Electronic supplementary materials *Mendeleev Commun*., 2019, **29**, 140–142

Alkylthio(4-methylpent-3-en-1-ynyl)carbenes: generation by the photolysis of 5-alkylthioethynyl-3,3-dimethyl-3*H*-pyrazoles and reactions with alkenes

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Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer using the solutions in $CDCl_3$. Residual signal of the solvent was used as a reference. High resolution mass spectra were recorded using a Bruker micrOTOF II instrument with electrospray ionization (ESI). The measurements were performed on the positive ions (capillary voltage 4500 V). Masses were scanned in the range of *m*/*z* from 50 to 3000 Da, using external or internal calibration (Electrospray Calibrant Solution, Fluka). Solutions of tested compounds in acetonitrile were injected using a syringe, the flow rate was 3 l min^{-1}. Nitrogen (4 l min^{-1}) was used as nebulizer gas, the interface temperature was 180 °C.

THF used for the synthesis of pyrazoles **2** was dried over $LiAlH_4$ at room temperature with following distillation in argon atmosphere. Starting 3,3-dimethyl-5-ethynyl-3*H*-pyrazole **1** was prepared by addition of 2-diazopropane to an excess of butadiyne, according to the procedure described earlier,[1] and purified by microdistillation *in vacuo*.

The cryostat used for matrix isolation was a CSW-208R Displex closed-cycle refrigeration system (APD Cryogenics, Inc.) fitted with KBr windows for IR range and CaF_2 windows for UV/vis photolysis. Cryostat case was equipped with two separate lines for independent supply of a matrix gas (argon) and a precursor. The polished surface of a copper cube was cooled to 10 K. The temperature of the cube was measured by a DT-470 silicon diode fixed at the Cu surface and was preset using a Lake Shore model 330-11 temperature controller. In a typical photolysis experiment pyrazole **2a** was evaporated at 40 °C and deposited through the high vacuum glass valve onto cooled surface along with argon (~1:1000) for 90–120 min. Pressure in the flow was ca. 10^{-4} Torr. Photolysis of the matrices was carried out using a DRSh-500 high pressure Hg arc lamp (500 W) equipped with a water filter and suitable cutoff (the wavelength of UV radiation was varied utilizing glass light filters).

IR spectra were recorded on a Bruker IFS 113v FTIR spectrometer (detector DTGS/KBr) in the range of 400–4000 cm^{-1} with resolution 0.5 cm^{-1} for matrix spectra and 2.0 cm^{-1} for spectra in KBr pellets. Quantum chemical computations were carried out using the Gaussian 09 quantum chemistry package. Density functional theory (DFT) B3LYP with aug-cc-PVTZ basis was used.

References

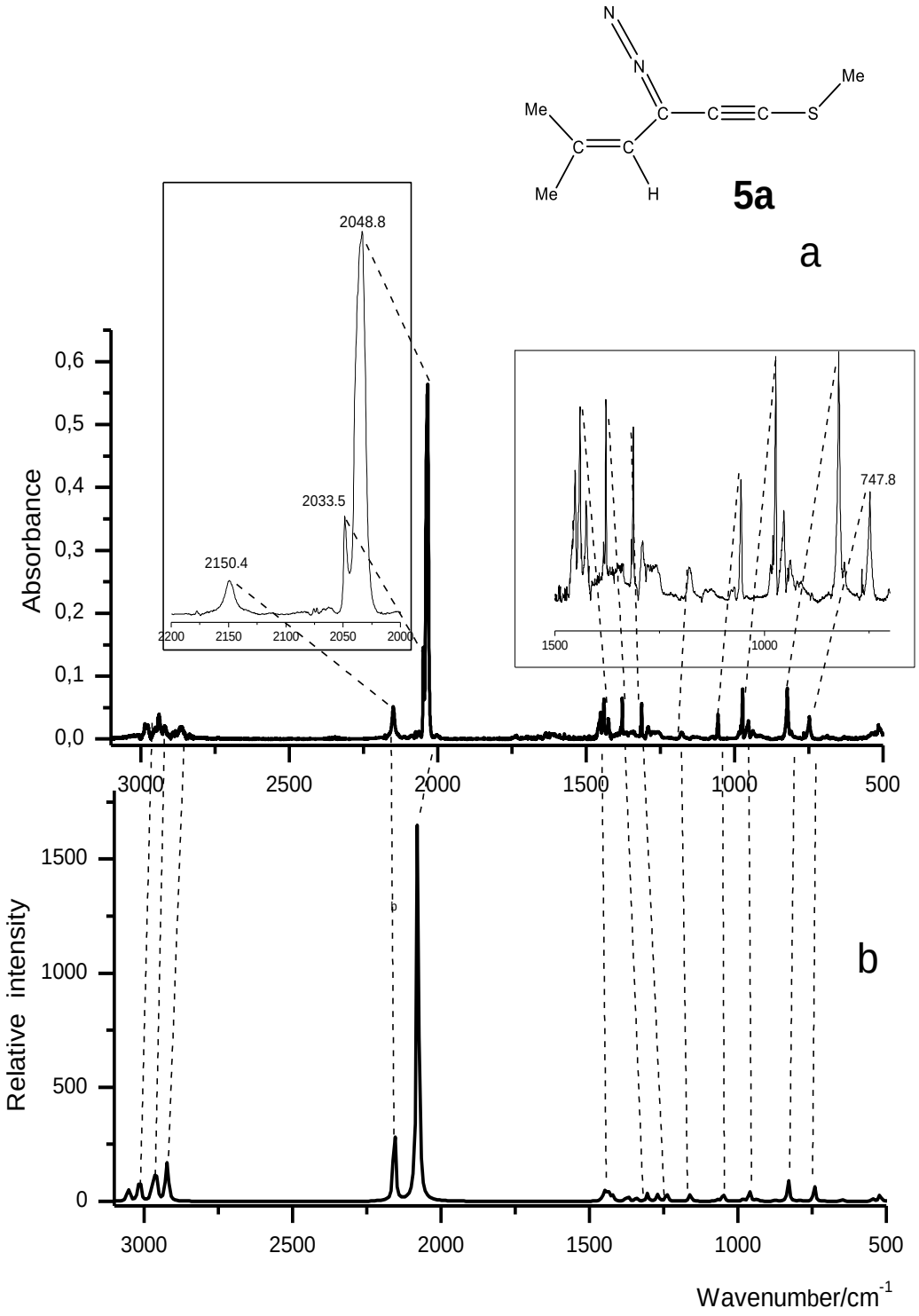
1. M. Franck-Neumann, P. Geoffroy and J. J. Lohmann, *Tetrahedron Lett*, 1983, **24**, 1775.

Characterization data for compounds **2b, 3b** *and* **3e.**

5-Ethylthioethynyl-3,3-dimethyl-3H-pyrazole **2b**. ^{1}H NMR, δ: 1.39 (s, 6H, 2Me), 1.42 (t, 3H, $SCH_2\mathit{Me}$, *J* 7.3 Hz), 2.82 (q, 2H, $SC\mathit{H}_2CH_3$, *J* 7.3 Hz), 6.85 (s, 1H, =CH-). ^{13}C NMR, δ: 14.8 ($SCH_2\mathit{Me}$), 20.4 (2Me), 29.9 (SCH_2CH_3), 85.0, 85.3 (C≡C), 94.6 ($C\mathit{C}Me_2$), 138.4 (=CC≡C), 146.0 (=CH-). HRMS, *m/z* 181.0789, calculated for $C_{10}H_{14}N_2S$, $[M+H]^+$: *m/z* 181.0794.

