Electronic Supplementary Information

Stereo-controlled *anti*-hydromagnesiation of aryl alkynes by magnesium hydrides

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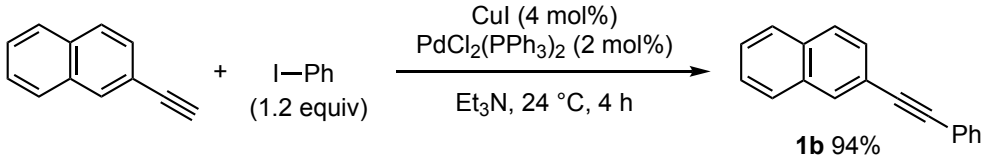
1. General

^{1}H NMR spectra (400 MHz) were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ [using TMS (for ^{1}H, δ = 0.00) as internal standard]. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, δ = 77.00) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad. High-resolution mass spectra were obtained with a Waters Q-Tof Premier mass spectrometer. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR spectrometer or on a Bruker alpha Platinum ATR inside a glovebox. Shimadzu GC-2010 was used for GC analysis. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Gel permeation chromatography (GPC) was performed on LaboACE LC-5060 recycling preparative HPLC. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and diethyl ether (Et_2O) were taken from a solvent purification system (PS-400-5, innovative technology Inc.). Other solvents and reagents, unless otherwise noted, were commercially available and used as received.

NaH (60% dispersion in mineral oil, product number: 452912) and NaH (dry, 95%, product number: 223441) were purchased from Sigma-Aldrich, Inc.

2.1. Synthesis and characterization of the starting materials

2.1.1. Synthesis of 2-(phenylethynyl)naphthalene (1b)[1]

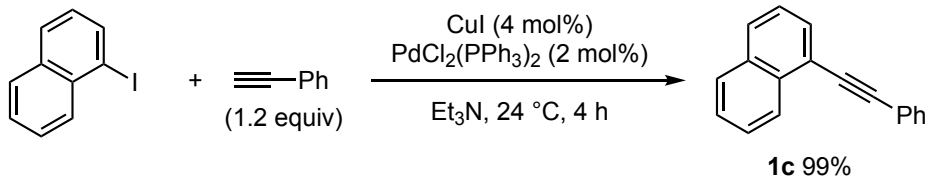


To a solution of 2-ethynylnaphthalene (615.2 mg, 4.042 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (60.5 mg, 0.086 mmol, 2 mol%) and CuI (31.9 mg, 0.168 mmol, 4 mol%) in triethylamine (10 mL) was added iodobenzene (0.54 mL, 4.825 mmol, 1.2 equiv), and the mixture was stirred at 24 °C for 4 h. The reaction mixture was filtrated through a celite pad. The volatile materials were then concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, *n*-Hexane) to give **1b** in 94% yield (871.3 mg, 3.817 mmol) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.05 (s, 1H), 7.82 – 7.91 (m, 3H), 7.62 – 7.54 (m, 3H), 7.53 – 7.44 (m, 2H), 7.41 – 7.30 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 133.0, 132.8, 131.7, 131.4, 128.41, 128.37, 128.3, 128.0, 127.8, 127.7, 126.6, 126.5, 123.3, 120.6, 89.8, 89.7.

2.1.2. Synthesis of 1-(phenylethynyl)naphthalene (1c)[2]

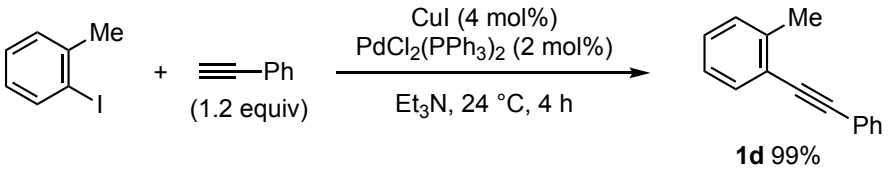


Alkyne of **1c** was synthesized using phenylacetylene (0.53 mL, 4.827 mmol) and 1-iodonaphthalene (0.60 mL, 4.110 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 99% yield (935.6 mg, 4.098 mmol) of **1c** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.44 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 8.8 Hz, 2H), 7.77 (d, J = 7.2 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.62 – 7.58 (m, 1H), 7.55 – 7.52 (m, 1H), 7.50 – 7.43 (m, 1H), 7.43 – 7.32 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 133.3, 133.2, 131.7, 130.4, 128.8, 128.42, 128.38, 128.3, 126.8, 126.4, 126.2, 125.3, 123.4, 120.9, 94.3, 87.5.

2.1.3. Synthesis of 1-methyl-2-(phenylethynyl)benzene (1d)[3]

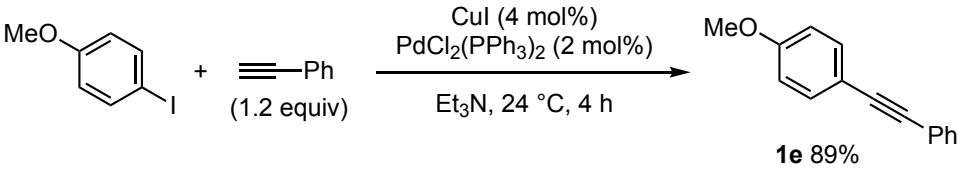


Alkyne of **1d** was synthesized using phenylacetylene (0.55 mL, 5.009 mmol) and 2-iodotoluene (0.51 mL, 4.008 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 99% yield (760.0 mg, 4.098 mmol) of **1d** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.58 – 7.45 (m, 3H), 7.37 – 7.27 (m, 3H), 7.26 – 7.20 (m, 2H), 7.20 – 7.09 (m, 1H), 2.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 140.2, 131.8, 131.5, 129.4, 128.33, 128.28, 128.2, 125.6, 123.6, 123.0, 93.3, 88.3, 20.7.

2.1.4. Synthesis of 1-methoxy-4-(phenylethynyl)benzene (1e)[4]

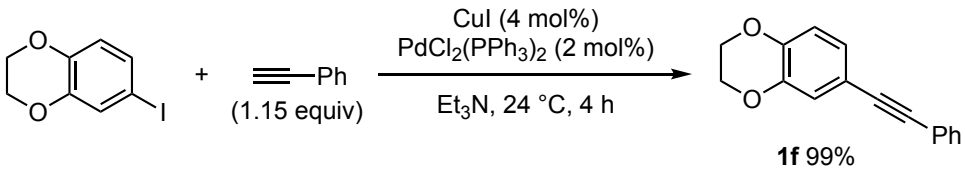


Alkyne of **1e** was synthesized using phenylacetylene (0.53 mL, 4.827 mmol) and 4-iodoanisole (964.1 mg, 4.120 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane:CH_2Cl_2 = 97.5:2.5) gave 89% yield (763.4 mg, 3.665 mmol) of **1e** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.52 – 7.50 (m, 2H), 7.49 – 7.44 (m, 2H), 7.37 – 7.28 (m, 3H), 6.91 – 6.84 (m, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.2.

2.1.5. Synthesis of 6-(phenylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (1f)



Alkyne of **1f** was synthesized using phenylacetylene (0.54 mL, 4.917 mmol) and 6-iodo-2,3-dihydrobenzo[b][1,4]dioxine (0.60 mL, 4.273 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 99% yield (1.00 g, 4.232 mmol) of **1f** as pale orange oil.

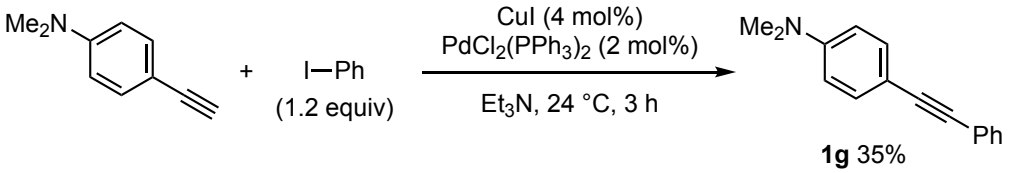
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.54 – 7.46 (m, 2H), 7.38 – 7.27 (m, 3H), 7.07 – 6.99 (m, 2H), 6.84 – 6.81 (m, 1H), 4.33 – 4.20 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 144.1, 143.2, 131.4, 128.3, 128.0, 125.2, 123.4, 120.4, 117.3, 116.1, 89.2, 87.8, 64.4, 64.2.

MS (HRMS ESI): Calcd for $C_{16}H_{13}O_2$ $[M+H]^+$ 237.0916, Found: 237.0922.

IR (neat, cm^{-1}): 2318 [ν(C≡C)], 1128 [ν(C-O)], 1196 [ν(C-O)].

2.1.6. Synthesis of *N,N*-dimethyl-4-(phenylethynyl)aniline (1g)[5]

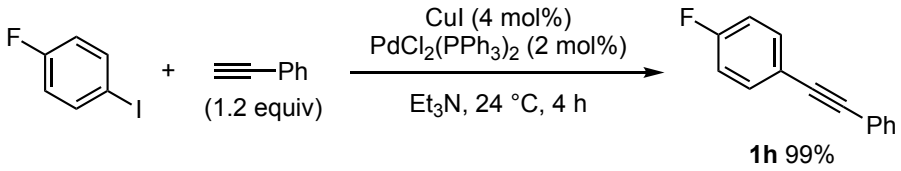


Alkyne of **1g** was synthesized using 4-ethynyl-*N,N*-dimethylaniline[5] (420 mg, 2.892 mmol) and iodobenzene (0.39 mL, 3.485 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 35% yield (222.0 mg, 1.004 mmol) of **1g** as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.50 – 7.48 (m, 2H), 7.42 – 7.39 (m, 2H), 7.34 – 7.24 (m, 3H), 6.60 – 6.34 (m, 2H), 2.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 150.1, 132.7, 131.3, 128.2, 127.4, 124.2, 111.8, 110.1, 90.6, 87.3, 40.2.

2.1.7. Synthesis of 1-fluoro-4-(phenylethynyl)benzene (1h)[4]



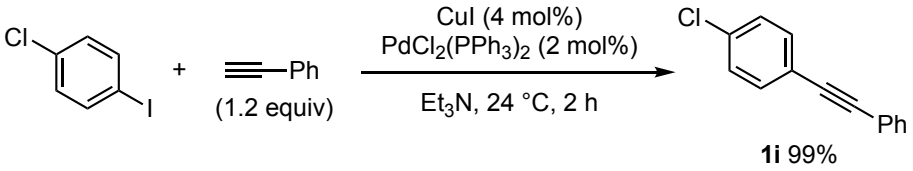
Alkyne of **1h** was synthesized using phenylacetylene (0.55 mL, 5.008 mmol) and 1-fluoro-4-iodobenzene (0.50 mL, 4.338 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 99% yield (842.1 mg, 4.291 mmol) of **1h** as pale orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.53 – 7.49 (m, 4H), 7.39 – 7.30 (m, 3H), 7.09 – 7.00 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 162.4 (d, $J_{C\text{-}F}$ = 248.0 Hz), 133.5 (d, $J_{C\text{-}F}$ = 8.3 Hz), 131.5, 128.4, 128.3, 123.1, 119.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 89.0, 88.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) –111.01.

2.1.8. Synthesis of 1-chloro-4-(phenylethynyl)benzene (1i)[4]



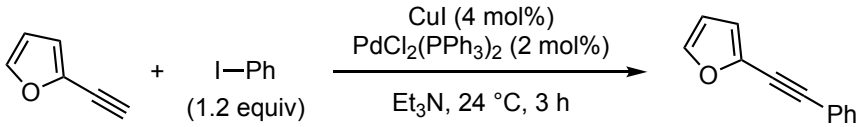
1i 99%

Alkyne of **1i** was synthesized using phenylacetylene (0.53 mL, 4.826 mmol) and 1-chloro-4-iodobenzene (969.7 mg, 4.025 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 99% yield (855.8, 4.024 mmol) of **1i** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.56 – 7.49 (m, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.29 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 134.3, 132.8, 131.6, 128.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.2.

2.1.9. Synthesis of 2-(phenylethynyl)furan (1j)[6]



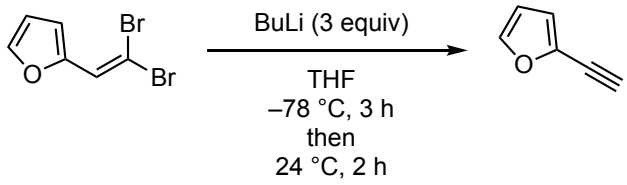
1j 55%

Alkyne of **1j** was synthesized using 2-ethynylfuran[6] (as the crude state including ca. 1.34 mmol of 2-ethynylfuran, that was prepared by the reported method shown below) and iodobenzene (0.42 mL, 3.753 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 55% yield (128.4 mg, 0.763 mmol) of **1j** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.56 – 7.48 (m, 2H), 7.43 – 7.42 (m, 1H), 7.36 – 7.33 (m, 3H), 6.66 (d, J = 3.6 Hz, 1H), 6.43 (dd, J = 3.6, 2.0 Hz, 1H).

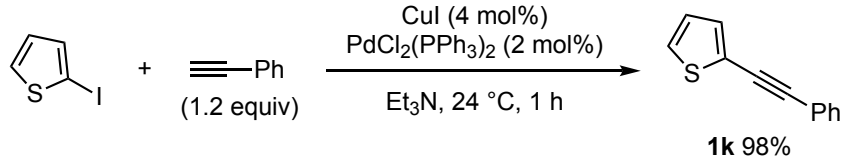
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 143.6, 137.2, 131.4, 128.7, 128.4, 122.3, 115.2, 111.0, 93.2, 79.4.

Synthesis of 2-ethynylfuran:



To a solution of 2-(2,2-dibromovinyl)furan (4.64 g, 18.419 mmol, 1.0 equiv) in THF (100 mL) was slowly added n-BuLi (36.0 mL, 1.5 M in hexane, 54.0 mmol, 3.0 equiv) at –78 °C, and the reaction mixture was stirred for 3 h at the same temperature. The reaction mixture was then stirred continuously for 2 h at 24 ºC before being quenched with saturated aqueous NH_4Cl solution. The organic materials were extracted thrice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated carefully *in vacuo*. The resulting crude residue including 2-ethynylfuran (24% yield calculated based on ^{1}H NMR) was used directly for Sonogashira coupling for synthesis of **1j** due to its volatile (b.p. 106 ºC at 760 mmHg) and unstable nature.

2.1.10. Synthesis of 2-(phenylethynyl)thiophene (1k)[7]



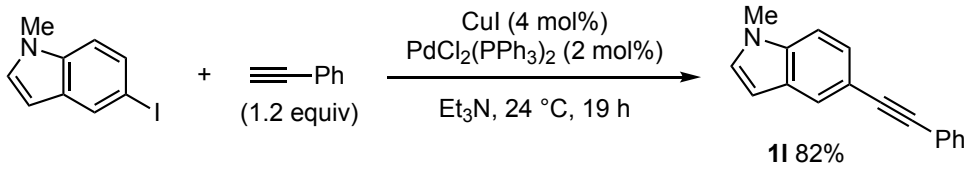
1k 98%

Alkyne of **1k** was synthesized using phenylacetylene (0.53 mL, 4.826 mmol) and 2-iodothiophene (0.44 mL, 3.984 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 98% yield (718.7 mg, 3.900 mmol) of **1k** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.56 – 7.46 (m, 2H), 7.38 – 7.29 (m, 3H), 7.29 – 7.24 (m, 2H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 131.9, 131.4, 128.4, 128.3, 127.2, 127.1, 123.3, 122.9, 93.0, 82.6.

2.1.11. Synthesis of 1-methyl-5-(phenylethynyl)-1*H*-indole (1l)[8]



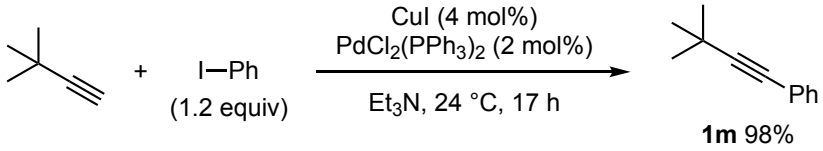
1l 82%

Alkyne of **1l** was synthesized using phenylacetylene (0.53 mL, 4.826 mmol) and 5-iodo-1-methyl-1*H*-indole[8] (1.025 g, 3.990 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave 82% yield (756.0 mg, 3.269 mmol) of **1l** as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.83 – 7.85 (m, 1H), 7.62 – 7.49 (m, 2H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.37 – 7.25 (m, 4H), 7.06 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 136.4, 131.4, 129.7, 128.4, 128.3, 127.6, 125.2, 124.8, 124.1, 113.8, 109.3, 101.3, 91.2, 87.0, 32.9.

2.1.12. Synthesis of (3,3-dimethylbut-1-yn-1-yl)benzene (1m)[6]



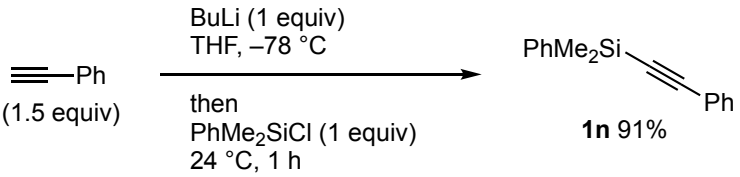
1m 98%

Alkyne of **1m** was synthesized using 3,3-dimethylbut-1-yne (1.35 mL, 10.962 mmol) and iodobenzene (1.12 mL, 10.008 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane) gave 98% yield (1.56 g, 9.857 mmol) of **1m** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.41 – 7.34 (m, 2H), 7.29 – 7.21 (m, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 131.5, 128.1, 127.4, 124.1, 98.5, 79.0, 31.0, 27.9.

2.1.13. Synthesis of dimethyl(phenyl)(phenylethynyl)silane (1n)[9]



1n 91%

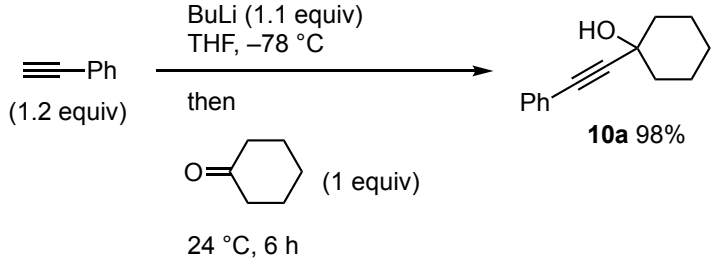
To a solution of phenylacetylene (1.0 mL, 9.106 mmol, 1.5 equiv) in THF (13 mL) was slowly added n-BuLi (2.4 mL, 2.5 M in hexane, 6.0 mmol, 1.02 equiv) at –78 °C, and the reaction mixture was stirred for 1 h at the same temperature. A solution of chlorodimethylphenylsilane (1.0 mL, 5.838 mmol, 1.0 equiv) in THF (2 mL) was then added at the same temperature. The mixture was slowly warmed up to 24 ºC and

stirred continuously for 1 h at 24 ºC before being quenched with saturated aqueous NH_4Cl solution. The organic materials were extracted thrice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude residue was purified by flash chromatography (silica gel, *n*-Hexane) to give **1n** in 91% yield (1.261 g, 5.332 mmol) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.71 – 7.68 (m, 2H), 7.54 – 7.46 (m, 2H), 7.42 – 7.36 (m, 3H), 7.34 – 7.25 (m, 3H), 0.49 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.0, 133.7, 132.1, 129.4, 128.7, 128.2, 127.9, 123.0, 106.8, 92.0, -0.8.

2.1.14. Synthesis of 1-(phenylethynyl)cyclohexan-1-ol (10a)[10]

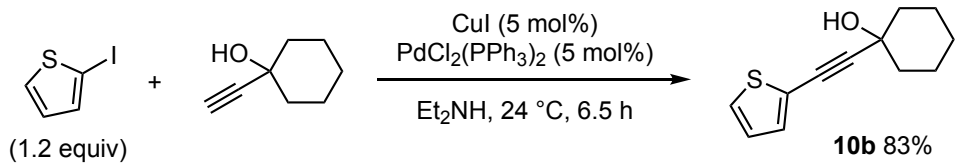


Propargyl alcohol **10a** was synthesized using phenylacetylene (2.5 mL, 22.763 mmol) and cyclohexanone (2.1 mL, 20.328 mmol) by following the procedure described in section 2.1.13. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) gave 98% yield (3.97 g, 19.822 mmol) of **10a** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.48 – 7.39 (m, 2H), 7.35 – 7.26 (m, 3H), 2.24 – 2.10 (m, 1H), 2.09 – 1.93 (m, 2H), 1.83 – 1.47 (m, 7H), 1.37 – 1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 131.6, 128.2, 128.1, 122.9, 92.8, 84.3, 69.1, 40.0, 25.2, 23.4.

2.1.15. Synthesis of 1-(thiophen-2-ylethynyl)cyclohexan-1-ol (10b)[11]



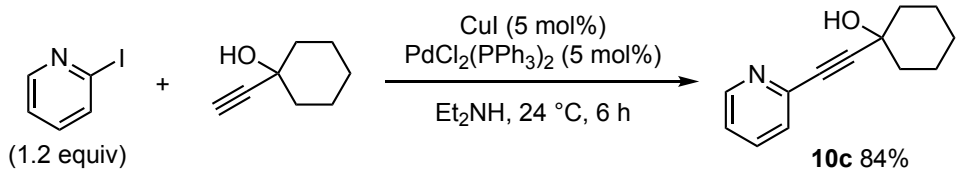
To a solution of 1-ethynylcyclohexan-1-ol[11] (496.8 mg, 4.001 mmol), $PdCl_2(PPh_3)_2$ (140.0 mg, 0.200 mmol, 5 mol%) and CuI (40.1 mg, 0.210 mmol, 5 mol%) in diethylamine (10 mL) was added 2-iodothiophene (0.46 mL, 4.751 mmol, 1.2 equiv),

and the mixture was stirred at 24 °C for 6.5 h. The reaction mixture was filtrated through a celite pad. The volatile materials were then concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, *n*-Hexane:EtOAc= 90:10) to give **10b** in 83% yield (682.5 mg, 3.308 mmol) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.24 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.18 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.08 (br s, 1H), 2.04 – 1.93 (m, 2H), 1.79 – 1.50 (m, 7H), 1.38 – 1.19 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 131.9, 126.94, 126.88, 122.8, 96.6, 77.5, 69.3, 39.9, 25.1, 23.3.

2.1.16. Synthesis of 1-(pyridin-2-ylethynyl)cyclohexan-1-ol (10c)[12]

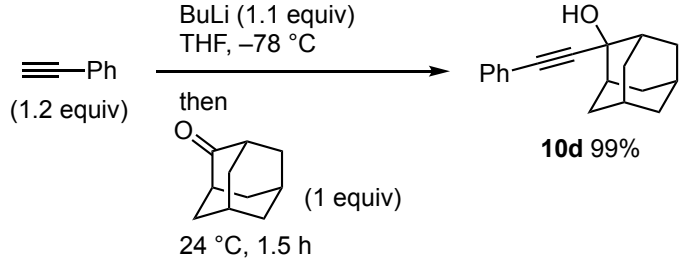


Propargyl alcohol **10c** was synthesized using 1-ethynylcyclohexan-1-ol[11] (49.2 mg, 4.004 mmol) and 2-iodopyridine (0.46 mL, 4.824 mmol) by following the procedure described in section 2.1.15. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 50:50) gave 84% yield (680.0 mg, 3.379 mmol) of **10c** as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.58 (br s, 1H), 7.64 (td, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 6.8, 5.2 Hz, 1H), 2.98 (br s, 1H), 2.07 – 2.03 (m, 3H), 1.83 – 1.48 (m, 6H), 1.39 – 1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 149.8, 143.0, 136.1, 127.2, 122.8, 93.3, 83.4, 68.7, 39.7, 25.1, 23.2.

2.1.17. Synthesis of (1*R**,3*S**,5*r*,7*r*)-2-((*E*)-styryl)adamantan-2-ol (10d)[13]



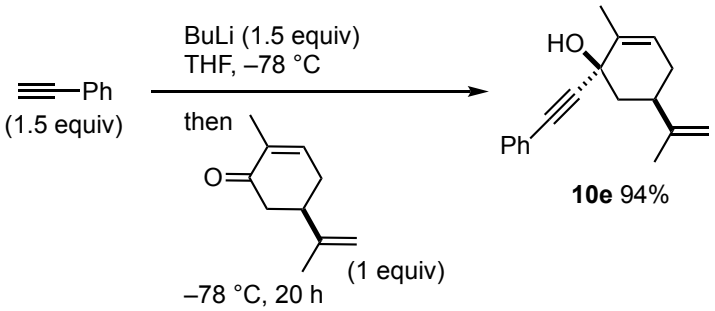
Propargyl alcohol **10d** was synthesized using phenylacetylene (0.51 mL, 4.635 mmol)

and 2-adamantanone (572.8 mL, 3.813 mmol) by following the procedure described in section 2.1.13. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave 99% yield (961.1 mg, 3.812 mmol) of **10d** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.44 – 7.42 (m, 2H), 7.30 – 7.29 (m, 3H), 2.22 (d, *J* = 12.0 Hz, 4H), 2.06 (s, 3H), 1.82 (d, *J* = 14.4 Hz, 4H), 1.73 (s, 3H), 1.60 (d, *J* = 11.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 131.6, 128.2, 128.1, 123.0, 93.8, 84.8, 72.9, 39.0, 37.6, 35.6, 31.6, 26.9, 26.8.

2.1.18. Synthesis of (1*R*,5*R*)-2-methyl-1-(phenylethynyl)-5-(prop-1-en-2-yl)cyclohex-2-en-1-ol (10e)



Propargyl alcohol **10e** was synthesized using phenylacetylene (1.0 mL, 9.106 mmol) and (*R*)-(-)-carvone (0.94 mL, 6.001 mmol) by following the procedure described in section 2.1.13 (in this case, the reaction of acetylide and ketone was conducted at – 78 °C). Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) gave 94% yield (1.414 g, 5.649 mmol) of **10e** as a single diastereomer as colorless oil. The stereochemistry of the propargylic stereogenic center of **10e** was confirmed by the NOESY correlation of **11e** (see section 4.2.5.).

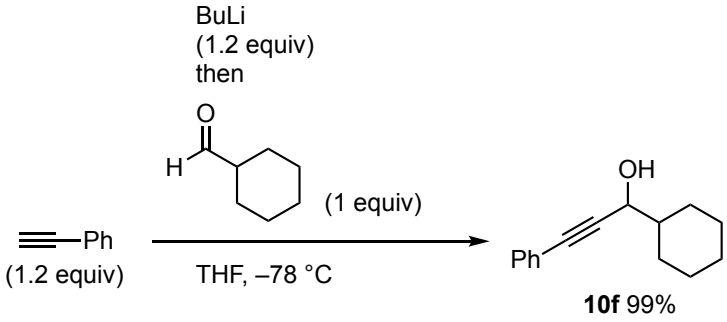
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.47 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 5.55 – 5.52 (m, 1H), 4.77 (s, 2H), 2.66 – 2.54 (m, 1H), 2.38 – 2.34 (m, 1H), 2.26 – 2.14 (m, 2H), 2.06 – 1.94 (m, 1H), 1.94 – 1.89 (m, 3H), 1.84 (dd, *J* = 12.4 Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 148.4, 135.8, 131.7, 128.3, 128.2, 124.5, 122.7, 109.2, 92.0, 84.1, 70.3, 43.6, 39.8, 31.0, 20.7, 17.3.

MS (HRMS ESI): Calcd for $C_{18}H_{21}O$ $[M+H]^+$ 253.1592, Found: 253.1598.

IR (neat, cm^{-1}): 3050 [ν(O-H)], 1645[ν(C=C)], 1170 [ν(C-O)], 891 [ν(C=CH_2)].

2.1.19. Synthesis of 1-cyclohexyl-3-phenylprop-2-yn-1-ol (10f)[10]

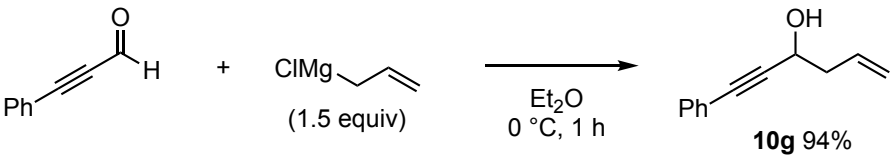


Propargyl alcohol **10f** was synthesized using phenylacetylene (1.30 mL, 11.837 mmol) and cyclohexanecarboxaldehyde (1.20 mL, 9.906 mmol) by following the procedure described in section 2.1.13. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave 99% yield (2.12 g, 9.900 mmol) of **10f** as sticky yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.48 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 4.38 (t, *J* = 6.0 Hz, 1H), 1.94 – 1.91 (m, 2H), 1.86 (d, *J* = 6.0 Hz, 1H), 1.82 – 1.78 (m, 2H), 1.74 – 1.60 (m, 2H), 1.39 – 1.05 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 131.6, 128.22, 128.19, 122.7, 89.2, 85.6, 67.6, 44.3, 28.6, 28.1, 26.3, 25.9, 25.8.

2.1.20. Synthesis of 1-phenylhex-5-en-1-yn-3-ol (10g)[14]



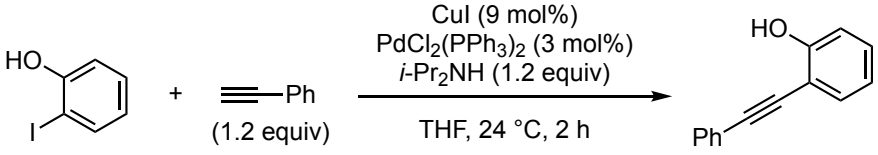
To a solution of 3-phenylpropiolaldehyde[14] (661.1 mg, 5.079 mmol) in Et_2O (10 mL) was added allylmagnesium chloride (1.0 M in Et_2O, 7.5 mL, 7.5 mmol) at 0 °C. After the reaction mixture was stirred at the same temperature for 1 h, the reaction was quenched with saturated aqueous NH_4Cl solution. Organic materials were extracted thrice with Et_2O and the combined extracts were washed with brine, and dried over $MgSO_4$. The volatile materials were removed *in vacuo* and the resulting crude material was purified by flash chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) to yield **10g** in 94% yield (825.7 mg, 4.794 mmol) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.44 – 7.41 (m, 2H), 7.35 – 7.27 (m, 3H), 5.96 (dddd, *J* = 17.2, 10.0, 7.2, 7.2 Hz, 1H), 5.27 – 5.21 (m, 2H), 4.66 (dd, *J* = 6.0, 6.0 Hz,

1H), 2.69 – 2.51 (m, 2H), 2.00 (d, J = 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 133.0, 131.7, 128.4, 128.3, 122.5, 119.1, 89.4, 85.2, 62.0, 42.2.

2.1.21. Synthesis of 2-(phenylethynyl)phenol (10h)[15]



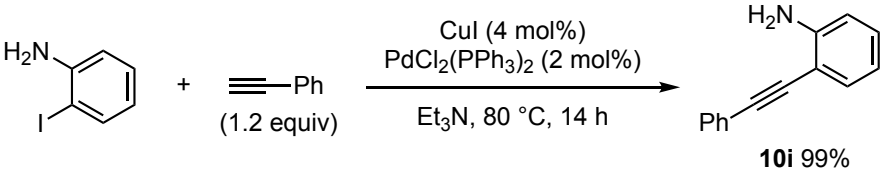
10h 98%

To a solution of 2-iodophenol (1359.0 mg, 6.177 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (127.9 mg, 0.182 mmol, 3 mol%), CuI (105.1 mg, 0.552 mmol, 9 mol%) and diisopropylamine (1.0 mL, 7.135 mmol, 1.2 equiv) in THF (15 mL) was added phenylacetylene (0.79 mL, 7.194 mmol, 1.2 equiv), and the mixture was stirred at 24 °C for 2 h. The reaction mixture was filtrated through a celite pad. The volatile materials were then concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, *n*-Hexane) to give **10h** in 98% yield (1.176 g, 6.055 mmol) as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.60 – 7.49 (m, 2H), 7.42 (dd, J = 8.0, 1.6 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.32 – 7.19 (m, 1H), 6.98 (dd, J = 8.0, 0.4 Hz, 1H), 6.91 (td, J = 7.6, 1.2 Hz, 1H), 5.84 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 156.5, 131.7, 131.6, 130.5, 128.8, 128.5, 122.4, 120.4, 114.7, 109.6, 96.4, 83.0.

2.1.22. Synthesis of 2-(phenylethynyl)aniline (10i)[16]



10i 99%

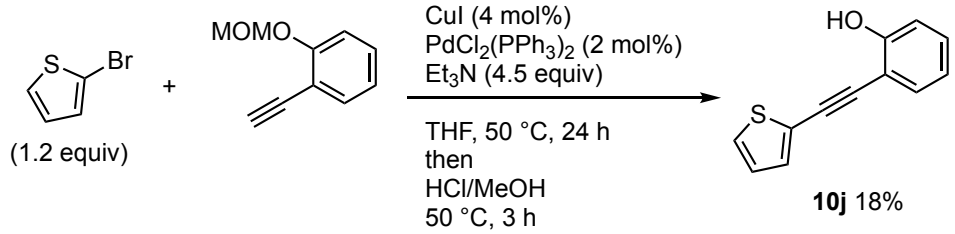
Alkyne of **10i** was synthesized using phenylacetylene (1.0 mL, 9.106 mmol) and 2-iodoaniline (1.31 g, 5.988 mmol) by following the procedure described in section 2.1.1. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave 99% yield (1147.7 mg, 5.939 mmol) of **10i** as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.55 – 7.51 (m, 2H), 7.42 – 7.27 (m, 4H), 7.18 – 7.07 (m, 1H), 6.78 – 6.65 (m, 2H), 4.26 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 147.8, 132.1, 131.4, 129.7, 128.4, 128.2,

123.3, 118.0, 114.3, 107.9, 94.7, 85.9.

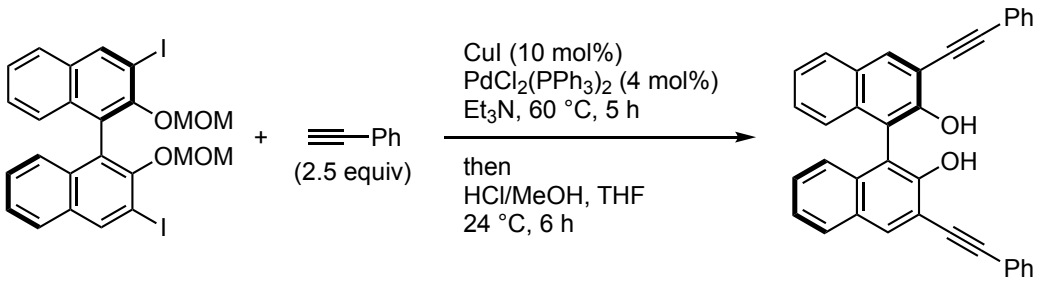
2.1.23. Synthesis of 2-(thiophen-2-ylethynyl)phenol (10j)[17]



To a solution of 1-ethynyl-2-(methoxymethoxy)benzene[17] (455.1 mg, 2.806 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (40.5 mg, 0.058 mmol, 2 mol%), CuI (21.0 mg, 0.110 mmol, 4 mol%) and triethylamine (1.80 mL, 12.914 mmol, 4.5 equiv) in THF (5 mL) was added 2-bromothiophene (0.35 mL, 3.615 mmol, 1.2 equiv), and the mixture was stirred at 50 °C for 24 h. The reaction mixture was filtrated through column chromatography (silica gel, *n*-Hexane:EtOAc= 99:1). The crude material was then dissolved in MeOH (5 mL) and conc. HCl (5 mL) was slowly added. The reaction mixture was stirred at 24°C for 3 h. The organic materials were extracted thrice with Et_2O and the combined extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) to give **10j** in 18% yield (108 mg, 0.503 mmol) over two steps as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.39 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.20 (m, 3H), 7.05 – 6.93 (m, 2H), 6.89 (t, *J* = 7.6 Hz, 1H), 5.83 (br s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 156.4, 132.5, 131.7, 130.7, 127.9, 127.2, 122.2, 120.4, 114.9, 109.3, 89.2, 86.7.

2.1.24. Synthesis of (*R*)-3,3'-bis(phenylethynyl)-[1,1'-binaphthalene]-2,2'-diol (10k)[18]



10k 66% (2 steps)

To a solution of 3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene[18b] (1174.0 mg, 2.917 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (84.0 mg, 0.120 mmol, 4 mol%), CuI (57.4 mg, 0.301 mmol, 10 mol%) in triethylamine (10 mL) was added phenylacetylene (0.80 mL, 7.284 mmol, 2.5 equiv), and the mixture was stirred at 60 °C for 5 h. The reaction mixture was filtrated through column chromatography (silica gel, *n*-Hexane:EtOAc= 95:5). The crude material was then dissolved in MeOH (4 mL) and THF (4 mL). Hydrochloric acid (36-38%, 2 mL) was slowly added and stirred at 24°C for 6 h. The organic materials were extracted thrice with Et_2O and the combined extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) to give **10k** in 66% yield (943.0 mg, 1.938 mmol) over two steps as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.20 (s, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.55 (m, 4H), 7.41 – 7.34 (m, 8H), 7.32 – 7.28 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.85 (s, 2H).

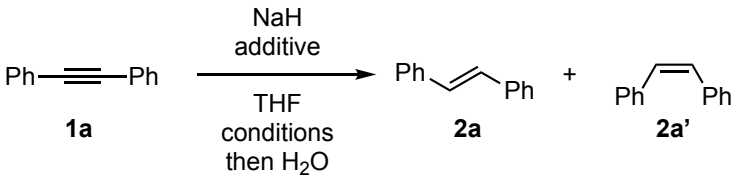
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 150.8, 133.9, 133.2, 131.7, 128.8, 128.7, 128.5, 128.2, 127.9, 124.7, 124.3, 122.4, 113.5, 112.2, 96.2, 83.9.

3. Hydromagnesiation of aryl alkynes by magnesium hydrides

3.1. Optimization of the reaction conditions using diphenylacetylene (1a)

The reactivity of main group metal hydrides was examined using diphenylacetylene (**1a**) (Table S1). Treatment of **1a** with NaH (3 equiv) and NaI (3 equiv) at 80 °C in THF for 24 h resulted in *trans*-selective semi-reduction to form *trans*-stilbene (**2a**) in 31% yield along with 5% yield of *cis*-stilbene (**2a'**), while poor mass balance was observed (entry 1). Use of LiI instead of NaI was detrimental, providing a complex mixture of unidentified compounds probably due to uncontrolled over-reduction/polymerization of **1a** (entry 2). Next, we examined the effect of magnesium iodide (MgI_2) for the semi-reduction of **1a**. Interestingly, we observed that the reaction with NaH (3 equiv) and MgI_2 (3 equiv) at 80 °C improved mass balance of the process, providing **2a** and **2a'** in 68% and 4% yield with 27% recovery of **1a** (entry 3). Further investigation revealed that the molar ratio of NaH and MgI_2 would be crucial to make the process efficient (entries 3-5): the reaction with NaH (3 equiv) and MgI_2 (2 equiv) resulted in poorer conversion (entry 4). Further lowering the amount of MgI_2 to 1.5 equiv gave similar outcome to entry 4 (entry 5). We found that the reaction with NaH (3 equiv) and MgI_2 (3 equiv) at 100 °C resulted in full conversion of **1a** within 24 h to afford **2a** and **2a'** in 92% and 6% yields, respectively (entry 6). Use of zinc iodide as well as metal iodides based on other alkaline earth metals (Ca, Ba, and Sr) resulted in poor conversion of **1a** (entries 7-10).

Table S1.[a]

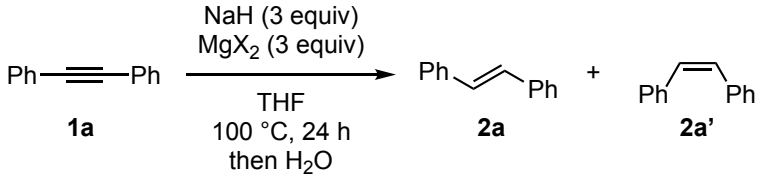


entry	NaH (equiv)	additive (equiv) [b]	Temp [°C]	*t* [h]	*Conv.* [%][c]	yield [%] [c]	
						2a	**2a'**
1	3	NaI (3)	80	24	>99	31	5
2	3	LiI (3)	80	24	>99	0	0
3	3	MgI_2 (3)	80	24	73	68	4
4	3	MgI_2 (2)	80	24	62	40	2
5	3	MgI_2 (1.5)	80	24	60	38	1
6	3	MgI_2 (3)	100	24	>99	92[d]	6
7	3	ZnI_2 (3)	80	24	<4	trace	trace
8	3	CaI_2 (3)	80	24	<20	8	<1
9	3	BaI_2 (3)	80	24	<5	2	1
10	3	SrI_2 (3)	80	24	<9	8	1

[a] All the reactions were conducted using 0.5 mmol of **1a** in THF (2.5 mL, 0.2M). [b] Grade of each reagent: NaI (>99%, crystalline powder, Sigma-Aldrich, 383112); LiI (>99%, beads, -10 mesh, anhydrous, Sigma-Aldrich, 439746); MgI_2 (98%, powder, Sigma-Aldrich, 394599); ZnI_2 (>99%, powder, anhydrous, Sigma-Aldrich, 466360); CaI_2 (>99%, beads, -10 mesh, anhydrous, Sigma-Aldrich, 516244); BaI_2 (>99%, beads, -10 mesh, anhydrous, Sigma-Aldrich, 413615); SrI_2 (>99%, beads, -10 mesh, anhydrous, Sigma-Aldrich, 400696). [c] GC yields with *n*-dodecane as an internal standard. [d] Isolated yield was 96% as a 94:6 *trans*/*cis*-mixture.

We then investigated effects of the counter ions on the magnesium and the reagent grade on the semi-hydride reduction of diphenylacetylene (**1a**) (Table S2). As for MgI_2, there is almost no reactivity difference between those of 98% and >99% purity (entries 1 and 2). The reaction in the presence of *t*-BuONa (1 equiv, generated in situ from *t*-BuOH and NaH) showed a similar performance (entry 3). The reaction with $MgBr_2$ of 98% purity was found detrimental with almost no conversion of **1a** (entry 4), whereas $MgBr_2$ of higher grade (>99% purity) performed similarly with MgI_2 (entry 5). The reaction with $MgCl_2$ in >99% purity provided slightly lower conversion of **1a** and isolated yield of **2a** (entry 6).

Table S2.[a]



entry	MgX_2	Grade	*Conv.* [%][b]	yield [%][b]	
				2a	**2a'**
1	MgI_2	98%，powder (Sigma-Aldrich, 394599)	>99	92	6
2	MgI_2	>99%, beads, –10 mesh, anhydrous (Sigma-Aldrich, 449911)	>99	93	6
3[c]	MgI_2	98%，powder (Sigma-Aldrich, 394599)	>99	89	11
4	$MgBr_2$	98%, powder (Sigma-Aldrich, 360074)	<3	trace	trace
5	$MgBr_2$	>99%, powder, anhydrous (Sigma-Aldrich, 495093)	>99	93[d]	5
6	$MgCl_2$	>99%, beads, –10 mesh, anhydrous (Sigma-Aldrich, 449164)	94	89	4

[a] All the reactions were conducted using 0.5 mmol of **1a**. [b] GC yields with *n*-dodecane as an internal standard. [c] *t*-BuOH (1 equiv) was added in the presence of 4 equiv of NaH and 3 equiv of MgI_2 for the purpose to examine the effect of *t*-butoxide for the reaction. [d] Isolated yield was 93% as a 94:6*trans*/*cis*-mixture.

GC calibration curve

All calibrations were performed using n-dodecane (0.5 mmol) as an internal standard. The GC oven temperature program was started from an initial temperature of 50 °C kept for 3 minutes, the temperature was then increased in a rate of 10 °C/min until 300 °C.

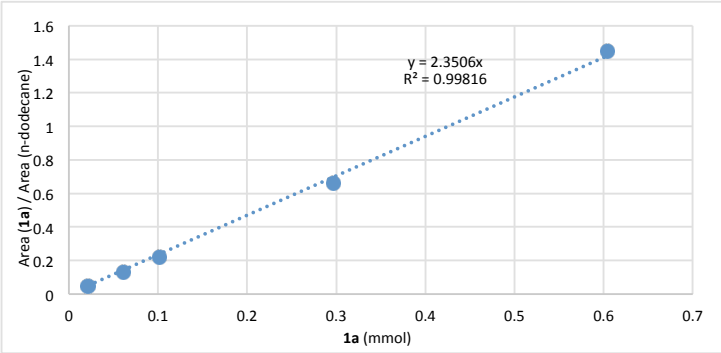


Figure S1. Calibration curve of diphenylacetylene (**1a**)

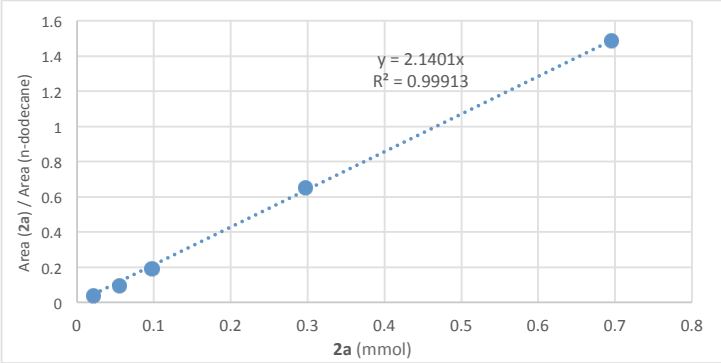


Figure S2. Calibration curve of *trans*-stilbene (**2a**)

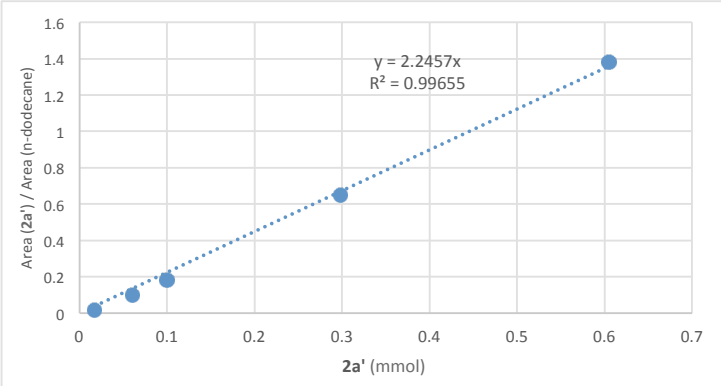
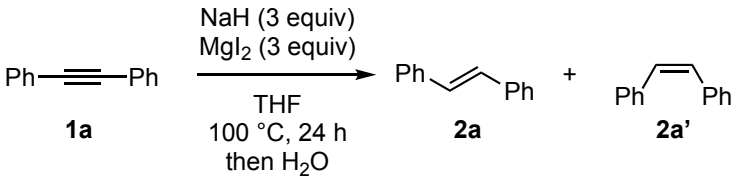


Figure S3. Calibration curve of *cis*-stilbene (**2a'**)

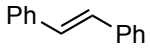
3.2. General procedure for synthesis of 2a



To a mixture of NaH (60 mg, 1.500 mmol) and MgI_2 (417.0 mg, 1.499 mmol) in 25 mL sealed tube was added a solution of 1,2-diphenylacetylene (**1a**) (89.0 mg, 0.499 mmol) in THF (2.5 mL) and the reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl solution. The organic materials were then extracted thrice with Et_2O and the combined extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. ^{1}H NMR analysis of the resulting crude material revealed that the ratio of **2a** and **2a'** is 94:6. The purification by flash column chromatography (silica gel, *n*-Hexane) gave a 94:6 mixture of **2a** and **2a'** in 96% yield (86.2 mg, 0.479 mmol) as white solid.

3.3. Characterization of the products

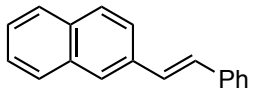
3.3.1. (*E*)-1,2-diphenylethene (2a) [CAS No.: 588-59-0]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.53 – 7.50 (m, 4H), 7.41 – 7.32 (m, 4H), 7.28 – 7.24 (m, 2H), 7.11 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.3, 128.69, 128.66, 127.6, 126.5.

3.3.2. (*E*)-2-styrylnaphthalene (2b)[19]



Prepared from **1b** (114.8 mg, 0.503 mmol) at 100 °C for 25 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2b** in 93% yield (108 mg, 0.469 mmol, *trans:cis* = 94:6) as white solid.

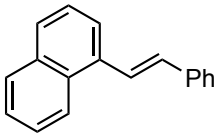
NMR data of the *trans*-isomer **2b** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.81 – 7.72 (m, 4H), 7.68 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.4, 134.8, 133.7, 133.0, 129.0, 128.8,

128.7, 128.3, 128.0, 127.68, 127.67, 126.6, 126.5, 126.3, 125.9, 123.5.

3.3.3. (*E*)-1-styrylnaphthalene (2c)[20]



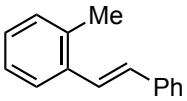
Prepared from **1c** (114.9 mg, 0.500 mmol) at 100 °C for 26 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2c** in 96% yield (110.5 mg, 0.480 mmol, *trans:cis* = 85:15) as colorless sticky oil.

NMR data of the *trans*-isomer **2c** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.22 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.28 (m, 1H), 7.15 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.6, 135.0, 133.7, 131.8, 131.4, 129.0, 128.7, 128.6, 128.0, 127.8, 126.7, 126.1, 125.8, 128.7, 123.8, 128.6.

3.3.4. (*E*)-1-methyl-2-styrylbenzene (2d)[21]



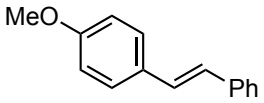
Prepared from **1d** (95.9 mg, 0.499 mmol) with 5 equiv of NaH and 5 equiv of MgI_2 at 100 °C for 58 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2d** in 91% yield (88.3 mg, 0.455 mmol, *trans:cis* = 85:15) as pale yellow oil.

NMR data of the *trans*-isomer **2d** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.59 – 7.57 (m, 1H), 7.52 – 7.50 (m, 2H), 7.38 – 7.28 (m, 3H), 7.28 – 7.22 (m, 1H), 7.22 – 7.07 (m, 3H), 6.99 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.7, 136.4, 135.8, 130.4, 130.0, 128.7, 127.6, 127.6, 126.5 (overlapped with 2C), 126.2, 125.4, 19.9.

3.3.5. (*E*)-1-methoxy-4-styrylbenzene (2e)[22]



Prepared from **1e** (103.6 mg, 0.500 mmol) at 100 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2e** in 92% yield (96.2 mg, 0.458

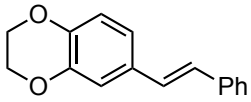
mmol, *trans:cis* = 94:6) as white solid.

NMR data of the *trans*-isomer **2e** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.49 – 7.43 (m, 4H), 7.36 – 7.32 (m, 2H), 7.26 – 7.19 (m, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.93 – 6.84 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 159.3, 137.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.1, 55.3.

3.3.6. (*E*)-6-styryl-2,3-dihydrobenzo[b][1,4]dioxine (2f)[23]



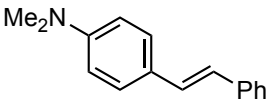
Prepared from **1f** (118.8 mg, 0.503 mmol) at 100 °C for 23 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2f** in 95% yield (113.8 mg, 0.478 mmol, *trans:cis* = 93:7) as white solid.

NMR data of the *trans*-isomer **2f** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.47 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.07 – 6.94 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 1H) 4.27 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 143.6, 143.4, 137.5, 131.2, 128.6, 128.1, 127.3, 127.2, 126.3, 120.0, 117.4, 114.9, 64.5, 64.4.

3.3.7. (*E*)-*N*,*N*-dimethyl-4-styrylaniline (2g)[24]



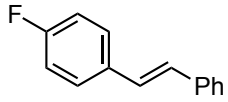
Prepared from **1g** (111.4 mg, 0.503 mmol) with 5 equiv of NaH and 5 equiv of MgI_2 at 100 °C for 68 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 97.5:2.5) gave **2g** in 64% yield (72.2 mg, 0.323 mmol, *trans:cis* = 93:7) as white solid.

NMR data of the *trans*-isomer **2g** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.50 – 7.46 (m, 2H), 7.42 – 7.40 (m, 2H), 7.34 – 7.30 (m, 2H), 7.21 – 7.17 (m, 1H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.91 (d, *J* = 16.4 Hz, 1H), 6.72 – 6.70 (m, 2H), 2.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 150.1, 138.2, 128.8, 128.6, 127.5, 126.6, 126.0, 125.8, 124.4, 112.4, 40.4.

3.3.8. (*E*)-1-fluoro-4-styrylbenzene (2h)[25]



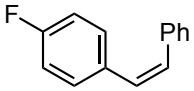
Prepared from **1h** (98.2 mg, 0.501 mmol) at 100 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2h** in 86% yield (85.6 mg, 0.432 mmol) as white solid, and *cis*-isomer **2h'** in 5% yield (5.4 mg, 0.027 mmol) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.53 – 7.41 (m, 4H), 7.36 – 7.33 (m, 2H), 7.27 – 7.22 (m, 1H), 7.12 – 6.95 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 162.3 (d, $J_{C\text{-}F}$ = 247.2 Hz), 137.2, 133.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.7, 128.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.6, 127.5, 126.4, 115.6 (d, $J_{C\text{-}F}$ = 21.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) -114.2.

(*Z*)-1-fluoro-4-styrylbenzene (2h')[25]

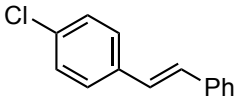


^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.25 – 7.15 (m, 7H), 6.95 – 6.85 (m, 2H), 6.59 (d, *J* = 12.0 Hz, 1H), 6.54 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 161.9 (d, $J_{C\text{-}F}$ = 246.7 Hz), 137.1, 133.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 130.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.3 (d, $J_{C\text{-}F}$ = 1.2 Hz), 129.1, 128.8, 128.3, 127.2, 115.1 (d, $J_{C\text{-}F}$ = 21.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ(ppm) -114.7.

3.3.9. (*E*)-1-chloro-4-styrylbenzene (2i)[26]

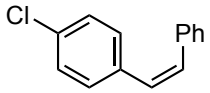


Prepared from **1i** (106.0 mg, 0.498 mmol) at 100 °C for 25 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2i** in 87% yield (93.1 mg, 0.434 mmol) as white solid, and *cis*-isomer **2i'** in 6% yield (6.2 mg, 0.029 mmol) of as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.49 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 7.11 – 6.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.0, 135.8, 133.2, 129.3, 128.8, 128.7, 127.8, 127.6, 127.4, 126.5.

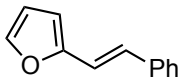
(*Z*)-1-chloro-4-styrylbenzene (2i')[26]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.30 – 7.12 (m, 9H), 6.62 (d, *J* = 12.4 Hz, 1H), 6.52 (d, *J* = 12.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 136.9, 135.6, 132.7, 130.9, 130.2, 128.9, 128.8, 128.4, 128.3, 127.3.

3.3.10. (*E*)-2-styrylfuran (2j)[27]

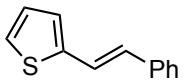


Prepared from **1j** (85.4 mg, 0.508 mmol) at 100 °C for 21 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2j** in 50% yield (43.0 mg, 0.253 mmol) as pale brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.46 – 7.44 (m, 2H), 7.40 – 7.38 (m, 1H), 7.35 – 7.31 (m, 2H), 7.25 – 7.21 (m, 1H), 7.03 (d, *J* = 16.4 Hz, 1H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.46 – 6.38 (m, 1H), 6.35 – 6.34 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 153.3, 142.1, 137.0, 128.7, 127.5, 127.1, 126.3, 116.5, 111.6, 108.5.

3.3.11. (*E*)-2-styrylthiophene (2k)[28]



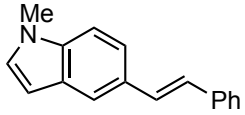
Prepared from **1k** (92.0 mg, 0.499 mmol) at 100 °C for 22 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2k** in 85% yield (78.6 mg, 0.422 mmol, *trans:cis* = 94:6) as white solid.

NMR data of the *trans*-isomer **2k** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.47 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 7.27 – 7.16 (m, 3H), 7.09 – 7.06 (m, 1H), 7.00 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 142.9, 136.9, 128.8, 128.7, 128.3, 127.6, 126.3, 126.1, 124.3, 121.8.

3.3.12. (*E*)-1-methyl-5-styryl-1*H*-indole (2l)[29]



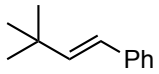
Prepared from **1l** (115.5 mg, 0.499 mmol) with 5 equiv of NaH and 5 equiv of MgI_2 at 100 °C for 50 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 98:2) gave **2l** in 79% yield (92.4 mg, 0.397 mmol, *trans*:*cis* = 97:3) as white solid.

NMR data of the *trans*-isomer of **2l** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.73 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.18 (m, 3H), 7.07 (d, *J* = 16.4 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.48 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 138.1, 136.6, 130.2, 129.4, 129.0, 128.8, 128.6, 126.9, 126.2, 125.9, 120.2, 119.7, 109.4, 101.4, 32.9.

3.3.13. (*E*)-(3,3-dimethylbut-1-en-1-yl)benzene (2m)[30]



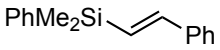
Prepared from **1m** (79.4 mg, 0.502 mmol) with 5 equiv of NaH and 5 equiv of MgI_2 at 120 °C for 70 h. Purification by flash column chromatography (silica gel, *n*-pentane) gave 70% yield (56.8 mg, 0.354 mmol, *trans:cis* = 93:7) of **2m** as colorless oil.

NMR data of the *trans*-isomer **2m** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.39 – 7.33 (m, 2H), 7.32 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 6.31 (d, *J* = 16.4 Hz, 1H), 6.25 (d, *J* = 16.4 Hz, 1H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 141.8, 138.1, 128.5, 126.7, 126.0, 124.6, 33.3, 29.6.

3.3.14. (*E*)-dimethyl(phenyl)(styryl)silane (2n)[9]



Prepared from **1n** (119.0 mg, 0.503 mmol) with 5 equiv of NaH and 5 equiv of MgI_2 at 120 °C for 70 h. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2n** in 35% yield (42 mg, 0.176 mmol, *trans:cis* = 96:4) as colorless oil.

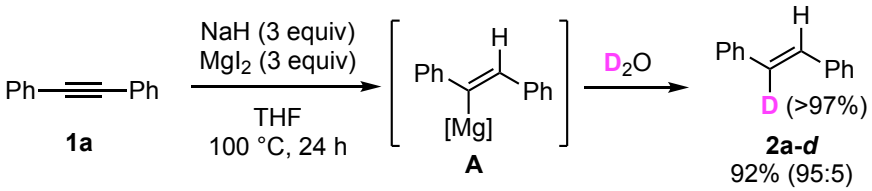
NMR data of the *trans*-isomer of **2n** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.58 – 7.56 (m, 2H), 7.45 – 7.43 (m, 2H), 7.41 – 7.28 (m, 5H), 7.28 – 7.18 (m, 1H), 6.94 (d, *J* = 19.2 Hz, 1H), 6.58 (d, *J* = 19.2 Hz, 1H), 0.43 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 145.3, 138.6, 138.2, 133.9, 129.0, 128.5, 128.1, 127.8, 127.1, 126.5, -2.5.

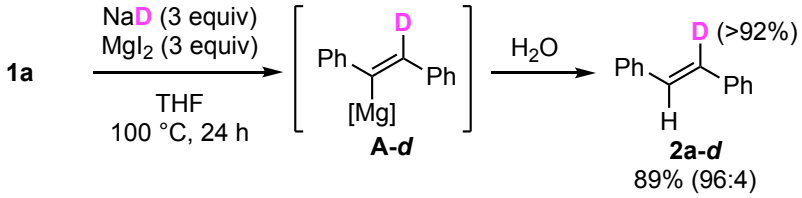
3.4. Deuterium-labelling experiments

3.4.1. Reduction of 1a quenched with D_2O



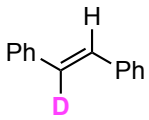
The reaction was conducted using **1a** (89.1 mg, 0.500 mmol) at 100 °C for 24 h by following the procedure described in section 3.2. The reaction was quenched by D_2O at 0 °C. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **2a-*d*** in 92% yield (82.9 mg, 0.457 mmol, *trans:cis* = 95:5) with >97% deuterium incorporation.

3.4.2. Reduction of 1a using NaD



The reaction was conducted using **1a** (89.0 mg, 0.499 mmol) with NaD (38 mg, 1.520 mmol) at 100 °C for 24 h by following the procedure described in section 3.2. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane) gave **2a-*d*** in 89% yield (80.1 mg, 0.444 mmol, *trans:cis* = 96:4) with >92% deuterium incorporation.

(*E*)-(ethene-1,2-diyl-1-*d*)dibenzene (2a-*d*)[31]

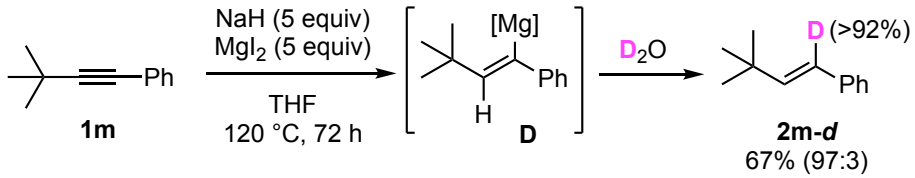


^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.59 – 7.45 (m, 4H), 7.38 – 7.34 (m, 4H), 7.27 – 7.22 (m, 2H), 7.10 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.3, 137.2, 128.65 (overlapped with 2C), 128.60 (t, J = 24.2 Hz), 128.58, 127.58, 127.57, 126.49, 126.47.

MS (HRMS ESI): Calcd for $C_{14}H_{22}DO$ $[M+H]^+$ 182.1080, Found: 182.1084.

3.4.3. Reduction of 1m quenched with D_2O



The reaction was conducted using **1m** (80.0 mg, 0.506 mmol) at 120 °C for 72 h by following the procedure described in section 3.2. The reaction was quenched by D_2O at 0 °C. Purification by flash column chromatography (silica gel, *n*-pentane) gave **2m-*d*** in 67% yield (54.3 mg, 0.337 mmol, *trans:cis* = 97:3) with >92% deuterium incorporation.

For **(*E*)-(3,3-dimethylbut-1-en-1-yl-1-*d*)benzene (2m-*d*)**:

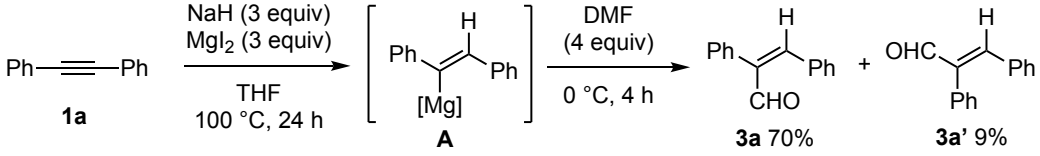
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.37 – 7.36 (m, 2H), 7.33 – 7.24 (m, 2H), 7.18 – 7.15 (m, 1H), 6.27 – 6.24 (m, 1H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 141.8, 138.0, 128.5, 126.7, 126.0, 124.32 (t, $J_{C\text{-}D}$ = 23.1 Hz), 33.3, 29.6.

MS (HRMS ESI): Calcd for $C_{12}H_{16}D$ $[M+H]^+$ 162.1393, Found: 162.1390.

3.5 Functionalization with various electrophiles in reduction of 1a

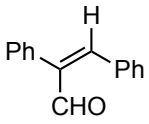
3.5.1. Formylation with DMF



The first reduction was conducted using **1a** (88.5 mg, 0.497 mmol) by following the procedure described in section 3.2. After full conversion of **1a** was confirmed by the

GC analysis, DMF (0.15 mL, 1.946 mmol) was added to the reaction mixture at 0 °C and the reaction mixture was stirred for another 4 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 97:3) gave **3a** (72.8 mg, 0.349 mmol) in 70% yield as white solid and **3a'** (9.0 mg, 0.0432 mmol) in 9% yield as white solid.

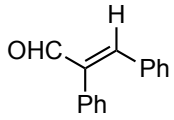
(*Z*)-2,3-diphenylacrylaldehyde (3a)[32]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 10.11 (s, 1H), 7.86 (s, 1H), 7.52 – 7.31 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 192.2, 147.1, 141.1, 136.2, 134.0, 130.3, 129.6, 128.7, 128.5, 128.4, 128.3.

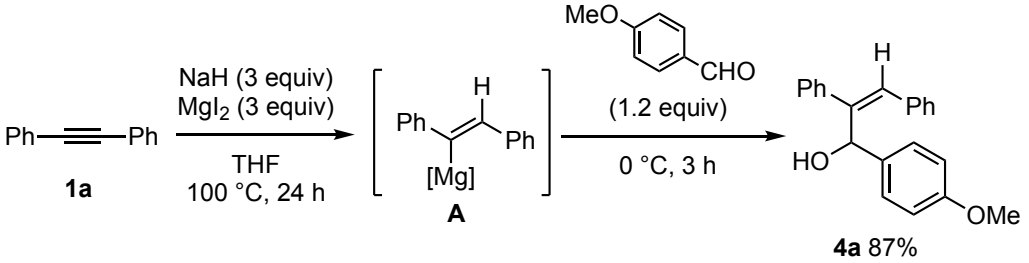
(*E*)-2,3-diphenylacrylaldehyde (3a')[32]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 9.77 (s, 1H), 7.44 – 7.33 (m, 4H), 7.33 – 7.26 (m, 1H), 7.27 – 7.14 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 193.9, 150.1, 141.8, 134.0, 133.3, 130.7, 130.2, 129.3, 128.8, 128.5, 128.3.

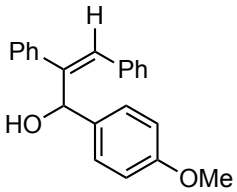
3.5.2. Addition to *p*-anisaldehyde (1.2 equiv)



The first reduction was conducted using **1a** (88.7 mg, 0.498 mmol) by following the procedure described in section 3.2. After full conversion of **1a** was confirmed by the

GC analysis, *p*-anisaldehyde (73 μL, 0.600 mmol) was added to the reaction mixture at 0 °C and the mixture was stirred for 3 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) gave **4a** (137.2 mg, 0.434 mmol) in 87% yield as pale yellow oil and **4a'** (11.8 mg, 0.038 mmol) in 7% yield as colorless oil.

(*Z*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (4a)



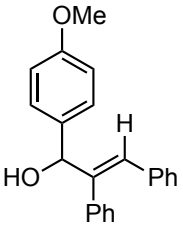
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.40 – 7.29 (m, 8H), 7.29 – 7.19 (m, 4H), 6.97 (s, 1H), 6.88 – 6.81 (m, 2H), 6.11 (s, 1H), 3.77 (s, 3H), 2.12 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 158.7, 142.8, 139.5, 136.7, 134.4, 131.6, 128.8, 128.5, 128.4, 128.1, 127.41, 127.40, 127.3, 113.7, 71.0, 55.2.

MS (HRMS ESI): Calcd for $C_{22}H_{21}O_2$ $[M+H]^+$ 317.1542, Found: 317.1536.

IR (neat, cm^{-1}): 3444 [ν(O-H)], 1610[ν(C=C)], 1051 [ν(C-O)], 1034 [ν(C-O)].

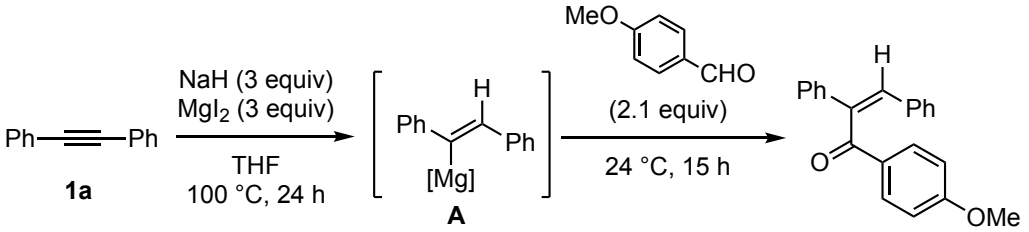
(*E*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (4a')[33]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.29 – 7.17 (m, 5H), 7.12 – 7.05 (m, 3H), 6.99 – 6.90 (m, 4H), 6.87 (s, 1H), 6.86 – 6.80 (m, 2H), 5.50 (s, 1H), 3.79 (s, 3H), 2.10 (d, *J* = 2.8 Hz, 1H).

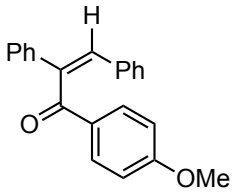
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 159.2, 144.2, 138.3, 136.5, 133.9, 129.4, 129.3, 128.4, 128.2, 127.9, 127.3, 126.80, 126.79, 113.7, 78.7, 55.2.

3.5.3. Addition to *p*-anisaldehyde (2.1 equiv)



The first reduction was conducted using **1a** (88.9 mg, 0.499 mmol) by following the procedure described in section 3.2. After full conversion of **1a** was confirmed by the GC analysis, *p*-anisaldehyde (128 μL, 1.052 mmol) was added to the reaction mixture at 24 °C and the mixture was stirred for 15 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **5a** (119.5 mg, 0.381 mmol, 92:8) in 76% yield as white solid.

(*Z*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-one (5a)[34]

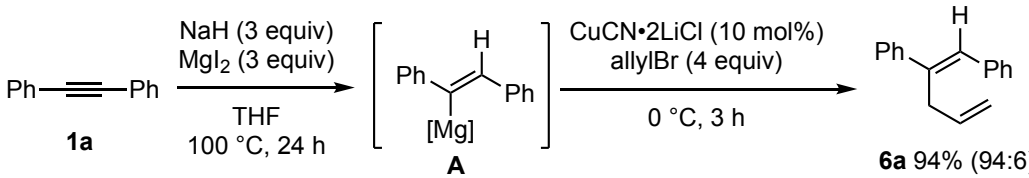


NMR data of the major isomer **5a** are described below:

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.98 – 7.95 (m, 2H), 7.48 – 7.45 (m, 2H), 7.36 – 7.25 (m, 5H), 7.22 – 7.08 (m, 4H), 6.84 – 6.81 (m, 2H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 197.8, 163.9, 140.9, 138.1, 135.5, 132.0, 129.5, 129.4, 128.8 (overlapped with 2C), 128.4, 128.1, 127.9, 126.2, 114.0, 55.3.

3.5.4. Cu-catalyzed allylation

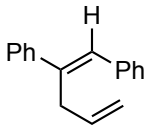


The first reduction was conducted using **1a** (90.3 mg, 0.507 mmol) by following the

procedure described in section 3.2. After full conversion of **1a** was confirmed by the GC analysis, allyl bromide (0.17 mL, 2.009 mmol) and CuCN•2LiCl (1 M solution in THF, 50 µL, 0.050 mmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 3 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel, *n*-Hexane) gave **6a** (104.8 mg, 0.476 mmol, 94:6) in 94% yield as colorless oil.

NMR data of the major isomer **6a** are described below:

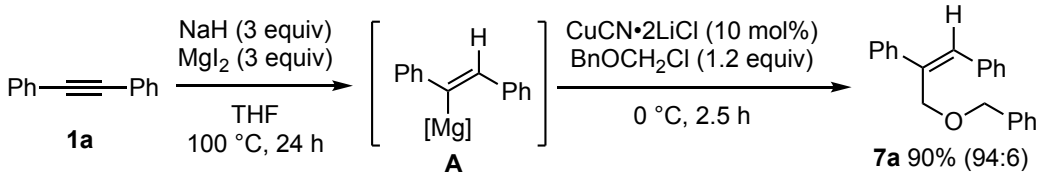
(*E*)-penta-1,4-diene-1,2-diyldibenzene (6a)[35]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.57 – 7.45 (m, 2H), 7.38 – 7.32 (m, 6H), 7.30 – 7.19 (m, 2H), 6.91 (s, 1H), 6.00 – 5.83 (m, 1H), 5.17 – 5.01 (m, 2H), 3.46 – 3.45 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 142.6, 139.2, 137.8, 136.0, 129.4, 128.7, 128.3, 128.2, 127.3, 126.8, 126.5, 116.3, 34.6.

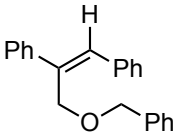
3.5.5. Cu-catalyzed benzyloxymethylation



The first reduction was conducted using **1a** (89.2 mg, 0.501 mmol) by following the procedure described in section 3.2. After full conversion of **1a** was confirmed by the GC analysis, benzyloxymethyl chloride (83 µL, 0.597 mmol) and CuCN•2LiCl (1 M solution in THF, 50 µL, 0.050 mmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 2.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 99:1) gave **7a** (134.7 mg, 0.448 mmol, 94:6) in 90% yield as colorless oil.

NMR data of the major isomer **7a** are described below:

(*Z*)-(3-(benzyloxy)prop-1-ene-1,2-diyl)dibenzene (7a)



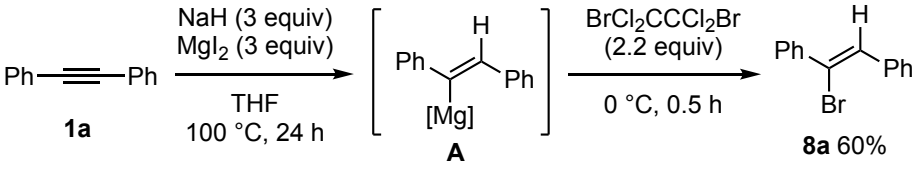
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.59 – 7.57 (m, 2H), 7.45 – 7.20 (m, 13H), 7.07 (s, 1H), 4.54 (s, 2H), 4.48 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 141.5, 138.0, 137.8, 137.0, 132.5, 129.0, 128.4, 128.3, 128.2, 128.1, 127.7, 127.4, 127.2, 126.4, 72.5, 67.6.

MS (HRMS ESI): Calcd for $C_{22}H_{21}O$ $[M+H]^+$ 301.1592, Found: 301.1596.

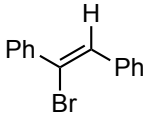
IR (neat, cm^{-1}): 1599[ν(C=C)], 1090 [ν(C-O)], 1070 [ν(C-O)].

3.5.6. Bromination



The first reduction was conducted using **1a** (89.6 mg, 0.503 mmol) by following the procedure described in section 3.2. After full conversion of **1a** was confirmed by the GC analysis, 1,2-dibromotetrachloroethane (355.5 mg, 1.092 mmol) was added to the reaction mixture at 0 °C and the mixture was stirred for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane) gave **8a** with inseparable impurity (85% yield, 93:7, calculated based on ^{1}H NMR). Further purification by GPC gave **8a** as a single isomer (78.3 mg, 0.302 mmol) in 60% yield as colorless oil.

(*Z*)-(1-bromoethene-1,2-diyl)dibenzene (8a)[36]

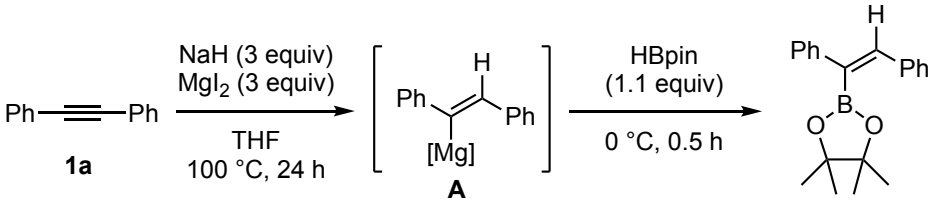


^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.75 – 7.60 (m, 4H), 7.44 – 7.28 (m, 6H), 7.21 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 141.0, 136.3, 129.9, 129.2, 128.7, 128.3,

128.2, 128.04, 127.79, 124.1.

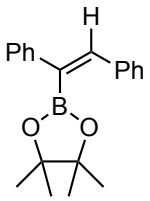
3.5.7. Borylation



The first reduction was conducted using **1a** (90.0 mg, 0.505 mmol) by following the procedure described in section 3.2. After full conversion of **1a** was confirmed by the GC analysis, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (80 μL, 0.551 mmol) was added to the reaction mixture at 0 °C and the mixture was stirred for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **9a** (141.3 mg, 0.461 mmol, 93:7) in 91% yield as white solid.

NMR data of the major isomer **9a** are described below:

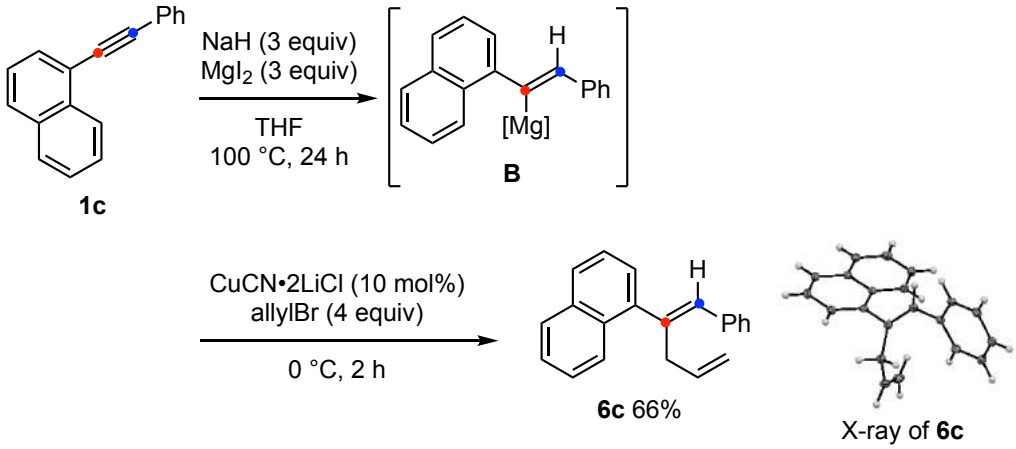
(*E*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a)[37]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.48 – 7.40 (m, 4H), 7.36 – 7.30 (m, 4H), 7.29 – 7.22 (m, 3H), 1.30 (s, 12H).

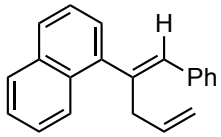
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 142.6, 140.8, 138.8, 128.4, 128.2, 128.1, 127.5, 126.93, 126.86, 84.0, 24.9. (The ^{13}C NMR signal attached to the B atom was not observed due to low intensity.)

3.5.8. Synthesis of 6c (Scheme 3B)



The first reduction was conducted using **1c** (115.6 mg, 0.506 mmol) by following the procedure described in section 3.2. After full conversion of **1c** was confirmed by the GC analysis, allyl bromide (0.17 mL, 2.009 mmol) and CuCN•2LiCl (1 M solution in THF, 50 µL, 0.050 mmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane) gave **6c** (91.0 mg, 0.337 mmol) in 66% yield as white solid, which was recrystallized from CH_2Cl_2:*n*-Hexane to afford colorless crystal. The structure of **6c** could be confirmed by X-ray crystallography analysis (CCDC-1987693).

(*E*)-1-(1-phenylpenta-1,4-dien-2-yl)naphthalene (6c)

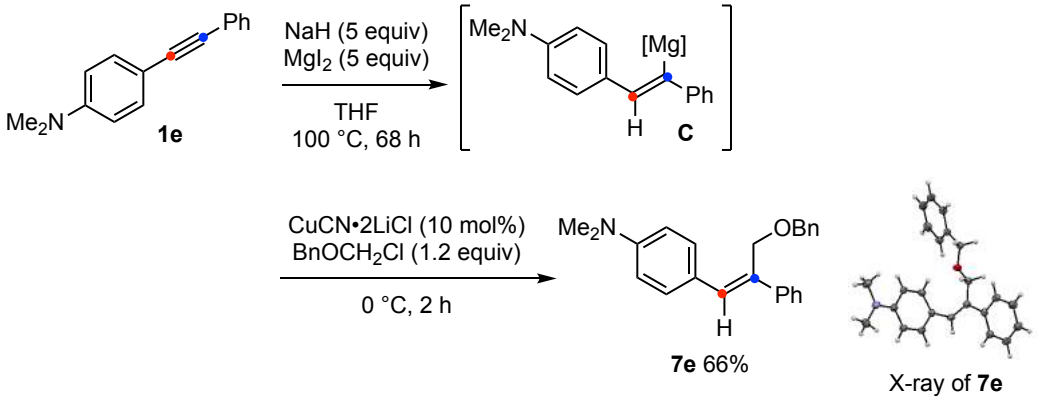


^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.21 – 8.01 (m, 1H), 7.88 – 7.86 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 5H), 7.43 – 7.38 (m, 3H), 7.32 – 7.28 (m, 1H), 6.64 (s, 1H), 5.80 (ddt, *J* = 16.8, 10.0, 6.4 Hz, 1H), 5.04 (dd, *J* = 16.8, 1.6 Hz, 1H), 4.96 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.53 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 141.8, 139.4, 137.5, 135.3, 133.9, 131.8, 131.6, 128.8, 128.4, 128.3, 127.3, 126.9, 125.81, 125.79, 125.7, 125.6, 125.2, 116.3, 38.0.

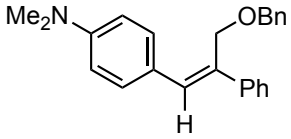
MS (HRMS ESI): Calcd for $C_{21}H_{19}$ $[M+H]^+$ 217.1487, Found: 217.1482.

3.5.9. Synthesis of 7e (Scheme 3B)



The first reduction was conducted using **1e** (111.1 mg, 0.502 mmol) by following the procedure described in section 3.2. After full conversion of **1e** was confirmed by the GC analysis, benzyloxymethyl chloride (83 μL, 0.597 mmol) and CuCN•2LiCl (1 M solution in THF, 50 μL, 0.050 mmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 3 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 99:1) gave **7e** (87.3 mg, 0.332 mmol) in 66% yield as pale yellow solid, which was recrystallized from CH_2Cl_2:*n*-Hexane to afford colorless crystal. The structure of **7e** was confirmed by X-ray crystallography analysis (CCDC-1987694).

(*Z*)-4-(3-(benzyloxy)-2-phenylprop-1-en-1-yl)-*N*,*N*-dimethylaniline (7e)

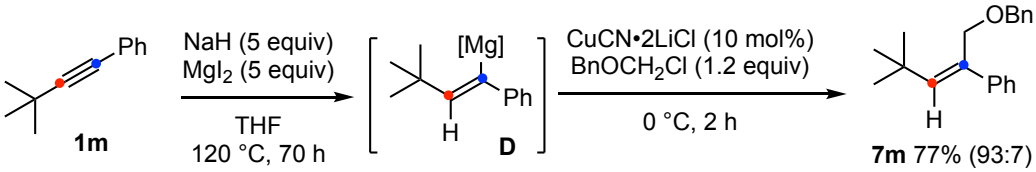


^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.60 – 7.53 (m, 2H), 7.38 – 7.22 (m, 10H), 7.01 (s, 1H), 6.69 – 6.66 (m, 2H), 4.58 (s, 2H), 4.51 (s, 2H), 2.98 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 149.7, 142.3, 138.2, 134.3, 133.1, 130.2, 128.30, 128.28, 128.2, 127.6, 126.8, 126.2, 125.3, 112.0, 72.5, 68.0, 40.4.

MS (HRMS ESI): Calcd for $C_{24}H_{26}ON$ $[M+H]^+$ 344.2014, Found: 344.2015.

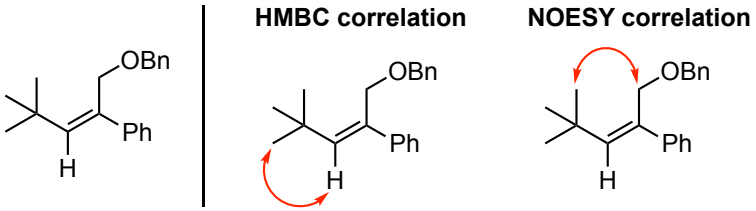
3.5.10. Synthesis of 7m (Scheme 3B)



The first reduction was conducted using **1m** (79.2 mg, 0.501 mmol) by following the procedure described in section 3.2. After full conversion of **1m** was confirmed by the GC analysis, benzyloxymethyl chloride (83 μL, 0.597 mmol) and CuCN•2LiCl (1 M solution in THF, 50 μL, 0.050 mmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 99:1) gave **7m** (107.5 mg, 0.383 mmol, 93:7) in 77% yield as colorless oil.

NMR data of the major isomer **7m** are described below:

(*Z*)-((2-benzylidene-3,3-dimethylbutoxy)methyl)benzene (7m)



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.41 – 7.21 (m, 10H), 5.92 (s, 1H), 4.50 (s, 2H), 4.49 (s, 2H), 1.21 (s, 9H).

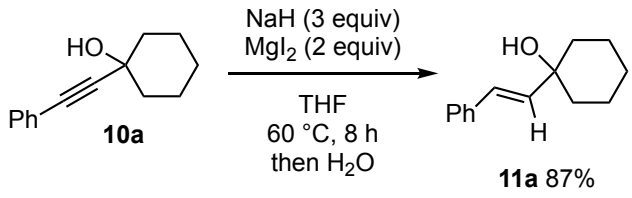
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 144.4, 143.4, 138.2, 135.8, 128.2, 128.0, 127.9, 127.5, 126.62, 126.58, 72.3, 66.9, 33.3, 31.5.

MS (HRMS ESI): Calcd for $C_{20}H_{25}O$ $[M+H]^+$ 281.1905, Found: 281.1914.

IR (neat, cm^{-1}): 1599 [ν(C=C)], 1091 [ν(C-O)], 1074 [ν(C-O)].

4. Guided hydromagnesiation of alkynes

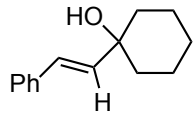
4.1. General procedure of guided reduction: synthesis of 11a



To a mixture of NaH (60 mg, 1.500 mmol) and MgI_2 (278.0 mg, 0.999 mmol) in 25 mL sealed tube was added a solution of **10a** (103.8 mg, 0.518 mmol) in THF (2.5 mL) and the reaction mixture was stirred at 60 °C for 8 h. The reaction mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl solution. The organic materials were then extracted thrice with Et_2O and the combined extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. ^{1}H NMR analysis of the resulting crude material revealed that the reaction gave *trans*-alkene **11a** as a single isomer. The purification by flash column chromatography (silica gel, *n*-Hexane to *n*-Hexane:EtOAc = 95:5) gave **11a** in 87% yield (91.3 mg, 0.451 mmol) as white solid.

4.2. Characterization of the products

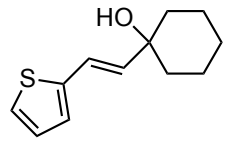
4.2.1. (*E*)-1-styrylcyclohexan-1-ol (11a)[38]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.43 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.18 (m, 1H), 6.63 (d, *J* = 16.4 Hz, 1H), 6.34 (d, *J* = 16.4 Hz, 1H), 1.80 – 1.52 (m, 9H), 1.43 (br s, 1H), 1.38 – 1.27 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.5, 137.1, 128.5, 127.4, 127.0, 126.4, 71.7, 38.0, 25.5, 22.1.

4.2.2. (*E*)-1-(2-(thiophen-2-yl)vinyl)cyclohexan-1-ol (11b)



Prepared from **10b** (103.0 mg, 0.499 mmol) at 60 °C for 7 h. Purification by flash

column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **11b** as a single *trans*-isomer in 85% yield (88.0 mg, 0.422 mmol) as pale brown solid.

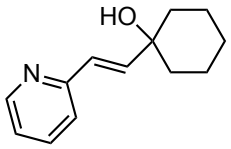
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.16 – 7.12 (m, 1H), 6.96 – 6.94 (m, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 1.76 – 1.51 (m, 9H), 1.41 (br s, 1H), 1.38 – 1.23 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 142.4, 137.1, 127.3, 125.5, 123.8, 120.5, 71.6, 37.9, 25.4, 22.0.

MS (HRMS ESI): Calcd for $C_{12}H_{17}OS$ $[M+H]^+$ 209.1000, Found: 209.0999.

IR (neat, cm^{-1}): 3429 [ν(O-H)], 1647 [ν(C=C)], 1078 [ν(C-O)].

4.2.3. (*E*)-1-(2-(pyridin-2-yl)vinyl)cyclohexan-1-ol (11c)



Prepared from **10c** (100.5 mg, 0.499 mmol) at 60 °C for 7.5 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 75:25) gave **11c** as a single *trans*-isomer in 56% yield (57.1 mg, 0.281 mmol) as pale yellow sticky oil.

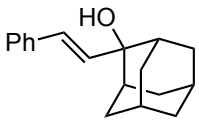
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.55 (d, *J* = 4.4 Hz, 1H), 7.62 (td, *J* = 7.6, 1.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.12 (dd, *J* = 7.2, 4.8 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 1.88 – 1.49 (m, 10H), 1.36 – 1.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 155.6, 149.5, 142.1, 136.5, 126.8, 122.0, 121.9, 71.8, 37.8, 25.4, 21.9.

MS (HRMS ESI): Calcd for $C_{13}H_{17}NONa$ $[M+Na]^+$ 226.1208, Found: 226.1207.

IR (neat, cm^{-1}): 3416 [ν(O-H)], 1651 [ν(C=C)], 1080 [ν(C-O)].

4.2.4. (1*R**,3*S**,5*r*,7*r*)-2-((*E*)-styryl)adamantan-2-ol (11d)[39]



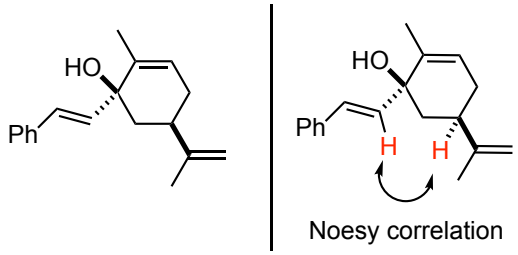
Prepared from **10d** (127.7 mg, 0.506 mmol) at 60 °C for 10 h. Purification by flash column chromatography (silica gel, *n*-Hexane to *n*-Hexane:EtOAc = 90:10) gave **11d** as a single *trans*-isomer in 56% yield (72.2 mg, 0.284 mmol) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.45 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.28 – 7.18 (m, 1H), 6.73 (d, *J* = 16.4 Hz, 1H), 6.62 (d, *J* = 16.4 Hz, 1H), 2.31 (d, *J* = 12.0

Hz, 2H), 1.96 – 1.94 (m, 4H), 1.85 – 1.84 (m, 2H), 1.82 – 1.67 (m, 4H), 1.62 (d, *J* = 12.4 Hz, 2H), 1.48 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.3, 136.4, 128.7, 128.6, 127.5, 126.4, 74.7, 38.3, 38.0, 34.8, 32.8, 27.3, 27.1.

4.2.5. (1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)-1-((*E*)-styryl)cyclohex-2-en-1-ol (11e)



Prepared from **10e** (125.8 mg, 0.502 mmol) at 60 °C for 8 h. Purification by flash column chromatography (silica gel, *n*-Hexane to *n*-Hexane:EtOAc = 90:10) gave **11e** as a single *trans*-isomer in 77% yield (98.9 mg, 0.389 mmol) as colorless oil.

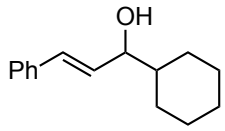
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.43 – 7.37 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.19 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 5.64 – 5.63 (m, 1H), 4.72 (s, 2H), 2.42 – 2.31 (m, 1H), 2.24 – 2.12 (m, 1H), 2.08 – 1.92 (m, 2H), 1.82 (s, 1H), 1.78 (t, *J* = 12.4 Hz, 1H), 1.72 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 148.7, 136.8, 135.8, 134.0, 129.2, 128.5, 127.5, 126.5, 125.2, 109.1, 75.5, 42.8, 38.7, 31.2, 20.7, 17.3.

MS (HRMS ESI): Calcd for $C_{18}H_{23}O$ $[M+H]^+$ 255.1749, Found: 255.1747.

IR (neat, cm^{-1}): 3373 [ν(O-H)], 1645 [ν(C=C)], 1069 [ν(C-O)], 891 [ν(C=CH_2)].

4.2.6. (*E*)-1-cyclohexyl-3-phenylprop-2-en-1-ol (11f)[40]

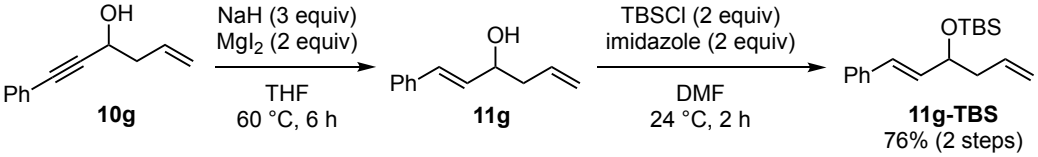


Prepared from **10f** (107.5 mg, 0.502 mmol) at 60 °C for 10.5 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) gave **11f** in 76% yield (82.9 mg, 0.383 mmol, *trans:cis* = 99:1) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.41 – 7.34 (m, 2H), 7.34 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 7.2 Hz, 1H), 4.01 (dd, *J* = 7.2, 7.2 Hz, 1H), 1.92 – 1.89 (m, 1H), 1.84 – 1.59 (m, 4H), 1.54 – 1.45 (m, 1H), 1.34 – 0.95 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 136.8, 131.2, 131.0, 128.5, 127.5, 126.4, 77.5, 43.9, 28.9, 28.6, 26.5, 26.1, 26.0.

4.2.7. (*E*)-tert-butyldimethyl((1-phenylhexa-1,5-dien-3-yl)oxy)silane (11g-TBS)[41]

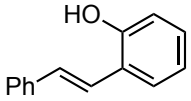


The first reduction was conducted using **10g** (84.8 mg, 0.498 mmol) by following the procedure described in section 4.1. After full conversion of **10g** was confirmed by the GC analysis, the reaction was quenched with saturated aqueous NH_4Cl solution, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was then dissolved in DMF (2 mL) and treated with *t*-butyldimethylsilyl chloride (TBSCl) (150.4 mg, 0.998 mmol, 2 equiv) and imidazole (61.0 mg, 1.015 mmol, 2 equiv) for 2 h at 24 °C. The mixture was diluted with water, and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 99:1) gave **11g-TBS** (109.0 mg, 0.378 mmol) as a single *trans*-isomer in 76% yield as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.37 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.19 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.84 (dddd, *J* = 17.2, 10.0, 7.2, 7.2 Hz, 1H), 5.14 – 4.99 (m, 2H), 4.32 (q, *J* = 6.2 Hz, 1H), 2.46 – 2.26 (m, 2H), 0.92 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.1, 134.9, 132.8, 129.2, 128.5, 127.3, 126.4, 117.0, 73.3, 43.2, 25.9, 18.3, -4.3, -4.7.

4.2.8. (*E*)-2-styrylphenol (11h)[42]



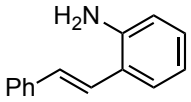
Prepared from **10h** (97.5 mg, 0.502 mmol) at 80 °C for 6 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **11h** as a single *trans*-isomer in 84% yield (83.0 mg, 0.423 mmol) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.54 – 7.52 (m, 3H), 7.41 – 7.31 (m, 3H), 7.30

– 7.21 (m, 1H), 7.18 – 7.08 (m, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.80 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.04 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 153.0, 137.6, 130.2, 128.6 (overlapped with 2C), 127.6, 127.2, 126.5, 124.7, 123.0, 121.1, 115.9.

4.2.9. (*E*)-2-styrylaniline (11i)[43]

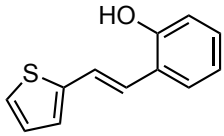


Prepared from **10i** (95.5 mg, 0.494 mmol) at 80 °C for 6.5 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) followed by recrystallized from *n*-Hexane:CH_2Cl_2 gave **11i** as a single *trans*-isomer in 55% yield (52.8 mg, 0.270 mmol) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.51 – 7.49 (m, 2H), 7.40 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 7.16 (d, *J* = 16.0 Hz, 1H), 7.10 (td, *J* = 8.0, 1.6 Hz, 1H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.82 – 6.78 (m, 1H), 6.70 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.69 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 143.9, 137.6, 130.3, 128.7, 128.6, 127.5, 127.2, 126.4, 124.2, 123.8, 119.2, 116.2.

4.2.10. (*E*)-2-(2-(thiophen-2-yl)vinyl)phenol (11j)



Prepared from **10j** (100.0 mg, 0.499 mmol) at 80 °C for 6 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) gave **11j** as a single *trans*-isomer in 86% yield (87.0 mg, 0.430 mmol) as white solid.

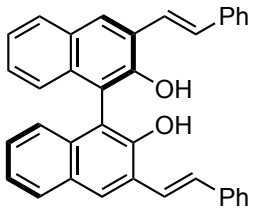
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.46 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 16.0 Hz, 1H), 7.22 – 7.03 (m, 4H), 7.03 – 6.97 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.01 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 152.9, 143.3, 128.6, 127.5, 127.2, 126.0, 124.34, 124.31, 123.3, 122.8, 121.2, 116.0.

MS (HRMS ESI): Calcd for $C_{12}H_{11}OS$ $[M+H]^+$ 203.0531, Found: 203.0528.

IR (neat, cm^{-1}): 3574 [ν(O-H)], 1603 [ν(C=C)], 1087 [ν(C-O)].

4.2.11. (*R*)-3,3'-di((*E*)-styryl)-[1,1'-binaphthalene]-2,2'-diol (11k)



Prepared from **10k** (237.5 mg, 0.488 mmol) with 6 equiv of NaH and 4 equiv of MgI_2 at 100 °C for 22 h. Purification by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **11k** in 51% yield (121.5 mg, 0.248 mmol) as a single *trans*-isomer as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.26 (s, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 6.0 Hz, 4H), 7.61 (d, *J* = 16.4 Hz, 2H), 7.45 (d, *J* = 16.4 Hz, 2H), 7.40 – 7.36 (m, 6H), 7.32 – 7.25 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.36 (s, 2H).

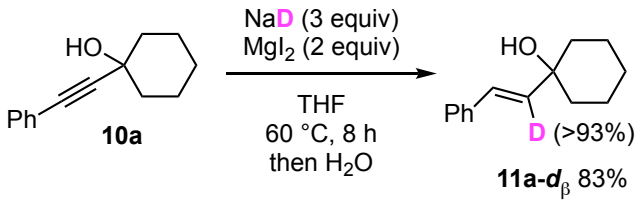
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 151.0, 137.6, 132.7, 131.2, 129.5, 128.7, 128.4, 128.0, 127.7, 127.3, 126.81, 126.77, 124.4, 124.0, 123.4, 111.1.

MS (HRMS ESI): Calcd for $C_{36}H_{27}O_2$ $[M+H]^+$ 491.2011, Found: 491.2017.

IR (neat, cm^{-1}): 3491 [ν(O-H)], 1634 [ν(C=C)], 1215 [ν(C-O)].

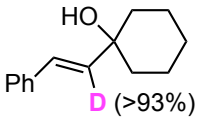
4.3. Deuterium-labelling experiments

4.3.1. With NaD



The reaction was conducted using **10a** (101.5 mg, 0.507 mmol), NaD (38.0 mg, 1.520 mmol) and MgI_2 (278.0 mg, 1.000 mmol) by following the procedure described in section 4.1. Purification of the crude material by flash column chromatography (silica gel, *n*-Hexane to *n*-Hexane:EtOAc = 95:5) gave *trans*-alkene **11a-*d*$_\beta$** (84.9 mg, 0.418 mmol, 83% yield) having a deuterium at the β-position on the styryl moiety in >93% incorporation rate.

(*E*)-1-(2-phenylvinyl-1-*d*)cyclohexan-1-ol (11a-*d*$_\beta$)

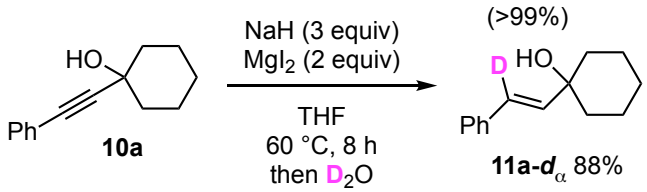


^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.40 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.13 (m, 1H), 6.62 (s, 1H), 1.77 – 1.47 (m, 10H), 1.39 – 1.22 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.08 (t, $J_{C\text{-}D}$ = 22.8 Hz), 137.07, 128.5, 127.2, 126.8, 126.3, 71.6, 37.9, 25.4, 22.0.

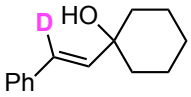
MS (HRMS ESI): Calcd for $C_{14}H_{17}DONa$ $[M+Na]^+$ 226.1318, Found: 226.1312.

4.3.2. With D_2O



The reaction was conducted using **10a** (100.8 mg, 0.503 mmol) by following the procedure described in section 4.1. and quenched with D_2O. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane to *n*-Hexane:EtOAc = 95:5) gave **11a-*d*$_\alpha$** (90.3 mg, 0.444 mmol, 88% yield) having a deuterium at the α-position on the styryl moiety in >99% incorporation rate.

(*E*)-1-(2-phenylvinyl-2-*d*)cyclohexan-1-ol (11a-*d*$_\alpha$)



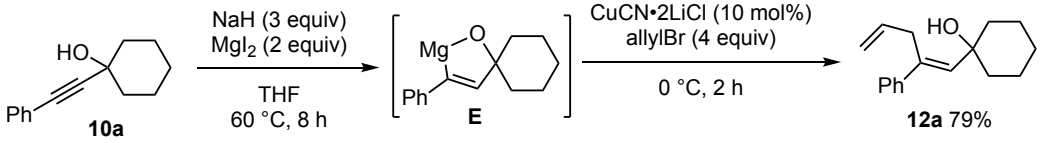
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.37 – 7.35 (m, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H), 6.31 (s, 1H), 1.83 – 1.44 (m, 10H), 1.42 – 1.16 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 137.3, 137.0, 128.4, 127.2, 126.6 (t, $J_{C\text{-}D}$ = 23.5 Hz), 126.3, 71.6, 37.9, 25.4, 22.0.

