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Electronic supporting information for:

Synthesis of spiroindolenines by intramolecular *ipso*-iodocyclization of indol ynones

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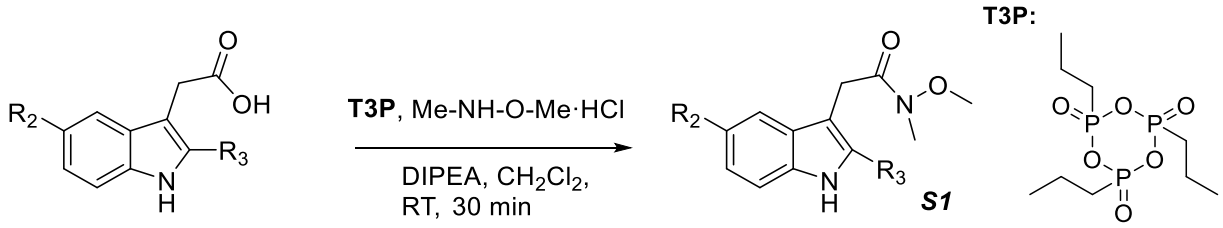
General Information

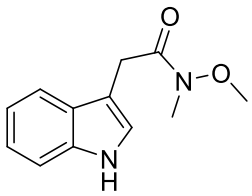
General Information NMR spectra were recorded on a 300 MHz, 400 MHz or 600 MHz instrument using $CDCl_3$ as solvent unless and otherwise stated (s = singlet, d = doublet, t = triplet, m = multiplet). The ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. IR spectra were recorded on Bruker Alpha FT-IR spectrometer. The IR data is presented for the maximal peaks. For the Mass spectrometry, ion source temperature was 150-250°C, as required. High-resolution EI mass spectra were performed with a resolution of 10,000. For chromatography, analytical TLC plates and 70-230 mesh silica gel were used. All the solvents and chemicals were purchased and used as available.

General procedure A for synthesis of Indole-3-ynones (S1)

First step: Weinreb amide formation

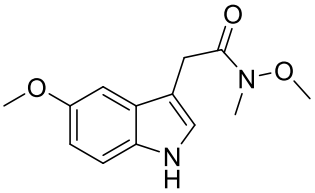


To a stirred solution of carboxylic acid (1.00 mmol), MeNHOMe·HCl (107 mg, 1.10 mmol) and DIPEA (0.52 mL, 3.00 mmol) in CH_2Cl_2 (2.5 mL) was added propylphosphonic anhydride solution (T3P) (50% in EtOAc; 955 mg, 1.5 mmol). The solution was stirred for 1 h at RT. The reaction mixture was poured into water (20 mL) and acidified using aq. 10% HCl (5 mL). The organics were collected and the aqueous was extracted with EtOAc (3 × 30 mL). The organics were combined, washed with aq. 2M NaOH (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to afford the Weinreb amide product.



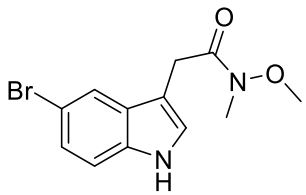
2-(1H-indol-3-yl)-N-methoxy-N-methylacetamide (**S1a**)

Pale brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 – 7.06 (m, 2H), 6.95 (s, 1H), 3.89 (s, 2H), 3.62 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.02, 136.11, 127.35, 123.42, 121.78, 119.32, 118.68, 111.31, 108.48, 61.35, 32.30, 28.95. Spectroscopic data matched those reported in the literature.[1,2]



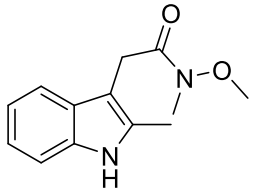
N-methoxy-2-(5-methoxy-1H-indol-3-yl)-N-methylacetamide (S1b)

Pale brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.03 (s, 1H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.87 (s, 2H), 3.85 (s, 3H), 3.65 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.96, 154.01, 131.27, 127.78, 124.04, 112.18, 111.96, 108.52, 100.61, 77.48, 77.06, 76.63, 61.38, 55.87, 32.30. Spectroscopic data matched those reported in the literature.[1,3]



2-(5-bromo-1H-indol-3-yl)-N-methoxy-N-methylacetamide (S1c)

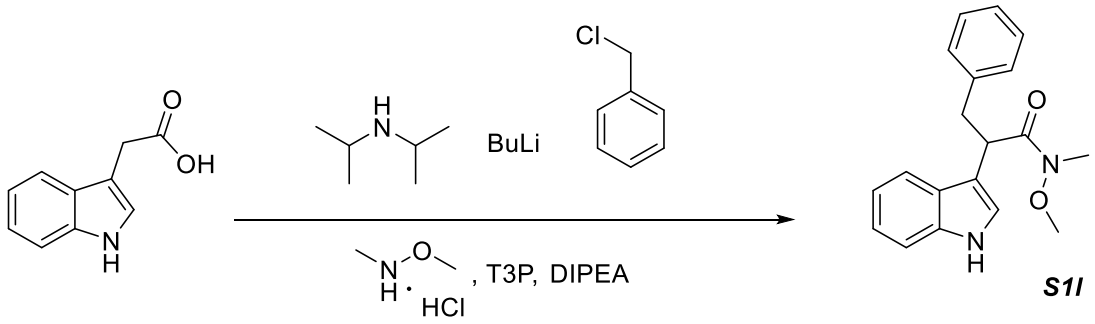
Pale brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.70 (s, 1H), 7.17 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.91 (s, 1H), 3.83 (s, 2H), 3.69 (s, 3H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.71, 134.78, 129.12, 124.83, 124.59, 121.18, 112.80, 112.62, 108.09, 61.43, 32.37, 28.60. Spectroscopic data matched those reported in the literature.[1,2]



N-methoxy-N-methyl-2-(2-methyl-1H-indol-3-yl)acetamide (S1d)

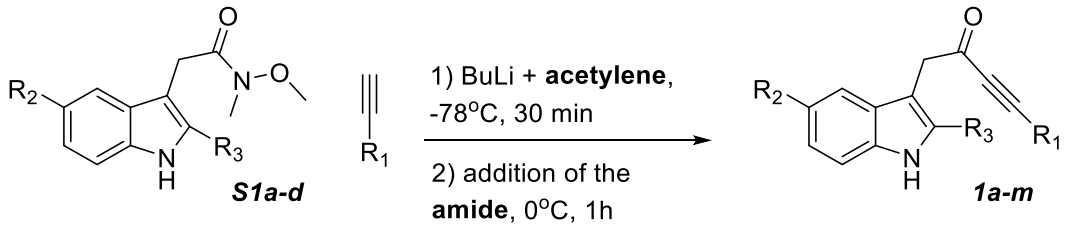
Pale brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.56 – 7.51 (m, 1H), 7.09 – 7.00 (m, 3H), 3.80 (s, 2H), 3.56 (s, 3H), 3.15 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.11, 135.26, 133.11, 128.66, 120.82, 119.19, 118.13, 110.48, 104.39, 61.23, 61.12, 32.36, 28.76, 11.63. Spectroscopic data matched those reported in the literature[1,2]

Synthetic procedure for the synthesis of S1l

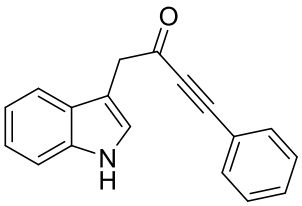


To a solution of diisopropylamine (6.44 ml, 45.6 mmol) in THF (23 ml) at a 0 °C under argon was added butyllithium (18.24 ml, 45.6 mmol) dropwise. The solution was stirred for 15 min before 2-(1H-indol-3-yl)acetic acid (2 g, 11.42 mmol) in THF (12 ml) was added dropwise to the solution, which was stirred at 0 °C for 2 h. (Chloromethyl)benzene (2.90 ml, 25.2 mmol) was then added dropwise to the mixture, which was allowed to warm to RT. The resulting mixture was stirred for 16 h. The reaction mixture was quenched with water (40 mL) and extracted with EtOAc (3 × 40 mL). The organics were combined, dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was dissolved in DCM (43 ml), to which N,O-dimethylhydroxylamine hydrochloride (1,225 g, 12,56 mmol), DIPEA (5.96 ml, 34.2 mmol) and T3P (10.20 ml, 17.14 mmol) were added successively. The mixture was stirred for 1h at RT. Then, the reaction mixture was poured into water (60 mL) and the organics were collected. The aqueous was extracted with EtOAc (2 × 60 mL). The organics were combined, washed with aq. 10% HCl (2 × 40 mL), aq. 2M NaOH (40 mL) and brine (40 mL), then dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography to afford the title compound as a pale brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.21 (m, 4H), 7.20 – 7.09 (m, 4H), 4.73 – 4.60 (m, 1H), 3.50 (dd, *J* = 13.3, 9.7 Hz, 1H), 3.26 (s, 3H), 3.15 – 3.07 (m, 4H). Spectroscopic data matched those reported in the literature.[1,2]

Second step: Weinreb ketone synthesis

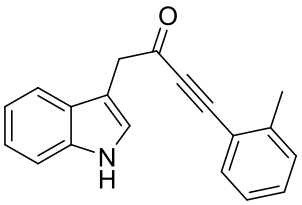


To a solution of terminal alkyne (3.0 mmol) in THF (3 mL) at −78 °C under nitrogen was added n-BuLi (1.0 mL, 2.5 mmol, 2.5 M in hexane). The resulting mixture was stirred at −78 °C for 30 min, then a solution of Weinreb amide (1.0 mmol) in THF (9 mL) was quickly added to the solution. The mixture was stirred at −78 °C for 5 min, then warmed to 0 °C and stirred for another 1 h. The reaction was then re-cooled to −78 °C and quenched with sat. aq. NH_4Cl (30 mL), allowed to warm to RT, diluted with water (70 mL), extracted with ethyl acetate (3 × 100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash column chromatography (20-40% of ethyl acetate in heptane) afforded the desired ynone.



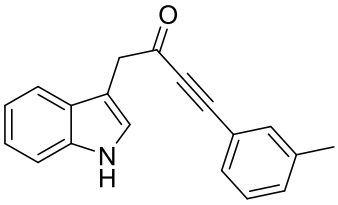
1-(1H-indol-3-yl)-4-phenylbut-3-yn-2-one (1a)

Light-brown solid; R_f=0.45 (Heptane/Ethyl acetate 1:1); Yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.66 (dd, *J* = 7.9, 0.5 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.13 (m, 2H), 4.08 (s, *J* = 0.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.66, 136.17, 133.08, 130.64, 128.49, 127.46, 123.72, 122.30, 119.91, 119.84, 118.92, 111.31, 107.61, 92.08, 87.99, 42.00; Spectroscopic data matched those reported in the literature.[1,2]



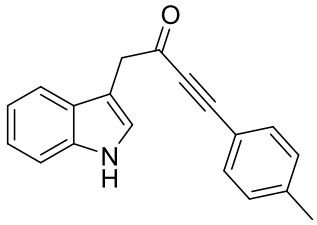
1-(1H-indol-3-yl)-4-(o-tolyl)but-3-yn-2-one (1b)

Brown solid; R_f=0.46 (Heptane/Ethyl acetate 1:1); Yield 67%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.19 (m, 4H), 7.18 – 7.07 (m, 4H), 4.08 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.95, 142.22, 136.19, 133.62, 130.70, 129.65, 127.45, 125.72, 123.76, 122.29, 119.82, 119.69, 118.83, 111.30, 107.63, 91.73, 91.19, 42.05, 20.26; Spectroscopic data matched those reported in the literature.[1]



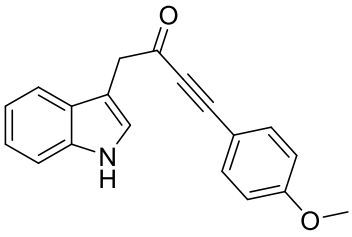
1-(1H-indol-3-yl)-4-(m-tolyl)but-3-yn-2-one (1c)

Brown solid; R_f=0.46 (Heptane/Ethyl acetate 1:1); Yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.13 (m, 6H), 7.10 (s, 1H), 4.07 (s, 2H), 2.28 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 185.81, 138.35, 136.23, 133.68, 131.63, 130.22, 128.41, 127.54, 123.79, 122.31, 119.86, 119.72, 118.99, 111.36, 107.70, 92.63, 87.83, 42.03, 21.13; Spectroscopic data matched those reported in the literature.[1]



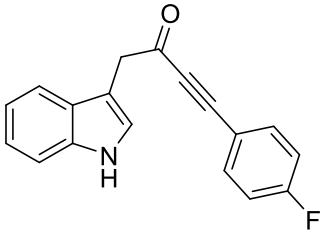
1-(1H-indol-3-yl)-4-(p-tolyl)but-3-yn-2-one (1d)

Brown solid; R_f=0.46 (Heptane/Ethyl acetate 1:1); Yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.08 (m, 7H), 4.07 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.76, 141.39, 136.17, 133.11, 129.30, 127.48, 123.71, 122.25, 119.79, 118.94, 116.79, 111.30, 107.71, 92.82, 87.90, 41.97, 21.69; Spectroscopic data matched those reported in the literature.[1]



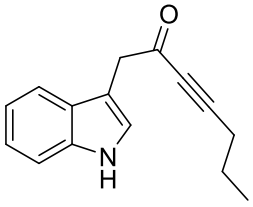
1-(1H-indol-3-yl)-4-(4-methoxyphenyl)but-3-yn-2-one (1e)

Light-brown solid; R_f=0.37 (Heptane/Ethyl acetate 1:1); Yield 70%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.12 (m, 5H), 6.83 – 6.76 (m, 2H), 4.06 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.75, 161.59, 136.18, 135.14, 127.53, 123.67, 122.25, 119.79, 118.98, 114.24, 111.70, 111.29, 107.93, 93.37, 87.98, 55.38, 41.88; Spectroscopic data matched those reported in the literature.[1,2]



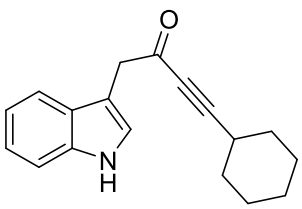
4-(4-fluorophenyl)-1-(1H-indol-3-yl)but-3-yn-2-one (1f)

Dark-orange solid; R_f=0.43 (Heptane/Ethyl acetate 1:1); Yield 62%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.12 (m, 5H), 7.02 – 6.93 (m, 2H), 4.07 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.61, 163.92 (d, *J* = 253.7 Hz), 136.21, 135.39 (d, *J* = 8.9 Hz), 127.50, 123.76, 122.36, 119.89, 118.94, 116.19, 116.04 (d, *J* = 22.3 Hz), 115.89, 111.38, 107.63, 91.13, 87.90, 41.95; Spectroscopic data matched those reported in the literature.[1,4]



1-(1H-indol-3-yl)hept-3-yn-2-one (1g)

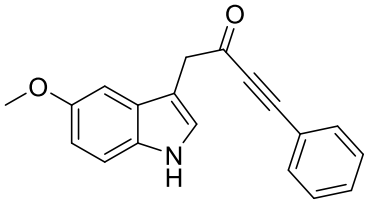
Light-brown solid; R_f=0.47 (Heptane/Ethyl acetate 1:1); Yield 64%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.06 (m, 2H), 7.05 (s, 1H), 3.95 (s, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.55 – 1.38 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.06, 136.13, 127.32, 123.71, 122.11, 119.60, 118.77, 111.32, 107.42, 95.73, 81.07, 42.09, 21.06, 20.88, 13.33; Spectroscopic data matched those reported in the literature.[1]



4-cyclohexyl-1-(1H-indol-3-yl)but-3-yn-2-one (1h)

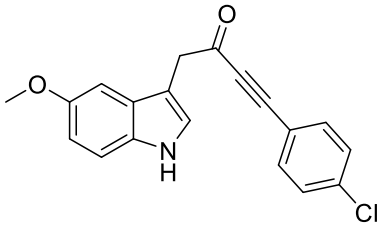
Orange solid; R_f=0.53 (Heptane/Ethyl acetate 1:1); Yield 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.15 – 7.10 (m, 2H), 3.96 (s, 2H), 2.50 – 2.40 (m, 1H), 1.75 – 1.65 (m, 2H), 1.63 – 1.52 (m, 2H), 1.50 – 1.42 (m, 1H), 1.41 – 1.31 (m, 2H), 1.30 – 1.20 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.06, 136.12, 127.45, 123.53, 122.21, 119.69, 118.94, 111.17, 107.93, 99.33, 80.85, 42.09, 31.36, 29.04, 25.59, 24.46; Spectroscopic data matched those reported in the literature.[1]



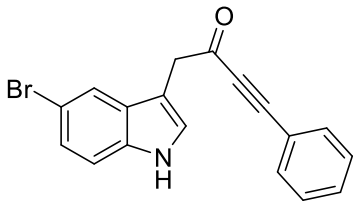
1-(5-methoxy-1H-indol-3-yl)-4-phenylbut-3-yn-2-one (1i)

Brown solid; R_f=0.37 (Heptane/Ethyl acetate 1:1); Yield 23%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.43 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.26 – 7.25 (m, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.05 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.61, 154.35, 133.06, 131.30, 130.66, 128.52, 127.89, 124.45, 119.94, 112.70, 112.07, 107.35, 100.61, 92.04, 88.01, 55.88, 42.13; Spectroscopic data matched those reported in the literature.[1]



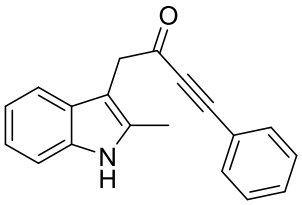
4-(4-chlorophenyl)-1-(5-methoxy-1H-indol-3-yl)but-3-yn-2-one (1j)

White solid; R_f=0.39 (Heptane/Ethyl acetate 1:1); Yield 37%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.33 – 7.25 (m, 1H), 7.29 – 7.20 (m, 4H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.03 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.42, 154.34, 137.03, 134.20, 131.32, 128.96, 127.86, 124.51, 118.35, 112.62, 112.12, 107.16, 100.64, 90.64, 88.65, 55.89, 42.06; MS (ESI) m/z: calculated for $C_{18}H_{13}NO^+$ $[M + H]^+$: 324.1, found: 324.1.



