SUPPORTING INFORMATION

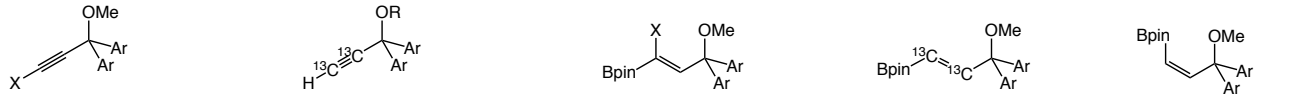
Table of contents

General Methods

Reactions were performed under a nitrogen atmosphere in flame dried glassware. NMR spectra were obtained on a Varian spectrometer operating at 400 or 500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P at 25 °C unless noted otherwise. ^{13}C NMR spectra were referenced relative to CD_2Cl_2 (δ 53.8) or $CDCl_3$ (δ 77.2), ^{1}H NMR spectra were referenced relative to residual $CHCl_3$ (δ 7.26) or $CHDCl_2$ (δ 5.32). ^{31}P NMR spectra was referenced to an external solution of triphenylphosphine oxide in CD_2Cl_2 (δ 26.9). Flash column chromatography was performed employing 200-400 mesh silica gel 60 (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F254. CD_2Cl_2 was dried over CaH_2 and degassed prior to use. Ether, methylene chloride, and THF were purified by passage through columns of activated alumina under nitrogen. Reagents and other materials were obtained through major chemical suppliers and were used as received unless noted otherwise. Room temperature is 25 °C. Glassware and NMR tubes used for generation of allenylidenes was silanized before use.[S1] Propargylic ethers **7a**

and 7**b** were prepared as white solids employing published procedures.[S2,S3] Acetylene-$^{13}C_2$ was prepared from amorphous carbon-^{13}C (99% ^{13}C) employing a published procedure and condensed at –78 °C.[S4] Elemental Analyses were performed by Atlantic Microlab, Inc.

Synthesis of Vinyl Boronic esters



7a (Ar = Ph, X = H)
7b (Ar = 4-C_6H_4OMe, X = H)
7b-d_1 (Ar = 4-C_6H_4OMe, X = D)

7b-1,2-$^{13}C_2$ (R = Me, Ar = 4-C_6H_4OMe)
S1-1,2-$^{13}C_2$ (R = H, Ar = 4-C_6H_4OMe)

(*E*)-**8a** (Ar = Ph, X = H)
(*E*)-**8b** (Ar = 4-C_6H_4OMe, X = H)
(*E*)-**8b**-d_1 (Ar = 4-C_6H_4OMe, X = D)

(*E*)-**8b**-1,2-$^{13}C_2$ (Ar = 4-C_6H_4OMe)

(*Z*)-**8b** (Ar = 4-C_6H_4OMe)

Scheme S1. Propargylic alcohols and ethers and vinyl boronic esters and their isotopomers.

(*E*)-Vinyl boronic esters were prepared employing a modification of the procedure published by Frost.[S5]

(*E*)-BpinC(H)=C(H)-C(OMe)(C_6H_4OMe)$_2$ [(*E*)-8b]. A yellow solution of **7b** (1.10 g, 3.90 mmol), Cp_2ZrHCl (100 mg, 0.39 mmol), HBPin (0.60 mL, 4.1 mmol) and Et_3N (55 μL, 0.39 mmol) in CH_2Cl_2 (5 mL) was stirred in a sealed tube at 60 °C for 2 days in the dark. The reaction mixture was diluted with hexanes, filtered through silica gel, and concentrated under vacuum. The resulting residue was chromatographed (SiO_2; hexanes–EtOAc = 85:15) to give a yellow oil, which was chromatographed a second time (SiO_2: hexanes–EtOAc = 9:1) to give yellow solid, which was then crystalized from ^{i}PrOH at –20 °C to give (*E*)-**S2** as white solid (0.35 g, 22%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.22 (d, *J* = 8.8 Hz, 4 H), 7.08 (d, *J* = 18.2 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 4H), 5.63 (d, *J* = 18.1 Hz, 1H), 3.79 (s, 6H), 3.08 (s, 3H), 1.26 (s, 12H). $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$): δ 158.74, 153.91, 135.82, 129.58, 113.37, 84.80, 83.42, 55.39, 52.07, 25.03. HRMS (ESI) calcd. (found) for $C_{23}H_{28}BO_4$ [M-OMe]$^+$: 379.2770 (379.2083).

(*E*)-BpinC(D)=C(H)-C(OMe)(C_6H_4OMe)$_2$ [(*E*)-8b-d_1]. A solution of **7b** (0.80 g, 2.8 mmol) in methanol-*O*-d (5 mL) was added into a solution of NaOMe (46 mg, 0.85 mmol) in methanol-*O*-*d* (2 mL)

at room temperature and stirred for 2 h and the resulting mixture was concentrated under reduced pressure and diluted with fresh methanol-*O*-*d* (4 mL). This procedure was repeated three times and the resulting suspension was treated with D_2O (4 mL) and extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated to give 4,4'-(1-methoxyprop-2-yne-1,1-diyl-3-*d*)bis(methoxybenzene) (**7b**-d_1) as white solid (0.61 g, 76%) with >95% deuterium incorporation at terminal alkynyl position. **7b**-d_1 was converted into (*E*)-**8b**-d_1 employing a procedure analogous to that used to synthesize (*E*)-**8b**. ^{1}H NMR analysis of (*E*)-**8b**-d_1 established >95% deuterium incorporation at C_1 position, with δ 7.08 (s, 1H) at C_2 position.

(*E*)-Bpin^{13}C(H)=^{13}C(H)-C(OMe)(C$_6$H$_4$OMe)$_2$ [(*E*)-8b-1,2-^{13}C$_2$]. THF (10 mL) was added to condensed H^{13}C≡^{13}CH [generated from reaction of carbon-^{13}C (0.47 g) with Ca(0) (2.1 g)][S4] at –116 °C and the resulting solution was treated sequentially with *n*-BuLi (2.1 mL, 2.5 M in hexanes, 5.3 mmol) at –78 °C and a solution of 4,4'-bismethoxybenzophenone (1.3 g, 5.4 mmol) in THF (20 mL). The resulting solution was stirred at –78 °C for 20 min, during which time the initially pale yellow solution became colorless. The solution was warmed gradually to room temperature, stirred for 12 h, and then treated with water (25 mL). The layers were separated, the aqueous phase was extracted with diethyl ether, and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated under vacuum. The resulting colorless oil was chromatographed (SiO_2: hexanes–EtOAc = 9:1) to give 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**S1**-1,2-^{13}C$_2$) (197 mg, 0.73 mmol). Bisanisyl ethynyl alcohol **S1**-1,2-^{13}C$_2$ was methylated with NaH/MeI employing a procedure analogous to that used to synthesize **7b** to give **7b**-1,2-^{13}C$_2$ in 59% yield. Zirconium-catalyzed hydroboration of **7b**-1,2-^{13}C$_2$ with HBpin employing a procedure analogous to that used to synthesize (*E*)-**8b** gave (*E*)-**8b**-1,2-^{13}C$_2$ as colorless oil (79%).

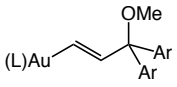
For S1-1,2-^{13}C$_2$: ^{1}H NMR (400 MHz; $CDCl_3$; selected resonances): δ 2.85 (dd, $^1J_{HC}$ = 250.5, $^2J_{HC}$ = 49.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$): δ 86.97 (d, $^1J_{CC}$ = 171.3 Hz), 75.18 (d, $^1J_{CC}$ = 171.3 Hz).

For (*E*)-8b-1,2-$^{13}C_2$: ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.62 (ddd, $^1J_{HC}$ = 142.5, $^3J_{HH}$ = 18.3, $^2J_{HC}$ = 7.3 Hz, 1H). $^{-13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$): δ 153.86 (d, $^1J_{CC}$ = 62.3 Hz), 117.96 (m). ^{13}C NMR (100 MHz; $CDCl_3$): δ 153.86 (ddd, $^1J_{HC}$ = 156.6, $^1J_{CC}$ = 62.4, $^2J_{HC}$ = 7.1 Hz).

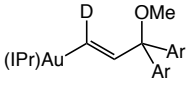
(*Z*)-BpinC(H)=C(H)-C(OMe)(C_6H_4OMe)$_2$ [(*Z*)-8b]. Compound (*Z*)-**8b** was prepared employing a modification of the procedure published by Miyaura.[S6] A mixture of **7b** (195 mg, 0.69 mmol), HBpin (0.11 mL, 0.79mmol), Et_3N (0.1 mL, 0.69 mmol), $[Rh(COD)Cl]_2$ (10.2 mg, 2.1×10^{-2} mmol), and PCy_3 (23.5 mg, 8.4×10^{-2} mmol) in cyclohexane (2.1 mL) was stirred at room temperature for 3.5 h. The resulting mixture was concentrated under vacuum and the resulting residue was chromatographed (SiO_2; hexanes–EtOAc = 90:10) to give (*Z*)-**8b** (110 mg, 39%) as a yellow oil. ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.31 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 4H), 6.44 (d, *J* = 13.9 Hz, 1H), 5.40 (d, *J* = 13.9 Hz, 1H), 3.81 (s, 6H), 2.95 (s, 3H), 1.31 (s, 12H). $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$): δ 158.80, 148.74, 134.57, 130.05, 113.42, 84.95, 83.16, 55.4, 52.26, 25.33. HRMS (ESI) calcd. (found) for $C_{24}H_{31}BO_5$ $[M+H]^+$: 411.2337 (411.2327). $[M+Na]^+$: 433.2157 (433.2152) $[M+K]^+$: 499.1896 (499.1895).

(*E*)-BpinC(H)=C(H)C(OMe)Ph_2 [(*E*)-8a]. Zirconium-catalyzed hydroboration of **7a** (1.0 g, 4.5 mmol) with HBpin employing a procedure similar to that used to synthesize (*E*)-**8b** led to isolation of (*E*)-**8a** (1.0 g, 64 %) as colorless oil, which solidified upon cooling at –20 °C. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.30 – 7.16 (m, 10H), 7.09 (d, *J* = 18.1 Hz, 1H), 5.62 (d, *J* = 18.1 Hz, 1H), 3.06 (s, 3H), 1.21 (s, 12H). $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$): δ 153.24, 143.61, 128.32, 128.10, 127.29, 119.02 (br), 85.30, 83.47, 52.26, 25.03. HRMS (ESI) calcd. (found) for $C_{22}H_{27}BO_3$ $[M-OMe]^+$: 319.1864 (319.1871).

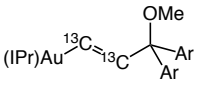
Synthesis of Gold Vinyl Complexes



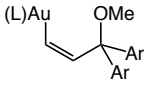
(*E*)-**6a** (L = IPr, Ar = Ph)
(*E*)-**6b** (L = IPr, Ar = 4-C_6H_4OMe)
(*E*)-**6c** [L = P(*t*-Bu)$_2$*o*-biphenyl, Ar = 4-C_6H_4OMe]



(*E*)-**6b**-d_1 (Ar = 4-C_6H_4OMe)



(*E*)-**6b**-1,2-$^{13}C_2$ (Ar = 4-C_6H_4OMe)



(*Z*)-**6b** (L = IPr, Ar = 4-C_6H_4OMe)

Scheme S2. Gold vinyl complexes and their isotopomers.

(*E*)-(IPr)Au[η^1-C(H)=C(H)-C(OMe)(C_6H_5)$_2$ [(*E*)-6a]. A suspension of **7a** (45 mg, 0.13 mmol), IPrAuCl (80 mg, 0.13 mmol) and Cs_2CO_3 (42 mg, 0.13 mmol) in iPrOH (1.3 mL) was stirred for one day at 60 °C. The reaction mixture was cooled to room temperature and concentrated under vacuum. The resulting white solid was dissolved in Et_2O and filtered through thin pad of basic alumina, concentrated, and the procedure was repeated with hexanes/EtOAc (v/v = 9/1). The resulting solid was recrystallized by layering a concentrated CH_2Cl_2 solution with pentane at –20 °C to give (*E*)-**6a** as colorless crystals (62 mg, 59%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.47 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.24 (m, 10H), 7.19 – 7.05 (m, 8H), 6.26 (d, *J* = 19.1 Hz, 1H), 5.76 (d, *J* = 19.2 Hz, 1H), 3.08 (s, 3H), 2.63 (h, *J* = 7.1 Hz, 4H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 7.0 Hz, 12H). $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$): δ 198.19, 161.01, 146.22, 145.93, 143.08, 134.88, 130.25, 128.22, 127.44, 126.00, 124.07, 122.87, 86.62, 51.22, 28.94, 24.56, 24.17. HRMS (ESI) calcd. (found) for $C_{43}H_{52}AuN_2O$ $(M)^+$: 809.3740 (809.3748).

(*E*)-(IPr)Au[η^1-C(H)=C(H)-C(OMe)(4-C_6H_4OMe)$_2$ [(*E*)-6b]. A suspension of (*E*)-**8b** (93 mg, 0.23 mmol), IPrAuCl (141 mg, 0.23 mmol) and Cs_2CO_3 (74 mg, 0.23 mmol) in iPrOH (2.3 mL) was stirred for one day at 60 °C. The reaction mixture was cooled to room temperature and concentrated under vacuum. The resulting white solid was dissolved in Et_2O and filtered through thin pad of basic alumina, concentrated, and the procedure was repeated. The resulting solid was recrystallized by layering a concentrated CH_2Cl_2 solution with pentane at –20 °C to give (*E*)-**6b** as colorless crystals (117 mg, 59%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 4H), 7.15 (d, *J* = 8.7 Hz, 4H),

7.09 (s, 2H), 6.71 (d, J = 8.8 Hz, 4H), 6.22 (d, J = 19.1 Hz, 1H), 5.75 (d, J = 19.1 Hz, 1H), 3.73 (s, 6H), 3.05 (s, 3H), 2.63 (hept, J = 6.8 Hz, 4H), 1.35 (d, J = 6.8 Hz, 12H), 1.21 (d, J = 6.9 Hz, 12H). $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$): δ 198.3, 160.2, 157.9, 145.9, 143.6, 138.6, 134.9, 130.2, 129.4, 124.1, 122.9, 112.8, 86.1, 55.3, 51.0, 24.6, 24.2. Anal. calcd. (found) for $C_{45}H_{56}AuN_2O_3$: C, 62.13 (62.20); H, 6.49 (6.25); N, 3.22 (3.21).

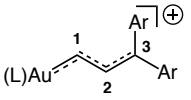
(*E*)-(IPr)Au[η^1-C(D)=C(H)-C(OMe)(4-$C_6H_4OMe)_2$] [(*E*)-6b-d_1]. Gold vinyl complex (*E*)-**6b**-d_1 was isolated as a white solid in 100 % yield from reaction of (*E*)-**8b**-d_1 (31 mg, 7.3×10^{-2} mmol) and (IPr)AuCl (45 mg, 7.3×10^{-2} mmol) employing a procedure analogous to that used to synthesize (*E*)-**6b**. ^{1}H NMR analysis of (*E*)-**6b**-d_1 established >95% deuterium incorporation at C_1 position.

(*E*)-(IPr)Au[η^1-^{13}C(H)=^{13}C(H)-C(OMe)(4-$C_6H_4OMe)_2$] [(*E*)-6b-1,2-$^{13}C_2$]. Complex (*E*)-**6b**-1,2-$^{13}C_2$ was isolated as a white solid in 62% yield from reaction of (*E*)-**8b**-1,2-$^{13}C_2$ (67 mg, 1.6×10^{-1} mmol) and (IPr)AuCl (101 mg, 1.6×10^{-1} mmol) employing a procedure analogous to that used to synthesize (*E*)-**6b**. ^{1}H NMR (400 MHz; $CDCl_3$, selected resonances): δ 6.14 (ddd, $^1J_{HC}$ = 171.7, $^3J_{HH}$ = 19.1, $^2J_{HC}$ = 5.8 Hz, 1H), 5.78 (ddd, $^1J_{HC}$ = 155.1, $^3J_{HH}$ = 19.1, $^2J_{HC}$ = 4.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$): δ 160.2 (d, J = 59.1 Hz), 143.5 (d, J = 58.7 Hz).

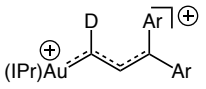
(*Z*)-(IPr)Au[η^1-C(H)=C(H)-C(OMe)(4-$C_6H_4OMe)_2$] [(*Z*)-6b]. Complex (*Z*)-**6b** was isolated as a white solid in 25% yield from reaction of (*Z*)-**8b** with (IPr)AuCl employing a procedure analogous to that used to synthesize (*E*)-**6b** after three successive recrystallizations from diethyl ether. ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.44 (t, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 4H), 7.14 (d, J = 8.7 Hz, 4H), 7.10 (s, 2H), 6.78 (d, J = 14.1 Hz, 1H), 6.62 (d, J = 13.4 Hz, 1H), 6.62 (d, J = 8.9 Hz, 4H), 3.73 (s, 6H), 2.32 (s, 3H), 1.38 (d, J = 6.9 Hz, 12H), 1.21 (d, J = 6.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (125 MHz; $CDCl_3$): δ 198.01, 157.61, 156.12, 146.02, 143.54, 140.44, 135.19, 130.20, 129.41, 124.47, 124.08, 122.95, 112.72, 84.09, 55.25, 50.71, 28.96, 24.54, 24.17.

(*E*)-(P1)Au[η^1-C(H)=C(H)-C(OMe)(4-C$_6$H$_4$OMe)$_2$] [(*E*)-6c]. Gold vinyl complex (*E*)-**6c** was isolated as a white solid in 71% yield from reaction of (*E*)-**8b** (67 mg, 1.6×10^{-1} mmol) and (**P1**)AuCl (86 mg, 1.6×10^{-1} mmol) employing a procedure analogous to that used to synthesize (*E*)-**6b**. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.86 (td, *J* = 7.0, 1.8 Hz, 1H), 7.45 - 7.40 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 4H), 7.25 – 7.21 (m, 3H), 7.13 (d, *J* = 6.9 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 4H), 5.93 (dd, *J* = 19.0, $^3J_{PH}$ = 6.6 Hz, 1H), 5.83 (dd, *J* = 18.9, $^4J_{PH}$ = 4.1 Hz, 1H), 3.81 (s, 6H), 3.18 (s, 3H), 1.39 (d, *J* = 14.3 Hz, 18H). ^{13}C{^{1}H} NMR (125 MHz; $CDCl_3$): δ 158.09, 150.56 (d, *J* = 18.4 Hz), 143.96, 142.66, 138.55, 135.20, 132.99 (d, *J* = 7.6 Hz), 129.91, 129.75, 129.59, 128.26, 127.51, 126.50 (d, *J* = 5.2 Hz), 112.81, 86.46 (d, *J* = 8.6 Hz), 55.40, 51.35, 37.38 (d, *J* = 18.4 Hz), 31.22 (d, *J* = 7.2 Hz). ^{31}P{^{1}H} (162 Hz; $CDCl_3$) δ 64.58. Anal. calcd. (found) for $C_{38}H_{46}AuO_3P$: C, 58.61 (58.76); H, 5.95 (5.88).

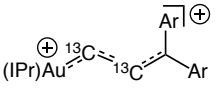
Ionization of gold vinyl complexes



(*E*)-**5a** (L = IPr, Ar = Ph)
(*E*)-**5b** (L = IPr, Ar = 4-C$_6$H$_4$OMe)
(*E*)-**5c** [L = P(*t*-Bu)$_2$*o*-biphenyl, Ar = 4-C$_6$H$_4$OMe]



(*E*)-**5b**-d_1 (Ar = 4-C$_6$H$_4$OMe)



(*E*)-**6b**-1,2-$^{13}C_2$ (Ar = 4-C$_6$H$_4$OMe)

Scheme S3. Gold vinyl carbene complexes and their isotopomers generated via ionization of gold vinyl complexes.

[(*E*)-(IPr)Au[η^1-C(H)=C(H)-C(4-C$_6$H$_4$OMe)$_2$]$^+$ OTf$^-$ [(*E*)-5b]. A solution of (*E*)-**6b** (14.5 mg, 1.7×10^{-2} mmol) in CD_2Cl_2 (0.35 mL) was added dropwise with constant agitation to an NMR tube containing a solution of TMSOTf (4.4 mg, 2.0×10^{-2} mmol) and CH_2Br_2 (0.77 mg, 4.4 μmol; internal standard) in CD_2Cl_2 (0.35 mL) at –95 °C to give a bright orange solution of (*E*)-**5b** that was analyzed without isolation by NMR spectroscopy at or below –85 °C. A yield of 96% for the conversion of (*E*)-**6b** to (*E*)-**5b** was determined by integrating the H_1 resonance of (*E*)-**5b** at δ 9.52 relative to the resonance of CH_2Br_2 at δ

4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; –95 °C): δ 9.51 (d, *J* = 17.8 Hz, 1H), 7.88 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.71 (d, *J* = 17.8 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.33 (s, 2H), 7.31 (d, *J* = 3.0 Hz, 4H), 7.29 (d, *J* = 8.9 Hz, 4H), 7.13 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 4H), 3.96 (s, 3H), 3.89 (s, 3H), 2.44 (sept, *J* = 6.9 Hz, 4H), 1.28 (d, *J* = 6.8 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –95 °C): δ 243.7, 188.7, 185.7, 168.3, 167.6, 146.9, 145.0, 142.4, 139.8, 136.4, 132.9, 129.8, 129.6, 123.5, 123.3, 116.0, 114.4, 56.6, 56.3, 28.0, 24.5, 22.6.

Fluxional behavior of (*E*)-5b. When a solution of (*E*)-**5b** was warmed above –95 °C, the aryl methoxy resonances at δ 3.96 and 3.89 broadened and coalesced at –42 °C (Figure S1). An energy barrier of $\Delta G^{\ddagger}_{231K}$ = 10.5 kcal/mol was determined for interconversion of the anisyl groups of (*E*)-**5b** from the slow-exchange peak separation ($\Delta\nu$ = 32 Hz) and coalescence temperature (T_c = –42 °C) according to the relationship [$k = \pi(\Delta\nu)/\sqrt{2}$].

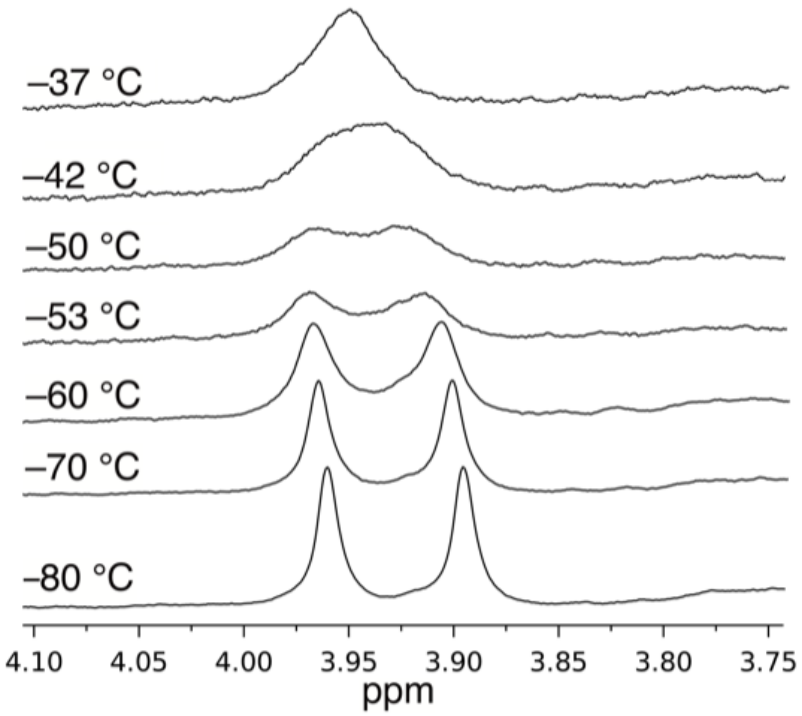


Figure S1. Temperature dependence of the methoxy ^{1}H NMR resonances of (*E*)-**5b** in CD_2Cl_2 from –80 °C to –37 °C in CD_2Cl_2.