MS (HRMS ESI): Calcd for $C_{14}H_{18}DO$ $[M+H]^+$ 204.1499, Found: 204.1506.

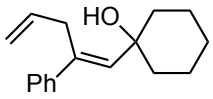
4.4. Functionalization with various electrophiles

4.4.1. Cu-catalyzed allylation starting from 10a



The first reduction was conducted using **10a** (100.4 mg, 0.501 mmol) by following the procedure described in section 4.1. After full conversion of **10a** was confirmed by the GC analysis, CuCN•2LiCl (1M solution in THF, 50 μL, 0.050 mmol) and allyl bromide (0.17 mL, 1.964 mmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **12a** (95.4 mg, 0.394 mmol) in 79% yield as colorless oil.

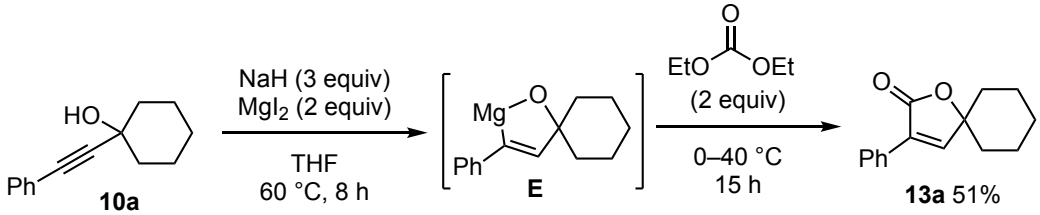
(*E*)-1-(2-phenylpenta-1,4-dien-1-yl)cyclohexan-1-ol (12a)[44]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.37 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.20 (m, 1H), 5.95 – 5.78 (m, 1H), 5.86 (s, 1H), 5.13 – 5.01 (m, 1H), 5.01 – 4.94 (m, 1H), 3.65 – 3.64 (m, 2H), 1.73 – 1.66 (m, 6H), 1.62 (s, 1H), 1.54 – 1.44 (m, 3H), 1.41 – 1.34 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 143.6, 139.6, 137.5, 136.3, 128.1, 126.9, 126.6, 115.5, 72.4, 39.5, 34.6, 25.4, 22.4.

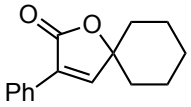
4.4.2. Lactonization with diethyl carbonate starting from 10a



The first reduction was conducted using **10a** (100.4 mg, 0.501 mmol) by following the procedure described in section 4.1. After full conversion of **10a** was confirmed by

the GC analysis, diethyl carbonate (0.12 mL, 0.996 mmol) was added to the reaction mixture at 0 °C and the reaction was then stirred at 40 °C for 15 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 95:5) gave **13a** (57.8 mg, 0.253 mmol) in 51% yield as white solid.

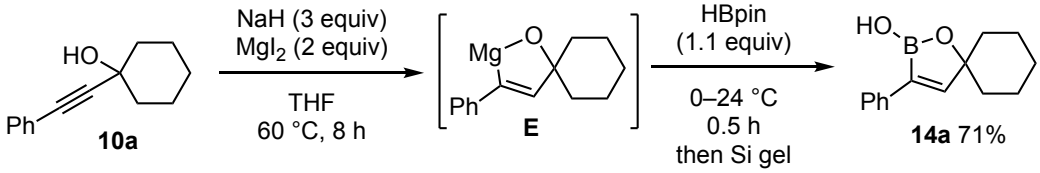
3-phenyl-1-oxaspiro[4.5]dec-3-en-2-one (13a)[45]



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.93 – 7.79 (m, 2H), 7.57 (s, 1H), 7.46 – 7.31 (m, 3H), 1.92 – 1.59 (m, 9H), 1.46 – 1.38 (m, 1H).

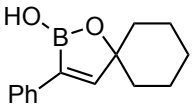
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 171.1, 152.4, 130.2, 129.7, 129.1, 128.5, 127.0, 85.3, 34.9, 24.6, 22.5.

4.4.3. Borylation starting from 10a



The first reduction was conducted using **10a** (100.4 mg, 0.501 mmol) by following the procedure described in section 4.1. After full conversion of **10a** was confirmed by the GC analysis, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (80 μL, 0.551 mmol) was added to the reaction mixture at 0 °C and the reaction was stirred at 24 °C for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 90:10) gave **14a** (78.3 mg, 0.356 mmol) in 71% yield as white solid. It should be noted that the ^{1}H NMR spectrum of the crude residue showed the presence of pinacol borane moiety in the product, which was removed during the column chromatography in silica gel to form **14a**.

3-phenyl-1-oxa-2-boraspiro[4.5]dec-3-en-2-ol (14a)



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.65 – 7.63 (m, 2H), 7.43 (s, 1H), 7.36 – 7.33 (m, 2H), 7.26 – 7.23 (m, 1H), 5.84 (s, 1H), 1.85 – 1.54 (m, 9H), 1.48 – 1.40 (m, 1H).

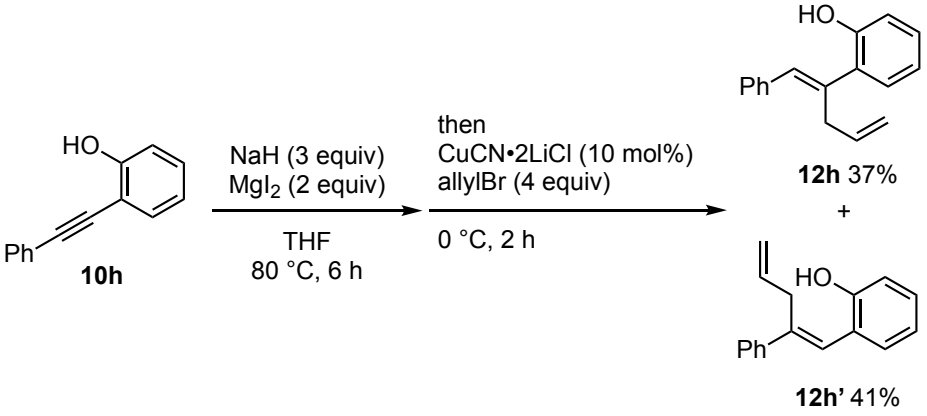
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 155.9, 136.1, 128.5, 127.3, 126.9, 85.5, 36.6, 25.2, 23.0. (The ^{13}C NMR signal attached to the B atom was not observed due to low intensity.)

^{11}B NMR (128 MHz, $CDCl_3$): δ(ppm) 31.68.

MS (HRMS ESI): Calcd for $C_{14}H_{18}O_2B$ $[M+H]^+$ 229.1400, Found: 229.1404.

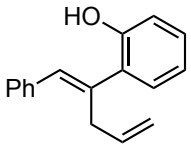
IR (neat, cm^{-1}): 3460 [ν(O-H)], 1600 [ν(C=C)], 1121 [ν(C-O)].

4.4.4. Cu-catalyzed allylation starting from 10h



The first reduction was conducted using **10h** (98.0 mg, 0.505 mmol) by following the procedure described in section 4.1. After full conversion of **10h** was confirmed by the GC analysis, CuCN•2LiCl (1M in THF, 50 μL, 10 mol%) and allyl bromide (0.17 mL, 1.964 mmol) were added to the reaction mixture at 0 °C and the reaction mixture was stirred for 3.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution and the organic materials were then extracted thrice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude residue by flash column chromatography (silica gel, *n*-Hexane:EtOAc = 98:2) gave **12h** (44.2 mg, 0.187 mmol) in 37% yield as pale yellow solid, and **12h'** (48.3 mg, 0.204 mmol) in 41% yield as colorless oil.

(*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



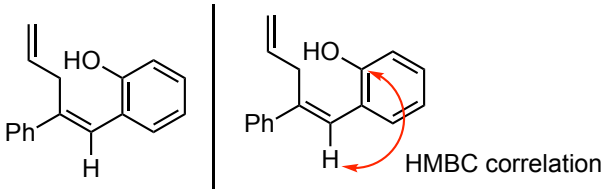
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.43 – 7.34 (m, 4H), 7.34 – 7.25 (m, 1H), 7.21 – 7.17 (m, 2H), 6.98 – 6.88 (m, 2H), 6.69 (s, 1H), 5.83 (ddt, *J* = 16.4, 10.0, 6.4 Hz, 1H), 5.55 (s, 1H), 5.16 – 5.01 (m, 2H), 3.42 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 152.5, 136.9, 136.6, 135.0, 131.9, 129.6, 128.7 (overlapped with 3C), 128.4, 127.3, 120.3, 116.7, 115.7, 36.9.

MS (HRMS ESI): Calcd for $C_{17}H_{17}O$ $[M+H]^+$ 237.1279, Found: 237.1277.

IR (neat, cm^{-1}): 3437 [ν(O-H)], 1639 [ν(C=C)], 1233 [ν(C-O)], 914 [ν(C=CH_2)].

(*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.59 – 7.49 (m, 2H), 7.39 – 7.53 (m, 2H), 7.34 – 7.27 (m, 1H), 7.27 – 7.14 (m, 2H), 6.95 – 6.91 (m, 2H), 6.78 (s, 1H), 5.81 (ddt, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.11 – 4.92 (m, 3H), 3.34 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 153.1, 143.7, 141.2, 135.6, 129.6, 128.9, 128.5, 127.8, 126.5, 124.3, 122.6, 120.4, 116.5, 115.3, 34.8.

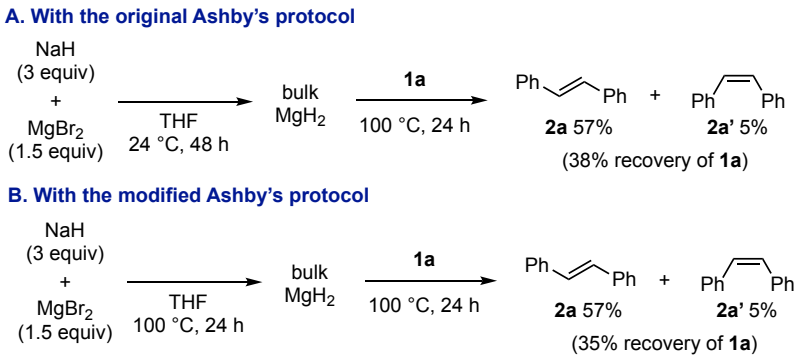
MS (HRMS ESI): Calcd for $C_{17}H_{17}O$ $[M+H]^+$ 237.1279, Found: 237.1282.

IR (neat, cm^{-1}): 3433 [ν(O-H)], 1637 [ν(C=C)], 1093 [ν(C-O)], 914 [ν(C=CH_2)].

5. Investigation of the reaction mechanism

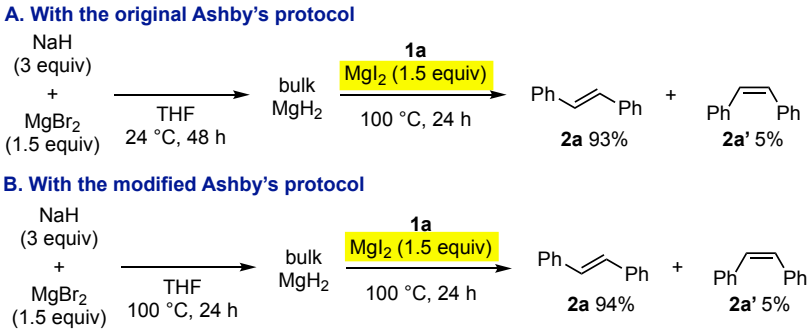
5.1. Control experiments

To elucidate the active hydride species responsible for the present *anti*-hydromagnesiation of alkynes, we conducted several control experiments. Ashby[46] reported preparation of magnesium hydride MgH_2 in bulk state by treatment of $MgBr_2$ with 2 equiv of NaH in THF at room temperature (in quantitative yield with elimination of inert sodium bromide). Diphenylacetylene (**1a**) was treated with the bulk MgH_2 (prepared by following the Ashby's protocol) at 100 °C for 24 h, that resulted in selective formation of *trans*-stilbene (**2a**) despite poor conversion of **1a** (Scheme S1-A). We found that preparation of the bulk MgH_2 could be conducted at higher temperature (100 °C for 24 h) without loss of reactivity (Scheme S1-B).



Scheme S1. The reaction of bulk MgH_2

We found that treatment of **1a** with the bulk MgH_2 (1.5 equiv) in the presence of MgI_2 (1.5 equiv) resulted in full conversion of **1a** at 100 °C, providing *trans*-stilbene (**2a**) selectively in excellent yields (Scheme S2-A and B).

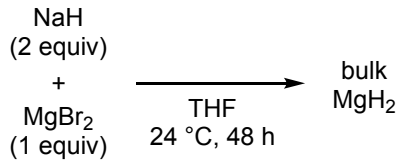


Scheme S2. The reaction of bulk MgH_2 in the presence of MgI_2

5.2. IR analyses

To further understand the active magnesium hydride species responsible for the present *anti*-hydromagnesiation of alkynes, we conducted IR spectroscopic analyses of the composite of NaH-MgX_2 prepared under the different conditions, that were discussed in section 5.1.

5.2.1. Bulk MgH_2 prepared by the original Ashby's protocol (Scheme S1-A)



To a mixture of NaH (dry; 36.2 mg, 1.508 mmol), $MgBr_2$ (139.1 mg, 0.755 mmol) in a 25 mL sealed tube was added 2.5 mL of THF, the reaction mixture was sealed and stirred at 24 °C for 48 h. The reaction mixture was transferred to the glovebox and a sample of the reaction mixture containing bulk MgH_2 and NaBr was directly taken for the IR spectroscopic analysis (Figure S4).

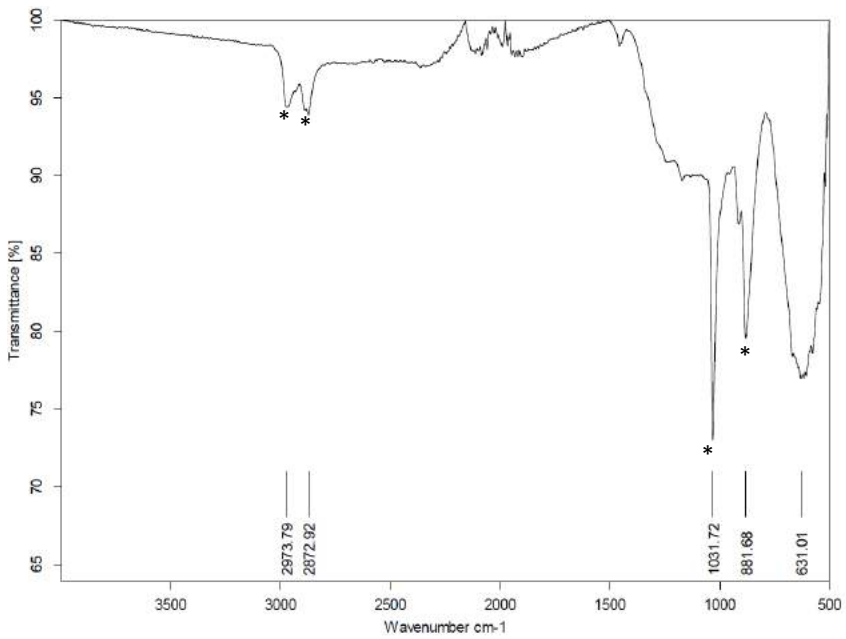
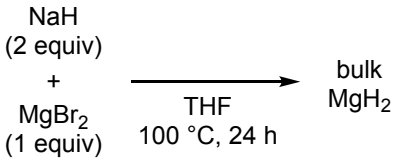


Figure S4. The peaks marked with * corresponds to IR absorptions of THF.

MgH_2 ν_{max}/cm^{-1}: 1400 – 790 (br), 790 – 500 (br).

5.2.2. Bulk MgH_2 prepared by the modified Ashby's protocol (Scheme S1-B)



To a mixture of NaH (dry; 36.1 mg, 1.504 mmol), $MgBr_2$ (138.6 mg, 0.753 mmol) in a 25 mL sealed tube was added 2.5 mL of THF, the reaction mixture was sealed and stirred at 100 °C for 24 h. Reaction mixture was transferred to a glovebox and a sample of the reaction mixture containing bulk MgH_2 and NaBr was directly taken for the IR spectroscopic analysis (Figure S5).

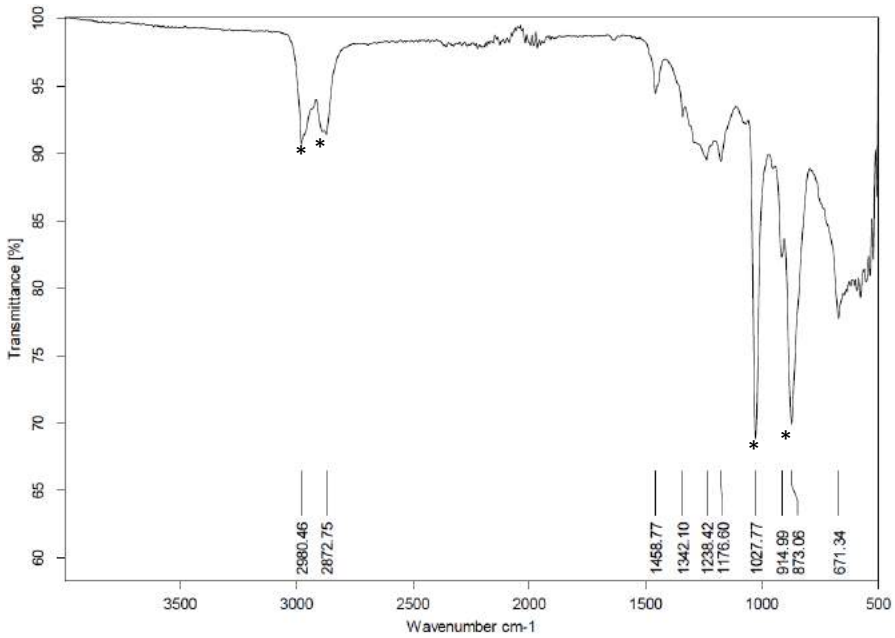
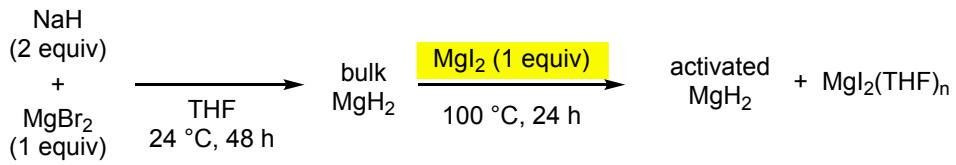


Figure S5. The peaks marked with * corresponds to IR absorptions of THF.

MgH_2 ν_{max}/cm^{-1}: 1450 – 790 (br), 790 – 500 (br).

5.2.3. Activated MgH_2 prepared from bulk MgH_2 and MgI_2 (Scheme S2-A)



To a mixture of NaH (dry; 36.2 mg, 1.508 mmol), $MgBr_2$ (139.1 mg, 0.755 mmol) in a 25 mL sealed tube was added 2.5 mL of THF, the reaction mixture was sealed and stirred at 24 °C for 48 h. MgI_2 (209.3 mg, 0.753 mmol) was then added to the reaction mixture and stirred at 100 °C for another 24 h. The resulting mixture was transferred to a glovebox and a sample of the reaction mixture containing MgH_2, MgI_2 and NaBr was directly taken for the IR spectroscopy analysis (Figure S6).

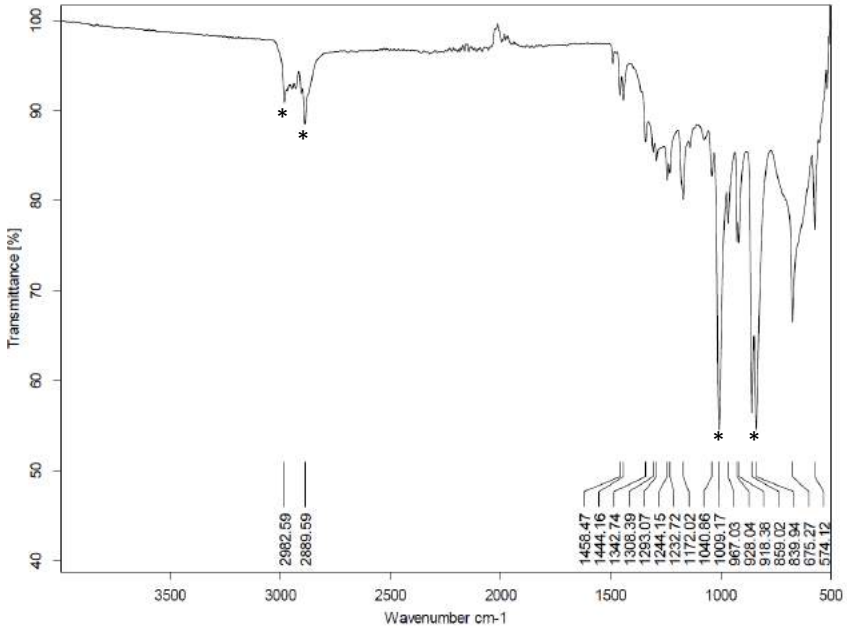
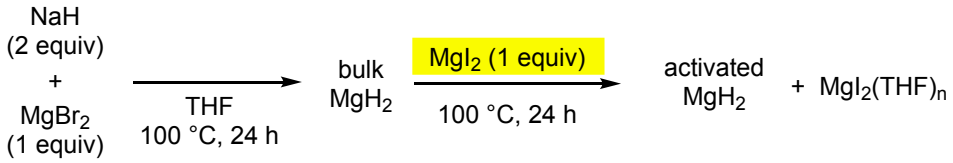


Figure S6. The peaks marked with * corresponds to IR absorptions of THF

MgH_2 ν_{max}/cm^{-1}: 1450 – 790 (br), 790 – 500 (br),

$MgI_2(THF)_n$ ν_{max}/cm^{-1}:1458, 1444, 1342, 1308, 1293, 1232, 1172, 928, 918, 675, 574 (see Section 5.2.5.).

5.2.4. Activated MgH_2 prepared from bulk MgH_2 (prepared from NaH and $MgBr_2$ at 100 °C) and MgI_2 (Scheme S2-B)



To a mixture of NaH (dry; 36.1 mg, 1.504 mmol), $MgBr_2$ (138.6 mg, 0.753 mmol) in a 25 mL sealed tube was added 2.5 mL of THF, the reaction mixture was sealed and stirred at 100 °C for 24 h. MgI_2 (208.7 mg, 0.750 mmol) was then added to the reaction mixture and stirred at 100 °C for another 24 h. The resulting mixture was transferred to a glovebox and a sample of the reaction mixture containing MgH_2, MgI_2 and NaBr was directly taken for the IR spectroscopic analysis (Figure S7).

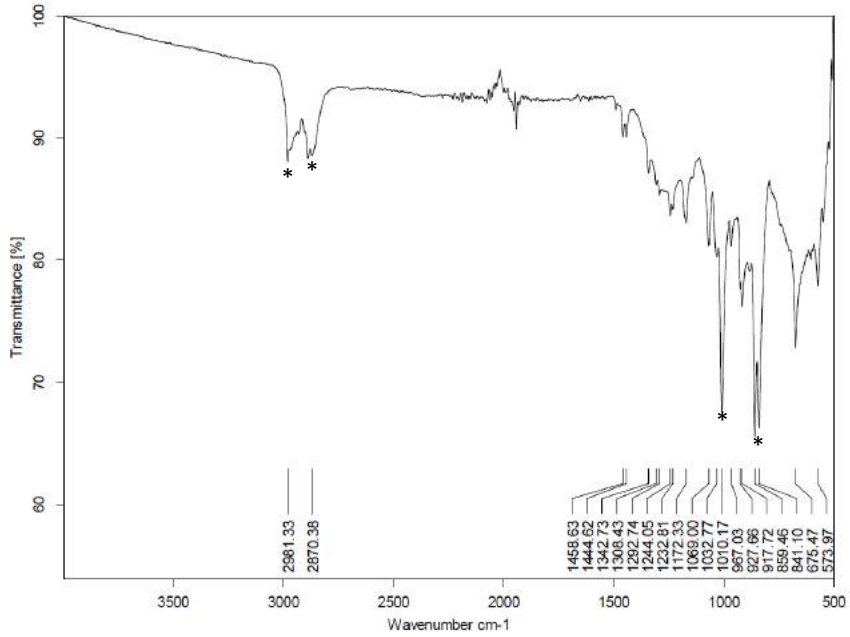


Figure S7. The peaks marked with * corresponds to IR absorptions of THF.

MgH_2 ν_{max}/cm^{-1}: 1450 – 790 (br), 790 – 500 (br).

$MgI_2(THF)_n$ ν_{max}/cm^{-1}:1459, 1445, 1343, 1308, 1293, 1232, 1172, 928, 918, 675, 574 (see Section 5.2.5.).

5.2.5. IR spectrum of $MgI_2(THF)_n$[47]

To a 10 mL sealed tube was added MgI_2 (250.0 mg, 0.750 mmol) and 1.5 mL of THF, the mixture was sealed and stirred at 100 °C for 6 h. The resulting suspension was transferred to a glovebox and a sample of the reaction mixture containing $MgI_2(THF)_n$ was directly taken for the IR spectroscopic analysis (Figure S8). It should be noted that $MgI_2(THF)_n$ is soluble in THF at higher temperature (>60 °C).

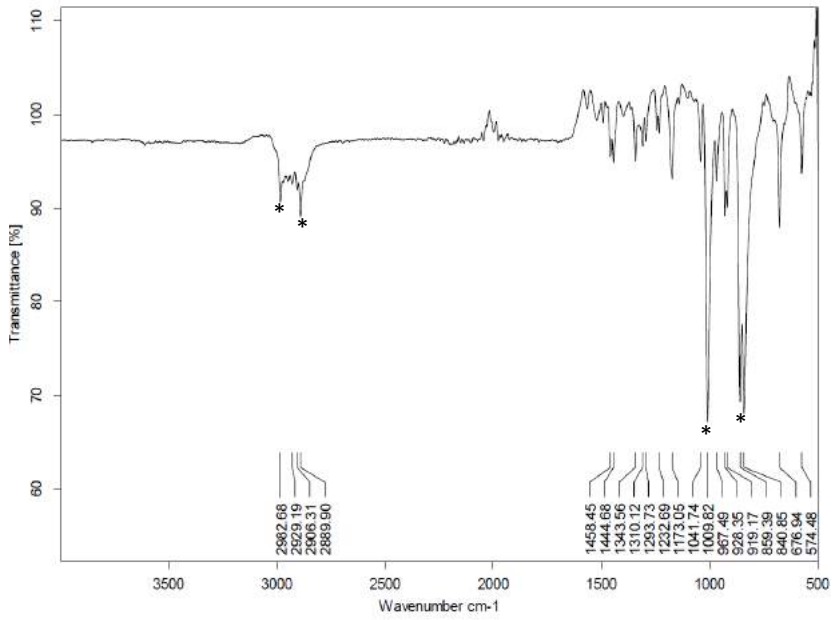
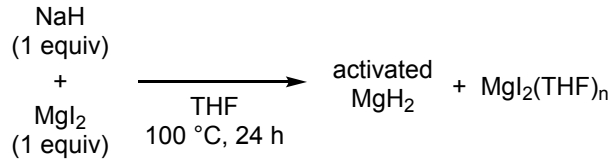


Figure S8. The peaks marked with * corresponds to IR absorptions of THF.

$MgI_2(THF)_n$ ν_{max}/cm^{-1}:1458, 1445, 1343, 1310, 1293, 1232, 1173, 928, 919, 677, 574.

5.2.6. The current protocol



To a mixture of NaH (dry; 36.3 mg, 1.513 mmol), MgI_2 (417.0 mg, 1.499 mmol) in a 25 mL sealed tube was added 2.5 mL of THF, the reaction mixture was sealed and stirred at 100 °C for 24 h. The resulting mixture was transferred to a glovebox and a sample of the reaction mixture was directly taken for the IR spectroscopic analysis (Figure S9).

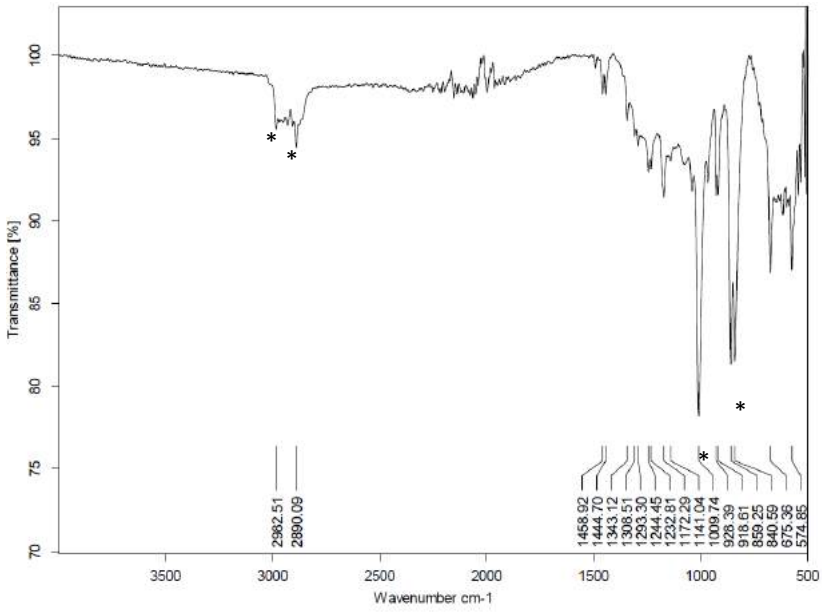


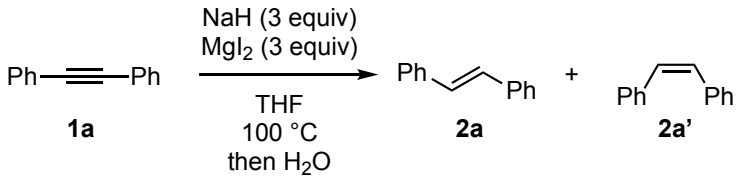
Figure S9. The peaks marked with * corresponds to IR absorptions of THF.

MgH_2 ν_{max}/cm^{-1}: 1440 – 790 (br), 790 – 500 (br),

$MgI_2(THF)_n$ ν_{max}/cm^{-1}:1459, 1445, 1343, 1309, 1294, 1233, 1172, 928, 918, 676, 574

Based on the IR analyses, MgH_2 prepared by the current protocol displayed the similar IR spectrum as those prepared by the protocols shown in sections 5.2.3. and 5.2.4. No other magnesium hydride species (e.g. HMgX)[54] was detected in the IR spectroscopy. Therefore, the current protocol should involve MgH_2 and the presence of $MgI_2(THF)_n$ is the key to keep activating MgH_2 through counter ion metathesis with $MgI_2(THF)_n$.

5.3. The reaction profile



To a mixture of NaH (60.0 mg, 1.500 mmol) and MgI_2 (417 mg, 1.499 mmol) in 25 mL sealed tube was added a solution of 1,2-diphenylacetylene (**1a**) (88.9 mg, 0.499 mmol) and *n*-dodecane (85.1 mg, 0.500 mmol) in THF (2.5 mL). The reaction mixture was stirred at 100 °C. The aliquots (0.05 mL of the solution) were taken from the reaction solution at 1 h intervals (for total 11 h), which were quenched by water (0.1 mL) and diluted with CH_2Cl_2 (1.0 mL). The organic layer was collected and filtered with syringe filter. The filtrates were subjected to the GC analysis. The consumption of **1a** and formation of **2a** and **2a'** were plotted in the Figure S10.

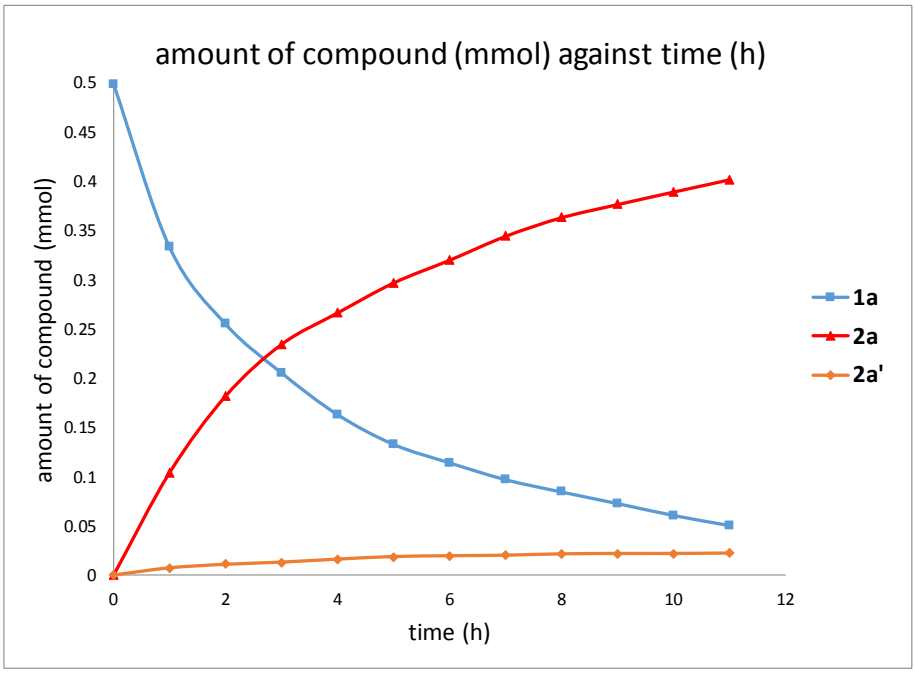


Figure S10. The reaction profile

5.4. DFT calculation

5.4.1. Computational details

All calculations were carried with the Gaussian 16 (revision B.01) program package.[48] Unless otherwise noted, the molecular structures and harmonic vibrational frequencies were obtained using the hybrid density functional method based on the long-range corrected hybrid density functional including a version of Grimme's D2 dispersion model developed by Chai and Head-Gordon (ωB97XD).[49] We used 6–31++G** basis set[50] for all other atoms. Geometry optimization and vibrational analysis were performed at the same level. All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The thermal corrections were computed at 298.15 K and 1 atm. Connectivity of the stationary points was the "pseudo" intrinsic reaction coordinate (IRC) method,[51] where IRC calculations were performed for 20 to 50 steps form the TS (in both forward and backward directions) and subsequent structures were optimized to obtain the corresponding local minima.[52] Single point energies were calculated at the ωB97XD/6-311++G** level of theory and the self-consistent reaction field (SCRF) method based on the SMD[53] was employed to evaluate the solvent reaction field (THF; $\varepsilon = 7.58$).

5.4.2. Reactivity of H-Mg-I species

Although the generation and involvement of the H-Mg-I species was excluded by the experimental results including the IR analyses (section 5.2.), we conducted the DFT calculation to examine the possible reactivity of the bridging hydride $[HMgI(thf)]_2$ as a model of H-Mg-I species toward the hydromagensiation.[54] As shown in Scheme S11, the computed results indicated that the reaction would preferentially proceed in a *syn*-selective manner. Thus, the possibility of involvement of H-Mg-I species was denied by both experimental and theoretical ways.

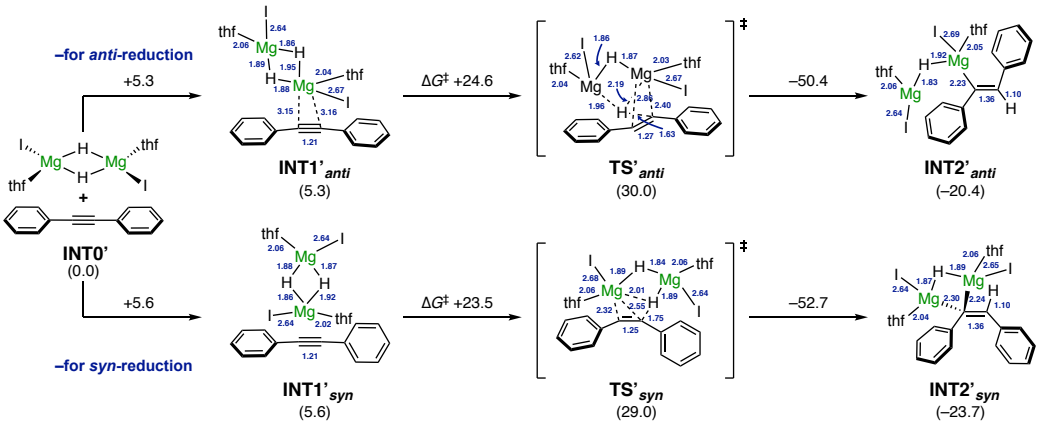


Figure S11. DFT calculations for model reactions of diphenylacetylene with MgHI•thf dimeric species. Energy changes and bond lengths at the *ω*B97XD/6-311++G** and SDD (for I)/SMD(THF)//*ω*B97XD/6-31++G** and SDD (for I) level of theory are shown in kcal/mol and Å, respectively. thf = tetrahydrofuran.

5.4.3. *Syn*-to-*anti* isomerization of alkenylmagnesium species

The DFT calculations were carried out to seek for the possibility of isomerization from *syn*-alkenylmagnesium species **INT2**$_{syn}$ to thermodynamically more stable *anti*-species **INT2**$_{anti}$ (Figure S12).[55] We observed that this process would require much higher activation energy ($\Delta G^{‡}$ +29.6 kcal/mol), than that of *anti*-hydromagnesiation ($\Delta G^{‡}$ +23.6 kcal/mol), indicating that *syn*-to-*anti* isomerization of alkenylmagnesium species is less likely involved during the reaction. This result is consistent with the results of reaction profile (section 5.3 and Figure S10).

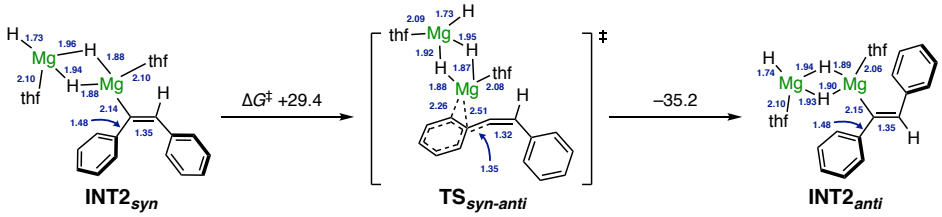
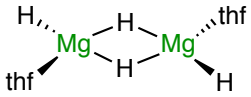


Figure S12. DFT calculations for model reaction of *syn*-to-*anti* isomerization process of alkenylmagnesium species. Energy changes and bond lengths at the *ω*B97XD/6-311++G**/SMD(THF)//*ω*B97XD/6-31++G** level of theory are shown in kcal/mol and Å, respectively. thf = tetrahydrofuran.

5.4.4. Cartesian coordinates and energies

MgH_2_THF dimer



at ωB97XD/6-31++G**

Energy = -867.350011145 A.U.

Thermal correction to Gibbs Free Energy = 0.214564 A.U.

Sum of electronic and thermal Free Energies = -867.135447 A.U.

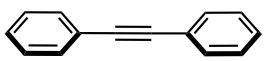
at ωB97XD/6-311++G**/SMD(THF)

Energy = -867.508767549 A.U.

Mg	-0.962492	-1.504706	-0.407537
H	-0.917640	-3.215423	-0.095917
H	-0.303897	-0.176190	0.827862
Mg	0.448749	0.939086	-0.520431
H	-0.165368	-0.408950	-1.741159
H	0.277354	2.670139	-0.647560
O	-2.922480	-0.728224	-0.507445
C	-3.172463	0.605123	-0.989352
C	-3.705263	-0.865997	0.690754
C	-3.283058	1.481396	0.267150
H	-2.351703	0.870593	-1.657981
H	-4.107589	0.585317	-1.561361
C	-3.537530	0.471732	1.412928
H	-4.746516	-1.053790	0.400612
H	-3.325666	-1.733064	1.235662
H	-4.095132	2.204727	0.163413
H	-2.358295	2.039086	0.433643
H	-4.419720	0.719568	2.007530
H	-2.672710	0.430085	2.078452
O	2.429873	0.351157	-0.321510
C	2.770359	-1.020932	-0.005807
C	3.556940	1.225171	-0.102368
C	4.267695	-1.004095	0.286918
H	2.176255	-1.316568	0.865030
H	2.491812	-1.642064	-0.860068
C	4.491357	0.425305	0.793343
H	4.013617	1.449354	-1.072862
H	3.179136	2.149725	0.338205
H	4.840829	-1.177407	-0.629379
H	4.548345	-1.767487	1.015188
H	5.528997	0.754395	0.706112
H	4.185434	0.515714	1.840437

---

diphenylacetylene



at ωB97XD/6-31++G**

Energy = -539.294849460 A.U.

Thermal correction to Gibbs Free Energy = 0.154358 A.U.

Sum of electronic and thermal Free

Energies = -539.140491 A.U.

at ωB97XD/6-311++G**/SMD(THF)

Energy = -539.406417593 A.U.

C -0.605937 -0.001736 0.001546

C 0.605936 -0.000610 -0.000520

C 2.037530 -0.000240 -0.000269

C 2.747800 -1.210190 0.000501

C 2.747159 1.210096 -0.001027

C 4.138197 -1.205784 0.000657

H 2.200091 -2.146756 0.000978

C 4.137557 1.206394 -0.000900

H 2.198958 2.146390 -0.001665

C 4.836878 0.000517 0.000002

H 4.678307 -2.147335 0.001138

H 4.677149 2.148158 -0.001569

H 5.922240 0.000813 0.000127

C -2.037531 -0.000831 0.000962

C -2.746633 1.209819 0.001344

C -2.748329 -1.210465 -0.000221

C -4.137029 1.206742 0.000366

H -2.198014 2.145860 0.002294

C -4.138724 -1.205448 -0.001161

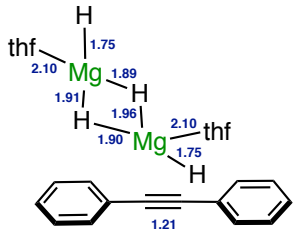
H -2.201040 -2.147263 -0.000434

C -4.836869 0.001094 -0.000851

H -4.676261 2.148821 0.000384

H -4.679239 -2.146683 -0.002233

H -5.922228 0.001842 -0.001601



INT1*anti*

at ωB97XD/6-31++G**

Energy = -1406.66618292 A.U.

Thermal correction to Gibbs Free Energy = 0.395931 A.U.

Sum of electronic and thermal Free Energies = -1406.270252 A.U.

at ωB97XD/6-311++G**/SMD(THF)

Energy = -1406.92967979 A.U.

C 1.412225 -2.058270 -0.161705

C 0.206516 -2.179449 -0.166680

C -1.217541 -2.311817 -0.122670

C -1.983768 -2.199728 -1.291644

C -1.858658 -2.539456 1.104406

C -3.366642 -2.333552 -1.234680

H -1.485990 -2.004265 -2.235400

C -3.242785 -2.675106 1.151215

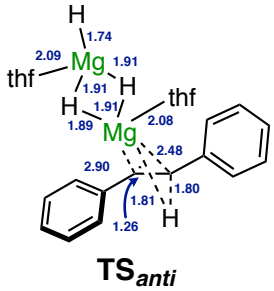
H -1.263095 -2.590293 2.009309

C -3.998921 -2.577683 -0.015647

H -3.952551 -2.252604 -2.145403

H -3.730903 -2.855731 2.103842

H	-5.078429	-2.689739	0.023882
Mg	0.241864	0.762778	1.201896
H	0.212514	-0.270465	2.609246
C	2.828945	-1.860497	-0.110629
C	3.425183	-1.431759	1.084714
C	3.621577	-2.044061	-1.252587
C	4.791816	-1.179675	1.126582
H	2.801474	-1.279284	1.960315
C	4.988477	-1.793126	-1.200450
H	3.156495	-2.375886	-2.175179
C	5.575898	-1.356325	-0.013442
H	5.246614	-0.843331	2.053090
H	5.596277	-1.936505	-2.088238
H	6.642596	-1.158445	0.024024
H	-0.520135	0.771921	-0.539836
Mg	-1.136839	2.577944	-0.452151
H	-0.485888	2.577574	1.318863
H	-0.945969	3.756931	-1.725120
O	2.121133	1.427606	0.554760
C	2.706919	2.603318	1.130995
C	2.558587	1.387433	-0.815485
C	2.581167	3.666579	0.039874
H	2.157080	2.833600	2.045472
H	3.752988	2.379731	1.377140
C	2.564767	2.851046	-1.276313
H	3.557794	0.935724	-0.836174
H	1.859007	0.749622	-1.357003
H	3.402605	4.385413	0.082792
H	1.642627	4.214664	0.157593
H	3.435439	3.057182	-1.903339
H	1.667102	3.083410	-1.855660
O	-3.116645	1.960527	-0.102712
C	-3.358850	1.058268	0.991075
C	-3.870049	1.445705	-1.213998
C	-4.856423	0.782961	0.910957
H	-2.771444	0.143885	0.831789
H	-3.026650	1.554364	1.903353
C	-5.165853	0.891778	-0.600929
H	-4.011711	2.269341	-1.914745
H	-3.281824	0.651182	-1.691141
H	-5.410669	1.537692	1.474197
H	-5.100649	-0.199532	1.319928
H	-6.008991	1.561477	-0.782790
H	-5.407454	-0.080862	-1.035887



TS*anti*

at ωB97XD/6-31++G**

Energy = -1406.63620062 A.U.

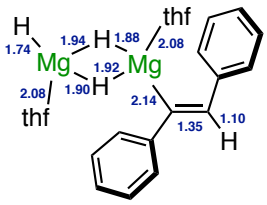
Thermal correction to Gibbs Free Energy = 0.397133 A.U.

Sum of electronic and thermal Free Energies = -1406.239068 A.U.

at ωB97XD/6-311++G**/SMD(THF)

Energy = -1406.89319732 A.U.

C	1.373422	-1.674051	0.150706
C	0.416371	-2.052560	-0.573129
C	-1.005326	-2.223608	-0.549666
C	-1.824692	-1.818959	-1.619487
C	-1.611855	-2.804520	0.581235
C	-3.199662	-2.004958	-1.564129
H	-1.364894	-1.360116	-2.488311
C	-2.990445	-3.005279	0.619961
H	-0.984919	-3.112265	1.411622
C	-3.788446	-2.610171	-0.450738
H	-3.817243	-1.693669	-2.402089
H	-3.439638	-3.474027	1.490684
H	-4.861405	-2.776696	-0.424015
Mg	0.362214	0.494336	0.806710
H	0.852222	-0.988597	1.727887
C	2.828421	-1.603825	0.250330
C	3.496122	-1.192935	1.406545
C	3.583866	-1.941154	-0.884718
C	4.885636	-1.112573	1.428920
H	2.909797	-0.932705	2.281701
C	4.970944	-1.858608	-0.858682
H	3.062934	-2.262838	-1.780734
C	5.629566	-1.439712	0.297569
H	5.388124	-0.793160	2.336903
H	5.539833	-2.122014	-1.745213
H	6.713048	-1.374536	0.316777
H	-0.646346	1.010528	-0.708811
Mg	-1.326522	2.598974	0.101320
H	-0.482537	1.960336	1.694121
H	-1.247397	4.187943	-0.608274
O	2.061342	1.555670	0.253590
C	2.463535	2.835814	0.767129
C	2.534759	1.488596	-1.102242
C	2.343385	3.805477	-0.419359
H	1.803331	3.068686	1.603949
H	3.495813	2.746092	1.125823
C	2.257682	2.882533	-1.659062
H	3.603005	1.239789	-1.079397
H	1.990109	0.684901	-1.601466
H	3.205941	4.474800	-0.460687
H	1.440621	4.415669	-0.336820
H	2.971136	3.154712	-2.440098
H	1.251661	2.919626	-2.085566
O	-3.225978	1.790929	0.433026
C	-3.345057	0.628266	1.273936
C	-4.070441	1.551501	-0.708969
C	-4.835050	0.314602	1.245549
H	-2.752668	-0.187852	0.839560
H	-2.946702	0.893739	2.253262
C	-5.270786	0.755521	-0.170551
H	-4.323407	2.526595	-1.127565
H	-3.499286	0.969358	-1.442669
H	-5.356788	0.896713	2.009390
H	-5.020660	-0.745164	1.430522
H	-6.172986	1.369451	-0.133515
H	-5.473611	-0.104183	-0.813172



INT2*anti*

at ωB97XD/6-31++G**

Energy = -1406.73072287 A.U.

Thermal correction to Gibbs Free Energy = 0.404319 A.U.

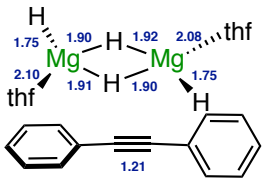
Sum of electronic and thermal Free Energies = -1406.326404 A.U.

at ωB97XD/6-311++G**/SMD(THF)

Energy = -1406.98536797 A.U.

C	-1.302281	-2.348216	0.015377
C	-0.304816	-1.485282	0.283419
C	1.089549	-1.973503	0.154464
C	1.993506	-1.802215	1.217222
C	1.577319	-2.563307	-1.023641
C	3.313028	-2.234669	1.121762
H	1.640516	-1.335821	2.134042
C	2.904074	-2.977337	-1.128783
H	0.904012	-2.681841	-1.867955
C	3.779444	-2.819885	-0.055441
H	3.980712	-2.114271	1.970937
H	3.254590	-3.427780	-2.053245
H	4.811035	-3.149863	-0.134054
Mg	-0.422776	0.637542	0.481753
H	-1.093748	-3.378570	-0.298288
C	-2.740068	-2.007536	0.110268
C	-3.637027	-2.398357	-0.894570
C	-3.244829	-1.284966	1.199138
C	-4.981455	-2.042771	-0.834200
H	-3.266948	-2.973576	-1.739542
C	-4.590756	-0.933195	1.266578
H	-2.570002	-1.015958	2.006528
C	-5.464302	-1.304071	0.246665
H	-5.655829	-2.345423	-1.629913
H	-4.958579	-0.375892	2.123324
H	-6.514832	-1.034821	0.299235
H	0.620634	1.699965	1.633942
Mg	1.372605	2.770008	0.194798
H	0.338741	1.664047	-0.952944
H	1.370581	4.510529	0.237329
O	-2.233602	1.667698	0.471426
C	-3.069633	1.508060	-0.692667
C	-2.257165	3.073895	0.787865
C	-2.719494	2.704845	-1.573725
H	-2.851953	0.531209	-1.129637
H	-4.115054	1.514488	-0.363867
C	-2.306317	3.801922	-0.563863
H	-3.151474	3.263701	1.392543
H	-1.368944	3.292175	1.384305
H	-3.564180	3.001351	-2.199658
H	-1.877647	2.454551	-2.222944
H	-3.023859	4.625128	-0.531164
H	-1.327992	4.219398	-0.813149
O	3.179041	1.769301	-0.075381
C	3.386633	0.795729	-1.118851

C	4.047528	1.425493	1.021284
C	4.890709	0.570817	-1.101220
H	2.831433	-0.116246	-0.877623
H	2.996964	1.225026	-2.042478
C	5.256046	0.710136	0.391608
H	4.298368	2.358586	1.529573
H	3.497381	0.771232	1.706014
H	5.393745	1.338011	-1.696133
H	5.151689	-0.410241	-1.503421
H	6.177048	1.280881	0.526682
H	5.393972	-0.270092	0.852461



INT1*syn*

at *ω*B97XD/6-31++G**

Energy = -1406.66988472 A.U.

Thermal correction to Gibbs Free Energy = 0.398714 A.U.

Sum of electronic and thermal Free Energies = -1406.271171 A.U.

at *ω*B97XD/6-311++G**/SMD(THF)

Energy= -1406.93185773 A.U.

C	-0.489819	2.011783	-0.009444
C	0.645074	1.920346	-0.422703
C	1.974230	1.707300	-0.914587
C	2.275235	0.507051	-1.575182
C	2.983887	2.664059	-0.735307
C	3.562601	0.262187	-2.038682
H	1.492972	-0.230124	-1.722383
C	4.269118	2.416620	-1.208130
H	2.753218	3.593840	-0.225543
C	4.562523	1.216832	-1.857448
H	3.771737	-0.681198	-2.533839
H	5.045373	3.162219	-1.067104
H	5.567700	1.028319	-2.221412
Mg	-1.402639	-2.495785	0.807724
H	-2.239909	-2.115263	2.295813
C	-1.829610	2.033205	0.498266
C	-2.234361	1.048380	1.410736
C	-2.750678	3.006433	0.084403
C	-3.535499	1.035886	1.900001
H	-1.532640	0.285087	1.729505
C	-4.051154	2.989332	0.578957
H	-2.440404	3.766931	-0.624678
C	-4.447031	2.006334	1.486814
H	-3.825855	0.255738	2.597247
H	-4.758685	3.745634	0.253746
H	-5.462985	1.997838	1.869137
H	-0.182347	-1.334088	-0.091000
Mg	1.182376	-2.643461	-0.307442
H	-0.083173	-3.833762	0.498054
H	2.148777	-2.897637	-1.742867
O	-2.778830	-2.425584	-0.775401
C	-2.291135	-2.105435	-2.091272

C -3.998777 -1.672658 -0.572622

C -2.548440 -0.612731 -2.211315

H -1.237469 -2.387279 -2.133874

H -2.856735 -2.691588 -2.826588

C -3.906021 -0.447653 -1.502379

H -4.842020 -2.323965 -0.823578

H -4.040576 -1.420723 0.488921

H -2.566417 -0.272429 -3.249079

H -1.762277 -0.071026 -1.676650

H -4.728175 -0.455791 -2.223343

H -3.958490 0.487399 -0.941509

O 2.358208 -1.793805 1.186304

C 1.822449 -0.769455 2.064214

C 3.793461 -1.661733 1.064182

C 3.040284 -0.124676 2.712382

H 1.256528 -0.063937 1.448652

H 1.145895 -1.256438 2.770864

C 4.110675 -0.284958 1.628389

H 4.257259 -2.464364 1.648462

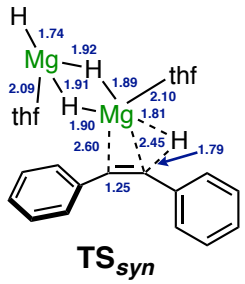
H 4.047357 -1.783159 0.008613

H 3.326640 -0.663166 3.621763

H 2.851041 0.918672 2.973665

H 5.129416 -0.226641 2.018136

H 3.990293 0.478274 0.854631



TS*syn*

at ωB97XD/6-31++G**

Energy = -1406.63511340 A.U.

Thermal correction to Gibbs Free Energy = 0.398261 A.U.

Sum of electronic and thermal Free Energies = -1406.236852 A.U.

at ωB97XD/6-311++G**/SMD(THF)

Energy= -1406.89018623 A.U.

C -1.004502 -0.673658 -0.613884

C 0.049536 -0.834109 0.028762

C 1.182078 -1.271865 0.770360

C 1.501593 -0.734971 2.032431

C 2.000405 -2.297289 0.254243

C 2.588777 -1.219041 2.750295

H 0.897541 0.070871 2.432153

C 3.085999 -2.771229 0.981728

H 1.761504 -2.727359 -0.713771

C 3.390028 -2.238050 2.233841

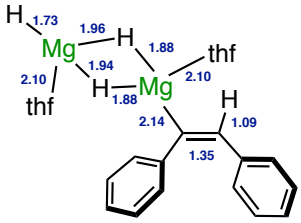
H 2.814659 -0.791177 3.722431

H 3.695982 -3.569263 0.568011

H 4.236346 -2.612712 2.800275

Mg -0.326343 1.679219 -0.538599

H	-1.163057	0.667436	-1.783549
C	-2.365166	-1.187419	-0.807750
C	-3.159821	-0.879464	-1.912290
C	-2.874057	-2.047437	0.176971
C	-4.441841	-1.409705	-2.029322
H	-2.757881	-0.212476	-2.668920
C	-4.158098	-2.569059	0.063480
H	-2.251382	-2.295247	1.031390
C	-4.949580	-2.249124	-1.039587
H	-5.046551	-1.164057	-2.896940
H	-4.541821	-3.225302	0.838528
H	-5.952632	-2.654653	-1.128102
H	0.747834	1.968511	0.999334
Mg	2.170147	2.799637	0.029994
H	0.910580	2.801155	-1.424168
H	3.333700	3.939761	0.640794
O	-2.044067	2.423497	0.408055
C	-2.181711	2.339141	1.837483
C	-3.360638	2.240624	-0.156954
C	-3.163033	1.192261	2.028256
H	-1.184104	2.177086	2.247562
H	-2.581101	3.292164	2.207660
C	-4.143560	1.380150	0.853589
H	-3.809080	3.230169	-0.294328
H	-3.221971	1.762783	-1.127886
H	-3.655895	1.222531	3.002647
H	-2.634896	0.238593	1.936602
H	-5.048753	1.901630	1.175804
H	-4.440369	0.422832	0.420206
O	3.135397	1.126659	-0.770318
C	2.853560	0.471464	-2.019806
C	4.331925	0.573181	-0.172209
C	4.219864	0.029637	-2.517853
H	2.189682	-0.381001	-1.831474
H	2.340468	1.194042	-2.655667
C	4.916543	-0.385309	-1.215428
H	4.988898	1.417255	0.055021
H	4.051286	0.065644	0.753947
H	4.738040	0.871119	-2.988386
H	4.153208	-0.785513	-3.242036
H	6.004361	-0.308274	-1.274345
H	4.659309	-1.416463	-0.959560



INT2*syn*

at ωB97XD/6-31++G**

Energy = -1406.72444425 A.U.

Thermal correction to Gibbs Free Energy = 0.404189 A.U.

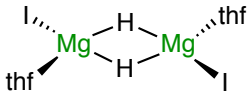
Sum of electronic and thermal Free Energies = -1406.320256 A.U.

at ωB97XD/6-311++G**/SMD(THF)

Energy = -1406.98047755 A.U.

C	-1.486369	0.309988	-1.007176
C	-0.326089	0.197335	-0.322563
C	-0.089686	-0.937629	0.599556
C	0.369038	-0.718637	1.908738
C	-0.231519	-2.272339	0.179937
C	0.612940	-1.776955	2.781025
H	0.533246	0.301816	2.248971
C	0.030293	-3.332541	1.041564
H	-0.570090	-2.468516	-0.833663
C	0.444239	-3.092609	2.352260
H	0.949054	-1.573323	3.793654
H	-0.094932	-4.352942	0.690410
H	0.643409	-3.919889	3.026111
Mg	1.123997	1.768152	-0.463557
H	-1.562455	1.099525	-1.761769
C	-2.745688	-0.471120	-0.896509
C	-3.534597	-0.668469	-2.038090
C	-3.218730	-0.971242	0.325361
C	-4.735261	-1.370357	-1.973315
H	-3.193274	-0.271541	-2.991376
C	-4.421001	-1.667883	0.394490
H	-2.637515	-0.813112	1.228035
C	-5.182567	-1.876693	-0.754709
H	-5.323194	-1.519250	-2.874177
H	-4.766616	-2.046760	1.351721
H	-6.119872	-2.421564	-0.698925
H	2.661813	1.885141	0.608252
Mg	3.846553	1.866872	-0.952671
H	2.207525	2.089172	-1.963546
H	5.423088	2.569908	-1.102138
O	0.068161	3.462328	0.194048
C	-0.140703	3.513281	1.617724
C	-1.186167	3.828851	-0.414193
C	-1.524648	2.903469	1.812351
H	0.680225	2.967033	2.088123
H	-0.098753	4.562416	1.935467
C	-2.287435	3.331984	0.539759
H	-1.197532	4.918053	-0.529463
H	-1.216402	3.368990	-1.403915
H	-1.999961	3.254395	2.730920
H	-1.449331	1.813585	1.852616
H	-3.003774	4.131121	0.744894
H	-2.829875	2.486382	0.112750
O	3.768092	-0.233285	-0.999628
C	2.900176	-1.082596	-1.788624
C	4.278356	-0.949948	0.150100
C	3.174611	-2.493459	-1.289001
H	1.860683	-0.786321	-1.607774
H	3.146389	-0.919613	-2.839521
C	3.494756	-2.254654	0.189120
H	5.351116	-1.105015	-0.004421
H	4.120450	-0.322288	1.031773
H	4.033854	-2.928034	-1.810679
H	2.310479	-3.146427	-1.429009
H	4.070837	-3.065337	0.640399
H	2.571089	-2.126897	0.758826

MgHI_THF dimer



at ωB97XD/6-31++G**&SDD (for I)

Energy = -889.212938911 A.U.

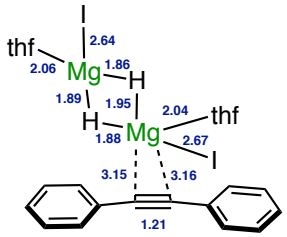
Thermal correction to Gibbs Free Energy = 0.197906 A.U.

Sum of electronic and thermal Free Energies = -889.015033 A.U.

at ωB97XD/6-311++G**&SDD (for I) /SMD(THF)

Energy = XXX A.U.

Mg	1.411790	-0.469089	-0.417450
H	0.131745	-0.209006	0.961211
Mg	-1.228100	0.307209	-0.228491
H	0.047339	0.026006	-1.609261
O	1.399025	-2.524580	-0.487200
C	0.137316	-3.203282	-0.684564
C	2.072581	-3.242153	0.568699
C	-0.305875	-3.662597	0.712710
H	-0.545854	-2.501666	-1.168067
H	0.318320	-4.043794	-1.362791
C	0.967584	-3.527689	1.582575
H	2.493884	-4.158238	0.138533
H	2.885410	-2.609989	0.932612
H	-0.673785	-4.690362	0.678355
H	-1.112698	-3.032180	1.092320
H	1.178945	-4.425879	2.166753
H	0.869325	-2.686094	2.272675
O	-1.223735	2.329295	-0.011613
C	0.036109	3.037638	0.150925
C	-2.349525	3.220035	0.183684
C	-0.353283	4.506190	0.268026
H	0.517140	2.656190	1.056746
H	0.664664	2.811285	-0.713545
C	-1.754517	4.431735	0.885152
H	-2.758151	3.471850	-0.800429
H	-3.103629	2.681235	0.760169
H	-0.395179	4.972269	-0.721334
H	0.357332	5.064720	0.880086
H	-2.345856	5.333878	0.715487
H	-1.692613	4.256074	1.963794
I	3.786925	0.618594	-0.147574
I	-3.619855	-0.784079	-0.182704



INT1'*anti*

at ωB97XD/6-31++G**&SDD (for I)

Energy = -1428.52811211 A.U.

Thermal correction to Gibbs Free Energy = 0.38031 A.U.

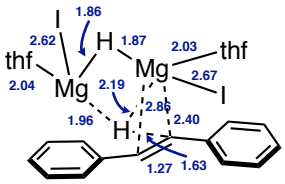
Sum of electronic and thermal Free Energies = -1428.147802 A.U.

at ωB97XD/6-311++G**&SDD (for I) /SMD(THF)

Energy = -1428.8019114 A.U.

Mg	1.414600	-1.781250	-0.524688
H	0.275425	-0.791122	0.612202
Mg	-0.414830	0.286898	-0.758530
H	0.826043	-0.686862	-1.902770
O	0.158102	-3.403751	-0.682438
C	-0.814380	-3.519508	-1.762000
C	-0.433505	-3.865021	0.554111
C	-2.129174	-3.943012	-1.101784
H	-0.885232	-2.539498	-2.240970
H	-0.431520	-4.250979	-2.477536
C	-1.915667	-3.592229	0.375556
H	-0.211284	-4.931992	0.668152
H	0.032888	-3.308173	1.371301
H	-2.293289	-5.018288	-1.222357
H	-2.977181	-3.407172	-1.533132
H	-2.533661	-4.191612	1.048247
H	-2.128882	-2.532638	0.550297
O	0.237350	2.119799	-1.369530
C	1.523003	2.364760	-1.991994
C	-0.586937	3.312889	-1.401635
C	1.292533	3.595721	-2.852320
H	2.256814	2.547918	-1.200942
H	1.792081	1.462390	-2.542903
C	0.302007	4.398226	-2.001712
H	-1.460835	3.089149	-2.020045
H	-0.912616	3.521887	-0.379366
H	0.843624	3.314967	-3.810356
H	2.221272	4.136046	-3.047693
H	-0.276691	5.119450	-2.582668
H	0.835573	4.935724	-1.212205
I	3.885099	-2.208866	0.289684
I	-2.969274	0.047085	-1.494413
C	-1.068107	1.580775	2.041479
C	0.036519	2.037244	1.831123
C	1.365708	2.499195	1.566919
C	2.412932	1.569106	1.473243
C	1.634006	3.861887	1.373049
C	3.703035	1.995898	1.176106
H	2.208983	0.514574	1.628799
C	2.928047	4.282117	1.080900
H	0.825926	4.582208	1.457687
C	3.963431	3.351999	0.978129
H	4.497130	1.260156	1.095478
H	3.130040	5.339155	0.936289
H	4.971008	3.684084	0.748431
C	-2.327413	0.951664	2.302721
C	-3.529822	1.660739	2.187195
C	-2.352946	-0.409296	2.642208
C	-4.740666	1.013765	2.402967
H	-3.507390	2.709922	1.911854
C	-3.568542	-1.048008	2.855746
H	-1.416075	-0.951843	2.718583
C	-4.763316	-0.340102	2.734062
H	-5.670084	1.564280	2.300411
H	-3.584518	-2.102656	3.112882

H -5.711594 -0.843714 2.892931



TS'*anti*

at ωB97XD/6-31++G**&SDD (for I)

Energy = -1428.49031964 A.U.

Thermal correction to Gibbs Free Energy = 0.379329 A.U.

Sum of electronic and thermal Free Energies = -1428.110991 A.U.

at ωB97XD/6-311++G**&SDD (for I) /SMD(THF)

Energy = -1428.76165838 A.U.

Mg 1.171011 -1.614389 -0.606015

H 0.571093 -0.460729 0.865312

Mg -0.337262 0.874475 -0.619568

H 0.752748 -0.182511 -1.709797

O -0.520952 -2.710541 -0.924931

C -1.334975 -2.663881 -2.129890

C -1.274771 -3.337048 0.136116

C -2.765748 -2.990567 -1.680871

H -1.237715 -1.656034 -2.539197

H -0.930298 -3.392179 -2.837802

C -2.702411 -2.912735 -0.148548

H -1.133112 -4.422365 0.071572

H -0.876881 -2.966179 1.082297

H -3.048158 -3.996540 -2.005128

H -3.480642 -2.276867 -2.094972

H -3.433586 -3.558631 0.341819

H -2.861527 -1.886758 0.198332

O 0.473606 2.695873 -1.016448

C 1.794616 2.945298 -1.554754

C -0.202757 3.937910 -0.698429

C 1.768270 4.412178 -1.955258

H 2.528211 2.748538 -0.766863

H 1.947011 2.249878 -2.381884

C 0.852814 5.020604 -0.886957

H -1.044858 4.039505 -1.389138

H -0.582927 3.859673 0.323774

H 1.332047 4.531311 -2.952092

H 2.768552 4.850156 -1.958758

H 0.409540 5.970706 -1.192222

H 1.409434 5.176393 0.041858

I 3.439756 -2.921615 -0.420170

I -2.836667 1.030483 -1.535825

C -0.855621 0.996238 2.193870

C 0.306690 0.917712 1.693491

C 1.611246 1.587118 1.703330

C 2.795025 0.928703 1.363139

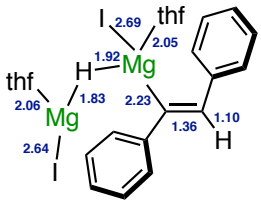
C 1.671707 2.939123 2.078707

C 4.013208 1.605961 1.375058

H 2.776439 -0.127465 1.115025

C 2.886921 3.612672 2.085765

H	0.755263	3.442985	2.369101
C	4.064161	2.951729	1.727064
H	4.919275	1.069480	1.112131
H	2.917939	4.657456	2.380931
H	5.012270	3.480138	1.736674
C	-1.980068	0.140446	2.444501
C	-3.307701	0.538125	2.213691
C	-1.737376	-1.144596	2.968074
C	-4.356195	-0.334967	2.472527
H	-3.503588	1.525344	1.810000
C	-2.796437	-2.001015	3.256268
H	-0.713712	-1.445183	3.170245
C	-4.107068	-1.603359	3.001314
H	-5.375204	-0.022202	2.267828
H	-2.595932	-2.981934	3.677696
H	-4.932813	-2.273570	3.219767



INT2'*anti*

at ωB97XD/6-31++G**&SDD (for I)

Energy = -1428.58481702 A.U.

Thermal correction to Gibbs Free Energy = 0.387532 A.U.

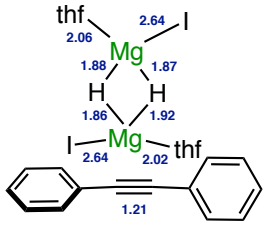
Sum of electronic and thermal Free Energies = -1428.197285 A.U.

at ωB97XD/6-311++G**&SDD (for I) /SMD(THF)

Energy = -1428.85014247 A.U.

Mg	1.117471	0.742382	-0.756324
H	0.749572	2.099907	2.420047
Mg	-1.234286	-0.662630	0.036692
H	-0.500864	0.265217	-1.470586
O	1.994507	-1.029046	-1.318592
C	1.523686	-1.810276	-2.447469
C	3.177439	-1.671572	-0.798930
C	2.084248	-3.227409	-2.242711
H	0.434500	-1.767998	-2.429541
H	1.894771	-1.339284	-3.363479
C	2.835281	-3.146462	-0.902613
H	4.031316	-1.391343	-1.428409
H	3.335319	-1.310347	0.216005
H	2.763670	-3.490028	-3.058246
H	1.281069	-3.966085	-2.209123
H	3.723249	-3.781857	-0.872335
H	2.175215	-3.423259	-0.076032
O	-3.126966	0.014712	-0.351382
C	-3.406464	0.997895	-1.379713
C	-4.349923	-0.494706	0.227772
C	-4.882001	0.808347	-1.697240
H	-3.191029	1.987545	-0.966212
H	-2.734961	0.797973	-2.215410
C	-5.457196	0.384785	-0.341916
H	-4.446336	-1.543920	-0.067633
H	-4.259299	-0.433101	1.315788

H	-5.015438	0.013322	-2.437646
H	-5.335267	1.723002	-2.085356
H	-6.402445	-0.155495	-0.425782
H	-5.613718	1.262577	0.292005
I	2.719435	2.797554	-1.155357
I	-1.508212	-3.324734	-0.190729
C	0.232757	0.277238	1.421118
C	0.046507	1.575768	1.762361
C	-1.146781	2.391318	1.407053
C	-1.036940	3.570089	0.656575
C	-2.401708	2.031200	1.912468
C	-2.159827	4.354179	0.403063
H	-0.066200	3.870078	0.270053
C	-3.520943	2.827697	1.678820
H	-2.484667	1.137297	2.525181
C	-3.404177	3.989922	0.919071
H	-2.059484	5.258858	-0.188570
H	-4.480651	2.547260	2.103603
H	-4.273603	4.614938	0.738971
C	1.449817	-0.392243	1.977499
C	1.403846	-1.764184	2.269935
C	2.662912	0.285217	2.201097
C	2.508674	-2.425696	2.798416
H	0.488000	-2.316481	2.079218
C	3.773107	-0.378607	2.718547
H	2.754450	1.337190	1.943541
C	3.700151	-1.736609	3.024338
H	2.440158	-3.485617	3.024778
H	4.699116	0.167289	2.871774
H	4.565416	-2.254784	3.426116



INT1'*syn*

at ωB97XD/6-31++G**&SDD (for I)

Energy = -1428.52647536 A.U.

Thermal correction to Gibbs Free Energy = 0.379041 A.U.

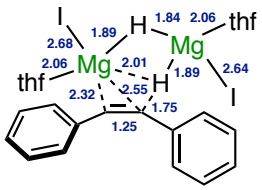
Sum of electronic and thermal Free Energies = -1428.147435 A.U.

at ωB97XD/6-311++G**&SDD (for I) /SMD(THF)

Energy = -1428.80024807 A.U.

Mg	-0.483340	0.565324	-1.447308
H	-0.090843	-0.632470	-0.080078
Mg	0.777989	-1.864026	-1.209439
H	0.329249	-0.726685	-2.619152
O	0.962722	1.979127	-1.366851
C	2.333044	1.748221	-1.784045
C	0.791979	3.322070	-0.844289
C	2.954860	3.135388	-1.838635
H	2.813189	1.110477	-1.035595
H	2.301867	1.227040	-2.742715
C	2.205366	3.875493	-0.725714

H	0.173912	3.877081	-1.556589
H	0.269092	3.245235	0.112216
H	2.768710	3.601523	-2.811546
H	4.033393	3.100455	-1.671070
H	2.226783	4.960916	-0.844735
H	2.629125	3.624417	0.249770
O	-0.677634	-3.315646	-1.081811
C	-2.036023	-2.850709	-1.279789
C	-0.703711	-4.099797	0.131875
C	-2.605055	-2.609721	0.127586
H	-1.993730	-1.958106	-1.908731
H	-2.574654	-3.634691	-1.821974
C	-1.584772	-3.284444	1.072240
H	-1.136156	-5.078330	-0.108083
H	0.329094	-4.232260	0.461665
H	-3.600973	-3.048319	0.219921
H	-2.690011	-1.542914	0.344039
H	-2.059180	-3.907588	1.833492
H	-0.984951	-2.523670	1.578759
I	-2.854833	1.560707	-2.037233
I	3.213354	-2.590006	-0.498717
C	0.116375	1.340287	2.418887
C	-1.017737	0.916255	2.466795
C	-2.325163	0.332370	2.536177
C	-2.537508	-0.804593	3.331816
C	-3.391020	0.862197	1.796506
C	-3.790971	-1.404767	3.372577
H	-1.712425	-1.210707	3.908385
C	-4.641124	0.252673	1.837716
H	-3.230813	1.734573	1.172991
C	-4.844444	-0.880676	2.622881
H	-3.946077	-2.283991	3.990598
H	-5.452278	0.662129	1.244482
H	-5.821065	-1.353992	2.652645
C	1.489754	1.745306	2.344504
C	2.420989	0.898834	1.724218
C	1.926698	2.953580	2.907275
C	3.765459	1.252228	1.673537
H	2.085380	-0.039109	1.293179
C	3.274039	3.300412	2.854320
H	1.207973	3.606650	3.391966
C	4.196064	2.452090	2.239829
H	4.472217	0.578073	1.198365
H	3.605779	4.233935	3.298237
H	5.246703	2.723546	2.207592



TS'*syn*

at *ω*B97XD/6-31++G**&SDD (for I)

Energy = -1428.49559031 A.U.

Thermal correction to Gibbs Free Energy = 0.37988 A.U.

Sum of electronic and thermal Free Energies = -1428.115710 A.U.

at *ω*B97XD/6-311++G**&SDD (for I)

/SMD(THF)

Energy = -1428.76365816 A.U.

Mg 1.019942 0.723704 -0.788177
H -0.848948 0.619917 -0.064681
Mg -1.513221 -0.487235 -1.442835
H 0.140034 -0.179224 -2.192546
O 2.877433 0.128336 -1.462650
C 3.040790 -1.117014 -2.185352
C 4.147502 0.595225 -0.947436
C 4.547048 -1.334058 -2.272225
H 2.545545 -1.904892 -1.609588
H 2.545947 -1.010878 -3.152169
C 5.057357 -0.620753 -1.016457
H 4.488873 1.417838 -1.584197
H 3.980467 0.971763 0.063532
H 4.952111 -0.864682 -3.174643
H 4.801221 -2.395971 -2.292613
H 6.111337 -0.341066 -1.079538
H 4.914147 -1.250180 -0.133162
O -2.954716 0.890922 -1.977481
C -2.544942 2.277534 -1.878850
C -4.230780 0.817173 -1.301803
C -3.017594 2.746675 -0.495823
H -1.461527 2.319154 -2.008625
H -3.029208 2.820744 -2.697190
C -4.029770 1.664982 -0.049080
H -4.989566 1.235351 -1.973769
H -4.447727 -0.236543 -1.117860
H -3.472158 3.737857 -0.560403
H -2.173587 2.803740 0.194655
H -4.971927 2.085404 0.309610
H -3.607228 1.053561 0.753629
I 1.331080 3.338946 -0.313776
I -2.555967 -2.881677 -1.073740
C 0.980549 -0.750382 1.001717
C -0.123347 -0.237659 1.283178
C -1.235995 0.106792 2.153348
C -2.159648 -0.876821 2.521568
C -1.381370 1.419833 2.618586
C -3.225379 -0.543251 3.355279
H -2.049265 -1.887147 2.141348
C -2.445881 1.741608 3.452221
H -0.667085 2.177507 2.308386
C -3.370458 0.762038 3.820459
H -3.943995 -1.306616 3.635985
H -2.556522 2.759246 3.813463
H -4.203233 1.018260 4.468108
C 2.177916 -1.456583 1.395608
C 2.400921 -2.776510 0.975620
C 3.144703 -0.820531 2.190725
C 3.556292 -3.449319 1.363162
H 1.653358 -3.272992 0.363681
C 4.301035 -1.498080 2.564000
H 2.975005 0.200769 2.518828
C 4.513045 -2.814925 2.154870
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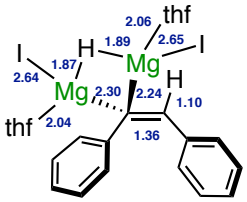
H 5.037173 -0.995558 3.184164
H 5.413703 -3.341948 2.452840



INT2'*syn*

at ωB97XD/6-31++G**&SDD (for I)

Energy = -1428.58682896 A.U.

Thermal correction to Gibbs Free Energy = 0.387352 A.U.

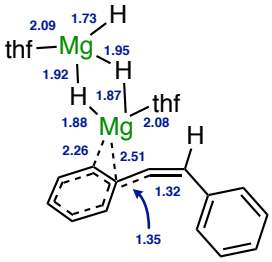
Sum of electronic and thermal Free Energies = -1428.199477 A.U.

at ωB97XD/6-311++G**&SDD (for I) /SMD(THF)

Energy = -1428.85517107 A.U.

Mg	0.572282	-0.997390	-1.426373
H	1.044084	1.614730	-0.689795
Mg	-1.621439	0.734233	-0.962288
H	-0.733975	-0.090608	-2.409120
O	-0.263686	-2.781226	-0.909685
C	-1.683532	-2.856417	-0.606749
C	0.457269	-3.855975	-0.248211
C	-1.871790	-4.204519	0.072462
H	-1.930034	-2.033775	0.071971
H	-2.232409	-2.738564	-1.542981
C	-0.525264	-4.401074	0.775753
H	0.726532	-4.592846	-1.011320
H	1.366188	-3.434197	0.185546
H	-2.042901	-4.991569	-0.669120
H	-2.717169	-4.187893	0.762983
H	-0.318137	-5.444346	1.023901
H	-0.482346	-3.806094	1.693008
O	-1.338279	2.724549	-1.422218
C	-0.367741	3.272050	-2.334884
C	-1.645830	3.757848	-0.466542
C	0.487030	4.241019	-1.498439
H	0.182358	2.433196	-2.765935
H	-0.911011	3.788112	-3.133771
C	-0.296646	4.407553	-0.175357
H	-2.356711	4.451732	-0.930185
H	-2.123559	3.283298	0.392825
H	0.609684	5.190940	-2.023464
H	1.484539	3.836990	-1.309511
H	-0.408707	5.453483	0.117820
H	0.209326	3.880113	0.637271
I	3.118862	-1.267985	-2.062596
I	-4.173795	0.452688	-0.296581
C	0.020230	0.191375	0.469383
C	0.968414	1.146286	0.299105
C	1.964218	1.712650	1.238731
C	1.679920	1.912338	2.596079
C	3.210308	2.113891	0.741470
C	2.626949	2.489268	3.435901
H	0.713611	1.615262	2.991285
C	4.163171	2.678126	1.585358
H	3.440634	1.952595	-0.309157
C	3.872487	2.868854	2.934996
H	2.392825	2.641983	4.484996

H	5.131318	2.967885	1.188871
H	4.611526	3.313918	3.594078
C	-0.021383	-0.626603	1.707597
C	-1.217427	-0.817991	2.414282
C	1.127475	-1.299496	2.159621
C	-1.254688	-1.615347	3.557193
H	-2.126174	-0.330217	2.069813
C	1.086988	-2.107532	3.291251
H	2.063912	-1.173372	1.620605
C	-0.103753	-2.263600	4.002280
H	-2.190211	-1.733631	4.095942
H	1.989961	-2.612285	3.622234
H	-0.134564	-2.889040	4.889087



TS*syn-anti*

at *ω*B97XD/6-31++G**

Energy = -1406.67113424 A.U.

Thermal correction to Gibbs Free Energy = 0.400657 A.U.

Sum of electronic and thermal Free Energies = -1406.270478 A.U.

at *ω*B97XD/6-311++G**/SMD(THF)

Energy = -1406.93013878 A.U.

C	-1.603182	-0.754344	-0.717695
C	-0.797618	-1.108002	0.265422
C	0.312204	-1.243975	1.020574
C	0.638759	-0.335359	2.132720
C	1.294205	-2.300821	0.775488
C	1.803862	-0.551522	2.913094
H	-0.191600	0.187147	2.603711
C	2.414351	-2.422932	1.542247
H	1.082779	-3.015296	-0.014036
C	2.712486	-1.538116	2.623194
H	1.967992	0.098974	3.769126
H	3.103087	-3.237173	1.326318
H	3.607899	-1.675644	3.218088
Mg	0.816423	1.141460	0.429308
H	-1.219796	-0.148348	-1.550860
C	-3.041168	-1.094399	-0.822963
C	-3.756254	-0.740459	-1.972940
C	-3.726993	-1.729979	0.220141
C	-5.118214	-1.013210	-2.082228
H	-3.235776	-0.245842	-2.790245
C	-5.085487	-2.003907	0.113318
H	-3.173601	-2.005373	1.114241
C	-5.789256	-1.644793	-1.037784
H	-5.654706	-0.732796	-2.983810
H	-5.601208	-2.498018	0.931564
H	-6.850831	-1.857095	-1.118431
H	2.381818	2.163853	0.356584
Mg	2.426589	2.215135	-1.589794
H	0.826686	1.160160	-1.452958

H 2.762954 3.594421 -2.584280

O -0.798355 2.413025 0.736231

C -1.529296 2.571506 1.963957

C -1.729987 2.700892 -0.337572

C -2.864389 1.910675 1.662835

H -0.948610 2.111658 2.764077

H -1.634277 3.644230 2.170563

C -3.126464 2.348949 0.209431

H -1.631775 3.762461 -0.584589

H -1.419758 2.103462 -1.194937

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H -2.760160 0.822480 1.717866

H -3.778380 3.225766 0.175240

H -3.597738 1.551515 -0.367080

O 3.716839 0.579369 -1.733855

C 3.270345 -0.784442 -1.944620

C 4.938243 0.599393 -0.960016

C 4.392199 -1.663775 -1.407042

H 2.338545 -0.927598 -1.388403

H 3.076646 -0.910995 -3.011904

C 5.013792 -0.778410 -0.322977

H 5.772529 0.791614 -1.643417

H 4.860233 1.414707 -0.235906

H 5.123003 -1.885629 -2.191600

H 4.005334 -2.606377 -1.014627

H 6.038262 -1.061197 -0.070861

H 4.405854 -0.805689 0.586989

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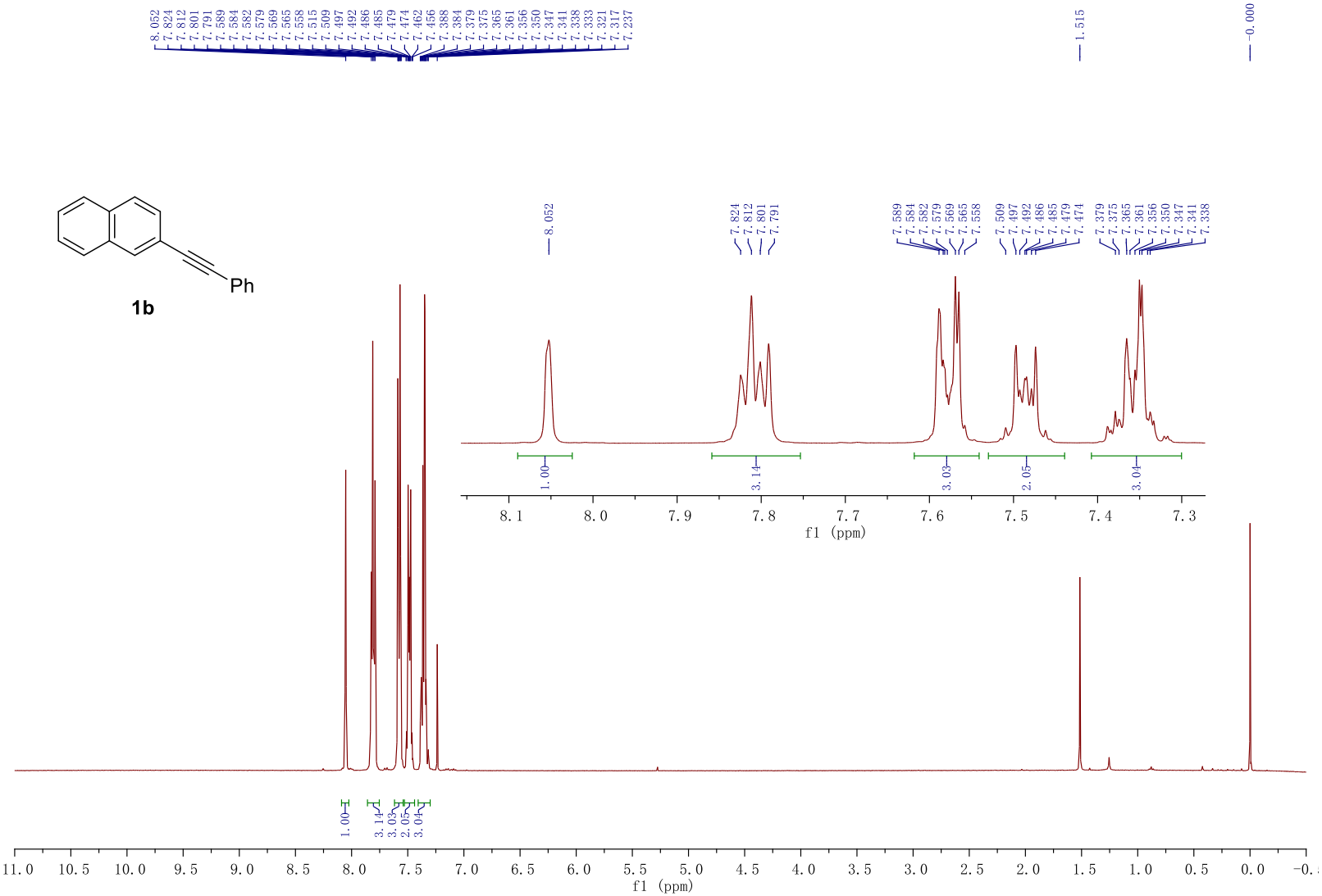
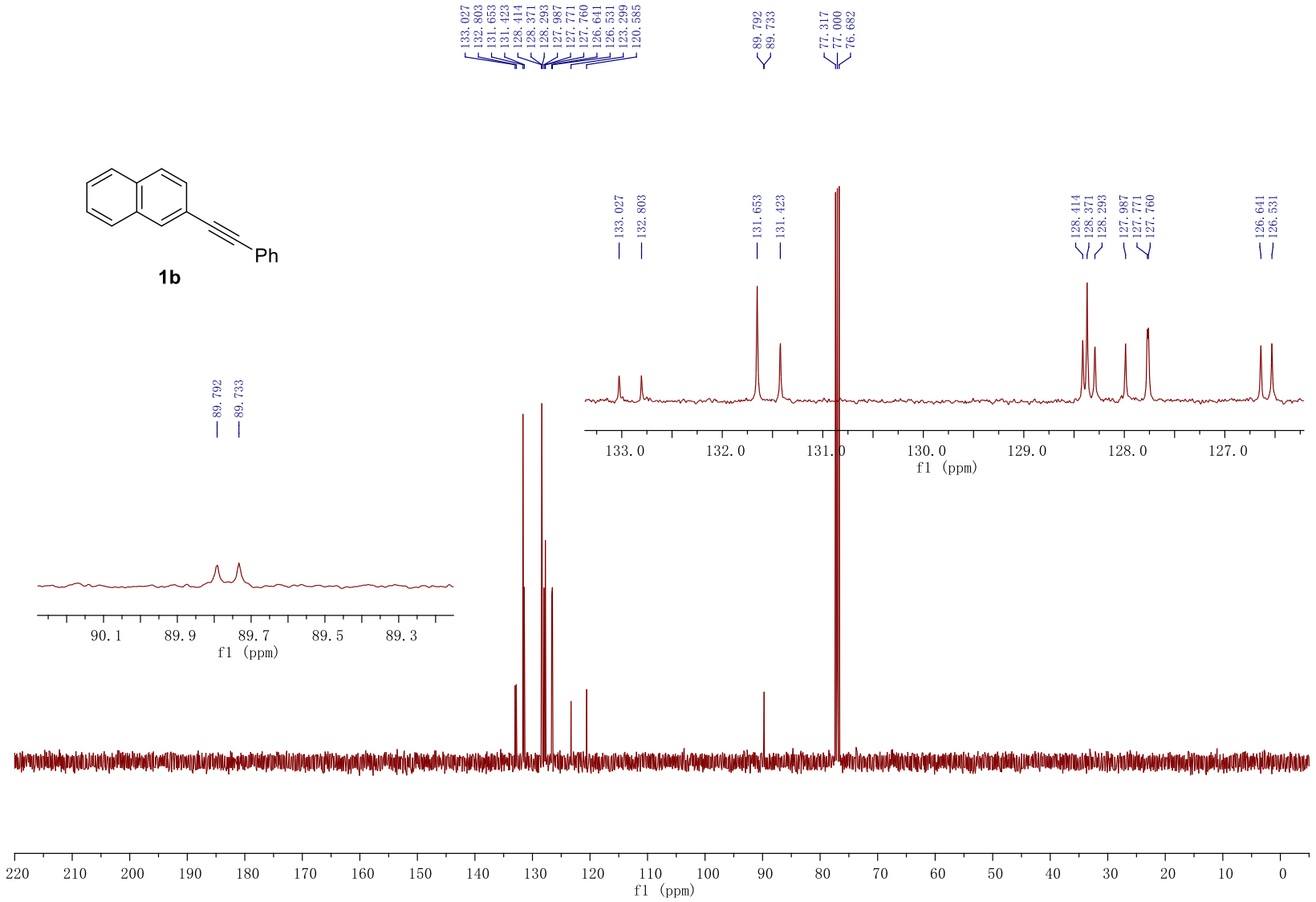
7. ^{1}H and ^{13}C NMR spectra of new compounds

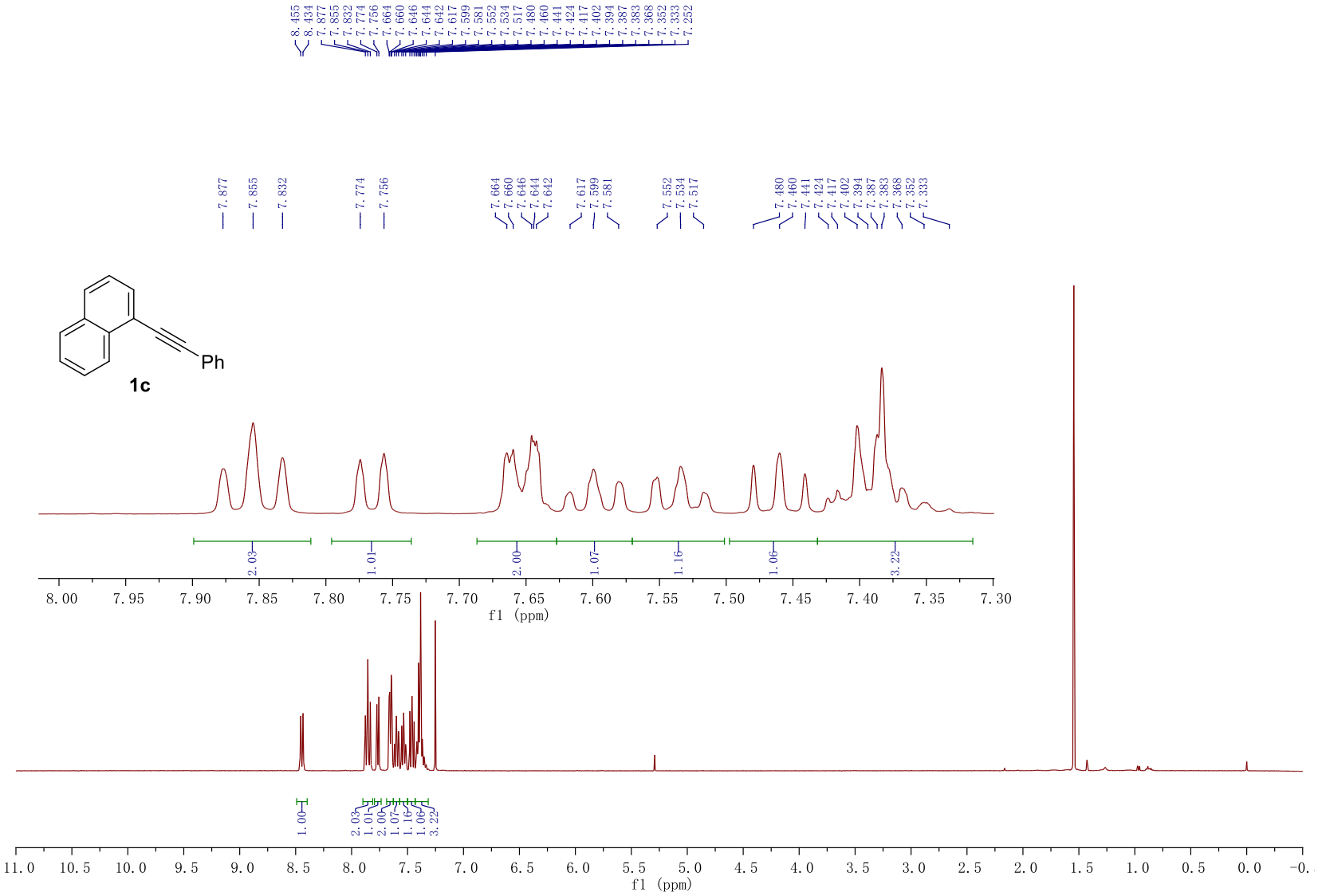
^{1}H NMR Spectrum of 2-(phenylethynyl)naphthalene (1b)



^{13}C NMR Spectrum of 2-(phenylethynyl)naphthalene (1b)



^{1}H NMR Spectrum of 1-(phenylethynyl)naphthalene (1c)



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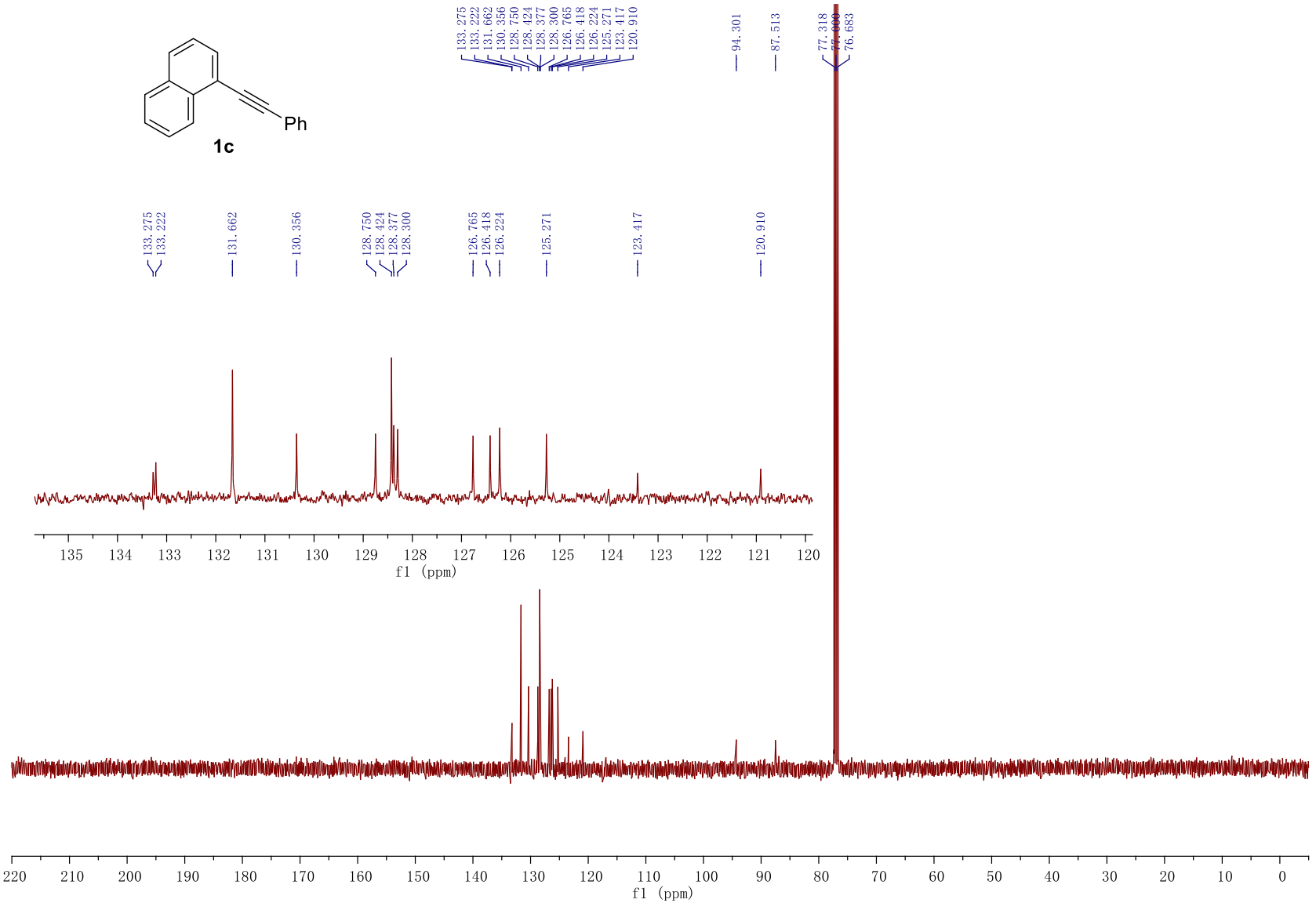
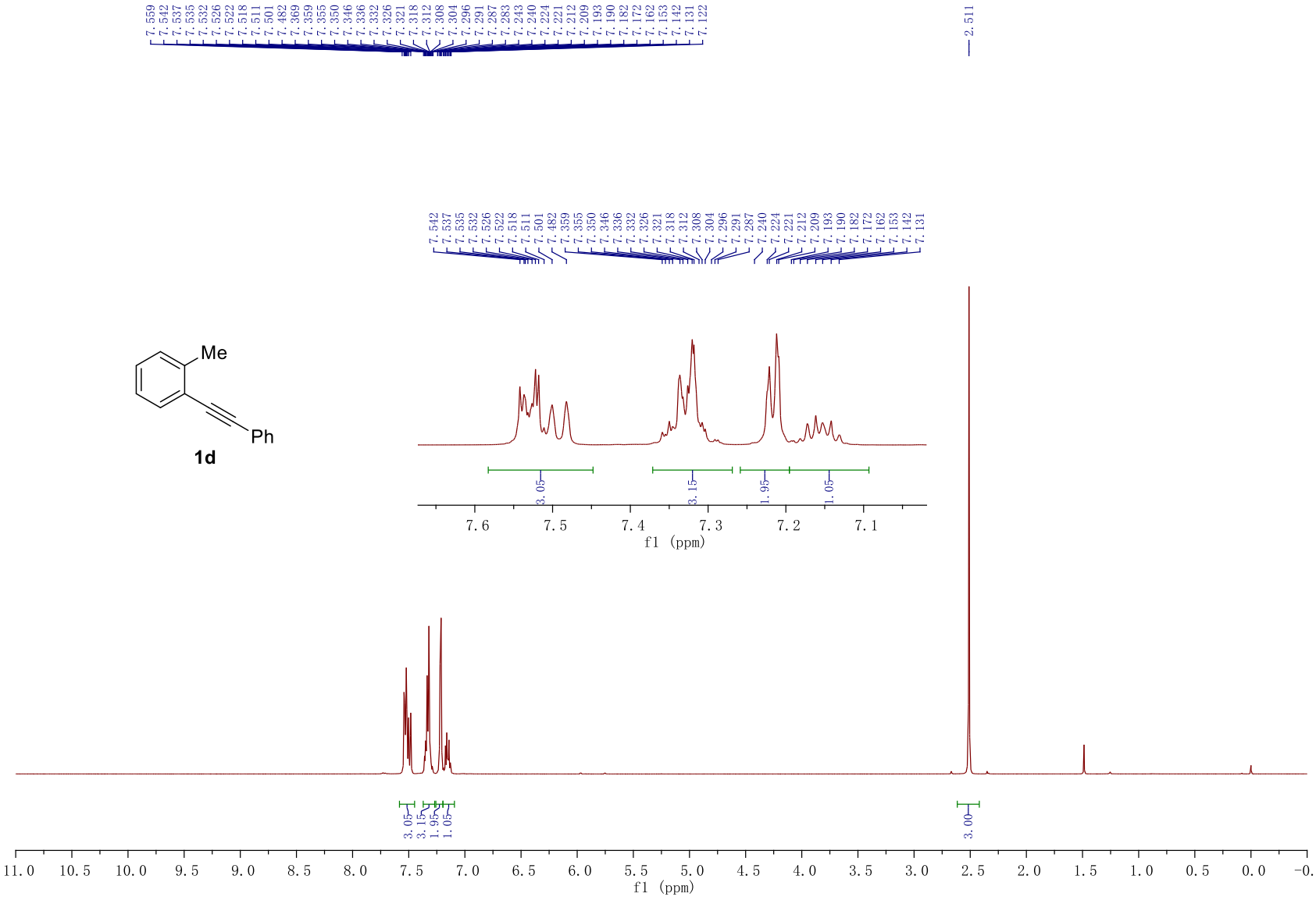


