# Convenient and efficient synthesis of functionalized unsymmetrical alkynyl sulfides
Supporting Information

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Contents :



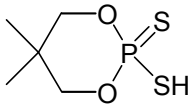
## General Information

All thiols and phosphorodithioic acid disulfane **2a** required for preparation of **2b-o** were purchased from ProChimia (www.prochimia.com). DDQ, *N, N, N', N'*-tetramethyletylenediamine (TMEDA), phenylethyne, 5-methylhex-1-yne, 4-methoxy-2-methylphenylethyne, ethyl propiolate and BuLi (2.5M in hexanes) are available from Aldrich. 5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)disulfanyl derivatives[1] **2a-b, 2i-k**, 1-benzyloxyprop-2-yne[2] and *N*-butoxycarbonylpropargylamine[3] were described previously and the analytical data of the obtained compounds were identical with the authentic samples. THF was dried before using by standard procedure. Column chromatography was performed using silica gel 60 (230–400 mesh, Merck). TLC was performed with silica gel Polygram SIL G/UV254 (Macherey-Nagel). Melting points were measured with a Gallenkamp 7936B apparatus and are uncorrected. NMR spectra were recorded on Varian Gemini 500 MHz, 200 MHz or Brucker 400 MHz spectrometers. The residual solvent peak was used as the internal reference ($CDCl_3$ : $\delta$ = 7.26 ppm for $^1H$, $\delta$ = 77.0 ppm for $^{13}C$). An external standard (85% $H_3PO_4$ : $\delta$ = 0 ppm) was used as the reference for recording the $^{31}P$ NMR spectra. ESI-MS spectra were recorded on a Mariner PerSeptive Biosystem.

**Improved synthesis of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphorinane and bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) disulfane 2a**

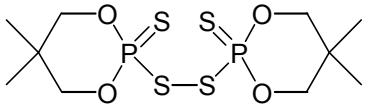
The purification of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphorinane has been accomplished previously by vacuum distillation.[7] The vacuum must be kept below 1.5 mmHg upon heating, otherwise content of the flask can decompose and sometimes explode. We have found that crude phosphorodithioic acid can be also purified by crystallization form carbon tetrachloride with 60% yield. Moreover, filtrate after crystallization can be used for preparation of ammonium salt required for preparation of phosphorodithioic acid disulfane **2a** (bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) disulfane). The modified procedures for preparation of phosphorodithioic acid and its disulfane make developed method more common and versatile.

**5,5-Dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphorinane**[7]



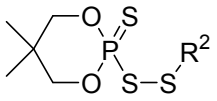

To a suspension of $P_4S_{10}$ 44.8 g (0.1 mol) in dry toluene (260 mL), a 2,2-dimethylpropane-1,3-diol 41.6 g (0.4 mol) was added. The reaction mixture was stirred at 60-80 $^oC$ for 15 h under nitrogen, then traces amount of unreacted $P_4S_{10}$ were filtered off. Solvent was evaporated under reduced pressure and residue was kept under vacuum at room temperature for 30 minutes. The obtained sticky solid was dissolved in hot $CCl_4$ (25 mL for each 10 g of crude product) and placed in the freezer (-15 $^oC$) for 6 h. Product was filtered off and dried under vacuum at room temperature to yield 47.6 g (0.24 mol, 60%), the residue from filtrate after evaporation of $CCl_4$ under reduced pressure can be used for preparation of phosphorodithioic acid ammonium salt.
mp 81-82 $^oC$ (Lit.[7c] 81-82 $^oC$), $^{31}P$ NMR ($CDCl_3$) = 77.68

**Bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfane 2a**[7]




A dry ammonia gas was passed through the solution of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphorinane 47.6 g (0.24 mol) (or residue from filtrate after evaporation of $CCl_4$, 32 g (0.16 mol)) in mixture of toluene (350 mL) and diethyl ether (50 mL) (ether is required to produce precipitate that is easier to filtered off) cooled in an ice bath for 30 minutes. White precipitate was filtered off and washed with toluene (50 mL) and ether (50 mL). After filtration ammonium salt was dried under vacuum to yield 49.5 g (0.23 mol, 96%) (or 28 g 0.13 mol, 81% from residue after evaporation filtrate) of white powder ($^{31}P$ NMR ($D_2O$) = 110.22).
A solution of the ammonium salt of phosphorodithioic acid 43 g (0.2 mol) in water (300 mL) was stirred at r.t. and a solution of $I_2$ 25.4 g (0.1 mol) and KI 50 g (0.31 mol) in water (200 mL) was added dropwise. The brown solid was filtered off, washed with water (400 mL) and dissolved in ethyl acetate (500 mL). Solution was washed with 10% $Na_2S_2O_3$ aqueous solution (50 mL), dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The residue was recrystallized from ethanol to yield bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) disulfane **2a** (33.5 g 0.085 mol, 85 %), mp 133-134 $^oC$ (Lit.[7c] 133.5-134 $^oC$), $^{31}P$ NMR ($CDCl_3$) = 80.87

**General procedure for the preparation of disulfanyl derivatives 2**[1]

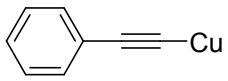


**2**

$R^2$ = $-(CH_2)_{11}CH_3$, **2b**
$-(CH_2)_{11}OH$, **2i**
$-(CH_2)_{10}CO_2H$, **2j**
$-C_6H_4$-4-$CH_3$, **2k**

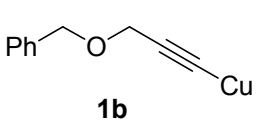
A thiol (1.0 mmol) and bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfane **2a** 394 mg (1.0 mmol) were dissolved in acetonitrile (2.0 mL) and cooled to 0 ºC in the ice bath. Then a solution of DDQ 114 mg (0.5 mmol) in acetonitrile (2.0 mL) was added slowly to the reaction mixture and stirred for 5 min at 0 ºC. The reaction was monitored by TLC analysis. Solvent was removed under reduced pressure and the residue was directly purified by column chromatography ($SiO_2$).
5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)disulfanyl derivatives **2b,**[4] **2i-j,**[5] **2k**,[6] were described previously and the analytical data of the obtained compounds were identical with the authentic samples.

**A typical procedure for the synthesis of copper(I) phenylethyne 1a.**[8]

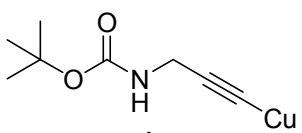


**1a**

To a stirred solution of $CuSO_4$ $5H_2O$ 25 g (100 mmol), aqueous ammonia (28%, 100 mL) and water (400 mL) at 0 ºC was added solid $NH_2OH$ HCl 13.9 g (200 mmol) under $N_2$. After 10 min, a solution of phenylethyne 10.25 g (100.5 mmol) in EtOH (95%, 500 mL) was added rapidly. The resultant suspension was stirred for 5 min and water (500 mL) was added. After 5 min without stirring, the yellow solid was collected on a sintered glass filter and washed successively with water (5 x 100 mL), EtOH (5 x 100 mL) and $Et_2O$ (5 x 100 mL). The solid was dried in vacuum for 6 h at room temperature to provide 14 g (85%) of copper(I) phenylethyne **1a** as bright yellow crystals.



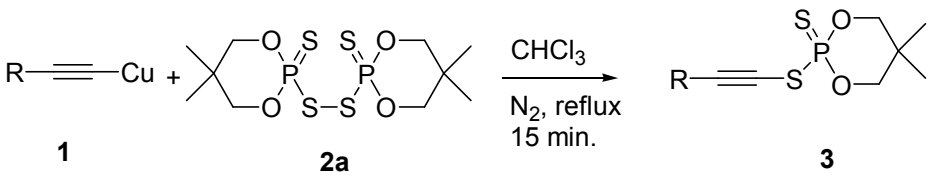
**1b**



**1c**

Copper(I) acetylides[9] **1b** and **1c** were described previously and the analytical data of the obtained compounds were identical with the authentic samples.

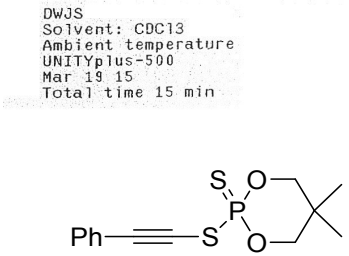
**Reaction of 1-Copper (I) acetylides 1 with disulfane 2a**




A suspension of copper (I) acetylide **1** (1.0 mmol) and bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfane **2a** 395 mg (1.0 mmol) in $CHCl_3$ (10 mL) was refluxed for 15 min under $N_2$. The reaction was monitored by TLC analysis (disappearance of starting material **2a**, toluene, $R_f = 0.3$). Solvent was removed under reduced pressure and the residue was directly purified by column chromatography ($SiO_2$).

**1-[(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)sulfanyl]-2-phenylethyne (3a)**

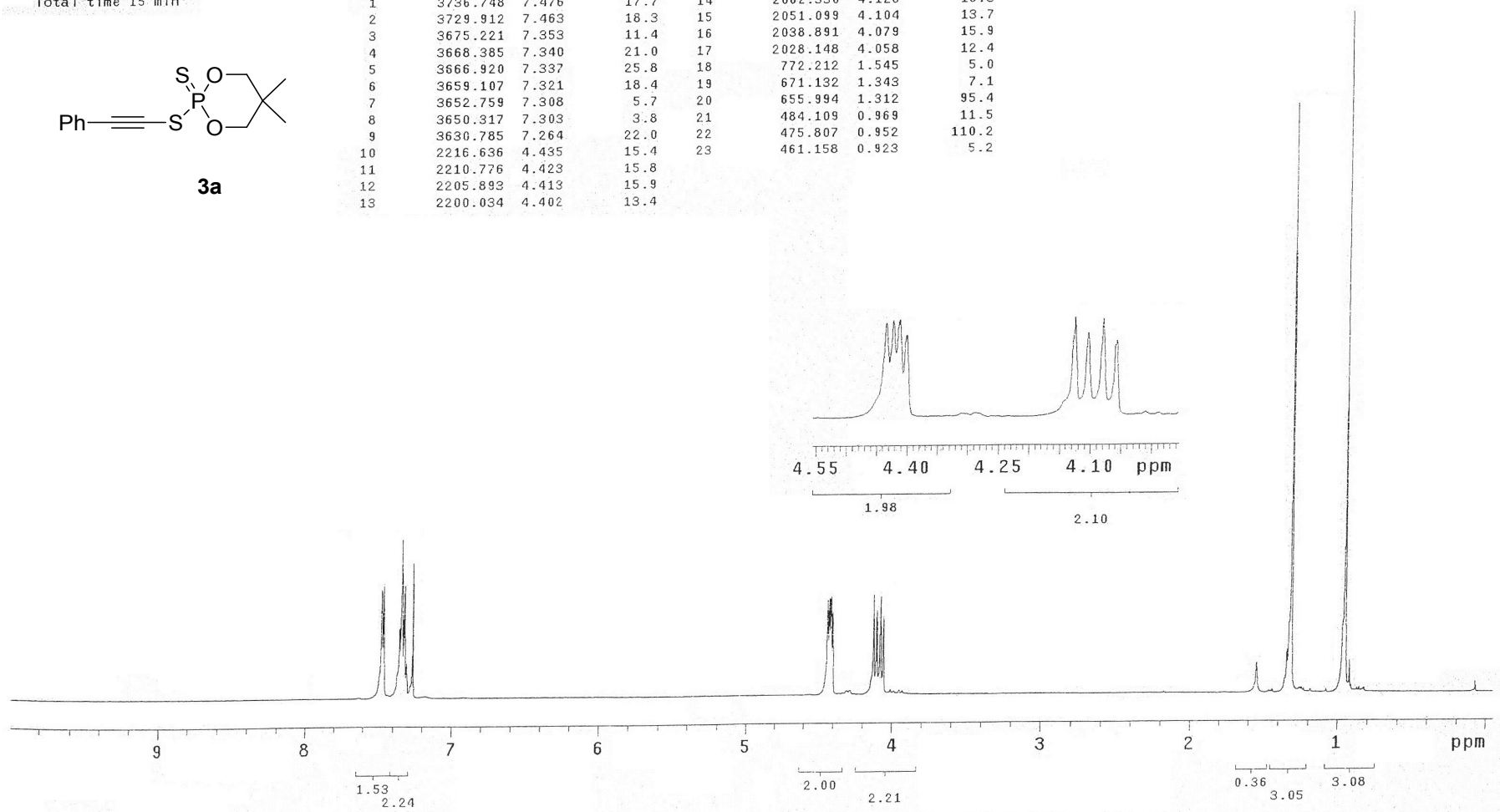
chromatography: $CH_2Cl_2$ : petroleum ether, 1:4, ($R_f$ = 0.2), then 1:2, white solid; mp 76-78 °C, yield: 200 mg, 0.67 mmol, (67%).



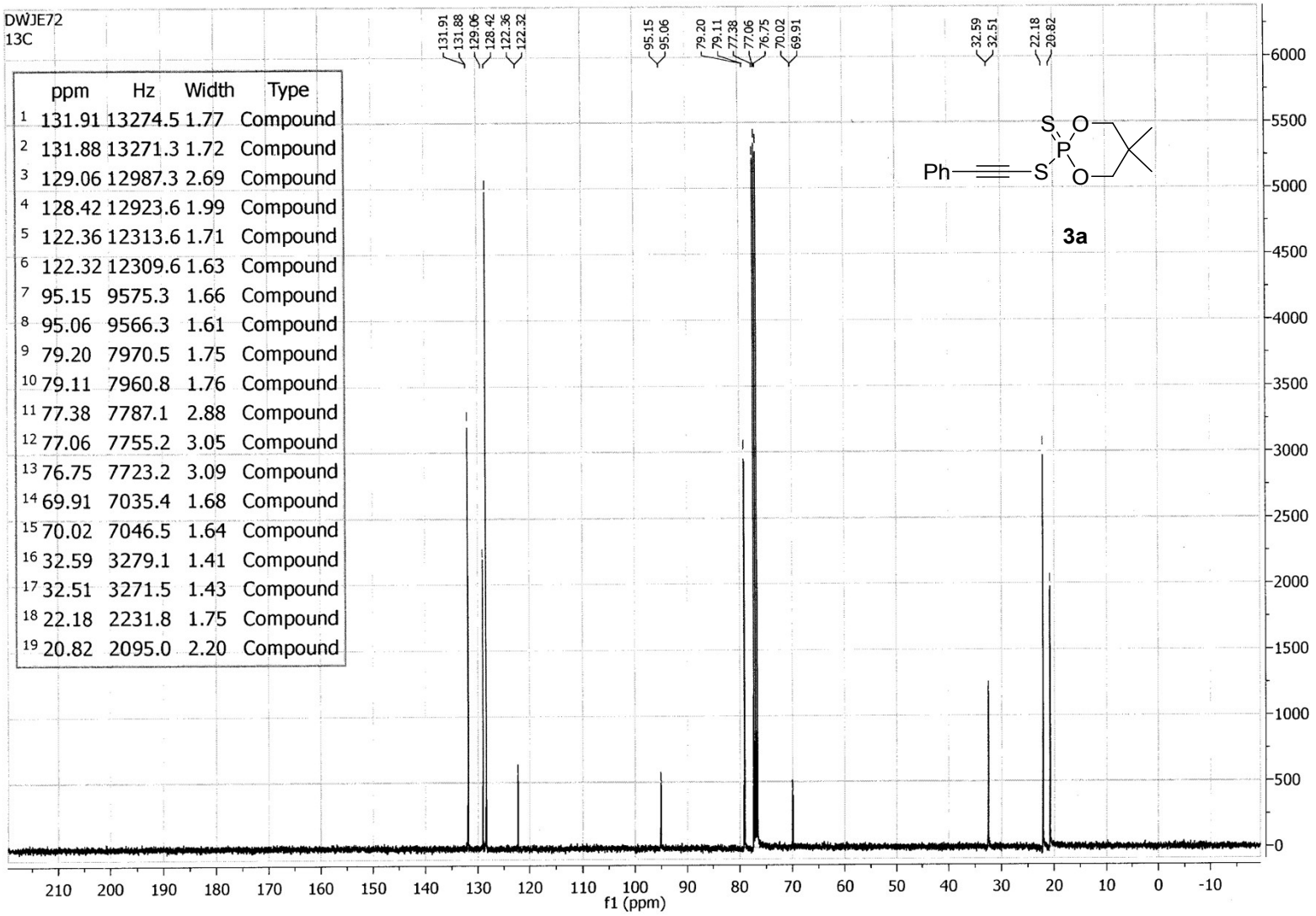

**3a**

DWJS
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Mar 19 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3736.748 | 7.476 | 17.7 | 14 | 2062.330 | 4.126 | 16.3 |
| 2 | 3729.912 | 7.463 | 18.3 | 15 | 2051.099 | 4.104 | 13.7 |
| 3 | 3675.221 | 7.353 | 11.4 | 16 | 2038.891 | 4.079 | 15.9 |
| 4 | 3668.385 | 7.340 | 21.0 | 17 | 2028.148 | 4.058 | 12.4 |
| 5 | 3666.920 | 7.337 | 25.8 | 18 | 772.212 | 1.545 | 5.0 |
| 6 | 3659.107 | 7.321 | 18.4 | 19 | 671.132 | 1.343 | 7.1 |
| 7 | 3652.759 | 7.308 | 5.7 | 20 | 655.994 | 1.312 | 95.4 |
| 8 | 3650.317 | 7.303 | 3.8 | 21 | 484.109 | 0.969 | 11.5 |
| 9 | 3630.785 | 7.264 | 22.0 | 22 | 475.807 | 0.952 | 110.2 |
| 10 | 2216.636 | 4.435 | 15.4 | 23 | 461.158 | 0.923 | 5.2 |
| 11 | 2210.776 | 4.423 | 15.8 | | | | |
| 12 | 2205.893 | 4.413 | 15.9 | | | | |
| 13 | 2200.034 | 4.402 | 15.4 | | | | |

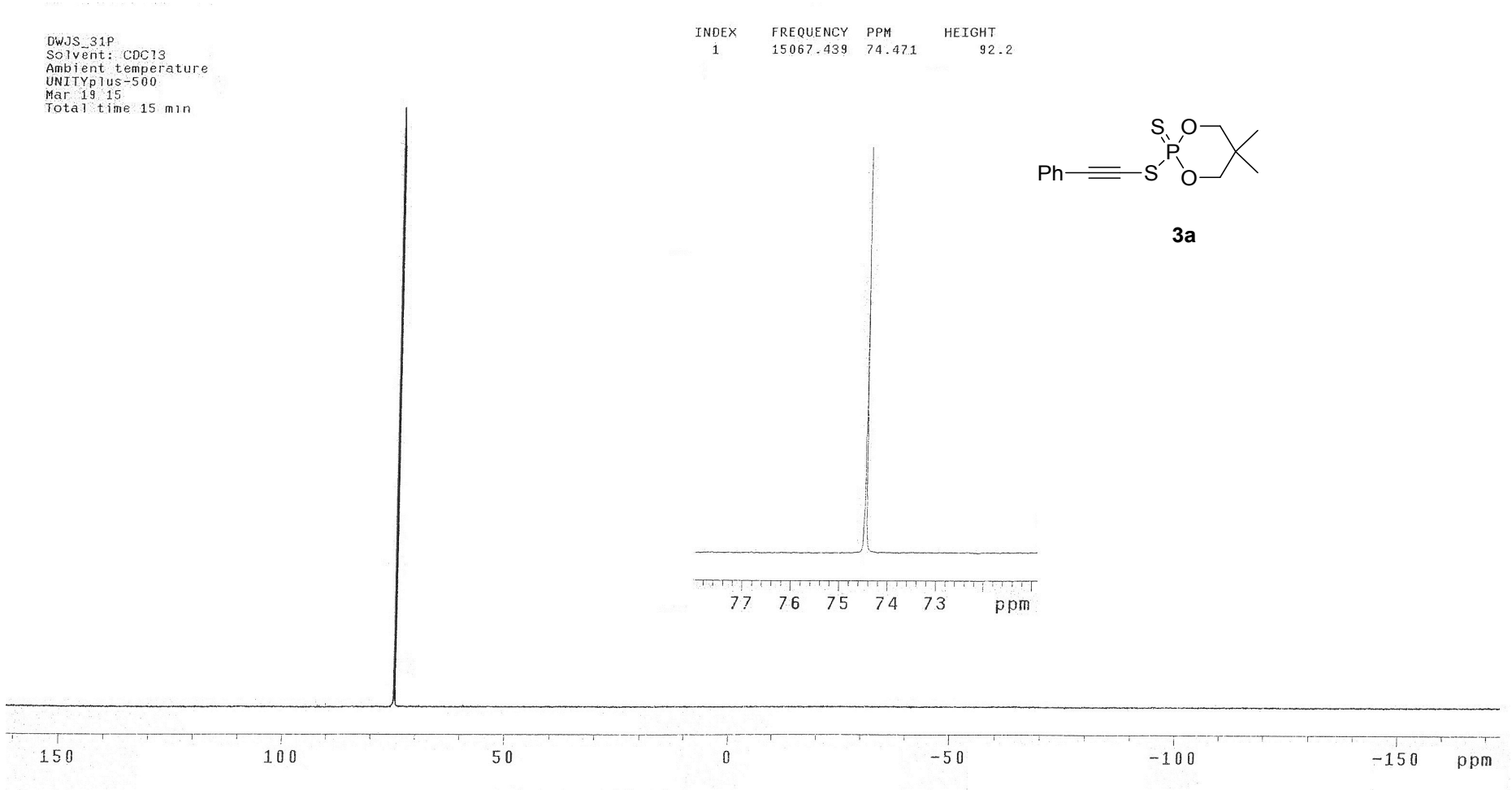



$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.95 (s, 3H, $CH_3$), 1.31 (s, 3H, $CH_3$), 4.00-4.15 (m, 2H, $OCH_2$), 4.38-4.48 (m, 2H, $OCH_2$), 7.26-7.38 (m, 3H, Ph), 7.40-7.48 (m, 2H, Ph).




| | ppm | Hz | Width | Type |
|---|---|---|---|---|
| 1 | 131.91 | 13274.5 | 1.77 | Compound |
| 2 | 131.88 | 13271.3 | 1.72 | Compound |
| 3 | 129.06 | 12987.3 | 2.69 | Compound |
| 4 | 128.42 | 12923.6 | 1.99 | Compound |
| 5 | 122.36 | 12313.6 | 1.71 | Compound |
| 6 | 122.32 | 12309.6 | 1.63 | Compound |
| 7 | 95.15 | 9575.3 | 1.66 | Compound |
| 8 | 95.06 | 9566.3 | 1.61 | Compound |
| 9 | 79.20 | 7970.5 | 1.75 | Compound |
| 10 | 79.11 | 7960.8 | 1.76 | Compound |
| 11 | 77.38 | 7787.1 | 2.88 | Compound |
| 12 | 77.06 | 7755.2 | 3.05 | Compound |
| 13 | 76.75 | 7723.2 | 3.09 | Compound |
| 14 | 69.91 | 7035.4 | 1.68 | Compound |
| 15 | 70.02 | 7046.5 | 1.64 | Compound |
| 16 | 32.59 | 3279.1 | 1.41 | Compound |
| 17 | 32.51 | 3271.5 | 1.43 | Compound |
| 18 | 22.18 | 2231.8 | 1.75 | Compound |
| 19 | 20.82 | 2095.0 | 2.20 | Compound |

$^{13}$C NMR (100 MHz, $CDCl_3$): δ= 131.9 (d, *J* = 3.2 Hz), 129.1, 128.4, 122.3 (d, *J* = 4.0 Hz), 95.1 (d, *J* = 9.0 Hz),79.2 (d, *J* = 9.7 Hz), 70.0 (d, *J* = 11.1 Hz), 32.6 (d, *J* = 7.6 Hz), 22.2, 20.8; signals: expected and observed 10.







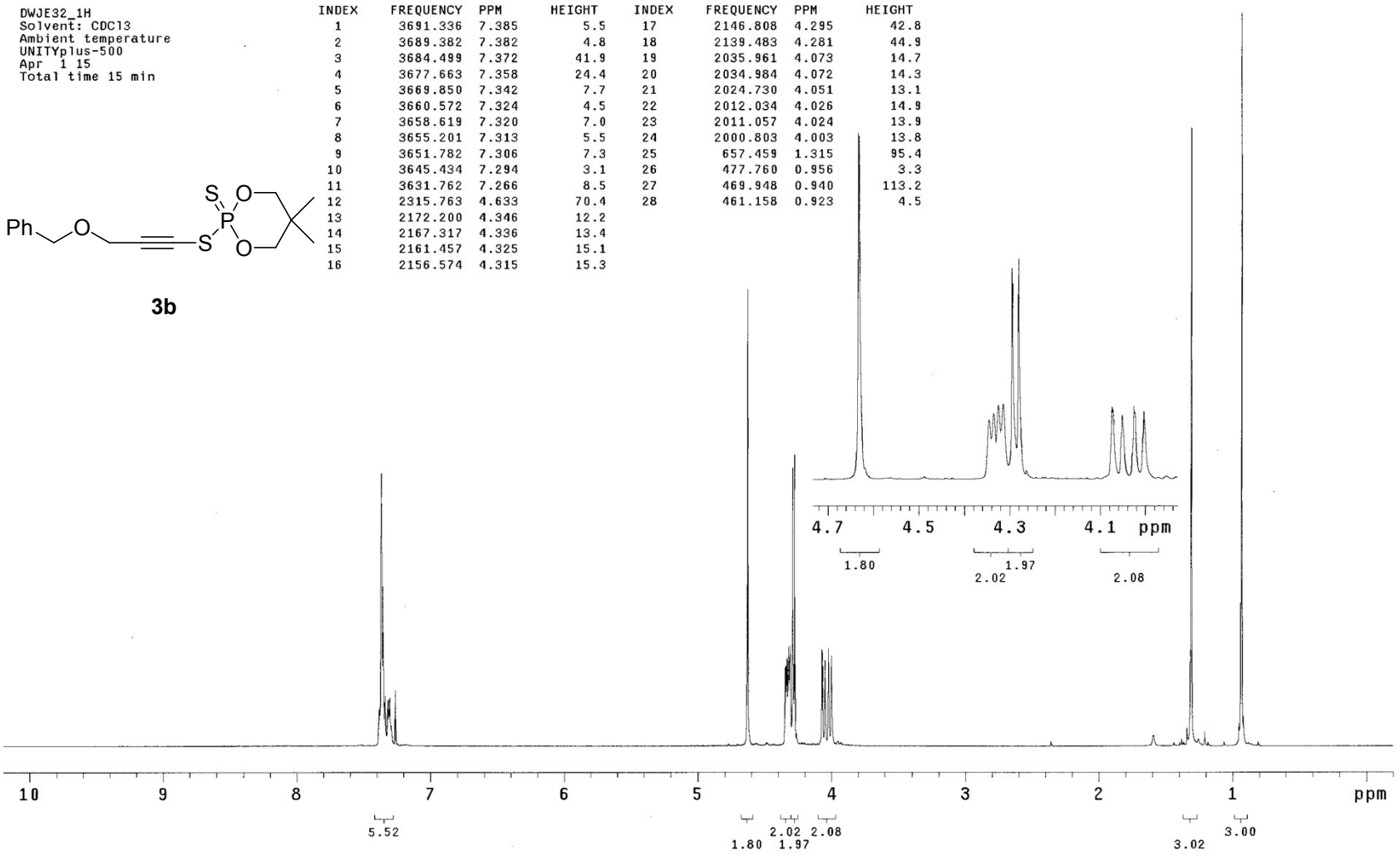
**3a**

$^{31}$P NMR (202 MHz, $CDCl_3$): δ = 74.47

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{13}H_{16}O_2PS_2$: 299.0329; found: 299.0336.

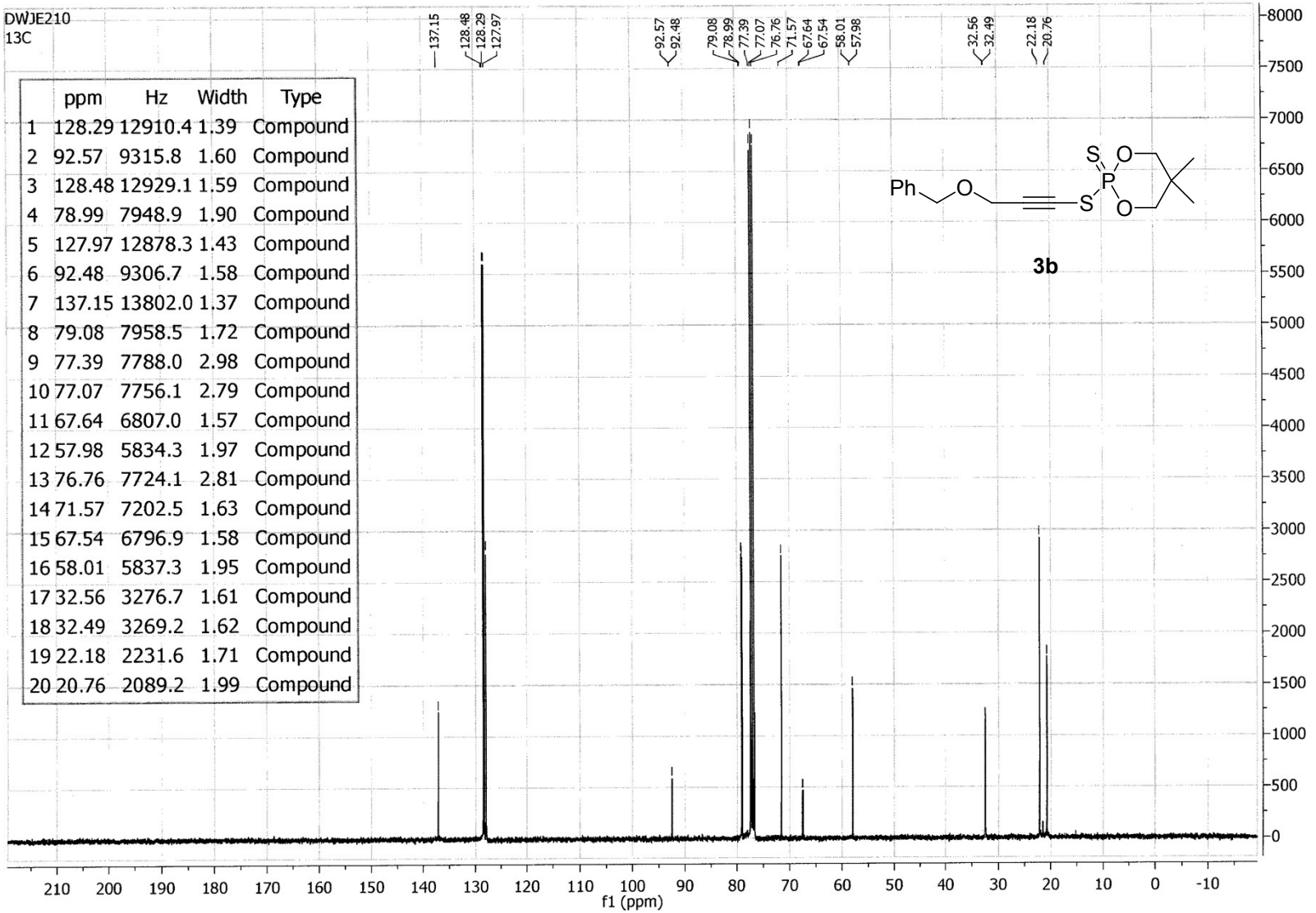
**1-[(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)sulfanyl]-3-benzyloxyprop-1-yne (3b)**

chromatography: $CH_2Cl_2$ : petroleum ether, 1:2, ($R_f$ = 0.2), then 1:1, white solid; mp 57.2-58.3 °C, yield: 137 mg, 0.40 mmol, (40%).