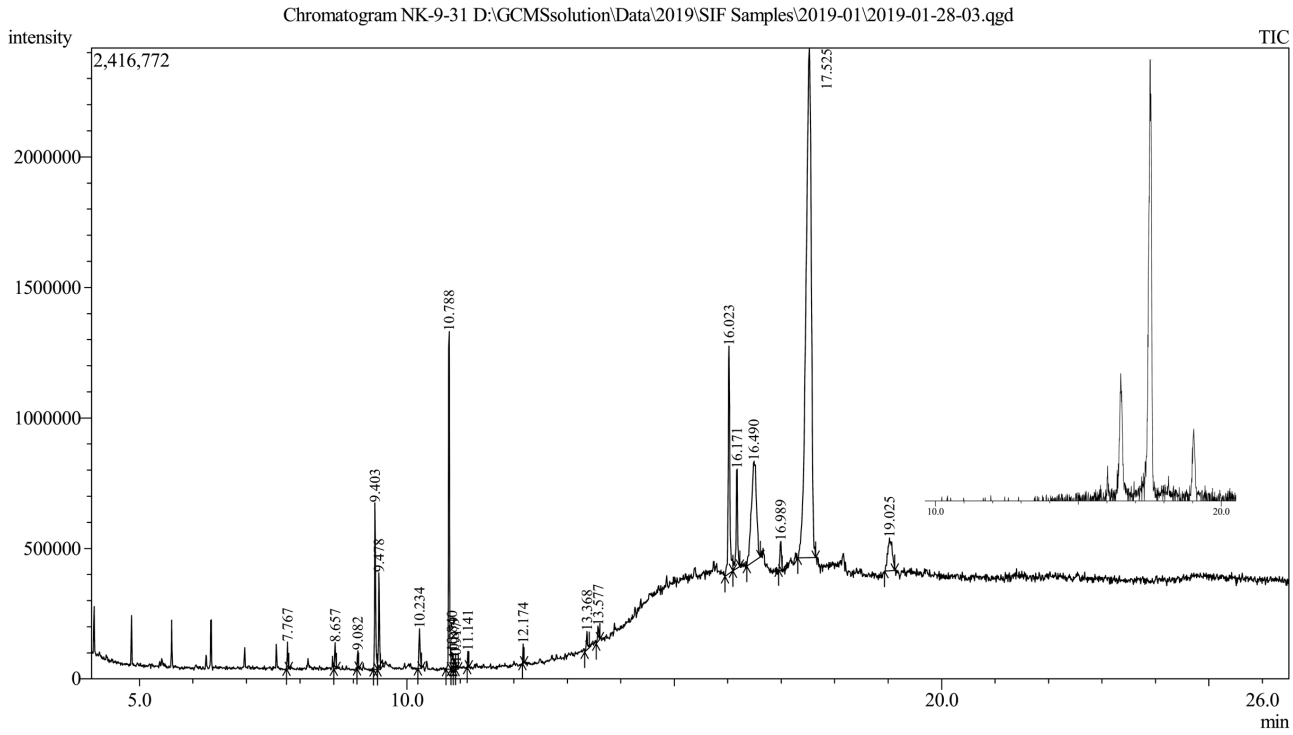
[(*E*)-(IPr)Au[η^1-^{13}C(H)=^{13}C(H)-C(C$_6$H$_4$OMe)$_2$]$^+$ OTf$^–$ [(*E*)-5b-1,2-^{13}C$_2$]. Complex (*E*)-**5b**-1,2-$^{13}C_2$ was generated *in situ* from (*E*)-**6b**-1,2-$^{13}C_2$ employing a procedure analogous to that used to synthesize (*E*)-**5b**. ^{1}H NMR (–95 °C, CD_2Cl_2, 500 MHz, selected resonances): δ 9.50 (dd, *J* = 135.8, 17.7 Hz, 1H; H_1), H_2 was obscured by aromatic protons. $^{13}C\{^1H\}$ NMR (–80 °C, CD_2Cl_2, 125 MHz, selected resonances): δ 243.9 (d, *J* = 47.9 Hz, C1), 188.8 (d, *J* = 38.3 Hz, C_{Ipr}), 185.8 (d, *J* = 48.0 Hz, C3), 146.9 (d, *J* = 47.9 Hz, C2). ^{13}C NMR (–80 °C, CD_2Cl_2, 125 MHz, selected resonances): δ 244.4 (dd, J_{CH} = 135.4, J_{CC} = 48.5 Hz), 147.04 (dd, J_{CH} = 163.0, J_{CC} = 47.7 Hz).

[(*E*)-(P1)Au[η^1-C(H)=C(H)-C(4-C$_6$H$_4$OMe)$_2$]$^+$ OTf$^–$ [(*E*)-5c]. Complex (*E*)-**5c** was synthesized in 95% yield from (*E*)-**6c** (^{1}H NMR) as a red solution employing a procedure analogous to that used to synthesize (*E*)-**5b**. ^{1}H NMR (500 MHz; CD_2Cl_2; –90 °C): δ 8.89 (d, *J* = 17.5 Hz, 1H), 8.16 (d, *J* = 9.1 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.83 (dd, *J* = 17.5, 4.4 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 4H), 7.26 – 7.01 (m, 7H), 4.03 (s, 3H), 4.00 (s, 3H), 1.36 (d, *J* = 14.8 Hz, 18H). $^{13}C\{^1H\}$ NMR (125 MHz; CD_2Cl_2; –90 °C): δ 252.33 (d, *J* = 93.7 Hz), 185.58, 168.29, 167.92, 148.15 (d, *J* = 16.1 Hz), 145.86, 142.70, 142.35, 140.03, 136.85 (br), 134.24, 131.71, 129.95 -124.95 (br), 115.97, 114.42, 56.53, 56.45, 36.32 (d, *J* = 21.8 Hz), 29.83 (br). $^{31}P\{^1H\}$ (202 Hz; CD_2Cl_2; –95 °C): δ 61.8.

[(*E*)-(IPr)Au[η^1-C(H)=C(H)-C(C$_6$H$_5$)$_2$]$^+$ OTf$^–$ [(*E*)-5a]. A solution of (*E*)-**6a** (11.2 mg, 1.4 × 10^{-2} mmol) in CD_2Cl_2 (0.2 mL) was added via syringe to an NMR tube containing a solution of TMSOTf (3.7 mg, 1.7 × 10^{-2} mmol) in ~1:1 mixture of $CDFCl_2/CD_2Cl_2$ at –116 °C to form a biphasic mixture consisting of a liquid phase of $CDFCl_2/CD_2Cl_2$ (bottom) and a solid phase of CD_2Cl_2 (top). As the top phase melted and dissolved in to the bottom layer, the bright orange color of (*E*)-**5a** was observed at the interface, ultimately forming a bright orange solution upon complete dissolution that was analyzed without isolation by NMR spectroscopy at –110 °C. ^{1}H NMR (500 MHz; $CDFCl_2/CD_2Cl_2$; –110 °C; selected resonances): δ 10.83 (d, *J* = 17.4 Hz, 1H), 8.18 (d, *J* = 17.5 Hz, 1H).

A solution of (*E*)-**6a** (11.8 mg, 1.5×10^{-2} mmol) in CD_2Cl_2 (0.3 mL) was added via syringe to a solution of TMSOTf (4.2 mg, 1.8×10^{-2} mmol) and CH_2Br_2 (0.75 mg, 4.3 μmol; internal standard) in CD_2Cl_2 (0.3 mL) at –95 °C to form a bright red solution that faded within 10 s. ^{1}H NMR analysis of the resulting solution revealed the formation of TMSOMe in 92 ± 5% yield, determined by integrating methoxy resonance of TMSOMe at δ 3.29 relative to the resonance of CH_2Br_2 at δ 4.96. ^{1}H NMR also revealed formation of corresponding to the known (*E*)-1,1,6,6-tetraphenylhexa-1,3,5-triene[S7] at δ 6.74 (dd, *J* = 7.6, 3.1 Hz) and δ 6.51 (dd, *J* = 7.5, 3.1 Hz) and for (*Z*)-1,1,6,6-tetraphenylhexa-1,3,5-triene at δ 6.10 (br d, *J* = 8.8 Hz) [Lit. for (*E*)-1,1,6,6-tetraphenylhexa-1,3,5-triene ($CDCl_3$, 400 MHz): δ 6.72 (dd, *J* = 7.6, 3.2 Hz), 6.51 (dd, *J* = 7.6, 3.2 Hz). Lit. for (*Z*)-1,1,6,6-tetraphenylhexa-1,3,5-triene ($CDCl_3$, 400 MHz): δ 6.08 (dd, *J* = 8.4, 2.4 Hz)].[S7] The yield of (*E*)-1,1,6,6-tetraphenylhexa-1,3,5-triene (64%) was determined by integrating vinyl proton at δ 6.51 relative to the resonance of CH_2Br_2 at δ 4.96 and the yield of (*Z*)-1,1,6,6-tetraphenylhexa-1,3,5-triene (6%) was determined by integrating vinyl proton at δ 6.10 relative to the resonance of CH_2Br_2 at δ 4.96.

To corroborate the NMR assignments of (*E*)- and (*Z*)-1,1,6,6-tetraphenylhexa-1,3,5-triene formed in the ionization of (*E*)-**6a**, a solution of (*E*)-**6a** (23.1 mg, 2.8×10^{-2} mmol) in CH_2Cl_2 (0.8 mL) was added via syringe to a solution of TMSOTf (7.6 mg, 3.4×10^{-2} mmol) in CH_2Cl_2 (1.2 mL) at –95 °C and warmed to room temperature. The resulting light green solution was concentrated under vacuum, extracted with hexanes/EtOAc (v/v = 9/1) and filtered through thin pad of silica gel to give yellow oil (5.2 mg). The resulting filtrate was dissolved in EtOAc and analyzed by GCMS on a standard non-polar column over temperature gradient 70 °C - 320 °C, with a hold at the high end. The GCMS trace displayed peaks at 16.49 min (10% mass yield) and 17.52 min (54% mass yield) with molecular weights (m/z = 384.8) consistent with a mixture of (*Z*)- and (*E*)-1,1,6,6-tetraphenylhexa-1,3,5-triene (Figure S2). No other resonances accounted for ≥5% of the reaction mixture. Mass yields were calculated from the total mass of isolated filtrate assuming that mass amount correlates to peak areas in the GC.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	7.767	7.750	7.792	103491	0.43	103320	1.49	1.00	MI	
2	8.657	8.633	8.683	139383	0.58	100763	1.45	1.38	MI	
3	9.082	9.067	9.100	68176	0.29	68743	0.99	0.99	MI	
4	9.403	9.375	9.450	873814	3.66	637830	9.19	1.37	MI	
5	9.478	9.450	9.508	501212	2.10	370695	5.34	1.35	MI	
6	10.234	10.208	10.275	232329	0.97	151983	2.19	1.53	MI	
7	10.788	10.733	10.825	1760463	7.37	1293318	18.63	1.36	MI	
8	10.840	10.825	10.867	125147	0.52	65337	0.94	1.92	MI	
9	10.879	10.867	10.908	69220	0.29	39886	0.57	1.74	MI	
10	10.917	10.908	10.958	36700	0.15	22027	0.32	1.67	MI	
11	11.141	11.125	11.158	57831	0.24	61394	0.88	0.94	MI	
12	12.174	12.158	12.192	62639	0.26	73193	1.05	0.86	MI	
13	13.368	13.325	13.408	107473	0.45	69880	1.01	1.54	MI	
14	13.577	13.542	13.608	95773	0.40	58393	0.84	1.64	MI	
15	16.023	15.950	16.100	1879935	7.87	871245	12.55	2.16	MI	
16	16.171	16.100	16.225	775549	3.25	380120	5.48	2.04	MI	
17	16.490	16.358	16.608	2586284	10.83	383238	5.52	6.75	MI	
18	16.989	16.950	17.017	212914	0.89	113240	1.63	1.88	MI	
19	17.525	17.308	17.642	13465499	56.39	1951846	28.11	6.90	MI	
20	19.025	18.933	19.125	724818	3.04	126171	1.82	5.74	MI	
				23878650	100.00	6942622	100.00			

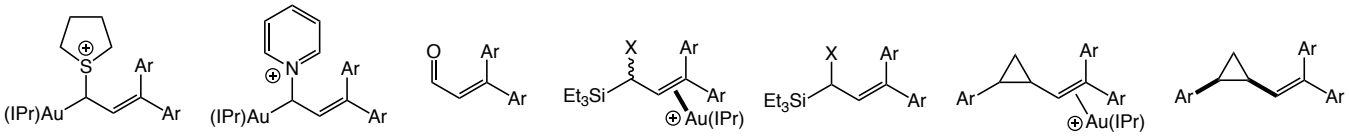
Figure S2. GCMS trace of the filtrated isolated from the reaction of (*E*)-**6a** with TMSOTf at –95 °C in CD_2Cl_2 with mass-selected (m/z = 384.8) GC trace (insert).

Ionization of (*Z*)-6b. A solution of (*Z*)-**6a** (10.0 mg, 1.2×10^{-2} mmol) in CD_2Cl_2 (0.3 mL) was added via syringe to a solution of TMSOTf (3.0 mg, 1.3×10^{-2} mmol) and CH_2Br_2 (0.62 mg, 3.5 μmol; internal standard) in CD_2Cl_2 (0.3 mL) at –95 °C to form an orange solution. ^{1}H NMR analysis of the

resulting solution displayed no resonances that could be attributed to the C1 or C2 vinyl protons of (*Z*)-**6b**, but displayed singlets at δ 4.63 and δ 4.59, as a small peak at δ 4.53 corresponding to the benzylic resonance of **9**. As the temperature was raised in 20 °C increments, the singlets at δ 4.63 and δ 4.59 disappeared and the benzylic resonance of **9** at δ 4.53 increased in intensity, ultimately accounting for a 58 ± 5% yield, as determined by integrating the δ 4.53 resonance relative to the resonance of CH_2Br_2 at δ 4.96. The crude reaction mixture was filtered through silica gel with hexanes–EtOAc = 9:1, concentrated, and the resulting residue was chromatographed (SiO_2; hexanes–EtOAc = 9:1) to give **9** (0.8 mg, 28%) as colorless oil, which solidified upon cooling at –20 °C.

For 9: ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.11 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 5.3, 2.2 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.58 (dd, *J* = 5.5, 1.9 Hz, 1H), 4.52 (t, *J* = 2.1 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz; $CDCl_3$): 159.1, 158.5, 145.5, 141.5, 140.8, 131.4, 131.0, 128.7, 124.2, 114.1, 111.0, 106.8, 55.5, 55.3, 55.0. HRMS (ESI) calcd. (found) for $C_{17}H_{16}O_2$ $[M+H]^+$: 253.1223 (253.1222).

Reactions of Nucleophiles with (*E*)-5b



10 **11** **12** **13** (X = H) **13**-d_1 (X = D) **14** (X = H) **14**-d_1 (X = D) **15** (dr = 3:1) **16** (dr = 3:1)

Scheme S4. Products and isotopomers generated from reaction of (*E*)-**5b** with nucleophiles (Ar = 4-C_6H_4OMe).

Reaction of (*E*)-5b with tetrahydrothiophene (THT). A solution of tetrahydrothiophene (1.9 mg, 2.21×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise to a freshly prepared solution of (*E*)-**5b** (1.44 $\times 10^{-2}$ mmol) in CD_2Cl_2 (0.60 mL) at –95 °C and the resulting solution mixed thoroughly for < 1 min to give a yellow solution of $^{(IPr)}Au[\eta^1\text{-}C(H)(\overline{SCH_2CH_2CH_2CH_2})=C(H)=C(4\text{-}C_6H_4OMe)_2]^+$ OTf^- (**10**) in 92 ± 5

yield (^{1}H NMR). The yield of **10** was determined by integrating the vinylic H_1 resonance of **10** at δ 5.61 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; 0 °C): δ 7.56 (t, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.33 (s, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 5.60 (d, *J* = 11.5 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.22 (d, *J* = 11.5 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.72 – 2.61 (m, 1H), 2.49 (h, *J* = 7.3 Hz, 4H), 2.08 - 1.95 (m, 1H), 1.81 - 1.72 (m, 1H), 1.35 - 1.20 (m, 24H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –80 °C): δ 185.8, 174.9, 157.7, 157.4, 145.3, 145.0, 137.3, 133.6, 133.0, 132.3, 130.6, 130.1, 128.7, 127.4, 123.9, 123.7, 123.5, 122.9, 120.6, 118.3, 112.9, 112.5, 54.9, 54.9, 49.7, 49.0, 43.9, 43.0, 31.3, 30.7, 28.6, 28.1, 24.7, 24.2, 23.1, 22.9, 22.8.

Reaction of (*E*)-5b with pyridine. A solution of pyridine (3.3 mg; 4.21×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise with agitation to a freshly prepared solution of (*E*)-**5b** (1.30×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) at –95 °C for <1 min to give a bright yellow solution of (IPr)Au[η^1-C(H)(NC_5H_5)=C(H)=C(4-$C_6H_4OMe)_2$]$^+$ OTf^- (**11**) in 94 ± 5% NMR yield. The yield of **11** was determined by integrating the vinylic proton resonance of **11** at δ 5.80 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; –20 °C): δ 8.23 (t, *J* = 7.8 Hz, 1H; py), 8.08 (d, *J* = 6.0 Hz, 2H; py), 7.68 – 7.53 (m, 4H), 7.46 – 7.38 (m, 2H), 7.38 – 7.30 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 5.7 Hz, 4H), 5.80 (d, *J* = 10.8 Hz, 1H), 4.90 (d, *J* = 10.7 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 2.49 (h, *J* = 7.1 Hz, 4H), 1.36 – 1.15 (m, 24H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –80 °C): δ ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –80 °C): δ 187.5, 157.5, 157.3, 150.4, 145.5, 145.0, 143.1, 133.8, 133.2, 131.7, 130.5, 130.3, 130. 1, 128.9, 127.7, 126.7, 126.5, 123.9, 123.7, 123.5, 122.8, 121.1, 118.6, 112.7, 112.4, 81.41, 54.8, 28.2, 28.1, 24.7, 24.6, 24.0, 23.2, 22.9, 22.8, 22.8, 21.1.

A concentrated solution (0.13 M) of **11** was layered with ten volumes of diethyl ether at room temperature and then maintained at –20 °C to give yellow crystals of **11** suitable for X-ray analysis. A yellow block-like crystal was used for the X-ray crystallographic analysis.

Conversion of 10 to 11. Pyridine (1.1 μL, 1.2 μmol, 16 mM) was added to a freshly prepared solution of **10** (17 mM) in CD_2Cl_2 at –80 °C, mixed thoroughly, and placed in the probe of an NMR spectrometer cooled at –80 °C. The probe was warmed at 0 °C and the solution was monitored periodically by ^{1}H NMR spectroscopy. The concentrations of **10** and **11** were determined by integrating the C2 vinylic protons of **10** and **11** at δ 5.59 and 5.82, respectively, relative to the resonance for CH_2Br_2 at δ 4.96 (Figure S3). After 120 min the ratio of **10**:**11** was 1.25, which remained unchanged after –20 °C for 24 h. From these data we determined an equilibrium constant for the conversion of **10** and pyridine to **11** and THT of $K_{eq} = [\mathbf{11}]_{eq}[THT]_{eq}/[\mathbf{10}]_{eq}[pyridine]_{eq} = 1.8 \pm 0.2$. The values for $[\mathbf{10}]_{eq} + [\mathbf{11}]_{eq}$ were determined from the ratio of **10**:**11** at equilibrium and from the initial concentration of **10** assuming that $[\mathbf{10}]_{eq} + [\mathbf{11}]_{eq} = [\mathbf{10}]_0 = 17$ mM, the value for $[THT]_{eq}$ was determined assuming that $[THT]_{eq} = [\mathbf{11}]_{eq}$, and the value for $[pyridine]_{eq}$ was determined assuming that $[pyridine]_{eq} = [pyridine]_0 - [\mathbf{11}]_{eq}$. A plot of $\ln([\mathbf{10}]_t - [\mathbf{10}]_\infty)$ versus time was linear to 2.5 half-lives with an observed rate constant of $k_{obs} = k_f + k_r = 6.3 \pm 0.3 \times 10^{-4}$ s^{-1} (Figure S4). From this value and from the equilibrium constant for the conversion of **10** to **11**, we determined values for the forward and reverse first-order rate constants for the conversion of **10** to **11** of $k_f = 4.1 \pm 0.9 \times 10^{-4}$ s^{-1} and $k_r = 2.3 \pm 0.5 \times 10^{-4}$ s^{-1}.

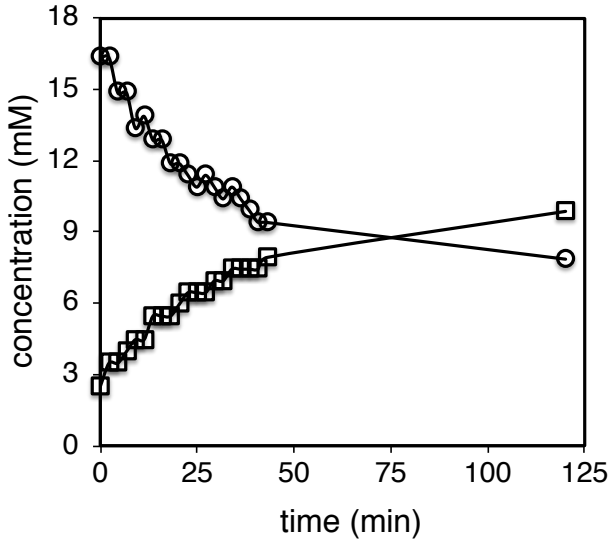


Figure S3. Concentration versus time plot for the reaction of **10** (17 mM; ○) with pyridine (16 mM) to form **11** (□) and THT in CD_2Cl_2 at 0 °C.

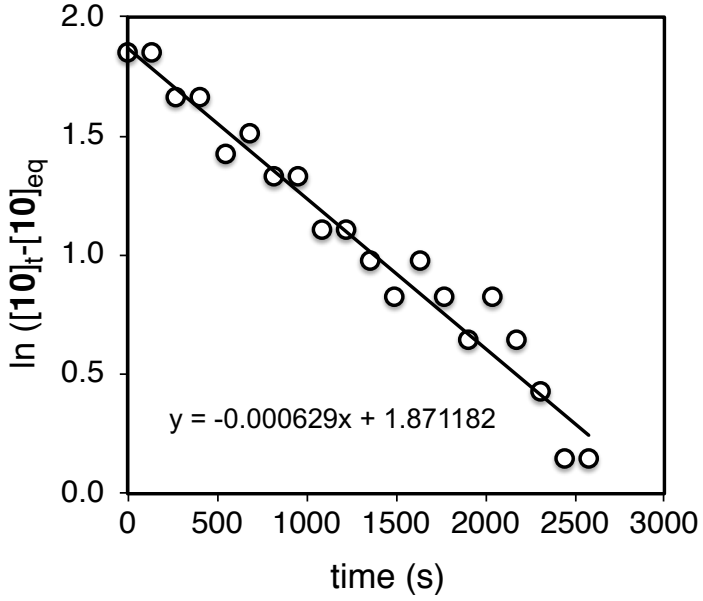


Figure S4. First-order plot of approach to equilibrium for the reaction of **10** (17 mM) with pyridine (16 mM) in CD_2Cl_2 at 0 °C.

