Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cobalt-catalyzed carboxylation of propargyl acetates with carbon dioxide

Keisuke Nogi, Tetsuaki Fujihara,* Jun Terao and Yasushi Tsuji*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

* To whom correspondence should be addressed.

E-mail: tfuji@scl.kyoto-u.ac.jp

E-mail: ytsuji@scl.kyoto-u.ac.jp

Table of Contents

1. Instrumentation and Chemicals

THF and toluene were dried and purified by usual procedures[1] DMA and DMI were distilled with CaH_2 and stored with activated MS-4A. Mn powder (99.99%) was purchased from Sigma-Aldrich and stored over nitrogen atmosphere. Zn powder was activated by washing with HCl aq. and stored in nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. IR spectra were obtained on a SHIMADZU FTIR-8300 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). EI-MS were recorded on a Shimadzu GCMS-QP5050A with a direct inlet. High-resolution mass spectra (EI-HRMS, ESI-HRMS and APCI-HRMS) were obtained with JEOL JMX-SX102A (EI-HRMS) and Thermo SCIENTIFIC Exactive LC-MS spectrometers (ESI-HRMS and APCI-HRMS). GC analysis was carried out using a Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-1, 0.25 mm i.d. × 25 m). Optical rotations were recorded on a JASCO DIP-1000 digital polarimeter at room temperature, using the sodium D line. Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63-210 μm). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Silica gel 60F_{254}.

2. Preparation of Substrates

2.1 General procedure for preparation of the cobalt complexes

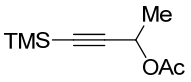
CoI_2(phen) was prepared according to a published method for $CoBr_2$(phen).[2] 50 mL Schlenk flask was dried with a heating-gun under vacuum. The flask was charged with CoI_2 (156 mg, 0.50 mmol), phen (90 mg, 0.50 mmol), and THF (2.0 mL) under Ar atmosphere. The resulting solution was stirred at room temperature for 10—12 h. A yellow solid was precipitated and isolated with filtration. After washing with Et_2O and drying in vacuo, the complex was obtained in 89% yield (220 mg, 0.45 mmol) and used without further purifitcation. Anal. Calcd for $C_{12}H_8CoI_2N_2 \cdot 2/3THF$: C, 32.56; H, 2.48; N, 5.18%. Found: C, 32.56; H, 2.63; N, 5.23%.

CoI_2(bpy), $CoI_2(PPh_3)_2$ and CoI_2(dppe) were prepared similarly.

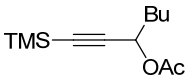
2.2 General procedure for preparation of the propargyl acetates

To a mixture of terminal acetylene (10 mmol) in THF (20 mL), *n*-BuLi (10 mmol, 1.64 M in hexane, 6.1 mL) was added dropwise at 0 ºC and the mixture was stirred for 30 min. Then, aldehyde (10 mmol) was added, and the solution was stirred for 30 min at 0 ºC.

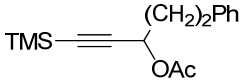
After adding Ac_2O (1.2 mL, 12 mmol), the resulting mixture was warmed to room temperature and stirred for 1 h. To the resulting solution, H_2O (10 mL) and Et_2O (10 mL) was added. The organic layer was washed with sat. $NaHCO_3$ aq. and brine, and dried over $MgSO_4$. After removal of volatile, the residue was purified with silica gel chromatography using hexane/EtOAc (30/1 w/w) as an eluent. **1j**[3] and **1q**[4] were prepared in the same way.



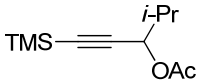
1a: Synthesized with 50 mmol scale. Colorless oil (3.5 g, 19 mmol, 38%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.47 (d, J = 6.8 Hz, 3H), 2.08 (s, 3H), 5.46 (q, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 21.1, 21.5, 60.6, 89.5, 103.5, 169.8. Anal. Calcd for $C_{19}H_{16}O_2Si$: C, 58.65; H, 8.75%. Found: C, 58.59; H, 8.99%.



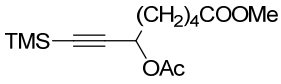
1b: Colorless oil (1.9 g, 8.2 mmol, 82%) ^{1}H NMR ($CDCl_3$): δ 0.17 (d, J = 0.9 Hz, 9H), 0.91 (t, J = 7.0 Hz, 3H), 1.32-1.44 (m, 4H), 1.71-1.77 (m, 2H), 2.08 (d, J = 0.9 Hz, 3H), 5.38 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 13.9, 21.1, 22.2, 27.1, 34.5, 64.4, 90.2, 102.8, 169.9. Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.66; H, 9.80%. Found: C, 63.42; H, 9.99%.



1c: Colorless oil (1.7 g, 6.2 mmol, 62%) ^{1}H NMR (400 MHZ, $CDCl_3$): δ 0.19 (s, 9H), 2.05-2.13 (m, 5H, two peaks were overlapped), 2.77 (t, J = 8.2 Hz, 2H), 5.39 (t, J = 6.6 Hz, 1H), 7.20 (t, J = 7.0 Hz, 3H), 7.31-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 21.0, 31.3, 36.4, 63.9, 90.8, 102.3, 126.1, 128.4, 128.5, 140.8, 169.8. Anal. Calcd for $C_{16}H_{22}O_2Si$: C, 70.03; H, 8.08%. Found: C, 70.15; H, 8.22%.

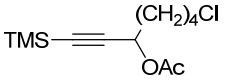


1d: Colorless oil (1.6 g, 7.5 mmol, 75%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 0.98 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H), 1.93-2.02 (m, 1H), 2.09 (s, 3H), 5.24 (d, J = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 17.4, 18.2, 21.0, 32.4, 69.2, 90.8, 101.4, 169.9. Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49%. Found: C, 62.44; H, 9.65%.

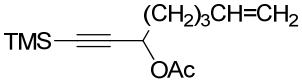


1e: Colorless oil (5 mmol scale, 1.0 g, 3.5 mmol, 70%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.43-1.50 (m, 2H), 1.64-1.79 (m, 4H), 2.08 (s, 3H), 2.33 (t, J = 7.5 Hz, 2H), 3.67 (s, 3H), 5.38 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.3, 21.0, 24.4, 24.5, 33.8, 34.4, 51.5, 64.0, 90.5, 102.4,

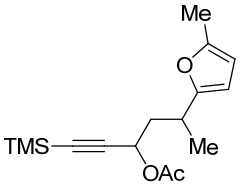
169.8, 173.8. Anal. Calcd for $C_{14}H_{24}O_4Si$: C, 59.12; H, 8.51%. Found: C, 58.89; H, 8.52%.



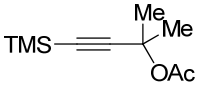
1f: Colorless oil (1.8 g, 6.9 mmol, 69%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.56-1.65 (m, 2H), 1.75-1.86 (m, 4H), 2.09 (s, 3H), 3.55 (t, J = 6.8 Hz, 2H), 5.40 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.3, 21.0, 22.3, 31.9, 33.9, 44.6, 64.0, 90.6, 102.2, 169.8. Anal. Calcd for $C_{12}H_{21}ClO_2Si$: C, 55.26; H, 8.12%. Found: C, 55.26; H, 8.41%.



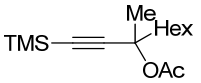
1g: Colorless oil (9 mmol scale, 1.3 g, 5.5 mmol, 61%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.49-1.55 (m, 2H), 1.72-1.79 (m, 2H), 2.07-2.12 (m, 5H), 4.96-5.05 (m, 2H), 5.39 (t, J = 6.6 Hz, 1H) 5.74-5.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 21.1, 24.2, 33.1, 34.2, 64.2, 90.4, 102.6, 115.0, 138.1, 169.9. APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{23}O_2Si$, 239.1462; found, 239.1458.



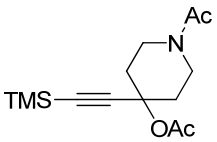
1h: Colorless oil (2.4 g, 8.2 mmol, 82%) ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers, dr = 4:5): δ 0.16 (d, J = 4.5 Hz, 9H), 1.25-1.27 (m, 3H), 1.83-2.21 (m, 5H), 2.24 (d, J = 4.1 Hz, 3H), 2.92-2.99 (m, 1H), 5.29-5.39 (m, 1H), 5.83-5.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 13.5, 13.5, 19.1, 19.4, 21.0, 21.0, 21.0, 29.7, 30.0, 40.6, 40.8, 62.7, 62.9, 90.2, 90.2, 90.4, 90.5, 102.5, 102.6, 104.7, 104.8, 105.7, 150.4, 150.4, 156.8, 169.7, 169.7. Anal. Calcd for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27%. Found: C, 65.53; H, 8.38%.



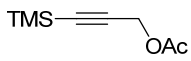
1i: Colorless oil (1.1 g, 5.5 mmol, 55%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 1.65 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 22.0, 29.0, 72.3, 88.2, 106.4, 169.1. Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15%. Found: C, 60.30; H, 9.40%.



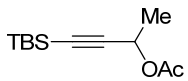
1k: Colorless oil (1.7 g, 6.3 mmol, 63%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H), 1.30-1.34 (m, 6H), 1.42-1.47 (m, 2H), 1.64 (s, 3H), 1.74-1.81 (m, 1H), 1.88-1.96 (m, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 14.1, 22.0, 22.5, 24.1, 26.4, 29.1, 31.7, 41.3, 75.7, 89.3, 105.8, 169.1 Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51%. Found: C, 66.88; H, 10.74%.



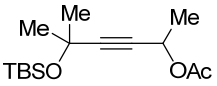
1l: White solid (610 mg, 2.2 mmol, 22%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.85-1.96 (m, 2H), 2.06 (s, 3H), 2.10 (s, 3H), 2.14-2.20 (m, 1H), 2.24-2.30 (m, 1H), 3.31 (ddd, J = 13.8, 10.0, 3.4 Hz, 1H), 3.43 (ddd, J = 13.7, 9.9, 3.3 Hz, 1H), 3.60-3.66 (m, 1H), 4.06-4.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 21.4, 21.8, 36.3, 36.8, 38.1, 43.0, 73.3, 92.6, 102.8, 168.8, 168.8. ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{24}NO_3Si$, 282.1520; found, 282.1523.



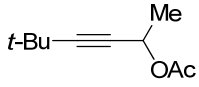
1m: To a mixture of 3-(trimethylsilyl)-2-propyn-1-ol (1.5 mL, 10 mmol) and acetyl chloride (850 μL, 12 mmol) in CH_2Cl_2 (20 mL), pyridine (1.2 mL, 15 mmol) was added dropwise at 0 ºC. The solution was sttired at room temperature for 1 h. After the addition of H_2O (20 mL), organic layer was washed with 1M HCl aq. (10 mL × 2) and brine (10 mL). The resulting organic layer was dried over $MgSO_4$ and all volatiles were removed by a rotary evaporator. The residue was purified with silica gel chromatography using hexane/EtOAc (30/1 w/w) as an eluent. Colorless oil (1.3 g, 7.6 mmol, 76%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 2.07 (s, 3H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.4, 20.7, 52.7, 92.0, 98.9, 170.1. Anal. Calcd for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29%. Found: C, 56.27; H, 8.18%.



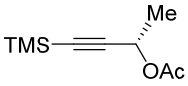
1n: Colorless oil (1.0 g, 4.4 mmol, 44%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 6H), 0.93 (s, 9H), 1.48 (d, J = 6.8 Hz, 3H), 2.07 (s, 3H), 5.46 (q, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.8, 16.5, 21.1, 21.5, 26.0, 60.6, 87.7, 104.3, 169.8. Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.66; H, 9.80%. Found: C, 63.76; H, 10.08%.



1o: Colorless oil (7 mmol scale, 920 mg, 3.2 mmol, 46%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 6H), 0.86 (s, 9H), 1.44 (s, 6H), 1.46 (d, J = 6.3 Hz, 3H), 2.06 (s, 3H), 5.48 (q, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –3.1, 17.9, 21.0, 21.3, 25.7, 32.8, 60.3, 66.1, 80.7, 90.0, 169.8. ESI-HRMS (*m/z*): $[M+NH_4]^+$ calcd for $C_{15}H_{32}O_3SiN$, 302.2146; found, 302.2148.



1p: Colorless oil (430 mg, 2.6 mmol, 26%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9H), 1.44 (d, J = 6.8 Hz, 3H), 2.06 (s, 3H), 5.46 (q, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 21.9, 27.3, 30.8, 60.8, 93.5, 169.9. EI-HRMS (*m/z*): $[M]^+$ calcd for $C_{10}H_{16}O_2$, 168.1150; found, 168.1154.



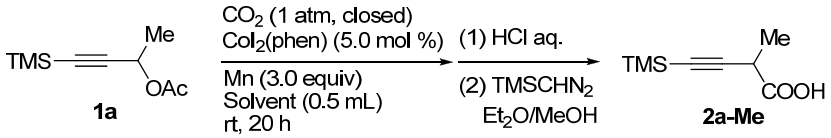
(*S*)-**1a**: To a solution of (*S*)-4-trimethylsilyl-3-butyn-2-ol[5] (3.2 mmol) and acetyl chloride (350 μL, 4 mmol) in CH_2Cl_2 (20 mL) was added pyridine (460 μL, 6 mmol) at 0 ºC and resulting mixture was stirred for 2 h. The reaction was quenched by addition of sat. $NaHCO_3$ aq. (10 mL) and organic layer was washed with 1M HCl aq. and brine, and dried over $MgSO_4$. After the removal of solvent, the residue was purified with silica-gel chromatography using hexane/EtOAc (30/1 w/w) as an eluent. Colorless oil (510 mg, 2.8 mmol, 86%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.47 (d, J = 6.8 Hz, 3H), 2.08 (s, 3H), 5.46 (q, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 21.1, 21.5, 60.6, 89.5, 103.5, 169.8. $[\alpha]^{25}_D$ –137.9 (c 1.070, $CHCl_3$, 98% ee). Enantiomeric excess of this compound was determined by GC analysis with a capillary column (CP-Chirasil Dex CB, 0.25 mm i.d. × 25 m)

3. Experimental Procedure

3.1. General procedure for carboxylation of 1a (entry 1, Table 1)

A 20 mL Schlenk flask was dried with a heating-gun under vacuum. The flask was charged with CoI_2(phen) (12.3 mg, 0.025 mmol) and Mn powder (82.4 mg, 1.5 mmol). The flask was evacuated and refilled with CO_2 five times. Then, DMA (0.5 mL) and 1-methyl-3-(trimethylsilyl)prop-2-ynyl acetate **1a** (101 μL, 0.50 mmol) were added via air-tight syringes, and the resulting mixture was stirred at room tempearture for 20 h. After the reaction, tridecane (50 μL, 0.21 mmol) as an internal standard, Et_2O (5.0 mL), and 1M HCl aq. (3.0 mL) were added to the reaction mixture. After stirring for 10 min, organic layer was transferred to a flask containing anhydrous $MgSO_4$ (50 mg). Then, methanol (1.0 mL) and $TMSCHN_2$ (2.0 M in Et_2O, 0.50 ml, 1.0 mmol) was added to the suspension, and it was stirred for 30 min. The yield of **2a-Me** was determined by GC analysis.

Table S1 Effect of solvents on the cobalt-catalyzed carboxylation of **1a**[a]



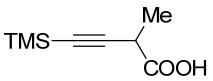
entry	Solvent	Yield of **2a-Me** (%)[b]
1	DMA	83
2	DMI	76
3	THF	26
4	Toluene	0

[a] Reaction conditions; **1a** (0.50 mmol), CoI_2(phen) (0.025 mmol, 5.0 mol %), Mn powder

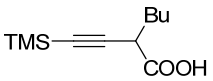
(1.5 mmol, 3.0 equiv), in Solvent (0.5 mL), at room temperature for 20 h. [b] Determined by GC analysis.

3.2. General procedure for the carboxylation of propargyl acetates (Table 2)

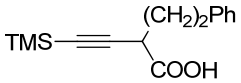
A 20 mL Schlenk flask was dried with a heating-gun under vacuum. The flask was charged with CoI_2(phen) (12.3 mg, 0.025 mmol) or CoI_2(bpy) (11.7 mg, 0.025 mmol) and Mn powder (82.4 mg, 1.5 mmol). The flask was evacuated and refilled with CO_2 five times. Then, DMA (0.5 mL) and **1** (0.50 mmol) were added via air-tight syringes, and the resulting mixture was stirred at room temperature for 20 h. After reaction, 1M HCl aq. (3 mL) and Et_2O (5 mL) was added, and stirred at room temperature for 10 min. The mixture was extracted with Et_2O (5 mL × 5). The collected organic layer was combined and dried over anhydrous $MgSO_4$. After removal of volatile, the residue was purified by silica gel chromatography using hexane/EtOAc (4/1, v/v) as an eluent.



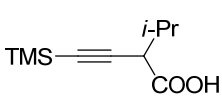
2a: Yellow oil (69.9 mg, 82%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.47 (d, J = 7.2 Hz, 3H), 3.49 (q, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 18.0, 33.2, 87.8, 102.4, 177.5. Anal. Calcd for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29%. Found: C, 56.58; H, 8.44%. IR (neat): 3300-2700 (br), 2179.2, 1719.2, 1413.6, 1286.3, 1250.6, 1224.6, 1120.4, 940.1, 844.7, 760.8 cm^{-1}.



2b: Yellow oil (84.9 mg, 80%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 0.92 (t, J = 7.2 Hz, 3H), 1.31-1.51 (m, 4H), 1.74-1.91 (m, 2H), 3.39 (dd, J = 6.3, 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 13.8, 22.1, 29.0, 32.0, 38.9, 88.9, 101.4, 177.1. Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49%. Found: C, 62.40; H, 9.59%. IR (KBr): 3300-2500 (br), 2179.2, 1717.3, 1414.7, 1250.6, 843.7, 759.8 cm^{-1}.

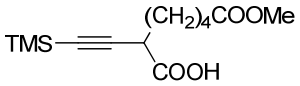


2c: Yellow oil (98.3 mg, 75%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H), 2.05-2.21 (m, 2H), 2.74-2.87 (m, 2H), 3.38 (dd, J = 5.9, 8.2 Hz, 1H), 7.19-7.22 (m, 3H), 7.27-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 32.9, 33.7, 38.1, 89.7, 100.9, 126.2, 128.5, 128.6, 140.6, 175.9. Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.19; H, 7.74%. Found: C, 69.31; H, 7.80%. IR (KBr): 3200-2500 (br), 1713.4, 1276.7, 1252.5, 1235.2, 840.8, 750.9, 747.3, 701.0 cm^{-1}.

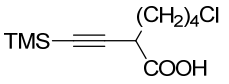


2d: Yellow oil (78.4 mg, 79%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.05 (dd, J = 2.3, 6.8 Hz, 6H), 2.18-2.30 (m, 1H), 3.26 (d, J =

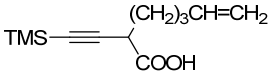
5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 18.8, 20.8, 31.0, 46.4, 89.9, 100.0, 176.8. Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15%. Found: C, 60.45; H, 9.23%. IR (neat): 3500-2500 (br), 2183.0, 1715.4, 1414.5, 1290.1, 1250.6, 1024.0, 843.7, 760.8 cm^{-1}.



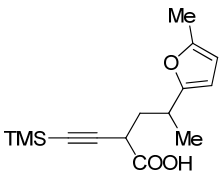
2e: Yellow oil (87.5 mg, 65%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.45-1.59 (m, 2H), 1.64-1.72 (m, 2H), 1.75-1.92 (m, 2H), 2.34 (t, J = 7.5 Hz, 2H), 3.39 (dd, J = 6.1, 7.9 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 24.3, 26.4, 31.8, 33.8, 38.7, 51.6, 89.0, 101.1, 174.0, 176.4. Anal. Calcd for $C_{13}H_{22}O_4Si$: C, 57.74; H, 8.20%. Found: C, 57.96; H, 8.37%. IR (neat): 3500-2700 (br), 1741.4, 1717.3, 1438.6, 1250.6, 1208.2, 1175.4, 844.7, 760.8 cm^{-1}.



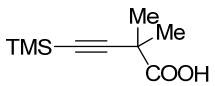
2f: Yellow oil (104.9 mg, 85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.60-1.69 (m, 2H), 1.77-1.90 (m, 4H), 3.41 (t, J = 6.8 Hz, 1H), 3.55 (t, J = 6.6 Hz, 2H), 10.89 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 24.2, 31.4, 31.9, 38.8, 44.5, 89.4, 100.8, 176.6, 176.8. Anal. Calcd for $C_{11}H_{19}ClO_2Si$: C, 53.53; H, 7.76%. Found: C, 53.58; H, 7.92%. IR (neat): 3500-2500 (br), 1717.3, 1415.5, 1288.2, 1250.6, 844.7, 760.8 cm^{-1}.



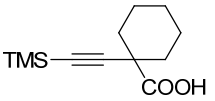
2g: Yellow oil (82.4 mg, 73%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.52-1.64 (m, 2H), 1.75-1.90 (m, 2H), 2.10 (q, J = 6.9 Hz, 2H), 3.40 (t, J = 7.0 Hz, 1H), 4.96-5.05 (m, 2H), 5.74-5.84 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ –0.1, 26.0, 31.6, 33.0, 38.8, 89.0, 101.1, 115.0, 138.0, 177.3. APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{21}O_2Si$, 225.1305; found, 225.1302. IR (neat): 3300-2800 (br), 2179.2, 1718.3, 1414.5, 1250.6, 843.7, 760.8 cm^{-1}.