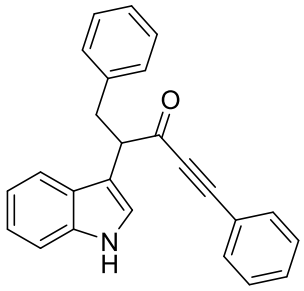
1-(5-bromo-1H-indol-3-yl)-4-phenylbut-3-yn-2-one (1k)

Beige solid; R_f=0.37 (Heptane/Ethyl acetate 1:1); Yield 44%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.79 (d, *J* = 1.7 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.34 – 7.24 (m, 3H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 4.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.17, 134.80, 133.14, 130.82, 129.18, 128.58, 125.18, 124.99, 121.57, 119.70, 113.15, 112.84, 107.24, 92.47, 87.91, 41.85; Spectroscopic data matched those reported in the literature.[1]



1-(2-methyl-1H-indol-3-yl)-4-phenylbut-3-yn-2-one (1l)

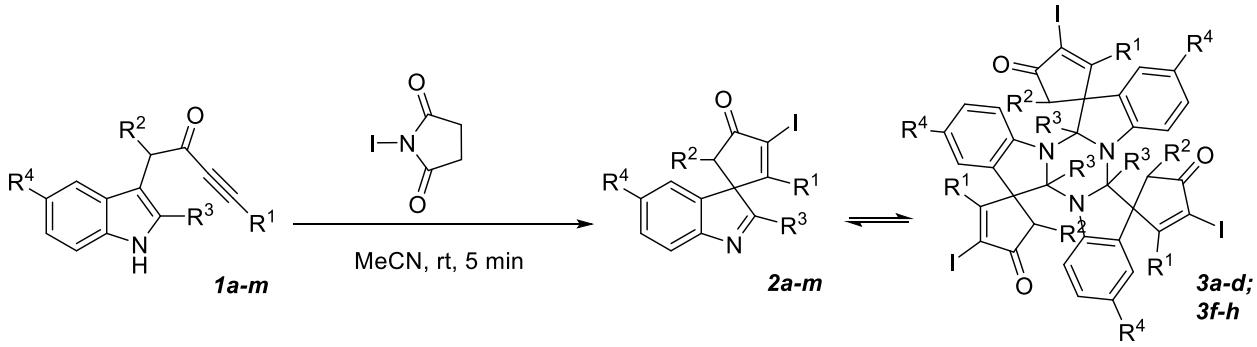
Light-orange solid; R_f=0.42 (Heptane/Ethyl acetate 1:1); Yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.59 – 7.54 (m, 1H), 7.37 – 7.31 (m, 1H), 7.28 – 7.20 (m, 2H), 7.14 – 7.08 (m, 1H), 3.96 (s, 1H), 2.35 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.56, 135.36, 133.71, 133.13, 130.71, 128.71, 128.56, 121.36, 119.94, 119.71, 118.14, 110.61, 103.31, 91.90, 88.18, 41.28, 11.81; Spectroscopic data matched those reported in the literature.[1,4]



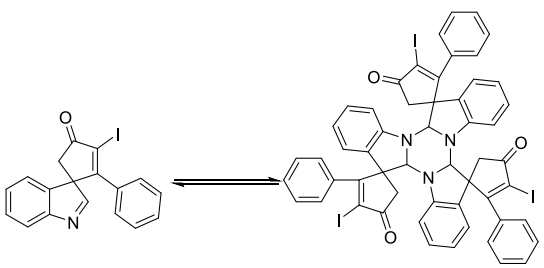
4-(1H-indol-3-yl)-1,5-diphenylpent-1-yn-3-one (1m)

Yellow solid; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.75 – 7.69 (m, 1H), 7.41 – 7.33 (m, 4H), 7.32 – 7.25 (m, 2H), 7.25 – 7.12 (m, 8H), 4.52 – 4.40 (m, 1H), 3.66 (dd, *J* = 14.0, 8.1 Hz, 1H), 3.26 (dd, *J* = 14.0, 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.98, 139.42, 136.29, 132.97, 130.51, 129.01, 128.45, 128.33, 126.74, 126.27, 123.01, 122.39, 120.03, 119.92, 119.24, 112.33, 111.33, 92.06, 87.80, 53.93, 37.04; Spectroscopic data matched those reported in the literature.[1]

General procedure B for the synthesis of iodocyclized spiro-indolenines (2a-l)



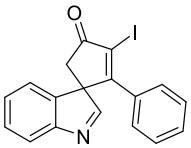
Corresponding ynone **1a-m** (0.3 mmol) was dissolved in acetonitrile (1.5 ml) to afford a concentration of 0.1 M, followed by addition of N-iodosuccinimide (1.05 equiv, 0.315 mmol) to afford the concentration of 0.05 M dropwise during 4 min. After the addition the solution was allowed to stir at room temperature for 1 min. Then the reaction was shaked with sat. sol. of NaS_2O_3 (50 ml) and extracted with ethyl acetate (50 ml). Then organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification was performed by column chromatography (20-30% of ethyl acetate in heptane, in a fast way) affording spiro-indolenines **2a-m**. After the isolation, the synthesized compounds were found to slowly trimerize. The successful reversal was achieved by addition of a few drops of TFA to the solution (or NMR tube).



2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one + the trimer (2a+3a)

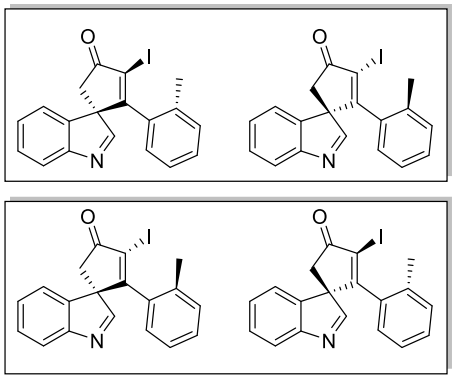
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.36 (m, 2H), 7.34 – 7.16 (m, 9H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.07 – 6.96 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 2H), 6.87 – 6.66 (m, 2H), 6.49 (d, *J* = 7.7 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 6.22 (d, *J* = 7.9 Hz, 0H), 5.57 (t, *J* = 8.9 Hz, 1H), 4.90 (s, 0H), 4.35 (s, 0H), 4.22 (s, 0H), 3.24 (d, *J* = 18.8 Hz, 1H), 2.94 (d, *J* = 18.6 Hz, 1H), 2.49 (d, *J* = 19.1 Hz, 0H), 2.04 – 1.80 (m, 1H), 1.78 – 1.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.08, 200.81, 200.24, 200.10, 179.67, 179.06, 178.48, 174.53, 171.48, 155.17,

150.19, 148.84, 145.33, 138.63, 134.65, 134.46, 133.52, 131.92, 130.36, 130.21, 130.16, 129.68, 129.55, 129.36, 129.14, 128.79, 128.53, 128.35, 128.15, 128.06, 127.99, 127.60, 126.63, 126.43, 126.17, 125.87, 123.66, 123.00, 122.40, 121.93, 121.83, 121.77, 121.26, 120.43, 114.79, 106.72, 105.93, 105.27, 105.15, 104.82, 103.85, 84.15, 81.00, 78.29, 68.84, 63.99, 61.41, 59.23, 41.83, 40.05, 39.93, 38.75.



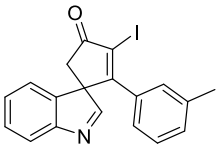
2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2a)

Brown amorphous solid; R_f=0.21 (Heptane/Ethyl acetate 1:1); Yield 98% (96% for 1.3 g scale); IR (neat, cm^{-1}): 1714.61, 1546.31, 1450.79, 1171.74, 1030.17, 752.42, 697.44, 523.92; ^{1}H NMR for the TFA salt (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 7.75 – 7.69 (m, 1H), 7.55 – 7.44 (m, 3H), 7.36 – 7.30 (m, 1H), 7.27 – 7.21 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 3.45 (d, *J* = 18.8 Hz, 1H), 3.03 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR for the TFA salt (101 MHz, CDCl3) δ 199.75, 174.29, 172.47, 148.56, 138.02, 132.75, 130.89, 130.31, 129.74, 128.81, 126.22, 122.58, 120.72, 106.27, 68.09, 38.51; HRMS (ESI) m/z: calculated for $C_{18}H_{13}NO^+$ $[M + H]^+$: 386.0038, found: 386.0035.



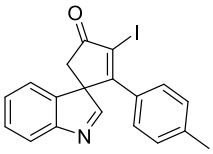
2-(o-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2b)

Brown amorphous solid; R_f=0.23 (Heptane/Ethyl acetate 1:1); Yield 93%; Isolated as an inseparatable mixture of diastereomers (approx. 1.2:1 ratio A/B, according ^{1}H NMR); IR (neat, cm^{-1}): 1713.16, 1600.15, 1456.78, 1177.50, 923.76, 737.02, 522.68, 469.08; ^{1}H NMR for the TFA salt (300 MHz, Chloroform-*d*) δ 9.54 (s, 0.45H), 9.28 (s, 0.55H), 7.80 – 7.53 (m, 4H), 7.27 – 7.21 (m, 1.45H), 7.18 – 7.06 (m, 1H), 6.88 – 6.80 (m, 1H), 6.06 (d, *J* = 7.7 Hz, 0.55H), 3.73 (d, *J* = 19.0 Hz, 1H), 3.69 (d, *J* = 19.1 Hz, 1H), 3.23 (d, *J* = 19.1 Hz, 1H), 3.21 (d, *J* = 19.0 Hz, 1H), 2.28 (s, 1.65H), 2.09 (s, 1.35H); ^{13}C NMR for the TFA salt (101 MHz, CDCl3) δ 200.13, 199.97, 176.73, 176.34, 173.00, 172.93, 143.57, 143.10, 136.62, 136.38, 134.31, 133.71, 131.29, 131.27, 131.25, 131.22, 131.20, 131.14, 131.10, 130.80, 130.70, 130.62, 130.56, 126.09, 125.77, 125.24, 124.52, 123.73, 123.59, 119.78, 119.58, 110.16, 110.10, 69.09, 68.87, 38.30, 38.12, 20.02, 19.70; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO^+$ $[M + H]^+$: 400.0194, found: 400.0195.



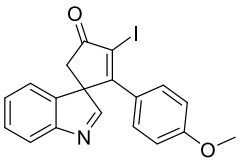
2-(m-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2c)

Brown solid; R_f=0.23 (Heptane/Ethyl acetate 1:1); Yield 93%; mp 164-166 °C; IR (neat, cm^{-1}): 1706.22, 1576.42, 1454.35, 1216.65, 926.92, 899.78, 772.23, 742.82, 698.24, 510.17; ^{1}H NMR for the TFA salt (300 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 7.83 – 7.71 (m, 1H), 7.63 – 7.47 (m, 3H), 7.20 – 7.05 (m, 2H), 6.70 (s, 1H), 6.67 – 6.56 (m, 1H), 3.53 (d, *J* = 18.8 Hz, 1H), 3.07 (d, *J* = 18.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 199.89, 175.43, 172.14, 146.50, 138.87, 137.85, 132.49, 131.88, 130.58, 130.35, 128.82, 126.67, 123.13, 122.86, 120.29, 106.30, 67.97, 38.45, 21.17; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO^+$ $[M + H]^+$: 400.0194, found: 400.0188.



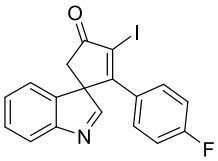
2-(p-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2d)

Brown amorphous solid; R_f=0.23 (Heptane/Ethyl acetate 1:1); Yield 95%; IR (neat, cm^{-1}): 1713.00, 1584.49, 1455.48, 1181.69, 899.75, 751.52, 509.10; ^{1}H NMR for the TFA salt (300 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.86 – 7.79 (m, 1H), 7.65 – 7.58 (m, 2H), 7.58 – 7.53 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 3.61 (d, *J* = 18.9 Hz, 1H), 3.09 (d, *J* = 18.8 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR for the TFA salt (101 MHz, CDCl3) δ 200.02, 176.65, 171.26, 144.37, 142.22, 137.80, 131.08, 130.89, 129.79, 129.46, 126.12, 123.09, 120.00, 106.05, 67.86, 38.59, 21.38; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO^+$ $[M + H]^+$: 400.0194, found: 400.0189.



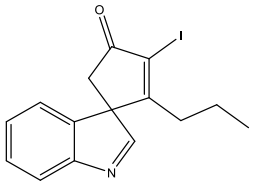
2-(4-methoxyphenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2e)

Brown amorphous solid; R_f=0.15 (Heptane/Ethyl acetate 1:1); Yield 96%; IR (neat, cm^{-1}): 1706.73, 1603.21, 1502.96, 1456.21, 1297.03, 1248.22, 1176.98, 1025.91, 929.12, 834.81, 754.80, 513.65; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.32 – 7.21 (m, 1H), 6.98 – 6.91 (m, 1H), 6.77 (s, 1H), 6.72 – 6.66 (m, 1H), 3.73 (s, *J* = 7.2 Hz, 1H), 3.02 (d, *J* = 18.6 Hz, 1H), 2.64 (d, *J* = 18.6 Hz, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 200.06, 173.25, 172.26, 161.19, 155.01, 139.32, 129.29, 128.53, 127.68, 125.62, 121.95, 121.71, 113.77, 103.47, 68.75, 55.20, 38.99; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO_2^+$ $[M + H]^+$: 416.0144, found: 416.0140.



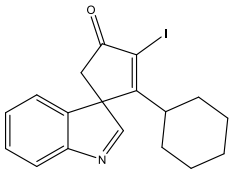
2-(4-fluorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2f)

Brown amorphous solid; R_f=0.21 (Heptane/Ethyl acetate 1:1); Yield 92%; IR (neat, cm^{-1}): 1710.54, 1602.19, 1500.93, 1458.18, 1234.44, 1156.09, 1018.96, 930.80, 839.61, 753.93, 577.05, 522.79, 457.04; ^{1}H NMR for the TFA salt (600 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.73 – 7.68 (m, 1H), 7.53 – 7.47 (m, 1H), 7.48 – 7.43 (m, 1H), 7.42 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.95 – 6.89 (m, 4H), 3.38 (d, *J* = 18.8 Hz, 1H), 3.00 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR for the TFA salt (151 MHz, CDCl3) δ 199.51, 173.45, 171.71, 163.70 (d, *J* = 252.9 Hz), 160.07, 159.79, 159.52, 159.25, 150.50, 138.16, 130.18, 129.26, 128.95 (d, *J* = 3.7 Hz), 128.71 (d, *J* = 8.7 Hz), 122.34, 121.16, 116.07 (d, *J* = 22.0 Hz), 106.38, 68.23, 38.51; HRMS (ESI) m/z: calculated for $C_{18}H_{12}FNO^+$ $[M + H]^+$: 403.9944, found: 403.9947.



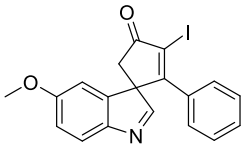
2-propylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2g)

Brown solid; R_f=0.45 (Heptane/Ethyl acetate 1:1); Yield 98%; mp 65-67 °C; IR (neat, cm^{-1}): 1708.38, 1586.53, 1456.47, 1161.08, 928.27, 729.24; ^{1}H NMR for the TFA salt (400 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 7.91 – 7.86 (m, 1H), 7.65 – 7.50 (m, 2H), 7.41 – 7.36 (m, 1H), 3.35 (d, *J* = 19.4 Hz, 1H), 2.97 (d, *J* = 19.1 Hz, 1H), 2.08 – 1.83 (m, 1H), 1.35 – 1.11 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR for the TFA salt (101 MHz, CDCl3) δ 200.16, 176.70, 175.23, 147.25, 137.46, 130.66, 130.15, 123.02, 120.46, 106.48, 67.83, 38.01, 34.36, 21.68, 14.24; HRMS (ESI) m/z: calculated for $C_{15}H_{15}NO^+$ $[M + H]^+$: 352.0195, found: 352.0192.



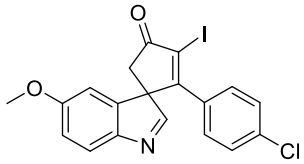
2-propylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2h)

Brown amorphous solid; R_f=0.32 (Heptane/Ethyl acetate 1:1); Yield 99%; IR (neat, cm^{-1}): 2928.74, 1709.79, 1581.17, 1544.28, 1447.85, 1207.15, 897.41, 757.83, 514.90, 424.30; ^{1}H NMR NMR for the TFA salt (600 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 3.44 (d, *J* = 19.0 Hz, 1H), 2.90 (d, *J* = 19.0 Hz, 1H), 2.33 – 2.24 (m, 1H), 1.72 – 1.55 (m, 3H), 1.50 – 1.40 (m, 2H), 1.31 – 1.13 (m, 2H), 1.13 – 0.94 (m, 3H); ^{13}C NMR NMR for the TFA salt (151 MHz, CDCl3) δ 200.30, 178.32, 177.02, 143.15, 137.64, 131.25, 131.16, 123.57, 119.98, 105.75, 67.50, 44.63, 38.24, 29.61, 29.30, 25.79, 25.72, 24.98. HRMS (ESI) m/z: calculated for $C_{15}H_{15}NO^+$ $[M + H]^+$: 392.0508, found: 392.0506.



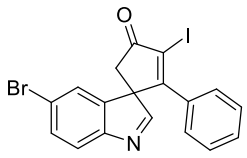
5'-methoxy-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2i)

Brown solid; R_f=0.21 (Heptane/Ethyl acetate 1:1); Yield 84%; mp 183-185 °C; IR (neat, cm^{-1}): 2933.84, 1705.06, 1578.27, 1472.83, 1288.31, 1211.12, 1151.24, 1027.58, 933.49, 867.66, 817.03, 729.42, 691.94, 515.90, 449.25; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.23 – 7.16 (m, 2H), 6.99 – 6.94 (m, 2H), 6.91 – 6.83 (m, 2H), 3.81 (s, 3H), 3.22 (d, *J* = 18.8 Hz, 1H), 2.91 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 200.19, 174.57, 169.30, 159.66, 148.83, 140.41, 133.51, 130.25, 128.37, 126.53, 122.36, 114.23, 107.90, 105.06, 68.85, 55.84, 39.18; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO_2^+$ $[M + H]^+$: 416.0144, found: 416.0135.



2-(4-chlorophenyl)-3-iodo-5'-methoxyspiro[cyclopentane-1,3'-indol]-2-en-4-one (2j)

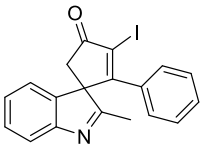
Yellow amorphous solid; R_f=0.23 (Heptane/Ethyl acetate 1:1); Yield 76%; IR (neat, cm^{-1}): 1710.25, 1592.57, 1486.14, 1471.31, 1279.48, 1208.35, 1093.49, 1013.47, 908.03, 832.54, 730.98, 513.21; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.22 – 7.16 (m, 2H), 6.95 – 6.88 (m, 3H), 6.82 (d, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 3.22 (d, *J* = 18.9 Hz, 1H), 2.91 (d, *J* = 18.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.95, 173.14, 169.03, 159.80, 148.82, 140.19, 136.46, 131.84, 128.85, 128.05, 122.64, 114.28, 108.00, 107.96, 105.56, 68.75, 39.14; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO_2^+$ $[M + H]^+$: 449.9754, found: 449.9760.



5'-bromo-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2k)

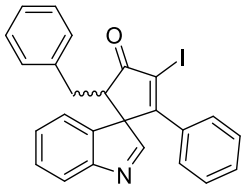
Brown amorphous solid; R_f=0.26 (Heptane/Ethyl acetate 1:1); Yield 99%; IR (neat, cm^{-1}): 1712.02, 1547.97, 1449.17, 1197.51, 901.98, 870.40, 742.10, 697.29, 511.85; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.34 (m, 1H), 7.37 – 7.22 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 3.24 (d, *J* = 18.7 Hz, 1H), 2.94 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 200.10, 174.52, 171.49, 155.16, 138.62, 133.51, 130.20, 129.35,

128.33, 127.59, 126.42, 121.91, 121.77, 105.16, 68.83, 38.73; HRMS (ESI) m/z: calculated for $C_{18}H_{12}BrNO^+$ [M + H]$^+$: 463.9144, found: 463.9142; 465.9149.



2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2l)

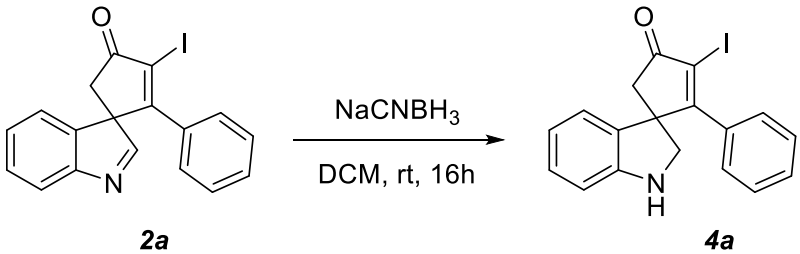
Brown solid; R_f=0.21 (Heptane/Ethyl acetate 1:1); Yield 99%; mp 182-184 °C; IR (neat, cm^{-1}): 1700.88, 1563.17, 1426.58, 1196.67, 922.26, 761.03, 740.46, 693.61, 507.42, 451.13; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.34 – 7.24 (m, 2H), 7.27 – 7.15 (m, 3H), 6.93 – 6.85 (m, 2H), 3.03 (d, *J* = 18.8 Hz, 1H), 2.96 (d, *J* = 18.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 200.43, 180.25, 175.09, 154.95, 139.59, 133.38, 130.46, 129.36, 128.47, 126.56, 121.92, 120.69, 104.97, 69.62, 41.21, 15.86; HRMS (ESI) m/z: calculated for $C_{19}H_{15}NO^+$ [M + H]$^+$: 400.0195, found: 400.0196.



5-benzyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2m)

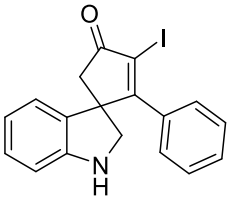
Light-brown amorphous solid; Isolated as an inseparatable mixture of diastereomers (approx. 3:2 ratio A/B according ^{1}H NMR); R_f=0.38 (Heptane/Ethyl acetate 1:1); Yield 98%; IR (neat, cm^{-1}): 1714.61, 1546.31, 1450.79, 1171.74, 1030.17, 752.42, 697.44, 523.92; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (s), 7.78 (s), 7.46 – 7.44 (m), 7.42 – 7.35 (m), 7.27 – 7.19 (m), 7.17 – 7.12 (m), 7.02 – 6.97 (m), 6.92 – 6.89 (m), 6.88 – 6.86 (m), 6.78 – 6.75 (m), 6.46 (d, *J* = 7.4 Hz), 3.64 – 3.61 (m), 3.38 – 3.30 (m), 2.62 (d, *J* = 14.9 Hz), 2.61 (d, *J* = 14.9 Hz), 2.25 (d, *J* = 14.4 Hz), 2.23 (d, *J* = 14.5 Hz); ^{13}C NMR (151 MHz, CDCl3) δ 201.06, 200.93, 173.79, 173.18, 171.19, 170.15, 156.59, 155.44, 138.20, 137.13, 137.08, 135.40, 133.53, 133.43, 130.15, 130.00, 129.58, 129.05, 128.36, 128.33, 128.21, 128.19, 128.06, 128.04, 127.19, 126.81, 126.50, 126.48, 126.47, 126.42, 123.45, 122.28, 121.84, 121.77, 104.70, 103.07, 73.26, 72.72, 54.55, 50.39, 33.16, 32.43; HRMS (ESI) m/z: calculated for $C_{25}H_{19}NO^+$ [M + H]$^+$: 476.0507, found: 476.0505.

