

Rhodium-Catalyzed [(3+2)+1] Carbocyclization Reactions of Alkynylidenecyclopropanes with Carbon Monoxide: Construction of Polysubstituted Bicyclohexa-2,5-dienones

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Contents of Supporting Information:

1.	General Information	S1
2.	Representative Experimental Procedures and Spectral Data for 1a-l , 2a-l and 3a	S2
3.	Photochemical Rearrangement of 2e to 4	S15
4.	Copies of all NMR Spectra	S16
5.	Structure Report for 4	S68

1. General Information

All reactions were carried out under an atmosphere of argon in anhydrous solvent and commercially available reagents were used as received unless otherwise stated. THF was distilled from sodium-benzophenone ketal or obtained from an in-house Grubbs solvent purification system. *p*-Xylene was distilled from CaH₂ and stored over 4Å molecular sieves under an atmosphere of argon. Anhydrous toluene was obtained from an in-house Grubbs solvent purification system. Photochemical reactions were conducted using an Ace Glass Inc. quartz mercury vapour lamp, powered by an Ace Glass Inc. 450 W power supply with voltage boost enabled, immersed in an Ace Glass Inc. water-cooled jacketed quartz immersion well and contained within an Ace Glass Inc. photochemical safety cabinet. Analytical thin layer chromatography (TLC) was performed on precoated aluminum-backed silica gel 60 F₂₅₄ plates (EMD Millipore, 200 μm thickness). TLC plates were visualized with ultraviolet light and treatment with KMnO₄ or vanillin stains followed by heating. All compounds were purified by flash chromatography using silica gel 60 (40-63 μm, SiliCycle) and gave spectroscopic data consistent with being ≥95% the assigned structure. Melting points (uncorrected) were obtained from a Büchi M-560 melting point instrument. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (CHCl₃: δ_H = 7.26 ppm and δ_C = 77.16 ppm). ¹H NMR data are reported as follows: chemical shift (multiplicity, 1st order spin system if available, coupling constant, integration). Coupling constants (*J*) are reported in Hz and splitting patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br. (broad), app. (apparent) and combinations thereof. ¹³C NMR data with complete proton decoupling were described with the aid of an APT sequence, separating methylene and quaternary carbons (e, even) from methyl

and methine (o, odd). IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer; wavenumbers (ν) are given in cm^{-1} ; and the abbreviations w (weak, <33%), m (medium, 33-66%), s (strong, >66%) and br. (broad) are used to describe the relative intensities of the IR absorbance bands. Mass spectra were obtained through the Chemistry Department Mass Spectrometry Service at Queen's University.

2. Representative Experimental Procedures and Spectral Data for 1a-1, 2a-1 and 3a.

General Procedure for the Synthesis of ACPs 1a-d: Diisopropyl azodicarboxylate (DIAD, 2.40 mmol) was added dropwise to a stirring solution of 2-cyclopropylidenepropan-1-ol¹ (2.00 mmol), the requisite propargyl sulfonamide (2.40 mmol) and triphenylphosphine (2.40 mmol) in THF (8.00 ml) at 0 °C. The reaction was then warmed to ambient temperature and stirred until consumption of the alcohol was complete (t.l.c. control). The reaction mixture was then concentrated *in vacuo* onto silica gel. Purification by flash chromatography (SiO_2 , eluting with a diethyl ether/pentane gradient) furnished the ACPs **1a-d**.

General Procedure for the Synthesis of ACPs 1e-l: Phosphorus tribromide (10.6 mmol) was added dropwise to a stirred solution of 2-cyclopropylidenepropan-1-ol (20.0 mmol) in diethyl ether (40 ml) at 0 °C. The reaction mixture was then allowed to warm to ambient temperature and stirred overnight *ca.* 16 hours. The reaction mixture was then cooled to 0 °C and carefully quenched with water (20 ml) and 5% aqueous K_2CO_3 solution (20 ml). The mixture was then warmed to ambient temperature and stirred for a further *ca.* 15 minutes. The phases were then separated and the aqueous phase extracted with diethyl ether (2 x 80 ml). The combined organic phases were then washed with saturated aqueous NaCl solution, dried (anhyd. Na_2SO_4), filtered and carefully concentrated *in vacuo* to afford (1-bromopropan-2-ylidene)cyclopropane as a colourless solution in diethyl ether (*ca.* 80 wt.%), which was used directly in the next step without further purification.

Sodium hydride (60 wt.% dispersion in mineral oil, 3.75 mmol) was suspended in THF (12.0 ml) and the suspension cooled with stirring to 0 °C. The requisite propargyl nucleophile (3.00 mmol) was then added dropwise and stirring at 0 °C continued until gas evolution ceased. The reaction mixture was warmed to ambient temperature and stirred for a further *ca.* 15 minutes, before the dropwise addition of the crude (1-bromopropan-2-ylidene)cyclopropane (*ca.* 80 wt.% solution in diethyl ether, 3.30 mmol). The reaction mixture was stirred until consumption of the nucleophile was complete (t.l.c. control), quenched with water and partitioned with diethyl ether. The combined organic phases were

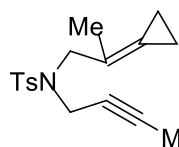
¹ (a) F. Huet, A. Lechevallier and J. M. Conia, *Tetrahedron Lett.*, 1977, **18**, 2521; (b) F. Huet, A. Lechevallier, M. Pellet and J. M. Conia, *Synthesis*, 1978, 63; (c) M. Hanack and F. Pradl, *Chem. Ber.*, 1986, **119**, 777.

then washed with water and saturated aqueous NaCl solution, dried (anhyd. Na₂SO₄), filtered and concentrated *in vacuo*. Purification by flash chromatography (SiO₂, eluting with a diethyl ether/pentane gradient) furnished the ACPs **1e-1**.

General Procedure for the Rhodium(I)-Catalyzed [(3+2)+1] Carbocyclization Reaction: In an argon-filled glove box, chlorocarbonylbis(triphenylphosphine)rhodium(I) (3.5 mg, 5.1 μmol) and silver trifluoroacetate (1.7 mg, 7.7 μmol) were weighed into a flame-dried glass tube equipped with a magnetic stirrer bar and capped with a rubber septum. The vessel was removed from the glove box, covered with aluminium foil and evacuated and back-filled with carbon monoxide from a balloon (3x). Anhydrous *p*-xylene (2 mL) was then added, and the resulting solution stirred at 120 °C for *ca.* 20 minutes. A solution of the requisite ACP **1** (0.25 mmol) in *p*-xylene (2 mL) was then added *via* syringe, and the mixture was stirred at 120 °C until the reaction was complete (t.l.c. control). The reaction mixture was then allowed to cool to ambient temperature, filtered through cotton wool and the volume partially reduced by concentration *in vacuo* to afford the crude product. Purification by flash chromatography (for **2a-b** and **2d-1**: SiO₂, eluting with a pentane/diethyl ether gradient; for **2c**: deactivated SiO₂,² eluting with a hexane/acetone gradient) furnished the desired compounds **2**.

Procedure for Gram-Scale Reaction of ACP 1e: In an argon-filled glove box, chlorocarbonylbis(triphenylphosphine)rhodium(I) (0.131 g, 0.181 mmol) and silver trifluoroacetate (0.063 g, 0.284 mmol) were weighed into a flame-dried 500 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar. The side neck was capped with a rubber septum and the centre neck sealed with a one-way ground glass stopcock adapter. The vessel was then removed from the glove box and covered with aluminium foil. A three-way glass stopcock adapter equipped with two balloons containing carbon monoxide was securely attached with Tygon[®] tubing to the stopcock adapter, and the reaction vessel evacuated and backfilled with CO from one of the balloons (3x). Anhydrous *p*-xylene (132 mL) was then added through the septum, and the resulting solution stirred at 120 °C for *ca.* 20 minutes. A solution of ACP **1e** (1.00 g, 3.78 mmol) in *p*-xylene (20 mL) was then added *via* syringe through the septum, and the mixture was stirred at 120 °C for *ca.* 24 hours. The stopcock adapter was then adjusted to expose the reaction mixture to the second balloon of CO, and the reaction mixture stirred for a further *ca.* 24 hours. The reaction mixture was then allowed to cool to ambient temperature, filtered through cotton wool and the volume partially reduced by concentration *in vacuo* to afford the crude product. Purification by flash chromatography (SiO₂, eluting with 20-35% diethyl ether/pentane) furnished the *cyclohexa-2,5-dienone* **2e** in 88% yield as a cream-coloured solid.

² Silica gel was deactivated by treatment with a 80:18:2 solution of pentane:diethyl ether:triethylamine. The deactivated silica gel was packed into a column, and then flushed with a 1:1 (v/v) solution of pentane:diethyl ether until no free amine remained.



***N*-(But-2-yn-1-yl)-*N*-(2-cyclopropylidenepropyl)-4-methylbenzenesulfonamide (1a).**

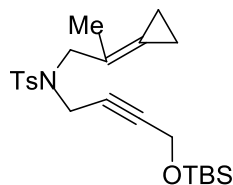
Colour and State: White solid; **mp** = 90-91 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.77-7.74 (m, 2H), 7.31-7.28 (m, 2H), 3.91 (q, *J* = 2.3 Hz, 2H), 3.87 (s, 2H), 2.42 (s, 3H), 1.83 (app. quintet, *J* = 1.6 Hz, 3H), 1.50 (t, *J* = 2.4 Hz, 3H), 1.05-1.03 (m, 4H).

¹³C NMR (125 MHz, CDCl₃) δ 143.12 (e), 136.57 (e), 129.26 (o), 128.06 (o), 122.56 (e), 118.72 (e), 81.18 (e), 71.98 (e), 51.73 (e), 36.01 (e), 21.63 (o), 18.25 (o), 3.31 (o), 2.81 (e), 2.28 (e).

IR (Neat) 3054 (w), 2965 (w), 2918 (w), 2851 (w), 1595 (w), 1442 (w), 1338 (m), 1327 (s), 1154 (s), 1087 (s), 1059 (m), 999 (w), 892 (s), 817 (m), 747 (s), 654 (s) cm⁻¹.

HRMS (EI, [M]⁺) calcd for C₁₇H₂₁NO₂S 303.1293, found 303.1289.



***N*-(4-((*tert*-Butyldimethylsilyloxy)but-2-yn-1-yl)-*N*-(2-cyclopropylidenepropyl)-4-methylbenzenesulfonamide (1b).**

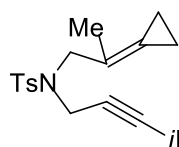
Colour and State: White solid; **mp** = 52-54 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.76-7.73 (m, 2H), 7.29-7.27 (m, 2H), 4.01 (t, *J* = 1.7 Hz, 2H), 3.98 (t, *J* = 1.7 Hz, 2H), 3.88 (s, 2H), 2.41 (s, 3H), 1.83 (app. quintet, *J* = 1.7 Hz, 3H), 1.08-1.01 (m, 4H), 0.85 (s, 9H), 0.01 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 143.23 (e), 136.57 (e), 129.41 (o), 127.98 (o), 122.83 (e), 118.56 (e), 83.86 (e), 77.59 (e), 51.86 (e), 51.43 (e), 35.84 (e), 25.87 (o), 21.65 (o), 18.34 (e), 18.23 (o), 2.96 (e), 2.31 (e), -5.18 (o).

IR (Neat) 2953 (w), 2927 (m), 2854 (m), 1596 (w), 1446 (w), 1342 (s), 1252 (m), 1159 (s), 1064 (s), 999 (m), 896 (m), 835 (s), 771 (s), 743 (s) cm⁻¹.

HRMS (EI, [M]⁺) calcd for C₂₃H₃₅NO₃SSi 433.2107, found 433.2100.



***N*-(2-Cyclopropylidenepropyl)-4-methyl-*N*-(4-methylpent-2-yn-1-yl)benzenesulfonamide (1c).**

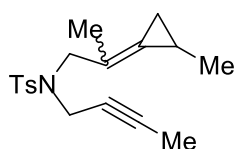
Colour and State: Pale yellow solid; **mp** = 54-56 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.76-7.73 (m, 2H), 7.29-7.27 (m, 2H), 3.95 (d, *J* = 2.0 Hz, 2H), 3.89 (s, 2H), 2.41 (s, 3H), 2.22 (septet of t, *J* = 6.9, 2.0 Hz, 1H), 1.84 (app. quintet, *J* = 1.6 Hz, 3H), 1.07-1.00 (m, 4H), 0.88 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 143.14 (e), 136.64 (e), 129.42 (o), 127.94 (o), 122.55 (e), 118.62 (e), 91.38 (e), 71.84 (e), 51.50 (e), 35.87 (e), 22.71 (o), 21.58 (o), 20.31 (o), 18.22 (o), 2.85 (e), 2.29 (e).

IR (Neat) 3048 (w), 2972 (w), 2917 (w), 2872 (w), 1597 (w), 1430 (m), 1340 (s), 1322 (s), 1159 (s), 1090 (s), 901 (s), 813 (m), 747 (s), 709 (m) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2\text{S}$ 331.1606, found 331.1611.



***N*-(But-2-yn-1-yl)-4-methyl-*N*-(2-(2-methylcyclopropylidene)propyl)benzenesulfonamide (1d).**

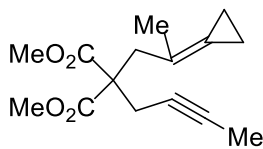
Colour and State: Colourless viscous oil. Isolated as a *ca.* 1:1 mixture of *E/Z* isomers.

^1H NMR (500 MHz, CDCl_3) δ 7.77-7.74 (m, 4H), 7.31-7.28 (m, 4H), 3.97 (dq, $J = 18:1, 2.3, 0.9$ Hz, 1H), 3.92-3.84 (m, 5H), 3.88 (dq, $J = 18.1, 2.3, 0.7$ Hz, 1H), 3.80 (app. d quintet, $J = 13.3, 1.0$ Hz, 1H), 2.42 (s, 3H), 2.42 (s, 3H), 1.81 (app. q, $J = 1.6$ Hz, 3H), 1.80 (app. q, $J = 1.6$ Hz, 3H), 1.50 (t, $J = 2.4$ Hz, 3H), 1.49 (t, $J = 2.4$ Hz, 3H), 1.46-1.39 (m, 2H), 1.21-1.15 (m, 2H), 1.10 (d, $J = 6.1$ Hz, 3H), 1.10 (d, $J = 6.1$ Hz, 3H), 0.67-0.62 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 143.10 (e), 136.72 (e), 136.61 (e), 129.54 (e), 129.34 (e), 129.26 (o), 128.09 (o), 128.07 (o), 118.86 (e), 118.51 (e), 81.18 (e), 81.13 (e), 72.08 (e), 51.68 (e), 51.48 (e), 35.95 (e), 21.64 (o), 18.14 (o), 17.98 (o), 17.91 (o), 17.54 (o), 10.71 (o), 10.45 (e), 10.01 (o), 9.95 (e), 3.32 (o), 3.30 (o).

IR (Neat) 3033 (w), 2965 (w), 2919 (w), 2860 (w), 1598 (w), 1443 (w), 1346 (m), 1159 (s), 1092 (m), 897 (m), 814 (w), 750 (m), 655 (m) cm^{-1} .

HRMS (ESI, $[\text{M}+\text{H}]^+$) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_2\text{S}$ 318.1522, found 318.1532.



Dimethyl 2-(but-2-yn-1-yl)-2-(2-cyclopropylidene)propylmalonate (1e).

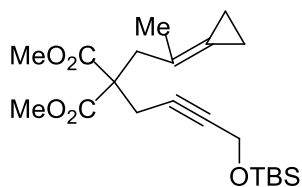
Colour and State: Colourless oil.

^1H NMR (500 MHz, CDCl_3) δ 3.73 (s, 6H), 2.98 (s, 2H), 2.73 (q, $J = 2.6$ Hz, 2H), 1.76 (t, $J = 2.6$ Hz, 3H), 1.73 (app. quintet, $J = 1.6$ Hz, 3H), 1.08-1.03 (m, 2H), 1.02-0.98 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 171.30 (e), 122.20 (e), 118.99 (e), 78.79 (e), 74.16 (e), 57.20 (e), 52.71 (o), 38.93 (e), 23.23 (e), 21.49 (o), 3.82 (e), 3.59 (o), 2.75 (e).

IR (Neat) 3041 (w), 2973 (w), 2952 (w), 2922 (w), 2855 (w), 1733 (s), 1435 (m), 1294 (m), 1226 (s), 1197 (s), 1159 (s), 1142 (s), 1065 (m), 888 (w), 841 (w) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4$ 264.1362, found 264.1369.



Dimethyl 2-(4-((*tert*-butyldimethylsilyloxy)but-2-yn-1-yl)-2-(2-cyclopropylidene)propylmalonate (1f).

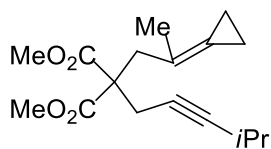
Colour and State: Colourless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.26 (t, $J = 2.1$ Hz, 2H), 3.72 (s, 6H), 2.98 (s, 2H), 2.82 (t, $J = 2.2$ Hz, 2H), 1.73 (app. quintet, $J = 1.6$ Hz, 3H), 1.08-1.04 (m, 2H), 1.02-0.97 (m, 2H), 0.89 (s, 9H), 0.09 (s, 6H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 171.04 (e), 122.39 (e), 118.89 (e), 81.84 (e), 80.18 (e), 57.01 (e), 52.78 (o), 51.89 (e), 39.01 (e), 25.94 (o), 23.27 (e), 21.55 (o), 18.40 (e), 3.97 (e), 2.79 (e), -5.07 (o).

IR (Neat) 2952 (w), 2930 (w), 2856 (w), 1737 (s), 1435 (m), 1255 (m), 1226 (m), 1197 (m), 1138 (s), 1069 (s), 834 (s), 776 (s) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{21}\text{H}_{34}\text{O}_5\text{Si}$ 394.2176, found 394.2183.



Dimethyl 2-(2-cyclopropylidene)propyl)-2-(4-methylpent-2-yn-1-yl)malonate (1g).

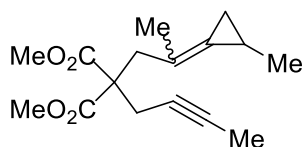
Colour and State: Colourless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.72 (s, 6H), 2.98 (s, 2H), 2.72 (d, $J = 2.1$ Hz, 2H), 2.48 (septet of t, $J = 6.8, 2.2$ Hz, 1H), 1.73 (app. quintet, $J = 1.6$ Hz, 3H), 1.11 (d, $J = 6.8$ Hz, 6H), 1.09-1.04 (m, 2H), 1.02-0.98 (m, 2H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 171.28 (e), 122.24 (e), 119.05 (e), 89.37 (e), 74.47 (e), 57.40 (e), 52.67 (o), 38.85 (e), 23.38 (o), 23.06 (e), 21.55 (o), 20.62 (o), 3.95 (e), 2.79 (e).

IR (Neat) 2969 (w), 2932 (w), 2872 (w), 1735 (s), 1435 (m), 1294 (m), 1225 (m), 1196 (s), 1154 (s), 1066 (m), 889 (w), 841 (w) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$ 292.1675, found 292.1669.



Dimethyl 2-(but-2-yn-1-yl)-2-(2-(2-methylcyclopropylidene)propyl)malonate (1h).

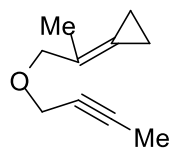
Colour and State: Colourless oil. Isolated as a *ca.* 1:1 mixture of *E/Z*-isomers.

¹H NMR (500 MHz, CDCl₃) δ 3.71 (s, 3H), 3.71 (s, 3H), 3.70 (s, 6H), 3.03 (d, A of AB, *J*_{AB} = 13.8 Hz, 1H), 2.93 (s, 2H), 2.83 (d, B of AB, *J*_{AB} = 13.8 Hz, 1H), 2.72 (q, *J* = 2.6 Hz, 2H), 2.70 (app. quintet, *J* = 2.5 Hz, 2H), 1.74 (t, *J* = 2.6 Hz, 3H), 1.73 (t, *J* = 2.6 Hz, 3H), 1.70 (app. q, *J* = 1.7 Hz, 3H), 1.67 (app. q, *J* = 1.6 Hz, 3H), 1.46-1.34 (m, 2H), 1.20-1.14 (m, 2H), 1.11 (d, *J* = 6.1 Hz, 3H), 1.07 (d, *J* = 6.0 Hz, 3H), 0.65-0.63 (m, 1H), 0.58-0.55 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 171.41 (e), 171.30 (e), 171.26 (e), 171.17 (e), 129.48 (e), 129.12 (e), 118.91 (e), 118.77 (e), 78.74 (e), 78.66 (e), 74.25 (e), 74.20 (e), 57.25 (e), 57.16 (e), 52.69 (o), 52.66 (o), 52.64 (o), 38.76 (e), 38.74 (e), 23.25 (e), 23.18 (e), 21.23 (o), 21.20 (o), 17.66 (o), 17.38 (o), 11.59 (o), 11.40 (e), 10.33 (o), 10.24 (e), 3.58 (o), 3.56 (o).

IR (Neat) 2953 (w), 2924 (w), 2857 (w), 1738 (s), 1436 (w), 1294 (m), 1227 (m), 1200 (m), 1163 (m), 1062 (w) cm⁻¹.

HRMS (ESI, [M+H]⁺) calcd for C₁₆H₂₃O₄ 279.1591, found 279.1593.



(1-(But-2-yn-1-yloxy)propan-2-ylidene)cyclopropane (1i).

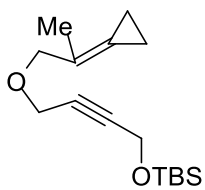
Colour and State: Pale yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 4.11 (s, 2H), 4.02 (qd, *J* = 2.3, 0.6 Hz, 2H), 1.85-1.83 (m, 6H), 1.10-1.05 (m, 2H), 1.04-1.00 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 121.42 (e), 121.06 (e), 82.08 (e), 75.54 (e), 73.38 (e), 57.28 (e), 18.25 (o), 3.69 (o), 2.58 (e), 1.90 (e).

IR (Neat) 3048 (w), 2976 (w), 2918 (w), 2851 (w), 1444 (w), 1351 (m), 1256 (w), 1134 (m), 1068 (s), 998 (m), 929 (w), 901 (w), 772 (w) cm⁻¹.

HRMS (ESI, [M+H]⁺) calcd for C₁₀H₁₅O 151.1117, found 151.1120.



tert-Butyl((4-(2-cyclopropylidenepropoxy)but-2-yn-1-yl)oxy)dimethylsilane

(1j).

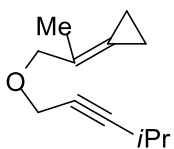
Colour and State: Colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 4.35 (t, *J* = 1.8 Hz, 2H), 4.13 (app. t, *J* = 0.9 Hz, 2H), 4.11 (t, *J* = 1.8 Hz, 2H), 1.85 (app. quintet, *J* = 1.6 Hz, 3H), 1.11-1.06 (m, 2H), 1.05-1.01 (m, 2H), 0.90 (s, 9H), 0.11 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 121.65 (e), 120.95 (e), 84.69 (e), 81.21 (e), 73.43 (e), 57.03 (e), 51.88 (e), 25.94 (o), 18.41 (e), 18.26 (o), 2.64 (e), 1.95 (e), -5.04 (o).

IR (Neat) 2951 (w), 2929 (w), 2887 (w), 2855 (w), 1462 (w), 1360 (w), 1253 (m), 1125 (m), 1065 (s), 1000 (m), 833 (s), 775 (s) cm⁻¹.

HRMS (ESI, [M+Na]⁺) calcd for C₁₆H₂₈O₂NaSi 303.1751, found 303.1757.



1-((4-Methylpent-2-yn-1-yl)oxy)propan-2-ylidene)cyclopropane (1k).

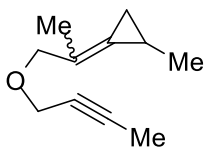
Colour and State: Colourless oil.

¹H NMR (500 MHz, CDCl₃) δ 4.13 (app. t, *J* = 0.9 Hz, 2H), 4.06 (d, *J* = 2.0 Hz, 2H), 2.59 (septet of t, *J* = 6.9, 2.0 Hz, 1H), 1.86 (app. quintet, *J* = 1.6 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 6H), 1.11-1.06 (m, 2H), 1.06-1.01 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 121.52 (e), 121.11 (e), 92.22 (e), 75.49 (e), 73.20 (e), 57.22 (e), 23.09 (o), 20.70 (o), 18.33 (o), 2.61 (e), 1.96 (e).

IR (Neat) 2970 (m), 2933 (w), 2851 (w), 1446 (w), 1359 (m), 1319 (m), 1256 (w), 1182 (w), 1076 (s), 997 (m), 902 (m), 719 (w) cm⁻¹.

HRMS (ESI, [M+Na]⁺) calcd for C₁₂H₁₈ONa 201.1250, found 201.1257.



1-(1-(But-2-yn-1-yloxy)propan-2-ylidene)-2-methylcyclopropane (1l).

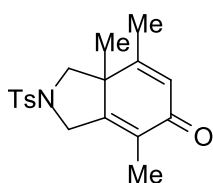
Colour and State: Colourless oil. Isolated as a *ca.* 1:1 mixture of *E/Z*-isomers.

¹H NMR (500 MHz, CDCl₃) δ 4.11 (s, 2H), 4.09 (s, 2H), 4.04-4.01 (m, 4H), 1.86-1.82 (m, 12H), 1.49-1.40 (m, 2H), 1.27-1.16 (m, 2H), 1.14-1.12 (m, 6H), 0.69 (app. t, *J* = 5.1 Hz, 1H), 0.66-0.63 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 128.40 (e), 128.24 (e), 121.06 (e), 120.87 (e), 82.07 (e), 82.05 (e), 75.67 (e), 75.66 (e), 73.43 (e), 73.19 (e), 57.25 (e), 57.10 (e), 18.02 (o), 18.00 (o), 17.49 (o), 10.39 (o), 10.29 (e), 9.69 (e), 9.68 (o), 3.73 (o), 3.71 (o).

IR (Neat) 3032 (w), 2952 (m), 2920 (m), 2854 (w), 1725 (w), 1642 (w), 1444 (m), 1353 (m), 1254 (w), 1134 (m), 1064 (s), 1013 (m), 965 (w), 905 (w), 771 (w) cm^{-1} .

HRMS (ESI, $[\text{M}+\text{H}]^+$) calcd for $\text{C}_{11}\text{H}_{17}\text{O}$ 165.1274, found 165.1282.



4,7,7a-Trimethyl-2-tosyl-2,3-dihydro-1H-isoindol-5(7aH)-one (2a).

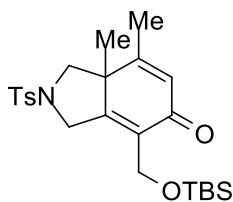
Colour and State: Beige solid; mp = 165-166 °C (decomp).

^1H NMR (500 MHz, CDCl_3) δ 7.74-7.71 (m, 2H), 7.35-7.33 (m, 2H), 6.00 (q, J = 1.4 Hz, 1H), 4.31 (dq, J = 15.8, 1.5 Hz, 1H), 3.93 (d, J = 15.7 Hz, 1H), 3.64 (d, A of AB, J_{AB} = 8.7 Hz, 1H), 2.87 (d, B of AB, J_{AB} = 8.7 Hz, 1H), 2.43 (s, 3H), 1.95 (d, J = 1.3 Hz, 3H), 1.71 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 185.90 (e), 159.26 (e), 156.80 (e), 144.22 (e), 133.48 (e), 130.09 (o), 128.54 (e), 127.56 (o), 127.03 (o), 55.29 (e), 48.82 (e), 47.99 (e), 26.83 (o), 21.69 (o), 19.22 (o), 11.59 (o).

IR (Neat) 2983 (w), 2962 (w), 2922 (w), 2866 (w), 1687 (w), 1635 (s), 1445 (w), 1339 (s), 1306 (m), 1229 (m), 1182 (m), 1156 (s), 1106 (s), 1092 (s), 1050 (s), 868 (m), 811 (m), 708 (m), 666 (s) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3\text{S}$ 331.1242, found 331.1253.



4-(((tert-Butyl)dimethylsilyloxy)methyl)-7,7a-dimethyl-2-tosyl-2,3-dihydro-1H-isoindol-5(7aH)-one (2b).

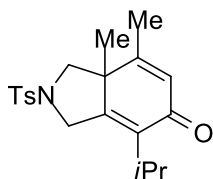
Colour and State: White solid; mp = 113-116 °C.

^1H NMR (500 MHz, CDCl_3) δ 7.72-7.69 (m, 2H), 7.33-7.31 (m, 2H), 5.97 (q, J = 1.3 Hz, 1H), 4.62 (dt, J = 14.7, 1.3 Hz, 1H), 4.49 (dt, J = 17.1, 1.7 Hz, 1H), 4.28 (ddd, J = 14.7, 2.0, 1.0 Hz, 1H), 4.22 (d, J = 17.1 Hz, 1H), 3.66 (d, A of AB, J_{AB} = 8.7 Hz, 1H), 2.83 (d, B of AB, J_{AB} = 8.7 Hz, 1H), 2.42 (s, 3H), 1.96 (d, J = 1.3 Hz, 3H), 1.37 (s, 3H), 0.90 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 184.80 (e), 159.69 (e), 158.65 (e), 144.10 (e), 133.33 (e), 131.16 (e), 130.00 (o), 127.68 (o), 127.00 (o), 58.99 (e), 54.54 (e), 49.31 (e), 48.82 (e), 27.25 (o), 26.05 (o), 21.68 (o), 19.26 (o), 18.35 (e), -5.36 (o), -5.43 (o).

IR (Neat) 2946 (w), 2930 (w), 2892 (w), 2856 (w), 1683 (w), 1642 (s), 1626 (m), 1595 (w), 1459 (w), 1405 (w), 1345 (s), 1295 (m), 1247 (m), 1158 (s), 1113 (s), 1091 (m), 1052 (m), 1028 (s), 973 (m), 840 (s), 820 (s), 781 (s), 662 (s) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{24}\text{H}_{35}\text{NO}_4\text{SSi}$ 461.2056, found 461.2042.



4-Isopropyl-7,7a-dimethyl-2-tosyl-2,3-dihydro-1H-isoindol-5(7aH)-one (2c).

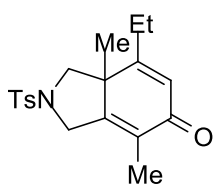
Colour and State: Colourless viscous oil.

^1H NMR (500 MHz, CDCl_3) δ 7.74-7.72 (m, 2H), 7.36-7.33 (m, 2H), 5.95 (q, $J = 1.3$ Hz, 1H), 4.36 (d, A of AB, $J_{\text{AB}} = 15.8$ Hz, 1H), 4.06 (d, B of AB, $J_{\text{AB}} = 15.7$ Hz, 1H), 3.60 (d, A of AB, $J_{\text{AB}} = 8.6$ Hz, 1H), 2.85 (d, B of AB, $J_{\text{AB}} = 8.7$ Hz, 1H), 2.79 (septet, $J = 7.1$ Hz, 1H), 2.43 (s, 3H), 1.92 (d, $J = 1.5$ Hz, 3H), 1.30 (s, 3H), 1.08 (d, $J = 7.2$ Hz, 3H), 1.06 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 185.50 (e), 158.14 (e), 155.71 (e), 144.24 (e), 137.51 (e), 133.38 (e), 130.08 (o), 127.97 (o), 127.59 (o), 54.96 (e), 48.49 (e), 48.25 (e), 27.71 (o), 27.19 (o), 21.69 (o), 20.31 (o), 20.27 (o), 19.01 (o).

