Electronic Supplementary Information

Simple and efficient *in situ* generated copper nanocatalyst for stereoselective semihydrogenation of alkynes

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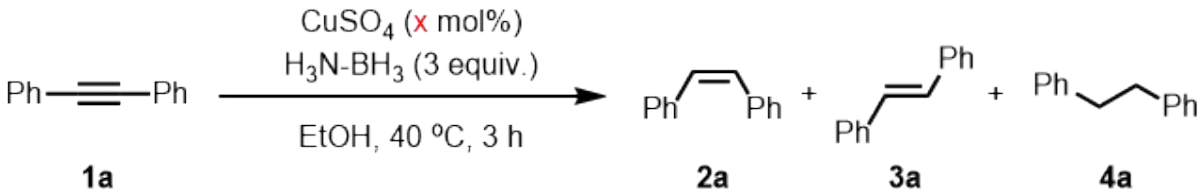
S.1. General Information

Unless stated otherwise, all reactions were carried out under atmospheric environment.
All chemical reagents were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), Alfa Aesar, Daejung Chemical Industry and Duksan. Unless otherwise stated, they were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded using a JEOL (400 MHz) NMR spectrometer. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and dt = doublets of triplets, dd = doublets of doublets. Mass Spectra (EI) was recorded on an Agilent Technologies 7693A instrument. High Resolution Mass Spectra (HRMS) was recorded on a Bruker impact II instrument (ESI-QToF). X-ray photoelectron spectroscopy (XPS) spectra was recorded using Thermo Fisher Scientific NEXSA spectrometer and an Al Kα X-ray source ($h\nu$ = 1486.7 eV). Transmission electron microscopy (TEM) and High-angle annular dark field-scanning transmission electron microscopy (HADDF-STEM) micrographs were obtained with a JEOL JEM-2100F microscope at 200kV. Energy dispersive X-ray spectroscopy (EDS) mapping images were collected using a JEOL JEM-2100F microscope and Aztec X-Max 80T (Oxford Instrument, UK). Scanning electron microscopy (SEM) micrographs were obtained with a JEOL JSM-7500F microscope. Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku Smartlab X-ray diffractometer with a Cu Kα radiation.

S.2. Optimization of reaction conditions

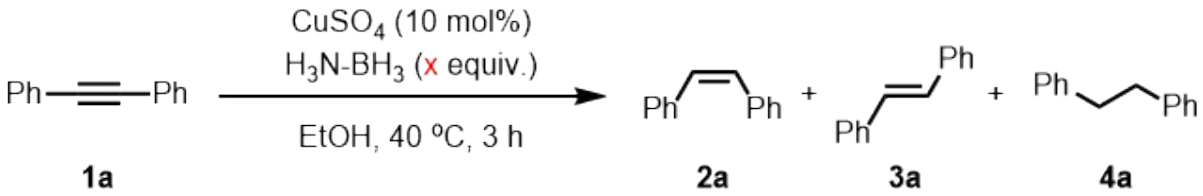
Table S1. Screening of the amount of copper sulfate ($CuSO_4$) for (Z)-selective semihydrogenation [a]



Entry	$CuSO_4$ (mol%)	Conversion (%)	Yield of **2a**/**3a**/**4a** (%)
1	0.5 %	11	11/0/0
2	1.0 %	40	39/1/0
3	2.0 %	43	41/1/0
4	3.0 %	69	67/1/0
5	4.0 %	90	88/2/0
6	5.0 %	98	96/1/1
7	10 %	99	97/2/1
8	20 %	98	96/2/1
9	1 equiv.	98	92/2/3

[a] Reaction conditions: **1a** (0.5 mmol), H_3N-BH_3 (3 equiv.), EtOH (2.0 mL), 40 ℃ for 3 h under aerobic condition otherwise noted. Yield was determined by ^{1}H-NMR by using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Screening of the amount of ammonia borane (H_3N-BH_3) for (Z)-selective semihydrogenation [a]



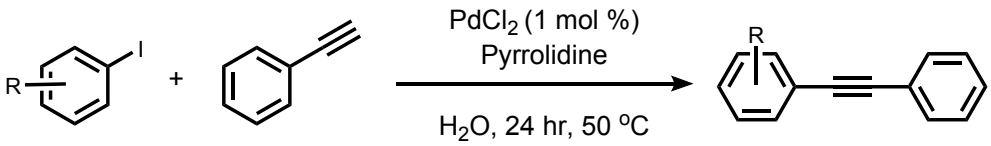
Entry	H_3N-BH_3 (equiv.)	Conversion (%)	Yield of **2a**/**3a**/**4a** (%)
1	0.1	0	0/0/0
2	0.5	28	27/0/0
3	1.0	98	95/1/0
4	2.0	99	97/1/1
5	3.0	99	97/1/0
6	4.0	99	96/1/0
7	5.0	98	96/2/0

[a] Reaction conditions: **1a** (0.5 mmol), $CuSO_4$ (10 mol%), EtOH (2.0 mL), 40 ℃ for 3 h under aerobic condition otherwise noted. Yield was determined by ^{1}H-NMR by using 1,3,5-trimethoxybenzene as an internal standard.

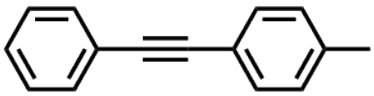
S.3. Experimental procedure and characterization of the products

S.3.1. General procedure for the preparation of internal alkynes via Sonogashira reaction

Alkynes **1b-c**, **1f-i** were prepared according to the following procedure [S1]:



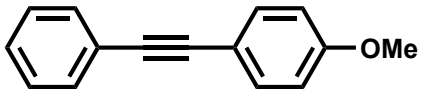
$PdCl_2$ (0.02 mmol), aryl iodide (2.0 mmol), H_2O (5.0 mL), and pyrrolidine (0.83 mL, 10 mmol) were added to a 50 mL round bottom flask under aerobic conditions, and the resulting mixture was stirred at 50 ℃ for 5 minutes. To this solution was added phenyl acetylene (2.4 mmol) and the reaction mixture was stirred at 50 ℃ for 24 h. The reaction mixture was then extracted with EtOAc (3 x 10 mL) and the combined organic layer was dried with Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography to give the desired product.



1-methyl-4-(phenylethynyl)benzene (1b)

Purified by column chromatography using Hexane as eluent. White solid. Yield 70%.

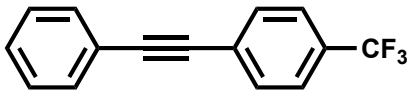
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50-7.54 (m, 2H), 7.42-7.44 (m, 2H), 7.29-7.36 (m, 3H), 7.14-7.16 (m, 2H), 2.37 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 138.5, 131.7, 131.6, 129.3, 128.5, 128.2, 123.6, 120.3, 89.7, 88.8, 21.7. **MS** (EI): m/z = 193(16), 192($[M]^+$, 100), 191(50), 190(12), 189(24), 165(13).



1-methoxy-4-(phenylethynyl)benzene (1c)

Purified by column chromatography using Hexane : EtOAc = 20 : 1 as eluent. Light yellow solid. Yield 70 %.

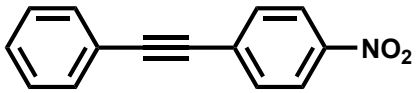
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45-7.52 (m, 4H), 7.28-7.36 (m, 3H), 6.86-6.90 (m, 2H), 3.83 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 159.7, 133.2, 131.6, 128.5, 128.1, 123.7, 115.5, 114.1, 89.5, 88.2, 55.5. **MS** (EI): m/z = 209(15), 208($[M]^+$, 100), 193(49), 165(40), 164(15), 163(11), 139(11), 28(17).



1-(phenylethynyl)-4-(trifluoromethyl)benzene (1f)

Purified by column chromatography using Hexane : EtOAc = 50 : 1 as eluent. White solid. Yield 45 %.

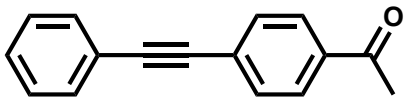
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52-7.64 (m, 6H), 7.35-7.39 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 131.96, 131.90, 129.0, 128.6, 127.3, 125.49, 125.45, 125.41, 125.38, 122.7, 91.9, 88.1. **MS** (EI): m/z = 247(16), 246($[M]^+$, 100).



1-nitro-4-(phenylethynyl)benzene (1g)

Purified by column chromatography using Hexane : EtOAc = 3 : 1 as eluent. Light yellow solid. Yield 36 %.

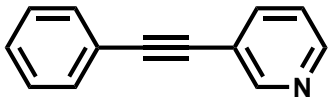
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (dt, J = 9.1, 2.1 Hz, 2H), 7.66 (dt, J = 9.2, 2.1 Hz, 2H), 7.53-7.59 (m, 2H), 7.36-7.43 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 147.1, 132.4, 132.0, 130.4, 129.4, 128.7, 123.8, 122.3, 94.9, 87.7. **MS** (EI): m/z = 224(16), 223($[M]^+$, 100), 194(12), 193(66), 177(22), 176(73), 165(33), 151(29), 150(21), 88(12), 32(16), 28(56).



1-(4-(phenylethynyl)phenyl)ethan-1-one (1h)

Purified by column chromatography using Hexane : EtOAc = 3 : 1 as eluent. Light brown solid. Yield 40 %

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (dt, J = 8.4, 1.8 Hz, 2H), 7.61 (dt, J = 8.4, 1.8 Hz, 2H), 7.53-7.58 (m, 2H), 7.35-7.39 (m, 3H), 2.62 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 197.5, 136.3, 131.89, 131.85, 129.0, 128.6, 128.4, 128.3, 122.8, 92.9, 88.7, 26.8. **MS** (EI): m/z = 221(11), 220($[M]^+$, 62), 206(16), 205(100), 177(22), 176(50), 151(18), 150(12), 88(12), 28(22).



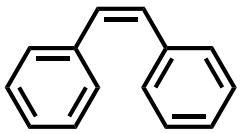
3-(phenylethynyl)pyridine (1i)

Purified by column chromatography using Hexane : EtOAc = 7 : 1 as eluent. Yellow solid. Yield 77 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.77 (s, 1H), 8.53-8.55 (m, 1H), 7.78-7.81 (m, 1H), 7.54-7.56 (m, 2H), 7.36-7.37 (m, 3H), 7.25-7.29 (m, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 152.4, 148.7, 138.5, 131.8, 128.9, 128.5, 123.1, 122.6, 120.5, 92.7, 86.0. **MS** (EI): m/z = 180(15), 179($[M]^+$, 100), 178(22), 152(10), 151(12), 126(15), 28(12).

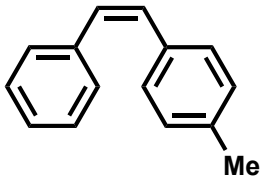
S.3.2. General procedure for the (Z)-selective semihydrogenation of alkynes

To a 5 mL vial, alkyne substrate (0.5 mmol), $CuSO_4$ (0.05 mmol), and ethanol (2 mL) was added. The reaction mixture was stirred at 40 ℃ until the alkyne substrate dissolved in ethanol. After, ammonia borane (1.5 mmol) was added and reaction mixture was stirred for 3 h at 40 ℃. The reaction mixture was then extracted with EtOAc (3 x 10 mL) and the combined organic layer was dried with Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography to give the desired (Z)-alkene.



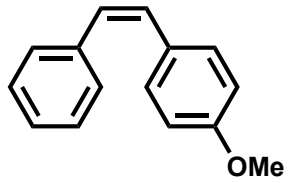
(Z)-1,2-diphenylethene (2a) [S2]

Purified by column chromatography using Hexane as eluent. Colorless oil. Yield 99 %.
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15-7.26 (m, 10H), 6.59 (s, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 137.4, 130.4, 129.0, 128.3, 127.2. **MS** (EI): m/z = 181(14), 180([M]$^+$, 96), 179(100), 178(68), 176(12), 165(49), 152(13), 89(20), 76(14).



(Z)-1-methyl-4-styrylbenzene (2b) [S2]

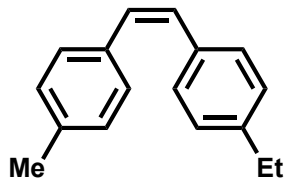
Purified by column chromatography using Hexane as eluent. Colorless oil. Yield 95 %.
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.13-7.27 (m, 7H), 7.02 (d, J = 7.9 Hz, 2H), 6.55 (s, 2H), 2.30 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 137.6, 137.0, 134.4, 130.3, 129.7, 129.03, 128.97, 128.9, 128.3, 127.1, 21.4. **MS** (EI): m/z = 195(14), 194([M]$^+$, 86), 193(21), 180(14), 179(100), 178(82), 165(12), 152(10), 115(13).



(Z)-1-methoxy-4-styrylbenzene (2c) [S3]

Purified by column chromatography using Hexane : EtOAc = 20 : 1 as eluent. Colorless oil. Yield 90 %.

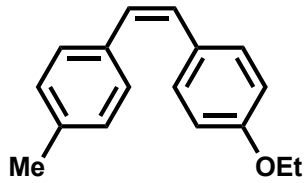
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15-7.28 (m, 7H), 6.72-6.76 (m, 2H), 6.47-6.54 (m, 2H), 3.76 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 158.8, 137.7, 130.3, 129.9, 129.8, 128.92, 128.86, 128.3, 127.0, 113.7, 55.3. **MS** (EI): m/z = 211(16), 210($[M]^+$, 100), 209(17), 195(18), 179(11), 167(27), 166(13), 165(42), 152(26).



(Z)-1-ethyl-4-(4-methylstyryl)benzene (2d) [S4]

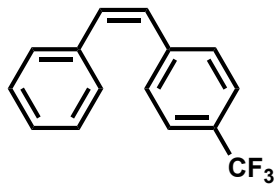
Purified by column chromatography using Hexane as eluent. Colorless oil. Yield 99 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15-7.20 (m, 4H), 7.02-7.06 (m, 4H), 6.51 (s, 2H), 2.60 (q, J = 7.6 Hz, 2H), 2.31 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 143.2, 136.8, 134.8, 134.6, 129.7, 129.6, 129.0, 128.93, 128.87, 127.8, 28.7, 21.4, 15.6. **MS** (EI): m/z = 223(19), 222($[M]^+$, 100), 208(14), 207(77), 193(34), 192(25), 191(28), 189(13), 179(15), 178(27), 165(12), 115(14), 91(10).



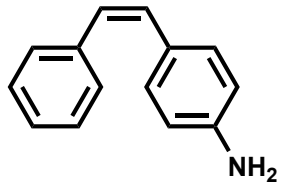
(Z)-1-ethoxy-4-(4-methylstyryl)benzene (2e)

Purified by column chromatography using Hexane : EtOAc = 15 : 1 as eluent. Light yellow solid. Yield 97 %. **HRMS (ESI):** m/z calcd for $C_{17}H_{19}O^+$ $[M+H]^+$ 239.1430; found 239.1429. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.15-7.20 (m, 4H), 7.03 (d, J = 7.9 Hz, 2H), 6.74 (dt, J = 9.4, 2.5 Hz, 2H), 6.46 (s, 2H), 4.00 (q, J = 7.0 Hz, 2H), 2.31 (s, 3H), 1.39 (t, J = 7.0 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 158.1, 136.7, 134.8, 130.2, 129.9, 129.3, 129.0, 128.9, 128.8, 114.2, 63.4, 21.4, 15.0.



(Z)-1-styryl-4-(trifluoromethyl)benzene (2f) [S5]

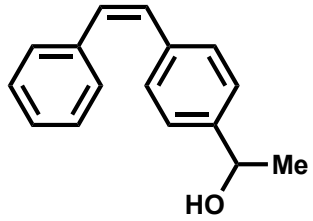
Purified by column chromatography using Hexane as eluent. Colorless oil. Yield 79 %. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.46 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.19-7.27 (m, 5H), 6.72 (d, J = 12.4 Hz, 1H), 6.59 (d, J = 12.4 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 141.1, 136.7, 132.5, 129.3, 129.0, 128.9, 128.6, 127.7, 125.7, 125.3 (q, J = 3.8 Hz), 123.0. **MS** (EI): m/z = 249(18), 248($[M]^+$, 100), 247(22), 233(19), 229(11), 227(20), 207(10), 180(14), 179(91), 178(8 4), 176(11), 152(10), 89(10).



(Z)-4-styrylaniline (2g) [S2]

Purified by column chromatography using Hexane : EtOAc = 5 : 1 as eluent. Yellow oil. Yield 93 %.

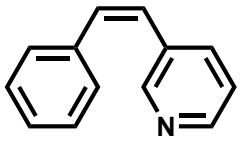
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15-7.31 (m, 5H), 7.06 (dt, J = 8.9, 2.3 Hz, 2H), 6.50-6.54 (m, 2H), 6.45 (q, J = 11.0 Hz, 2H), 3.65 (s, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 145.6, 137.9, 130.3, 130.2, 128.9, 128.3, 127.7, 127.5, 126.8, 114.8. **MS** (EI): m/z = 196(15), 195([M]$^+$, 100), 194(52), 193(18), 180(13), 178(12), 177(13), 165(14), 97(10), 28(17).



(Z)-1-(4-styrylphenyl)ethan-1-ol (2h) [S4]

Purified by column chromatography using Hexane : EtOAc = 5 : 1 as eluent. Light yellow oil. Yield 85 %.

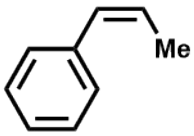
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16-7.26 (m, 9H), 6.57 (q, J = 9.3 Hz, 2H), 4.83 (q, J = 6.4 Hz, 1H), 1.96 (s, 1H), 1.46 (d, J = 6.4 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 144.7, 137.4, 136.5, 130.3, 130.0, 129.1, 128.9, 128.4, 127.2, 125.4, 70.3, 25.1. **MS** (EI): m/z = 224([M]$^+$, 9), 209(12), 207(28), 206(100), 205(32), 204(14), 203(24), 202(20), 191(31), 190(15), 189(16), 179(30), 178(50), 166(11), 165(24), 152(12), 103(15), 101(11), 89(13), 77(11), 32(29), 28(98).



(Z)-3-styrylpyridine (2i) [S6]

Purified by column chromatography using Hexane : EtOAc = 3 : 1 as eluent. Yellow oil. Yield 95 %.

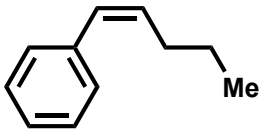
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47 (d, J = 2.3 Hz, 1H), 8.39-8.41 (m, 1H), 7.50 (dt, J = 7.8, 1.8 Hz, 1H), 7.18-7.26 (m, 5H), 7.09-7.12 (m, 1H), 6.74 (d, J = 12.4 Hz, 1H), 6.53 (d, J = 12.4 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 150.3, 148.2, 136.6, 135.9, 133.1, 132.8, 128.8, 128.6, 127.7, 126.5, 123.1. **MS** (EI): m/z = 181($[M]^+$, 40), 180(100), 152(18).



(Z)-prop-1-en-1-ylbenzene (2j) [S7]

Yield 94 % (^{1}H NMR yield relative to 1,3,5-trimethoxybenzene (0.5 mmol) as an internal standard.)

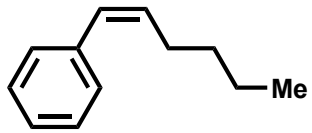
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28-7.34 (m, 4H), 7.18-7.22 (m, 1H), 6.43 (dd, J = 11.7, 1.8 Hz, 1H), 5.78 (dq, J = 16.6, 4.8 Hz, 1H), 1.89 (dd, J = 7.3, 1.8 Hz, 3H).



(Z)-pent-1-en-1-ylbenzene (2k) [S5]

Purified by column chromatography using Hexane as eluent. Colorless oil. Yield 94 %.

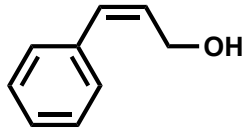
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.18-7.34 (m, 5H), 6.41 (d, J = 11.6 Hz, 1H), 5.66 (dt, J = 13.5, 5.8 Hz, 1H), 2.28-2.34 (m, 2H), 1.43-1.52 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 138.0, 133.2, 129.0, 128.9, 128.2, 126.5, 30.7, 23.3, 14.0. **MS** (EI): m/z = 146($[M]^+$, 35), 118(10), 117(100), 116(13), 115(53), 104(34), 91(31).



(Z)-hex-1-en-1-ylbenzene (2l) [S8]

Purified by column chromatography using Hexane as eluent. Colorless oil. Yield 89 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16-7.34 (m, 5H), 6.40 (d, J = 11.6 Hz, 1H), 5.66 (td, J = 9.5, 5.9 Hz, 1H), 2.30-2.36 (m, 2H), 1.30-1.48 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 138.0, 133.4, 128.9, 128.8, 128.2, 126.5, 32.3, 28.5, 22.6, 14.1. **MS** (EI): m/z = 160($[M]^+$, 30), 118(12), 117(100), 116(13), 115(51), 104(64), 91(34).



(Z)-3-phenylprop-2en-1-ol (2m) [S9]

Purified by column chromatography using Hexane : EtOAc = 3 : 1 as eluent. Colorless oil. Yield 88 %.

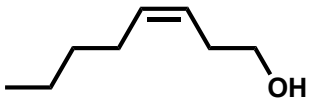
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.19-7.36 (m, 5H), 6.56 (d, J = 11.9 Hz, 1H), 5.86 (dt, J = 12.4, 5.8 Hz, 1H), 4.43 (dd, J = 6.4, 1.5 Hz, 2H), 1.81 (s, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 136.6, 131.3, 131.0, 128.9, 128.4, 127.4, 59.8. **MS** (EI): m/z = 134($[M]^+$, 42), 133(18), 117(12), 116(44), 115(82), 105(48), 103(28), 92(100), 91(78), 89(14), 79(29), 78(56), 77(51), 65(12), 63(18), 55(16), 51(28), 50(13), 39(13).

(Z)-dec-5-ene (2n) [S10]

Yield 93 % (^{1}H NMR yield relative to 1,3,5-trimethoxybenzene (0.5 mmol) as an internal standard.)

Purified by column chromatography using Hexane as eluent. Colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.31-5.39 (m, 2H), 1.98-2.08 (m, 4H), 1.29-1.36 (m, 8H), 0.87-0.92 (m, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 130.0, 32.1, 27.1, 22.5, 14.2. **MS** (EI): m/z = 140([M]$^+$, 22), 97(12), 84(11), 83(14), 70(37), 67(12), 57(12), 56(48), 55(100), 54(13), 43(21), 42(17), 41(51), 39(19), 29(11), 27(14).

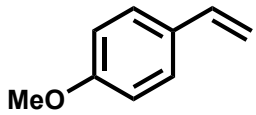


(Z)-oct-3-en-1-ol (2o) [S11]

Yield 93 % (^{1}H NMR yield relative to 1,3,5-trimethoxybenzene (0.5 mmol) as an internal standard.)

Purified by column chromatography using Hexane : EtOAc = 3 : 1 as eluent. Yellow oil.

