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Supporting Information

Catalytic Halodefluorination of Aliphatic C–F Bonds

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Experimental Details

General Procedures and Materials

All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and glove box techniques.Reactions were performed in a J. Young NMR tube in a nitrogen atmosphere glovebox. Glassware were flame-dried under vacuum prior to use. All solvents, including deuterated NMR solvents were distilled, degassed and dried with calcium hydride before use. NMR spectra were recorded at 25°C on Bruker Avance 400 MHz and Bruker AMX 500 MHz spectrometers. The chemical shifts (δ) for ^{1}H-NMR spectra are given in ppm relative to residual signals of the solvent, ^{19}F relative to an internal C_6F_6 reference. All GC-MS studies were performed on an Agilent GC/MS (Agilent 7890A GC/Agilent 5975C MS) system. HRMS were obtained with a Finnigan IMAT 95XL-T mass spectrometer. Aluminium chloride and aluminium bromide were purified by sublimation. Benzotrifluoride was distilled, degassed and dried with calcium hydride before use. 1-Fluorooctane, trimethylsilyl chloride, trimethylsilylbromide, trimethylsilyl iodide, silicon tetrachloride, 1,3-Bis(trifluoromethyl)benzene, 1,4-Bis(trifluoromethyl)benzene, trifluoromethoxybenzene, chlorotriphenylmethane, aluminium fluoride and aluminium iodide were purchased from Sigma-Aldrich or Alfa-Aesar and used without further purification. $[CPh_3][B(C_6F_5)_4]$ and $[SiEt_3][B(C_6F_5)_4]$ were prepared according to reported methods.[1]

GC/MS Run Method

GC Method

Column: DB-5MS 30 m x 250 µm x 0.25 µm

Oven Program: 50°C for 3 min, 10°C/min to 150°C for 2 min, 25°C/min to 250°C for 5 min

Split Ratio: 100:1

In*J*ection Volume: 1 µL

MS Method

Mass range: 36-500amu

General Procedure A for the Halodefluorination of Fluoroalkanes

To an oven-dried J. Young's NMR tube in a glove box was added chlorobenzene, d-benzene, trimethylsilyl halide, hexafluorobenzene and fluoroalkane. The reaction NMR tube was first subjected to screening of its initial ^{1}H and ^{19}F NMR spectra. Aluminium halide was then added to the reaction tube in a glove box and the reaction was carried out by heating in a pre-heated silicon oil bath at 80 °C. The reaction was monitored *via* ^{19}F NMR on the consumption of the fluoroalkane periodically. Conversion was based on comparing the integral ratios of unconsumed fluoroalkane to hexafluorobenzene as an internal standard. The reaction was quenched with a few drops of water before washing with CH_2Cl_2 to a 5 mL volumetric flask, followed by extraction of a 1 mL aliquot for GCMS analysis. The ratio of halodefluorinated products to starting fluoroalkane were determined by GCMS.

General Procedure B for the Bromodefluorination of Trifluoroalkanes

To an oven-dried J. Young's NMR tube in a glove box was added chlorobenzene (0.8 mL), d-benzene (0.2 mL), bromotrimethylsilane (2.8mol, 2.8 equiv), hexafluorobenzene (70 uL) and fluoroalkane (1 mmol, 1.0 equiv). The reaction NMR tube was first subjected to screening of their initial ^{1}H and ^{19}F NMR spectra. Aluminium bromide (0.2 mmol, 0.2 equiv) was then added to the reaction tube in the glove box and the reaction was carried out by heating in a pre-heated silicon oil bath at 80 °C. The reaction was monitored *via* ^{19}F NMR on the consumption of the fluoroalkane periodically. Conversion was based on comparing the integral ratios of unconsumed fluoroalkane to hexafluorobenzene as an internal standard. The reaction was quenched with a few drops of water before washing with CH_2Cl_2 to a 5 mL volumetric flask, followed by extraction of a 1 mL aliquot for GCMS analysis. The ratio of halodefluorinated products to starting fluoroalkane were determined by GCMS. The combined washed crude mixture was then evaporated and was further purified *via* silica gel column chromatography using hexane as eluant to give the title compounds.

General Procedure C for the Chlorodefluorination of Trifluoroalkanes

To an oven-dried J. Young's NMR tube in a glove box was added d-benzene (0.2 mL), silicon tetrachloride (0.7 mmol, 0.7 equiv), hexafluorobenzene (70 uL) and fluoroalkane (1 mmol, 1.0 equiv). The reaction NMR tube was first subjected to screening of their initial ^{1}H and ^{19}F NMR spectra. Aluminium chloride (0.05 mmol, 0.05 equiv) was then added to the reaction tube in the glove box and the reaction was carried out by heating in a pre-heated silicon oil bath at 80 °C. The reaction was monitored *via* ^{19}F NMR on the consumption of the fluoroalkane periodically. Conversion was based on comparing the integral ratios of unconsumed fluoroalkane to hexafluorobenzene as an internal standard. The reaction was quenched with a few drops of water before washing with CH_2Cl_2 to a 5 mL volumetric flask, followed by extraction of a 1 mL aliquot for GCMS analysis. The ratio of halodefluorinated products to starting fluoroalkane were determined by GCMS. The combined washed crude mixture was then evaporated and was further purified *via* silica gel column chromatography using hexane as eluant to give the title compounds.

Scale-up synthesis of benzotribromide from benzotrifluoride *via* aluminum catalysis.

To an oven-dried 25 mL reaction schlenk tube fitted with a stirrer bar under argon was added trimethylsilyl bromide (2.14 g, 14.00 mmol) and benzotrifluoride (0.73 g, 5.00 mmol). The reaction tube was then transferred to a glovebox and added aluminium bromide (0.27 g, 1.00 mmol). The resulting mixture was then heated at 80 °C over 21 hours. Caution was taken to slowly release the built-up trimethylsilyl fluoride from the reaction tube, followed by quenching with a few drops of water. The crude mixture was filtered through a short plug of silica gel with further washing with CH_2Cl_2 (10 mL x 3) and evaporated to give the crude product which was further purified *via* silica gel column chromatography using hexane as eluant to afford the product as a yellow oil (1.58

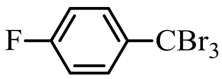
g, 4.82 mmol, 96% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.00–8.03 (m, 2H), 7.38–7.43 (m, 2H), 7.31–7.36 (m, 1H) ppm. The data are in agreement with literature values.[2]

Scale-up synthesis of benzotrichloride from benzotrifluoride *via* aluminum catalysis.

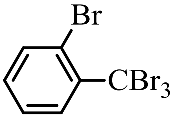
To an oven-dried 25 mL reaction schlenk tube fitted with a stirrer bar under argon was added silicon tetrachloride (0.64 g, 3.75 mmol) and benzotrifluoride (0.73 g, 5.00 mmol). The reaction tube was then transferred to a glovebox and added aluminium chloride (0.13 g, 1.00 mmol). The resulting mixture was then heated at 80 °C over 21 hours. Caution was taken to slowly release the built-up volatile fluorosilanes from the reaction tube, followed by quenching with a few drops of water. The crude mixture was filtered through a short plug of silica gel with further washing with CH_2Cl_2 (10 mL x 3) and evaporated to give the crude product which was further purified *via* silica gel column chromatography using hexane as eluant to afford the product as a colorless oil (0.92 g, 4.70 mmol, 94% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.93–7.95 (m, 2H), 7.43–7.45 (m, 3H) ppm. The data are in agreement with literature.[3]

Scale-up synthesis of 1-iodooctane from 1-fluorooctane *via* aluminum catalysis.

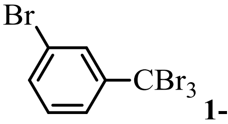
To an oven-dried 25 mL reaction schlenk tube fitted with a stirrer bar under argon was added trimethylsilyl iodide (0.90 g, 4.50 mmol) and 1-fluorooctane (0.66 g, 5.00 mmol). The reaction tube was then transferred to a glovebox and added aluminium iodide (0.2 mg, 0.50 mmol). The resulting mixture was then stirred at room temperature over 3 hours in the dark. Caution was taken to slowly release the built-up volatile fluorosilanes from the reaction tube, followed by quenching with a few drops of water. The crude mixture was filtered through a short plug of silica gel with further washing with CH_2Cl_2 (10 mL x 3) and evaporated to give the crude product without further purification as a black oil (1.09 g, 4.55 mmol, 91% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 3.19 (t, 2H, J = 7.1 Hz), 1.79–1.86 (m, 2H), 1.28–1.41 (m, 10H), 0.89 (t, 3H, J = 6.9 Hz) ppm. Data matched with those obtained from commercially available samples. CAS: 629-27-6.



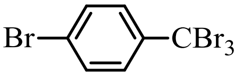
1-Fluoro-4-(tribromomethyl)benzene (14-Br); 278 mg, 80% yield, light yellow oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 7.59–7.65 (m, 2H), 6.44–6.50 (m, 2H) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 162.2 (d, J_{CF} = 251.7 Hz), 142.4 (d, J_{CF} = 3.2 Hz), 127.9 (d, 2C, J_{CF} = 8.8 Hz), 113.7 (d, 2C, J_{CF} = 22.1 Hz), 33.7 ppm; **^{19}F NMR** (C_6D_6, 400 MHz): δ -111.0 ppm. The data are in agreement with reported values.[4]



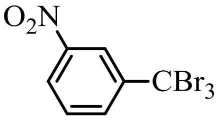
1-Bromo-2-(tribromomethyl)benzene (8-Br); 358 mg, 88% yield, light yellow oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 8.06 (dd, 1H, J = 8.2 Hz, J = 1.5 Hz), 7.31 (dd, 1H, J = 7.9 Hz, J = 1.4 Hz), 6.67 (ddd, 1H, J = 8.2 Hz, J = 7.4 Hz, J = 1.4 Hz), 6.42–6.46 (m, 1H) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 140.6, 136.0, 130.3, 128.6, 125.9, 121.9, 33.0 ppm. **HRMS** (EI, $C_7H_4Br_4$ $(M)^+$): calcd.: 403.7046; found: 403.7043. (New compound)



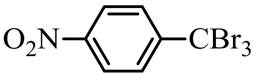
1-Bromo-3-(tribromomethyl)benzene (9-Br); 310 mg, 76% yield, light yellow oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 8.15 (t, 1H, *J* = 2.0 Hz), 7.61 (ddd, 1H, *J* = 8.1 Hz, *J* = 2.2 Hz, *J* = 0.9 Hz), 6.95 (ddd, 1H, *J* = 8.0 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz), 6.52 (t, 1H, *J* = 8.1 Hz) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 148.0, 132.1, 128.6, 128.6, 124.4, 121.1, 33.1 ppm. **HRMS** (EI, $C_7H_4Br_4$ $(M)^+$): calcd.: 403.7046; found: 403.7030. The data are in agreement with reported values.[5]



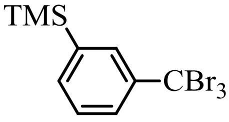
1-Bromo-4-(tribromomethyl)benzene (10-Br); 314 mg, 77% yield, light yellow oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 7.46 (d, 2H, *J* = 9.0 Hz), 6.98 (d, 2H, *J* = 9.0 Hz) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 145.2, 130.2 (2C), 127.3 (2C), 123.6, 33.9 ppm. **HRMS** (EI, $C_7H_4Br_4$ $(M)^+$): calcd.: 403.7046; found: 403.7032. The data are in agreement with reported values.[6]



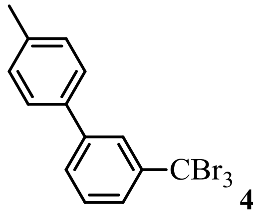
1-Nitro-3-(tribromomethyl)benzene (11-Br); 194 mg, 52% yield, light yellow oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 8.67 (t, 1H, *J* = 2.1 Hz), 7.75 (ddd, 1H, *J* = 8.3 Hz, *J* = 2.2 Hz, *J* = 0.7 Hz), 7.52 (ddd, 1H, *J* = 8.2 Hz, *J* = 2.0 Hz, *J* = 0.7 Hz), 6.61 (t, 1H, *J* = 8.1 Hz) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 147.2, 146.5, 131.0, 128.2, 123.5, 120.4, 32.0 ppm. The data are in agreement with reported values.[5]



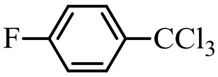
1-Nitro-4-(tribromomethyl)benzene (12-Br); 225 mg, 60% yield, dark brown oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.25 (d, 1H, *J* = 9.2 Hz), 8.19 (d, 1H, *J* = 9.2 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.0, 148.2, 127.7 (2C), 123.2 (2C), 32.6 ppm. The data are in agreement with reported values.[7]



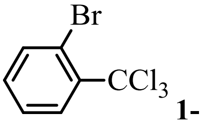
Trimethyl(3-(tribromomethyl)phenyl)silane (13-Br); 340 mg, 85% yield, colorless oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 8.27–8.28 (m, 1H), 7.92 (ddd, 1H, *J* = 8.1 Hz, *J* = 2.5 Hz, *J* = 1.0 Hz), 7.19 (td, 1H, *J* = 7.3 Hz, *J* = 1.0 Hz), 7.00–7.04 (m, 1H) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 145.8, 140.0, 134.2, 130.0, 126.7, 126.4, 36.7, -2.2 ppm. **HRMS** (EI, $C_9H_{10}Br_3Si$ $(M\text{-}CH_3)^+$): calcd.: 382.8101; found: 382.8109. (New compound)



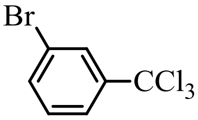
4'-Methyl-3-(tribromomethyl)-1,1'-biphenyl (15-Br); 364mg, 87% yield, white solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.26 (t, 1H, *J* = 1.9 Hz), 8.01 (ddd, 1H, *J* = 8.0 Hz, *J* = 2.3 Hz, *J* = 0.9 Hz), 7.55–7.58 (m, 3H), 7.47 (t, 1H, *J* = 7.8Hz), 7.33 (d, 2H, *J* = 7.8Hz), 2.46 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.4, 141.2, 137.8, 137.1, 129.7 (2C), 128.6, 128.4, 127.1 (2C), 125.2, 125.0, 36.3, 21.1 ppm. (New compound)



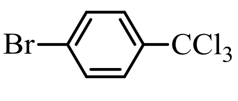
1-Fluoro-4-(trichloromethyl)benzene (14-Cl); 167 mg, 78% yield, colorless oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 7.49 (dd, 2H, *J* = 9.1 Hz, *J* = 4.9 Hz), 6.52 (dd, 2H, *J* = 9.1 Hz, *J* = 8.2 Hz) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 162.6 (d, J_{CF} = 251.3 Hz), 139.5 (d, J_{CF} = 3.5 Hz), 127.1 (2C), 114.2 (d, 2C, J_{CF} = 22.8 Hz), 96.2 ppm; **^{19}F NMR** (C_6D_6, 400 MHz): δ -110.5 ppm. **HRMS** (EI, $C_7H_4Cl_3F$ $(M)^+$): calcd.: 211.9362; found: 211.9370. The data are in agreement with reported values.[8]



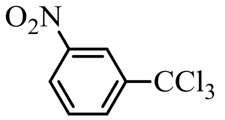
1-Bromo-2-(trichloromethyl)benzene (8-Cl); 215 mg, 78% yield, colorless oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 7.88 (dd, 1H, *J* = 1.6 Hz, *J* = 8.1 Hz), 7.34 (dd, 1H, *J* = 1.4 Hz, *J* = 7.9 Hz), 6.70 (ddd, 1H, *J* = 1.4 Hz, *J* = 7.5 Hz, *J* = 8.1 Hz), 6.52–6.56 (m, 1H) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 139.5, 135.7, 130.5, 126.9, 126.0, 121.0, 96.5 ppm. **HRMS** (EI, $C_7H_4BrCl_3$ $(M)^+$): calcd.: 271.8561; found: 271.8562.The data are in agreement with reported values.[9]



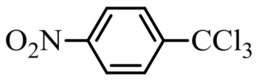
1-Bromo-3-(trichloromethyl)benzene (9-Cl); 198 mg, 72% yield, colorless oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 8.03 (t, 1H, *J* = 2.0 Hz), 7.47 (ddd, 1H, *J* = 8.1 Hz, *J* = 2.1 Hz, *J* = 0.9 Hz), 7.03 (ddd, 1H, *J* = 8.0 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz), 6.54 (t, 1H, *J* = 8.0 Hz) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 145.2, 132.4, 129.0, 127.7, 123.3, 121.6, 95.5 ppm. **HRMS** (EI, $C_7H_4BrCl_3$ $(M)^+$): calcd.: 271.8561; found: 271.8559. (New compound)



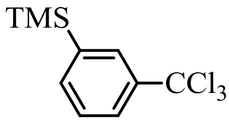
1-Bromo-4-(trichloromethyl)benzene (10-Cl); 212 mg, 77% yield, colorless oil; **^{1}H NMR** (C_6D_6, 400 MHz): δ 7.33 (d, 2H, *J* = 8.9 Hz), 7.02 (d, 2H, *J* = 9.0 Hz) ppm; **^{13}C NMR** (C_6D_6, 100 MHz): δ 142.4, 130.6 (2C), 126.3 (2C), 123.9, 96.2 ppm. **HRMS** (EI, $C_7H_4BrCl_3$ $(M)^+$): calcd.: 271.8561; found: 271.8559. The data are in agreement with reported values.[10]



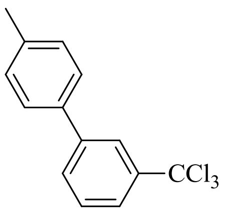
1-Nitro-3-(trichloromethyl)benzene (11-Cl); 140 mg, 58% yield, light brown oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.79 (t, 1H, J = 2.1 Hz), 8.26–8.31 (m, 2H), 7.67 (t, 1H, J = 8.1 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.9, 145.9, 131.4, 129.8, 125.1, 120.8, 95.4 ppm. **HRMS** (EI, $C_7H_4O_2NCl_3$ $(M)^+$): calcd.: 238.9307; found: 283.9298. The data are in agreement with reported values.[11]



1-Nitro-4-(trichloromethyl)benzene (12-Cl); 130 mg, 54% yield, light yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.30 (d, 2H, J = 9.2 Hz), 8.13 (d, 2H, J = 9.2 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.5, 147.6, 125.9 (2C), 122.7 (2C), 94.6 ppm. **HRMS** (EI, $C_7H_4O_2NCl_3$ $(M)^+$): calcd.: 238.9307; found: 238.9305.The data are in agreement with reported values.[9]



Trimethyl(3-(trichloromethyl)phenyl)silane (13-Cl); 211 mg, 79% yield, colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.11 (d, 1H, J = 2.3 Hz), 7.95 (ddd, 1H, J = 8.0 Hz, J = 2.3 Hz, J = 1.0 Hz), 7.61 (td, 1H, J = 7.3 Hz, J = 0.9 Hz), 7.45 (t, 1H, J = 7.7 Hz), 0.36 (s, 9H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.5, 141.4, 135.3, 129.8, 127.7, 126.0, 98.2, -1.2 ppm. **HRMS** (EI, $C_9H_{10}Cl_3Si$ $(M\text{-}CH_3)^+$): calcd.: 250.9617; found: 250.9613. (New compound)



4'-Methyl-3-(trichloromethyl)-1,1'-biphenyl (15-Cl); 233mg, 82% yield, light yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.22 (t, 1H, J = 1.9 Hz), 7.96 (ddd, 1H, J = 8.0 Hz, J = 2.2 Hz, J = 0.9Hz), 7.67 (ddd, 1H, J = 7.7 Hz, J = 1.6 Hz, J = 1.1 Hz), 7.58 (d, 2H, J = 8.0 Hz), 7.53 (t, 1H, J = 7.8 Hz), 7.34 (d, 2H, J = 8.0 Hz), 2.47 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.7, 141.5, 137.8, 137.1, 129.7 (2C), 128.8, 128.7, 127.1 (2C), 124.1, 124.0, 97.7, 21.1 ppm. **HRMS** (EI, $C_{14}H_{11}Cl_3$ $(M)^+$): calcd.: 283.9926; found: 283.9928. (New compound)

Compounds **2-Cl** (CAS: 111-85-3), **2-Br** (CAS: 111-83-1), **4-Cl** (CAS: 622-24-2), **4-Br** (CAS: 103-63-9), **5-Cl**,[12] **5-Br**,[5] **6-Cl**,[13] **6-Br**,[14] **7-Cl**,[15] and **8-Br**[16] were not isolated, and were identified by a combination of GC-MS and ^{1}H NMR, where data were compared to either commercially obtained authentic samples, or literature values.

Figure S1. Sample ^{1}H NMR and GC-MS spectra for quantifying yield of **4-Cl**

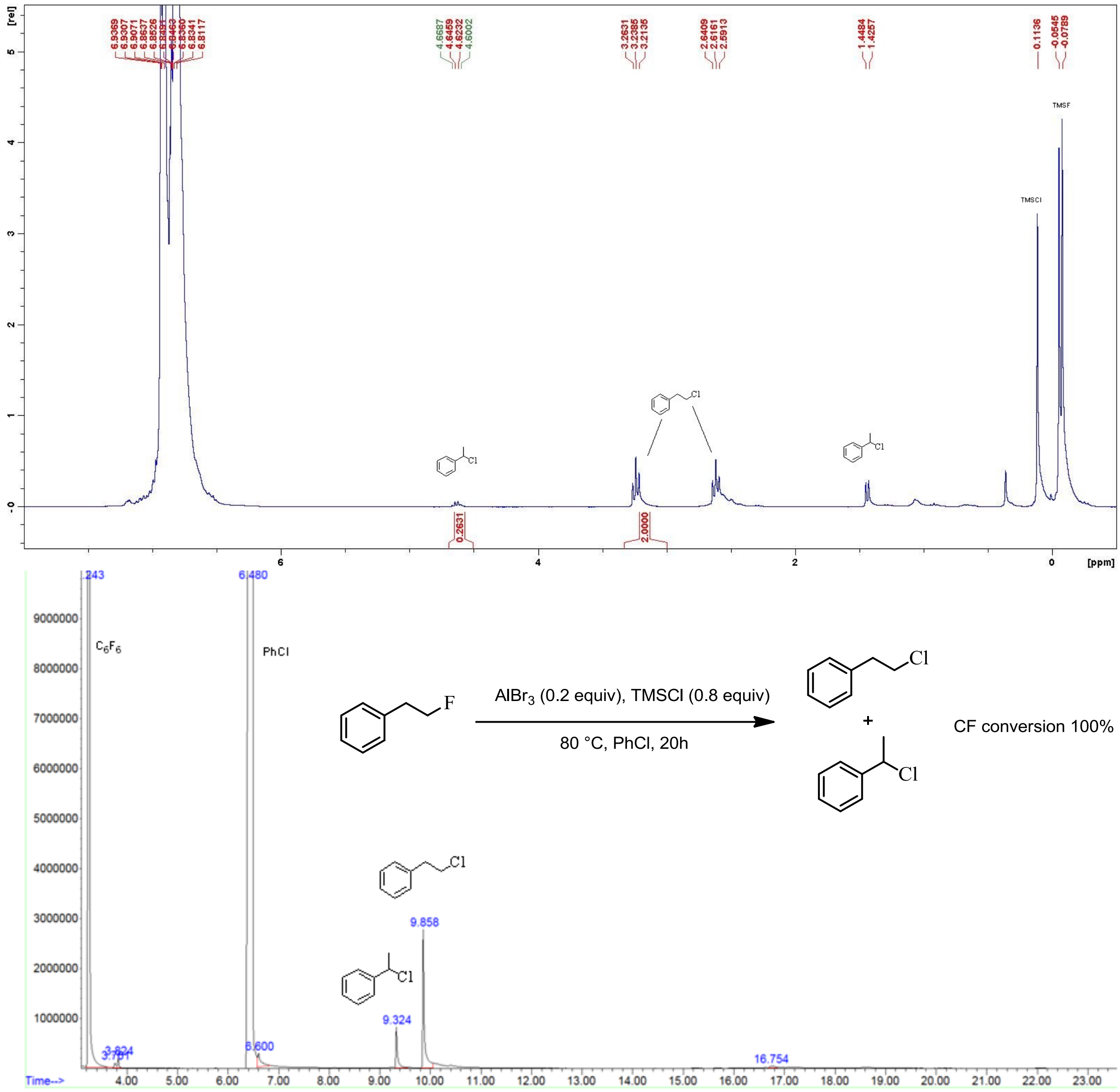
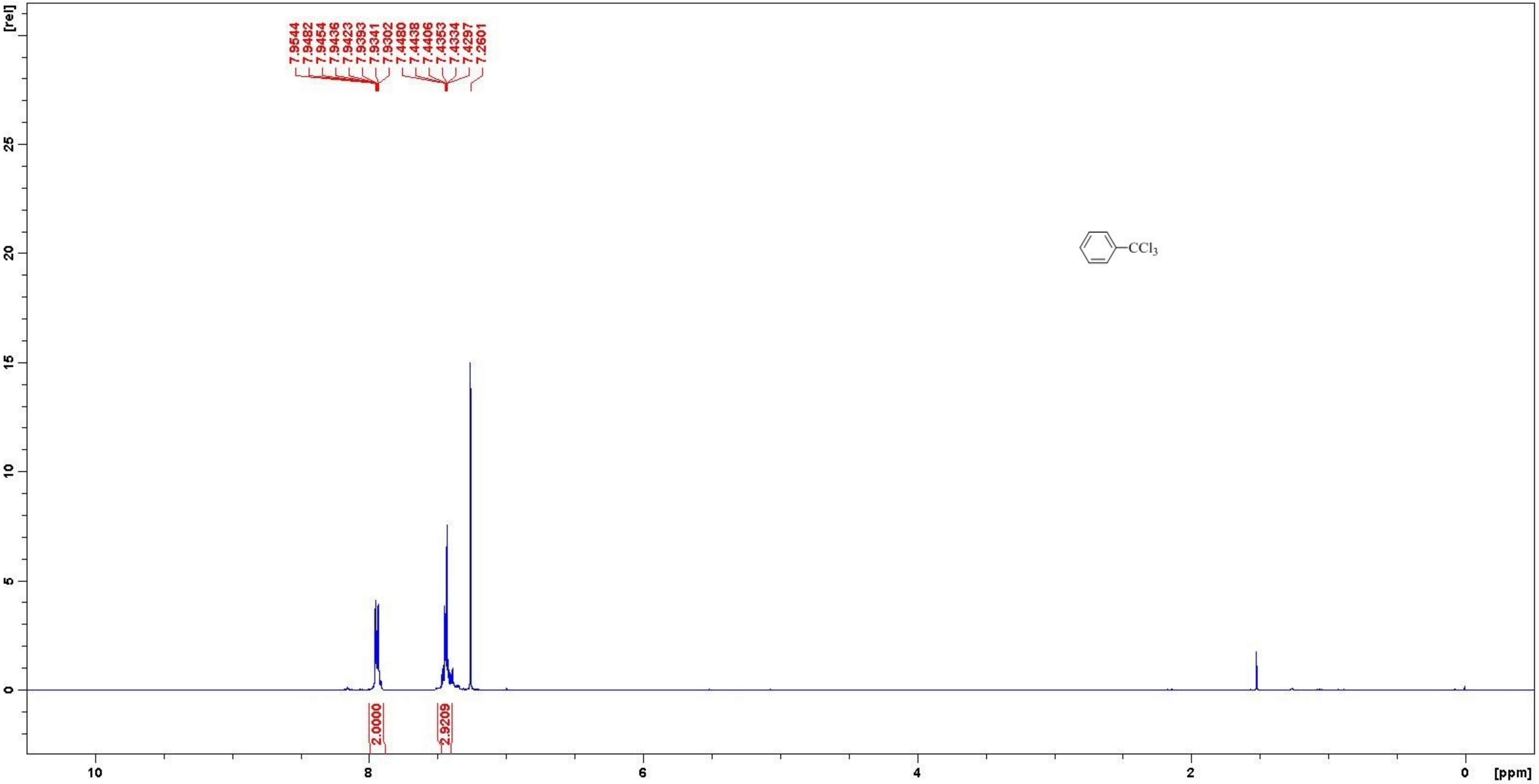


Figure S2. ^{1}H NMR spectrum of **1-Cl** in $CDCl_3$.



