SUPPORTING INFORMATION

Improved Ruthenium Catalysts for *Z*-Selective Olefin Metathesis

Benjamin K. Keitz‡, Koji Endo‡, Paresma R. Patel, Myles B. Herbert, Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, 91125

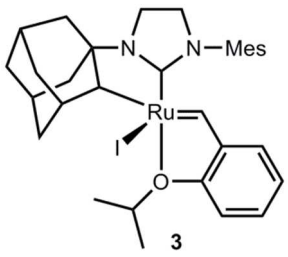
General Information.

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk line 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 with argon.[1] NMR solvents for air-sensitive compounds were dried over CaH_2 and vacuum transferred or distilled into a dry Schlenk flask and subsequently degassed with argon. Commercially available reagents were used as received unless otherwise noted. Substrates for olefin cross-metathesis (**12**, **15**, **17**-**24, 26, 27**) were degassed with argon and passed through a plug of neutral alumina (Brockmann I) prior to use. Complex **2** was synthesized according to the literature procedure.[2]

Standard NMR spectroscopy experiments were conducted on a Varian Inova 400 MHz spectrometer, while kinetic experiments were conducted on a Varian 500 MHz spectrometer equipped with an AutoX probe. Experiments and pulse sequences from Varian's Chempack 4 software were used. 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.[3]

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with a DB-Wax Polyethylene Glycol capillary column (J&W Scientific).

High-resolution mass spectrometry (HRMS) data was obtained on a JEOL MSRoute mass spectrometer using FAB+ ionization, except where specified.

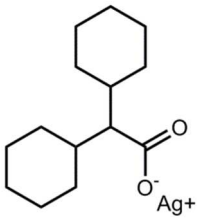


3

(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.
(3) www.mestrelab.com

Preparation of 3.

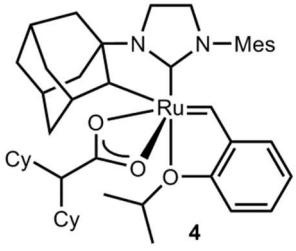
In a glovebox, a 250 mL RB flask was charged with **2** (491 mg, 0.731 mmol), NaI (548 mg, 3.65 mmol), and THF (25 mL). The resulting suspension was stirred for 1 h, at which point a color change from purple to brown had occurred. The solution was concentrated and the residue was dissolved in CH_2Cl_2 (ca. 100 mL), filtered through celite, and concentrated to a brown residue which was triturated with Et_2O until the washes were colorless to give **3** (332 mg, 65%) as a brown solid. ^{1}H NMR (400 MHz, C_6D_6) δ 13.42 (s, 1H), 7.38 (dd, *J* = 8, 4 Hz, 1H), 7.15 (m, 1H), 6.97 (br s, 1H), 6.80 (dt, *J* = 8, 1 Hz, 1H), 6.76 (br s, 1H), 6.64 (d, *J* = 8 Hz, 1H), 4.81 (sept, *J* = 4 Hz, 1H), 3.46 (q, *J* = 8 Hz, 1H), 3.37-3.30 (m, 1H), 3.11-3.06 (m, 2H), 2.61 (br s, 1H), 2.56 (s, 3H), 2.41 (s, 3H), 2.40 (br s, 1H), 2.13 (s, 3H), 2.03 (br s, 1H), 1.91 (d, *J* = 4 Hz, 3H), 1.86-1.79 (m, 2H), 1.65 (br s, 2H), 1.62 (d, *J* = 4 Hz, 3H), 1.59-1.57 (m, 1H),1.43-1.37 (m, 3H), 2.30 (br d, *J* = 8 Hz, 2H), 0.54 (br d, *J* = 16 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 236.56, 215.48, 154.59, 141.54, 139.13, 138.09, 137.45, 135.36, 125.96, 123.47, 122.63, 112.99, 81.52, 75.78, 63.40, 52.52, 42.24, 41.09, 39.39, 38.12, 37.54, 37.25, 33.81, 30.63, 29.64, 22.72, 21.76, 21.16, 20.99, 19.28. HRMS (FAB+): Calculated – 698.1316, Found – 698.1343.



4-Ag

Preparation of silver(I) 2,2-dicyclohexylacetate (4-Ag).

To 2,2-dicyclohexylcarboxylic acid (1.24 g, 5.54 mmol) and NaOH (193 mg, 4.82 mmol) was added H_2O (2.7 mL) and the solution was stirred for 15 min. $AgNO_3$ (676 mg, 3.99 mmol) dissolved in H_2O (2.6 mL) was added dropwise which caused immediate precipitation of a white solid. The suspension was stirred for 15 min after which the white precipitate was collected on a medium porosity frit and washed with H_2O, MeOH, and hexanes. After drying, **4-Ag** was recovered as a white solid (937 mg, 71%). Insolubility precluded analysis using NMR spectroscopy. MS (Laser Desorption Ionization): Calculated – 223.1704, Found – 223.1788.

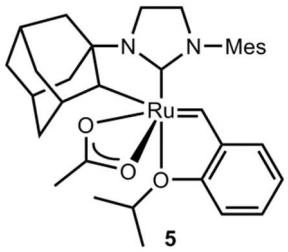


4

Preparation of 4.

In a glovebox, a 20 mL scintillation vial was charged with **3** (24 mg, 0.035 mmol) and **4-Ag** (13 mg, 0.038 mmol). THF (ca. 1 mL) was added and the color of the solution immediately changed from brown to deep purple. The reaction was stirred for 1 h and concentrated. The resulting purple residue was dissolved in C_6H_6, filtered through celite, and concentrated to give **4** (25 mg, 93%).

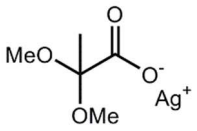
Note: Catalyst **4** would change colors from purple to brown upon the addition of solvents which were not rigorously purified of oxygen. Recrystallization from Et_2O at −35°C was used to purify **4** when this occurred. ^{1}H NMR (400 MHz, C_6D_6) δ 14.94 (s, 1H), 7.41 (dd, *J* = 8, 4 Hz, 1H), 7.25 (dt, *J* = 8, 4 Hz, 1H), 6.87-6.83 (m, 2H), 6.80 (br s, 1H), 6.72 (br d, *J* = 8 Hz, 1H), 4.78 (sept, *J* = 8 Hz, 1H), 4.08 (s, 1H), 3.45-3.13 (m, 4H), 2.47 (br s, 1H), 2.44 (s, 3H), 2.33 (s, 1H), 2.25 (s, 1H), 2.10-1.30 (m, 10H), 2.07 (br s, 1H), 1.98 (br d, *J* = 8 Hz, 3H), 1.88 (br d, *J* = 8 Hz, 4H), 1.79 (br s, 3H), 1.76 (br s, 2H), 1.64 (br s, 4H), 1.60 (d, *J* = 4 Hz, 4H), 3.34 (br d, *J* = 16 Hz, 3H), 1.39 (br s, 1H), 1.36 (d, *J* = 4 Hz, 5H), 1.17 (br d, *J* = 8 Hz, 2H), 1.07 (br d, *J* = 8 Hz, 2H), 0.63 (br d, *J* = 12 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 258.83, 214.74, 183.61, 153.90, 143.52, 137.70, 136.58, 136.43, 136.03, 129.47, 129.20, 124.98, 122.86, 122.83, 113.34, 73.83, 67.67, 62.30, 57.15, 51.31, 42.77, 40.96, 40.04, 37.88, 37.58, 36.76, 33.30, 30.71, 29.60, 21.68, 21.35, 20.86, 18.65, 18.49. HRMS (FAB+, (M+H)−H_2): Calculated – 793.3883, Found – 793.3894.



5

Preparation of 5.

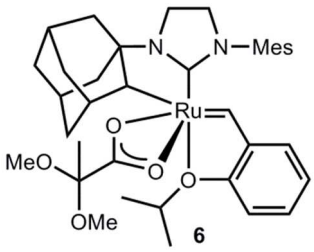
Catalyst **5** (23 mg, 80%) was prepared in a manner analogous to catalyst **4**. **3** (32 mg, 0.046 mmol), AgOAc (11 mg, 0.069 mmol), THF (ca. 1 mL). ^{1}H NMR (400 MHz, C_6D_6) δ 14.95 (s, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.88 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.77 (br s, 1H), 6.70 (br s, 1H), 6.65 (br d, *J* = 8.4 Hz, 1H), 4.76 (sept, *J* = 6.0 Hz, 1H), 4.06 (s, 1H), 3.47 (q, *J* = 8.8 Hz, 1H), 3.38-3.21 (m, 4H), 2.43 (s, 3H), 2.40 (br s, 1H), 2.33 (s, 3H), 2.15 (br s, 4H), 2.15-1.04 (m, 2H), 1.98-1.95 (m, 1H), 1.87-1.83 (m, 1H), 1.78 (s, 3H), 1.69 (br s, 1H), 1.57 (d, *J* = 6.4 Hz, 3H), 1.56-1.53 (m, 2H), 1.22-1.15 (m, 2H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.73 (br d, *J* = 12 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 259.69, 215.65, 180.15, 154.57, 143.79, 137.76, 137.41, 136.81, 136.42, 129.55, 129.24, 125.51, 123.20, 123.19, 112.90, 74.01, 68.79, 67.84, 62.82, 51.44, 43.38, 41.62, 40.64, 38.27, 37.97, 37.72, 33.59, 31.21, 30.03, 25.84, 24.43, 21.35, 21.04, 20.73, 18.75, 18.48. HRMS (FAB+, (M+H)−H_2): Calculated – 629.2318, Found – 629.2345.



6-Ag

Preparation of silver(I) 2,2-dimethoxypropanoate (6-Ag).

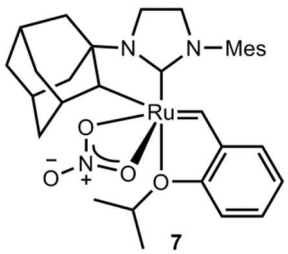
A 100 mL RB flask was charged with 2,2-dimethoxypropanoic acid (488 mg, 3.64 mmol), Ag_2O (507 mg, 2.19 mmol), MeCN (20 mL), and H_2O (6 mL). The solution was shielded from light and stirred at RT under Ar for 5 h. The suspension was filtered through celite, washing with MeCN, and the filtrate was concentrated to a white solid which was washed with hexanes and collected by filtration to give **6-Ag** (469 mg, 53%). ^{1}H NMR (400 MHz, D_2O) δ 3.21 (s, 6H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, D_2O) δ 176.37, 101.51, 49.34, 20.26. MS (Laser Desorption Ionization): Calculated – 133.0506, Found – 133.0539.



6

Preparation of 6.

Catalyst **6** (31 mg, 89%) was prepared in a manner analogous to catalyst **4**. **3** (35 mg, 0.050 mmol), **6-Ag** (13 mg, 0.055 mmol), THF (ca. 1 mL). ^{1}H NMR (600 MHz, C_6D_6) δ 14.88 (s, 1H), 7.43 (br d, *J* = 12 Hz, 1H), 7.23 (t, *J* = 6 Hz, 1H), 6.94 (br s, 1H), 6.86 (t, *J* = 6 Hz, 1H), 6.74-6.71 (m, 2H), 4.87 (br s, 1H), 4.16 (s, 1H), 3.50-3.19 (m, 10H), 2.47 (br s, 1H), 2.45 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H), 2.13-2.08 (m, 2H), 2.01 (br d, *J* = 12 Hz, 1H), 1.96 (br d, *J* = 12 Hz, 1H), 1.82 (br d, *J* = 12 Hz, 1H), 1.66 (br s, 1H), 1.63 (d, *J* = 6 Hz, 3H), 1.57-1.54 (m, 1H), 1.50-1.48 (m, 1H), 1.43 (br d, *J* = 12 Hz, 1H), 1.38 (s, 3H), 1.27 (br d, *J* = 6 Hz, 3H), 1.17 (br d, *J* = 12 Hz, 1H), 1.10-1.09 (m, 2H), 0.68 (br d, *J* = 6 Hz, 1H). ^{13}C NMR (151 MHz, C_6C_6) δ 259.06, 216.37, 177.95, 154.78, 144.04, 138.48, 137.86, 136.61, 136.38, 130.46, 129.48, 125.96, 123.52, 123.39, 113.89, 99.58, 75.37, 69.60, 63.10, 51.94, 43.58, 41.83, 40.83, 38.50, 38.32, 37.63, 33.94, 31.45, 30.30, 21.70, 21.41, 21.17, 20.99, 19.11, 18.88. HRMS (FAB+, (M+H)–H_2): Calculated – 703.2685, Found – 703.2682.

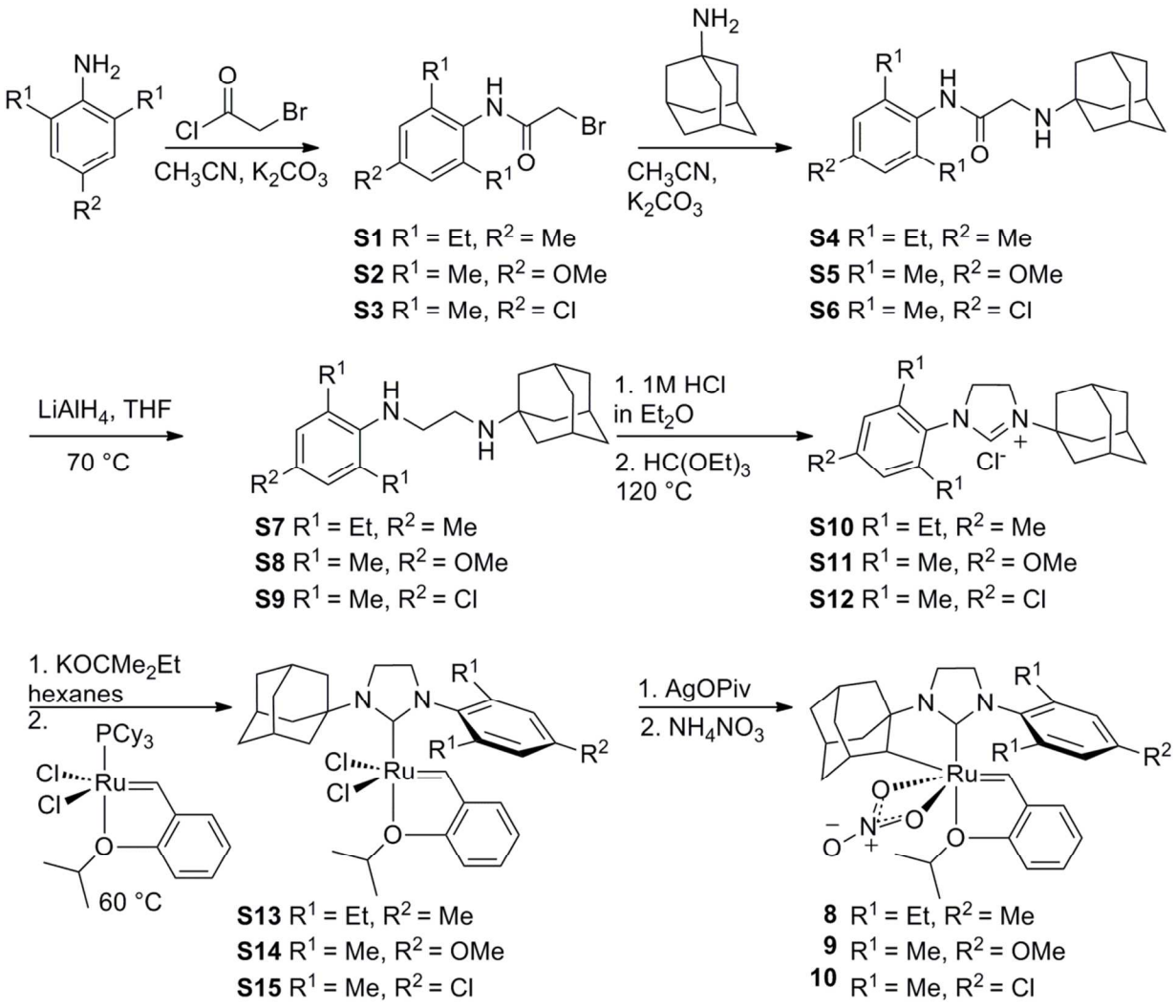


7

Preparation of 7.

Method A: In a glovebox, a 20 mL scintillation vial was charged with **3** (112 mg, 0.161 mmol), $AgNO_3$ (409 mg, 2.41 mmol), and THF (6 mL). The reaction was stirred vigorously until a color change from brown to dark purple was observed (ca. 3-5 min). At this point, the reaction was immediately concentrated and the resulting residue was dissolved in C_6H_6, filtered, and concentrated. The crude product was triturated with Et_2O several times, until the washes were colorless, to give **7** (73 mg, 72%) as a purple solid. ^{1}H NMR (400 MHz, C_6D_6) δ 15.22 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 4.57 (sept, *J* = 6.0 Hz, 1H), 4.17 (s, 1H), 3.43 (q, *J* = 9.6 Hz, 1H), 3.28 – 3.15 (m, 3H), 2.38 (d, *J* = 8.4 Hz, 6H), 2.25 (br s, 1H), 2.15 – 2.09 (m, 4H), 2.03 – 1.97 (m, 2H), 1.90 – 1.87 (m, 1H), 1.77 (br d, *J* = 15.2 Hz, 1H), 1.65 (br s, 1H), 1.55 – 1.47 (m, 2H), 1.42 (d, *J* = 5.2 Hz, 3H), 1.14 – 1.10 (m, 3H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.58 (br d, *J* = 12 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 265.80, 265.55, 214.16, 154.72, 143.60, 137.69, 137.40, 136.24, 135.45, 130.11, 129.36, 126.83, 123.38, 123.35, 113.00, 74.32, 66.78, 63.05, 51.36, 43.14, 41.84, 40.34, 37.95, 37.81, 37.65, 33.33, 30.98, 29.83, 21.25, 21.09, 20.28, 18.56, 17.44. HRMS (FAB+, M–NO_3): Calculated – 571.2263, Found – 571.2273.