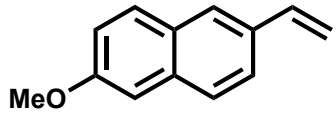
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.53-5.60 (m, 1H), 5.33-5.40 (m, 1H), 3.64 (t, J = 6.6 Hz, 2H), 2.31-2.36 (m, 2H), 2.05-2.10 (m, 2H), 1.61 (s, 1H), 1.28-1.38 (m, 4H), 0.87-0.93 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 133.6, 125.1, 62.4, 32.0, 30.9, 27.2, 22.5, 14.1. **MS** (EI): m/z = 128([M]$^+$, 0.5), 111(1.2), 110(13), 109(0.7), 100(1.3), 99(0.8), 98(0.5), 97(1.6), 96(1.5), 95(17), 93(1.0), 91(1.1), 86(0.6), 85(1.9), 84(2.6), 83(3.4), 82(22), 81(70), 80(2.4), 79(12), 78(0.7), 77(3.2), 72(0.9), 71(3.7), 70(5.8), 69(20), 68(55), 67(51), 66(6.8), 65(4.8), 63(0.9), 58(1.5), 57(16), 56(23), 55(100), 54(27), 53(16), 52(2.1), 51(3.9), 50(1.7), 45(1.7), 44(5.3), 43(19), 42(11), 41(54), 40(4.6), 39(29), 38(1.6), 31(19), 30(0.8), 29(15), 28(4.3), 27(17), 26(1.3).



1-methoxy-4-vinylbenzene (2p) [S8]

Purified by column chromatography using Hexane : EtOAc = 25 : 1 as eluent. Colorless oil. Yield 70 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33-7.36 (m, 2H), 6.84-6.88 (m, 2H), 6.66 (dd, J = 17.5, 10.8 Hz, 1H), 5.60 (dd, J = 17.7, 0.9 Hz, 1H), 5.12 (dd, J = 11.0, 0.9 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 159.5, 136.4, 130.6, 127.5, 114.0, 111.7, 55.4. **MS** (EI): m/z = 135(10), 134($[M]^+$, 100), 119(53), 91(58), 65(27), 63(12).



2-methoxy-6-vinylnaphthalene (2q) [S12]

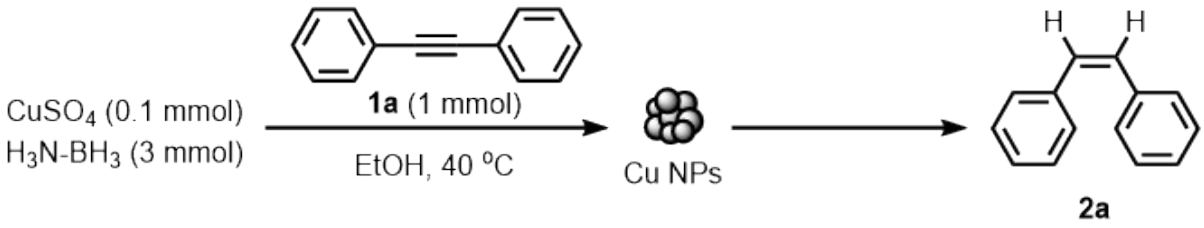
Purified by column chromatography using Hexane : EtOAc = 25 : 1 as eluent. White solid. Yield 81 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68-7.71 (m, 3H), 7.60 (dd, J = 8.7, 1.7 Hz, 1H), 7.11-7.14 (m, 2H), 6.85 (dd, J = 17.5, 10.8 Hz, 1H), 5.81 (dd, J = 17.5, 0.8 Hz, 1H), 5.27 (dd, J = 11.0, 0.6 Hz, 1H), 3.92 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ (ppm) 157.9, 137.1, 134.5, 133.1, 129.7, 129.1, 127.1, 126.3, 123.9, 119.1, 113.2, 106.0, 55.4. **MS** (EI): m/z = 185(14), 184($[M]^+$, 100), 169(21), 141(66), 139(16), 115(31).

S.4. *In situ* generation of copper nanoparticle in the presence and absence of alkyne substrate

To two 20 mL reaction vials, copper sulfate (0.1 mmol) was added. 1 mmol of diphenylacetylene was added to one of the vials. Then, 6 mL of ethanol was added to the vials and stirred at 40 ℃ until copper sulfate and diphenylacetylene dissolved. After, 3 mmol of ammonia borane was added to the vials. One hour after ammonia borane was added, the *in situ* generated copper nanoparticles were filtered and washed with acetone and water. The nanoparticles were then dried in vacuum and analyzed with X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), and high-angle annular dark field scanning transmission electron microscopy (HADDF-STEM).

For time-course observation of the *in situ* generated copper nanoparticles in the presence and absence of alkyne substrate, same reactions were run as above without isolation of the nanoparticles. Also, the reaction sample with the alkyne substrate was monitored via thin-layer chromatography (TLC) using hexane as an eluent.



Scheme S1. *In situ* generation of copper nanoparticle in the presence and absence of alkyne substrate **1a**.

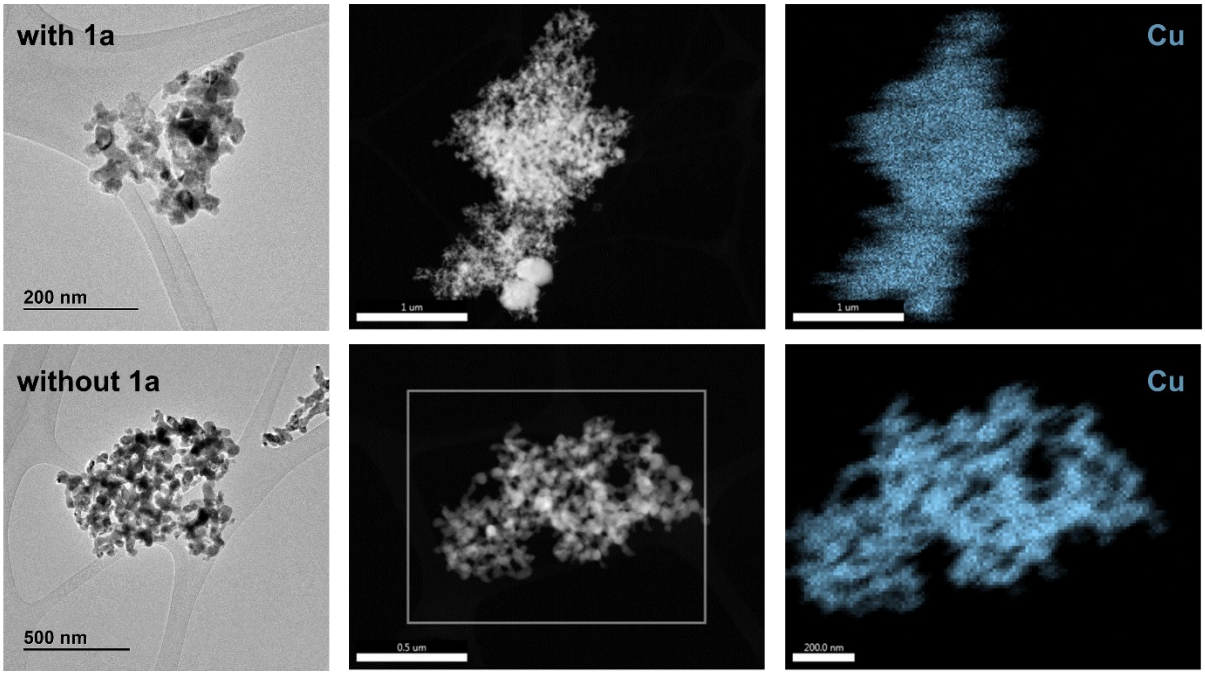


Figure S1. (a) TEM, (b) HADDF-STEM, and (c) elemental mapping image of copper of the *in situ* generated copper nanoparticle in the presence and absence of alkyne substrate **1a**.

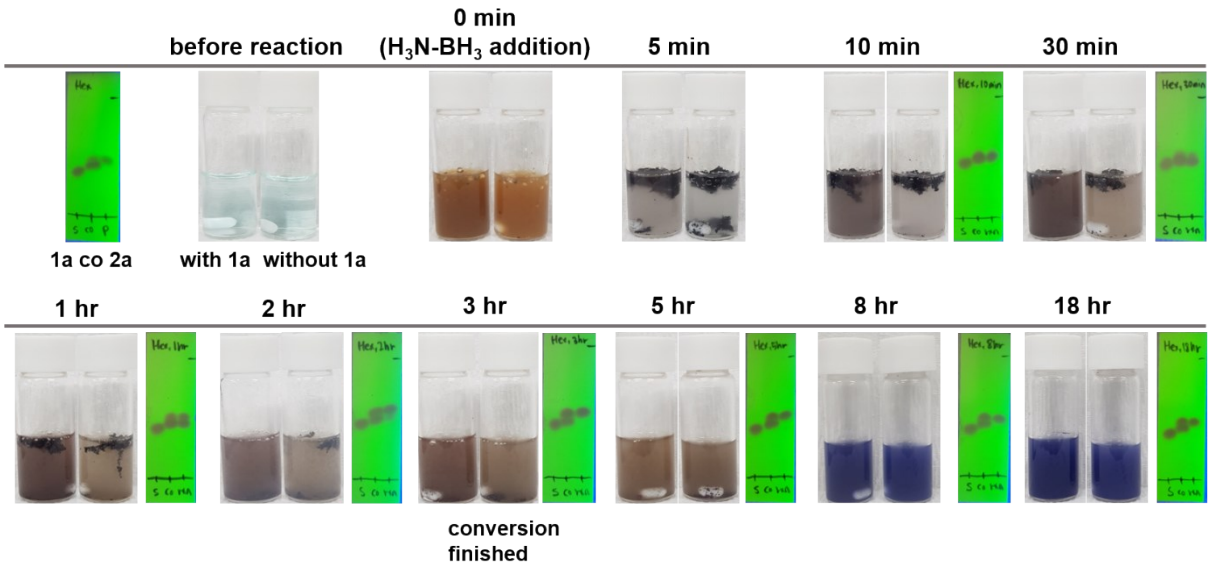
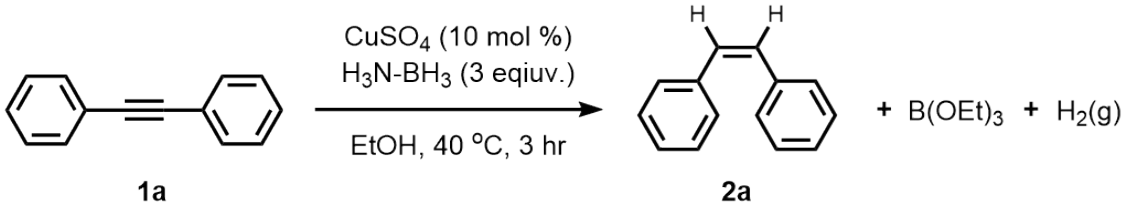


Figure S2. Time-course observation of *in situ* generated copper nanoparticles in the presence and absence of alkyne substrate **1a**.

S.5. Determination of the dehydrogenation product of ammonia borane [S13]



S.5.1. Determination of $B(OEt)_3$

To a 5 mL reaction vial, alkyne **1a** (0.5 mmol), copper sulfate (0.05 mmol), and ethanol (2.0 mL) was added. The reaction mixture was stirred at 40 ℃ until **1a** and copper sulfate dissolved completely. Then, ammonia borane (1.5 mmol) was added to the reaction mixture. After 30 minutes, the crude reaction mixture was analyzed by ^{11}B NMR using D_8-THF as solvent. A quartet at δ -23 ppm corresponds to remaining ammonia borane and a peak at δ 17 ppm was expected to be $B(OEt)_3$.

S.5.2. Determination of $H_2(g)$

To a 20 mL reaction vial, alkyne **1a** (3.0 mmol), copper sulfate (0.3 mmol), and ethanol (10 mL) was added. The reaction mixture was stirred until **1a** and copper sulfate dissolved completely to ethanol. Then, ammonia borane (9.0 mmol) was added to the reaction mixture. As soon as ammonia borane was added to the reaction mixture, generation of gaseous product was monitored. For the first 30 minutes, the generated gas was vented inside a fume hood to remove air inside the vial. After 30 minutes, the gas was collected by a gas-tight syringe and qualitatively analyzed by GC which showed the presence of H_2 gas at retention time at 1.71 min.

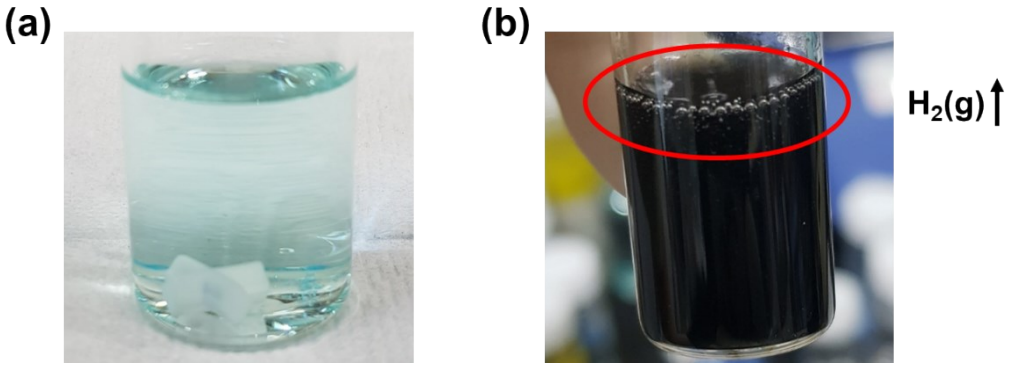


Figure S3. Ethanol solution containing **1a** and copper sulfate (a) before adding ammonia-borane (b) 30 minute after adding ammonia borane showing production of H_2 bubbles by the Cu^0 NPs.

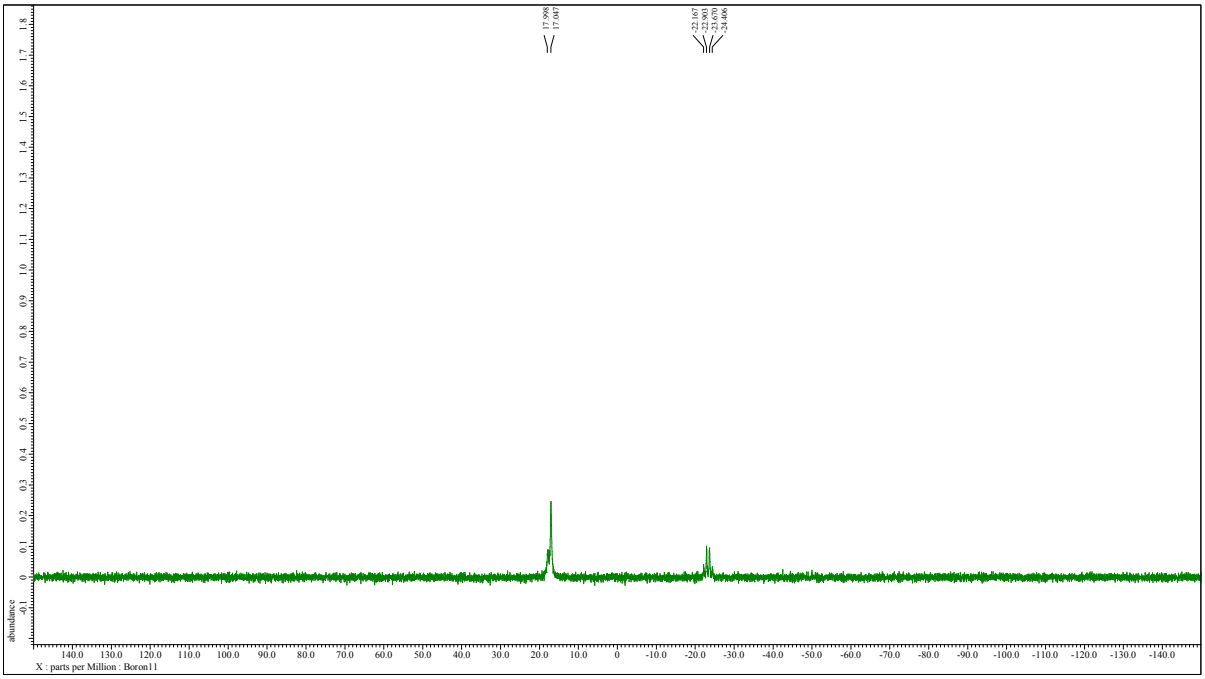


Figure S4. ^{11}B NMR spectrum of crude reaction mixture.

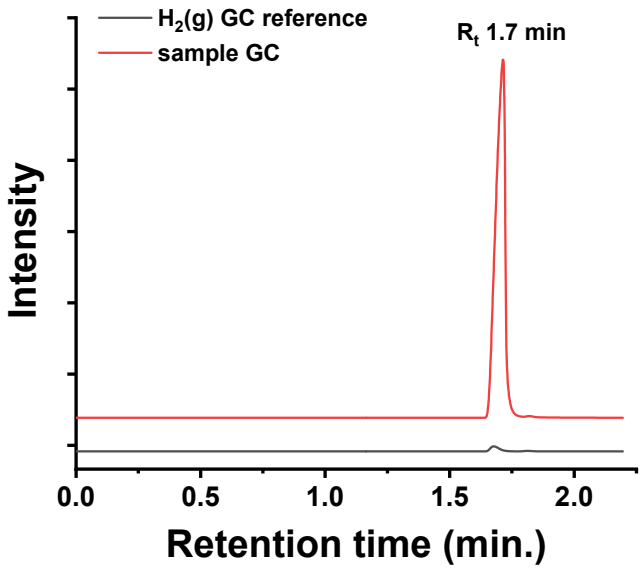
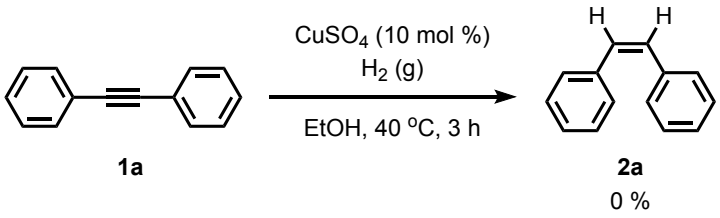


Figure S5. Chromatography of the generated gaseous species (red), and reference H_2(g) (black).

S.6. Semihydrogenation under gaseous H_2



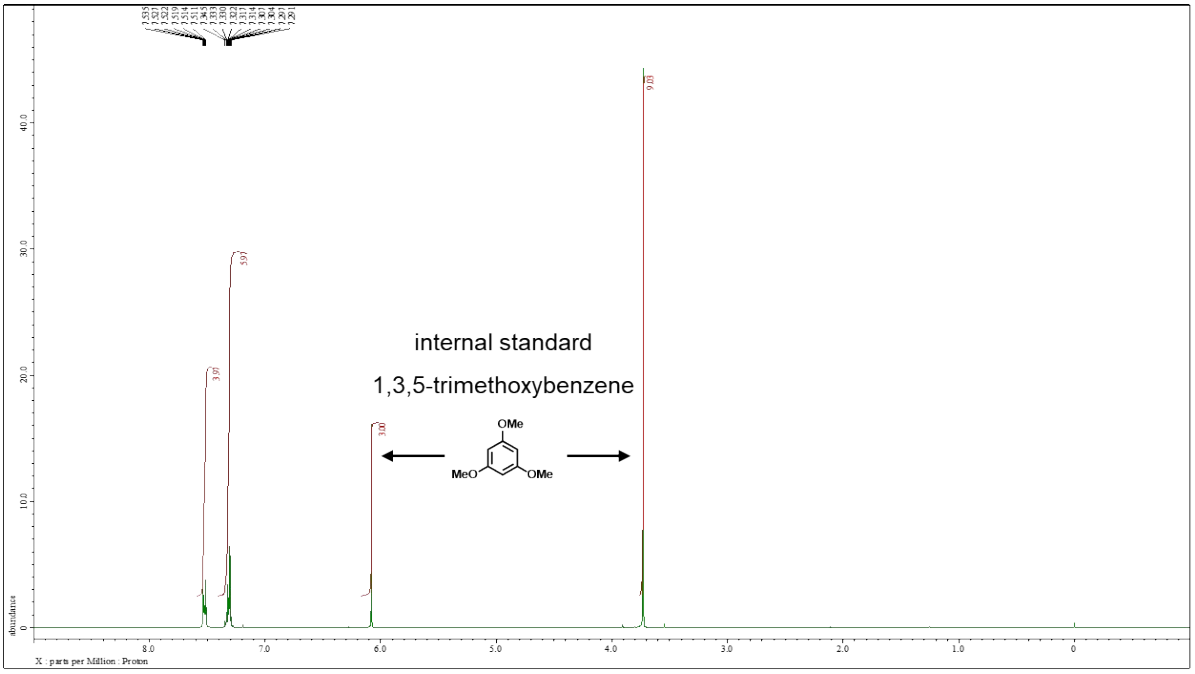
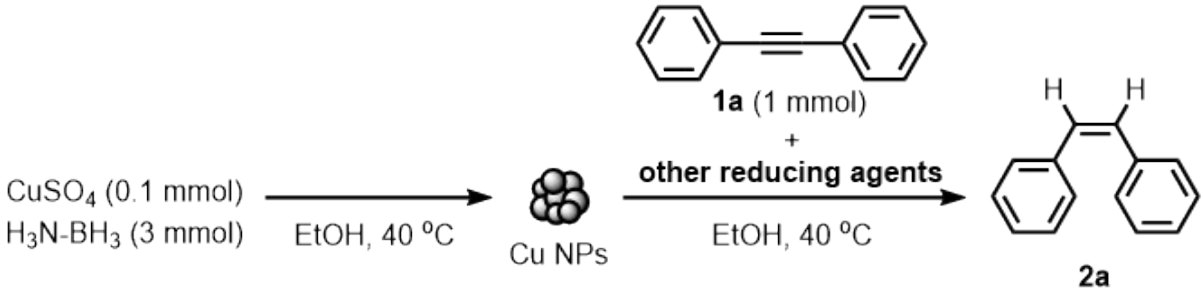


Figure S6. ^{1}H NMR spectrum of the crude reaction mixture under $CuSO_4$ and gaseous H_2.

S.7. Semihydrogenation using isolated copper nanoparticles and gaseous H_2

First, copper nanoparticles were generated by adding 3 mmol of ammonia borane to the ethanol solution (6 mL) of copper sulfate (0.1 mmol). After one hour, the *in situ* generated copper nanoparticles were filtered, washed with acetone and water, and dried in vacuum. Then to a new 20 mL reaction vial, alkyne substrate **1a** (1.0 mmol), isolated copper nanoparticles, 1,3,5-trimethoxybenzene (^{1}H NMR standard) (1.0 mmol), ethanol (6 mL), and other reducing agents were added to verify whether copper nanoparticles already prepared with ammonia borane and copper sulfate would tolerate alternative reducing agents.



Scheme S2. Generation of copper nanoparticles and semihydrogenation of **1a** using the generated copper nanoparticles and other reducing agents.

