Supporting Information for

Synthesis of Benzothienofuranones and dihydrobenzothienopyranones by palladium iodide–catalyzed carbonylative double cyclization

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Table of Contents

Preparation and characterization of 3-(2-(methylthio)phenyl)prop-2-yn-1-ols 1a-k and 4-(2-(methylthio)phenyl)but-3-yn-1-ols 3a-3l

Synthesis of 3-(2-(methylthio)phenyl)prop-2-yn-1-ols 1a-k

3-(2-(methylthio)phenyl)prop-2-yn-1-ols **1a**, **1c**, **1f-h** and **1k** were prepared as we already reported [1]. 3-(2-(methylthio)phenyl)prop-2-yn-1-ols **1b**, **1d**, **1e**, **1i** and **1j** were prepared by Sonogashira coupling of 2-iodothioanisole (commercially available), 2-bromo-4-fluorothioanisole (prepared by methylation of commercially available 2-bromo-4-fluorobenzenethiol, according to a literature procedure [2]) and 2-bromo-4-methylthioanisole (prepared by methylation of commercially available 2-bromo-4-methylbenzenethiol, according to a literature procedure [2]) with prop-2-yn-1-ols (commercially available), as described below.

General procedure for the synthesis of 3-(2-(methylthio)phenyl)prop-2-yn-1-ols 1b, 1i and 1j

A solution of 2-iodothioanisole (1.0 g, 4.0 mmol), $PdCl_2(PPh_3)_2$ (60 mg, 0.085 mmol), CuI (20 mg, 0.11 mmol), and the terminal alkyne (4.8 mmol; 4-methylpent-1-yn-3-ol, 470 mg; 2-phenylbut-3-yn-2-ol, 700 mg; 1,1-diphenylprop-2-yn-1-ol, 1.0 g) in anhydrous triethylamine (16 mL) was allowed to stir under nitrogen at 25 °C for 24 h. Water (50 mL) was then added, and the mixture extracted with diethyl ether (3 × 50 mL). The organic layer was washed with a saturated solution of NH_4Cl (100 mL) and water until neutral pH. After drying over Na_2SO_4, the solvent was evaporated, and the residue purified by column chromatography on silica gel using 99:1 to 9:1 hexane-AcOEt as eluent.

4-Methyl-1-(2-(methylthio)phenyl)pent-1-yn-3-ol (**1b**). Yield: 637 mg, starting from 1.0 g of 2-iodothioanisole (72%). Yellow oil. IR (film): ν = 3406 (m, br), 2226 (vw), 1466 (m), 1435 (m), 1234 (w), 1072 (w), 1026 (m), 988 (w), 752 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (dd, *J* = 7.5, 1.0, 1H, H-6), 7.32-7.23 (m, 1H, H-4), 7.12 (dist d, *J* = 7.9, 1H, H-3), 7.09-7.02 (m, 1H, H-5), 4.47 (d, *J* = 5.5, 1H, C*H*OH), 2.46 (s, 3H, SMe), 2.10-1.92 (m, 1H, CH_3CHCH_3), 1.12 (d, *J* = 6.8, 3H, CH_3CHCH_3), 1.08 (d, *J* = 6.8, 3H, CH_3CHCH_3) (Note: the –OH signal was too broad to be detected); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 141.6, 132.5, 128.8, 124.1, 123.8, 120.7, 95.6, 82.9, 68.5, 34.6, 18.3, 17.5, 14.9; GC-MS (EI, 70 eV) *m/z* = 220 (M^+, 5), 205 (19), 187 (8), 172 (20), 163 (60), 162 (38), 149 (59), 147 (68), 149 (59), 147 (68), 134 (100), 116 (100), 115 (45), 89 (20); HRMS-ESI (*m/z*): [$(M-H_2O+H)^+$] cald for $(C_{13}H_{15}S)^+$: 203.0888; found: 203.0906.

4-(2-(Methylthio)phenyl)-2-phenylbut-3-yn-2-ol (**1i**). Yield: 749 mg, starting from 1.0 g of 2-iodothioanisole (70%). Yellow solid, mp = 63-64 °C. IR (KBr): ν = 3414 (m, br), 2226 (vw), 1493 (w), 1462 (m), 1435 (m), 1366 (w), 1142 (w), 1088 (w), 1069 (m), 937 (w), 895 (w), 752 (s), 698 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.86-7.74 (m, 2H, aromatic), 7.49-7.25 (m, 5H, aromatic), 7.20-7.02 (m, 2H, aromatic), 2.79 (s, 1H, OH), 2.46 (s, 3H, SMe), 1.90 (s, 3H, CH_3COH); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 145.5, 141.9, 132.4, 129.0, 128.3, 127.7, 125.2, 124.2, 123.9, 120.5, 98.9, 82.5, 70.6, 33.4, 15.0; GC-MS (EI, 70 eV) *m/z* = 268 (M^+, 3), 250 (29), 235 (100), 234 (60), 202 (22), 189 (7), 147 (14), 105 (21); HRMS-ESI (*m/z*): [$(M-H_2O+H)^+$] cald for $(C_{17}H_{15}S)^+$: 251.0889; found: 251.0906.

3-(2-(Methylthio)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1j**). Yield: 864 mg, starting from 1.0 g of 2-iodothioanisole (65%). Yellow solid, mp = 109-110 °C. IR (KBr): ν = 3426 (m, br), 2214 (vw), 1489 (w), 1462 (m), 1450 (m), 1435 (w), 1165 (m), 1072 (w), 1022 (m), 992 (m), 918 (w), 883 (w), 752 (s), 702 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.81-7.65 (m, 4H, aromatic), 7.46-7.37 (m, 1H, aromatic), 7.37-7.20 (m, 7H, aromatic), 7.20-7.11 (m, 1H, aromatic), 7.10-7.01 (m, 1H, aromatic), 3.02 (s, 1H, OH), 2.42 (s, 3H, SMe); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 145.1, 142.1, 132.7, 129.1, 128.3, 127.7, 126.3, 124.7, 124.4, 121.1, 98.1, 82.0,

15.3; GC-MS (EI, 70 eV) *m/z* = 330 (M^+, 10), 329 (23), 315 (12), 283 (8), 237 (19), 225 (9), 210 (11), 165 (8), 105 (100), 77 (53); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] cald for ($C_{22}H_{17}S$)$^+$: 313.1045; found: 313.1070.

General procedure for the synthesis of 3-(2-(methylthio)phenyl)prop-2-yn-1-ols 1d and 1e

A solution of the substituted 2-iodothioanisole (2.0 mmol; 2-bromo-4-fluorothioanisole, 450 mg; 2-bromo-4-methylthioanisole, 440 mg), $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol), CuI (57 mg, 0.3 mmol), and 2-methylbut-3-yn-2-ol (340 mg, 4.0 mmol) in anhydrous diisopropylamine (20 mL) was allowed to stir under nitrogen at 80 °C for 24 h. Water (50 mL) was then added, and the mixture extracted with diethyl ether (3 × 50 mL). The organic layer was washed with a saturated solution of NH_4Cl (100 mL) and water until neutral pH. After drying over Na_2SO_4, the solvent was evaporated, and the residue purified by column chromatography on silica gel using hexane to 8:2 hexane–AcOEt as eluent.

4-(5-Fluoro-2-(methylthio)phenyl)-2-methylbut-3-yn-2-ol (**1d**). Yield: 410 mg, starting from 450 mg of 2-bromo-4-fluorothioanisole (90%). Yellow oil. IR (film): ν = 3397 (m, br), 2230 (w), 1593 (m), 1572 (m), 1460 (s), 1437 (m), 1408 (w), 1364 (w), 1207 (m), 1167 (m), 1153 (m), 1121 (m), 1067 (w), 986 (w), 966 (s), 874 (m), 806 (m), 633 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.12-7.07 (m, 2H, H-6 + H-3), 6.99 (td, *J* = 8.5, 2.9, 1H, H-5), 2.45 (s, 3H, SMe), 1.65 (s, 6 H., MeCMe) (Note: the –OH signal was too broad to be detected); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 160.1 (d, *J* = 244.5), 136.8, 127.5-126.0 (m), 122.8 (d, *J* = 9.1), 119.5-118.5 (m), 117.0-115.5 (m), 101.3, 78.8, 31.3, 15.8; GC-MS (EI, 70 eV) *m/z* = 234 (M^+, 100), 209 (26), 191 (16), 181 (18), 165 (30), 133 (27); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] cald for ($C_{11}H_{12}FS$)$^+$: 207.0683; found: 207.0643.

2-Methyl-4-(5-methyl-2-(methylthio)phenyl)but-3-yn-2-ol (**1e**). Yield: 325 mg, starting from 440 mg of 2-bromo-4-methylthioanisole (73%). Yellow oil. IR (film): ν = 3397 (m, br), 1462 (m), 1435 (m), 1362 (w), 1292 (w), 1211 (m), 1161 (s), 1065 (m), 962 (w), 939 (m), 868 (w), 806 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.21 (d, *J* = 1.6, 1H, H-6), 7.08 (dist dd, *J* = 8.3, 1.6, 1H, H-4), 7.04 (dist d, *J* = 8.3, 1H, H-3), 2.45 (s, 3H, SMe), 2.27 (s, 3H, Me at C-5), 1.65 (s, 6H, MeCMe) (Note: the –OH signal was too broad to be detected); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 137.9, 134.2, 133.0, 129.8, 124.7, 121.0, 99.9, 79.9, 65.8, 31.4, 20.6, 15.3; GC-MS (EI, 70 eV): *m/z* = 203 (M^+, 100), 210 (25), 189 (20), 173 (21), 163 (46), 148 (46), 130 (58), 115 (25), 103 (12); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] cald for ($C_{13}H_{15}S$)$^+$: 203.0889; found: 203.0903.

Synthesis of 4-(2-(methylthio)phenyl)but-3-yn-1-ols 3a-3l

4-(2-(Methylthio)phenyl)but-3-yn-1-ols **3a-3l** were prepared by Sonogashira coupling of 2-iodothioanisole (commercially available), 2-bromo-5-fluorothioanisole (prepared by methylation of commercially available 2-bromo-5-fluorobenzenethiol, according to a literature procedure [2]) with but-3-yn-1-ols, as described below. But-3-yn-1-ol, pent-4-yn-2-ol and hex-5-yn-3-ol are commercially available; 1-phenylbut-3-yn-1-ol, 1-mesitylbut-3-yn-1-ol, 1-(4-methoxyphenyl)but-3-yn-1-ol, 4-(1-hydroxybut-3-yn-1-yl)benzonitrile, 1-(furan-2-yl)but-3-yn-1-ol, 2-phenylpent-4-yn-2-ol and 1-(prop-2-yn-1-yl)cyclohexan-1-ol were prepared by Barbier reaction between an alkynyl bromide and an aldehyde or a ketone in the presence of activated zinc [3]. *trans*-2-Ethynylcyclohexan-1-ol and *trans*-2-ethynylcyclopentan-1-ol were synthesized as reported in the literature [4].

General procedure for the synthesis of 4-(2-(methylthio)phenyl)but-3-yn-1-ols 3a and 3c-3l

A solution of 2-iodothioanisole (500 mg, 2.0 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol), CuI (11.4 mg, 0.06 mmol), and the terminal alkyne (2.4 mmol; but-3-yn-1-ol, 168 mg; pent-4-yn-2-ol, 202 mg; hex-5-yn-3-ol, 235 mg; 1-phenylbut-3-yn-1-ol, 350 mg; 1-mesitylbut-3-yn-1-ol, 452 mg; 1-(4-methoxyphenyl)but-3-yn-1-ol, 422 mg; 1-(furan-2-yl)but-3-yn-1-ol, 327 mg; 2-phenylpent-4-yn-2-ol, 385 mg; 1-(prop-2-yn-1-yl)cyclohexan-1-ol,

332 mg; *trans*-2-ethynylcyclohexan-1-ol, 300 mg; *trans*-2-ethynylcyclopentan-1-ol, 265 mg) in anhydrous triethylamine (8 mL) was allowed to stir under nitrogen at 25 °C for 15 h. The mixture was washed with a saturated solution of NH_4Cl (3 x 20 mL); the aqueous layer was extracted with ethyl acetate (3 x 20 mL), and the combined organic layers was washed with a saturated solution of NH_4Cl until pH was neutral, then dried with Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified via chromatography on silica gel using 9:1 hexane–AcOEt to 6:4 hexane–AcOEt as eluent.

4-(2-(Methylthio)phenyl)but-3-yn-1-ol (**3a**). Yield: 370 mg, starting from 500 mg of 2-iodothioanisole (96%). Yellow oil. IR (film): ν = 3410 (s, br), 2230 (w), 1466 (m), 1435 (m), 1327 (w), 1041 (s), 957 (w), 849 (w), 756 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38-7.35 (m, 1H, H-6), 7.29-7.24 (m, 1H, H-4), 7.14 (dist d, *J* = 7.9, 1H, H-3), 7.06 (td, *J* = 7.5, 0.8, 1H, H-5), 3.84 (q, *J* = 6.2, 2H, C*H*$_2$OH), 2.75 (t, *J* = 6.2, 2H, C*H*$_2$CH$_2$OH), 2.47 (s, 3H, SMe), 2.38 (t, *J* = 6.2, 1H, OH); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.3, 132.0, 128.5, 124.3, 124.1, 121.5, 93.5, 80.3, 61.1, 24.2, 15.0; GC-MS (EI, 70 eV) *m/z* = 192 (M^+, 62), 147 (100), 128 (60), 115 (29); HRMS-ESI (*m/z*): [(M+H)$^+$] cald for $(C_{11}H_{13}OS)^+$: 193.0681; found: 193.0684. The spectroscopic data agreed with those reported [5].

5-(2-(Methylthio)phenyl)pent-4-yn-2-ol (**3c**). Yield: 406 mg, starting from 500 mg of 2-iodothioanisole (98%). Yellow oil. IR (film): ν = 3395 (m, br), 2230 (w), 1582 (w), 1466 (m), 1435 (s), 1273 (w), 1111 (m), 1080 (m), 934 (m), 748 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.36 (dist dd, *J* = 7.6, 1.2, 1H, H-6), 7.30-7.25 (m, 1H, H-4), 7.14 (dist d, *J* = 8.0, 1H, H-3), 7.10-7.04 (m, 1H, H-5), 4.13-4.04 (m, 1H, C*H*OH), 2.71 (dist dd, *J* = 16.7, 5.1, 1H, ≡CC*H*H), 2.60 (dist dd, *J* = 16.7, 6.8, 1H, ≡CCH*H*), 2.52-2.47 (m, 1H, OH), 2.48 (s, 3H, SMe), 1.35 (d, *J* = 6.2, C*H*$_3$CHOH); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.3, 132.0, 128.5, 124.3, 124.0, 121.4, 93.2, 80.8, 66.6, 30.3, 22.3, 15.1; GC-MS (EI, 70 eV) *m/z* = 206 (M^+, 22), 162 (19), 147 (100), 128 (17), 115 (25); HRMS-ESI (*m/z*): [(M+H)$^+$] cald for $(C_{12}H_{15}OS)^+$: 207.0838; found, 207.0840.

6-(2-(Methylthio)phenyl)hex-5-yn-3-ol (**3d**). Yield: 430 mg, starting from 500 mg of 2-iodothioanisole (98%). Yellow oil. IR (film): ν = 3410 (m, br), 2222 (w), 1582 (w), 1466 (m), 1435 (s), 1111 (m), 1072 (w), 1081 (w), 980 (m), 748 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.36 (dist dd, *J* = 7.6, 1.3, 1H, H-6), 7.27 (dist dd, *J* = 7.6, 1.3, 1H, H-4), 7.14 (dist d, *J* = 7.9, 1H, H-3), 7.06 (td, *J* = 7.6, 0.9, 1H, H-5), 3.84-3.76 (m, 1H, C*H*OH), 2.72 (dist dd, *J* = 16.7, 4.5, 1H, ≡CC*H*H), 2.60 (dist dd, *J* = 16.7, 7.0, 1H, ≡CCH*H*), 2.47 (s, 3H, SMe), 2.48-2.44 (m, 1H, OH), 1.71 -1.62 (m, 2H, C*H*$_2$CH$_3$), 1.00 (t, *J* = 7.4, 3H, CH$_2$C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.3, 132.0, 128.5, 124.3, 124.1, 121.6, 93.3, 80.8, 71.6, 29.2, 28.3, 15.1, 10.1; GC-MS (EI, 70 eV) *m/z* = 220 (M^+, 8), 187 (7), 162 (26), 147 (100), 128 (14), 115 (23); HRMS-ESI (*m/z*): [(M+H)$^+$] cald for $(C_{13}H_{17}OS)^+$: 221.0994; found, 221.1004.

4-(2-(Methylthio)phenyl)-1-phenylbut-3-yn-1-ol (**3e**). Yield: 375 mg, starting from 500 mg of 2-iodothioanisole (70%). Yellow oil. IR (film): ν = 3418 (m, br), 2230 (vw), 1582 (m), 1458 (m), 1435 (m), 1196 (w), 1042 (m), 748 (s), 702 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.48-7.42 (m, 2H, aromatic), 7.39-7.32 (m, 3H, aromatic), 7.32-7.23 (m, 2H, aromatic), 7.14 (dist d, *J* = 7.9, 1H, H-3), 7.06 (td, *J* = 7.5, 0.9, 1H, H-5), 5.02-4.92 (m, 1H, C*H*OH), 2.99-2.91 (m, 2H, ≡CC*H*H + OH), 2.89 (dist dd, *J* = 16.7, 7.8, 1H, ≡CCH*H*), 2.46 (s, 3H, SMe); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 142.6, 141.4, 132.1, 128.6, 128.5, 127.8, 125.8, 124.4, 124.3, 121.5, 93.0, 88.1, 72.5, 31.1, 15.2; GC-MS (EI, 70 eV): *m/z* = 268 (M^+, 5), 267 (13), 235 (7), 162 (20), 147 (100), 128 (11), 115 (12), 107 (22), 79 (41); HRMS-ESI (*m/z*): [(M-H$_2$O+H)$^+$] calcd for $(C_{17}H_{15}S)^+$: 251.0889; found, 251.0880.

1-Mesityl-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3f**). Yield: 550 mg, starting from 500 mg of 2-iodothioanisole (89%). Yellow solid, mp = 73-74 °C. IR (KBr): ν = 3426 (m, br), 2222 (vw), 1612 (w), 1582 (w), 1466 (m), 1435 (m), 1381 (m), 1034 (s), 849 (m), 748 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35 (d, *J* = 7.6, 1H, H-6), 7.27 (t, *J* = 7.7, 1H, H-4), 7.14 (dist d, *J* = 8.0, 1H, H-3), 7.08-7.04 (m, 1H, H-5), 6.83 (s, 2H, mesityl ring), 5.45-5.40 (m, 1H, C*H*OH), 3.14 (dist dd, *J* = 17.0, 9.9, 1H, ≡CC*H*H), 2.80 (dist dd, *J* = 17.0, 4.4, 1H, ≡CCH*H*), 2.76-2.72 (m, 1H,

OH), 2.47 (s, 3H, SMe), 2.45 (s, 6H, 2 *o*-Me on mesityl ring), 2.25 (s, 3H, *p*-Me on mesityl ring); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.3, 136.9, 136.2, 134.6, 132.1, 130.2, 128.5, 124.3, 124.2, 121.5, 93.8, 80.5, 70.1, 27.6, 20.8, 15.1; GC-MS (EI, 70 eV): *m/z* = 310 (M^+, <0.5), 262 (6), 162 (55), 149 (100), 147 (33), 121 (43); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] calcd for ($C_{20}H_{21}S$)$^+$: 293.1358; found, 293.1370.

1-(4-Methoxyphenyl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3g**). Yield: 508 mg, starting from 500 mg of 2-iodothioanisole (85%). Yellow oil. IR (film): ν = 3433 (m, br), 2230 (vw), 1612 (m), 1512 (m), 1466 (m), 1435 (m), 1304 (w), 1250 (s), 1173 (m), 1034 (s), 833 (m), 756 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.41-7.32 (m, 3H, aromatic), 7.28-7.24 (m, 1H, H-4), 7.14 (dist d, *J* = 7.7, 1H, H-3), 7.06 (td, *J* = 7.5, 0.8, 1H, H-5), 6.92-6.87 (m, 2H, aromatic), 4.98-4.92 (m, 1H, C*H*OH), 3.80 (s, 3H, OMe), 2.91-2.88 (m, 3H, ≡CCH_2 + OH), 2.47 (s, 3H, SMe); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 159.3, 141.3, 134.8, 132.1, 128.6, 127.1, 124.4, 124.3, 121.5, 113.8, 93.2, 81.0, 72.1, 55.5, 31.1, 15.2; GC-MS (EI, 70 eV): *m/z* = 298 (M^+, 0.6), 280 (46), 264 (39), 250 (28), 234 (27), 221 (43), 189 (21), 162 (32), 137 (100), 109 (36); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] calcd for ($C_{18}H_{17}OS$)$^+$: 281.0994; found, 281.0995.

1-(Furan-2-yl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3h**). Yield: 488 mg, starting from 500 mg of 2-iodothioanisole (94%). Yellow oil. IR (film): ν = 3418 (m, br), 2230 (vw), 1582 (w), 1504 (w), 1466 (w), 1435 (m), 1227 (w), 1142 (w), 1042 (m), 1011 (m), 748 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.41-7.38 (m, 1H, furyl ring), 7.35 (dd, *J* = 7.6, 1.2, 1H, H-6), 7.29-7.24 (m, 1H, H-4), 7.14 (dist d, *J* = 8.0, 1H, H-3), 7.06 (td, *J* = 7.6, 1.0, 1H, H-5), 64.1-6.39 (m, 1H, furyl ring), 6.36-6.33 (m, 1H, furyl ring), 5.00 (q, *J* = 5.9, 1H, C*H*OH), 3.06 (dist d, *J* = 5.9, 2H, ≡CCH_2), 2.92 (d, *J* = 5.9, 1H, OH), 2.46 (s, 3H, SMe); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 154.8, 142.2, 141.4, 132.1, 128.6, 124.39, 124.38, 121.5, 110.3, 106.8, 92.1, 81.3, 66.4, 27.6, 15.3; GC-MS (EI, 70 eV): *m/z* = 258 (M^+, 2), 243 (33), 197 (5), 162 (32), 147 (100), 115 (13), 97 (84); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] calcd for ($C_{15}H_{13}OS$)$^+$: 241.0681; found, 241.0690.

5-(2-(Methylthio)phenyl)-2-phenylpent-4-yn-2-ol (**3i**). Yield: 453 mg, starting from 500 mg of 2-iodothioanisole (80%). Yellow oil. IR (film): ν = 3443 (m, br), 2232 (vw), 1582 (w), 1493 (m), 1464 (m), 1435 (w), 1180 (w), 1099 (m), 1028 (m), 912 (m), 766 (m), 719 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57-7.52 (m, 2H, aromatic), 7.37-7.32 (m, 2H, aromatic), 7.31 (dd, *J* = 7.6, 1.3, 1H, aromatic), 7.28-7.22 (m, 2H, aromatic), 7.13 (dist d, *J* = 8.6, 1H, H-3), 7.04 (dist td, *J* = 7.5, 1.0, 1H, H-5), 3.04 (dist d, *J* = 16.7, 1H, ≡CC*H*H), 2.97 (dist d, *J* = 16.7, 1H, ≡CCH*H*), 2.93 (s, 1H, OH), 2.43 (s, 3H, SMe), 1.73 (s, 3H, Me); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 146.6, 141.4, 132.1, 128.5, 128.2, 127.0, 124.8, 124.4, 121.6, 92.7, 81.7, 73.6, 36.0, 29.5, 15.3; GC-MS (EI, 70 eV): *m/z* = 282 (M^+, 2), 263 (54), 248 (44), 234 (72), 215 (26), 202 (16), 162 (60), 147 (100), 121 (8), 115 (47), 105 (41); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] calcd for ($C_{18}H_{17}S$)$^+$: 265.1045; found, 265.1053.

1-(3-(2-(Methylthio)phenyl)prop-2-yn-1-yl)cyclohexan-1-ol (**3j**). Yield: 495 mg, starting from 500 mg of 2-iodothioanisole (95%). Yellow oil. IR (film): ν = 3451 (m, br), 2228 (w), 1582 (w), 1464 (m), 1435 (m), 1265 (w), 1151 (m), 1074 (m), 980 (m), 955 (m), 750 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37 (dist d, *J* = 7.4, 1H, H-6), 7.27 (dist t, *J* = 7.4, 1H, H-4), 7.14 (dist d, *J* = 7.8, 1H, H-3), 7.07 (t, *J* = 7.4, 1H, H-5), 2.65 (s, 2H, ≡CCH_2), 2.47 (s, 3H, SMe), 2.23 (s, 1H, OH), 1.82-1.44 (m, 9H, aliphatic), 1.36-1.24 (m, 1H, aliphatic); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.4, 132.1, 128.4, 124.3, 124.1, 121.6, 93.1, 81.4, 70.9, 37.0, 34.1, 25.7, 22.3, 15.2; GC-MS (EI, 70 eV) *m/z* = 260 (M^+, 3), 227 (29), 185 (8), 162 (30), 147 (100), 99 (18), 81 (28); HRMS-ESI (*m/z*): [(M-H_2O+H)$^+$] calcd for ($C_{16}H_{19}S$)$^+$: 243.1202; found, 243.1216.

trans-2-((2-(Methylthio)phenyl)ethynyl)cyclohexan-1-ol (**3k**). Yield: 443 mg, starting from 500 mg of 2-iodothioanisole (90%). Yellow oil. IR (film): ν = 3426 (m, br), 2222 (w), 1582 (w), 1435 (m), 1273 (w), 1111 (m), 1042 (w), 856 (w), 748 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37 (dist dd, *J* = 7.6, 1.0, 1H, H-6), 7.27 (dist td, *J* = 7.7, 1.2, 1H, H-4), 7.14 (dist d, *J* = 8.0, 1H, H-3), 7.09-7.04 (m, 1H, H-5), 3.63-3.54 (m, 1H, C*H*OH),

2.89 (s, 1H, OH), 2.55-2.40 (m, 1H, aliphatic), 2.47 (s, 3H, SMe), 2.15-2.01 (m, 2H, aliphatic), 1.85-1.66 (m, 2H, aliphatic), 1.55-1.45 (m, 1H, aliphatic), 1.37-1.17 (m, 3H, aliphatic); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.3, 131.9, 128.5, 124.3, 124.0, 121.5, 98.0, 80.3, 73.8, 40.0, 32.9, 30.8, 24.9, 24.3, 15.1; GC-MS (EI, 70 eV) *m/z* = 246 (M^+, 15), 203 (18), 147 (100), 135 (23), 115 (14); HRMS-ESI (*m/z*): [$(M+H)^+$] calcd for $(C_{15}H_{19}OS)^+$: 247.1151; found, 247.1158.

trans-2-((2-(Methylthio)phenyl)ethynyl)cyclopentan-1-ol (**3l**). Yield: 350 mg, starting from 500 mg of 2-iodothioanisole (75%). Yellow oil. IR (film): ν = 3379 (m, br), 2220 (w), 1582 (w), 1463 (m), 1435 (m), 1317 (w), 1300 (w), 1236 (w), 1165 (m), 1001 (m), 750 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (dist d, *J* = 7.5, 1H, H-6), 7.27-7.21 (m, 1H, H-4), 7.11 (dist d, *J* = 8.0, 1H, H-3), 7.05 (dist t, *J* = 7.5, 1H, H-5), 4.34 (q, *J* = 5.6, 1H, C*H*OH), 2.89-2.82 (m, 1H, aliphatic), 2.46 (s, 3H, SMe), 2.27 (s, 1H, OH), 2.21-2.05 (m, 2H, aliphatic), 1.87-1.75 (m, 3H, aliphatic), 1.68-1.57 (m, 1H, aliphatic), 1.37-1.17 (m, 1H, aliphatic); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 141.4, 132.0, 128.3, 124.1, 123.8, 121.6, 98.7, 79.5, 79.4, 40.5, 33.3, 30.8, 21.8, 14.9; GC-MS (EI, 70 eV) *m/z* = 232 (M^+, 24), 217 (11), 189 (45), 173 (58), 147 (100), 115 (27); HRMS-ESI (*m/z*): [$(M+H)^+$] calcd for $(C_{14}H_{17}OS)^+$: 233.0995; found, 233.1003.

Procedure for the synthesis of 4-(4-fluoro-2-(methylthio)phenyl)but-3-yn-1-ol 3b.

A solution of 2-bromo-5-fluorothioanisole (440 mg, 2.0 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol), CuI (57 mg, 0.3 mmol), and but-3-yn-1-ol (280.4 mg, 4.0 mmol) in anhydrous diisopropylamine (20 mL) was allowed to stir under nitrogen at 80 °C for 24 h. Water (50 mL) was then added, and the mixture extracted with diethyl ether (3 × 50 mL). The organic layer was washed with a saturated solution of NH_4Cl (100 mL) and water until neutral pH. After drying over Na_2SO_4, the solvent was evaporated, and the residue purified by column chromatography on silica gel using 9:1 hexane–AcOEt to 6:4 hexane–AcOEt as eluent.

4-(4-Fluoro-2-(methylthio)phenyl)but-3-yn-1-ol (**3b**). Yield: 307 mg, starting from 440 mg of 2-bromo-5-fluorothioanisole (73%). Yellow oil. IR (film): ν = 3397 (m, br), 2230 (w), 1591 (m), 1568 (w), 1477 (s), 1435 (m), 1250 (m), 1202 (m), 1044 (s), 897 (w), 847 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32 (dd, *J* = 8.4, 5.9, 1H, H-6), 6.82 (dd, *J* = 9.7, 2.5, 1H, H-3), 6.75 (td, *J* = 8.4, 2.5, 1H, H-5), 3.84 (q, *J* = 6.1, 2H, CH_2OH), 2.74 (t, *J* = 6.1, 2H, CH_2CH$_2$OH), 2.46 (s, 3H, SMe), 2.27-2.21 (m, 1H, OH); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 162.7 (d, *J* = 250.2), 144.3 (d, *J* = 8.4), 133.5 (d, *J* = 8.9), 117.1 (d, *J* = 2.9), 113.3 (d, *J* = 22.2), 111.0 (d, *J* = 24.8), 93.2, 79.3, 61.1, 24.1, 14.9 (d, *J* = 3.1); GC-MS (EI, 70 eV) *m/z* = 210 (M^+, 61), 179 (12), 165 (100), 146 (55), 133 (36), 115 (33); HRMS-ESI (*m/z*): [$(M+H)^+$] cald for $(C_{11}H_{12}FOS)^+$: 211.0587; found: 211.0595.

X-Ray crystallographic data collection and structure refinement for products 2a, 4a, 4k, and 4l

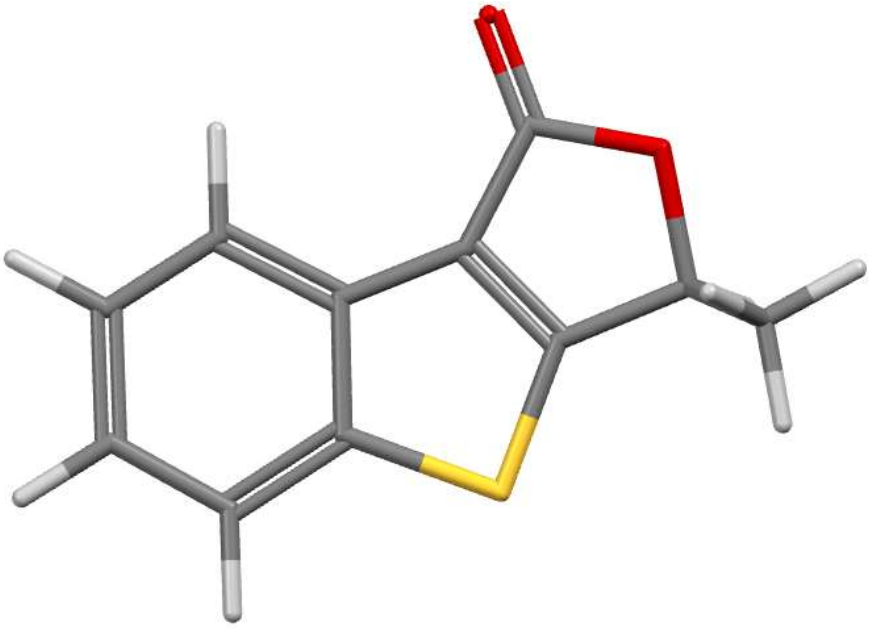

Figure S1. The asymmetric unit of the **2a** compound with the atom labelling scheme for non-H atoms. Color legend: carbon (light grey), hydrogen (white), oxygen (red), sulfur (yellow).

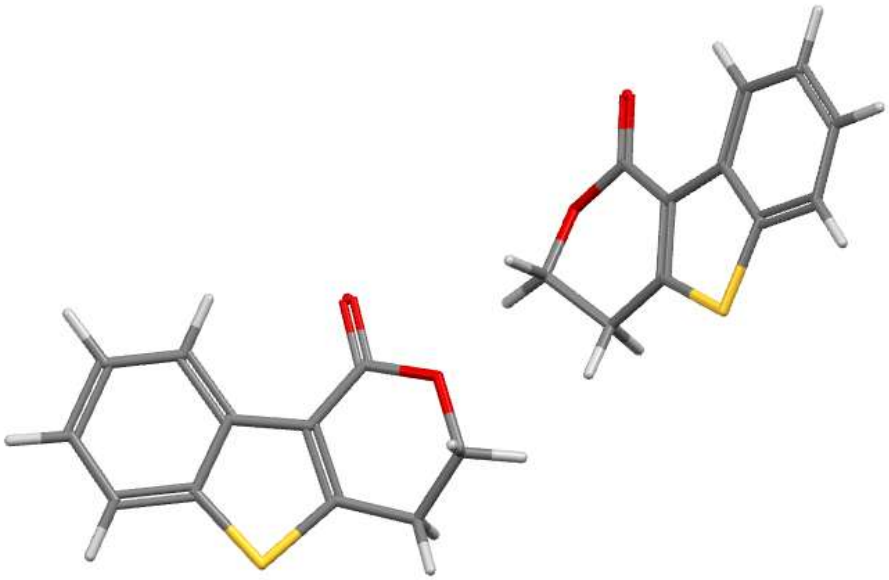

Figure S2. The asymmetric unit of the **4a** compound with the atom labelling scheme for non-H atoms. Color legend: carbon (light grey), hydrogen (white), oxygen (red), sulfur (yellow).

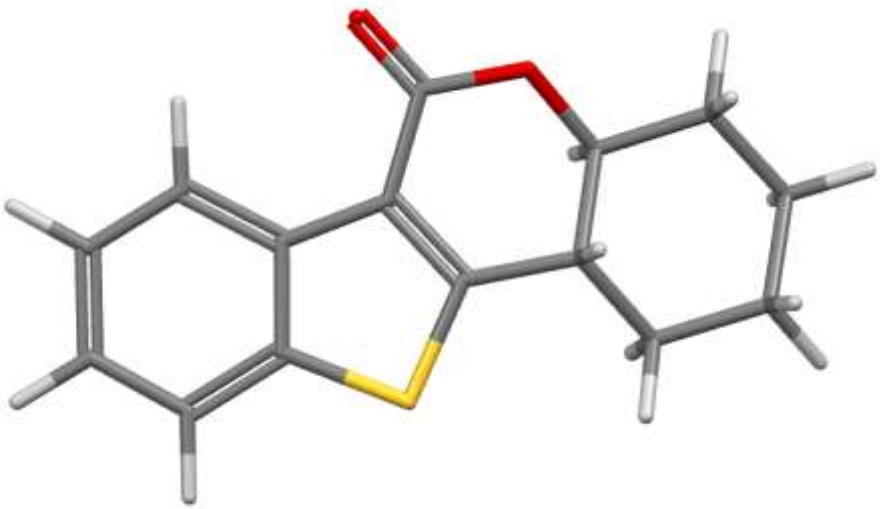

Figure S3. The asymmetric unit of the **4k** compound with the atom labelling scheme for non-H atoms. Color legend: carbon (light grey), hydrogen (white), oxygen (red), sulfur (yellow).

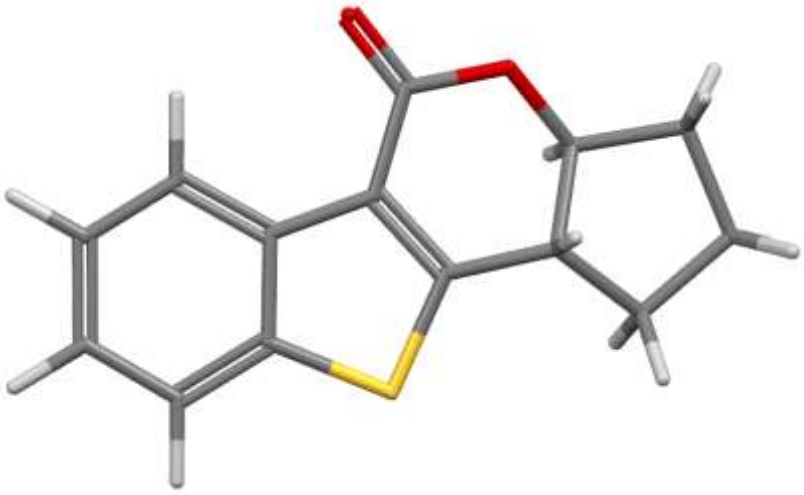

Figure S4. The asymmetric unit of the **4l** compound with the atom labelling scheme for non-H atoms. Color legend: carbon (light grey), hydrogen (white), oxygen (red), sulfur (yellow).

	2a	**4a**	**4k**	**4l**
Crystal data				
Chemical formula	$C_{11}H_8O_2S$	$C_{11}H_8O_2S$	$C_{15}H_{14}O_2S$	$C_{14}H_{12}O_2S$
Formula weight (g/mol)	204.25	204.25	258.34	244.31
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbca*	$P2_1ab$	$P2_1/n$	$P2_12_12_1$
Temperature (K)	293	293	293	293
Cell parameters (Å,°)	*a* = 19.5159 (10) *b* = 10.1378 (5) *c* = 9.7013 (5)	*A* = 31.834 (4) *b* = 14.3017 (16) *c* = 3.9833 (3)	*a* = 12.4146 (4) *b* = 9.1475 (2) *c* = 11.7305 (4)	*a* = 9.1412 (3) *b* = 17.5180 (7) *c* = 7.1796 (2)

			β = 108.6794 (16)	
Volume (Å^3)	1919.39 (16)	1813.5 (3)	1261.98 (7)	1149.70 (7)
Z	8	8	4	4
Z'	1	2	1	1
Radiation type	Cu *Kα* radiation, λ = 1.540560 Å	Cu *Kα* radiation, λ = 1.540560 Å	Cu *Kα* radiation, λ = 1.540560 Å	Cu *Kα* radiation, λ = 1.540560 Å
Data collection				
Diffractometer	Rigaku RINT2500			
Specimen mounting	special glass capillary			
Data collection mode	transmission			
2θ (°)	$2\theta_{min}$ = 8.00, $2\theta_{max}$ = 70.00	$2\theta_{min}$ = 5.00, $2\theta_{max}$ = 80.00	$2\theta_{min}$ = 8.00, $2\theta_{max}$ = 60.00	$2\theta_{min}$ = 6.00, $2\theta_{max}$ = 100.00
Structure solution				
Methods	Direct space method, direct methods	Direct space method	Direct space method, direct methods	Direct space method, direct methods
Parameters	6+1 DOF, 14 non-hydrogen atoms	6+5+0 DOF, 18 non-hydrogen atoms	6+0 DOF, 18 non-hydrogen atoms	6+0 DOF, 17 non-hydrogen atoms
Cost function	R_{wp} = 4.984	R_{wp} = 17.139	R_{wp} = 6.652	R_{wp} = 9.189
Refinement				
R_p	1.753	7.685	2.237	3.420
R_{wp}	2.605	12.104	3.301	5.507
R_{exp}	2.098	2.892	2.357	2.960
R_{Bragg}	4.361	14.914	3.492	7.717
χ^2	1.542	17.513	1.962	3.462
No. of data points	3101	3751	2601	4701
No. of reflections	417	573	355	714
Profile function	Pearson VII	Pearson VII	Pearson VII	Pearson VII
Refinement parameters				
Lattice	3	3	4	4
Positional	42	83	54	51
ADP	14	1	18	17
Profile	10	10	10	10
Background	20	19	20	20

Peak-shift	3	3	3	3
Restraints	40	78	52	50
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Programs				
Indexing	N-TREOR09 [7], DICVOL04 [8]			
Space group determination	EXPO2014 [9]			
Structure solution and refinement	EXPO2014			
Model building	ChemSketch [10], MOPAC2016 [11]			
Structure validation	Quantum ESPRESSO [12]			
Structure visualization	Mercury [13]			

The *ab initio* solution and structure refinement process were automatically performed by EXPO software [9], a package capable of carrying out the following steps: a) determination of unit-cell parameters and identification of the space group; b) structure solution by direct methods and/or a real-space approach; d) structure model refinement by the Rietveld method [14]. The first low-angle well-defined peaks in the experimental diffraction pattern were selected and actively used for indexing *via* N-TREOR09 [7] and DICVOL04 [8] programs embedded in EXPO. The space group determination was determined on the evaluation of the systematic absences.

The structures were solved with a real-space method based on the simulated annealing algorithm implemented in EXPO. The starting model was assembled using the sketching facilities of ACD/ChemSketch [10] and the geometry optimization was achieved by the program MOPAC2016 [11]. The simulated annealing algorithm was run 100 times under Linux workstation in default mode and parallel calculation over 20 CPUs. The best solution with the lowest cost function value was selected. The criterion to accept the solution was also based on the soundness of the crystal packing. The solutions obtained by the direct-space method were also confirmed by direct methods for structures **2a**, **4k**, **4l**.

Density-functional theory (DFT) geometry optimization with Quantum ESPRESSO was only performed on hydrogen atoms to improve their positions [12]. The structures derived were refined by the Rietveld method. Restraints were applied to bond distances to stabilize the refinement of structures 2a, 4a ,4k, 4l. All H atoms bonded to C atoms were treated as riding under the constraint on atomic displacement parameters $U_{iso}(H) = 1.2U_{iso}(C)$. Peak shape was modelled using the Pearson VII function. The atomic displacement parameters were refined isotropically and, only for the structure 4a, only an overall atomic displacement parameter was refined. To validate the refined crystal structures, they were subjected to periodic, solid-state calculations performed by Quantum ESPRESSO, an *ab initio* quantum-mechanical program employing plane waves and density-functional theory to simulate the properties of solids. The following execution parameters were used: PBE potentials from the SSSP Efficiency PBE (version 1.1) library [15], an optional cut-off controlling the accuracy of the calculations set to 60 Ry, k-point spacing was 0.15 $Å^{-1}$, van der Waals interactions were corrected by means of a Grimme's D3 dispersion correction [16]. Atomic-coordinate-only optimization of the

structures were performed using the experimental cell parameters and atomic positions obtained from the Rietveld refinement. The root-mean-square (RMS) displacements of non-H atoms between the DFT-optimized and experimental crystal structures were 0.055 Å, 0.306 Å, 0.054 Å and 0.196 Å respectively, providing strong evidence that the experimental structures were correct [17].

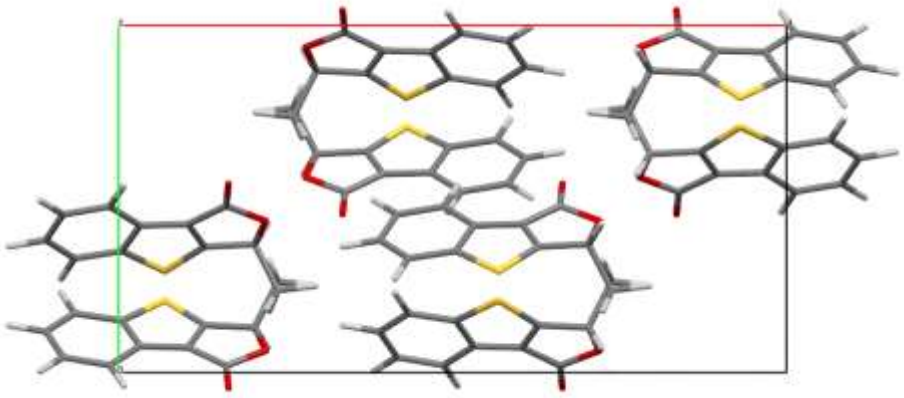

Figure S5. View of the packing of **2a** molecules along the c axis.

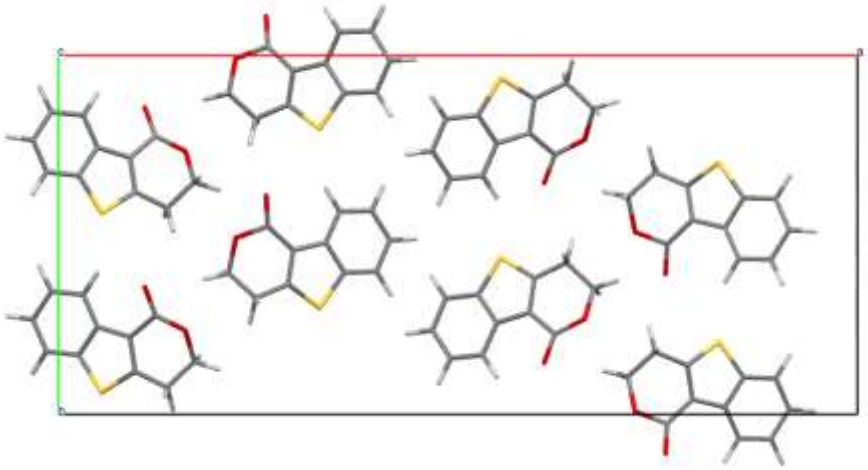

Figure S6. View of the packing of **4a** molecules along the c axis.

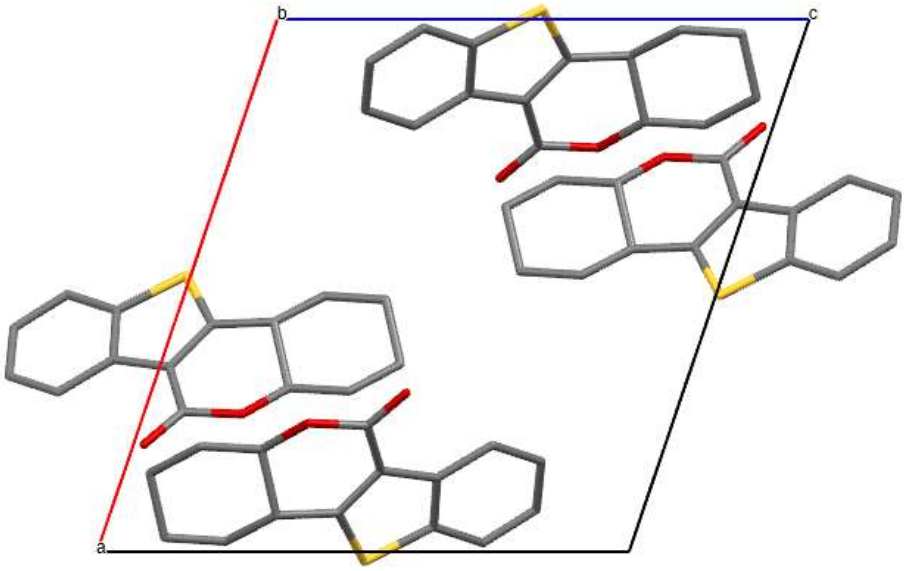

Figure S7. View of the packing of **4k** molecules along the b axis. All hydrogen atoms have been removed for clarity.

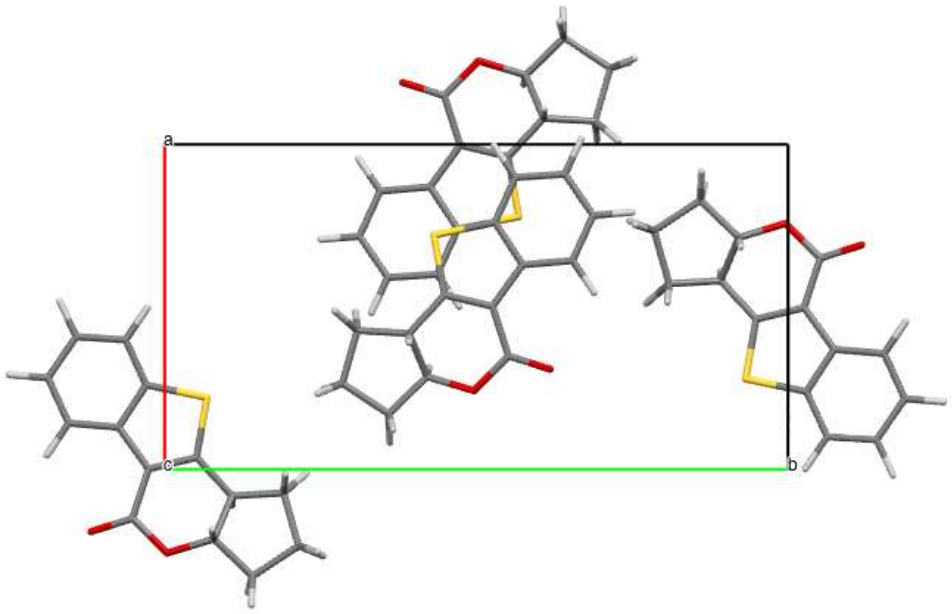

Figure S8. View of the packing of **4l** molecules along the c axis.

