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Acyl-tetrahydroindolyl-capped 1,3-diynes in oxidative [4+2]-cycloaddition with benzylamine: a one-pot access to 2-acyl-6-phenyl-5-tetrahydroindolyl-pyridines

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1. Materials and Methods

1.1. General Procedures

IR spectra were obtained on a "Bruker IFS-25" spectrometer (KBr pellets in 400-4000 cm^{-1} region). ^{1}H (400 MHz), ^{13}C (100 MHz), ^{15}N (41 MHz) NMR spectra were recorded on a "Bruker Avance 400" instrument in $CDCl_3$. 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. The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment. The ^{1}H chemical shifts (δ) were referenced to residual solvent: 7.26 ppm ($CDCl_3$) for ^{1}H, 77.10 ppm ($CDCl_3$) for ^{13}C and ^{15}N - $MeNO_2$ (0.0 ppm), respectively. Coupling constant(s) in hertz (Hz) were measured from one-dimensional spectra. The chemical shifts were recorded in ppm. Elemental analyses (C, H, N) were performed on an EA FLASH 1112 Series (CHN Analyzer) instrument. Melting points (uncorrected) were determined with melting point SMP3 (Stuart Scientific).

1.2. Synthetic Procedures

1-Acyl-4-tetrahydroindolyldiynes **1a-c,e** were obtained from 4,5,6,7-tetrahydro-1*H*-indoles and acyl(alkoxycarbonyl)-4-bromodiynes as reported [D. N. Tomilin, B. Pigulski, N. Gulia, A. Arendt, L. N. Sobenina, A. I. Mikhaleva, S. Szafert and B. A. Trofimov, *RSC Advances*, 2015, 73241].

1.2.1. Synthesis of 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpenta-2,4-diyn-1-one (1d). 1-Methyl-4,5,6,7-tetrahydro-1*H*-indole (1.0 mmol, 0.135 g) and 5-bromo-1-phenylpenta-2,4-diyn-1-one (1.1 mmol, 0.256 g) were grounded at room temperature with K_2CO_3 (3.91 g, 10-fold amount by weight) in a mortar for 10 min, the reaction mixture turned yellow. After 1 h, the mixture was placed on the column with silica gel and eluted with mixture of *n*-hexane and diethyl ether (5/1; v/v) to afford pure 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpenta-2,4-diyn-1-one as yellow crystals (0.118 g, yield 41%), mp 112-115 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.16-8.14 (m, 2H, Ph), 7.63-7.60 (m, 1H, Ph), 7.52-7.48 (m, 2H, Ph), 6.53 (s, 1H, H-pyrrole), 3.55 (s, 3H, NMe), 2.56-2.53 (m, 2H, CH_2-4), 2.50-2.47 (m, 2H, CH_2-7), 1.88-1.82 (m, 2H, CH_2-5), 1.76-1.70 (m, 2H, CH_2-6).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 176.9, 136.9, 135.3, 134.1, 129.5 (2C), 128.6 (2C), 119.3, 118.9, 111.5, 83.5, 81.8, 80.2, 79.8, 31.2, 23.2, 22.9, 22.8, 22.5.

IR (KBr): 2926, 2163, 1627, 1468, 1361, 1279, 1209, 911, 791, 695 cm^{-1}.

Anal. Calcd for $C_{20}H_{17}NO$ (287.36): C 83.59, H 5.96, N 4.87%. Found: C 83.48, H 5.91, N 4.78%.

1.2.2. The reaction of 1-acyl(alkoxycarbonyl)-4-tetrahydroindolyldiynes 1a-d with benzylamine in the KOH/DMSO system

A. A mixture of methyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-yl)penta-2,4-diynoate **1a** (241 mg, 1 mmol), $KOH·0.5H_2O$ (20 mg, 0.30 mmol) and benzylamine (161 mg, 1.50 mmol) in DMSO (2.5 ml) were heated at 80 ºC for 4 h. After cooling to room temperature, the reaction mixture was diluted with brine (5 ml), extracted with diethyl ether (5×3-5 ml). The ether extracts were washed with water (5×5 ml) and dried over K_2CO_3. The residue after removing solvent was fractionated by column chromatography (SiO_2) to give (eluent – *n*-hexane) enoate **4a**, then (eluent – *n*-hexane-diethyl ether, 9:1) pyridine **2a** and (eluent – *n*-hexane-diethyl ether, 5:1) pyridine **3a**. Re-cleaning of products by preparative thin-layer chromatography (SiO_2, *n*-hexane-diethyl ether, 1:1) gave 35 mg (10%) of enoate **4a**, 142 mg (41%) of pyridine **2a** and 21 mg (5%) of pyridine **3a**.

Methyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinate **2a**, yellow crystals, mp 113-115 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.1 Hz, 1H, H-3 pyridine), 7.84 (d, *J* = 8.1 Hz, 1H, H-4 pyridine), 7.44-7.41 (m, 2H, Ph), 7.25-7.23 (m, 3H, Ph), 6.01 (s, 1H, H-3 pyrrole), 3.99 (s, 3H, COMe), 2.59 (s, 3H, NMe), 2.54-2.50 (m, 2H, CH_2-4), 2.34-2.31 (m, 2H, CH_2-7), 1.79-1.78 (m, 2H, CH_2-5), 1.73-1.71 (m, 2H, CH_2-6).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 166.1, 156.7, 146.3, 140.5, 140.0, 131.4, 130.5, 129.0 (3C), 128.4, 128.2 (2C), 123.3, 118.1, 109.1, 52.9, 30.5, 23.7, 23.3, 23.1, 22.1.

^{15}N NMR (40.5 MHz, $CDCl_3$) δ: -238.4 (NMe), -68.4 (N).

IR (film): 2921, 2851, 1950, 1717, 1555, 1439, 1318, 1212, 1144, 1077, 860, 742, 699, 625 cm^{-1}.

Anal. Calcd for $C_{22}H_{22}N_2O_2$ (346.43): C 76.28, H 6.40, N 8.09%. Found: C 76.01, H 6.13, N 7.88%.

N-Benzyl-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinamide **3a**, yellow crystals, mp 124-125 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.50 (t, *J* = 6.4 Hz, 1H, NH), 8.19 (d, *J* = 7.9 Hz, 1H, H-3 pyridine), 7.91 (d, *J* = 7.9 Hz, 1H, H-4 pyridine), 7.40-7.28 (m, 10H, 2Ph), 6.02 (s, 1H, H-pyrrole), 4.72 (d, *J* = 6.4 Hz, 2H, C$\underline{H_2}$-Ph), 2.63 (s, 3H, NMe), 2.57-2.53 (m, 2H, CH_2-4), 2.37-2.34 (m, 2H, CH_2-7), 1.86-1.80 (m, 2H, CH_2-5), 1.78-1.74 (m, 2H, CH_2-6).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 164.5, 155.1, 148.2, 141.1, 140.0, 138.6, 130.8, 130.3, 129.1, 128.9 (2C), 128.8 (2C), 128.4, 128.2 (2C), 127.8 (2C), 127.5, 120.7, 118.1, 108.9, 43.4, 30.4, 23.7, 23.3, 23.1, 22.1.

IR (film): 3293, 2925, 2851, 1651, 1520, 1449, 1364, 1231, 1161, 980, 780, 696 cm^{-1}.

Anal. Calcd for $C_{28}H_{27}N_3O$ (421.54): C 79.78, H 6.46, N 9.97%. Found: C 79.61, H 6.40, N 9.94%.

Methyl (*Z*)-3-benzylamino-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)pent-2-en-4-ynoate **4a**, yellow solid, mp 114-115 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.67 (t, *J* = 6.4 Hz, 1H, NH), 7.35-7.30 (m, 4H, Ph), 7.27-7.24 (m, 1H, Ph), 6.31 (s, 1H, H-3 pyrrole), 4.95 (s, 1H, =CH), 4.64 (d, *J* = 6.4 Hz, 2H, C$\underline{H_2}$-Ph), 3.66 (s, 3H, CO_2Me), 3.38 (s, 3H, NMe), 2.51-2.45 (m, 4H, CH_2-4,7), 1.85-1.79 (m, 2H, CH_2-5), 1.74-1.68 (m, 2H, CH_2-6).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 170.6, 146.2, 139.1, 133.1, 128.7 (2C), 127.4, 127.1 (2C), 118.7, 115.5, 111.7, 89.7, 88.4, 86.9, 50.4, 48.9, 30.9, 23.4, 23.0, 22.9, 22.4.

IR (KBr): 3305, 3031, 2936, 2846, 2190, 1641, 1576, 1554, 1293, 1168, 1032, 778, 696, 522 cm^{-1}.

Anal. Calcd for $C_{22}H_{24}N_2O_2$ (348.45): C 75.83, H 6.94, N 8.04%. Found: C 75.58, H 6.76, N 7.95%.

B. Analogously, from ethyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)penta-2,4-diynoate **1b** (255 mg, 1 mmol), KOH·0.5H_2O (20 mg, 0.30 mmol) and benzylamine (161 mg, 1.50 mmol) after column and preparative thin-layer chromatography ethyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinate **2b** (151 mg, 42%) was isolated as yellow solid, mp 58-60 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.1 Hz, 1H, H-3 pyridine), 7.86 (d, *J* = 8.1 Hz, 1H, H-4 pyridine), 7.49-7.46 (m, 2H, Ph), 7.30-7.27 (m, 3H, Ph), 6.04 (s, 1H, H-3 pyrrole), 4.51-4.46 (m, 2H, CH_2), 2.62 (s, 3H, NMe), 2.57-2.54 (m, 2H, CH_2-4), 2.37-2.34 (m, 2H, CH_2-7), 1.86-1.80 (m, 2H, CH_2-5), 1.78-1.74 (m, 2H, CH_2-6), 1.46 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 165.5, 156.8, 146.7, 140.4, 140.1, 131.1, 130.4, 129.1 (2C), 129.0, 128.4, 128.1 (2C), 123.1, 118.1, 109.0, 61.8, 30.4, 23.7, 23.3, 23.1, 22.1, 14.4.

IR (film): 2929, 2849, 1953, 1714, 1556, 1447, 1307, 1210, 1140, 1015, 861, 743, 698, 626 cm^{-1}.