Method B: In a glovebox, a 20 mL scintillation vial was charged with **2** (128 mg, 0.190 mmol), NH_4NO_3 (457 mg, 5.71 mmol), and THF (ca. 10 mL). The reaction was stirred until completion as determined by ^{1}H NMR spectroscopy (ca. 1h) and concentrated. The residue was purified as described in Method A to give **7** (98 mg, 82%).



Scheme S1. Synthesis of catalysts **8**, **9**, and **10**.

Preparation of S1.

A solution of 2,6-diethyl-4-methylaniline (1.63 g, 10.0 mmol) and CH_3CN (20 mL) was treated with K_2CO_3 (2.76 g, 20.0 mmol). Bromoacetyl chloride (830 ul, 10.0 mmol) was added dropwise, and the reaction mixture was stirred at 25 °C over 12-16 h. The mixture was filtered over celite, concentrated under reduced pressure, and recrystallized from CH_2Cl_2-hexanes providing **S1** (1.55 g, 55%) as a white powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.68 (s, 1H), 6.95 (s, 2H), 4.08 (s, 2H), 2.54 (q, 4H, *J* = 7.5 Hz), 2.32 (s, 3H), 1.19 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.8, 141.2, 138.2, 129.1, 127.4, 29.2, 24.8, 21.3, 14.6; HRMS (FAB+) *m/z*: Calculated ([M + H]) 284.0650, Found 284.0654 ([M + H]).

Preparation of S2.

Prepared from 4-methoxy-2,6-dimethylaniline[4] (520 mg, 3.44 mmol) and bromoacetyl chloride (286 ul, 3.44 mmol) following the procedure detailed for **S1** providing **S2** (750 mg, 80%) as a white powder: 1H NMR (CDCl3, 500 MHz) δ 7.66 (s, 1H), 6.62 (s, 2H), 4.04 (s, 2H), 3.77 (s, 3H), 2.20 (s, 6H); 13C NMR (CDCl3, 125 MHz) δ 164.5, 158.7, 136.9, 125.9, 113.6, 55.4, 29.2, 18.6; HRMS (EI+) m/z: Calculated 271.0208, Found 271.0198.

Preparation of S3.

Prepared from 4-chloro-2,6-dimethylaniline (1.55 g, 3.44 mmol) and bromoacetyl chloride (286 ul, 10.0 mmol) following the procedure detailed for **S1** providing **S3** (0.75 g, 28%) as a white powder: 1H NMR (CDCl3, 300 MHz) δ 7.10 (s, 2H), 4.07 (s, 2H), 2.22 (s, 6H); 13C NMR ((CD3)2SO, 125 MHz) δ 164.9, 137.5, 133.3, 130.7, 127.3, 29.1, 17.6; HRMS (FAB+) m/z: Calculated 277.9761, Found 277.9755.

Preparation of S4.

A solution of **S1** (950 mg, 3.36 mmol) and 1-adamantylamine (760 mg, 5.0 mmol) in CH_3CN (10 mL) was treated with K_2CO_3 (700 mg, 5.1 mmol) and allowed to stir at 85 °C for 16 h. The reaction mixture was then filtered over celite and concentrated under reduced pressure. Flash chromatography (SiO_2, 4% MeOH-DCM) provided S4 (1.11 g, 93%) as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.04 (s, 1H), 6.93 (s, 2H), 3.42 (s, 2H), 2.54 (q, 4H, *J* = 7.5 Hz), 2.31 (s, 3H), 2.11 (br s, 3H), 1.58-1.73 (m, 13H), 1.17 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.2, 140.9, 137.1, 130.2, 127.2, 51.1, 44.1, 42.9, 36.5, 29.5, 25.1, 21.2, 14.7; HRMS (FAB+) *m/z*: Calculated ([M + H]) 355.2749, Found 355.2758 ([M + H]).

Preparation of S5.

Prepared from **S2** (700 mg, 2.58 mmol) and 1-adamantylamine (590 mg, 3.9 mmol) following the procedure detailed for **S4** providing **S5** (800 mg, 91%) as an off-white solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.94 (s, 1H), 6.62 (s, 2H), 3.75 (s, 3H), 3.40 (s, 2H), 2.18 (s, 6H), 2.10 (br m, 3H), 1.57-1.71 (m, 13H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.9, 158.1, 136.4, 127.0, 113.4, 55.3, 51.1, 44.0, 42.9, 36.5, 29.5, 18.9; HRMS (EI+) *m/z*: Calculated 342.2307, Found 342.2292.

Preparation of S6.

Prepared from **S3** (750 mg, 2.73 mmol) and 1-adamantylamine (620 mg, 4.1 mmol) following the procedure detailed for **S4** providing **S6** (715 mg, 77%) as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.06 (s, 1H), 7.05 (s, 2H), 3.41 (s, 2H), 2.18 (s, 6H), 2.10 (br m, 3H), 1.57-1.71 (m, 13H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.6, 136.9, 132.8, 132.1, 128.0, 51.2, 44.1, 42.9, 36.5, 29.5, 18.6; HRMS (EI+) *m/z*: Calculated 347.1890, Found 347.1905.

(4) Blum, A. P.; Ritter, T.; Grubbs, R. H. *Organometallics* **2007**, *26*, 2122.

Preparation of S7.

Under an atmosphere of argon, a solution of **S4** (1.0 g, 2.82 mmol) in THF (15 mL) at 0 °C was treated with $LiAlH_4$ (325 mg, 8.5 mmol). The reaction mixture was allowed to warm to 25 °C and stirred at 65 °C for 36 h. The reaction mixture was allowed to cool to 0 °C and 1 mL H_2O and 1 mL NaOH were added slowly. The mixture was diluted with EtOAc, filtered, and partitioned between EtOAc-H_2O. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure providing **S7** (0.95 g, 99%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.88 (s, 2H), 2.98 (m, 2H), 2.85 (m, 2H), 2.70 (q, 4H, *J* = 7.5 Hz), 2.30 (s, 3H), 2.11 (br s, 3H), 1.62-1.74 (m, 13H), 1.27 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.88, 136.3, 131.5, 127.3, 51.1, 50.2, 43.0, 40.6, 36.8, 29.6, 24.4, 20.8, 15.0; HRMS (FAB+) *m/z*: Calculated ([M + H]) 341.2957, Found 341.2966 ([M + H]).

Preparation of S8.

Prepared from **S5** (735 mg, 2.15 mmol) and $LiAlH_4$ (245 mg, 6.45 mmol) following the procedure detailed for **S7** providing **S8** (685 mg, 98%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.56 (s, 2H), 3.73 (s, 3H), 2.93 (dd, 2H, *J* = 6.5, 5.0 Hz), 2.79 (dd, 2H, *J* = 6.5, 5.0 Hz), 2.29 (s, 6H), 2.07 (br s, 3H), 1.58-1.71 (m, 13H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.5, 139.8, 131.4, 113.8, 55.3, 50.2, 50.0, 43.0, 40.7, 36.8, 29.6, 18.8; HRMS (FAB+) *m/z*: Calculated ([M + H]) 329.2593, Found 329.2577 ([M + H]).

Preparation of S9.

Prepared from **S6** (660 mg, 1.91 mmol) and $LiAlH_4$ (218 mg, 5.73 mmol) following the procedure detailed for **S7** providing **S9** (634 mg, 99%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.92 (s, 2H), 2.96 (m, 2H), 2.75 (m, 2H), 2.25 (s, 6H), 2.05 (br s, 3H), 1.58-1.71 (m, 13H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.2, 130.4, 128.1, 125.5, 50.1, 49.2, 42.9, 40.3, 36.6, 29.5, 18.6; HRMS (FAB+) *m/z*: Calculated ([M + H]) 333.2098, Found 333.2094 ([M + H]).

Preparation of S10.

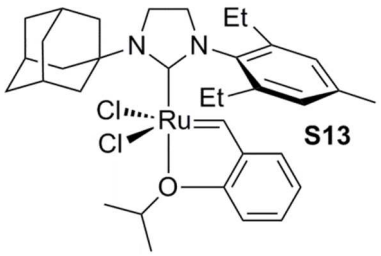
A solution of **S7** (950 mg, 2.79 mmol) in Et_2O (5 mL) was treated with 2M HCl in Et_2O (2.80 mL) to provide a white solid that was filtered and dried. A solution of triethylorthoformate (5 mL) was added to this white solid and the mixture was allowed to stir at 120 °C for 30 min. The reaction mixture was concentrated under reduced pressure to provide an off-white powder that was filtered, washed with hexanes and dried to provide **S10** (0.55 g, 52%) as a white powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.65 (s, 1H), 6.97 (s, 2H), 4.48 (t, 2H, *J* = 10.0 Hz), 4.31 (t, 2H, *J* = 10.0 Hz), 2.53-2.69 (m, 4H), 2.33 (s, 3H), 2.26 (br m, 3H), 2.10 (d, 6H, *J* = 2.5 Hz), 1.73 (t, 6H, *J* = 2.5 Hz), 1.26 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.2, 140.9, 140.3, 129.6, 127.6, 57.9, 52.1, 45.4, 41.0, 35.3, 29.1, 24.0, 21.3, 14.8; HRMS (FAB+) *m/z*: Calculated ([M+]) 351.2800, Found 351.2817 ([M+]).

Preparation of S11.

Prepared from **S8** (685 mg, 2.10 mmol) and triethylorthoformate (5 mL) following the procedure detailed for **S10** providing **S11** (565 mg, 72%) as a white powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.04 (s, 1H), 6.49 (s, 2H), 4.27 (dd, 2H, *J* = 9.2, 12.3 Hz), 4.12 (dd, 2H, *J* = 9.2, 12.3 Hz), 3.66 (s, 3H), 2.21 (s, 6H), 2.13 (br m, 3H), 2.01 (d, 6H, *J* = 3.0 Hz), 1.62 (t, 6H, *J* = 2.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.7, 156.8, 137.0, 126.5, 114.0, 57.8, 55.3, 50.9, 45.1, 40.8, 35.3, 29.1, 18.4; HRMS (FAB+) *m/z*: Calculated ([M+]) 339.2436, Found 339.2448 ([M+]).

Preparation of S12.

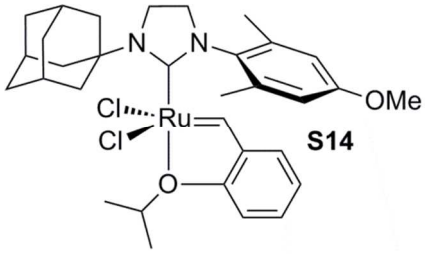
Prepared from **S9** (630 mg, 1.91 mmol) and triethylorthoformate (5 mL) following the procedure detailed for **S10** providing **S12** (600 mg, 83%) as a white powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.47 (s, 1H), 6.98 (s, 2H), 4.26 (m, 2H), 4.14 (m, 2H), 2.24 (s, 6H), 2.14 (br s, 3H), 2.01 (d, 6H, *J* = 3.0 Hz), 1.63 (t, 6H, *J* = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.3, 137.7, 135.1, 132.3, 128.8, 58.1, 50.6, 45.1, 40.9, 35.3, 29.1, 18.2; HRMS (FAB+) *m/z*: Calculated ([M+]) 343.1941, Found 343.1932 ([M+]).



S13

Preparation of S13.

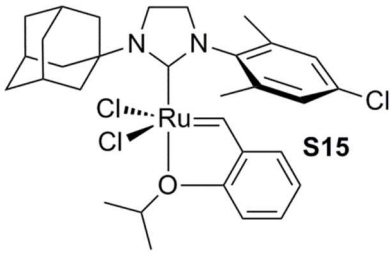
In a glove box, a solution of **S10** (200 mg, 0.52 mmol) in hexanes (6 mL) was treated with $KCOMe_2Et$ (75 mg, 0.57 mmol), and the mixture was allowed to stir at 35 °C for 1 h. The reaction mixture was then treated with $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O^iPrC_6H_4)$ (312 mg, 0.52 mmol), removed from the glove box, and allowed to stir at 65 °C for 3 h. The precipitated solids were filtered and washed well with hexanes to provide **S13** (335 mg, 96%) as a green powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 16.87 (s, 1H), 7.55 (ddd, 1H, *J* = 1.7, 7.4, 8.8 Hz), 7.15 (s, 2H), 6.91 (m, 2H), 6.83 (dd, 1H, *J* = 1.5, 7.5 Hz), 5.06 (hept, 1H, *J* = 6.1 Hz), 4.02 (dd, 2H, *J* = 8.4, 11.4 Hz), 3.85 (dd, 2H, *J* = 8.4, 11.4 Hz), 2.95 (br s, 6H), 2.70 (dq, 2H, *J* = 7.6, 15.3 Hz), 2.55 (dq, 2H, *J* = 7.6, 15.3 Hz), 2.53 (s, 3H), 2.41 (br s, 3H), 1.94 (d, 3H, *J* = 12.0 Hz), 1.83 (d, 3H, *J* = 12.0 Hz), 1.63 (d, 6H, *J* = 6.1 Hz), 1.13 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 311.7, 208.6, 152.4, 145.6, 143.1, 138.63, 138.59, 130.7, 127.1, 123.6, 122.6, 113.3, 74.2, 57.7, 52.8, 44.5, 42.2, 36.2, 30.0, 23.3, 22.5, 21.7, 14.1; HRMS (FAB+) *m/z*: Calculated 670.2031, Found 670.2019.



S14

Preparation of S14.

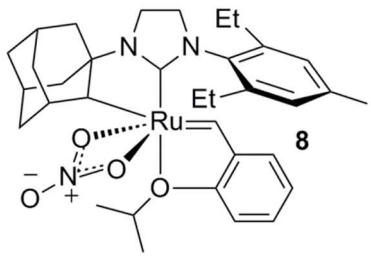
Prepared from **S11** (100 mg, 0.27 mmol) and $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O^iPrC_6H_4)$ (160 mg, 0.27 mmol) following the procedure detailed for **S13** providing **S14** (138 mg, 78%) as a green powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 16.98 (s, 1H), 7.56 (ddd, 1H, *J* = 1.9, 7.2, 8.9 Hz), 6.93 (m, 3H), 6.78 (s, 2H), 5.09 (hept, 1H, *J* = 6.1 Hz), 4.04 (dd, 2H, *J* = 8.5, 11.9 Hz), 1.89 (s, 3H), 3.85 (dd, 2H, *J* = 8.5, 11.9 Hz), 2.95 (br s, 6H), 2.41 (s, 3H), 2.26 (s, 6H), 1.93 (d, 3H, *J* = 12.0 Hz), 1.83 (d, 3H, *J* = 12.0 Hz), 1.63 (d, 6H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 312.4, 208.3, 159.4, 152.4, 145.92, 145.90, 139.6, 135.3, 130.8, 124.0, 122.8, 114.0, 113.3, 74.2, 57.2, 55.7, 51.3, 44.6, 42.2, 36.2, 30.0, 22.5, 18.8; HRMS (FAB+) *m/z*: Calculated 658.1667, Found 658.1645.



S15

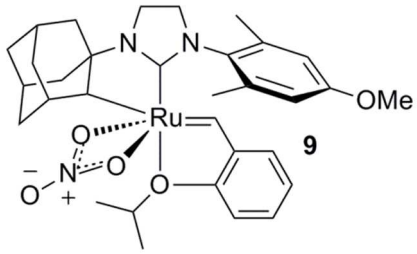
Preparation of S15.

Prepared from **S12** (100 mg, 0.27 mmol) and $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O^iPrC_6H_4)$ (160 mg, 0.27 mmol) following the procedure detailed for **S13** providing **S15** (136 mg, 78%) as a green powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 16.89 (s, 1H), 7.59 (m, 1H), 7.26 (m, 2H), 6.96 (m, 3H), 5.10 (hept, 1H, *J* = 6.2 Hz), 4.05 (dd, 2H, *J* = 8.4, 11.6 Hz),), 3.83 (dd, 2H, *J* = 8.5, 11.6 Hz), 2.93 (br s, 6H), 2.41 (s, 3H), 2.28 (s, 6H), 1.93 (d, 3H, *J* = 12.0 Hz), 1.84 (d, 3H, *J* = 12.5 Hz), 1.63 (d, 6H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 310.8, 208.2, 152.4, 145.8, 140.7, 140.4, 133.9, 131.0, 128.8, 124.0, 122.9, 113.3, 74.3, 57.4, 50.9, 44.7, 42.1, 36.1, 30.0, 22.4, 18.4; HRMS (FAB+) *m/z*: Calculated 664.1143, Found 664.1151.