1,1,2,2-Tetramethyl-3-(4-methylpent-3-en-1-yn-1-yl)-3-(methylthio)cyclopropane **3b** was prepared from pyrazole **2a** and 2,3-dimethylbut-2-ene and isolated in 52 % yield. ^{1}H NMR, δ: 1.22 (2Me), 1.24 (2Me), 1.79, 1.88 (2 br. s, each 3H, $=CMe_2$), 2.20 (s, 3H, SMe), 5.35 (br. s, 1H, -CH=). ^{13}C NMR, δ: 15.2 (SMe), 18.3 (2Me), 20.6 (2Me), 21.0, 24.7 ($=C\mathit{Me}_2$), 24.0 (C≡$C\mathit{C}$), 31.1 ($2\mathit{C}Me_2$), 79.8, 91.7 (C≡C), 105.6 (-CH=), 146.9 ($=\mathit{C}Me_2$). HRMS, *m/z* 223.1508, 245.1329, calculated for $C_{14}H_{22}S$, $[M+H]^+$: *m/z* 223.1515, $[M+Na]^+$: *m/z* 245.1334.

1-Ethylthio-1-(4-methylpent-3-en-1-yn-1-yl)spiro[2.4]heptane **3e** was prepared from pyrazole **2b** and methylenecyclopentane and isolated in 55 % yield. ^{1}H NMR, δ: 1.03 (d, 1H, C*H*H, *J* 4.6 Hz), 1.24 (d, 1H, C*H*H, *J* 4.6 Hz), 1.31 (t, 3H, $SCH_2\mathit{Me}$, *J* 7.4 Hz), 1.49-1.78 (m, 6H, *cyclo*-C_5), 1.79, 1.88 (2 br. s, each 3H, $=CMe_2$), 1.97-2.15 (m, 2H, *cyclo*-C_5), 2.78 (q, 2H, $SC\mathit{H}_2Me$, *J* 7.4 Hz), 5.31 (br. s, 1H, -CH=). ^{13}C NMR, δ: 14.5 ($SCH_2\mathit{Me}$), 21.0, 24.7 ($=C\mathit{Me}_2$), 25.7 (C≡$C\mathit{C}$), 26.6, 26.7, 26.8, 31.8, 32.4, 34.5 ($6CH_2$), 38.0 (quaternary C), 78.8, 93.1 (C≡C), 105.5 (-CH=), 147.4 ($=\mathit{C}Me_2$). HRMS, *m/z* 235.1509, 257.1330, calculated for $C_{15}H_{22}S$, $[M+H]^+$: *m/z* 235.1515, $[M+Na]^+$: *m/z* 257.1334.



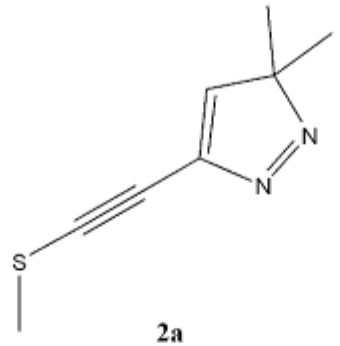
IR spectrum of (3-diazo-5-methylhex-4-en-1-ynyl)(methyl)sulfane **5a.** (a)-experimental spectrum isolated in an argon matrix at 10 K; (b)- spectrum of *gauche*-conformer calculated using B3LYP/aug-cc-PVTZ, scaling factor (3500−1000 cm^{-1}) 0.9676, scaling factor (1000−500 cm^{-1}) 0.9891. Diazo compound **5a** mainly occurs as the *s-gauche* conformer (this conformer preserves in the main geometry of the parent 3H-pyrazole **2a** and should be formed initially).

Table S1 Assignment for the infrared bands of (3-diazo-5-methylhex-4-en-1-ynyl)(methyl)sulfane **5a**, observed in Ar matrices, and corresponding calculated (B3LYP/aug-cc-pVTZ) frequencies (cm^{-1}), with their IR intensities.

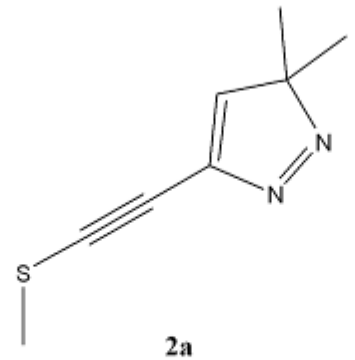
Approximate assignment[a]	Experimental frequencies[b]	Calculated[c]			
		Gauche-**5a**		*Anti*-**5a**	
		Freq	Int	Freq	Int
ν (SCH_3) as		3050.0	4.5	3049.3	2.3
ν (CH)		3045.7	11.0	3046.4	4.1
ν (SCH_3) as		3040.3	5.9	3036.7	5.7
ν $(CH_3)_2$ as	2983.1 m	3012.2	16.4	3034.6	14.9
ν $(CH_3)_2$ as	2942 m	3005.4	19.4	2996.3	20.3
ν $(CH_3)_2$ s	2936.6 m	2965.9	21.8	2952.5	27.4
ν (SCH_3)s		2956.2	29.3	2942.4	40.7
ν $(CH_3)_2$ as		2951.0	17.1	2940.8	0.3
ν $(CH_3)_2$ s	2919.6 m	2919.1	46.2	2911.8	84.9
ν $(CH_3)_2$ s	2866 m	2913.4	29.3	2905.7	26.3
ν (C≡C). ν (N=N) s	2150.4 m	2149.4	112.6	2146.8	228.3
ν (C≡C). ν (N=N) as	2048.8 m. 2033.5 vs	2068.2	622.5	2064.0	798.5
ν (C=C)		1640.1	0.3	1648.4	5.5
δ $(CH_3)_2$ as	1451.3 w	1453.1	5.9	1449.5	3.4
δ $(CH_3)_2$ s	1444.7 vw sh	1444.5	10.7	1447.4	9.7
δ $(CH_3)_2$ as	1440.2 m	1438.4	2.7	1435.7	2.1
δ $(CH_3)_2$ as	1425.6 w	1434.0	10.2	1430.9	9.4
δ $(CH_3)_2$ s		1428.7	6.7	1425.5	2.0
δ (CH_3) as	1424.0 w sh	1418.4	8.0	1415.9	8.1
δ (CH_3) as	1383.7 vw	1376.3	2.0	1381.3	5.4
δ $(CH_3)_2$ s. δ (CH)	1378.3 m	1365.5	7.6	1368.9	12.2
δ (CH)		1338.0	5.6	1356.4	6.3
δ (CH3) s	1312.9 w	1300.1	9.1	1307.2	2.3
ν (CC) s	1257.1 vw	1266.2	11.3	1296.7	12.4
ν (C–N)	1250 w	1237.3	11.9	1209.0	23.5
ν C–$(CH_3)_2$ a. δ (CH)	1176.6 wb	1157.7	11.1	1137.7	21.5
r $(CH_3)_2$ s		1067.3	2.6	1066.8	0.0
r $(CH_3)_2$ s	1056.9 w	1047.1	11.4	1056.8	20.8
r $(CH_3)_2$ as		979.9	3.5	982.6	3.2
r (CH_3) s	972.9 w	978.1	14.1	978.0	12.8
r $(CH_3)_2$ as		959.8	0.9	959.3	0.8
r (CH_3) as	953.7 w	952.6	1.8	952.0	1.6
r $(CH_3)_2$. *w*(CH)		889.4	1.2	912.3	1.8
w(CH)	822.6 m	843.9	28.7	850.0	10.9
ν C–$(CH_3)_2$		806.3	1.4	835.0	2.5
δ (C–N=N).ν (C–S)	747.8 m	754.5	21.1	677.8	23.0
ν (S–CH_3)	687.0 vw	660.3	2.5	658.1	5.8
w(NNN) *w*(CH)		553.8	2.8	558.7	4.5
w(NNN) *w*(CH)	515.0 w	529.3	10.4	537.7	1.6

[a]ν – bond stretching, δ – bending, *r* – rocking, τ – torsion; s – symmetric, as – antisymmetric. [b]vs – very strong, s – strong, sh – shoulder, m – medium, w – weak, vw- very weak, [c] calculated harmonic wavenumbers are scaled by 0.9676 (from 3500 to 1000 cm^{-1}) and 0.9891 (below 1000 cm^{-1}).