[1]H NMR Spectrum of 1-methyl-2-(phenylethynyl)benzene (1d)



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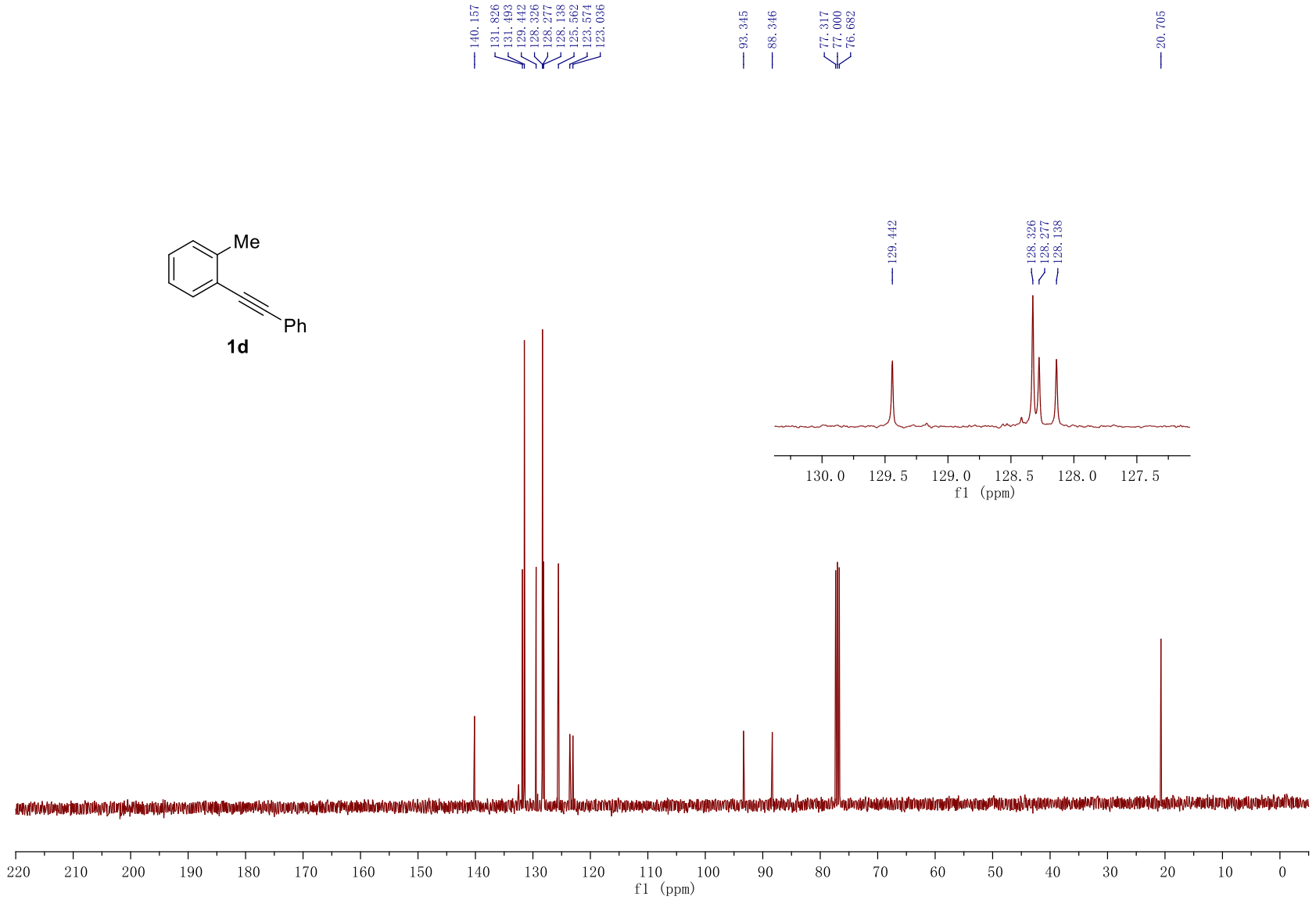
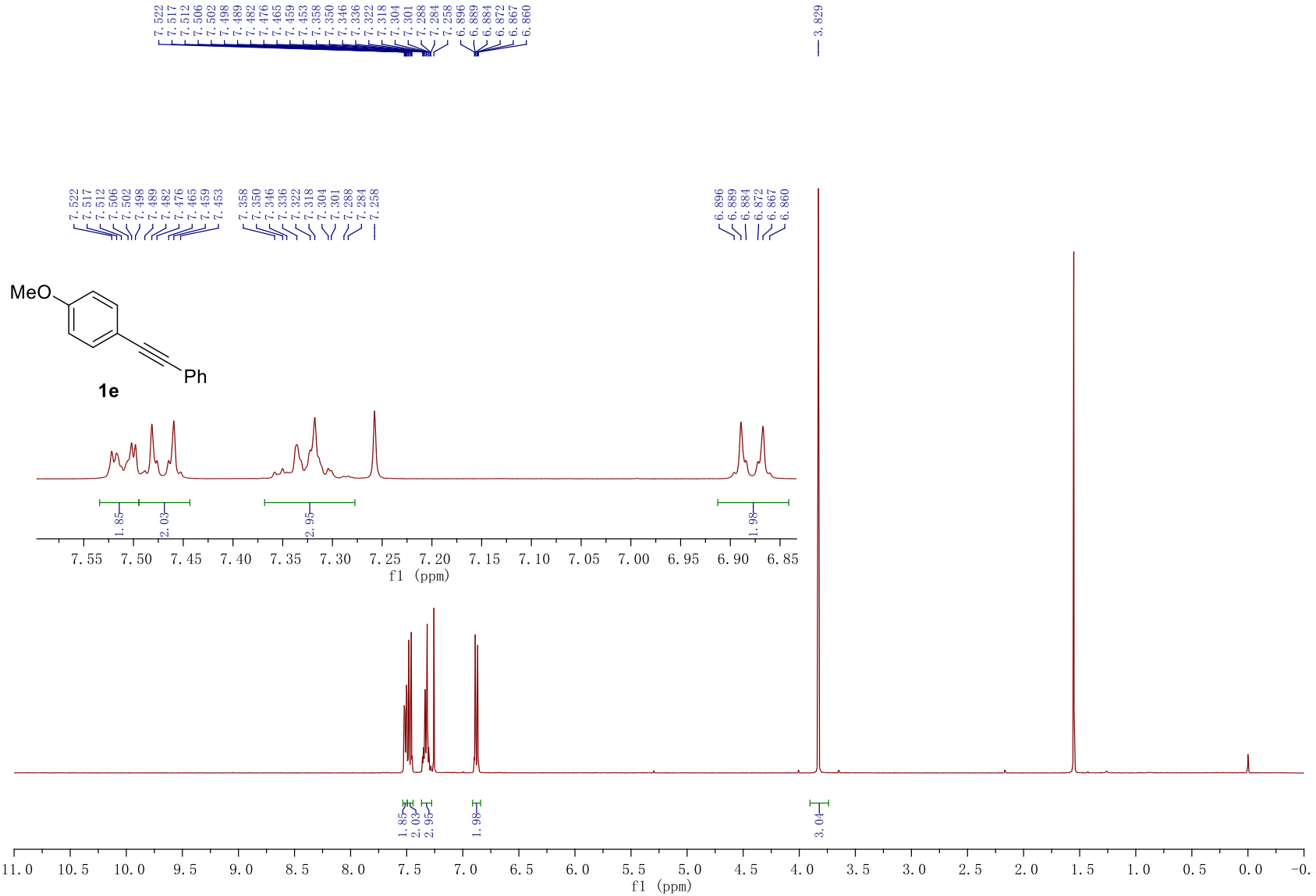


^{1}H NMR Spectrum of 1-methoxy-4-(phenylethynyl)benzene (1e)



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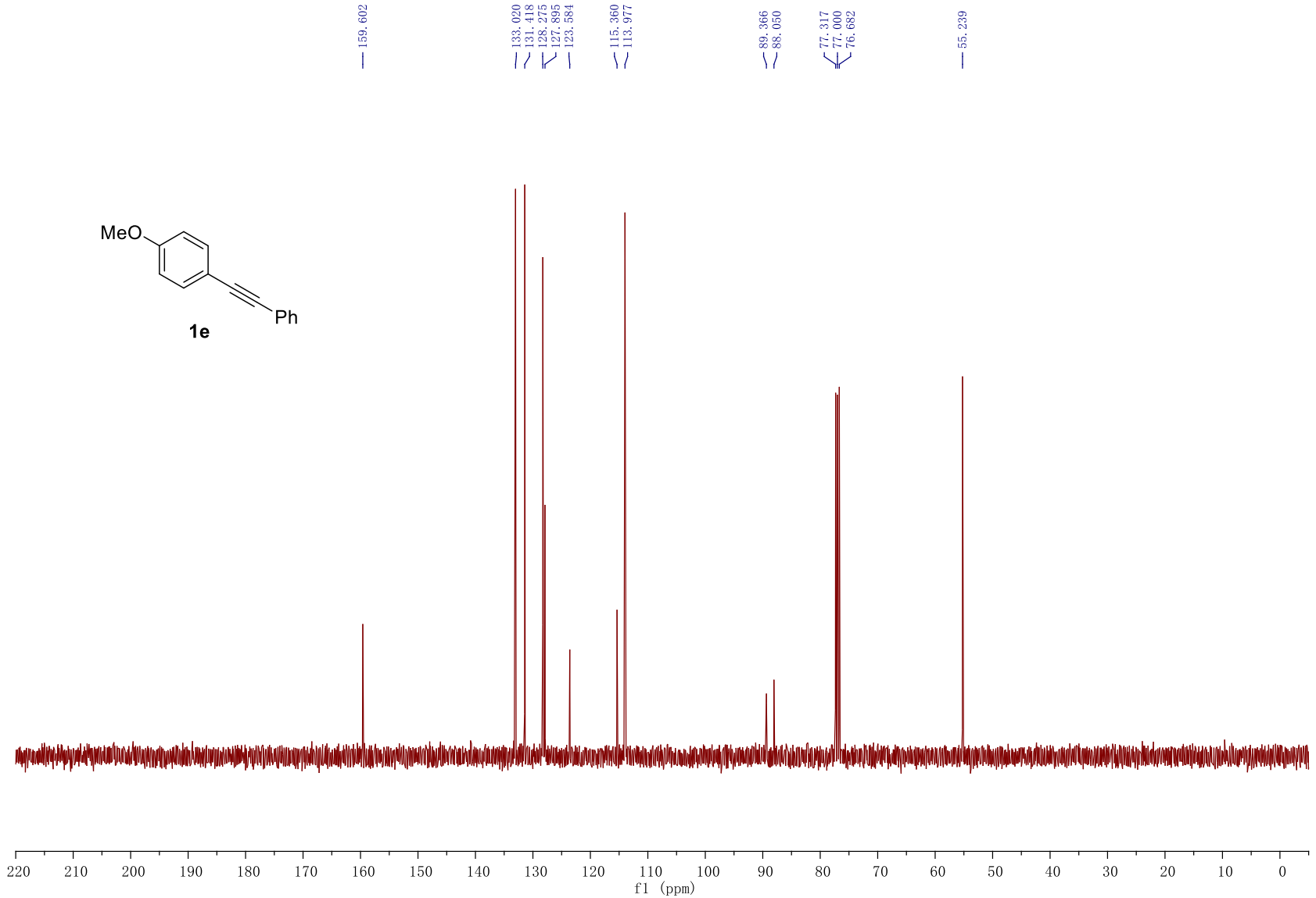
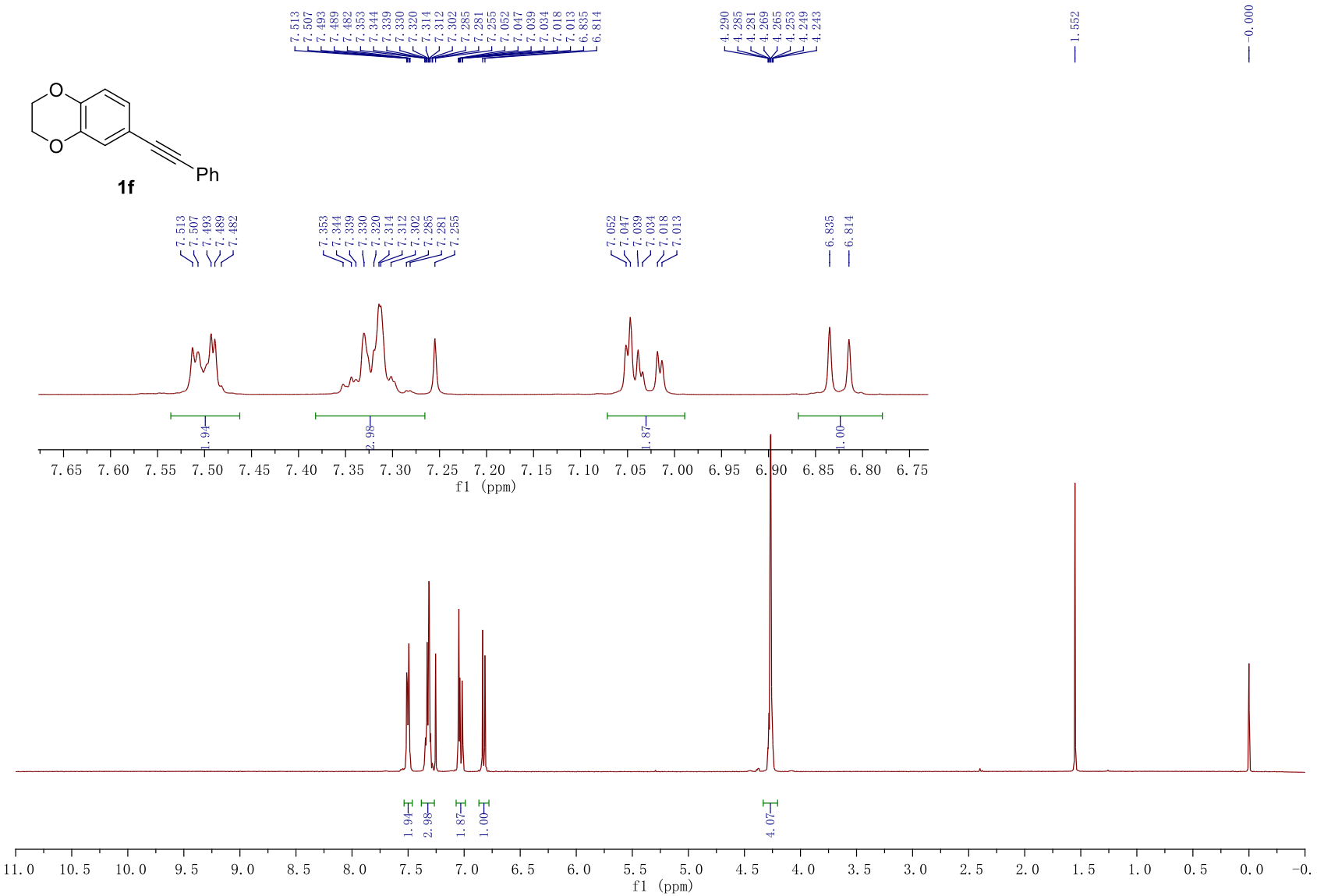
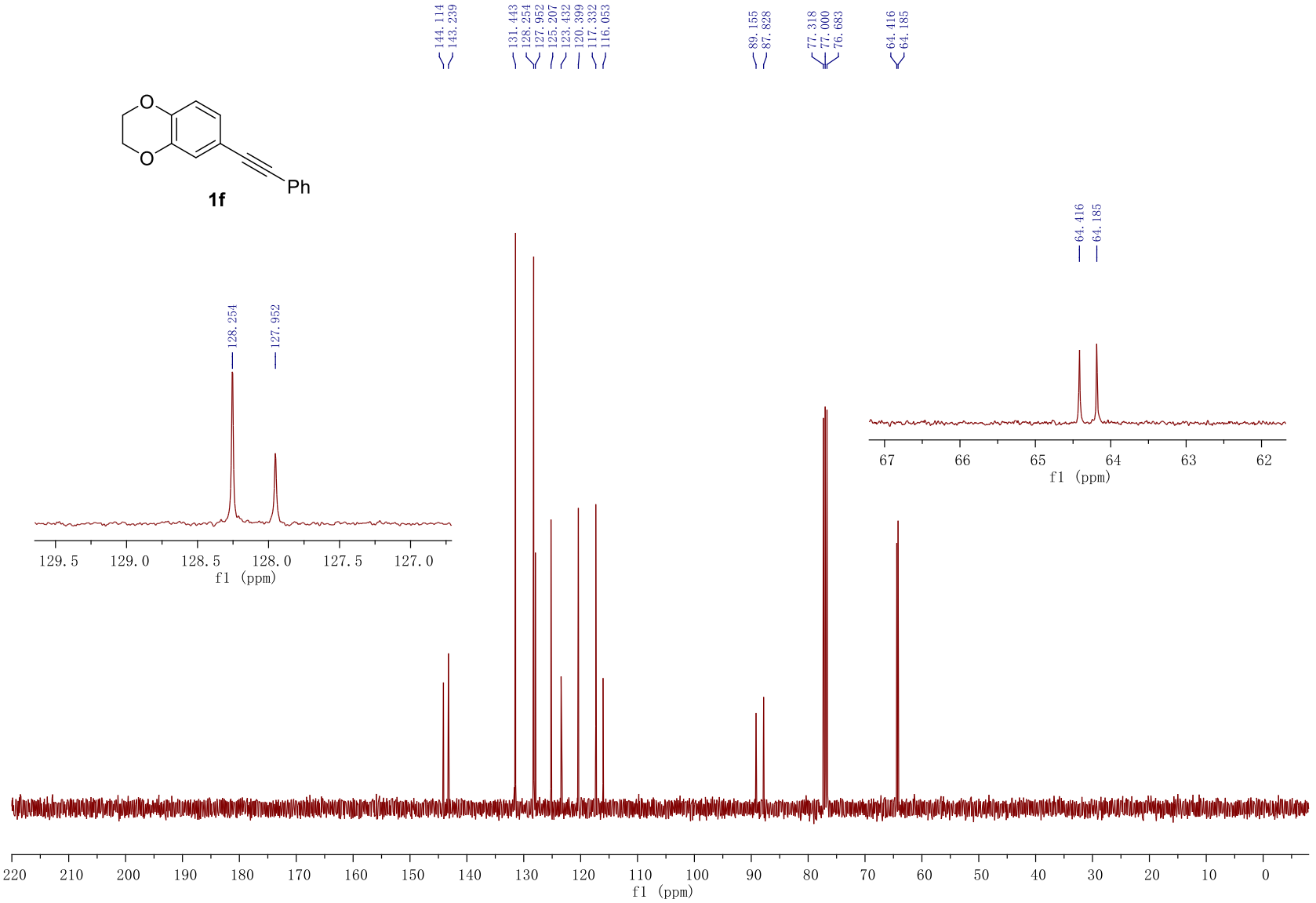


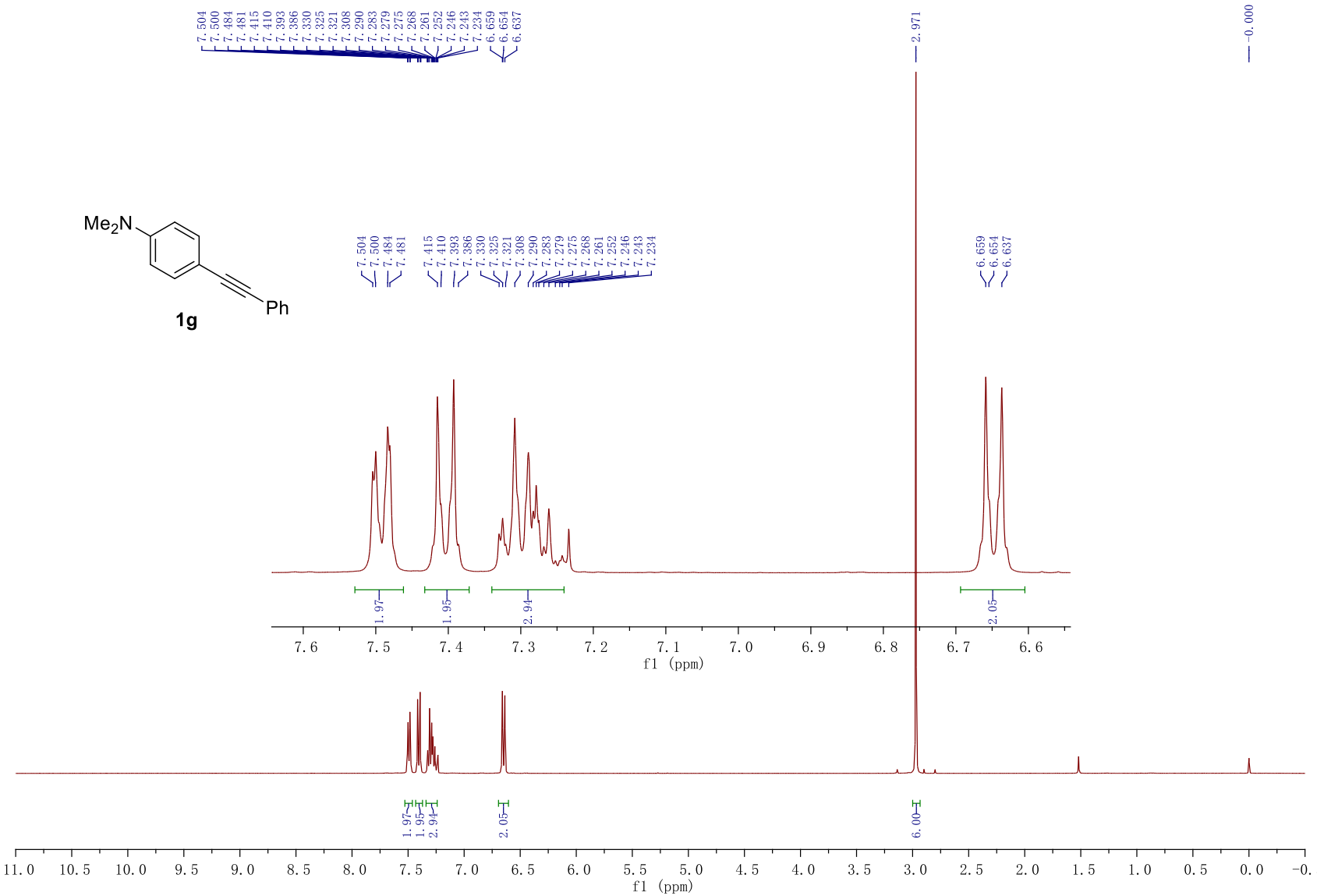
^{1}H NMR Spectrum of 6-(phenylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (1f)



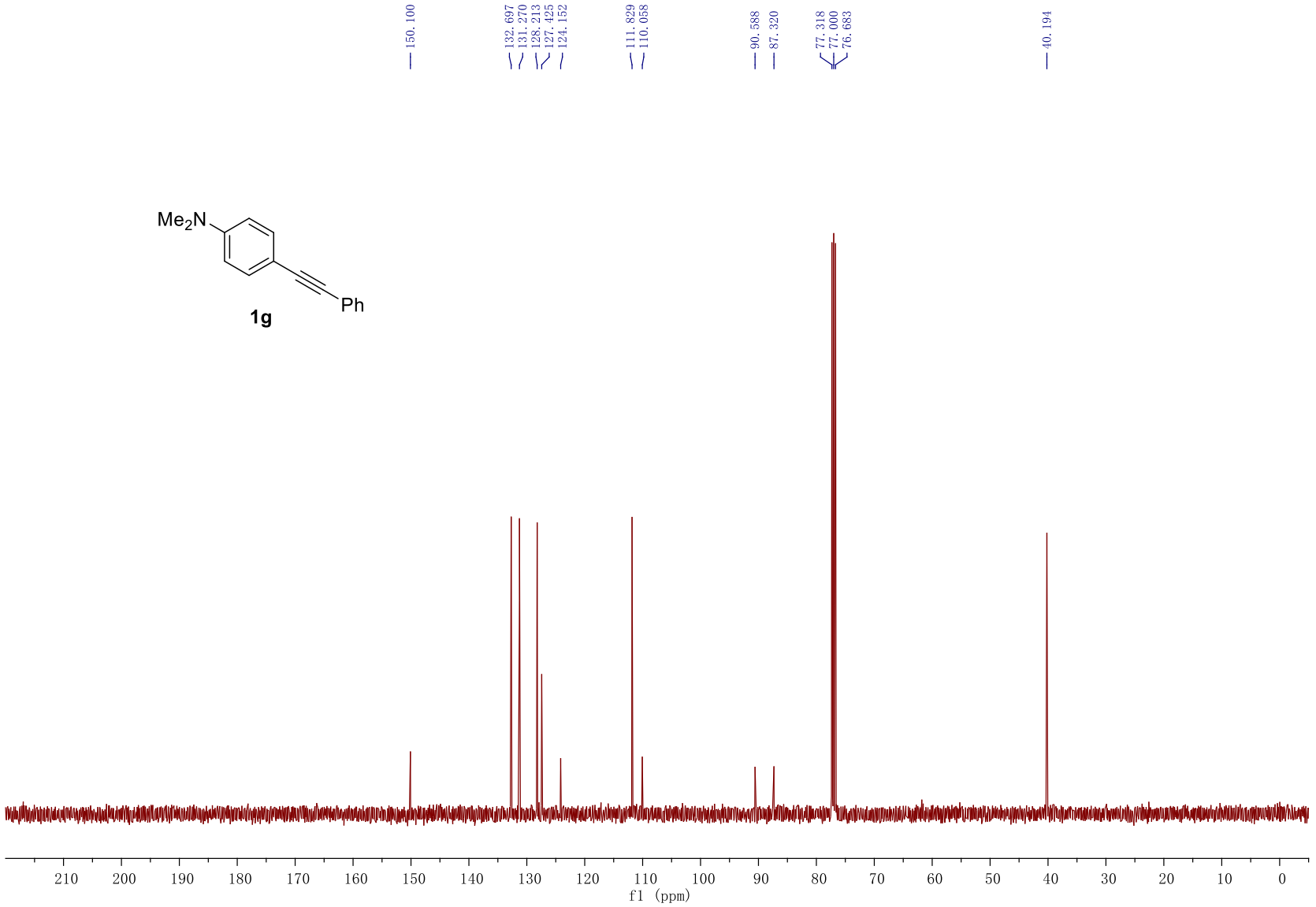
^{13}C NMR Spectrum of 6-(phenylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (1f)



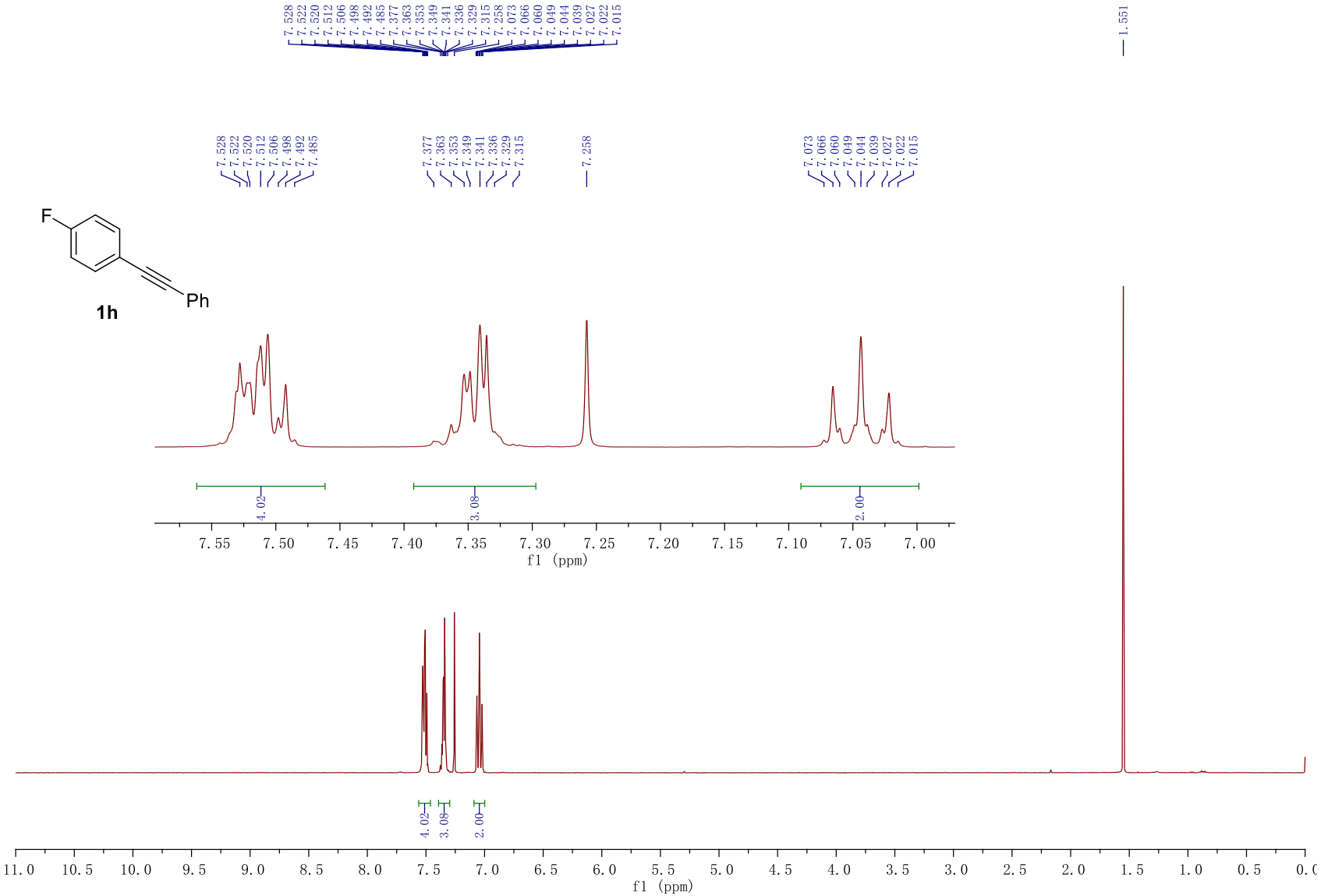
^{1}H NMR Spectrum of *N,N*-dimethyl-4-(phenylethynyl)aniline (1g)



^{13}C NMR Spectrum of *N,N*-dimethyl-4-(phenylethynyl)aniline (1g)



^{1}H NMR Spectrum of 1-fluoro-4-(phenylethynyl)benzene (1h)



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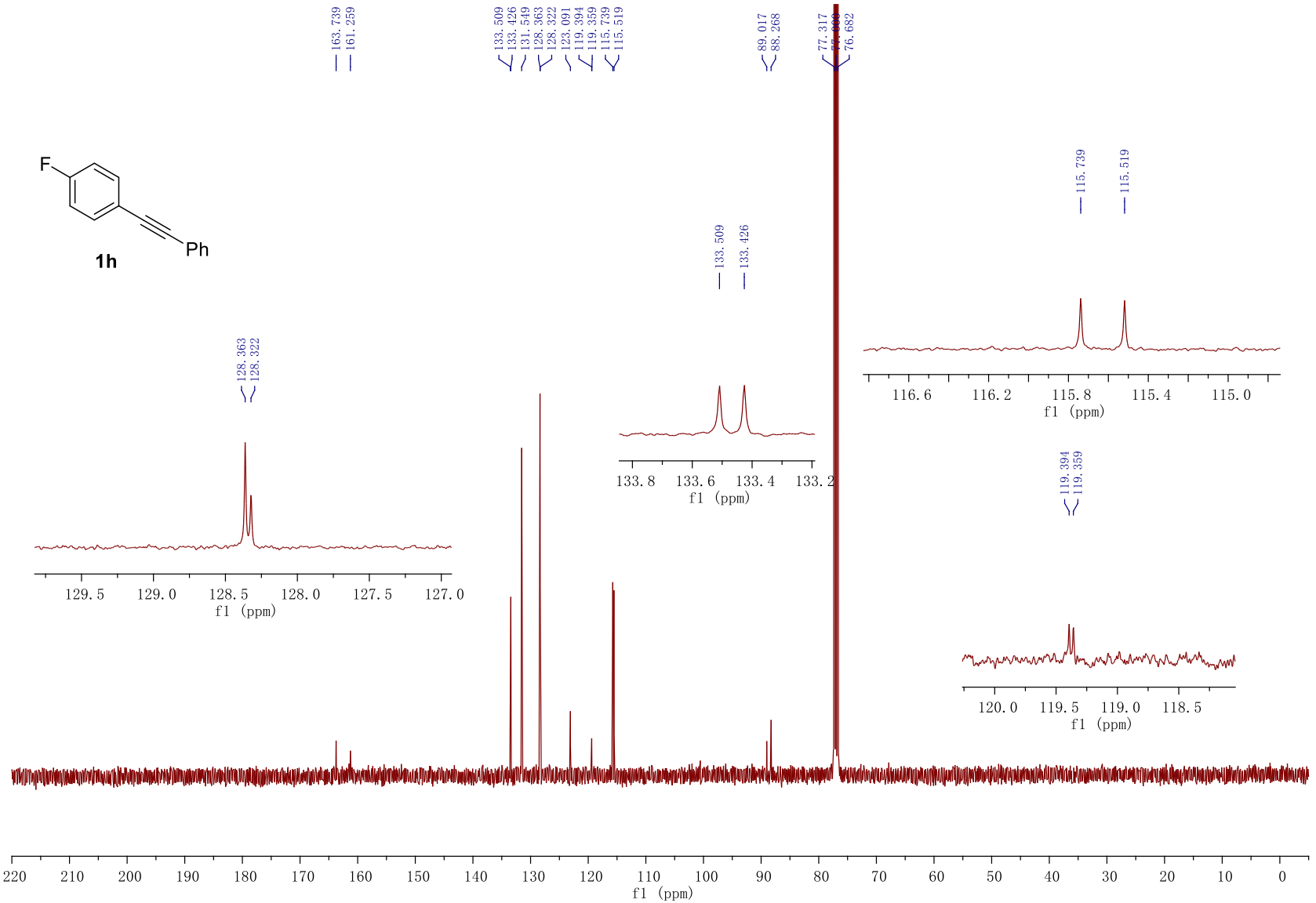
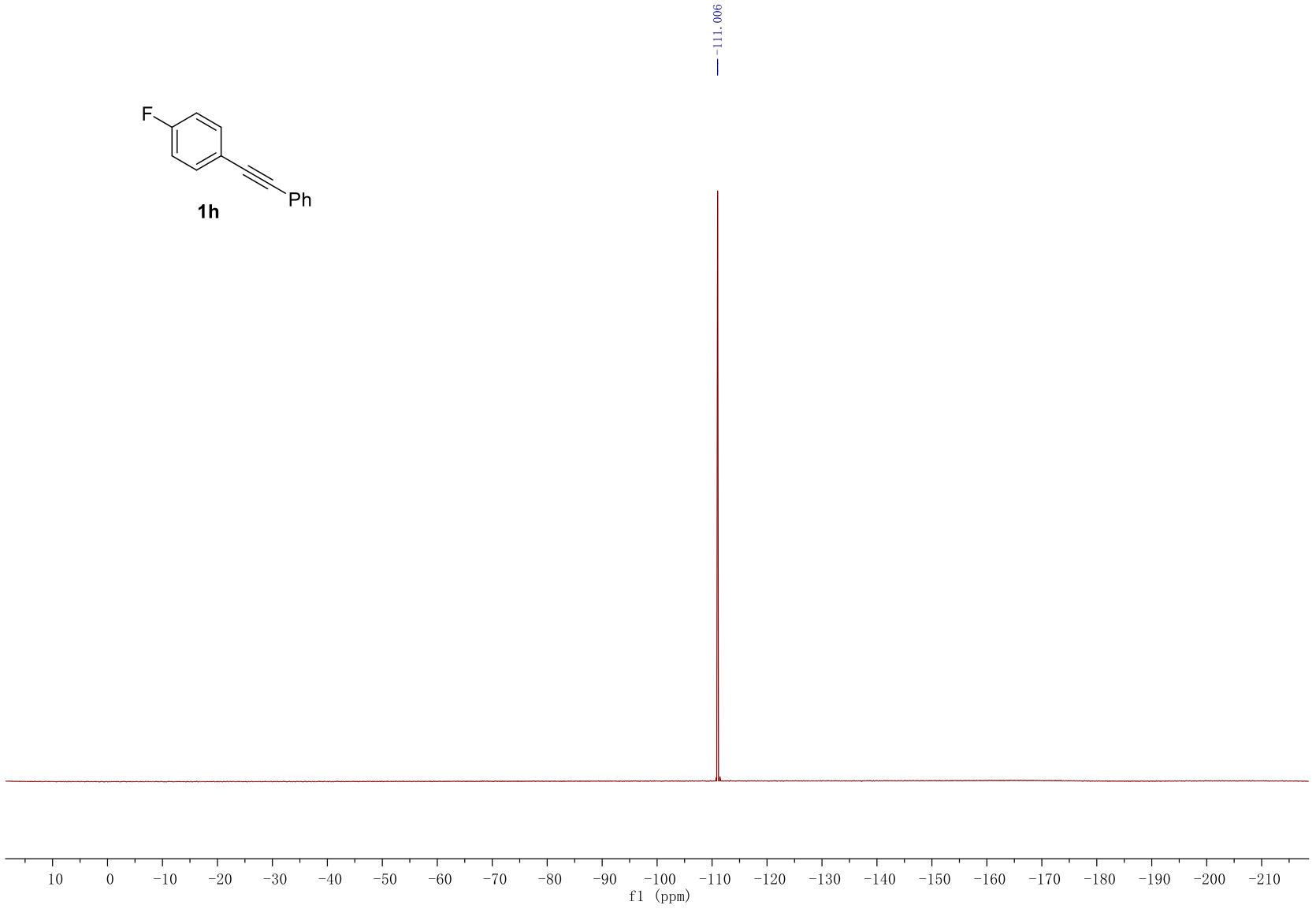


^{19}F NMR Spectrum of 1-fluoro-4-(phenylethynyl)benzene (1h)



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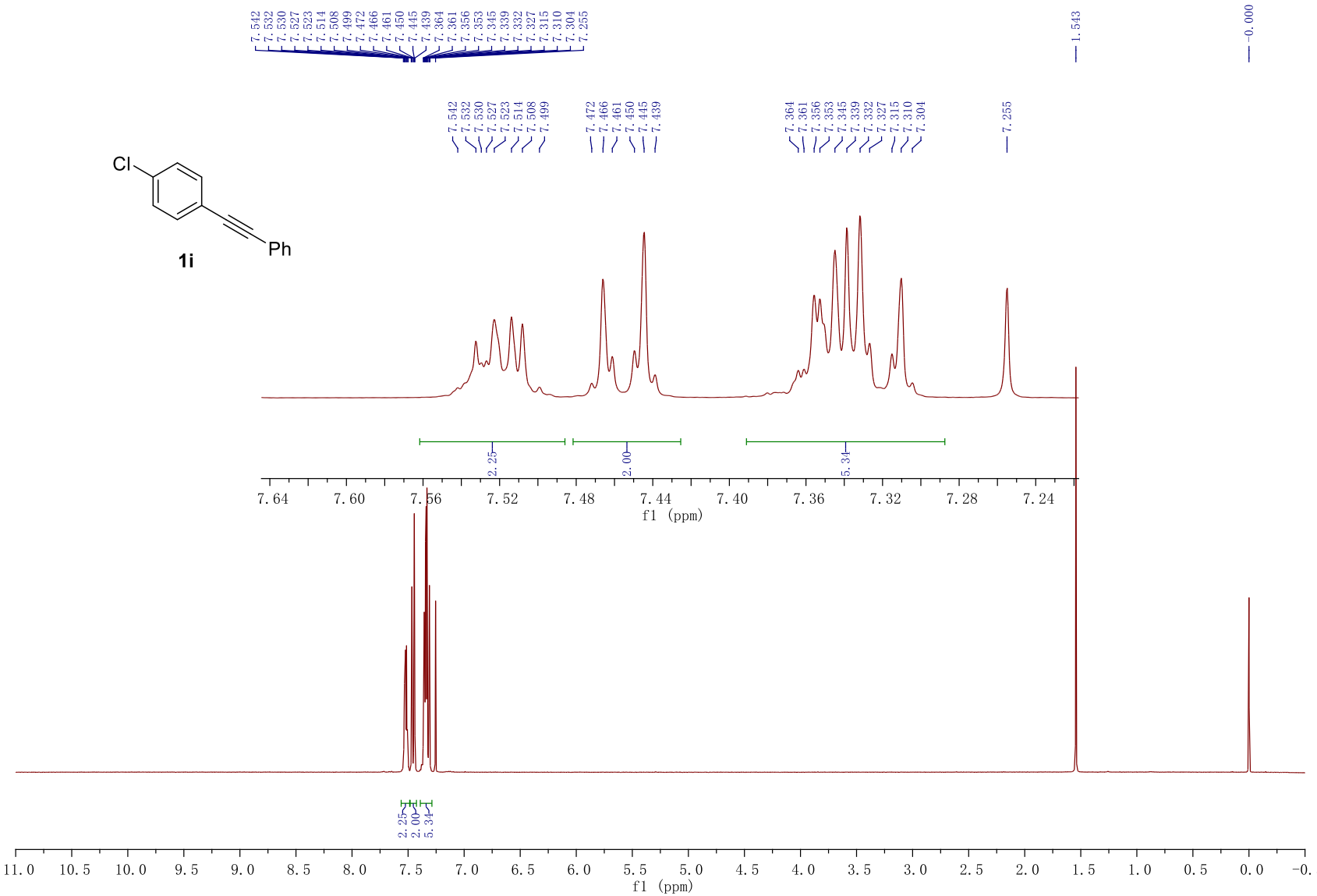
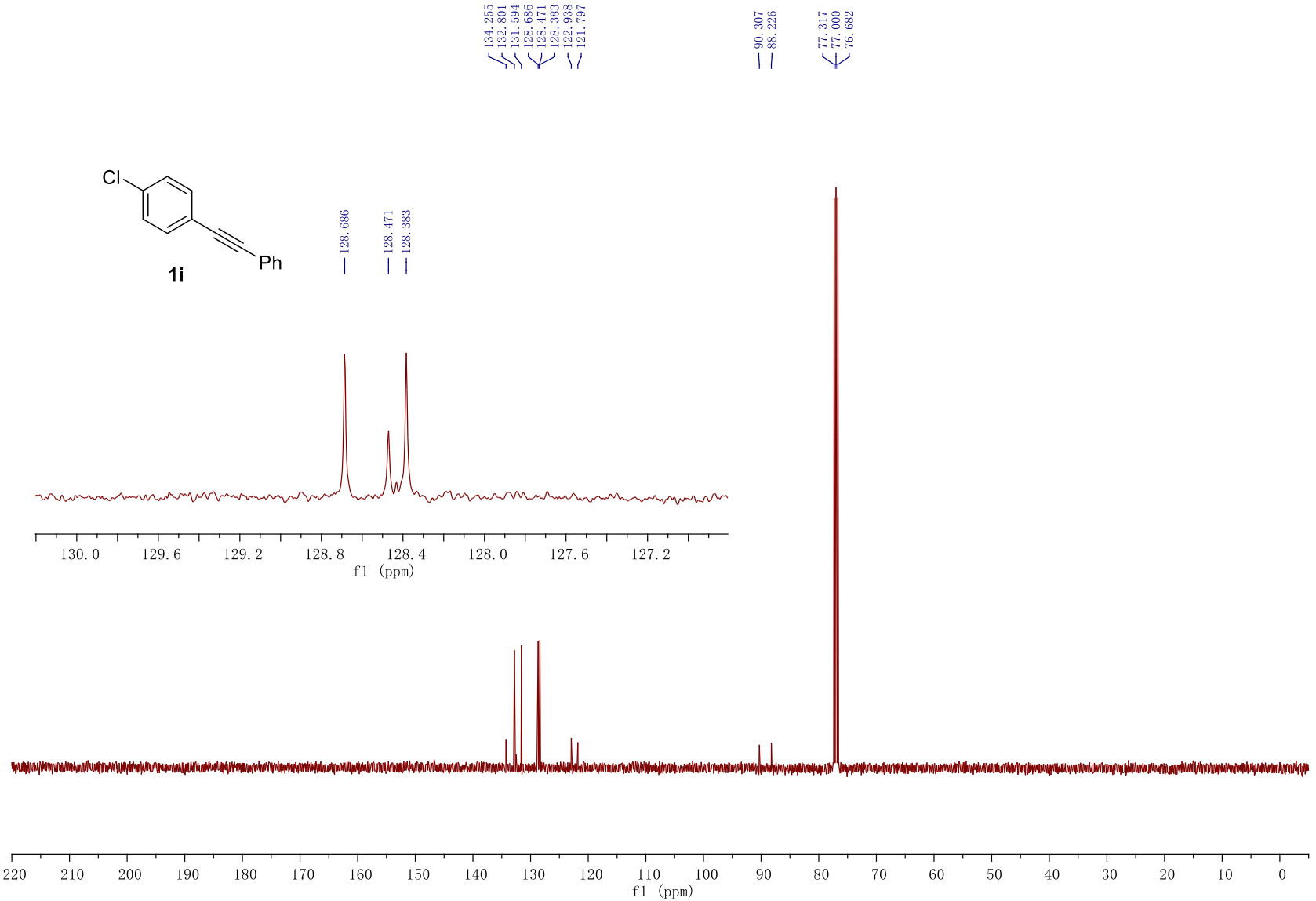
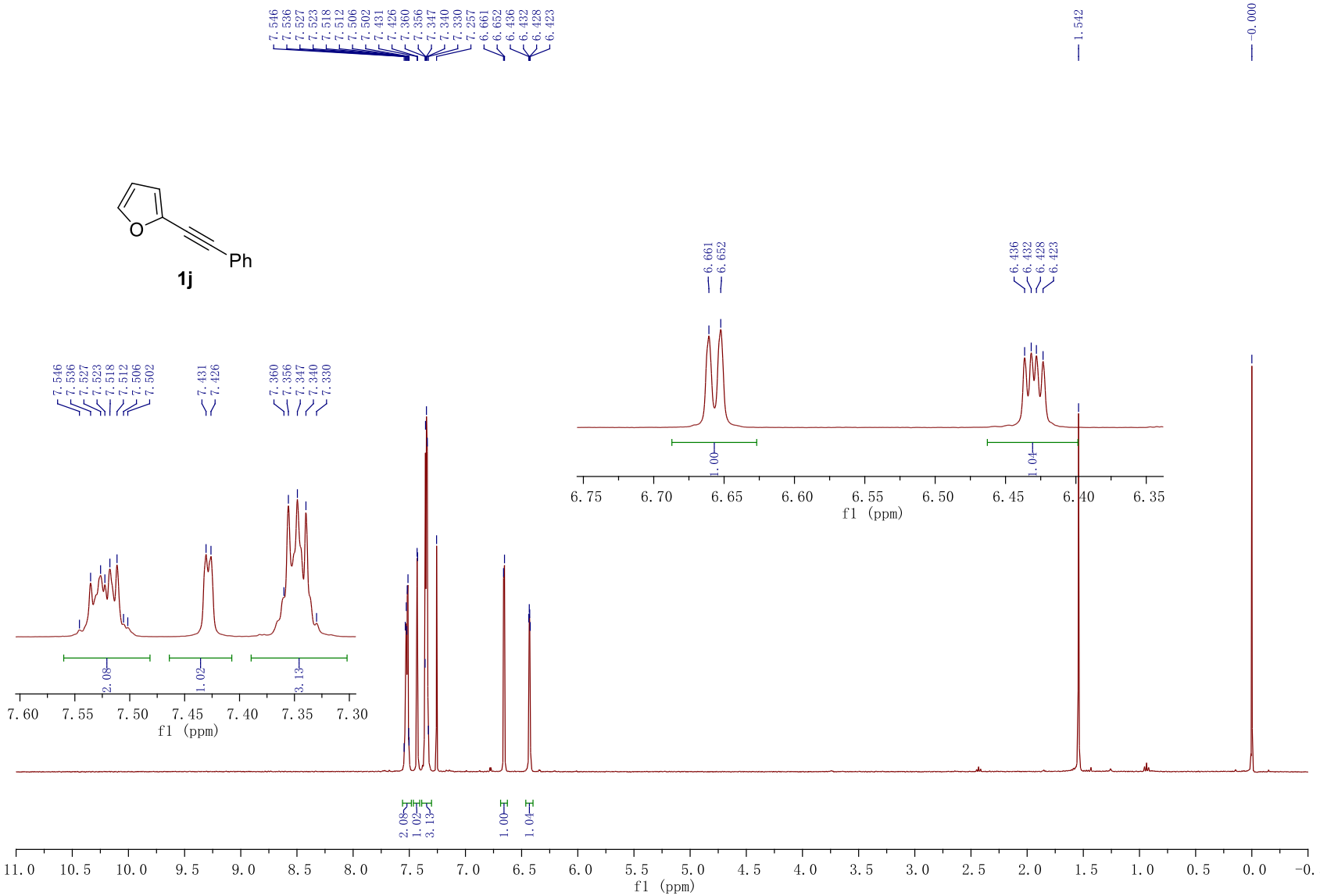


^{13}C NMR Spectrum of 1-chloro-4-(phenylethynyl)benzene (1i)



[1]H NMR Spectrum of 2-(phenylethynyl)furan (1j)



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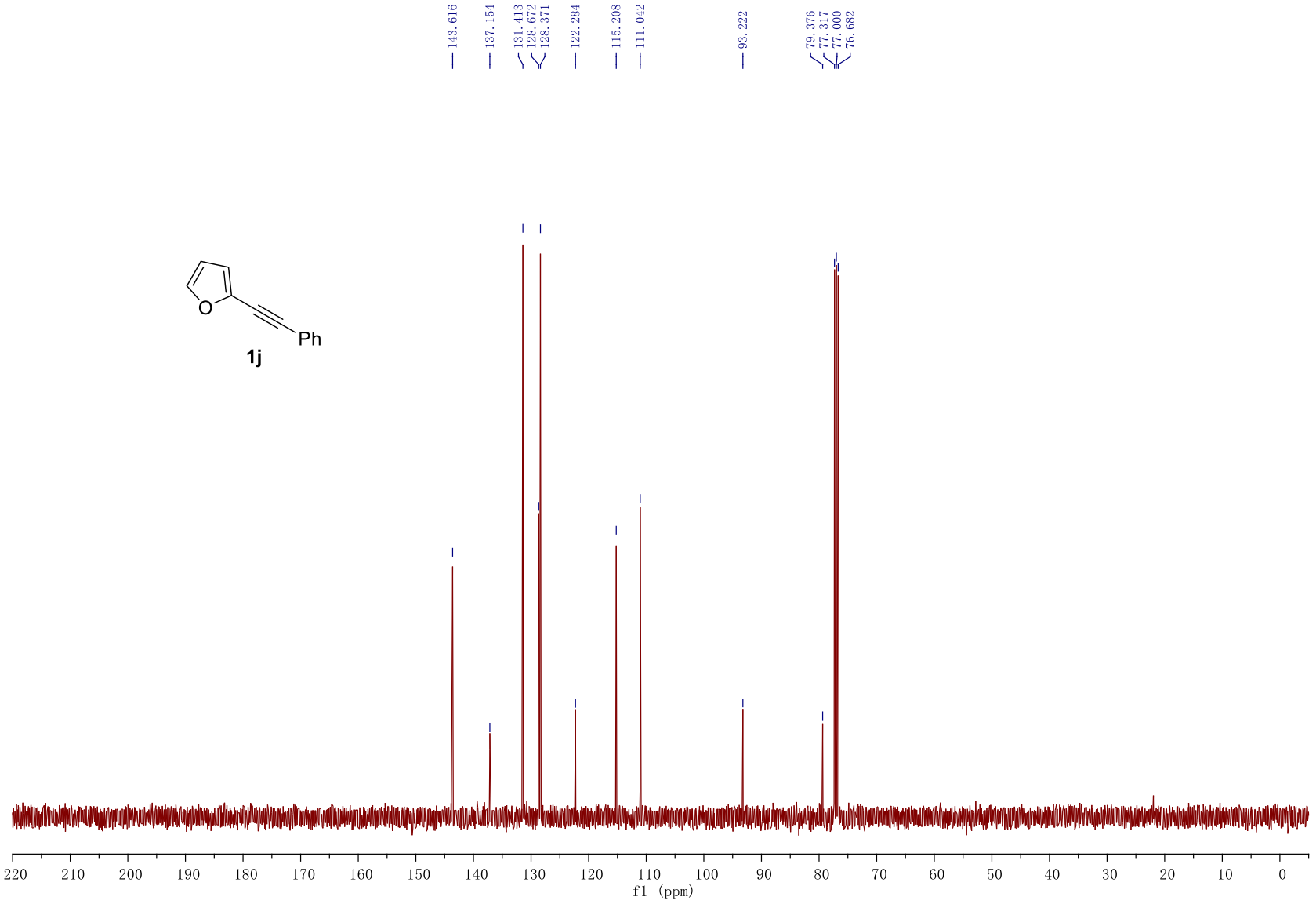
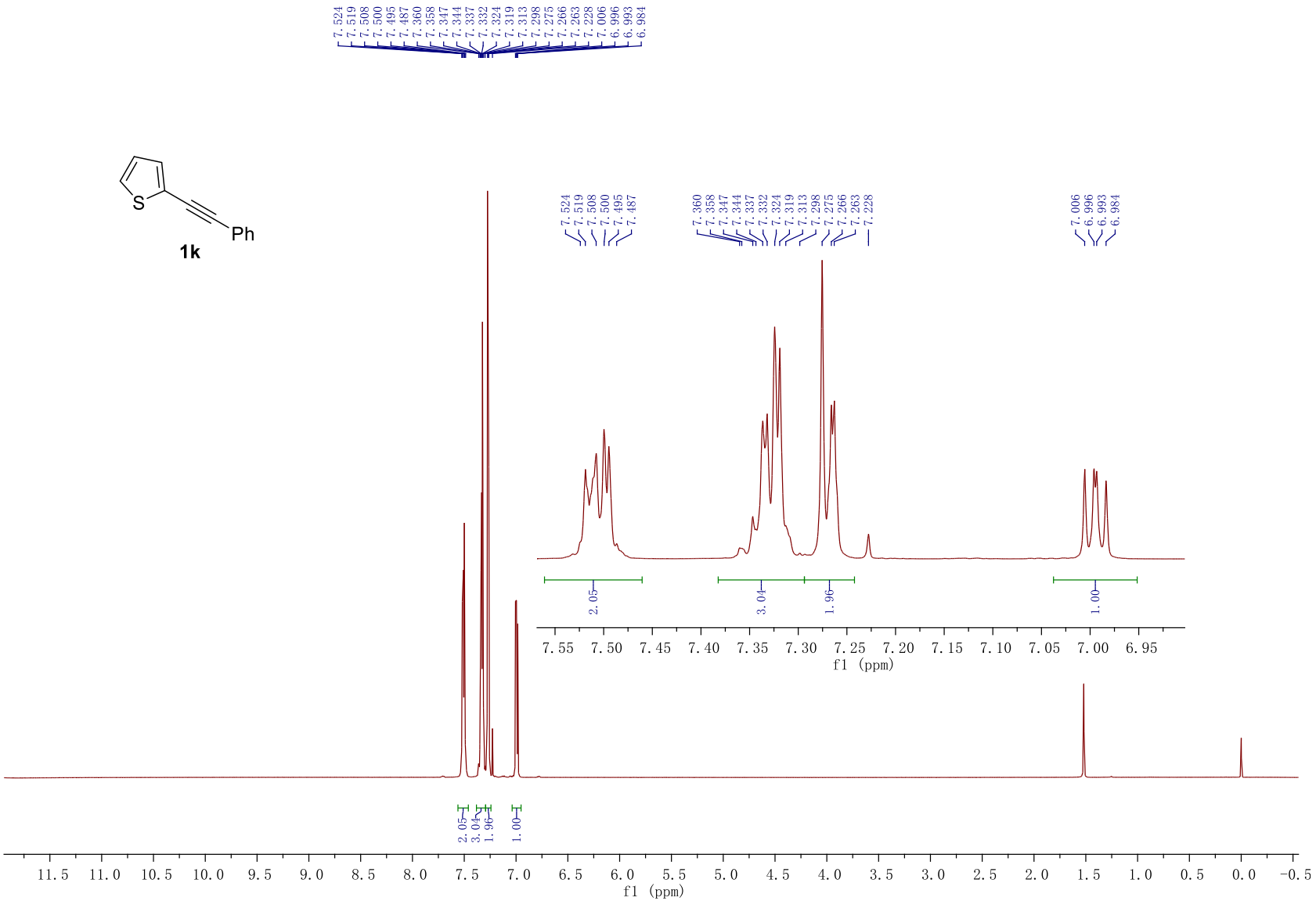
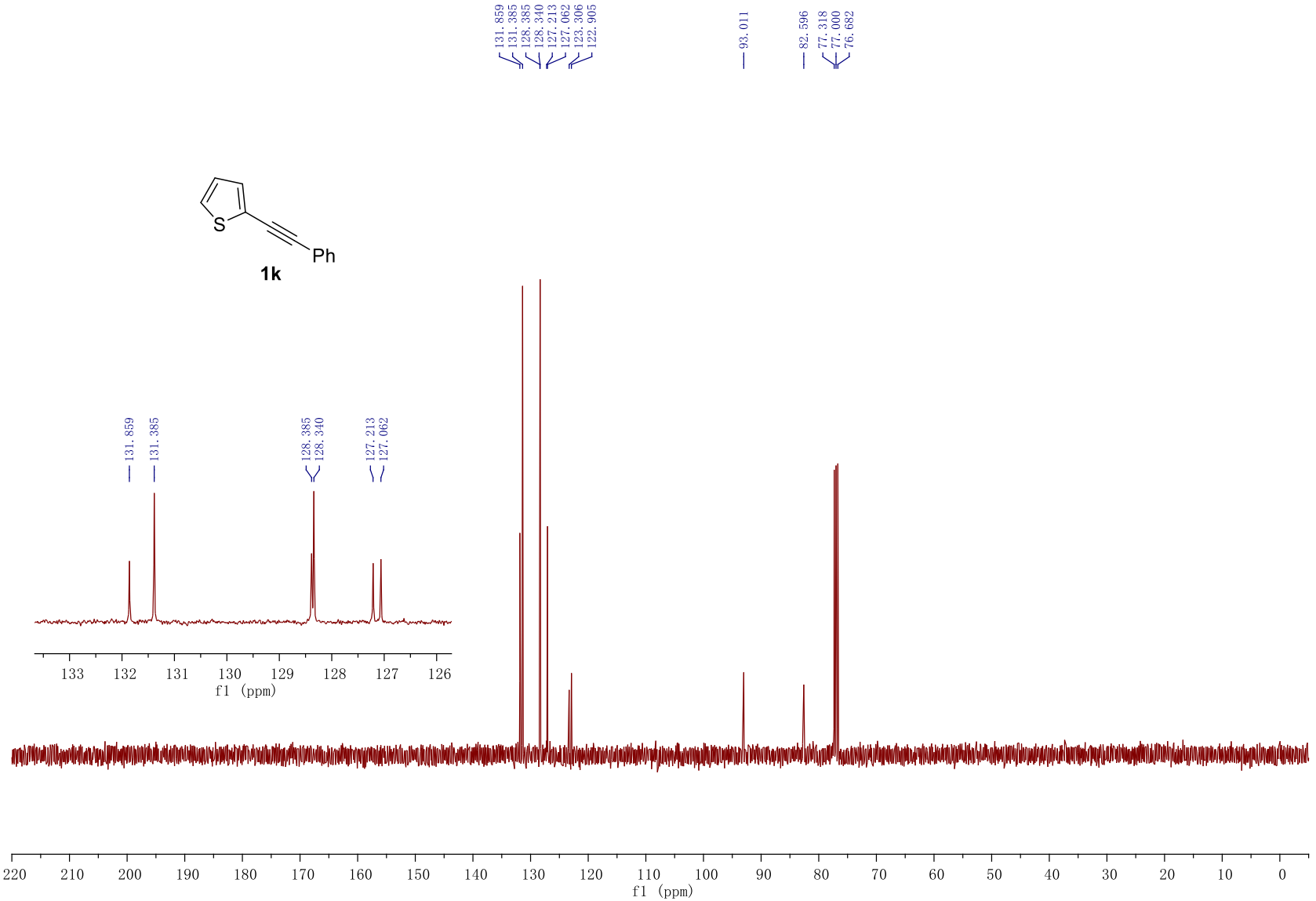


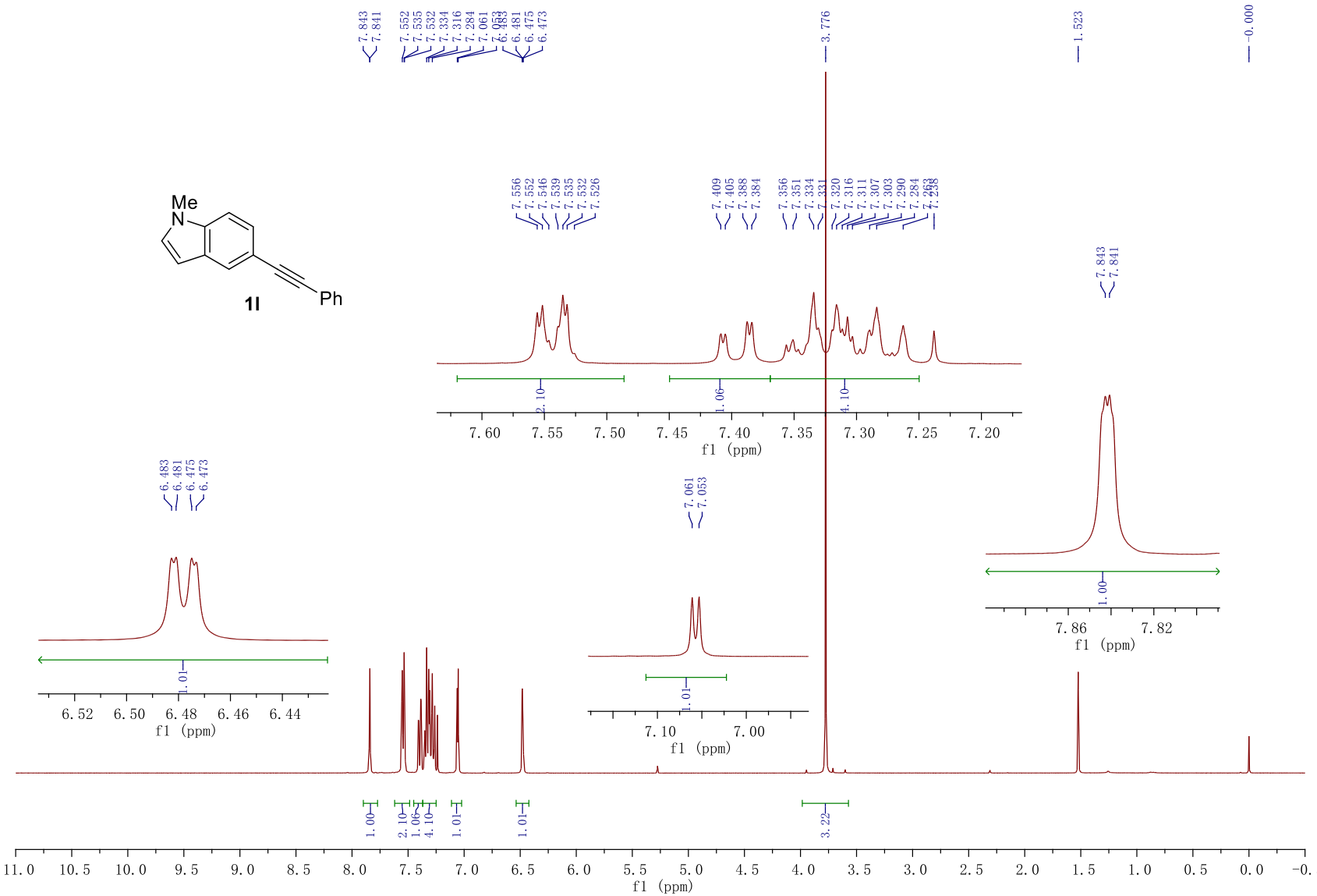
^{1}H NMR Spectrum of 2-(phenylethynyl)thiophene (1k)



^{13}C NMR Spectrum of 2-(phenylethynyl)thiophene (1k)



^{1}H NMR Spectrum of 1-methyl-5-(phenylethynyl)-1*H*-indole (1l)



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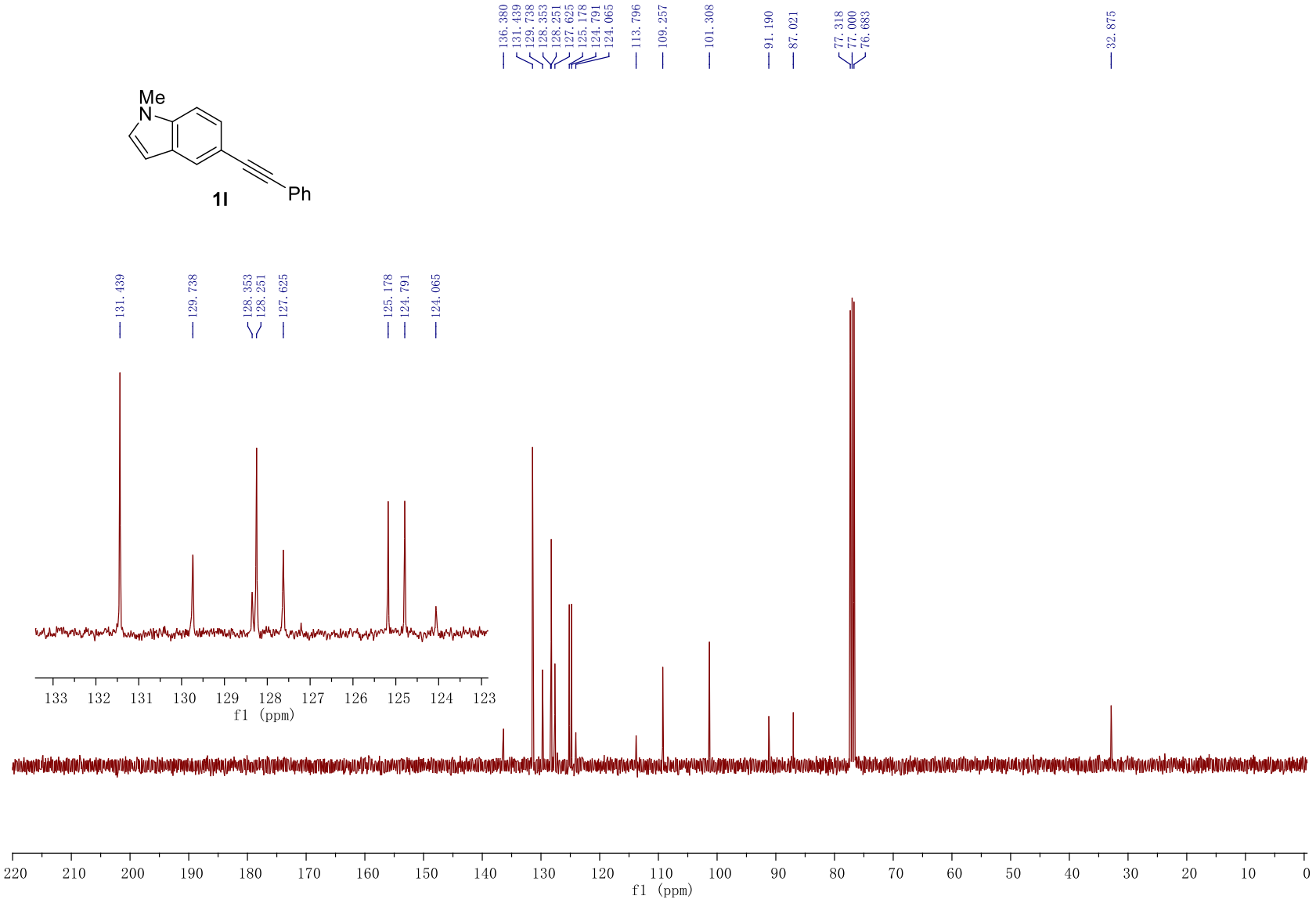
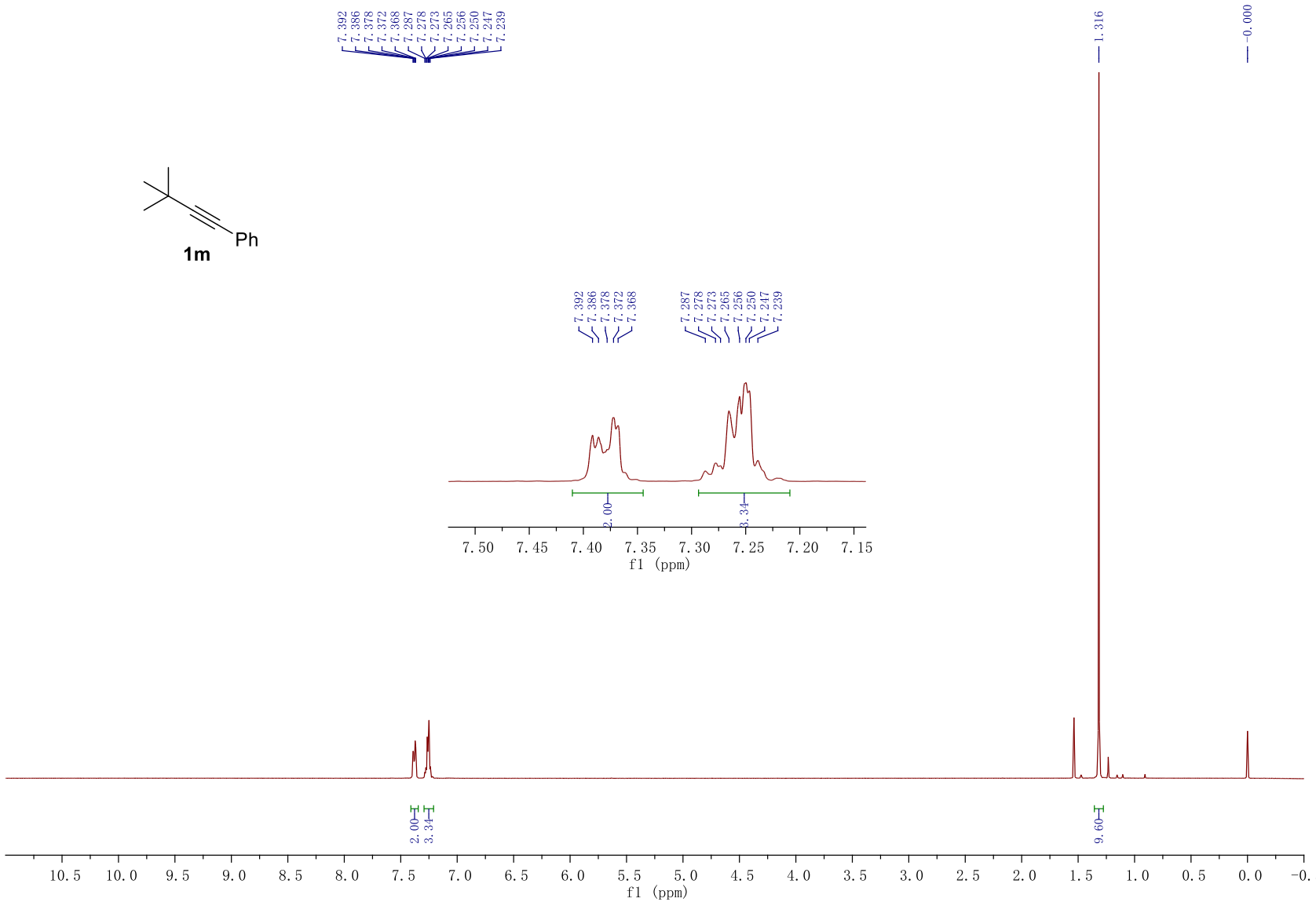


^{1}H NMR Spectrum of (3,3-dimethylbut-1-yn-1-yl)benzene (1m)



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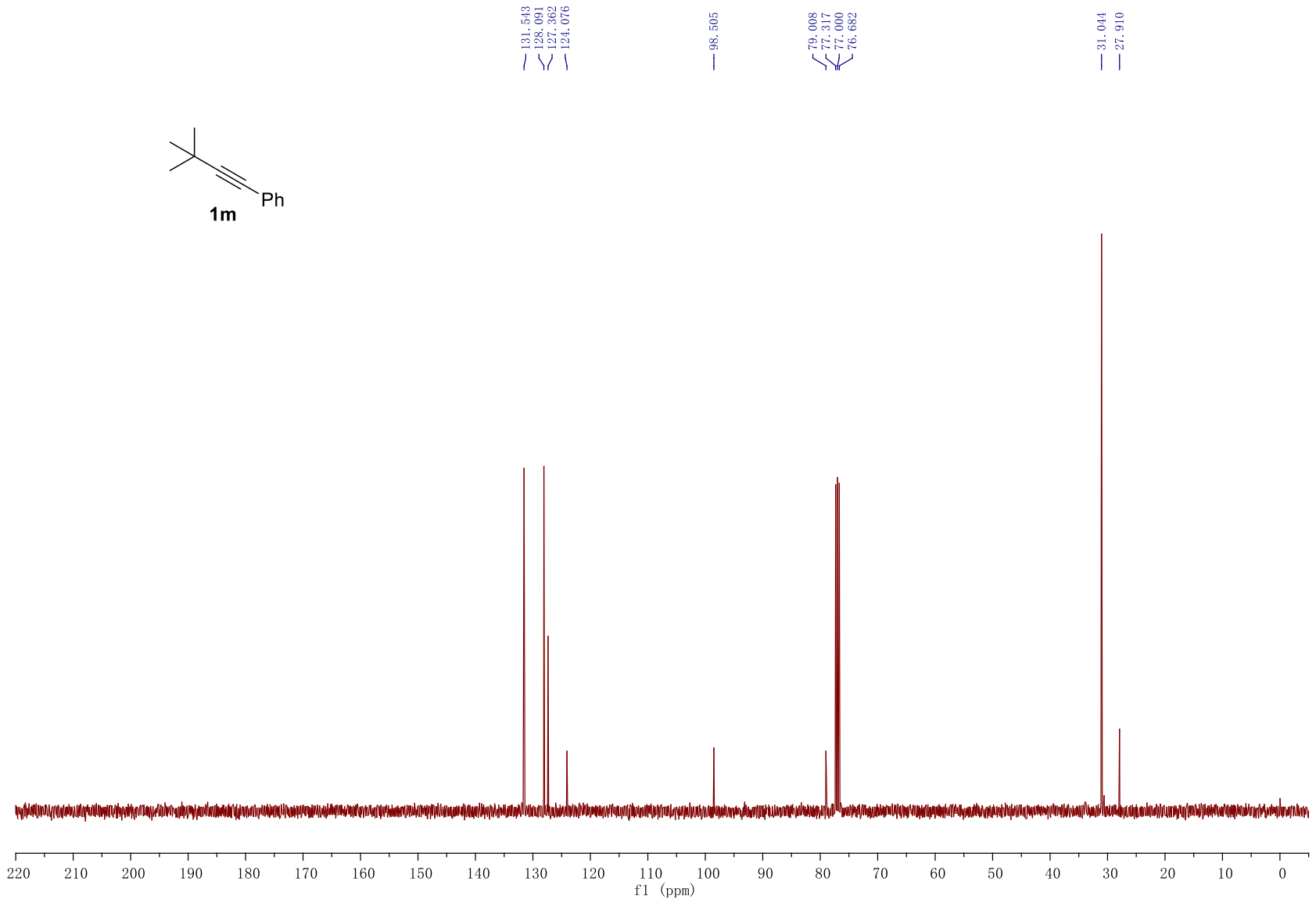
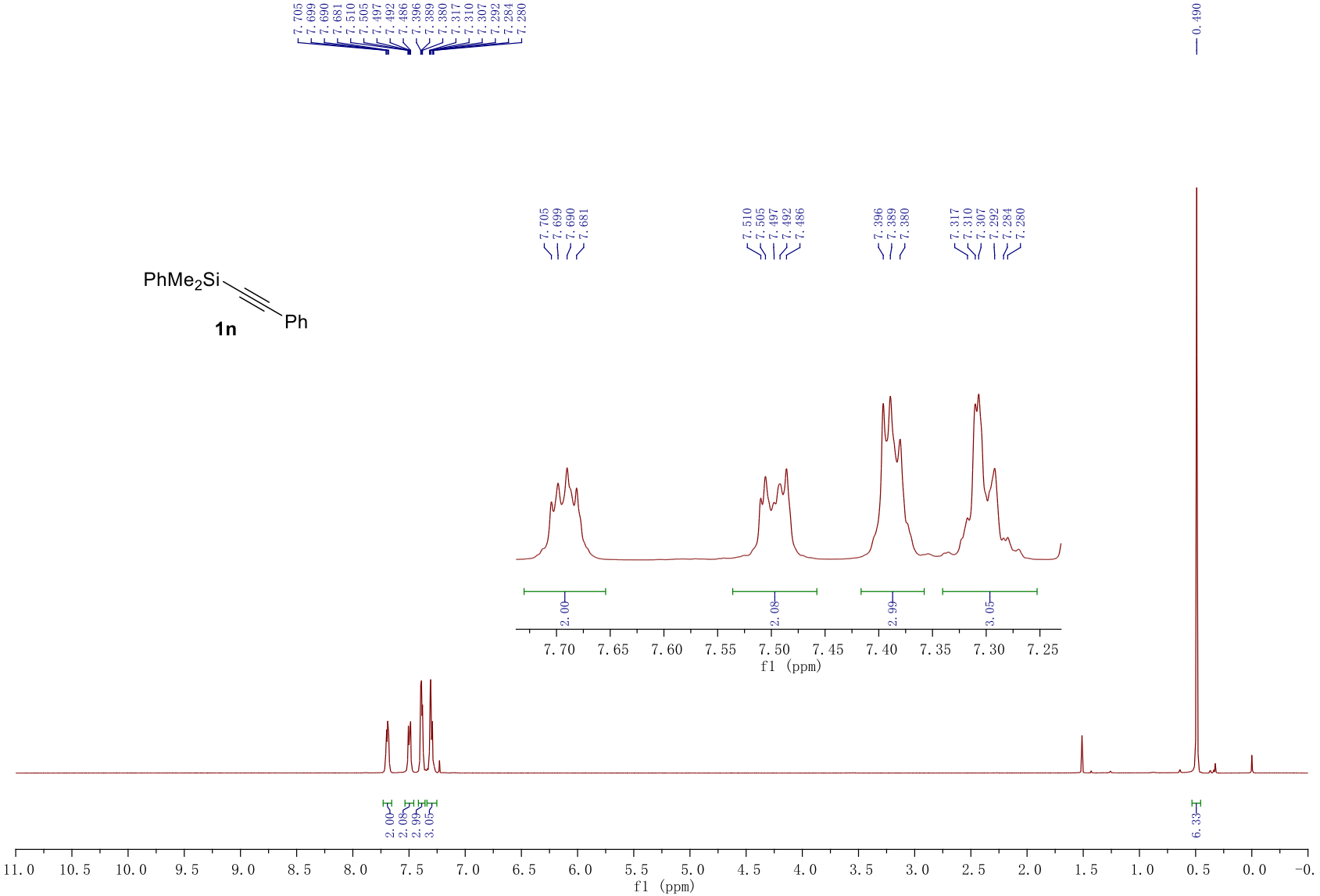
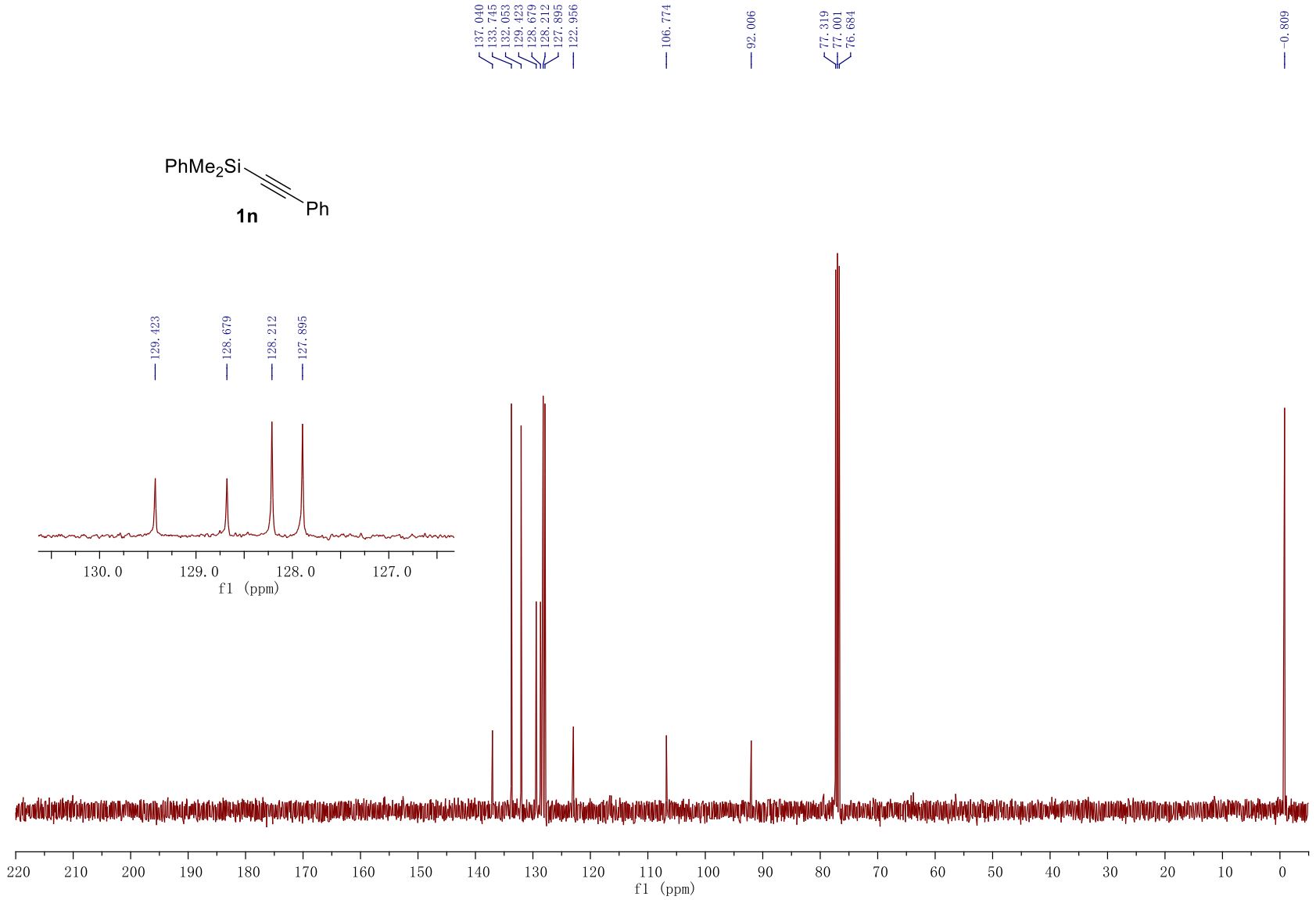


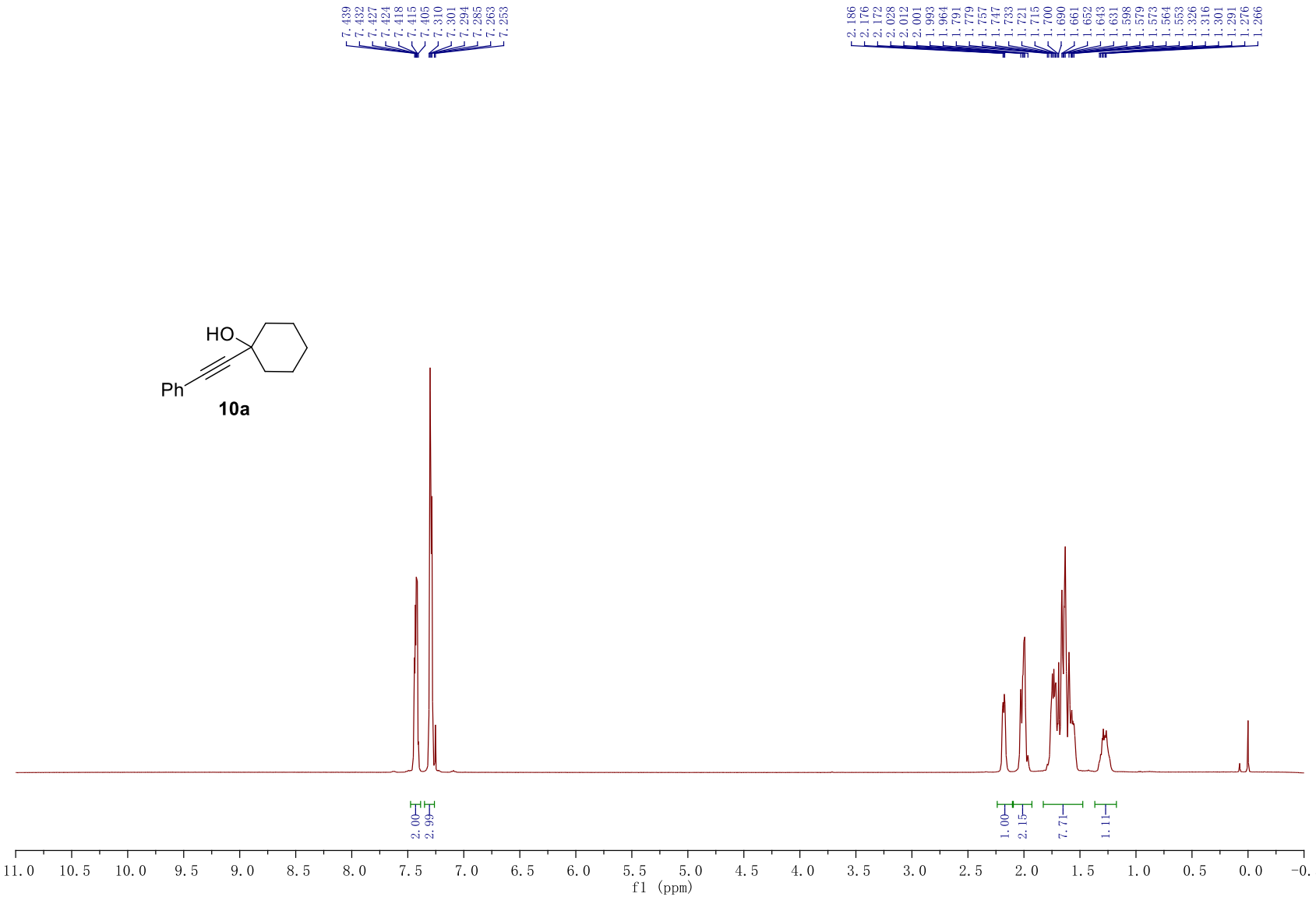
^{1}H NMR Spectrum of dimethyl(phenyl)(phenylethynyl)silane (1n)



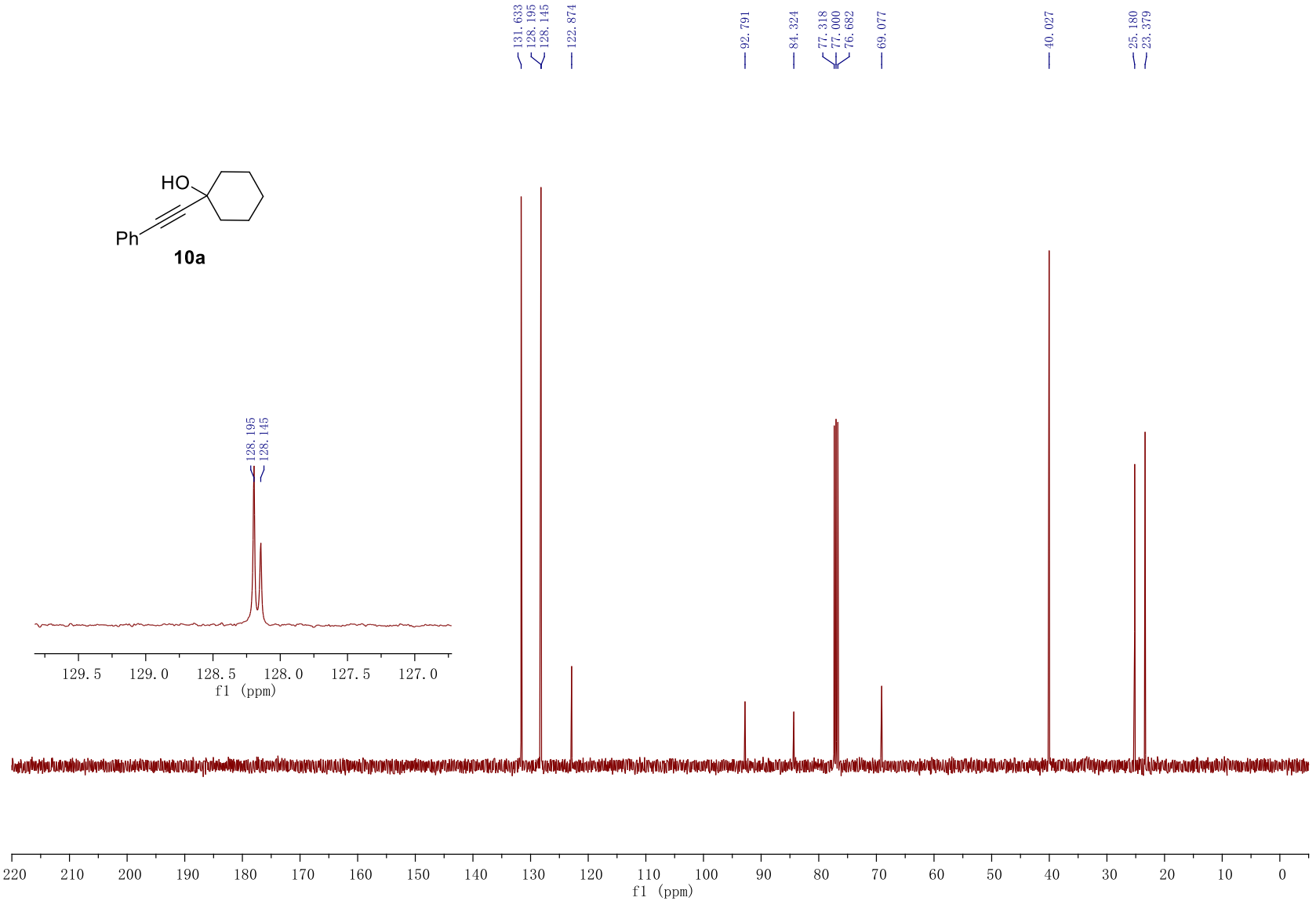
^{13}C NMR Spectrum of dimethyl(phenyl)(phenylethynyl)silane (1n)



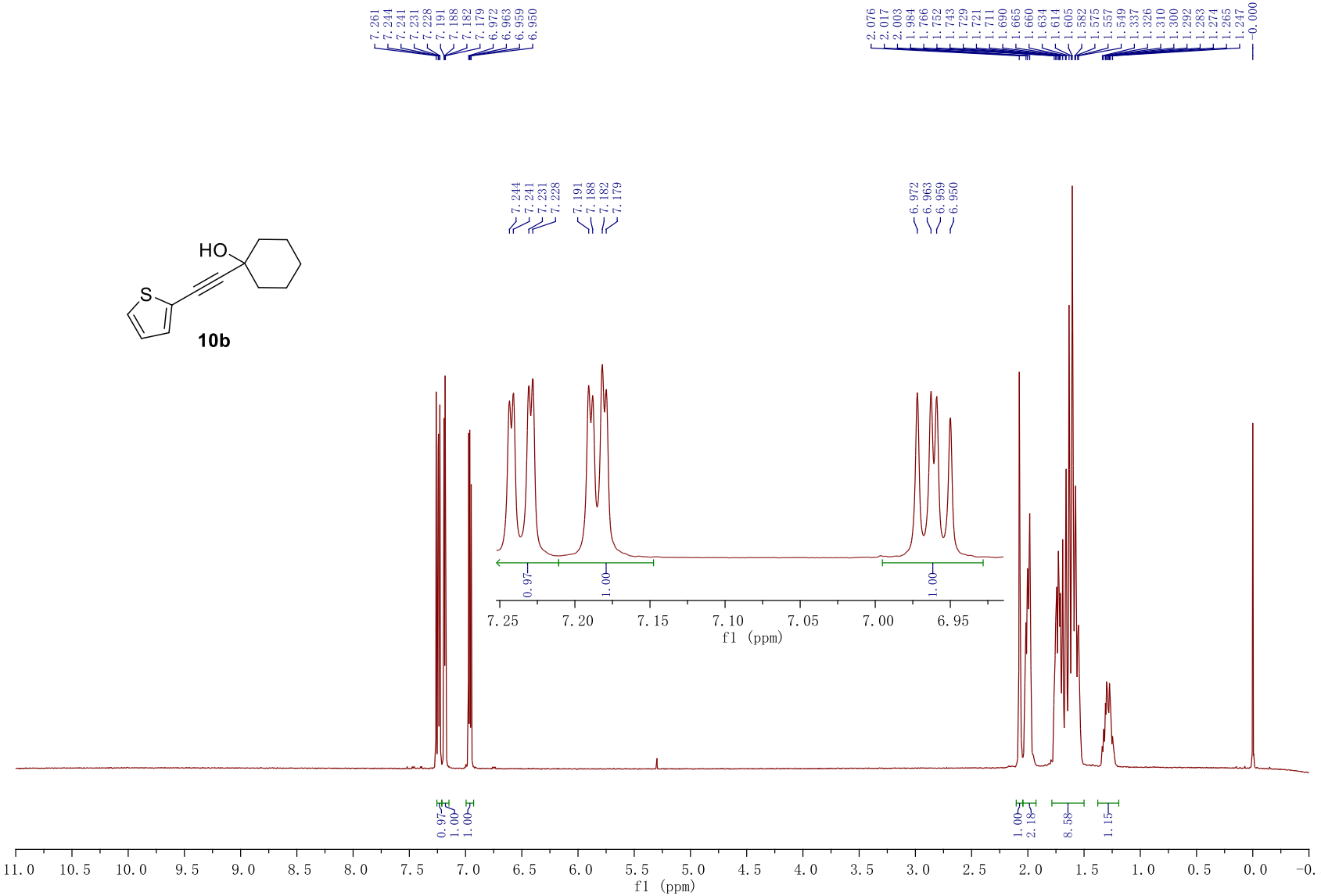
^{1}H NMR Spectrum of 1-(phenylethynyl)cyclohexan-1-ol (10a)



^{13}C NMR Spectrum of 1-(phenylethynyl)cyclohexan-1-ol (10a)



^{1}H NMR Spectrum of 1-(thiophen-2-ylethynyl)cyclohexan-1-ol (10b)



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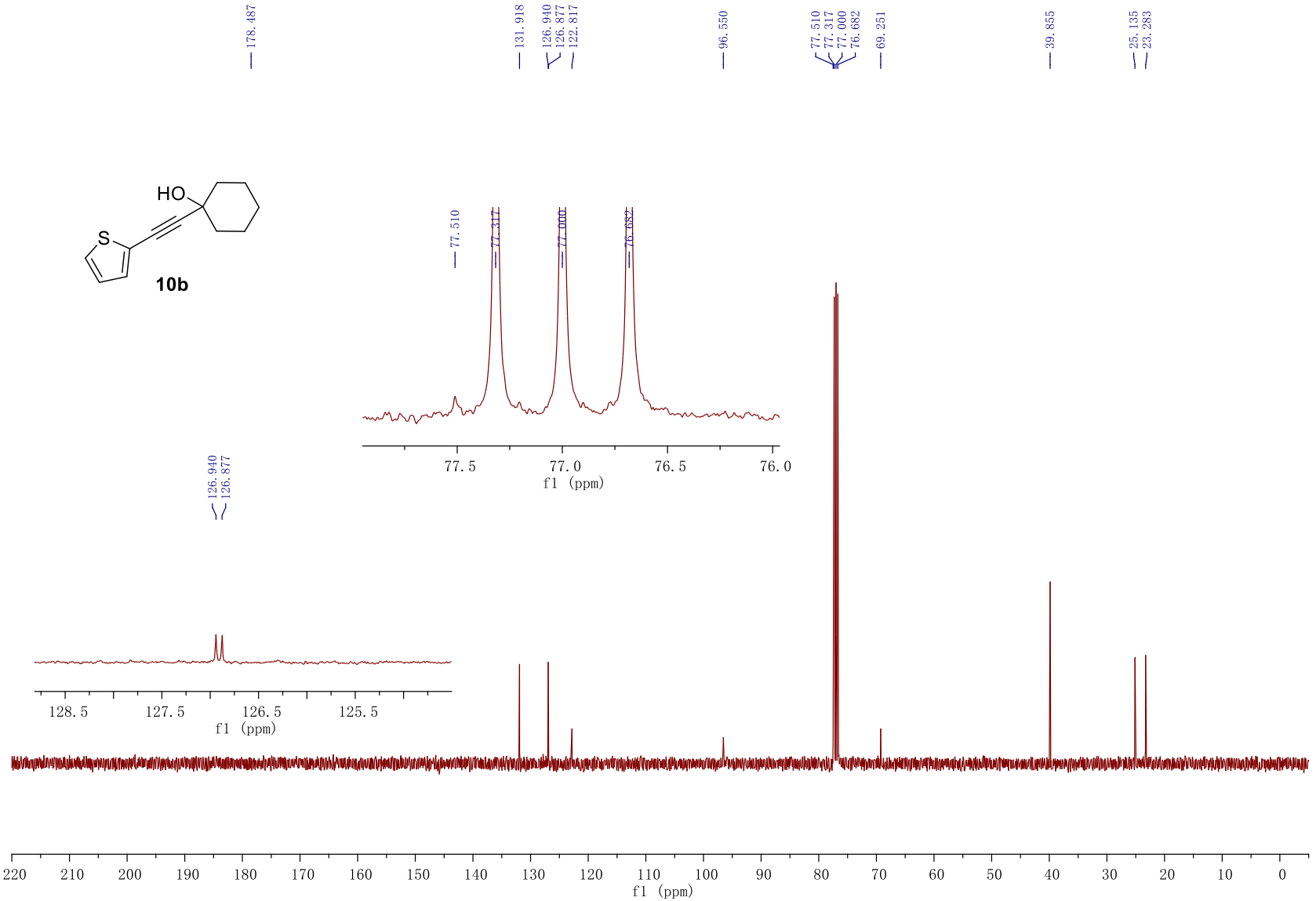

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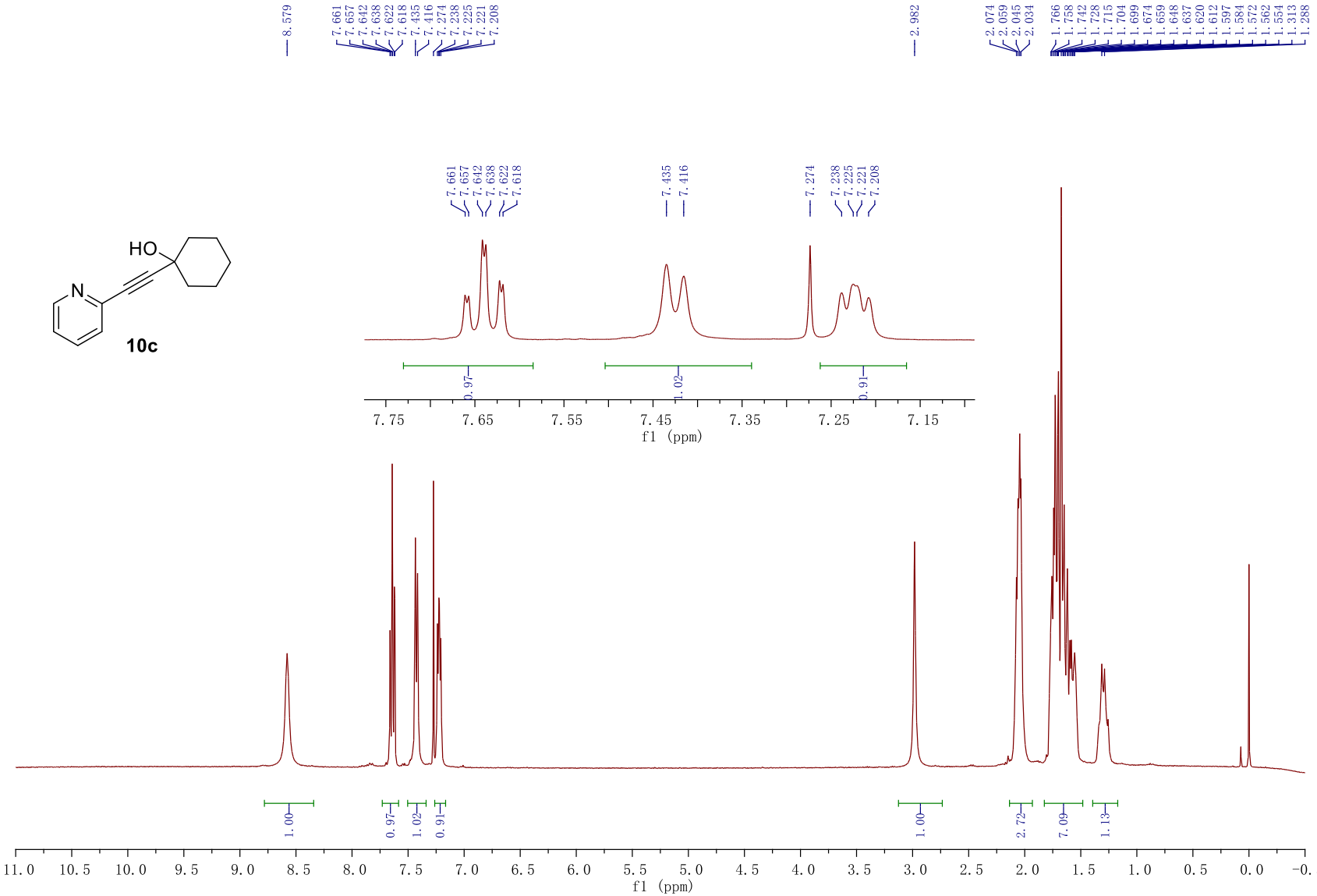