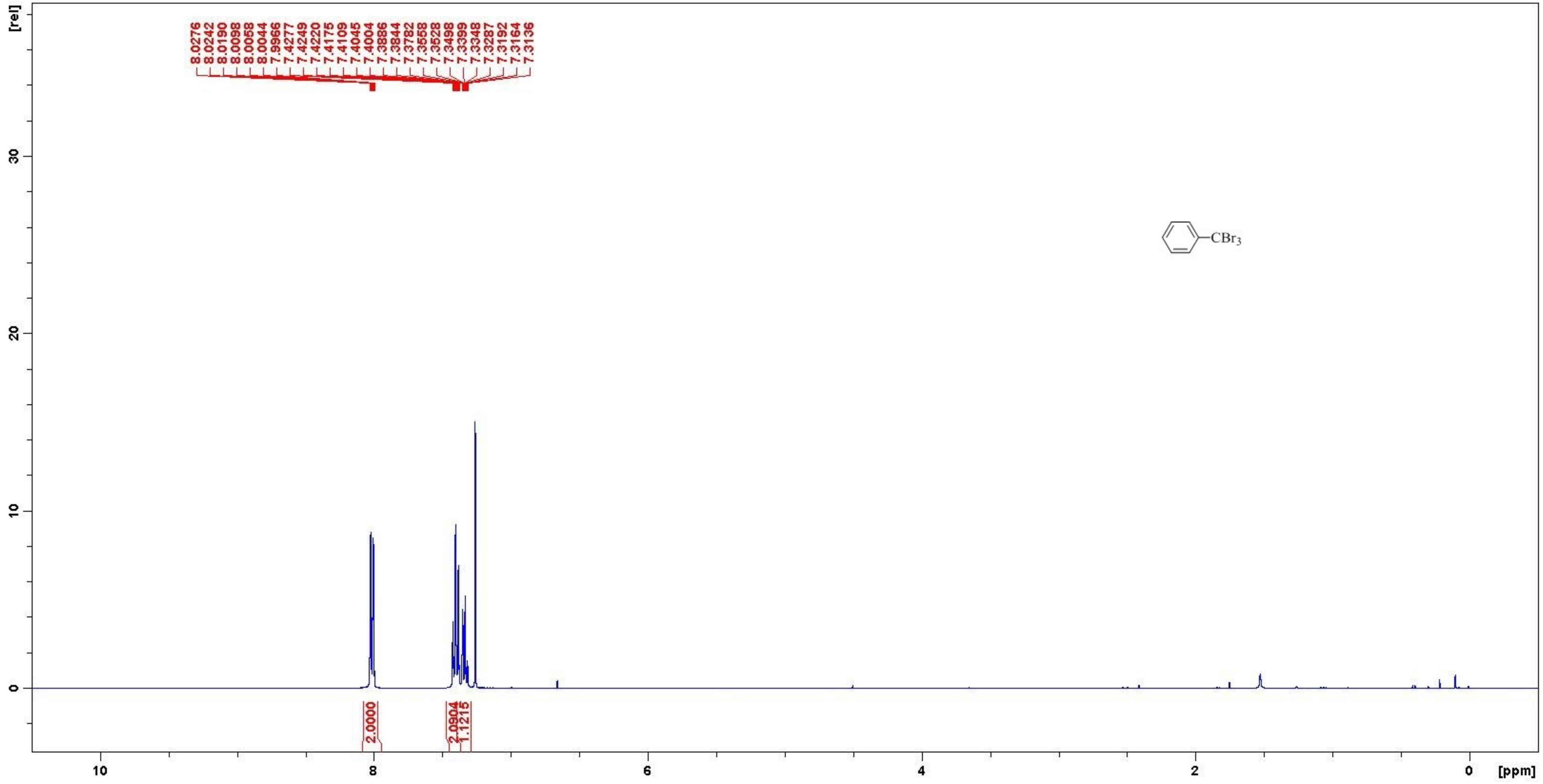


Figure S3. ^{1}H NMR spectrum of **1-Br** in $CDCl_3$.

Figure S4. ^{1}H NMR spectrum of **2-I** in $CDCl_3$.

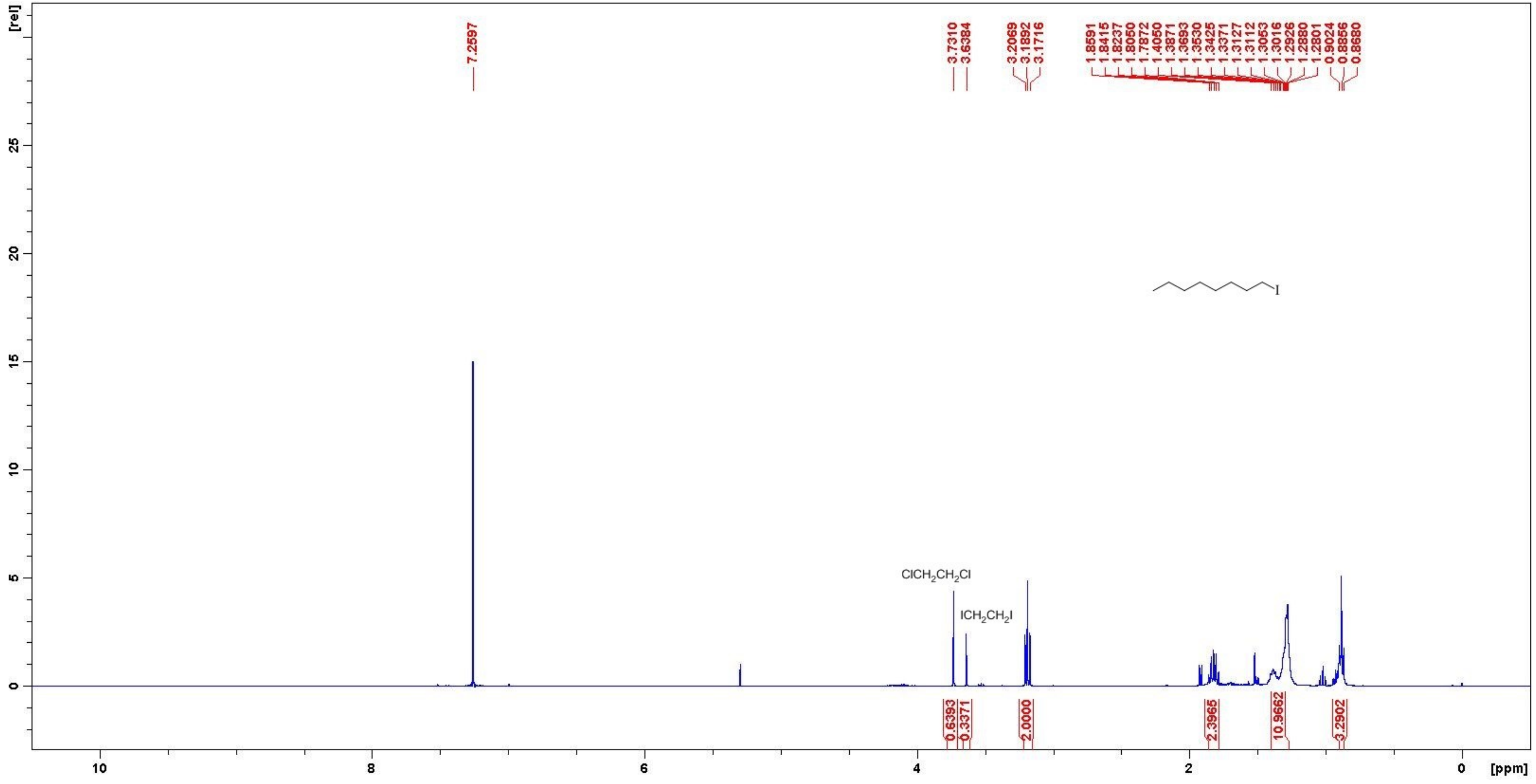


Figure S5. ^{1}H NMR spectrum of **14-Br** in C_6D_6.

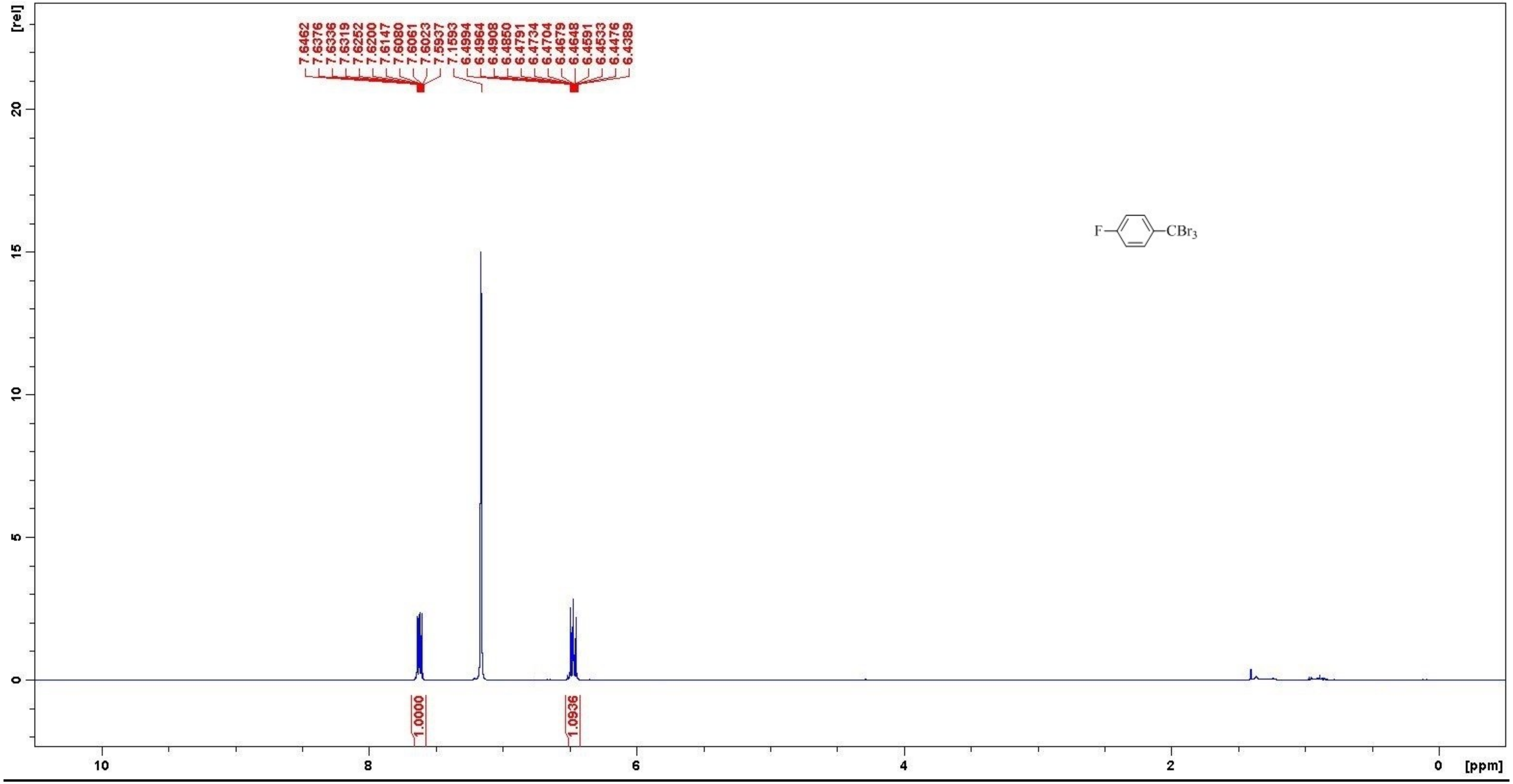


Figure S6. ^{13}C NMR spectrum of **14-Br** in C_6D_6.

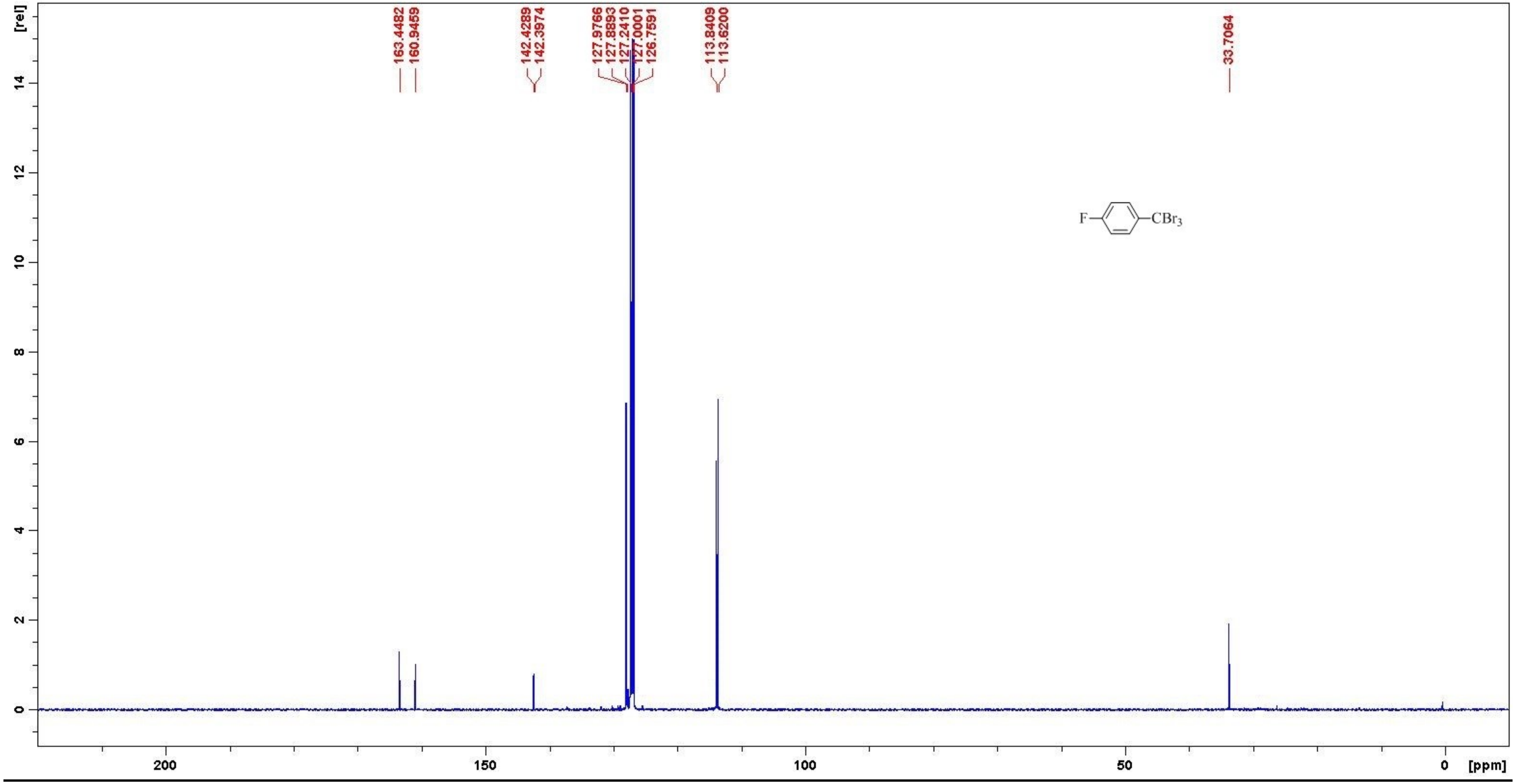


Figure S7. ^{19}F NMR spectrum of **14-Br** in C_6D_6.

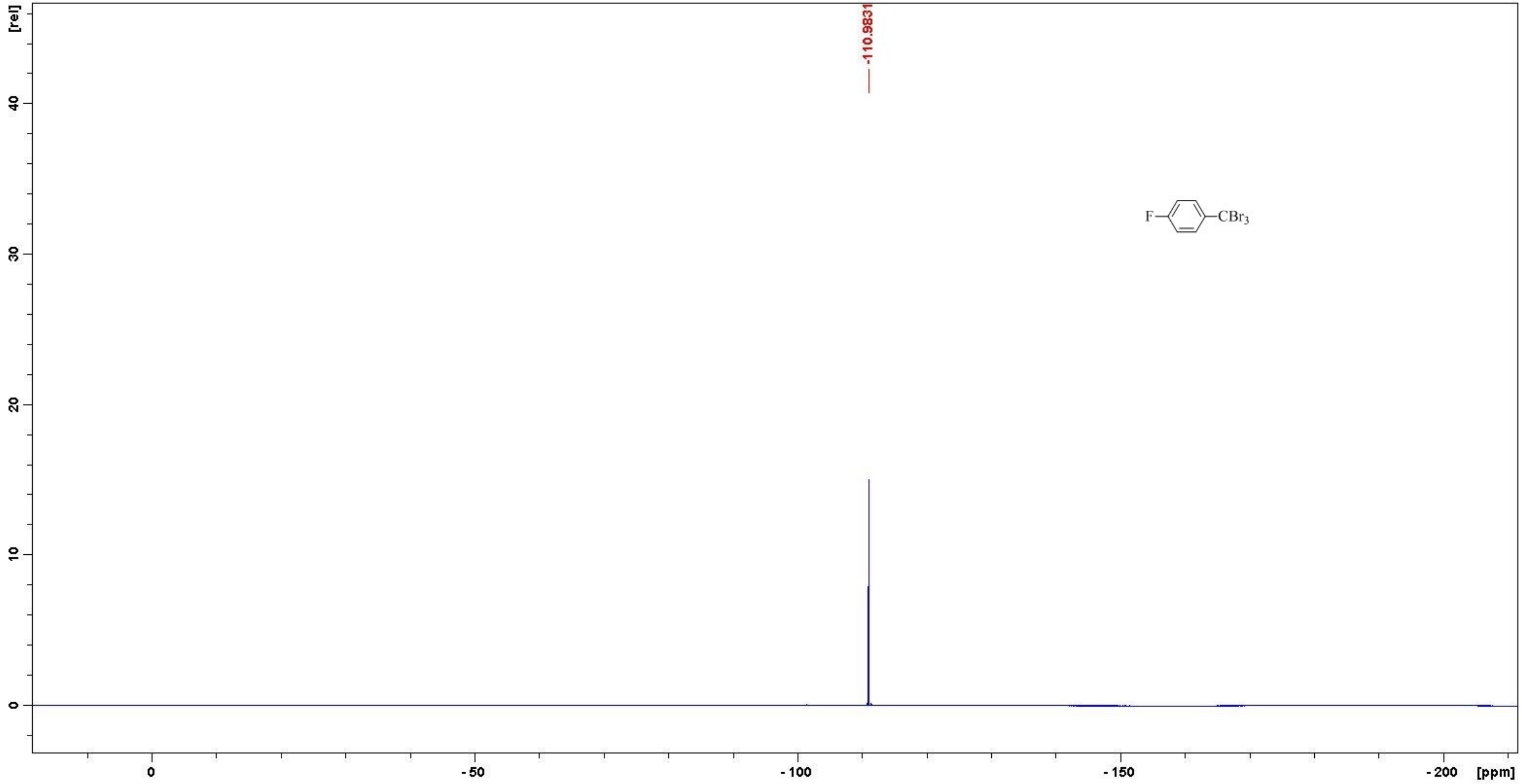


Figure S8. ^{1}H NMR spectrum of **8-Br** in C_6D_6.

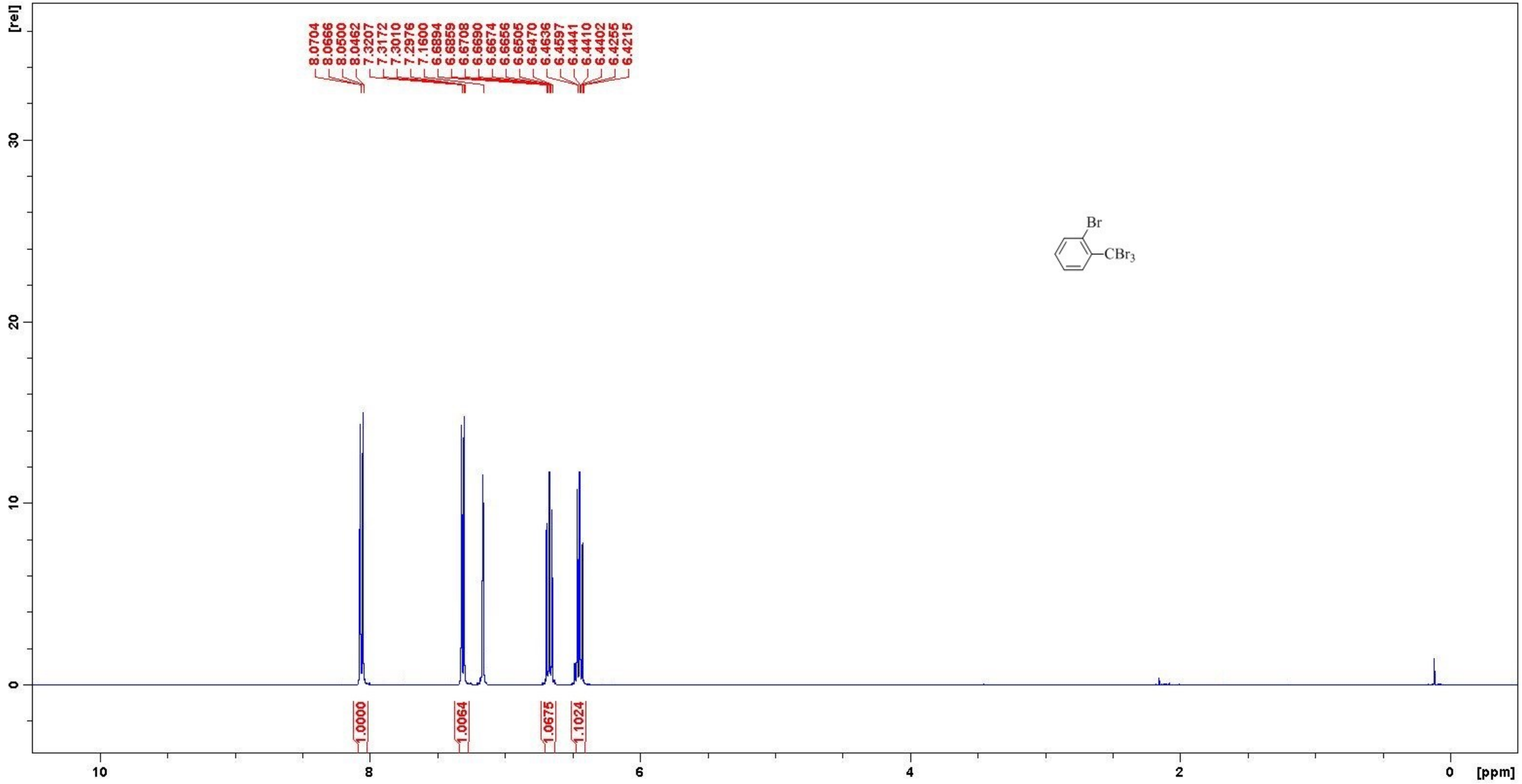


Figure S9. ^{13}C NMR spectrum of **8-Br** in C_6D_6.

