SUPPORTING INFORMATION

Highly Active Ruthenium Metathesis Catalysts Exhibiting Unprecedented Activity and *Z*-selectivity

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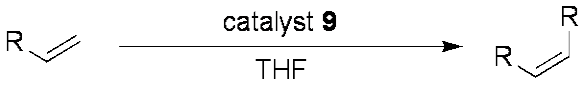
Table S1. Isolated Yields for Homodimerizations Using Catalyst **9.**



subtrate	loading, mol %	conc., M	temp, °C	time, h	isolated yield, %	*Z*, %	TON
10	0.1	3.3	35	2	84	>95	840
	0.1	1	23	6.5	91	>95	910
	0.01	7[b]	35	2.5	74	>95	7400
13	0.1	3.3	35	6.5	87	>95	870
	0.1	1	23	12	85	>95	850
	0.01	3.3	35	12	58	>95	5800
14	0.1	3.3	35	2.5	81	>95	810
	0.1	1	23	12	80	>95	800
	0.01	3.3	35	4.5	15	>95	1500

[a]Determined by ^{1}H NMR spectroscopy. [b]Run at a higher substrate concentration to increase catalyst initiation and activity. Due to insufficient solubility of **9** in **13** and **14**, however, homodimerizations of those substrates at 0.01 mol % were run at the maximum concentration achievable (3.3M).

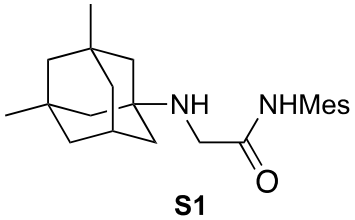
General Information.

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ and CD_2Cl_2 were used as received. All substrates for olefin cross-metathesis (**10**, **13**, and **14**) were degassed with argon and filtered through a plug of neutral alumina prior to use. $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O^iPrC_6H_4)$ (**S4**) was obtained from Materia, Inc. **4** was synthesized according to the literature procedure.[1] Other commercially available reagents and silica gel were used as received.

^1H NMR spectra were acquired at 400 or 500 MHz and ^{13}C NMR spectra at 101 or 126 MHz as $CDCl_3$ or C_6D_6 solutions unless otherwise noted. 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 (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. All HRMS were by positive-ion EI or FAB.

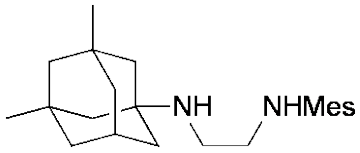
[1] Herbert, M. B.; Lan, Y.; Keitz, B. K.; Liu, P.; Endo, K.; Day, M. W.; Houk, K. N.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 7861.



S1

Preparation of S1.

A 3-neck 250 mL RB flask equipped with a condenser was flame dried and charged with 2-chloro-*N*-mesitylacetamide (3.5 g, 17 mmol), memantine hydrochloride (3.0 g, 14 mmol, OChem Incorp.), and K_2CO_3 (4.8 g, 35 mmol). MeCN (110 mL) was added and the suspension was heated to 100°C under an argon atmosphere for 24 h. After cooling to RT, the mixture was filtered through celite, washing with CH_2Cl_2, and the filtrate was concentrated to a white powder. The crude mixture was dry loaded onto a silica gel column and purified via flash chromatography using Et_2O as eluant to give **S1** (3.0 g, 60%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (br s, 1H), 6.88 (s, 2H), 3.38 (s, 2H), 2.26 (s, 3H), 2.18 (s, 6H), 2.17 (m, 1H), 1.53 (br s, 1H), 1.49 (br d, *J* = 3.2 Hz, 2H), 1.31–1.27 (m, 8H), 1.14 (br q, *J* = 11.6 Hz, 2H), 0.86 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 136.4, 134.7, 131.4, 128.8, 52.8, 50.7, 49.0, 44.3, 42.8, 41.3, 32.4, 30.2, 30.1, 20.9, 18.5. HRMS (FAB+): Calculated—355.2749, Found—355.2766.

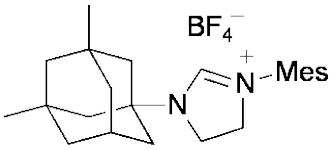


S2

Preparation of S2.

A 2-neck 100 mL RB flask equipped with a condenser was dried and charged with $LiAlH_4$ (1.3 g, 34 mmol) while a separate 25 mL RB flask was dried and charged with **S1** (3.0 g, 8.4 mmol). THF (50 mL) was added to the $LiAlH_4$ while **S1** was dissolved in THF (20 mL) and added dropwise to the $LiAlH_4$ suspension. After the addition was complete, the suspension was heated to 80 °C for 24 h, after which it was cooled to RT and carefully quenched via the dropwise addition of H_2O (1.3 mL), 15% NaOH solution (1.3 mL), and H_2O (4.0 mL). The quenched reaction was stirred

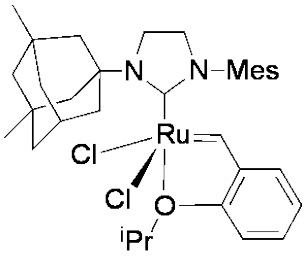
for 5 h under air and filtered through celite, washing with Et_2O. The filtrate was concentrated to give **S2** (2.8 g, 98%), which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 3.04 (t, *J* = 4.4 Hz, 2H), 2.85 (t, *J* = 4.8 Hz, 2H), 2.34 (s, 6H), 2.28 (s, 3H), 2.20 (br s, 1H), 1.55 (s, 2H), 1.38–1.32 (m, 8H), 1.19–1.17 (m, 2H), 0.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 130.6, 129.4, 129.2, 52.1, 51.0, 49.5, 49.2, 43.1, 41.4, 40.9, 32.4, 30.4, 30.3, 20.6, 18.6. HRMS (FAB+): Calculated—341.2957, Found—341.2964.



S3

Preparation of S3.

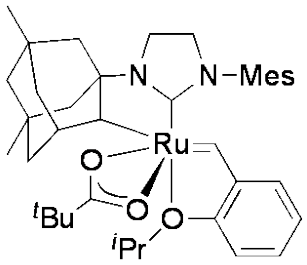
A 100 mL RB flask was dried and charged with **S2** (1.0 g, 2.9 mmol), NH_4BF_4 (0.34 g, 3.2 mmol), and $CH(OMe)_3$ (6.0 mL, 28 mmol). The solution was heated to 100 °C for 4 h, cooled to RT and concentrated. The resulting orange-red residue was washed with cold ^{n}BuOH:Toluene (1:1) to give a white precipitate that was collected by filtration. Drying the precipitate under vacuum gave **S3** (0.49 g, 44%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 6.89 (s, 2H), 4.31–4.13 (m, 4H), 2.27 (m, 1H), 2.26 (s, 3H), 2.22 (s, 6H), 1.65 (br s, 2H), 1.61 (br q, *J* = 11.6 Hz, 4H), 1.36 (br q, *J* = 14.4 Hz, 4H), 1.21 (br s, 2H), 0.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 139.9, 135.2, 130.7, 129.6, 59.3, 50.4, 49.6, 46.3, 44.9, 41.6, 39.0, 32.6, 29.7, 29.4, 20.8, 17.4. HRMS (FAB+): Calculated—351.2800, Found—351.2755.



S5

Preparation of S5.

In a glovebox, a solution of **S3** (0.49 g, 1.1 mmol) in hexanes (30 mL) was treated with $KCOMe_2Et$ (0.14 g, 0.91 mmol), and the mixture was allowed to stir at 35 °C for 1.5 h. To the reaction mixture was then added **S4** (0.64 g, 1.1 mmol), upon which the mixture was removed from the glove box and allowed to stir at 65 °C for 3.5 h. The precipitated solids were filtered and washed well with warm hexanes and pentane to give **S5** as a green powder: ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.90 (s, 1H), 7.55 (ddd, *J* = 8.8, 7.3, 1.9 Hz, 1H), 7.06 (s, 2H), 6.95–6.88 (m, 2H), 6.86 (dd, *J* = 7.5, 1.8 Hz, 1H), 5.09 (hept, *J* = 6.3 Hz, 1H), 4.12 (s, 2H), 4.06–3.98 (m, 2H), 3.90–3.82 (m, 2H), 2.70 (p, *J* = 3.1 Hz, 1H), 2.46 (s, 3H), 2.25 (s, 6H), 2.04 (dd, *J* = 11.9, 1.8 Hz, 2H), 1.81 (d, *J* = 12.2 Hz, 2H), 1.74 (dt, *J* = 12.6, 2.8 Hz, 2H), 1.63 (d, *J* = 6.1 Hz, 6H), 1.47 (dt, *J* = 12.6, 2.4 Hz, 2H), 1.31–1.17 (m, 2H), 0.97 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 312.4, 207.8, 152.4, 145.9, 139.6, 138.5, 138.1, 130.8, 129.8, 123.9, 122.8, 113.5, 74.4, 58.9, 51.2, 50.7, 47.3, 44.7, 42.4, 42.2, 33.0, 31.3, 30.4, 22.6, 21.3, 18.5. HRMS (FAB+): Calculated—670.2031, Found—670.2028.

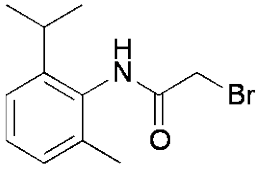


7

Preparation of 7.

In a glovebox, a 20ml scintillation vial was charged with **S5** (0.10 g, 0.16 mmol), NaOPiv (0.19 g, 1.5 mmol), THF (2.0 mL), and MeOH (2.0 mL). The vial was capped, removed from the glovebox, and heated to 40 °C for 4.5 h at which point a

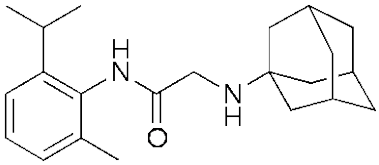
color change from green to brown to dark purple was observed. The vial was returned to the box, where the solvent was removed under high vacuum and the residue dissolved in CH_2Cl_2 (15 mL), filtered through celite, and concentrated to a deep purple residue. The residue was recrystallized from Et_2O at -35 °C. The resulting crystals were washed with cold Et_2O (3 x 5 mL) to give **7** as a bright purple solid (20 mg, 18%). ^{1}H NMR (400 MHz, C_6D_6) δ 14.83 (s, 1H), 7.46 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.83 (br s, 1H), 6.76 (br s, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.79 (sept, *J* = 6.8 Hz, 1H), 3.91 (s, 1H), 3.47–3.40 (m, 2H), 3.27–3.14 (m, 2H), 2.57 (br s, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 1.73 (br d, *J* = 11.2 Hz, 1H), 1.60 (br d, *J* = 10.8 Hz, 1H), 1.53–1.51 (m, 4H), 1.43–1.39 (m, 2H), 1.26 (s, 9H), 1.18 (q, *J* = 6.4 Hz, 4H), 1.03 (d, *J* = 9.6 Hz, 1H), 0.89 (br s, 4H), 0.77 (br d, *J* = 12.8 Hz, 1H), 0.67 (br d, *J* = 10.4 Hz, 1H), 0.62 (s, 3H), 0.31 (br d, *J* = 9.6 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 259.0, 214.9, 154.2, 143.8, 138.0, 137.0, 136.8, 136.5, 129.9, 129.7, 125.6, 123.1, 122.8, 113.9, 74.5, 66.5, 64.1, 52.1, 51.7, 48.8, 46.6, 42.6, 41.3, 39.8, 39.1, 38.6, 33.4, 32.1, 30.8, 30.7, 28.9, 27.8, 21.6, 21.2, 21.0, 19.1, 19.0. HRMS (FAB+): Calculated—700.3178, Found—700.3181.



S6

Preparation of S6.