Procedure C for the reduction of the spiroindolenine 2a



2a ***4a***

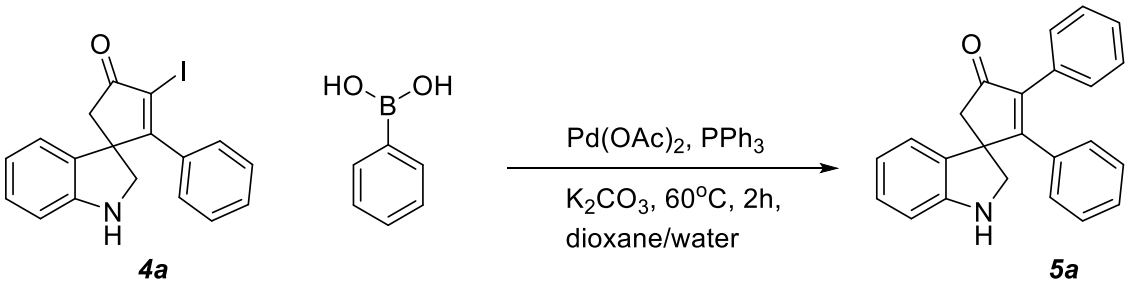
Spiroindolenine **2a** (0.3 mmol) was dissolved in dichloromethane (6 ml) followed by thy addition of sodium cyanoborohydride (2 equiv, 0.6 mmol). The solution was degassed, flushed with nitrogen and allowed to stir at rt for 16h. Then the reaction was dissolved in ethyl acetate (50 ml) and washed with water (50 ml) and brine (50 ml). Organic layer was dried under Na_2SO_4 and concentrated *in vacuo*. Purification was performed by column chromatography (20-30% of ethyl acetate in heptane) affording the spiroindoline **4a**.



5-benzyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (4a)

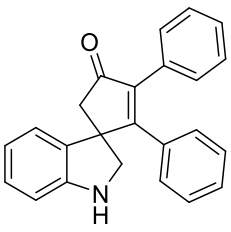
Light-brown amorphous solid; R_f=0.25 (Heptane/Ethyl acetate 1:1); Yield 67%; IR (neat, cm^{-1}): 1704.03, 1602.67, 1487.39, 1410.28, 1242.80, 1177.01, 1028.40, 907.85, 733.19, 696.89, 505.23, 455.15; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 3H), 7.17 – 7.11 (m, 1H), 7.09 – 7.04 (m, 1H), 6.97 – 6.91 (m, 2H), 6.86 – 6.80 (m, 1H), 6.63 – 6.58 (m, 1H), 3.74 (d, *J* = 9.9 Hz, 1H), 3.56 (d, *J* = 9.9 Hz, 1H), 3.15 (d, *J* = 18.7 Hz, 1H), 2.96 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl3) δ 202.08, 179.85, 150.92, 135.30, 130.59, 129.53, 129.34, 128.25, 127.53, 122.94, 119.79, 110.47, 104.24, 59.07, 57.15, 49.95; HRMS (ESI) m/z: calculated for $C_{25}H_{19}NO^+$ $[M + H]^+$: 388.0194, found: 388.0190.

Procedure D for the Suzuki reaction



4a ***5a***

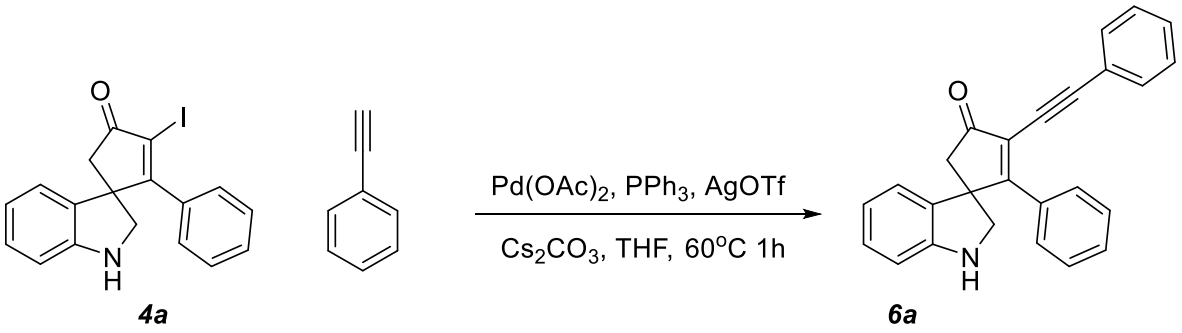
The spiroindoline **4a** (0.3 mmol), phenylboronic acid (2 equiv, 0.6 mmol), palladium acetate (0.1 equiv, 0.03 mmol), triphenylphosphine (0.2 equiv, 0.06 mmol) and potassium carbonate (2 equiv, 0.6 mmol) were dissolved in dioxane/water 4:1 (3 ml). The solution was degassed and flushed with nitrogen and subjected to stirring at 60ºC for 2 h. Then the reaction mixture was diluted with ethyl acetate (50 ml) and washed with water (50 ml) and brine (50 ml). Organic layer was dried under Na_2SO_4 and concentrated *in vacuo*. Purification was performed by column chromatography (20-30% of ethyl acetate in heptane) affording **5a**.



2,3-diphenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one (5a)

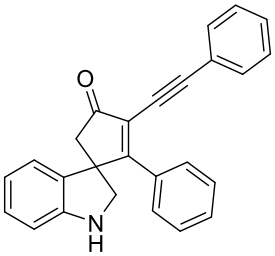
Light-brown amorphous solid; R_f=0.25 (Heptane/Ethyl acetate 1:1); Yield 97%; IR (neat, cm^{-1}): 1690.34, 1599.78, 1484.78, 1342.69, 1250.98, 1160.70, 1028.54, 740.82, 692.76, 513.31; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 6H), 7.17 – 7.09 (m, 4H), 6.88 – 6.79 (m, 3H), 6.67 (d, *J* = 7.8 Hz, 1H), 3.81 (d, *J* = 9.7 Hz, 1H), 3.61 (d, *J* = 9.8 Hz, 1H), 3.08 (d, *J* = 18.7 Hz, 1H), 3.00 (d, *J* = 18.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 205.92, 171.36, 151.09, 139.95, 134.81, 132.59, 131.23, 129.88, 128.92, 128.87, 128.78, 128.19, 128.13, 127.91, 122.78, 119.72, 110.29, 77.43, 77.11, 76.80, 57.18, 55.33, 53.49; HRMS (ESI) m/z: calculated for $C_{25}H_{19}NO^+$ $[M + H]^+$: 338.1539, found: 338.1540.

Procedure E for the Sonogashira reaction



4a ***6a***

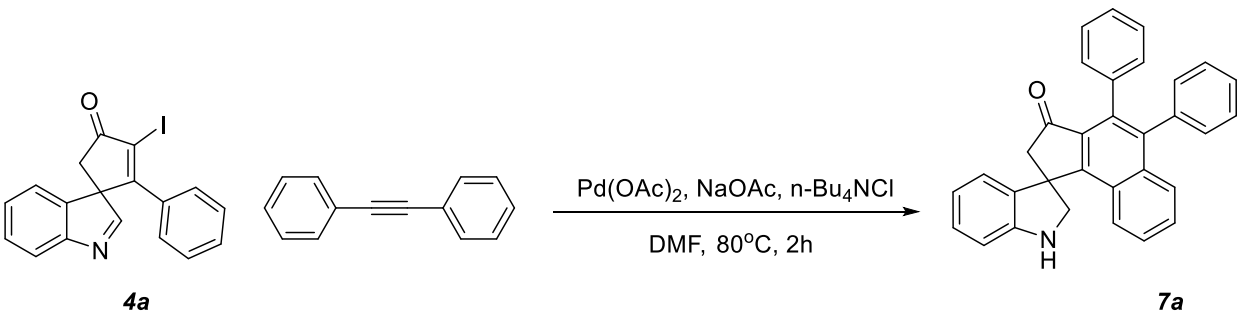
The spiroindoline **4a** (0.3 mmol), phenylacetylene (2 equiv, 0.6 mmol), palladium acetate (0.05 equiv, 0.015 mmol), triphenylphosphine (0.1 equiv, 0.03 mmol), silver triflate (0.1 equiv, 0.03 mmol) and cesium carbonate (2 equiv, 0.6 mmol) were dissolved in THF (3 ml). The solution was degassed and flushed with nitrogen and allowed to stir at 60ºC for 1 h. Then the reaction mixture was diluted with ethyl acetate (50 ml) and washed with water (50 ml) and brine (50 ml). Organic layer was dried under Na_2SO_4 and concentrated *in vacuo*. Purification was performed by column chromatography (20-30% of ethyl acetate in heptane) affording **6a**.



2-phenyl-3-(phenylethynyl)spiro[cyclopentane-1,3'-indolin]-2-en-4-one (6a)

Light-brown amorphous solid; R_f=0.26 (Heptane/Ethyl acetate 1:1); Yield 94%; IR (neat, cm^{-1}): 1704.17, 1599.21, 1484.79, 1348.01, 1202.99, 1028.67, 746.56, 688.75, 522.90; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.52 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.29 (m, 6H), 7.18 – 7.13 (m, 1H), 7.04 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.91 (d, *J* = 9.8 Hz, 1H), 3.58 (d, *J* = 9.8 Hz, 1H), 3.02 – 2.91 (m, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 203.45, 174.29, 150.45, 133.69, 132.84, 131.90, 131.51, 130.24, 129.17, 128.97, 128.83, 128.35, 128.28, 128.17, 128.10, 126.48, 125.06, 122.72, 122.56, 119.79, 110.17, 98.10, 81.49, 58.23, 55.71, 53.65; HRMS (ESI) m/z: calculated for $C_{25}H_{19}NO^+$ $[M + H]^+$: 362.1539, found: 362.1532.

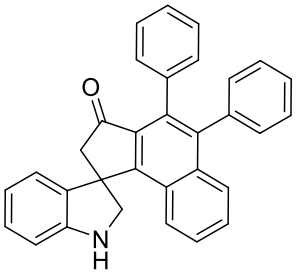
Procedure F for the alkyne carboannulation



4a ***7a***

The spiroindoline **4a** (0.3 mmol), diphenylacetylene (2 equiv, 0.6 mmol), palladium acetate (0.05 equiv, 0.015 mmol), sodium acetate (2 equiv, 0.6 mmol) and tetra-*n*-butylammonium chloride were dissolved in

DMF (3 ml). The solution was degassed and flushed with nitrogen and allowed to stir at 80ºC for 2 h. Then the reaction mixture was diluted with ethyl acetate (50 ml) and washed with water (50 ml) and brine (50 ml). Organic layer was dried under Na_2SO_4 and concentrated *in vacuo*. Purification was performed by column chromatography (20-30% of ethyl acetate in heptane) affording **7a**.



4,5-diphenylspiro[cyclopenta[a]naphthalene-1,3'-indolin]-3(2H)-one (7a)

Brown amorphous solid; R_f=0.28 (Heptane/Ethyl acetate 1:1); Yield 74%; IR (neat, cm^{-1}): 1704.20, 1602.05, 1486.82, 1409.65, 1243.20, 1176.35, 1027.81, 906.10, 728.54, 696.31, 504.82, 454.63; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 1H), 7.62 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.43 – 7.34 (m, 1H), 7.30 – 7.13 (m, 7H), 7.15 – 7.05 (m, 4H), 6.91 – 6.82 (m, 2H), 6.76 – 6.67 (m, 1H), 4.38 (d, *J* = 9.7 Hz, 1H), 3.76 (d, *J* = 9.7 Hz, 1H), 3.22 (d, *J* = 18.8 Hz, 1H), 2.99 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 203.42, 157.18, 150.27, 140.97, 137.95, 137.40, 136.98, 134.87, 134.45, 132.81, 131.03, 131.01, 130.02, 128.93, 128.71, 128.58, 128.42, 127.67, 127.59, 127.05, 126.83, 126.50, 126.34, 126.23, 123.14, 119.73, 110.07, 61.00, 56.30, 52.03; HRMS (ESI) m/z: calculated for $C_{25}H_{19}NO^+$ $[M + H]^+$: 438.1852, found: 438.1849.

References

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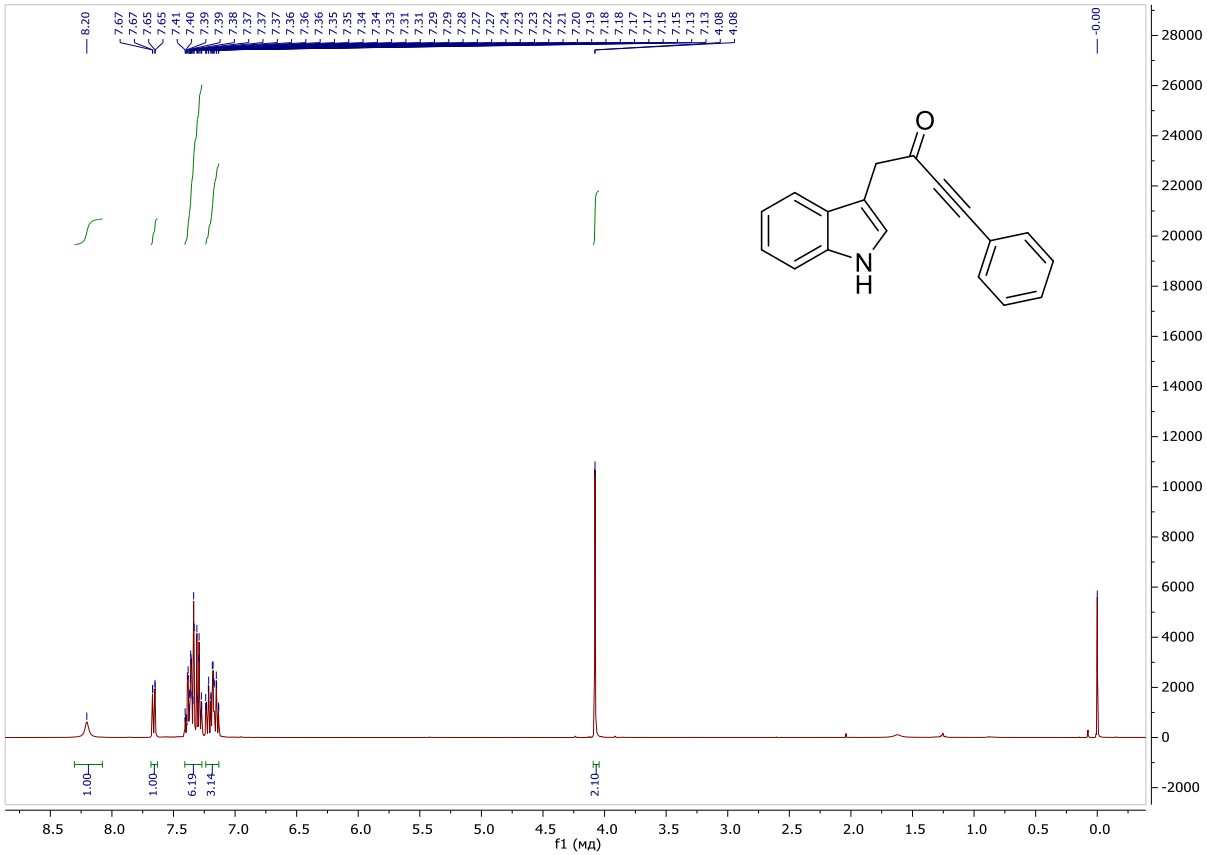
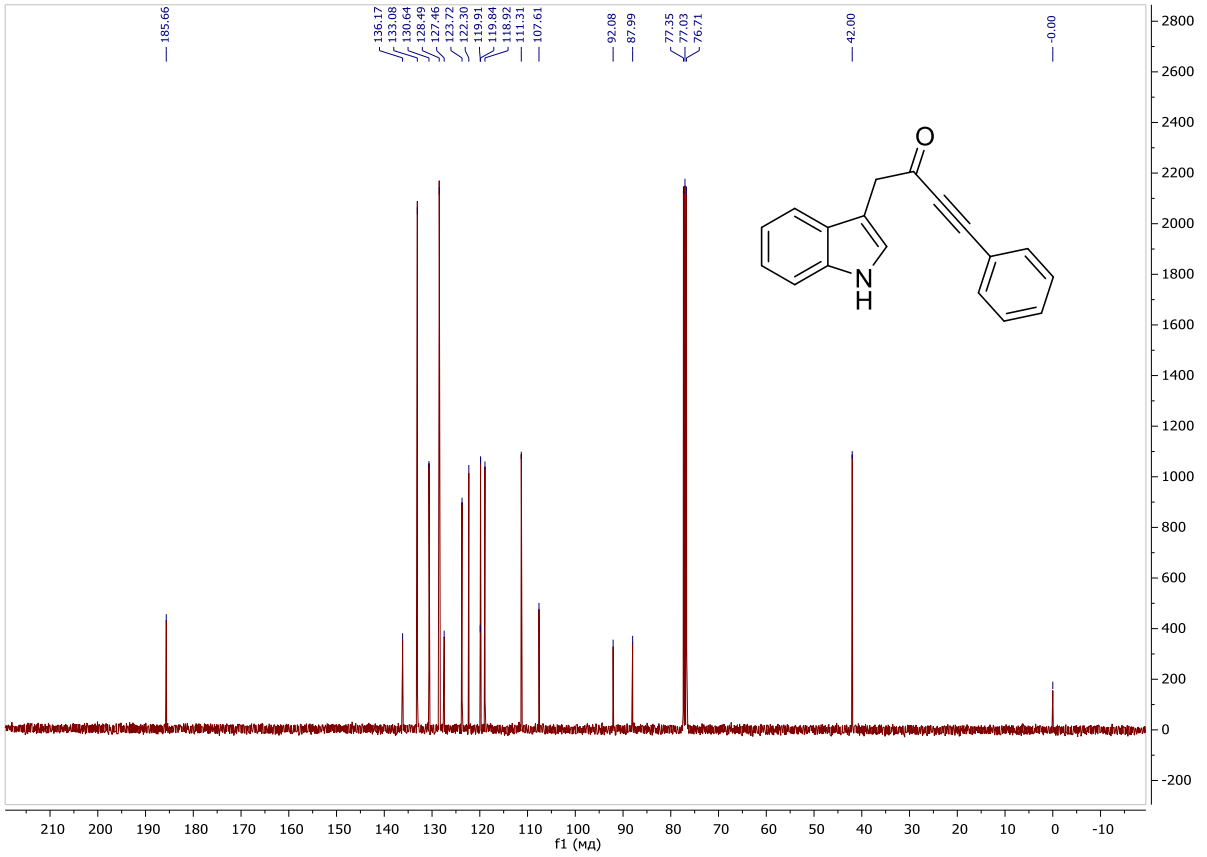
2 M. J. James, J. D. Cuthbertson, P. O'Brien, R. J. K. Taylor and W. P. Unsworth, *Angew. Chem. Int. Ed.*, 2015, **54**, 7640–7643.