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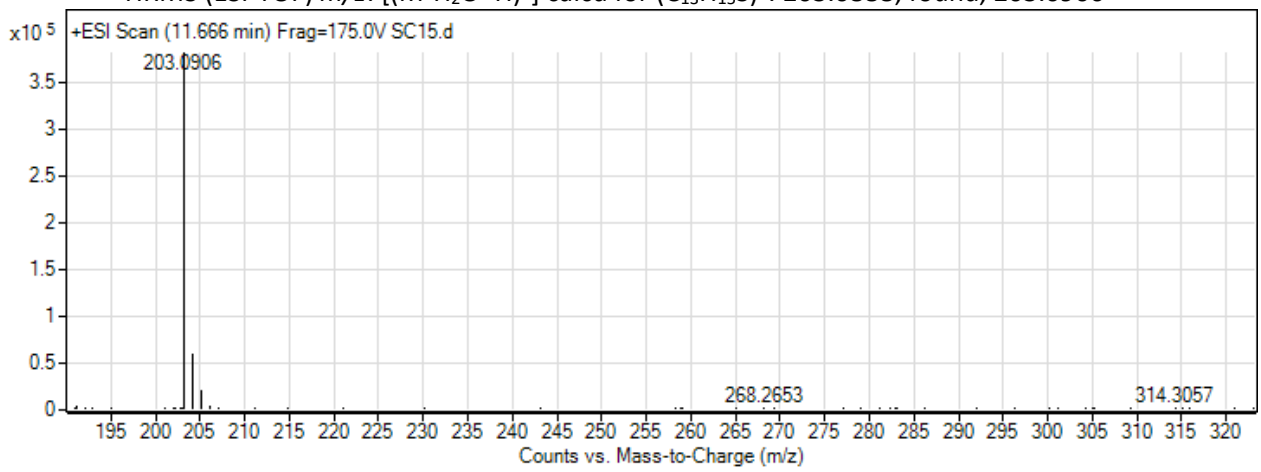
Copies of HRMS spectra

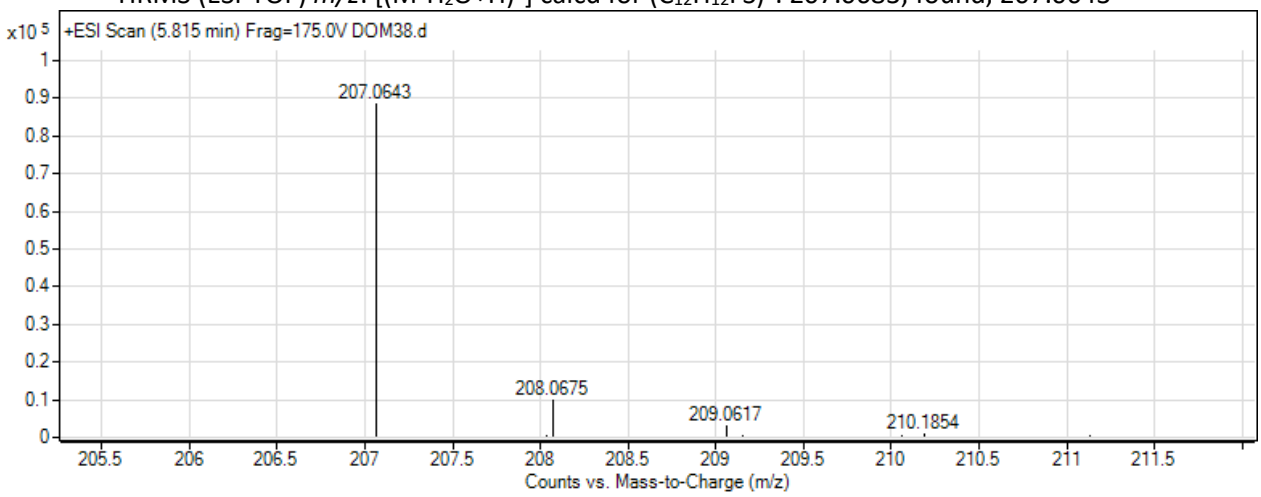
4-Methyl-1-(2-(methylthio)phenyl)pent-1-yn-3-ol (1b)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{13}H_{15}S$)$^+$: 203.0888; found, 203.0906



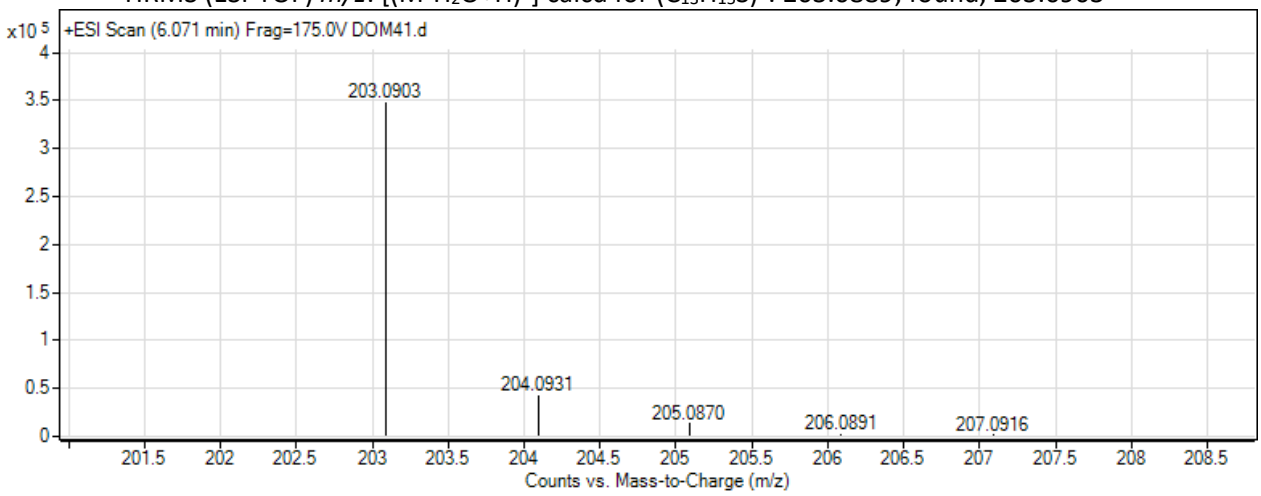
4-(5-Fluoro-2-(methylthio)phenyl)-2-methylbut-3-yn-2-ol (1d)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{12}H_{12}FS$)$^+$: 207.0683; found, 207.0643



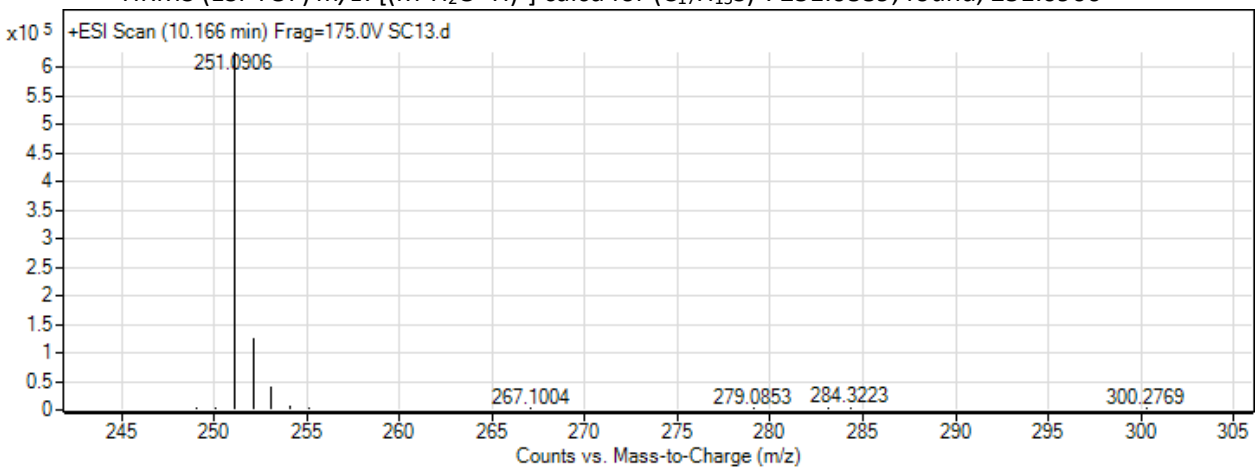
2-Methyl-4-(5-methyl-2-(methylthio)phenyl)but-3-yn-2-ol (1e)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{13}H_{15}S$)$^+$: 203.0889; found, 203.0903



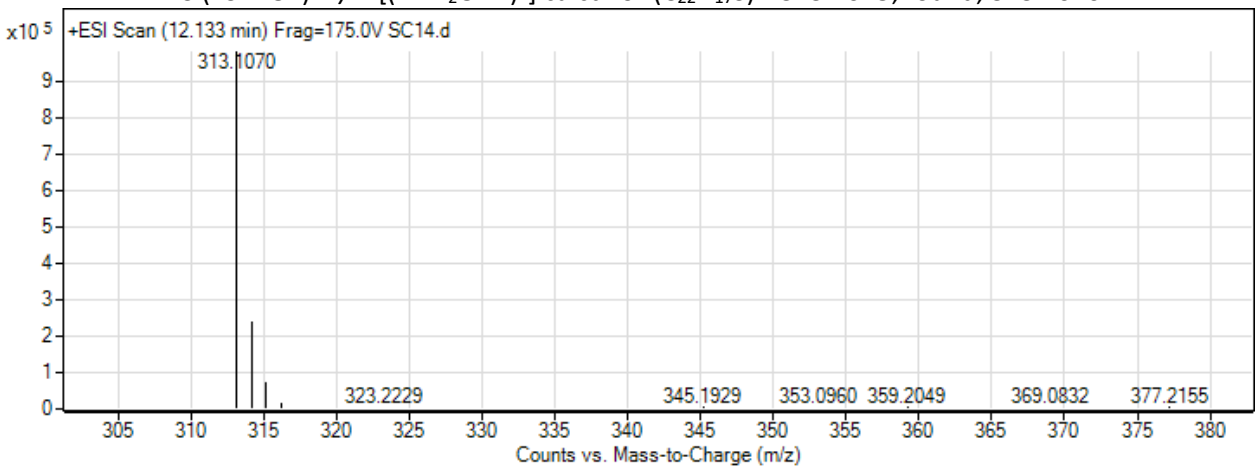
4-(2-(Methylthio)phenyl)-2-phenylbut-3-yn-2-ol (1i)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{17}H_{15}S$)$^+$: 251.0889; found, 251.0906



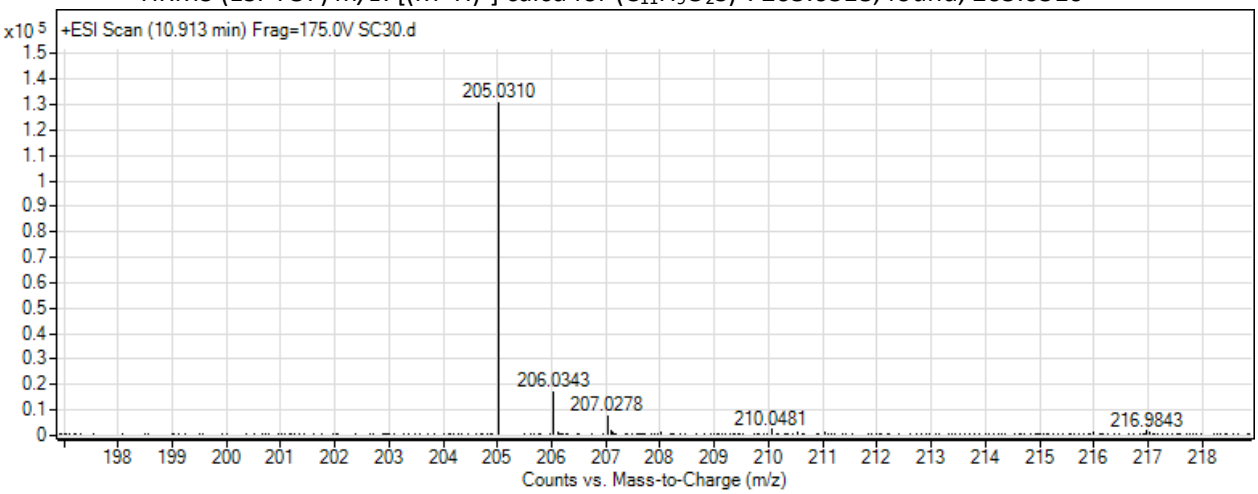
3-(2-(Methylthio)phenyl)-1,1-diphenylprop-2-yn-1-ol (1j)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{22}H_{17}S$)$^+$: 313.1045; found, 313.1070



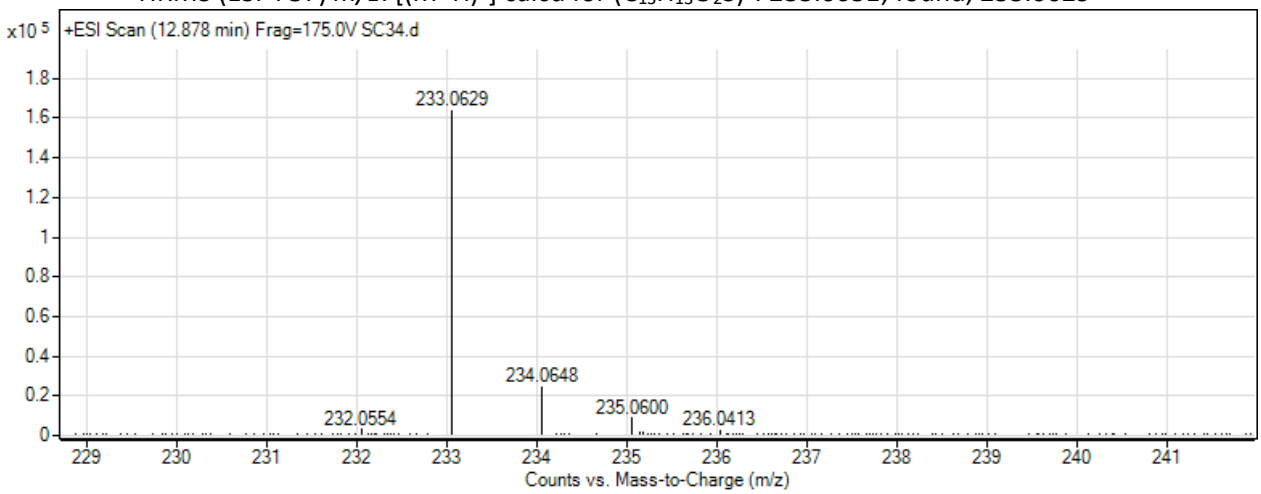
3-Methylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2a)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{11}H_9O_2S$)$^+$: 205.0318; found, 205.0310



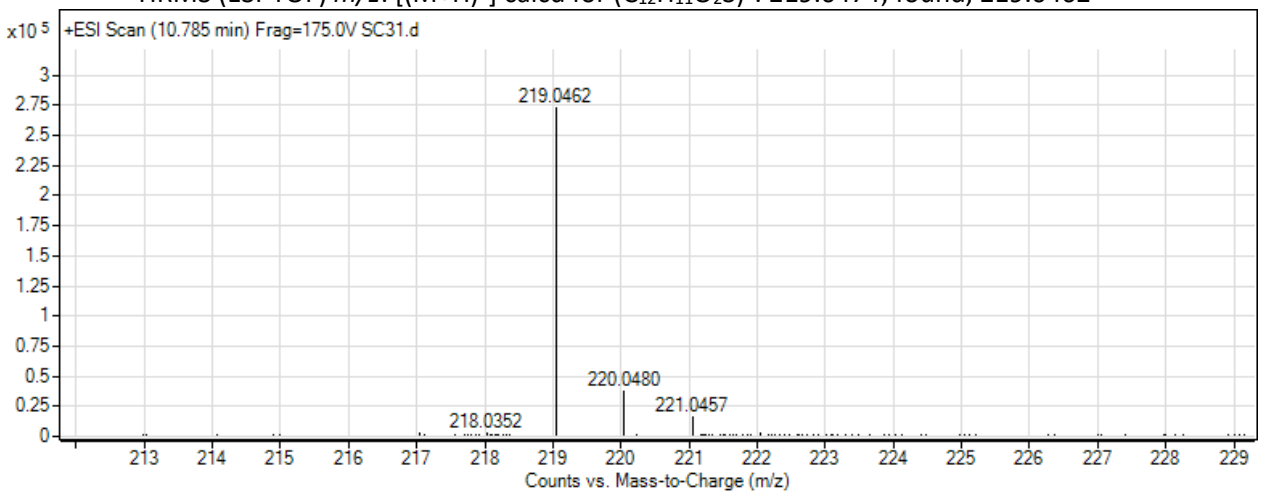
3-Isopropylbenzo[4,5]thieno[2,3-c]furan-1(3*H*)-one (2b)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{13}H_{13}O_2S$)$^+$: 233.0631; found, 233.0629



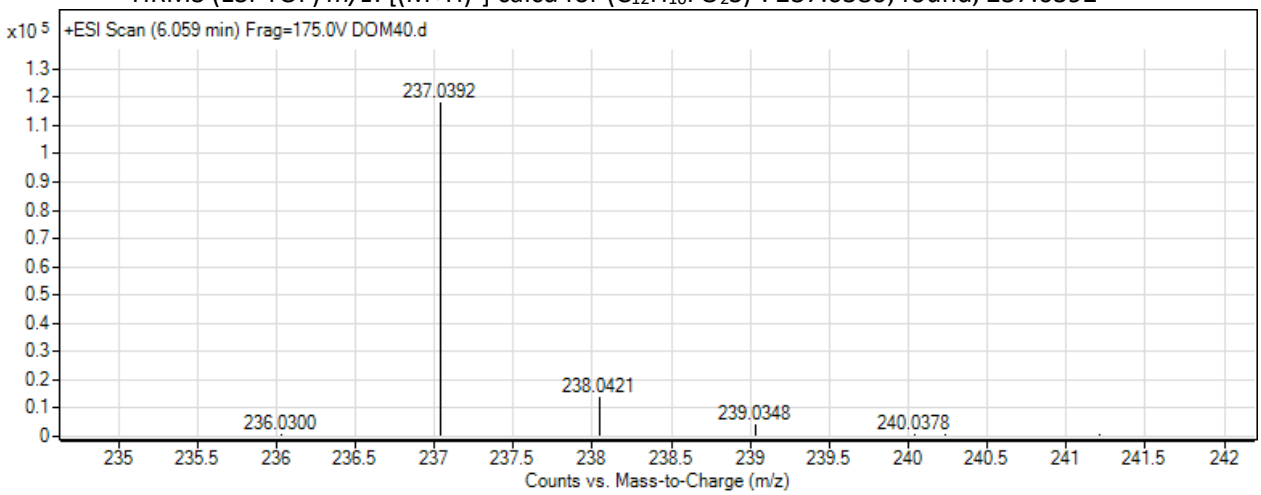
3,3-Dimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2c)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{12}H_{11}O_2S$)$^+$: 219.0474; found, 219.0462



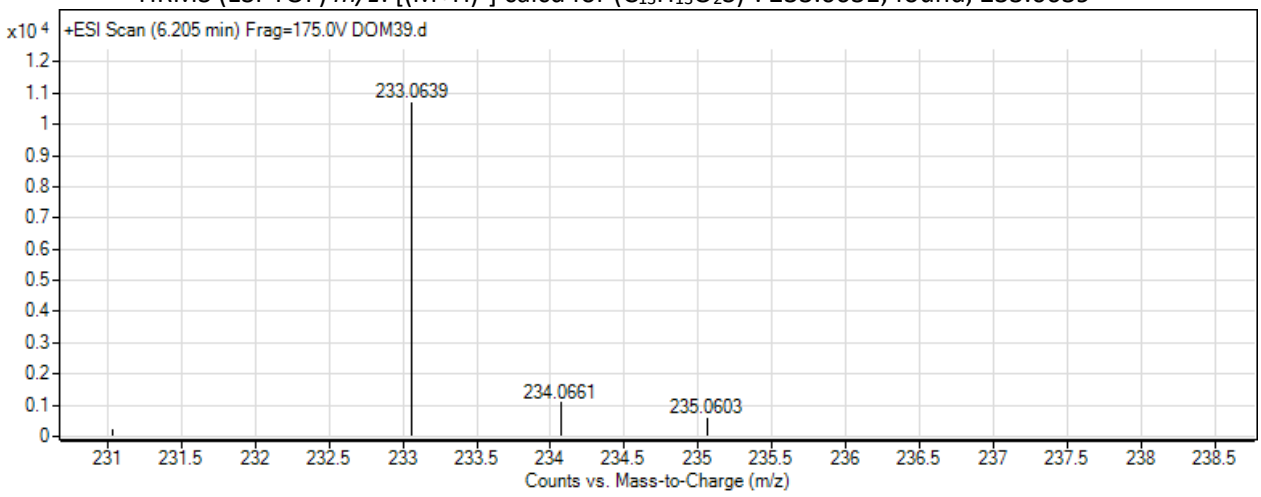
7-Fluoro-3,3-dimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2d)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{12}H_{10}FO_2S$)$^+$: 237.0380; found, 237.0392



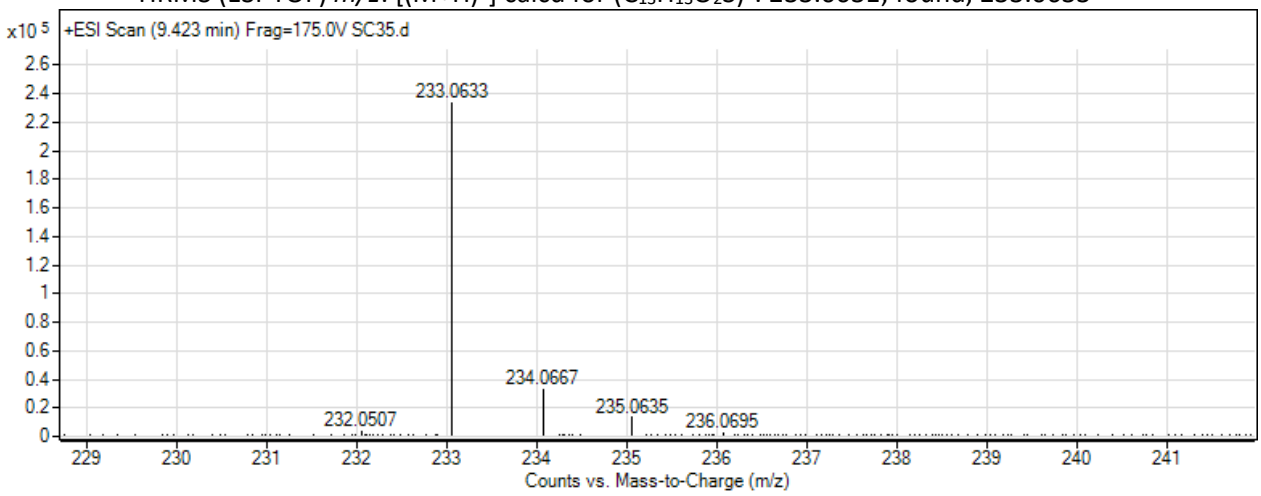
3,3,7-Trimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2e)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{13}H_{13}O_2S$)$^+$: 233.0631; found, 233.0639



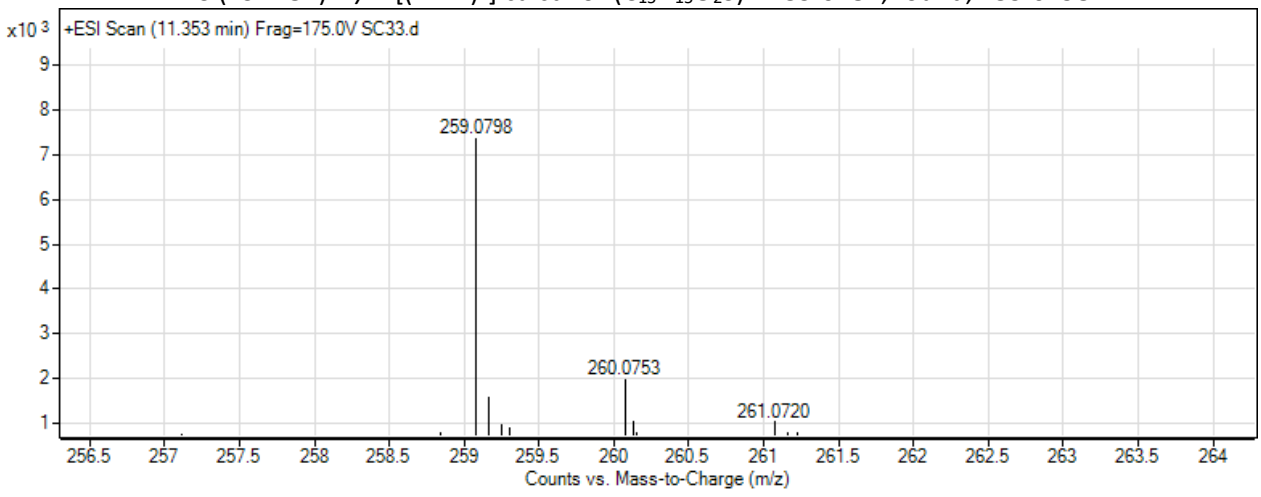
3-Ethyl-3-methylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2f)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{13}H_{13}O_2S$)$^+$: 233.0631; found, 233.0633



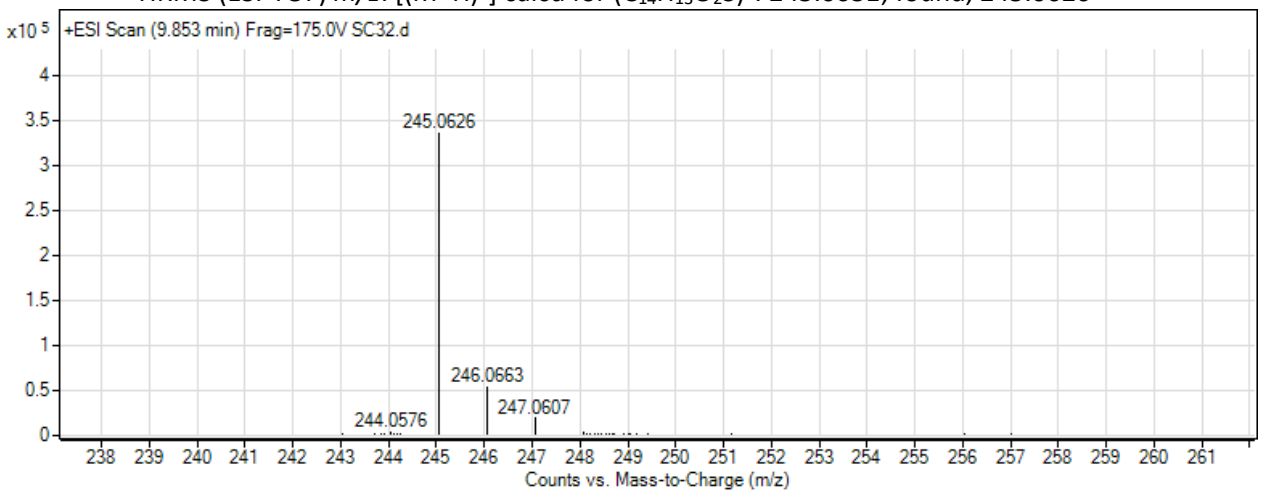
1*H*-Spiro[benzo[4,5]thieno[2,3-*c*]furan-3,1'-cyclohexan]-1-one (2g)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{15}H_{15}O_2S$)$^+$: 259.0787; found, 259.0798



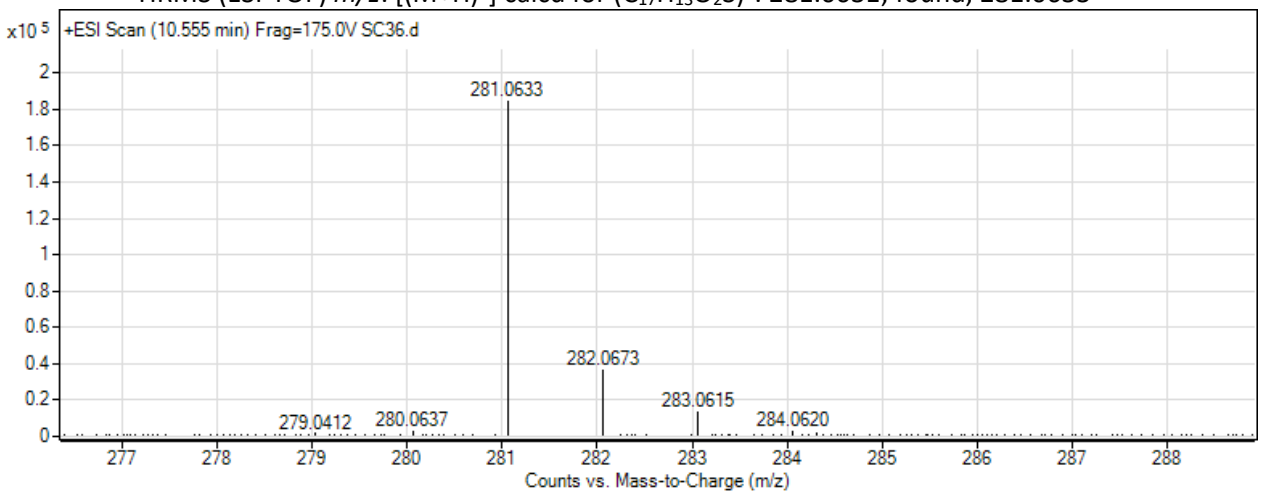
1*H*-Spiro[benzo[4,5]thieno[2,3-*c*]furan-3,1'-cyclopentan]-1-one (2h)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{14}H_{13}O_2S$)$^+$: 245.0631; found, 245.0626



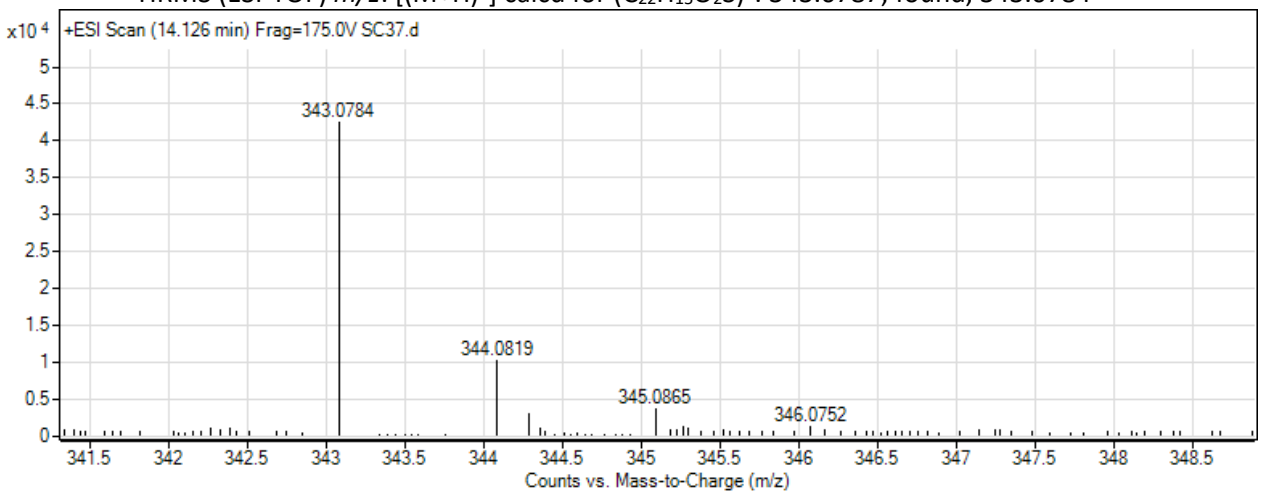
3-Methyl-3-phenylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2i)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{17}H_{13}O_2S$)$^+$: 281.0631; found, 281.0633



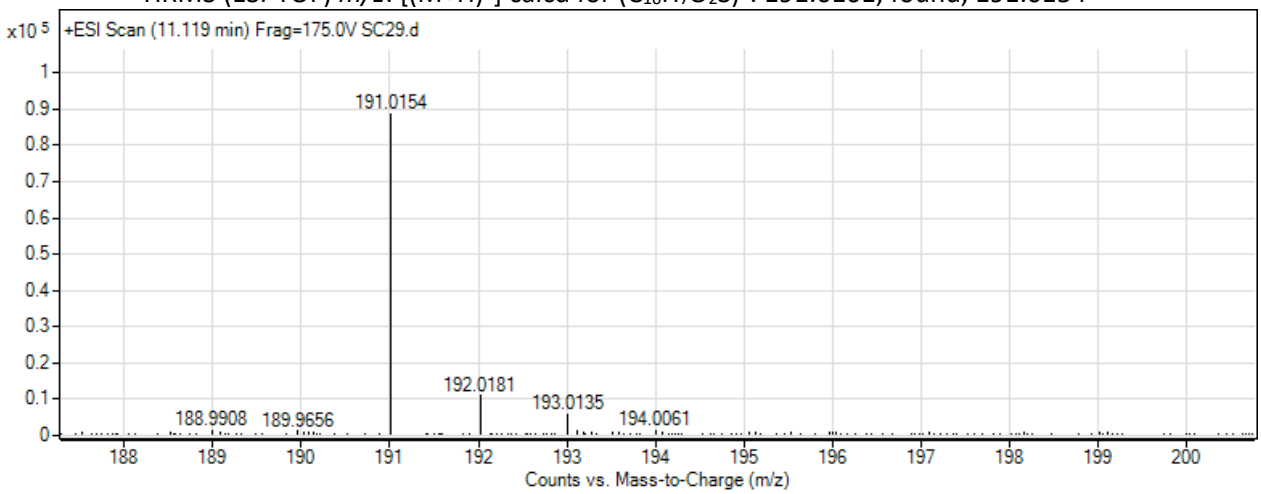
3,3-Diphenylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2j).

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{22}H_{15}O_2S$)$^+$: 343.0787; found, 343.0784



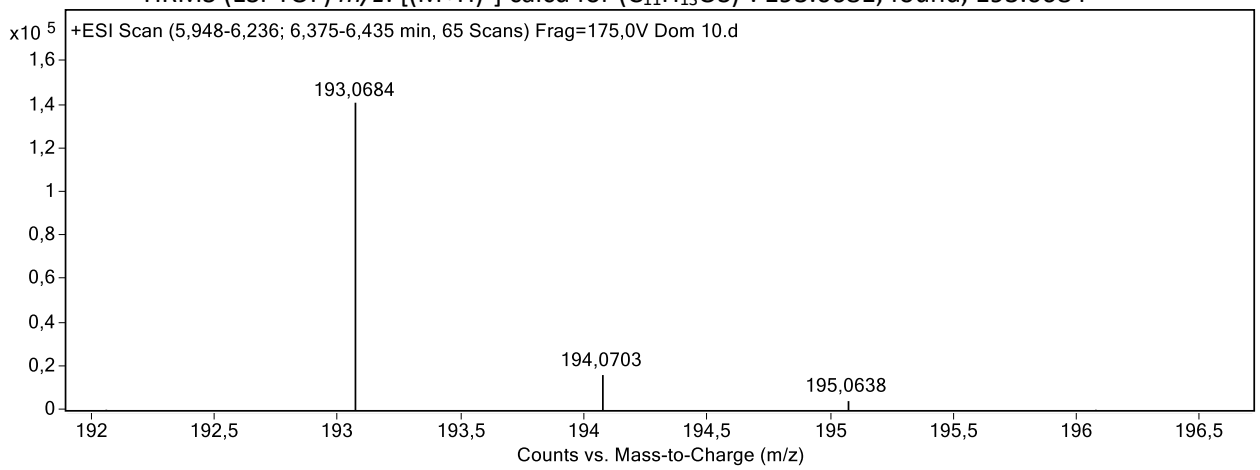
Benzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (2k)

HRMS (ESI-TOF) *m/z*: $[(M+H)^+]$ calcd for $(C_{10}H_7O_2S)^+$: 191.0161; found, 191.0154



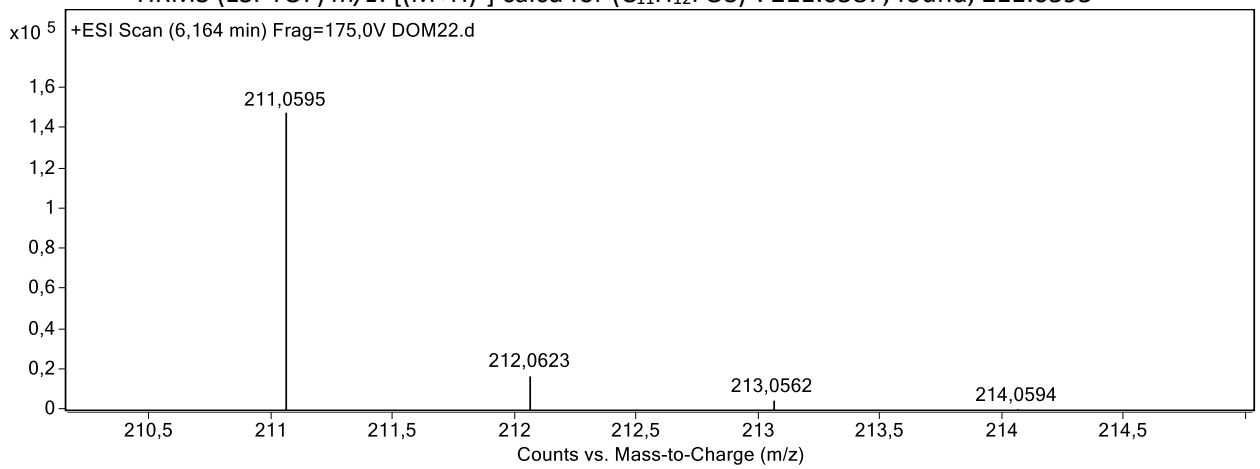
4-(2-(Methylthio)phenyl)but-3-yn-1-ol (3a)

HRMS (ESI-TOF) *m/z*: $[(M+H)^+]$ calcd for $(C_{11}H_{13}OS)^+$: 193.0681; found, 193.0684



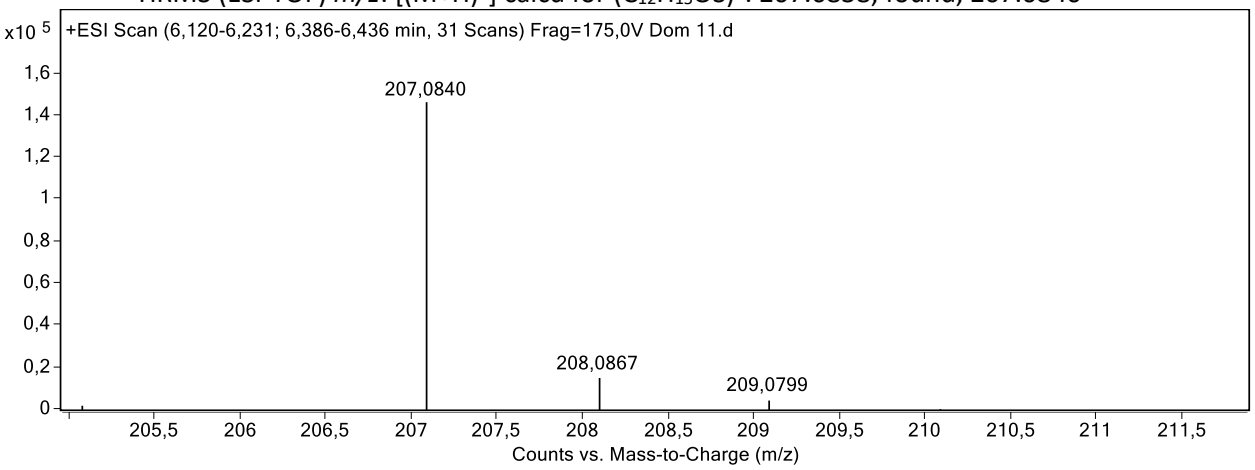
4-(4-Fluoro-2-(methylthio)phenyl)but-3-yn-1-ol (3b)

HRMS (ESI-TOF) *m/z*: $[(M+H)^+]$ calcd for $(C_{11}H_{12}FOS)^+$: 211.0587; found, 211.0595



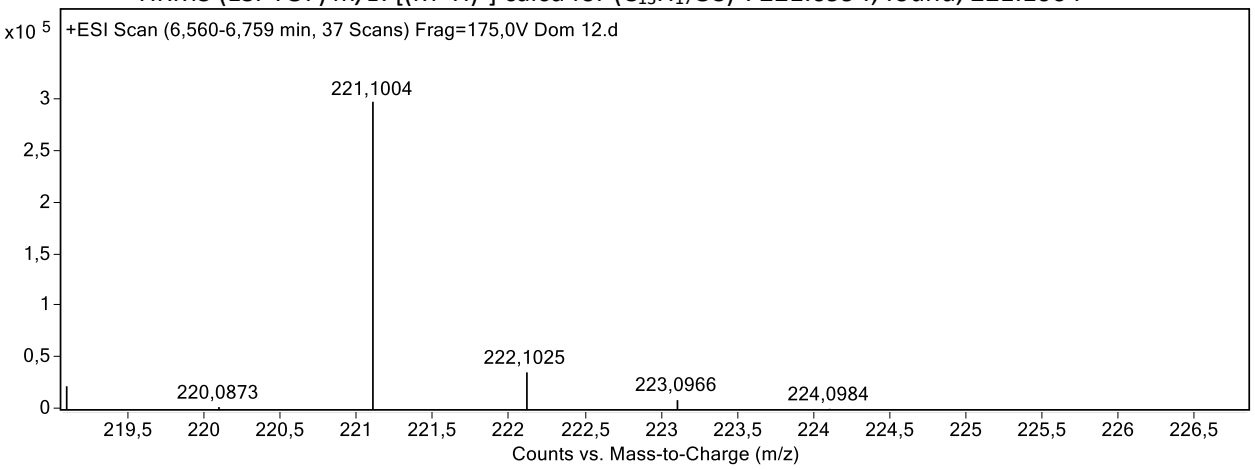
5-(2-(Methylthio)phenyl)pent-4-yn-2-ol (3c)

HRMS (ESI-TOF) *m/z*: $[(M+H)^+]$ calcd for $(C_{12}H_{15}OS)^+$: 207.0838; found, 207.0840



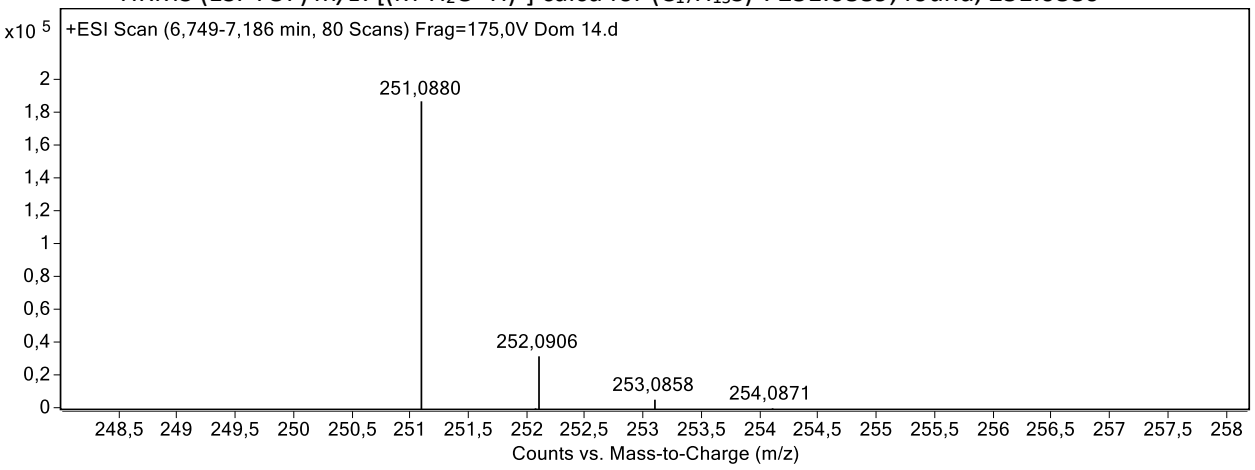
6-(2-(Methylthio)phenyl)hex-5-yn-3-ol (3d)

HRMS (ESI-TOF) *m/z*: $[(M+H)^+]$ calcd for $(C_{13}H_{17}OS)^+$: 221.0994; found, 221.1004



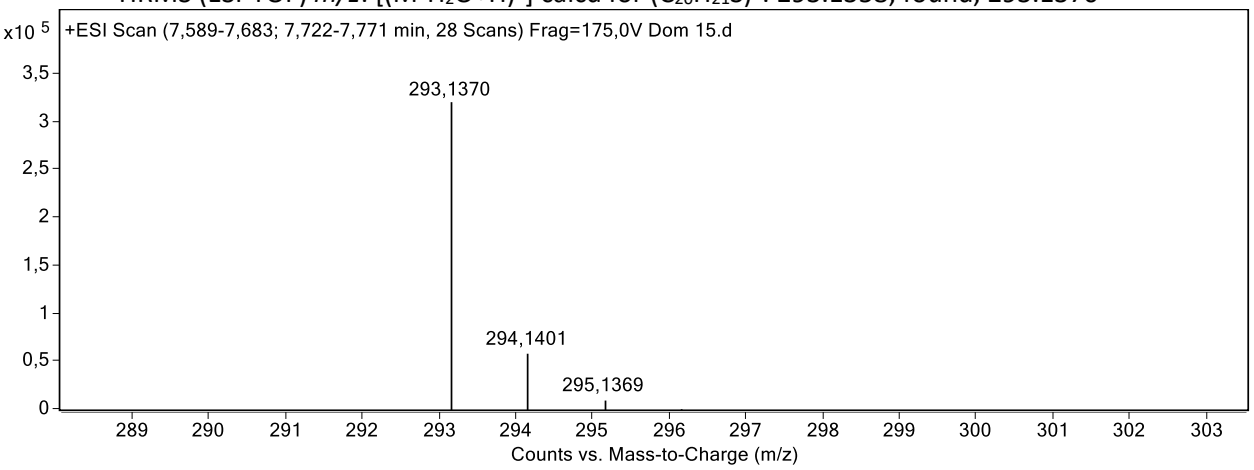
4-(2-(Methylthio)phenyl)-1-phenylbut-3-yn-1-ol (3e)

HRMS (ESI-TOF) *m/z*: $[(M-H_2O+H)^+]$ calcd for $(C_{17}H_{15}S)^+$: 251.0889; found, 251.0880



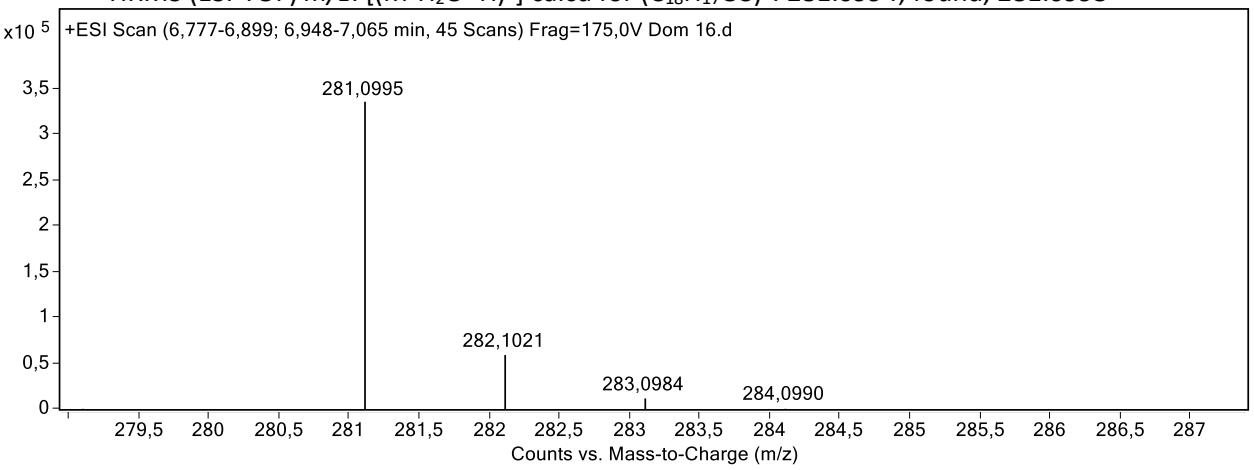
1-Mesityl-4-(2-(methylthio)phenyl)but-3-yn-1-ol (3f)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{20}H_{21}S$)$^+$: 293.1358; found, 293.1370



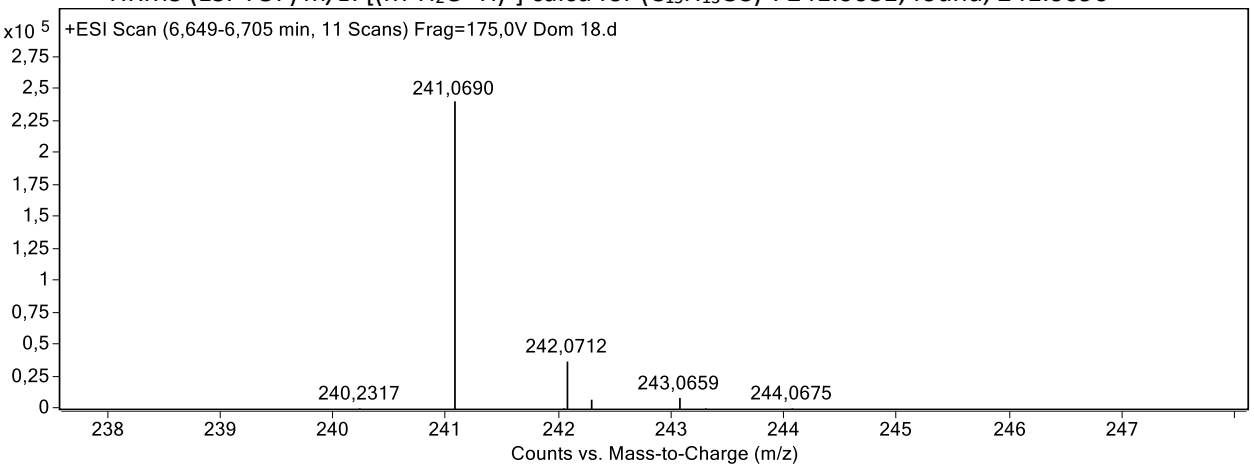
1-(4-Methoxyphenyl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (3g)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{18}H_{17}OS$)$^+$: 281.0994; found, 281.0995



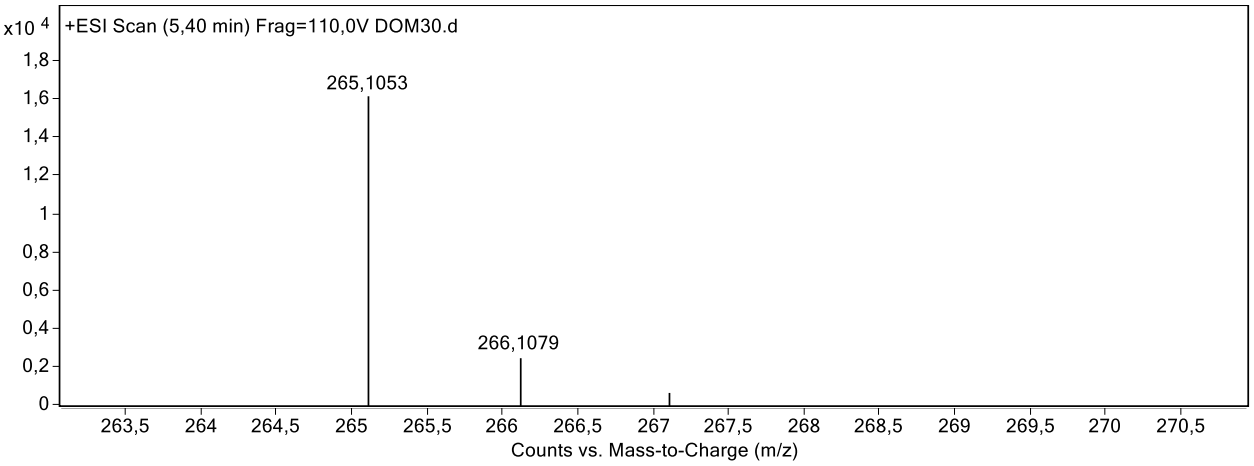
1-(Furan-2-yl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (3h)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{15}H_{13}OS$)$^+$: 241.0681; found, 241.0690



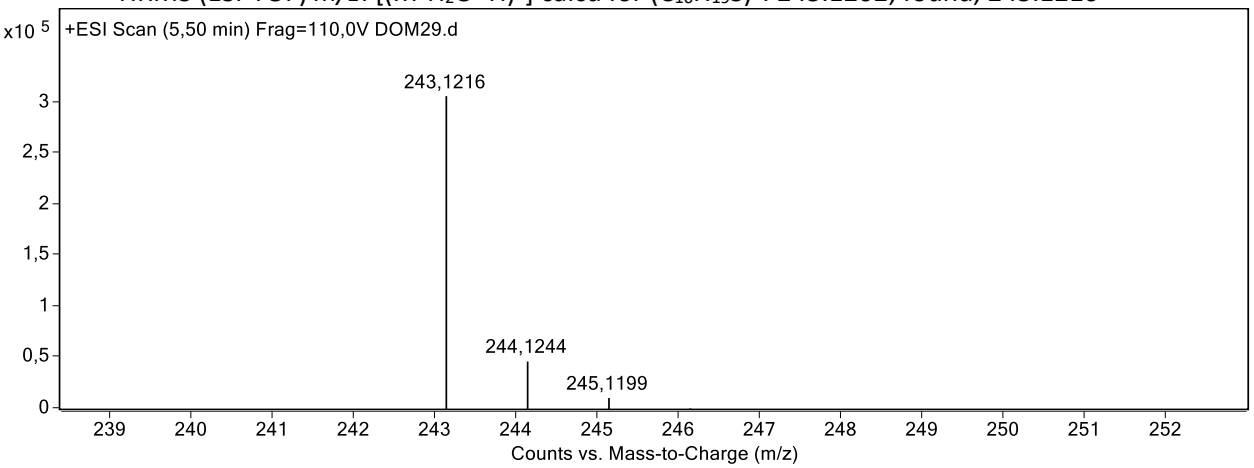
5-(2-(Methylthio)phenyl)-2-phenylpent-4-yn-2-ol (3i)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{18}H_{17}S$)$^+$: 265.1045; found, 265.1053



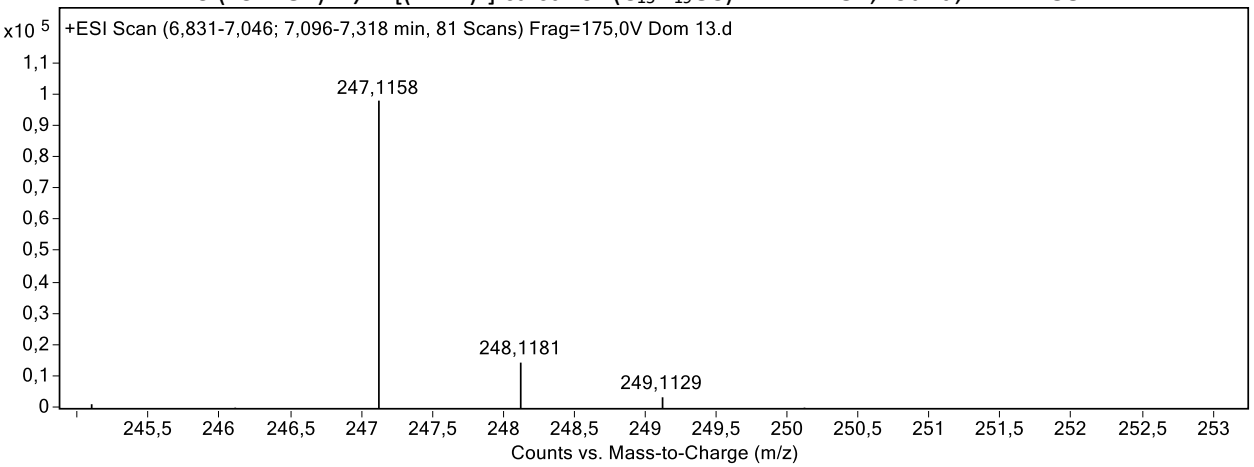
1-(3-(2-(Methylthio)phenyl)prop-2-yn-1-yl)cyclohexan-1-ol (3j)

HRMS (ESI-TOF) *m/z*: [(M-H_2O+H)$^+$] calcd for ($C_{16}H_{19}S$)$^+$: 243.1202; found, 243.1216



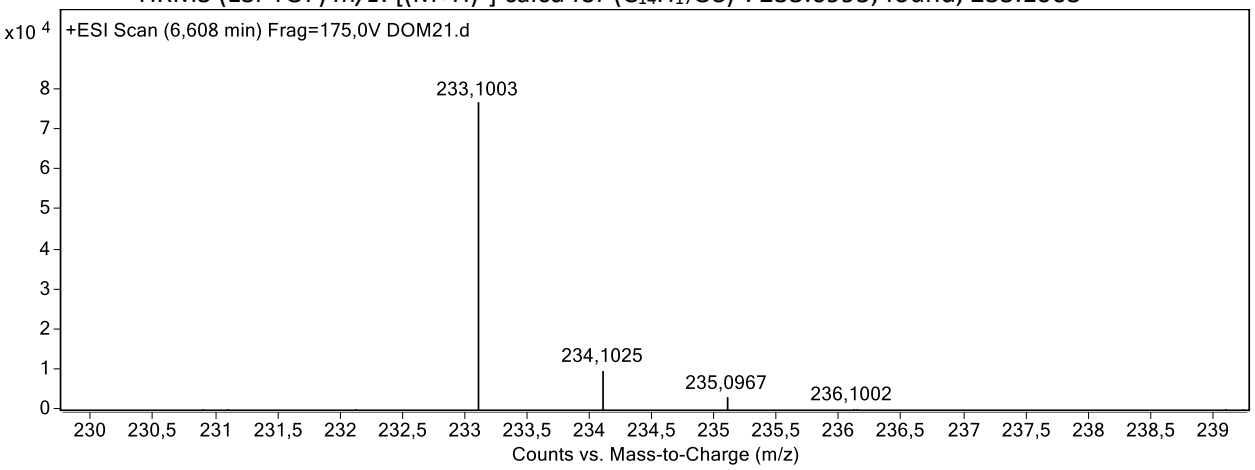
***trans*-2-((2-(Methylthio)phenyl)ethynyl)cyclohexan-1-ol (3k)**

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{15}H_{19}OS$)$^+$: 247.1151; found, 247.1158



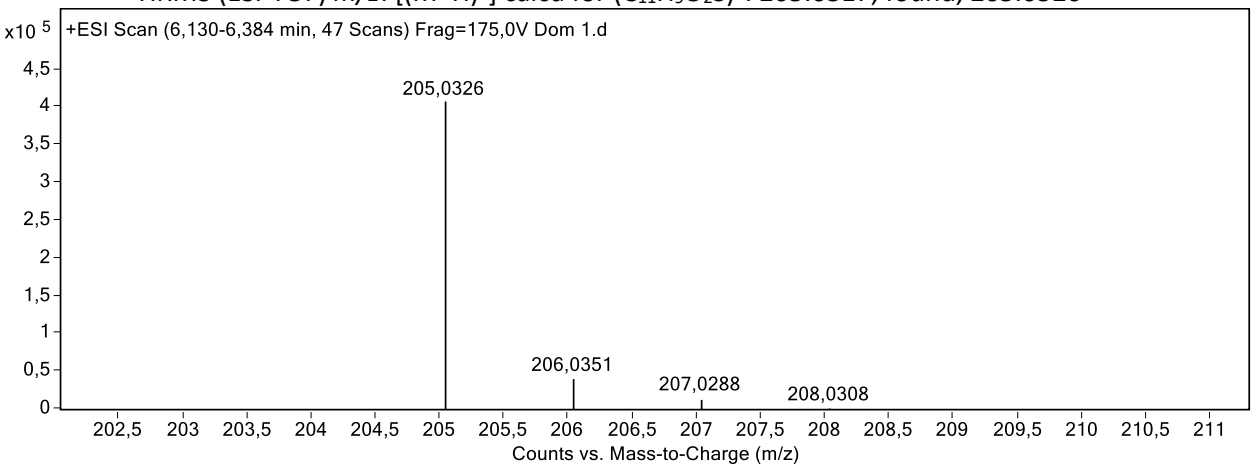
trans-2-((2-(Methylthio)phenyl)ethynyl)cyclopentan-1-ol (3l)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{14}H_{17}OS$)$^+$: 233.0995; found, 233.1003



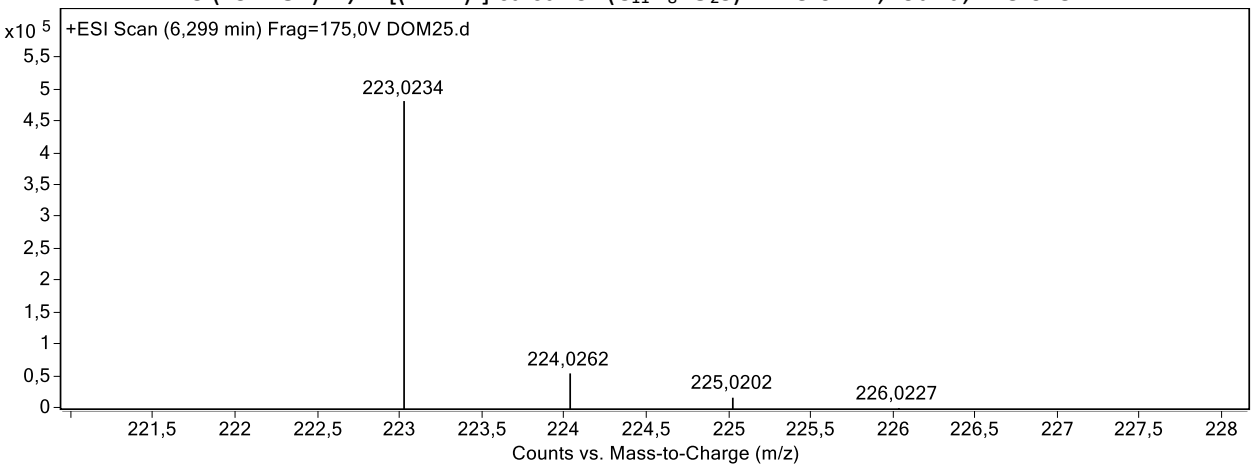
3,4-Dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4a)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{11}H_9O_2S$)$^+$: 205.0317; found, 205.0326