IR (Neat) 2961 (w), 2931 (w), 2871 (w), 1669 (m), 1637 (m), 1453 (w), 1345 (m), 1309 (m), 1158 (s), 1092 (s), 1050 (m), 1011 (m), 913 (m), 876 (m), 813 (m), 729 (s), 665 (s) cm^{-1} .

HRMS (ESI, $[\text{M}+\text{H}]^+$) calcd for $\text{C}_{20}\text{H}_{26}\text{O}_3\text{NS}$ 360.1628, found 360.1633.



7-Ethyl-4,7a-dimethyl-2-tosyl-2,3-dihydro-1H-isoindol-5(7aH)-one (2d).

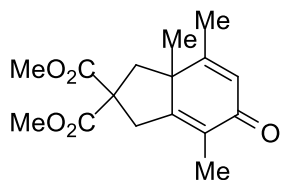
Colour and State: White solid; **mp** = 166-168 $^{\circ}\text{C}$ (decomp).

^1H NMR (500 MHz, CDCl_3) δ 7.74-7.72 (m, 2H), 7.36-7.33 (m, 2H), 6.04 (t, $J = 1.7$ Hz, 1H), 4.32 (dq, $J = 15.9, 1.5$ Hz, 1H), 3.92 (d, $J = 15.7$ Hz, 1H), 3.66 (d, A of AB, $J_{\text{AB}} = 8.6$ Hz, 1H), 2.88 (d, B of AB, $J_{\text{AB}} = 8.8$ Hz, 1H), 2.43 (s, 3H), 2.38 (dq, $J = 17.9, 7.4, 1.8$ Hz, 1H), 2.11 (dq, $J = 17.9, 7.3, 1.7$ Hz, 1H), 1.72 (app. t, $J = 1.1$ Hz, 3H), 1.31 (s, 3H), 1.13 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 186.17 (e), 164.73 (e), 157.02 (e), 144.22 (e), 133.50 (e), 130.10 (o), 128.40 (e), 127.59 (o), 124.31 (o), 55.27 (e), 48.77 (e), 48.28 (e), 27.46 (o), 24.58 (e), 21.70 (o), 11.57 (o), 11.00 (o).

IR (Neat) 2975 (w), 2921 (w), 2851 (w), 1686 (w), 1638 (s), 1615 (m), 1595 (m), 1450 (m), 1341 (s), 1306 (m), 1227 (m), 1157 (s), 1107 (s), 1091 (s), 1050 (s), 878 (m), 812 (s), 708 (m), 667 (s) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3\text{S}$ 345.1399, found 345.1389.



Dimethyl 4,7,7a-trimethyl-5-oxo-5,7a-dihydro-1H-indene-2,2(3H)-dicarboxylate (2e).

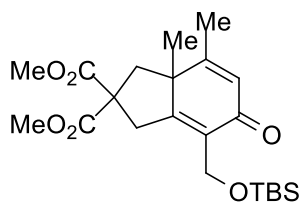
Colour and State: Cream-coloured solid; **mp** = 114-115 °C.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.97 (q, $J = 1.3$ Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.49 (dq, $J = 18.3, 1.7$ Hz, 1H), 3.22 (d, $J = 18.2$ Hz, 1H), 2.64 (d, A of AB, $J_{\text{AB}} = 13.4$ Hz, 1H), 2.23 (d, B of AB, $J_{\text{AB}} = 13.4$ Hz, 1H), 1.98 (d, $J = 1.4$ Hz, 3H), 1.81 (d, $J = 1.4$ Hz, 3H), 1.20 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 186.76 (e), 172.46 (e), 172.02 (e), 162.26 (e), 162.20 (e), 128.10 (e), 125.76 (o), 57.46 (e), 53.45 (o), 53.43 (o), 48.86 (e), 41.72 (e), 36.32 (e), 27.83 (o), 19.39 (o), 11.44 (o).

IR (Neat) 2992 (w), 2972 (w), 2954 (w), 2931 (w), 2878 (w), 2843 (w), 1725 (s), 1674 (m), 1635 (s), 1615 (s), 1431 (s), 1380 (m), 1274 (s), 1249 (s), 1200 (s), 1176 (s), 1067 (s), 1046 (m), 949 (s), 883 (m), 820 (m), 716 (m) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5$ 292.1311, found 292.1319.



Dimethyl 4-(((tert-butyl)dimethylsilyl)oxy)methyl-7,7a-dimethyl-5-oxo-5,7a-dihydro-1H-indene-2,2(3H)-dicarboxylate (2f).

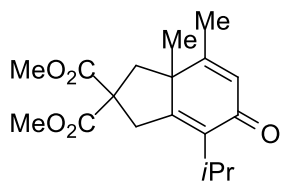
Colour and State: Pale yellow oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.95 (q, $J = 1.4$ Hz, 1H), 4.59 (d, $J = 13.0$ Hz, 1H), 4.36 (dd, $J = 13.0, 1.7$ Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.65 (d, A of AB, $J_{\text{AB}} = 19.2$ Hz, 1H), 3.51 (d, B of AB, $J_{\text{AB}} = 19.0$ Hz, 1H), 2.58 (d, A of AB, $J_{\text{AB}} = 13.5$ Hz, 1H), 2.30 (d, B of AB, $J_{\text{AB}} = 13.5$ Hz, 1H), 1.98 (d, $J = 1.3$ Hz, 3H), 1.22 (s, 3H), 0.86 (s, 9H), 0.47 (s, 3H), 0.37 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 185.23 (e), 172.56 (e), 171.95 (e), 165.83 (e), 162.18 (e), 131.17 (e), 125.87 (o), 57.48 (e), 57.08 (e), 53.42 (o), 53.33 (o), 49.45 (e), 41.29 (e), 36.28 (e), 27.94 (o), 26.00 (o), 19.42 (o), 18.33 (e), -5.32 (o), -5.25 (o).

IR (Neat) 2952 (w), 2930 (w), 2884 (w), 2855 (w), 1734 (s), 1674 (m), 1639 (s), 1460 (m), 1434 (m), 1391 (m), 1252 (s), 1164 (m), 1059 (s), 834 (s), 775 (s) cm^{-1} .

HRMS (EI, $[M]^+$) calcd for $C_{22}H_{34}O_6Si$ 422.2125, found 422.2118.



Dimethyl 4-isopropyl-7,7a-dimethyl-5-oxo-5,7a-dihydro-1H-indene-2,2(3H)-dicarboxylate (2g).

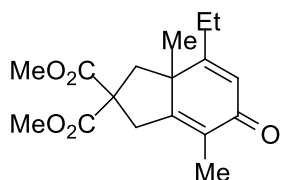
Colour and State: Colourless oil.

1H NMR (500 MHz, $CDCl_3$) δ 5.90 (q, $J = 1.3$ Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.44 (d, A of AB, $J_{AB} = 18.0$ Hz, 1H), 3.38 (d, B of AB, $J_{AB} = 18.1$ Hz, 1H), 2.98 (septet, $J = 7.1$ Hz, 1H), 2.60 (d, A of AB, $J_{AB} = 13.4$ Hz, 1H), 2.18 (d, B of AB, $J_{AB} = 13.4$ Hz, 1H), 1.94 (d, $J = 1.4$ Hz, 3H), 1.19 (s, 3H), 1.16 (d, $J = 7.0$ Hz, 3H), 1.14 (d, $J = 7.1$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.25 (e), 172.40 (e), 172.06 (e), 161.41 (e), 161.10 (e), 137.22 (e), 126.64 (o), 57.41 (e), 53.37 (o), 53.32 (o), 49.15 (e), 41.31 (e), 36.08 (e), 28.25 (o), 27.11 (o), 20.62 (o), 20.55 (o), 19.17 (o).

IR (Neat) 2954 (w), 2873 (w), 1731 (s), 1664 (m), 1631 (s), 1623 (s), 1433 (m), 1385 (m), 1257 (s), 1196 (s), 1172 (s), 1068 (m), 954 (m), 913 (m), 876 (m), 860 (m), 730 (m) cm^{-1} .

HRMS (EI, $[M]^+$) calcd for $C_{18}H_{24}O_5$ 320.1624, found 320.1631.



Dimethyl 7-ethyl-4,7a-dimethyl-5-oxo-5,7a-dihydro-1H-indene-2,2(3H)-dicarboxylate (2h).

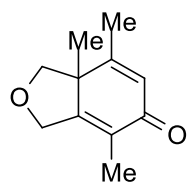
Colour and State: Off-white solid; **mp** = 98-101 $^{\circ}C$.

1H NMR (500 MHz, $CDCl_3$) δ 6.03 (t, $J = 1.6$ Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.51 (dq, $J = 18.3, 1.6$ Hz, 1H), 3.23 (d, $J = 18.3$ Hz, 1H), 2.67 (d, A of AB, $J_{AB} = 13.4$ Hz, 1H), 2.38 (dq, $J = 17.8, 7.4, 1.7$ Hz, 1H), 2.26 (dq, $J = 17.8, 7.3, 1.6$ Hz, 1H), 2.25 (d, B of AB, $J_{AB} = 13.6$ Hz, 1H), 1.83 (d, $J = 1.4$ Hz, 3H), 1.21 (s, 3H), 1.15 (t, 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 187.00 (e), 172.53 (e), 172.11 (e), 167.59 (e), 162.42 (e), 128.05 (e), 123.17 (o), 57.69 (e), 53.43 (o), 53.42 (o), 49.23 (e), 41.88 (e), 36.33 (e), 28.41 (o), 24.62 (e), 11.42 (o), 11.29 (o).

IR (Neat) 2977 (w), 2950 (w), 2915 (w), 2891 (w), 2844 (w), 1726 (s), 1673 (m), 1633 (s), 1614 (m), 1430 (m), 1379 (w), 1272 (s), 1246 (s), 1199 (m), 1177 (s), 1072 (m), 950 (m), 893 (m), 822 (w), 716 (w) cm^{-1} .

HRMS (EI, $[M]^+$) calcd for $C_{17}H_{22}O_5$ 306.1467, found 306.1460.



4,7,7a-Trimethyl-1,7a-dihydroisobenzofuran-5(3H)-one (2i).

Colour and State: White solid; **mp** = 66-68 °C.

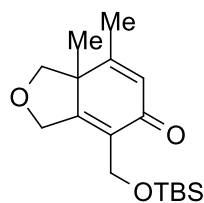
¹H NMR (500 MHz, CDCl₃) δ 6.07 (q, *J* = 1.3 Hz, 1H), 4.74 (dq, *J* = 15.4, 1.4 Hz, 1H), 4.52 (d, *J* = 15.4 Hz, 1H), 3.93 (d, A of AB, *J*_{AB} = 7.7 Hz, 1H), 3.56 (d, B of AB,

*J*_{AB} = 7.8 Hz, 1H), 1.97 (d, *J* = 1.4 Hz, 3H), 1.77 (t, *J* = 1.1 Hz, 3H), 1.41 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 186.92 (e), 161.41 (e), 159.58 (e), 127.40 (o), 126.62 (e), 74.72 (e), 68.07 (e), 49.15 (e), 26.39 (o), 19.50 (o), 11.68 (o).

IR (Neat) 2973 (w), 2919 (w), 2875 (w), 2851 (m), 1685 (m), 1630 (s), 1612 (s), 1445 (m), 1391 (m), 1366 (m), 1312 (m), 1222 (m), 1183 (m), 1108 (m), 1035 (s), 911 (s), 891 (s), 823 (m), 721 (w), 681 (m) cm⁻¹.

HRMS (EI, [M]⁺) calcd for C₁₁H₁₄O₂ 178.0994, found 178.0999.



4-(((*tert*-Butyldimethylsilyl)oxy)methyl)-7,7a-dimethyl-1,7a-dihydroisobenzofuran-5(3H)-one (2j).

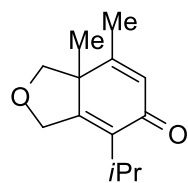
Colour and State: White solid; **mp** = 52-53 °C.

¹H NMR (500 MHz, CDCl₃) δ 6.03 (q, *J* = 1.3 Hz, 1H), 4.93 (dt, *J* = 16.6, 1.9 Hz, 1H), 4.77 (d, *J* = 16.7 Hz, 1H), 4.71 (dt, *J* = 14.9, 1.4 Hz, 1H), 4.38 (dt, *J* = 14.8 Hz, 1.8 Hz, 1H), 3.91 (d, A of AB, *J*_{AB} = 7.7 Hz, 1H), 3.53 (d, B of AB, *J*_{AB} = 7.8 Hz, 1H), 1.98 (d, *J* = 1.3 Hz, 3H), 1.43 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 185.75 (e), 162.95 (e), 159.97 (e), 129.77 (e), 127.34 (o), 73.78 (e), 68.78 (e), 59.49 (e), 50.03 (e), 26.88 (o), 26.09 (o), 19.49 (o), 18.42 (e), -5.34 (o), -5.40 (o).

IR (Neat) 2952 (w), 2929 (m), 2855 (m), 1678 (m), 1632 (s), 1614 (m), 1459 (m), 1440 (m), 1398 (m), 1304 (m), 1253 (m), 1100 (s), 1036 (s), 834 (s), 774 (s), 668 (m) cm⁻¹.

HRMS (EI, [M]⁺) calcd for C₁₇H₂₈O₃Si 308.1808, found 308.1817.



4-Isopropyl-7,7a-dimethyl-1,7a-dihydroisobenzofuran-5(3H)-one (2k).

Colour and State: Colourless oil.

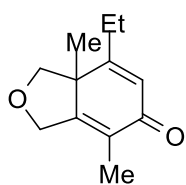
¹H NMR (500 MHz, CDCl₃) δ 6.01 (q, *J* = 1.3 Hz, 1H), 4.79 (d, A of AB, *J*_{AB} = 15.4 Hz, 1H), 4.61 (d, B of AB, *J*_{AB} = 15.3 Hz, 1H), 3.89 (d, A of AB, *J*_{AB} = 7.9 Hz, 1H),

3.55 (d, B of AB, $J_{AB} = 7.7$ Hz, 1H), 2.86 (septet, $J = 7.1$ Hz, 1H), 1.94 (d, $J = 1.3$ Hz, 3H), 1.38 (s, 3H), 1.13 (d, $J = 7.1$ Hz, 3H), 1.11 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 186.47 (e), 160.27 (e), 158.54 (e), 135.92 (e), 128.18 (o), 74.23 (e), 67.66 (e), 49.38 (e), 27.49 (o), 26.88 (o), 20.50 (o), 20.29 (o), 19.23 (o).

IR (Neat) 2962 (m), 2931 (w), 2868 (w), 1668 (m), 1636 (s), 1622 (s), 1452 (m), 1387 (m), 1369 (m), 1313 (m), 1279 (m), 1247 (w), 1189 (w), 1050 (s), 1010 (m), 981 (m), 921 (s), 873 (m), 722 (w), 686 (w) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ 206.1307, found 206.1300.



7-Ethyl-4,7a-dimethyl-1,7a-dihydroisobenzofuran-5(3H)-one (2l).

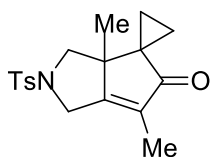
Colour and State: White solid; **mp** = 70-75 °C.

^1H NMR (500 MHz, CDCl_3) δ 6.10 (t, $J = 1.7$ Hz, 1H), 4.74 (dq, $J = 15.4, 1.4$ Hz, 1H), 4.51 (dt, $J = 15.4, 0.8$ Hz, 1H), 3.94 (dd, $J = 7.7, 0.6$ Hz, 1H), 3.58 (dd, $J = 7.7, 0.6$ Hz, 1H), 2.42 (dq, $J = 17.8, 7.4, 1.7$ Hz, 1H), 2.11 (dq, $J = 17.8, 7.3, 1.7$ Hz, 1H), 1.77 (app. t, $J = 1.2$ Hz, 3H), 1.40 (d, $J = 0.4$ Hz, 3H), 1.15 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 187.22 (e), 165.10 (e), 161.60 (e), 126.43 (e), 124.69 (o), 74.68 (e), 67.99 (e), 49.39 (e), 27.00 (o), 25.02 (e), 11.64 (o), 11.09 (o).

IR (Neat) 2966 (m), 2928 (m), 2860 (m), 1728 (w), 1683 (m), 1628 (s), 1610 (s), 1447 (m), 1381 (m), 1319 (m), 1250 (m), 1177 (m), 1110 (m), 1029 (s), 909 (s), 824 (m), 722 (m), 685 (w) cm^{-1} .

HRMS (ESI, $[\text{M}+\text{H}]^+$) calcd for $\text{C}_{12}\text{H}_{17}\text{O}_2$ 193.1223, found 193.1220.



3a,6-Dimethyl-2-tosyl-3,3a-dihydro-1H-spiro[cyclopenta[c]pyrrole-4,1'-cyclopropan]-5(2H)-one (3a).

Colour and State: Beige solid; **mp** = 126-128 °C.

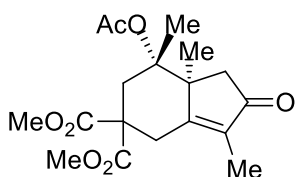
^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 4.28 (dd, $J = 15.1$ Hz, $J = 1.3$ Hz, 1H), 4.08 (d, $J = 15.0$ Hz, 1H), 3.33 (d, A of AB, $J_{AB} = 8.9$ Hz, 1H), 2.72 (d, B of AB, $J_{AB} = 8.9$ Hz, 1H), 2.43 (s, 3H), 1.68 (br. s, 3H), 1.29 (ddd, $J = 9.6, 7.2, 3.9$ Hz, 1H), 1.00 (s, 3H), 0.97-0.91 (m, 2H), 0.86 (ddd, $J = 9.0, 7.7, 4.0$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 207.17 (e), 173.10 (e), 144.04 (e), 134.19 (e), 133.18 (e), 130.03 (o), 127.41 (o), 56.87 (e), 49.55 (e), 46.08 (e), 37.67 (e), 23.13 (o), 21.68 (o), 15.50 (e), 12.87 (e), 9.21 (o).

IR (Neat) 2993 (w), 2961 (w), 2922 (w), 2860 (w), 1702 (m), 1675 (m), 1594 (w), 1450 (w), 1335 (s), 1292 (m), 1193 (m), 1155 (s), 1091 (s), 1033 (m), 1006 (m), 951 (m), 813 (m), 707 (m), 664 (s) cm^{-1} .

HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3\text{S}$ 331.1242, found 331.1233.

3. Photochemical Rearrangement of **2e** to **4**.



(7S,7aS)-Dimethyl 7-acetoxy-3,7,7a-trimethyl-2-oxo-4,6,7,7a-tetrahydro-

1H-indene-5,5(2H)-dicarboxylate (4). A 50 mL flame-dried thin-walled

glass tube, equipped with a magnetic stirrer bar and capped with a rubber

septum, was charged with a solution of dimethyl 4,7,7a-trimethyl-5-oxo-5,7a-

dihydro-1H-indene-2,2(3H)-dicarboxylate (**2e**, 29 mg, 0.1 mmol) in acetic acid (40 mL) under argon.

The reaction mixture was then irradiated with UV light (254 nm) at ambient temperature with vigorous stirring for *ca.* 4.5 hours (t.l.c. control). The reaction mixture was then concentrated *in vacuo* to afford the crude product.

Purification by flash chromatography (SiO_2 , eluting with 20-40% diethyl ether/pentane) afforded the *bicyclopentenone* **4** in 45% yield (average over 3 runs) as a white crystalline solid; **mp**: = 135-139 °C.

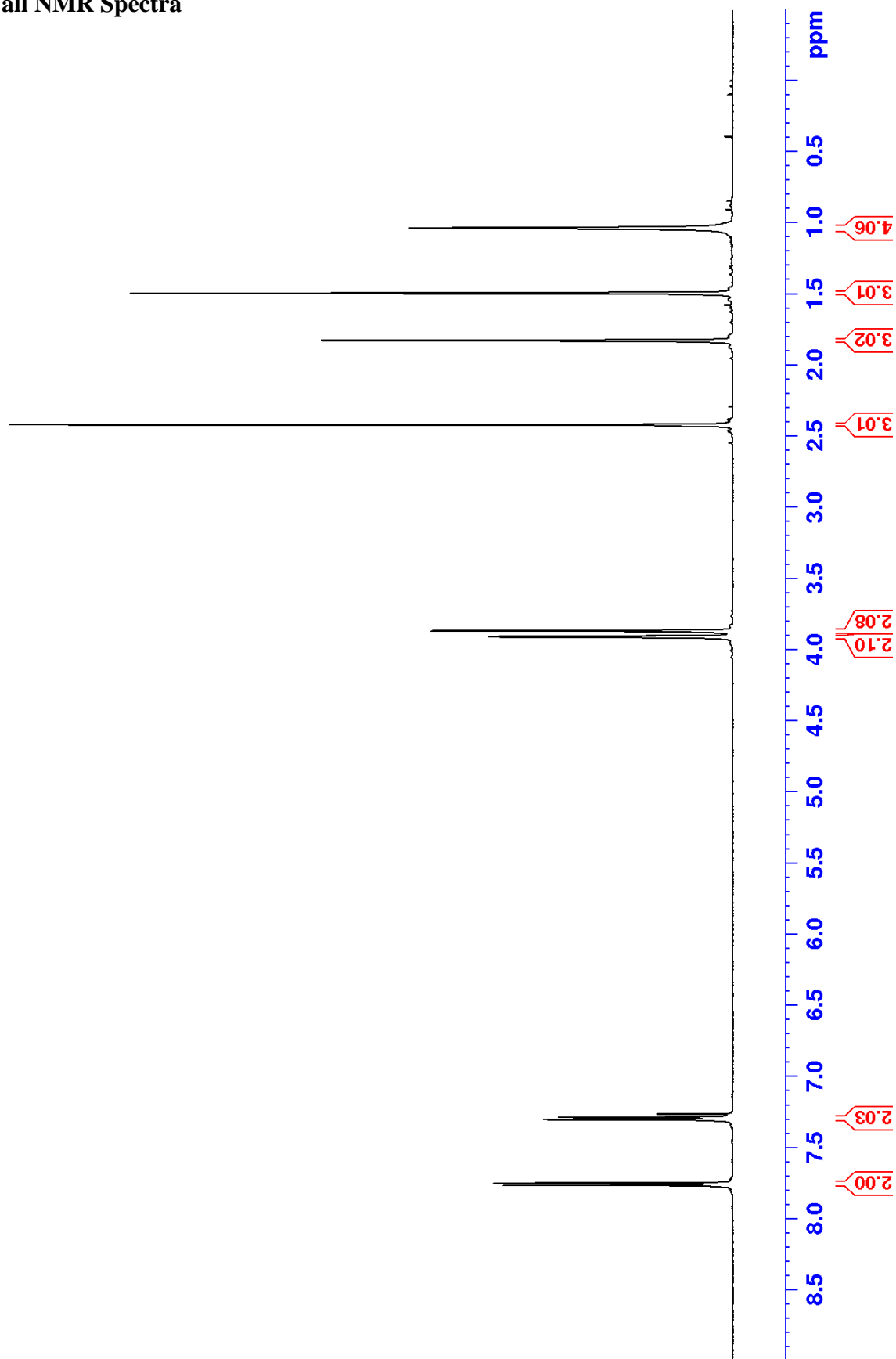
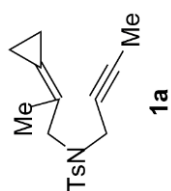
^1H NMR (500 MHz, CDCl_3) δ 3.77 (s, 3H), 3.70 (s, 3H), 3.47 (dd, $J = 14.2, 1.9$ Hz, 1H), 3.35 (dd, $J = 14.4, 2.0$ Hz, 1H), 2.74 (d, A of AB, $J_{\text{AB}} = 19.4$ Hz, 1H), 2.62 (dd, $J = 14.4, 0.5$ Hz, 1H), 2.44 (dd, $J = 14.1, 0.9$ Hz, 1H), 2.02 (s, 3H), 2.01 (d, B of AB, $J_{\text{AB}} = 19.5$ Hz, 1H), 1.82 (d, $J = 1.5$ Hz, 3H), 1.35 (s, 3H), 1.23 (s, 3H).

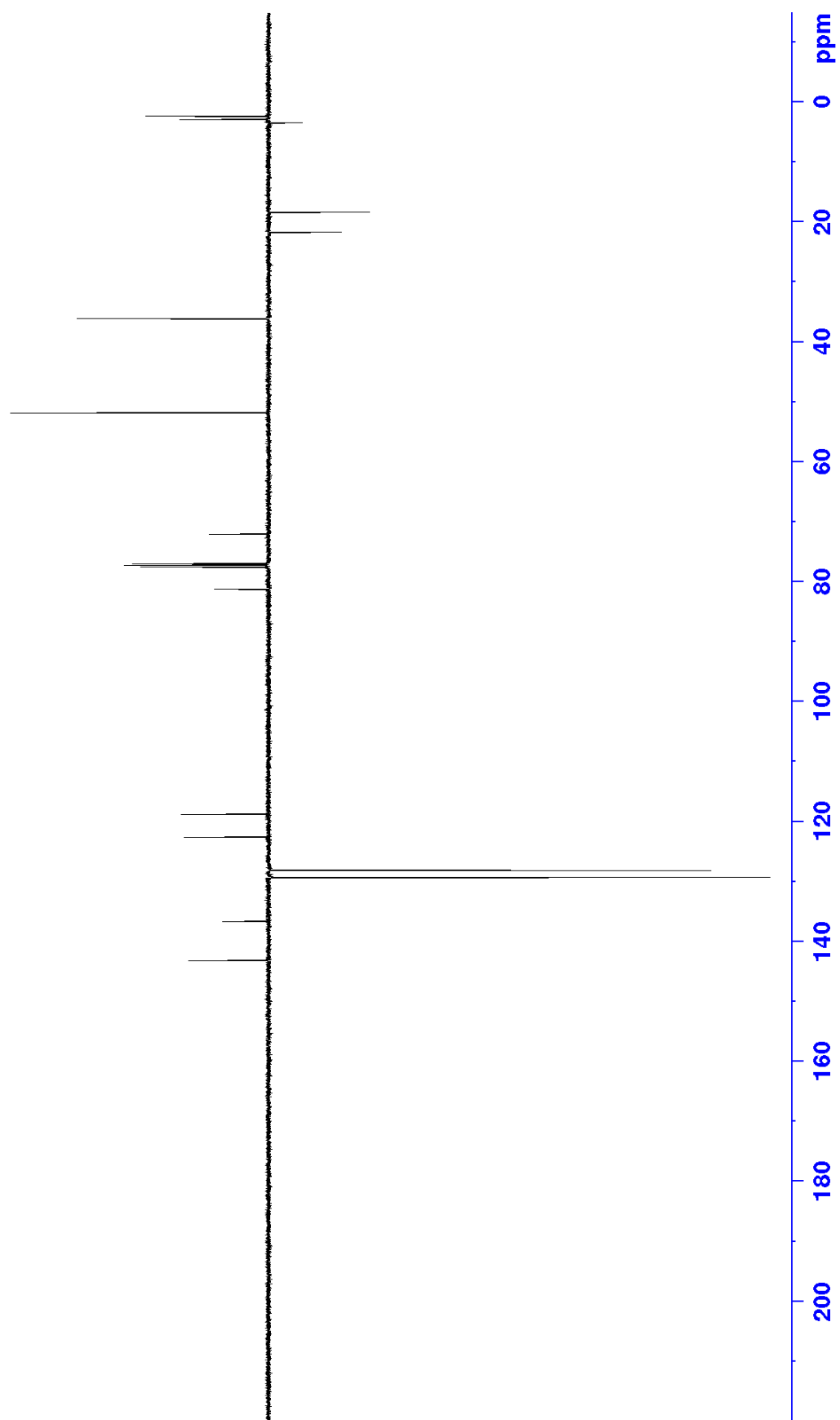
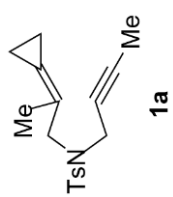
^{13}C NMR (125 MHz, CDCl_3) δ 207.79 (e), 171.02 (e), 170.92 (e), 169.92 (e), 169.43 (e), 137.88 (e), 83.86 (e), 54.57 (e), 53.49 (o), 53.00 (o), 49.31 (e), 45.09 (e), 36.16 (e), 29.08 (e), 22.34 (o), 22.33 (o), 19.54 (o), 8.22 (o).

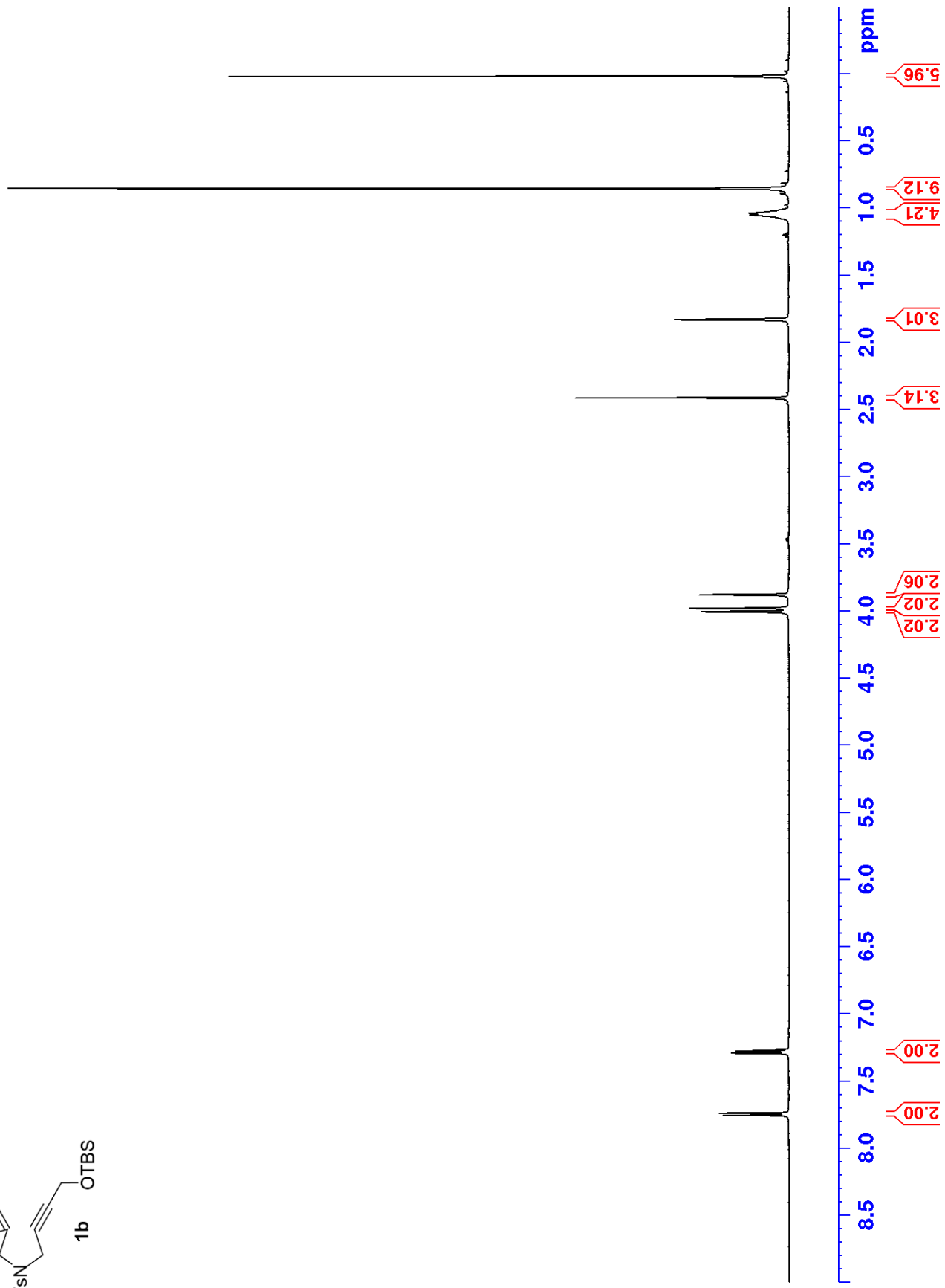
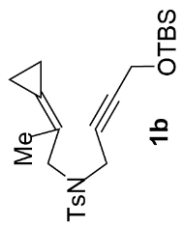
IR (Neat) 3001 (w), 2955 (w), 2922 (w), 2851 (w), 1739 (s), 1721 (s), 1698 (s), 1657 (m), 1431 (m), 1363 (m), 1314 (m), 1236 (s), 1149 (s), 1016 (s), 946 (s), 819 (m), 720 (m) cm^{-1} .

