BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Kinetic resolution of racemic planar-chiral vinylcymantrenes by molybdenum-catalyzed asymmetric metathesis dimerization

Haruna Imazu, Hitoshi Izu, Yasuhiro Ohki and Masamichi Ogasawara

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Experimental procedures, NMR spectra (^{1}H and ^{13}C) for all the new compounds, and chiral HPLC chromatograms

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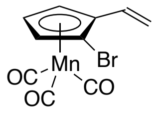
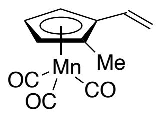
Experimental section.

General information. All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. C_6D_6 was distilled from Na/K under vacuum and stored in a glovebox. Following compounds were prepared as reported: *rac*-1-bromo-2-formylcymantrene (*rac*-**5a**) [S1], *rac*-2-methyl-1-formylcymantrene (*rac*-**5b**) [S2], *rac*-2-iodo-1-formylcymantrene (*rac*-**5c**) [S3], (pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=N-C$_6$H$_3$-2,6-^{i}Pr$_2$) [S4], (*R*)-3,3'-(Ph$_2$CH)$_2$-H$_8$-binaphthol (**L1**) [S5], (*R*)-3,3'-[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$-2,2'-binaphthol (**L3**) [S6]. All the other chemicals were obtained from commercial sources and used as received unless otherwise noted.

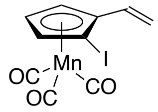
***rac*-1-Bromo-2-vinylcymantrene (*rac*-1a).** Methyltriphenylphosphonium iodide (1.08 g, 2.67 mmol) and ^{t}BuOK (299 mg, 2.66 mmol) were suspended in dry THF (20 mL) and the suspension was stirred for 15 min at room temperature. To this was added a THF (3 mL) solution of *rac*-1-bromo-2-formylcymantrene (*rac*-**5a**, 921 mg, 2.96 mmol) dropwise at room temperature. After stirring the mixture for 4 h, the reaction mixture was extracted with hexane. The organic extracts were combined and filtered through a pad of silica gel. The filtrate was evaporated to dryness. The residue was chromatographed on silica gel (hexane/benzene = 4/1) to give *rac*-**1a** as a yellow oil. Yield: 620 mg, (68%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.14 (dd, *J* = 17.5 and 11.0 Hz, 1H), 5.15 (d, *J* = 17.5 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.09−4.08 (m, 1H), 4.04−4.03 (m, 1H), 3.77−3.75 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 224.4, 127.2, 117.1, 99.3, 86.8, 82.5, 82.1, 76.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{10}H_7MnBrO_3^+$: 308.8954. Found: 308.8959.



***rac*-1-Methyl-2-vinylcymantrene (*rac*-1b).** This compound was prepared in the same way with *rac*-**1a** starting with methyltriphenylphosphonium iodide (4.17 g, 10.3 mmol), ^{t}BuOK (1.11 g, 9.89 mmol), and *rac*-2-methyl-1-formylcymantrene (*rac*-**5b**, 1.94 g, 7.88 mmol). The crude compound was chromatographed on silica gel (hexane/dichloromethane = 3/1) to give *rac*-**1b** as a yellow oil. Yield:1.43 g, (74%). ^{1}H NMR (400 MHz, C_6D_6): δ 5.90 (dd, *J* = 17.5 and 11.0 Hz, 1H), 5.12 (d, *J* = 17.5 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.27 (m, 1H), 3.96−3.95 (m, 1H), 3.78 (s, 1H), 1.48 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 223.7, 126.0, 113.3, 99.4, 96.0, 79.5, 79.2, 76.7, 9.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{11}H_{10}MnO_3^+$: 245.0005 Found: 245.0018.

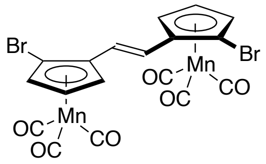


***rac*-1-Iodo-2-vinylcymantrene (*rac*-1c).** This compound was prepared in the same way with *rac*-**1a** starting with methyltriphenylphosphonium iodide (820 mg, 2.03 mmol), ^{t}BuOK (228 mg, 2.03 mmol), and *rac*-2-iodo-1-formylcymantrene (*rac*-**5c**, 760 mg, 2.13 mmol). The crude compound was chromatographed on silica gel (hexane/diethyl ether = 9/1) to give *rac*-**1b** as a yellow solid. Yield: 598 mg, (79%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.08 (dd, *J* = 17.5 and 10.9 Hz, 1H), 5.11 (dd, *J* = 17.5 and 0.7 Hz, 1H), 4.87 (dd, *J* = 10.9 and 0.9 Hz, 1H), 4.17−4.15 (m, 1H), 4.07−4.06 (m, 1H), 3.83−3.82 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 224.7, 129.4, 117.3, 103.3, 88.2, 84.4, 77.2, 49.6. HRMS (ESI) m/z: [M] Calcd for $C_{10}H_6MnIO_3$: 355.8742. Found: 355.8754.



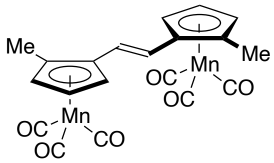
General procedure for the molybdenum-catalyzed asymmetric metathesis dimerization/kinetic resolution of 1a–c. The reaction conditions and the results are summarized in Table 1. The reactions were conducted in a manner similar to ref.-S7. In a glovebox under purified argon, Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(NC$_4$H$_4$)$_2$, (12.2 mg, 22.8 μmol) and (*R*)-3,3'-(Ph$_2$CH)$_2$-H$_8$-2,2'-binaphthol (**L1**; 14.3 mg, 22.8 μmol) were dissolved in dry benzene (1.0 mL) in a 20 mL Schlenk flask. After stirring the solution for 15 min at room temperature, to this was added a solution of *rac*-**1a** (70.0 mg, 227 μmol) in benzene (2.5 mL). The Schlenk flask was sealed tightly and taken out of the glovebox. The mixture was stirred for 48 h at the given temperature. After quenching the reaction by the addition of acetone (ca. 100 μL), the reaction mixture was evaporated to dryness under reduced pressure. The conversion of the AMD/kinetic resolution reaction was determined by the ^{1}HNMR analysis of the crude product. The crude product was chromatographed on silica gel (hexane/dichloromethane = 3/1) under nitrogen to give remaining **1a** (23.6 mg, 34%) and AMD product **2a** (26.6 mg, 38%). The characterization data of **2a–c** and the conditions for chiral HPLC analysis of **1a–c** and **2a–c** are listed below.

(*R*,*R*)-(*E*)-1,2-Di(2-bromocymantrenyl)ethylene (*chiral*-2a). ^{1}H NMR (400 MHz, C_6D_6): δ 6.32 (s, 2H), 4.09−4.07 (m, 2H), 3.95−3.94 (m, 2H), 3.74−3.73 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 224.0, 121.8, 97.4, 87.5, 82.6, 82.3, 77.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_9Mn_2Br_2O_6^+$: 590.7501. Found: 590.7496. $[\alpha]^{28}_{D} = -371$ (*c* 2.41, CH_2Cl_2, for (*R*,*R*)-isomer of >99% ee). Chiral HPLC analysis conditions: Chiralpak IE; eluent: hexane/ethyl acetate/^{i}PrOH = 90/5/1; flow rate: 0.5 mL/min; t_1 = 11.6 min ((*S*,*S*)-isomer), t_2 = 12.1 min ((*R*,*R*)-isomer).



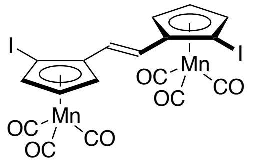
(*S*)-1-Bromo-2-vinylcymantrene ((*S*)-1a). $[\alpha]^{27}_{D} = +85$ (*c* 1.34, CH_2Cl_2, 63% ee). Chiral HPLC analysis conditions: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 50/1; flow rate: 1.0 mL/min; t_1 = 35.4 min ((*S*)-isomer), t_2 = 43.0 min ((*R*)-isomer).

(*S*,*S*)-(*E*)-1,2-Di(2-methylcymantrenyl)ethylene (*chiral*-2b). ^{1}H NMR (400 MHz, C_6D_6): δ 6.07 (s, 2H), 4.24−4.23 (m, 2H), 3.97−3.95 (m, 2H), 3.80−3.79 (m, 2H), 1.56 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 225.4, 121.4, 101.4, 97.1, 81.6, 81.5, 79.3, 12.1. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{20}H_{14}Mn_2O_6^+$: 459.9546. Found: 459.9543. $[\alpha]^{28}_{D} = -391$ (*c* 2.32, CH_2Cl_2, for (*S*,*S*)-isomer of 93% ee). Chiral HPLC analysis conditions: Chiralpak IC; eluent: hexane/^{i}PrOH = 100/1; flow rate: 0.5 mL/min; t_1 = 13.8 min ((*R*,*R*)-isomer), t_2 = 14.9 min ((*S*,*S*)-isomer).



(*R*)-1-Methyl-2-vinylcymantrene ((*R*)-1b). $[\alpha]^{23}_{D} = +113$ (*c* 4.89, CH_2Cl_2, 62% ee). Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 10/1; flow rate: 0.5 mL/min; t_1 = 45.9 min ((*R*)-isomer), t_2 = 49.9 min ((*S*)-isomer).

(*R*,*R*)-(*E*)-1,2-Di(2-iodocymantrenyl)ethylene (*chiral*-2c). ^{1}H NMR (400 MHz, C_6D_6): δ 6.24 (s, 2H), 4.15 (m, 2H), 4.00 (m, 2H), 3.80−3.79 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 224.4, 124.1, 101.3, 88.3, 84.8, 78.0, 50.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_9Mn_2I_2O_6^+$: 684.7244. Found: 684.7238. $[\alpha]^{29}_{D} = -172$ (*c* 2.17, CH_2Cl_2, for (*R*,*R*)-isomer of 99% ee). Chiral HPLC analysis conditions: Chiralpak IB; eluent: hexane/ethyl acetate/^{i}PrOH = 90/5/1; flow rate: 0.5 mL/min; t_1 = 21.2 min ((*S*,*S*)-isomer), t_2 = 22.2 min ((*R*,*R*)-isomer).



(*S*)-1-Iodo-2-vinylcymantrene ((*S*)-1c). $[\alpha]^{28}_{D} = +124$ (*c* 3.91, CH_2Cl_2, 40% ee). Chiral HPLC Analysis Conditions: Chiralpak IB; eluent: hexane/ethyl acetate/^{i}PrOH = 900/60/1; flow rate: 0.5 mL/min; t_1 = 12.1 min ((*S*)-isomer), t_2 = 12.6 min ((*R*)-isomer).

X-ray crystallographic structure determinations. Single crystal X-ray diffraction data of (*S*,*S*)-**2b** was collected on a Rigaku RA-Micro 7 equipped with a Rigaku HyPix-6000HE detector that uses mirror-monochromated MoKα radiation (λ = 0.71073 Å) at –150 °C under a cold N_2 stream. Single crystals of the compound were coated with oil (Immersion Oil, Type B: code 1248, Cargille Laboratories, Inc.) and placed on Polyimide crystal mounts. The crystal quality and preliminary cell parameters were determined by eighteen data frames measured at 0.5° increments of ω. Afterward, the full data sets were also measured at 0.5° intervals of ω. Each frame of data was integrated using the CrysAlisPro program package [S8], followed by the data correction for absorption using an REQAB program. The structure was solved with Intrinsic Phasing using SHELXT [S9] and refined by full-matrix least-square on F^2 using SHELXL [S10] in Olex2 [S11]. Anisotropic refinement was applied to all non-hydrogen. Hydrogen atoms were placed using a riding model. The absolute structure was determined by refinement of the Flack parameter using the method of Parsons, Flack, and Wagner based on quotients of Friedel pairs [S12].

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Deposition numbers CCDC 2525244 (for (*S*,*S*)-**2b**) contain the supplementary crystallographic data for this paper. This data is provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

References.

