Electronic Supplementary Material (ESI) for RSC Advances.

Tellurium-promoted stereoselective hydrodebromination of 1,1-dibromoalkenes: Synthesis of (*E*)-bromoalkenes

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Support Information

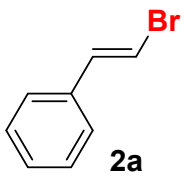
Contents

General Remarks

The reactions were monitored by low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 mass spectrometer. The *E*:*Z* ratio was determined by GC/MS for crude products. Baker silica gel (particle size 0.040-0.063 mm) was used for filtration. NMR spectra were recorded with Bruker DPX 400 (400 MHz) instrument using $CDCl_3$ as solvent and calibrated using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in ppm, coupling constants (*J*) are reported in Hertz. High resolution mass spectra (HRMS) were obtained for all compounds on a LTQ Orbitrap Discovery mass spectrometer (Thermo Scientific). This hybrid system meets the LTQ XL linear ion trap mass spectrometer and an Orbitrap mass analyzer.

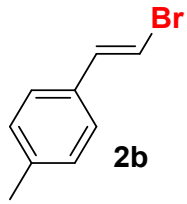
General procedure to hydrodebromination of 1,1-dibromoalkenes 1

Into the solution of powdered tellurium (0.064 g, 0.05 mmol) in ethanol (1.0 mL) under argon atmosphere, $NaBH_4$ (0.027 g, 0.7 mmol) was added at 50 °C and the mixture was stirred for 0.5 h. The tellurium reduction reaction was accompanied by change of colors. Initially, the color of solution gradually changes of grey suspension to pale purple and finally colorless. After this, the mixture was cooled at room temperature and 1,1-dibromoalkene[1] **1** (0.5 mmol) was added and the temperature was maintained at same temperature. The reaction progress was monitored by CG. After the time indicated in Table 2, the reaction mixture was quenched with water (10.0 mL) and extracted with ethyl acetate (3x 15.0 mL). The organic phase was separated, dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was isolated by filtration using silica gel 60 Å (0.060-0.200 mm-Across) and hexane (100 mL) as eluent. The compounds were characterized and the spectral data are listed below:



2a

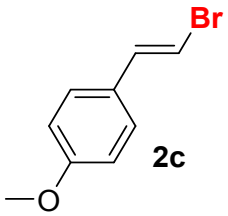
(2-Bromovinyl)benzene **2a**:[2] Yield: 0.082 g (90%); *E*:*Z* ratio = 96:4; colorless oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.15 (m, 5H); 7.02 (d, *J* = 14.4 Hz, 1H); 6.67 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.0, 128.8, 128.2, 126.1, 106.5. MS (rel. int.) *m*/*z*: 184 [$(M+2)^+$, 57.9], 182 (M^+, 60.5), 103 (100.0), 77 (58.4). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 184 [$(M+2)^+$, 57.9], 182 (M^+, 58.7), 103 (100.0), 77 (60.7).



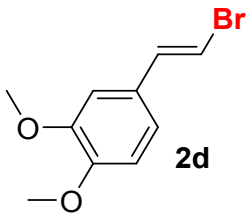
2b

1-(2-Bromovinyl)-4-methylbenzene **2b**:[2b,c,3] Yield: 0.085 g (87%); *E*:*Z* ratio = 97:3; white solid. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 2H), 7.03

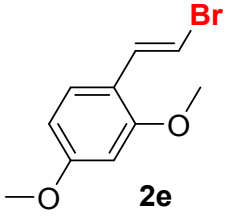
(d, *J* = 8.4 Hz, 2H); 6.98 (d, *J* = 14.0 Hz, 1H); 6.60 (d, *J* = 14.0 Hz, 1H); 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.0, 133.2, 129.5, 126.0, 105.4, 21.2. MS (rel. int.) *m*/*z*: 198 [$(M+2)^+$, 80.8], 196 (M^+, 86.2), 117 (100.0), 115 (83.3), 91 (39.8). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 198 [$(M+2)^+$, 64.3], 196 (M^+, 65.3), 117 (100.0), 115 (82.7), 91 (34.6).



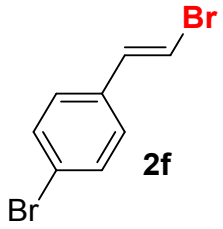
1-(2-Bromovinyl)-4-methoxybenzene **2c**:[2b,c,3] Yield: 0.101 g (95%); *E*:*Z* ratio = 96:4; white solid. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H); 6.94 (d, *J* = 14.0 Hz, 1H); 6.76 (d, *J* = 8.8 Hz, 2H); 6.51 (d, *J* = 14.0 Hz, 1H); 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 136.5, 128.8, 127.3, 114.2, 104.0, 55.3. MS (rel. int.) *m*/*z*: 214 [$(M+2)^+$, 94.2], 212 (M^+, 100.0), 199 (34.6), 197 (35.9), 133 (35.8), 118 (19.6), 90 (41.9). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 214 [$(M+2)^+$, 96.6], 212 (M^+, 100.0), 199 (37.7), 197 (38.1), 133 (44.0), 118 (24.1), 90 (51.3).



4-(2-Bromovinyl)-1,2-dimethoxybenzene **2d**:[4] Yield: 0.106 g (87%); *E*:*Z* ratio = 99:1; yellowish oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 14.0 Hz, 1H); 6.78-6.71 (m, 3H); 6.54 (d, *J* = 14.0 Hz, 1H); 3.80 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 149.2, 136.8; 129.0, 119.3, 111.3, 108.7, 104.2, 55.9, 55.8. MS (rel. int.) *m*/*z*: 244 [$(M+2)^+$, 95.6], 242 (M^+, 100.0), 229 (37.0), 227 (38.1), 120 (86.8), 91 (32.9), 77 (21.2). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 244 [$(M+2)^+$, 85.1], 242 (M^+, 87.2), 229 (33.7), 227 (35.6), 120 (100.0), 91 (43.5), 77 (22.1).

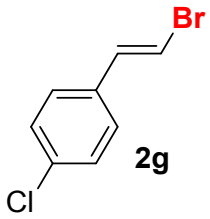


1-(2-Bromovinyl)-2,4-dimethoxybenzene **2e**: Yield: 0.097 g (80%); *E*:*Z* ratio = 93:7; yellowish oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 14.0 Hz, 1H); 7.05 (d, *J* = 8.4 Hz, 1H); 6.67 (d, *J* = 14.0 Hz, 1H); 6.36-6.34 (m, 2H); 3.72 (s, 3H); 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 157.9, 132.7, 128.8, 118.1, 105.4, 105.0, 98.7, 55.43, 55.39. MS (rel. int.) *m*/*z*: 244 [$(M+2)^+$, 79.3], 242 (M^+, 83.0), 163 (56.0), 148 (100.0), 133 (52.2), 121 (17.0), 105 (35.5), 91 (17.0), 77 (33.2). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 244 [$(M+2)^+$, 73.8], 242 (M^+, 77.0), 163 (64.0), 148 (100.0), 133 (50.1), 121 (15.8), 105 (34.3), 91 (15.5), 77 (30.1). HRMS (EI): *m*/*z* calcd for $C_{10}H_{12}BrO_2$ $[M+H]^+$: 243.0021; found: 243.0015.



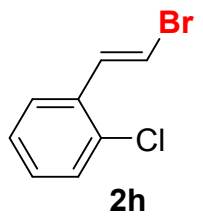
2f

1-Bromo-4-(2-bromovinyl)benzene **2f**:[2a] Yield: 0.118 g (91%); *E*:*Z* ratio = 97:3; yellowish solid. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H); 7.07 (d, *J* = 8.8 Hz, 2H); 6.95 (d, *J* = 14.0 Hz, 1H); 6.69 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 134.8, 131.9, 127.5, 122.2, 107.3. MS (rel. int.) *m*/*z*: 264 [$(M+4)^+$, 45.9], 262 [$(M+2)^+$, 95.5], 260 (M^+, 51.2), 183 (37.3), 181 (38.1), 102 (100.0). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 264 [$(M+4)^+$, 41.1], 262 [$(M+2)^+$, 85.7], 260 (M^+, 42.5), 183 (35.4), 181 (36.6), 102 (100.0).



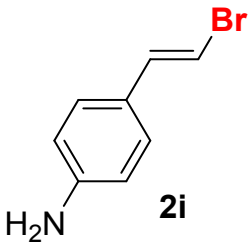
2g

1-(2-Bromovinyl)-4-chlorobenzene **2g**:[2a,b] Yield: 0.104 g (96%); *E*:*Z* ratio = 97:3; white solid. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H); 7.12 (d, *J* = 8.4 Hz, 2H); 6.96 (d, *J* = 14.4 Hz, 1H); 6.66 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 134.4, 134.0, 129.0, 127.3, 107.2. MS (rel. int.) *m*/*z*: 220 [$(M+4)^+$, 24.8], 218 [$(M+2)^+$, 100.0], 216 (M^+, 78.8), 137 (88.5), 102 (62.9), 75 (39.4). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 220 [$(M+4)^+$, 23.2], 218 [$(M+2)^+$, 93.0], 216 (M^+, 72.3), 137 (100.0), 102 (68.6), 75 (39.5).



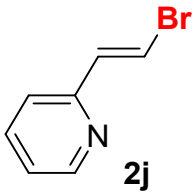
2h

1-(2-Bromovinyl)-2-chlorobenzene **2h**:[2b] Yield: 0.097 g (90%); *E*:*Z* ratio = 96:4; colorless oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 14.0 Hz, 1H); 7.30-7.25 (m, 2H); 7.15-7.11 (m, 2H); 6.70 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.8, 132.5, 129.9, 129.3, 126.99, 126.95, 109.2. MS (rel. int.) *m*/*z*: 220 [$(M+4)^+$, 10.2], 218 [$(M+2)^+$, 40.5], 216 (M^+, 31.6), 137 (100.0), 102 (39.9), 75 (31.3). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 220 [$(M+4)^+$, 9.2], 218 [$(M+2)^+$, 36.4], 216 (M^+, 27.4), 137 (100.0), 102 (40.8), 75 (30.2).



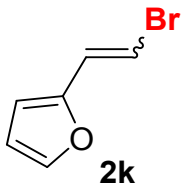
2i

(*E*)-4-(2-bromovinyl)aniline **2i**: Yield: 0.050 g (51%); *E*:*Z* ratio = 94:6; orange solid. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$ and DMSO-d_6) δ 7.00 (d, *J* = 7.6 Hz, 2H); 6.85 (d, *J* = 13.6 Hz, 1H); 6.57 (d, *J* = 13.6 Hz, 1H); 6.47 (d, *J* = 7.6 Hz, 2H); 5.06 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$ and DMSO-d_6) δ 147.1, 135.3, 125.4, 121.8, 112.1, 99.1. MS (rel. int.) *m*/*z*: 199 [$(M+2)^+$, 95.5], 197 (M^+, 100.0), 118 (98.5), 91 (50.4), 75 (3.3). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 199 [$(M+2)^+$, 71.9], 197 (M+, 77.7), 118 (100.0), 91 (46.4), 75 (4.2). HRMS (EI): *m*/*z* calcd for C_8H_8BrN $[M+H]^+$: 197.9913; found: 197.9939.



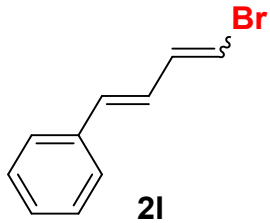
2j

2-(2-Bromovinyl)pyridine **2j**: Yield: 0.062 g (68%); *E*:*Z* ratio = 98:2; yellowish oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 1H); 7.56 (td, *J* = 7.6 Hz and 1.6 Hz, 1H); 7.31 (d, *J* = 13.6 Hz, 1H); 7.11-7.07 (m, 2H); 7.06 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.7, 136.7, 136.5, 122.7, 121.7, 112.7. MS (rel. int.) *m*/*z*: 185 [$(M+2)^+$, 14.1], 183 (M^+, 14.8), 104 (100.0), 78 (38.4). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 185 [$(M+2)^+$, 10.9], 183 (M^+, 11.4), 104 (100.0), 78 (35.9). HRMS (EI): *m*/*z* calcd for C_7H_6BrN $[M+H]^+$: 183.9762; found: 183.9766.



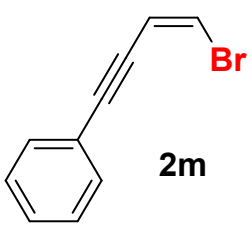
2k

2-(2-Bromovinyl)furane **2k**:[2c] Yield: 0.046 g (53%); *E*:*Z* ratio = 74:26; yellowish oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1,6 Hz, 1H); 6.81 (d, *J* = 14.0 Hz, 1H); 6.64 (d, *J* = 14.0 Hz, 1H); 6.29 (dd, *J* = 3.2 Hz and 1.6 Hz, 1H); 6.18 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 142.6, 125.5, 111.3, 108.6, 105.3. MS (rel. int.) *m*/*z*: 174 [$(M+2)^+$, 96.8], 172 (M^+, 100.0), 93 (22.3), 65 (96.9). (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (d, *J* = 1.6 Hz, 1H); 7.00 (d, *J* = 3.2 Hz, 1H); 6.97 (d, *J* = 8.4 Hz, 1H); 6.40 (dd, *J* = 3.2 Hz and 1.6 Hz, 1H); 6.23 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 142.1, 122.2, 111.6, 111.4, 104.2. MS (rel. int.) *m*/*z*: 174 [$(M+2)^+$, 94.8], 172 (M^+, 100.0), 93 (20.2), 65 (89.0).



2l

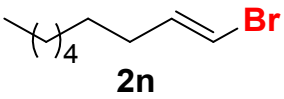
[(1*E*)-4-Bromobuta-1,3-dien-1-yl]benzene **2l**:[5] Yield: 0.098 g (94%); *E*:*Z* ratio = 78:22; yellowish solid. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.14 (m, 5H); 6.78 (dd, *J* = 13.4 Hz and 10.4 Hz, 1H); 6.57 (dd, *J* = 15.6 Hz and 10.4 Hz, 1H); 6.47 (d, *J* = 15.6 Hz, 1H); 6.32 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.7, 133.3, 128.7, 128.0, 126.5, 126.0, 108.9. MS (rel. int.) *m*/*z*: 210 [$(M+2)^+$, 22.6], 208 (M^+, 23.2), 129 (100.0), 102 (10.5), 77 (13.9). (*Z*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H); 7.30-7.14 (m, 3H); 7.02 (ddd, *J* = 16.0 Hz, 10.4 Hz and 1.2 Hz, 1H); 6.69 (ddd, *J* = 10.4 Hz, 7.2 Hz and 0.8 Hz, 1H); 6.65 (d, *J* = 16 Hz, 1H); 6.13 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.1, 132.7, 128.7, 128.3, 126.8, 124.4, 108.5. MS (rel. int.) *m*/*z*: 210 [$(M+2)^+$, 19.1], 208 (M^+, 19.7), 129 (100.0), 102 (9.4), 77 (12.7).