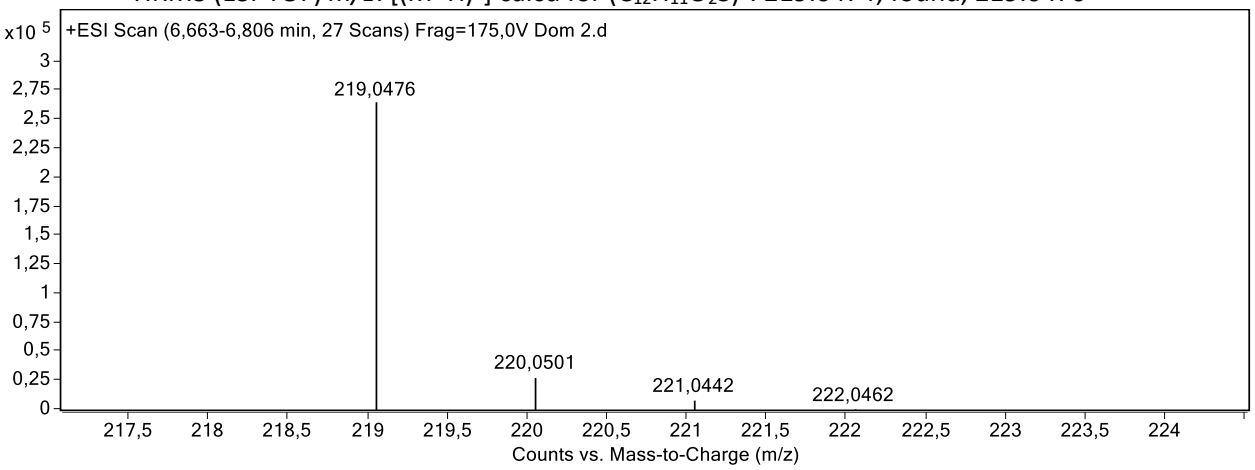
7-Fluoro-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4b)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{11}H_8FO_2S$)$^+$: 223.0224; found, 223.0234



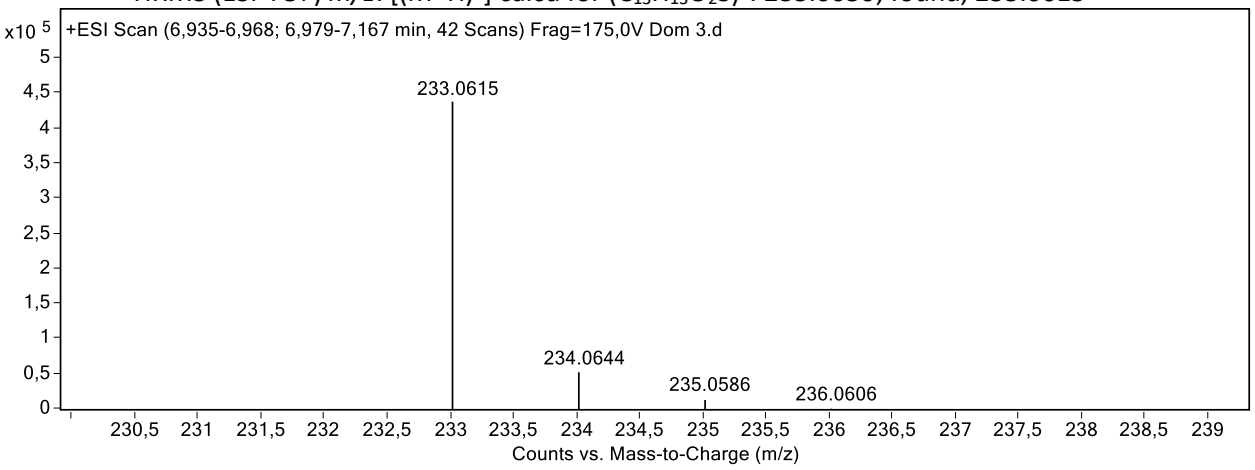
3-Methyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4c)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{12}H_{11}O_2S$)$^+$: 219.0474; found, 219.0476



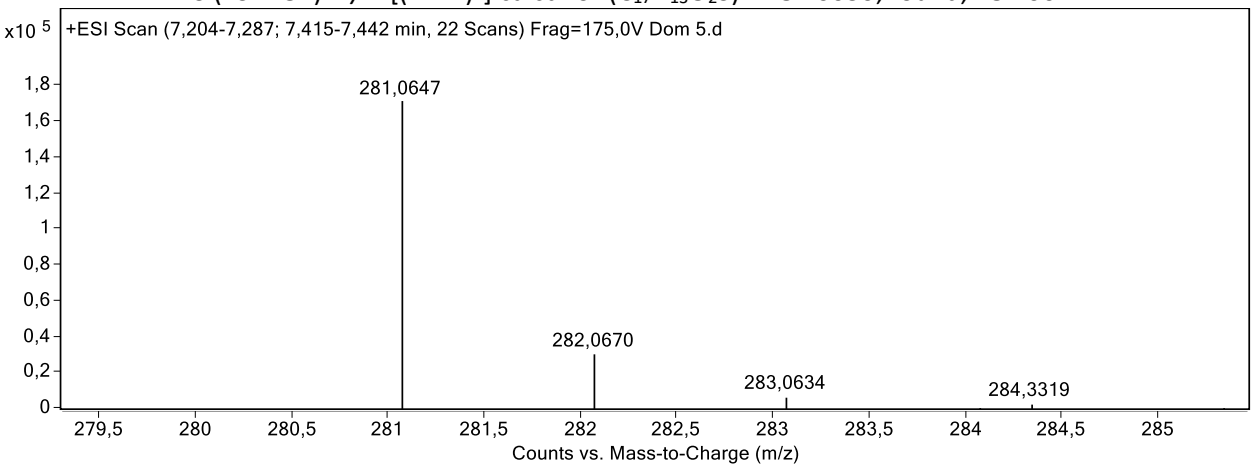
3-Ethyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4d)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{13}H_{13}O_2S$)$^+$: 233.0630; found, 233.0615



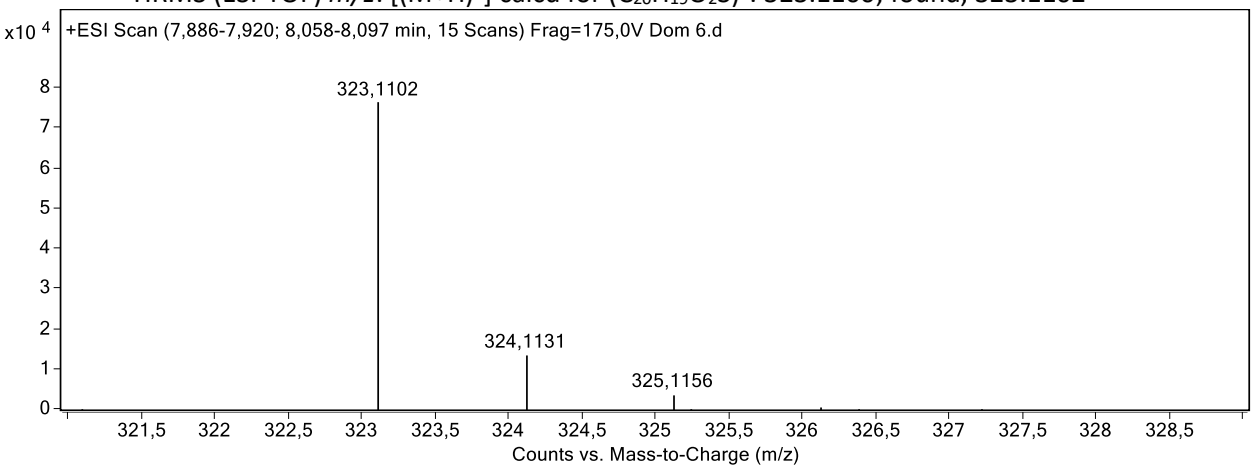
3-Phenyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4e)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{17}H_{13}O_2S$)$^+$: 281.0630; found, 281.0647



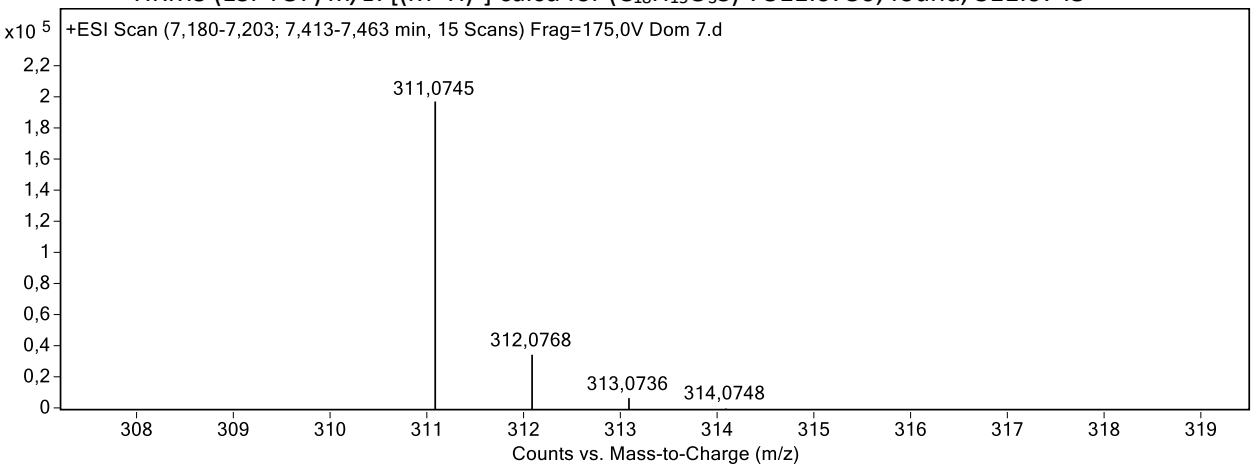
3-Mesityl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4f)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{20}H_{19}O_2S$)$^+$: 323.1100; found, 323.1102



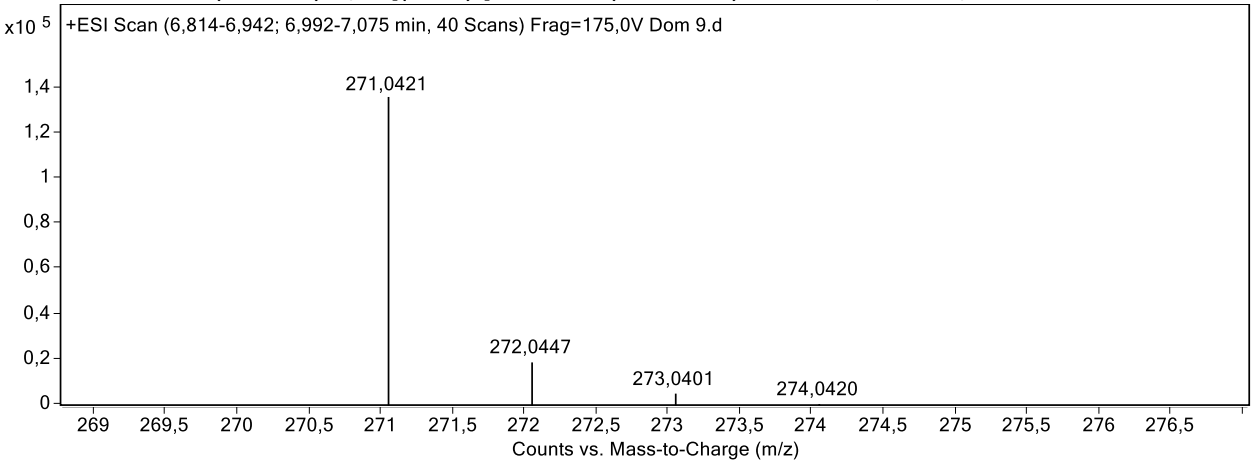
3-(4-Methoxyphenyl)-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4g)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{18}H_{15}O_3S$)$^+$: 311.0736; found, 311.0745



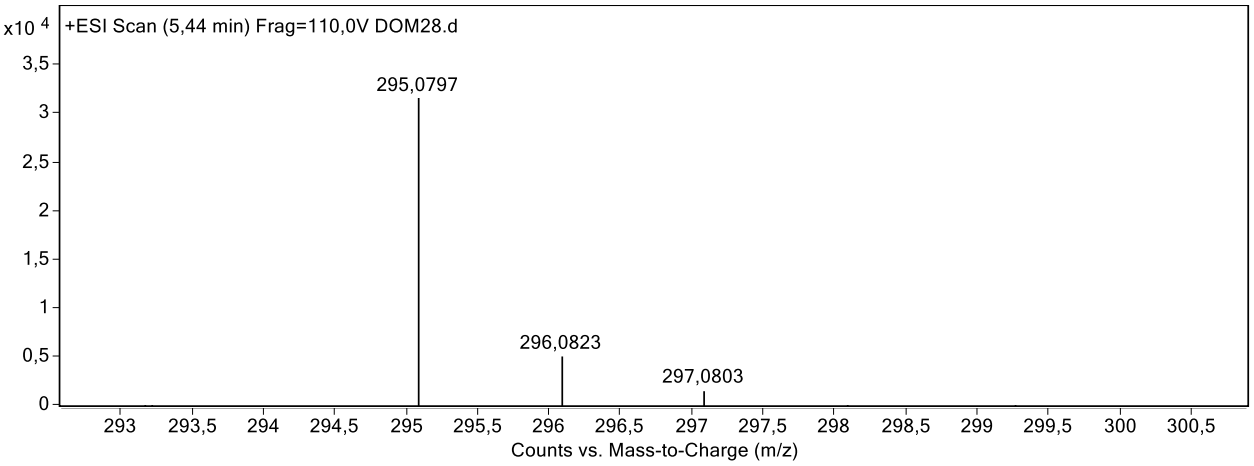
3-(Furan-2-yl)-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4h)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{15}H_{11}O_3S$)$^+$: 271.0423; found, 271.0421



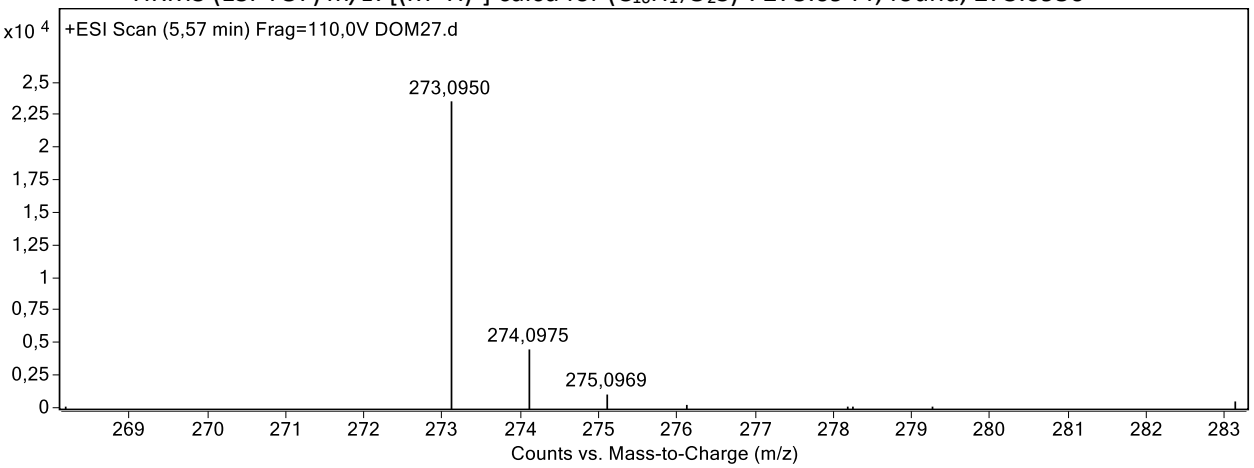
3-Methyl-3-phenyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (4i)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{18}H_{15}O_2S$)$^+$: 295.0787; found, 295.0797



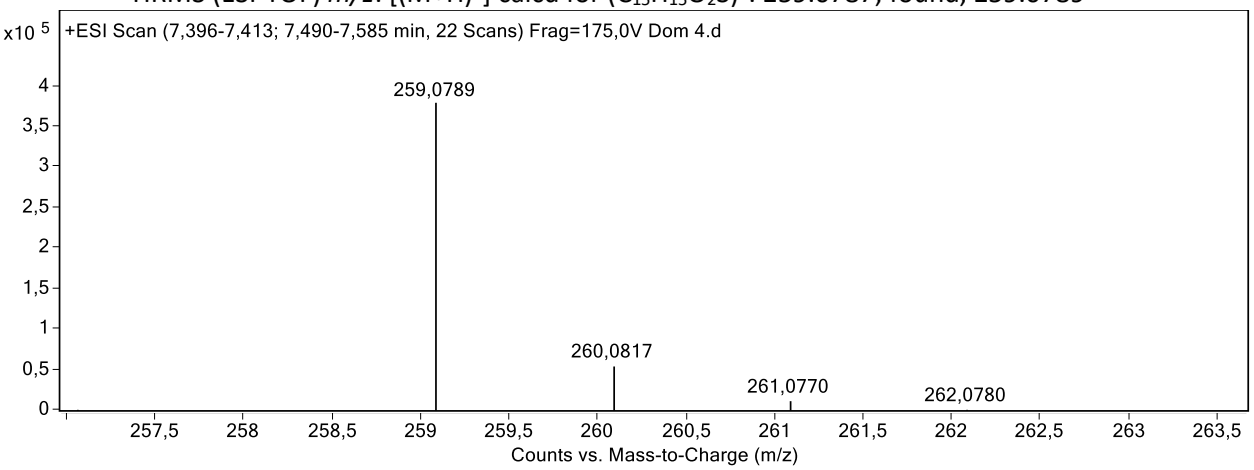
Spiro[benzo[4,5]thieno[3,2-*c*]pyran-3,1'-cyclohexan]-1(4*H*)-one (4j)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{16}H_{17}O_2S$)$^+$: 273.0944; found, 273.0950



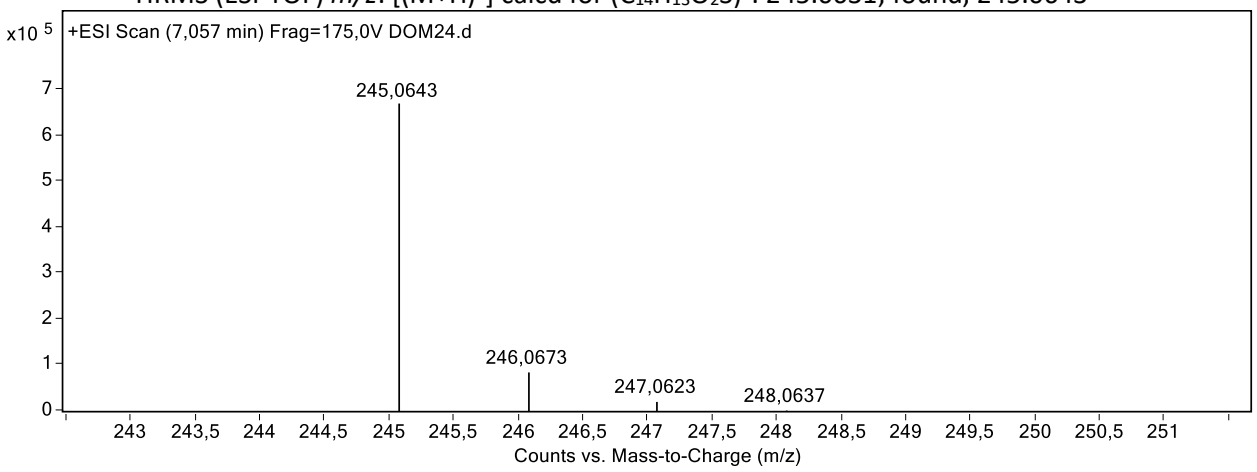
(4a*RS*, 11b*RS*)-1,2,3,4,4a,11b-Hexahydro-6*H*-benzo[4,5]thieno[3,2-*c*]chromen-6-one (4k)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{15}H_{15}O_2S$)$^+$: 259.0787; found, 259.0789



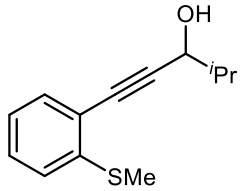
(3a*RS*, 10b*RS*)-2,3,3a,10b-Tetrahydrobenzo[4,5]thieno[3,2-*d*]cyclopenta[*b*]pyran-5(1*H*)-one (4l)

HRMS (ESI-TOF) *m/z*: [(M+H)$^+$] calcd for ($C_{14}H_{13}O_2S$)$^+$: 245.0631; found, 245.0643

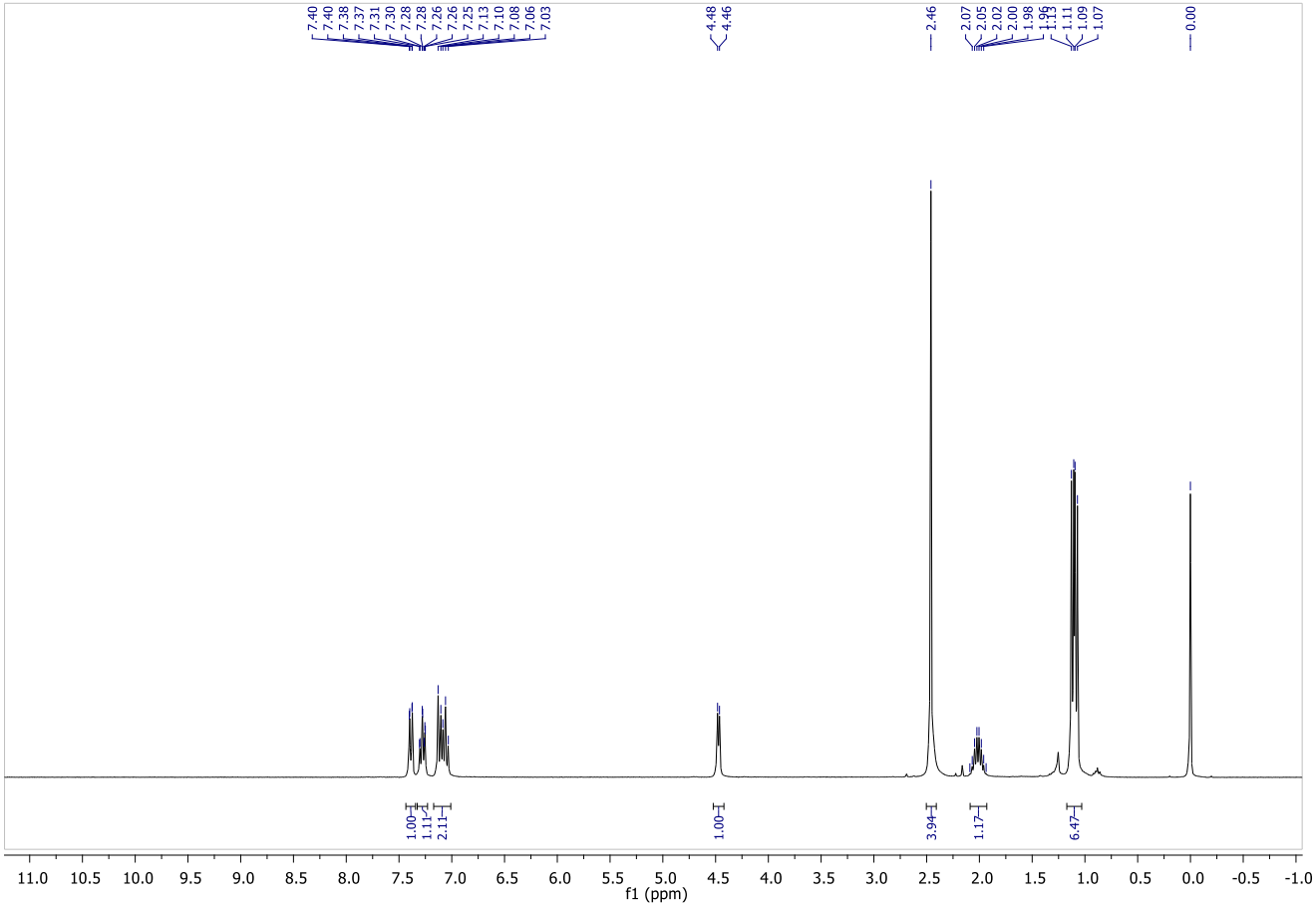


Copies of ^{1}H NMR and ^{13}CNMR Spectra

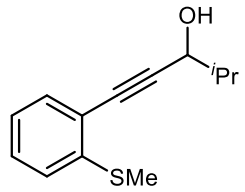
4-Methyl-1-(2-(methylthio)phenyl)pent-1-yn-3-ol (**1b**)



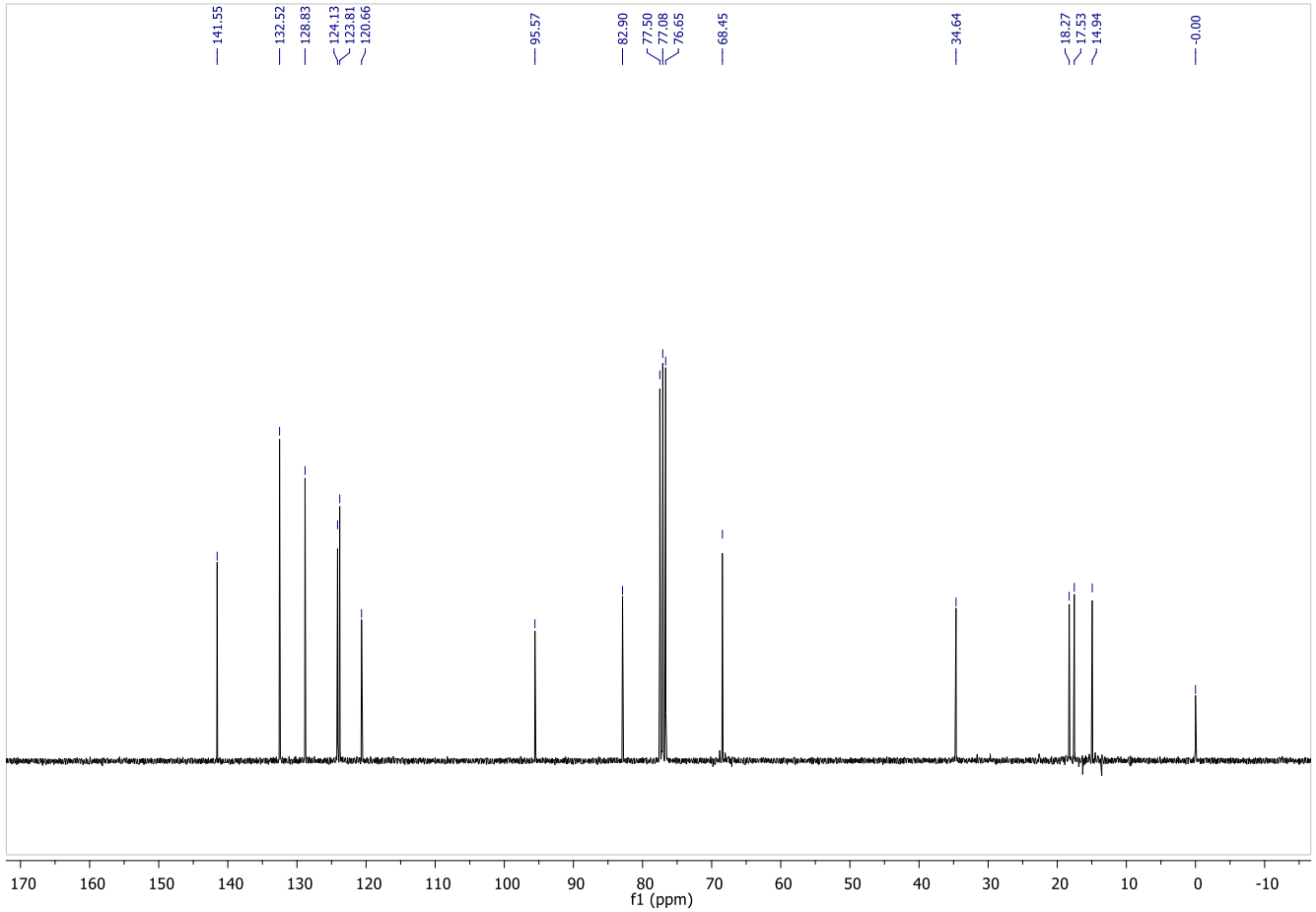
^{1}H NMR ($CDCl_3$, 300 MHz)



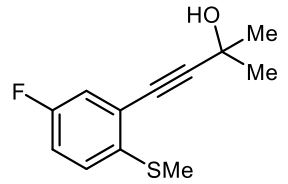
4-Methyl-1-(2-(methylthio)phenyl)pent-1-yn-3-ol (**1b**)



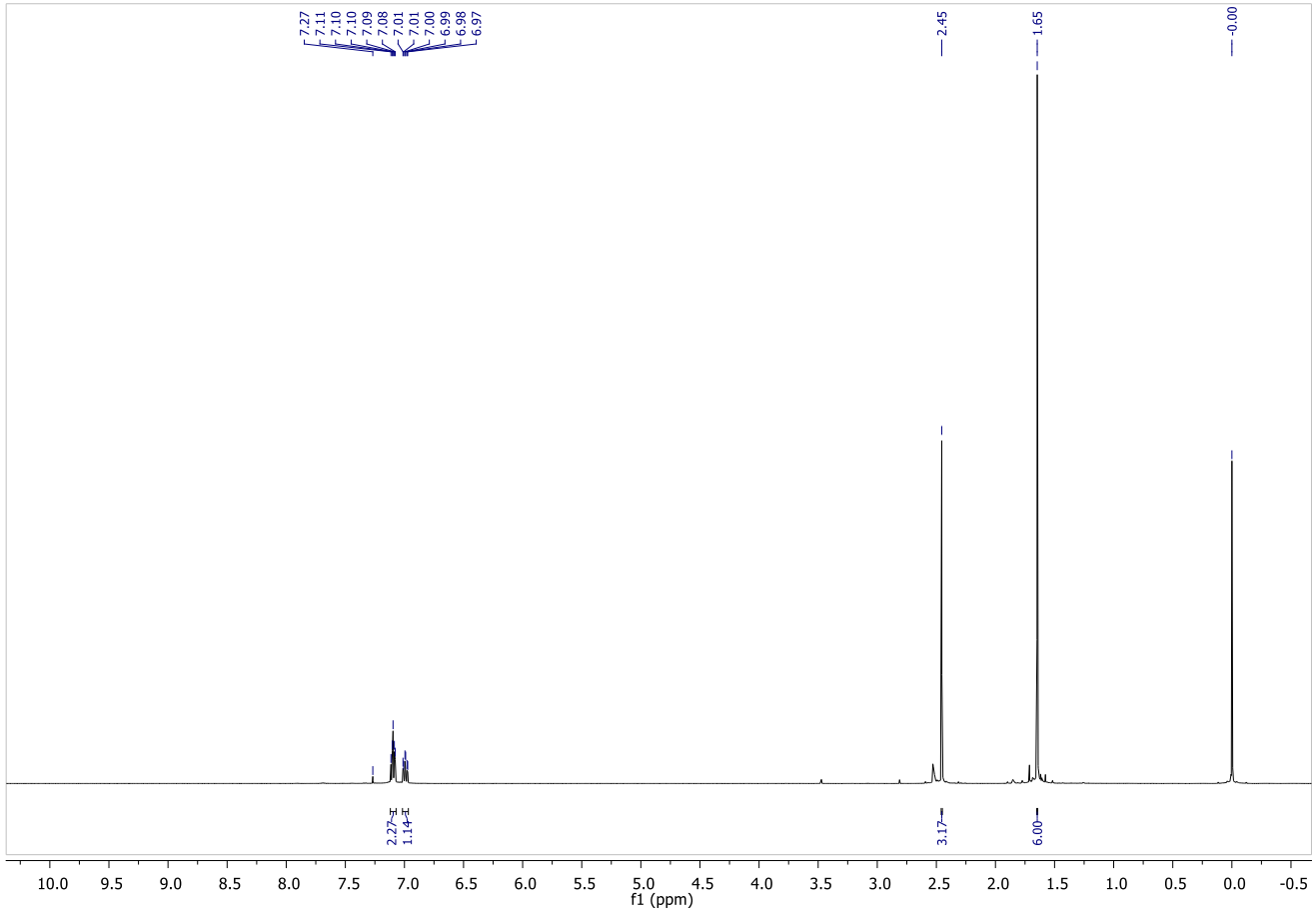
^{13}C NMR ($CDCl_3$, 75MHz)



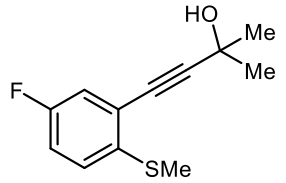
4-(5-Fluoro-2-(methylthio)phenyl)-2-methylbut-3-yn-2-ol (**1d**)



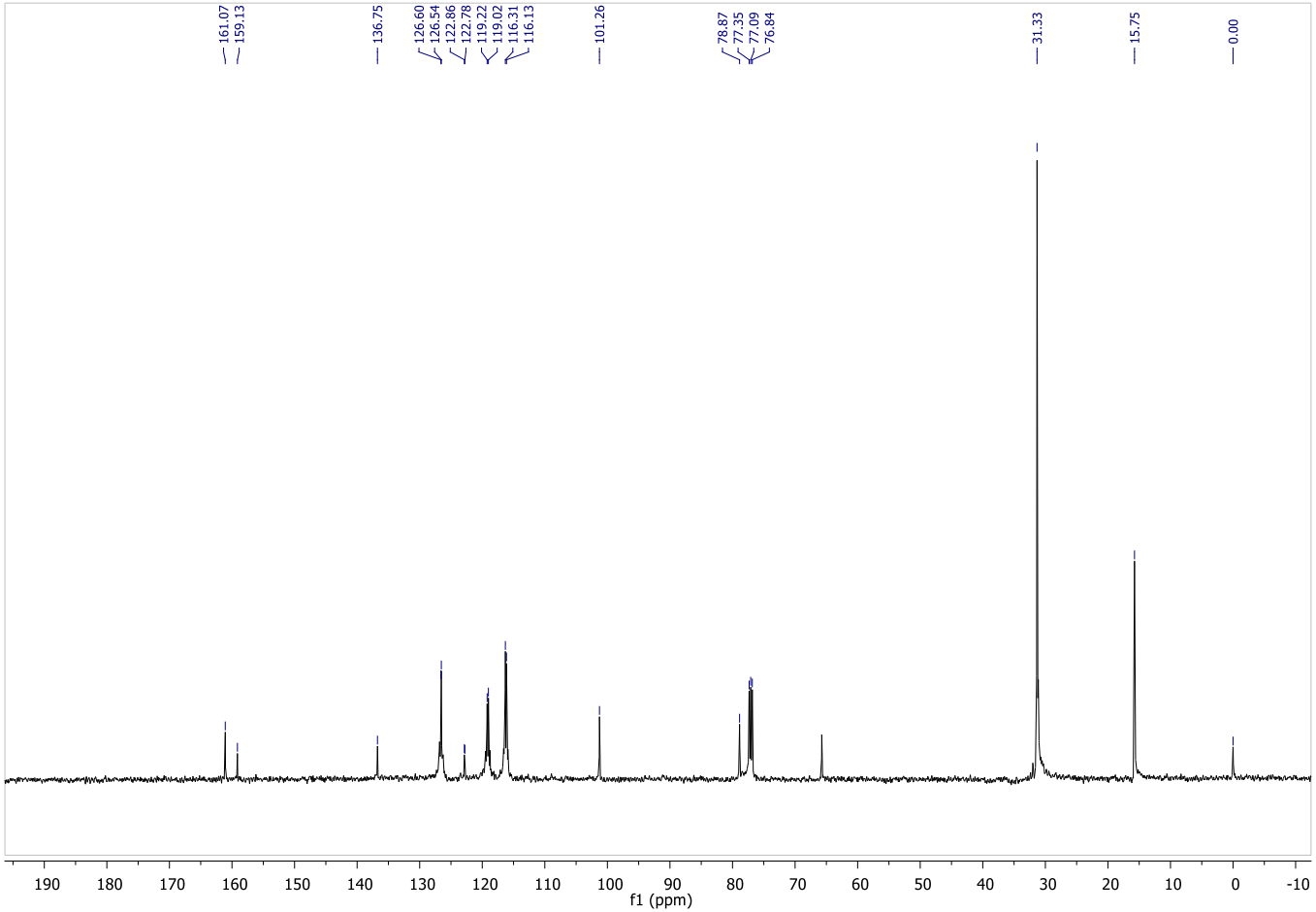
^{1}H NMR ($CDCl_3$, 500 MHz)



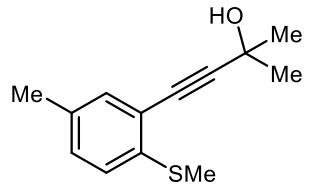
4-(5-Fluoro-2-(methylthio)phenyl)-2-methylbut-3-yn-2-ol (**1d**)



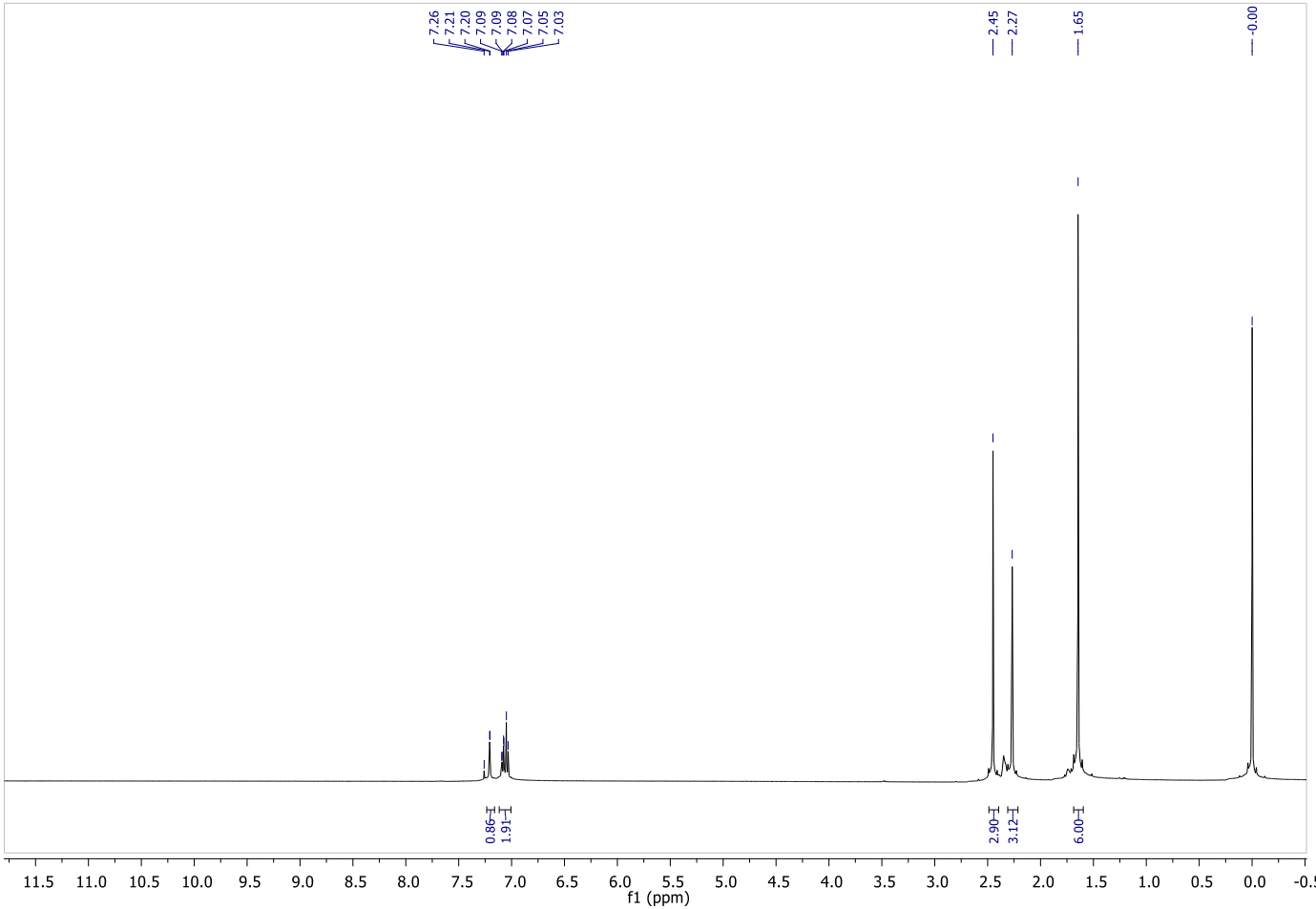
^{13}C NMR ($CDCl_3$, 125 MHz)



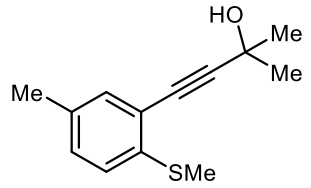
2-Methyl-4-(5-methyl-2-(methylthio)phenyl)but-3-yn-2-ol (**1e**)



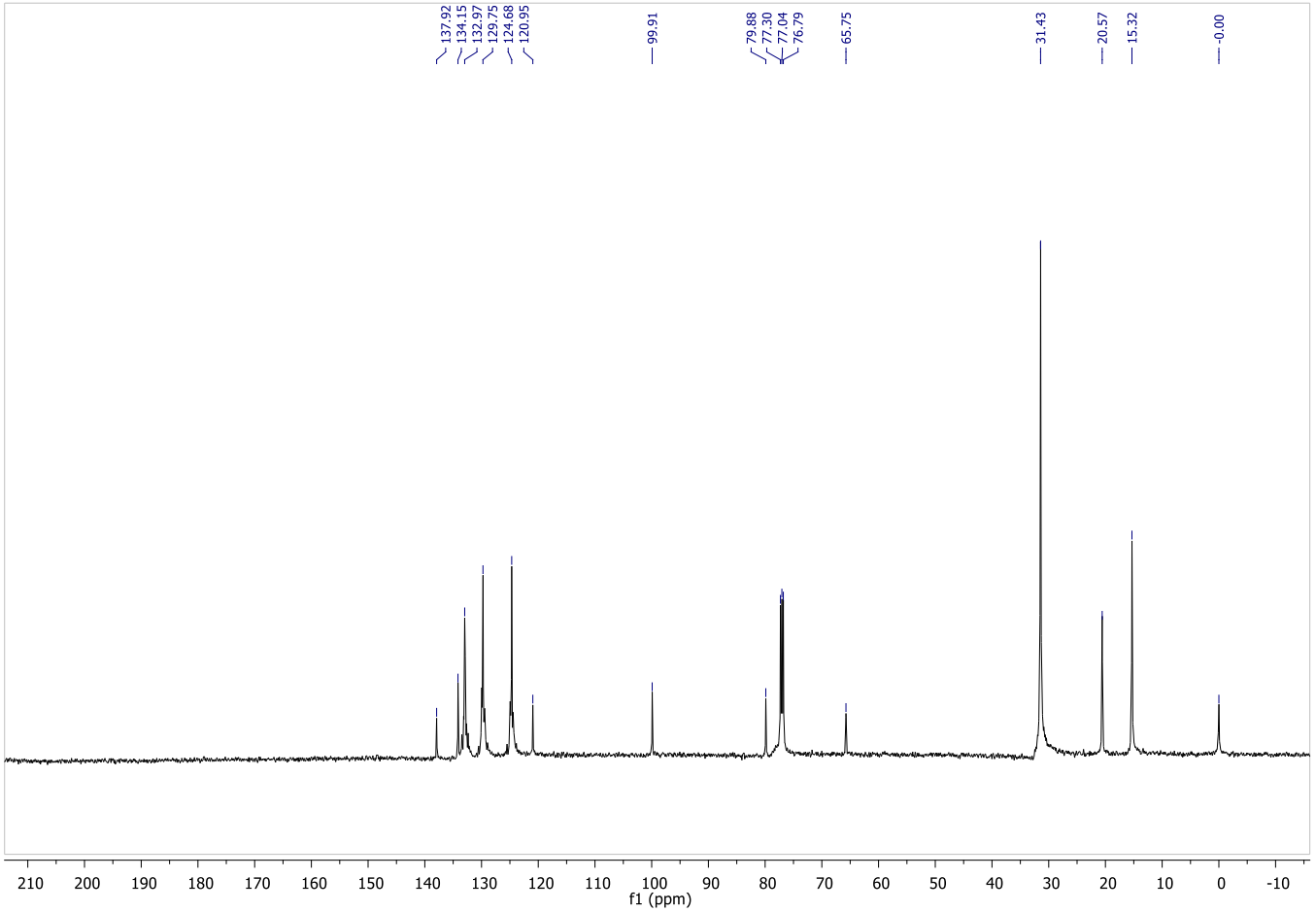
^{1}H NMR ($CDCl_3$, 500 MHz)



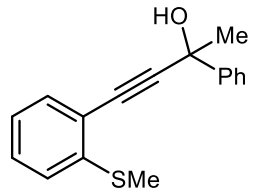
2-Methyl-4-(5-methyl-2-(methylthio)phenyl)but-3-yn-2-ol (**1e**)



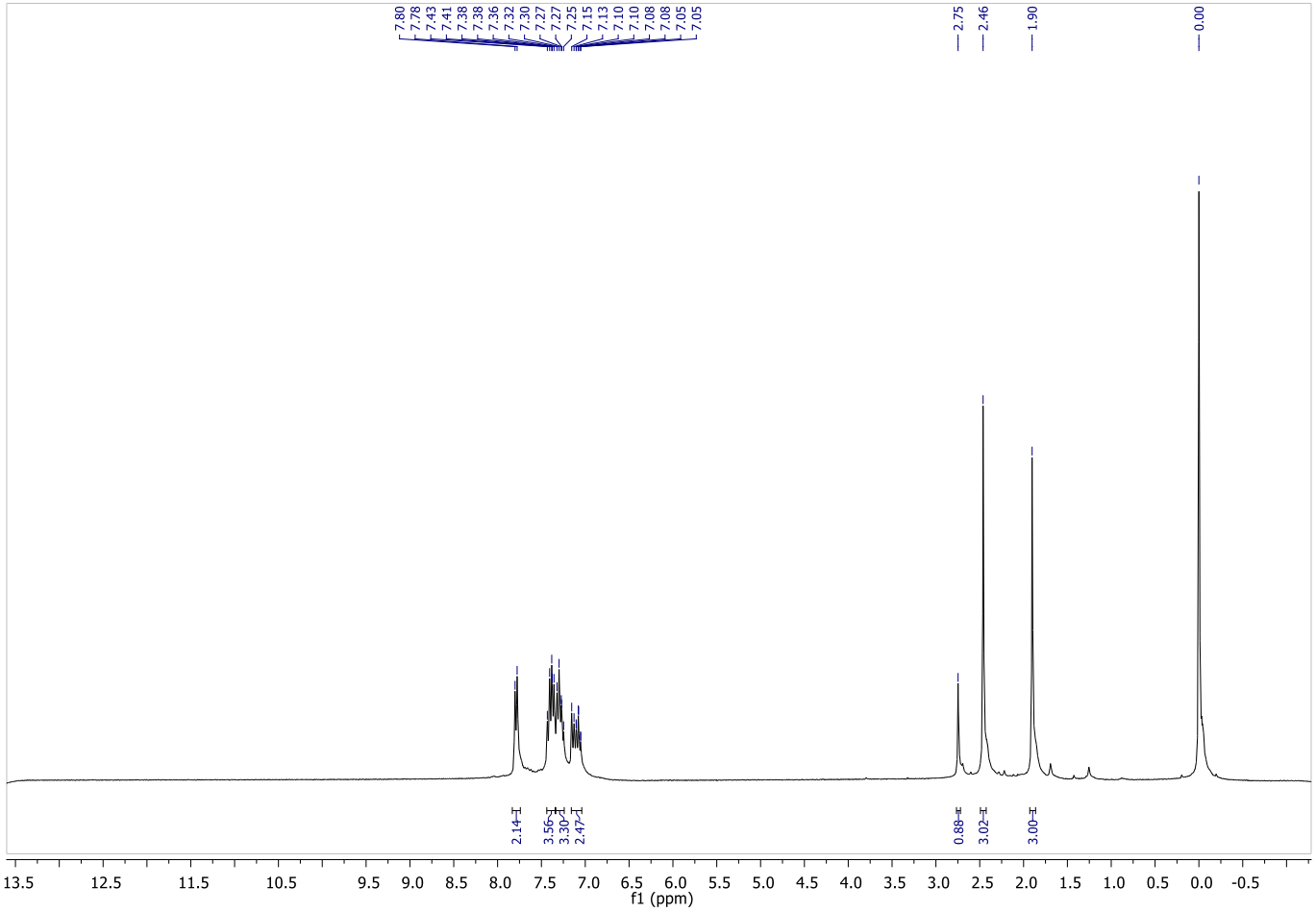
^{13}C NMR ($CDCl_3$, 125 MHz)



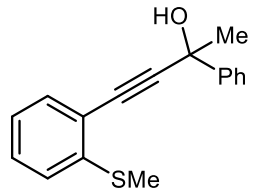
4-(2-(Methylthio)phenyl)-2-phenylbut-3-yn-2-ol (**1i**)



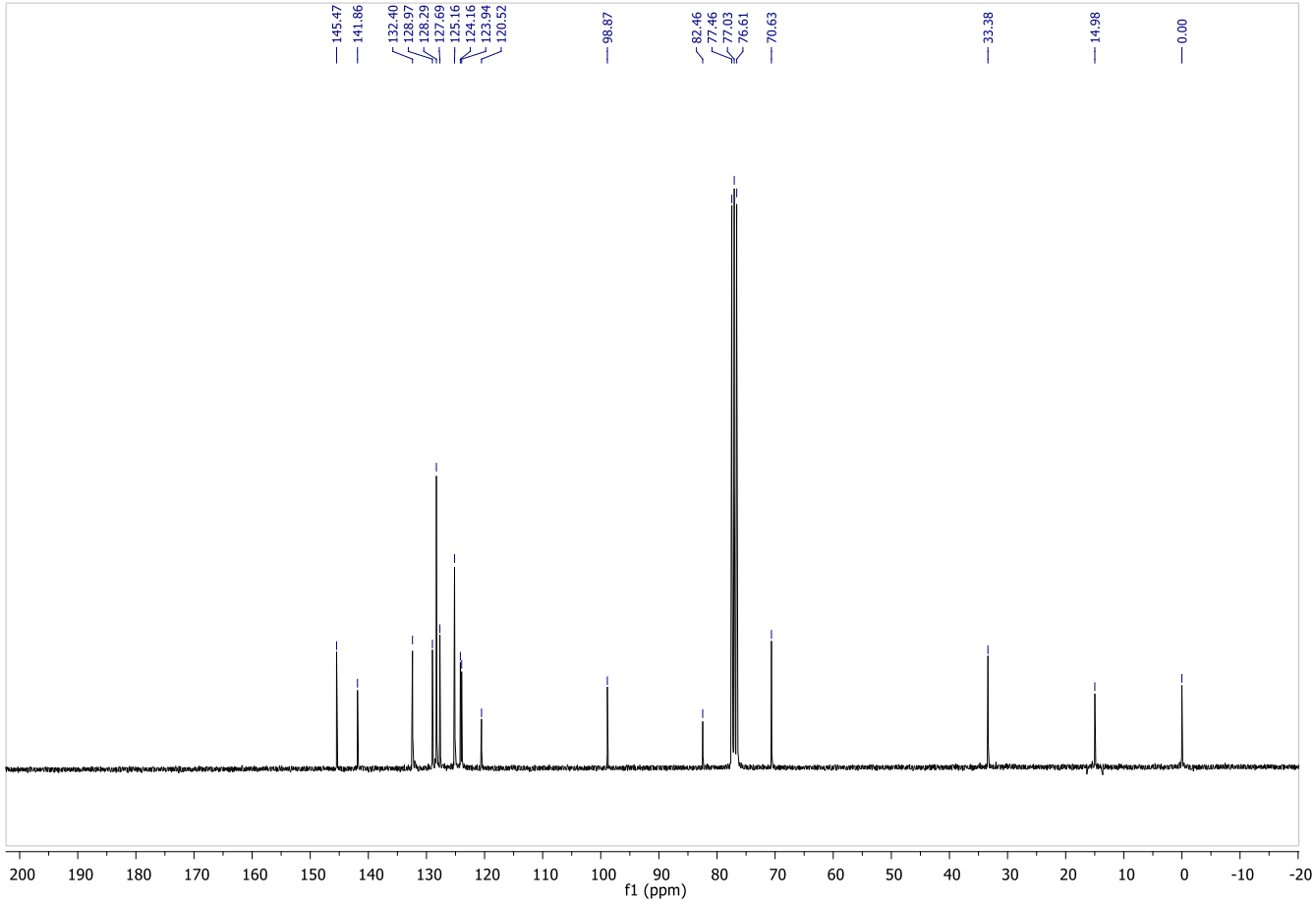
^{1}H NMR ($CDCl_3$, 300 MHz)



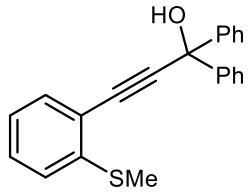
4-(2-(Methylthio)phenyl)-2-phenylbut-3-yn-2-ol (**1i**)



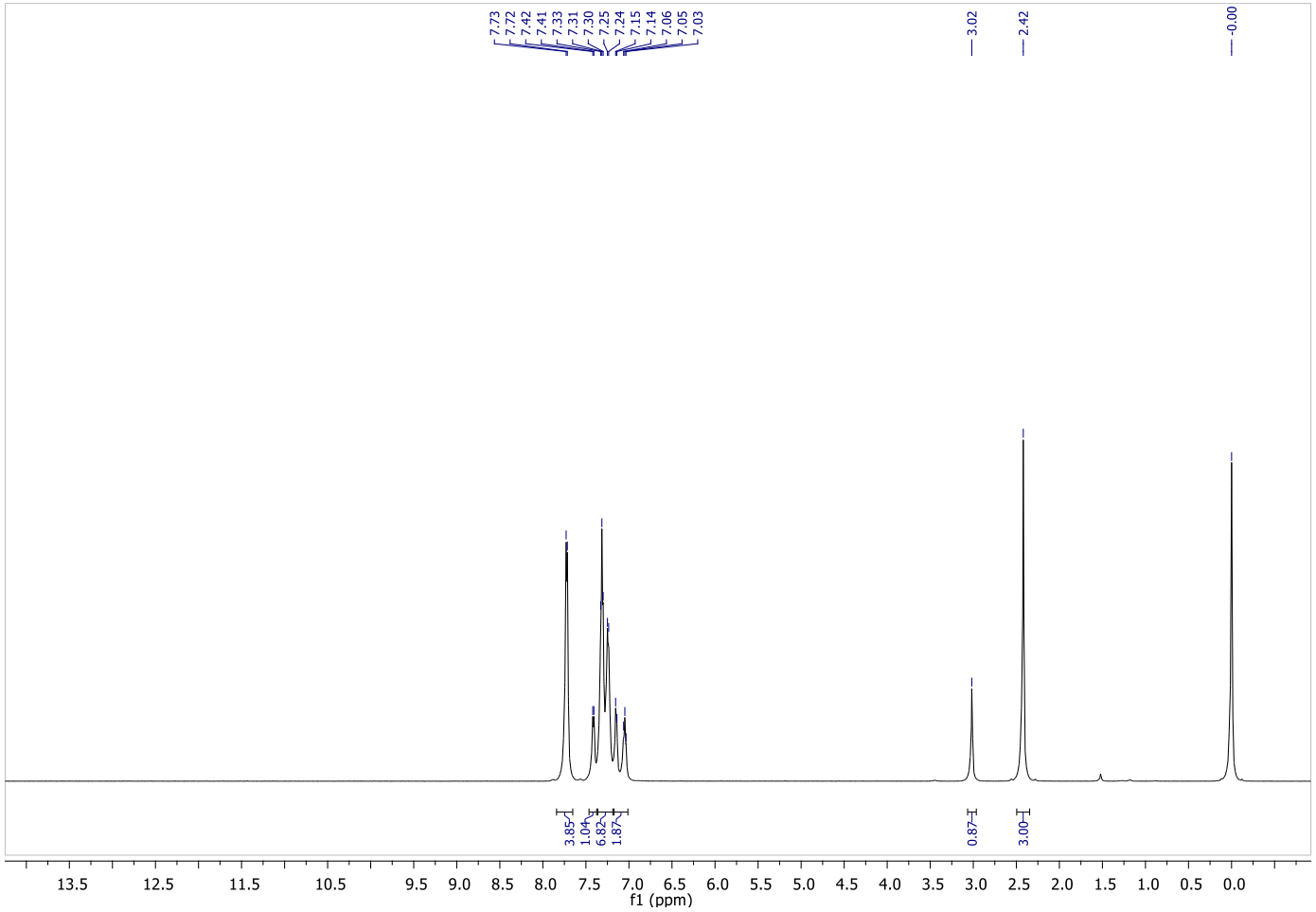
^{13}C NMR ($CDCl_3$, 75 MHz)



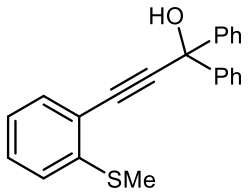
3-(2-(Methylthio)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1j**)