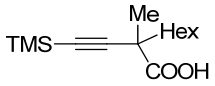
2h: Yellow oil (121.1 mg, 87%) ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers, dr = 4:5): δ 0.19 (d, J = 5.9 Hz, 9H), 1.28 (dd, J = 12.9, 7.0 Hz, 3H), 1.88-2.22 (m, 2H), 2.26 (s, 3H), 2.97-3.10 (m, 1H), 3.31-3.45 (m, 1H), 5.83-5.85 (m, 1H), 5.90 (dd, J = 7.7, 3.2 Hz, 1H), 11.08 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, –0.1, 13.5, 13.5, 18.5, 19.8, 30.8, 31.2, 36.8, 37.5, 38.0, 38.1, 88.8, 89.1, 101.0, 101.1, 105.2, 105.5, 105.6, 150.6, 150.7, 156.0, 156.6, 177.0, 177.1. ESI-HRMS (*m/z*): $[M–H]^-$ calcd for $C_{15}H_{21}O_3Si$, 277.1265; found, 277.1269. IR (neat): 3500-2500 (br), 1718.3, 1413.6, 1250.6, 1219.8, 1020.2, 844.7, 783.0, 760.8 cm^{-1}.



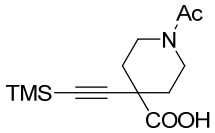
2i: Pale orange solid (65.8 mg, 71%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 1.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 27.1, 39.0, 86.4, 107.3, 180.2. Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75%. Found: C, 58.41; H, 8.87%. IR (KBr): 3300-2500 (br), 1707.7, 1295.0, 1251.6, 899.6, 841.8, 761.7 cm^{-1}.



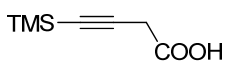
2j: Pale orange solid (89.2 mg, 80%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.19-1.26 (m, 1H), 1.66-1.74 (m, 7H), 1.94 (d, J = 9.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 22.2, 25.3, 34.6, 44.6, 89.4, 105.4, 179.3. Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98%. Found: C, 64.03; H, 9.19%. IR (KBr): 3300-2500 (br), 1699.0, 1278.6, 1249.7, 868.8, 840.8, 760.8 cm^{-1}.



2k: Yellow oil (101.1 mg, 80%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H), 1.29-1.44 (m, 8H), 1.47 (s, 3H), 1.65 (dt, J = 4.5, 11.8 Hz, 1H), 1.83 (dt, J = 4.7, 12.5, Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 14.0, 22.5, 25.1, 25.5, 29.2, 31.5, 40.0, 43.8, 87.9, 106.5, 179.5. Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30%. Found: C, 65.84; H, 10.58%. IR (neat): 3500-2500 (br), 2173.4, 1709.6, 1459.9, 1408.8, 1277.6, 1250.6, 881.3, 843.7, 759.8 cm^{-1}.

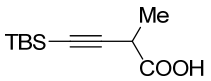


2l: White solid (62.5 mg, 46%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 9H), 1.80-1.96 (m, 4H), 2.12 (s, 3H), 3.12 (t, J = 11.6 Hz, 1H), 3.46 (t, J = 11.3 Hz, 1H), 3.69 (d, J = 13.6 Hz, 1H), 4.37 (d, J = 13.6 Hz, 1H), 11.75 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 21.0, 33.6, 34.1, 38.4, 42.7, 43.1, 90.6, 103.4, 169.9, 174.6. ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{22}NO_3Si$, 268.1363; found, 268.1361. IR (KBr): 3700-2500 (br), 1726.0, 1602.6, 1480.1, 1457.0, 1442.5, 1254.5, 1050.1, 858.2, 839.8 cm^{-1}.

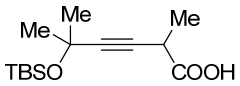


2m: Orange oil (31.6 mg, 40%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H), 3.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 26.9, 89.1, 96.3, 174.2. ESI-HRMS (*m/z*): $[M-H]^-$ calcd for $C_7H_{11}O_2Si$, 155.0534; found, 155.0535. IR (neat): 3300-2700 (br), 2187.8, 1714.4, 1392.4, 1255.4, 1244.8, 1220.7, 1048.1, 845.6, 760.8 cm^{-1}.

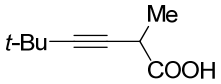
2n: Yellow oil (93.5 mg, 88%) ^{1}H NMR (400 MHz, Acetone-D_6): δ 0.08 (s, 6H), 0.94 (s, 9H), 1.38 (d, J = 7.2 Hz, 3H), 3.49 (q, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-



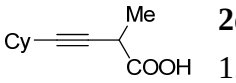
D$_6$): δ –4.5, 17.1, 18.4, 26.3, 33.3, 84.7, 106.2, 172.0. Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49%. Found: C, 61.98; H, 9.78%. IR (neat): 3500-2500 (br), 1720.2, 1250.6, 838.9, 810.9, 776.2 cm^{-1}.



2o: Yellow oil (75.0 mg, 55%) ^{1}H NMR (400 MHz, Acetone-D$_6$): δ 0.16 (s, 6H), 0.84 (s, 9H), 1.35 (d, J = 7.2 Hz, 3H), 1.41 (s, 6H), 3.44 (q, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-D$_6$): δ –2.9 (d, J = 1.9 Hz), 18.2, 18.4, 26.1, 32.2, 33.4 (d, J = 1.9 Hz), 66.9, 81.9, 87.7, 172.2. Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69%. Found: C, 62.41; H, 9.92%. IR (neat): 3500-2500 (br), 1720.2, 1245.8, 1163.8, 1041.4, 777.2 cm^{-1}.



2p: Yellow oil (43.9 mg, 57%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21(s, 9H), 1.42 (d, J = 7.2 Hz, 3H), 3.41 (q, J = 7.2 Hz, 1H), 11.64 (brs, 1H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 27.3, 31.0, 32.2, 75.3, 91.8, 178.7. EI-HRMS (m/z): [M]$^+$ calcd for $C_9H_{14}O_2$, 154.0994; found, 154.0993. IR (neat): 3300-2500 (br), 1715.4, 1457.9, 1415.5, 1364.4, 1288.2, 1204.3 cm^{-1}.

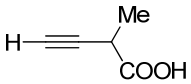


2q: Yellow oil (23.3 mg, 26%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26-1.33 (m, 3H), 1.39-1.52 (m, 6H), 1.65-1.72 (m, 2H), 1.75-1.81 (m, 2H), 2.34-2.41 (m, 1H), 3.44 (dq, J = 1.8, 7.1 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 24.8, 25.9, 29.0, 32.3, 32.6, 76.8, 87.8, 178.2. ESI-HRMS (*m/z*): [M–H]$^-$ calcd for $C_{11}H_{15}O_2$, 179.1078; found, 179.1079. IR (neat): 3700-2500 (br), 1712.5, 1451.2, 1381.8, 1256.4, 967.1 cm^{-1}. IR (neat): 3700-2500 (br), 1712.5, 1451.2, 1381.8, 1256.4, 967.1 cm^{-1}.

3.3. Experimental procedure for transformation of Product 2

3.3.1. Procedure for desilylation of 2a using TBAF (Scheme 1a)

To a solution of propargyl carboxylic acid **2a** (85.1 mg, 0.50 mmol) in THF (1.0 mL), TBAF (0.50 mmol, 1 M in THF, 0.50 mL) was added and then the mixture was stirred overnight at room temperature. The resulting mixture was extracted with Et_2O (10 mL) and H_2O (10 mL) and the combined organic layers were dried over $MgSO_4$. Et_2O and THF were removed with carefully evaporation. The residue was purified by reduced distillation with Kugel-roll oven (6 Torr, 100 ºC) and **2r** was obtained.

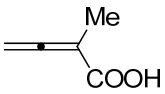


2r: Colorless oil (38.1 mg, 78%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, J = 7.2 Hz, 3H), 2.29 (d, J = 2.7 Hz, 1H), 3.49 (dq, J = 2.3, 7.2 Hz, 1H).

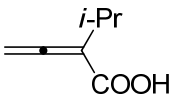
^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 32.0, 71.5, 80.7, 177.2. APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_5H_7O_2$, 99.0441; found, 99.0449. IR (neat): 3700-2700 (br), 1727.9, 1640.2, 1218.8, 659.5 cm^{-1}.

3.3.2. Procedure for desilylation of 2a and 2d using KOH (Scheme 1b)

To a solution of propargyl carboxylic acid **2a** (0.50 mmol) in methanol (1.0 mL), crushed KOH (140 mg, 2.5 mmol) was added and then the mixture was stirred overnight at room temperature. The resulting mixture was diluted with Et_2O (20 mL) and extracted with H_2O three times. The combined basic aqueous layer was acidified to pH = 1 using 1 M HCl aq. and extracted with CH_2Cl_2. The combined organic layers were dried with anhydrous $MgSO_4$ and evaporated to yield **2s**. Carboxylic acid **2t** was obtained similarly using **2d** as the substrate.



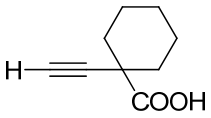
2s: White solid (39.2 mg, 80%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (t, *J* = 2.9 Hz, 3H), 5.15 (q, *J* = 2.9 Hz, 2H), 11.18 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 78.3, 95.1, 173.0, 215.0. Anal. Calcd for $C_5H_6O_2$: C, 61.22; H, 6.16%. Found: C, 61.42; H, 6.39%. IR (KBr): 3300-2500 (br), 1962.2, 1684.5, 1423.2, 1309.4, 1142.6, 869.7 cm^{-1}.



2t: Orange oil (41.2 mg, 65%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 6.8 Hz, 6H), 2.60-2.72 (m, 1H), 5.22 (d, *J* = 2.3 Hz, 2H), 10.98 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 26.5, 80.4, 106.7, 172.9, 213.7. ESI-HRMS (*m/z*): $[M-H]^-$ calcd for $C_7H_9O_2$, 125.0608; found, 125.0608. IR (neat): 3300-2500 (br), 2661.3, 1962.2, 1936.2, 1683.6, 1466.6, 1411.64, 1385.6, 1280.5, 1046.2, 846.6, 752.1 cm^{-1}.

3.3.3. Procedure for desilylation reactions of 2i and 2j (Scheme 1c)

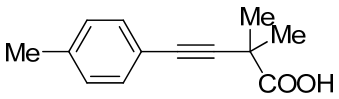
To a solution of carboxylic acid **2i** (570 mg, 3.1 mmol) in methanol (30 mL), K_2CO_3 (2.1 g, 15 mmol) was added in one portion, and the resulting mixture was stirred overnight at room temperature. After the reaction, Et_2O (20 mL) and saturated $NaHCO_3$ aq. (20 mL) were added to the reaction mixture, and the organic layer was washed with saturated $NaHCO_3$ aq. three times. The combined aqueous phase was acidified again to pH = 1 using 1M HCl aq. and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to yield **2u** as pale yellow oil (340 mg, 3.0 mmol, 98%). All the resonances in NMR spectrums were in good agreement with the literature values.[6] Carboxylic acid **2v** was obtained similarly using **2j** as the substrate.



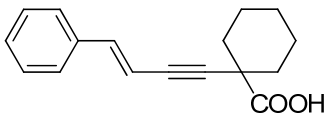
2v: The reaction was carried out on 8.0 mmol scale. Yellow solid (956 mg, 6.3 mmol, 79%) ^{1}H NMR (400 MHz, Acetone-D_6): δ 1.24-1.90 (m, 10H), 2.77 (d, J = 0.9 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-D_6): δ 23.0, 25.9, 35.3, 43.6, 73.3, 85.4, 174.0. APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{13}O_2$, 153.0910; found, 153.0909. IR (KBr): 3300-2800 (br), 1700.9, 1451.2, 1294.0, 1256.4, 1063.6, 930.5, 752.1, 651.8, 556.4, 498.5, 429.1 cm^{-1}.

3.3.4. Procedure for Sonogashira-Coupling reactions of 2u and 2v (Scheme 1d, e)

To a solution of 4-iodotoluene (110 mg, 0.50 mmol), $Pd(PPh_3)_4$ (57 mg, 0.025 mmol) and CuI (9.5 mg, 0.050 mmol) in piperidine/THF (1.5 mL, 2/1, v/v), was added **2u** (59 mg, 0.50 mmol). The resulting mixture was then stirred at 25 ºC for 20 h under Ar atmosphere. After addition of 1M HCl aq., the aqueous layer was washed with Et_2O (20 mL) three times and the combined organic layers were dried over anhydrous $MgSO_4$. After removal of volatile, the residue was purified by silica gel chromatography using hexane/EtOAc (5/1, v/v) as an eluent, and then, **2w** was obtained. Coupling product **2x** was also obtained under the similarly using **2v** and β-bromostyrene (*E*/*Z* = 93/7).



2w: Pale orange solid (76.2 mg, 75%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 6H), 2.33 (s, 3H), 7.09 (d, J = 7.7 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 27.1, 38.7, 82.4, 90.0, 119.8, 128.9, 131.6, 138.2, 179.8. ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{15}O_2$, 203.1067; found, 203.1065. IR (KBr): 3100-2900 (br), 1789.6, 1290.1, 1246.8, 1091.5, 1004.7, 925.7, 798.4 cm^{-1}.

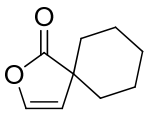


2x: Pale yellow solid (68.0 mg, 53%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23-1.31 (m, 1H), 1.63-1.86 (m, 7H), 2.01 (d, J = 12.2 Hz, 2H), 6.20 (d, J = 16.3 Hz, 1H), 6.95 (d, J = 16.3 Hz, 1H), 7.24-7.38 (m, 5H), 9.96 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 25.3, 34.7, 44.5, 83.8, 91.2, 107.9, 126.2, 128.5, 128.5, 136.2, 141.3, 179.6. APCI-HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{19}O_2$, 255.1380; found, 255.1375. IR (KBr): 3300-2800 (br), 1703.8, 1448.3, 1280.5, 1256.4, 955.6, 751.1, 693.3, 521.7 cm^{-1}.

3.3.5. Procedure for intramolecular cyclization reaction of 2v (Scheme 1f)

In a 20 mL Schrenk flask, AuCl (5.8 mg, 5.0 mol %) and PPh_3 (6.6 mg, 5.0 mol %)

were dissolved in CH_2Cl_2 (5.0 mL) and stirred for 5 min under Ar atmosphere. The solution was further stirred for additional 10 min after adding AgOTf (6.4 mg, 5.0 mol %). Then, carboxylic acid **2v** (76.1 mg, 0.50 mmol) was added and the resulting mixture was stirred at room temperature for 8 h. After removal of volatile, the residue was purified by silica gel chromatography using hexane/EtOAc (50/1, v/v) as an eluent to afford **2y**.

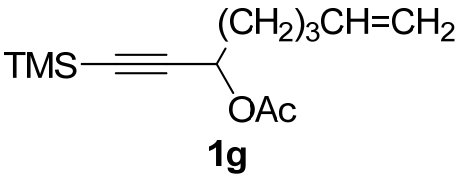


2y: Colorless oil (46.4 mg, 61%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35-1.86 (m, 10H), 5.84 (d, J = 3.6 Hz, 1H), 6.81 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 22.2, 33.4, 47.4, 114.5, 141.2, 181.6. APCI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{13}O_2$, 153.0910; found, 153.0908. IR (neat): 3116.4, 2934.2, 2858.0, 1791.6, 1616.1, 1452.1, 1348.0, 1285.3, 1265.1, 1183.1, 1162.9, 1119.5, 1079.9, 1051.0, 994.1, 918.0, 849.5, 724.1, 569.9 cm^{-1}.

3.4. Experimental procedure for carboxylation of (*S*)-1a (eqn (1))

A 20 mL Schlenk flask was dried with a heating-gun under vacuum. The flask was charged with CoI_2(phen) (12.3 mg, 0.025 mmol) and Mn powder (82.4 mg, 1.5 mmol). The flask was evacuated and refilled with CO_2 five times. Then, DMA (0.50 mL) and (*S*)-**1a** (101 μL, 0.50 mmol) were added via air-tight syringes, and the resulting mixture was stirred at room tempearture for 20 h. After reaction, 1M HCl aq. (3 mL) and Et_2O (5 mL) was added, and stirred at room temperature for 10 min. The mixture was extracted with Et_2O (5 mL × 5). The collected organic layer was combined and dried over anhydrous $MgSO_4$. After removal of volatile, the residue was purified by silica gel chromatography using hexane/EtOAc (4/1, v/v) as an eluent to afford **2a**. Yellow oil (60.9 mg, 72%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.47 (d, J = 7.2 Hz, 3H), 3.49 (q, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.1, 18.0, 33.2, 87.8, 102.4, 177.5. $[\alpha]^{24}_D$ +0.6 (c 0.932, $CHCl_3$). This compound was identified as racemic mixture by GC analysis with a capillary column (CP-Chirasil Dex CB, 0.25 mm i.d. × 25 m) after the derivatization of the corresponding methyl ester.

4. NMR Charts



1g

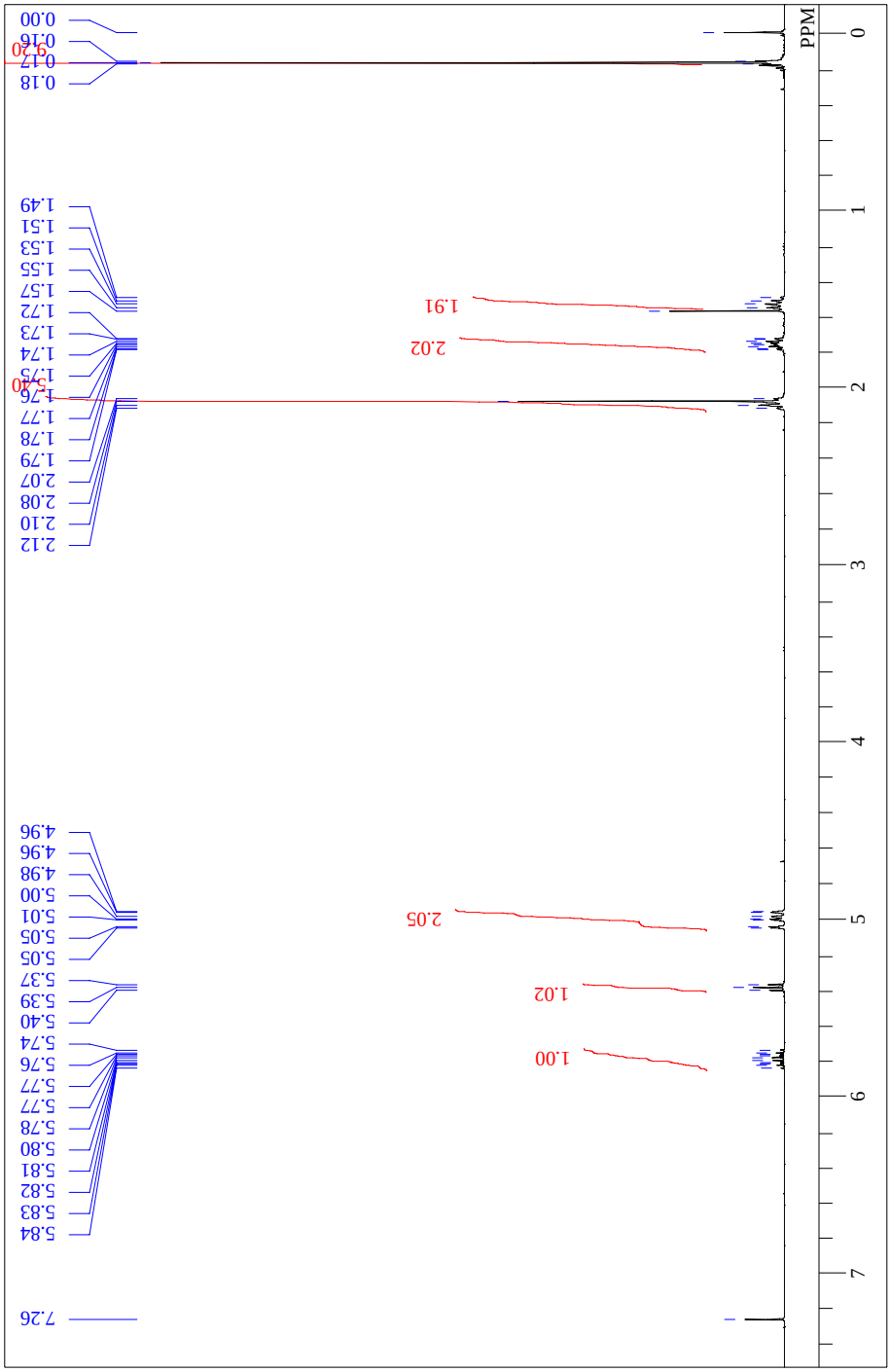
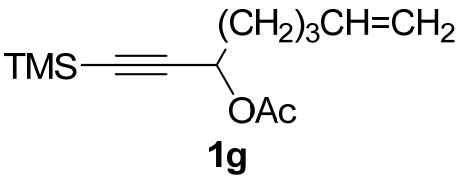


Fig. S1 ^{1}H NMR spectrum of **1g** in $CDCl_3$.