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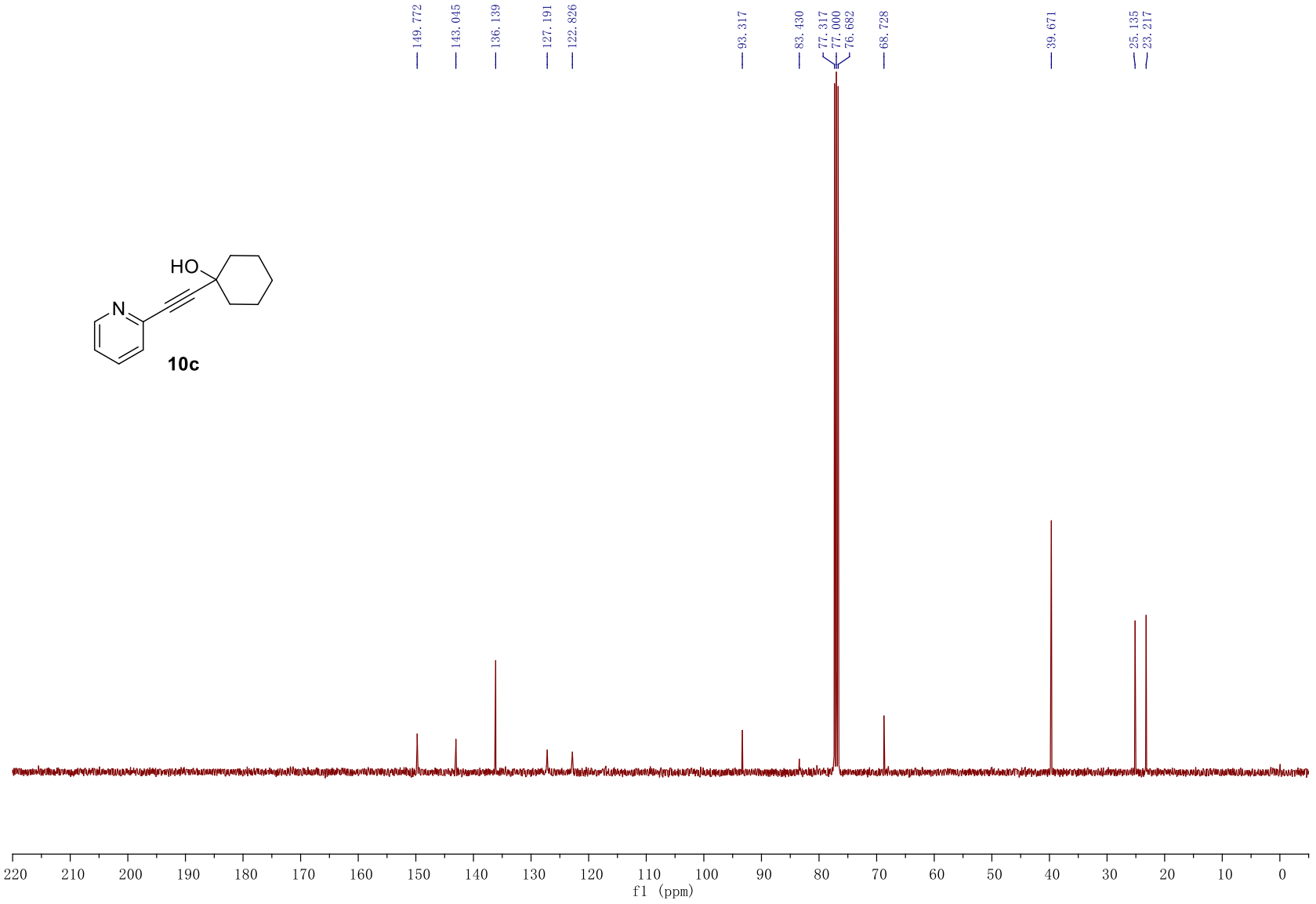
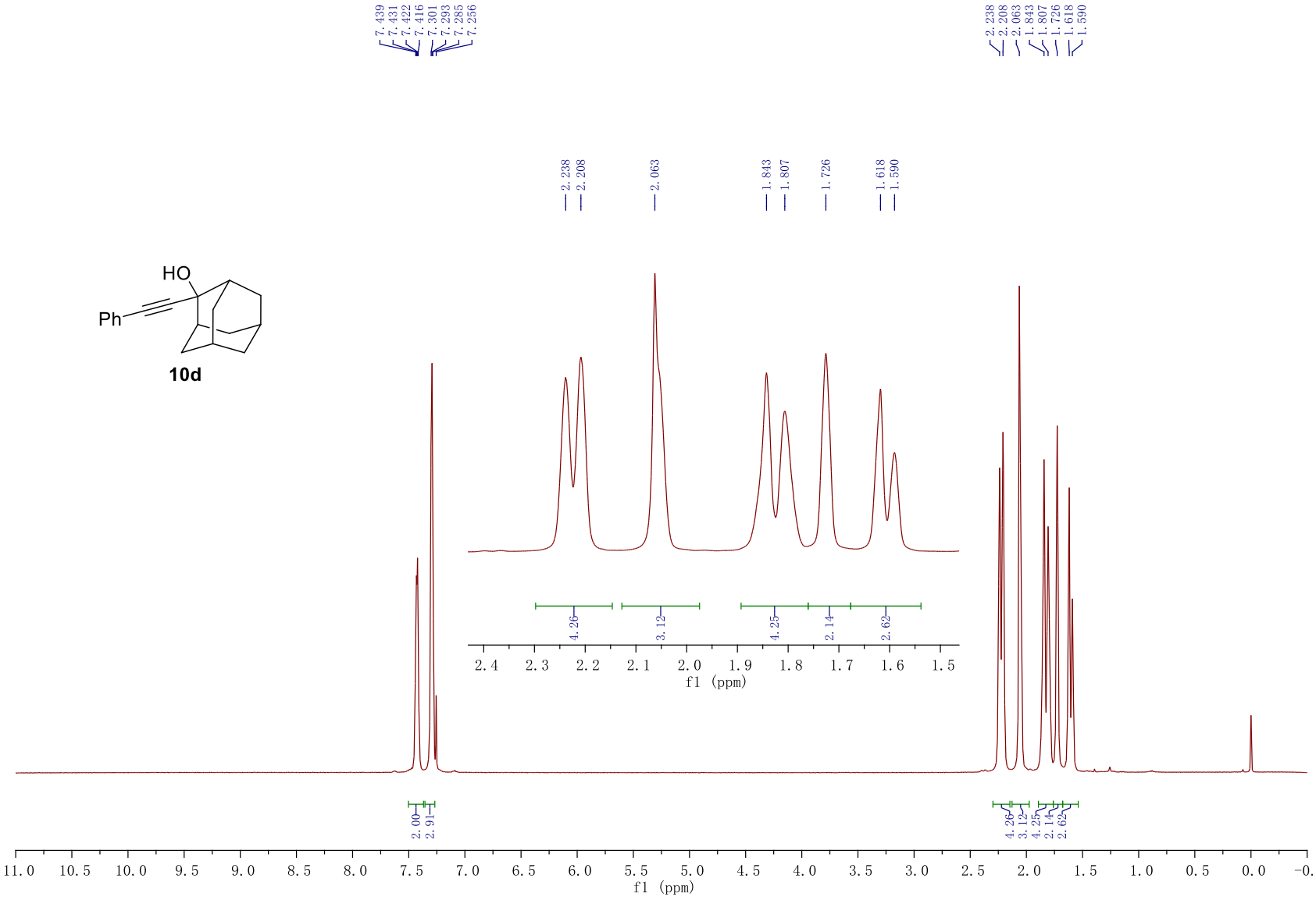
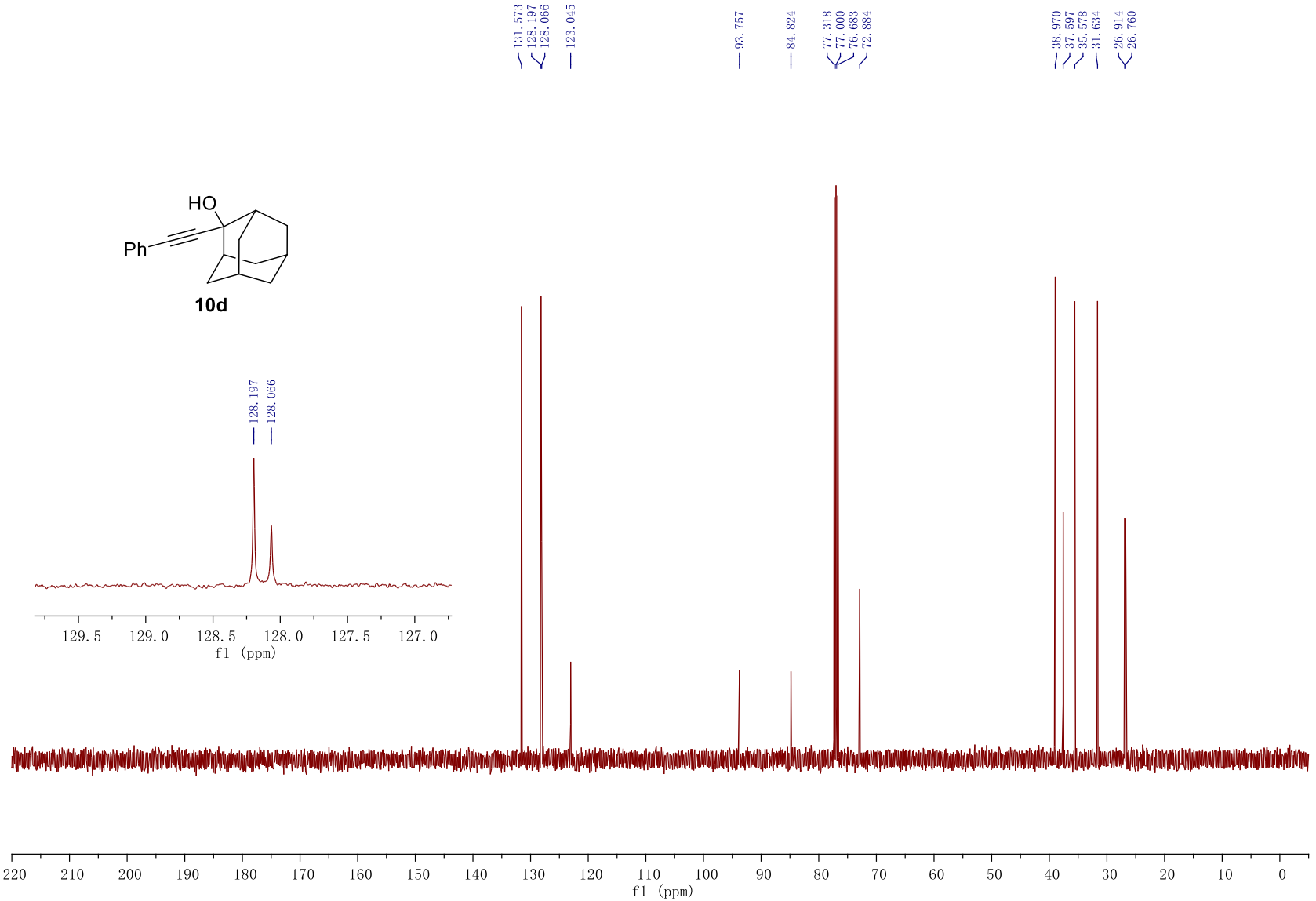


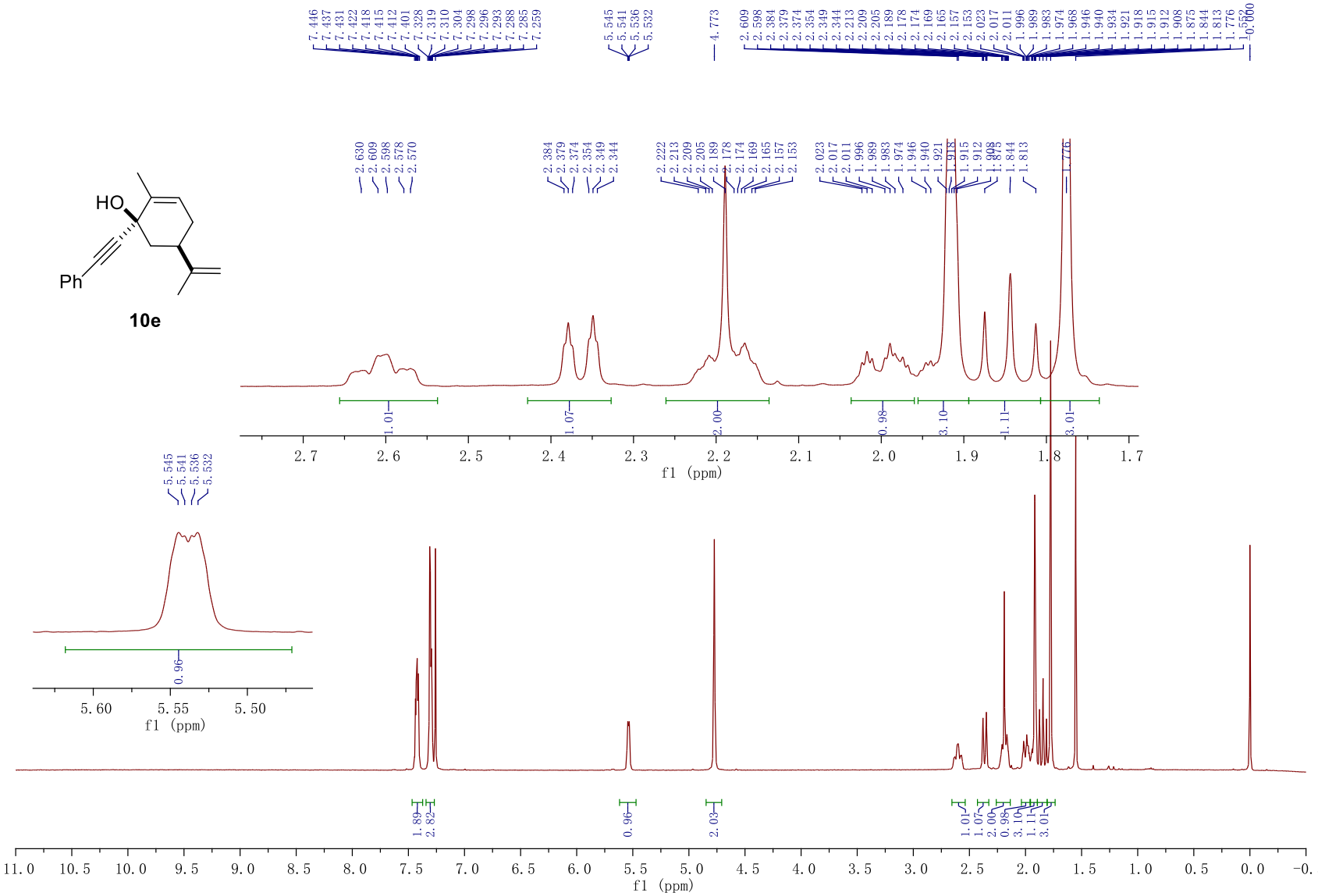
^{1}H NMR Spectrum of (1*R,3*S**,5*r*,7*r*)-2-((*E*)-styryl)adamantan-2-ol (10d)**



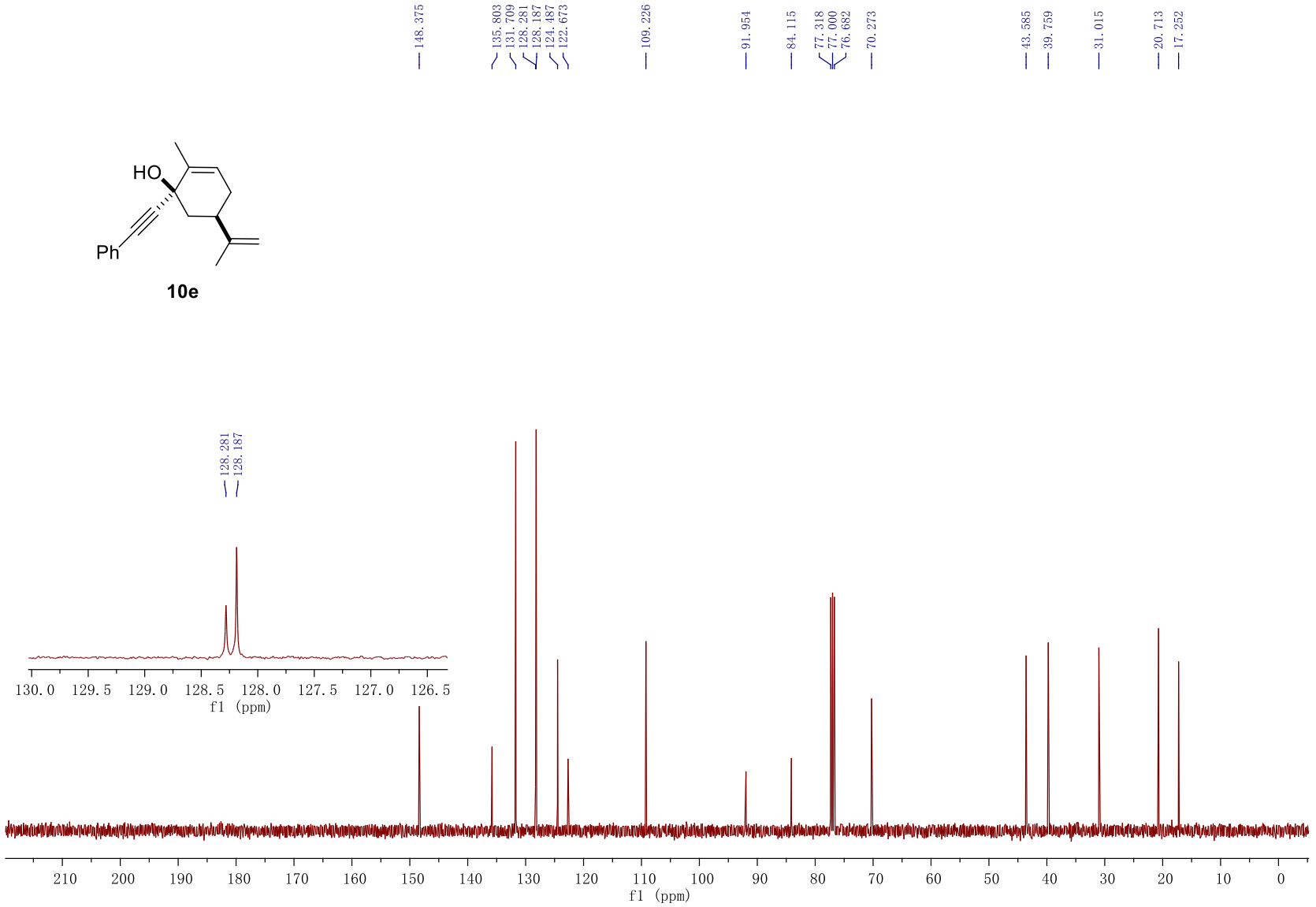
^{13}C NMR Spectrum of (1*R,3*S**,5*r*,7*r*)-2-((*E*)-styryl)adamantan-2-ol (10d)**



^{1}H NMR Spectrum of (1*R*,5*R*)-2-methyl-1-(phenylethynyl)-5-(prop-1-en-2-yl)cyclohex-2-en-1-ol (10e)



^{13}C NMR Spectrum of (1*R*,5*R*)-2-methyl-1-(phenylethynyl)-5-(prop-1-en-2-yl)cyclohex-2-en-1-ol (10e)



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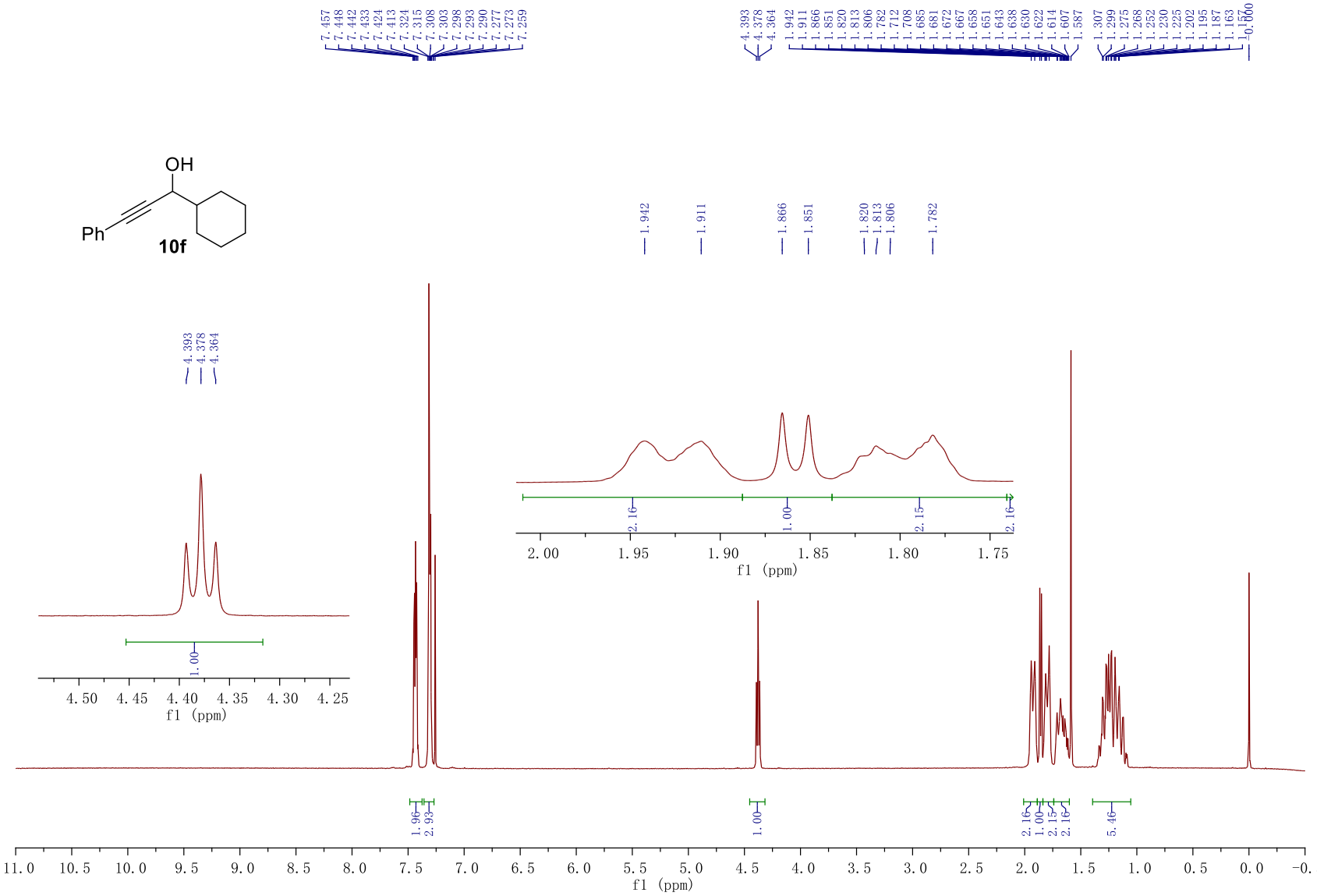
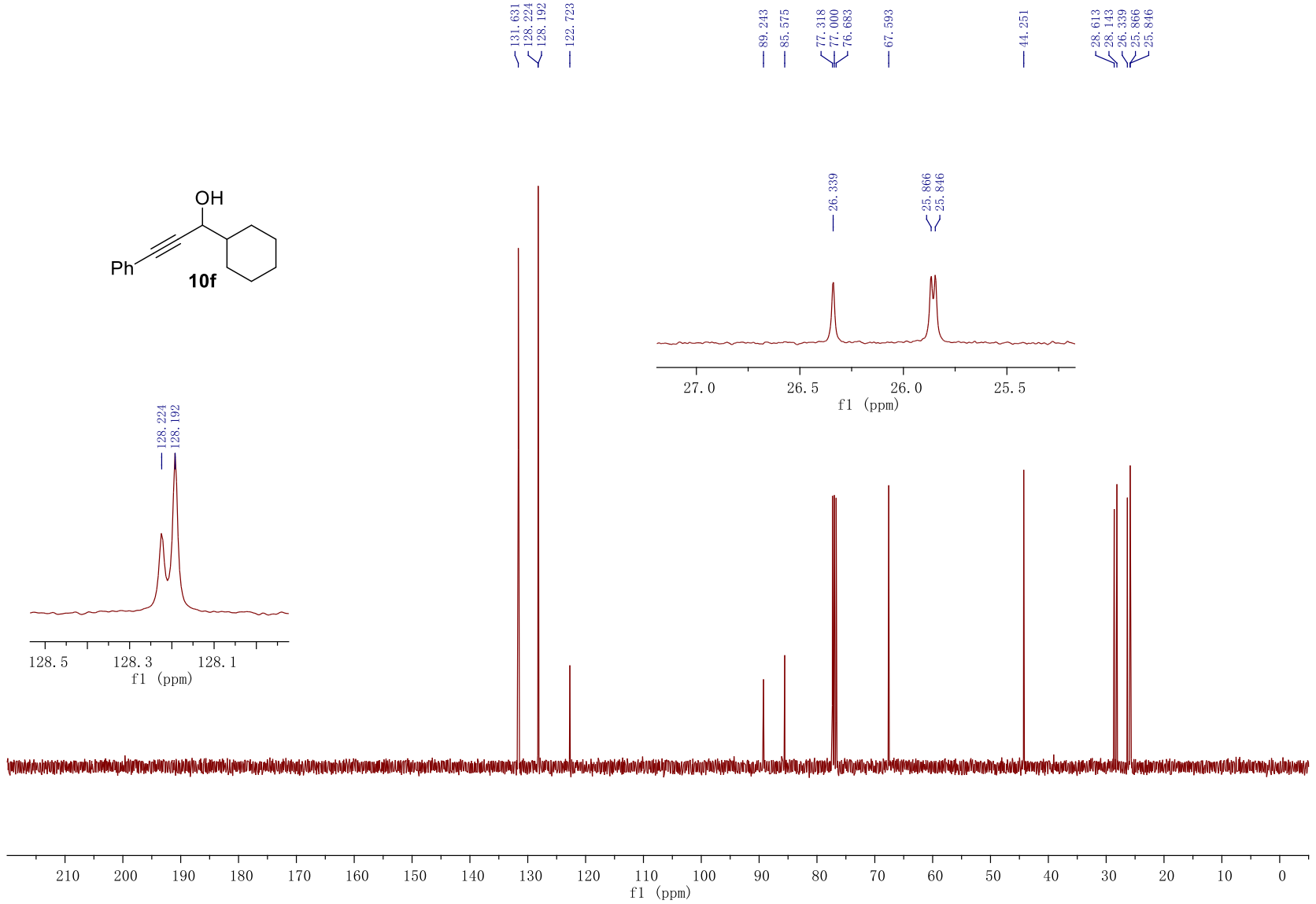
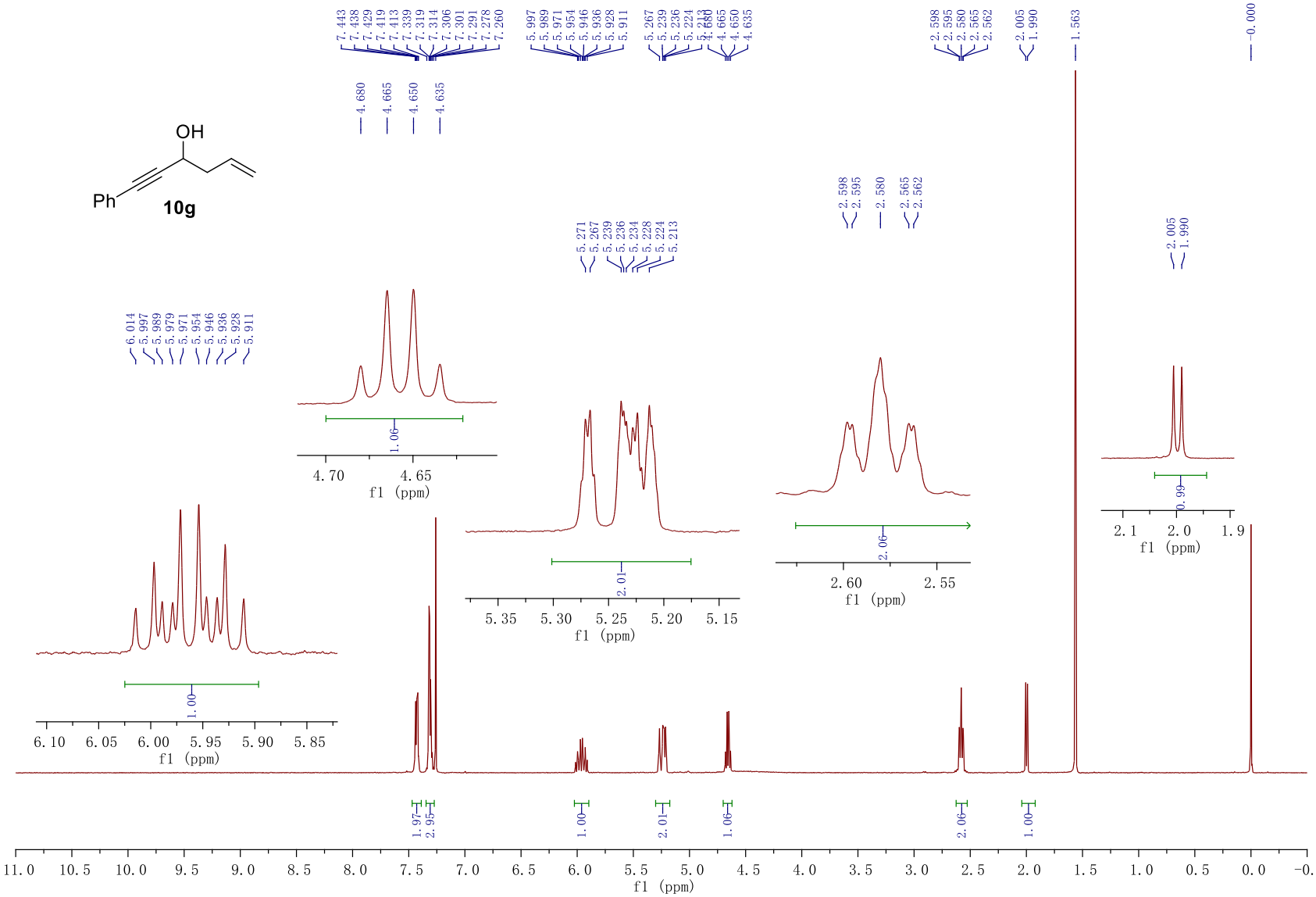


^{13}C NMR Spectrum of 1-cyclohexyl-3-phenylprop-2-yn-1-ol (10f)



^{1}H NMR Spectrum of 1-phenylhex-5-en-1-yn-3-ol (10g)



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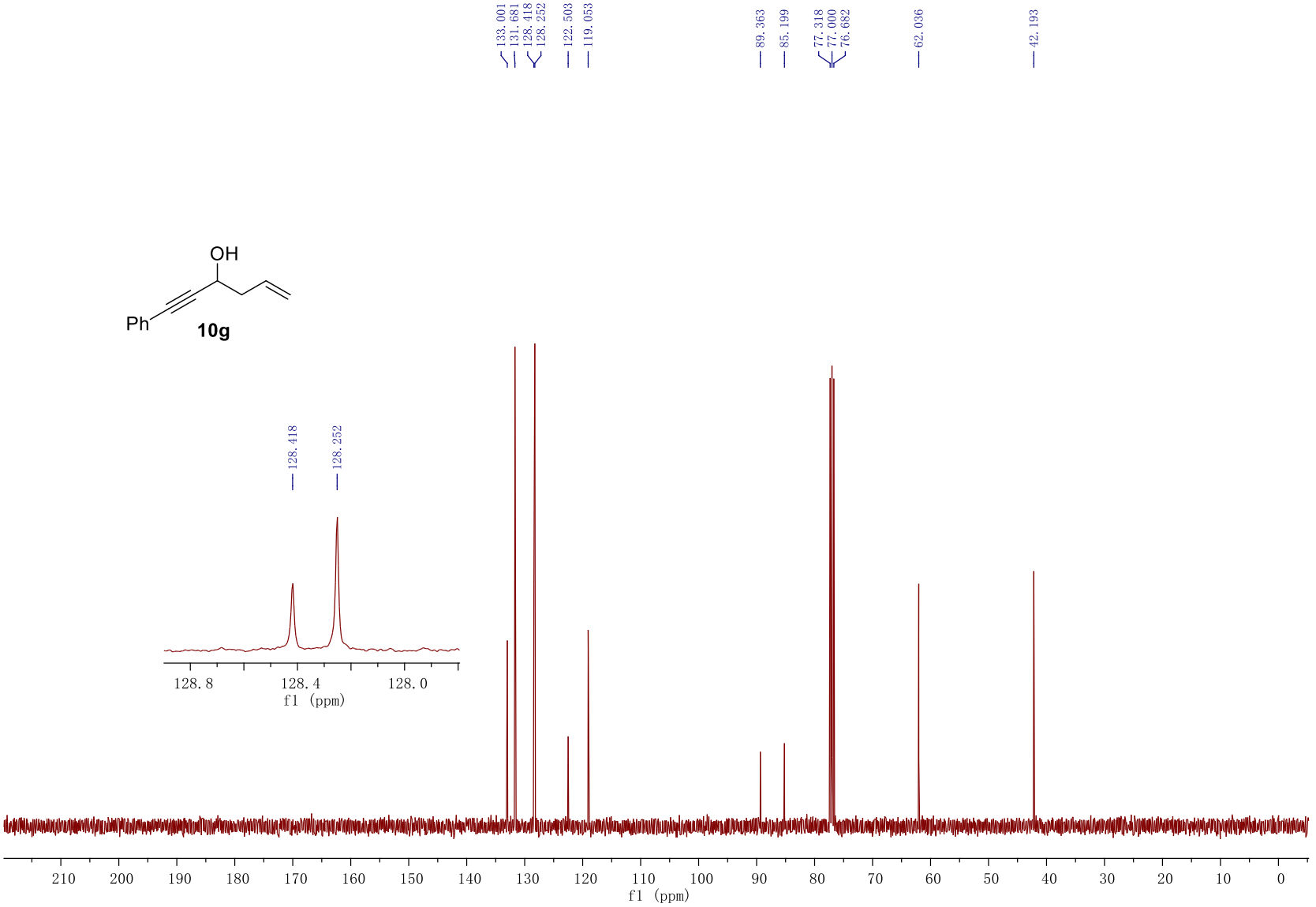
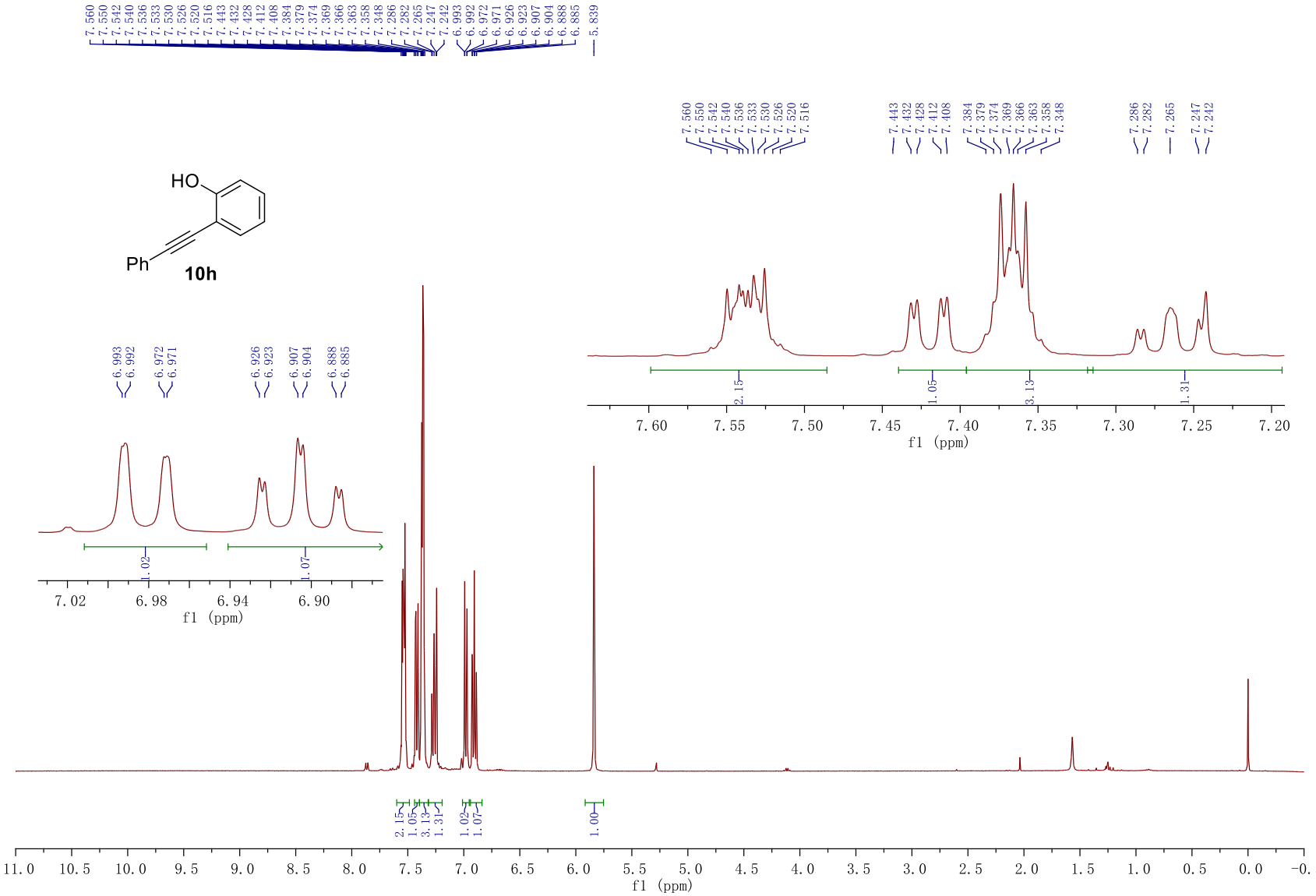
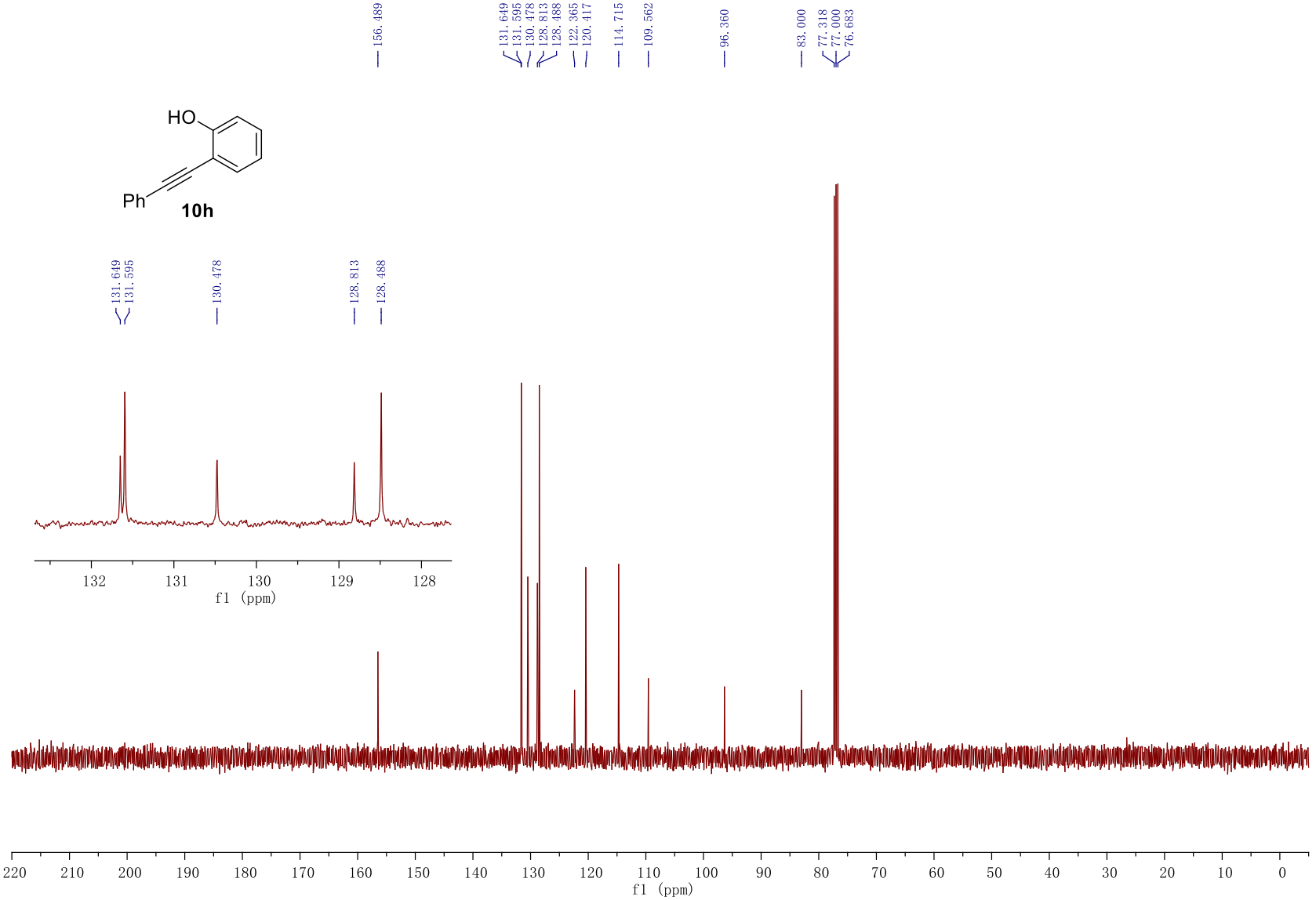


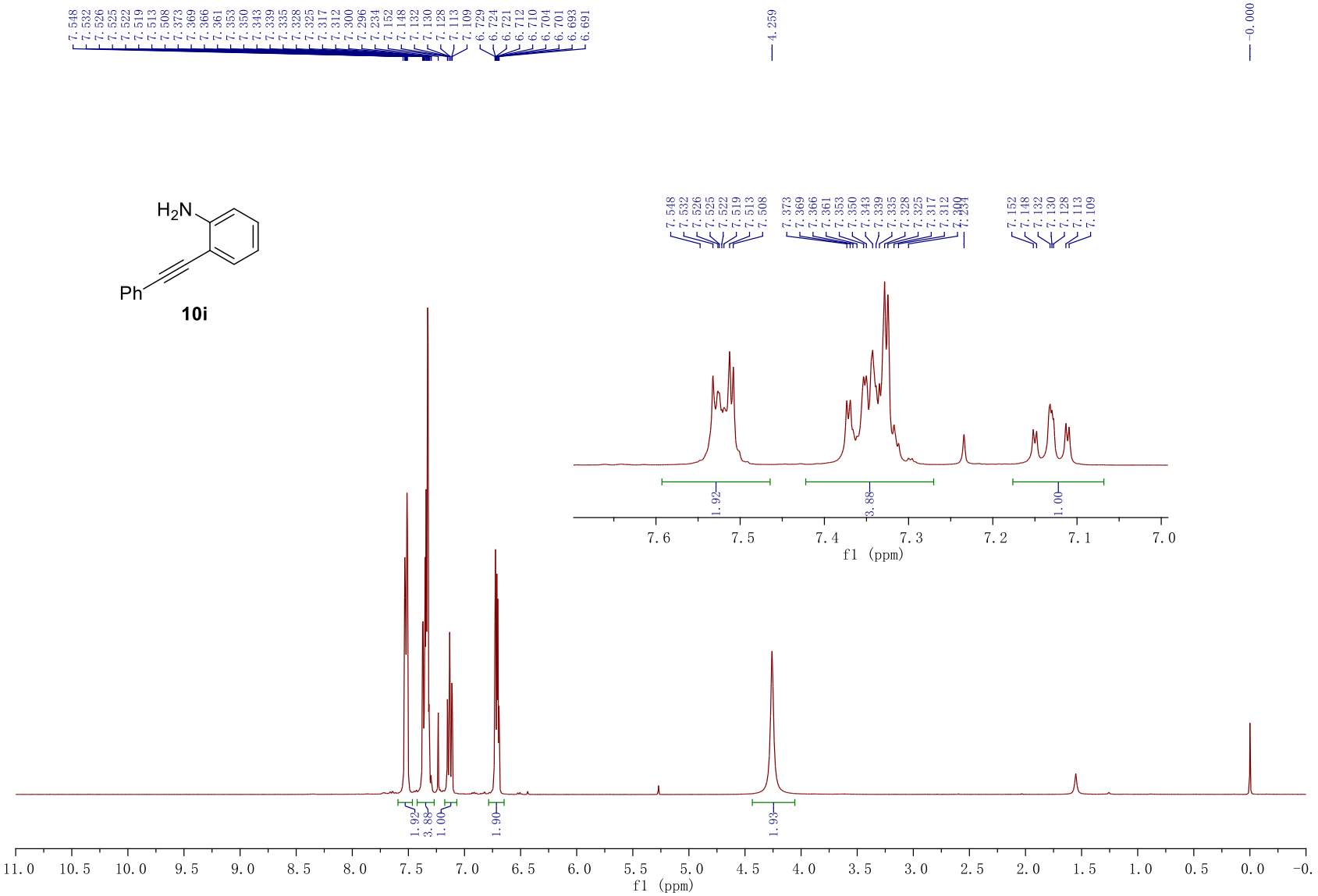
^{1}H NMR Spectrum of 2-(phenylethynyl)phenol (10h)



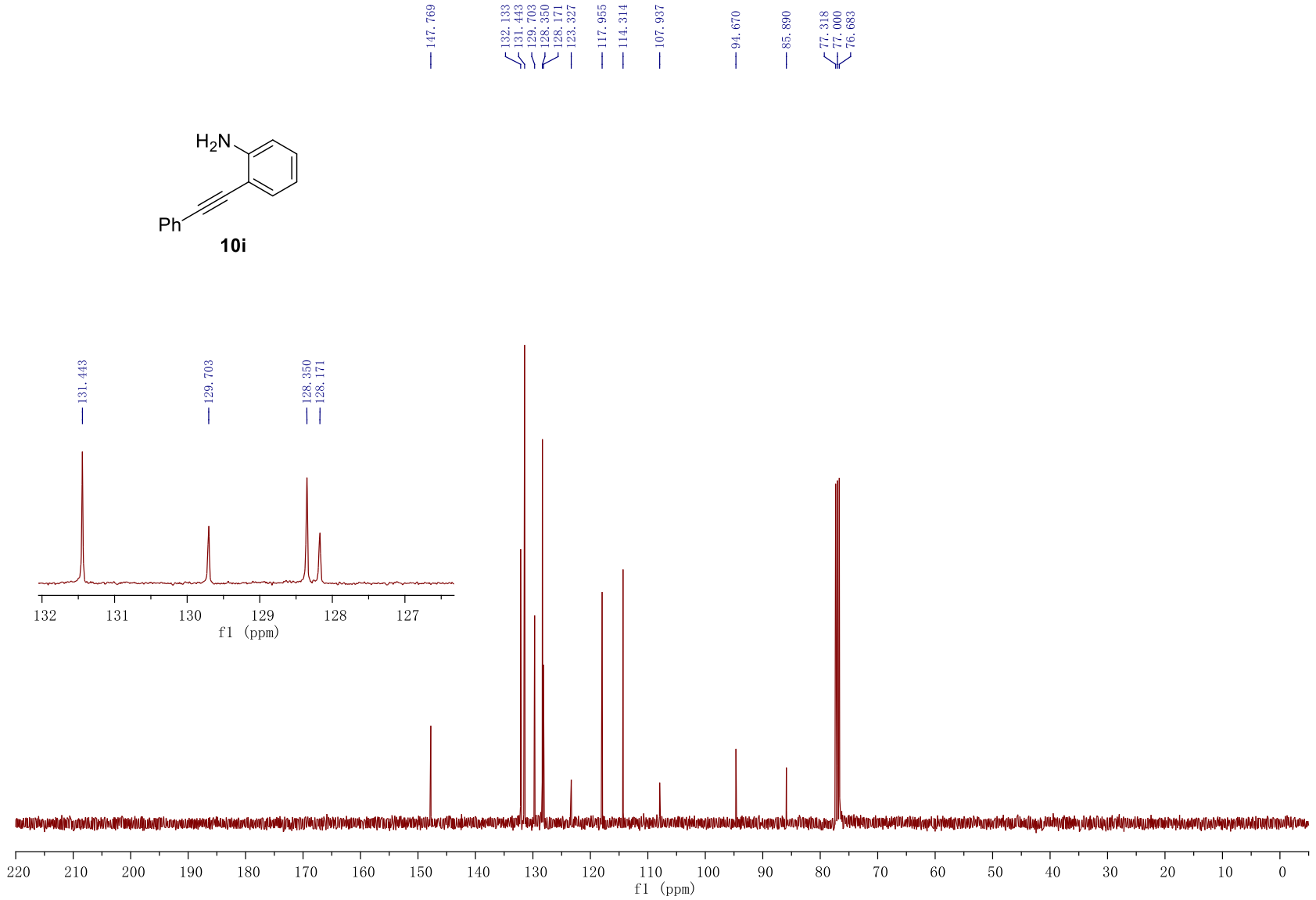
^{13}C NMR Spectrum of 2-(phenylethynyl)phenol (10h)



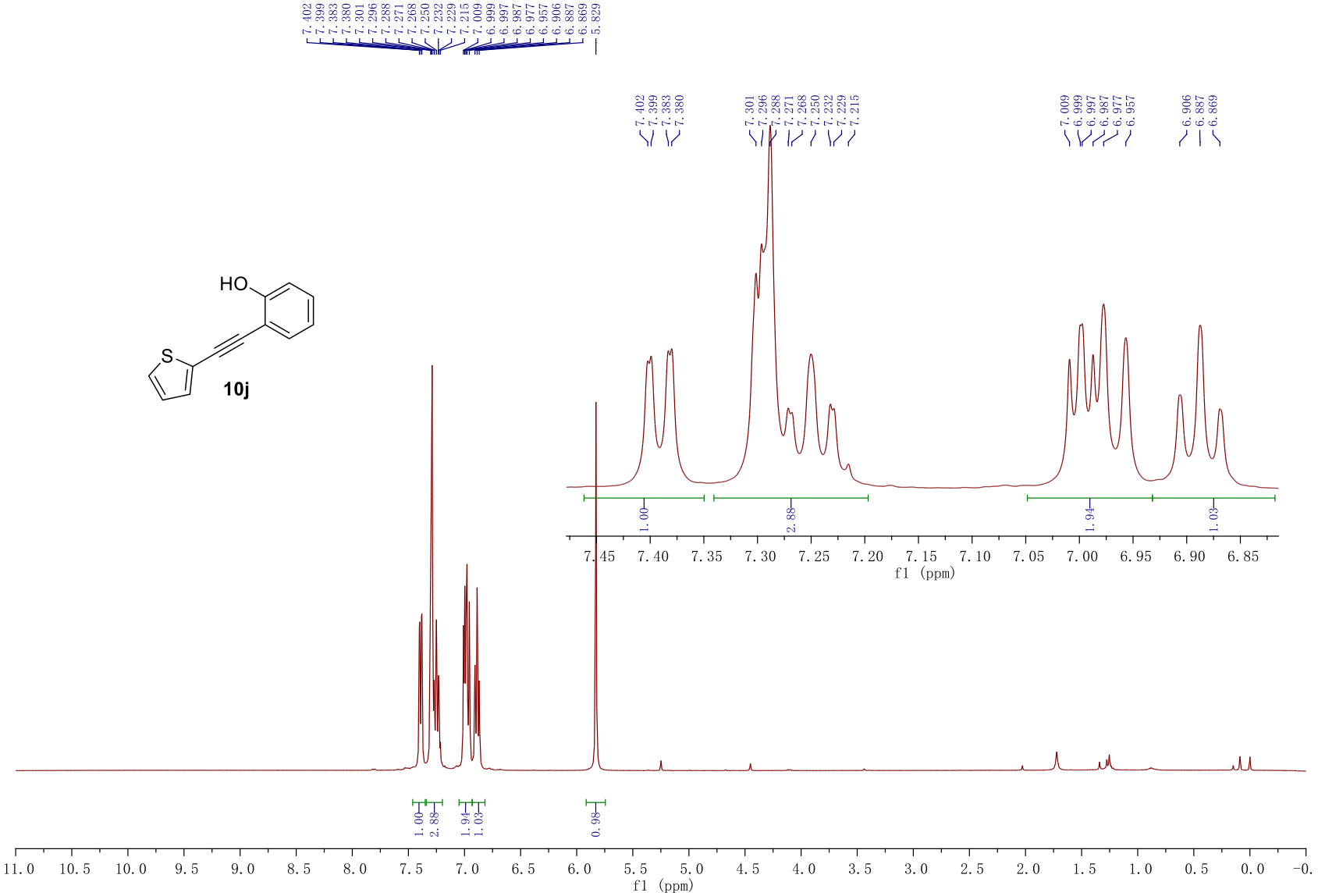
^{1}H NMR Spectrum of 2-(phenylethynyl)aniline (10i)



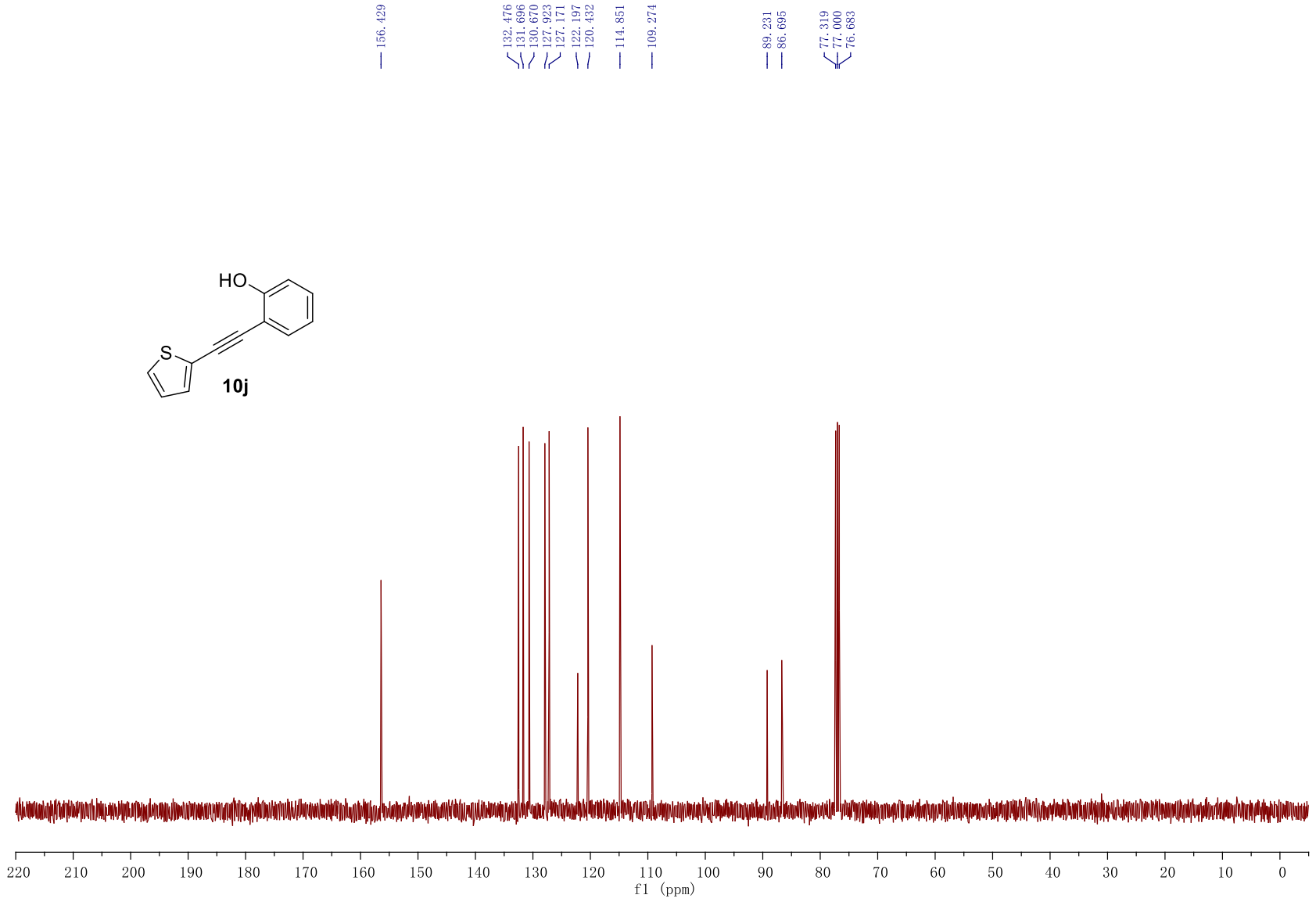
^{13}C NMR Spectrum of 2-(phenylethynyl)aniline (10i)



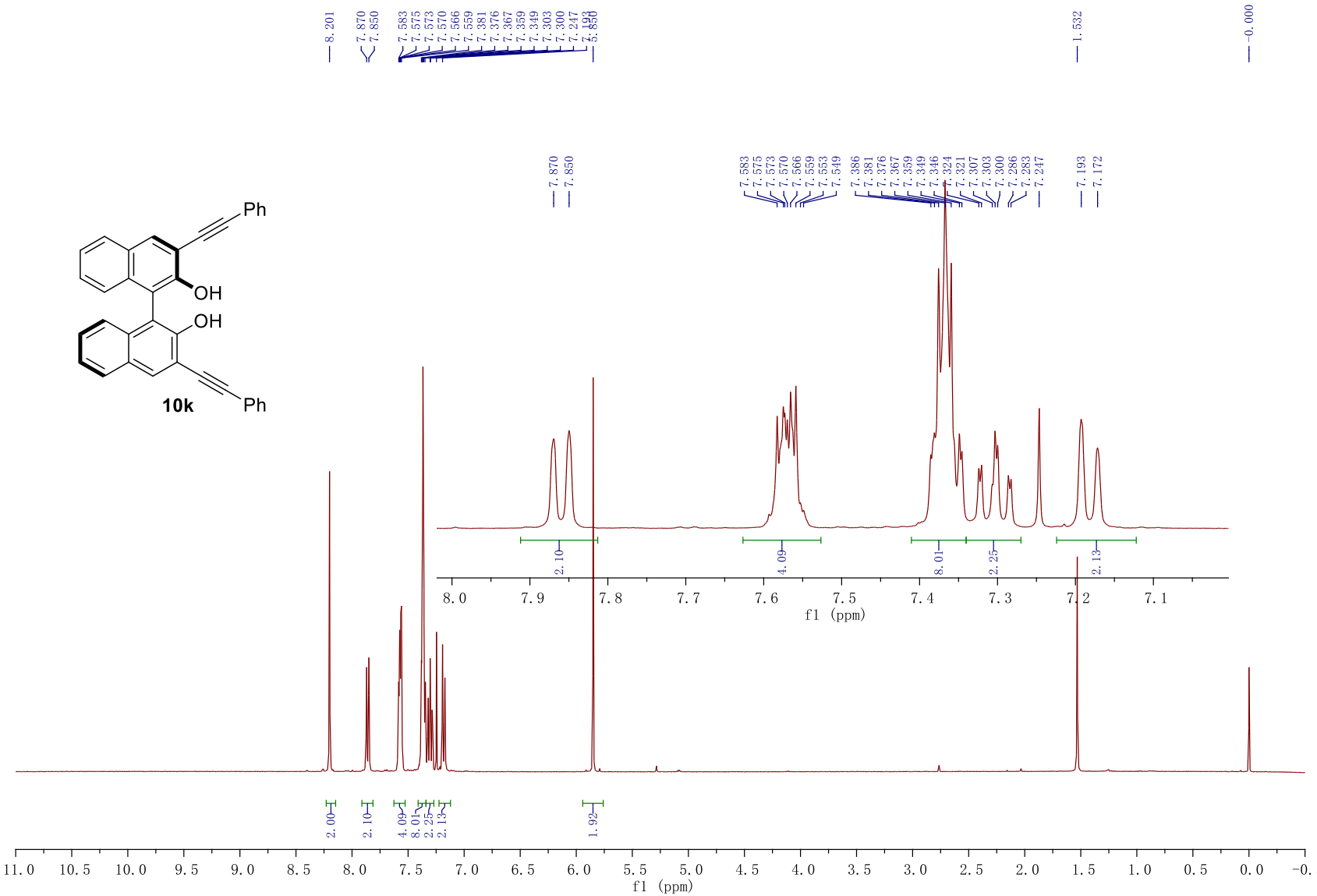
^{1}H NMR Spectrum of 2-(thiophen-2-ylethynyl)phenol (10j)



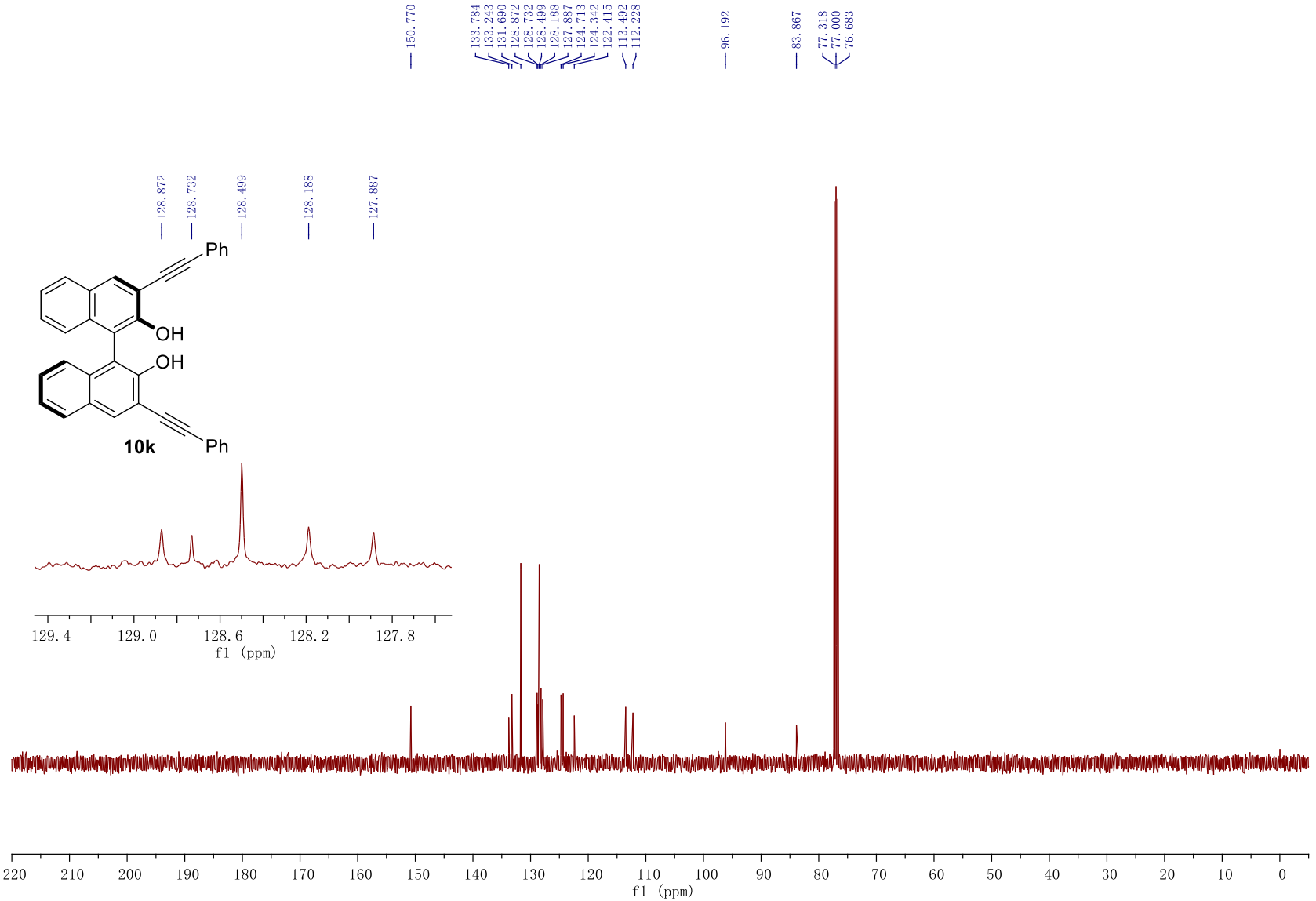
^{13}C NMR Spectrum of 2-(thiophen-2-ylethynyl)phenol (10j)



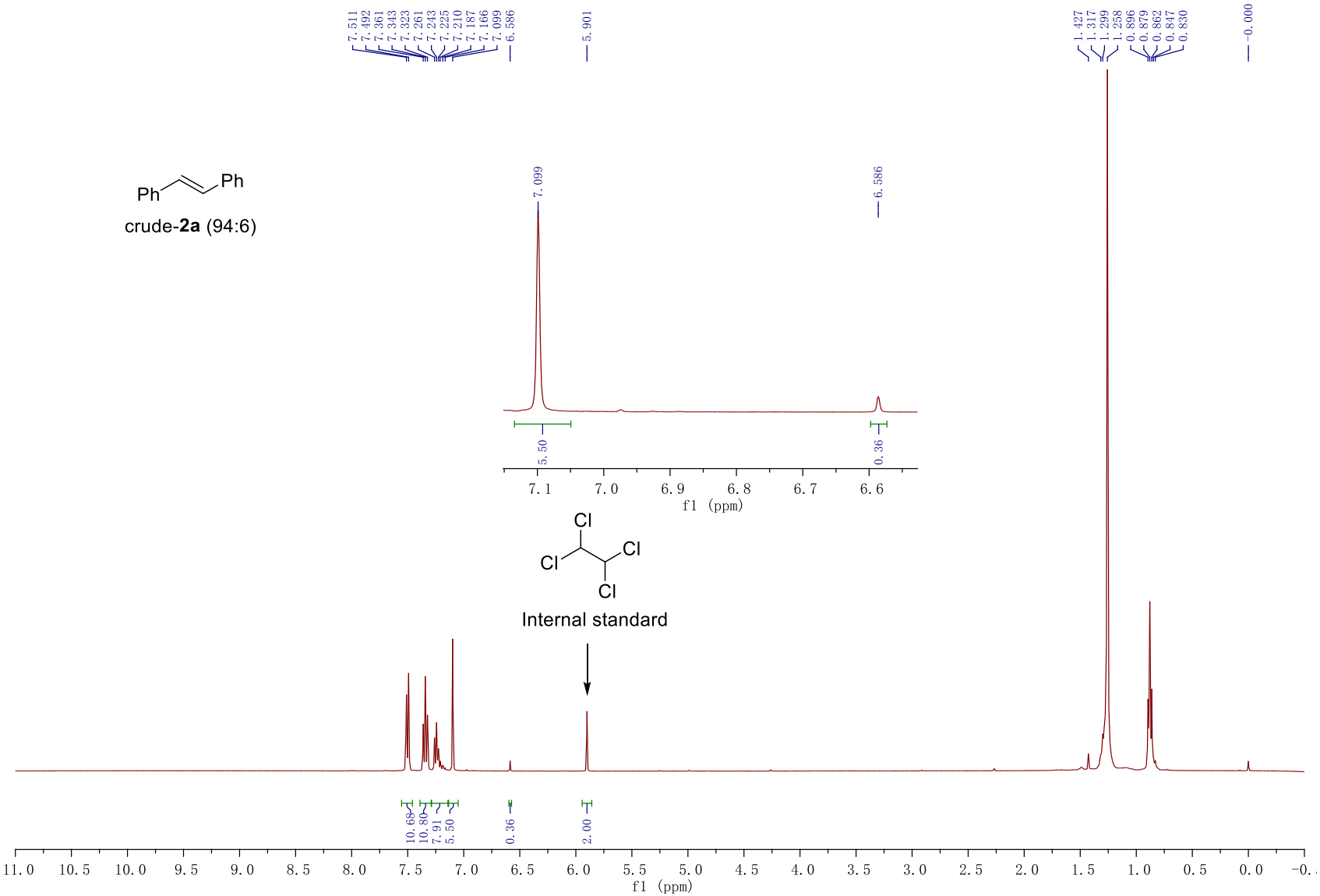
^{1}H NMR Spectrum of (*R*)-3,3'-bis(phenylethynyl)-[1,1'-binaphthalene]-2,2'-diol (10k)



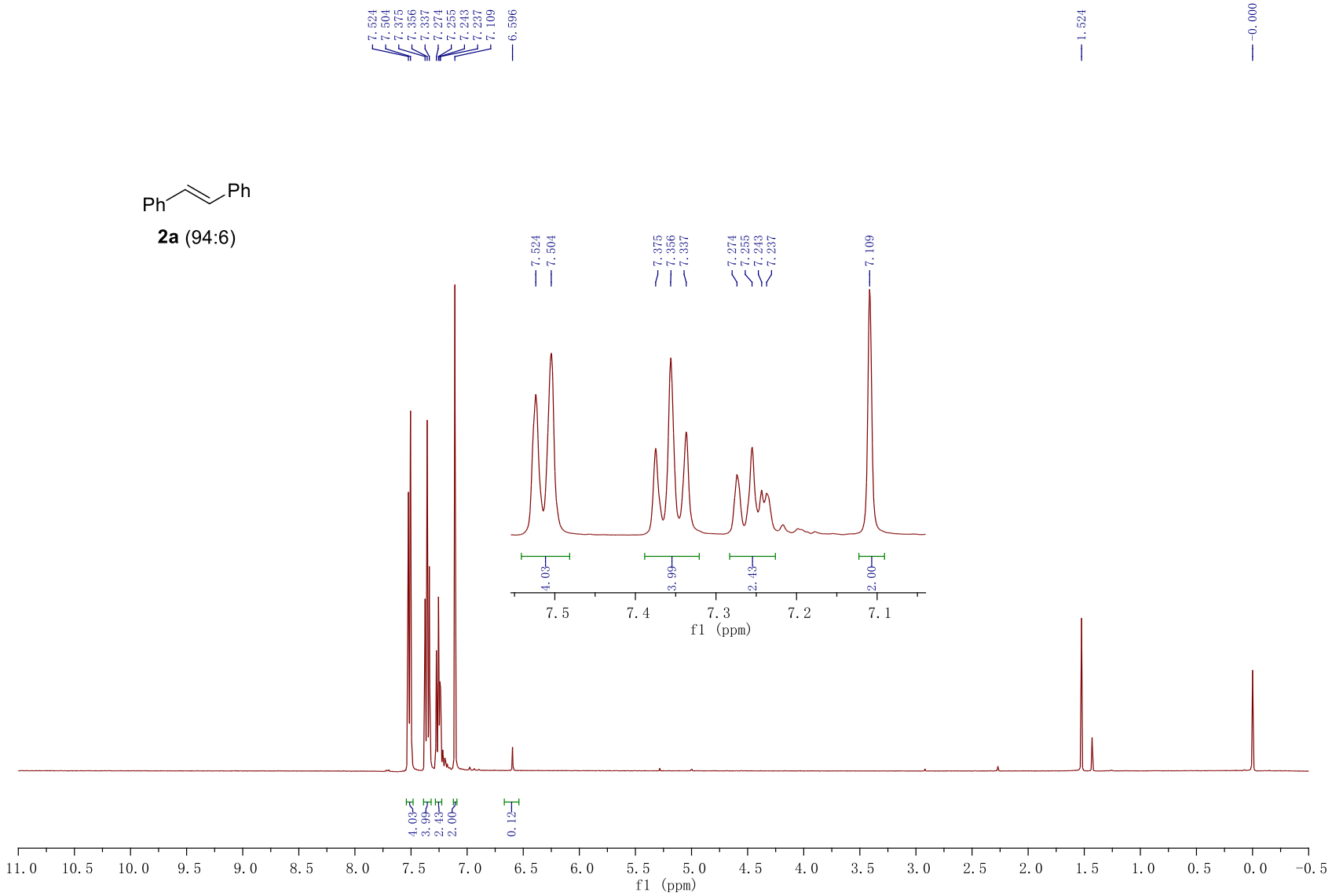
^{13}C NMR Spectrum of (*R*)-3,3'-bis(phenylethynyl)-[1,1'-binaphthalene]-2,2'-diol (10k)



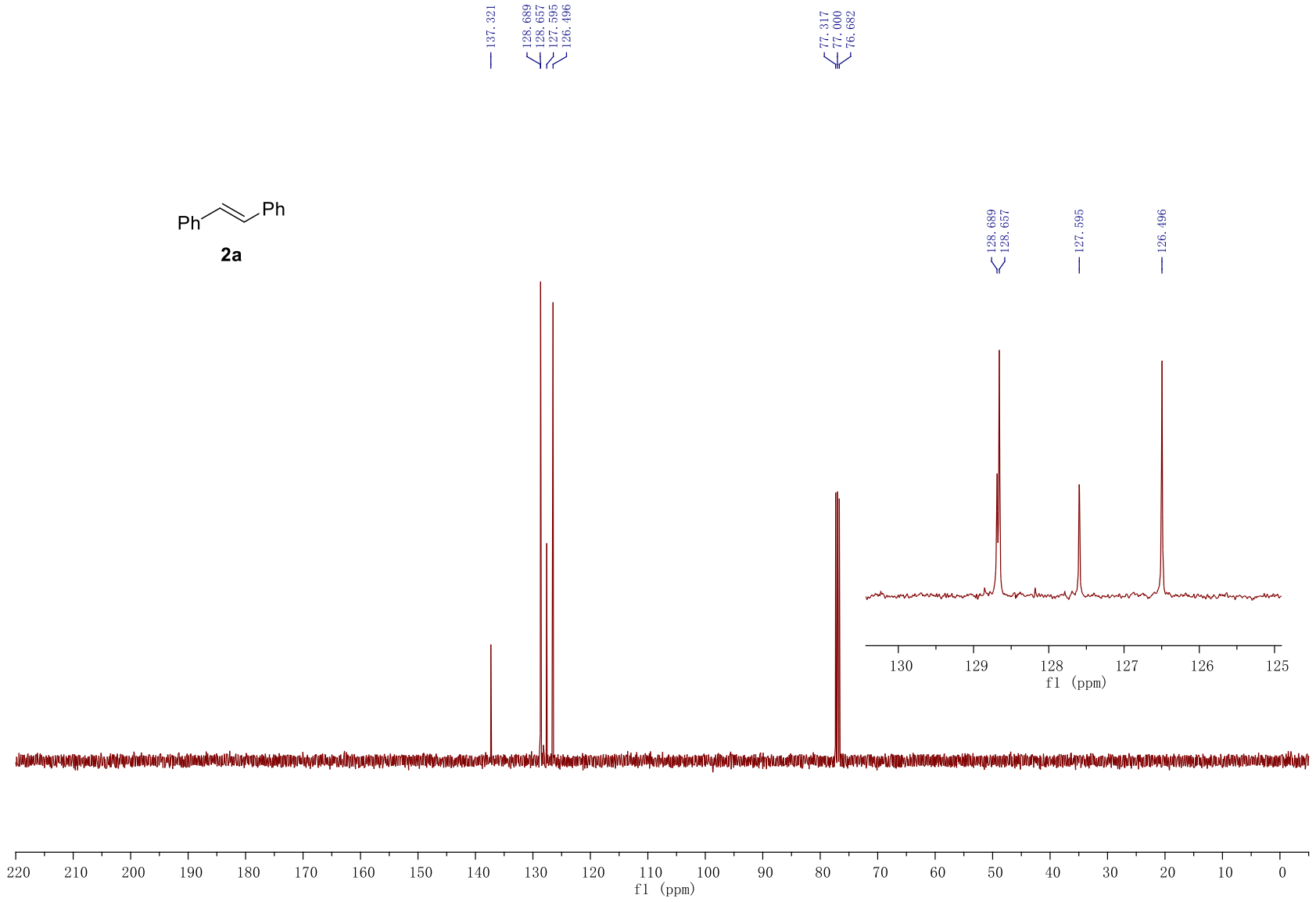
^{1}H NMR Spectrum of crude (*E*)-1,2-diphenylethene (2a)



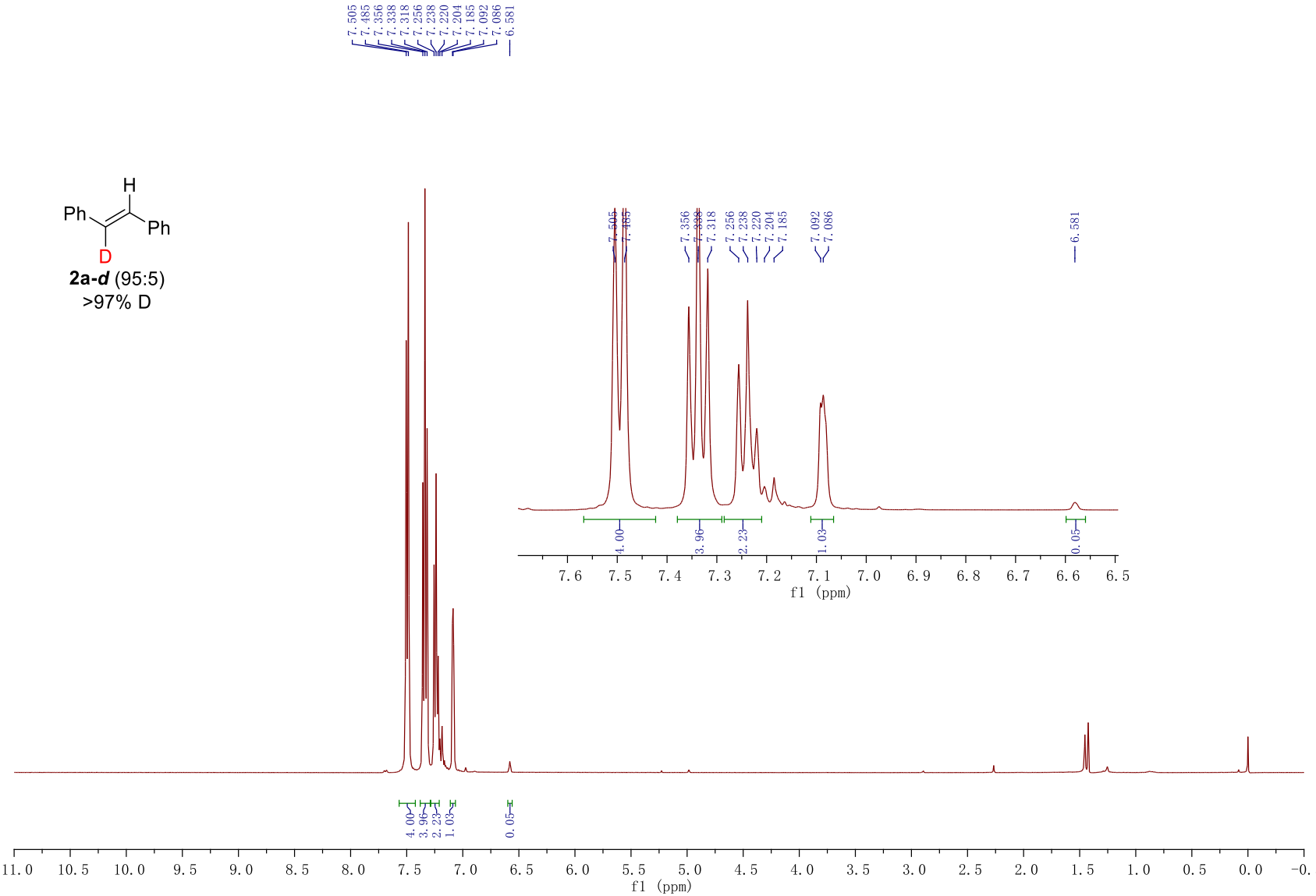
^{1}H NMR Spectrum of (*E*)-1,2-diphenylethene (2a)



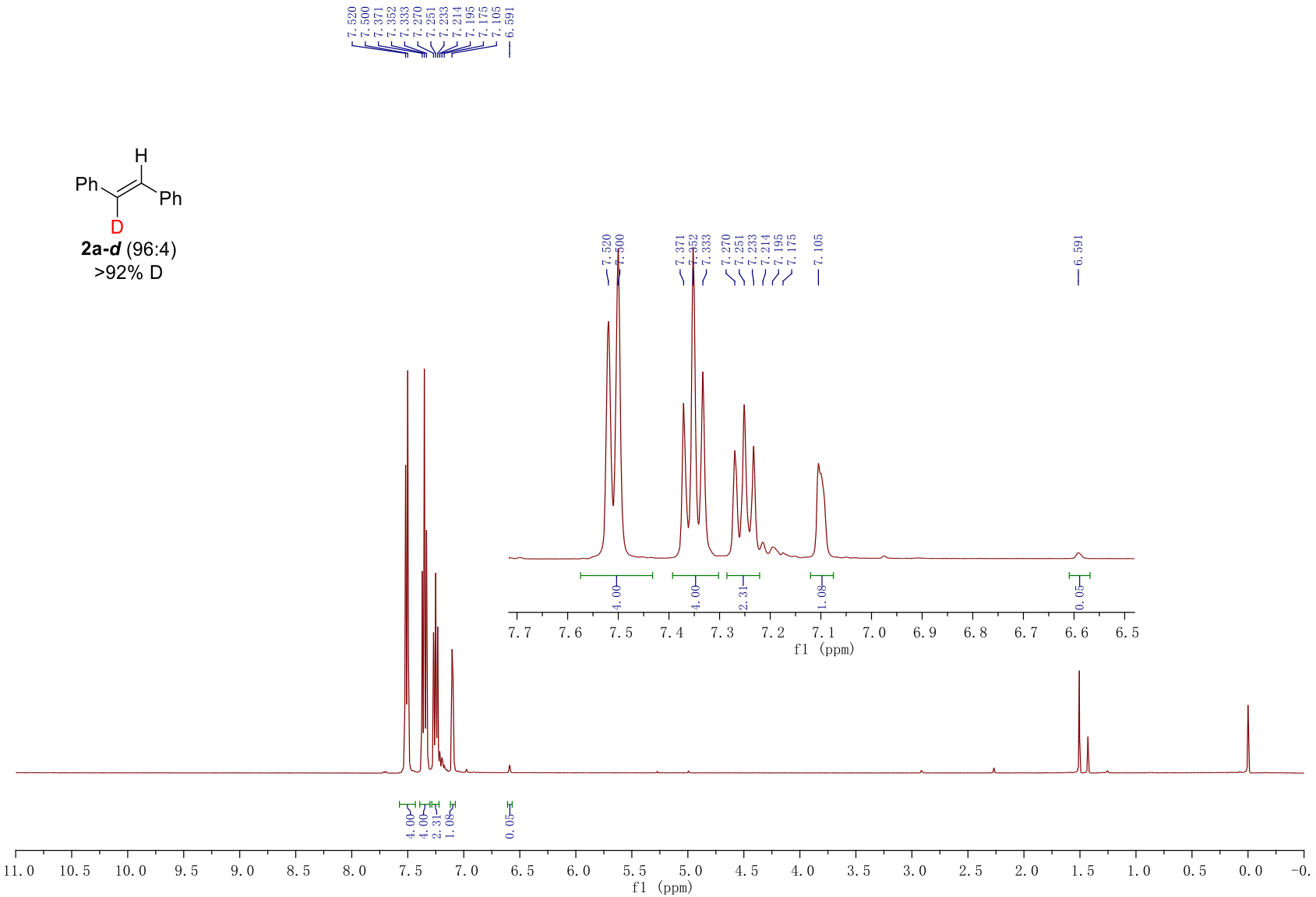
^{13}C NMR Spectrum of (*E*)-1,2-diphenylethene (2a)



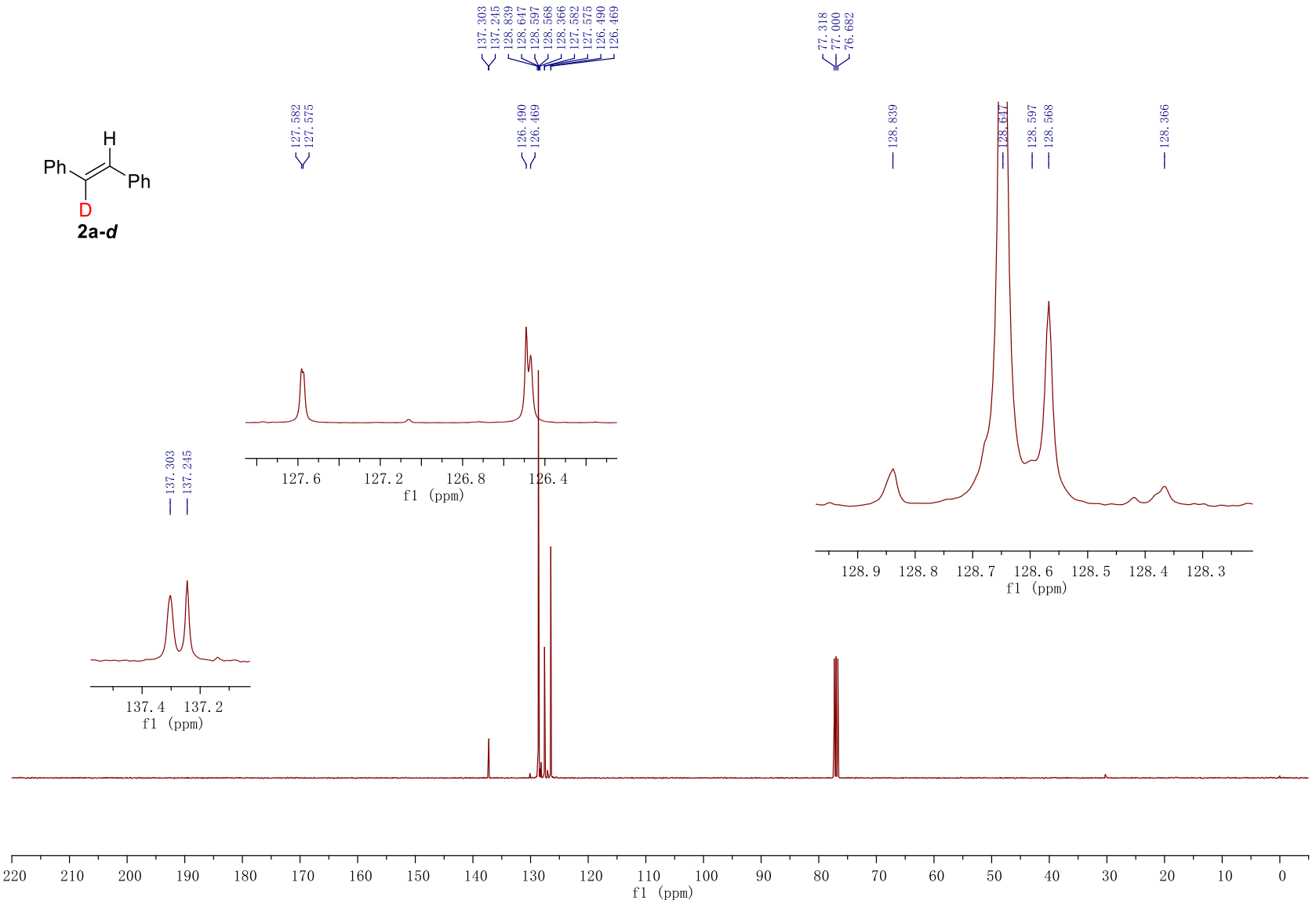
[1]H NMR Spectrum of (*E*)-(ethene-1,2-diyl-1-*d*)dibenzene (2a-*d*)



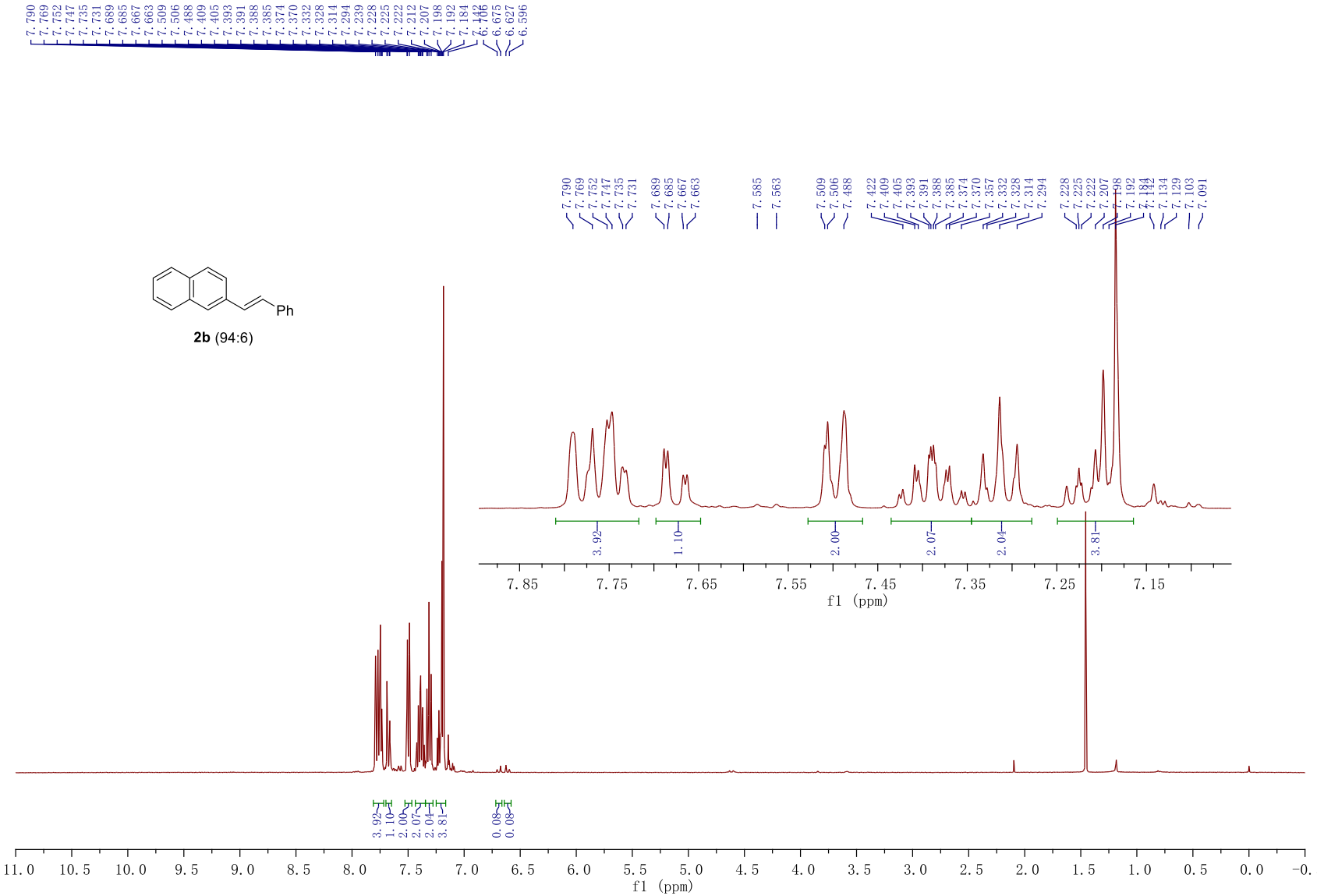
^{1}H NMR Spectrum of (*E*)-(ethene-1,2-diyl-1-*d*)dibenzene (2a-*d*)



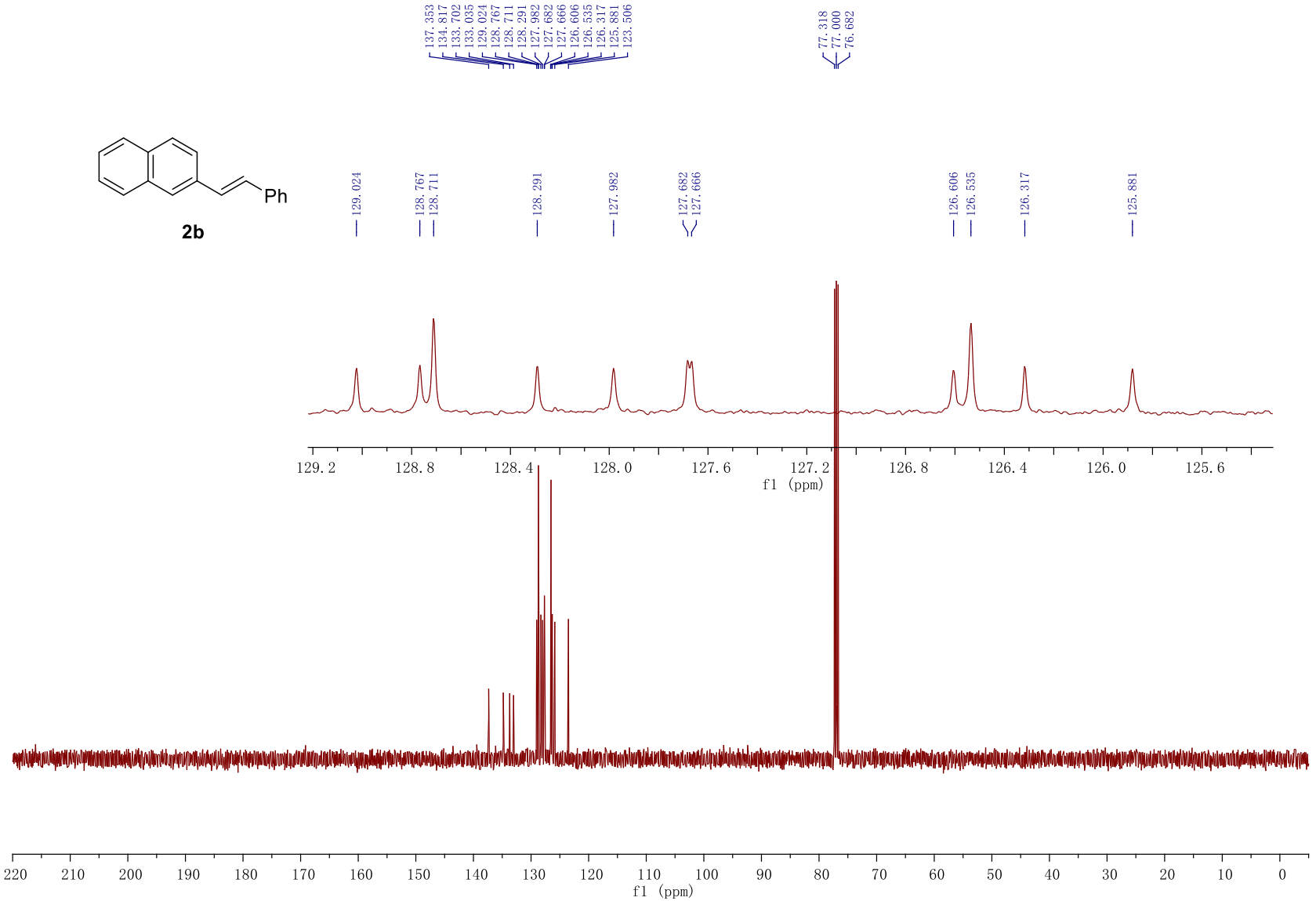
^{13}C NMR Spectrum of (*E*)-(ethene-1,2-diyl-1-*d*)dibenzene (2a-*d*)



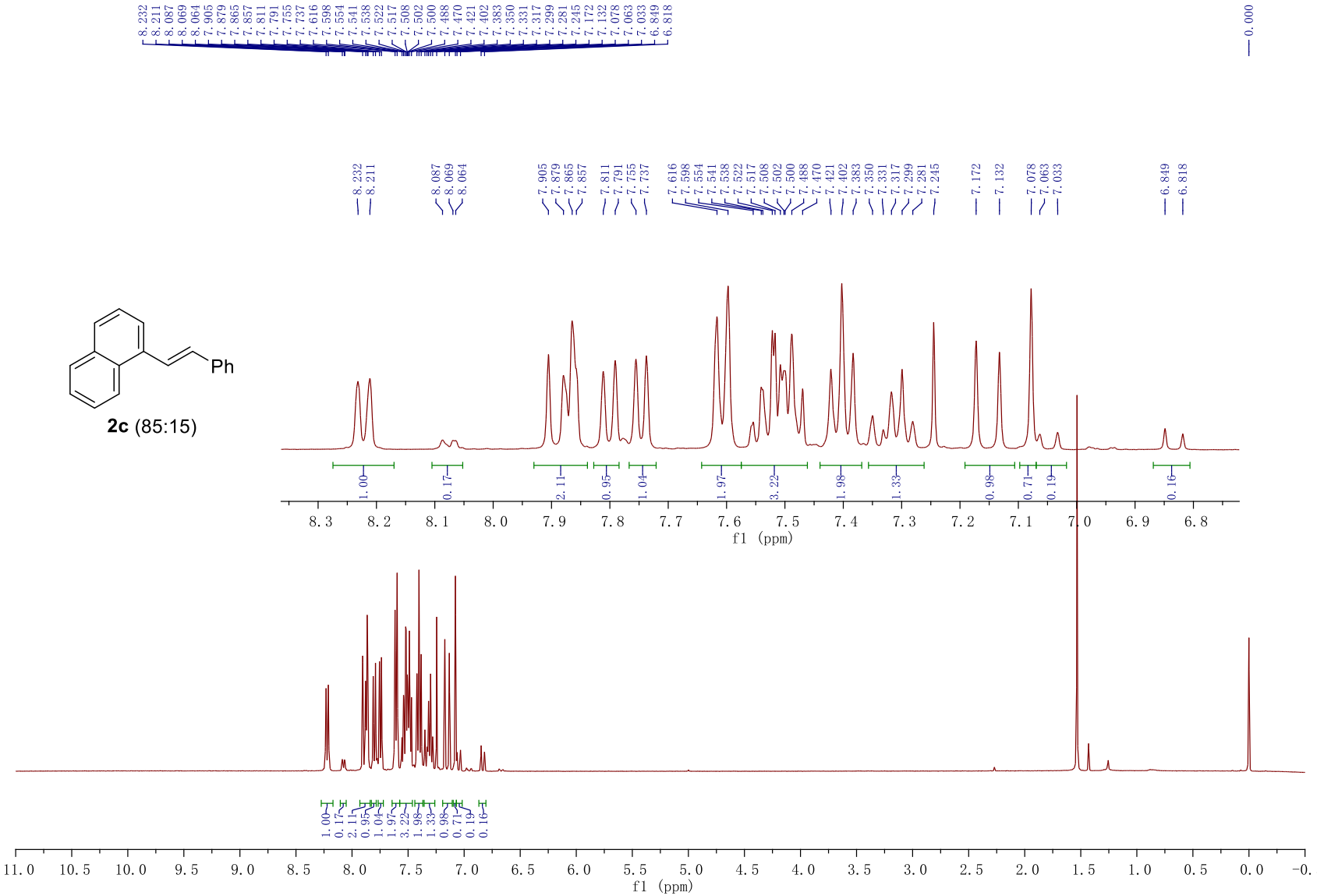
^{1}H NMR Spectrum of (*E*)-2-styrylnaphthalene (2b)



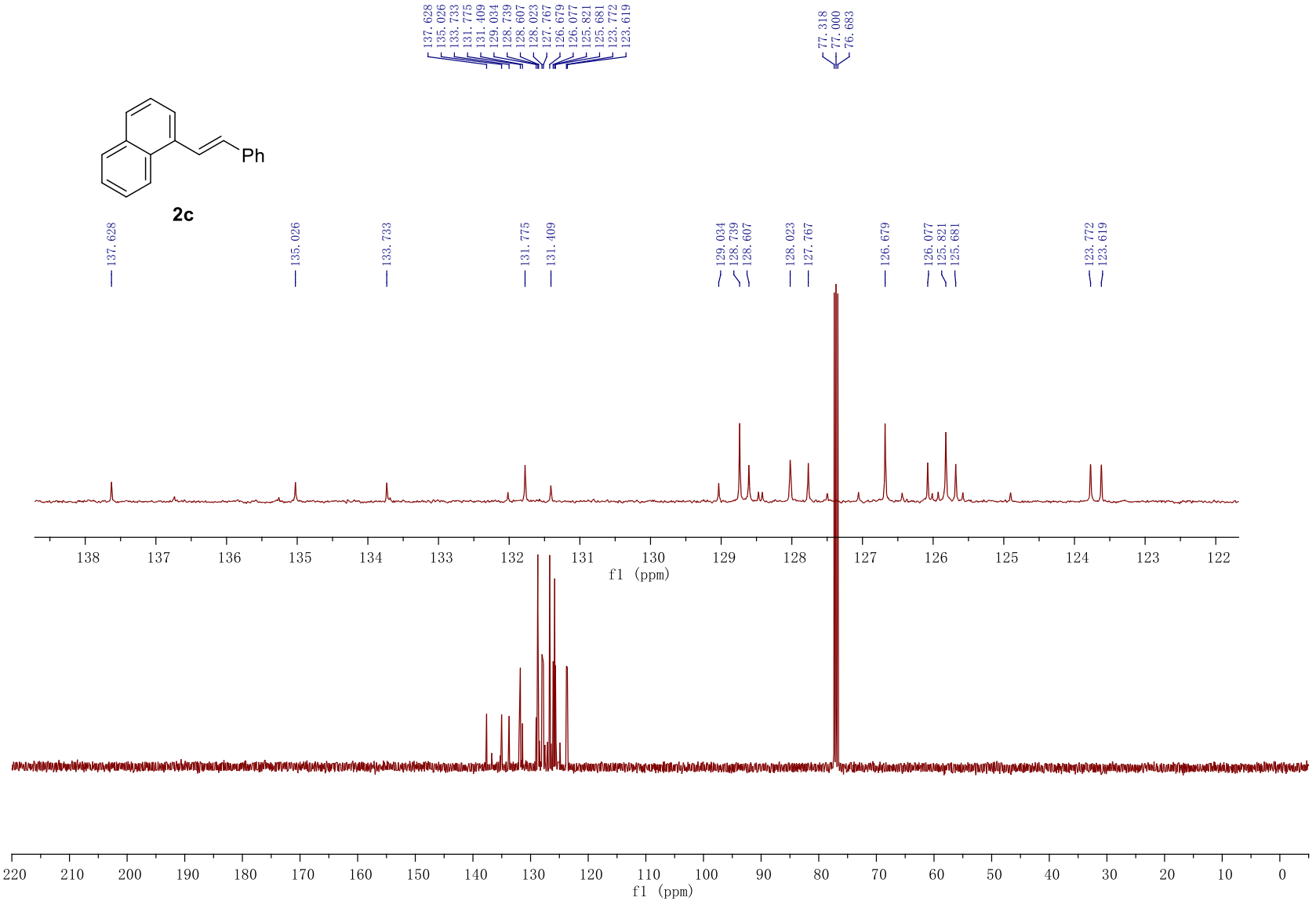
^{13}C NMR Spectrum of (*E*)-2-styrylnaphthalene (2b)



