Supporting Information

Tosyl/pyrrolyl-capped 1,3-enynes via *t*-BuOK-assisted reaction of TosMIC with acylethynylpyrroles: a new feature of the popular reagent

Maxim D. Gotsko, Ivan V. Saliy, Igor A. Ushakov, Lyubov' N. Sobenina, Boris A. Trofimov

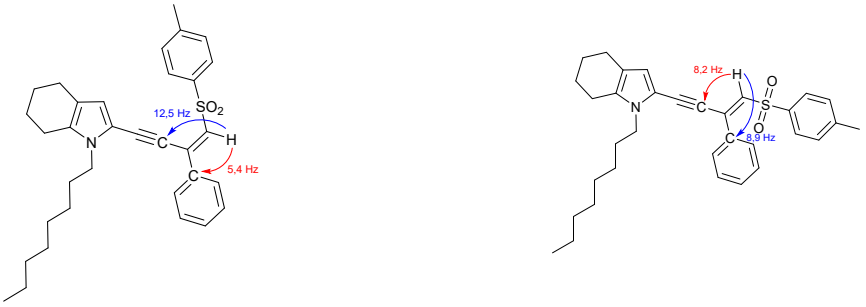
A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky St., Irkutsk 664033, Russian Federation

**Corresponding author: Tel.: 7 (3952) 51-14-31; fax 7 (3952) 41-93-46; e-mail: boris_trofimov@irioch.irk.ru*

Table of contents

1. General information

IR spectra were obtained with a Bruker Vertex 70 spectrometer (400–4000 cm^{-1}, films). ^{1}H (400.13 MHz), ^{13}C (100.6 MHz) spectra were recorded on a Bruker DPX-400 spectrometer at ambient temperature in $CDCl_3$ solutions and referenced to $CDCl_3$ (residual protons of $CDCl_3$ in ^{1}H NMR δ = 7.26 ppm; ^{13}C NMR δ = 77.1 ppm). The assignment of signals in the ^{1}H NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^{1}H- ^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. In the HMBC spectra of compound **2a**, cross-peaks between the signals of the olefin proton and the *C-ipso* of benzene ring and C-2 of enine chain are observed (Figure S1). Evidence for the configurational assignment of the olefinic fragment is the comparison of the vicinal constants $^{3}J_{C\text{-}ipso,H}$ and $^{3}J_{C\text{-}2,H}$. For the *E*-isomer, the coupling $^{3}J_{C\text{-}ipso,H}$ constant is 5.4 Hz and $^{3}J_{C\text{-}2,H}$ is 12.5 Hz. Vicinal $^{3}J_{C2,H}$ (8.2 Hz) and $^{3}J_{C\text{-}ipso,H}$ (8.9 Hz) coupling constants correspond to a *cis* position of the olefinic proton with respect to C-*2*, that is, Z- configuration of adduct **2a** (Figure S1). The similar effects in the NMR spectra of other tosylpyrrolylenines **2** were also observed.



E-isomer Z-isomer

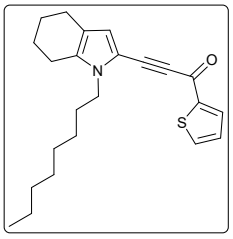
Figure 1. Main HMBC correlations of 1-octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2a**)

The C, H, N microanalyses were performed on a Flash EA 1112 CHNS-O/MAS analyzer. Sulfur was determined by complexometric titration with Chlorasenazo III. Fluorine content was determined on a SPECOL 11 (Carl Zeiss Jena, Germany) spectrophotometer. Clorine was determined by mercurimetric titration. Melting point (uncorrected) was determined on a Kofler micro hot-stage apparatus.

2. Starting materials

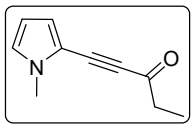
Acylethynylpyrroles **1a-m,p,q** were prepared from corresponding pyrroles and acylbromoacetylenes in the presence of Al_2O_3 according to the reported procedure.[1] 1,3-Diphenylprop-2-yn-1-one (**1n**), 1-(furan-2-yl)-3-phenylprop-2-yn-1-one (**1o**), 1-phenylpent-1-yn-3-one (**1r**), tosylmethylisocyanide (TosMIC), *t*-BuOK and THF are commercial products.

*3-(1-Octyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-1-(thiophen-2-yl)prop-2-yn-1-one (**1i**)*



Yield 276 mg (75%), yellow crystals; m.p. 58-60°C. Anal. Calcd for $C_{23}H_{29}NOS$: C, 75.16; H, 7.95; N, 3.81; S, 8.72%. Found: C, 75.3; H, 8.09; N, 3.98; S, 8.54%. ν_{max} (KBr) 3092, 2926, 2854, 2158, 1605, 1558, 1515, 1489, 1441, 1411, 1391, 1354, 1308, 1265, 1230, 1207, 1196, 1144, 1101, 1080, 1048, 1008, 987, 954, 929, 856, 824, 802, 720, 631 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.88-7.87 (m, 1H, H5-thiophene), 7.65-7.64 (m, 1H, H3-thiophene), 7.16-7.14 (m, 1H, H4-thiophene), 6.61 (s, 1H, pyrrole), 4.00-3.96 (m, 2H, NCH_2), 2.59-2.55 (m, 2H, CH_2-7), 2.52-2.49 (m, 2H, CH_2-4), 1.85-1.83 (m, 2H, CH_2-5), 1.76-1.75 (m, 4H, CH_2, CH_2-6), 1.33-1.24 (m, 10H, $5CH_2$), 0.86 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 169.1, 145.5, 135.5, 133.8, 133.2, 128.2, 119.9 (2C), 110.2, 95.8, 89.0, 45.1, 31.8, 31.3, 29.4, 29.3, 26.9, 23.3, 23.0, 22.9, 22.8, 22.7, 14.1.

*1-(1-Methyl-1H-pyrrol-2-yl)pent-1-yn-3-one (**1q**)*



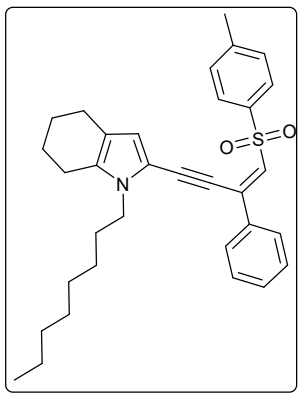
Yield 217 mg (67%), yellow crystals; m.p. 48-50°C. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69%. Found: C, 74.68; H, 7.01; N, 8.87%. ν_{max} (KBr) 3285, 3130, 3106, 2982, 2942, 2898, 2171, 1767, 1653, 1572, 1482, 1454, 1421, 1404, 1377, 1343, 1317, 1244, 1189, 1122, 1041, 1014, 985, 984, 798, 756, 635, 604, 545, 496, 453 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 6.80-6.79 (m, 1H, pyrrole), 6.70 (dd, J = 1.6, 3.9 Hz, 1H, pyrrole), 6.14 (dd, J = 2.6, 3.9 Hz, 1H, pyrrole), 3.72 (s, 3H, N-CH_3), 2.64 (q, J = 7.4 Hz, 2H, CH_2), 1.21 (t, J = 4.0 Hz, 3H, CH_3). ^{13}C NMR (100,6 MHz, $CDCl_3$) δ 187.9, 127.4, 120.8, 112.8, 109.5, 95.2, 85.2, 38.3, 34.8, 8.5.

(1) Trofimov, B. A.; Stepanova, Z. V.; Sobenina, L. N.; Mikhaleva, A. b. I.; Ushakov, I. A., Ethynylation of pyrroles with 1-acyl-2-bromoacetylenes on alumina: a formal 'inverse Sonogashira coupling'. Tetrahedron Lett. 2004, 45, 6513-6516.

3. The reaction of 2-acylethynylpyrroles (1a-o) with TosMIC

A solution of acylethynylpyrrole **1** (1 mmol) and TosMIC (395 mg, 2 mmol) in THF (10 mL) was heated to reflux. Then, under reflux, solution of *t*-BuOK (224 mg, 2 mmol) in THF (10 mL) was added dropwise to reaction mixture for 1 hour. The residue, after removing solvent, was fractionated by column chromatography (SiO_2, *n*-hexane : diethyl ether, 5 : 1) to afford the tosylpyrrolylenines **2a-o**.

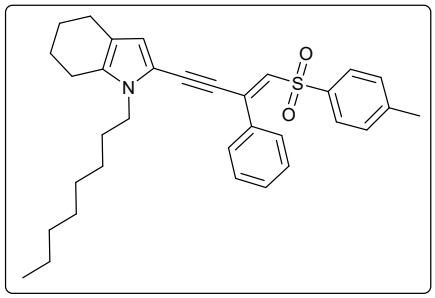
*(E) 1-Octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2a**), E/Z = 10:1.*



Yield 334 mg (65%), yellow crystals; m.p. 48-50°C. Anal. Calcd for $C_{33}H_{39}NO_2S$: C, 77.15; H, 7.65; N, 2.73; S, 6.24%. Found: C, 77.33; H, 7.82; N, 2.92; S, 6.09%. ν_{max} (KBr) 3060, 2926, 2853, 2167, 1595, 1565, 1545, 1489, 1464, 1390, 1316, 1301, 1239, 1184, 1145, 1084, 1016, 913, 823, 810, 746, 666, 565, 538 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.97-7.95 (m, 2H, Ph), 7.66-7.64 (m, 2H, Ph), 7.40-7.29 (m, 5H, Ph), 6.79 (s, 1H, =CH), 6.53 (s, 1H, H-3, pyrrole), 4.02-3.99 (m, 2H,

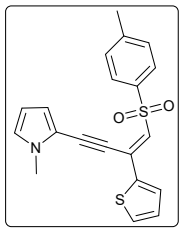
NCH_2), 2.60-2.57 (m, 2H, CH_2-7), 2.55-2.52 (m, 2H, CH_2-4), 2.41 (s, 3H, CH_3), 1.90-1.84 (m, 2H, CH_2), 1.78-1.67 (m, 4H, CH_2-5,6), 1.31-1.21 (m, 10H, $5CH_2$), 0.84 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1, 139.4, 136.6, 136.3, 133.7, 130.4, 129.8 (2C), 128.8 (2C), 127.9, 127.7 (2C), 127.3 (2C), 119.5, 117.2, 112.2, 101.4, 91.1, 45.1, 31.9, 31.6, 29.5, 29.3, 26.8 (2C), 23.5, 23.2, 22.7 (2C), 21.7, 14.2.

*(Z) 1-Octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2a**) , E/Z = 10:1.*



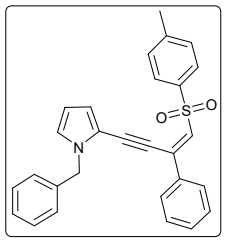
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H, Ph), 7.66-7.64 (m, 2H, Ph), 7.40-7.29 (m, 3H, Ph), 7.20-7.18 (m, 2H, Ph), 6.75 (s, 1H, =CH), 6.29 (s, 1H, H-3, pyrrole), 3.37-3.35 (m, 2H, NCH_2), 2.60-2.57 (m, 2H, CH_2-7), 2.55-2.52 (m, 2H, CH_2-4), 2.39 (s, 3H, CH_3), 1.90-1.84 (m, 2H, CH_2), 1.78-1.67 (m, 4H, CH_2-5,6), 1.31-1.21 (m, 10H, $5CH_2$), 0.84 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.0, 139.4 (2C), 138.9, 137.9, 134.9, 133.4, 130.8, 130.6, 128.7 (2C), 127.9 (2C), 127.2 (2C), 118.6, 116.1, 111.7, 94.7, 93.5, 45.1, 31.9, 31.6, 29.5, 29.3, 26.8 (2C), 23.5, 23.2, 22.7 (2C), 21.7, 14.2.

*1-Methyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1H-pyrrole (**2b**), E/Z = 4:1.*



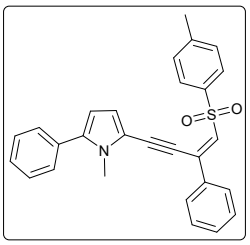
Yield 213 mg (58%), yellow crystals; m.p. 66-68°C. Anal. Calcd for $C_{20}H_{17}NO_2S_2$: C, 65.37; H, 4.66; N, 3.81; S, 17.45%. Found: C, 65.5; H, 4.85; N, 3.95; S, 17.27%. ν_{max} (KBr) 3106, 3051, 2923, 2853, 2183, 1595, 1558, 1521, 1511, 1473, 1418, 1361, 1318, 1290, 1232, 1200, 1182, 1145, 1083, 1052, 1020, 980, 966, 910, 855, 826, 811, 774, 732, 656, 600, 553, 535 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H, Ph), 7.50-7.49 (m, 1H, H-5, thiophene), 7.41-7.39 (m, 1H, H-3, thiophene), 7.32-7.30 (m, 2H, Ph), 7.07-7.04 (m, 1H, H-4, thiophene), 6.83 (s, 1H, =CH), 6.80-6.79 (m, 1H, H-5, pyrrole), 6.71-6.70 (m, 1H, H-4, pyrrole), 6.21-6.19 (m, 1H, H-3, pyrrole), 3.88 (s, 3H, N-CH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.4, 140.4, 139.3, 133.2, 129.9 (2C), 129.3, 129.1, 128.9, 128.3, 127.7 (2C), 126.4, 126.1, 118.6, 109.5, 97.3, 89.0, 35.3, 21.8.

*1-Benzyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1H-pyrrole (**2c**), E/Z = 9:1.*



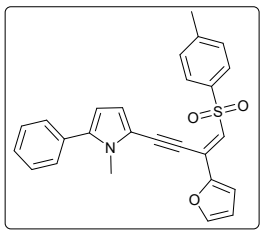
Yield 241 mg (55%), yellow crystals; m.p. 53-55°C. Anal. Calcd for $C_{28}H_{23}NO_2S$: C, 76.86; H, 5.30; N, 3.20; S, 7.33%. Found: C, 76.98; H, 5.49; N, 3.32; S, 7.23%. ν_{max} (KBr) 3059, 3032, 2959, 2924, 2854, 2180, 1596, 1558, 1521, 1494, 1467, 1454, 1417, 1316, 1300, 1233, 1182, 1144, 1093, 1031, 911, 807, 732, 695, 672, 612, 570, 540 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.84-7.82 (m, 2H, Ph), 7.57-5.55 (m, 2H, Ph), 7.40-7.38 (m, 1H, Ph), 7.35-7.31 (m, 4H, Ph, Ph), 7.28-7.27 (m, 1H, Ph), 7.23-7.21 (m, 2H, Ph), 7.16-7.14 (m, 2H, Ph), 6.86 (s, 1H, =CH), 6.85-6.84 (m, 1H, H-5, pyrrole), 6.79-6.78 (m, 1H, H-4, pyrrole), 6.29-6.27 (m, 1H, H-3, pyrrole), 5.43 (s, 2H, CH_2Ph), 2.40 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.1, 138.8, 138.0, 135.9, 135.5, 130.4, 129.6 (2C), 129.4, 128.7 (4C), 127.6 (2C), 127.5, 127.2 (2C), 126.9 (2C), 125.6, 118.6, 114.7, 110.0, 98.8, 90.1, 51.3, 21.6.

*1-Methyl-2-phenyl-5-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1H-pyrrole (**2d**), E/Z = 4:1.*



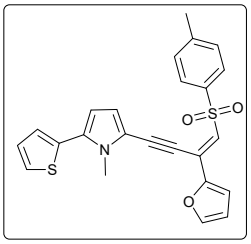
Yield 271 mg (62%), yellow crystals; m.p. 76-78°C. Anal. Calcd for $C_{28}H_{23}NO_2S$: C, 76.86; H, 5.30; N, 3.20; S, 7.33%. Found: C, 77.04; H, 5.48; N, 3.35; S, 7.17%. ν_{max} (KBr) 3061, 2923, 2853, 2175, 1597, 1559, 1534, 1491, 1458, 1395, 1376, 1315, 1303, 1231, 1216, 1185, 1145, 1084, 1019, 1001, 911, 827, 812, 755, 734, 699, 666, 591, 565, 538 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): 7.99-7.96 (m, 2H, Ph), 7.69-7.68 (m, 2H, Ph), 7.45-7.32 (m, 10H, Ph), 6.88 (s, 1H, =CH), 6.81-6.79 (m, 1H, H-4, pyrrole), 6.31-6.30 (m, 1H, H-3, pyrrole), 3.87 (s, 3H, N-CH_3), 2.43 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.4, 139.1, 136.2, 135.8, 132.4, 130.6, 129.9 (2C), 129.6, 129.1, 128.9 (2C), 128.8 (2C), 128.7 (2C), 127.9, 127.7 (2C), 127.3 (2C), 118.5, 116.3, 110.2, 99.8, 91.0, 33.8, 21.8.

*(E)-2-(3-(Furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-5-phenyl-1H-pyrrole (**2e**).*



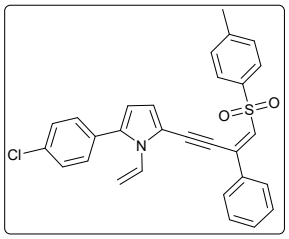
Yield 222 mg (52%), green crystals; m.p. 98-100°C. Anal. Calcd for $C_{26}H_{21}NO_3S$: C, 73.05; H, 4.95; N, 3.28; S, 7.50%. Found: C, 73.26; H, 5.18; N, 3.45; S, 7.39%. ν_{max} (KBr) 3123, 3064, 2956, 2922, 2852, 2185, 1582, 1531, 1500, 1471, 1456б 1392, 1345, 1314, 1302, 1292, 1219, 1145, 1084, 1018, 999, 910, 825, 811, 771, 757, 734, 563, 532, 498 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.95-7.93 (m, 2H, Ph), 7.46-7.45 (m, 5H, Ph), 7.39-7.36 (m, 1H, H-5, furan), 7.33-7.31 (m, 2H, Ph), 6.94 (s, 1H, =CH), 6.92-6.91 (m, 1H, H-3, furan), 6.77 (d, *J* = 3.9 Hz, 1H, H-3, pyrrole), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H, H-4, furan), 6.30 (d, *J* = 3.9 Hz, 1H, H-4, pyrrole), 3.89 (s, 3H, N-CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): 150.2, 145.1, 144.3, 139.4, 139.0, 132.4, 129.9 (2C), 128.9 (2C), 128.7 (2C), 127.9, 127.6 (2C), 124.6, 123.8, 118.2, 116.1, 114.8, 112.7, 110.1, 96.2, 88.1, 33.8, 21.7.

*(E)-2-(3-(Furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-5-(thiophen-2-yl)-1H-pyrrole (**2f**).*



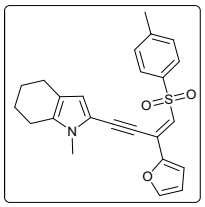
Yield 282 mg (65%), yellow crystals; m.p. 60-62°C. Anal. Calcd for $C_{24}H_{19}NO_3S_2$: C, 66.49; H, 4.42; N, 3.23; S, 14.79%. Found: C, 66.66; H, 4.53; N, 3.33; S, 14.62%. ν_{max} (KBr) 3111, 3068, 2948, 2921, 2185, 1582, 1545, 1506, 1467, 1445, 1417, 1390, 1351, 1317, 1304, 1219, 1197, 1184, 1145, 1084, 1049, 1026, 1011, 982, 911, 880, 825, 812, 768, 732, 702, 674, 652, 590, 561, 531 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): 7.93-7.91 (m, 2H, Ph), 7.47-7.45 (m, 1H, H-5, thiophene), 7.35-7.31 (m, 3H, Ph, H-5, furan), 7.17-7.16 (m, 1H, H-3, thiophene), 7.12-7.10 (m, 1H, thiophene), 6.93 (s, 1H, =CH), 6.90-8.89 (m, 1H, H-3, furan), 6.72 (d, *J* = 3.9 Hz, 1H, H4-pyrrole), 6.49 (dd, *J* = 3.2, 1.7 Hz, 1H, H-4, furan), 6.39 (d, *J* = 3.9 Hz, 1H, H-3, pyrrole), 3.98 (s, 3H, N-CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 149.6, 144.6, 143.8, 138.8, 133.4, 131.1, 129.3 (2C), 127.2, 127.1, 127.0 (2C), 125.5, 125.2, 124.2, 123.1, 117.6, 114.2, 112.1, 110.3, 95.2, 87.6, 33.3, 21.2.

*(E)-2-(4-Chlorophenyl)-5-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1-vinyl-1H-pyrrole (**2g**).*



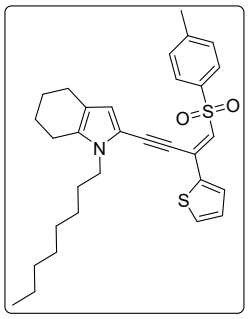
Yield 179 mg (37%), yellow crystals; m.p. 58-60°C. Anal. Calcd for $C_{29}H_{22}ClNO_2S$: C, 71.97; H, 4.58; Cl, 7.32; N, 2.89; S, 6.62%. Found: C, 72.11; H, 4.73; Cl, 7.48; N, 3.00; S, 6.47%. ν_{max} (KBr) 3061, 2922, 2852, 2162, 1670, 1643, 1596, 1558, 1532, 1492, 1460, 1421, 1385, 1319, 1303, 1237, 1220, 1182, 1146, 1087, 1015, 964, 909, 830, 812, 780, 734, 695, 664, 597, 565, 541, 502 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.98-7.96 (m, 2H, Ph), 7.66-7.64 (m, 2H, Ph), 7.42-7.39 (m, 6H, Ph), 7.33-7.31 (m, 3H, Ph), 7.03 (dd, *J* = 8.9, 15.8, Hz, 1H, H_x), 6.93 (s, 1H, =CH), 6.88 (d, *J* = 3.9 Hz, 1H, H-4, pyrrole), 6.35 (d, *J* = 3.8 Hz, 1H, H-3, pyrrole), 5.41 (d, *J* = 15.8 Hz, 1H, H_b), 5.09 (d, *J* = 8.9 Hz, 1H, H_a), 2.42 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.4, 139.0, 136.4, 135.9, 135.6, 134.1, 130.9, 130.7, 130.6, 130.4, 130.3 (2C), 129.8 (2C), 128.9 (3C), 128.8, 127.9 (2C), 127.4 (2C), 120.7, 115.7, 112.1, 109.4, 99.0, 91.1, 21.8.

*(E)-2-(3-(Furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-4,5,6,7-tetrahydro-1H-indole (**2h**).*



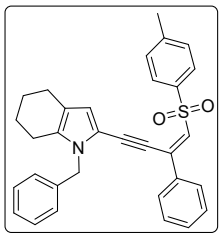
Yield 264 mg (65%), green crystals; m.p. 88-90°C. Anal. Calcd for $C_{24}H_{23}NO_3S$: C, 71.09; H, 5.72; N, 3.45; S, 7.91%. Found: C, 70.96; H, 5.93; N, 3.64; S, 7.76%. ν_{max} (KBr) 3373, 3166, 3068, 2927, 2853, 2177, 1584, 1548, 1530, 1480, 1459, 1448, 1394, 1370, 1316, 1261, 1222, 1144, 1083, 1028, 914, 859, 836, 801, 745, 670, 652, 561, 532 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.93-7.91 (m, 2H, Ph), 7.45-7.42 (m, 1H, H-5, furan), 7.30-7.28 (m, 2H, Ph), 6.86 (s, 1H, =CH), 6.86-6.85 (m, 1H, H-5, H-3, furan), 6.48 (s, 1H, H-3, pyrrole), 6.47-6.46 (m, 1H, H-4, furan), 3.71 (s, 3H, N-CH_3), 2.59-2.56 (m, 2H, CH_2-7), 2.54-2.51 (m, 2H, CH_2-4), 2.40 (s, 3H, CH_3), 1.89-1.84 (m, 2H, CH_2-5), 1.78-1.73 (m, 2H, CH_2-6). ^{13}C NMR (100.6 MHz, $CDCl_3$): 150.5, 145.0, 144.1, 139.6, 134.3, 129.8 (2C), 127.5 (2C), 124.3, 123.4, 119.3, 116.5, 114.6, 112.6 (2C), 97.4, 88.2, 31.4, 23.5, 23.1, 23.0, 22.6, 21.7.

*1-Octyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2i**), E/Z = 10:1.*



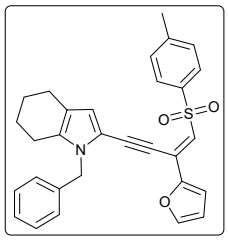
Yield 353 mg (68%), yellow crystals; m.p. 110-112°C. Anal. Calcd for $C_{31}H_{37}NO_2S_2$: C, 71.64; H, 7.18; N, 2.69; S, 12.34%. Found: C, 71.77; H, 7.28; N, 2.81; S, 12.15%. ν_{max} (KBr) 3101, 3058, 2926, 2853, 2171, 1596, 1568, 1543, 1497, 1464, 1420, 1392, 1314, 1291, 1233, 1202, 1145, 1084, 1057, 836, 911, 740, 706, 656, 554, 535, 464 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): 7.95-7.93 (m, 2H, Ph), 7.47-7.46 (m, 1H, H-5, thiophene), 7.39-7.38 (m, 1H, H-3, thiophene), 7.31-7.29 (m, 2H, Ph), 7.04 (dd, *J* = 4.9, 3.8 Hz, 1H, H-4, thiophene), 6.76 (s, 1H, =CH), 6.56 (s, 1H, H-3, pyrrole), 4.06-4.02 (m, 2H, NCH_2), 2.61-2.58 (m, 2H, CH_2-7), 2.56-2.53 (m, 2H, CH_2-4), 2.41 (s, 3H, CH_3), 1.89-1.84 (m, 2H, CH_2-5), 1.80-1.70 (m, 4H, CH_2-6, CH_2), 1.31-1.21 (m, 10H, $5CH_2$), 0.84 (t, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.0, 140.8, 139.6, 133.8, 129.7 (2C), 129.4, 129.0, 128.6, 128.1, 127.6 (2C), 124.4, 119.5, 117.3, 111.9, 99.5, 90.1, 45.2, 31.9, 31.6, 29.5, 29.3, 26.8, 23.5, 23.1 (2C), 22.7 (2C), 21.7, 14.2.

*1-Benzyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2j**), E/Z = 6:1.*



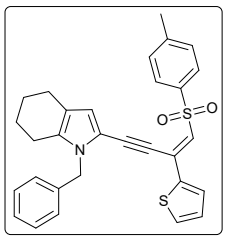
Yield 231 mg (47%), green crystals; m.p. 68-70°C. Anal. Calcd for $C_{32}H_{29}NO_2S$: C, 78.18; H, 5.95; N, 2.85; S, 6.52%. Found: C, 78.41; H, 6.29; N, 3.03; S, 6.38%. ν_{max} (KBr) 3086, 3061, 3031, 2924, 2852, 2168, 1654, 1595, 1546, 1465, 1392, 1383, 1315, 1260, 1214, 1181, 1144, 1114, 1084, 1027, 911, 824, 809, 732, 697, 567, 538, 456 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.76-7.74 (m, 2H, Ph), 7.53-7.51 (m, 2H, Ph), 7.32-7.23 (m, 6H, Ph), 7.15-7.13 (m, 2H, Ph), 7.04-7.02 (m, 2H, Ph), 6.74 (s, 1H, =CH), 6.61 (s, 1H, H-3, pyrrole), 5.35 (s, 2H, CH_2-Ph), 2.57-2.54 (m, 2H, CH_2-7), 2.44-2.41 (m, 2H, CH_2-4), 2.37 (s, 3H, CH_3), 1.80-1.72 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.9, 139.1, 138.4, 136.3, 136.0, 134.4, 130.3, 129.7 (2C), 128.8 (2C), 128.7 (2C), 127.7, 127.6 (2C), 127.3 (2C), 127.2, 126.4 (2C), 120.1, 117.3, 113.0, 100.8, 91.1, 48.1, 23.4, 23.1, 22.9, 22.6, 21.7.

*(E)-1-Benzyl-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2k**).*



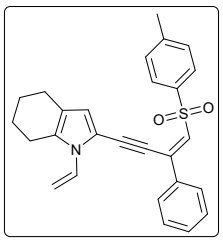
Yield 327 mg (68%), green crystals; m.p. 148-150°C. Anal. Calcd for $C_{30}H_{27}NO_3S$: C, 74.82; H, 5.65; N, 2.91; S, 6.66 %. Found: C, 75.06; H, 5.80; N, 3.03; S, 6.54%. ν_{max} (KBr) 3130, 3064, 3031, 2928, 2852, 2179, 1583, 1538, 1490, 1457, 1396, 1380, 1316, 1303, 1220, 1145, 1115, 1084, 1036, 1014, 984, 917, 837, 813, 765, 732, 699, 652, 591, 562, 532 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.70 (m, 2H, Ph), 7,41-7,36 (m, 1H, H-5, furan), 7.32-7,23 (m, 3H, Ph), 7.12-7.10 (m, 2H, Ph), 7.07-7.05 (m, 2H, -Ph), 6.82 (s, 1H, =CH), 6.66-6.65 (m, 1H, H-3, furan), 6.58 (s, 1H, H-3, pyrrole), 6.42-6.39 (m, 1H, H-4, furan), 5.39 (s, 2H, CH_2-Ph), 2.56-2.54 (m, 2H, CH_2-7), 2.44-2.41 (m, 2H, CH_2-4), 2.36 (s, 3H, CH_3), 1.79-1.73 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): 150.3, 144.9, 143.9, 139.4, 138.4, 134.3, 130.6, 129.7 (2C), 128.8 (2C), 127.5 (2C), 127.2, 126.5 (2C), 124.1, 123.4, 119.9, 117.1, 114.5, 112.5, 97.1, 88.1, 48.1, 23.4, 23.1, 23.0, 22.6, 21.7.