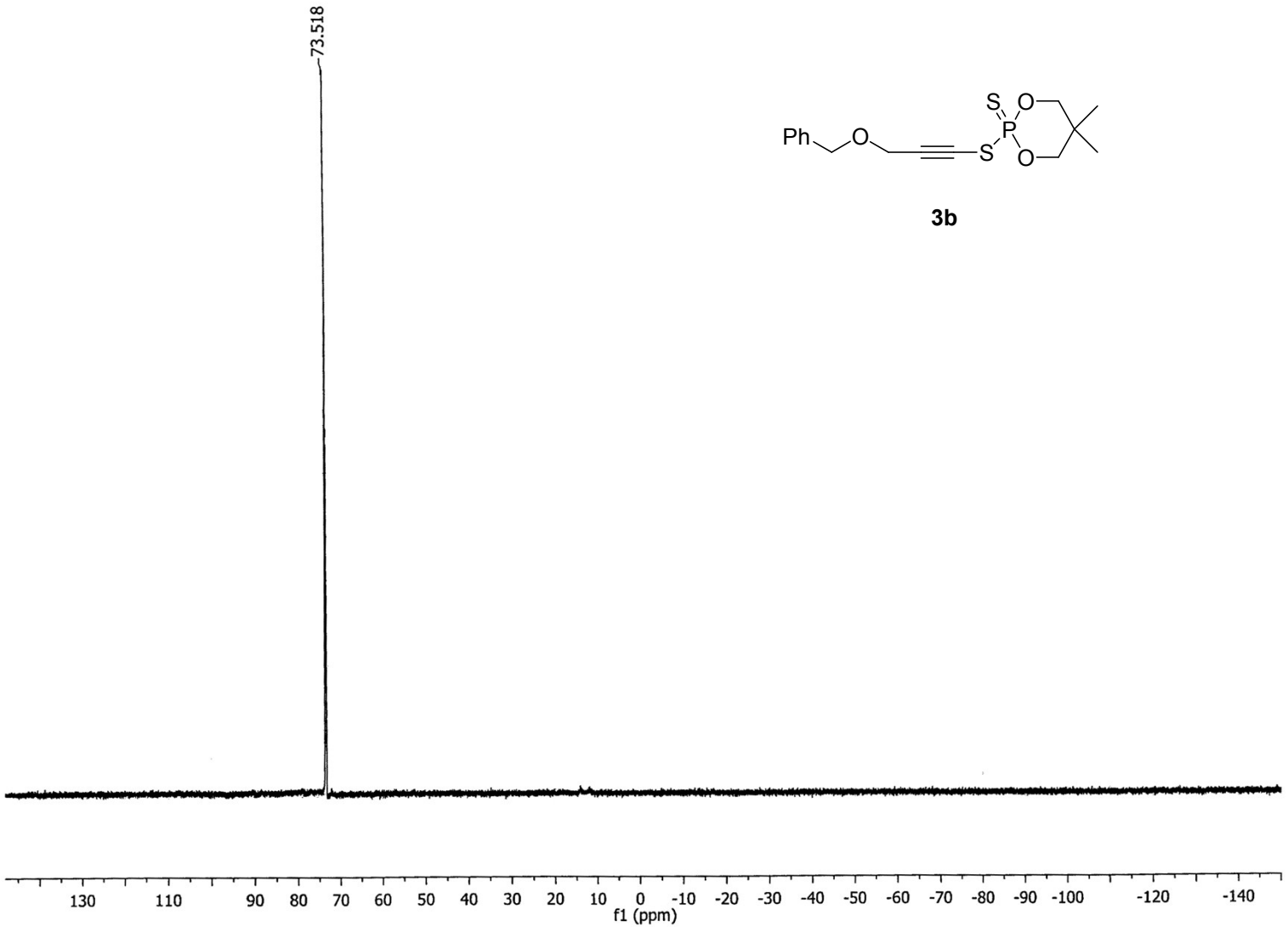

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3691.336 | 7.385 | 5.5 | 17 | 2146.808 | 4.295 | 42.8 |
| 2 | 3689.382 | 7.382 | 4.8 | 18 | 2139.483 | 4.281 | 44.9 |
| 3 | 3684.499 | 7.372 | 41.9 | 19 | 2035.961 | 4.073 | 14.7 |
| 4 | 3677.663 | 7.358 | 24.4 | 20 | 2034.984 | 4.072 | 14.3 |
| 5 | 3669.850 | 7.342 | 7.7 | 21 | 2024.730 | 4.051 | 13.1 |
| 6 | 3660.572 | 7.324 | 4.5 | 22 | 2012.034 | 4.026 | 14.9 |
| 7 | 3658.619 | 7.320 | 7.0 | 23 | 2011.057 | 4.024 | 13.9 |
| 8 | 3655.201 | 7.313 | 5.5 | 24 | 2000.803 | 4.003 | 13.8 |
| 9 | 3651.782 | 7.306 | 7.3 | 25 | 657.459 | 1.315 | 95.4 |
| 10 | 3645.434 | 7.294 | 3.1 | 26 | 477.760 | 0.956 | 3.3 |
| 11 | 3631.762 | 7.266 | 8.5 | 27 | 469.948 | 0.940 | 113.2 |
| 12 | 2315.763 | 4.633 | 70.4 | 28 | 461.158 | 0.923 | 4.5 |
| 13 | 2172.200 | 4.346 | 12.2 | | | | |
| 14 | 2167.317 | 4.336 | 13.4 | | | | |
| 15 | 2161.457 | 4.325 | 15.1 | | | | |
| 16 | 2156.574 | 4.315 | 15.3 | | | | |

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.94 (s, 3H, $CH_3$), 1.32 (s, 3H, $CH_3$), 3.98-4.10 (m, 2H, $POCH_2$), 4.29 (d, $J$ = 7.3 Hz, 2H, $OCH_2$) 4.30-4.36 (m, 2H, $POCH_2$), 4.63 (s, 2H, $OCH_2$), 7.26-7.40 (m, 5H, Ph).




| | ppm | Hz | Width | Type |
|---|---|---|---|---|
| 1 | 128.29 | 12910.4 | 1.39 | Compound |
| 2 | 92.57 | 9315.8 | 1.60 | Compound |
| 3 | 128.48 | 12929.1 | 1.59 | Compound |
| 4 | 78.99 | 7948.9 | 1.90 | Compound |
| 5 | 127.97 | 12878.3 | 1.43 | Compound |
| 6 | 92.48 | 9306.7 | 1.58 | Compound |
| 7 | 137.15 | 13802.0 | 1.37 | Compound |
| 8 | 79.08 | 7958.5 | 1.72 | Compound |
| 9 | 77.39 | 7788.0 | 2.98 | Compound |
| 10 | 77.07 | 7756.1 | 2.79 | Compound |
| 11 | 67.64 | 6807.0 | 1.57 | Compound |
| 12 | 57.98 | 5834.3 | 1.97 | Compound |
| 13 | 76.76 | 7724.1 | 2.81 | Compound |
| 14 | 71.57 | 7202.5 | 1.63 | Compound |
| 15 | 67.54 | 6796.9 | 1.58 | Compound |
| 16 | 58.01 | 5837.3 | 1.95 | Compound |
| 17 | 32.56 | 3276.7 | 1.61 | Compound |
| 18 | 32.49 | 3269.2 | 1.62 | Compound |
| 19 | 22.18 | 2231.6 | 1.71 | Compound |
| 20 | 20.76 | 2089.2 | 1.99 | Compound |

$^{13}$C NMR (100 MHz, $CDCl_3$): δ= 137.2, 128.5, 128.3, 128.0, 92.5 (d, $J$ = 9.1 Hz), 79.0 (d, $J$ = 9.6 Hz), 71.6, 67.6 (d, $J$ = 10.1 Hz), 58.0 (d, $J$ = 3.0 Hz), 32.5 (d, $J$ = 7.5 Hz), 22.2, 20.8; signals: expected and observed 12.




**3b**

$^{31}$P NMR (202 MHz, $CDCl_3$): δ = 73.52

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{15}H_{20}O_3PS_2$: 343.0591; found: 343.0585.

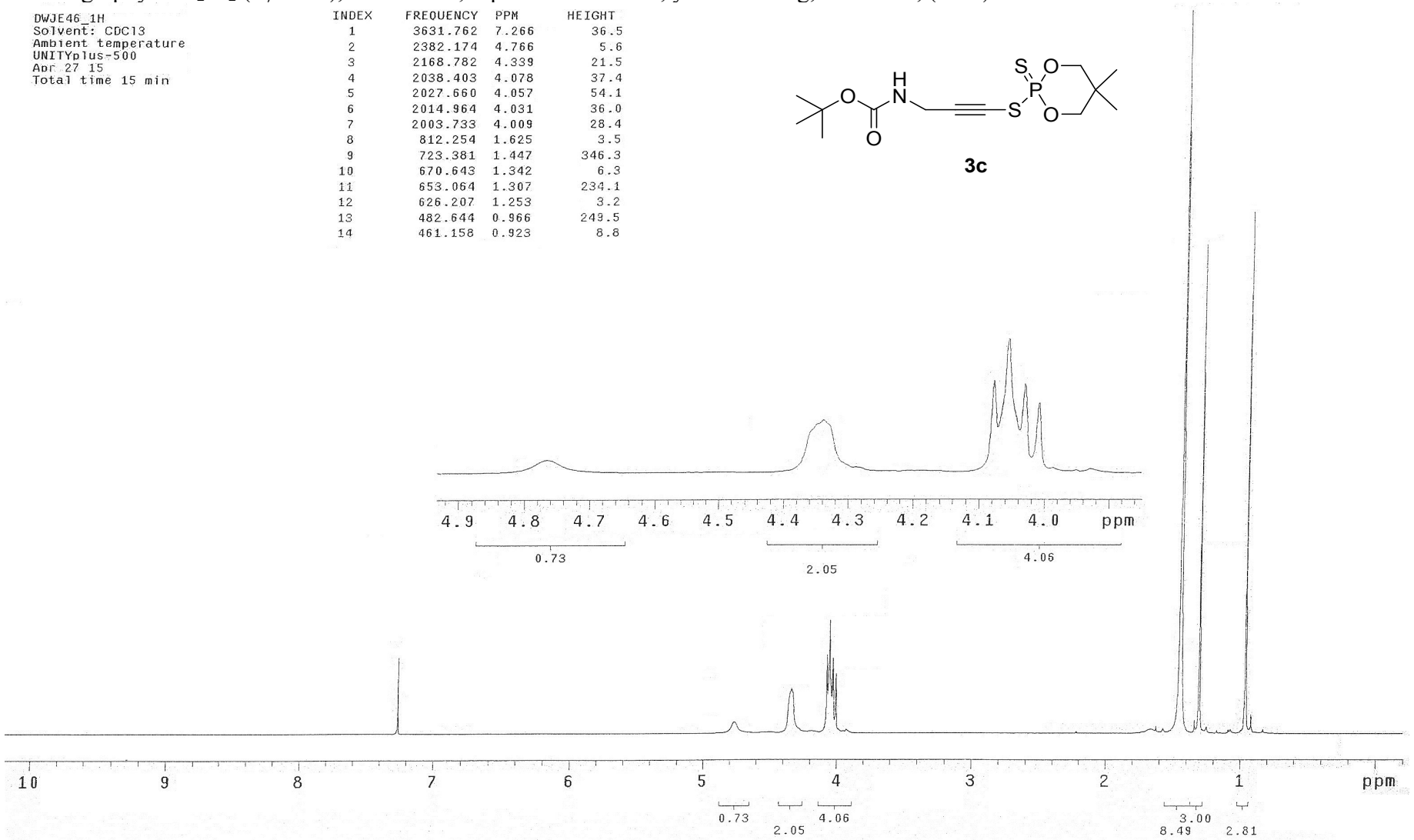
**3-[(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)sulfanyl]-*N*-butoxycarbonyl-prop-2-ynylamine (3c)**
chromatography: $CH_2Cl_2$ ($R_f$ = 0.3), white solid; mp 110.1-110.9 °C, yield: 105 mg, 0.3 mmol, (30%).

DWJE46_1H
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Apr 27 15
Total time 15 min

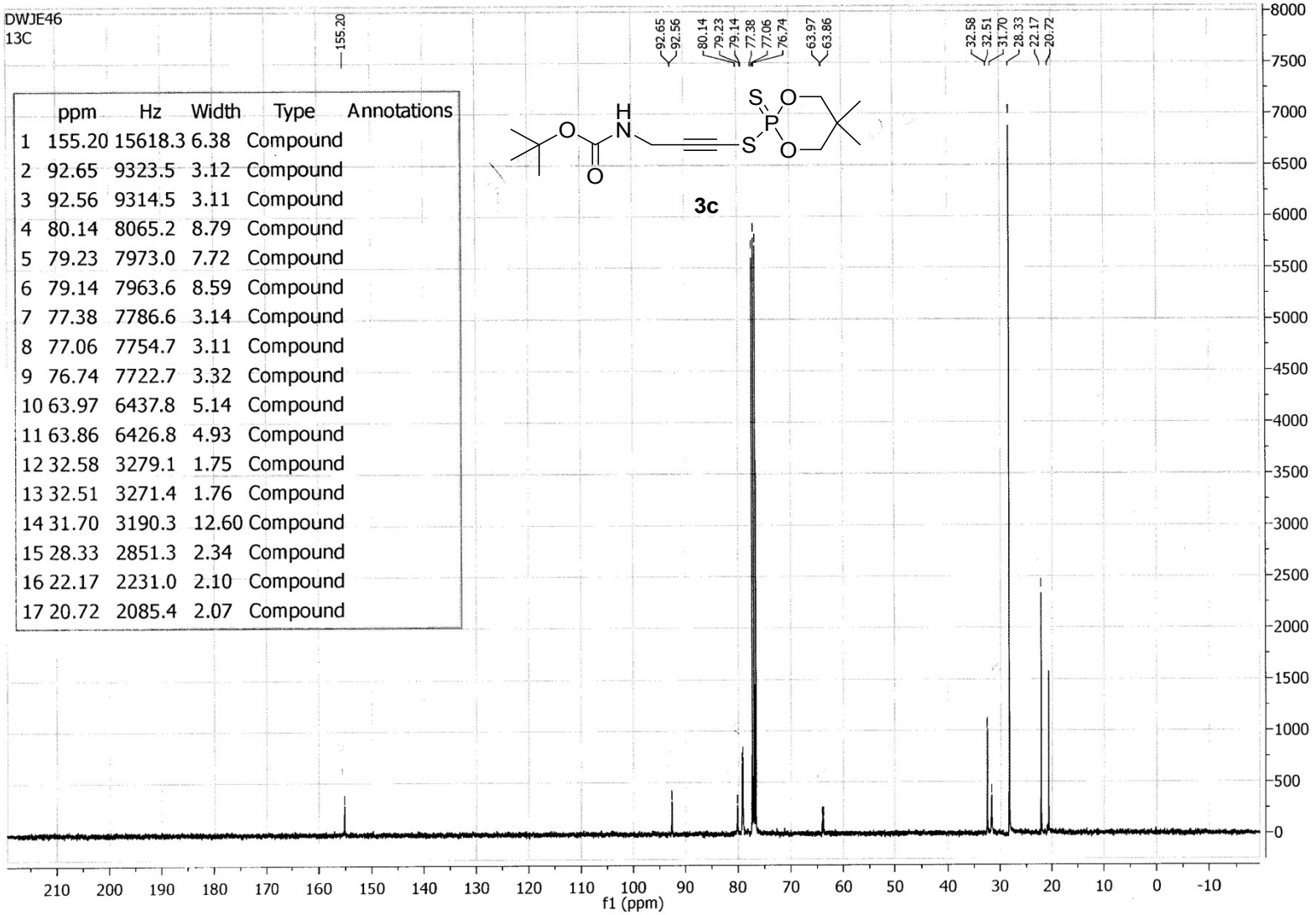
| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 3631.762 | 7.266 | 36.5 |
| 2 | 2382.174 | 4.766 | 5.6 |
| 3 | 2168.782 | 4.339 | 21.5 |
| 4 | 2038.403 | 4.078 | 37.4 |
| 5 | 2027.660 | 4.057 | 54.1 |
| 6 | 2014.964 | 4.031 | 36.0 |
| 7 | 2003.733 | 4.009 | 28.4 |
| 8 | 812.254 | 1.625 | 3.5 |
| 9 | 723.381 | 1.447 | 346.3 |
| 10 | 670.643 | 1.342 | 6.3 |
| 11 | 653.064 | 1.307 | 234.1 |
| 12 | 626.207 | 1.253 | 3.2 |
| 13 | 482.644 | 0.966 | 249.5 |
| 14 | 461.158 | 0.923 | 8.8 |




**3c**




$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.97 (s, 3H, $CH_3$), 1.31 (s, 3H, $CH_3$), 4.00-4.10 (m, 4H, $POCH_2$), 4.34 (bs, 2H, $NCH_2$), 4.77 (bs, 1H, NH).




| | ppm | Hz | Width | Type | Annotations |
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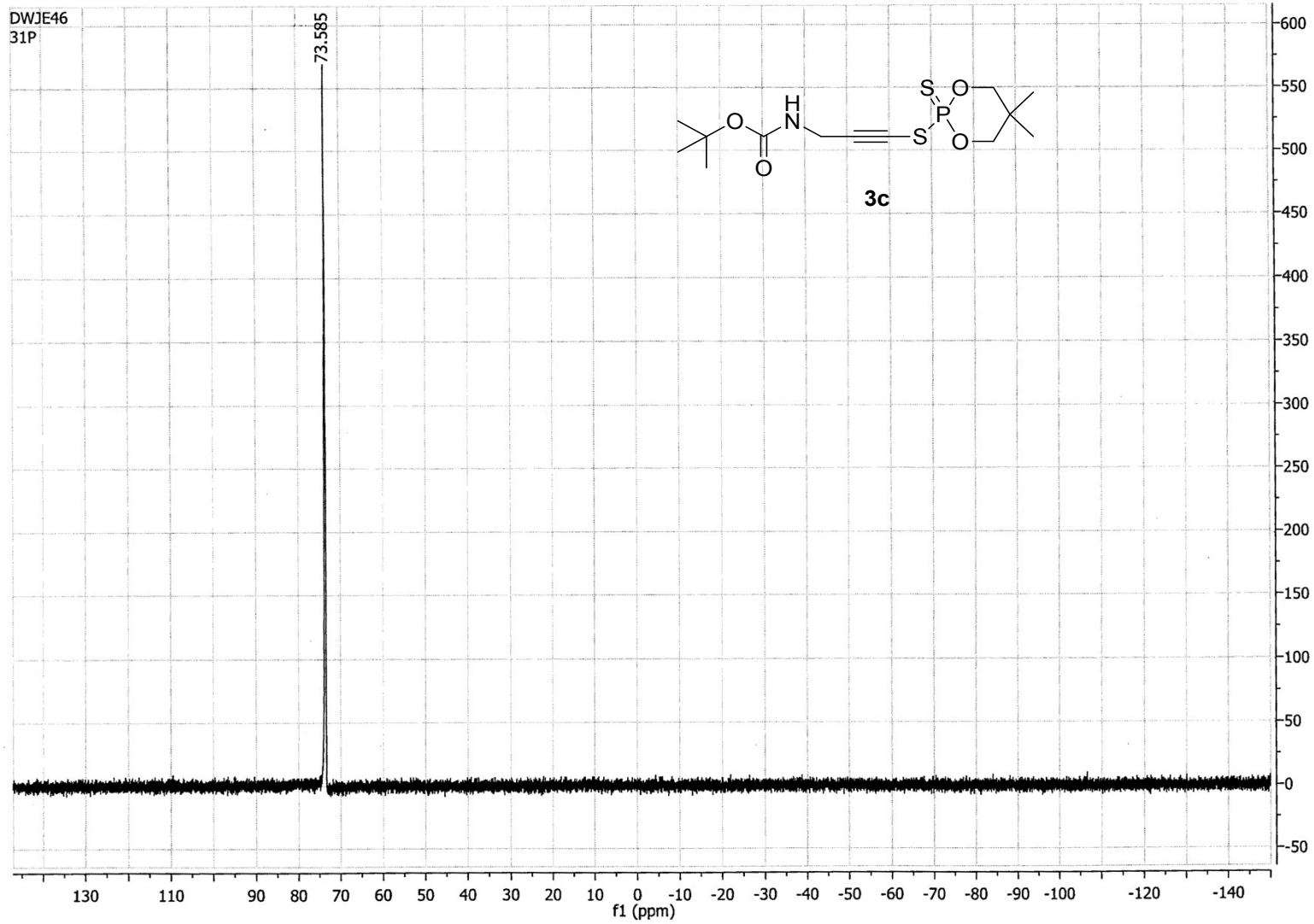
| 2 | 92.65 | 9323.5 | 3.12 | Compound | |
| 3 | 92.56 | 9314.5 | 3.11 | Compound | |
| 4 | 80.14 | 8065.2 | 8.79 | Compound | |
| 5 | 79.23 | 7973.0 | 7.72 | Compound | |
| 6 | 79.14 | 7963.6 | 8.59 | Compound | |
| 7 | 77.38 | 7786.6 | 3.14 | Compound | |
| 8 | 77.06 | 7754.7 | 3.11 | Compound | |
| 9 | 76.74 | 7722.7 | 3.32 | Compound | |
| 10 | 63.97 | 6437.8 | 5.14 | Compound | |
| 11 | 63.86 | 6426.8 | 4.93 | Compound | |
| 12 | 32.58 | 3279.1 | 1.75 | Compound | |
| 13 | 32.51 | 3271.4 | 1.76 | Compound | |
| 14 | 31.70 | 3190.3 | 12.60 | Compound | |
| 15 | 28.33 | 2851.3 | 2.34 | Compound | |
| 16 | 22.17 | 2231.0 | 2.10 | Compound | |
| 17 | 20.72 | 2085.4 | 2.07 | Compound | |

$^{13}$C NMR (100 MHz, $CDCl_3$): δ= 155.2, 92.6 (d, *J* = 9.0 Hz), 80.1, 79.2 (d, *J* = 9.4 Hz), 63.9 (d, *J* = 11.0 Hz), 32.6 (d, *J* = 7.7 Hz), 31.7, 28.3, 22.2, 20.7; signals: expected and observed 10.




$^{31}$P NMR (162 MHz, $CDCl_3$): δ = 73.59

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{13}H_{23}NO_4PS_2$: 352.0806; found: 352.0811.

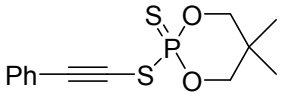
**General procedure for the preparation of alkynyl sulfides 3 and representative analytical data**

BuLi (2.5M, 0.44 mL, 1.1 mmol) (Note 1) was added to a solution of terminal alkyne (1.0 mmol) (phenylacetylene, 1-benzyloxyprop-2-yne, *N*-butoxycarbonylpropargylamine) and *N,N,N,'N,'*-tertamethylethylenediamine (TMEDA) (0.15 mL, 1.0 mmol) in anhydrous THF (10 mL) at 0 °C under $N_2$. After 5 min, a solution of disulfane **2** (1.1 mmol) (Note 2) in anhydrous THF (2 mL) was added. The mixture was stirred at r.t. for 30 min. The reaction was quenched by addition of MeOH (1 mL) and evaporated under vacuum. The residue was purified by column chromatography ($SiO_2$) to give alkynyl sulfide **3a-u**; yields are summarized in Table 1.

Note 1. BuLi (2.2 mmol) were used to generate **5c** from *N*-butoxycarbonylpropargylamine.

Note 2. In the case of disulfanes **2i** and **2j** with acidic protons (OH and $CO_2H$ respectively) the two fold excess of **5a** and **5b** was used. It was also possible to treat **2i** and **2j** with NaH before addition to solution of **5a** or **5b** in THF. Both methods provided appropriate alkynyl sulfides **3g**, **3h** and **3j**, **3k** with comparable yield respectively.

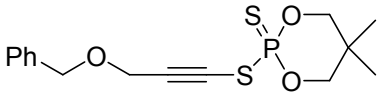
**1-[(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)sulfanyl]-2-phenylethyne (3a)**




**3a**

chromatography: $CH_2Cl_2$ : petroleum ether, 1:4, ($R_f$ = 0.2), then 1:2,
white solid; mp 76-78 °C, yield: 233 mg, 0.78 mmol, (78%).

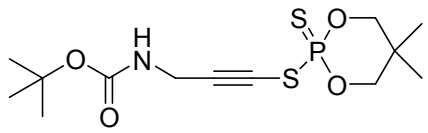
**1-[(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)sulfanyl]-3-benzyloxyprop-1-yne (3b)**




**3b**

chromatography: $CH_2Cl_2$ : petroleum ether, 1:2, ($R_f$ = 0.2), then 1:1,
white solid; mp 57.2-58.3 °C, yield: 257 mg, 0.75 mmol, (75%).

**3-[(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)sulfanyl]-*N*-butoxycarbonyl-prop-2-ynylamine (3c)**

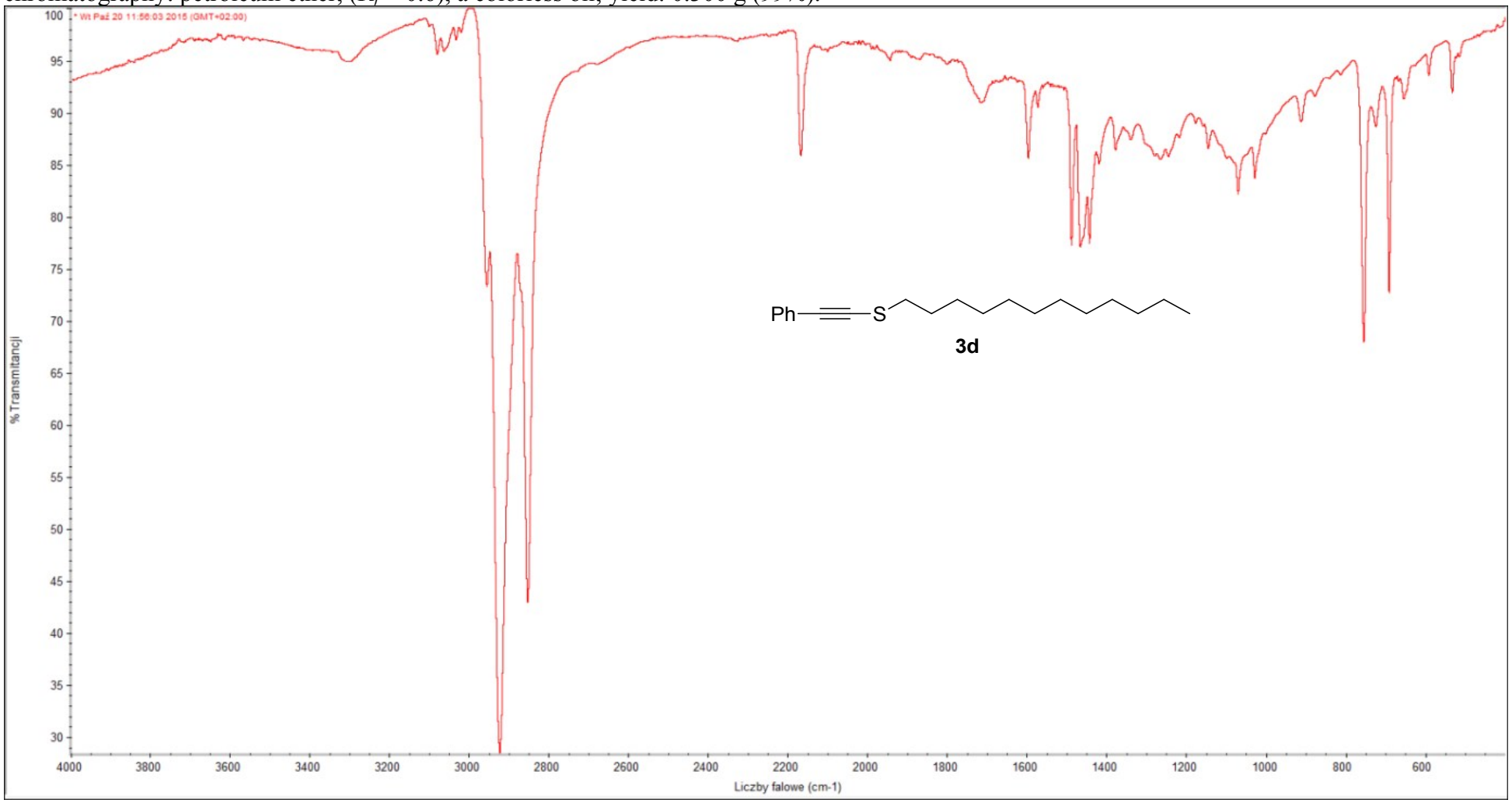



**3c**

chromatography: $CH_2Cl_2$ ($R_f$ = 0.3),
white solid; mp 110.1-110.9 °C, yield: 211 mg, 0.60 mmol, (60%).

**1-(Dodec-1-ylsulfanyl)-2-phenylethyne (3d)**

chromatography: petroleum ether, ($R_f$ = 0.6), a colorless oil; yield: 0.300 g (99%).



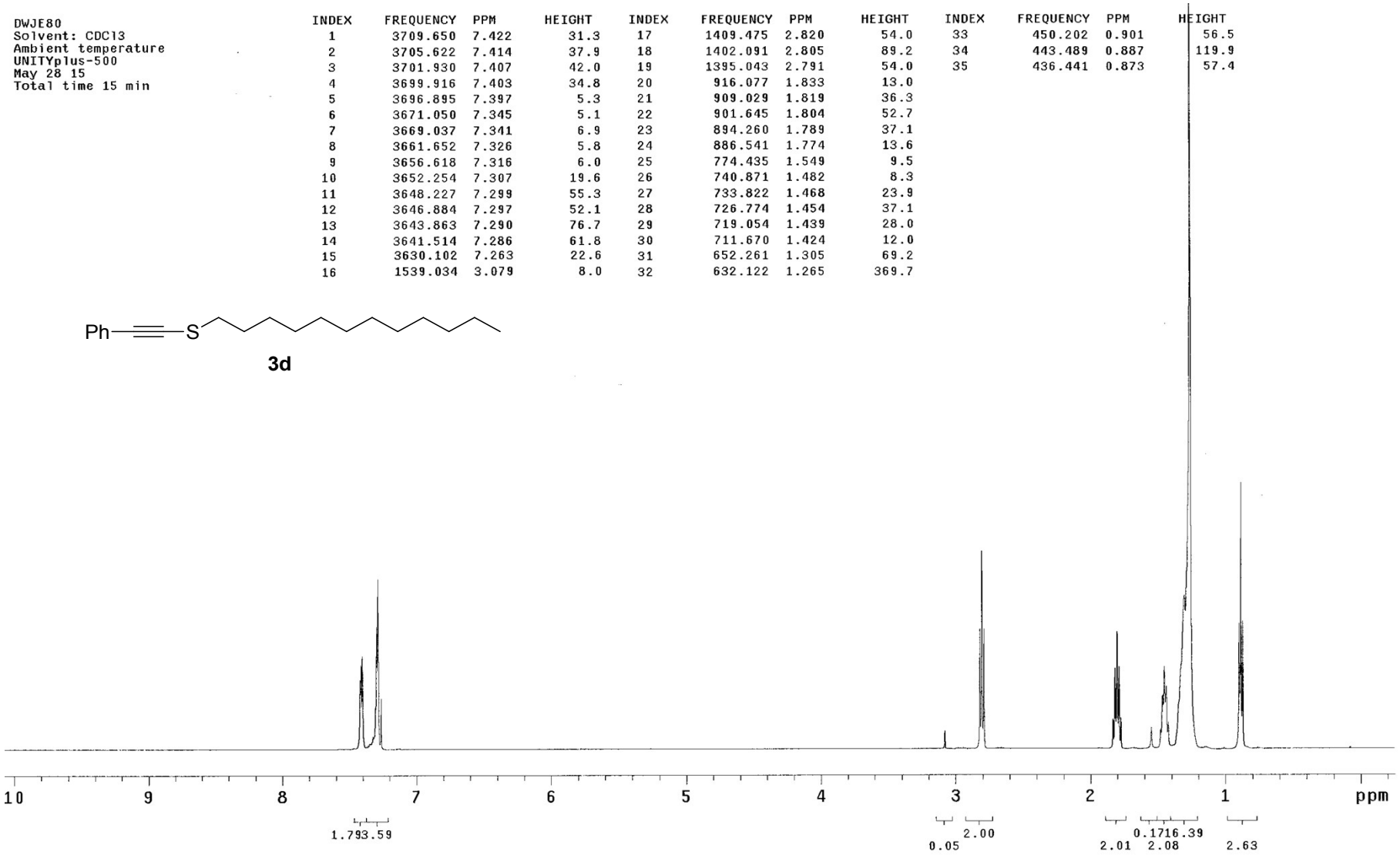

IR (ATR): 2900 (s), 2850 (s) (C-H), 2170 (w) (C≡C), 1600 (w), 1450 (w), 1370 (w), 750 (m), 700 (m) $cm^{-1}$

DWJE80
Solvent: CDCl3
Ambient temperature
UNITYplus-500
May 28 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3709.650 | 7.422 | 31.3 | 17 | 1409.475 | 2.820 | 54.0 | 33 | 450.202 | 0.901 | 56.5 |
| 2 | 3705.622 | 7.414 | 37.9 | 18 | 1402.091 | 2.805 | 89.2 | 34 | 443.489 | 0.887 | 119.9 |
| 3 | 3701.930 | 7.407 | 42.0 | 19 | 1395.043 | 2.791 | 54.0 | 35 | 436.441 | 0.873 | 57.4 |
| 4 | 3699.916 | 7.403 | 34.8 | 20 | 916.077 | 1.833 | 13.0 | | | | |
| 5 | 3696.895 | 7.397 | 5.3 | 21 | 909.029 | 1.819 | 36.3 | | | | |
| 6 | 3671.050 | 7.345 | 5.1 | 22 | 901.645 | 1.804 | 52.7 | | | | |
| 7 | 3669.037 | 7.341 | 6.9 | 23 | 894.260 | 1.789 | 37.1 | | | | |
| 8 | 3661.652 | 7.326 | 5.8 | 24 | 886.541 | 1.774 | 13.6 | | | | |
| 9 | 3656.618 | 7.316 | 6.0 | 25 | 774.435 | 1.549 | 9.5 | | | | |
| 10 | 3652.254 | 7.307 | 19.6 | 26 | 740.871 | 1.482 | 8.3 | | | | |
| 11 | 3648.227 | 7.299 | 55.3 | 27 | 733.822 | 1.468 | 23.9 | | | | |
| 12 | 3646.884 | 7.297 | 52.1 | 28 | 726.774 | 1.454 | 37.1 | | | | |
| 13 | 3643.863 | 7.290 | 76.7 | 29 | 719.054 | 1.439 | 28.0 | | | | |
| 14 | 3641.514 | 7.286 | 61.8 | 30 | 711.670 | 1.424 | 12.0 | | | | |
| 15 | 3630.102 | 7.263 | 22.6 | 31 | 652.261 | 1.305 | 69.2 | | | | |
| 16 | 1539.034 | 3.079 | 8.0 | 32 | 632.122 | 1.265 | 369.7 | | | | |



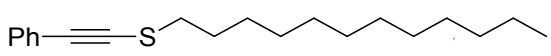

**3d**



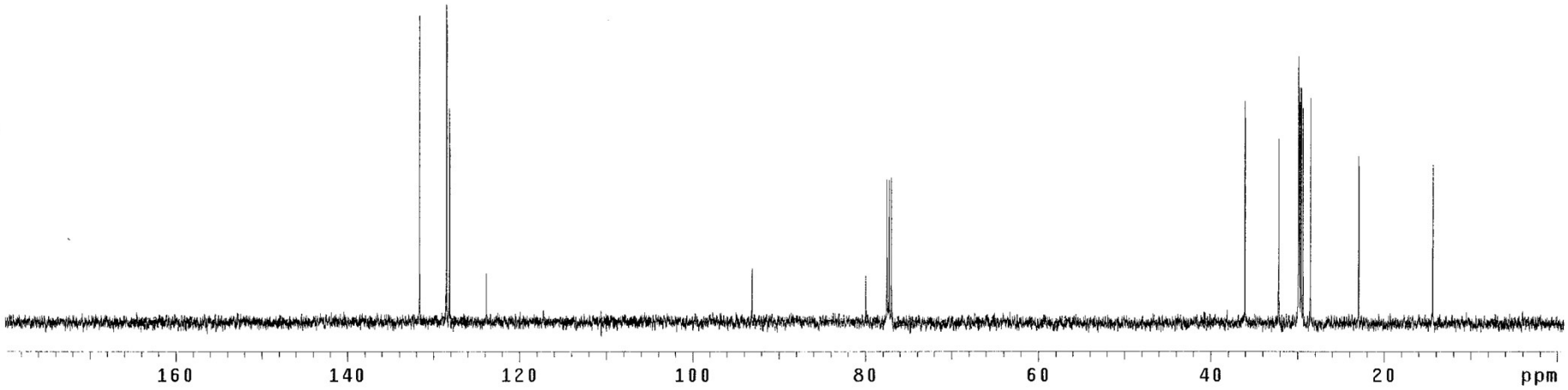

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3H, $CH_3$), 1.20-1.40 (m, 16H, $CH_2$), 1.46 (qu, *J* = 7.4 Hz, 2H, $CH_2$), 1.8 (qu, *J* = 7.4 Hz, 2H, $CH_2$), 2.81 (t, *J* = 7.3 Hz, 2H, $SCH_2$), 7.26-7.35 (m, 3H, Ph), 7.40-7.45 (m, 2H, Ph).