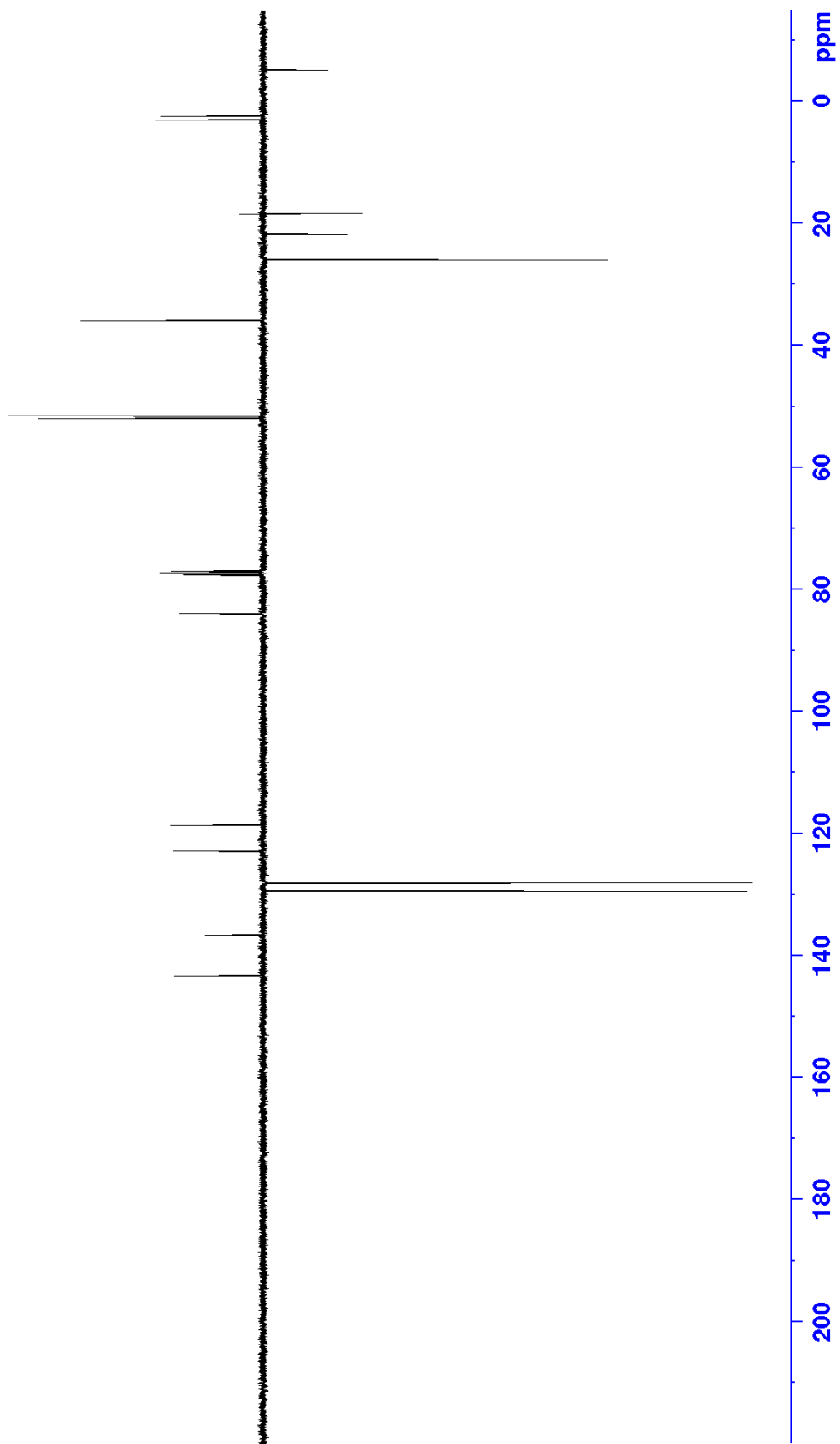
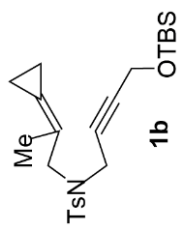
HRMS (EI, $[\text{M}]^+$) calcd for $\text{C}_{18}\text{H}_{24}\text{O}_7$ 352.1522, found 352.1529.

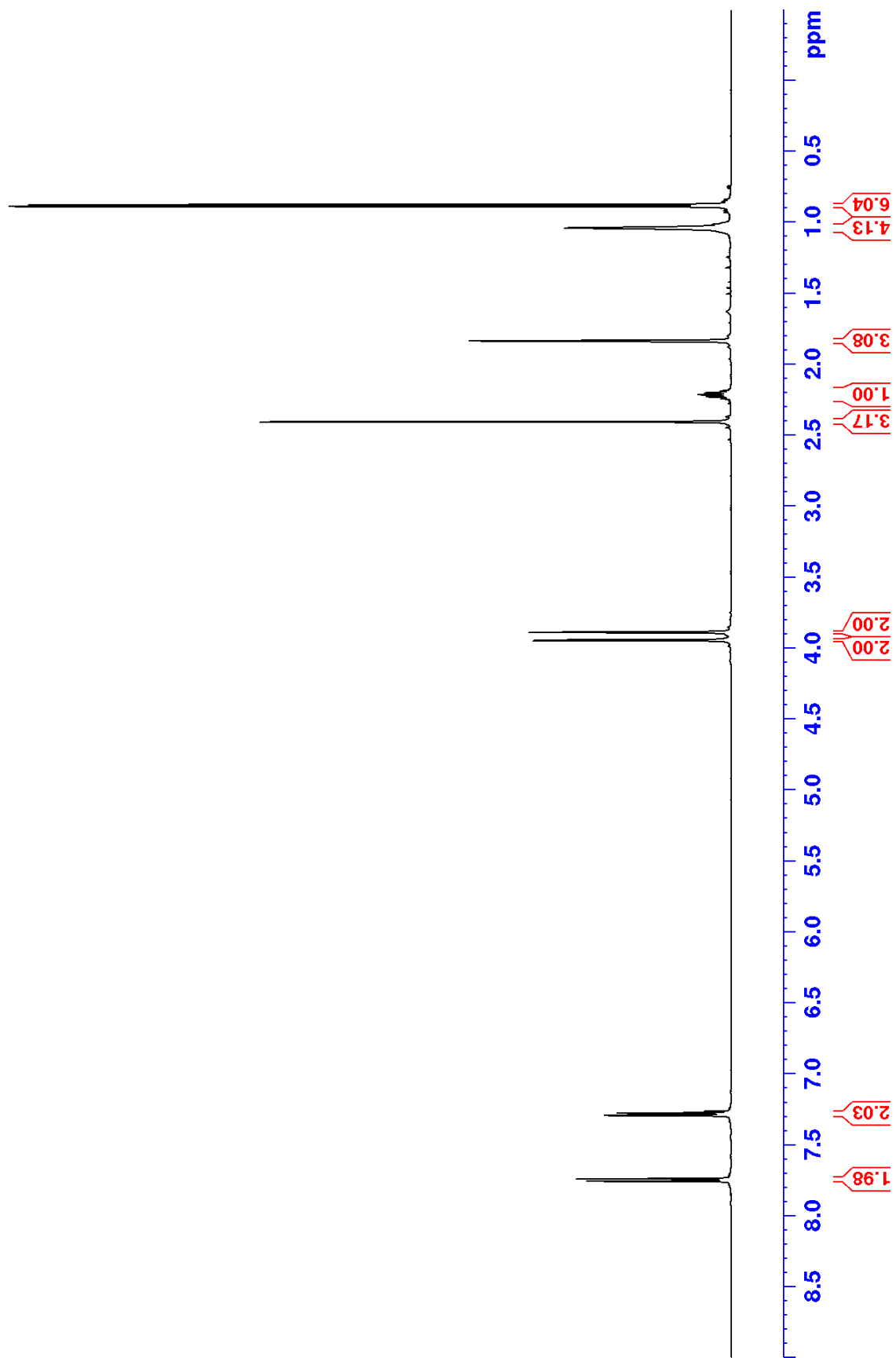
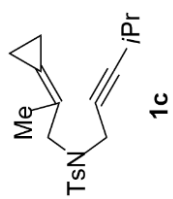
4. Copies of all NMR Spectra

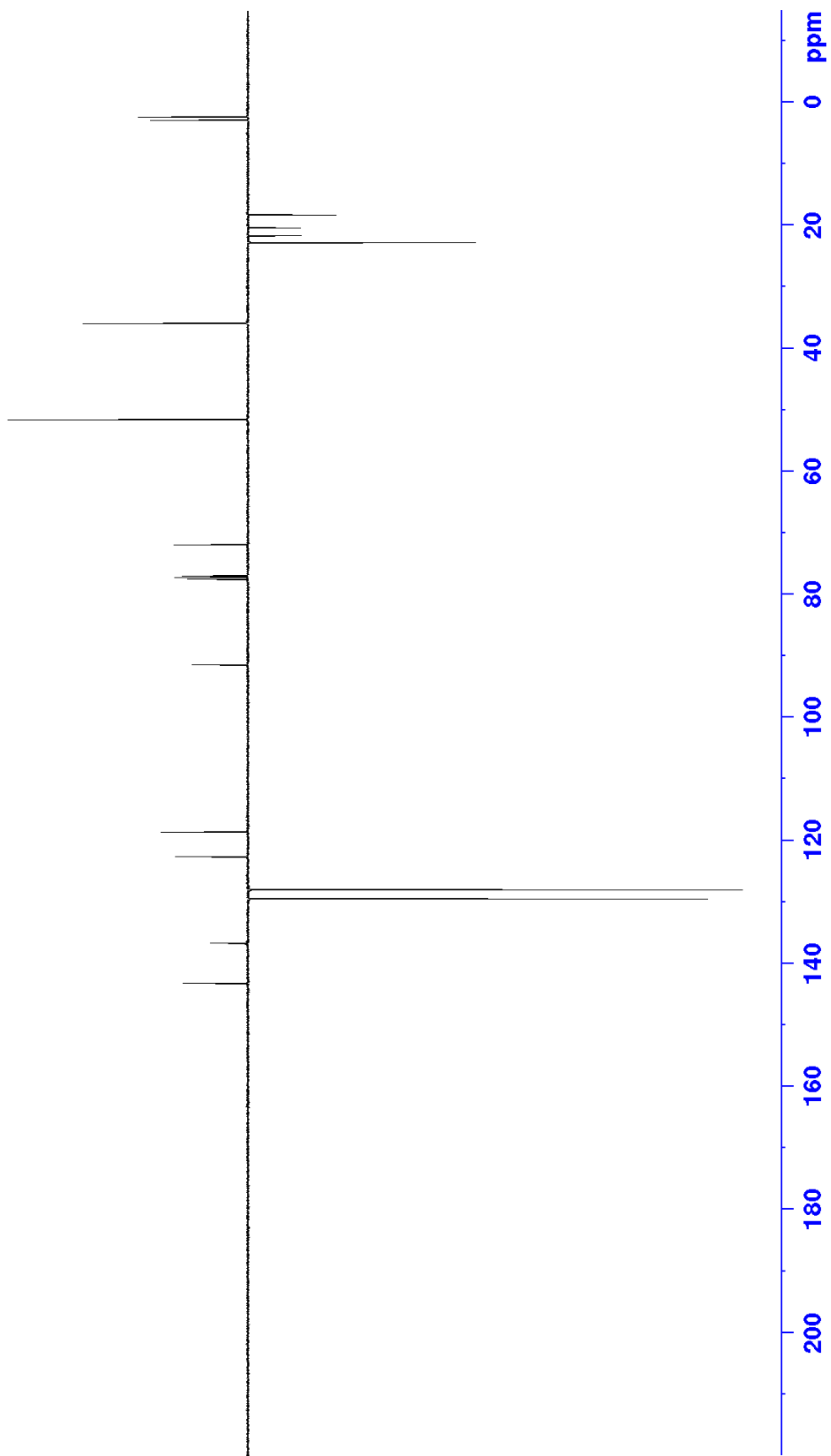
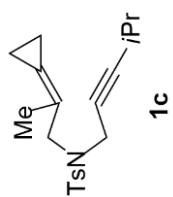


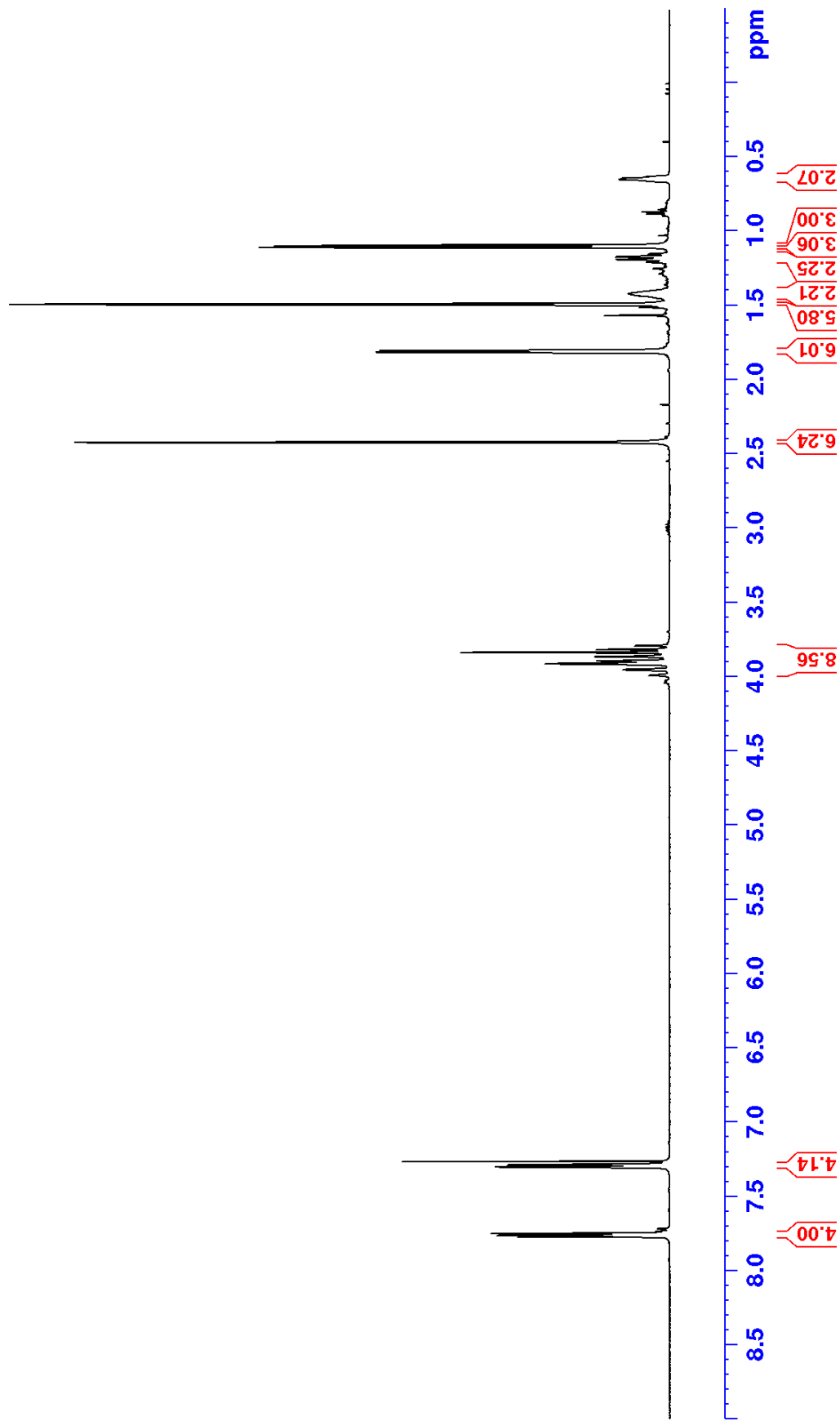
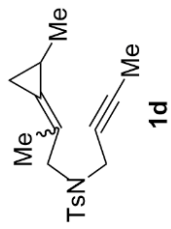


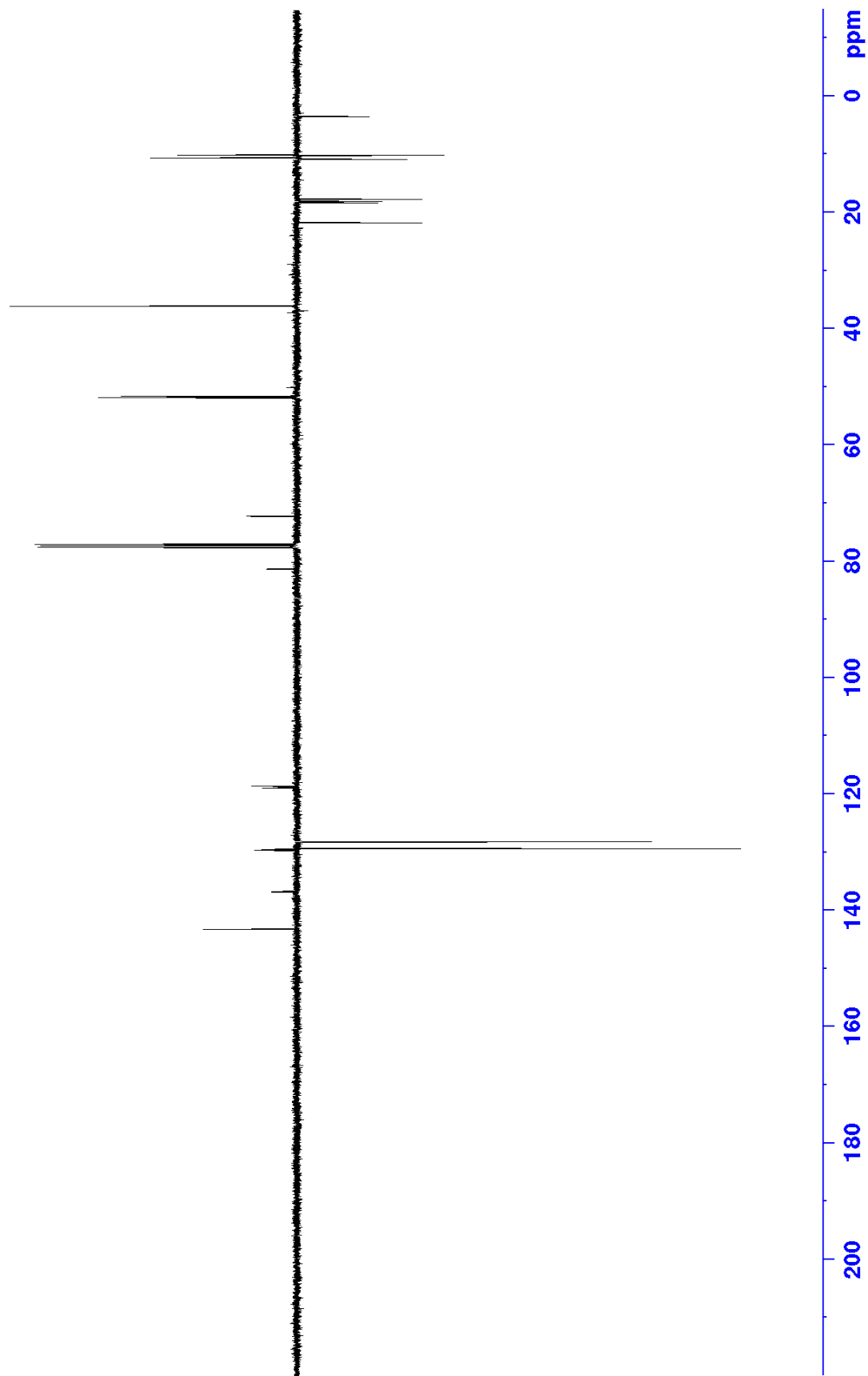
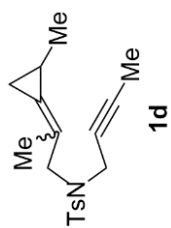


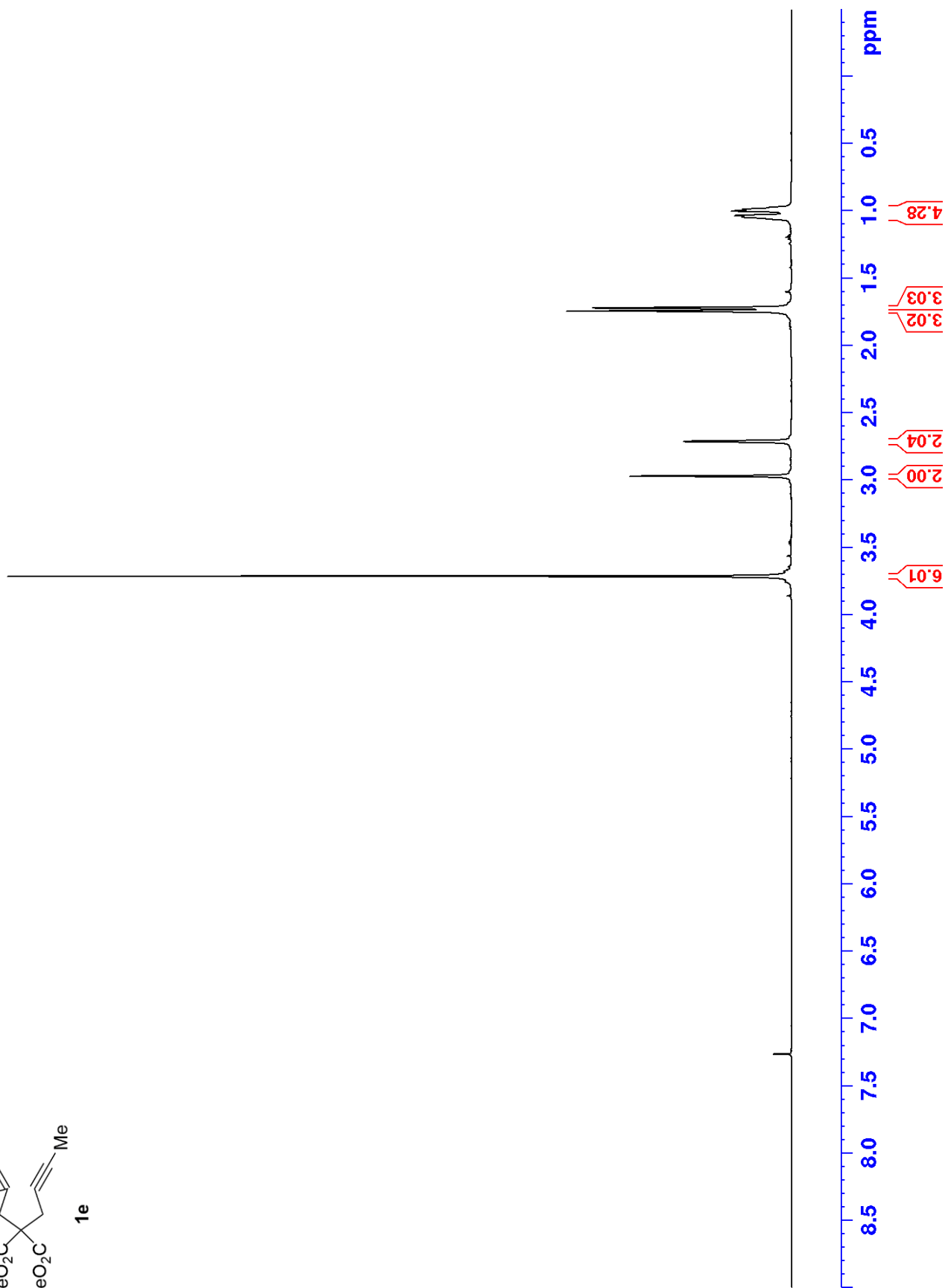
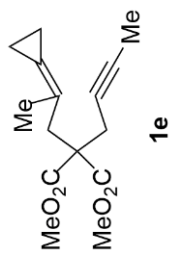


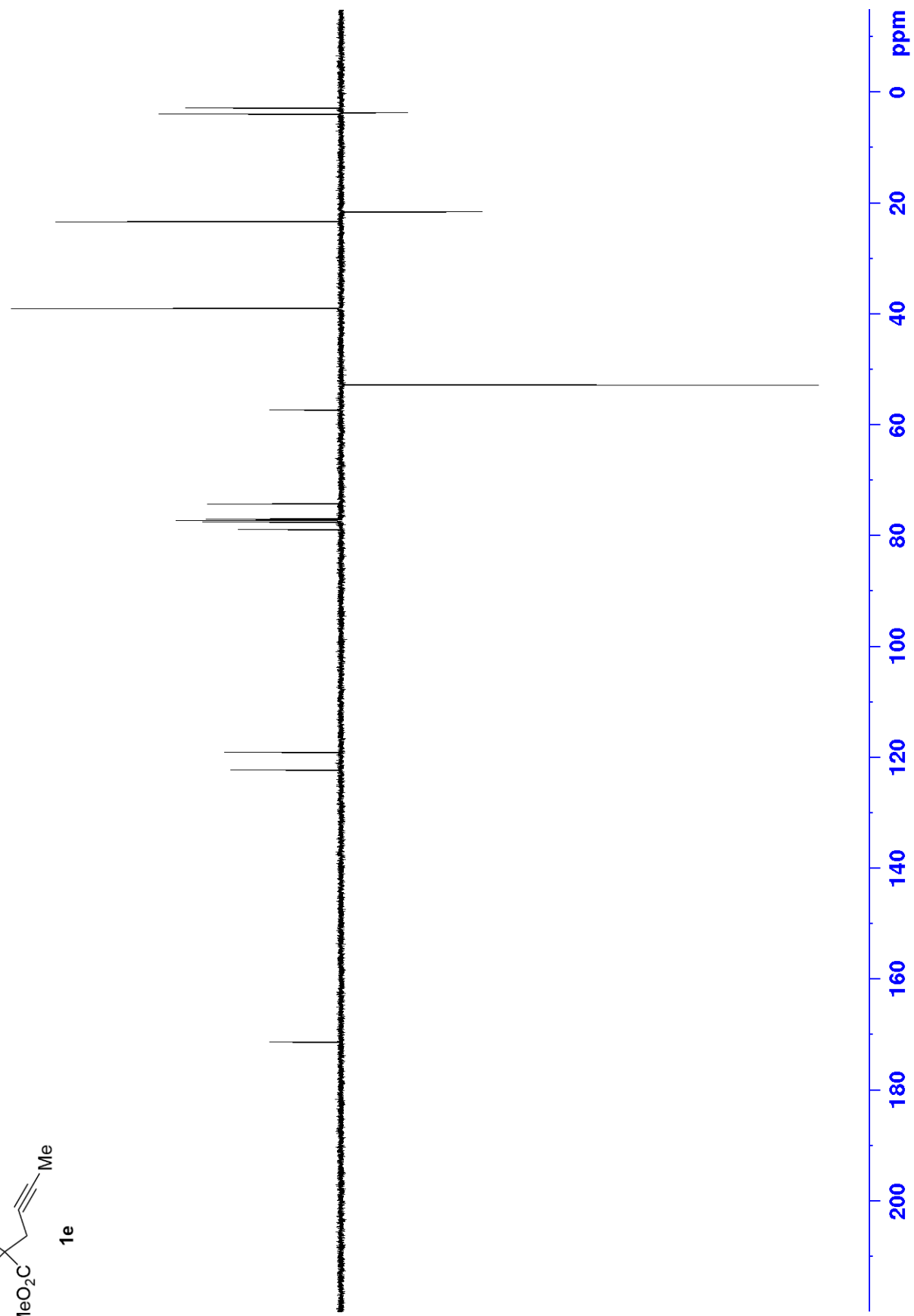
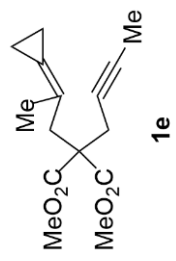


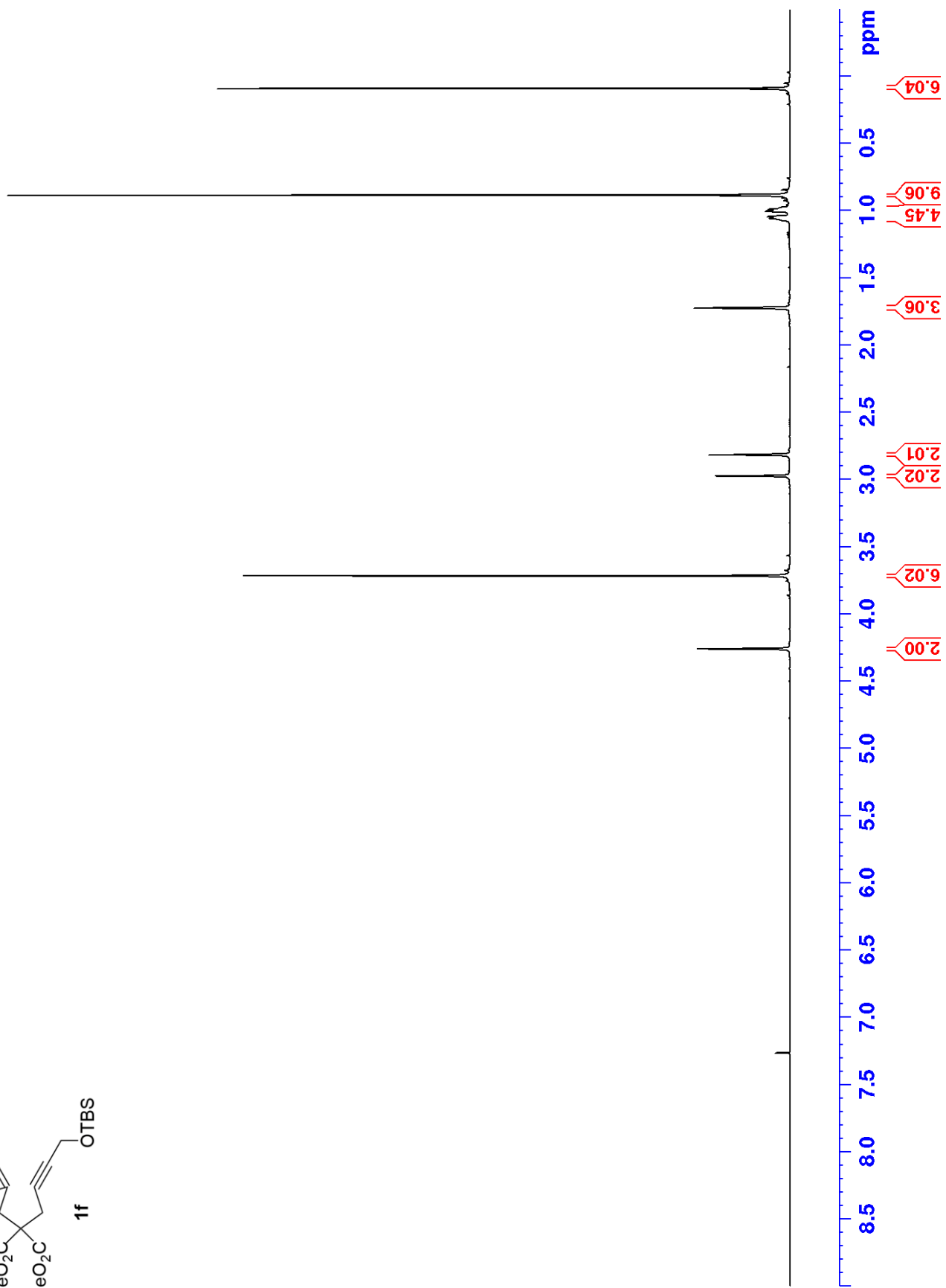
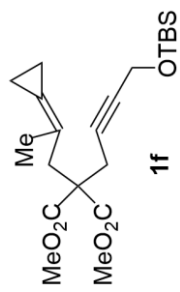