*(E)-1-Benzyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2l**).*



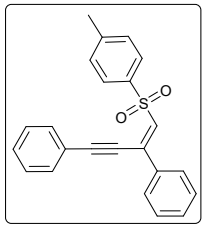
Yield 314 mg (63%), green crystals; m.p. 93-95°C. Anal. Calcd for $C_{30}H_{27}NO_2S_2$: C, 72.40; H, 5.47; N, 2.81; S, 12.88%. Found: C, 72.53; H, 5.61; N, 2.95; S, 12.68; %. ν_{max} (KBr) 3154, 3063, 3034, 2924, 2852, 2254, 2172, 1634, 1597, 1546, 1572, 1546, 1463, 1418, 1393, 1359, 1309, 1296, 1235, 1144, 1083, 1024, 909, 957, 837, 808, 732, 653, 555, 461 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H, Ph), 7.33-7.24 (m, 5H, Ph, H-3,5-thiophene), 7.14-7.12 (m, 2H, Ph), 7.06-7.05 (m, 2H, Ph), 6.97-6.94 (m, 1H, H-4, thiophene), 6.71 (s, 1H, =CH), 6.63 (s, 1H, H-3, pyrrole), 5.38 (s, 2H, CH_2-Ph), 5.87-2.55 (m, 2H, CH_2-7), 2.44-2.41 (m, 2H, CH_2-4), 2.36 (s, 3H, CH_3), 1.79-1.72 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): 143.9, 140.6, 139.3, 138.3, 134.6, 129.7 (2C), 129.2, 129.0, 128.9, 128.8 (2C), 128.1, 127.5 (2C), 127.2, 126.5 (2C), 124.4, 120.1, 117.5, 112.8, 99.0, 90.1, 48.2, 23.4, 23.1, 22.9, 22.6, 21.7.

*(E)-2-(3-Phenyl-4-tosylbut-3-en-1-yn-1-yl)-1-vinyl-4,5,6,7-tetrahydro-1H-indole (**2m**).*



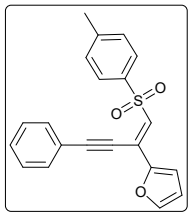
Yield 171 mg (40%), green crystals; m.p. 116-118°C. Anal. Calcd for $C_{27}H_{25}NO_2S$: C, 75.85; H, 5.89; N, 3.28; S, 7.50%. Found: C, 76.02; H, 6.08; N, 3.41; S, 7.34 %. ν_{max} (KBr) 3059, 2931, 2851, 2171, 1643, 1595, 1586, 1570, 1548, 1478, 1442, 1384, 1360, 1317, 1298, 1218, 1203, 1184, 1145, 1084, 1018, 1004, 910, 870, 840, 811, 733, 694, 664, 645, 566, 539, 465 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H, Ph), 7.64-7.63 (m, 2H, Ph), 7.40-7.36 (m, 3H, Ph, H_x), 7.31-7.26 (m, 3H, Ph), 6.85 (s, 1H, =CH), 6.59 (s, 1H, H-3, pyrrole), 5.32 (d, J = 16.8 Hz, 1H, H_b), 4.93 (d, J = 10.0 Hz, 1H, H_a), 2.75-2.72 (m, 2H, CH_2-7), 2.55-2.52 (m, 2H, CH_2-4), 2.41 (s, 3H, CH_3), 1.88-1.83 (m, 2H, CH_2-5), 1.79-1.74 (m, 2H, CH_2-6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.2, 139.1, 136.1, 136.0, 133.5, 130.9, 130.5, 129.8 (2C), 128.9, 128.8 (2C), 127.8 (2C), 127.3 (2C), 121.4, 119.3, 112.5, 103.3, 100.2, 91.3, 24.6, 23.3, 23.1, 22.9, 21.7.

*(Z)-(4-Tosylbut-3-en-1-yne-1,3-diyl)dibenzene (**2n**)*



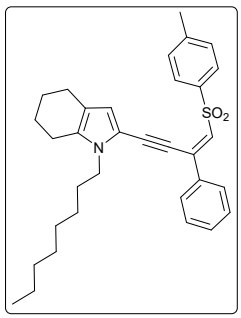
Yield 151 mg (42%), yellow crystals; m.p. 53-55°C. Anal. Calcd for $C_{23}H_{18}O_2S$: C, 77.07; H, 5.06; S, 8.94%. Found: C, 77.21; H, 5.18; S, 8.77%. ν_{max} (KBr) 3058, 2923, 2853, 2187, 1659, 1596, 1552, 1490, 1445, 1319, 1145, 1085, 1025, 1006, 912, 843, 811, 755, 733, 692, 664, 642, 562, 530 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): 7.96-7.94 (m, 2H, Ph), 7.71-7.69 (m, 2H, Ph), 7.64-7.62 (m, 2H, Ph), 7.46-7.40 (m, 6H, Ph), 7.30-7.28 (m, 2H, Ph), 7.11 (s, 1H, =CH), 2.40 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.5, 138.7, 135.7, 135.6, 133.1, 132.3 (2C), 130.9, 130.0, 129.8 (2C), 129.0 (2C), 128.7 (2C), 128.2 (2C), 127.3 (2C), 122.1, 105.8, 84.2, 21.8.

*(E)-2-(4-Phenyl-1-tosylbut-1-en-3-yn-2-yl)furan (**2o**)*



Yield 275 mg (79%), yellow crystals; m.p. 98-100°C. Anal. Calcd for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63; S, 9.20%. Found: C, 72.57; H, 4.79; S, 9.05 %. ν_{max} (KBr) 3131, 3058, 2923, 2854, 2148, 1916, 1723, 1654, 1593, 1581, 1539, 1489, 1471, 1444, 1396, 1349, 1319, 1303, 1293, 1212, 1145, 1084, 1027, 1006, 920, 884, 836, 811, 801, 756, 690, 651, 590, 561, 531 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H, Ph), 7.64-7.62 (m, 2H, Ph), 7.46-7.42 (m, 4H, Ph, H-5, furan), 7.30-7.28 (m, 2H, Ph), 7.11 (s, 1H, =CH), 6.92-6.91 (m, 1H, H-3, furan), 6.49-6.48 (m, 1H, H-4, furan), 2.40 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.2, 145.4, 144.4, 139.0, 132.3 (2C), 130.0, 129.8 (2C), 128.7 (2C), 128.4, 128.0 (2C), 123.8, 121.9, 115.2, 112.7, 102.2, 81.7, 21.7.

4. Scale reaction



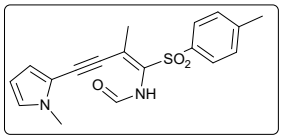
A solution of acylethynylpyrrole **1a** (1 g, 2.77 mmol) and TosMIC (1.08 g, 5.53 mmol) in THF (50 mL) was heated to reflux. Then, under reflux, solution of *t*-BuOK (621 mg, 5.53 mmol) in THF (20 mL) was added dropwise to reaction mixture for 1 hour. The residue, after removing solvent, was fractionated by column chromatography (SiO_2, *n*-

hexane : diethyl ether, 5 : 1) to afford the 426 mg (59%) of (*Z*)-1-octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole **2a**.

5. The reaction of 4-(1-methyl-1H-pyrrol-2-yl)but-3-yn-2-one (1p) with TosMIC

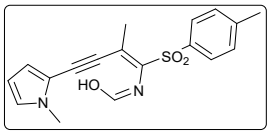
A solution of 4-(1-methyl-1*H*-pyrrol-2-yl)but-3-yn-2-one **1p** (147 mg, 1 mmol) and TosMIC (395 mg, 2 mmol) in THF (10 mL) was stirred at 66°C. Then solution of *t*-BuOK (224 mg, 2 mmol) in THF (10 mL) was added dropwise to reaction mixture for 1 hour. The residue, after removing solvent, was fractionated by column chromatography (SiO_2, n-hexane : diethyl ether, 2 : 1) to afford the 154 mg (45%) the mixture of isomers (*E*)-N-(2-methyl-4-(1-methyl-1*H*-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formamide **3a** and (*Z*)-N-((*E*)-2-methyl-4-(1-methyl-1*H*-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formimidic acid **3b** (**3a** : **3b** = 2 : 1).

*(E)-N-(2-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formamide (**3a**)*



Yield 154 mg (45%), brown crystals; m.p. 130-132°C. Anal. Calcd for $C_{18}H_{18}N_2O_3S$: C, 63.14; H, 5.30; N, 8.18; S, 9.36%. Found: C, 63.32; H, 5.41; N, 8.38; S, 9.25%. ν_{max} (KBr) 3302, 3130, 2924, 2856, 2181, 1700, 1597, 1525, 1476, 1420, 1370, 1324, 1305, 1259, 1215, 1146, 1086, 1055, 1019, 1000, 912, 845, 814, 731, 679, 647, 598, 582, 568, 529, 468 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.15 (s, 1H, CHO), 7.85-7.83 (m, 2H, Ph), 7.47 (br.s, 1H, NH), 7.29-7.27 (m, 2H, Ph), 6.77-6.73 (m, 1H, H5-pyrrole), 6.60-6.58 (m, 1H, H3-pyrrole), 6.17-6.15 (m, 1H, H4-pyrrole), 3.77 (s, 3H, NCH_3), 2.39 (s, 3H, Ph$\underline{CH_3}$), 2.06 (s, 3H, =CCH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.1, 145.0, 136.8, 129.9 (2C), 129.5, 128.2, 127.8 (2C), 125.9, 118.0, 115.1, 109.3, 96.5, 91.3, 35.0, 23.1, 21.8.

*(Z)-N-((E)-2-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formimidic acid (**3b**)*



^1H NMR (400.13 MHz, $CDCl_3$): only some signals are visible. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.9, 145.5, 136.0, 133.4, 131.4 (2C), 130.3 (2C), 128.5, 126.4, 118.6, 114.8, 109.5, 98.1, 91.1, 35.1, 22.8, 22.4.

6. The reaction of 1-(1-methyl-1*H*-pyrrol-2-yl)pent-1-yn-3-one (1q) with TosMIC

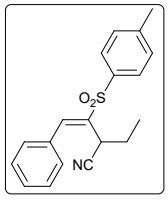
A solution of 1-(1-methyl-1*H*-pyrrol-2-yl)pent-1-yn-3-one **1q** (200 mg, 1 mmol) and TosMIC (395 mg, 2 mmol) in THF (10 mL) was heated to reflux. Then , under reflux, solution of *t*-BuOK (224 mg, 2 mmol) in THF (10 mL) was added dropwise to reaction mixture for 1 hour. The residue, after removing solvent, was fractionated by column chromatography (SiO_2, n-hexane : diethyl ether, 2 : 1) to afford the 89 mg (32%) 4-tosyloxazole **4**. The 4-tosyloxazole **4** is a known substance.[2]

(2) Leusen, D. V.; Leusen, A. M. V., Synthetic Uses of Tosylmethyl Isocyanide (TosMIC). In Org. React., John Wiley & Sons, Inc.2001; pp 417-666.

7. The reaction of 1-phenylpent-1-yn-3-one (1r) with TosMIC

A solution of 1-phenylpent-1-yn-3-one **1r** (158 mg, 1 mmol) and TosMIC (395 mg, 2 mmol) in THF (10 mL) was heated to reflux. Then , under reflux, solution of *t*-BuOK (224 mg, 2 mmol) in THF (10 mL) was added dropwise to reaction mixture for 1 hour. The residue, after removing solvent, was fractionated by column chromatography (SiO_2, n-hexane : diethyl ether, 2 : 1) to afford the 234 mg (72%) (*E*)-2-ethyl-4-phenyl-3-tosylbut-3-enenitrile **6**.

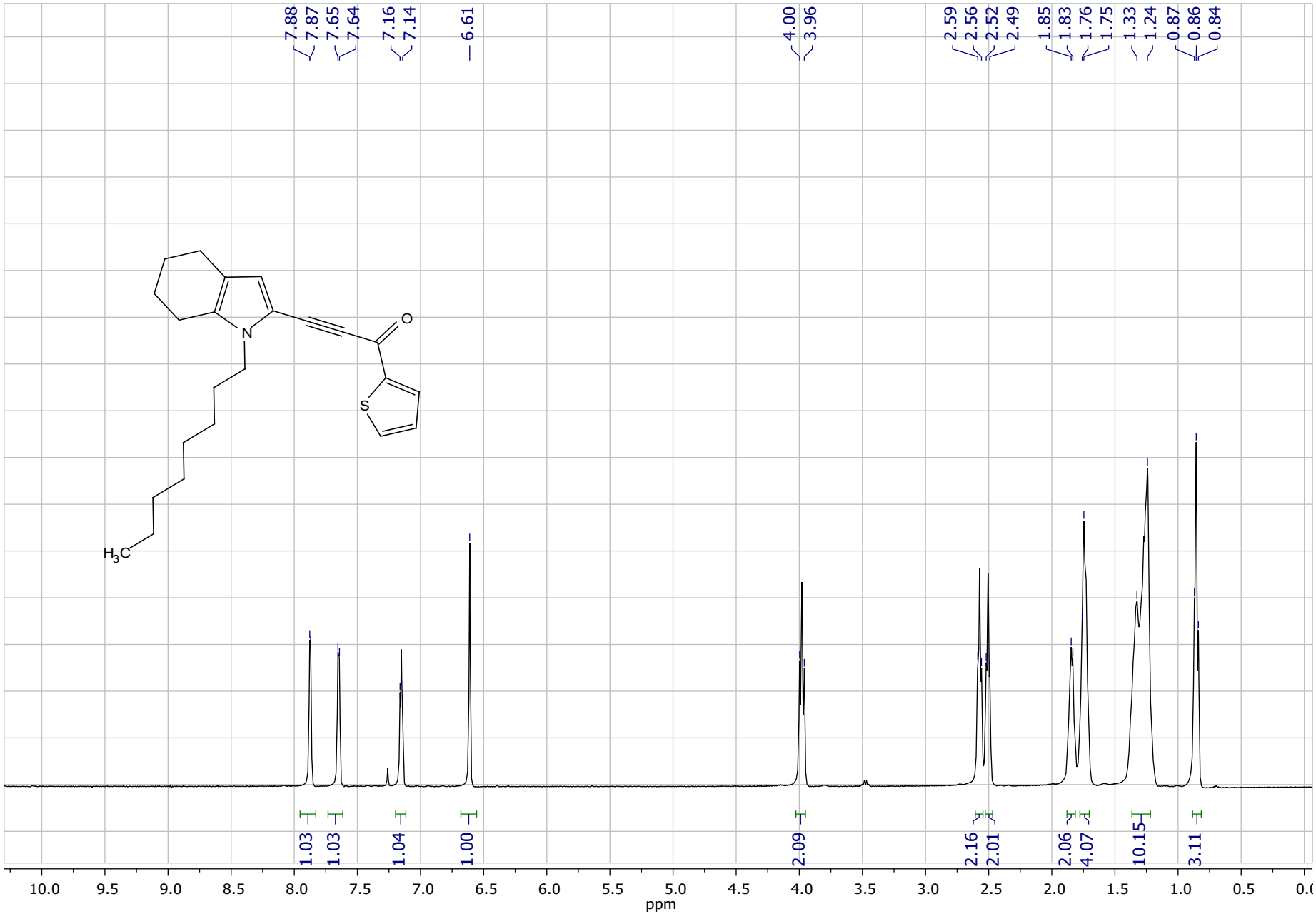
*(E)-2-Ethyl-4-phenyl-3-tosylbut-3-enenitrile (**6**)*



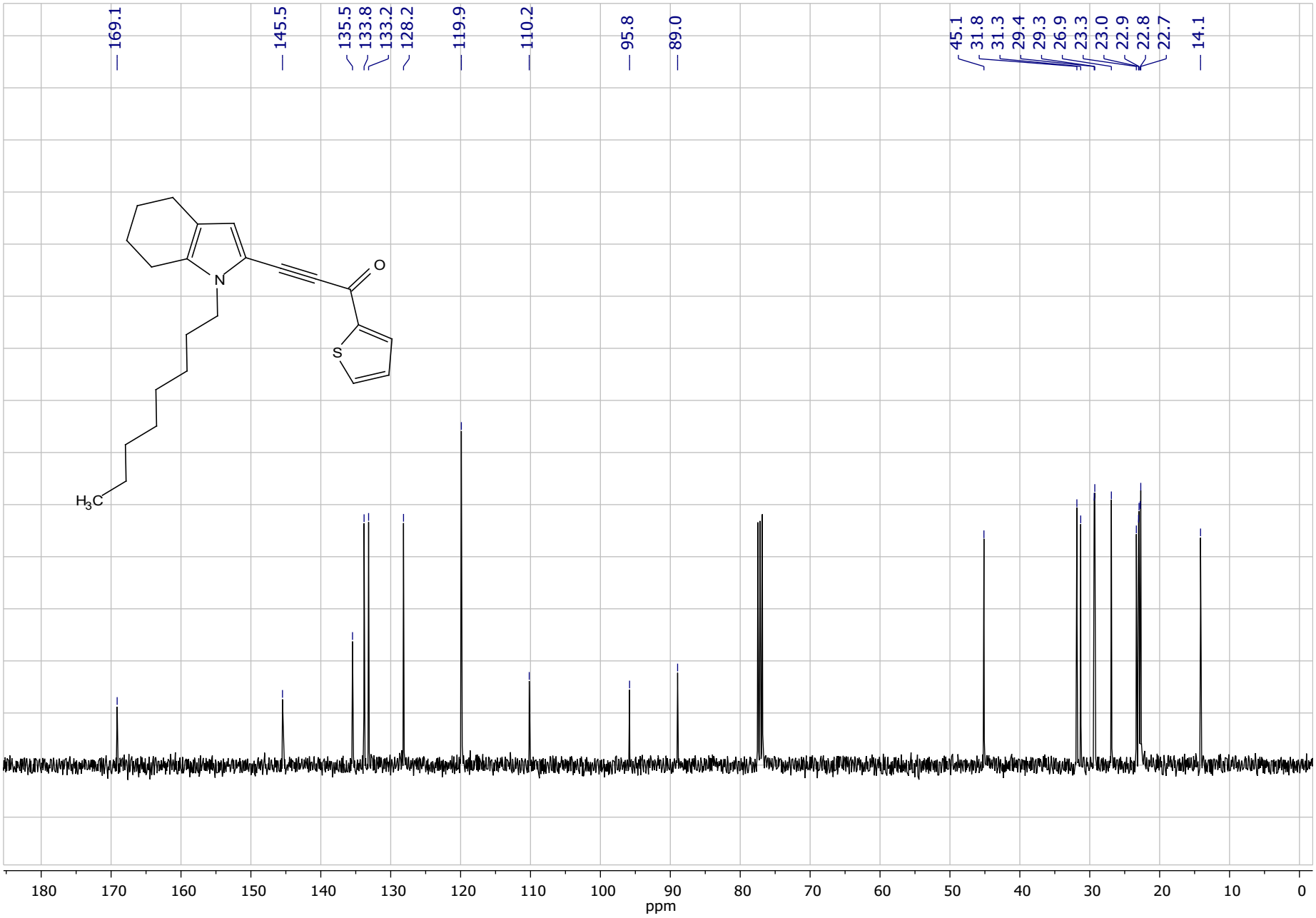
Yield 234 mg (72%), white crystals; m.p. 128-130°C. Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.89; N, 4.30; S, 9.85%. Found: C, 70.25; H, 6.04; N, 4.44; S, 9.65%. ν_{max} (KBr) 3060, 2976, 2934, 2879, 2242, 1622, 1597, 1493, 1450, 1402, 1384, 1317, 1305, 1210, 1183, 1150, 1121, 1085, 1019, 1002, 944, 912, 814, 757, 733, 698, 670, 608, 560, 532, 473 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.09 (s, 1H, =CH), 7.87-7.85 (m, 2H, *o*-Ph), 7.48-7.38 (m, 7H, Ph), 3.81 (dd, *J* = 6.6, 9.5 Hz, 1H, CHCN), 2.46 (s, 3H, CH_3), 2.06-1.98 (m, 1H, CH_2), 1.80-1.73 (m, 1H, HCH), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.3, 143.0, 137.0, 136.2, 132.4, 130.3(2C), 130.2, 129.3 (2C), 129.2 (2C), 128.5 (2C), 118.2, 31.4, 25.2, 21.8, 12.2.

8. ^1H and ^{13}C NMR spectra:

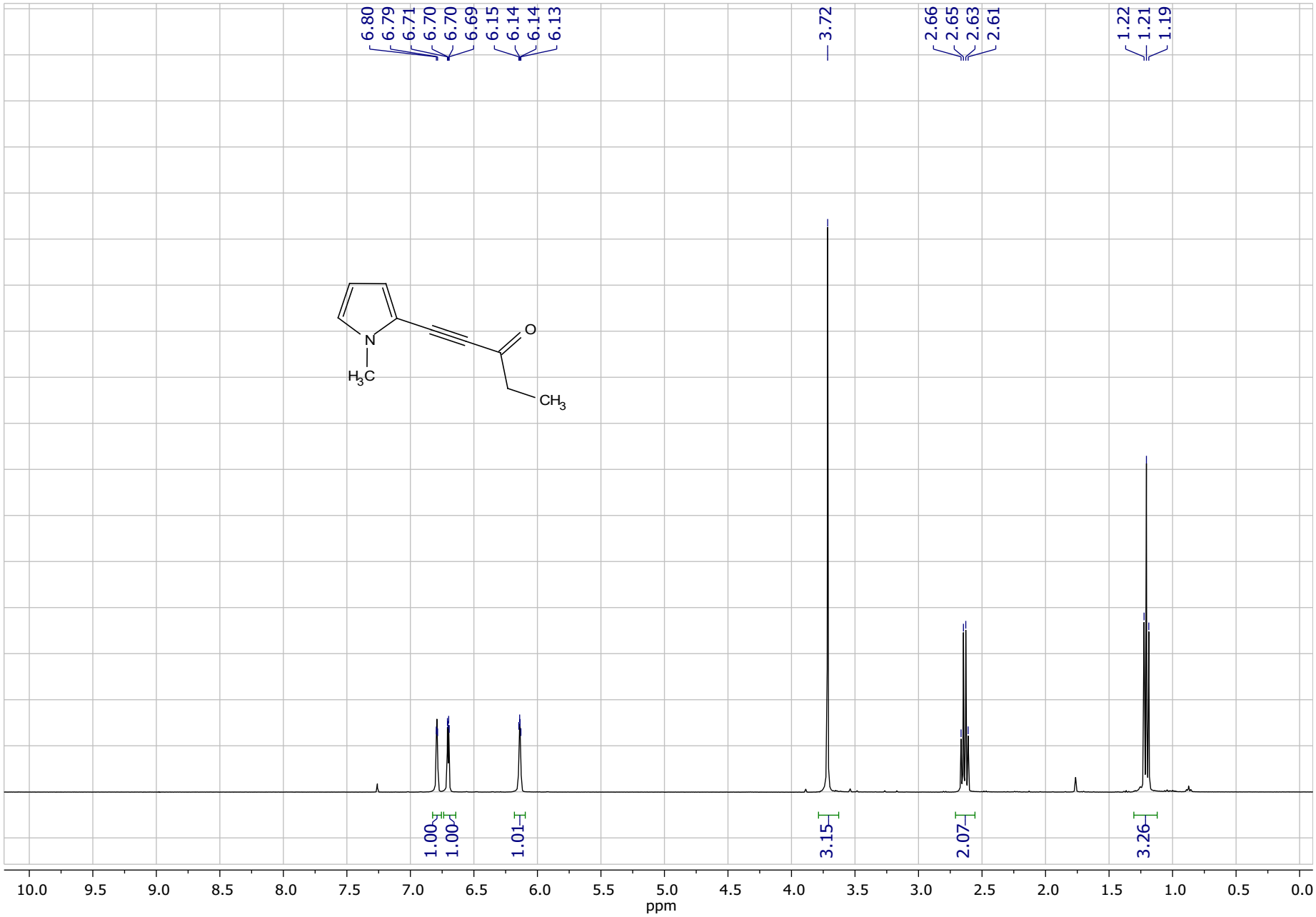
^{1}H NMR spectrum of 3-(1-octyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-(thiophen-2-yl)prop-2-yn-1-one (**1a**) in $CDCl_3$.



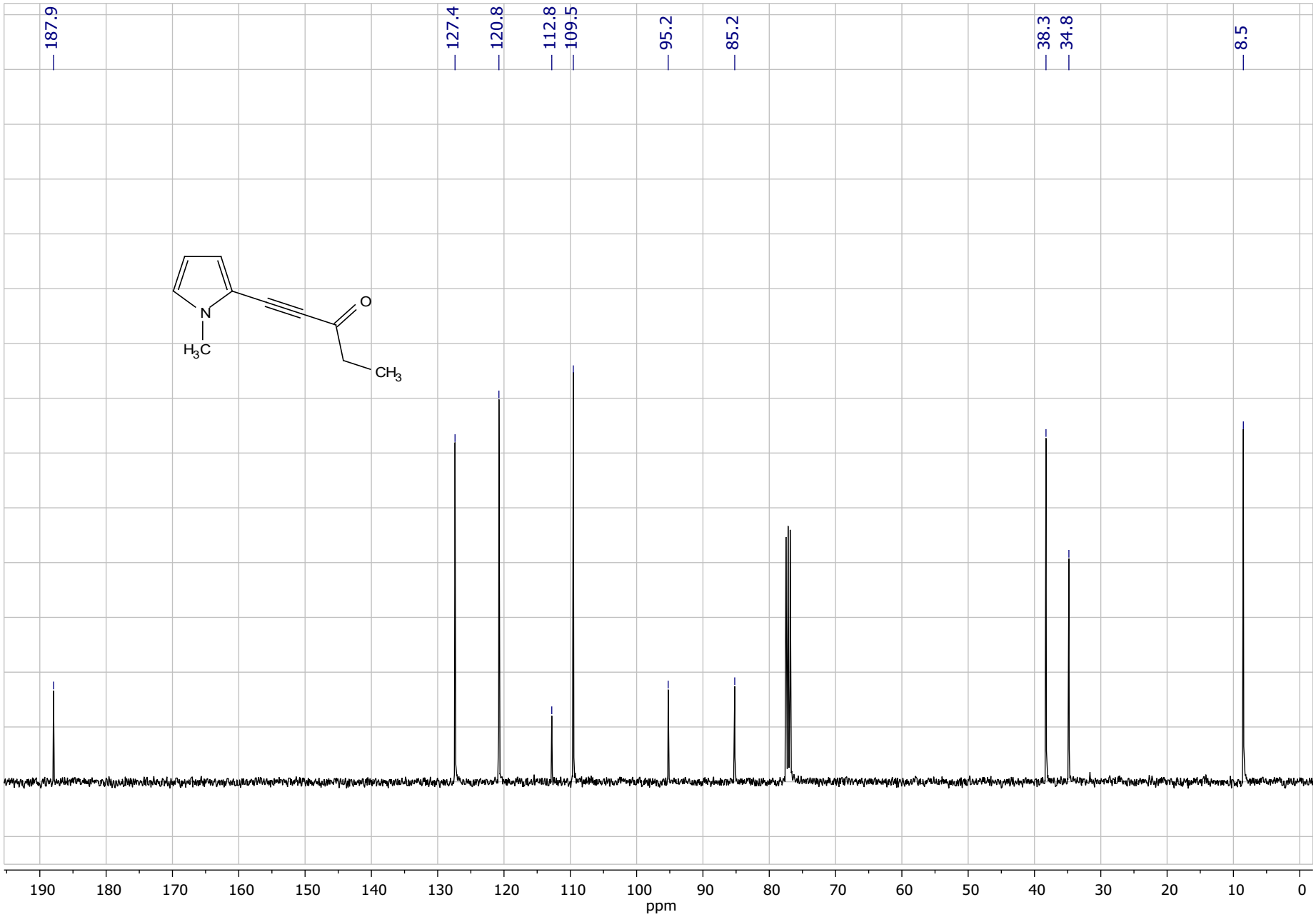
^{13}C NMR spectrum of 3-(1-octyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-(thiophen-2-yl)prop-2-yn-1-one (**1a**) in $CDCl_3$.