Anal. Calcd for $C_{23}H_{24}N_2O_2$ (360.46): C 76.64, H 6.71, N 7.77%. Found: C 76.31, H 6.33, N 7.88%.

C. Analogously, from ethyl 5-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)penta-2,4-diynoate **1c** (267 mg, 1 mmol), KOH·0.5H_2O (20 mg, 0.30 mmol) and benzylamine (151 mg, 1.50 mmol) after column (SiO_2, *n*-hexane-diethyl ether, 9:1) and preparative thin-layer (SiO_2, *n*-hexane-diethyl ether, 1:1) ethyl 6-phenyl-5-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)picolinate **2c** (149 mg, 40%) was isolated as yellow crystals, mp 86-88 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 7.9 Hz, 1H, H-3 pyridine), 7.87 (d, *J* = 7.9 Hz, 1H, H-4 pyridine), 7.41-7.38 (m, 2H, Ph), 7.26-7.23 (m, 3H, Ph), 6.08-6.02 (m, 2H, H-3 pyrrole, H_X), 4.51-4.46 (m, 2H, CH_2), 4.39-4.35 (m, 2H, H_B, H_A), 2.54-2.47 (m, 4H, CH_2-4,7), 1.82-1.75 (m, 4H, CH_2-5,6), 1.47-1.44 (m, 3H, CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 165.5, 157.2, 146.7, 139.9, 139.8, 131.2, 130.1, 129.8, 129.3 (2C), 128.4, 128.2, 127.8 (2C), 123.0, 119.6, 112.0, 104.6, 61.8, 23.4 (2C), 23.3, 23.1, 14.4.

IR (film): 2929, 2850, 1951, 1716, 1642, 1558, 1432, 1304, 1213, 1140, 1019, 864, 735, 698 cm^{-1}.

Anal. Calcd for $C_{24}H_{24}N_2O_2$ (372.47): C 77.39, H 6.50, N 7.52%. Found: C 77.25, H 6.38, N 7.44%.

D. Analogously, from 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpenta-2,4-diyn-1-one **1d** (287 mg, 1 mmol), KOH·0.5H_2O (20 mg, 0.30 mmol) and benzylamine (151 mg, 1.50 mmol) after column chromatography (SiO_2, *n*-hexane) (Z)-3-(benzylamino)-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpent-2-en-4-yn-1-one **4d** and (SiO_2, *n*-hexane-diethyl ether, 9:1) [5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpyridin-2-yl](phenyl)-methanone **2d** were isolated. After re-purification by preparative thin-layer chromatography (SiO_2, *n*-hexane-diethyl ether, 1:1) pyridine **2d** was isolated in low yield (8%) and ~ 80% purity. Enone **4d** was isolated as yellow oil in 17% yield.

[5-(1-Methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpyridin-2-yl](phenyl)methanone **2d**.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.27-8.25 (m, 2H, Ph), 8.03 (d, *J* = 8.0 Hz, 1H, H-3 pyridine), 7.93 (d, *J* = 8.0 Hz, 1H, H-4 pyridine), 7.61-7.58 (m, 1H, Ph), 7.51-7.43 (m, 4H, Ph), 7.30-7.26 (m, 3H, Ph), 6.07 (s, 1H, H-pyrrole), 2.68 (s, 3H, NMe), 2.59-2.56 (m, 2H, CH_2-4), 2.41-2.37 (m, 2H, CH_2-7), 1.88-1.82 (m, 2H, CH_2-5), 1.80-1.74 (m, 2H, CH_2-6).

(*Z*)-3-Benzylamino-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpent-2-en-4-yn-1-one **4d**, yield 67 mg (17%), yellow oil.

^{1} H NMR (400.13 MHz, $CDCl_3$) δ: 11.60 (t, *J* = 6.4 Hz, 1H, NH), 7.86-7.84 (m, 2H, Ph), 7.40-7.33 (m, 3H, Ph), 7.30-7.26 (m, 2H, Ph), 7.22-7.19 (m, 3H, Ph), 6.08 (s, 1H, H-pyrrole), 5.82 (s, 1H, =CH), 4.49 (d, *J* = 6.4 Hz, 2H, C$\underline{H_2}$-Ph), 3.39 (s, 3H, NMe), 2.53-2.49 (m, 2H, CH_2-4), 2.48-2.45 (m, 2H, CH_2-7), 1.86-1.80 (m, 2H, CH_2-5), 1.74-1.68 (m, 2H, CH_2-6).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 187.9, 158.6, 140.4, 138.7, 132.2, 130.6, 128.7 (2C), 128.2 (2C), 127.3, 127.1 (2C), 127.0 (2C), 125.2, 117.9, 110.2, 94.6, 48.7, 31.3, 23.5, 23.1, 23.0, 22.2.

IR (film): 3191, 3029, 2927, 2850, 1956, 1592, 1455, 1388, 1286, 1056, 1024, 760, 695, 593 cm^{-1}.

Anal. Calcd for $C_{27}H_{26}N_2O$ (394.52): C 82.20, H 6.64, N 7.10%. Found: C 82.12, H 6.59, N 7.05%.

1.2.3. Synthesis of methyl (*E*)-5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-(benzylamino)pent-2-en-4-ynoate 5

A. Benzylamine (129 mg, 1.2 mmol) was added to a solution of methyl 5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)penta-2,4-diynoate **1e** (317 mg, 1 mmol) in MeOH (3 ml). The reaction mixture was refluxed in methanol for 12 h. The solvent was evaporated and the residue was fractionated by column chromatography (SiO_2, *n*-hexane-diethyl ether, 9:1) to give of compound **5** (170 mg, 40%) as yellow oil.

B. Benzylamine (214 mg, 2 mmol) was added to a solution of methyl 5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)penta-2,4-diynoate **1e** (317 mg, 1 mmol) and DABCO (112 mg, 1 mmol) in MeCN (12 ml). The reaction mixture was refluxed for 2 h and, after cooling to room temperature, was diluted with brine (15 ml) and extracted with diethyl ether (5×5 ml). The ether extracts were washed with water (5×5 ml) and dried over K_2CO_3. After removing the solvent, the residue was fractionated by column chromatography (SiO_2, *n*-hexane-diethyl ether, 9:1) to give enoate **5** (166 mg, 39%) as yellow oil.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 7.33-7.22 (m, 8H, 2Ph), 7.04-7.02 (m, 2H, Ph), 6.23 (s, 1H, H-pyrrole), 5.75 (s, 1H, =CH), 5.04-5.01 (m, 3H, N-C$\underline{H_2}$-Ph, NH), 4.74 (d, *J* = 5.9 Hz, 2H, C$\underline{H_2}$-Ph), 3.80 (s, 3H, CO_2Me), 2.52-2.49 (m, 2H, CH_2-4), 2.40-2.37 (m, 2H, CH_2-7), 1.77-1.71 (m, 4H, CH_2-5,6).

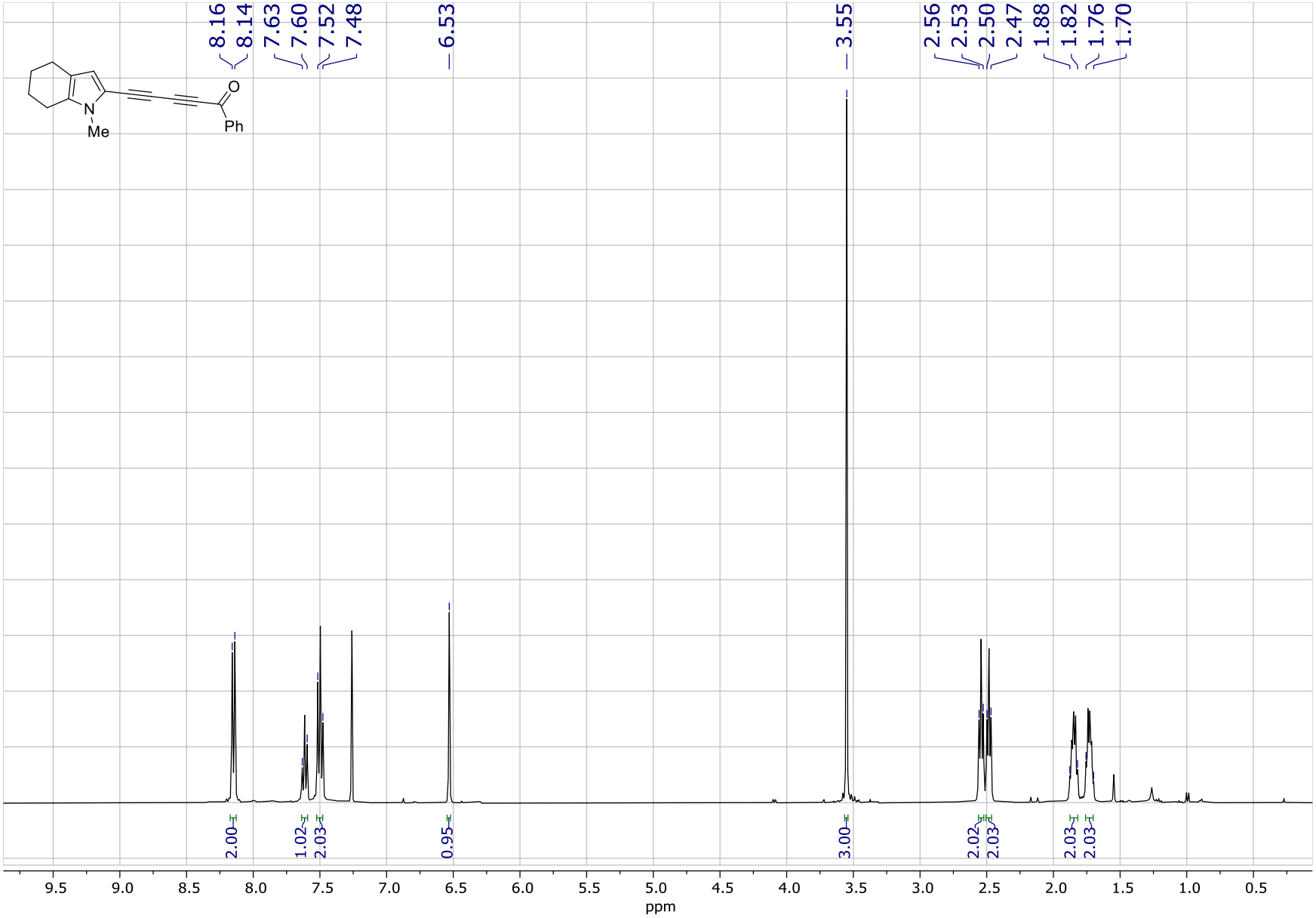
^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 165.5, 139.7, 138.6, 138.3, 131.0, 128.7 (2C), 128.6 (2C), 127.8 (2C), 127.3, 127.2, 126.5 (2C), 118.5, 114.6, 113.0, 91.1, 90.4, 85.5, 52.8, 48.6, 47.9, 23.5, 23.1, 23.0, 22.4. ^{15}N NMR (40.5 MHz, $CDCl_3$) δ: -303.4 (NH), -223.2 (NBn).