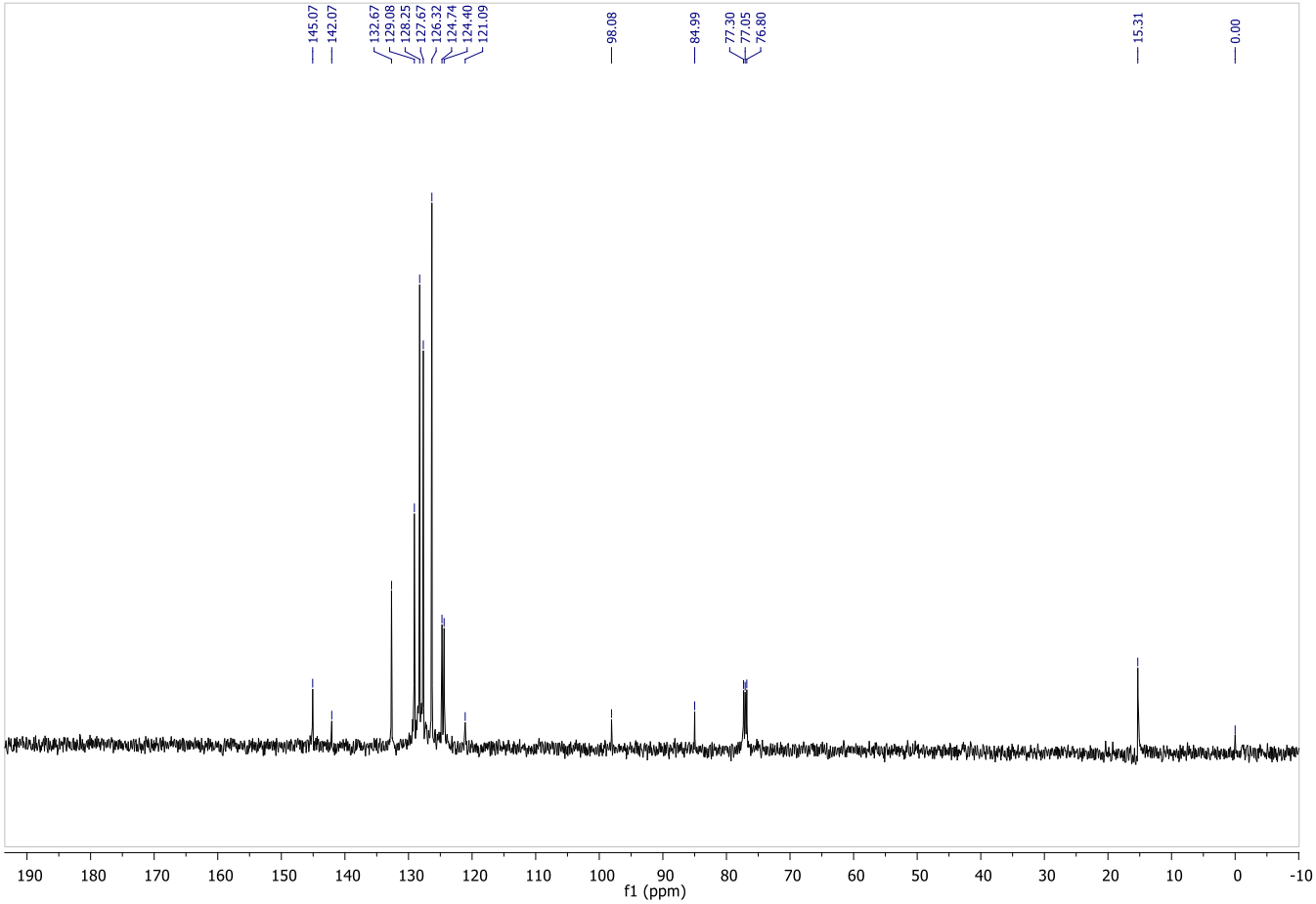
^{1}H NMR ($CDCl_3$, 500 MHz)



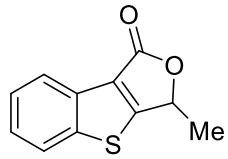
3-(2-(Methylthio)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1j**)



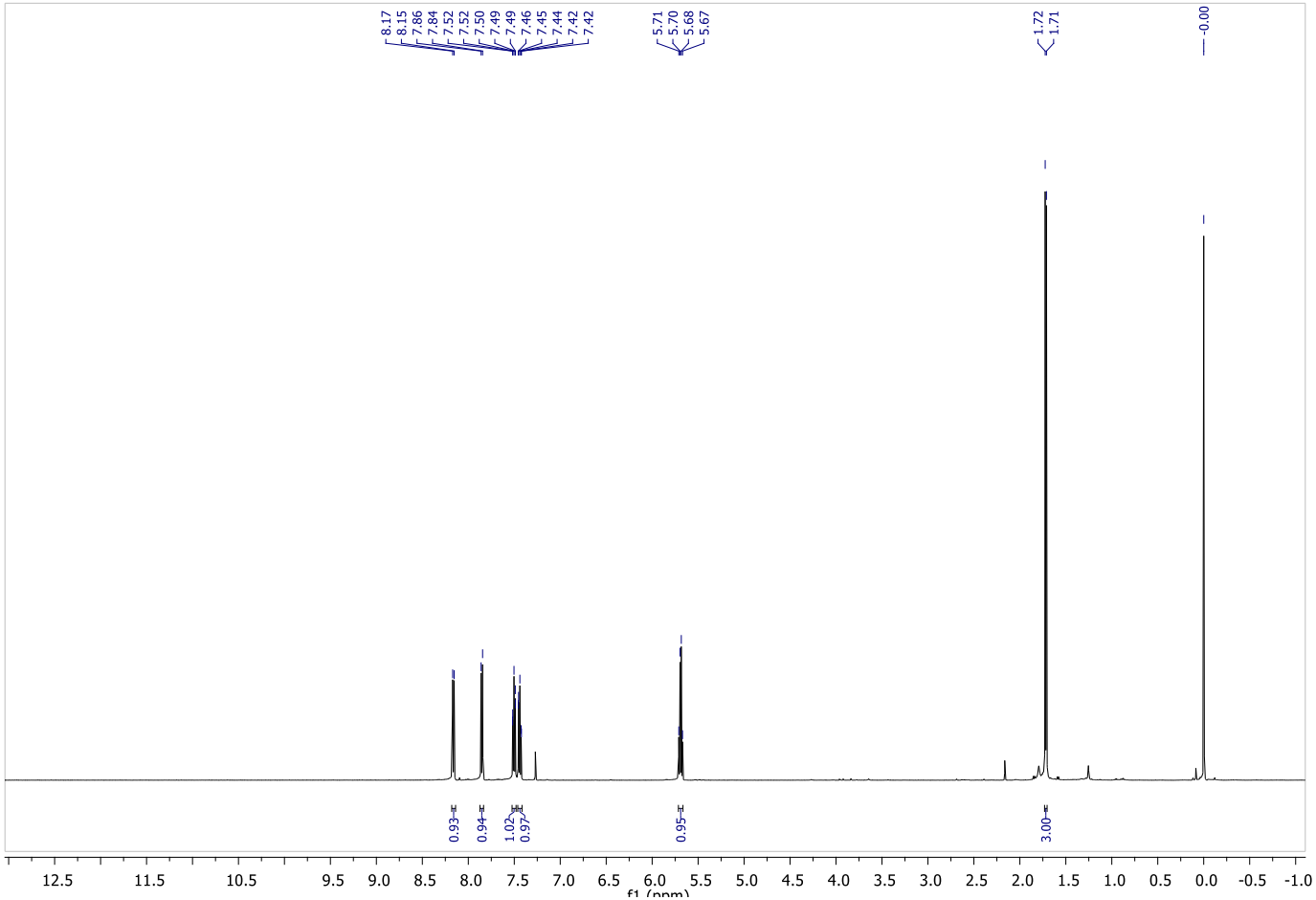
^{13}C NMR ($CDCl_3$, 125 MHz)



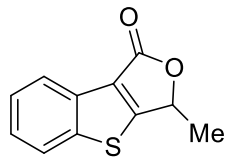
3-Methylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2a**)



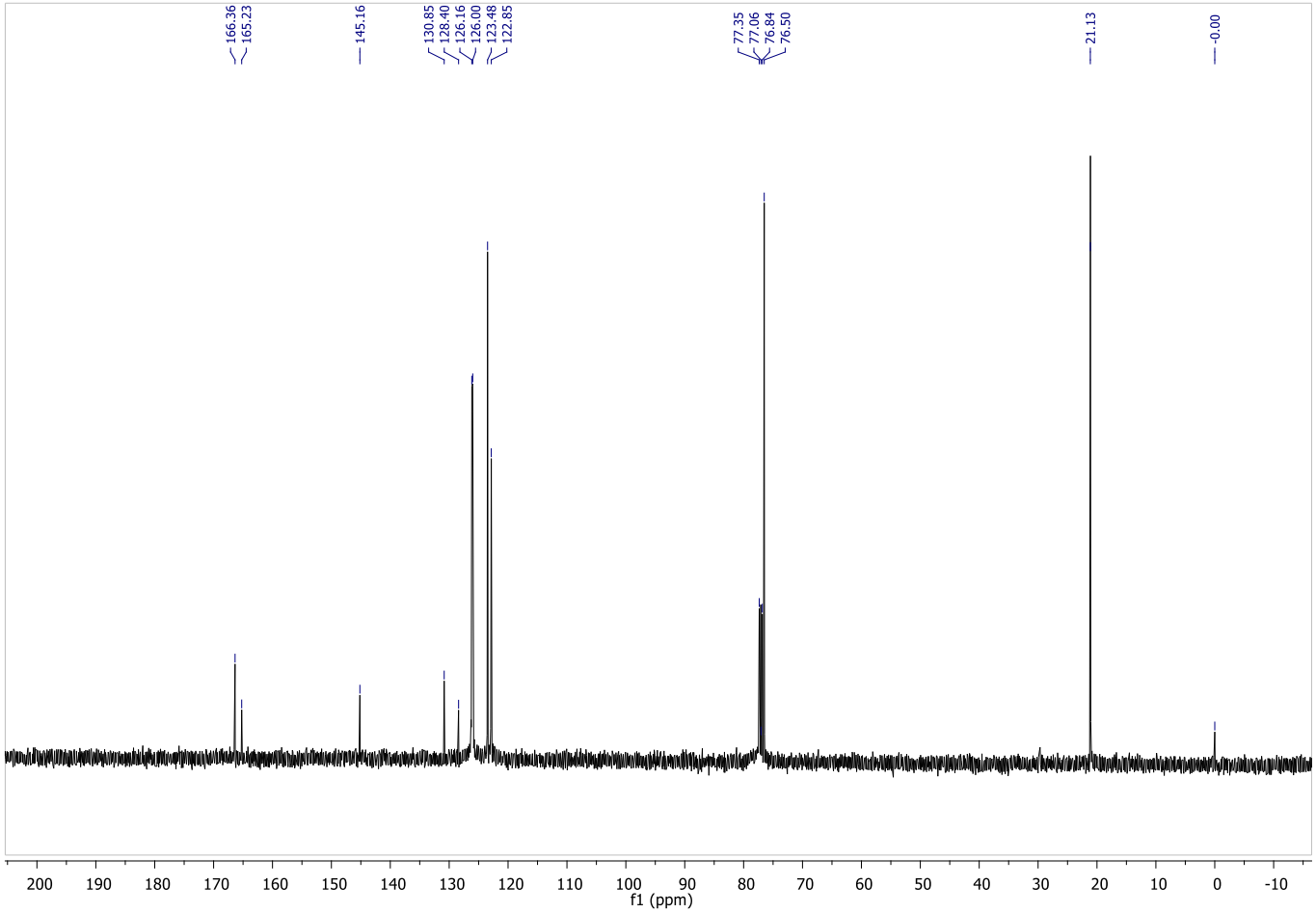
^{1}H NMR ($CDCl_3$, 500 MHz)



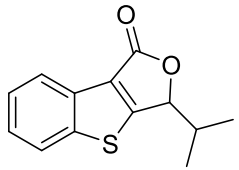
3-Methylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2a**)



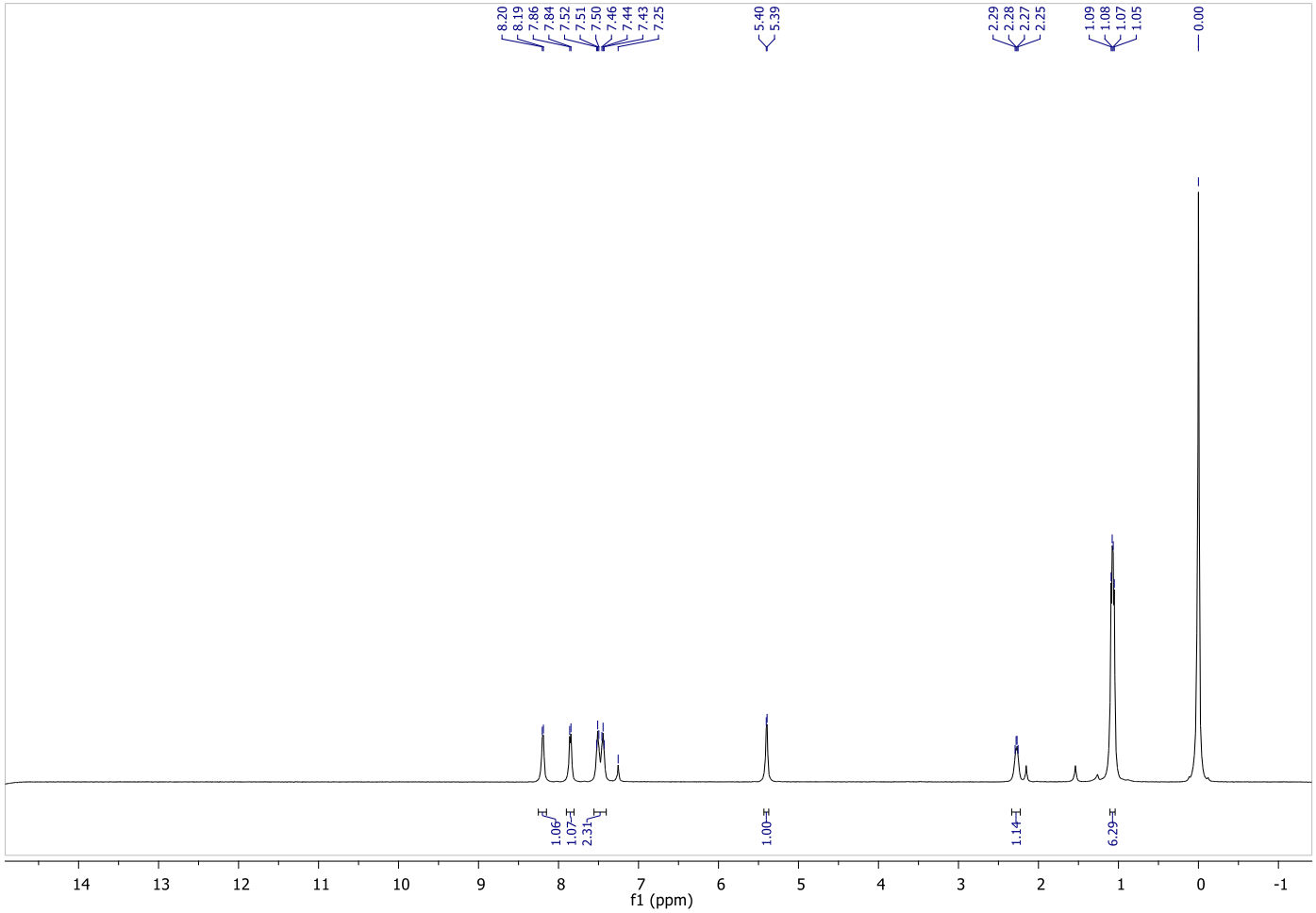
^{13}C NMR ($CDCl_3$, 125 MHz)



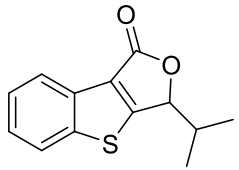
3-Isopropylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2b**)



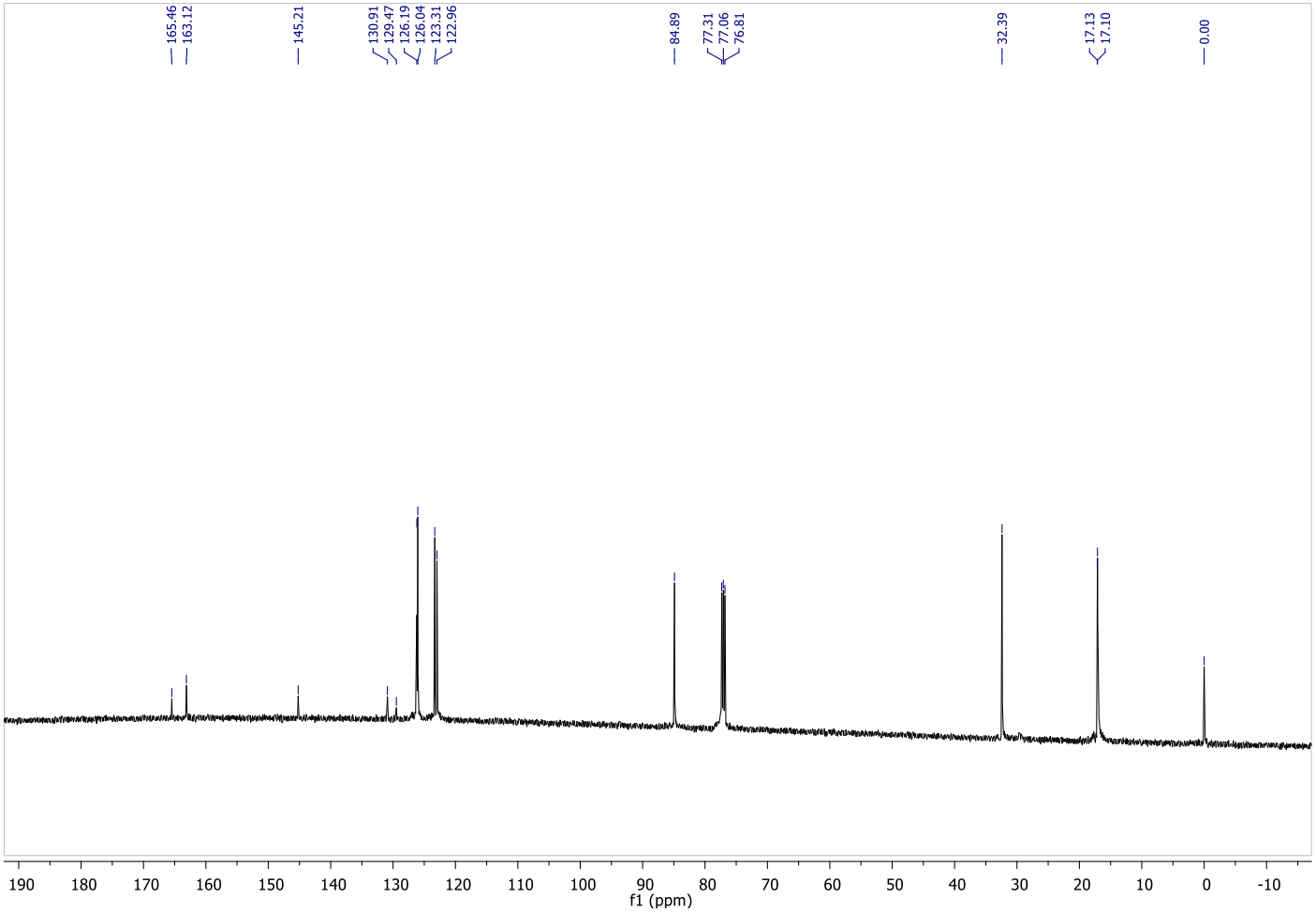
^{1}H NMR ($CDCl_3$, 500 MHz)



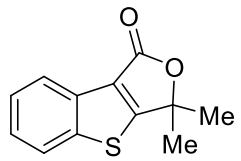
3-Isopropylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2b**)



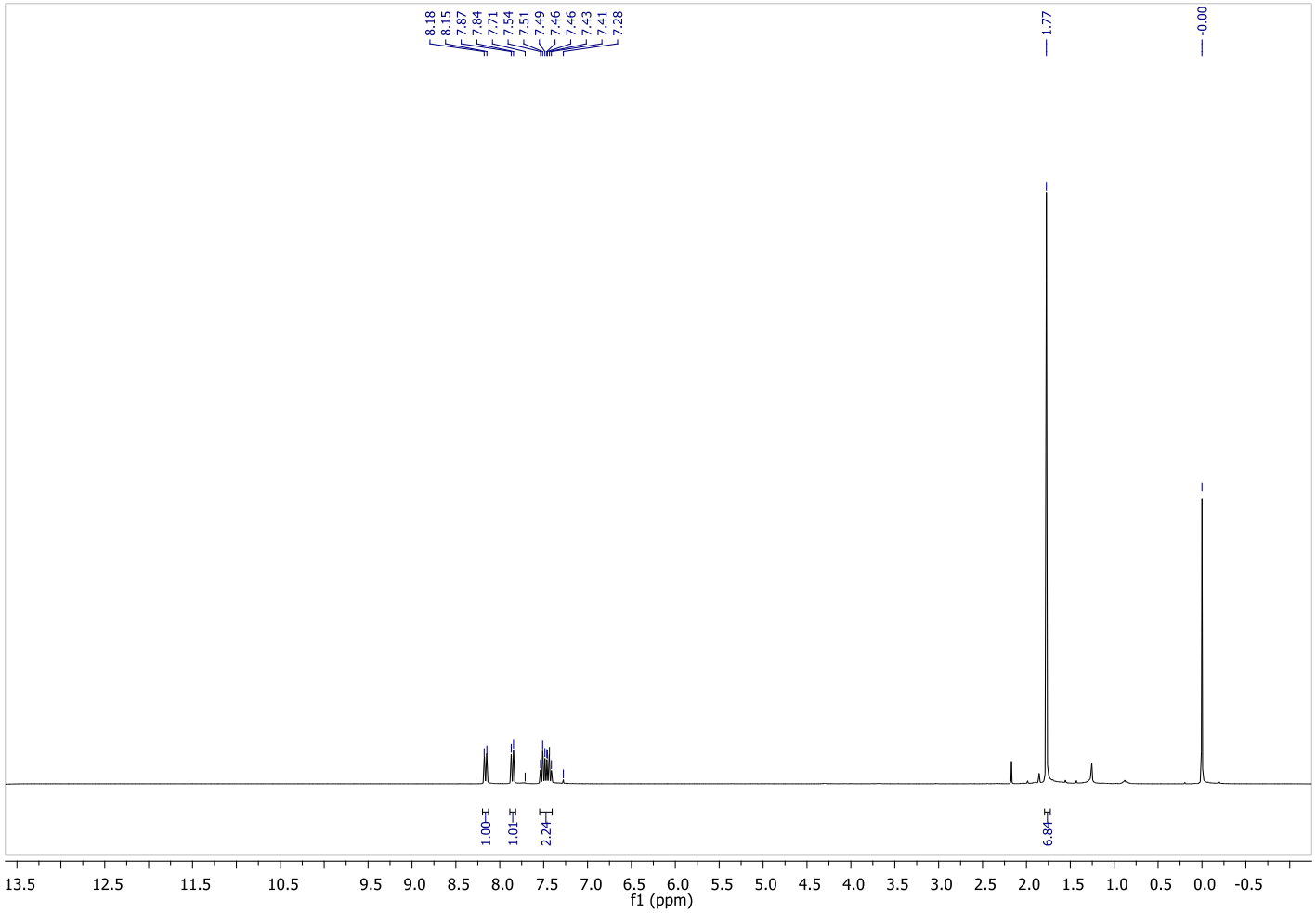
^{13}C NMR ($CDCl_3$, 125 MHz)



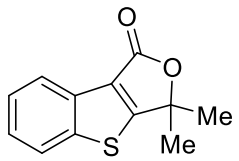
3,3-Dimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2c**)



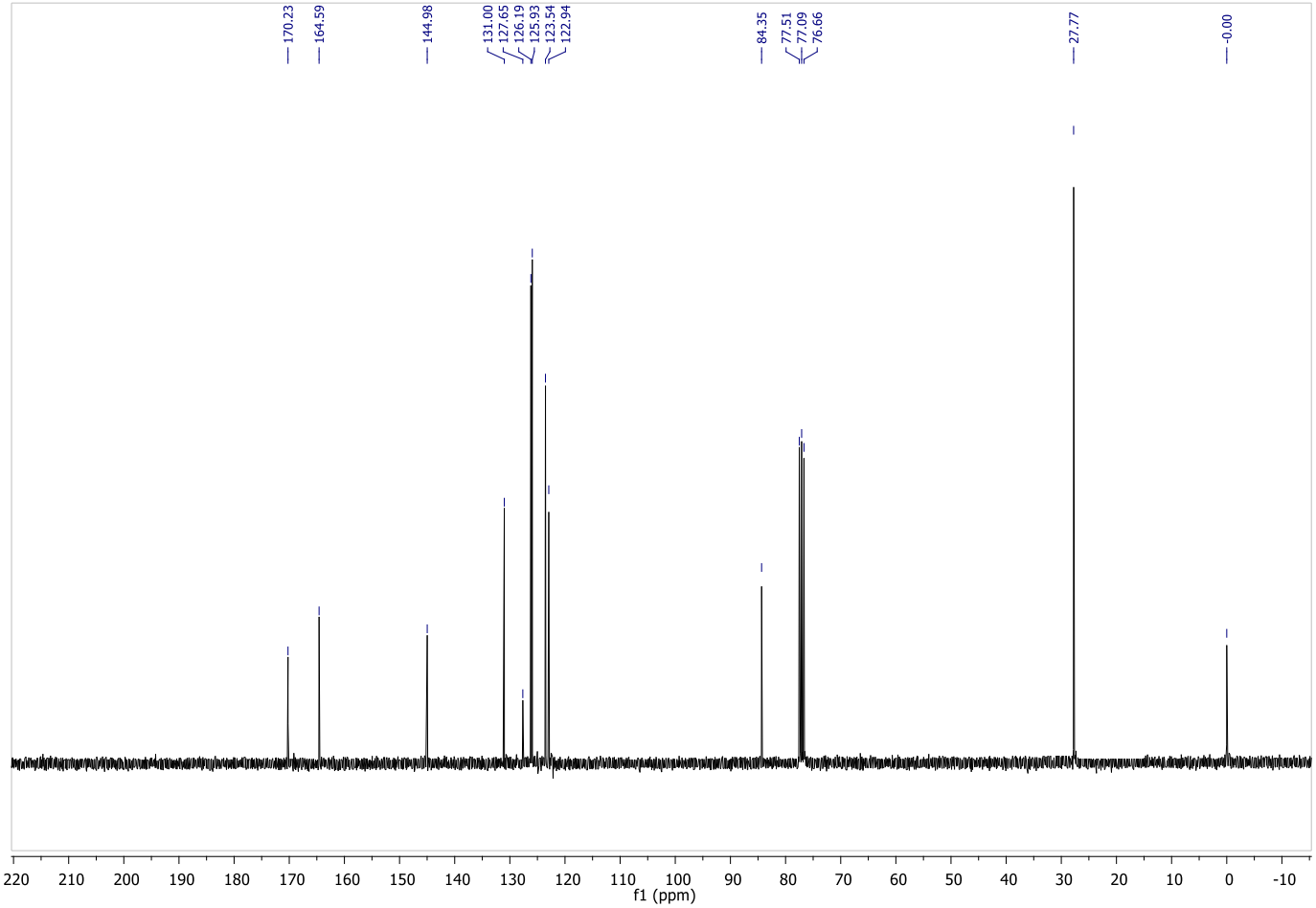
^{1}H NMR ($CDCl_3$, 500 MHz)



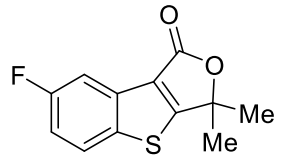
3,3-Dimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2c**)



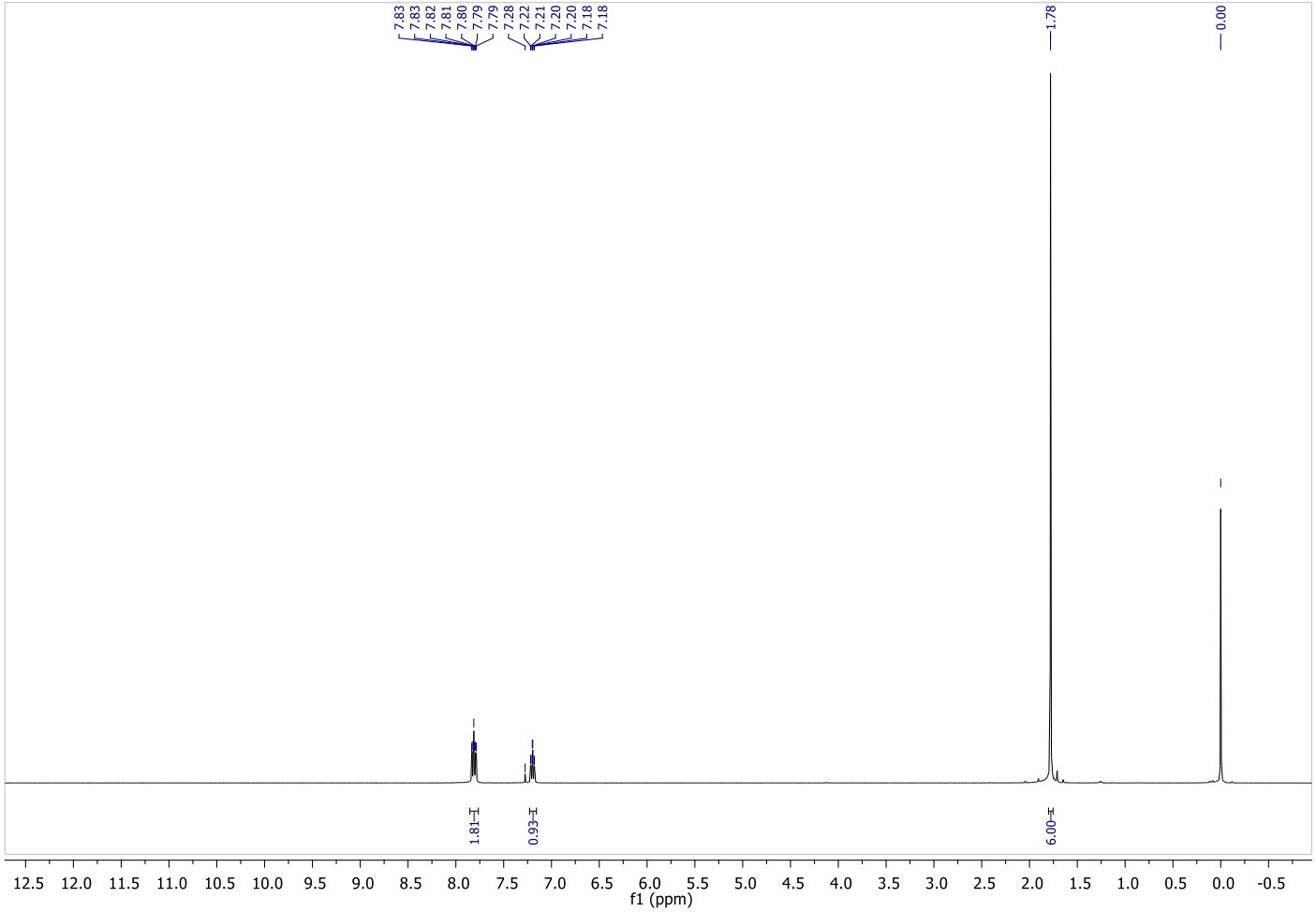
^{13}C NMR ($CDCl_3$, 125 MHz)



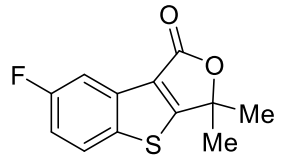
7-Fluoro-3,3-dimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2d**)



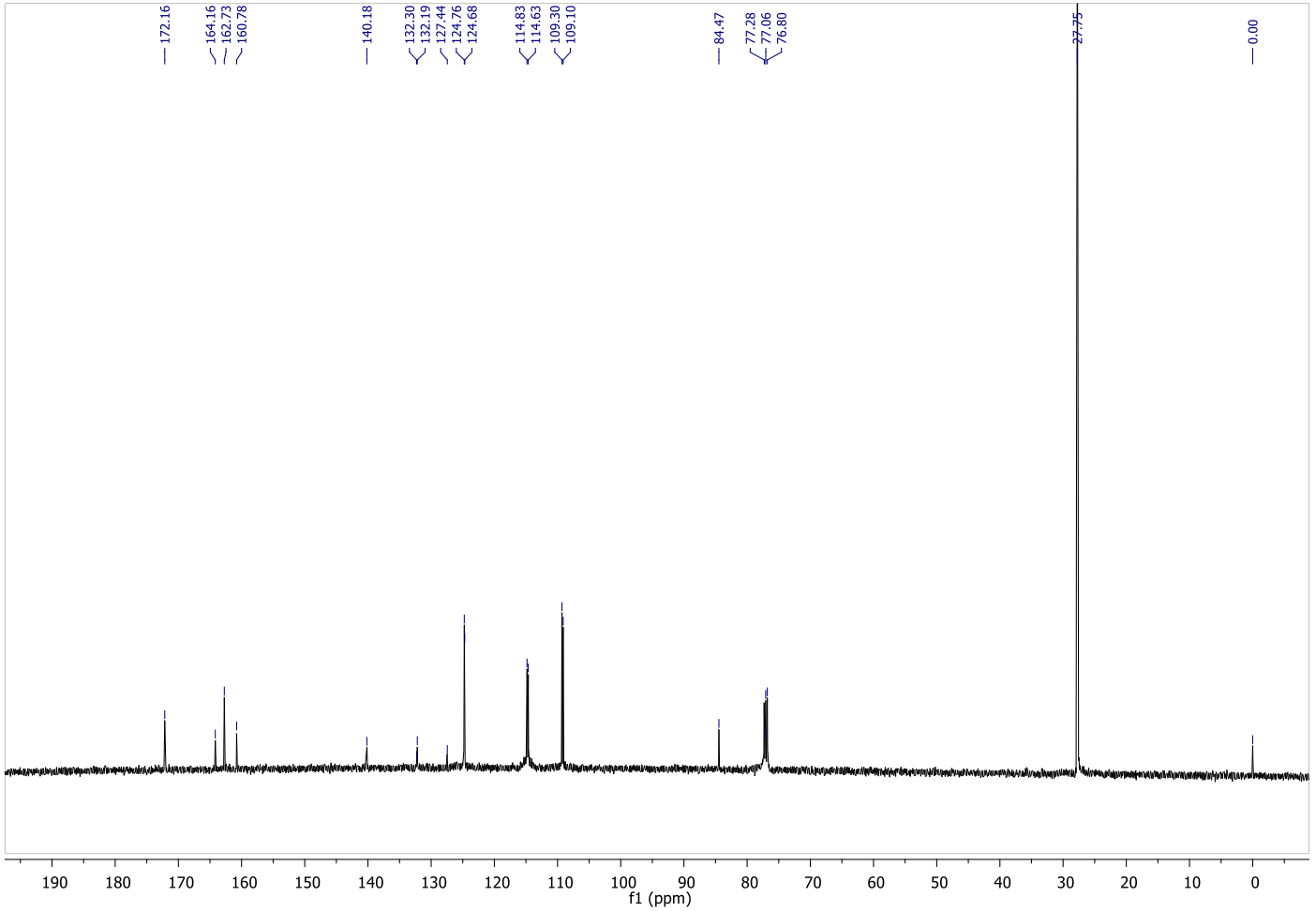
^{1}H NMR ($CDCl_3$, 500 MHz)



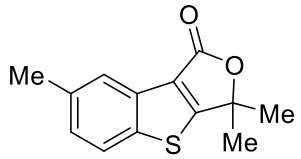
7-Fluoro-3,3-dimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2d**)



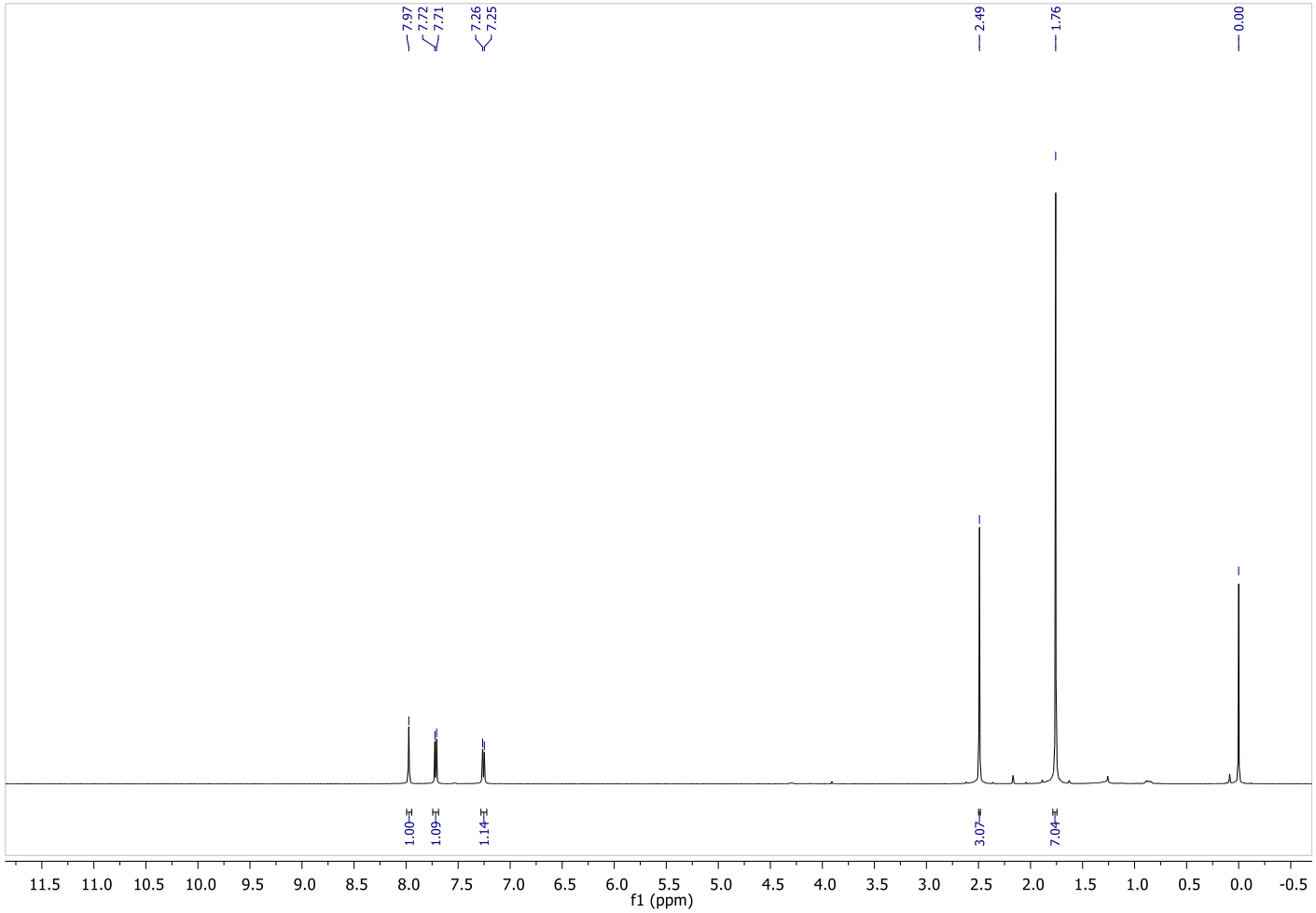
^{13}C NMR ($CDCl_3$, 125 MHz)



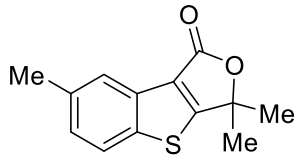
3,3,7-trimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2e**)



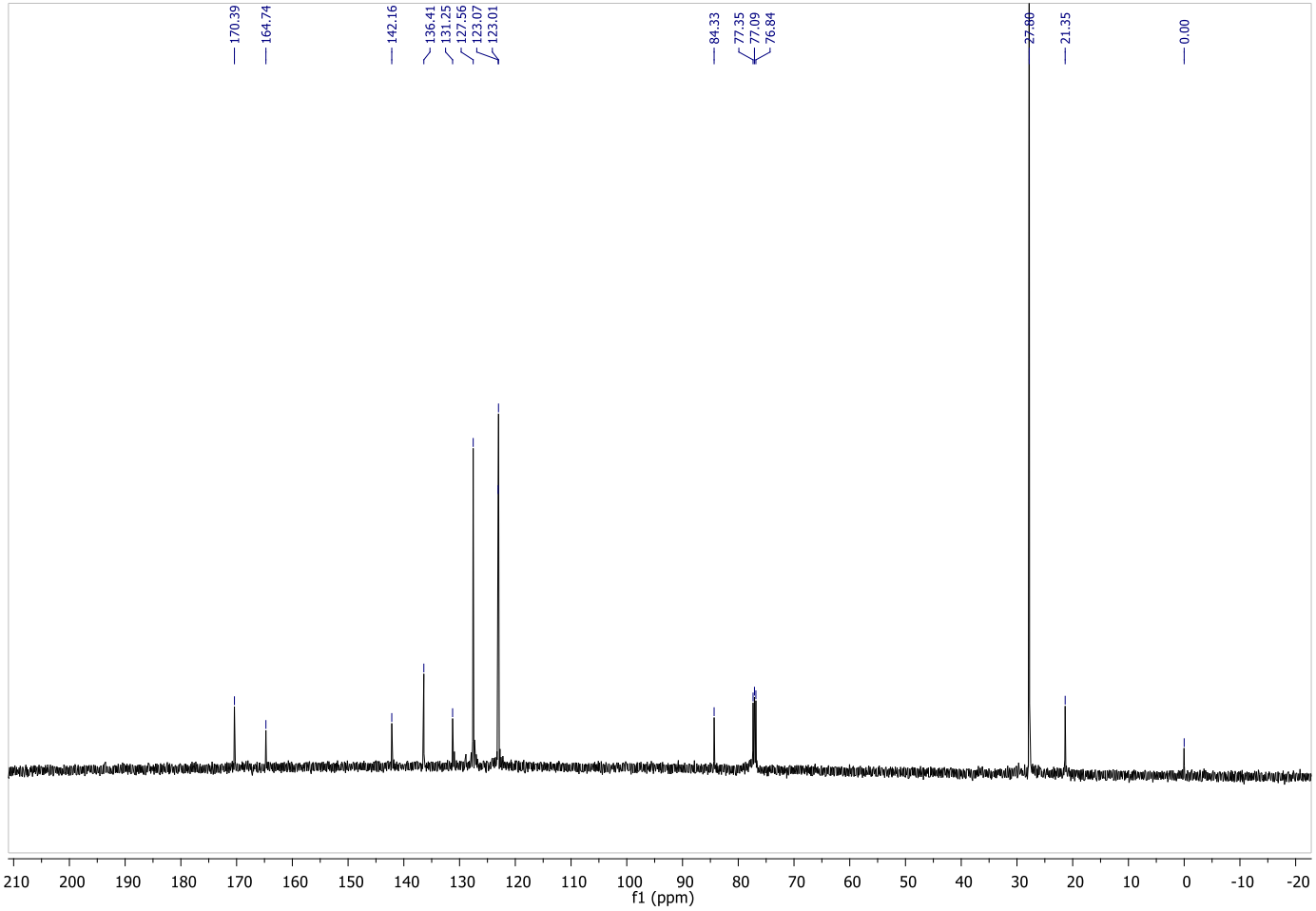
^{1}H NMR ($CDCl_3$, 500 MHz)



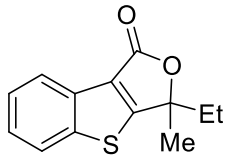
3,3,7-trimethylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2e**)



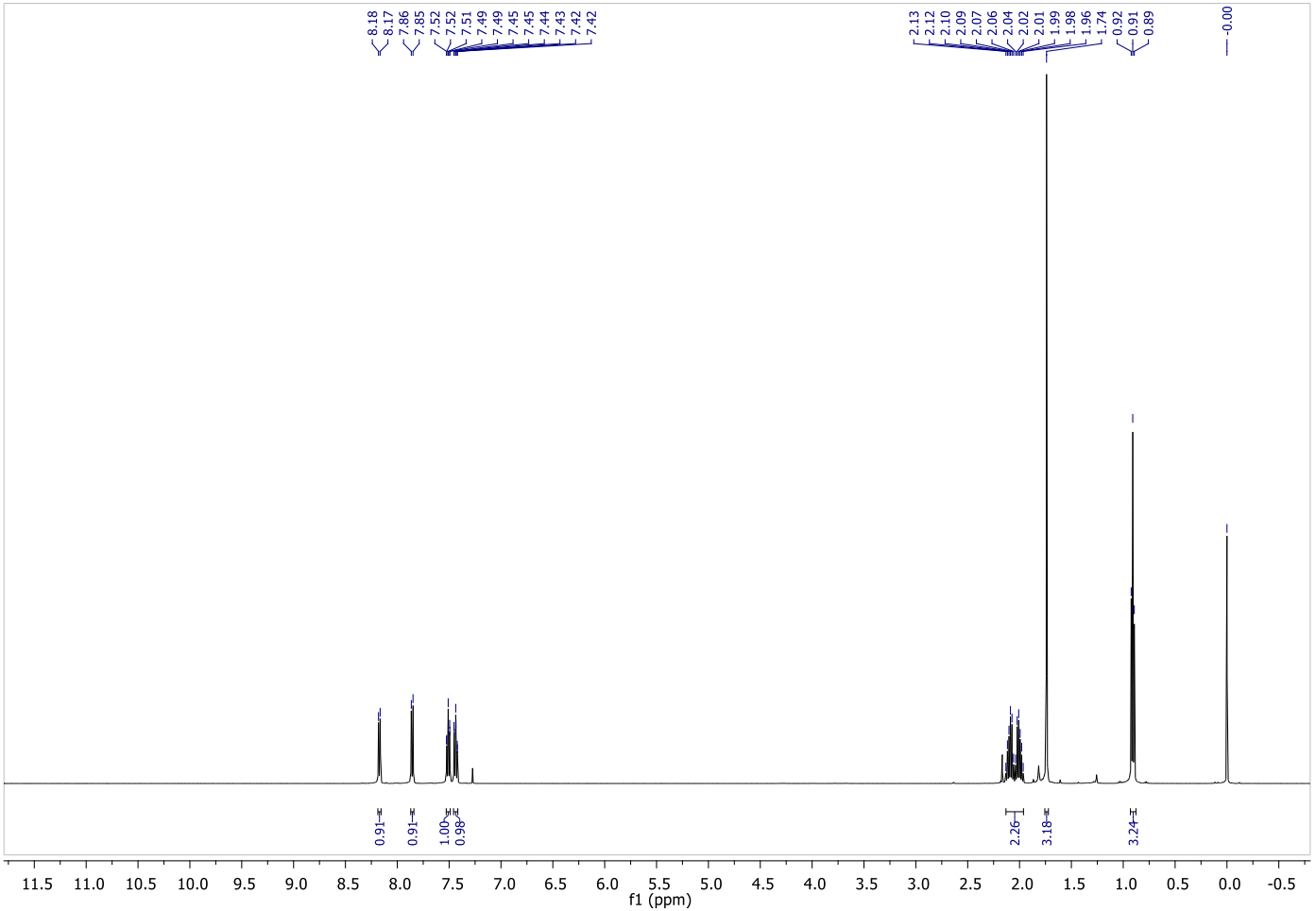
^{13}C NMR ($CDCl_3$, 125 MHz)



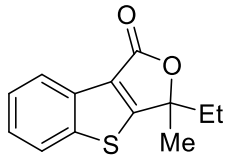
3-Ethyl-3-methylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2f**)



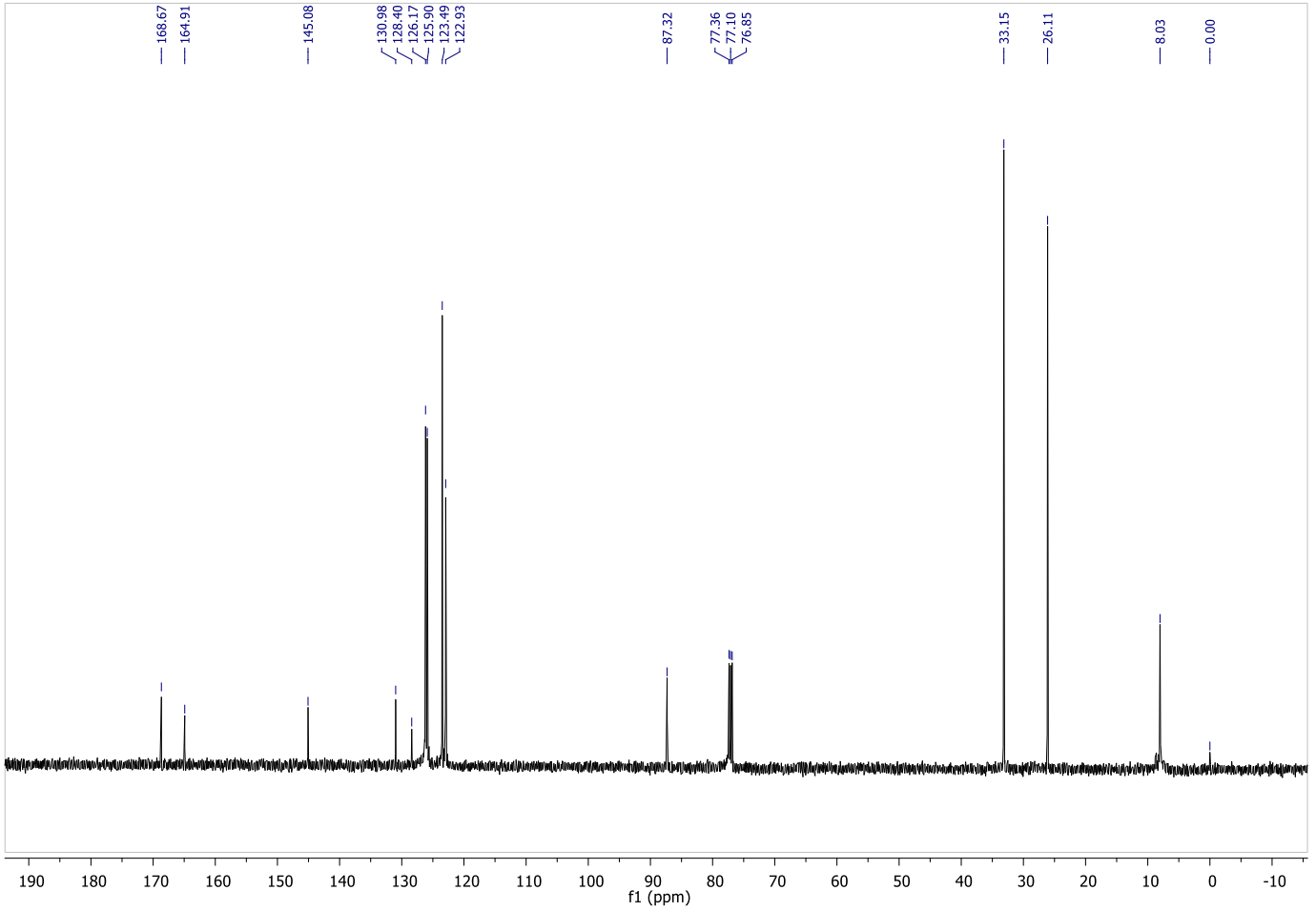
^{1}H NMR ($CDCl_3$, 500 MHz)



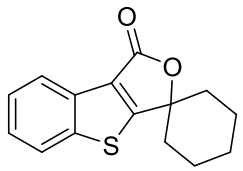
3-Ethyl-3-methylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2f**)



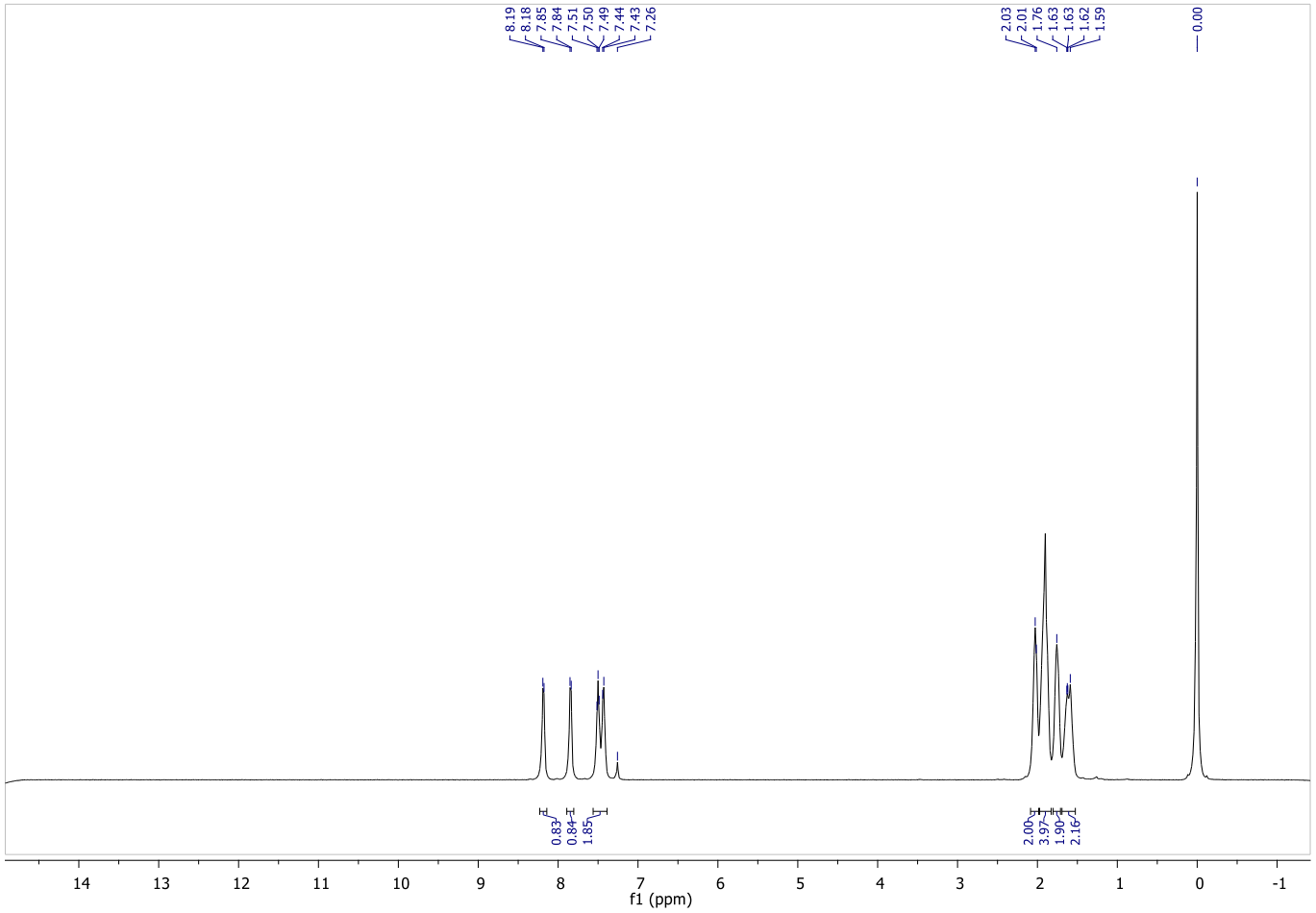
^{13}C NMR ($CDCl_3$, 125 MHz)



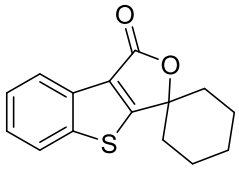
1*H*-Spiro[benzo[4,5]thieno[2,3-*c*]furan-3,1'-cyclohexan]-1-one (**2g**)