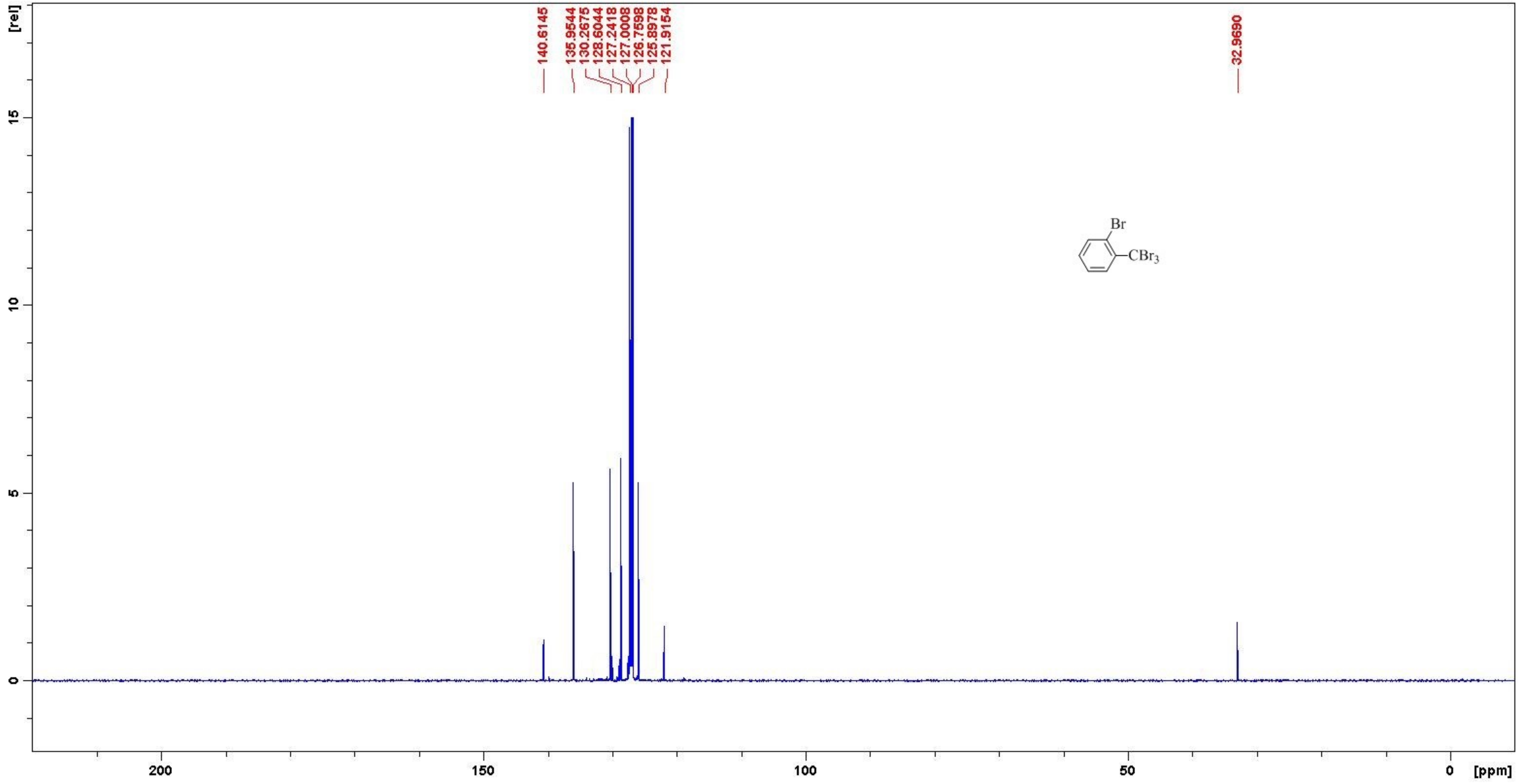


Figure S10. ^{1}H NMR spectrum of **9-Br** in C_6D_6.

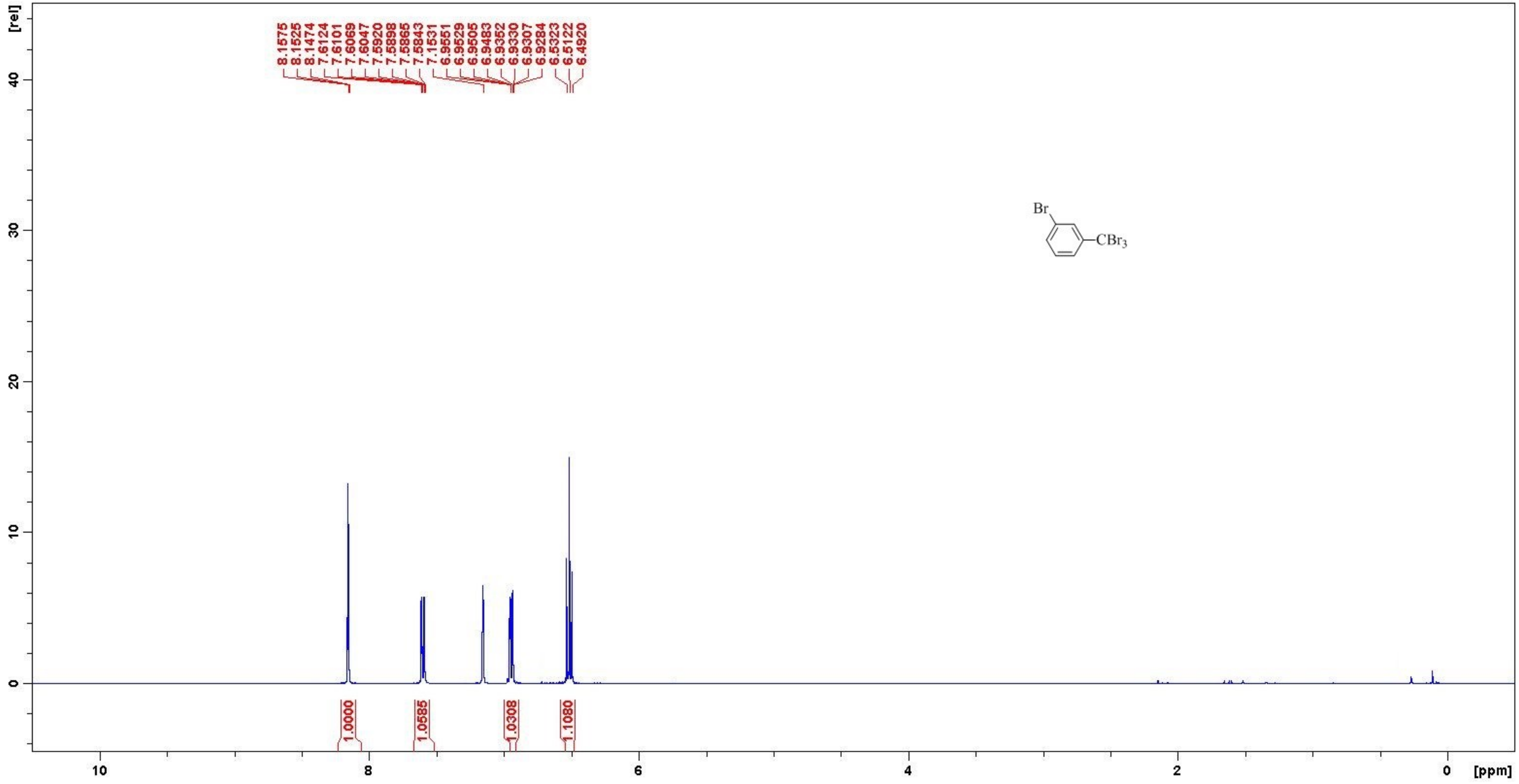


Figure S11. ^{13}C NMR spectrum of **9-Br** in C_6D_6.

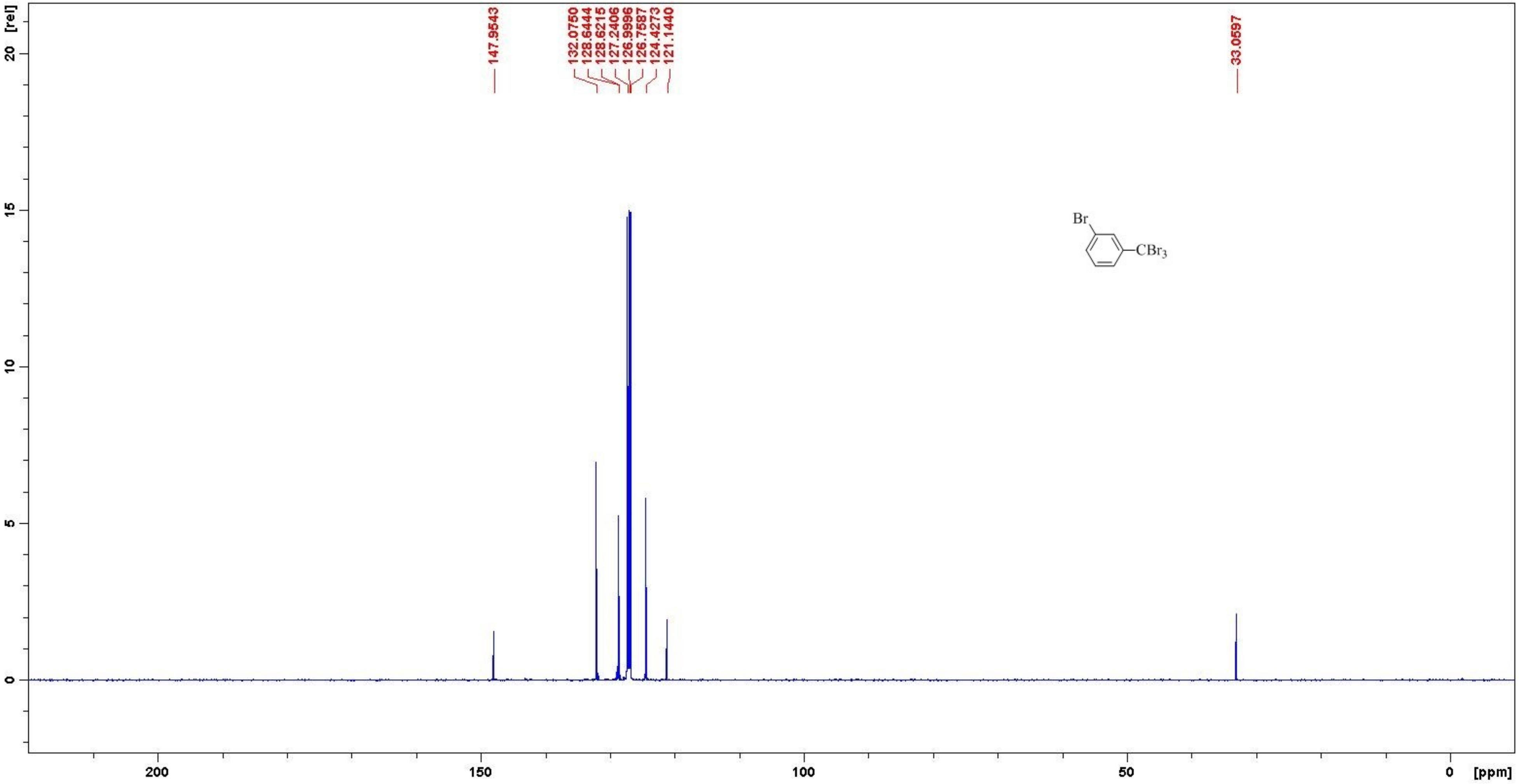


Figure S12. ^{1}H NMR spectrum of **10-Br** in C_6D_6.

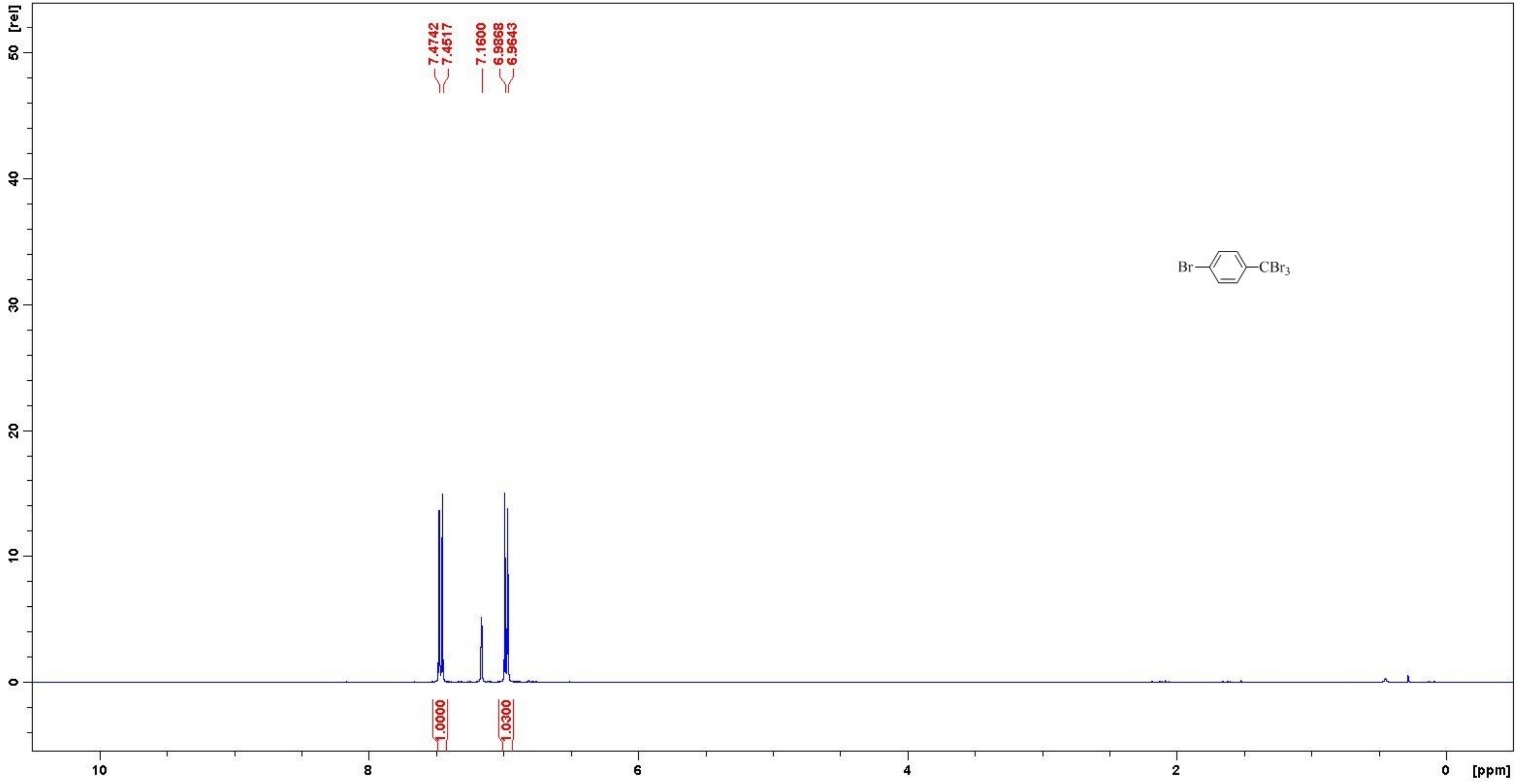


Figure S13. ^{13}C NMR spectrum of **10-Br** in C_6D_6.

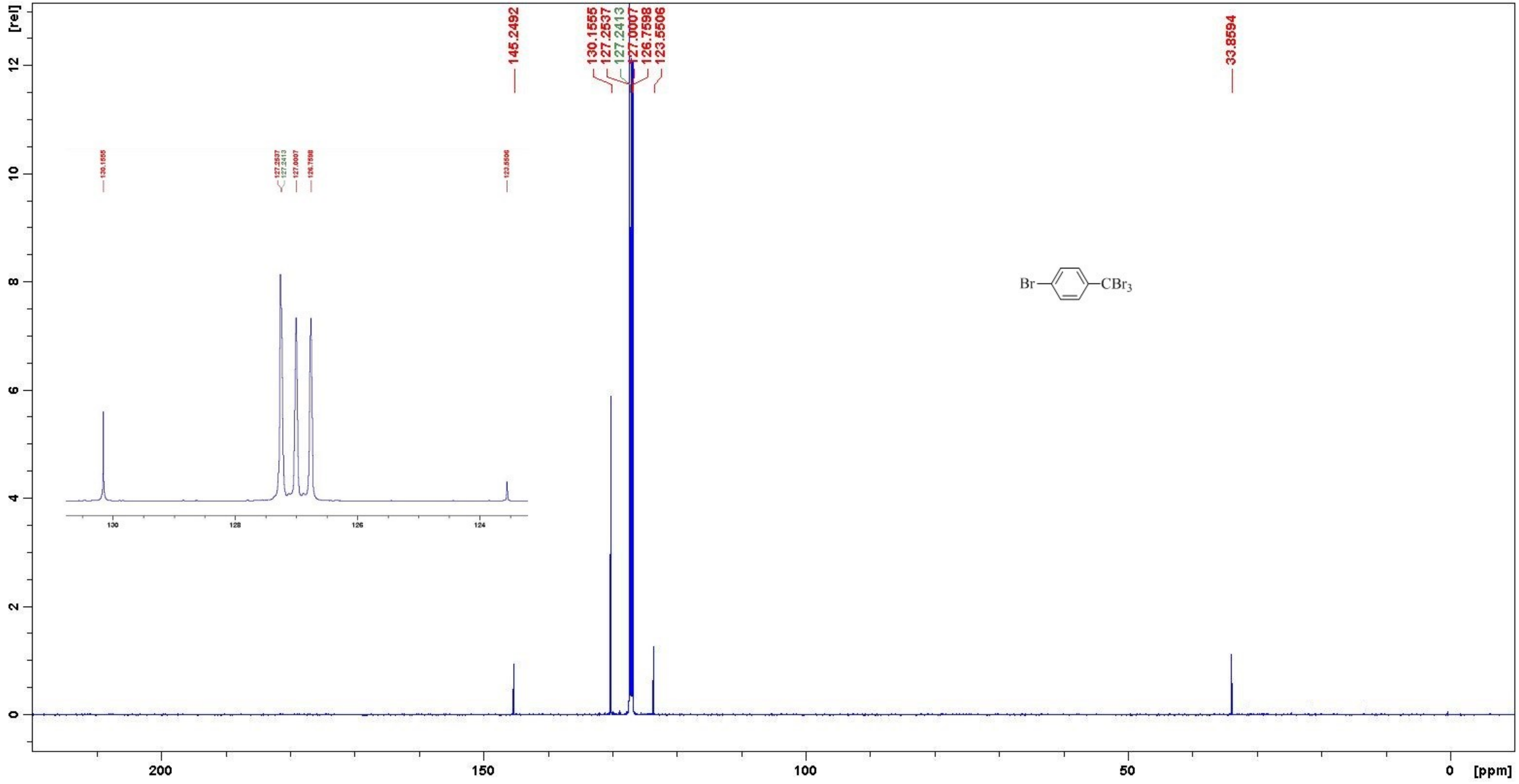


Figure S14. ^{1}H NMR spectrum of **11-Br** in C_6D_6.

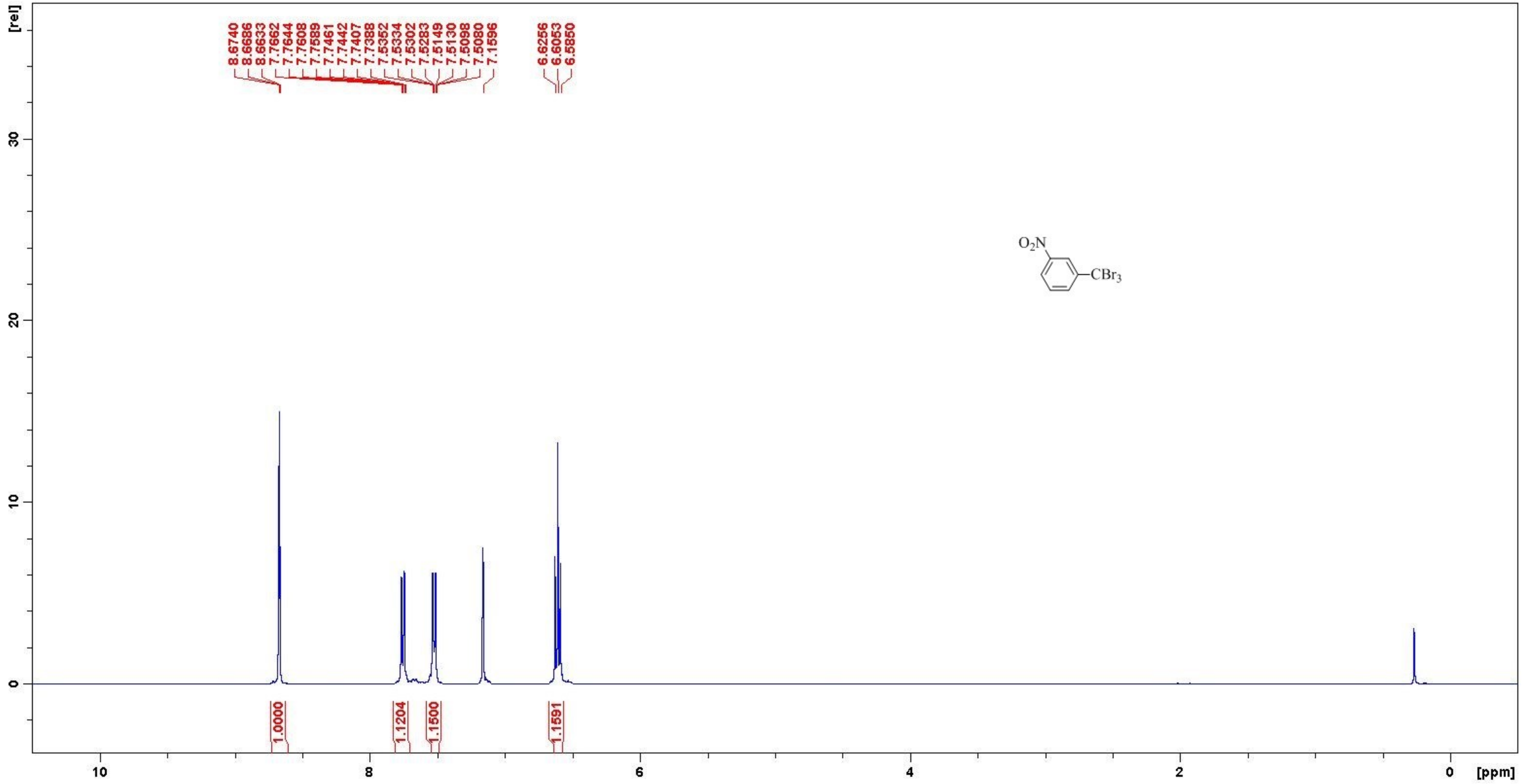


Figure S15. ^{13}C NMR spectrum of **11-Br** in C_6D_6.

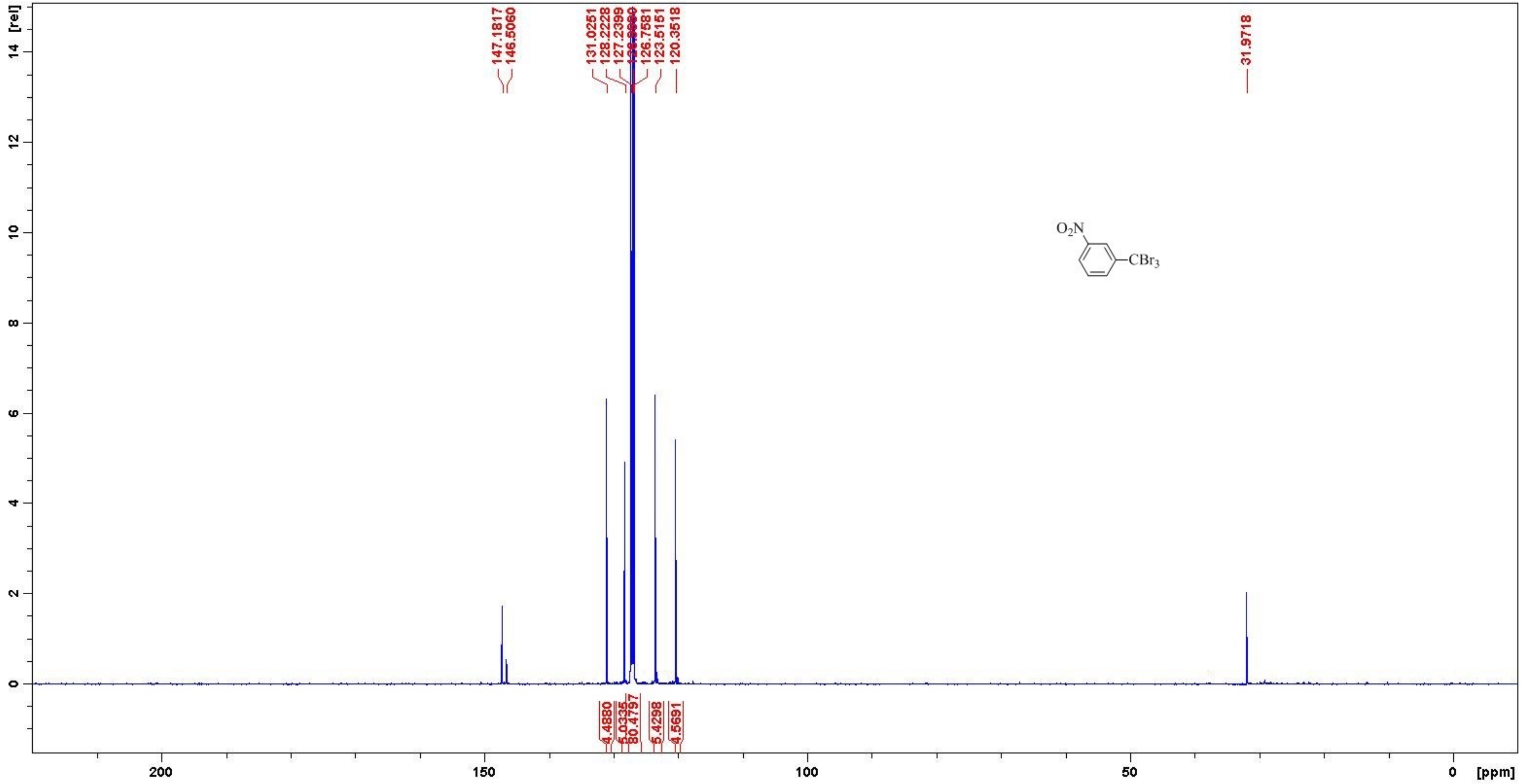


Figure S16. ^{1}H NMR spectrum of **12-Br** in CDCl$_3$.