Reaction of (*E*)-5b with 4-picoline *N*-oxide (4-PNO). A solution of 4-methylpyridine N-oxide (3.1 mg, 2.8×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise with constant agitation to a freshly prepared solution of (*E*)-**5b** (1.5×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) at –95 °C and mixed thoroughly to give transparent, pale green solution within 1 min. ^{1}H NMR analysis of the resulting solution revealed a mixture of the known 3,3-bis(4-methoxyphenyl)acrylaldehyde (**12**)[S8] in 88 ± 5% yield and [(IPr)Au(4-pic)]$^+$ OTf$^-$ in quantitative yield, both of which were characterized in solution without isolation. The yield of **12** was determined by integrating the aldehyde resonance of **12** at δ 9.37 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum.

For [(IPr)Au(4-pic)]$^+$ OTf$^-$: ^{1}H NMR (500 MHz; CD_2Cl_2; 25 °C): δ 7.73 (d, *J* = 5.6 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.41 (s, 2H), 7.38 (d, *J* = 7.8 Hz, 4H), 7.30 (d, *J* = 5.8 Hz, 2H), 2.56 (h, *J* = 7.0 Hz, 4H), 2.39 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 12H), 1.28 (d, *J* = 6.9 Hz, 12H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; 25 °C): δ 168.1, 155.0, 150.2, 146.09, 133.7, 131.5, 127.9, 125.0, 124.9, 29.3, 24.8, 24.1 21.7.

Reaction of (*E*)-5b with triethylsilane. A solution of triethylsilane (3.0 mg, 2.6×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added to a freshly prepared solution of (*E*)-**5b** (1.4×10^{-2} mmol) and CH_2Br_2 (0.83 mg, 4.8 μmol; internal standard) in CD_2Cl_2 (0.60 mL) at –95 °C to give transparent, pale orange solution immediately upon mixing. ^{1}H NMR analysis of the resulting solution revealed formation of (IPr)Au(η^2-$Et_3SiCH_2C(H)=C(4\text{-}C_6H_4OMe)_2]^+$ OTf^- (**13**) as the exclusive product in 97% yield as determined by integrating vinyl resonance of **13** at δ 5.99 relative to the resonance of CH_2Br_2 at δ 4.96. Complex **13** was thermally unstable and was therefore characterized by NMR spectroscopy in solution without isolation and through isotopic labelling and independent synthesis (see below).

When the solution was warmed to –40 °C, conversion of **13** to (3,3-bis(4-methoxyphenyl)allyl)triethylsilane (**14**) was observed and further warming the solution at 0 °C for 5 min. led to formation of **14** in 100% yield as determined by integrating the vinylic resonance of **14** at δ 6.00 relative to the resonance for CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. The resulting solution was concentrated and chromatographed (SiO_2; hexanes–EtOAc = 95: 5) to give **14** as colorless oil (3.5 mg, 67%).

Independent synthesis of 13. A solution of **14** (5.0 mg, 1.4×10^{-2} mmol) in CD_2Cl_2 (0.4 mL) was added to a suspension of IPrAuCl (8.4 mg, 1.4×10^{-2} mmol) and $AgSbF_6$ (5.0 mg, 1.5×10^{-2} mmol) in CD_2Cl_2 (0.3 mL) at –78 °C. ^{1}H NMR analysis of the resulting solution revealed formation of **13** in ~65% yield, determined by integrating the vinylic proton resonance of **13** at δ 5.98 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum, along with free **14**. Complex **13** synthesized in this manner was indistinguishable from **13** generated from the reaction of (*E*)-**5b** with $HSiEt_3$. ^{1}H NMR spectrum of **13** displayed a doublet at δ 5.97 (J = 13 Hz) assigned to the vinylic proton and a triplet at δ 1.40 (J = 13 Hz) assigned to one of the diastereotopic allylic protons, with the second diastereotopic allylic proton presumably obscured by IPr resonances. This coupling pattern is consistent with strong and coincidentally equivalent (J = 13 Hz) coupling between the vinylic proton and the allylic proton at δ 1.40

and between the two allylic protons and weak ($J \leq 2$ Hz) coupling between the vinylic proton and the obscured allylic resonance (Figure S5).

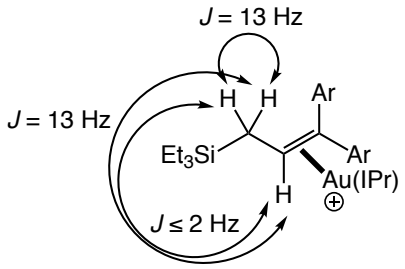


Figure S5. Assignment of allylic and vinylic couplings in **13**.

For 13: ^{1}H NMR (500 MHz; CD_2Cl_2; –80 °C): δ 7.59 (t, J = 7.7 Hz, 2H), 7.49 (t, J = 8.0 Hz, 0.5 H), 7.43 (s, 2H), 7.29 (d, J = 8.6 Hz, 4H), 7.27 (d, J = 8.3 Hz, 4H), 7.20 (d, J = 7.9 Hz, 0.5 H), 5.98 (d, J = 12.9 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 2.23 (sept, J = 13.6 Hz, 4H), 1.40 (t, J = 13.0 Hz, 1H), 0.52 (t, J = 7.8 Hz, 9H), 0.33 – 0.12 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –80 °C): δ 174.0, 159.9, 158.8, 144.8, 144.7, 132.1, 131.2, 131.0, 130.9, 130.6, 128.8, 127.1, 124.0, 123.8, 113.4, 112.9, 103.4, 55.2, 55.1, 49.7, 28.1, 24.0, 23.4, 22.9.

For 14: ^{1}H NMR (500 MHz; CD_2Cl_2; 25 °C): δ 7.10 (dd, J = 8.7, 1.9 Hz, 4H), 6.90 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.00 (t, J = 8.7 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 1.65 (d, J = 8.7 Hz, 2H), 0.87 (t, J = 7.9 Hz, 9H), 0.52 (q, J = 7.9 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; 25 °C): δ 158.43, 158.36, 138.50, 136.91, 133.20, 131.51, 128.14, 124.80, 113.75, 113.60, 55.46, 55.40, 15.92, 7.54, 3.59. HRMS (ESI) calcd. (found) for $C_{23}H_{32}O_2Si$ $(M)^+$: 369.2244 (369.2243).

Reactions of (*E*)-5b with $DSiEt_3$ and (*E*)-5b-d_1 with $HSiEt_3$. A solution of $DSiEt_3$ (3.4 mg, 2.9×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added to a freshly prepared solution of (*E*)-**5b** (1.4×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) containing CH_2Br_2 (4.7×10^{-3} mmol) at –95 °C to give transparent, pale orange mixture of (IPr)Au(η^2-$Et_3SiCHDC(H)=C(4\text{-}C_6H_4OMe)_2]^+$ OTf^- (**13**-d_1) in quantitative yield. In a separate experiment, a solution of $HSiEt_3$ (2.8 μL) in CD_2Cl_2 was added via syringe to a solution of (*E*)-**5b**-d_1 (11.9

mg, 1.4×10^{-2} mmol) in CD_2Cl_2 containing CH_2Br_2 (4.3×10^{-3} mmol) to form **13**-d_1 in 95% yield, which was indistinguishable from **13**-d_1 generated in the reaction of (*E*)-**5b** with $DSiEt_3$. The ^{1}H NMR spectrum of **13**-d_1 displayed a broad singlet at δ 5.97 assigned to the vinylic proton and a doublet at δ 1.40 (J = 13 Hz) assigned to one of the diastereotopic allylic protons, which integrated to 0.5 H relative to the vinylic resonance at δ 5.97. This observation is consistent with exclusive incorporation of deuterium into the allylic position of **13**-d_1 with the deuterium atom distributed equally between the diastereomeric positions.

Warming a solution of **13**-d_1 to 0 °C led to quantitative formation of **14**-d_1 with ≥95% deuterium incorporation at the allylic position as determined by integrating the allylic resonance at δ 1.63 relative to the vinylic resonance at δ 5.99.

For 13-d_1: ^{1}H NMR (CD_2Cl_2, –80 °C, selected resonances): δ 5.97 (br s, 1H), 1.38 (d, J = 13.0 Hz, 0.5H).

For 14-d_1: ^{1}H NMR (CD_2Cl_2, 25 °C, selected resonances): δ 5.99 (d, J = 8.7 Hz, 1H), 1.63 (d, J = 8.6 Hz, 1H).

Reaction of (*E*)-5b with 4-methoxystyrene. A solution of 4-methoxystyrene (6.5 mg, 4.8×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise via syringe with constant agitation to a freshly prepared solution of (*E*)-**5b** (1.6×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) at –95 °C to generate a transparent red solution. ^{1}H NMR analysis of the crude reaction mixture at –90 °C showed a distinct resonance at δ 4.99 (J = 10.2 Hz, 1H) assigned to the vinyl proton of **15**, which corresponded to a 75% yield from (*E*)-**5b** as determined by integrating vinylic resonance of **15** at δ 4.99 relative to the resonance of CH_2Br_2 at δ 4.96. Upon warming the solution above –40 °C, decomplexation of *cis*-**15** was observed with the concomitant appearance of **16**, as indicated by the appearance of a resonance at 5.44 (d, J = 9.6 Hz, 1H) assigned to the vinylic resonance of **16**. However, direct integration of this resonance was precluded by the presence of both excess 4-methoxystyrene and byproducts, presumably resulting from polymerization of 4-methoxystyrene. Therefore, the reaction mixture was filtered through a thin pad of silica gel, eluted with hexanes–EtOAc, and concentrated under vacuum. ^{1}H NMR analysis of the resulting residue established

the presence of **16** along with minor impurities. In a separate experiment, 4-methoxystyrene (9.2 mg, 6.8×10^{-2} mmol) was added dropwise with stirring to a freshly prepared solution of (*E*)-**5b** (1.6×10^{-2} mmol) and anthracene (2.3 mg, 1.3×10^{-2} mmol; internal standard) in CH_2Cl_2 (3.0 mL) at –95 °C and the resulting mixture was warmed slowly to room temperature. The crude reaction mixture was filtered through silica gel with hexanes–EtOAc and analyzed by ^{1}H NMR spectroscopy, which revealed formation of **16** in 67% yield as a ~3:1 mixture of cis/trans isomers as determined by integrating the vinylic proton resonance of *cis*-**16** at δ 5.44 and *trans*-**16** at δ 5.17 relative to the H9/H10 proton resonance of anthracene at δ 8.44. The solvent was evaporated and the resulting residue was chromatographed (SiO_2; hexanes–EtOAc = 9:1) to give **16** (8.4 mg, 51%, 3:1 cis/trans) as a colorless oil.

The cis and trans isomers of **16** (*cis*-**16** and *trans*-**16**, respectively) were unambiguously assigned by ^{1}H-^{1}H NOESY analysis. In particular, *cis*-**16** displayed a strong cross peak correlating the benzylic proton resonance at δ 2.03 (ddd, *J* = 8.7, 5.8, 4.3 Hz, 1H) with the allylic proton resonance at δ 1.75 (dddd, *J* = 9.8, 8.4, 5.6, 4.3 Hz, 1H), which was absent for *trans*-**16** (Figure S6).

Spectroscopic analysis was performed on a 3:1 mixture of *cis*-**16** and *trans*-**16** without further purification.

For *cis*-16: ^{1}H NMR (500 MHz; $CDCl_3$; 25 °C): δ 7.19 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 7.4 Hz, 2H), 5.44 (d, *J* = 9.6 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.03 (ddd, *J* = 8.7, 5.8, 4.3 Hz, 1H), 1.75 (dddd, *J* = 9.8, 8.4, 5.6, 4.3 Hz, 1H), 1.19 - 1.10 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz; $CDCl_3$; 25 °C): δ 158.82 (*p*), 158.64 (*p*), 157.88 (*p*), 139.73 (*ipso*), 136.04 (*ipso*), 134.14 (*ipso*), 132.80 (vinyl), 131.64 (*o*), 128.59 (*o*), 128.46 (vinyl), 127.10 (*o*), 113.96 (*m*), 113.65 (*m*), 113.61 (*m*), 55.44 (*C*H_3O–), 25.72 (benzylic), 24.85 (allylic), 18.00.

For *trans*-16: δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.92 (dd, *J* = 8.6, 6.2 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 5.17 (d, *J* = 9.9 Hz, 1H), 3.81 (s, 11H), 3.85 (s, 3H), 3.74 (s, 3H), 2.28 (td, *J* = 8.5, 6.3 Hz, 1H), 1.89 (dtd, *J* = 10.0, 8.5, 5.5 Hz, 1H), 1.31 – 1.24 (m, 2H). Remaining aromatic resonances were obscured by those

of *cis*-**16**. $^{13}C\{^{1}H\}$ NMR (125 MHz; $CDCl_3$; 25 °C, distinct resonances only): δ 158.07, 140.52, 136.15, 133.24, 131.17, 130.93, 130.39, 128.46, 127.98, 23.90, 20.33, 13.86.

For *cis*-16/*trans*-16: HRMS (ESI) calcd. (found) for $C_{26}H_{26}O_3(M)^+$: 387.1955 (387.1952).

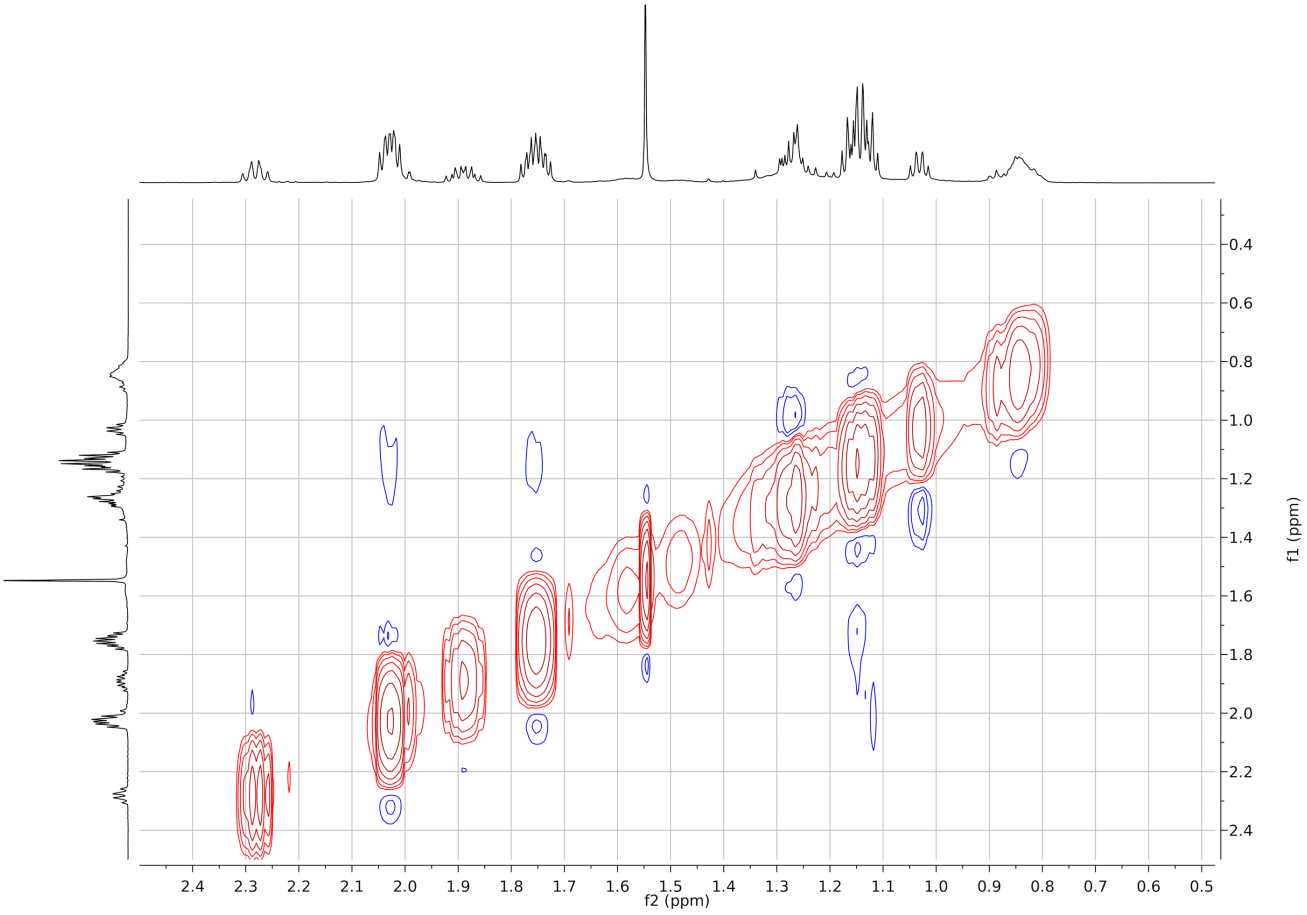


Figure S6. Partial ^{1}H-^{1}H NOESY spectrum of a 3:1 mixture of *cis*-**12** and *trans*-**12**.

Independent synthesis of 15. A solution of **16** (3.0 mg, 7.8×10^{-3} mmol; *cis*:*trans* = 3:1) in CD_2Cl_2 (0.35 mL) was added to a suspension of IPrAuCl (4.8 mg, 7.8×10^{-3} mmol) and $AgSbF_6$ (3.0 mg, 8.7×10^{-3} mmol) in CD_2Cl_2 (0.3 mL) at –80 °C to give dark purple solution. Although the ^{1}H NMR spectrum of the resulting was broadened, distinct resonances were observed for the vinylic protons of **15** and *cis*-**16** at δ 5.54 (*J* = 9.6 Hz) and δ 4.99 (*J* = 10.2 Hz), respectively, in ~4:1 ratio. Upon gradual warming of

solution above –40 °C to room temperature over 5 h, the vinylic resonances for both **15** and *cis*-**16** were significantly reduced in intensity and eventually disappeared to give deep blue solution.

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S1) B. Seed, *Curr. Protoc. Mol. Biol*. **1994**, A.3B.1–A.3B.2.

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Figure S7. ^{1}H NMR spectrum of (*E*)-**8b** ($CDCl_3$, 25 °C).

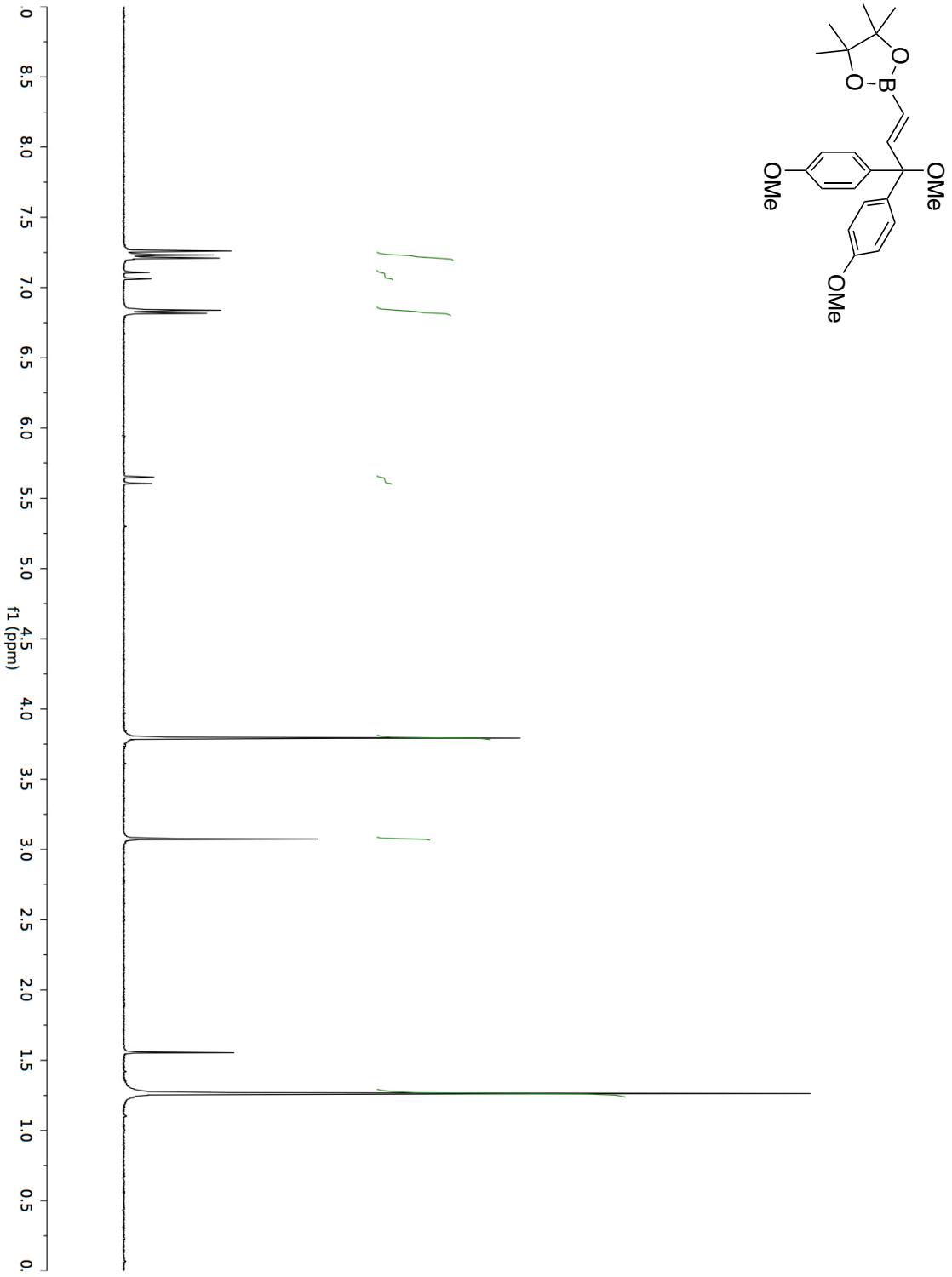

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**8b** ($CDCl_3$, 25 °C).