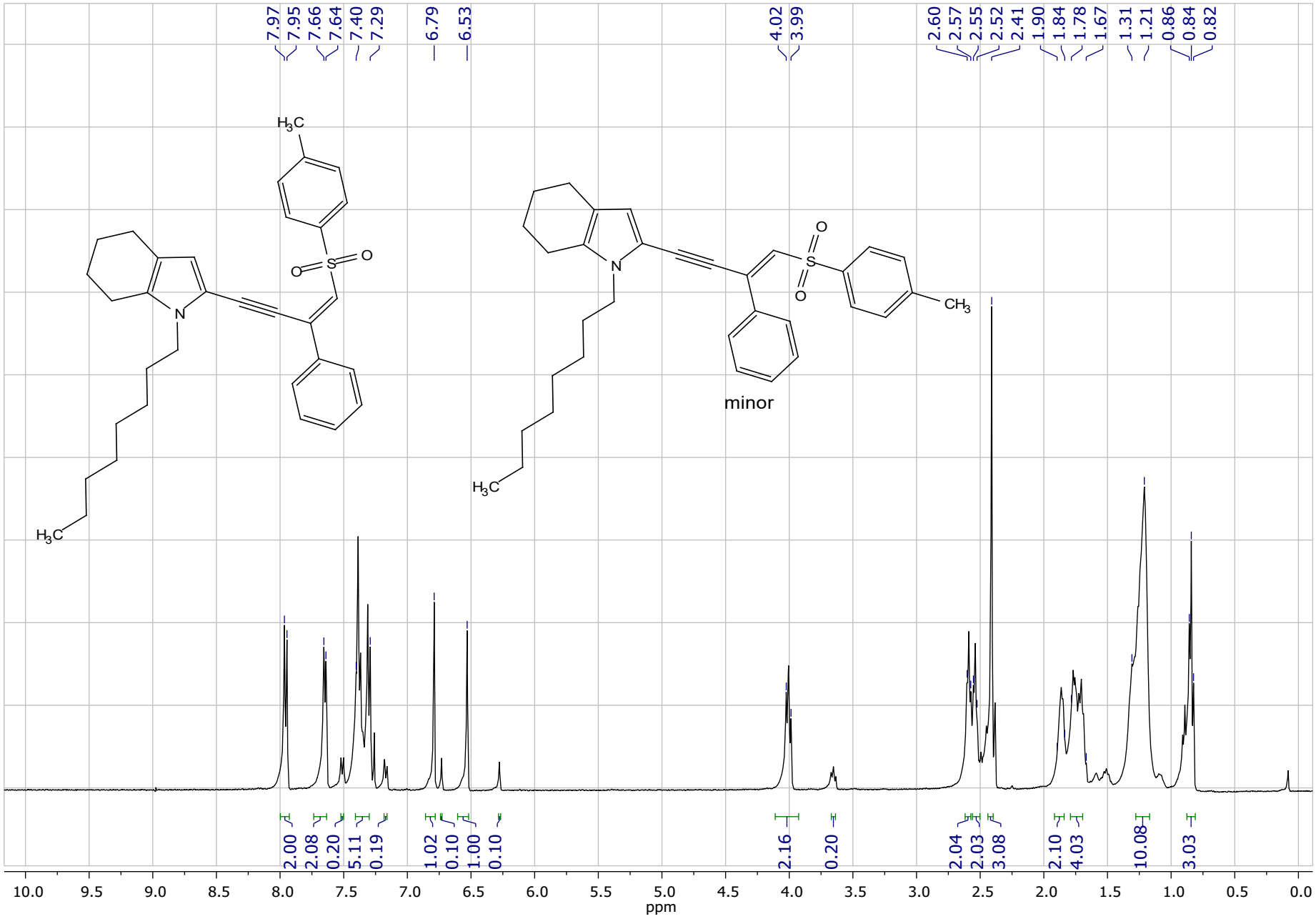
^{1}H NMR spectrum of 1-(1-methyl-1*H*-pyrrol-2-yl)pent-1-yn-3-one (**1q**) in $CDCl_3$.



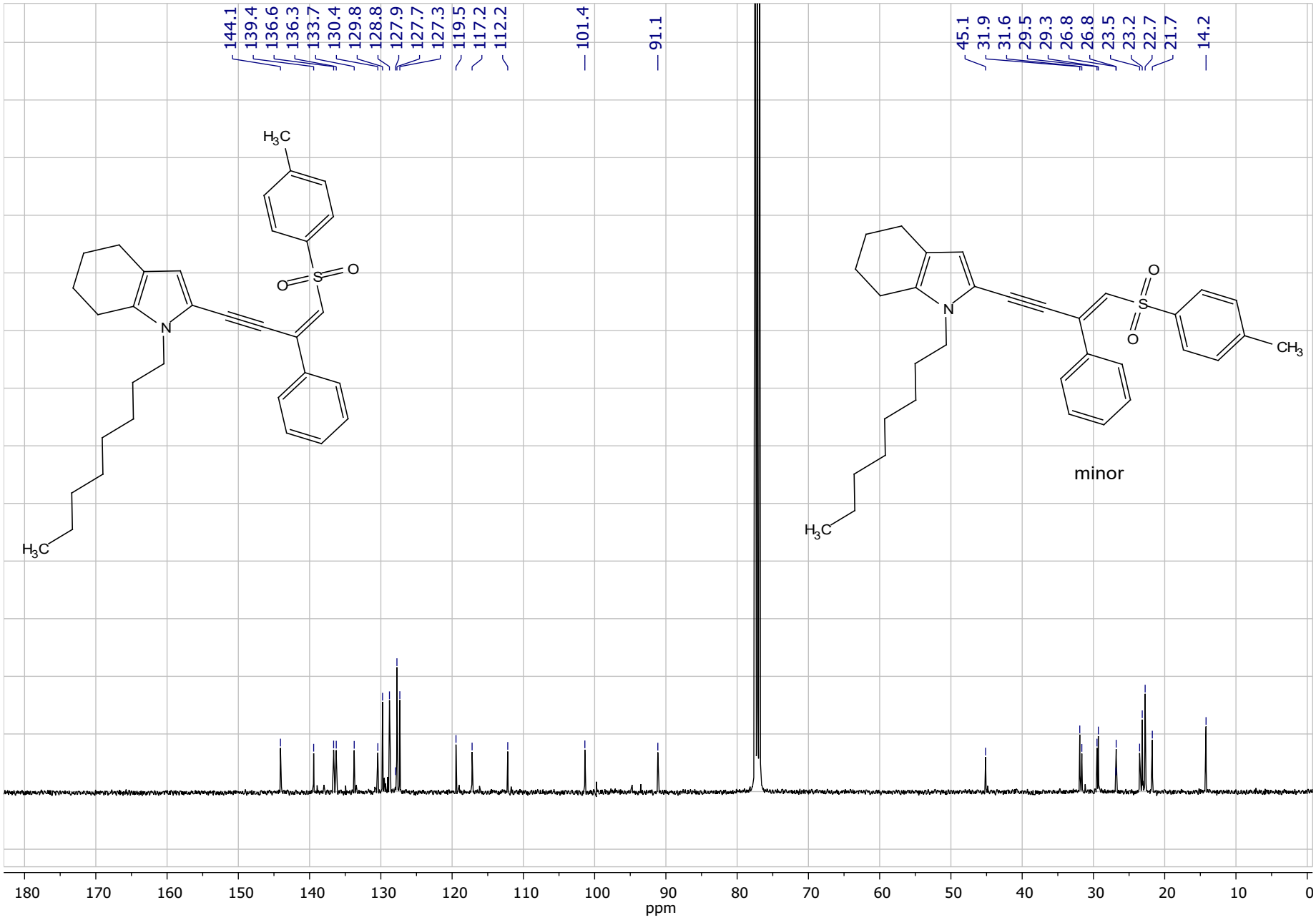
^{13}C NMR spectrum of 1-(1-methyl-1*H*-pyrrol-2-yl)pent-1-yn-3-one (**1q**) in $CDCl_3$.



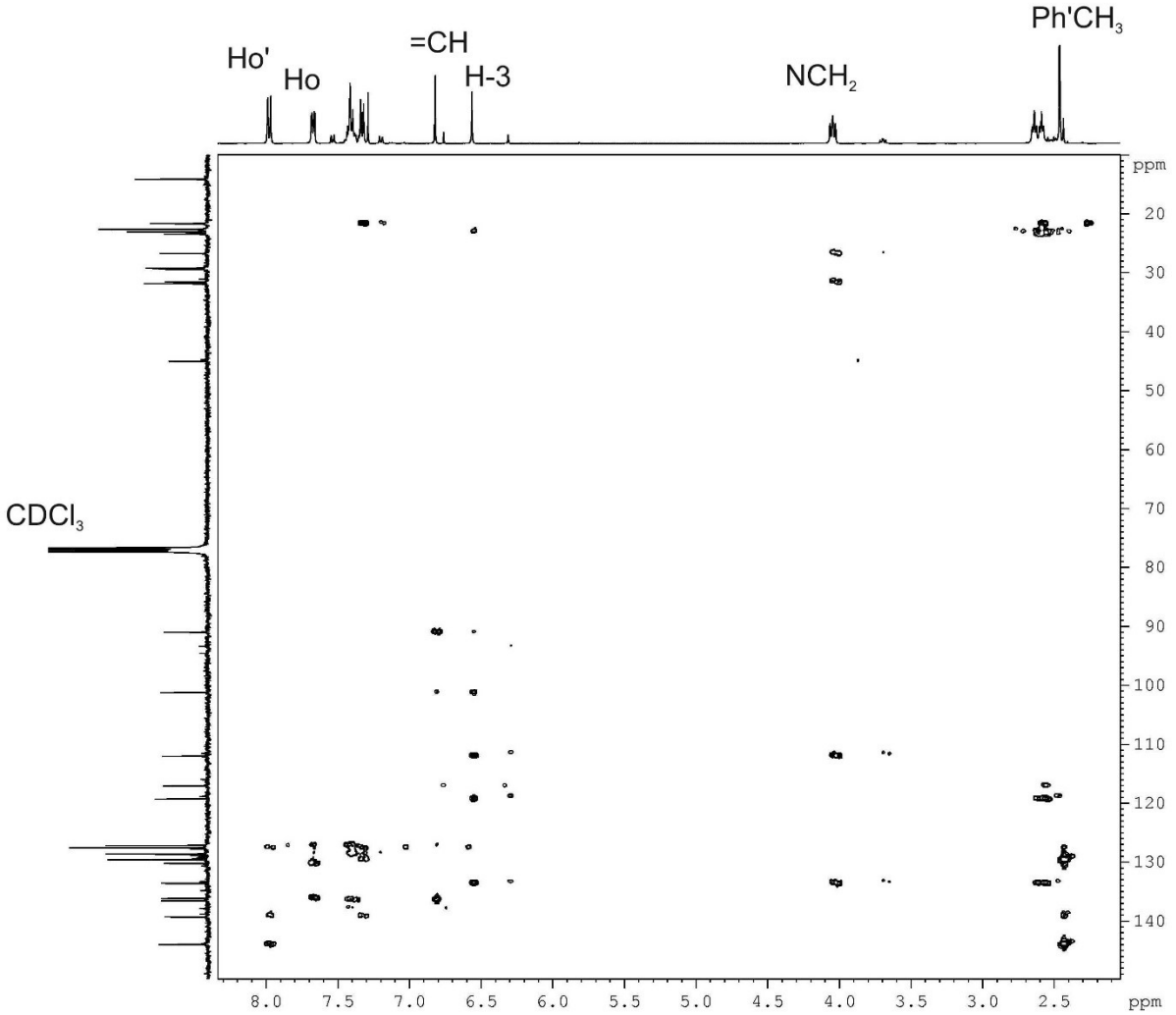
^{1}H NMR spectrum of (*Z*/*E*)-1-octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2a**) in $CDCl_3$.



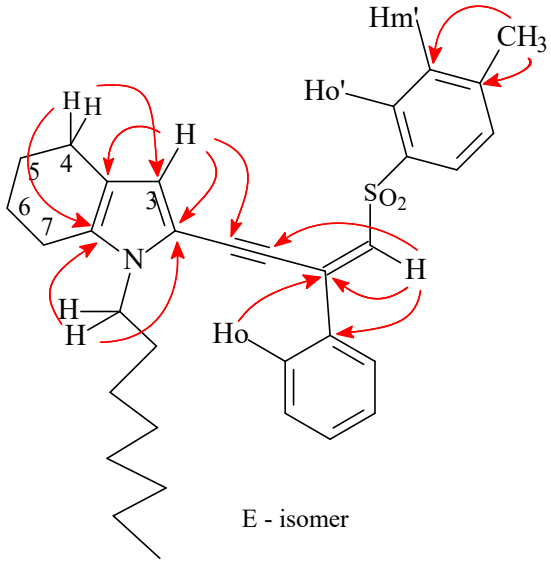
^{13}C NMR spectrum of (*Z*/*E*)-1-octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole in $CDCl_3$. (**2a**)



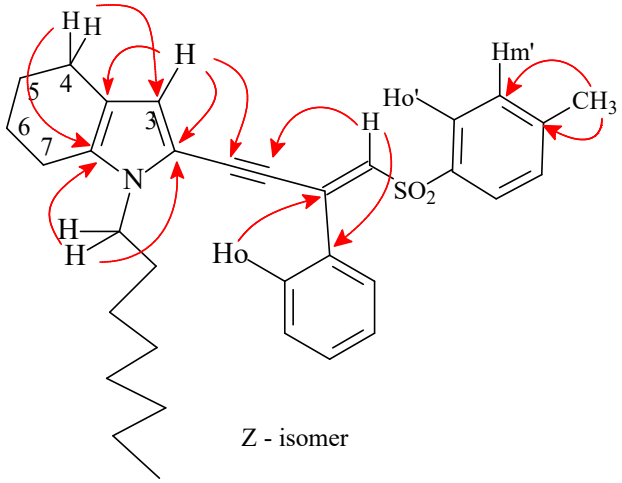
*2D NMR Spectra of 1-octyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1H-indole (**2a**) in $CDCl_3$, E/Z = 10:1.*



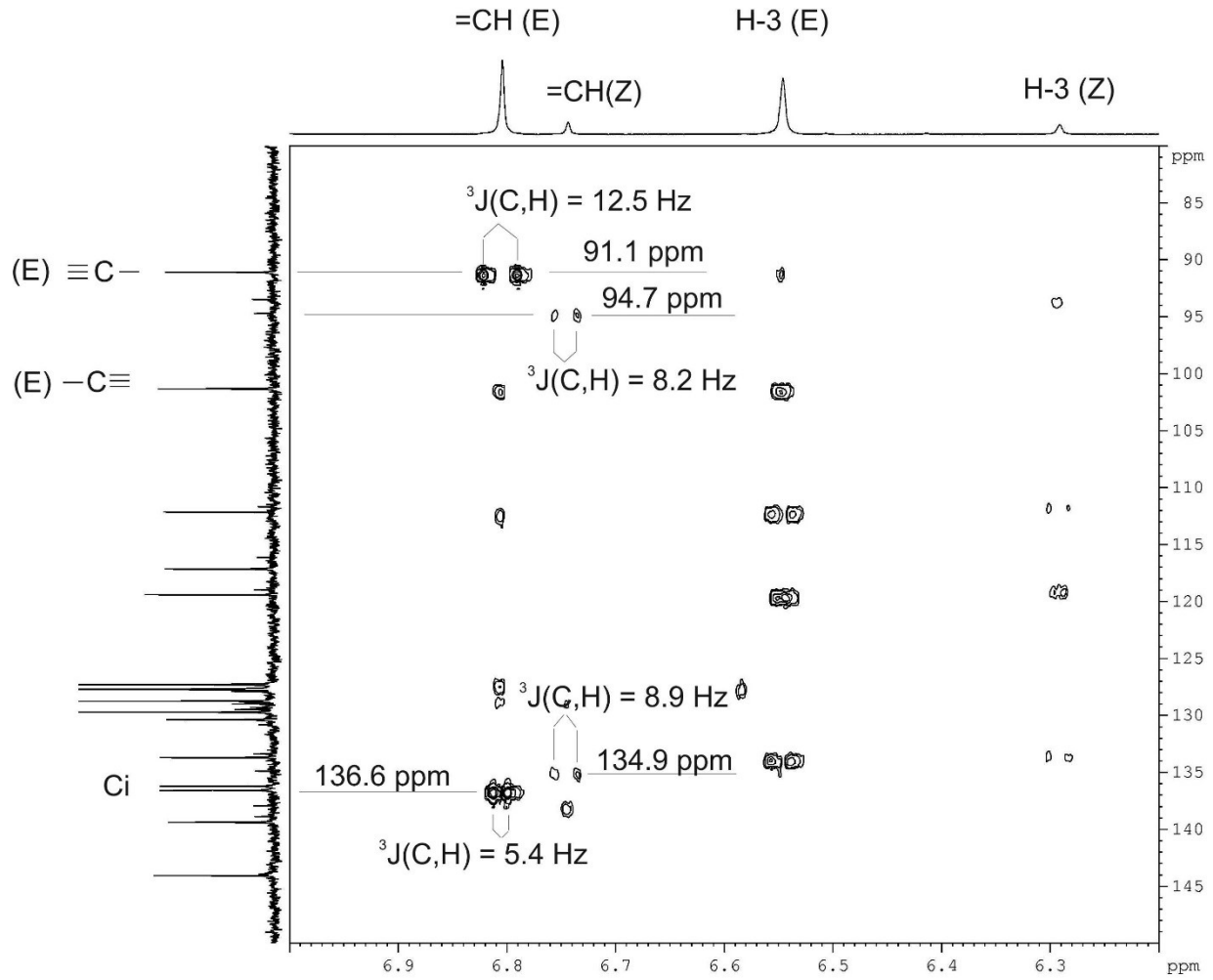
2D ^{1}H-^{13}C HMBC spectrum of mixture *E*- and *Z*- isomers of **2a** ($CDCl_3$), significant correlations observed in the spectrum are presented in the scheme below:



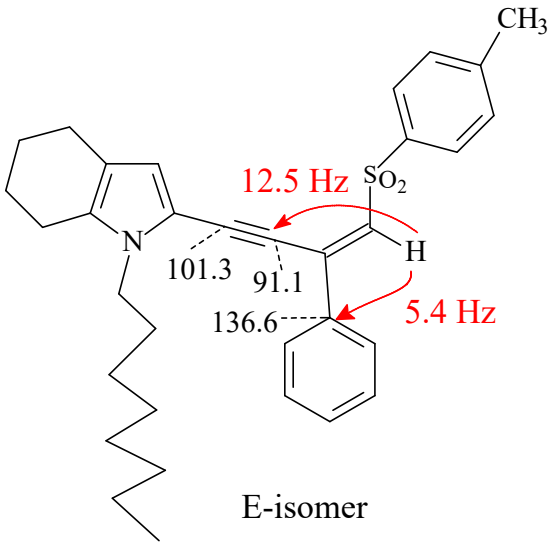
E - isomer



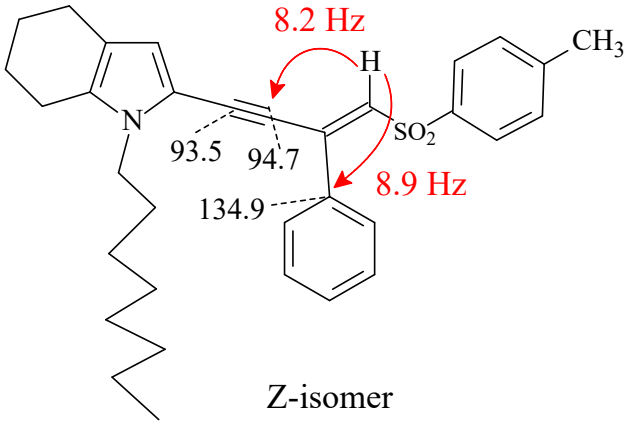
Z - isomer



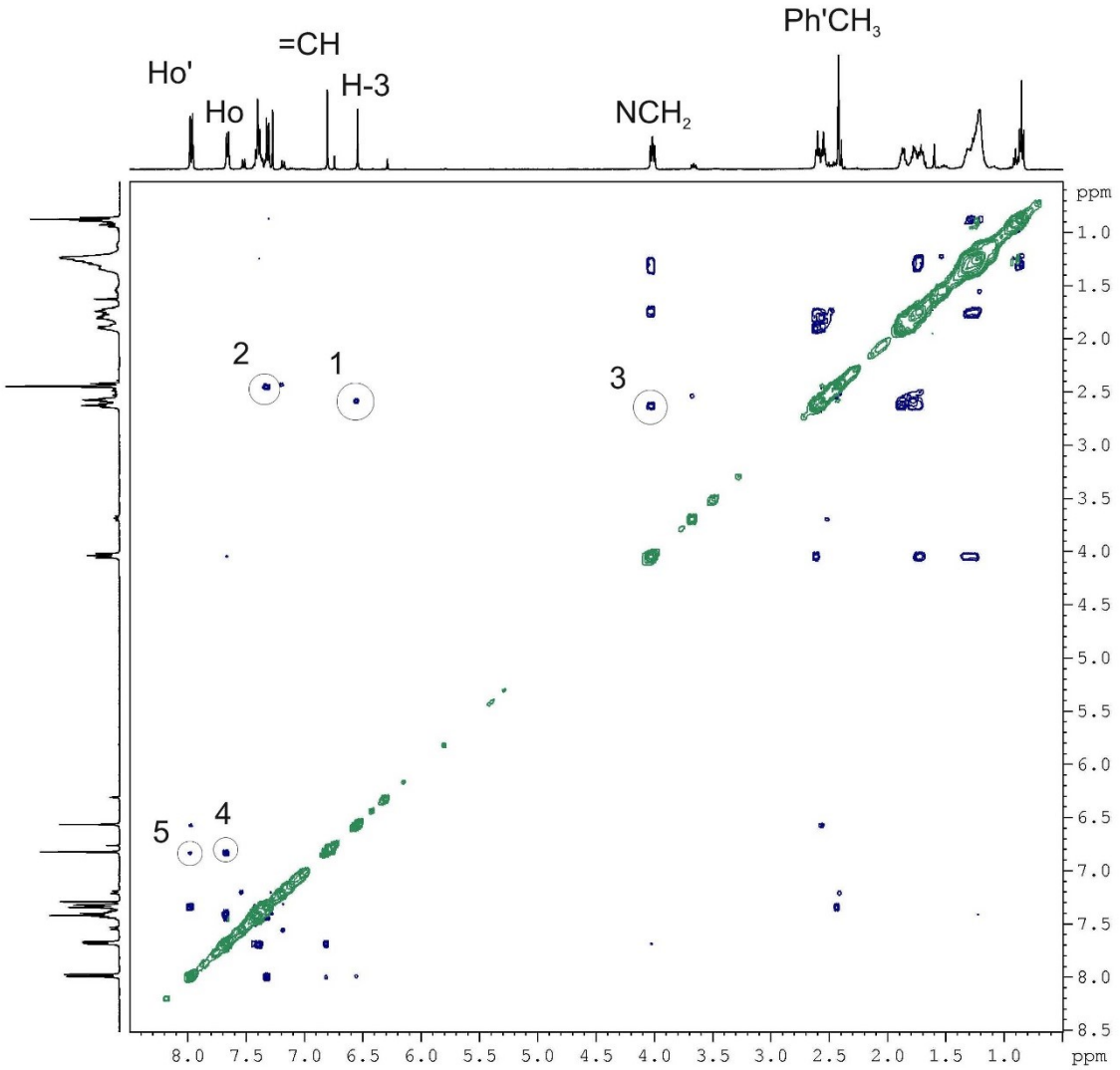
Fragment of 2D ^{1}H-^{13}C HMBC spectrum of mixture *E*- and *Z*- isomers of **2a** ($CDCl_3$). The values of the vicinal spin spin coupling constants ^{3}J(C,H) were measured from the cross sections of the corresponding cross peaks.



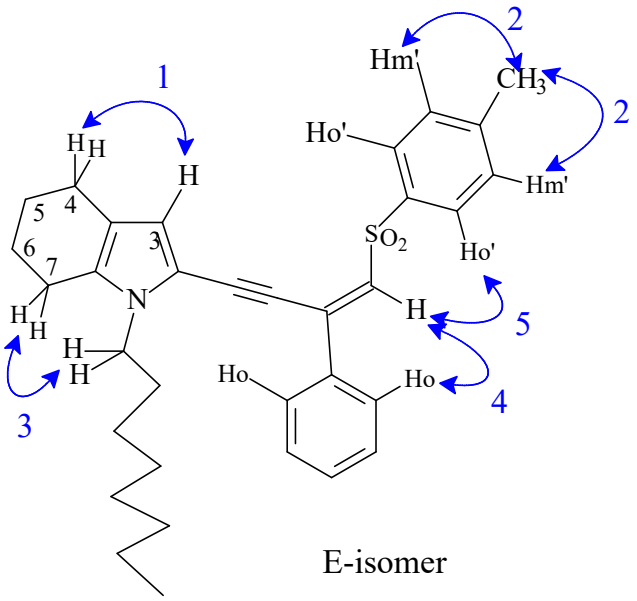
E-isomer



Z-isomer

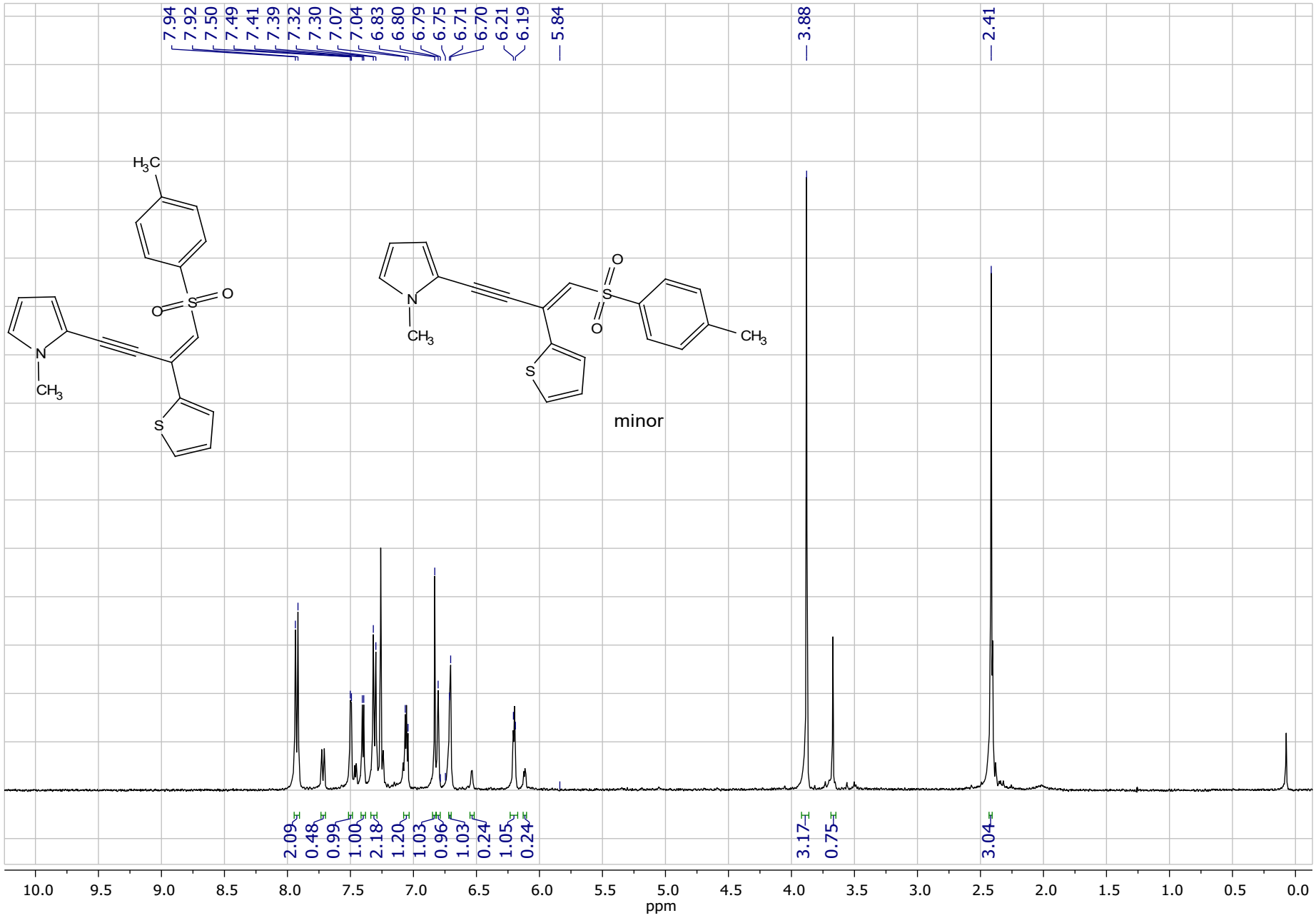


2D NOESY spectrum of mixture *E*- and *Z*- isomers of **2a** (400.1 MHz, $CDCl_3$), significant correlations observed in the spectrum are presented in the scheme below:

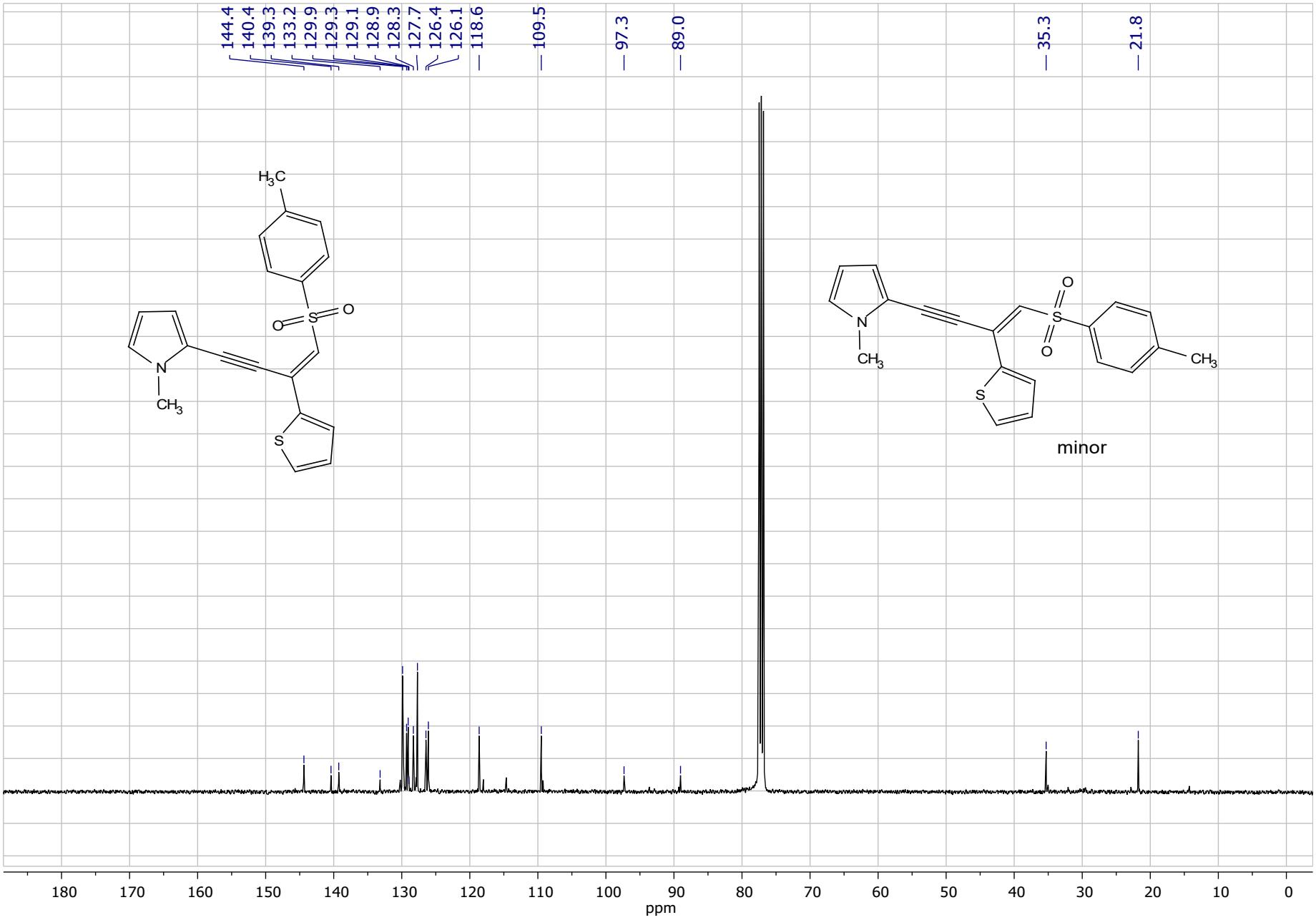


E-isomer

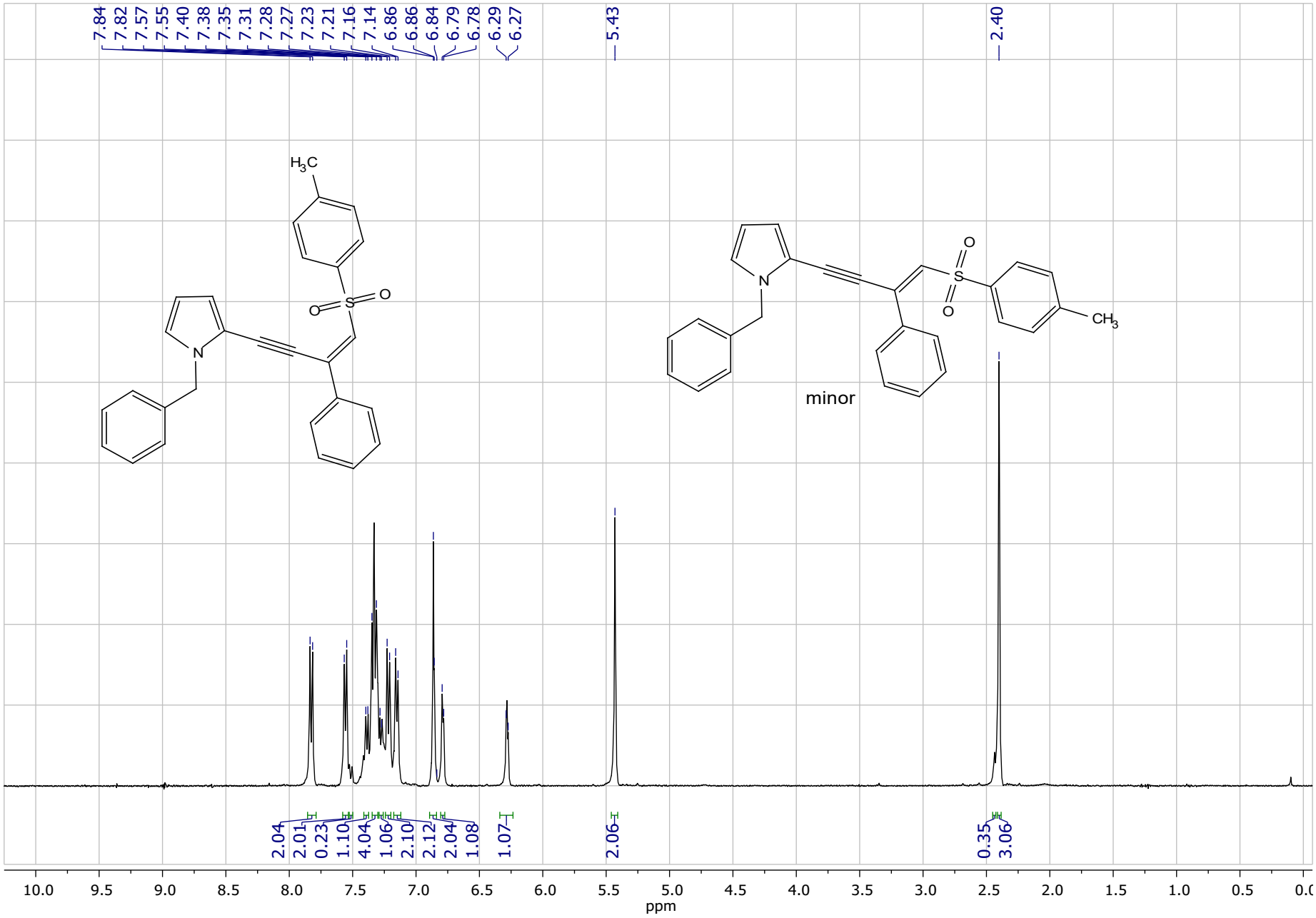
^{1}H NMR spectrum of (*Z*/*E*)-1-methyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2b**) in $CDCl_3$.



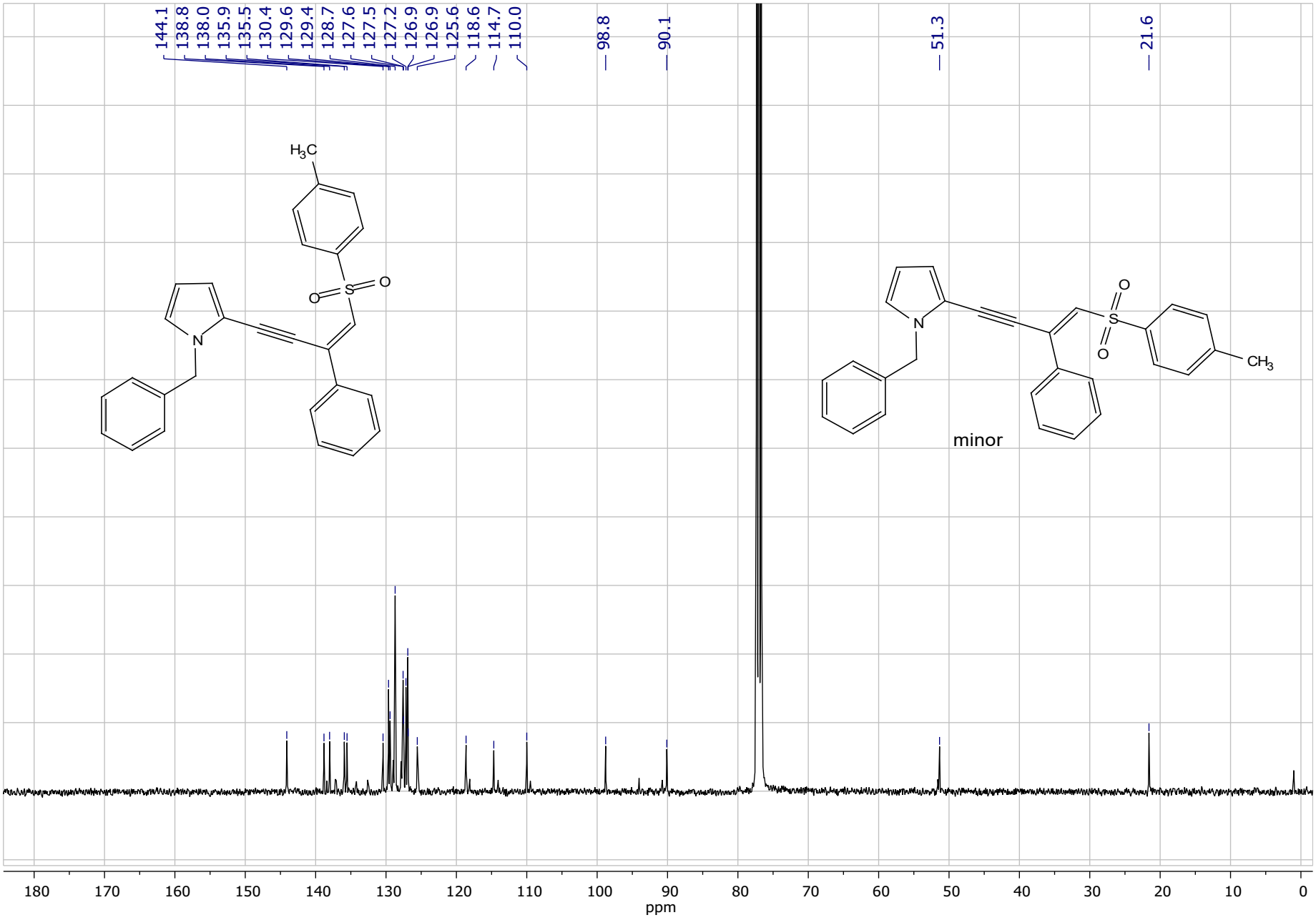
^{13}C NMR spectrum of (*Z*/*E*)-1-methyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2b**) in $CDCl_3$.



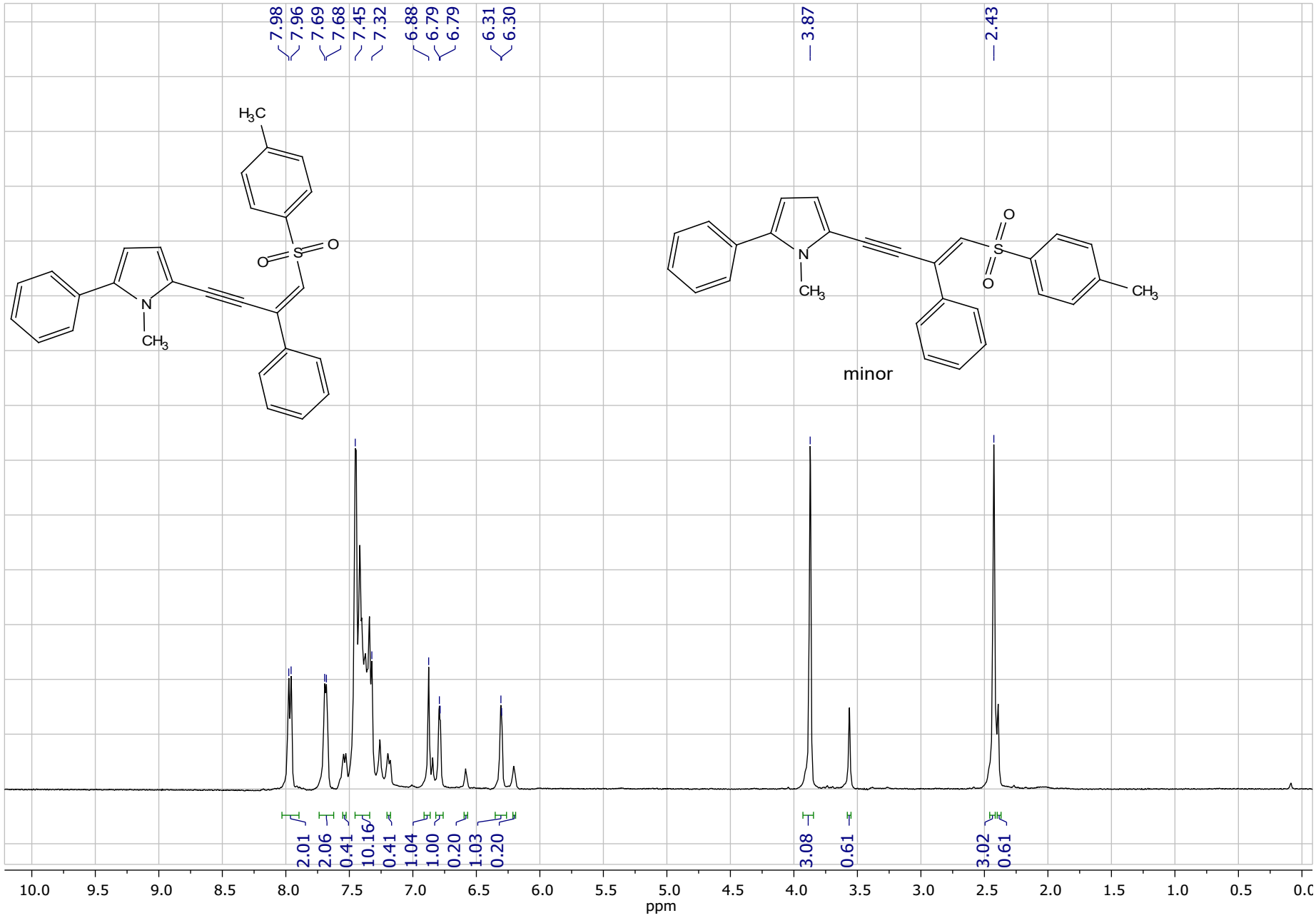
^{1}H NMR spectrum of (*Z*/*E*)-1-benzyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2c**) in $CDCl_3$.



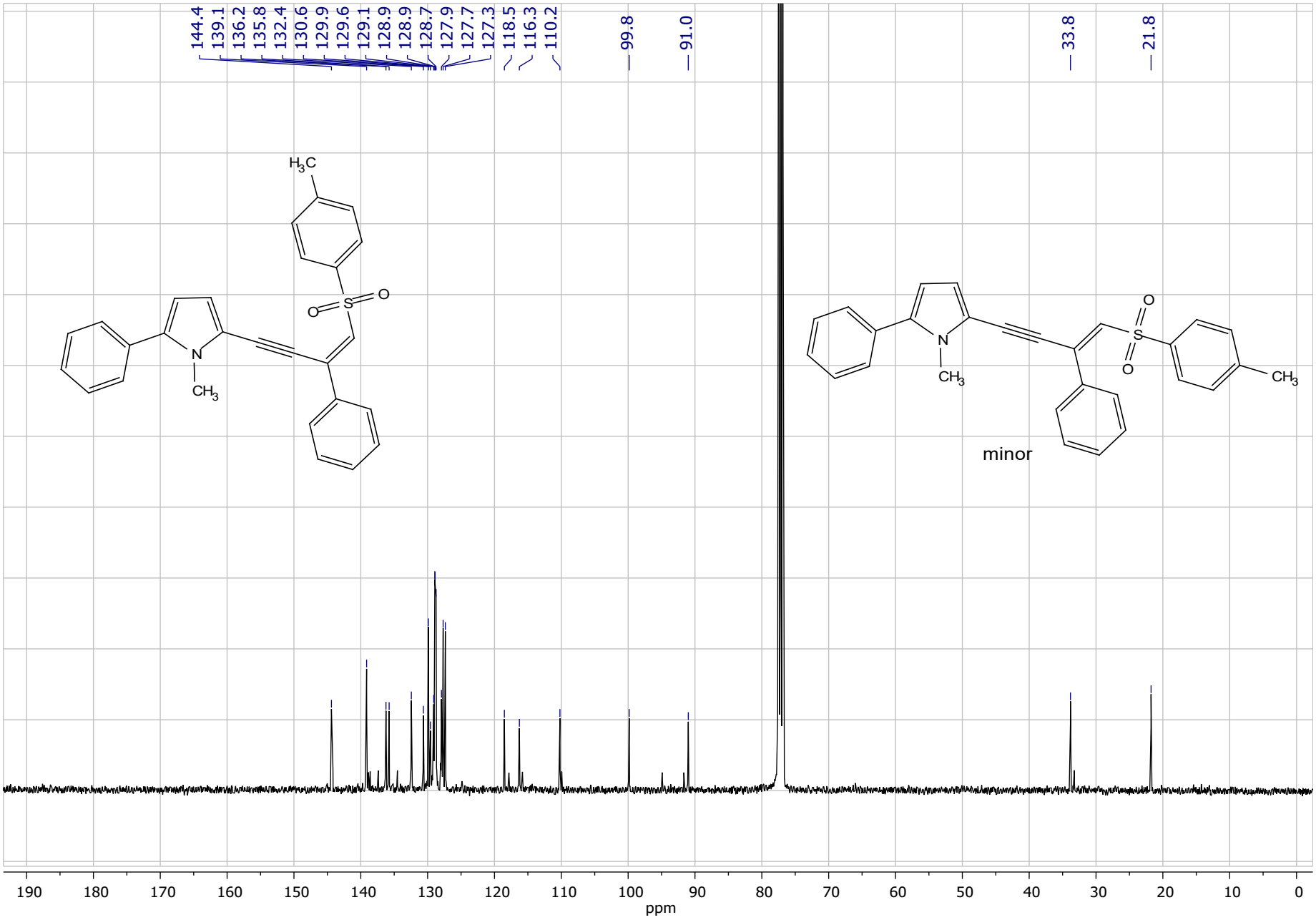
^{13}C NMR spectrum of (*Z*/*E*)-1-benzyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2c**) in $CDCl_3$.



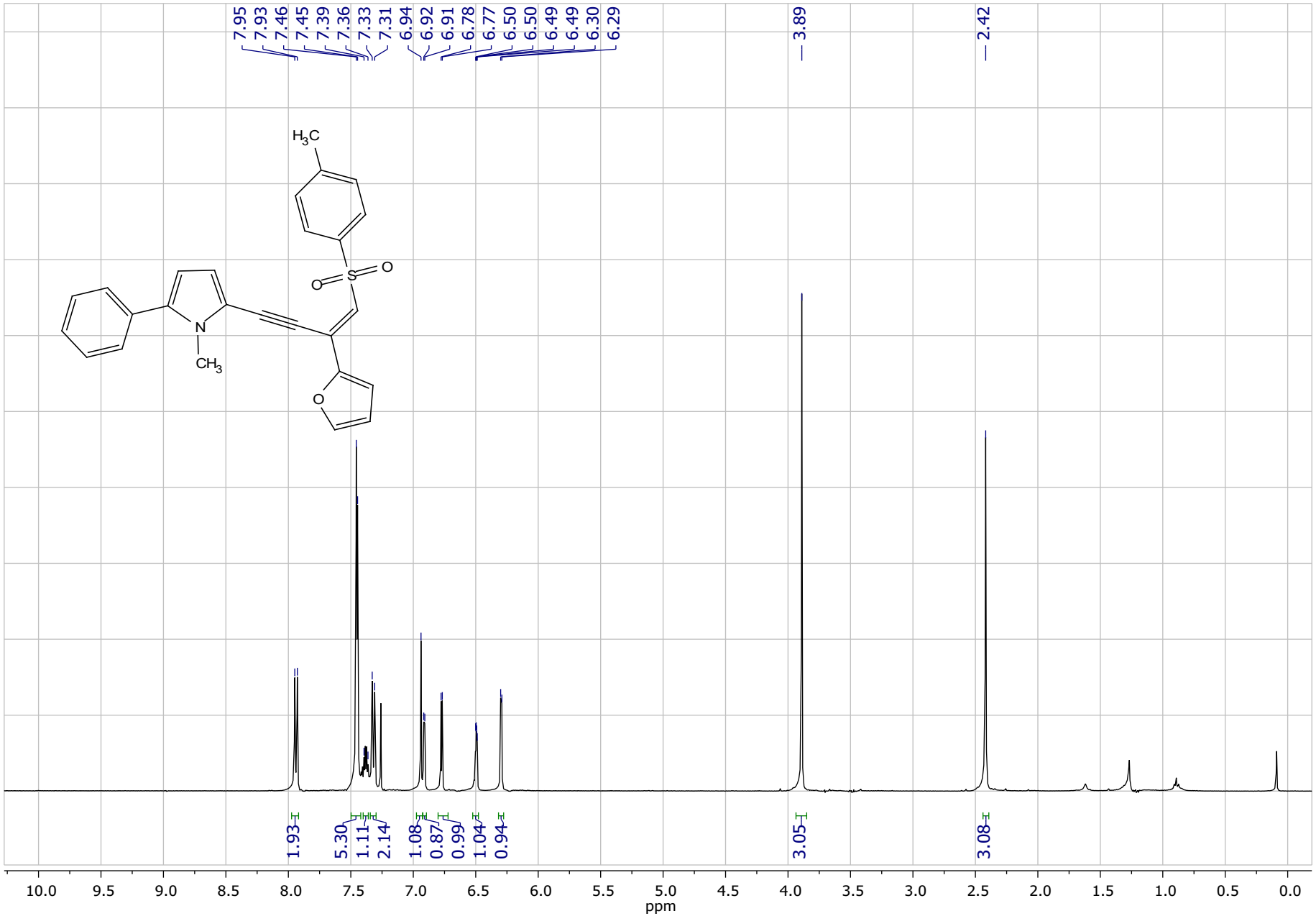
^{1}H NMR spectrum of (*Z*/*E*)-1-methyl-2-phenyl-5-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2d**) in $CDCl_3$.



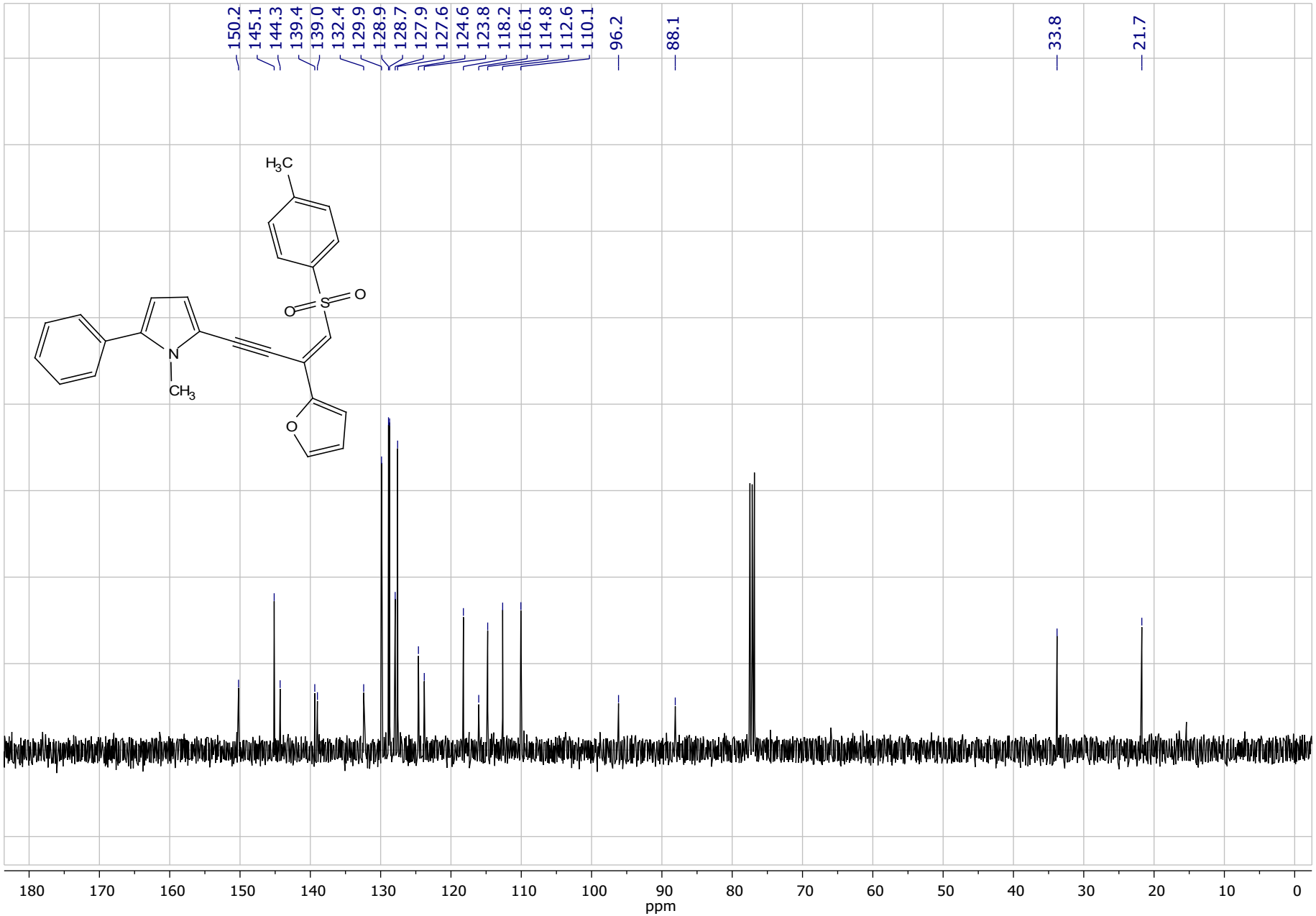
^{13}C NMR spectrum of (*Z*/*E*)-1-methyl-2-phenyl-5-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1*H*-pyrrole (**2d**) in $CDCl_3$.