2m

(*Z*)-(4-bromobut-3-en-1-yn-1-yl)benzene **2m**:[6] Yield: 0.093 g (90%); *E*:*Z* ratio = 95:5; colorless oil. (*Z*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H); 7.27-7.24 (m, 3H); 6.55 (d, *J* = 7.6 Hz, 1 H); 6.44 (d, *J* = 7.6 Hz, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 131.7, 128.8, 128.4, 122.7, 117.8, 115.7, 97.1, 85.2 MS (rel. int.) *m*/*z*: 208 [(M+2)$^+$, 66.1], 206 (M$^+$, 70.5), 127 (100.0), 101 (10.0), 77 (29.1). (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H); 7.27-7.24 (m, 3H); 6.70 (d, *J* = 14.0 Hz, 1 H); 6.35 (d, *J* = 14.0 Hz, 1H). HRMS (EI): *m*/*z* calcd for $C_{10}H_7Br$ [M+H]$^+$: 206.9804; found: 206.9843.

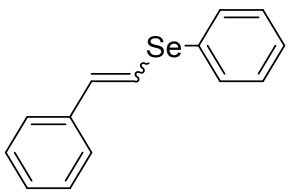


2n

(*E*/*Z*)1-Bromonon-1-ene **2n**:[2a] Yield: 0.066 g (65%); *E*:*Z* ratio = 51:49; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13-5.91 (m, 4H) 2.15-1.93 (m, 4H); 1.37-1.20 (m, 20H); 0.83-0.80 (m, 6H). (*E*)-isomer: MS (rel. int.) *m*/*z*: 206 [(M+2)$^+$, 7.2], 204 (M$^+$, 7.3), 125 (5.1), 83 (50.9), 81 (8.0), 69 (100.0), 43 (96.8), 41 (58.0). (*Z*)-isomer: MS (rel. int.) *m*/*z*: 206 [(M+2)$^+$, 5.4], 204 (M$^+$, 5.4), 125 (4.5), 83 (48.6), 81 (7.2), 69 (93.0), 43 (100.0), 41 (54.1).

General procedure to synthesis of (*E*)-phenylselenoalkene 3

To a solution of diphenyl diselenide **4** (0.3 mmol) in PEG-400 (1.0 mL) under Ar atmosphere, $NaBH_4$ (0.034 g, 0.9 mmol) was added at room temperature and the mixture was stirred for 0.5 h. Then, the 1,1-bromoalkene **2a** (0.5 mmol) was added and the temperature was slowly raised to 120 ºC and stirred for 4 h. The reaction progress was monitored by TLC. The reaction mixture was quenched with water (10.0 mL) and extracted with ethyl acetate (3x 15.0 mL). The organic phase was separated, dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was isolated by column chromatography using silica gel 60 Å (0.060-0.200 mm-Across) and hexane as the eluent. The compound was characterized and the spectral data are listed below:



3a

Phenyl(styryl)selane **3a**:[7] Yield: 0.094 g (72%); *E*:*Z* ratio = 95:5; yellowish oil. (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H); 7.33-7.27 (m, 7H); 7.24-7.21 (m, 1H); 7.16 (d, *J* = 15.7 Hz, 1H); 6.86 (d, *J* = 15.7 Hz, 1H). MS (rel. int.) *m*/*z*: 260 (M$^+$, 84.7), 180 (100.0), 169 (32.2), 102 (32.8), 77 (79.1). (*Z*)-isomer: *m*/*z*: 260 (M$^+$, 74.8), 180 (100.0), 169 (30.4), 102 (35.1), 77 (88.4).

References

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Selected Spectra

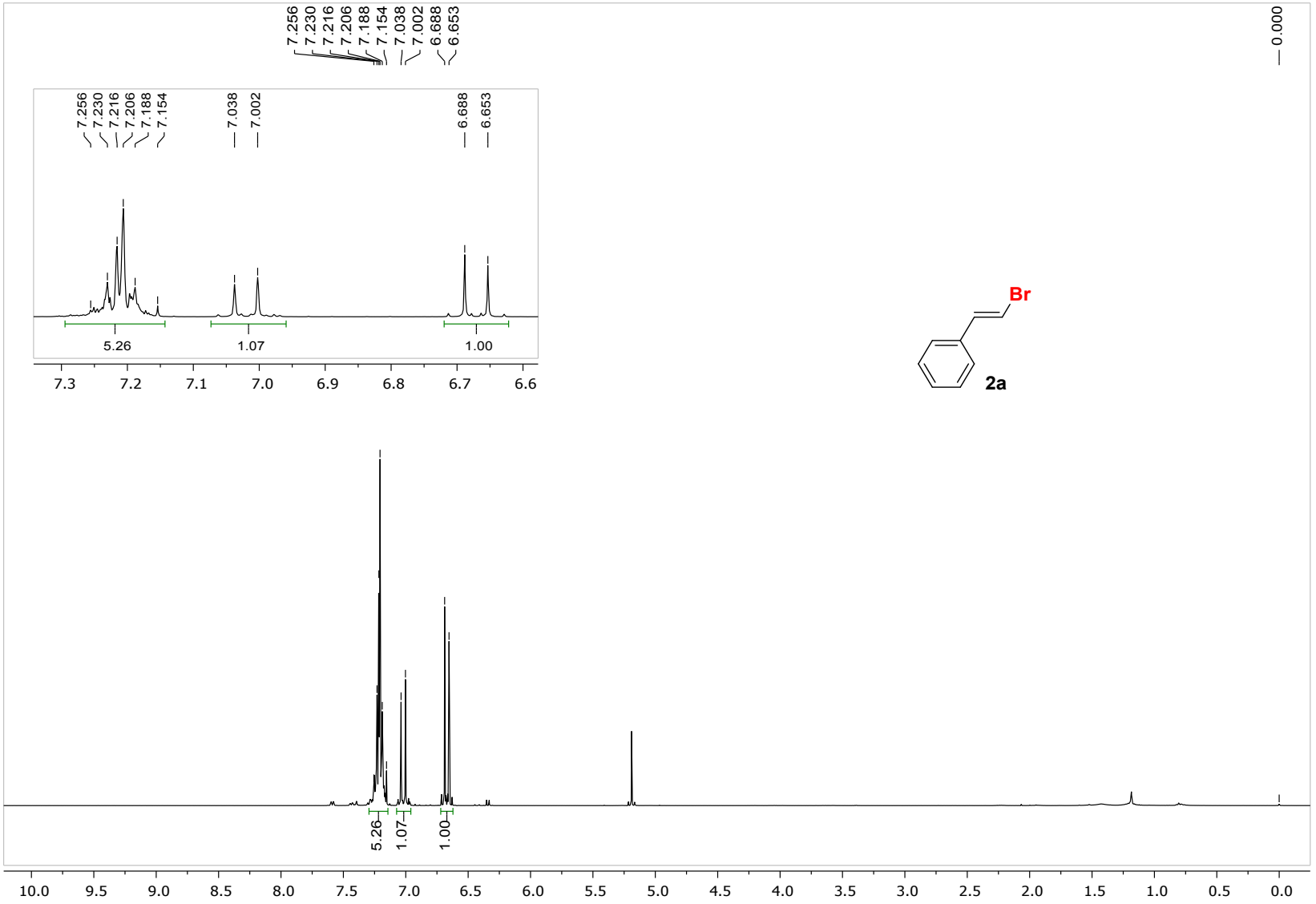

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2a**.

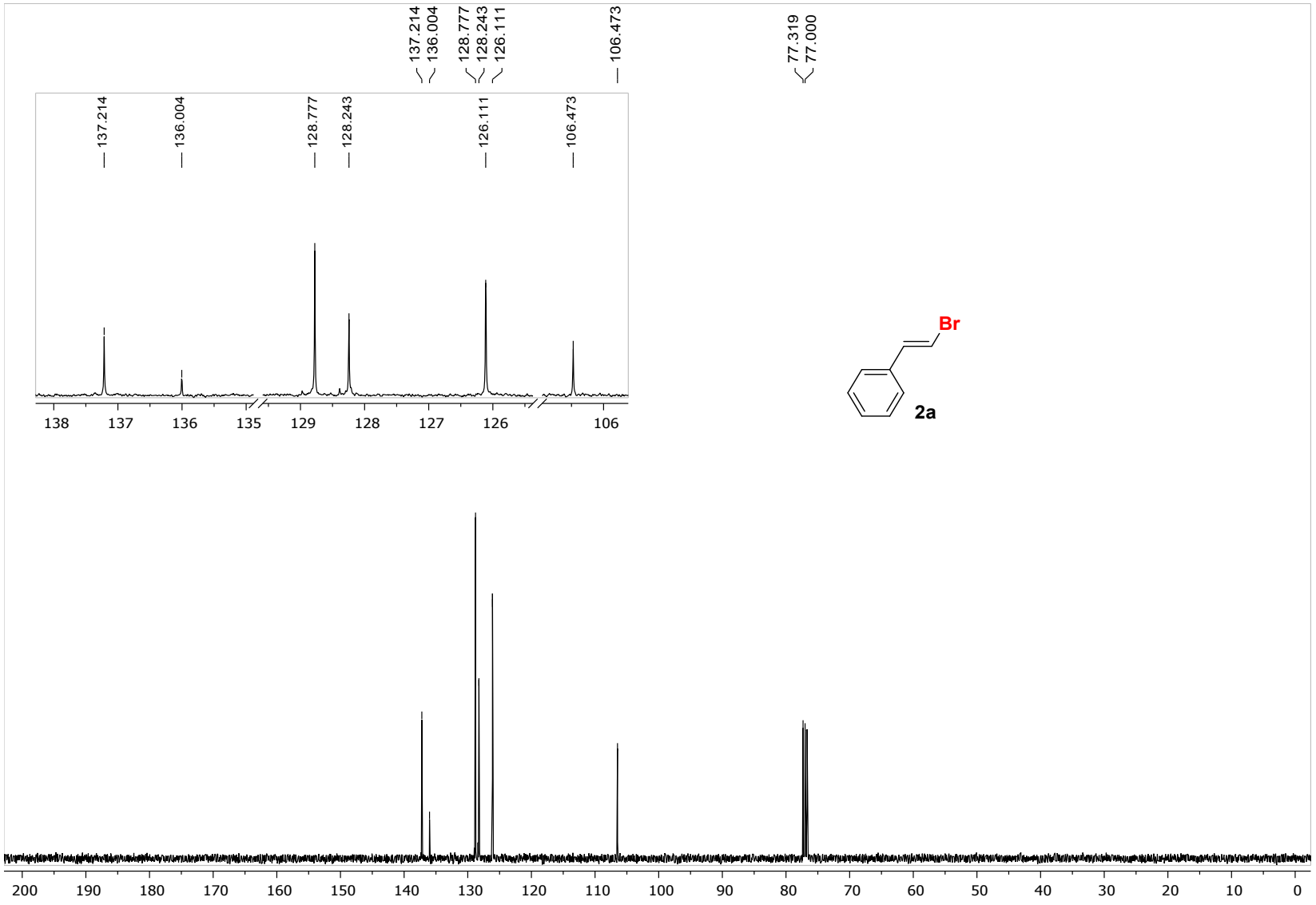

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2a**.

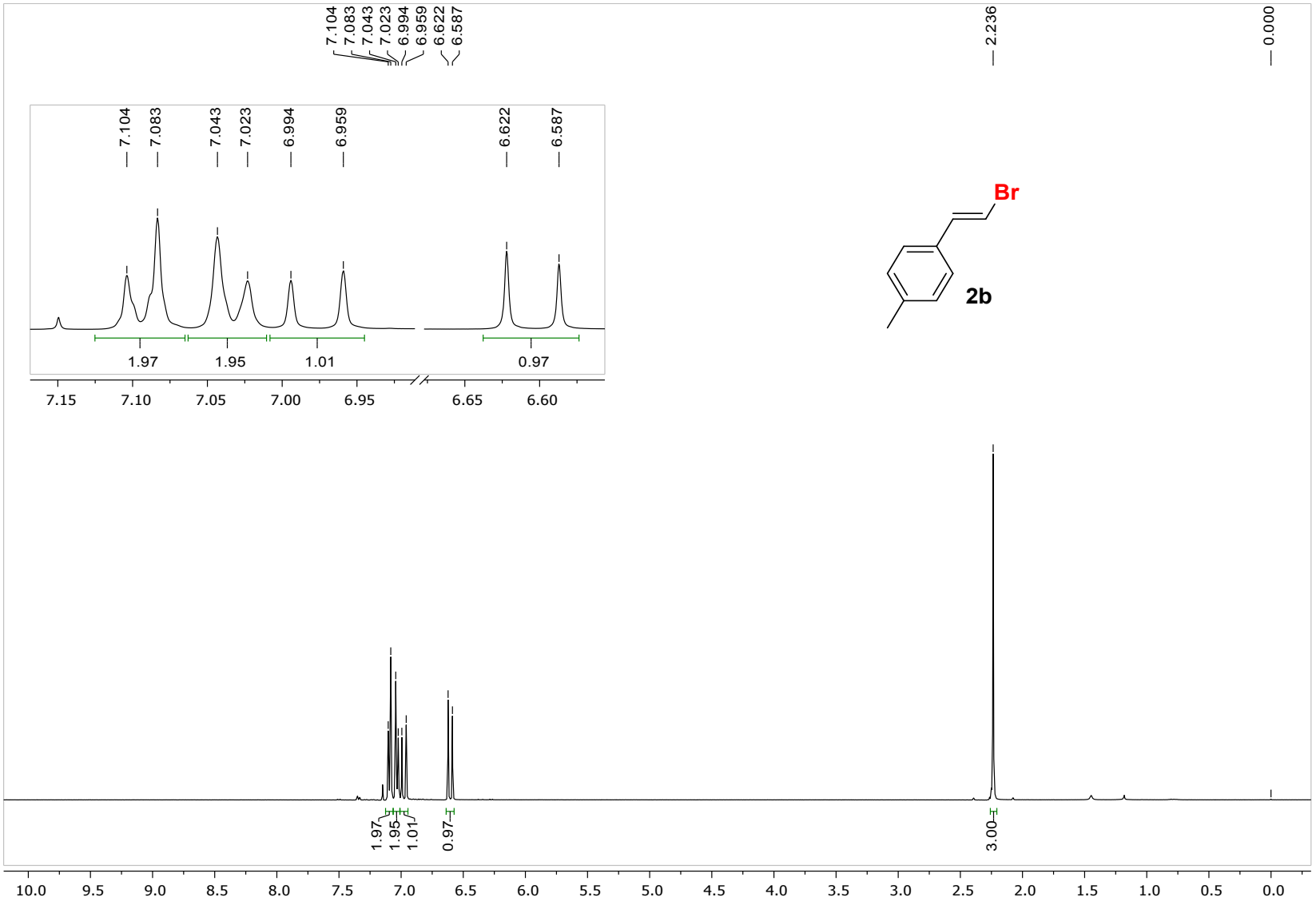

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2b**.