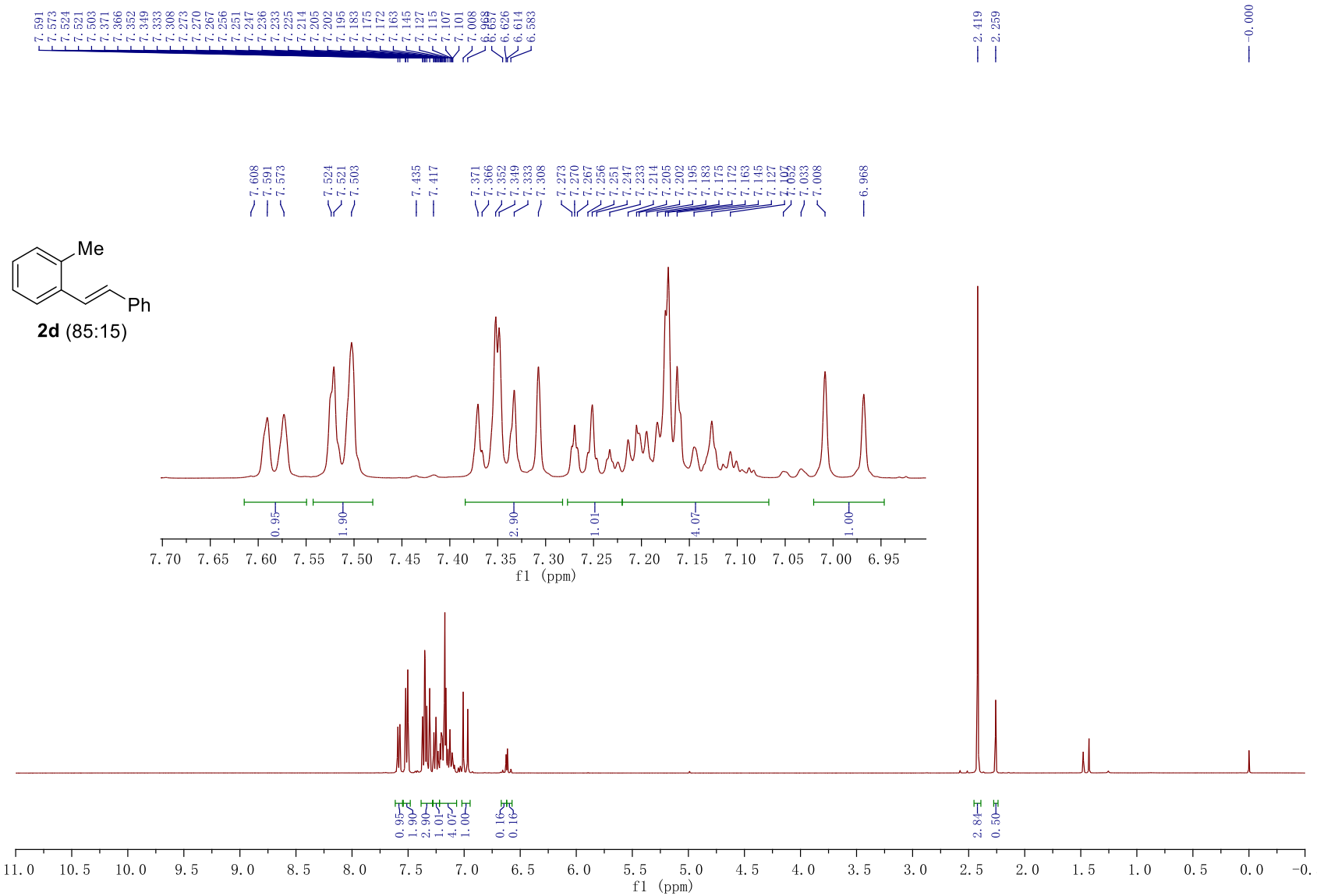
^{1}H NMR Spectrum of (*E*)-1-styrylnaphthalene (2c)



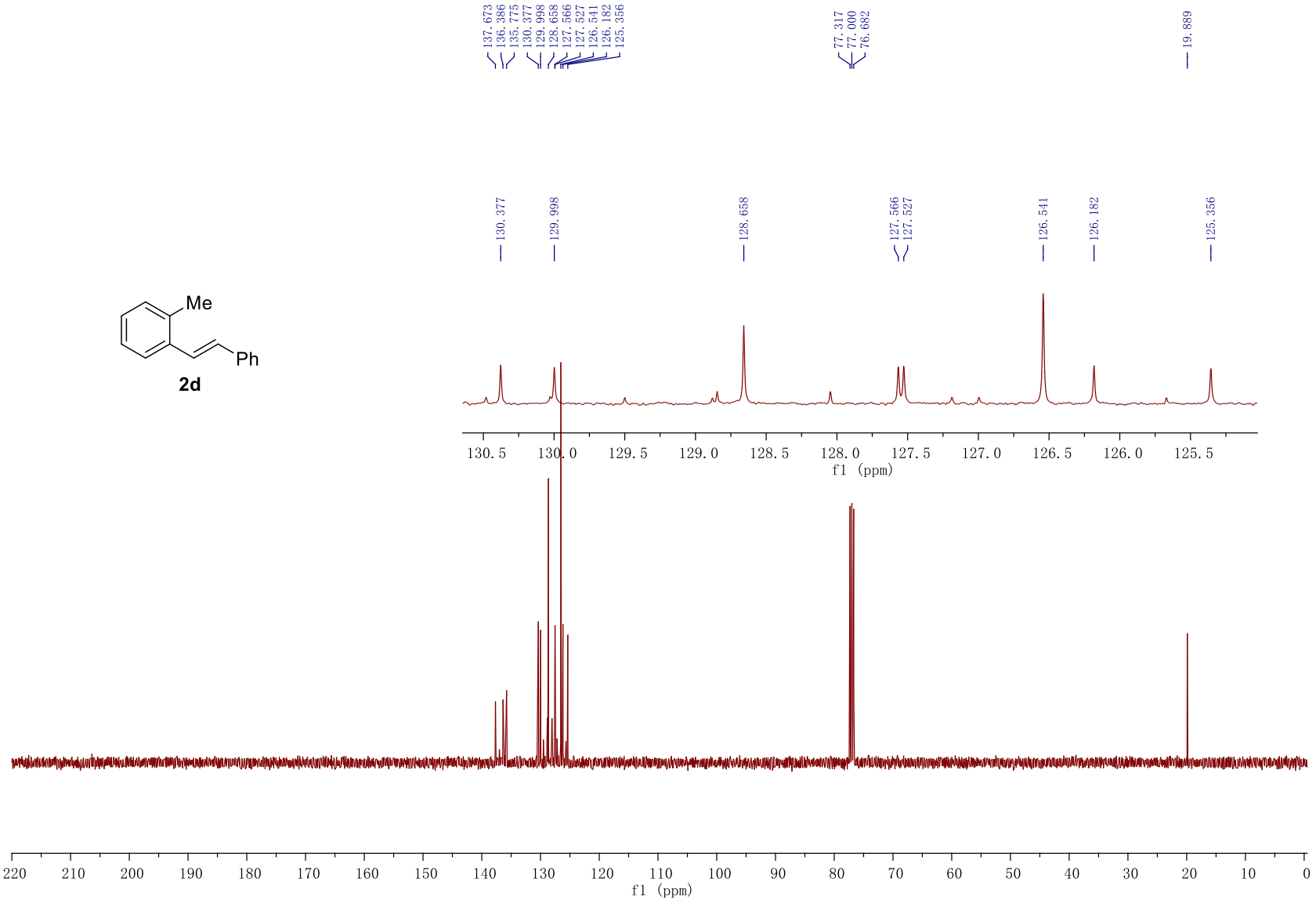
^{13}C NMR Spectrum of (*E*)-1-styrylnaphthalene (2c)



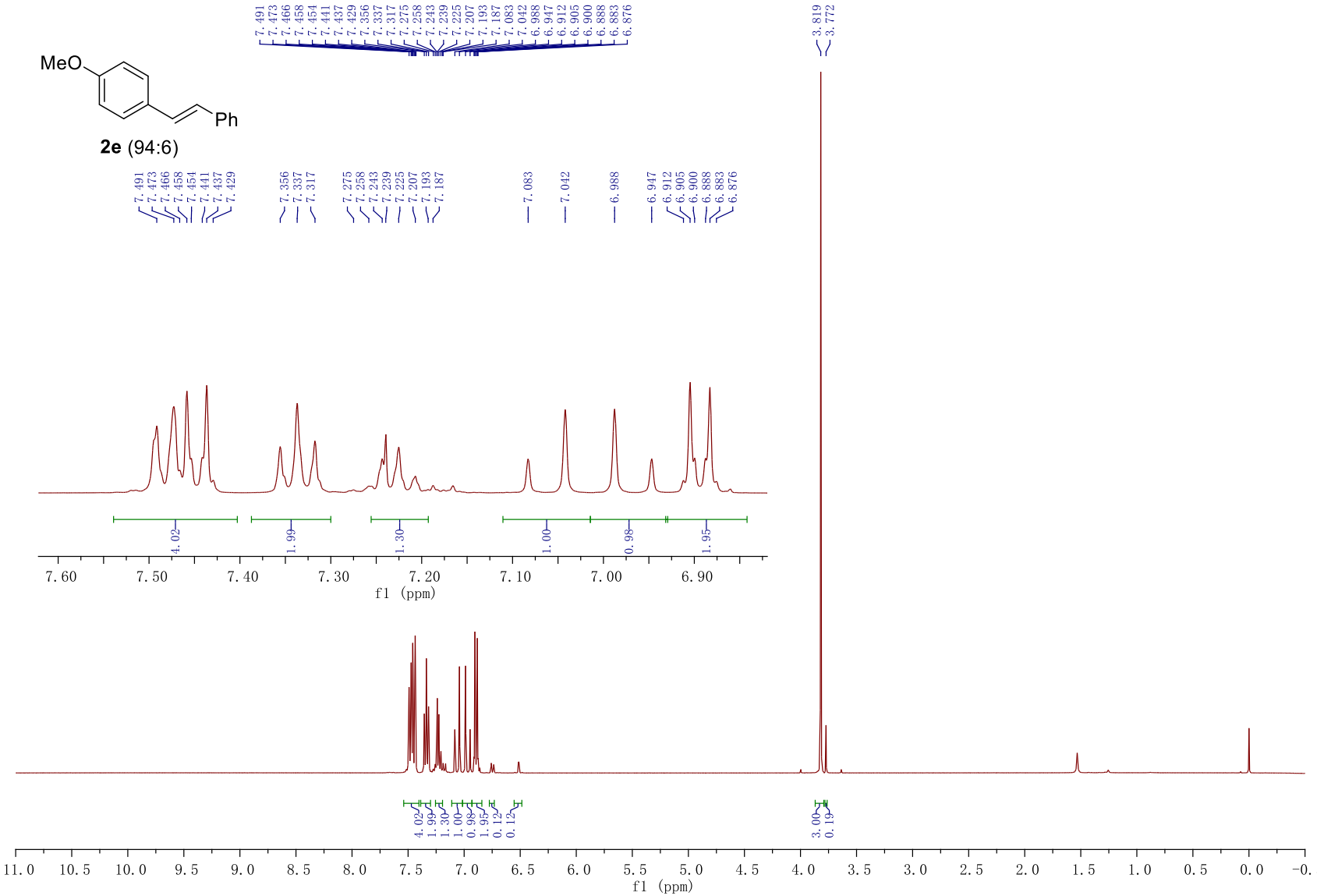
^{1}H NMR Spectrum of (*E*)-1-methyl-2-styrylbenzene (2d)



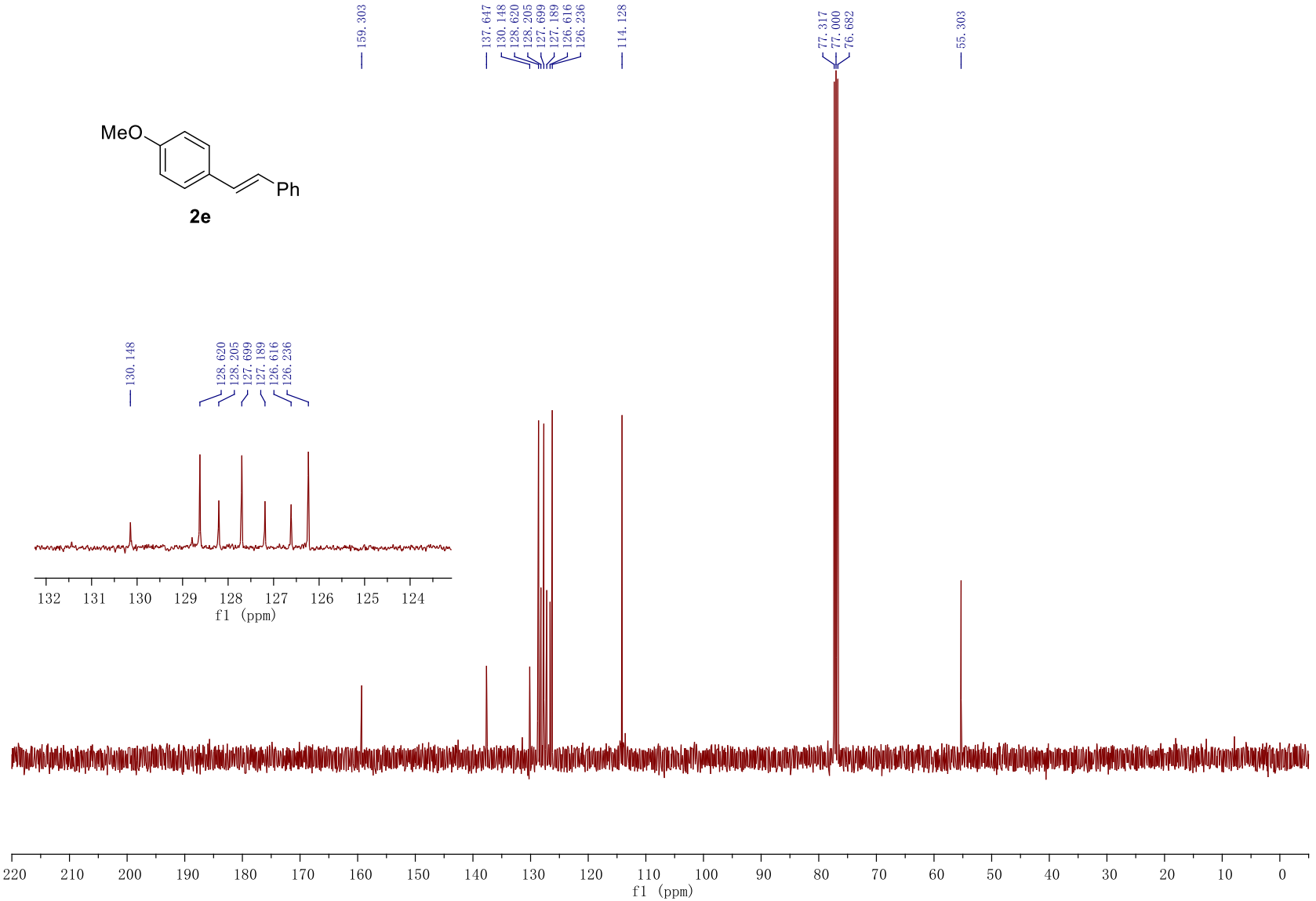
^{13}C NMR Spectrum of (*E*)-1-methyl-2-styrylbenzene (2d)



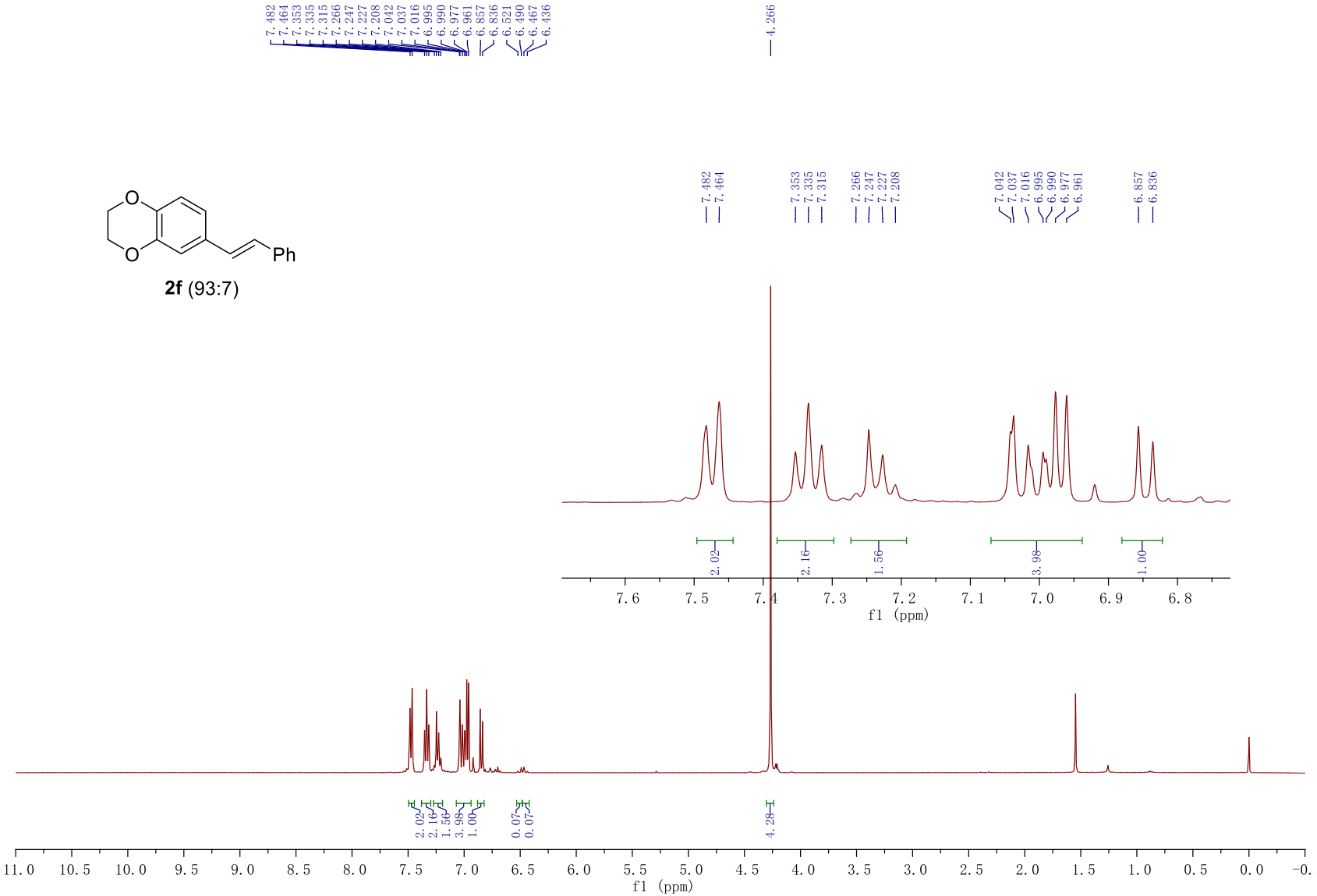
^{1}H NMR Spectrum of (*E*)-1-methoxy-4-styrylbenzene (2e)



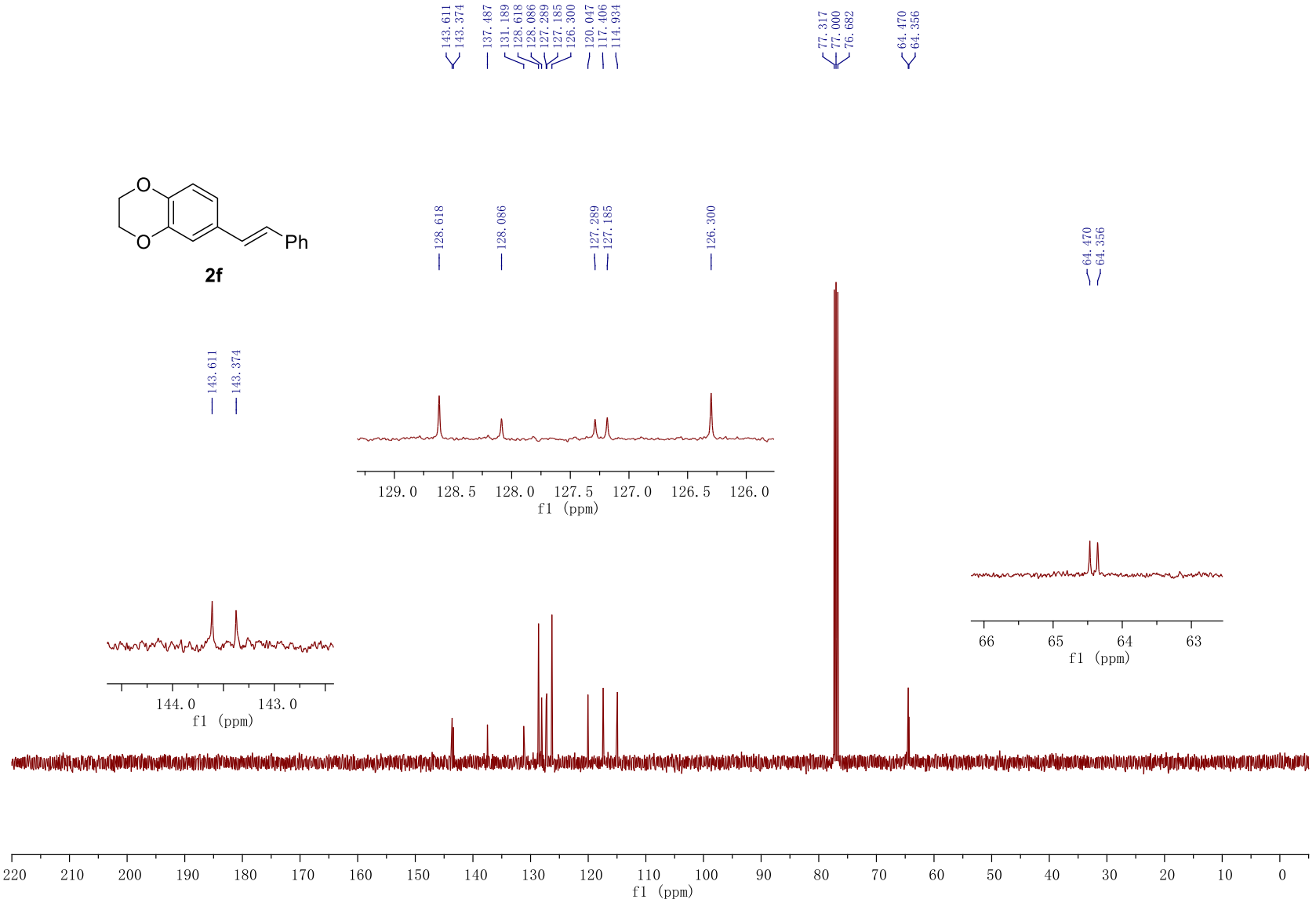
^{13}C NMR Spectrum of (*E*)-1-methoxy-4-styrylbenzene (2e)



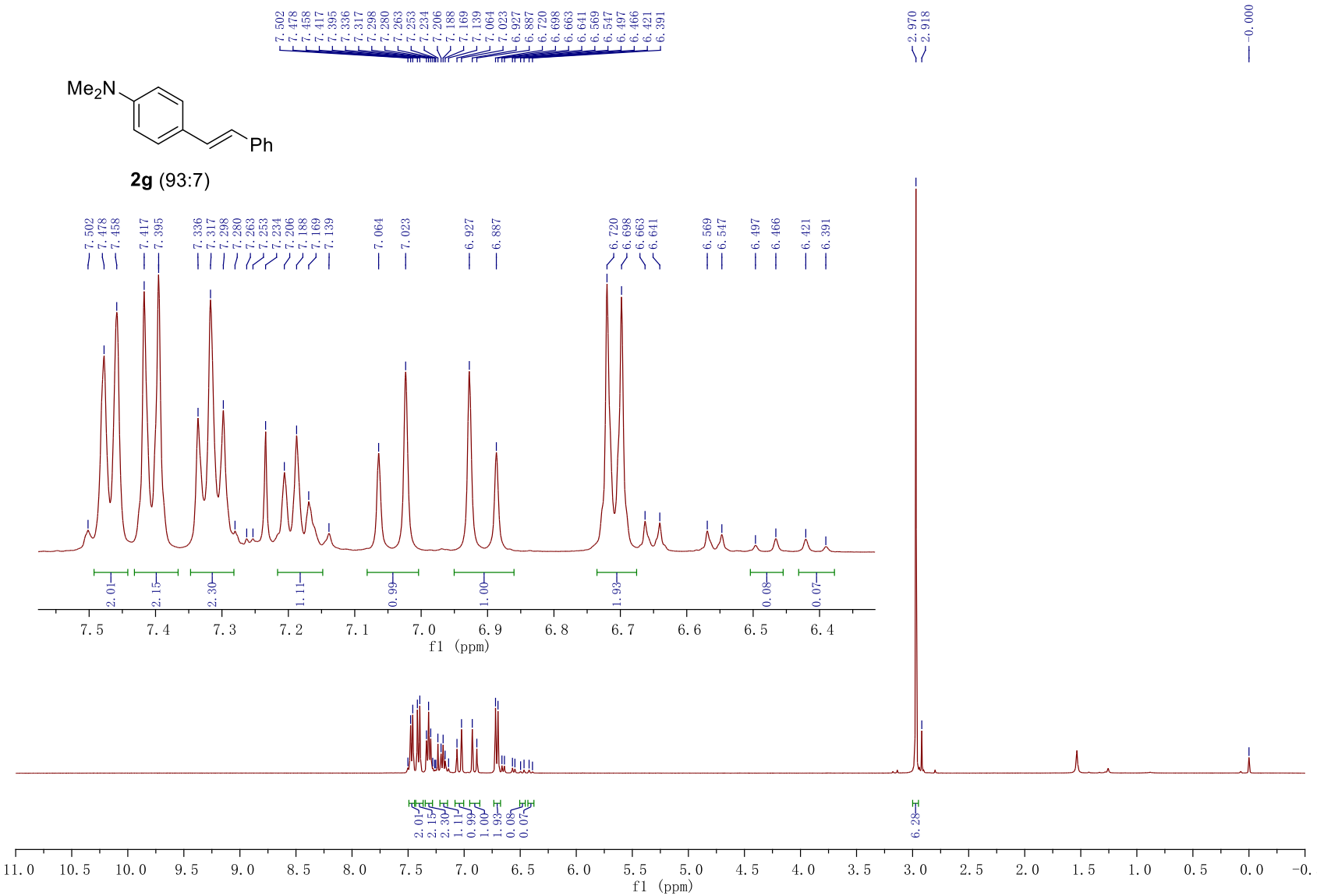
^{1}H NMR Spectrum of (*E*)-6-styryl-2,3-dihydrobenzo[b][1,4]dioxine (2f)



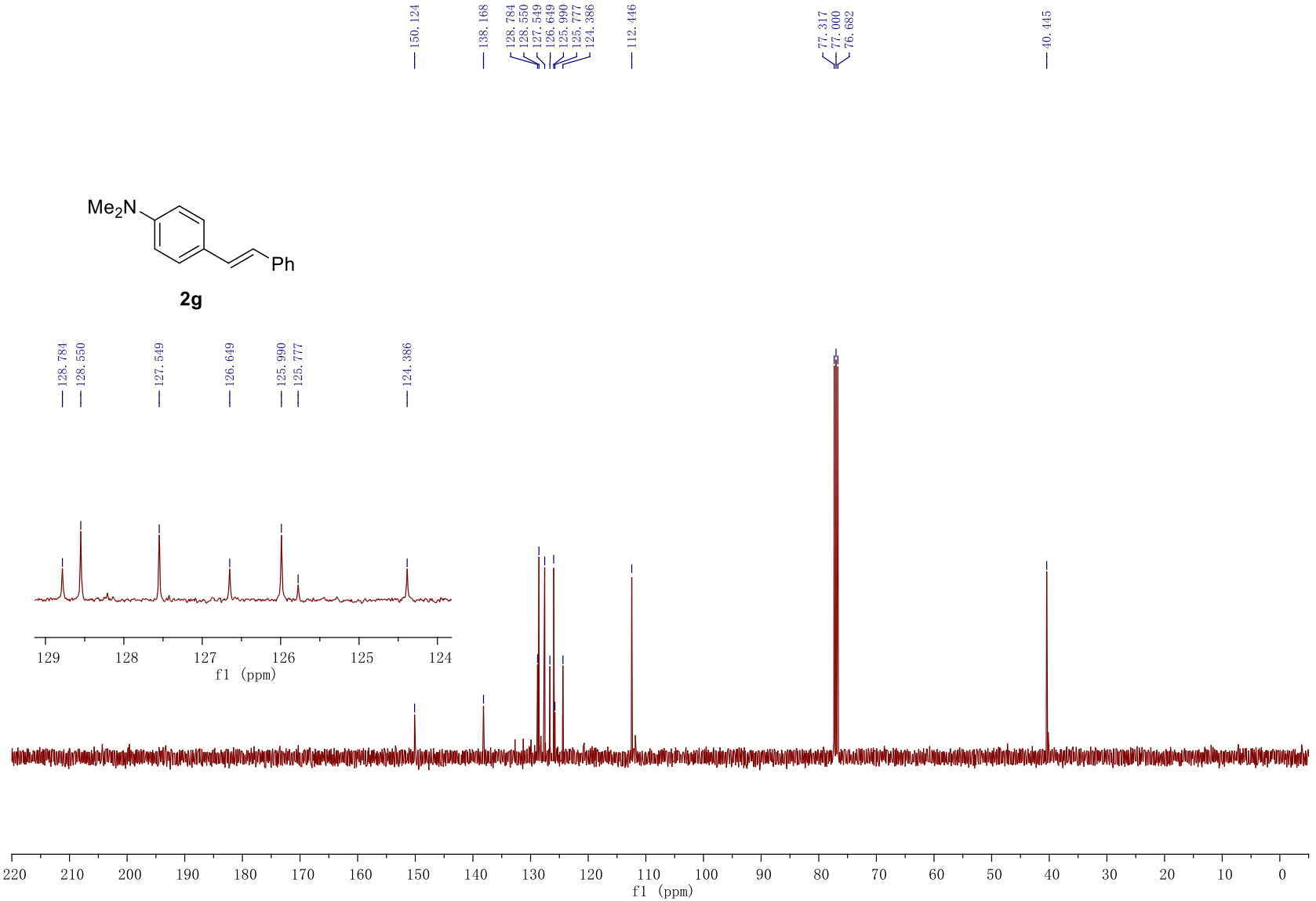
^{13}C NMR Spectrum of (*E*)-6-styryl-2,3-dihydrobenzo[b][1,4]dioxine (2f)



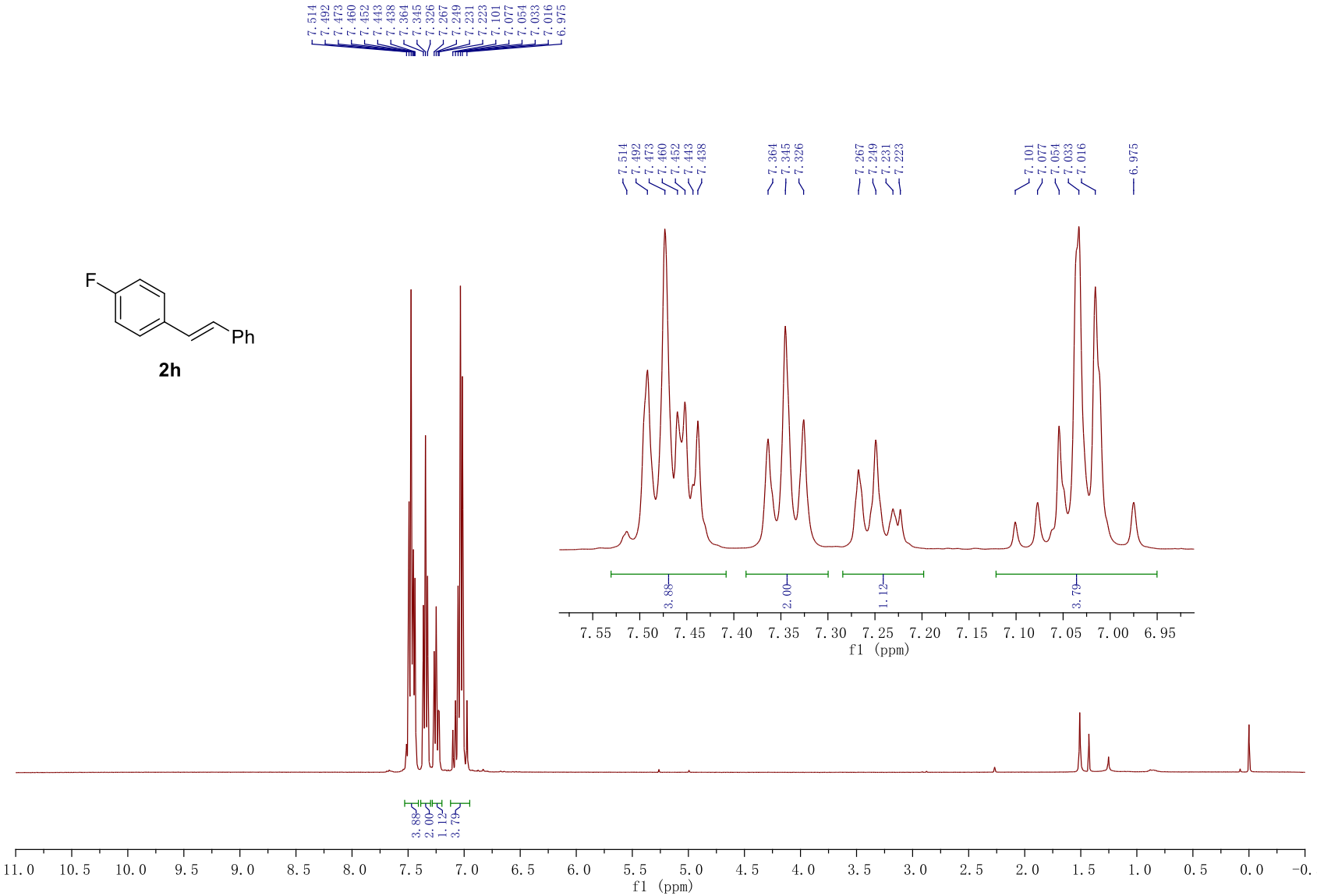
^{1}H NMR Spectrum of (*E*)-*N*,*N*-dimethyl-4-styrylaniline (2g)



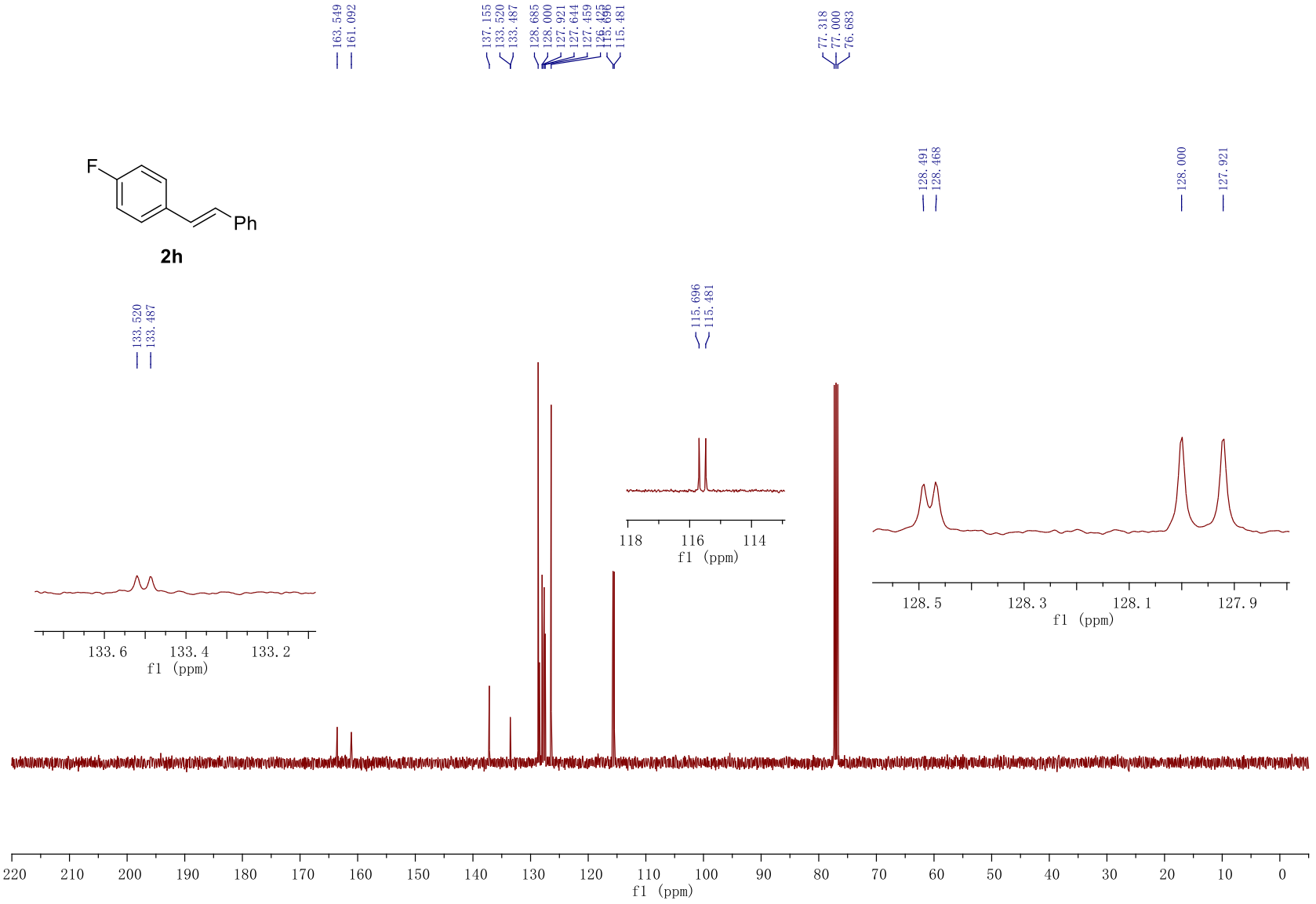
^{13}C NMR Spectrum of (*E*)-*N*,*N*-dimethyl-4-styrylaniline (2g)



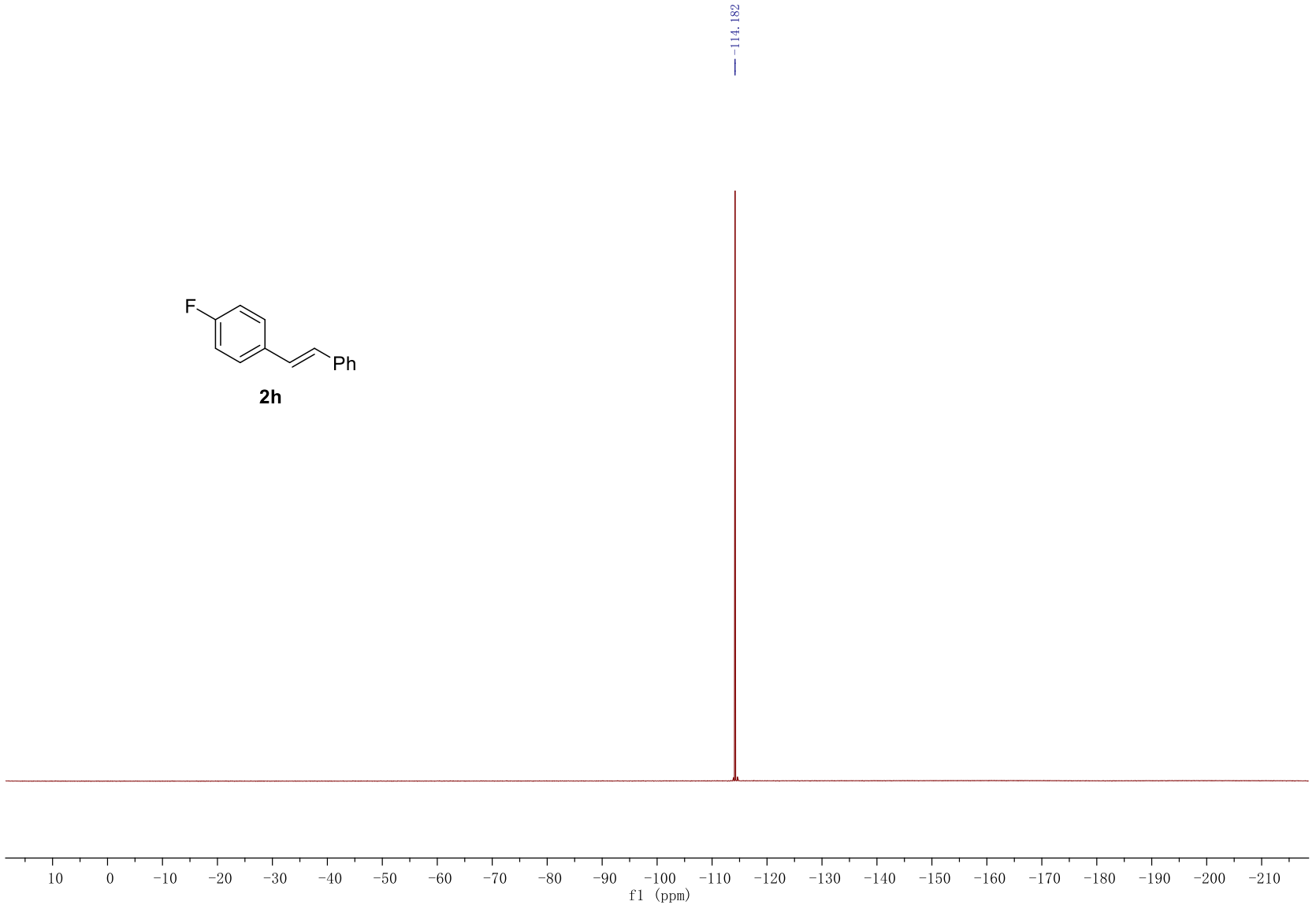
^{1}H NMR Spectrum of (*E*)-1-fluoro-4-styrylbenzene (2h)



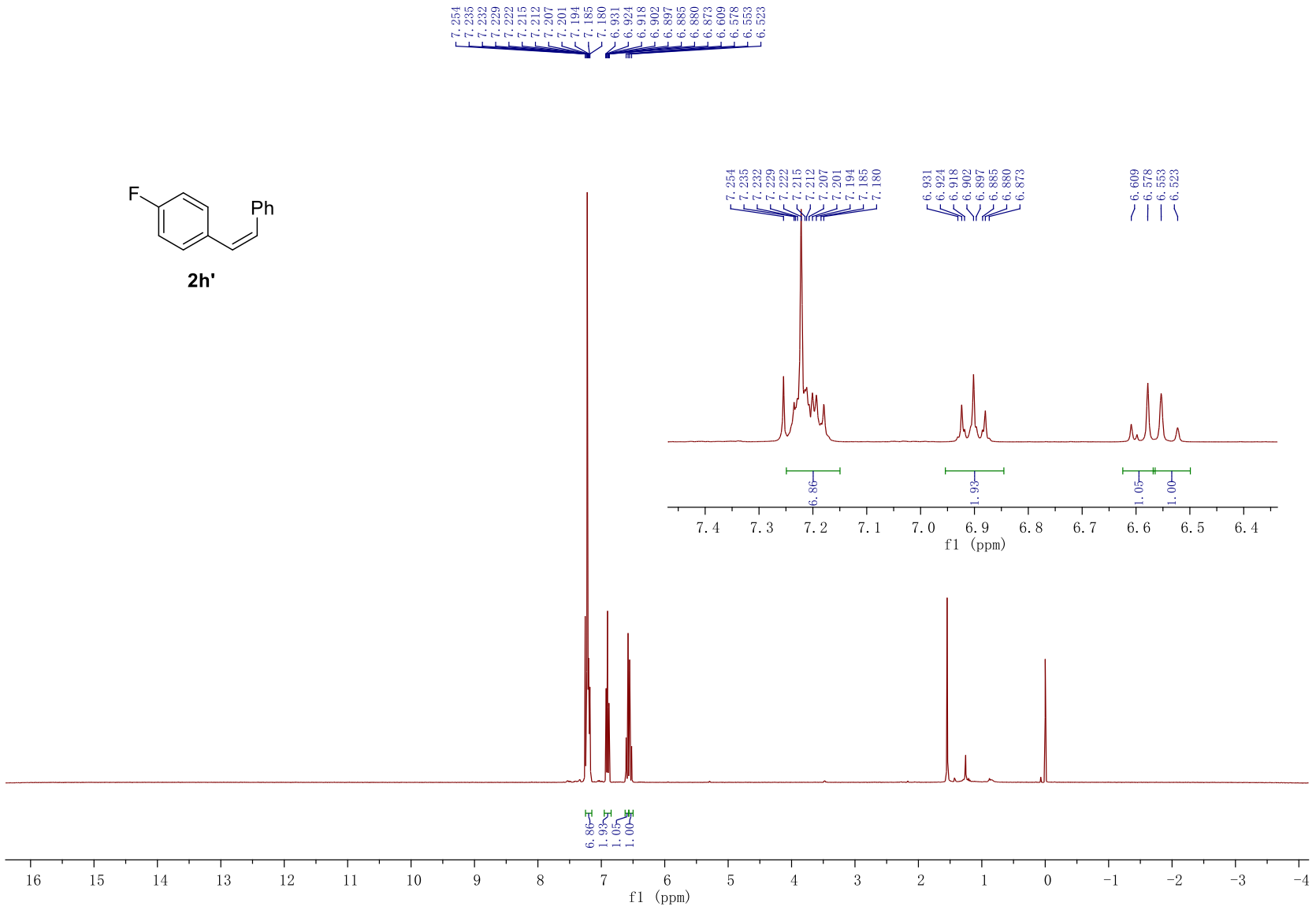
^{13}C NMR Spectrum of (*E*)-1-fluoro-4-styrylbenzene (2h)



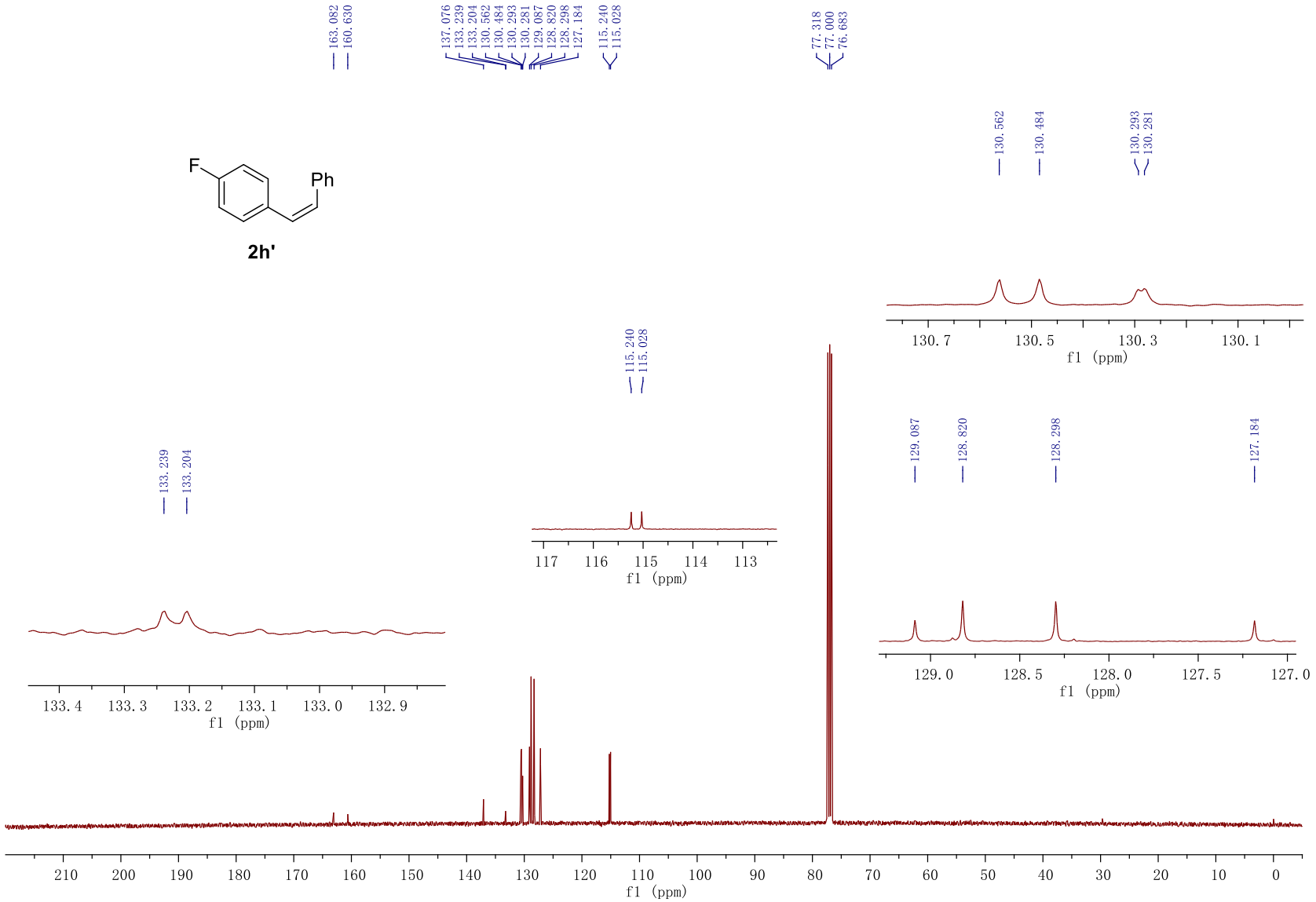
^{19}F NMR Spectrum of (*E*)-1-fluoro-4-styrylbenzene (2h)



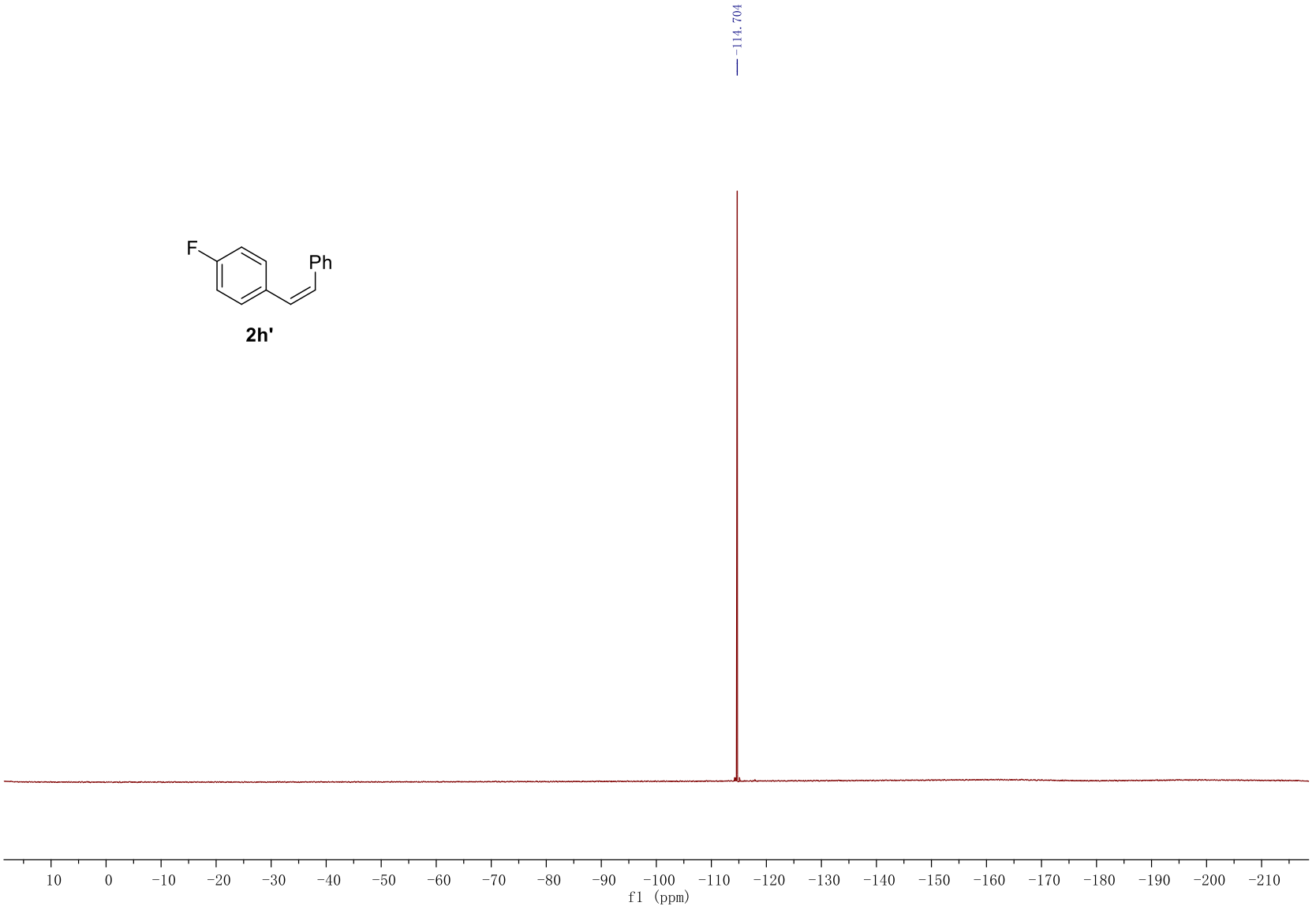
^{1}H NMR Spectrum of (*Z*)-1-fluoro-4-styrylbenzene (2h')



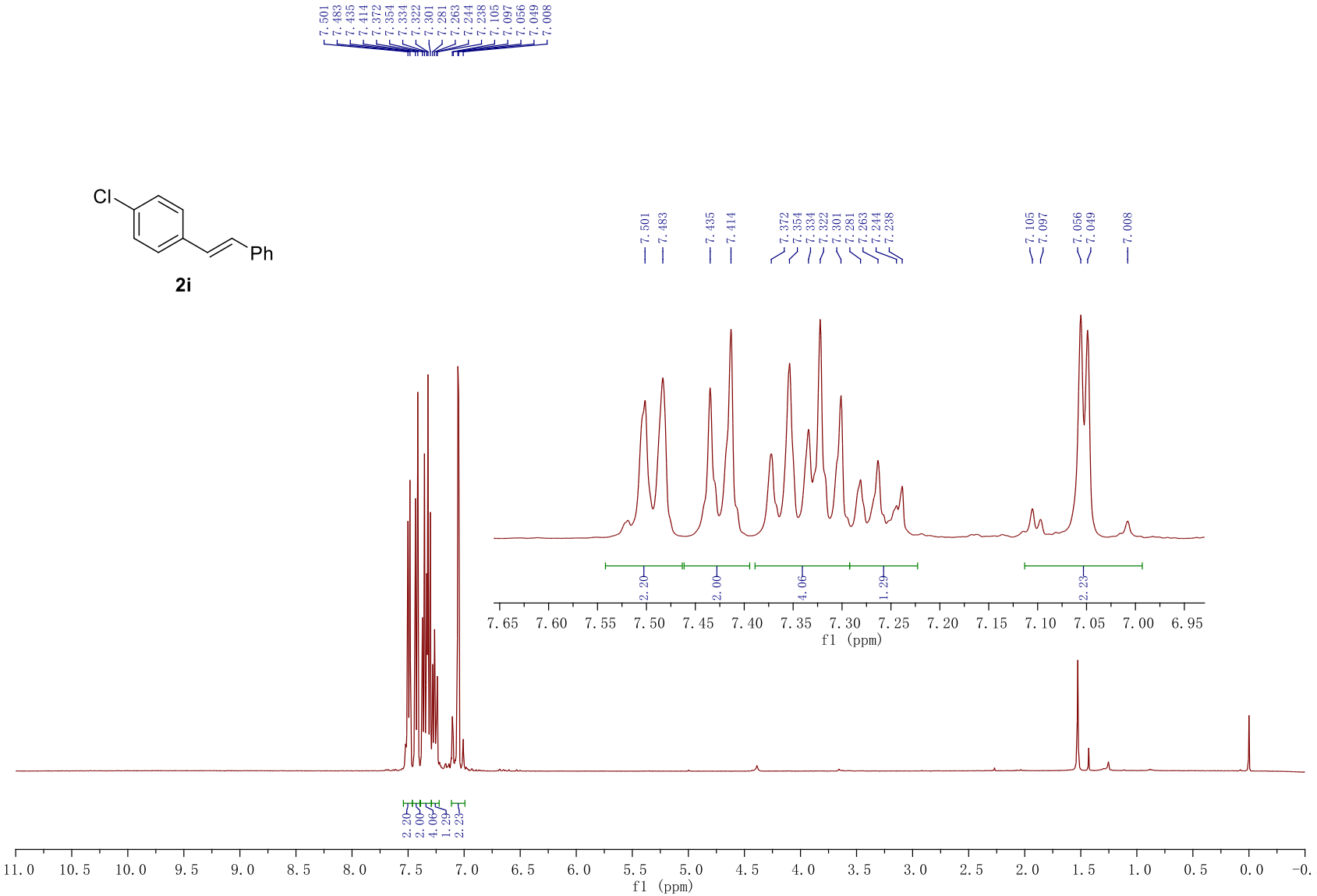
^{13}C NMR Spectrum of (*Z*)-1-fluoro-4-styrylbenzene (2h')



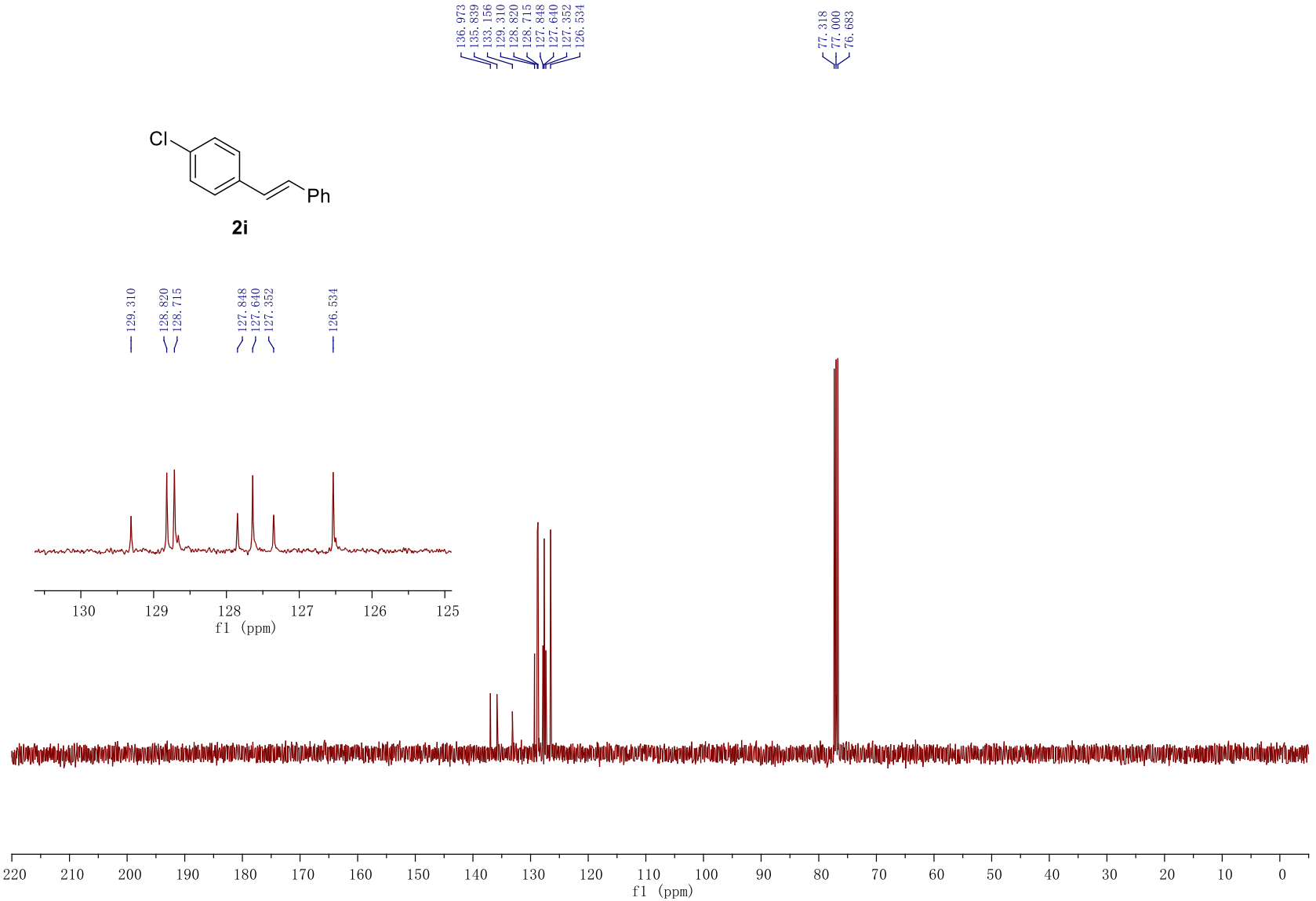
^{19}F NMR Spectrum of (*Z*)-1-fluoro-4-styrylbenzene (2h')



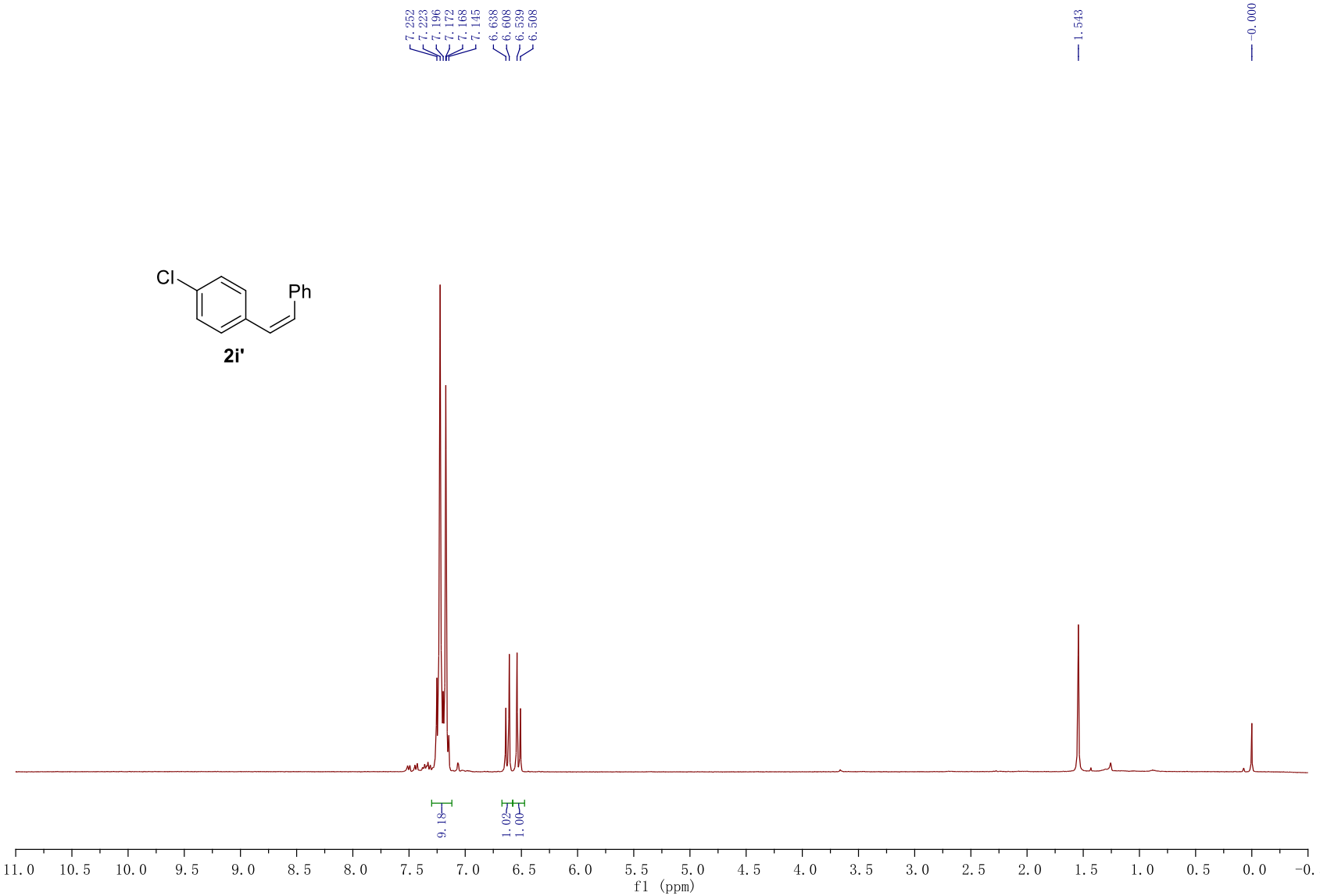
^{1}H NMR Spectrum of (*E*)-1-chloro-4-styrylbenzene (2i)



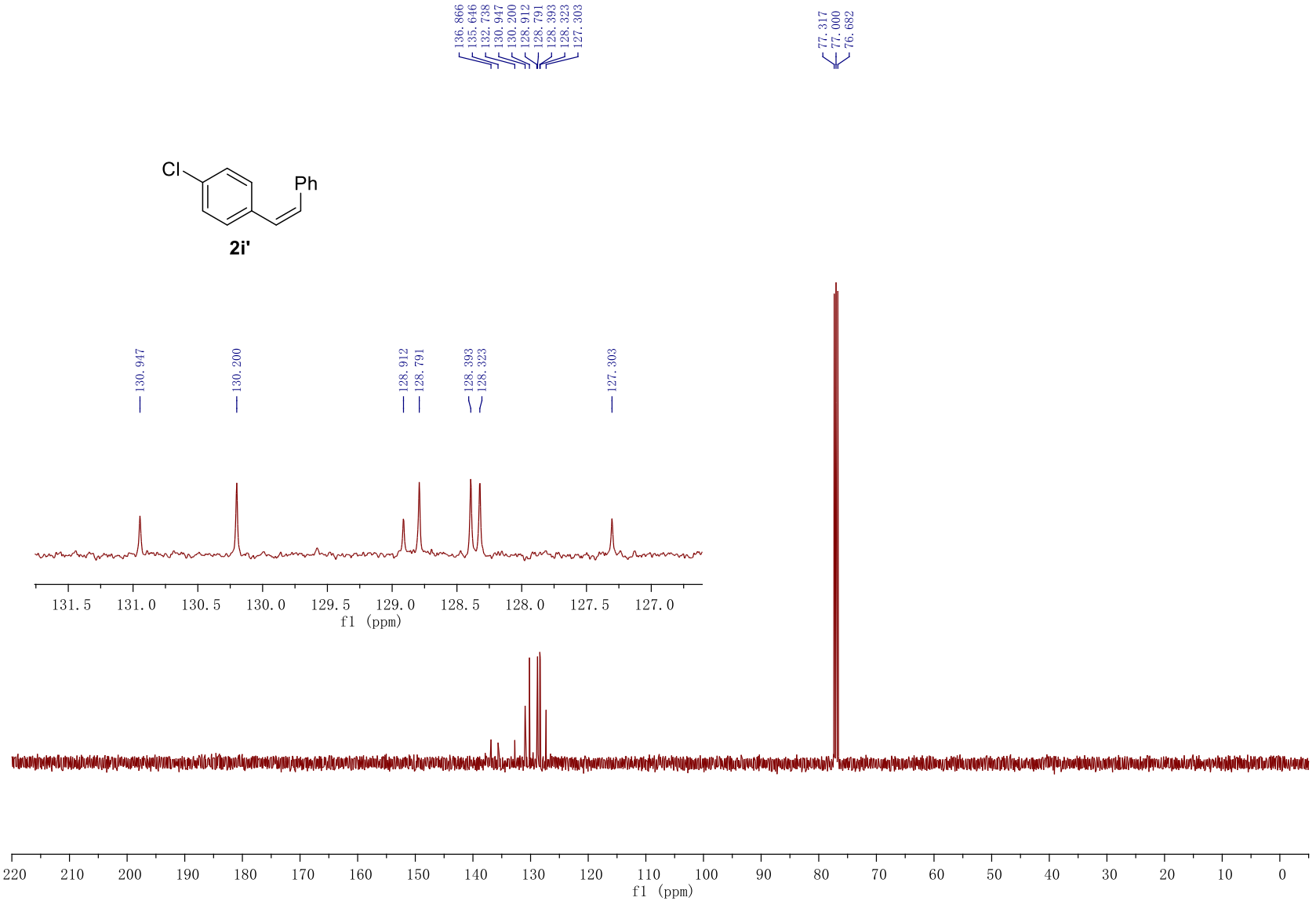
^{13}C NMR Spectrum of (*E*)-1-chloro-4-styrylbenzene (2i)



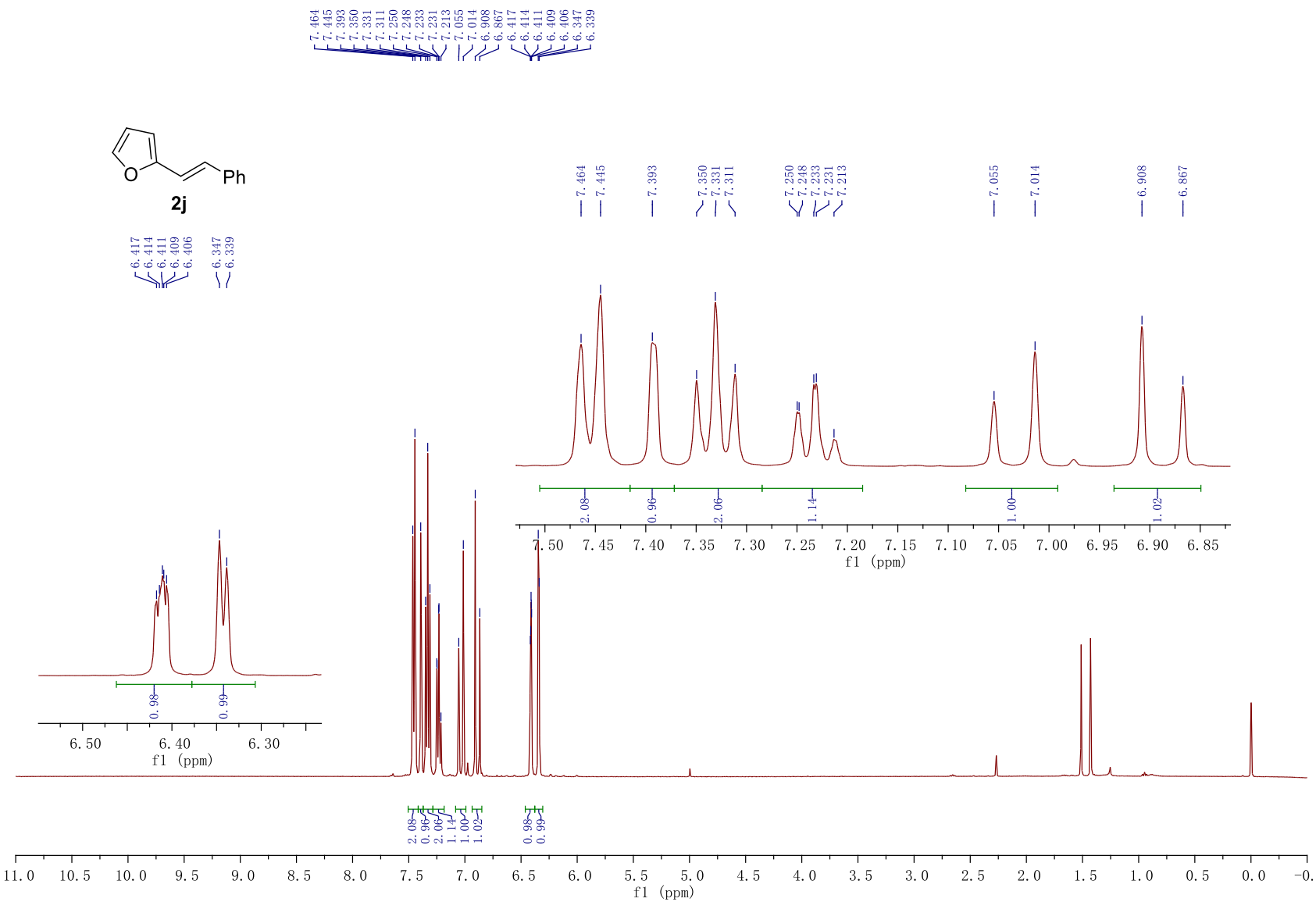
^{1}H NMR Spectrum of (*Z*)-1-chloro-4-styrylbenzene (2i')



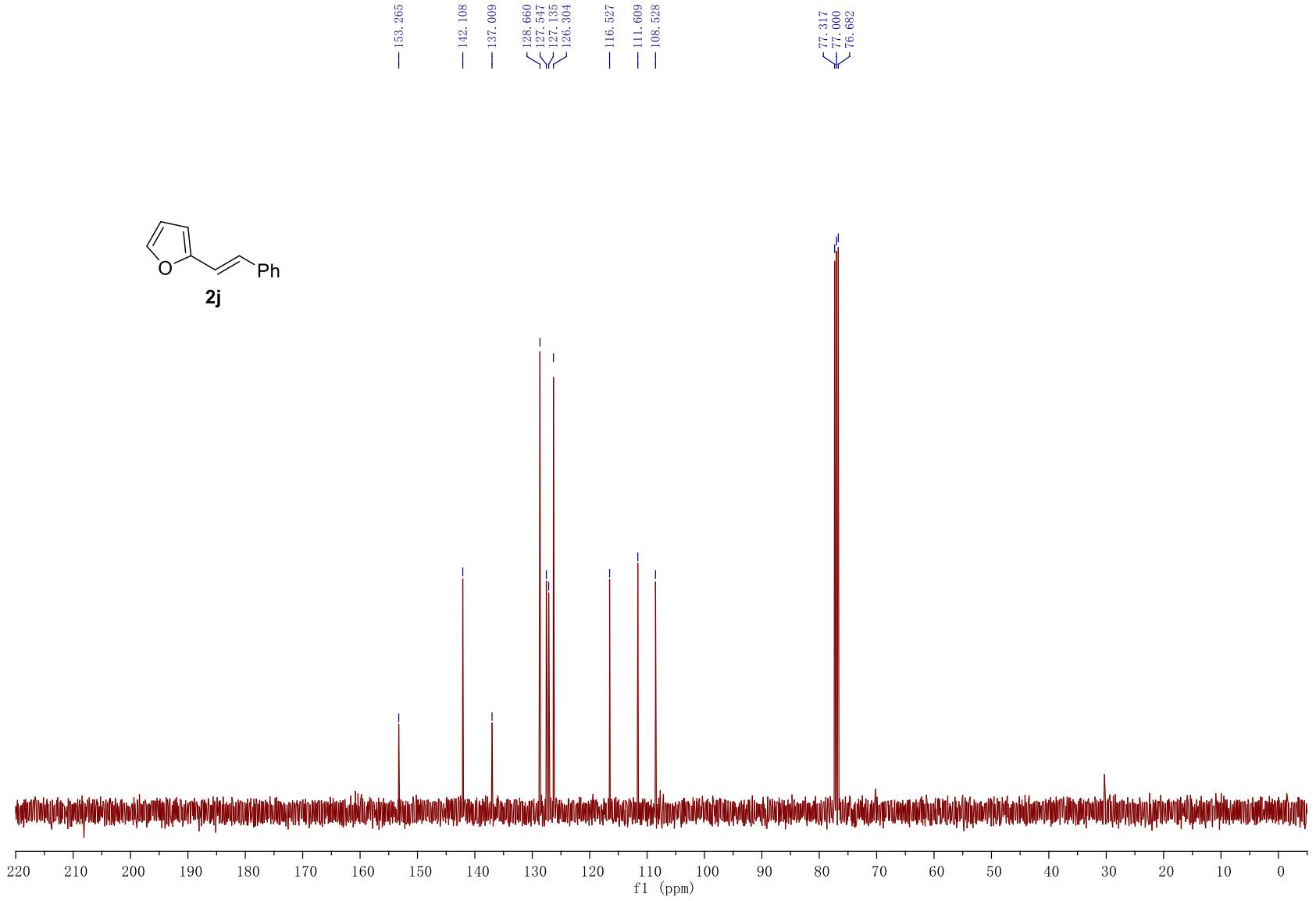
^{13}C NMR Spectrum of (*Z*)-1-chloro-4-styrylbenzene (2i')



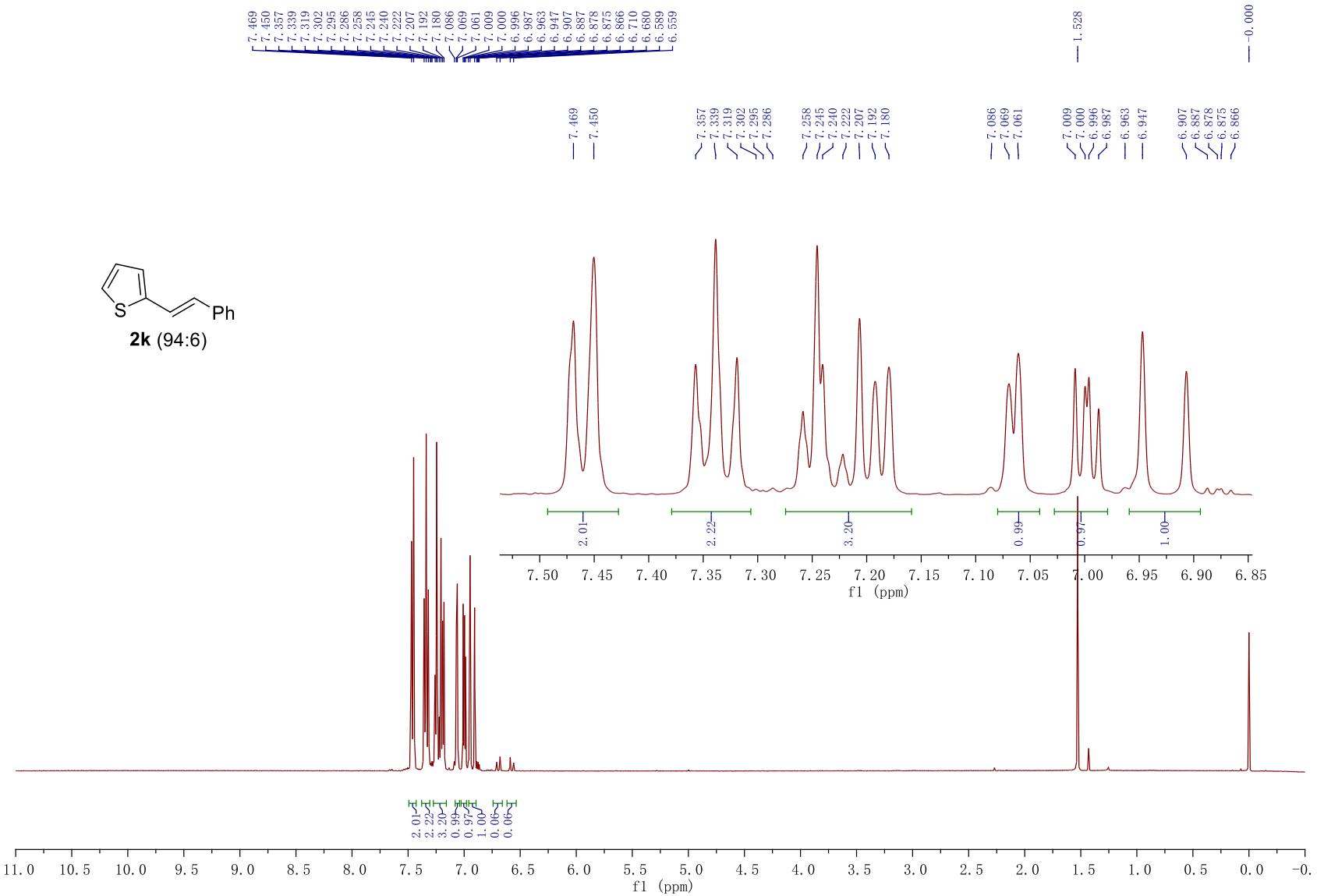
^{1}H NMR Spectrum of (*E*)-2-styrylfuran (2j)



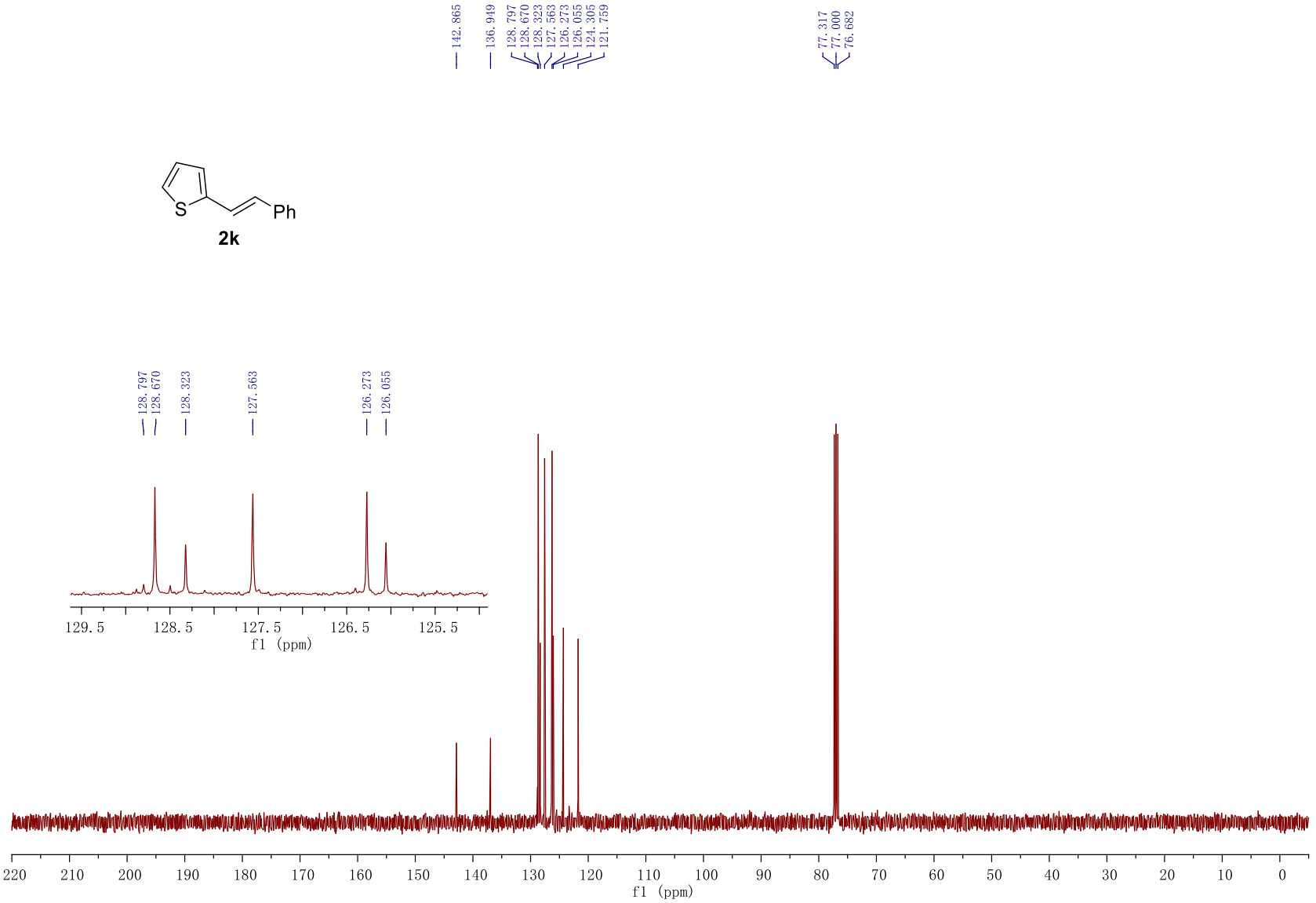
^{13}C NMR Spectrum of (*E*)-2-styrylfuran (2j)



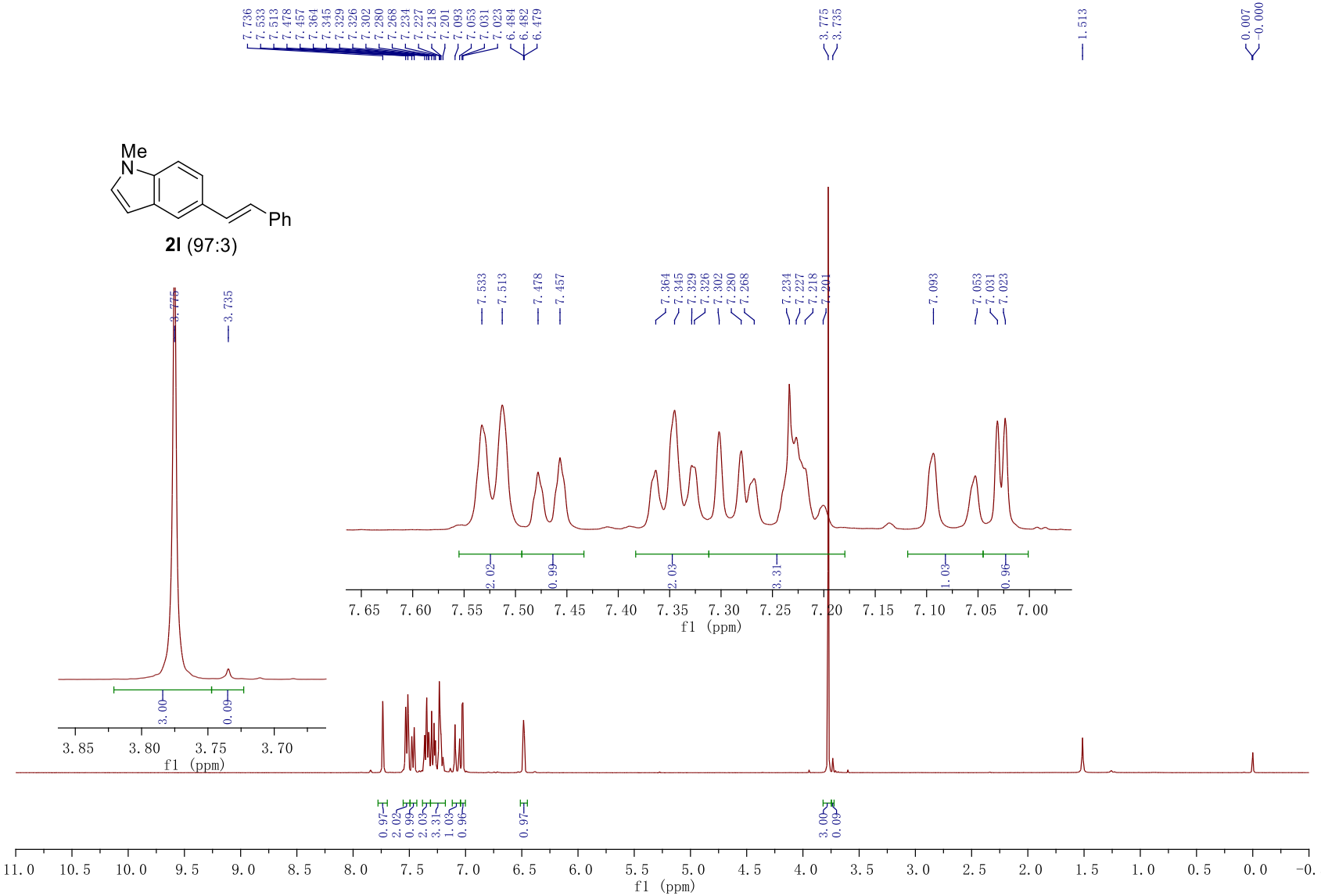
[1]H NMR Spectrum of (*E*)-2-styrylthiophene (2k)



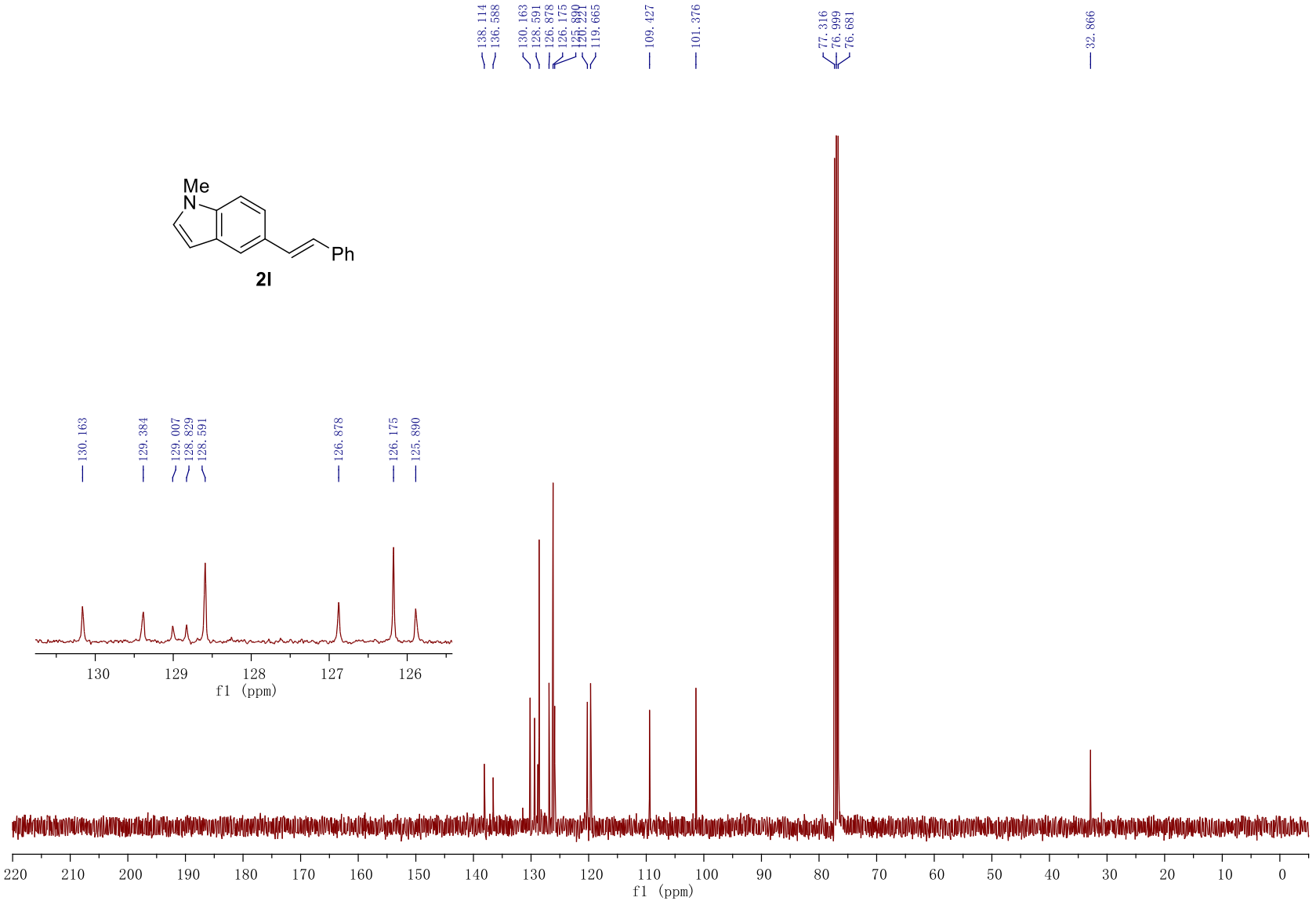
^{13}C NMR Spectrum of (*E*)-2-styrylthiophene (2k)



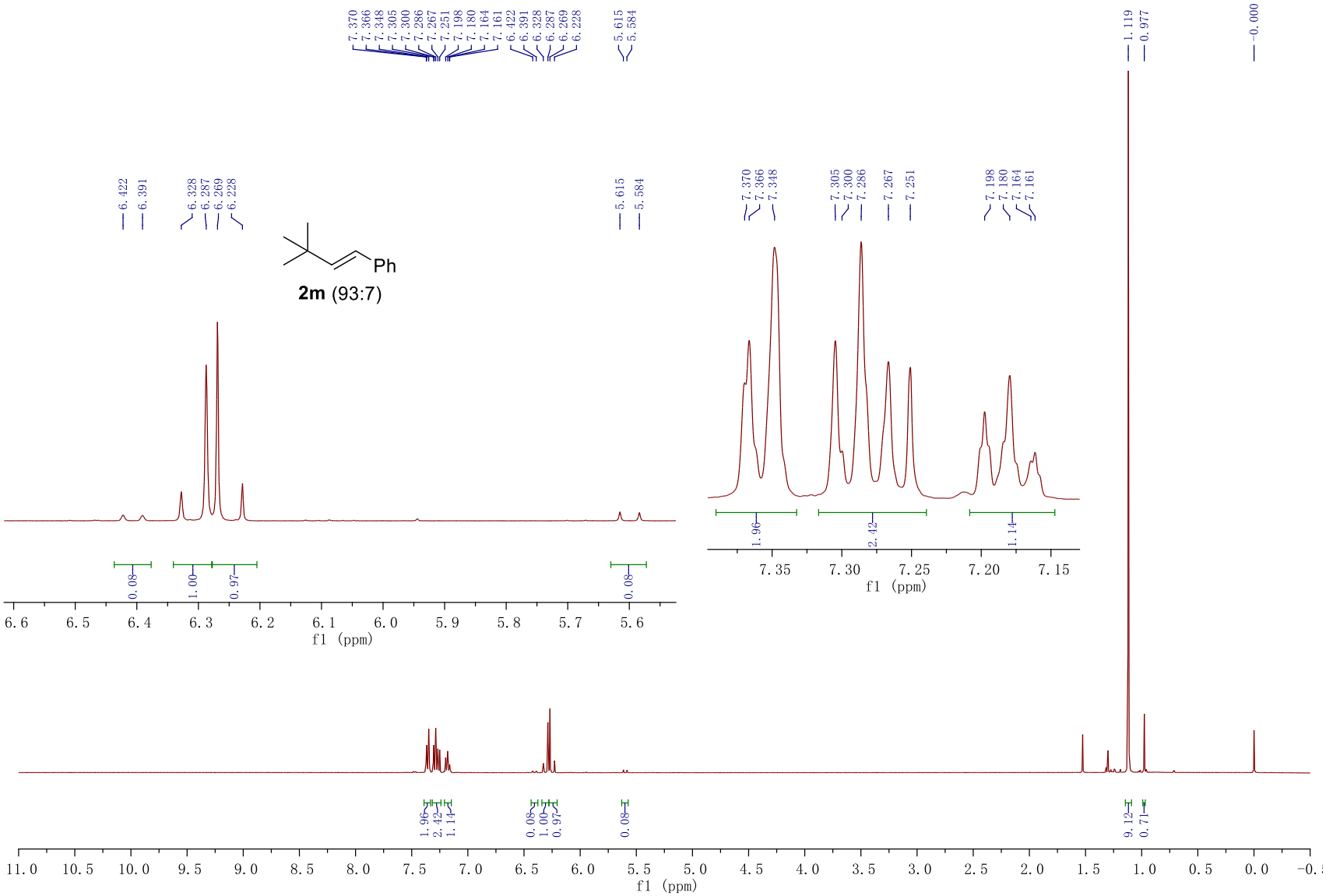
^{1}H NMR Spectrum of (*E*)-1-methyl-5-styryl-1*H*-indole (2l)



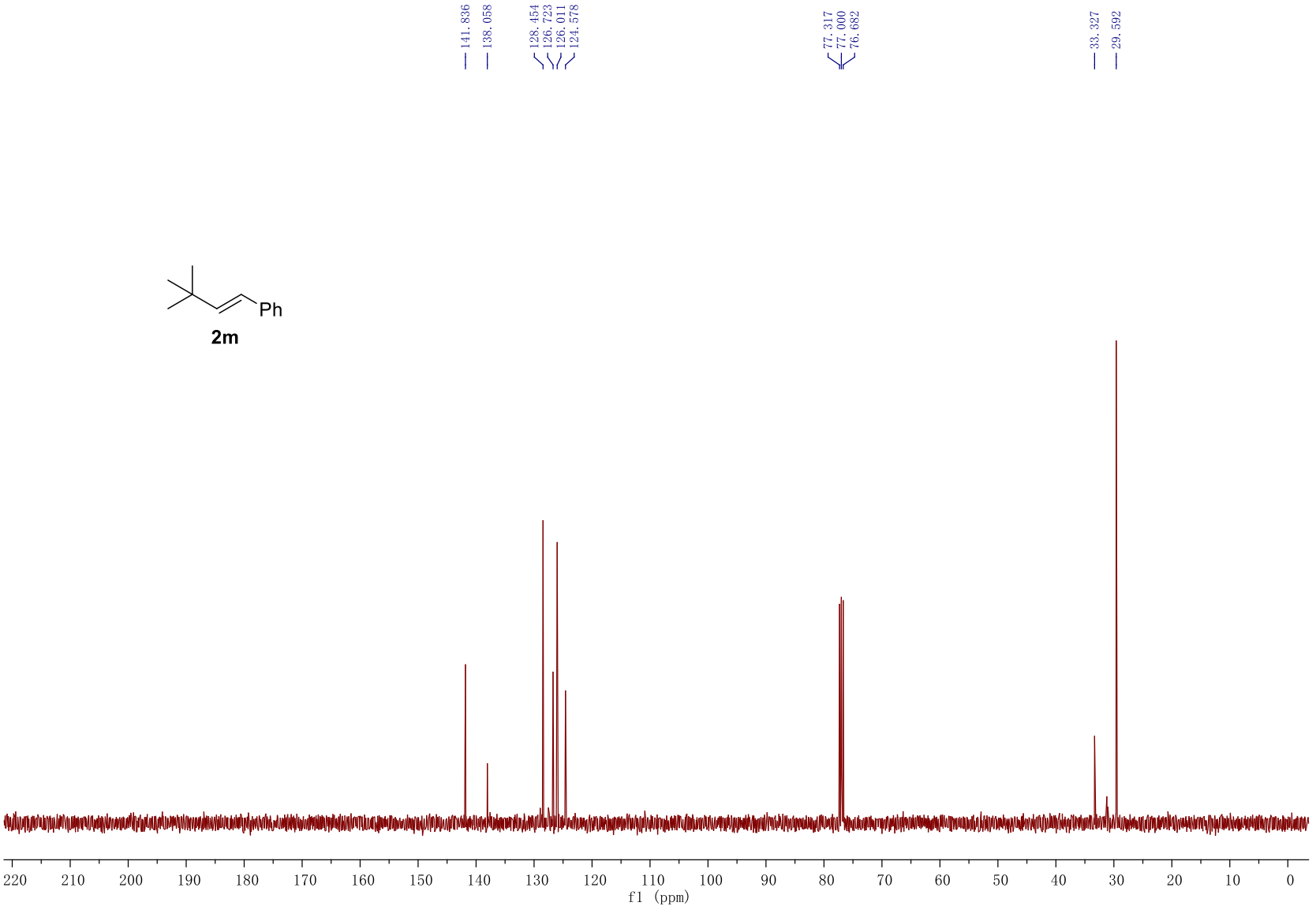
^{13}C NMR Spectrum of (*E*)-1-methyl-5-styryl-1*H*-indole (2l)