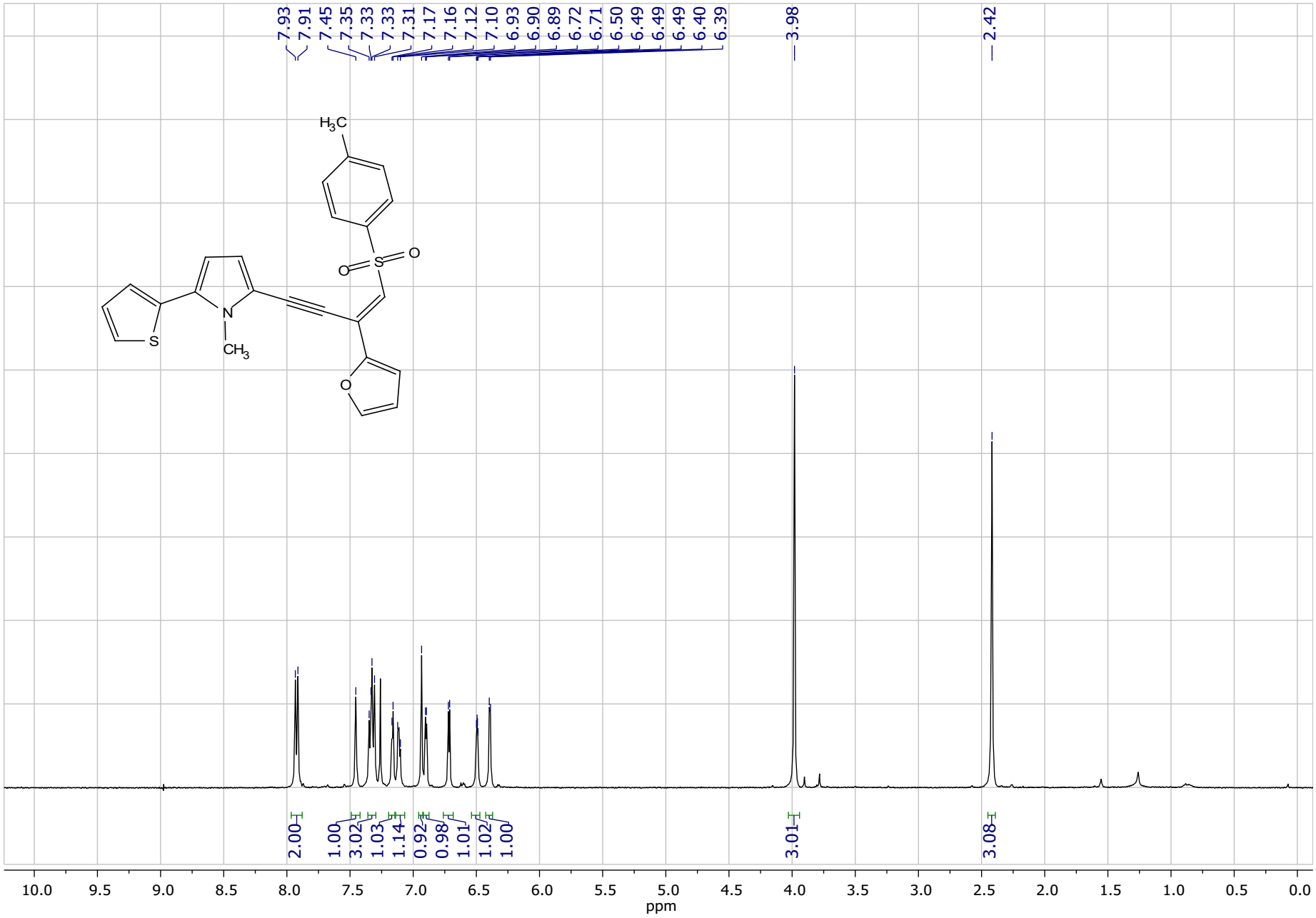
^{1}H NMR spectrum of (*E*)-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-5-phenyl-1*H*-pyrrole (**2e**) in $CDCl_3$.



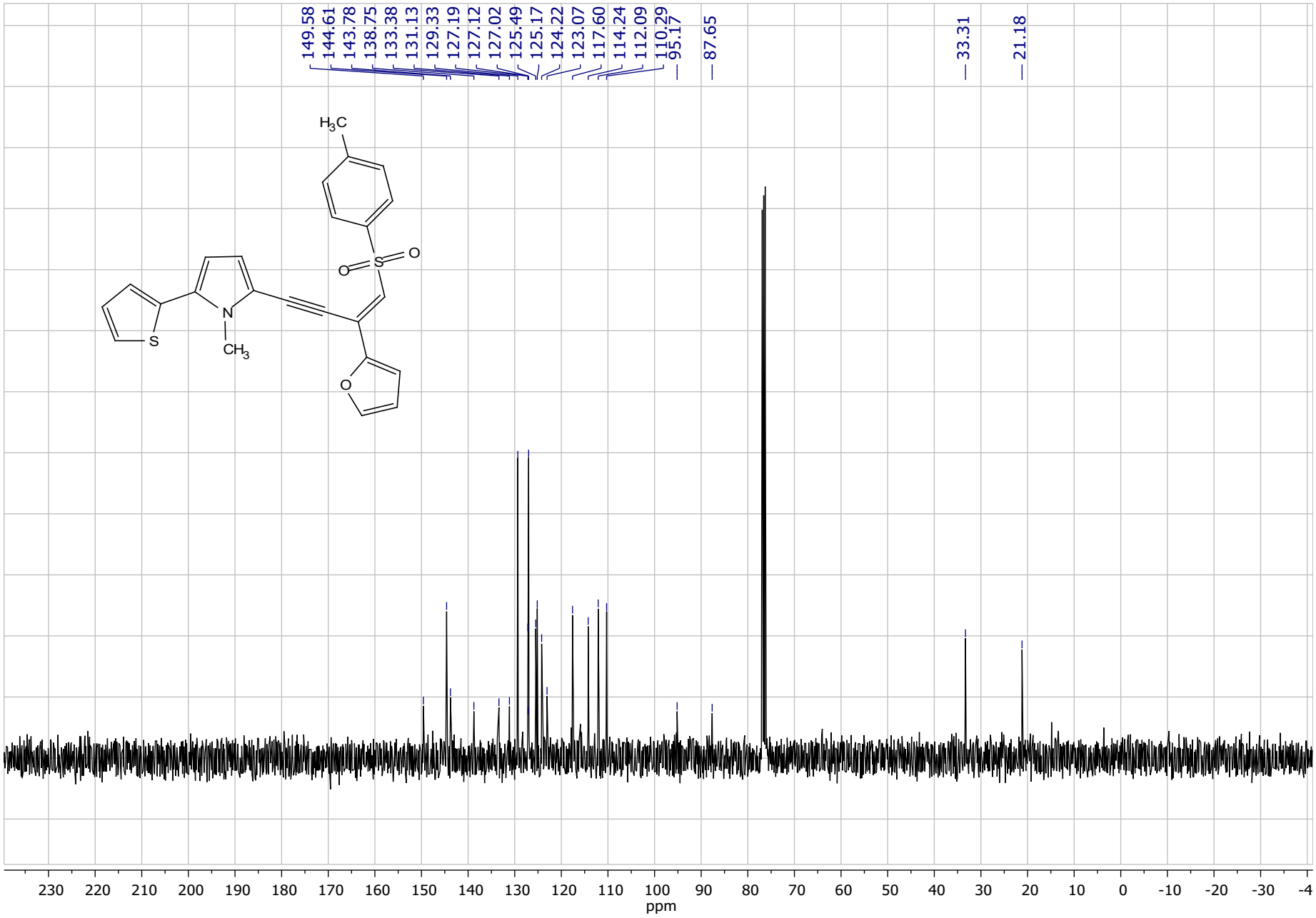
^{13}C NMR spectrum of (*E*)-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-5-phenyl-1*H*-pyrrole (**2e**) in $CDCl_3$.



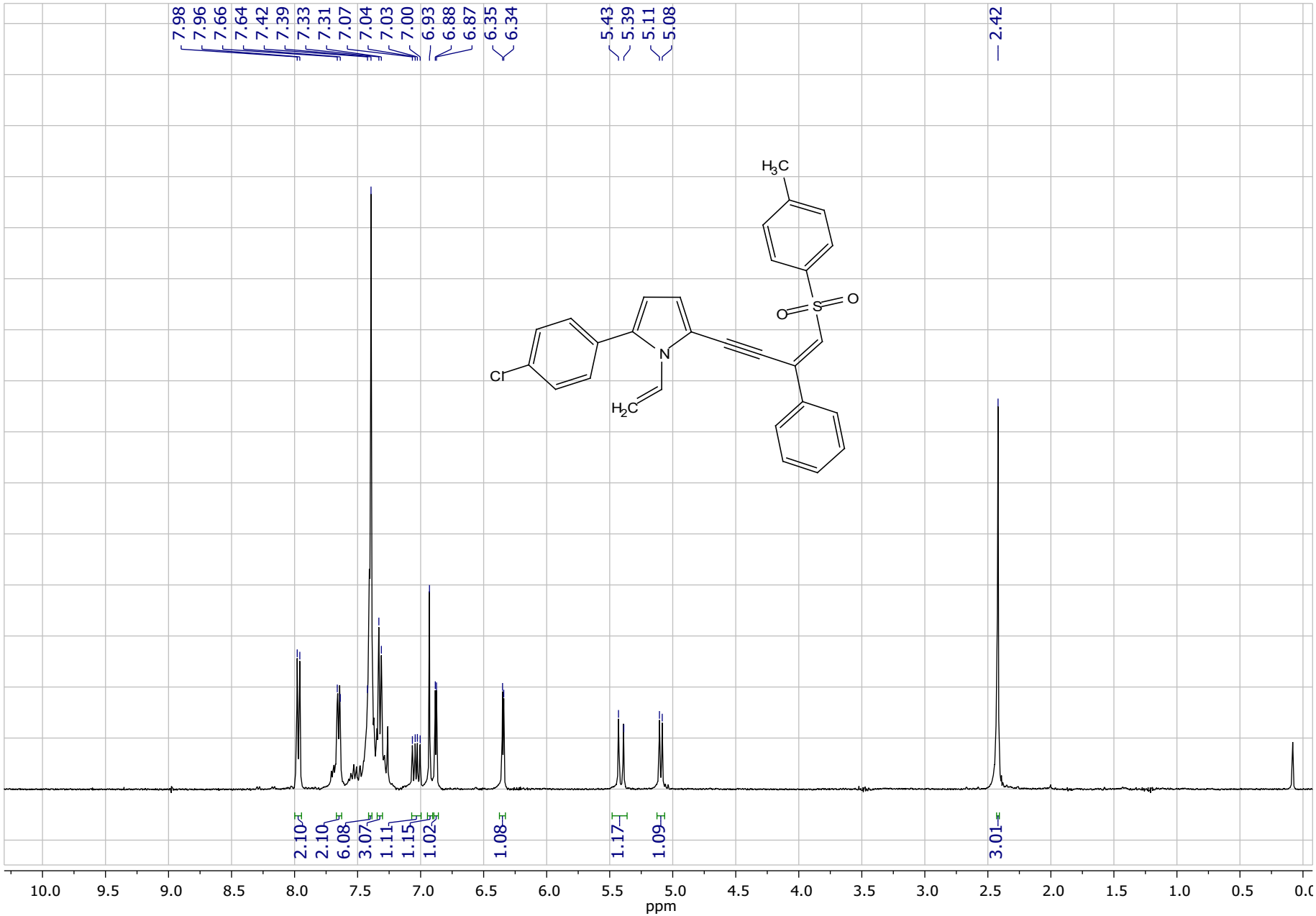
^{1}H NMR spectrum of (*E*)-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-5-(thiophen-2-yl)-1*H*-pyrrole (**2f**) in $CDCl_3$.



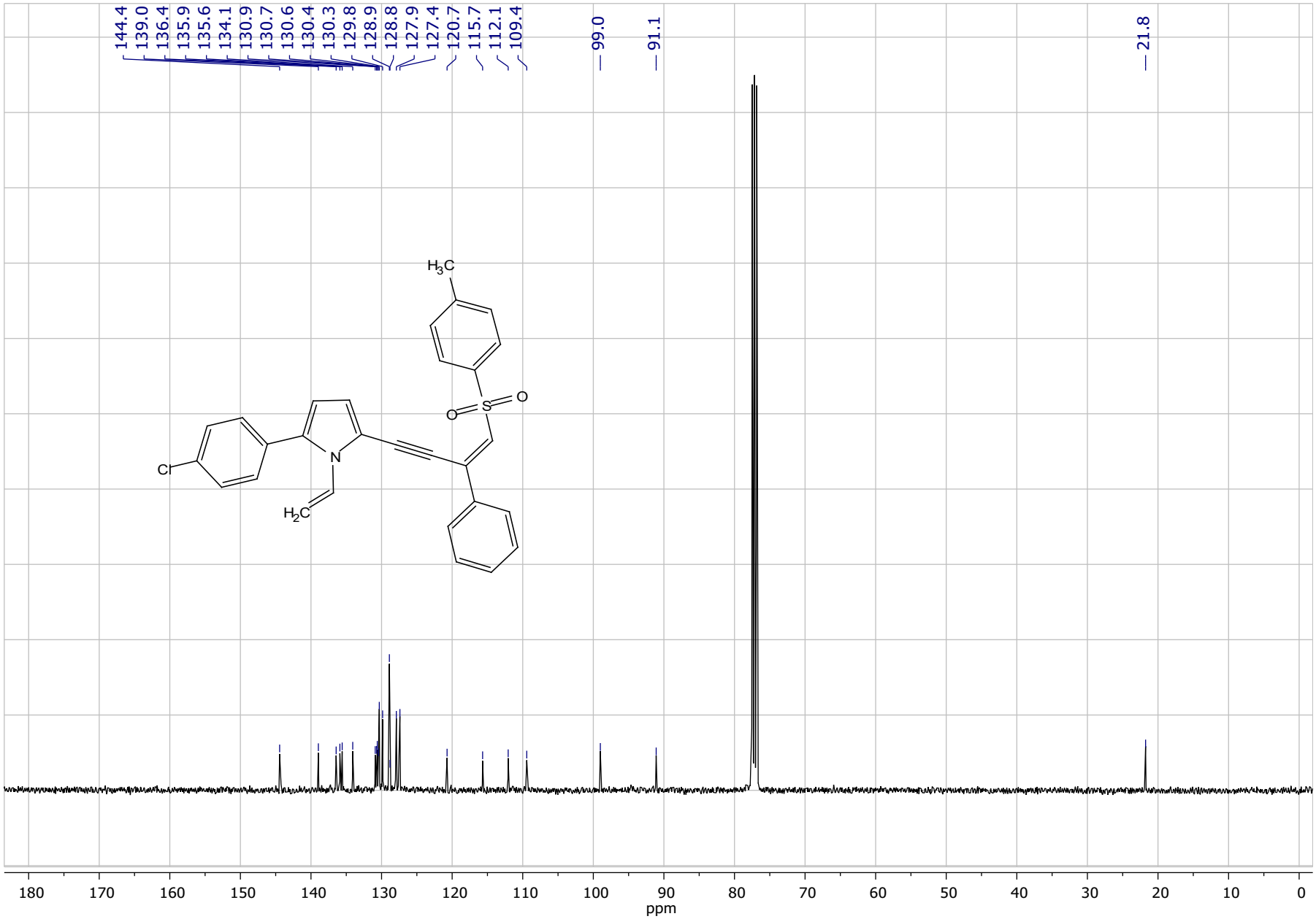
^{13}C NMR spectrum of (*E*)-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-5-(thiophen-2-yl)-1*H*-pyrrole (**2f**) in $CDCl_3$.



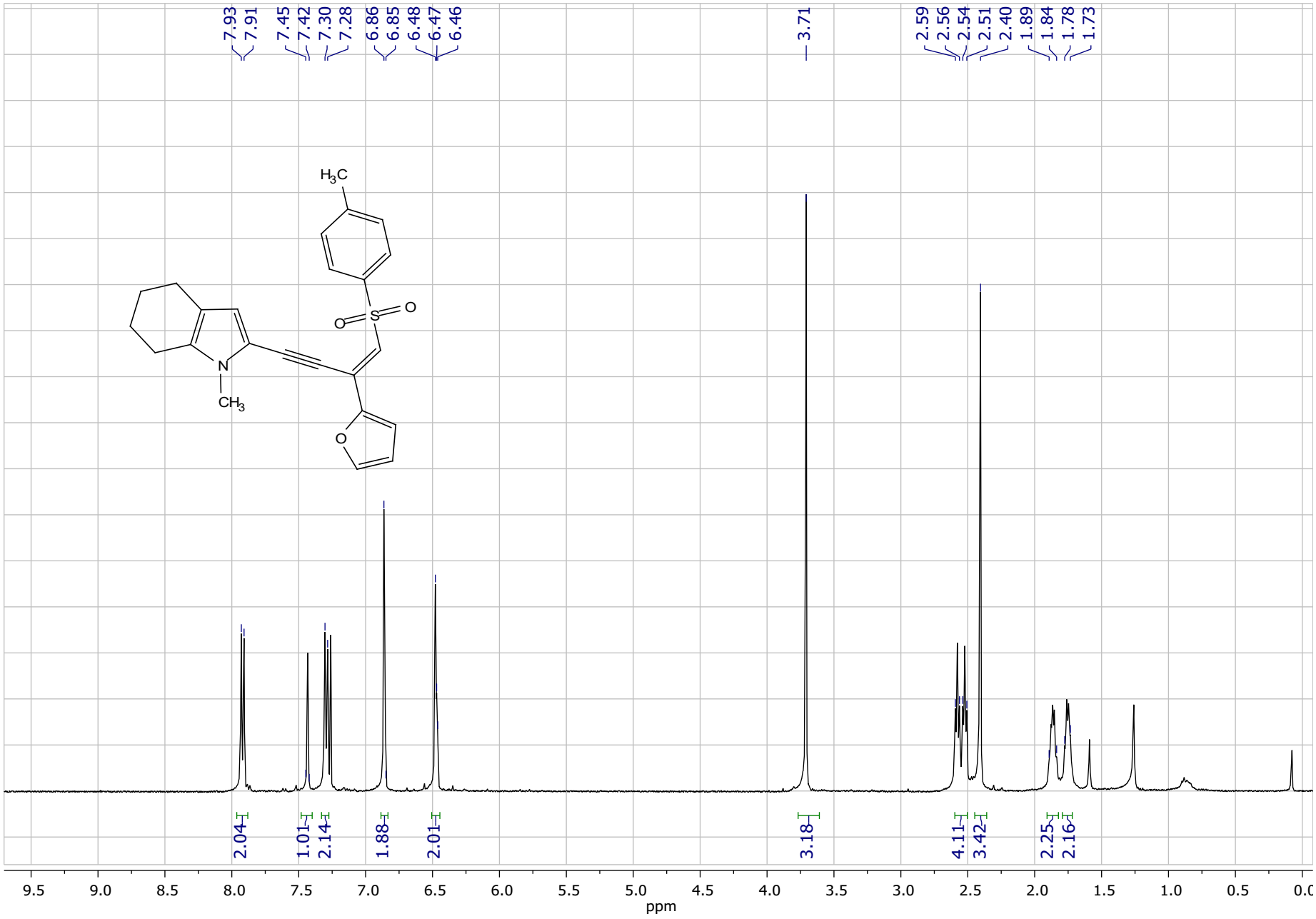
^{1}H NMR spectrum of (*Z*)-2-(4-chlorophenyl)-5-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1-vinyl-1*H*-pyrrole (**2g**) in $CDCl_3$.



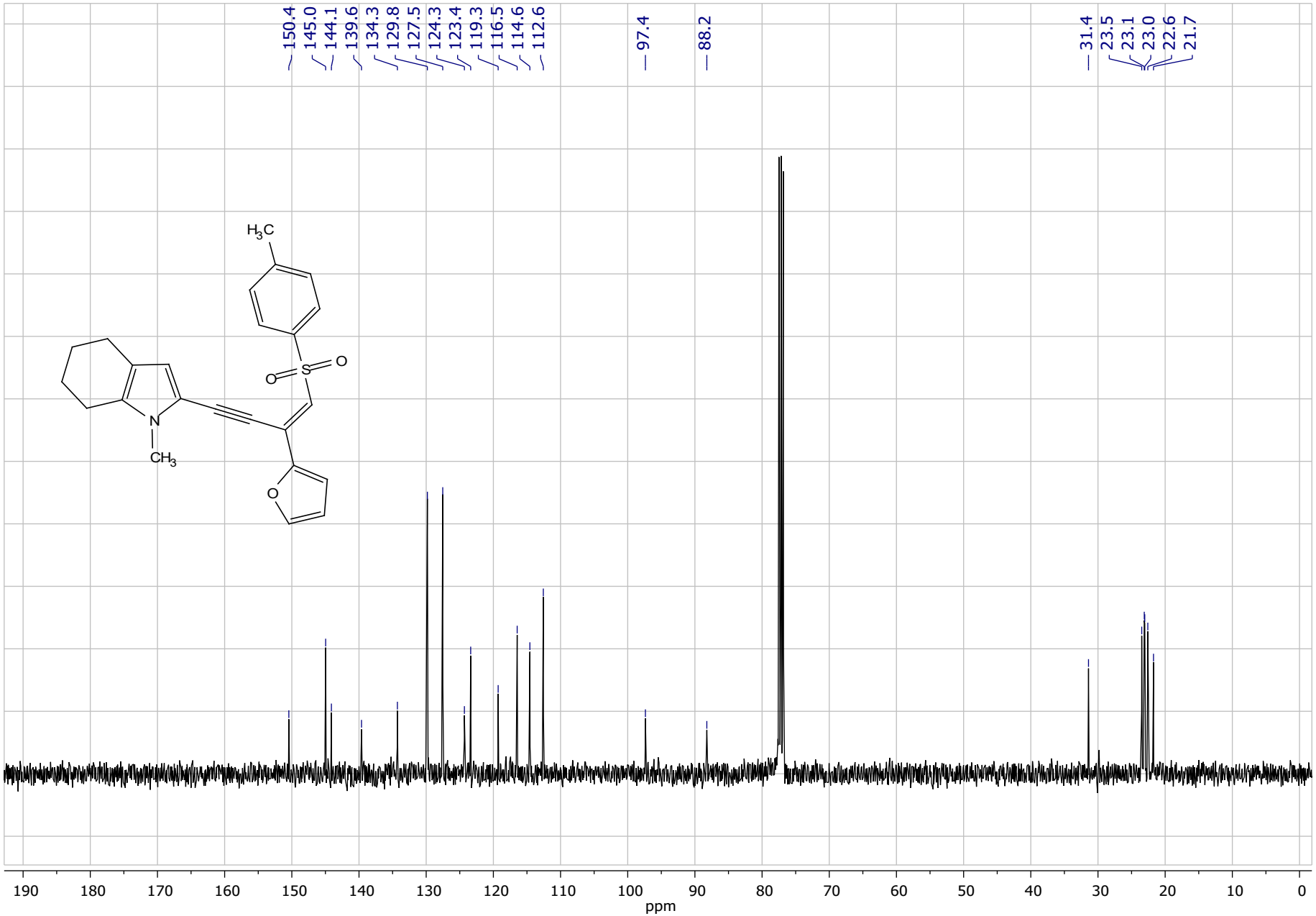
^{13}C NMR spectrum of (*Z*)-2-(4-chlorophenyl)-5-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1-vinyl-1*H*-pyrrole (**2g**) in $CDCl_3$.



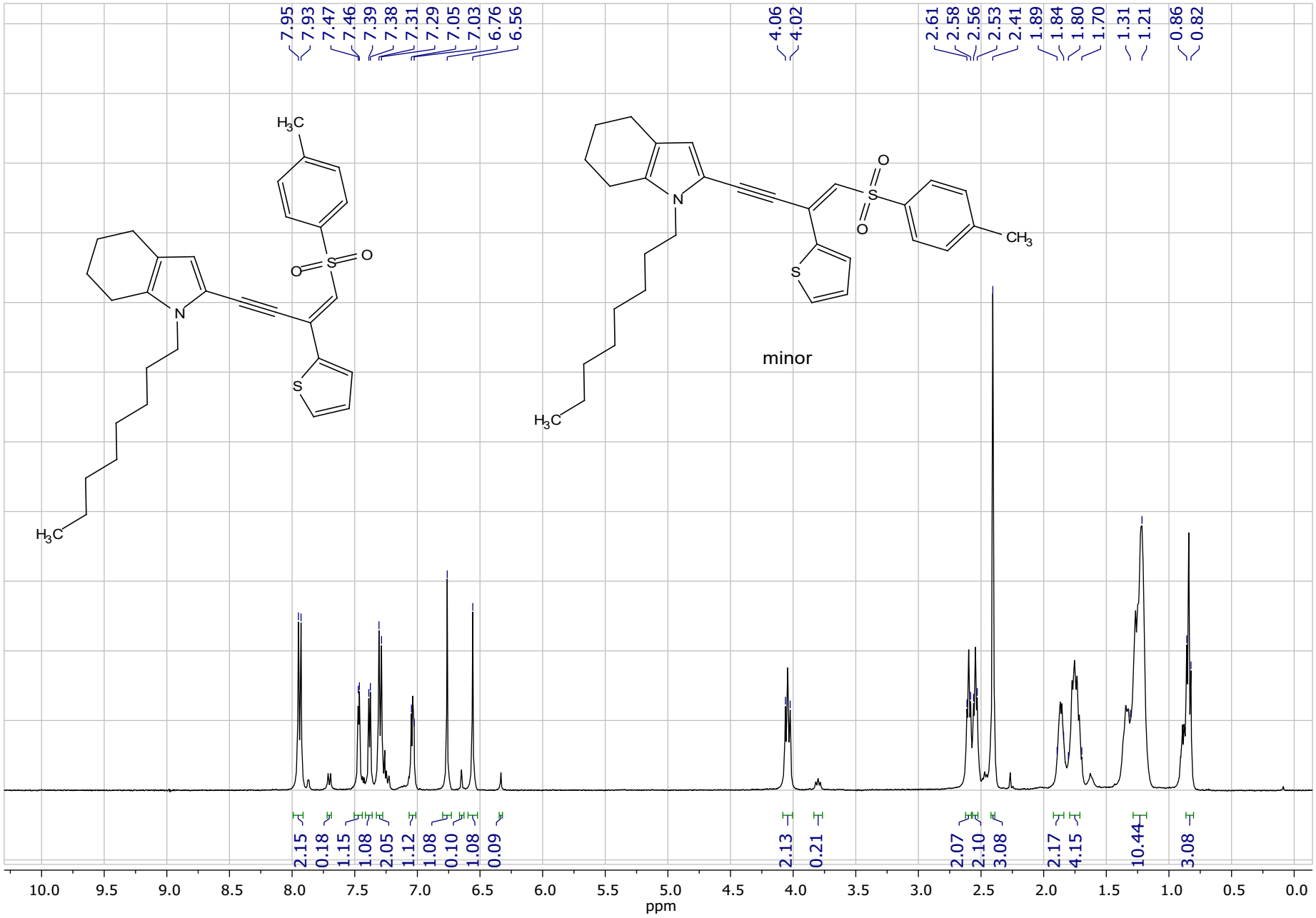
^{1}H NMR spectrum of (*E*)-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-4,5,6,7-tetrahydro-1*H*-indole (**2h**) in $CDCl_3$.



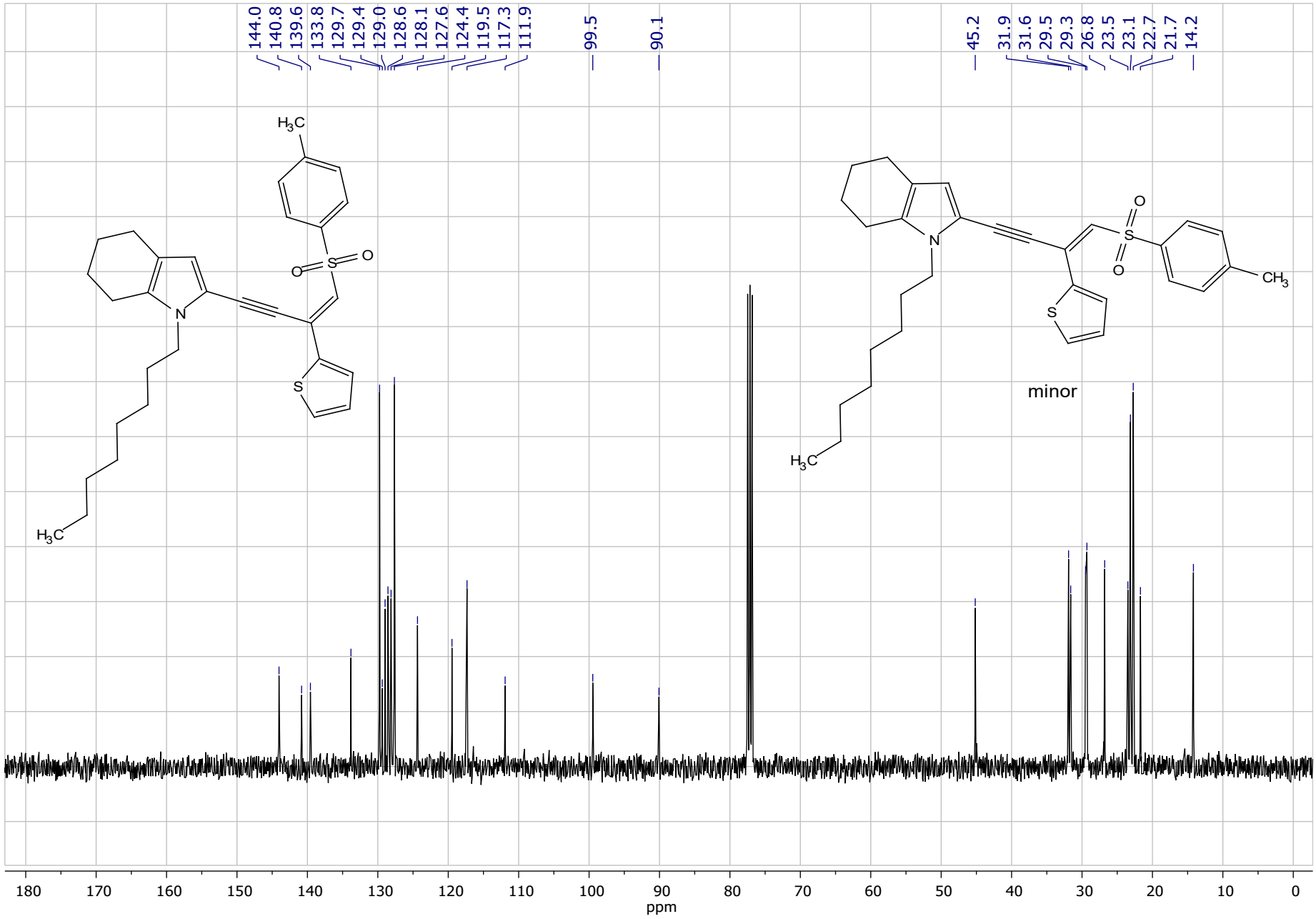
^{13}C NMR spectrum of (*E*)-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-1-methyl-4,5,6,7-tetrahydro-1*H*-indole (**2h**) in $CDCl_3$.