1g

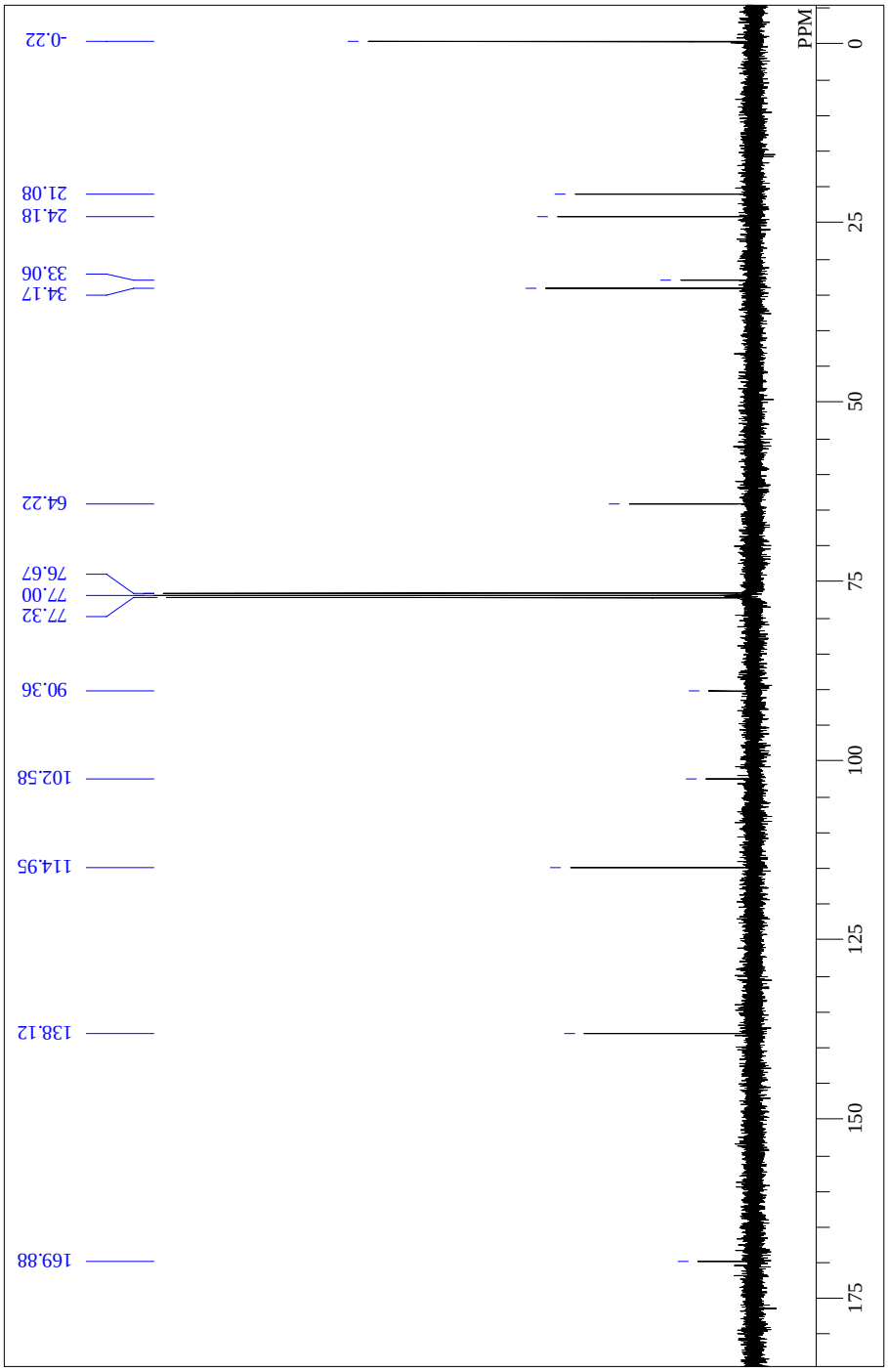
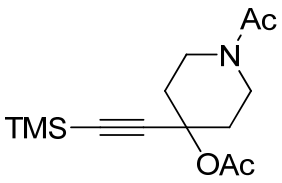


Fig. S2 ^{13}C NMR spectrum of **1g** in $CDCl_3$.



1l

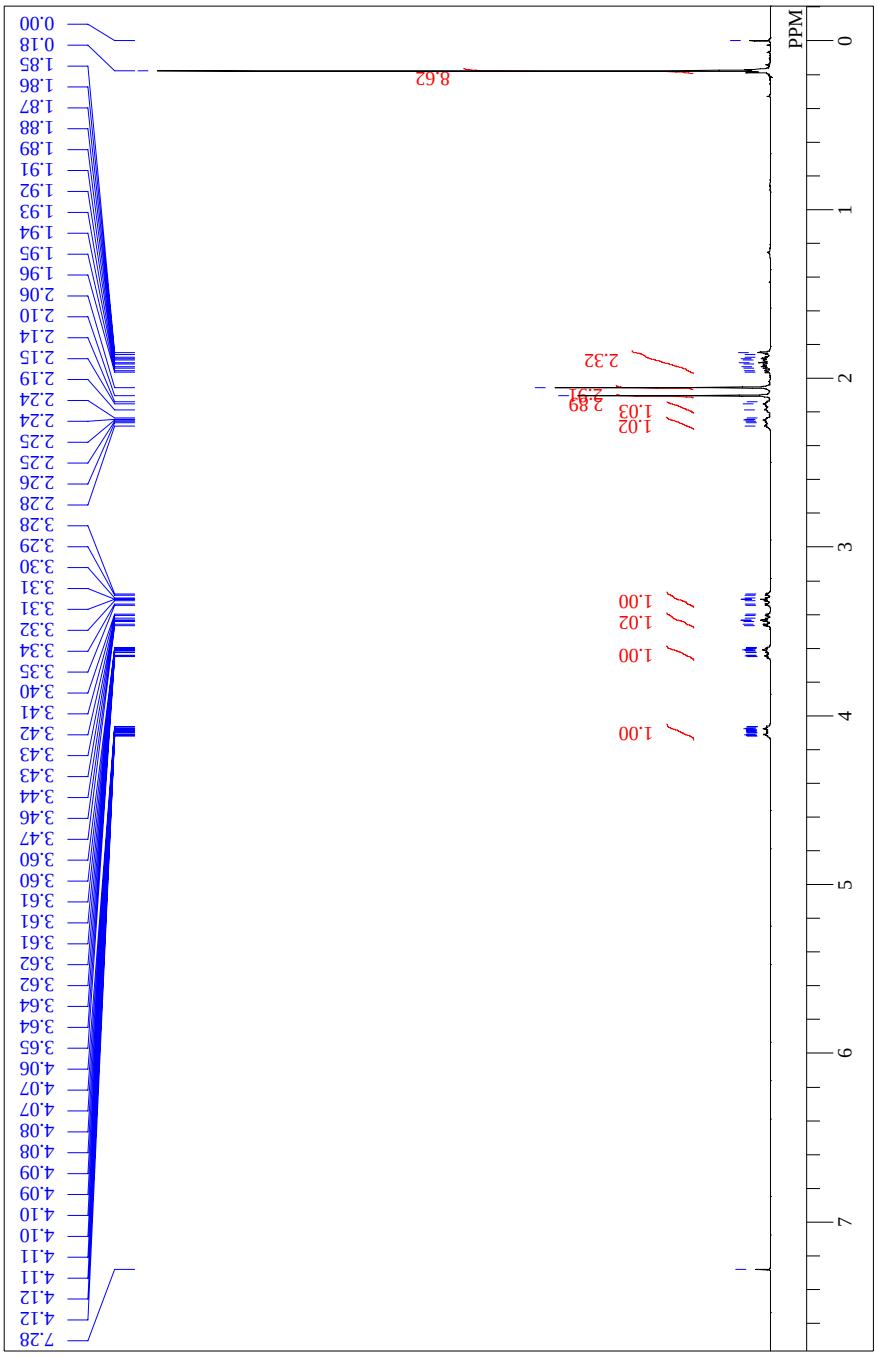


Fig. S3 ^{1}H NMR spectrum of **1l** in $CDCl_3$.

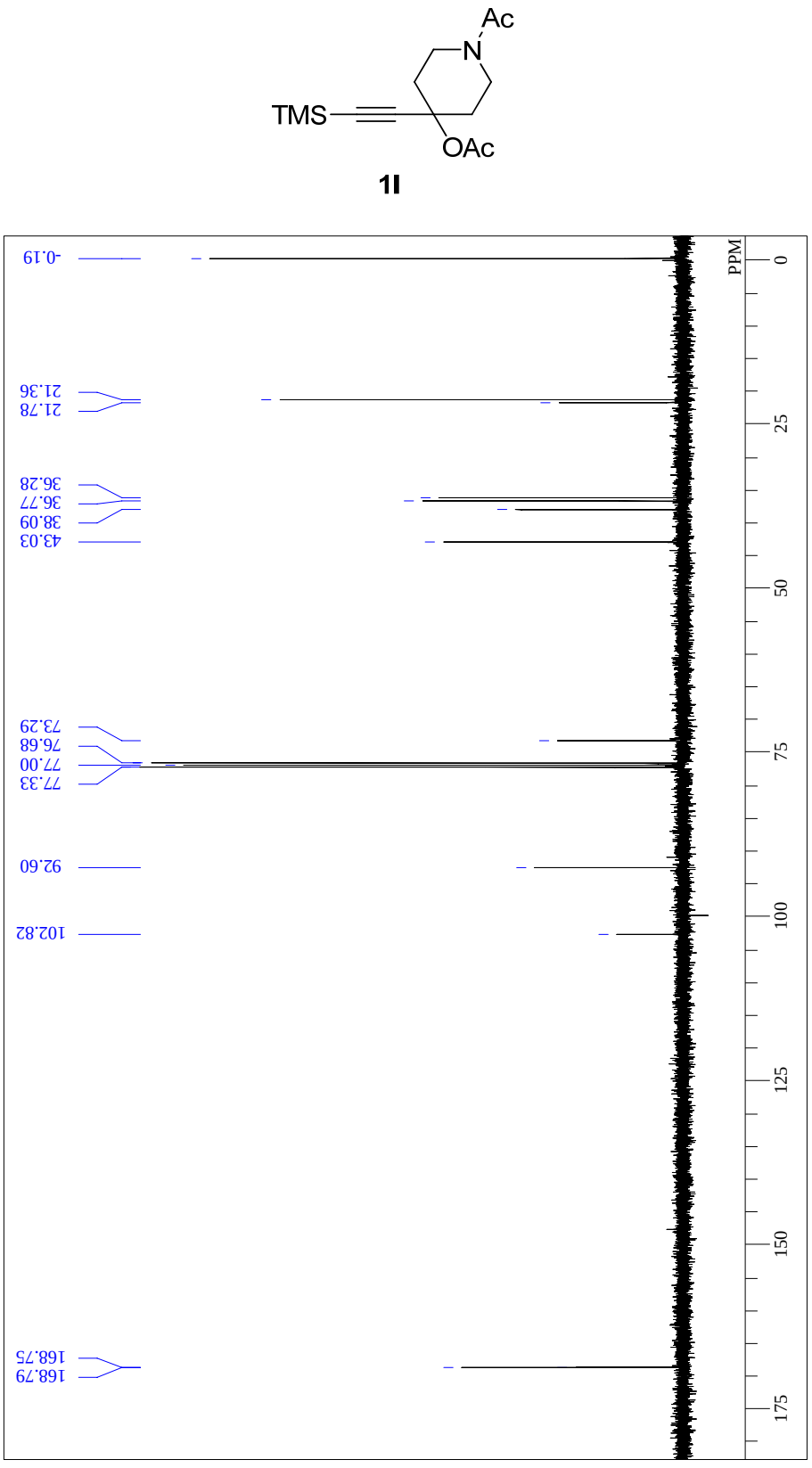


Fig. S4 ^{13}C NMR spectrum of **1l** in $CDCl_3$.

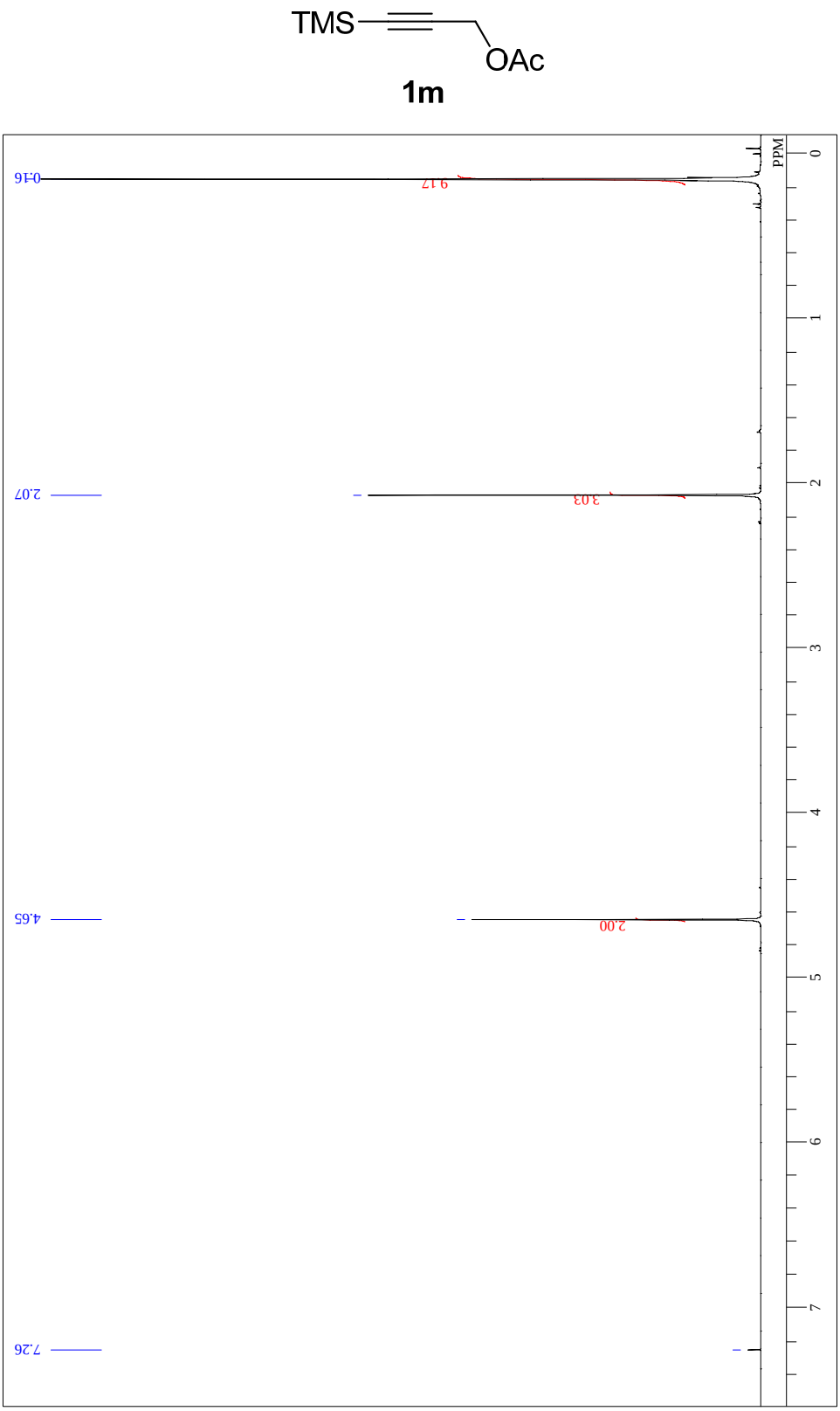


Fig. S5 ^{1}H NMR spectrum of **1m** in $CDCl_3$.

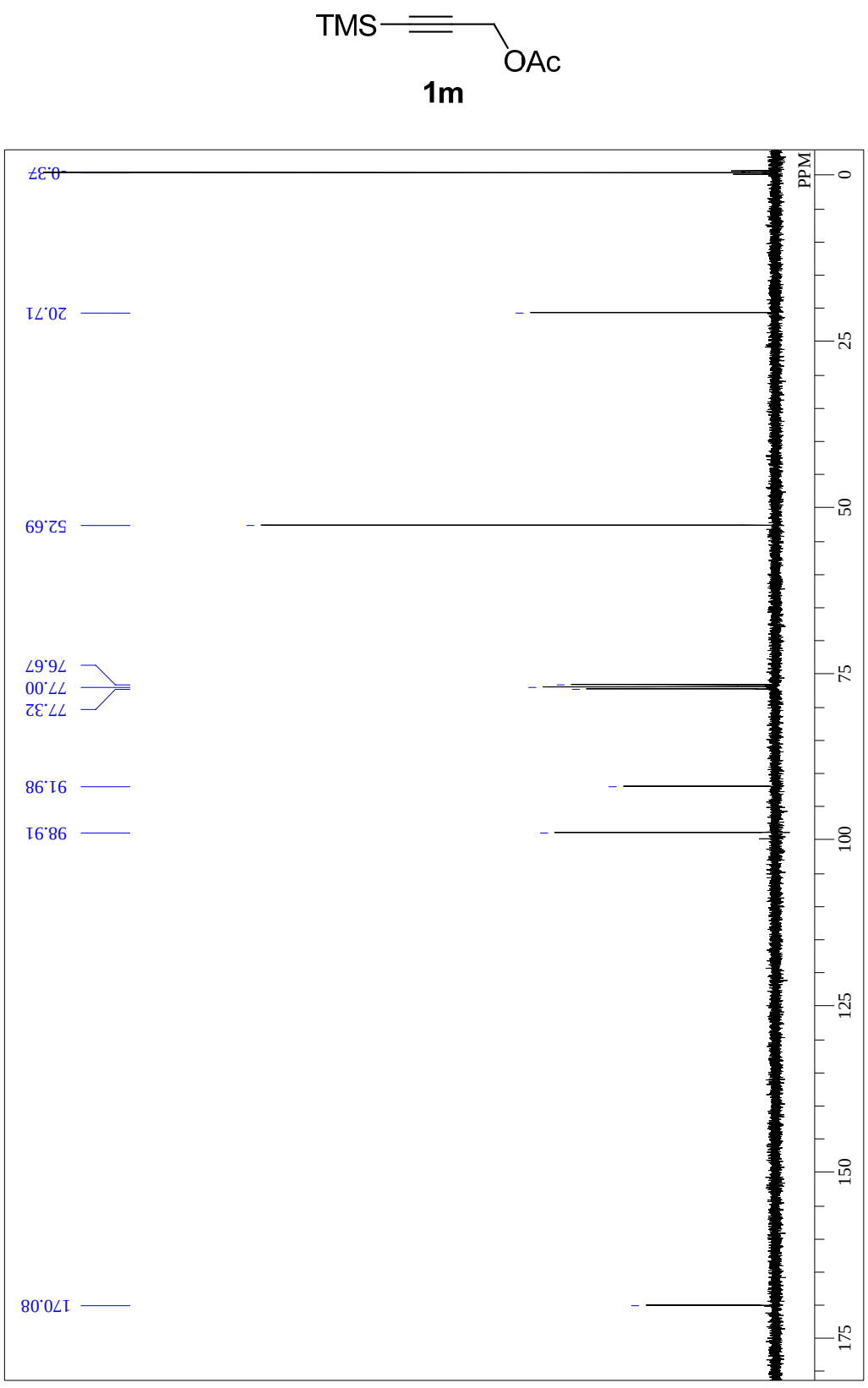
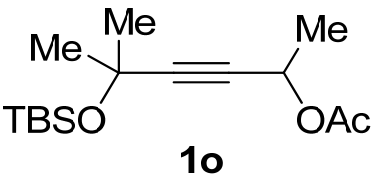


Fig. S6 ^{13}C NMR spectrum of **1m** in $CDCl_3$.



1o

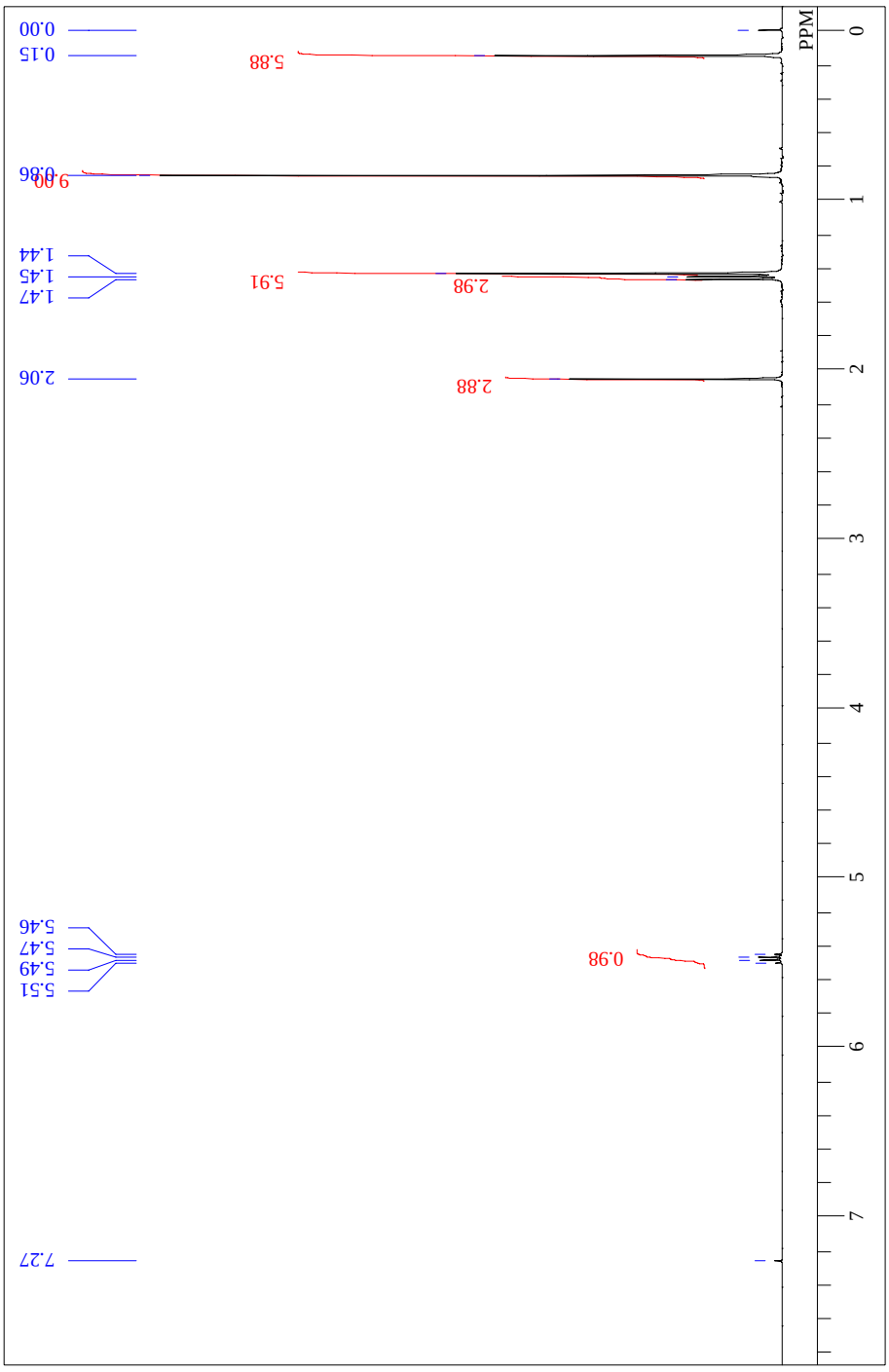
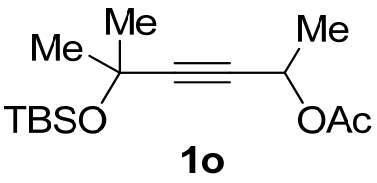


Fig. S7 ^{1}H NMR spectrum of **1o** in $CDCl_3$.