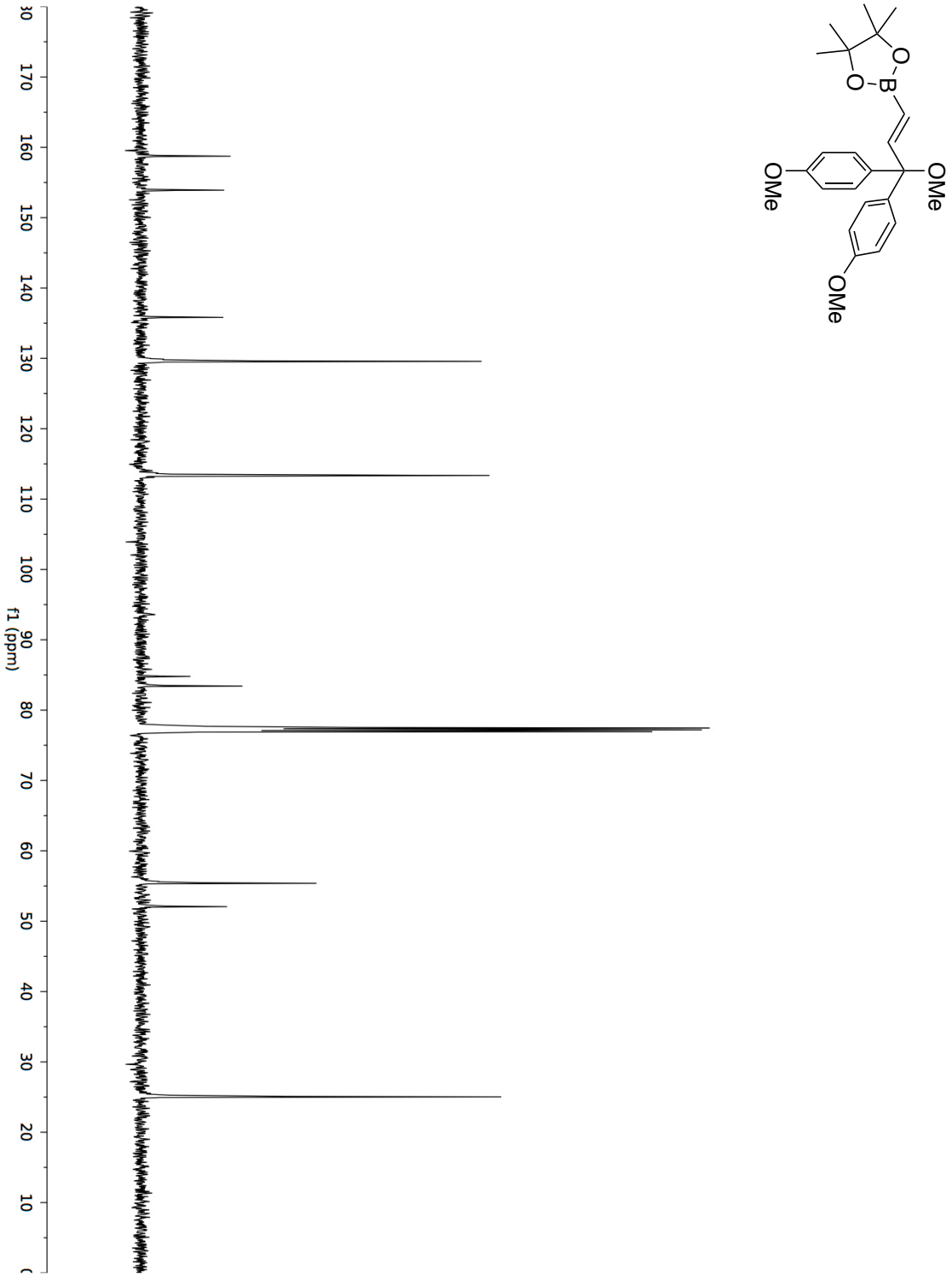

Figure S9. ^{1}H NMR spectrum of (*E*)-**8a** ($CDCl_3$, 25 °C).

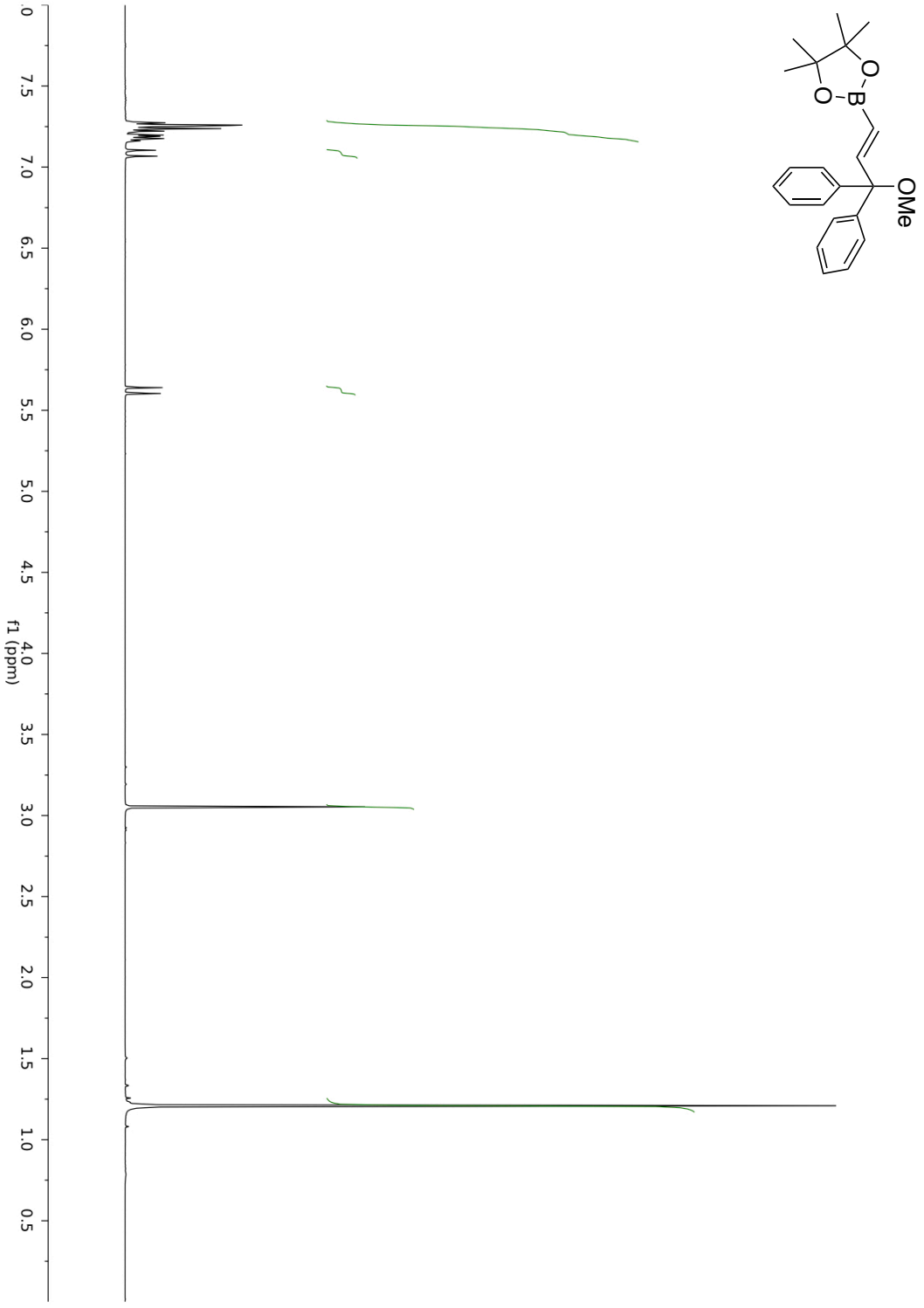

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**8a** ($CDCl_3$, 25 °C).

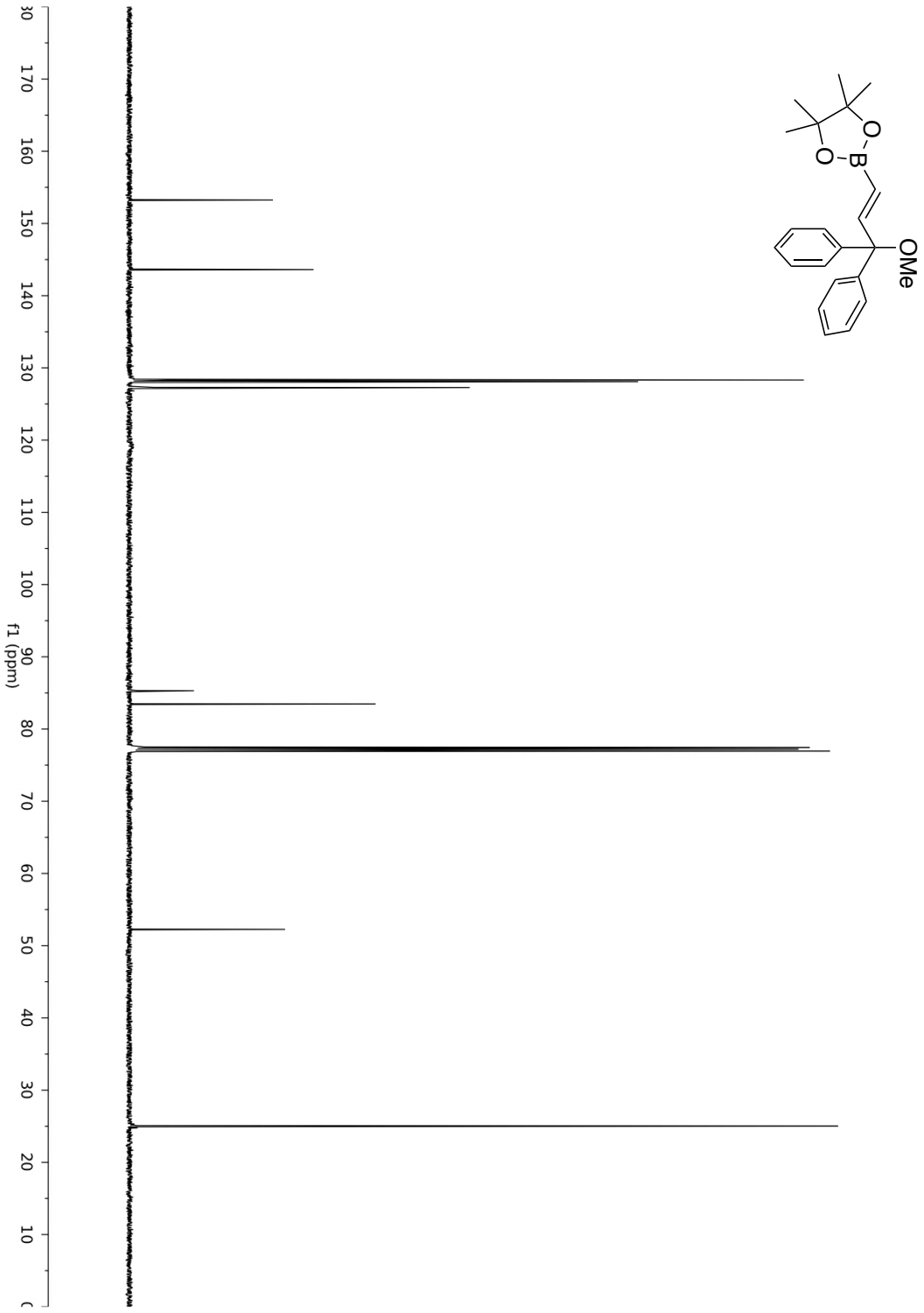

Figure S11. ^{1}H NMR spectrum of (*Z*)-**8b** ($CDCl_3$, 25 °C).

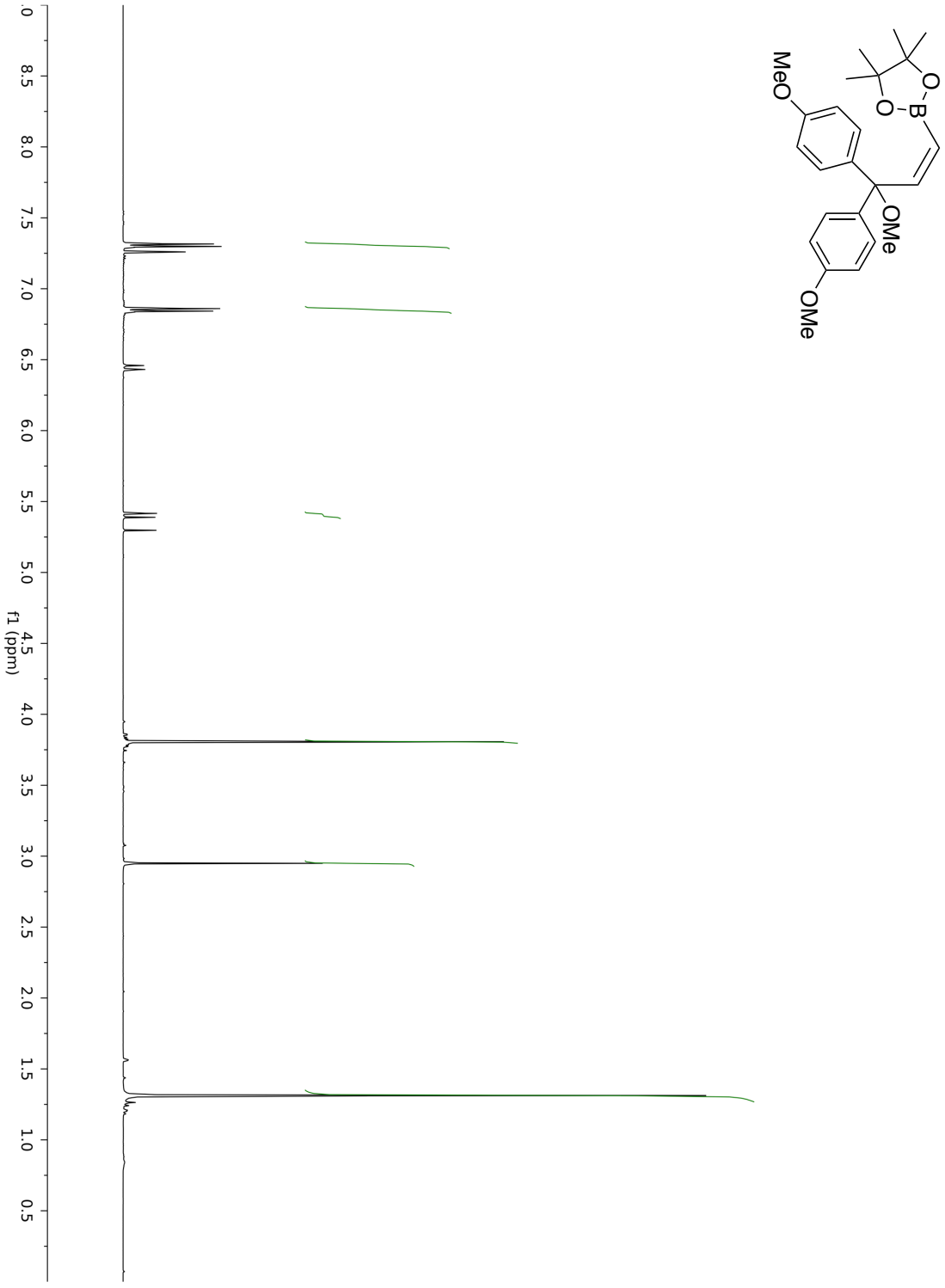

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of (*Z*)-**8b** ($CDCl_3$, 25 °C).

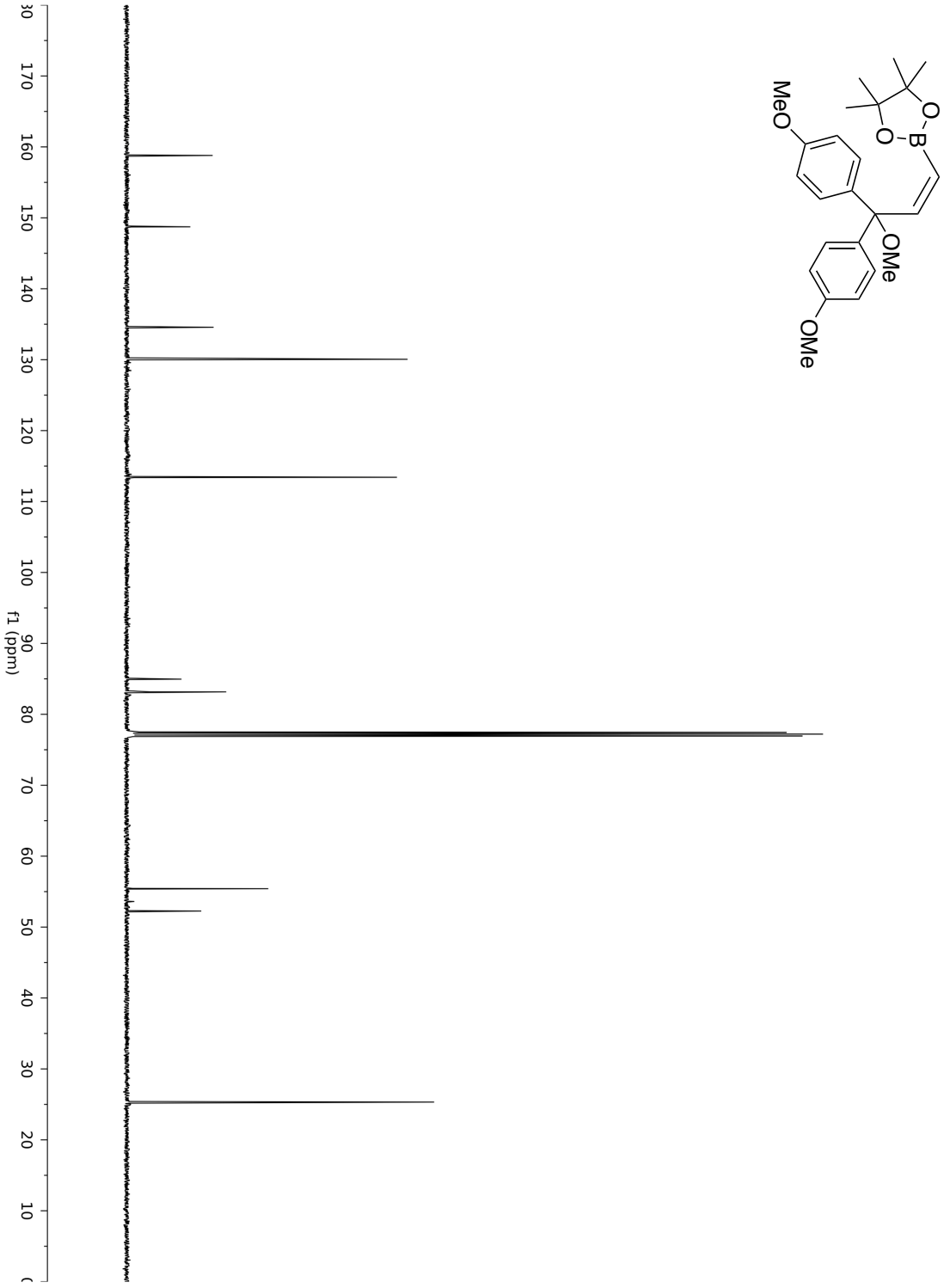

Figure S13. ^{1}H NMR spectrum of (*E*)-**6a** ($CDCl_3$, 25 °C).

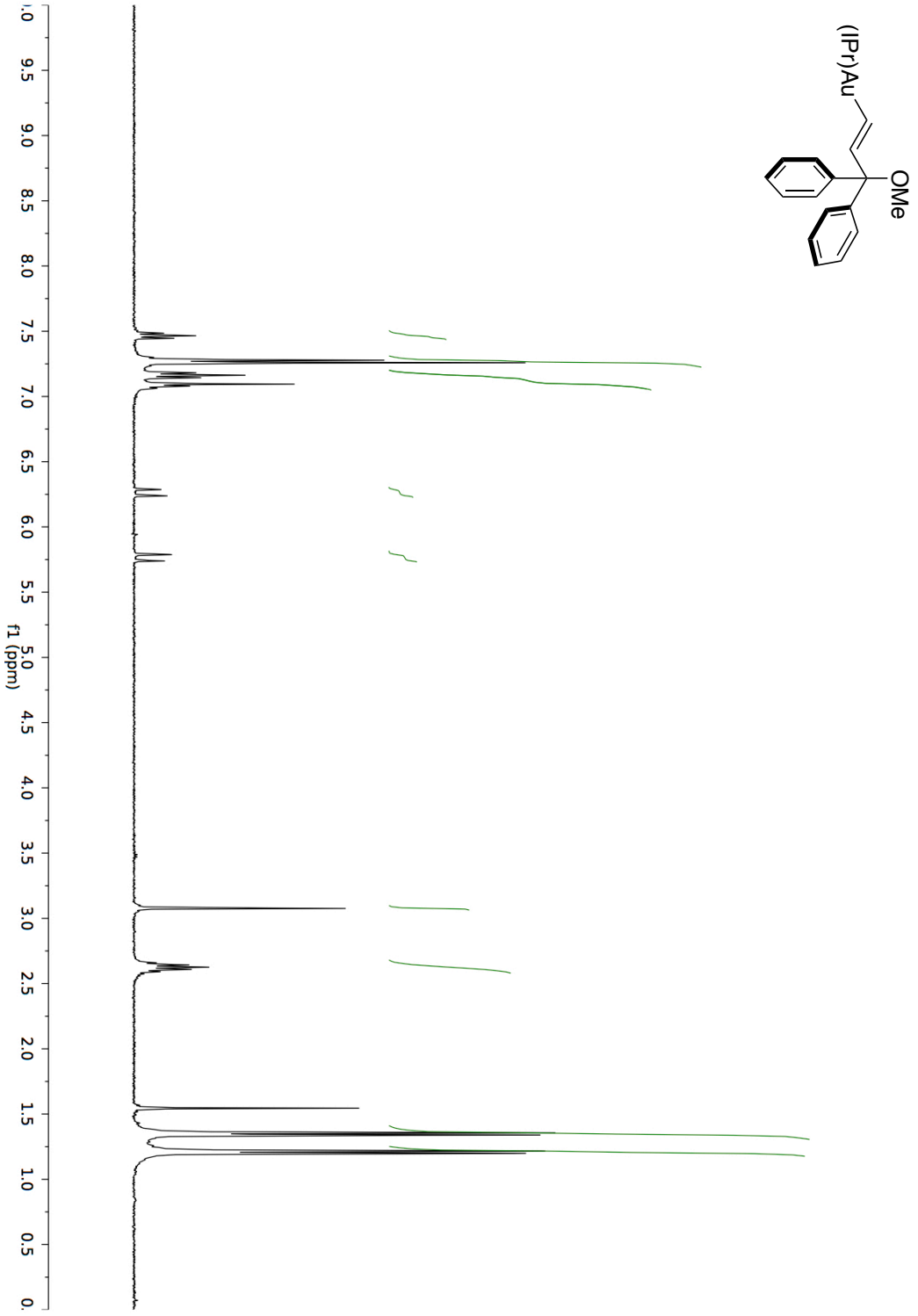

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**6a** ($CDCl_3$, 25 °C).

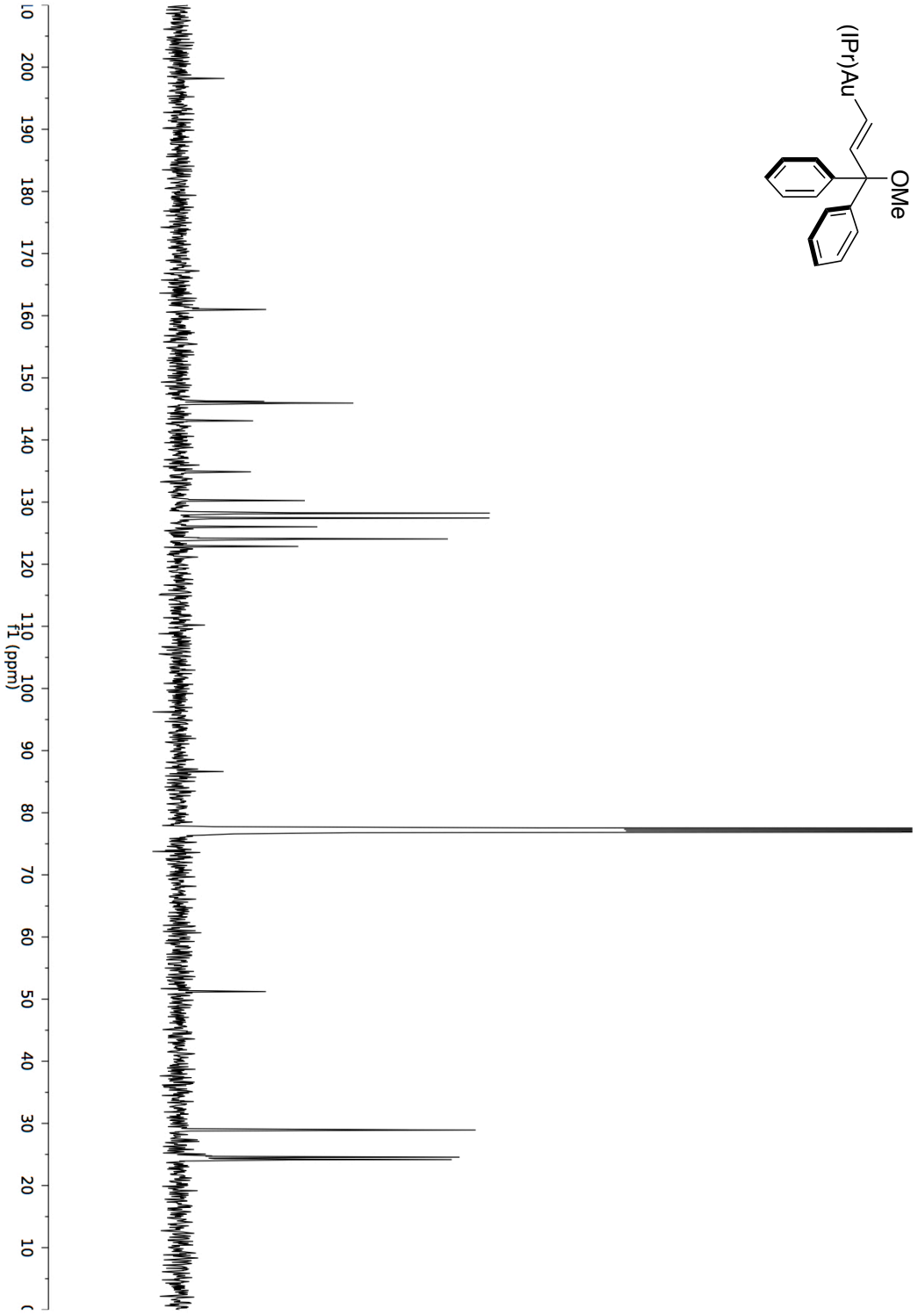

Figure S15. ^{1}H NMR spectrum of (*E*)-**6b** ($CDCl_3$, 25 °C).