IR (KBr): 3424, 2928, 2851, 2165, 1704, 1635, 1437, 1377, 1254, 731, 697 cm^{-1}.

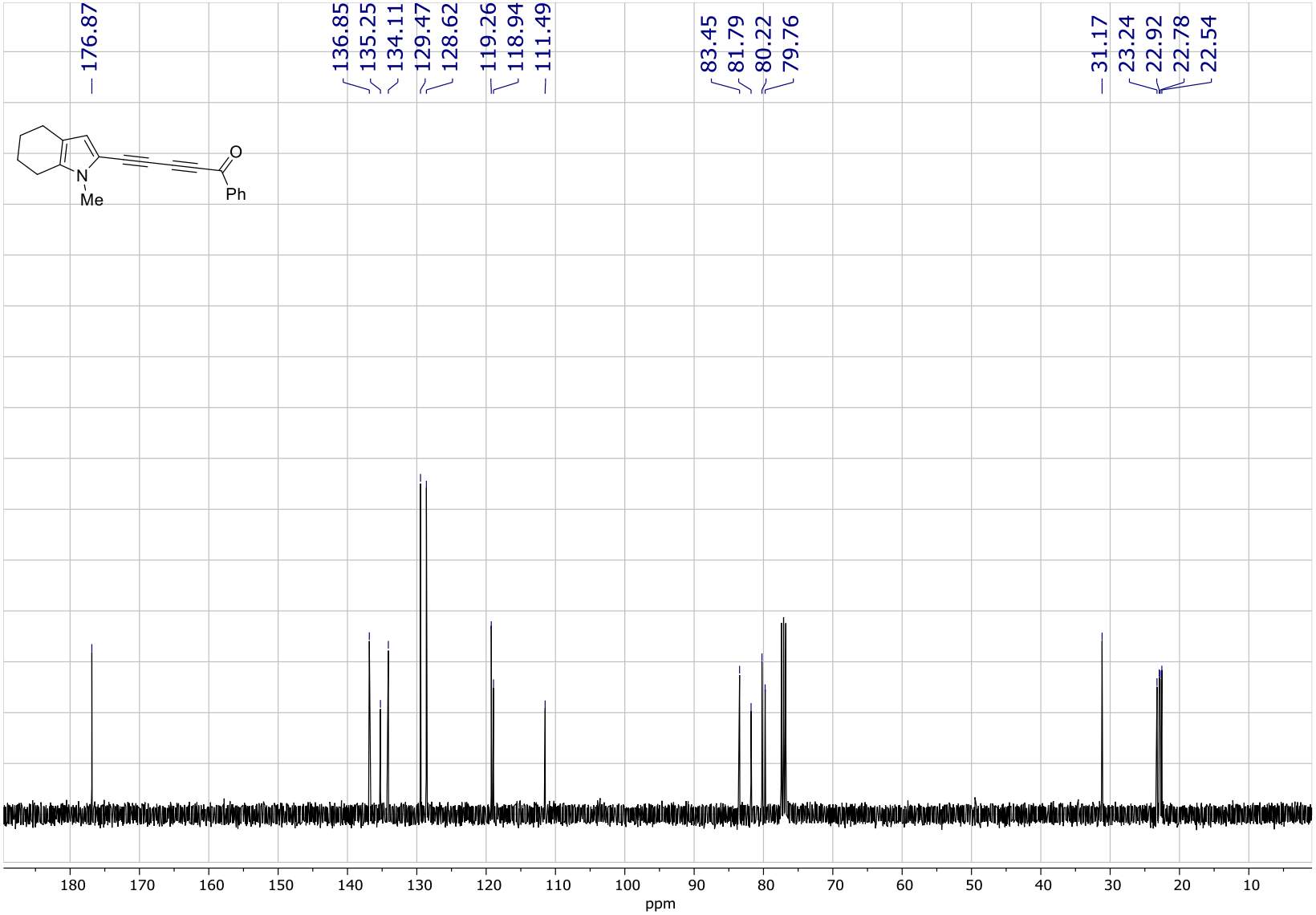
Anal. Calcd for $C_{28}H_{28}N_2O_2$ (424.54): C 79.22, H 6.65, N 6.60%. Found: C 79.07, H 6.52, N 6.24%.

3. Copies of ^{1}H and ^{13}C NMR spectra

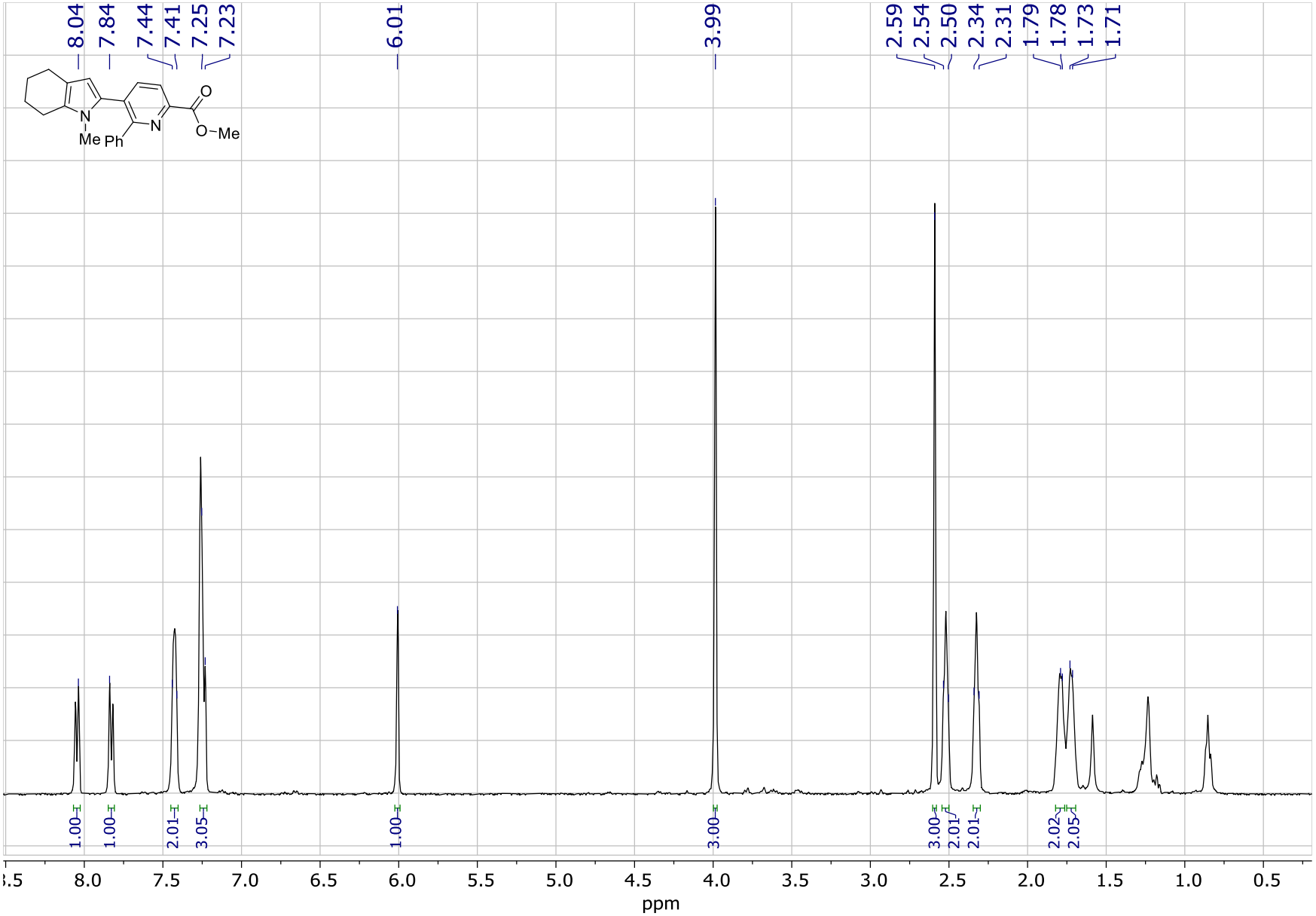
^{1}H NMR spectrum of 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpenta-2,4-diyn-1-one **(1d)** ($CDCl_3$).