1o

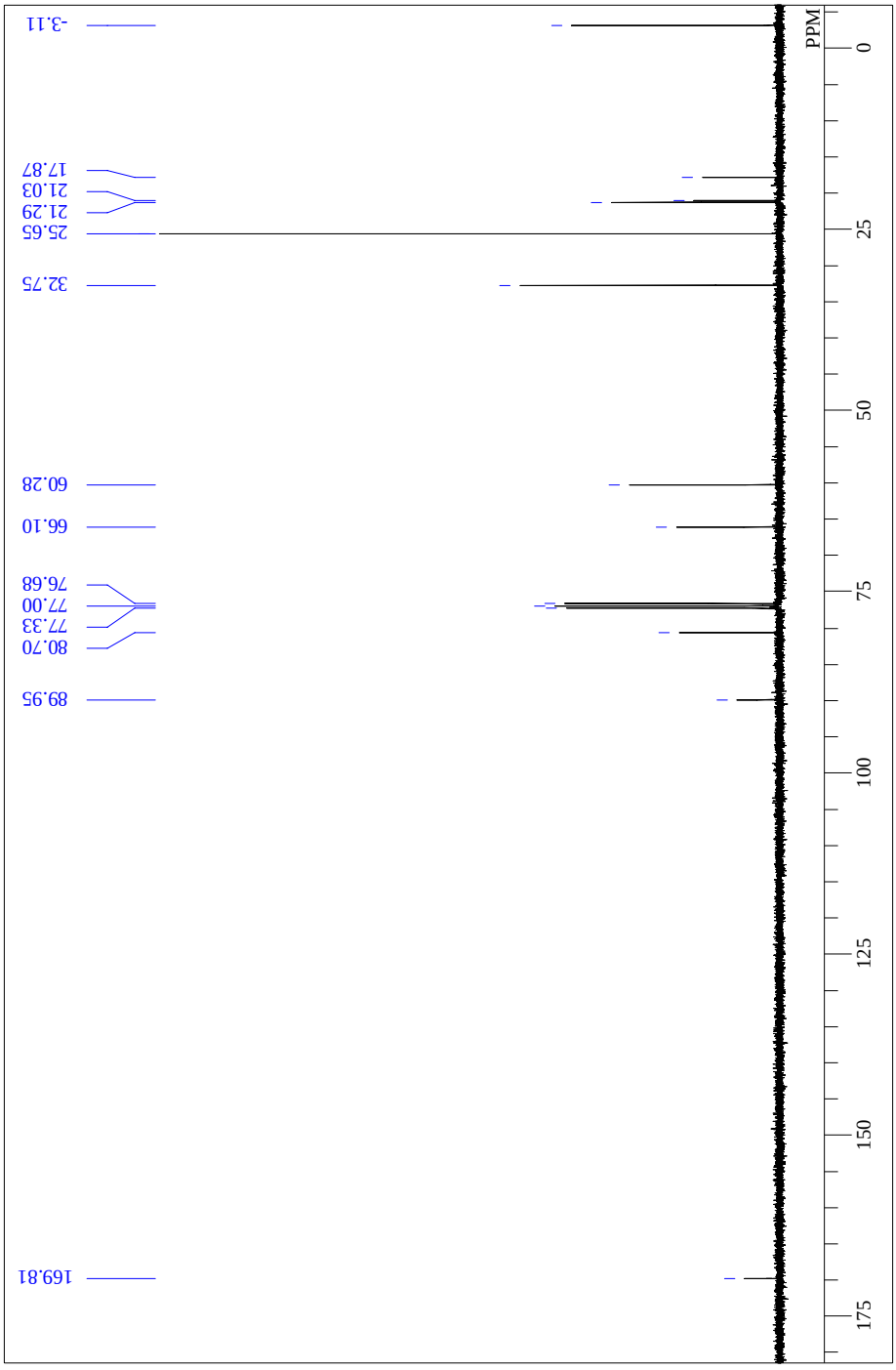
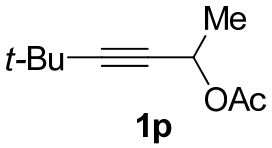


Fig. S8 ^{13}C NMR spectrum of **1o** in $CDCl_3$.



1p

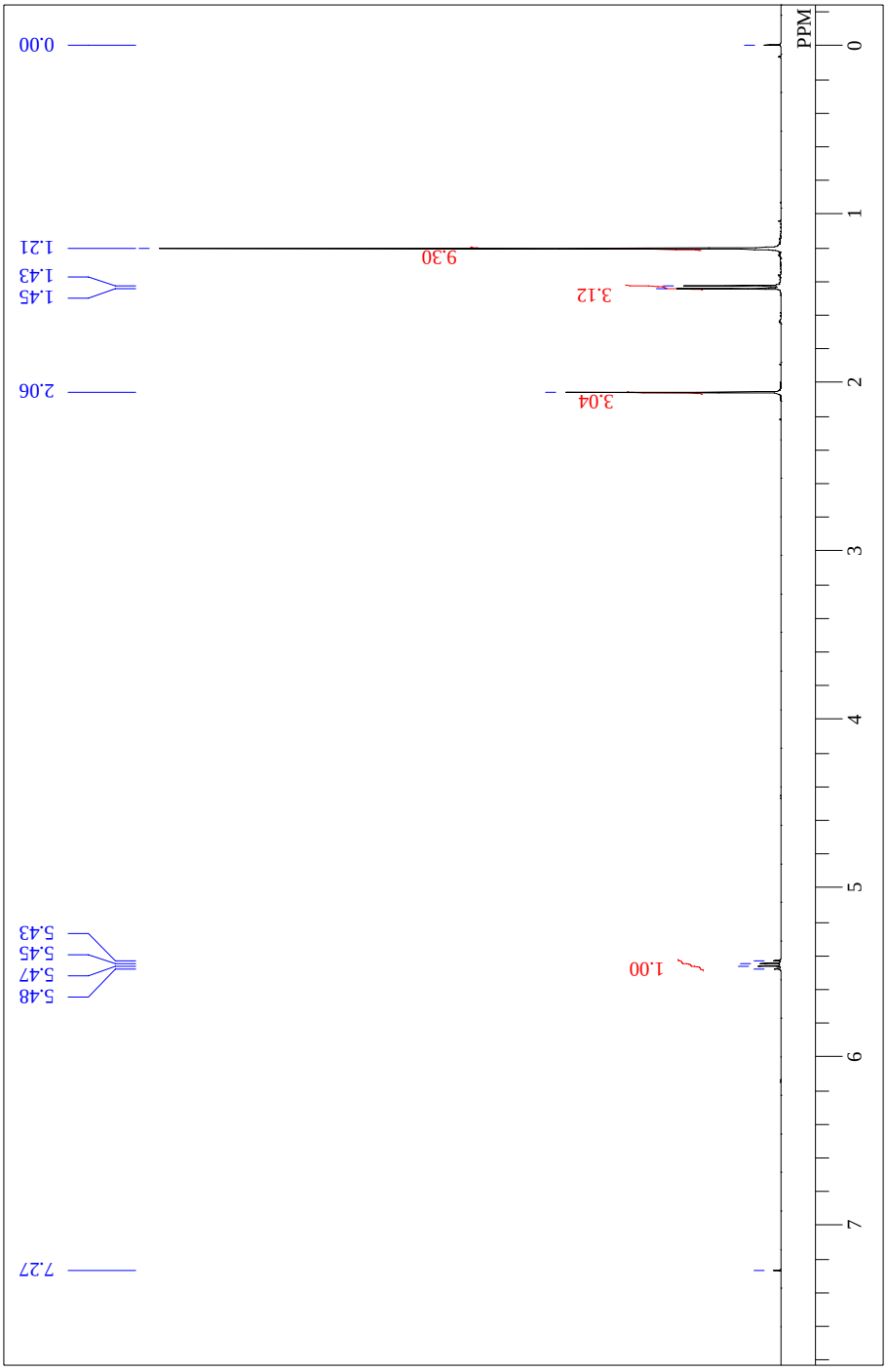


Fig. S9 ^{1}H NMR spectrum of **1p** in $CDCl_3$.

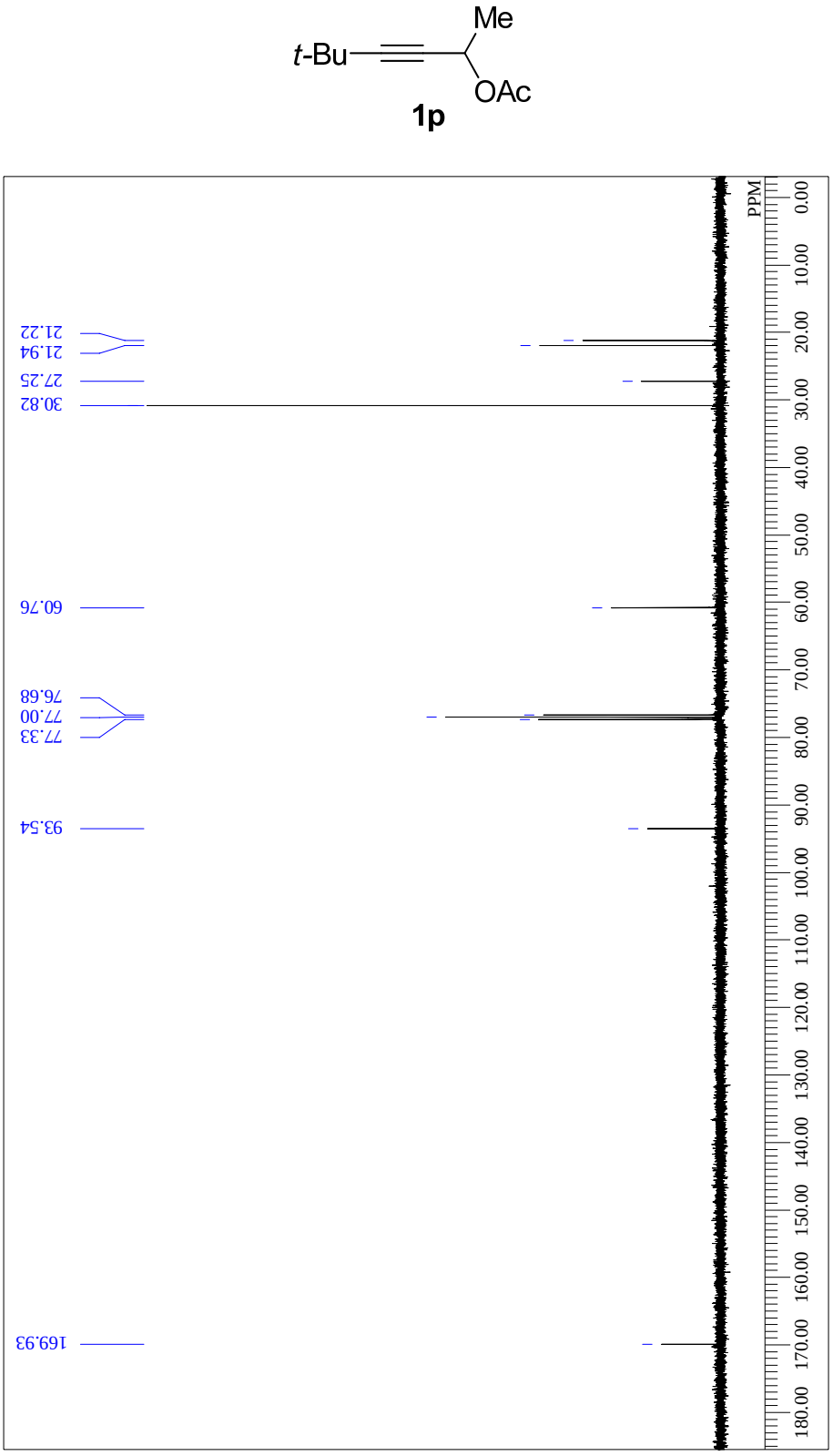
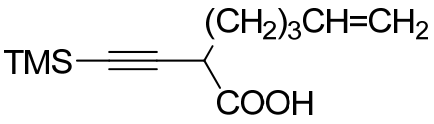


Fig. S10 ^{13}C NMR spectrum of **1p** in $CDCl_3$.



2g

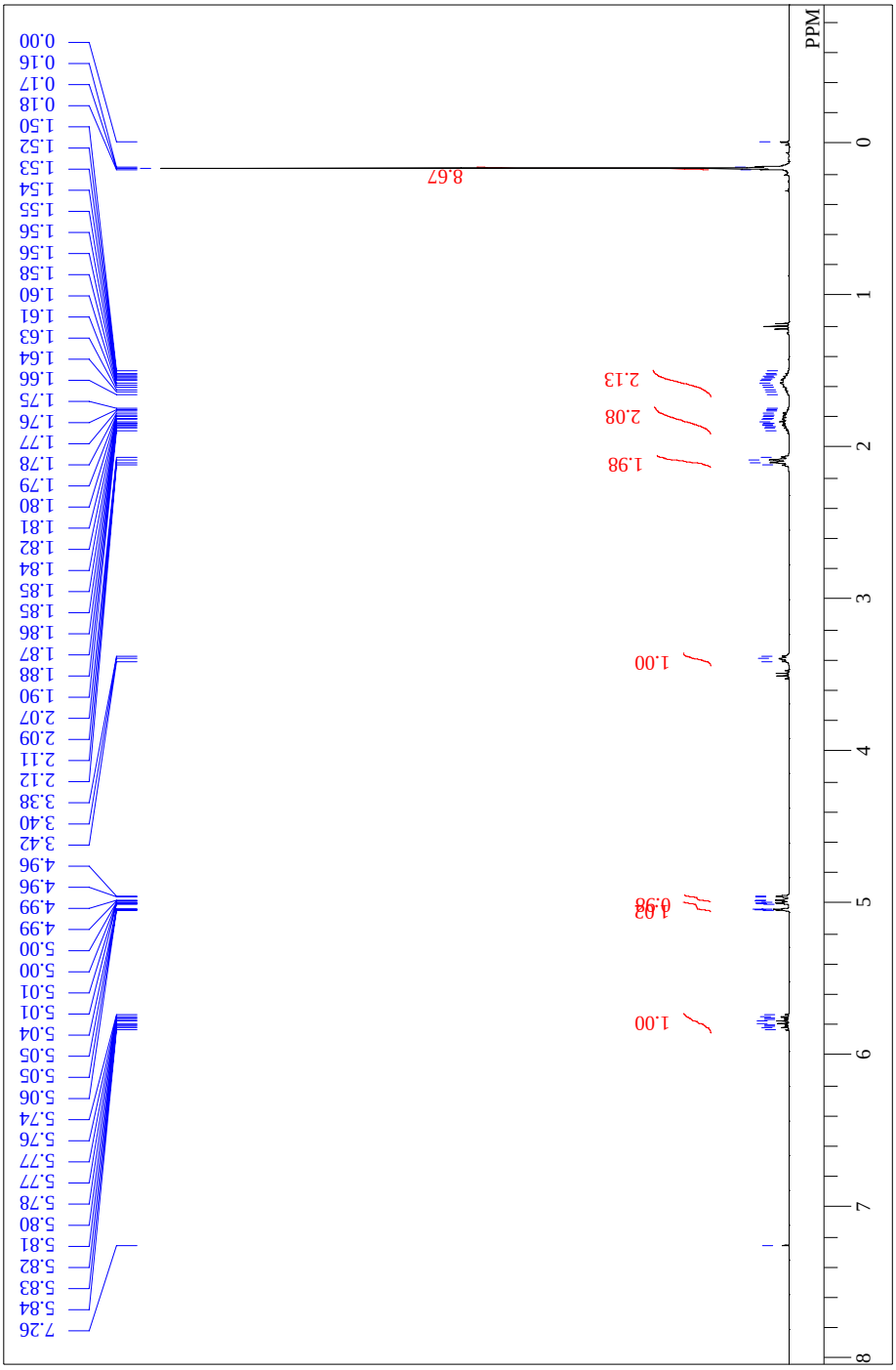
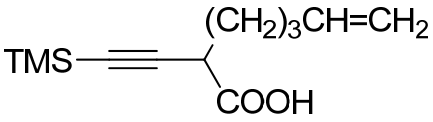


Fig. S11 ^{1}H NMR spectrum of **2g** in $CDCl_3$.



2g

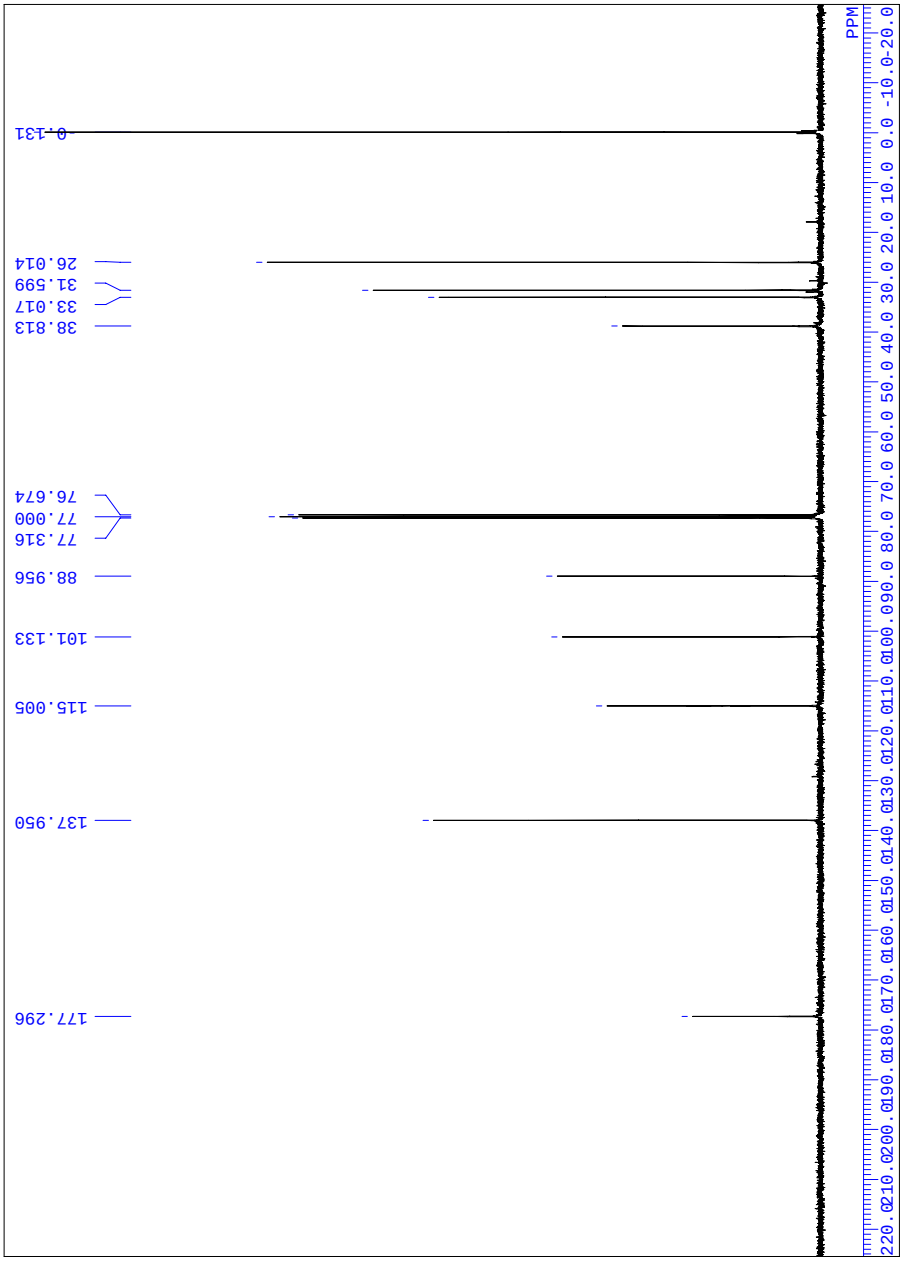
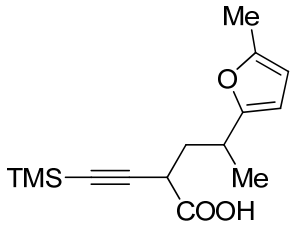


Fig. S12 ^{13}C NMR spectrum of **2g** in $CDCl_3$.