Preparation of 8.

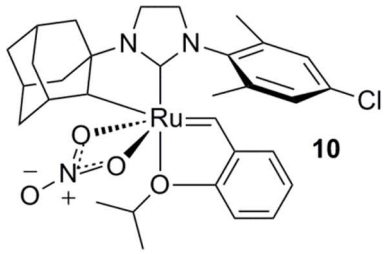
In a glovebox, a solution of **S13** (98 mg, 0.14 mmol) and THF (5 mL) was treated with AgOPiv (92 mg, 0.44 mmol). The reaction mixture was allowed to stir at 25 °C for 30 min and a color change from brown to purple was observed. The mixture was immediately filtered over celite and concentrated. The residue was triturated with Et_2O and dried to provide a purple solid. The purple solid was then taken up in THF (3 mL), treated with NH_4NO_3 (350 mg, 4.4 mmol) and allowed to stir for 1 h. The reaction mixture was concentrated, taken up in benzene, and filtered over celite. The filtrate was dried and triturated with Et_2O until the washes were colorless providing **8** (30 mg, 31%) as a purple powder: ^{1}H NMR (C_6D_6, 500 MHz) δ 15.19 (s, 1H), 7.42 (dd, 1H, *J* = 1.5, 7.5 Hz) 7.18 (ddd, 1H, *J* = 1.5, 7.5, 8.5 Hz), 7.06 (d, 1H, *J* = 1.0 Hz), 6.83 (dt, 1H, *J* = 1.0, 7.5 Hz), 6.79 (d, 1H, *J* = 1.5 Hz), 6.47 (d, 1H, *J* = 8.5 Hz), 4.55 (hept, 1H, *J* = 6.3 Hz), 4.18 (s, 1H), 3.55 (q, 1H, *J* = 10.7 Hz), 3.39 (m, 1H), 3.17-3.29 (m, 2H), 3.06 (dq, 1H, *J* = 7.7, 15.3 Hz), 2.86-3.00 (m, 2H), 2.63 (dq, 1H, *J* = 7.5, 15.0 Hz), 2.24 (m, 1H), 2.15 (s, 3H), 2.10 (m, 1H), 1.96-2.02 (m, 2H), 1.89 (d, 1H, *J* = 11.0 Hz), 1.77 (dd, 1H, *J* = 1.5, 12.0 Hz), 1.66 (m, 1H), 1.44-1.55 (m, 3H),1.42 (d, 3H, *J* = 6.5 Hz), 1.28 (t, 3H, *J* = 7.5 Hz), 1.20 (t, 3H, *J* = 7.5 Hz), 1.10 (m, 2H), 0.94 (d, 3H, *J* = 6.0 Hz), 0.59 (d, 1H, *J* = 12.0 Hz); ^{13}C NMR (C_6D_6, 100 MHz) δ 214.3, 154.7, 143.54, 143.50, 141.1, 137.8, 134.9, 128.5, 127.0, 126.8, 123.37, 123.33, 113.0, 74.3, 66.7, 63.0, 52.9, 43.0, 41.8, 40.3, 37.9, 37.77, 37.73, 33.3, 30.9, 29.8, 24.1, 23.4, 21.4, 21.2, 20.2, 15.7, 15.3; HRMS (FAB+) *m/z*: Calculated 661.2454, Found 661.2422.



Preparation of 9.

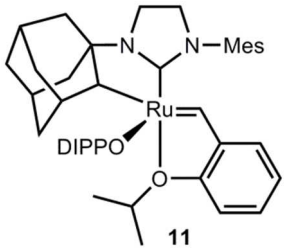
Prepared from **S14** (118 mg, 0.179 mmol) and AgOPiv (112 mg, 0.54 mmol) following the procedure detailed for **8** providing **9** (16.5 mg, 14%) as a purple powder: ^{1}H NMR (C_6D_6, 400 MHz) δ 15.21 (s, 1H), 7.37 (dd, 1H, *J* = 1.6, 7.6 Hz), 7.19 (m, 1H), 6.82 (m, 2H), 6.44 (d, 1H, *J* = 2.8 Hz), 6.49 (d,

1H, *J* = 8.4 Hz), 4.58 (hept, 1H, *J* = 6.3 Hz), 4.16 (s, 1H), 3.40 (m, 1H), 3.33 (s, 3H), 3.10-3.30 (m, 3H), 2.37 (d, 6H, *J* = 2.8 Hz), 2.24 (m, 1H), 2.11 (m, 1H), 1.96-2.01 (m, 2H), 1.85-1.92 (m, 1H), 1.73-1.81 (m, 1H), 1.65 (m, 1H), 1.48 (m, 3H), 1.44 (d, 3H, *J* = 6.4 Hz), 1.06 (m, 2H), 0.97 (d, 3H, *J* = 6.0 Hz), 0.58 (d, 1H, *J* = 12.4 Hz); ^{13}C NMR (C_6D_6, 100 MHz) δ 214.4, 159.2, 154.7, 143.6, 139.3, 137.0, 131.8, 128.5, 126.8, 123.38, 123.35, 114.2, 113.0, 74.3, 66.7, 63.0, 54.8, 51.5, 43.1, 41.8, 40.3, 37.9, 37.8, 37.6, 33.3, 30.9, 29.8, 21.2, 20.2, 18.8, 17.8; HRMS (FAB+) *m/z*: Calculated 648.2012, Found 648.2036.



Preparation of 10.

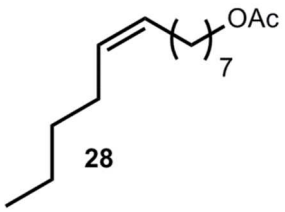
Prepared from **S15** (195 mg, 0.294 mmol) and AgOPiv (185 mg, 0.865 mmol) following the procedure detailed for **8** providing **10** (55 mg, 28%) as a purple powder: ^{1}H NMR (C_6D_6, 400 MHz) δ 15.08 (s, 1H), 7.36 (dd, 1H, *J* = 1.6, 7.6 Hz), 7.16-7.24 (m, 2H), 6.81-6.87 (m, 2H), 6.51 (d, 1H, *J* = 8.4 Hz), 4.58 (hept, 1H, *J* = 6.2 Hz), 4.09 (s, 1H), 3.10-3.33 (m, 4H), 2.21 (m, 1H), 2.19 (d, 6H, *J* = 6.0 Hz), 2.10 (m, 1H), 1.96 (m, 1H), 1.85 (m, 2H), 1.75 (m, 1H), 1.63 (m, 1H), 1.46 (m, 3H), 1.41 (d, 3H, *J* = 6.4 Hz), 1.07 (m, 2H), 0.96 (d, 3H, *J* = 6.0 Hz), 0.54 (d, 1H, *J* = 12.4 Hz); ^{13}C NMR (C_6D_6, 100 MHz) δ 265.9, 214.2, 154.7, 143.5, 140.0, 138.0, 137.4, 133.4, 129.2, 128.6, 127.1, 123.4, 123.3, 113.0, 74.4, 66.7, 63.2, 51.0, 43.0, 41.8, 40.2, 37.8, 37.7, 37.6, 33.2, 30.9, 29.7, 21.2, 20.2, 18.3, 17.3; HRMS (FAB+) *m/z*: Calculated 652.1517, Found 652.1529.



Preparation of 11.

In a glove box, **2** (52.1 mg, 77.5 μmol), potassium 2,6-diisopropylphenoxide (83.9 mg, 388 μmol) and C6H6 (5.0 ml) were added into a 20 ml vial equipped with a stir bar. The reaction mixture was stirred at room temperature for 30 min and filtered. The filtrate was evaporated and the resulting solid was dissolved in small amount of Et_2O and recrystallized at −35 °C. **11** was obtained as dark brown crystals

(54 mg, 93%). ^{1}H NMR (500 MHz, C_6D_6): δ 14.02 (s, 1H), 7.39 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.15 (br s, 1H), 7.06 (dt, *J* = 6.5, 2 Hz, 1H), 6.95 (br s, 1H), 6.83 (q, *J* = 7.5 Hz, 2H), 6.77 (s, 1H), 6.58-6.57 (m, 2H), 4.32 (sept, *J* = 6.4 Hz, 1H), 4.0 (br s, 1H), 3.89 (s, 1H), 3.40 (q, *J* = 11 Hz, 1H), 3.27 (dt, *J* = 10.5, 5 Hz, 1H), 3.10 (m, 2H), 2.57 (s, 3H), 2.33 (s, 3H), 2.30 (br s, 1H), 2.20 (br s, 1H), 2.11 (br s, 1H), 2.03 (s, 3H), 2.01 (br s, 1H), 1.94-1.93 (m, 1H), 1.82 (br t, *J* = 9 Hz, 2H), 1.62 (br s, 1H), 1.55-1.38 (m, 9H), 1.25 (d, *J* = 6.4 Hz, 3H), 1.11 (br d, *J* = 10.5 Hz, 2H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.59-0.41 (br m, 7H). ^{13}C NMR (126 MHz, C_6D_6) δ 234.91, 214.14, 150.56, 140.03, 136.31, 134.41, 134.07, 132.39, 127.15, 126.11, 121.95, 119.99, 119.76, 112.66, 110.58, 72.80, 66.00, 60.25, 49.43, 40.14, 38.44, 37.35, 34.95, 34.83, 34.23, 30.62, 27.99, 26.83, 18.48, 18.15, 17.71, 15.97, 15.73. HRMS (FAB+): Calculated: 748.3542, Found: 748.3576.



28

Preparation of 28.

In a glovebox, a 20 mL vial was charged with **27** (520 μL, 2.5 mmol), **26** (3.13 mL, 25 mmol), and THF (1.35 mL). **7** (7.9 mg, 0.0125 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 and the solvent was removed *in vacuo*. The crude mixture was chromatographed through silica gel with hexane: ethyl acetate (9:1) to give a mixture of the desired product and the 8-nonenyl acetate starting material. This mixture was chromatographed on silica gel impregnated with silver (I) nitrate (10%) prepared by the following procedure with a mobile phase of hexane: ethyl acetate (9:1). The solvent was removed *in vacuo* to yield pure **28** (404 mg, 67%). IR (NaCl), ν, cm^{-1}: 3005, 2928, 2865, 1745, 1456, 1386, 1365, 1238, 1038, 967, 725. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.35 (m, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.94-2.06 (m, 7H), 1.55-1.67 (m, 2H), 1.23-1.41 (m, 12H), 0.84-0.93 (m, 3H).^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.45, 130.43, 130.31, 65.04, 32.57, 30.26, 29.73, 29.20, 27.69, 27.46, 26.47, 22.93, 21.32, 14.34. HRMS (EI+): Calculated – 241.2168 Found – 241.2211.

Preparation of silica impregnated with silver (I) nitrate (10%).

In a procedure modified from the literature,[5] silver (I) nitrate (5.0 g) was added to ethanol (300 mL) and enough water (ca. 100 mL) to dissolve the solid. Silica gel (50 g) was then added to this solution and vigorously shaken. The solvent was removed under reduced pressure in a rotary evaporator and the

(5) Norin, T.; Westfelt, L. *Acta Chem. Scand*. **1963**, *17*, 1828.

remaining slurry was covered in foil and dried in an oven at 150°C for 6 hours to yield a light gray powder. Columns were loaded as with ordinary silica and shielded from light.

General Procedure for the Determination of Initiation Rates.

In a glovebox, a 1 mL volumetric flask was charged with **2** (8.1 mg, 0.012 mmol) and filled to the line with C_6D_6 to create a stock solution (ca. 0.012 M). A portion of the stock solution (0.25 mL, 0.003 mmol **2**) was added to a NMR tube and diluted with C_6D_6 (0.35 mL). The NMR tube was sealed with a septa cap and placed in the NMR spectrometer at 30 °C. Butyl vinyl ether (12 μL, 0.09 mmol) was added and the disappearance of the benzylidene proton resonance was monitored by arraying the 'pad' function in VNMRj.

All reactions, with the exception of **11**, showed clean first-order kinetics over a period of at least three half-lives. Spectra were baseline corrected and integrated with MestReNova. Estimation of error was determined from the average of three different kinetic runs.

General Procedure for Homodimerization Reactions.

In a glovebox, a 1 mL volumetric flask was charged with catalyst (0.0981 mmol) and filled to the line with THF to create a stock solution (0.0981 M). A portion of the catalyst stock solution (50 μL, ca. 5 μmol) was added to a 4 mL vial containing substrate (5 mmol) and THF (1.1 mL, ca. 3 M). The vial was placed into an aluminum block (IKA #3904400) preheated to 35 °C using a temperature controlled hotplate and the reaction was stirred while open to the glovebox atmosphere. After completion of the reaction (determined by ^{1}H NMR spectroscopy), the vial was removed from the glovebox, quenched with oxygen, and the product was isolated via flash chromatography on silica gel according to literature procedures.[6] The percentage of *Z*-olefin product was determined by ^{1}H and ^{13}C NMR spectroscopy, and all spectra were consistent with previous literature reports.[6]

General Procedure for Cross-metathesis of 12 and 24.

In a glovebox, a 4 mL vial was charged with **12** (1.33 mL, 10 mmol) and tridecane (internal standard, 1.22 mL, 5 mmol). A portion (89 μL, 0.35 mmol **12**) of this stock solution was added to a second 4 mL vial followed by **24** (111 μL, 0.69 mmol) and THF (0.45 mL). This mixture was stirred for several minutes before taking a t_0 timepoint. An aliquot (50 μL, 0.0035 mmol) of a catalyst solution prepared from **7** (44 mg, 0.069 mmol) in THF (1 mL) was added to the substrate solution and the vial was sealed and heated to the desired temperature. Periodically, the reaction was cooled to RT, and an aliquot (20 μL) was removed from the glovebox, diluted with a solution of ethyl vinyl ether in CH_2Cl_2, and analyzed via GC.

(6) Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9686.

GC response factors for all starting materials and products (ethylene excluded) were obtained in order to determine accurate conversions (Figure S1) and the GC data was worked up according to the literature.[7]

GC instrument conditions: Inlet temperature – 250 °C; Detector temperature – 250 °C; hydrogen flow – 32 mL/min; air flow – 400 mL/min; consant col + makeup flow – 30 mL/min.

GC Method: 50 °C for 5 min, followed by a temperature increase of 10 °C/min to 240 °C and a subsequent isothermal period at 240 °C for 5 min (total run time = 29 min).

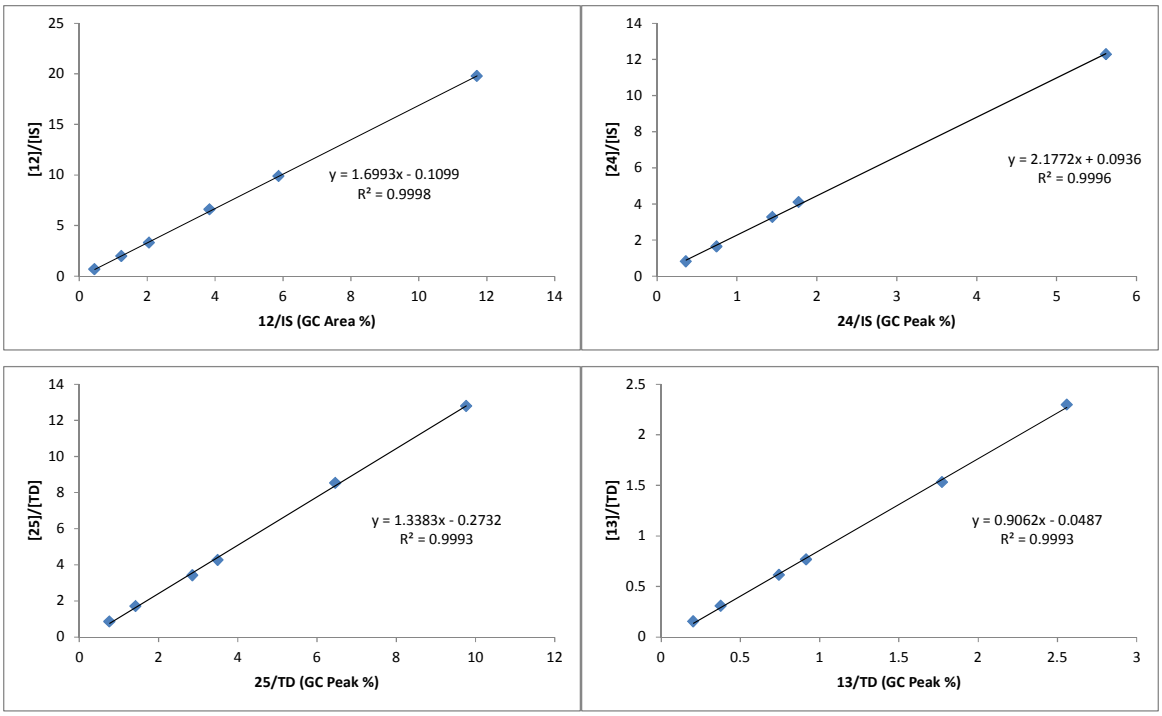


Figure S1. Response factors for **12** (top left), **24** (top right), **25** (bottom left), and **13** (bottom right).

(7) Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740.