DWJE80_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 16543.896 | 131.638 | 1.7 | 17 | 3717.535 | 29.580 | 1.3 |
| 2 | 16149.137 | 128.497 | 1.7 | 18 | 3693.384 | 29.388 | 1.2 |
| 3 | 16106.104 | 128.155 | 1.2 | 19 | 3584.924 | 28.525 | 1.2 |
| 4 | 15564.244 | 123.843 | 0.3 | 20 | 2884.546 | 22.952 | 0.9 |
| 5 | 11699.211 | 93.089 | 0.3 | 21 | 1807.852 | 14.385 | 0.9 |
| 6 | 10048.602 | 79.956 | 0.3 | | | | |
| 7 | 9743.861 | 77.531 | 0.8 | | | | |
| 8 | 9711.806 | 77.276 | 0.8 | | | | |
| 9 | 9679.751 | 77.021 | 0.8 | | | | |
| 10 | 4533.838 | 36.075 | 1.2 | | | | |
| 11 | 4043.354 | 32.173 | 1.0 | | | | |
| 12 | 3759.689 | 29.915 | 1.4 | | | | |
| 13 | 3756.616 | 29.891 | 1.4 | | | | |
| 14 | 3750.907 | 29.846 | 1.3 | | | | |
| 15 | 3739.490 | 29.755 | 1.2 | | | | |
| 16 | 3721.487 | 29.611 | 1.3 | | | | |




**3d**

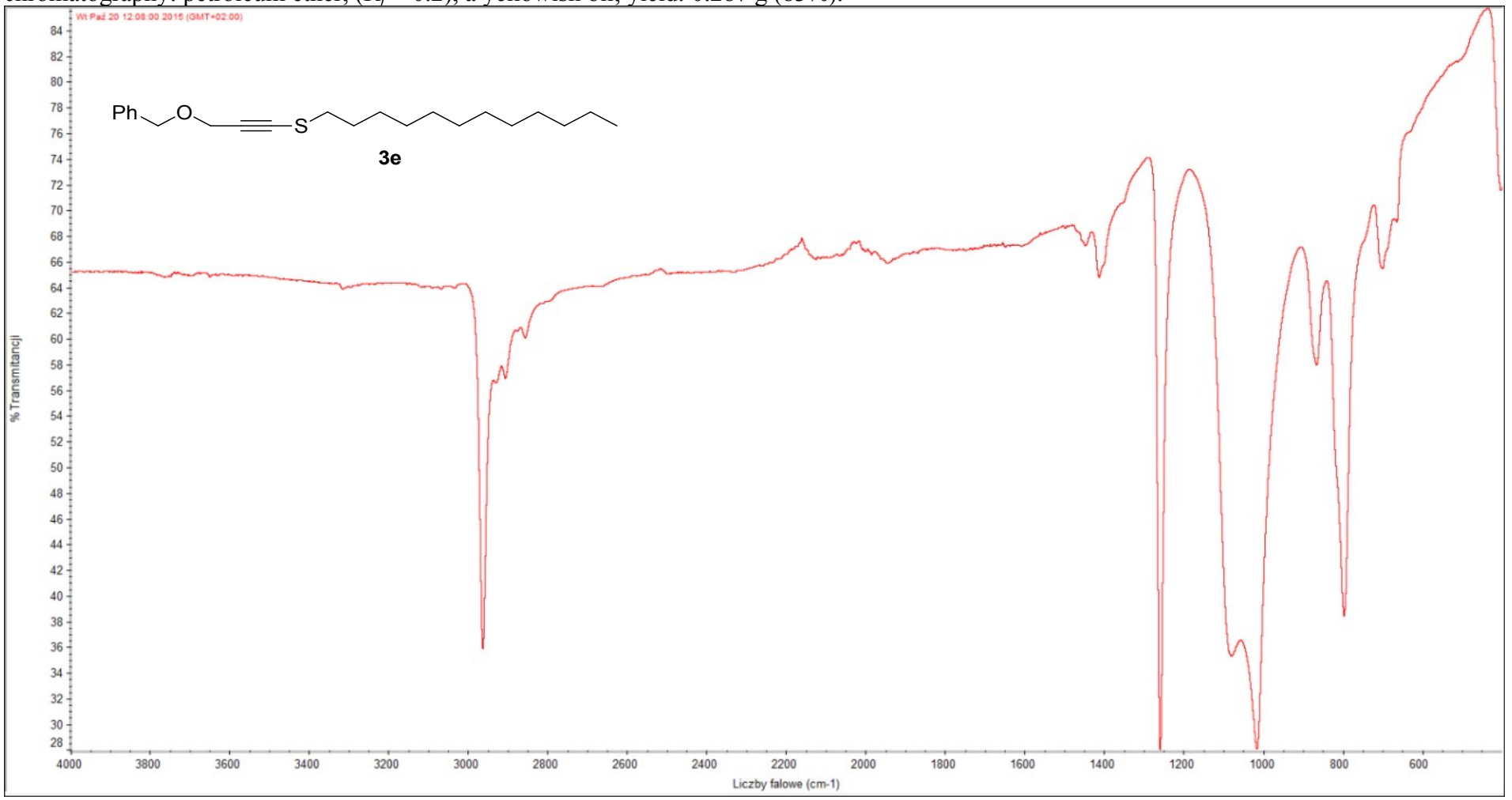



$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 131.4, 128.2, 127.9, 123.6, 92.8, 79.7, 35.8, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 28.2, 22.7, 14.1; signals: 19 expected, 18 observed.

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{20}H_{31}S$: 303.2146; found: 303.2152.

**1-(Dodec-1-ylsulfanyl)-3-benzyloxyprop-1-yne (3e)**

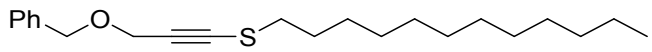
chromatography: petroleum ether, ($R_f$ = 0.2), a yellowish oil; yield: 0.287 g (83%).



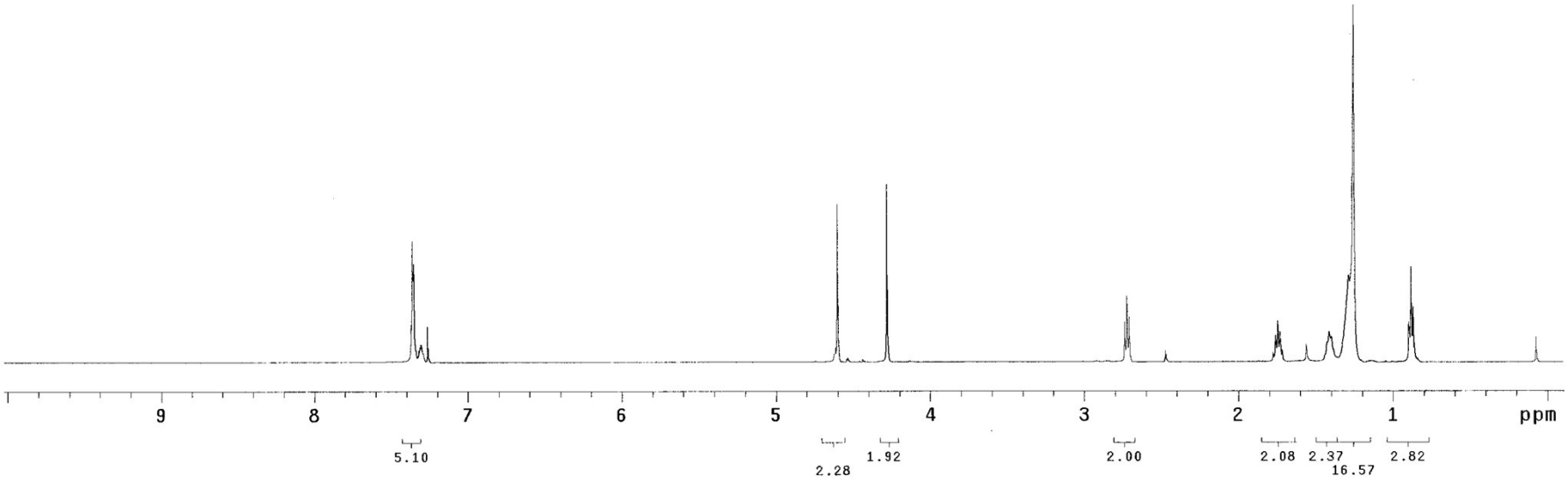

IR (ATR): 2900 (s), 2850 (s) (C-H), 1600 (w), 1260 (s), 1100 (s), 1025 (s), 800 (s) $cm^{-1}$

DWJE83
Solvent: CDCl3
Ambient temperature
UNITYplus-500
May 29 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3684.011 | 7.371 | 11.0 | 17 | 2140.948 | 4.284 | 52.3 | 33 | 630.602 | 1.262 | 105.0 |
| 2 | 3681.081 | 7.365 | 35.5 | 18 | 1368.928 | 2.739 | 11.8 | 34 | 449.438 | 0.899 | 11.5 |
| 3 | 3677.663 | 7.358 | 26.7 | 19 | 1361.603 | 2.724 | 19.3 | 35 | 443.090 | 0.887 | 27.9 |
| 4 | 3675.710 | 7.354 | 29.0 | 20 | 1354.279 | 2.710 | 13.1 | 36 | 437.719 | 0.876 | 9.0 |
| 5 | 3668.873 | 7.341 | 3.6 | 21 | 1237.084 | 2.475 | 3.2 | 37 | 435.766 | 0.872 | 16.1 |
| 6 | 3667.408 | 7.338 | 3.3 | 22 | 887.453 | 1.776 | 2.8 | 38 | 431.371 | 0.863 | 5.4 |
| 7 | 3658.619 | 7.320 | 3.5 | 23 | 880.129 | 1.761 | 7.7 | 39 | 38.281 | 0.077 | 7.1 |
| 8 | 3655.201 | 7.313 | 4.2 | 24 | 872.804 | 1.746 | 12.0 | | | | |
| 9 | 3653.736 | 7.310 | 5.1 | 25 | 865.479 | 1.732 | 8.8 | | | | |
| 10 | 3652.271 | 7.307 | 4.4 | 26 | 858.155 | 1.717 | 3.7 | | | | |
| 11 | 3649.829 | 7.302 | 5.1 | 27 | 780.513 | 1.562 | 5.1 | | | | |
| 12 | 3647.388 | 7.298 | 3.4 | 28 | 713.615 | 1.428 | 5.8 | | | | |
| 13 | 3644.946 | 7.293 | 2.7 | 29 | 707.755 | 1.416 | 8.8 | | | | |
| 14 | 3630.785 | 7.264 | 10.4 | 30 | 700.430 | 1.401 | 7.4 | | | | |
| 15 | 3628.832 | 7.260 | 4.0 | 31 | 693.106 | 1.387 | 3.9 | | | | |
| 16 | 2301.602 | 4.605 | 46.4 | 32 | 644.275 | 1.289 | 25.5 | | | | |



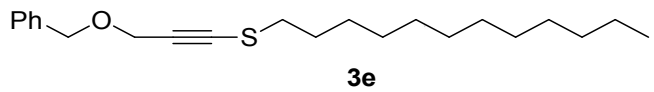

**3e**



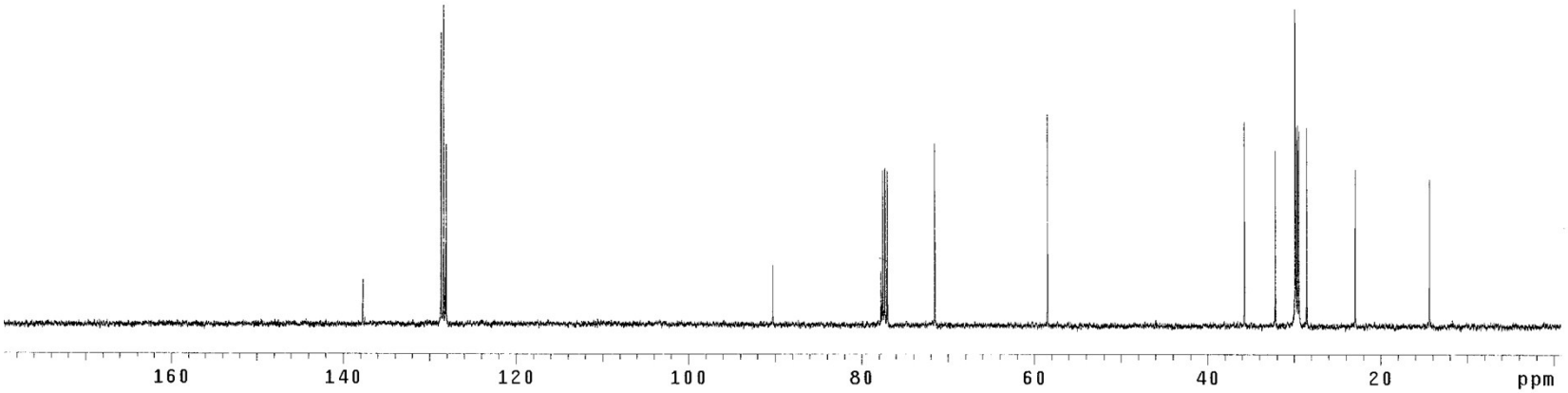

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3H, $CH_3$), 1.20-1.38 (m, 16H, $CH_2$), 1.38-1.48 (m, 2H, $CH_2$), 1.75 (qu, *J* =7.4 Hz, 2H, $CH_2$), 2.72 (t, *J* =7.3 Hz, 2H, $SCH_2$), 4.28 (s, 2H, $OCH_2$), 4.61 (s, 2H, $OCH_2$), 7.26-7.40 (m, 5H, Ph).

DWJE83_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 30 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 17310.140 | 137.735 | 0.2 | 17 | 3720.170 | 29.601 | 1.0 |
| 2 | 16170.653 | 128.668 | 1.5 | 18 | 3713.144 | 29.545 | 1.0 |
| 3 | 16132.012 | 128.361 | 1.6 | 19 | 3694.262 | 29.395 | 1.0 |
| 4 | 16096.883 | 128.081 | 0.9 | 20 | 3585.363 | 28.528 | 1.0 |
| 5 | 11343.533 | 90.259 | 0.3 | 21 | 2883.668 | 22.945 | 0.8 |
| 6 | 9772.842 | 77.761 | 0.3 | 22 | 1807.413 | 14.381 | 0.7 |
| 7 | 9745.178 | 77.541 | 0.8 | | | | |
| 8 | 9713.123 | 77.286 | 0.8 | | | | |
| 9 | 9681.507 | 77.035 | 0.8 | | | | |
| 10 | 8988.155 | 71.518 | 0.9 | | | | |
| 11 | 7346.767 | 58.457 | 1.1 | | | | |
| 12 | 4491.244 | 35.736 | 1.0 | | | | |
| 13 | 4042.475 | 32.166 | 0.9 | | | | |
| 14 | 3757.055 | 29.894 | 1.6 | | | | |
| 15 | 3750.907 | 29.846 | 1.1 | | | | |
| 16 | 3740.369 | 29.762 | 1.0 | | | | |




**3e**

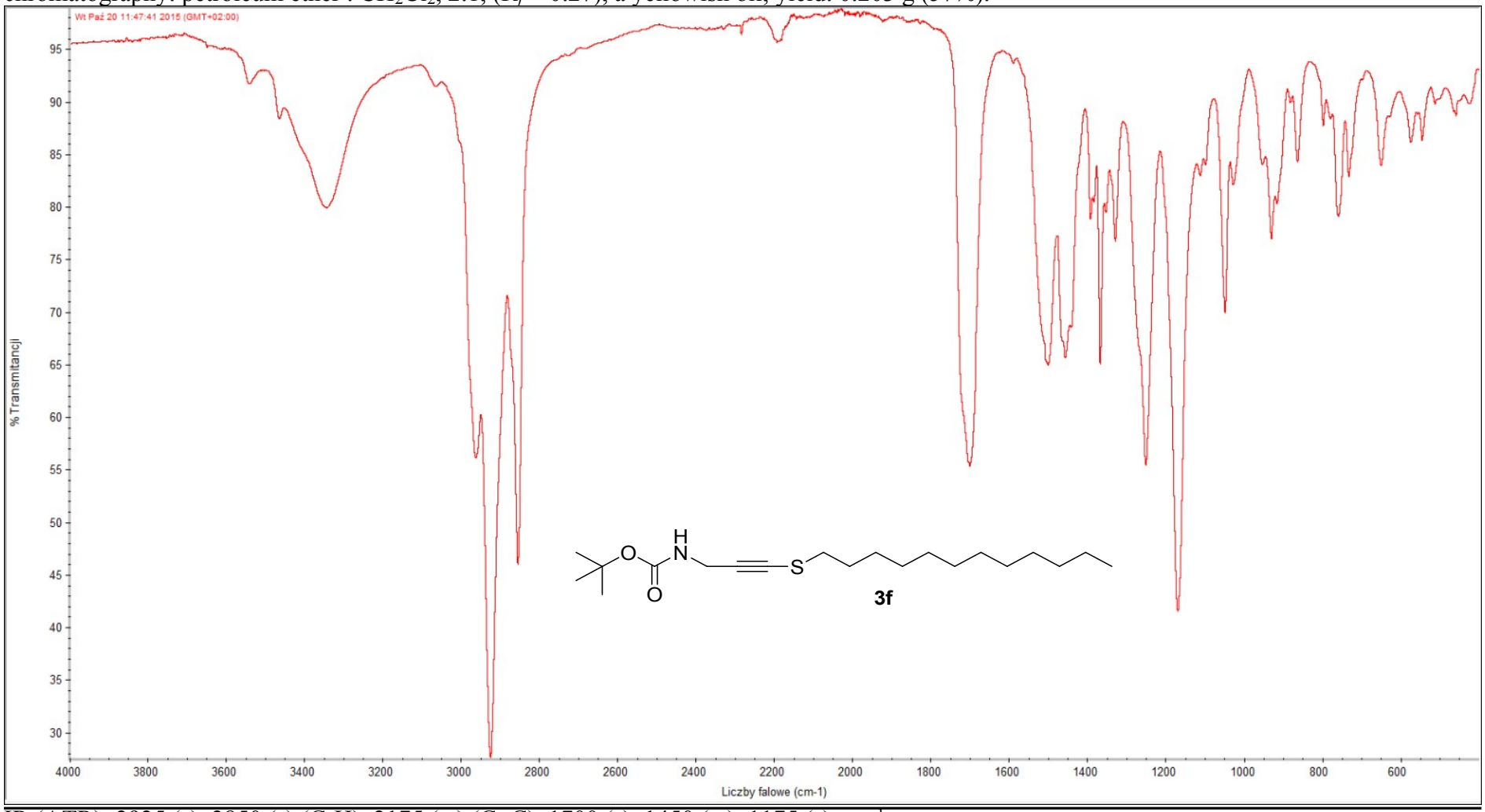



$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 137.4, 128.4, 128.1, 127.8, 90.0, 77.5, 71.2, 58.2, 35.5, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 28.2, 22.7, 14.1; signals: 20 expected, 19 observed.

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{22}H_{35}OS$: 347.2409; found: 347.2413.

**3-(Dodec-1-ylsulfanyl)-*N*-t-butoxycarbonyl-prop-2-ynylamine (3f)**

chromatography: petroleum ether : $CH_2Cl_2$, 2:1, ($R_f$ = 0.27), a yellowish oil; yield: 0.203 g (57%).



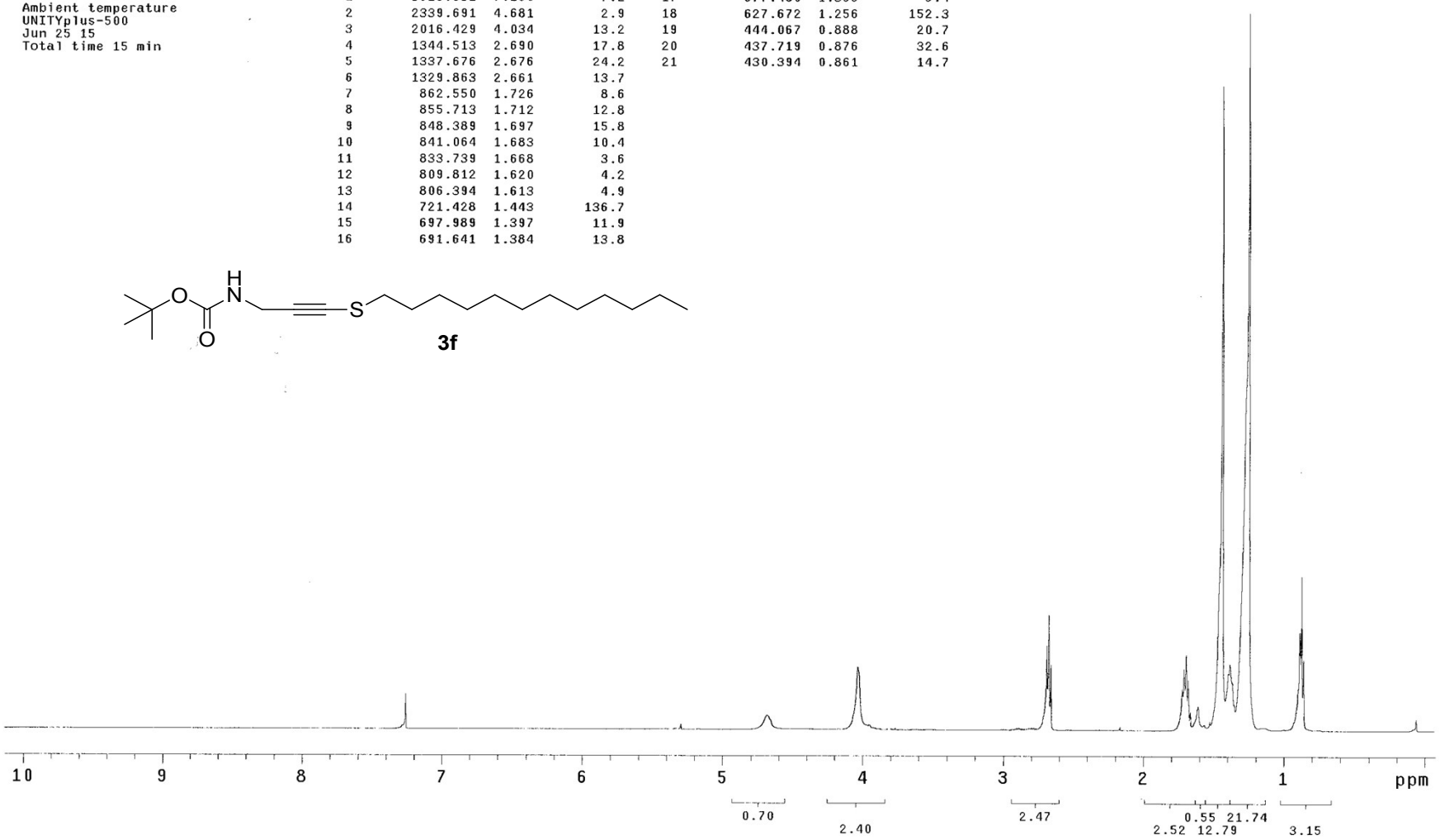

IR (ATR): 2925 (s), 2850 (s) (C-H), 2175 (w) (C≡C), 1700 (s), 1450 (w), 1175 (s) $cm^{-1}$

DWJE108
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 25 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3628.832 | 7.260 | 7.2 | 17 | 677.480 | 1.355 | 5.4 |
| 2 | 2339.691 | 4.681 | 2.9 | 18 | 627.672 | 1.256 | 152.3 |
| 3 | 2016.429 | 4.034 | 13.2 | 19 | 444.067 | 0.888 | 20.7 |
| 4 | 1344.513 | 2.690 | 17.8 | 20 | 437.719 | 0.876 | 32.6 |
| 5 | 1337.676 | 2.676 | 24.2 | 21 | 430.394 | 0.861 | 14.7 |
| 6 | 1329.863 | 2.661 | 13.7 | | | | |
| 7 | 862.550 | 1.726 | 8.6 | | | | |
| 8 | 855.713 | 1.712 | 12.8 | | | | |
| 9 | 848.389 | 1.697 | 15.8 | | | | |
| 10 | 841.064 | 1.683 | 10.4 | | | | |
| 11 | 833.739 | 1.668 | 3.6 | | | | |
| 12 | 809.812 | 1.620 | 4.2 | | | | |
| 13 | 806.394 | 1.613 | 4.9 | | | | |
| 14 | 721.428 | 1.443 | 136.7 | | | | |
| 15 | 697.989 | 1.397 | 11.9 | | | | |
| 16 | 691.641 | 1.384 | 13.8 | | | | |




**3f**



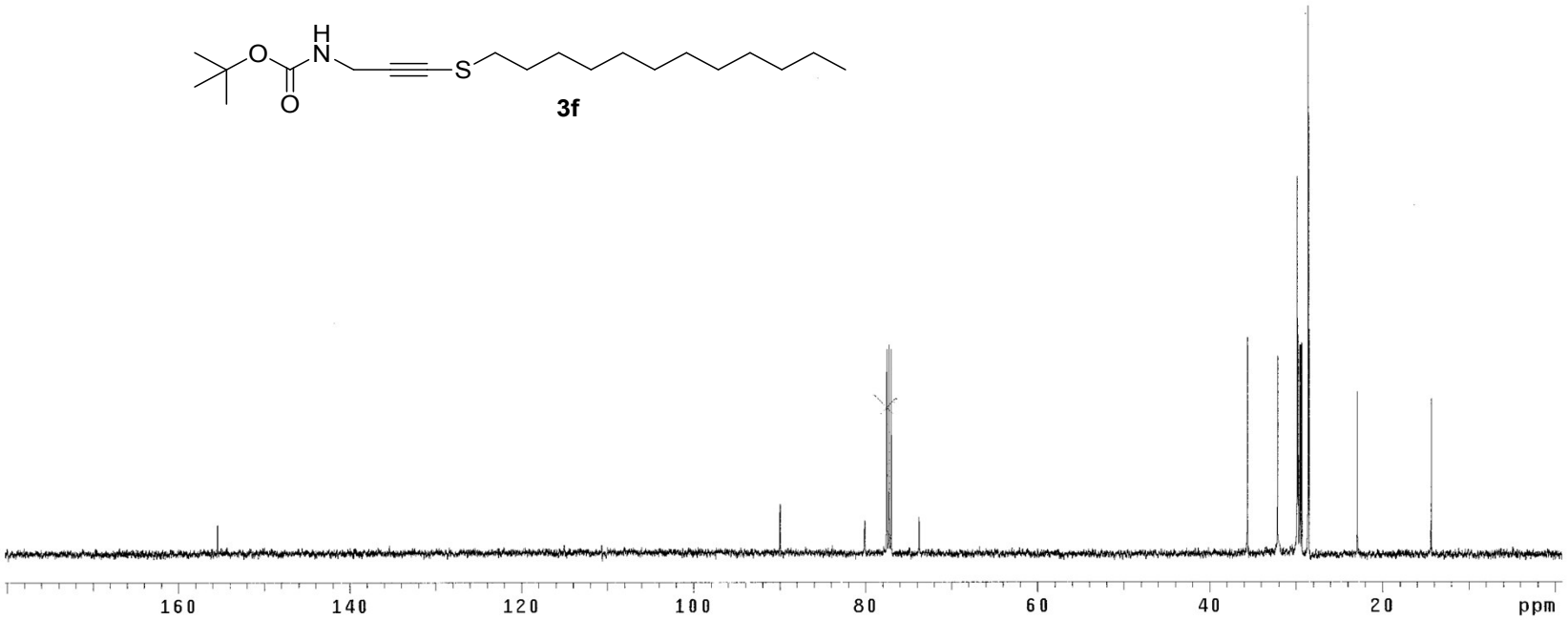

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* =7.0 Hz, 3H, $CH_3$), 1.22-1.43 (m, 18H, $CH_2$), 1.44 (s, 9H, tBu), 1.64-1.75 (m, 2H, $CH_2$), 2.68 (t, *J* = 7.4 Hz, 2H, $SCH_2$), 4.03 (bs, 2H, $NCH_2$), 4.68 (bs, 1H, NH)

DWJE108_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 25 15
Total time 30 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 19534.664 | 155.435 | 0.1 | 17 | 3582.729 | 28.507 | 1.6 |
| 2 | 11307.087 | 89.969 | 0.4 | 18 | 2880.155 | 22.917 | 1.2 |
| 3 | 10067.484 | 80.106 | 0.1 | 19 | 1803.900 | 14.353 | 1.1 |
| 4 | 9742.104 | 77.517 | 1.5 | | | | |
| 5 | 9710.488 | 77.265 | 1.5 | | | | |
| 6 | 9678.433 | 77.010 | 1.5 | | | | |
| 7 | 9270.502 | 73.764 | 0.2 | | | | |
| 8 | 4474.558 | 35.604 | 1.6 | | | | |
| 9 | 4039.402 | 32.141 | 1.5 | | | | |
| 10 | 3753.542 | 29.867 | 2.8 | | | | |
| 11 | 3746.516 | 29.811 | 1.7 | | | | |
| 12 | 3737.295 | 29.737 | 1.6 | | | | |
| 13 | 3716.657 | 29.573 | 1.5 | | | | |
| 14 | 3706.557 | 29.493 | 1.5 | | | | |
| 15 | 3687.676 | 29.342 | 1.6 | | | | |
| 16 | 3591.072 | 28.574 | 4.0 | | | | |




**3f**

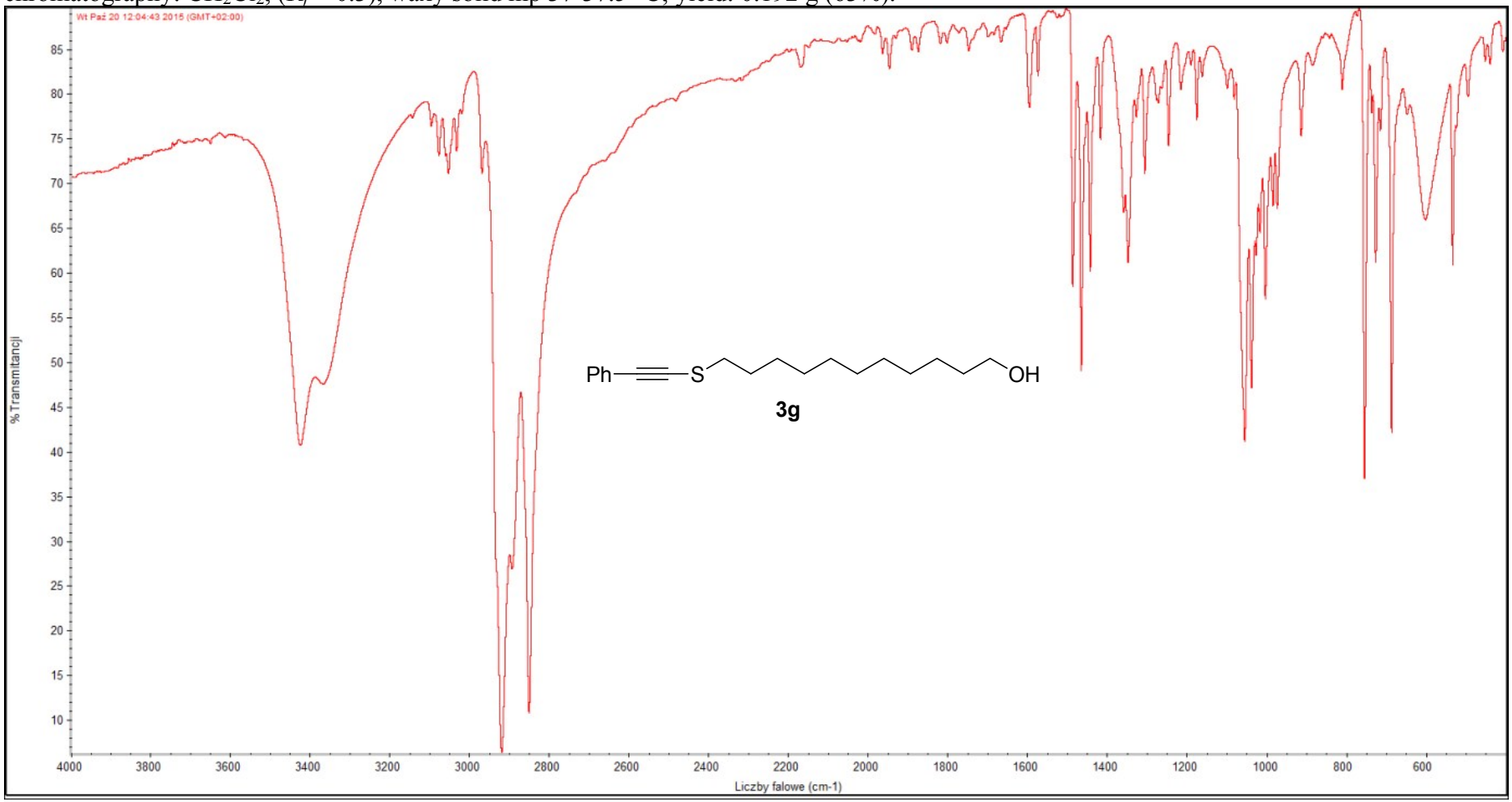



$^{13}C$ NMR (125 MHz, $CDCl_3$): δ=155.2, 89.7, 79.8, 73.5, 35.3, 31.9, 29.6, 29.5, 29.5, 29.3, 29.2, 29.1, 28.3, 28.2, 22.7, 14.1; signals: 18 expected, 16 observed.