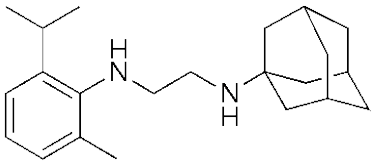
Bromoacetyl chloride (2.8 mL, 34 mmol) was added dropwise to a 0 °C solution of 2-isopropyl-6-methylaniline (5.0 g, 34 mmol) and K_2CO_3 (9.4 g, 68 mmol) in MeCN (70 mL). The solution was warmed to room temperature, stirred overnight, filtered over celite, and concentrated. Recrystallization from CH_2Cl_2/hexanes provided **S6** (5.5 g, 60%) as a colorless solid. ^{1}H NMR δ 7.77 (br s, 1H), 7.24 (m, 1H), 7.18 (m, 1H), 7.11 (m, 1H), 4.08 (s, 2H), 3.06 (m, 1H), 2.24 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR δ 164.3, 145.7, 135.9, 131.6, 128.4, 128.3, 123.7, 29.2, 28.7, 23.5, 18.5. HRMS (FAB+): Calculated—270.0493, Found—270.0480.



S7

Preparation of S7.

Compound **S6** (2.4 g, 8.9 mmol) and 1-adamantylamine (2.0 g, 13 mmol) were dissolved in MeCN (30 mL), K_2CO_3 (1.9 g, 14 mmol) was added, and the solution was refluxed for 24 hours. After cooling to room temperature, the mixture was filtered over celite and concentrated. The residue was then dissolved in CH_2Cl_2 and filtered over a pad of silica gel (eluent 10% MeOH in CH_2Cl_2). Removal of the solvent *in vacuo* provided **S7** (3.0 g, 94%) as a peach solid. ^{1}H NMR δ 9.15 (br s, 1H), 7.18 (m, 1H), 7.16 (m, 1H), 7.09 (m, 1H), 3.44 (s, 2H), 3.04 (m, 1H), 2.23 (s, 3H), 2.11 (m, 3H), 1.58–1.72 (m, 14H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR δ 171.9, 145.2, 135.6, 132.8, 128.1, 127.5, 123.3, 51.1, 44.0, 42.9, 36.5, 29.5, 28.7, 23.4, 18.8. HRMS (FAB+): Calculated—341.2593, Found—341.2603.

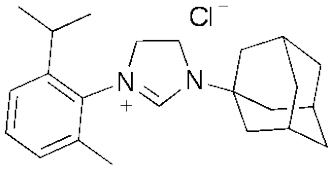


S8

Preparation of S8.

Lithium aluminum hydride (1.0 g, 26 mmol) was added portion-wise to a 0 °C solution of compound **S7** (3.0 g, 8.8 mmol) in THF (45 mL), and the solution was brought to room temperature, then refluxed for 72 hours. The mixture was then cooled to 0 °C, and water (1.0 mL), 10% *aq.* NaOH (1.0 mL), then additional water (1.0 mL) were added sequentially. The solution was dried with $MgSO_4$, filtered, and concentrated. Flash chromatography of the residue (SiO_2, using 66% Et_2O in pentanes) provided **S8** (1.8 g, 62%) as a yellow oil. ^{1}H NMR δ 7.08 (m, 1H), 6.98 (m, 1H), 6.91 (m, 1H), 3.30 (m, 1H), 3.06 (m, 2H), 2.86 (m, 2H), 2.32 (s, 3H), 2.08 (m, 3H), 1.59–1.73 (m, 15H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR δ 145.1, 140.8, 130.6,

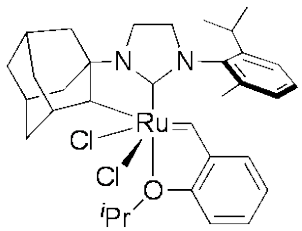
128.4, 123.6, 122.4, 51.1, 50.1, 42.9, 42.5, 40.7, 36.6, 29.5, 27.5, 24.0, 19.1. HRMS (FAB+): Calculated—327.2800, Found—327.2800.



S9

Preparation of S9.

A solution of compound **S8** (1.3 g, 4.0 mmol) in Et_2O (7.0 mL) was treated with HCl (4.0 mL, 2.0 M in Et_2O), and stirred for 15 minutes at room temperature. The solid was then filtered, washed with Et_2O, dried, suspended in $CH(OEt)_3$, and refluxed for 2 hours. The solution was cooled to room temperature and then concentrated. The resulting solid residue was washed rigorously with Et_2O to provide **S9** (0.75 g, 50%) as a tan solid. ^{1}H NMR δ 8.79 (br s, 1H), 7.32 (m, 1H), 7.22 (m, 1H), 7.13 (m, 1H), 4.55 (m, 1H), 4.43 (m, 2H), 4.25 (m, 1H), 2.93 (m, 1H), 2.41 (s, 3H), 2.27 (m, 3H), 2.18–2.08 (m, 6H), 1.74 (m, 6H), 1.28 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR δ 156.0, 146.5, 135.9, 132.0, 130.6, 129.2, 124.8, 58.2, 52.1, 45.5, 41.1, 35.4, 29.2, 28.7, 24.8, 24.2, 18.7. HRMS (FAB+): Calculated—337.2644, Found—337.2652.

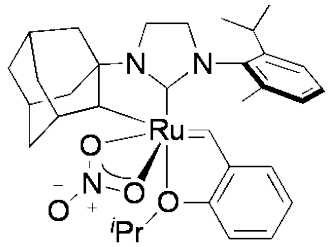


S10

Preparation of S10.

In a glovebox, $KCOMe_2Et$ (75 mg, 0.57 mmol) was added to a suspension of compound **S9** (0.19 g, 0.52 mmol) in hexanes (6.0 mL). The solution was stirred at 35 °C for 30 minutes, and then **S4** (0.31 g, 0.52 mmol) was added, at which point the solution was removed from the glovebox. The solution was stirred for 2 hours at 65 °C and then cooled to room temperature. The resulting precipitate was filtered and washed thoroughly with warm hexanes to provide **S10** (0.22 g, 65%) as a green solid. ^{1}H NMR δ 16.9 (s, 1H), 7.54 (m, 1H), 7.49 (m, 1H), 7.22 (m, 1H), 6.92 (m, 1H),

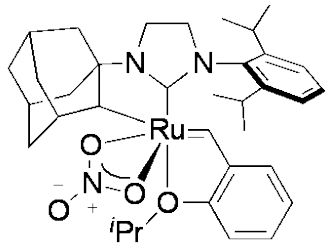
6.87 (m, 1H), 6.85 (m, 1H), 5.07 (m, 1H), 3.98–4.11 (m, 2H), 3.84–3.92 (m, 2H), 3.15 (m, 1H), 2.96 (m, 5H), 2.42 (m, 2H), 2.32 (s, 3H), 1.94 (m, 3H), 1.83 (m, 3H), 1.69 (d, *J* = 6.2 Hz, 3H), 1.60 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR δ 310.5, 208.2, 152.5, 148.7, 145.2, 140.6, 137.9, 130.6, 129.1, 128.9, 124.8, 123.8, 122.5, 113.2, 74.2, 57.2, 52.7, 44.5, 42.2, 36.1, 30.0, 27.6, 25.5, 23.8, 22.7, 22.3, 18.9. HRMS (FAB+): Calculated—656.1875, Found—656.1894.



8

Preparation of 8.

In a glovebox, a solution of NaOPiv (0.30 g, 1.5 mmol) in MeOH (2.0 mL) was added to a solution of **S10** (0.15 g, 0.15 mmol) in THF (2.0 mL). The mixture was removed from the glovebox, heated at 50 °C for 21 hours, and then brought back into the glovebox and concentrated. The residue was taken in CH_2Cl_2, filtered over a pad of celite, dissolved in THF (8.0 mL), and then ammonium nitrate (0.12 g, 1.5 mmol) was added. Following stirring for 3 hours, the mixture was concentrated. The residue was then taken in CH_2Cl_2, filtered over a pad of celite, and concentrated. Rigorous washing of the resulting solid with Et_2O provided **8** (0.70 g, 72%) as a purple solid. ^{1}H NMR δ 15.0 (s, 1H), 7.48 (m, 1H), 7.42 (m, 1H), 7.13 (m, 1H), 7.08 (m, 1H), 6.99 (m, 1H), 6.97 (m, 1H), 5.10 (m, 1H), 3.95 (m, 1H), 3.78–3.99 (m, 4H), 3.72 (m, 1H), 3.15 (m, 1H), 2.23 (m, 1H), 2.18 (s, 3H), 2.18 (*overlapped*, 1H), 2.06 (m, 1H), 1.99 (m, 1H), 1.92 (m, 1H), 1.72 (m, 1H), 1.65 (m, 1H), 1.59 (m, 1H), 1.55 (m, 2H), 1.48 (d, *J* = 6.2 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.98 (m, 2H), 0.24 (m, 1H). ^{13}C NMR δ 266.4, 213.1, 154.7, 147.6, 143.1, 138.0, 137.3, 128.7, 128.3, 127.1, 124.0, 123.4, 123.4, 112.9, 74.4, 67.6, 52.6, 43.2, 42.3, 40.3, 37.9, 37.7, 37.6, 33.3, 31.0, 29.8, 28.3, 26.3, 23.6, 21.4, 20.6, 17.5. HRMS (FAB+): Calculated—646.2219, Found—646.2239.



9

Preparation of 9.

In a glovebox, a 250 mL Schlenk flask was charged with **4** (0.50 g, 0.73 mmol), NaOPiv (0.92 g, 7.4 mmol), THF (32 mL), and MeOH (16 mL). The flask was sealed, removed from the box, and heated to 40 °C for 4 days at which point the solution was a deep purple color. The solvent was removed under high vacuum and the Schlenk flask transferred back into the glovebox where the reside was dissolved in CH_2Cl_2 (80 mL), filtered through celite, and concentrated to a deep purple residue consisting of a mixture of the C-H activated product and pivalic acid. To this residue was added ammonium nitrate (0.72 g, 9.0 mmol) and THF (35 mL). The reaction was allowed to stir for 3 h inside the glovebox, after which the solvent was removed under vacuum. The residue was dissolved in C_6H_6 (70 mL), filtered through celite, and concentrated. The resulting residue was triturated with Et_2O (3 x 15 mL) to give **9** as a bright purple powder (100 mg, 20%). ^{1}H NMR (500 MHz, C_6D_6) δ 15.21 (s, 1H), 7.45 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.19 (qd, *J* = 5.8, 5.2, 2.5 Hz, 3H), 7.00 (dd, *J* = 6.8, 2.5 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 4.54 (hept, *J* = 6.3 Hz, 1H), 4.10 (s, 1H), 3.83–3.71 (m, 2H), 3.59 (ddd, *J* = 11.7, 10.1, 8.1 Hz, 1H), 3.36 (ddd, *J* = 11.0, 9.7, 8.1 Hz, 1H), 3.26–3.15 (m, 2H), 2.25 (t, *J* = 3.0 Hz, 1H), 2.06 (p, *J* = 3.3 Hz, 1H), 1.94 (tt, *J* = 11.9, 2.4 Hz, 2H), 1.77 (*overlapped*, 2H), 1.75 (d, *J* = 6.7 Hz, 3H), 1.63 (p, *J* = 3.4 Hz, 1H), 1.55–1.44 (m, 2H), 1.43 (*overlapped*, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.14 (*overlapped*, 1H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.10 (*overlapped*, 1H), 0.97 (d, *J* = 6.1 Hz, 3H), 0.58 (dt, *J* = 12.2, 2.6 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 267.5, 211.9, 154.8, 147.5, 147.4, 143.4, 135.6, 129.2, 126.9, 124.8, 124.2, 123.4, 123.4, 113.2, 74.4, 66.4, 63.2, 54.1, 43.0, 41.6, 40.3, 38.0, 37.8, 37.7, 33.3, 30.9, 29.8, 29.0, 28.7, 27.9, 26.8, 23.6, 23.1, 21.1, 20.3. HRMS (FAB+): Calculated—674.2566, Found—674.2532.

General Procedure for Homodimerization Reactions.