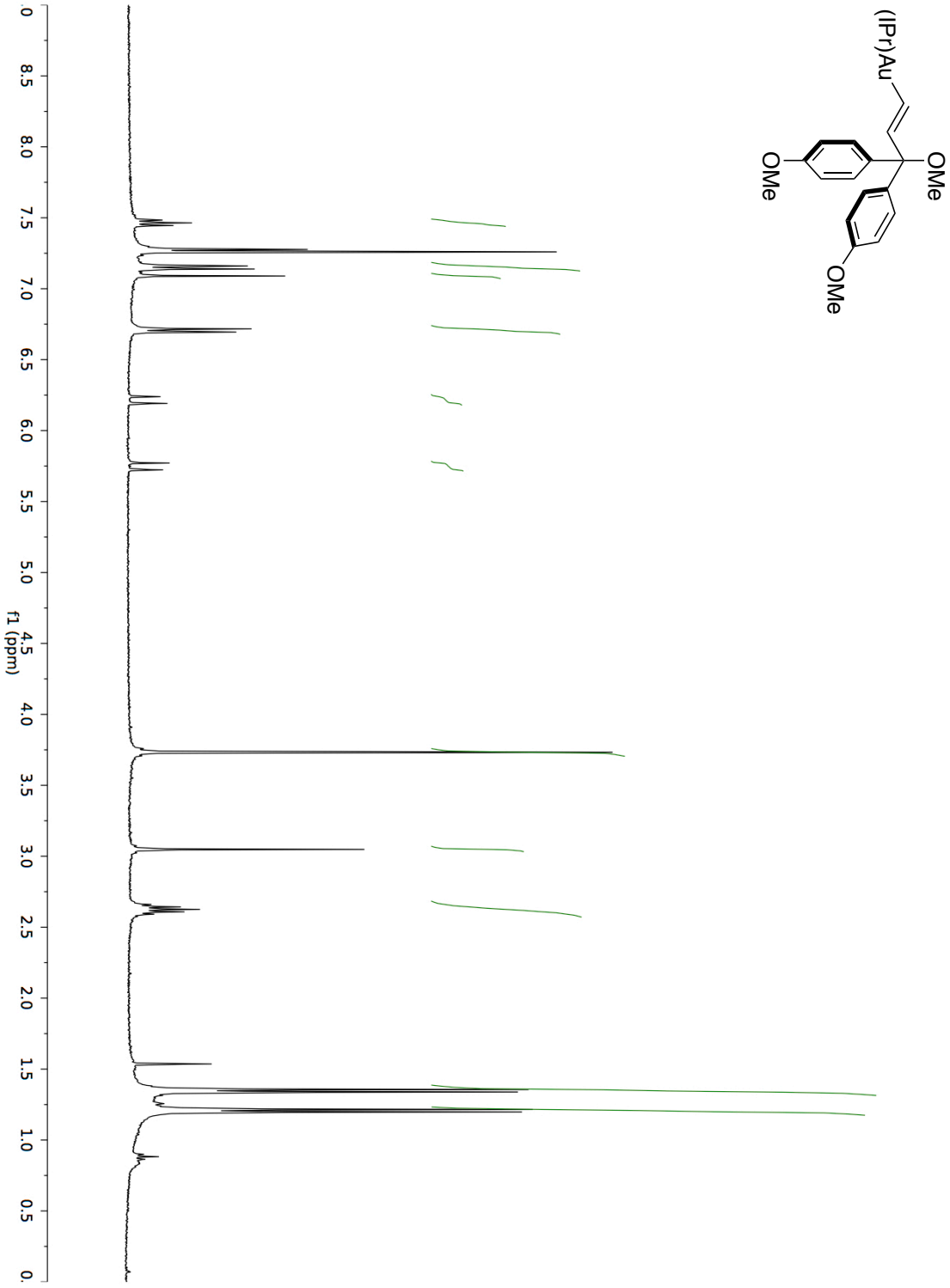

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**6b** ($CDCl_3$, 25 °C).

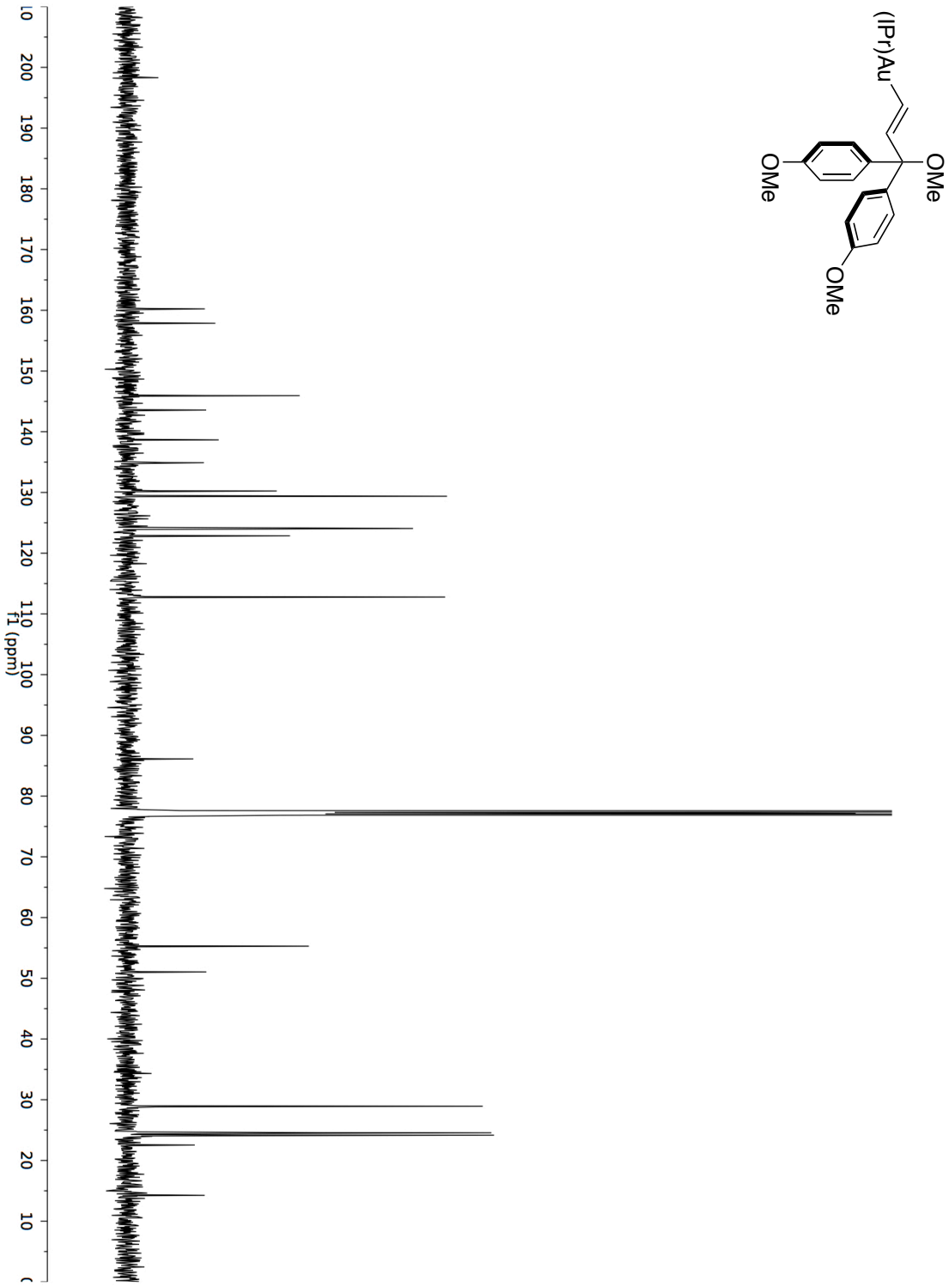

Figure S17. ^{1}H NMR spectrum of (*E*)-**6c** ($CDCl_3$, 25 °C).

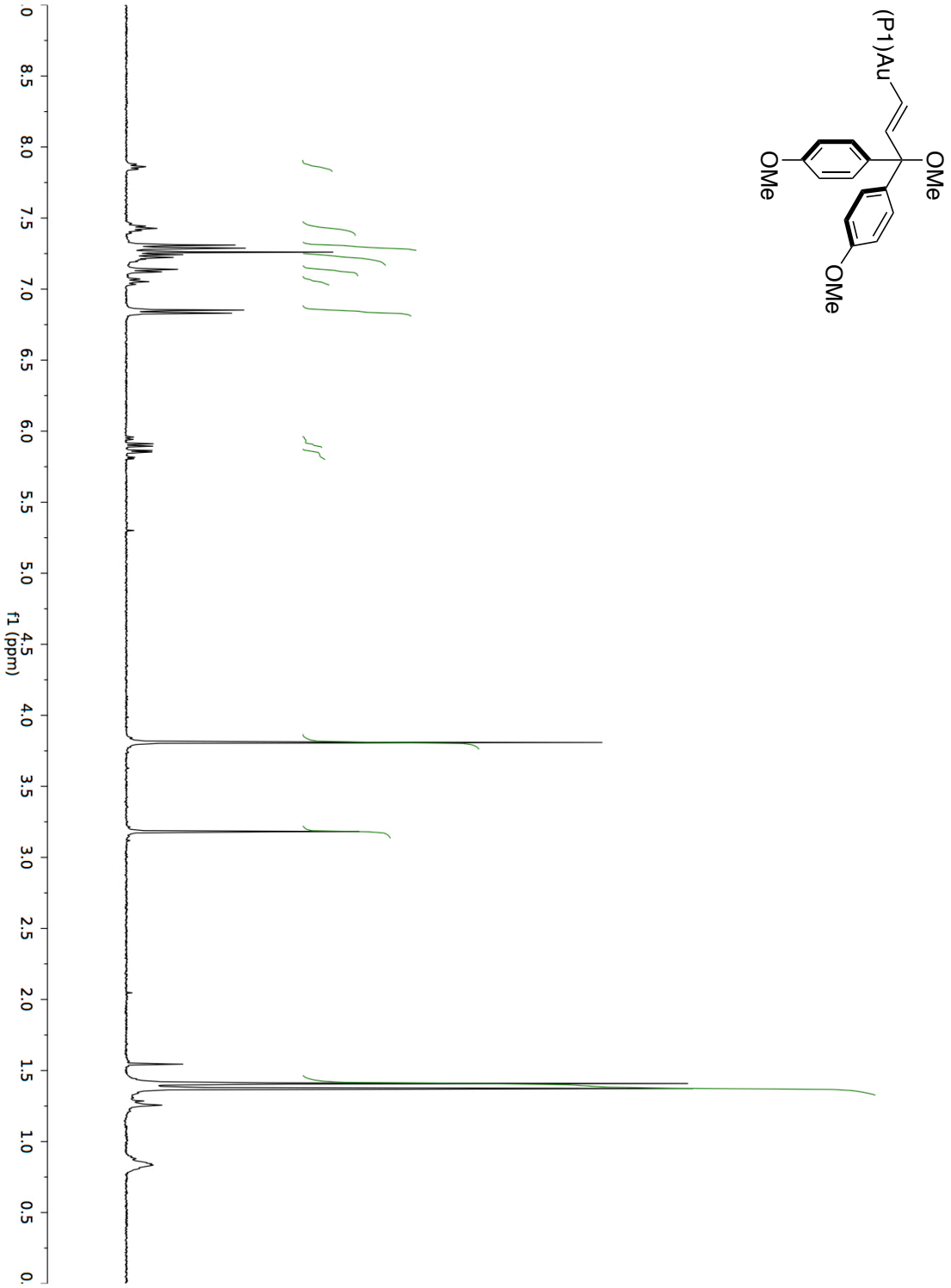

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**6c** ($CDCl_3$, 25 °C).

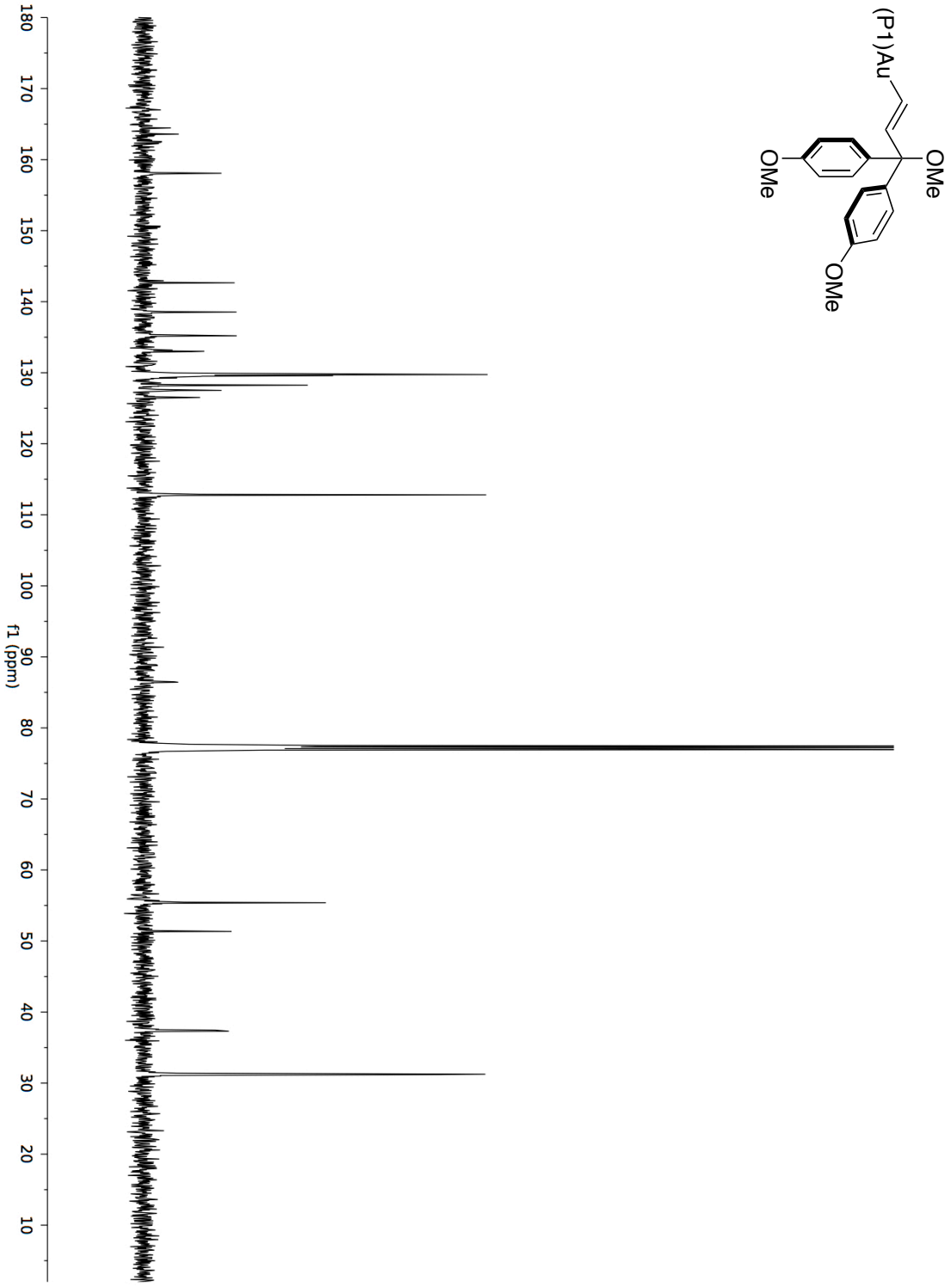

Figure S19. ^{1}H NMR spectrum of (*Z*)-**6b** ($CDCl_3$, 25 °C).

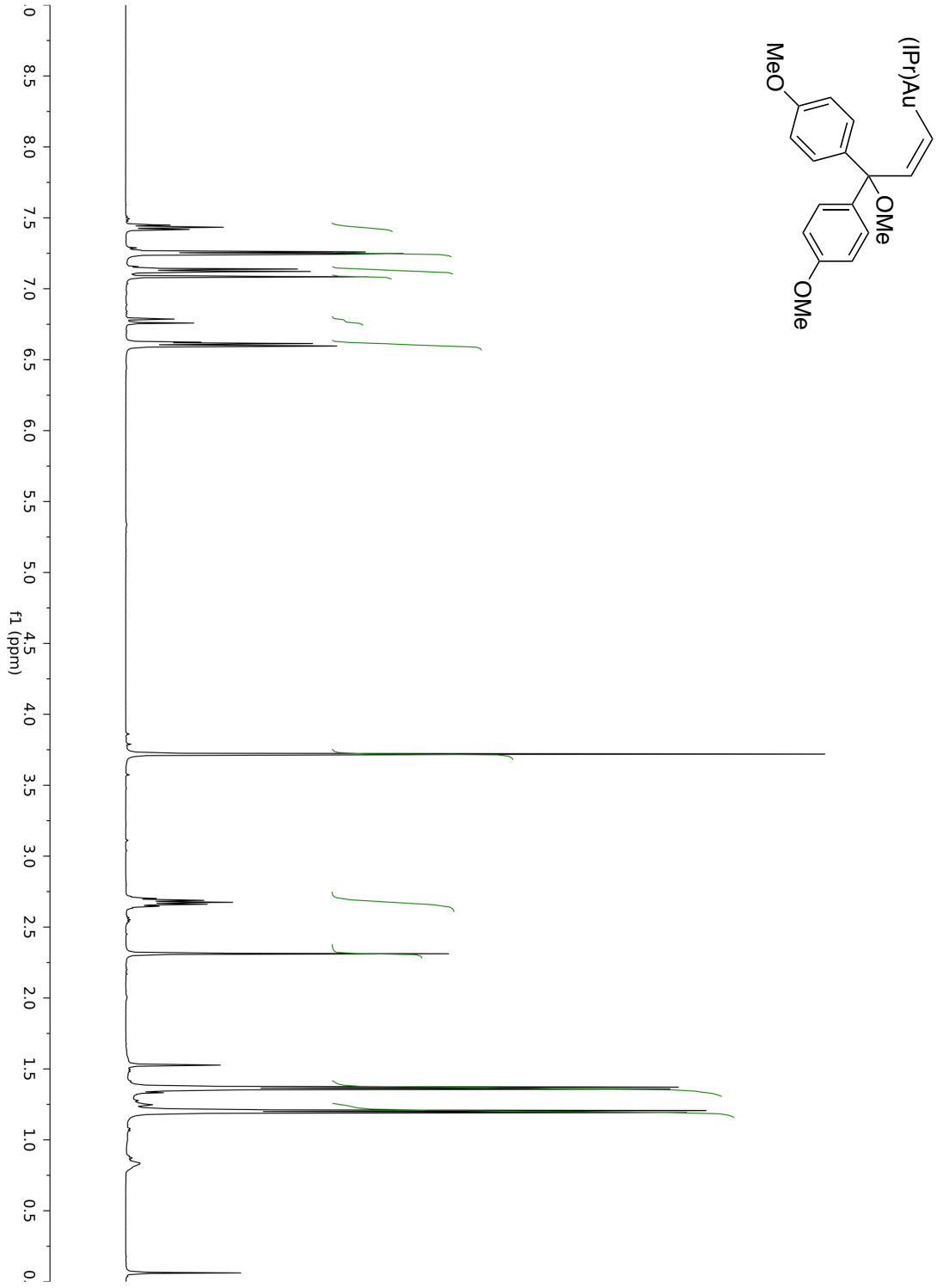

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of (*Z*)-**6b** ($CDCl_3$, 25 °C).

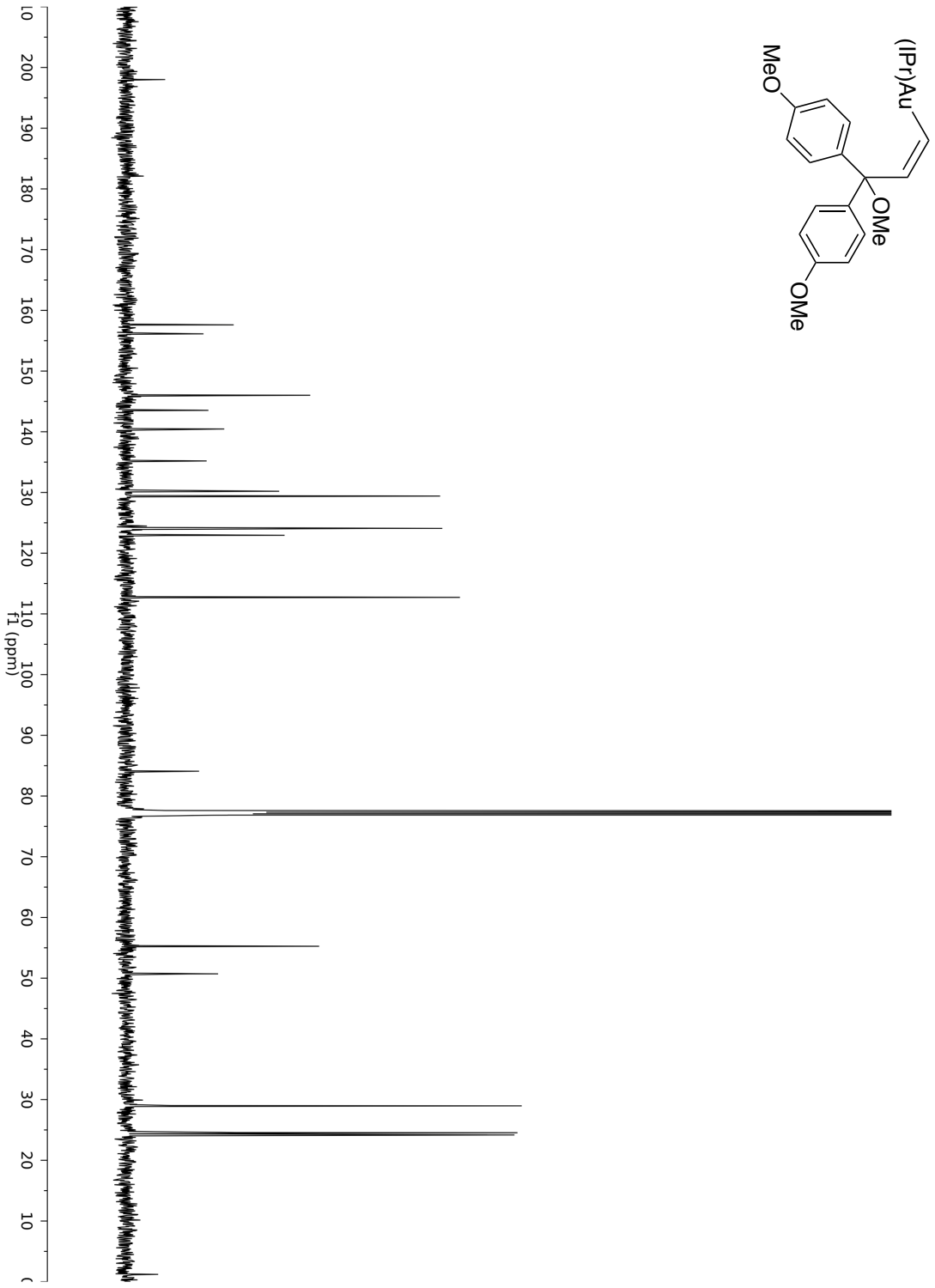

Figure S21. ^{1}H NMR spectrum of (*E*)-**5b** (CD_2Cl_2, –95 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), δ 0.43 (s, TMSOTf), 0.02 (s, TMSOMe).