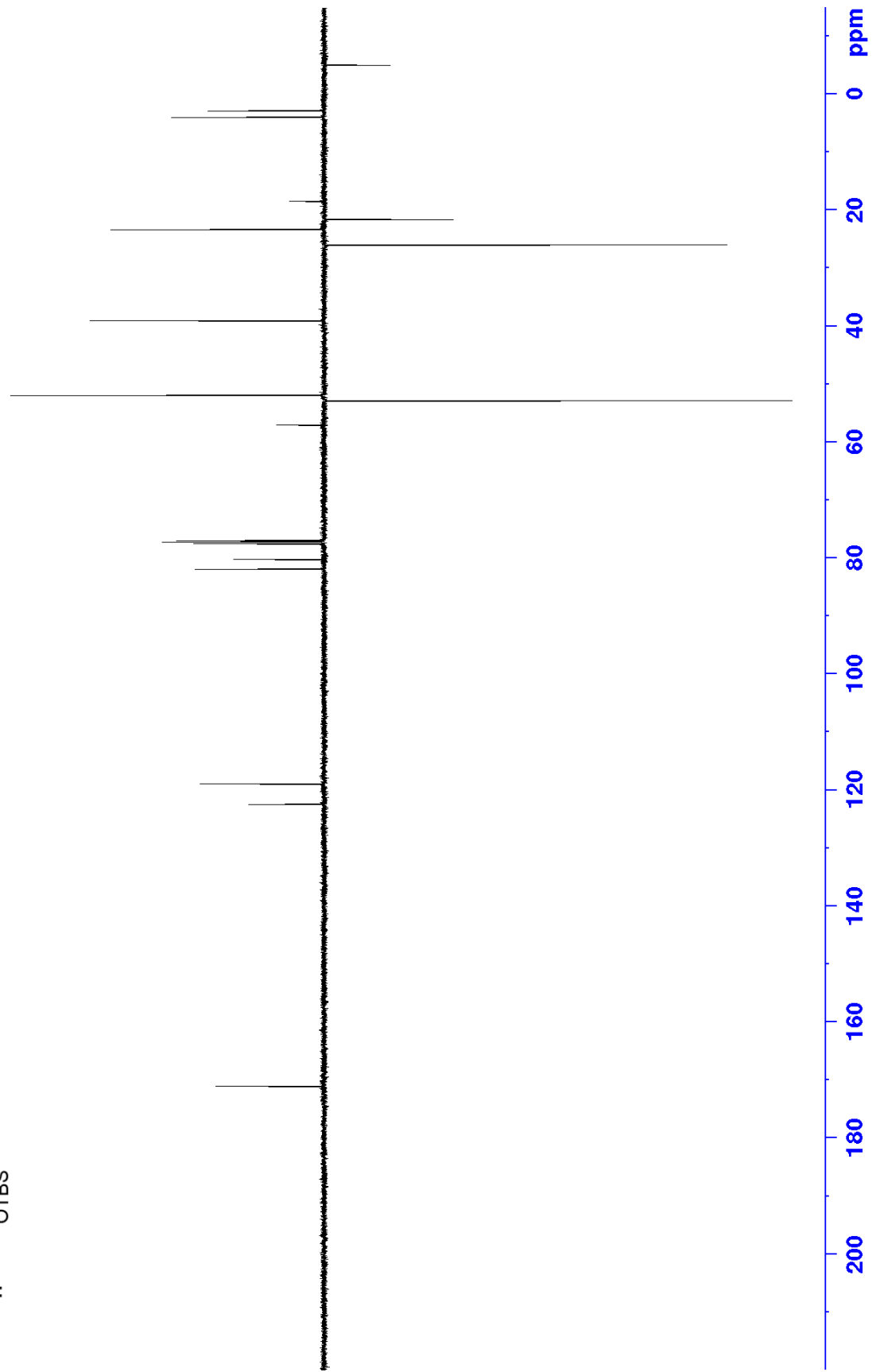
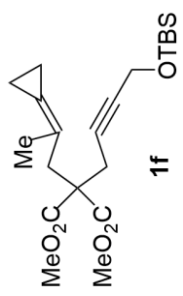


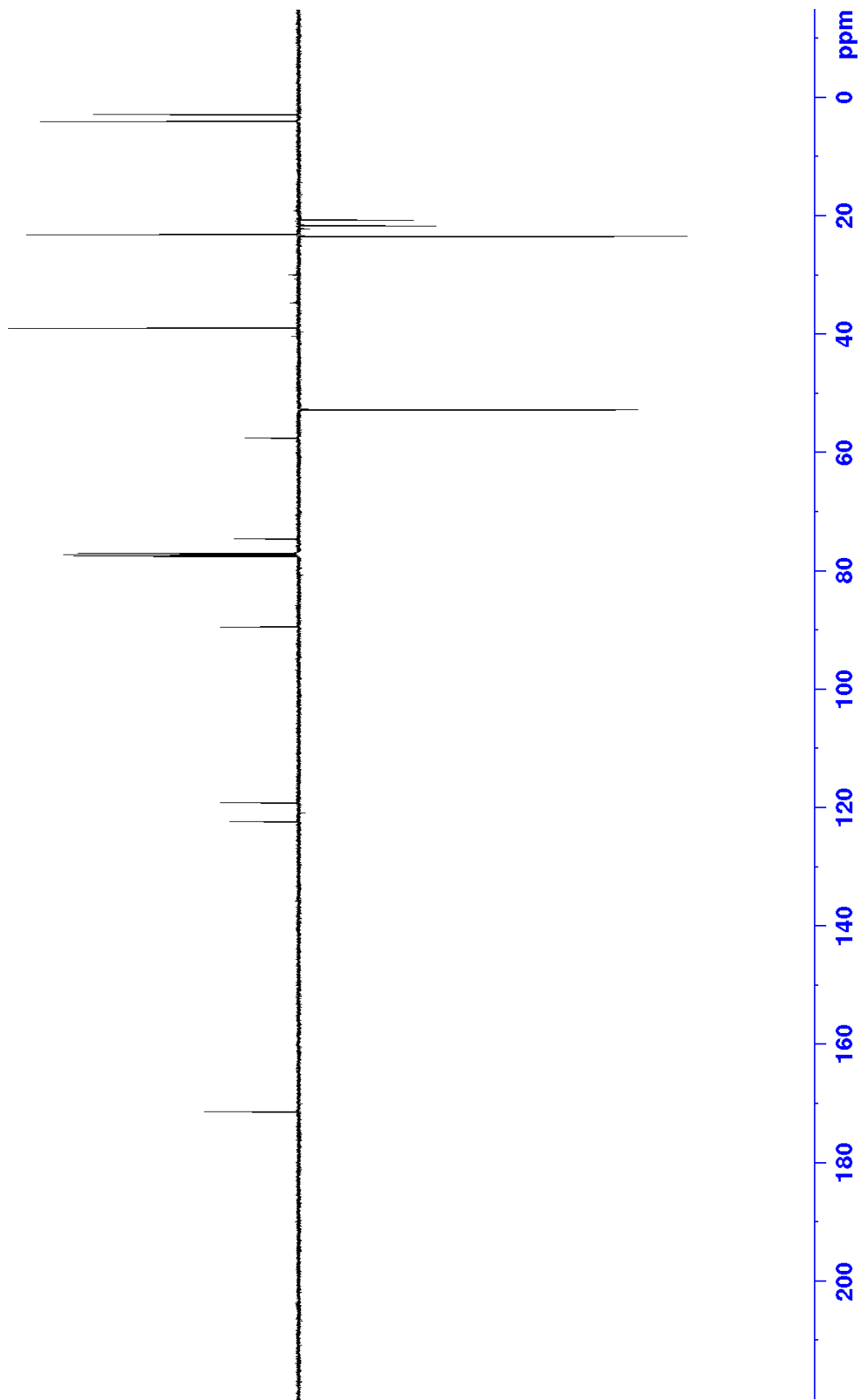
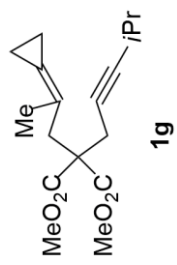


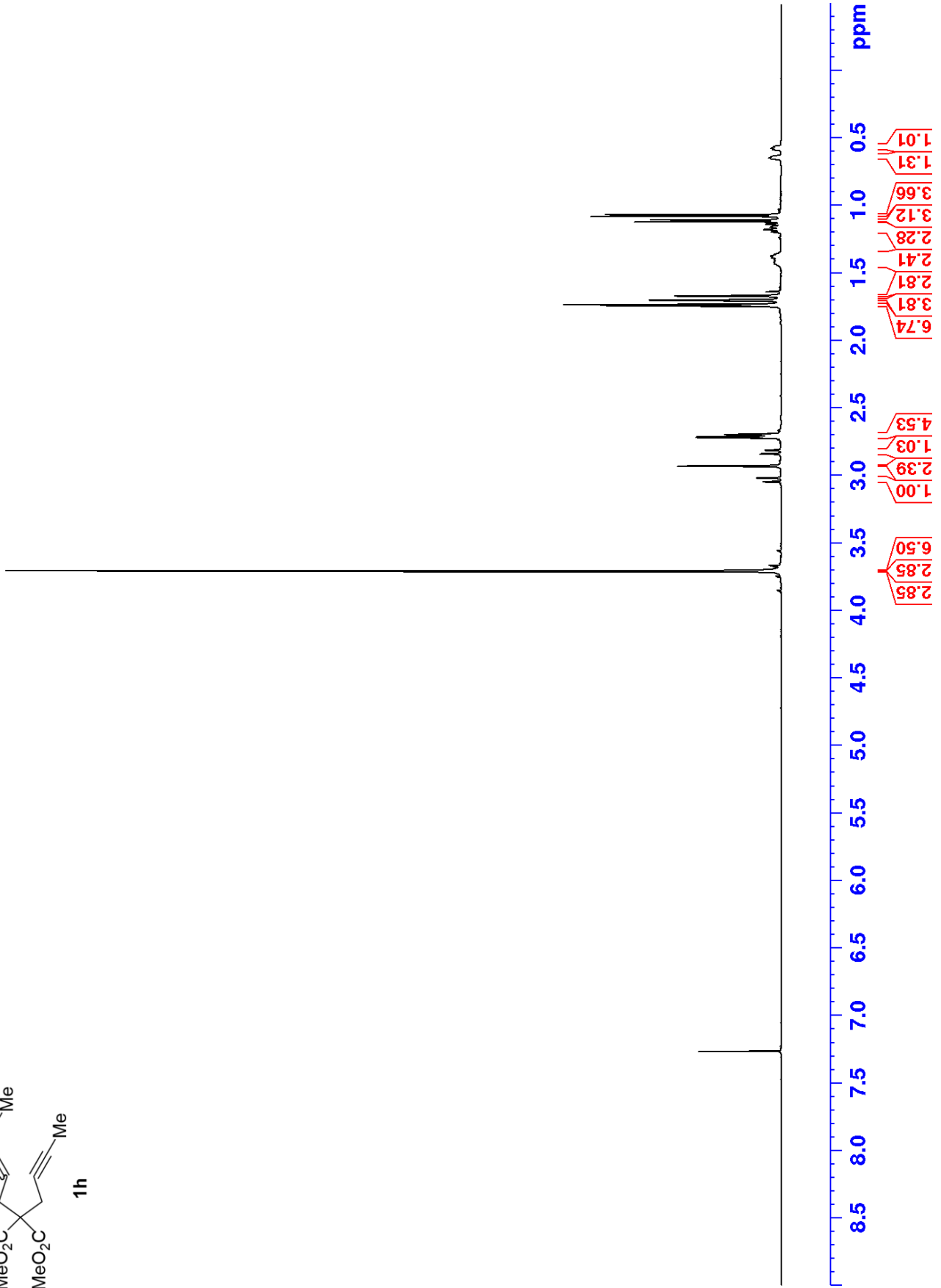
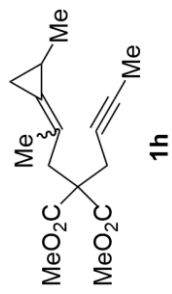


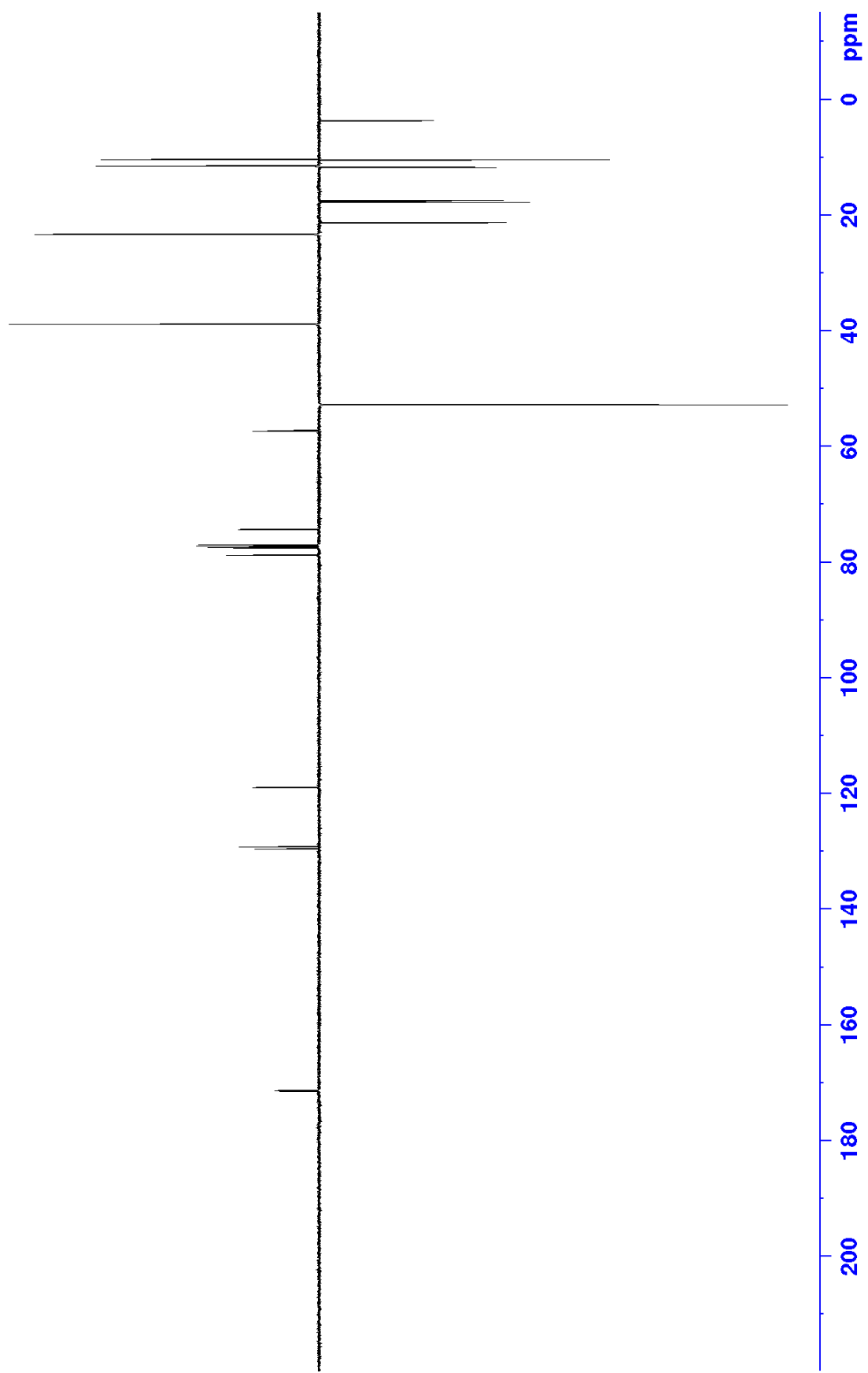
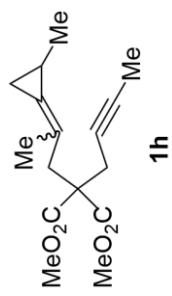


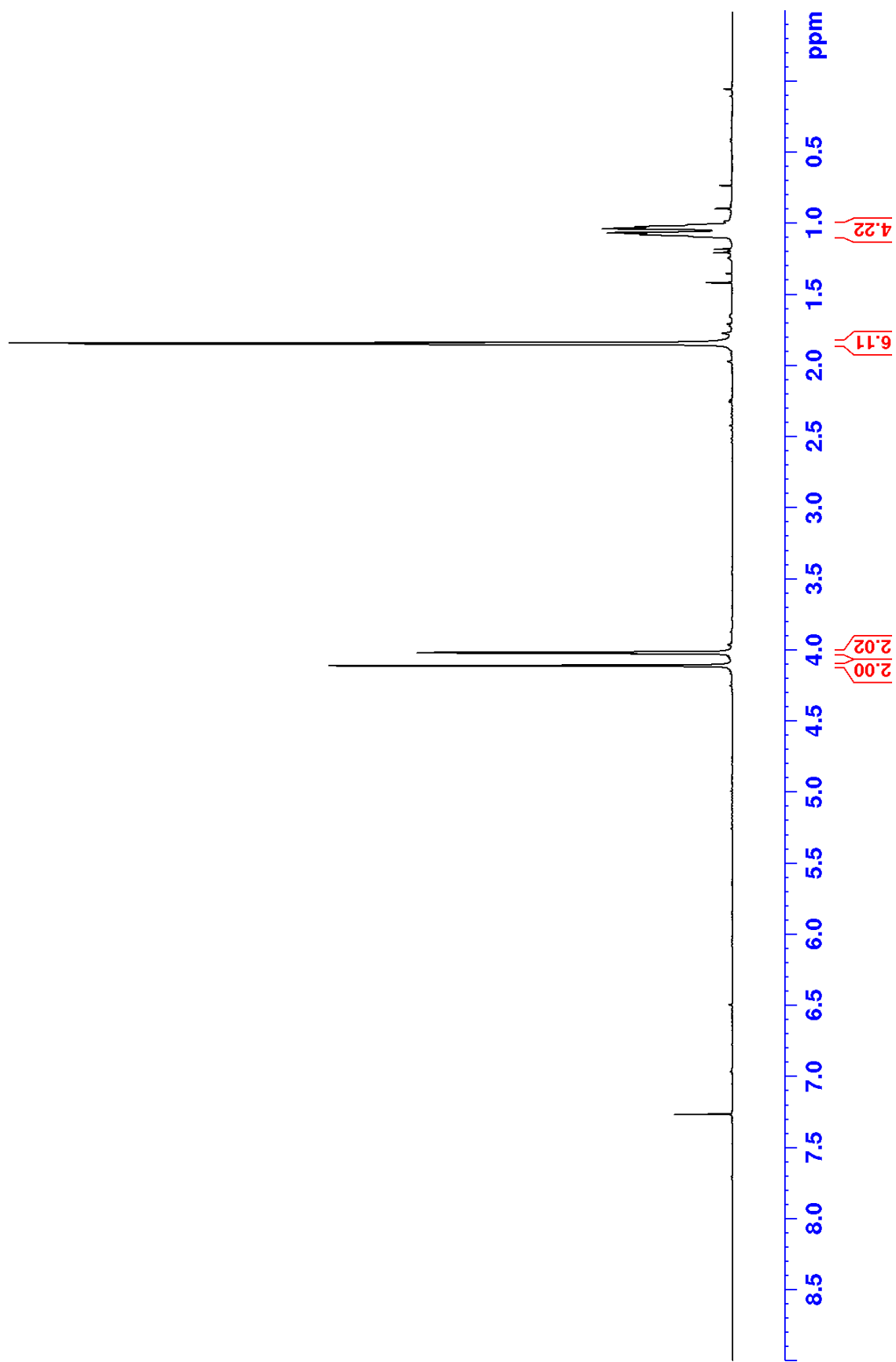
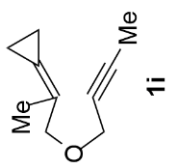


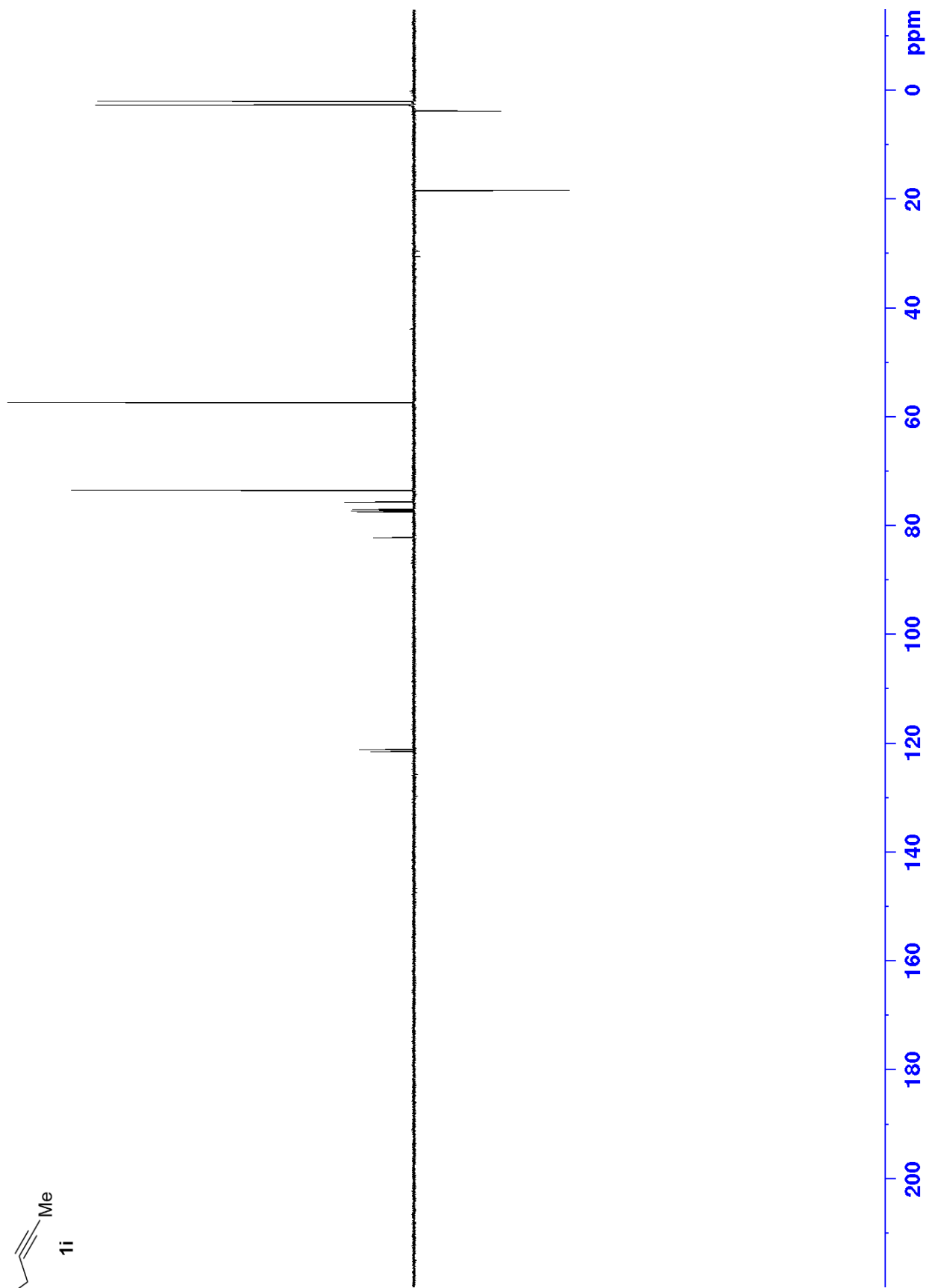
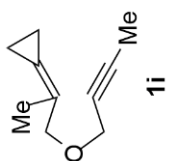


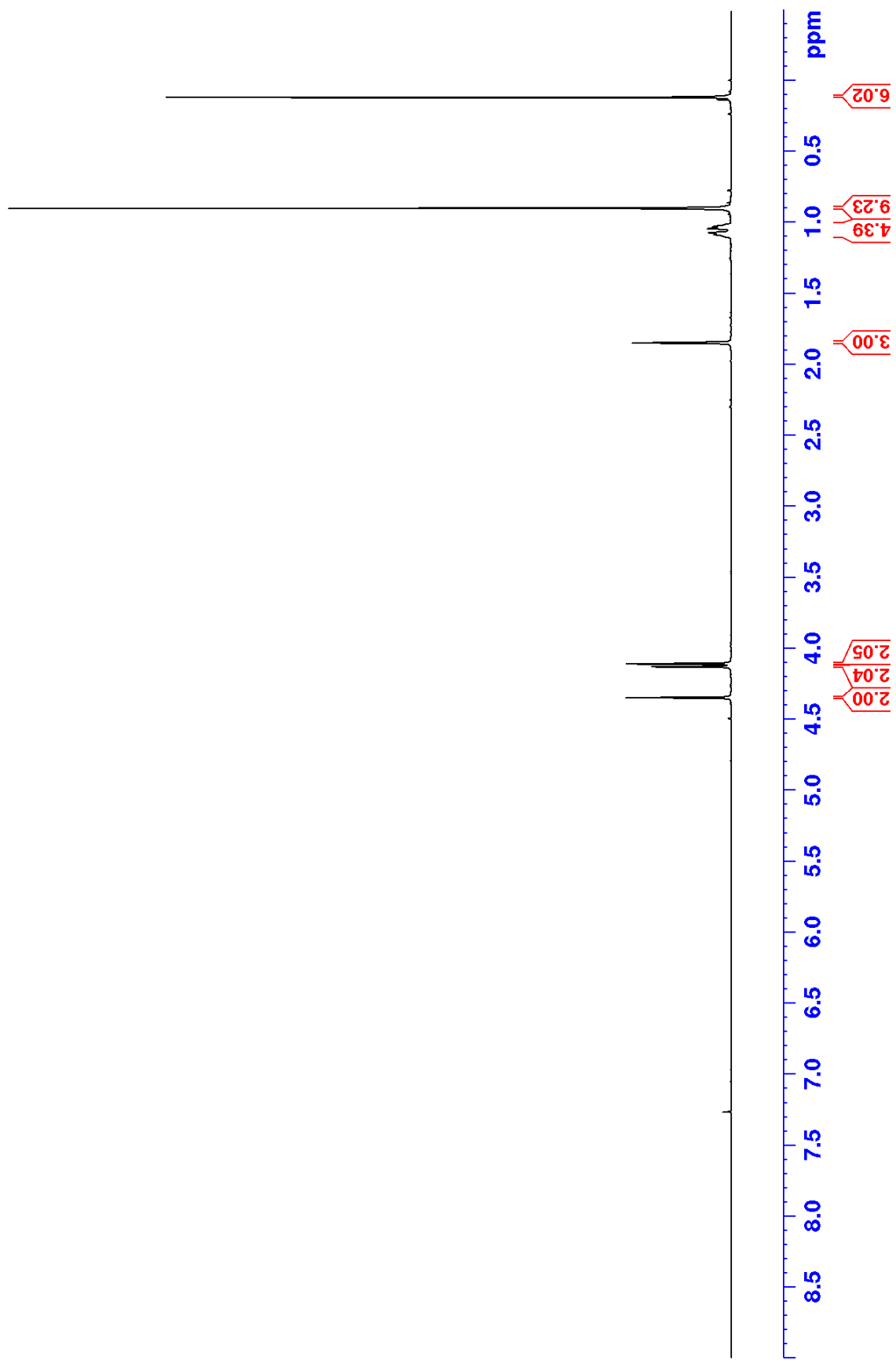
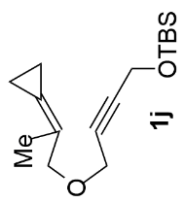


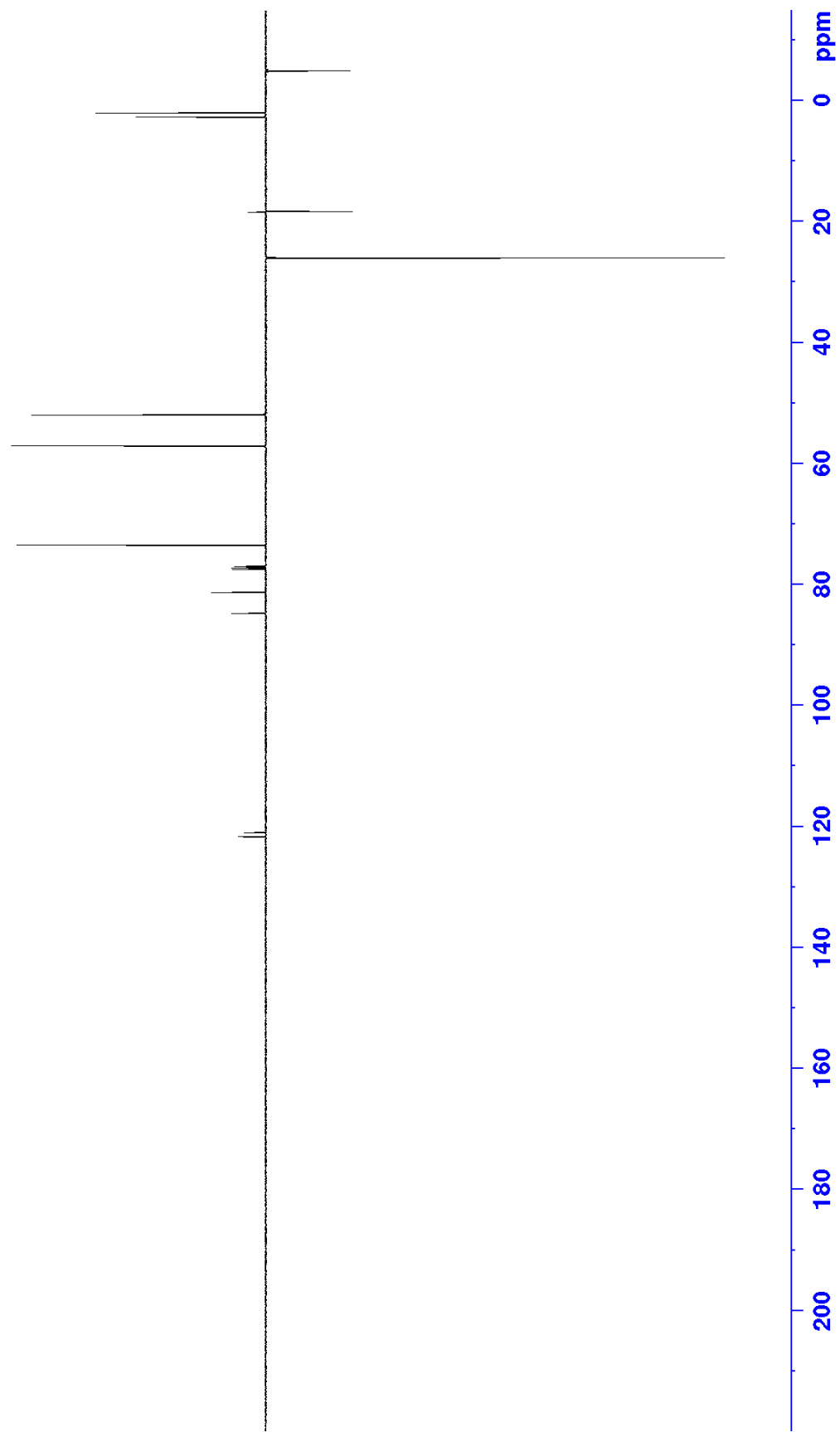
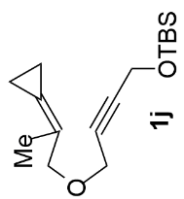