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[S7] Masaoka, K.; Taue, H.; Wakioka, M.; Ohki, Y.; Ogasawara, M. *Organometallics* **2023**, *42*, 1629−1638.

[S8] Rigaku Oxford Diffraction, CrysAlisPrO, version 1.171.43.130a, Rigaku Corporation, Oxford, UK, **2024**)

[S9] Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3−8.

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[S11] Dolomanov, O. V.; Bourhis, L. J.; Howard, J. A. K.; Puschmann, H. *Acta Cryst.* **2009**, *42*, 339−341.

[S12] Parsons, S.; Flack, H. D.; Wagner, T. *Acta Cryst.* **2013**, *B69*, 249−259.

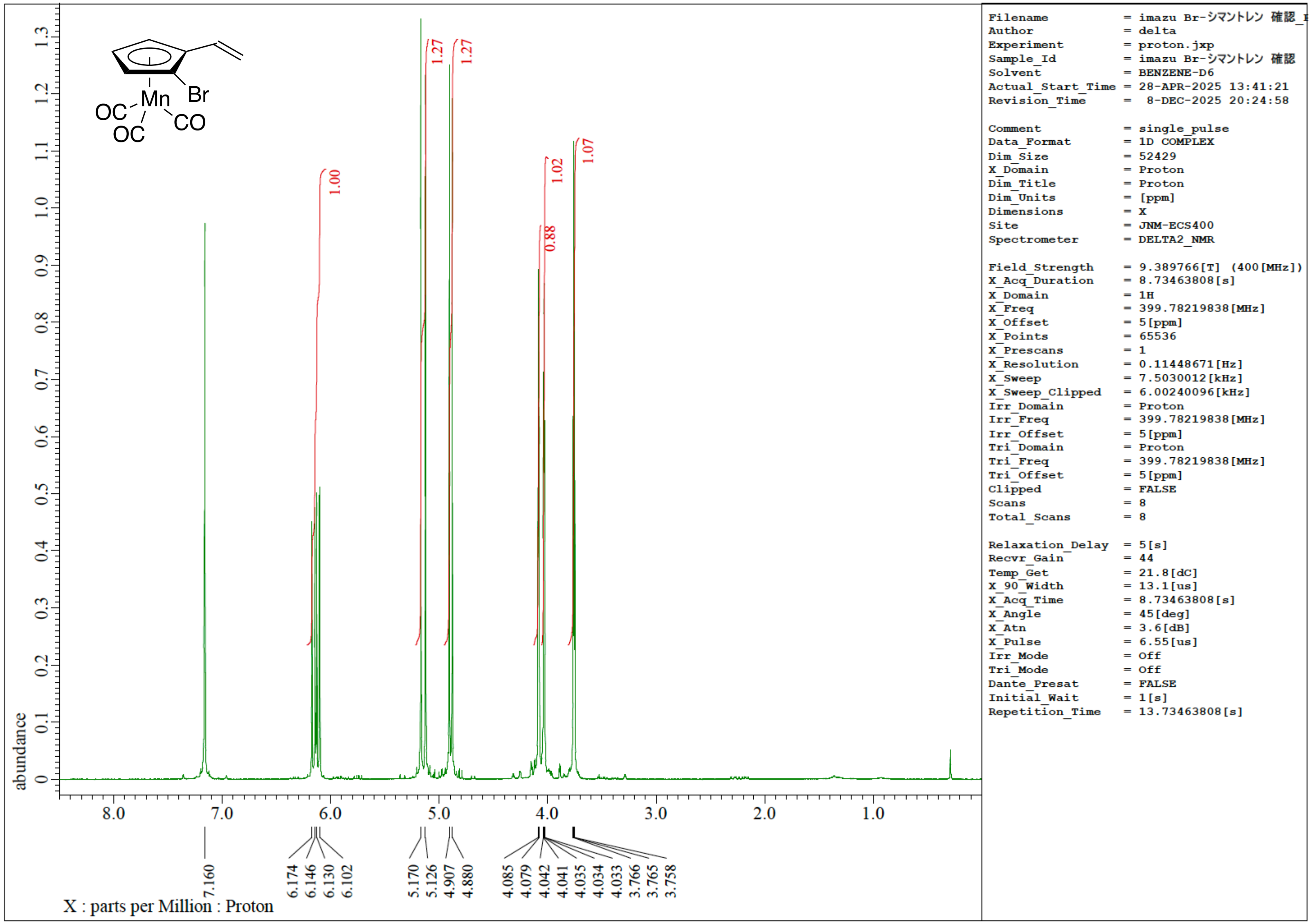

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Figure S1. ^{1}H NMR Spectrum of **1a** in C_6D_6 at 400 MHz.

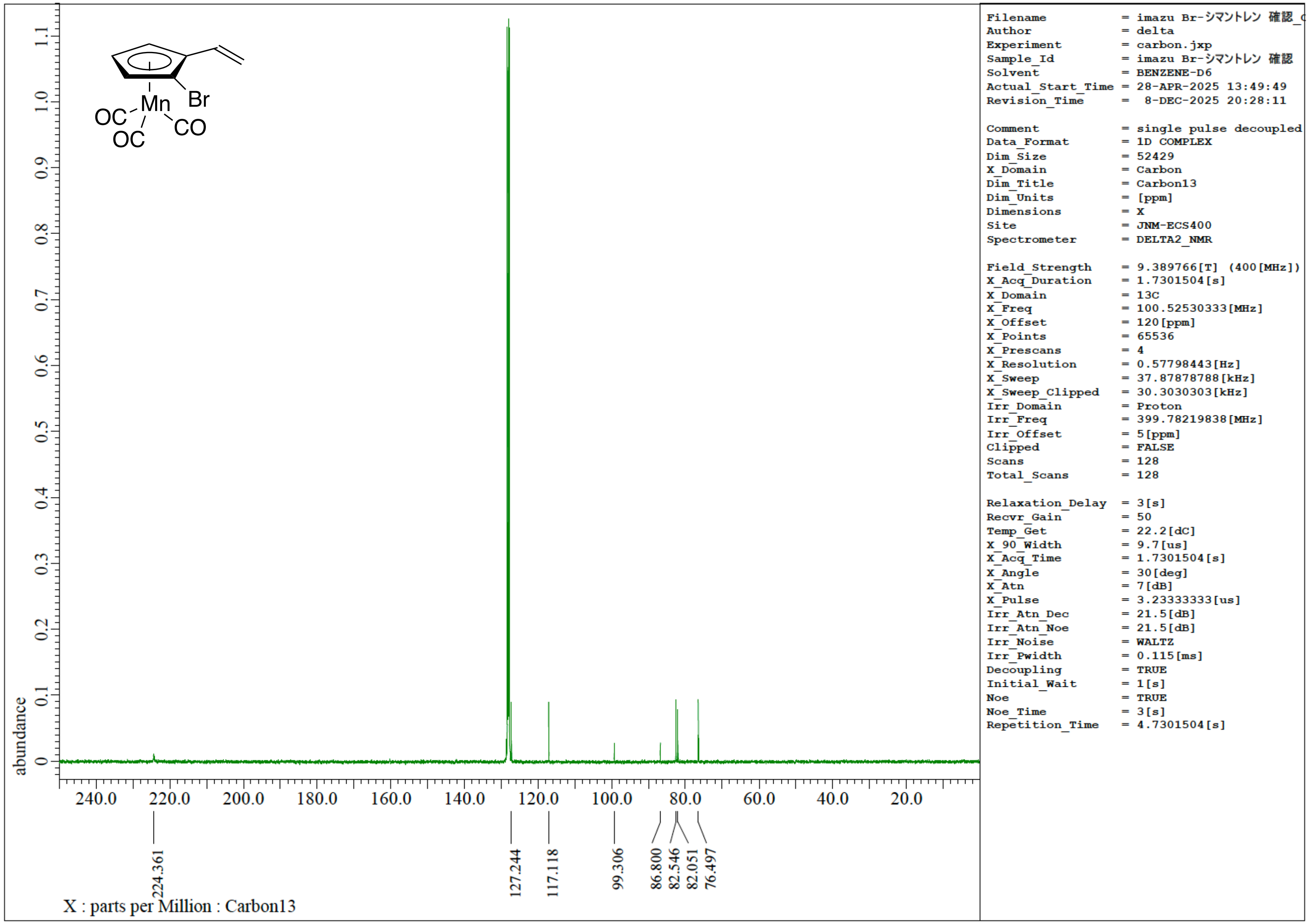

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Figure S2. ^{13}C NMR Spectrum of **1a** in C_6D_6 at 101 MHz.

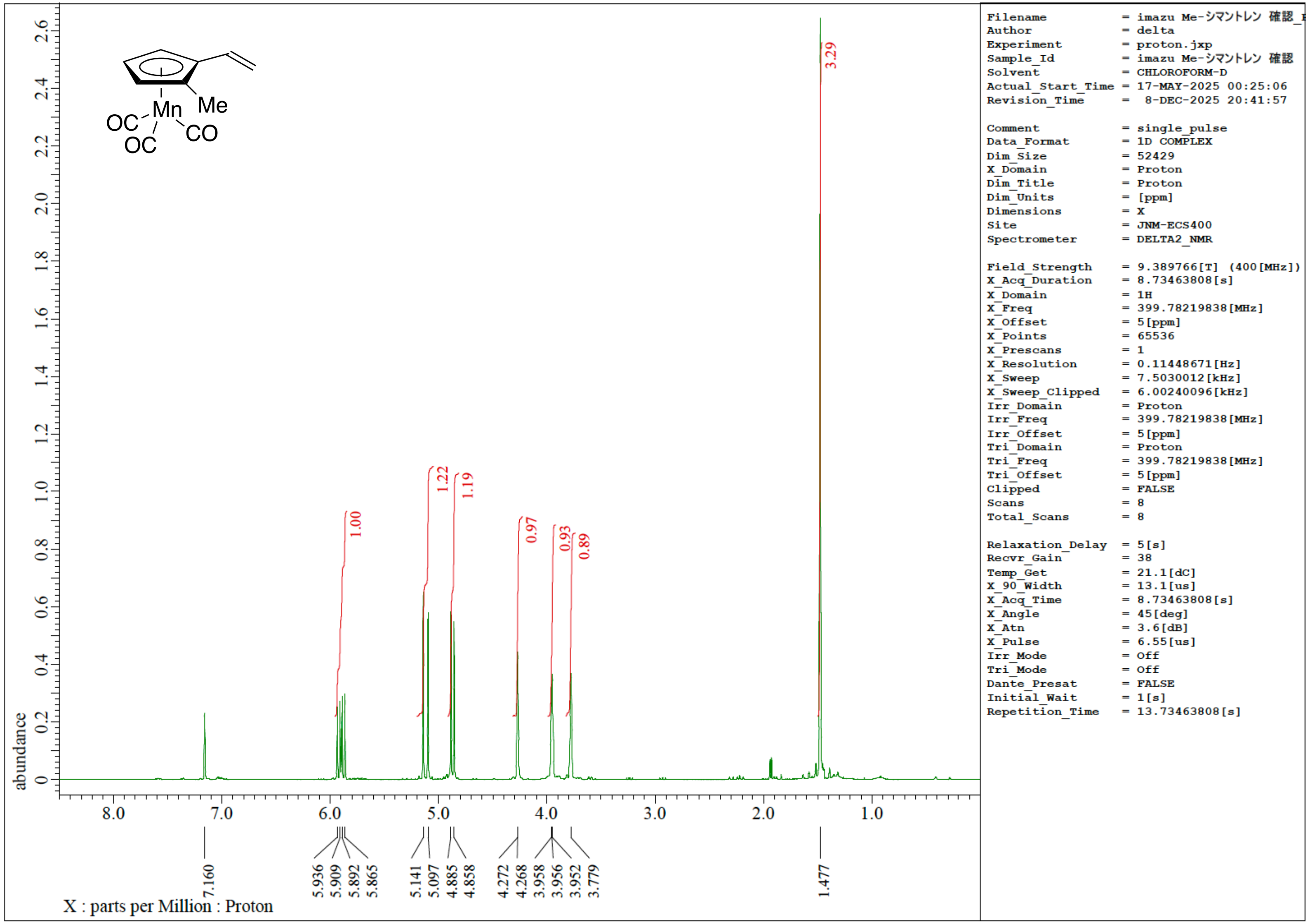

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Figure S3. ^{1}H NMR Spectrum of **1b** in C_6D_6 at 400 MHz.