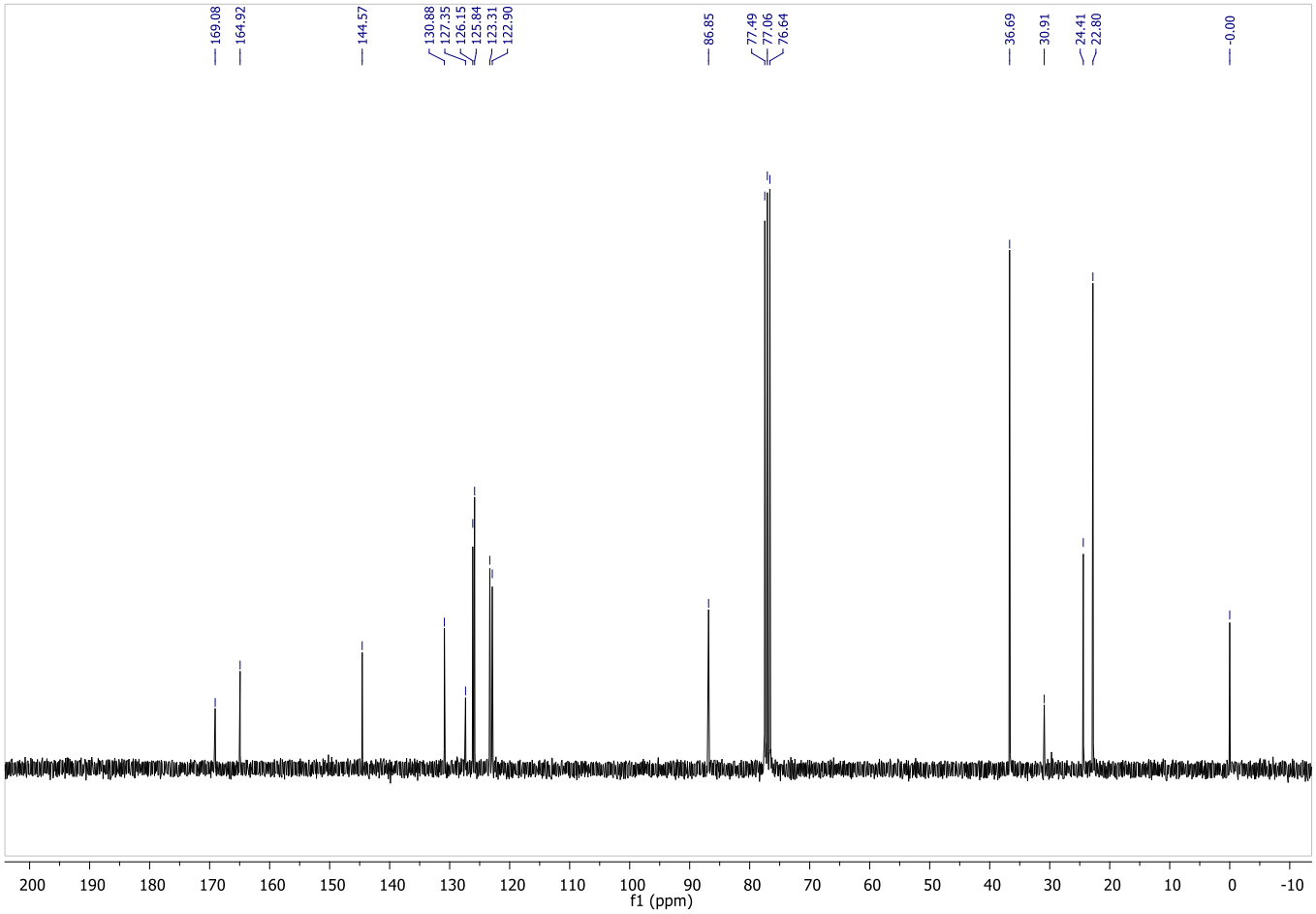
^{1}H NMR ($CDCl_3$, 500 MHz)



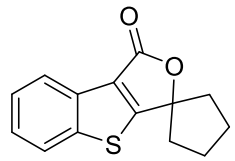
1*H*-Spiro[benzo[4,5]thieno[2,3-*c*]furan-3,1'-cyclohexan]-1-one (**2g**)



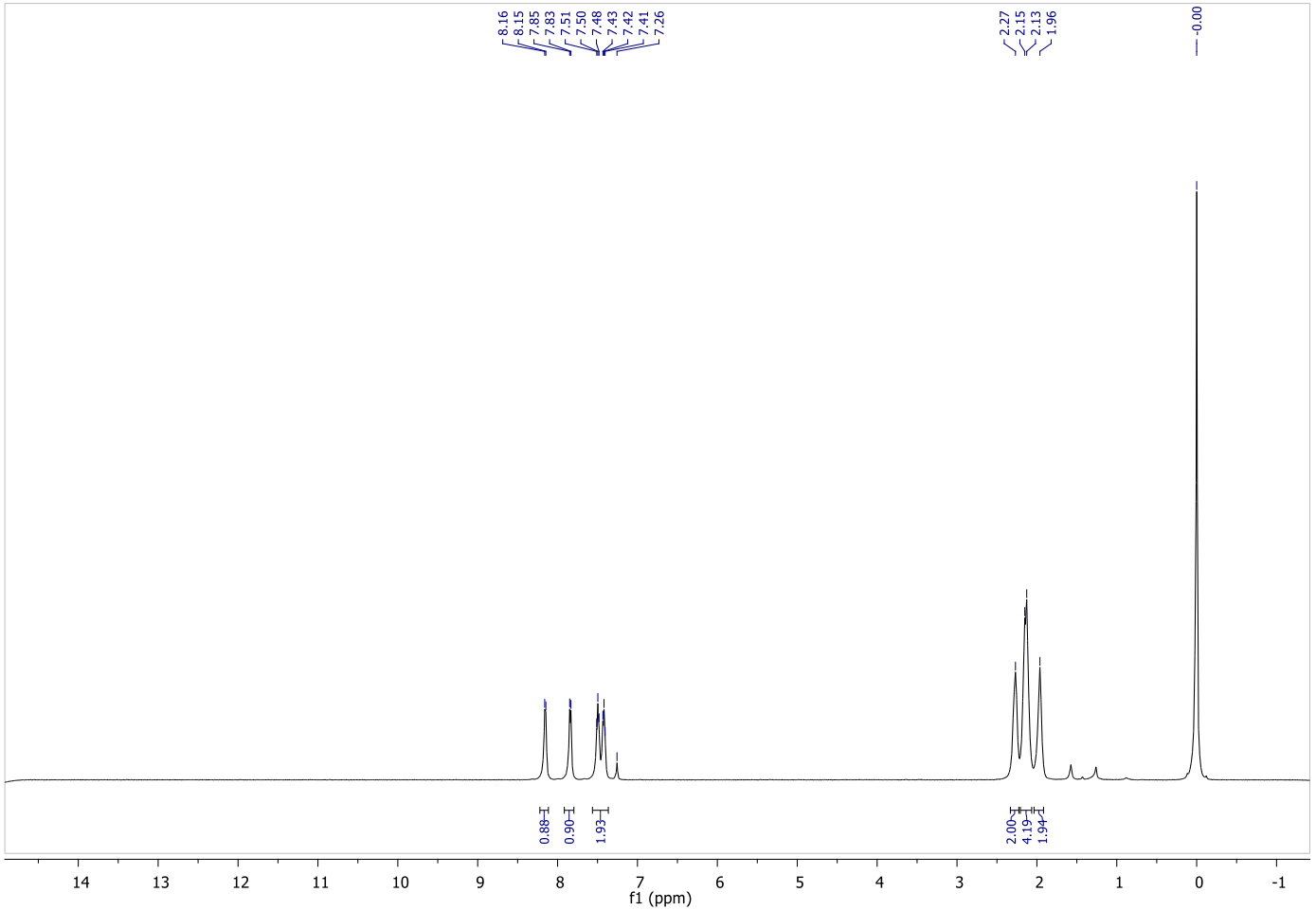
^{13}C NMR ($CDCl_3$, 125 MHz)



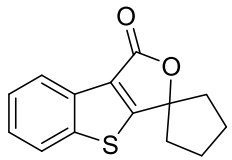
1*H*-Spiro[benzo[4,5]thieno[2,3-*c*]furan-3,1'-cyclopentan]-1-one (**2h**)



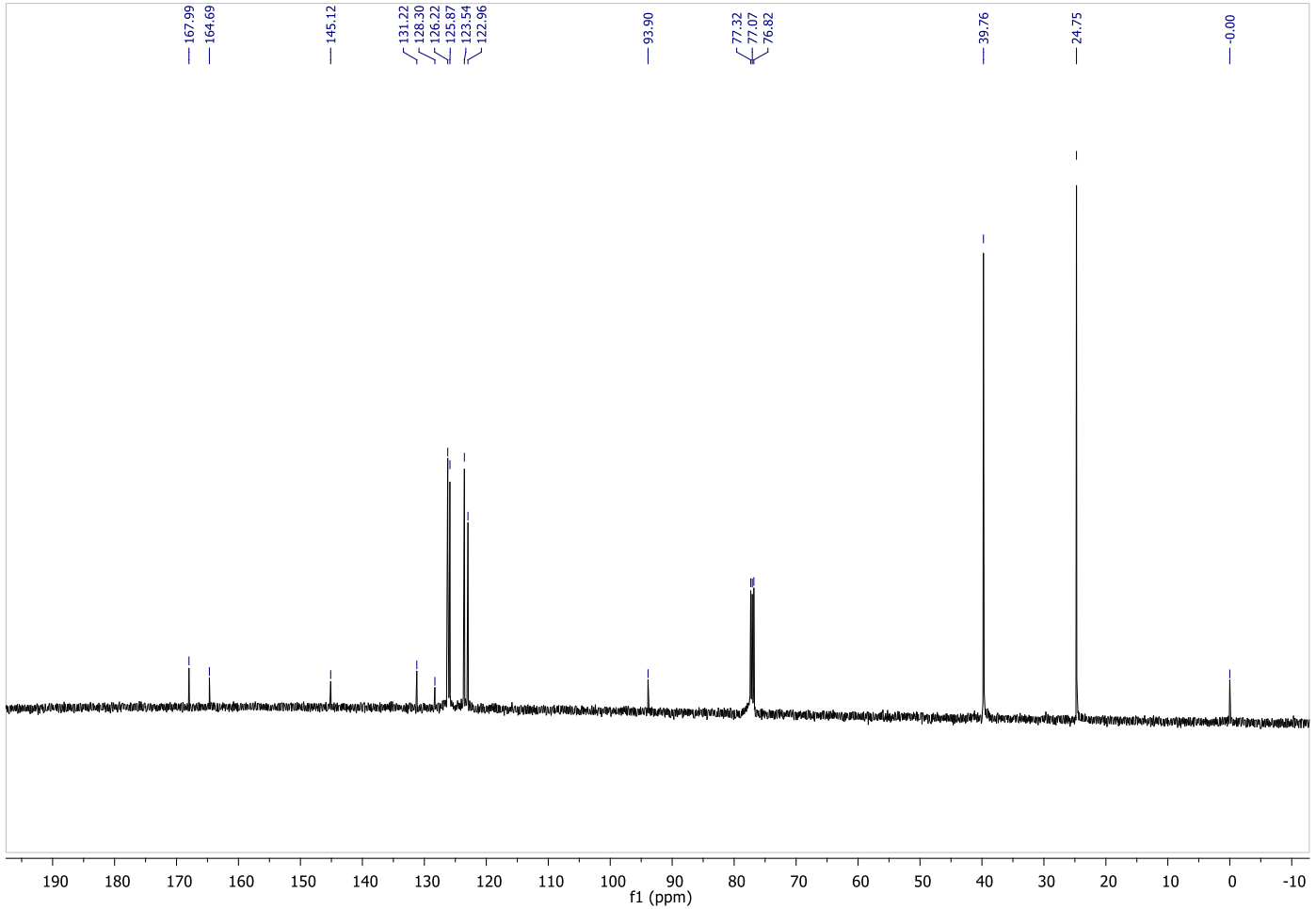
^{1}H NMR ($CDCl_3$, 500 MHz)



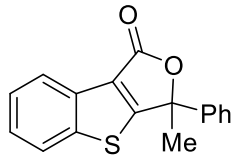
1*H*-Spiro[benzo[4,5]thieno[2,3-*c*]furan-3,1'-cyclopentan]-1-one (**2h**)



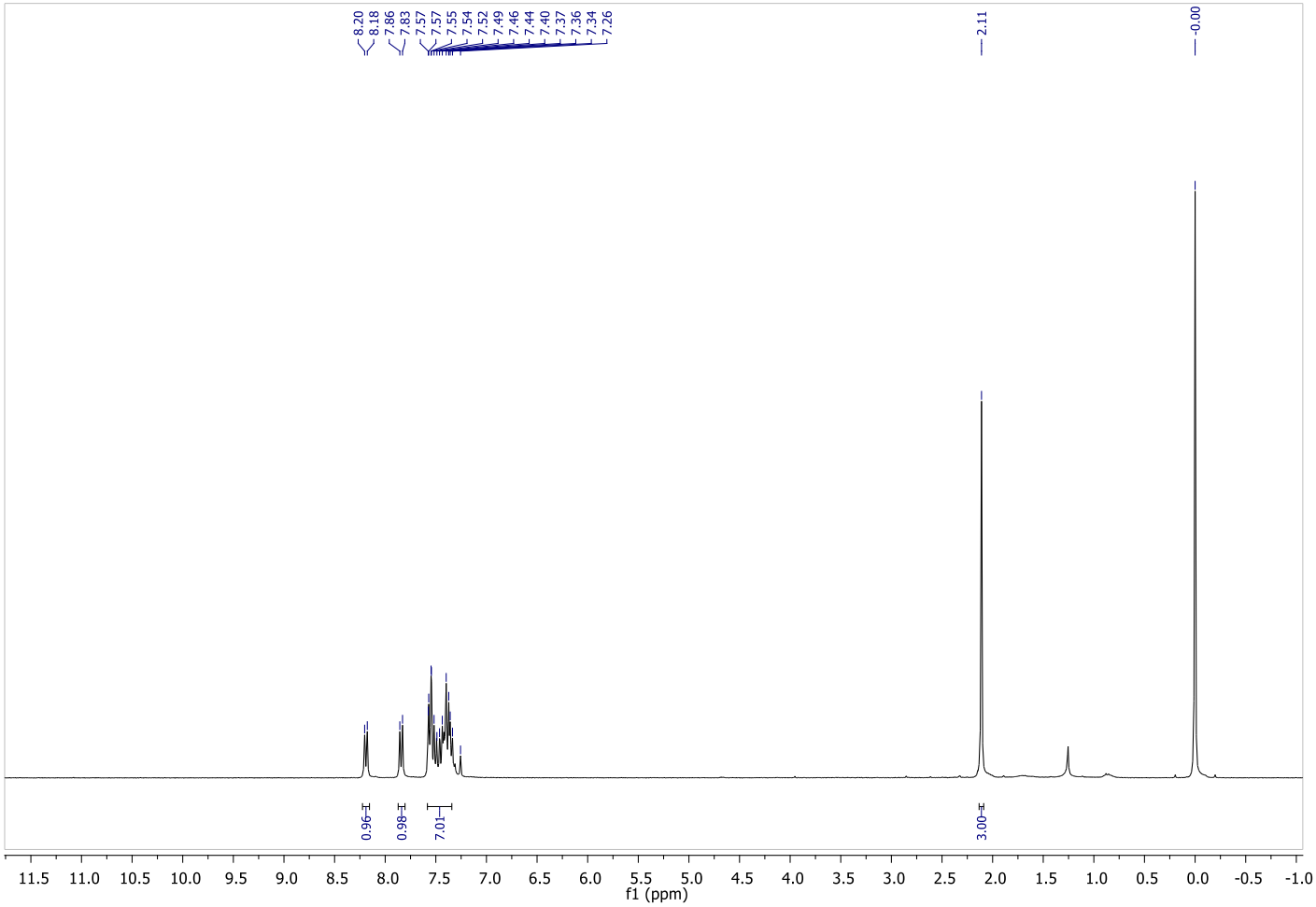
^{13}C NMR ($CDCl_3$, 125 MHz)



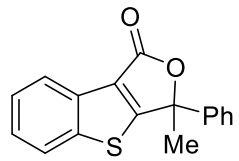
3-Methyl-3-phenylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2i**)



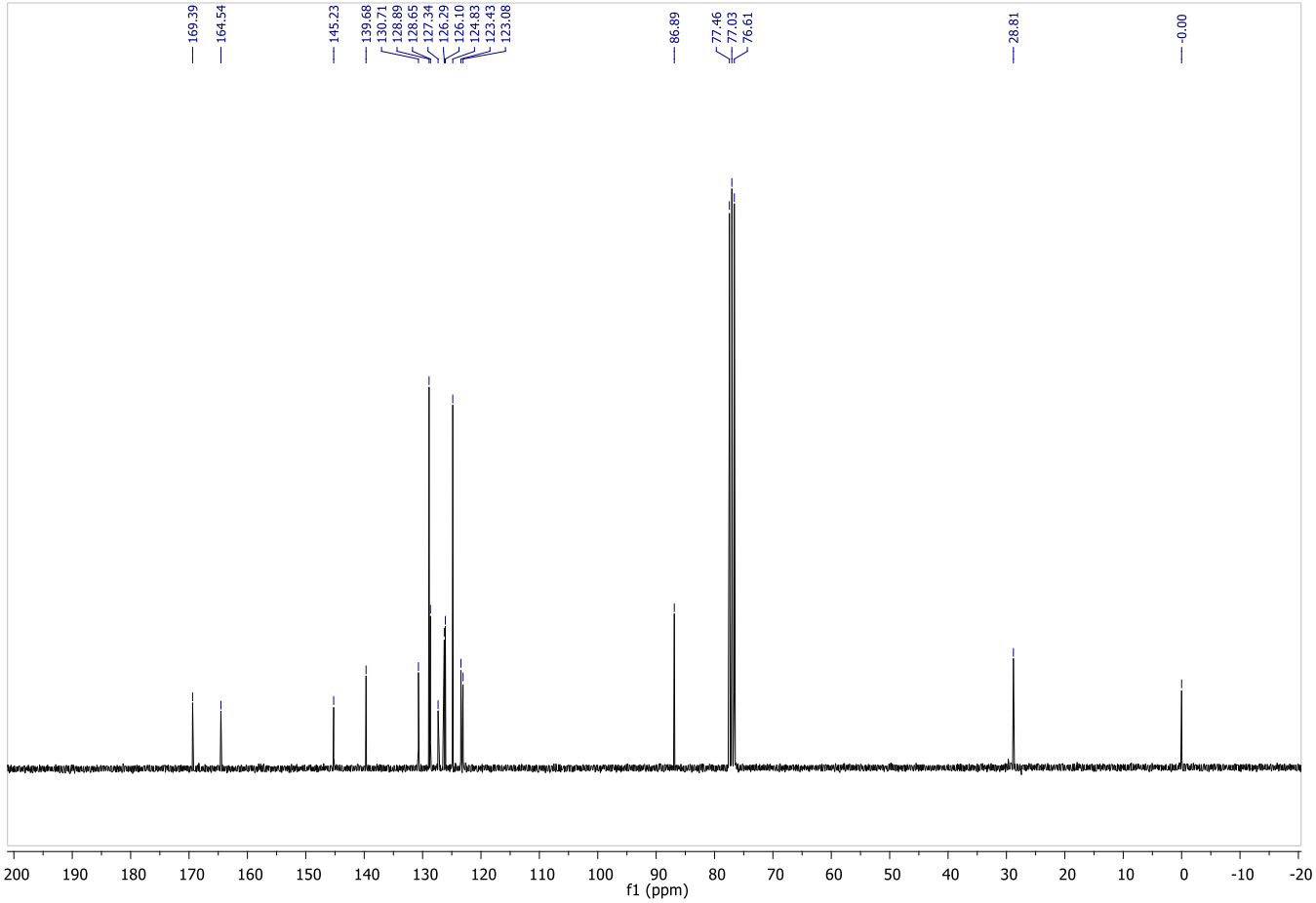
^{1}H NMR ($CDCl_3$, 300 MHz)



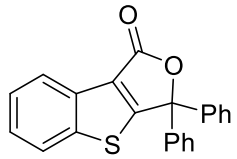
3-Methyl-3-phenylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2i**)



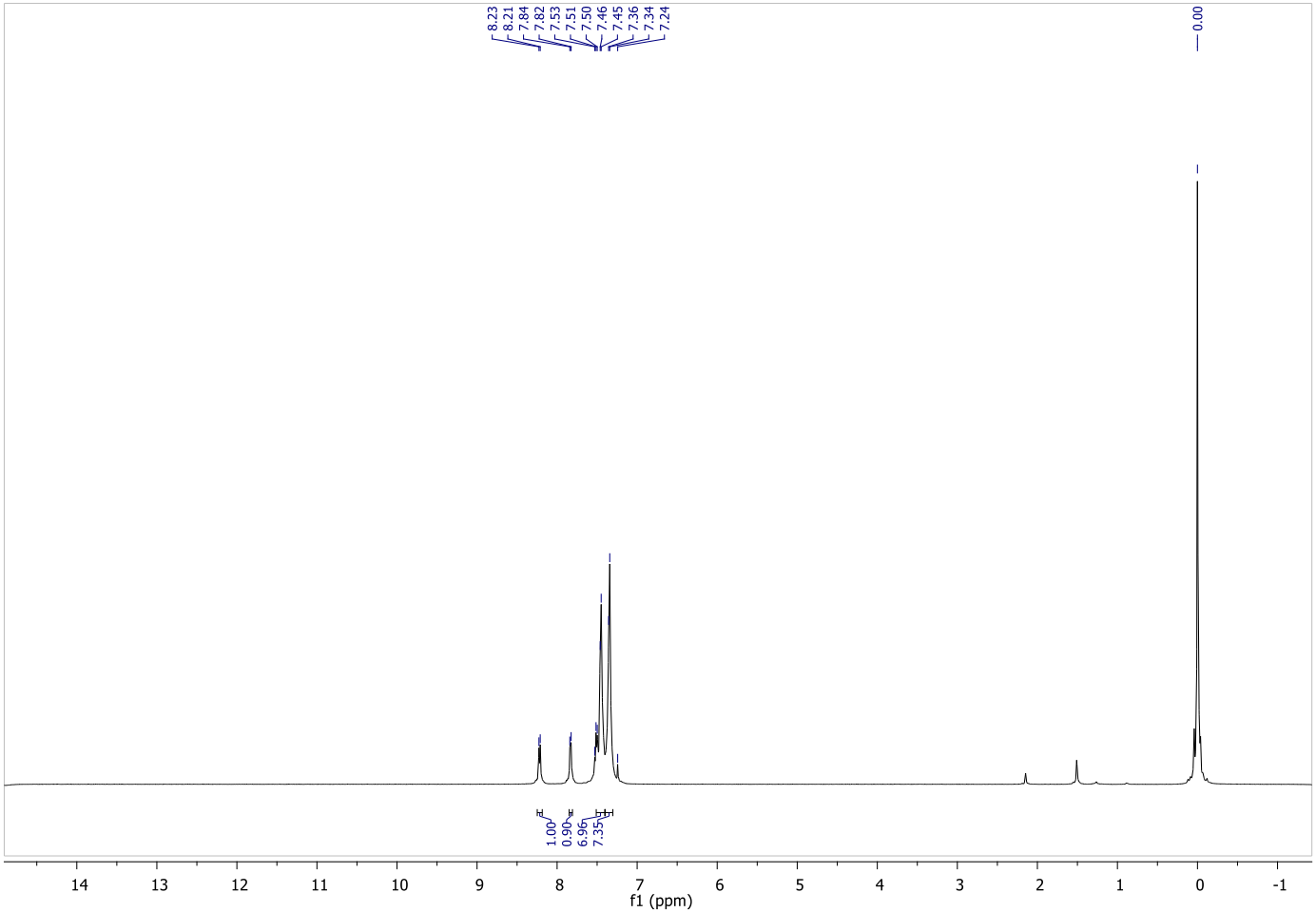
^{13}C NMR ($CDCl_3$, 75 MHz)



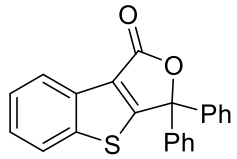
3,3-Diphenylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2j**)



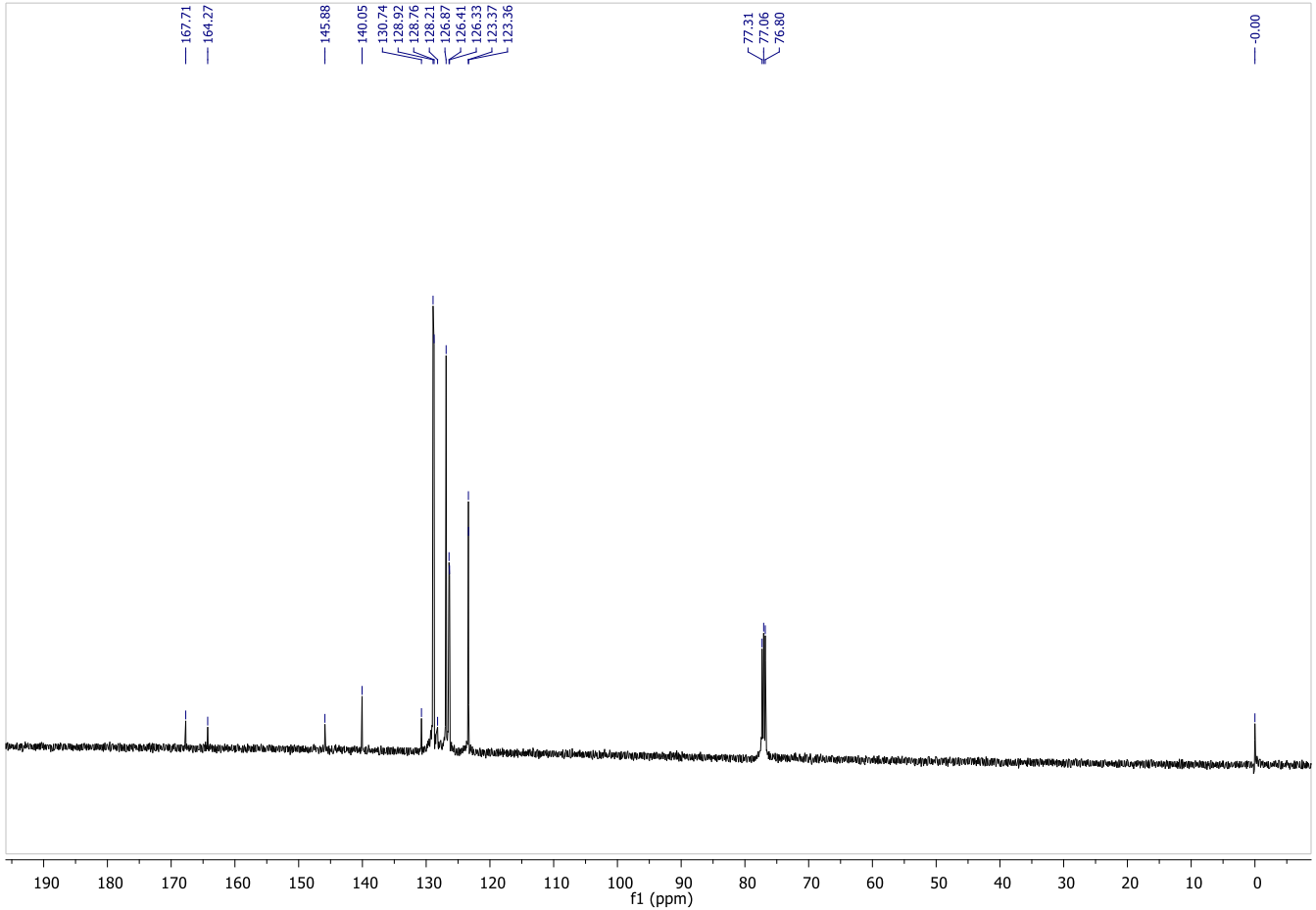
^{1}H NMR ($CDCl_3$, 500 MHz)



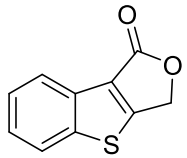
3,3-Diphenylbenzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2j**)



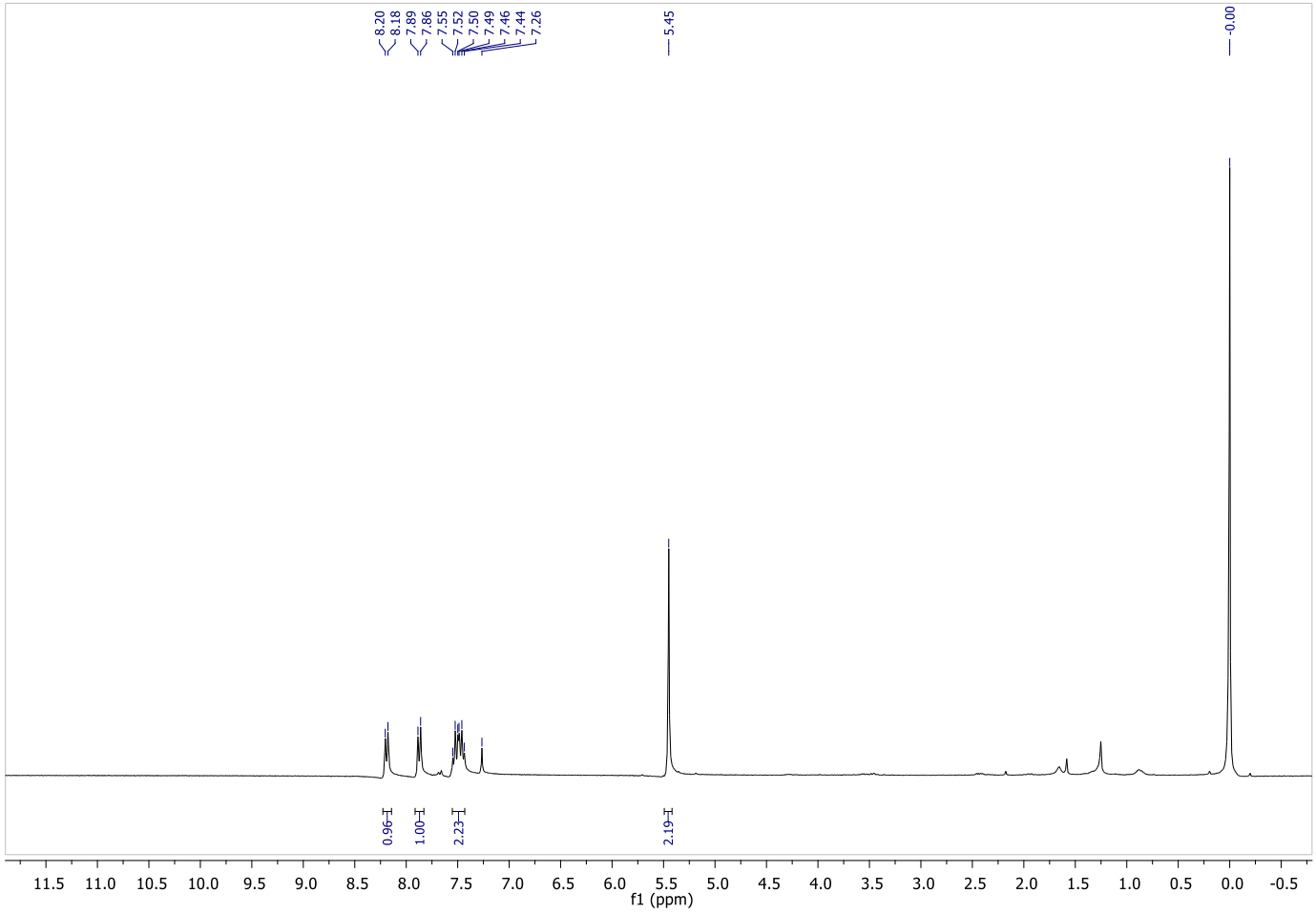
^{13}C NMR ($CDCl_3$, 125 MHz)



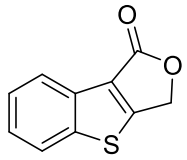
Benzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2k**)



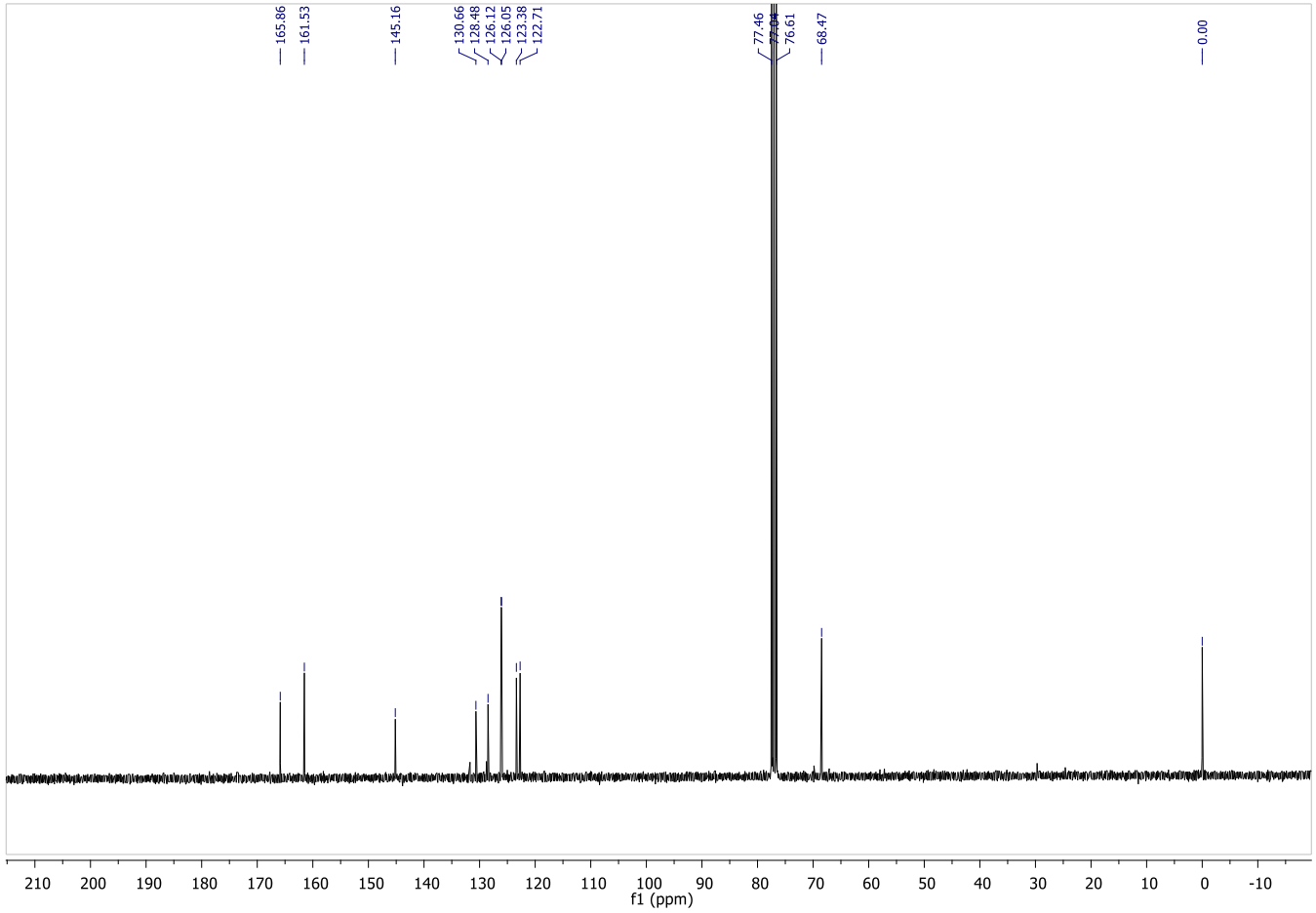
^{1}H NMR ($CDCl_3$, 300 MHz)



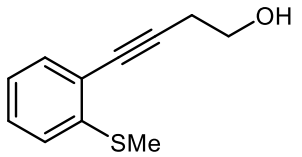
Benzo[4,5]thieno[2,3-*c*]furan-1(3*H*)-one (**2k**)



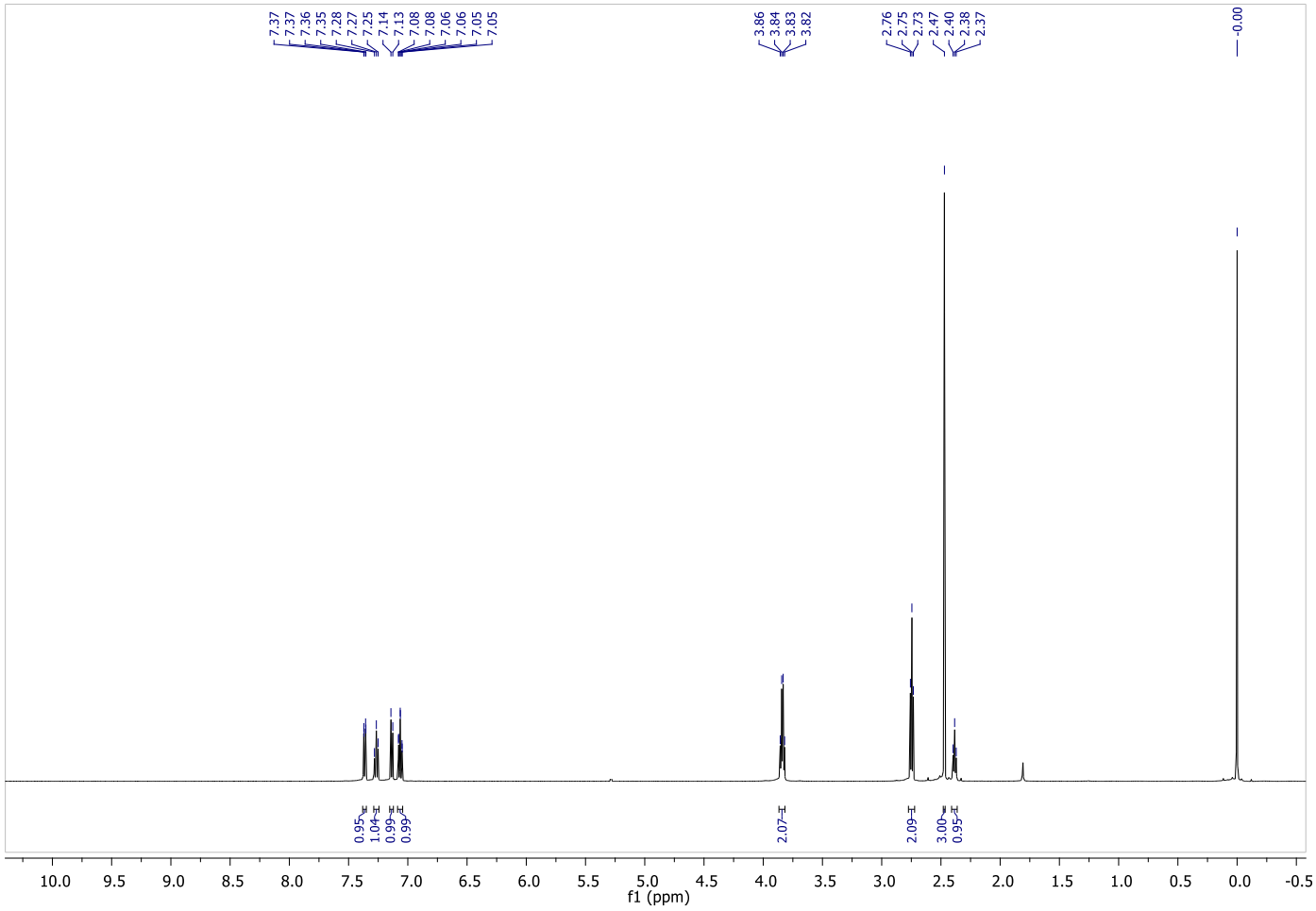
^{13}C NMR ($CDCl_3$, 75 MHz)



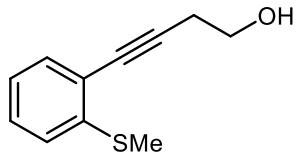
4-(2-(Methylthio)phenyl)but-3-yn-1-ol (**3a**)



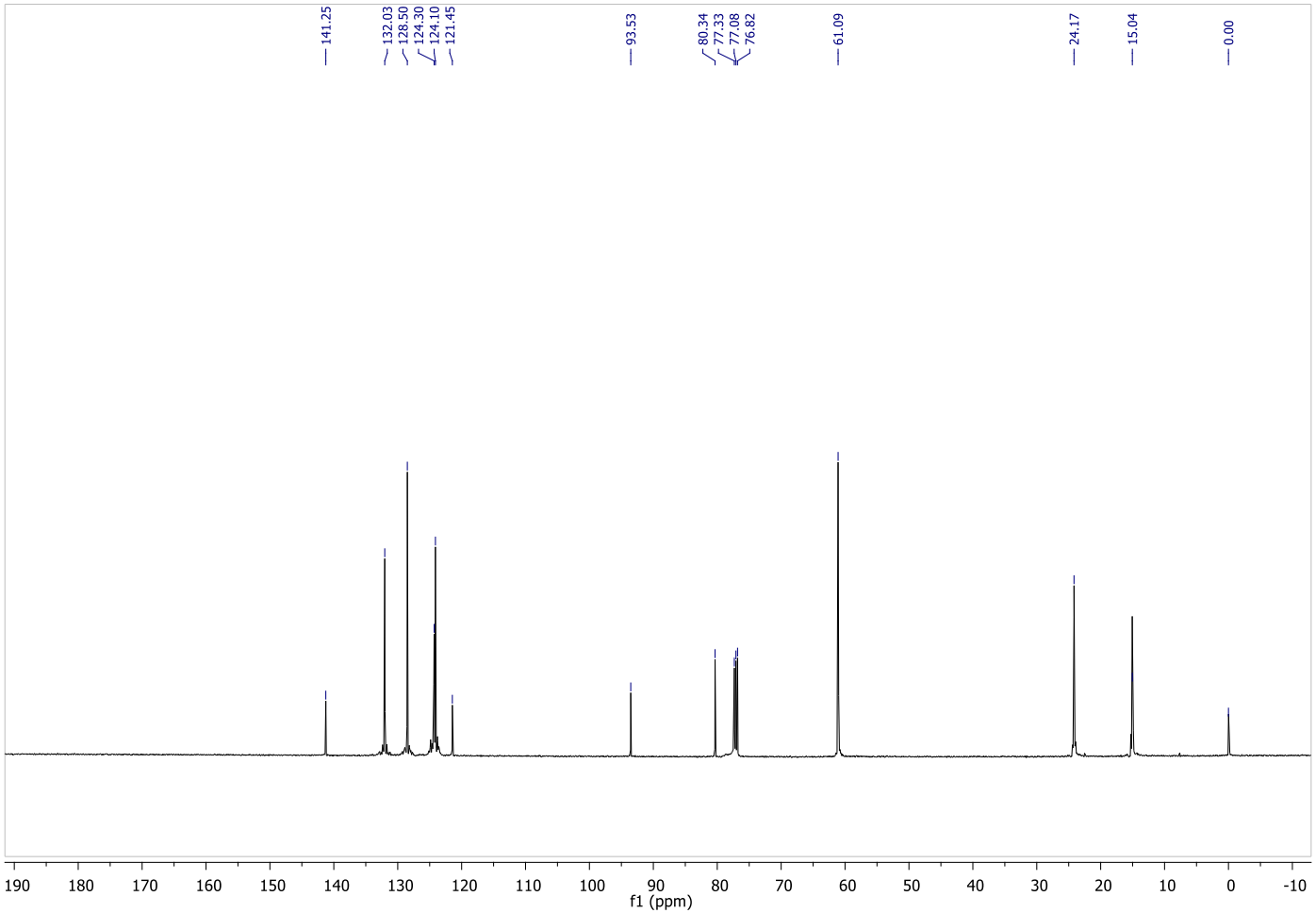
^{1}H NMR ($CDCl_3$, 500 MHz)



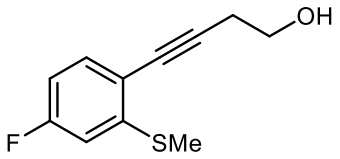
4-(2-(Methylthio)phenyl)but-3-yn-1-ol (**3a**)



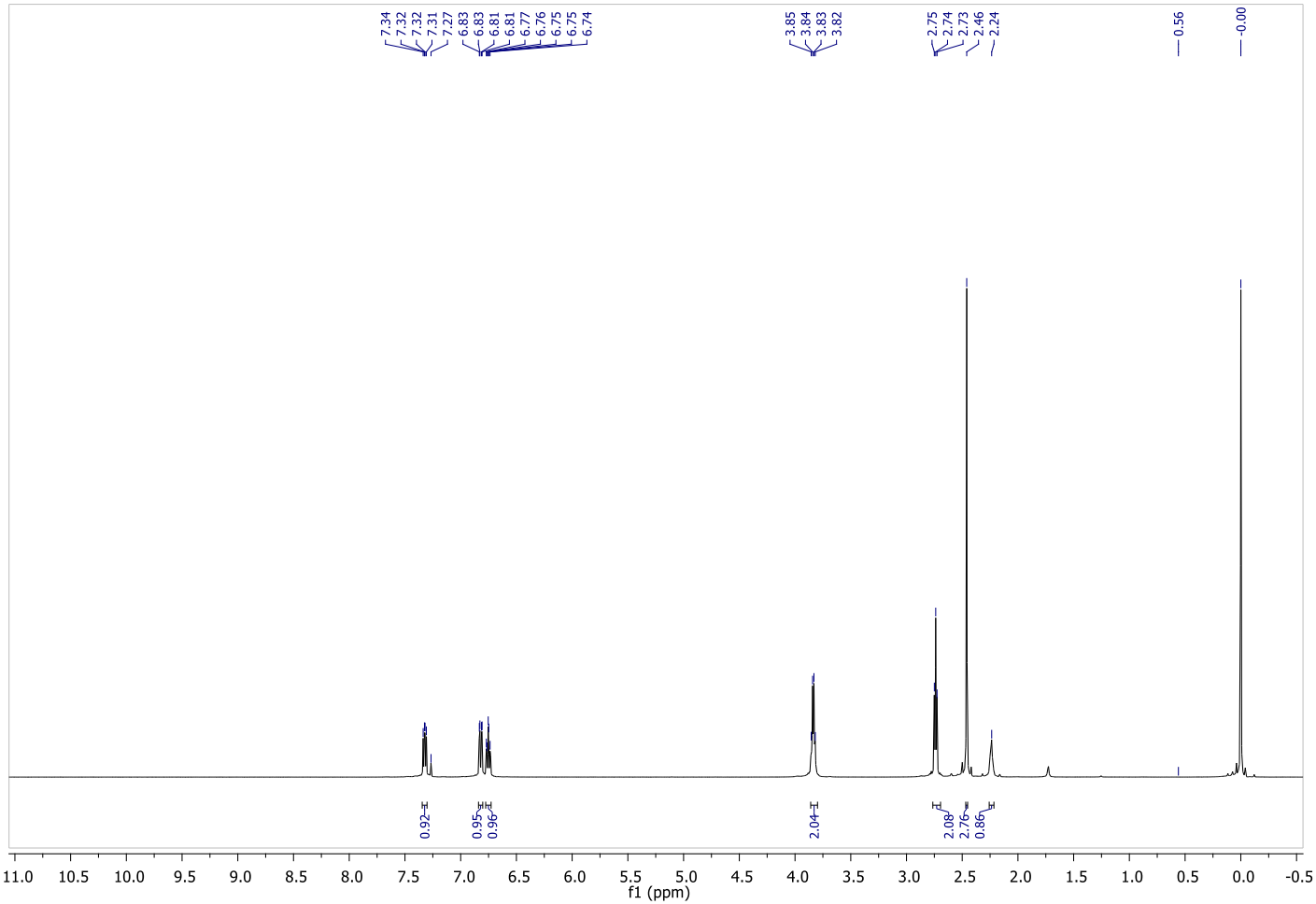
^{13}C NMR ($CDCl_3$, 125 MHz)



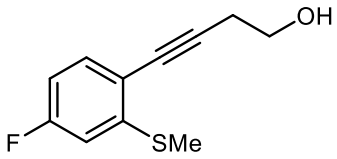
4-(4-Fluoro-2-(methylthio)phenyl)but-3-yn-1-ol (**3b**)



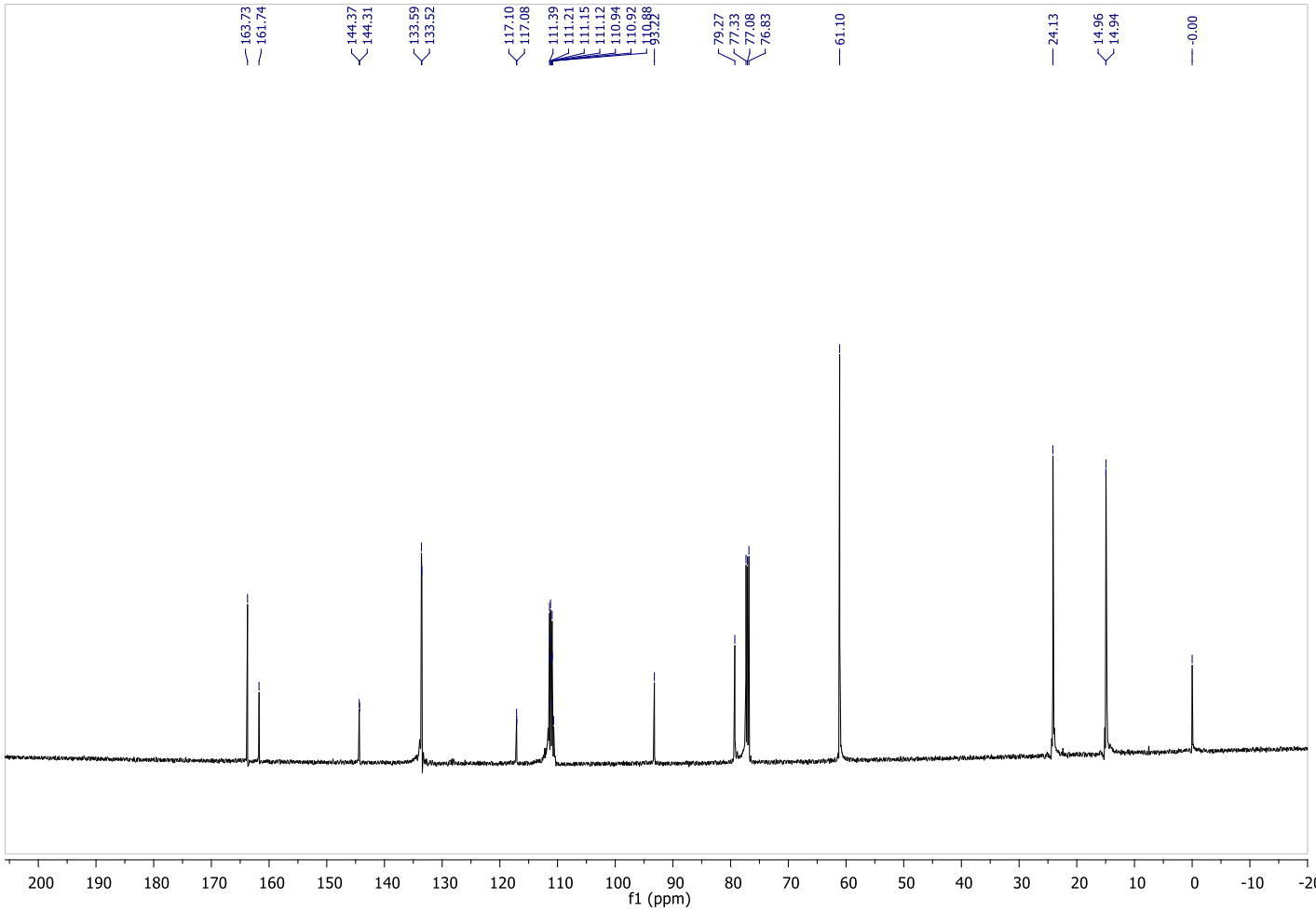
^{1}H NMR ($CDCl_3$, 500 MHz)



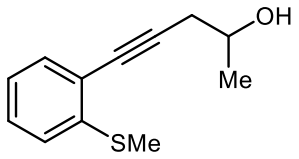
4-(4-Fluoro-2-(methylthio)phenyl)but-3-yn-1-ol (**3b**)



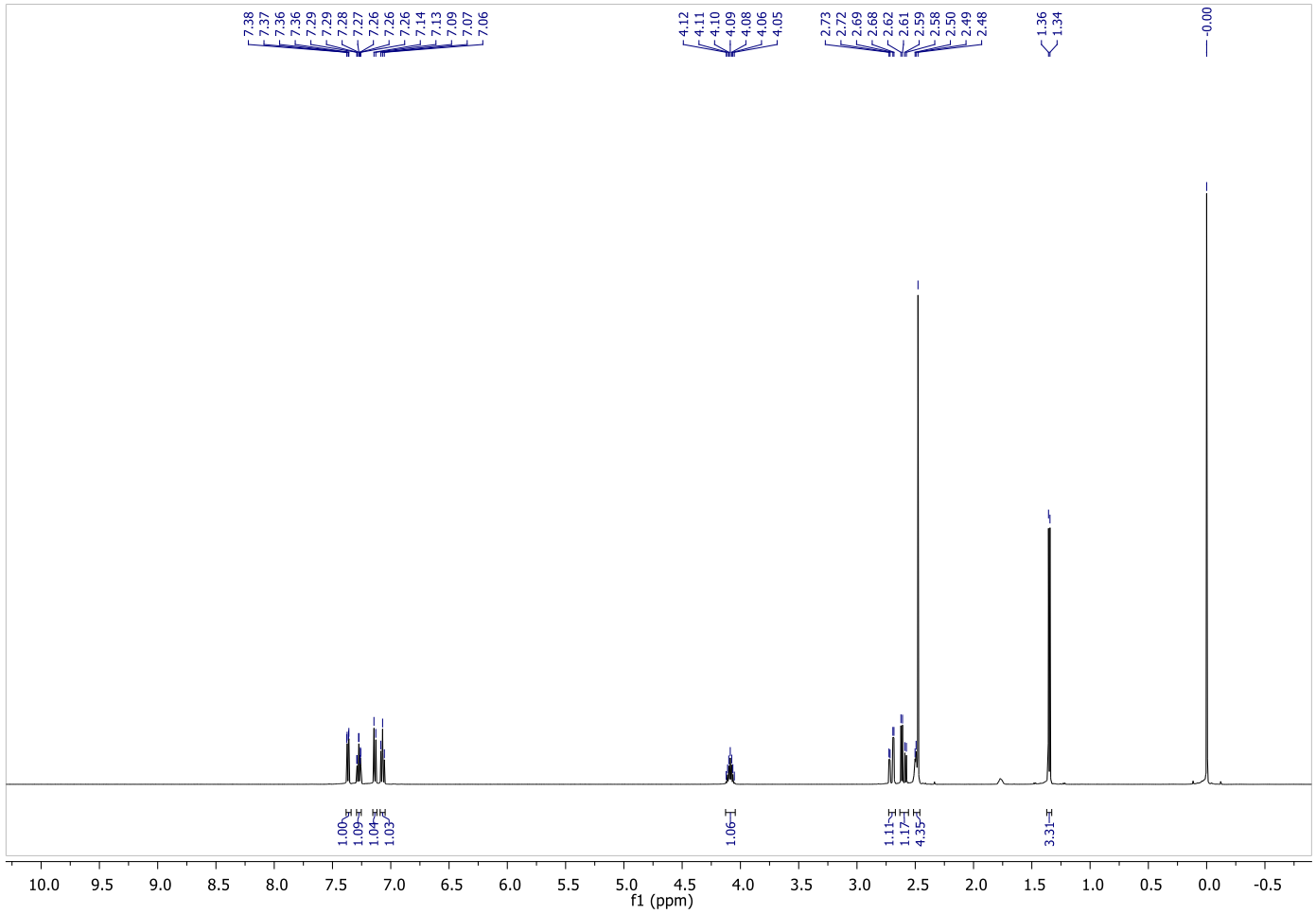
^{13}C NMR ($CDCl_3$, 125 MHz)



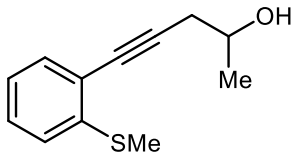
5-(2-(Methylthio)phenyl)pent-4-yn-2-ol (**3c**)