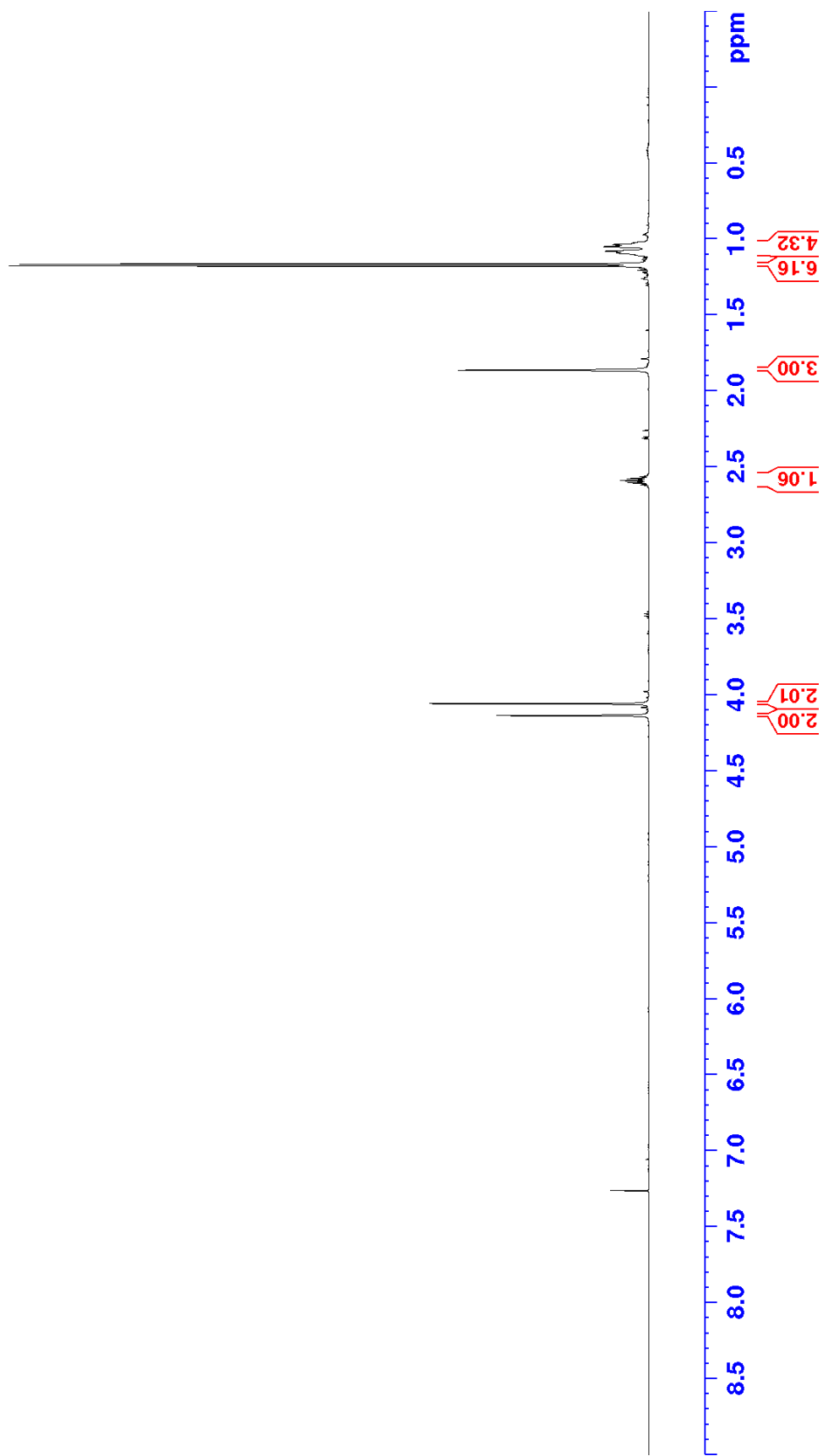
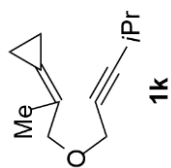


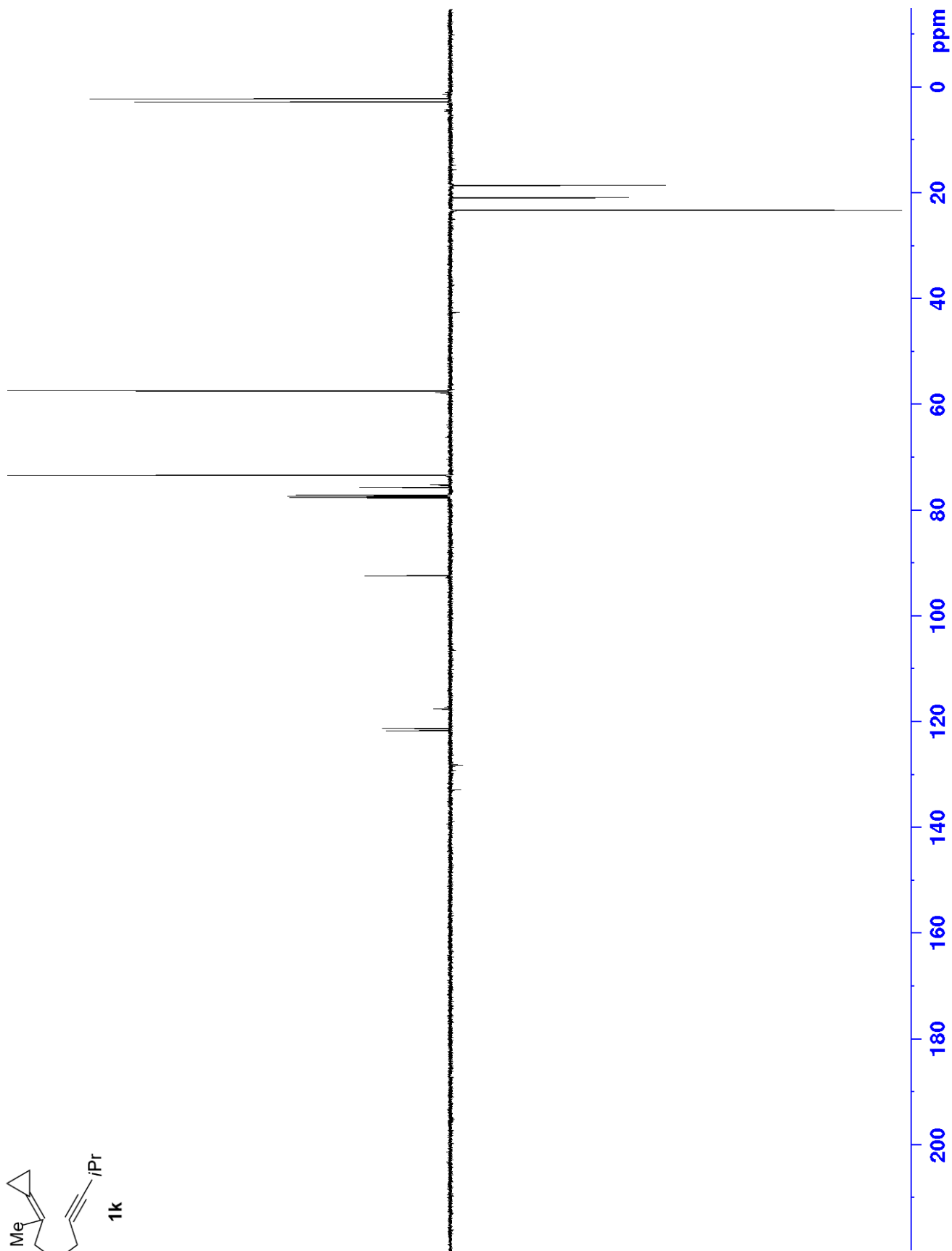
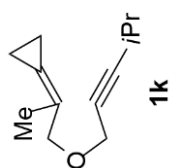


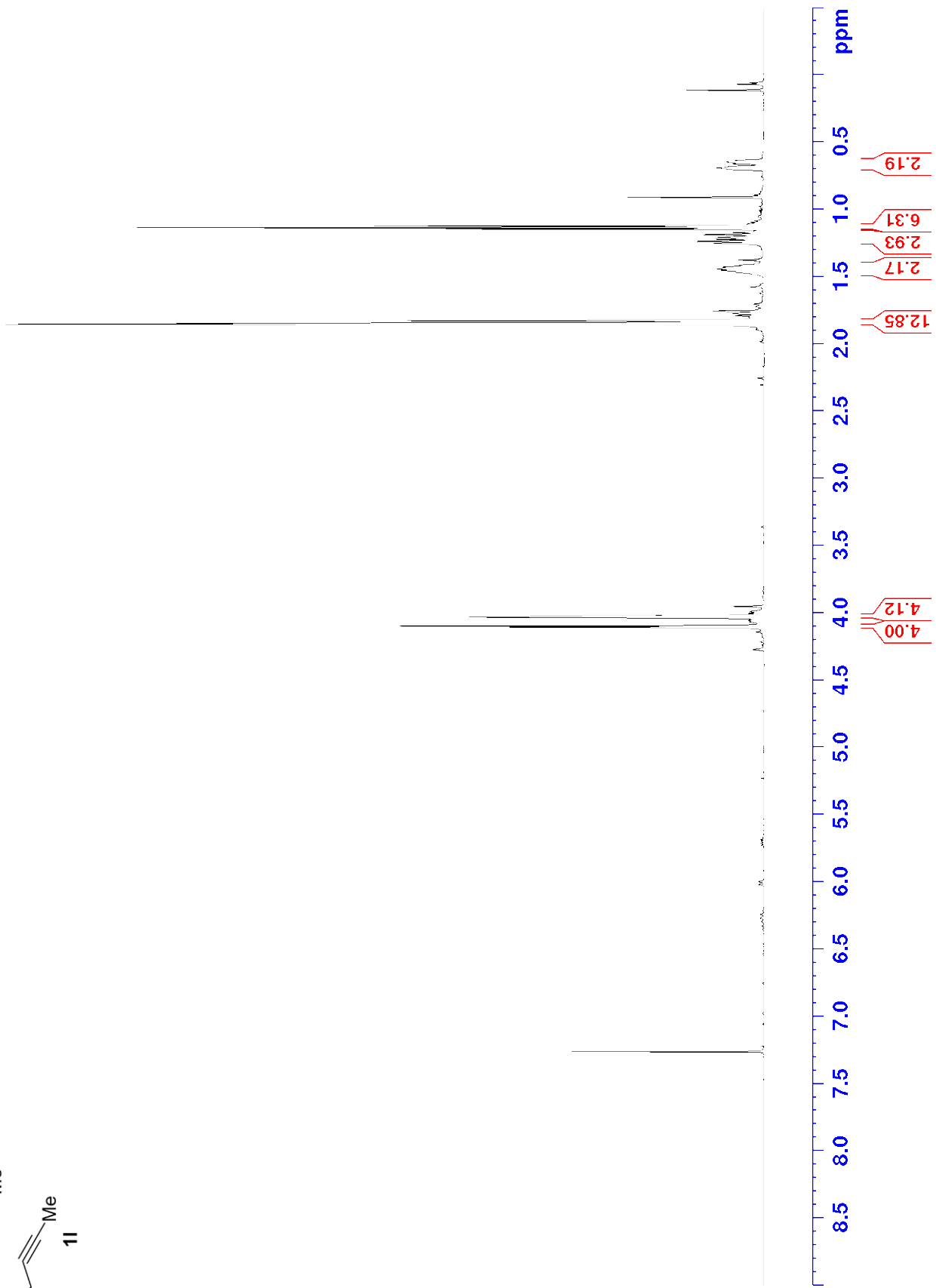
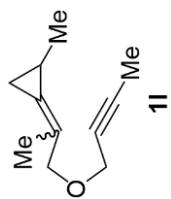


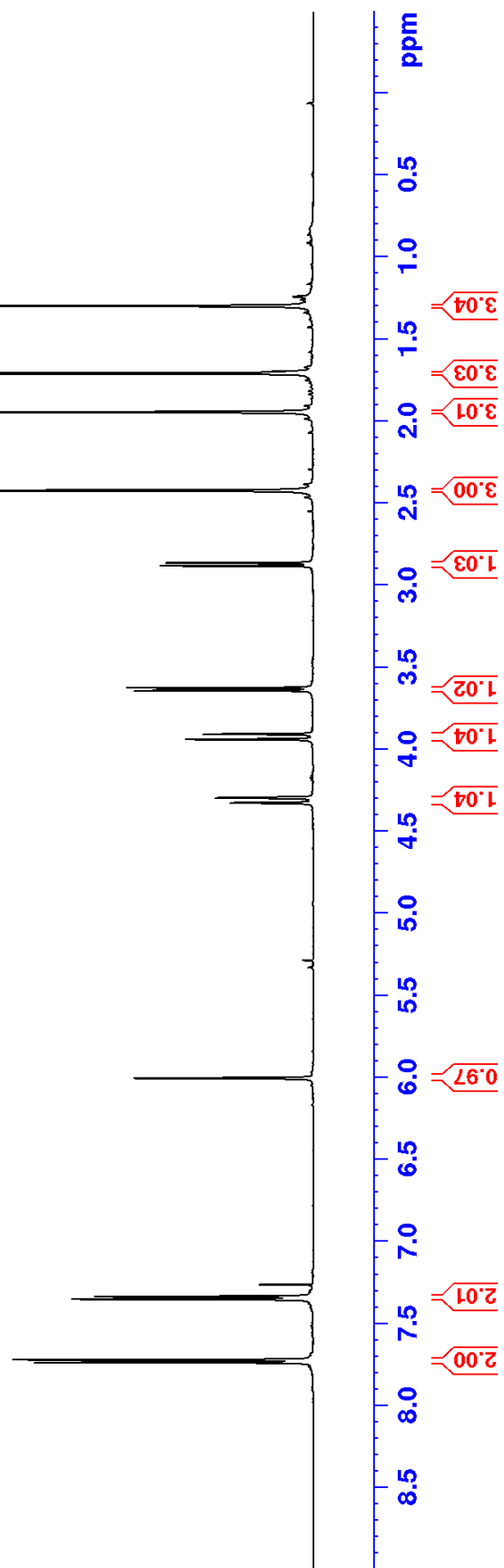
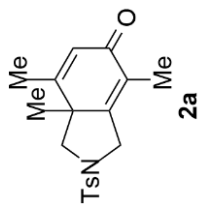


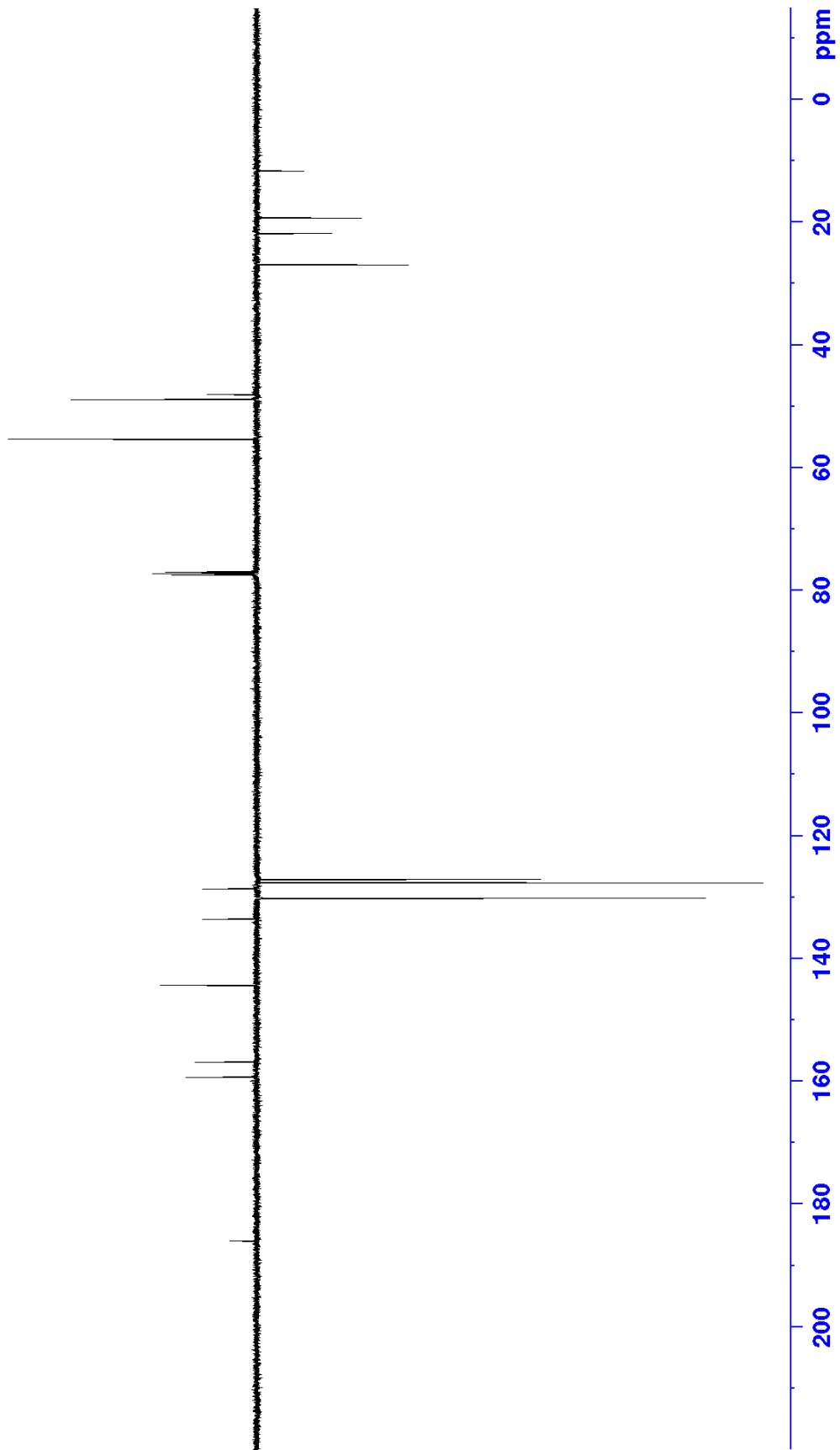
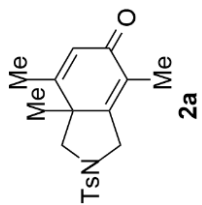


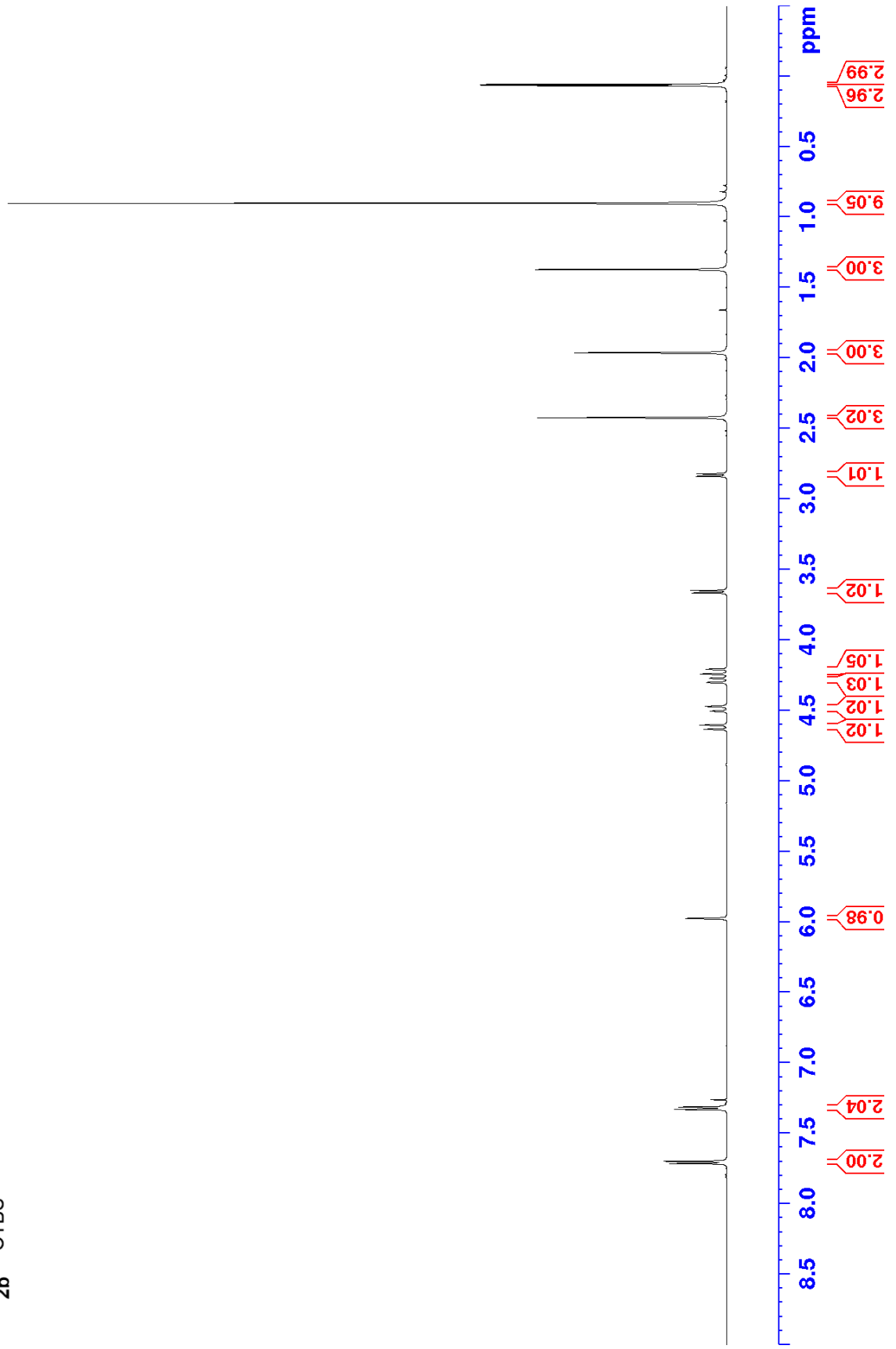
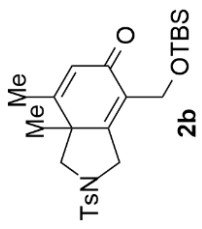


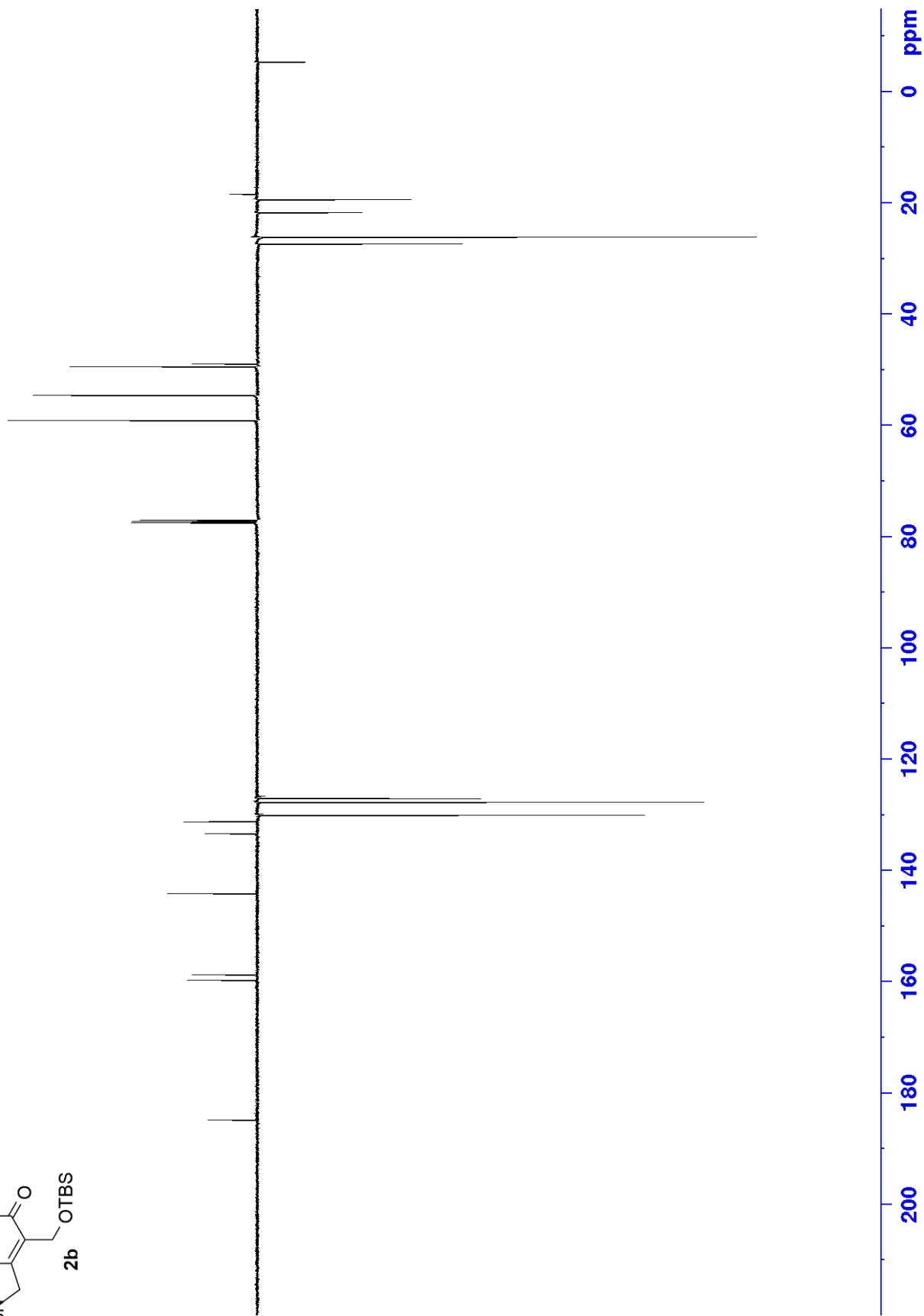
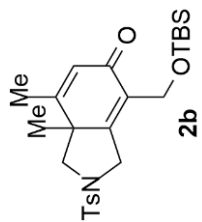


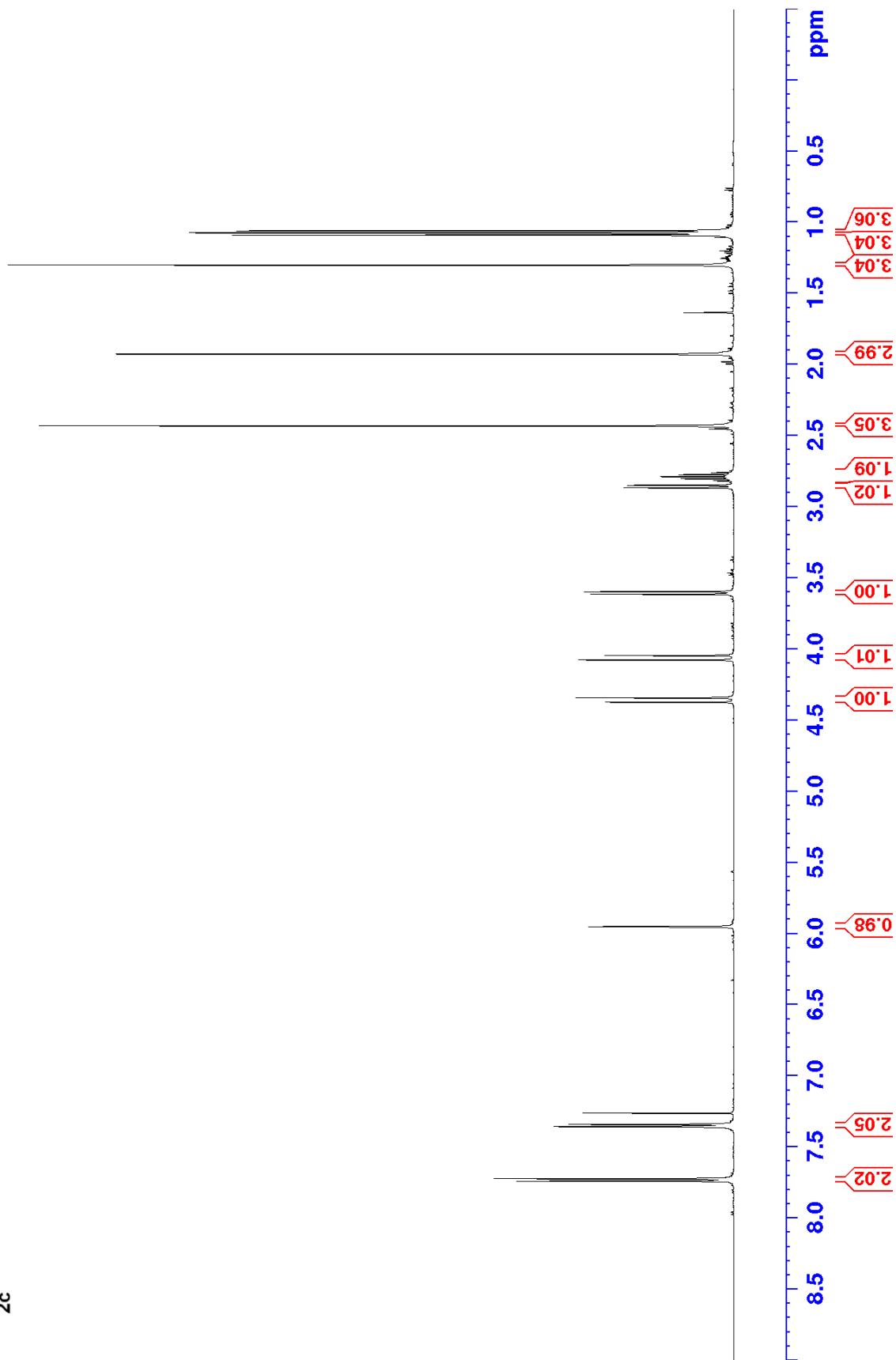
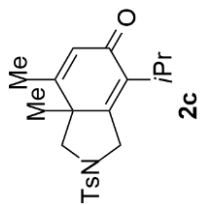