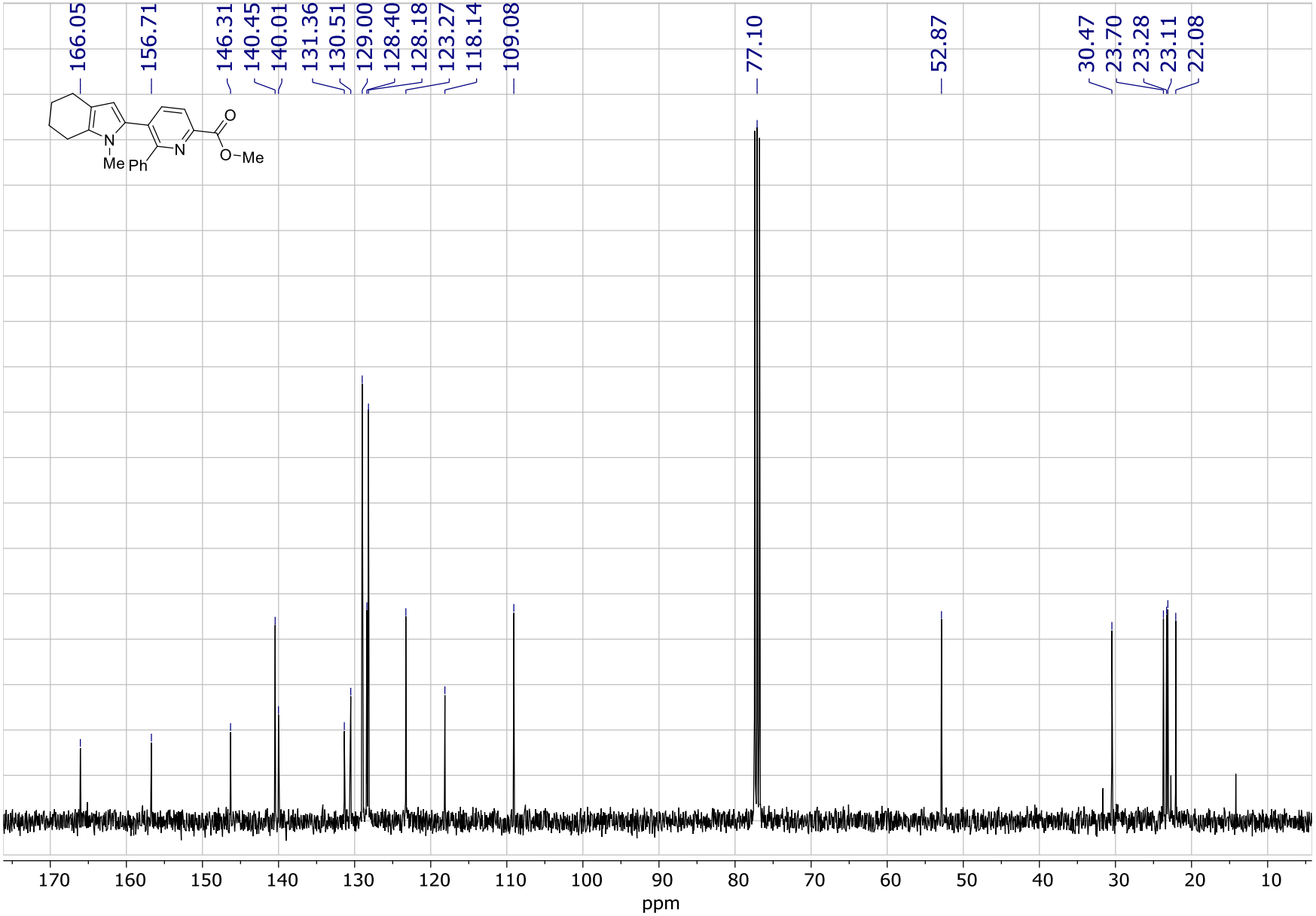
^{13}C NMR spectrum of 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpenta-2,4-diyn-1-one **(1d)** ($CDCl_3$).



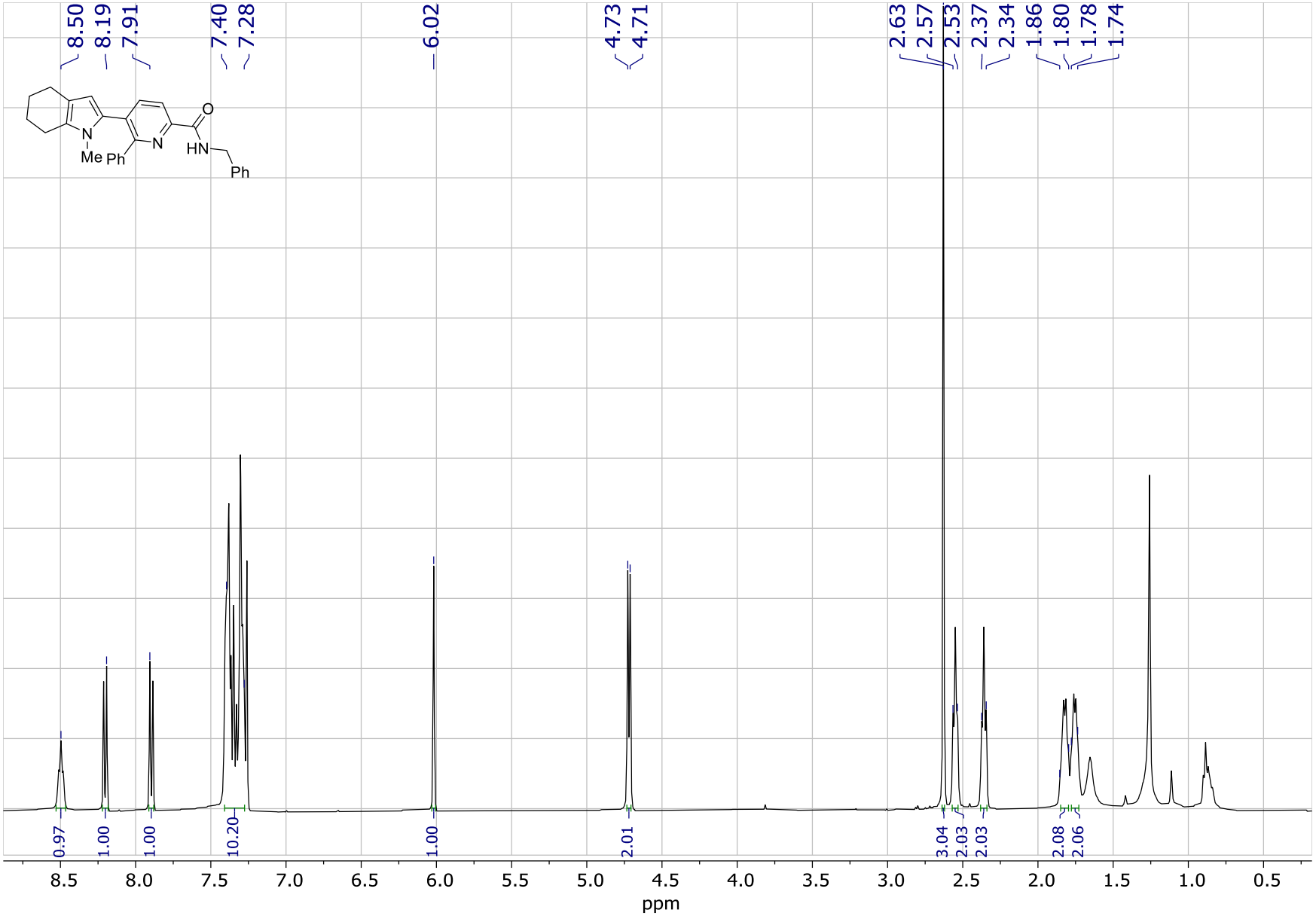
^{1}H NMR spectrum of methyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinate (**2a**) ($CDCl_3$).



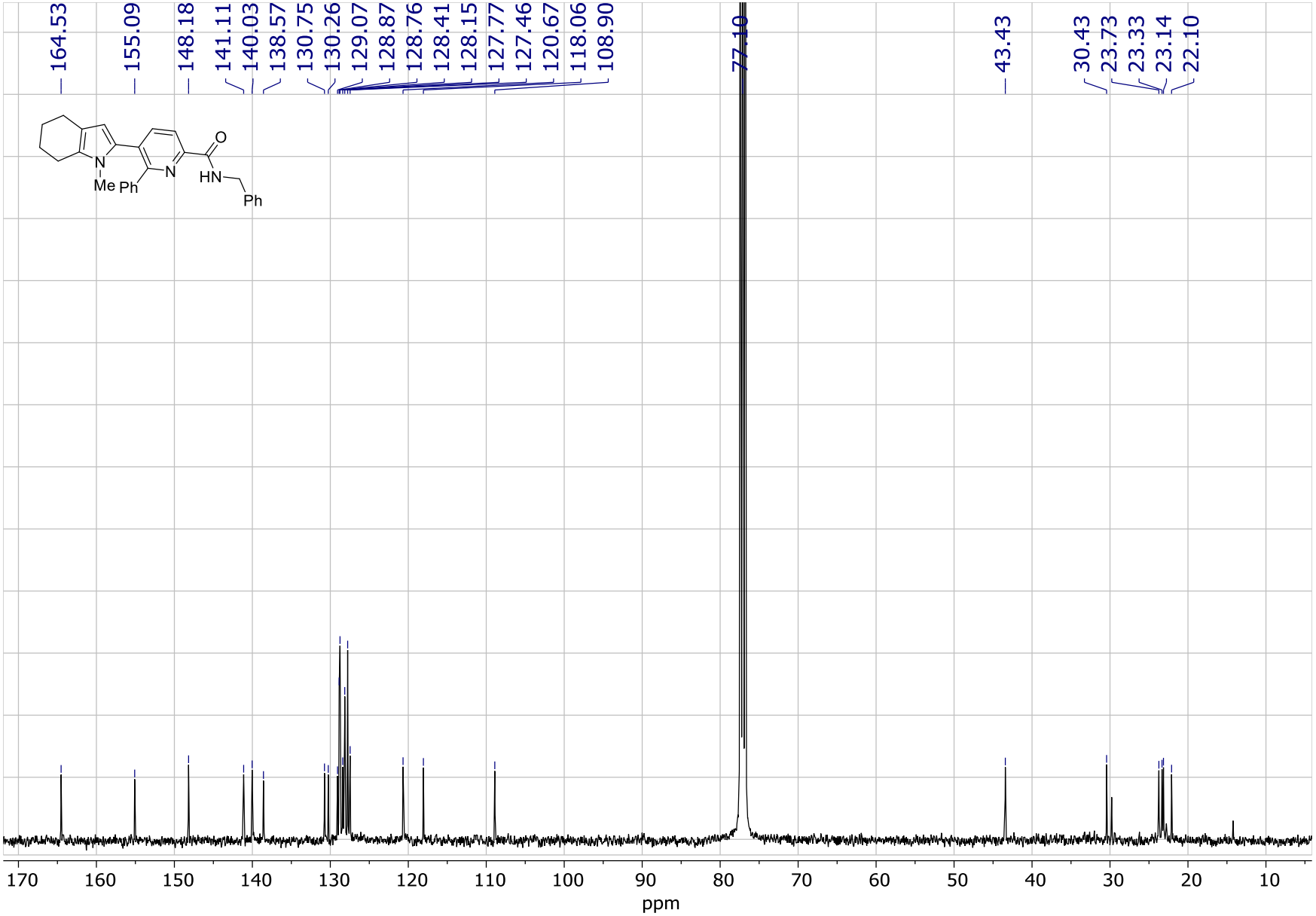
^{13}C NMR spectrum of methyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinate (**2a**) ($CDCl_3$).