2h

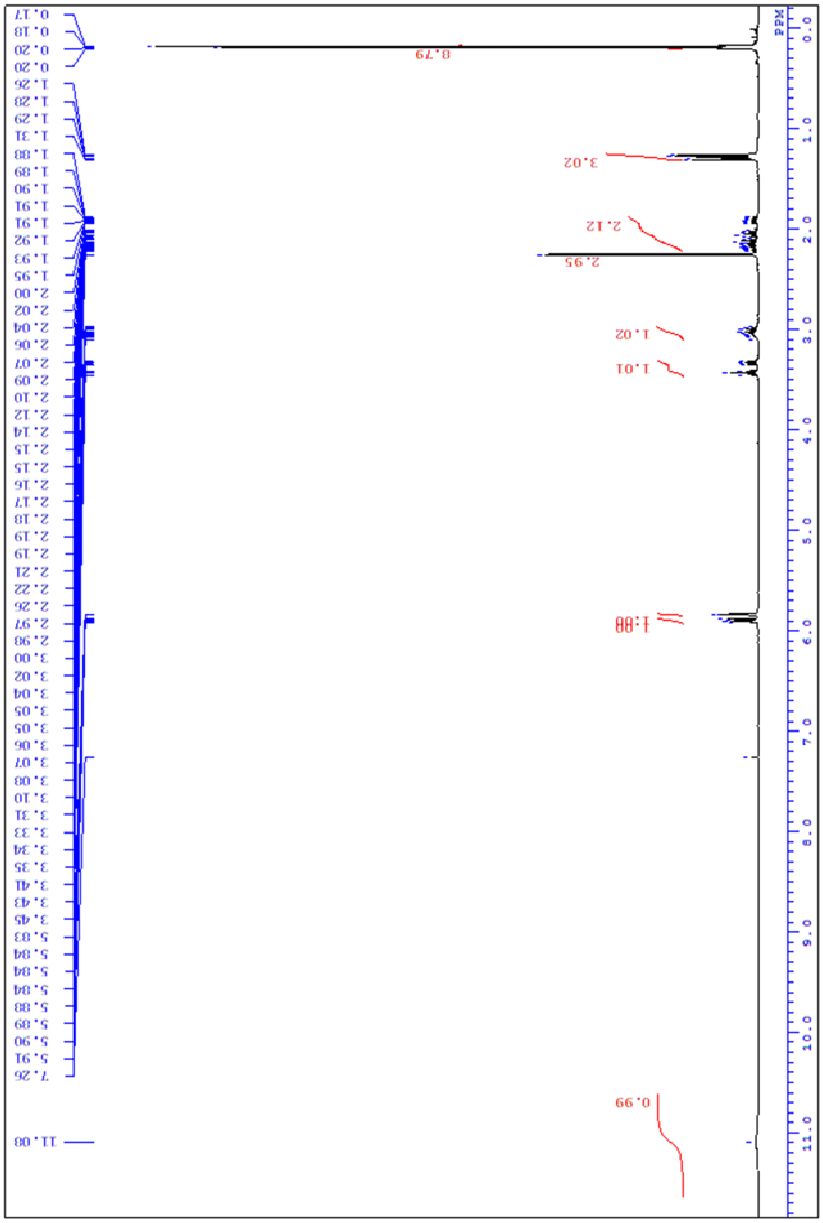
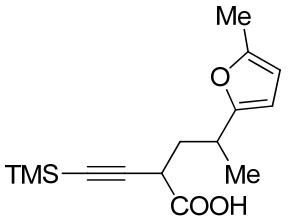


Fig. S13 ^{1}H NMR spectrum of **2h** in $CDCl_3$.



2h

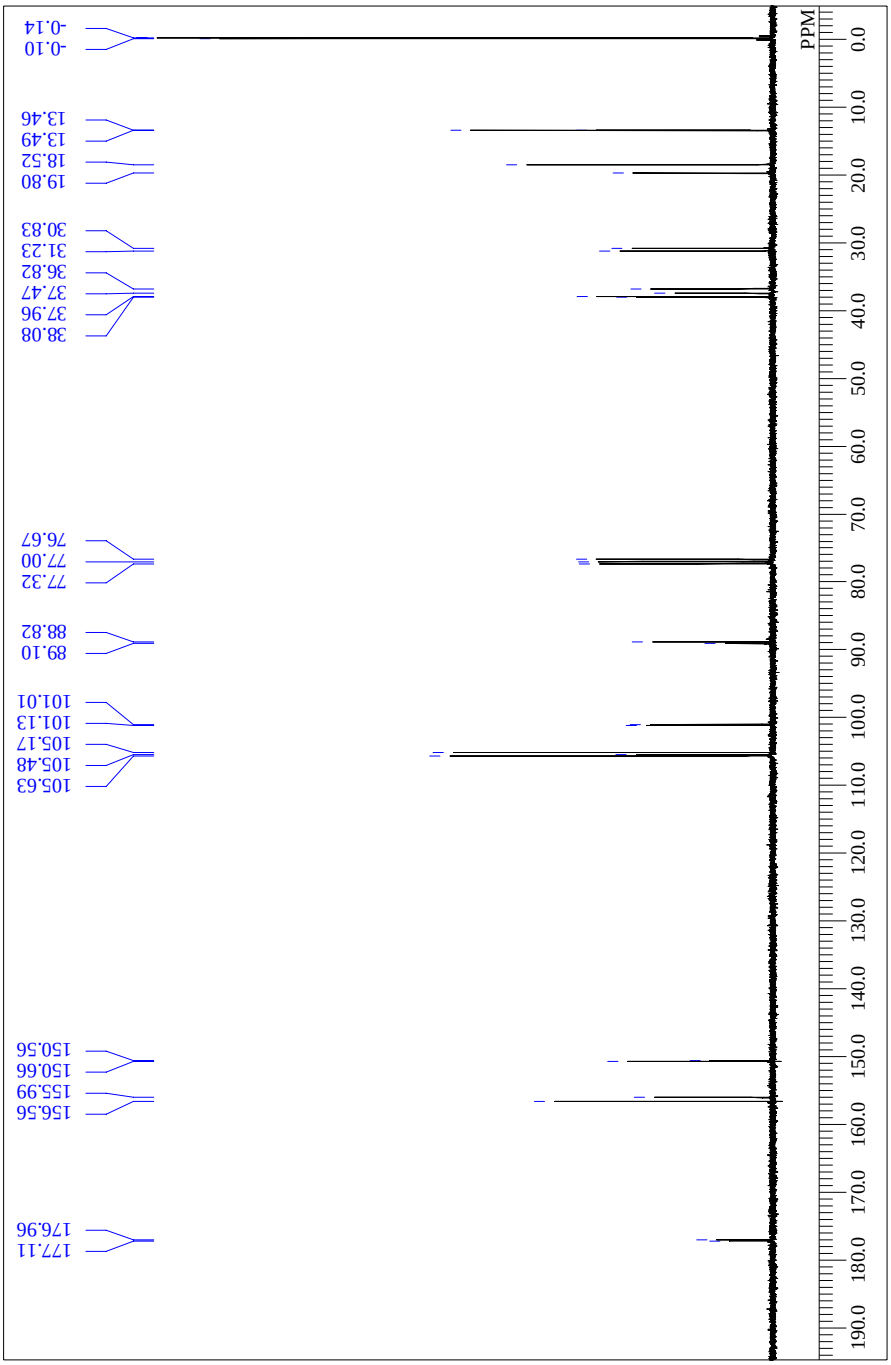


Fig. S14 ^{13}C NMR spectrum of **2h** in $CDCl_3$.

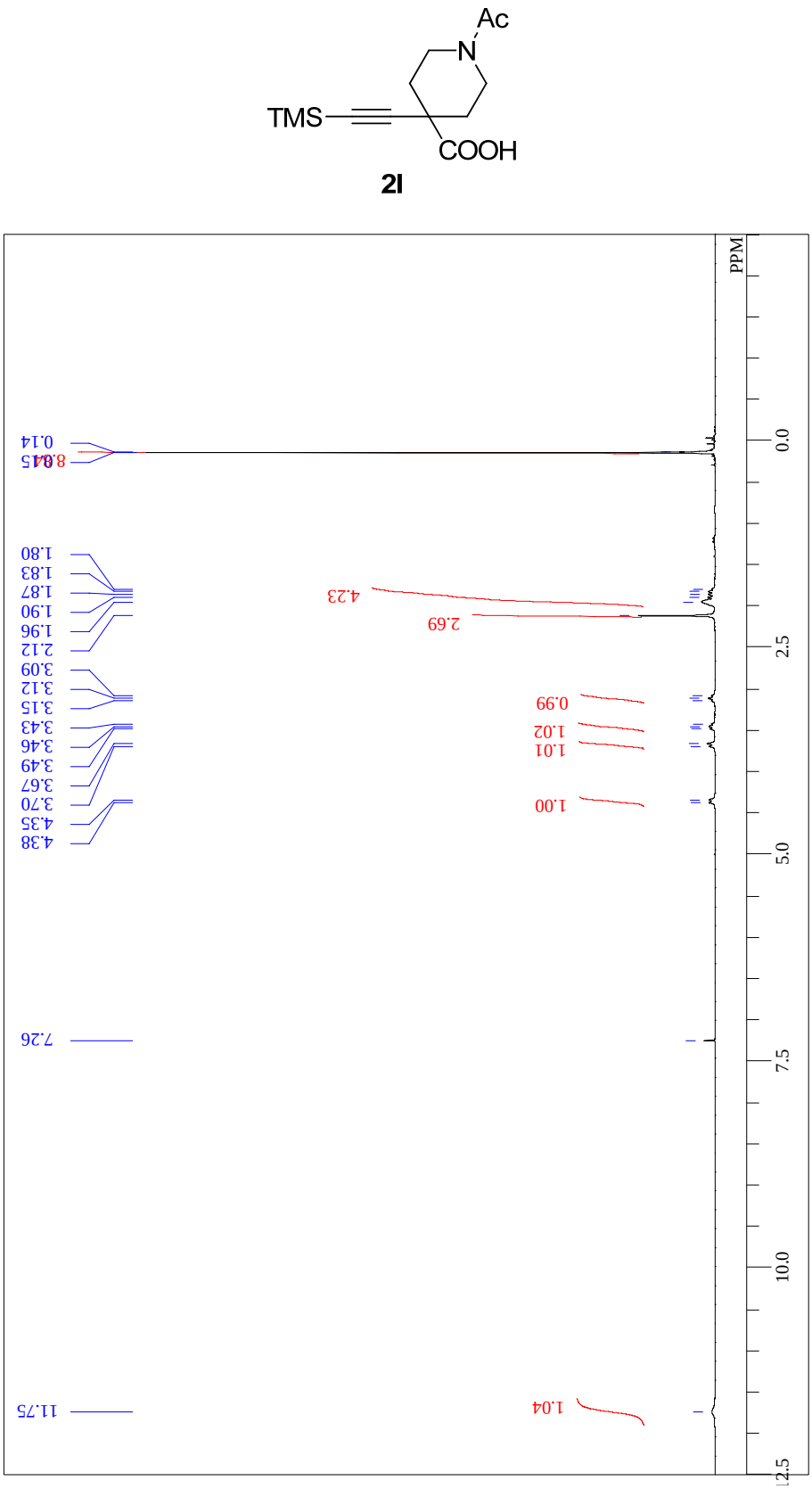


Fig. S15 ^{1}H NMR spectrum of **2l** in $CDCl_3$.

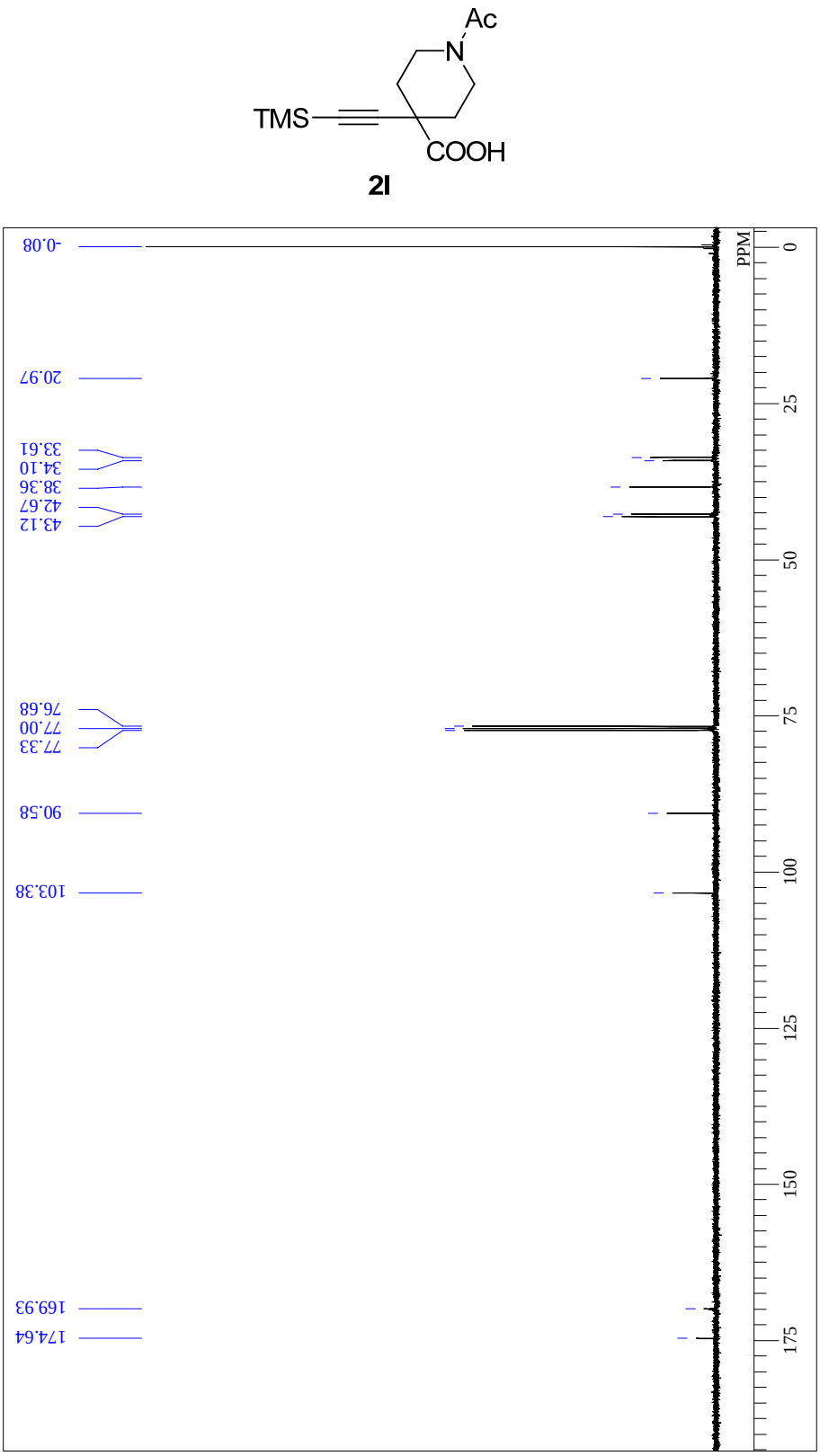
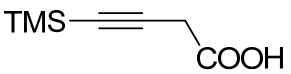


Fig. S16 ^{13}C NMR spectrum of **2l** in $CDCl_3$.



2m

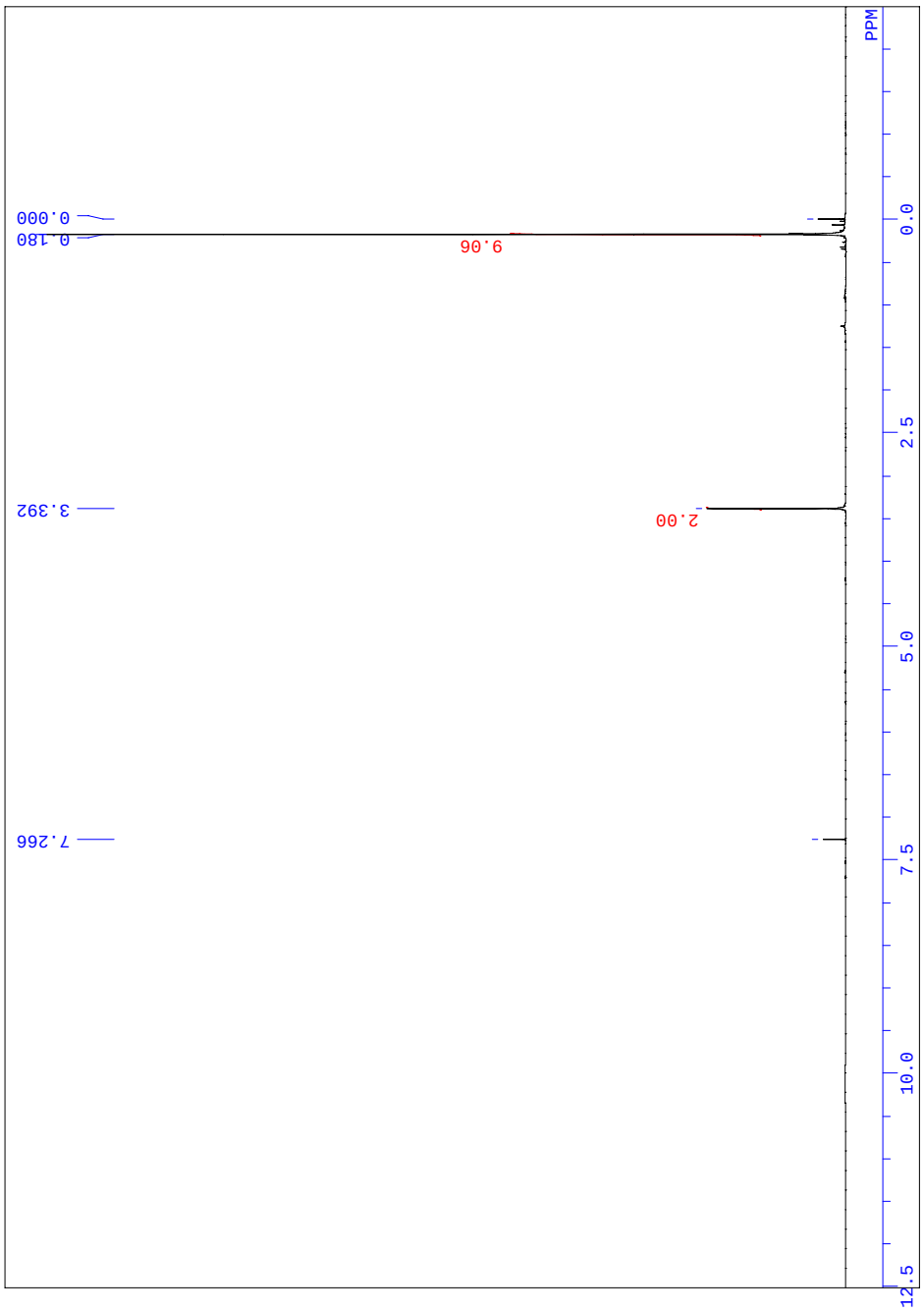
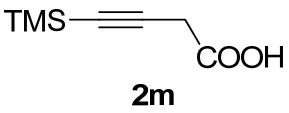


Fig. S17 ^{1}H NMR spectrum of **2m** in $CDCl_3$.



2m

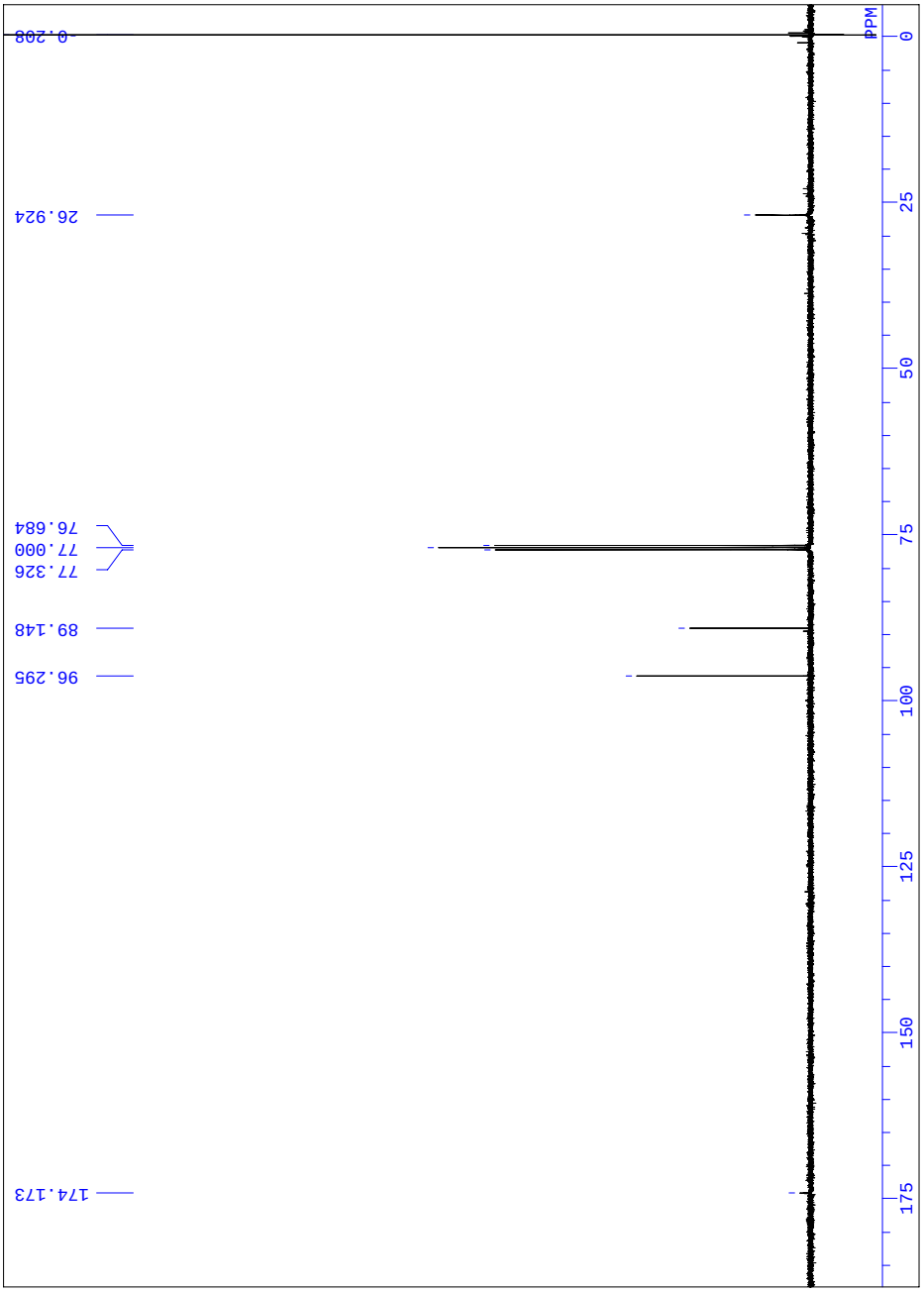
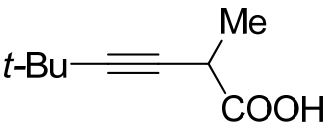


Fig. S18 ^{13}C NMR spectrum of **2m** in $CDCl_3$.