Copies of NMR-spectra for compounds **2a,b** *and* **3a-c,e**



2a


N
N
S

2a

20.53
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138.46
94.77
86.92
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77.79
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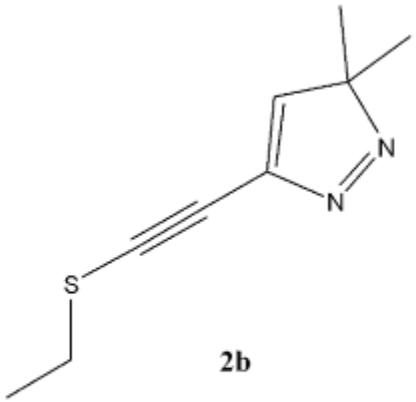
76.52
20.67
19.12
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


N
N
S

2b

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6.5
6.0
5.5
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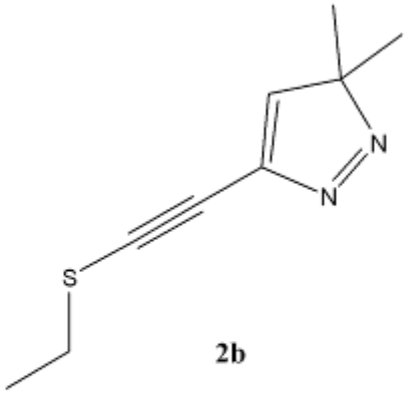
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


N
N
S

2b

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77.10
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20.38
14.79
152
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96
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80
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40
32
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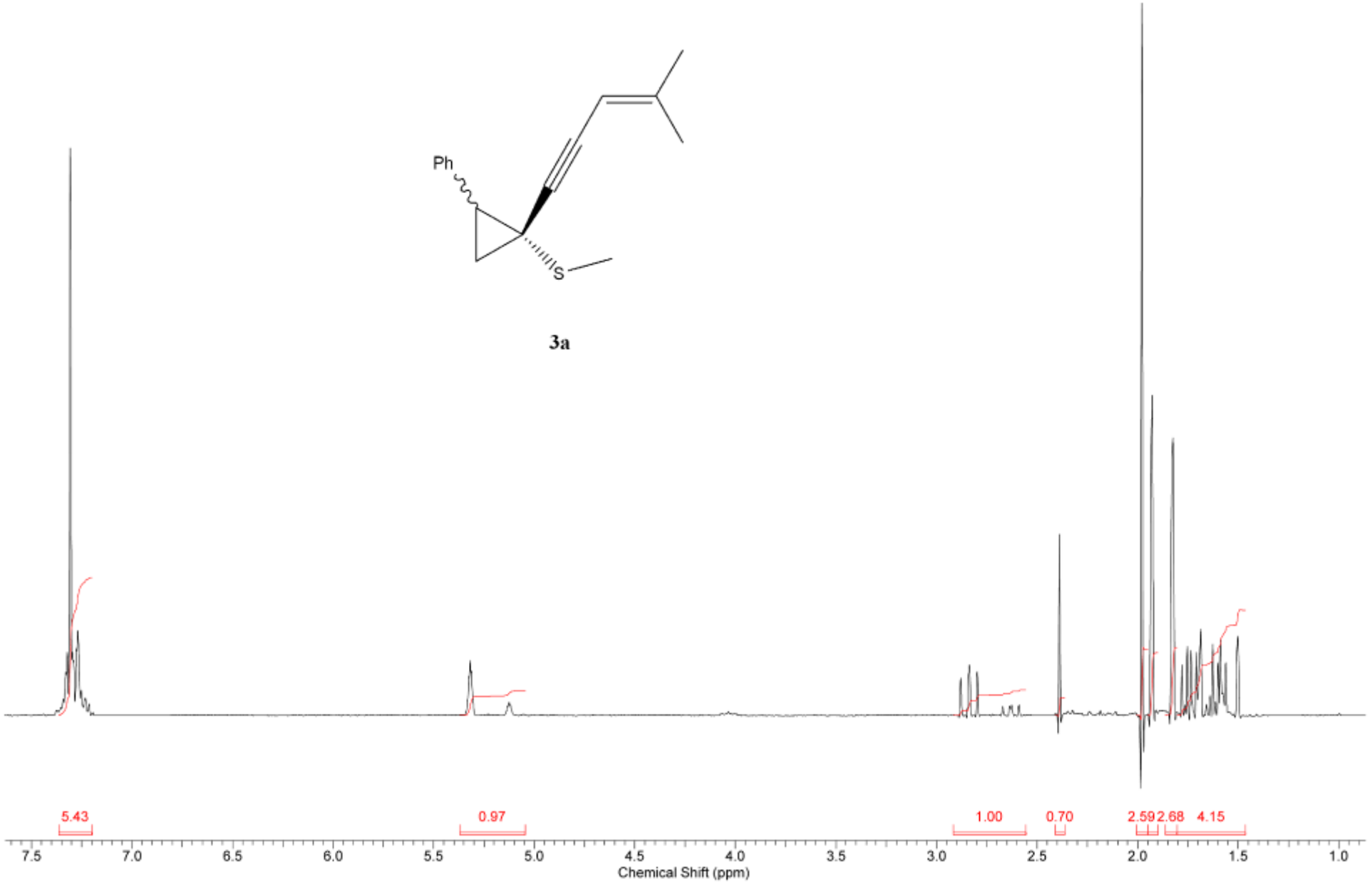
16
8
Chemical Shift (ppm)