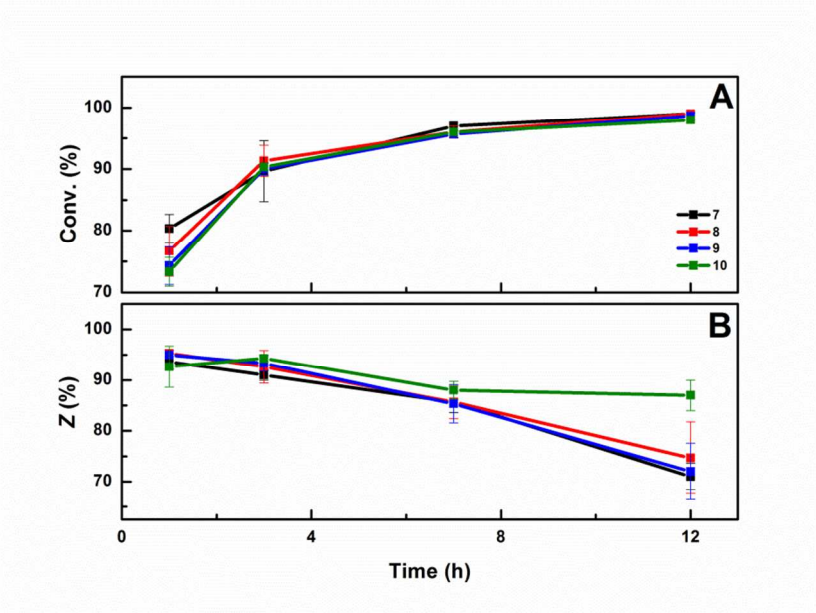


Figure S2. Time-course plot for the conversion (**A**) and selectivity (**B**) of **12** to **13** with catalysts **7**-**10**.

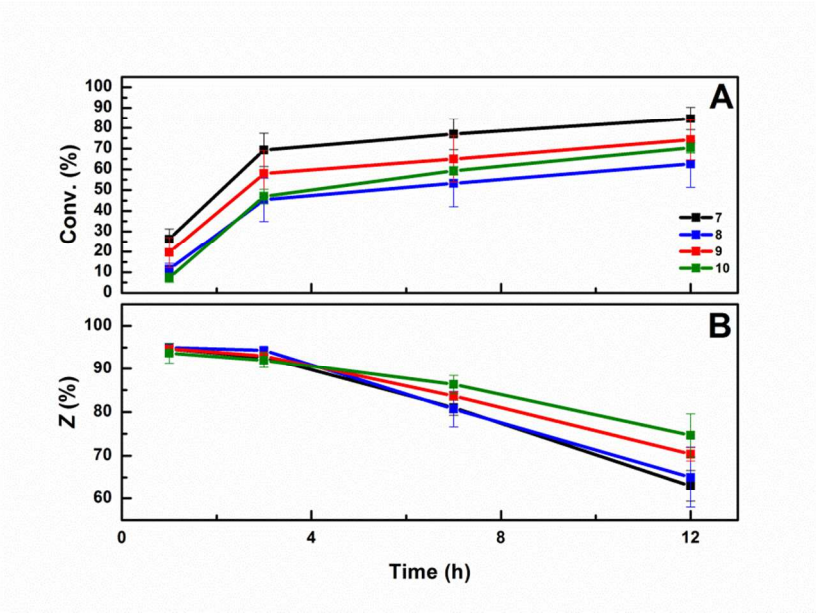


Figure S3. Time-course plot for the conversion (**A**) and selectivity (**B**) of **18** with catalysts **7**-**10**.

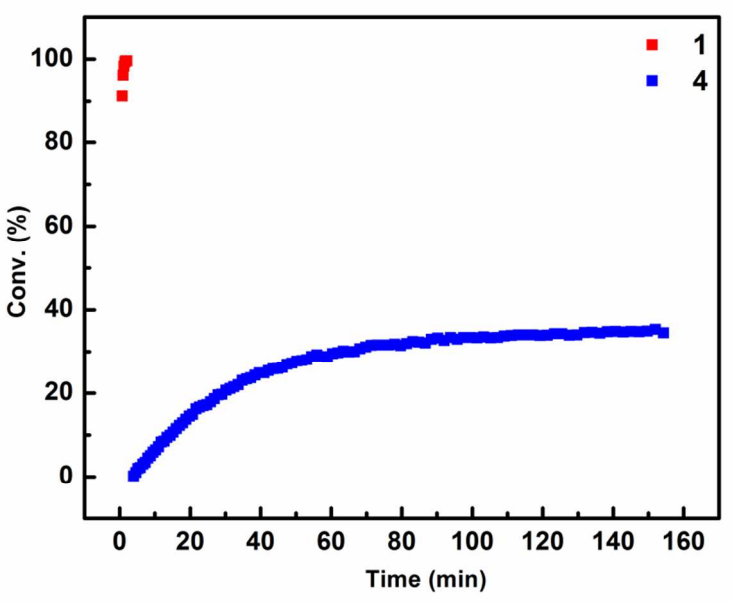


Figure S4. ROMP comparison of cyclooctadiene (COD) with catalysts **1** and **4**. Conditions were **1** or **4** (0.1 mol%) and COD (53 μL, 0.4 mmol) C_6D_6 (0.8 mL).

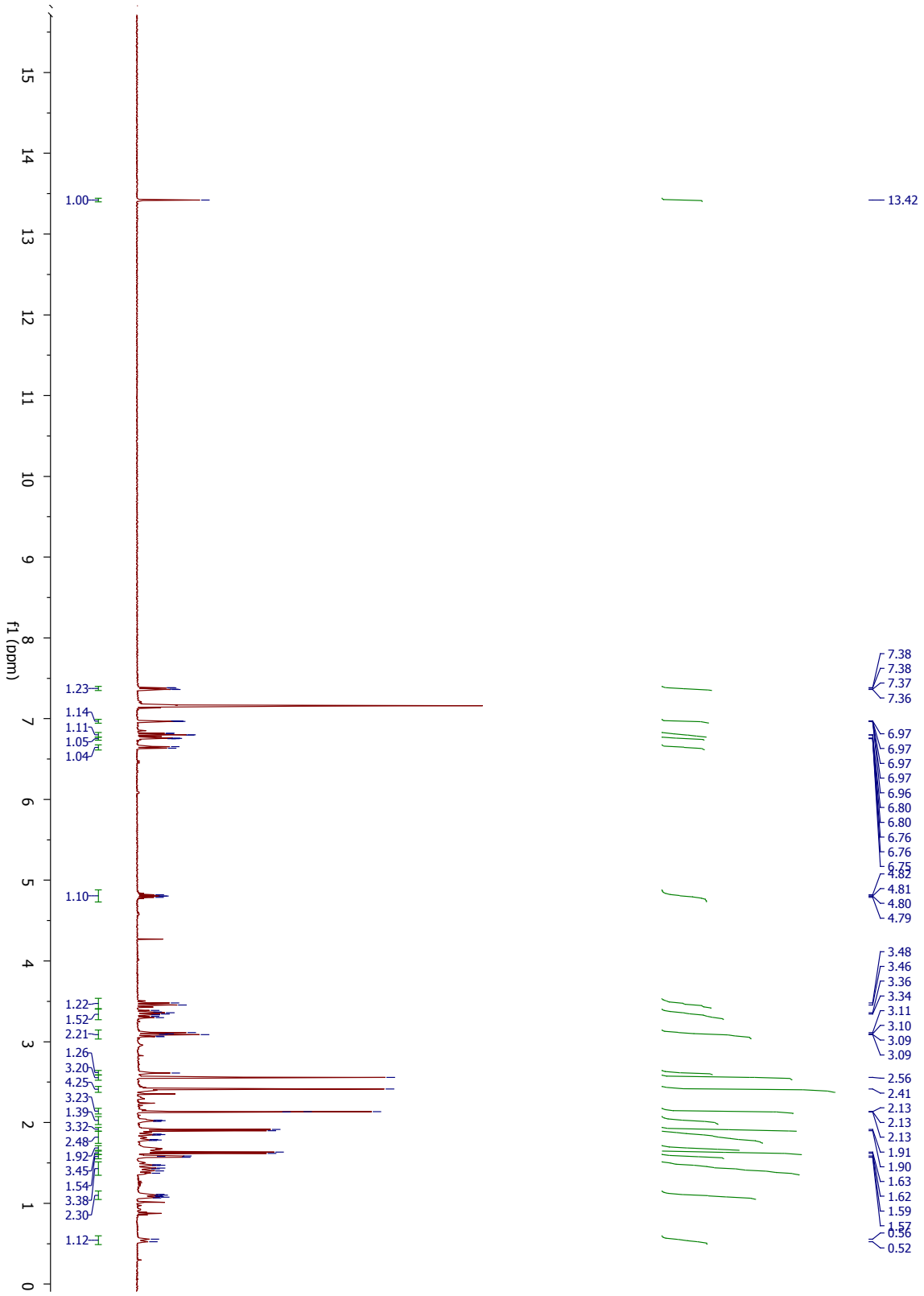


Figure S5. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **3**.

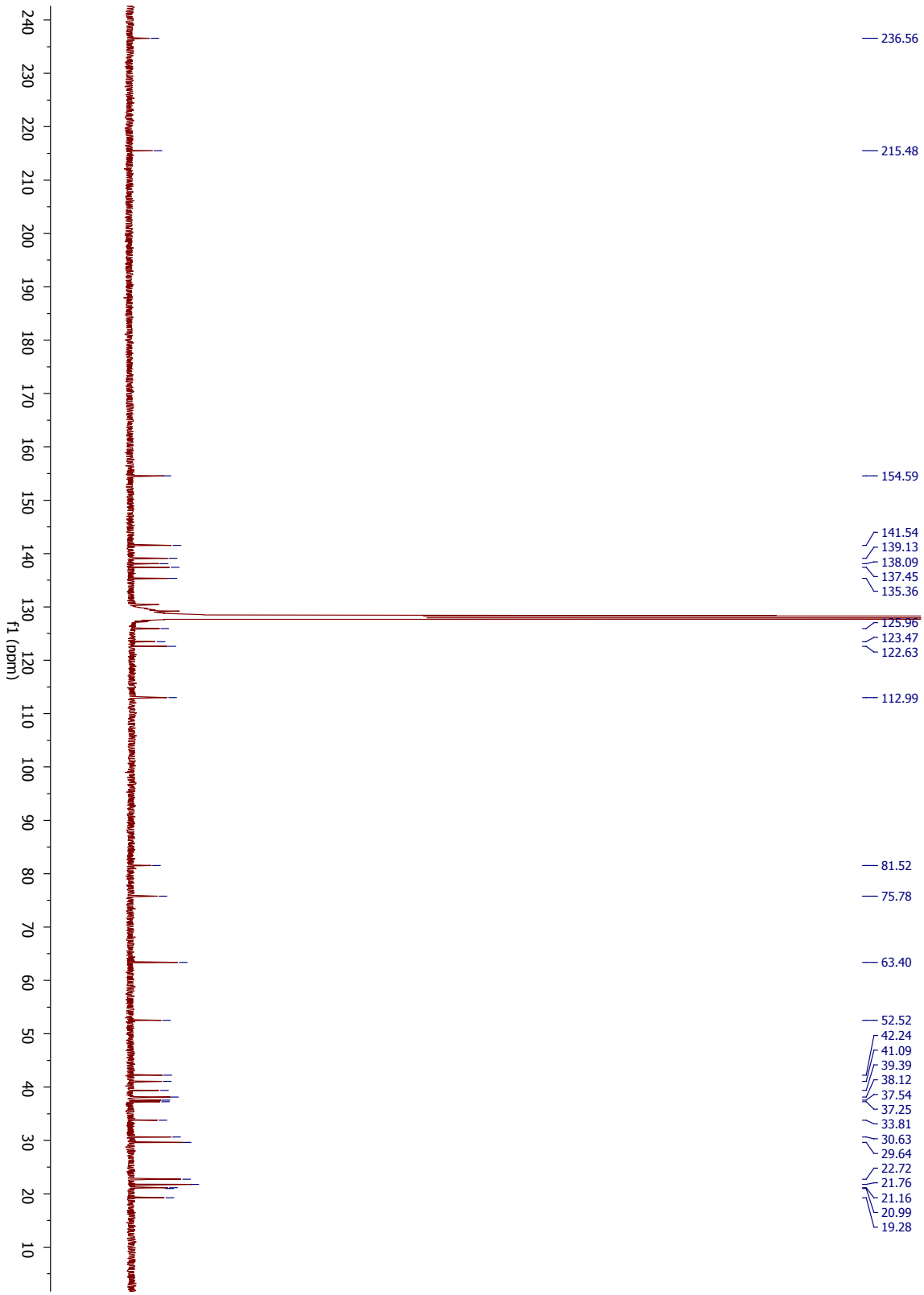


Figure S6. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **3**.

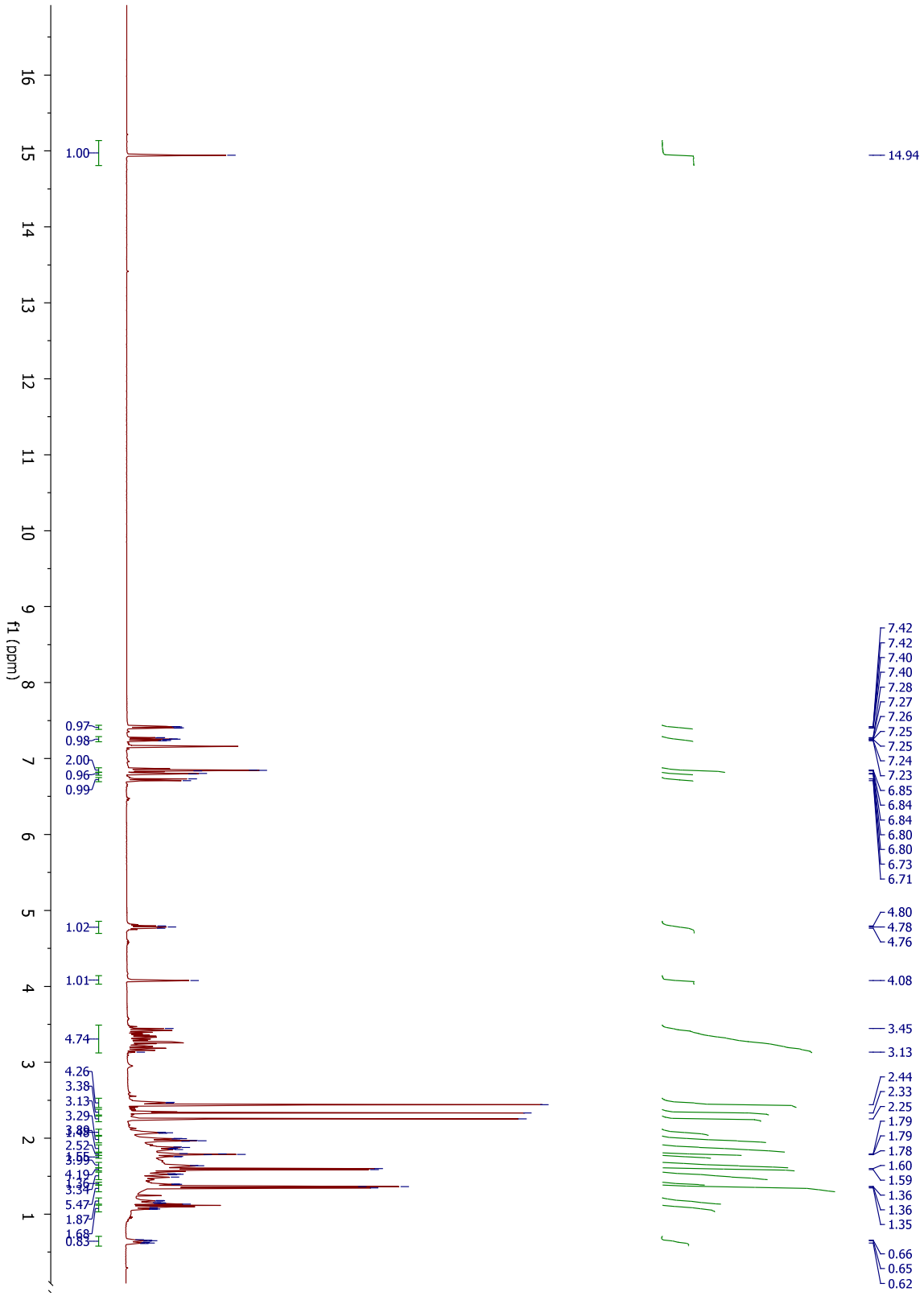


Figure S7. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **4**.