2p

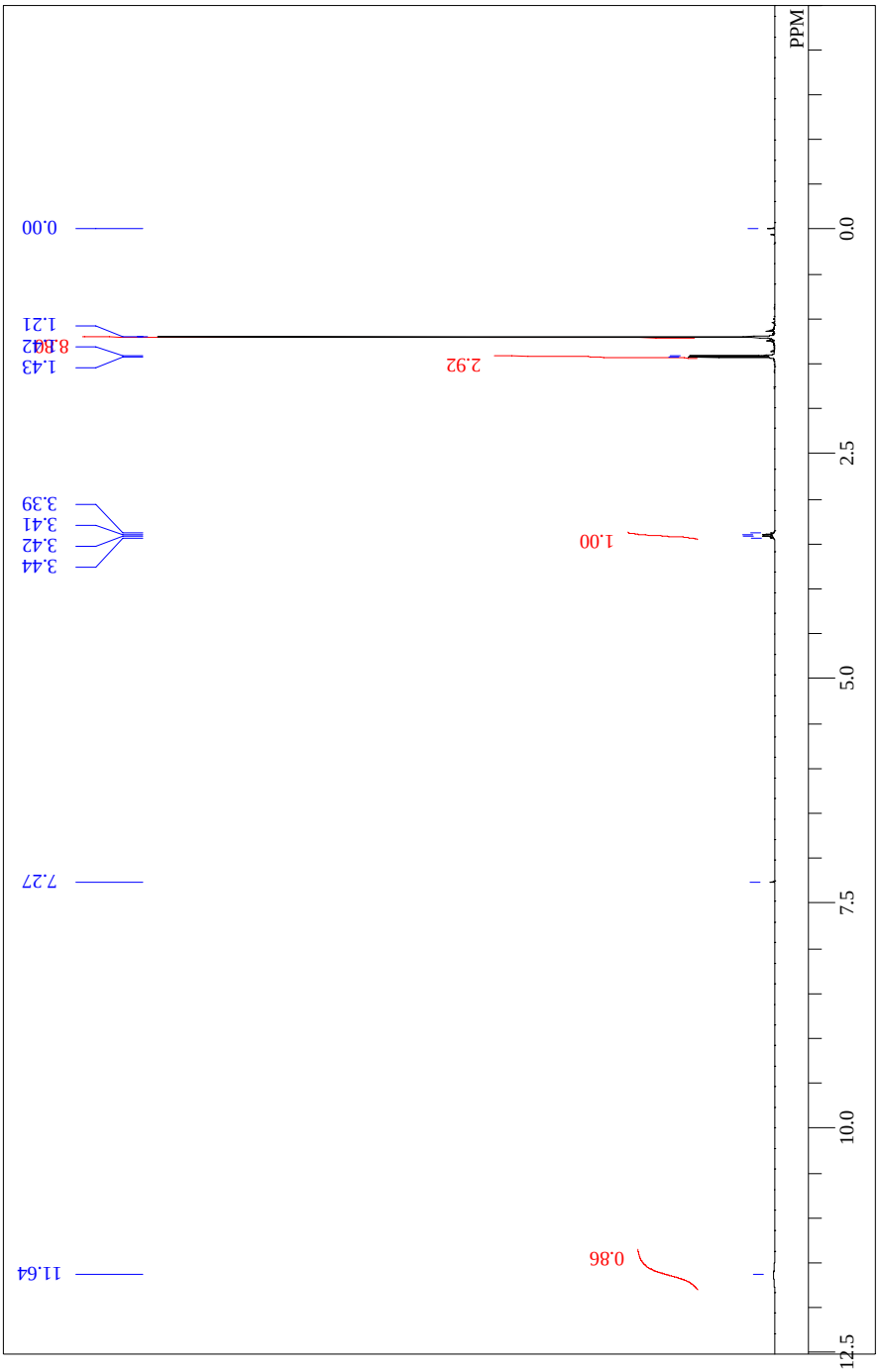
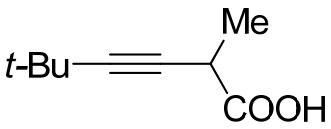


Fig. S19 ^{1}H NMR spectrum of **2p** in $CDCl_3$.



2p

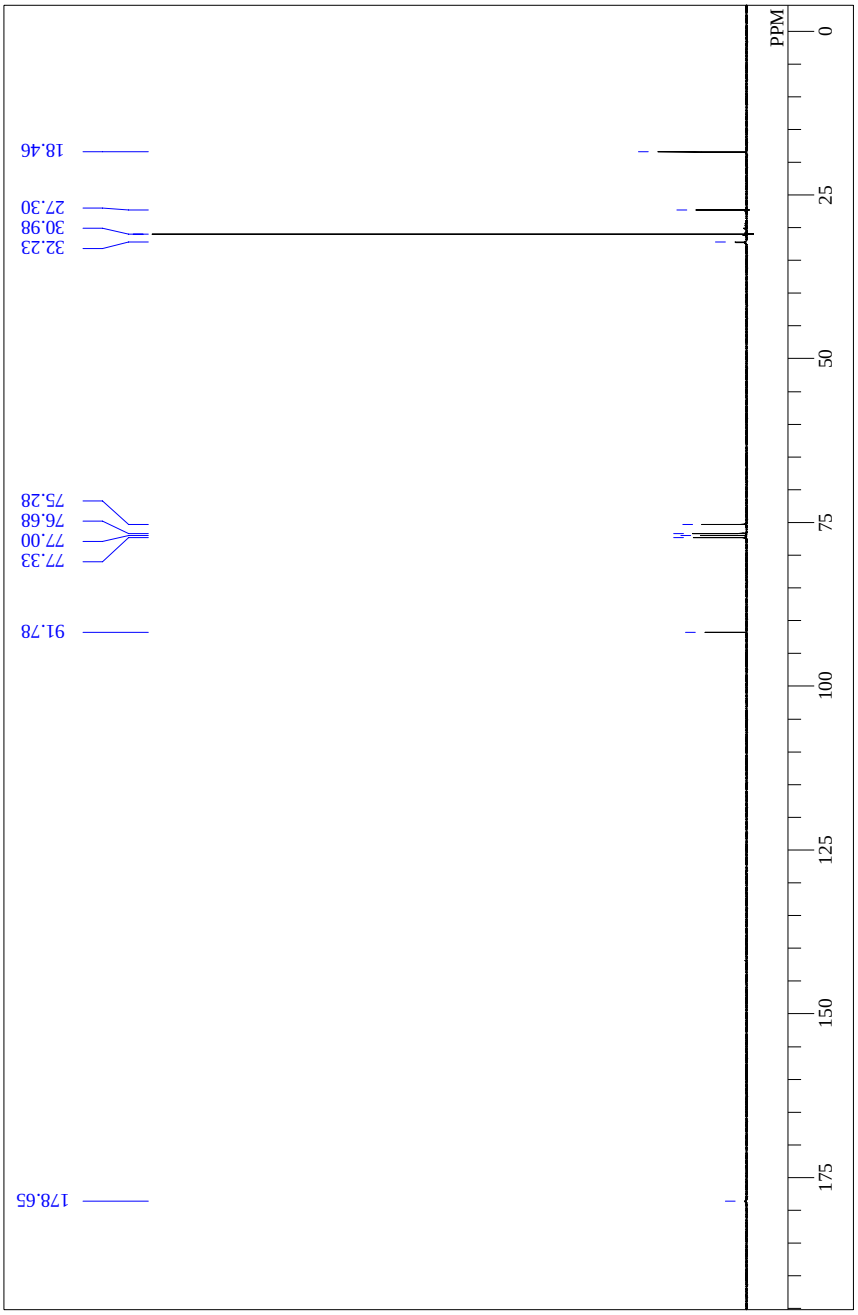
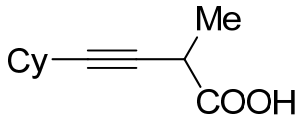


Fig. S20 ^{13}C NMR spectrum of **2p** in $CDCl_3$.



2q

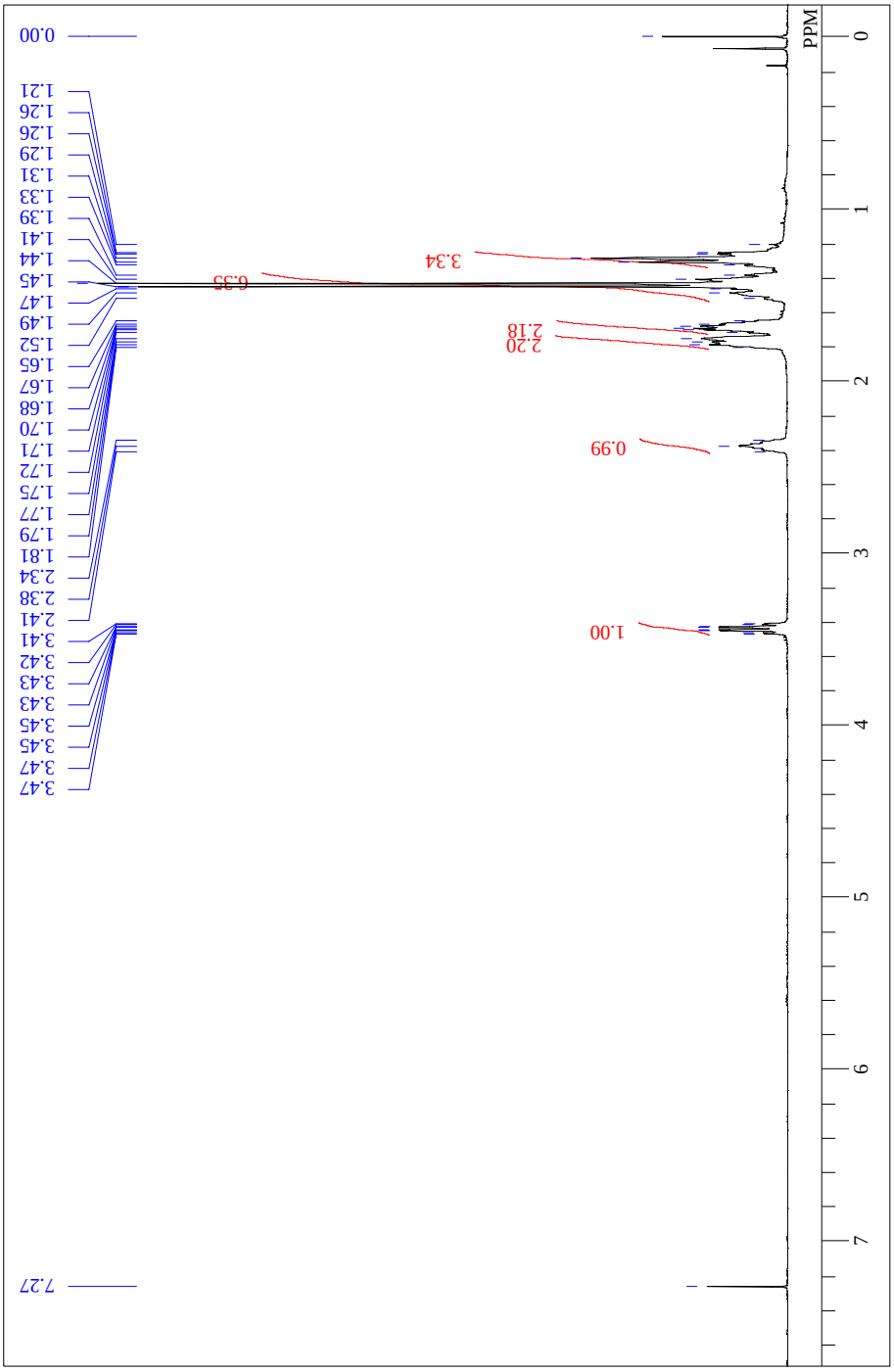


Fig. S21 ^{1}H NMR spectrum of **2q** in $CDCl_3$.

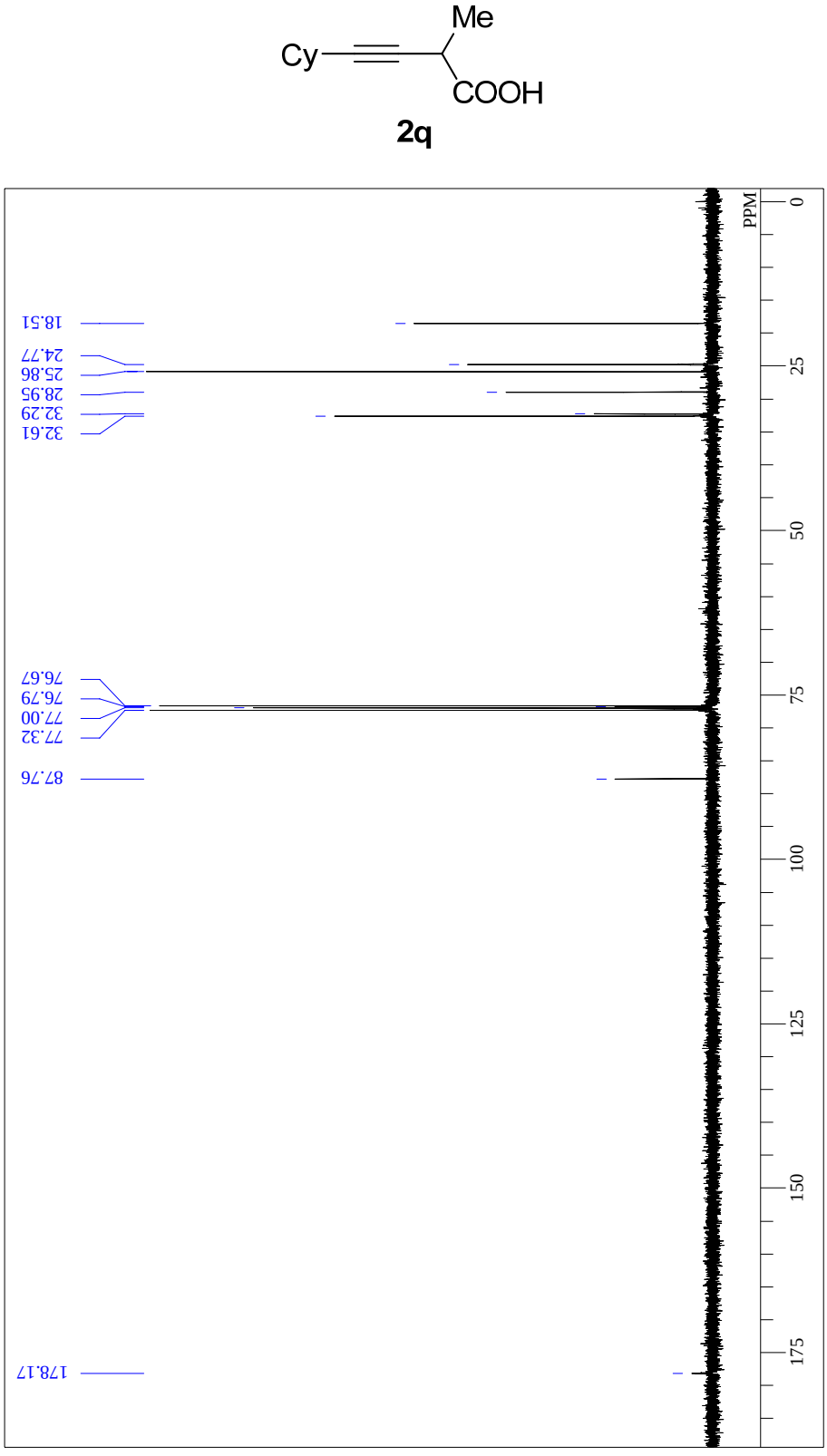
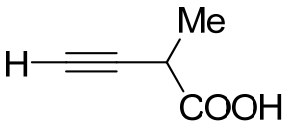


Fig. S22 ^{13}C NMR spectrum of **2q** in $CDCl_3$.



2r

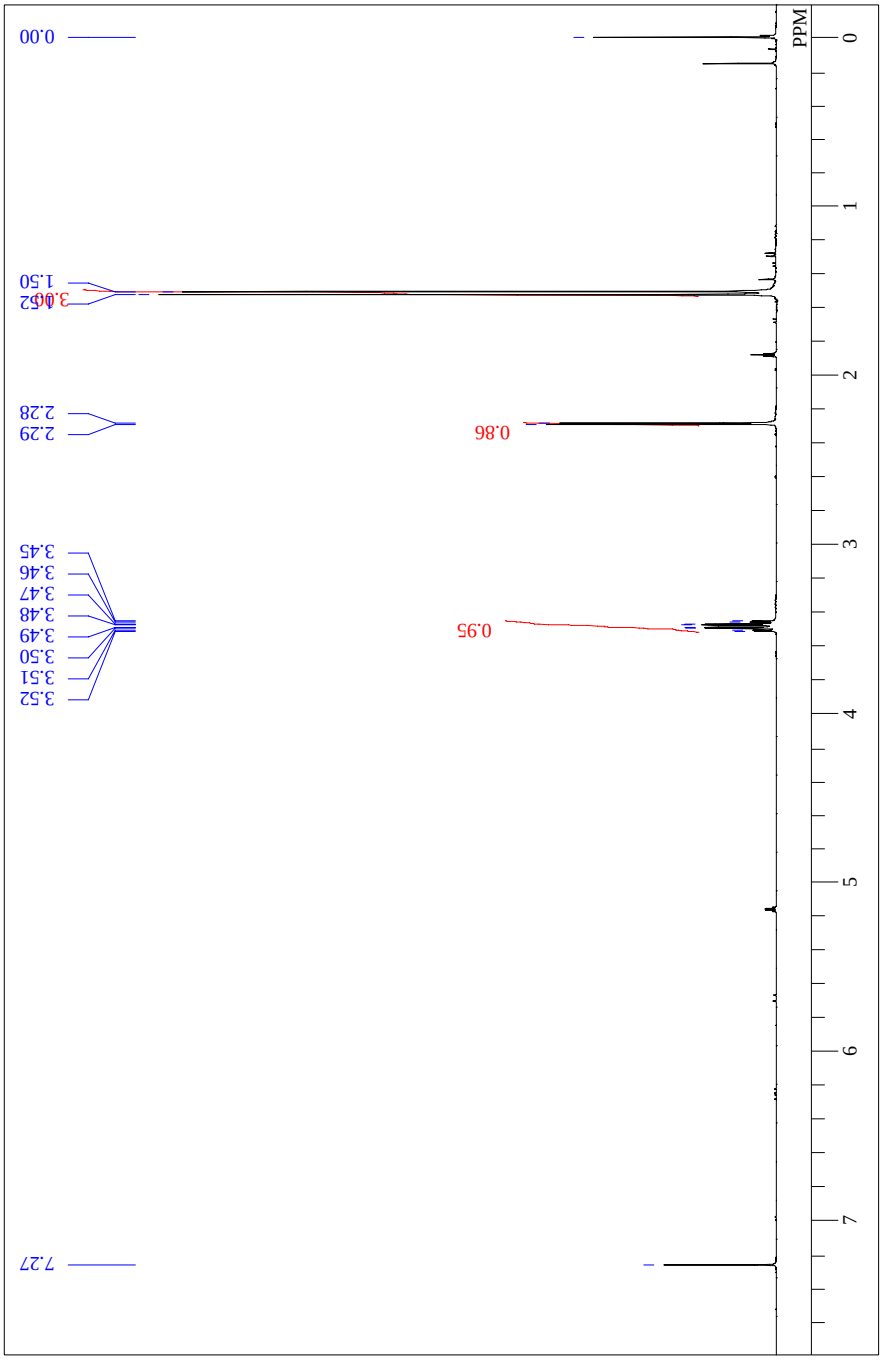
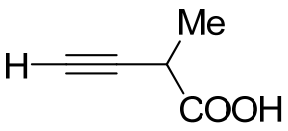


Fig. S23 ^{1}H NMR spectrum of **2r** in $CDCl_3$.