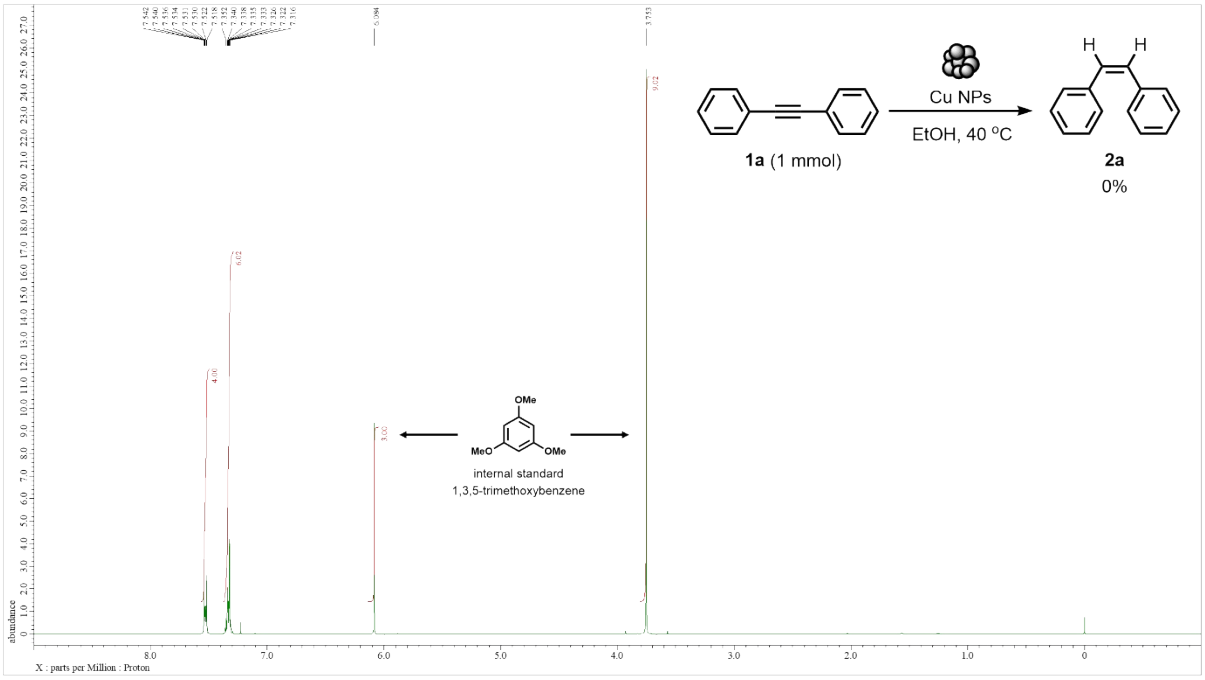


Figure S7. ^{1}H NMR spectrum of the crude reaction mixture in the presence of **1a** and copper nanoparticles.

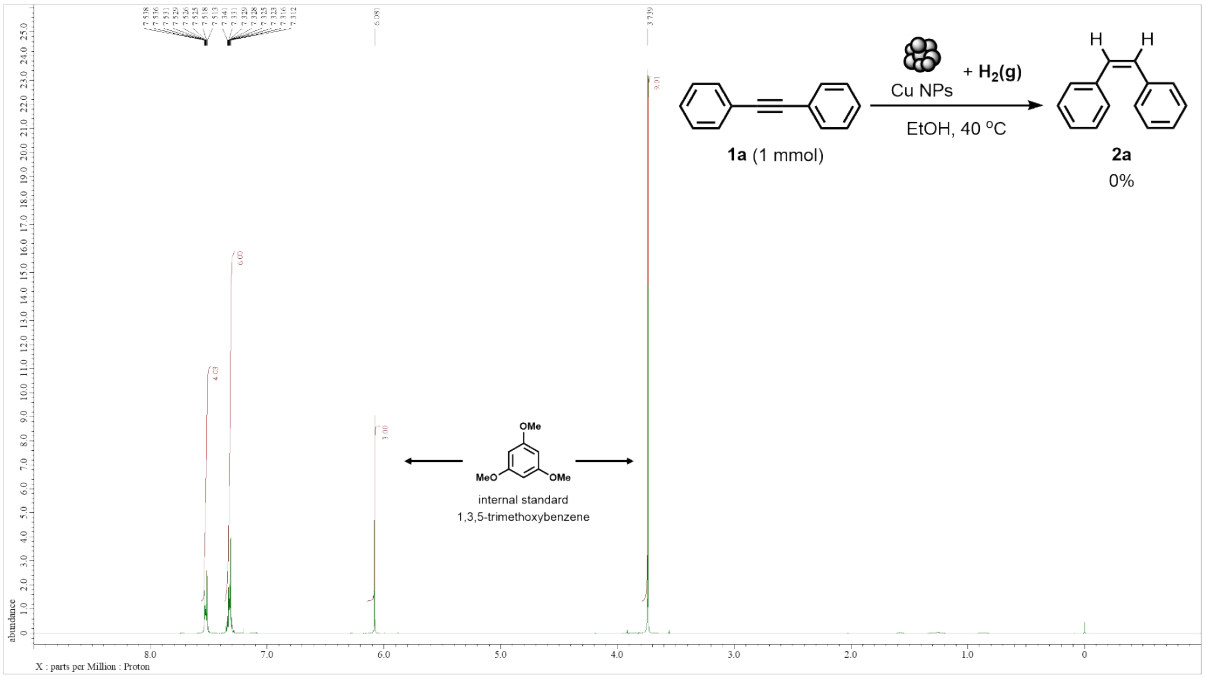


Figure S8. ^{1}H NMR spectrum of the crude reaction mixture in the presence of **1a**, copper nanoparticles, and H_2(g).

S.8. Spectra

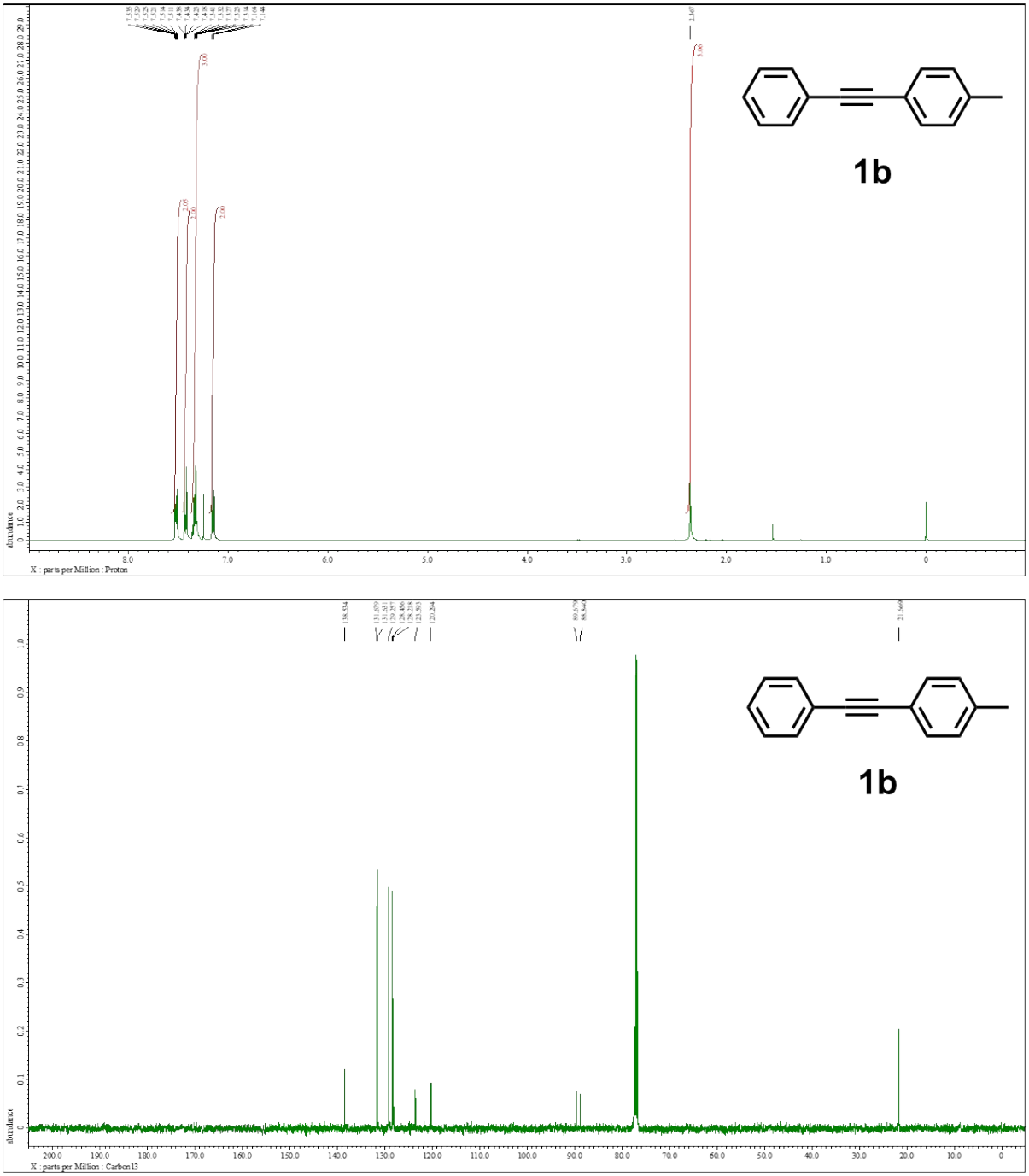


Figure S9. ^{1}H, ^{13}C spectrum of **1b**.

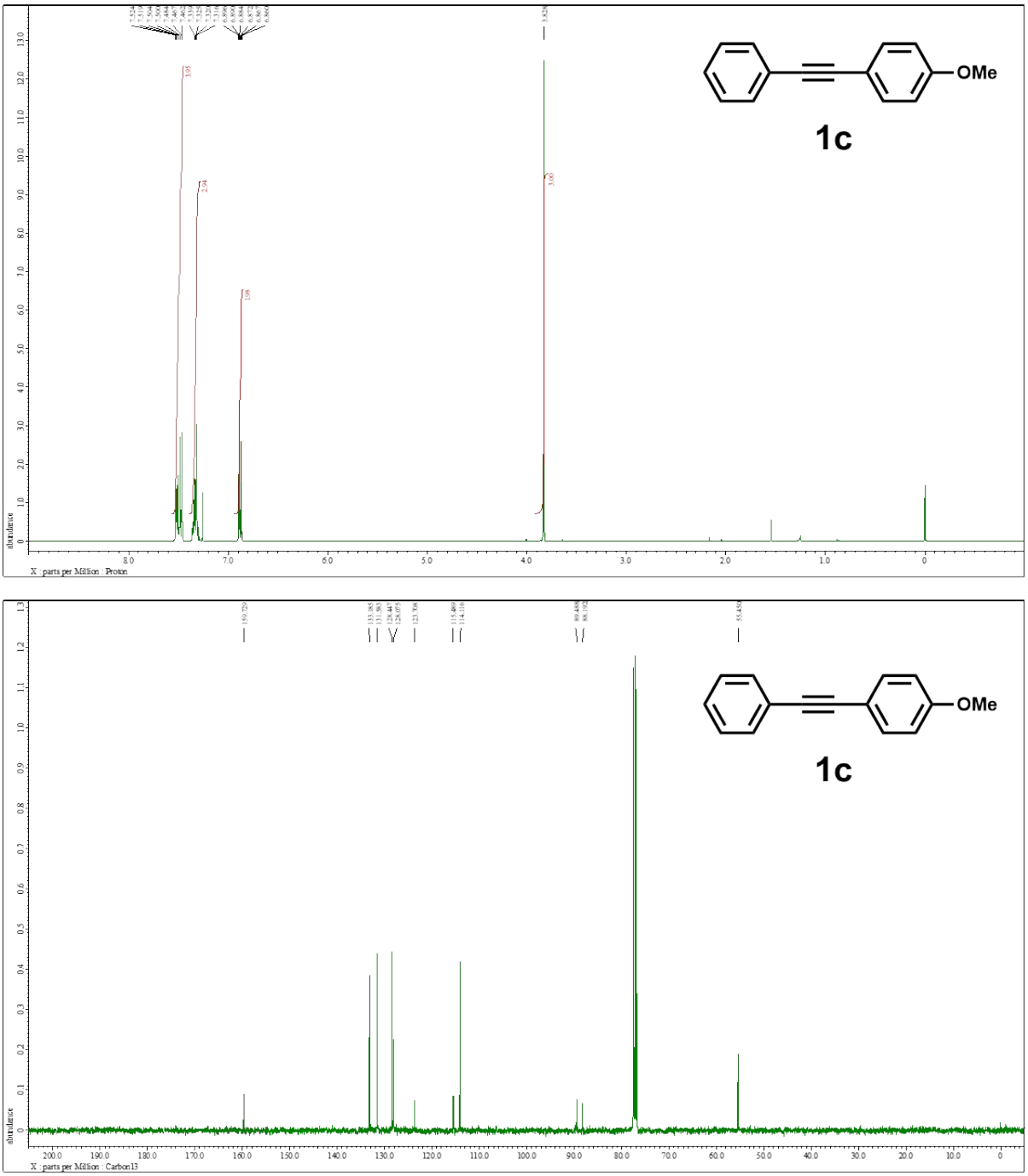


Figure S10. ^{1}H, ^{13}C spectrum of **1c**.

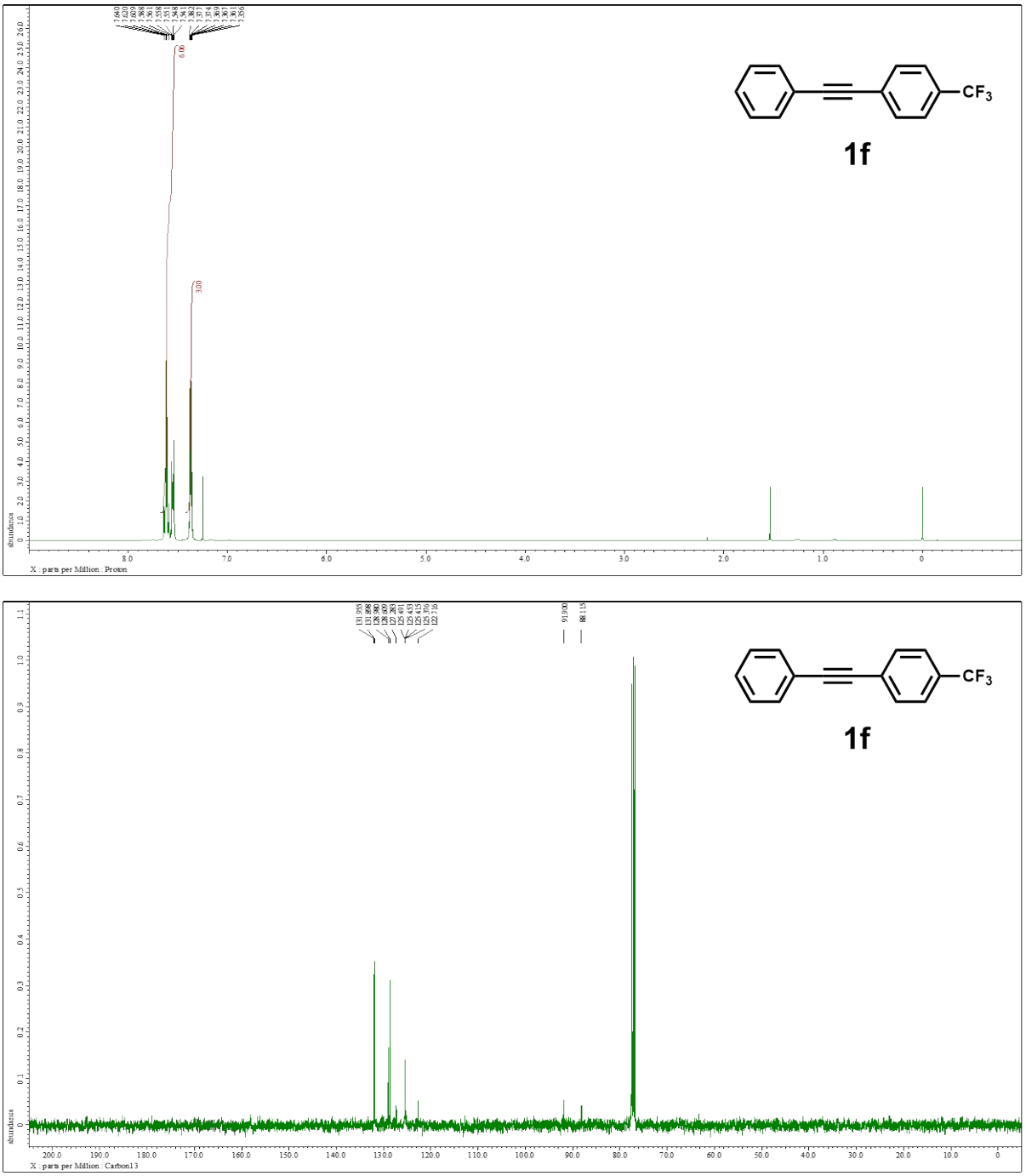


Figure S11. ^{1}H, ^{13}C spectrum of **1f**.

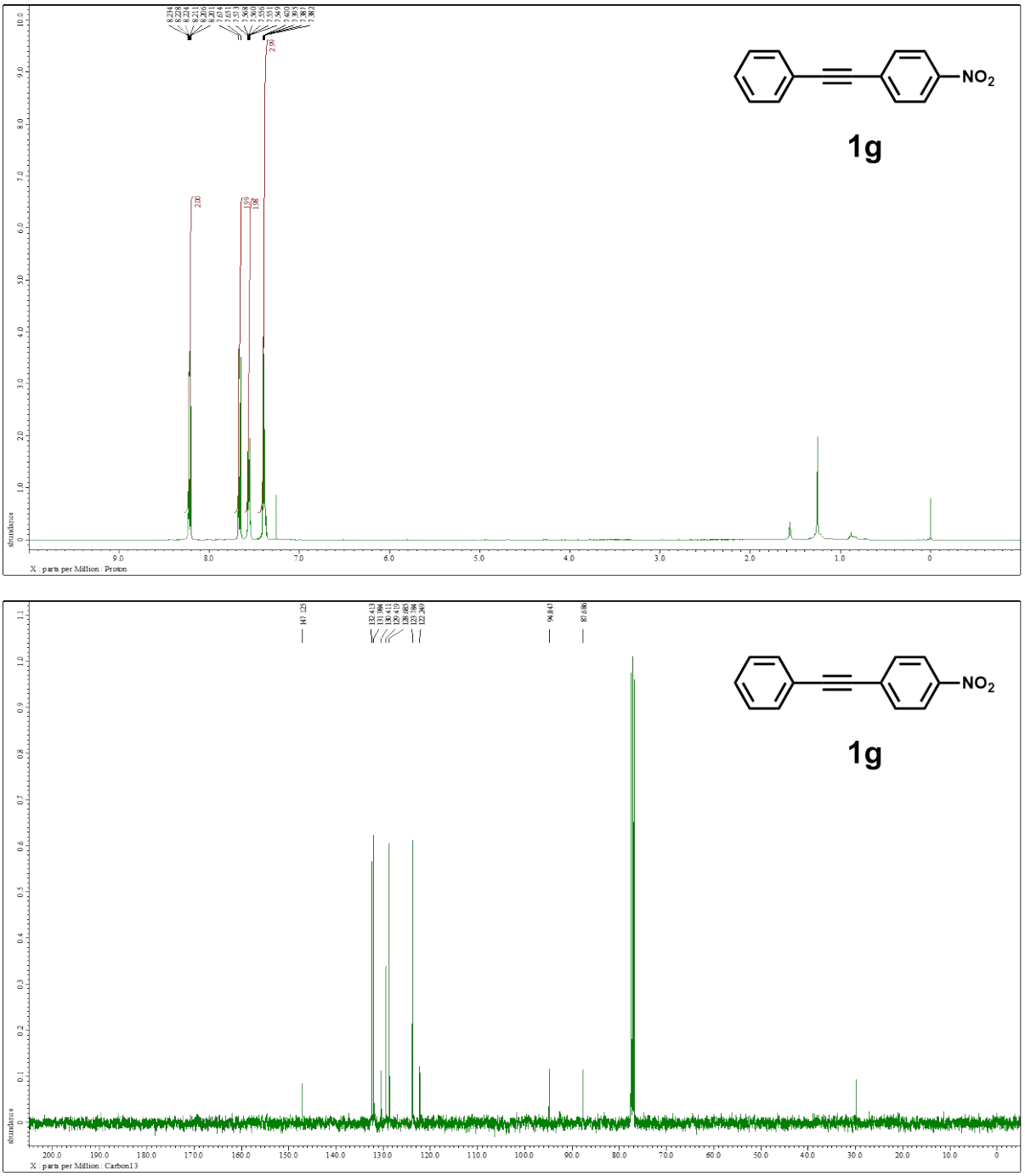


Figure S12. ^{1}H, ^{13}C spectrum of **1g**.

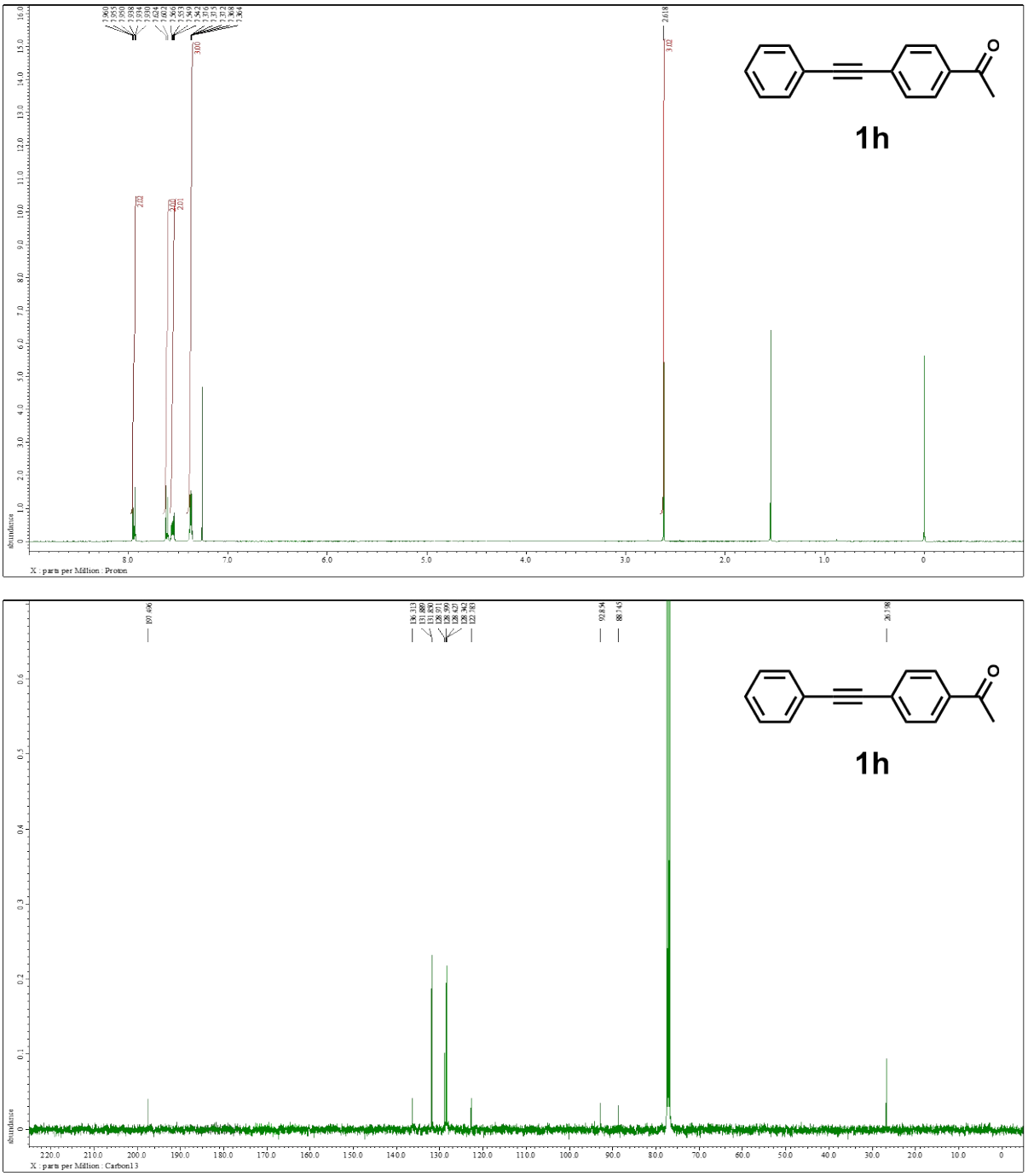


Figure S13. ^{1}H, ^{13}C spectrum of **1h**.