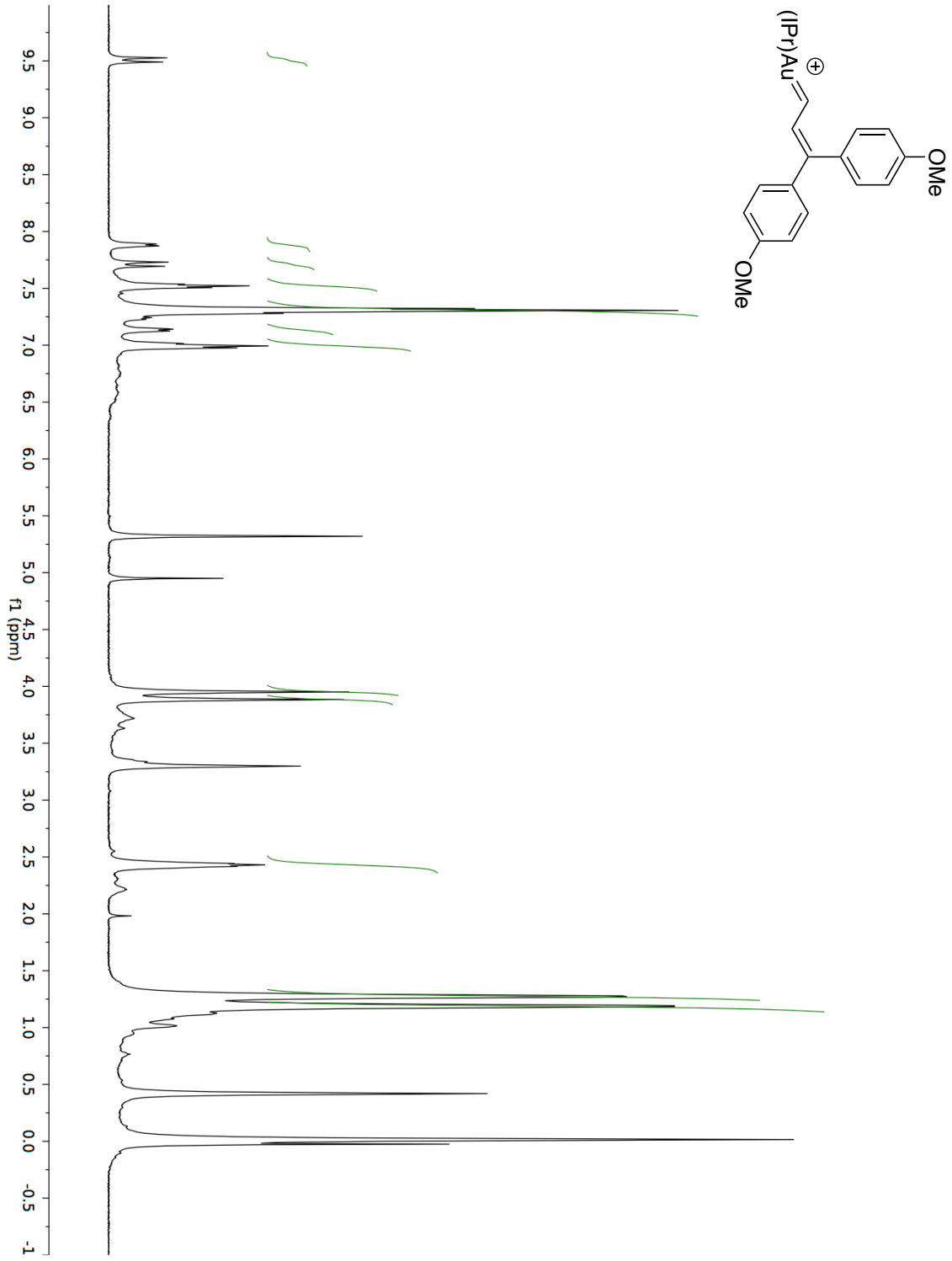

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**5b** (CD_2Cl_2, –95 °C). Additional peaks observed at δ 21.3 (CH_2Br_2; internal standard), δ 49.6 (TMSOMe), –2.1 (TMSOMe), δ –0.5 (TMSOTf).

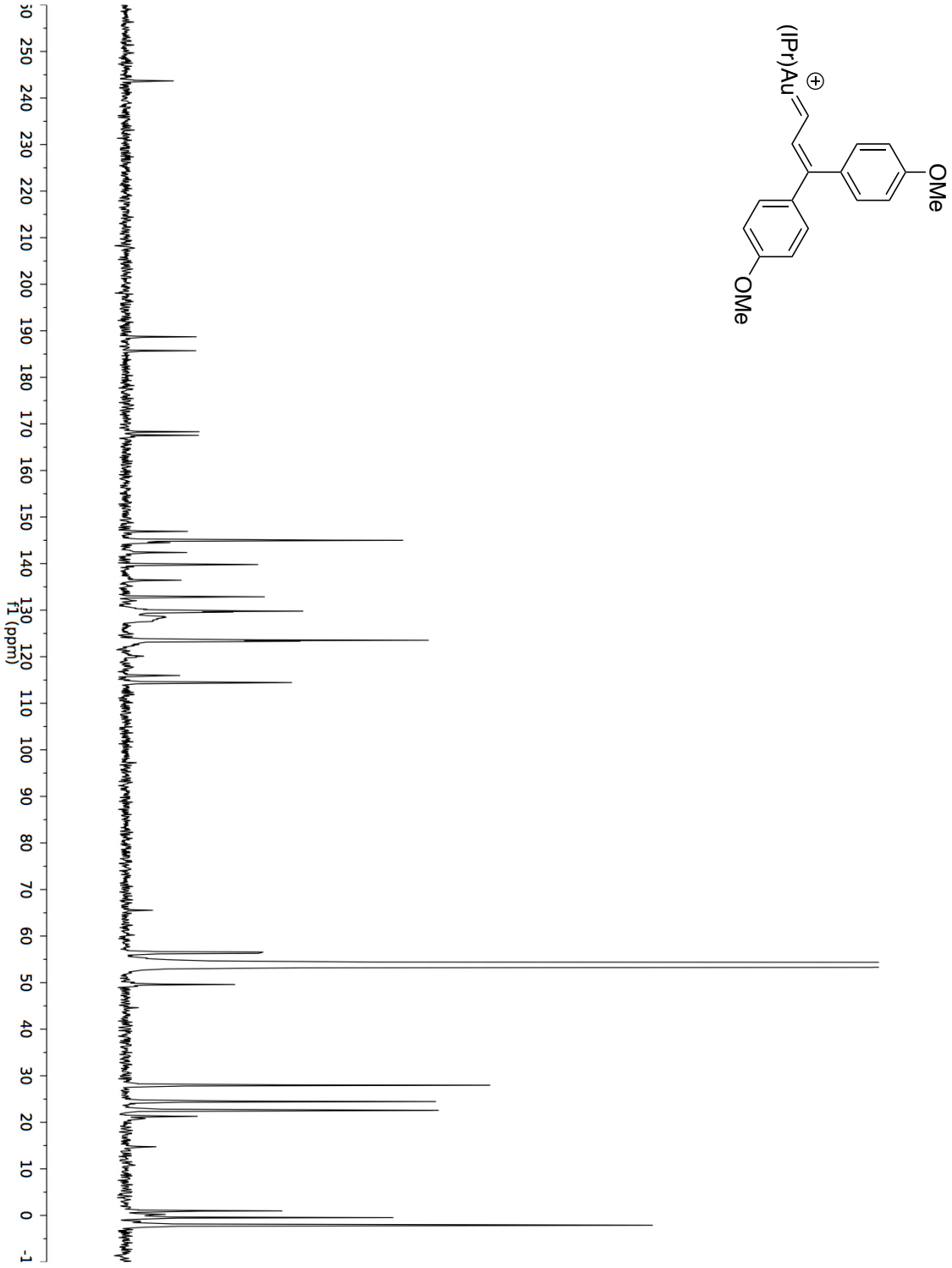

Figure S23. ^{1}H NMR spectrum of (*E*)-**5c** (CD_2Cl_2, –90 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), δ 0.43 (s, TMSOTf), 0.02 (s, TMSOMe).

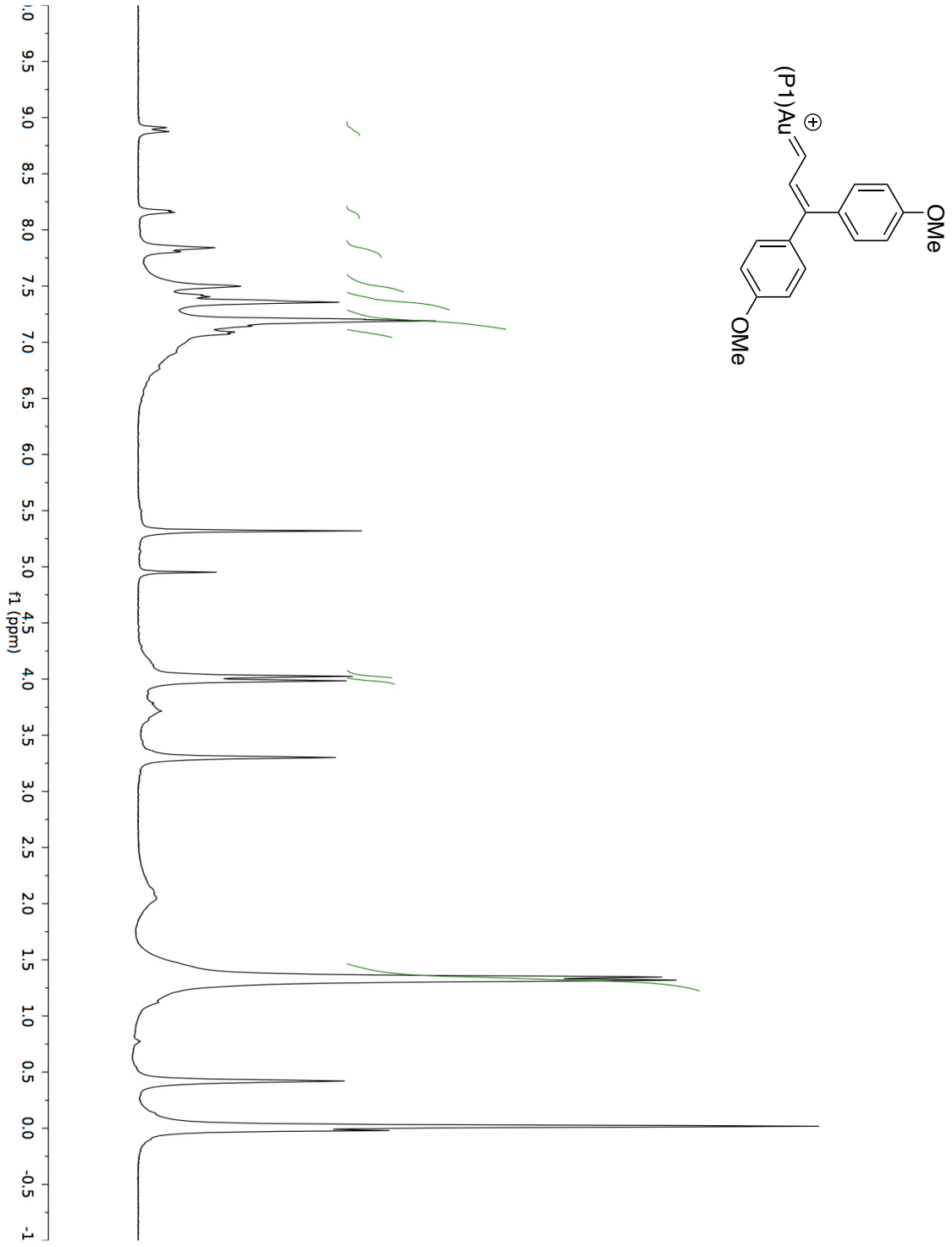

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-**5c** (CD_2Cl_2, –90 °C).

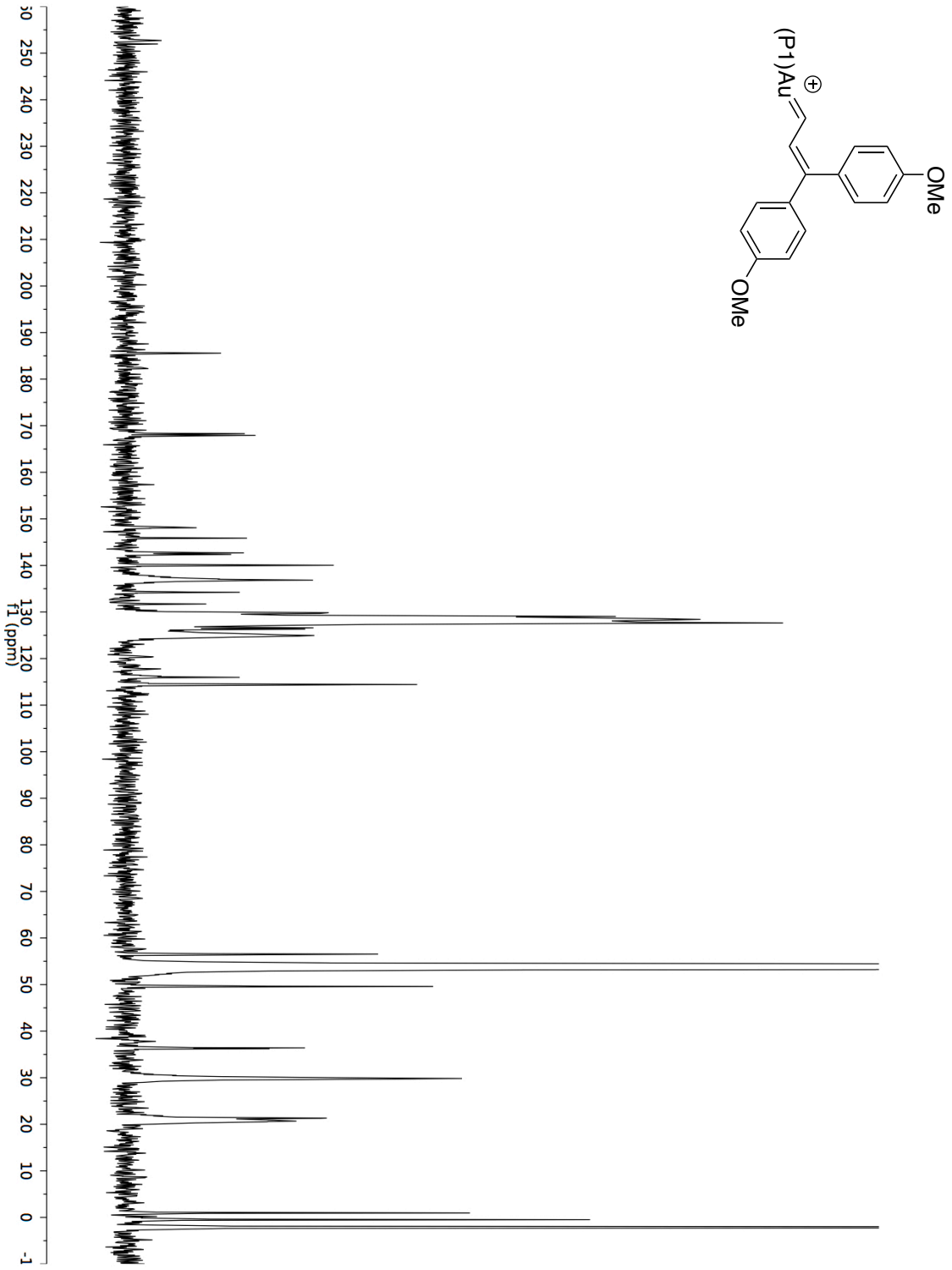

Figure S25. ^{1}H NMR spectrum of (*E*)-**5a** (CD_2Cl_2, –110 °C).

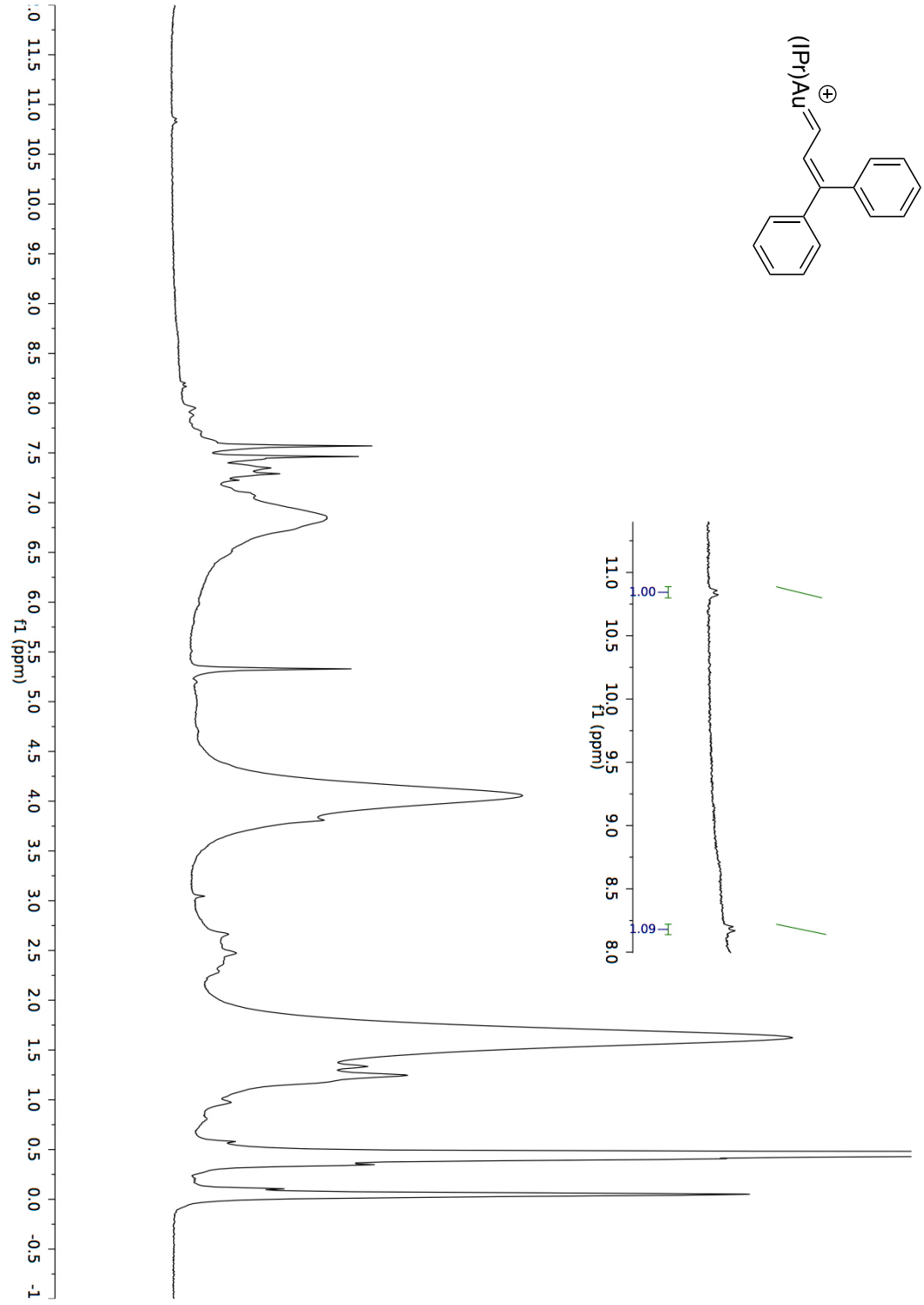

Figure S26. ^{1}H NMR spectrum of **9** ($CDCl_3$, 25 °C).

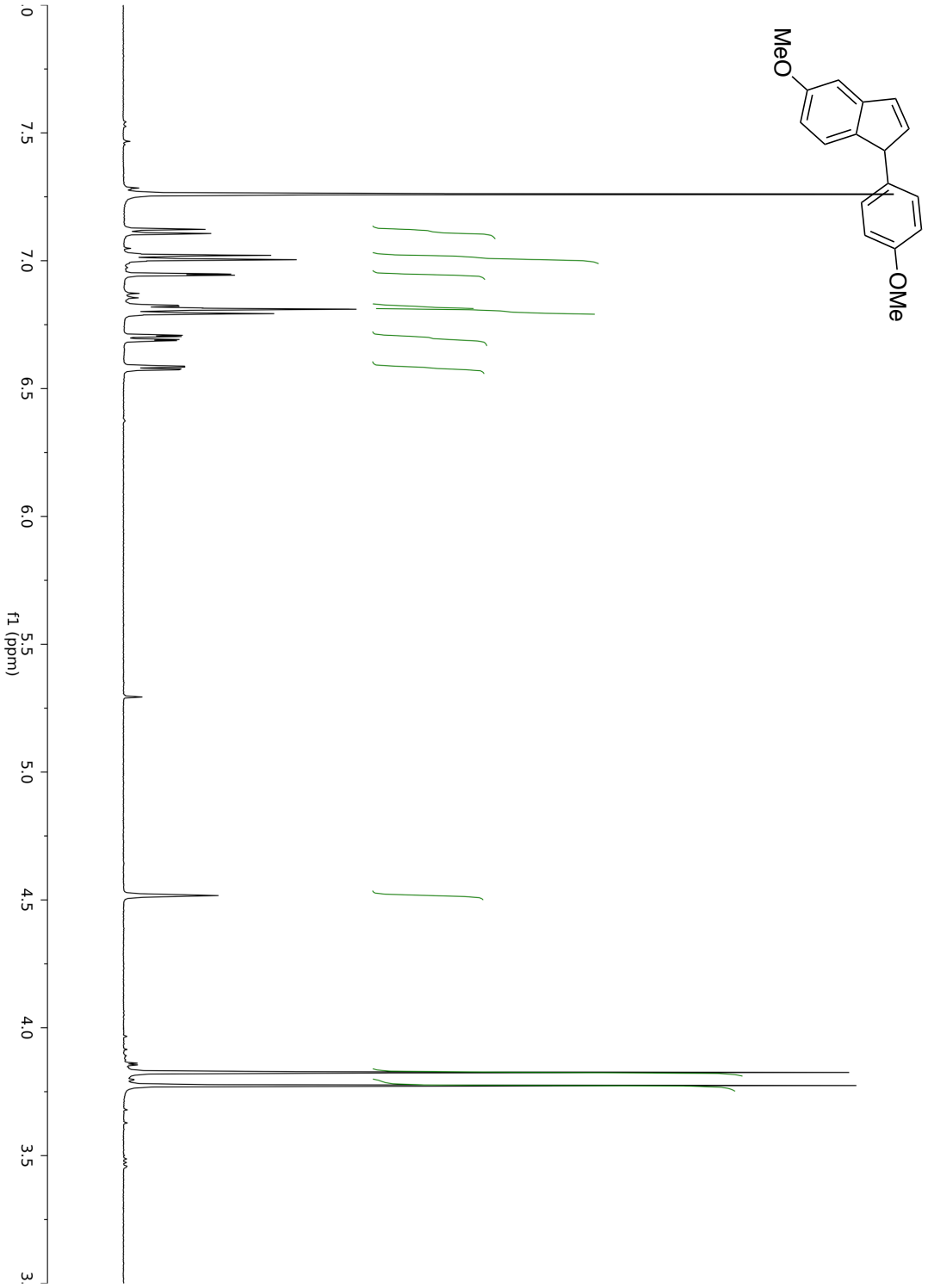

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **9** ($CDCl_3$, 25 °C).