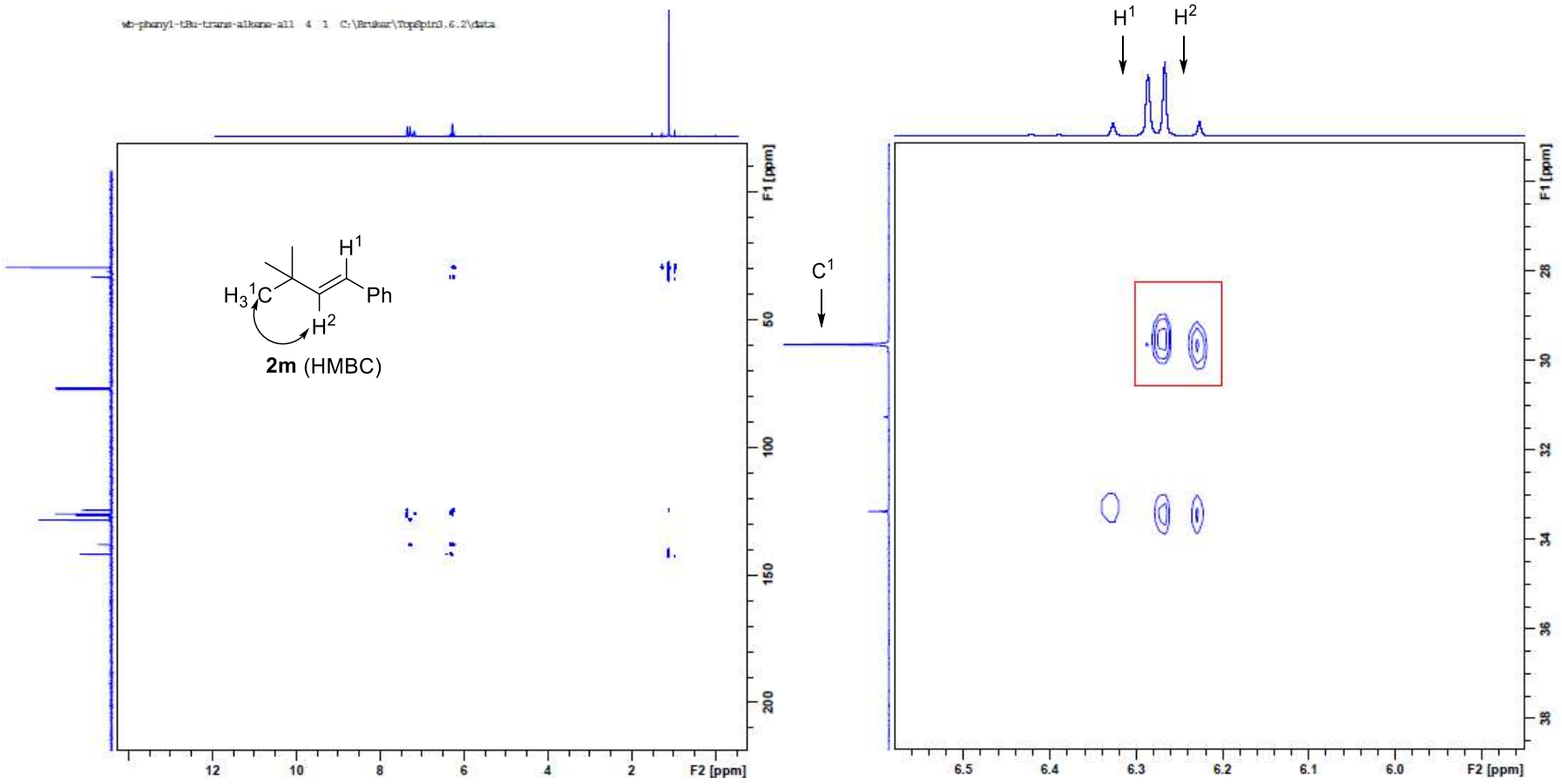
^{1}H NMR Spectrum of (*E*)-(3,3-dimethylbut-1-en-1-yl)benzene (2m)



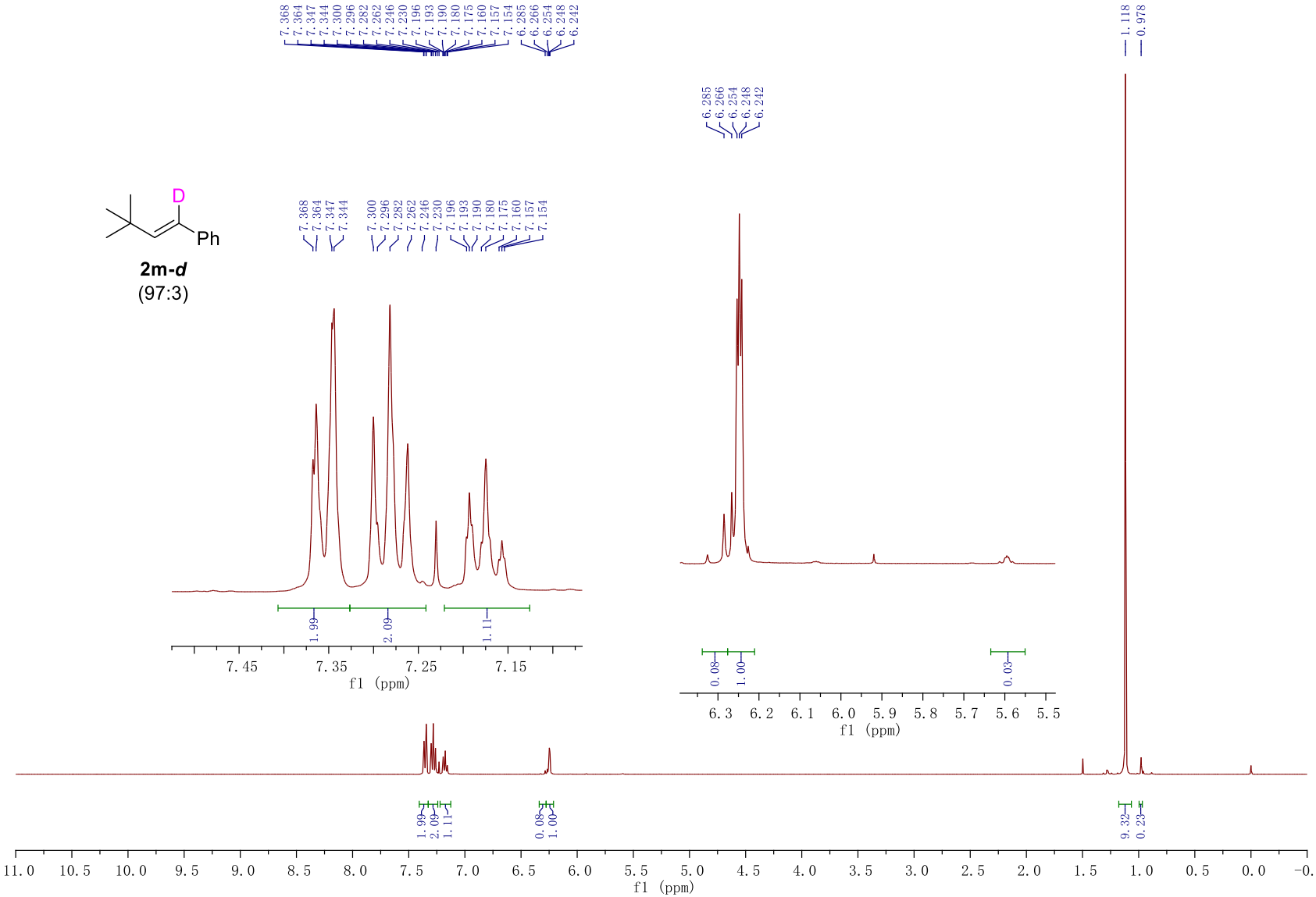
^{13}C NMR Spectrum of (*E*)-(3,3-dimethylbut-1-en-1-yl)benzene (2m)



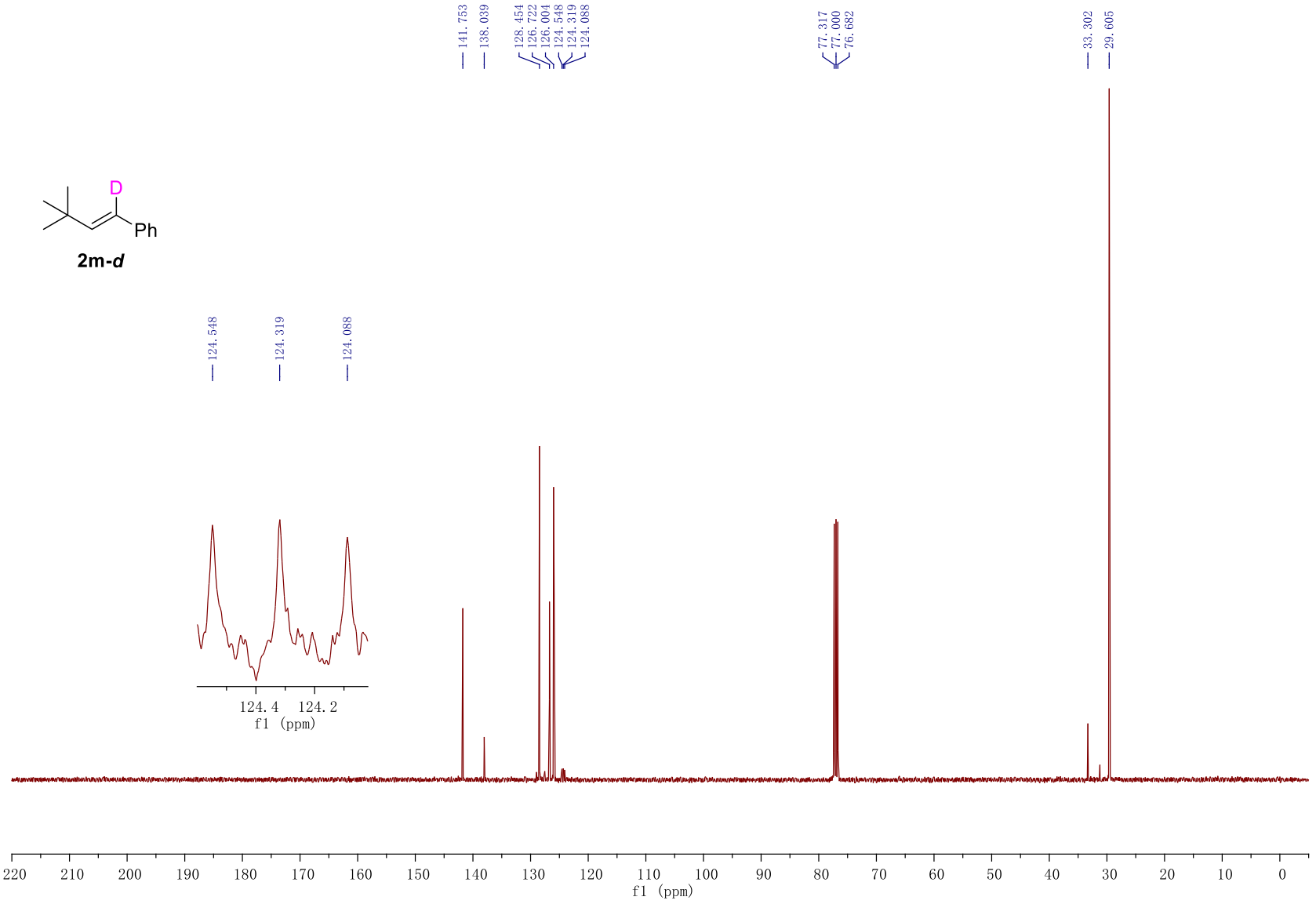
HMBC of (*E*)-(3,3-dimethylbut-1-en-1-yl)benzene (2m)



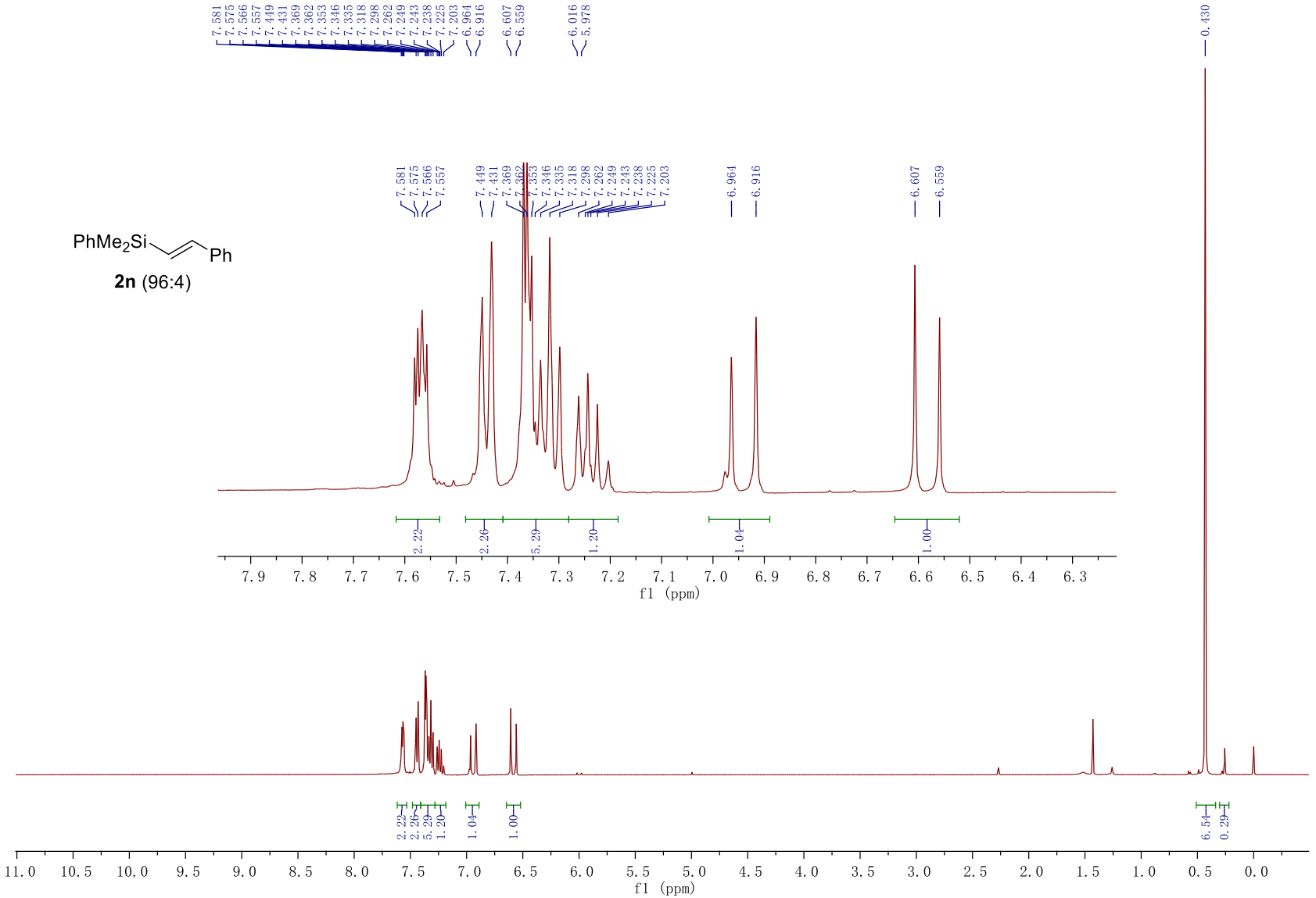
^{1}H NMR Spectrum of (*E*)-(3,3-dimethylbut-1-en-1-yl-1-*d*)benzene (2m-*d*)



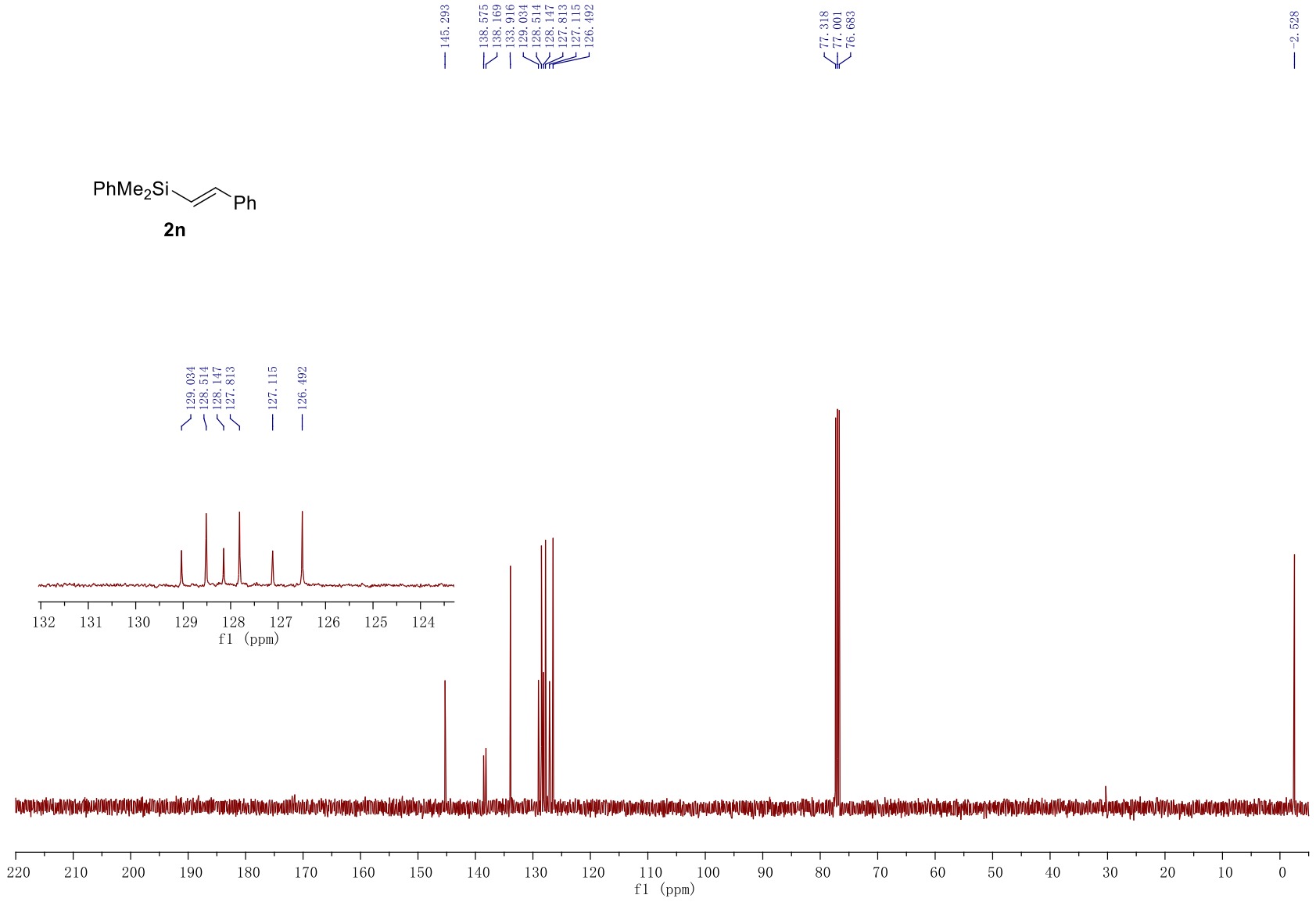
^{13}C NMR Spectrum of (*E*)-(3,3-dimethylbut-1-en-1-yl-1-*d*)benzene (2m-*d*)



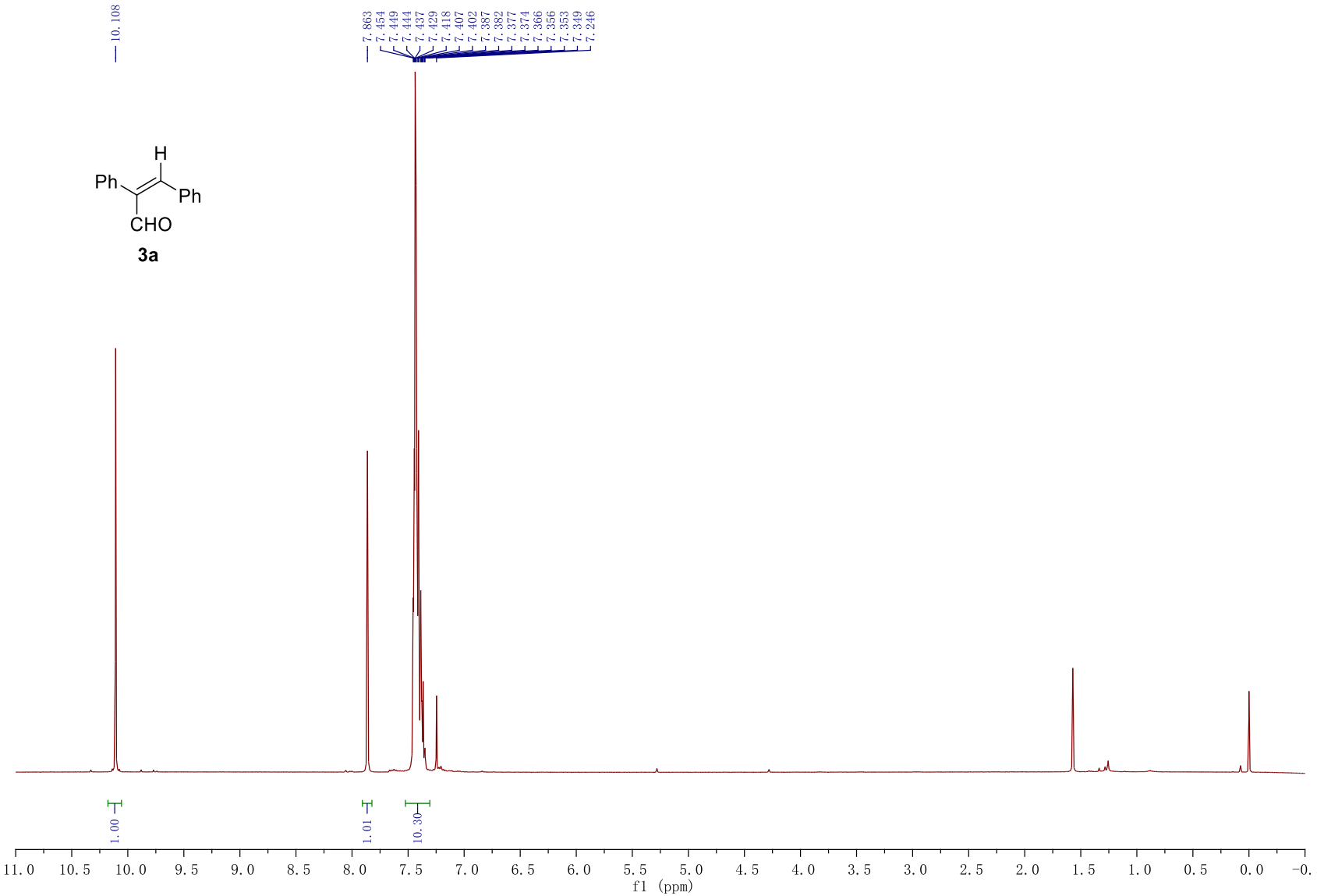
^{1}H NMR Spectrum of (*E*)-dimethyl(phenyl)(styryl)silane (2n)



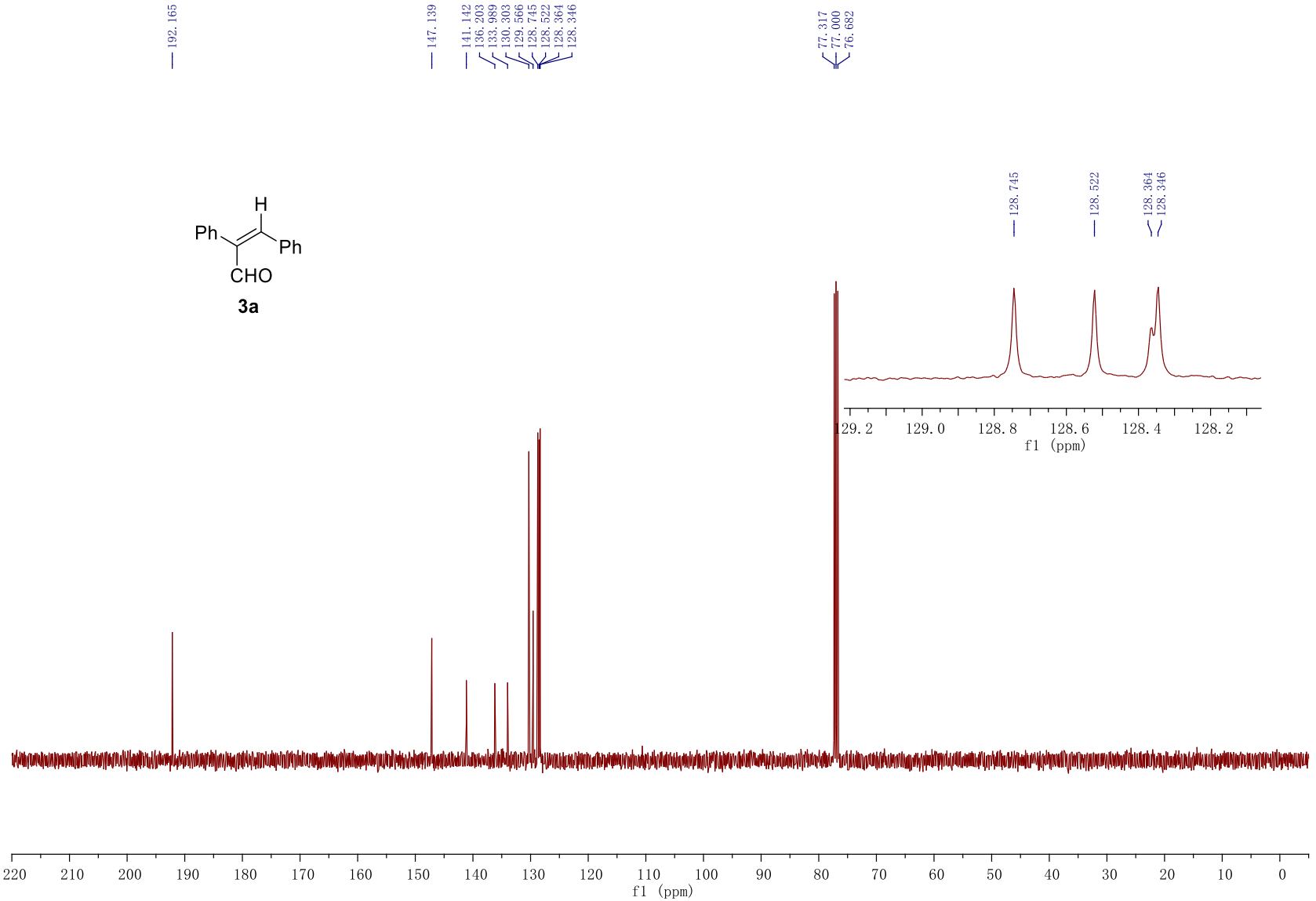
^{13}C NMR Spectrum of (*E*)-dimethyl(phenyl)(styryl)silane (2n)



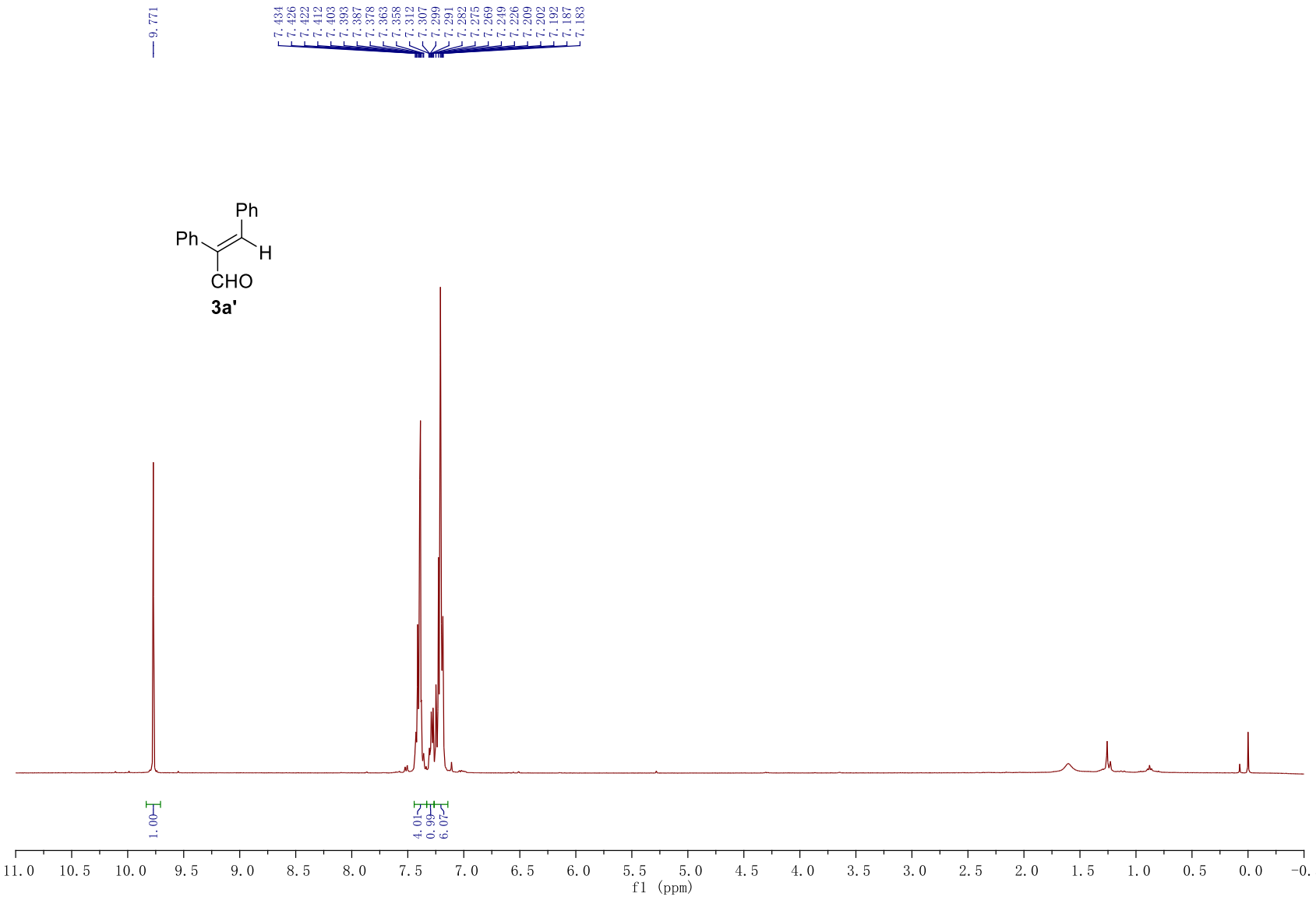
^{1}H NMR Spectrum of (*Z*)-2,3-diphenylacrylaldehyde (3a)



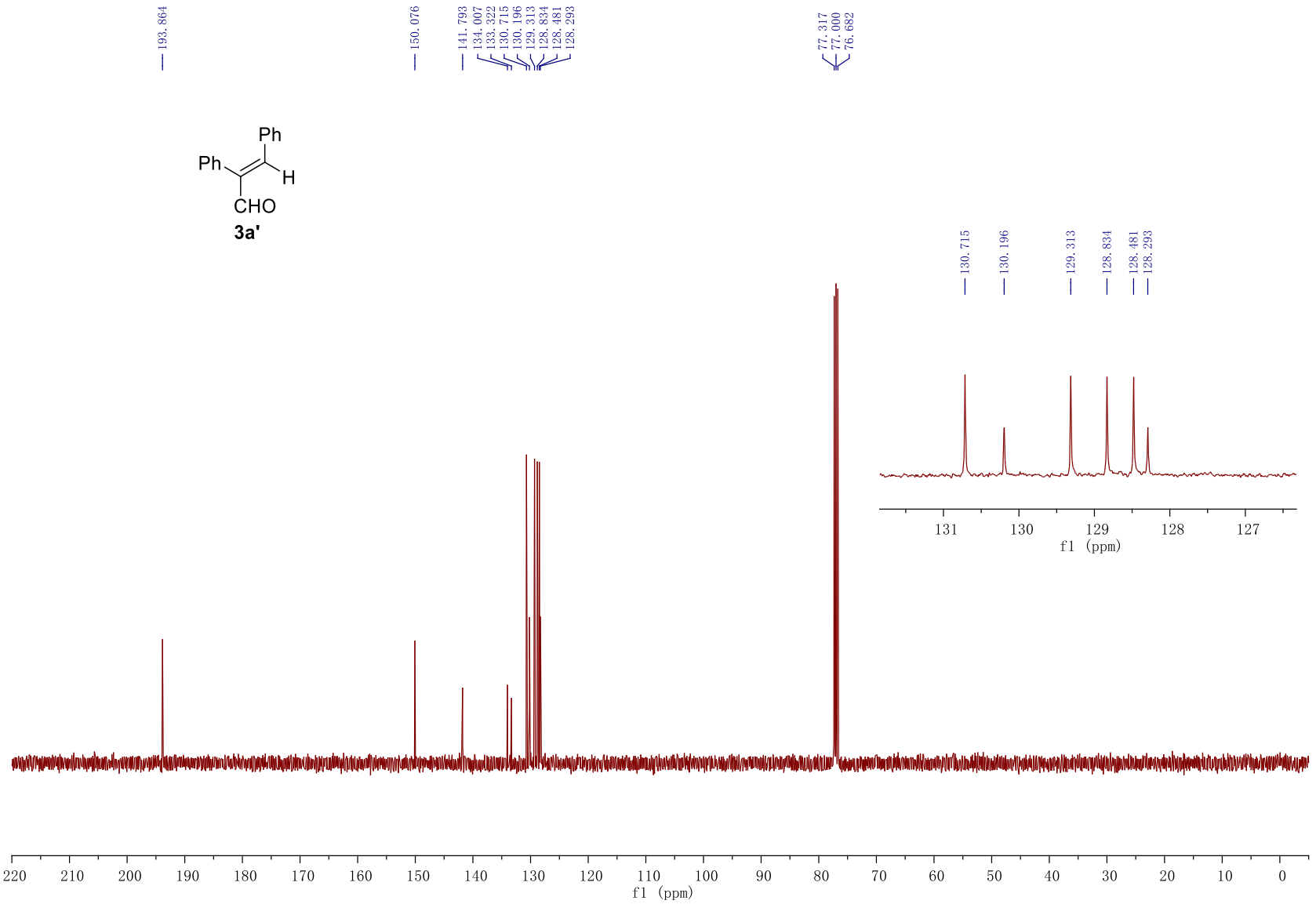
^{13}C NMR Spectrum of (*Z*)-2,3-diphenylacrylaldehyde (3a)



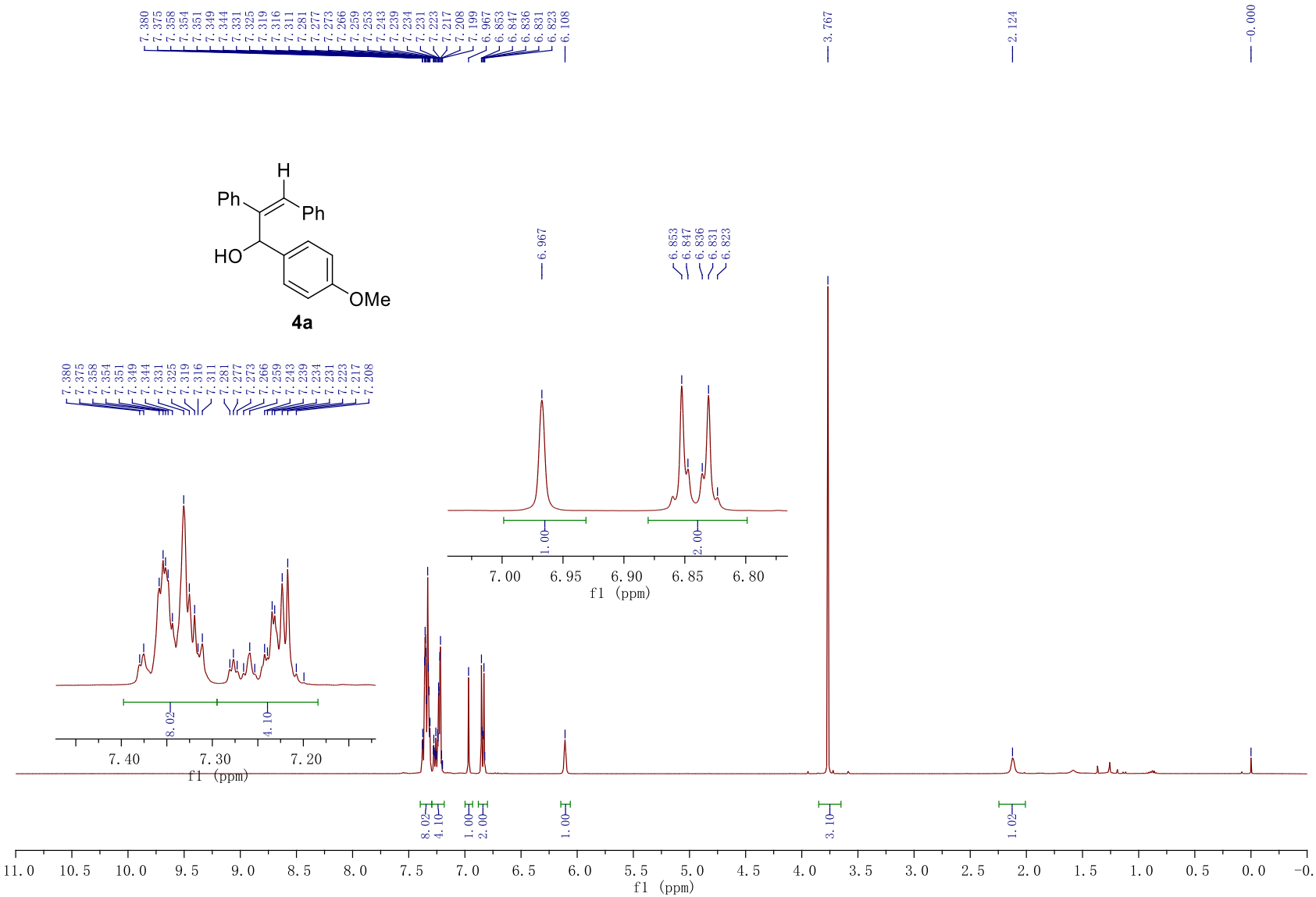
^{1}H NMR Spectrum of (*E*)-2,3-diphenylacrylaldehyde (3a')



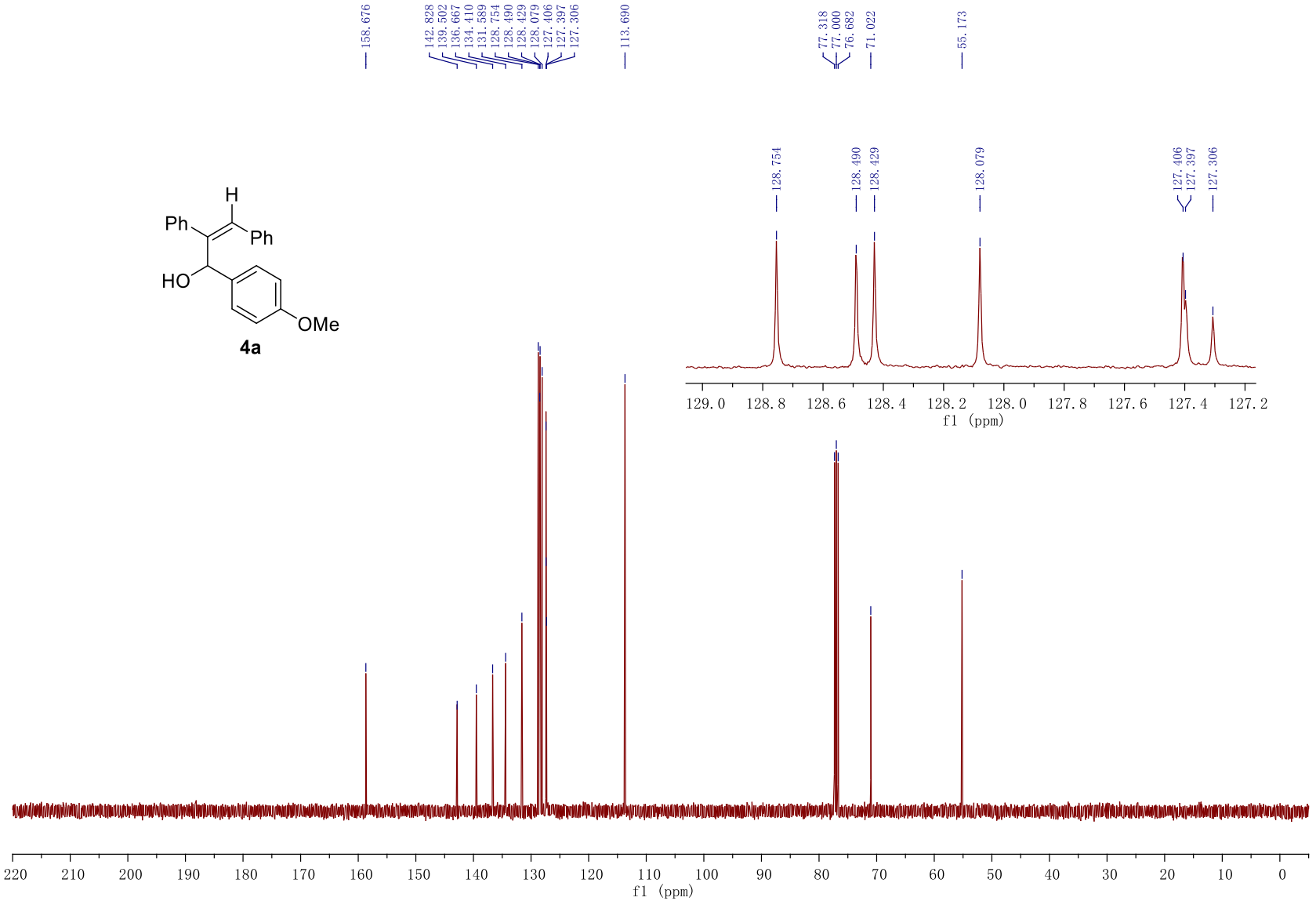
^{13}C NMR Spectrum of (*E*)-2,3-diphenylacrylaldehyde (3a')



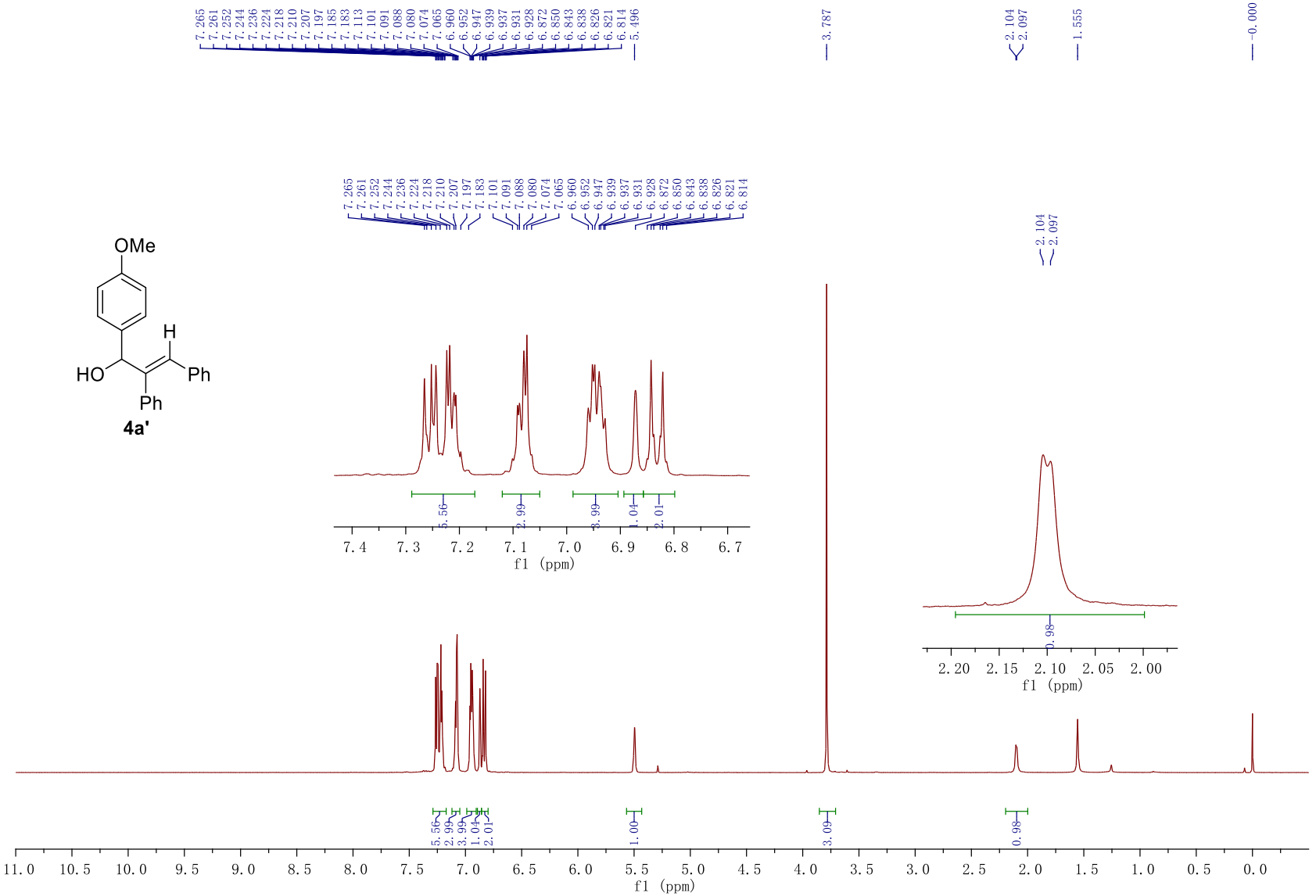
^{1}H NMR Spectrum of (*Z*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (4a)



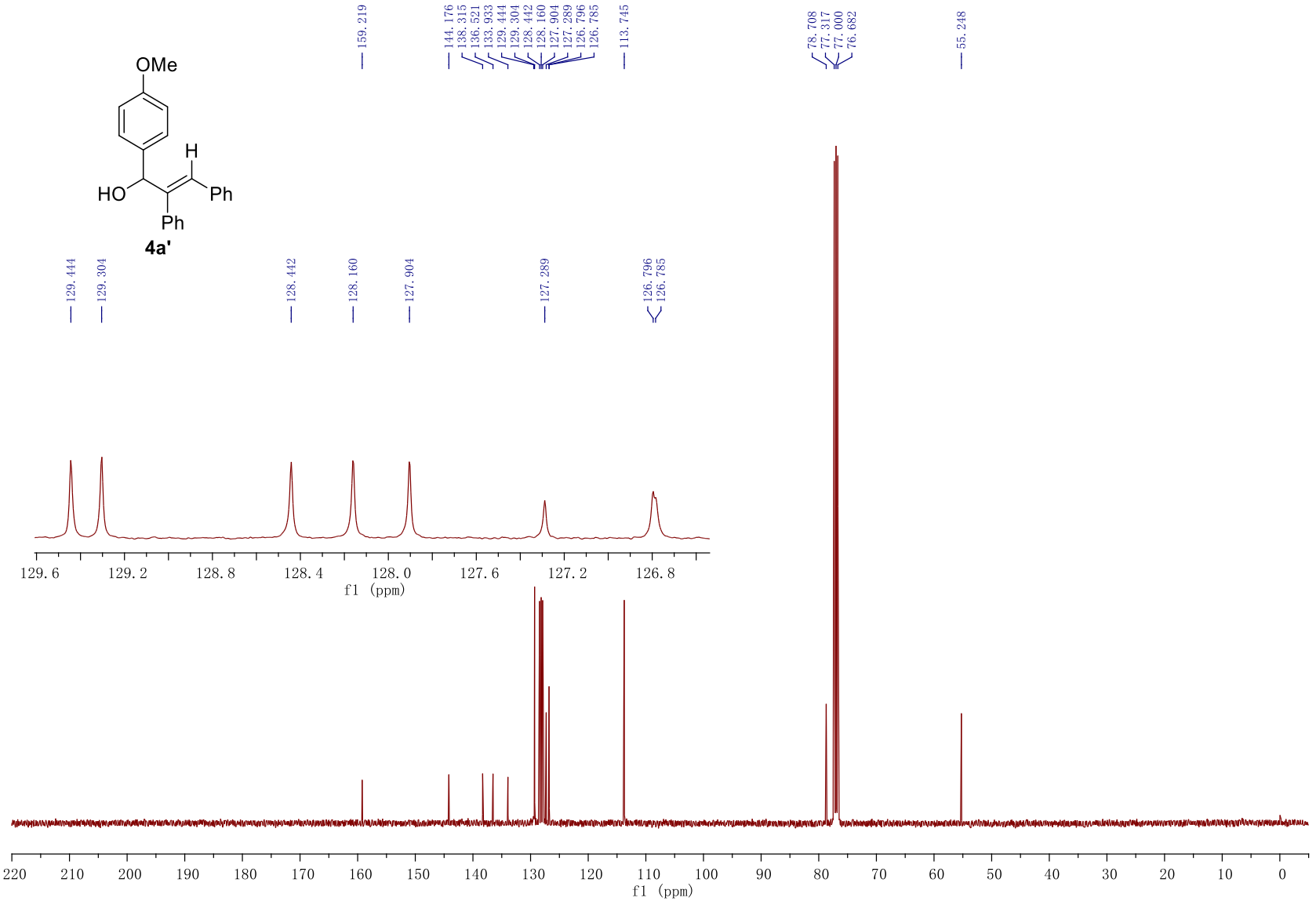
^{13}C NMR Spectrum of (*Z*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (4a)



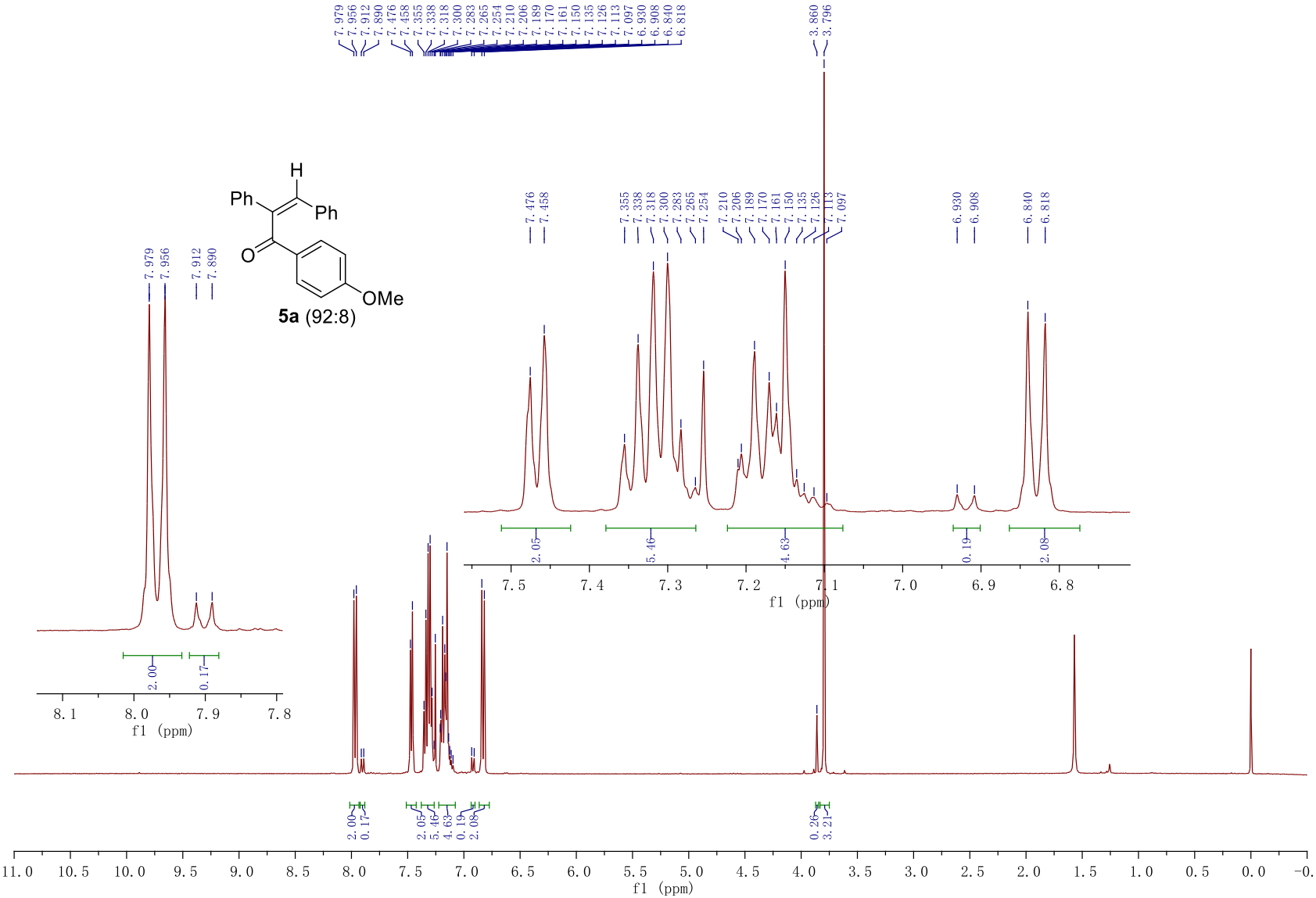
^{1}H NMR Spectrum of (*E*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (4a')



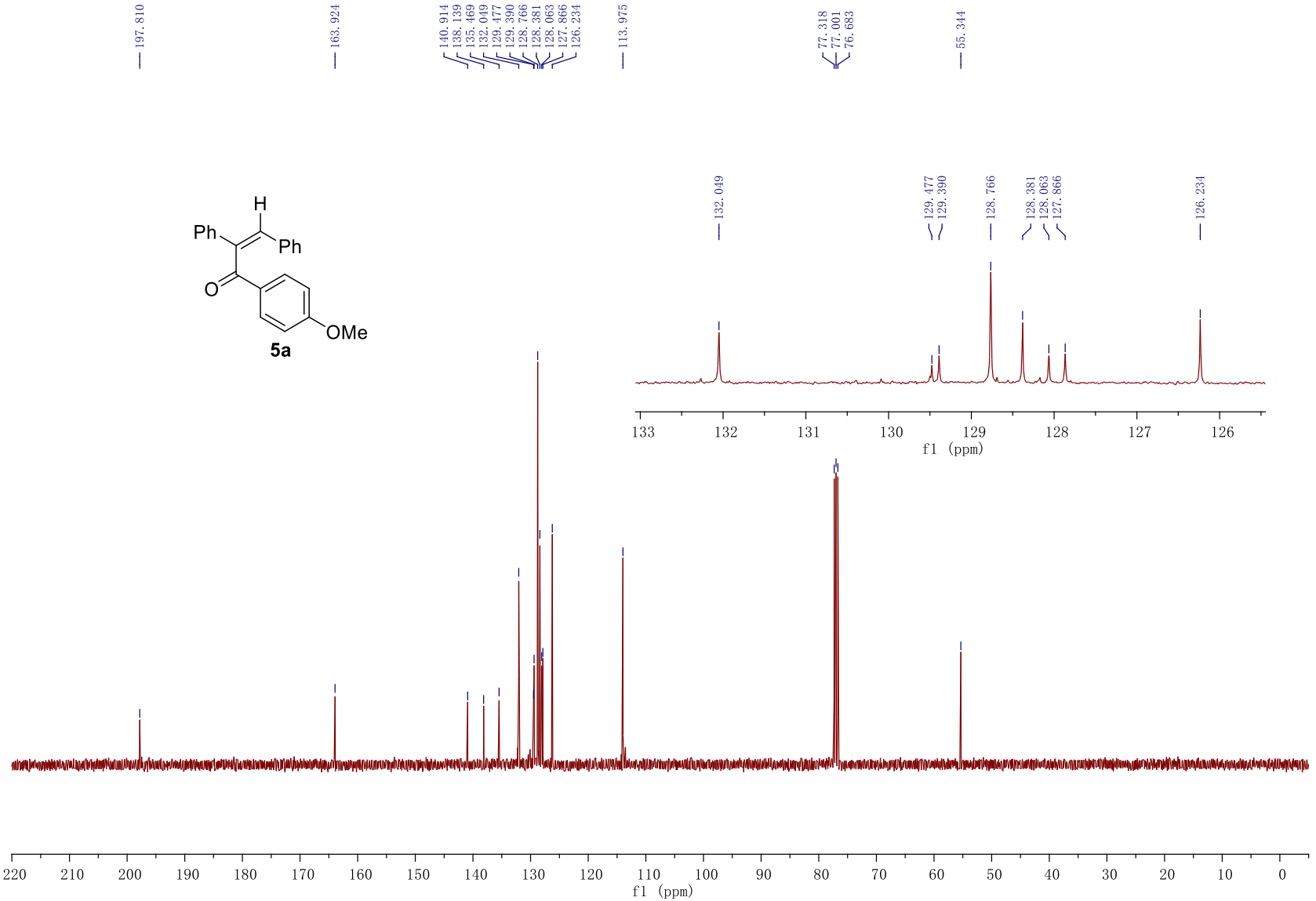
^{13}C NMR Spectrum of (*E*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (4a')



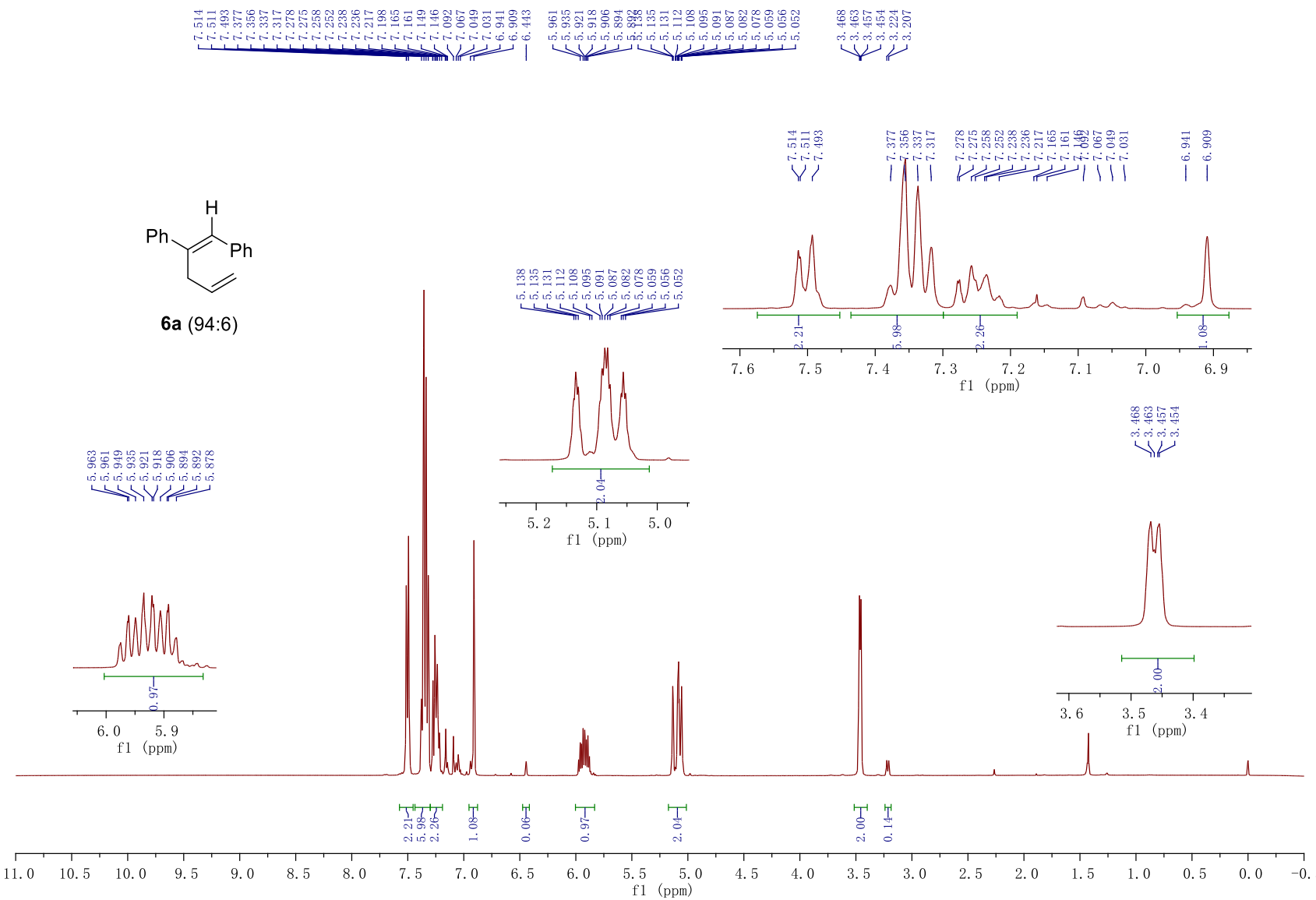
^{1}H NMR Spectrum of (*Z*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-one (5a)



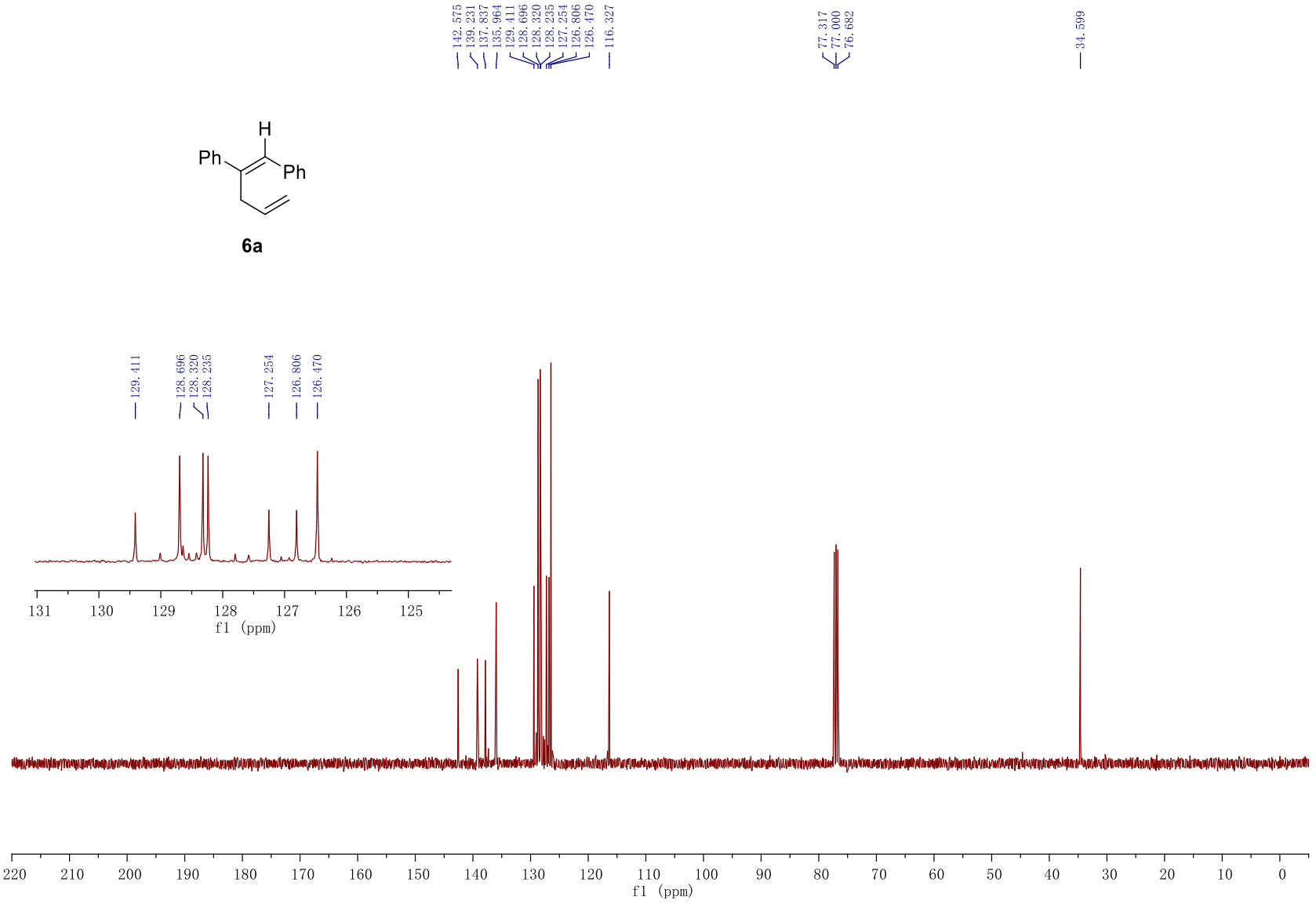
^{13}C NMR Spectrum of (*Z*)-1-(4-methoxyphenyl)-2,3-diphenylprop-2-en-1-one (5a)



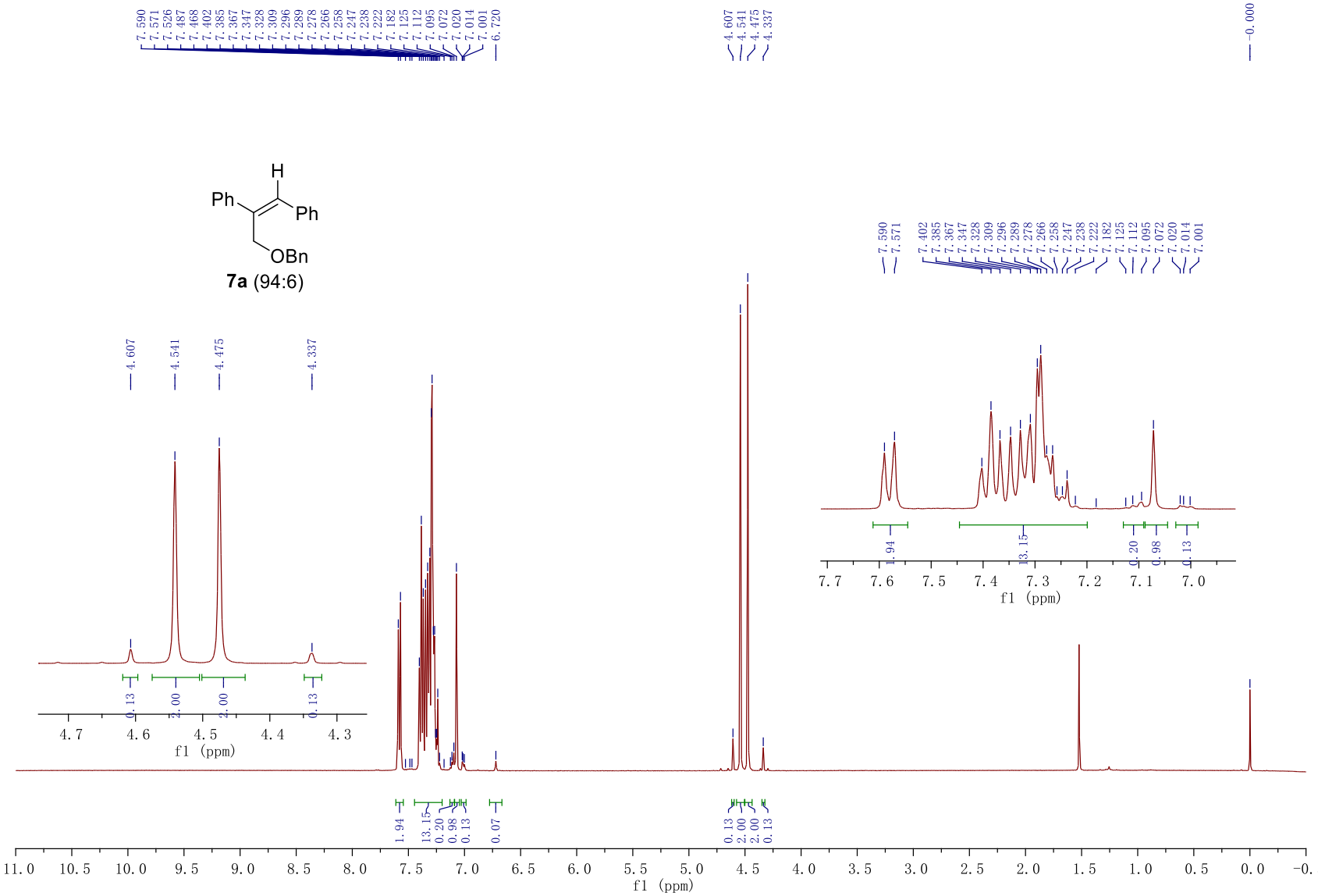
^{1}H NMR Spectrum of (*E*)-penta-1,4-diene-1,2-diyldibenzene (6a)



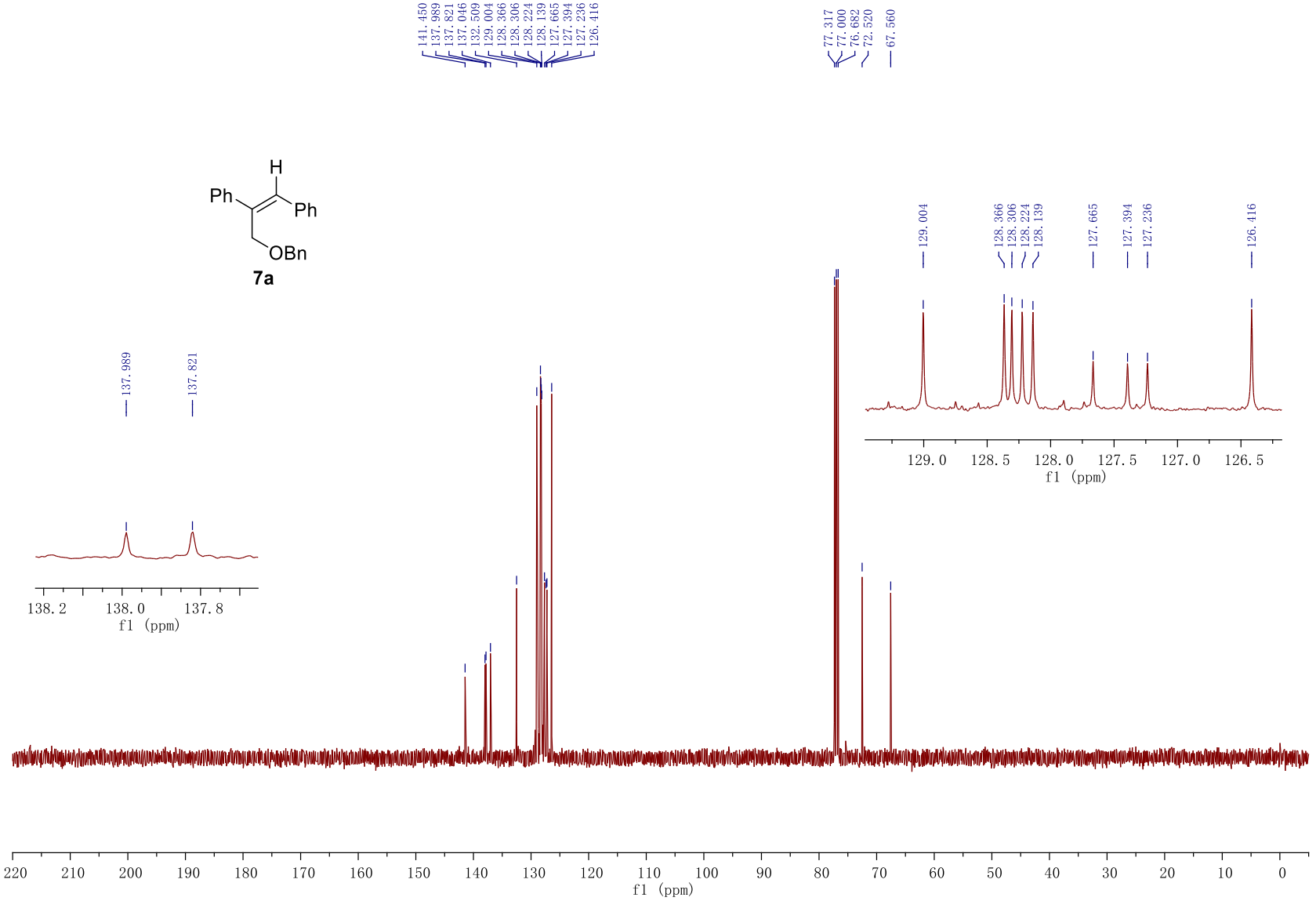
^{13}C NMR Spectrum of (*E*)-penta-1,4-diene-1,2-diyldibenzene (6a)



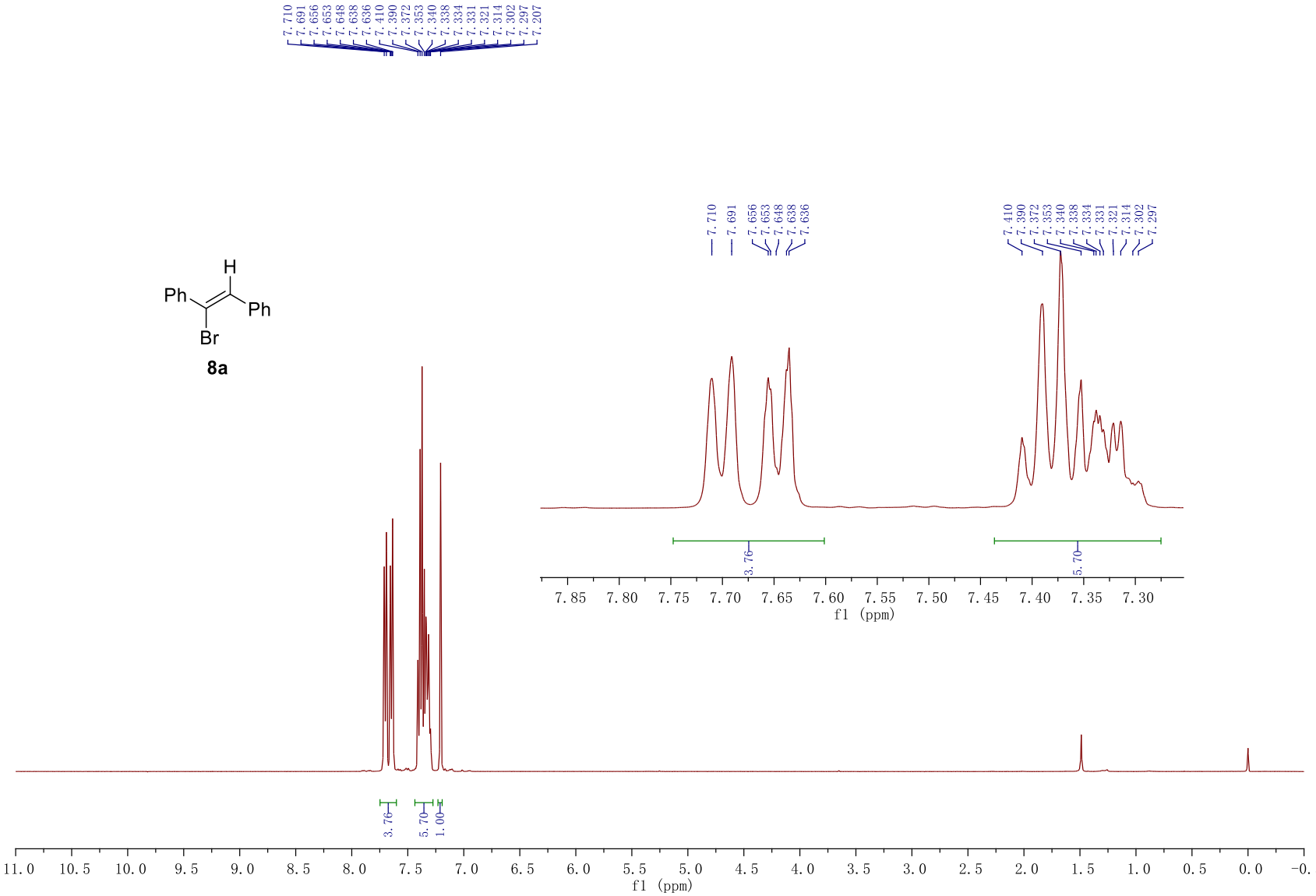
^{1}H NMR Spectrum of (*Z*)-(3-(benzyloxy)prop-1-ene-1,2-diyl)dibenzene (7a)



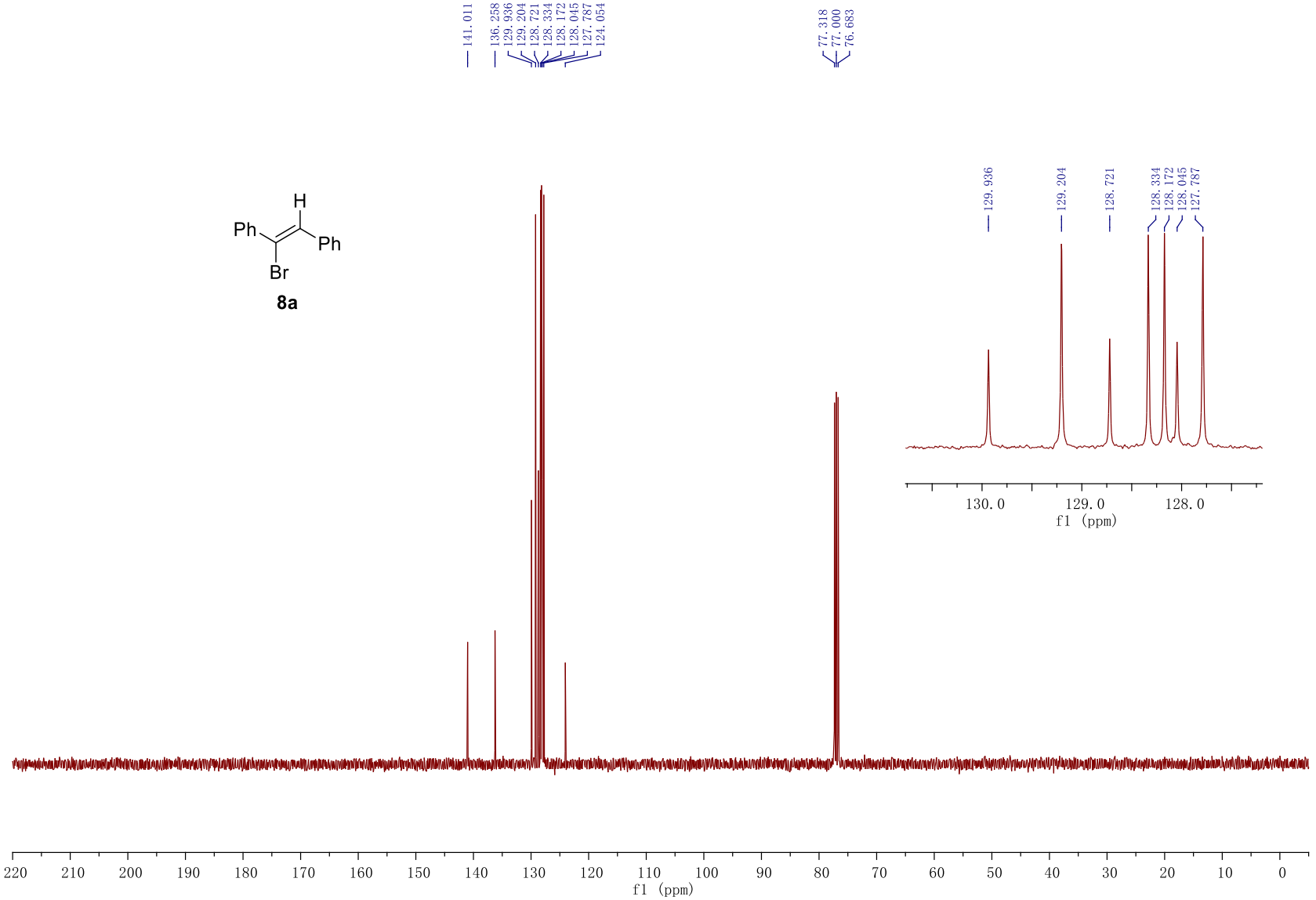
^{13}C NMR Spectrum of (*Z*)-(3-(benzyloxy)prop-1-ene-1,2-diyl)dibenzene (7a)



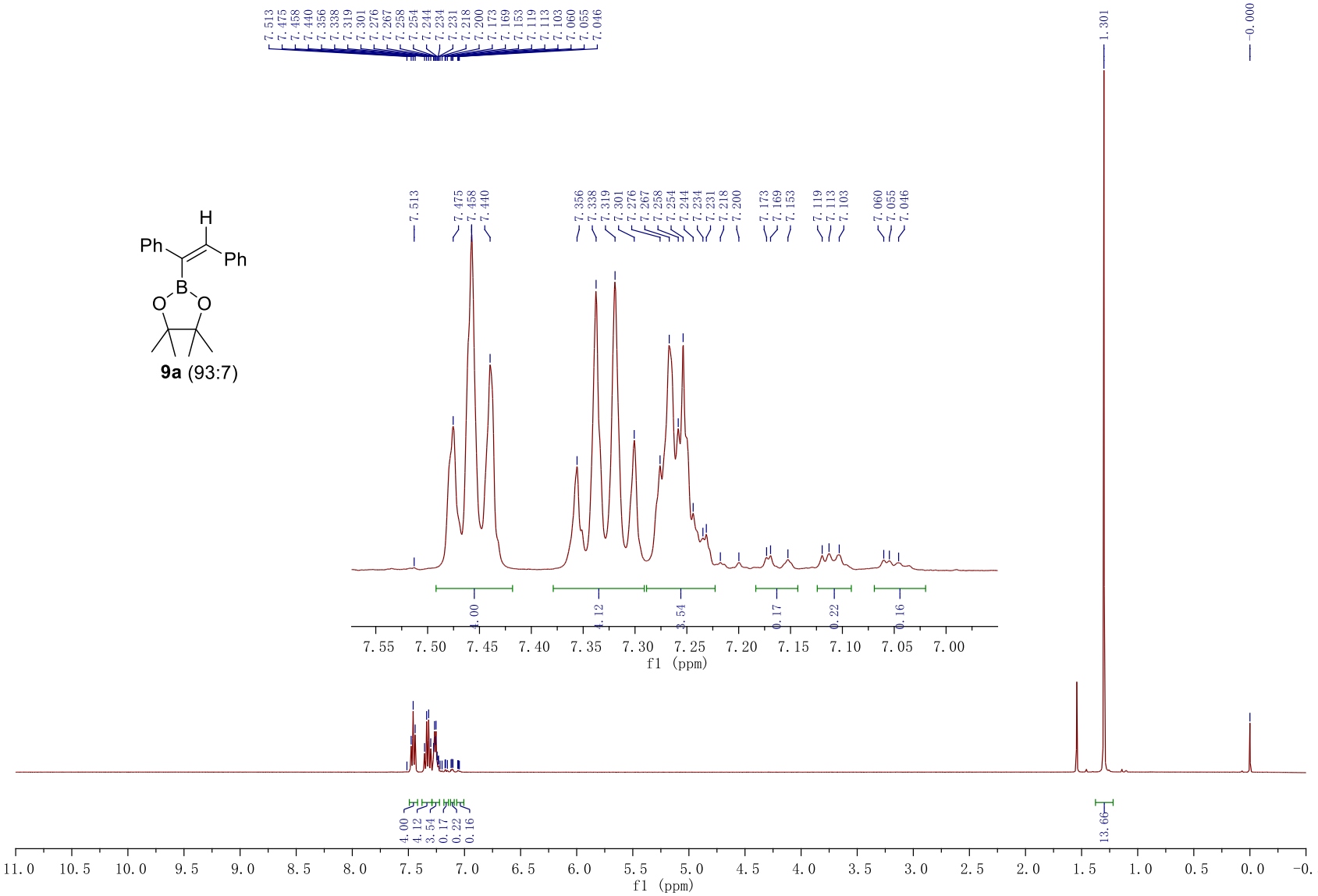
^{1}H NMR Spectrum of (*Z*)-(1-bromoethene-1,2-diyl)dibenzene (8a)



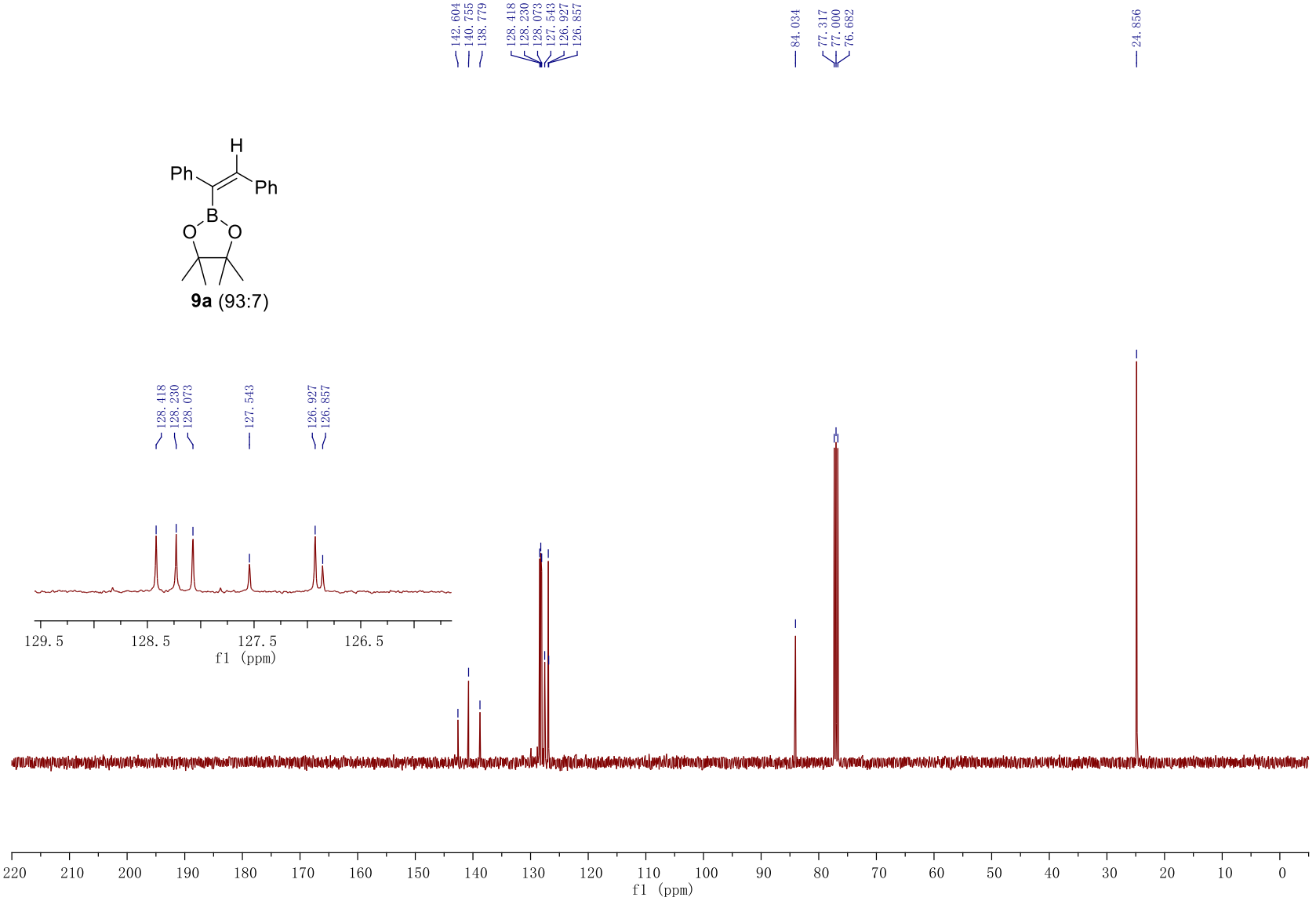
^{13}C NMR Spectrum of (*Z*)-(1-bromoethene-1,2-diyl)dibenzene (8a)



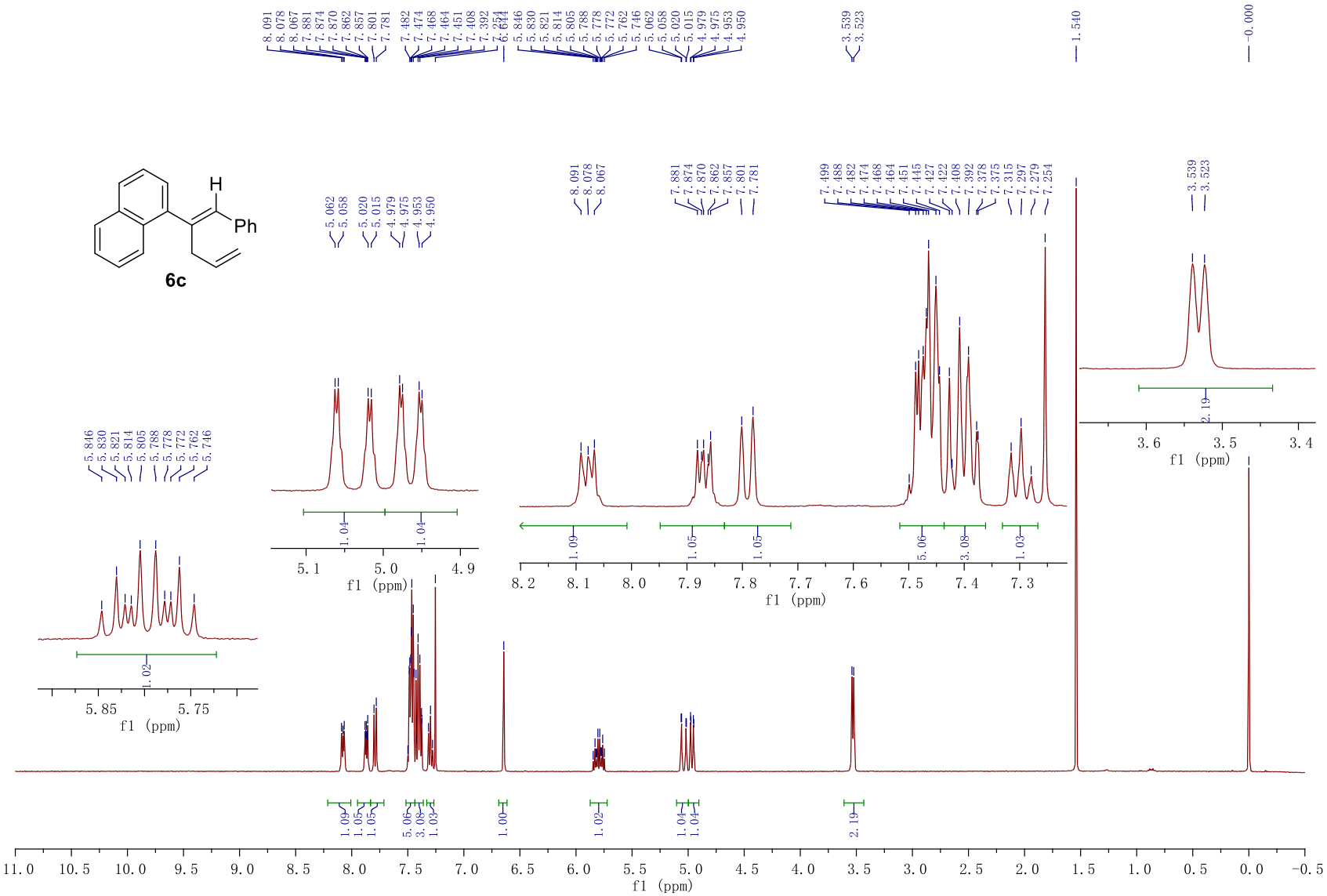
[1]H NMR Spectrum of (*E*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a)



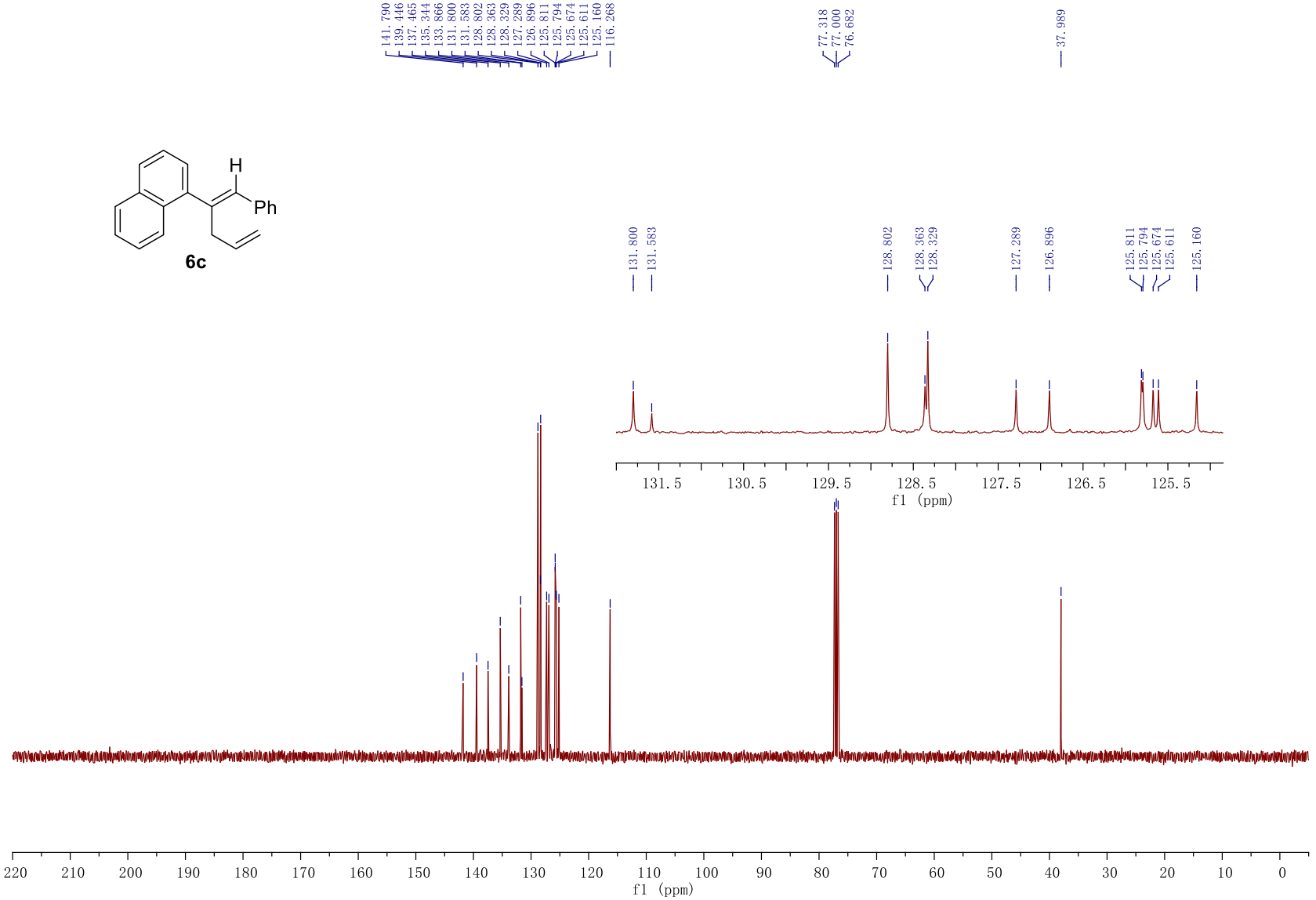
^{13}C NMR Spectrum of (*E*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a)



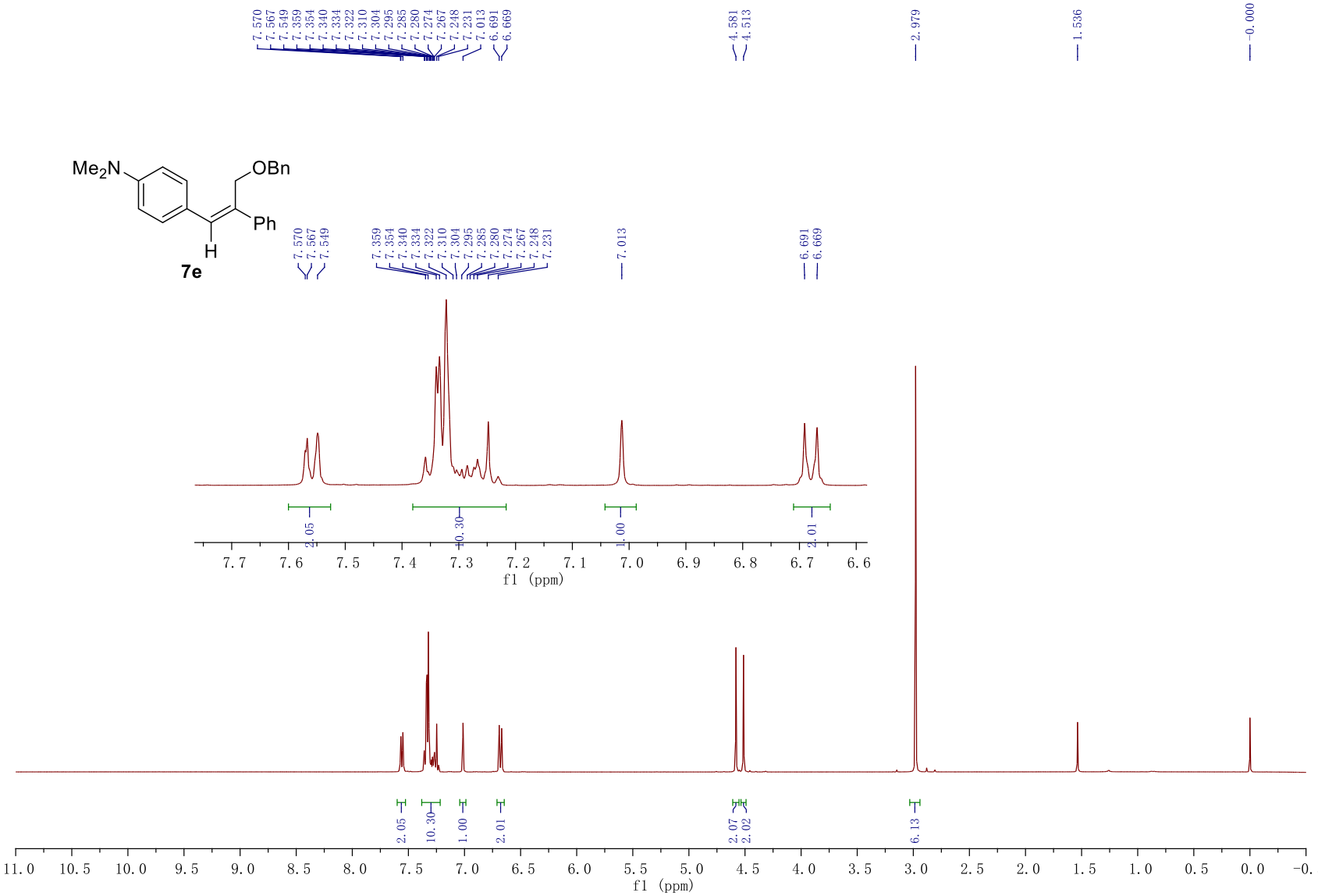
^{1}H NMR Spectrum of (*E*)-1-(1-phenylpenta-1,4-dien-2-yl)naphthalene (6c)



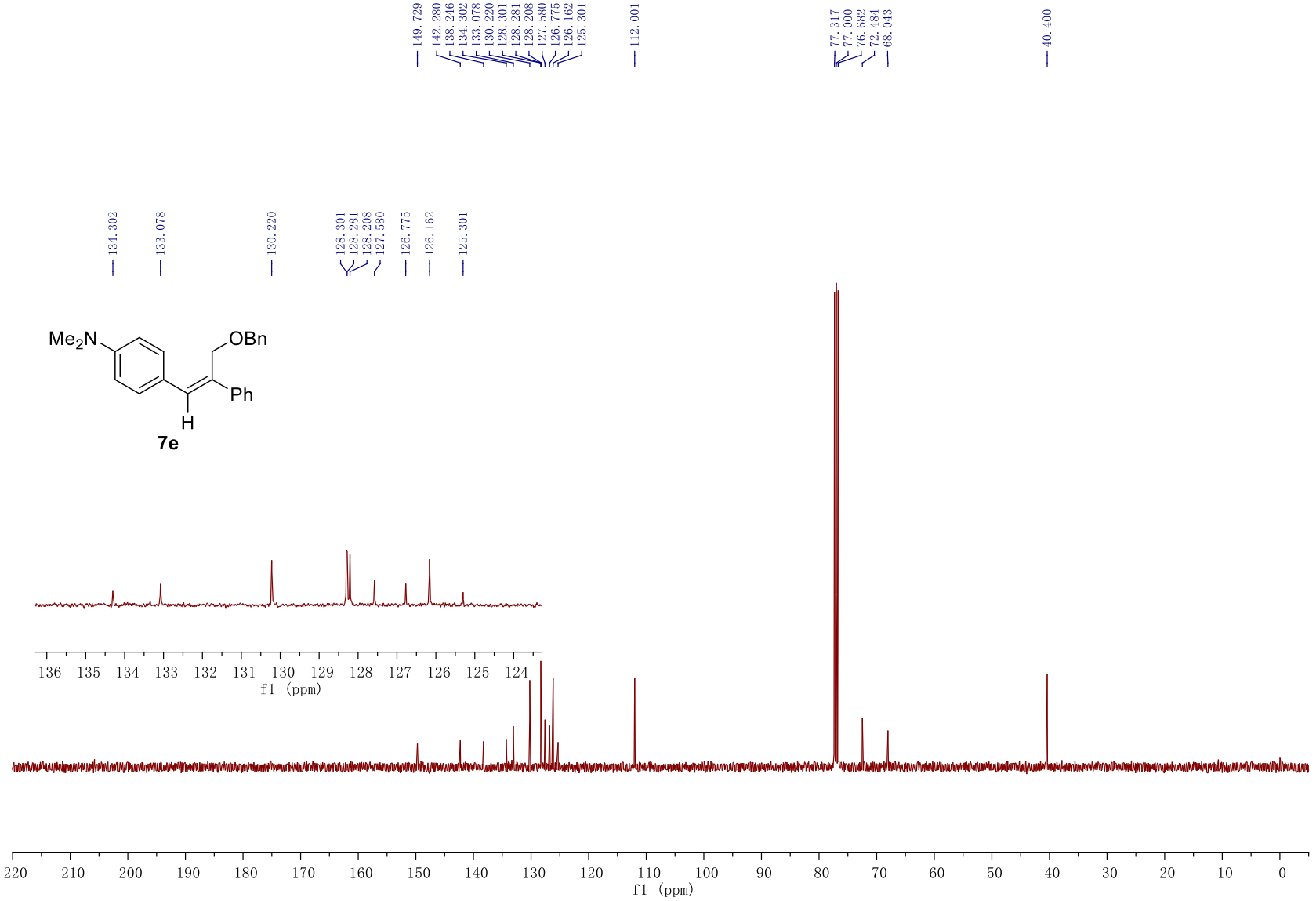
^{13}C NMR Spectrum of (*E*)-1-(1-phenylpenta-1,4-dien-2-yl)naphthalene (6c)