HRMS (ESI): m/z $[M + Na]^+$calcd for $C_{20}H_{37}NNaO_2S$: 378.2443; found: 378.2450.

**1-(11-Hydroxyundec-1-ylsulfanyl)-2-phenylethyne (3g)**

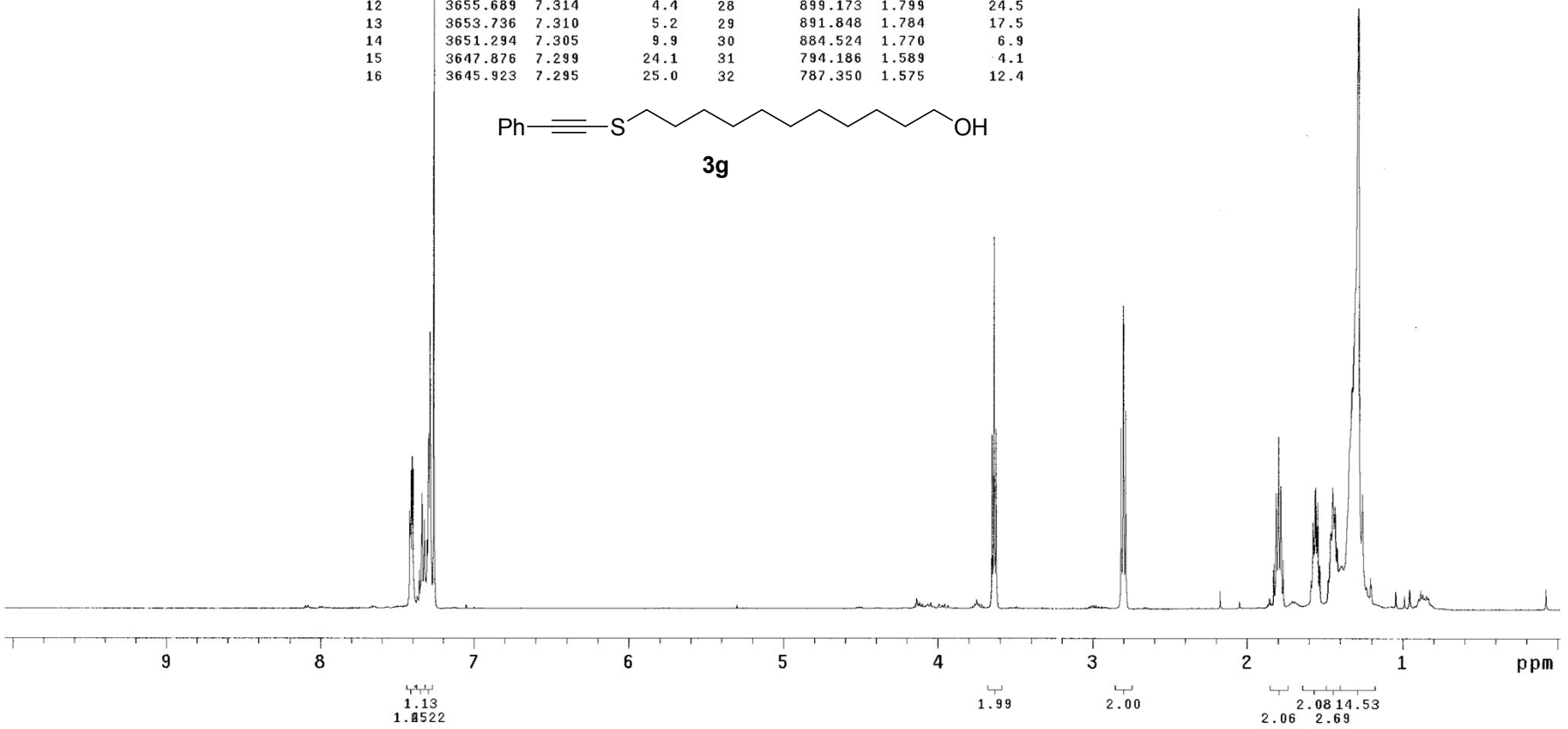
chromatography: $CH_2Cl_2$, ($R_f$ = 0.3), waxy solid mp 37-37.5 °C; yield: 0.192 g (63%).




IR (ATR): 3400 (s), 2910 (s), 2850 (s) (C-H), 2170 (w) (C≡C), 1450 (w), 1370 (w), 750 (m), 700 (m) $cm^{-1}$

DWJE85_1H
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 2 15
Total time 15 min

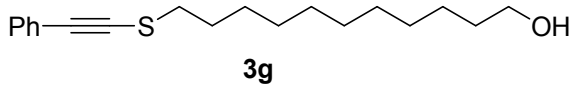
| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3707.938 | 7.419 | 13.9 | 17 | 3642.993 | 7.289 | 39.4 | 33 | 780.513 | 1.562 | 17.3 |
| 2 | 3703.543 | 7.410 | 19.7 | 18 | 3641.039 | 7.285 | 32.6 | 34 | 773.189 | 1.547 | 15.2 |
| 3 | 3700.125 | 7.403 | 21.7 | 19 | 3630.297 | 7.263 | 95.0 | 35 | 766.352 | 1.533 | 6.2 |
| 4 | 3698.172 | 7.399 | 19.9 | 20 | 1825.011 | 3.651 | 24.7 | 36 | 738.519 | 1.478 | 4.1 |
| 5 | 3694.754 | 7.392 | 4.2 | 21 | 1818.174 | 3.638 | 52.9 | 37 | 731.682 | 1.464 | 11.0 |
| 6 | 3676.686 | 7.356 | 5.5 | 22 | 1811.338 | 3.624 | 25.6 | 38 | 724.358 | 1.449 | 17.3 |
| 7 | 3673.756 | 7.350 | 3.3 | 23 | 1407.993 | 2.817 | 25.7 | 39 | 717.033 | 1.435 | 14.6 |
| 8 | 3671.803 | 7.346 | 6.4 | 24 | 1400.668 | 2.802 | 43.1 | 40 | 709.708 | 1.420 | 8.8 |
| 9 | 3670.338 | 7.343 | 10.6 | 25 | 1393.344 | 2.788 | 28.2 | 41 | 697.012 | 1.395 | 6.1 |
| 10 | 3667.897 | 7.339 | 16.4 | 26 | 913.822 | 1.828 | 6.4 | 42 | 662.830 | 1.326 | 31.5 |
| 11 | 3660.084 | 7.323 | 12.6 | 27 | 906.498 | 1.814 | 16.4 | | | | |
| 12 | 3655.689 | 7.314 | 4.4 | 28 | 899.173 | 1.799 | 24.5 | | | | |
| 13 | 3653.736 | 7.310 | 5.2 | 29 | 891.848 | 1.784 | 17.5 | | | | |
| 14 | 3651.294 | 7.305 | 9.9 | 30 | 884.524 | 1.770 | 6.9 | | | | |
| 15 | 3647.876 | 7.299 | 24.1 | 31 | 794.186 | 1.589 | 4.1 | | | | |
| 16 | 3645.923 | 7.295 | 25.0 | 32 | 787.350 | 1.575 | 12.4 | | | | |



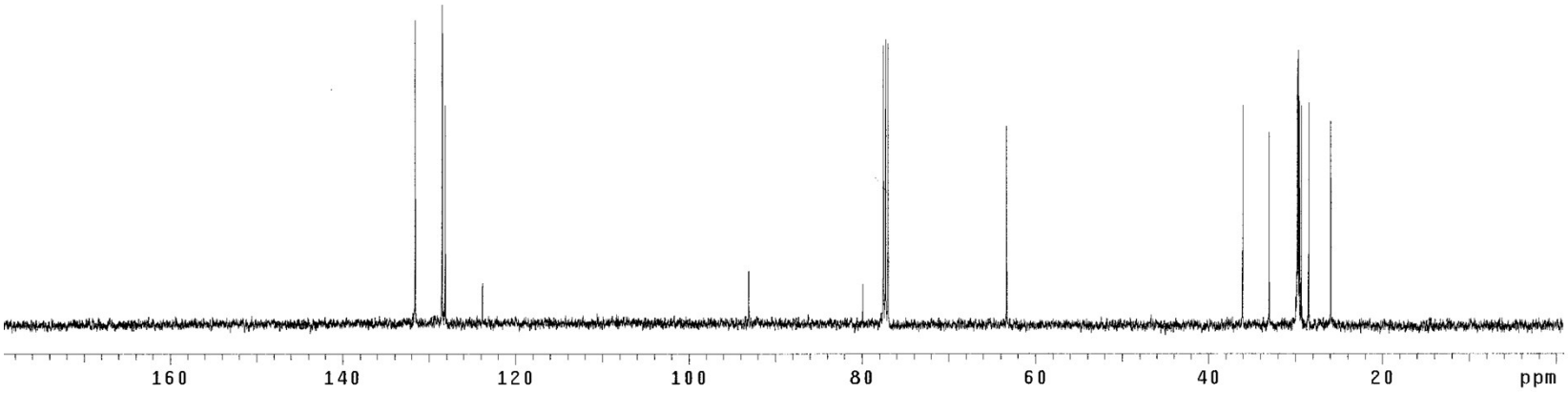

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.20-1.50 (m, 15H, OH, $CH_2$), 1.50-1.60 (m, 2H, $CH_2$), 1.80 (qu, *J* = 7.3 Hz, 2H, $CH_2$), 2.80 (t, *J* = 7.4 Hz, 2H, $SCH_2$), 3.64 (t, *J* = 6.8 Hz, 2H, $OCH_2$), 7.25-7.45 (m, 5H, Ph).

DWJE85_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 45 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 16542.139 | 131.624 | 0.8 | 17 | 3713.583 | 29.549 | 0.6 |
| 2 | 16149.137 | 128.497 | 0.9 | 18 | 3687.676 | 29.342 | 0.6 |
| 3 | 16106.983 | 128.161 | 0.6 | 19 | 3579.655 | 28.483 | 0.6 |
| 4 | 15560.292 | 123.812 | 0.1 | 20 | 3263.058 | 25.964 | 0.6 |
| 5 | 11697.894 | 93.079 | 0.1 | | | | |
| 6 | 10044.650 | 79.924 | 0.1 | | | | |
| 7 | 9743.422 | 77.527 | 0.8 | | | | |
| 8 | 9711.806 | 77.276 | 0.8 | | | | |
| 9 | 9679.751 | 77.021 | 0.8 | | | | |
| 10 | 7956.689 | 63.310 | 0.5 | | | | |
| 11 | 4531.642 | 36.058 | 0.6 | | | | |
| 12 | 4150.496 | 33.025 | 0.5 | | | | |
| 13 | 3746.077 | 29.807 | 0.6 | | | | |
| 14 | 3735.099 | 29.720 | 0.7 | | | | |
| 15 | 3731.586 | 29.692 | 0.7 | | | | |
| 16 | 3725.439 | 29.643 | 0.6 | | | | |




**3g**

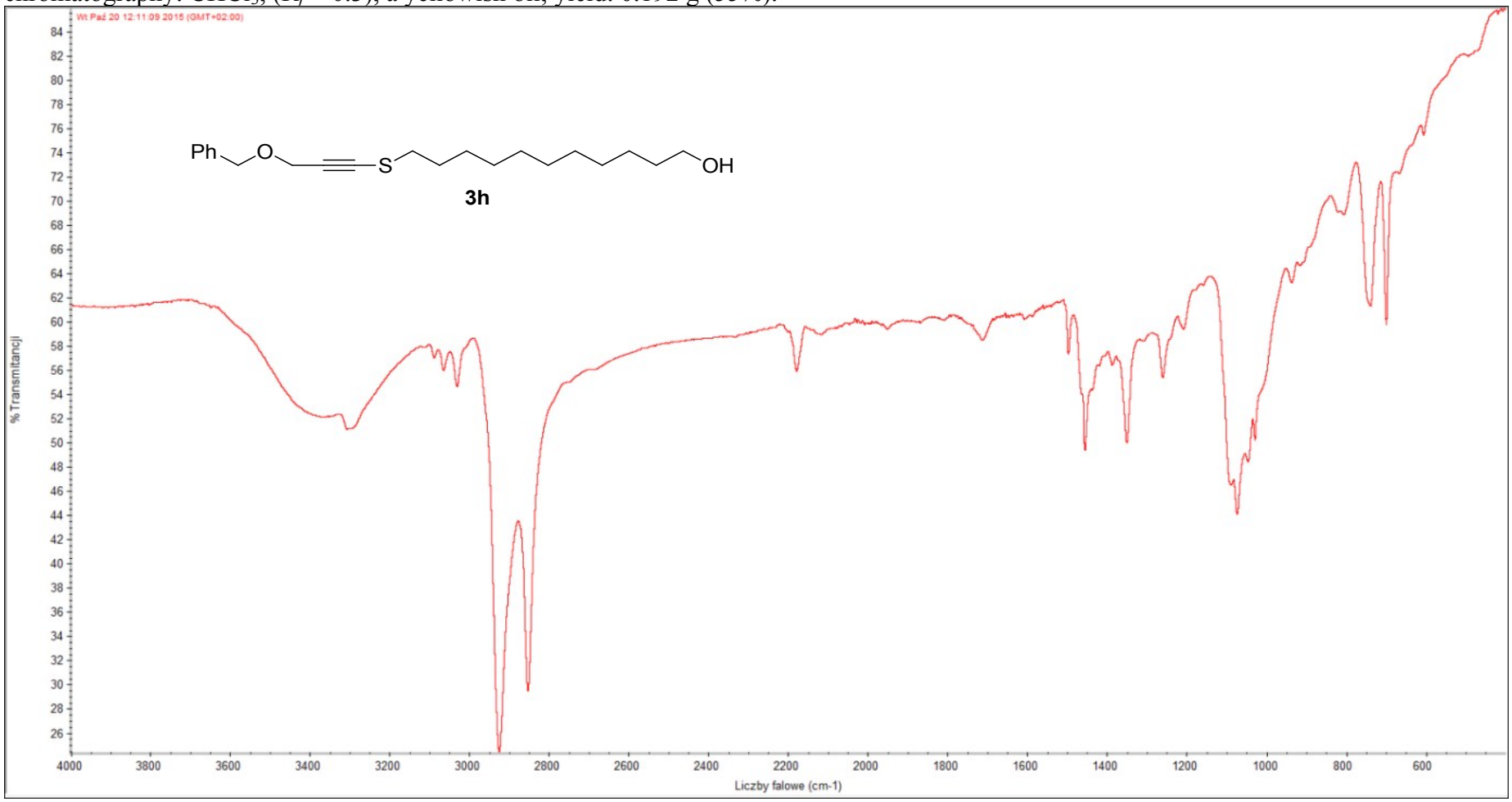



$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 131.4, 128.2, 127.9, 123.5, 92.8, 79.6, 63.0, 35.8, 32.8, 29.5, 29.4, 29.4, 29.4, 29.3, 29.1, 28.2, 25.7; signals: expected and observed 17.

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{19}H_{29}OS$: 305.1939; found: 305.1946.

**1-(11-Hydroxyundec-1-ylsulfanyl)-3-benzyloxyprop-1-yne (3h)**

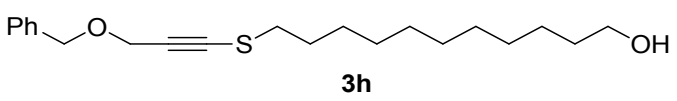
chromatography: $CHCl_3$, ($R_f$ = 0.3), a yellowish oil; yield: 0.192 g (55%).



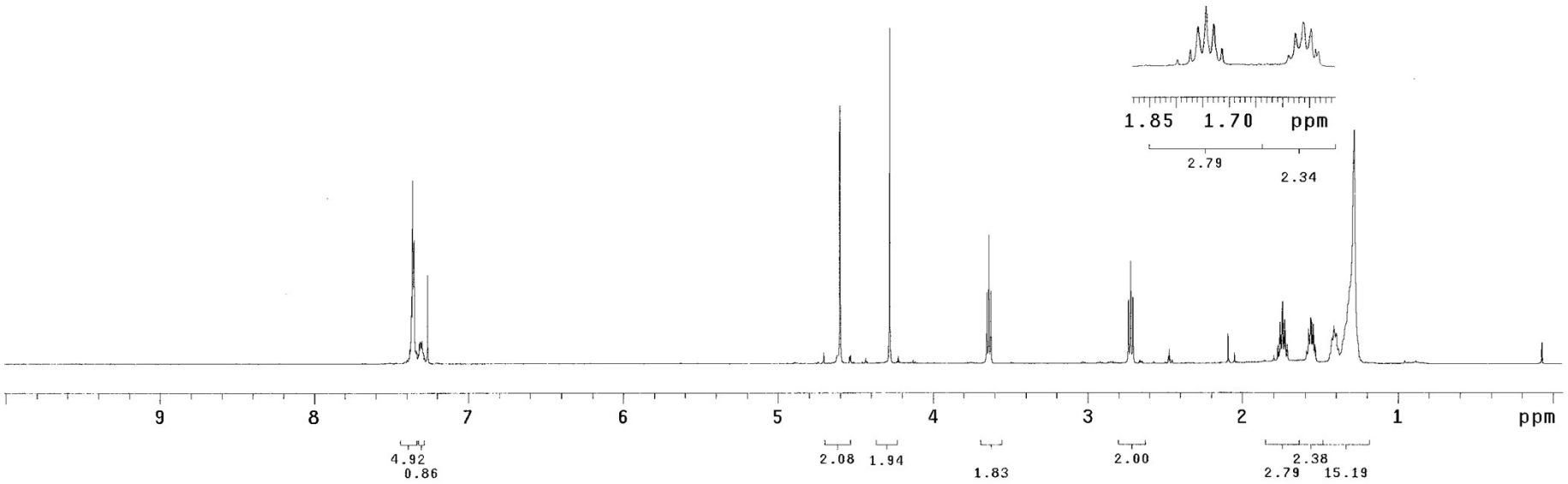

IR (ATR): 3400 (m), 2910 (s), 2850 (s) (C-H), 2175 (w) (C≡C), 1600 (w), 1450 (w), 1370 (w), 750 (w), 700 (w) $cm^{-1}$

DWJE99
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 17 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3682.546 | 7.368 | 10.1 | 17 | 661.854 | 1.324 | 9.0 |
| 2 | 3679.616 | 7.362 | 27.6 | 18 | 641.345 | 1.283 | 35.1 |
| 3 | 3675.710 | 7.354 | 18.3 | | | | |
| 4 | 3674.733 | 7.352 | 18.6 | | | | |
| 5 | 3630.297 | 7.263 | 13.3 | | | | |
| 6 | 2299.649 | 4.601 | 38.9 | | | | |
| 7 | 2139.483 | 4.281 | 50.5 | | | | |
| 8 | 1824.522 | 3.650 | 10.6 | | | | |
| 9 | 1817.686 | 3.637 | 19.3 | | | | |
| 10 | 1811.338 | 3.624 | 10.9 | | | | |
| 11 | 1367.463 | 2.736 | 9.6 | | | | |
| 12 | 1360.627 | 2.722 | 15.4 | | | | |
| 13 | 1353.302 | 2.708 | 10.0 | | | | |
| 14 | 871.339 | 1.743 | 9.3 | | | | |
| 15 | 864.015 | 1.729 | 6.6 | | | | |
| 16 | 781.002 | 1.563 | 6.9 | | | | |



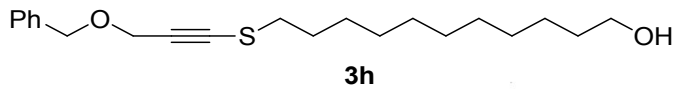

**3h**



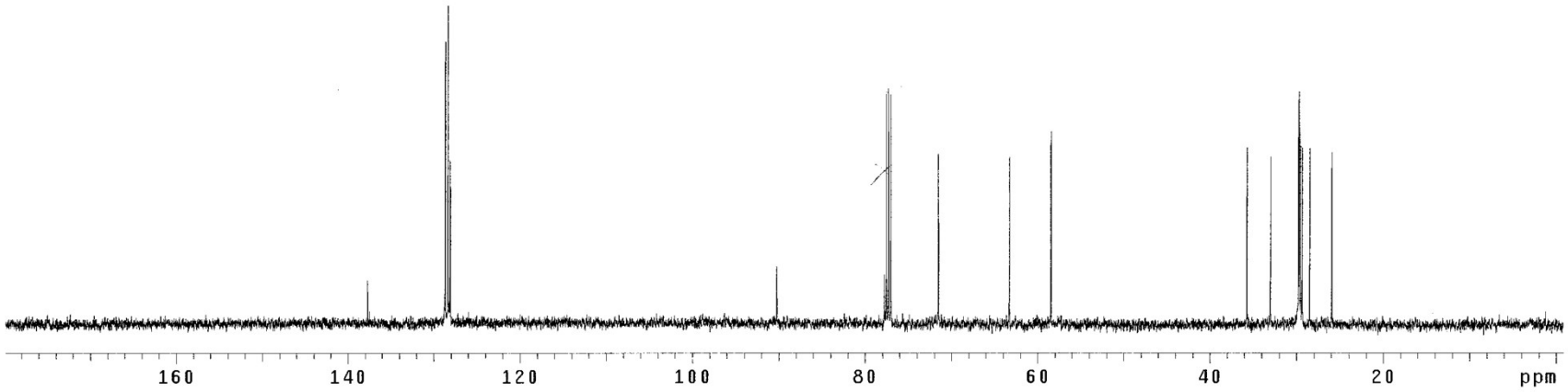

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.22-1.45 (m, 15H, OH, $CH_2$), 1.56 (qu, *J* = 5.5 Hz, 2H, $CH_2$), 1.74 (qu, *J* = 7.4 Hz, 2H, $CH_2$), 2.72 (t, *J* = 7.4 Hz, 2H, $SCH_2$), 3.63 (t, *J* = 6.7 Hz, 2H, $OCH_2$), 4.28 (s, 2H, $OCH_2$), 4.60 (s, 2H, $OCH_2$), 7.27-7.40 (m, 5H, Ph).

DWJE99_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 17305.310 | 137.696 | 0.2 | 17 | 3732.904 | 29.702 | 0.9 |
| 2 | 16171.092 | 128.672 | 1.1 | 18 | 3725.439 | 29.643 | 0.7 |
| 3 | 16133.768 | 128.375 | 1.2 | 19 | 3709.631 | 29.517 | 0.7 |
| 4 | 16098.639 | 128.095 | 0.6 | 20 | 3689.432 | 29.356 | 0.7 |
| 5 | 11341.777 | 90.245 | 0.2 | 21 | 3580.533 | 28.490 | 0.7 |
| 6 | 9772.842 | 77.761 | 0.2 | 22 | 3262.619 | 25.960 | 0.7 |
| 7 | 9746.056 | 77.548 | 0.9 | | | | |
| 8 | 9714.001 | 77.293 | 0.9 | | | | |
| 9 | 9681.946 | 77.038 | 0.9 | | | | |
| 10 | 8987.716 | 71.514 | 0.6 | | | | |
| 11 | 7952.298 | 63.276 | 0.6 | | | | |
| 12 | 7345.011 | 58.443 | 0.7 | | | | |
| 13 | 4489.488 | 35.722 | 0.7 | | | | |
| 14 | 4146.983 | 32.997 | 0.6 | | | | |
| 15 | 3744.760 | 29.797 | 0.7 | | | | |
| 16 | 3735.538 | 29.723 | 0.9 | | | | |



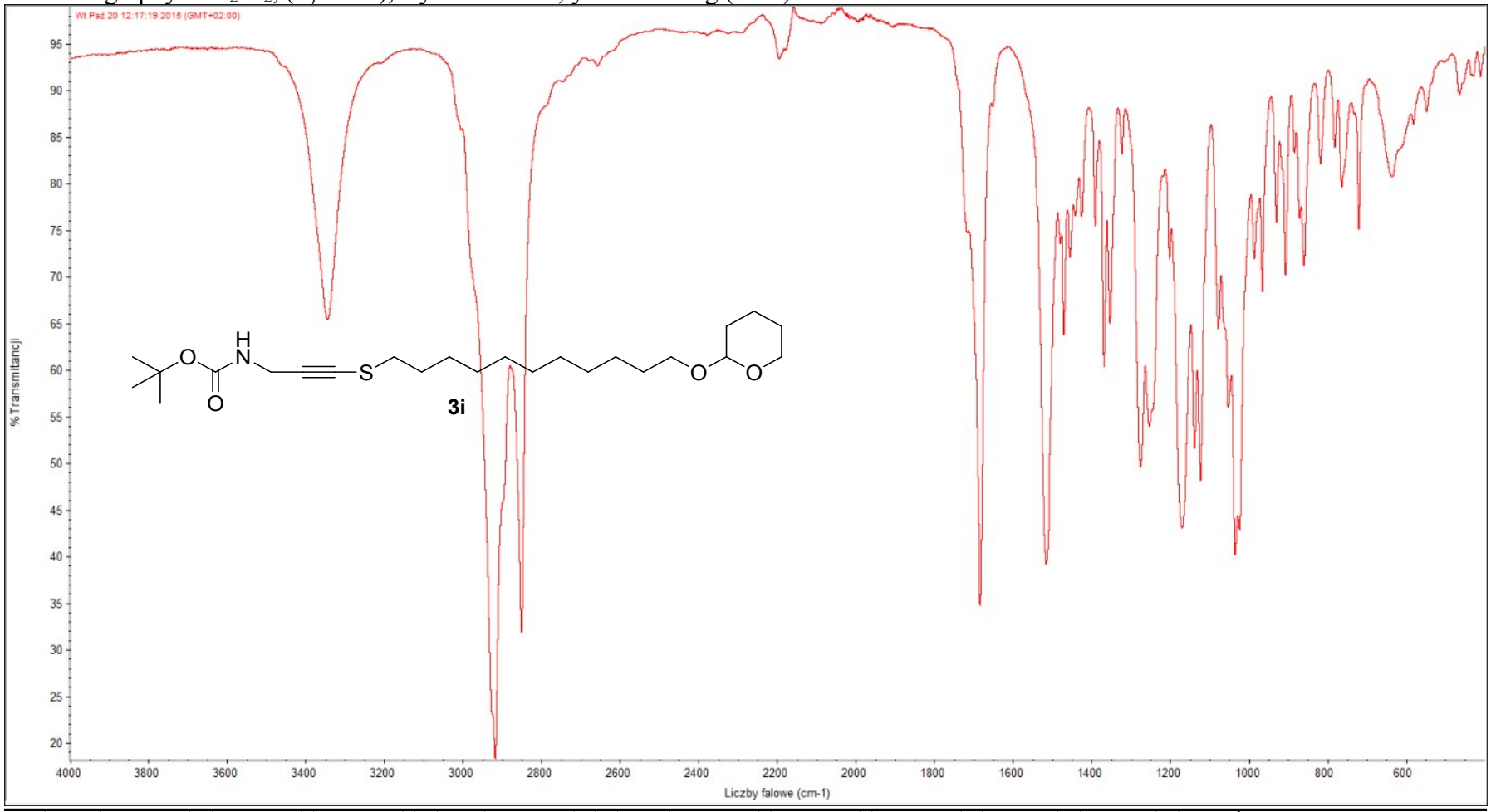

**3h**



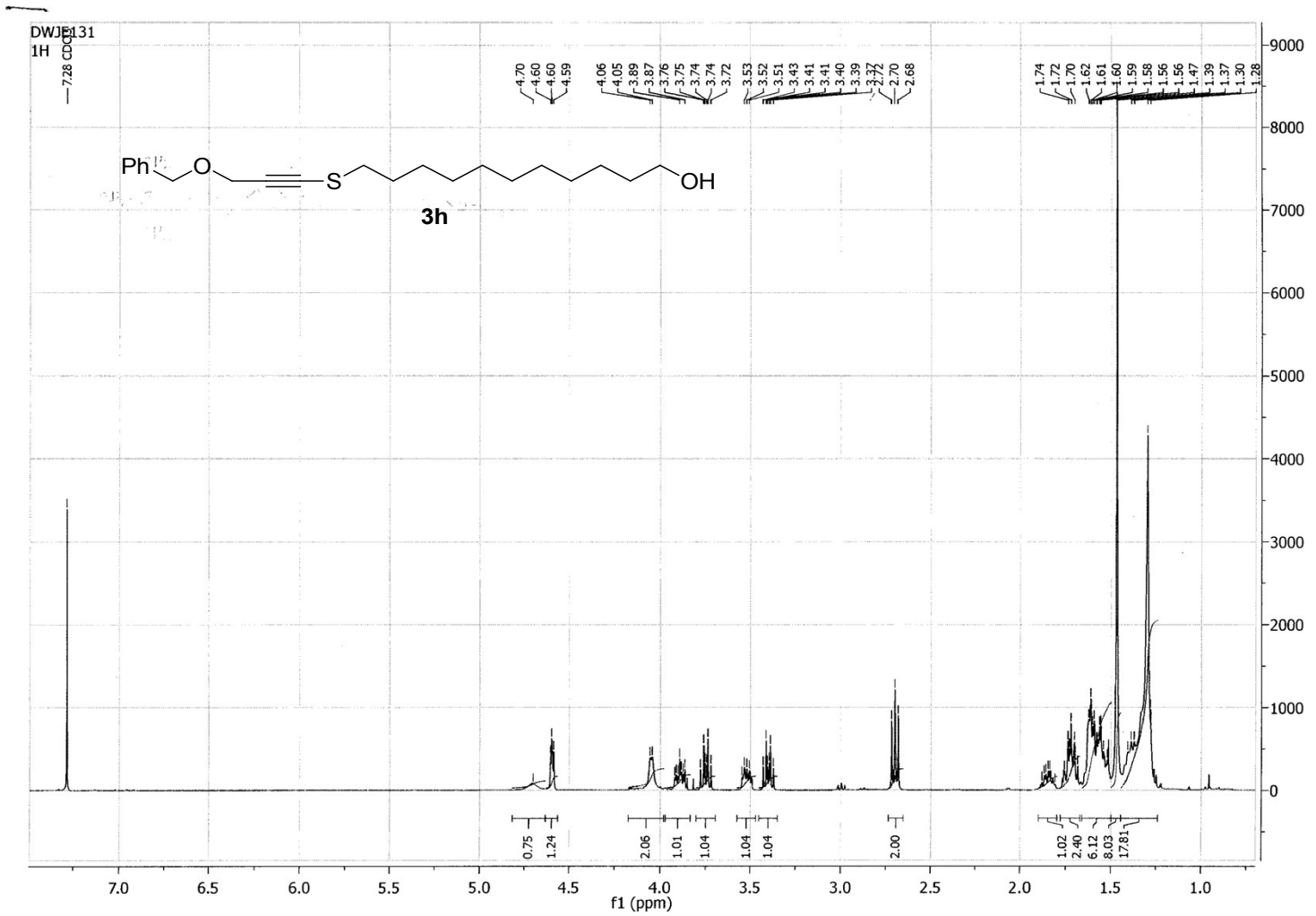

$^{13}C$ NMR (125 MHz, $CDCl_3$): δ=137.4, 128.4, 128.1, 127.8, 90.0, 77.5, 71.2, 63.0, 58.2, 35.4, 32.7, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 28.2, 25.7; signals: expected and observed 19.
HRMS (ESI): m/z $[M + H]^+$calcd for $C_{21}H_{33}O2S$: 349.2201; found: 349.2209.