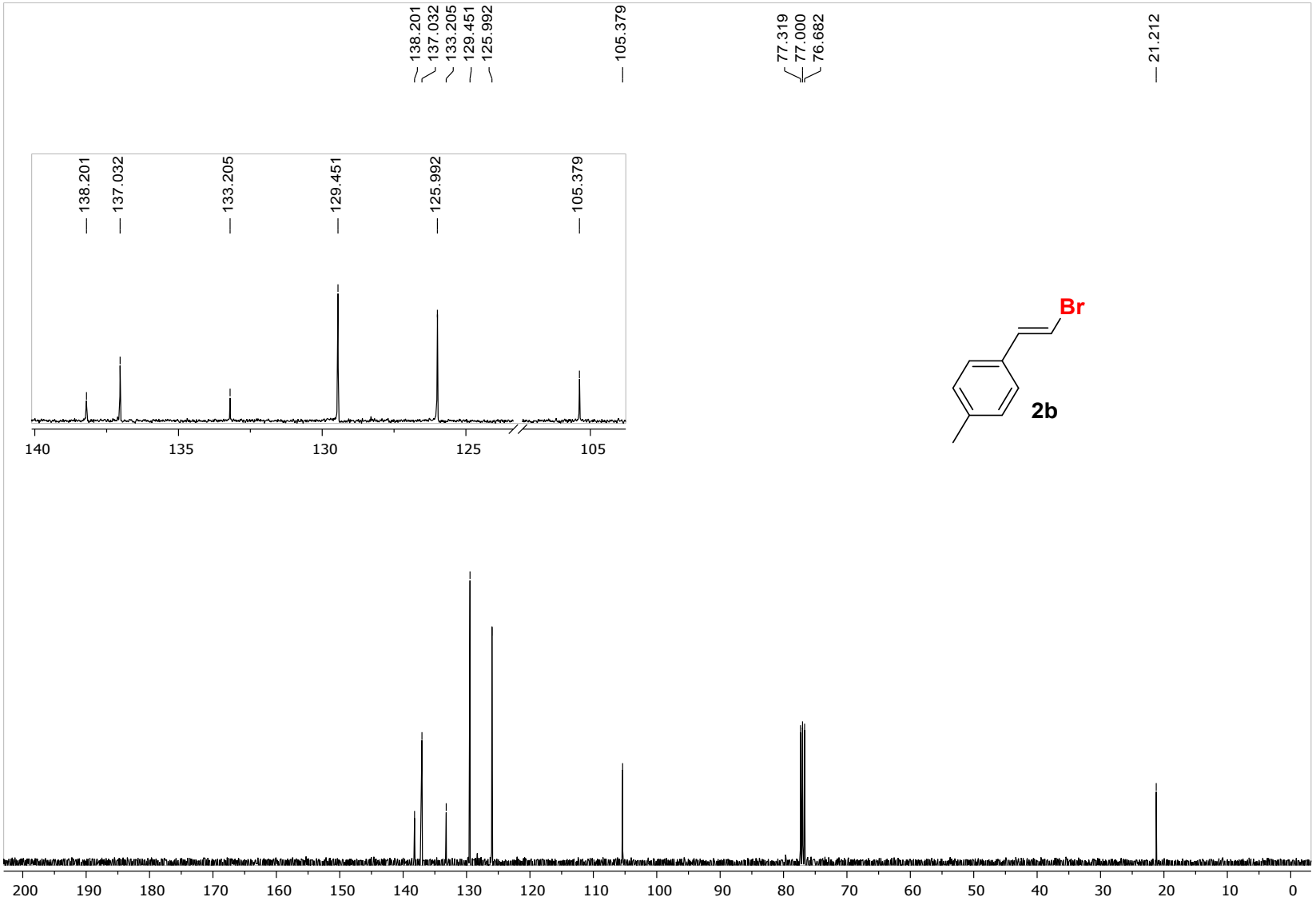

Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2b**.

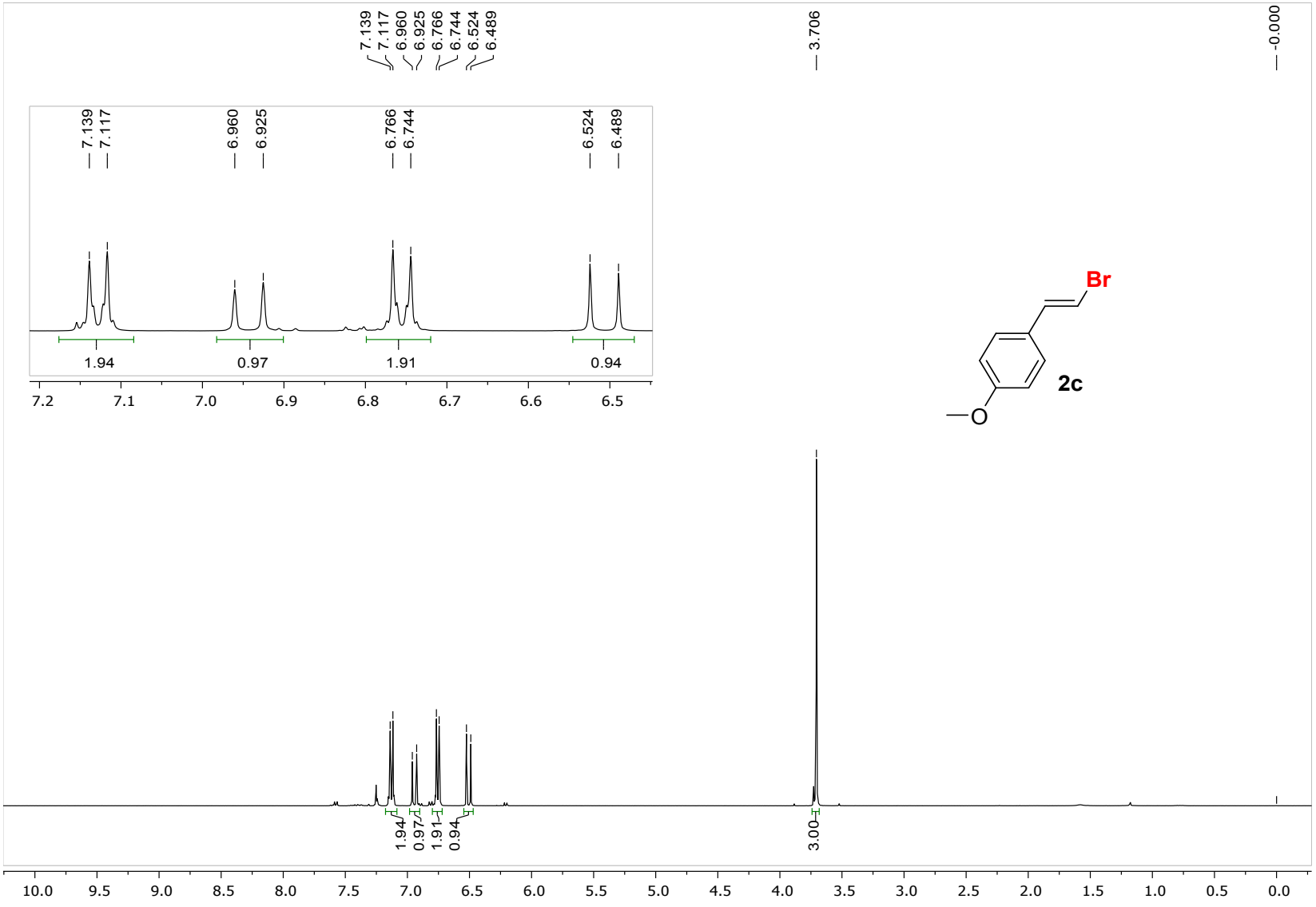

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2c**.

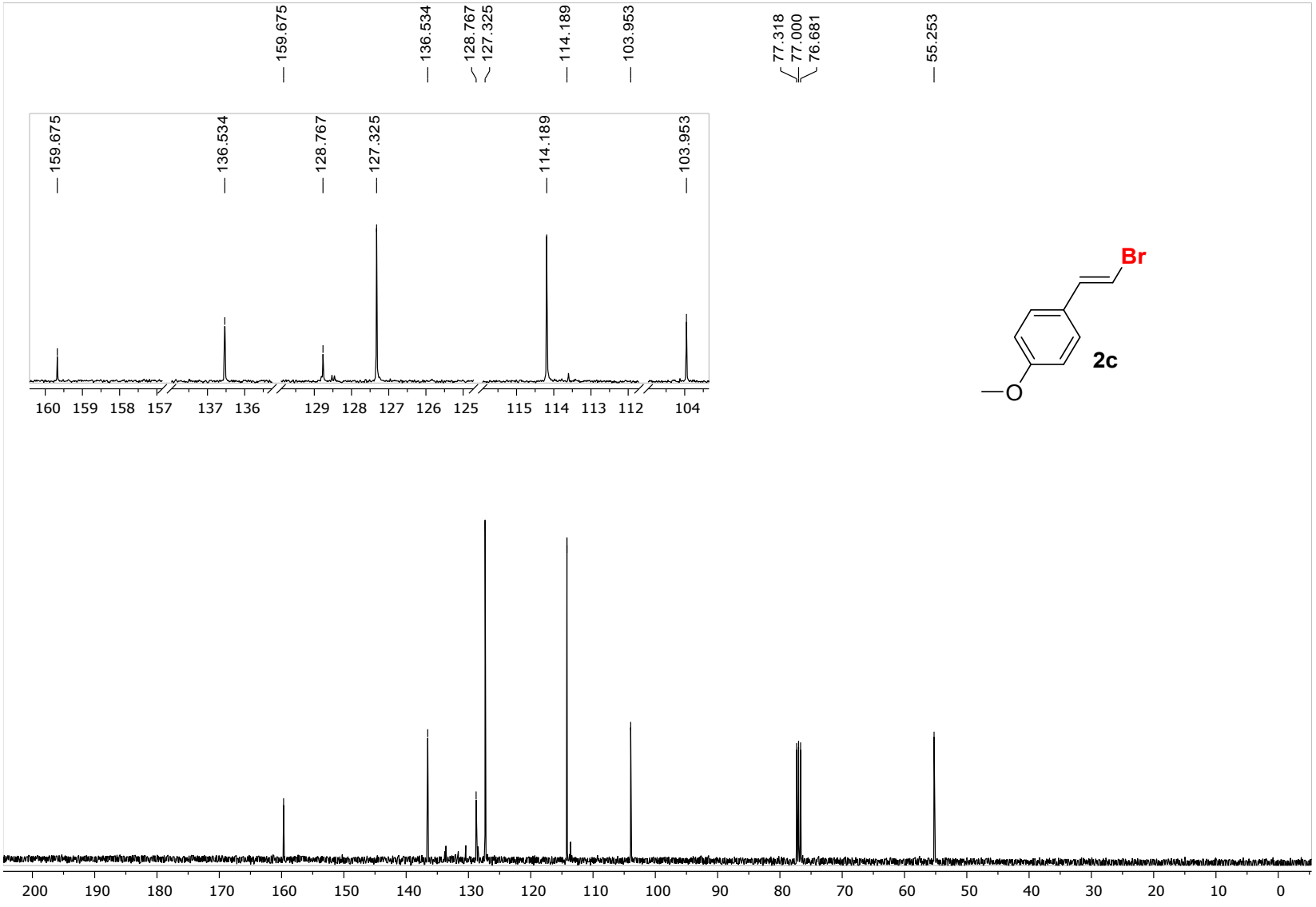

Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2c**.

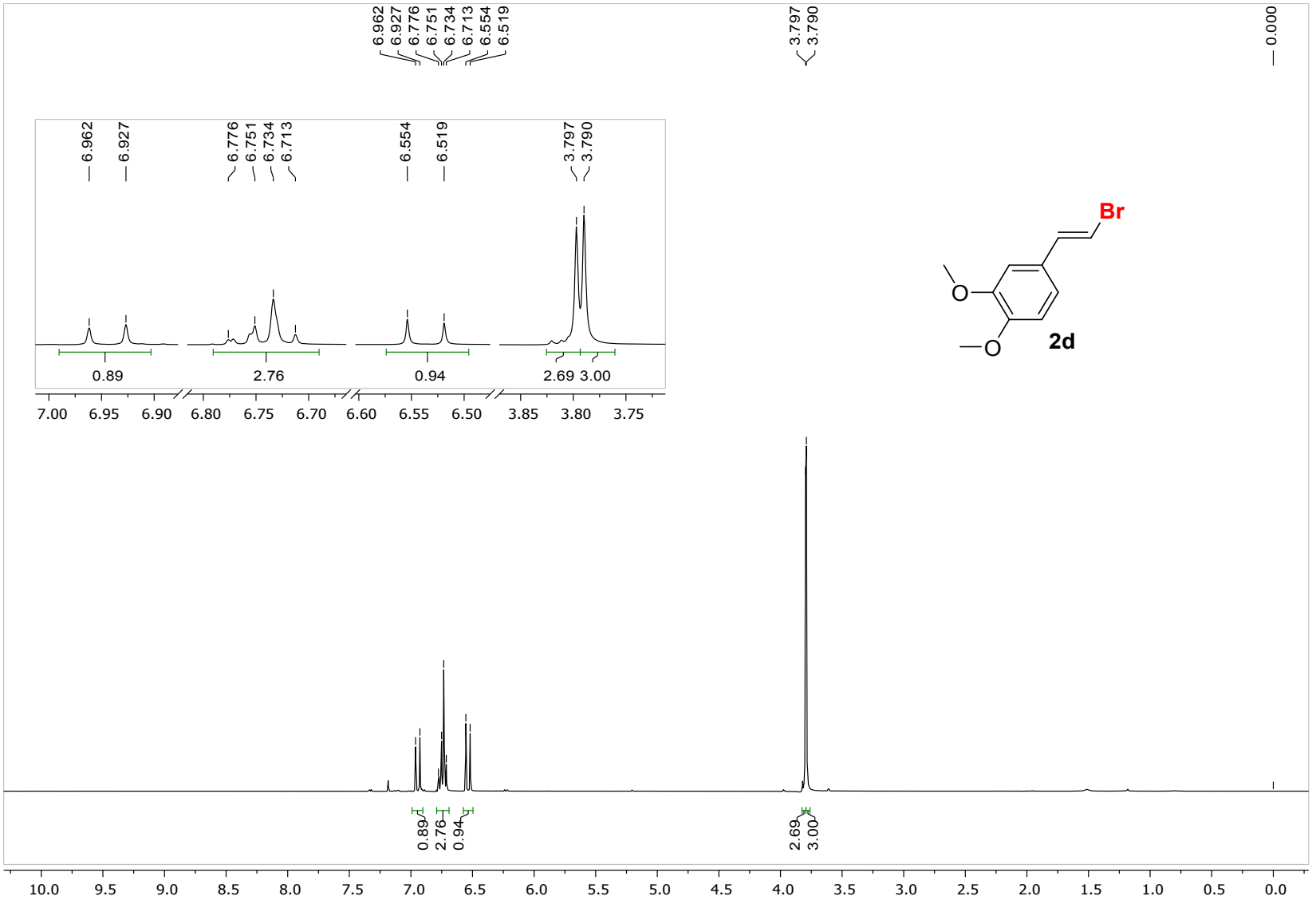

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2d**.