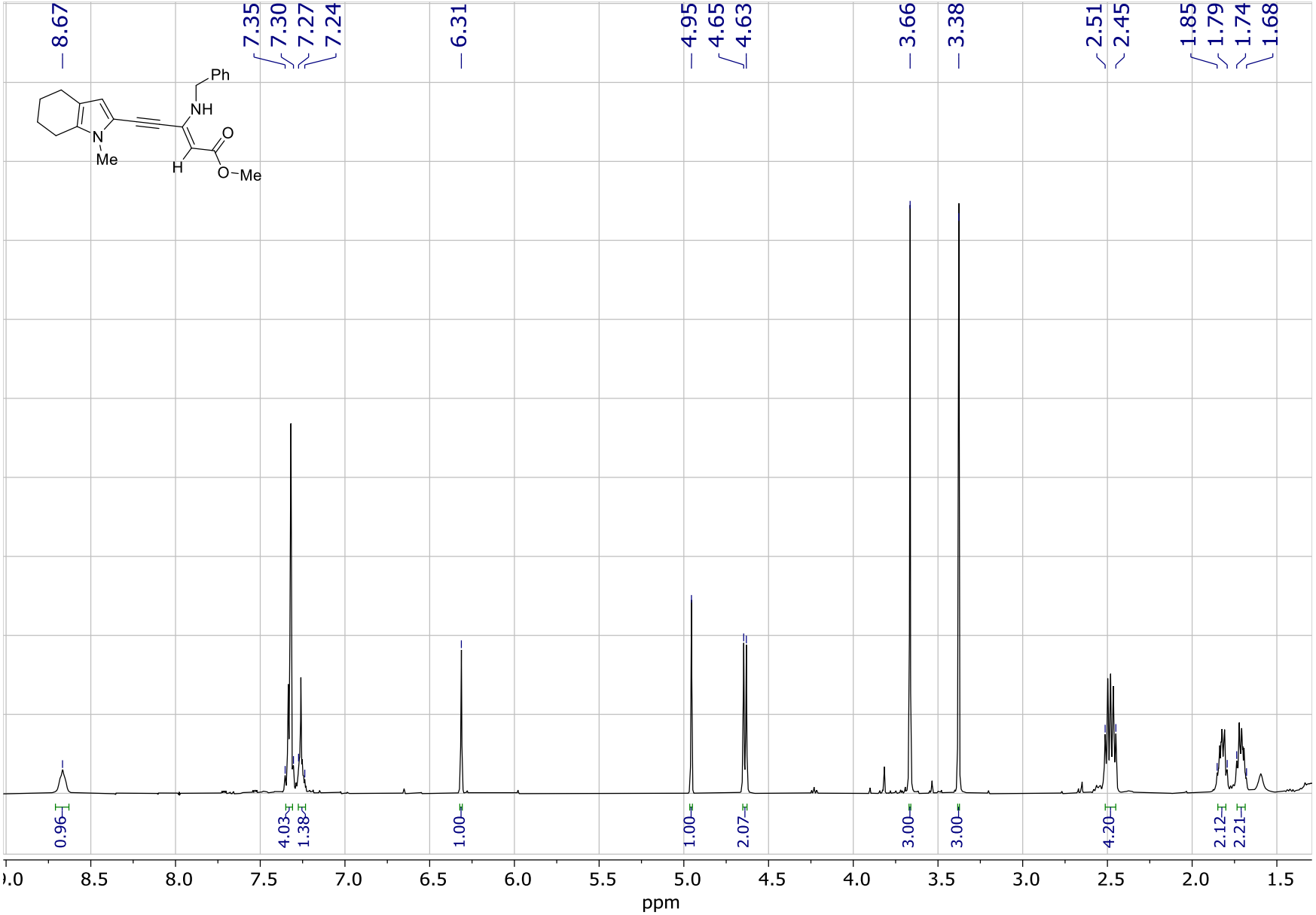
^{1}H NMR spectrum of *N*-benzyl-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinamide (**3a**) ($CDCl_3$).



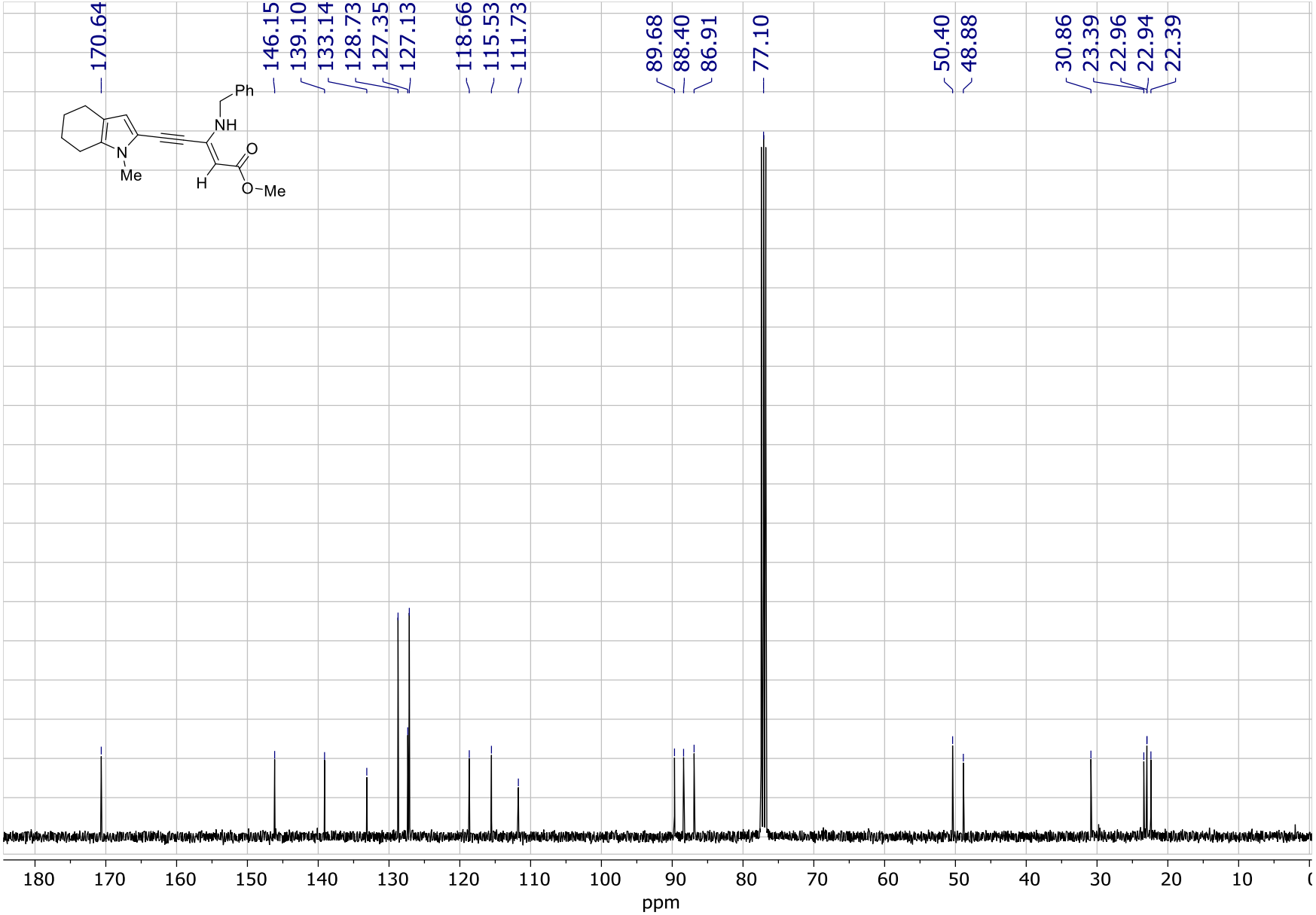
^{13}C NMR spectrum of *N*-benzyl-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinamide (**3a**) ($CDCl_3$).