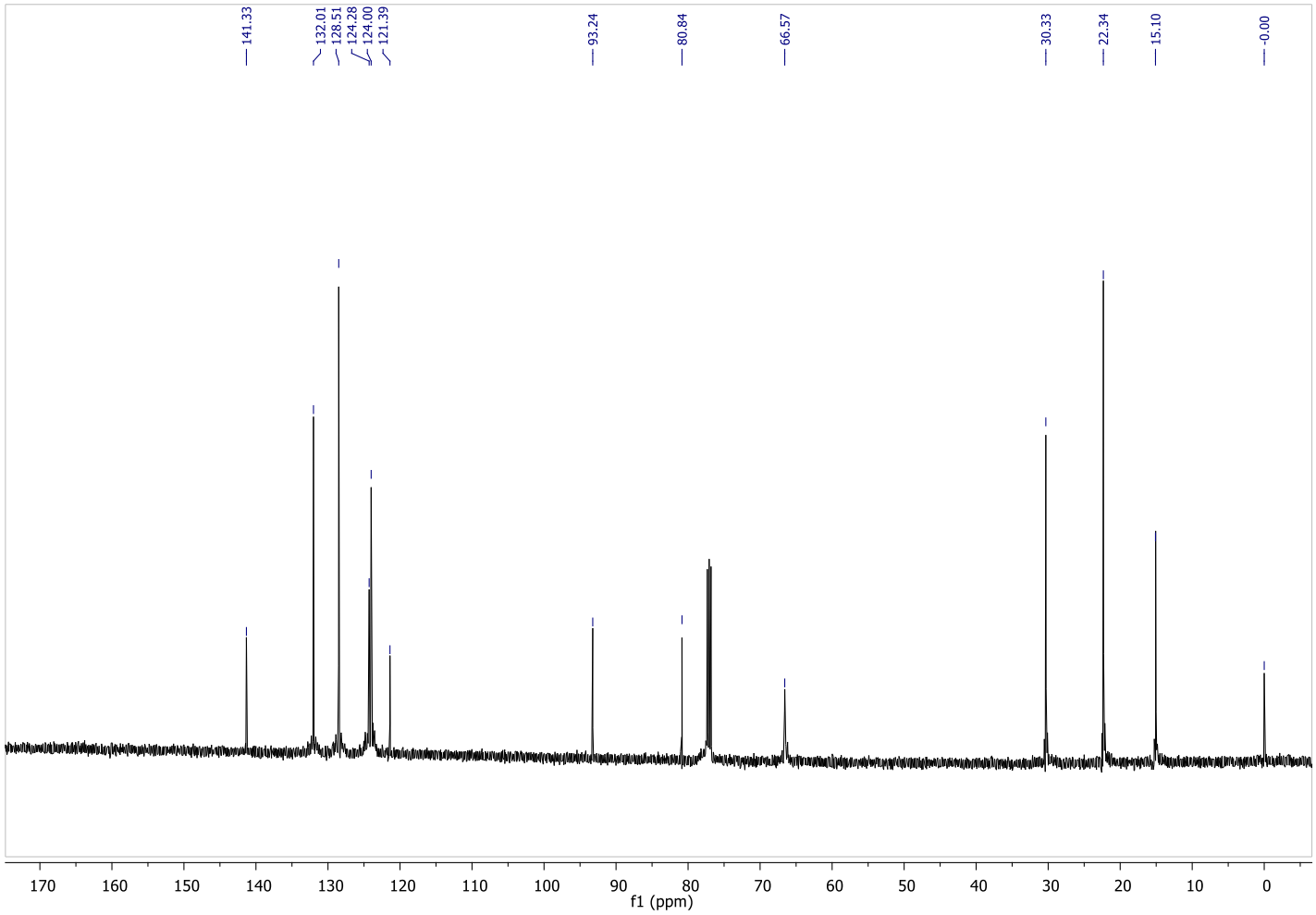
^{1}H NMR ($CDCl_3$, 500 MHz)



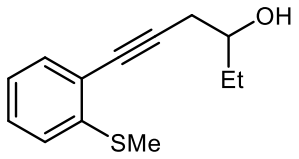
5-(2-(Methylthio)phenyl)pent-4-yn-2-ol (**3c**)



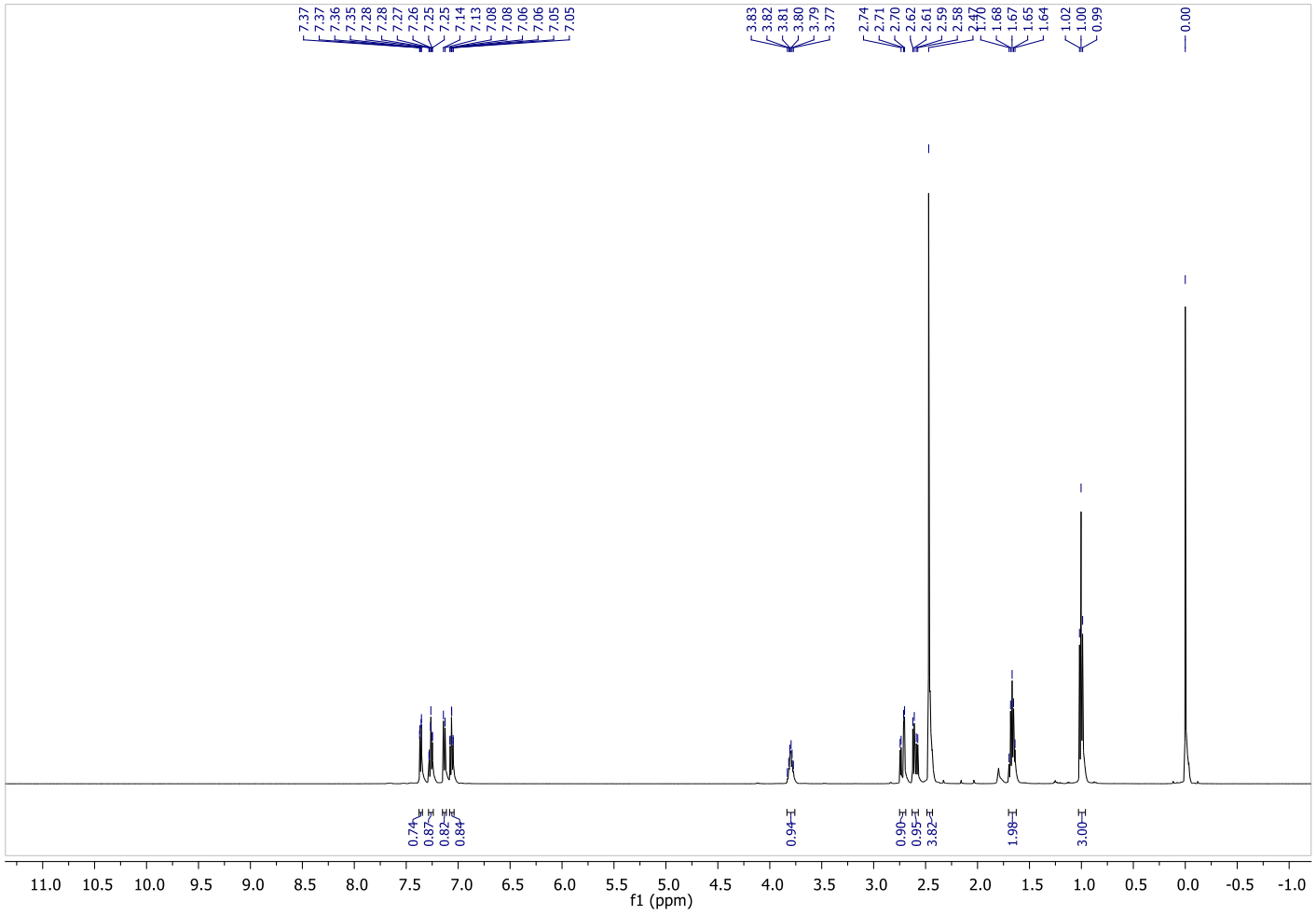
^{13}C NMR ($CDCl_3$, 125 MHz)



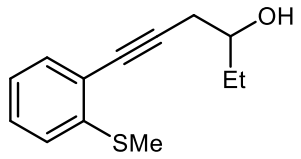
6-(2-(Methylthio)phenyl)hex-5-yn-3-ol (**3d**)



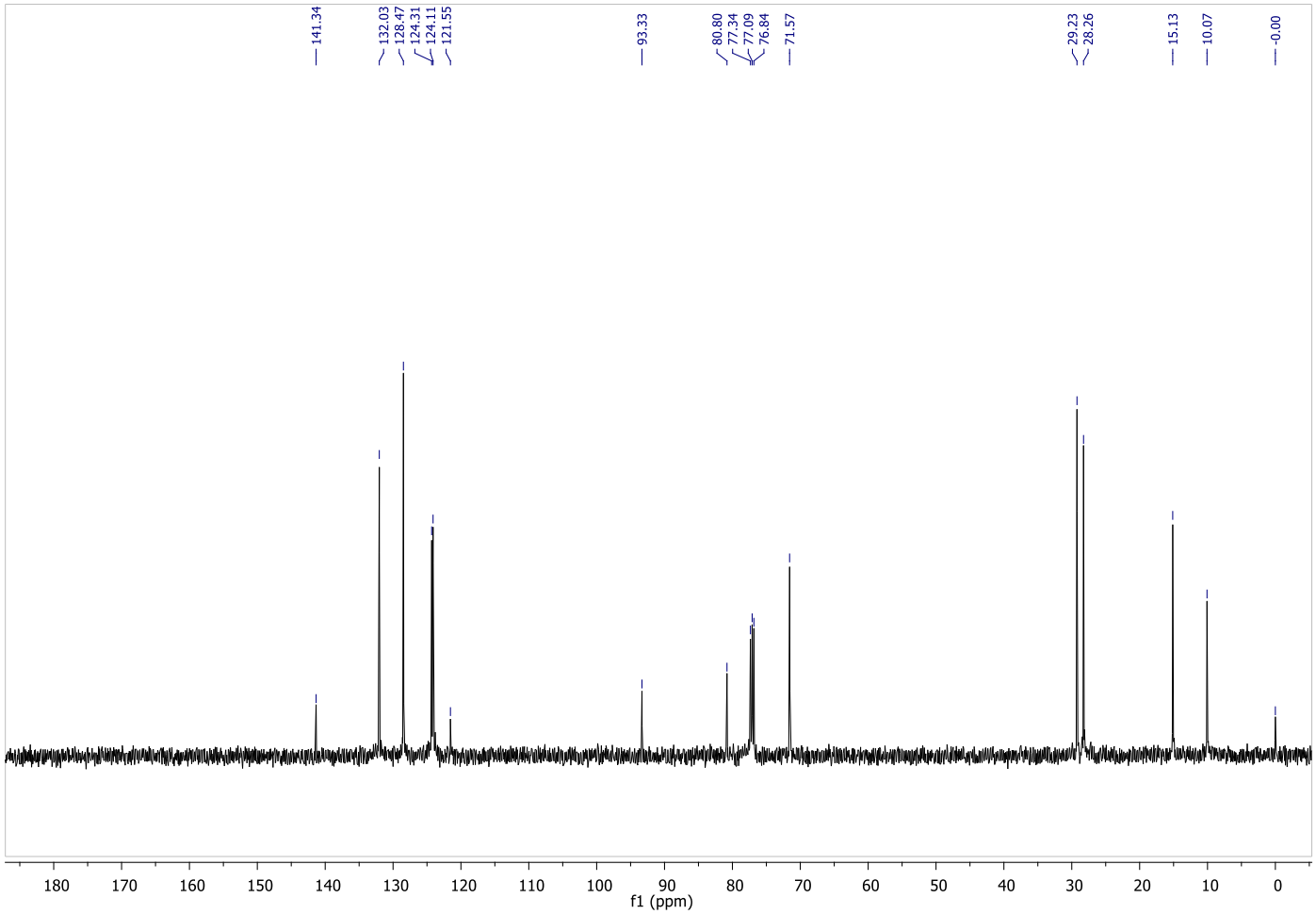
^{1}H NMR ($CDCl_3$, 500 MHz)



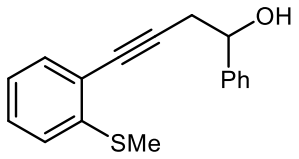
6-(2-(Methylthio)phenyl)hex-5-yn-3-ol (**3d**)



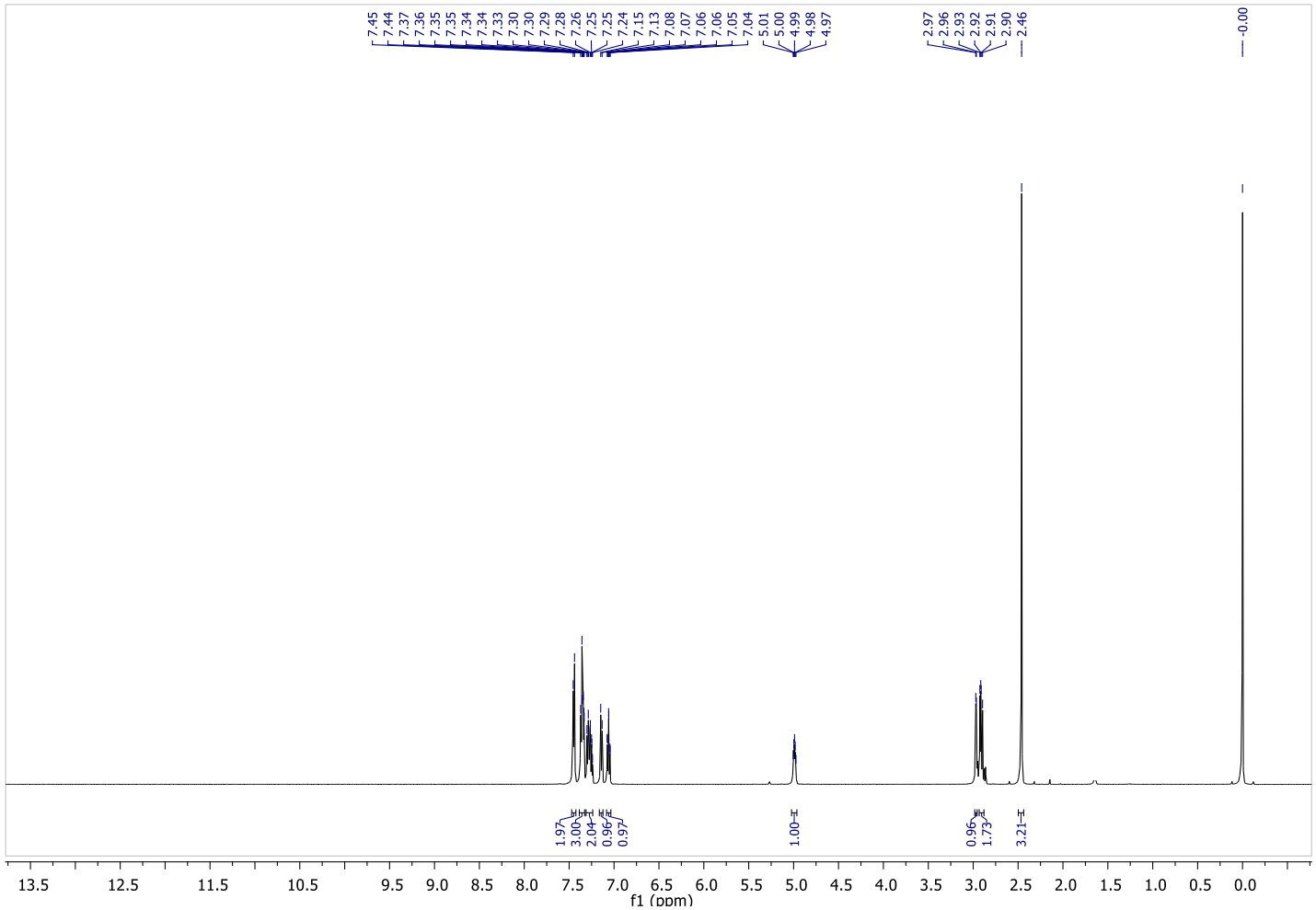
^{13}C NMR ($CDCl_3$, 125 MHz)



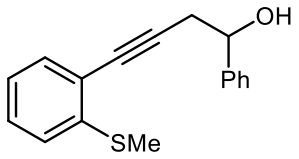
4-(2-(Methylthio)phenyl)-1-phenylbut-3-yn-1-ol (**3e**)



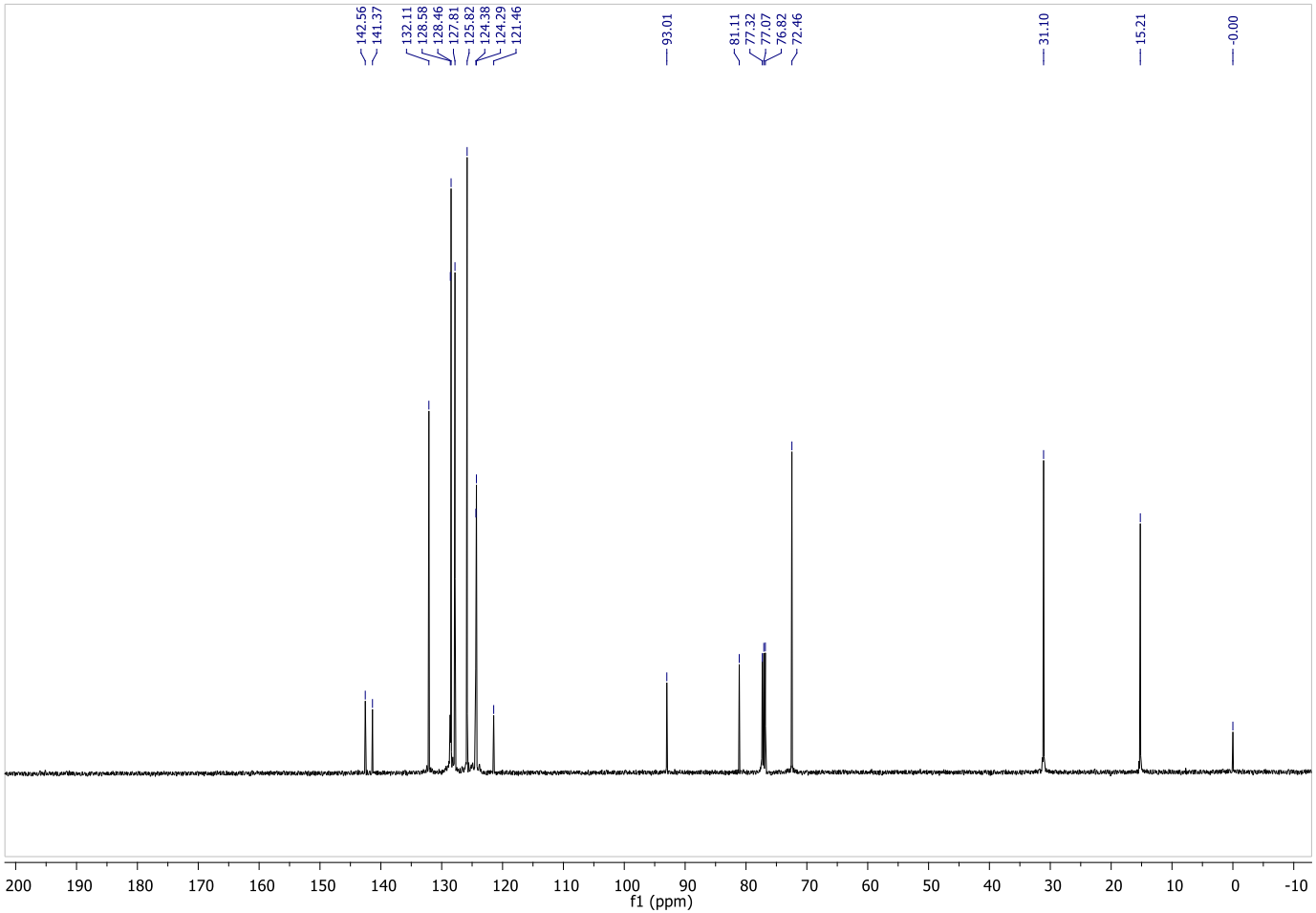
^{1}H NMR ($CDCl_3$, 500 MHz)



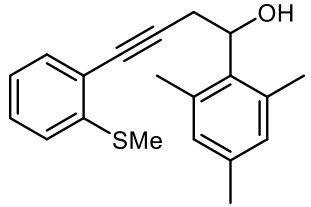
4-(2-(Methylthio)phenyl)-1-phenylbut-3-yn-1-ol (**3e**)



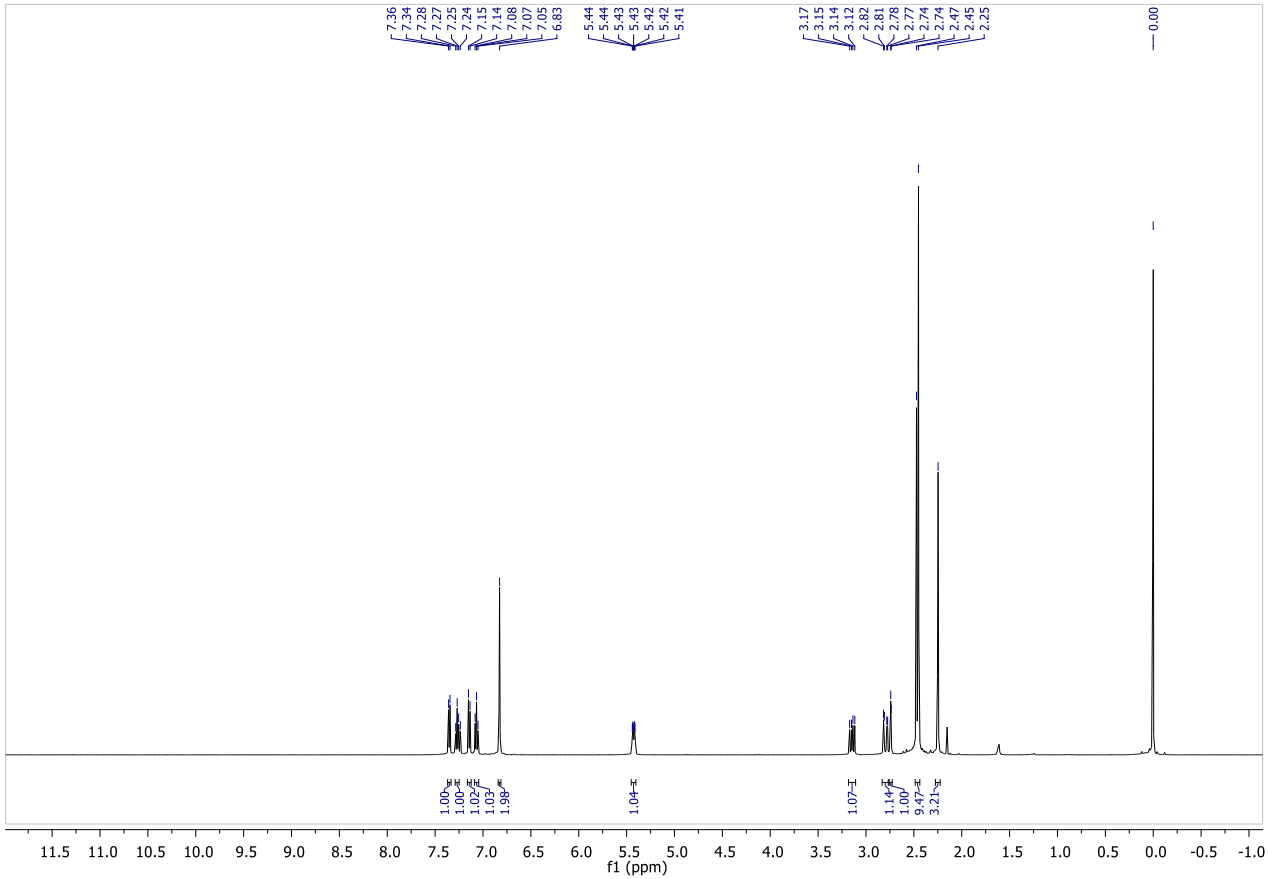
^{13}C NMR ($CDCl_3$, 125 MHz)



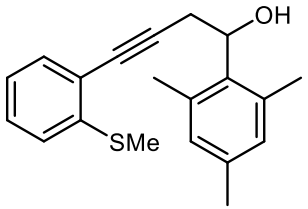
1-Mesityl-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3f**)



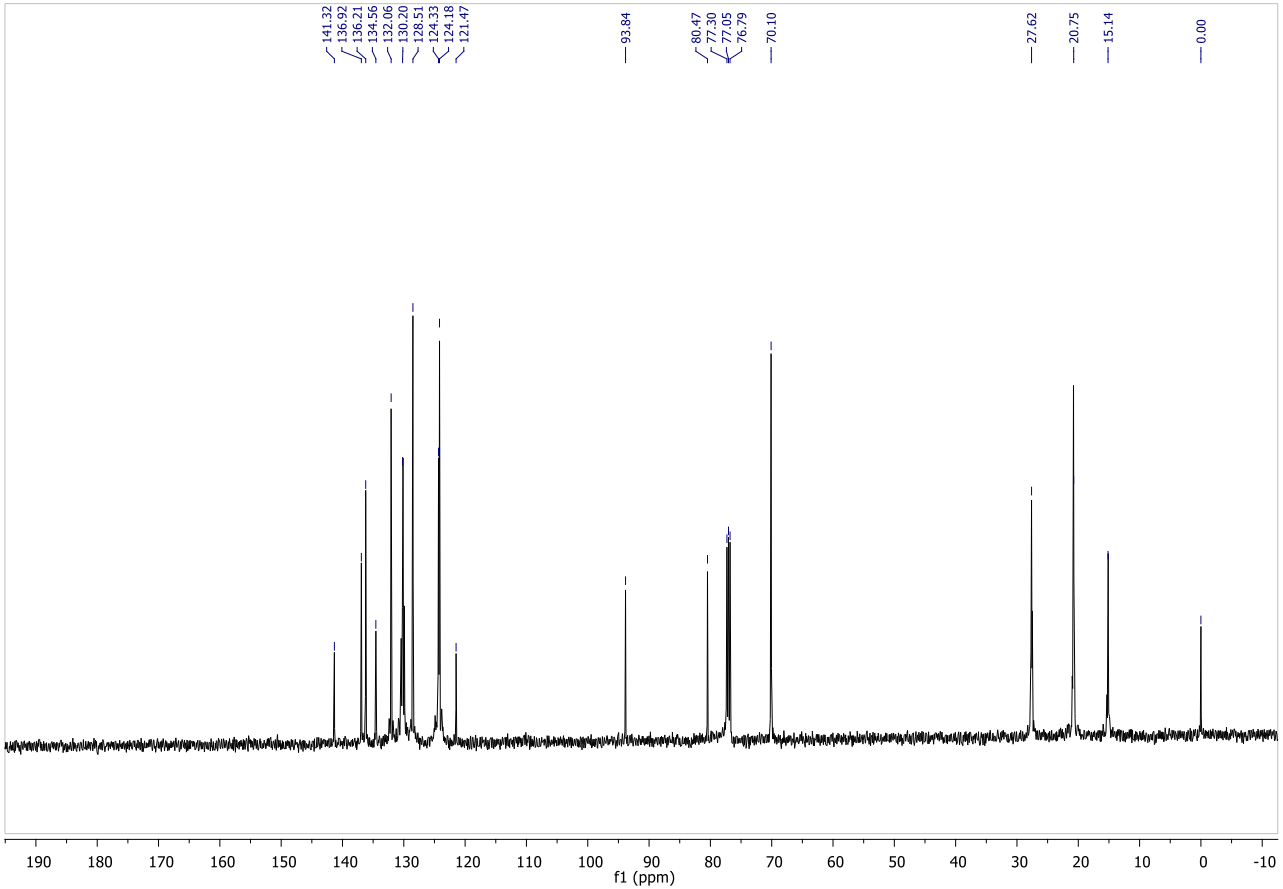
^{1}H NMR ($CDCl_3$, 500 MHz)



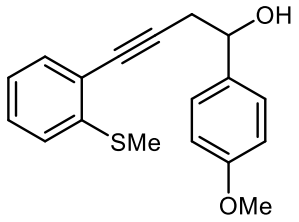
1-Mesityl-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3f**)



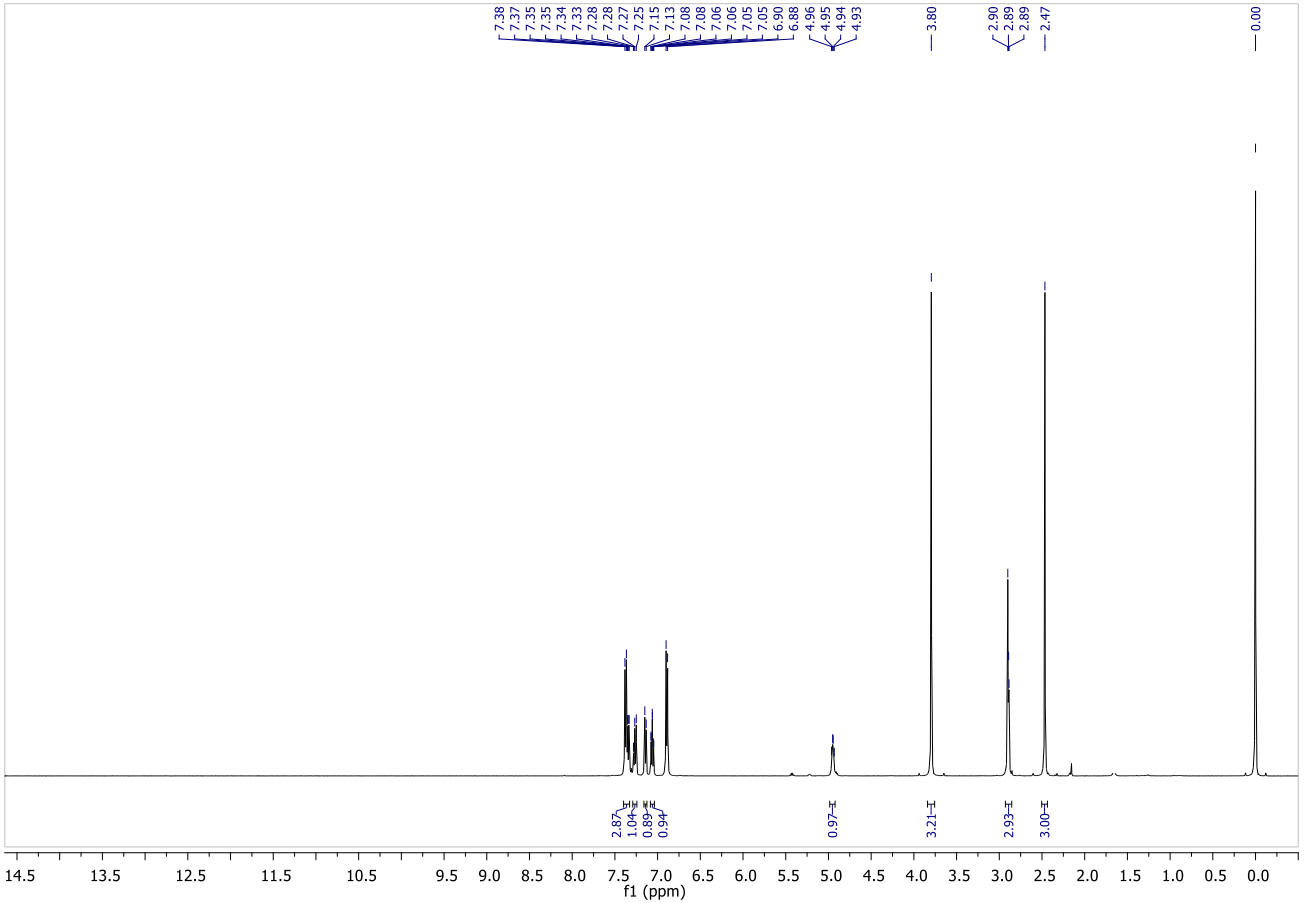
^{13}C NMR ($CDCl_3$, 125 MHz)



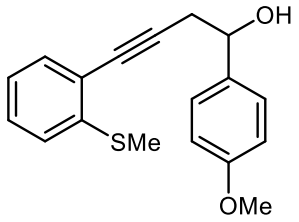
1-(4-Methoxyphenyl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3g**)



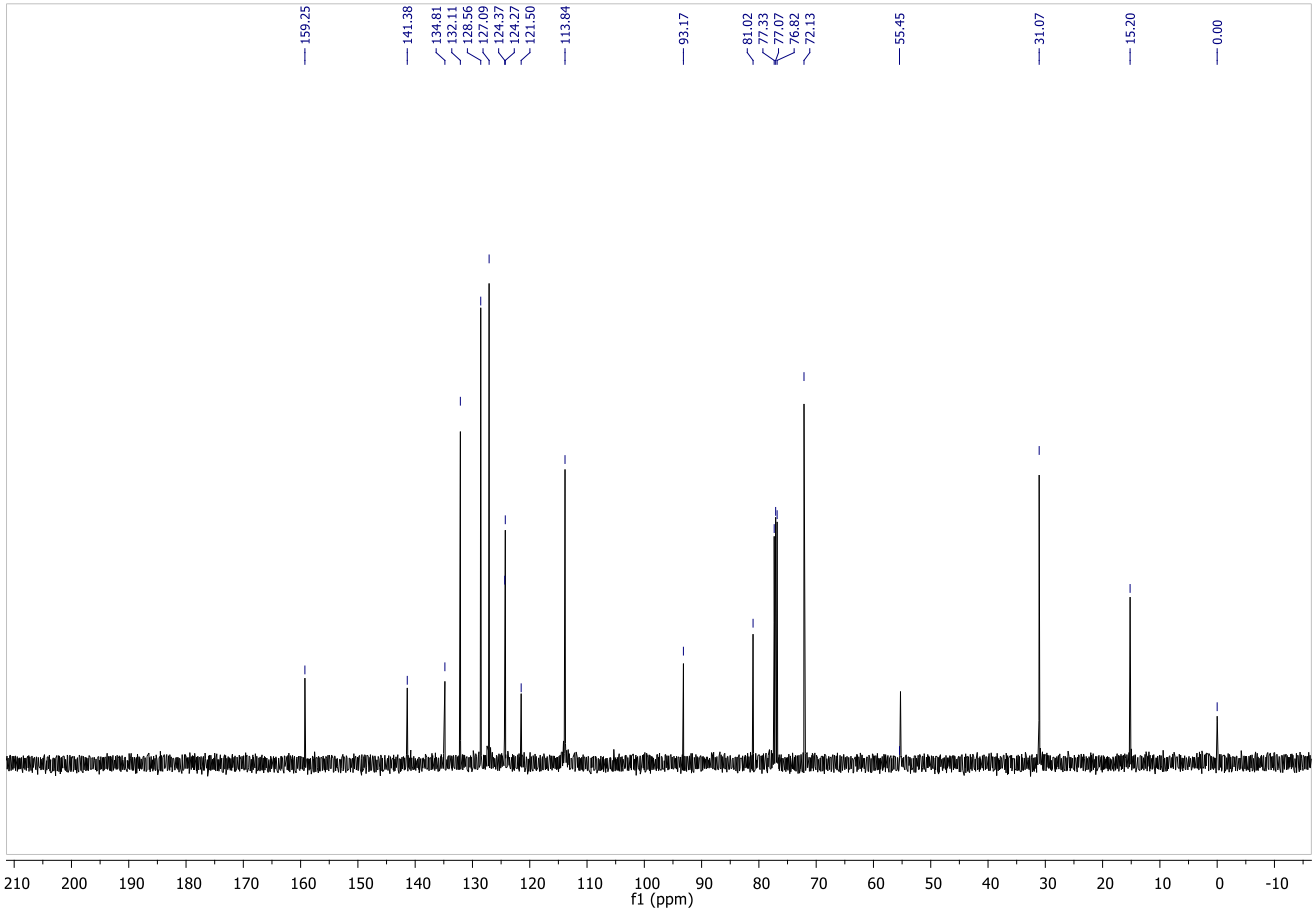
^{1}H NMR ($CDCl_3$, 500 MHz)



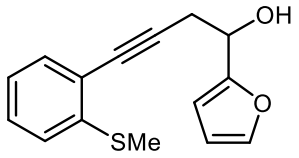
1-(4-Methoxyphenyl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3g**)



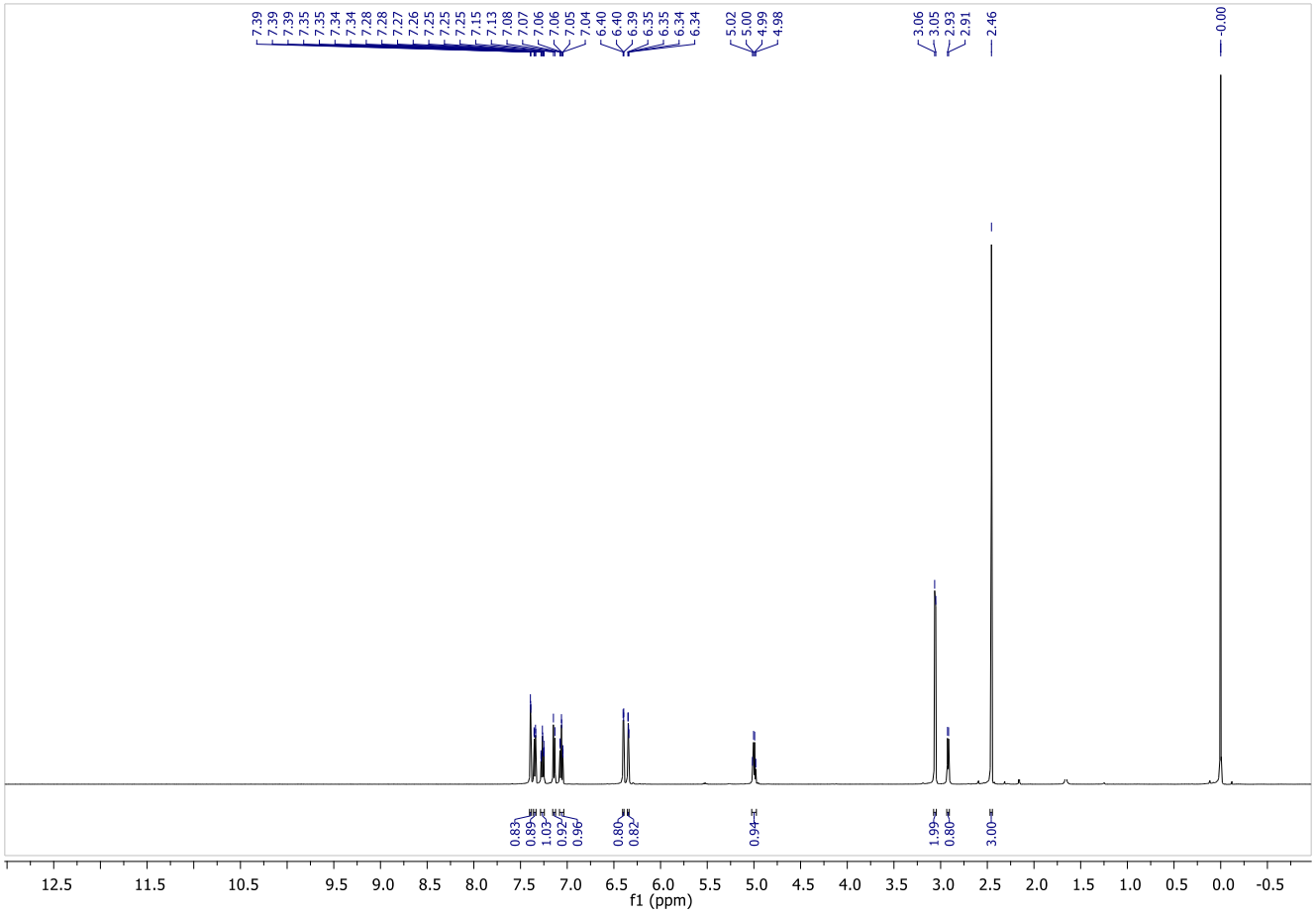
^{13}C NMR ($CDCl_3$, 125 MHz)



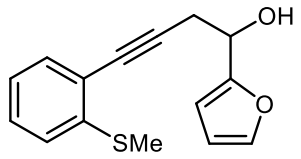
1-(Furan-2-yl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3h**)



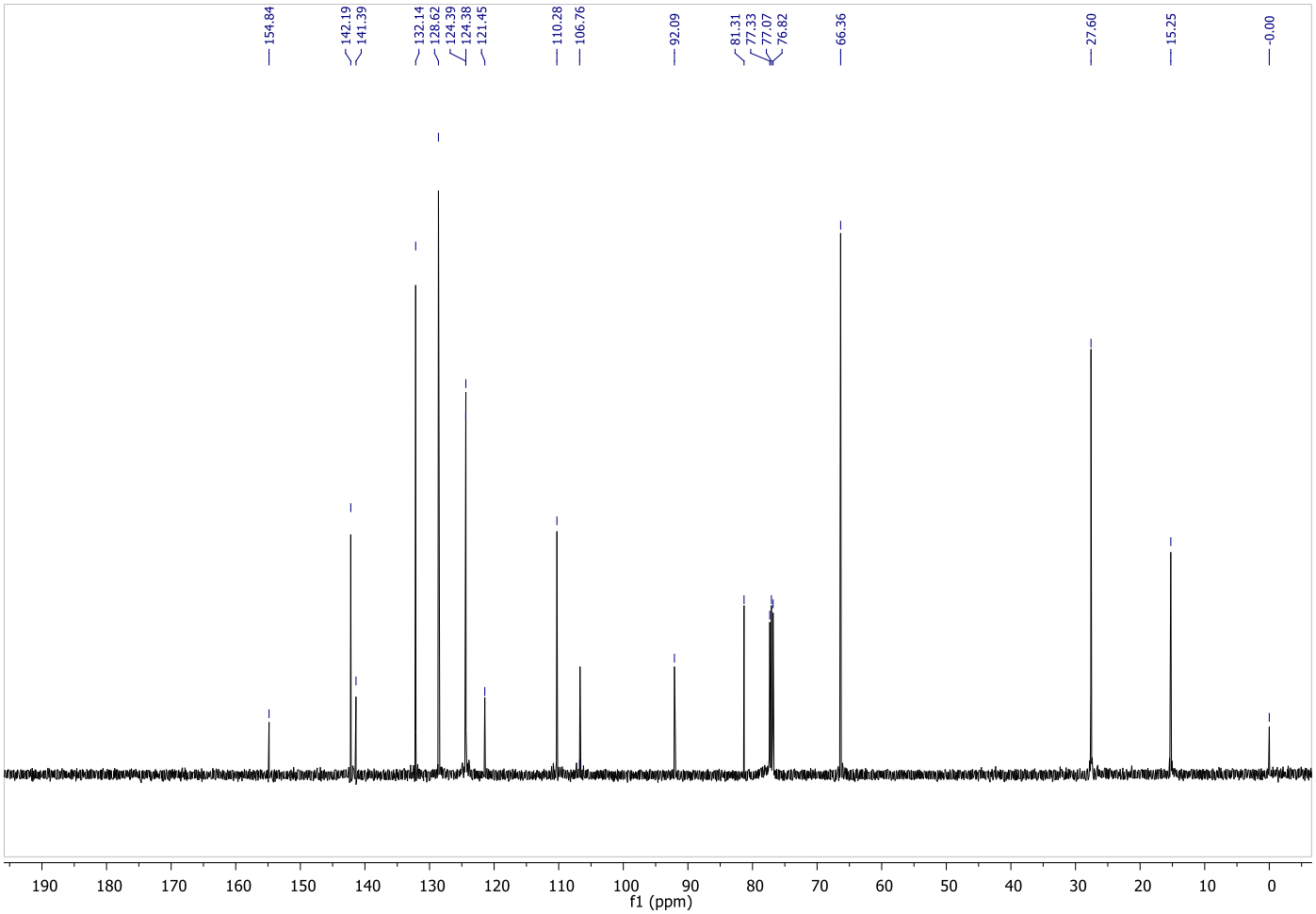
^{1}H NMR ($CDCl_3$, 500 MHz)



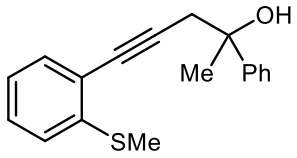
1-(Furan-2-yl)-4-(2-(methylthio)phenyl)but-3-yn-1-ol (**3h**)



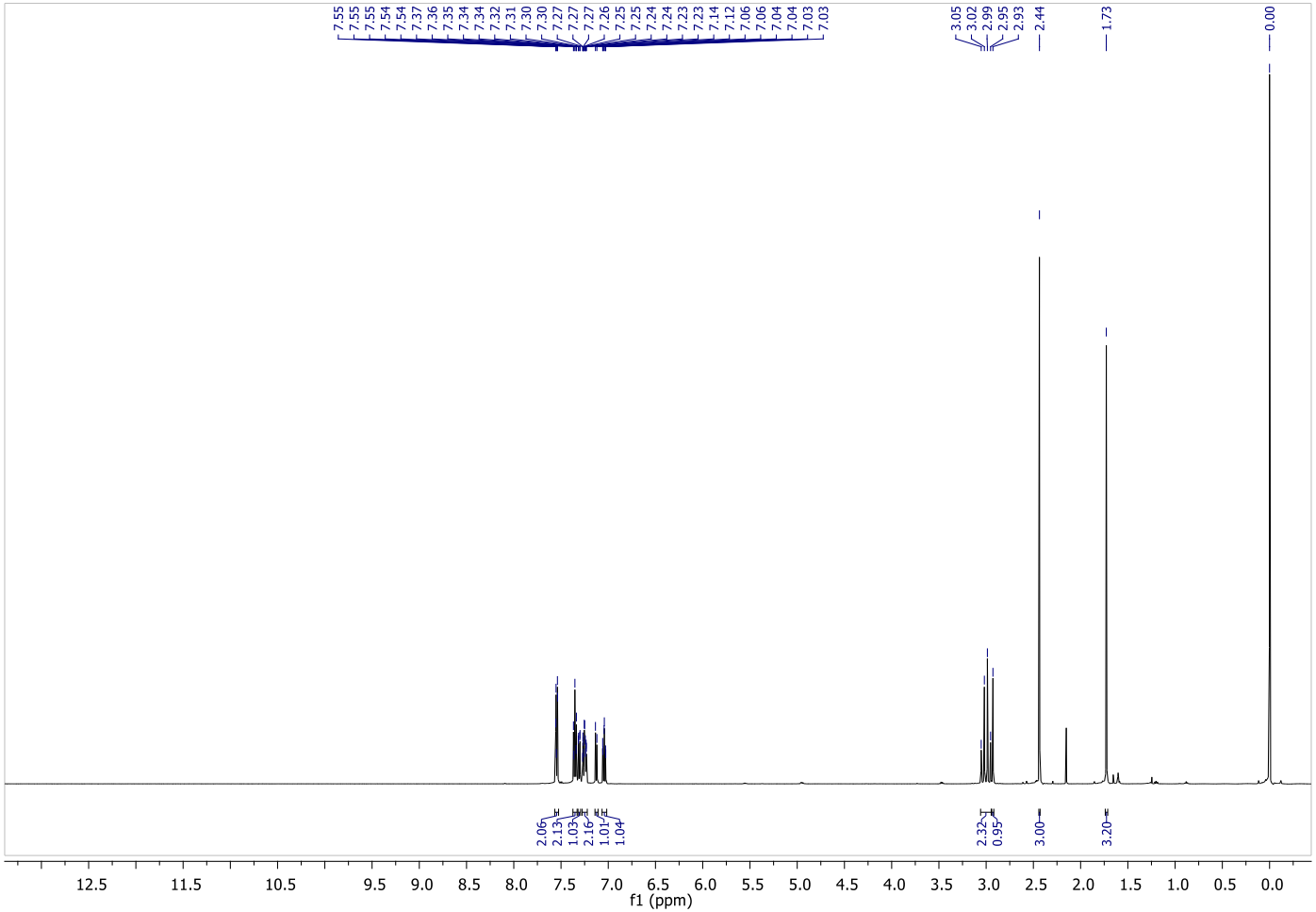
^{13}C NMR ($CDCl_3$, 125 MHz)



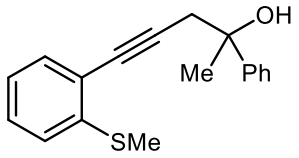
5-(2-(Methylthio)phenyl)-2-phenylpent-4-yn-2-ol (**3i**)



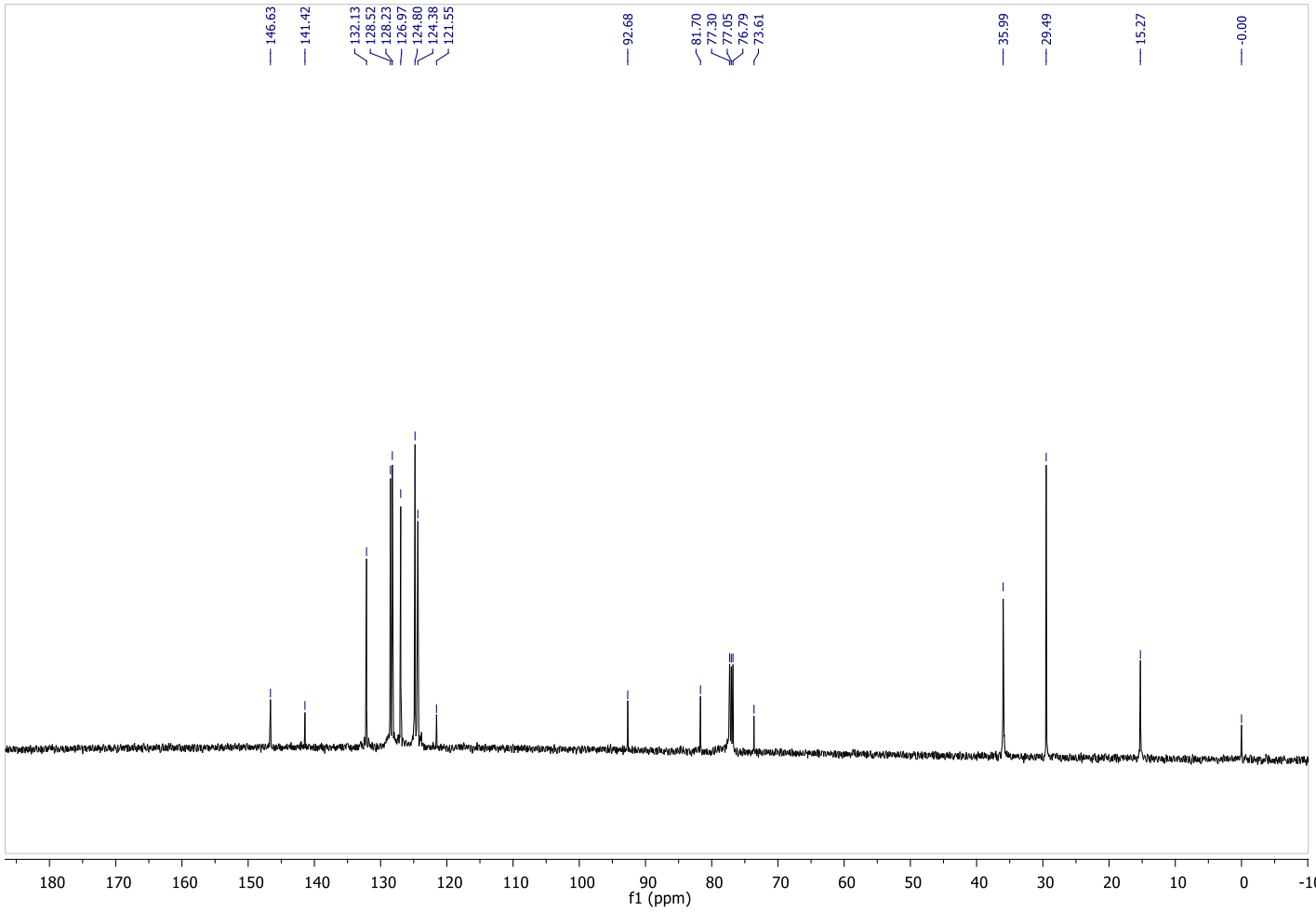
^{1}H NMR ($CDCl_3$, 500 MHz)



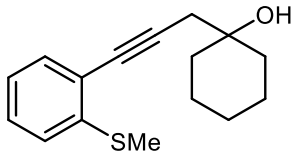
5-(2-(Methylthio)phenyl)-2-phenylpent-4-yn-2-ol (**3i**)



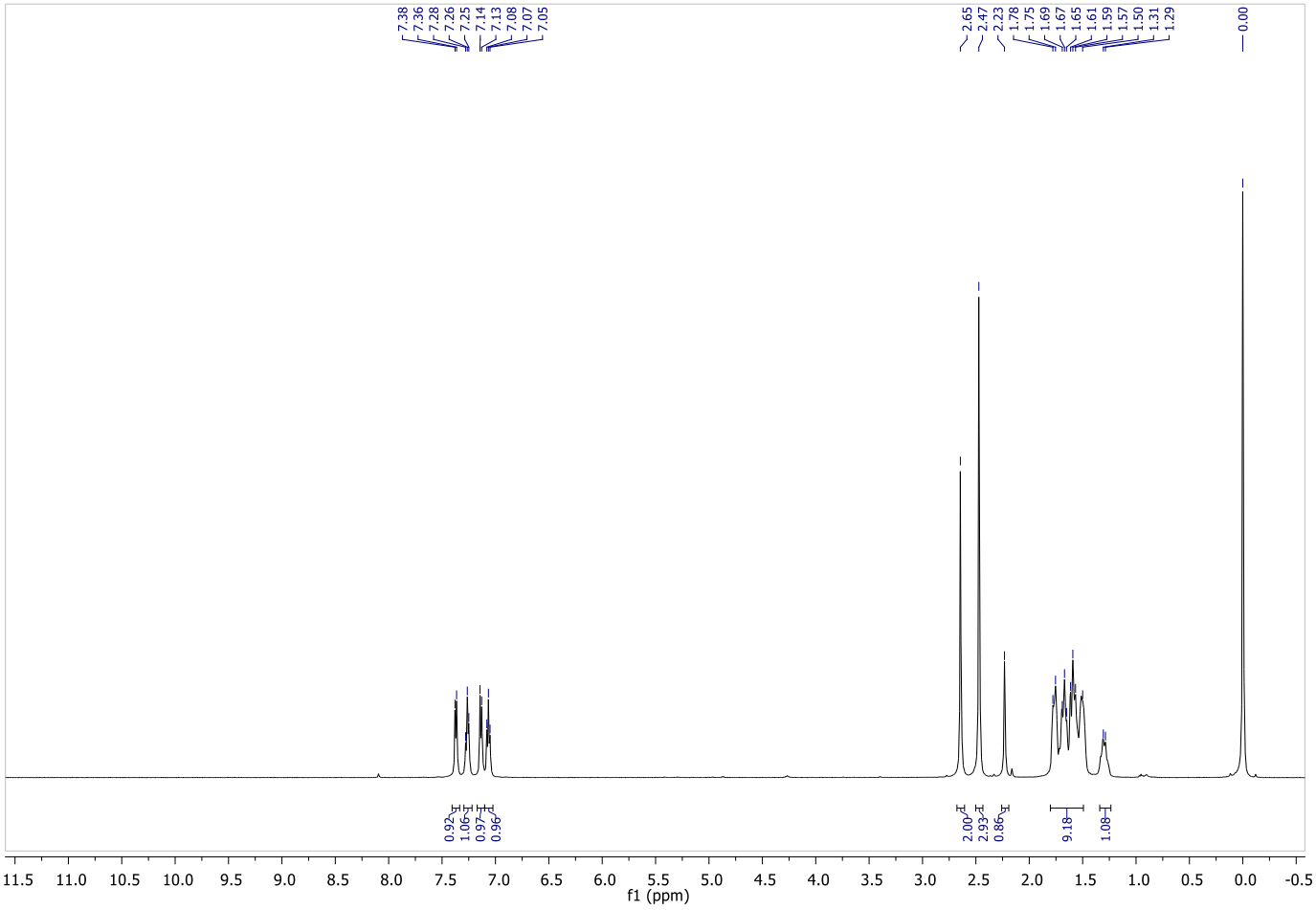
^{13}C NMR ($CDCl_3$, 125 MHz)



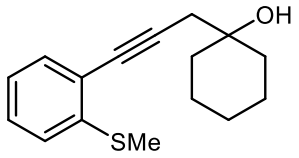
1-(3-(2-(Methylthio)phenyl)prop-2-yn-1-yl)cyclohexan-1-ol (**3j**)