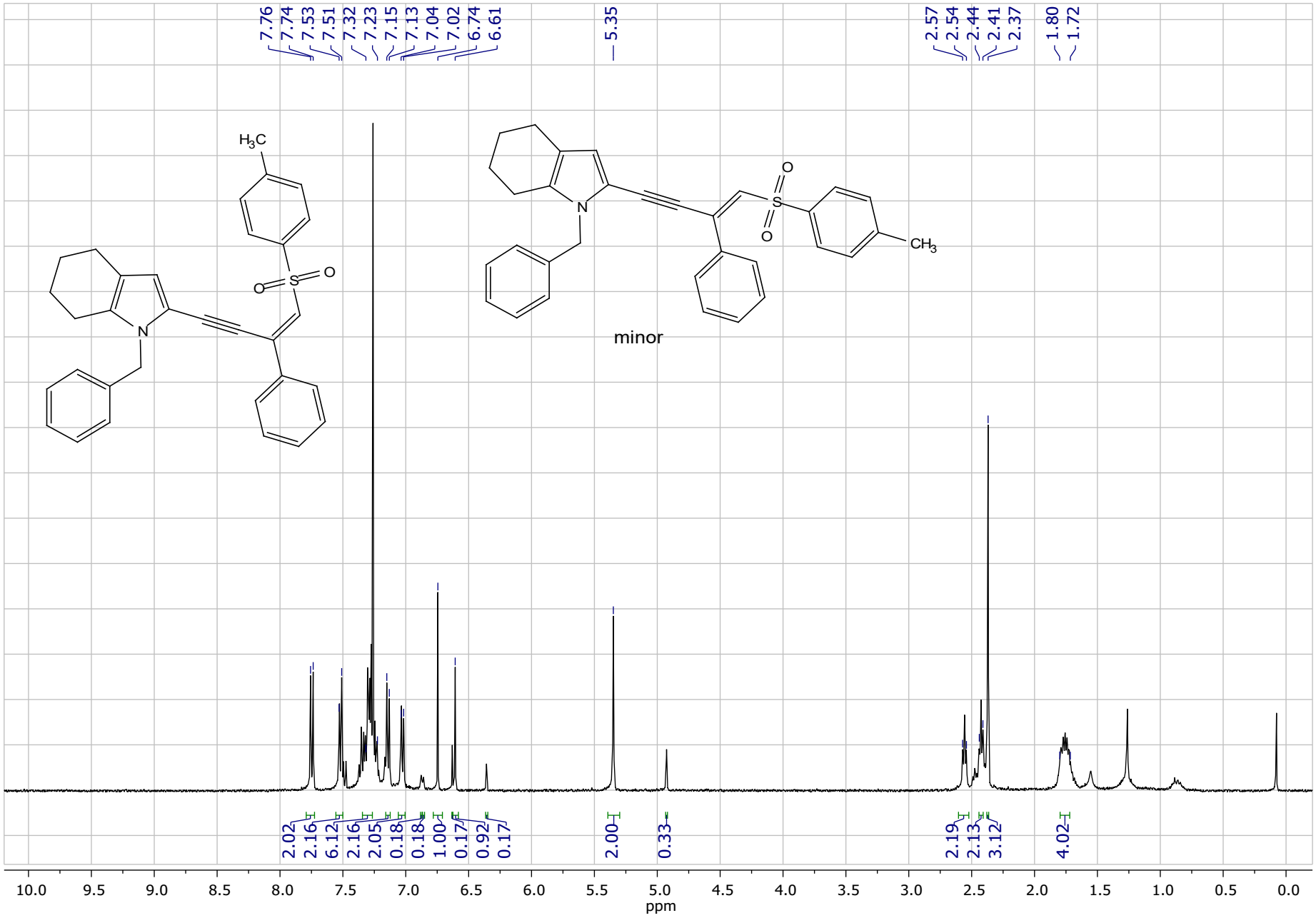
^{1}H NMR spectrum of (*E/Z*)-1-octyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2i**) in $CDCl_3$.



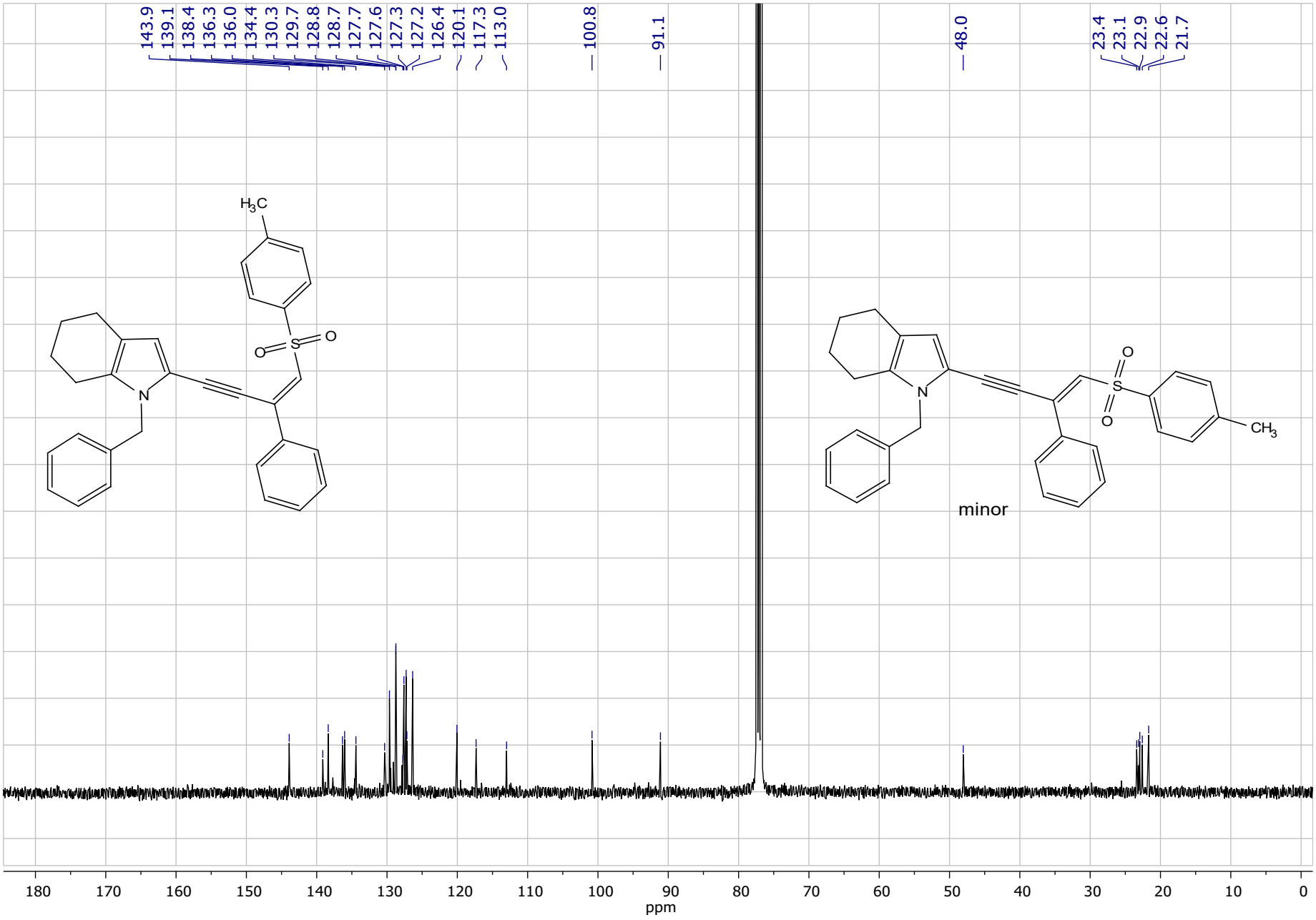
^{13}C NMR spectrum of (*E/Z*)-1-octyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2i**) in $CDCl_3$.



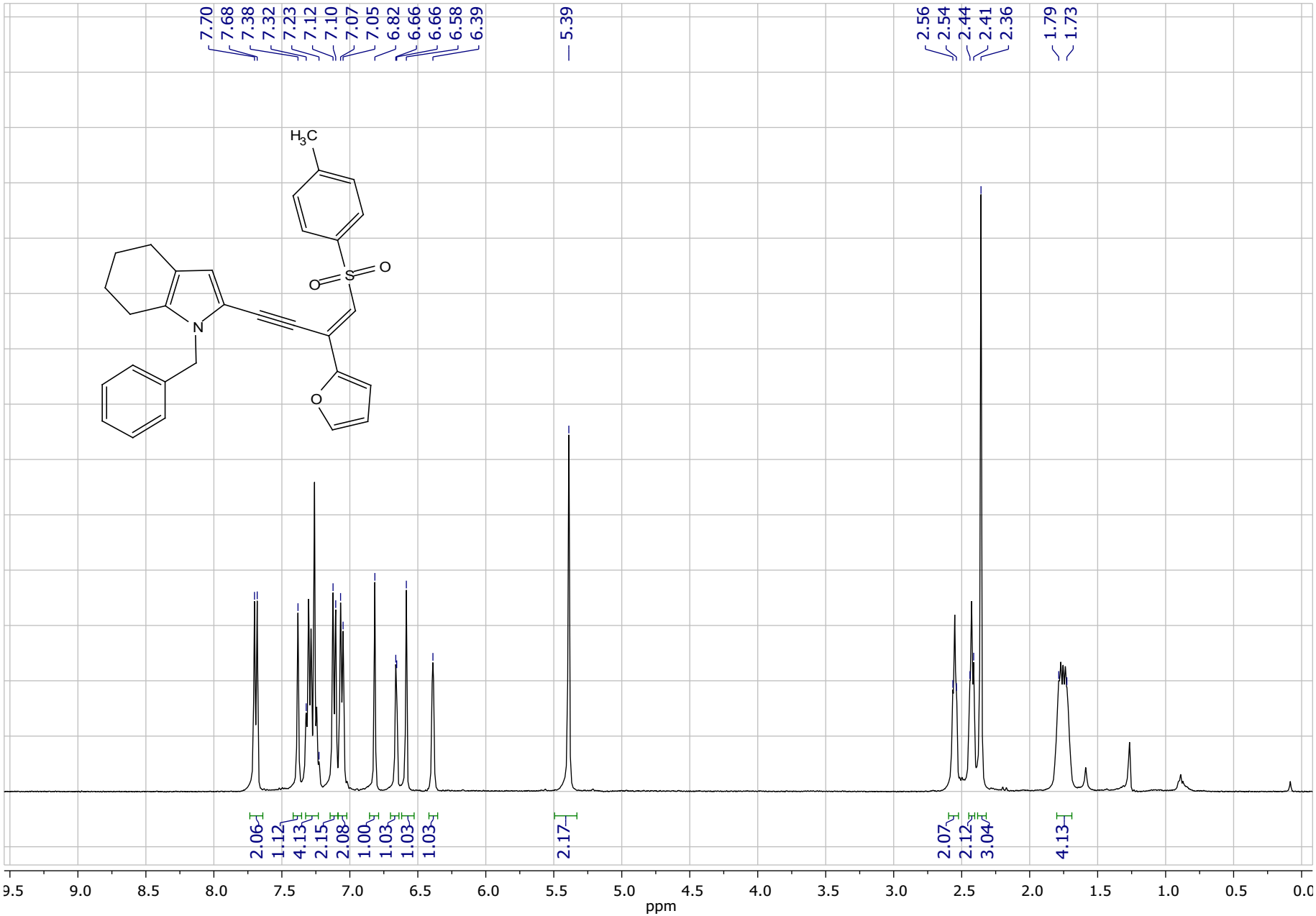
^{1}H NMR spectrum of (*Z*/*E*)-1-benzyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2j**) in $CDCl_3$.



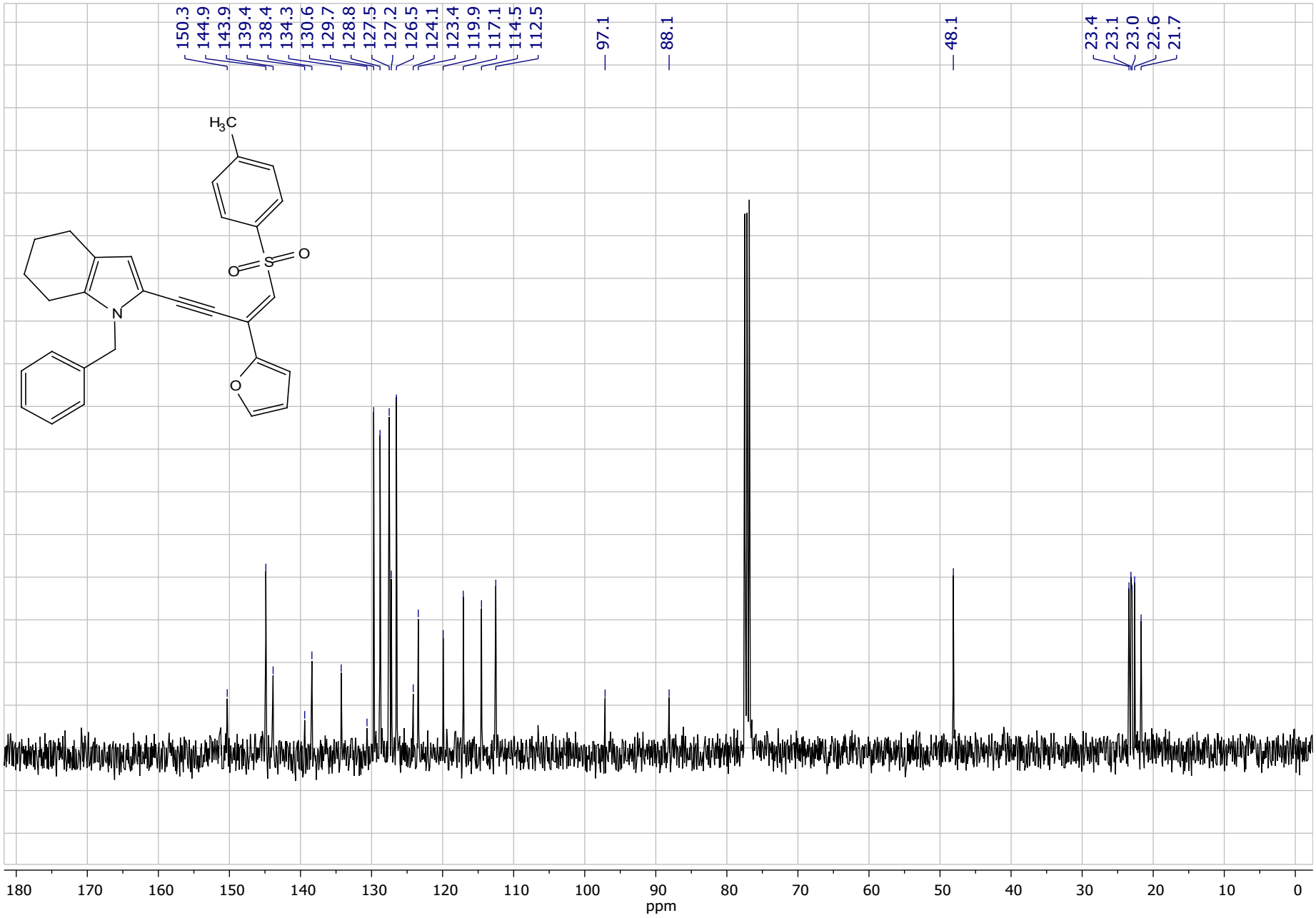
^{13}C NMR spectrum of (*Z*/*E*)-1-benzyl-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2j**) in $CDCl_3$.



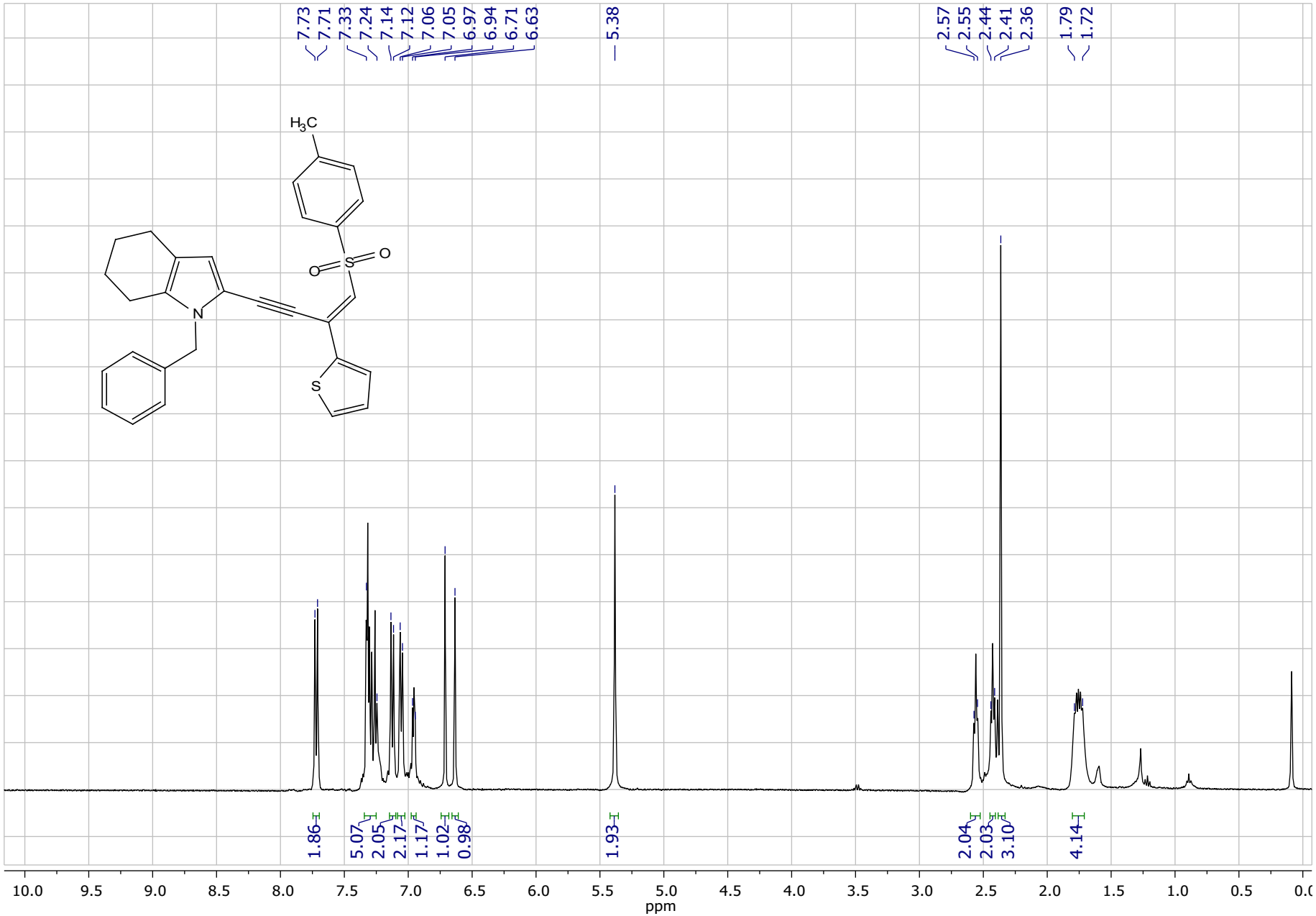
^{1}H NMR spectrum of (*E*)-1-benzyl-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2k**) in $CDCl_3$.



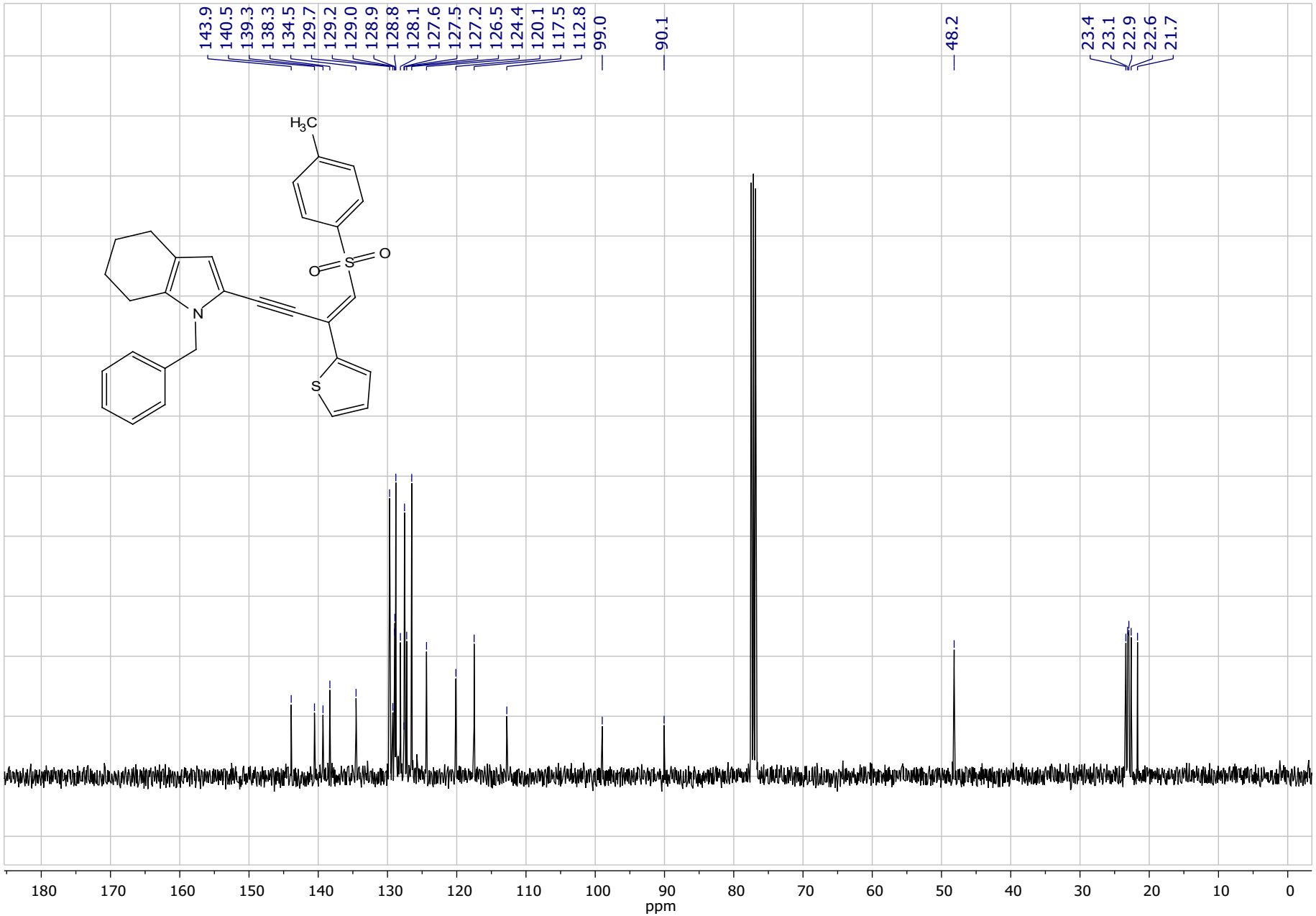
^{13}C NMR spectrum of (*E*)-1-benzyl-2-(3-(furan-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2k**) in $CDCl_3$.



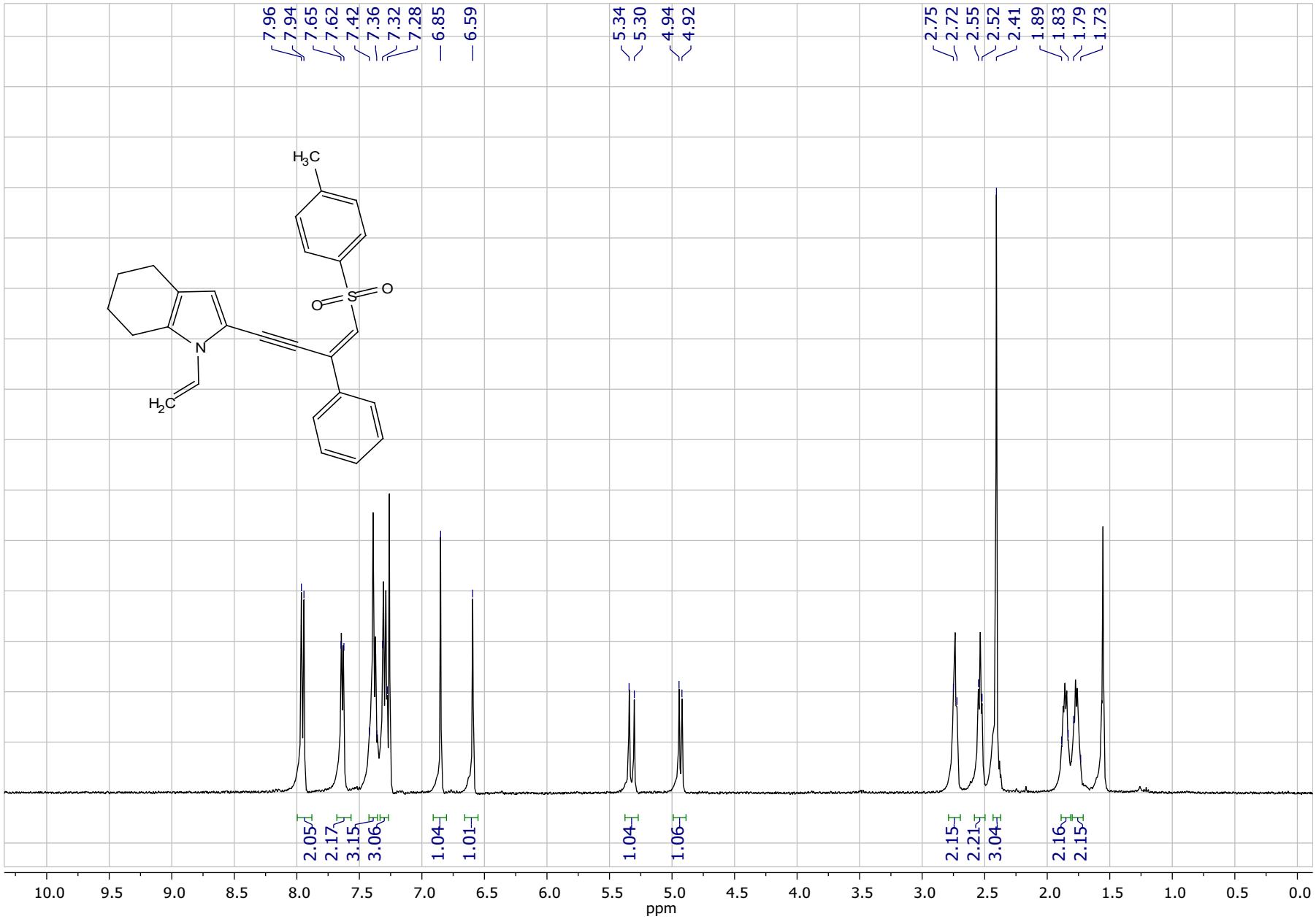
^{1}H NMR spectrum of (*E*)-1-benzyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**2l**) in $CDCl_3$.