**3-(11-Tetrahydropyranyloxyundec-1-ylsulfanyl)-*N*-t-butoxycarbonylprop-2-ynylamine (3i)**

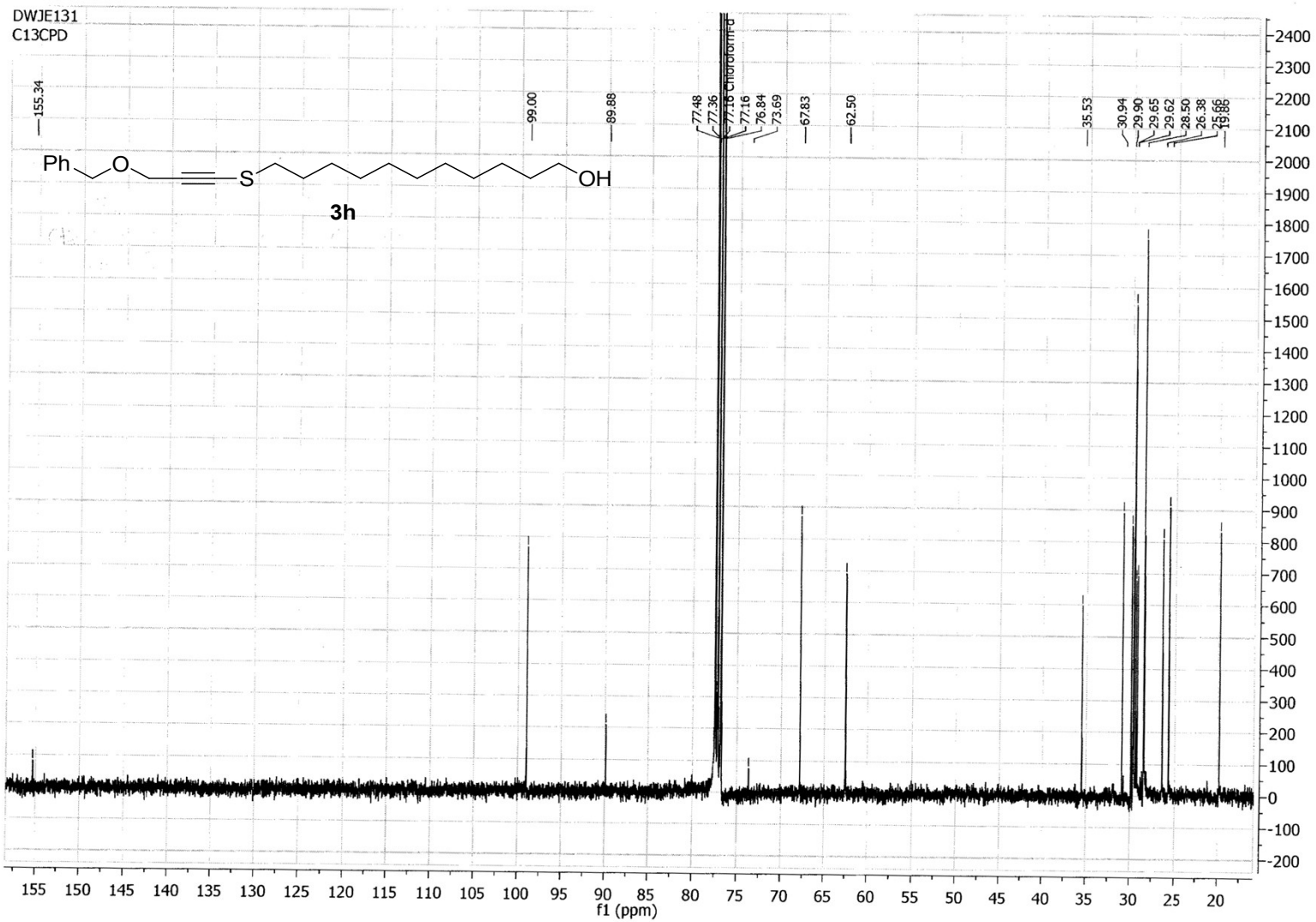
chromatography: $CH_2Cl_2$, ($R_f$ = 0.4), a yellowish oil; yield: 0.221 g (50%).




IR (ATR): 3375 (m), 2910 (s), 2835 (s) (C-H), 2175 (w) (C≡C), 1700 (s), 1450 (s), 1370 (w), 750 (m), 700 (m) $cm^{-1}$




$^1$H NMR (400 MHz, $CDCl_3$): δ =1.25-1.44 (m, 15H, $CH_2$), 1.45 (s, 9H, tBu), 1.50-1.65 (m, 6H, $CH_2$), 1.65-1.77 (m, 2H, $CH_2$), 1.77-1.90 (m, 1H, $CH_2$), 2.70 (t, J = 7.4 Hz, 2H, $SCH_2$), 3.35-3.45 (m, 1H, $OCH_2$), 3.45-3.57 (m, 1H, $OCH_2$), 3.70-3.80 (m, 1H, $OCH_2$), 3.85-3.95 (m, 1H, $OCH_2$), 4.05 (bs, 2H, $NCH_2$), 4.60 (t, *J* = 7.4 Hz, 1H, OCH), 4.70 (bs, 1H, NH)

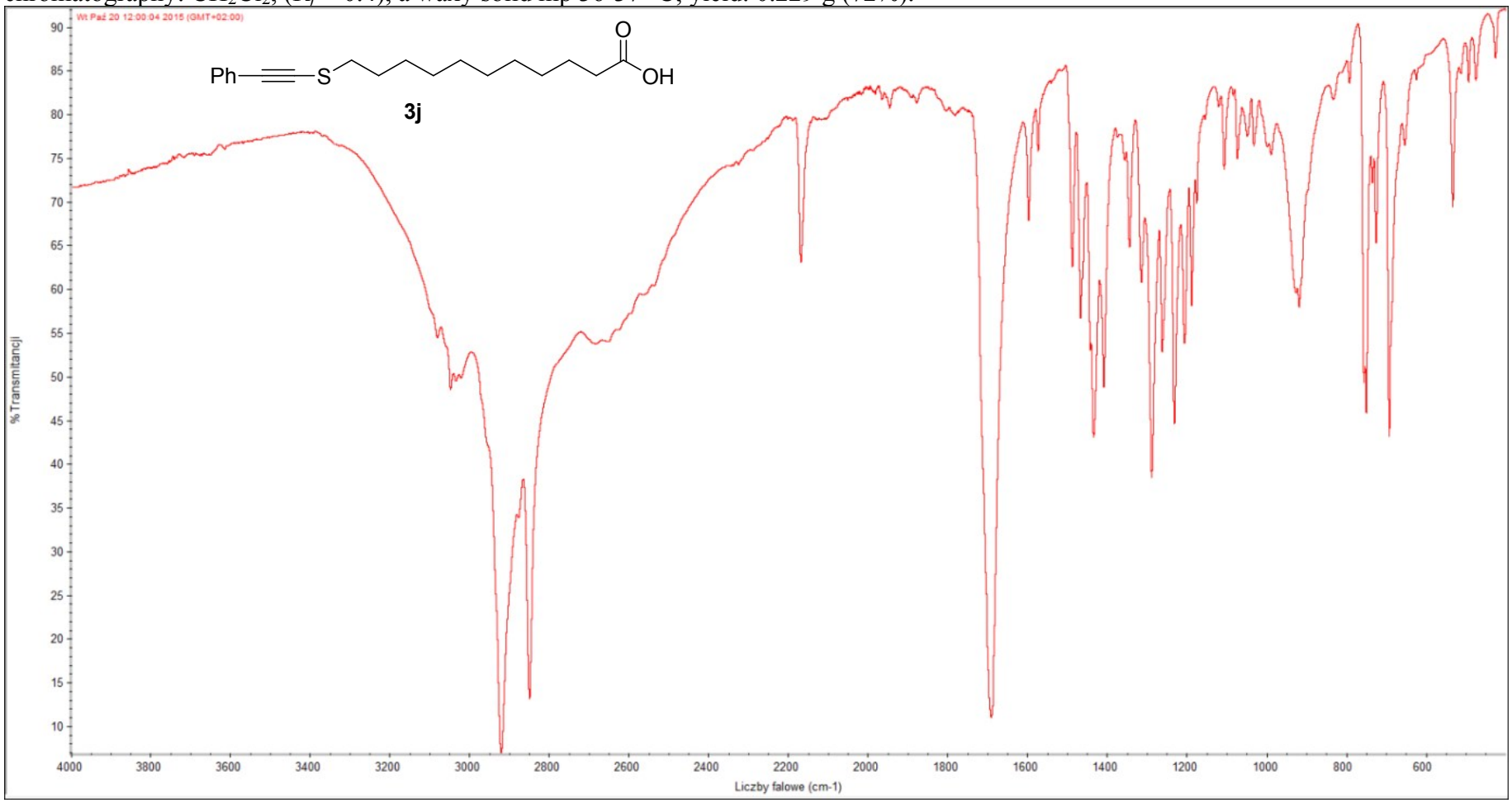



$^{13}C$ NMR (101 MHz, $CDCl_3$): δ= 155.2, 98.9, 89.8, 77.2, 73.6, 67.7, 62.4, 35.4, 31.8, 30.8, 29.8, 29.6, 29.5, 29.5, 29.3, 29.1, 28.4, 28.3, 26.2, 25.5, 19.7; signals: 22 expected, 21 observed.

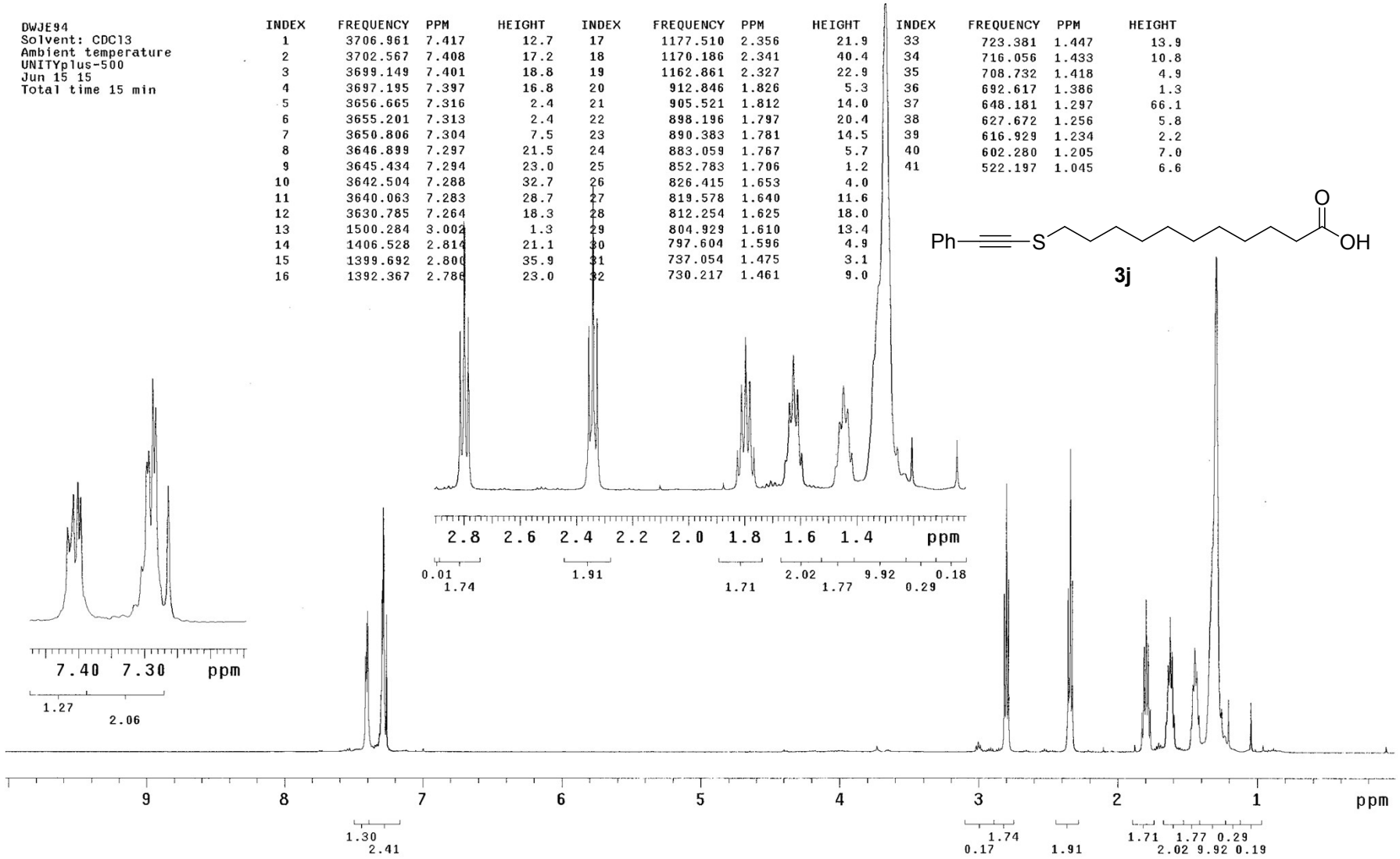
HRMS (ESI): m/z $[M + Na]^+$calcd for $C_{24}H_{43}NNaO_4S$: 464.2810; found: 464.2825.

**1-(10-Carboxydec-1-ylsulfanyl)-2-phenylethyne (3j)**

chromatography: $CH_2Cl_2$, ($R_f$ = 0.4), a waxy solid mp 36-37 °C; yield: 0.229 g (72%).



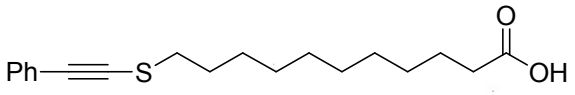

IR (ATR): 2910 (s), 2820 (s) (C-H), 2175 (w) (C≡C), 1700 (s), 1450 (w), 1370 (w), 750 (m), 700 (m) $cm^{-1}$



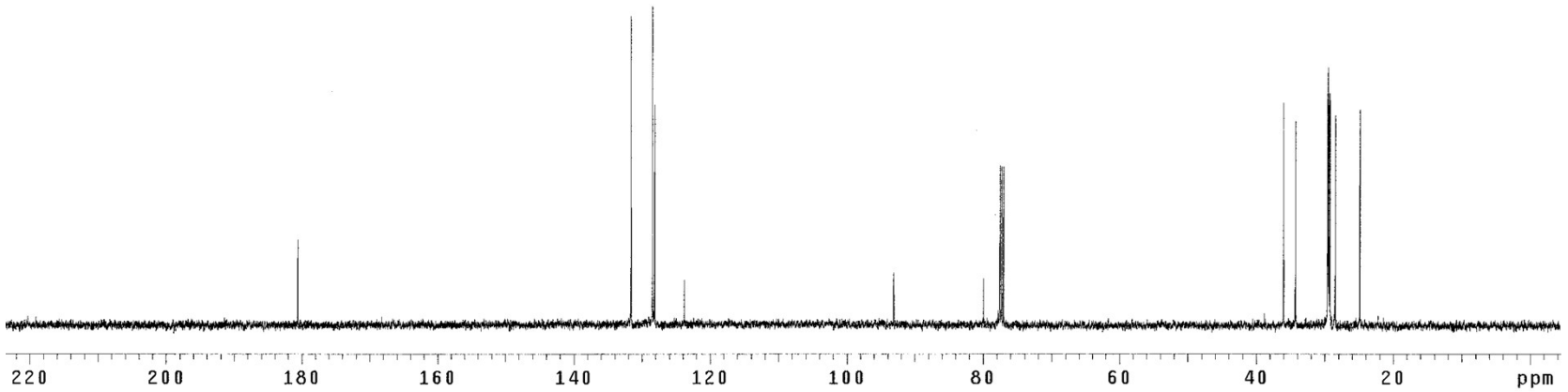

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.20-1.40 (m, 10H, $CH_2$), 1.40-1.50 (m, 2H, $CH_2$), 1.56-1.68 (m, 2H, $CH_2$), 1.80 (qu, $J$ = 7.5 Hz, 2H, $CH_2$), 2.34 (t, $J$ = 7.5 Hz, 2H, $CH_2CO$), 2.8 (t, $J$ = 7.3 Hz, 2H, $SCH_2$), 7.25-7.33 (m, 3H, Ph), 7.37-7.44 (m, 2H, Ph).

DWJE94_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 22699.758 | 180.619 | 0.5 | 17 | 3684.602 | 29.318 | 1.3 |
| 2 | 16543.017 | 131.631 | 1.8 | 18 | 3678.015 | 29.266 | 1.3 |
| 3 | 16150.015 | 128.504 | 1.8 | 19 | 3577.898 | 28.469 | 1.2 |
| 4 | 16108.300 | 128.172 | 1.3 | 20 | 3127.812 | 24.888 | 1.2 |
| 5 | 15560.732 | 123.815 | 0.3 | | | | |
| 6 | 11700.089 | 93.096 | 0.3 | | | | |
| 7 | 10045.089 | 79.928 | 0.3 | | | | |
| 8 | 9746.056 | 77.548 | 0.9 | | | | |
| 9 | 9714.001 | 77.293 | 0.9 | | | | |
| 10 | 9681.946 | 77.038 | 0.9 | | | | |
| 11 | 4529.886 | 36.044 | 1.3 | | | | |
| 12 | 4313.405 | 34.321 | 1.2 | | | | |
| 13 | 3725.000 | 29.639 | 1.3 | | | | |
| 14 | 3716.218 | 29.570 | 1.5 | | | | |
| 15 | 3713.144 | 29.545 | 1.5 | | | | |
| 16 | 3700.849 | 29.447 | 1.3 | | | | |



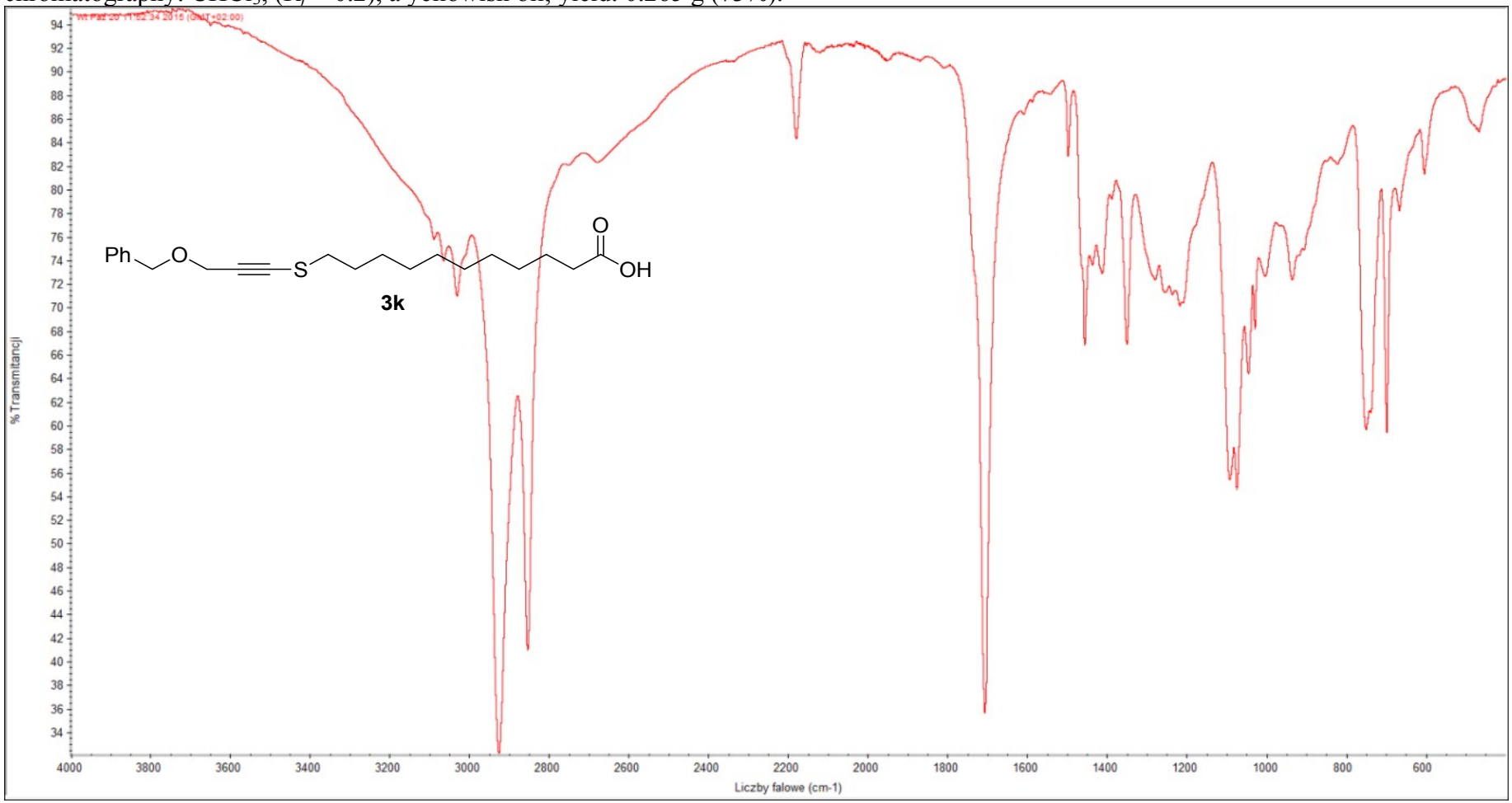

**3j**




$^{13}C$ NMR (125 MHz, $CDCl_3$): δ=180.3, 131.3, 128.2, 127.9, 123.5, 92.8, 79.6, 35.8, 34.0, 29.3, 29.3, 29.2, 29.0, 29.0, 29.0, 28.2, 24.6; signals expected and observed 17.
HRMS (ESI): m/z $[M + Na]^+$calcd for $C_{19}H_{26}NaO_2S$: 341.1551; found: 341,1545.

**1-(10-Carboxydec-1-ylsulfanyl)-3-benzyloxyprop-1-yne (3k)**

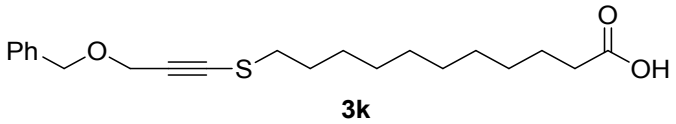
chromatography: $CHCl_3$, ($R_f$ = 0.2), a yellowish oil; yield: 0.265 g (73%).



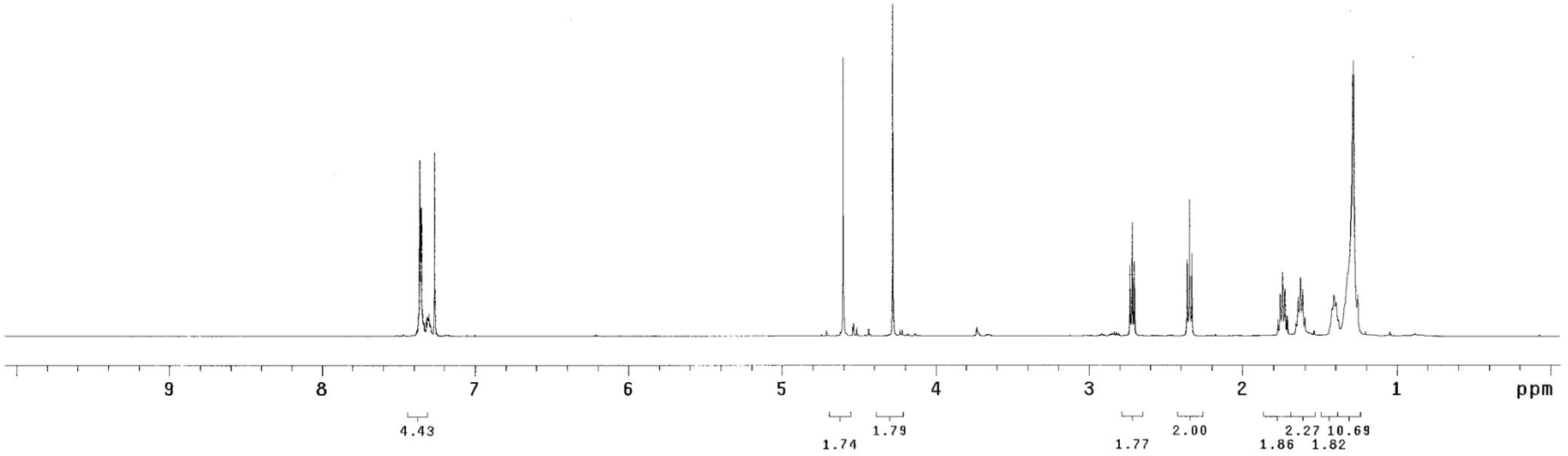

IR (ATR): 2925 (s), 2825 (s) (C-H), 2170 (w) (C≡C), 1700 (s), 1450 (w), 1370 (w), 750 (m), 700 (m) $cm^{-1}$

DWJE97
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 17 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3679.128 | 7.361 | 26.1 | 17 | 813.719 | 1.628 | 8.7 |
| 2 | 3675.710 | 7.354 | 18.9 | 18 | 806.394 | 1.613 | 6.8 |
| 3 | 3674.245 | 7.351 | 19.2 | 19 | 705.802 | 1.412 | 6.1 |
| 4 | 3630.297 | 7.263 | 27.3 | 20 | 644.275 | 1.289 | 41.0 |
| 5 | 2300.626 | 4.603 | 41.5 | 21 | 627.672 | 1.256 | 6.1 |
| 6 | 2139.971 | 4.282 | 49.4 | | | | |
| 7 | 1366.487 | 2.734 | 10.5 | | | | |
| 8 | 1359.162 | 2.719 | 16.9 | | | | |
| 9 | 1351.837 | 2.705 | 11.0 | | | | |
| 10 | 1179.952 | 2.361 | 11.3 | | | | |
| 11 | 1172.139 | 2.345 | 20.3 | | | | |
| 12 | 1164.814 | 2.331 | 12.2 | | | | |
| 13 | 878.176 | 1.757 | 6.3 | | | | |
| 14 | 870.363 | 1.741 | 9.4 | | | | |
| 15 | 863.038 | 1.727 | 6.9 | | | | |
| 16 | 820.555 | 1.642 | 5.7 | | | | |



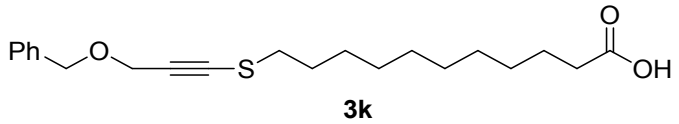

**3k**



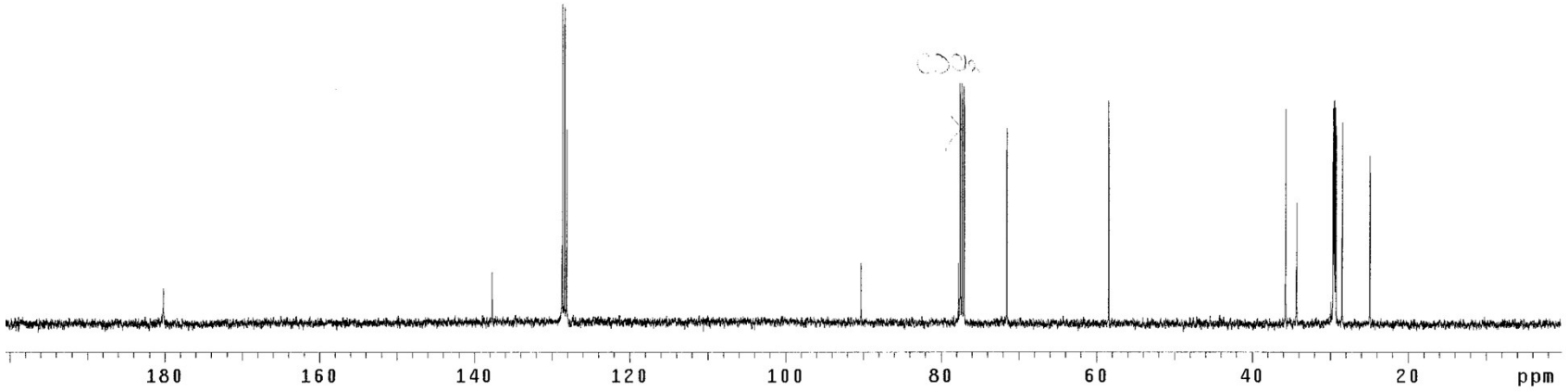

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.22-1.43 (m, 12H, $CH_2$), 1.63 (qu, *J* = 7.5 Hz, 2H, $CH_2$), 1.74 (qu, *J* = 7.4 Hz, 2H, $CH_2$), 2.35 (t, *J* = 7.5 Hz, 2H, $CH_2CO$), 2.72 (t, *J* = 7.3 Hz, 2H, $SCH_2$), 4.28 (s, 2H, $OCH_2$), 4.6 (s, 2H, $OCH_2$), 7.26-7.40 (m, 5H, Ph).