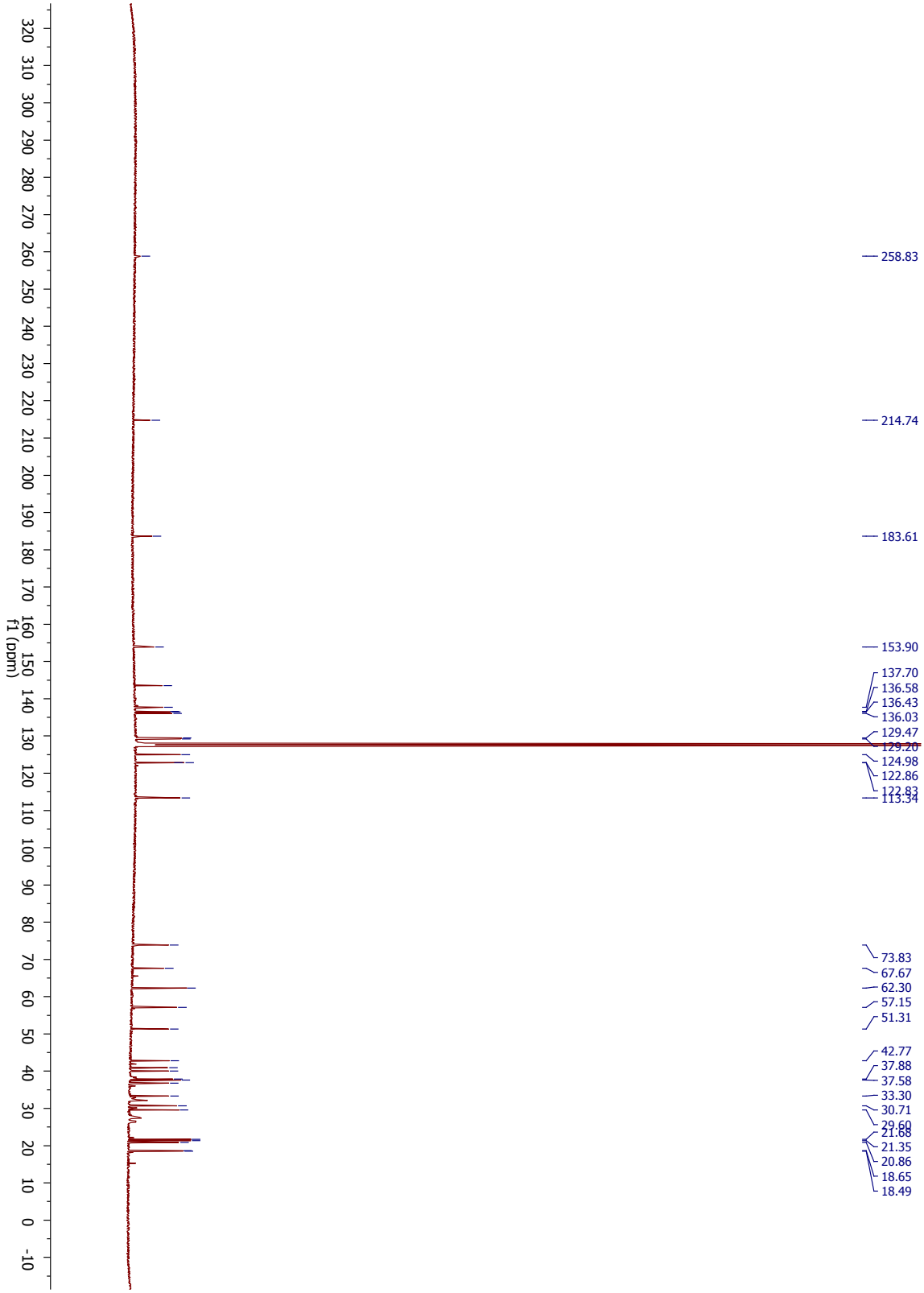


Figure S8. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **4**.

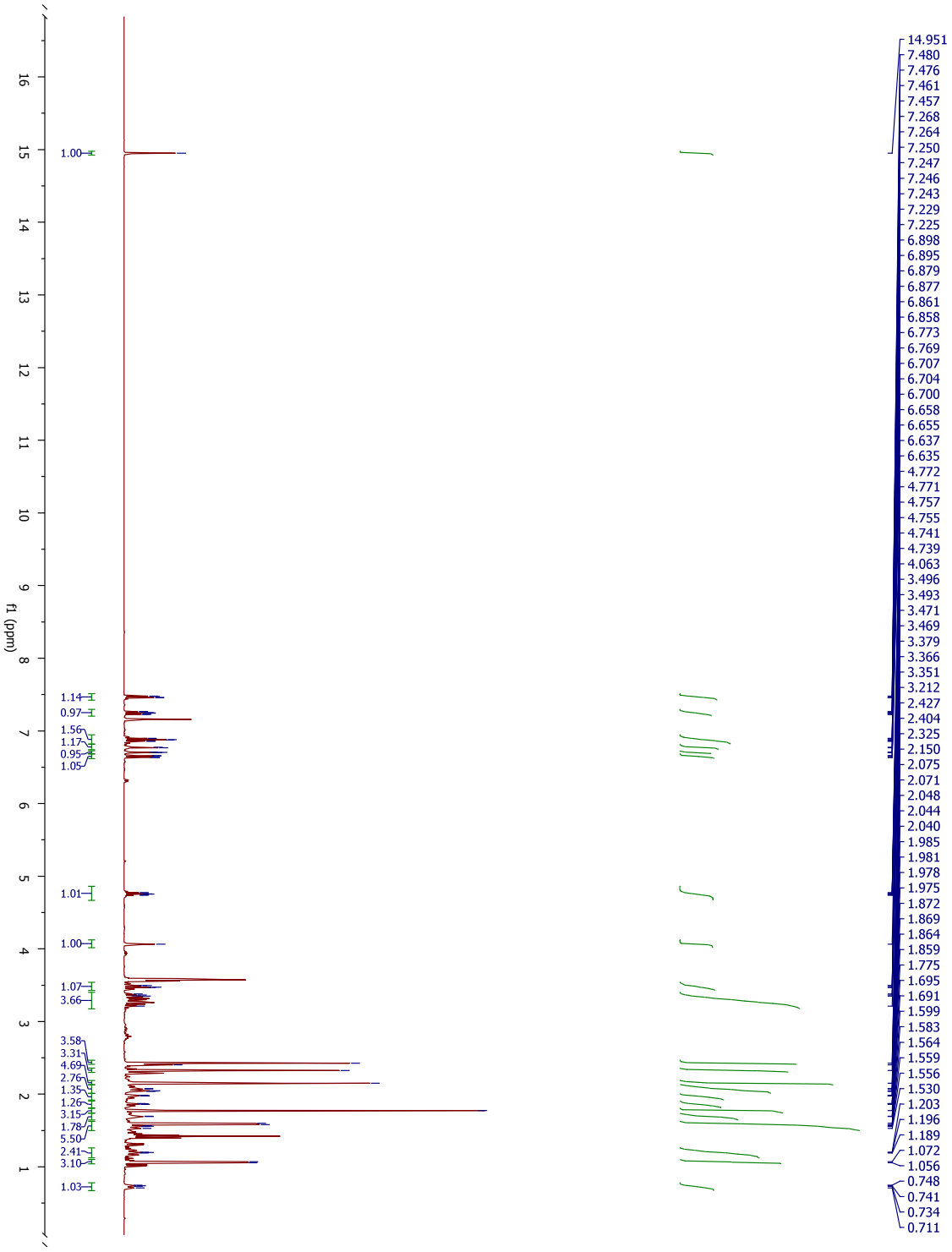


Figure S9. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **5**.

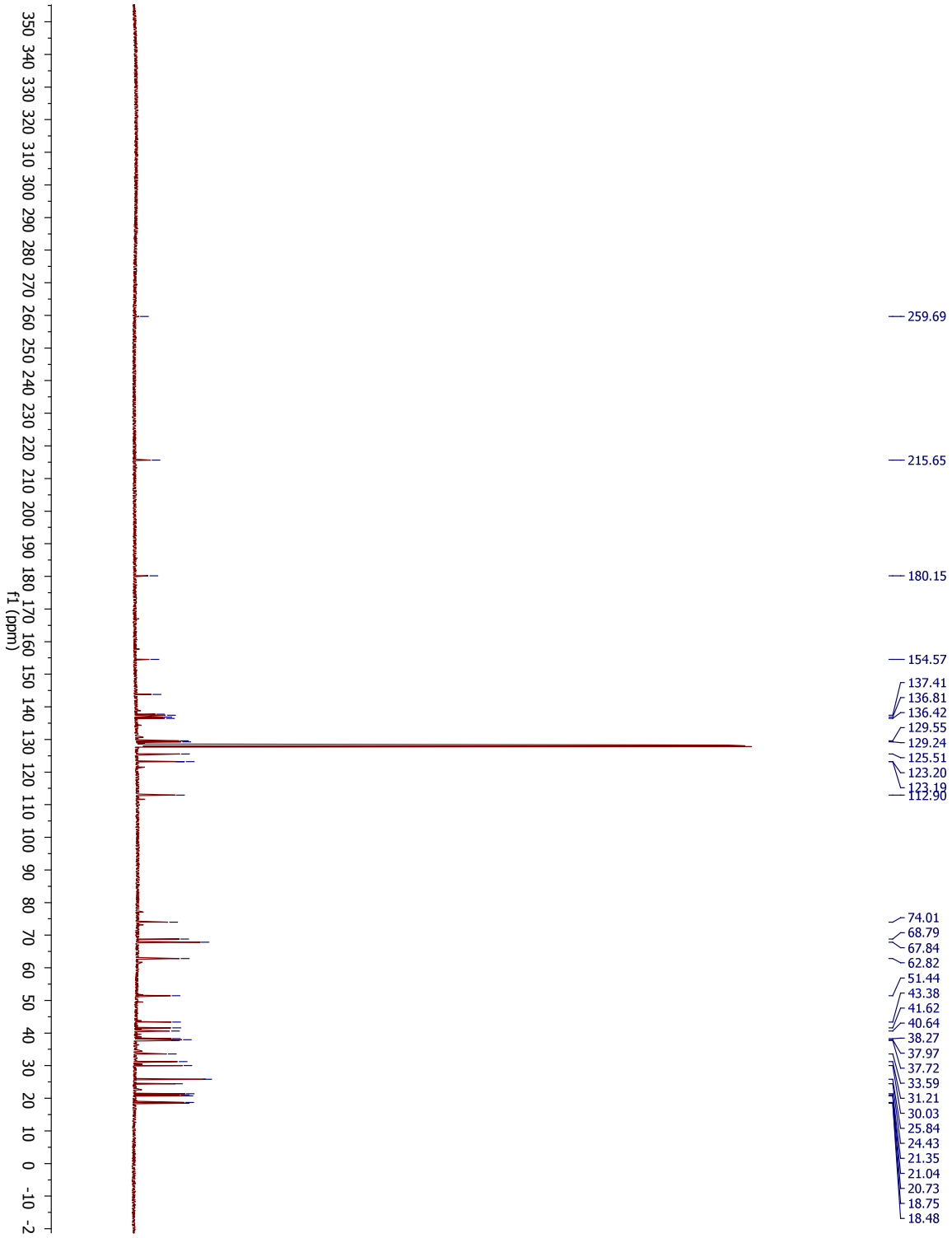


Figure S10. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **5**.

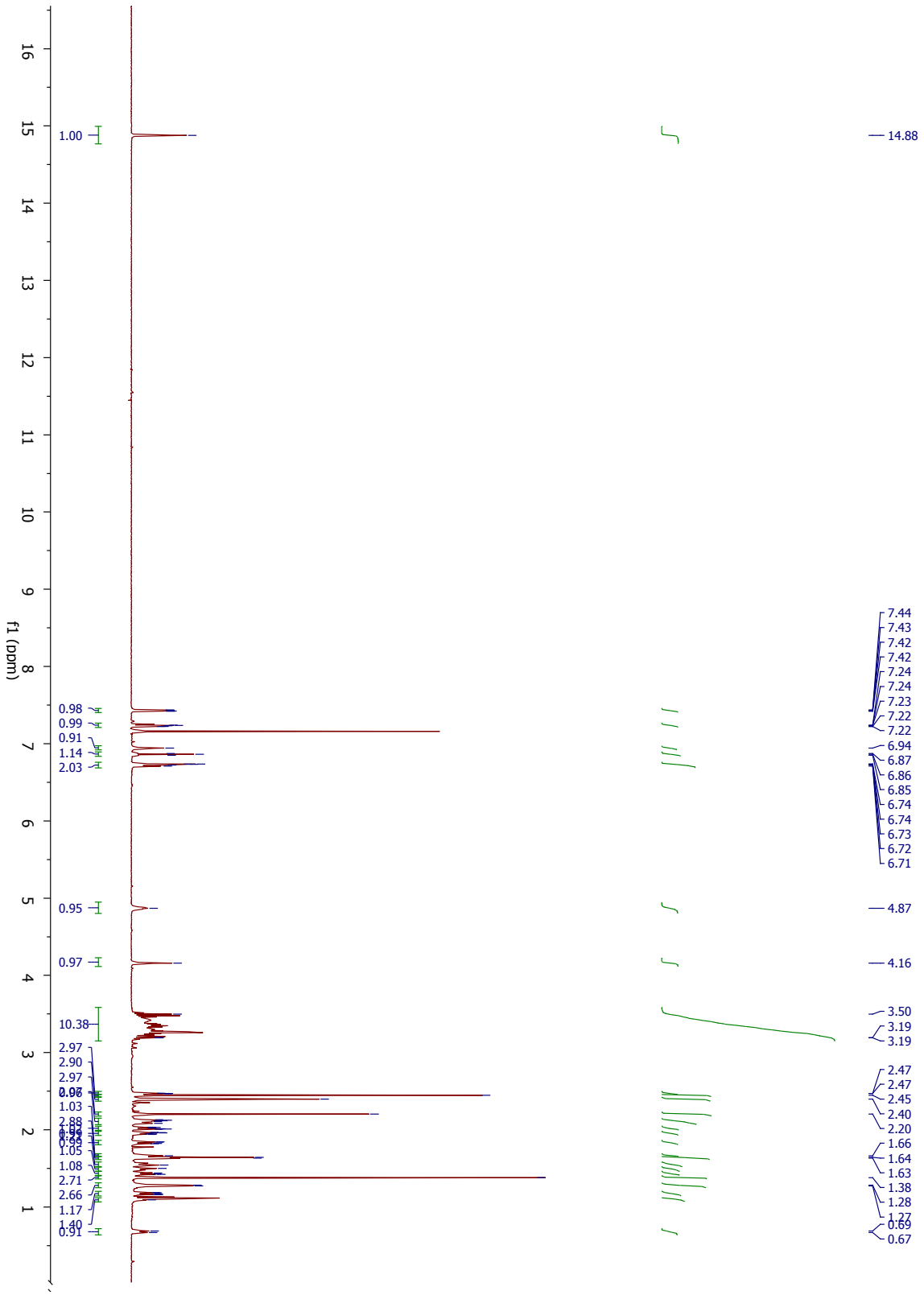


Figure S11. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **6**.

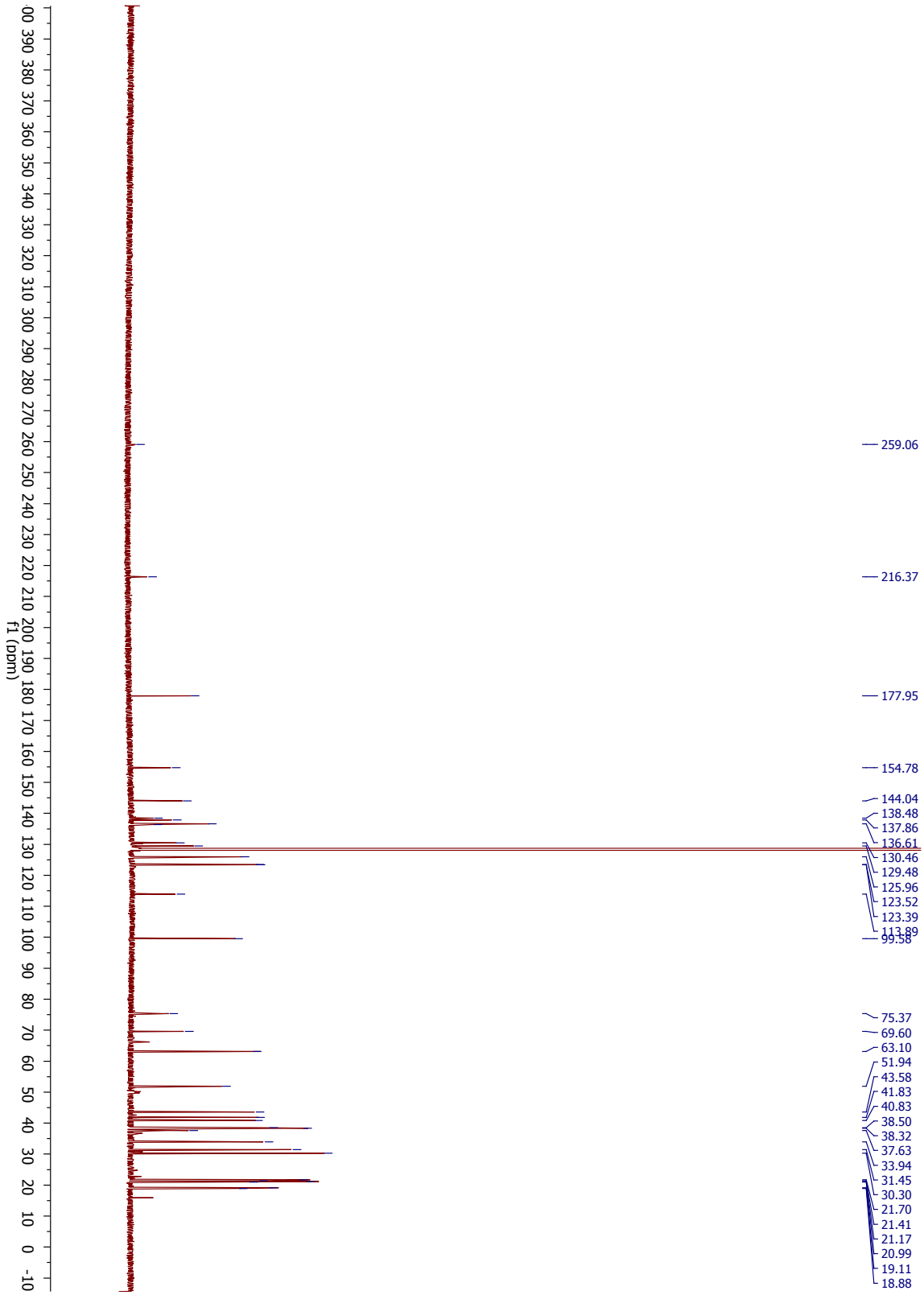


Figure S12. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **6**.