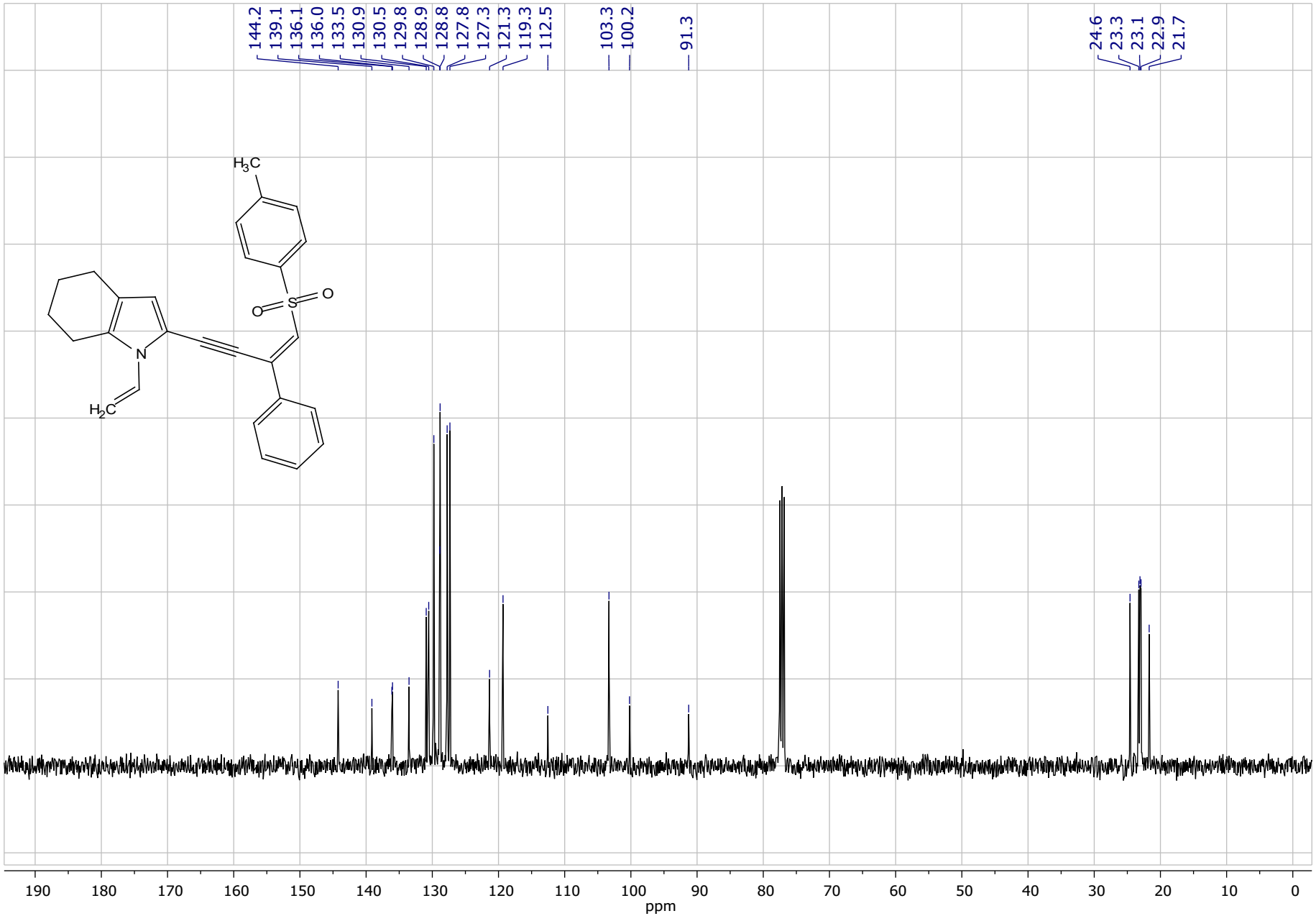
^{13}C NMR spectrum of (*E*)-1-benzyl-2-(3-(thiophen-2-yl)-4-tosylbut-3-en-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-indole (**21**) in $CDCl_3$.



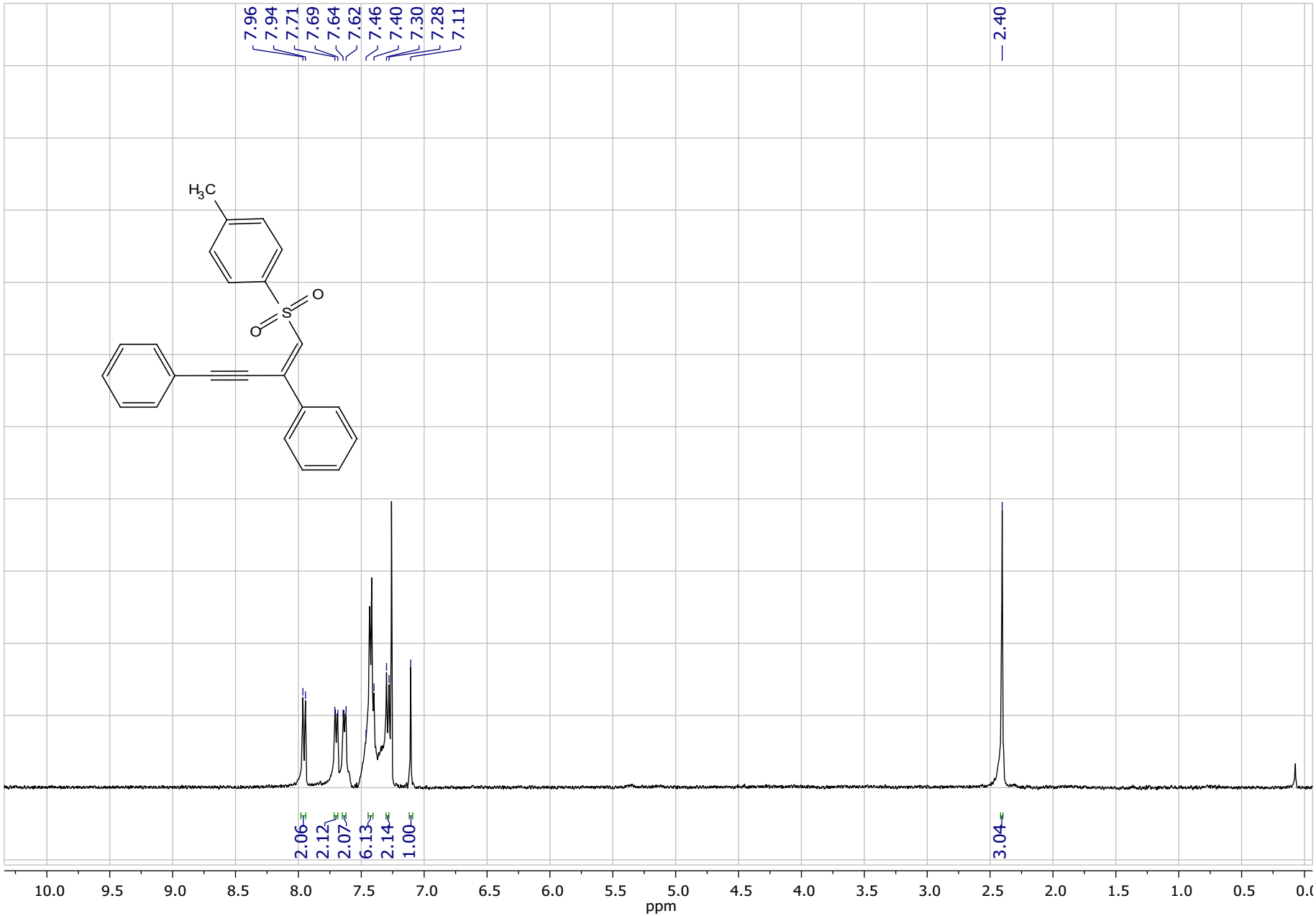
^{1}H NMR spectrum of (*Z*)-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (**2m**) in $CDCl_3$.



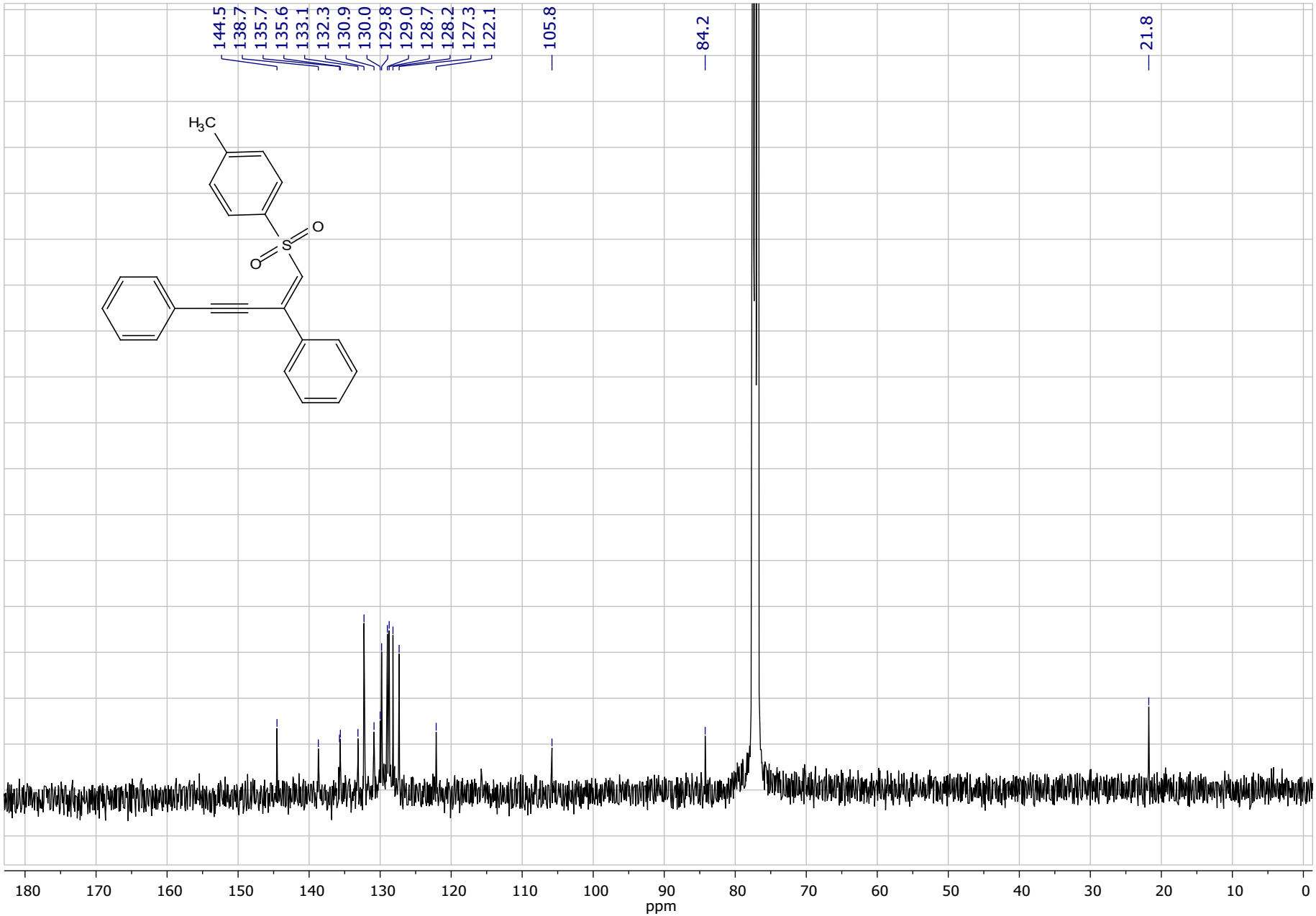
^{13}C NMR spectrum of (*Z*)-2-(3-phenyl-4-tosylbut-3-en-1-yn-1-yl)-1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (**2m**) in $CDCl_3$.



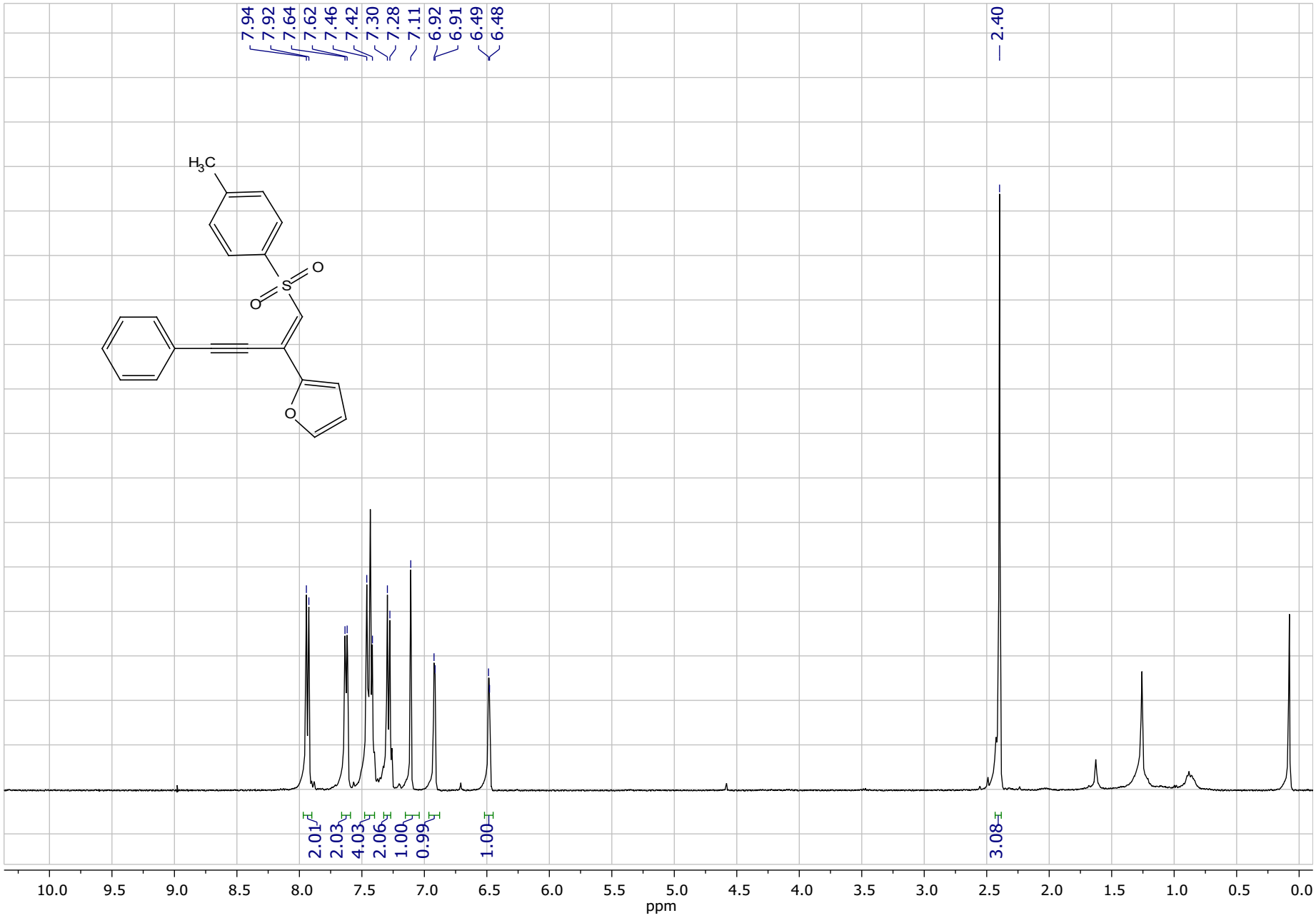
^{1}H NMR spectrum of (*Z*)-(4-tosylbut-3-en-1-yne-1,3-diyl)dibenzene (**2n**) in $CDCl_3$.



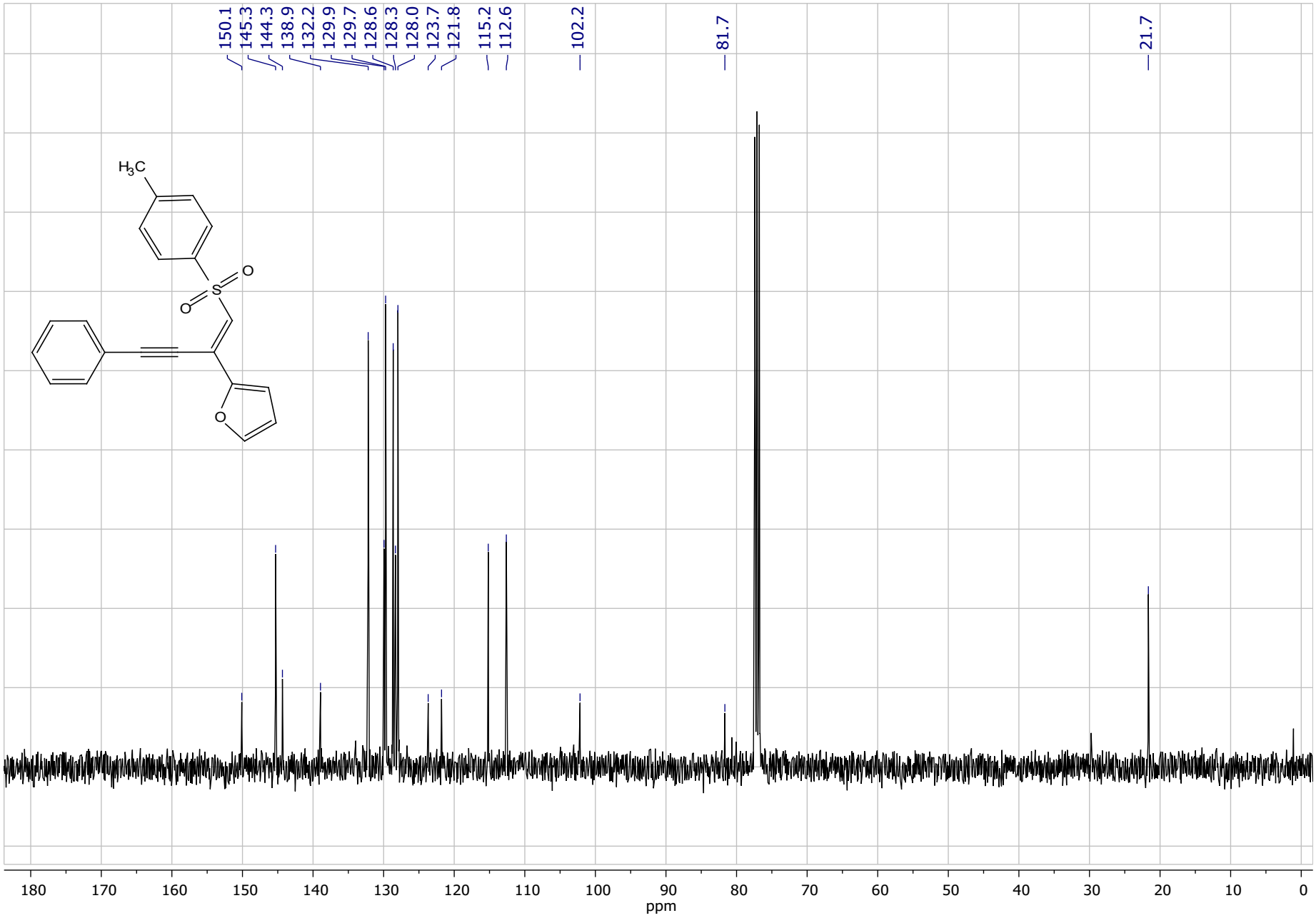
^{13}C NMR spectrum of (*Z*)-(4-tosylbut-3-en-1-yne-1,3-diyl)dibenzene (**2n**) in $CDCl_3$.



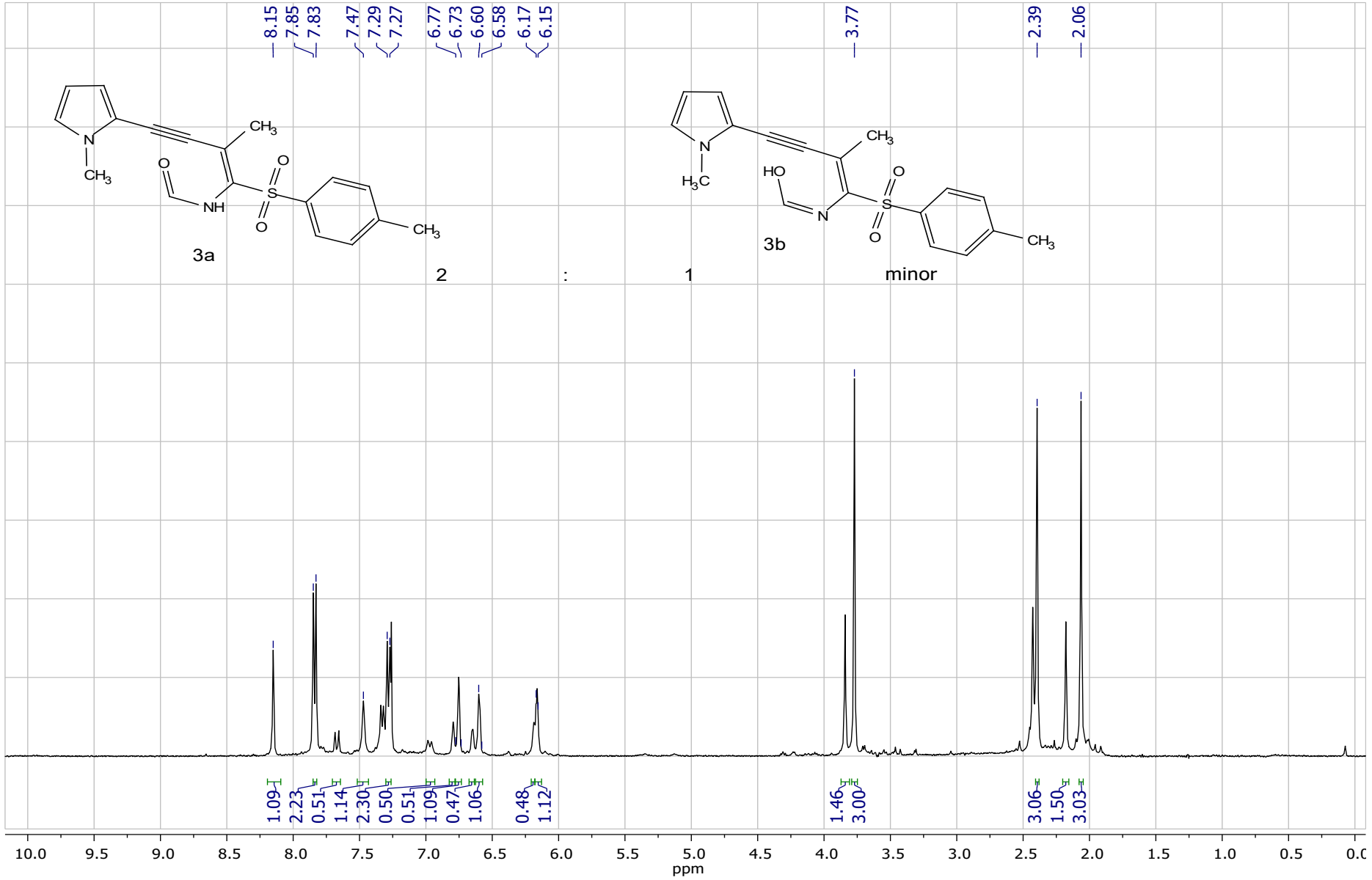
^{1}H NMR spectrum of (*E*)-2-(4-phenyl-1-tosylbut-1-en-3-yn-2-yl)furan (**2o**) in $CDCl_3$.



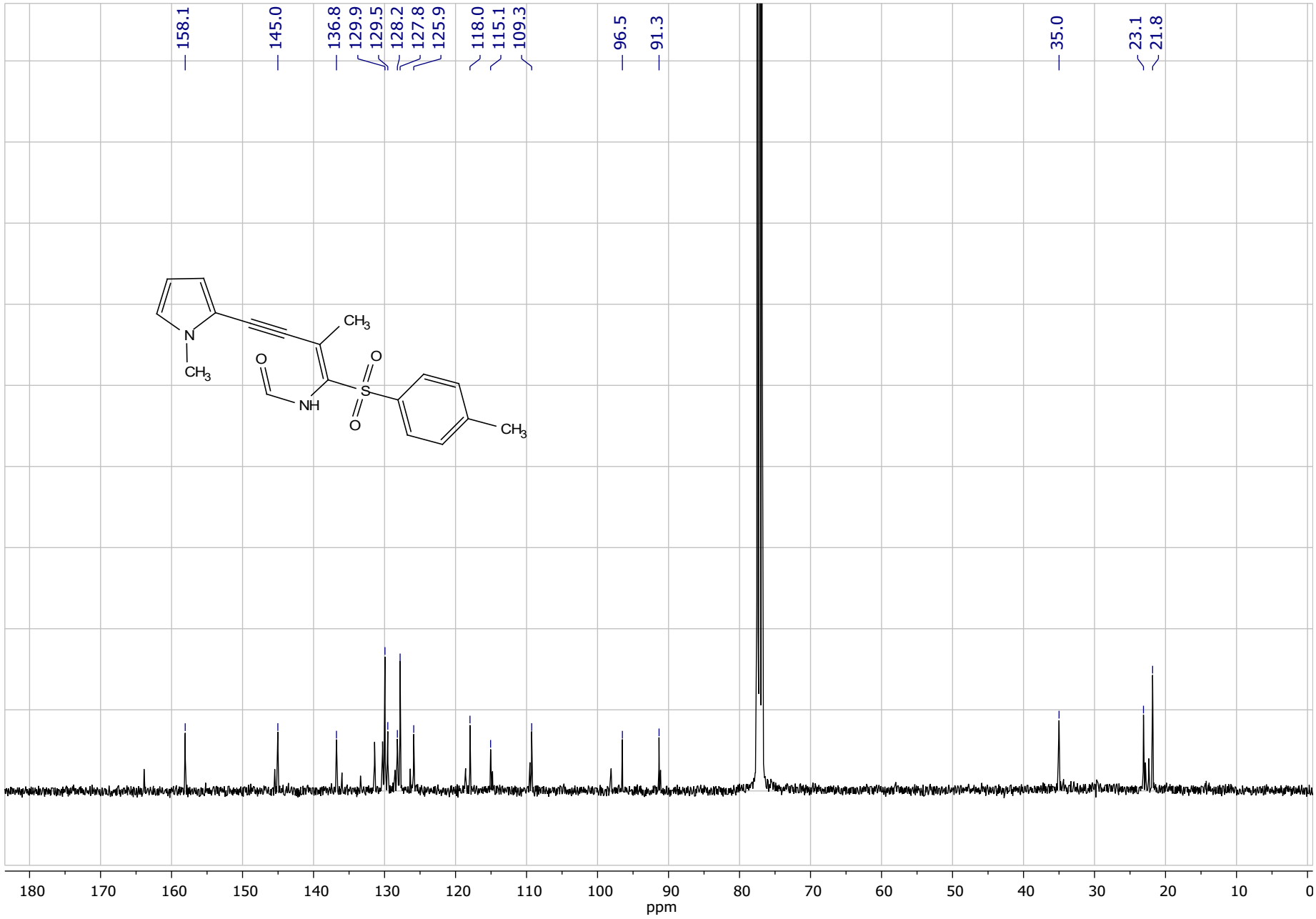
^{13}C NMR spectrum of (*E*)-2-(4-phenyl-1-tosylbut-1-en-3-yn-2-yl)furan (**2o**) in $CDCl_3$.



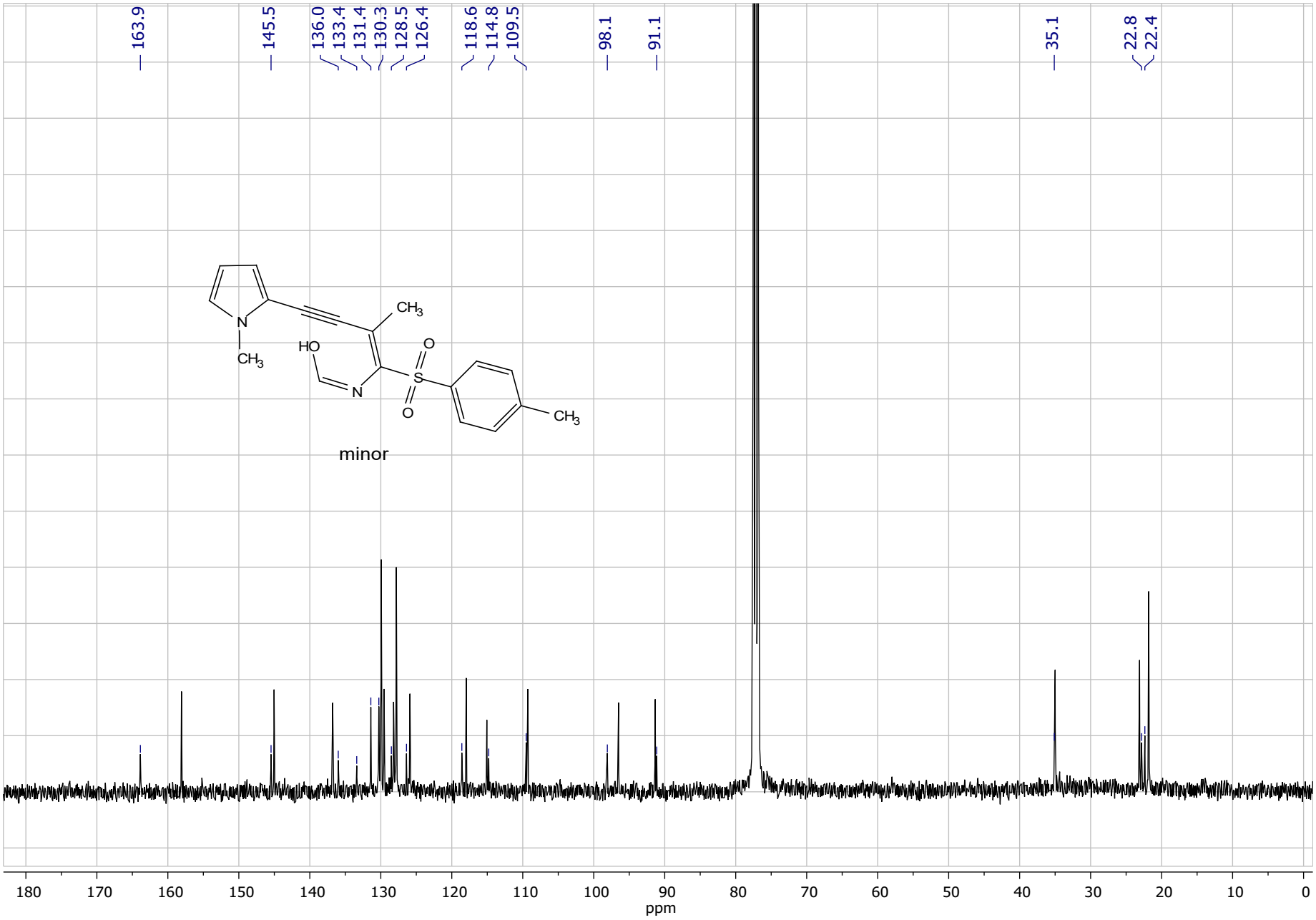
^{1}H NMR spectrum of (*E*)-N-(2-methyl-4-(1-methyl-1*H*-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formamide (**3a**) and (*Z*)-N-((*E*)-2-methyl-4-(1-methyl-1*H*-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formimidic acid (**3b**) in $CDCl_3$.