In a glovebox, a 4 ml vial was charged with catalyst (0.014 mmol) and THF (1.0 mL) to make a stock solution (0.014 M). A portion of the catalyst stock solution (70 μL, *ca.* 1.0 μmol) was added to a 4 mL vial containing substrate (1.0 mmol) and THF (100 μL, *ca.* 3.3 M). The vial was then placed into an aluminum block on an IKA temperature-controlled hotplate preheated to 35 °C, and the reaction was stirred while open to the glovebox atmosphere. After completion of the reaction (as determined by ^{1}H NMR spectroscopy), the vial was removed from the glovebox, quenched with oxygen, and the product was isolated either via flash chromatography on silica gel or by removal of starting material *in vacuo* according to literature procedures.[2] The percentage of *Z*-olefin product was determined by ^{1}H NMR spectroscopy. All spectra were consistent with previous literature reports.[2]

General Procedure for the Synthesis of 17 Using Catalyst 9.

In a glovebox, a 20 mL vial was charged with **16** (520 μL, 2.5 mmol), **15** (3.1 mL, 25 mmol), and THF (1.4 mL). **9** (8.5 mg, 0.013 mmol, 0.5 mol %) was added and the reaction was stirred at 35 ˚C in an open vial for 2 hours. The vial was removed from the glovebox, quenched with ethyl vinyl ether (1.5 mL) and stirred for 1 hour. The solvent was then removed *in vacuo*. The crude mixture was purified by flash column chromatography (SiO_2, hexane to 4% ethyl acetate in hexanes) two times to provide the pure *Z*-isomer of **17** (430 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (m, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.00–2.04 (m, 7H), 1.60–1.63 (m, 2H), 1.29–1.36 (m, 12H), 0.88–0.91 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 130.1, 129.9, 64.8, 32.1, 29.8, 29.3, 28.7, 27.3, 27.1, 26.0, 22.5, 21.2, 14.1. HRMS (EI+): Calculated—241.2168, Found—241.2174.

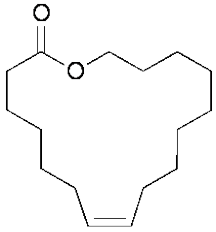
Synthesis of 17 at 1 mol % Catalyst Loading: Following the general procedure, **9** (1.7 mg, 0.0025 mmol, 0.1 mol %) was added to a solution of **16** (520 μL, 2.5 mmol), **15** (3.1 mL, 25 mmol) in THF (1.4 mL) to produce **17** (360 mg, 60%).

[2] Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc*. **2011**, *133*, 9686.

General Procedure for Macrocyclizations Using Catalyst 9.

In a glovebox, a 500 mL Strauss flask was charged with a solution of diene[3] (1 equiv, *ca.* 0.45 mmol) in dichloroethane (5.0 mM, 90 mL), and a solution of **9** (7.5 mol %) dissolved in dichloroethane (1.0 mL) was added. The flask was sealed, brought out of the glovebox, and subjected to a single freeze/pump/thaw cycle. The flask was kept under a static vacuum of *ca.* 20 mtorr and heated at 60 °C. After 24 hours, the mixture was cooled, quenched with excess ethyl vinyl ether, and concentrated. Flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes for compounds **18** and **19,** and 10% Et_2O in pentanes for compound **20**) provided the product. *E/Z* ratios were determined by quantitative ^{13}C NMR.[4] Quantitative ^{13}C measurements were acquired at 126 MHz (decoupled, without NOE, 13 second delay time).

Preparation of 18.



18

According to the general procedure for macrocyclizations, diene **18a** (62 mg, 0.22 mmol) was reacted with **9** (12 mg, 0.018 mmol) to provide **18** (35 mg, 64% yield, >95% *Z* as determined by ^1H- and ^{13}C-NMR) as a colorless oil. ^1H NMR δ 5.32

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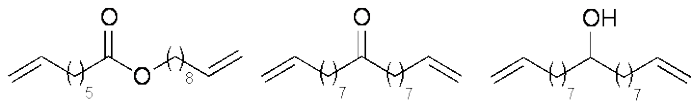
[3] Dienes **18a** – **20a** were synthesized as disclosed previously: Marx, V. M.; Herbert, M. B.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 94.

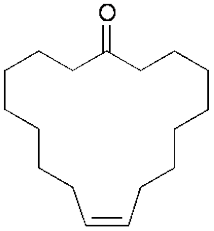


18a **19a** **20a**

[4] *E/Z* macrocycles can be readily differentiated through careful analysis of their ^1H, ^{13}C, and HSQC spectra, as the carbon atoms α to the olefin moiety in the *E*-isomers are located significantly more downfield then the corresponding carbon atoms in the *Z*-isomers, see: Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry.* Verlag Chemie: Weinheim, **1987**.

(m, 2H), 4.13 (t, *J* = 5.4 Hz, 2H), 2.33 (t, *J* = 6.5 Hz, 2H), 2.04 (m, 4H), 1.63 (m, 4H), 1.21–1.43 (m, 14H). ^{13}C NMR δ 174.0, 130.2, 130.0, 63.7, 34.6, 29.4, 28.8, 28.7, 28.5 (2C), 28.4, 27.7, 27.0, 26.8, 25.3 (2C). HRMS (EI+): Calculated—252.2089, Found—252.2084.

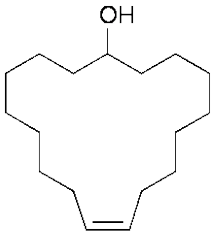
Preparation of 19.



19

According to the general procedure for macrocyclizations, diene **19a** (60 mg, 0.22 mmol) was reacted with **9** (12 mg, 0.018 mmol) to provide **19** (20 mg, 36% yield, >95% *Z* as determined by ^{1}H- and ^{13}C-NMR) as a colorless solid. ^{1}H NMR δ 5.34 (m, 2H), 2.40 (t, *J* = 6.7 Hz, 4H), 2.01 (m, 4H), 1.62 (m, 4H), 1.21–1.39 (m, 16H). ^{13}C NMR δ 212.6, 130.2 (2C), 42.5 (2C), 29.0 (2C), 28.6 (2C), 28.2 (2C), 28.1 (2C), 26.7 (2C), 23.9 (2C). HRMS (EI+): Calculated—250.2297, Found—250.2289.

Preparation of 20.



20

According to the general procedure for macrocyclizations, diene **20a** (62 mg, 0.22 mmol) was reacted with **9** (12 mg, 0.018 mmol) to provide **20** (23 mg, 42% yield, >95% *Z* as determined by ^{1}H- and ^{13}C-NMR) as a colorless solid. ^{1}H NMR δ 5.34 (m, 2H), 3.72 (m, 1H), 2.04 (m, 4H), 1.50 (m, 4H), 1.22–1.40 (m, 21H). ^{13}C NMR δ 130.2 (2C), 70.4, 35.7 (2C), 29.0 (2C), 28.2 (2C), 28.0 (2C), 27.9 (2C), 26.8 (2C), 23.5 (2C). HRMS (EI+): Calculated—252.2453, Found—252.2463.

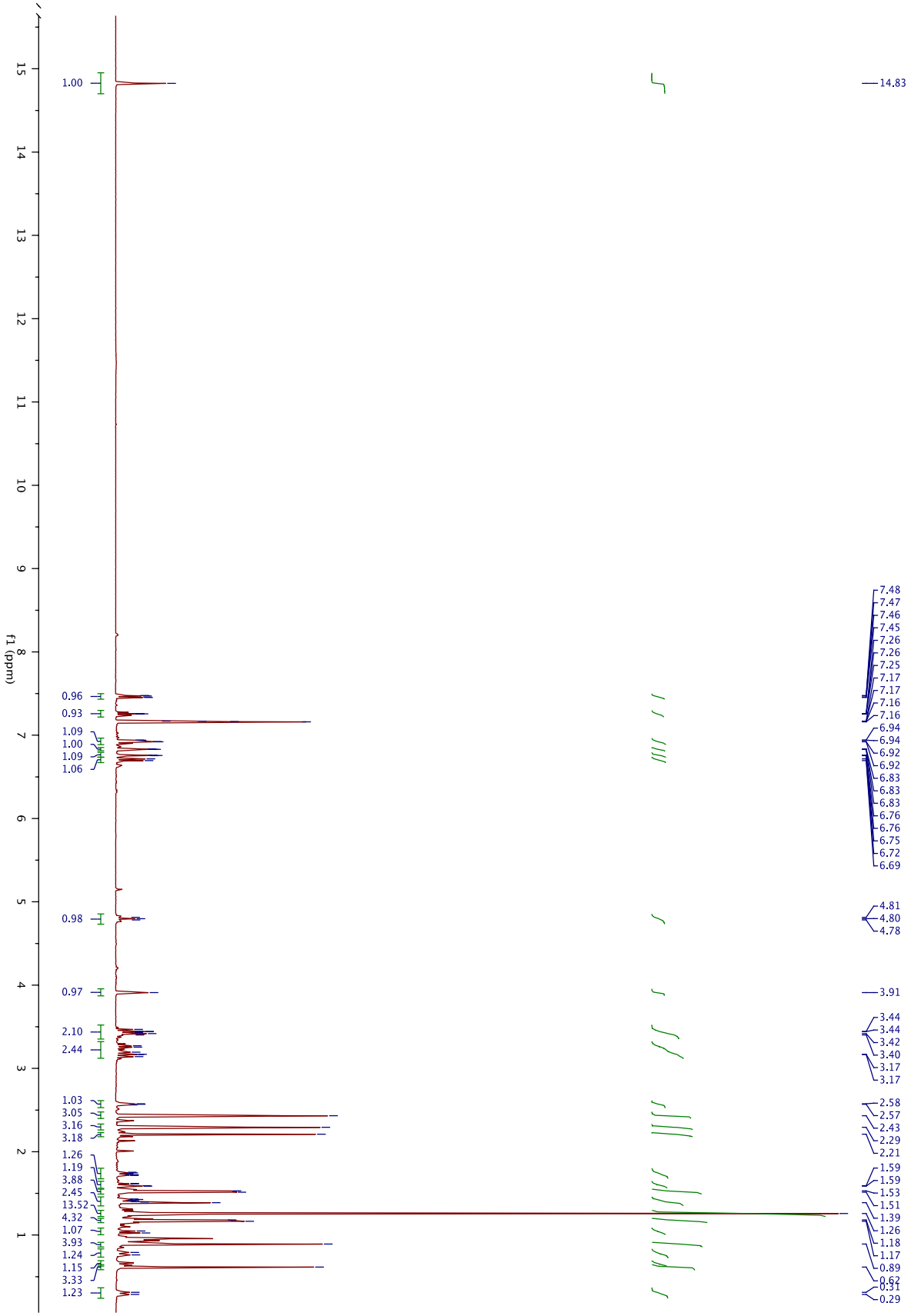


Figure S1. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **7**.