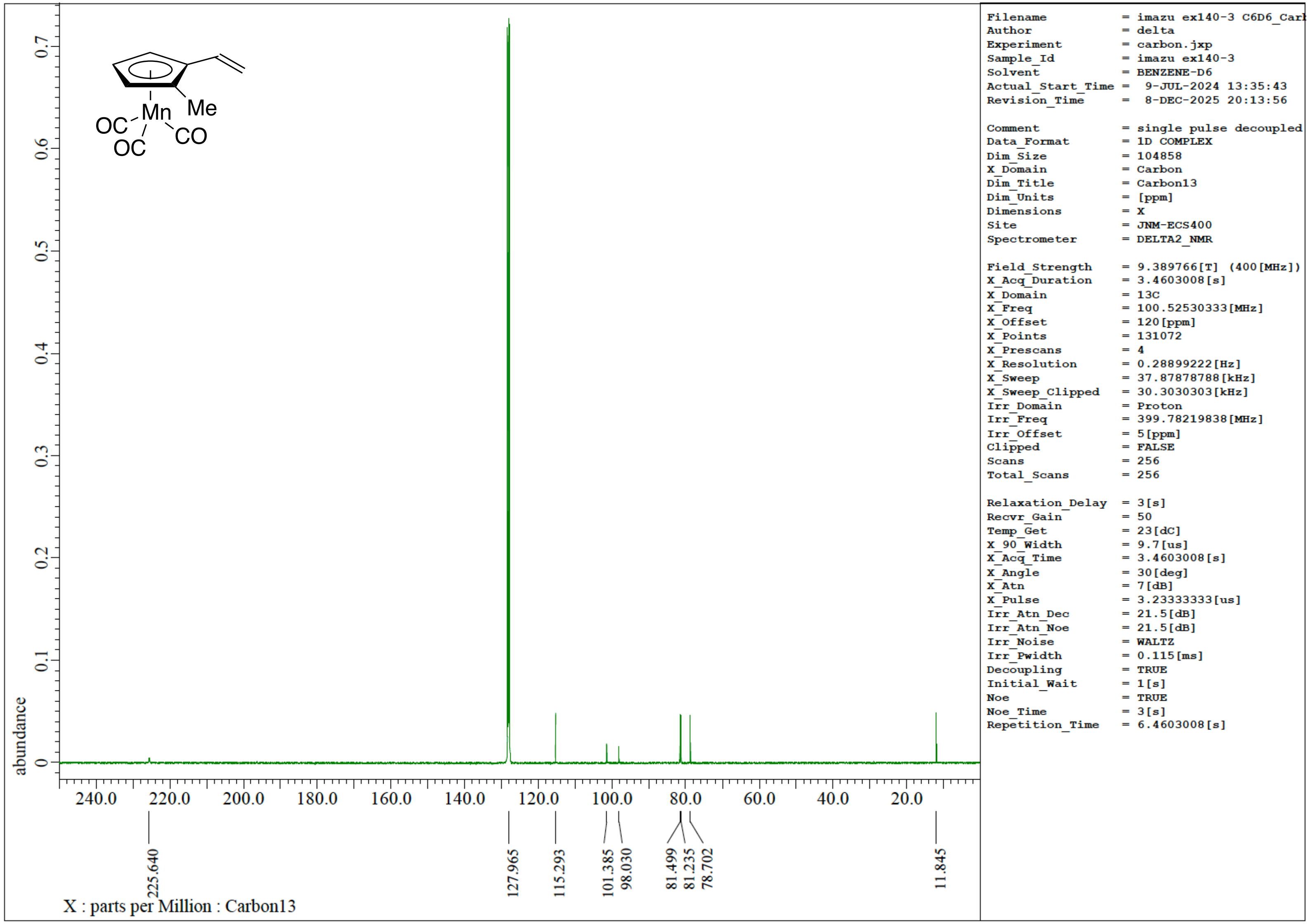

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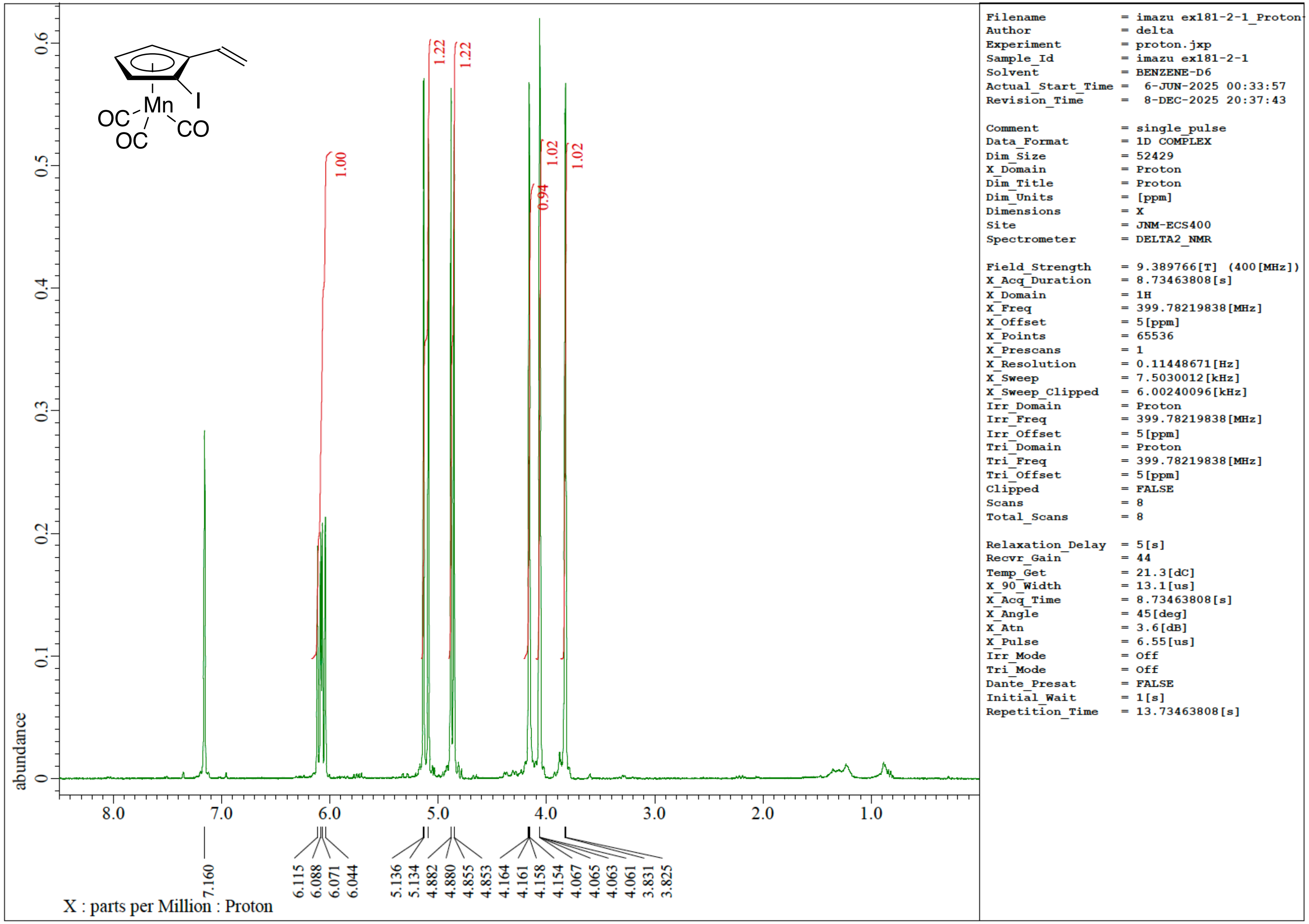
Figure S4. ^{13}C NMR Spectrum of **1b** in C_6D_6 at 101 MHz.



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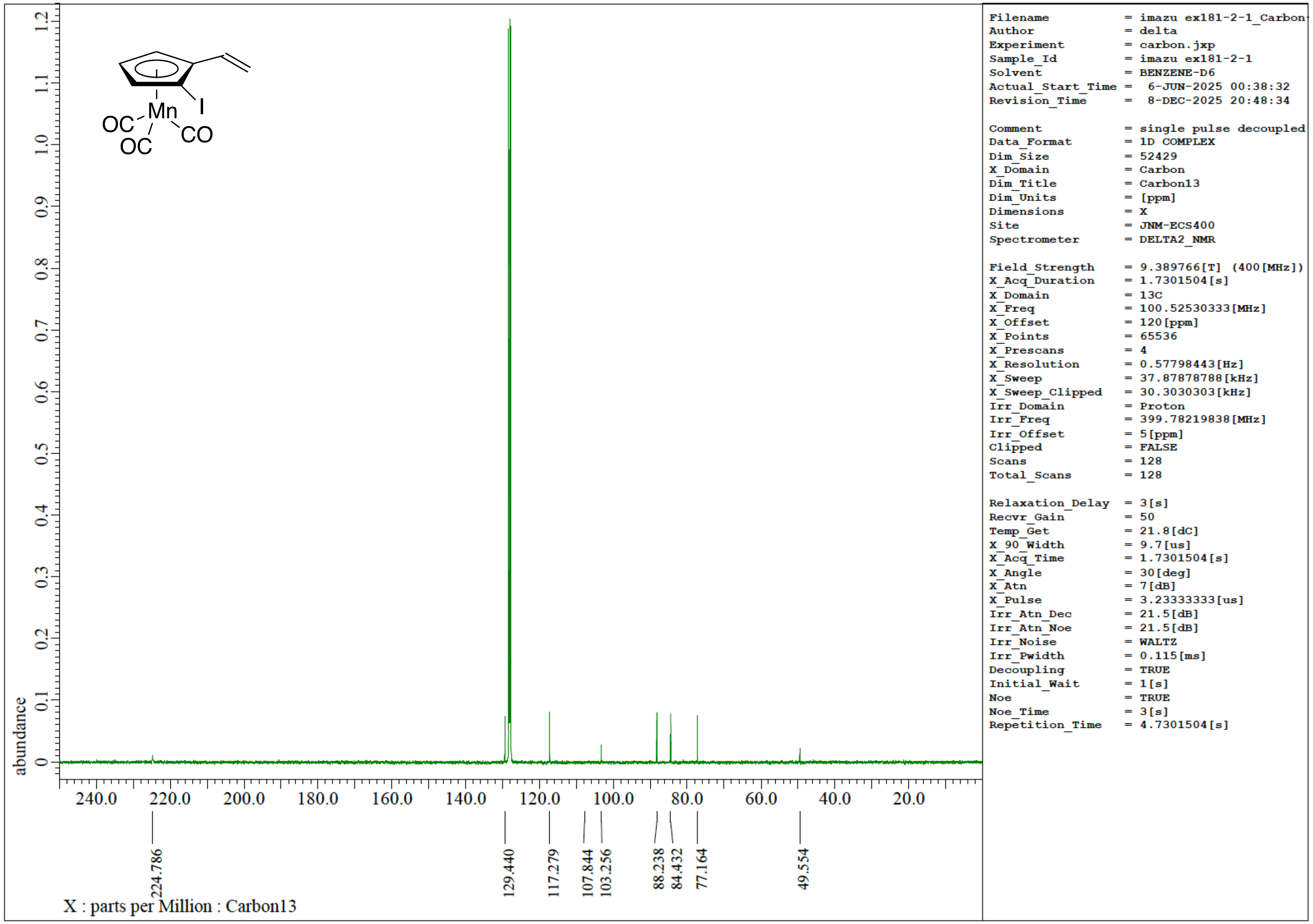
Author               = delta
Experiment           = proton.jxp
Sample_Id            = imazu ex181-2-1
Solvent              = BENZENE-D6
Actual_Start_Time    =  6-JUN-2025 00:33:57
Revision_Time        =  8-DEC-2025 20:37:43