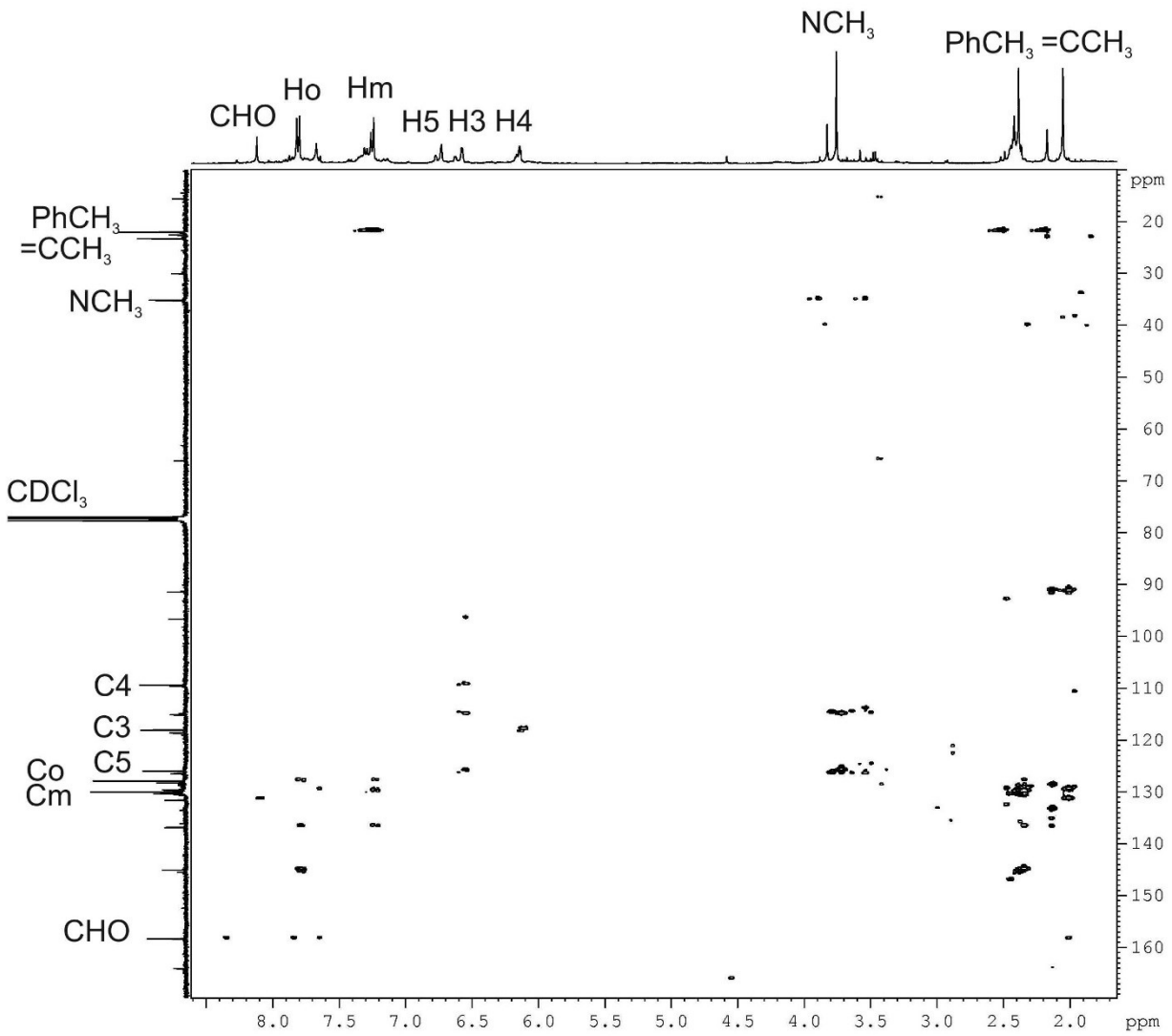
^{13}C NMR spectrum of (*E*)-N-(2-methyl-4-(1-methyl-1*H*-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formamide (**3a**) (in the mixture of **3a** and **3b**) in $CDCl_3$.



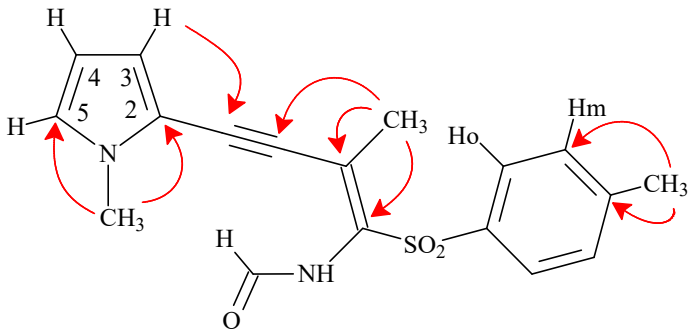
^{13}C NMR spectrum of (*Z*)-N-((*E*)-2-methyl-4-(1-methyl-1*H*-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formimidic acid (**3b**) (in the mixture of **3a** and **3b**) in $CDCl_3$.

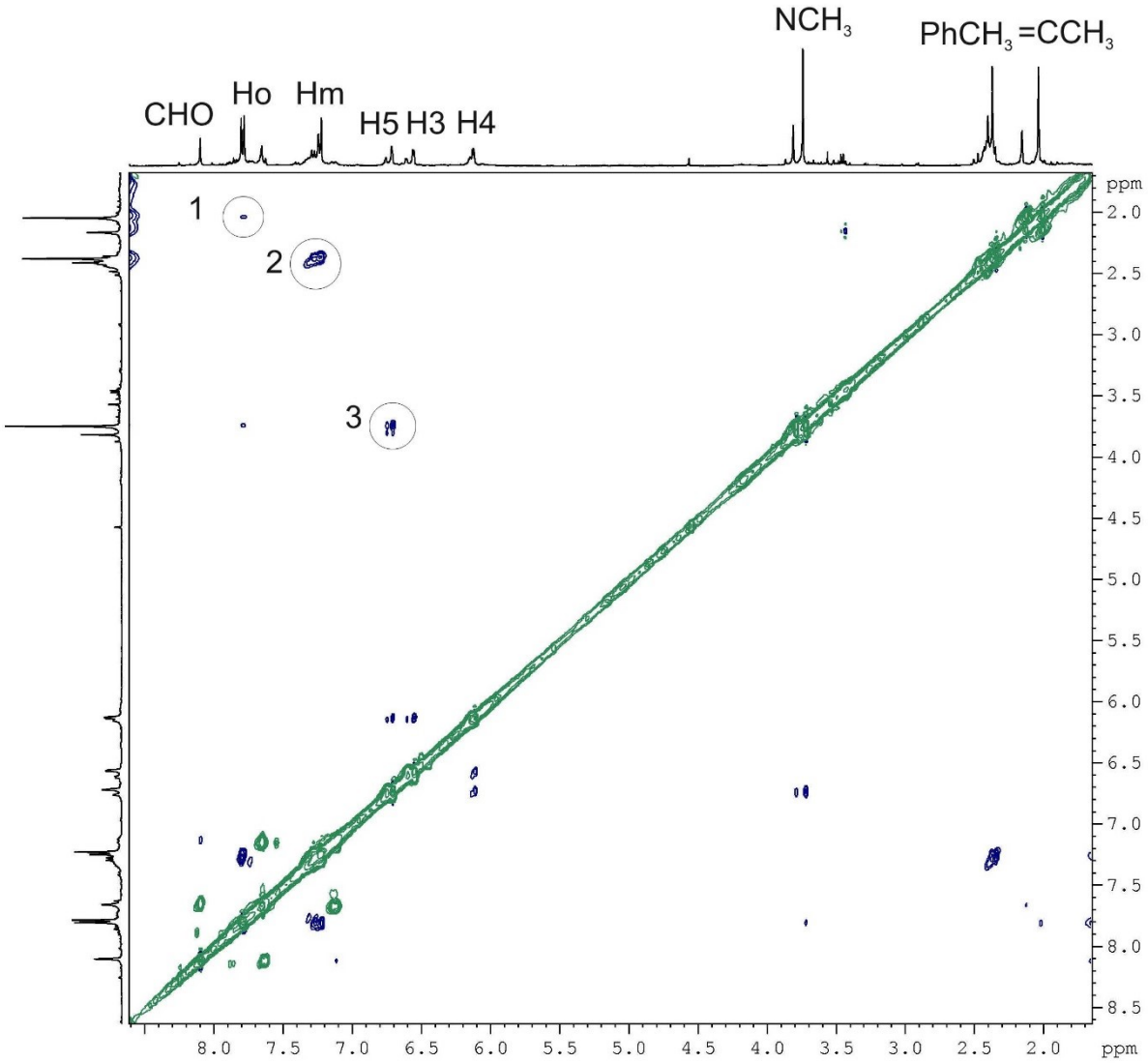


*2D NMR Spectra of (E)-N-(2-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formamide (**3a**) and (Z)-N-((E)-2-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1-tosylbut-1-en-3-yn-1-yl)formimidic acid in $CDCl_3$ (**3b**):*

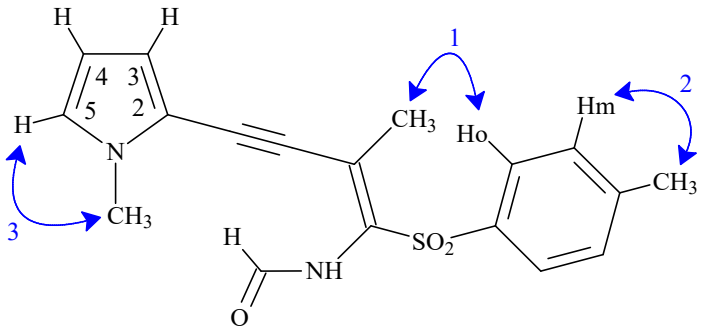


2D ^{1}H-^{13}C HMBC spectrum of mixture of **3a** and **3b** ($CDCl_3$), significant correlations observed in the spectrum are presented in the scheme below:

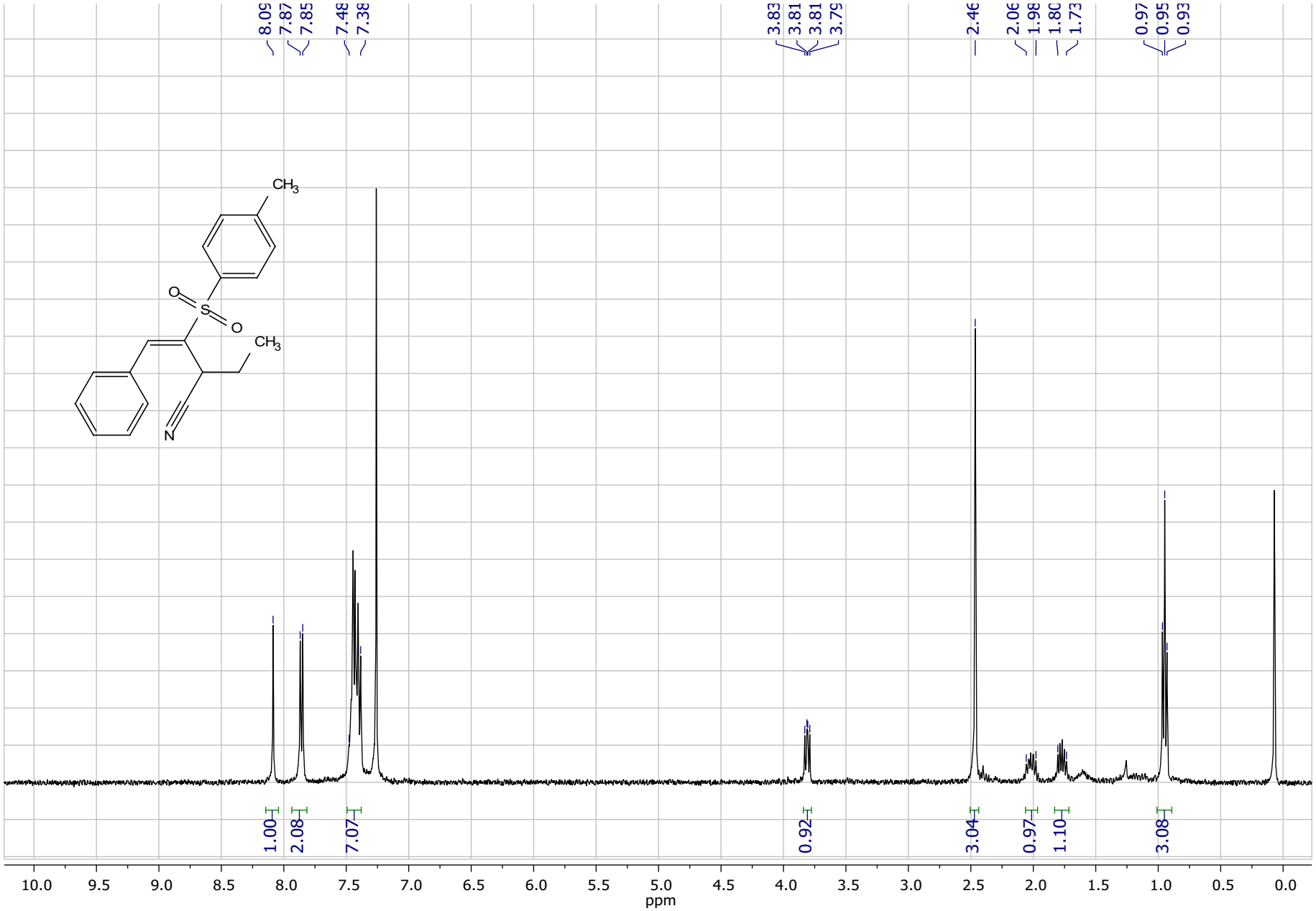

H
H
4
3
5
2
H
N
CH3
CH3
Ho
Hm
CH3
H
NH
SO2
O



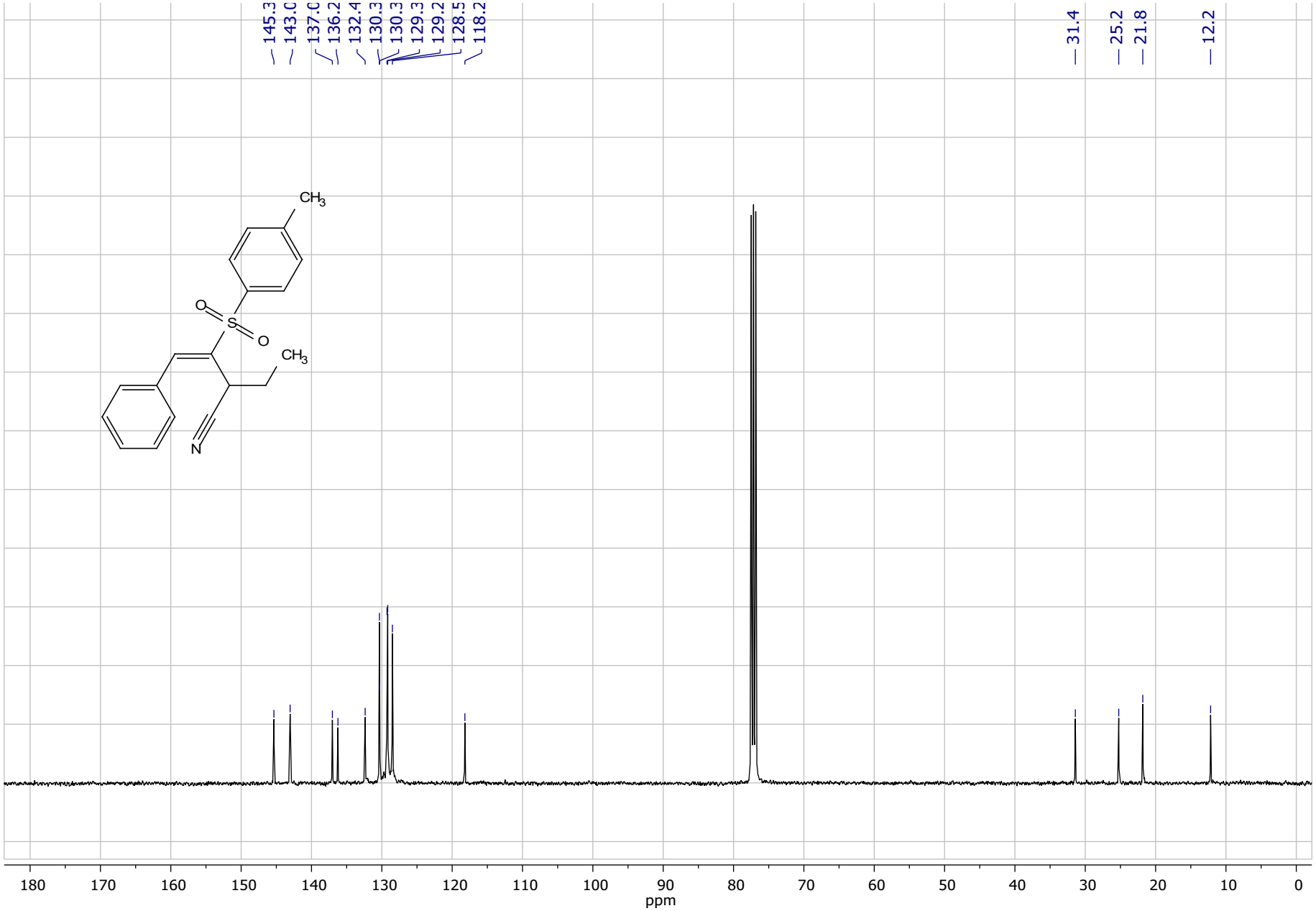
2D NOESY spectrum of mixture of **3a** and **3b** (400.1 MHz, $CDCl_3$), significant correlations observed in the spectrum are presented in the scheme below:


H
H
4
3
5
2
H
N
CH3
3
CH3
1
Ho
Hm
2
CH3
H
NH
SO2
O

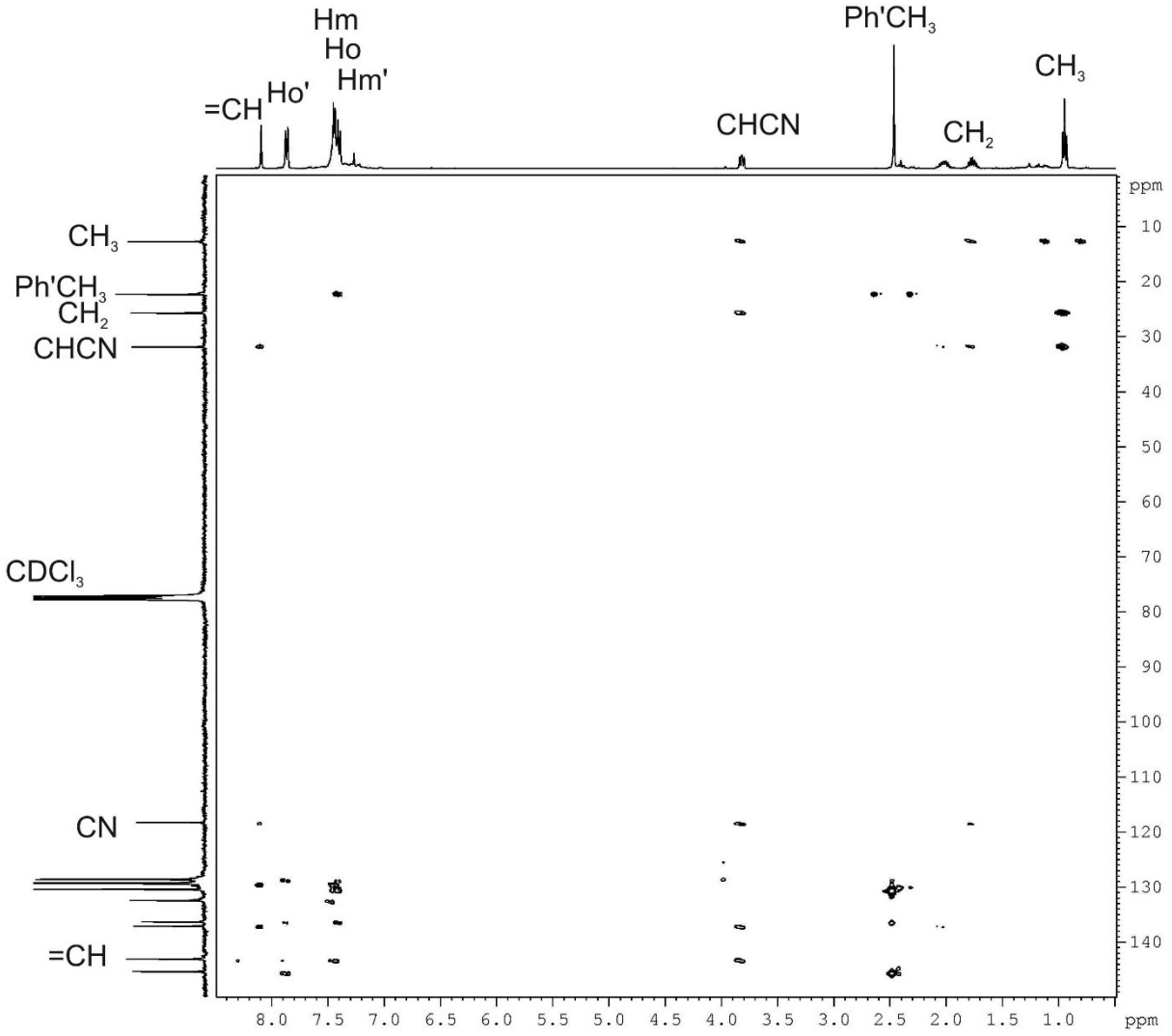
^{1}H NMR spectrum of (*E*)-2-ethyl-4-phenyl-3-tosylbut-3-enenitrile (**6**) in $CDCl_3$.



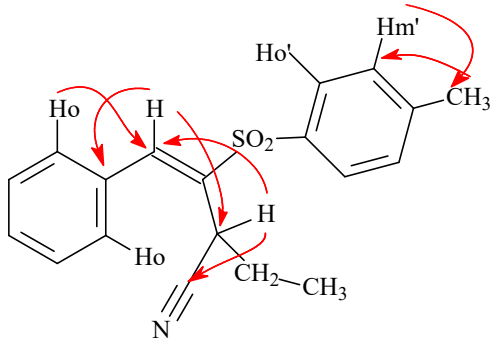
^{13}C NMR spectrum of (*E*)-2-ethyl-4-phenyl-3-tosylbut-3-enenitrile (**6**) in $CDCl_3$.

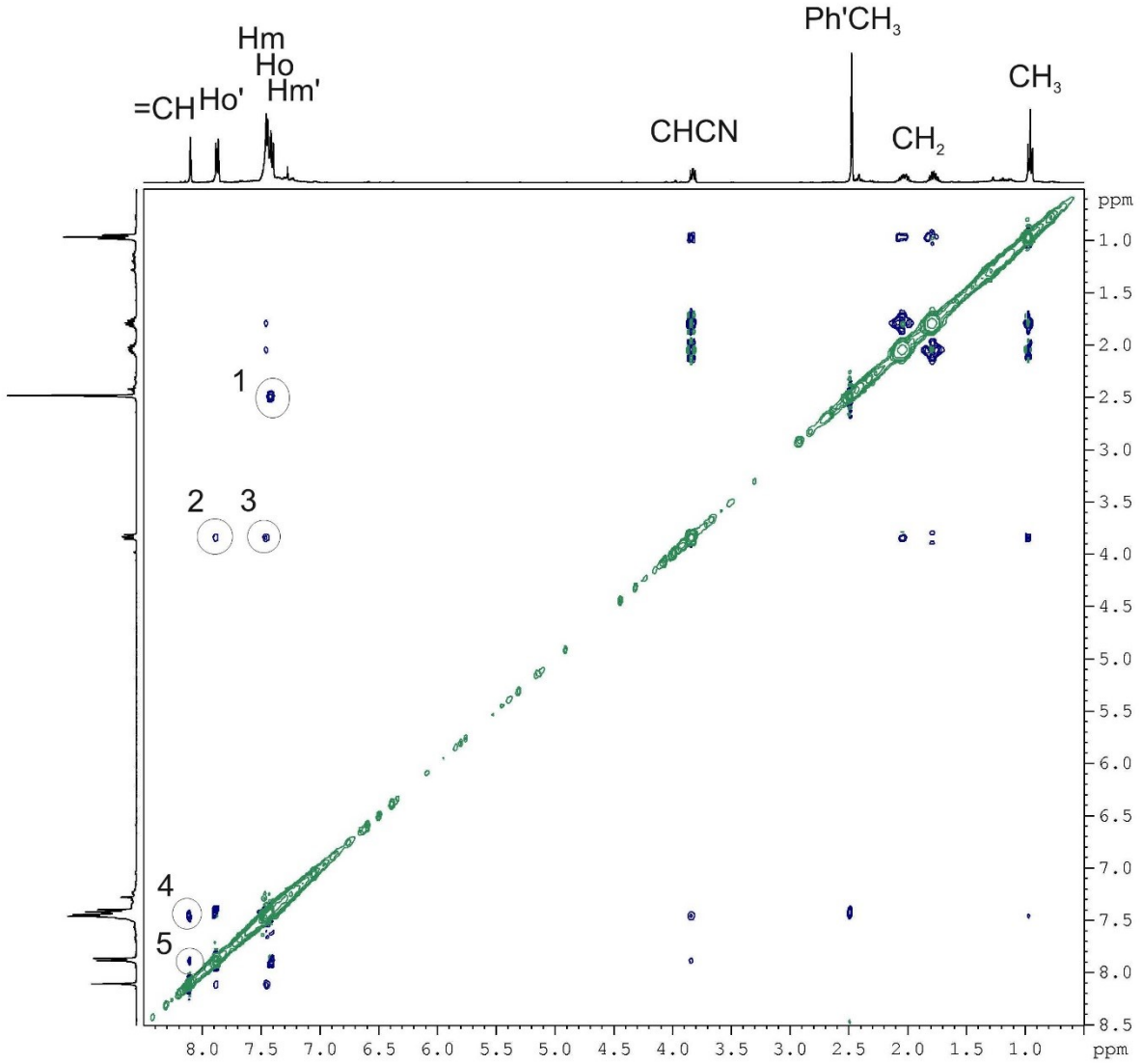


*2D NMR Spectra of(E)-2-Ethyl-4-phenyl-3-tosylbut-3-enenitrile in $CDCl_3$ (**6**)*

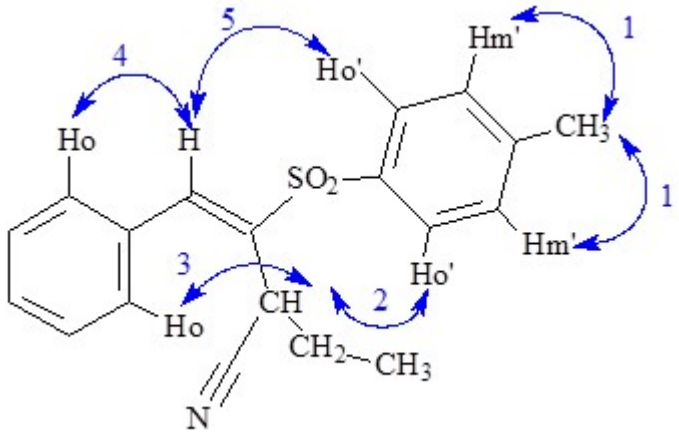


2D ^{1}H-^{13}C HMBC spectrum of **6** ($CDCl_3$), significant correlations observed in the spectrum are presented in the scheme below:


Hm'
Ho'
CH3
Ho
H
SO2
H
Ho
CH2
CH3
N



2D NOESY spectrum of **6** (400.1 MHz, $CDCl_3$), significant correlations observed in the spectrum are presented in the scheme below:


5
4
Ho'
Hm'
1
Ho
H
CH3
SO2
1
Hm'
3
Ho'
CH
2
Ho
CH2
CH3
N