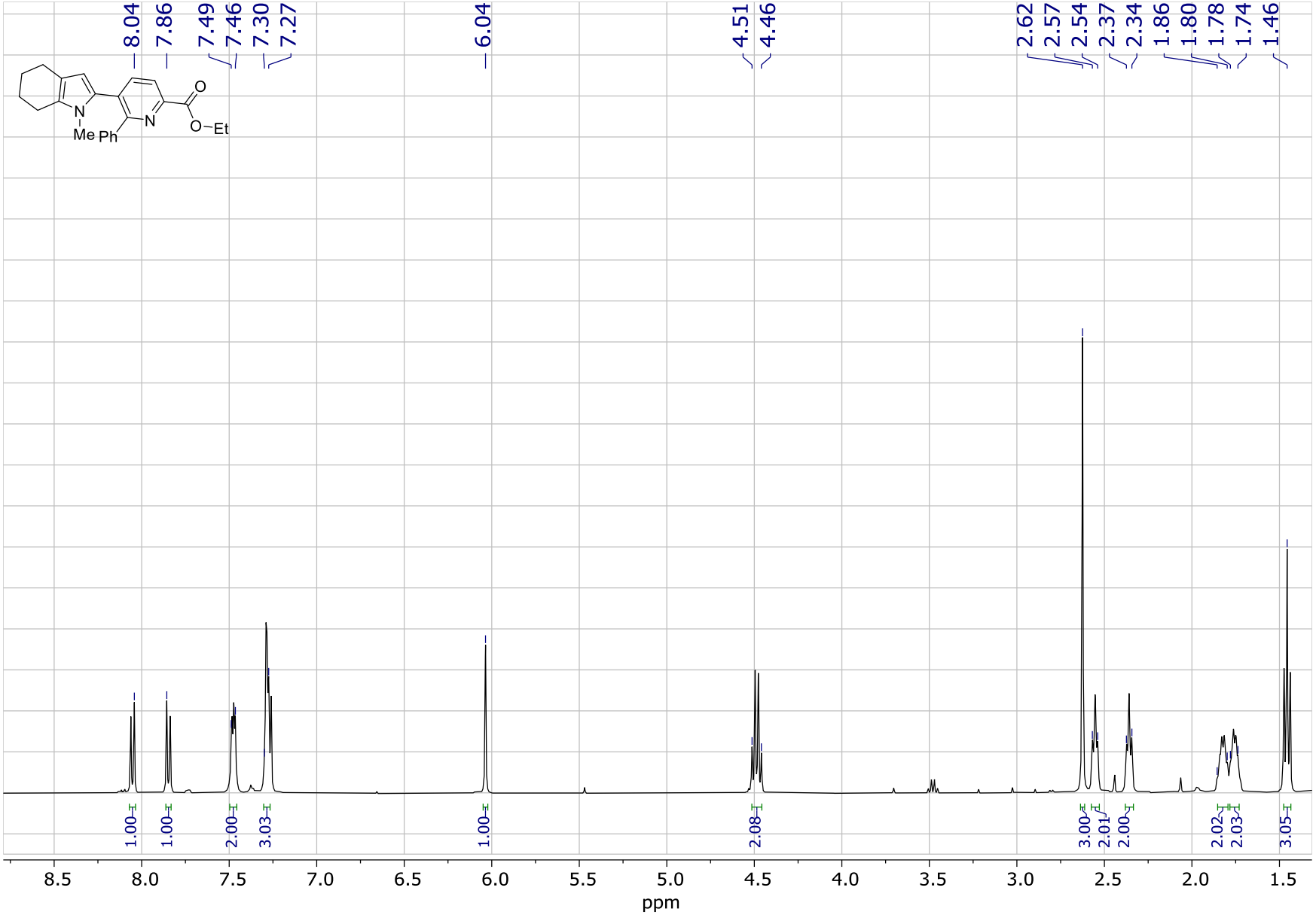
H NMR spectrum of methyl (*Z*)-3-(benzylamino)-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)pent-2-en-4-ynoate (**4a**) ($CDCl_3$).



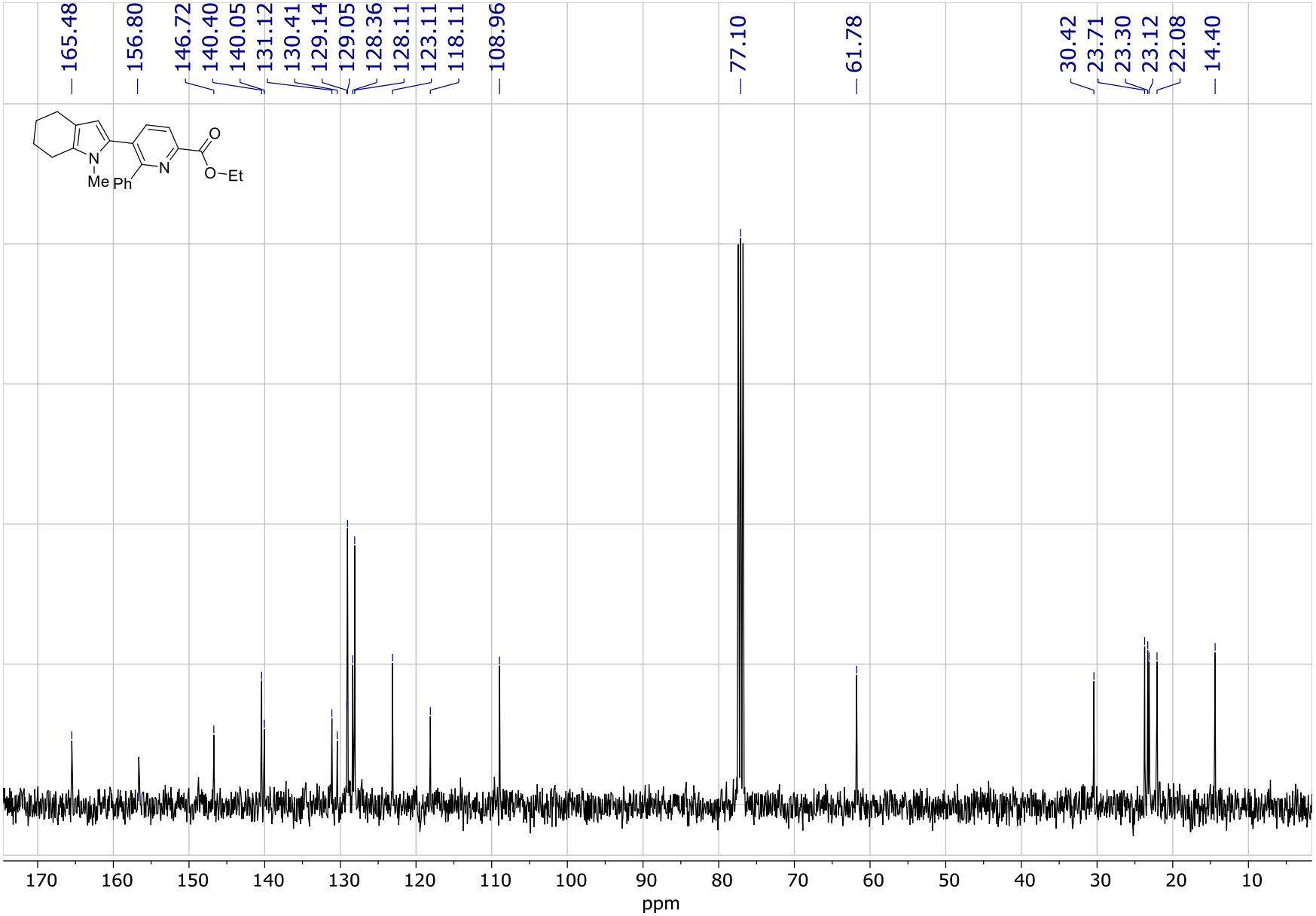
^{13}C NMR spectrum of methyl (*Z*)-3-(benzylamino)-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)pent-2-en-4-ynoate (**4a**) ($CDCl_3$).



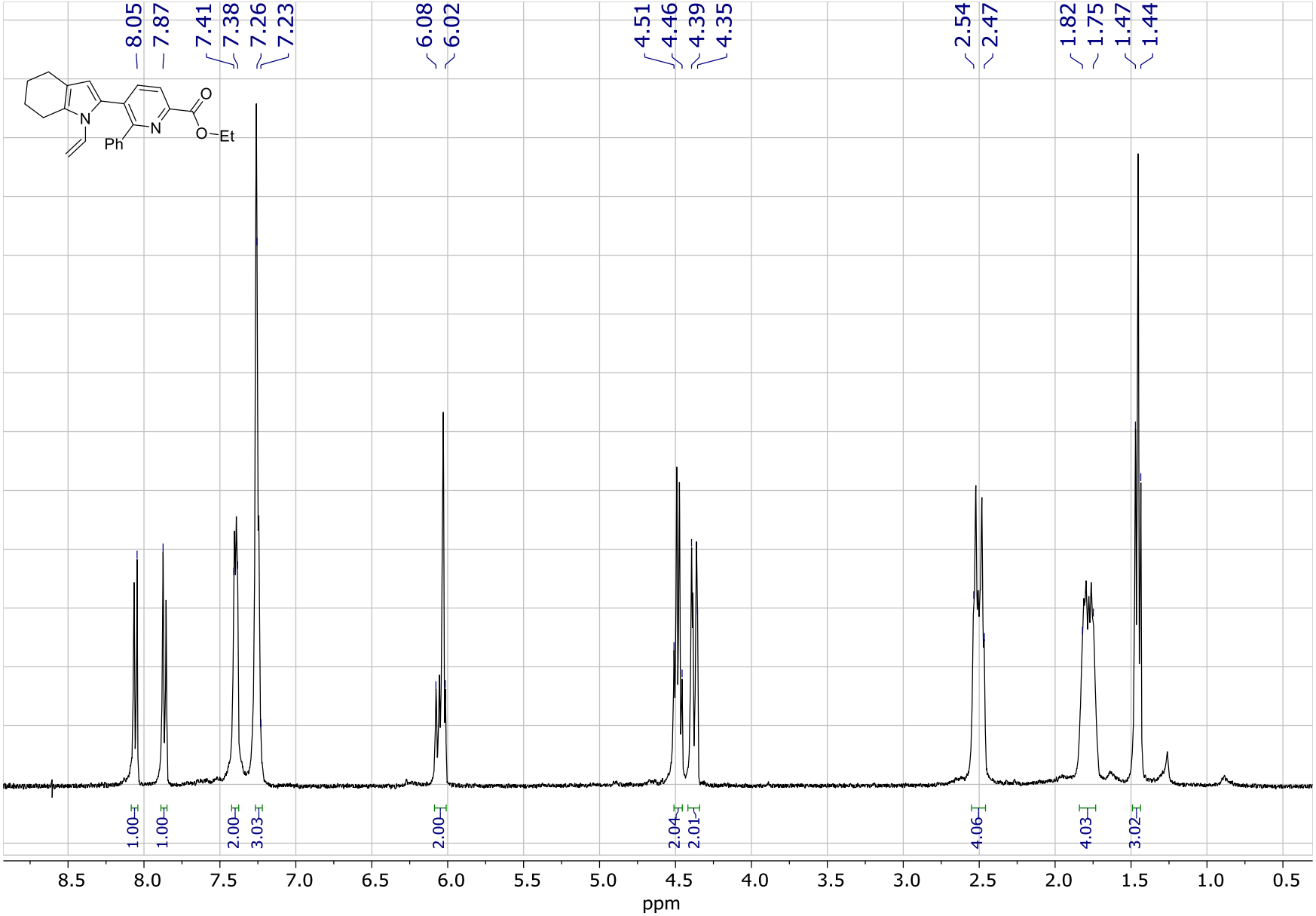
^{1}H NMR spectrum of ethyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinate (**2b**) ($CDCl_3$).