DWJE97_13C
Solvent: CDCl3
Ambient temperature
File: DWJE97_13C
UNITYplus-500
Jun 23 15
Total time 30 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 22651.017 | 180.232 | 0.1 | 17 | 3708.314 | 29.507 | 0.7 |
| 2 | 17303.114 | 137.679 | 0.2 | 18 | 3698.653 | 29.430 | 0.7 |
| 3 | 16171.092 | 128.672 | 1.0 | 19 | 3685.919 | 29.328 | 0.7 |
| 4 | 16133.768 | 128.375 | 1.0 | 20 | 3678.015 | 29.266 | 0.6 |
| 5 | 16099.079 | 128.099 | 0.6 | 21 | 3579.216 | 28.479 | 0.6 |
| 6 | 11341.338 | 90.242 | 0.2 | 22 | 3130.008 | 24.905 | 0.5 |
| 7 | 9772.403 | 77.758 | 0.2 | | | | |
| 8 | 9744.739 | 77.538 | 0.8 | | | | |
| 9 | 9712.684 | 77.283 | 0.8 | | | | |
| 10 | 9680.629 | 77.028 | 0.8 | | | | |
| 11 | 8987.277 | 71.511 | 0.6 | | | | |
| 12 | 7344.132 | 58.436 | 0.7 | | | | |
| 13 | 4487.731 | 35.708 | 0.7 | | | | |
| 14 | 4311.649 | 34.307 | 0.4 | | | | |
| 15 | 3725.000 | 29.639 | 0.7 | | | | |
| 16 | 3716.218 | 29.570 | 0.7 | | | | |



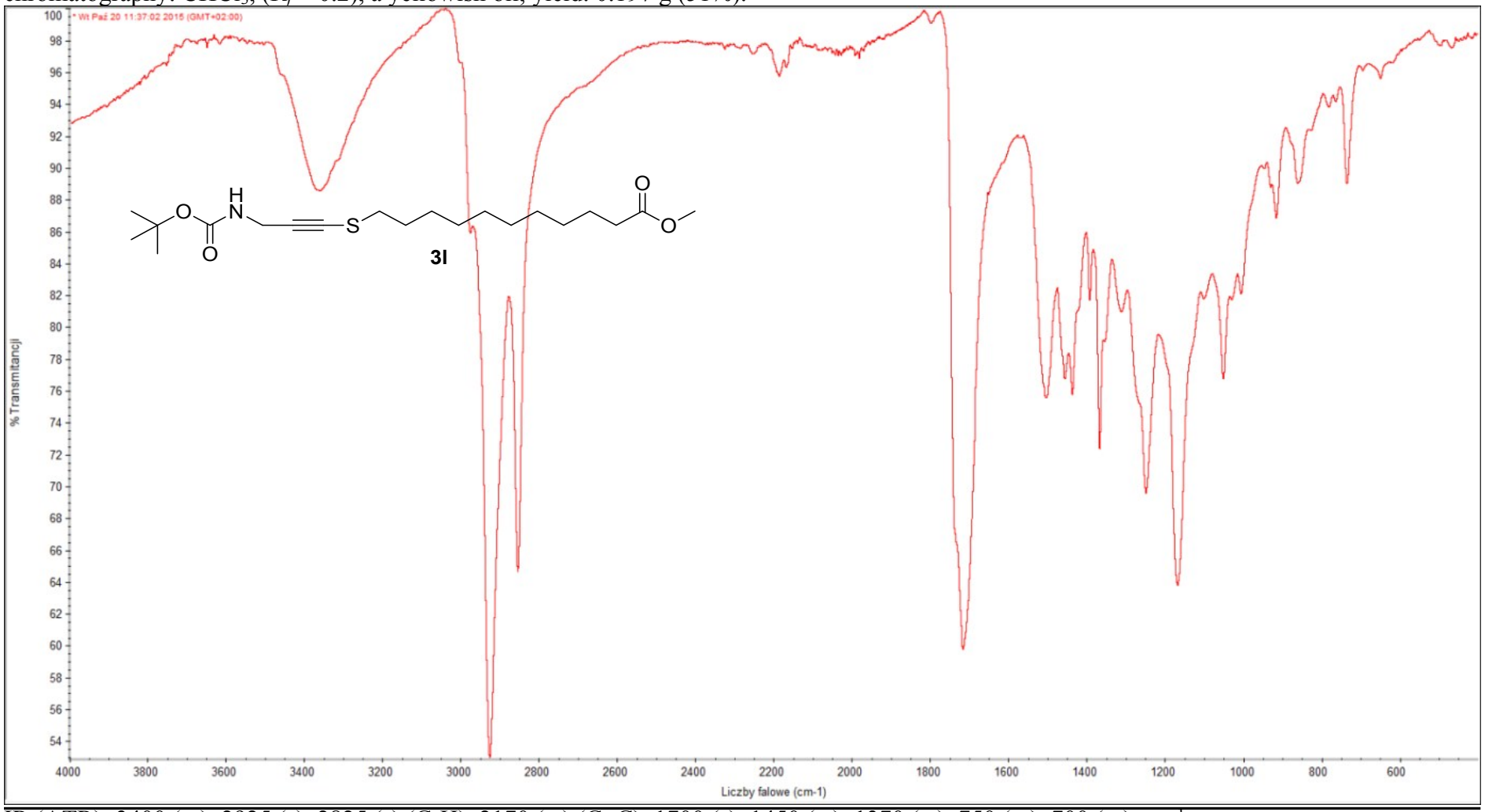

**3k**



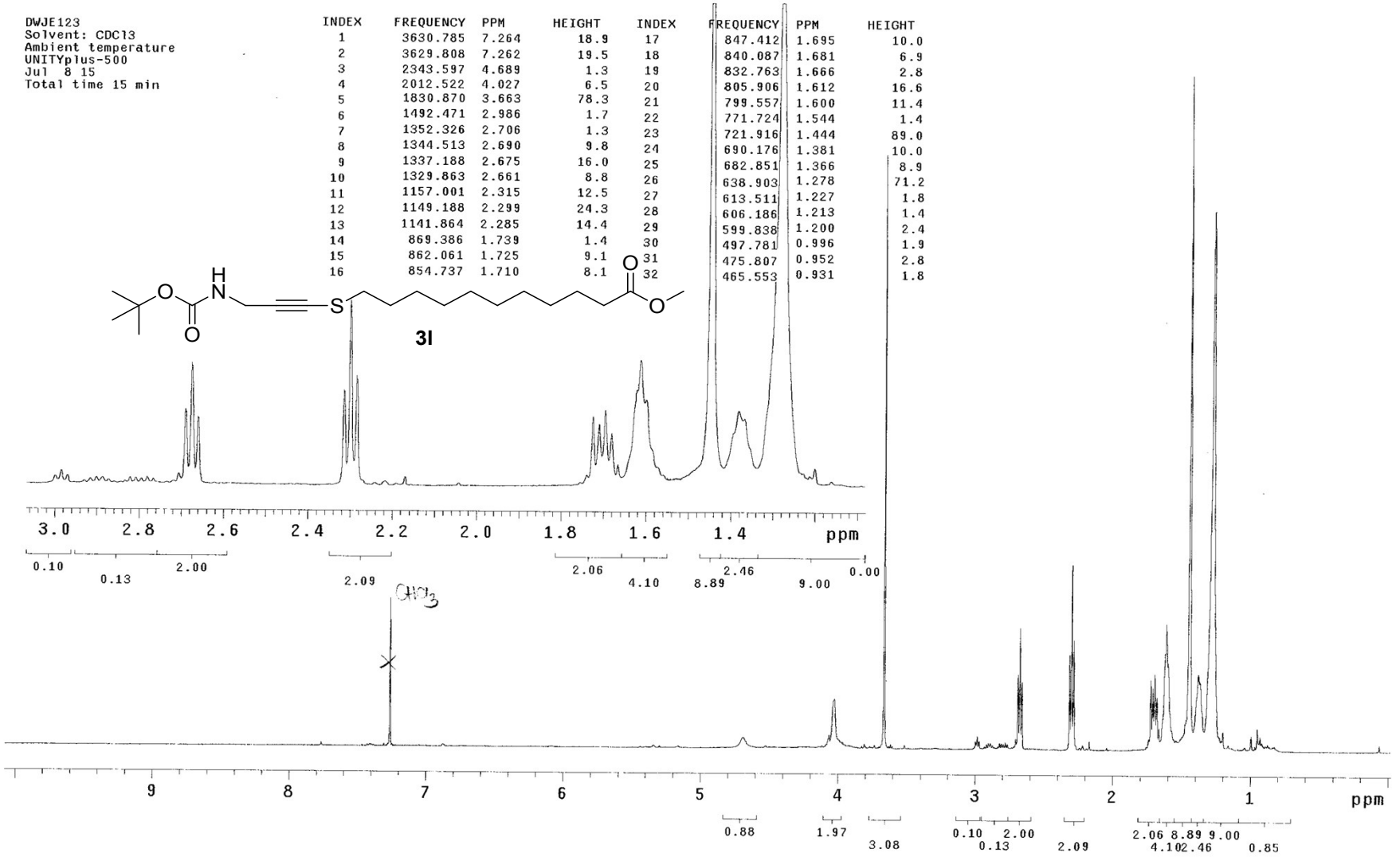

$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 179.9, 137.4, 128.4, 128.1, 127.8, 90.0, 77.5, 71.2, 58.2, 35.4, 34.0, 29.4, 29.3, 29.2, 29.1, 29.0, 29.0, 28.2, 24.6; signals expected and observed 19.
HRMS (ESI): m/z $[M + Na]^+$calcd for $C_{21}H_{30}NaO_3S$: 385.1813; found: 385.1805.

**3-(10-Methoxycarbonyldec-1-ylsulfanyl)-*N*-t-butoxycarbonylprop-2-ynylamine (3l)**

chromatography: $CHCl_3$, ($R_f$ = 0.2), a yellowish oil; yield: 0.197 g (51%).




IR (ATR): 3400 (m), 2925 (s), 2825 (s) (C-H), 2170 (w) (C≡C), 1700 (s), 1450 (w), 1370 (w), 750 (m), 700 (m) $cm^{-1}$



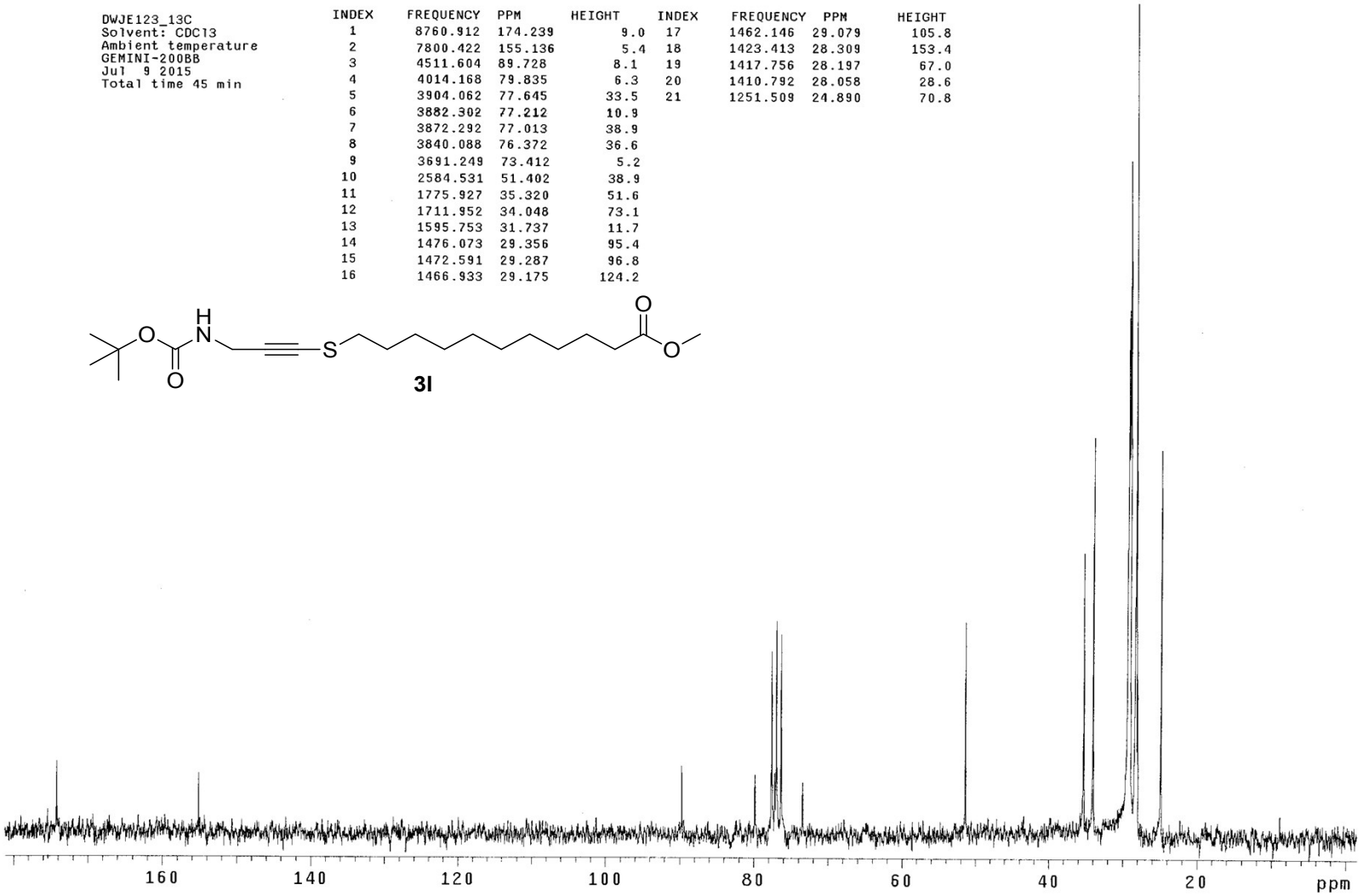

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.28-1.42 (m, 10H, $CH_2$), 1.44 (s, 9H, tBu), 1.61-1.68 (m, 4H, $CH_2$), 1.68-1.73 (m, 2H, $CH_2$), 2.30 (t, *J*=7.5 Hz, 2H, $CH_2CO$), 2.61 (t, *J* = 7.4 Hz, 2H, $SCH_2$), 3.66 (s, 3H, $OCH_3$), 4.03 (s, 2H, $NCH_2$), 4.69 (bs, 1H, NH).

DWJE123_13C
Solvent: CDCl3
Ambient temperature
GEMINI-200BB
Jul 9 2015
Total time 45 min

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 8760.912 | 174.239 | 9.0 | 17 | 1462.146 | 29.079 | 105.8 |
| 2 | 7800.422 | 155.136 | 5.4 | 18 | 1423.413 | 28.309 | 153.4 |
| 3 | 4511.604 | 89.728 | 8.1 | 19 | 1417.756 | 28.197 | 67.0 |
| 4 | 4014.168 | 79.835 | 6.3 | 20 | 1410.792 | 28.058 | 28.6 |
| 5 | 3904.062 | 77.645 | 33.5 | 21 | 1251.509 | 24.890 | 70.8 |
| 6 | 3882.302 | 77.212 | 10.9 | | | | |
| 7 | 3872.292 | 77.013 | 38.9 | | | | |
| 8 | 3840.088 | 76.372 | 36.6 | | | | |
| 9 | 3691.249 | 73.412 | 5.2 | | | | |
| 10 | 2584.531 | 51.402 | 38.9 | | | | |
| 11 | 1775.927 | 35.320 | 51.6 | | | | |
| 12 | 1711.952 | 34.048 | 73.1 | | | | |
| 13 | 1595.753 | 31.737 | 11.7 | | | | |
| 14 | 1476.073 | 29.356 | 95.4 | | | | |
| 15 | 1472.591 | 29.287 | 96.8 | | | | |
| 16 | 1466.933 | 29.175 | 124.2 | | | | |



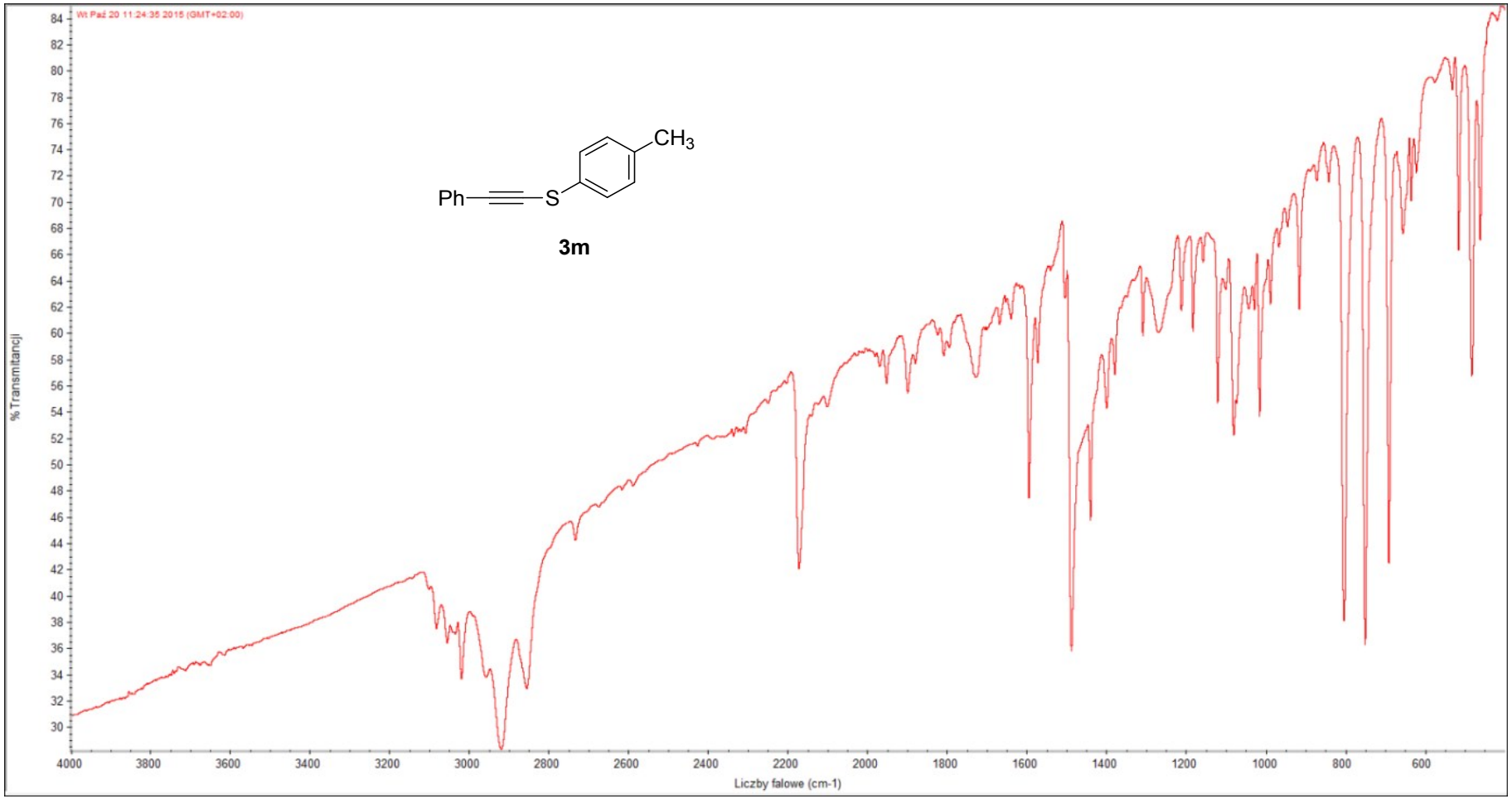

**3l**




$^{13}C$ NMR (50 MHz, $CDCl_3$): δ= 174.2, 155.1, 89.7, 79.8, 73.4, 51.4, 35.3, 34.0, 31.7, 29.3, 29.3, 29.2, 29.1, 28.3, 28.2, 28.0, 24.9; signals: 18 expected, 17 observed.

HRMS (ESI): m/z $[M + Na]^+$calcd for $C_{20}H_{35}NNaO_4S$: 408.2184; found: 408.2176.

**1-(4-Methylphenylsulfanyl)-2-phenylethyne (3m)**
chromatography: hexanes, ($R_f$ = 0.5), a yellowish oil; yield: 0.220 g (98%).



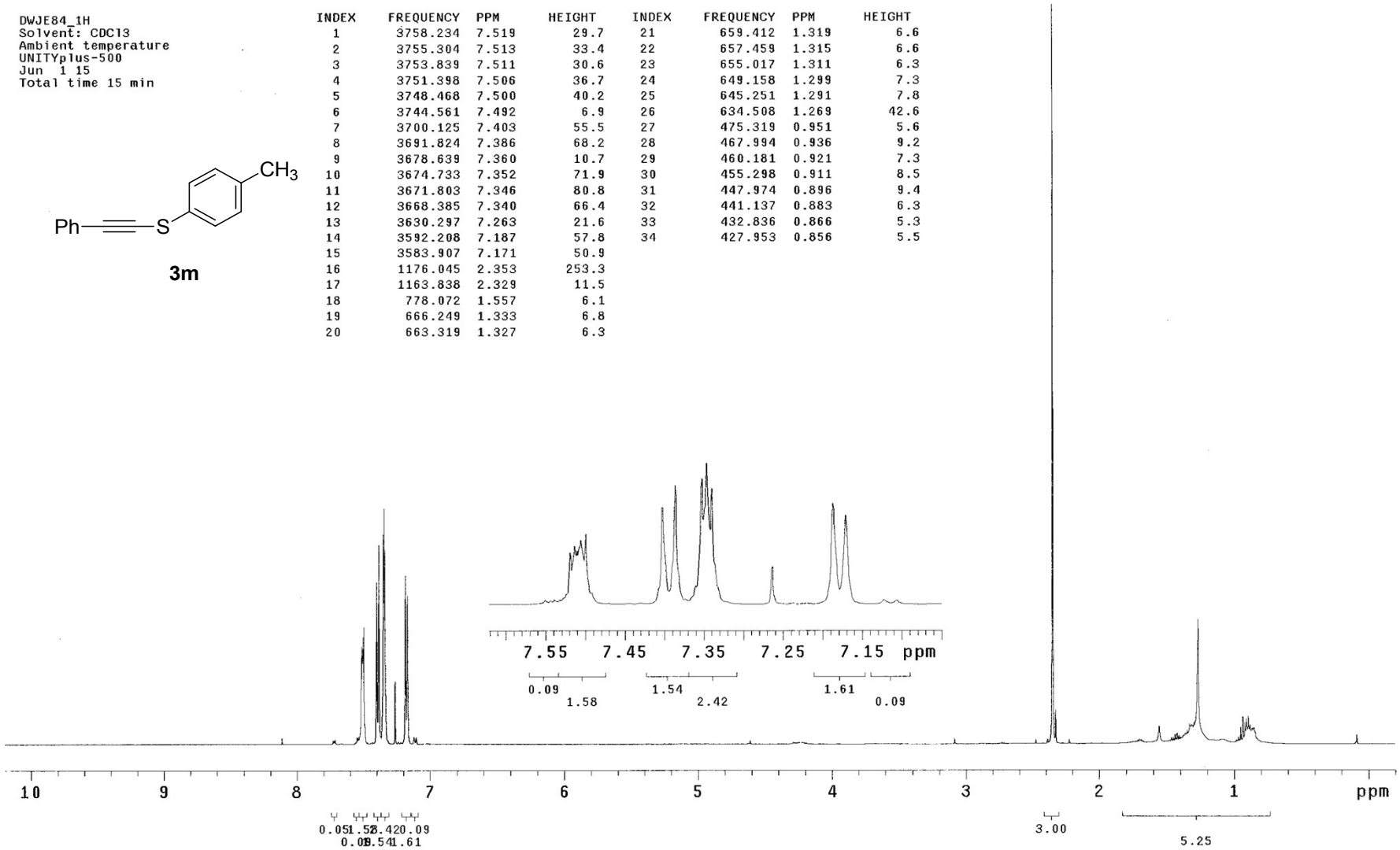

IR (ATR): 2910 (s), 2835 (s) (C-H), 2190 (m) (C≡C), 1600 (w), 1500 (s), 800 (s), 750 (s), 700 (s) $cm^{-1}$

DWJE84_1H
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 1 15
Total time 15 min




**3m**

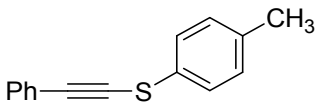
| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3758.234 | 7.519 | 29.7 | 21 | 659.412 | 1.319 | 6.6 |
| 2 | 3755.304 | 7.513 | 33.4 | 22 | 657.459 | 1.315 | 6.6 |
| 3 | 3753.839 | 7.511 | 30.6 | 23 | 655.017 | 1.311 | 6.3 |
| 4 | 3751.398 | 7.506 | 36.7 | 24 | 649.158 | 1.299 | 7.3 |
| 5 | 3748.468 | 7.500 | 40.2 | 25 | 645.251 | 1.291 | 7.8 |
| 6 | 3744.561 | 7.492 | 6.9 | 26 | 634.508 | 1.269 | 42.6 |
| 7 | 3700.125 | 7.403 | 55.5 | 27 | 475.319 | 0.951 | 5.6 |
| 8 | 3691.824 | 7.386 | 68.2 | 28 | 467.994 | 0.936 | 9.2 |
| 9 | 3678.639 | 7.360 | 10.7 | 29 | 460.181 | 0.921 | 7.3 |
| 10 | 3674.733 | 7.352 | 71.9 | 30 | 455.298 | 0.911 | 8.5 |
| 11 | 3671.803 | 7.346 | 80.8 | 31 | 447.974 | 0.896 | 9.4 |
| 12 | 3668.385 | 7.340 | 66.4 | 32 | 441.137 | 0.883 | 6.3 |
| 13 | 3630.297 | 7.263 | 21.6 | 33 | 432.836 | 0.866 | 5.3 |
| 14 | 3592.208 | 7.187 | 57.8 | 34 | 427.953 | 0.856 | 5.5 |
| 15 | 3583.907 | 7.171 | 50.9 | | | | |
| 16 | 1176.045 | 2.353 | 253.3 | | | | |
| 17 | 1163.838 | 2.329 | 11.5 | | | | |
| 18 | 778.072 | 1.557 | 6.1 | | | | |
| 19 | 666.249 | 1.333 | 6.8 | | | | |
| 20 | 663.319 | 1.327 | 6.3 | | | | |



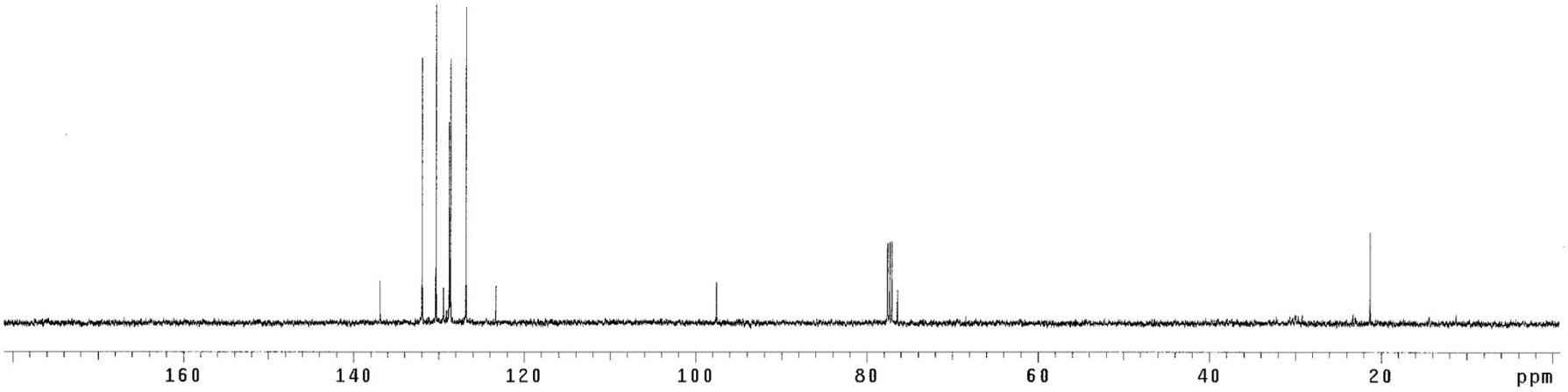

$^1$H NMR (500 MHz, $CDCl_3$): δ =2.35 (s, 3H, $CH_3$), 7.18 (d, *J* = 8.3 Hz, 2H, Ar), 7.32-7.37 (m, 3H, Ph), 7.39 (d, *J* = 8.3 Hz, 2H, Ar), 7.48-7.54 (m, 2H, Ph).