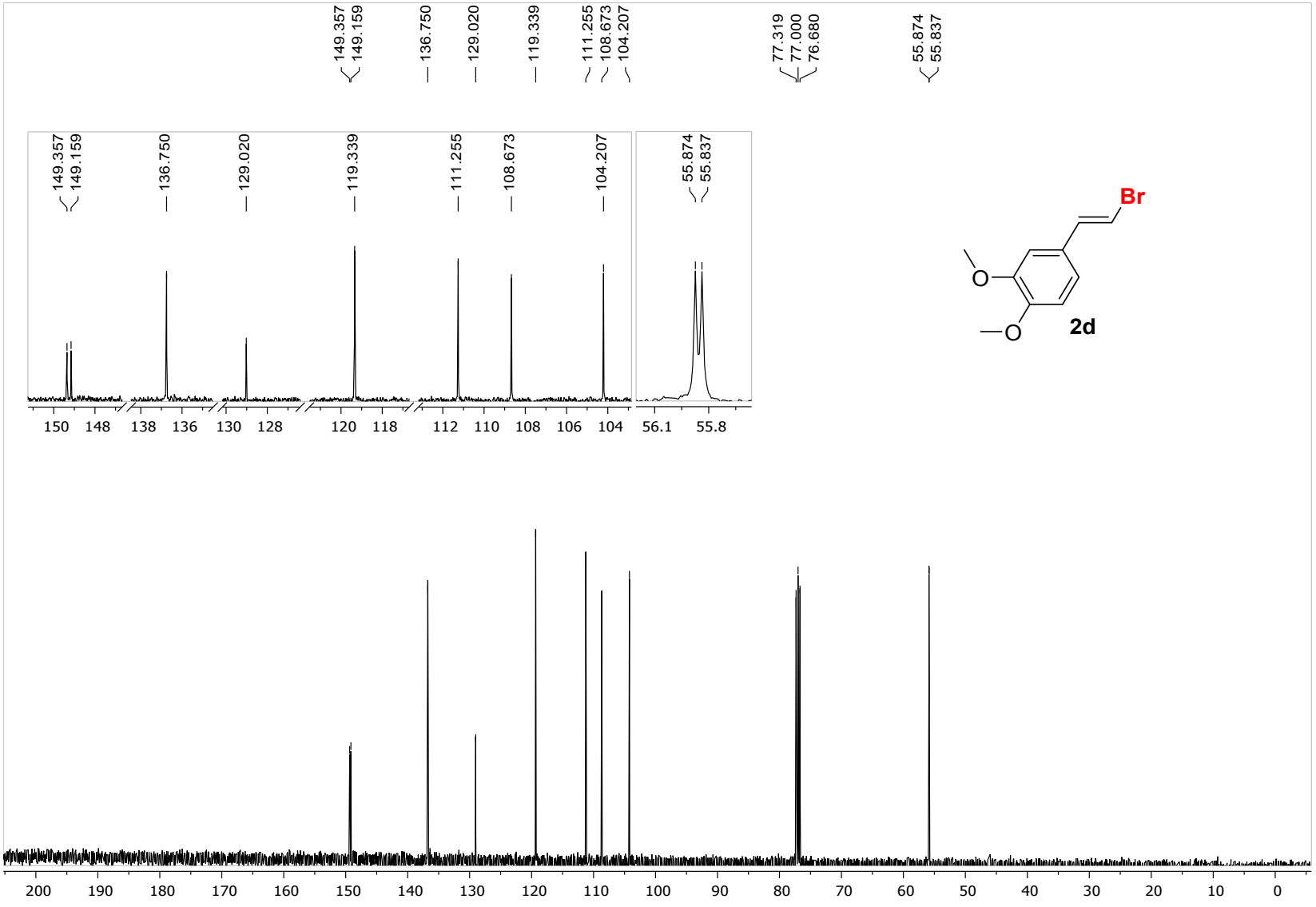

Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2d**.

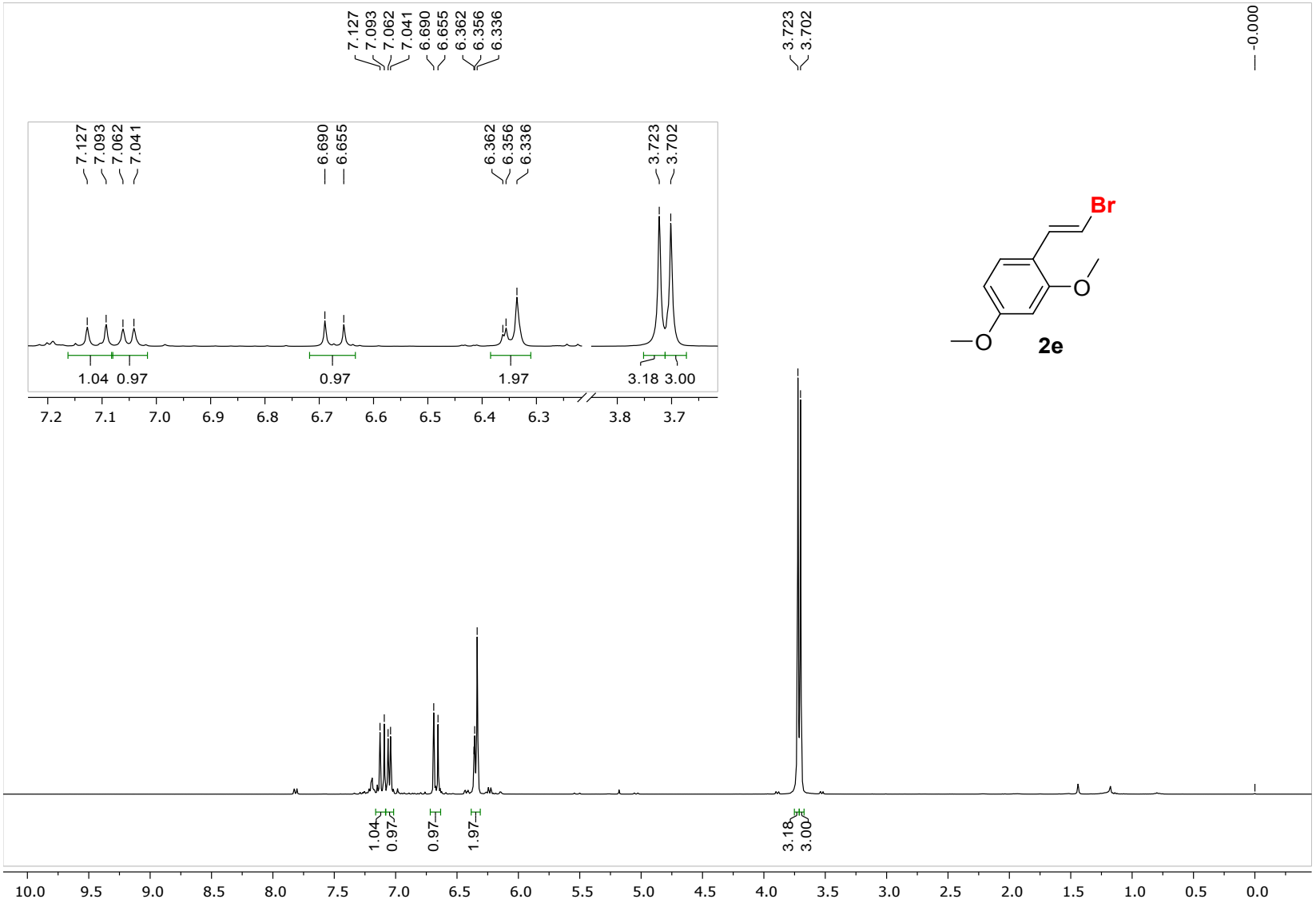

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2e**.

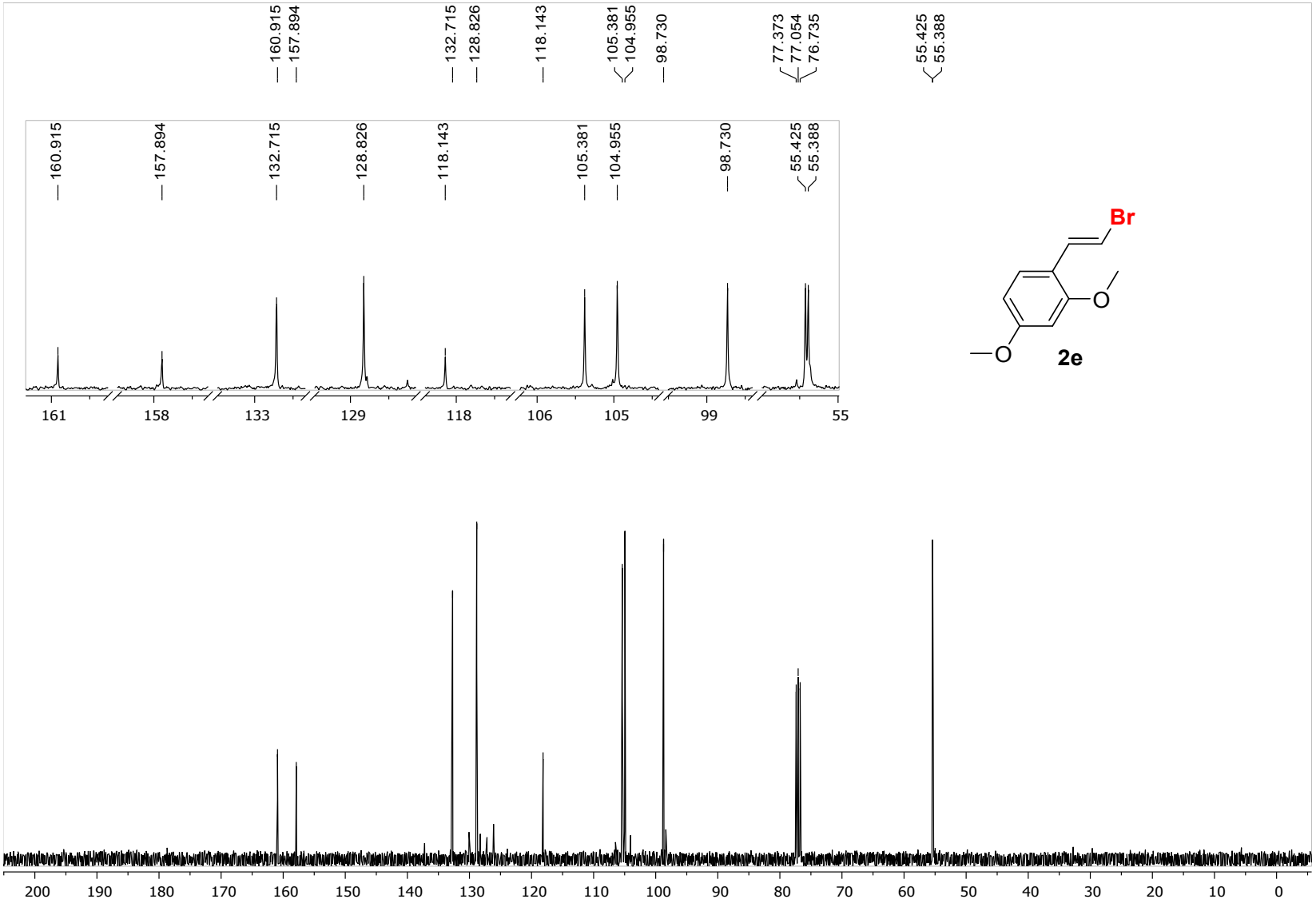

Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2e**.

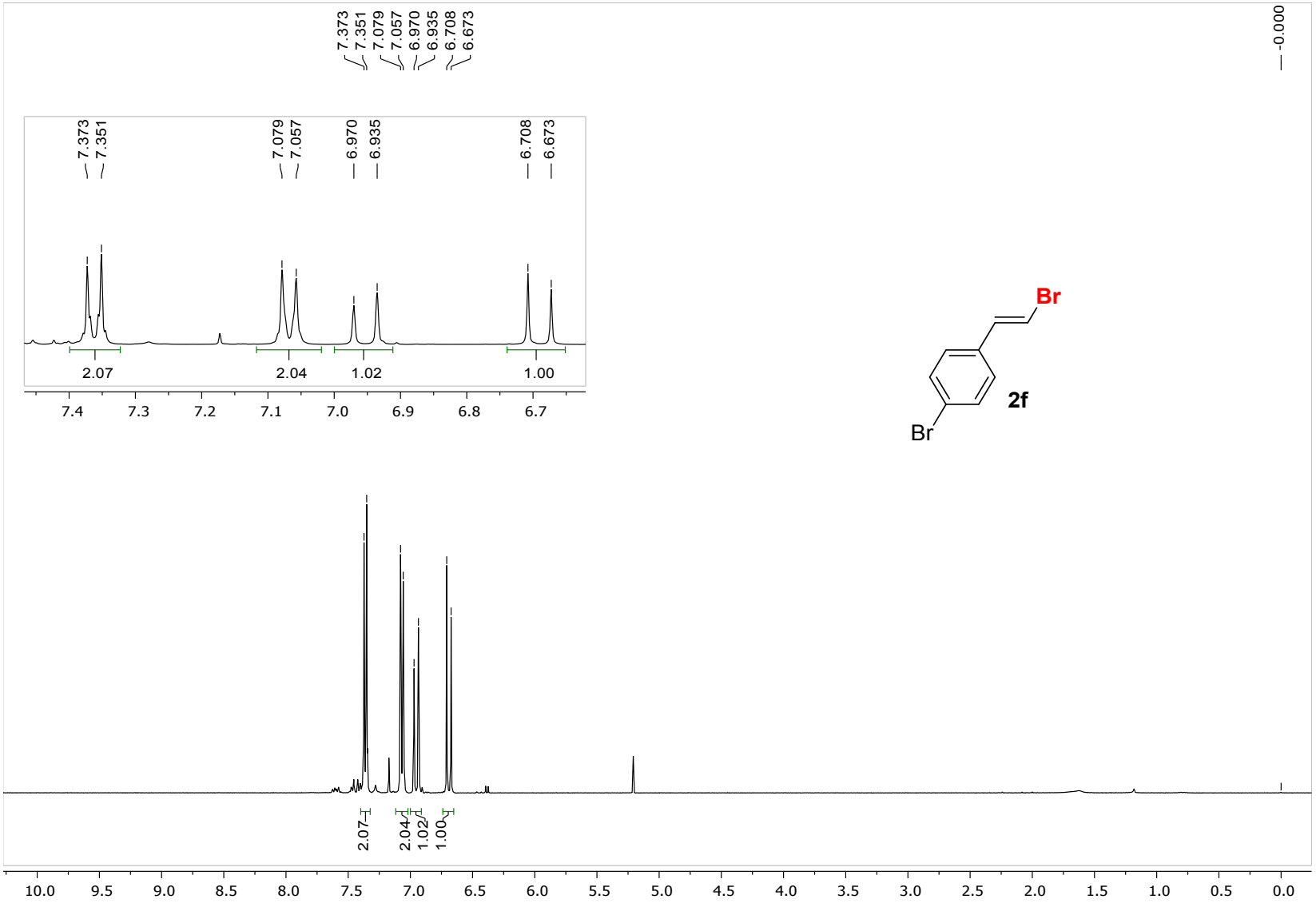

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2f**.