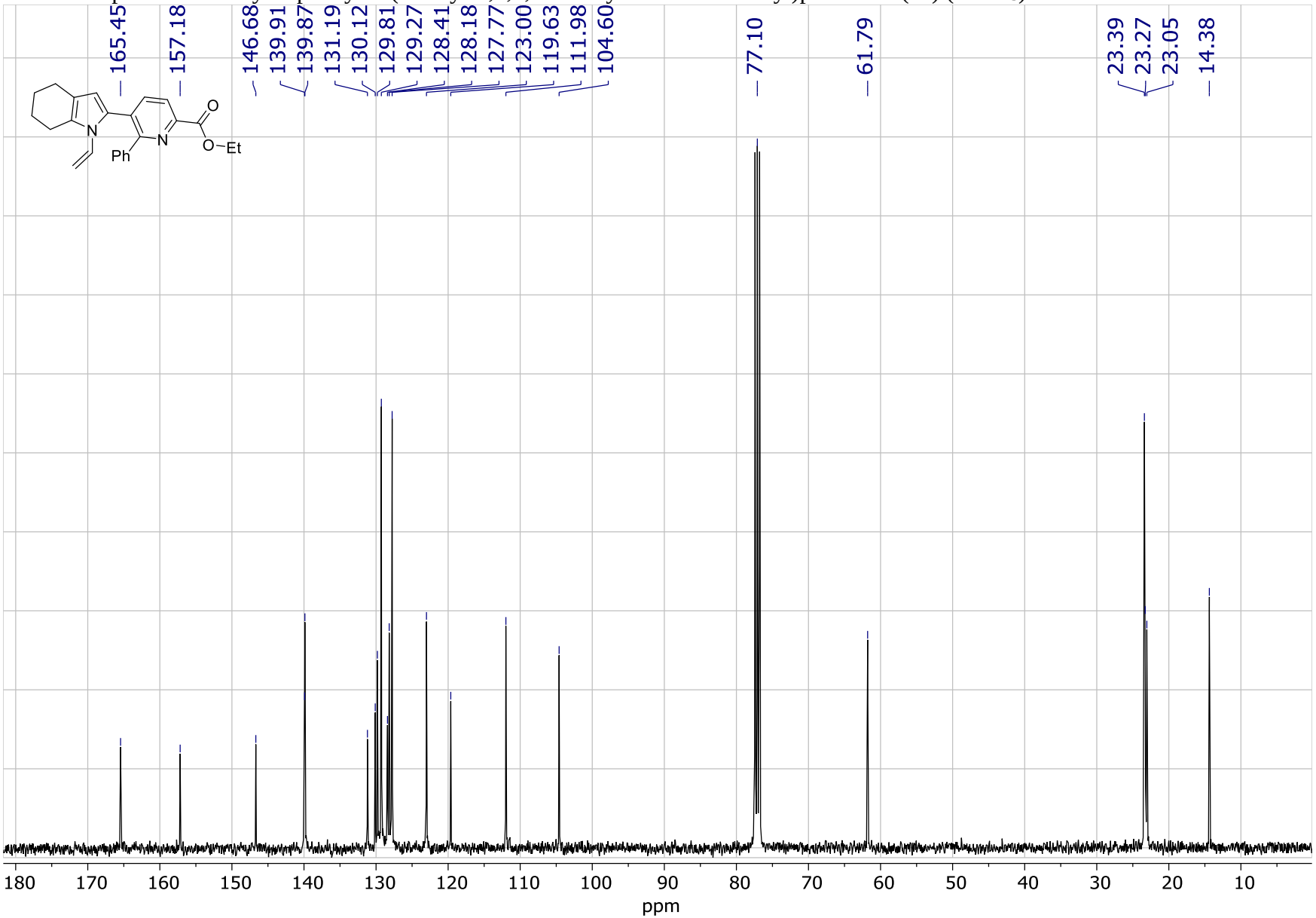
^{13}C NMR spectrum of ethyl 5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpicolinate (**2b**) ($CDCl_3$).



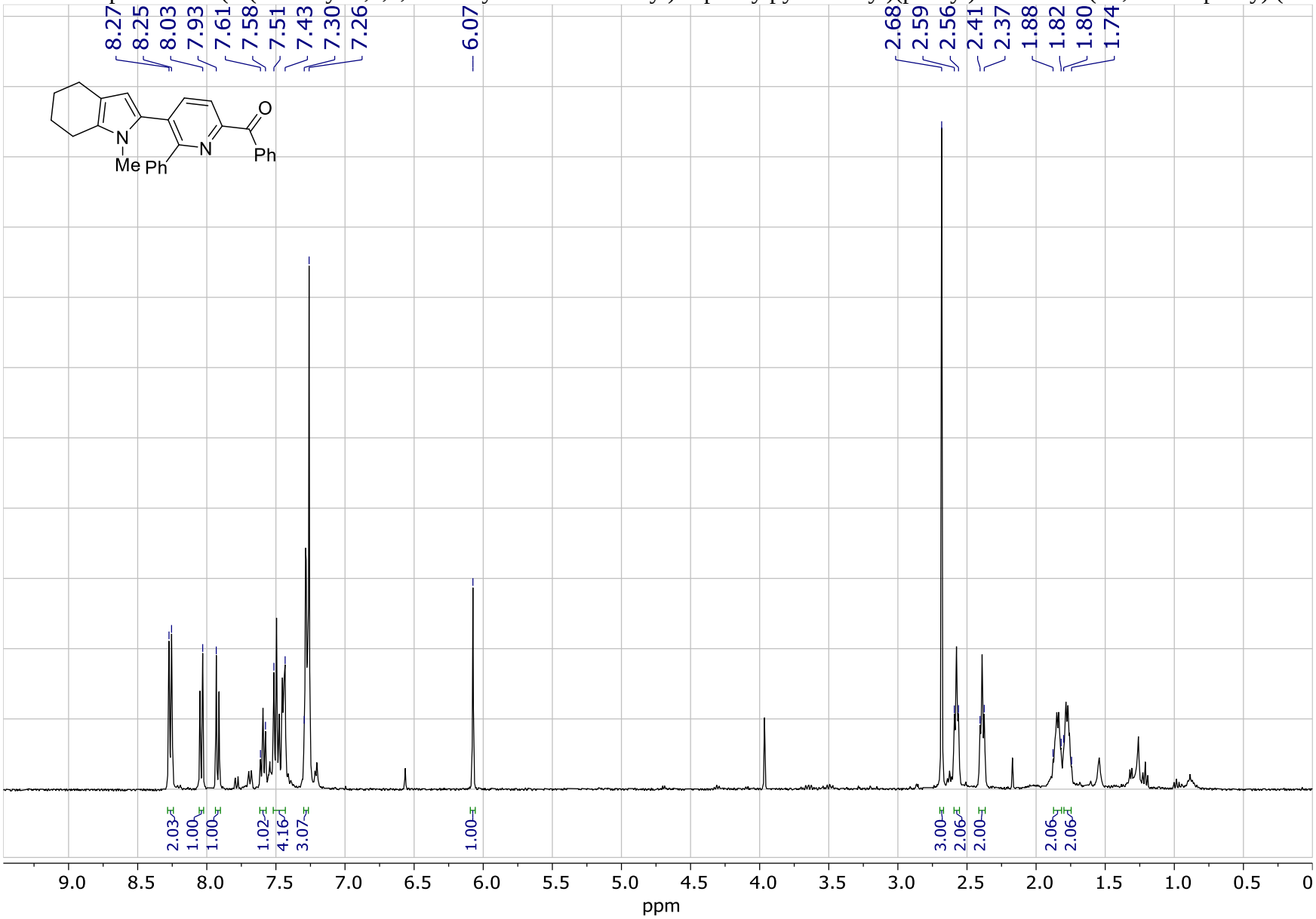
^{1}H NMR spectrum of ethyl 6-phenyl-5-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)picolinate (**2c**) ($CDCl_3$).



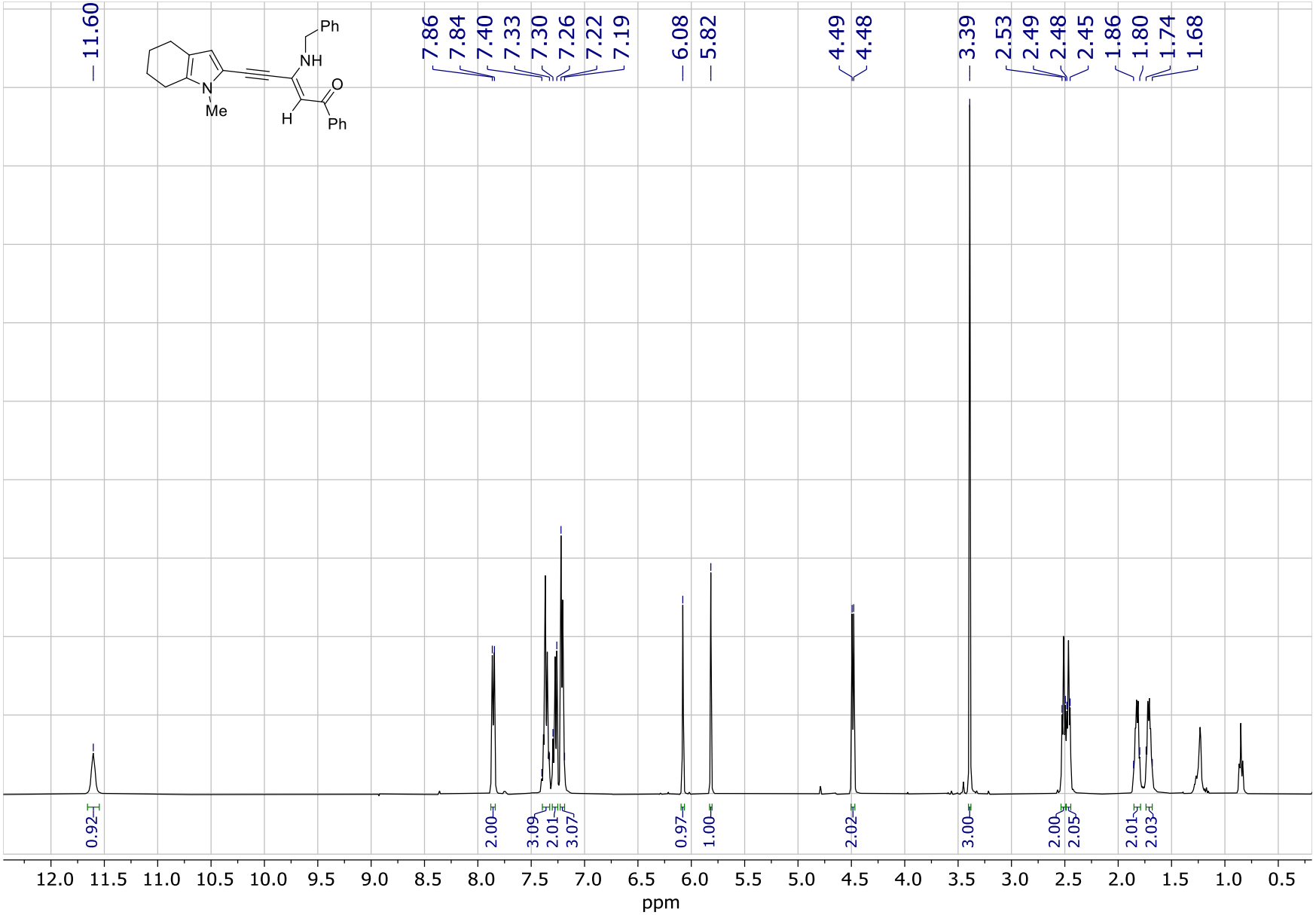
^{13}C NMR spectrum of ethyl 6-phenyl-5-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)picolinate (**2c**) ($CDCl_3$).