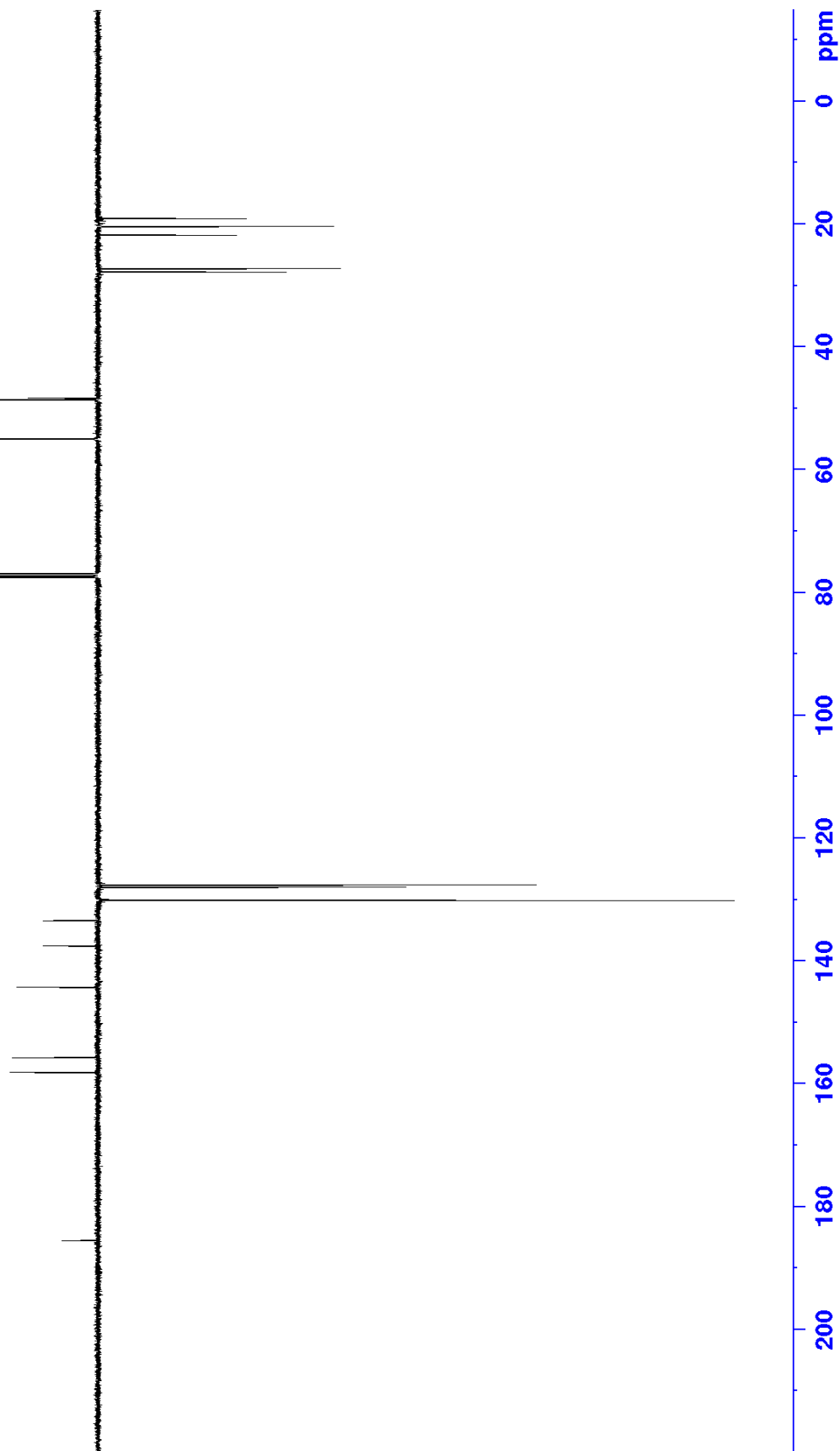
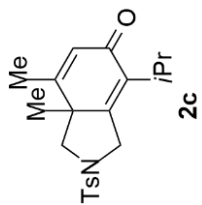


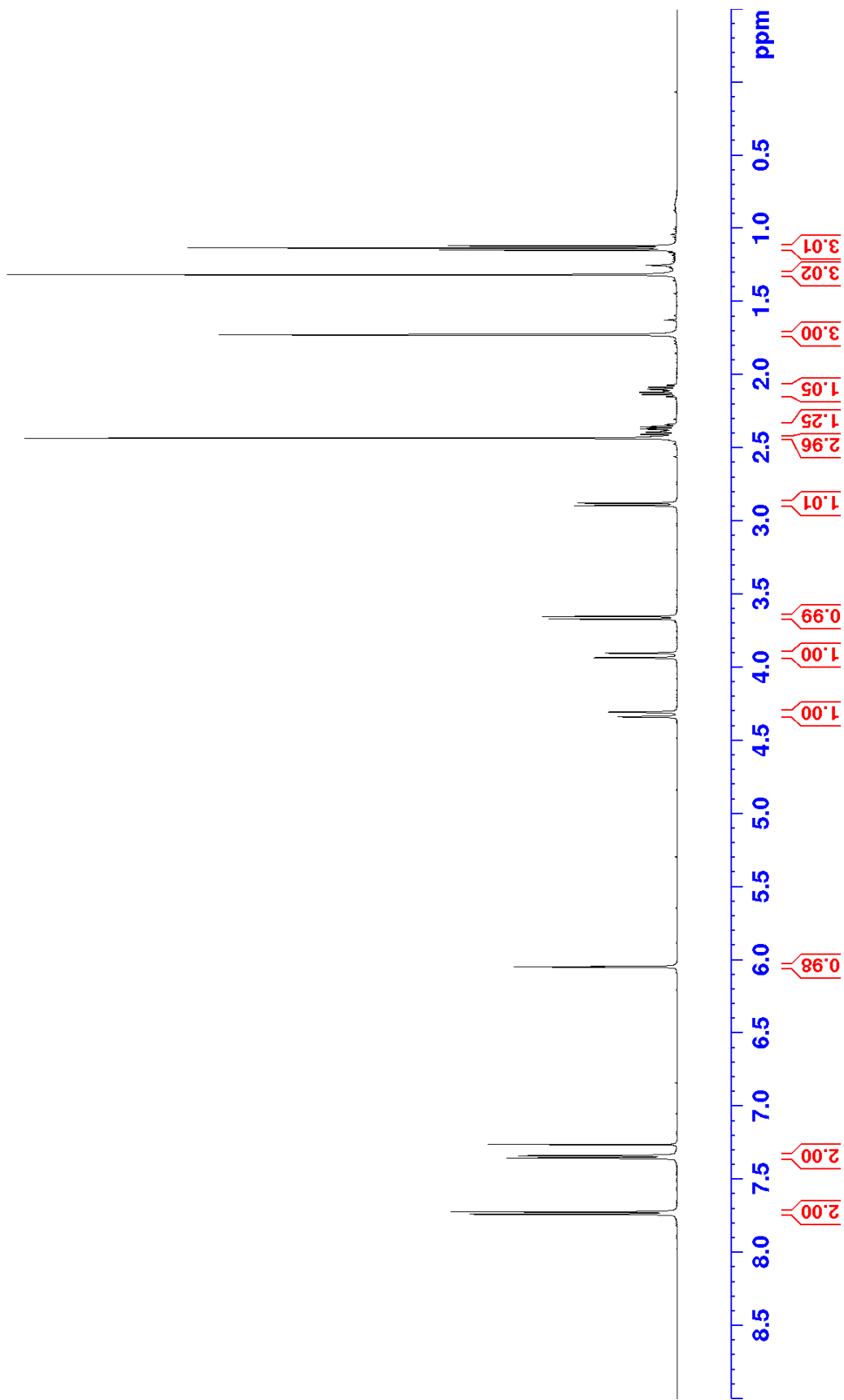
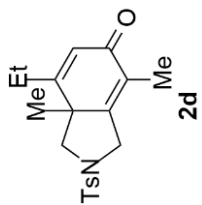


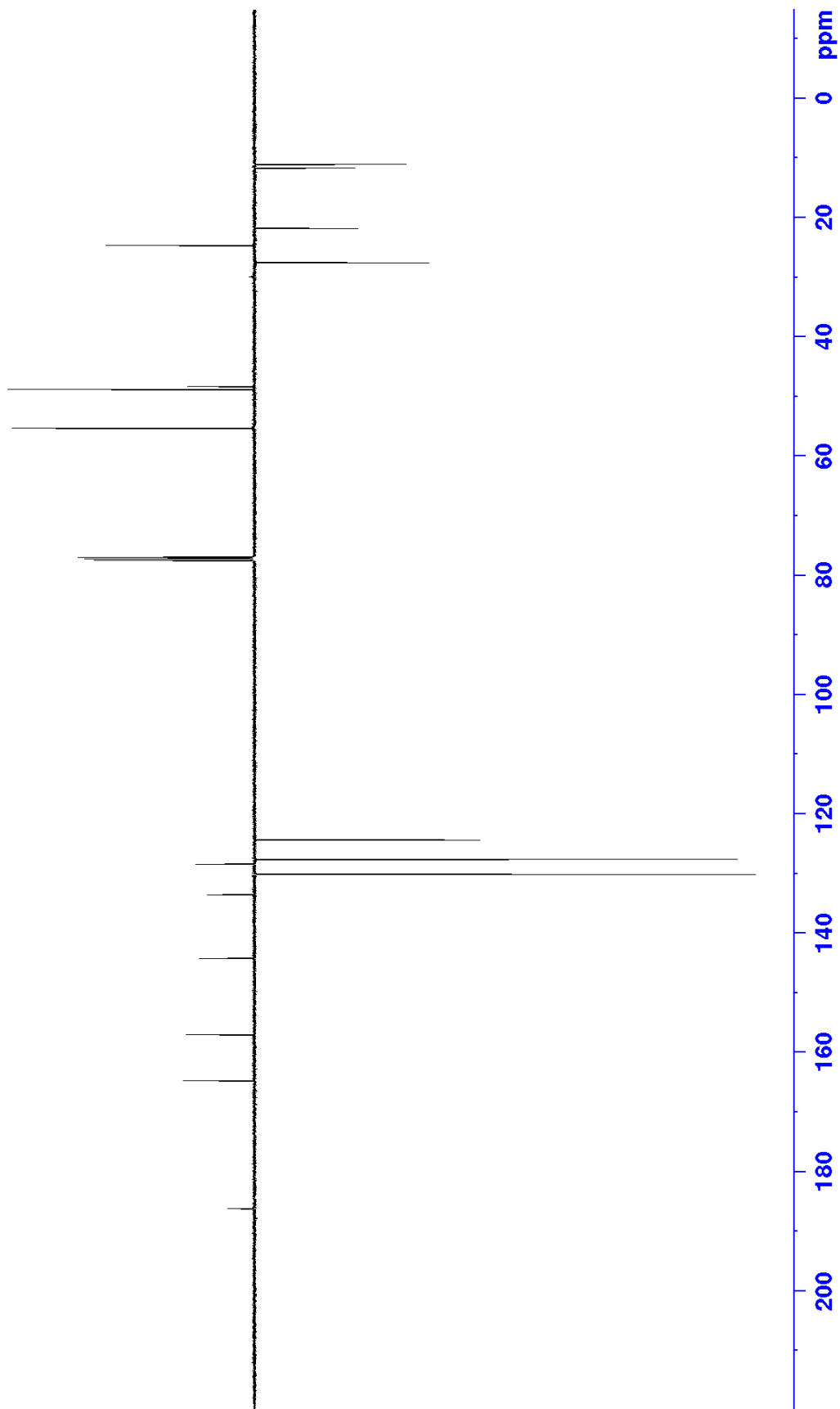
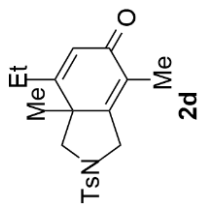


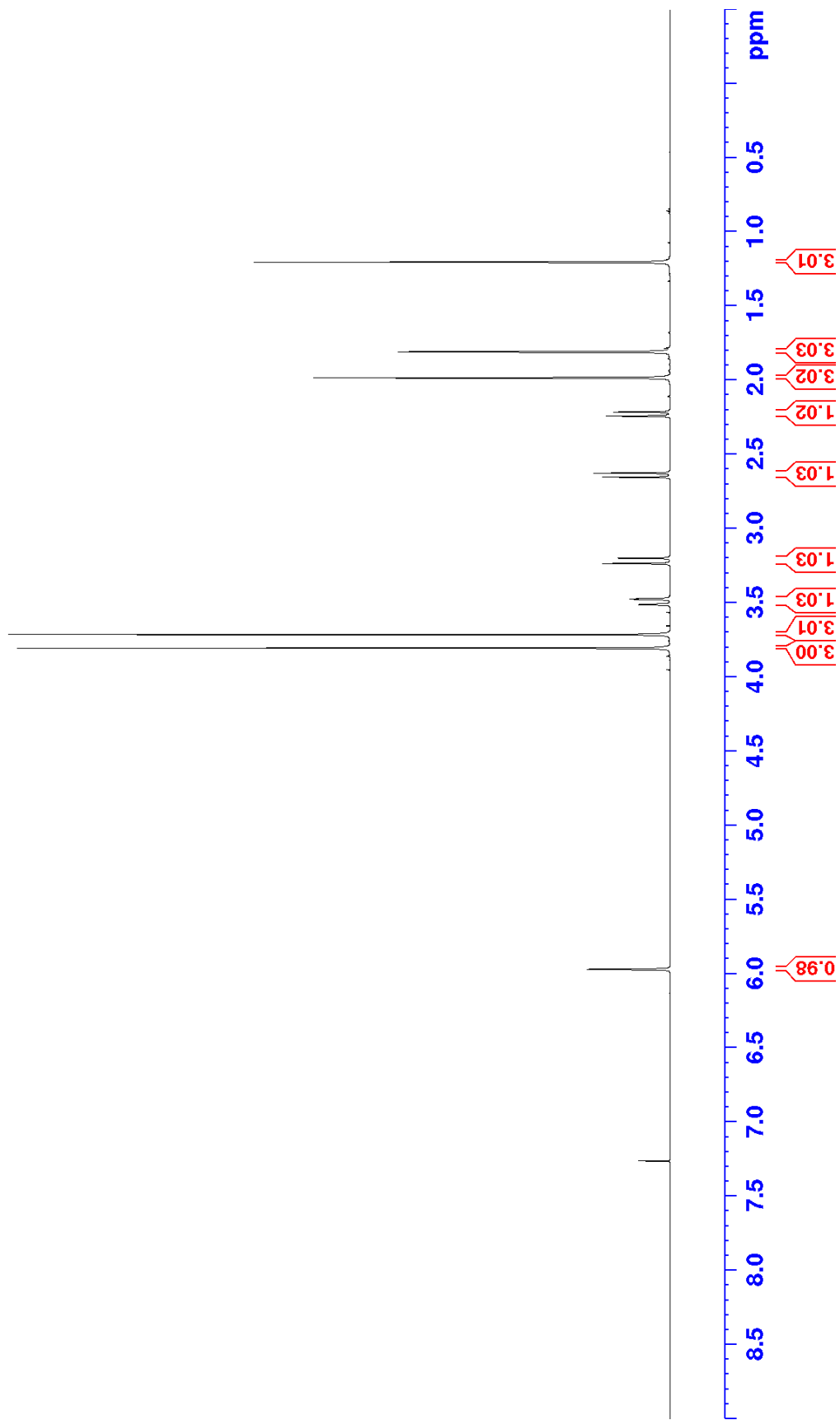
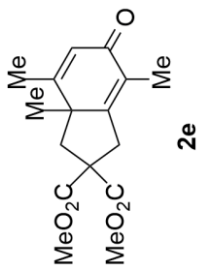


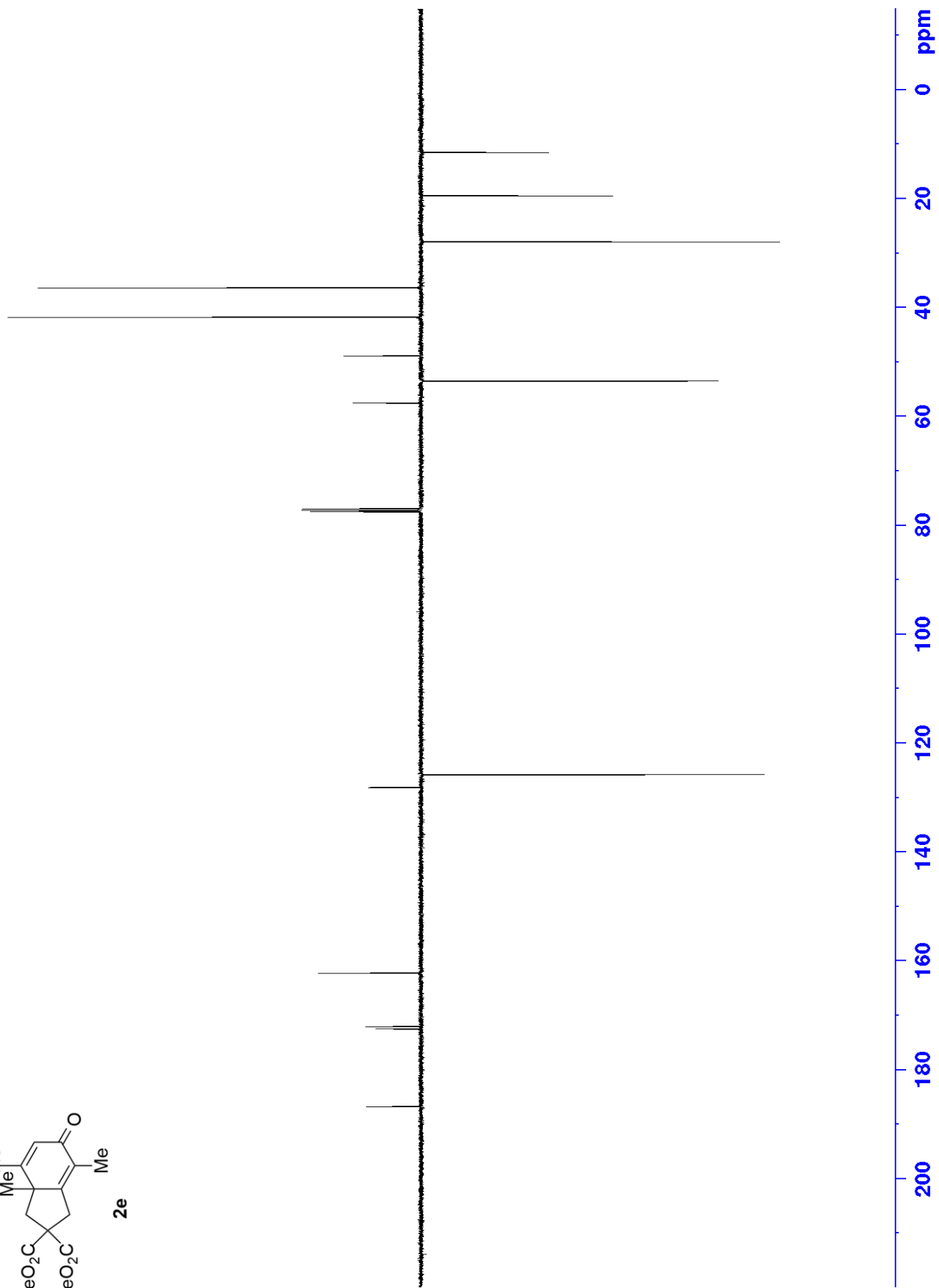
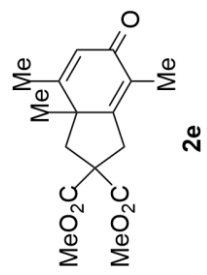


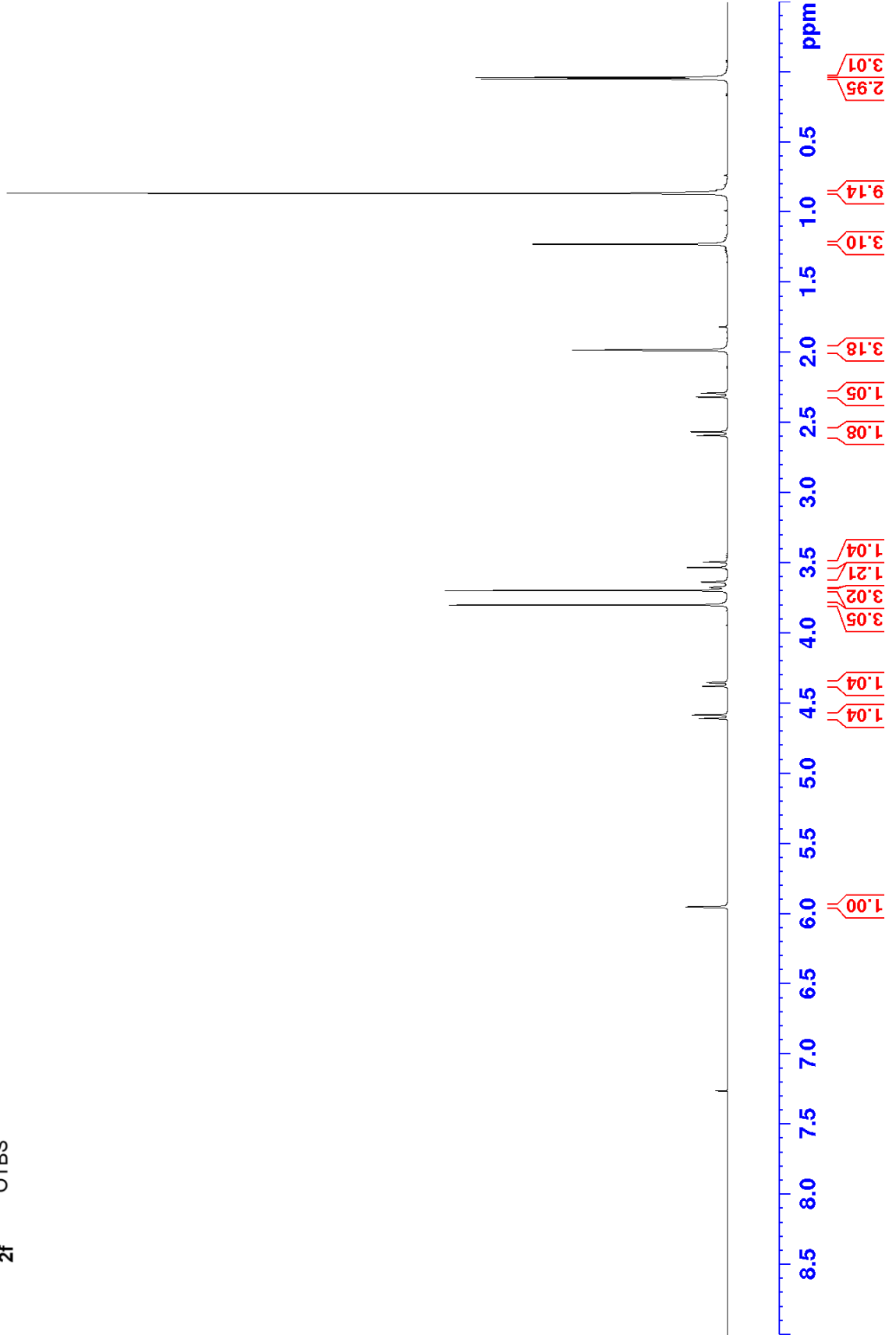
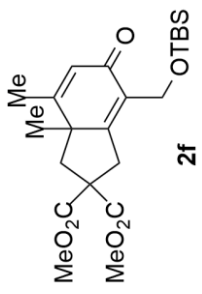


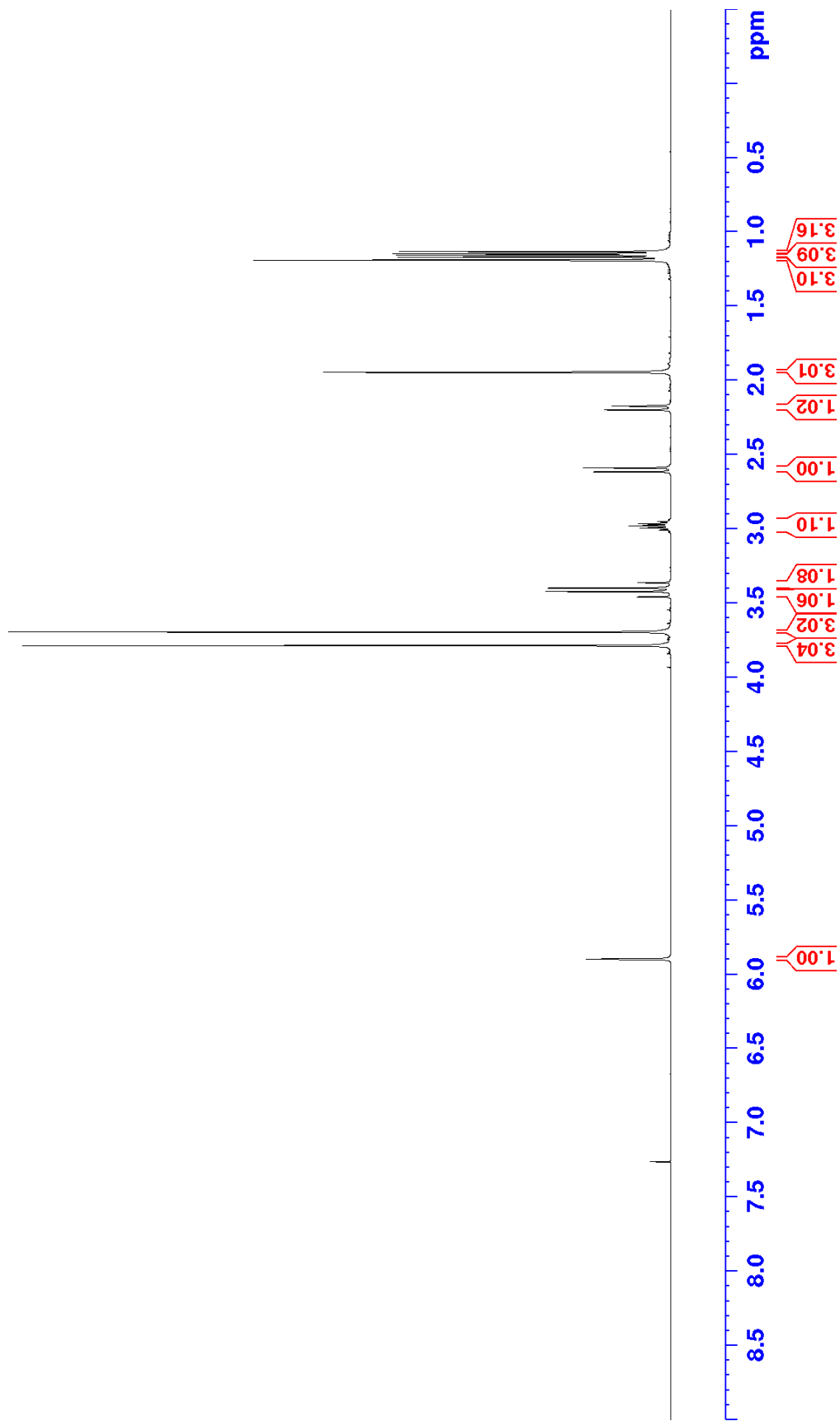
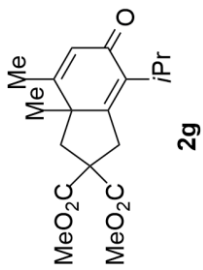


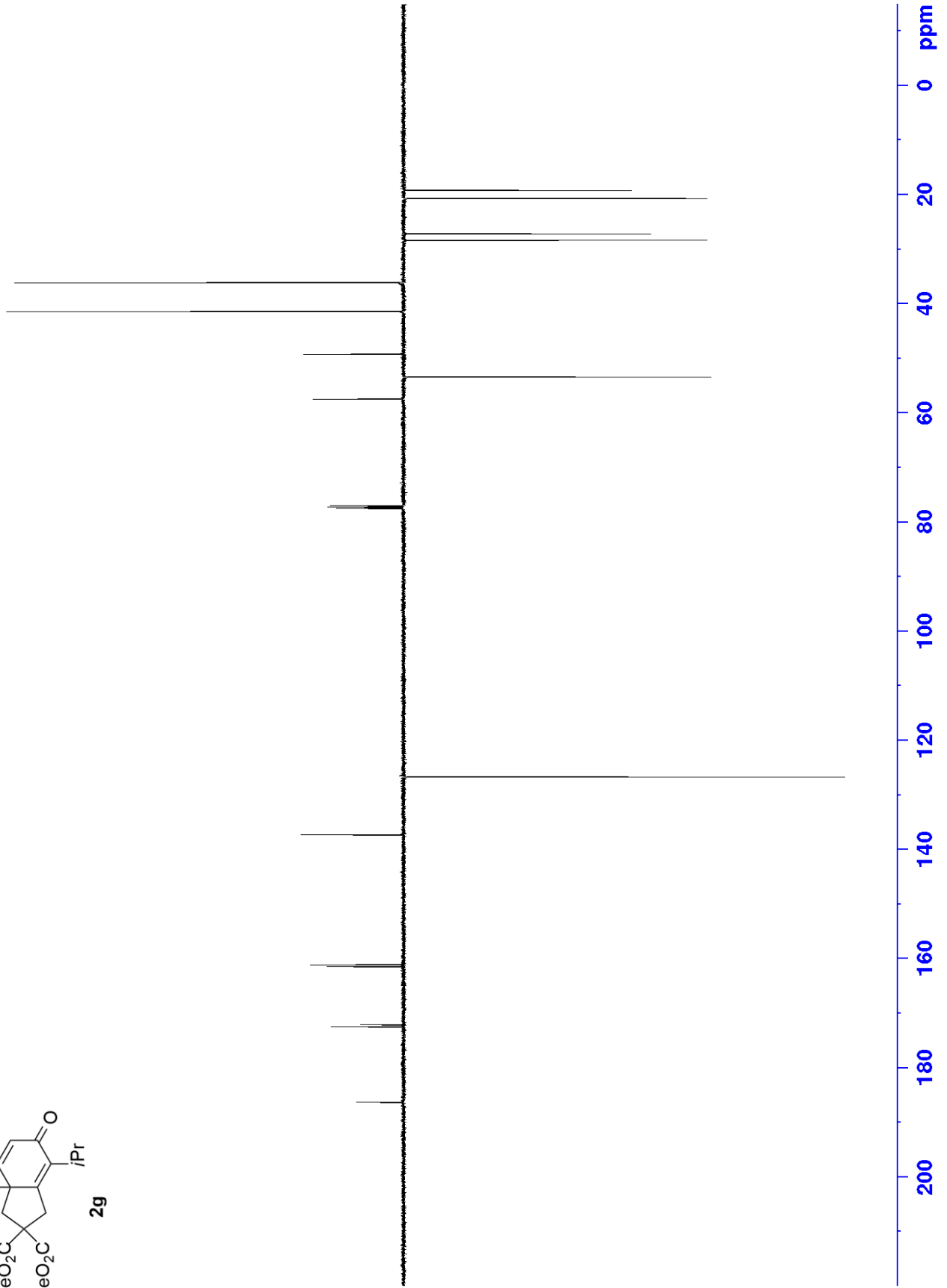
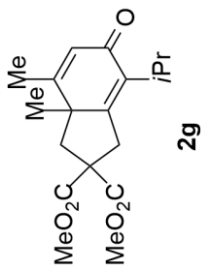