Ph
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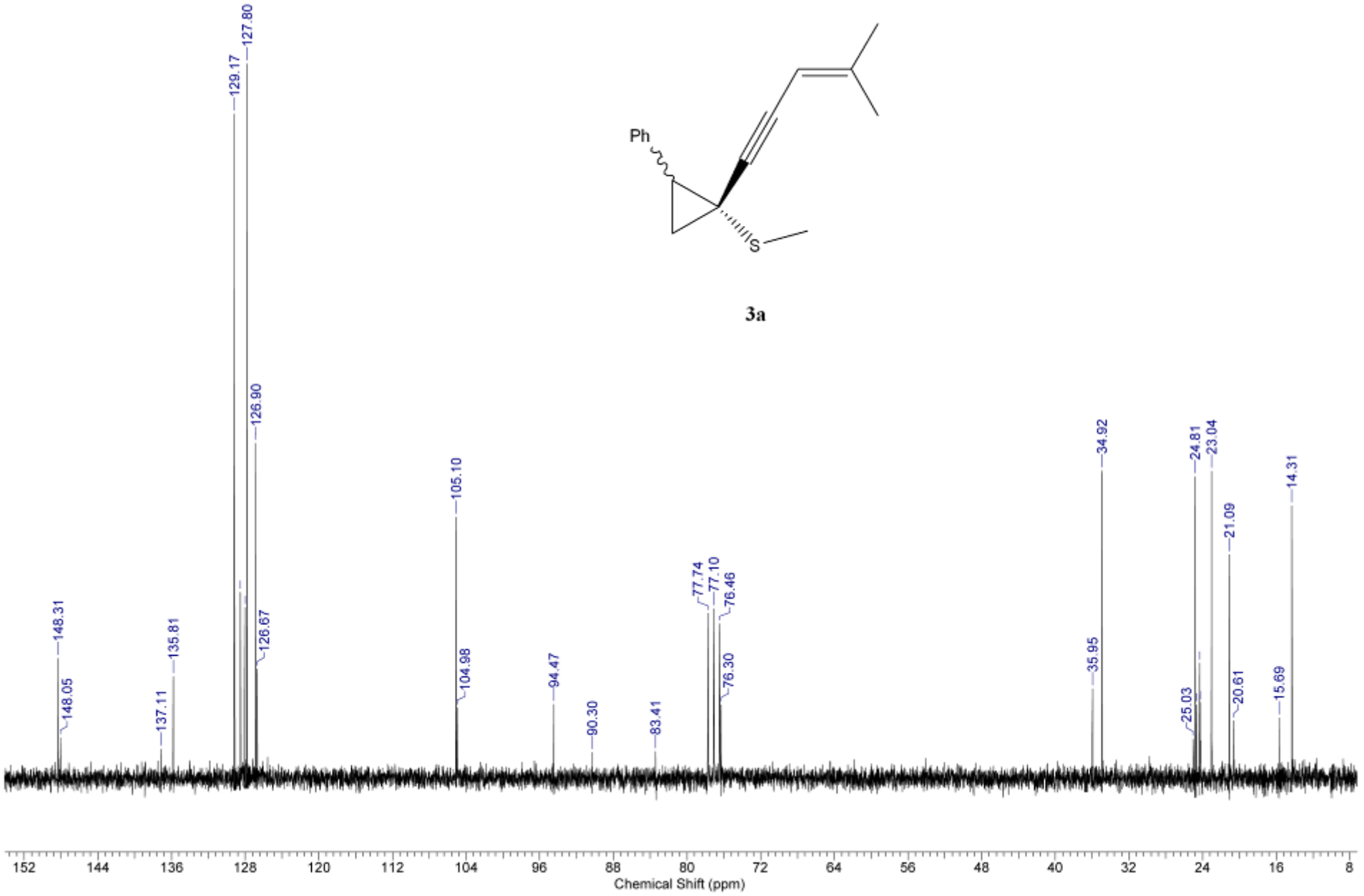
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

3a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135.81
105.10
104.98
94.47
90.30
83.41
77.74
77.10
76.46
76.30
34.92
35.95
24.81
23.04
21.09
20.61
25.03
15.69
14.31
152
144
136
128
120
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96
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72
64
56
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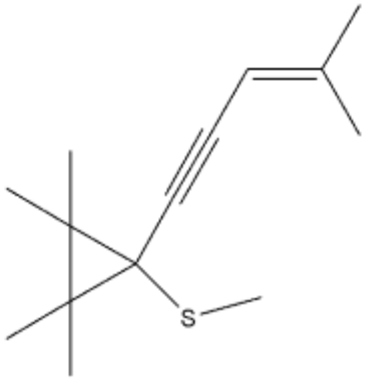
40
32
24
16
8
Chemical Shift (ppm)

3a


S

3b

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6.5
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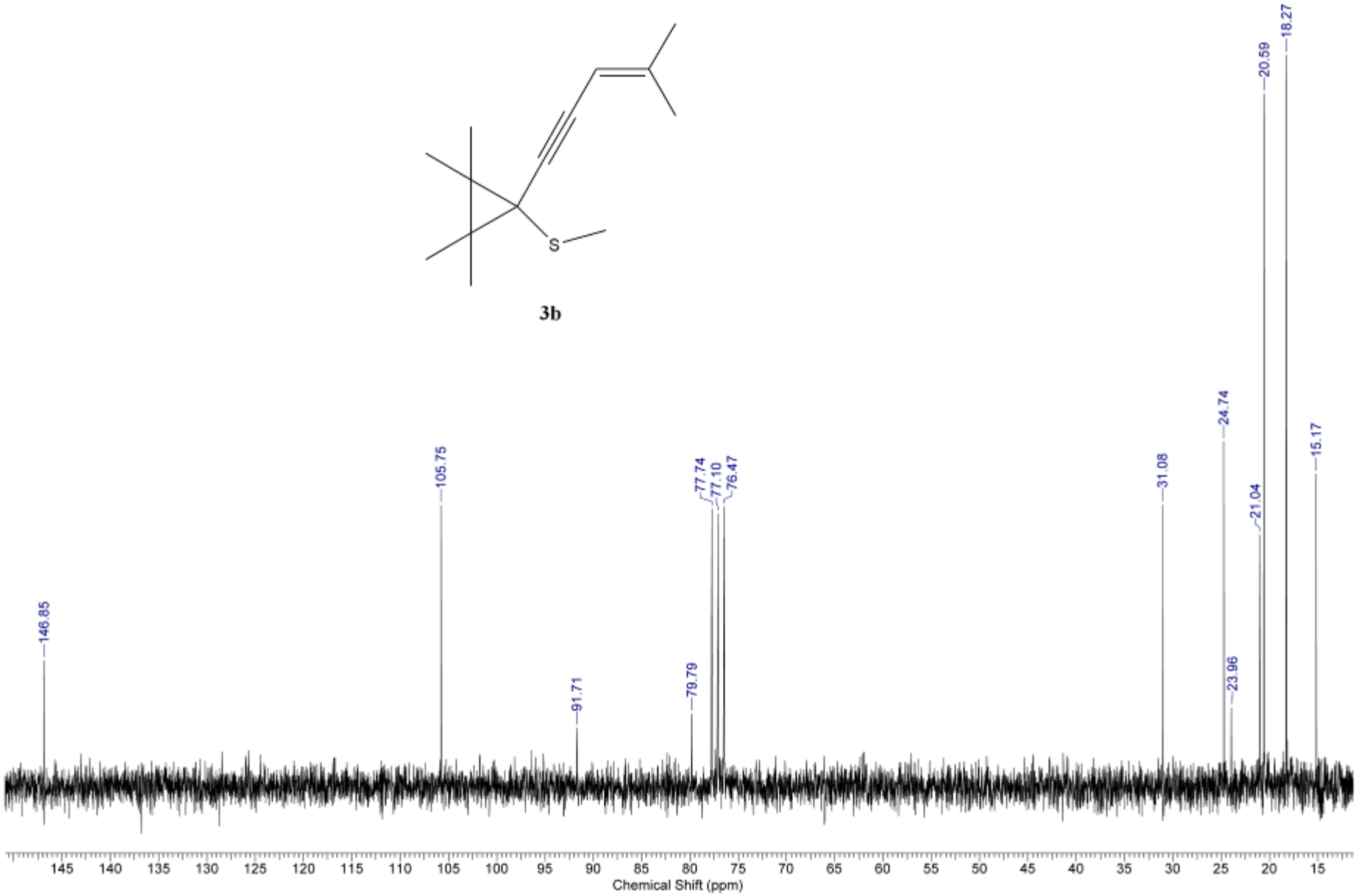
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