DWJE84_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 17203.436 | 136.886 | 0.4 |
| 2 | 16583.415 | 131.952 | 2.5 |
| 3 | 16379.230 | 130.328 | 3.1 |
| 4 | 16268.574 | 129.447 | 0.3 |
| 5 | 16186.022 | 128.790 | 1.9 |
| 6 | 16167.579 | 128.644 | 2.5 |
| 7 | 15940.121 | 126.834 | 3.0 |
| 8 | 15495.743 | 123.298 | 0.4 |
| 9 | 12260.831 | 97.558 | 0.4 |
| 10 | 9749.569 | 77.576 | 0.8 |
| 11 | 9717.514 | 77.321 | 0.8 |
| 12 | 9685.459 | 77.066 | 0.8 |
| 13 | 9602.467 | 76.406 | 0.3 |
| 14 | 2674.652 | 21.282 | 0.9 |

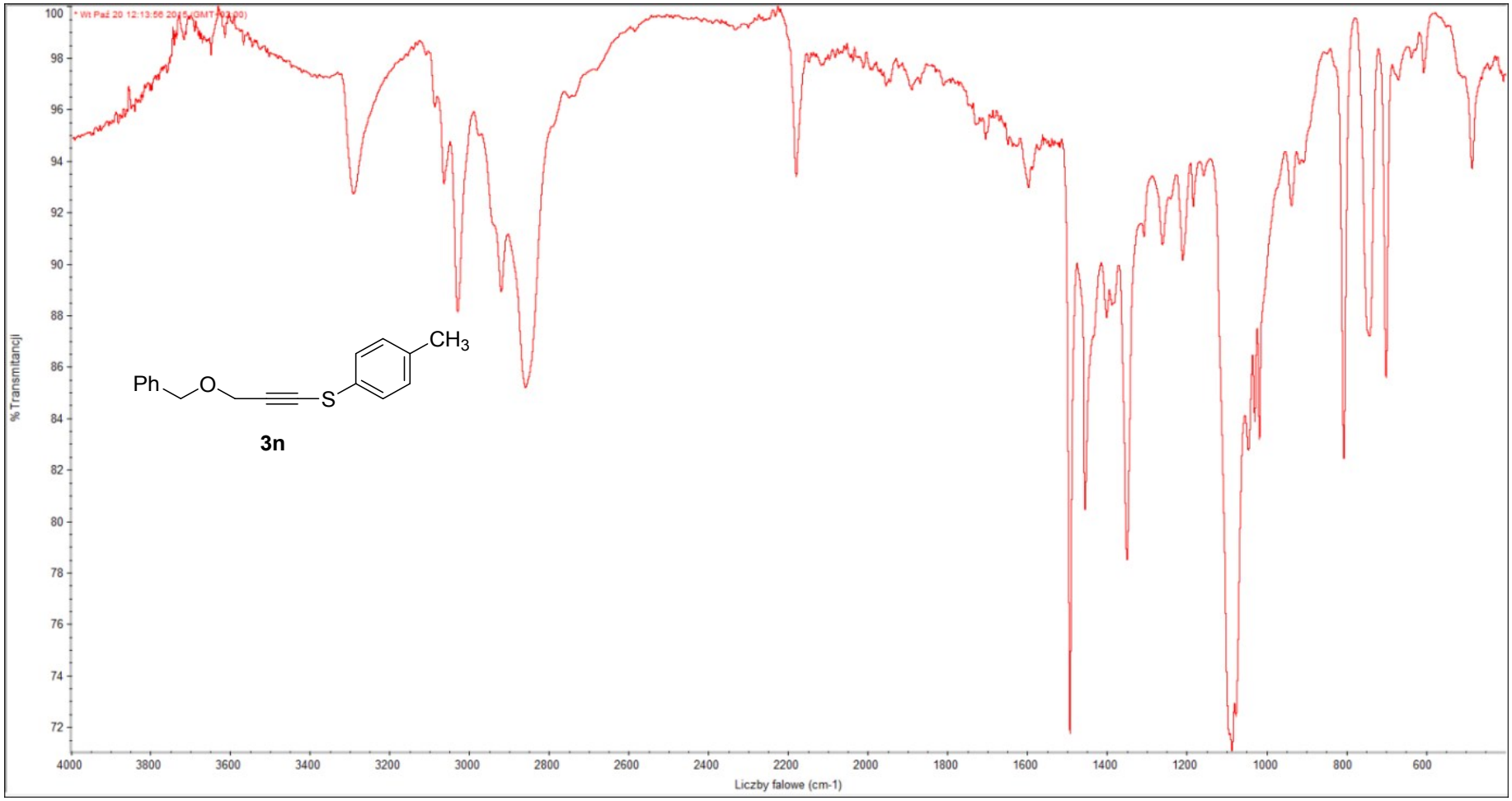



**3m**

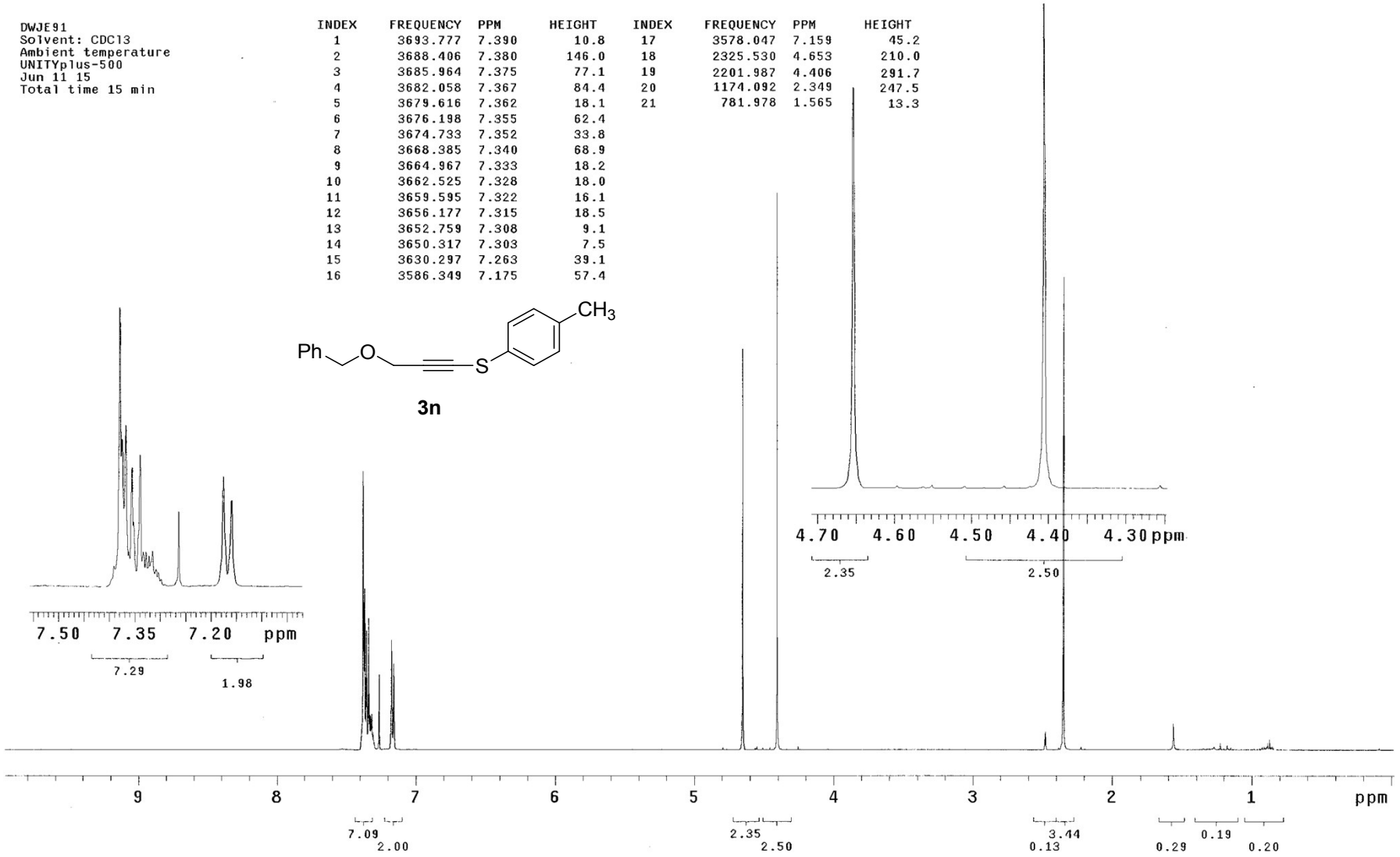



$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 136.6, 131.6, 130.0, 129.1, 128.5, 128.3, 126.5, 123.0, 97.2, 76.1, 21.0; signals expected and observed 11.
HRMS (ESI): m/z $[M + H]^+$calcd for $C_{15}H_{13}S$: 225.0738; found: 225.0740.

**1-(4-Methylphenylsulfanyl)-3-benzyloxyprop-1-yne (3n)**
chromatography: petroleum ether, ($R_f$ = 0.15), a yellowish oil; yield: 0.239 g (89%).



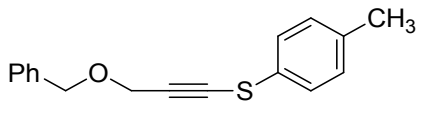

IR (ATR): 2900 (s), 2850 (s) (C-H), 2170 (w) (C≡C), 1500 (s), 1450 (w), 1100 (s), 750 (m), 700 (m) $cm^{-1}$



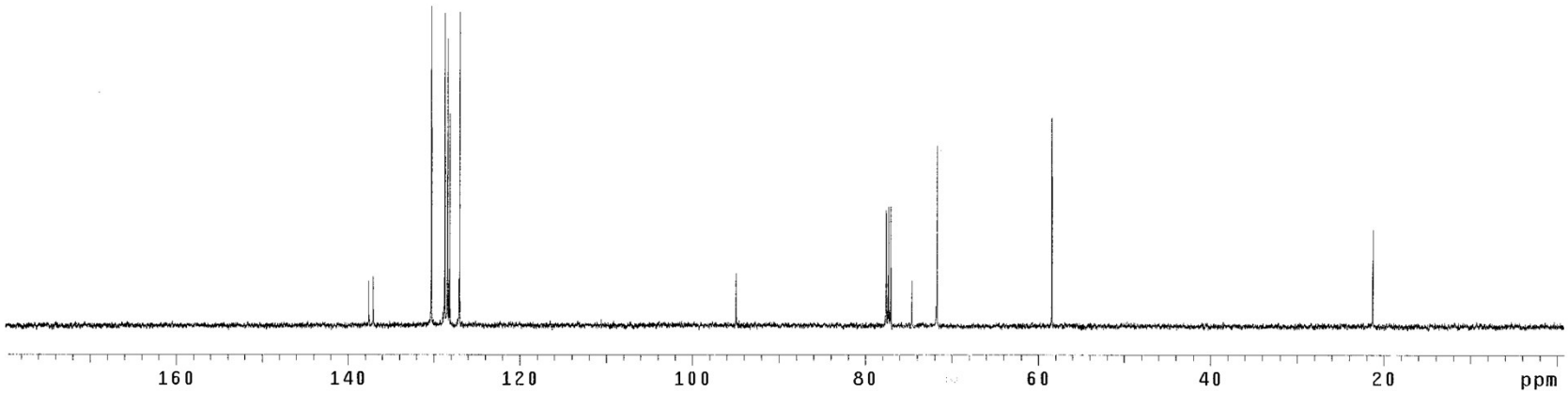

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3H, $CH_3$), 4.41 (s, 2H, $OCH_2$), 4.65 (s, 2H, $OCH_2$), 7.17 (d, *J* = 8.3 Hz, 2H, Ar), 7.30-7.40 (m, 7H, Ar, Ph).

DWJE91_13C
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 23 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 17292.136 | 137.592 | 0.3 |
| 2 | 17226.270 | 137.068 | 0.4 |
| 3 | 16375.278 | 130.296 | 2.3 |
| 4 | 16179.435 | 128.738 | 2.2 |
| 5 | 16141.233 | 128.434 | 2.1 |
| 6 | 16136.403 | 128.396 | 0.5 |
| 7 | 16110.935 | 128.193 | 1.5 |
| 8 | 15965.150 | 127.033 | 2.3 |
| 9 | 11931.499 | 94.938 | 0.4 |
| 10 | 9750.008 | 77.580 | 0.8 |
| 11 | 9717.953 | 77.325 | 0.9 |
| 12 | 9685.898 | 77.070 | 0.9 |
| 13 | 9376.766 | 74.610 | 0.3 |
| 14 | 9012.306 | 71.710 | 1.3 |
| 15 | 7345.889 | 58.450 | 1.5 |
| 16 | 2673.774 | 21.275 | 0.7 |



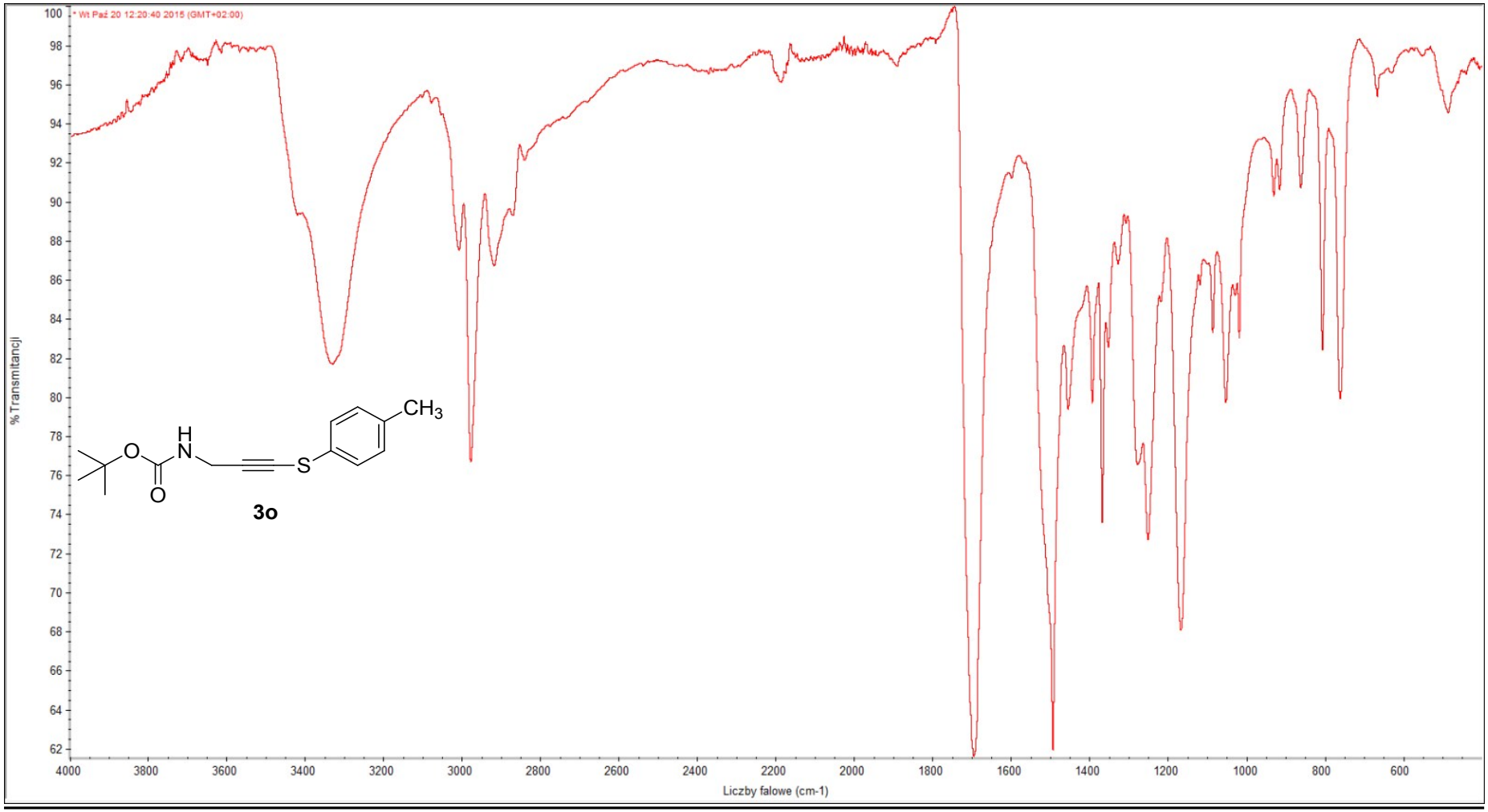

**3n**




$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 137.3, 136.7, 130.0, 128.4, 128.1, 128.1, 127.9, 126.7, 94.6, 74.3, 71.4, 58.1, 21.0; signals expected and observed 13.

HRMS (ESI): m/z $[M + H]^+$calcd for $C_{17}H_{17}OS$: 269.1000; found: 269.1009.

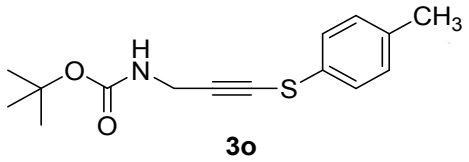
**3-(4-Methylphenylsulfanyl)-*N*-t-butoxycarbonylprop-2-ynylamine (3o)**
chromatography: $CH_2Cl_2$ :petroleum ether, 1:2 ($R_f$ = 0.2), a yellowish oil; yield: 0.216 g (78%).



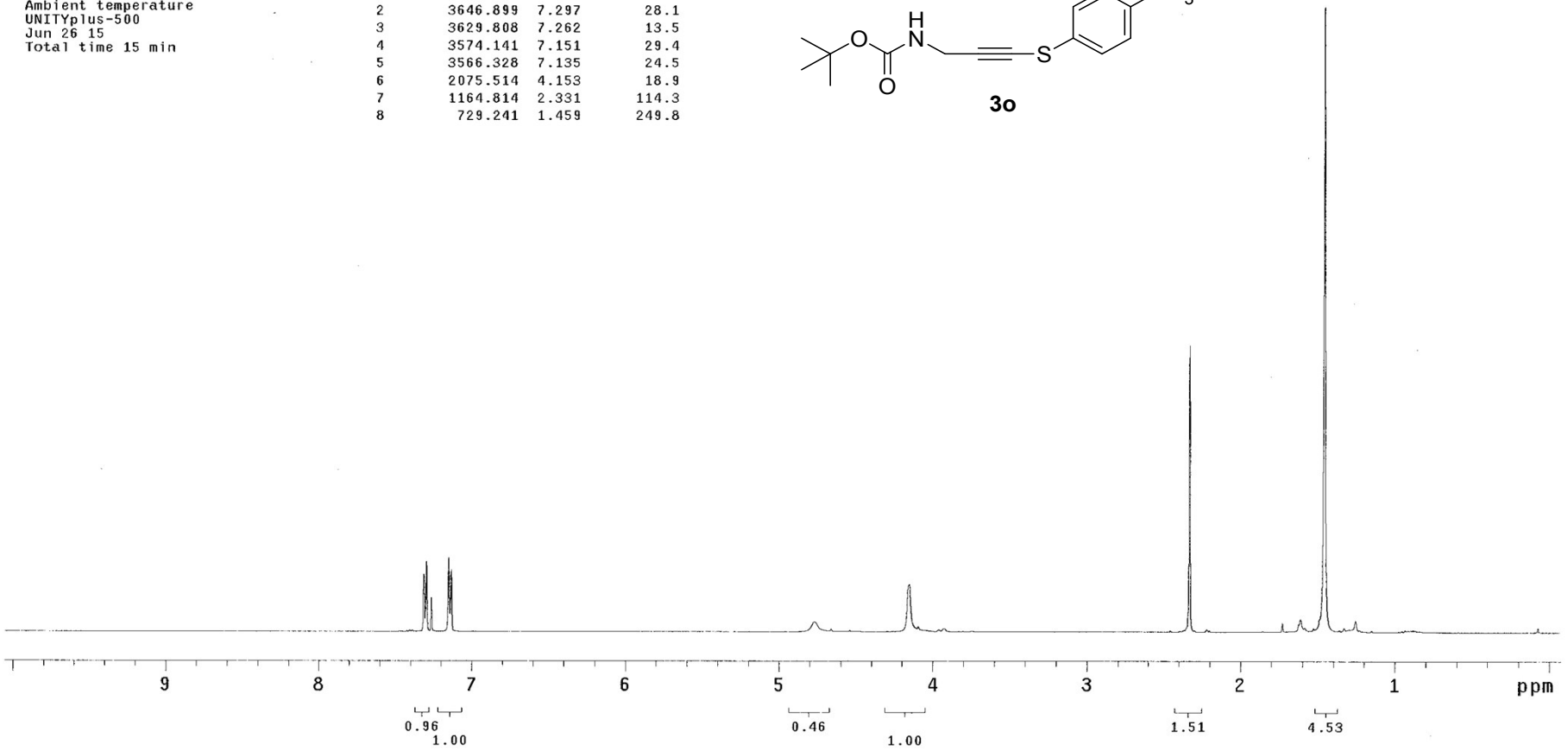

IR (ATR): 3400 (s), 2900 (s), 2850 (m) (C-H), 2170 (w) (C≡C), 1700 (s), 1500 (s), 1370 (w), 750 (m), 700 (m) $cm^{-1}$

DWJE112
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 26 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 3654.224 | 7.311 | 22.9 |
| 2 | 3646.899 | 7.297 | 28.1 |
| 3 | 3629.808 | 7.262 | 13.5 |
| 4 | 3574.141 | 7.151 | 29.4 |
| 5 | 3566.328 | 7.135 | 24.5 |
| 6 | 2075.514 | 4.153 | 18.9 |
| 7 | 1164.814 | 2.331 | 114.3 |
| 8 | 729.241 | 1.459 | 249.8 |




**3o**



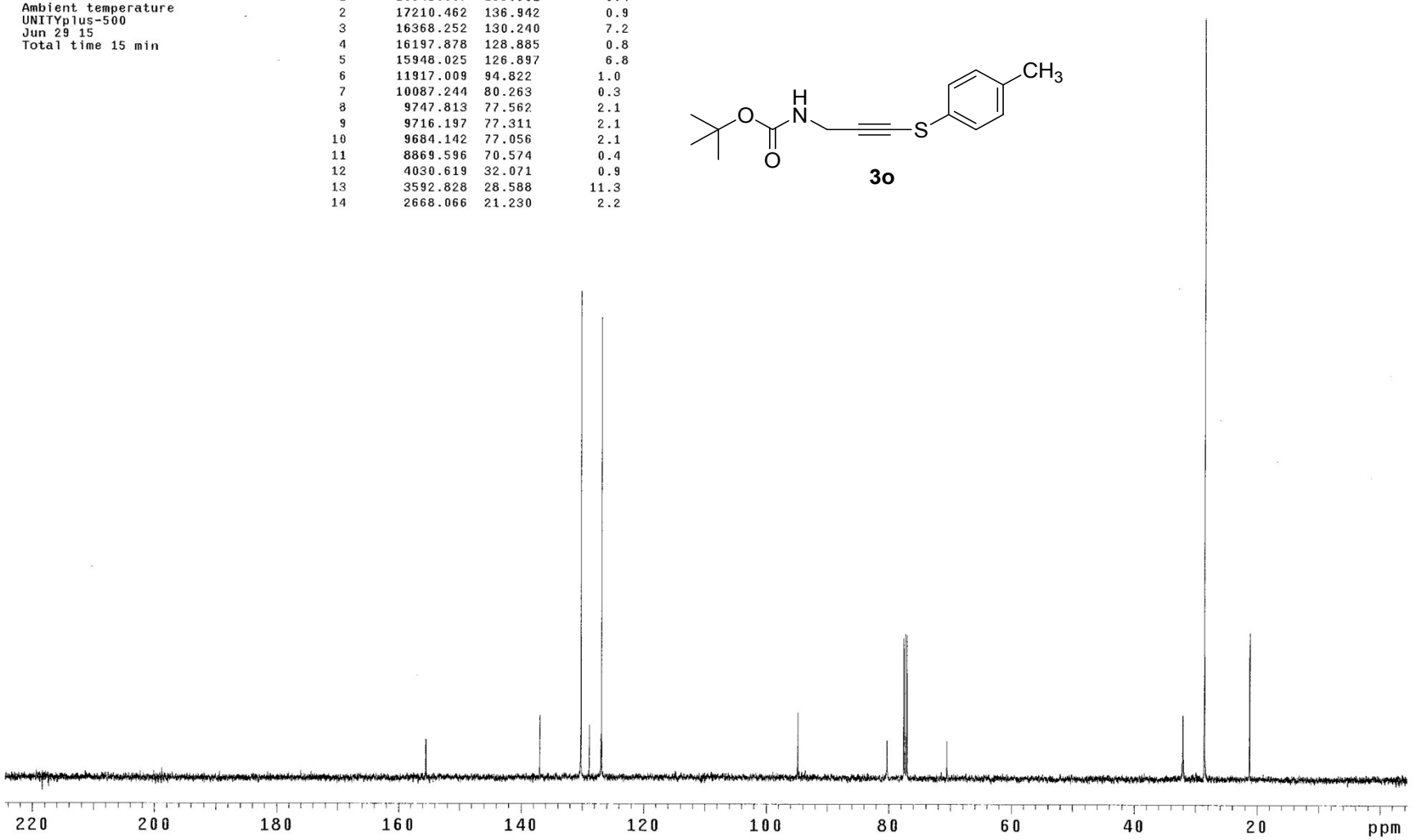

$^1$H NMR (500 MHz, $CDCl_3$): δ =1.46 (s, 9H, tBu), 2.33 (s, 3H, $CH_3$), 4.15 (s, 2H, $NCH_2$), 4.78 (bs, 1H, NH), 7.14 (d, *J* = 7.5 Hz, 2H, Ar), 7.30 (d, *J* = 7.5 Hz, 2H, Ar).

DWJE112_13C_290615
Solvent: CDCl3
Ambient temperature
UNITYplus-500
Jun 29 15
Total time 15 min

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 19543.007 | 155.502 | 0.4 |
| 2 | 17210.462 | 136.942 | 0.9 |
| 3 | 16368.252 | 130.240 | 7.2 |
| 4 | 16197.878 | 128.885 | 0.8 |
| 5 | 15948.025 | 126.897 | 6.8 |
| 6 | 11917.009 | 94.822 | 1.0 |
| 7 | 10087.244 | 80.263 | 0.3 |
| 8 | 9747.813 | 77.562 | 2.1 |
| 9 | 9716.197 | 77.311 | 2.1 |
| 10 | 9684.142 | 77.056 | 2.1 |
| 11 | 8869.596 | 70.574 | 0.4 |
| 12 | 4030.619 | 32.071 | 0.9 |
| 13 | 3592.828 | 28.588 | 11.3 |
| 14 | 2668.066 | 21.230 | 2.2 |



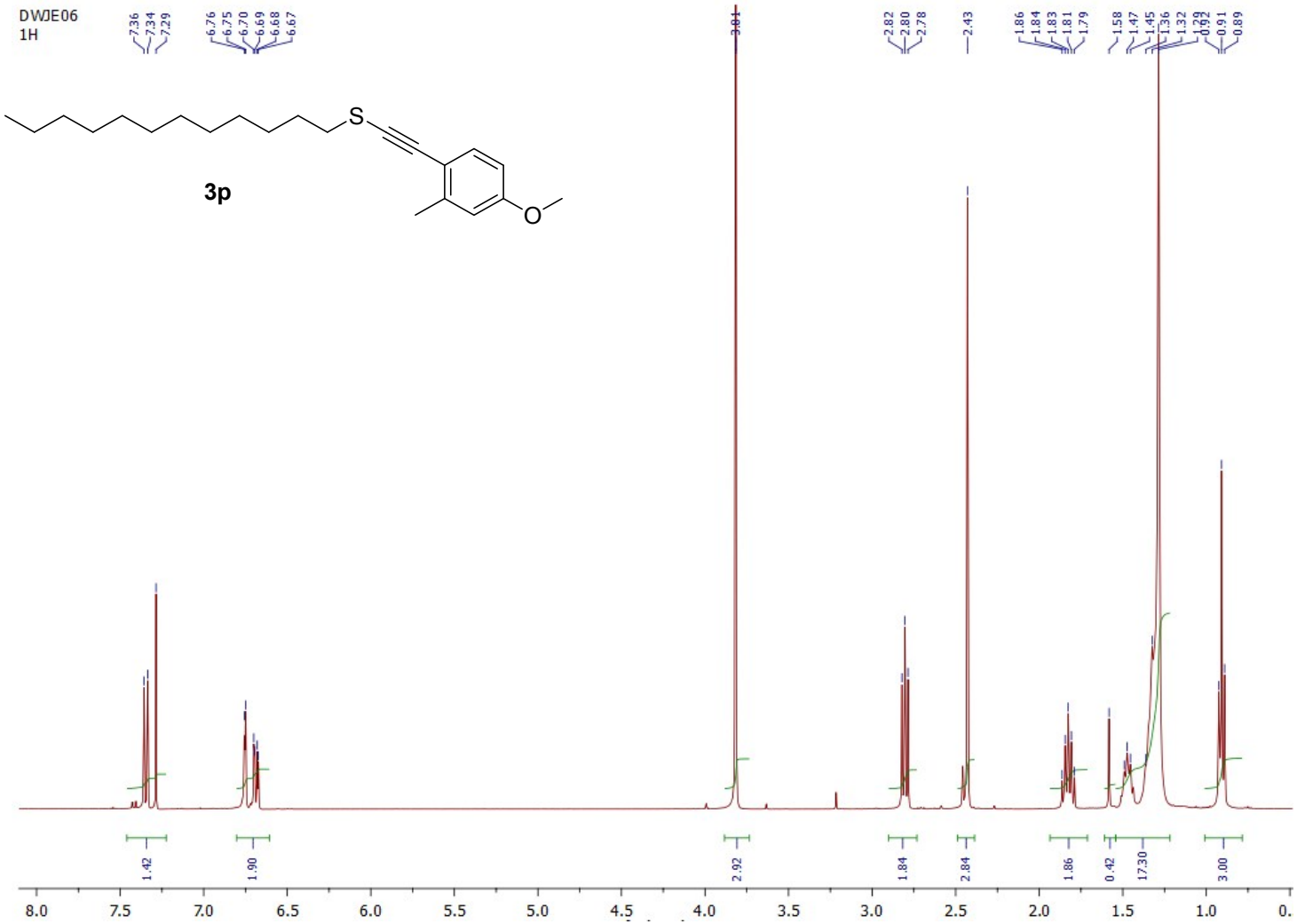

**3o**



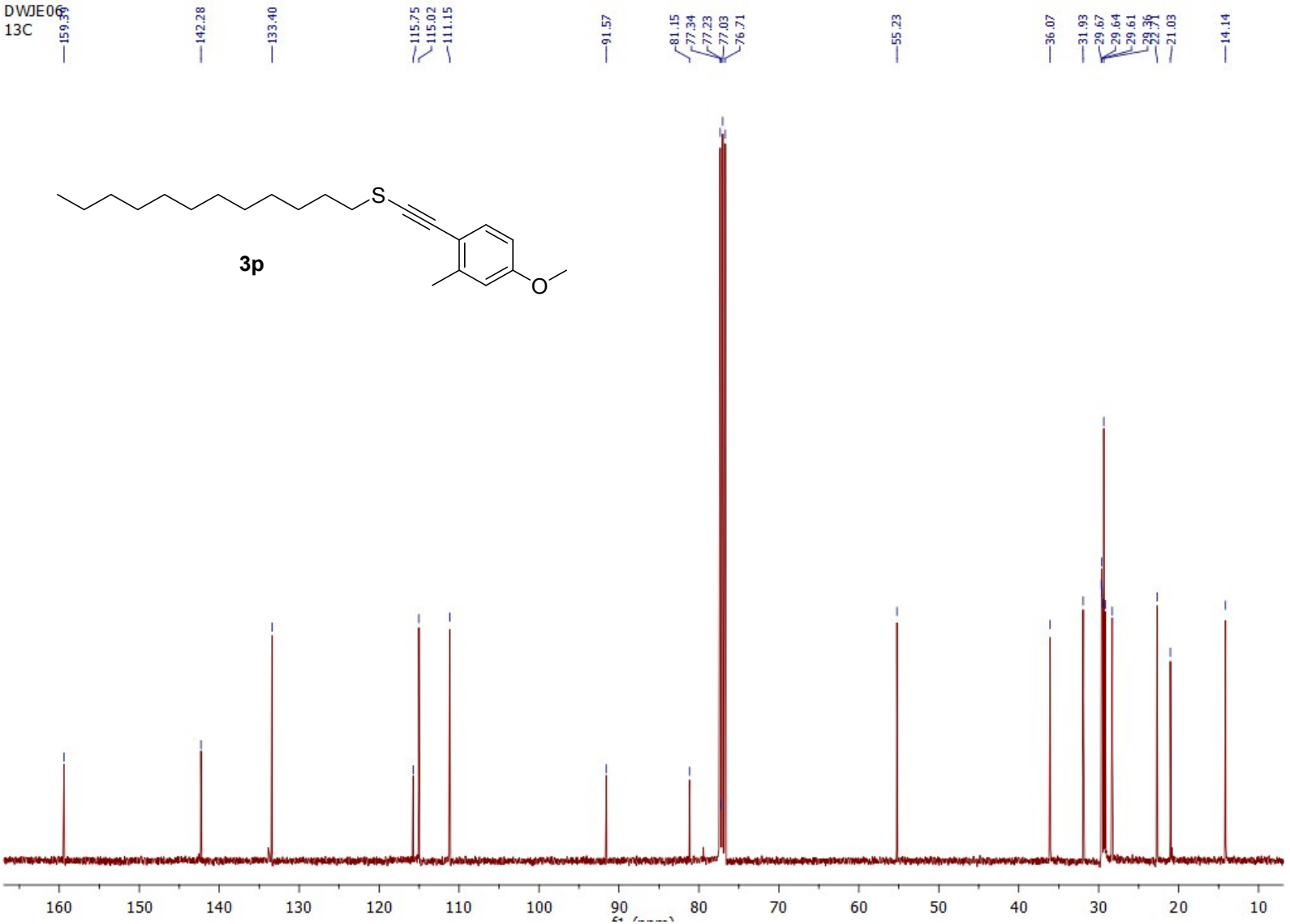

$^{13}C$ NMR (125 MHz, $CDCl_3$): δ= 155.2, 136.6, 129.9, 128.6, 126.6, 94.5, 80.0, 70.3, 31.8, 28.3, 20.9; signals expected and observed 11.

HRMS (ESI): m/z $[M + Na]^+$calcd for $C_{15}H_{19}NNaO_2S$: 300.1034; found: 300.1043.

**1-(Dodec-1-ylsulfanyl)-2-(4-methoxy-2-methylphenyl)ethyne (3p)**
chromatography: petroleum ether, ($R_f$ = 0.3), an oil; yield: 0.315 g (91%).