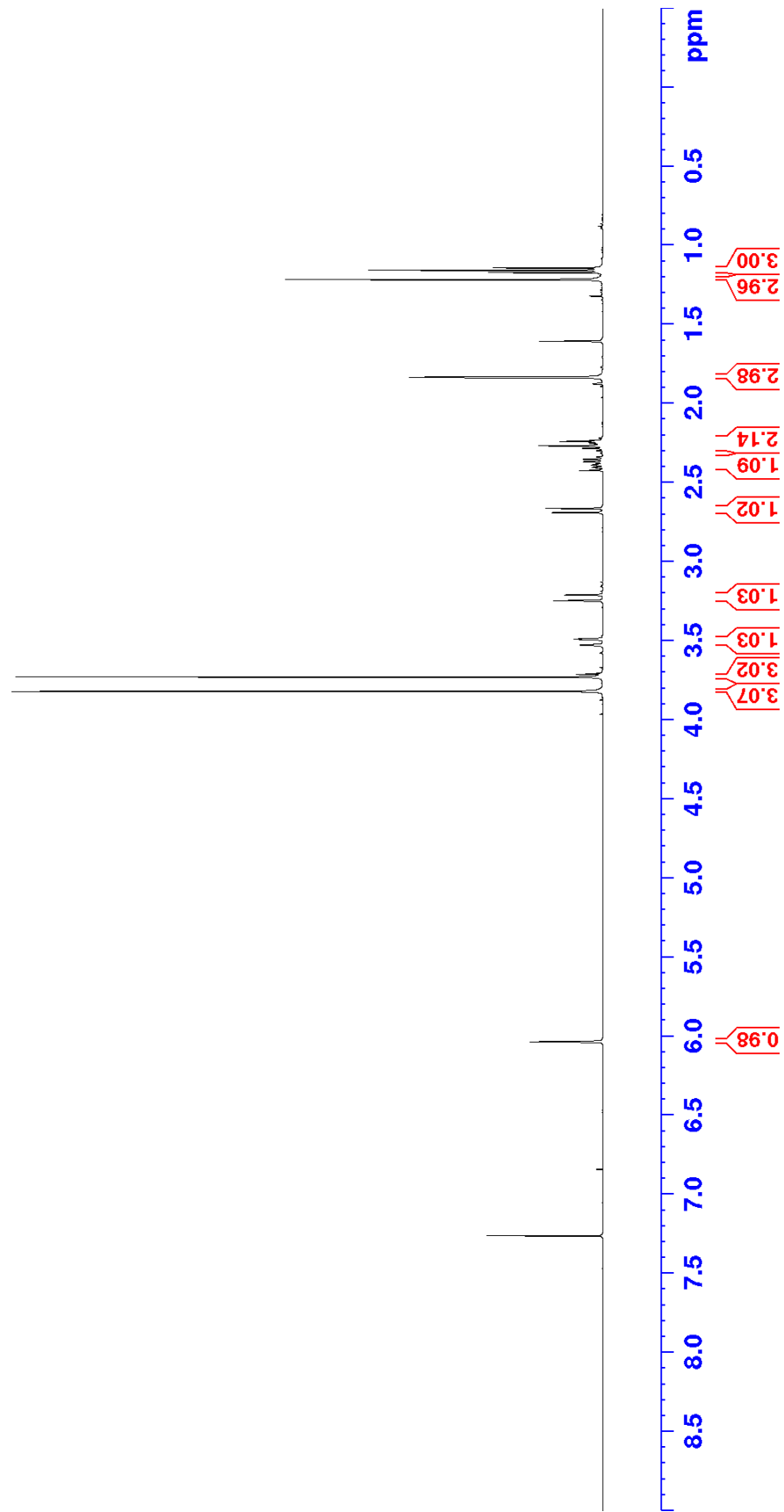
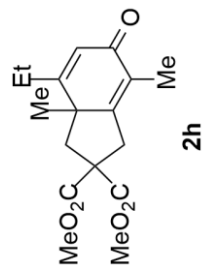


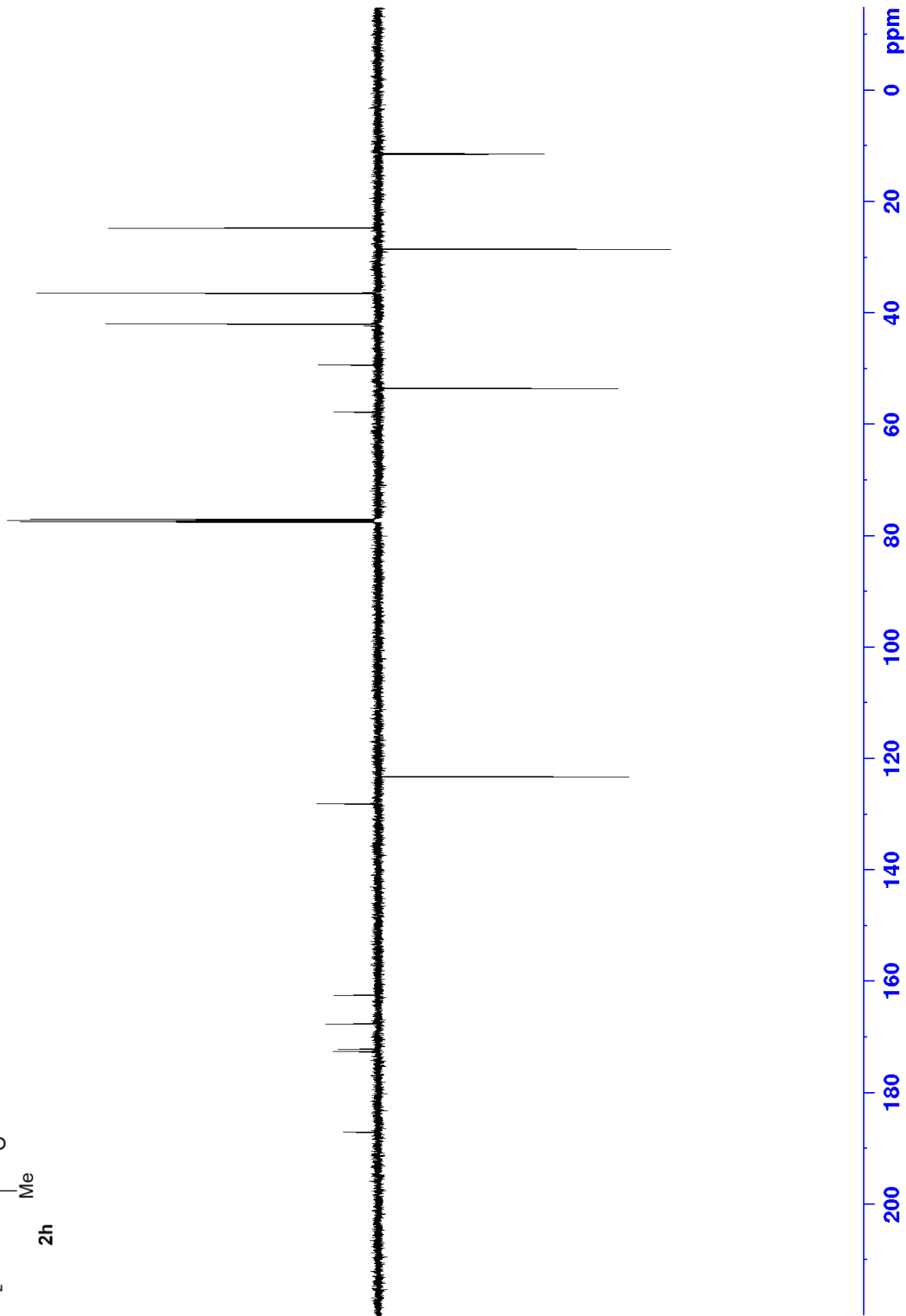
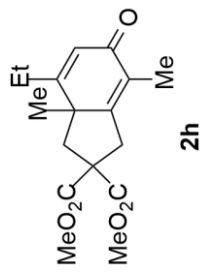


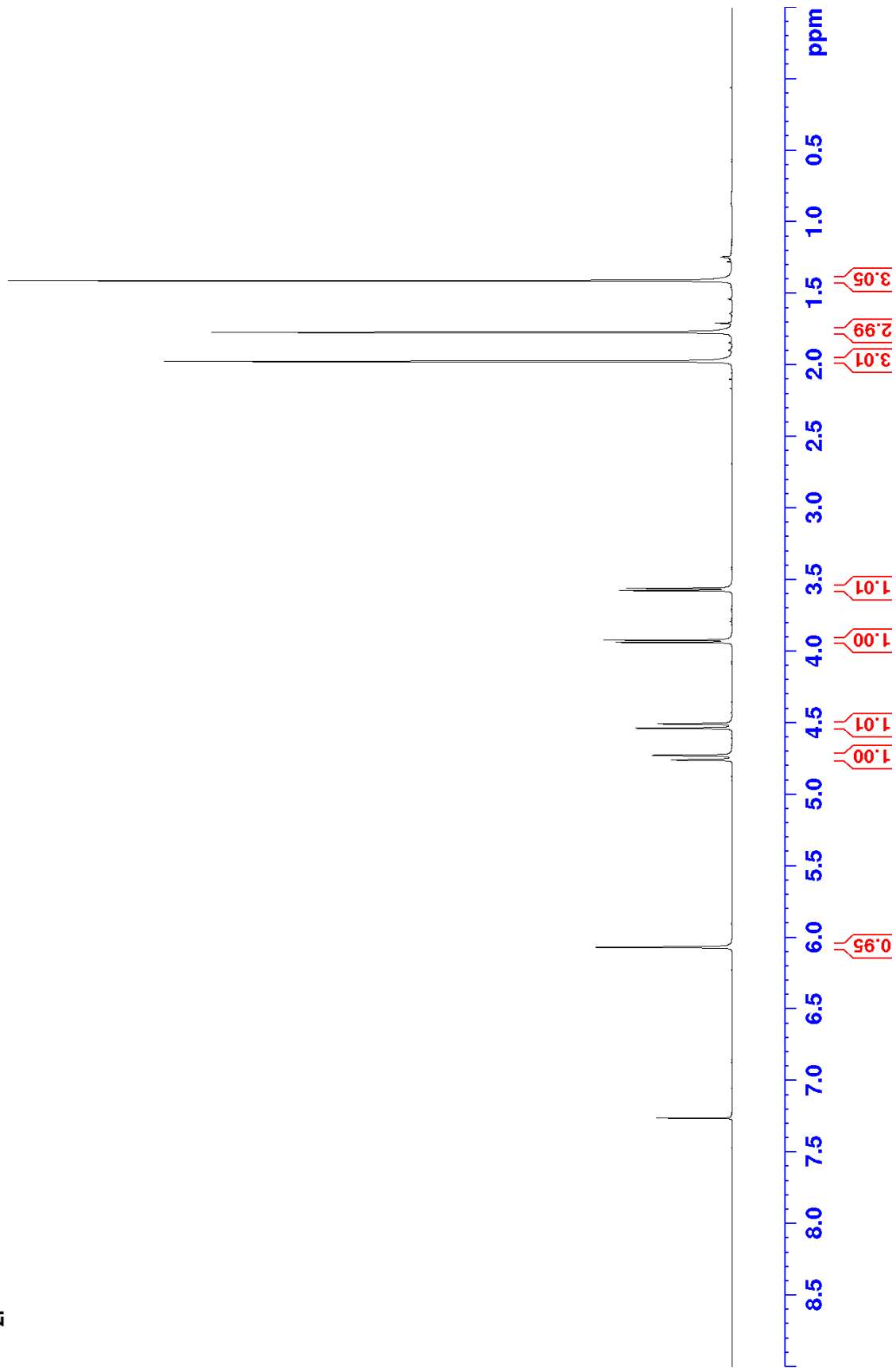
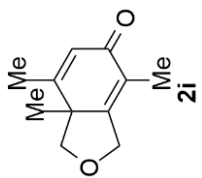


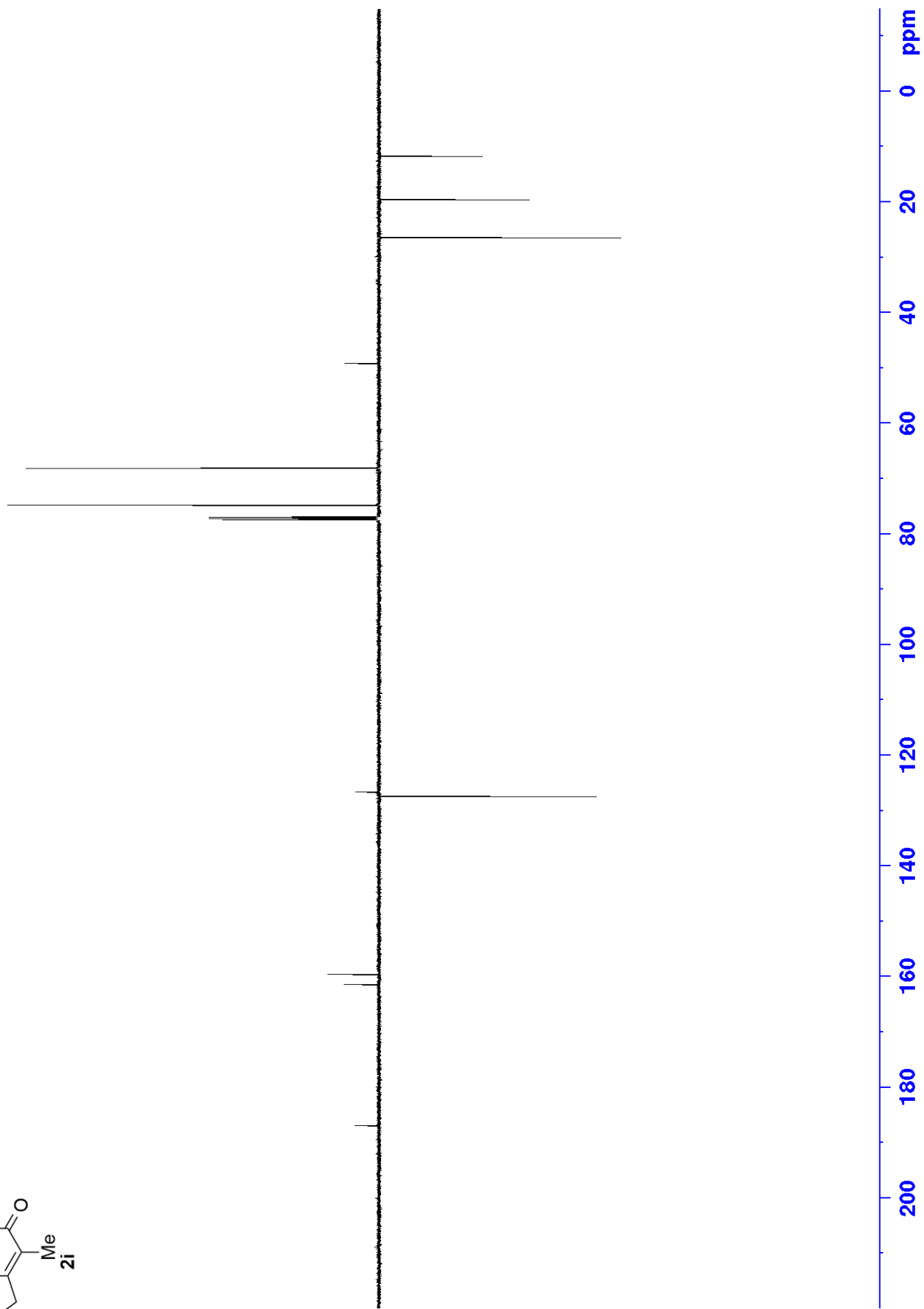
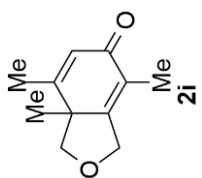


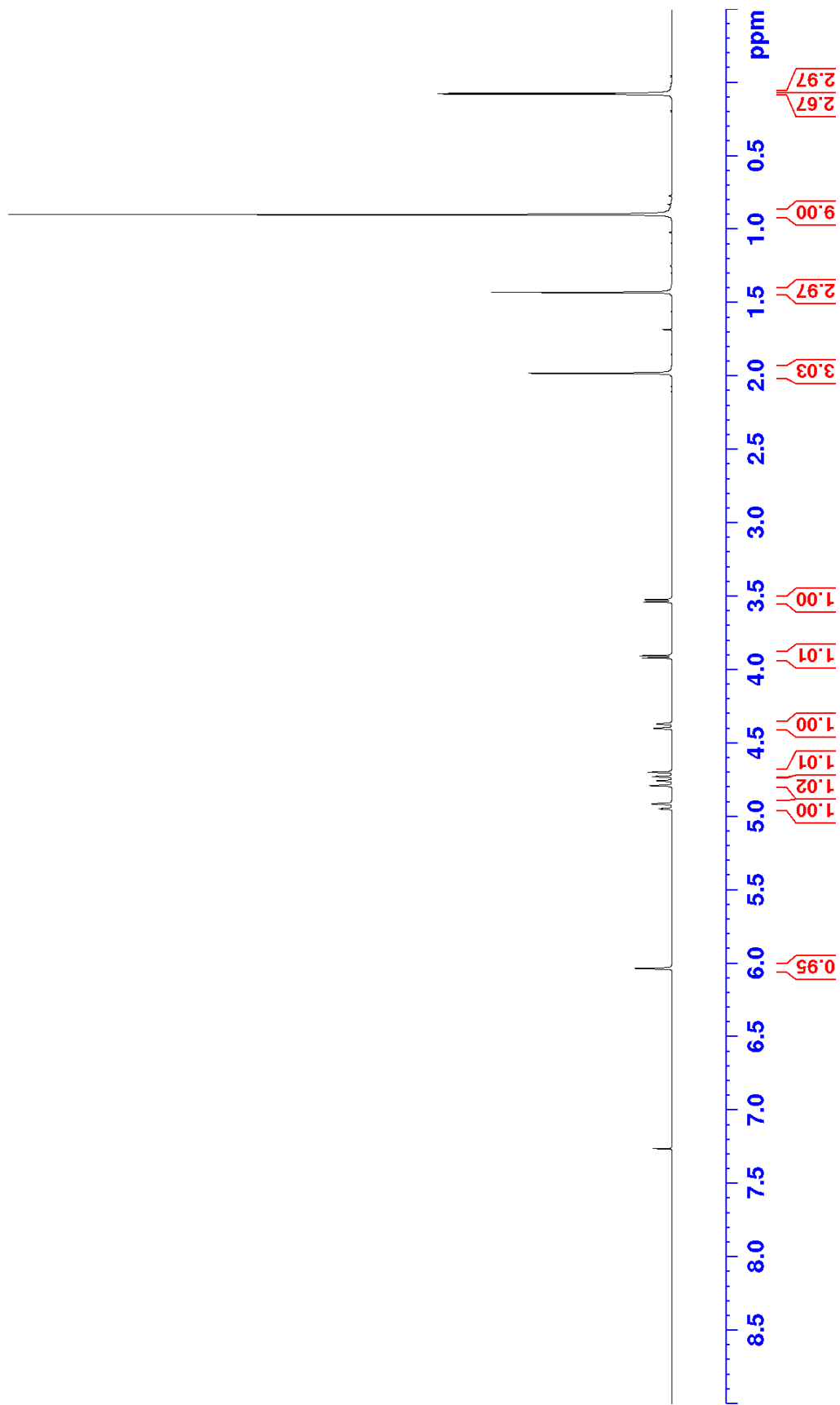
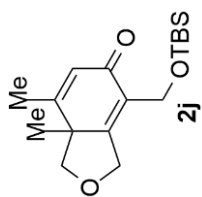


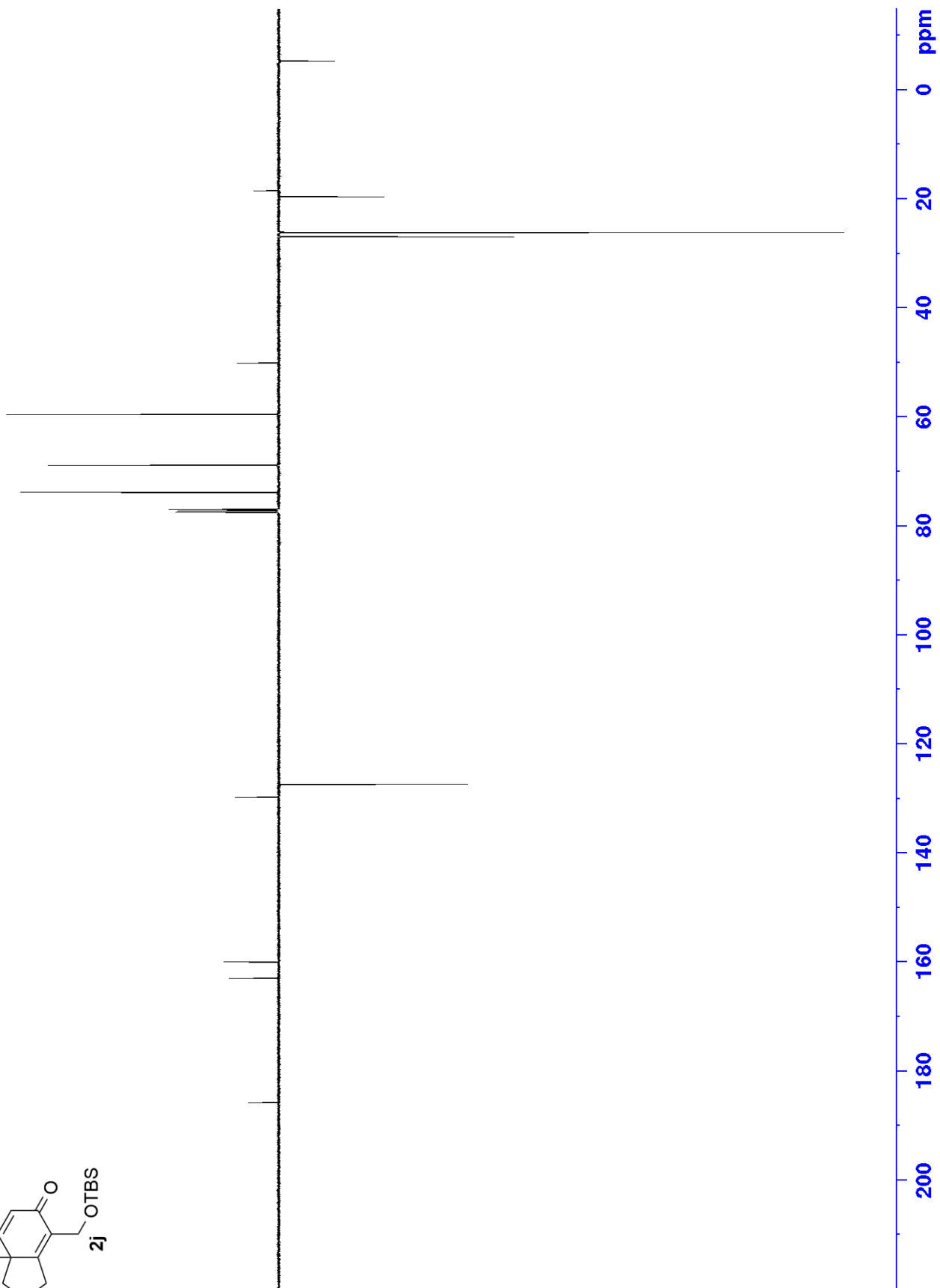
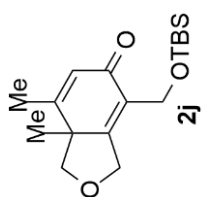


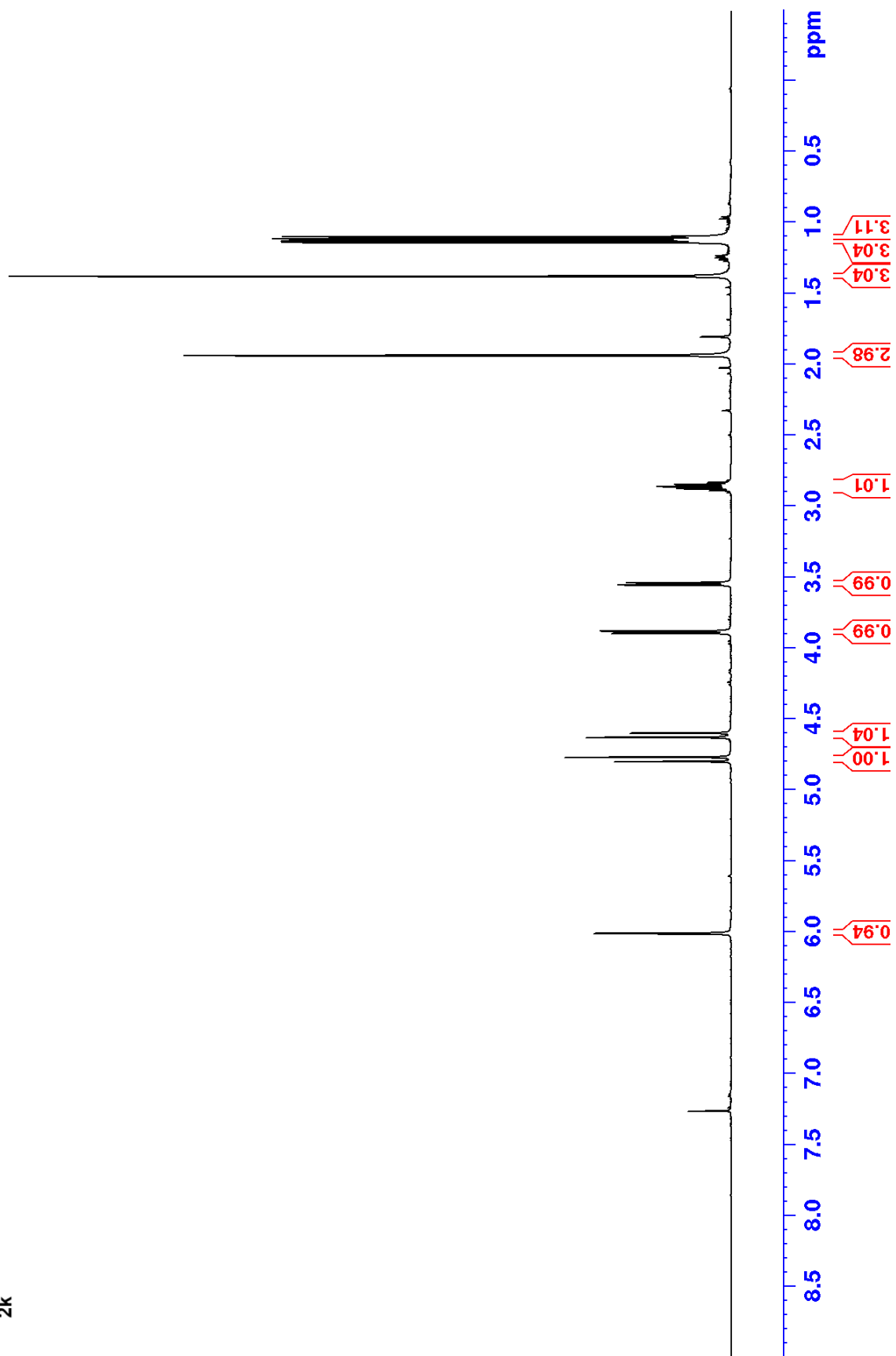
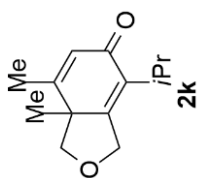


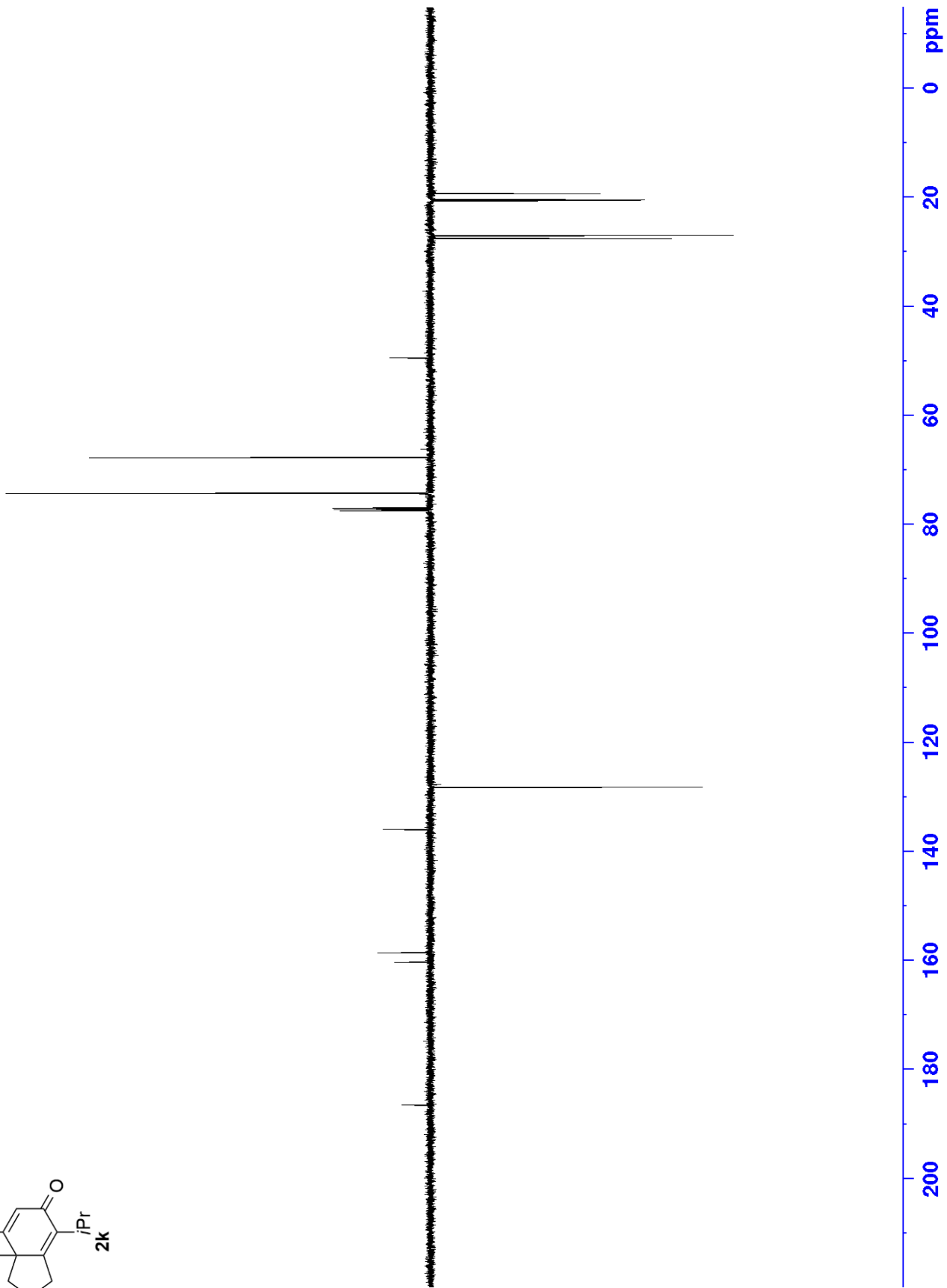
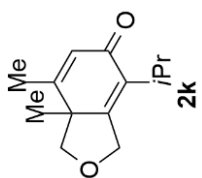