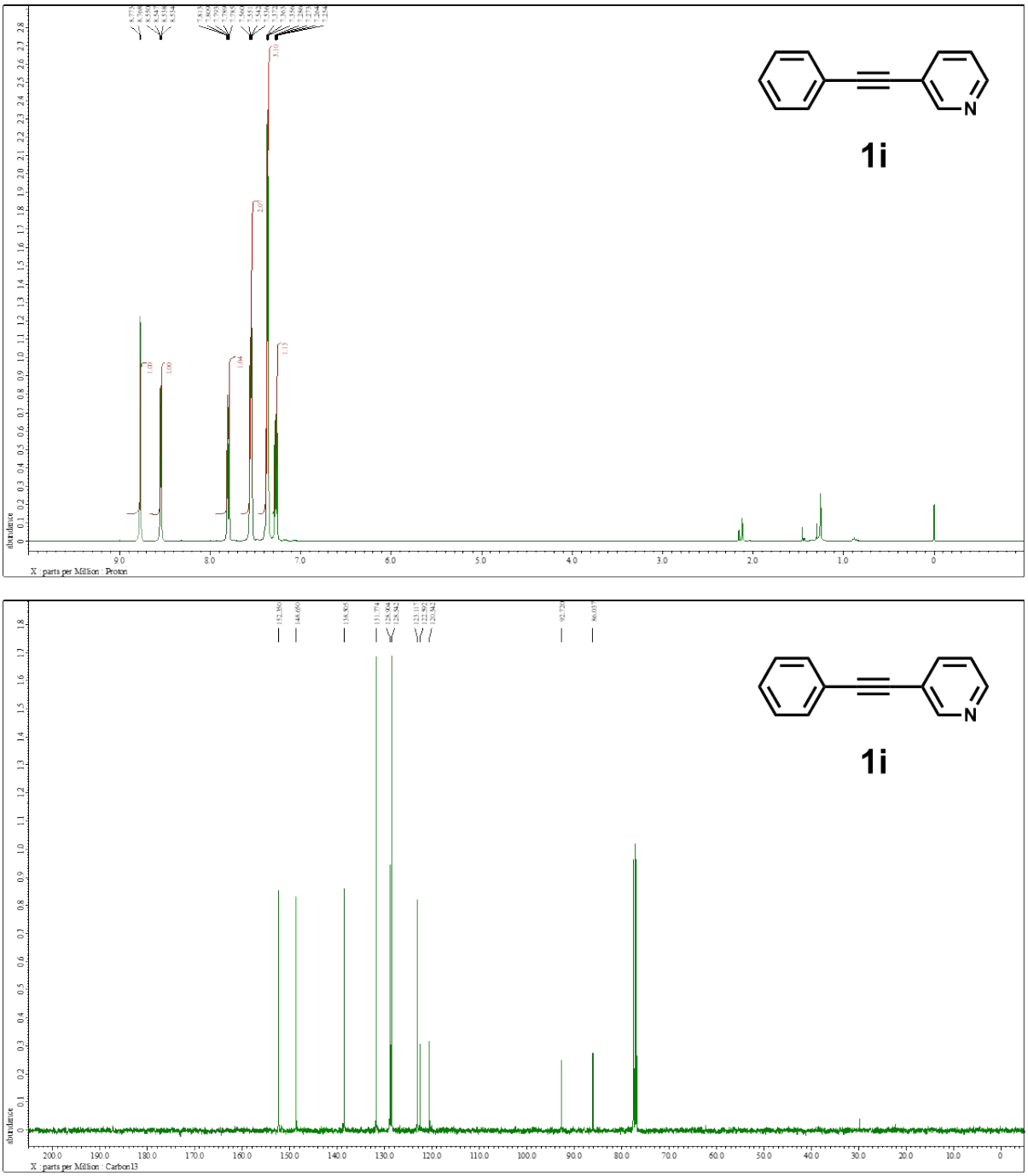


Figure S14. ^{1}H, ^{13}C spectrum of **1i**.

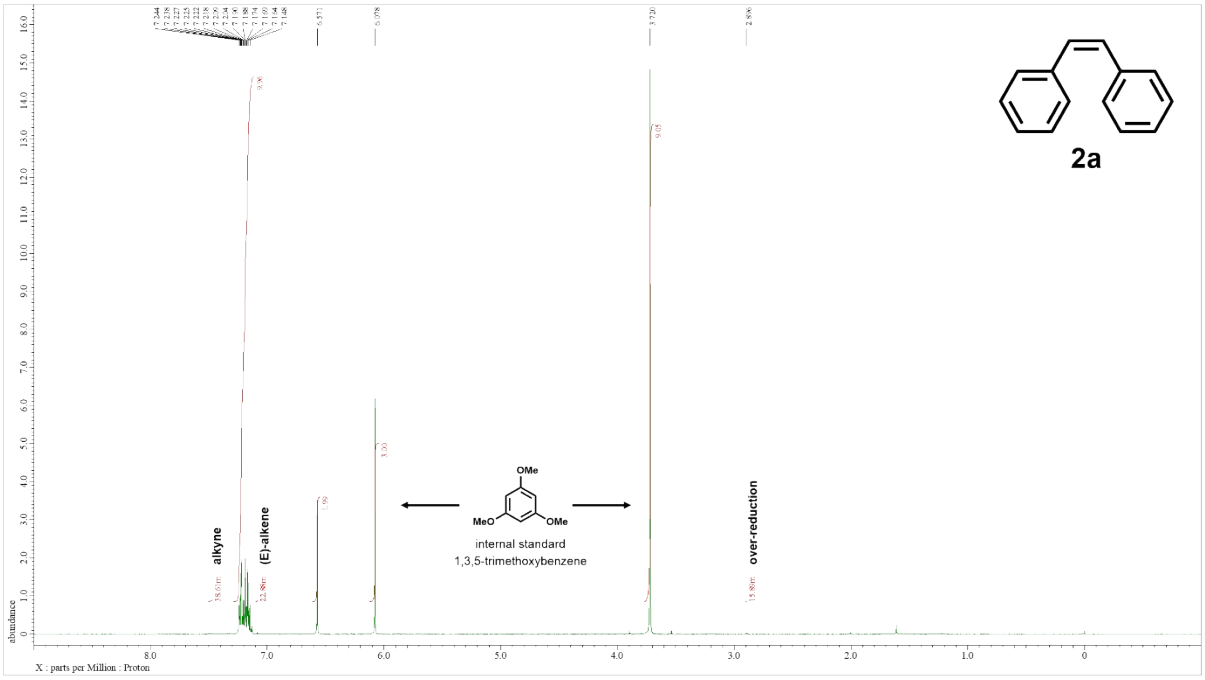


Figure S15. Crude ^{1}H spectrum of **2a**.

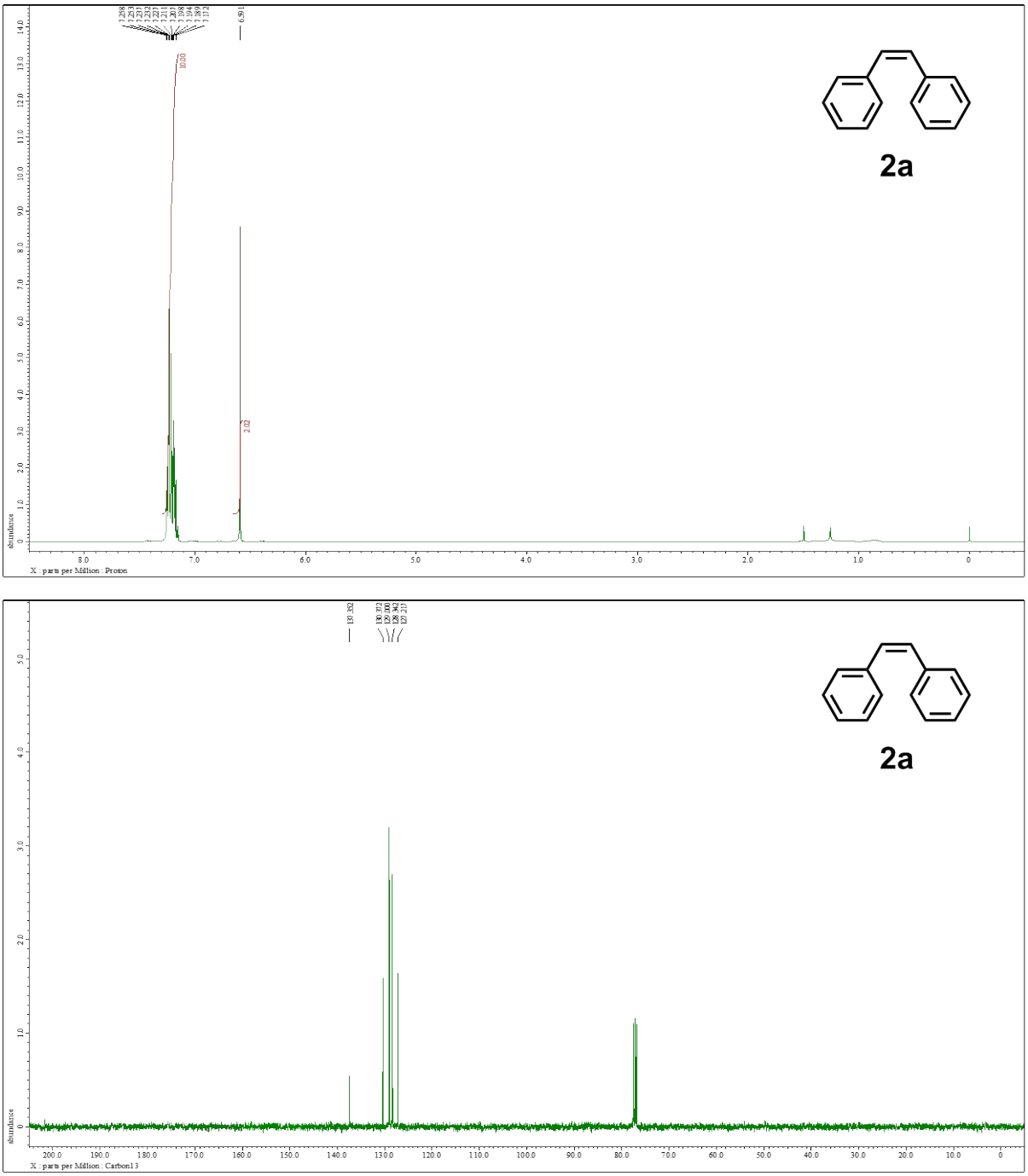


Figure S16. ^{1}H, ^{13}C spectrum of **2a**.

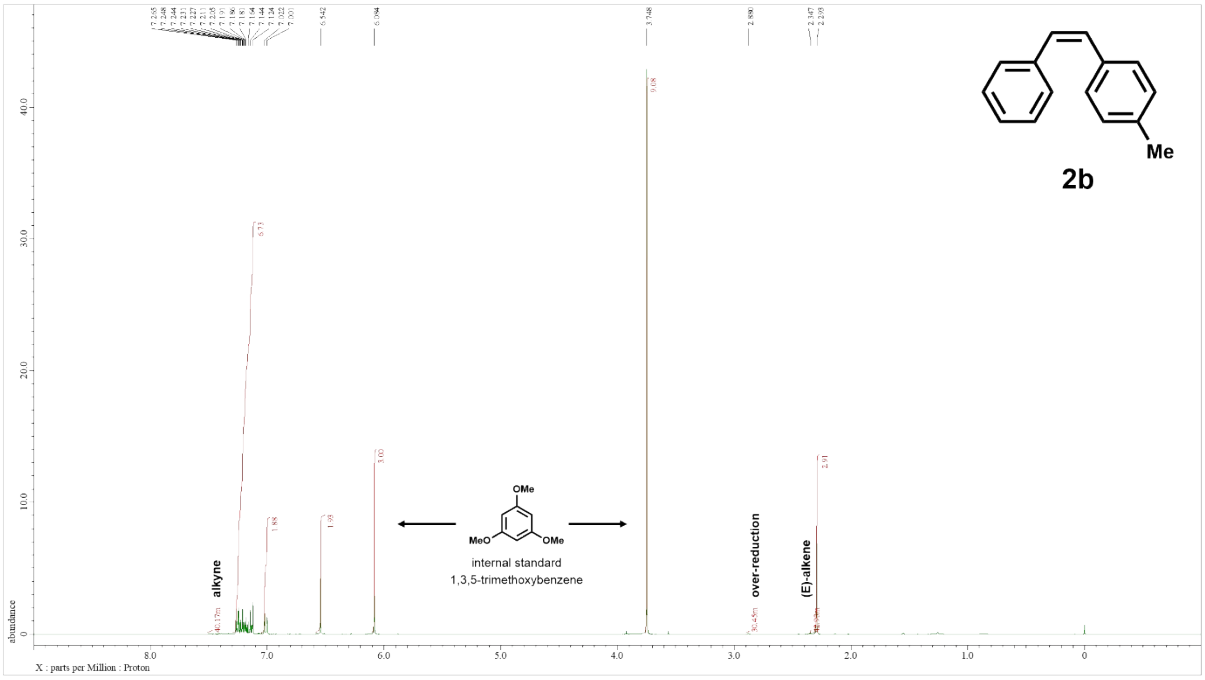


Figure S17. Crude ^{1}H spectrum of **2b**.

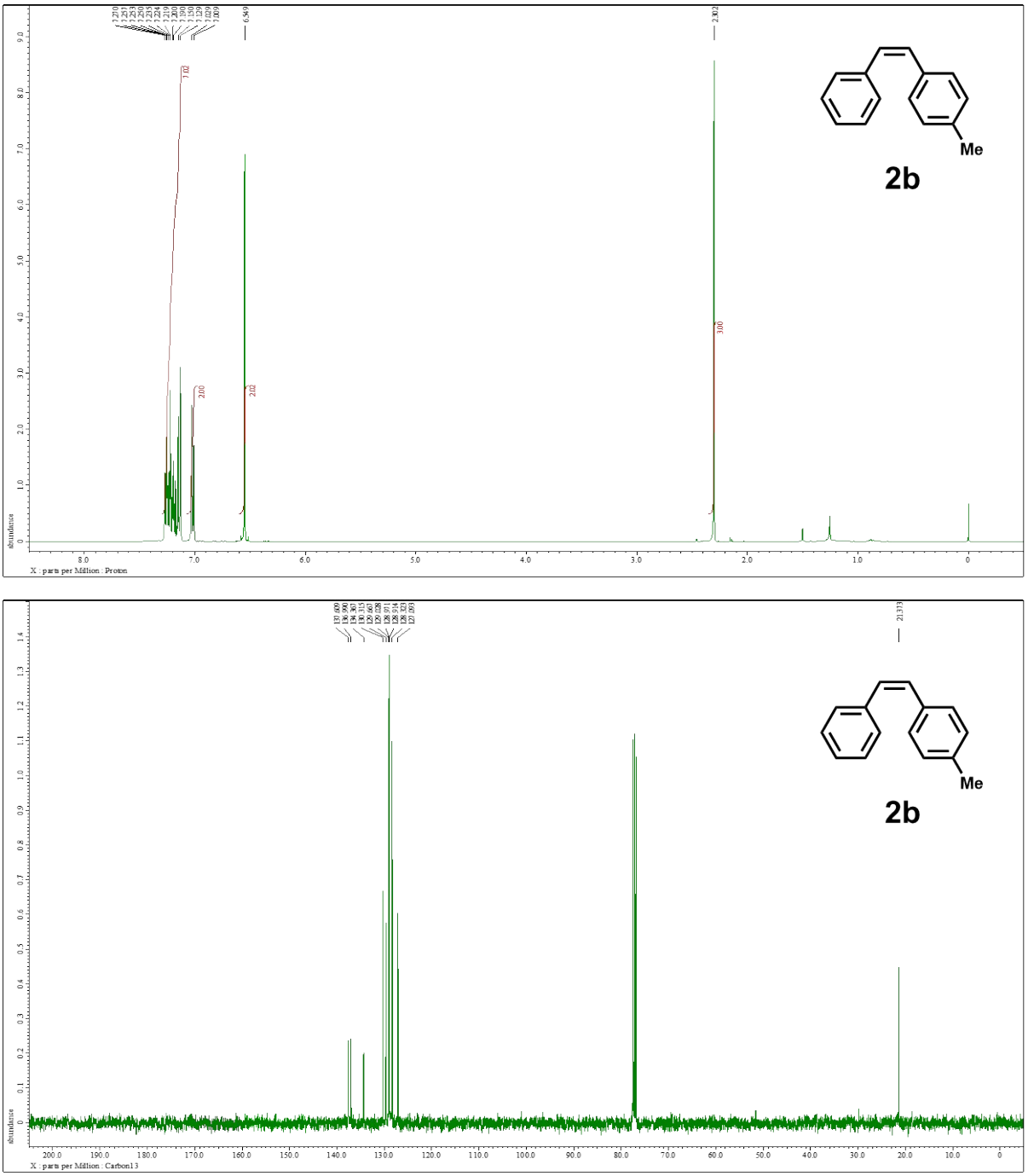


Figure S18. ^{1}H, ^{13}C spectrum of **2b**.

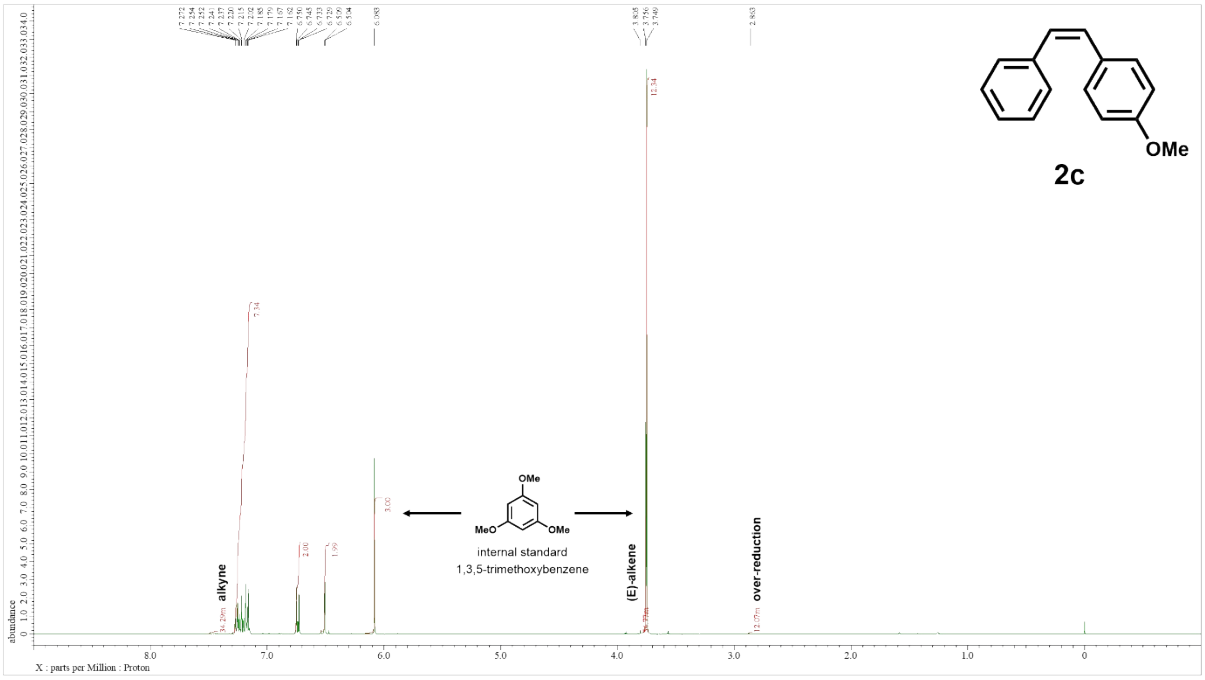


Figure S19. Crude ^{1}H spectrum of **2c**.

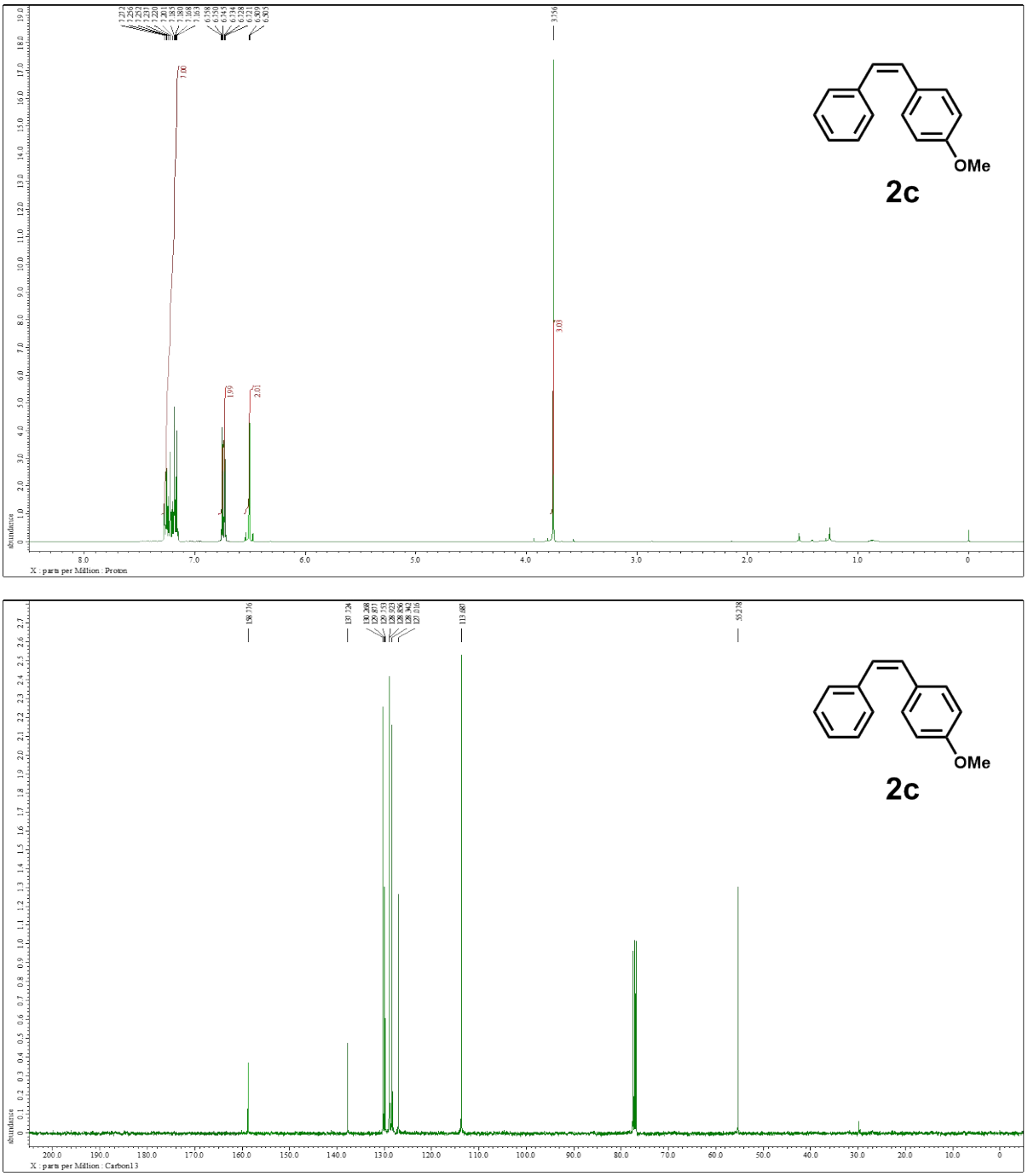


Figure S20. ^{1}H, ^{13}C spectrum of **2c**.