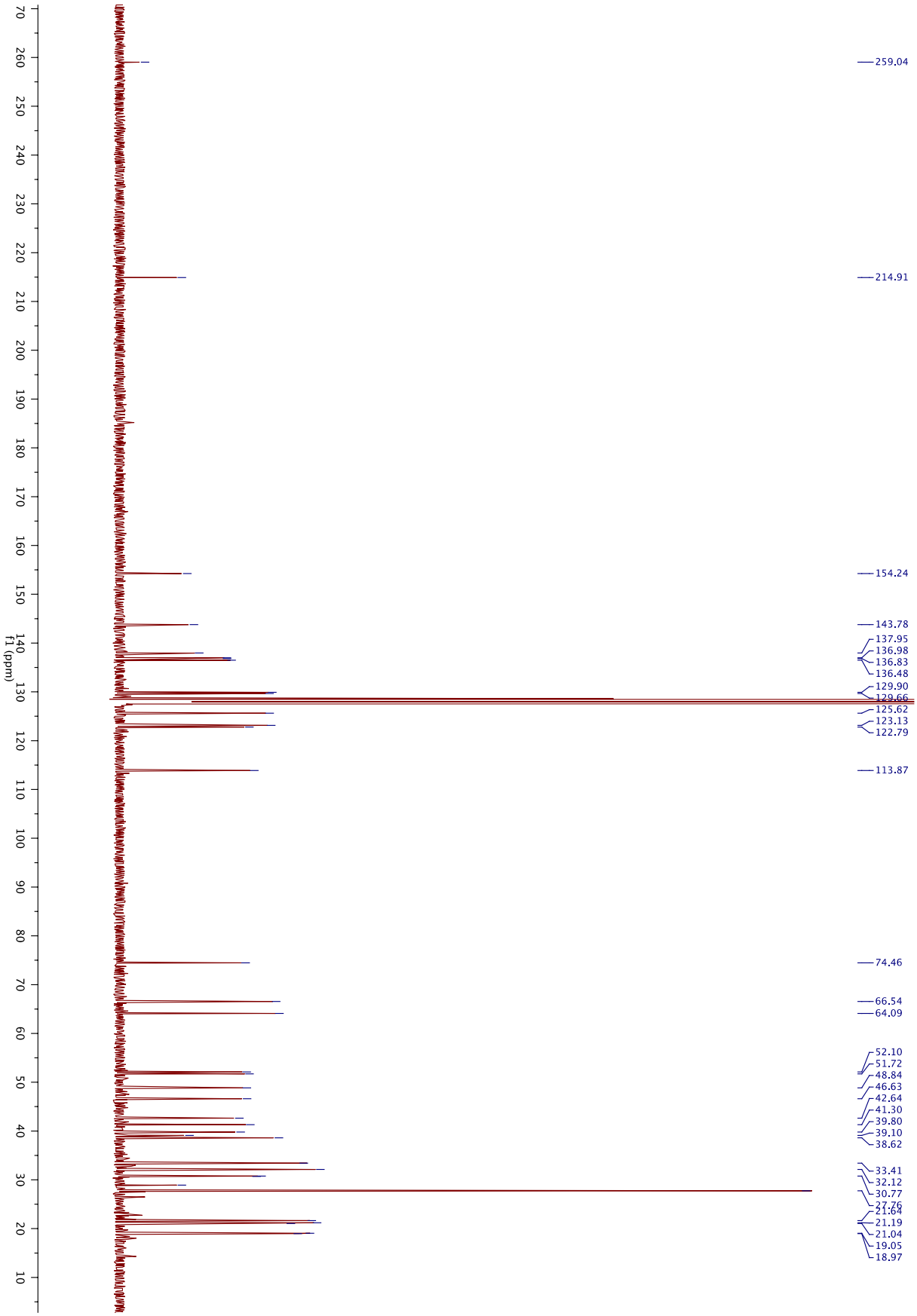


Figure S2. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **7**.

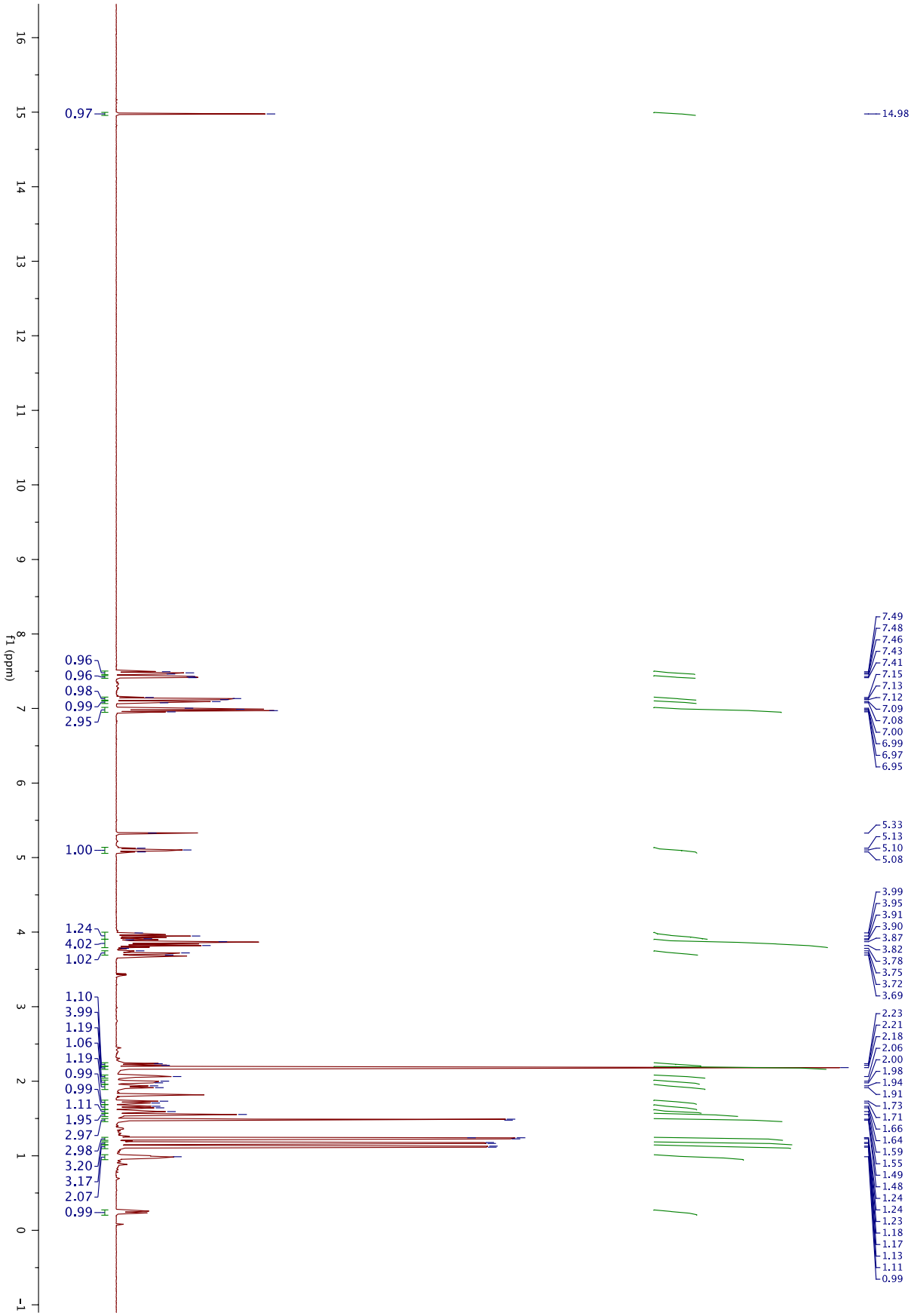


Figure S3. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **8**.

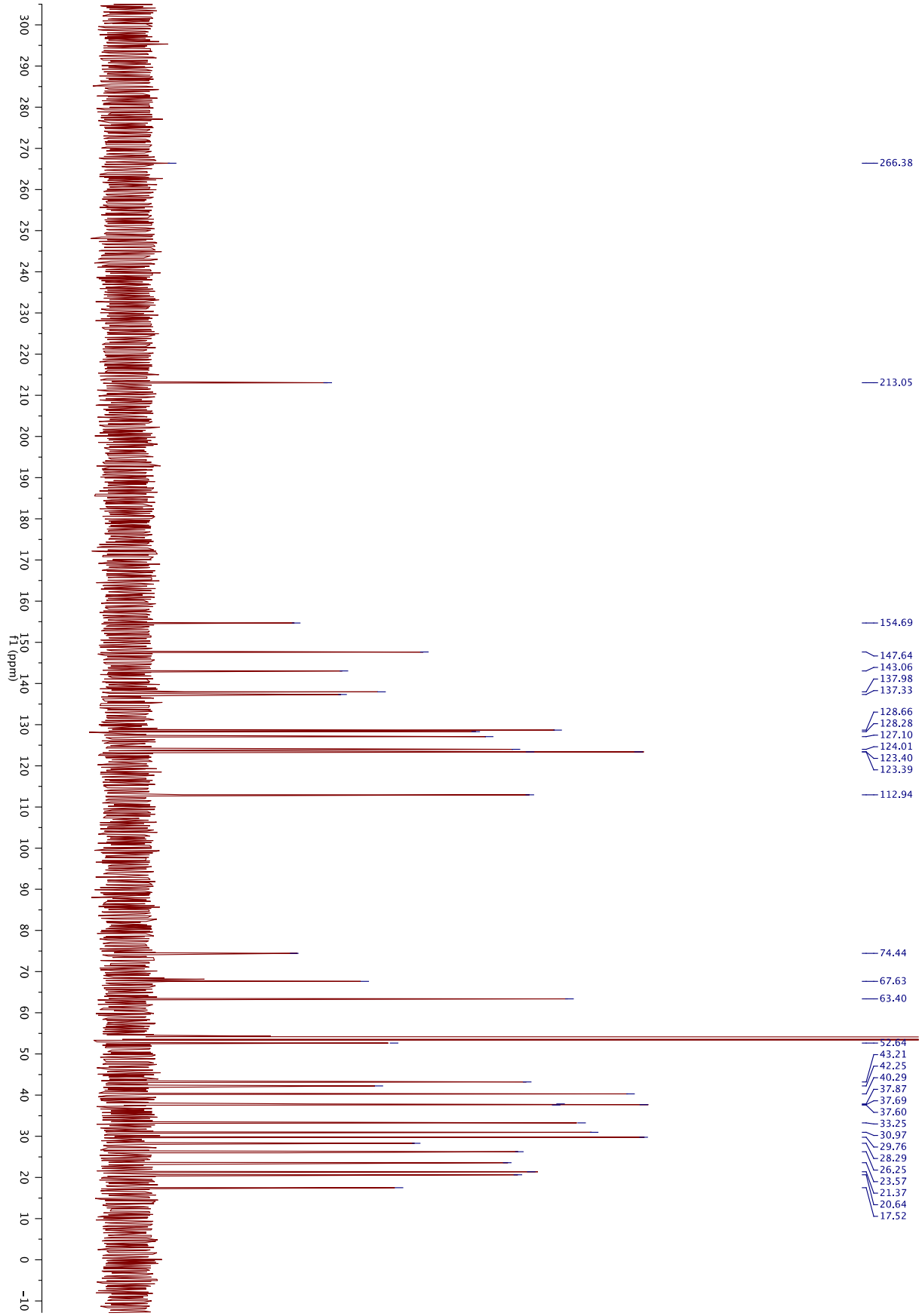


Figure S4. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of **8**.