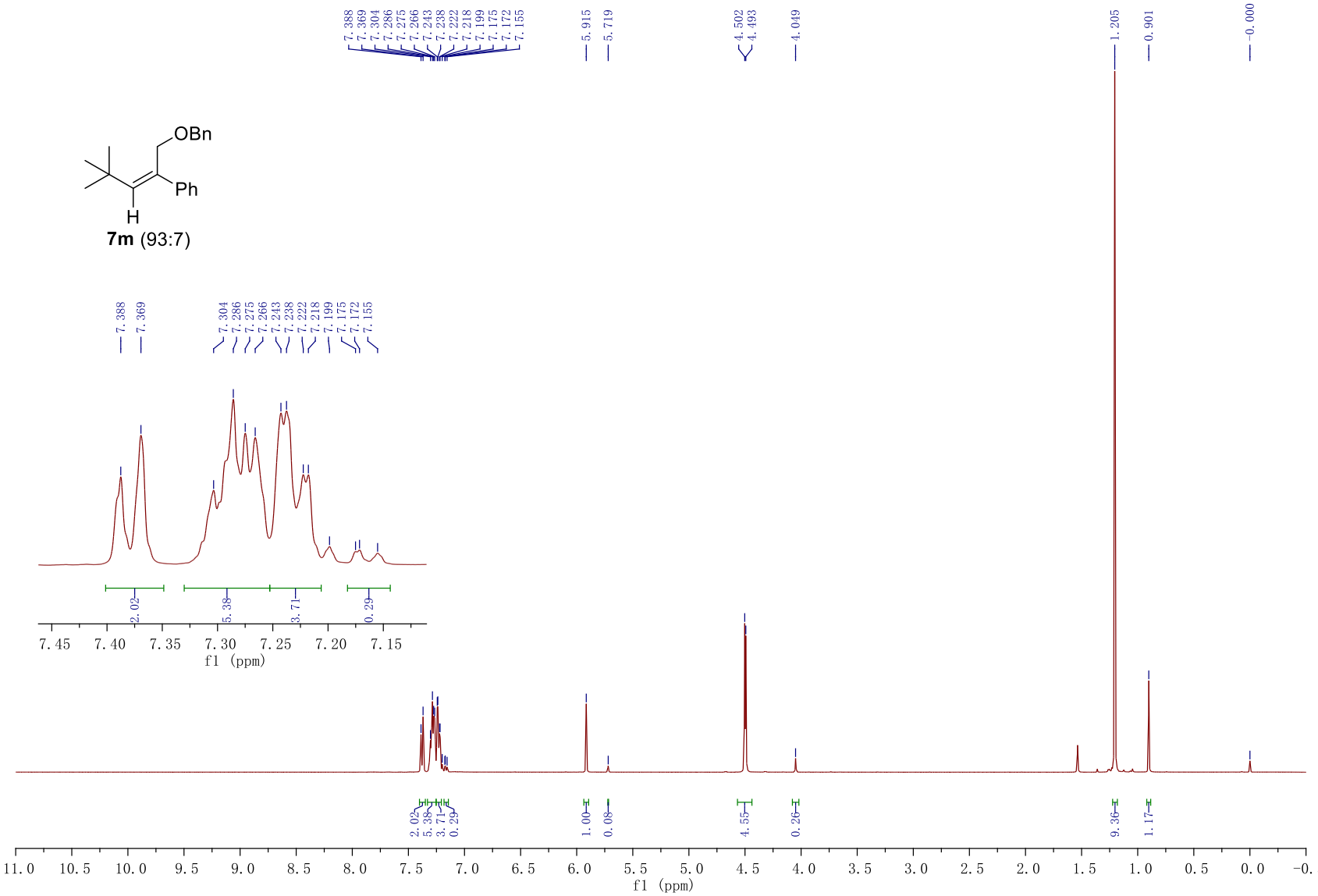
^{1}H NMR Spectrum of (*Z*)-4-(3-(benzyloxy)-2-phenylprop-1-en-1-yl)-*N*,*N*-dimethylaniline (7e)



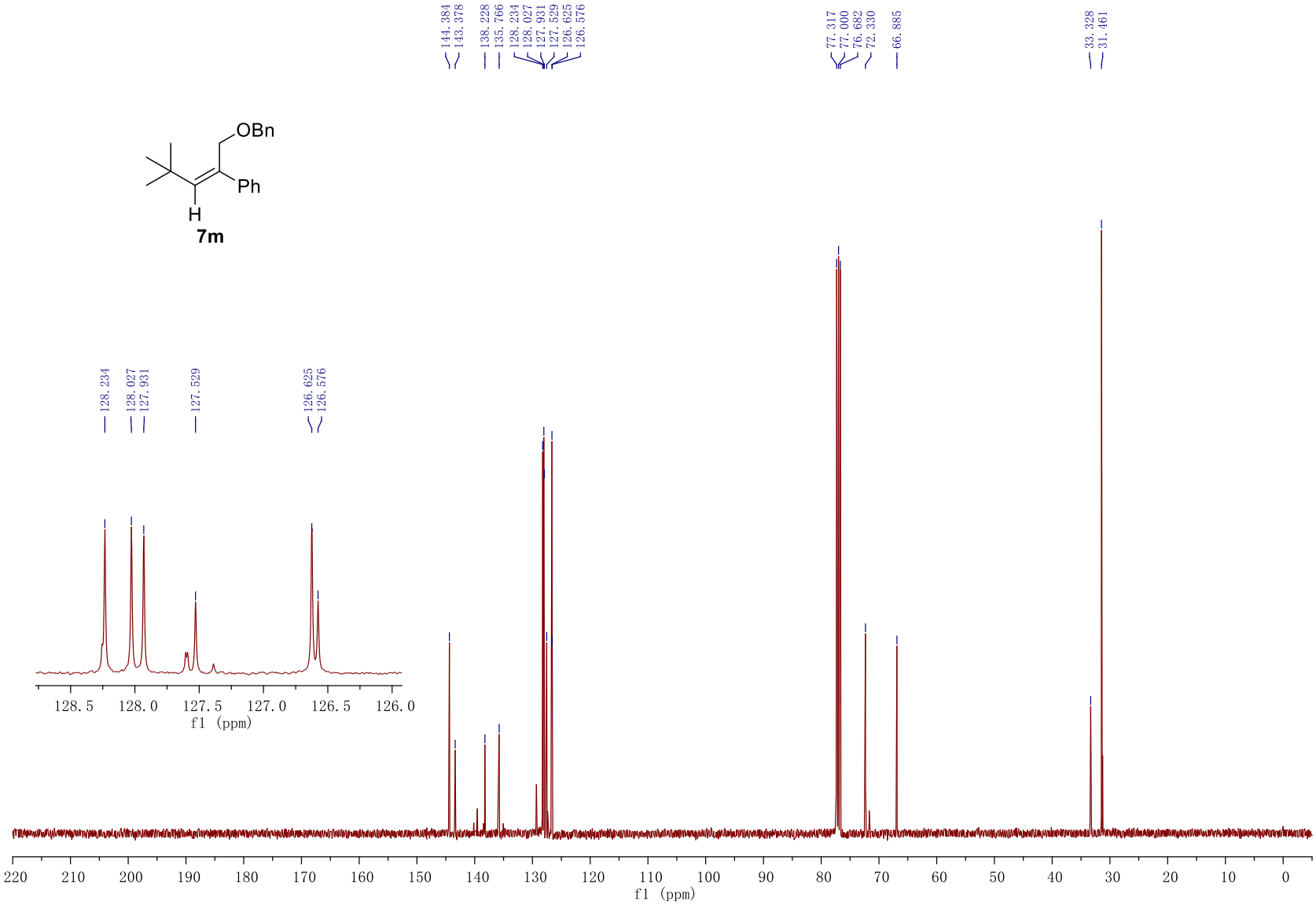
^{13}C NMR Spectrum of (*Z*)-4-(3-(benzyloxy)-2-phenylprop-1-en-1-yl)-*N*,*N*-dimethylaniline (7e)



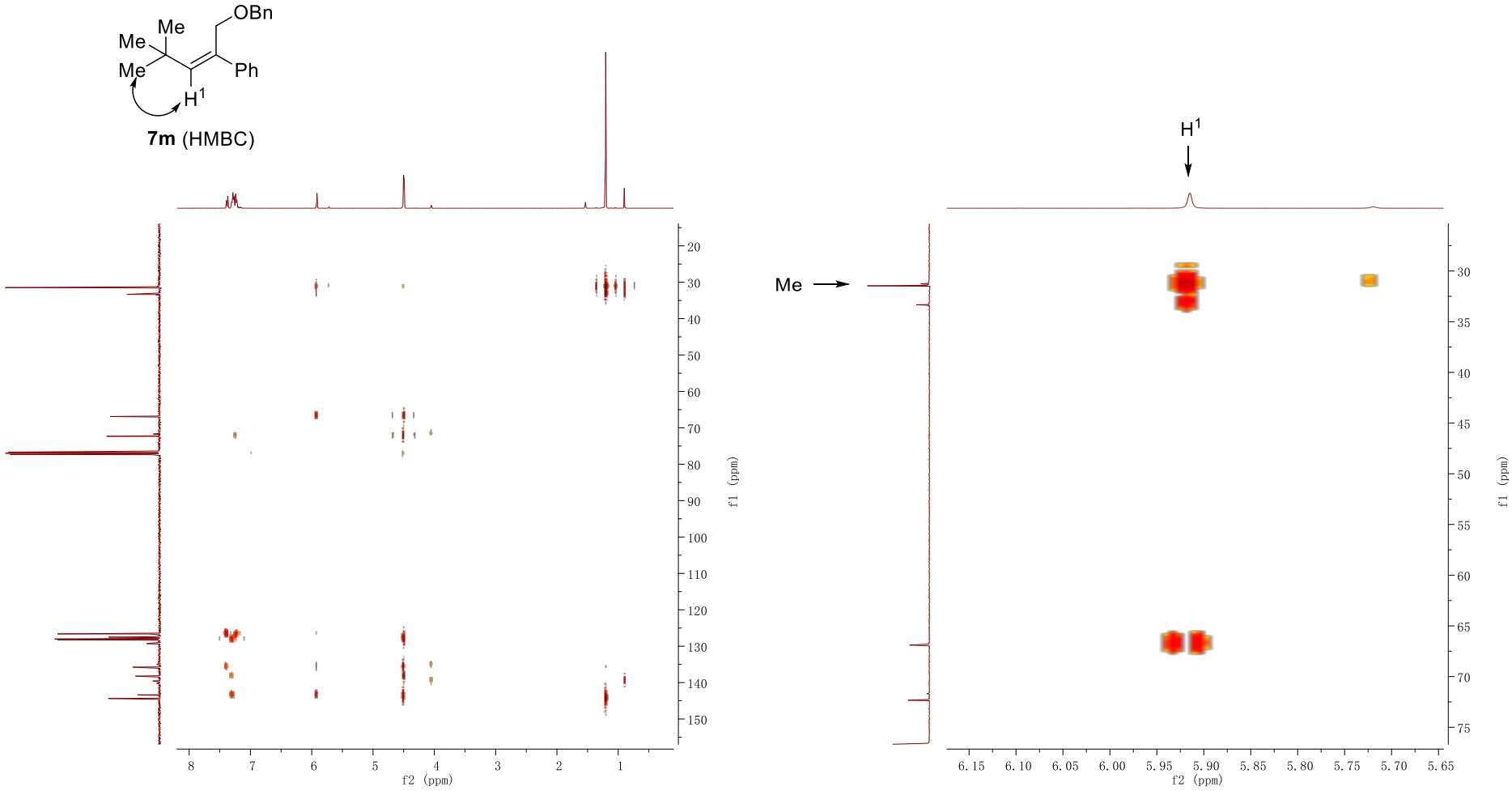
[1]H NMR Spectrum of (*Z*)-((2-benzylidene-3,3-dimethylbutoxy)methyl)benzene (7m)



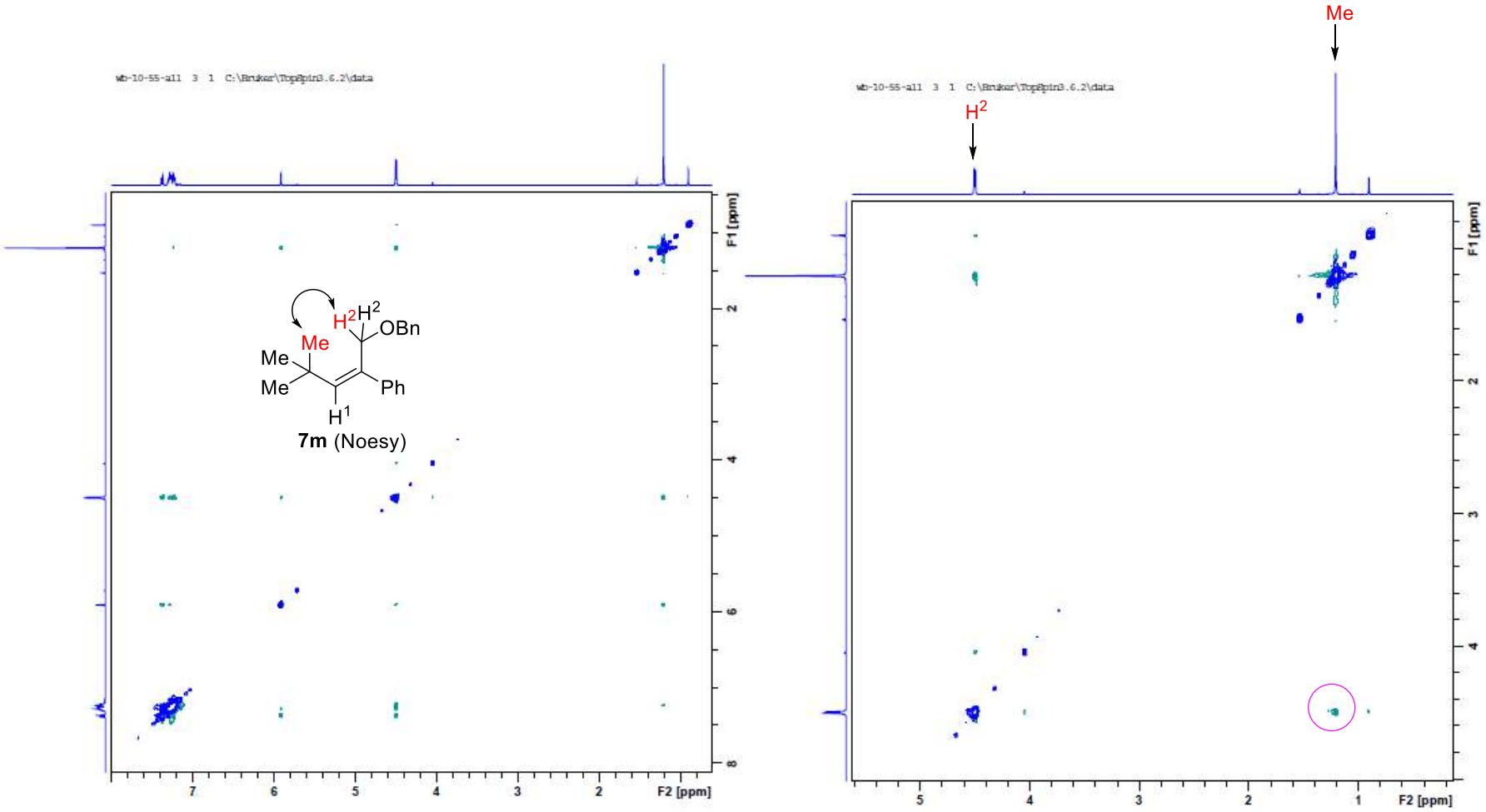
^{13}C NMR Spectrum of (*Z*)-((2-benzylidene-3,3-dimethylbutoxy)methyl)benzene (7m)



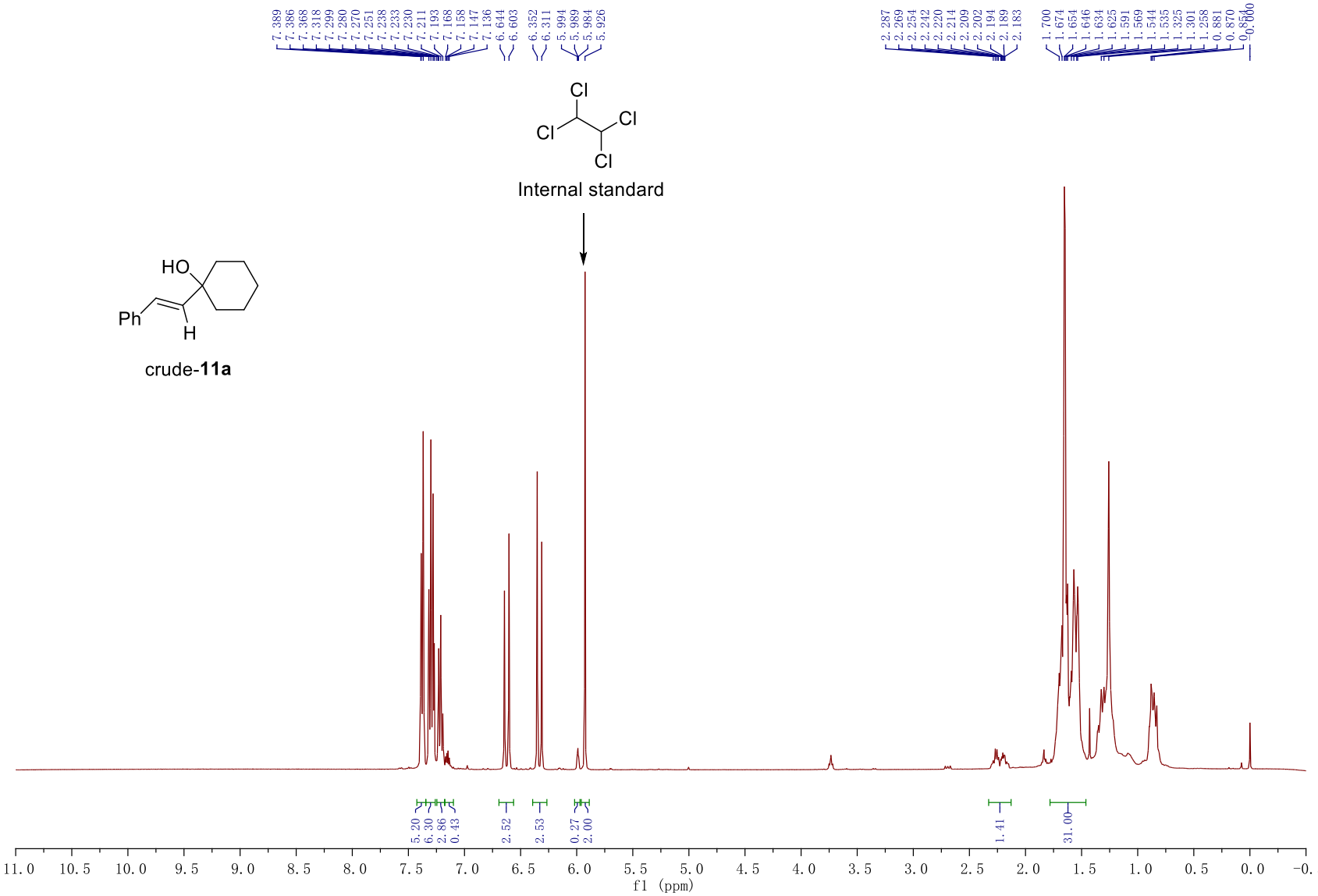
HMBC of (*Z*)-((2-benzylidene-3,3-dimethylbutoxy)methyl)benzene (7m)



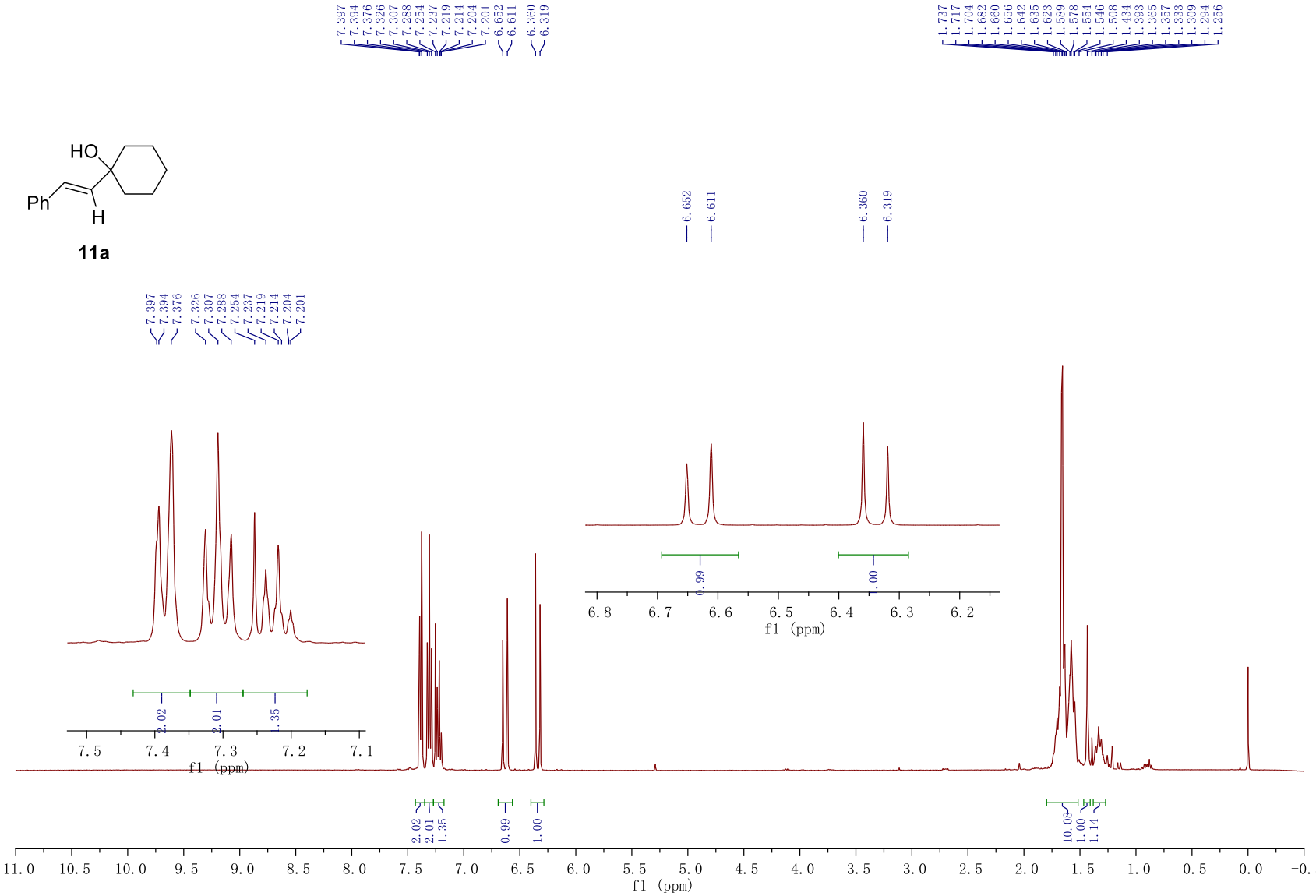
Noesy of (*Z*)-((2-benzylidene-3,3-dimethylbutoxy)methyl)benzene (7m)



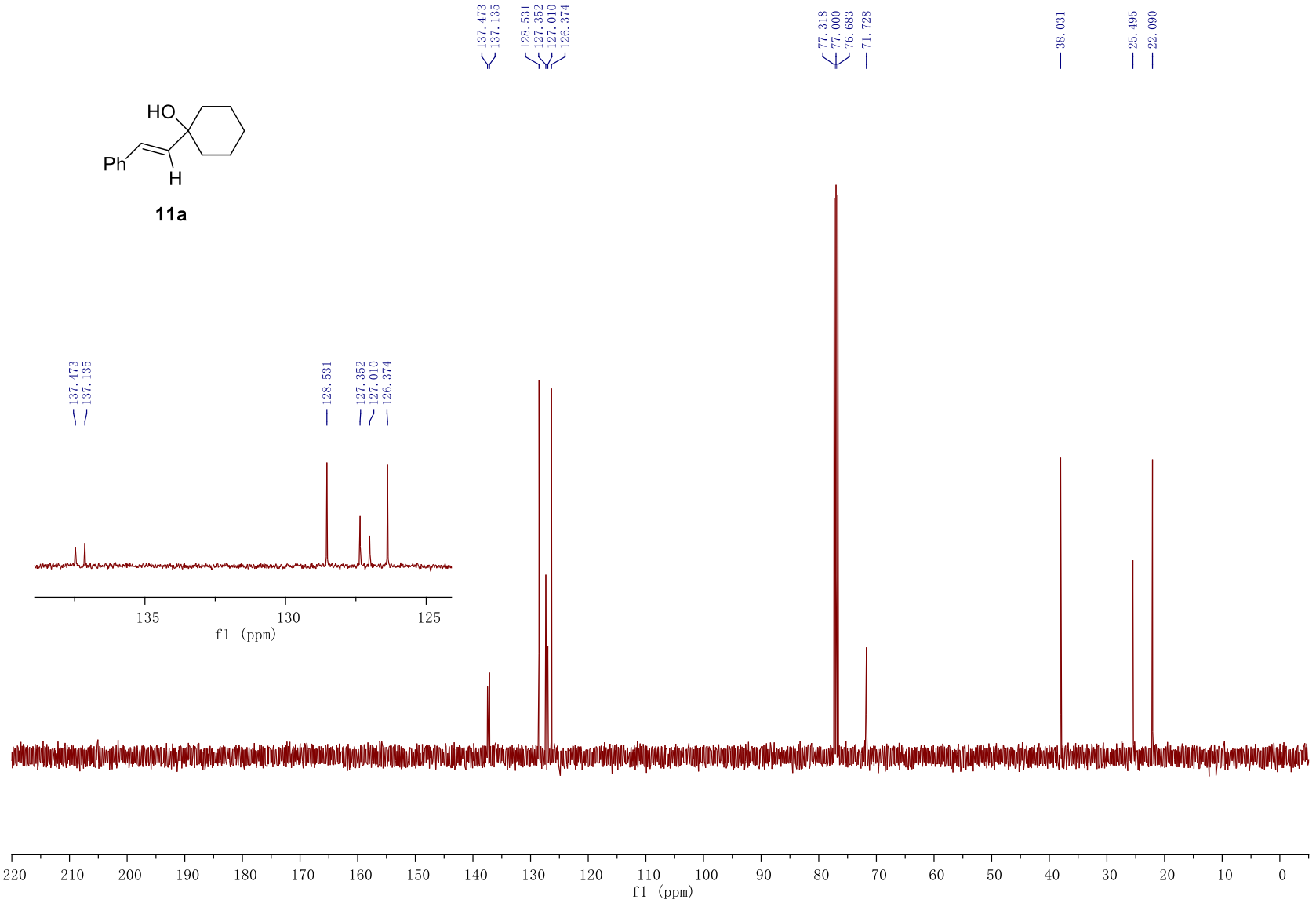
^{1}H NMR Spectrum of crude (*E*)-1-styrylcyclohexan-1-ol (11a)



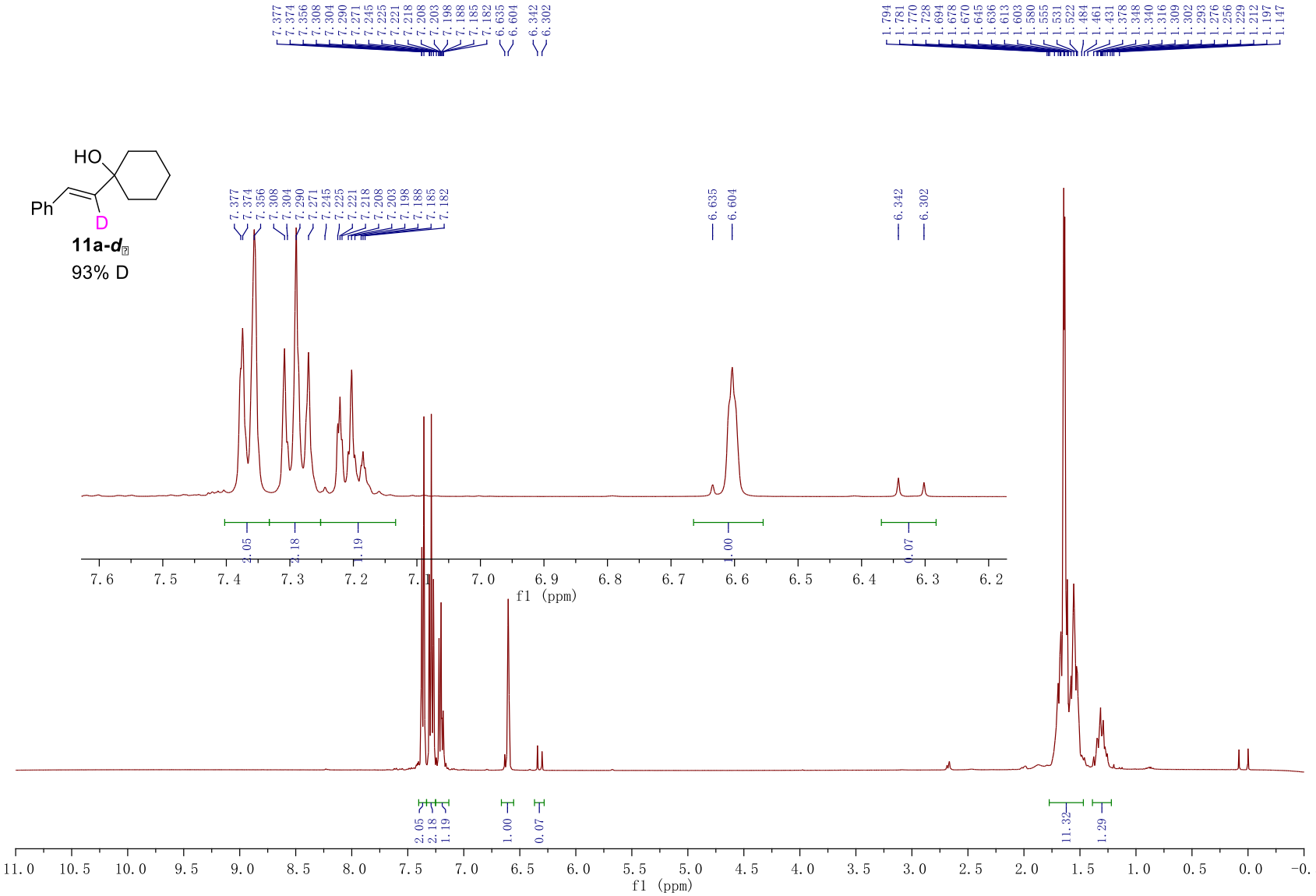
^{1}H NMR Spectrum of (*E*)-1-styrylcyclohexan-1-ol (11a)



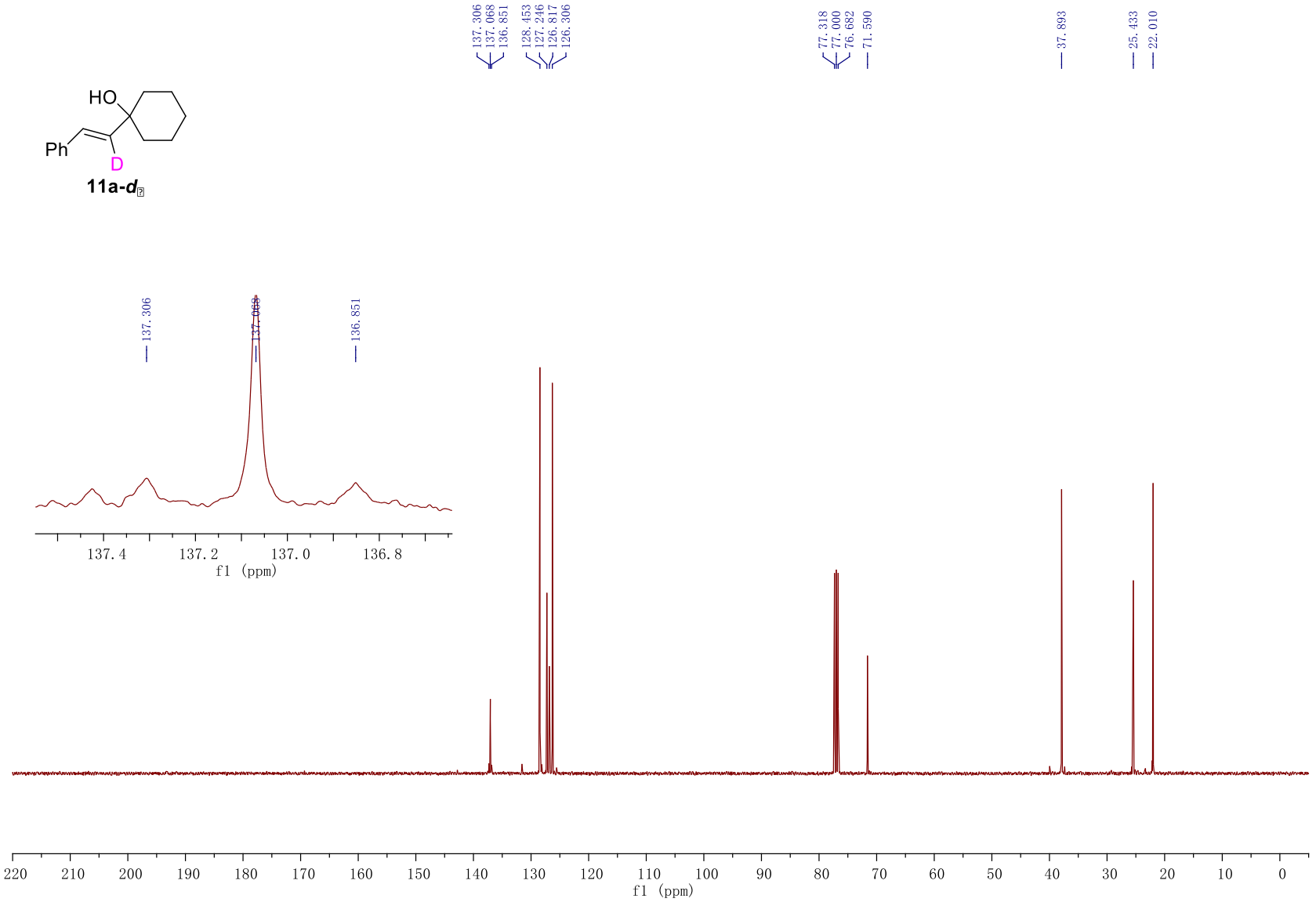
^{13}C NMR Spectrum of (*E*)-1-styrylcyclohexan-1-ol (11a)



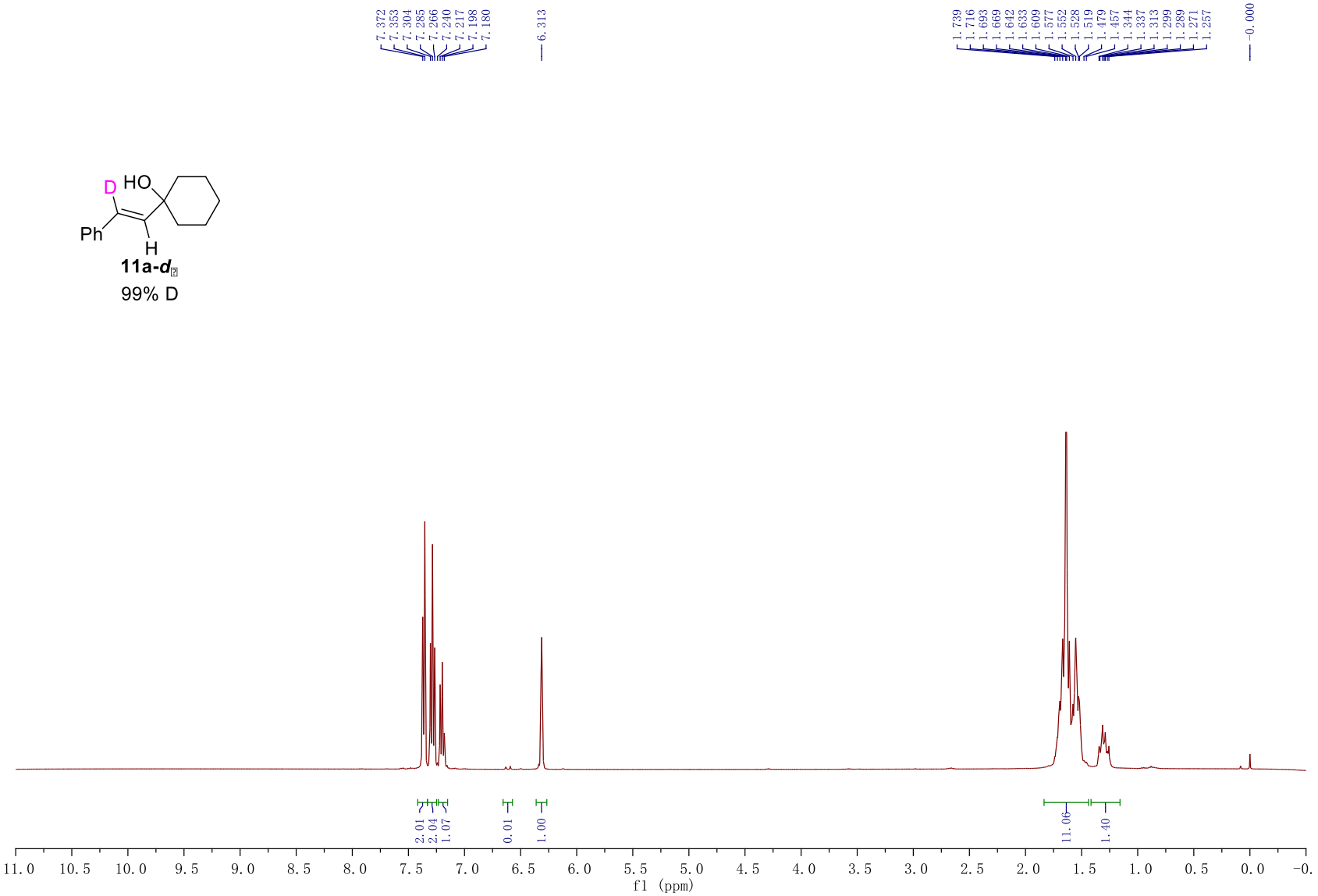
^{1}H NMR Spectrum of (*E*)-1-(2-phenylvinyl-1-*d*)cyclohexan-1-ol (11a-d_1)



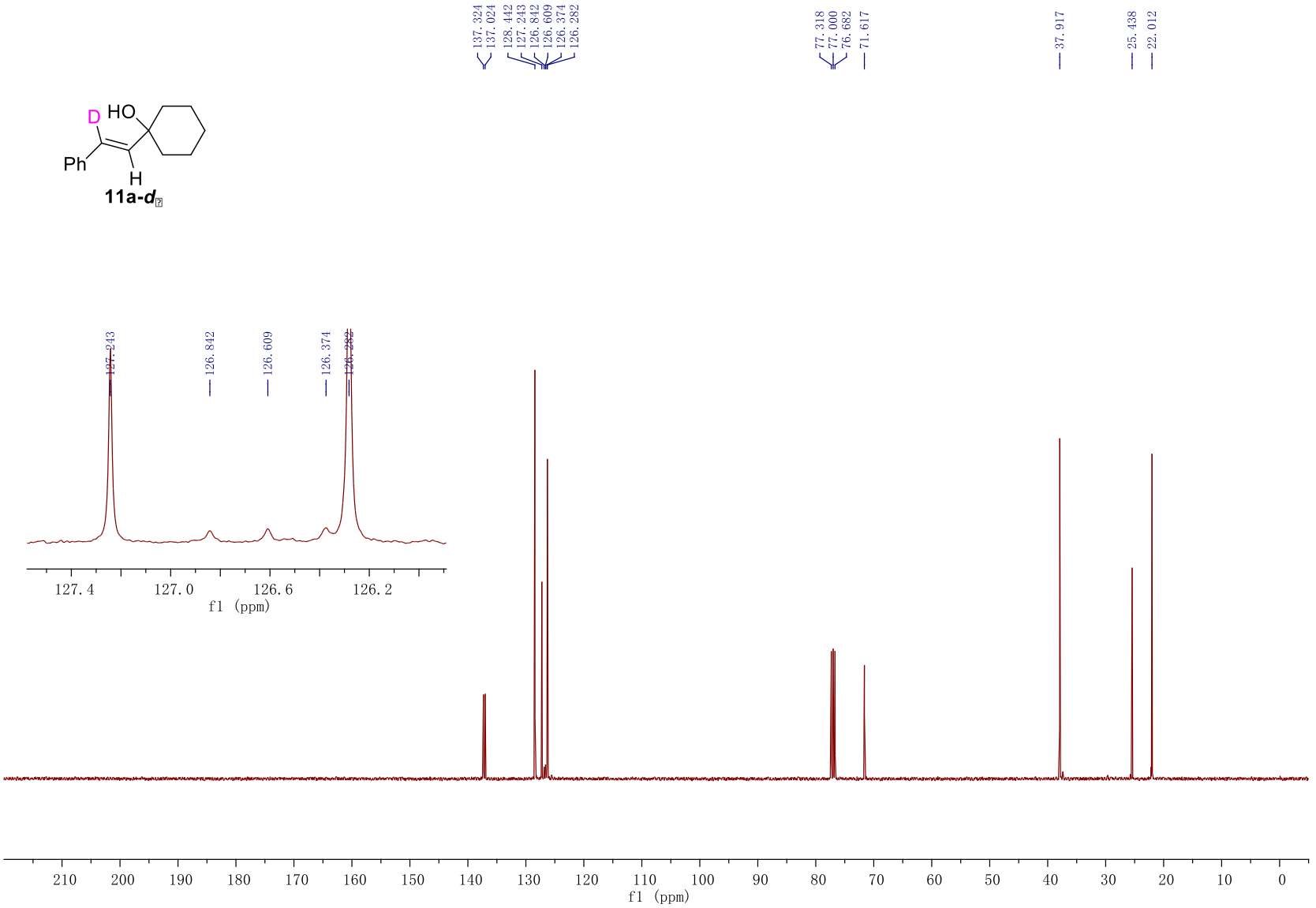
^{13}C NMR Spectrum of (*E*)-1-(2-phenylvinyl-1-*d*)cyclohexan-1-ol (11a-d_1)



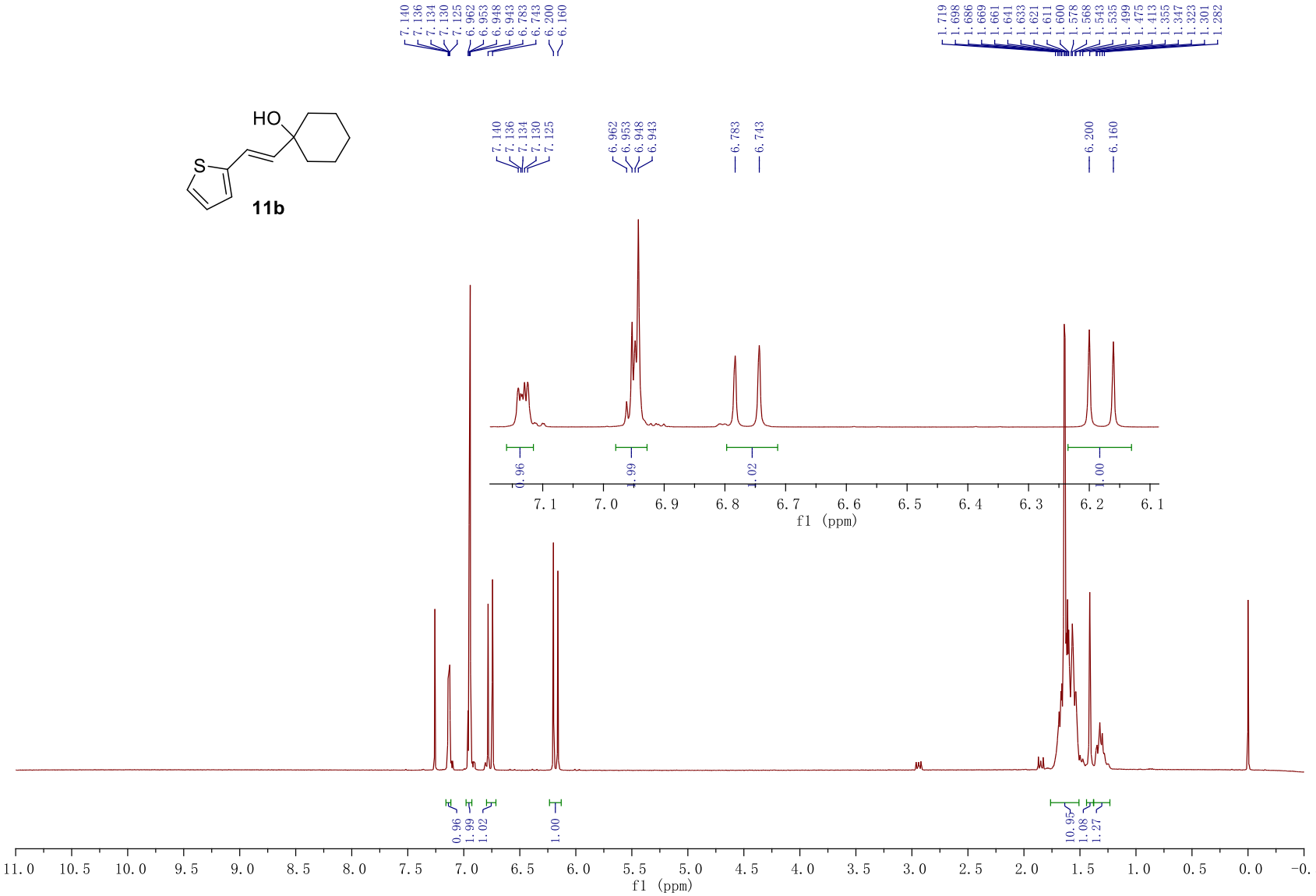
^{1}H NMR Spectrum of (*E*)-1-(2-phenylvinyl-2-*d*)cyclohexan-1-ol (11a-d_a)



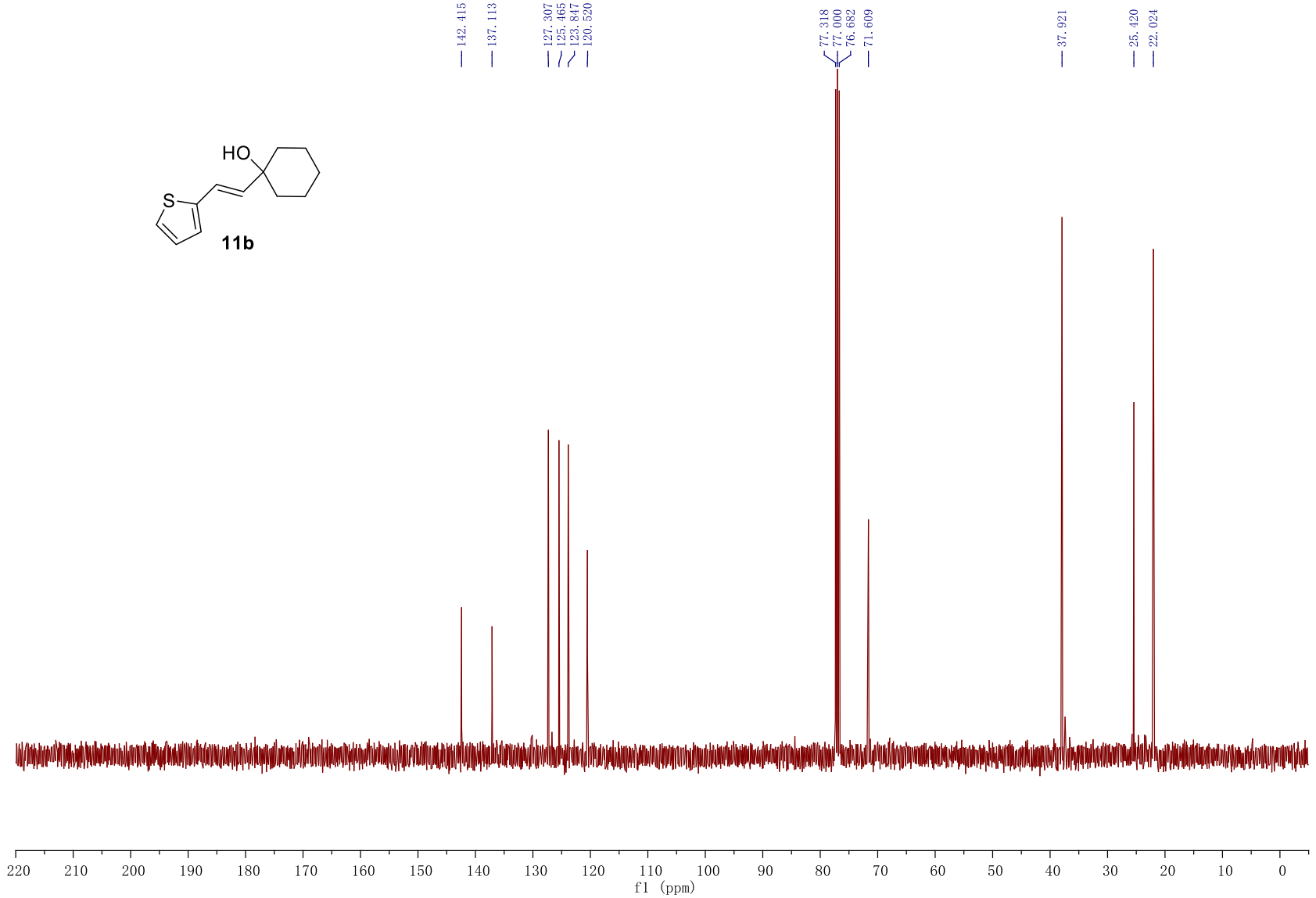
^{13}C NMR Spectrum of (*E*)-1-(2-phenylvinyl-2-*d*)cyclohexan-1-ol (11a-d_1)



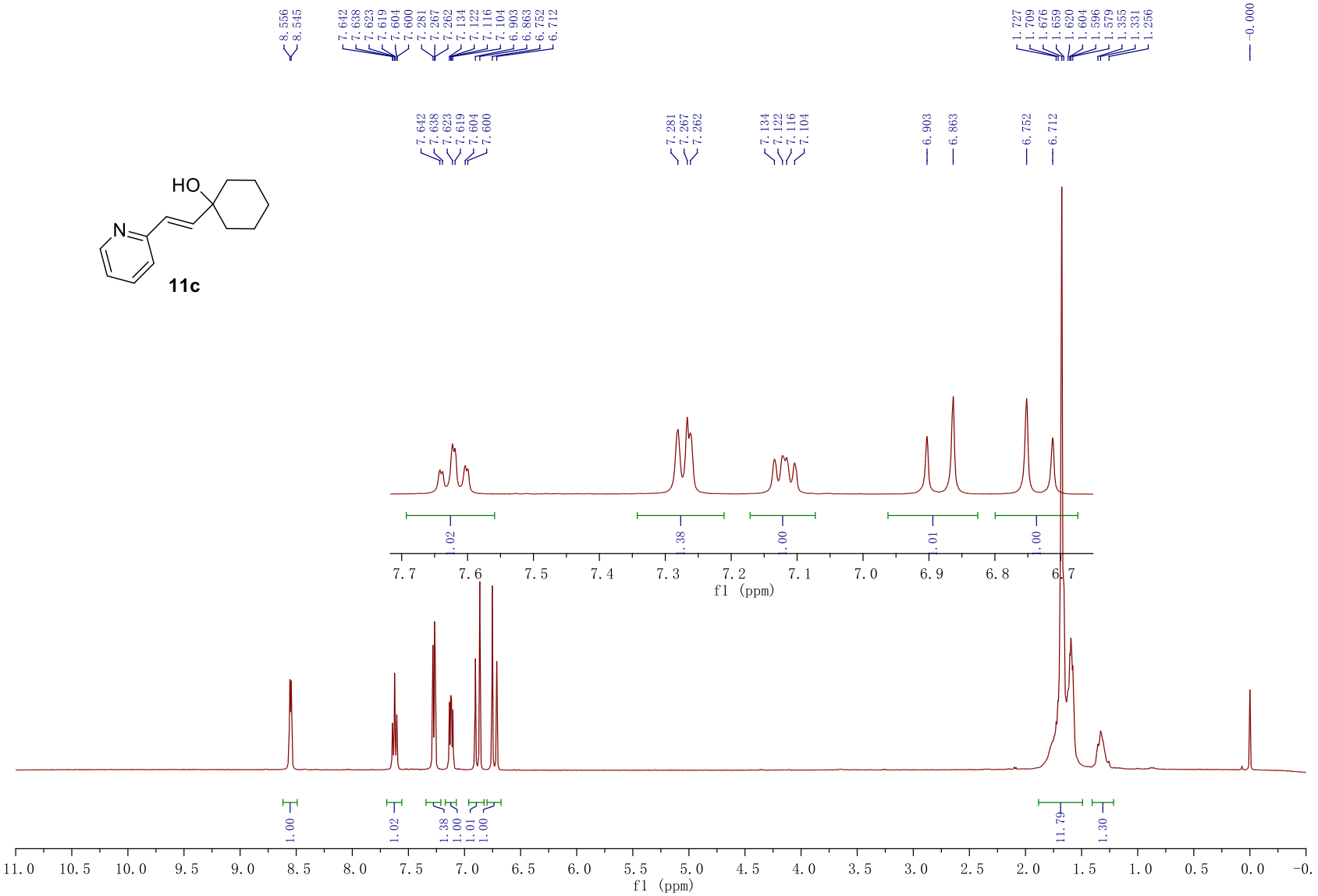
^{1}H NMR Spectrum of (*E*)-1-(2-(thiophen-2-yl)vinyl)cyclohexan-1-ol (11b)



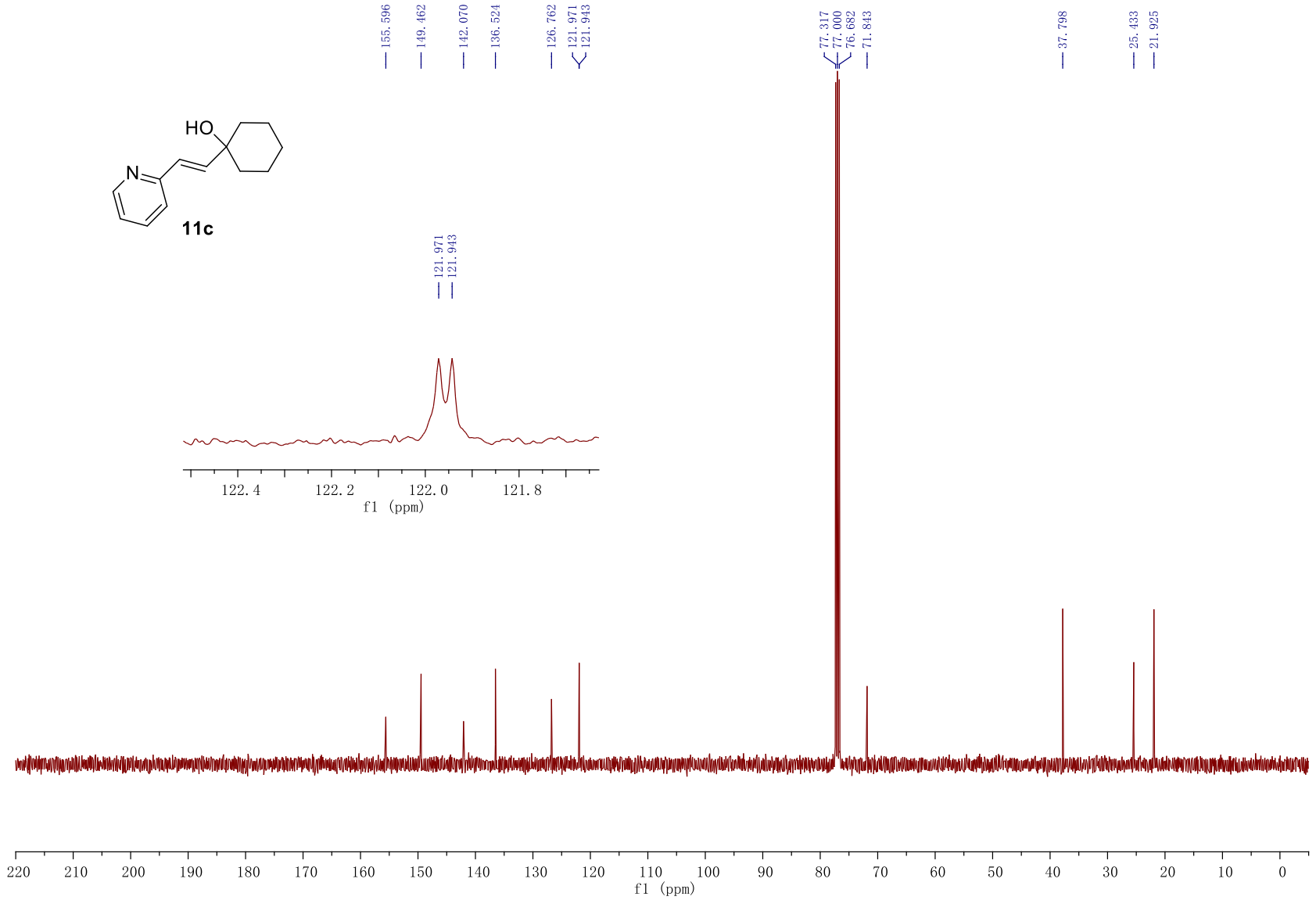
^{13}C NMR Spectrum of (*E*)-1-(2-(thiophen-2-yl)vinyl)cyclohexan-1-ol (11b)



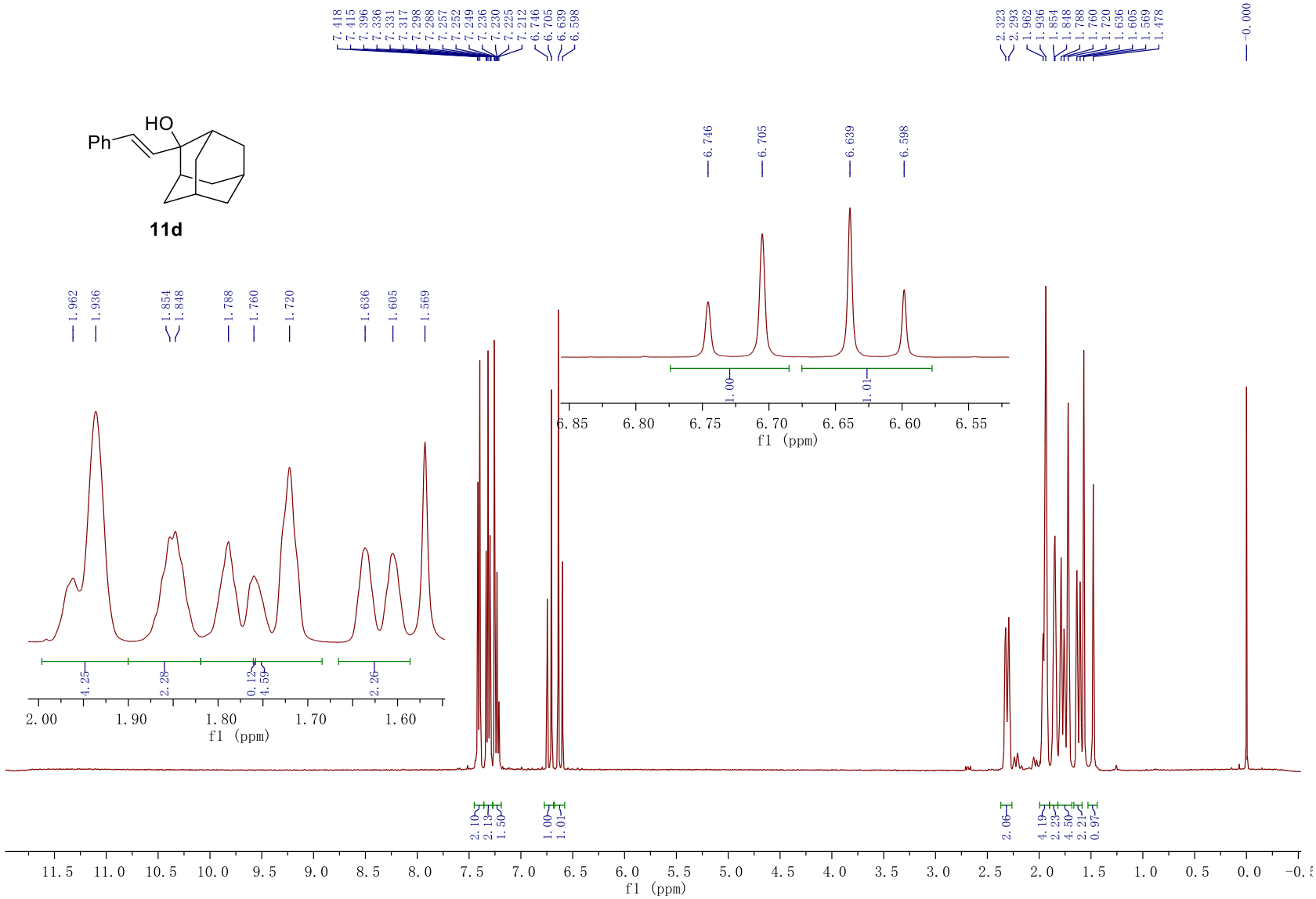
^{1}H NMR Spectrum of (*E*)-1-(2-(pyridin-2-yl)vinyl)cyclohexan-1-ol (11c)



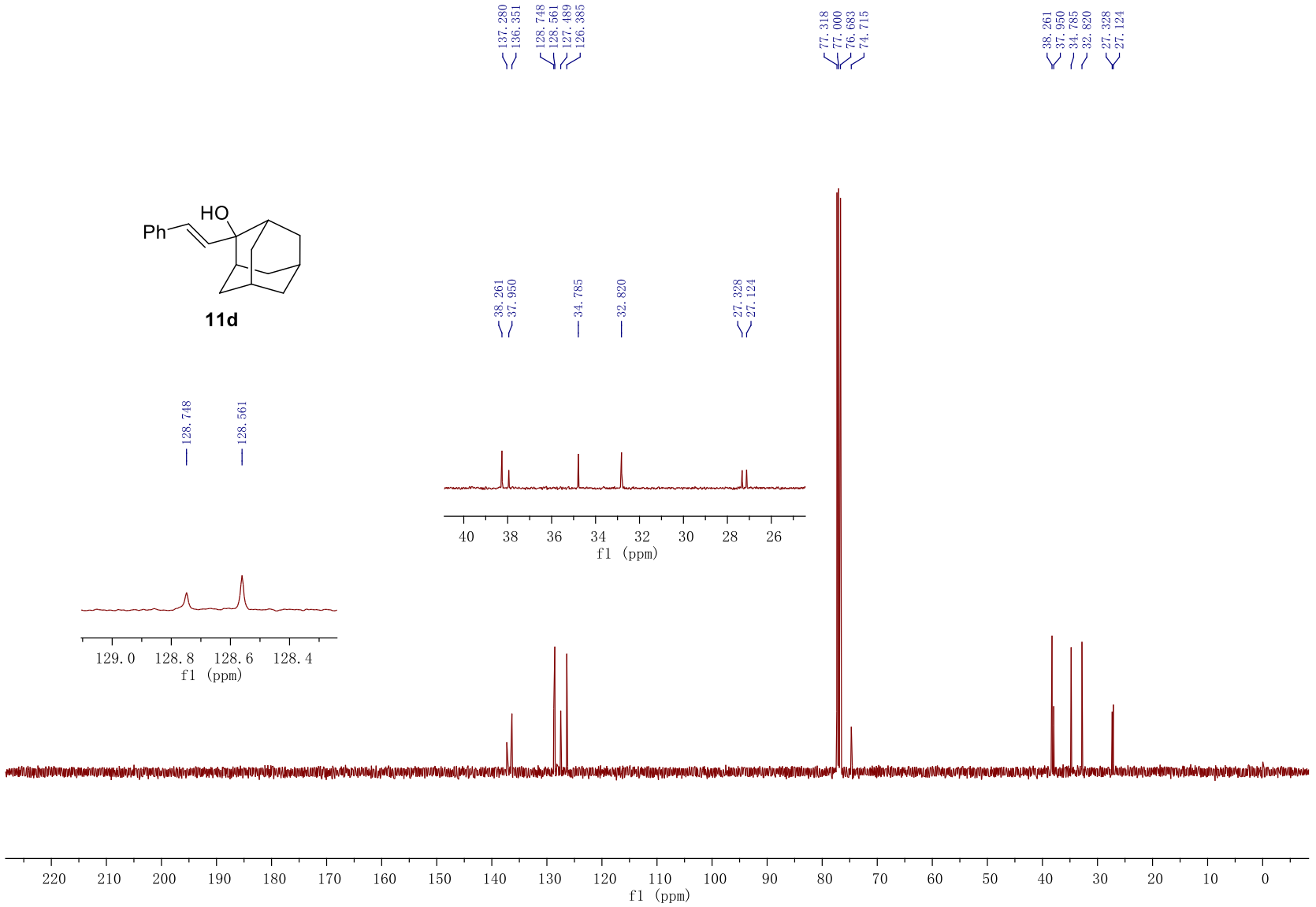
^{13}C NMR Spectrum of (*E*)-1-(2-(pyridin-2-yl)vinyl)cyclohexan-1-ol (11c)



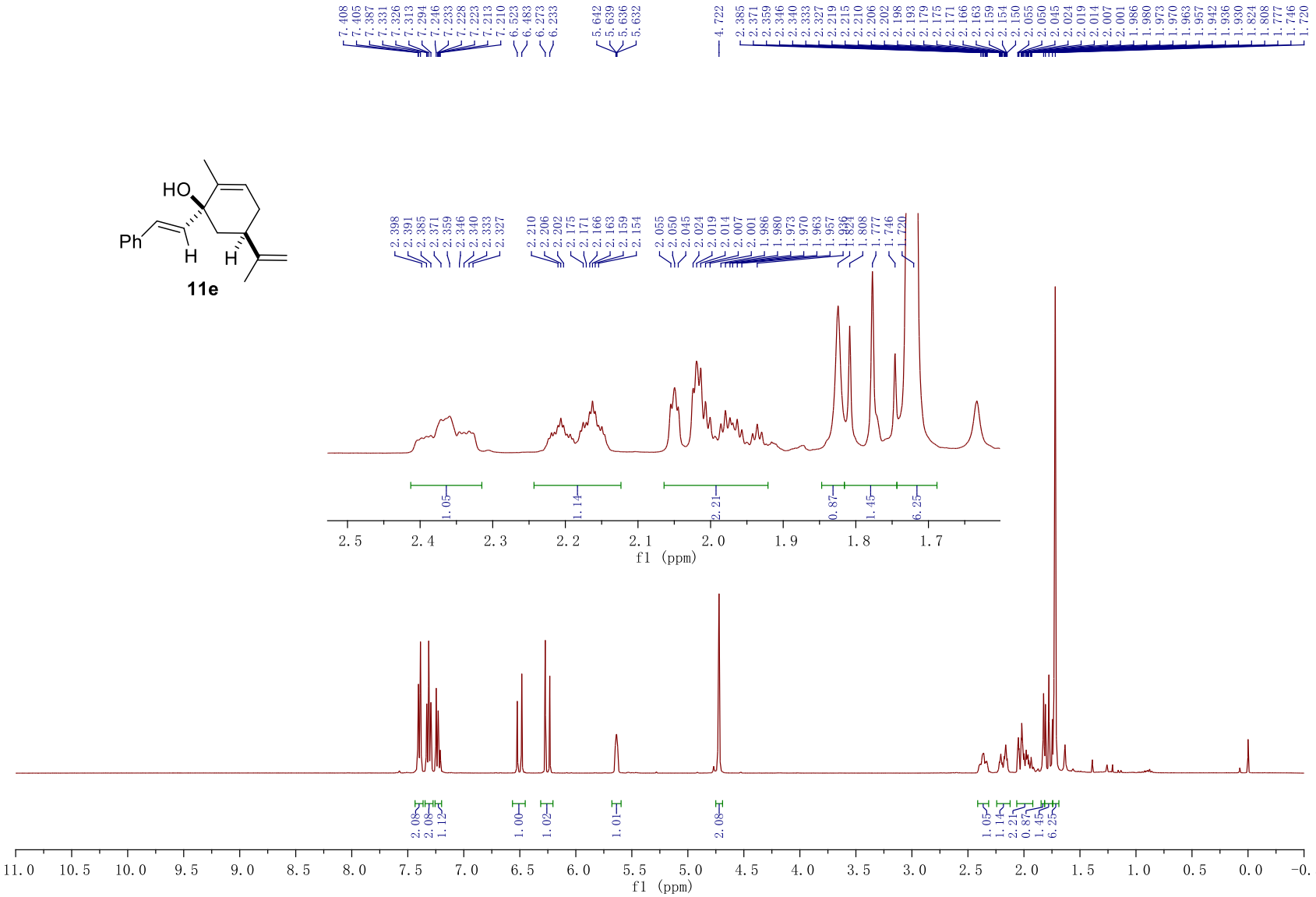
^{1}H NMR Spectrum of (1*R,3*S**,5*r*,7*r*)-2-((*E*)-styryl)adamantan-2-ol (11d)**



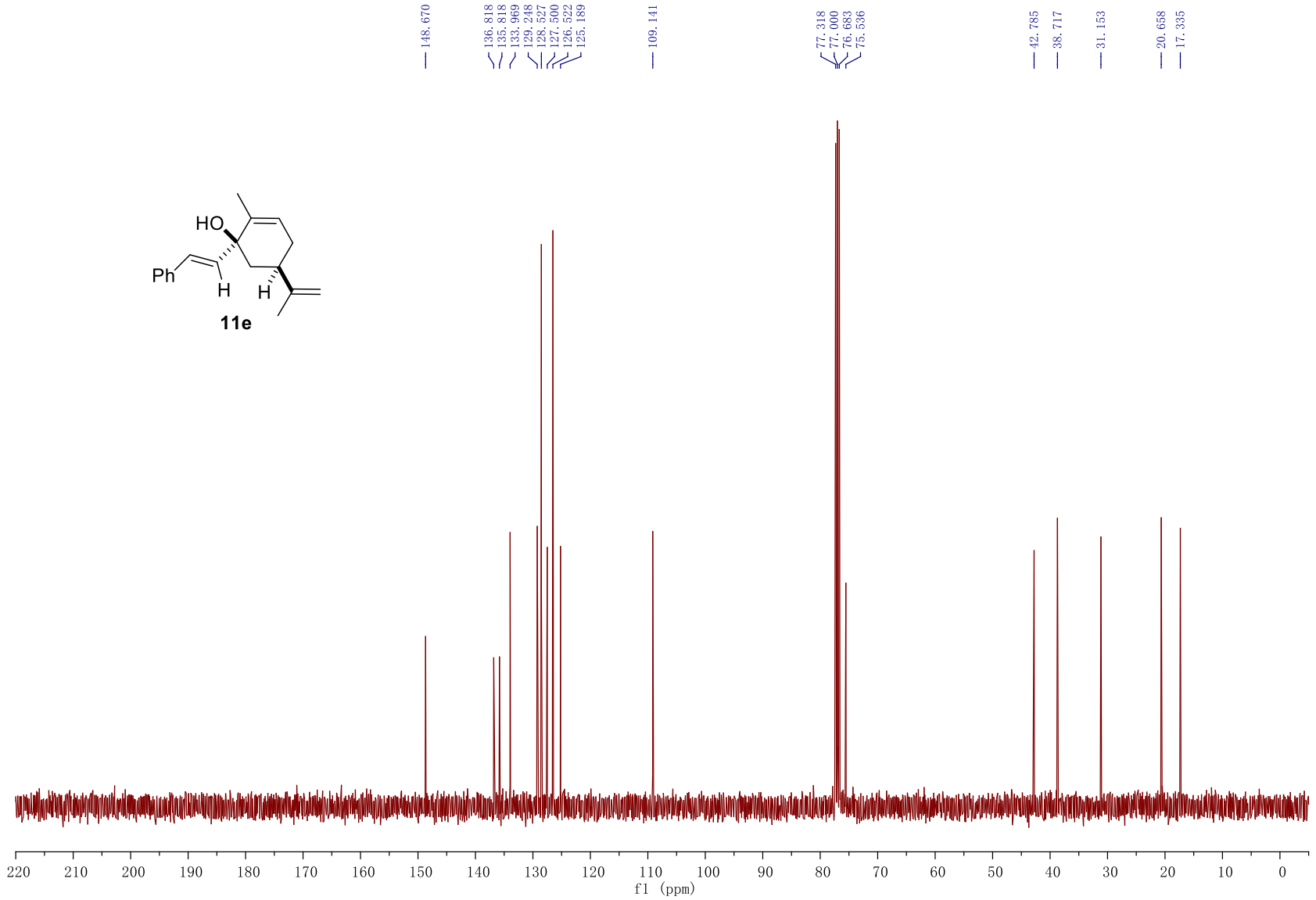
^{13}C NMR Spectrum of (1*R,3*S**,5*r*,7*r*)-2-((*E*)-styryl)adamantan-2-ol (11d)**



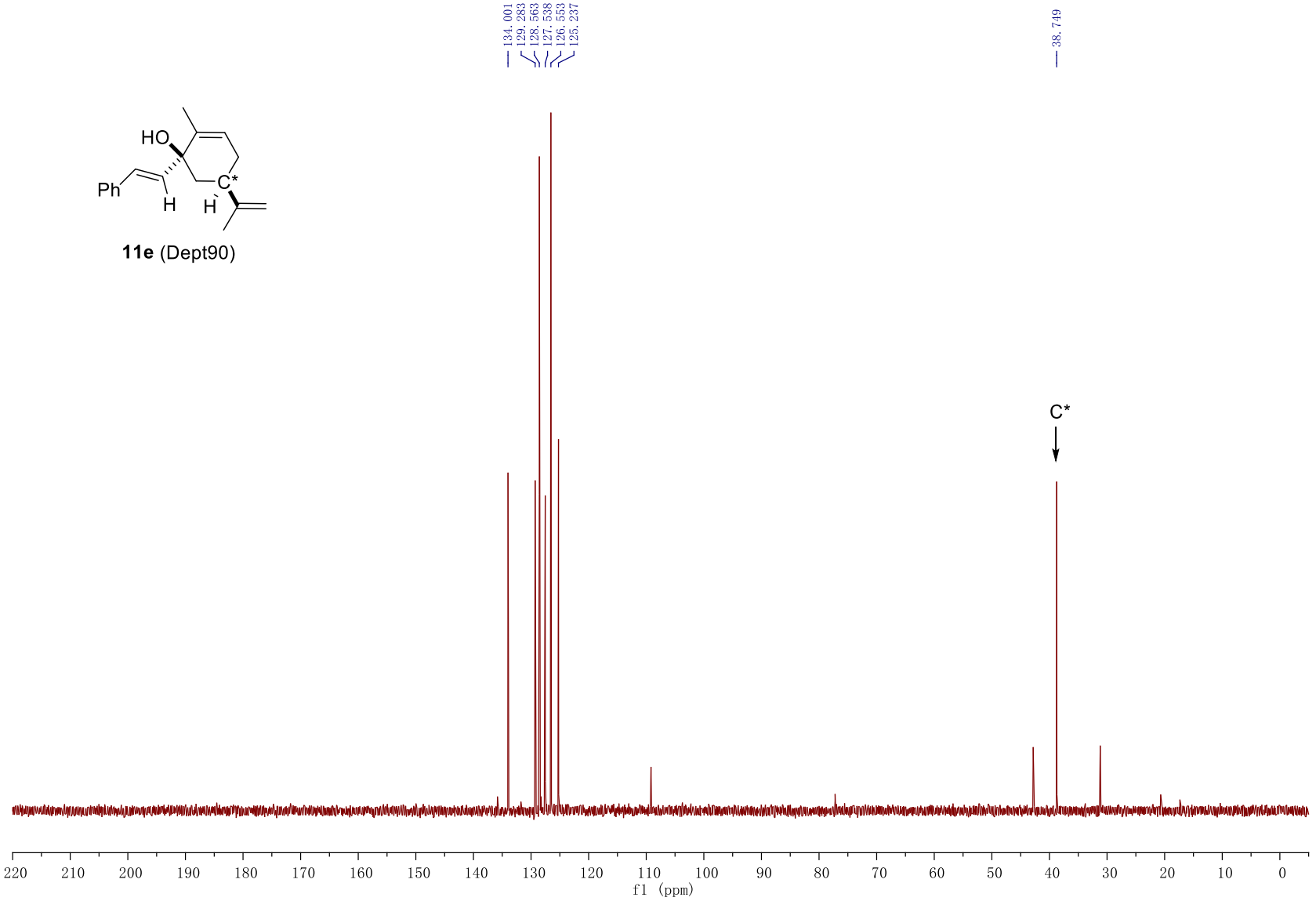
[1]H NMR Spectrum of (1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)-1-((*E*)-styryl)cyclohex-2-en-1-ol (11e)



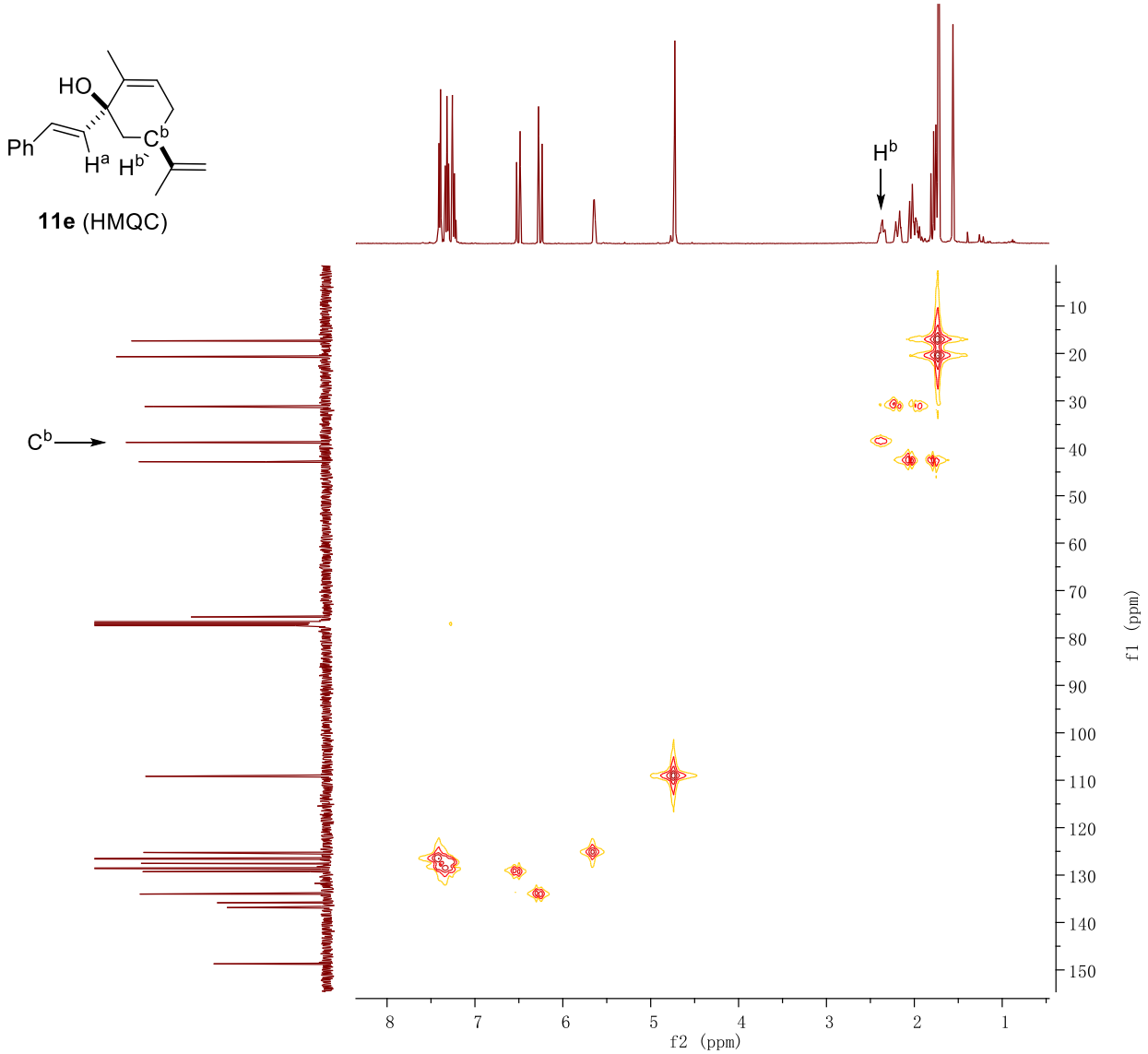
^{13}C NMR Spectrum of (1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)-1-((*E*)-styryl)cyclohex-2-en-1-ol (11e)



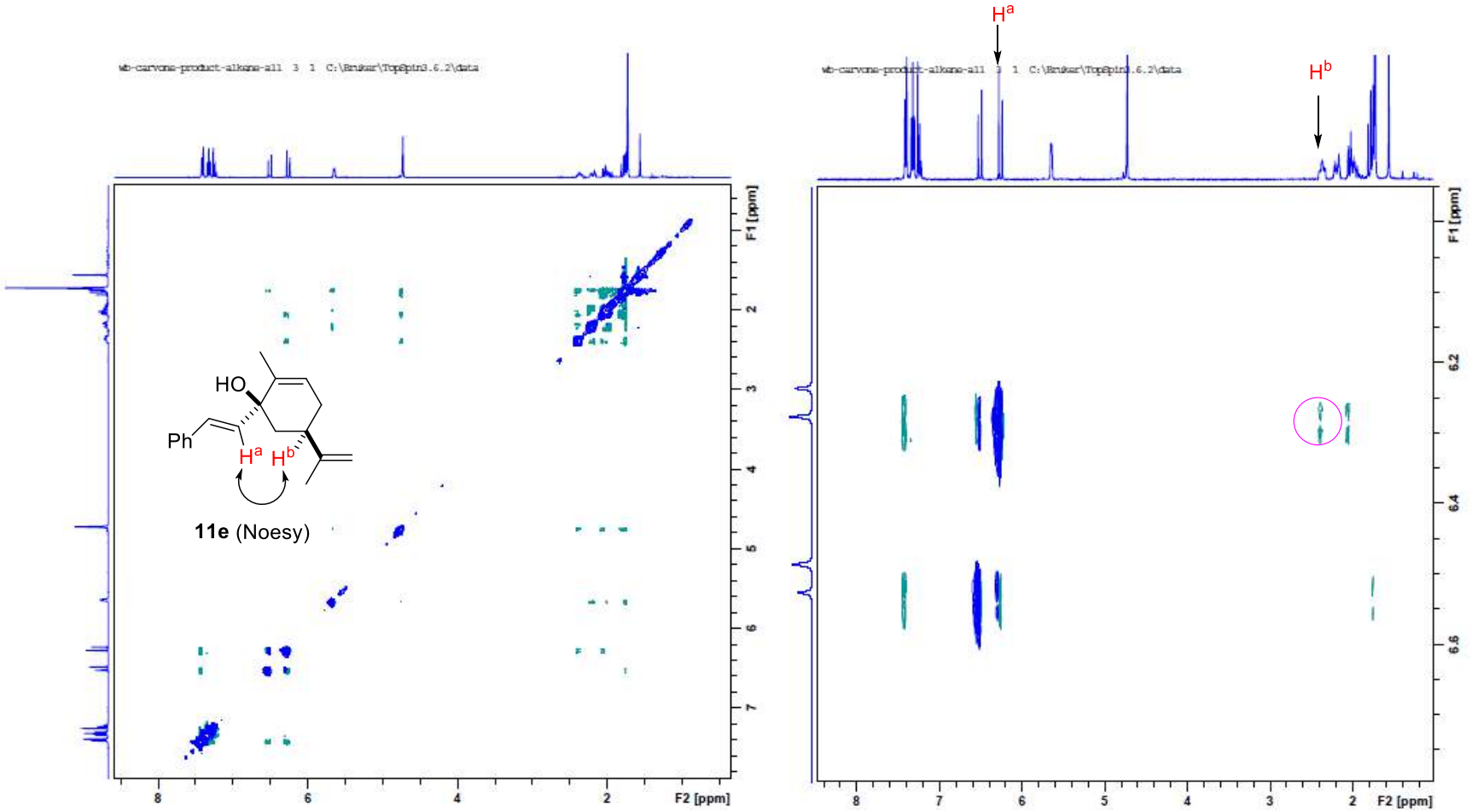
Dept90 NMR Spectrum of (1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)-1-((*E*)-styryl)cyclohex-2-en-1-ol (11e)



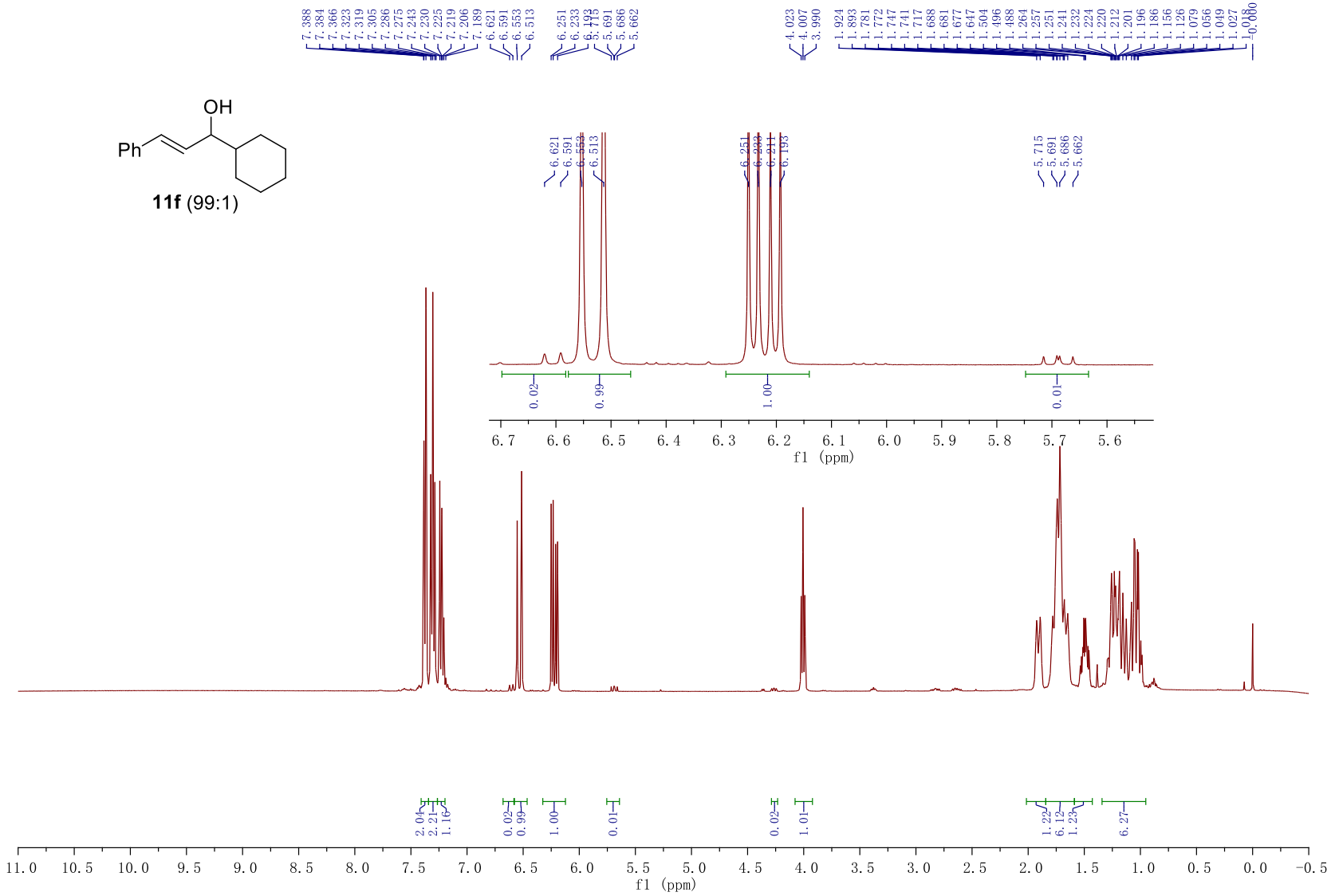
HMQC of (1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)-1-((*E*)-styryl)cyclohex-2-en-1-ol (11e)



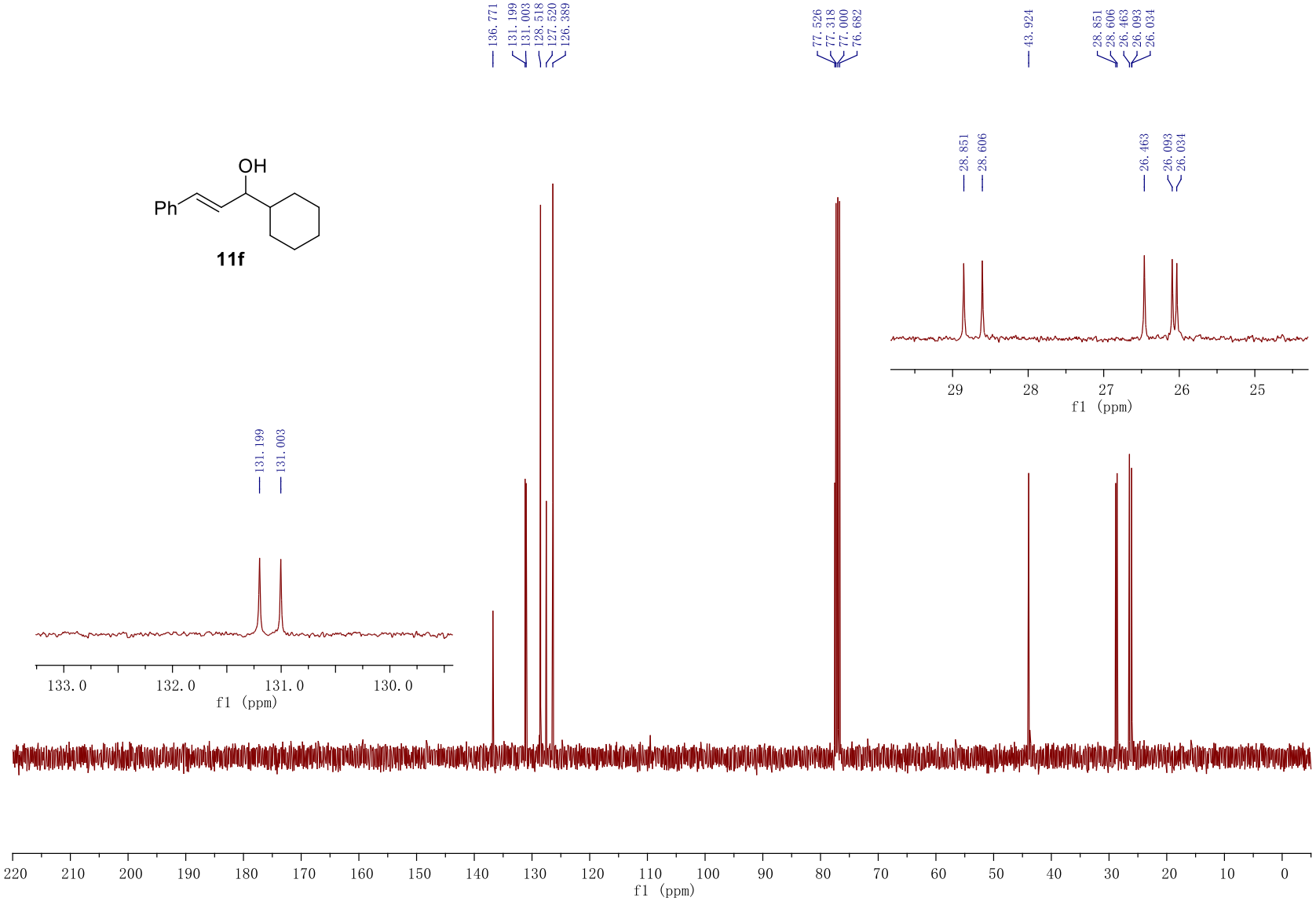
Noesy of (1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)-1-((*E*)-styryl)cyclohex-2-en-1-ol (11e)



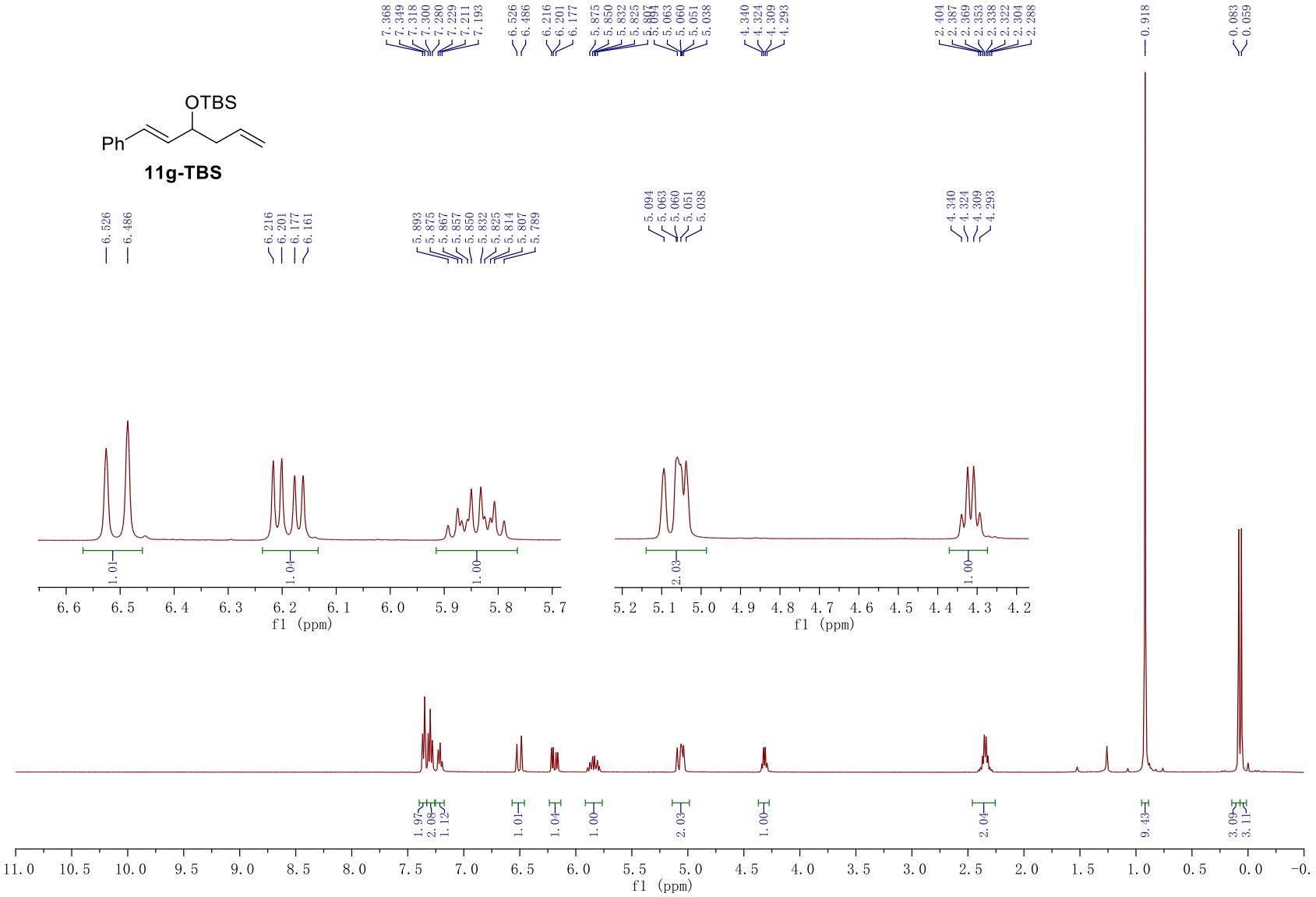
[1]H NMR Spectrum of (*E*)-1-cyclohexyl-3-phenylprop-2-en-1-ol (11f)



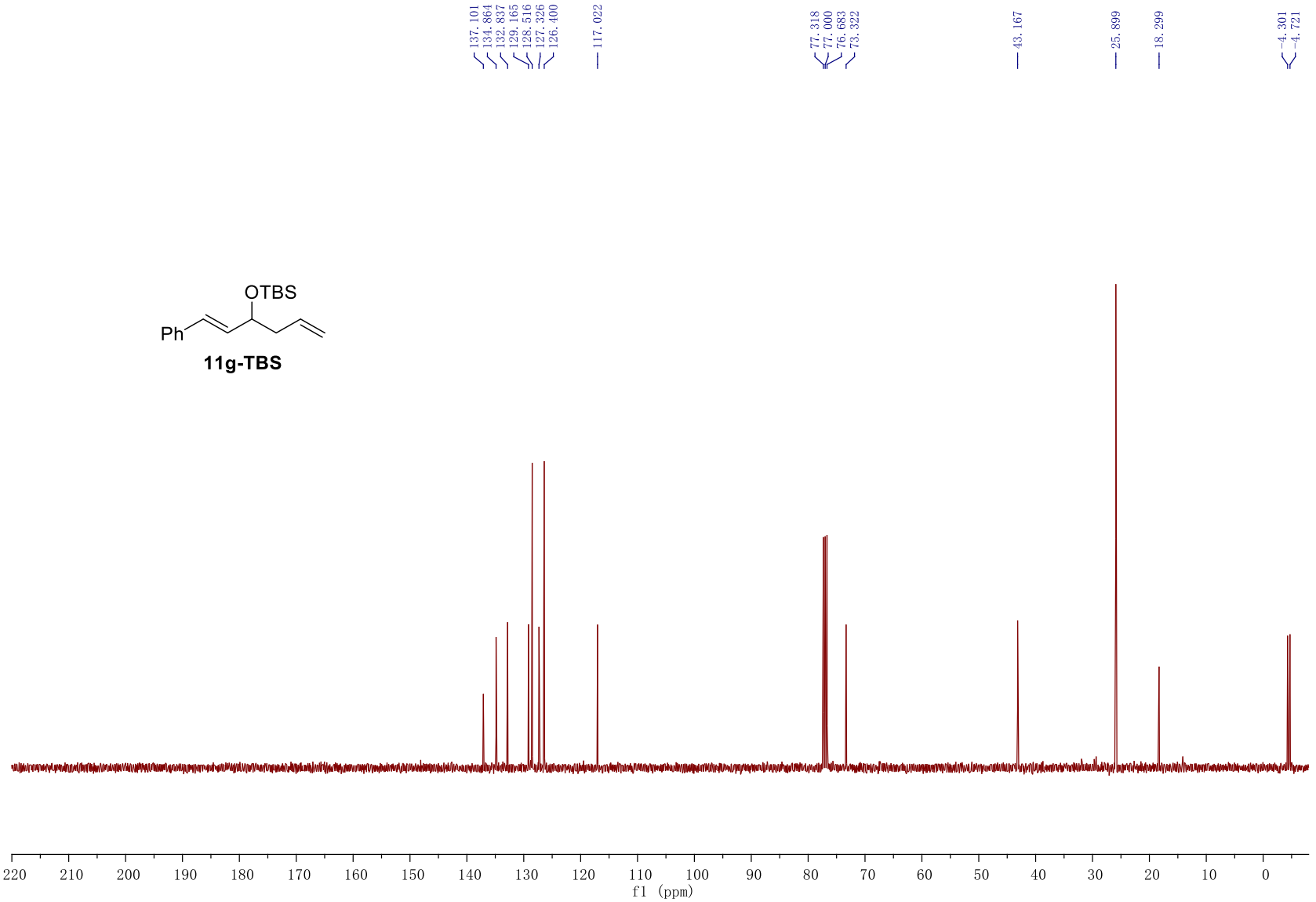
^{13}C NMR Spectrum of (*E*)-1-cyclohexyl-3-phenylprop-2-en-1-ol (11f)