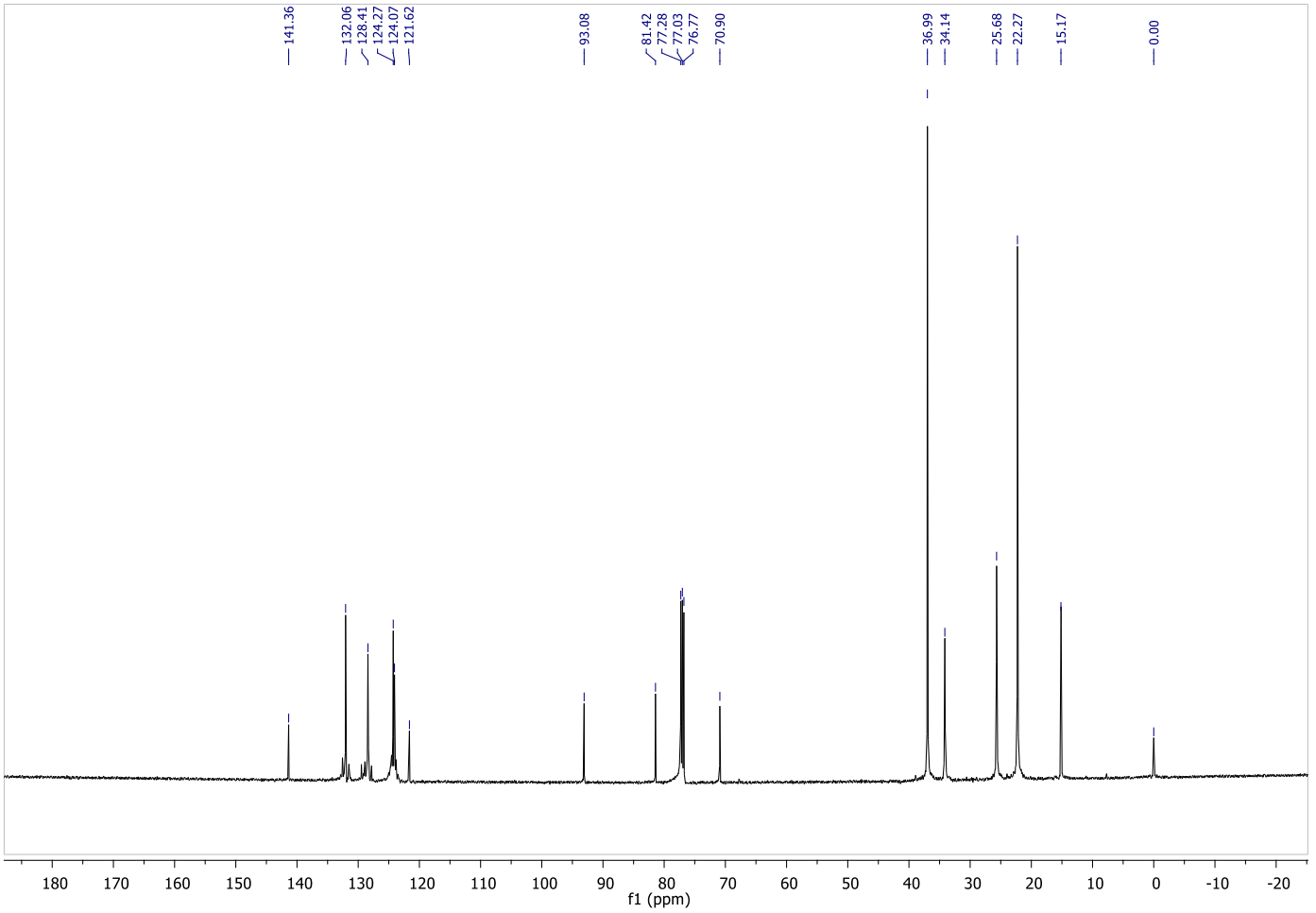
^{1}H NMR ($CDCl_3$, 500 MHz)



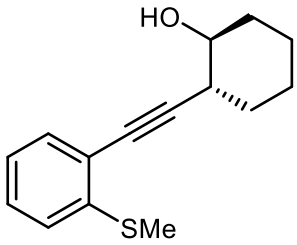
1-(3-(2-(Methylthio)phenyl)prop-2-yn-1-yl)cyclohexan-1-ol (**3j**)



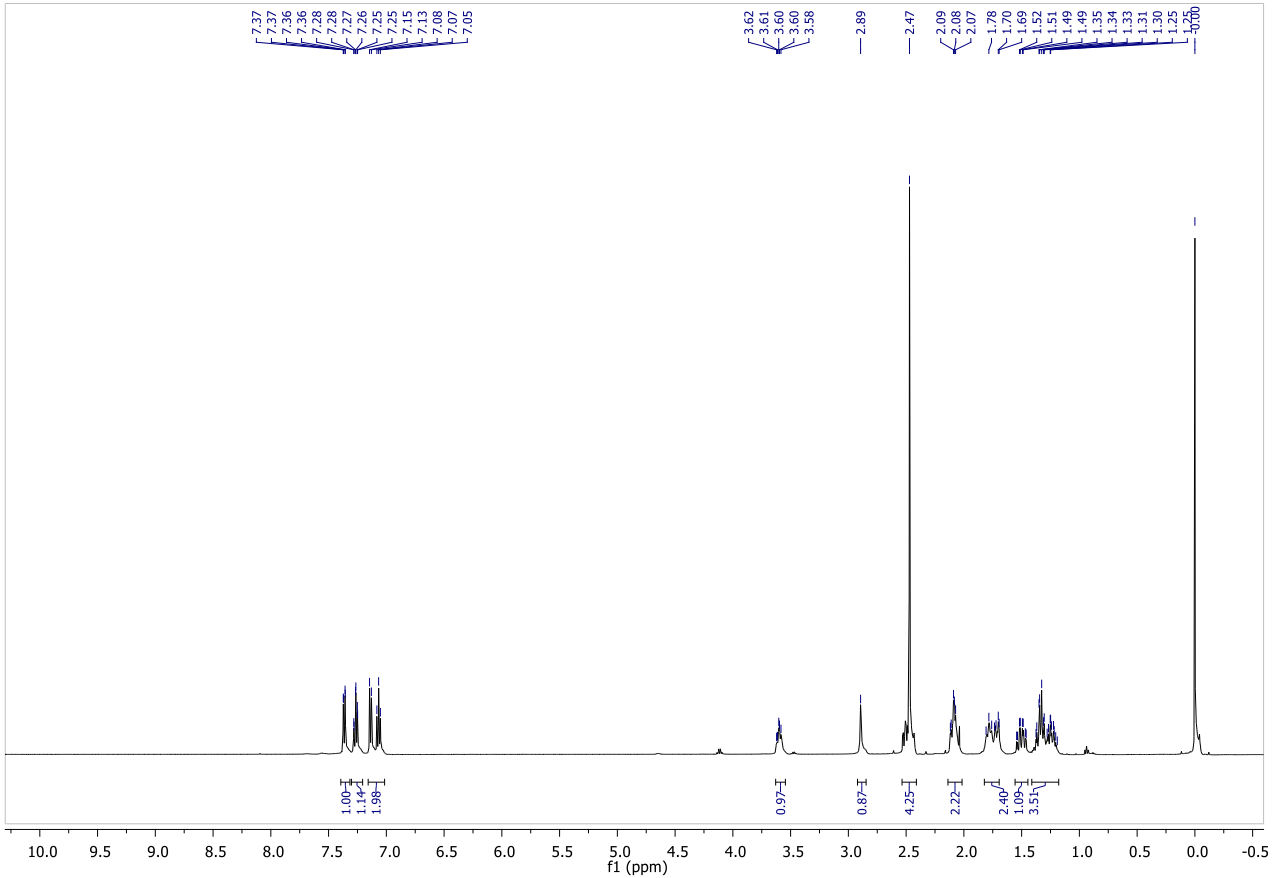
^{13}C NMR ($CDCl_3$, 125 MHz)



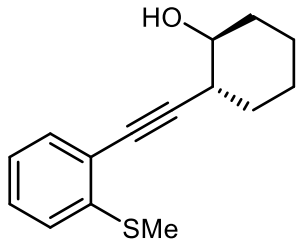
trans-2-((2-(Methylthio)phenyl)ethynyl)cyclohexan-1-ol (**3k**)



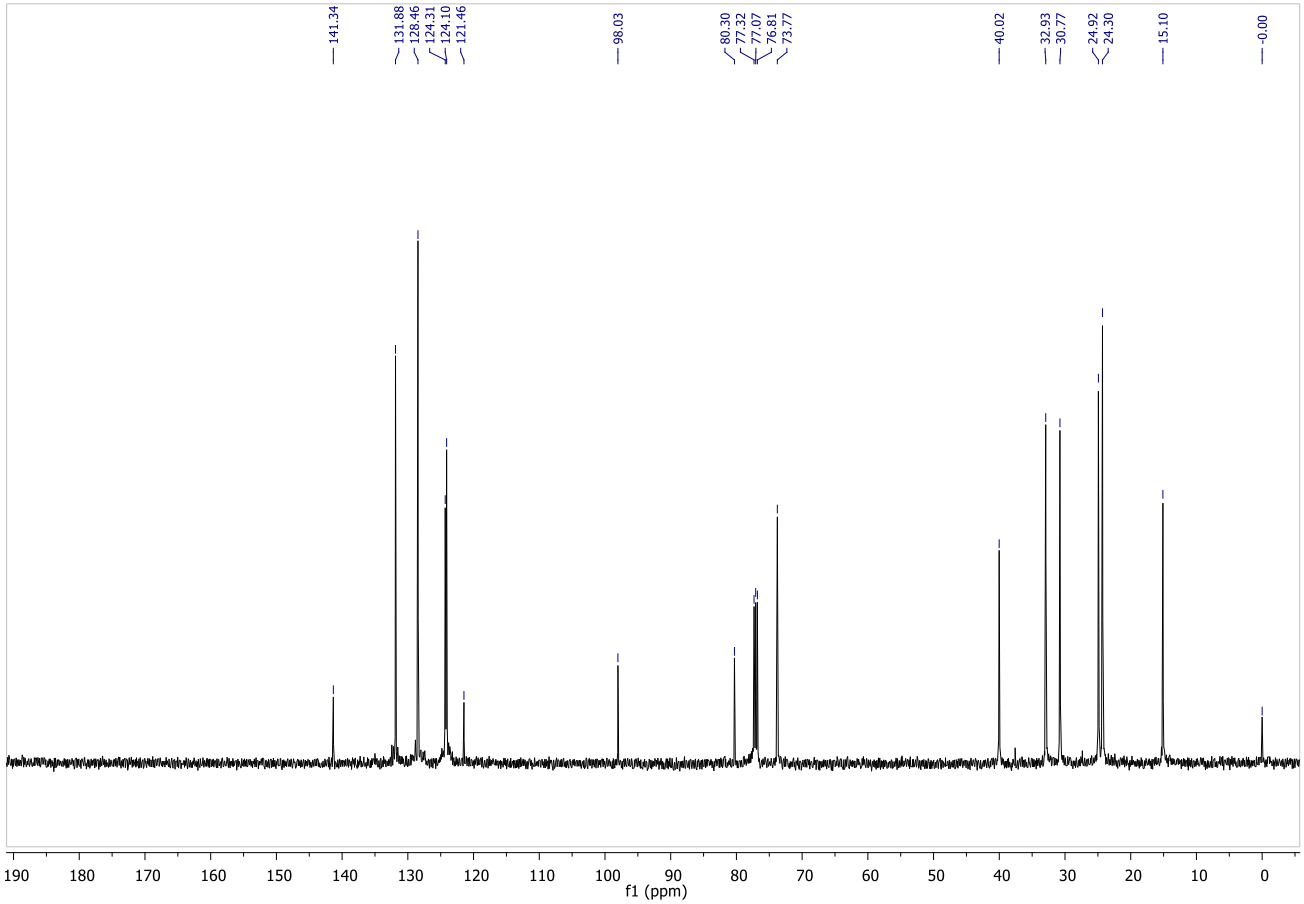
^{1}H NMR ($CDCl_3$, 500 MHz)



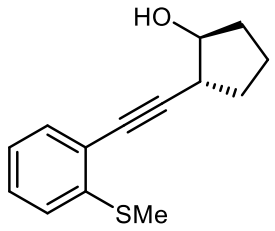
trans-2-((2-(Methylthio)phenyl)ethynyl)cyclohexan-1-ol (**3k**)



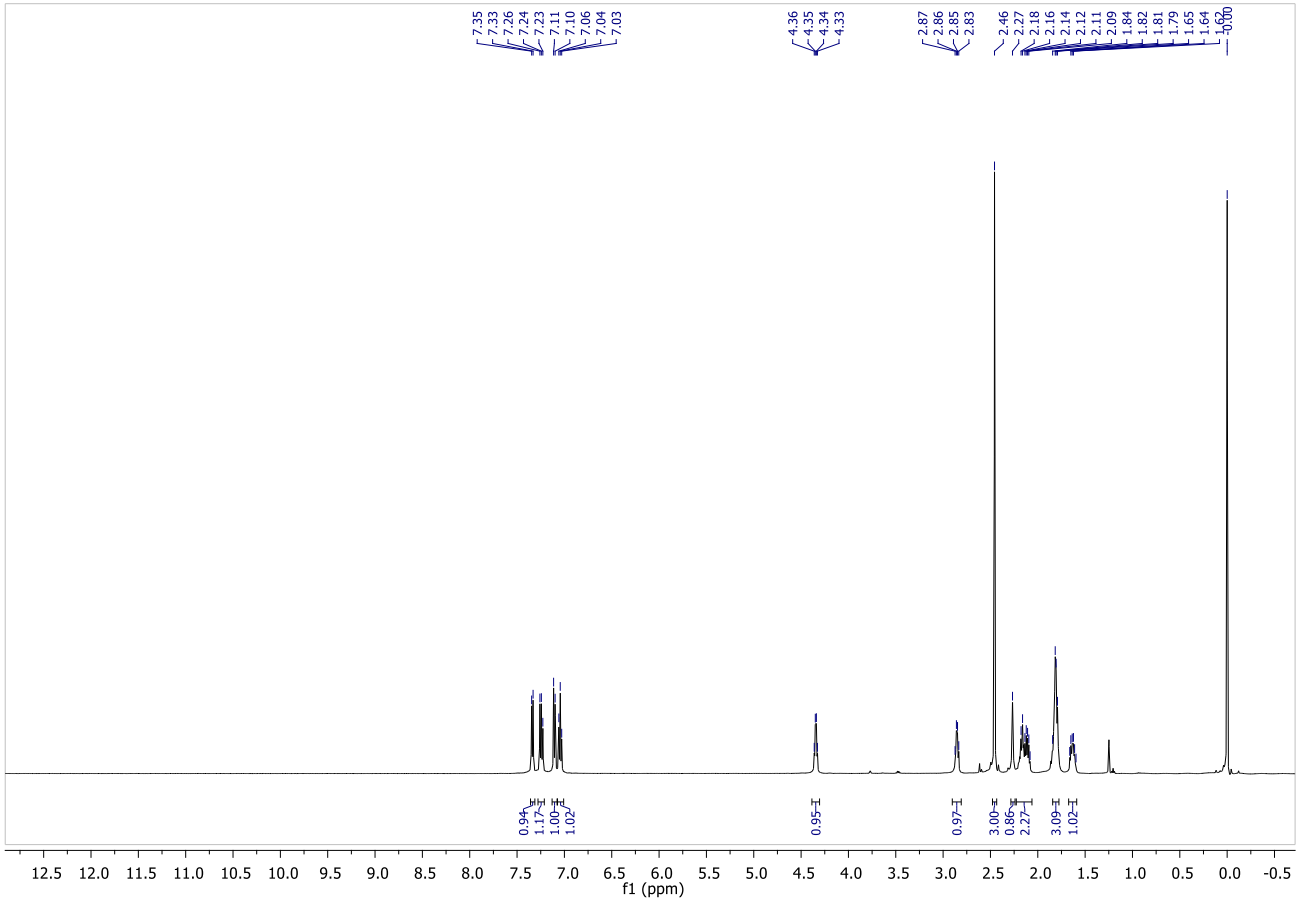
^{13}C NMR ($CDCl_3$, 125 MHz)



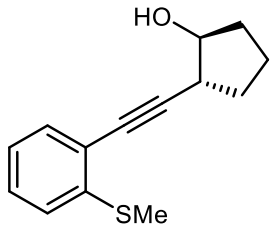
trans-2-((2-(Methylthio)phenyl)ethynyl)cyclopentan-1-ol (**3l**)



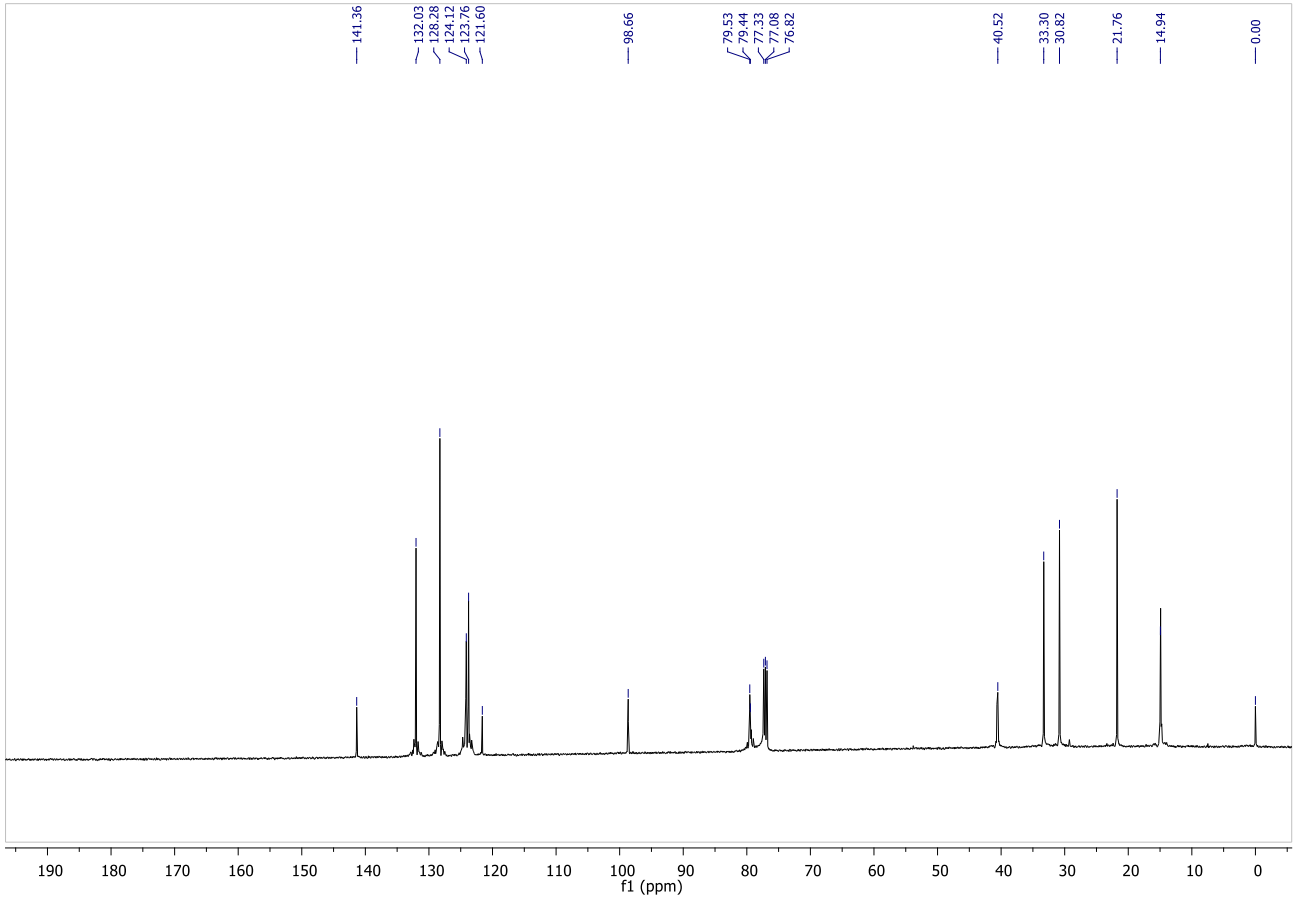
^{1}H NMR ($CDCl_3$, 500 MHz)



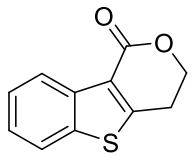
trans-2-((2-(Methylthio)phenyl)ethynyl)cyclopentan-1-ol (**3l**)



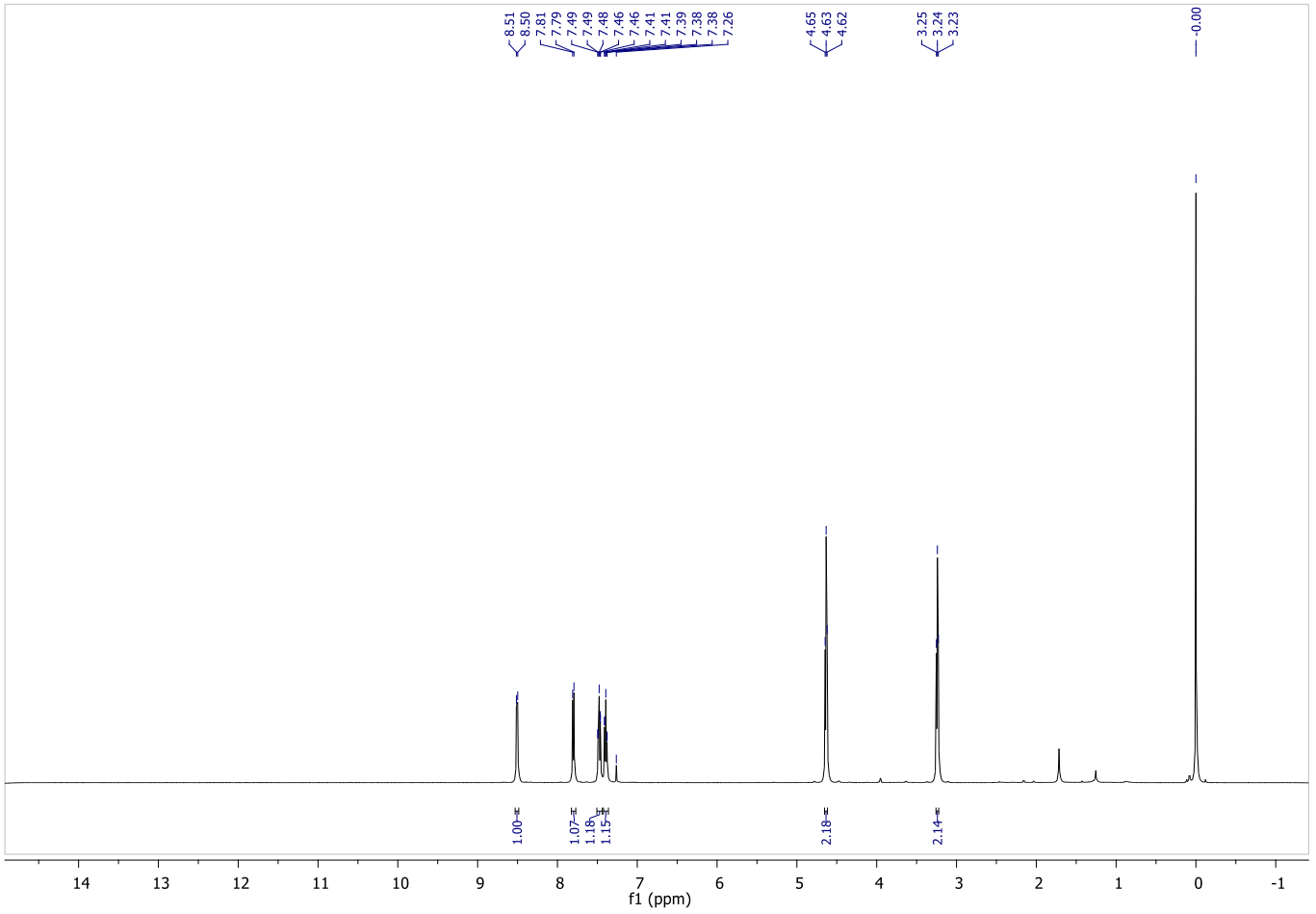
^{13}C NMR ($CDCl_3$, 125 MHz)



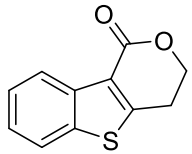
3,4-Dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4a**)



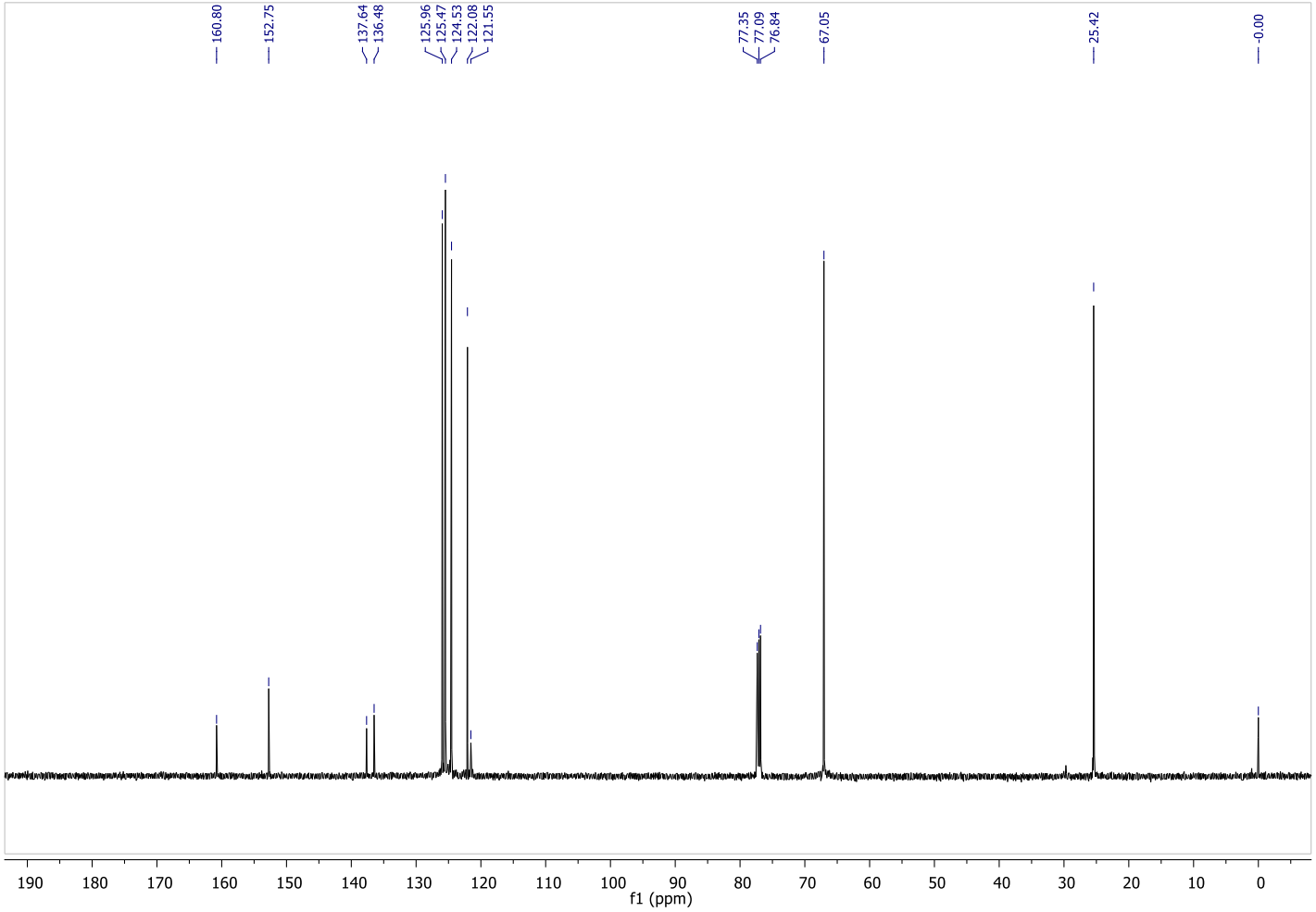
^{1}H NMR ($CDCl_3$, 500 MHz)



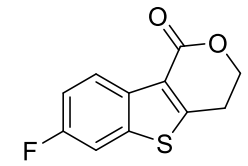
3,4-Dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4a**)



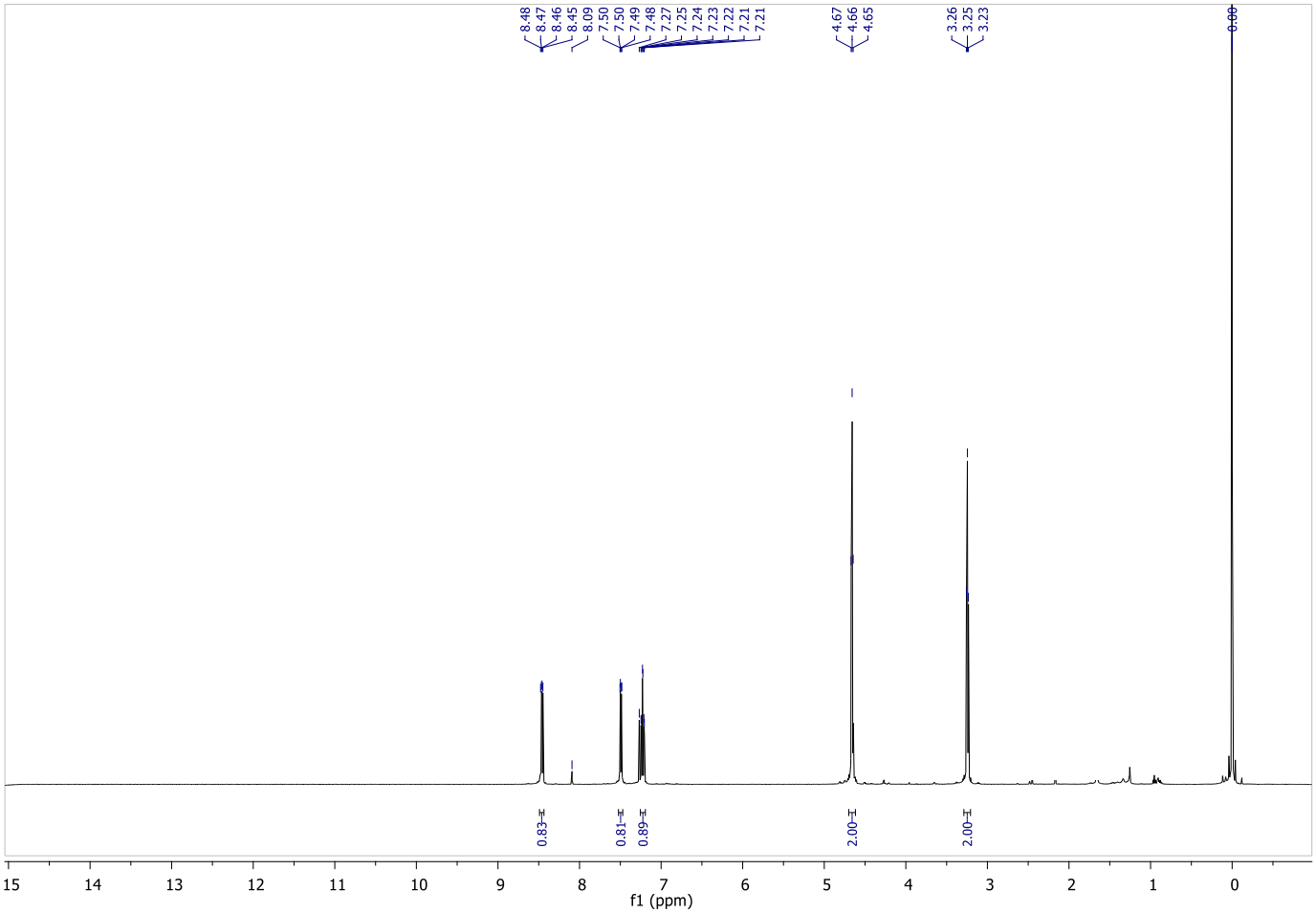
^{13}C NMR ($CDCl_3$, 125 MHz)



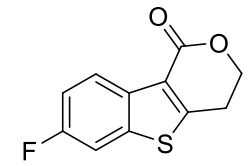
7-Fluoro-3,4-Dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4b**)



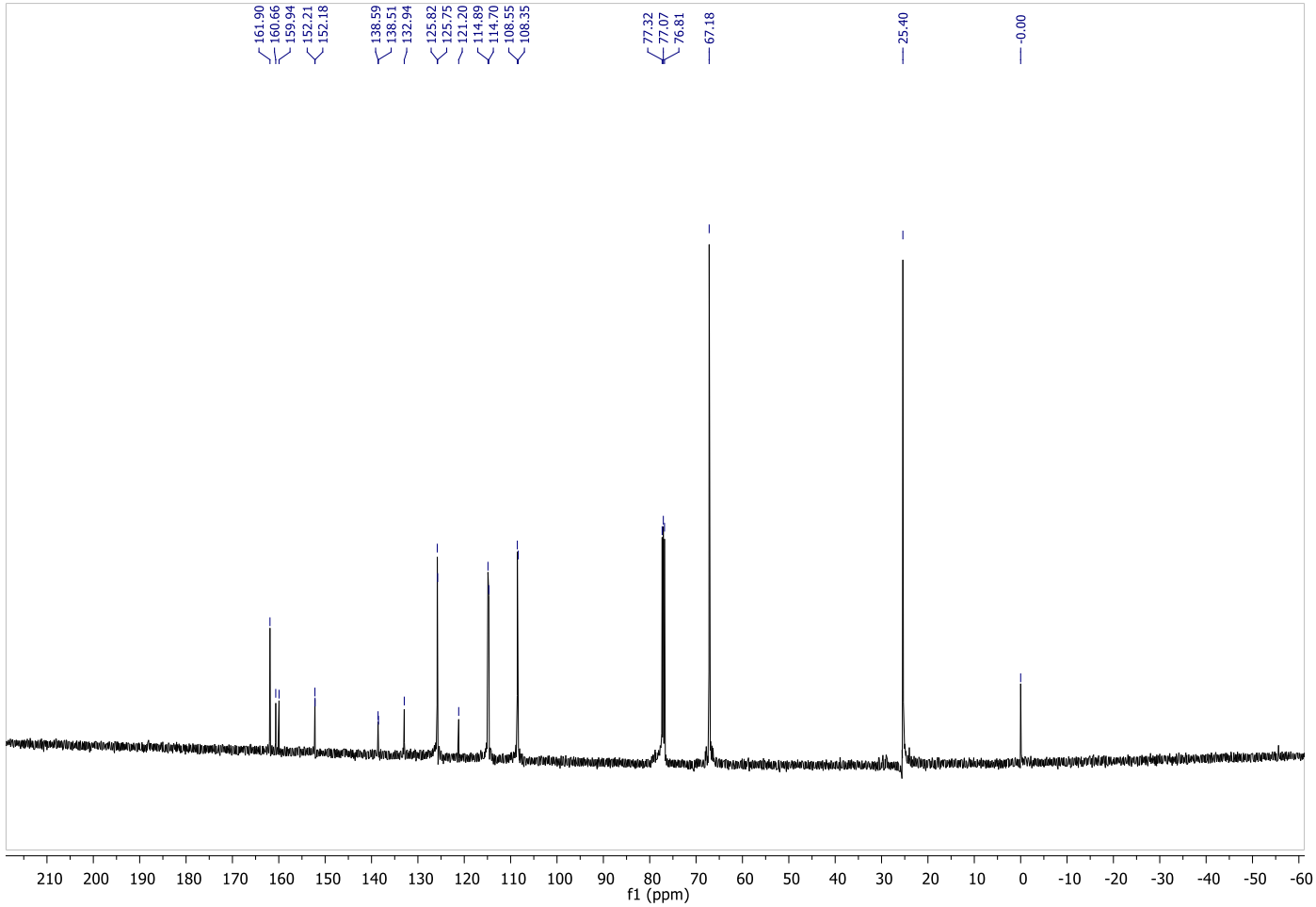
^{1}H NMR ($CDCl_3$, 500 MHz)



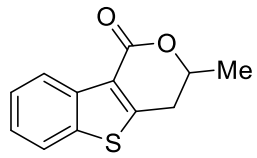
7-Fluoro-3,4-Dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4b**)



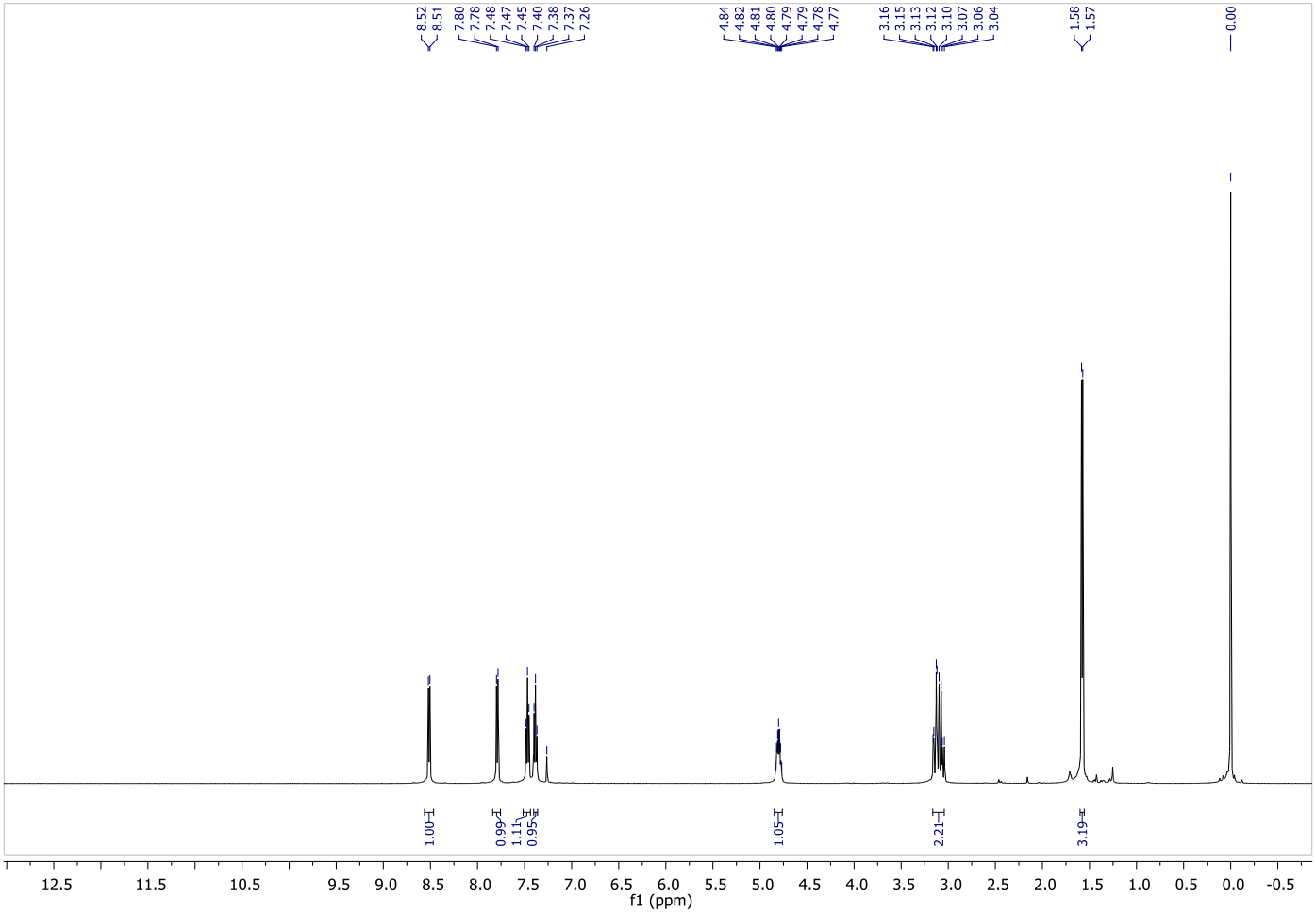
^{13}C NMR ($CDCl_3$, 125 MHz)



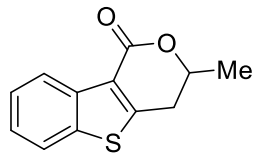
3-Methyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4c**)



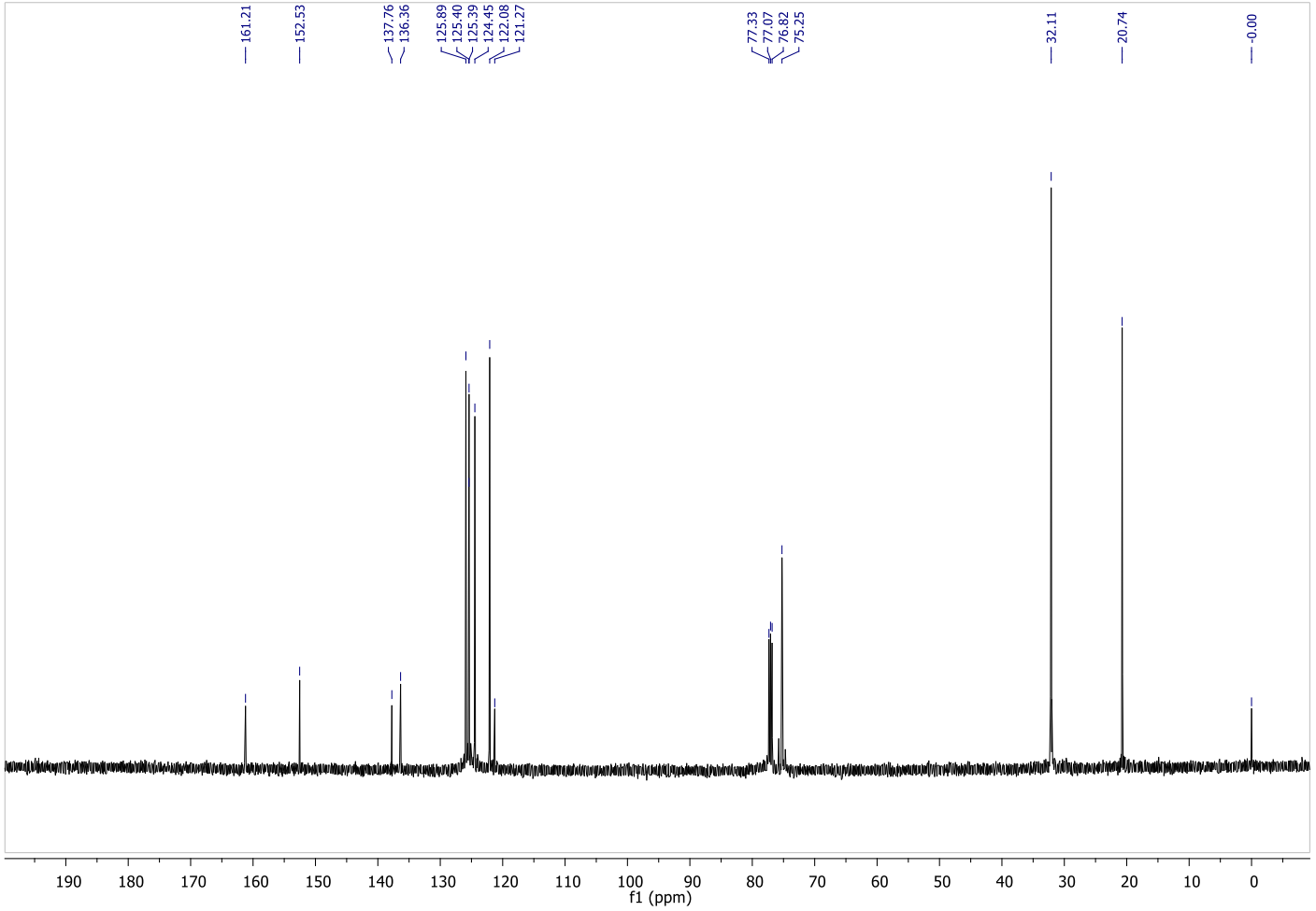
ù^{1}H NMR ($CDCl_3$, 500 MHz)



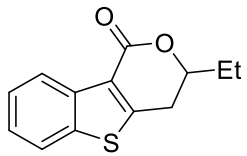
3-Methyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4c**)



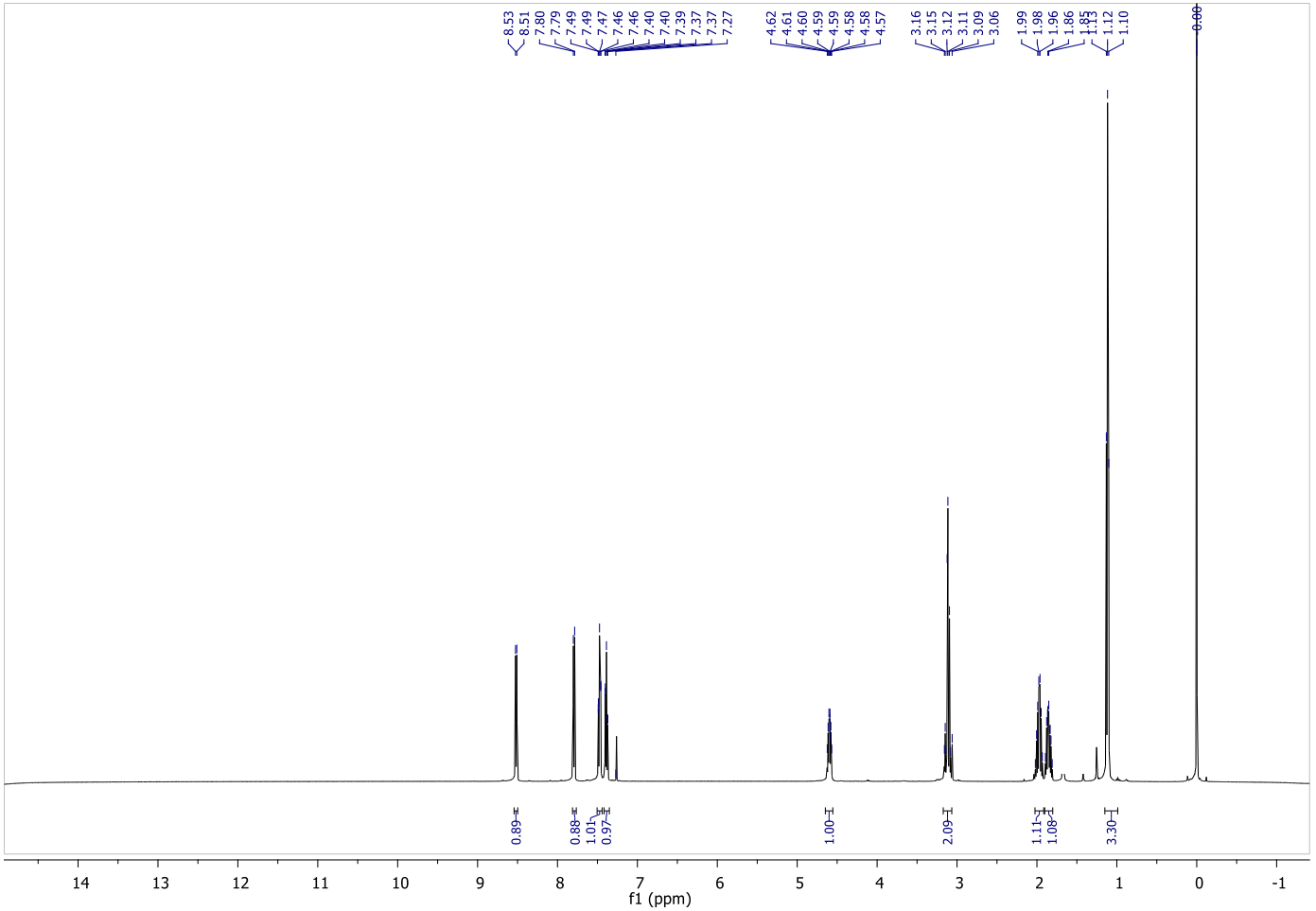
^{13}C NMR ($CDCl_3$, 125 MHz)



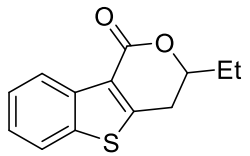
3-Ethyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4d**)



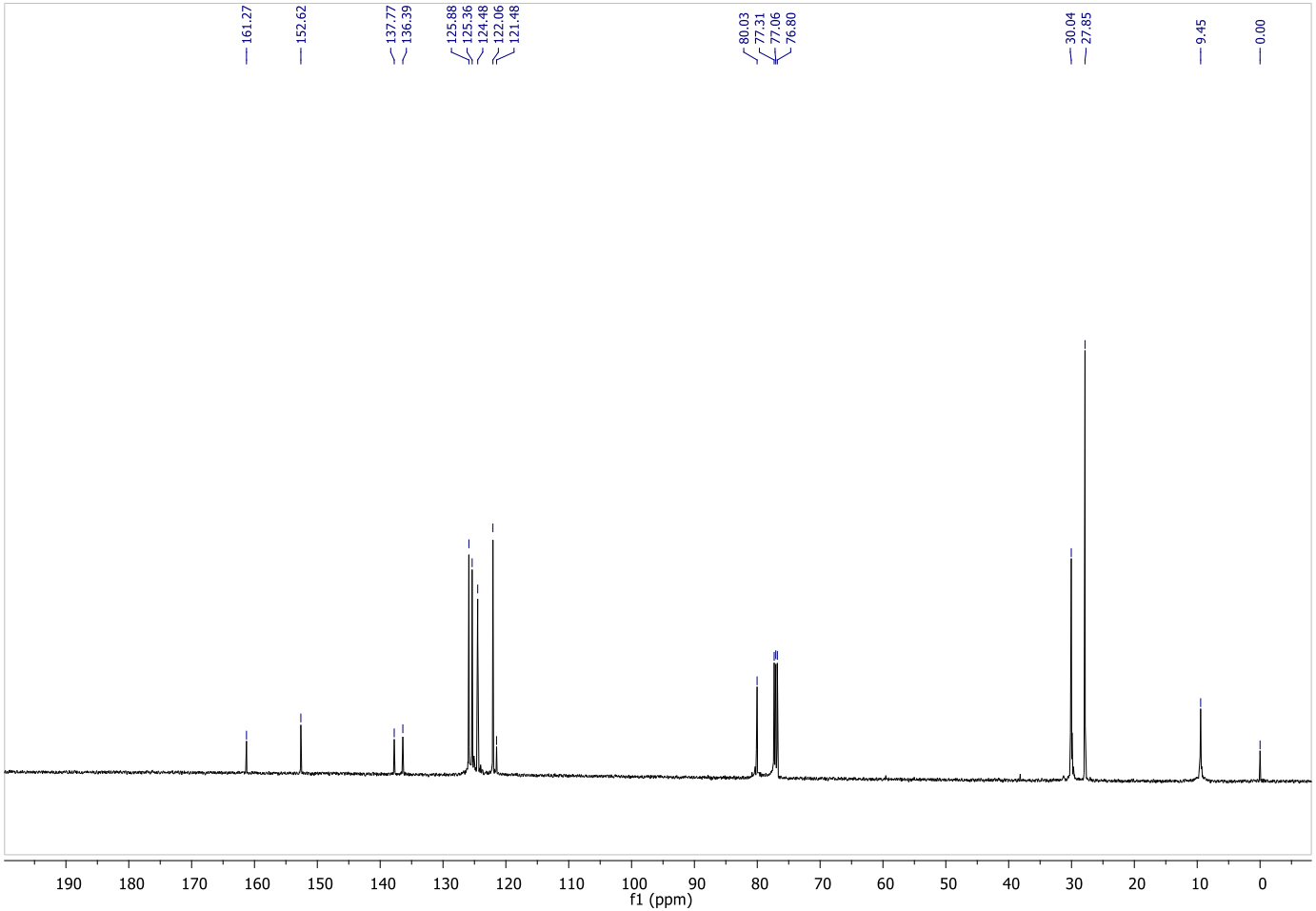
^{1}H NMR ($CDCl_3$, 500 MHz)



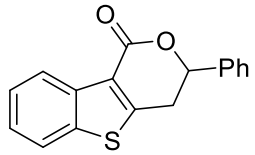
3-Ethyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4d**)



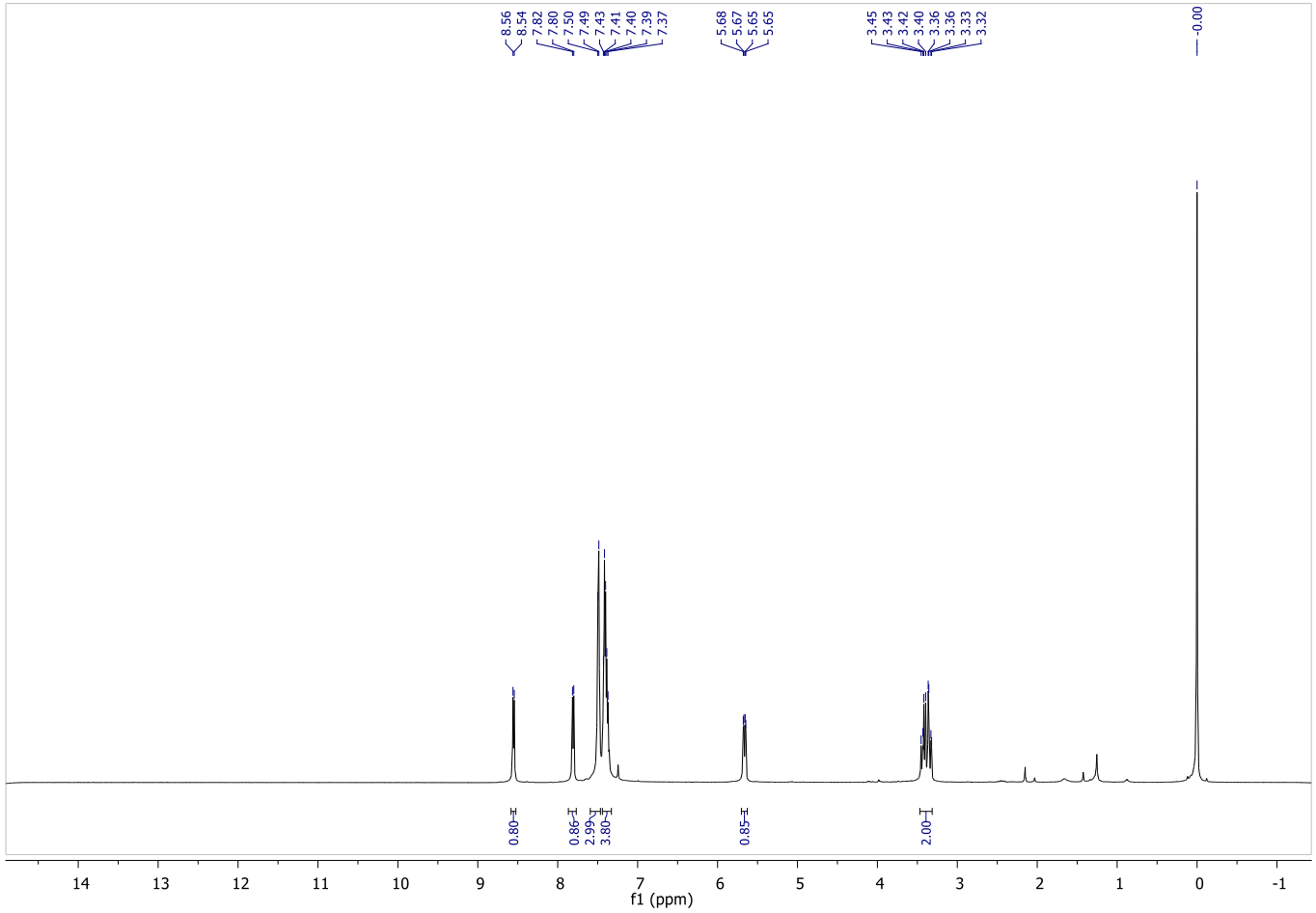
^{13}C NMR ($CDCl_3$, 125 MHz)



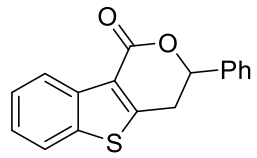
3-Phenyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4e**)