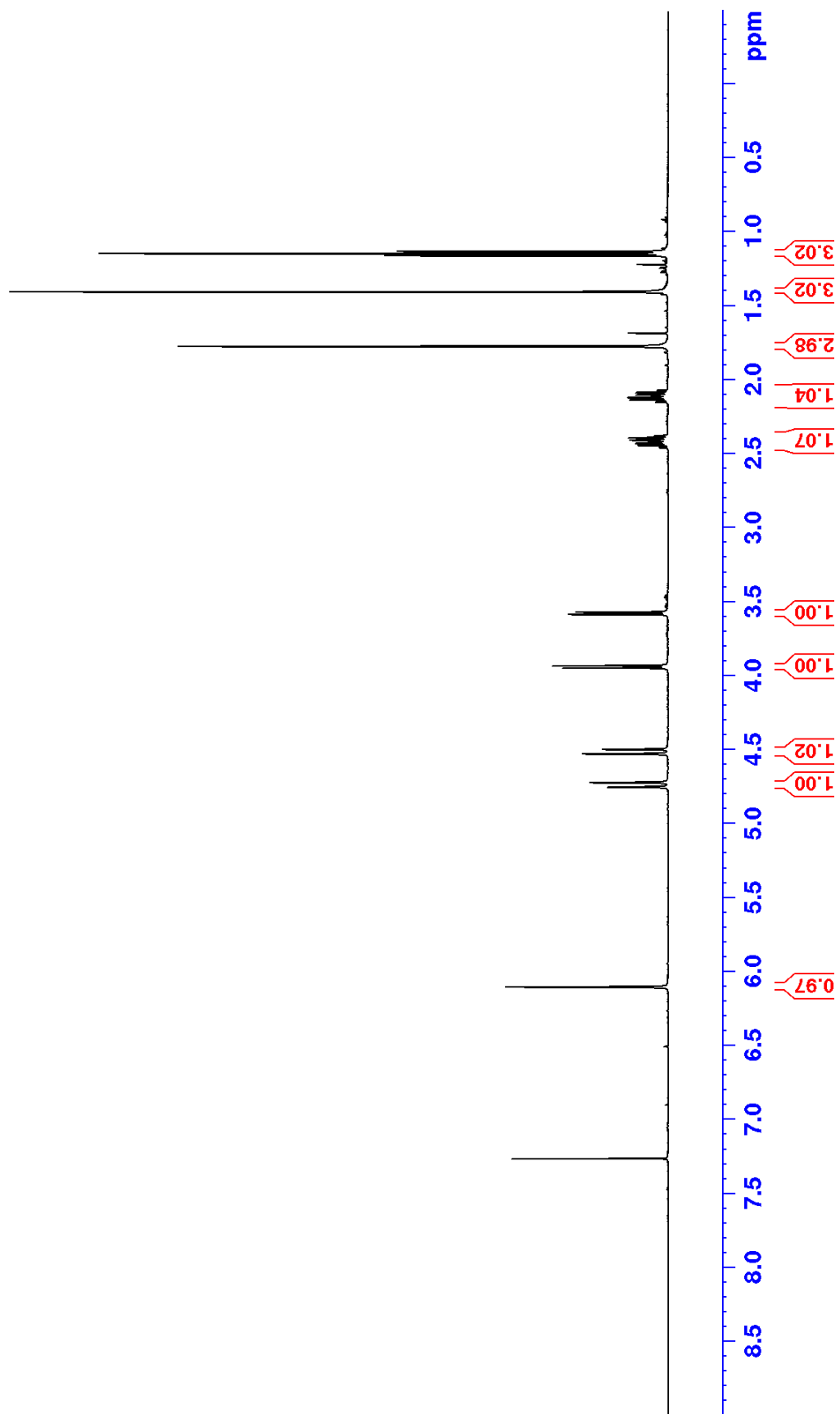
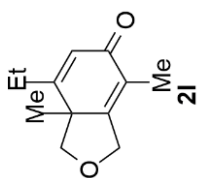


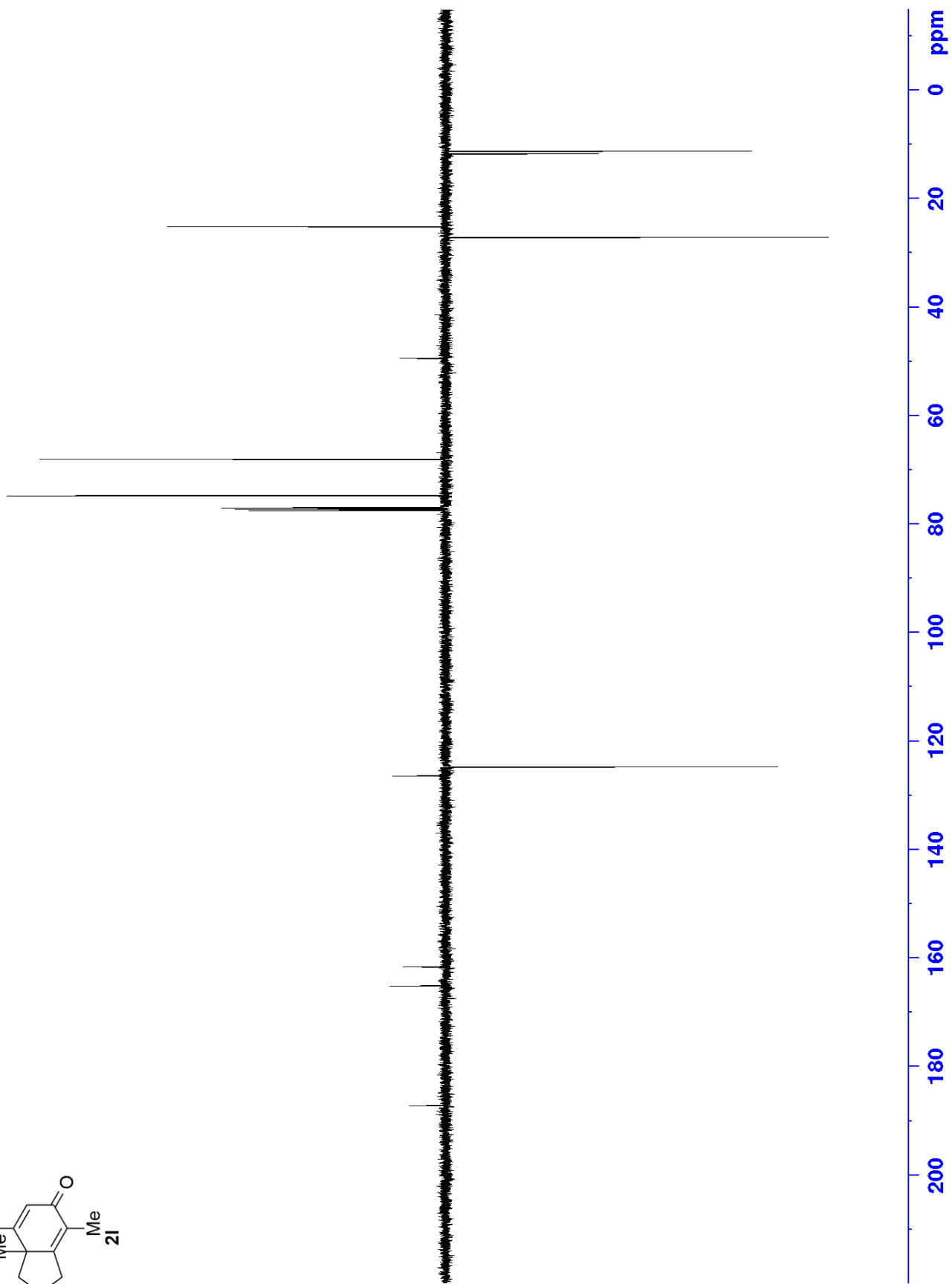
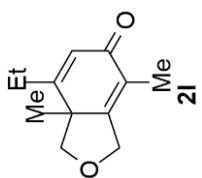


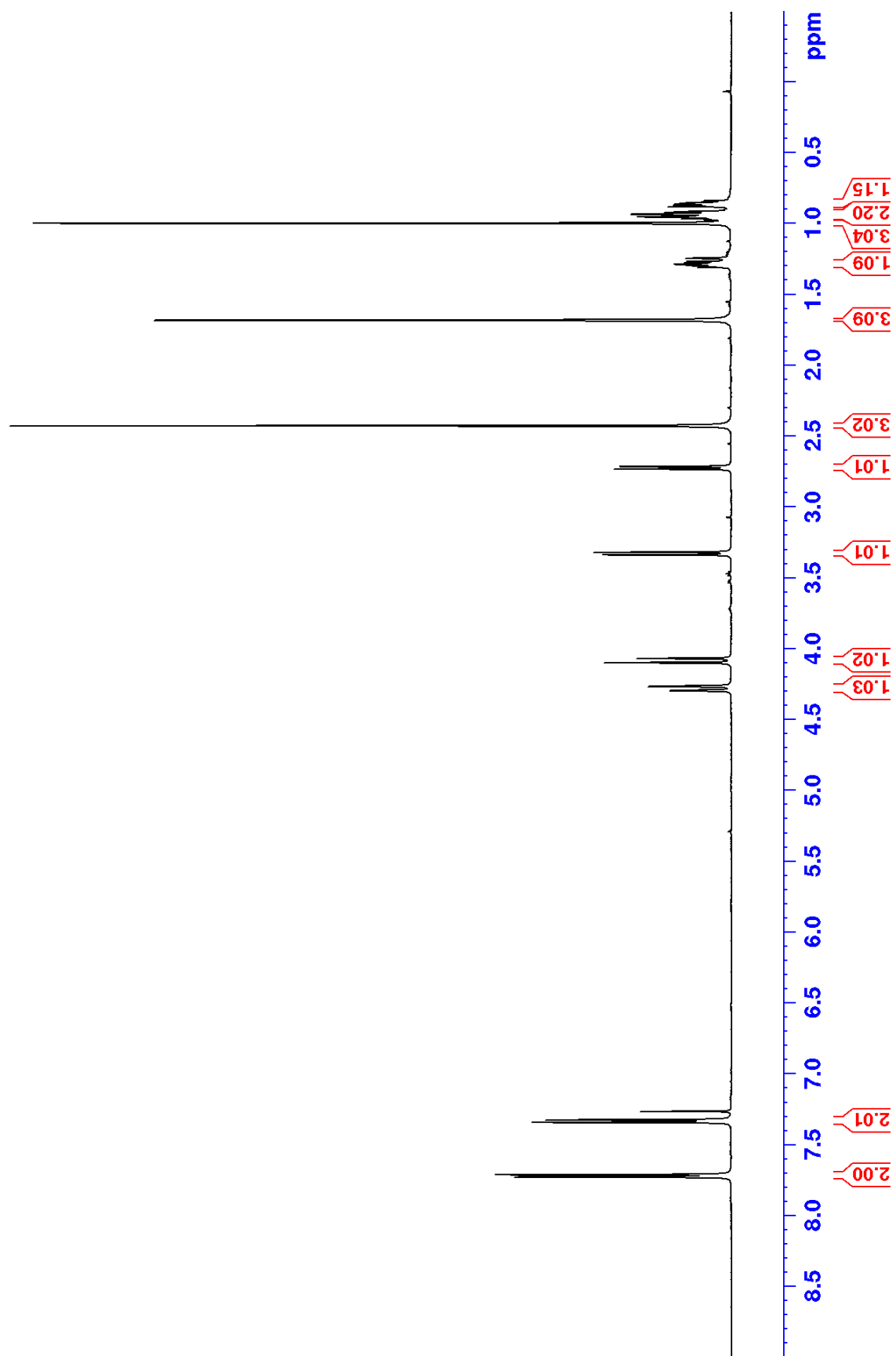
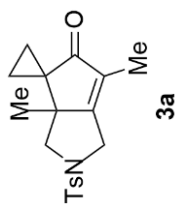


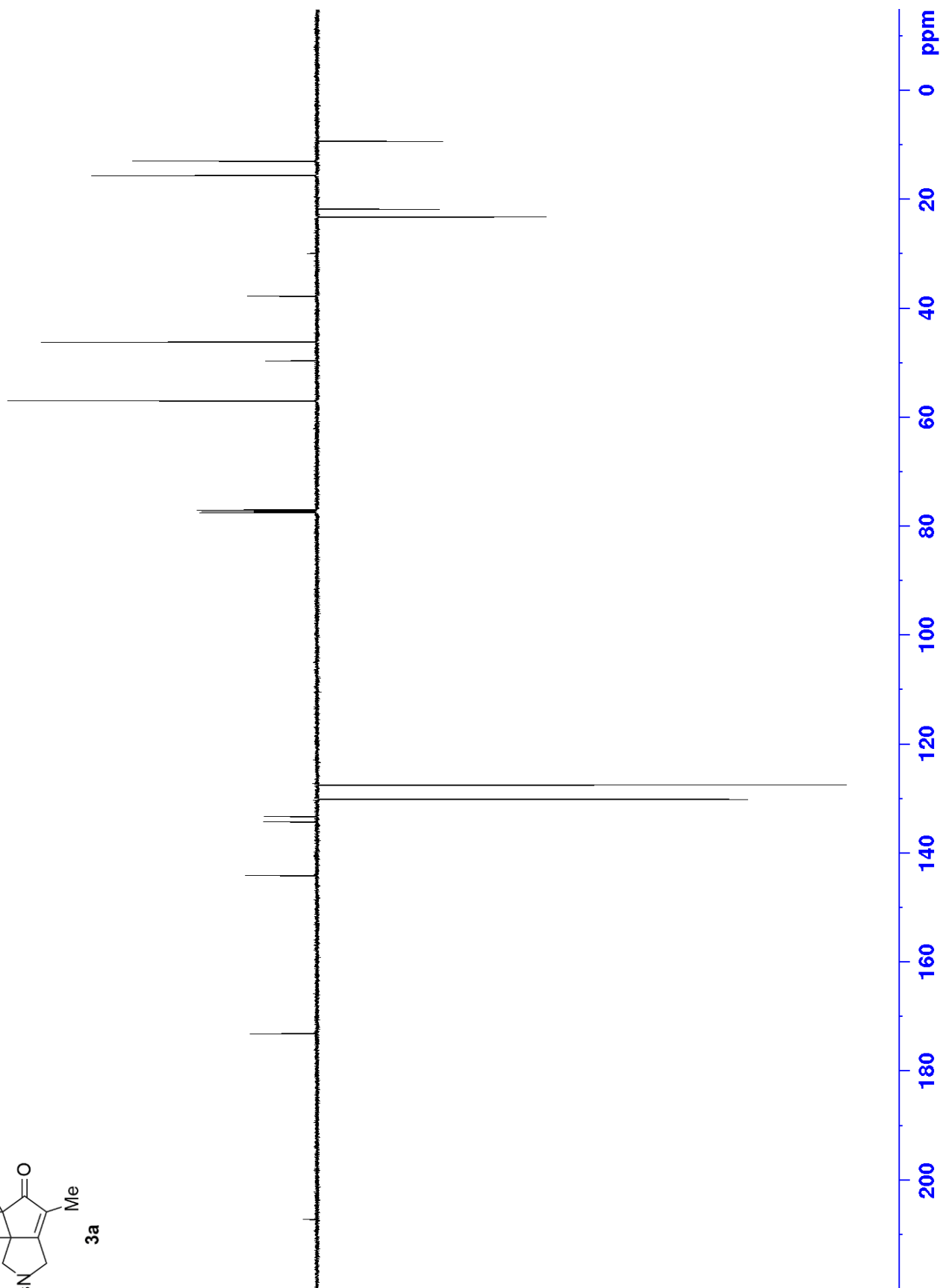
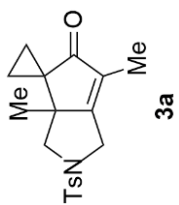


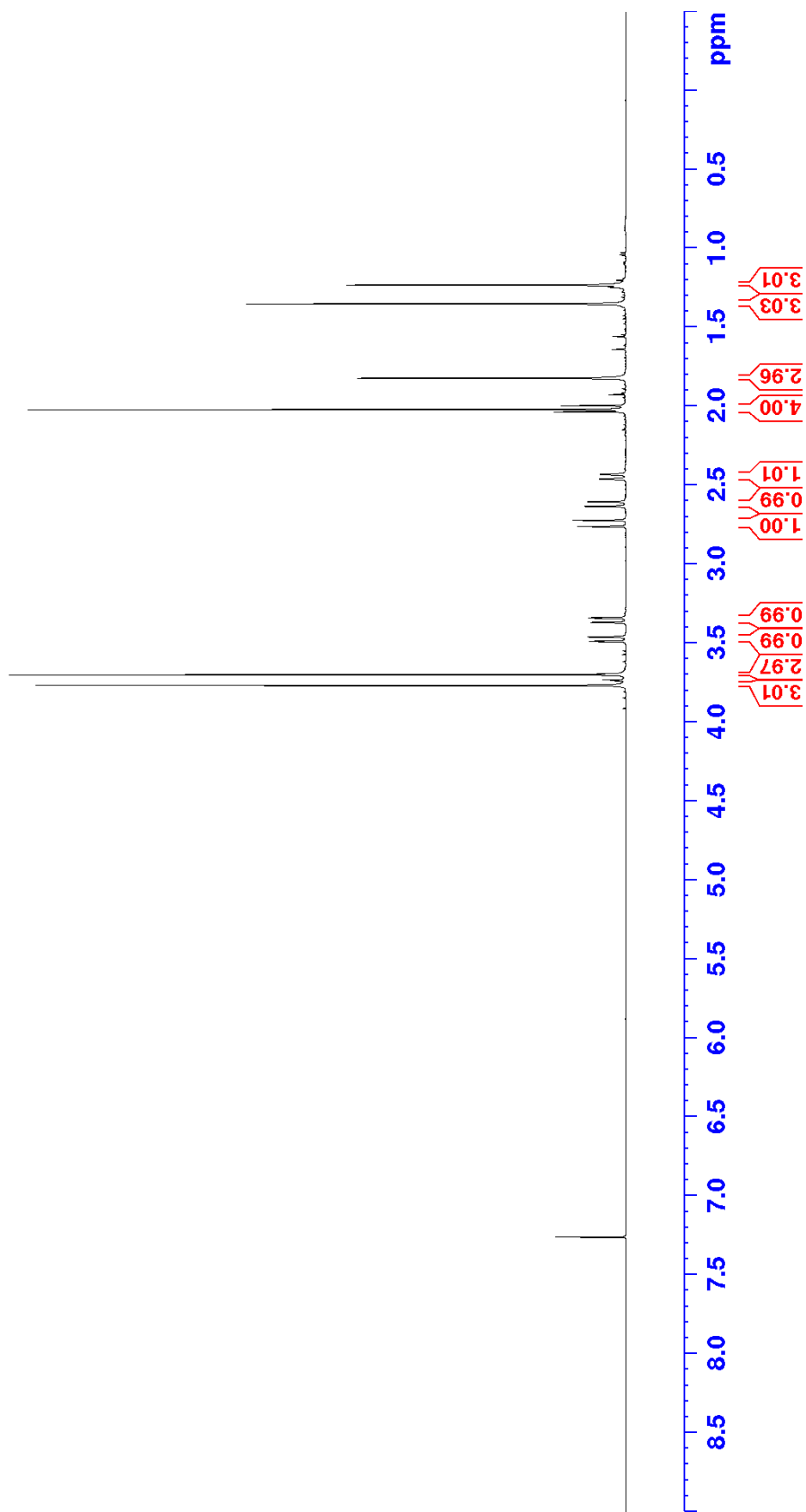
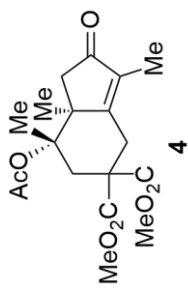


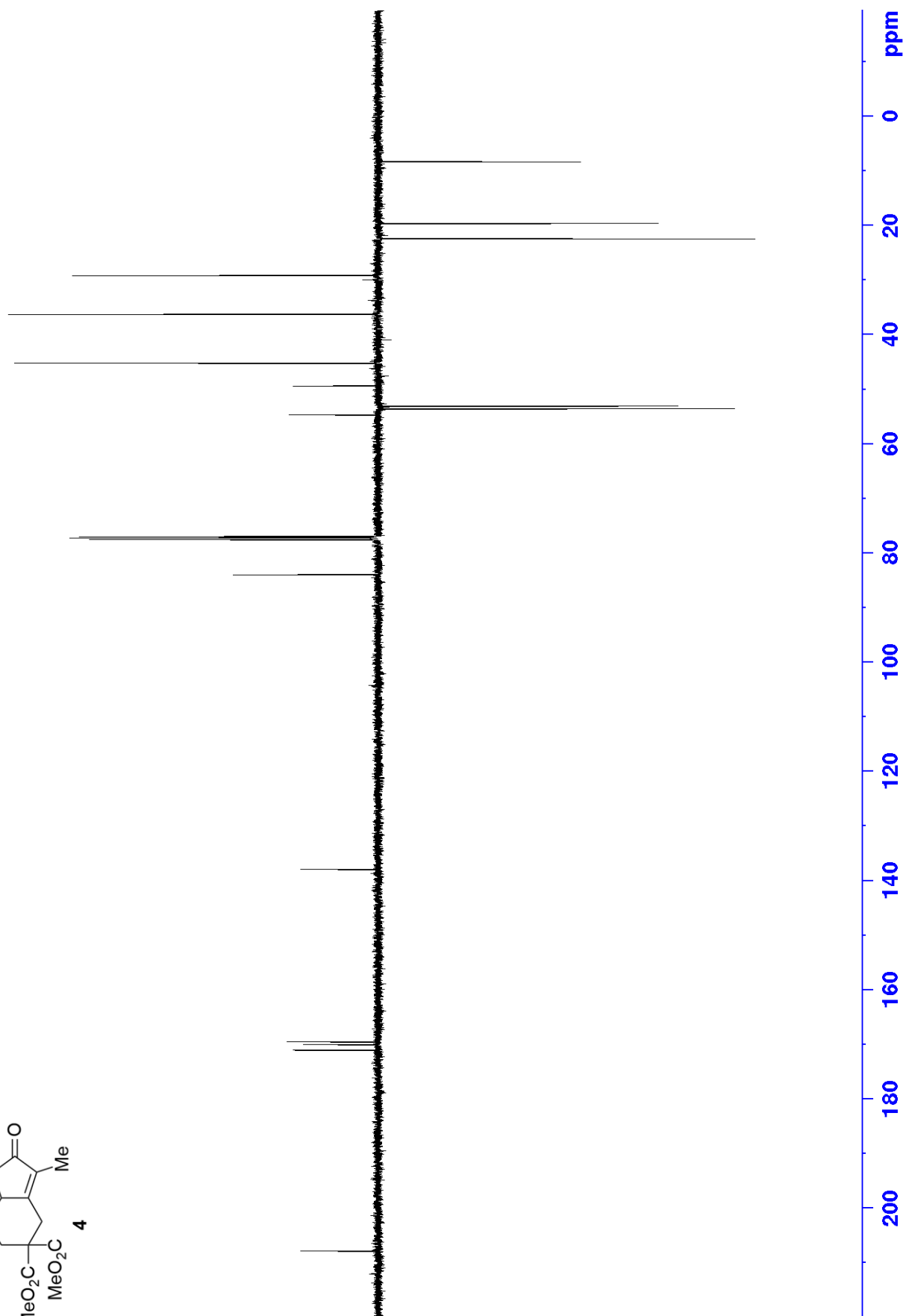
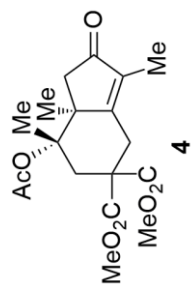










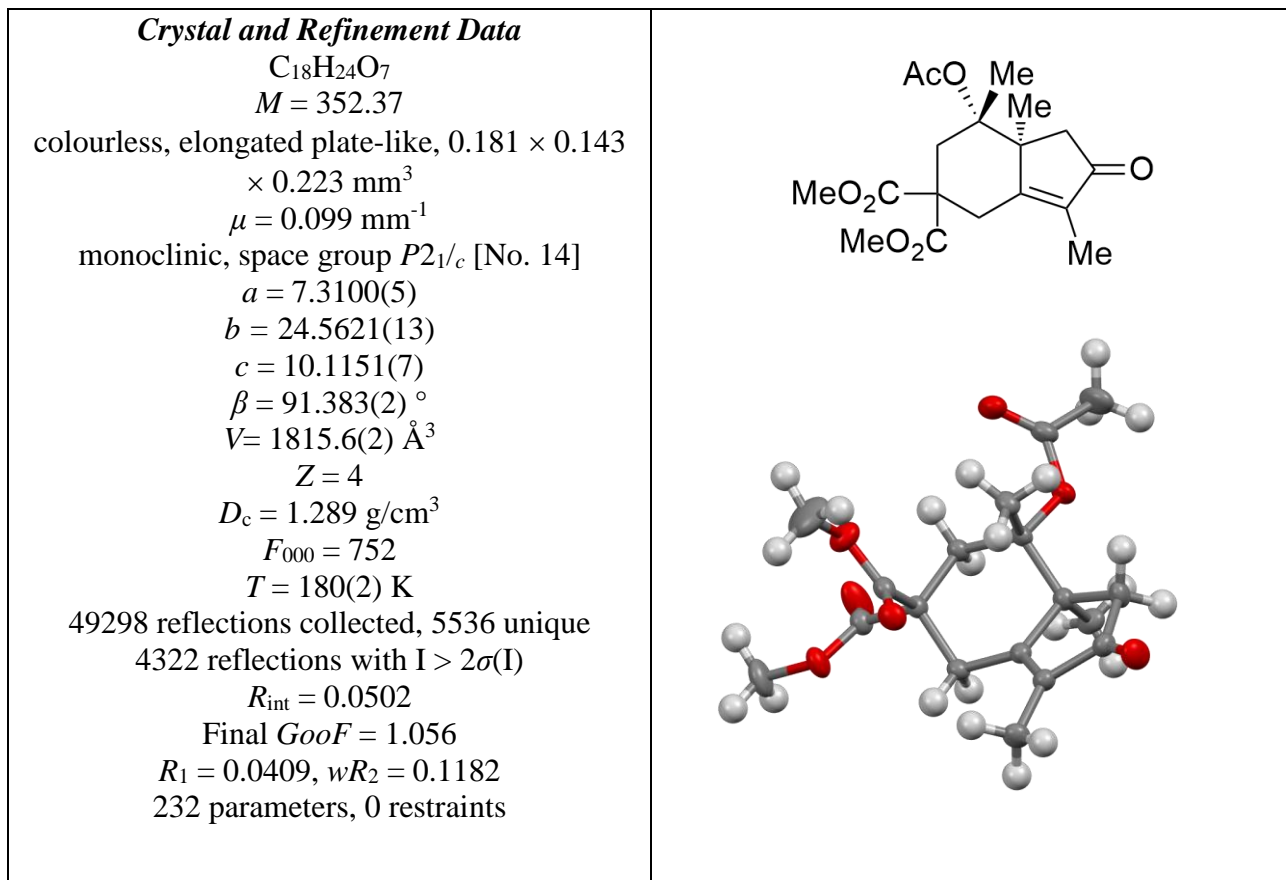


5. Structure Report for 4

X-Ray Crystallography Laboratory (Dr. Gabriele Schatte)

Department of Chemistry, Queen's University

Structure Report for (7*S*,7*aS*)-Dimethyl 7-acetoxy-3,7,7*a*-trimethyl-2-oxo-4,6,7,7*a*-tetrahydro-1*H*-indene-5,5(2*H*)-dicarboxylate (**4**)



Data collection, structure solution and refinement

A colourless, elongated plate-like crystal of **4**, having the approximate dimensions of $0.181 \times 0.143 \times 0.223 \text{ mm}$, coated with oil (Paratone 8277, Exxon), was collected onto the aperture of a mounted MicromountTM (diameter of the aperture: 100 microns; *MiTeGen* – Microtechnologies for Structural Genomics; USA) and quickly transferred to the cold nitrogen gas stream of the Oxford Cryostream 800 operating at $-93.16 \text{ }^\circ\text{C}$. The mounted MicromountTM had previously been inserted into reusable magnetic goniometer base (B3S-R, *MiTeGen* – Microtechnologies for Structural Genomics; USA). All measurements were made on a Bruker-AXS D8 Venture Duo diffractometer using Mo $K\alpha$ radiation (λ

= 0.71073 Å) generated by a high brilliance Incoatec Iµs microfocus tube equipped with a HELIOS multilayer mirror optics (power: 50 kV × 1 mA). Data were recorded with a Bruker AXS PHOTON II Charge-Integrating Pixel Array Detector (CPAD) (frame size: 768 × 1024).

An initial orientation matrix and cell was determined from a fast-scan with 180 frames using ϕ -scans (1° per frame, 5 s exposures per degree at $dx = 40$ mm). Data were measured using ϕ - and ω -scans³ and four sets of frames were collected (0.7° rotation per frame; exposure per frame: 10 s; $dx = 40.011$ mm). A total of 665 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.⁴ The integration of the data using a monoclinic unit cell yielded a total of 55239 reflections to a maximum θ angle of 31.616° (0.68 Å resolution). The final cell constants are based upon the refinement of the XYZ-centroids of 9866 reflections with $5.22^\circ < 2\theta < 62.48^\circ$. Data reduction was performed with the Bruker SAINT software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. The linear absorption coefficient, μ , is 0.099 mm⁻¹. A multi-scan absorption correction was applied (Bruker SADABS).⁵ The value for $wR_2(int)$ was 0.0982 before and 0.0564 after correction. The ratio of minimum to maximum transmission is 0.8849.

The structure was solved using direct methods in the space group P2₁/c (No. 14) (SHELXT-2014/5)⁶ and refined by full-matrix least-squares method on F^2 with SHELXL-2014/7⁷ using ShelXle⁸ as the graphical user interface (GUI). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the CH₂- and CH₃- groups were included at geometrically idealized positions (C–H bond distances 0.99/0.98 Å) and were not refined. The isotropic thermal parameters of these hydrogen atoms were fixed at 1.2 times (CH₂ groups) and 1.5 times (CH₃ groups) of that of the preceding carbon atom, respectively. The final cycle of full-matrix least squares refinement using F^2 (SHELXL-2014/7) was based on 5536 reflections, 0 restraints, 232 variable parameters and converged (largest parameter shift was 0.000 times its esd) with an unweighted factor of $R_1 = 0.0409$ for $I > 2\sigma(I)$. The standard deviation of an observation of unit weight (*goodness-of-fit*) was 1.056.⁹ The maximum and minimum peaks in the final difference Fourier map corresponded to 0.322 and -0.234 e⁻/Å³, respectively. Neutral atom scattering factors for non-hydrogen atoms and anomalous dispersion coefficients are contained in the SHELXTL program library.

³ APEX3 software package v2016.5-0, Bruker AXS Inc.: Madison, WI, 2016.

⁴ Bruker SAINT v8.37A: Part of the APEX3 software package v2016.5-0, Bruker AXS Inc.: Madison, WI, 2016.

⁵ Bruker SADABS v2016/2: Part of the APEX3 software package v2016.5-0, Bruker AXS Inc.: Madison, WI, 2015. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3.

⁶ G. M. Sheldrick, *SHELXT-2014, Program for the Solution of Crystal Structures*; University of Göttingen, Göttingen, Germany, 2014. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.

⁷ G.M. Sheldrick, *SHELXL-2014/7, Program for the Solution and Refining of Crystal Structures*: University of Göttingen, Göttingen, Germany, 2014. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

⁸ ShelXle v4.8.0 (2013): A Qt Graphical User Interface for SHELXL. C. B. Hübschle, G. M. Sheldrick and B Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281.

⁹ Standard deviation of an observation of unit weight (*goodness-of-fit* on F^2):

$$GooF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$$

$$n = \text{number of reflections, } p = \text{number of parameters}$$