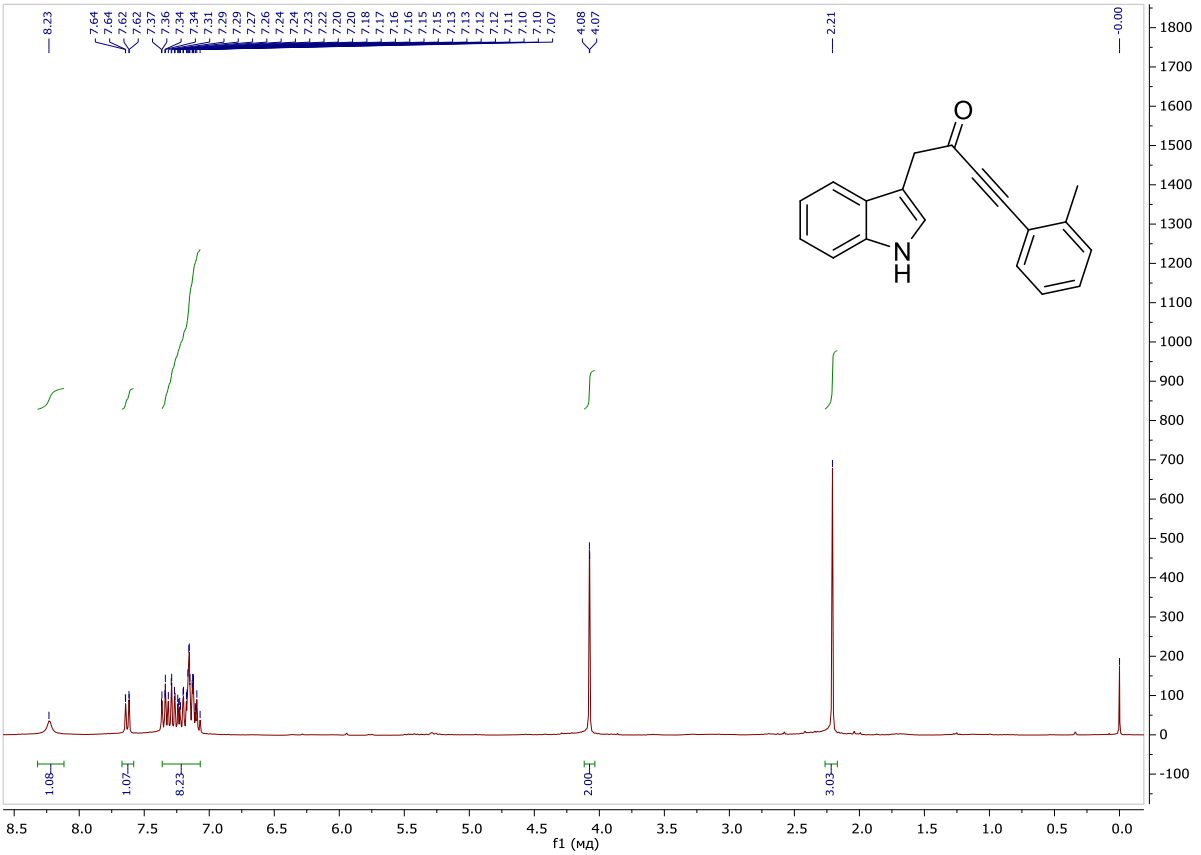
3 P. Wanga, J. Z. Zhaoa, H. F. Lia, X. M. Lianga, Y. L. Zhanga and C.S.Da, *Tetrahedron Letters* 2017, **58**, 129-133.

4 M. J. James, R. E. Clubley, K. Y. Palate, T. J. Procter, A. C. Wyton, P. O'Brien, R. J. K. Taylor and W. P. Unsworth, *Org. Lett.*, 2015, **17**, 4372–4375.