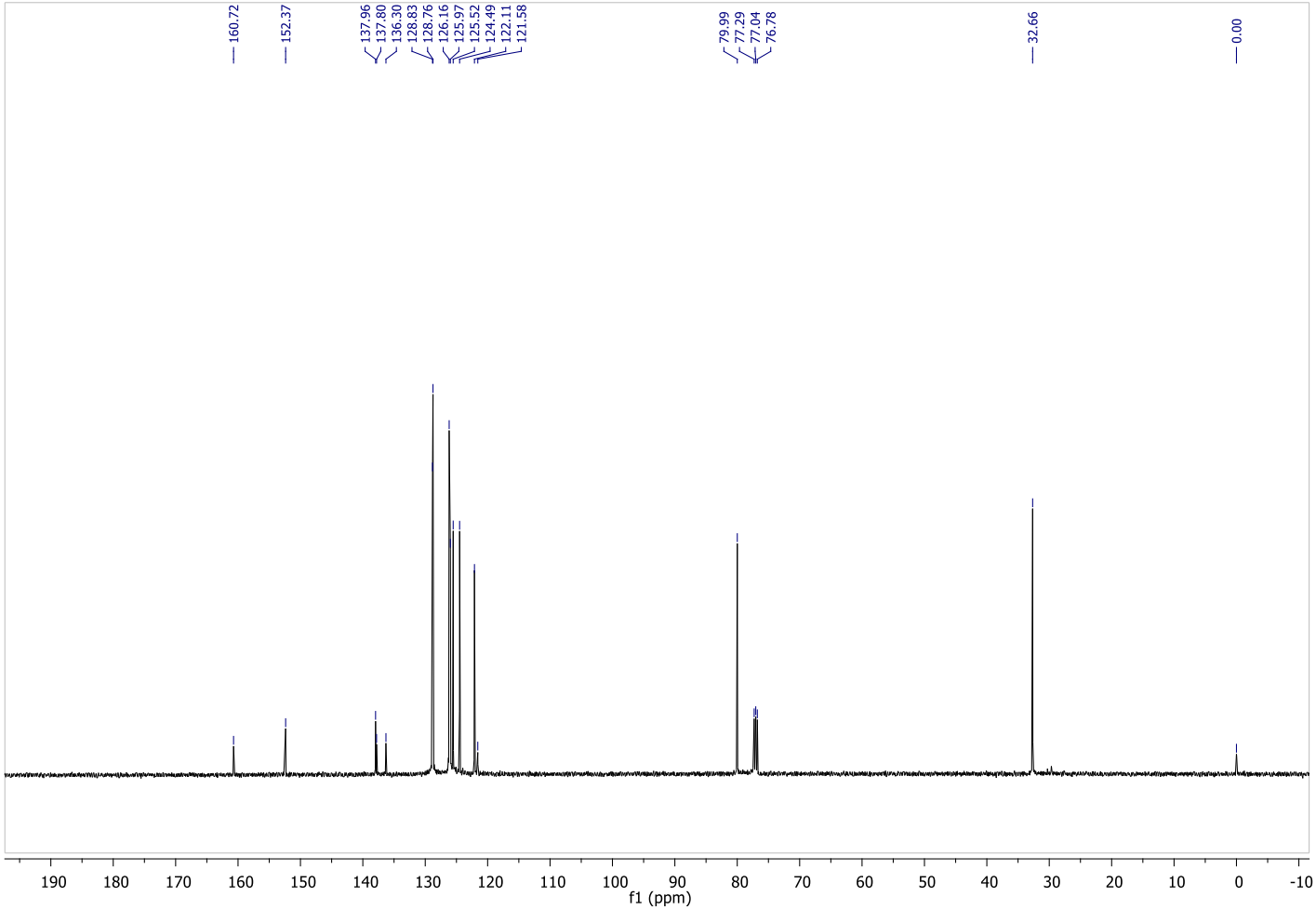
^{1}H NMR ($CDCl_3$, 500 MHz)



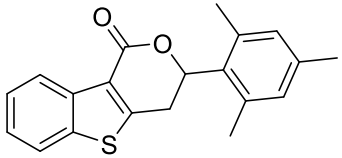
3-Phenyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4e**)



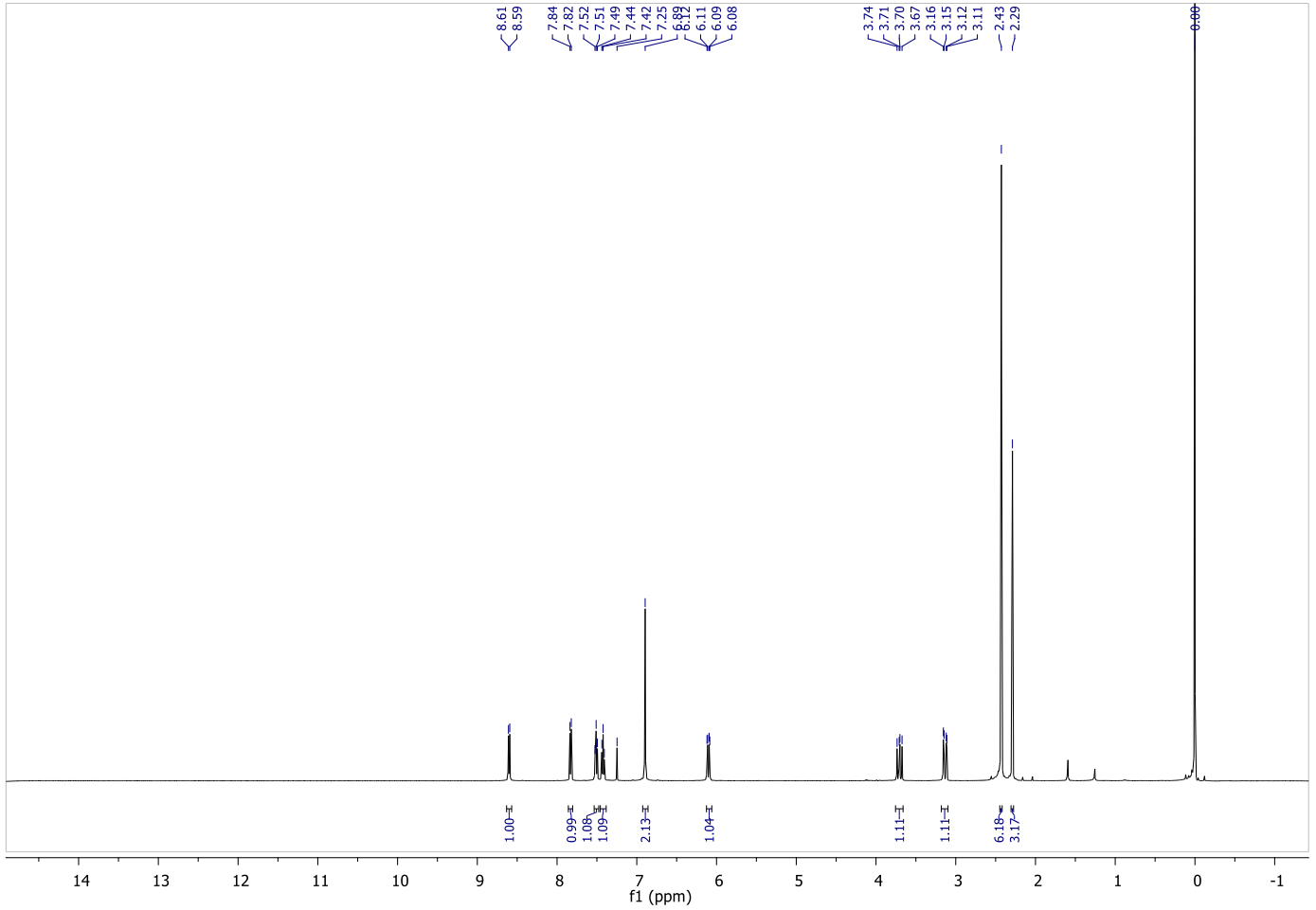
^{13}C NMR ($CDCl_3$, 125 MHz)



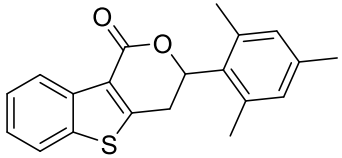
3-Mesityl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4f**)



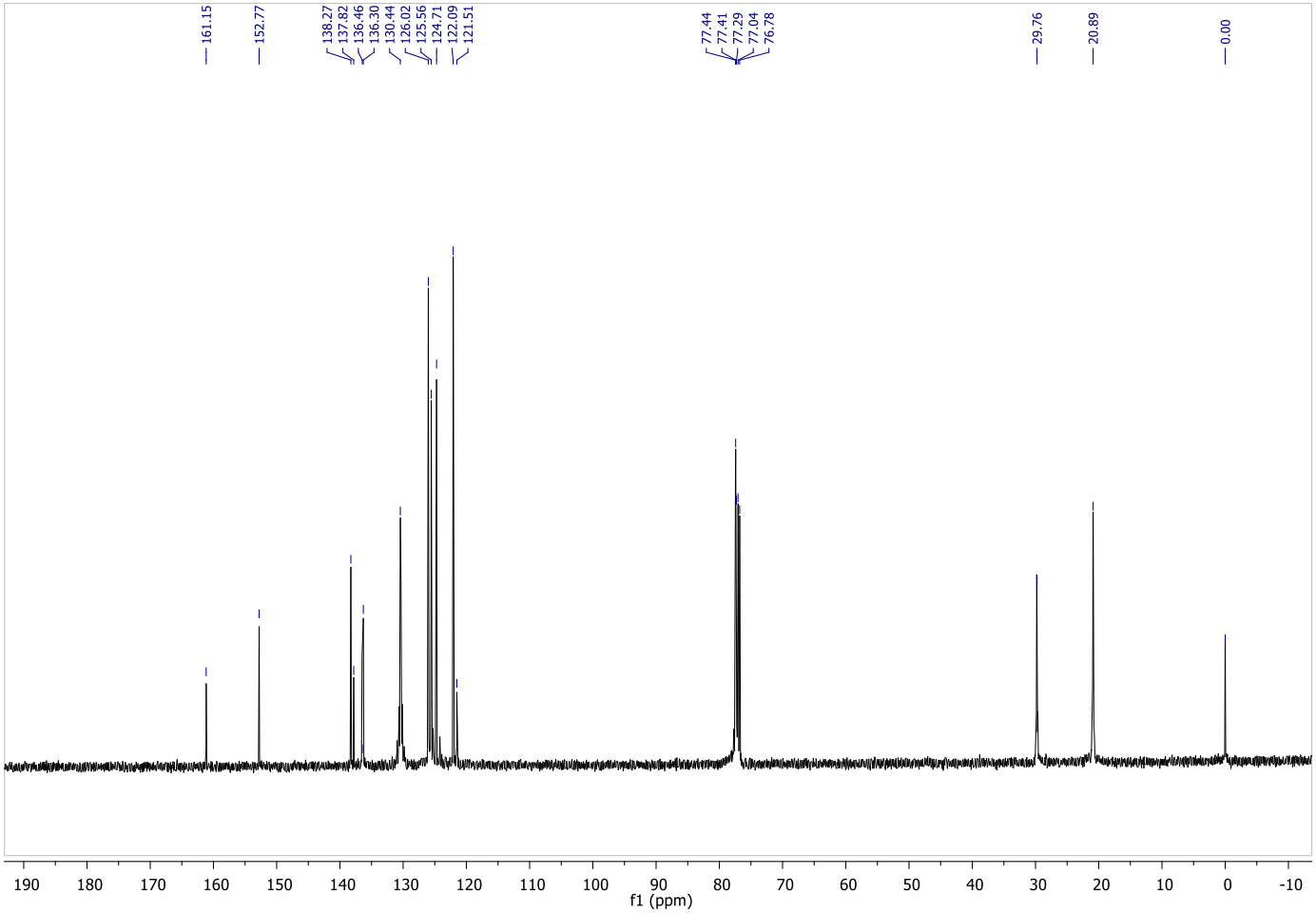
^{1}H NMR ($CDCl_3$, 500 MHz)



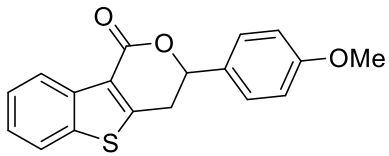
3-Mesityl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4f**)



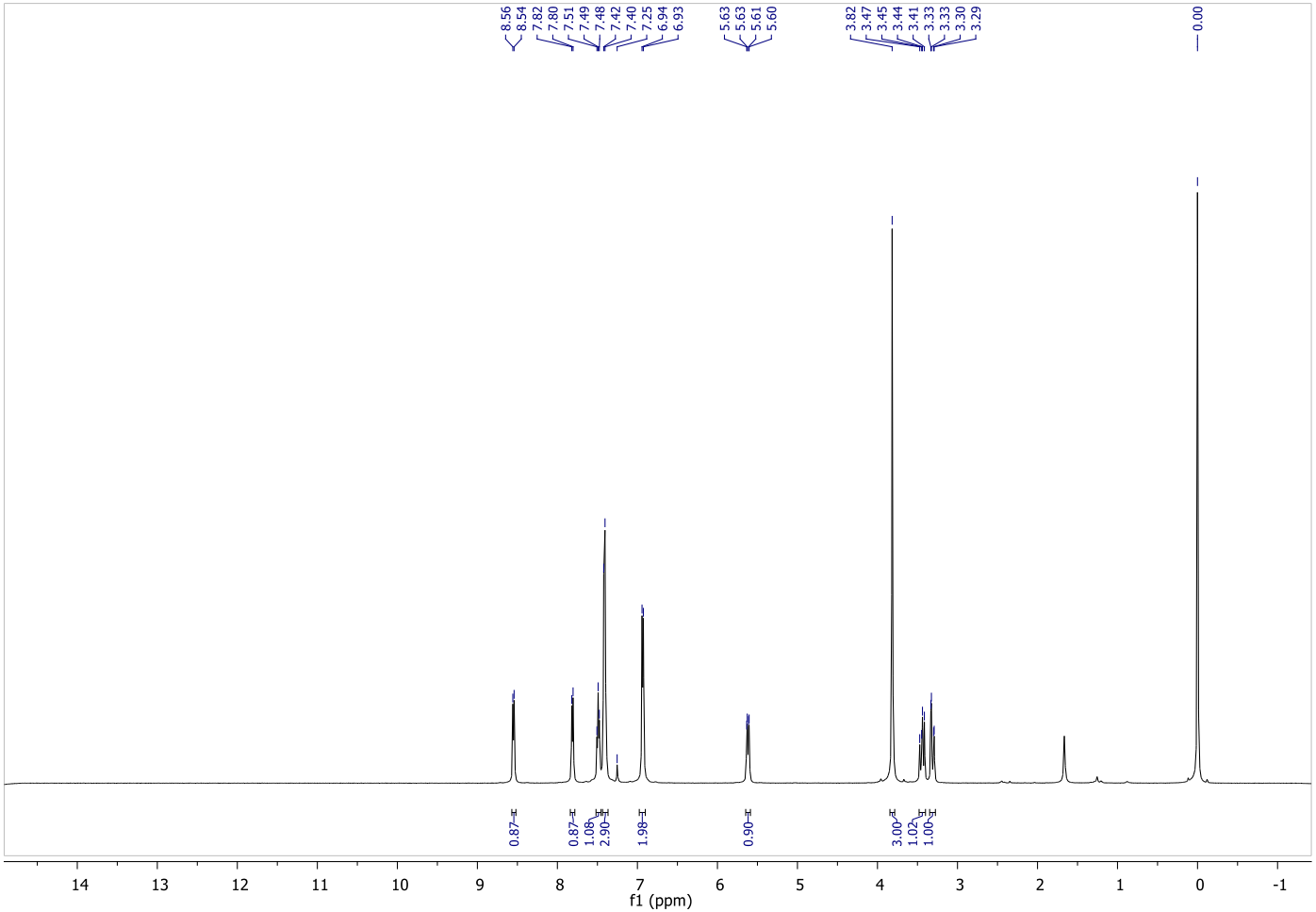
^{13}C NMR ($CDCl_3$, 125 MHz)



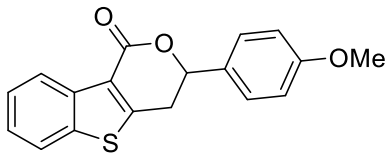
3-(4-Methoxyphenyl)-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4g**)



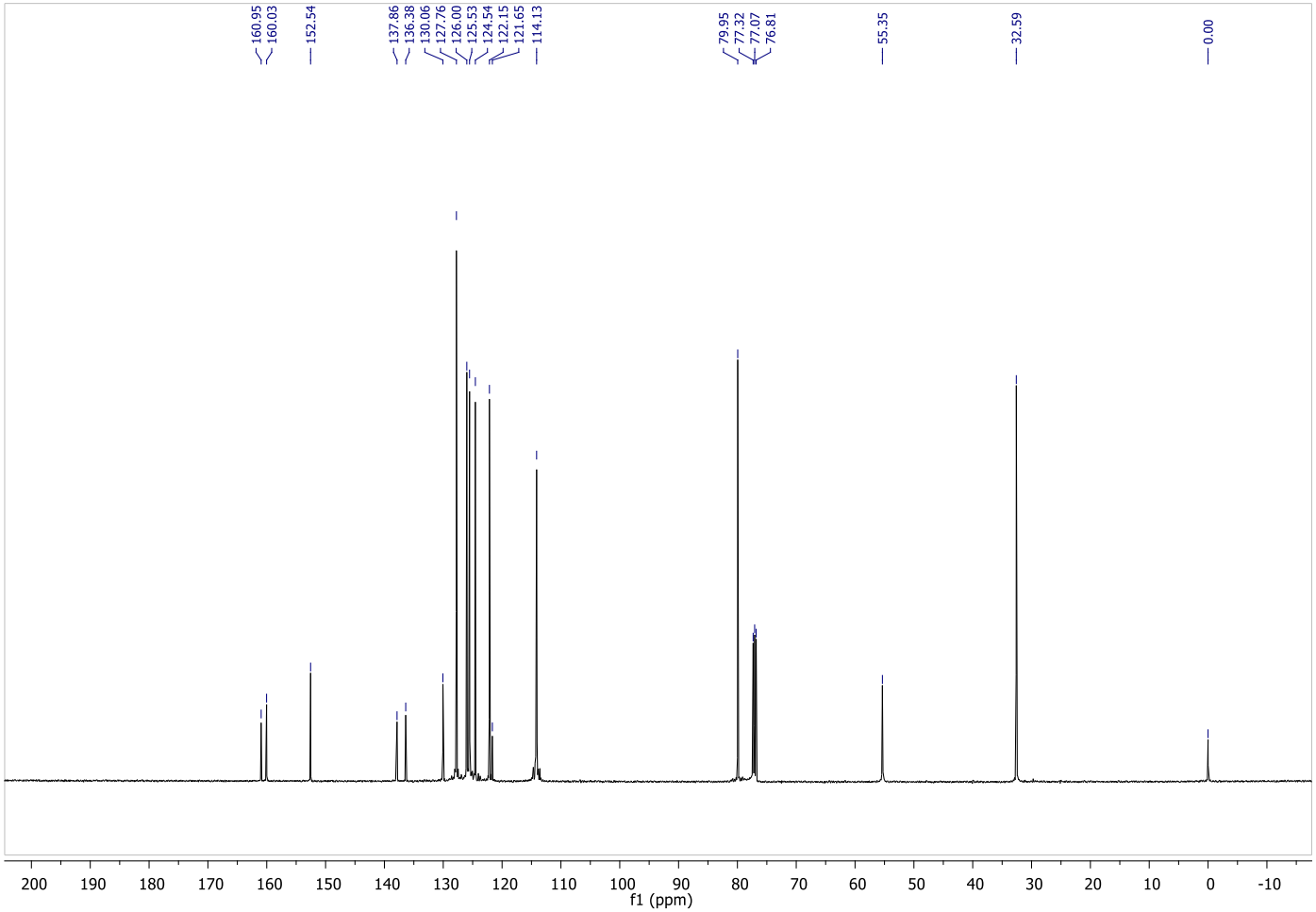
^{1}H NMR ($CDCl_3$, 500 MHz)



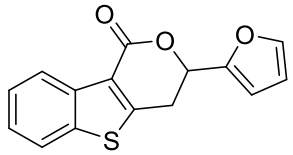
3-(4-Methoxyphenyl)-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4g**)



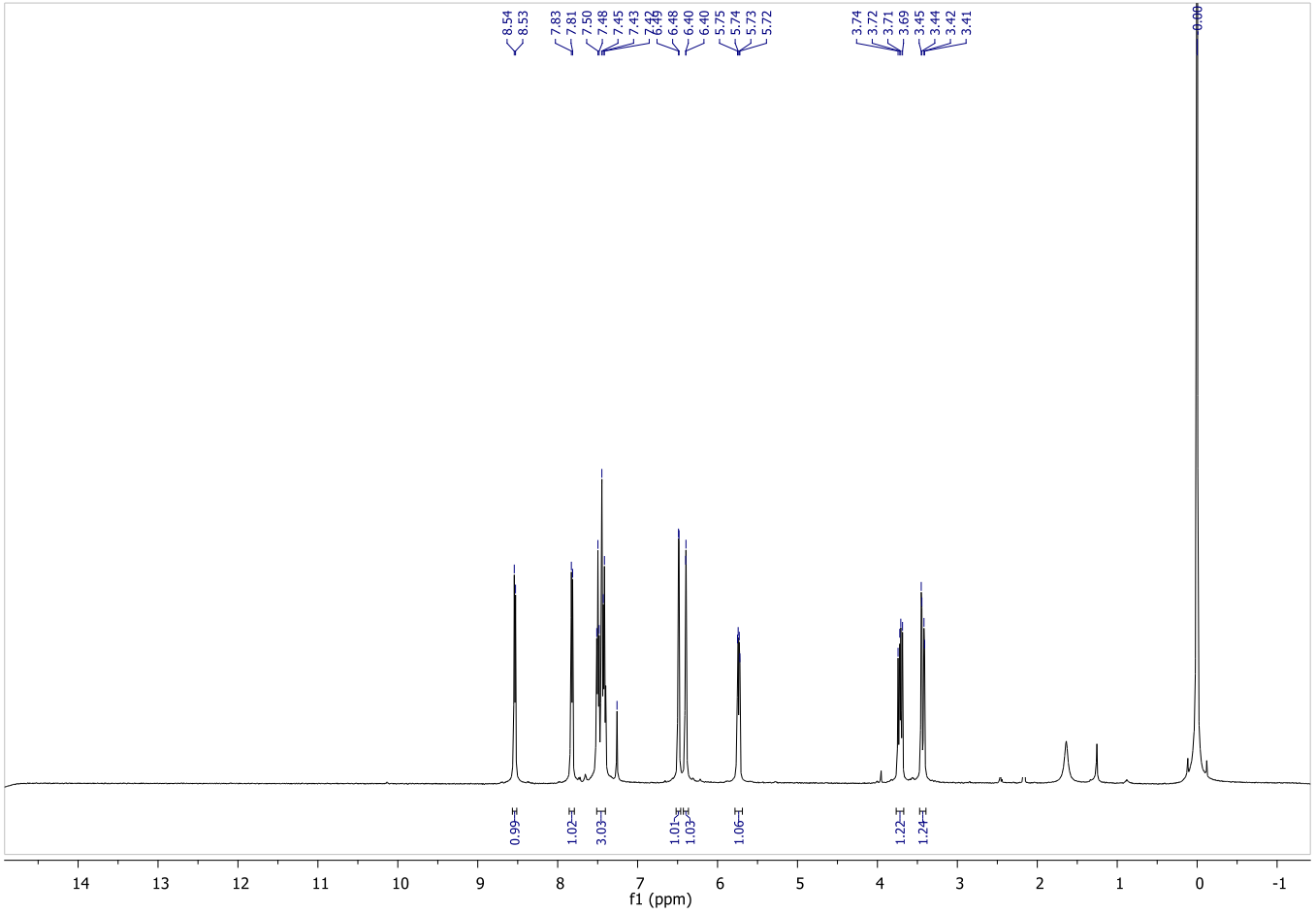
^{13}C NMR ($CDCl_3$, 125 MHz)



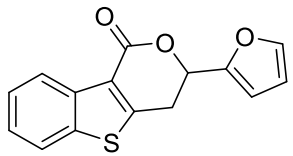
3-(Furan-2-yl)-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4h**)



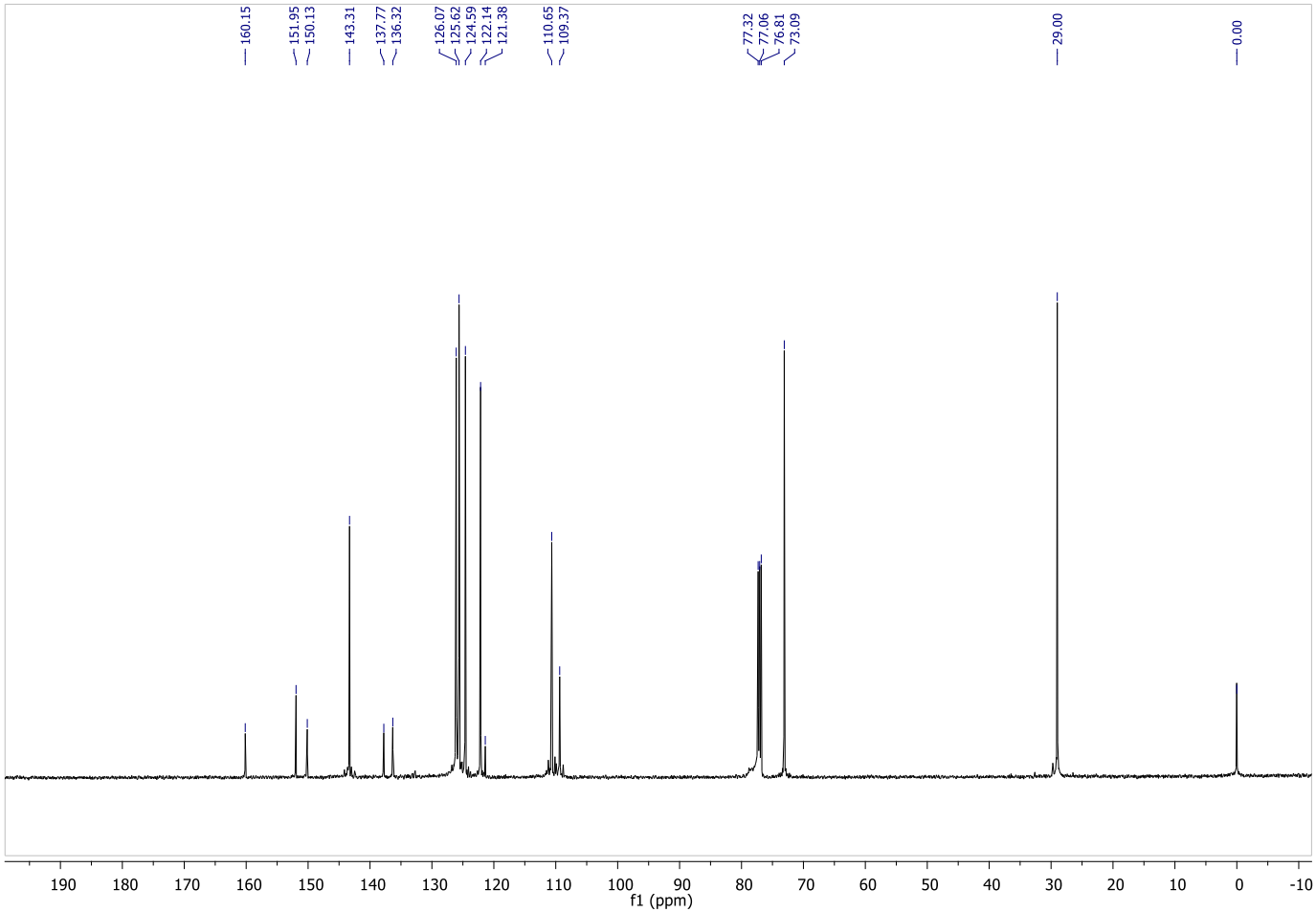
^{1}H NMR ($CDCl_3$, 500 MHz)



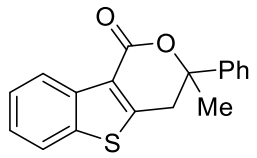
3-(Furan-2-yl)-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4h**)



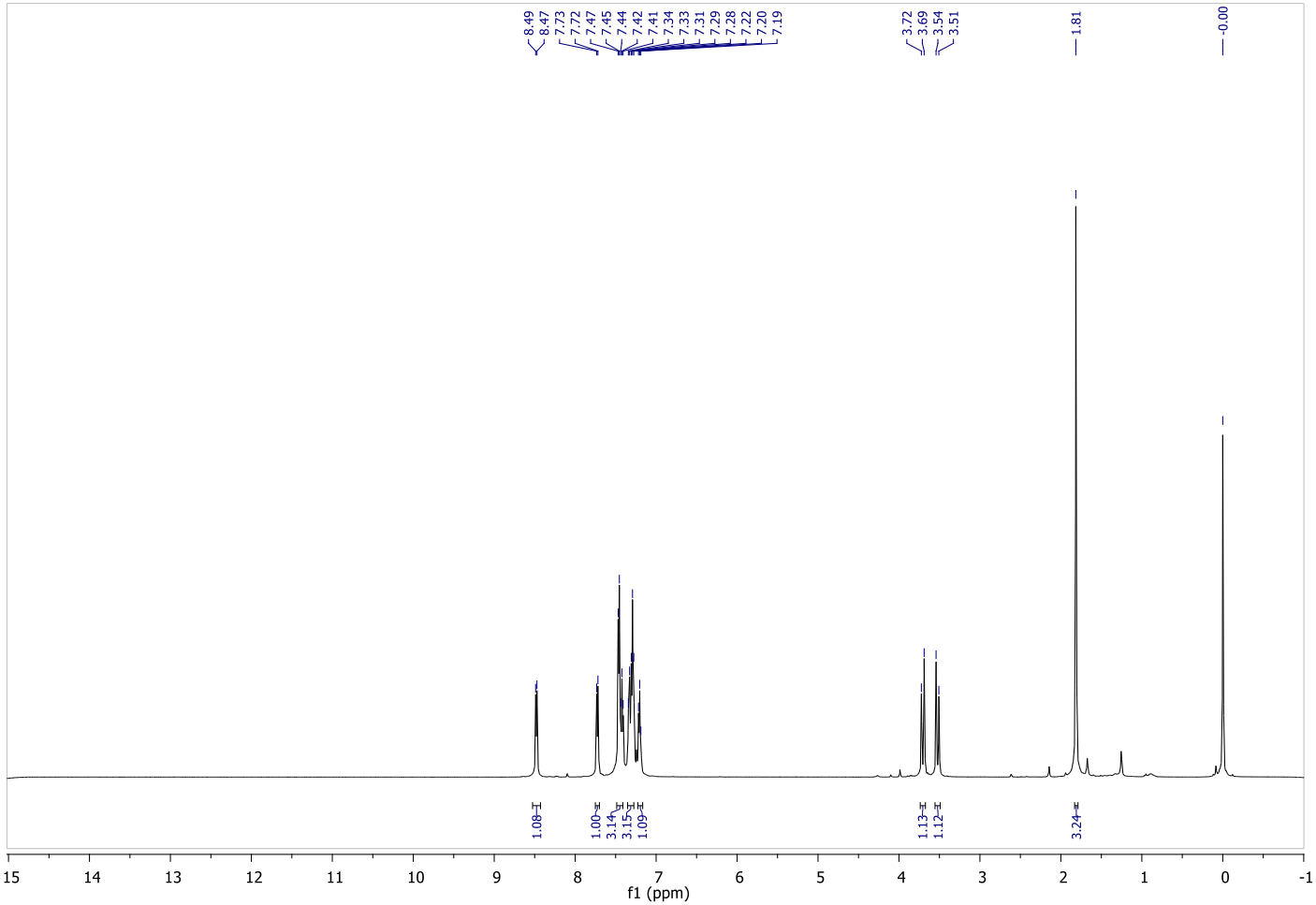
^{13}C NMR ($CDCl_3$, 125 MHz)



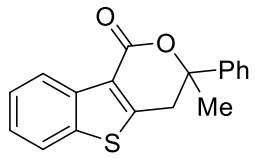
3-Methyl-3-phenyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4i**)



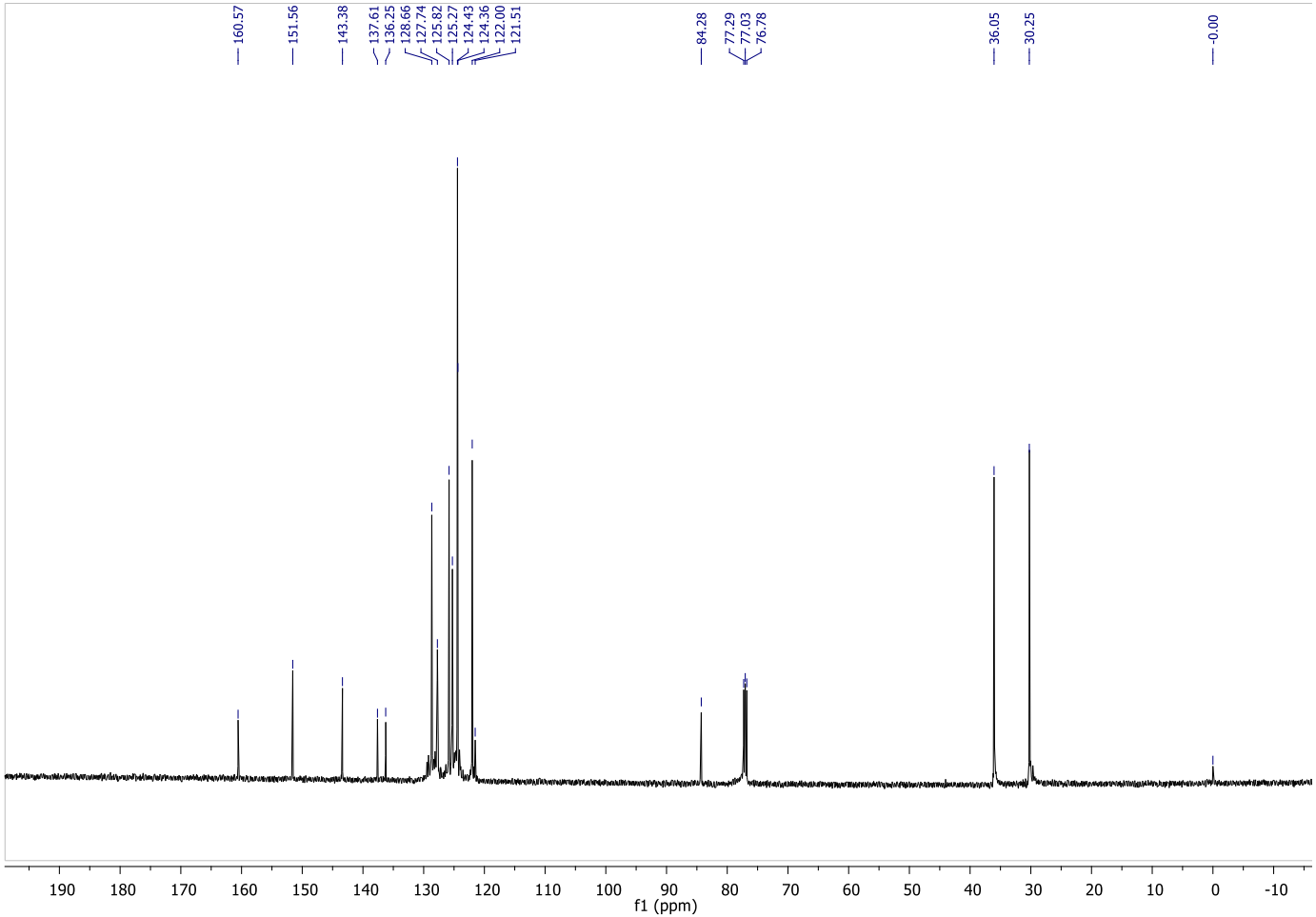
^{1}H NMR ($CDCl_3$, 500 MHz)



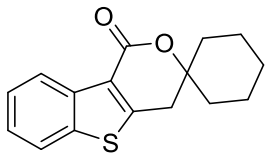
3-Methyl-3-phenyl-3,4-dihydro-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (**4i**)



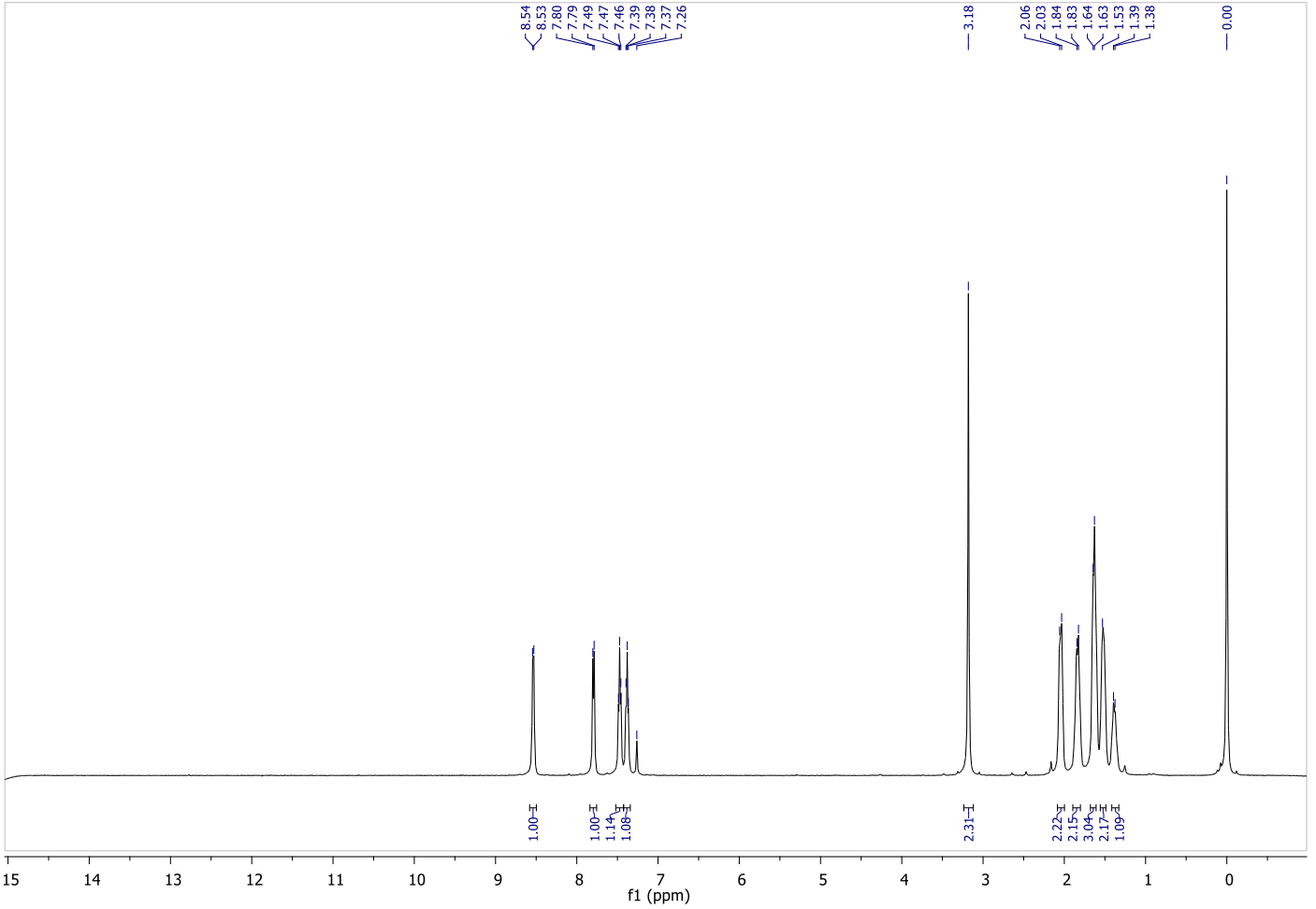
^{13}C NMR ($CDCl_3$, 125 MHz)



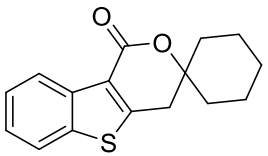
Spiro[benzo[4,5]thieno[3,2-*c*]pyran-3,1'-cyclohexan]-1(4*H*)-one (**4j**)



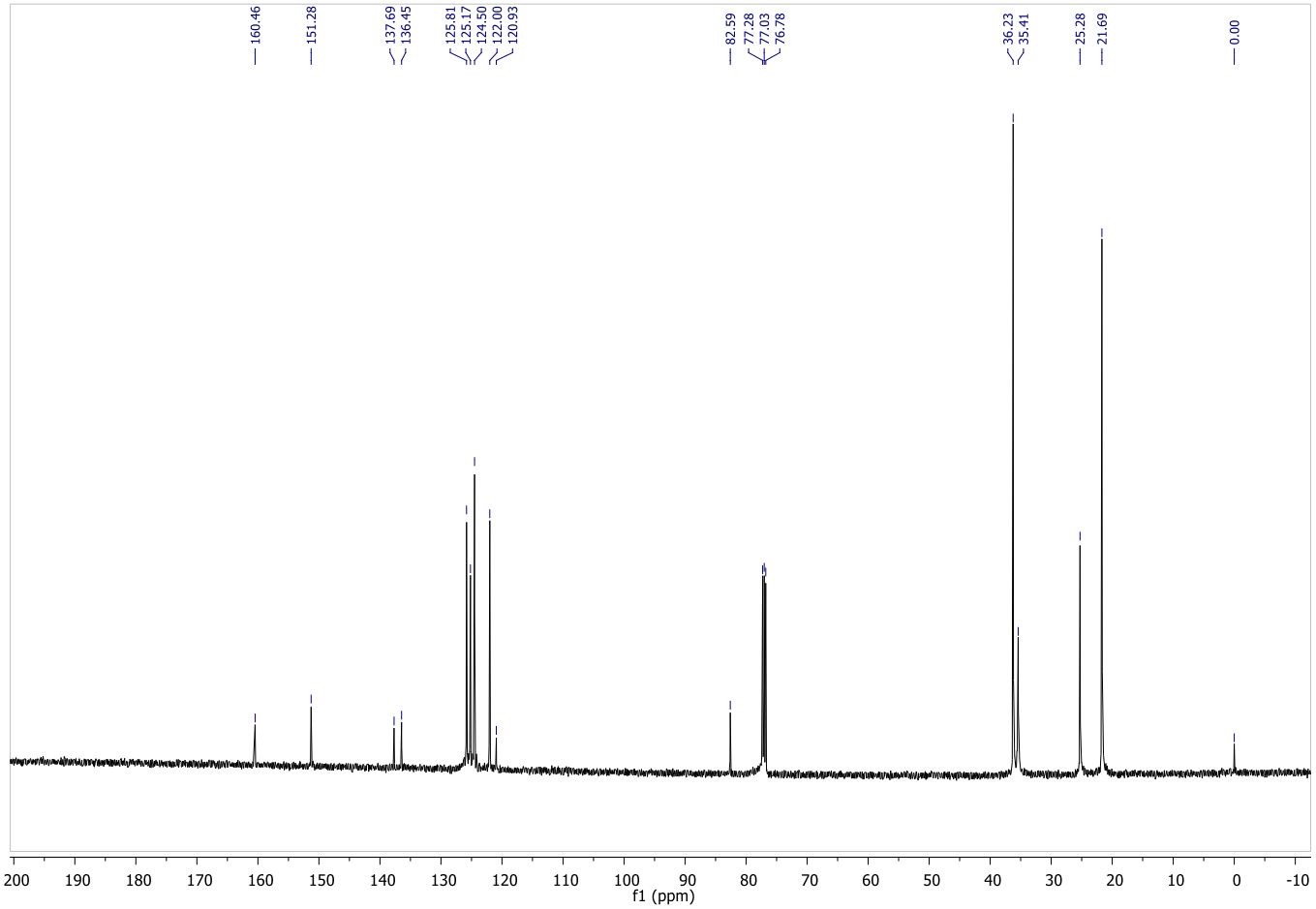
^{1}H NMR ($CDCl_3$, 500 MHz)



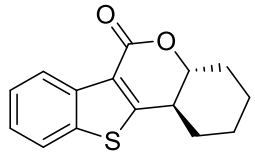
Spiro[benzo[4,5]thieno[3,2-*c*]pyran-3,1'-cyclohexan]-1(4*H*)-one (**4j**)



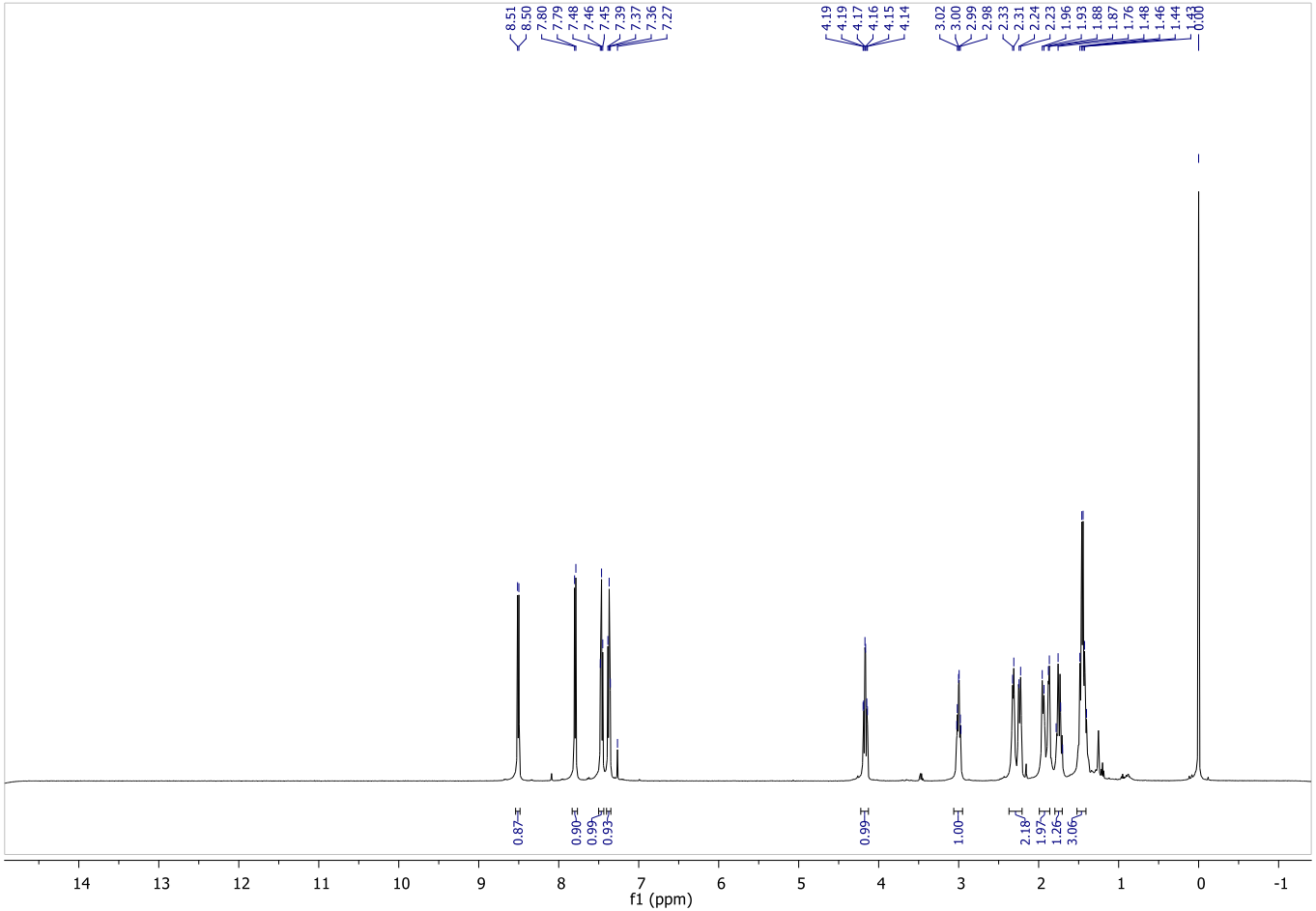
^{13}C NMR ($CDCl_3$, 125 MHz)



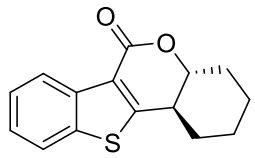
(4a*RS*, 11b*RS*)-1,2,3,4,4a,11b-Hexahydro-6*H*-benzo[4,5]thieno[3,2-*c*]chromen-6-one (**4k**)



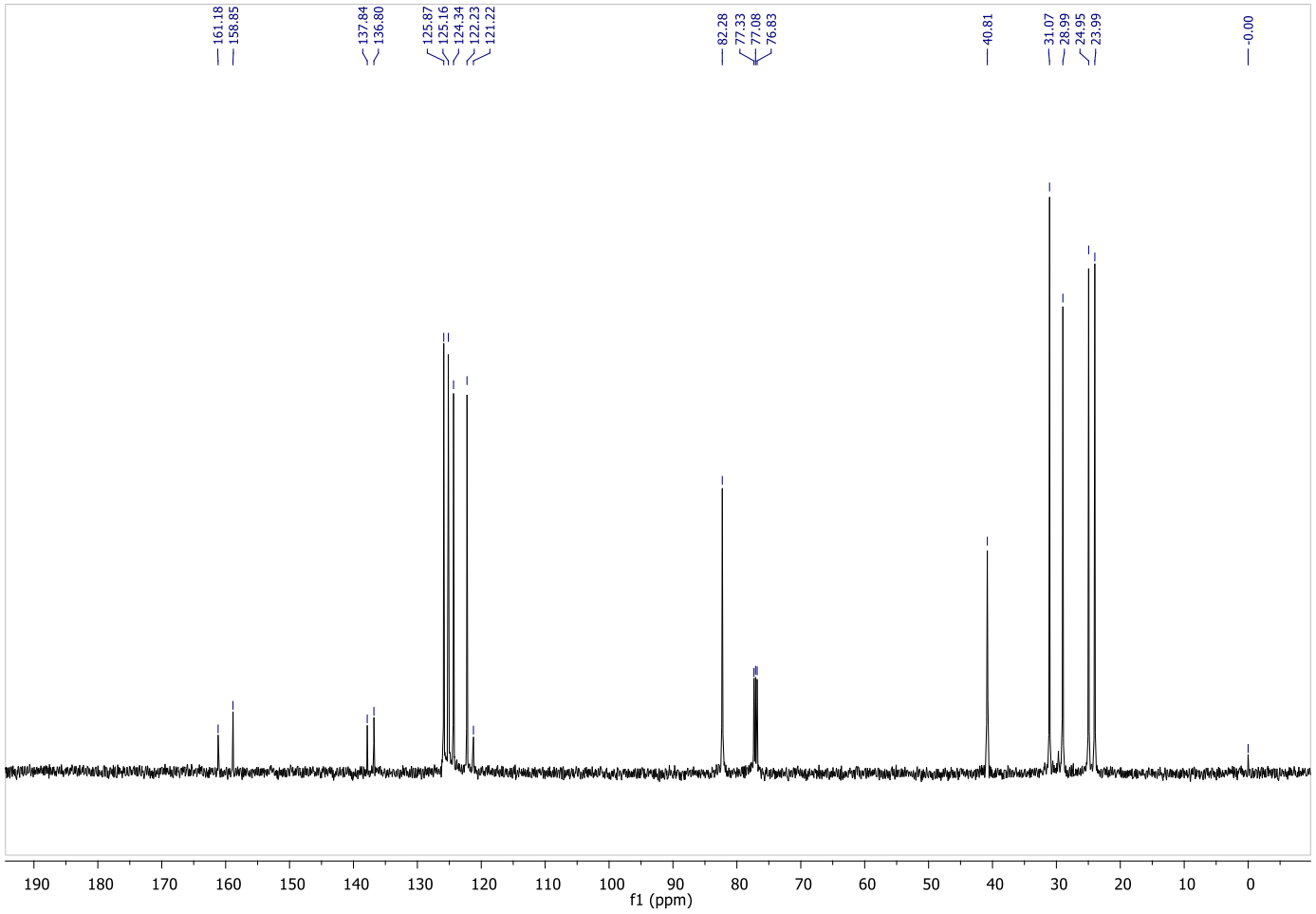
^{1}H NMR ($CDCl_3$, 500 MHz)



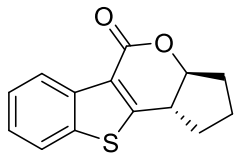
(4a*RS*, 11b*RS*)-1,2,3,4,4a,11b-Hexahydro-6*H*-benzo[4,5]thieno[3,2-*c*]chromen-6-one (**4k**)



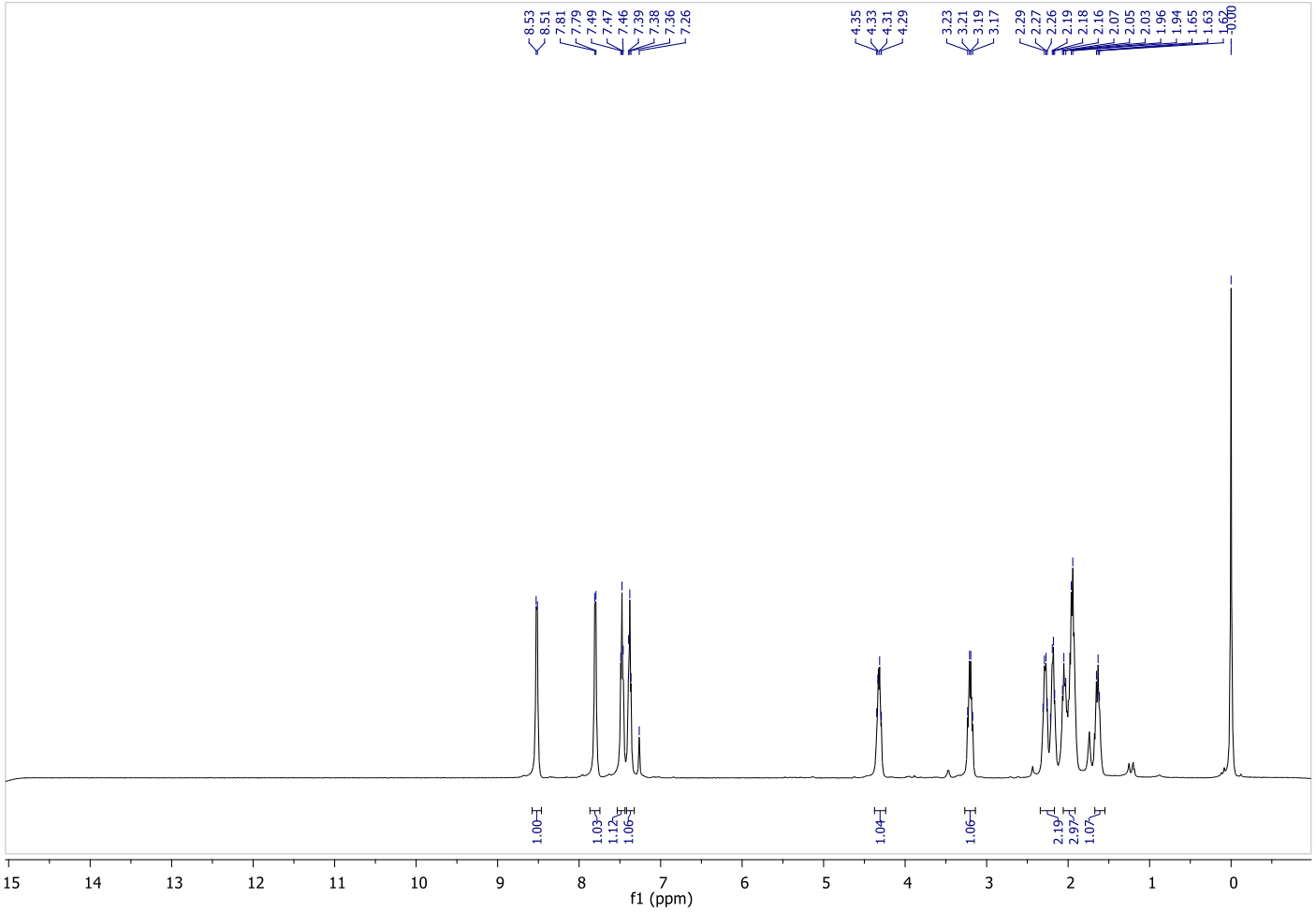
^{13}C NMR ($CDCl_3$, 125 MHz)



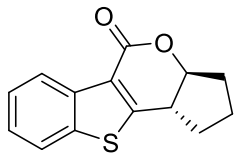
(3a*RS*, 10b*RS*)-2,3,3a,10b-Tetrahydrobenzo[4,5]thieno[3,2-*d*]cyclopenta[*b*]pyran-5(1*H*)-one (**4l**)



^{1}H NMR ($CDCl_3$, 500 MHz)



(3a*RS*, 10b*RS*)-2,3,3a,10b-Tetrahydrobenzo[4,5]thieno[3,2-*d*]cyclopenta[*b*]pyran-5(1*H*)-one (**4l**)



^{13}C NMR ($CDCl_3$, 125 MHz)