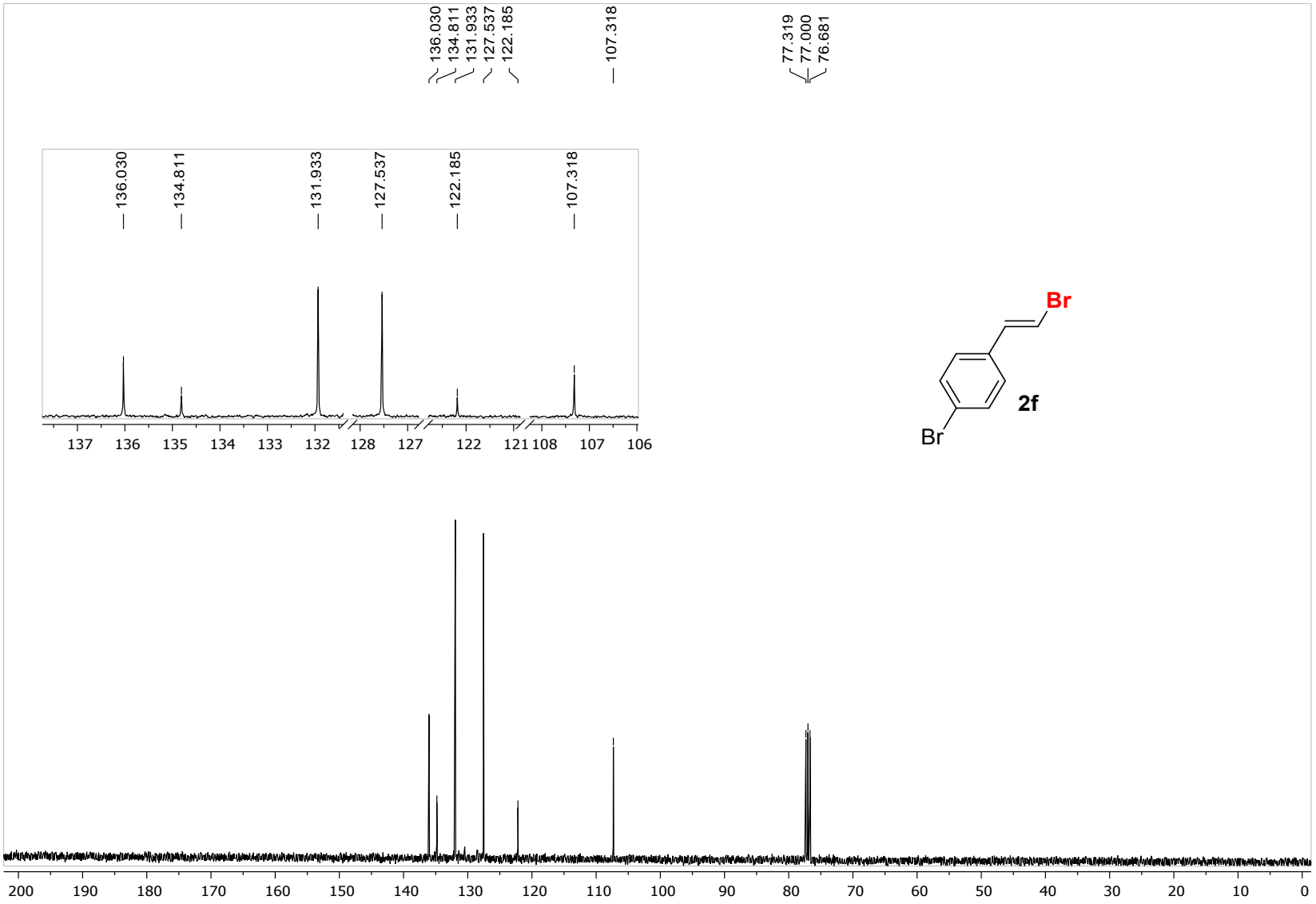

Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2f**.

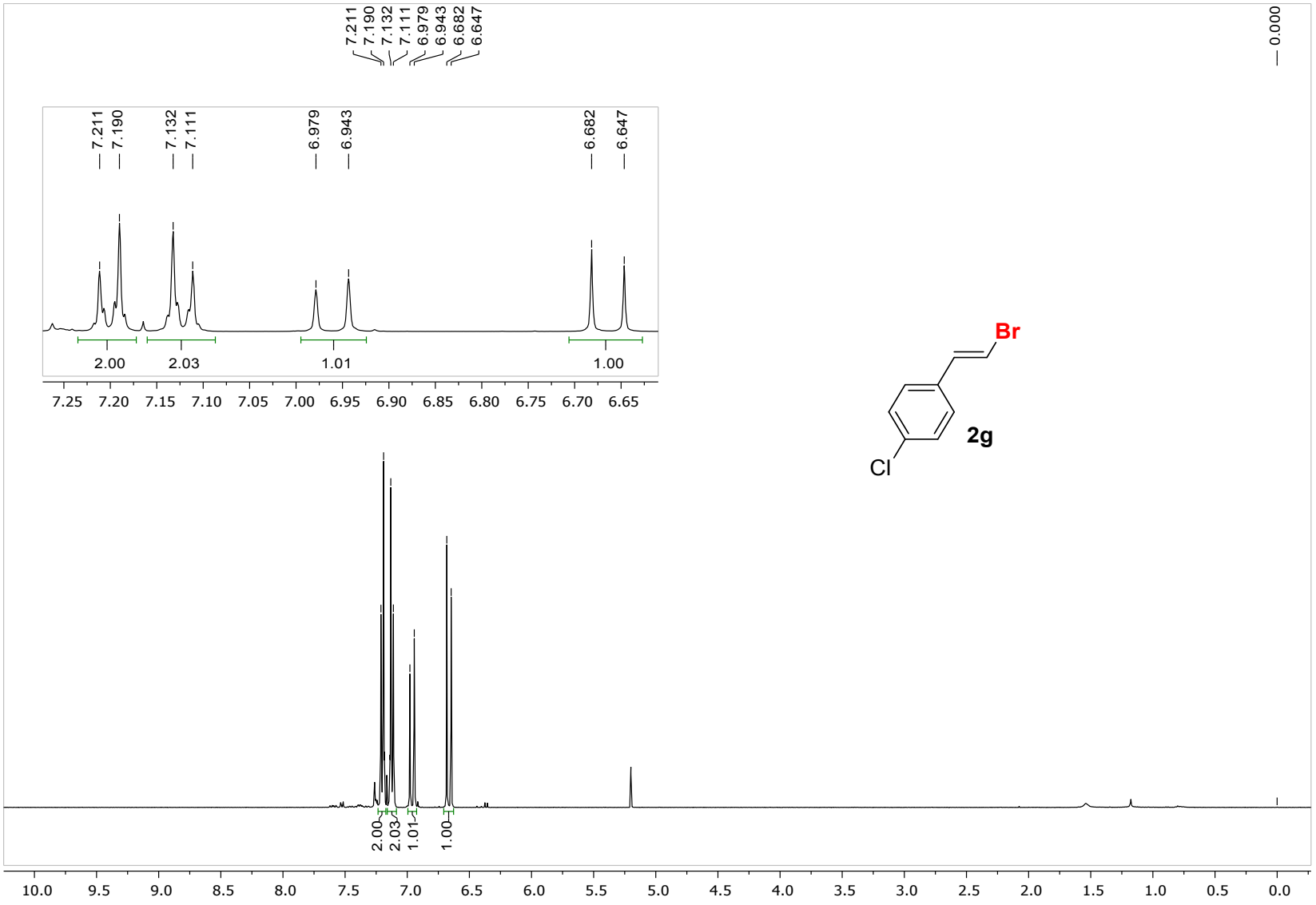

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2g**.

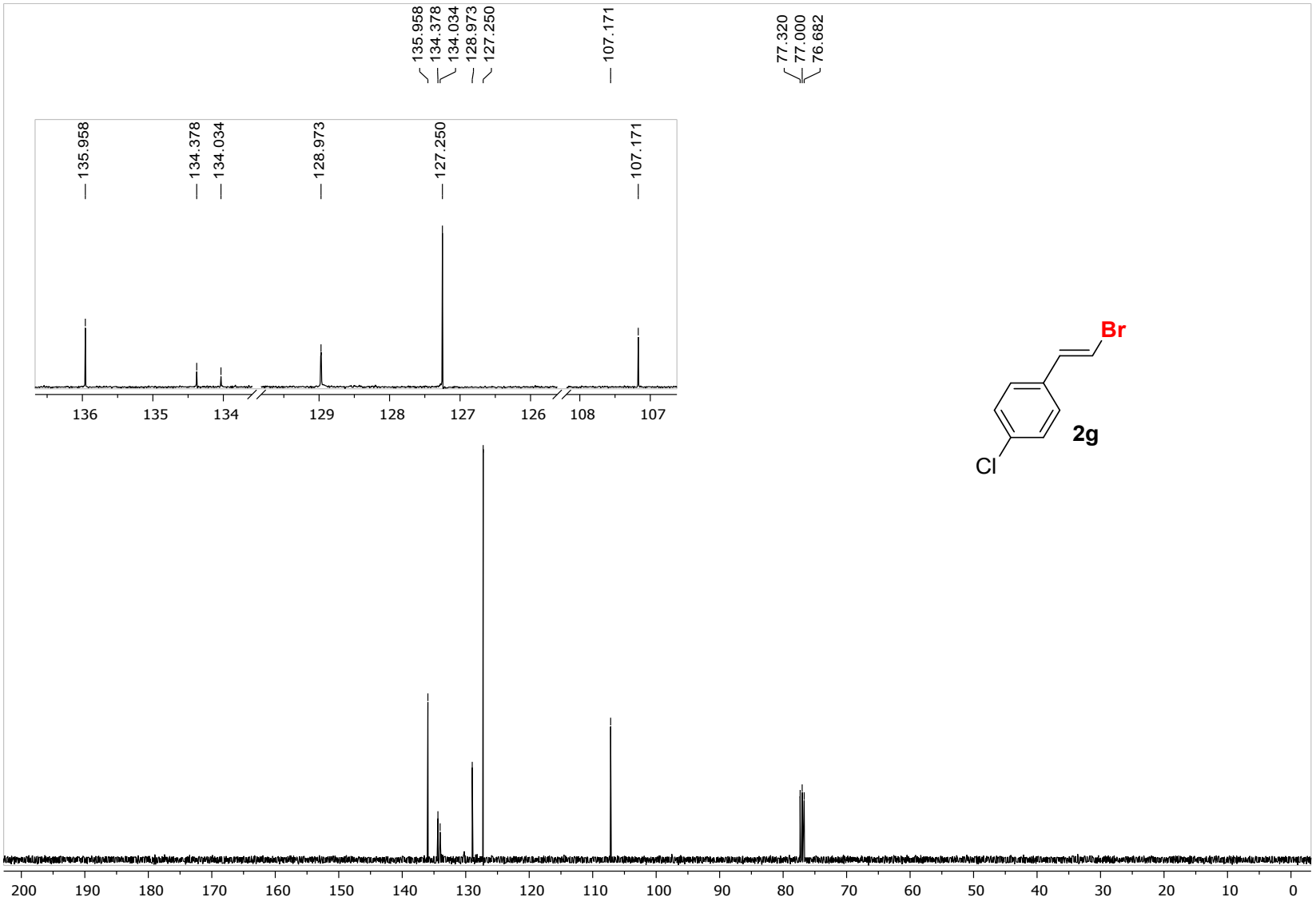

Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2g**.

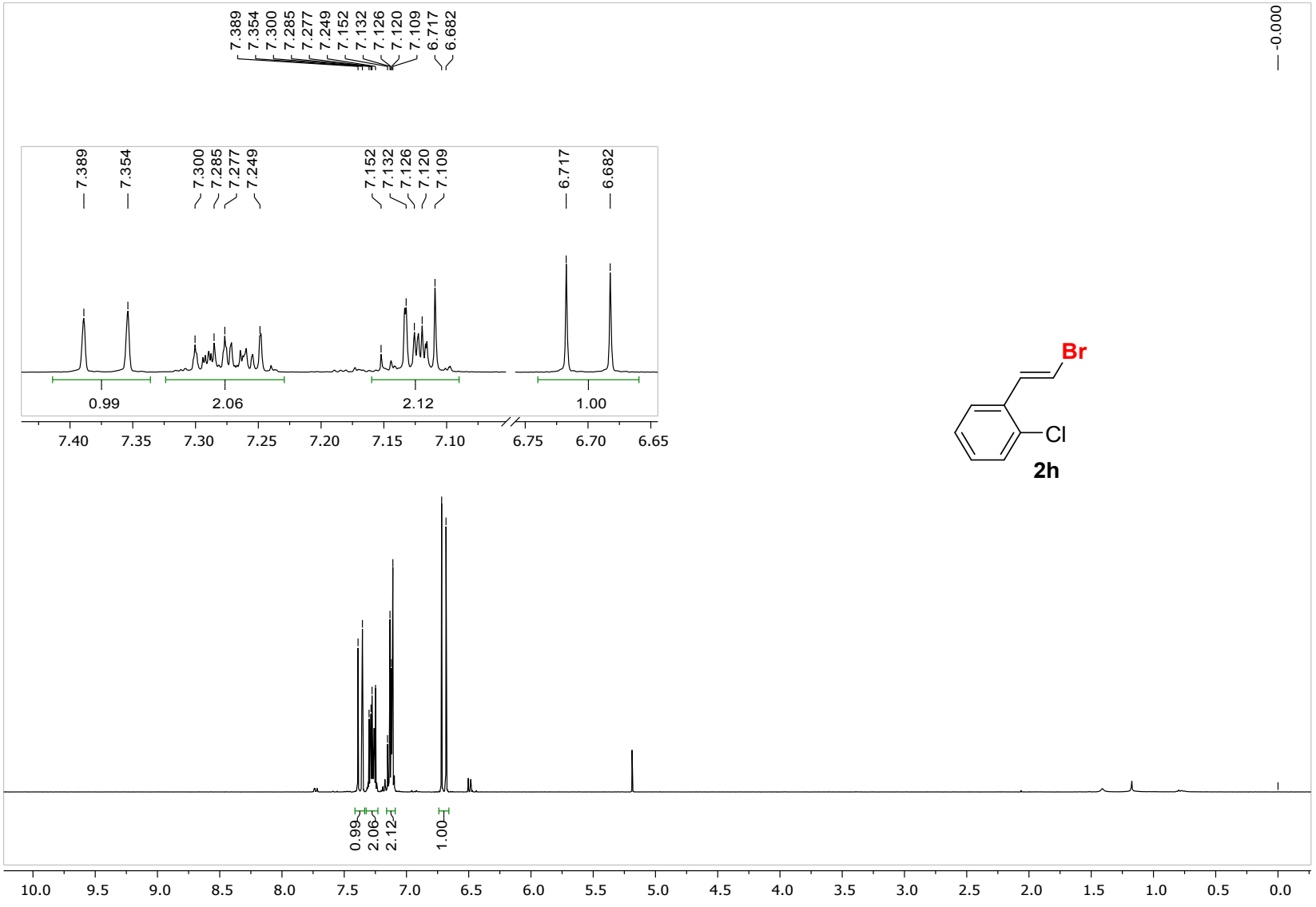

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2h**.