S
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31.08
24.74
23.96
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20.59
18.27
15.17
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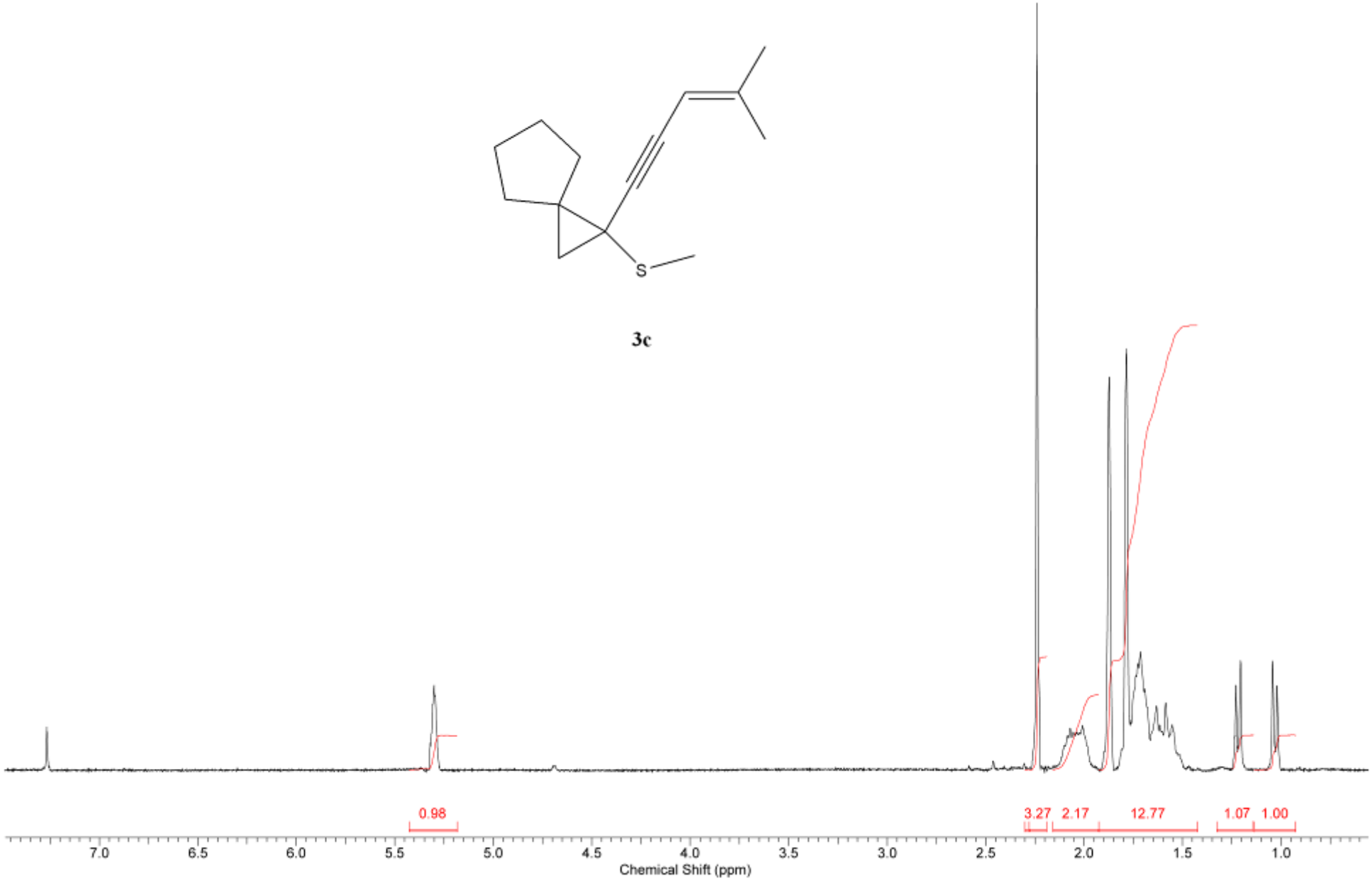
Chemical Shift (ppm)

3b


S
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3.27
2.17
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7.0
6.5
6.0
5.5
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4.5
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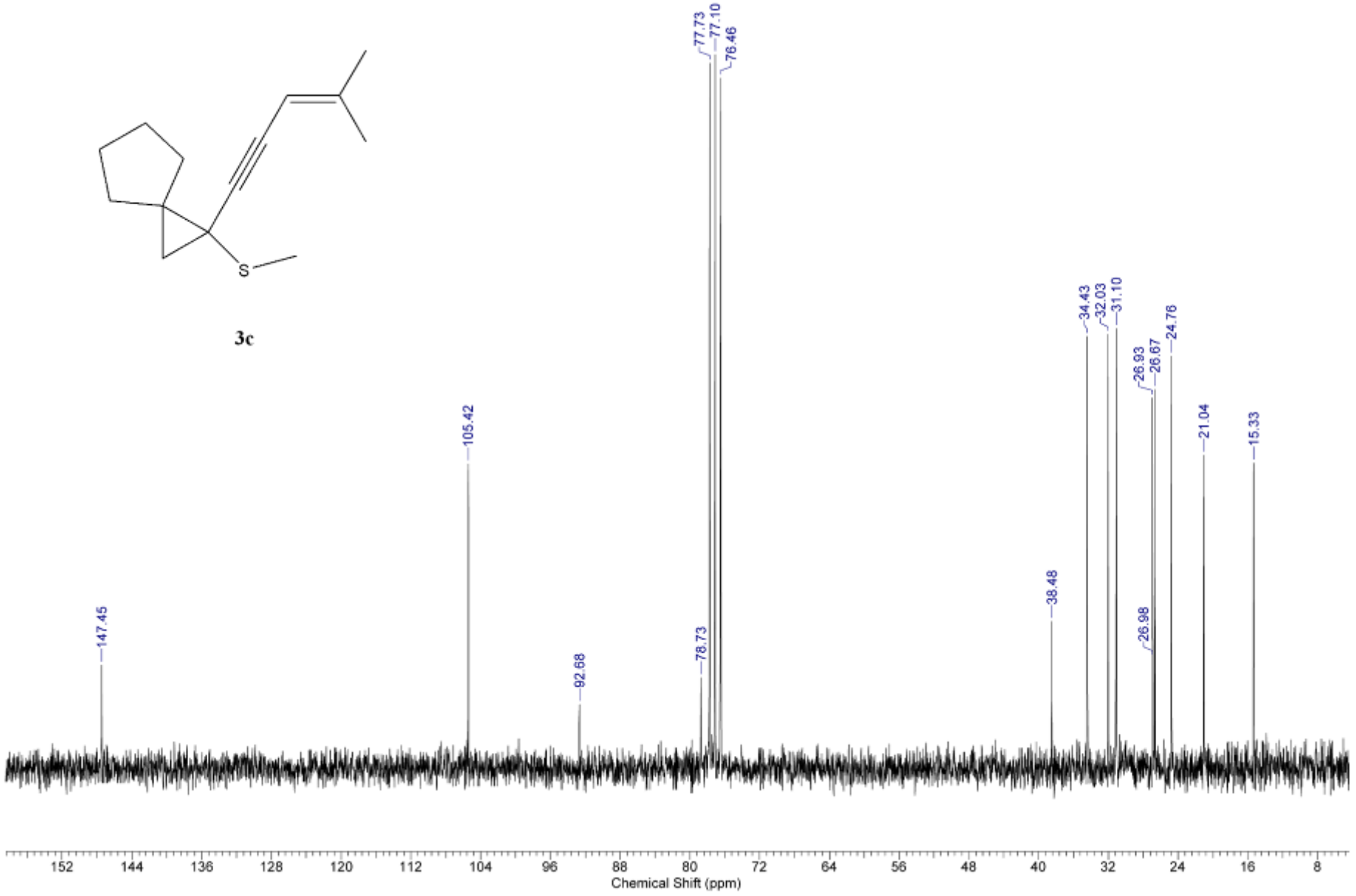
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