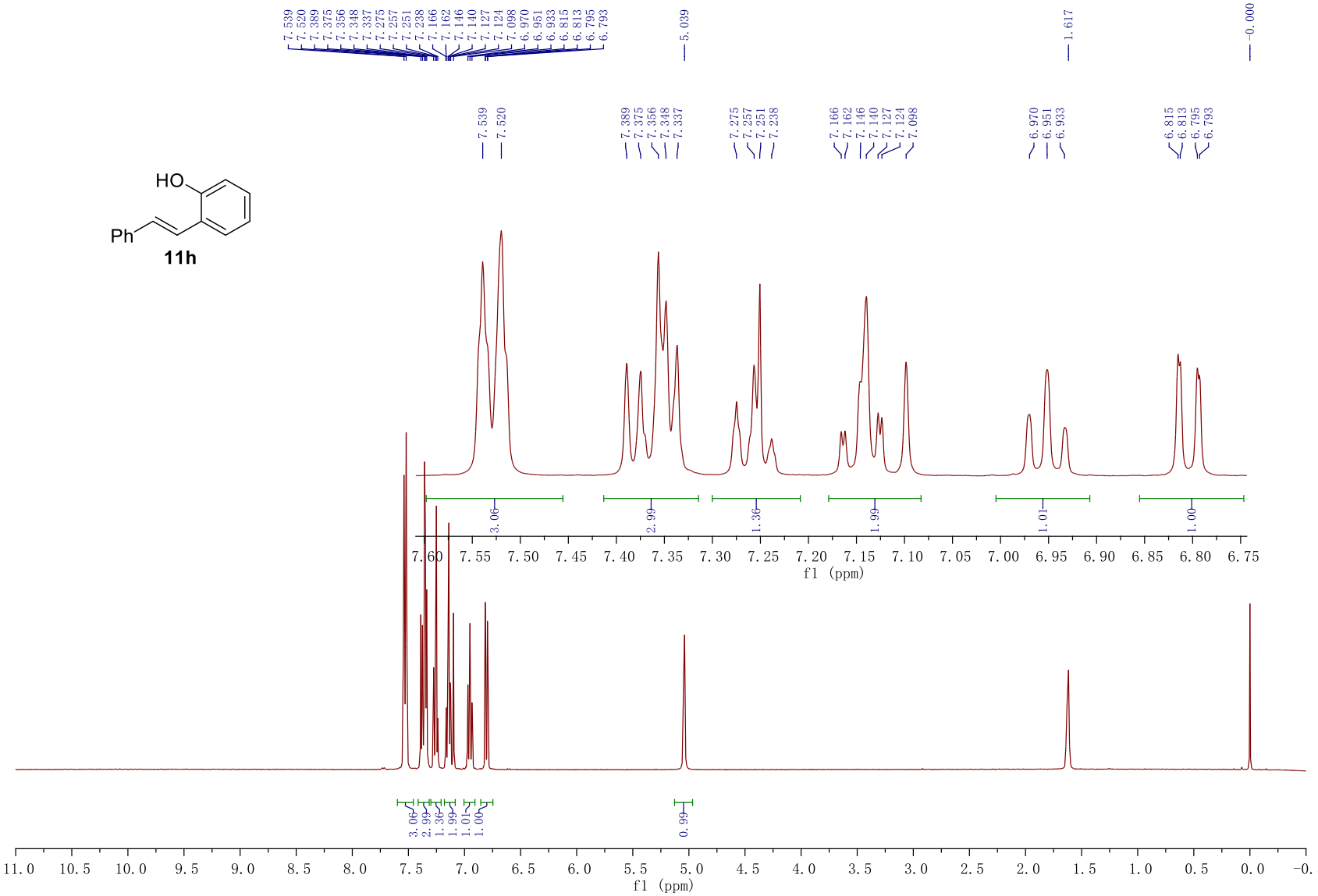
^{1}H NMR Spectrum of (*E*)-tert-butyldimethyl((1-phenylhexa-1,5-dien-3-yl)oxy)silane (11g-TBS)



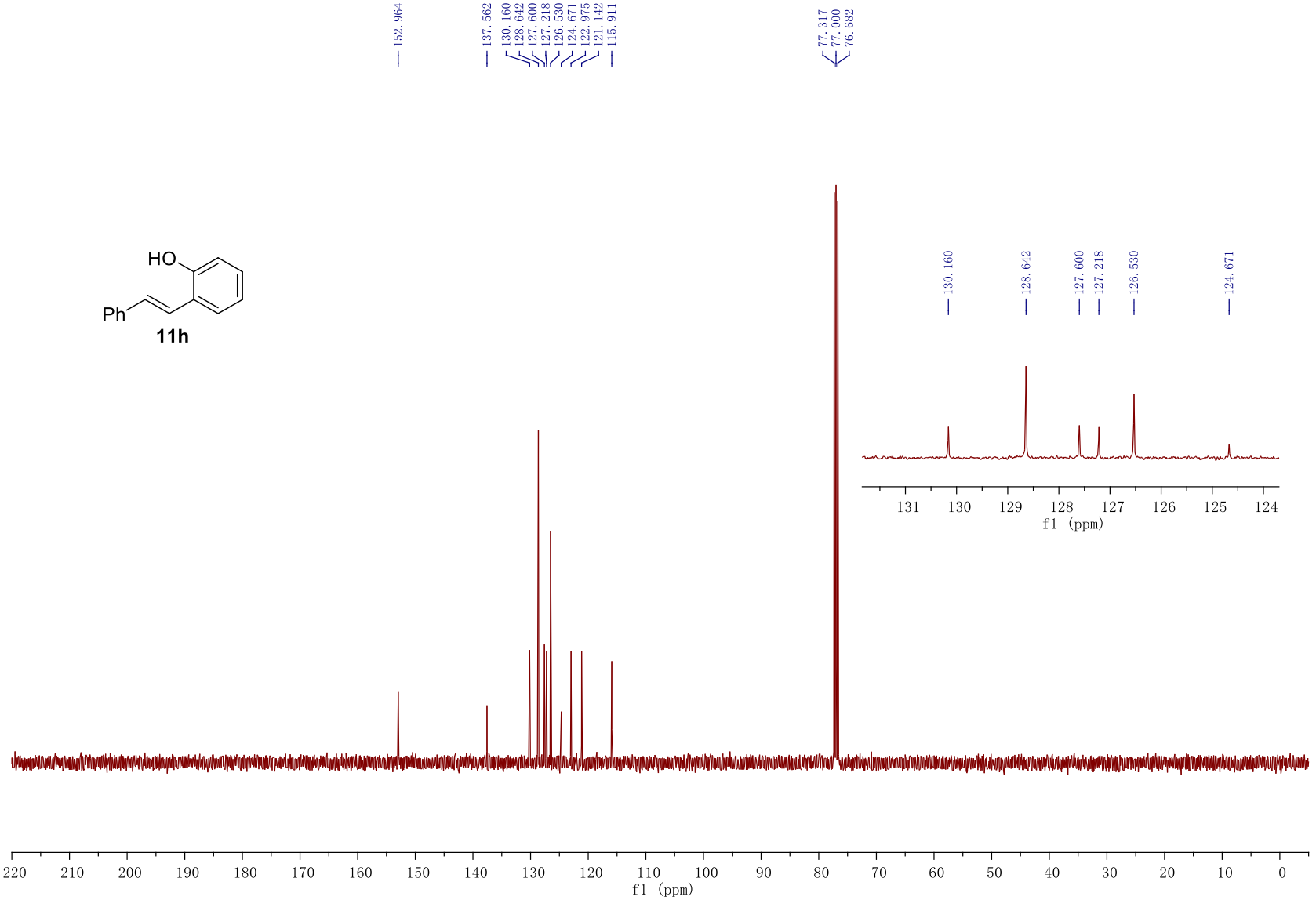
^{13}C NMR Spectrum of (*E*)-tert-butyldimethyl((1-phenylhexa-1,5-dien-3-yl)oxy)silane (11g-TBS)



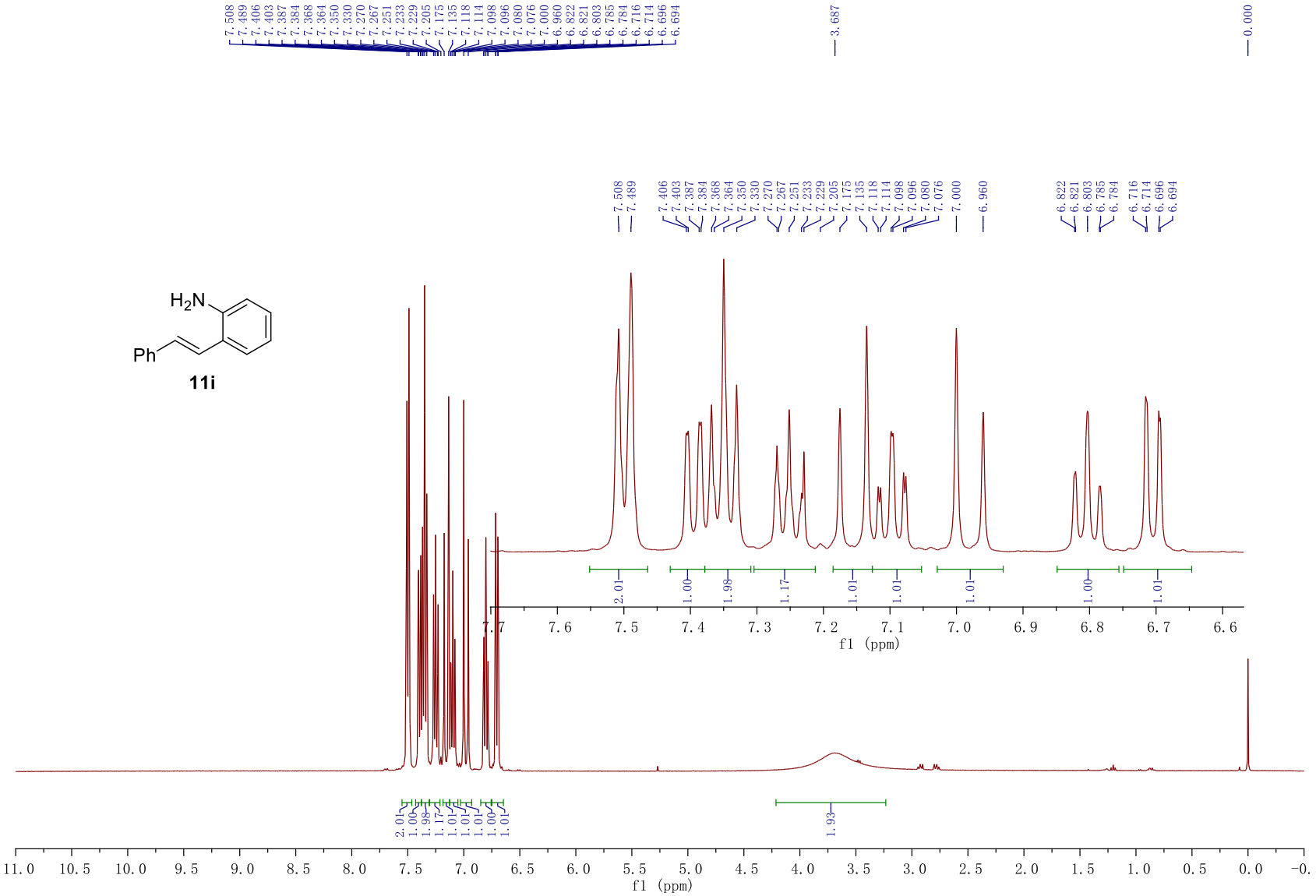
^{1}H NMR Spectrum of (*E*)-2-styrylphenol (11h)



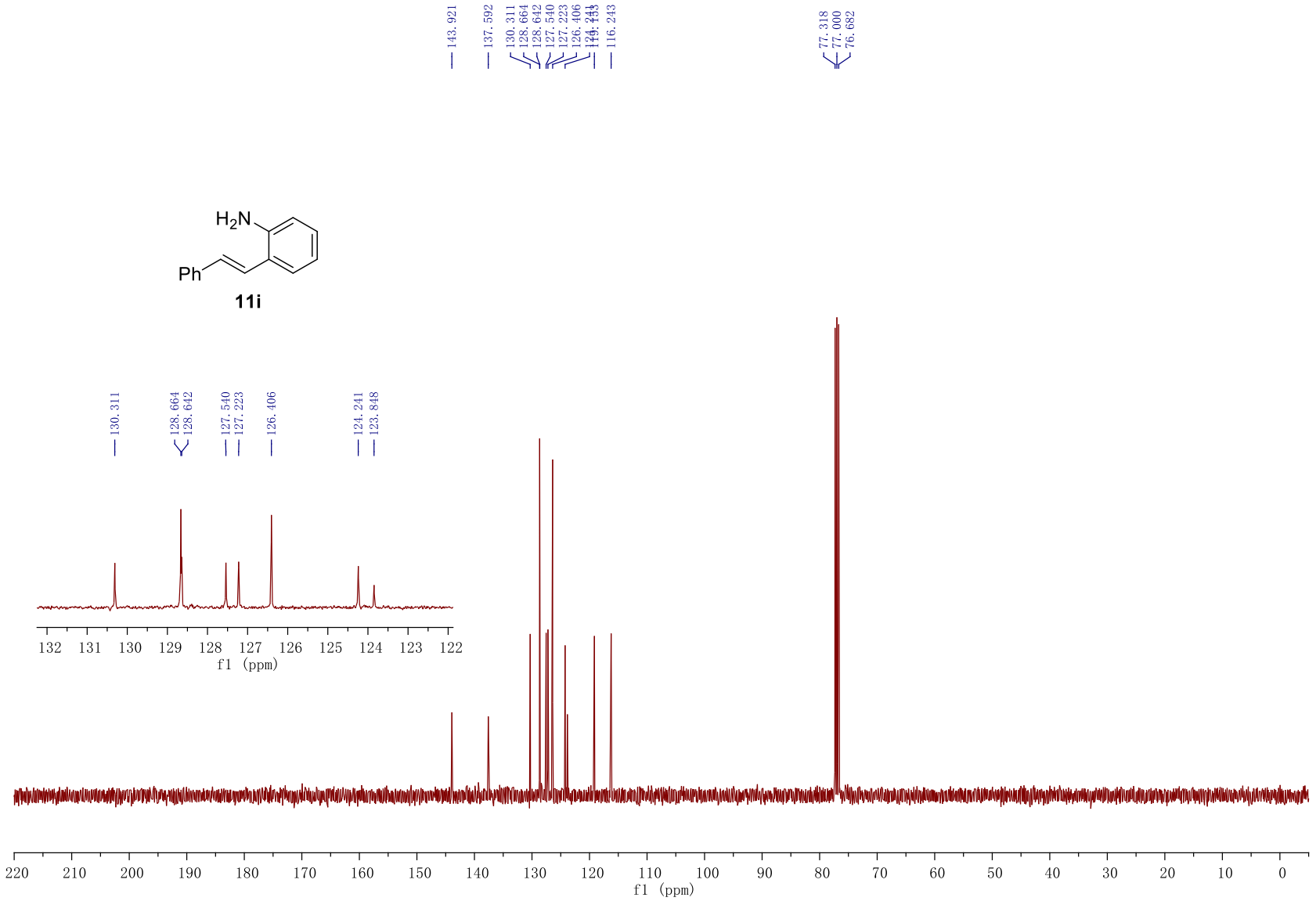
^{13}C NMR Spectrum of (*E*)-2-styrylphenol (11h)



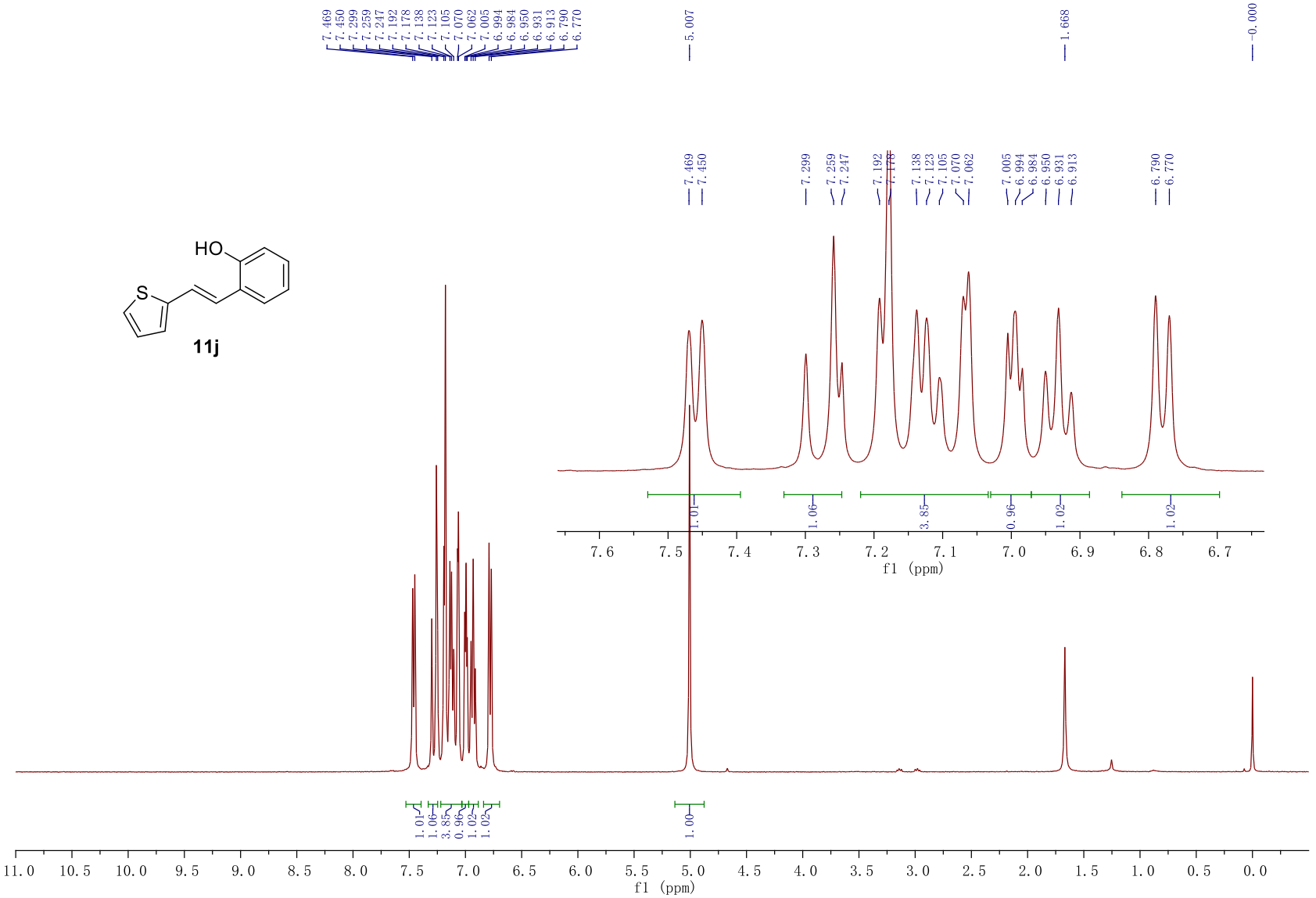
^{1}H NMR Spectrum of (*E*)-2-styrylaniline (11i)



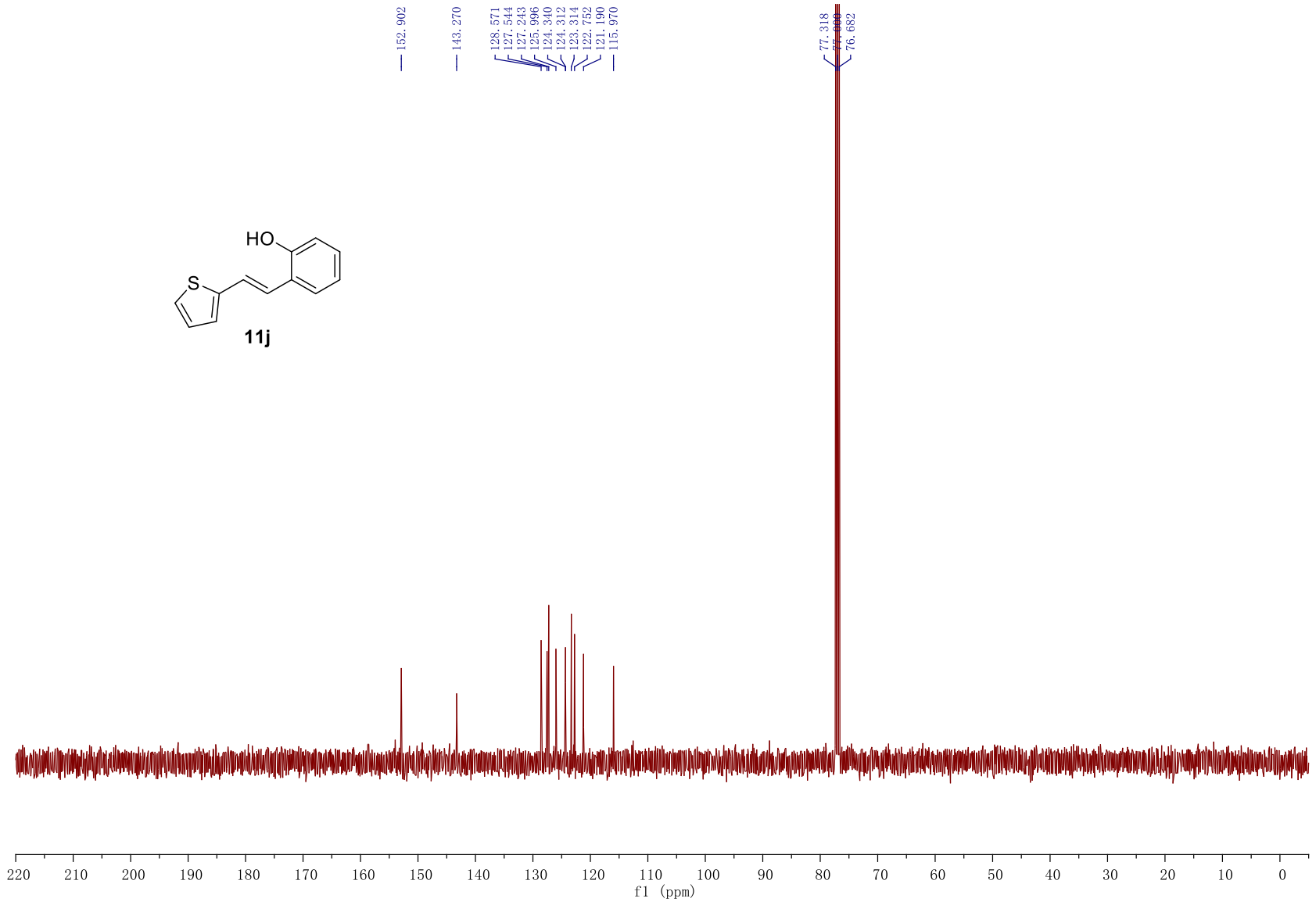
^{13}C NMR Spectrum of (*E*)-2-styrylaniline (11i)



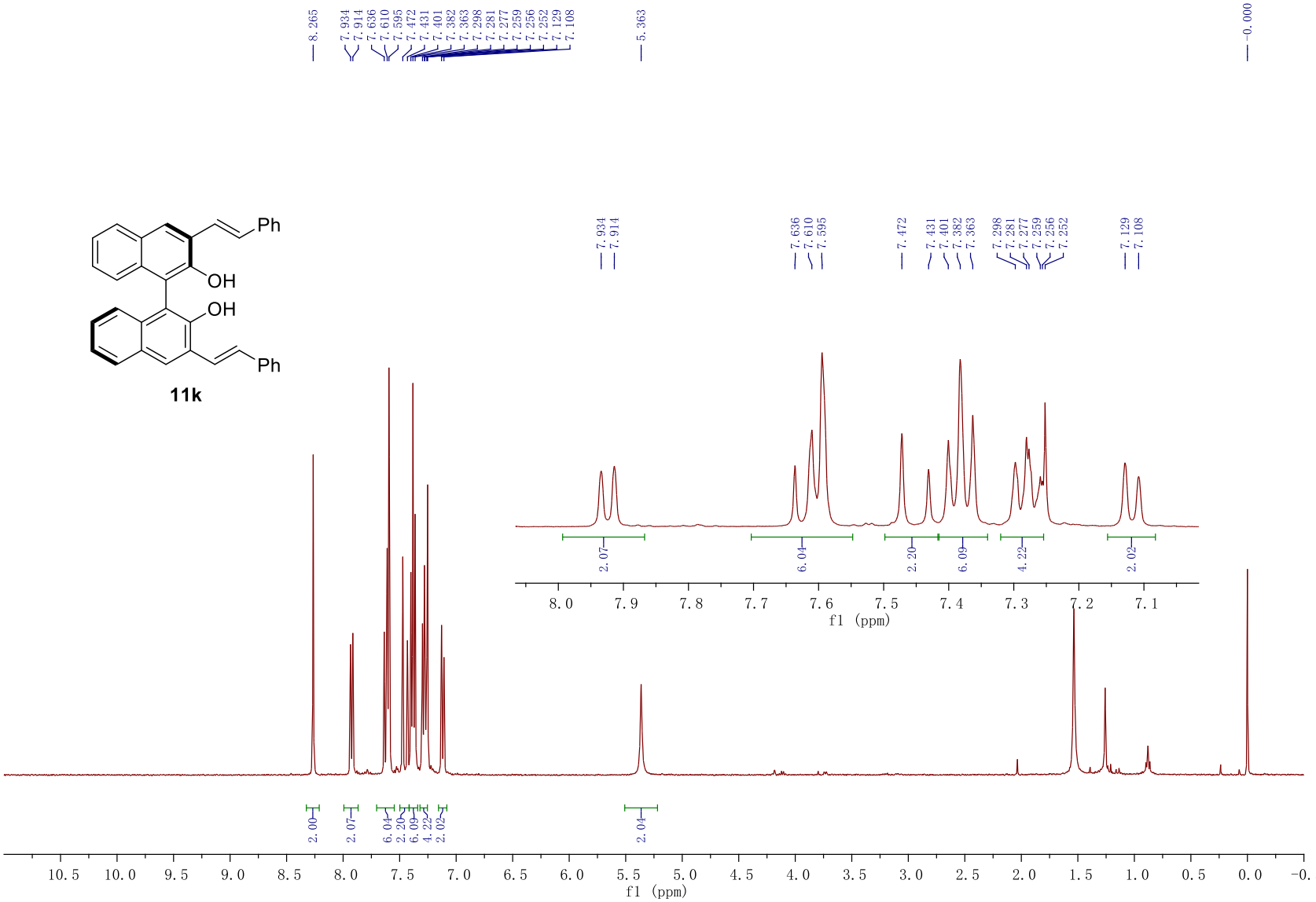
^{1}H NMR Spectrum of (*E*)-2-(2-(thiophen-2-yl)vinyl)phenol (11j)



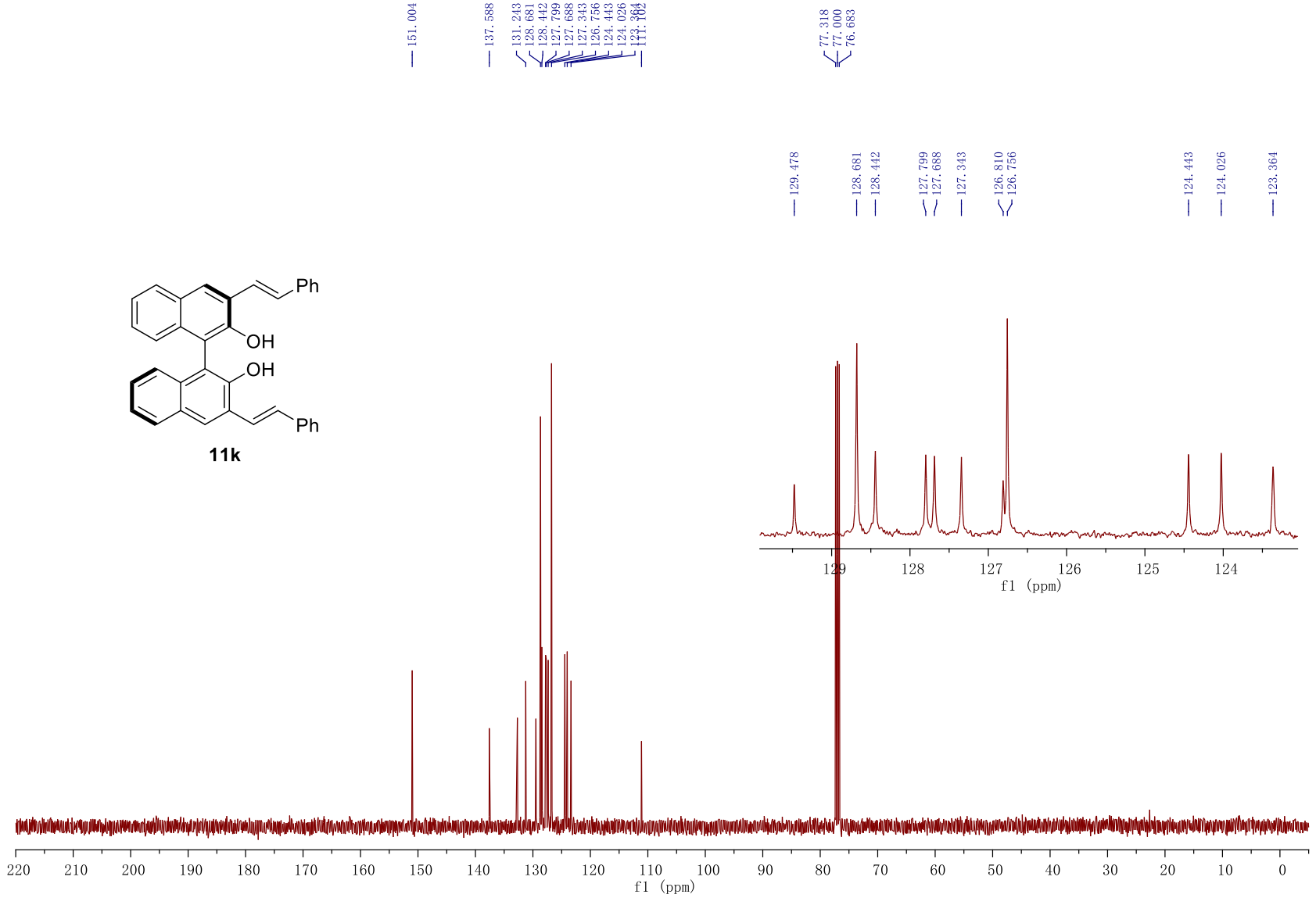
^{13}C NMR Spectrum of (*E*)-2-(2-(thiophen-2-yl)vinyl)phenol (11j)



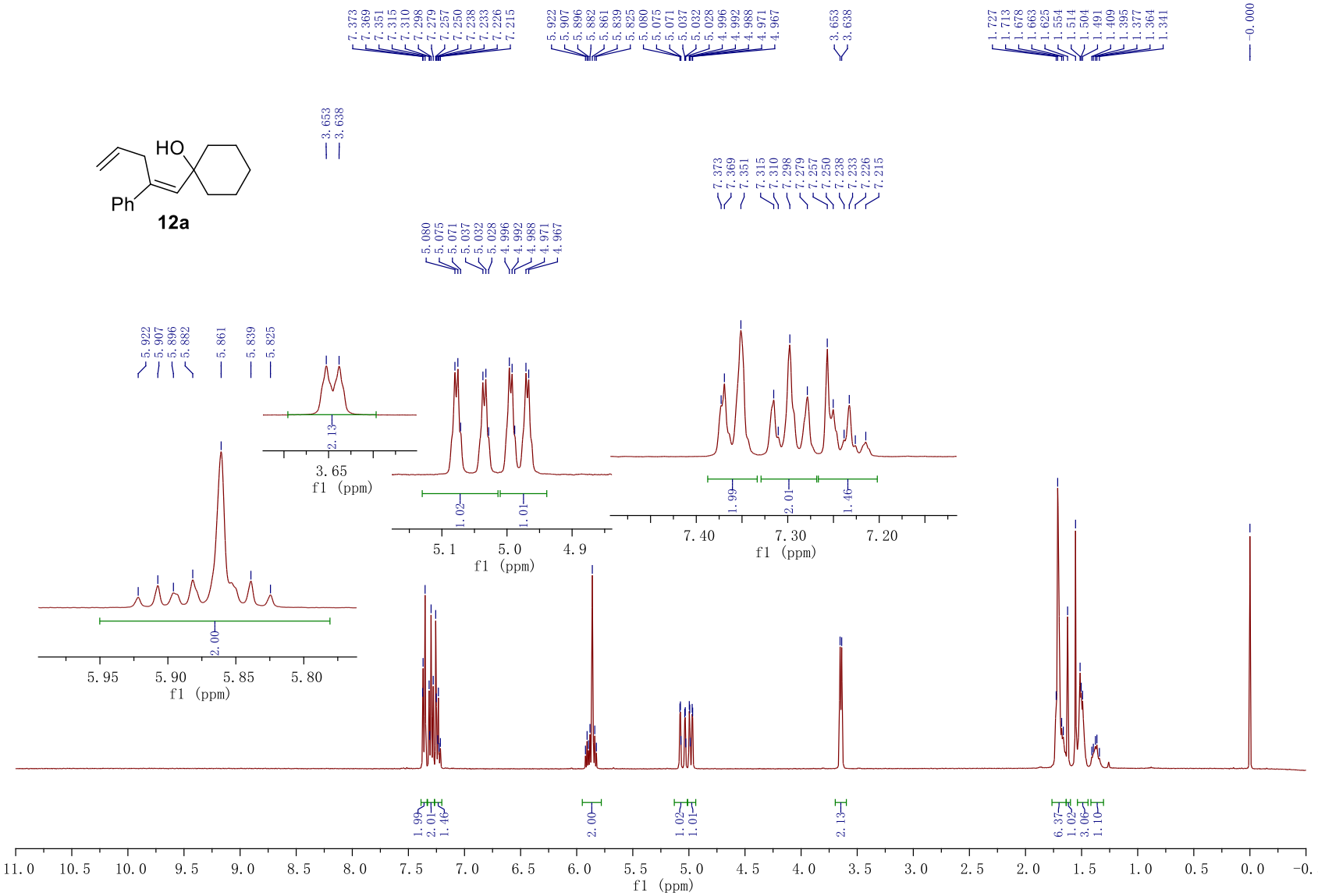
[1]H NMR Spectrum of (*R*)-3,3'-di((*E*)-styryl)-[1,1'-binaphthalene]-2,2'-diol (11k)



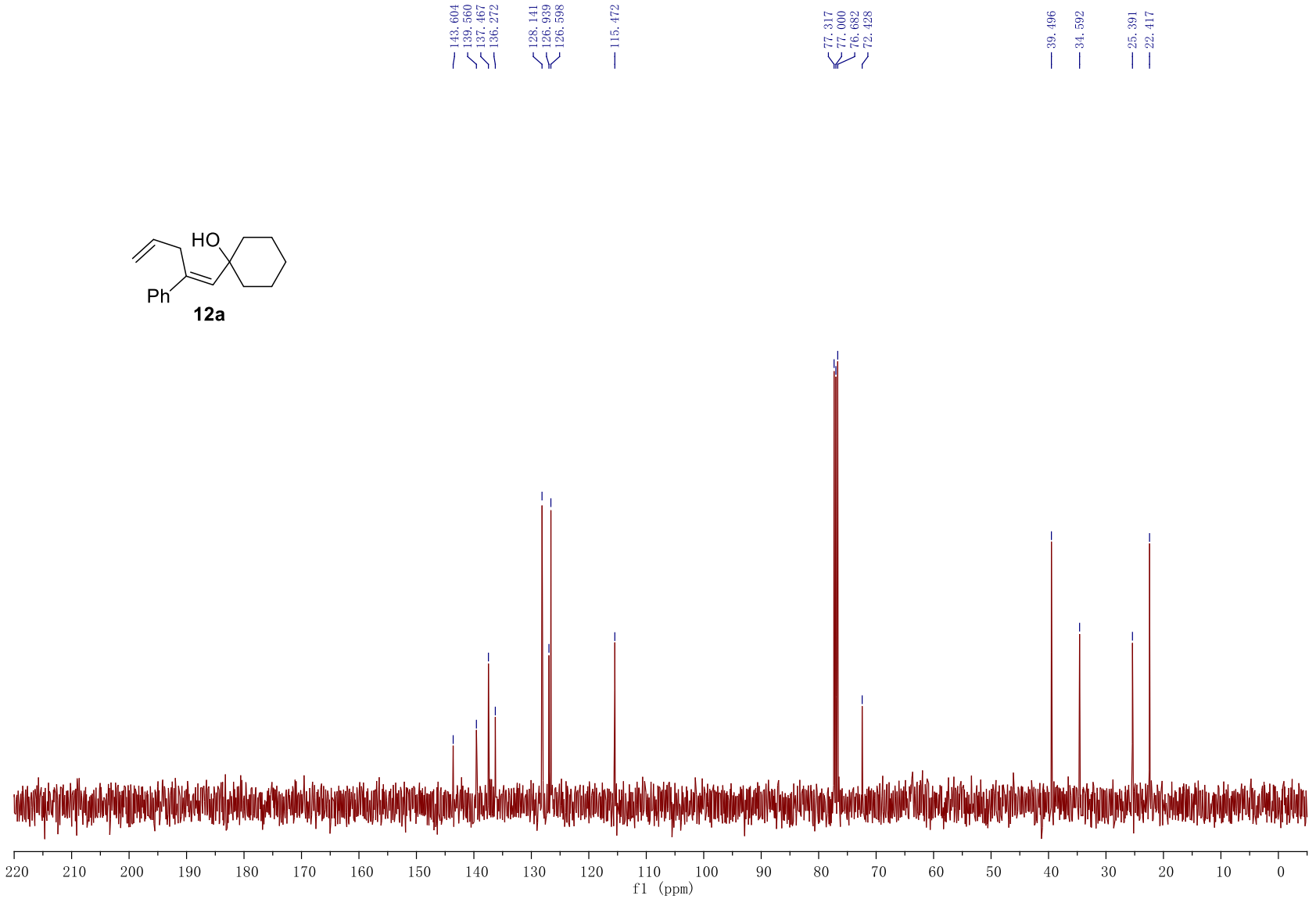
^{13}C NMR Spectrum of (*R*)-3,3'-di((*E*)-styryl)-[1,1'-binaphthalene]-2,2'-diol (11k)



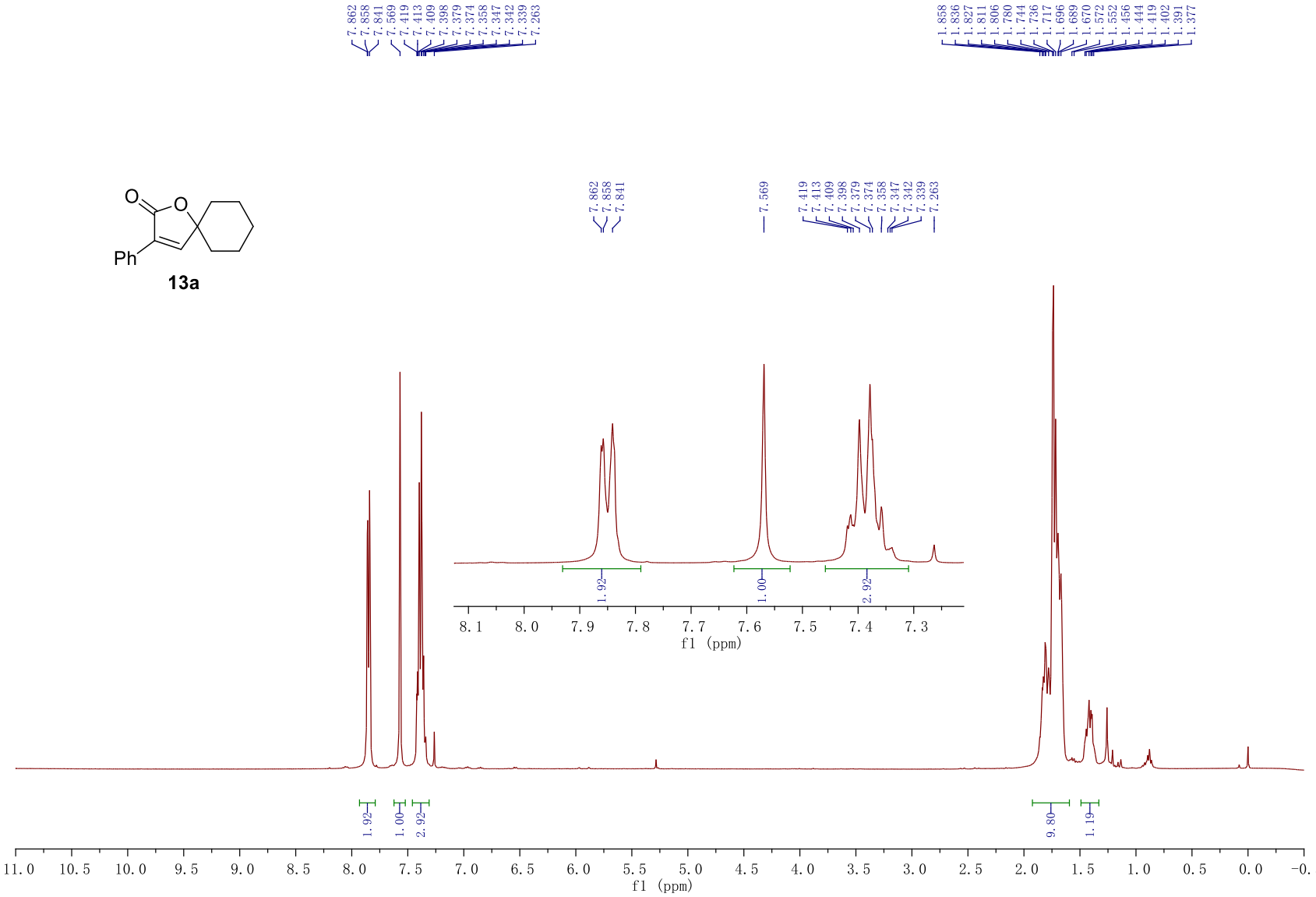
^{1}H NMR Spectrum of (*E*)-1-(2-phenylpenta-1,4-dien-1-yl)cyclohexan-1-ol (12a)



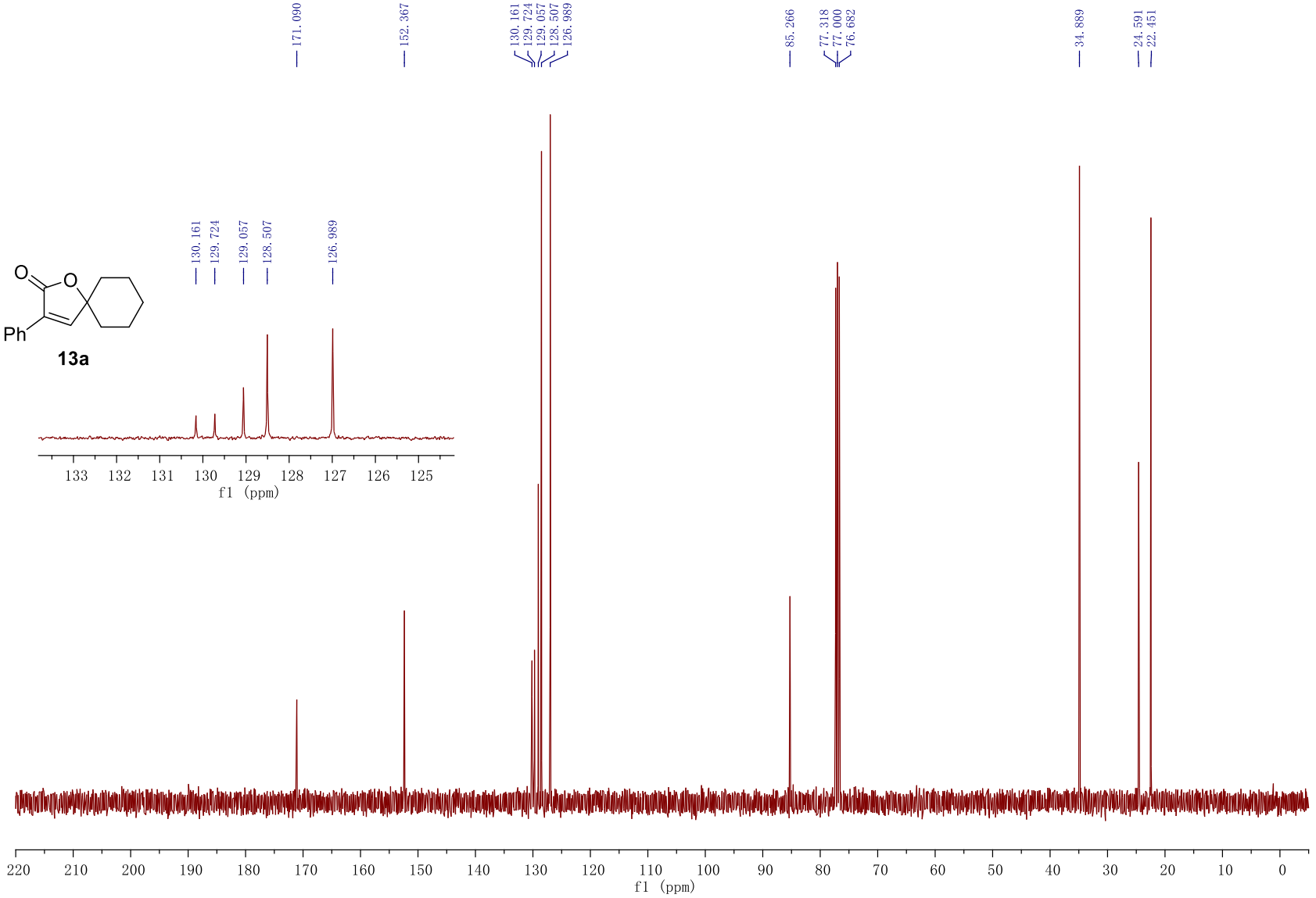
^{13}C NMR Spectrum of (*E*)-1-(2-phenylpenta-1,4-dien-1-yl)cyclohexan-1-ol (12a)



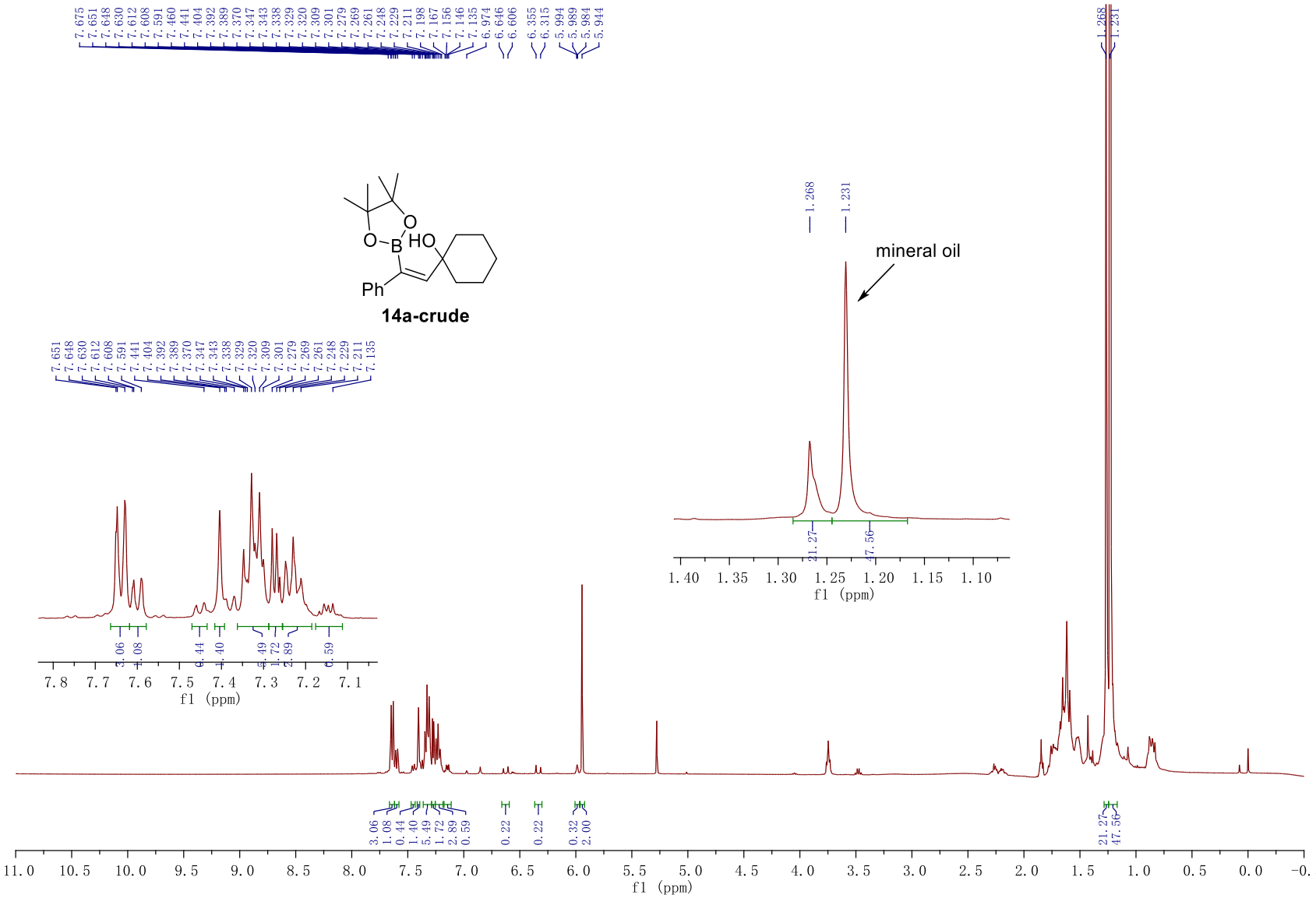
^{1}H NMR Spectrum of 3-phenyl-1-oxaspiro[4.5]dec-3-en-2-one (13a)



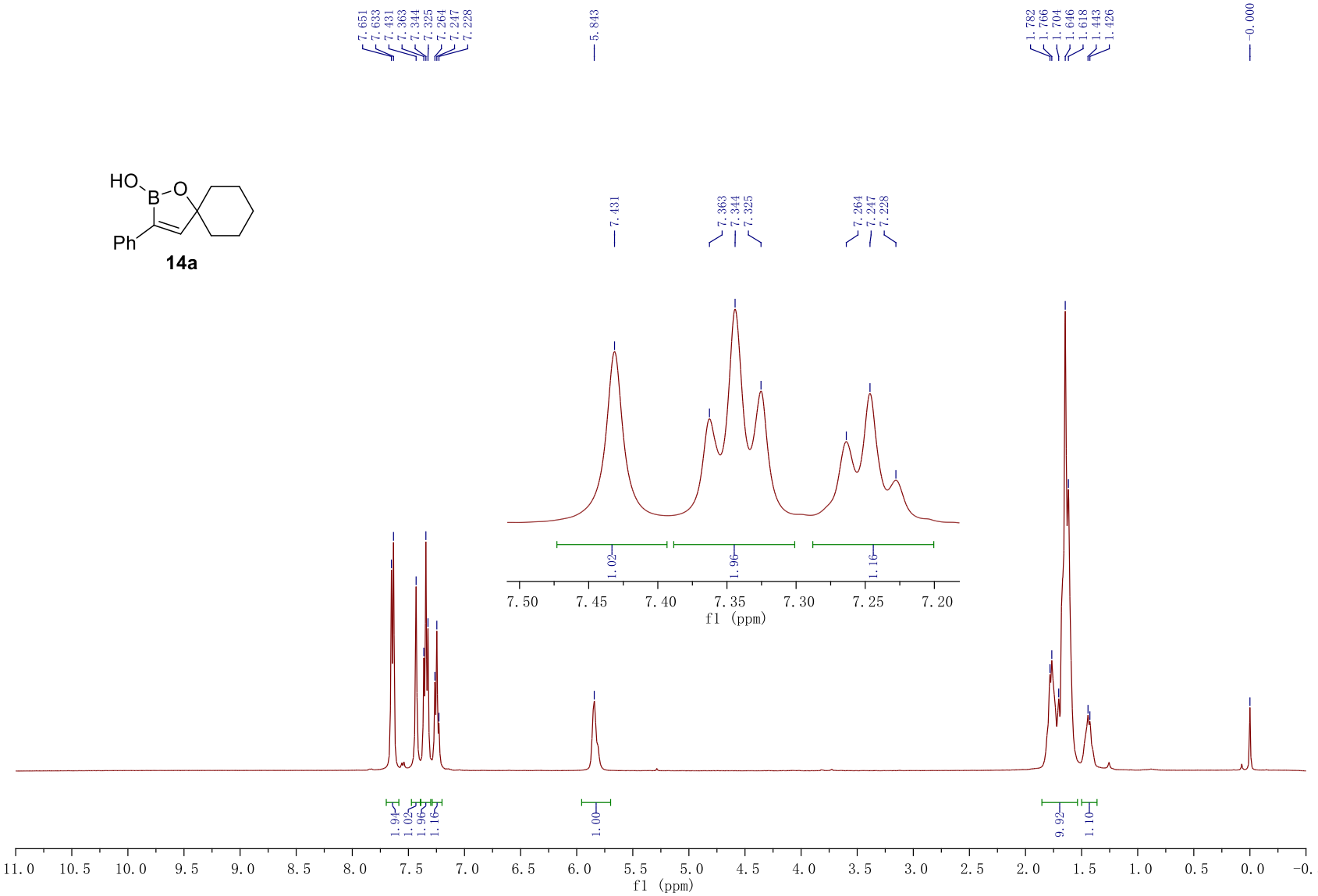
^{13}C NMR Spectrum of 3-phenyl-1-oxaspiro[4.5]dec-3-en-2-one (13a)



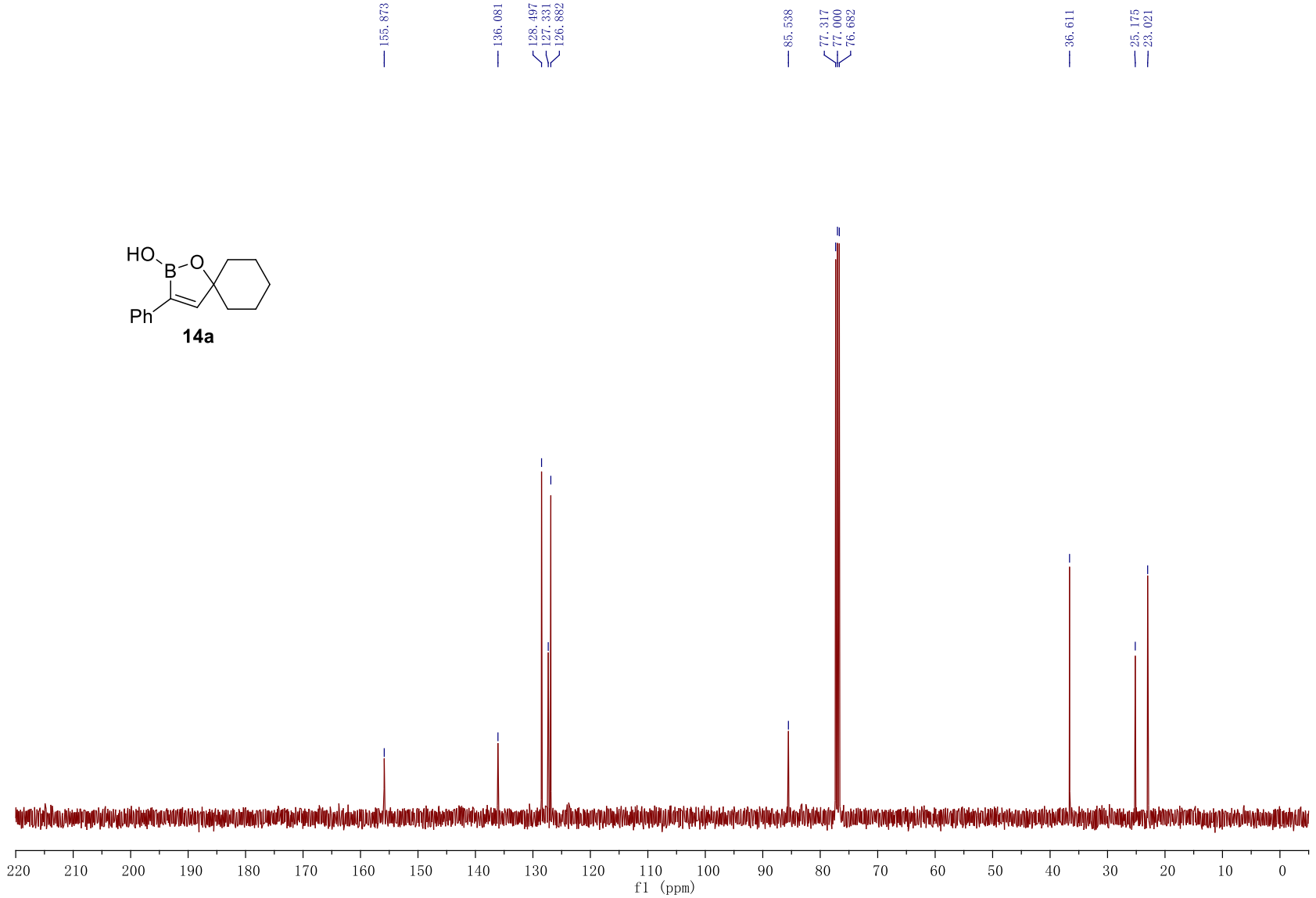
[1]H NMR Spectrum of crude borylation product starting from 10a (14a-crude)



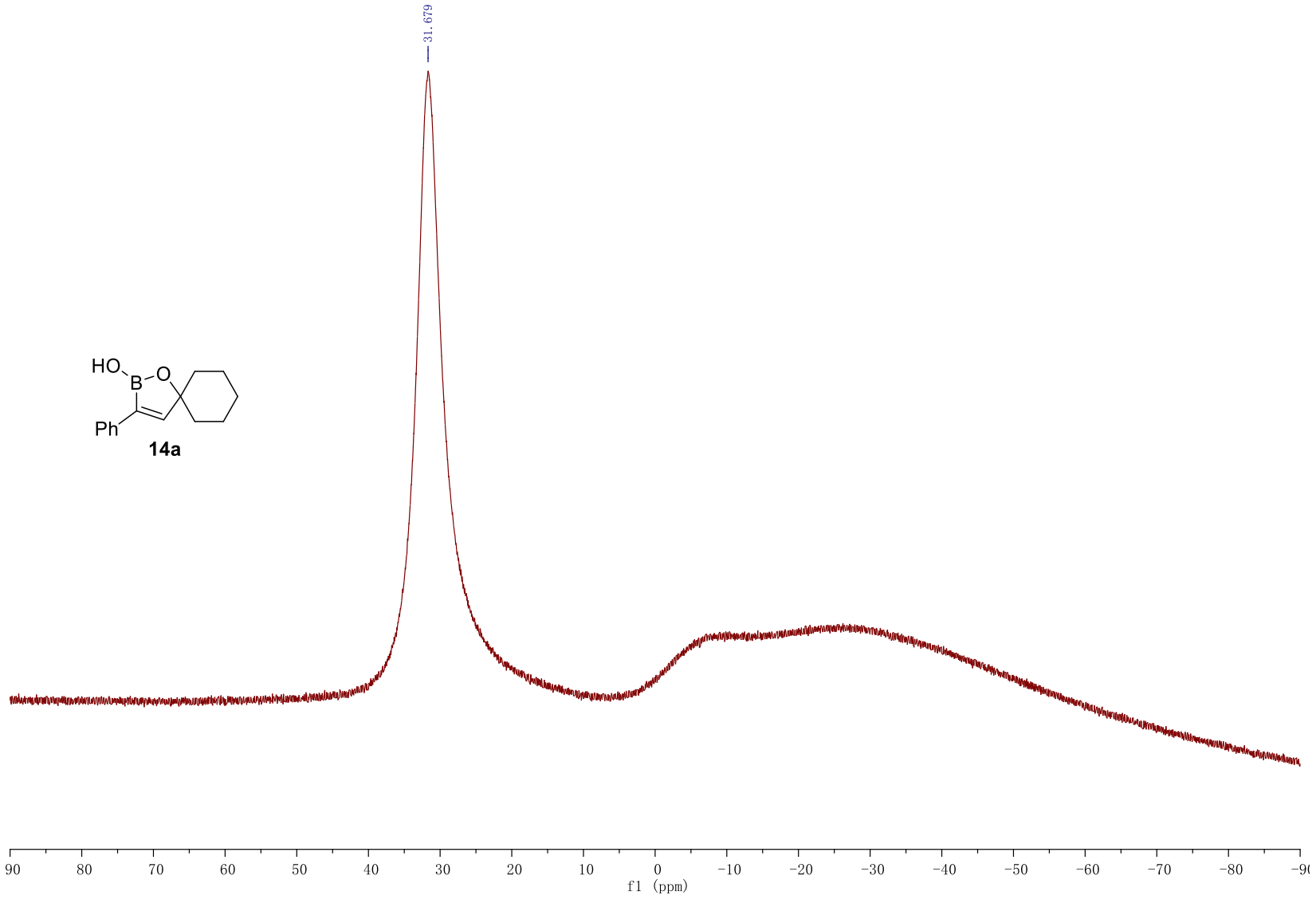
[1]H NMR Spectrum of 3-phenyl-1-oxa-2-boraspiro[4.5]dec-3-en-2-ol (14a)



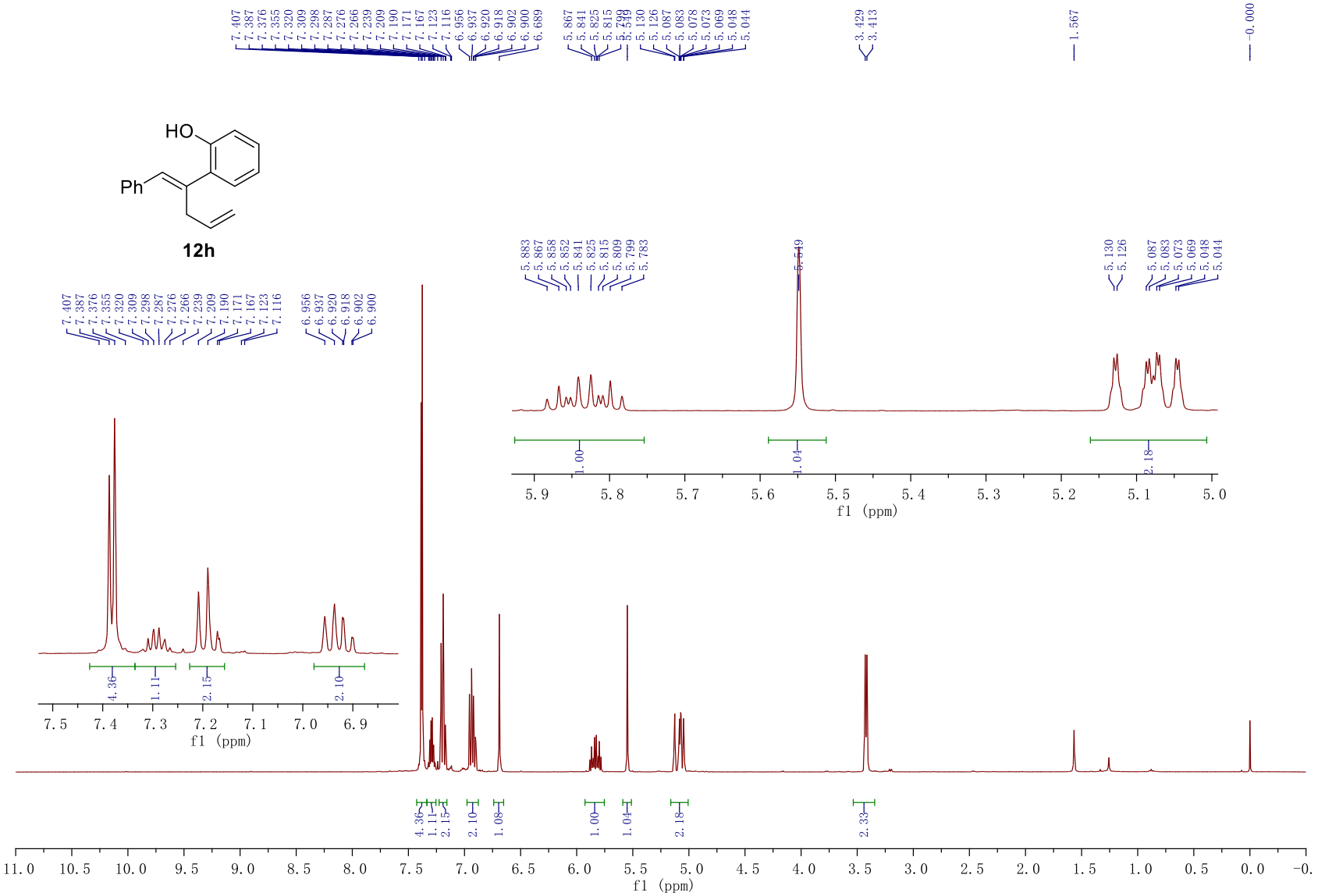
^{13}C NMR Spectrum of 3-phenyl-1-oxa-2-boraspiro[4.5]dec-3-en-2-ol (14a)



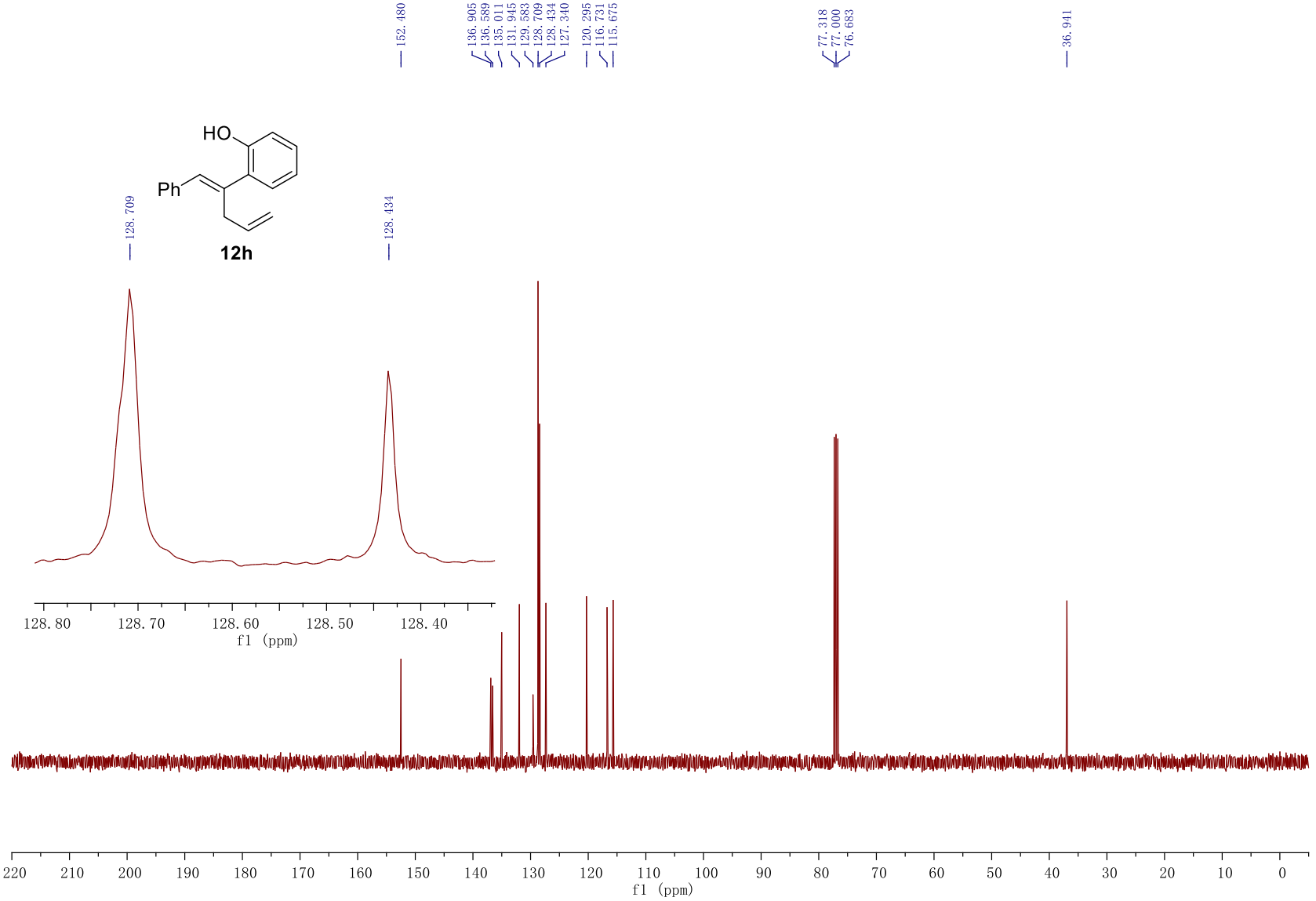
^{11}B NMR Spectrum of 3-phenyl-1-oxa-2-boraspiro[4.5]dec-3-en-2-ol (14a)



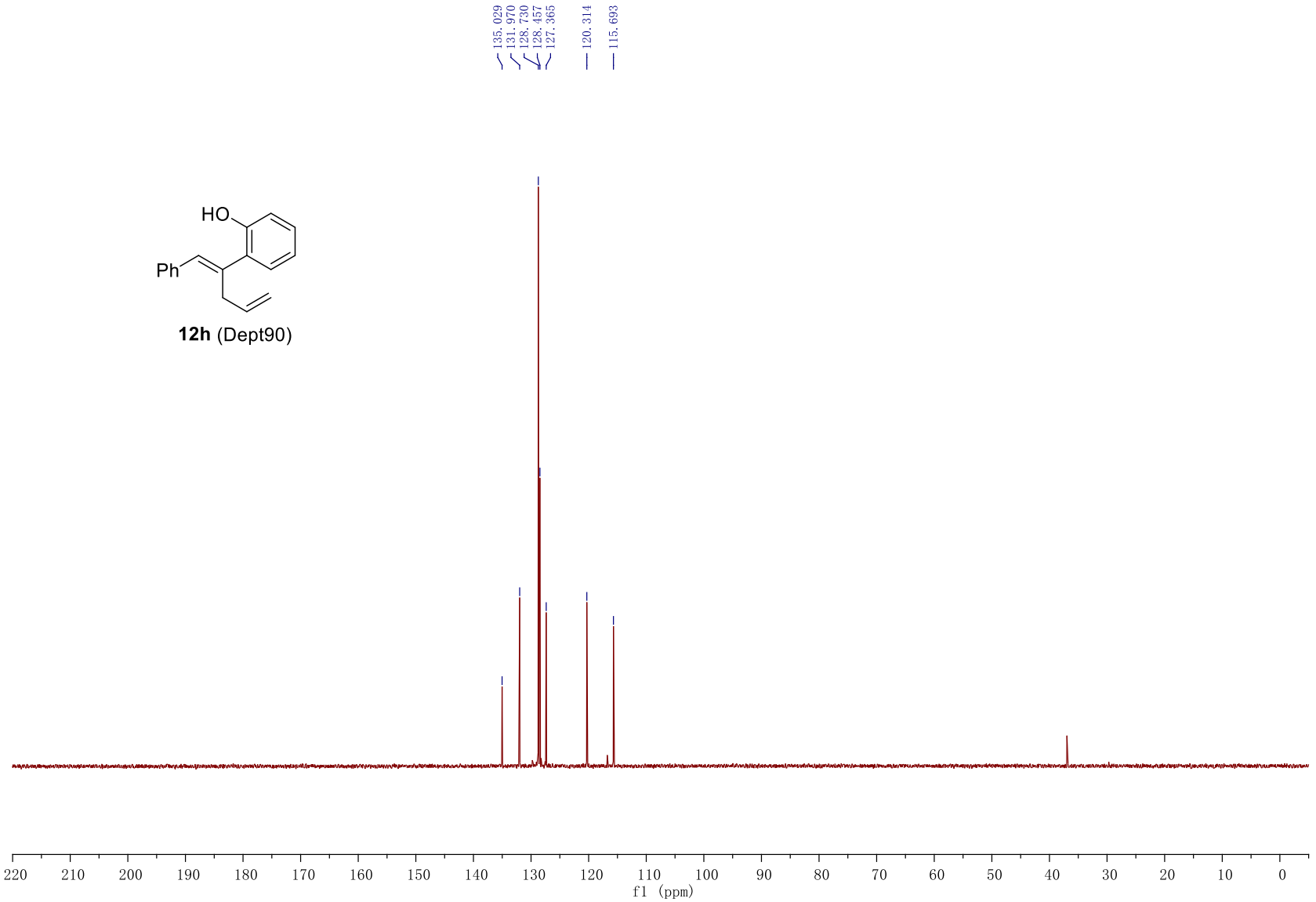
^{1}H NMR Spectrum of (*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



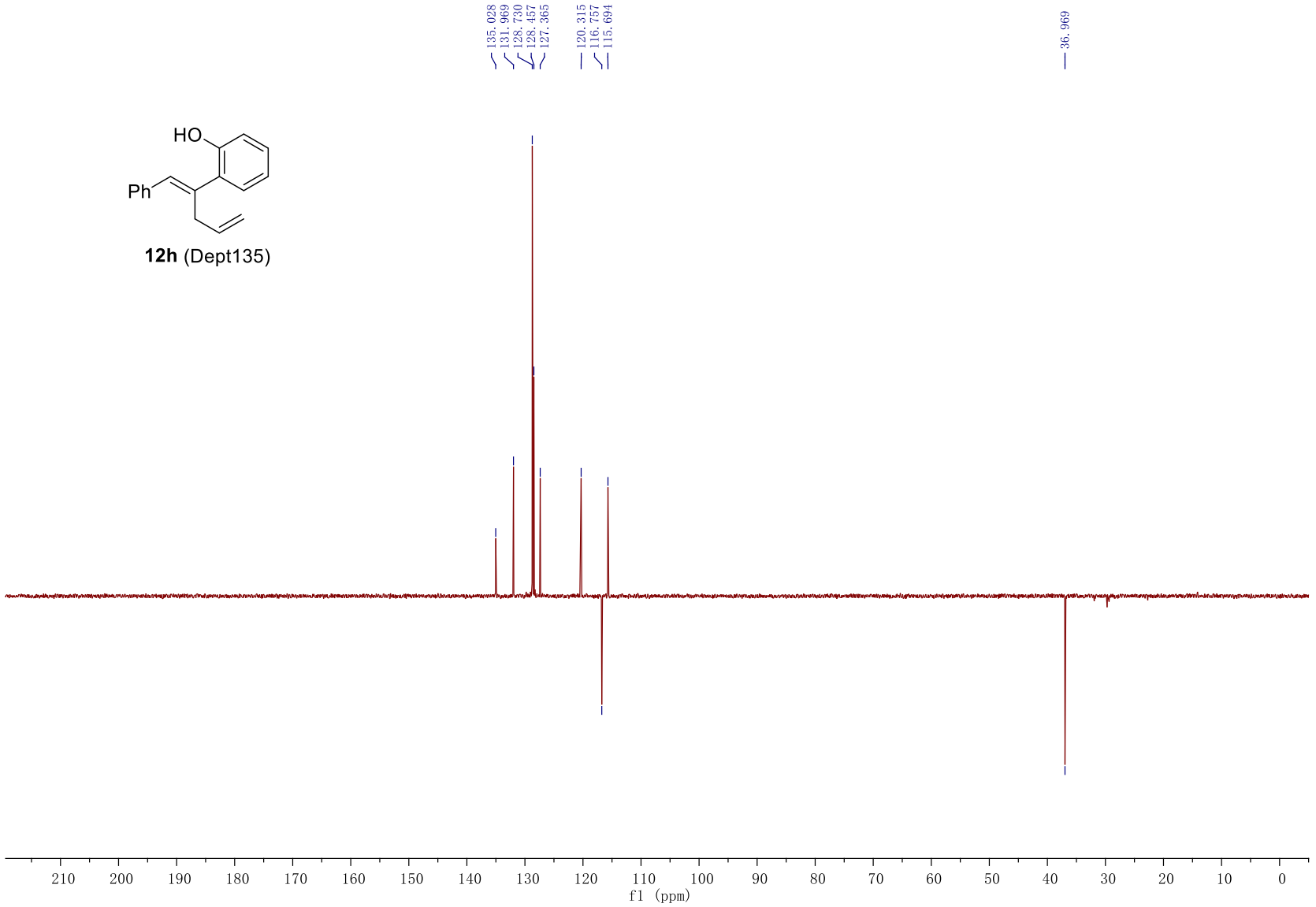
^{13}C NMR Spectrum of (*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



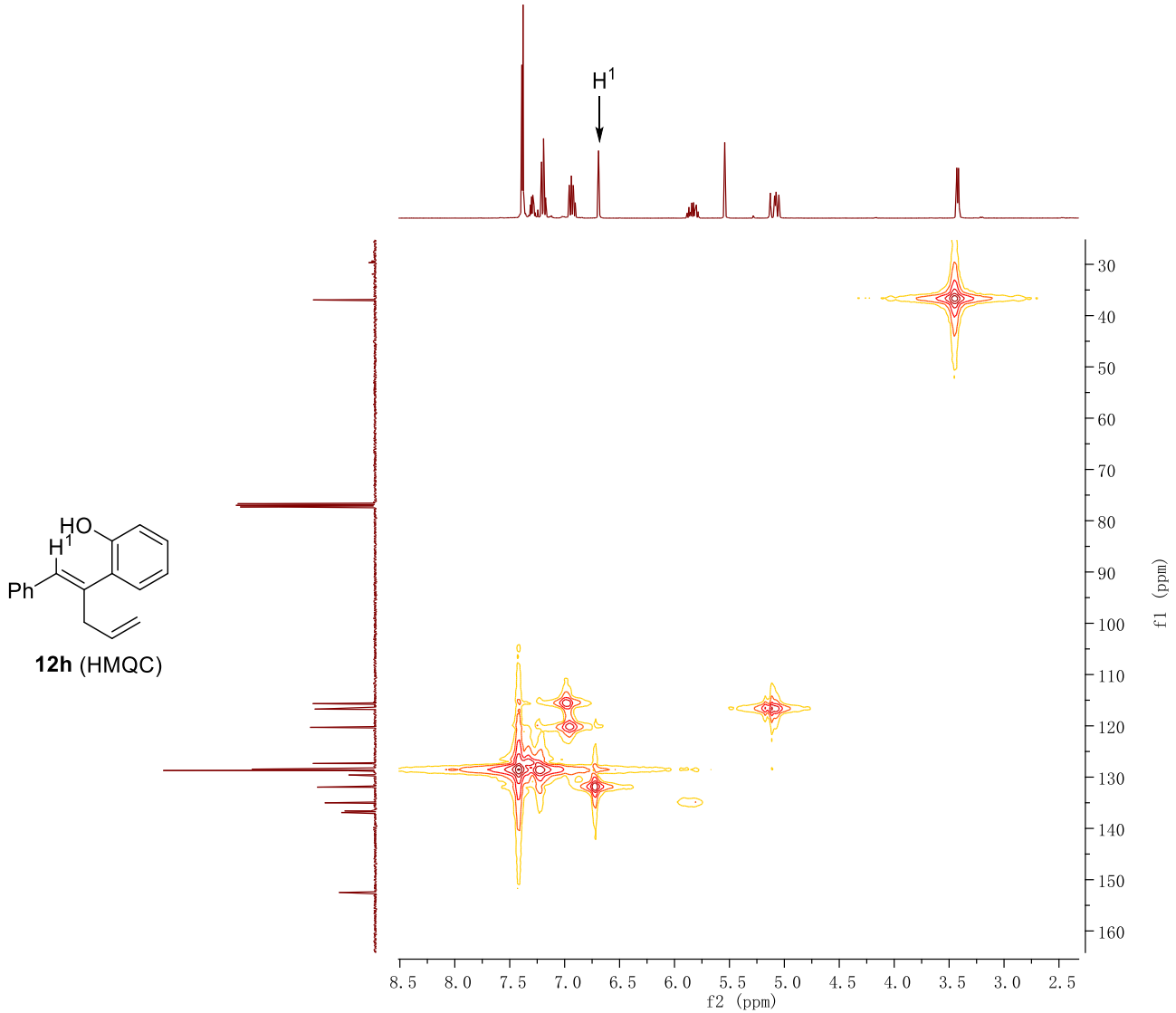
Dept90 NMR Spectrum of (*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



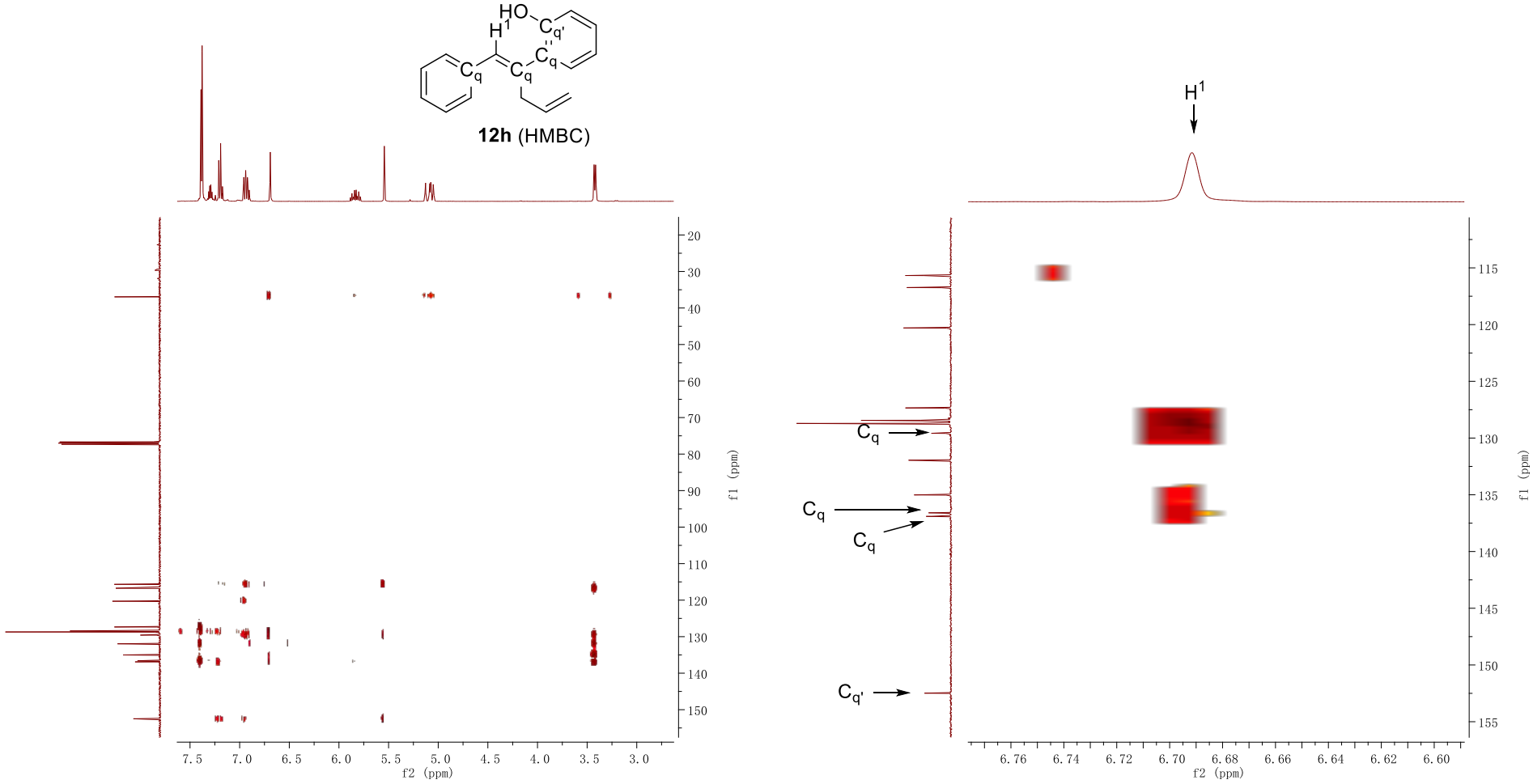
Dept135 NMR Spectrum of (*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



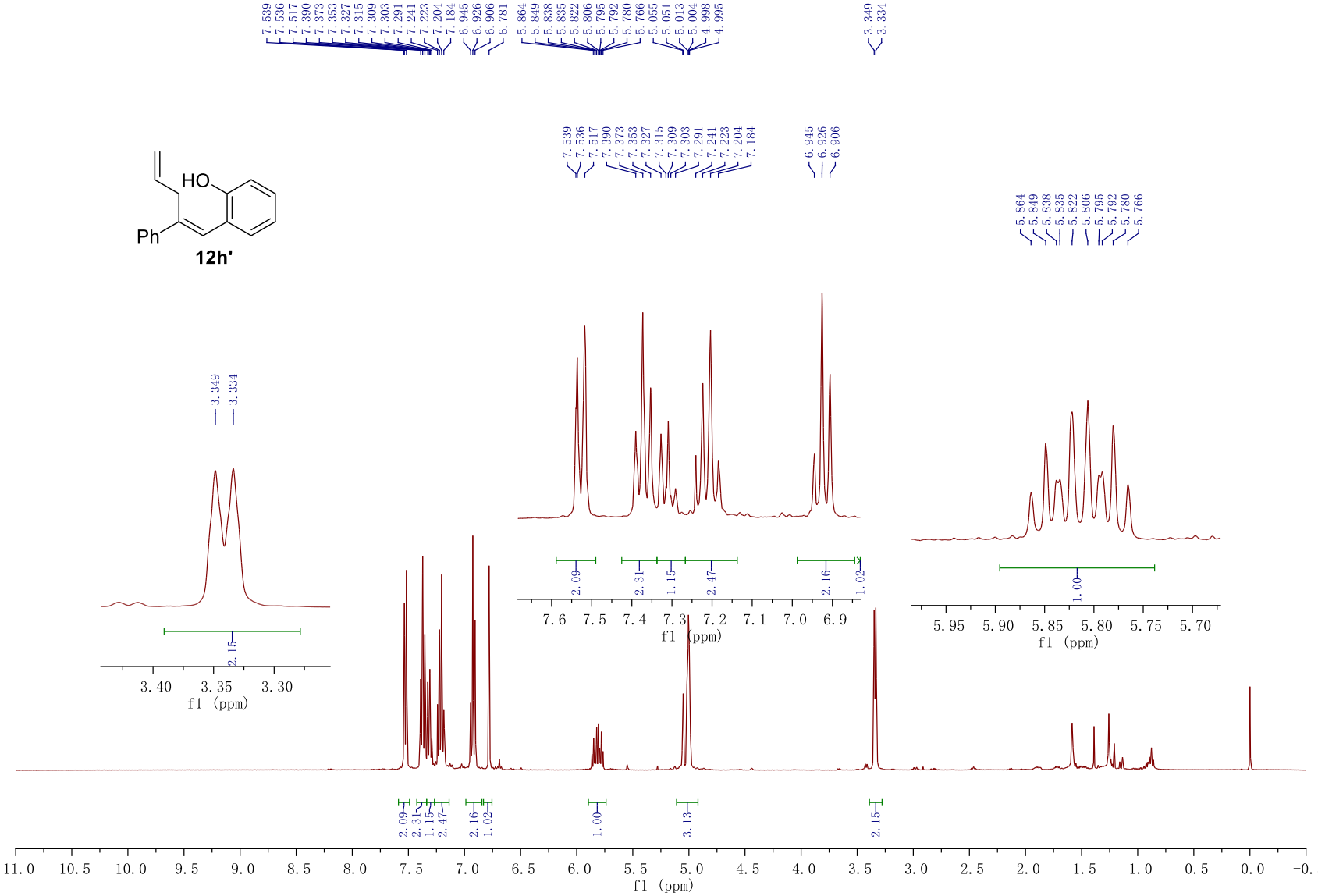
HMQC of (*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



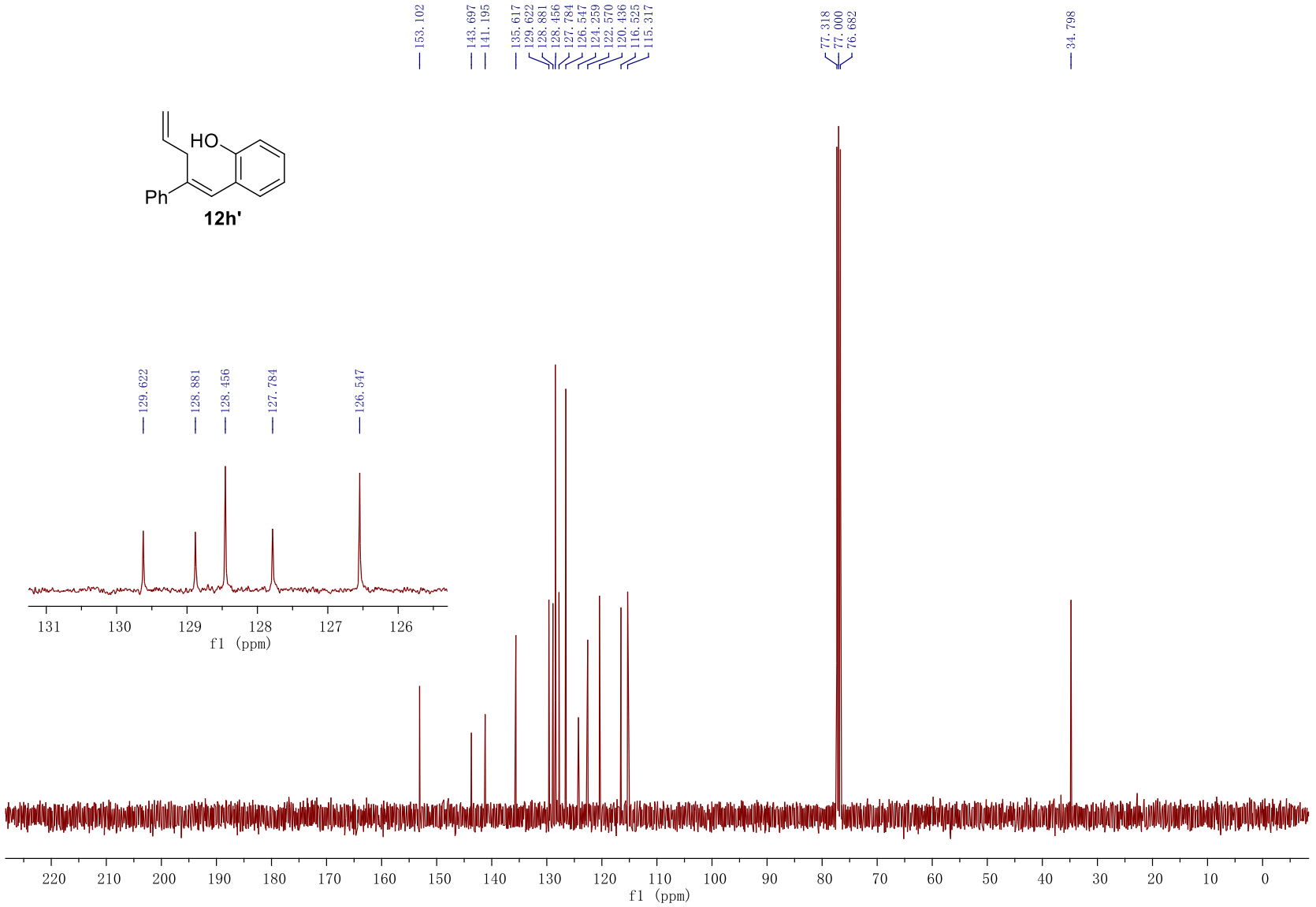
HMBC of (*E*)-2-(1-phenylpenta-1,4-dien-2-yl)phenol (12h)



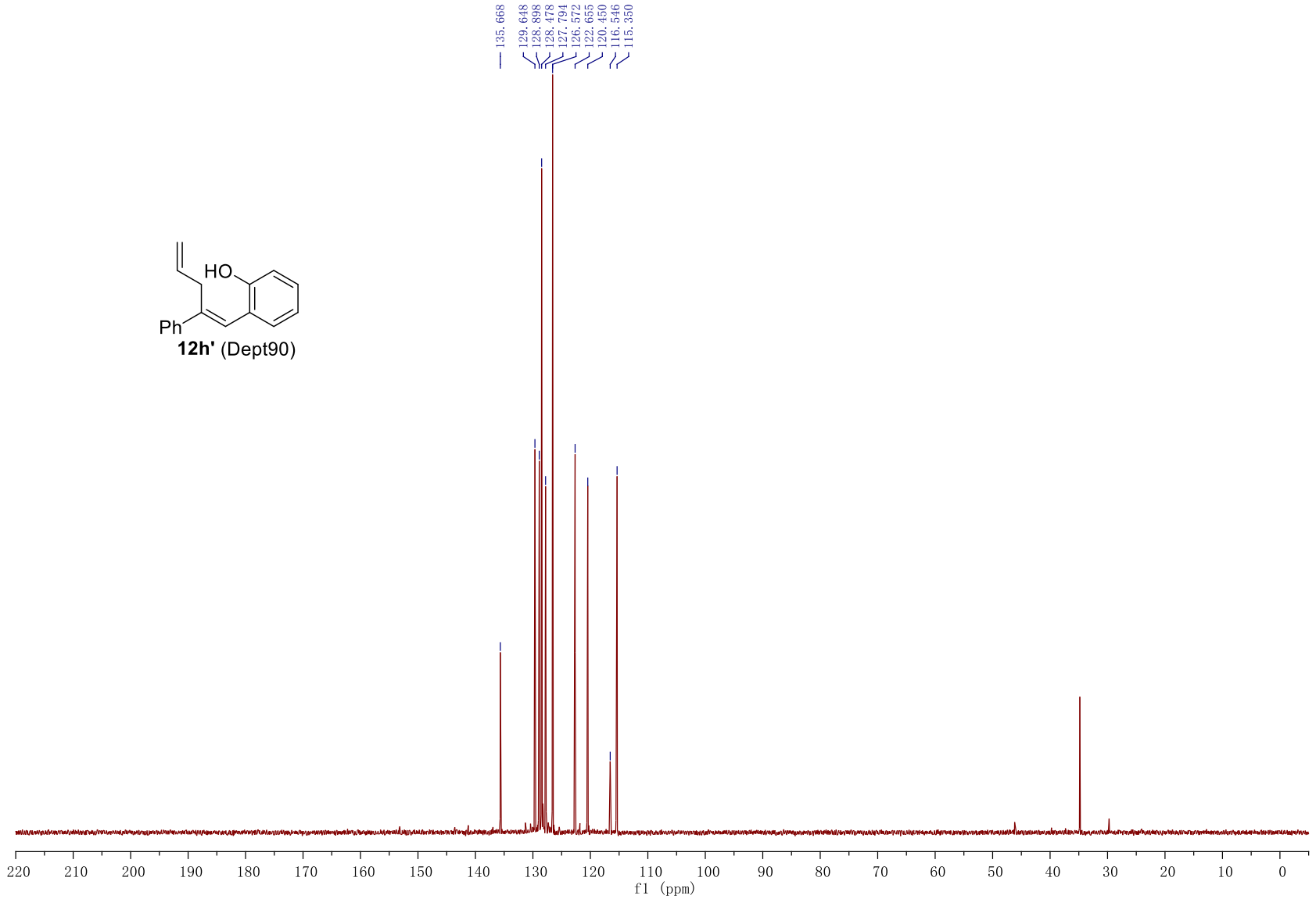
^{1}H NMR Spectrum of (*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')



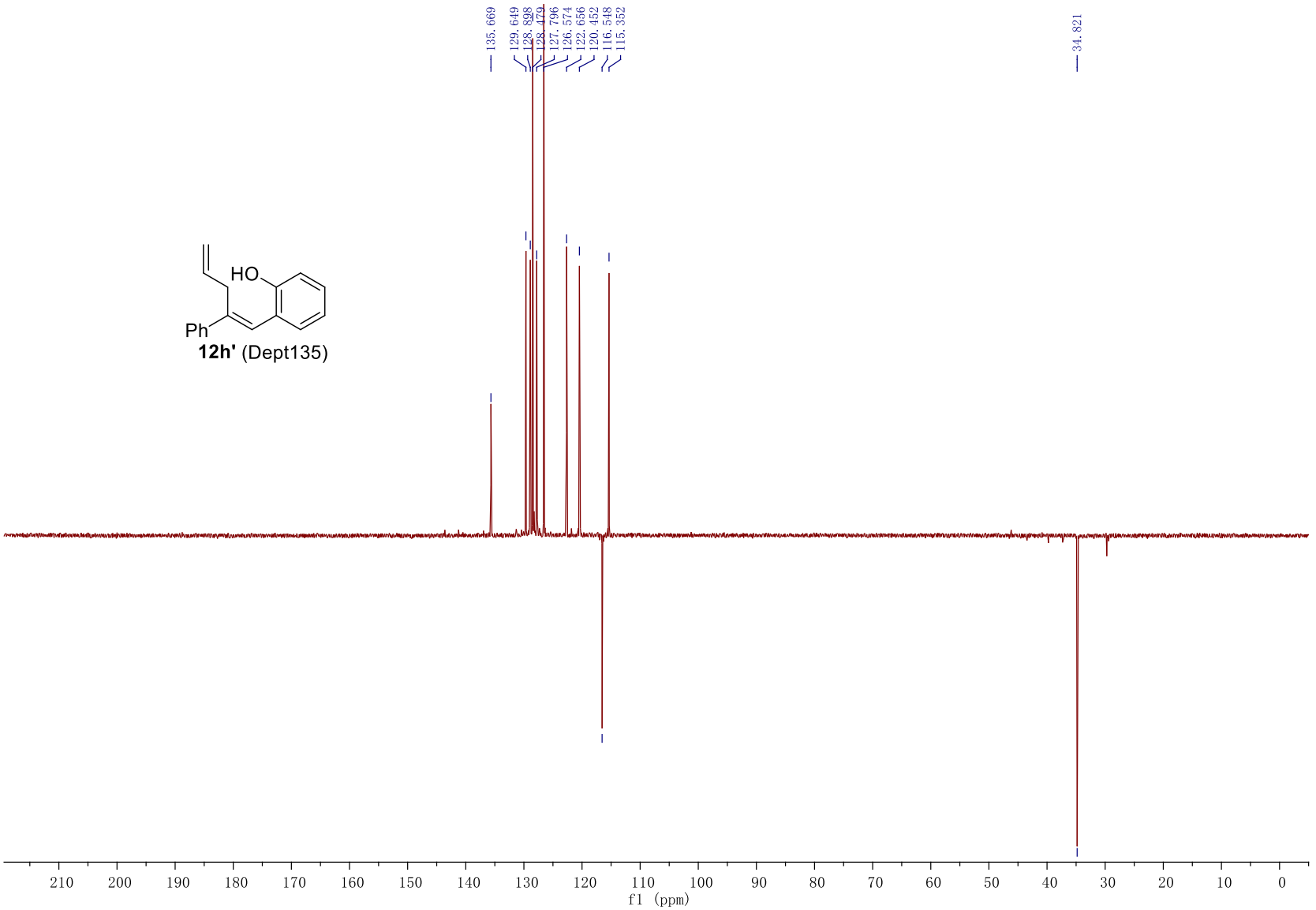
^{13}C NMR Spectrum of (*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')



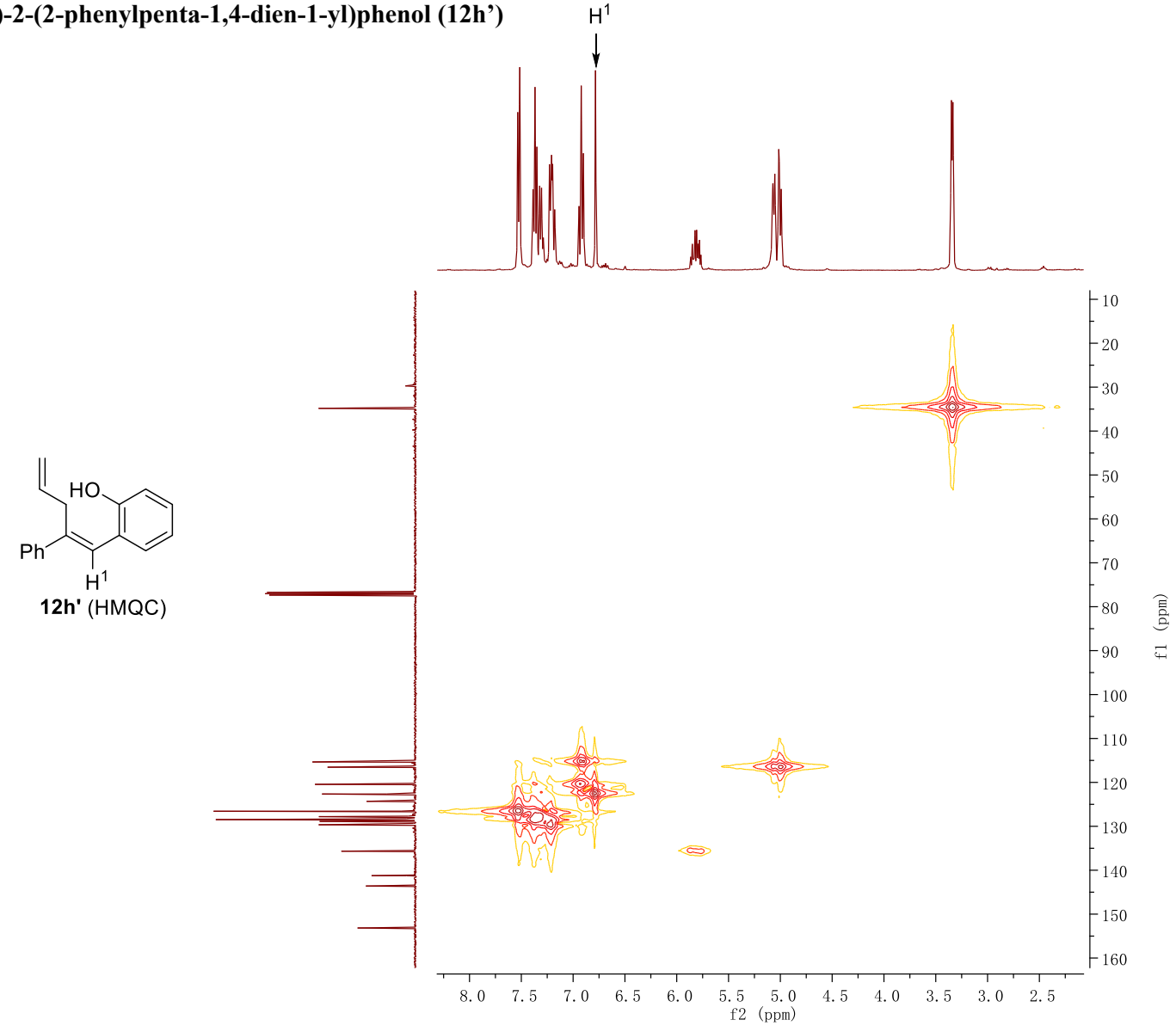
Dept90 NMR Spectrum of (*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')



Dept135 NMR Spectrum of (*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')



HMQC of (*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')



HMBC of (*E*)-2-(2-phenylpenta-1,4-dien-1-yl)phenol (12h')