Comment              = single_pulse
Data_Format          = 1D COMPLEX
Dim_Size             = 52429
X_Domain             = Proton
Dim_Title            = Proton
Dim_Units            = [ppm]
Dimensions           = X
Site                 = JNM-ECS400
Spectrometer         = DELTA2_NMR

Field_Strength       = 9.389766[T] (400[MHz])
X_Acq_Duration       = 8.73463808[s]
X_Domain             = 1H
X_Freq               = 399.78219838[MHz]
X_Offset             = 5[ppm]
X_Points             = 65536
X_Prescans           = 1
X_Resolution         = 0.11448671[Hz]
X_Sweep              = 7.5030012[kHz]
X_Sweep_Clipped      = 6.00240096[kHz]
Irr_Domain           = Proton
Irr_Freq             = 399.78219838[MHz]
Irr_Offset           = 5[ppm]
Tri_Domain           = Proton
Tri_Freq             = 399.78219838[MHz]
Tri_Offset           = 5[ppm]
Clipped              = FALSE
Scans                = 8
Total_Scans          = 8

Relaxation_Delay     = 5[s]
Recvr_Gain           = 44
Temp_Get             = 21.3[dC]
X_90_Width           = 13.1[us]
X_Acq_Time           = 8.73463808[s]
X_Angle              = 45[deg]
X_Atn                = 3.6[dB]
X_Pulse              = 6.55[us]
Irr_Mode             = Off
Tri_Mode             = Off
Dante_Presat         = FALSE
Initial_Wait         = 1[s]
Repetition_Time      = 13.73463808[s]
```

Figure S5. ^{1}H NMR Spectrum of **1c** in C_6D_6 at 400 MHz.



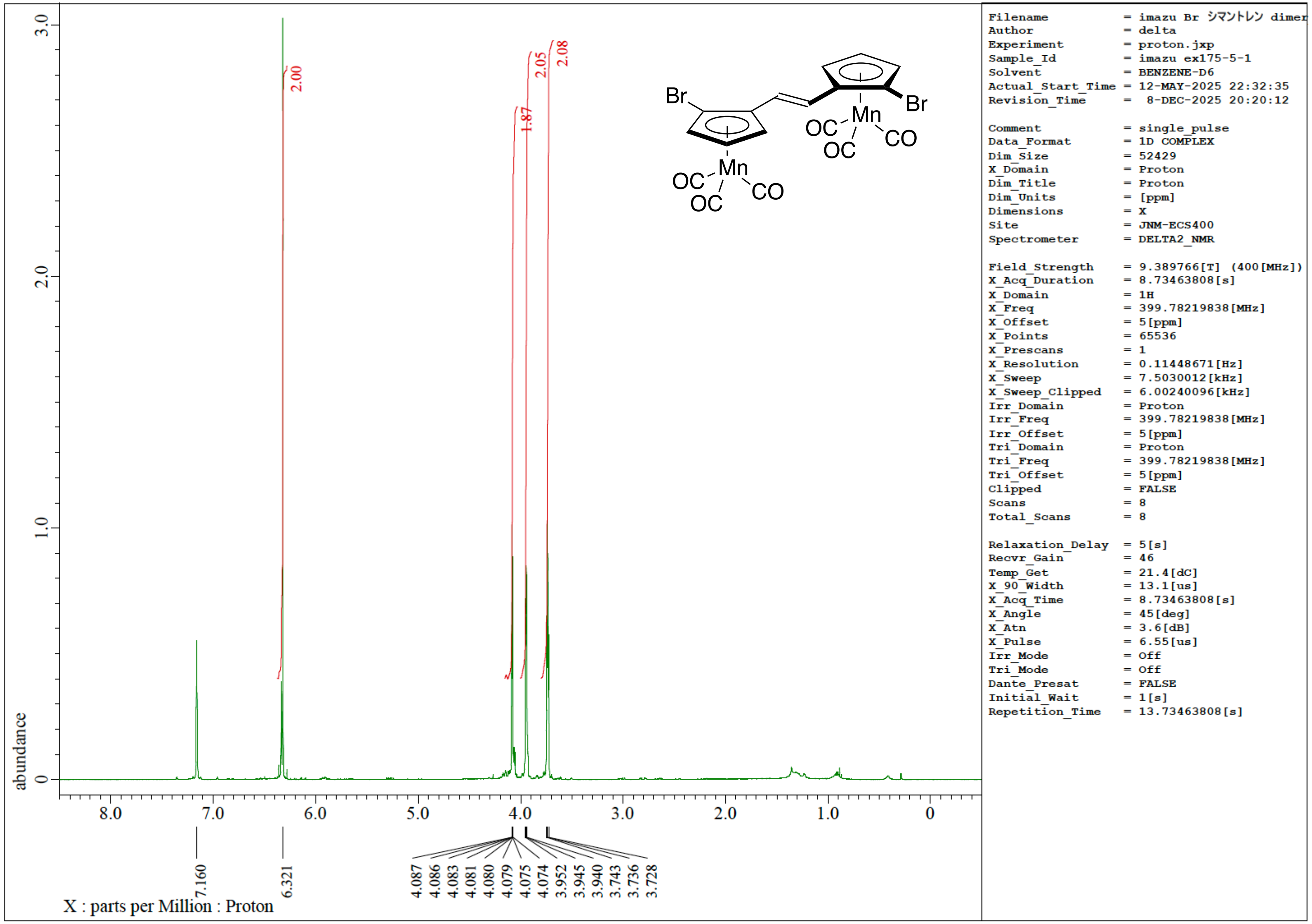
```
Filename            = imazu ex181-2-1_Carbon-
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = imazu ex181-2-1
Solvent             = BENZENE-D6
Actual_Start_Time   =  6-JUN-2025 00:38:32
Revision_Time       =  8-DEC-2025 20:48:34

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.7301504[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 120[ppm]
X_Points            = 65536
X_Prescans          = 4
X_Resolution        = 0.57798443[Hz]
X_Sweep             = 37.87878788[kHz]
X_Sweep_Clipped     = 30.3030303[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 128
Total_Scans         = 128

Relaxation_Delay    = 3[s]
Recvr_Gain          = 50
Temp_Get            = 21.8[dC]
X_90_Width          = 9.7[us]
X_Acq_Time          = 1.7301504[s]
X_Angle             = 30[deg]
X_Atn               = 7[dB]
X_Pulse             = 3.23333333[us]
Irr_Atn_Dec         = 21.5[dB]
Irr_Atn_Noe         = 21.5[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 3[s]
Repetition_Time     = 4.7301504[s]
```

Figure S6. ^{13}C NMR Spectrum of **1c** in C_6D_6 at 101 MHz.



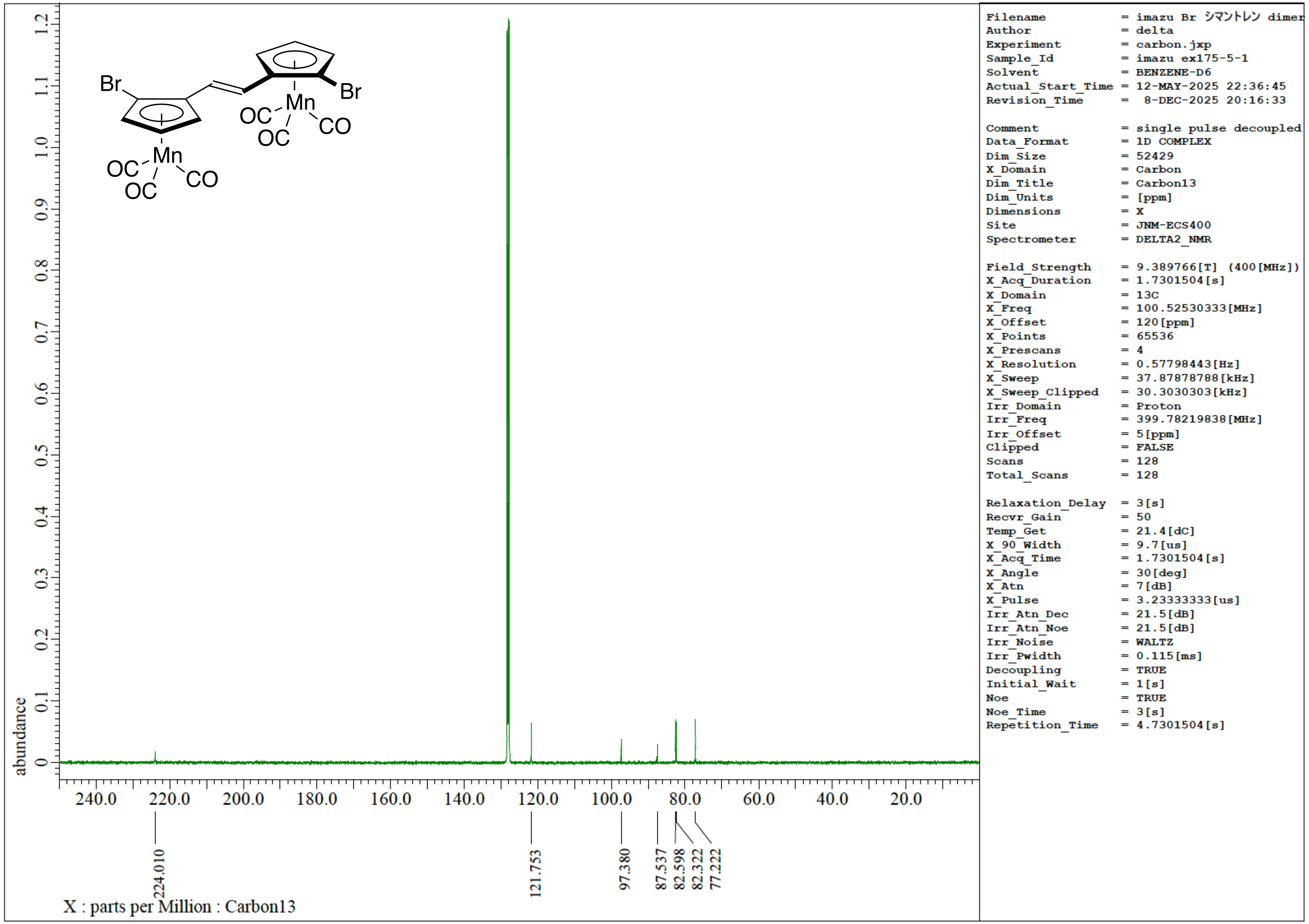
```
Filename            = imazu Br シマントレン dimer
Author              = delta
Experiment          = proton.jxp
Sample_Id           = imazu ex175-5-1
Solvent             = BENZENE-D6
Actual_Start_Time   = 12-MAY-2025 22:32:35
Revision_Time       =  8-DEC-2025 20:20:12