^{1}H and ^{13}C NMR spectra



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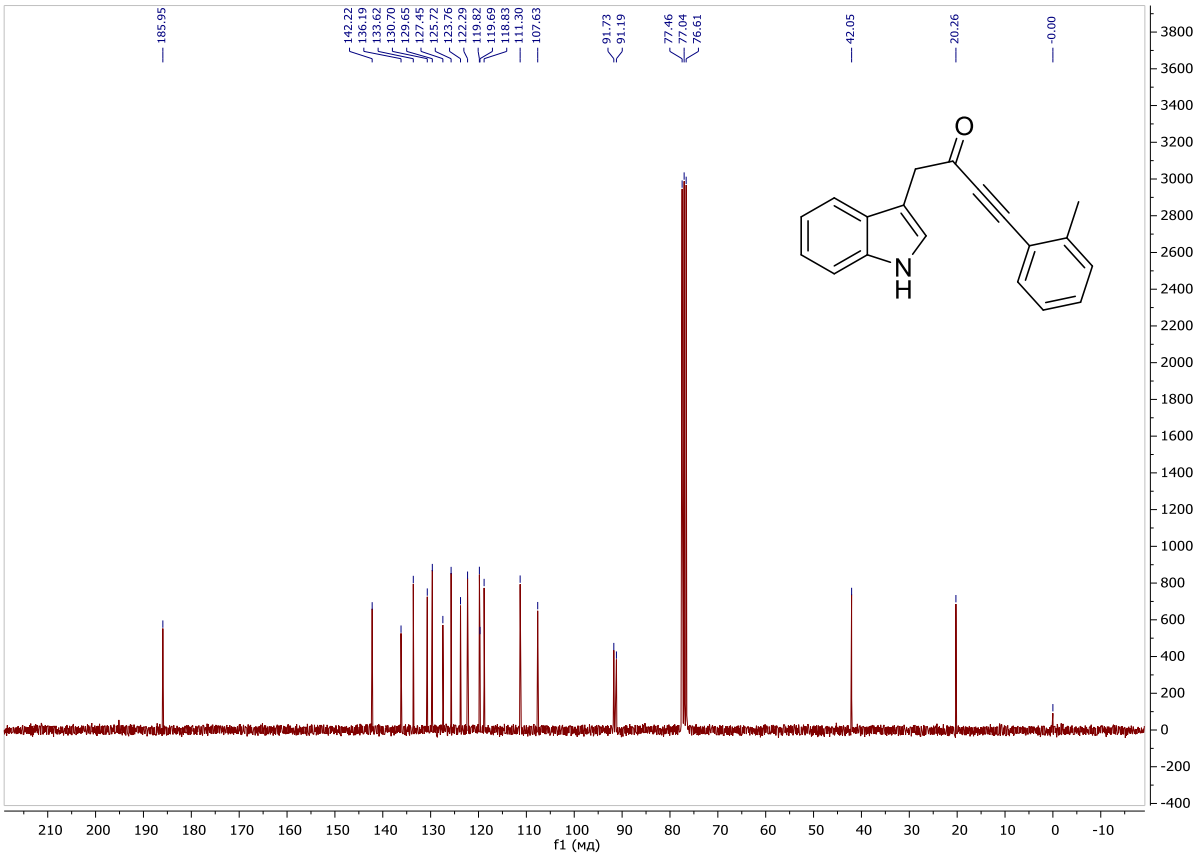
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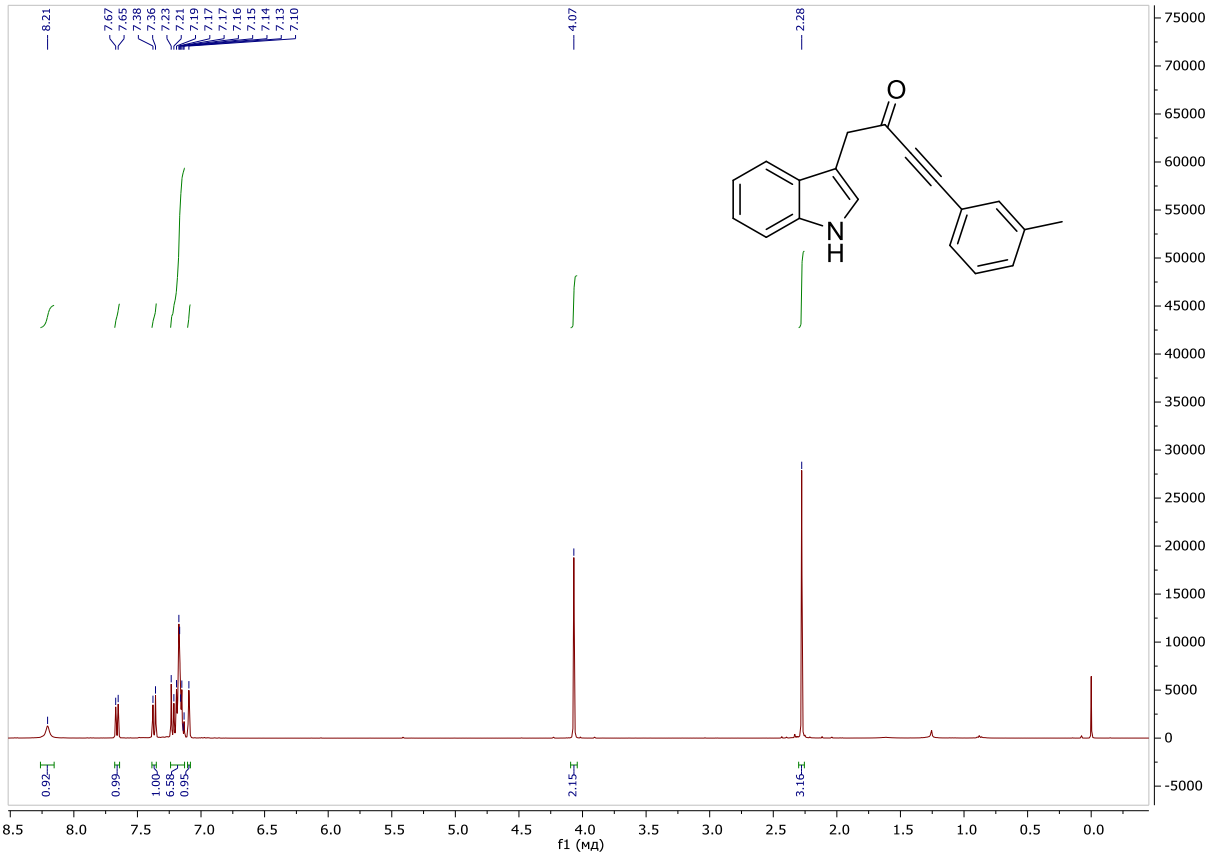
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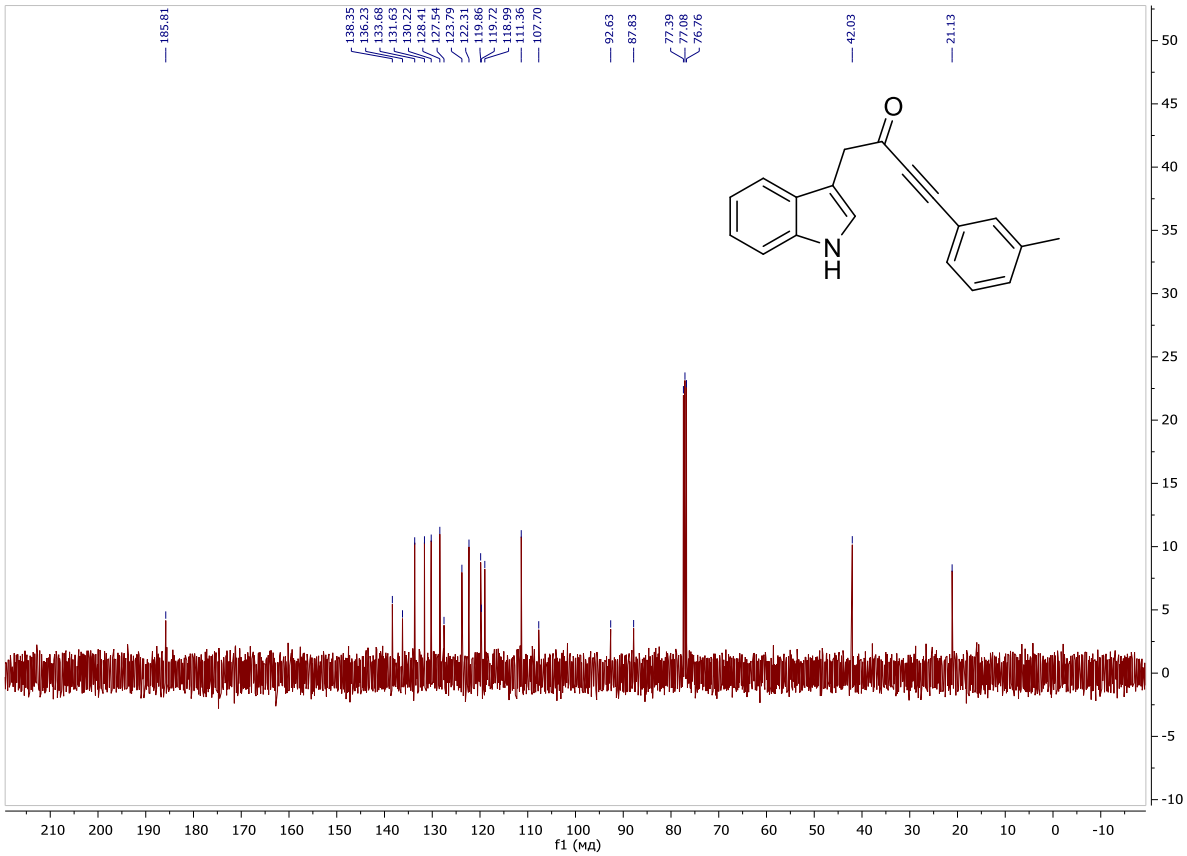
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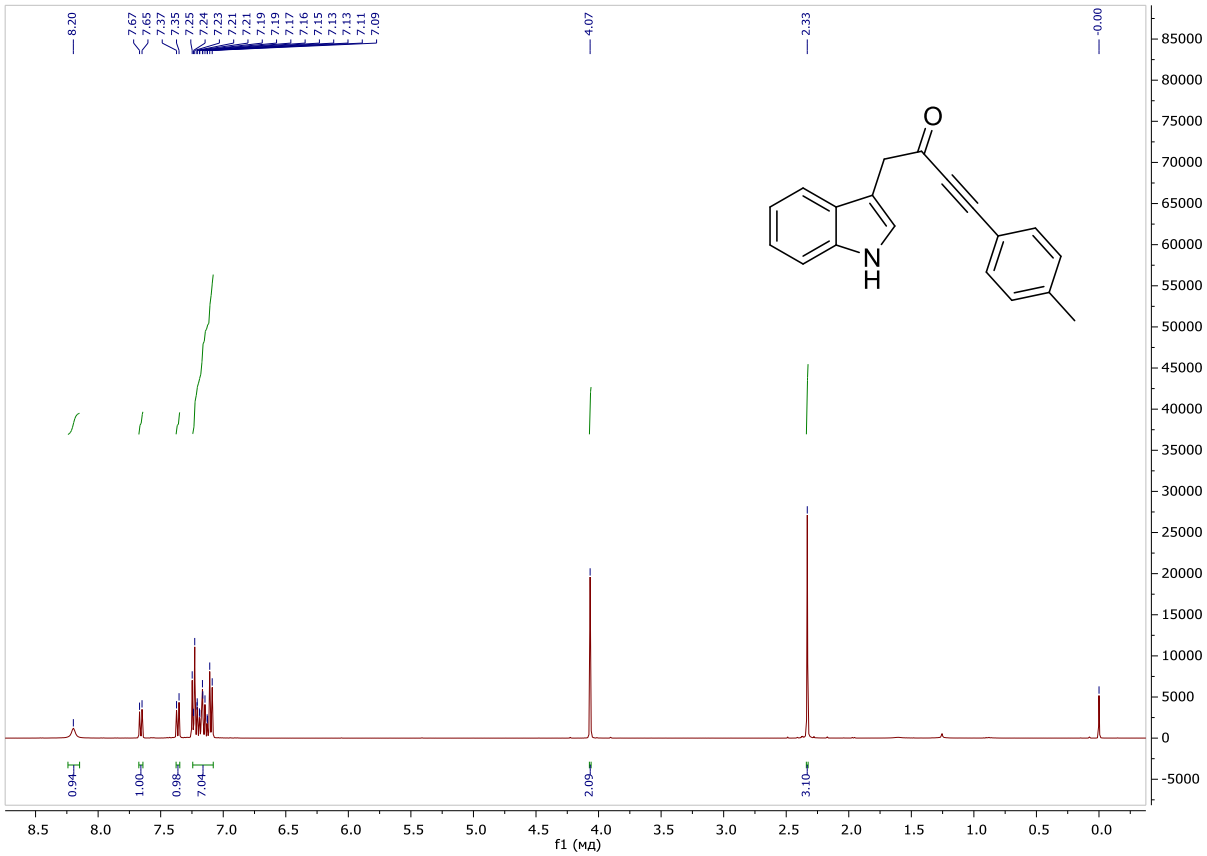
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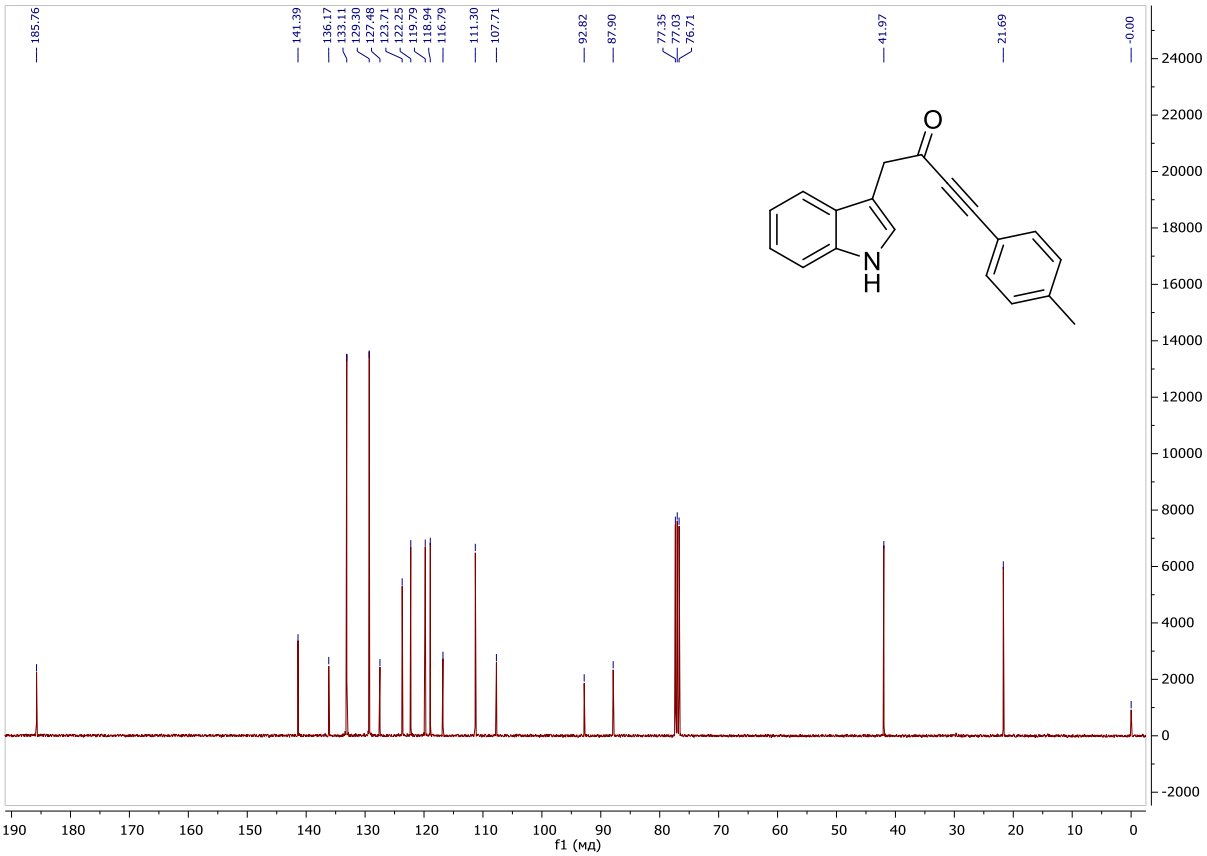
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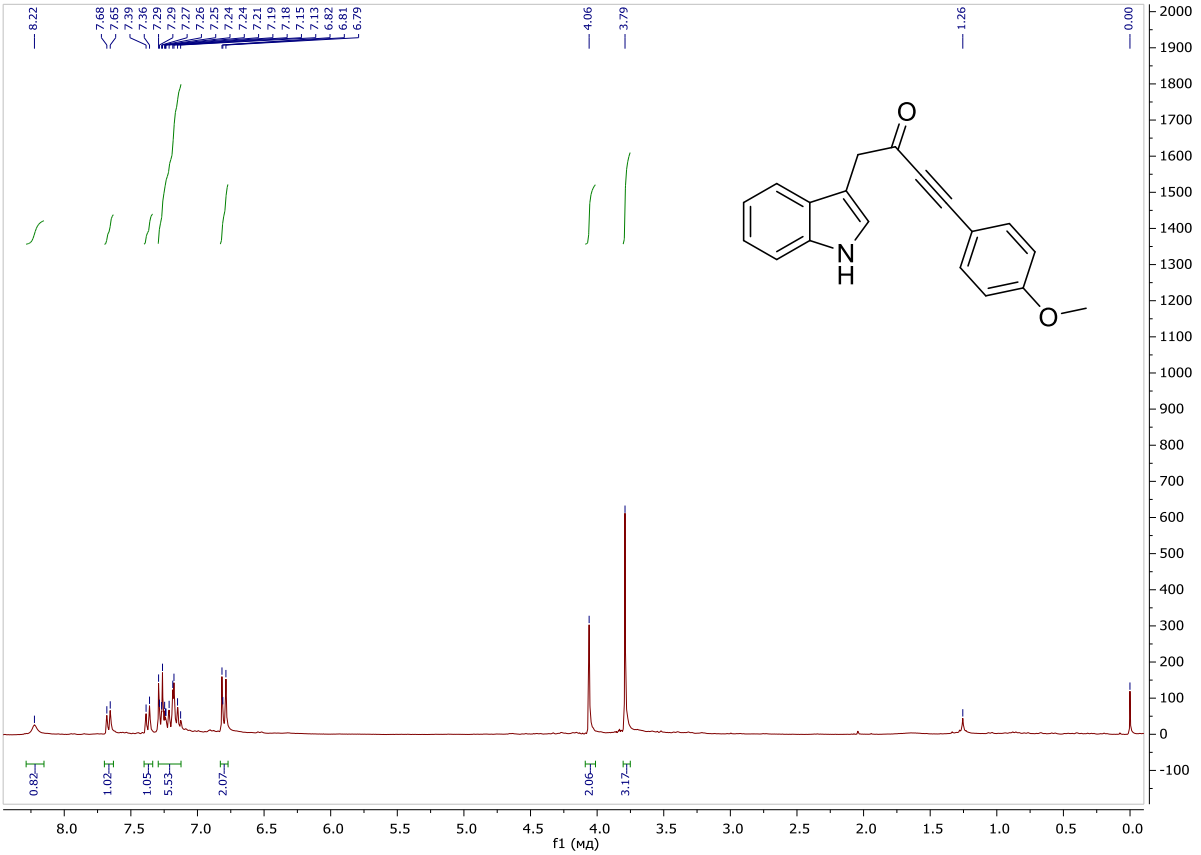
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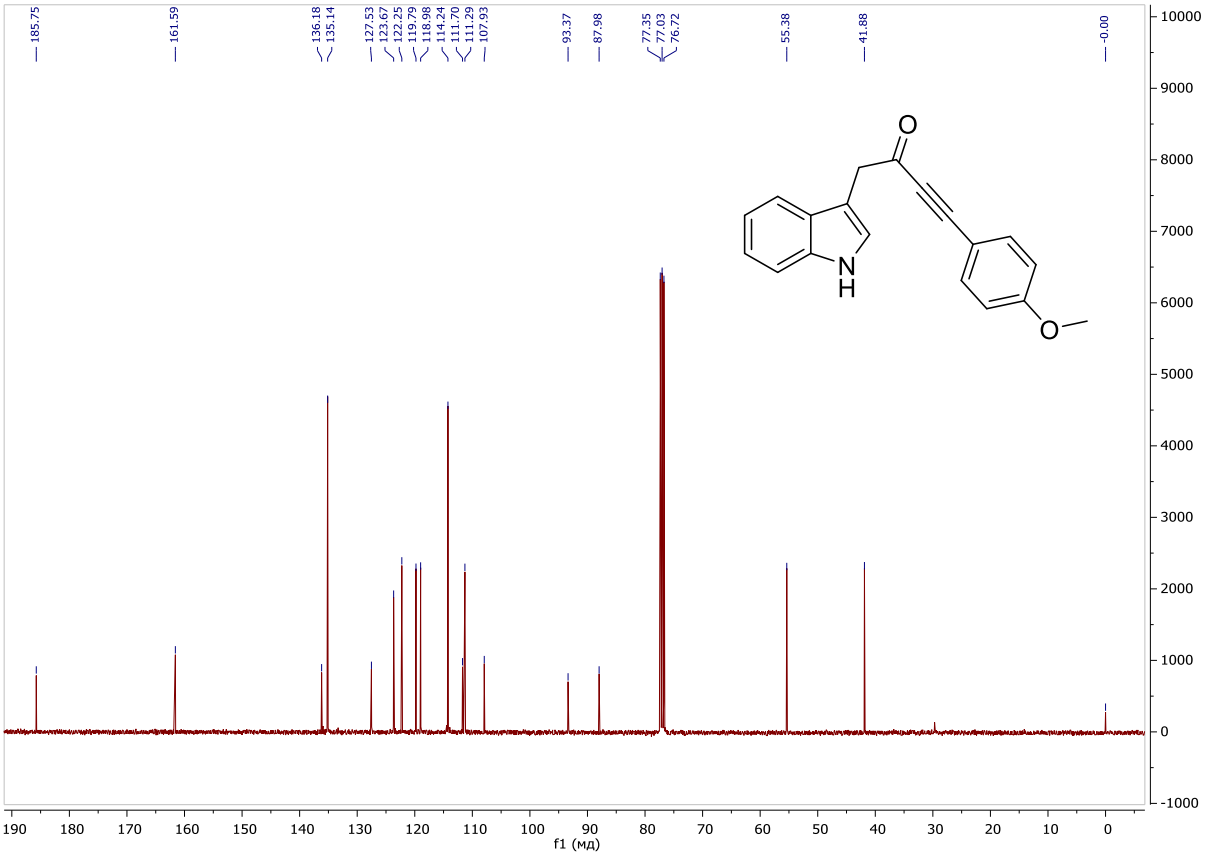
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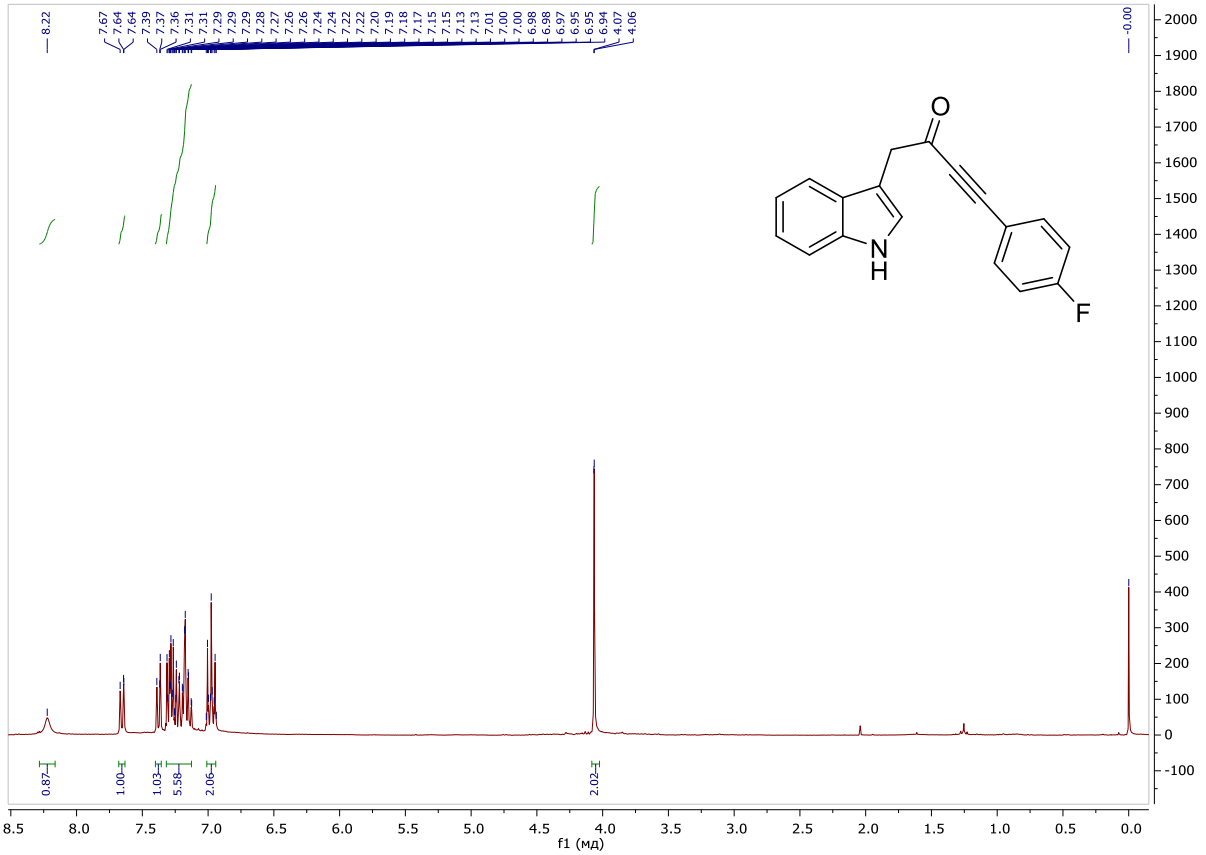
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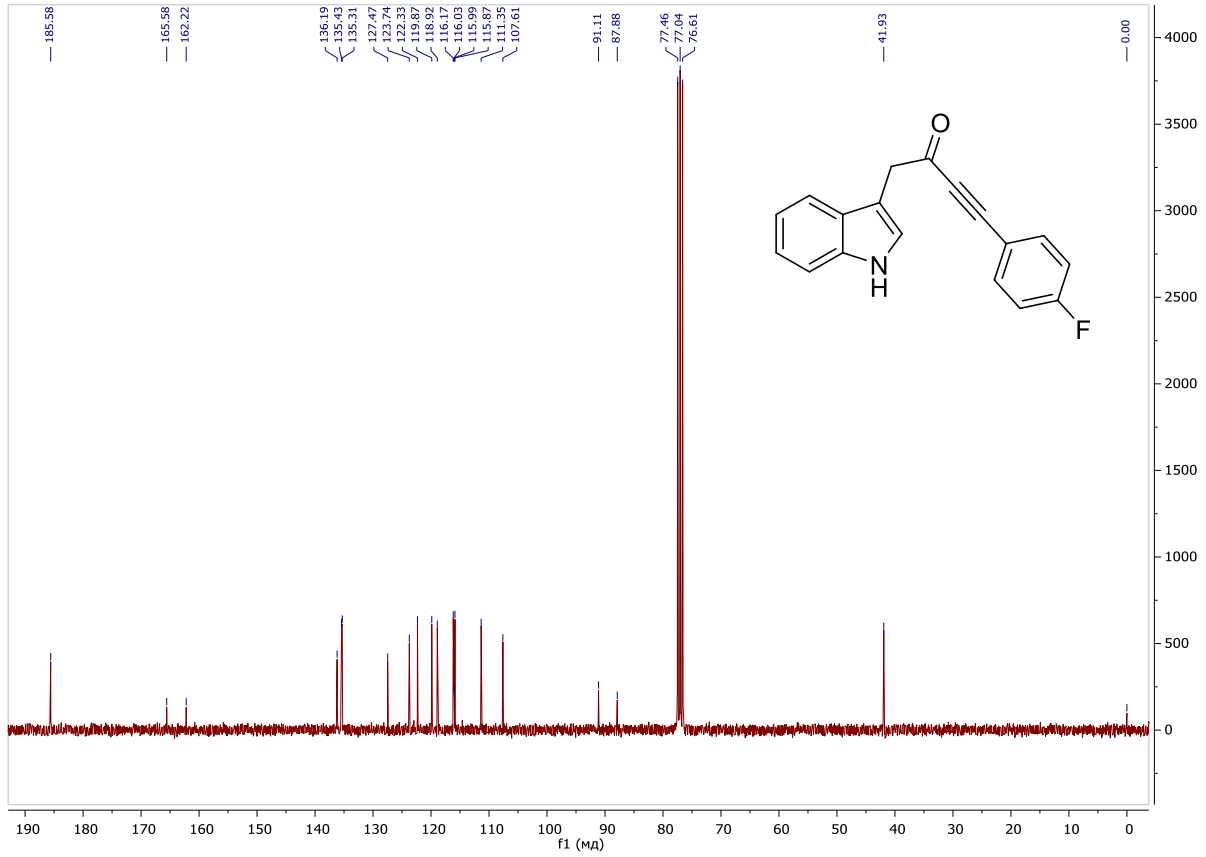
f1 (мд)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111.35
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77.04
76.61