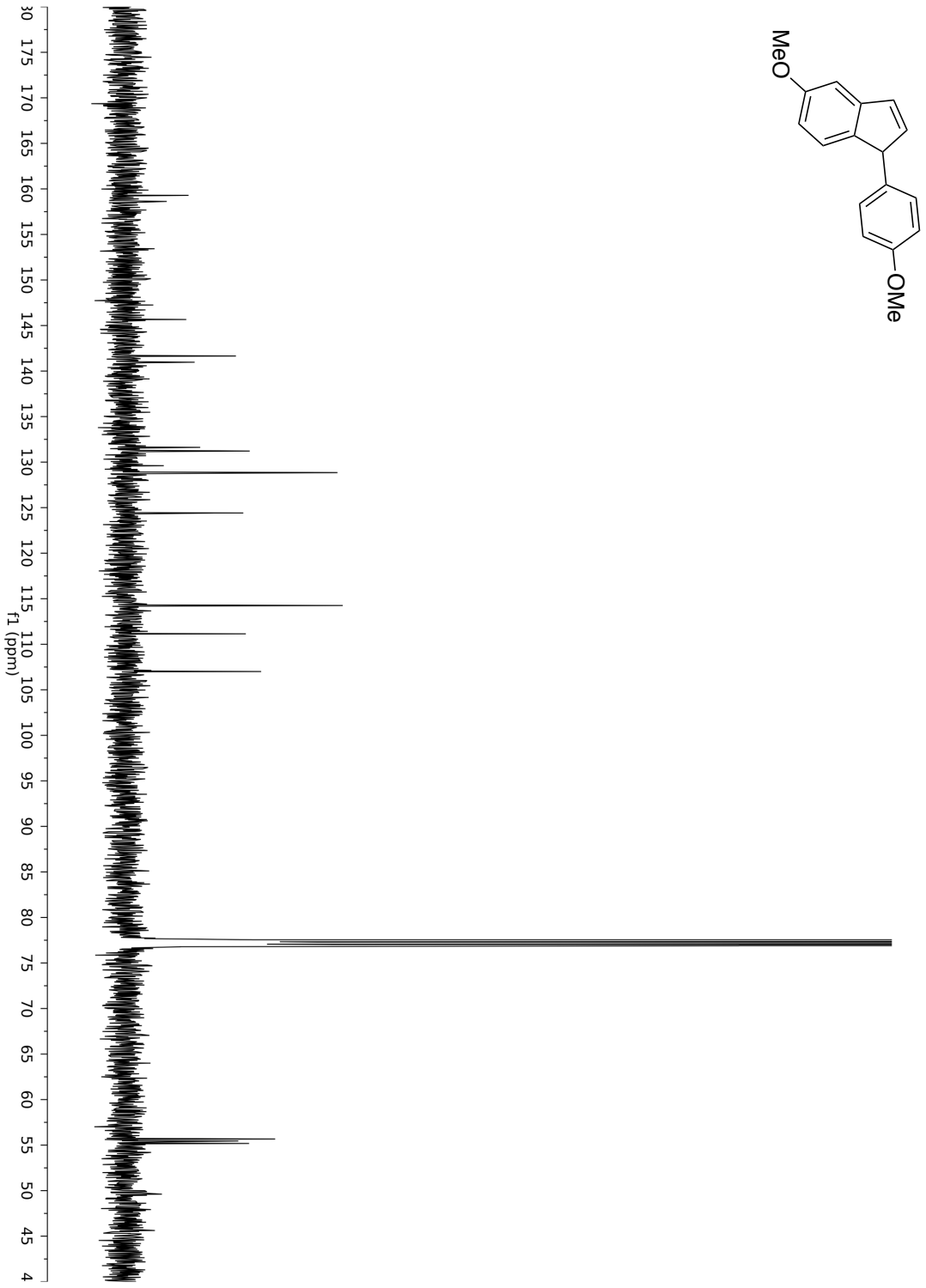

Figure S28. ^{1}H NMR spectrum of **10** (CD_2Cl_2, 0 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), 0.02 (s, TMSOMe).

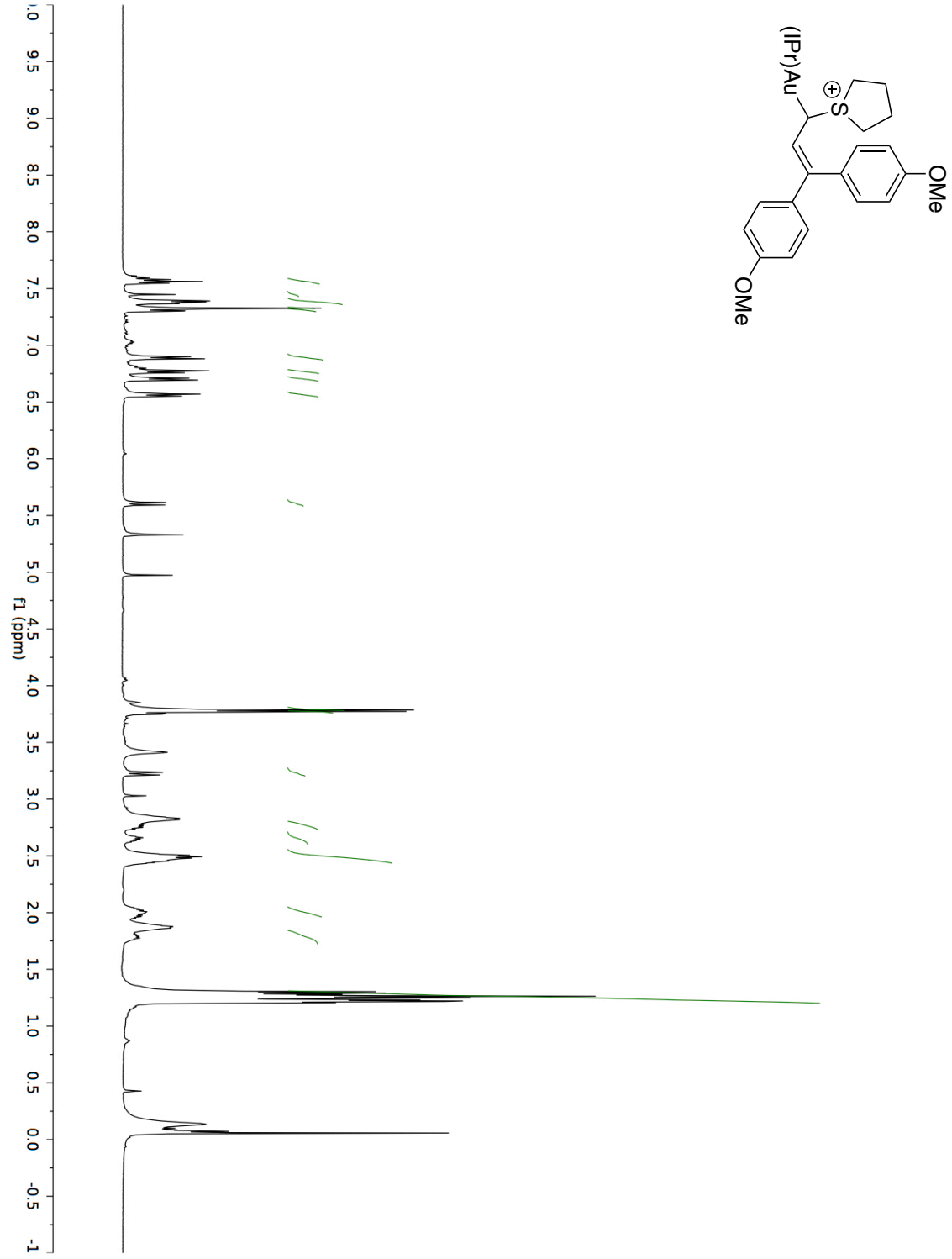

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **10** (CD_2Cl_2, –80 °C).

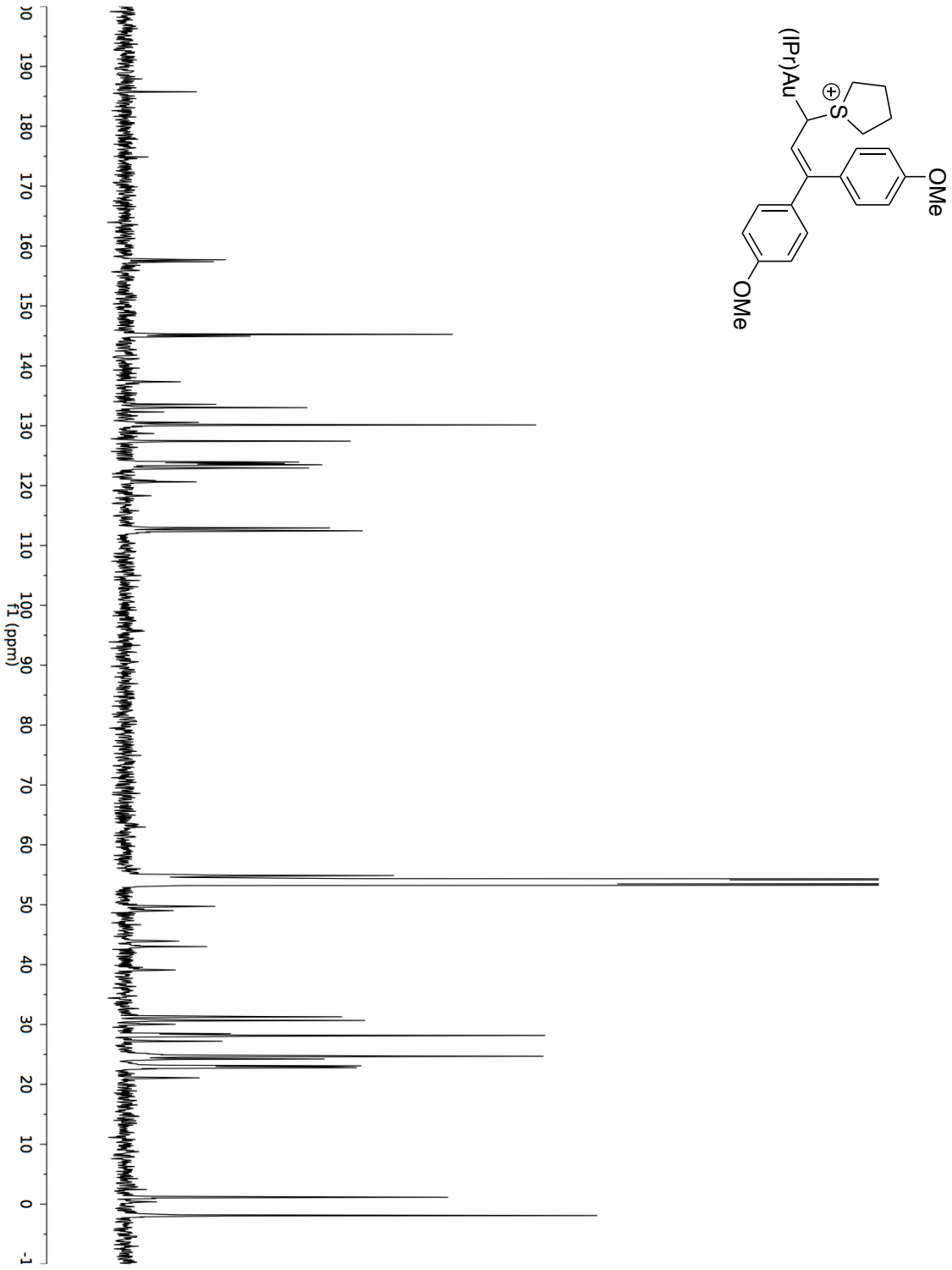

Figure S30. ^{1}H NMR spectrum of **11** (CD_2Cl_2, –20 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), 0.02 (s, TMSOMe).

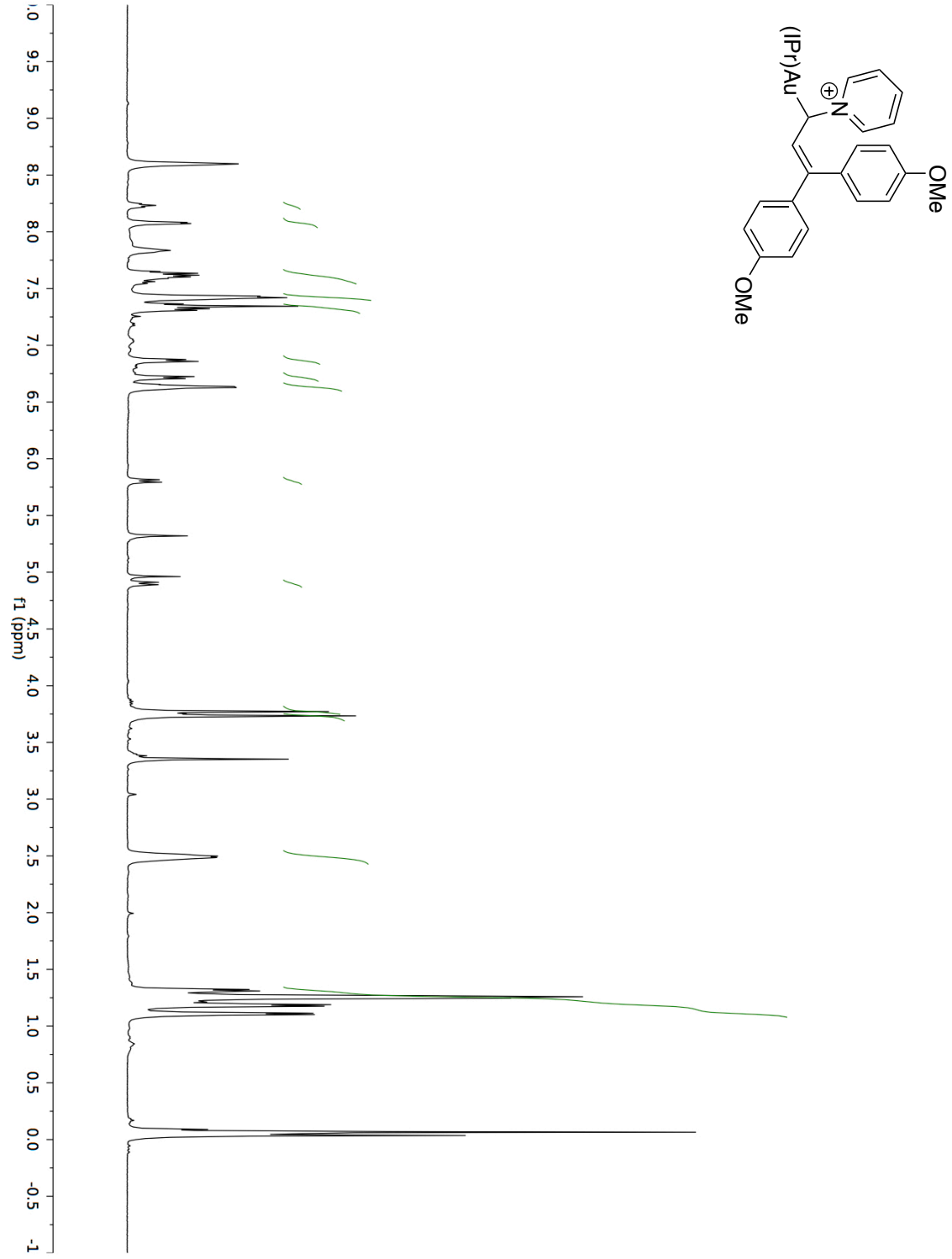

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **11** (CD_2Cl_2, –80 °C).

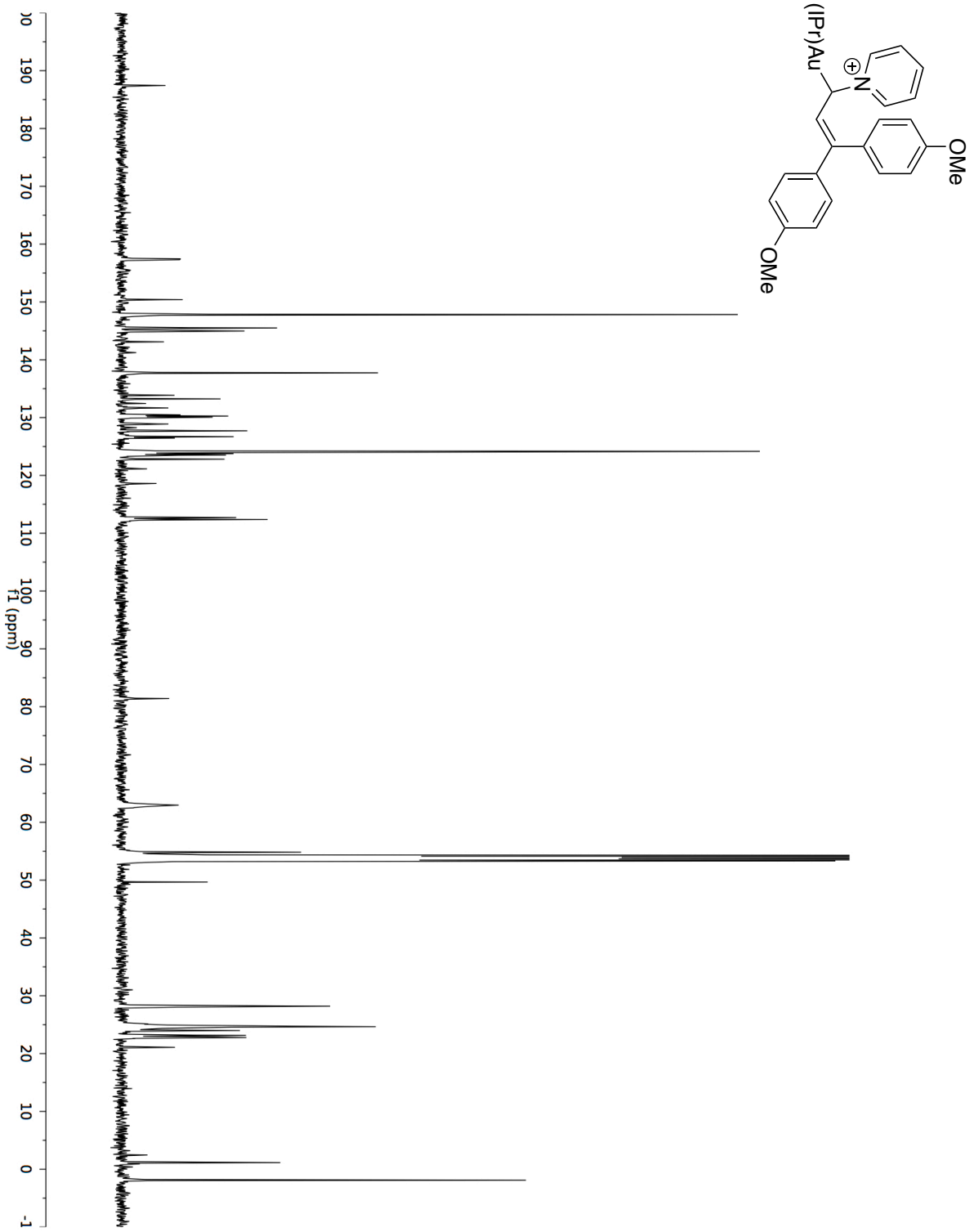

Figure S32. ^{1}H NMR spectrum of $[(IPr)Au(4\text{-pic})]^{+}\ OTf^{-}$ (CD_2Cl_2, 25 °C).

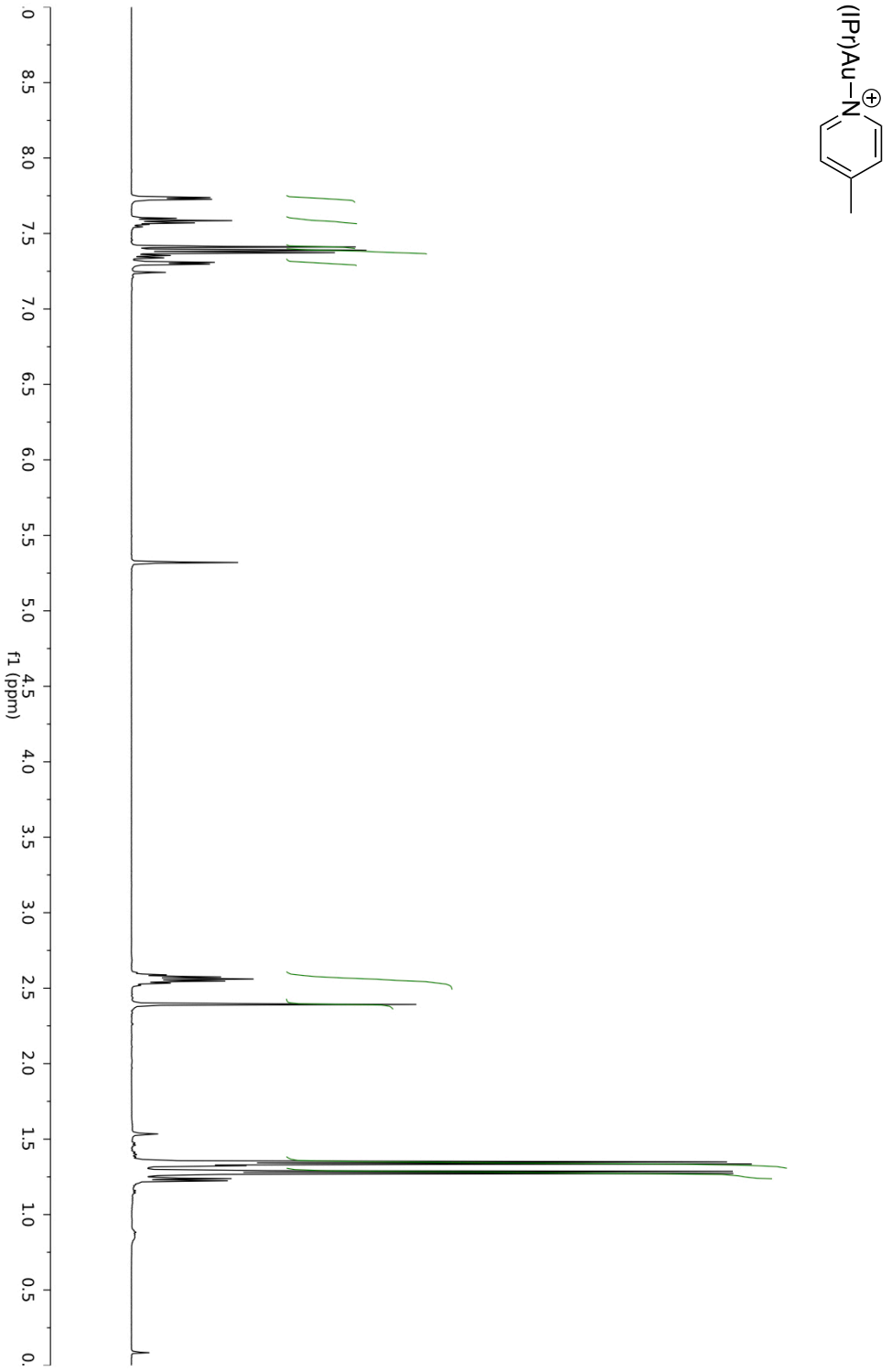

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of $[(IPr)Au(4\text{-pic})]^{+}\ OTf^{-}$ (CD_2Cl_2, 25 °C).