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 8.73463808[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 0.11448671[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 21.4[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 8.73463808[s]
X_Angle             = 45[deg]
X_Atn               = 3.6[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 13.73463808[s]
```

Figure S7. ^{1}H NMR Spectrum of **2a** in C_6D_6 at 400 MHz.



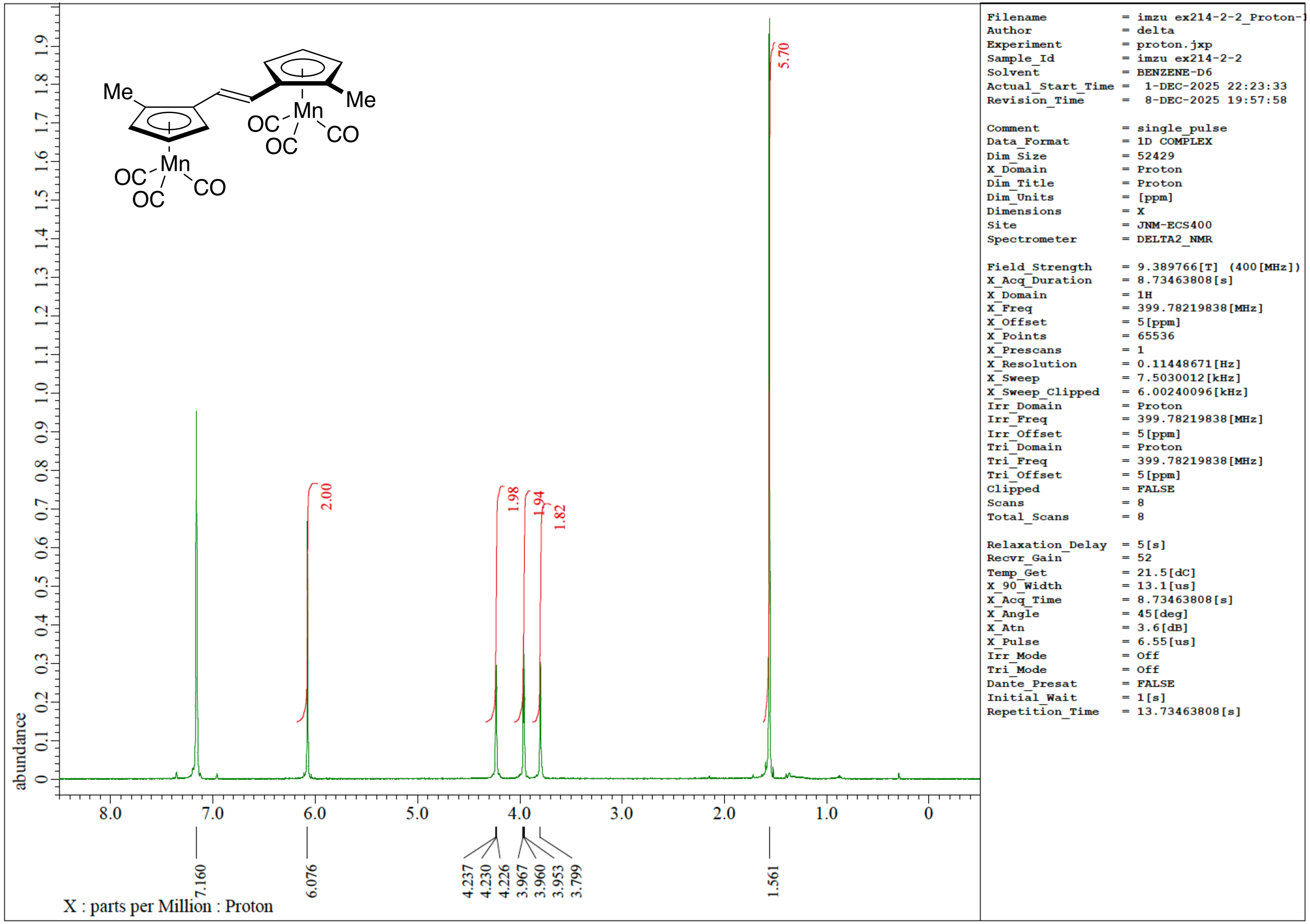
```
Filename            = imazu Br シマントレン dimer
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = imazu ex175-5-1
Solvent             = BENZENE-D6
Actual_Start_Time   = 12-MAY-2025 22:36:45
Revision_Time       =  8-DEC-2025 20:16:33

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.7301504[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 120[ppm]
X_Points            = 65536
X_Prescans          = 4
X_Resolution        = 0.57798443[Hz]
X_Sweep             = 37.87878788[kHz]
X_Sweep_Clipped     = 30.3030303[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 128
Total_Scans         = 128

Relaxation_Delay    = 3[s]
Recvr_Gain          = 50
Temp_Get            = 21.4[dC]
X_90_Width          = 9.7[us]
X_Acq_Time          = 1.7301504[s]
X_Angle             = 30[deg]
X_Atn               = 7[dB]
X_Pulse             = 3.23333333[us]
Irr_Atn_Dec         = 21.5[dB]
Irr_Atn_Noe         = 21.5[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 3[s]
Repetition_Time     = 4.7301504[s]
```

Figure S8. ^{13}C NMR Spectrum of **2a** in C_6D_6 at 101 MHz.



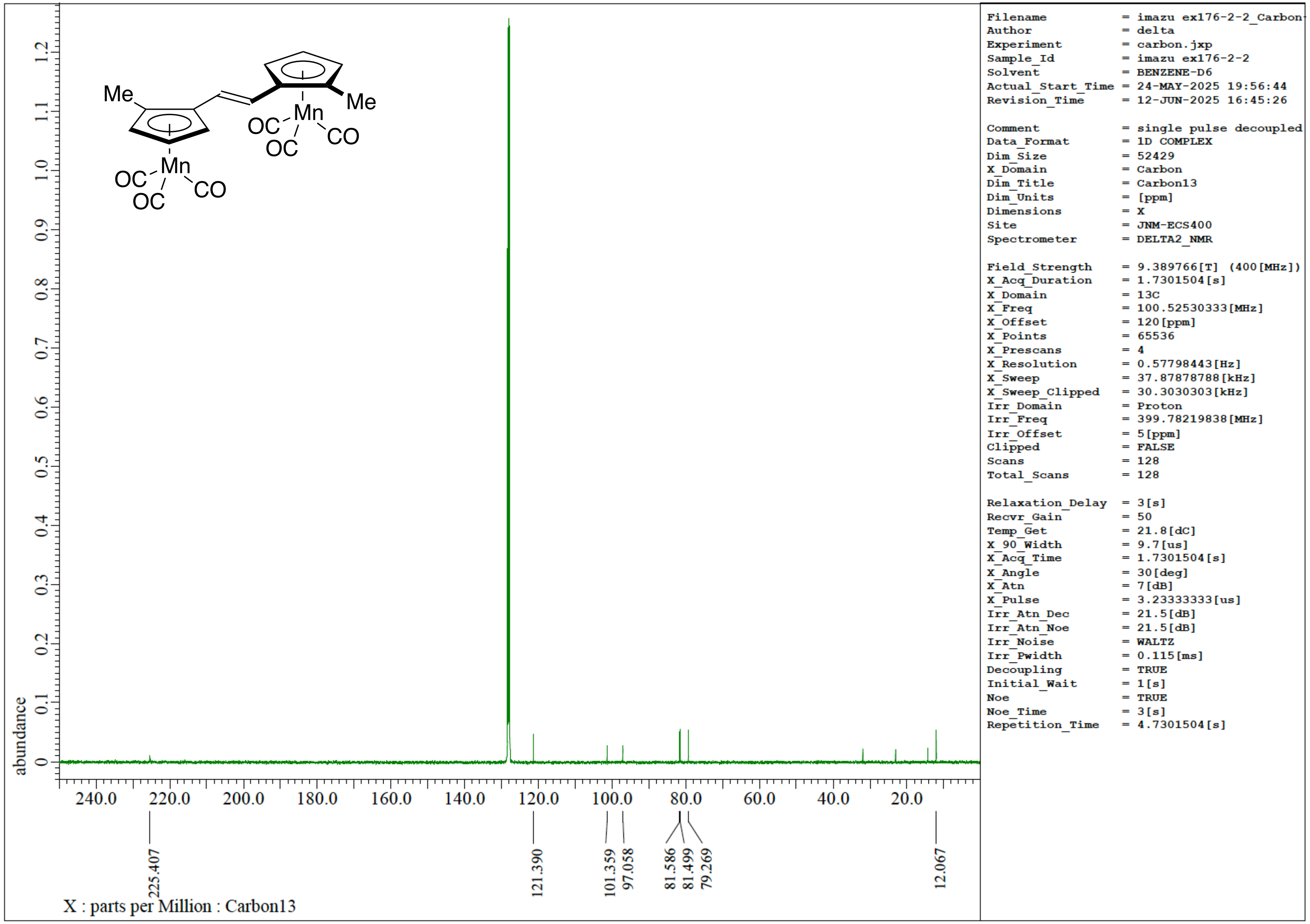
```
Filename            = imzu ex214-2-2_Proton-
Author              = delta
Experiment          = proton.jxp
Sample_Id           = imzu ex214-2-2
Solvent             = BENZENE-D6
Actual_Start_Time   =  1-DEC-2025 22:23:33
Revision_Time       =  8-DEC-2025 19:57:58

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 8.73463808[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 0.11448671[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 52
Temp_Get            = 21.5[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 8.73463808[s]
X_Angle             = 45[deg]
X_Atn               = 3.6[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 13.73463808[s]
```

Figure S9. ^{1}H NMR Spectrum of **2b** in C_6D_6 at 400 MHz.



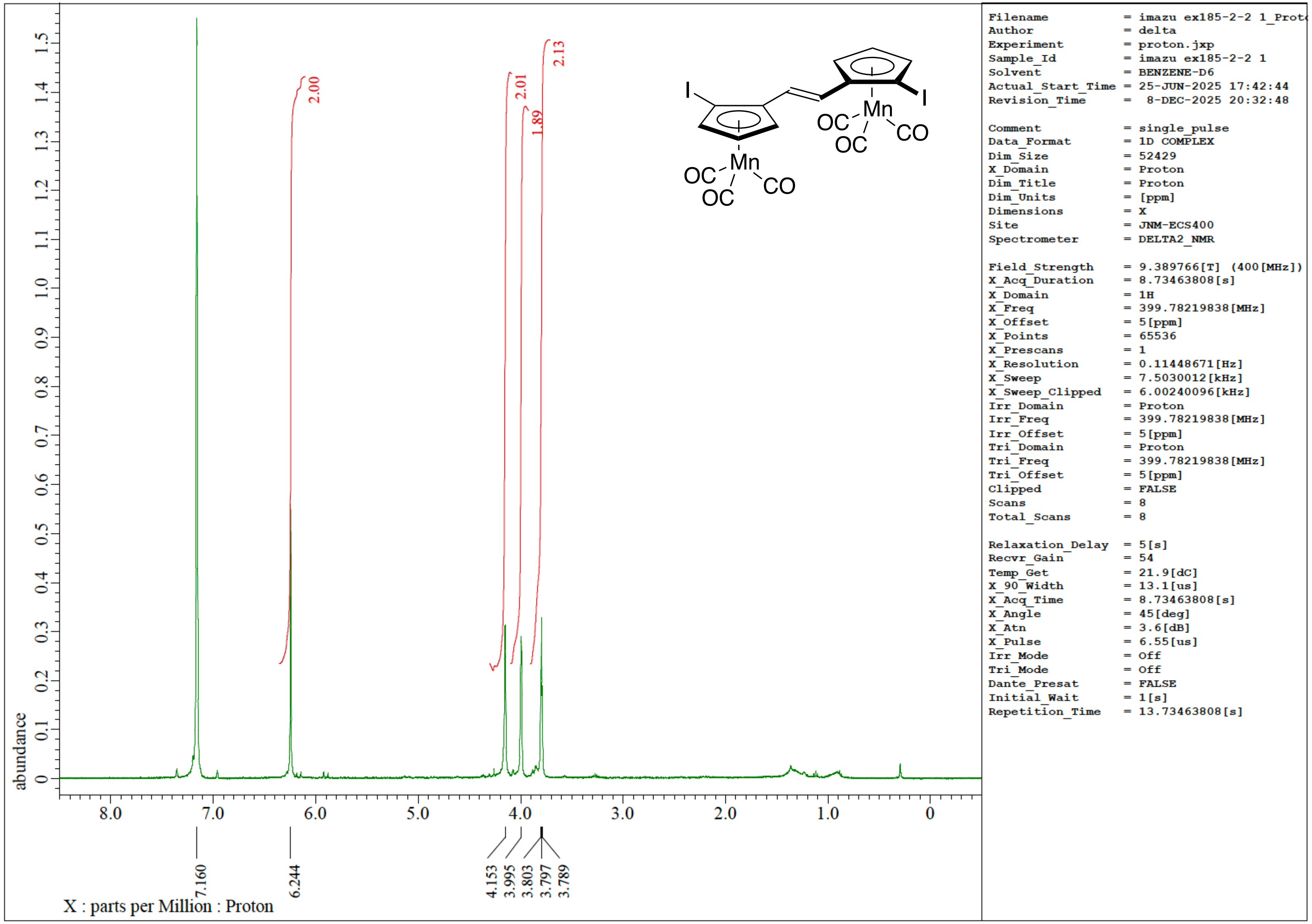
```
Filename           = imazu ex176-2-2_Carbon
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = imazu ex176-2-2
Solvent            = BENZENE-D6
Actual_Start_Time  = 24-MAY-2025 19:56:44
Revision_Time      = 12-JUN-2025 16:45:26