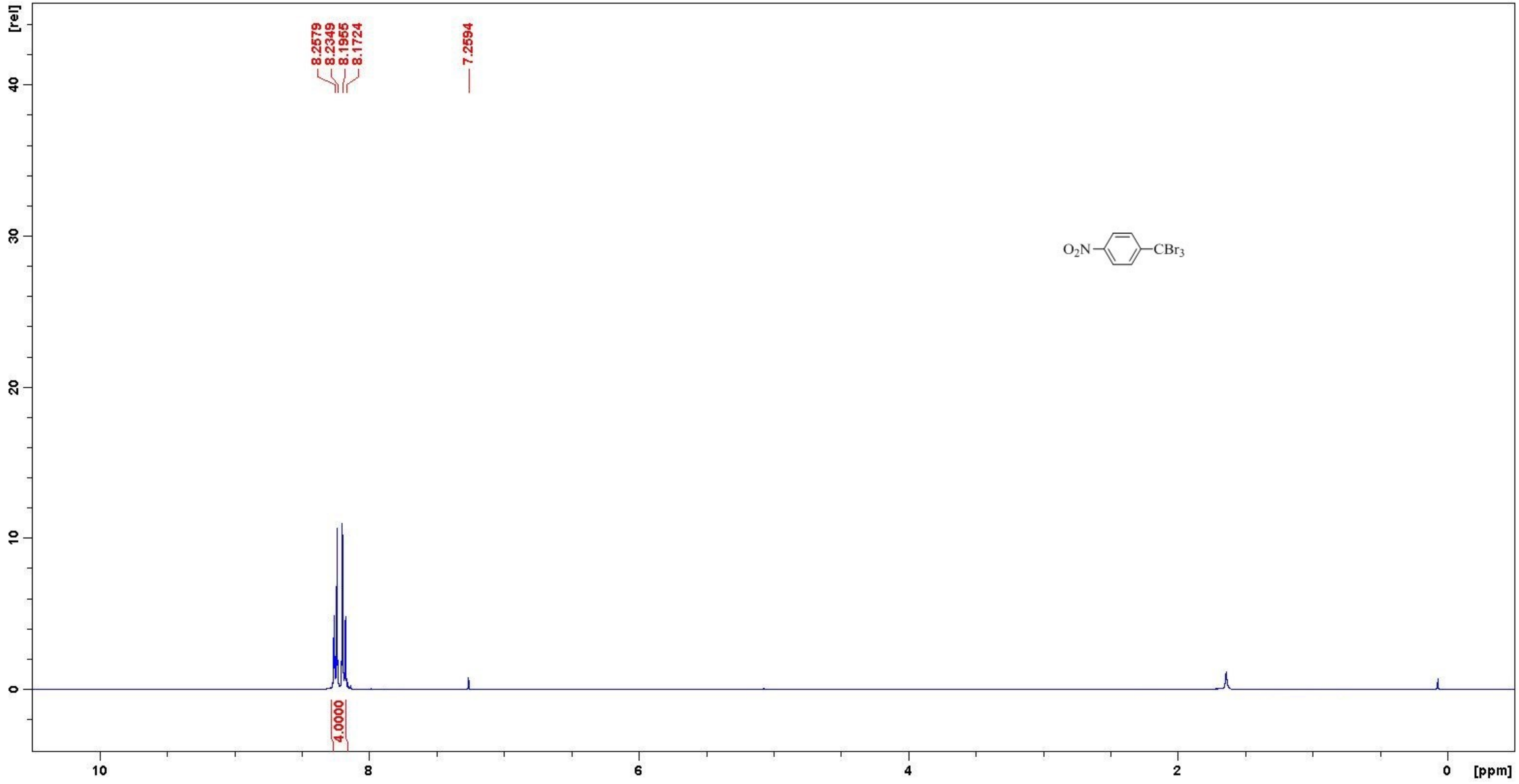


Figure S17. ^{13}C NMR spectrum of **12-Br** in $CDCl_3$.

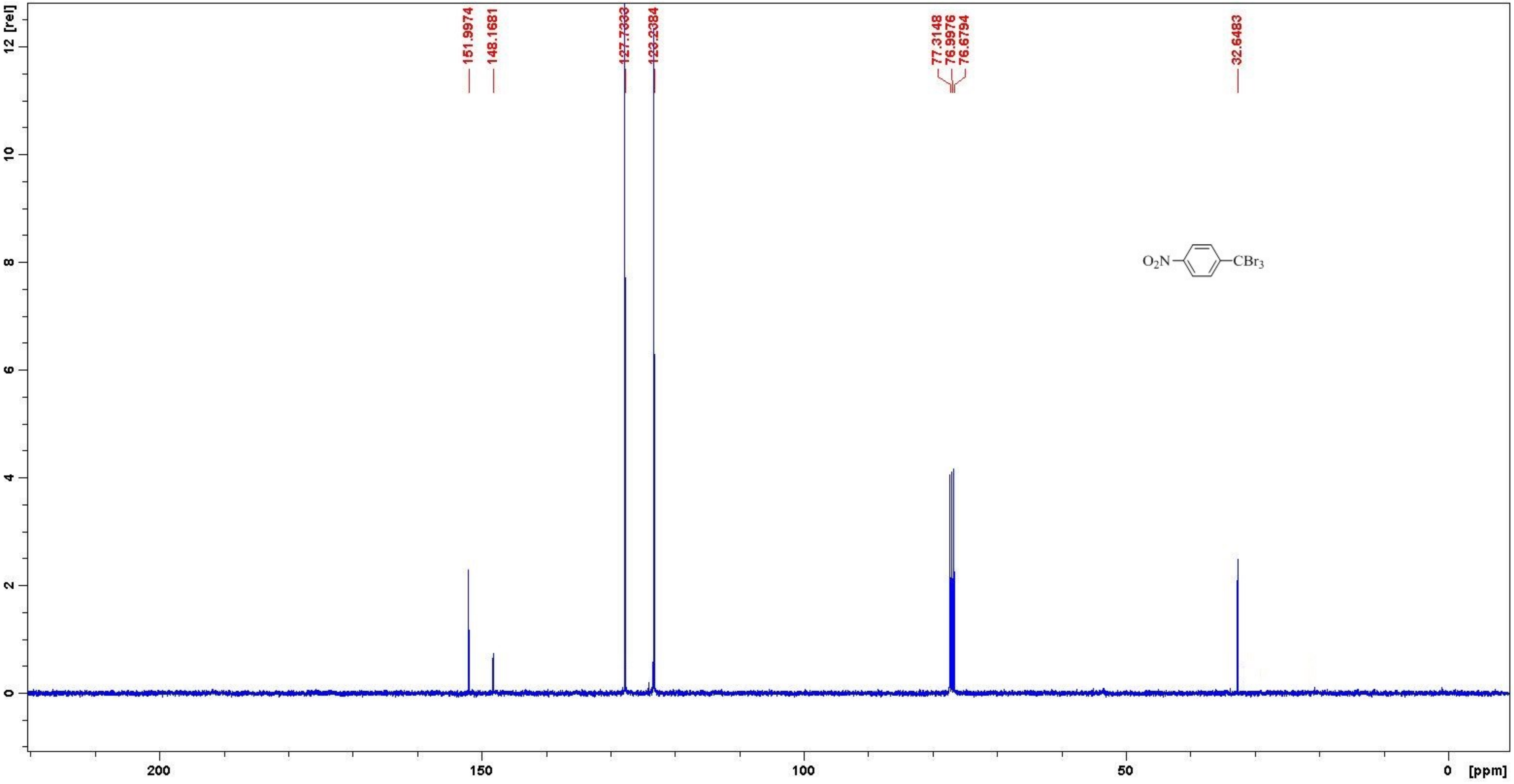


Figure S18. ^{1}H NMR spectrum of **13-Br** in C_6D_6.

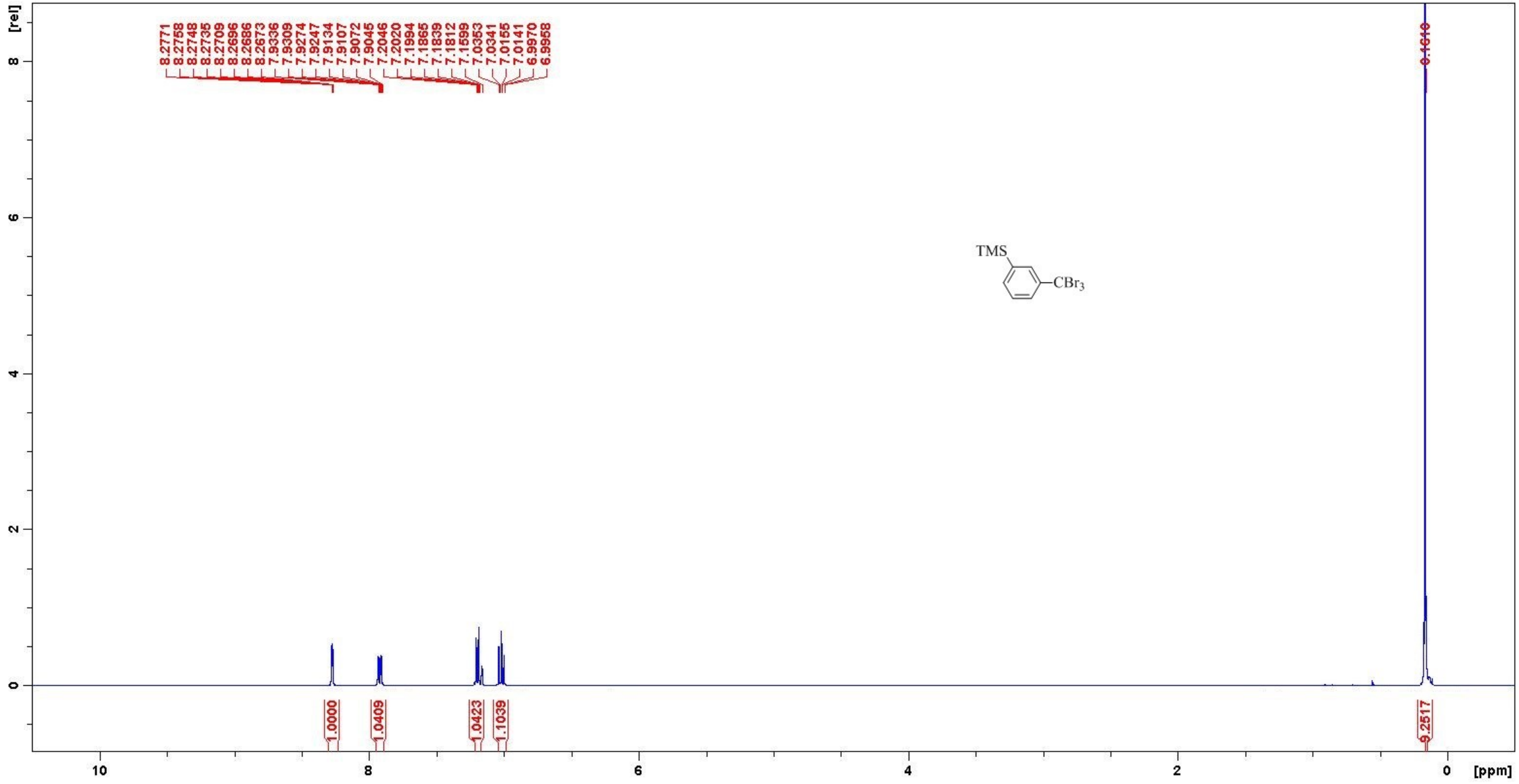


Figure S19. ^{13}C NMR spectrum of **13-Br** in C_6D_6.

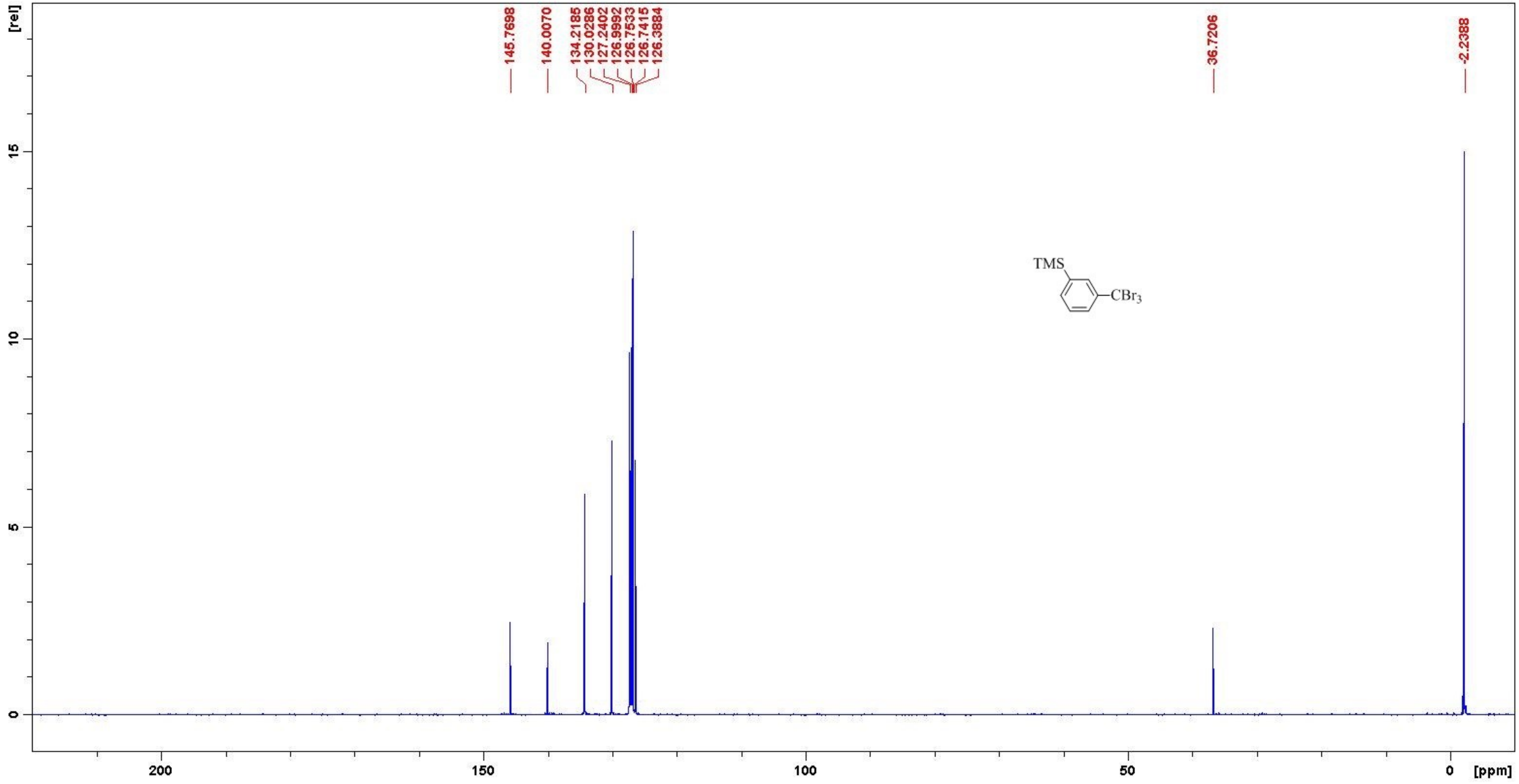


Figure S20. ^{1}H NMR spectrum of **15-Br** in $CDCl_3$.

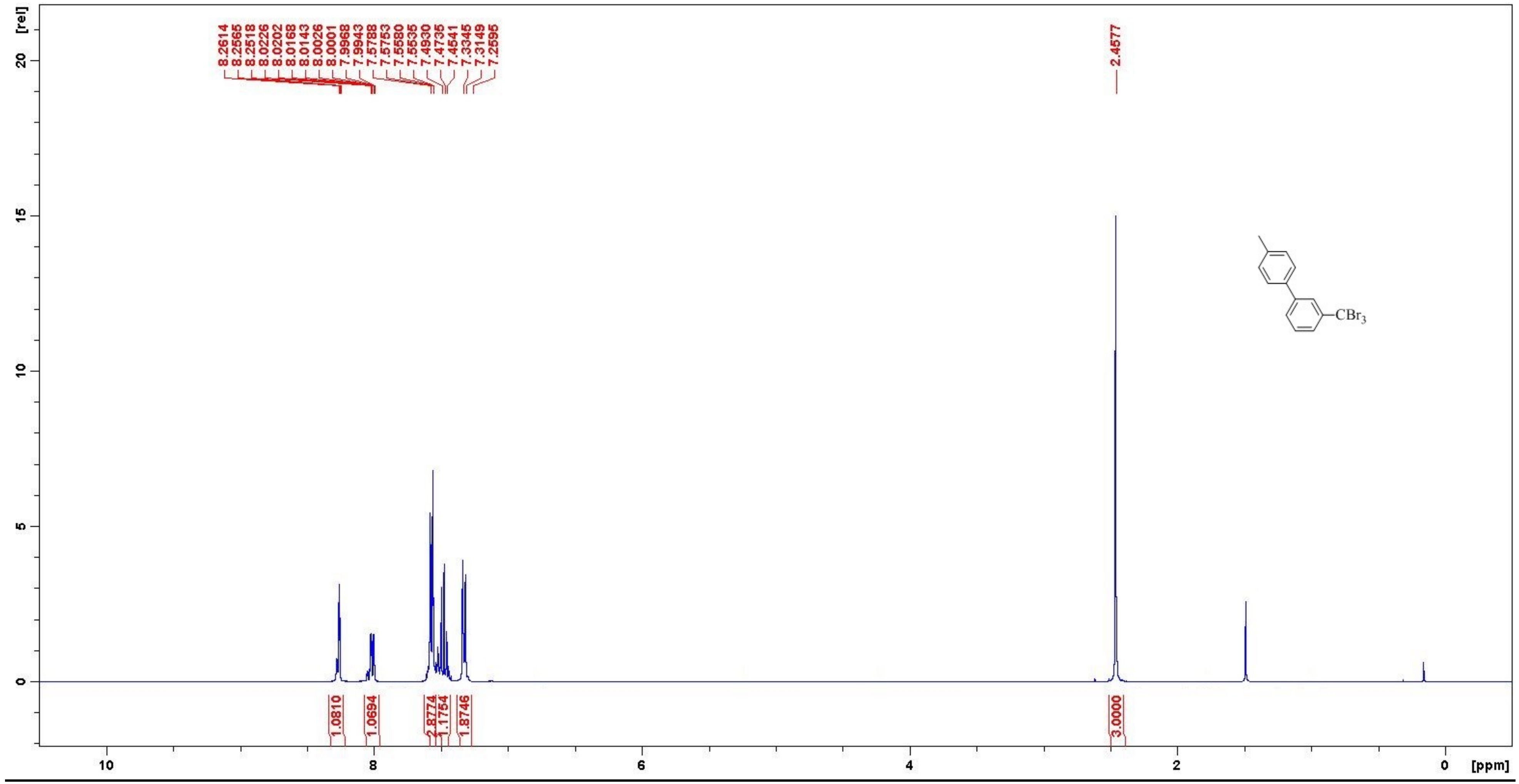


Figure S21. ^{13}C NMR spectrum of **15-Br** in $CDCl_3$.

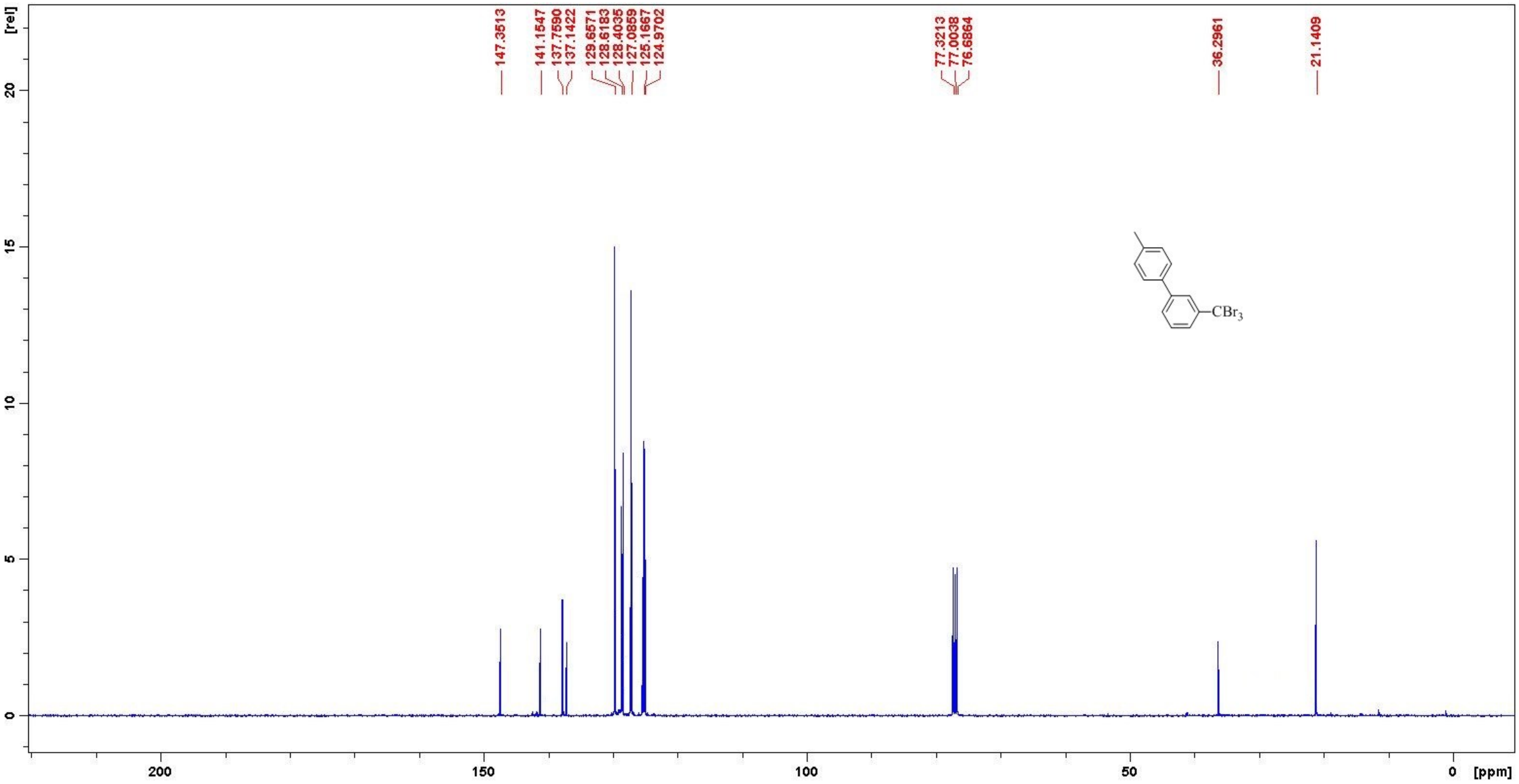


Figure S22. ^{1}H NMR spectrum of **14-Cl** in C_6D_6.

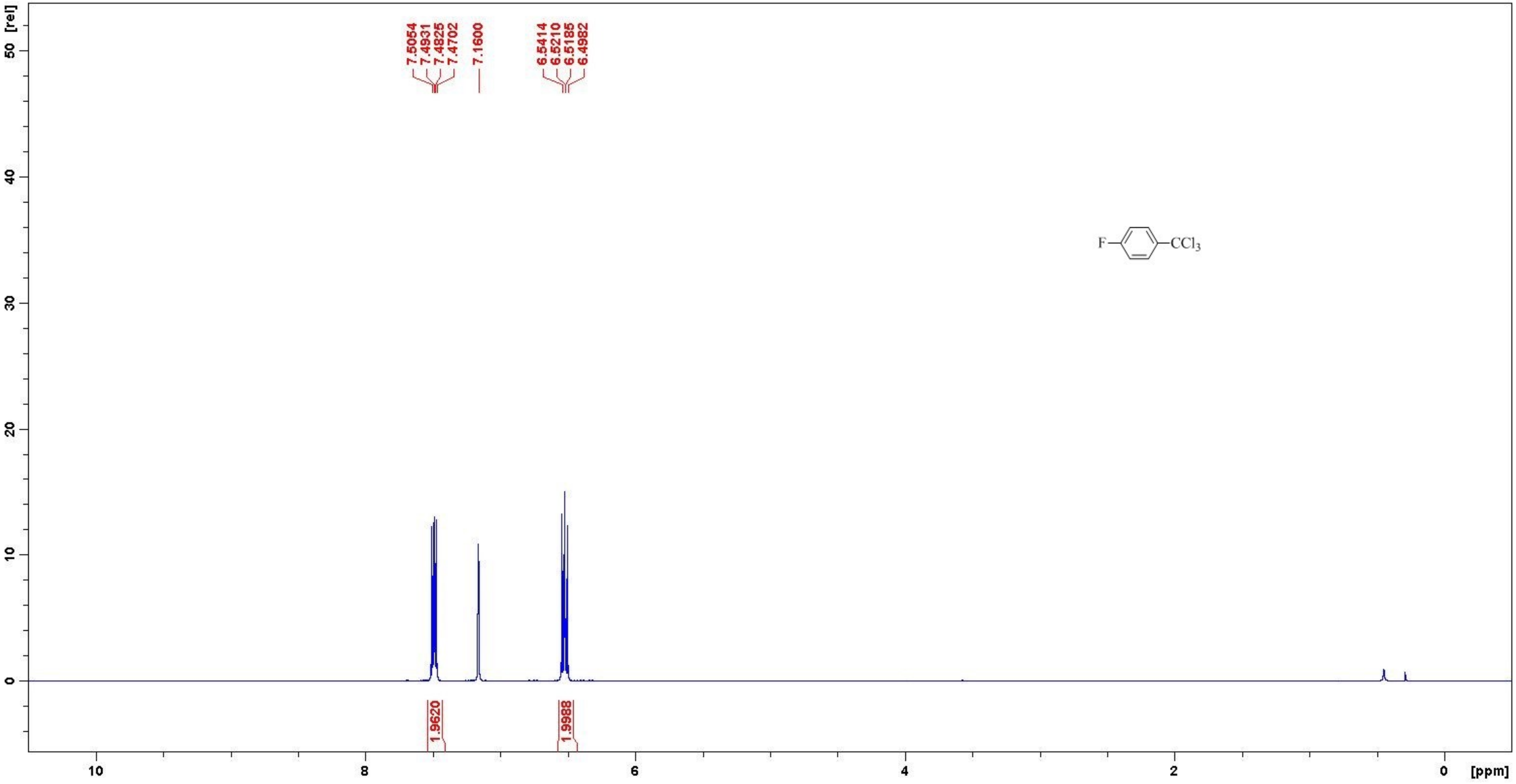


Figure S23. ^{13}C NMR spectrum of **14-Cl** in C_6D_6.