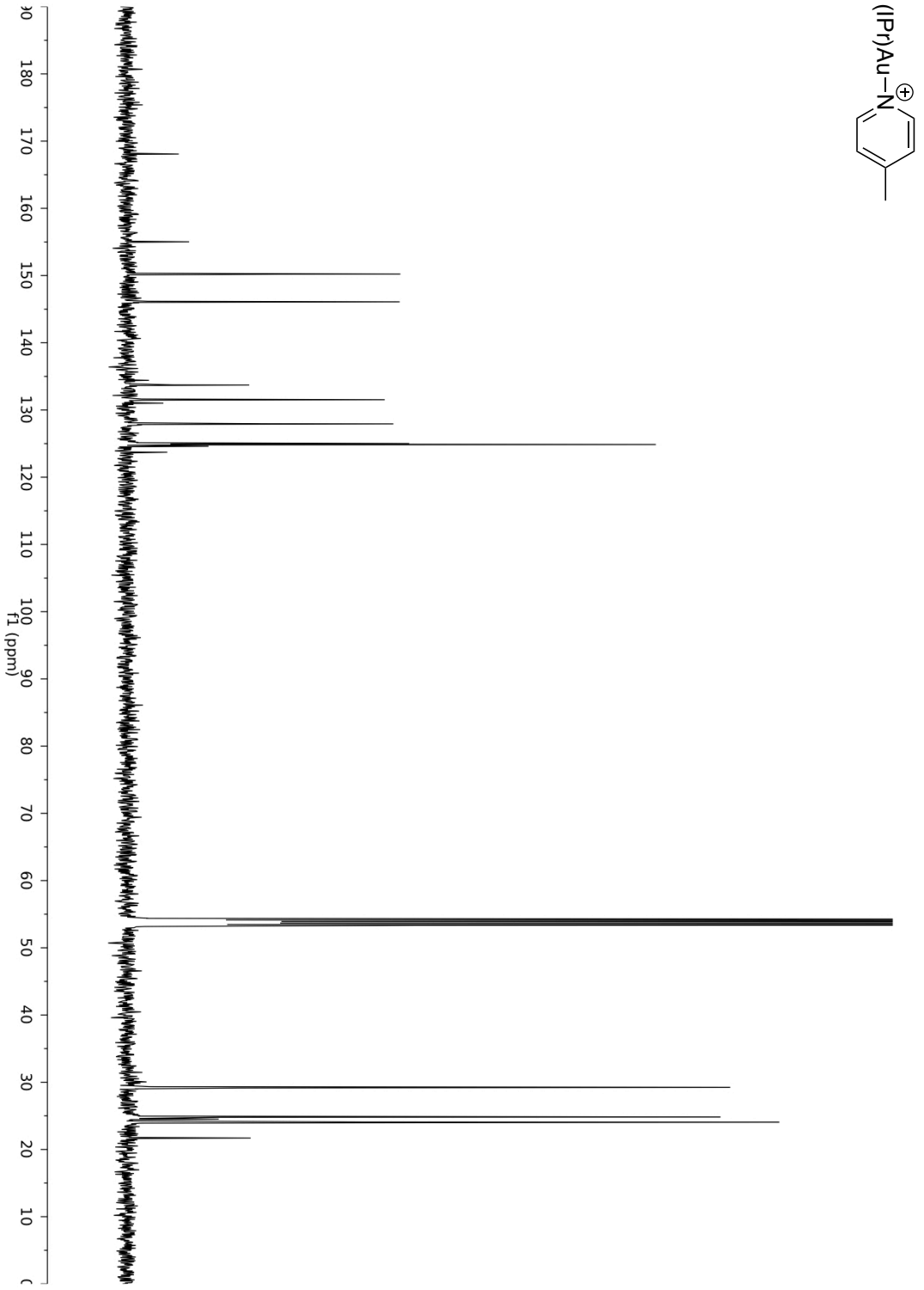

Figure S34. ^{1}H NMR spectrum of **13** (CD_2Cl_2, –80 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), δ 0.43 (s, TMSOTf), 0.02 (s, TMSOMe).

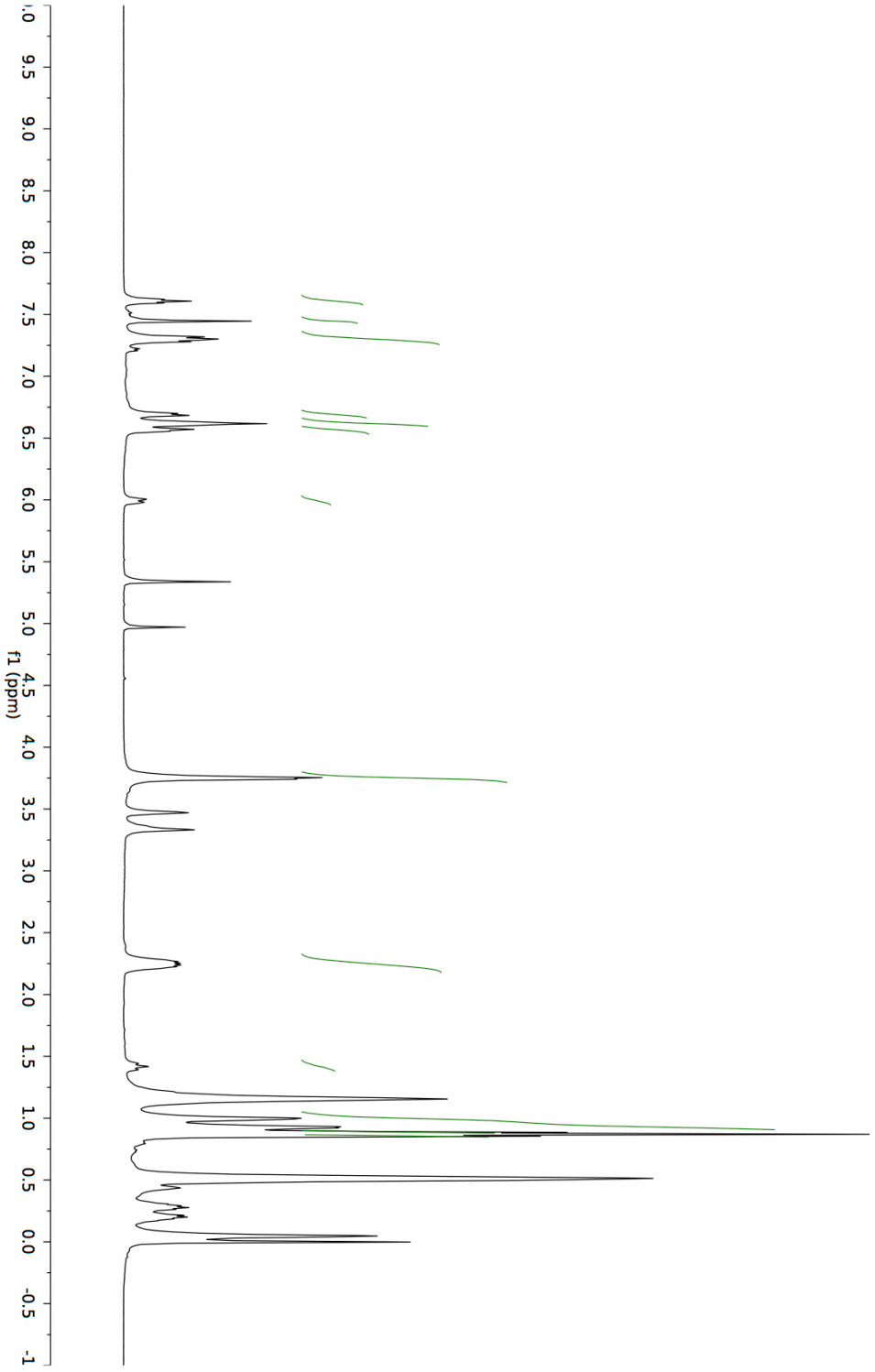

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **13** (CD_2Cl_2, –80 °C). Additional peaks observed at δ 21.3 (CH_2Br_2; internal standard), δ 49.6 (TMSOMe), –2.1 (TMSOMe), δ –0.5 (TMSOTf).

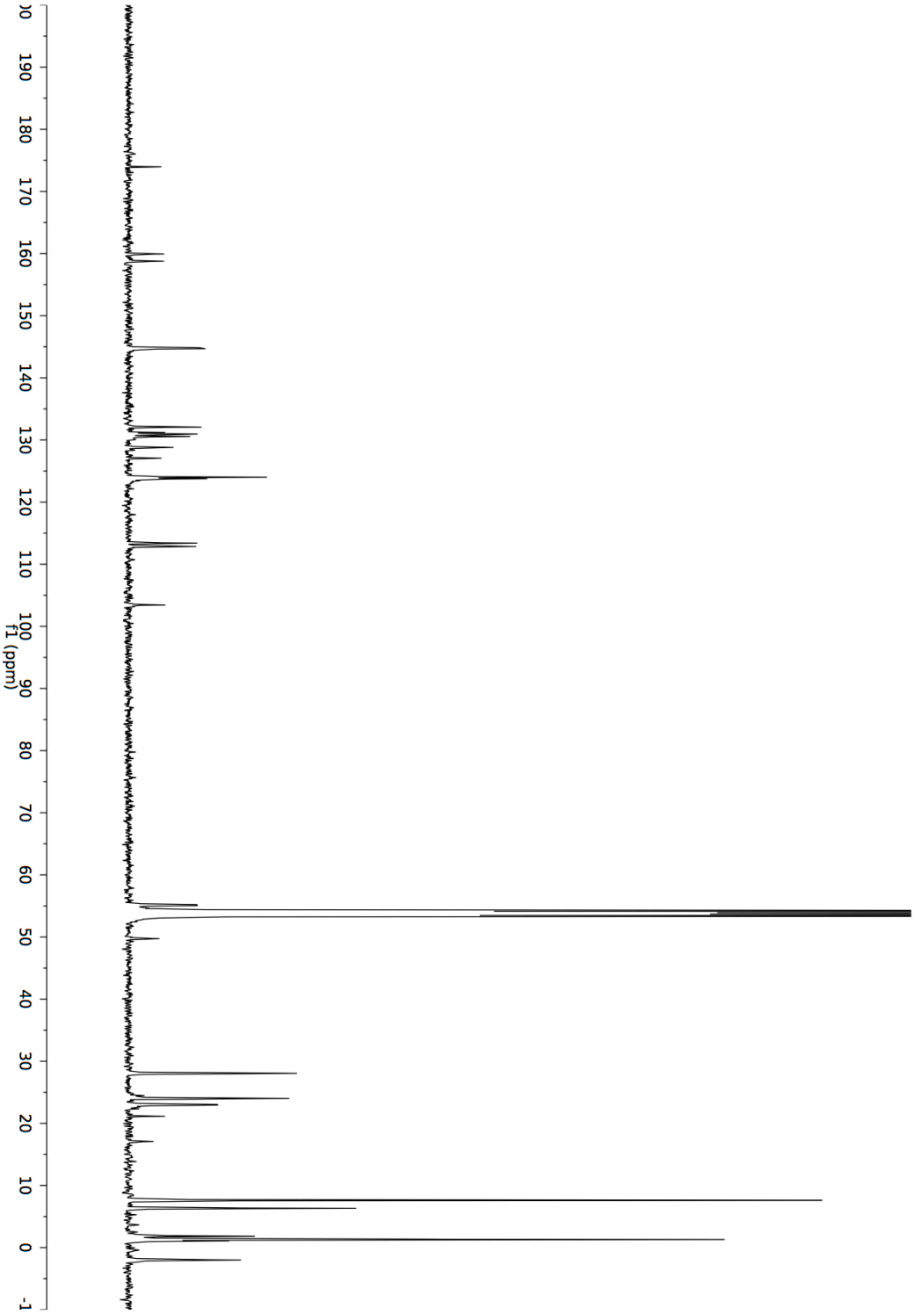

Figure S36. ^{1}H NMR spectrum of **14** ($CDCl_3$, 25 °C).

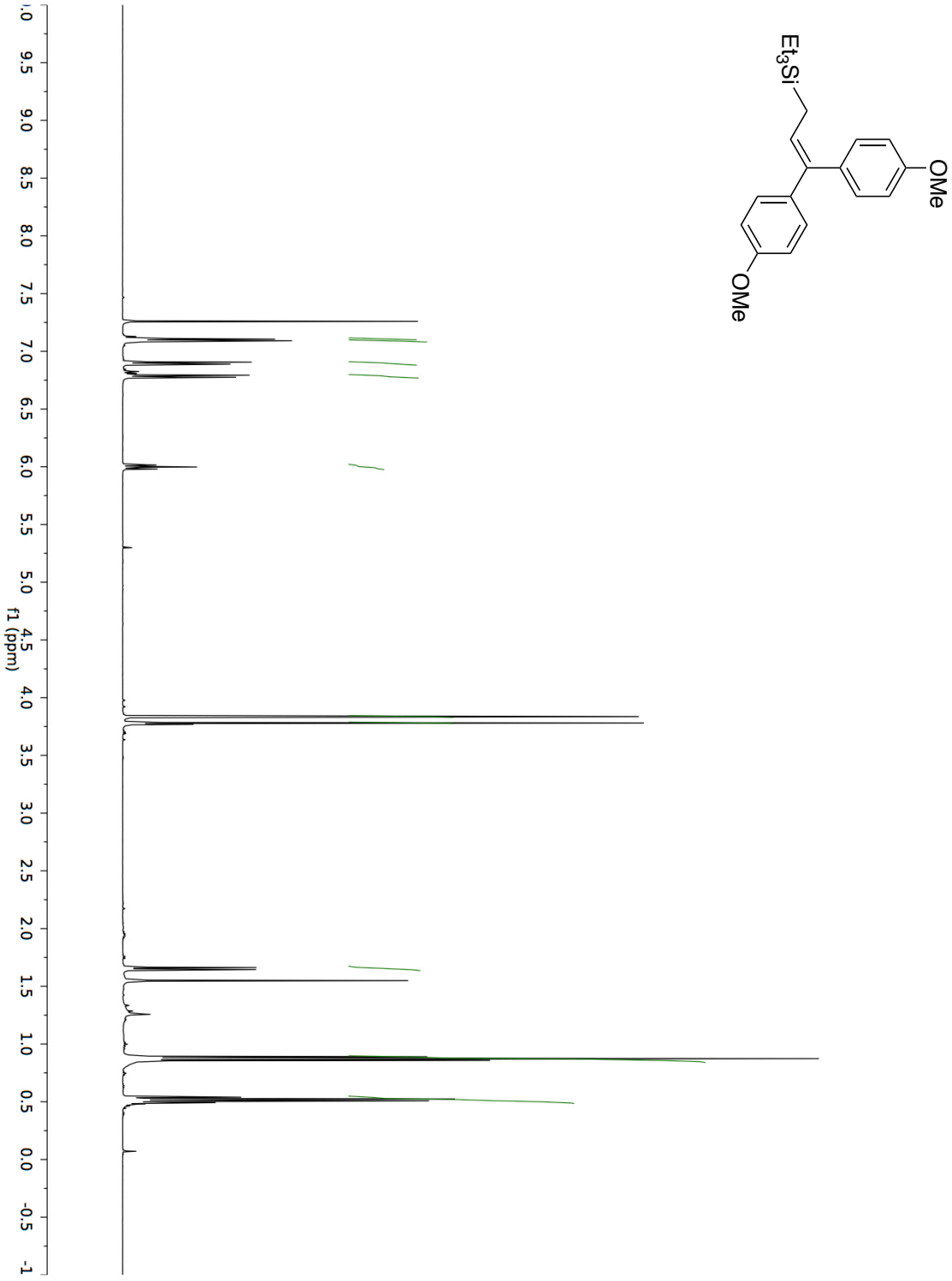

Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **14** ($CDCl_3$, 25 °C).

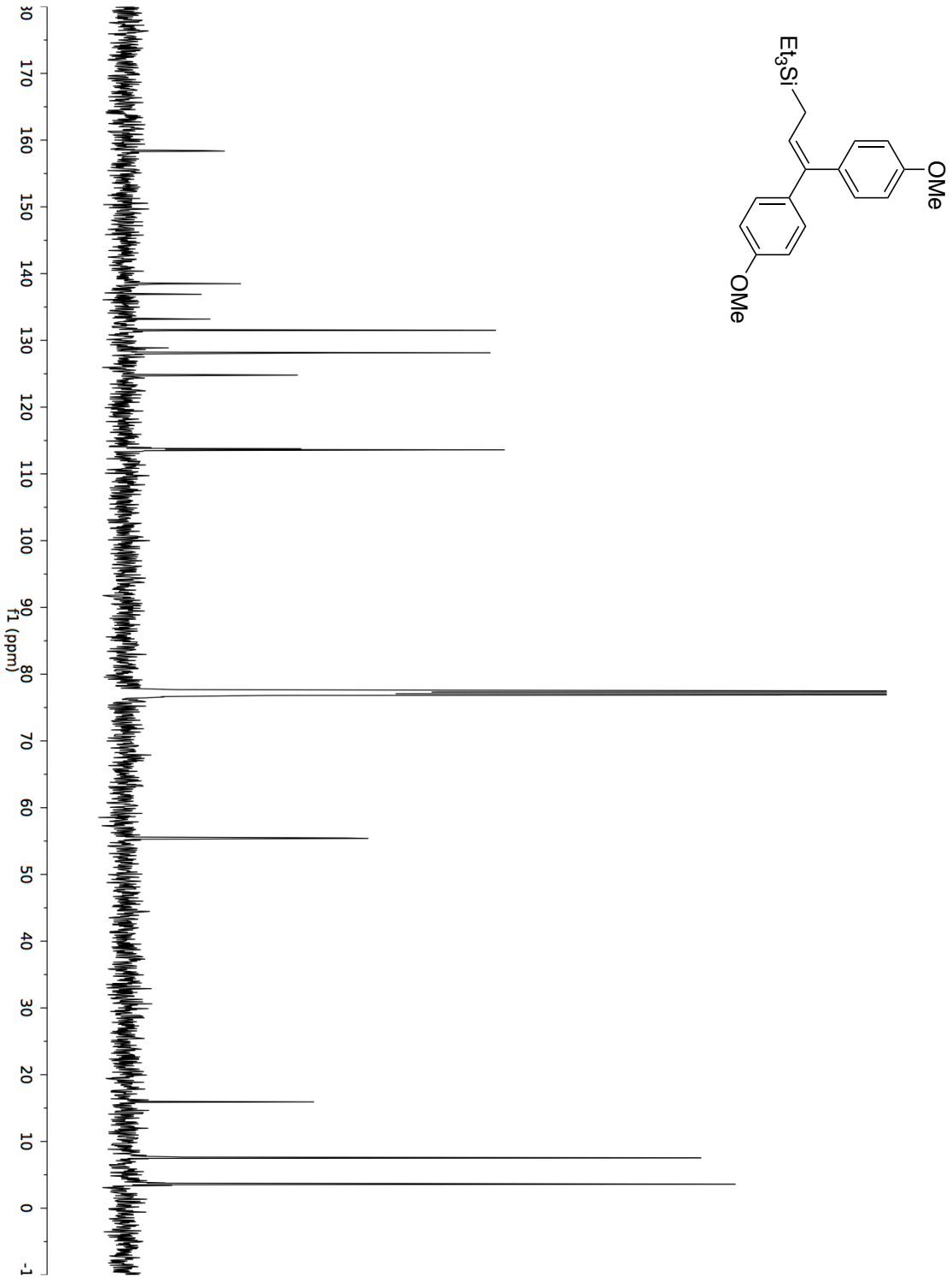

Figure S38. ^{1}H NMR spectrum of a 3:1 mixture of *cis*-**16** and *trans*-**16** ($CDCl_3$, 25 °C).

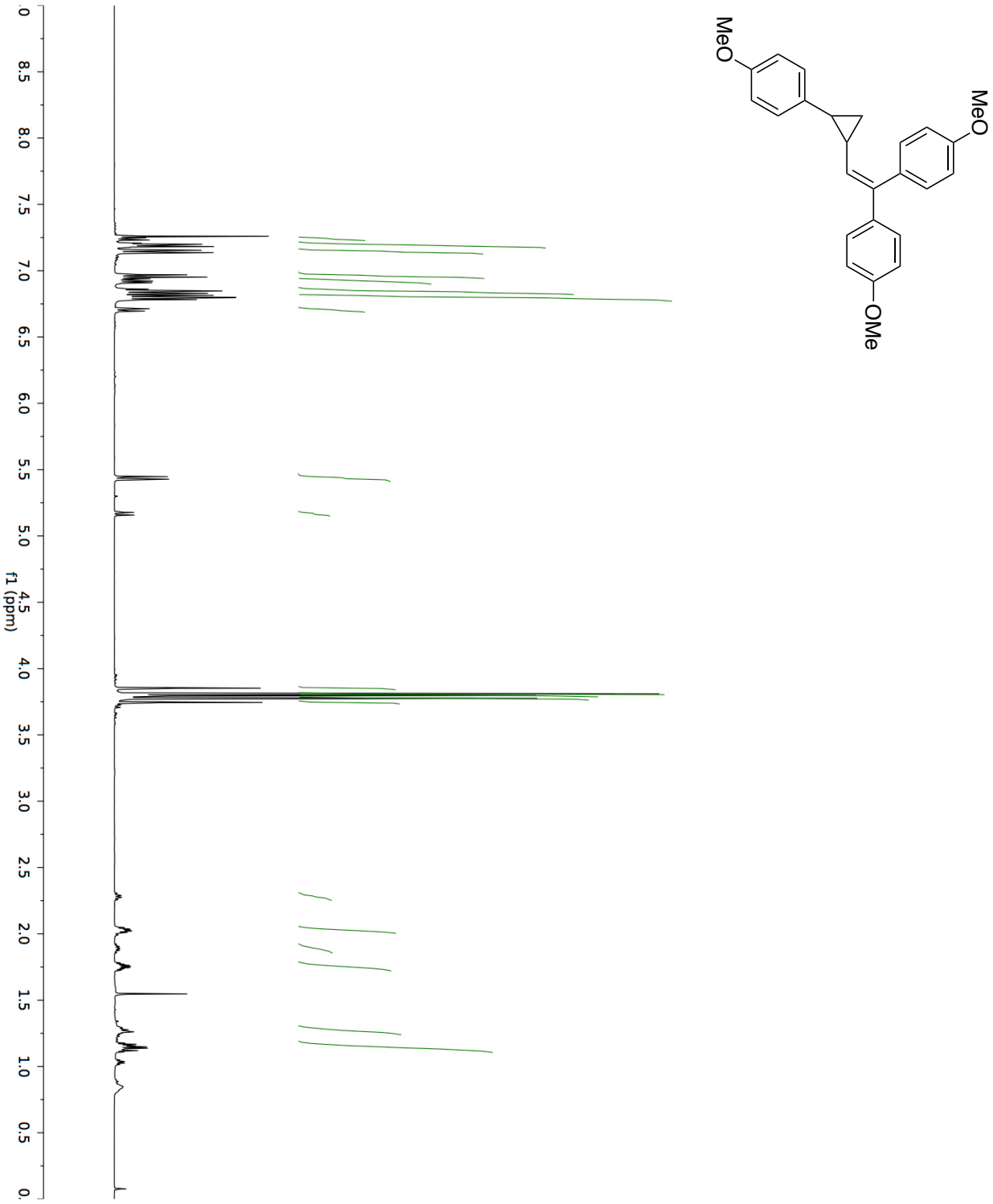

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **16** ($CDCl_3$, 25 °C).