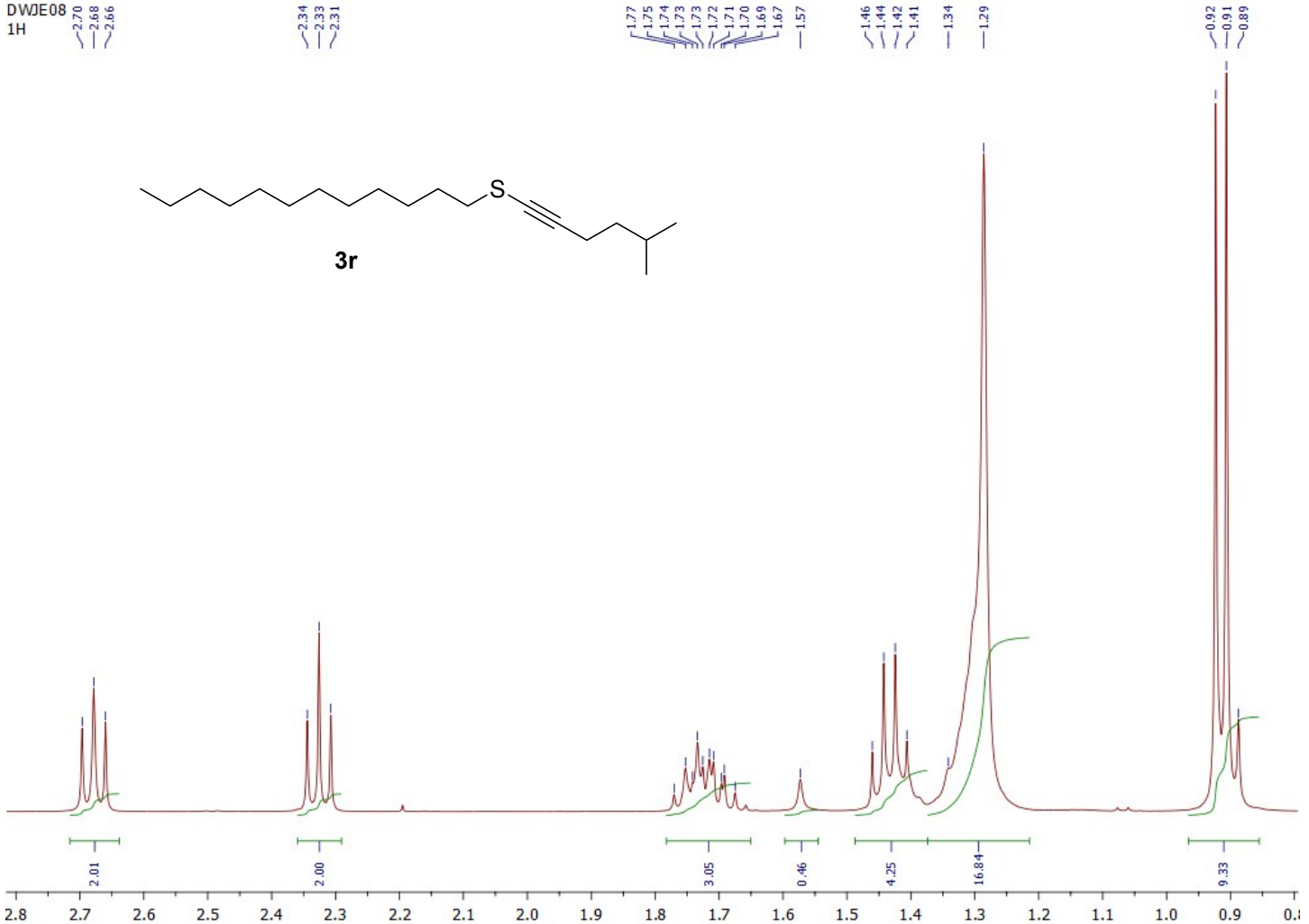

$^1$H NMR (400 MHz, $CDCl_3$) : δ= 0.91 (t, *J*=7.0 Hz, 3H, $CH_3$), 1.29-1.58 (m, 18H, $CH_2$), 1.83 (qu, *J*=7.4 Hz, 2H, $CH_2$), 2.45 (d, *J*= 11.3 Hz, 3H, $CH_3$), 2.8 (t, *J*=7.3 Hz, 2H, $SCH_2$), 3.82 (s, 3H, $OCH_3$), 6.67-6.76 (m, 2H, Ph), 7.35 (d, *J*=8.5 Hz, 1H, Ph).



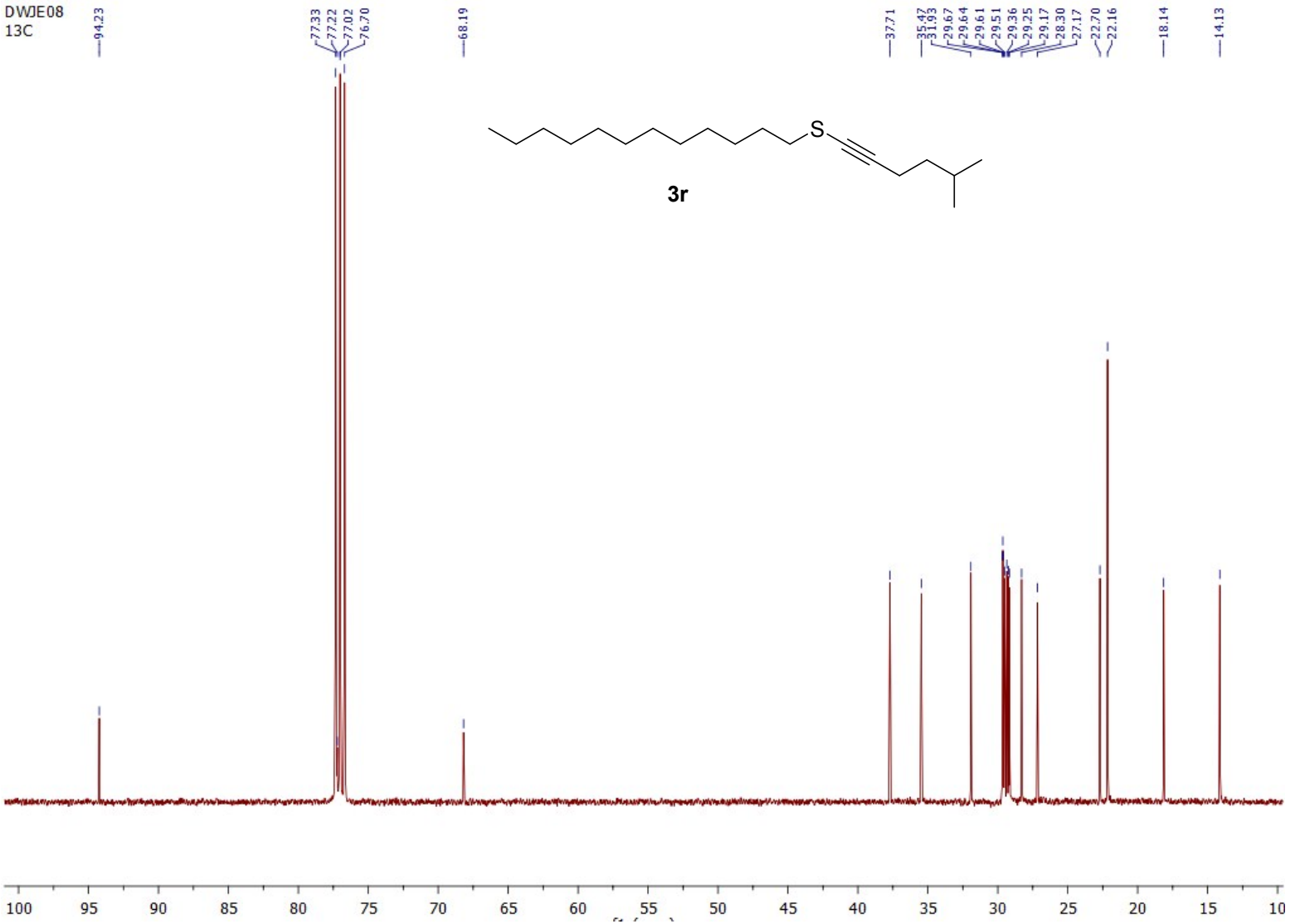

$^{13}C$ NMR (400 MHz,$CDCl_3$): δ= 159.4, 142.3, 133.4, 115.8, 115, 111.2, 91.6, 81.2, 77.2, 55.2, 36, 32, 29.7, 29.6, 29.6, 29.4, 22.7, 21, 14; signals: 22 expected, 19 observed.

**1-(Dodec-1-ylsulfanyl)-5-methylhex-1-yne (3r)**

chromatography: petroleum ether, ($R_f$ = 0.75), an oil; yield: 0.296 g (100%).



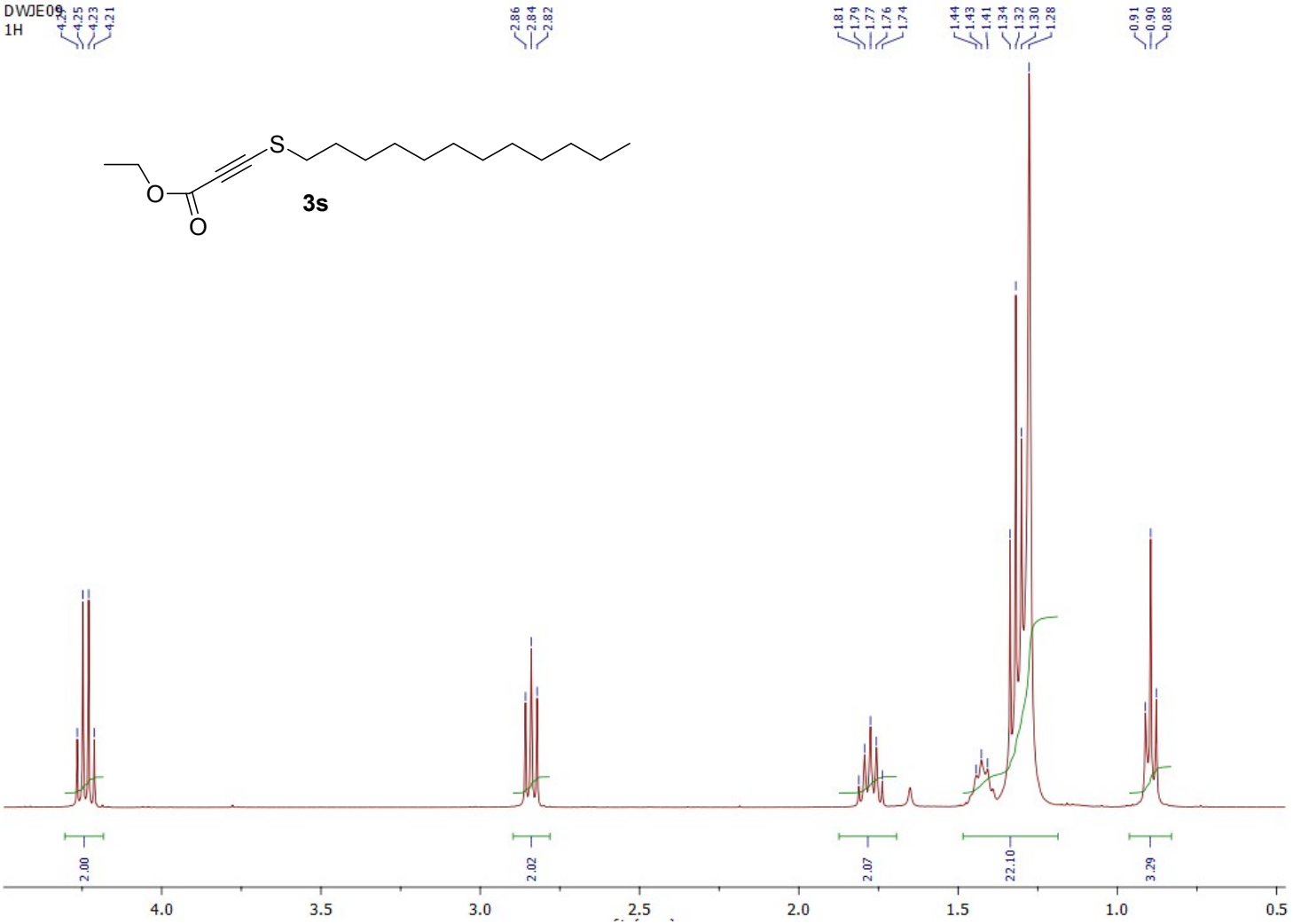

$^1$H NMR (400 MHz, $CDCl_3$) : δ= 0.91 (m, 9H, $CH_3$), 1.29-1.34 (m, 16H, $CH_2$), 1.43 (q, *J*=7.3 Hz, 4H, $CH_2$), 1.67-1.77 (m, 3H), 2.33 (t, *J*=7.2 Hz, 2H, $CH_2$), 2.68 (t, *J*=7.2 Hz, 2H, $SCH_2$).



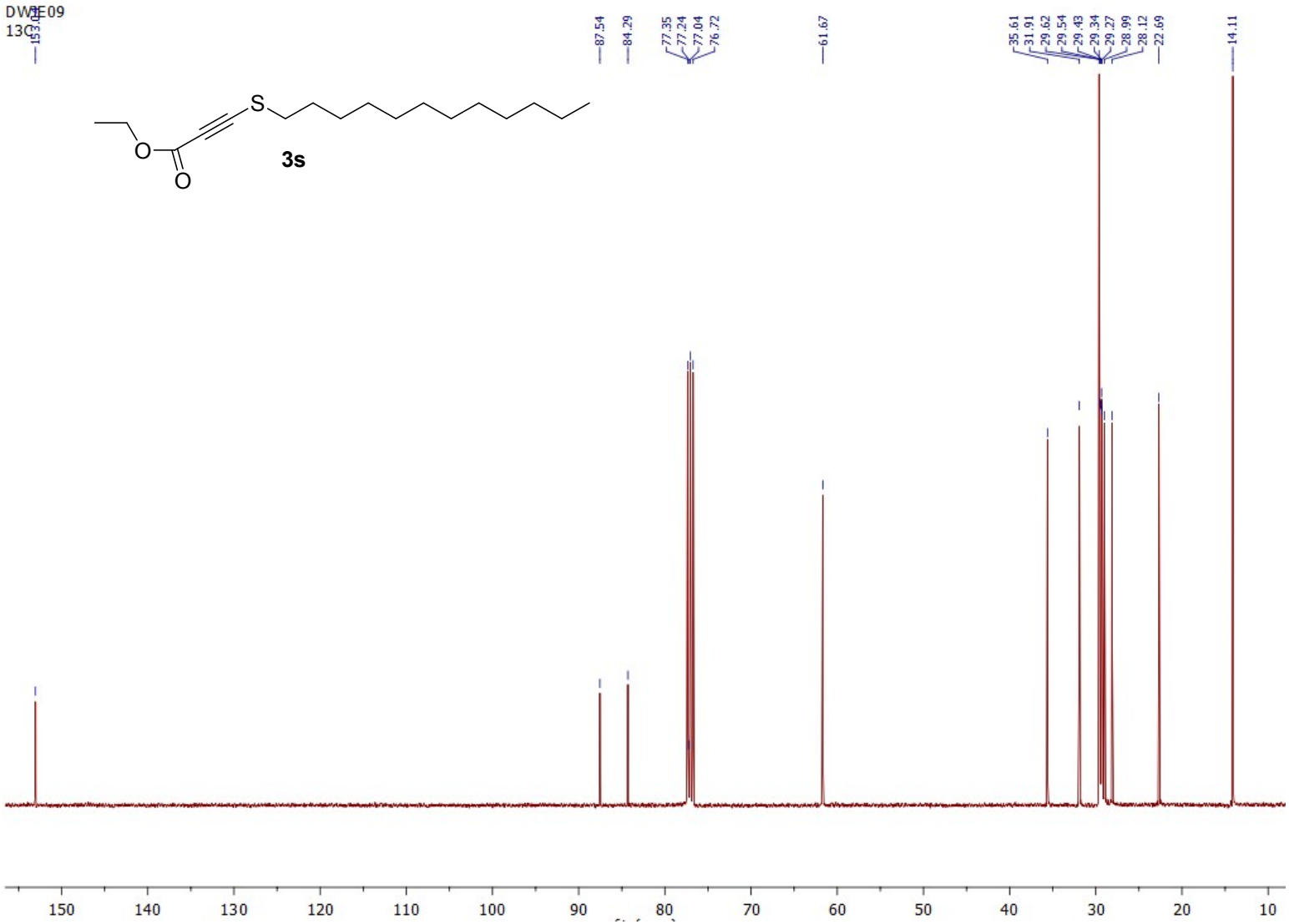

$^{13}C$ NMR (400 MHz, $CDCl_3$) : δ= 94.2, 77.2, 68.2, 7.7, 35.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.3, 27.2, 22.7, 22.2, 18.1, 14.1; signals: 19 expected, 19 observed.

**Ethyl 3-(dodec-1-ylsulfanyl)-propiolate (3s)**

chromatography: petroleum ether, ($R_f$ = 0.3), an oil; yield: 0.161 g (54%).



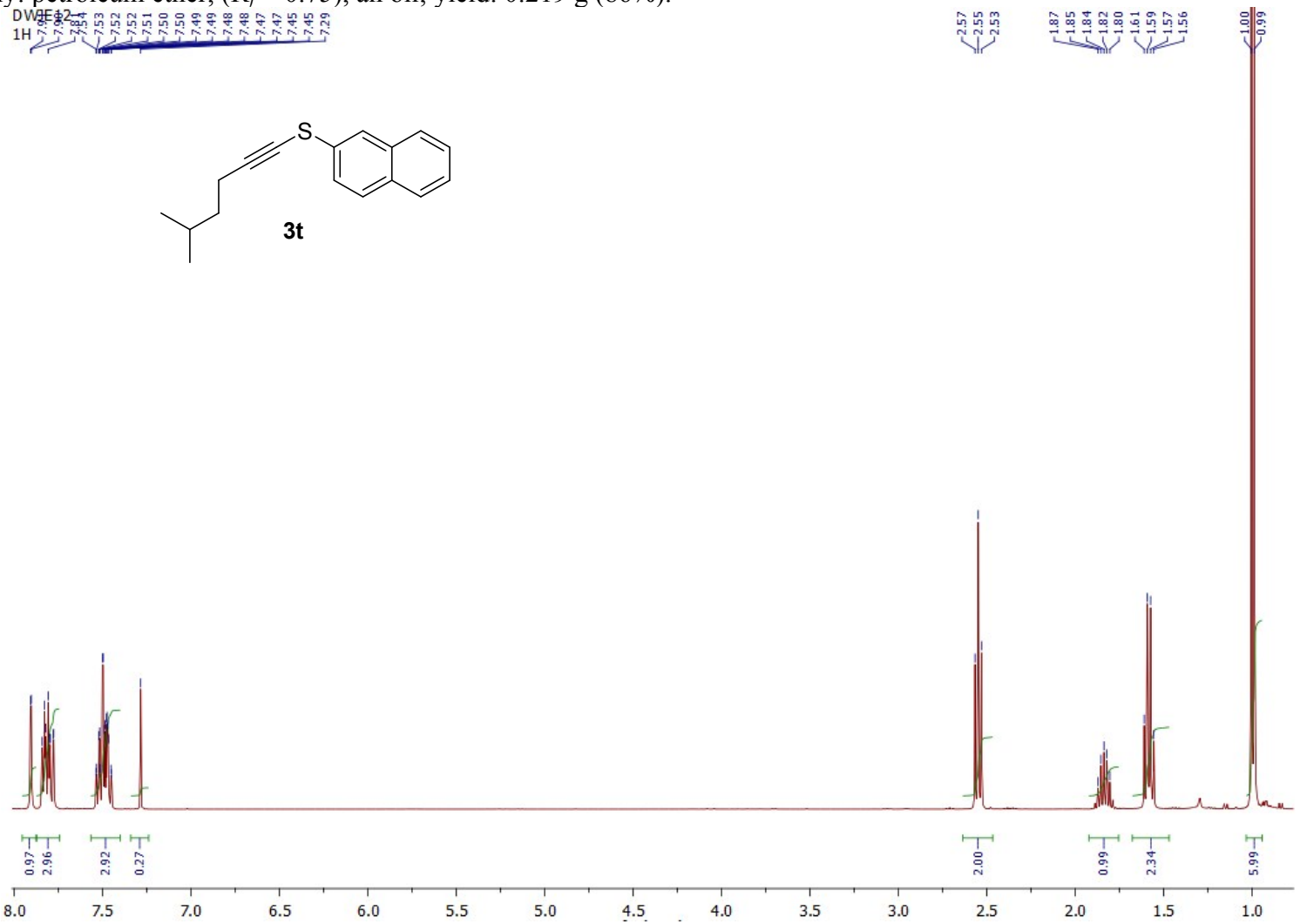

$^1$H NMR (400 MHz, $CDCl_3$) : δ= 0.9 (t, *J*=6.7 Hz, 3H, $CH_3$), 1.29-1.44 (m, 21H), 1.77 (qu, *J*=7.5 Hz, 2H, $CH_2$), 2.84 (t, *J*=7.3 Hz, 2H, $SCH_2$), 4.24 (q, *J*= 7.2 Hz, 2H, $OCH_2$).



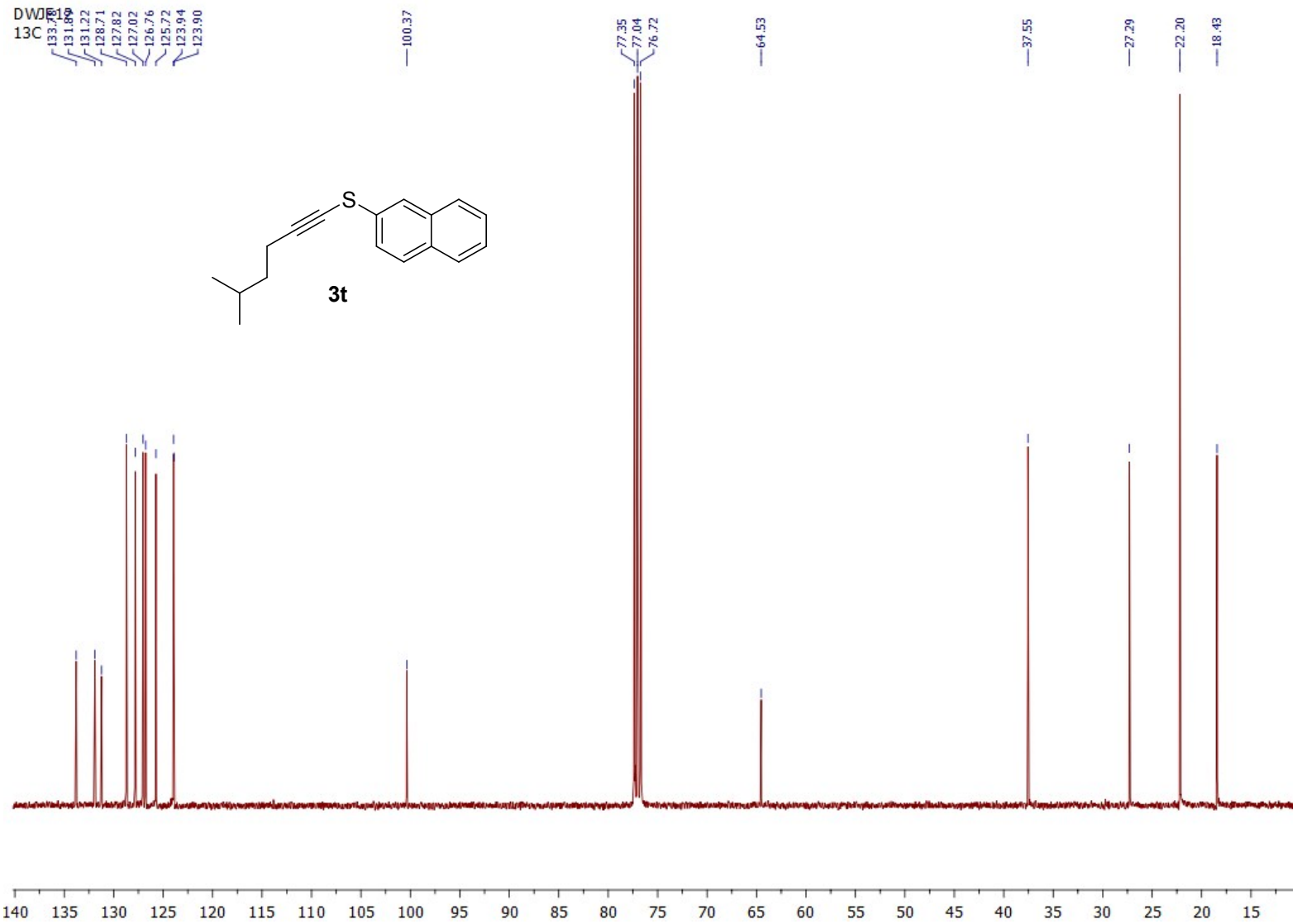

$^{13}C$ NMR (400 MHz, $CDCl_3$) : δ= 153, 87.5, 84.3, 77.2, 67.7, 35.6, 31.9, 29.6, 29.5, 29.4, 29.3, 29.3, 29, 28.1, 22.1, 14.1; signals: 17 expected, 16 observed.

**1-(2-Naphthylsulfanyl)-5-methylhex-1-yne (3t)**

chromatography: petroleum ether, ($R_f$ = 0.75), an oil; yield: 0.219 g (86%).



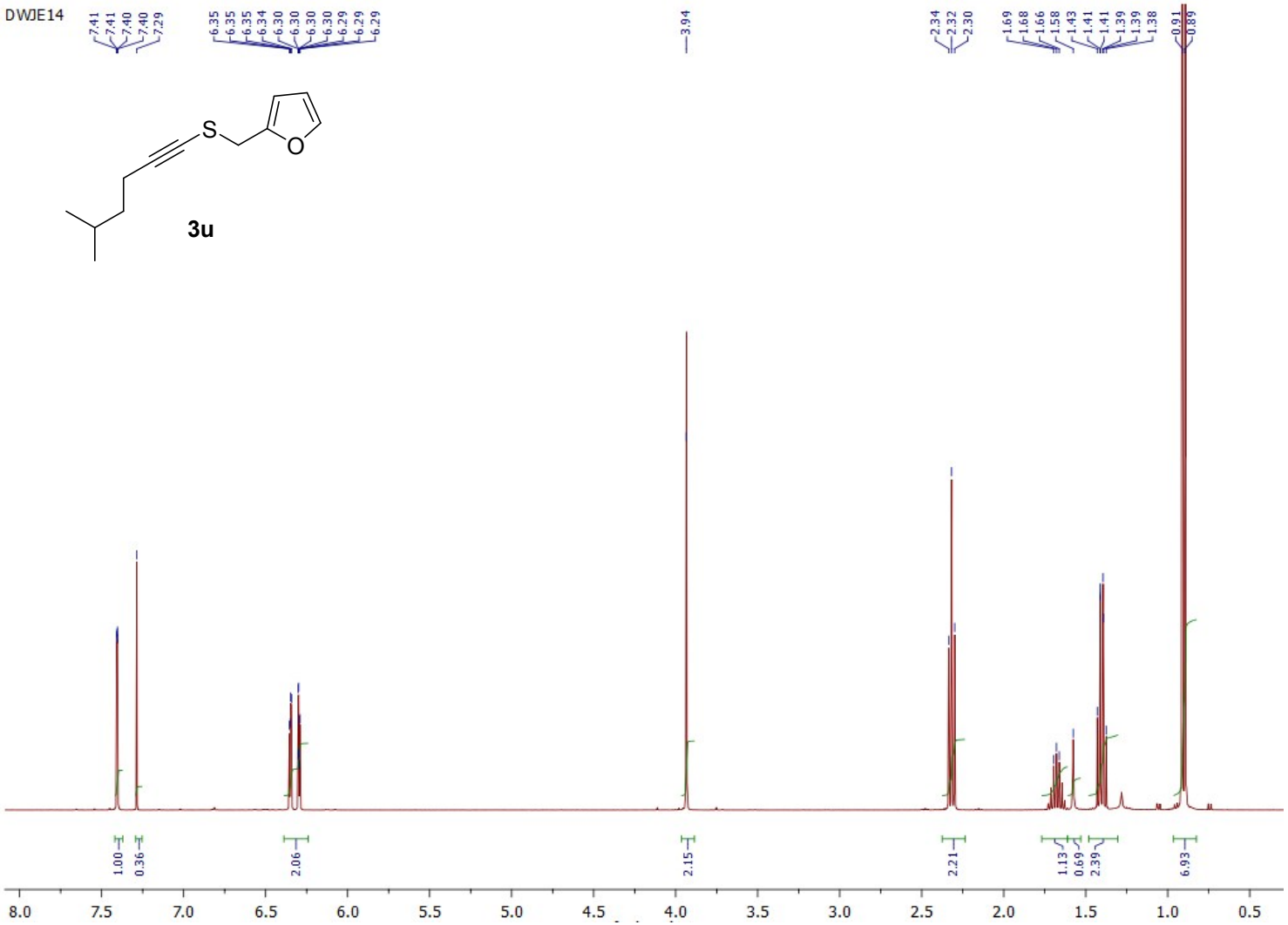

$^1$H NMR (400 MHz, $CDCl_3$) : δ= 1.0 (d, *J*=6.7 Hz, 6H, $CH_3$) , 1.6 (q, *J*=7.2 Hz, 2H, $CH_2$), 1.84 (qu, *J*=6.7 Hz, 1H, CH), 2.55 (t, *J*=7.4 Hz, 2H, $CH_2$), 7.45-7.54 (m, 3H, Ar), 7.78-7.91 (m, 4H, Ar).



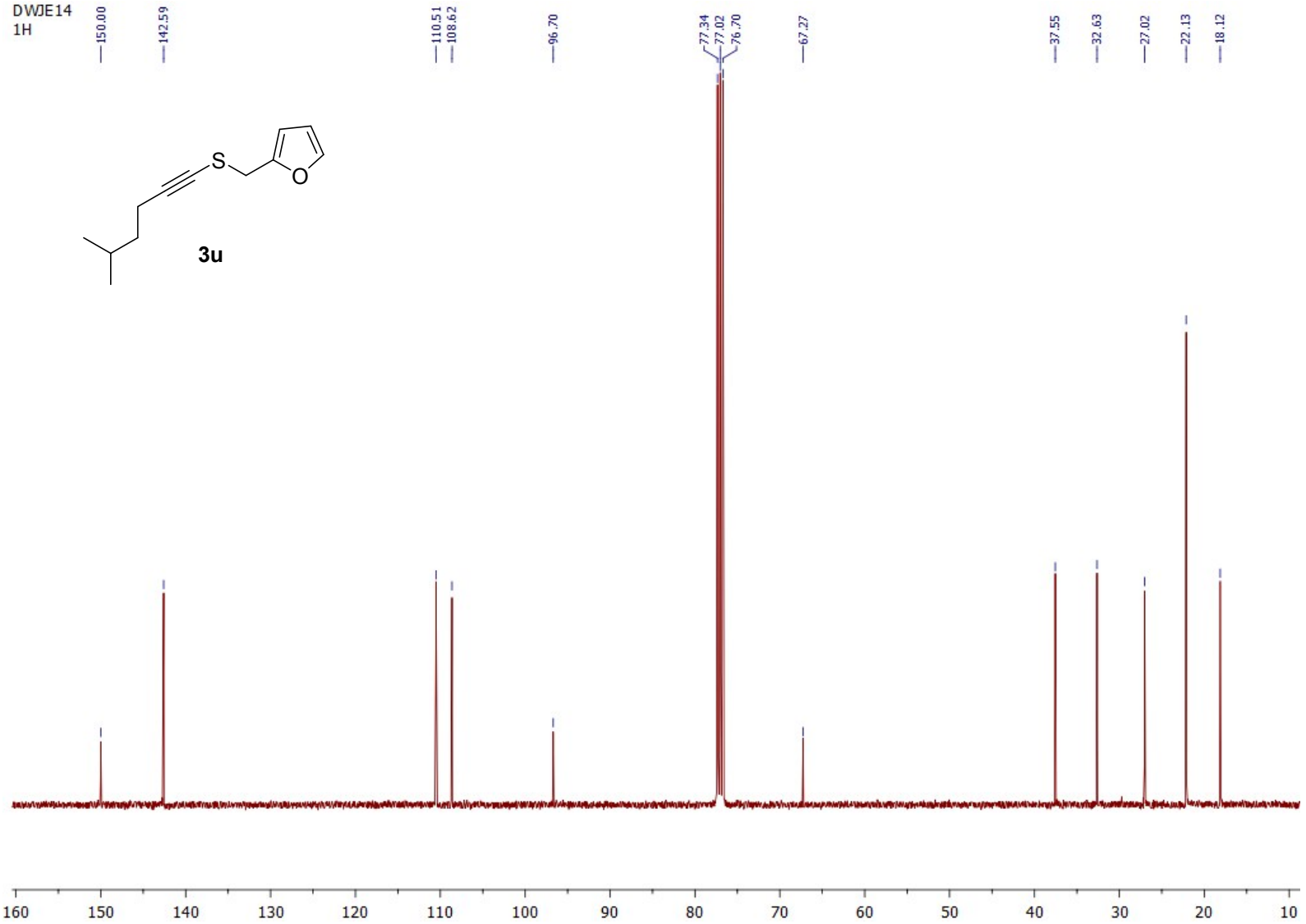

$^{13}C$ NMR (400 MHz, $CDCl_3$) : δ= 133.8, 131.9, 131.2, 128.7, 127.8, 127, 126.8, 125.7, 123.9, 123.9, 100.4, 64.5, 37.6, 27.3, 22.2, 18.4; signals: 16 expected, 16 observed.

**1-(2-Furylmethylsulfanyl)-5-methylhex-1-yne (3u)**

chromatography: petroleum ether, ($R_f$ = 0.5), an oil; yield: 0.208 g (100%)




$^1$H NMR (400 MHz, $CDCl_3$) : δ=0.91 (t, *J*=6.1 Hz, 6H, $CH_3$), 1.38-1.43 (m, 2H, $CH_2$), 1.58-1.69 (m, 1H, CH), 2.32 (t, *J*=7.4 Hz, 2H, $CH_2$), 3.93 (s, 2H, $SCH_2$), 6.29-6.35 (m, 2H, Ar), 7.4-7.41 (m, 1H, Ar).




$^{13}C$ NMR (400 MHz, $CDCl_3$) : δ= 150, 142.6, 110.5, 108.6, 96.7, 67.3, 37.6, 32.6, 27.0, 22.1, 18.1; signals: 11 expected, 11 observed.

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