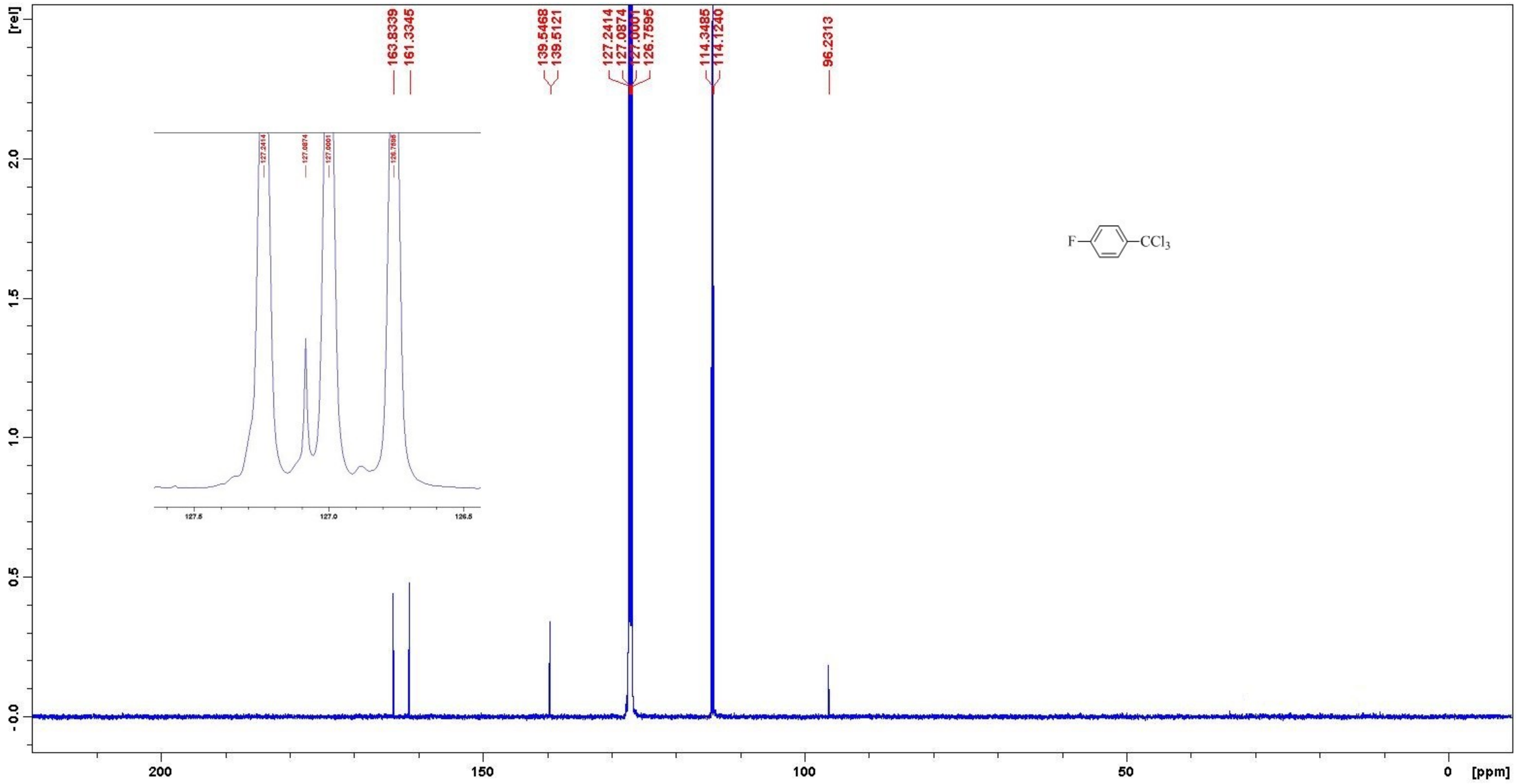


Figure S24. ^{19}F NMR spectrum of **14-Cl** in C_6D_6.

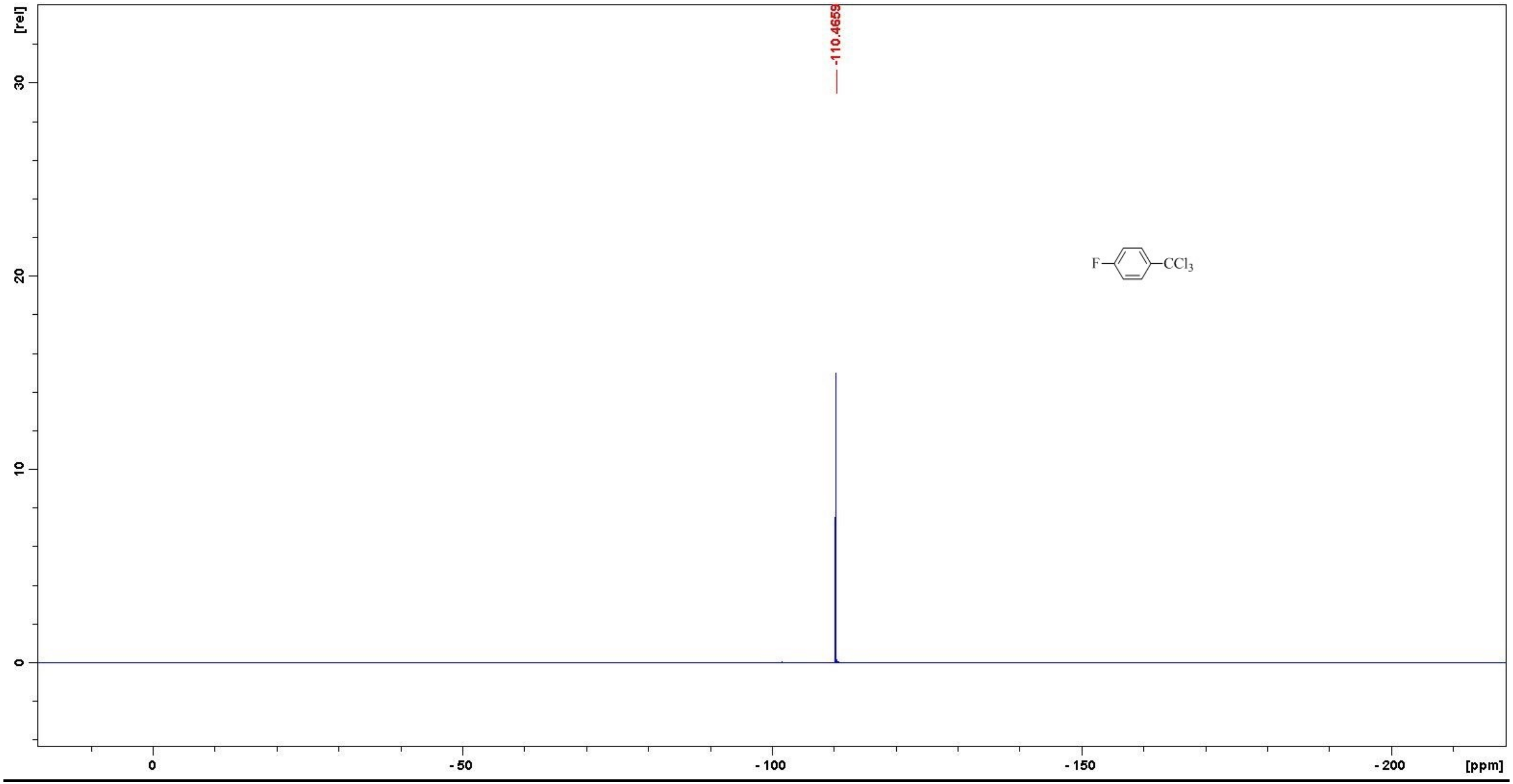


Figure S25. ^{1}H NMR spectrum of **8-Cl** in C_6D_6.

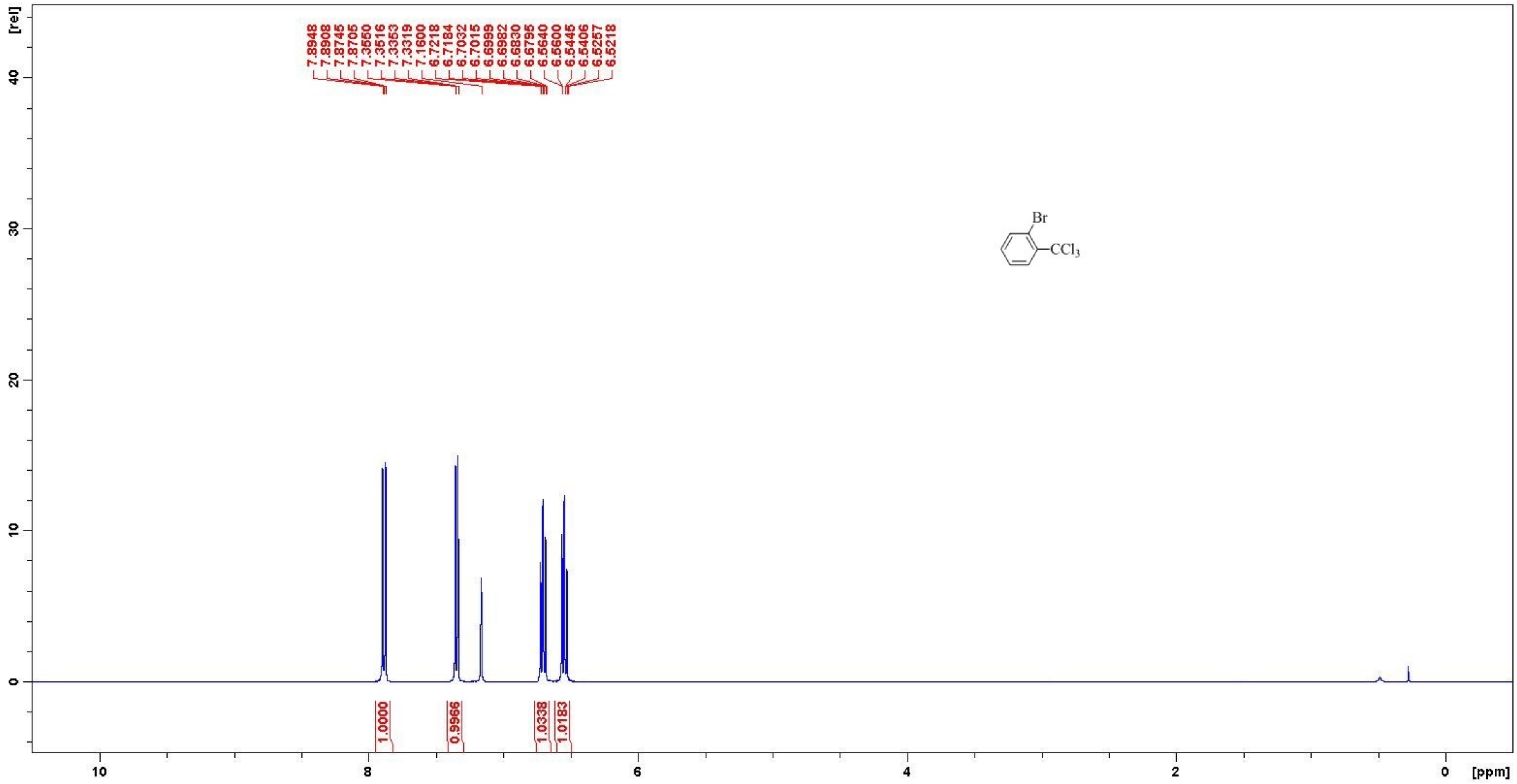


Figure S26. ^{13}C NMR spectrum of **8-Cl** in C_6D_6.

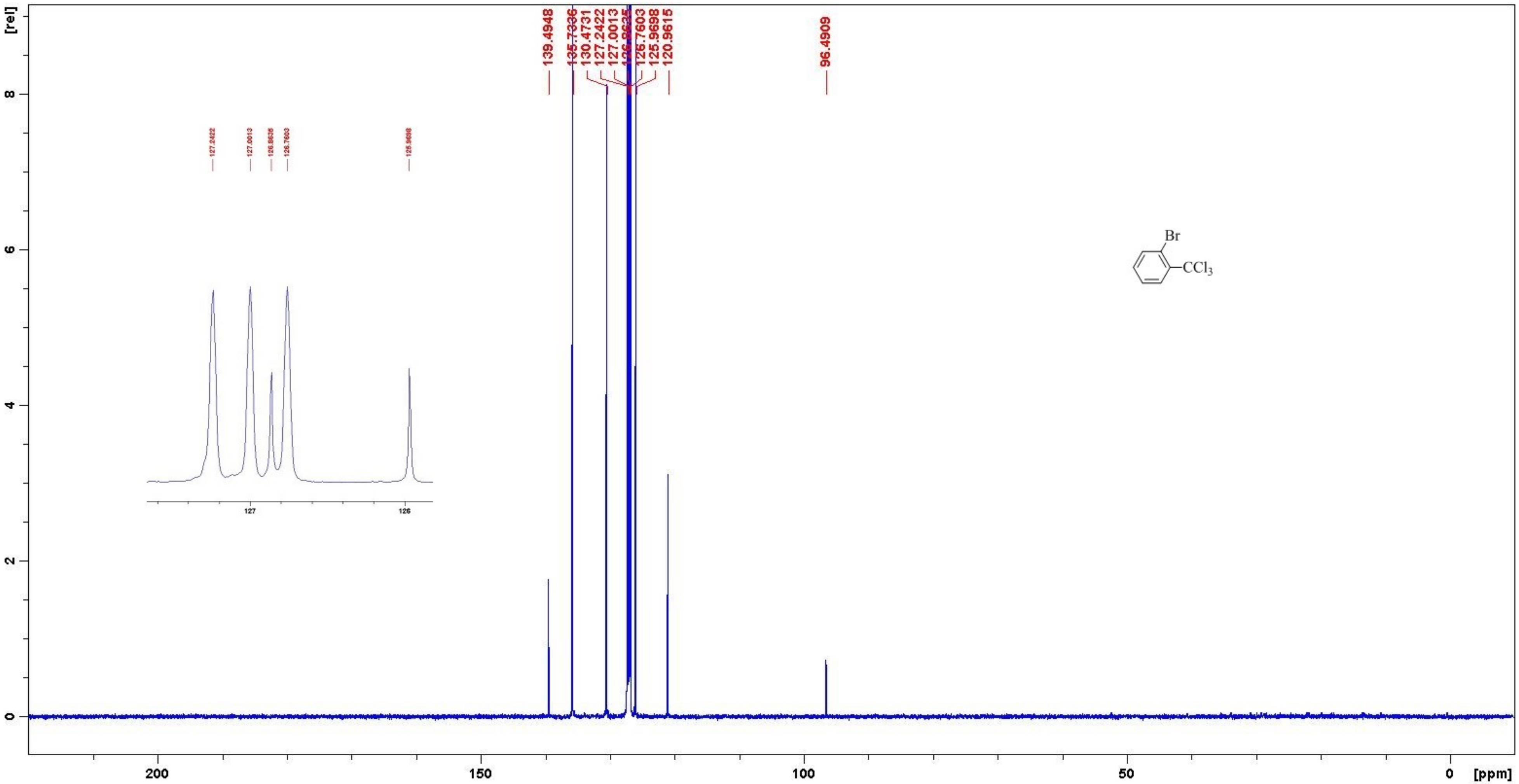


Figure S27. ^{1}H NMR spectrum of **9-Cl** in C_6D_6.

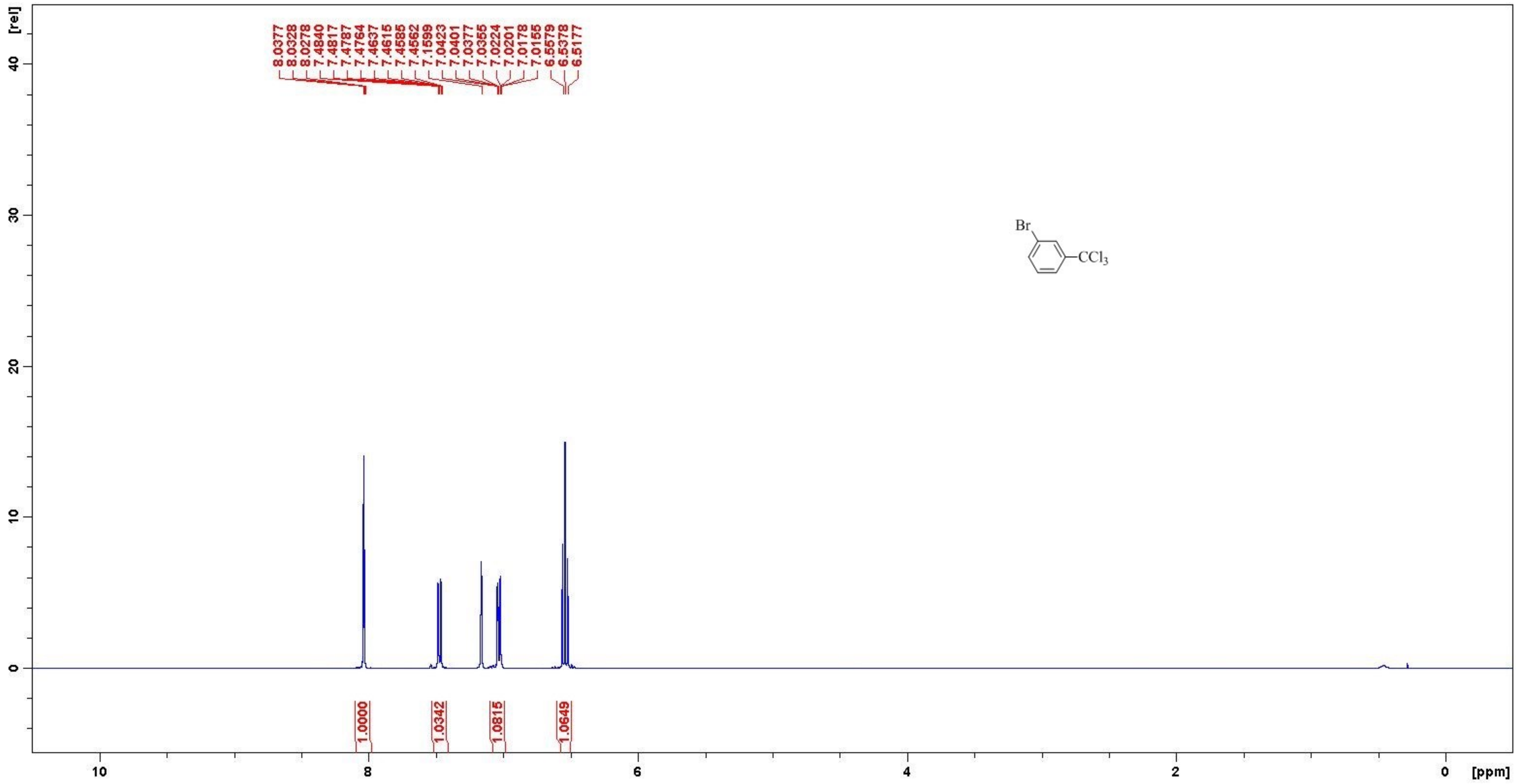


Figure S28. ^{13}C NMR spectrum of **9-Cl** in C_6D_6.

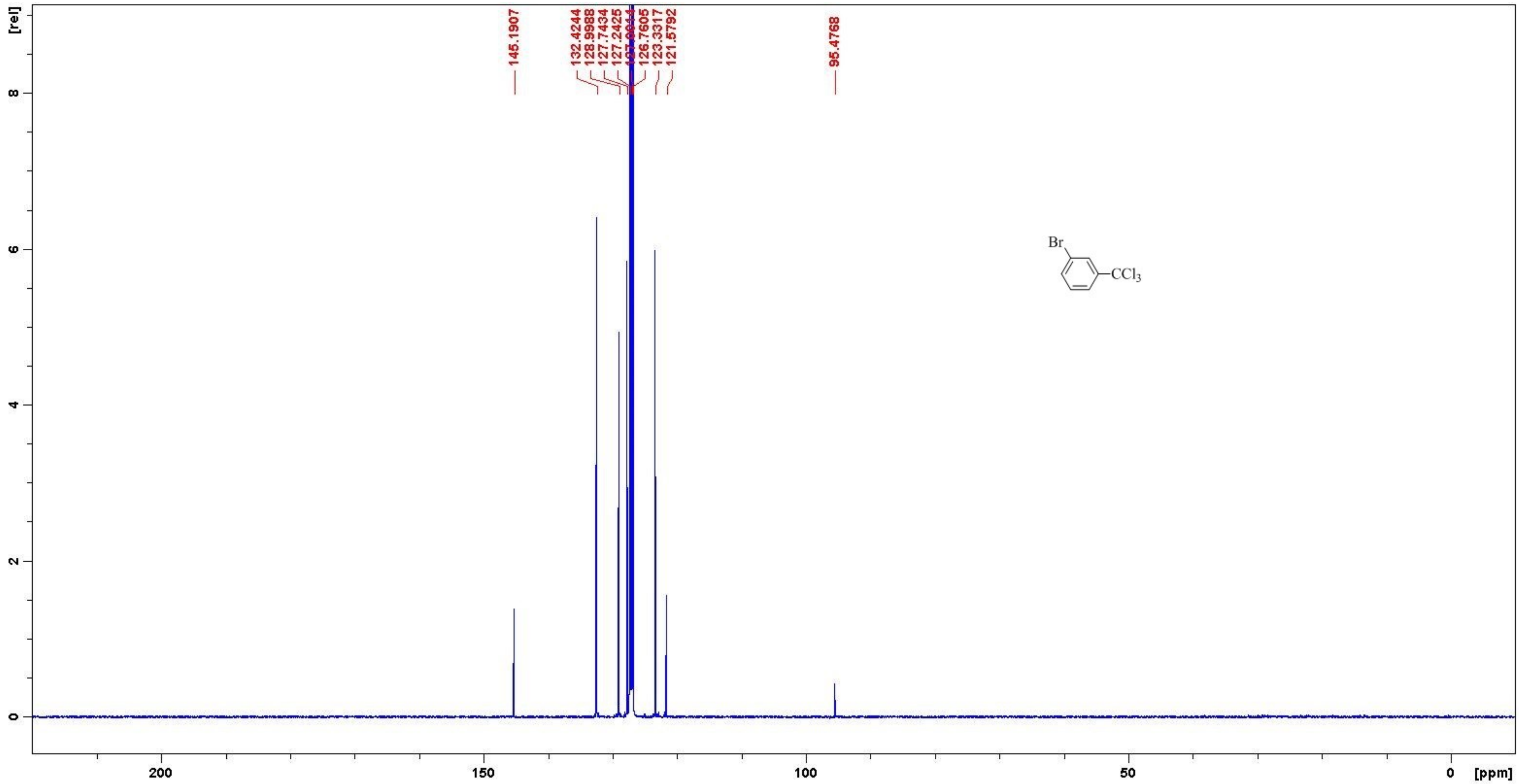


Figure S29. ^{1}H NMR spectrum of **10-Cl** in C_6D_6.

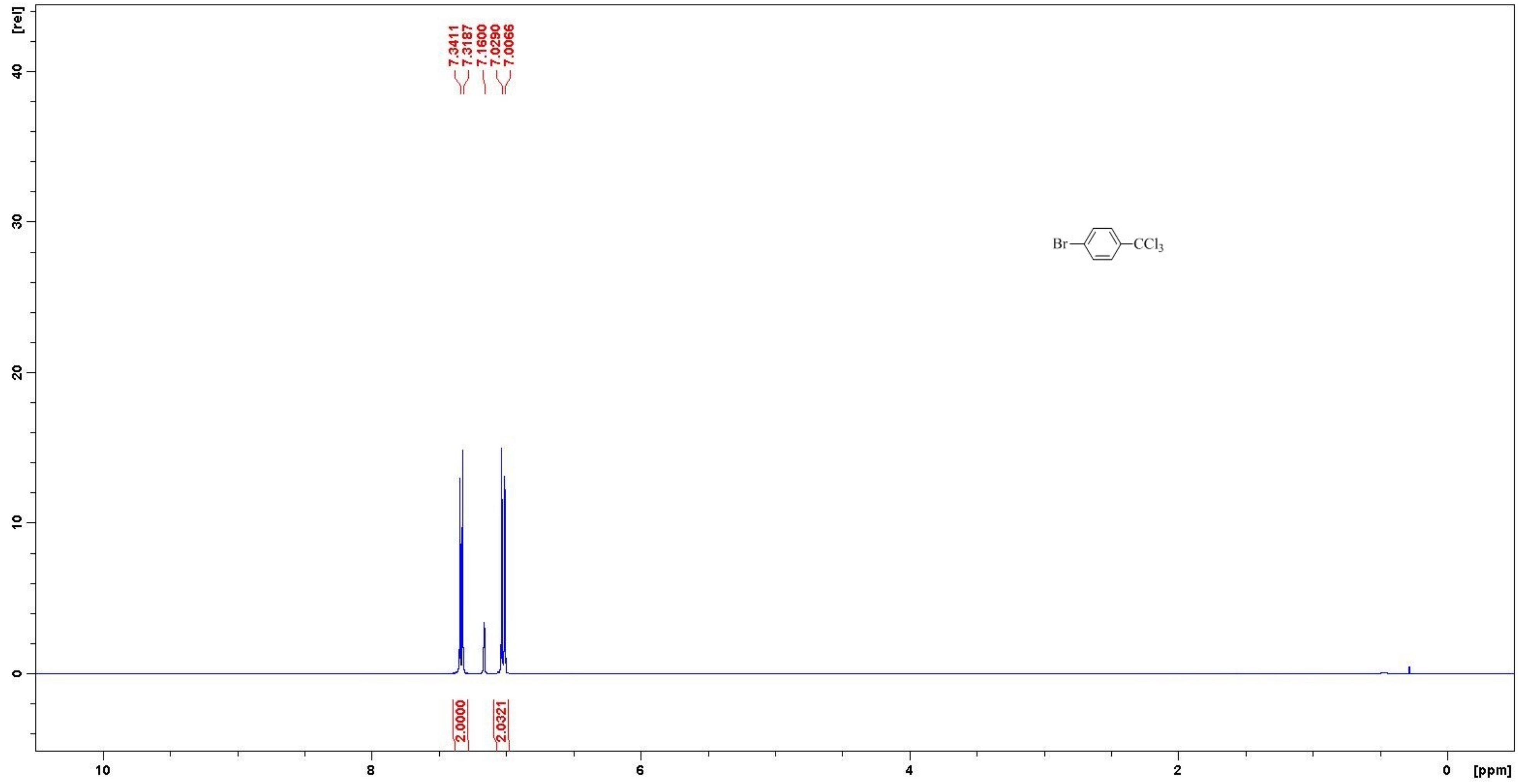


Figure S30. ^{13}C NMR spectrum of **10-Cl** in C_6D_6.