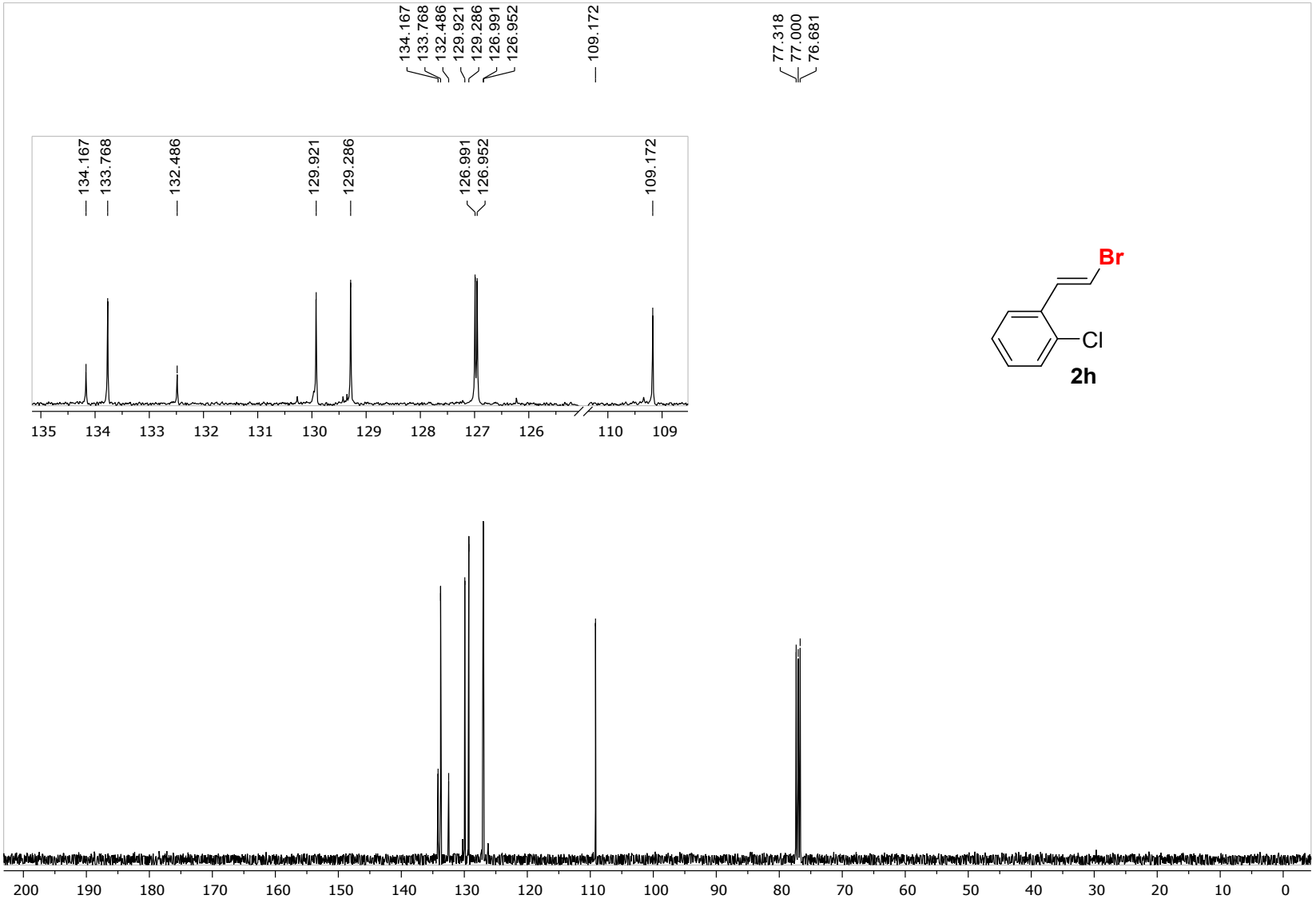

Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2h**.

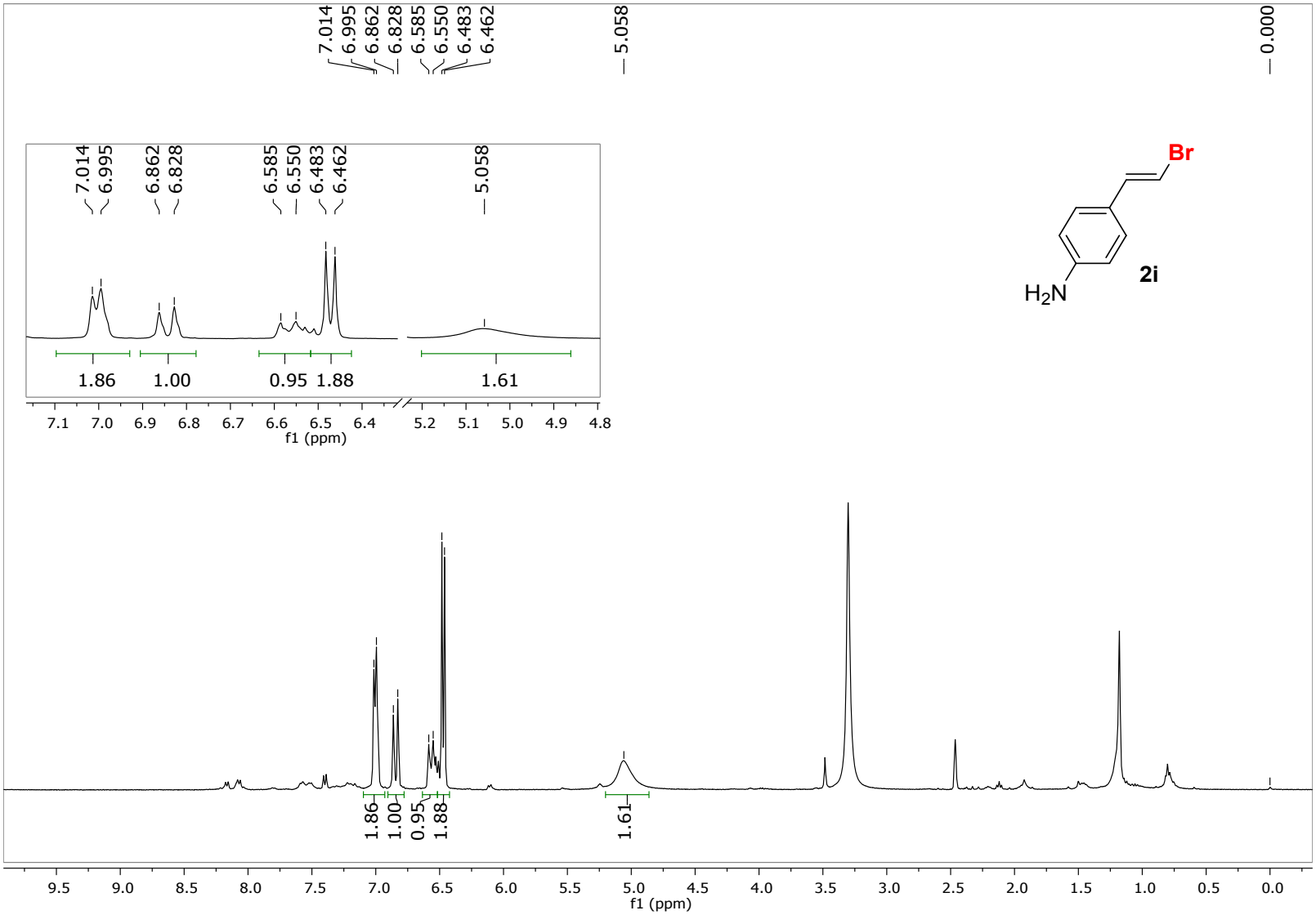

Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$ and DMSO-d_6) of the product **2i**.

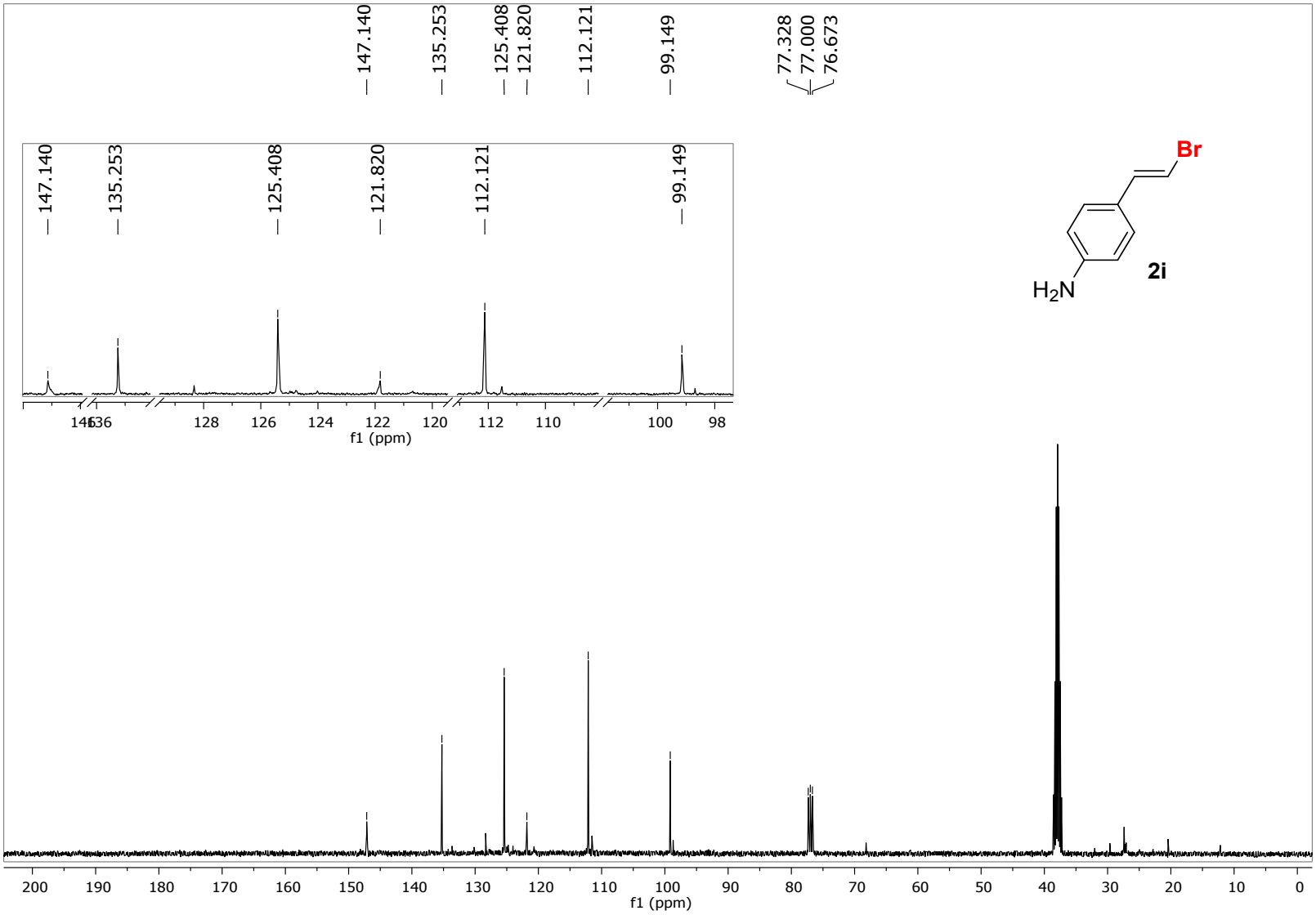

Figure S18. ^{13}C NMR (100 MHz, $CDCl_3$ and DMSO-d_6) of the product **2i**.

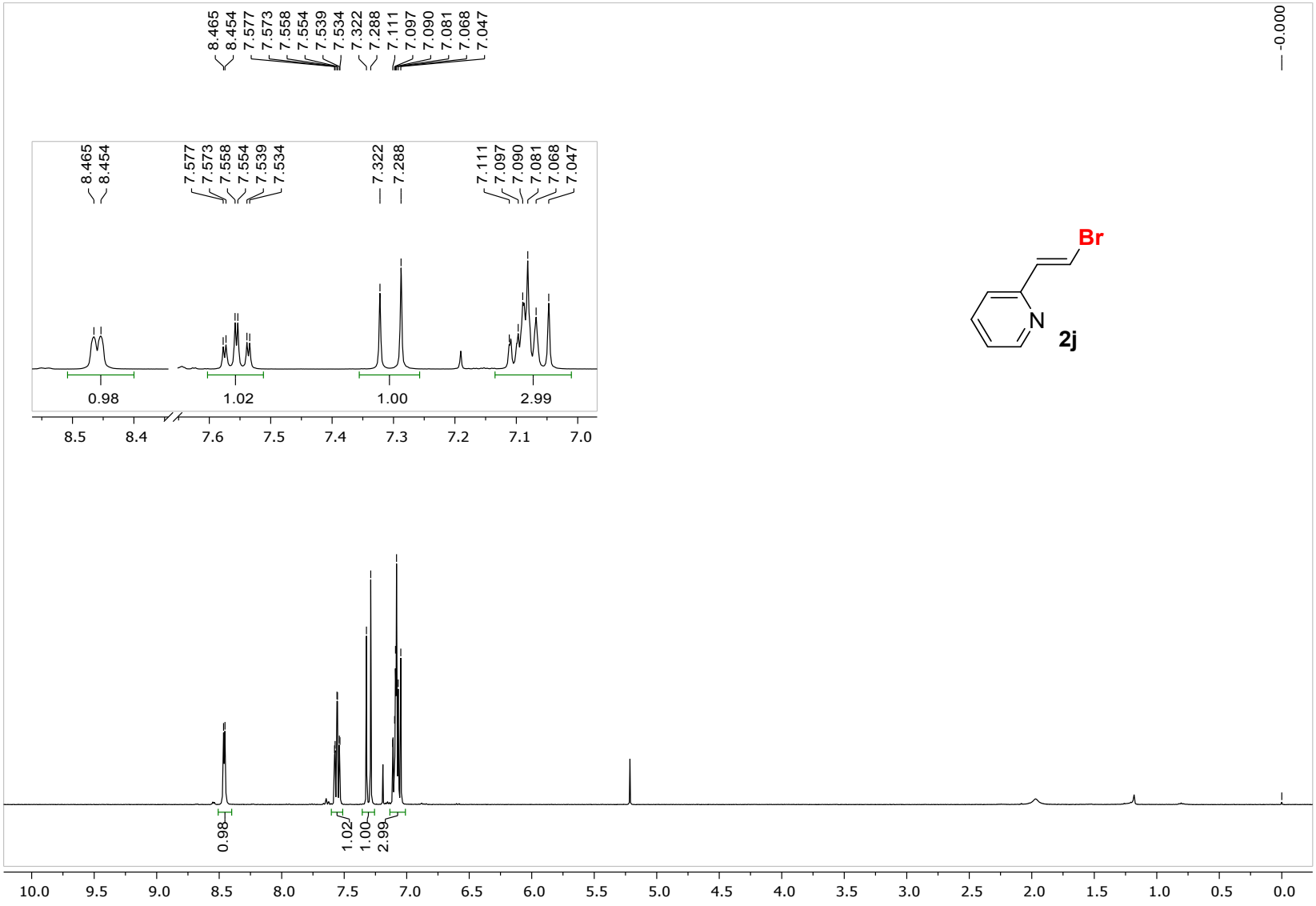

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2j**.