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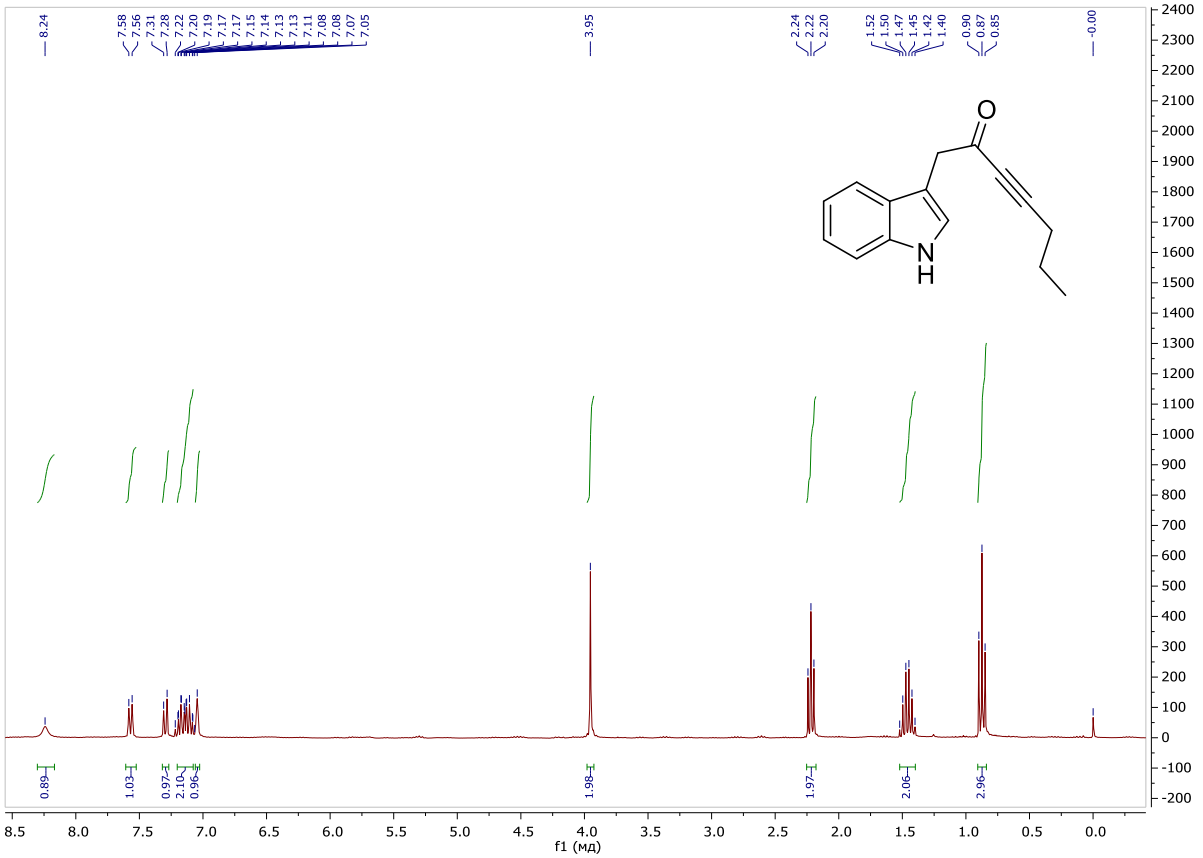
N
H
F
f1 (мд)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2.20
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1.50
1.47
1.45
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0.85
-0.00
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1.98
1.97
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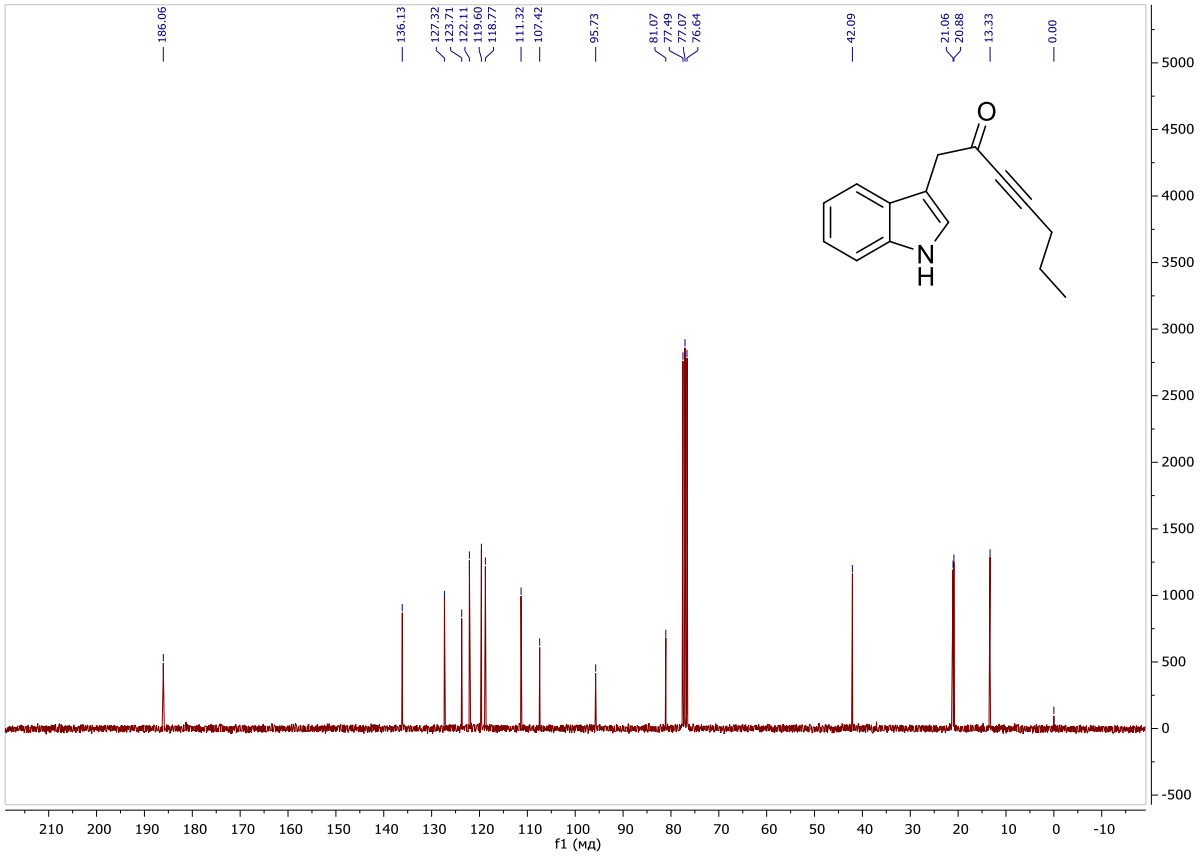
2.96
f1 (мд)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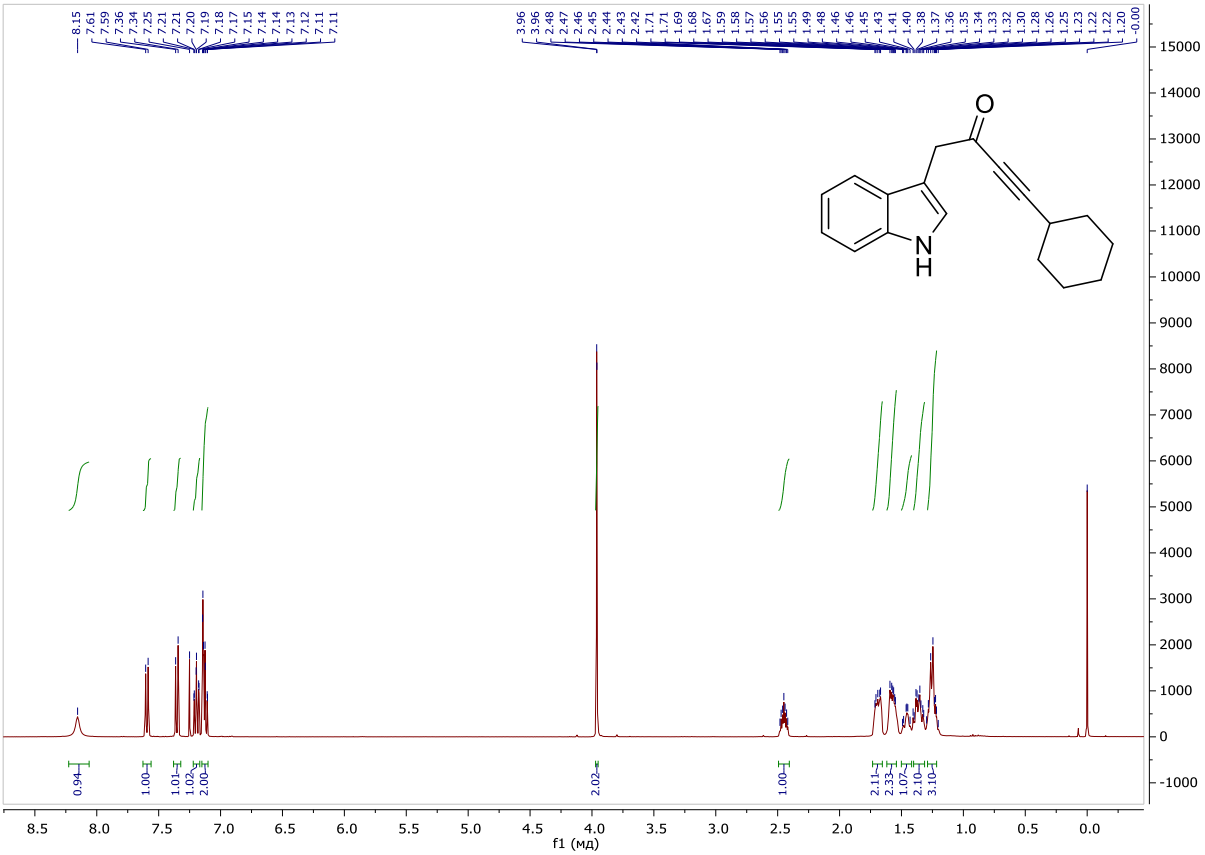
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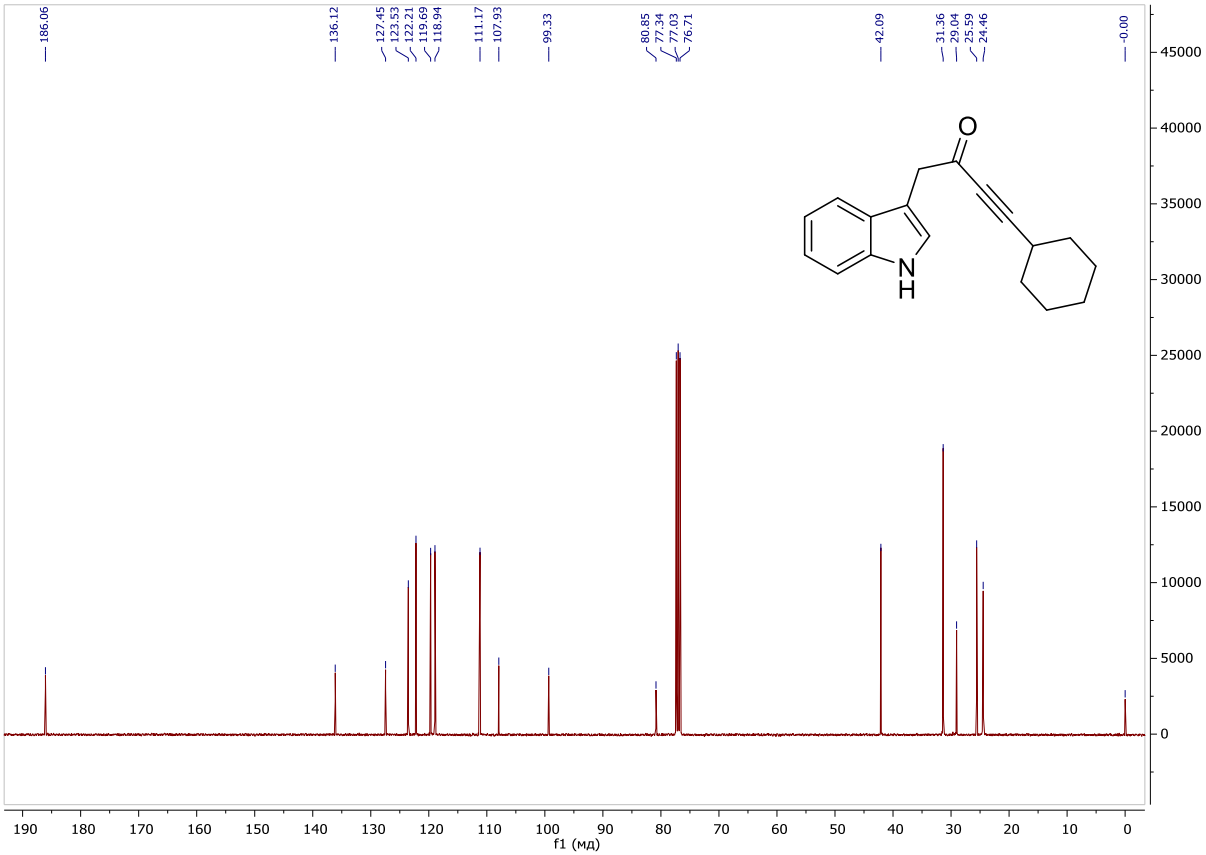
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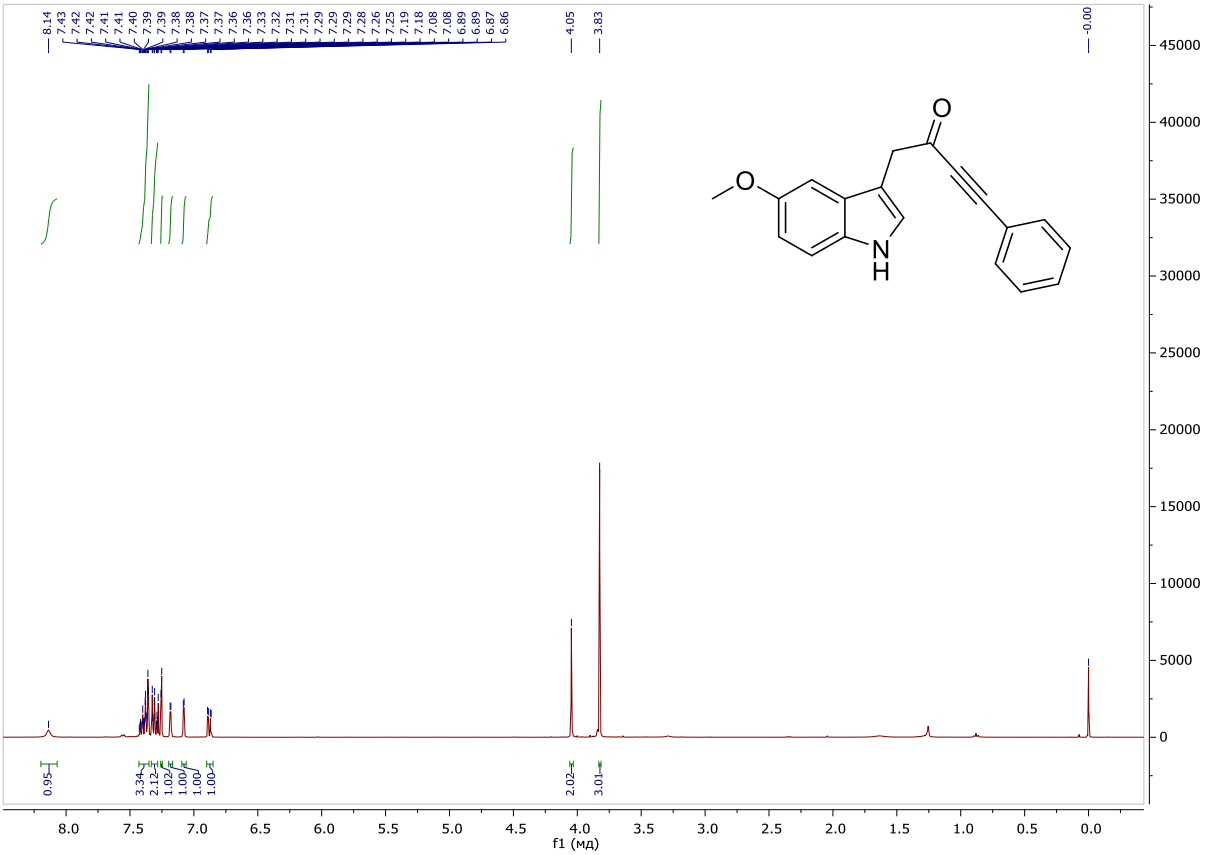
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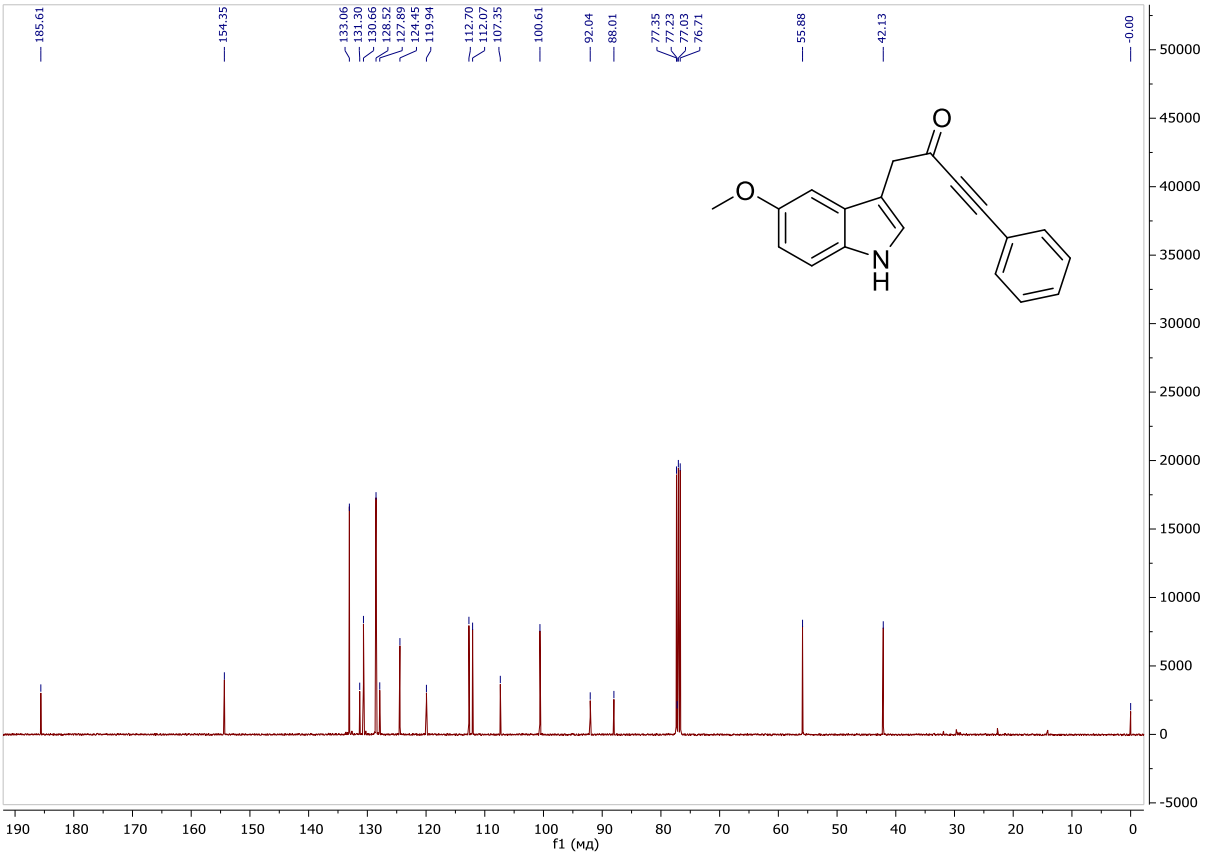
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92.04
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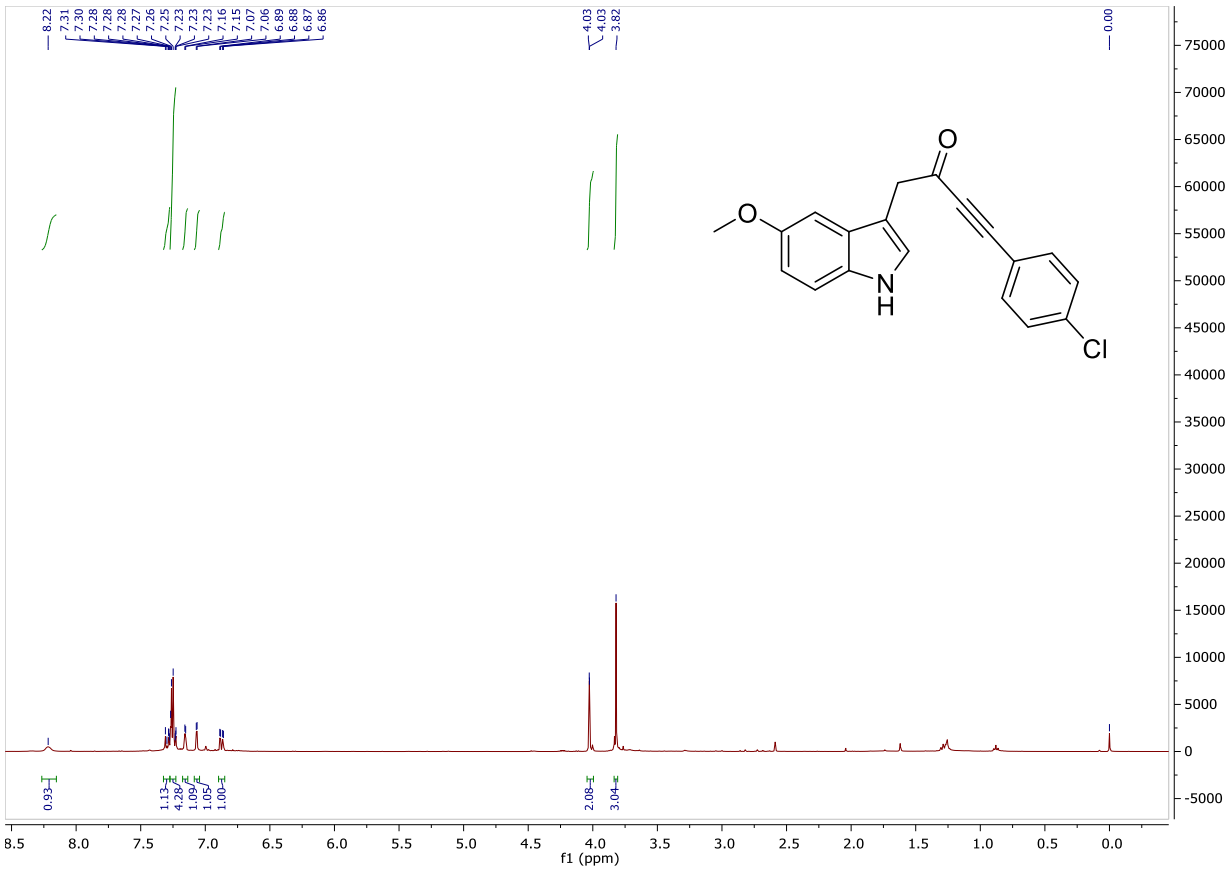
N
H
f1 (мд)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7.07