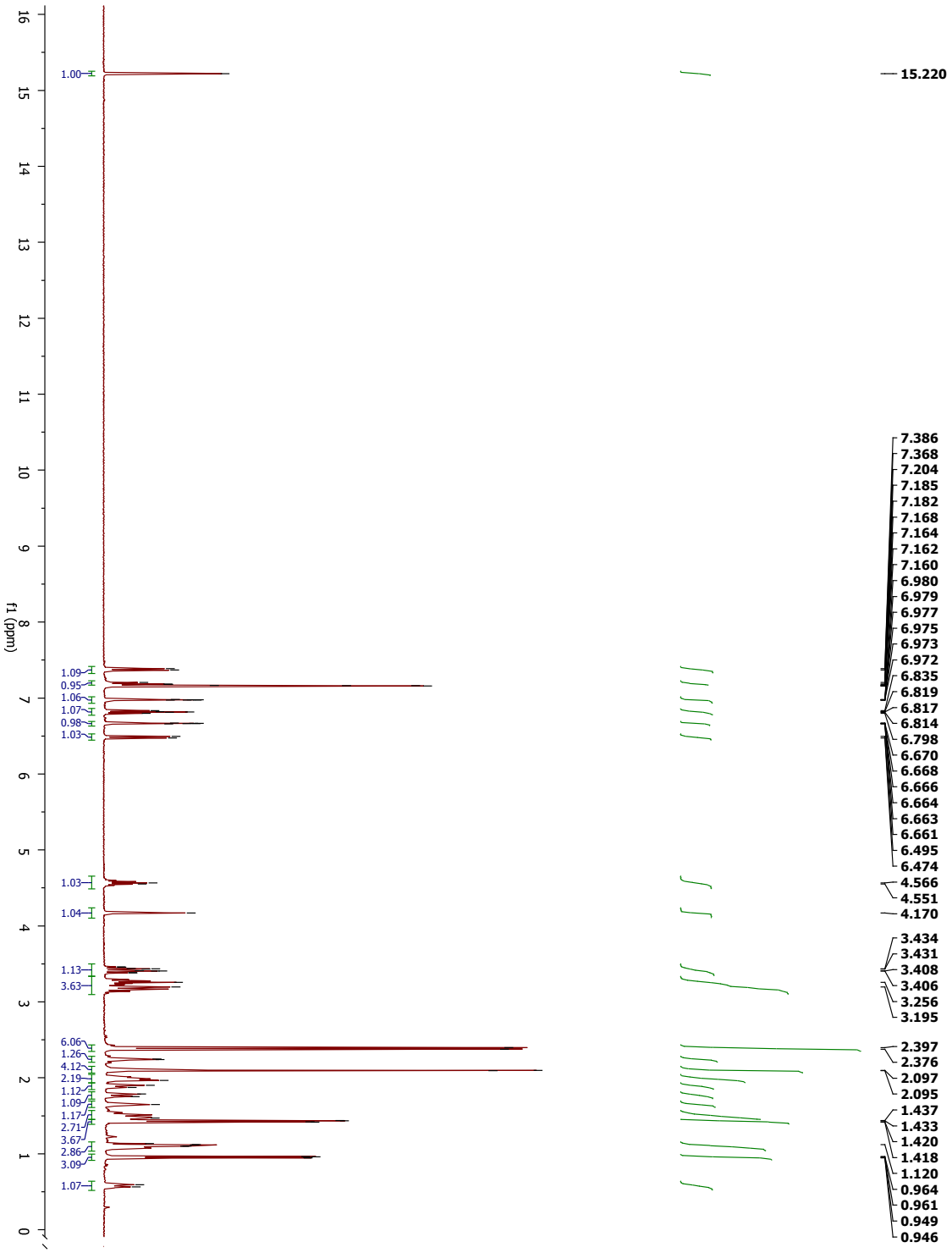


Figure S13. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **7**.

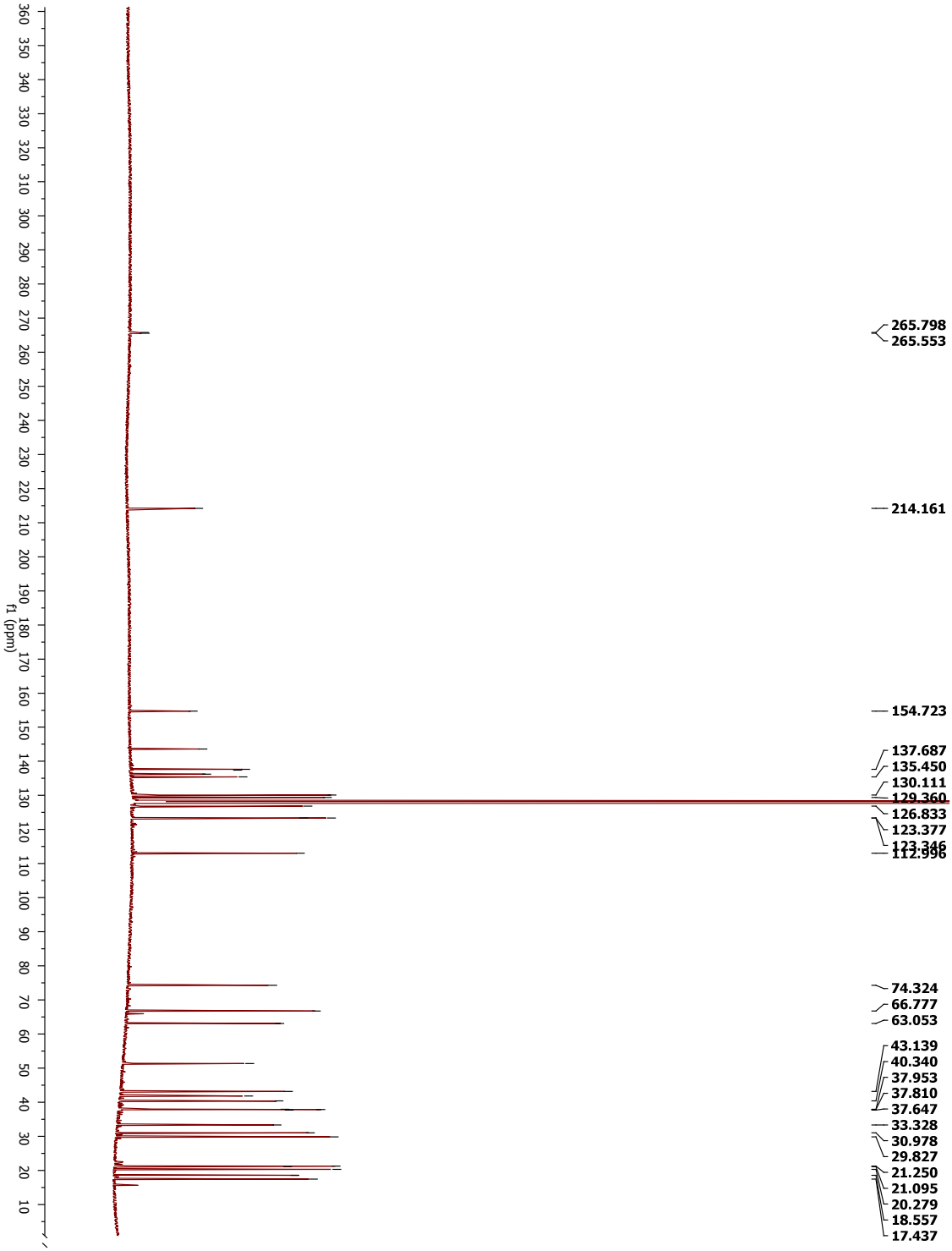


Figure S14. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **7**.

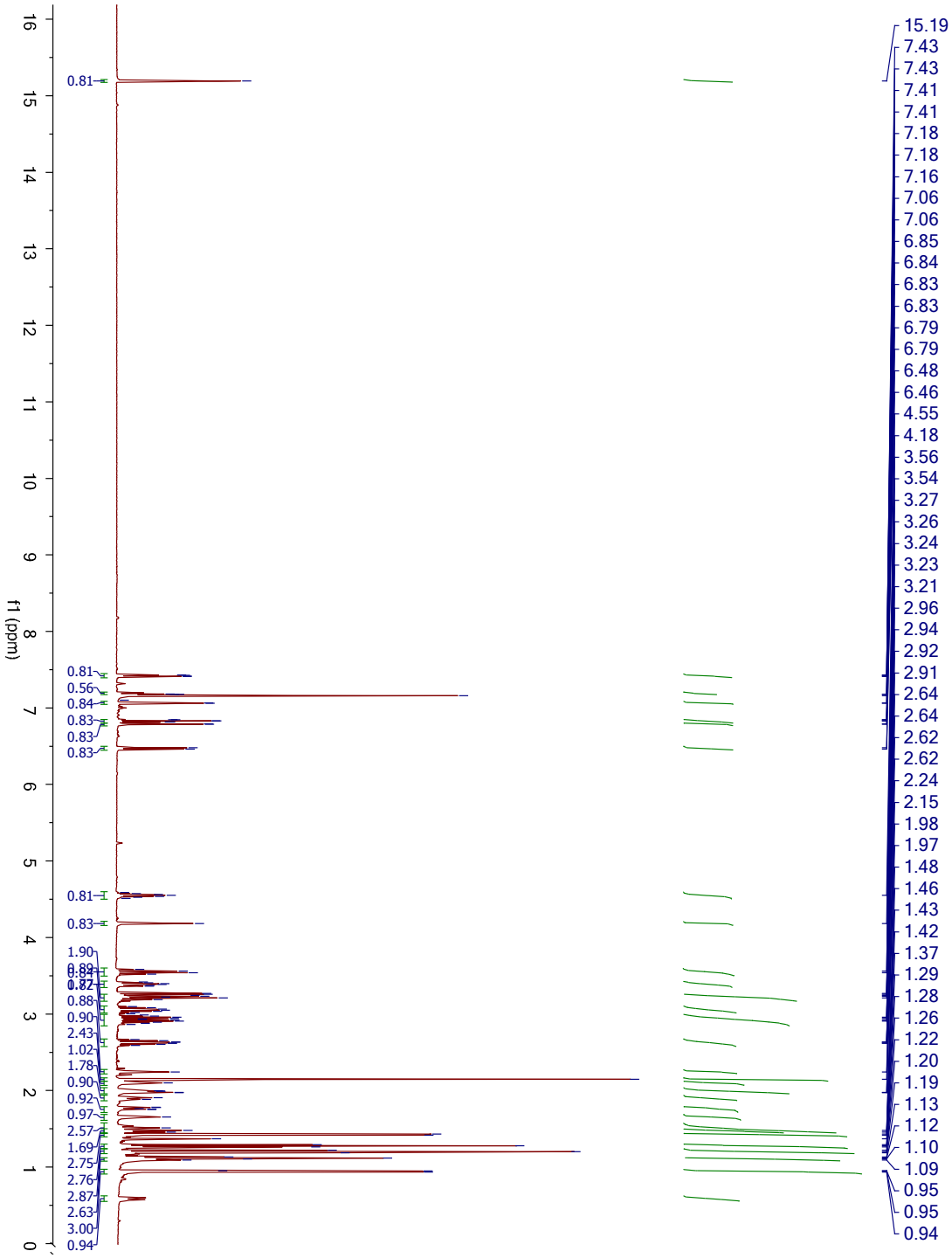


Figure S15. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **8**.

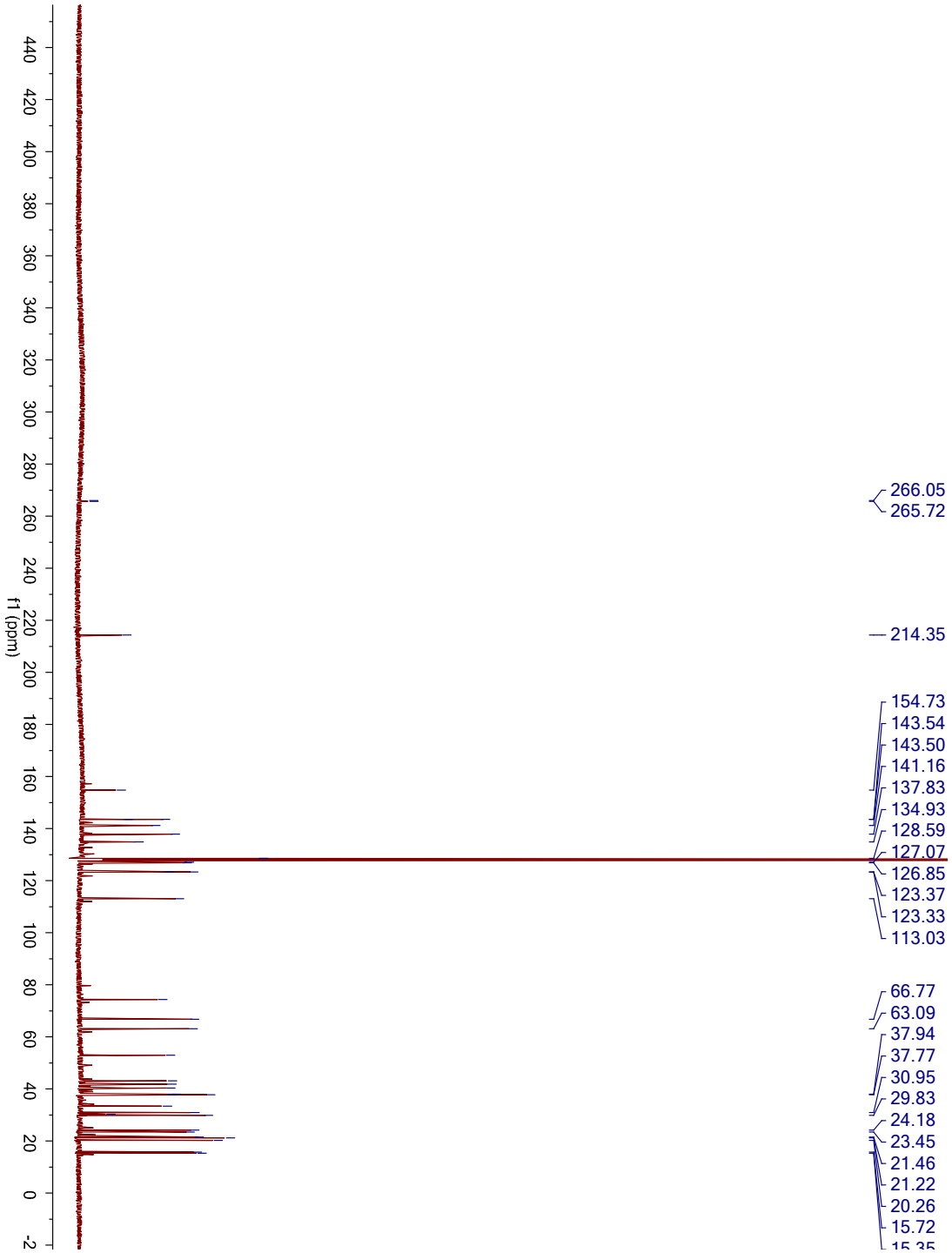


Figure S16. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **8**.