S
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31.10
26.93
26.67
26.98
24.76
21.04
15.33
152
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80
72
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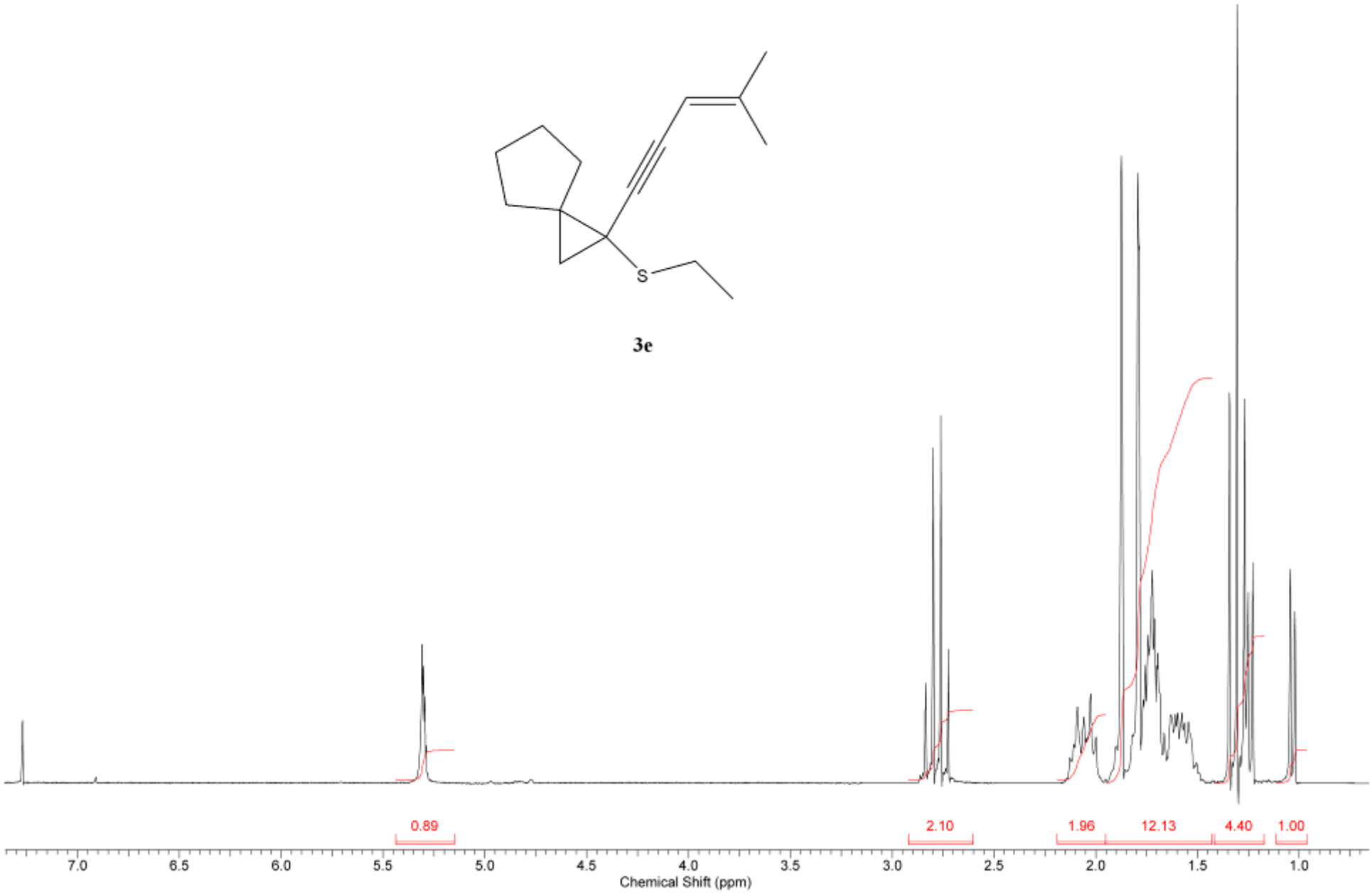
40
32
24
16
8
Chemical Shift (ppm)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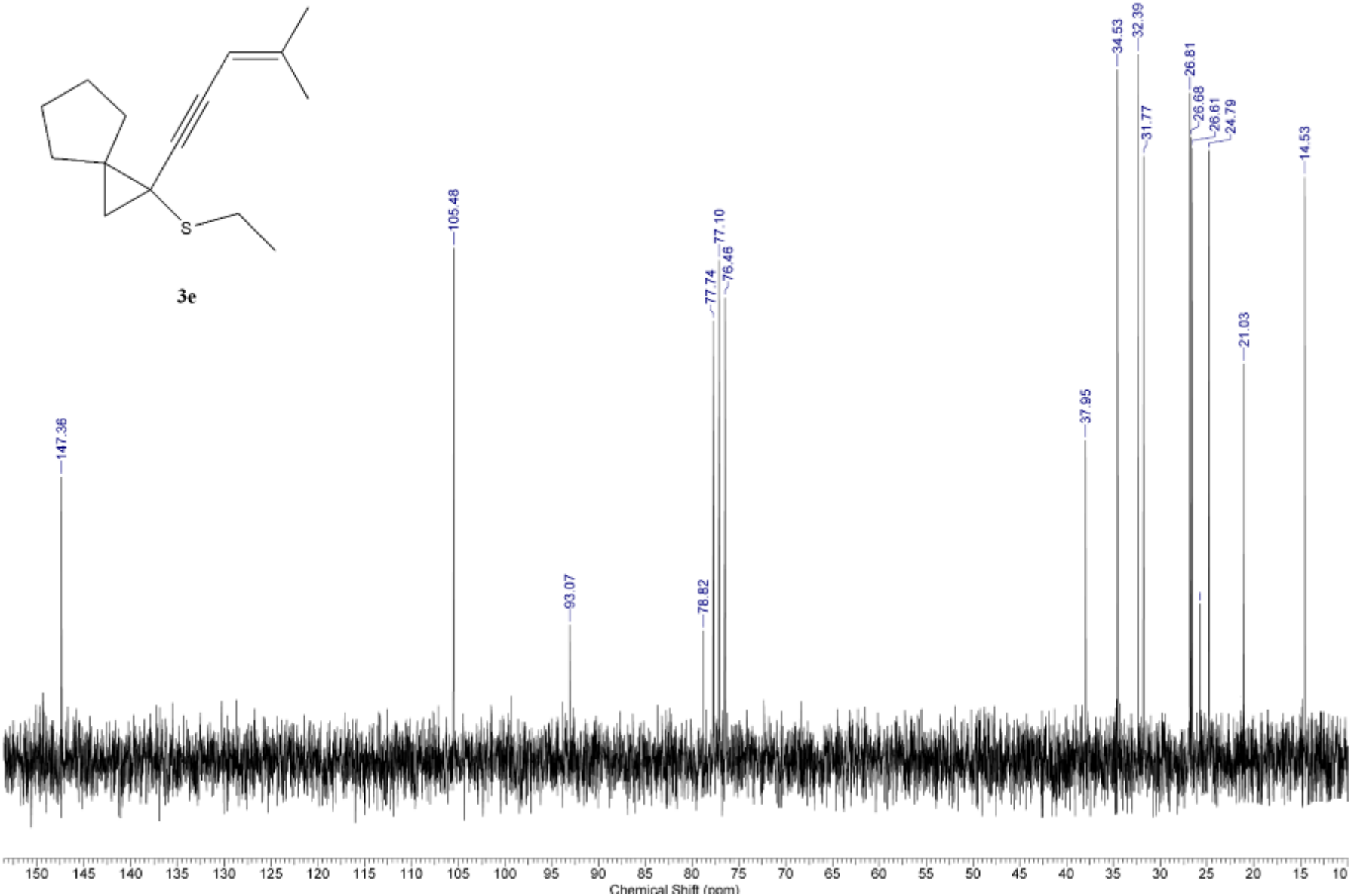
1.5
1.0
Chemical Shift (ppm)