2r

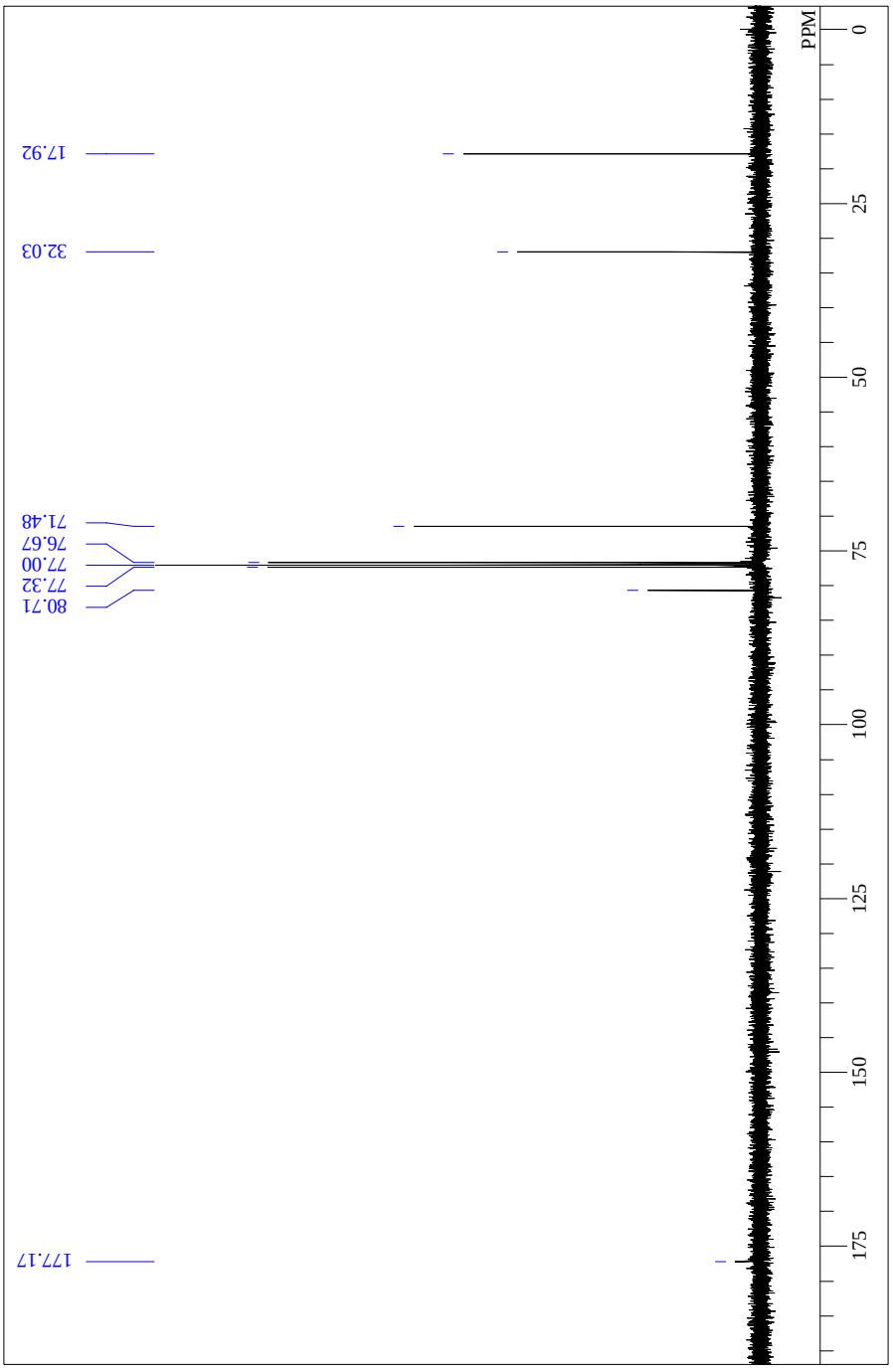
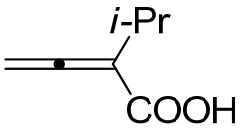


Fig. S24 ^{13}C NMR spectrum of **2r** in $CDCl_3$.



2t

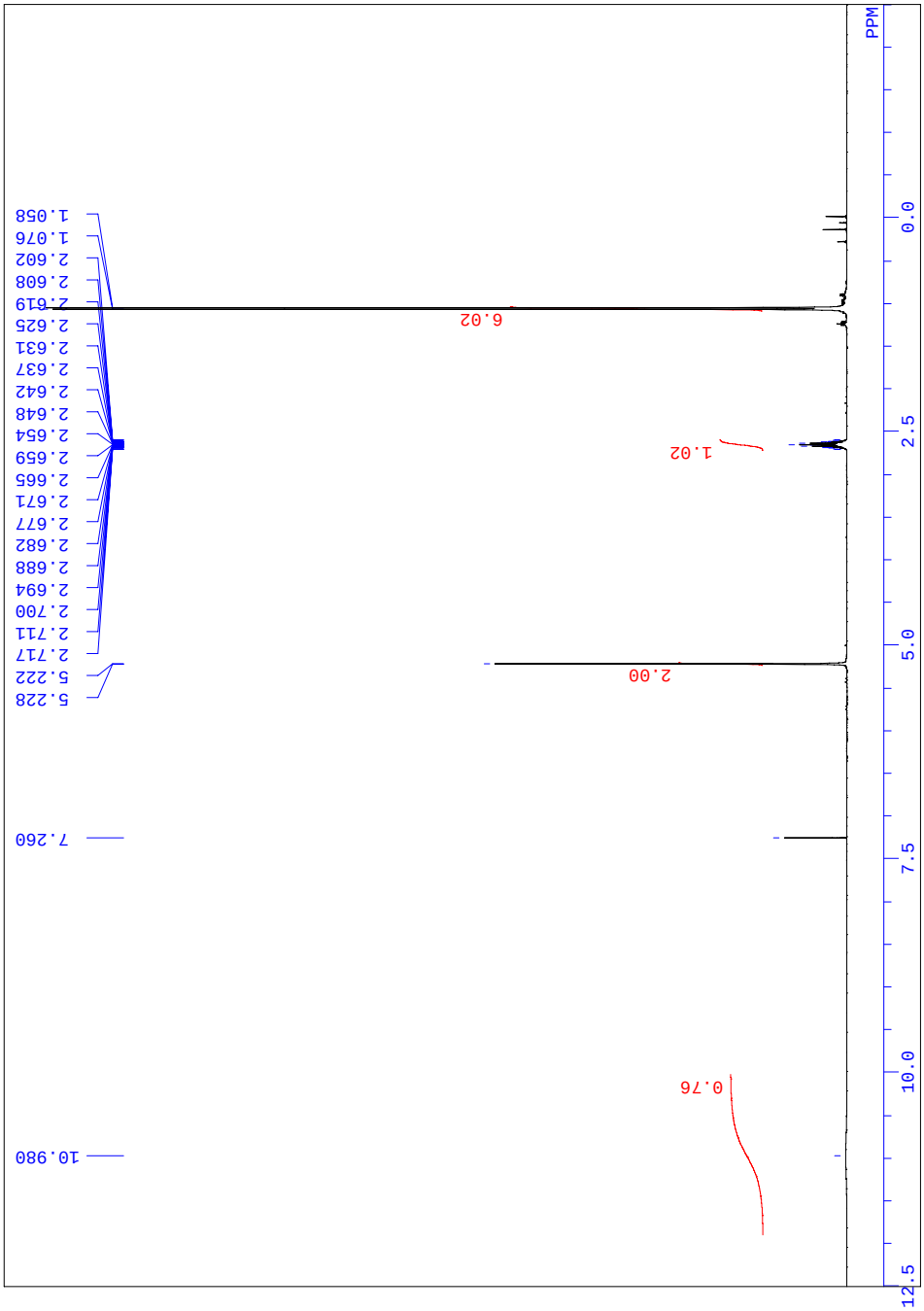
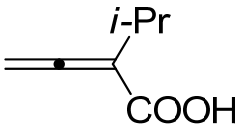


Fig. S25 ^{1}H NMR spectrum of **2t** in $CDCl_3$.



2t

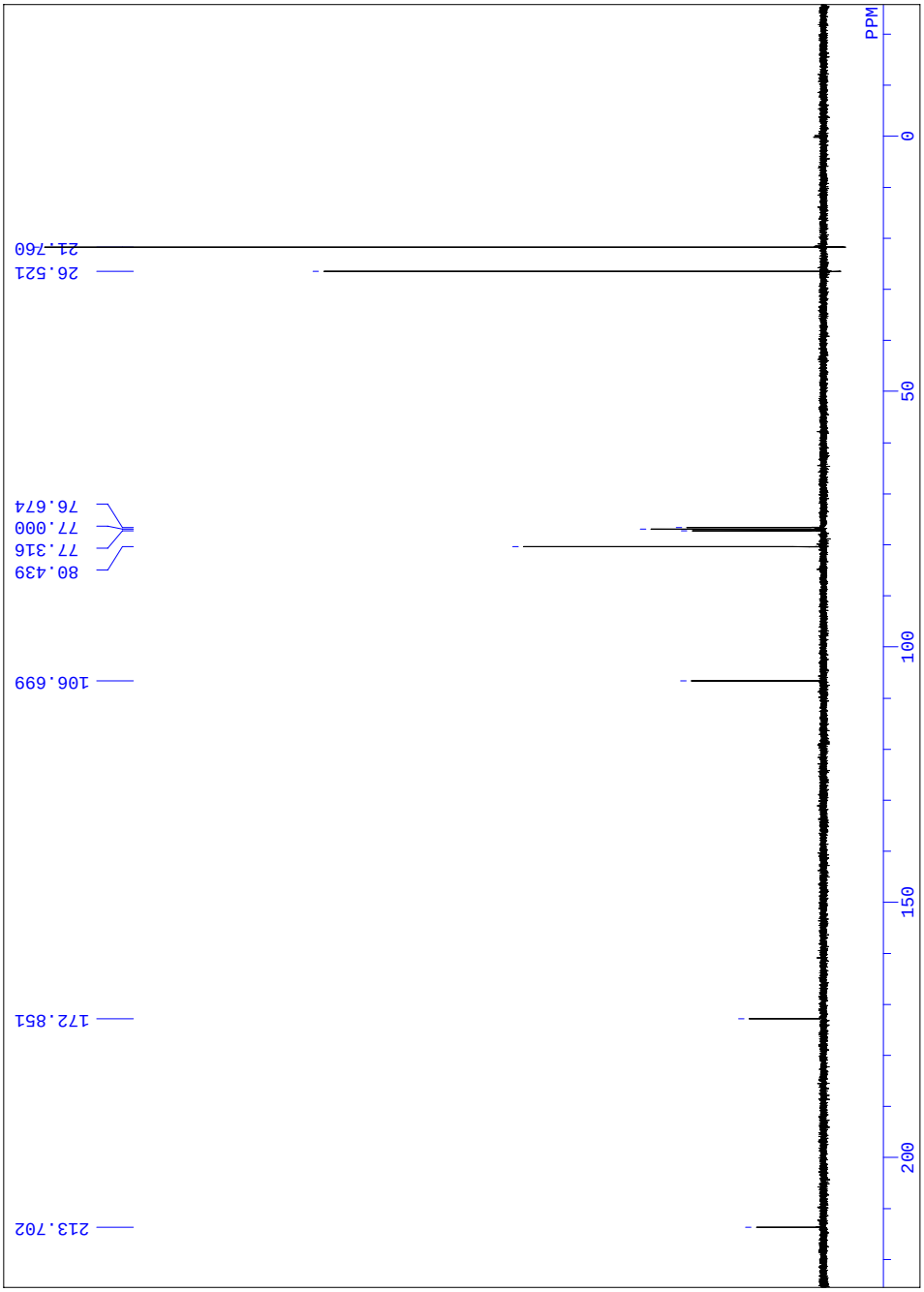
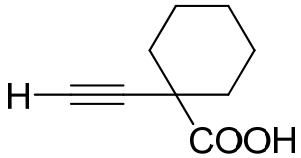


Fig. S26 ^{13}C NMR spectrum of **2t** in $CDCl_3$.



2v

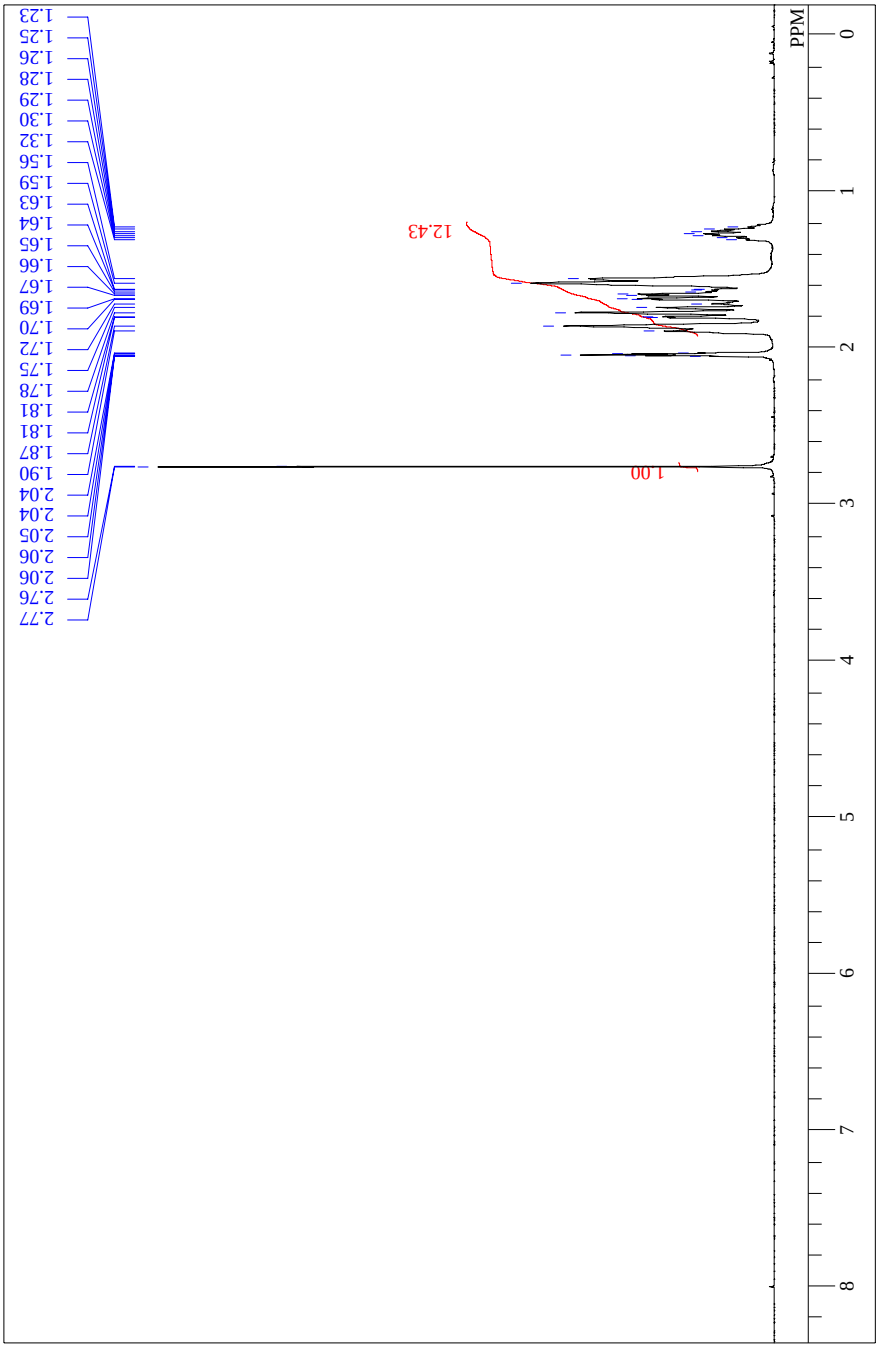
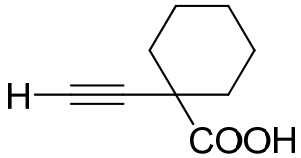


Fig. S27 ^{1}H NMR spectrum of **2v** in Acetone-D_6.



2v

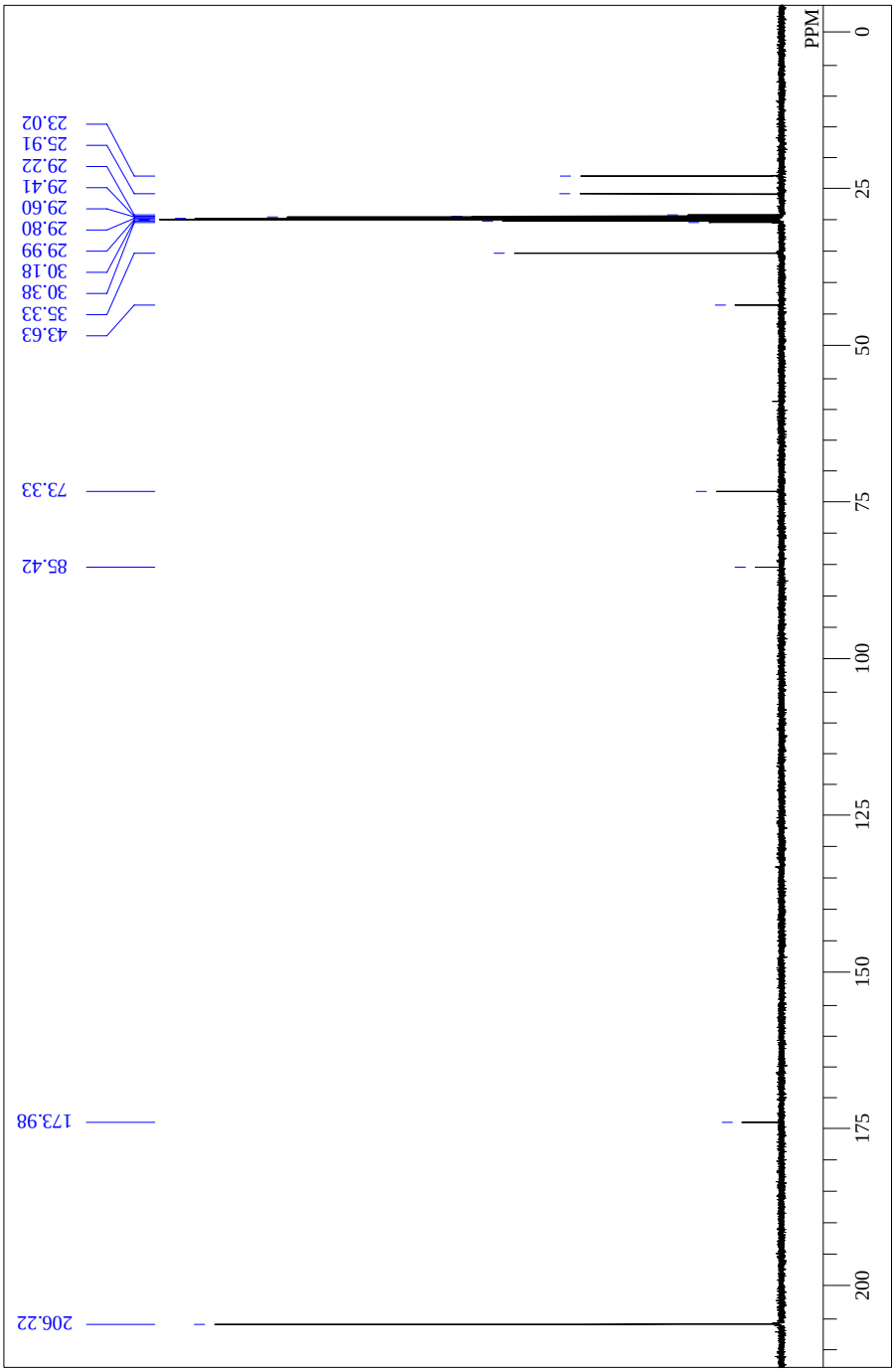


Fig. S28 ^{13}C NMR spectrum of **2v** in Acetone-D_6.

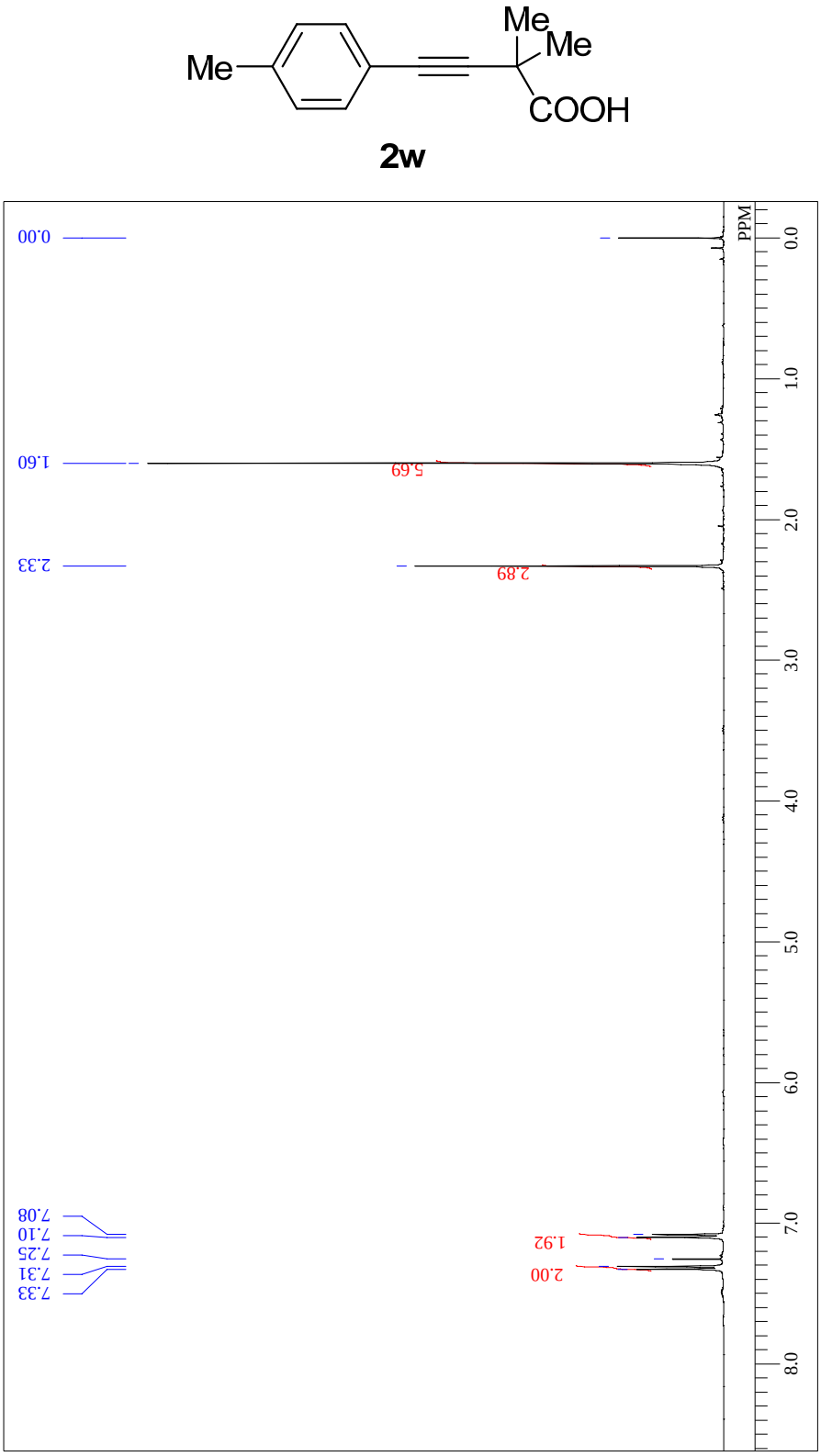
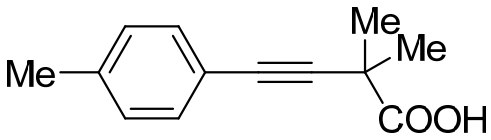


Fig. S29 ^{1}H NMR spectrum of **2w** in $CDCl_3$.