Comment            = single pulse decoupled
Data_Format        = 1D COMPLEX
Dim_Size           = 52429
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.7301504[s]
X_Domain           = 13C
X_Freq             = 100.52530333[MHz]
X_Offset           = 120[ppm]
X_Points           = 65536
X_Prescans         = 4
X_Resolution       = 0.57798443[Hz]
X_Sweep            = 37.87878788[kHz]
X_Sweep_Clipped    = 30.3030303[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 128
Total_Scans        = 128

Relaxation_Delay   = 3[s]
Recvr_Gain         = 50
Temp_Get           = 21.8[dC]
X_90_Width         = 9.7[us]
X_Acq_Time         = 1.7301504[s]
X_Angle            = 30[deg]
X_Atn              = 7[dB]
X_Pulse            = 3.23333333[us]
Irr_Atn_Dec        = 21.5[dB]
Irr_Atn_Noe        = 21.5[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.115[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 3[s]
Repetition_Time    = 4.7301504[s]
```

Figure S10. ^{13}C NMR Spectrum of **2b** in C_6D_6 at 101 MHz.



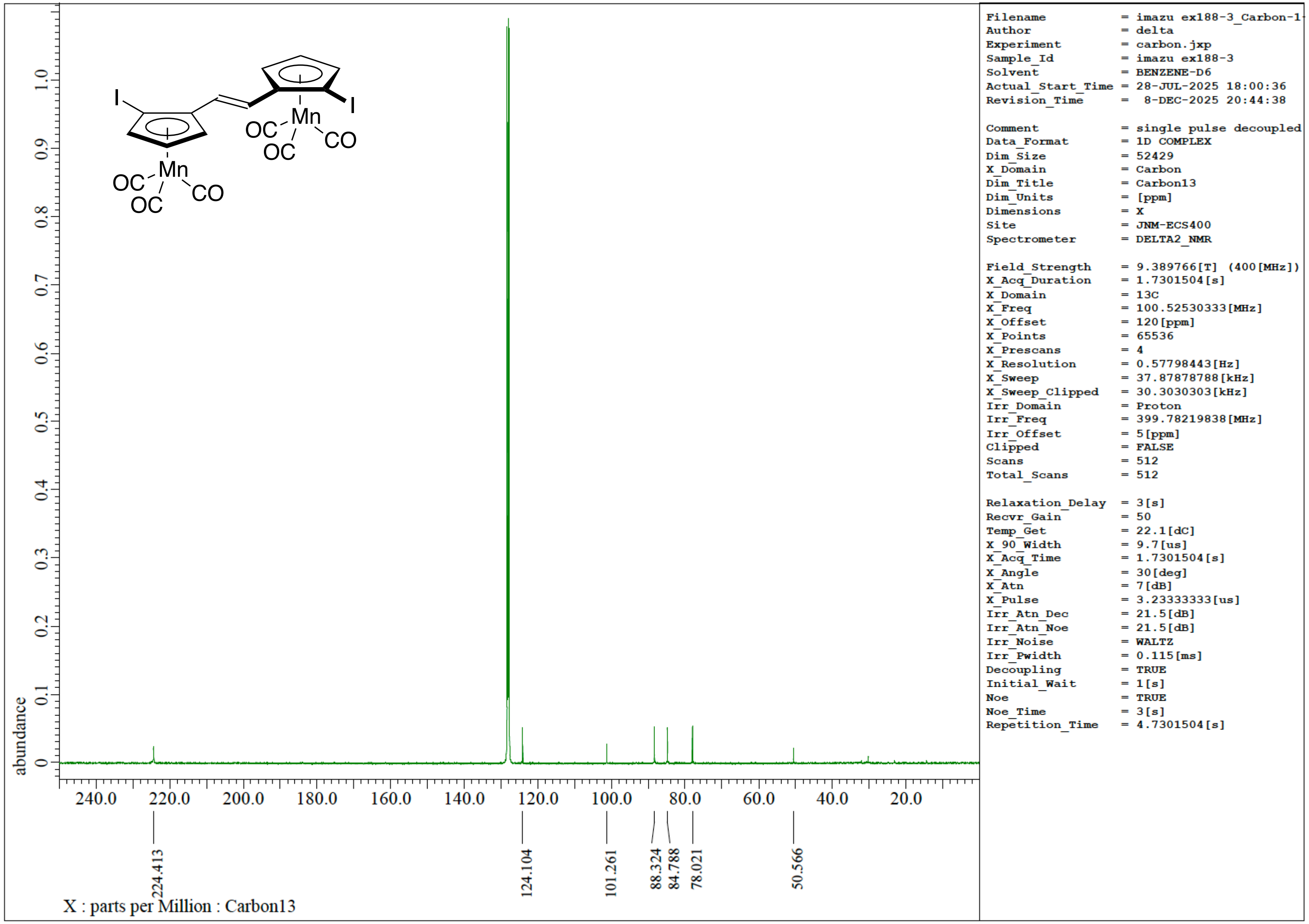
```
Filename            = imazu ex185-2-2 1_Prot
Author              = delta
Experiment          = proton.jxp
Sample_Id           = imazu ex185-2-2 1
Solvent             = BENZENE-D6
Actual_Start_Time   = 25-JUN-2025 17:42:44
Revision_Time       =  8-DEC-2025 20:32:48

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 8.73463808[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 0.11448671[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 54
Temp_Get            = 21.9[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 8.73463808[s]
X_Angle             = 45[deg]
X_Atn               = 3.6[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 13.73463808[s]
```

Figure S11. ^{1}H NMR Spectrum of **2c** in C_6D_6 at 400 MHz.



```
Filename           = imazu ex188-3_Carbon-1
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = imazu ex188-3
Solvent            = BENZENE-D6
Actual_Start_Time  = 28-JUL-2025 18:00:36
Revision_Time      =  8-DEC-2025 20:44:38

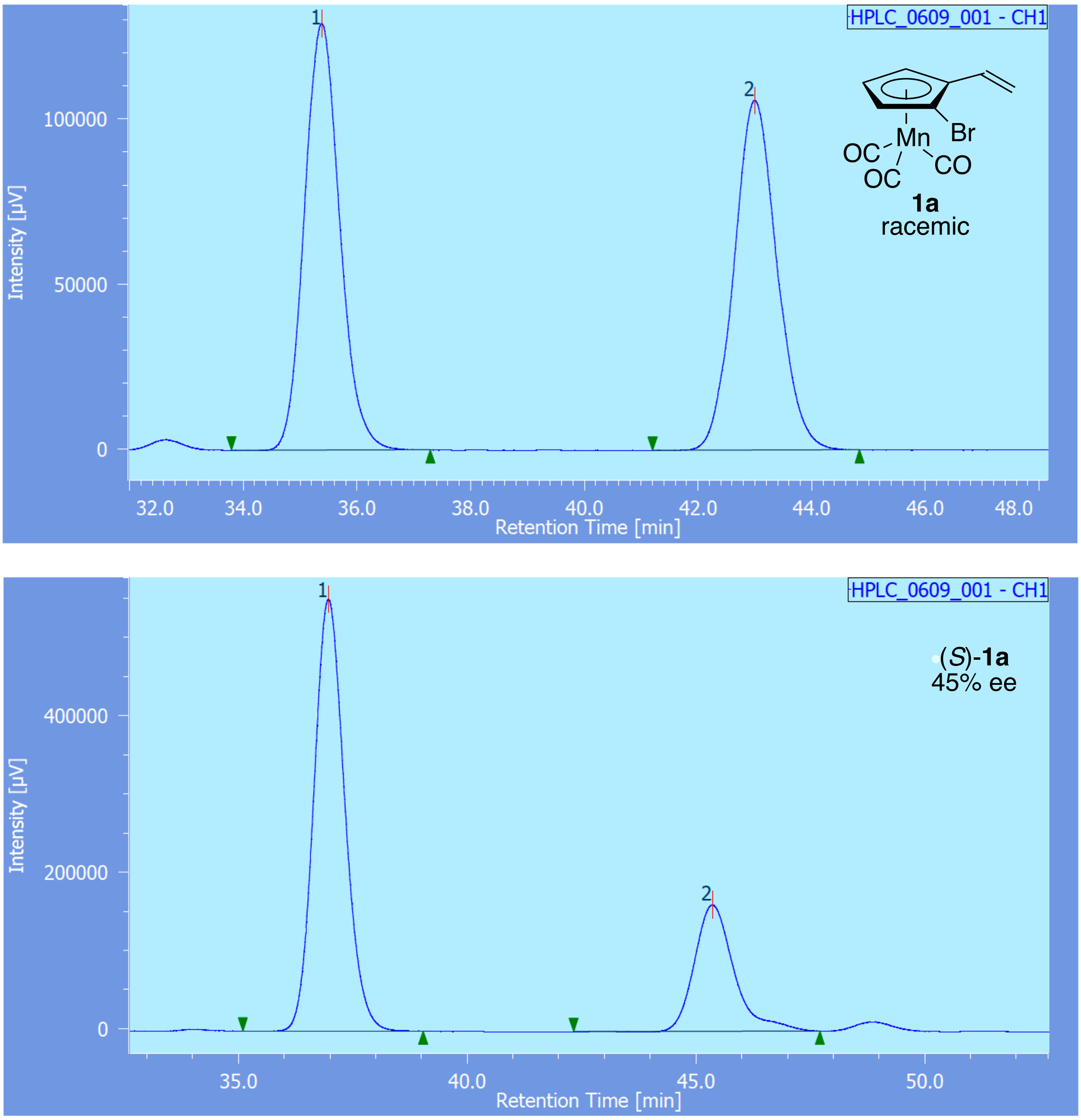
Comment            = single pulse decoupled
Data_Format        = 1D COMPLEX
Dim_Size           = 52429
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.7301504[s]
X_Domain           = 13C
X_Freq             = 100.52530333[MHz]
X_Offset           = 120[ppm]
X_Points           = 65536
X_Prescans         = 4
X_Resolution       = 0.57798443[Hz]
X_Sweep            = 37.87878788[kHz]
X_Sweep_Clipped    = 30.3030303[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 512
Total_Scans        = 512