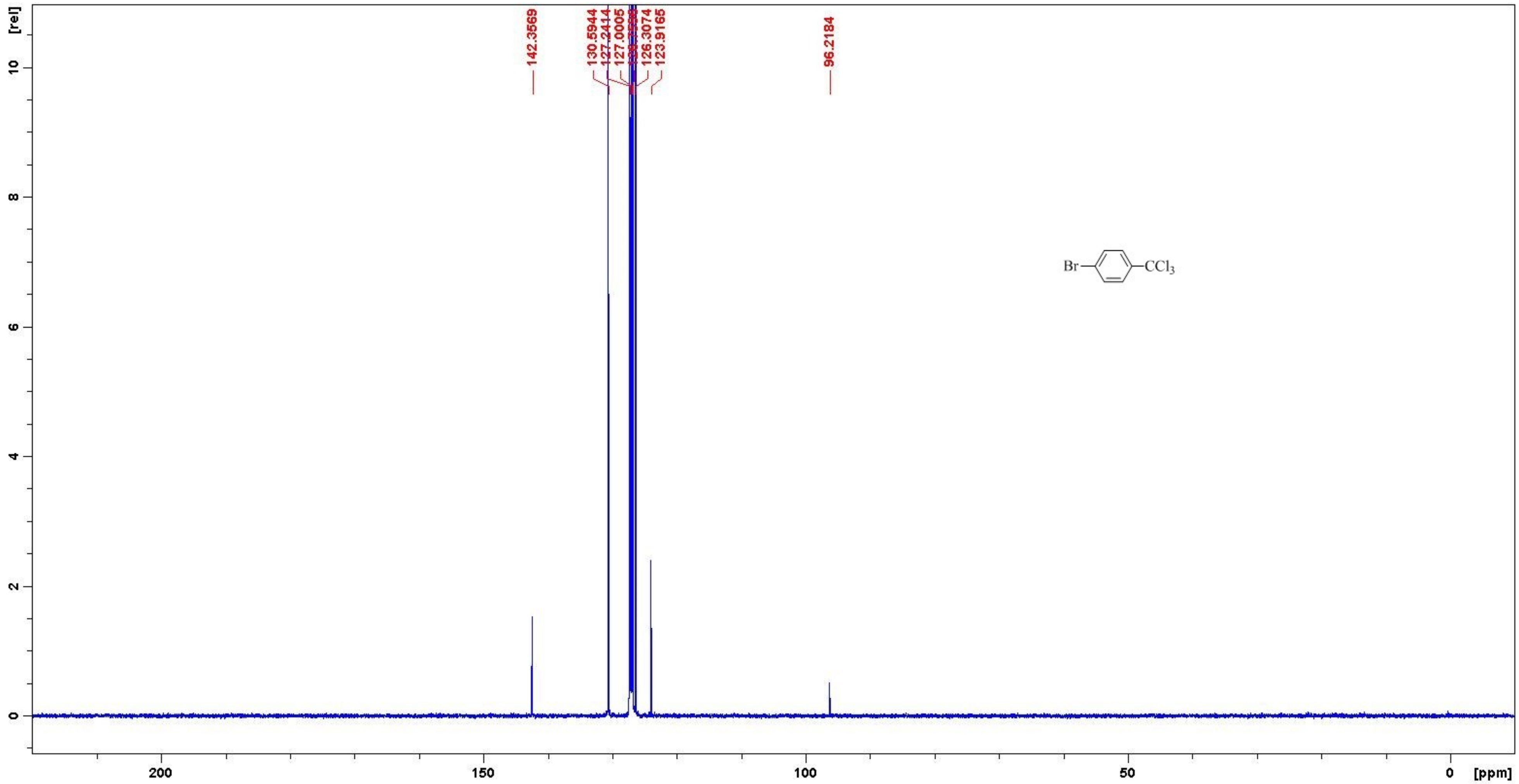


Figure S31. ^1H NMR spectrum of **11-Cl** in $CDCl_3$.

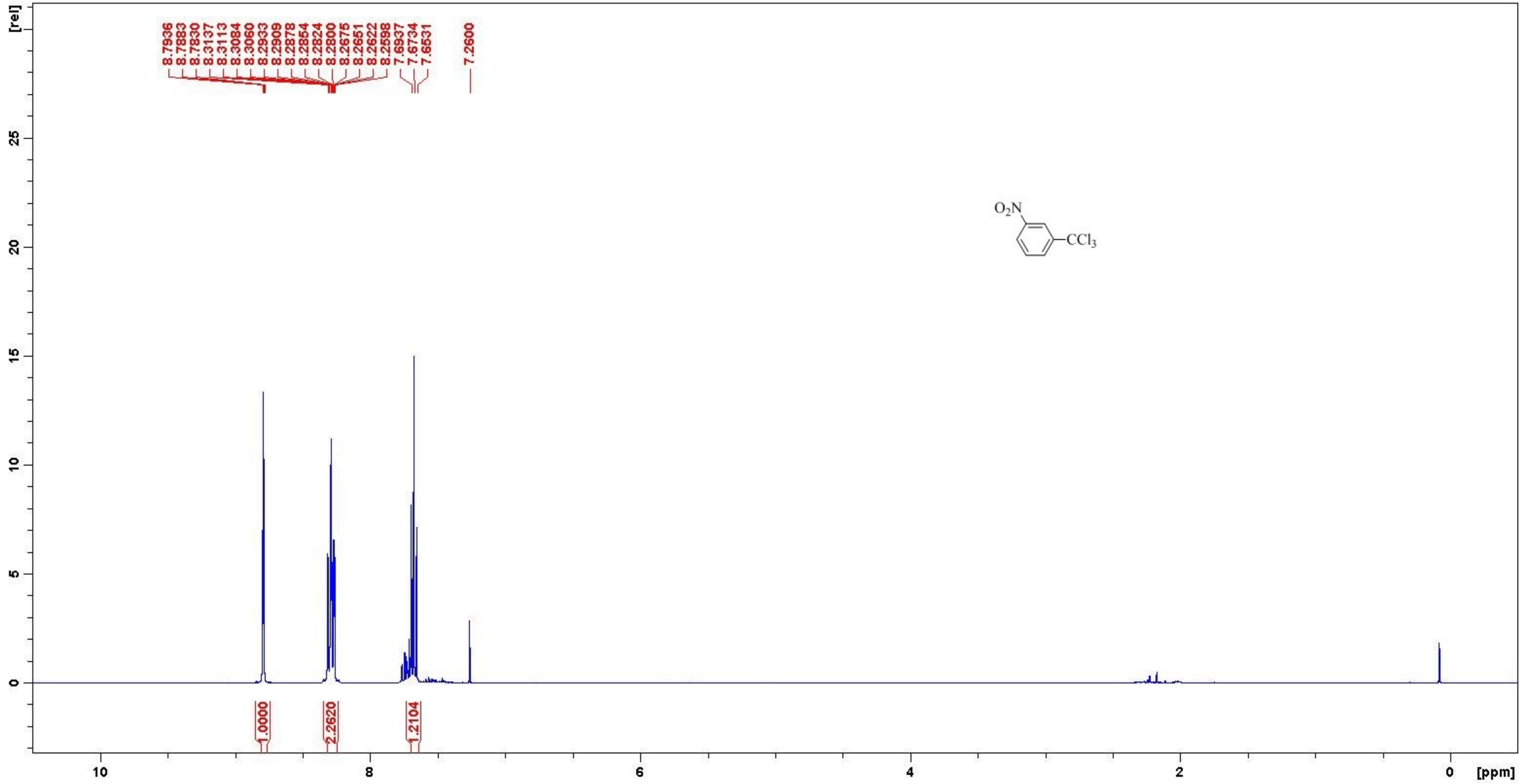


Figure S32. ^{13}C NMR spectrum of **11-Cl** in $CDCl_3$.

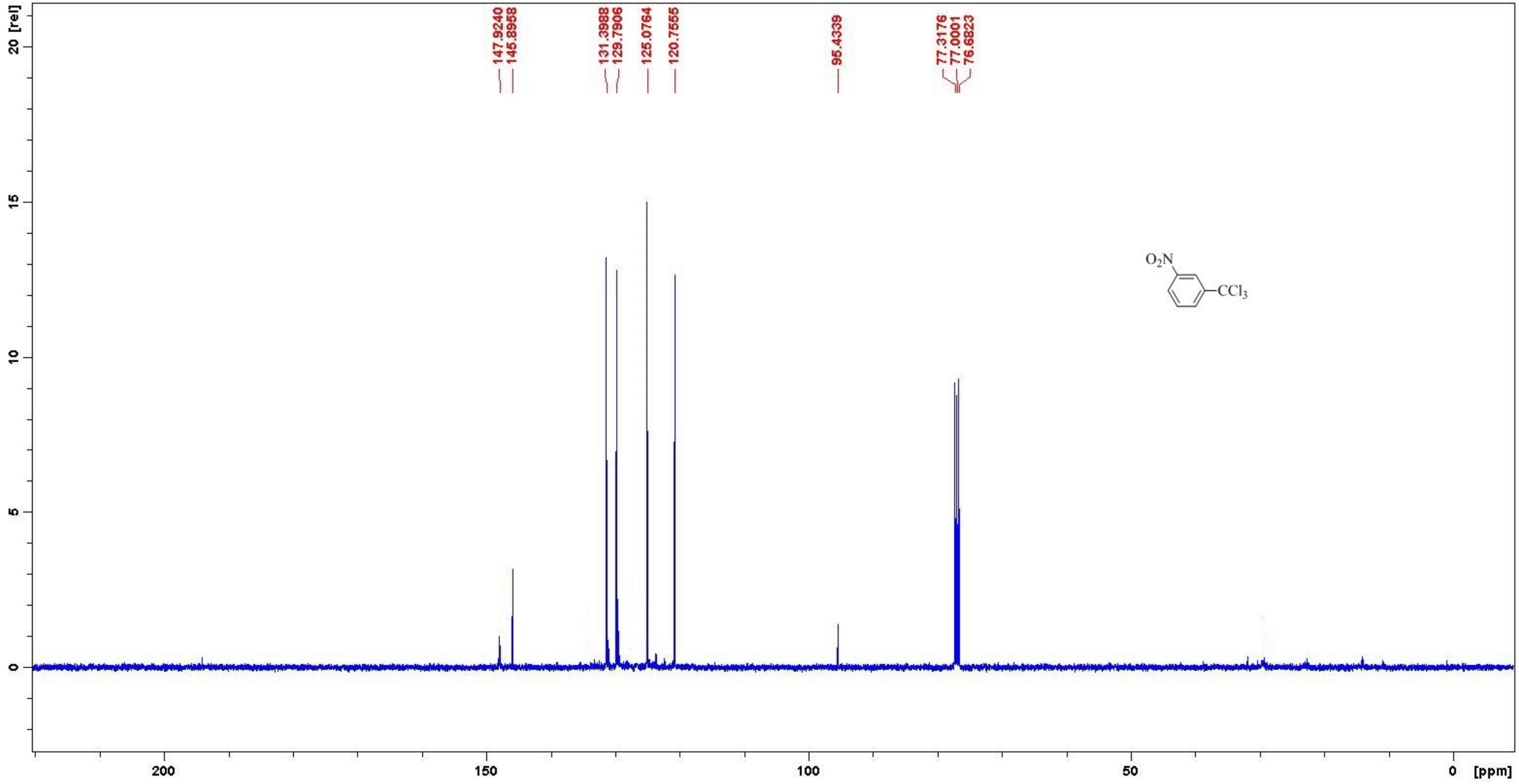


Figure S33. ^{1}H NMR spectrum of **12-Cl** in $CDCl_3$.

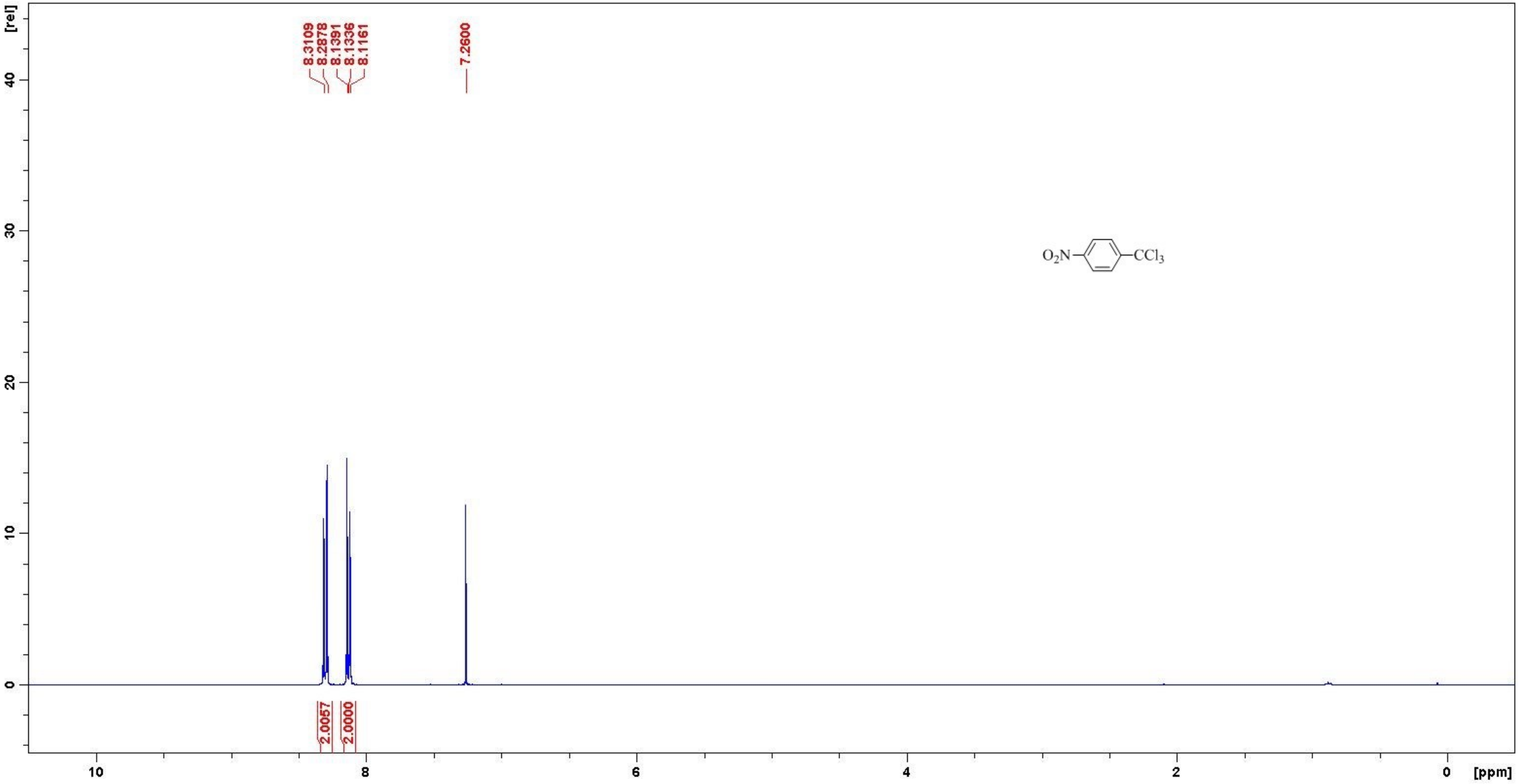


Figure S34. ^{13}C NMR spectrum of **12-Cl** in CDCl$_3$.

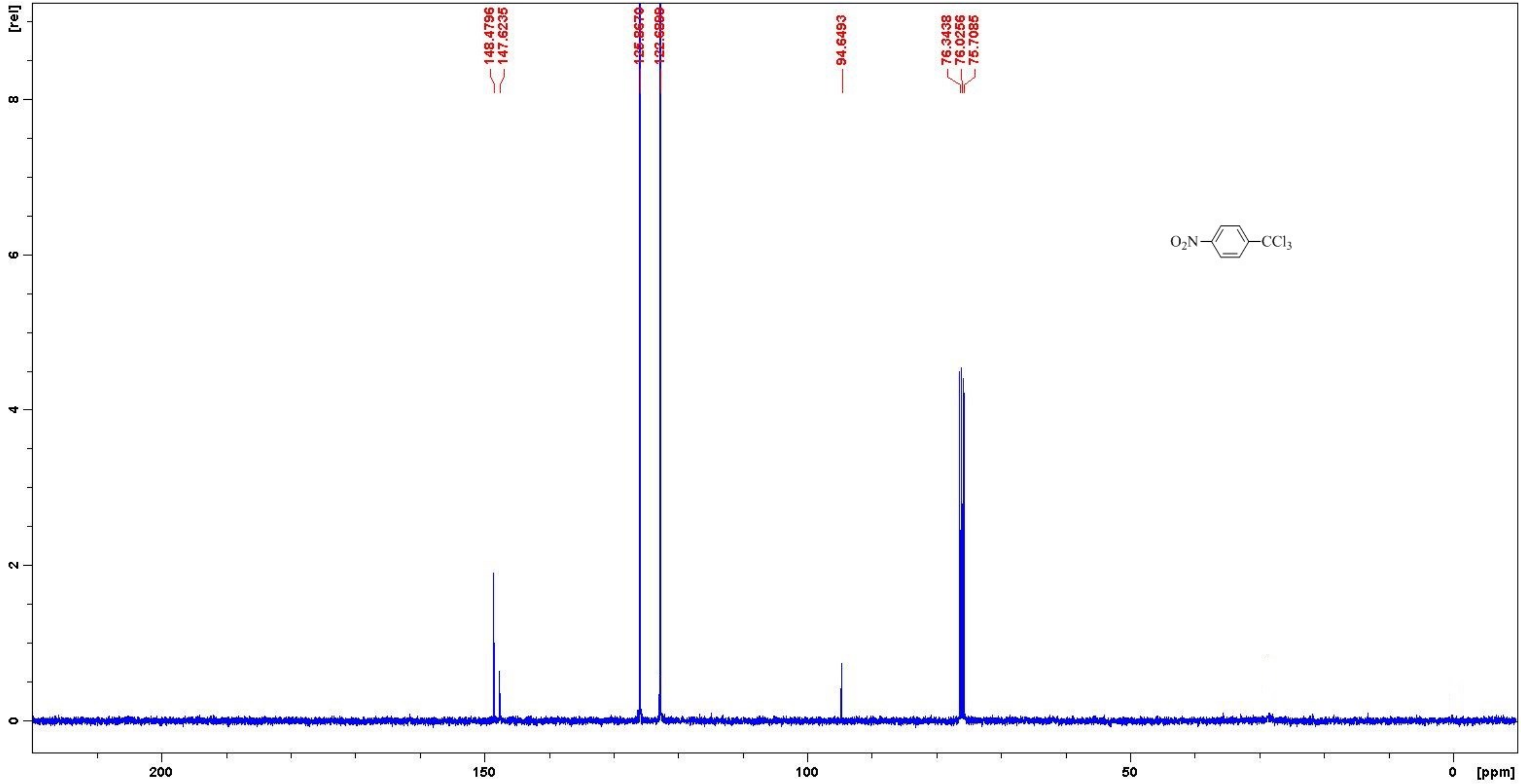


Figure S35. ^{1}H NMR spectrum of **13-Cl** in $CDCl_3$.

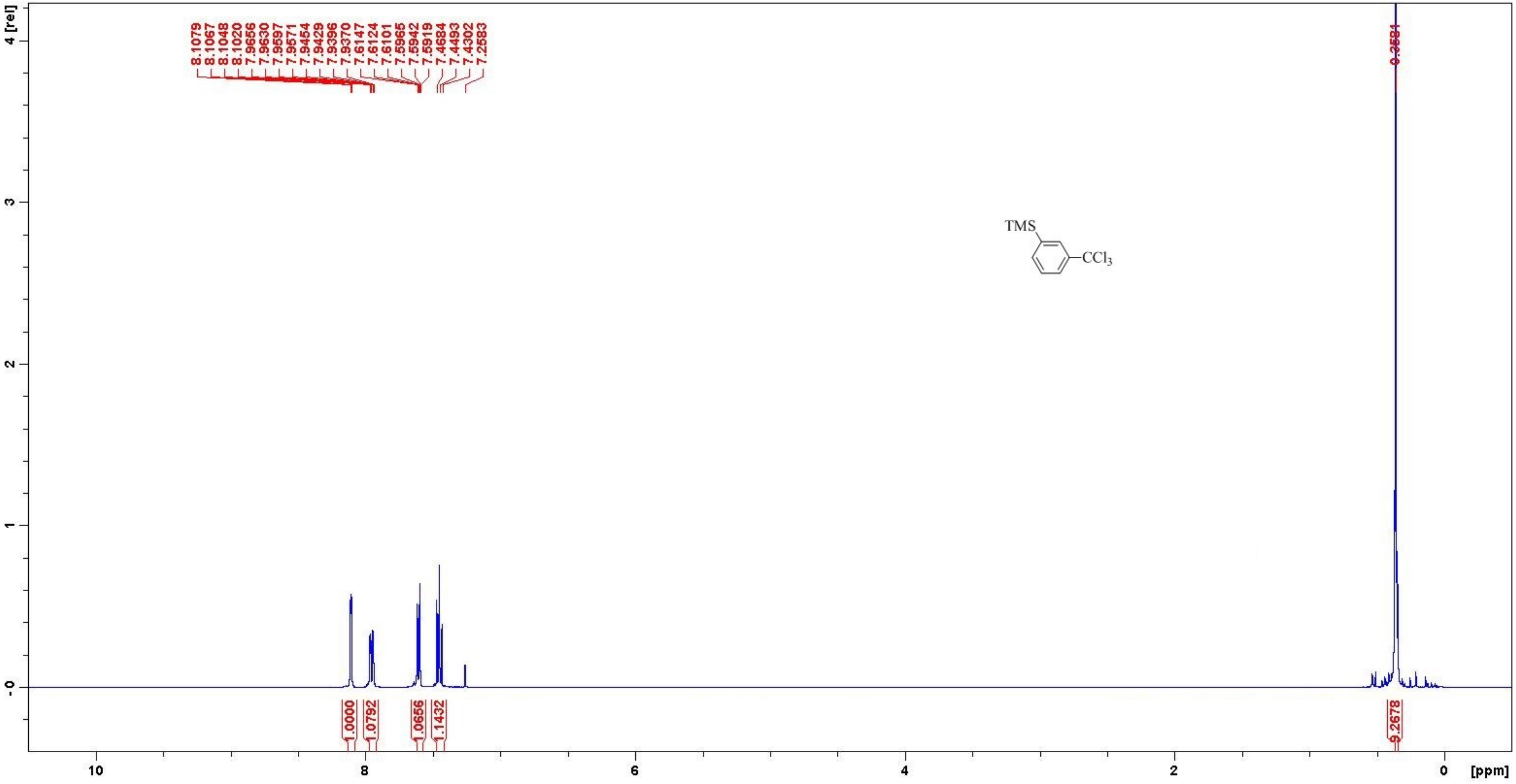


Figure S36. ^{13}C NMR spectrum of **13-Cl** in $CDCl_3$.