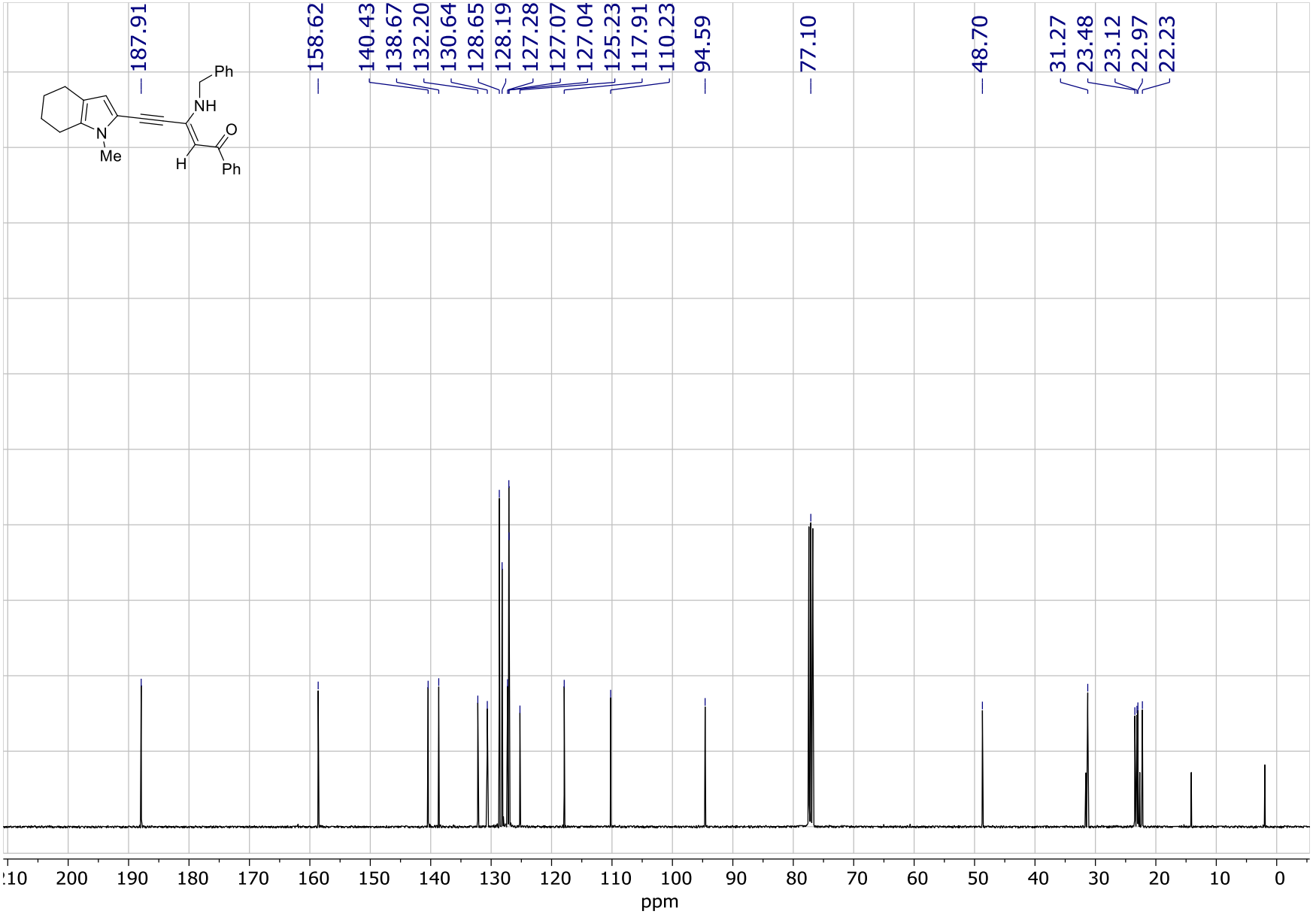
^{1}H NMR spectrum of (5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-6-phenylpyridin-2-yl)(phenyl)methanone (**2d**, ~ 80% purity) ($CDCl_3$).



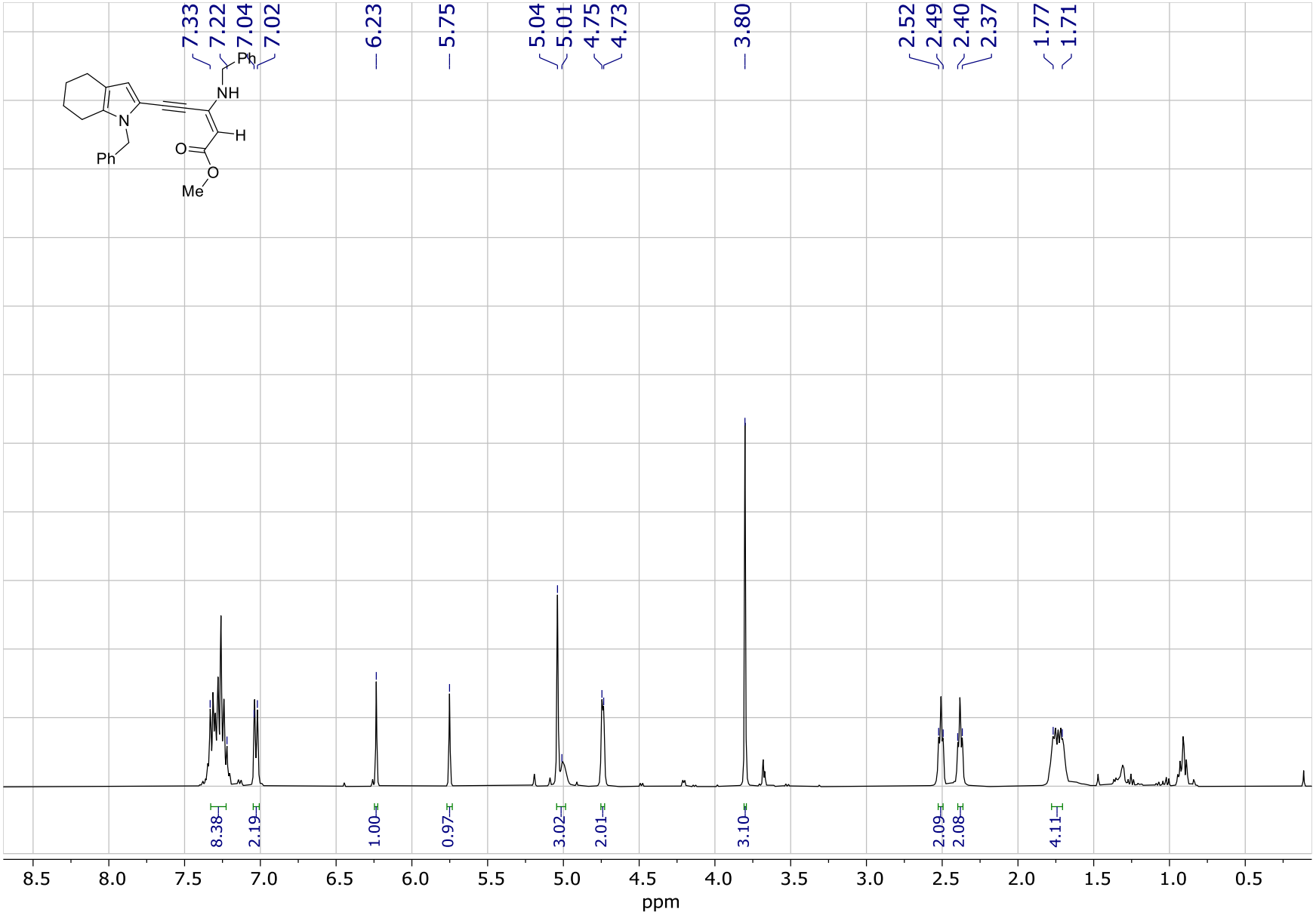
^{1}H NMR spectrum of (*Z*)-3-(benzylamino)-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpent-2-en-4-yn-1-one (**4d**) ($CDCl_3$).



^{13}C NMR spectrum of (*Z*)-3-(benzylamino)-5-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpent-2-en-4-yn-1-one (**4d**) ($CDCl_3$).



^{1}H NMR spectrum of methyl (*E*)-5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-(benzylamino)pent-2-en-4-ynoate (**5**) ($CDCl_3$).



^{13}C NMR spectrum of methyl (*E*)-5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-(benzylamino)pent-2-en-4-ynoate (**5**) ($CDCl_3$).