7.06
6.89
6.88
6.87
6.86
4.03
4.03
3.82
0.00
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1.09
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1.00
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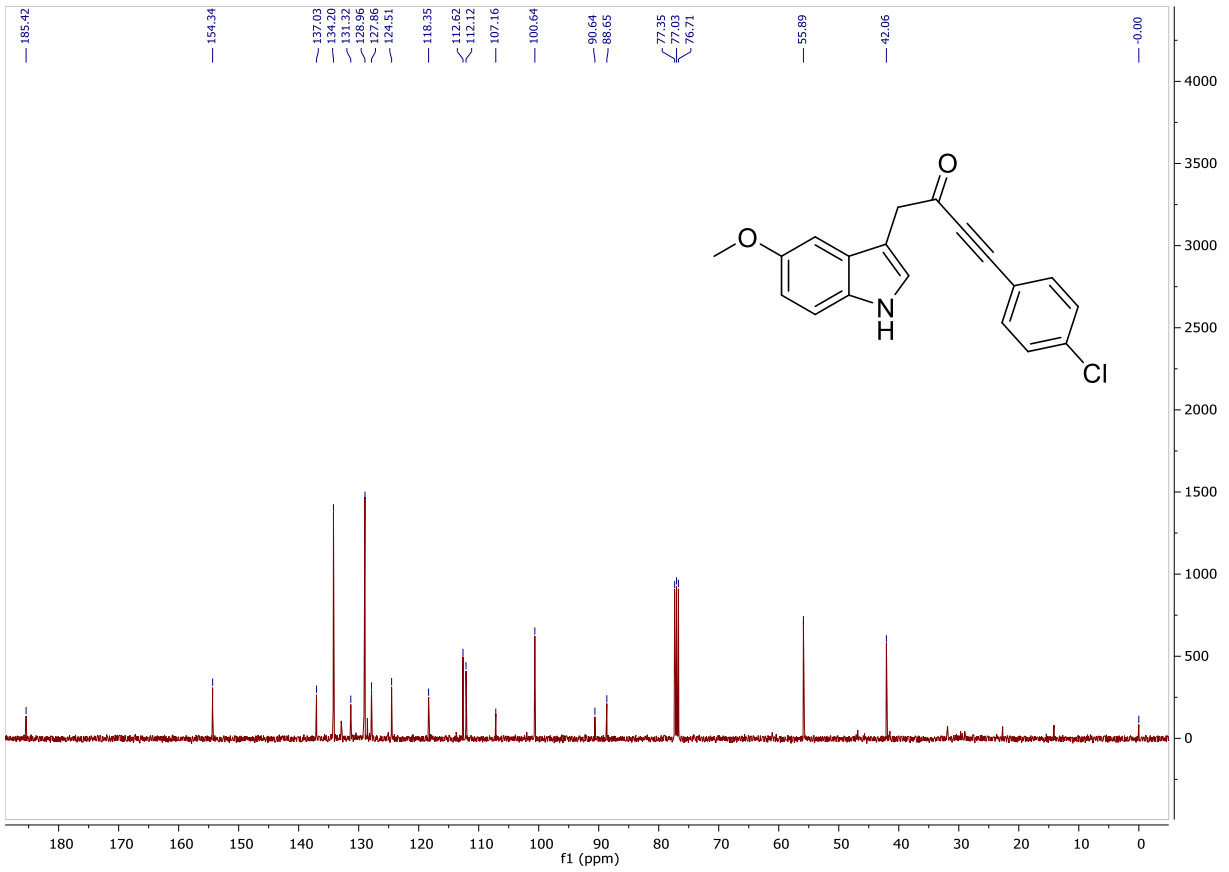
3.04
f1 (ppm)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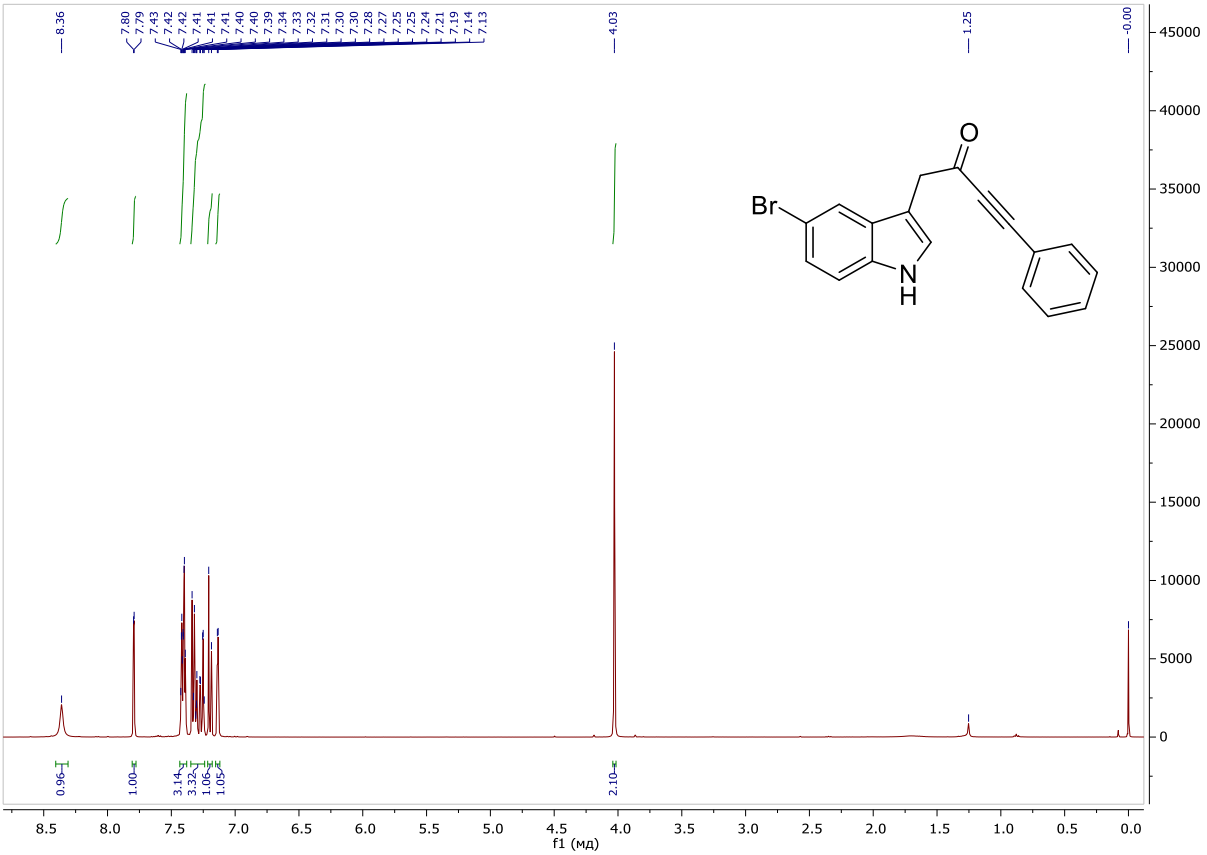
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4.03
1.25
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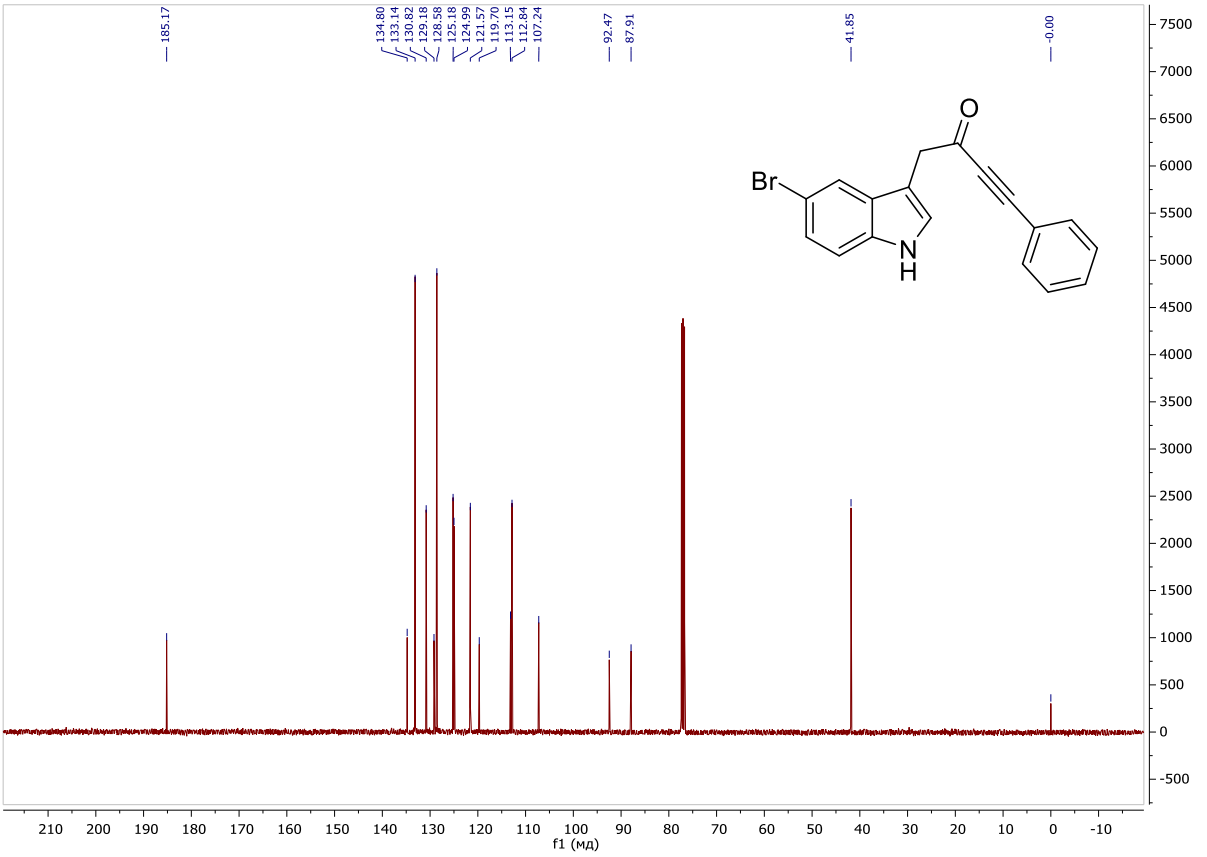
1.05
2.10
f1 (мд)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Br
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N
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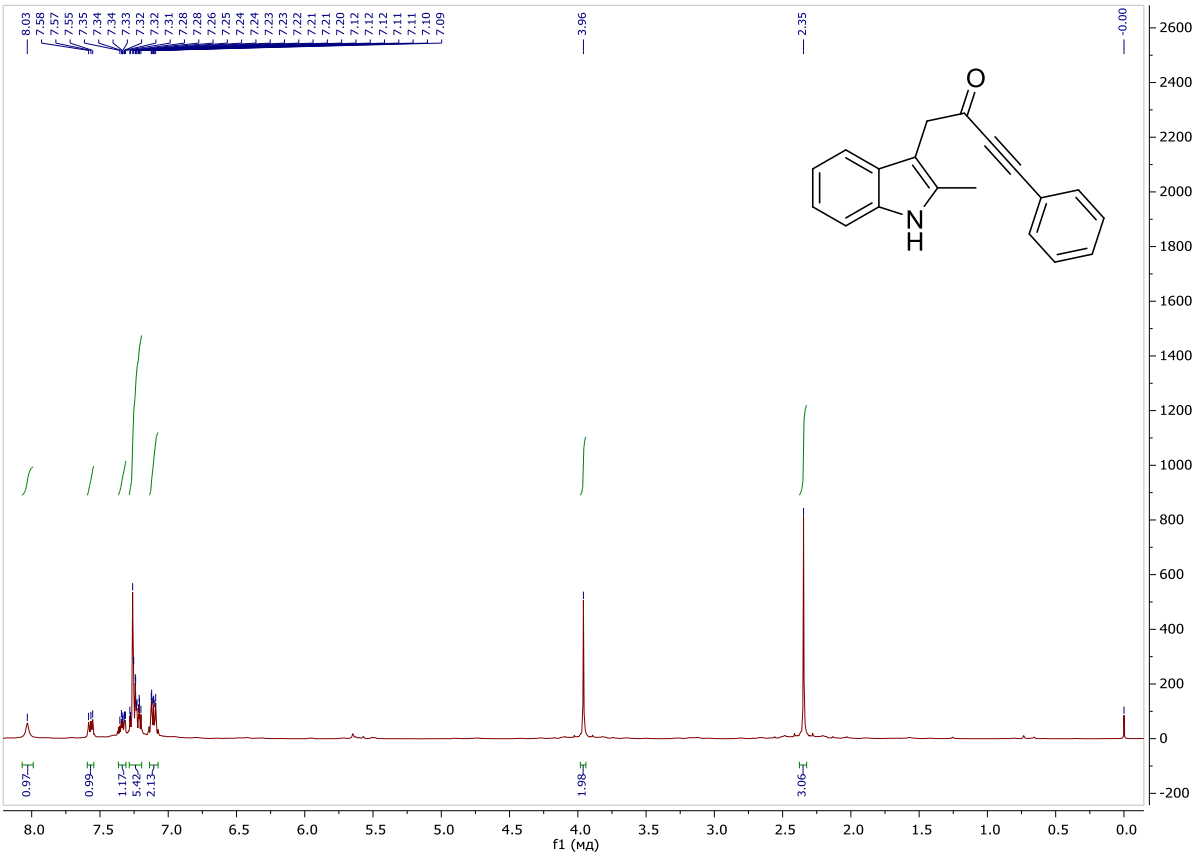
f1 (мд)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7.10
7.09
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N
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0.99
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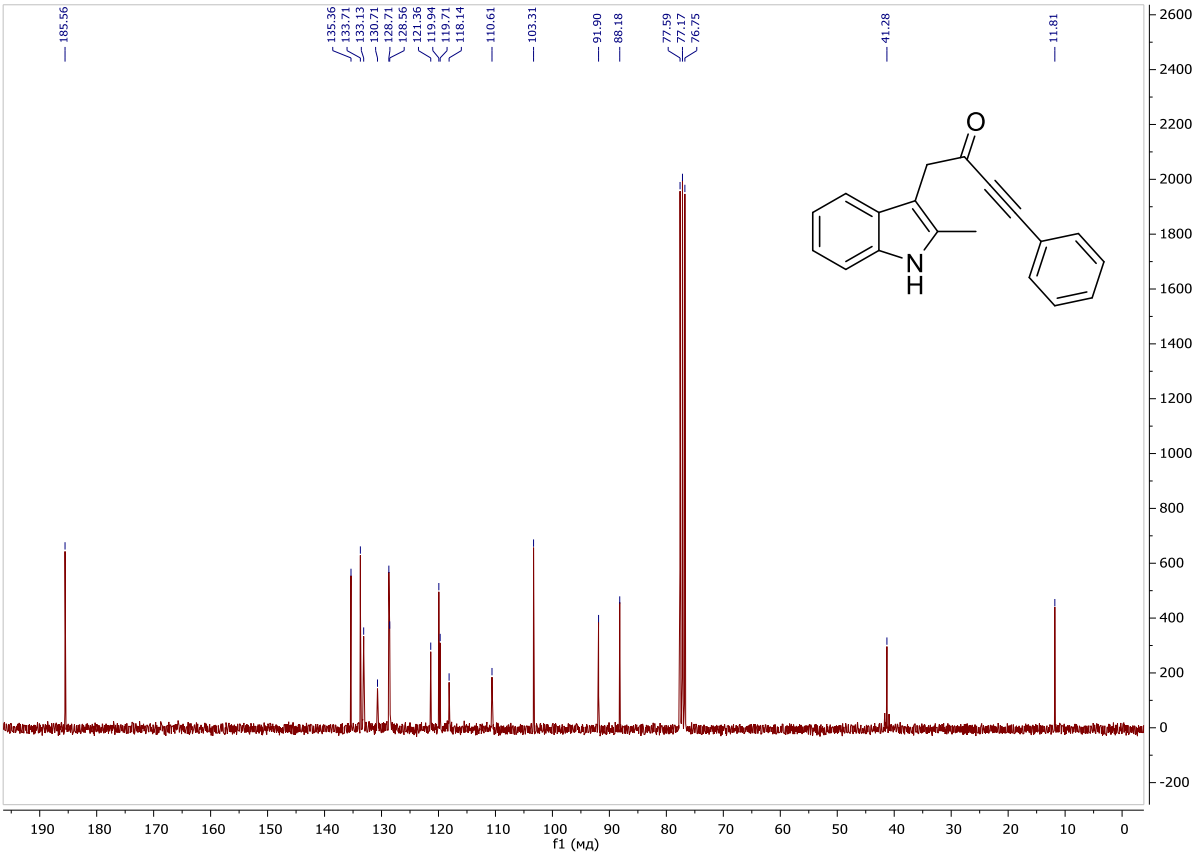