Relaxation_Delay   = 3[s]
Recvr_Gain         = 50
Temp_Get           = 22.1[dC]
X_90_Width         = 9.7[us]
X_Acq_Time         = 1.7301504[s]
X_Angle            = 30[deg]
X_Atn              = 7[dB]
X_Pulse            = 3.23333333[us]
Irr_Atn_Dec        = 21.5[dB]
Irr_Atn_Noe        = 21.5[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.115[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 3[s]
Repetition_Time    = 4.7301504[s]
```

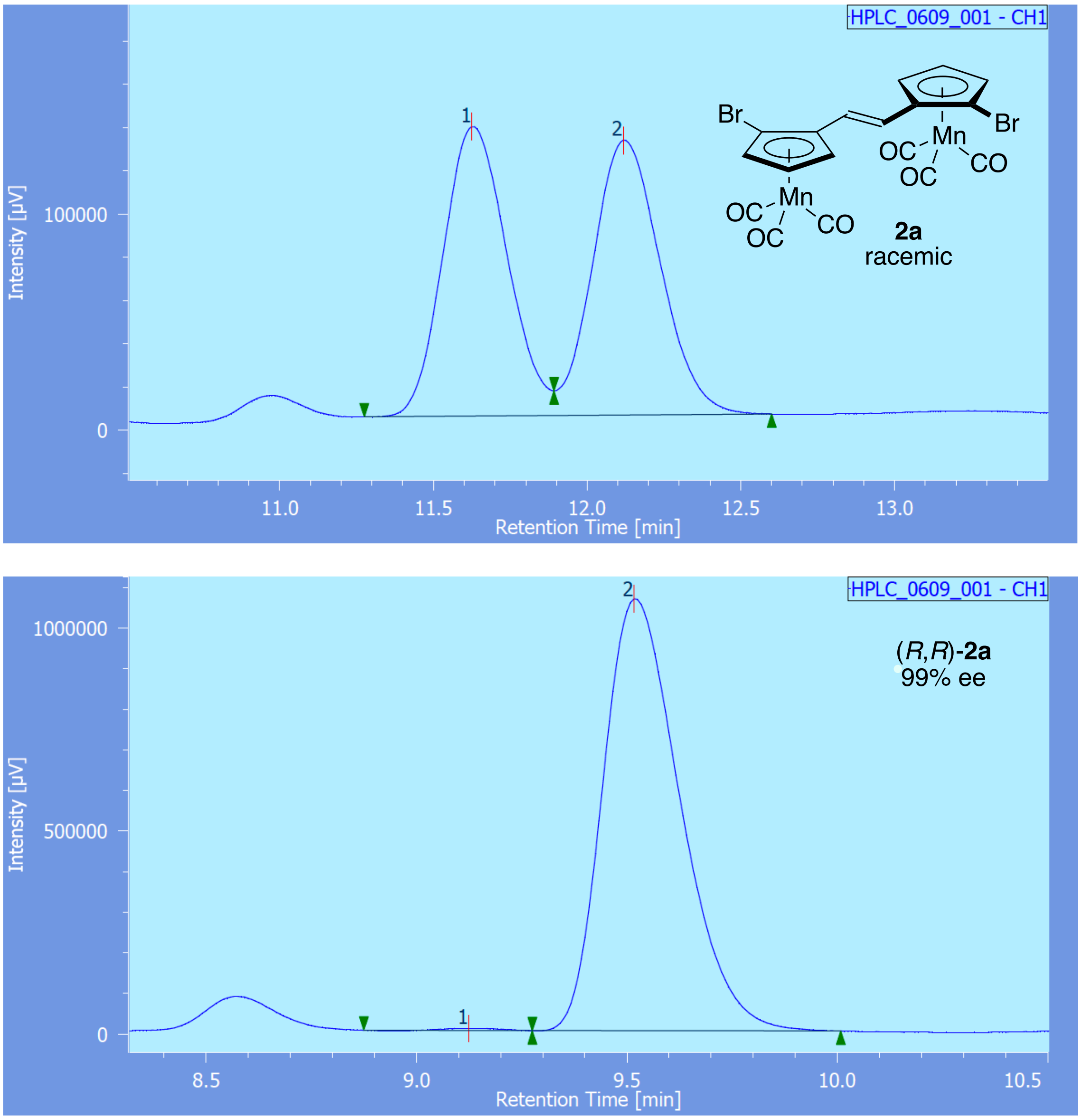
Figure S12. ^{13}C NMR Spectrum of **2c** in C_6D_6 at 101 MHz.

Figure S13. Chiral HPLC Analysis of (*S*)-**1a** (Table 1, entry 4); Chiralcel OD-H; eluent: hexane/^{i}PrOH = 50/1; flow rate: 1.0 mL/min.



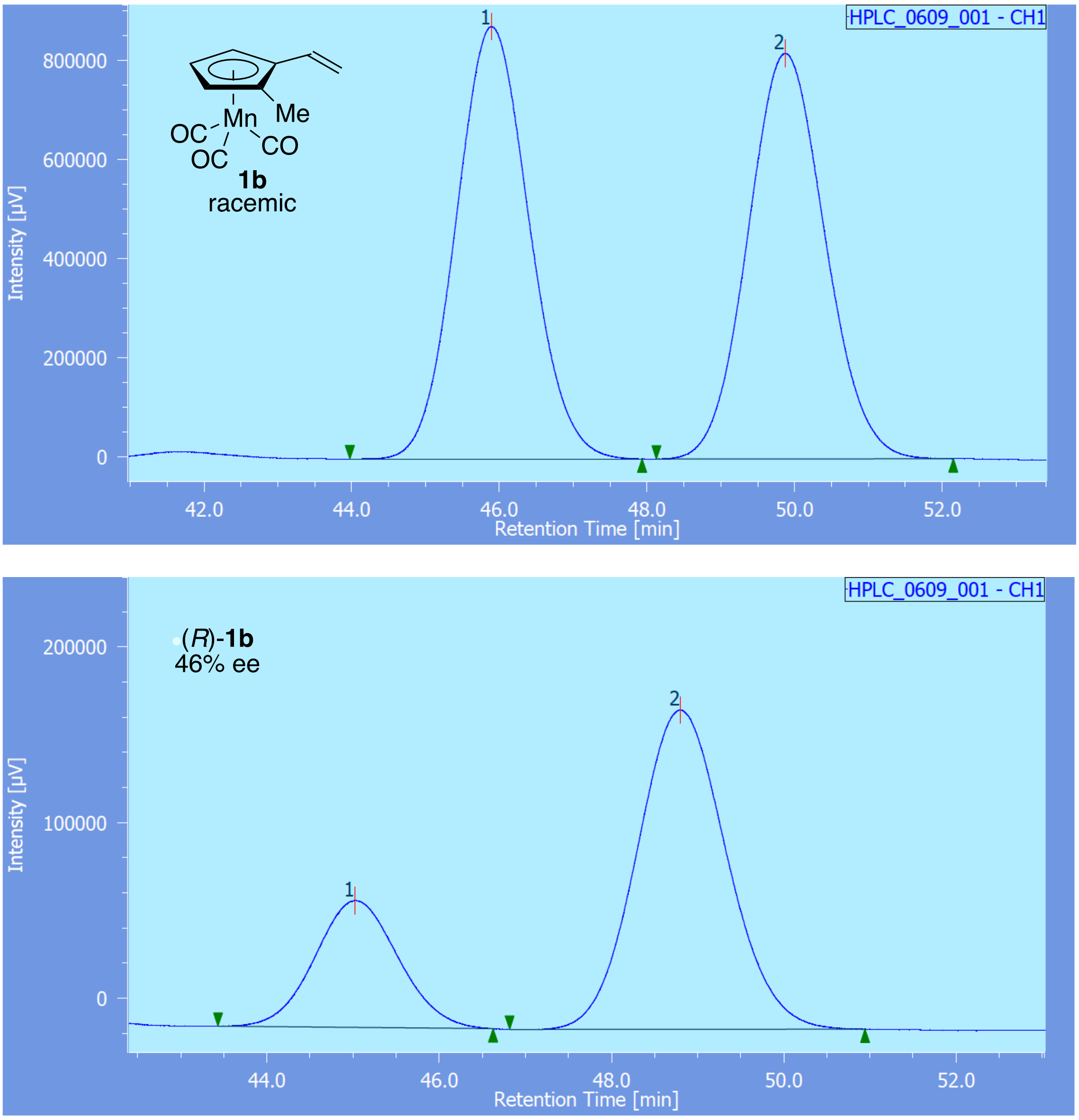
#	peak name	CH	tR [min]	area [µV•sec]	height [µV]	area %	height %	NTP	resolution	symmetry coefficient
1	(*S*)-**isomer**	1	36.967	25817677	551940	72.594	77.353	14618	6.185	1.133
2	(*R*)-**isomer**	1	45.358	9746652	161590	27.406	22.647	14672	N/A	1.426

Figure S14. Chiral HPLC Analysis of (*R*,*R*)-**2a** (Table 1, entry 4); Chiralpak IE; eluent: hexane/ethyl acetate/^{i}PrOH = 90/5/1; flow rate: 0.5 mL/min.



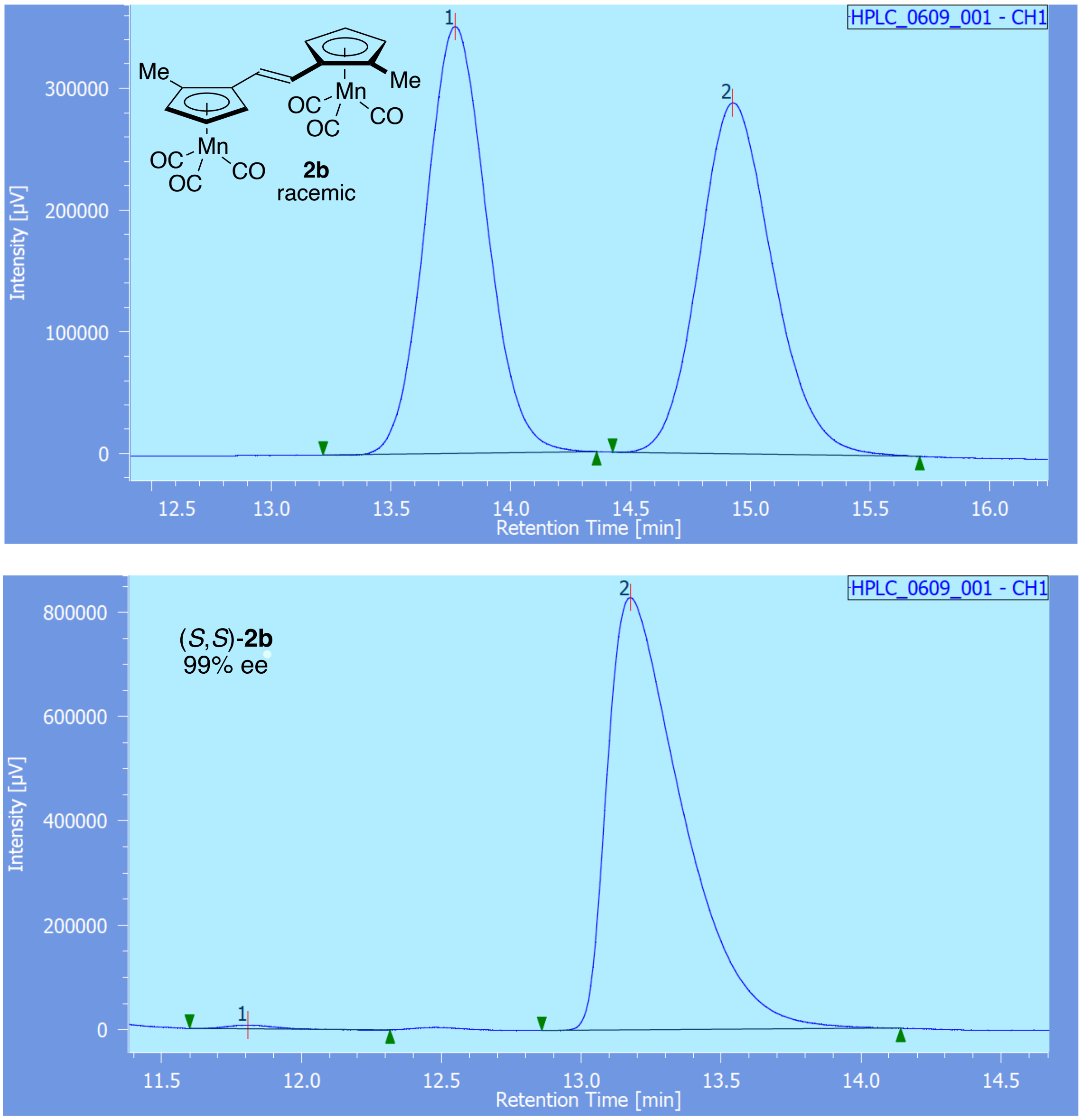
#	peak name	CH	tR [min]	area [µV•sec]	height [µV]	area %	height %	NTP	resolution	symmetry coefficient
1	(*S*,*S*)-**isomer**	1	9.125	45036	4803	0.331	0.450	17571	1.283	1.060
2	(*R*,*R*)-**isomer**	1	9.517	13553796	1063401	99.669	99.550	12787	N/A	1.351

Figure S15. Chiral HPLC Analysis of (*R*)-**1b** (Table 1, entry 8); Chiralcel OD-H; eluent: hexane/^{i}PrOH = 10/1; flow rate: 0.5 mL/min.



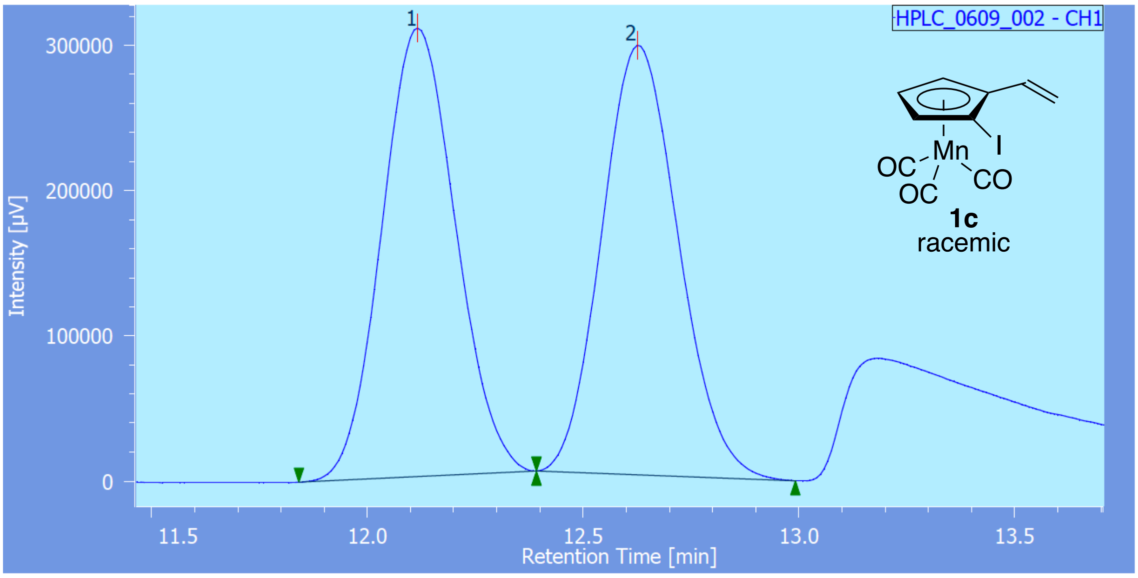