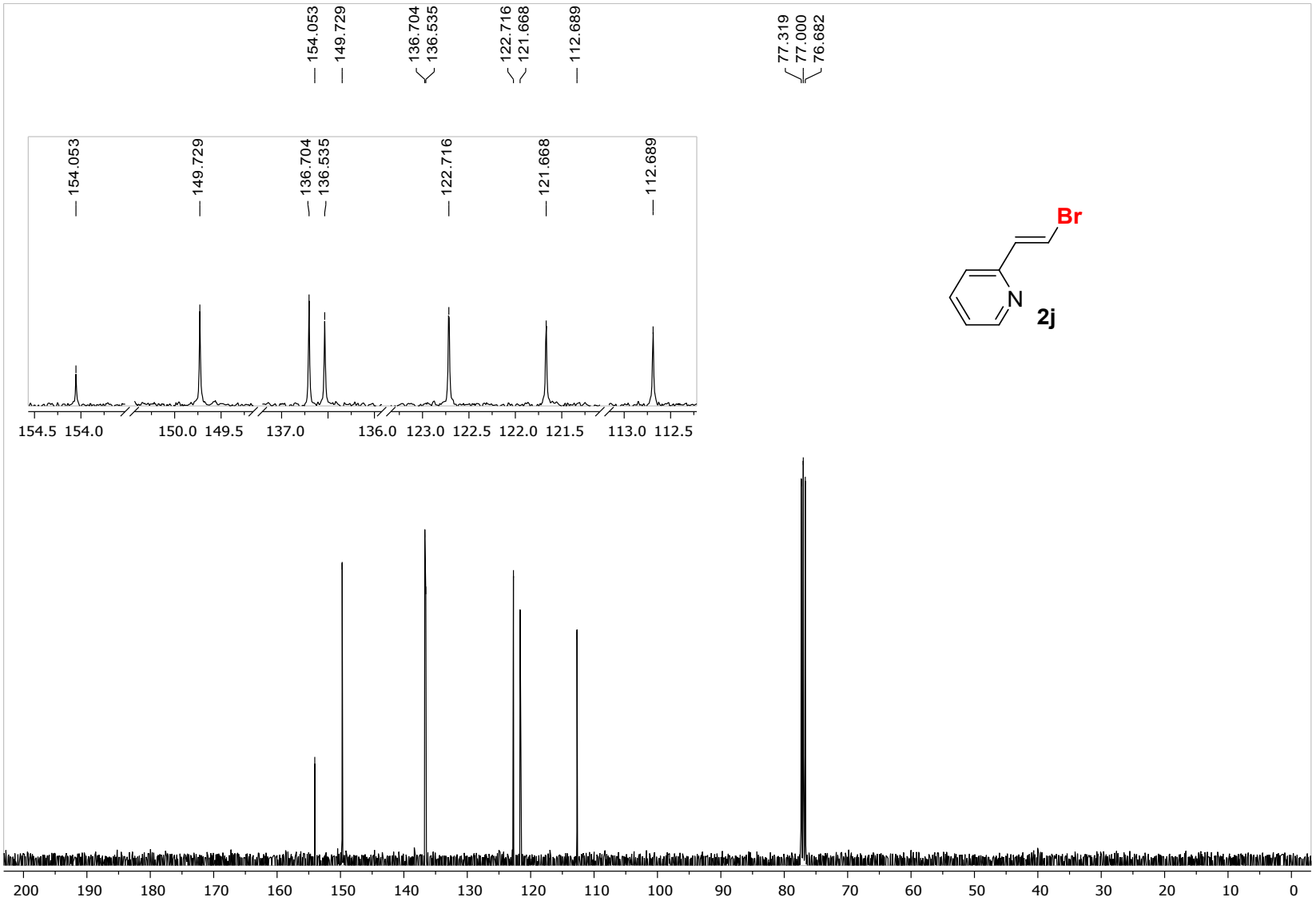

Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2j**.

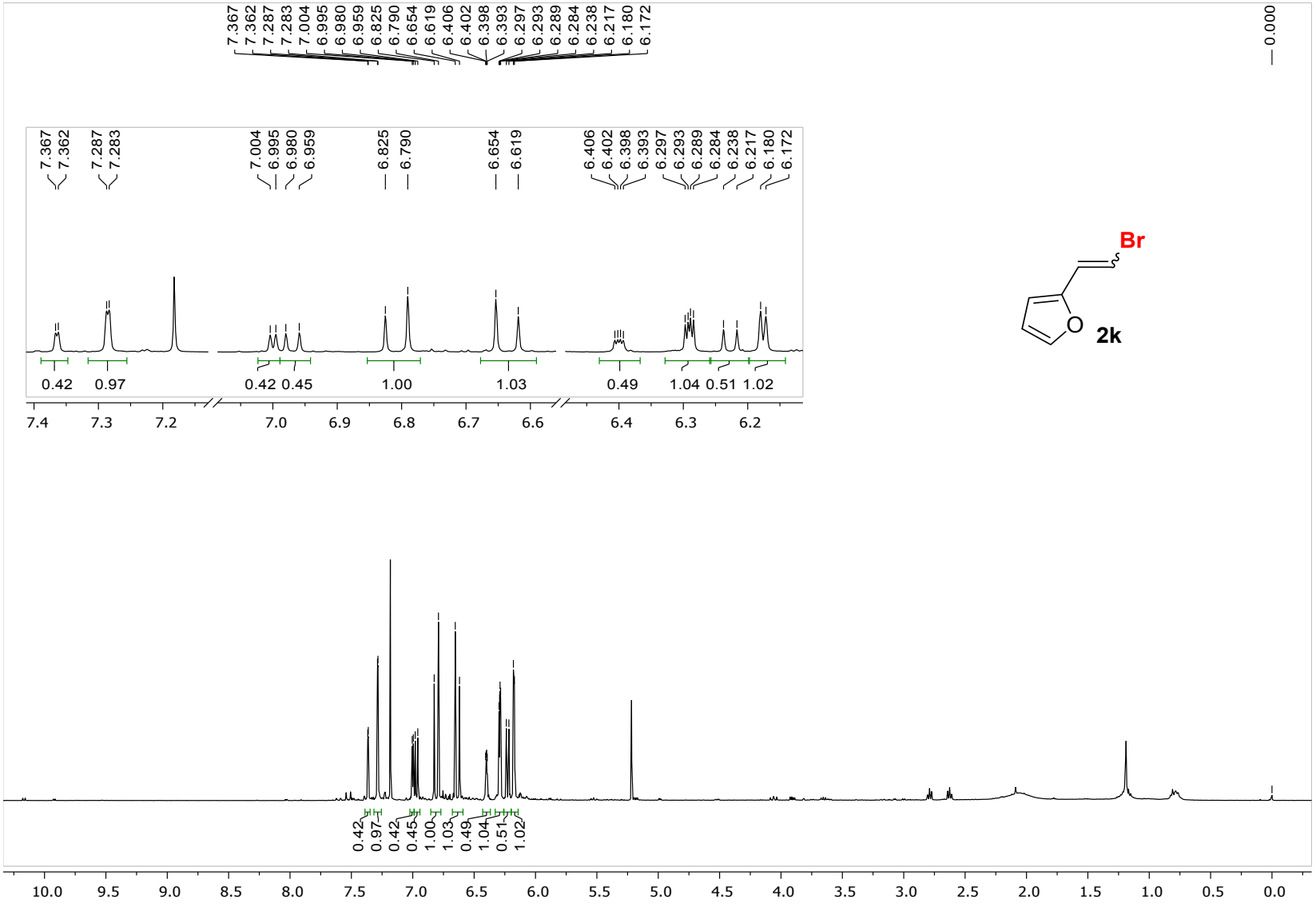

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2k**.

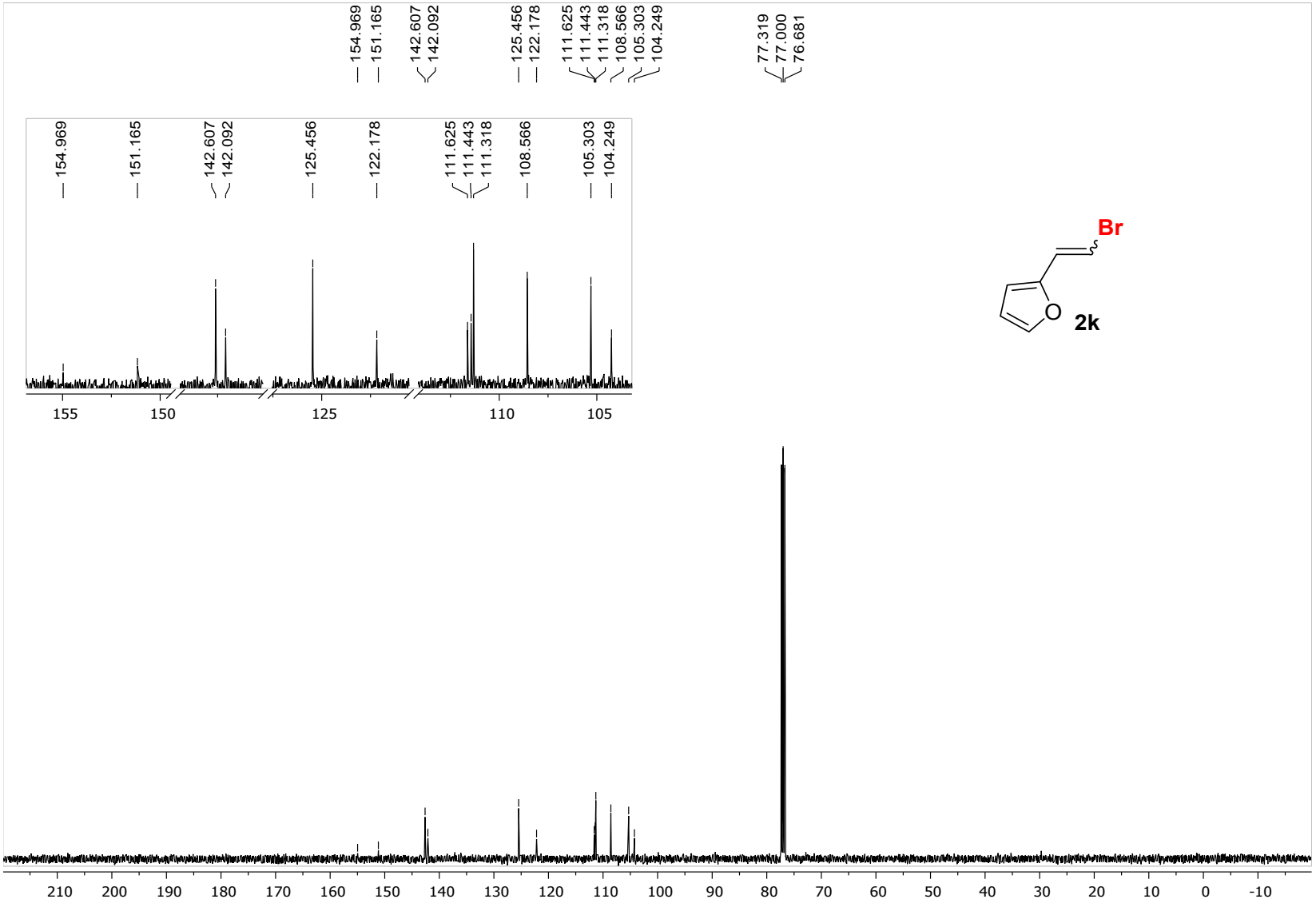

Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2k**

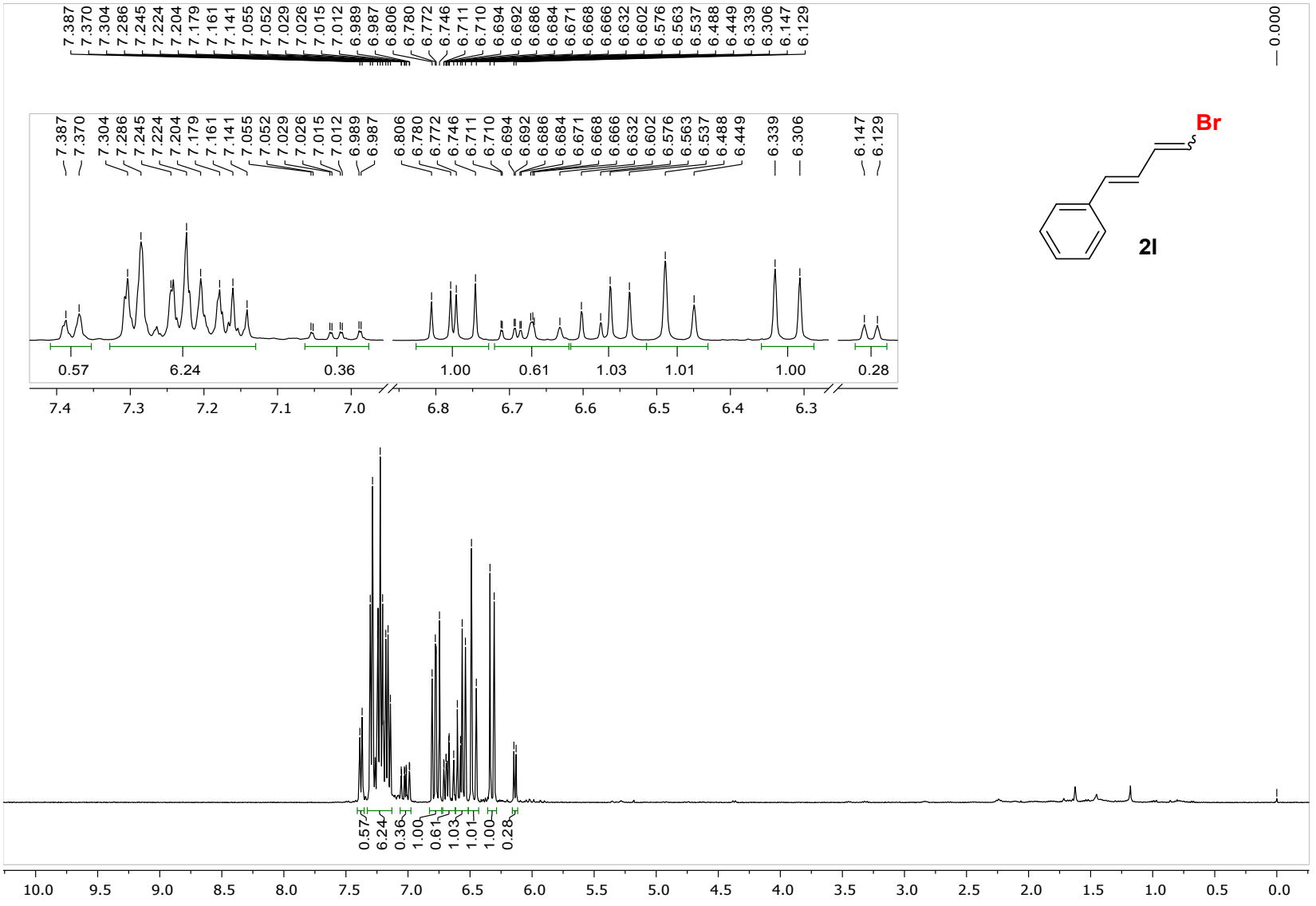

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2l**.