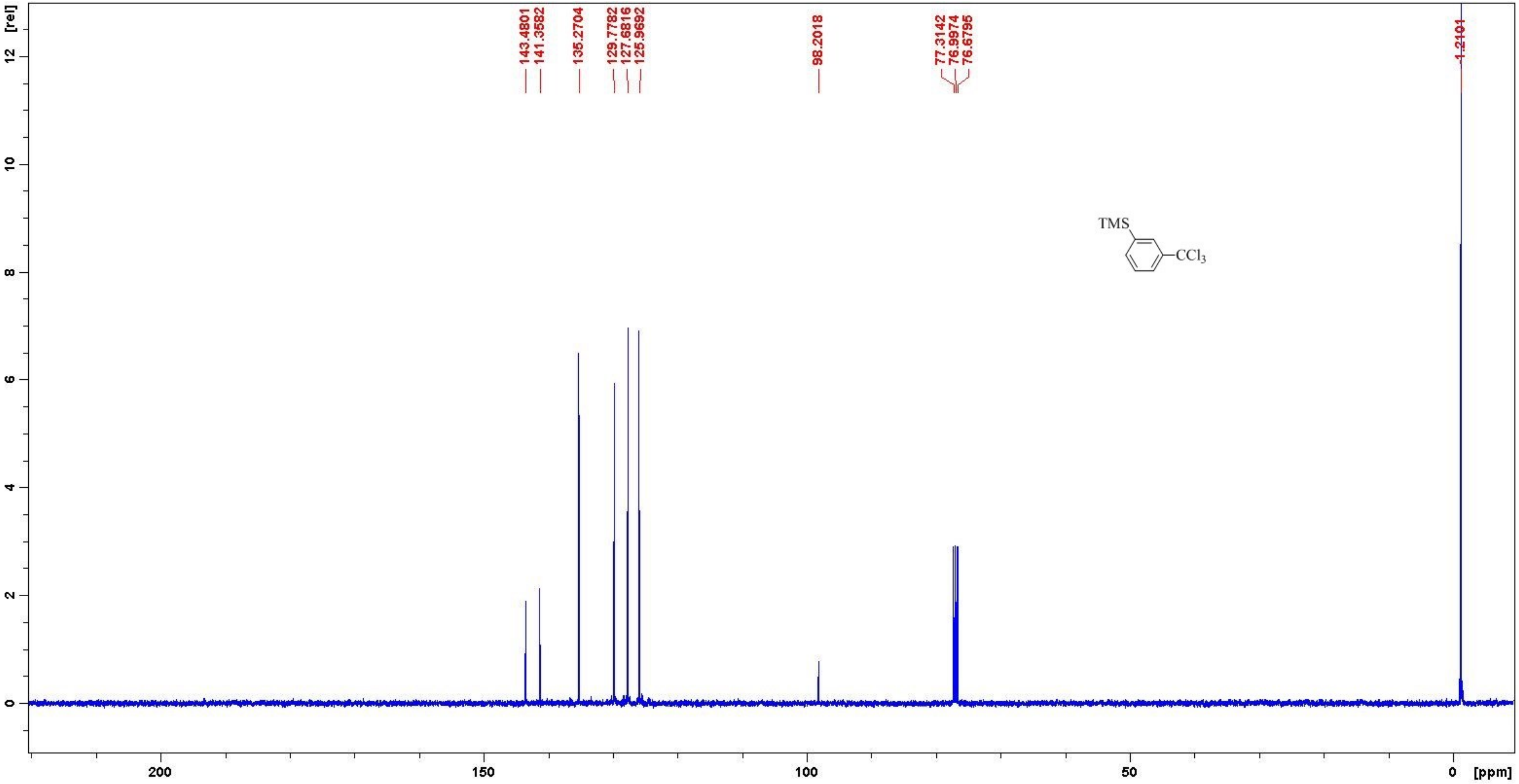


Figure S37. ^{1}H NMR spectrum of **15-Cl** in $CDCl_3$.

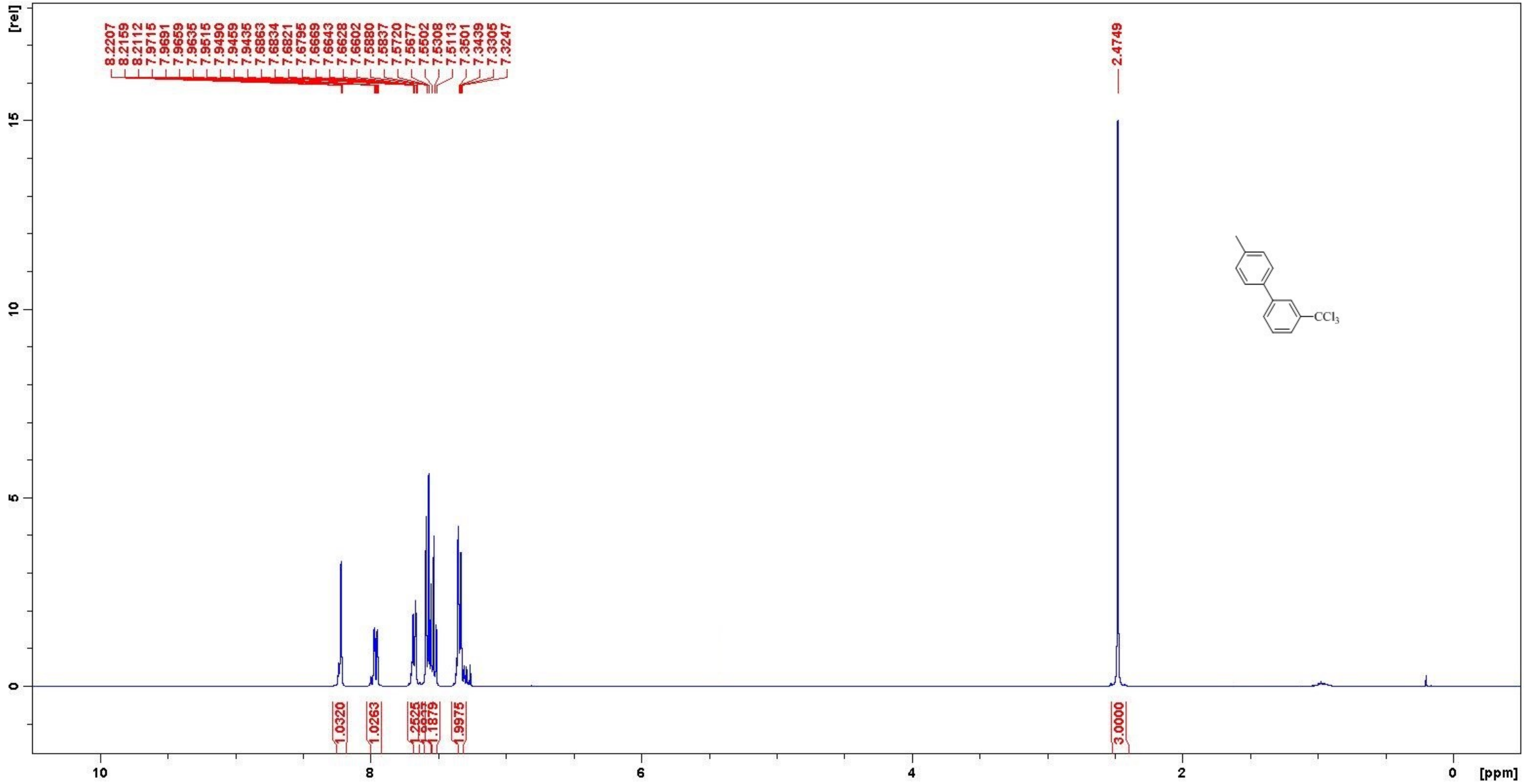


Figure S38. ^{13}C NMR spectrum of **15-Cl** in $CDCl_3$.

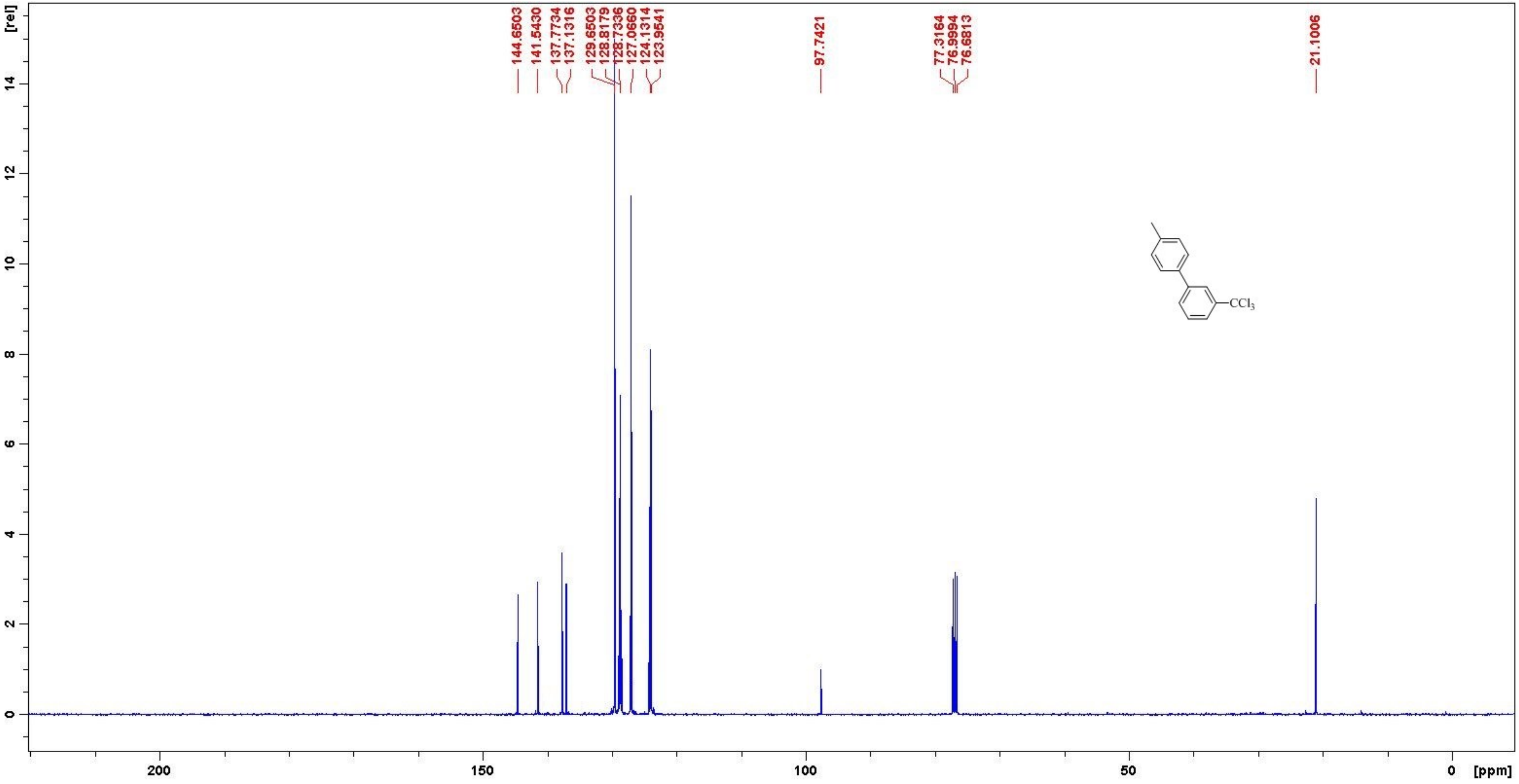


Figure S39. ^{1}H NMR spectra detailing the total conversion from trifluorotoluene to trichlorotoluene *via* $AlCl_3$ and $SiCl_4$

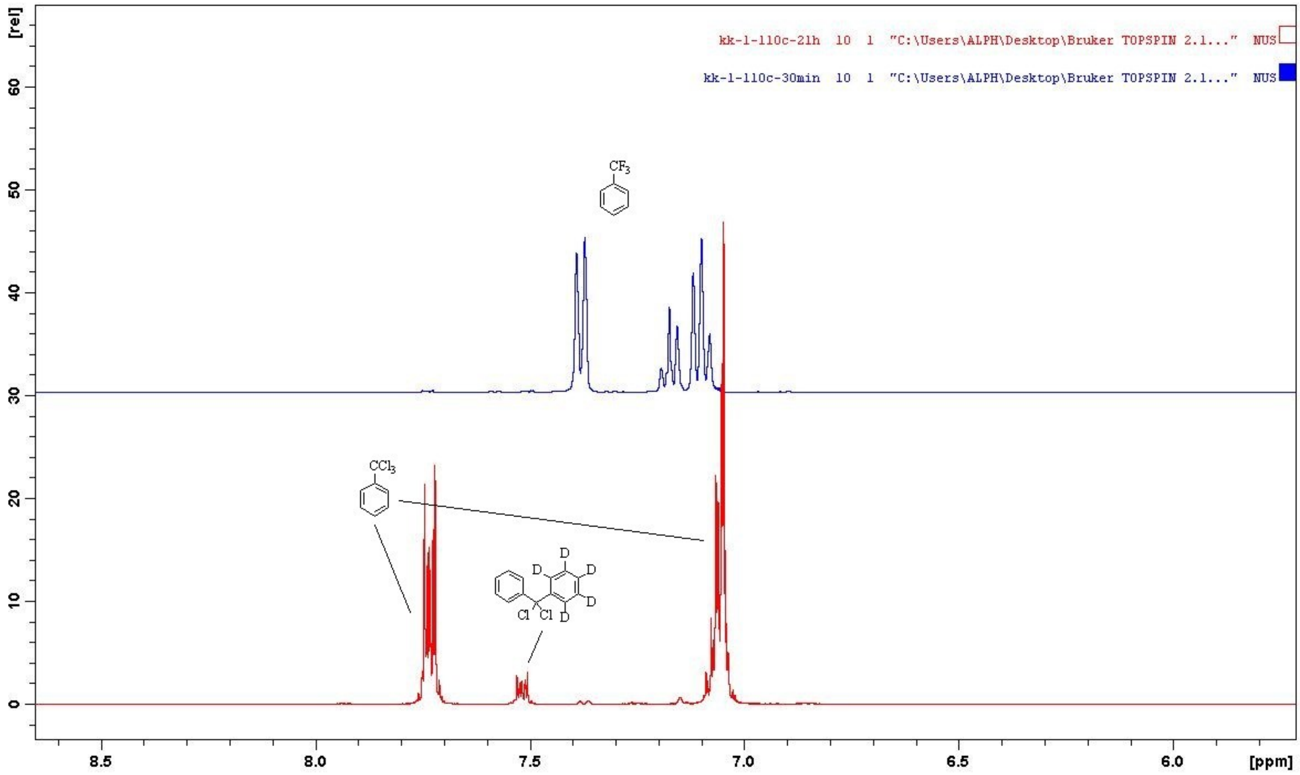


Figure S40. GCMS chromatogram of the reaction to convert trifluorotoluene to trichlorotoluene *via* $AlCl_3$ and $SiCl_4$

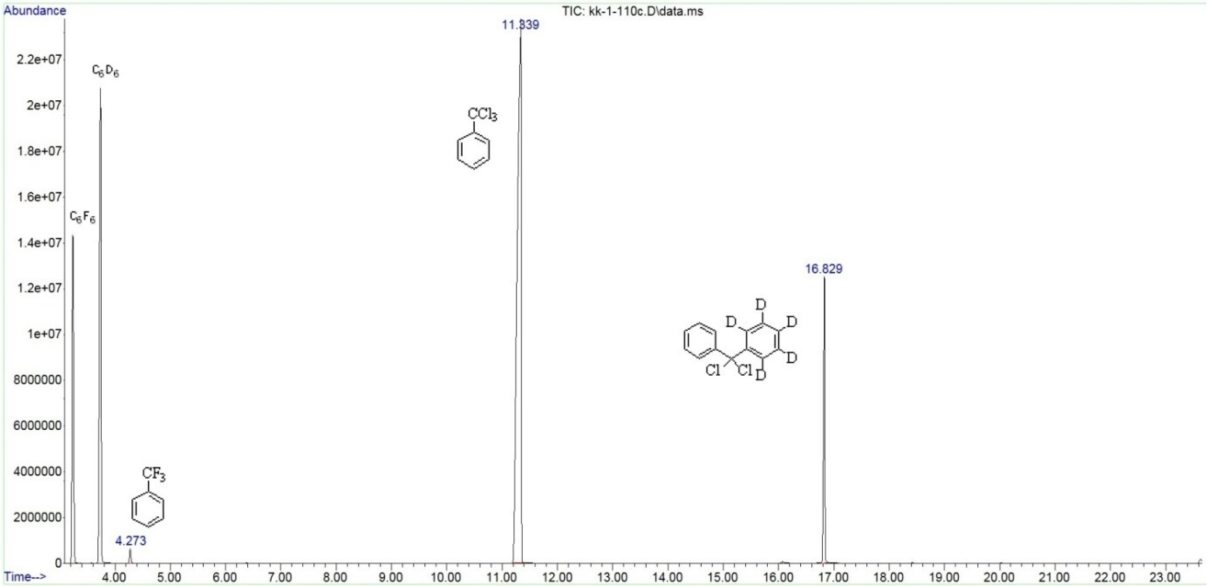
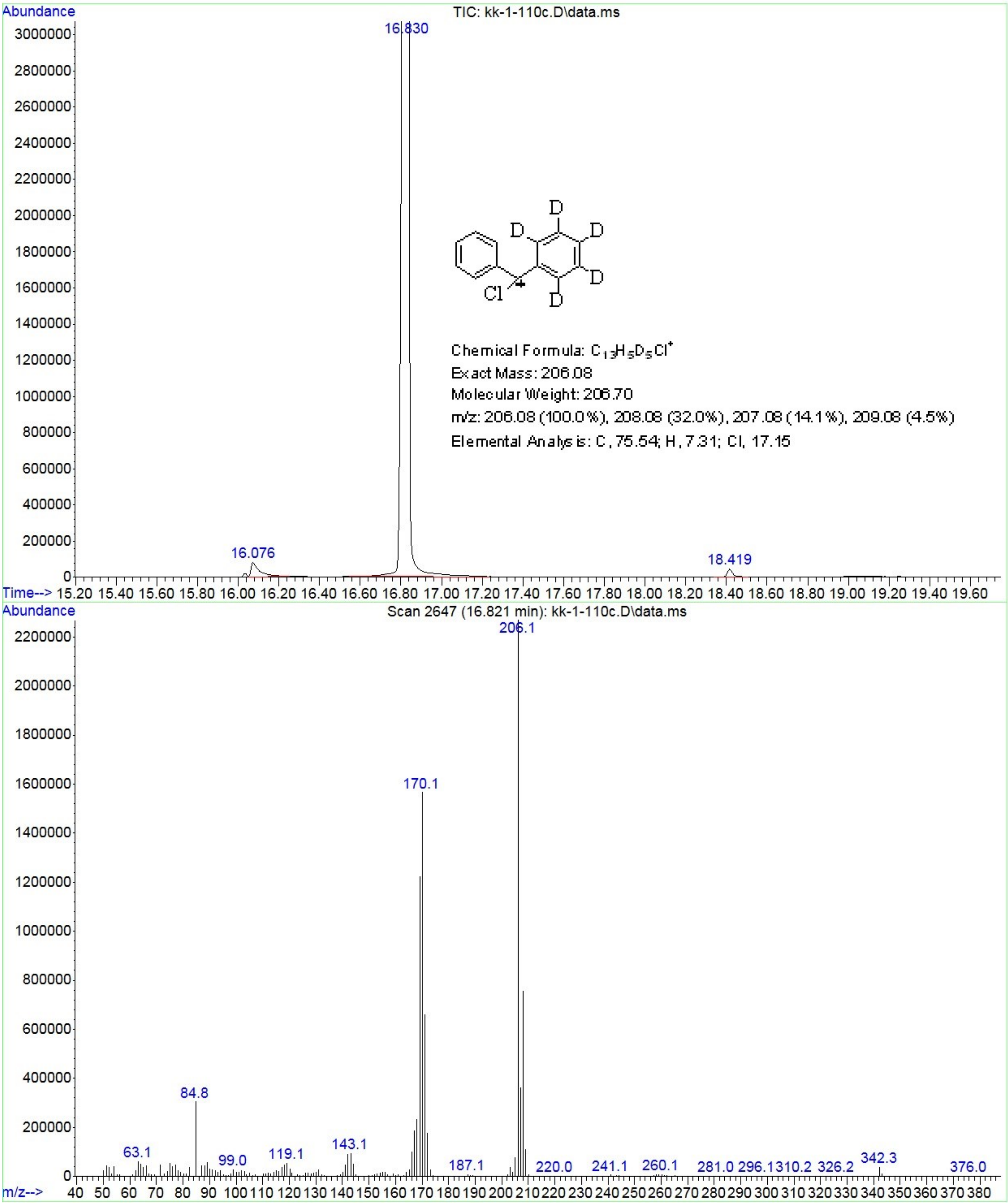


Figure S41. GCMS chromatogram and mass fragmentation spectra of ion peak at 16.821 min indicating the likely formation of Friedel-Craft's product of trichlorotoluene with d-benzene.



```
Signal     : TIC: kk-1-110c.D\data.ms

Peak R.T. first  max last  PK   peak      corr.   corr.    % of

  #   min   scan scan scan  TY  height     area    % max.   total

 ---  ----- ----- ---- ---- ---  -------    -------  ------  -------

  1   4.273    222  229  241    M    651645  11509630   0.97%    0.822%

  2  11.339  1562 1591 1604    M  24412795 1181691764 100.00%  84.361%

  3  16.829  2638 2648 2664    M  12745968 207561405  17.56%  14.818%

                           Sum of corrected areas:  1400762800
```

Figure S42. Bottom: ^{13}C NMR spectra of Ph_3C-Cl in C_6D_6 (ca 60 mM);Top:[Ph_3C][$B(C_6F_5)_4$] + Me_3Si-Cl in C_6D_6 after 3 hrs at room temperature (ca 25 mM). Note, the highlighted resonance at 82 ppm identifies the central tertiary carbon of trityl chloride, which is absent in the top spectrum.

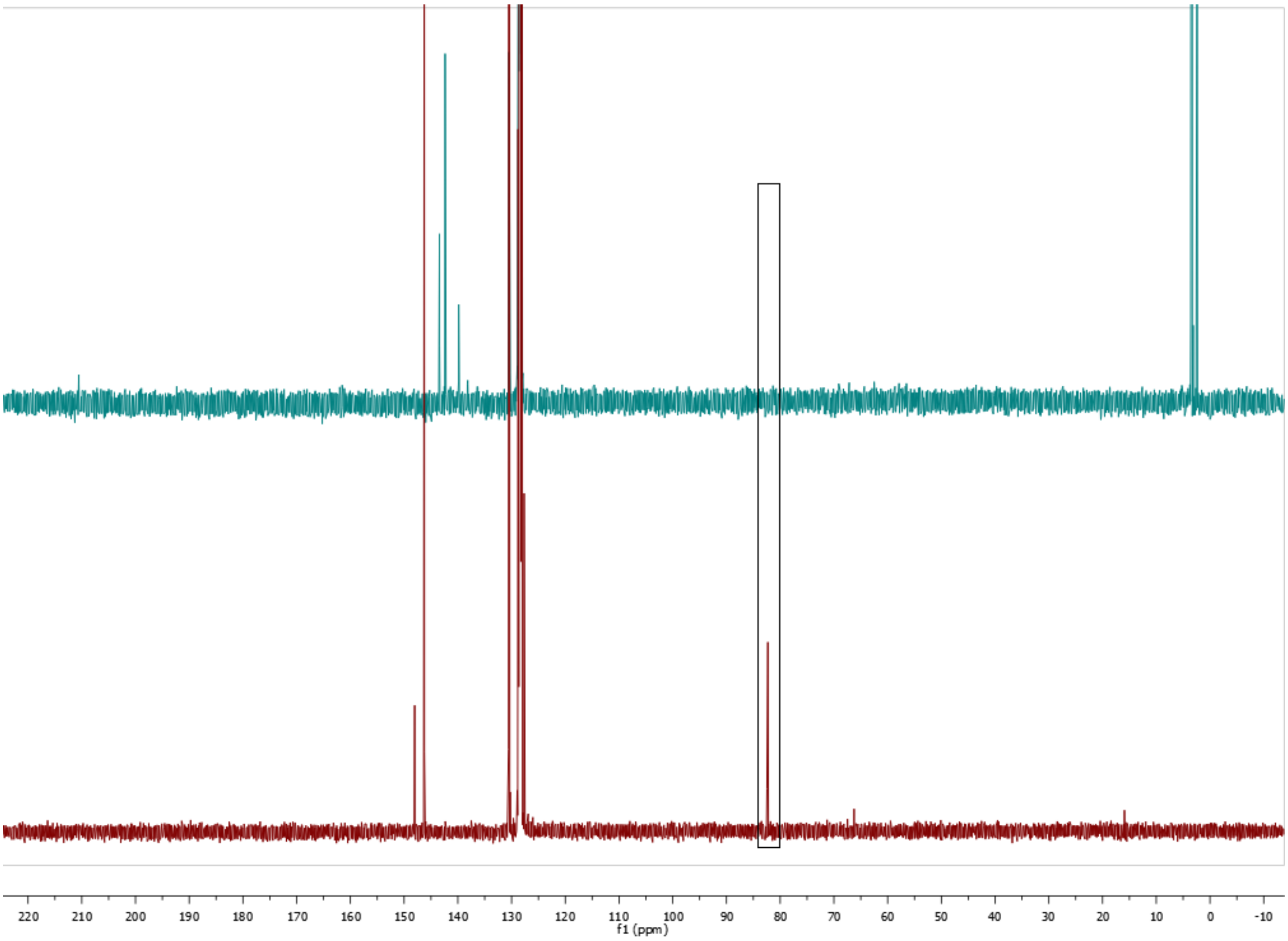


Figure S43a. GCMS chromatogram of reaction between [CPh$_3$][B(C$_6$F$_5$)$_4$] and TMSCl in C$_6$D$_6$.

```
peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #   min   scan scan scan  TY  height     area   % max.   total
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   3.726    10   19   28 rBV  15014697  27137735 100.00%  99.292% benzene-d6
  2   5.139   207  212  222 rM      11944     25455   0.09%   0.093% toluene
  3  18.121  1982 1985 2000 rM      90733    129442   0.48%   0.474%
  4  18.780  2072 2075 2086 rM      21074     38473   0.14%   0.141%
```

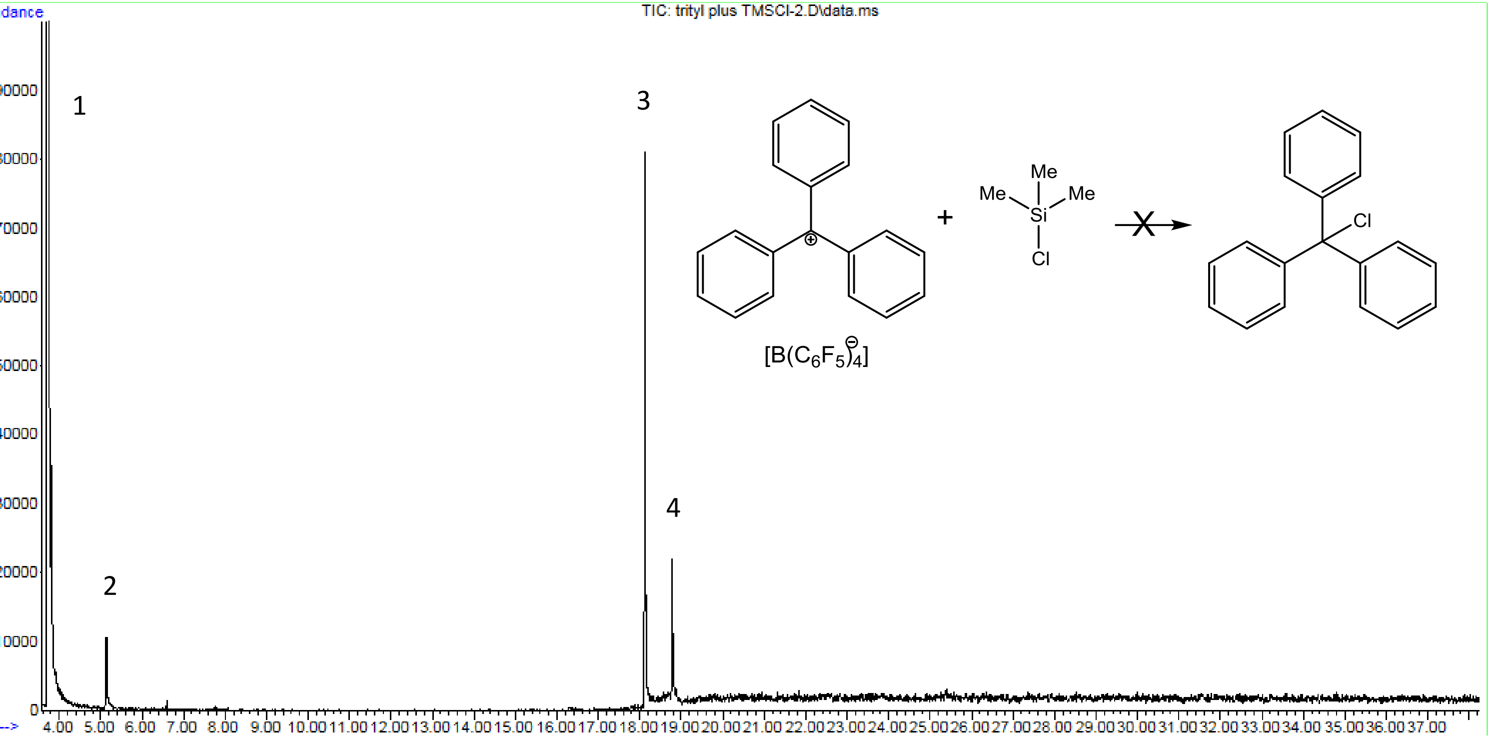


Figure S43b. Mass fragmentation of band at retention time 18.121 minutes from reaction between $[CPh_3][B(C_6F_5)_4]$ and TMSCl in C_6D_6, assigned as triphenyl methane.