#	peak name	CH	tR [min]	area [µV•sec]	height [µV]	area %	height %	NTP	resolution	symmetry coefficient
1	(*R*)-**isomer**	1	45.025	4867701	72197	26.995	28.428	10211	2.046	1.054
2	(*S*)-**isomer**	1	48.800	13164482	181771	73.005	71.572	10364	N/A	1.073

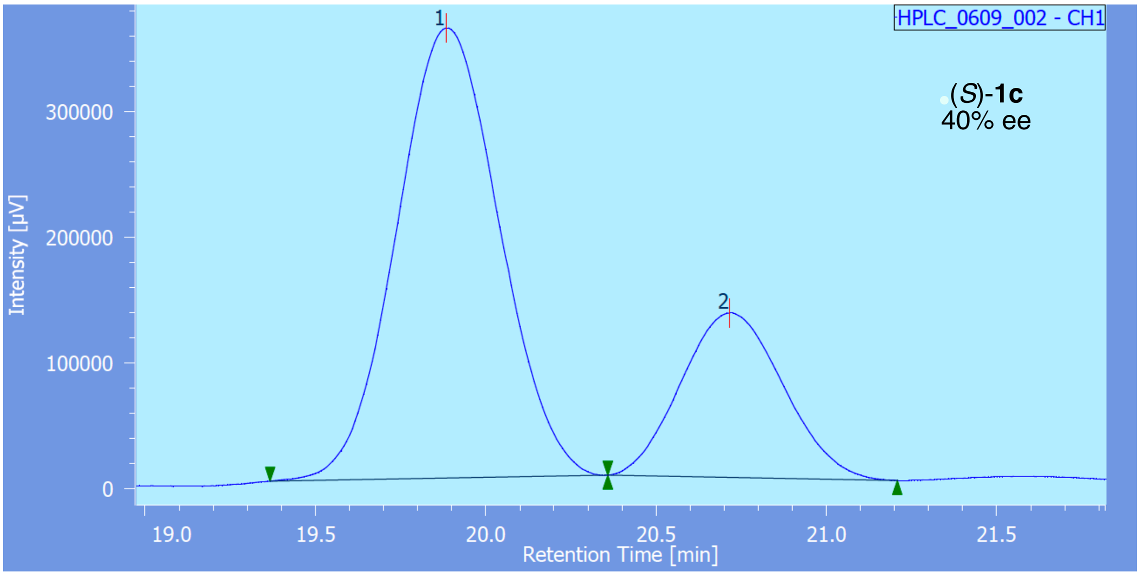
Figure S16. Chiral HPLC Analysis of (*S*,*S*)-**2b** (Table 1, entry 8); Chiralpak IC; eluent: hexane/^{i}PrOH = 100/1; flow rate: 0.5 mL/min.



#	peak name	CH	tR [min]	area [μV•sec]	height [μV]	area %	height %	NTP	resolution	symmetry coefficient
1	(*R*,*R*)-**isomer**	1	11.808	84773	7087	0.545	0.846	21349	3.410	1.299
2	(*S*,*S*)-**isomer**	1	13.175	15468192	828833	99.455	99.152	12037	N/A	2.058

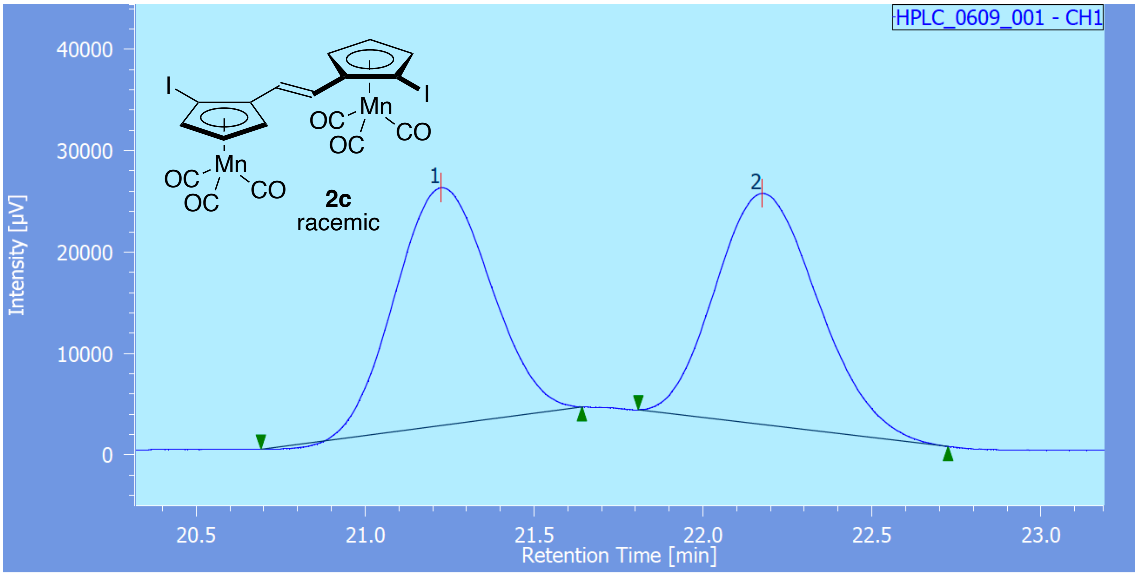
Figure S17. Chiral HPLC Analysis of (*S*)-**1c** (Table 1, entry 10); ChiralPAK IB; eluent: hexane/ethyl acetate/^{i}PrOH = 900/60/1; flow rate: 0.5 mL/min.

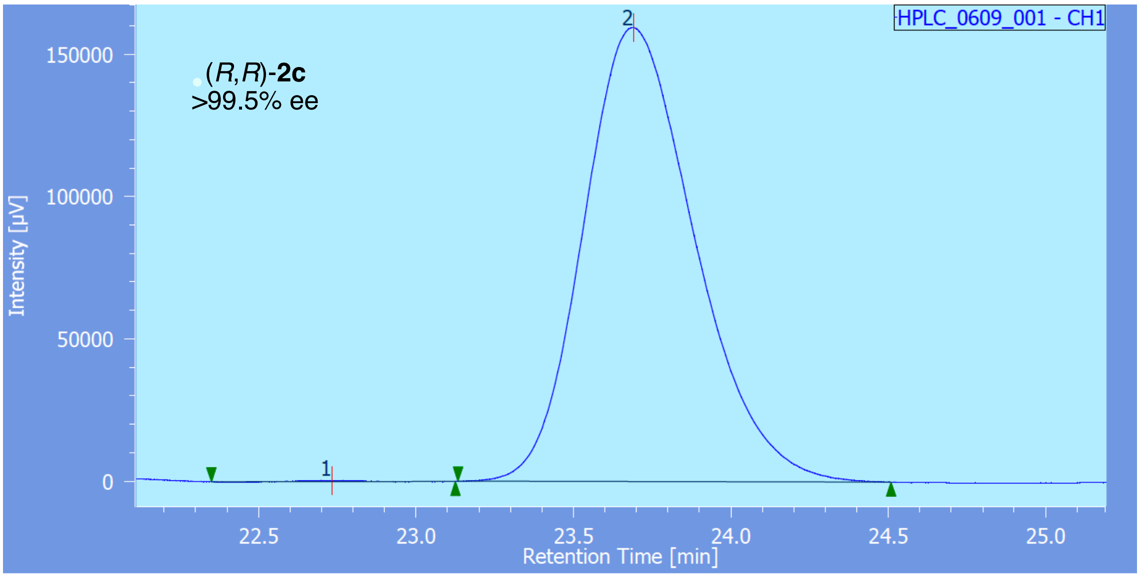




#	peak name	CH	tR [min]	area [μV•sec]	height [μV]	area %	height %	NTP	resolution	symmetry coefficient
1	(*S*)-**isomer**	1	19.883	7496491	358455	73.336	73.250	20179	1.486	1.046
2	(*R*)-**isomer**	1	20.717	2725569	130903	26.664	26.750	21550	N/A	1.089

Figure S18. Chiral HPLC Analysis of (*R*,*R*)-**2c** (Table 1, entry 10); Chiralpak IB; eluent: hexane/ethyl acetata/^{i}PrOH = 90/5/1; flow rate: 0.5 mL/min.





#	peak name	CH	tR [min]	area [µV•sec]	height [µV]	area %	height %	NTP	resolution	symmetry coefficient
1	(*S*,*S*)-**isomer**	1	22.733	5360	400	0.136	0.250	54248	1.854	0.937
2	(*R*,*R*)-**isomer**	1	23.692	3927596	159488	99.864	99.750	21513	N/A	1.209