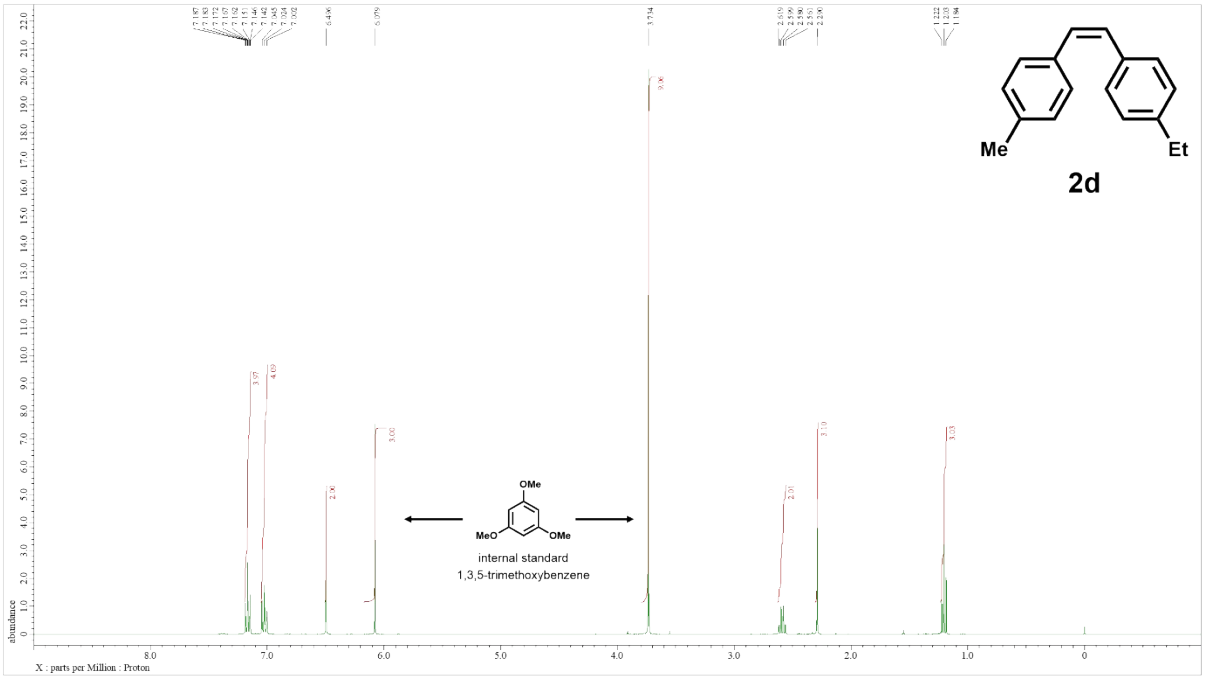


Figure S21. Crude ^{1}H spectrum of **2d**.

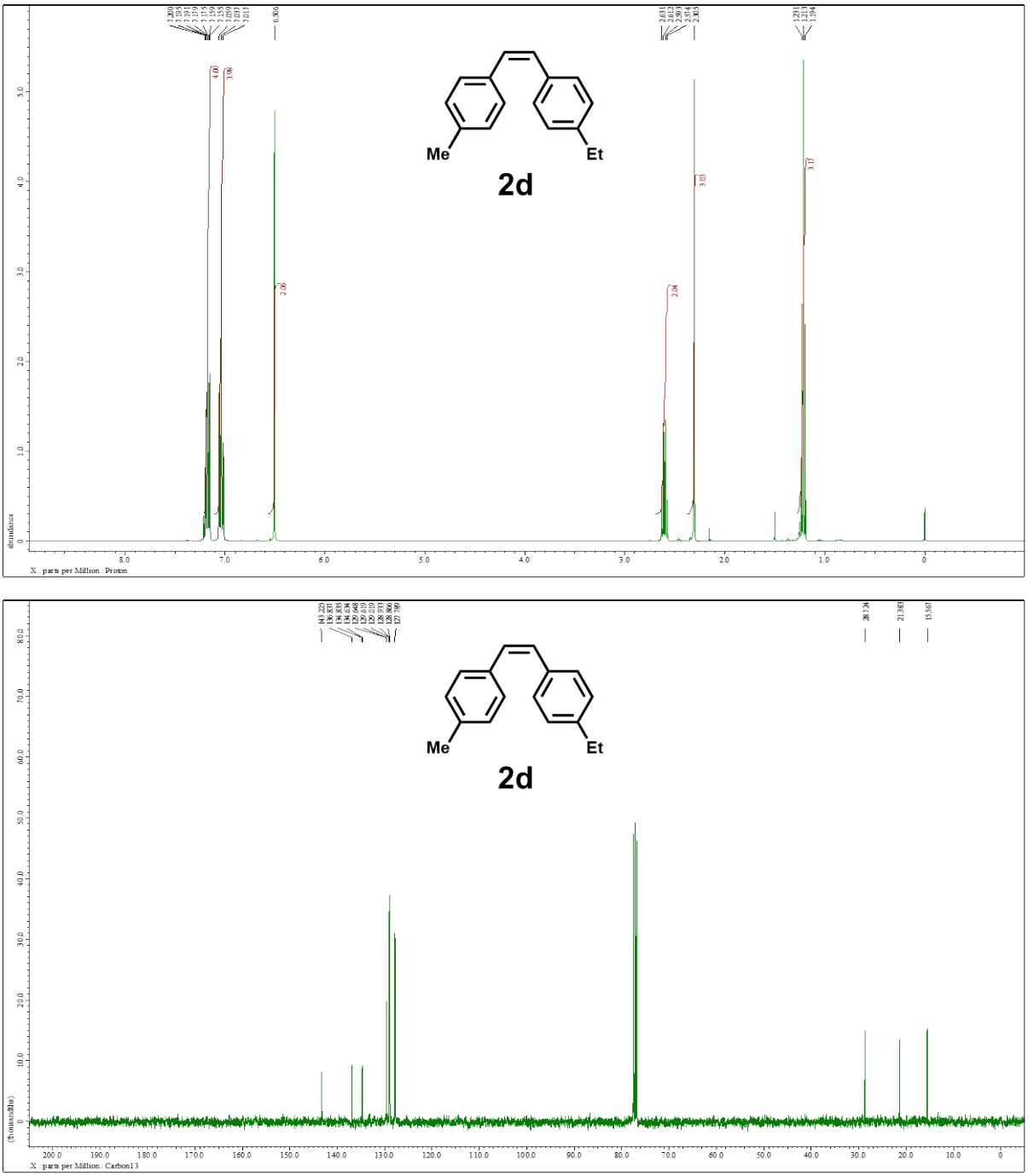


Figure S22. ^{1}H, ^{13}C spectrum of **2d**.

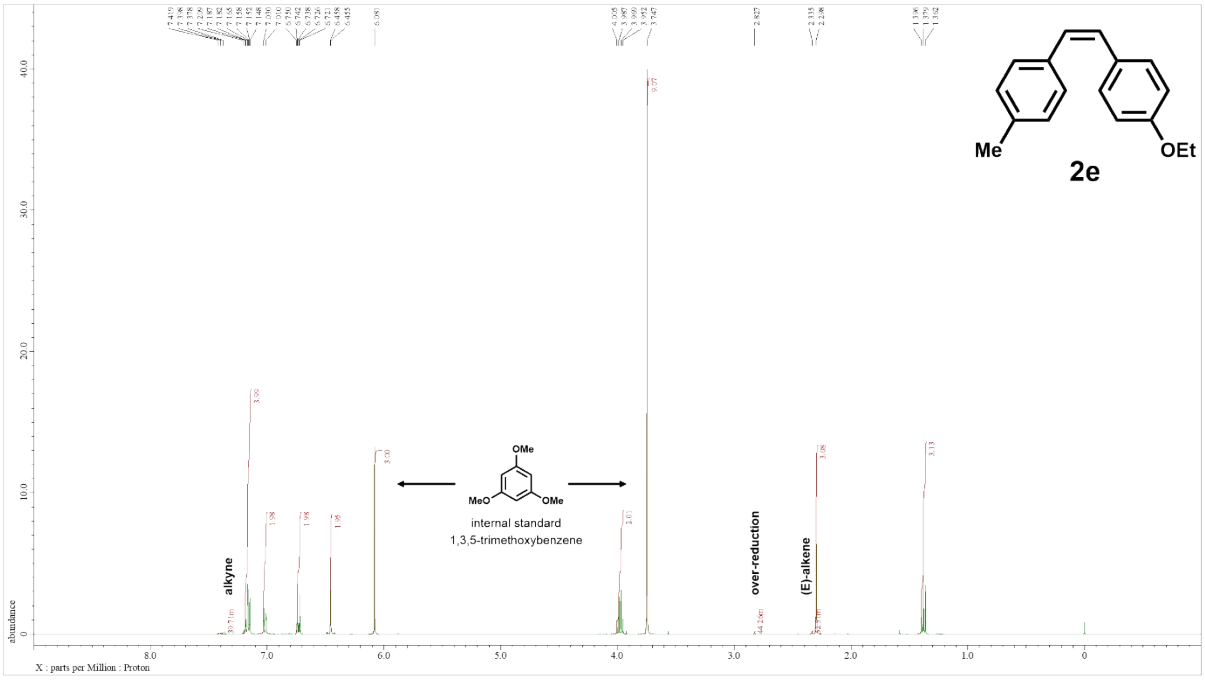


Figure S23. Crude ^{1}H spectrum of **2e**.

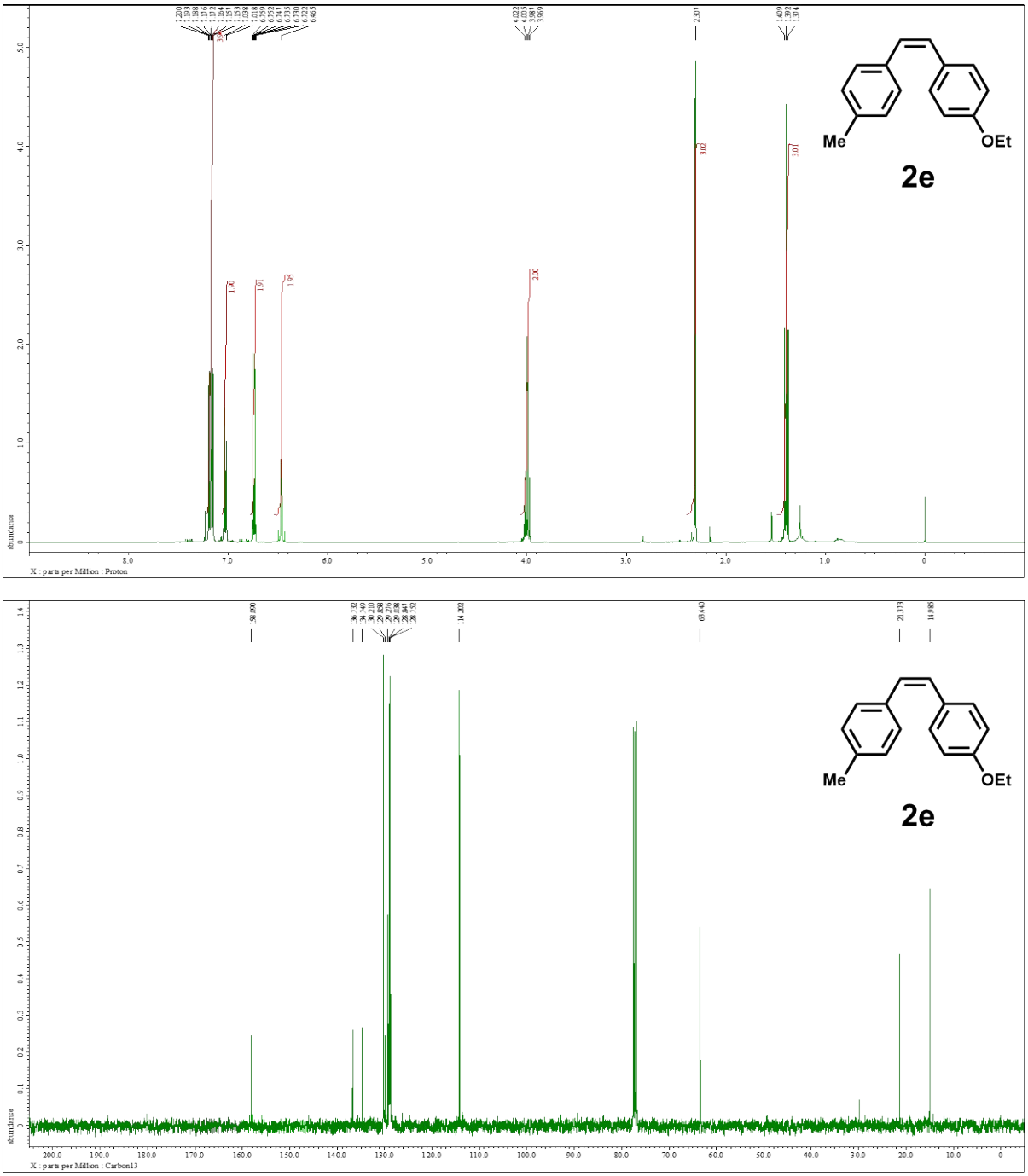


Figure S24. ^{1}H, ^{13}C spectrum of **2e**.

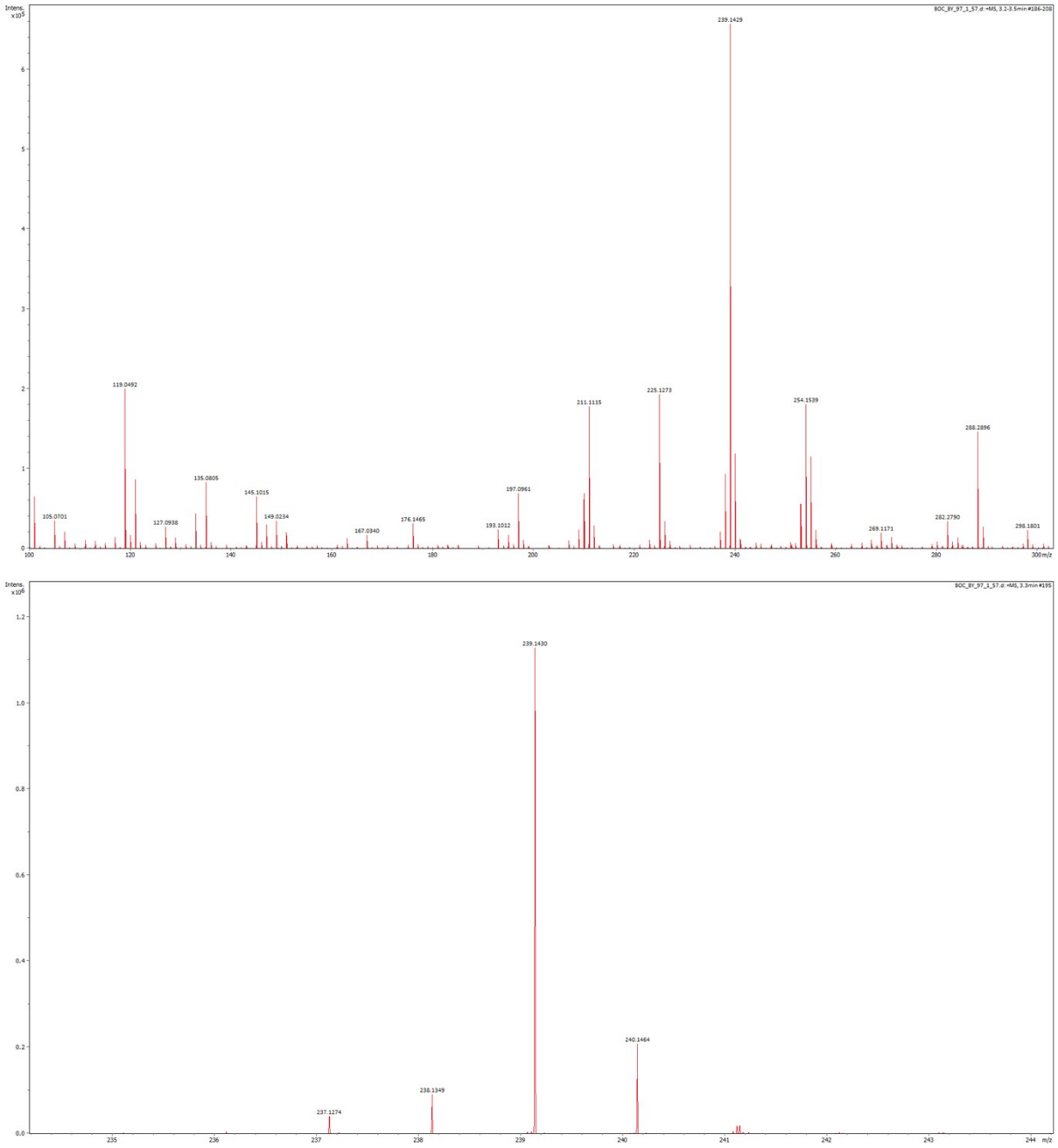


Figure S25. HRMS spectrum and isotope distribution pattern of **2e**.

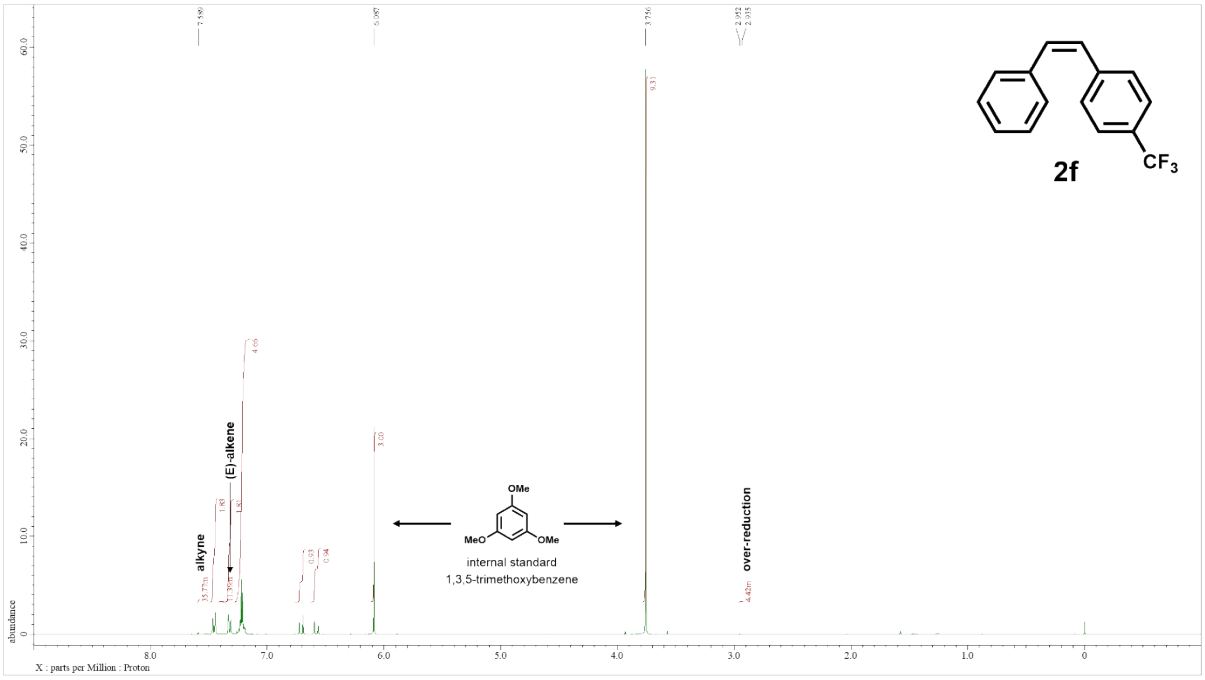


Figure S26. Crude ^{1}H spectrum of **2f**.

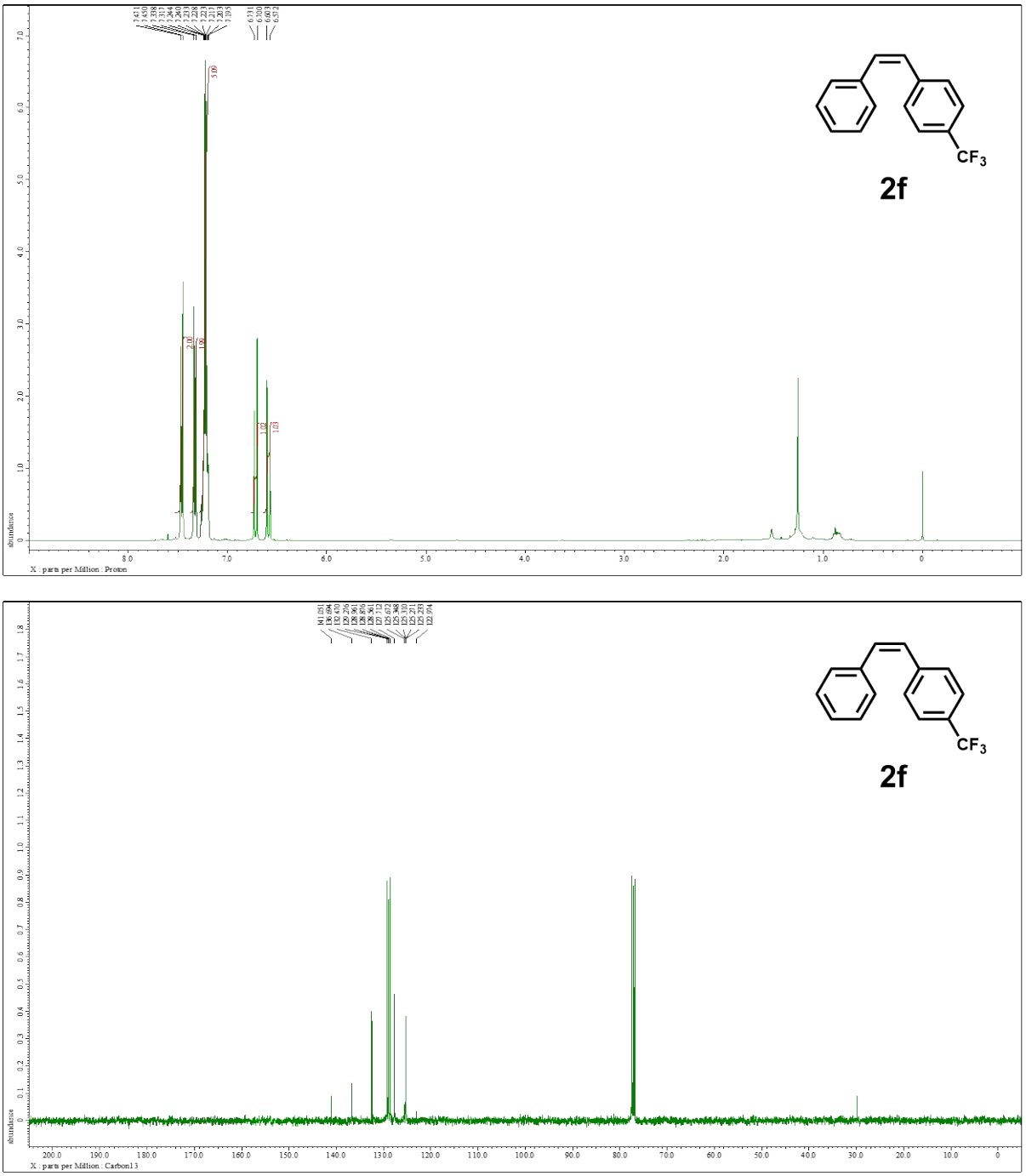


Figure S27. ^{1}H, ^{13}C spectrum of **2f**.