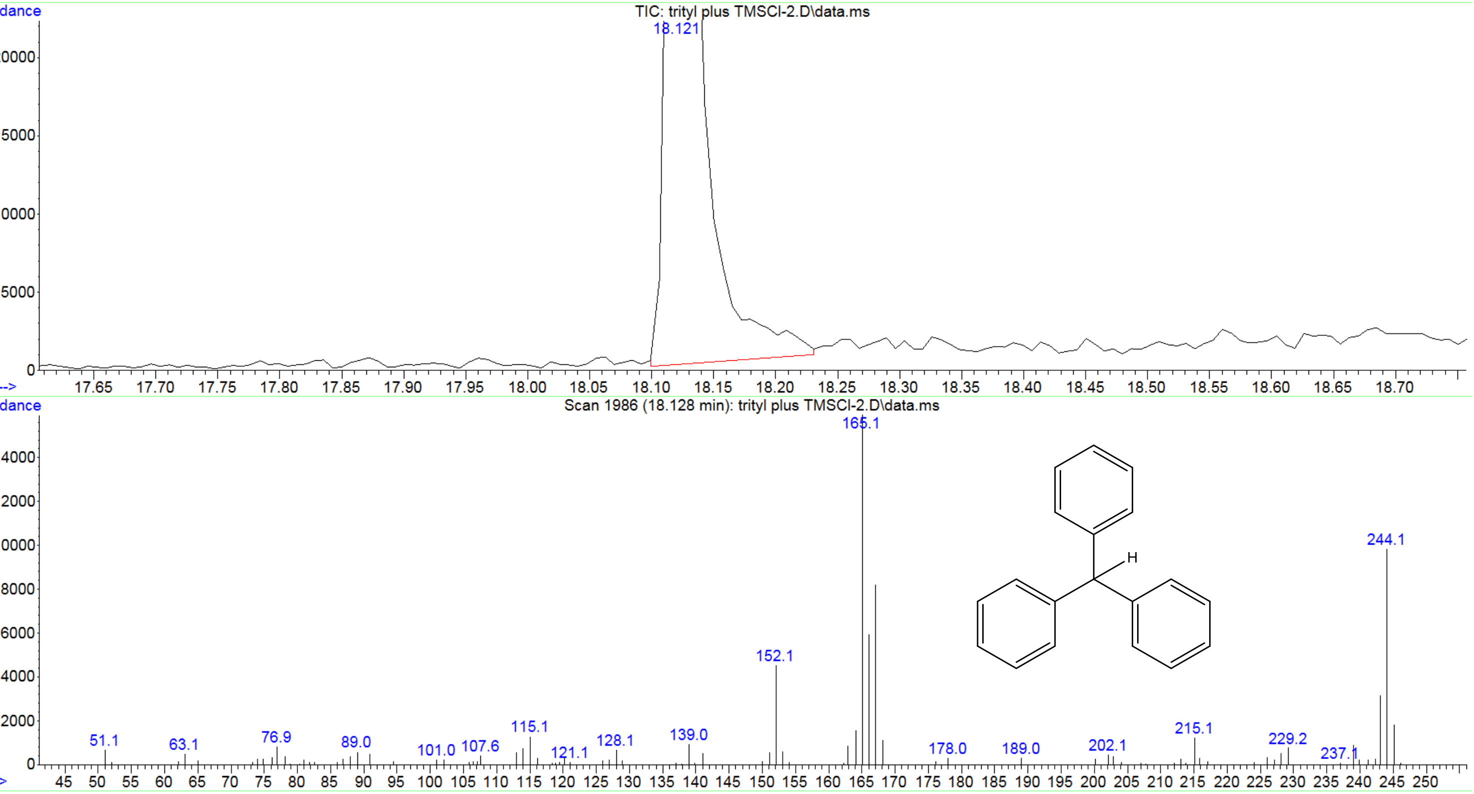


Figure S43c. Mass fragmentation of band at retention time 18.780 minutes from reaction between $[CPh_3][B(C_6F_5)_4]$ and TMSCl in C_6D_6, assigned as triphenyl methanol.

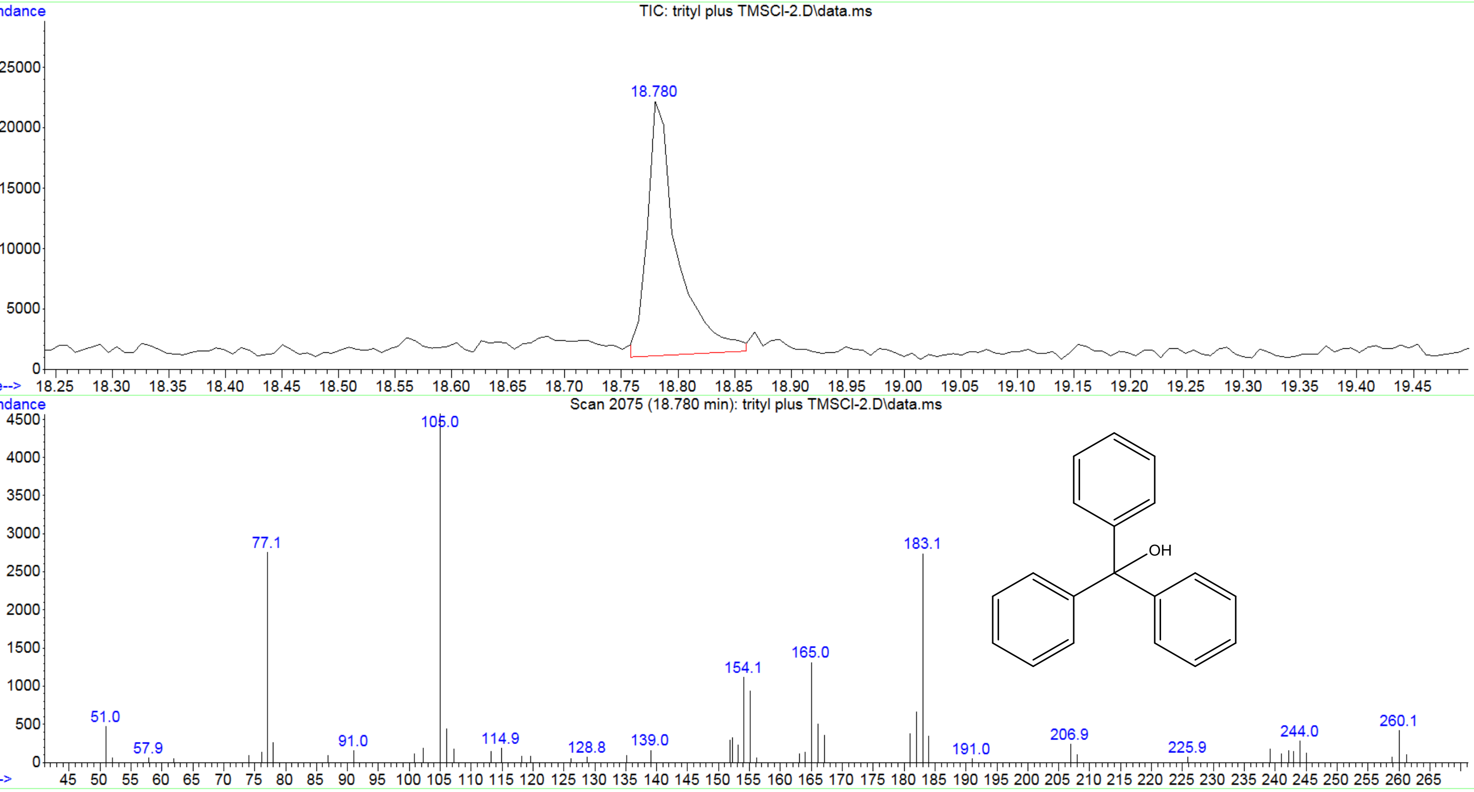
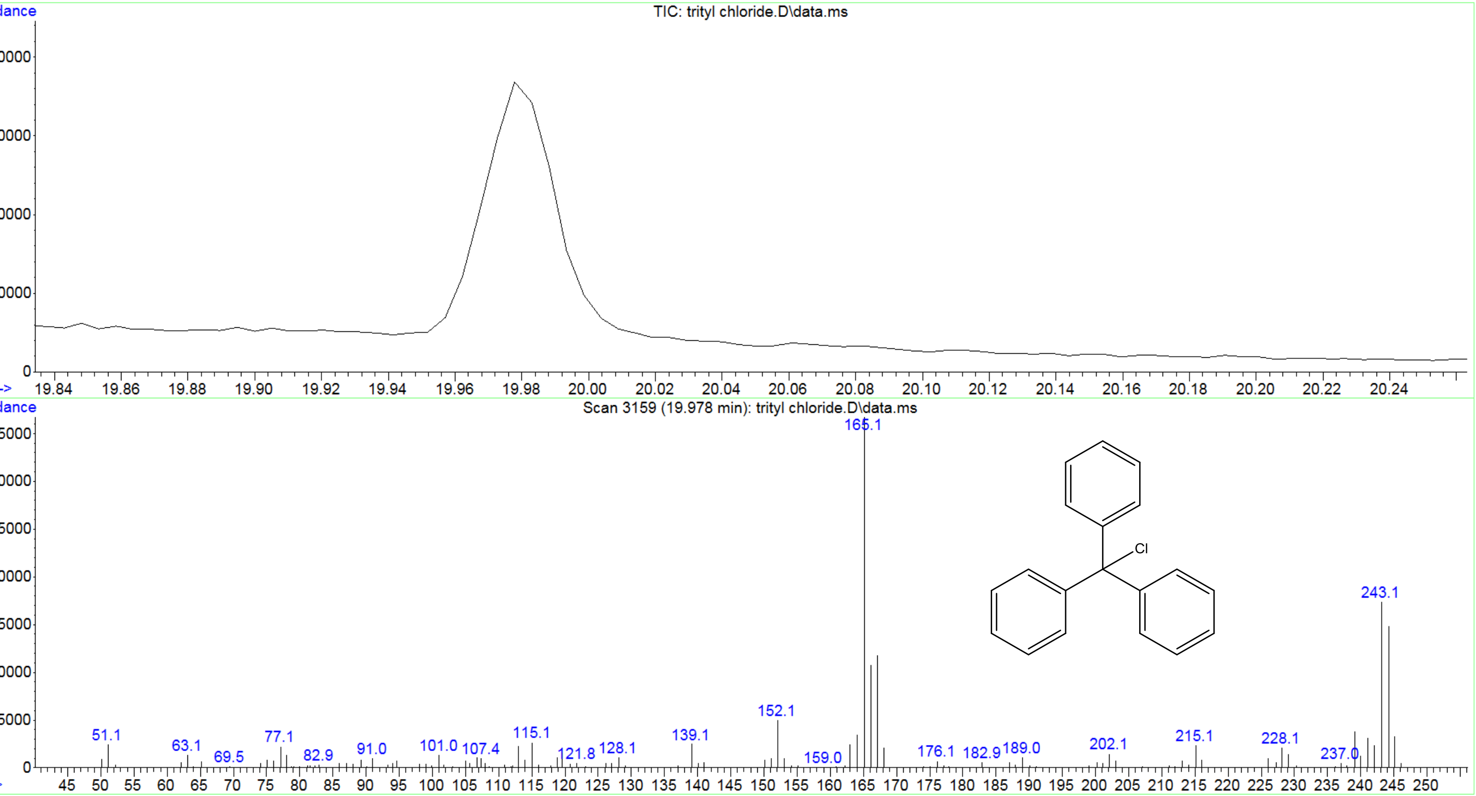


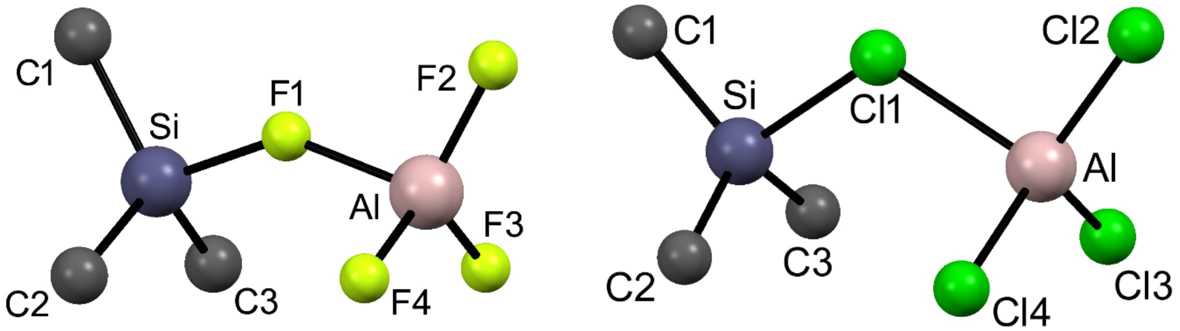
Figure S43d. Mass fragmentation and retention time of authentic sample of trityl chloride.



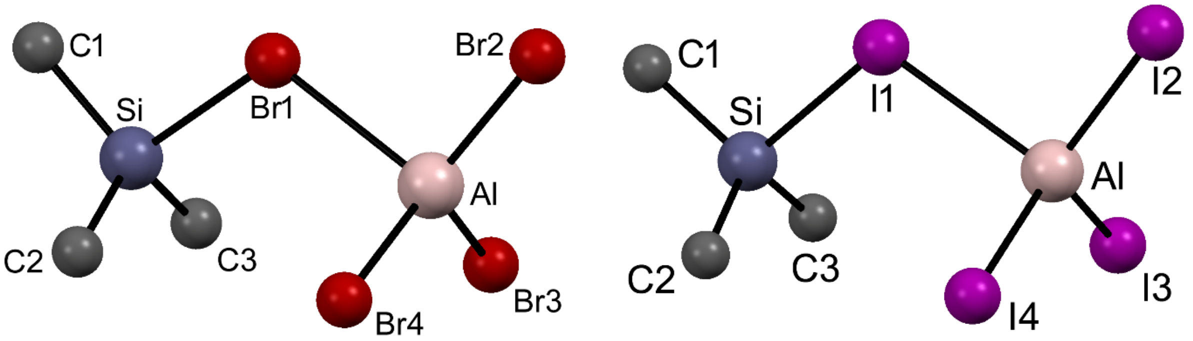
Computational Details

All computational works were performed by using Gaussian 09,[17] 2 revision A.02 on the Tiger 2 cluster at the National University of Singapore HPC clusters. Full geometry optimization were carried out using the Density Functional Theory (DFT) calculations using the three-parameter hybrid functional of Becke and the correlation functional of Lee, Yang and Parr (B3LYP)[18] in con*J*unction with thedouble-ζ basis set of Hay and Wadt (LanL2DZ)[19] with effective core potential (ECP) for chlorine, bromine and iodine and 6-311++g(d,p) for other atoms. The input geometries were generated by using GaussView 05 software and the optimizations started without symmetry restraints with the standard convergence criteria for the Gaussian 09, revision A.02. Vibrational frequencies were calculated at the same level of theory as the corresponding geometry optimization. All optimized structures are the local minima on the potential energy surface with no imaginary frequency.The thermodynamic energies of the optimized structures were calculated standard procedures. The modified Complete Basis Set (CBS) method CBS-QB3[20] was used to get accurate free energies.This method contains following five steps: i) B3LYP/6-311G(2d,d,p) geometry optimization; ii) B3LYP/6-311G(2d,d,p) frequencies; iii) CCSD(T)/6-31+G(d’) energy; iv) MP4(SDQ)/CBSB4 energy and v) MP2/CBSB3 energy and CBS extrapolation.

Figure S44. DFT Optimized Structures of the Halosilane-Aluminium Trihalide Complexes



$Me_3Si–F–AlF_3$ (X) **$Me_3Si–Cl–AlCl_3$ (X)**



$Me_3Si–Br–AlBr_3$ (X) **$Me_3Si–I–AlI_3$ (X)**

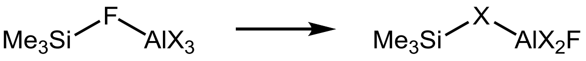
Table S1. Calculated Free Energy Change for the Defluorination Reaction

$$Me_3SiX + CH_3F \longrightarrow Me_3SiF + CH_3X$$

X = H, Cl, Br

	CBS-QB3	B3LYP
ΔG_{HDF}(kcal/mol)	-59.75	-53.31
ΔG_{ClDF} (kcal/mol)	-15.08	-10.85
ΔG_{BrDF} (kcal/mol)	-20.61	-15.49

Table S2. Calculated Free Energy Change for the Halogen Exchange Reaction



X = Cl, Br

	CBS-QB3	B3LYP
$\Delta G_{F\text{-}Cl}$ (kcal/mol)	9.52	13.29
$\Delta G_{F\text{-}Br}$ (kcal/mol)	10.68	14.08

Table S3. Calculated Free Energy Change for the Halogen Exchange Reaction

$$Me_3SiF + AlX_3 \longrightarrow AlX_2F + Me_3SiX$$

X = Cl, Br, I

	CBS-QB3	B3LYP
$\Delta G_{F\text{-}Cl}$ (kcal/mol)	3.38	2.42
$\Delta G_{F\text{-}Br}$ (kcal/mol)	3.71	2.97

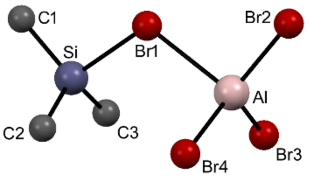
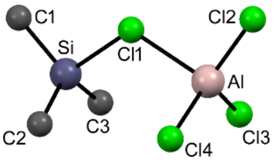
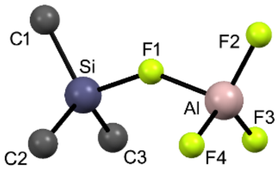
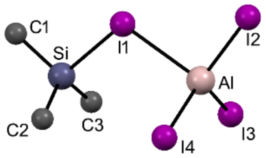
Table S4: B3LYP optimized coordinates for $Me_3Si–Br–AlBr_3$			
			
Si	0.272000	3.091000	0.000000
C	1.262000	2.931000	1.570000
H	1.956000	3.776000	1.641000
H	0.617000	2.947000	2.451000
H	1.845000	2.009000	1.593000
C	-0.933000	4.516000	0.000000
H	-0.375000	5.460000	0.000000
H	-1.571000	4.504000	-0.886000
H	-1.571000	4.504000	0.886000
C	1.262000	2.931000	-1.570000
H	0.617000	2.947000	-2.451000
H	1.956000	3.776000	-1.641000
H	1.845000	2.009000	-1.593000
Br	-1.241000	1.195000	0.000000
Br	-1.822000	-2.538000	0.000000
Br	1.262000	-1.076000	-1.942000
Br	1.262000	-1.076000	1.942000
Al	0.015000	-1.163000	0.000000

Table S5: B3LYP optimized coordinates for $Me_3Si–Cl–AlCl_3$			
			
Si	0.127000	2.448000	0.000000
C	1.115000	2.332000	1.571000

H	1.762000	3.212000	1.655000
H	0.464000	2.305000	2.448000
H	1.745000	1.441000	1.590000
C	-1.184000	3.772000	0.000000
H	-0.706000	4.758000	0.000000
H	-1.819000	3.705000	-0.886000
H	-1.819000	3.705000	0.886000
C	1.115000	2.332000	-1.571000
H	0.464000	2.305000	-2.448000
H	1.762000	3.212000	-1.655000
H	1.745000	1.441000	-1.590000
Al	-0.042000	-1.597000	0.000000
Cl	-1.156000	0.580000	0.000000
Cl	1.115000	-1.502000	1.791000
Cl	1.115000	-1.502000	-1.791000
Cl	-1.726000	-2.882000	0.000000

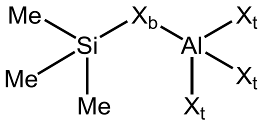
<table>
<tr><td colspan="4">Table S6: B3LYP optimized coordinates for $Me_3Si–F–AlF_3$</td></tr>
<tr><td colspan="4">
</td></tr>
<tr><td>Si</td><td>-0.061000</td><td>1.653000</td><td>0.000000</td></tr>
<tr><td>C</td><td>0.927000</td><td>1.793000</td><td>1.568000</td></tr>
<tr><td>H</td><td>1.357000</td><td>2.796000</td><td>1.656000</td></tr>
<tr><td>H</td><td>0.304000</td><td>1.614000</td><td>2.448000</td></tr>
<tr><td>H</td><td>1.745000</td><td>1.069000</td><td>1.584000</td></tr>
<tr><td>C</td><td>-1.677000</td><td>2.574000</td><td>0.000000</td></tr>
<tr><td>H</td><td>-1.496000</td><td>3.654000</td><td>0.000000</td></tr>
<tr><td>H</td><td>-2.271000</td><td>2.336000</td><td>-0.886000</td></tr>
<tr><td>H</td><td>-2.271000</td><td>2.336000</td><td>0.886000</td></tr>
</table>

C	0.927000	1.793000	-1.568000
H	0.304000	1.614000	-2.448000
H	1.357000	2.796000	-1.656000
H	1.745000	1.069000	-1.584000
Al	0.021000	-1.798000	0.000000
F	-0.585000	-0.016000	0.000000
F	-1.409000	-2.669000	0.000000
F	0.927000	-1.770000	1.418000
F	0.927000	-1.770000	-1.418000

Table S7: B3LYP optimized coordinates for Me$_3$Si–I–AlI$_3$			
			
Si	0.413000	3.539000	0.000000
C	1.408000	3.340000	1.567000
H	2.137000	4.156000	1.630000
H	0.771000	3.385000	2.453000
H	1.953000	2.395000	1.589000
C	-0.677000	5.060000	0.000000
H	-0.043000	5.954000	0.000000
H	-1.314000	5.101000	-0.886000
H	-1.314000	5.101000	0.886000
C	1.408000	3.340000	-1.567000
H	0.771000	3.385000	-2.453000
H	2.137000	4.156000	-1.630000
H	1.953000	2.395000	-1.589000
Al	0.053000	-0.984000	0.000000
I	-1.337000	1.598000	0.000000
I	1.408000	-0.917000	2.128000

I	1.408000	-0.917000	-2.128000
I	-1.976000	-2.467000	0.000000

Table S8. Important Metrical Parameters for the DFT Optimized Structures of the Halosilane-Aluminium Trihalide Complexes



X = F, Cl, Br, I

	$Me_3Si–F–AlF_3$ (**X**)	$Me_3Si–Cl–AlCl_3$ (**X**)	$Me_3Si–Br–AlBr_3$ (**X**)	$Me_3Si–I–AlI_3$ (**X**)
		Bond Length (Å)		
Me–Si	1.859, 1.858, 1.858	1.863, 1.859, 1.859	1.867, 1.862, 1.862	1.871, 1.866, 1.866
Si–X_b	1.749	2.267	2.426	2.613
X_b–Al	1.882	2.445	2.672	2.933
Al–X_t	1.674, 1.682, 1.682	2.118, 2.134, 2.134	2.294, 2.309, 2.309	2.513, 2.523, 2.523
		Bond Angle (°)		
Si–X_b–Al	143.79	118.41	113.36	109.68
X_b–Al–X_t	102.55, 99.04, 99.04	100.24, 101.97, 101.97	98.77, 102.73, 102.73	97.67, 103.34, 103.34
Me–Si–X_b	102.25, 103.35, 103.35	100.79, 104.43, 104.43	101.19, 105.34, 105.34	102.32, 106.12, 106.12

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