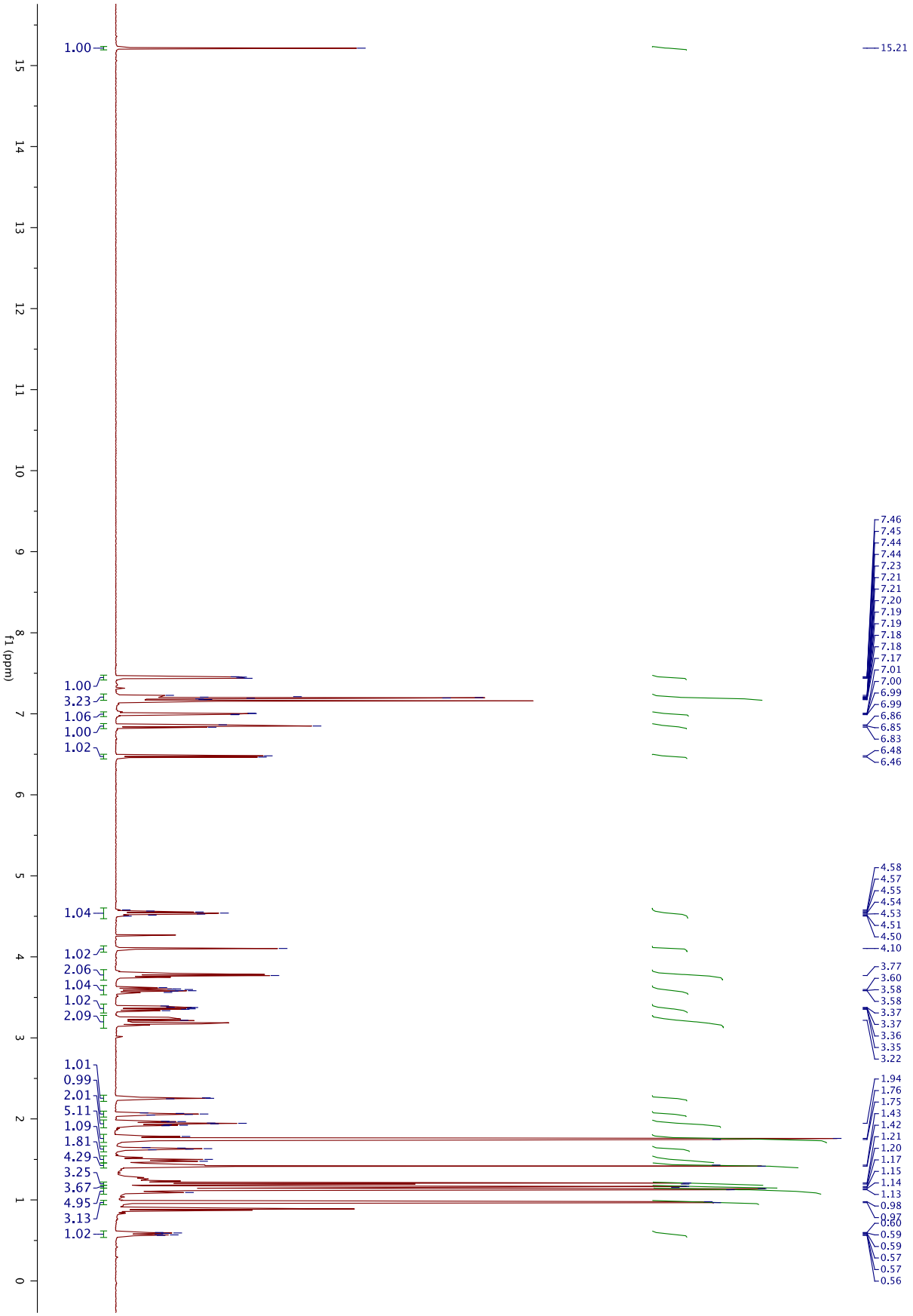


Figure S5. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **9**.

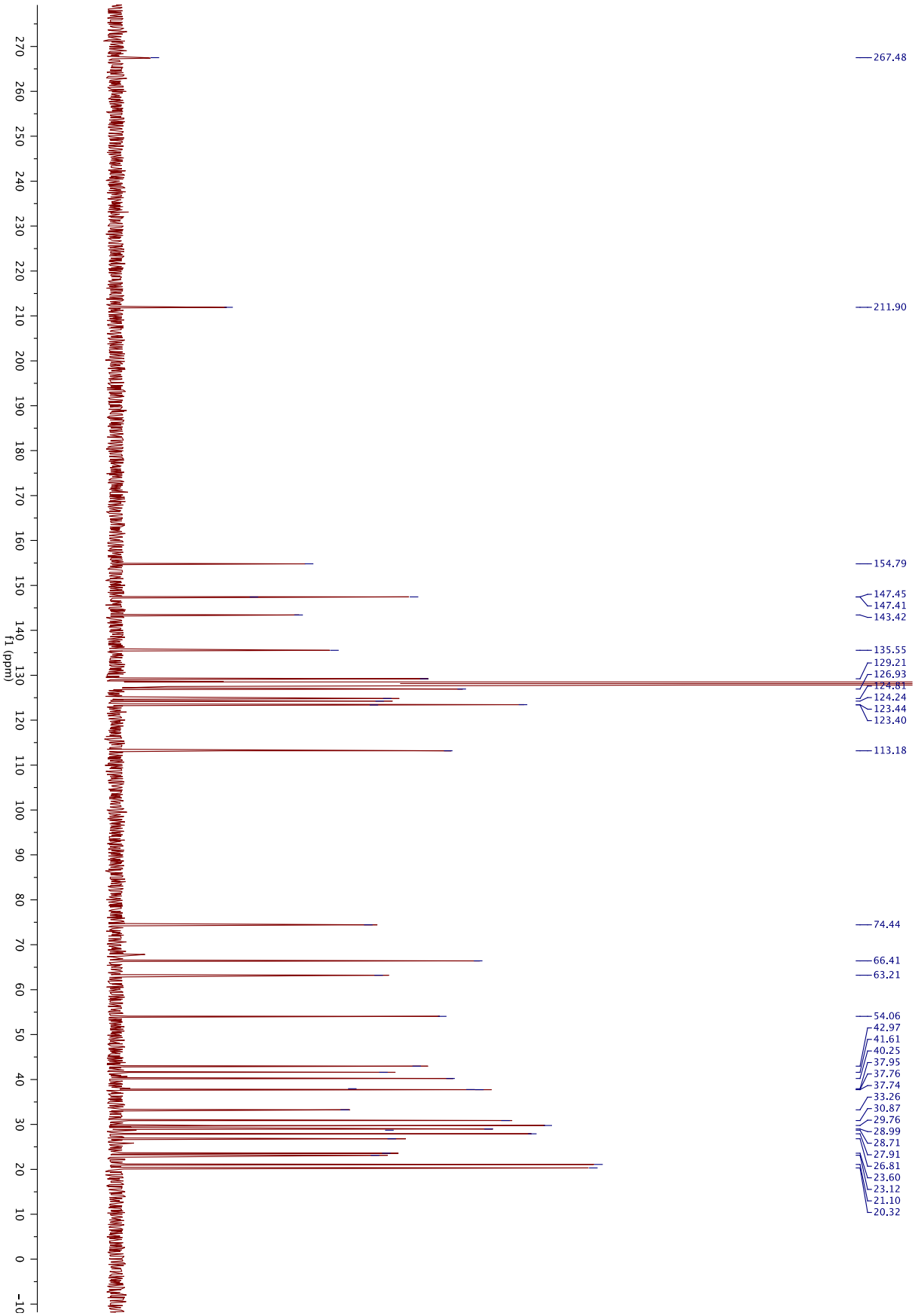


Figure S6. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **9**.

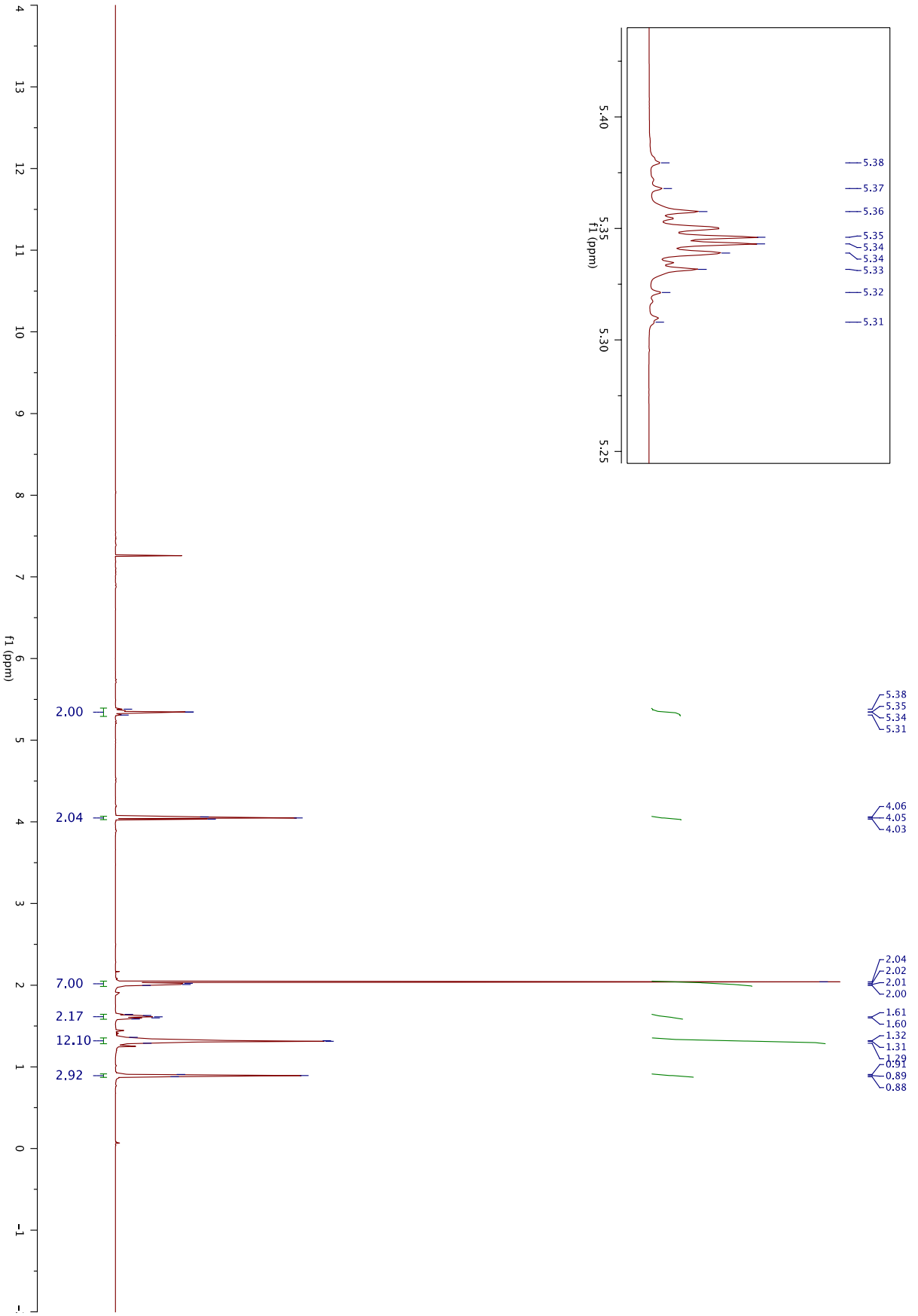


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **17**.

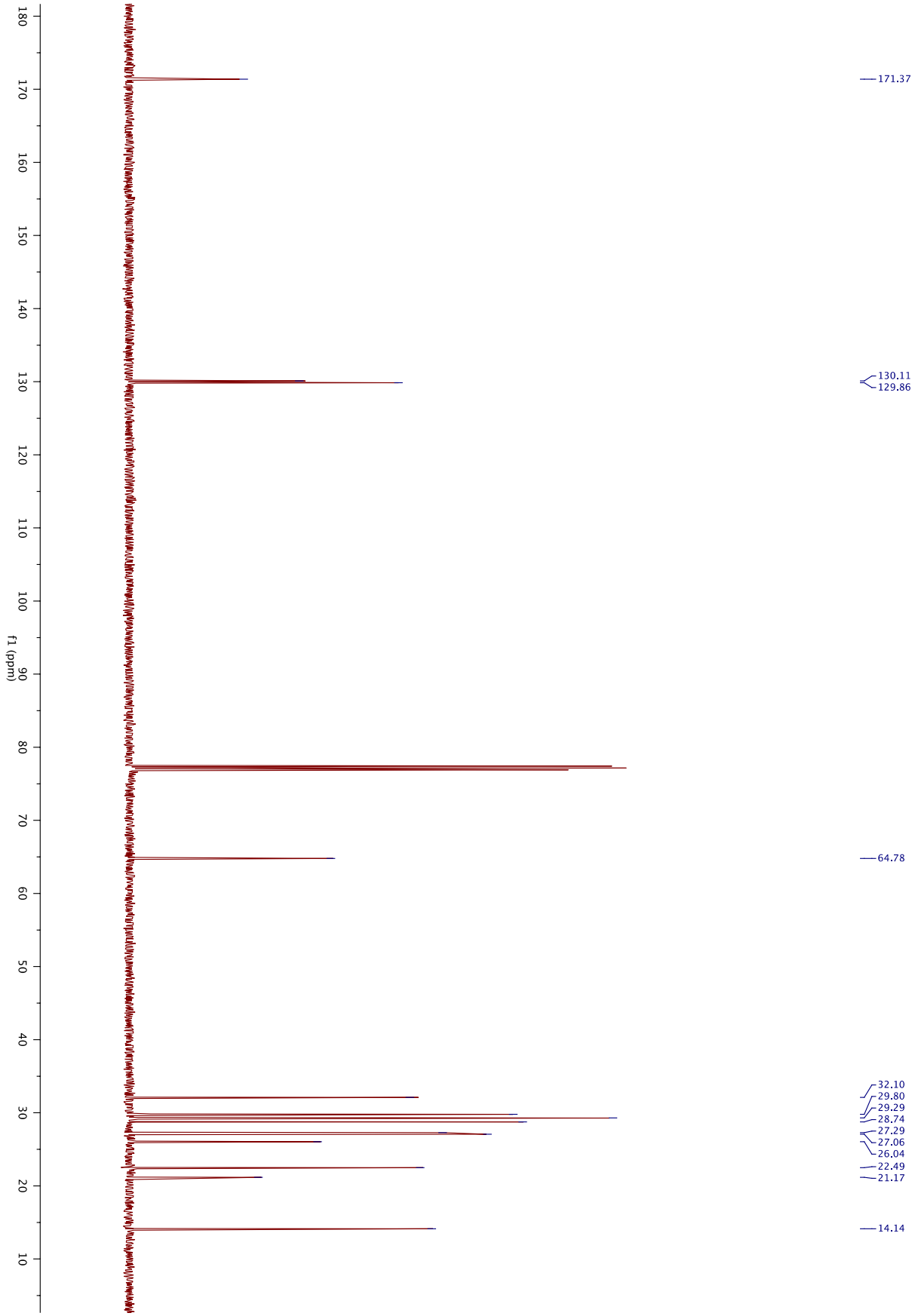


Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **17**.