3e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32.39
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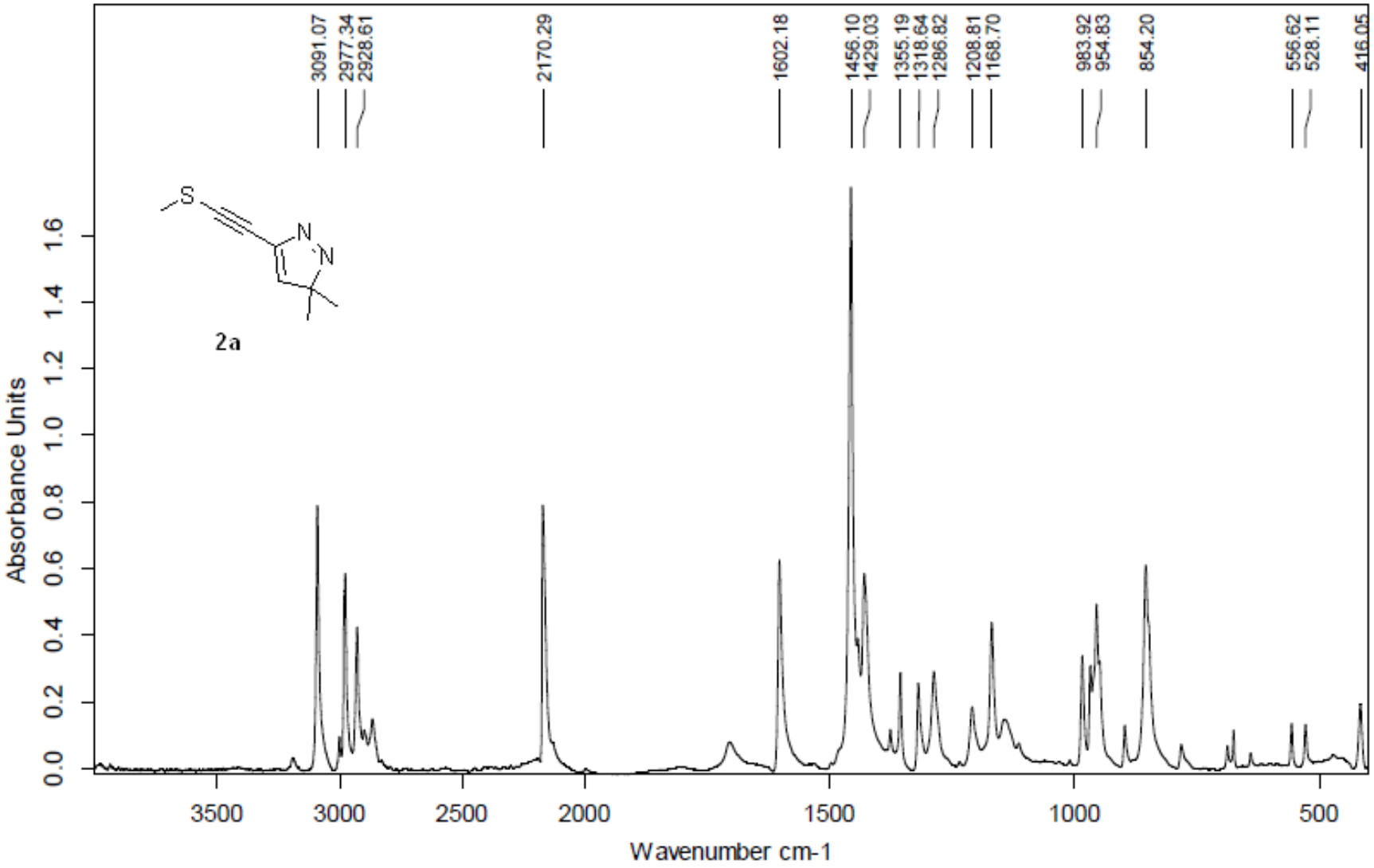
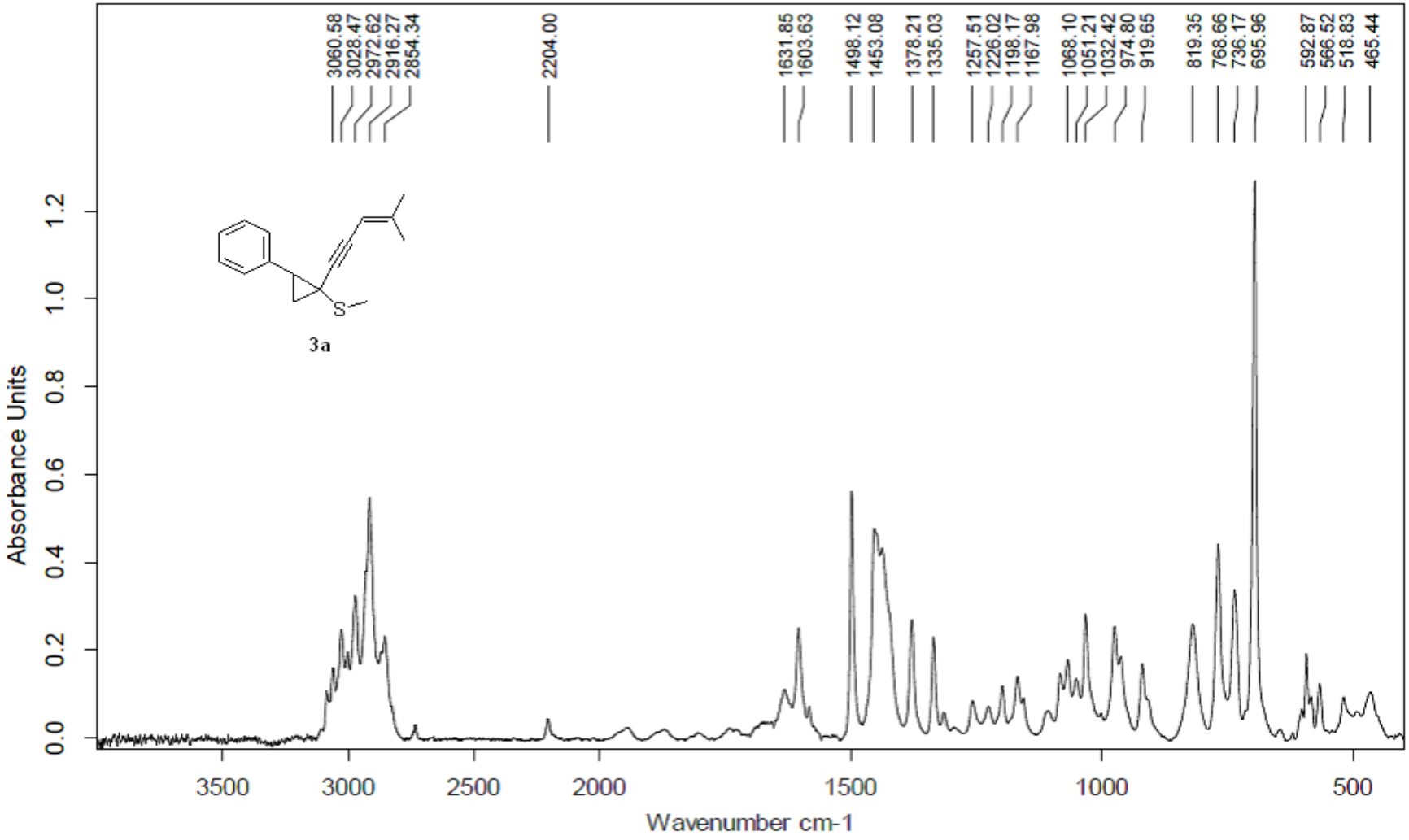
26.81
26.68
26.61
24.79
21.03
14.53
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
Chemical Shift (ppm)