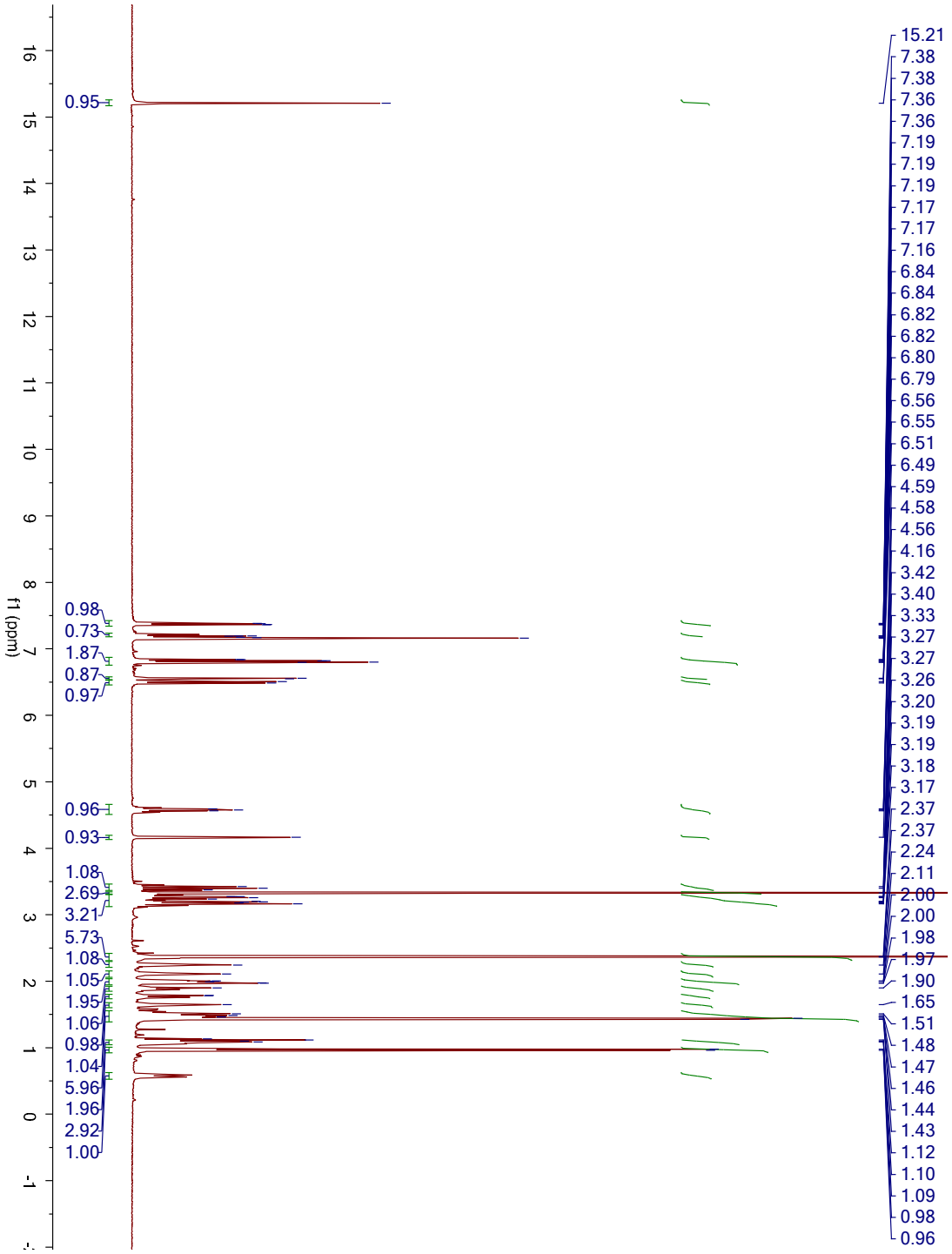


Figure S17. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **9**.

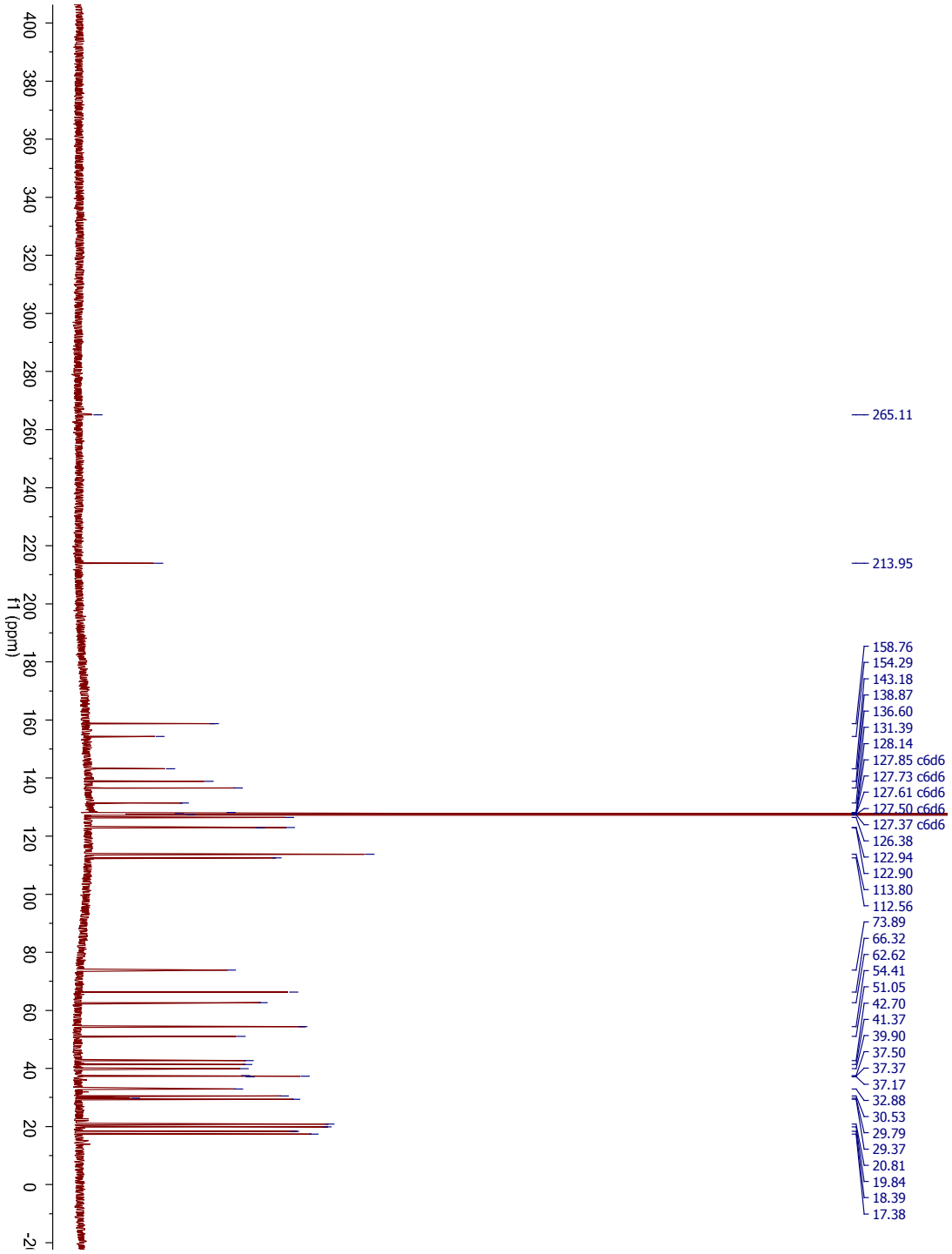


Figure S18. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **9**.

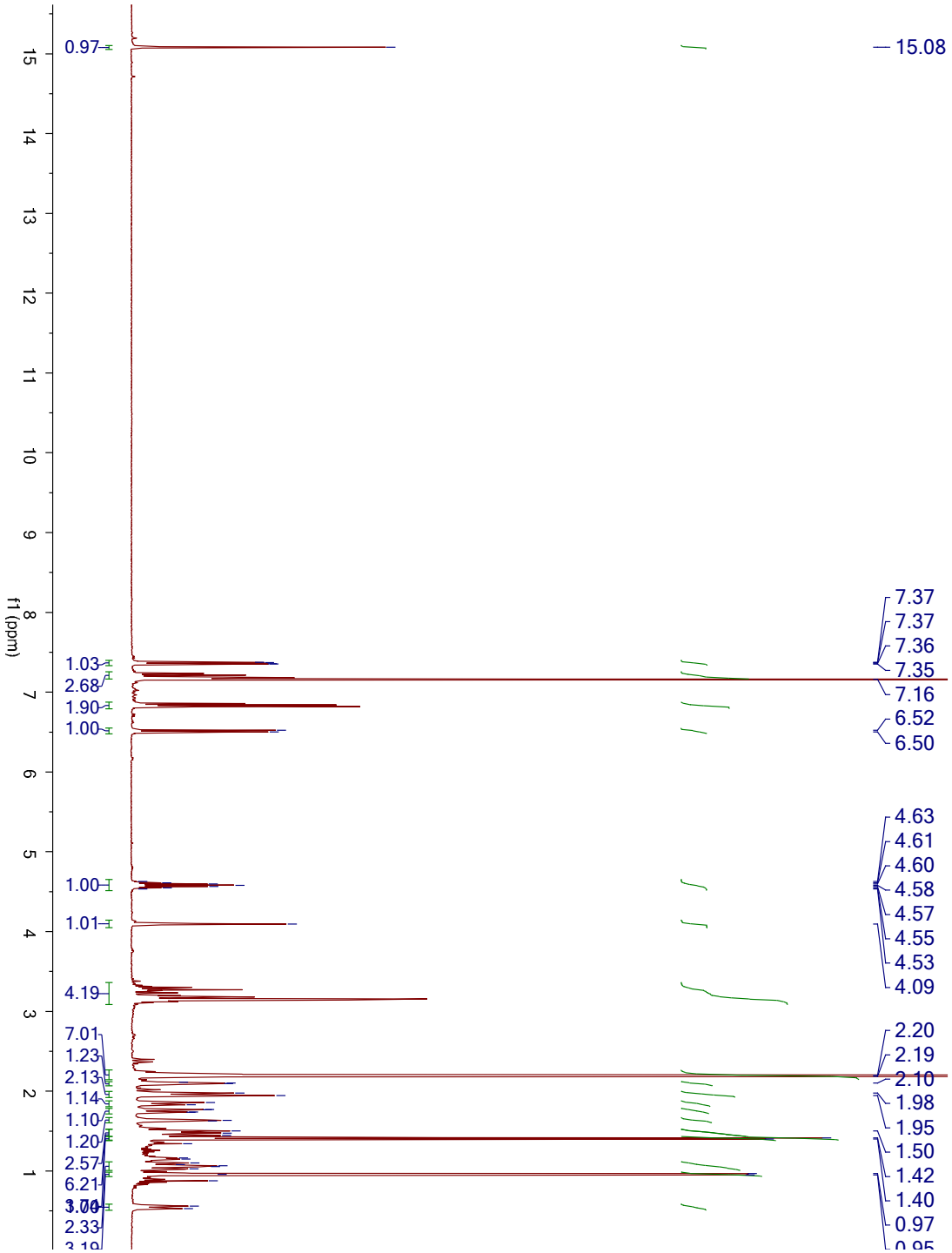


Figure S19. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **10**.

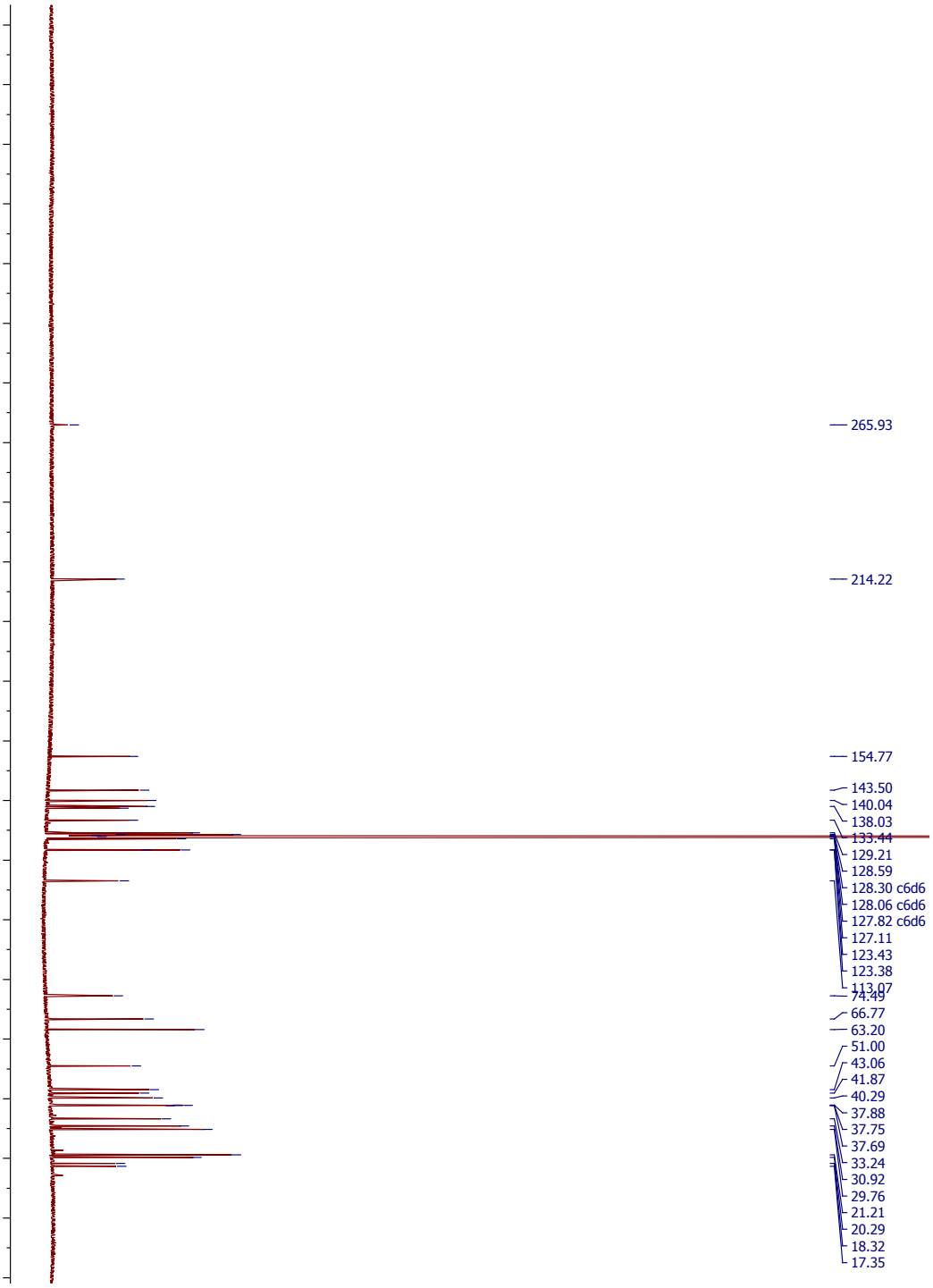


Figure S20. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **10**.

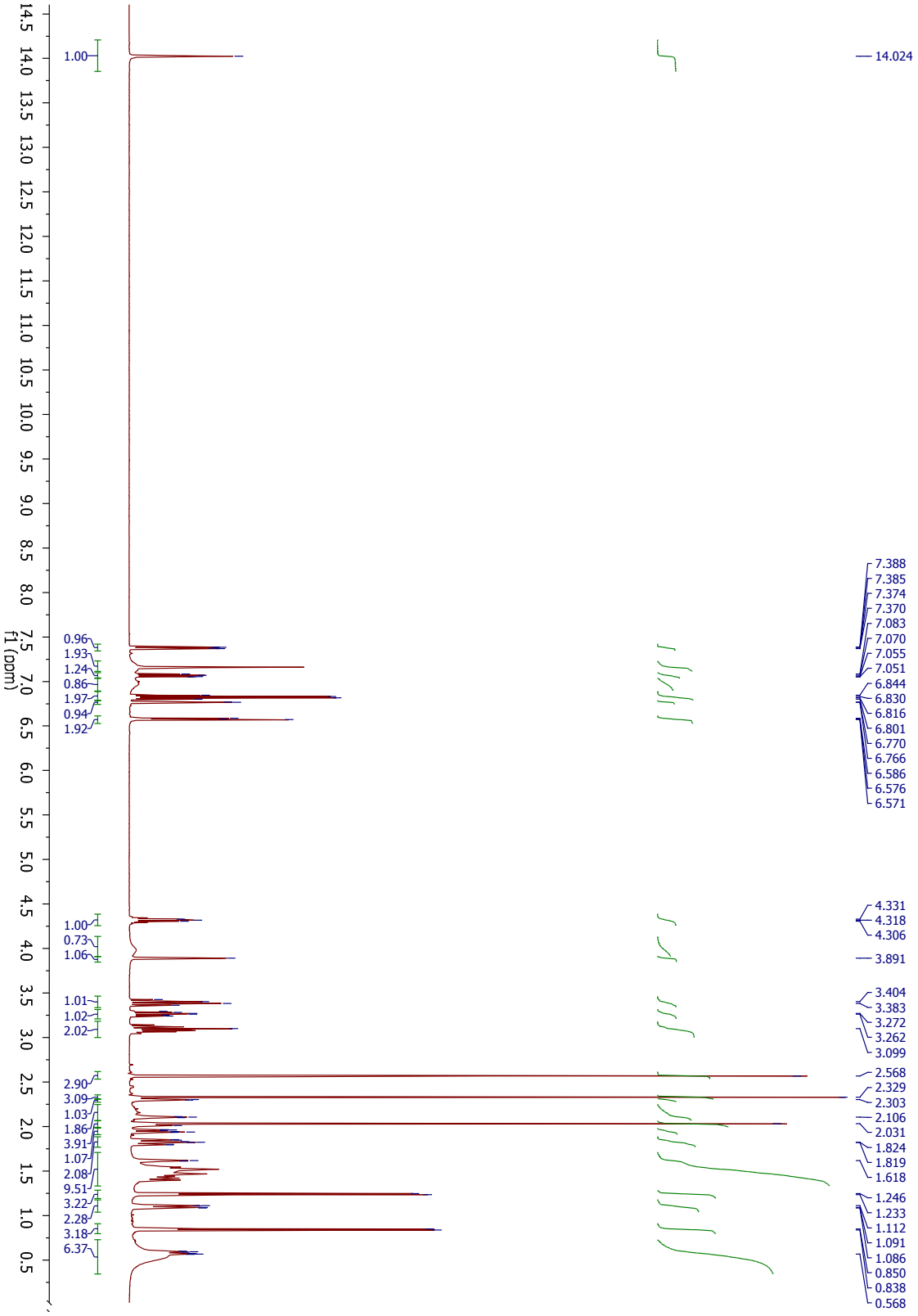


Figure S21. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **11**.