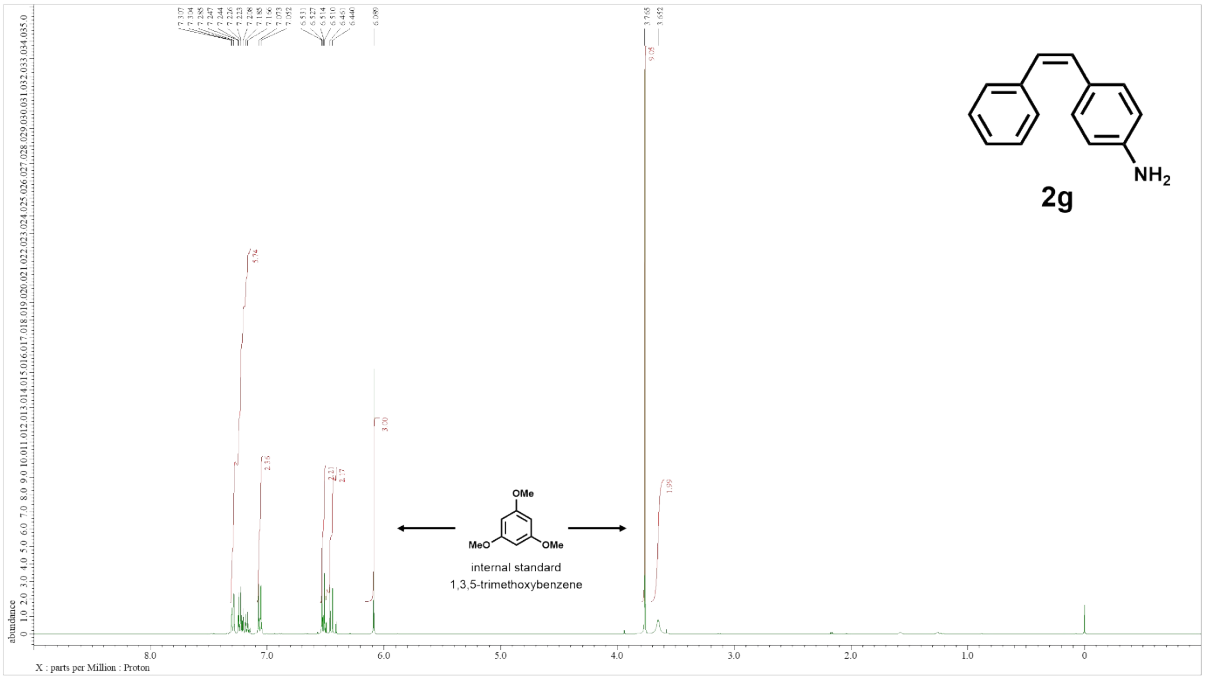


Figure S28. Crude ^{1}H spectrum of **2g**.

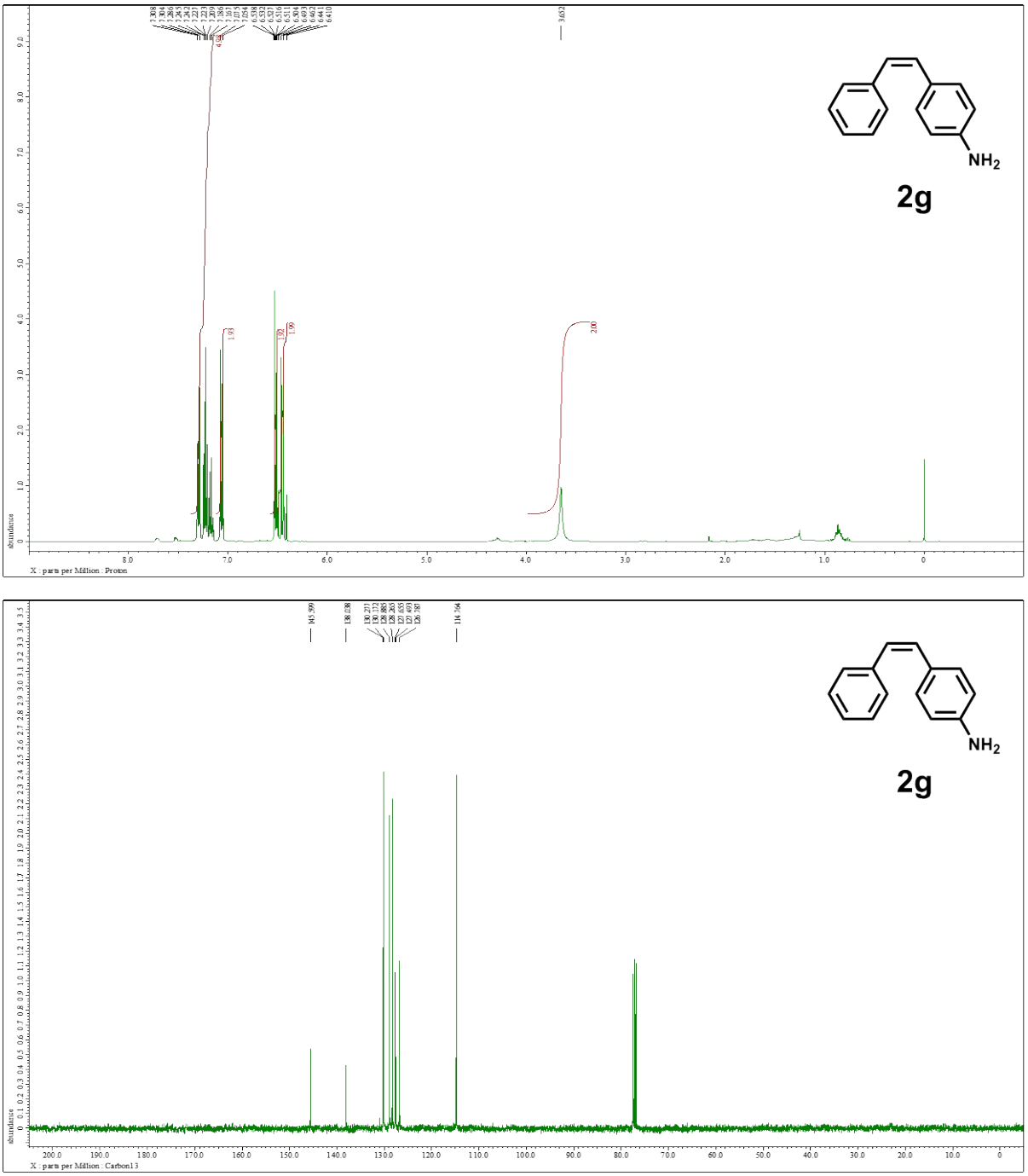


Figure S29. ^{1}H, ^{13}C spectrum of **2g**.

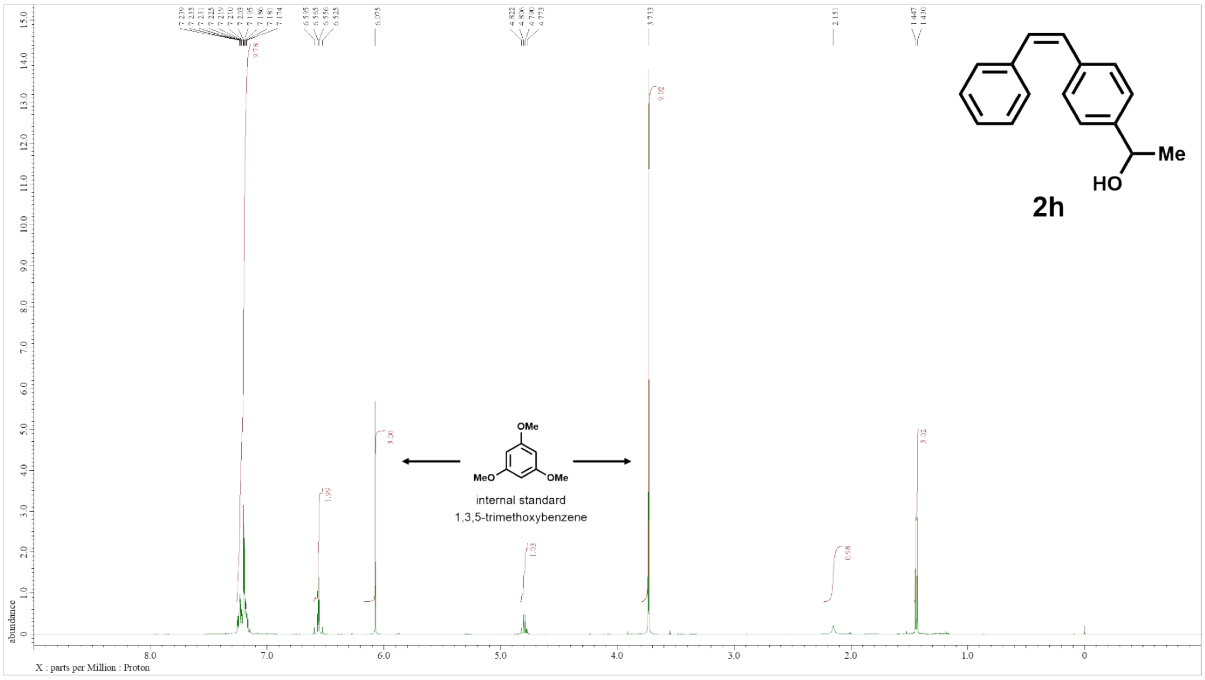


Figure S30. Crude ^{1}H spectrum of **2h**.

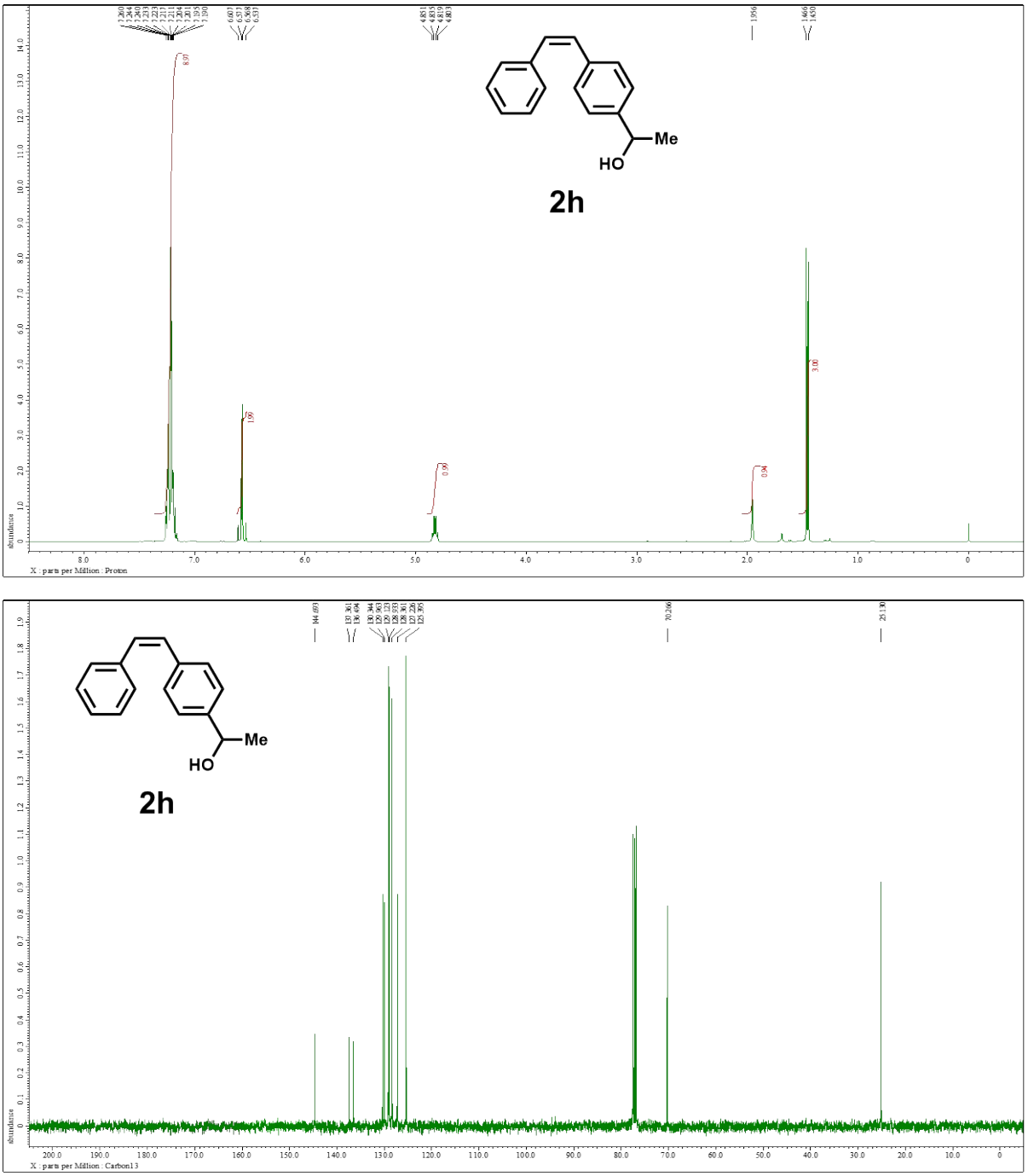


Figure S31. ^{1}H, ^{13}C spectrum of **2h**.

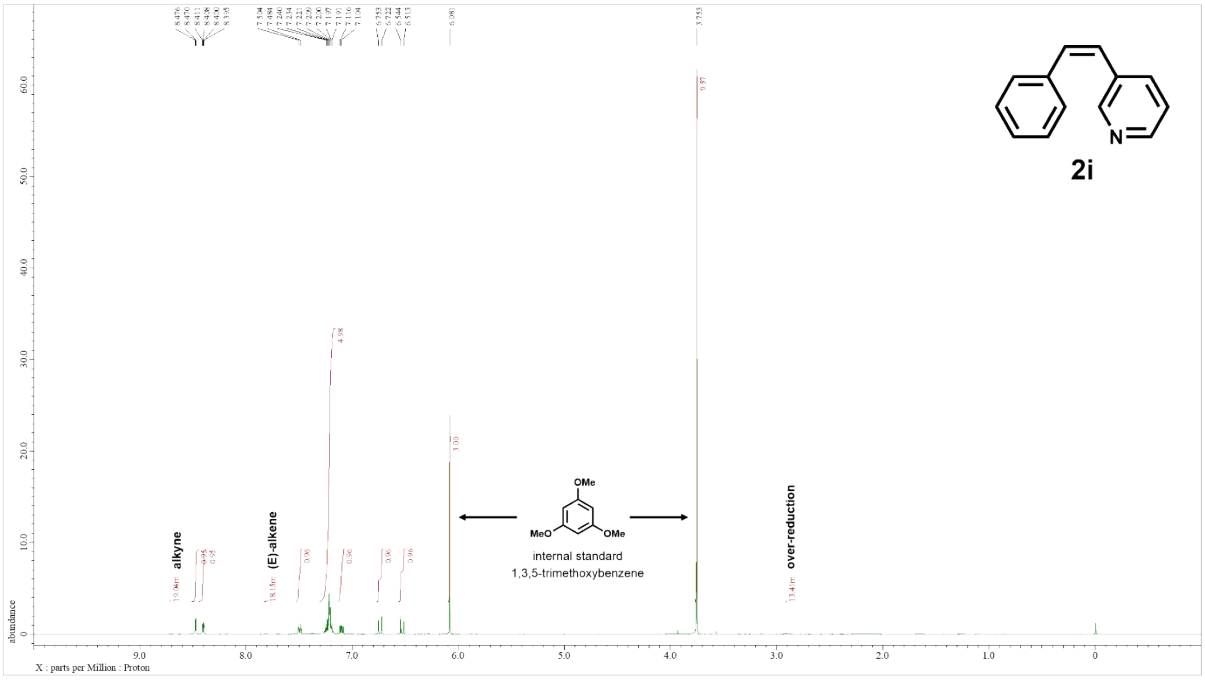


Figure S32. Crude ^{1}H spectrum of **2i**.

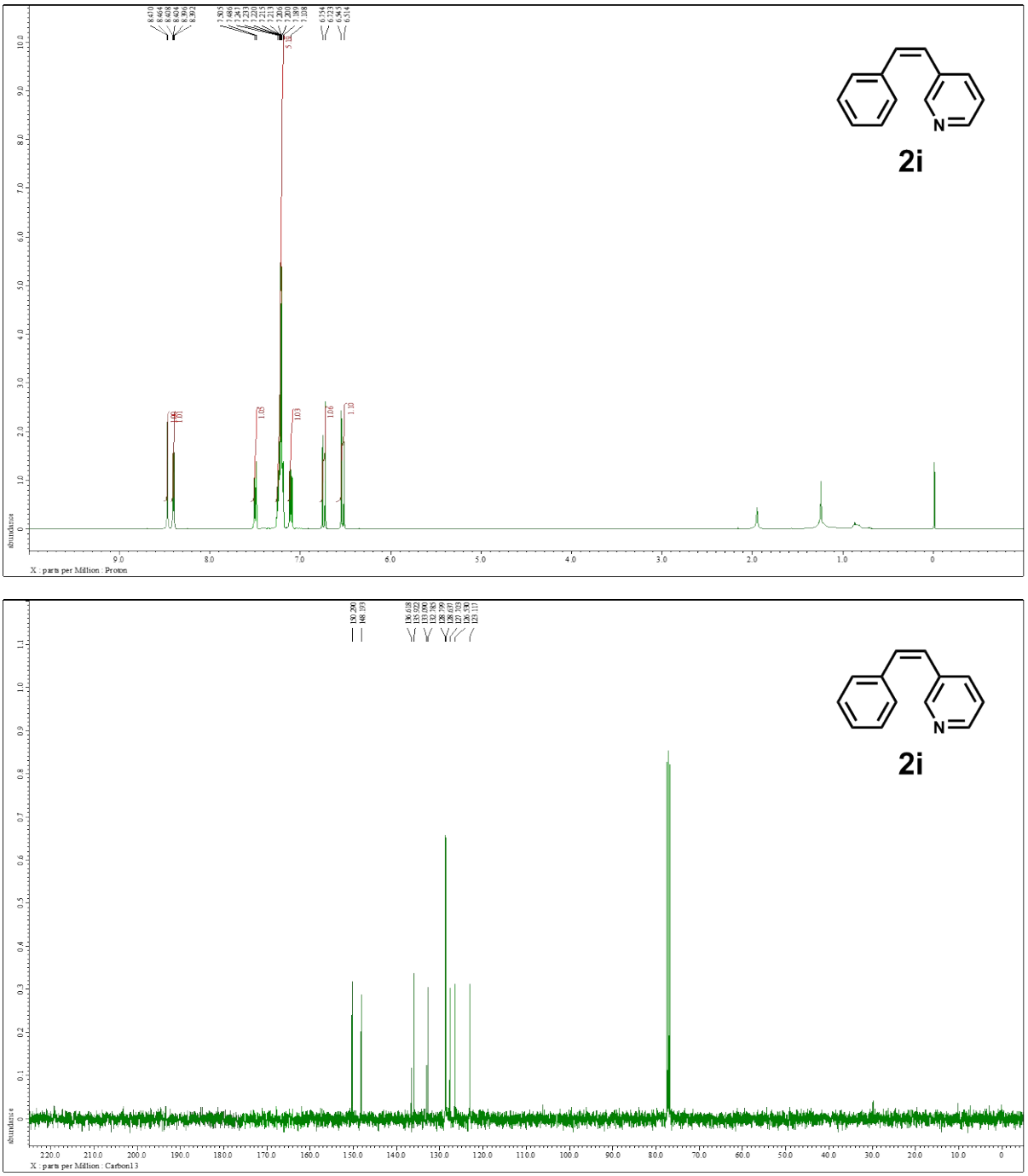


Figure S33. ^{1}H, ^{13}C spectrum of **2i**.

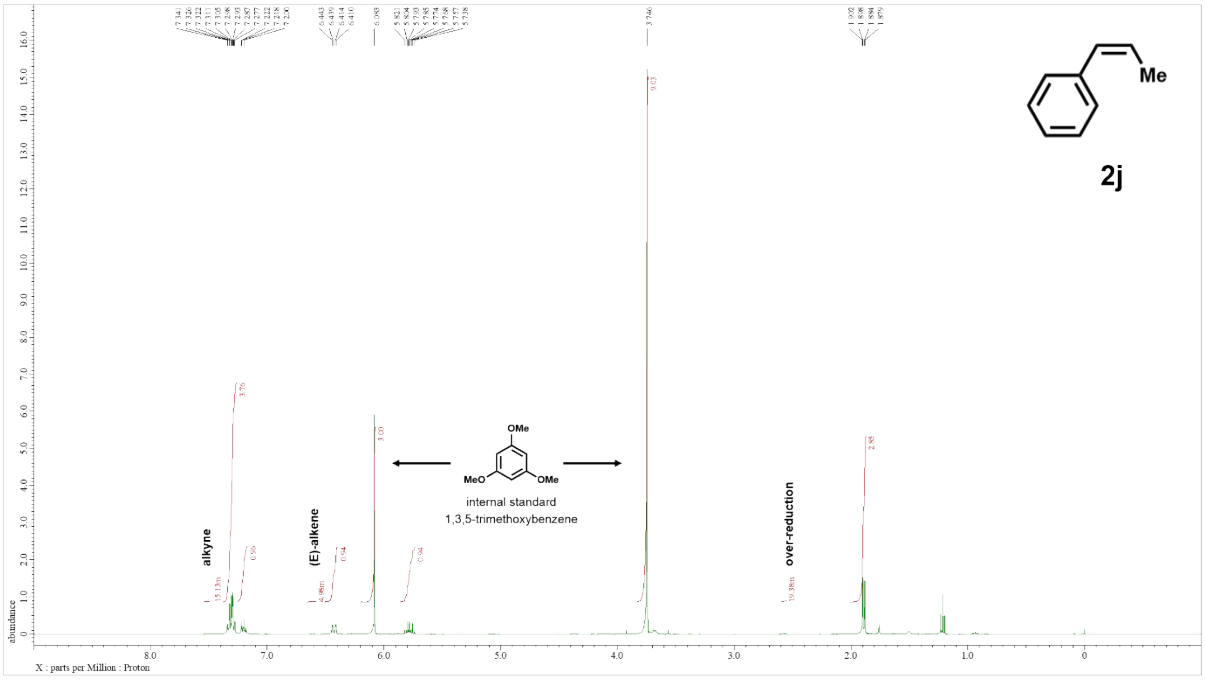


Figure S34. Crude ^{1}H spectrum of **2j**.