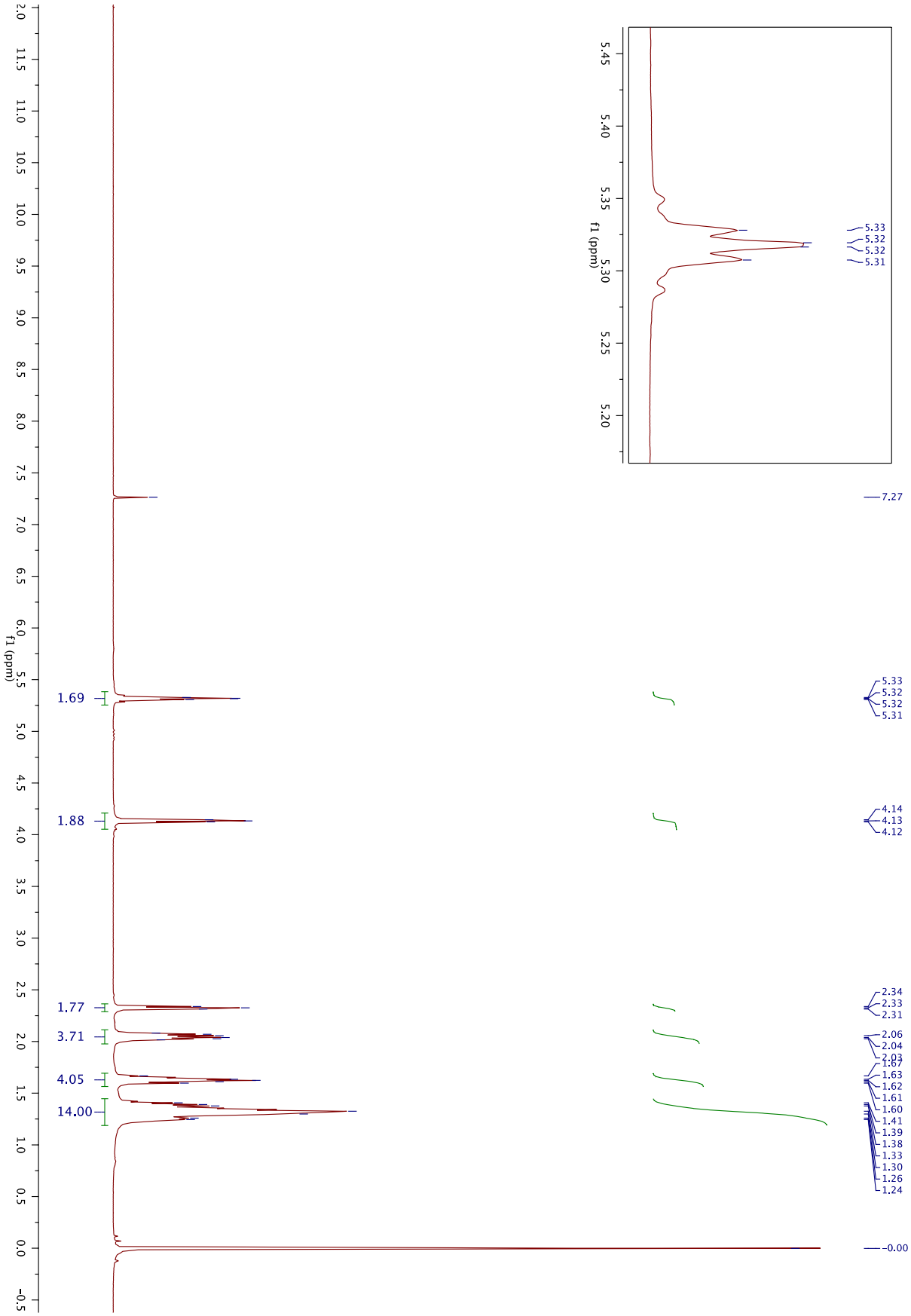


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **18**.

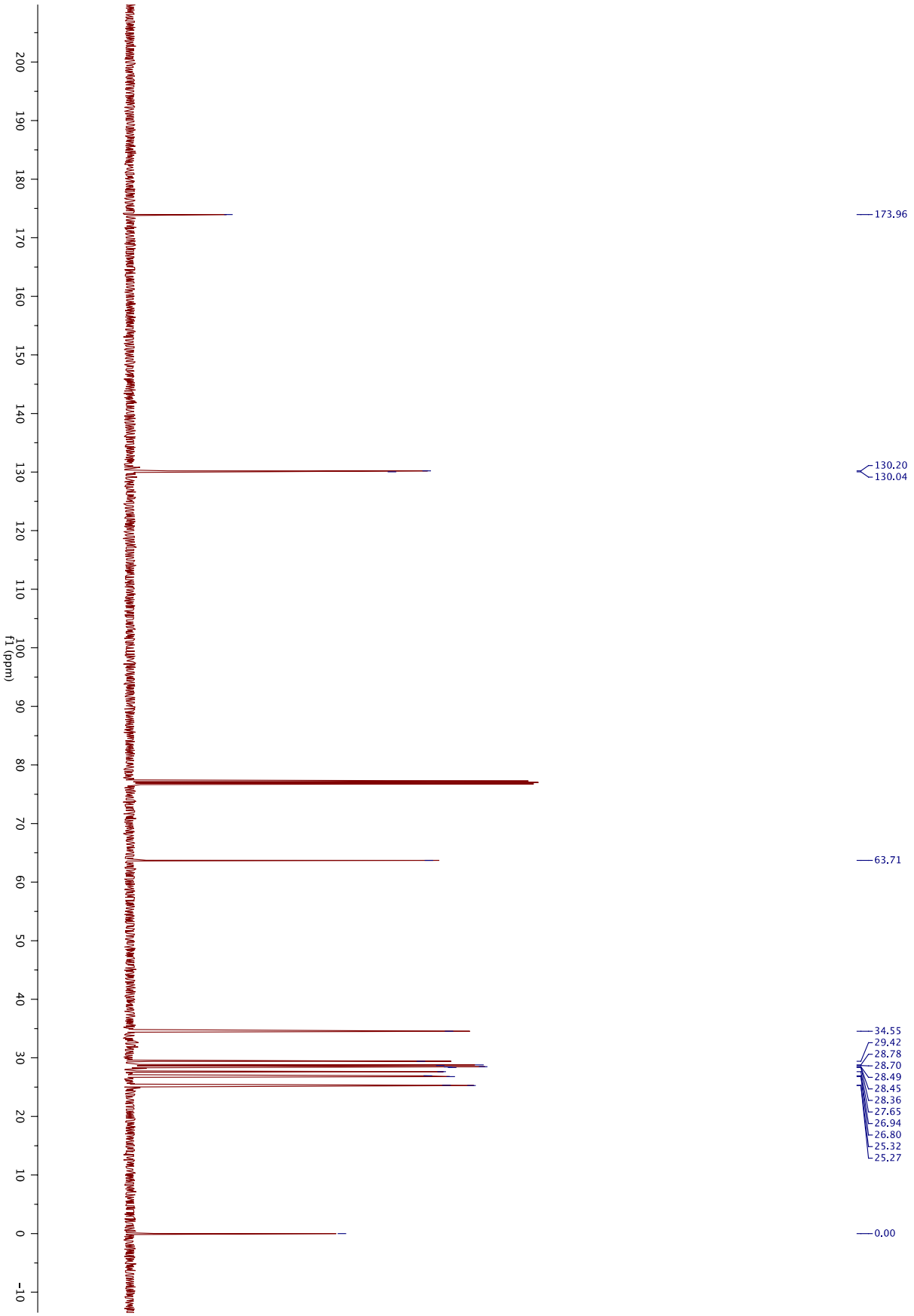


Figure S10. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **18**.

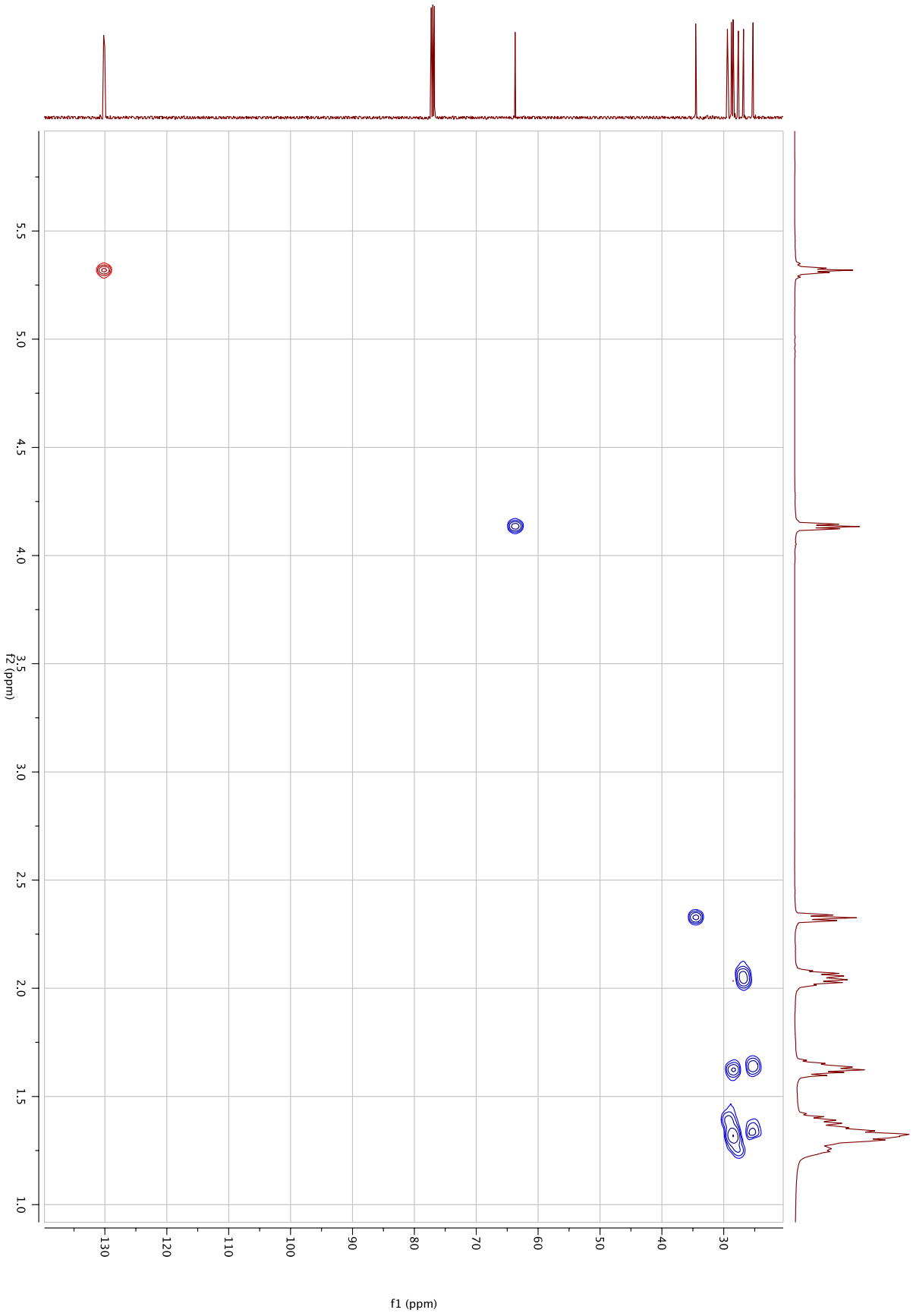


Figure S11. ^{1}H-^{13}C HSQC ($CDCl_3$) of **18**.