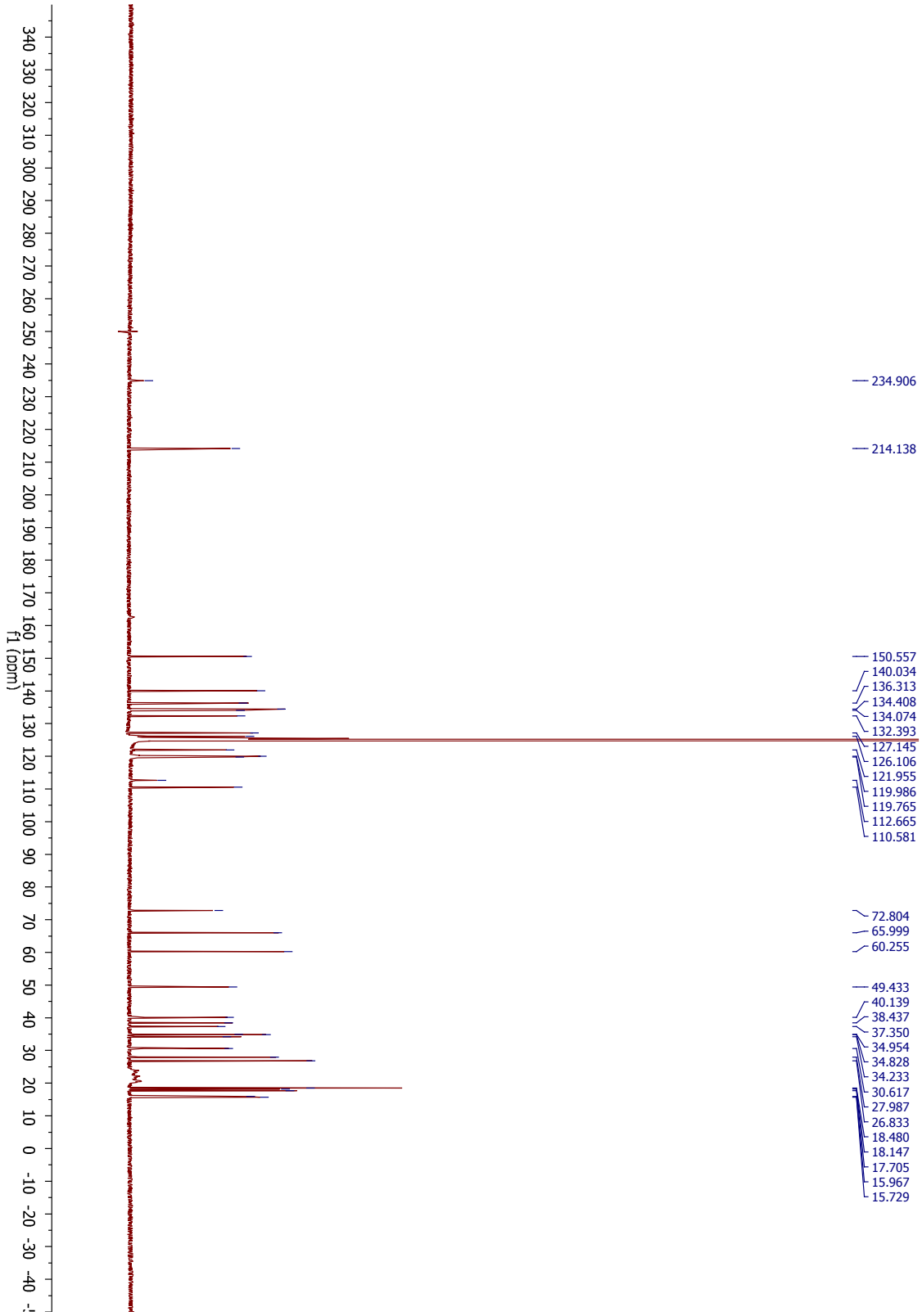


Figure S22. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **11**.

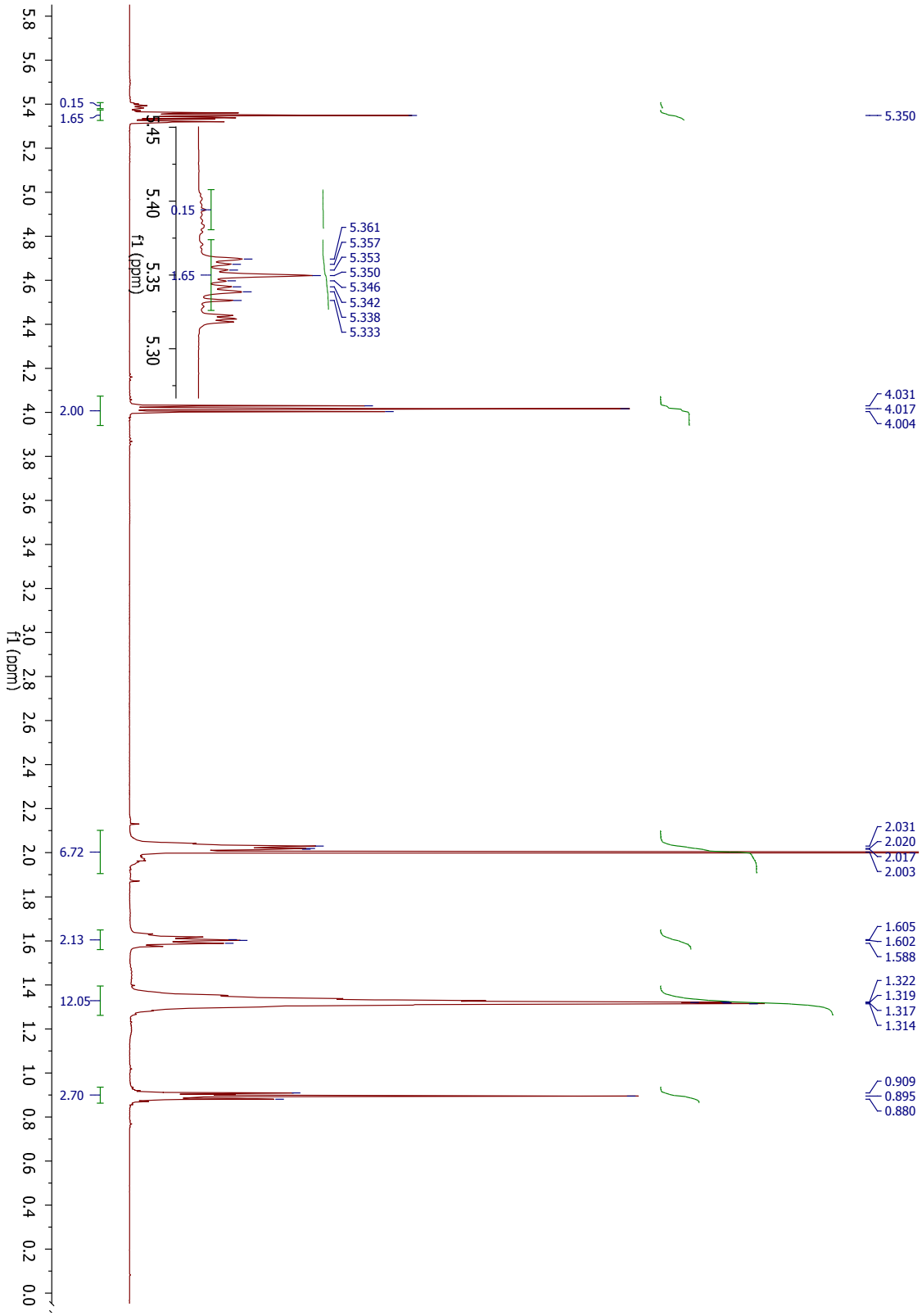


Figure S23. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **28**.

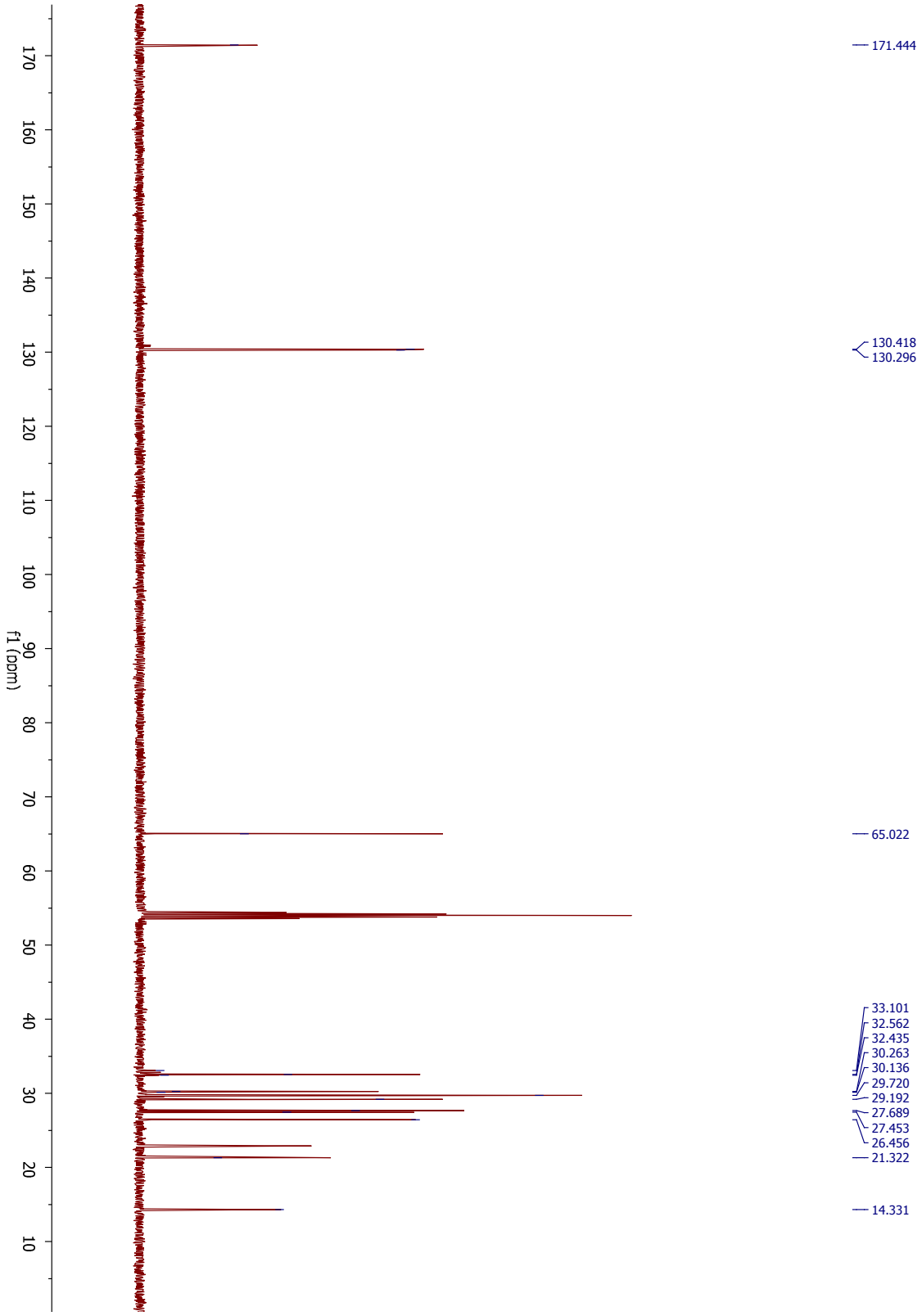


Figure S24. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of **28**.

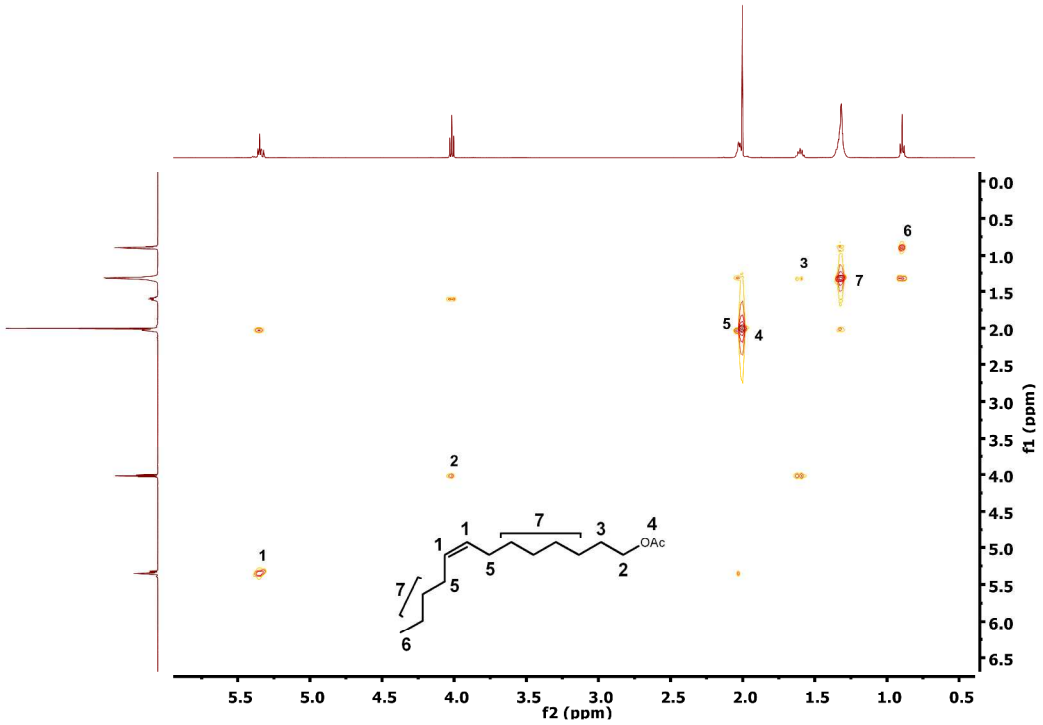


Figure S25. ^{1}H-^{1}H COSY (CD_2Cl_2) of **28**.

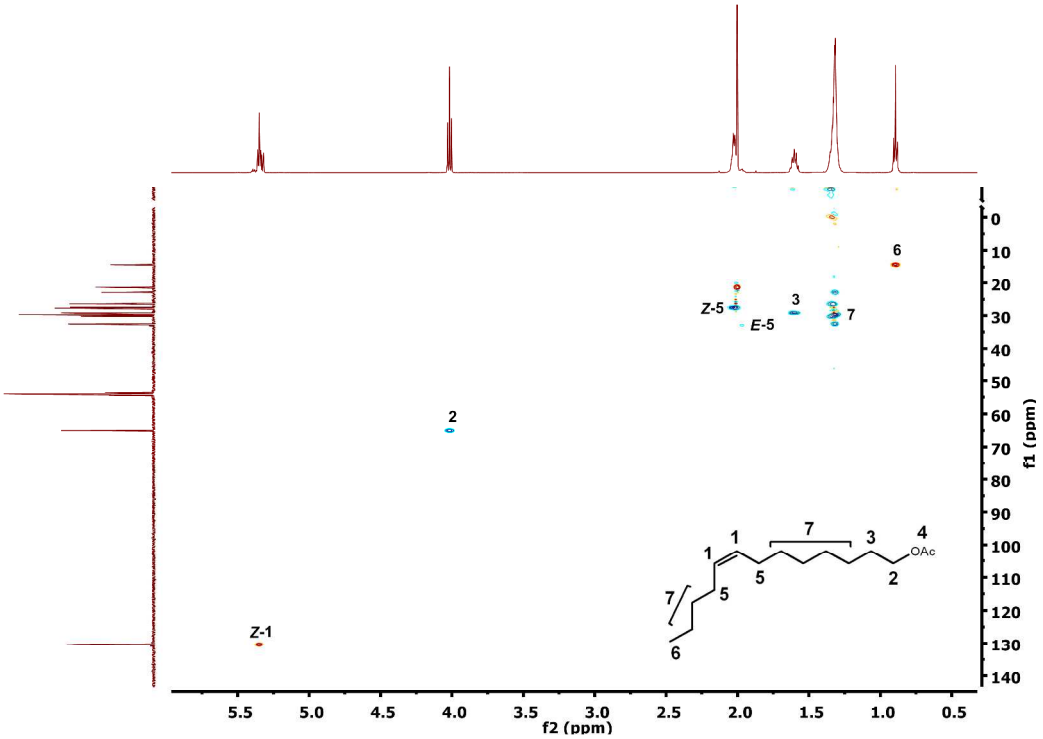


Figure S26. ^{1}H-^{13}C HSQC (CD_2Cl_2) of **28**.