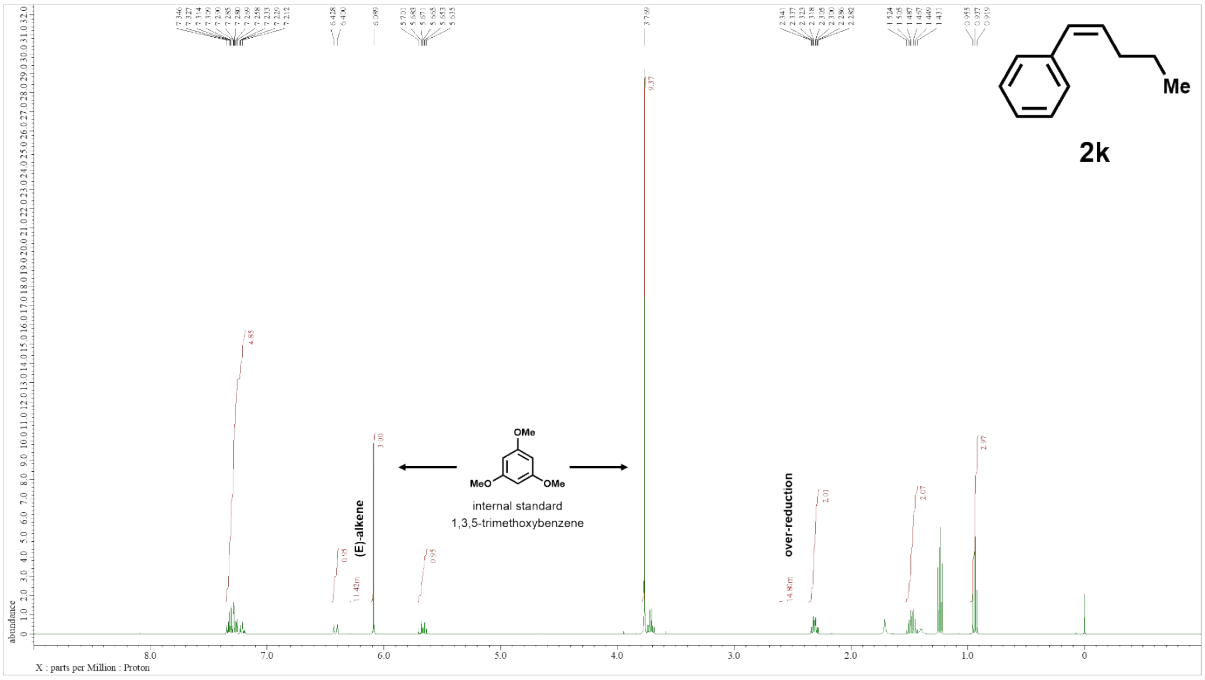


Figure S35. Crude ^{1}H spectrum of **2k**.

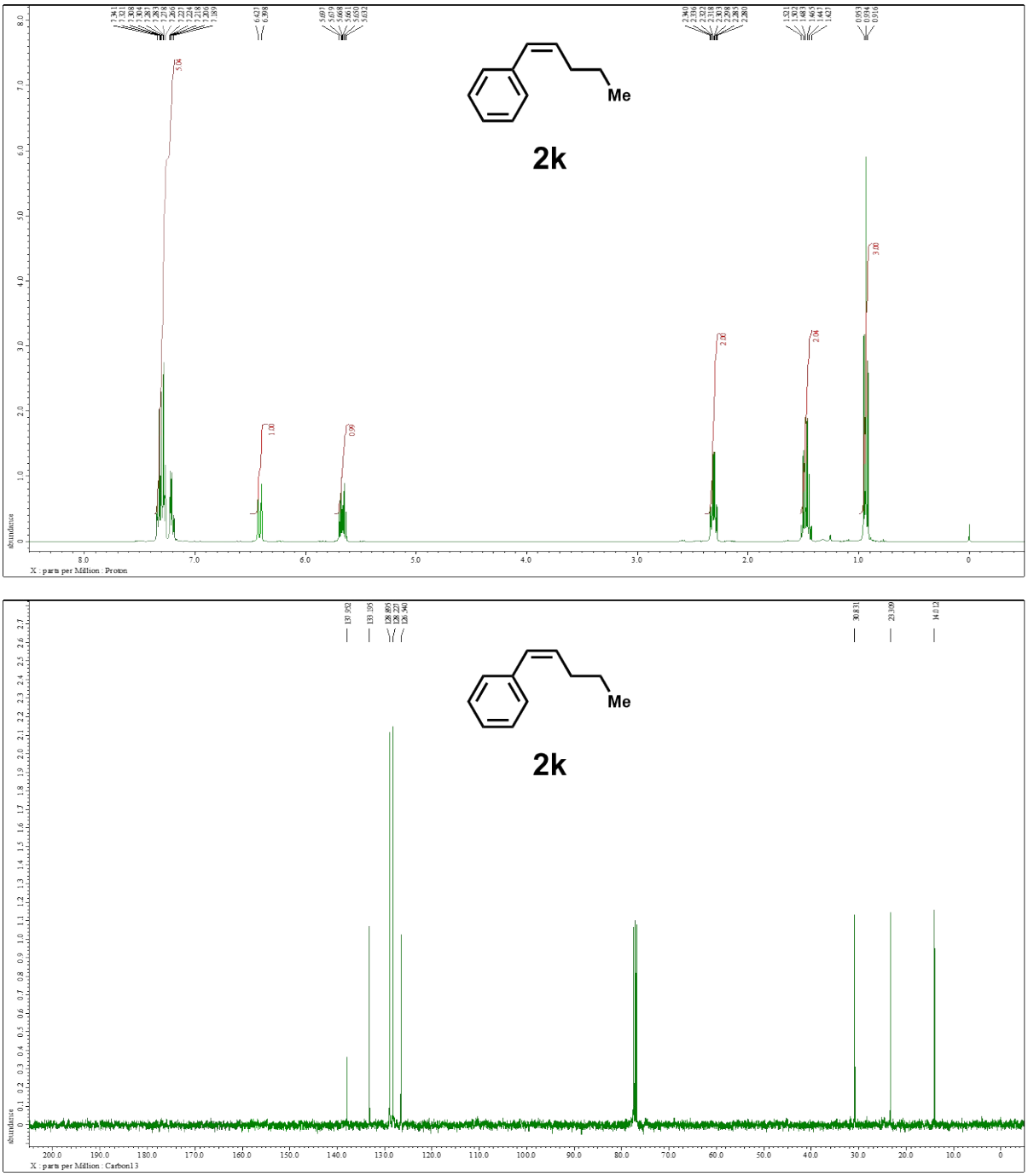


Figure S36. ^{1}H, ^{13}C spectrum of **2k**.

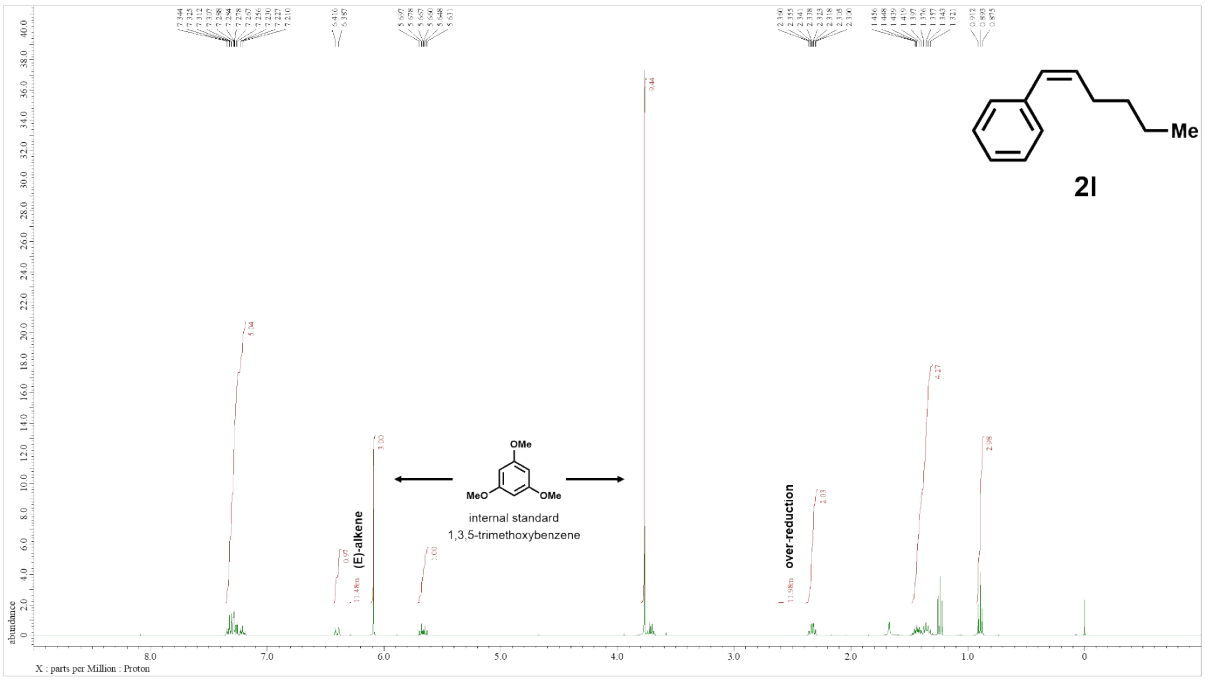


Figure S37. Crude ^{1}H spectrum of **2l**.

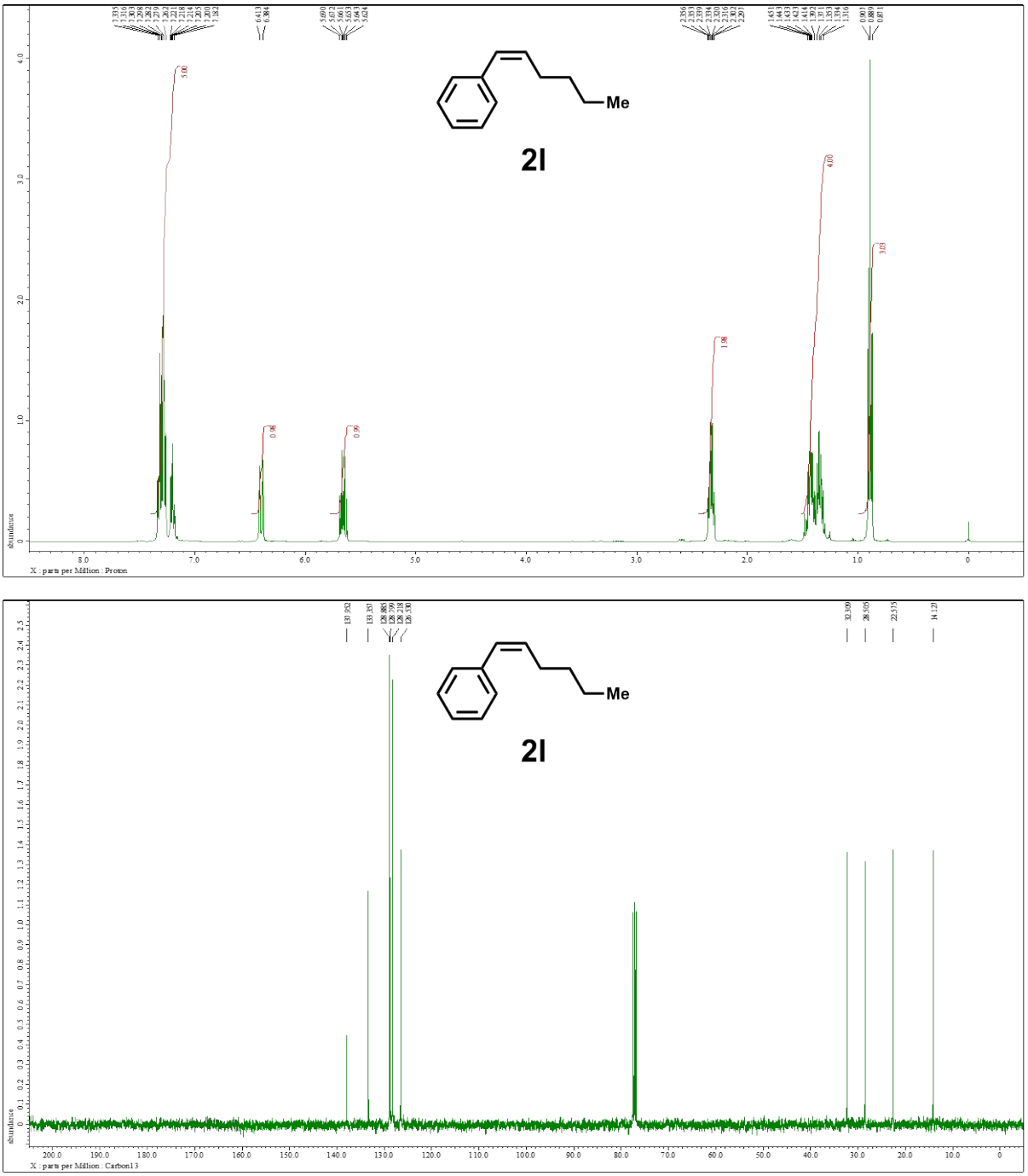


Figure S38. ^{1}H, ^{13}C spectrum of **2l**.

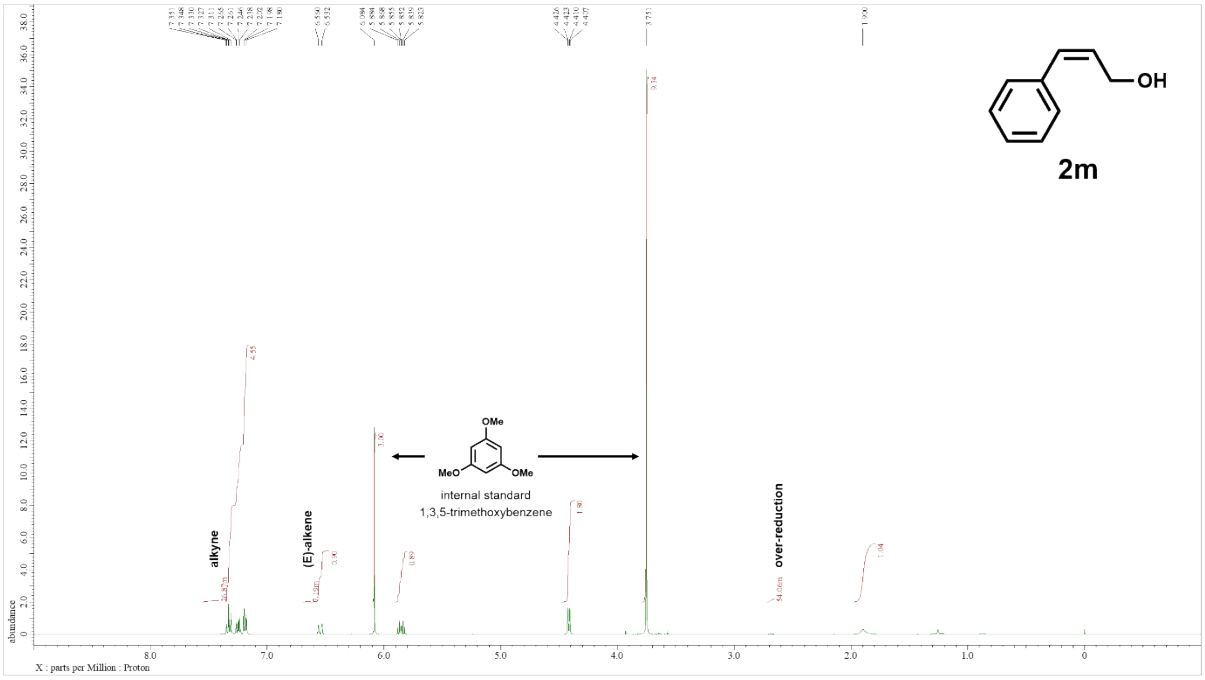


Figure S39. Crude ^{1}H spectrum of **2m**.

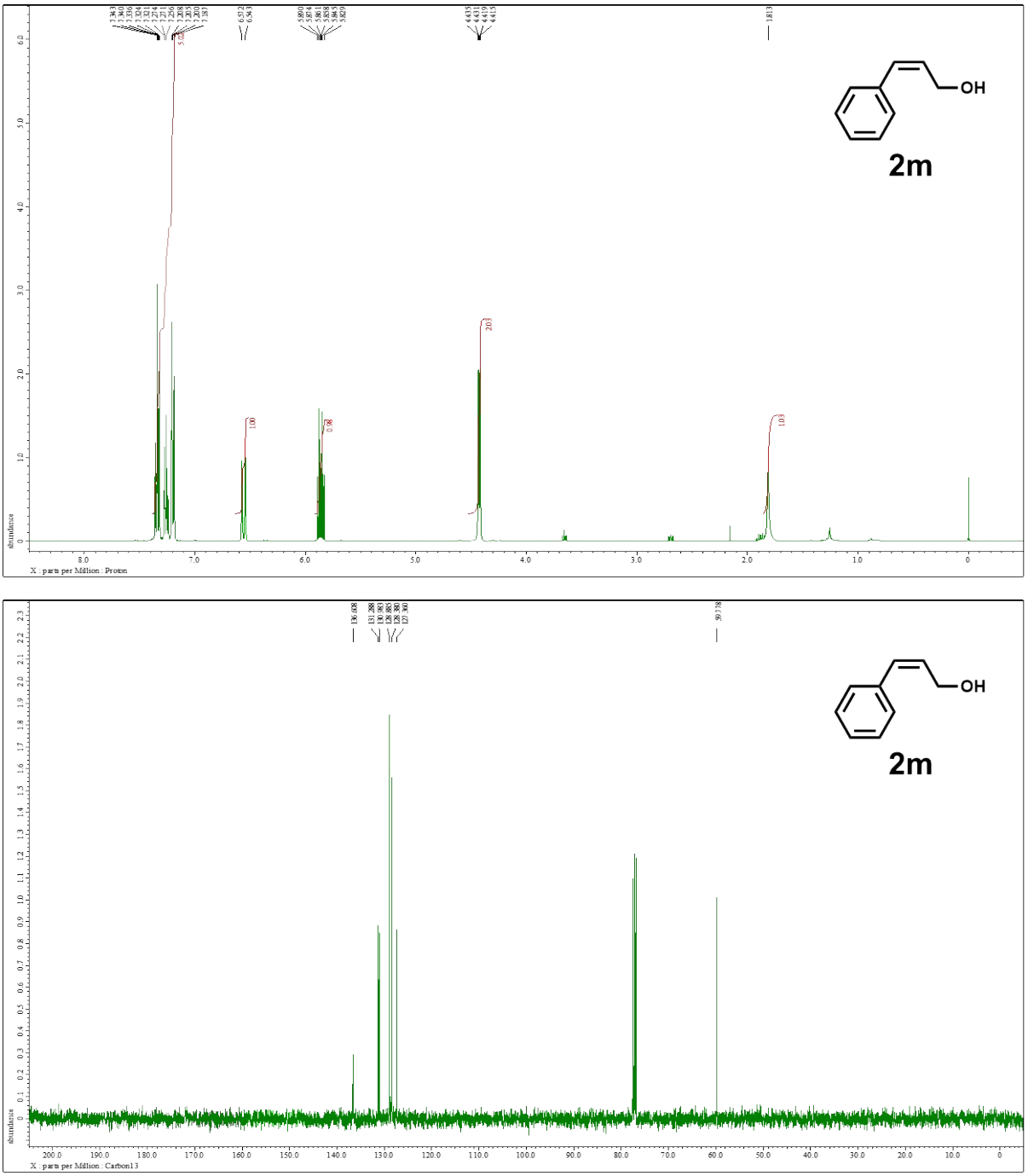


Figure S40. ^{1}H, ^{13}C spectrum of **2m**.

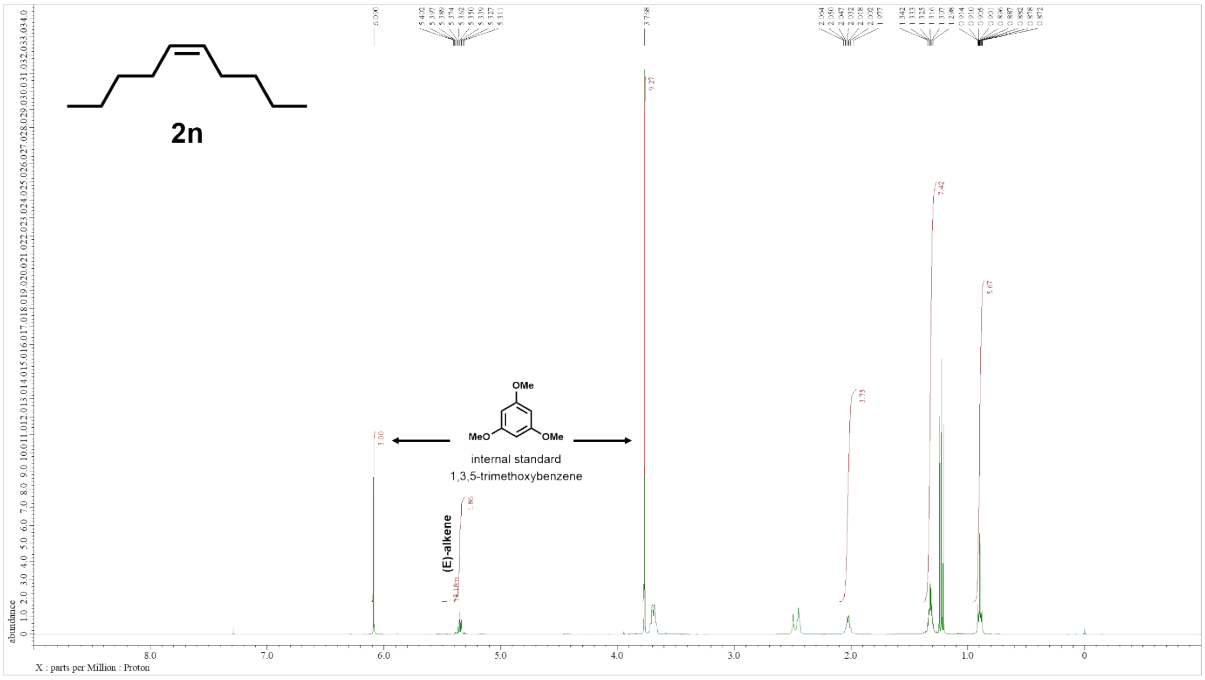


Figure S41. Crude ^{1}H spectrum of **2n**.