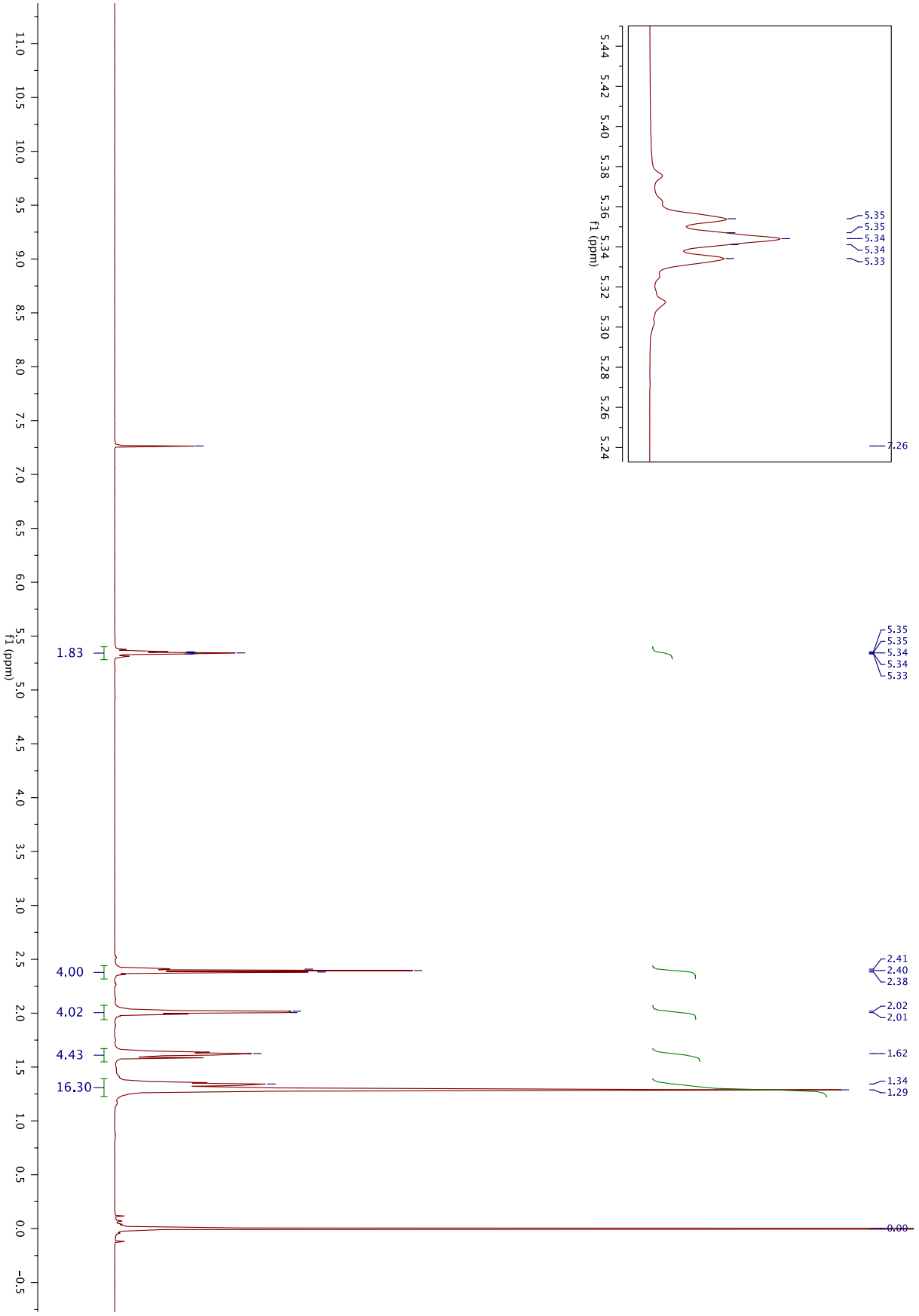


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **19**.

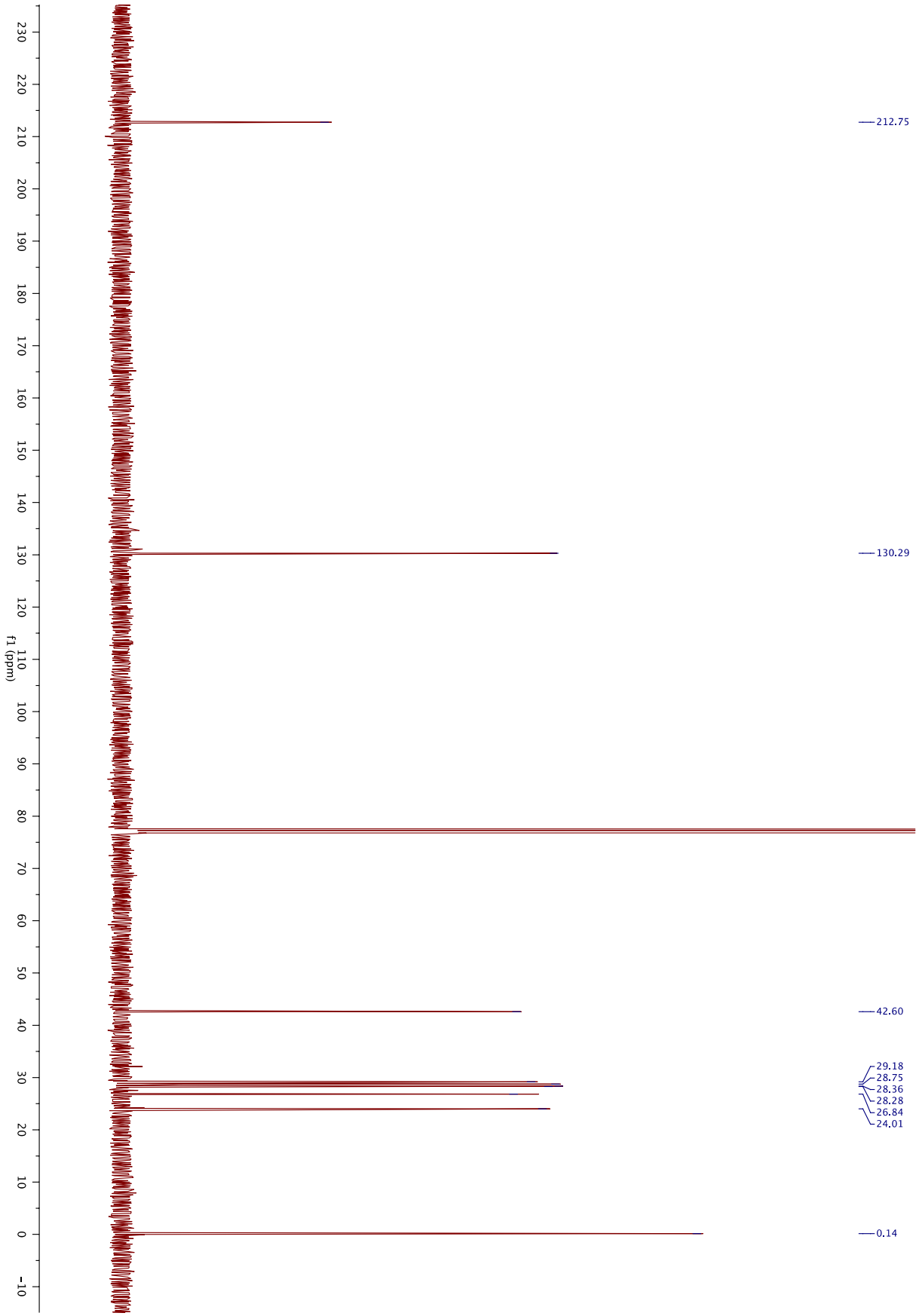


Figure S13. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **19**.

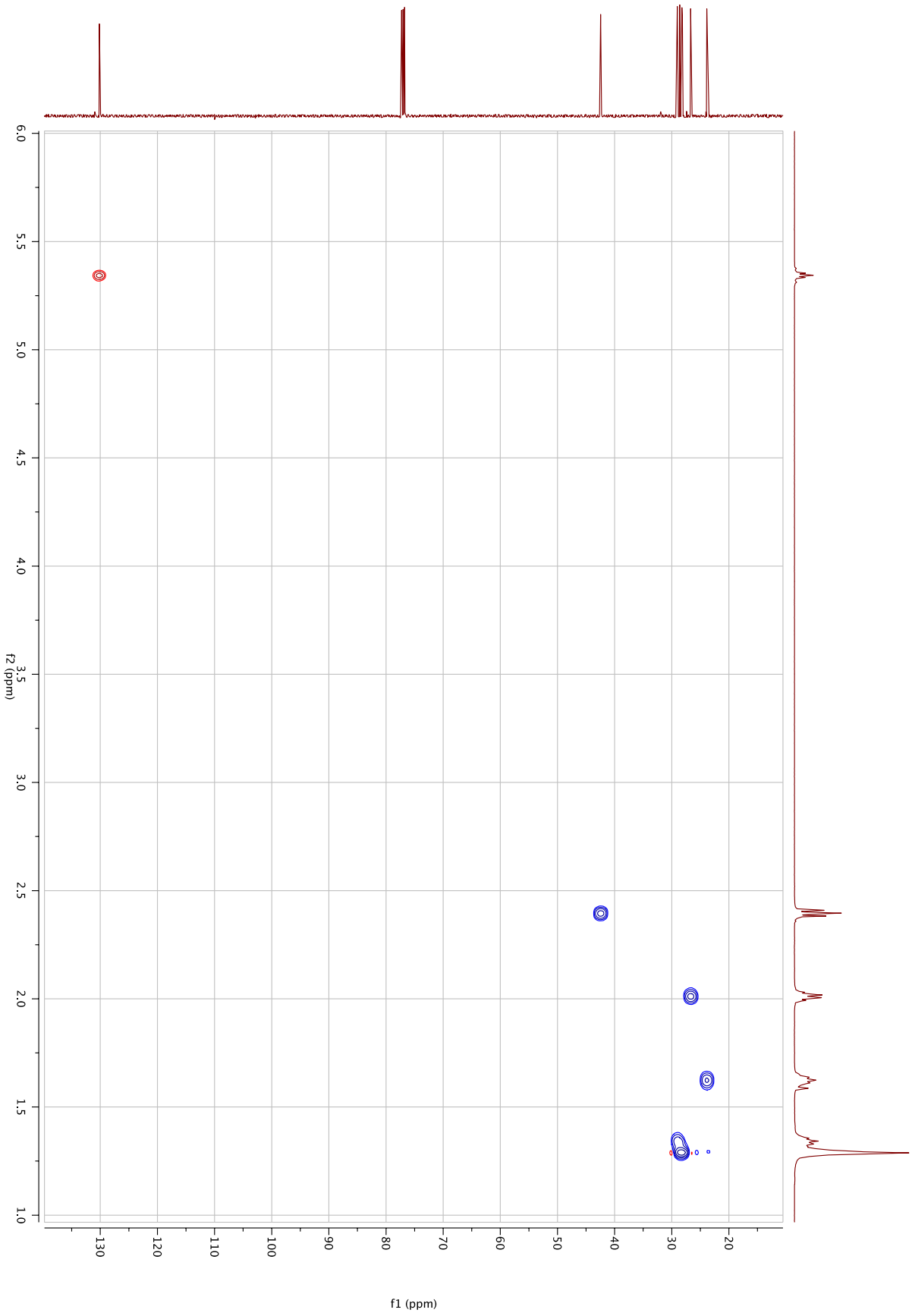


Figure S14. ^{1}H-^{13}C HSQC ($CDCl_3$) of **19**.