Copies of IR-spectra for compounds **2a** *and* **3a,b,e** in KBr pellets

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1335.03
1257.51
1226.02
1198.17
1167.98
1068.10
1051.21
1032.42
974.80
919.65
819.35
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695.96
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S
3a
Absorbance Units
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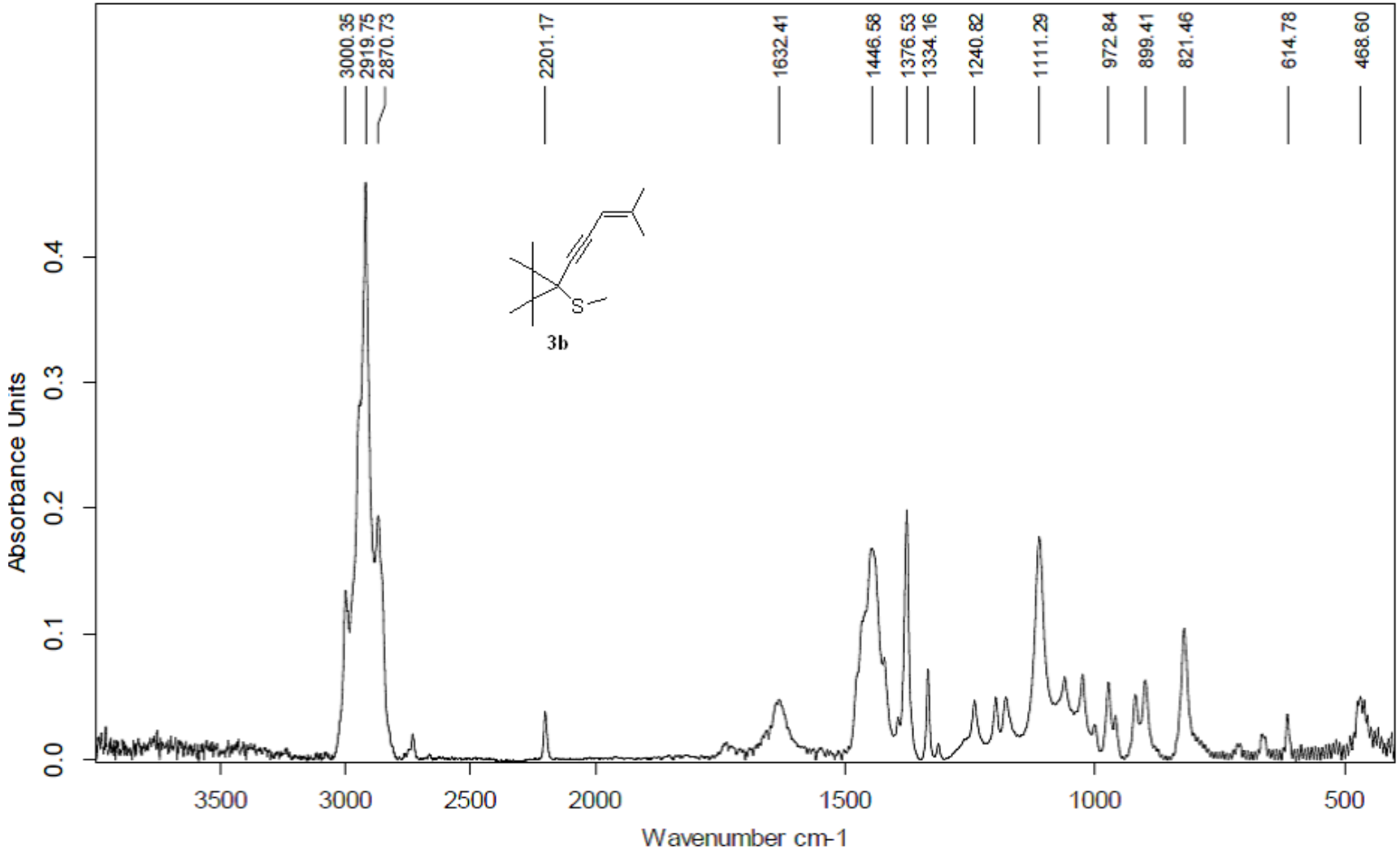
1500
1000
500
Wavenumber cm-1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614.78
468.60
S
3b
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1500
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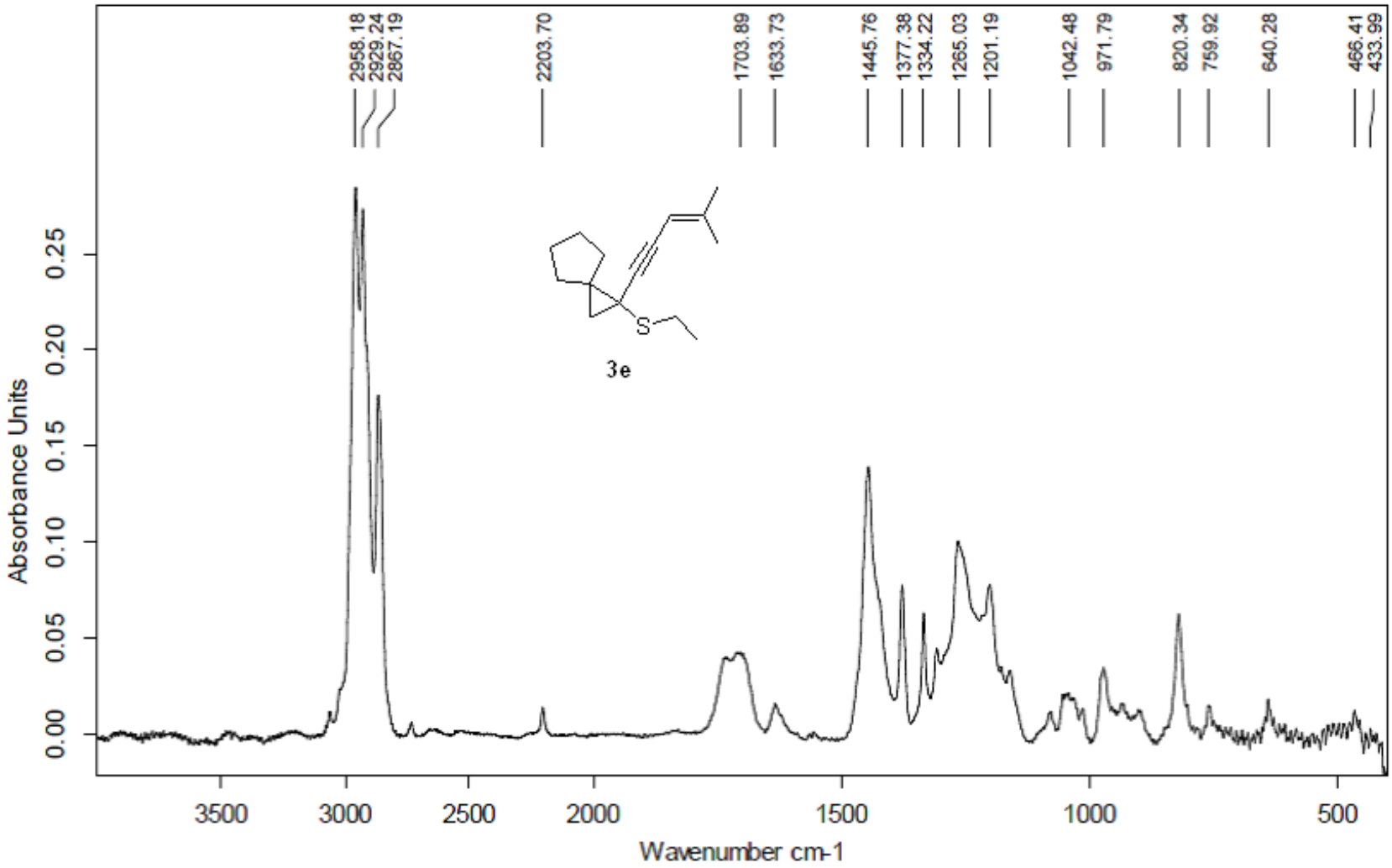
Wavenumber cm-1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S
3e
Absorbance Units
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0.25
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1