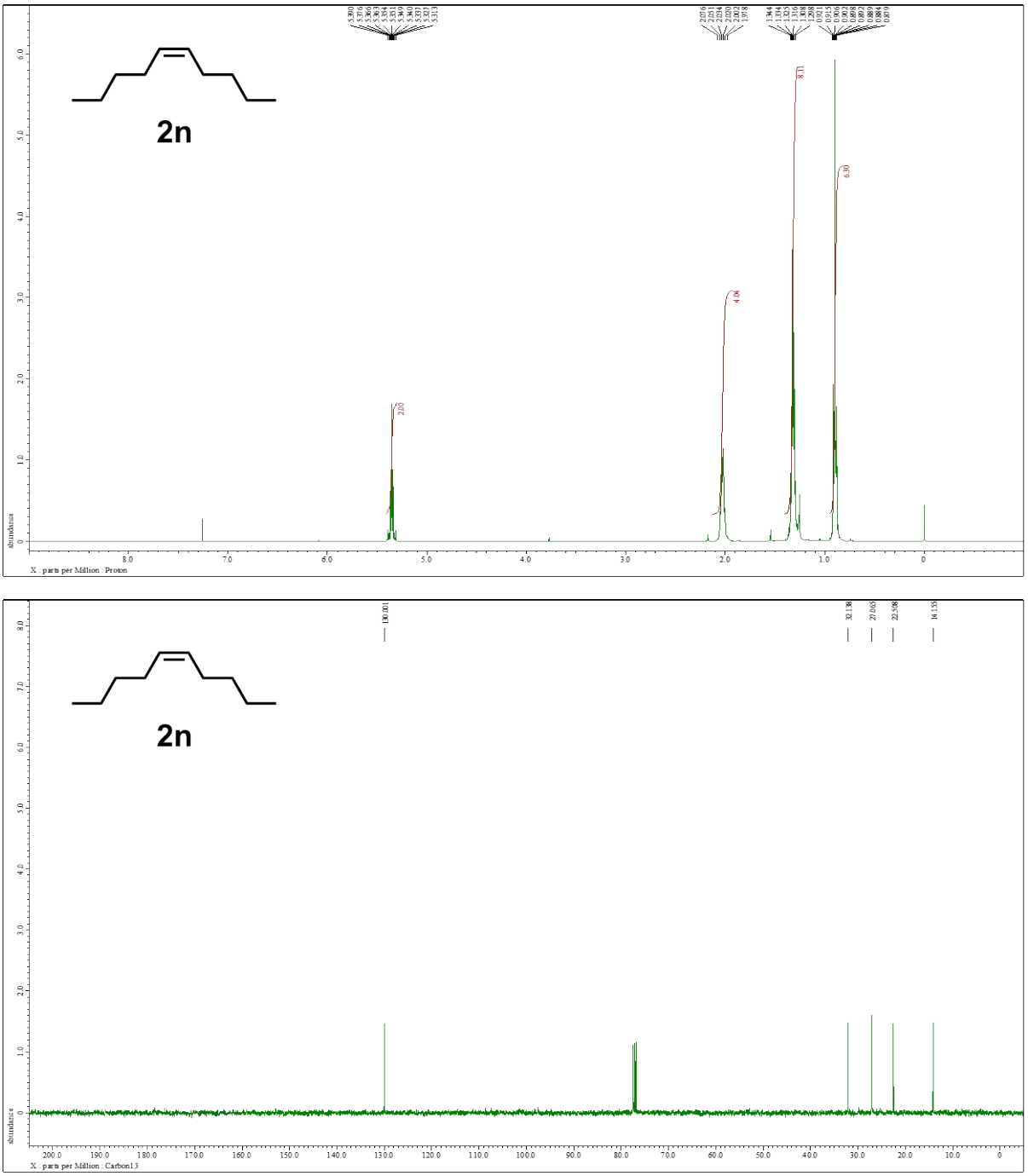


Figure S42. ^{1}H, ^{13}C spectrum of **2n**.

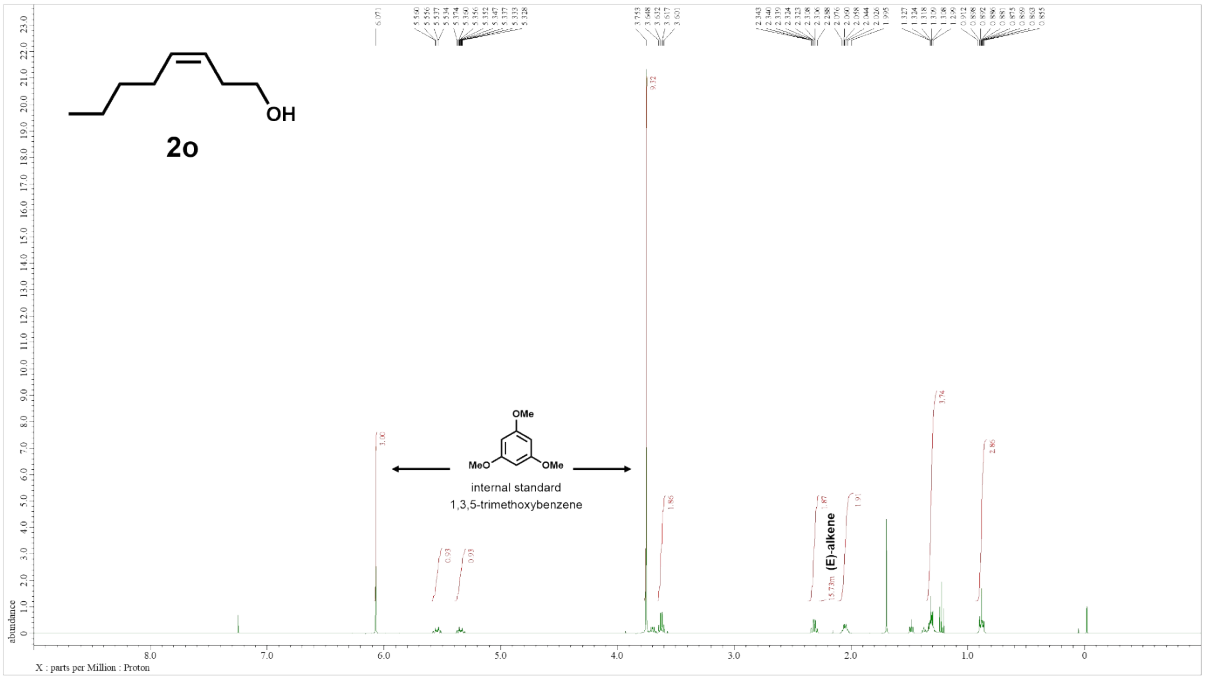


Figure S43. Crude ^{1}H spectrum of **2o**.

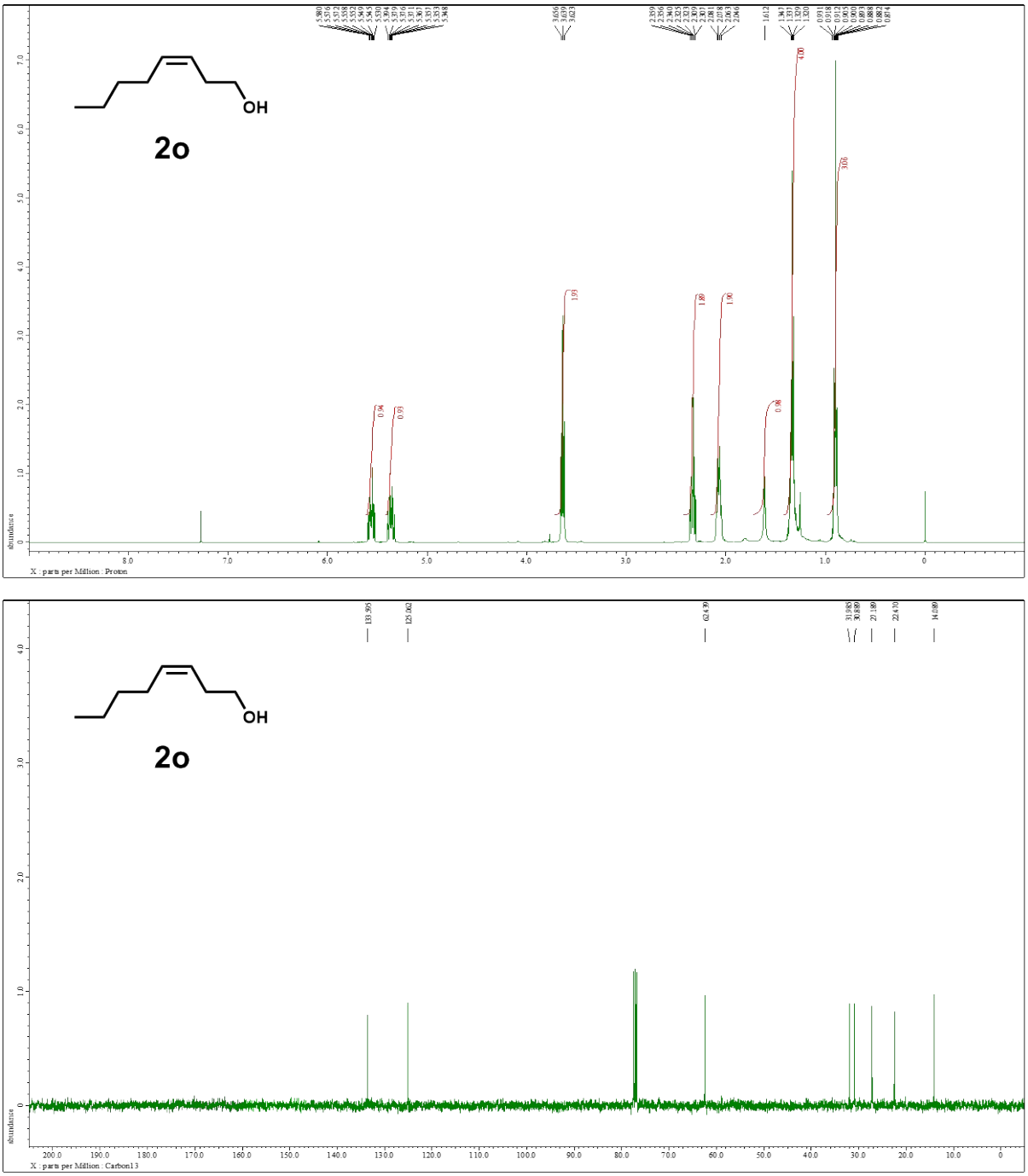


Figure S44. ^{1}H, ^{13}C spectrum of **2o**.

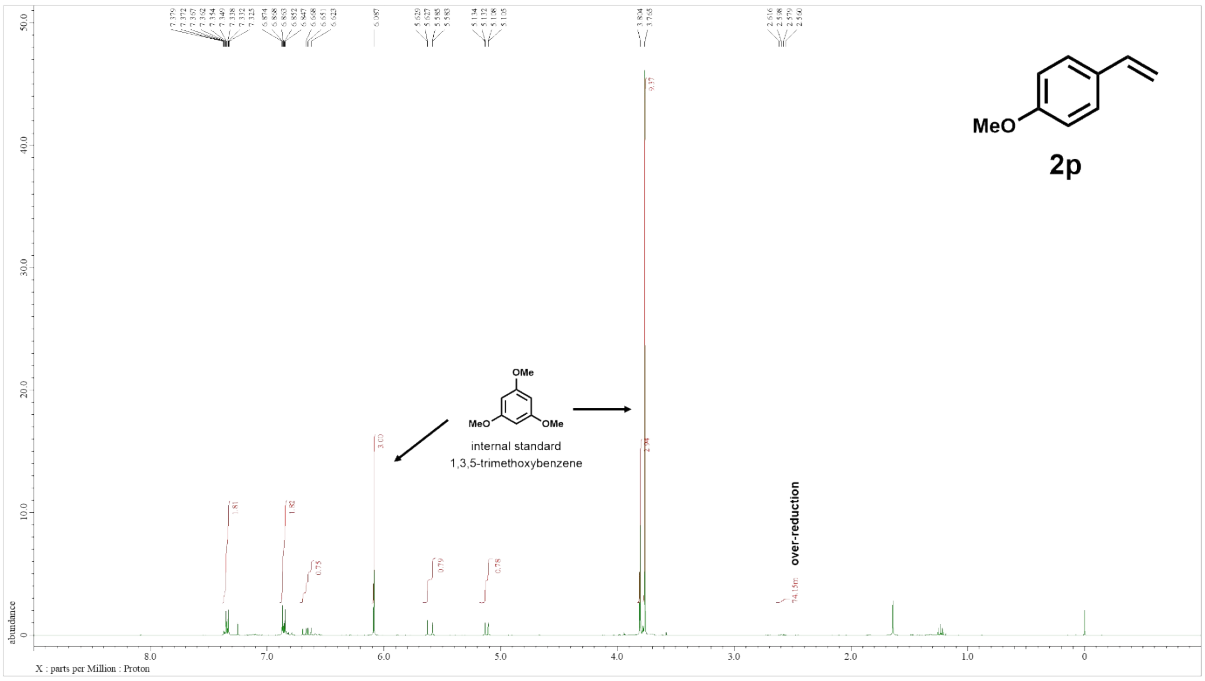


Figure S45. Crude ^{1}H spectrum of **2p**.

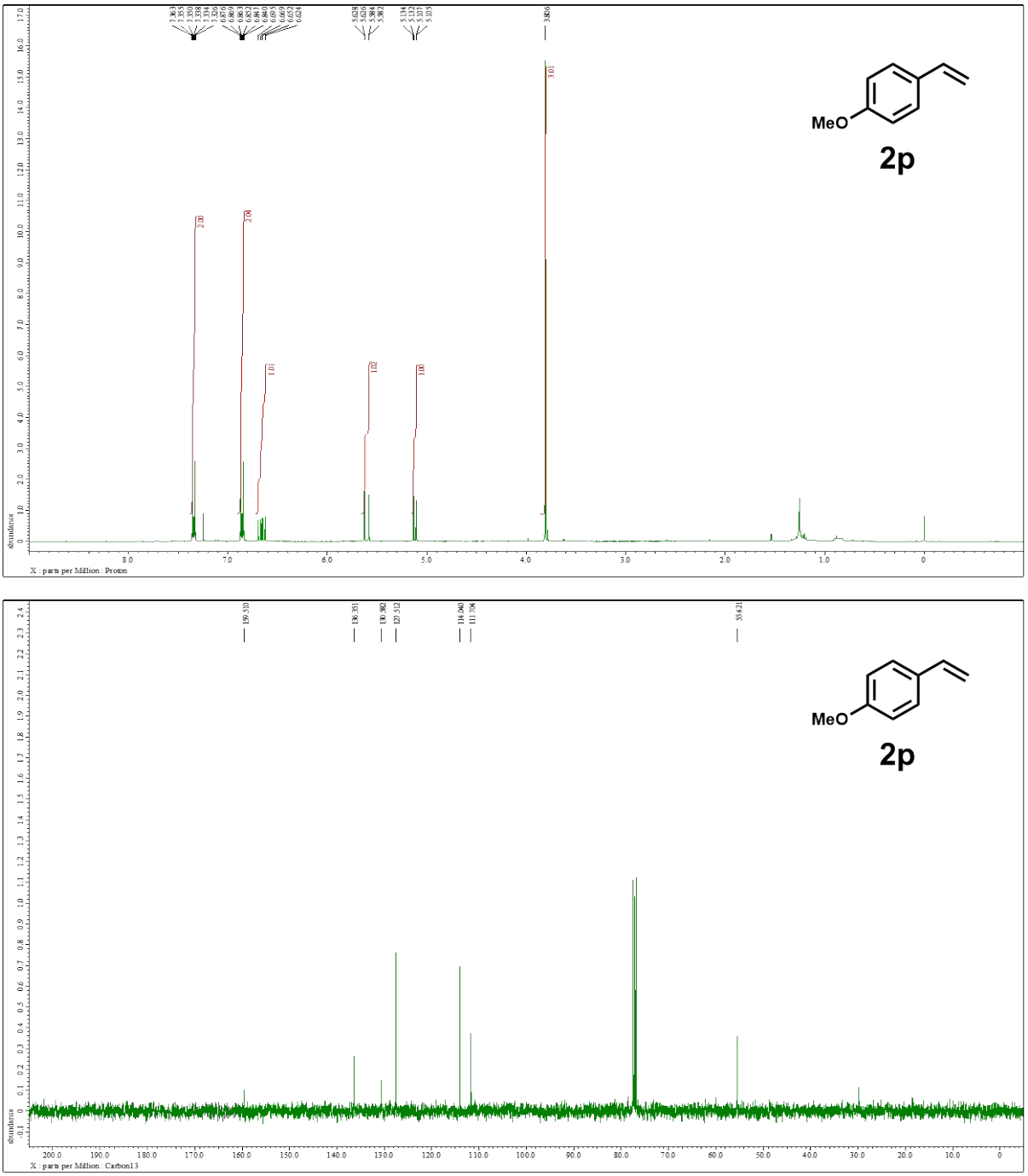


Figure S46. ^{1}H, ^{13}C spectrum of **2p**.

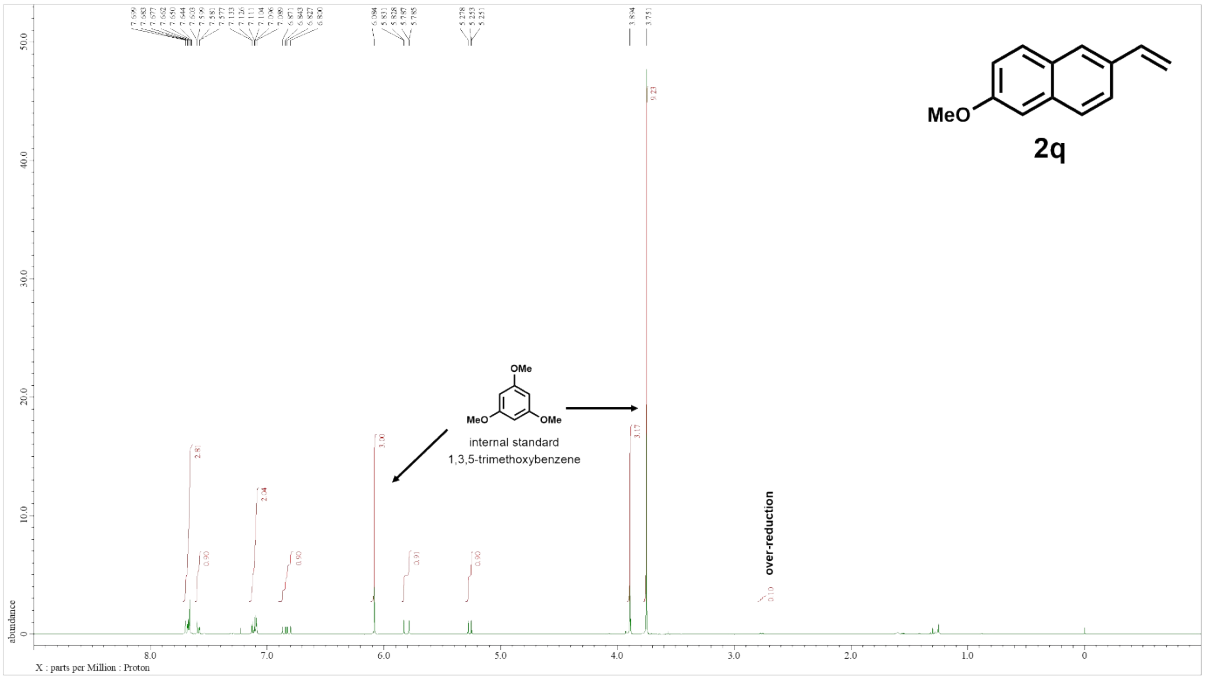


Figure S47. Crude ^{1}H spectrum of **2q**.

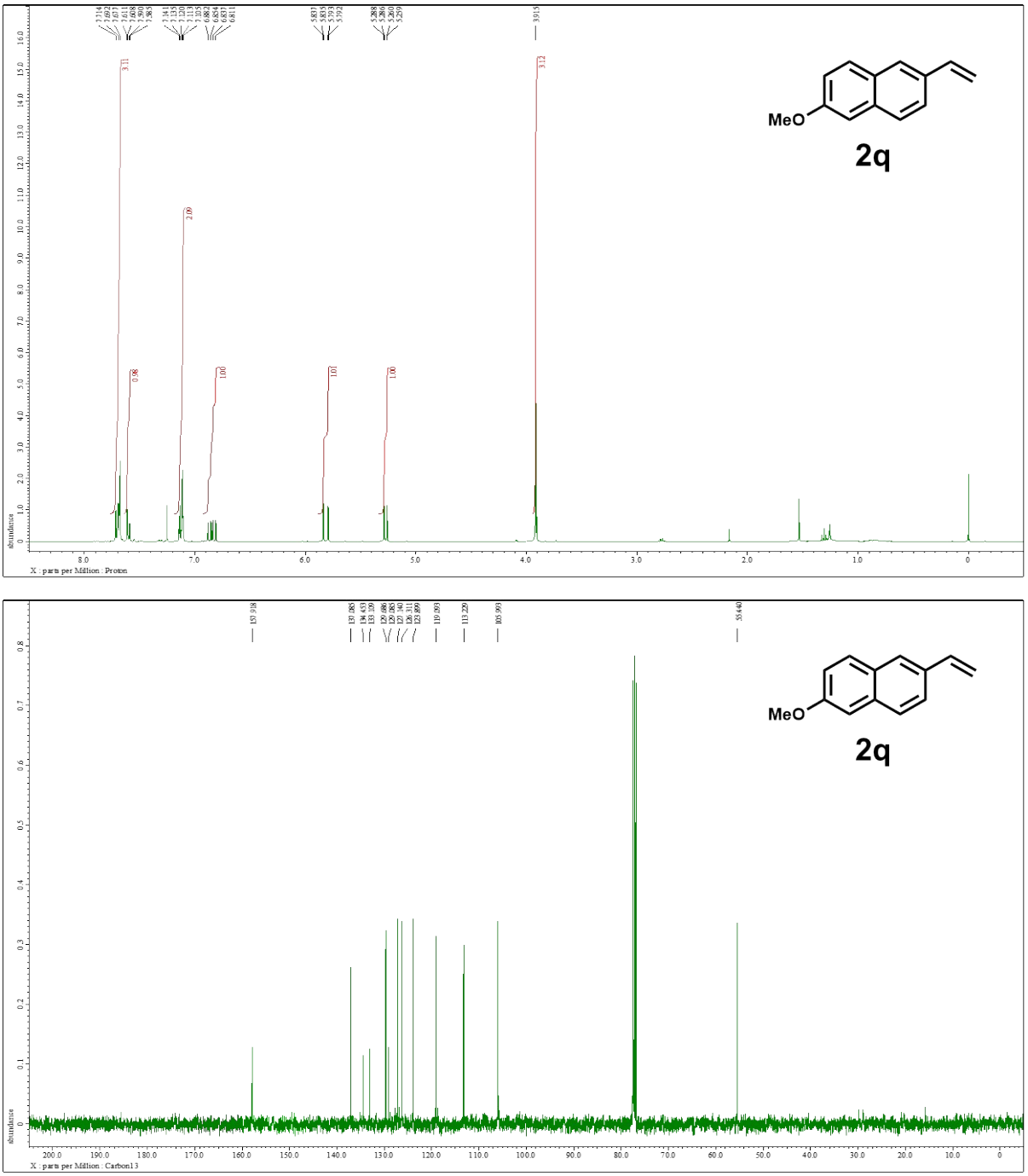


Figure S48. ^{1}H, ^{13}C spectrum of **2q**.

S.9. References

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