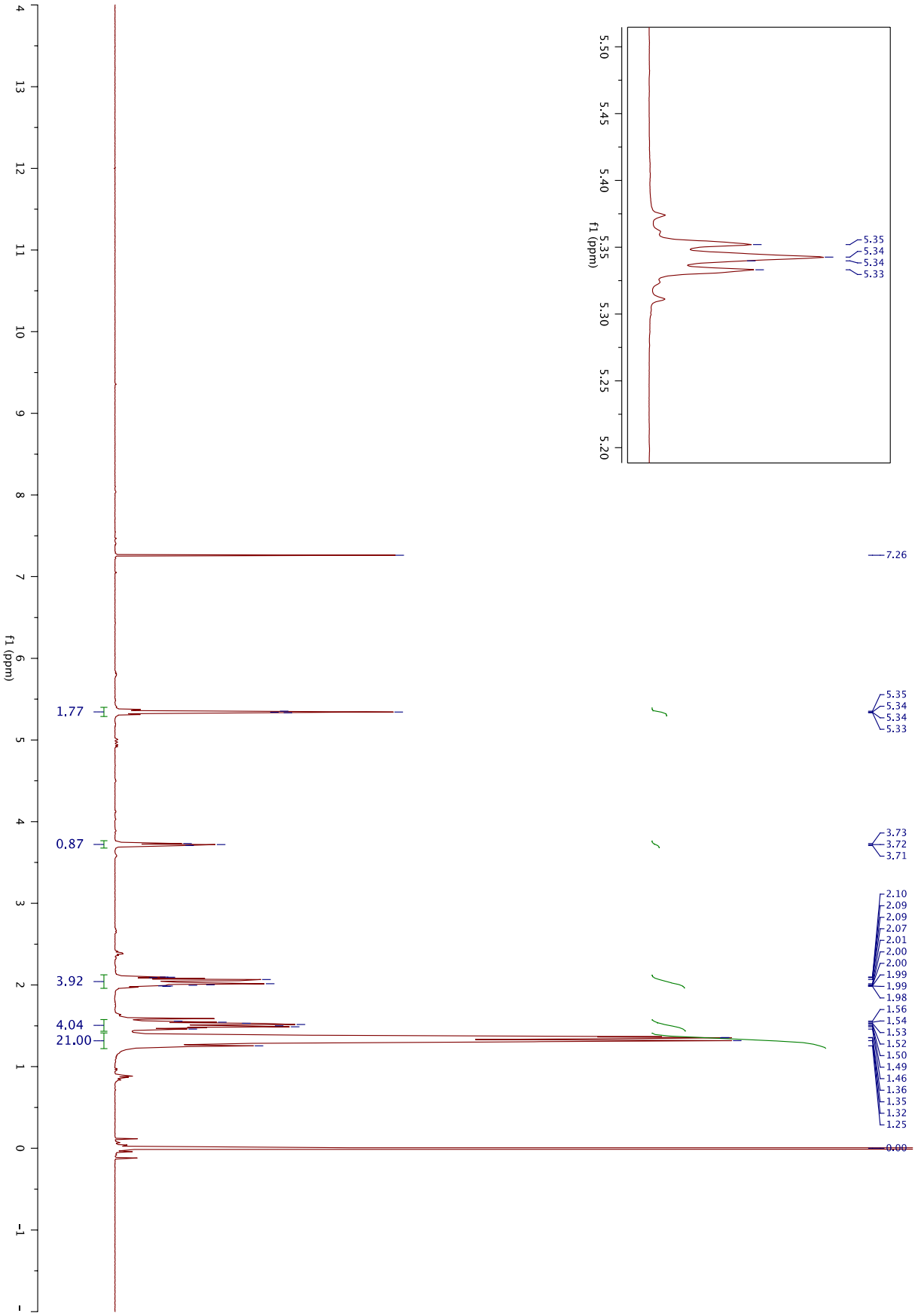


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **20**.

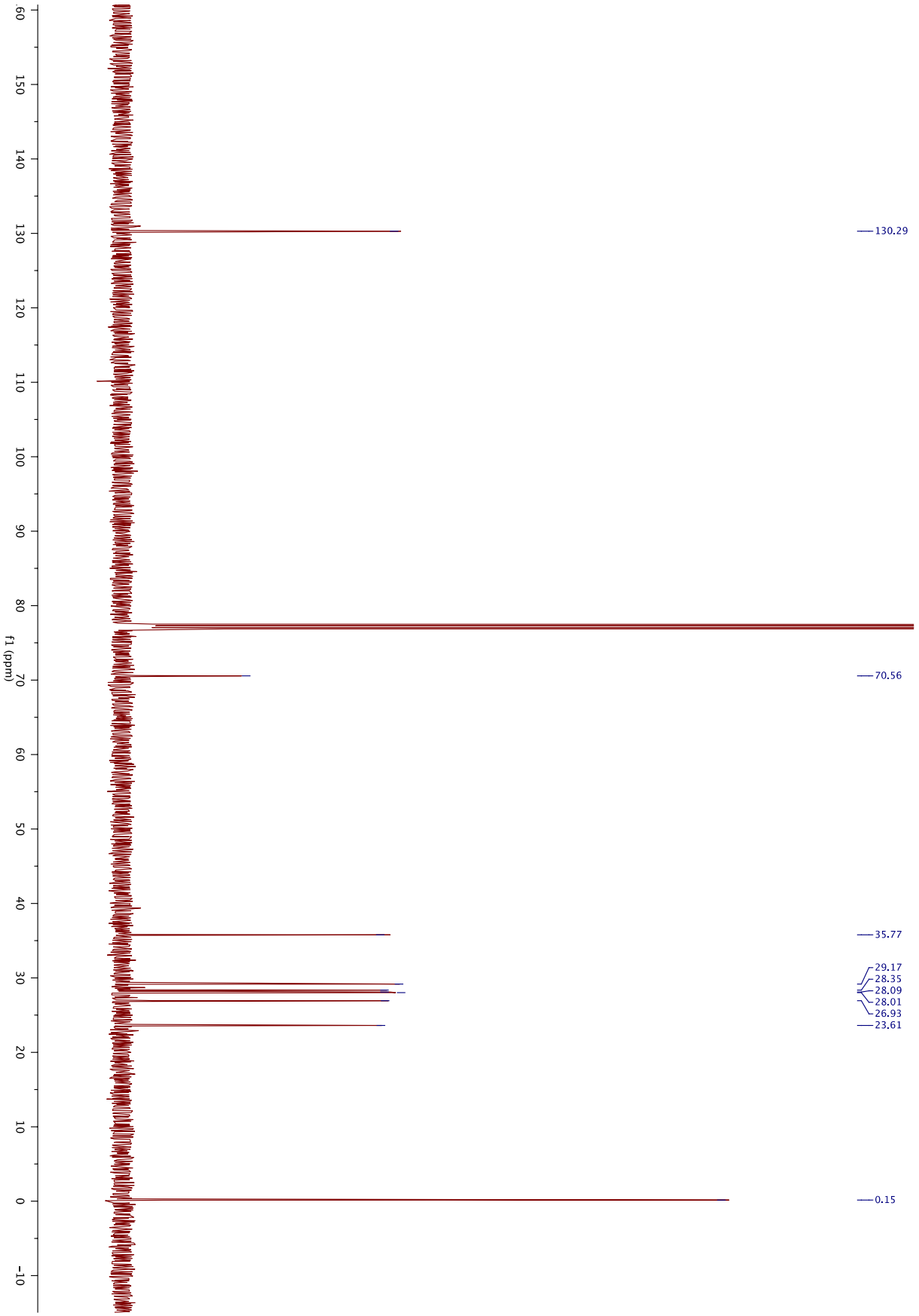


Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **20**.

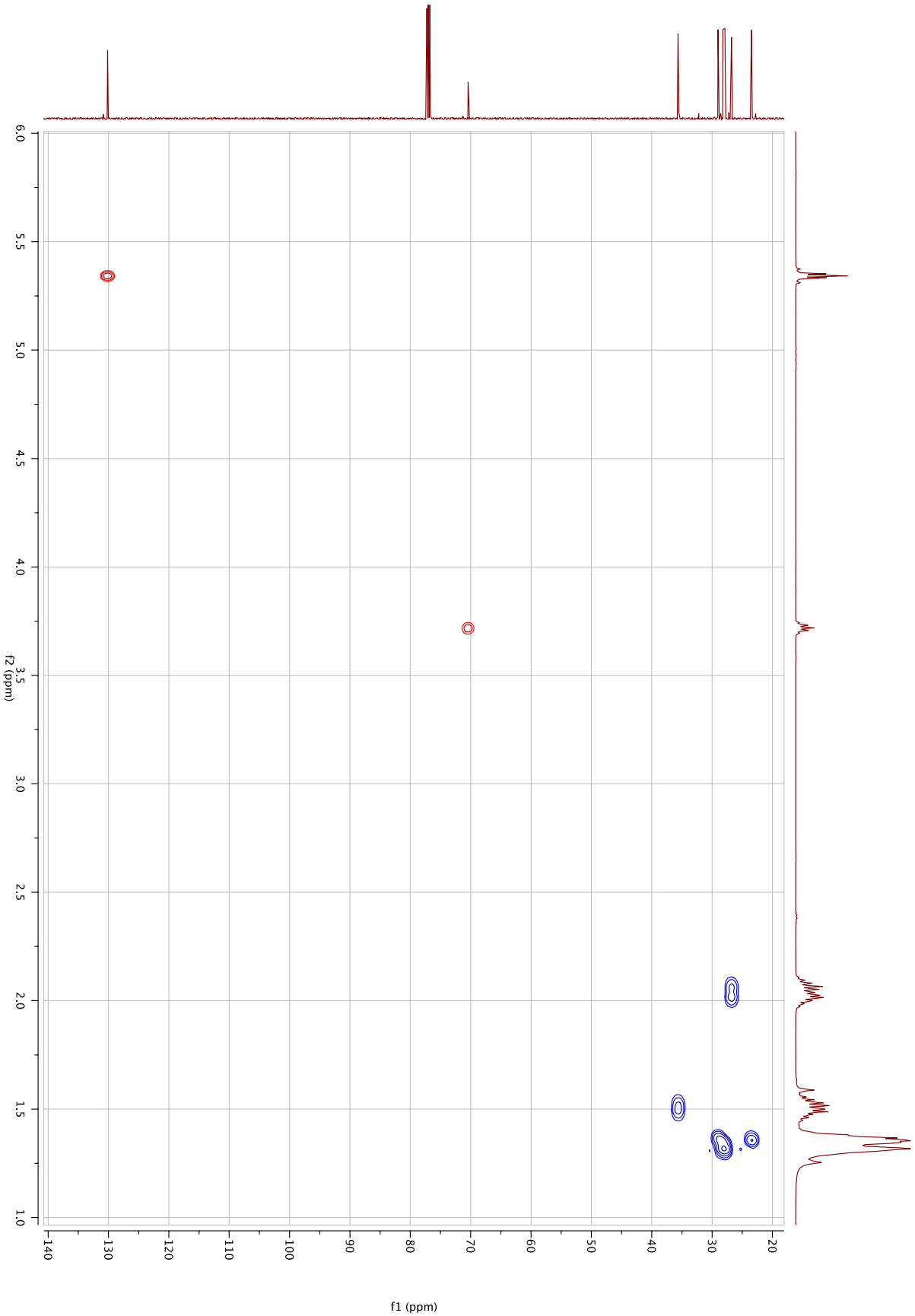


Figure S17. ^{1}H-^{13}C HSQC ($CDCl_3$) of **20**.