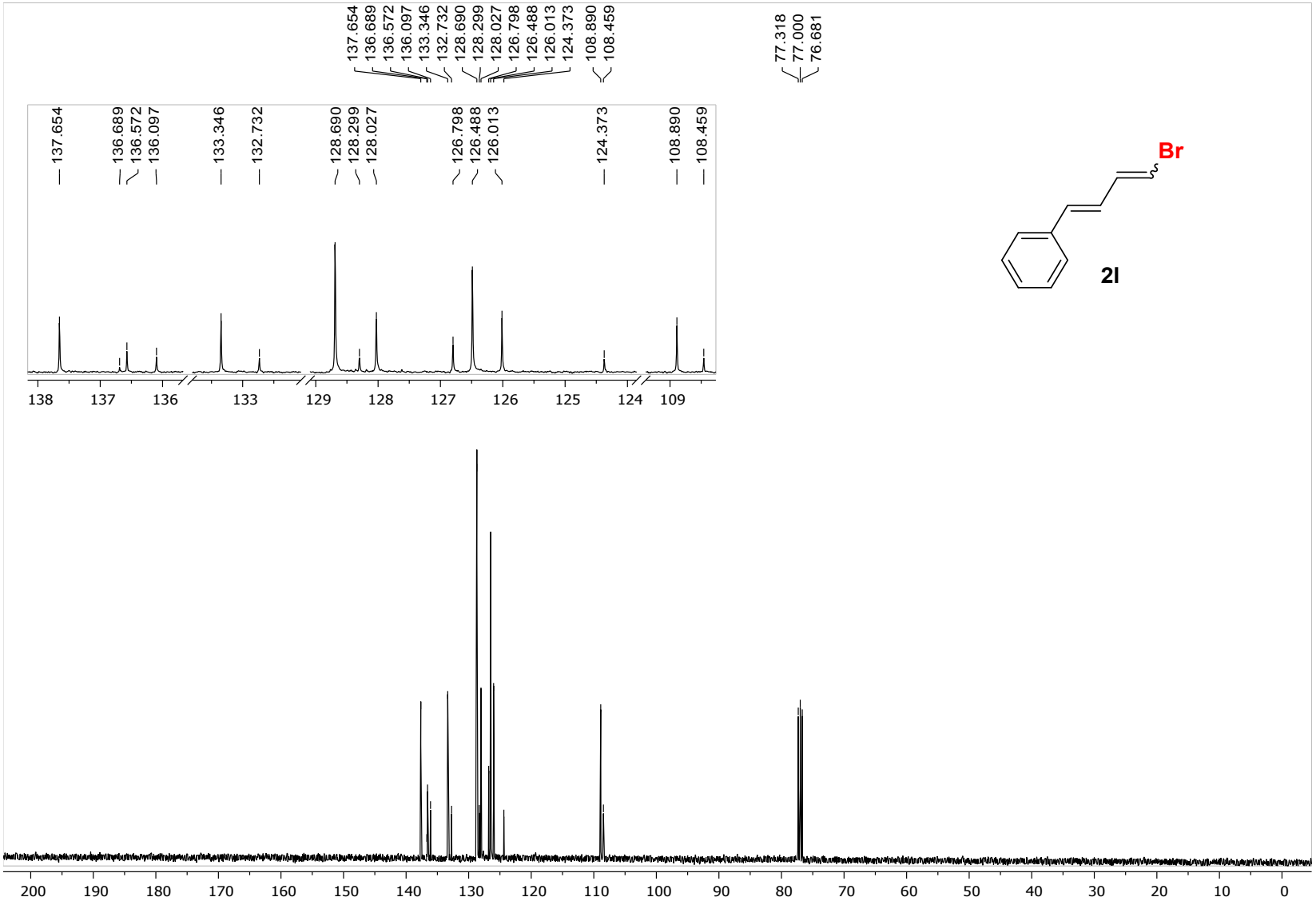

Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2l**.

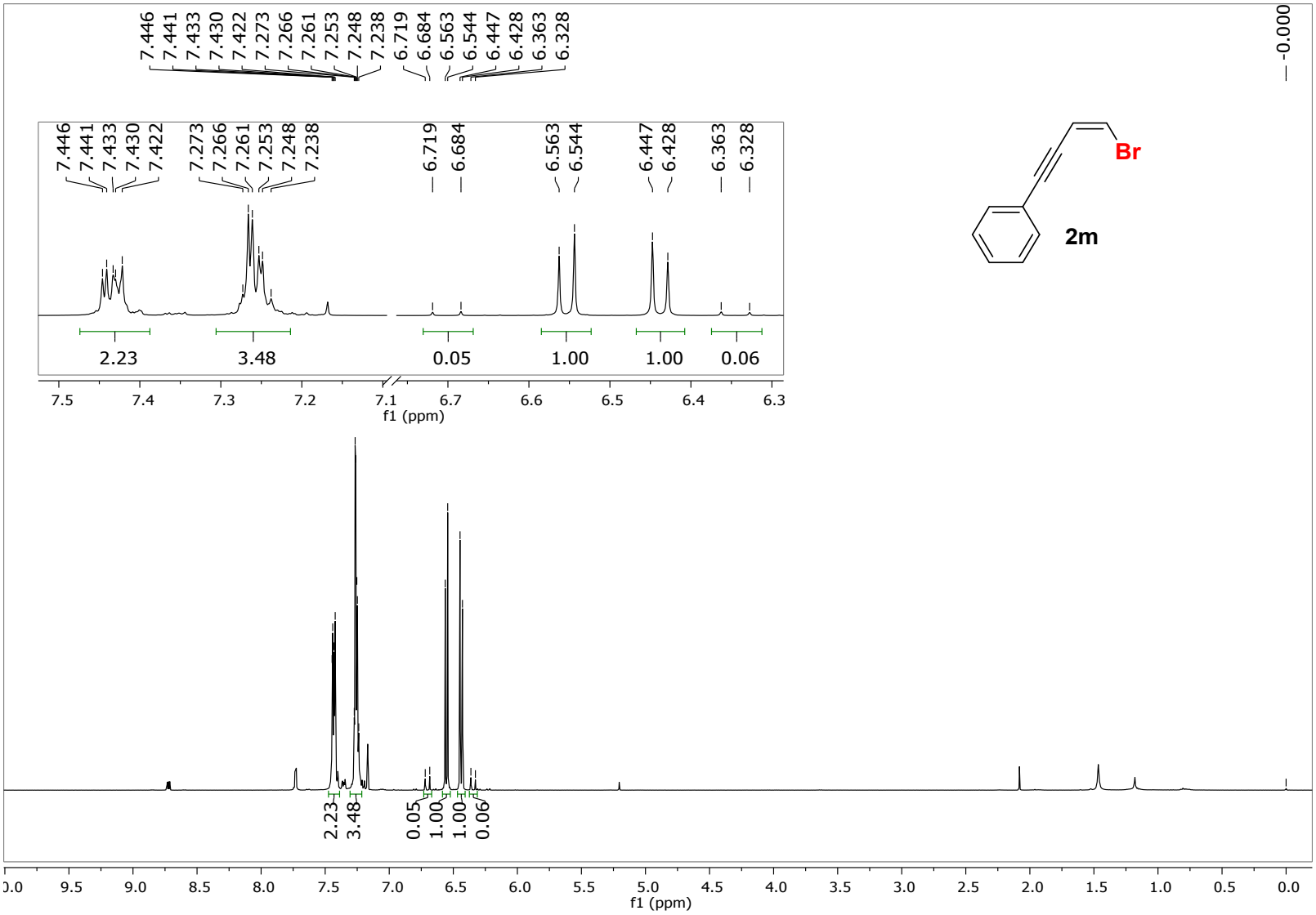

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **2m**.

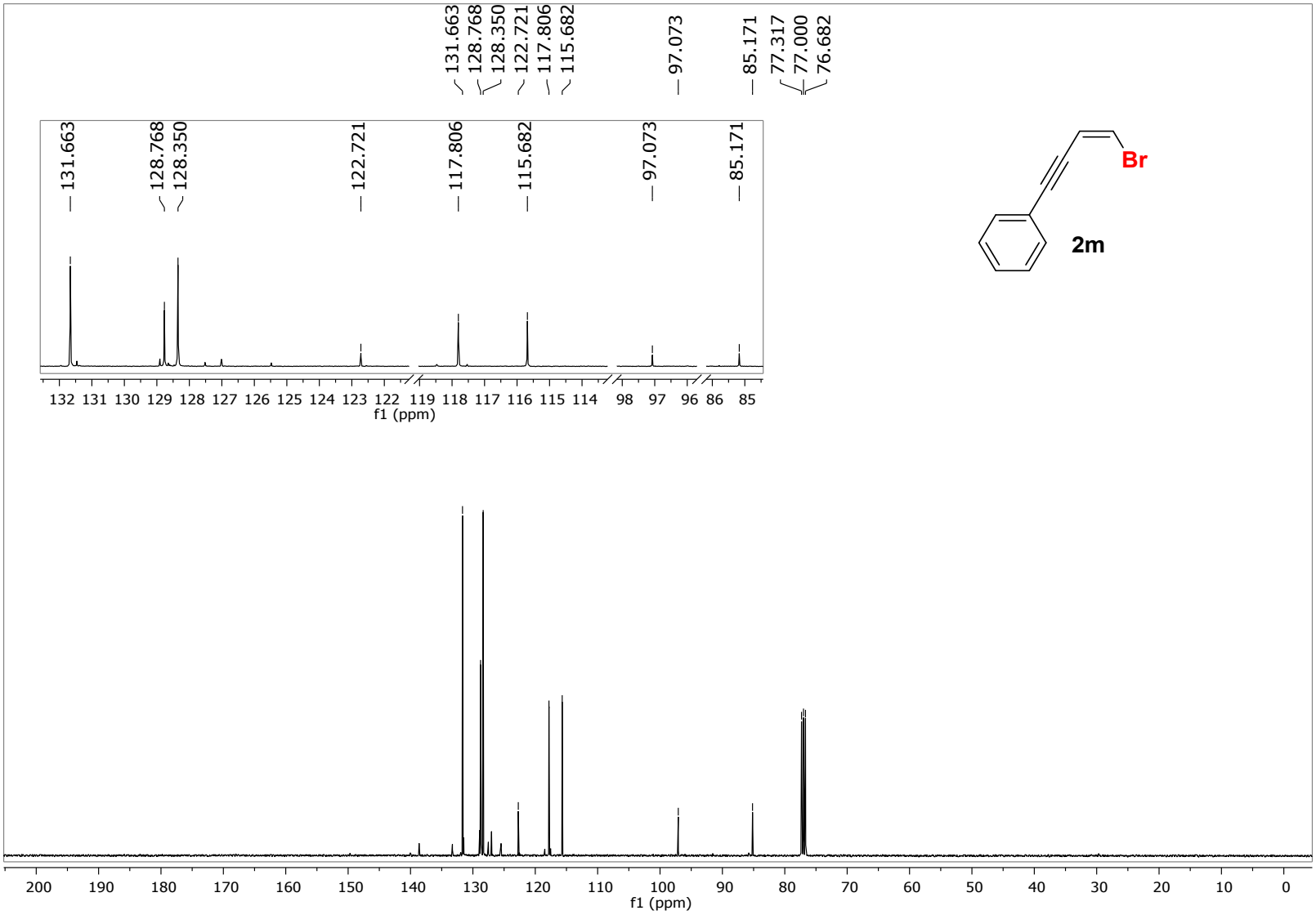

Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) of the product **2m**.

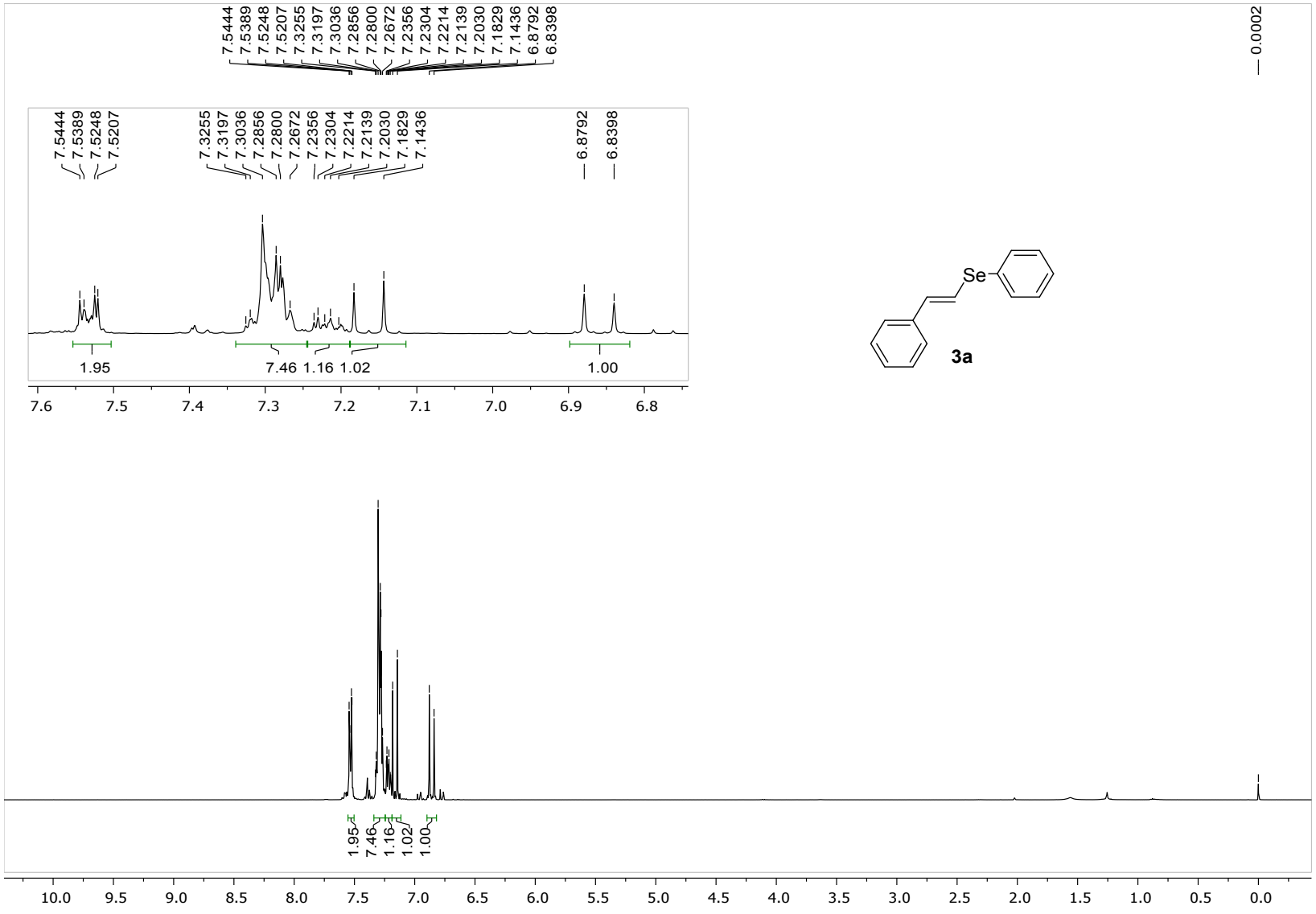

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of the product **3a**.