2w

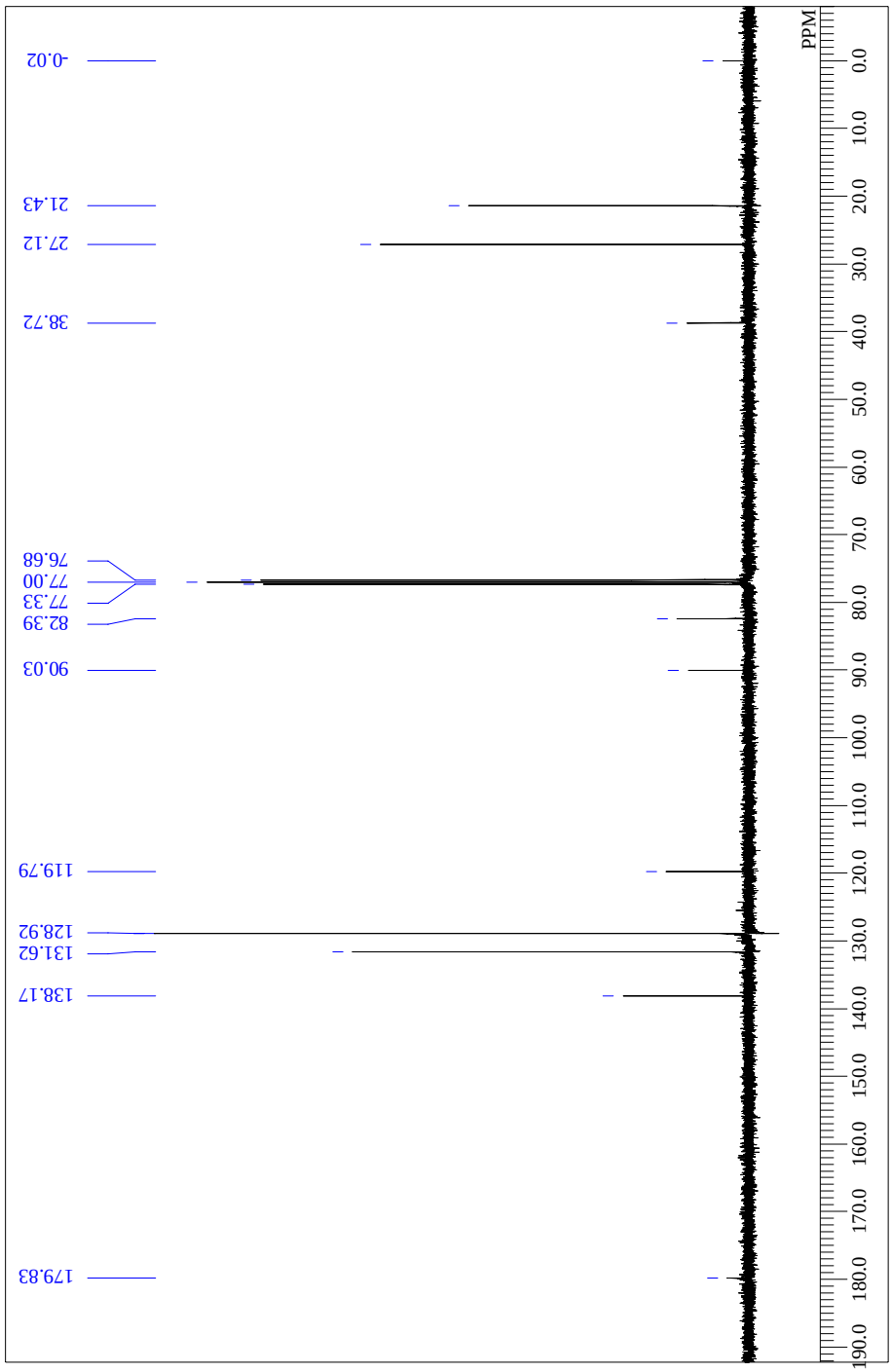
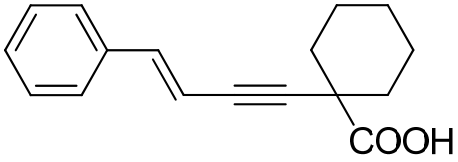


Fig. S30 ^{13}C NMR spectrum of **2w** in $CDCl_3$.



2x

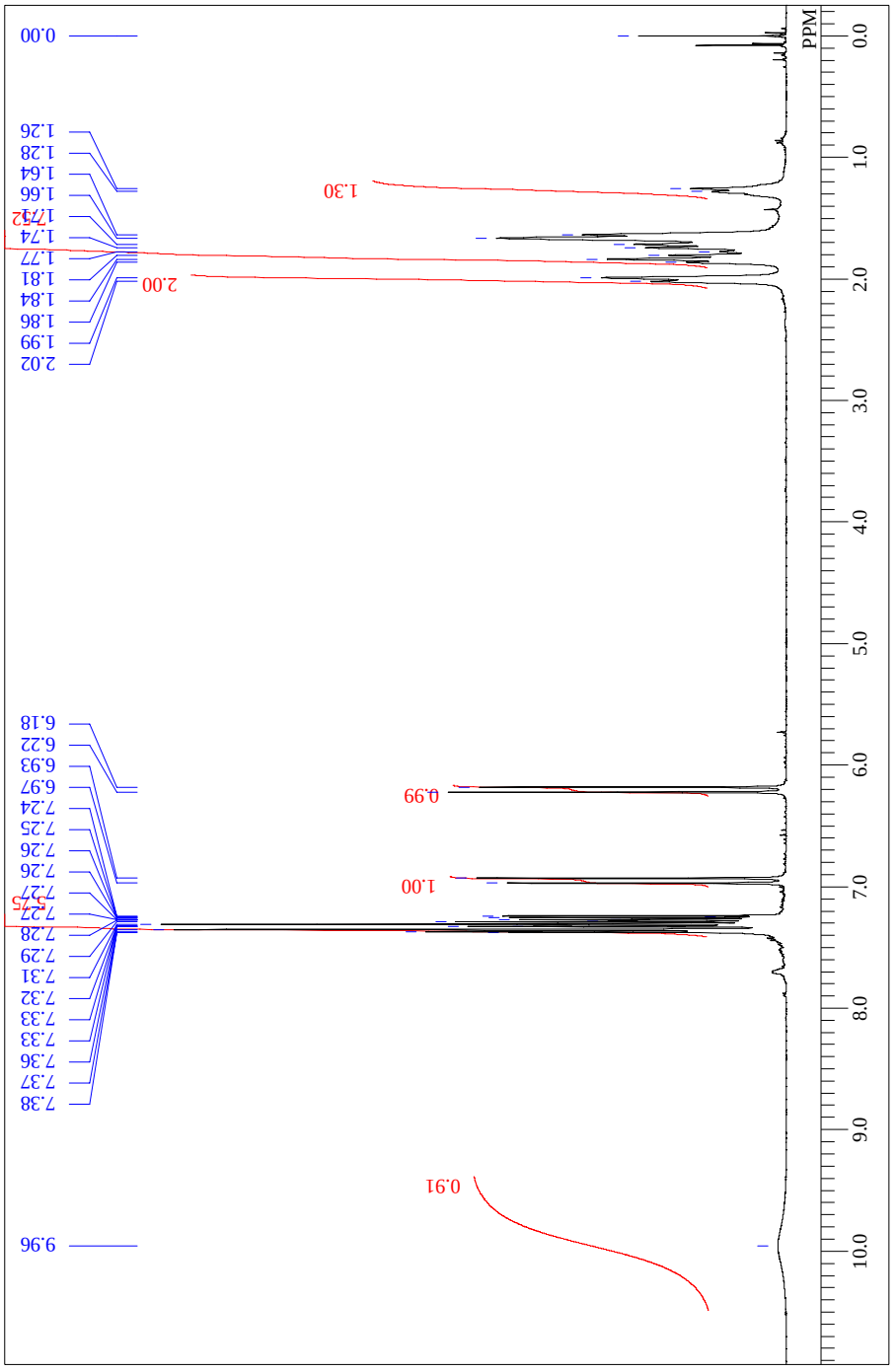
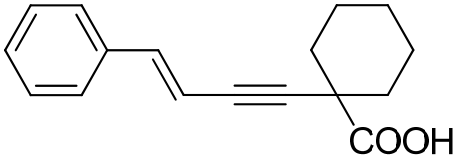


Fig. S31 ^{1}H NMR spectrum of **2x** in $CDCl_3$.



2x

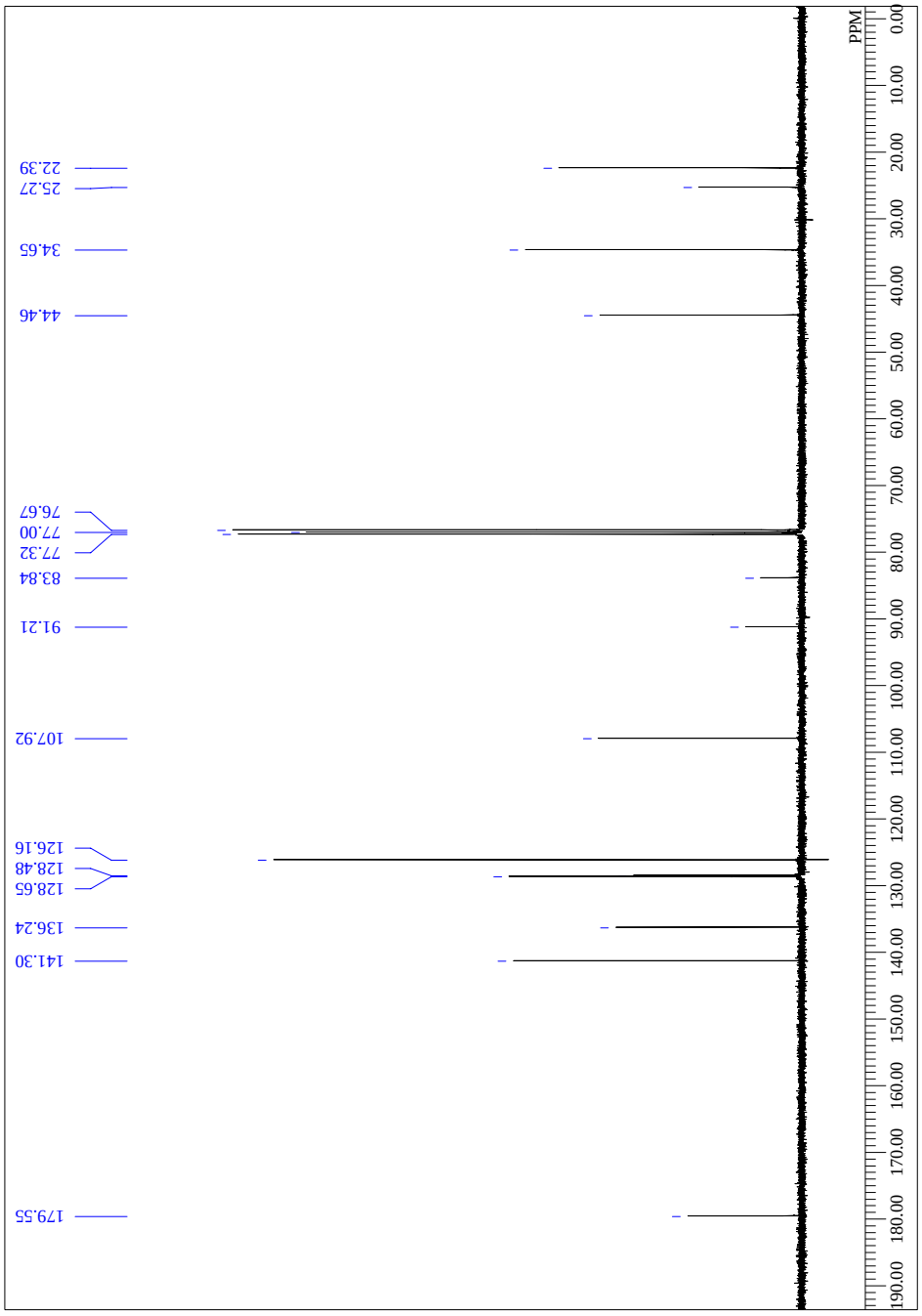
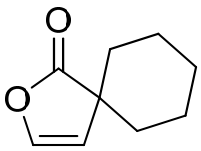


Fig. S32 ^{13}C NMR spectrum of **2x** in $CDCl_3$.



2y

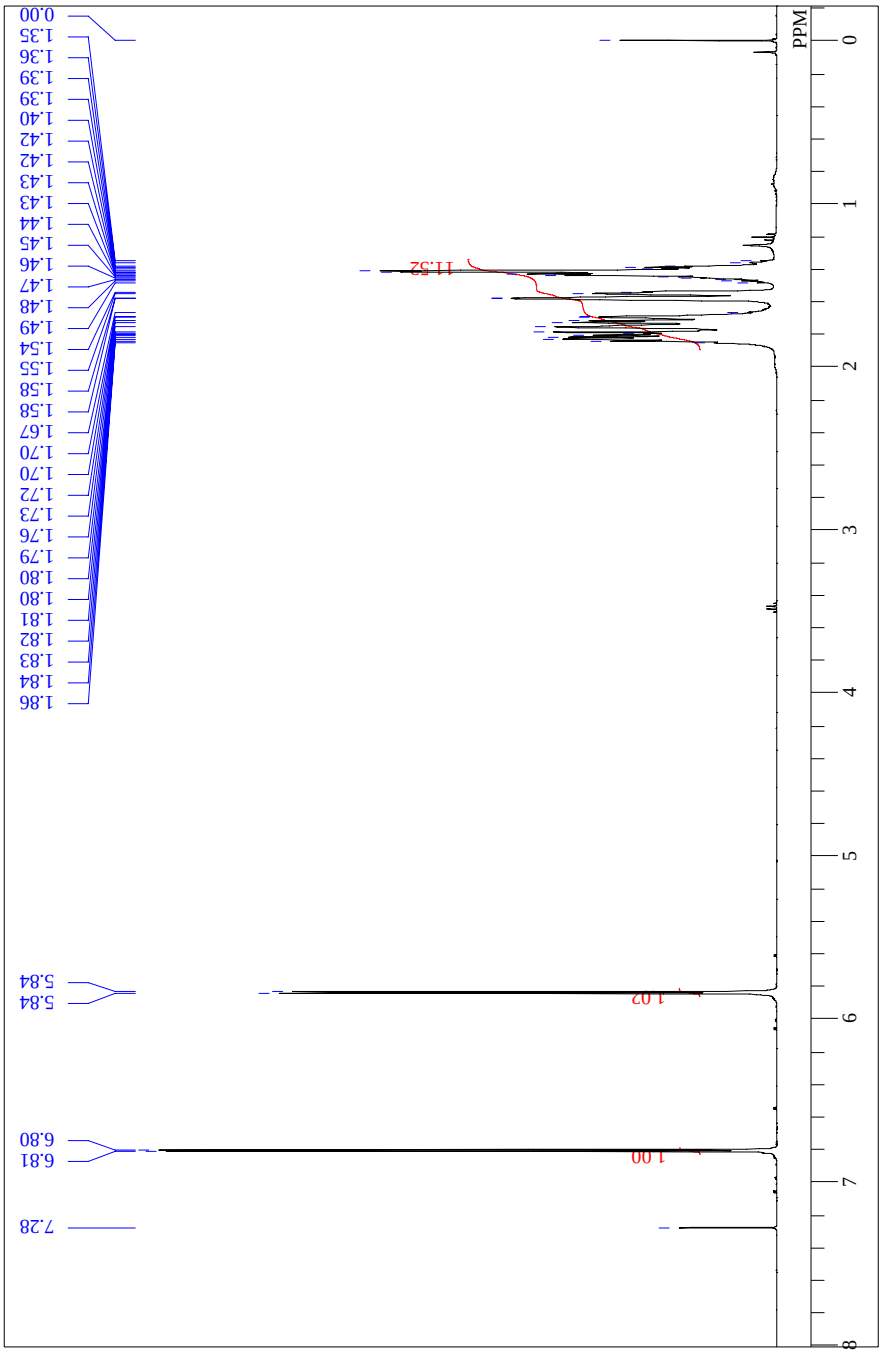
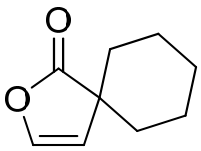


Fig. S33 ^{1}H NMR spectrum of **2y** in $CDCl_3$.



2y

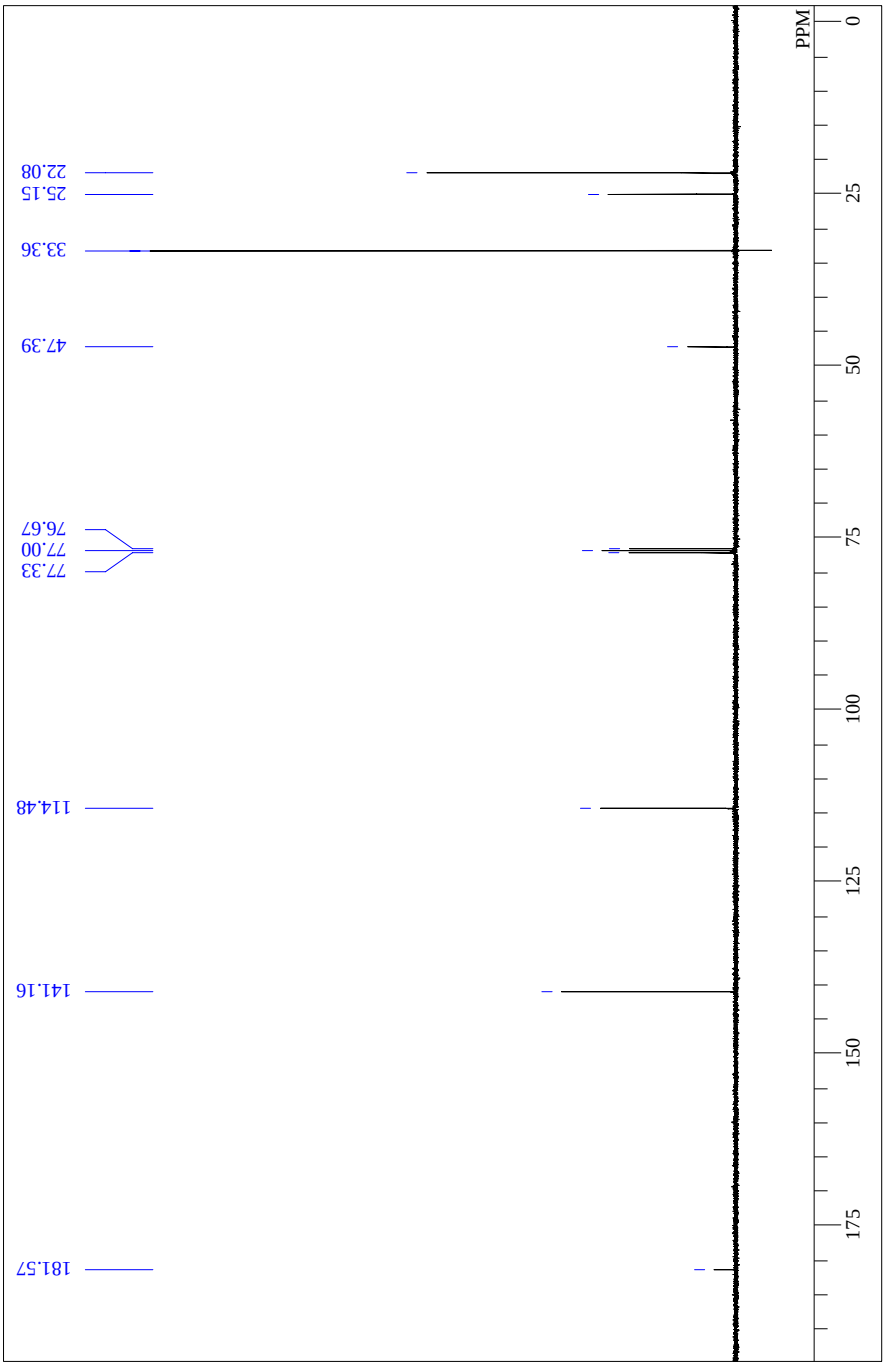


Fig. S34 ^{13}C NMR spectrum of **2y** in $CDCl_3$.

5. References

1 W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals, 5th ed.*; Burrerworth-Heinemann: Oxford, U. K., 2003.

2 G. Hilt, W. Hess, T. Vogler and C. Hengst, *J. Organomet. Chem.*, 2005, **690**, 5170–5181.

3 N. Ghosh, S. Nayak and A. K. Sahoo, *J. Org. Chem.*, 2011, **76**, 500–511.

4 M. Yu, G. Zhang and L. Zhang, *Org. Lett*., 2007, **9**, 2147–2150.

5 G.-R.Peh, and P. E. Eloreancig, *Org. Lett*. 2012, **14**, 5614–5617.

6 P. L. Wash, E. Maverick, J. Chiefari and D. A. Lightner, *J. Am. Chem. Soc*., 1997, **119**, 3802–3806.