1.98
3.06
f1 (мд)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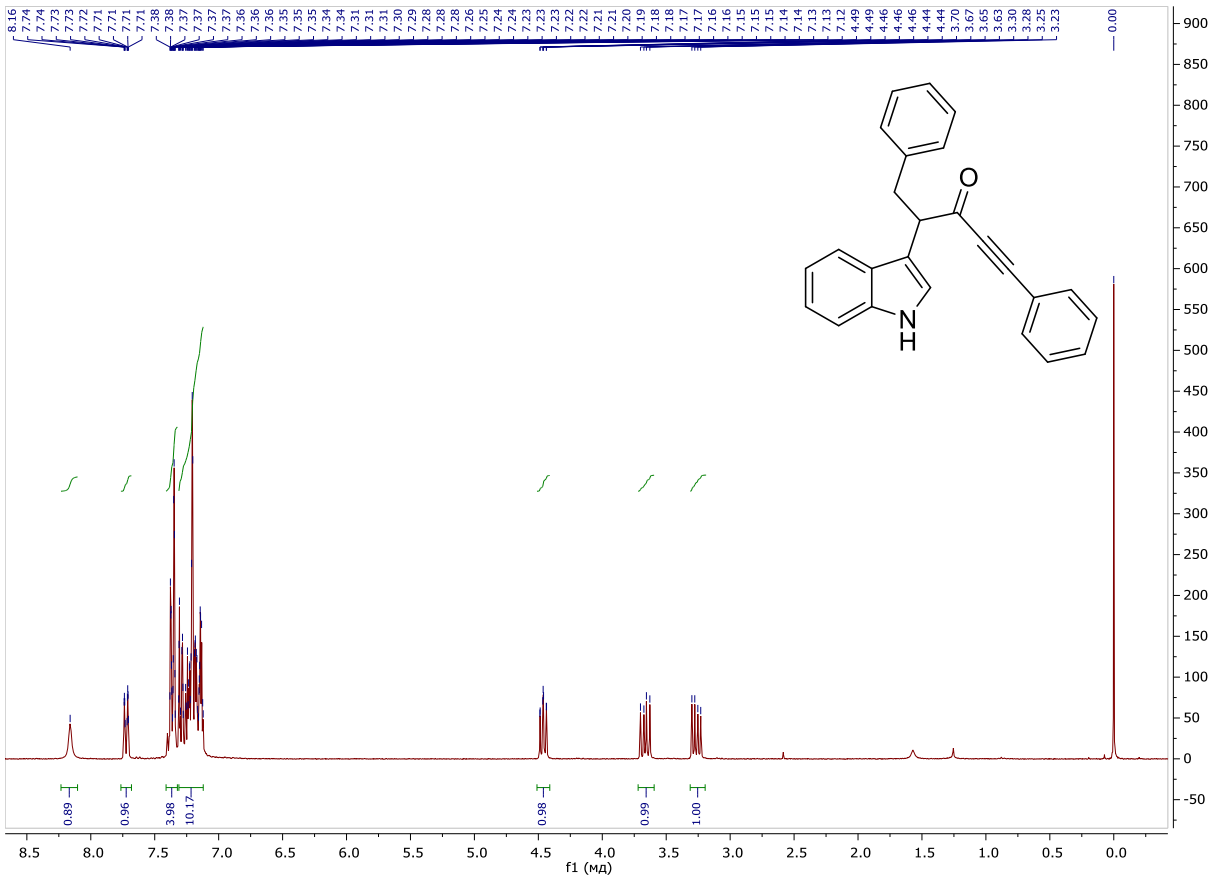
N
H
f1 (мд)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N
H
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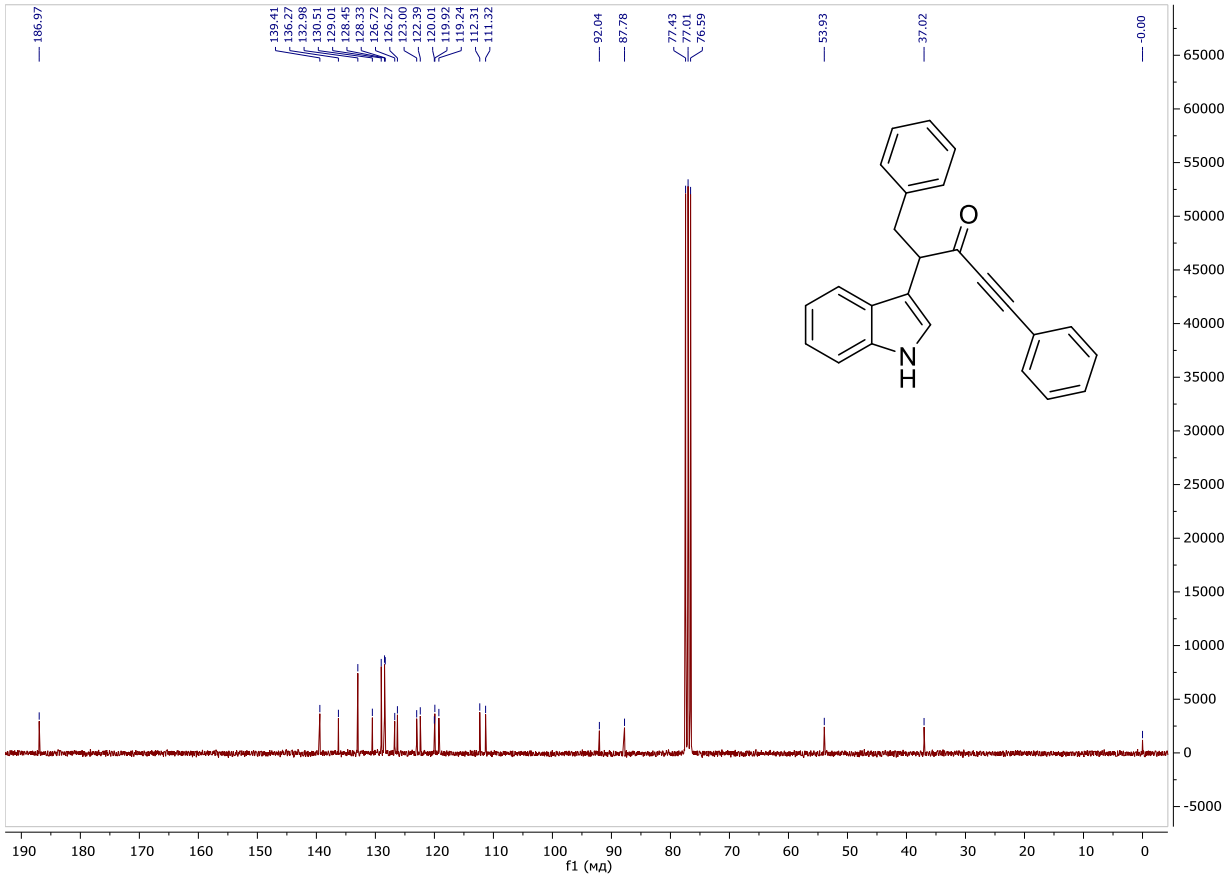
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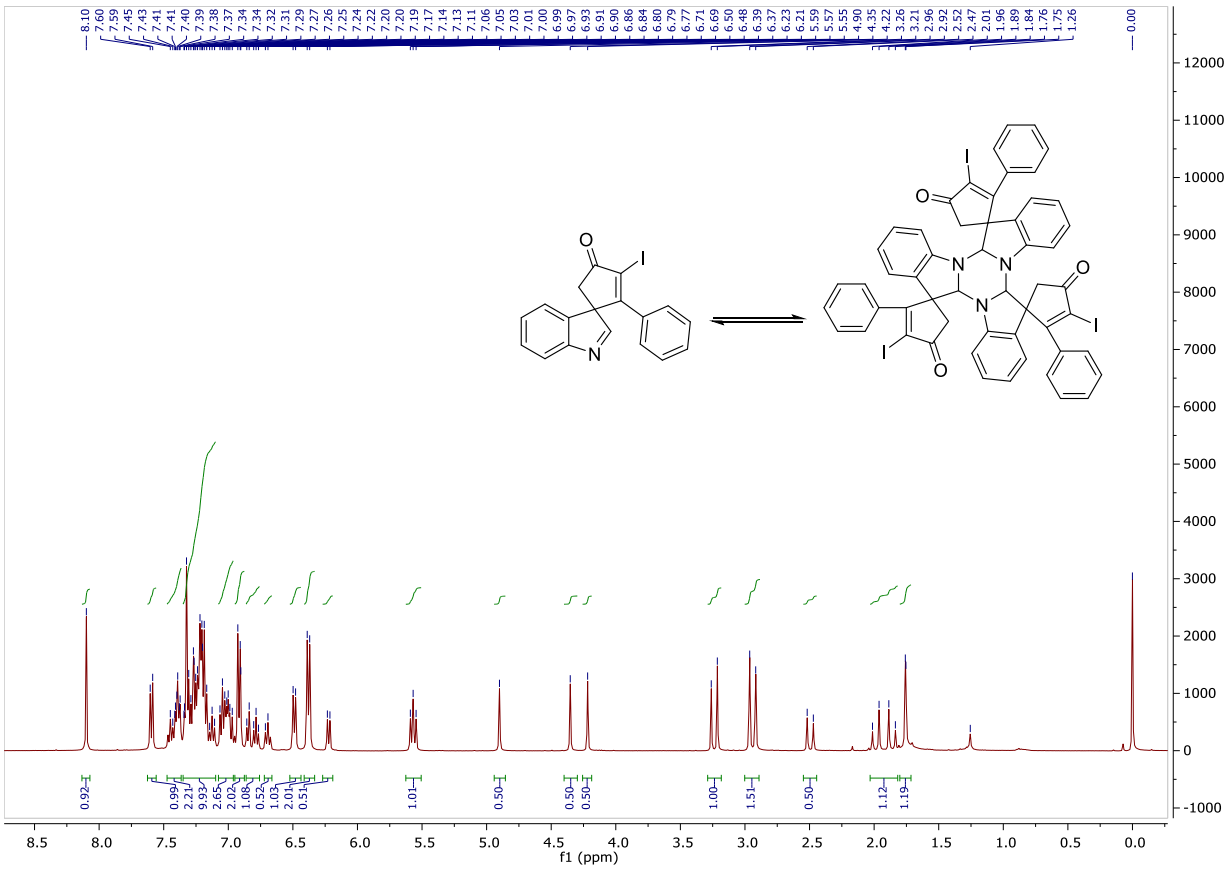
N
H
f1 (мд)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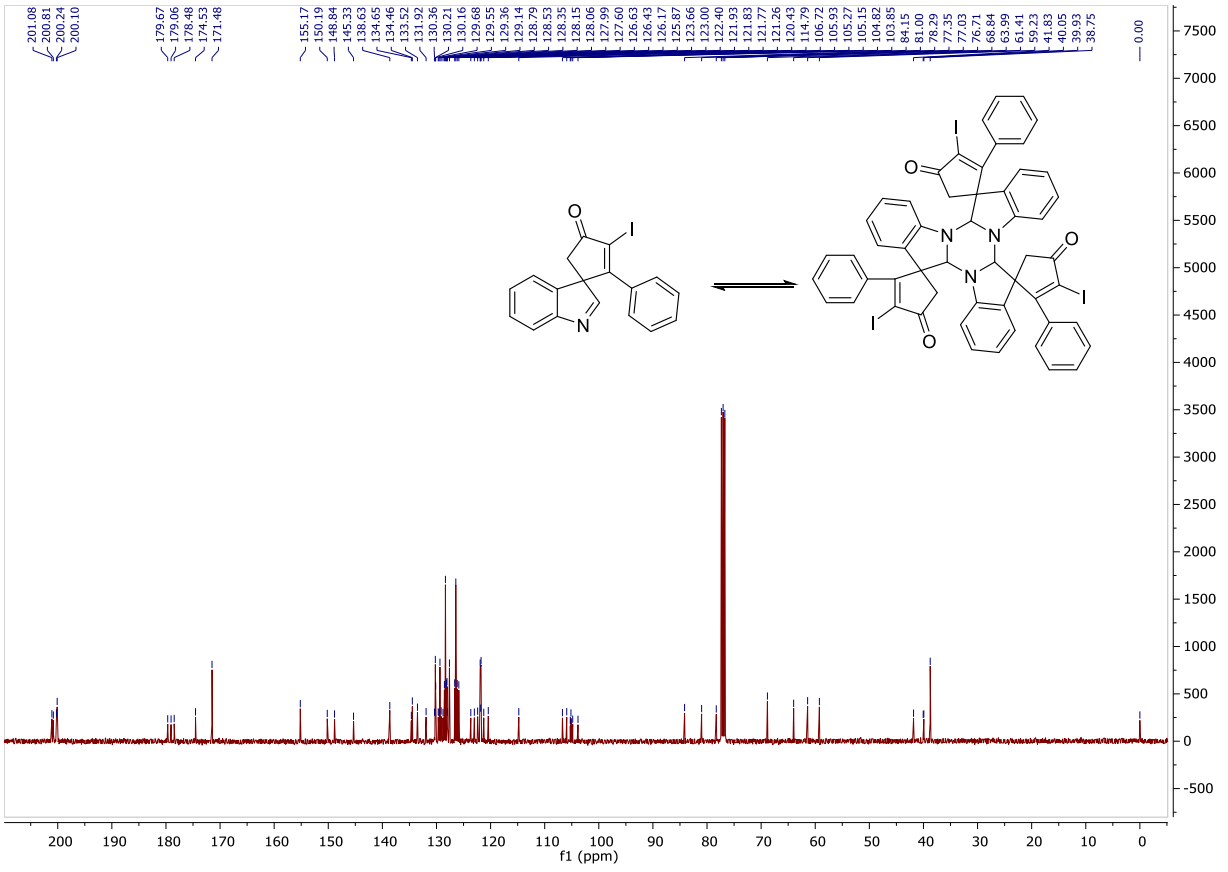
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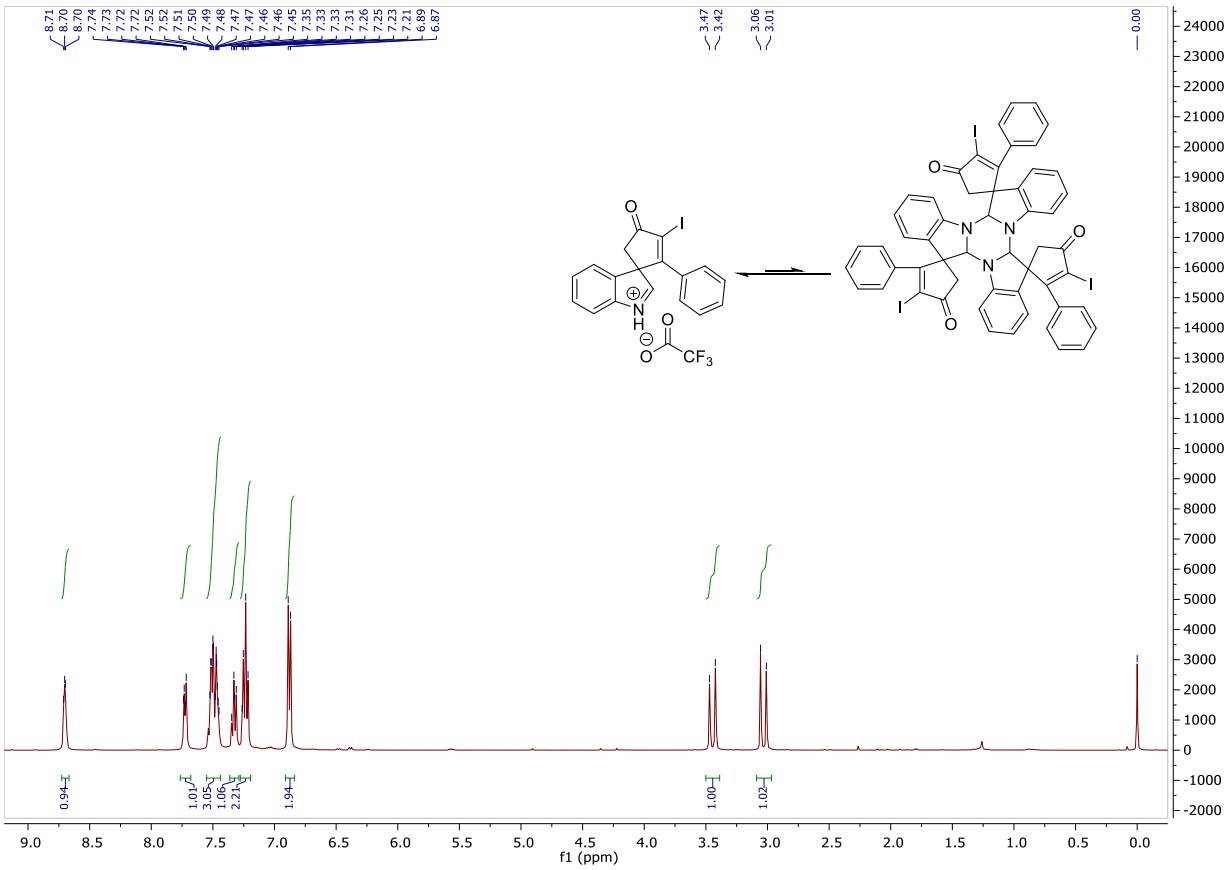
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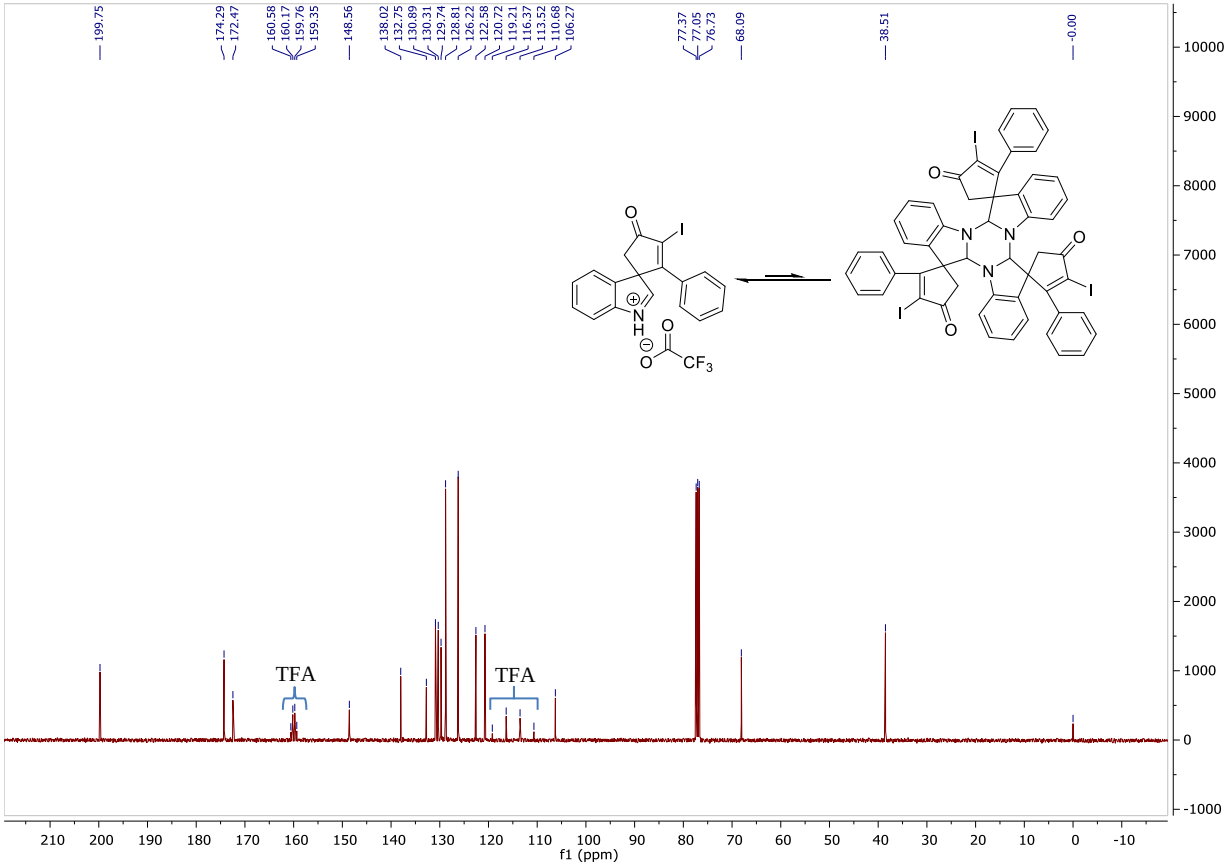
1.02
f1 (ppm)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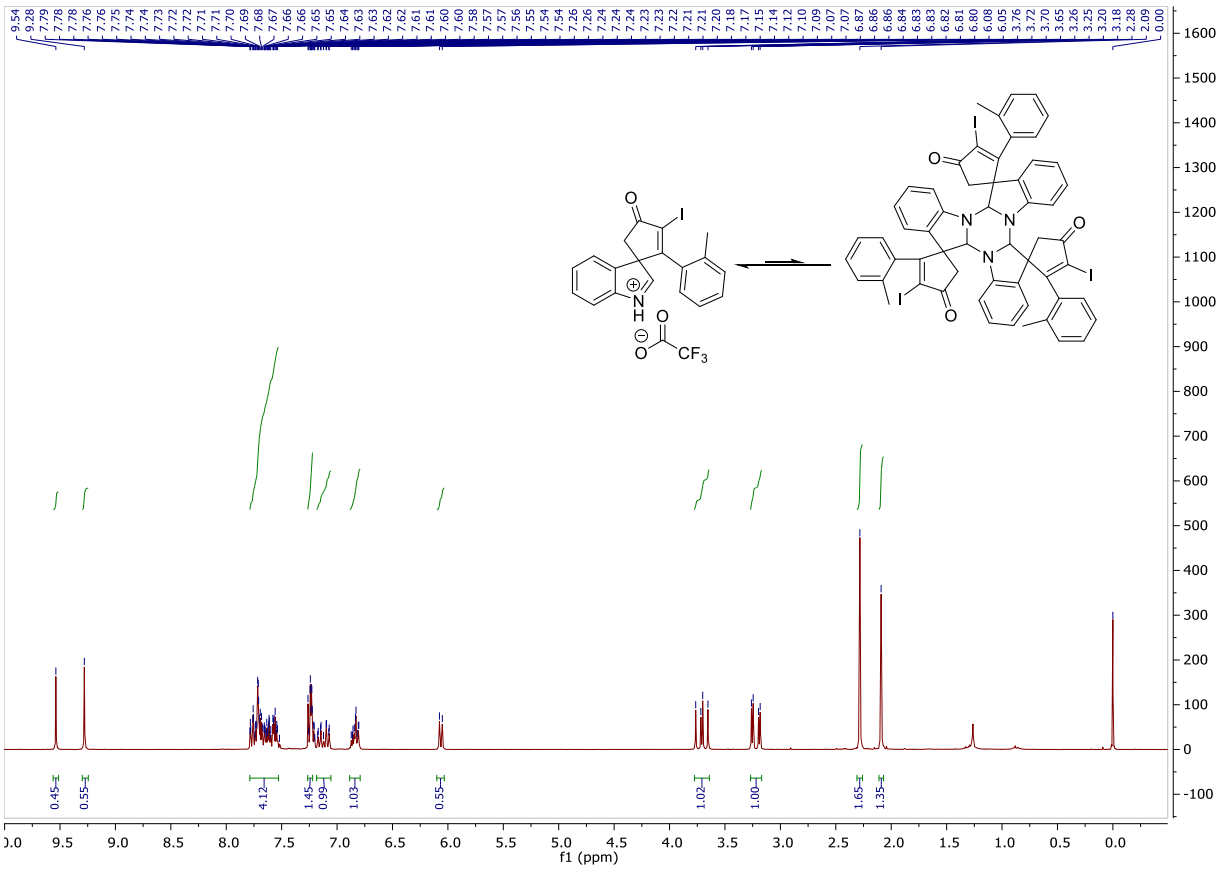
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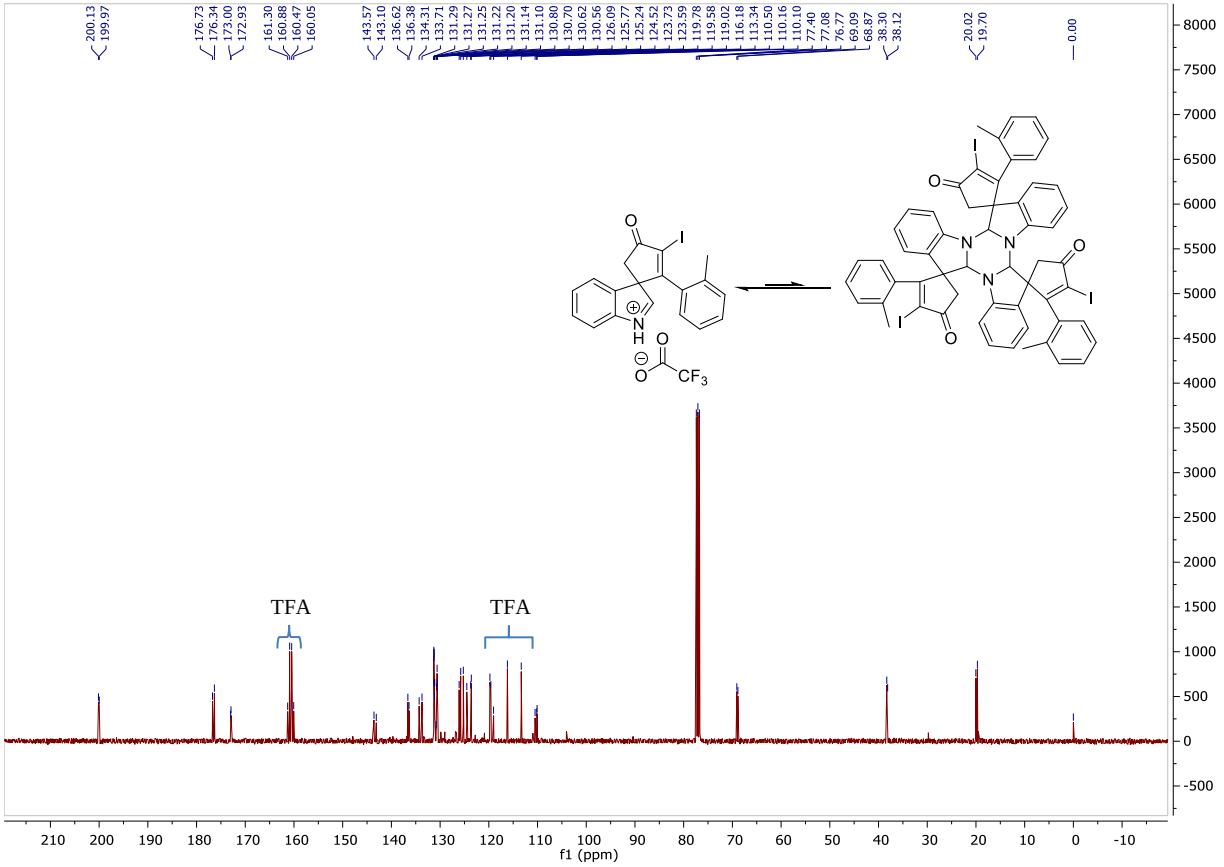
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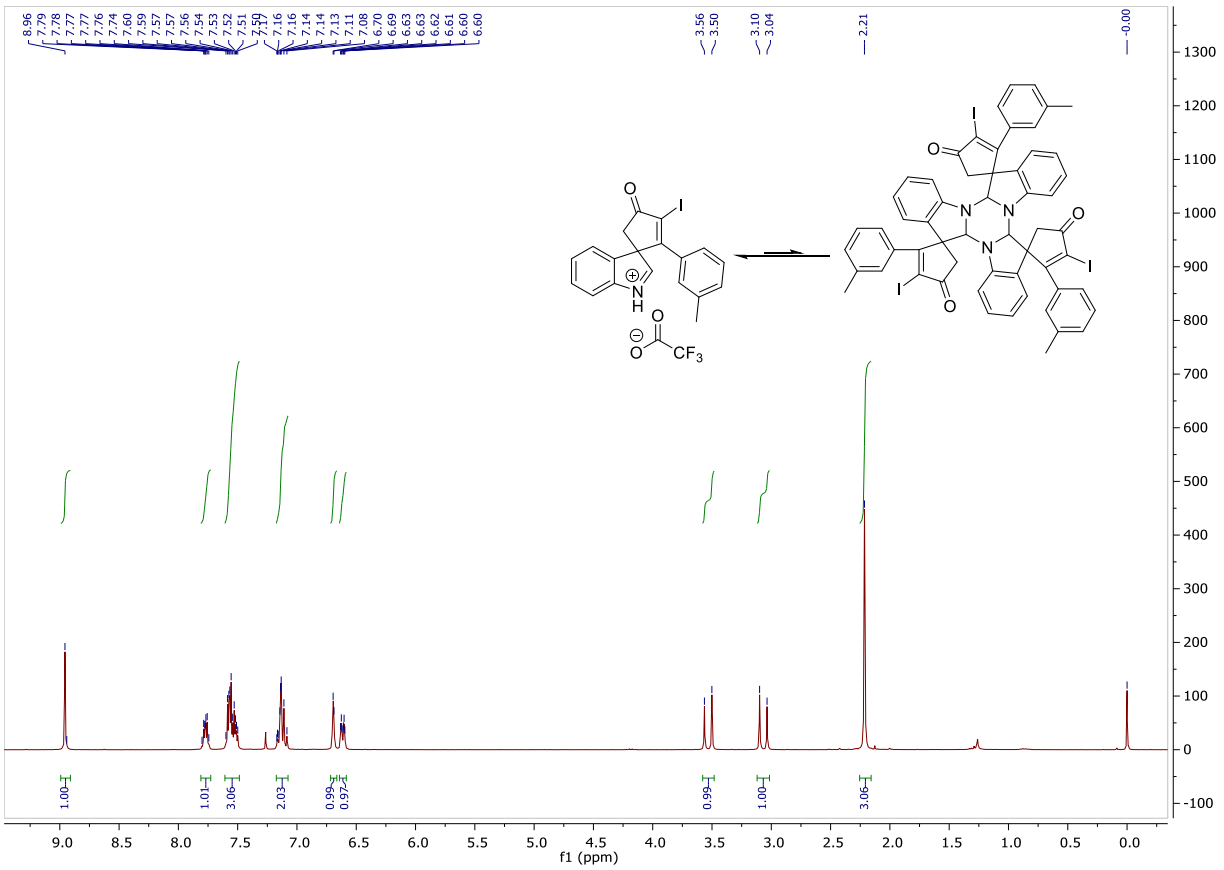
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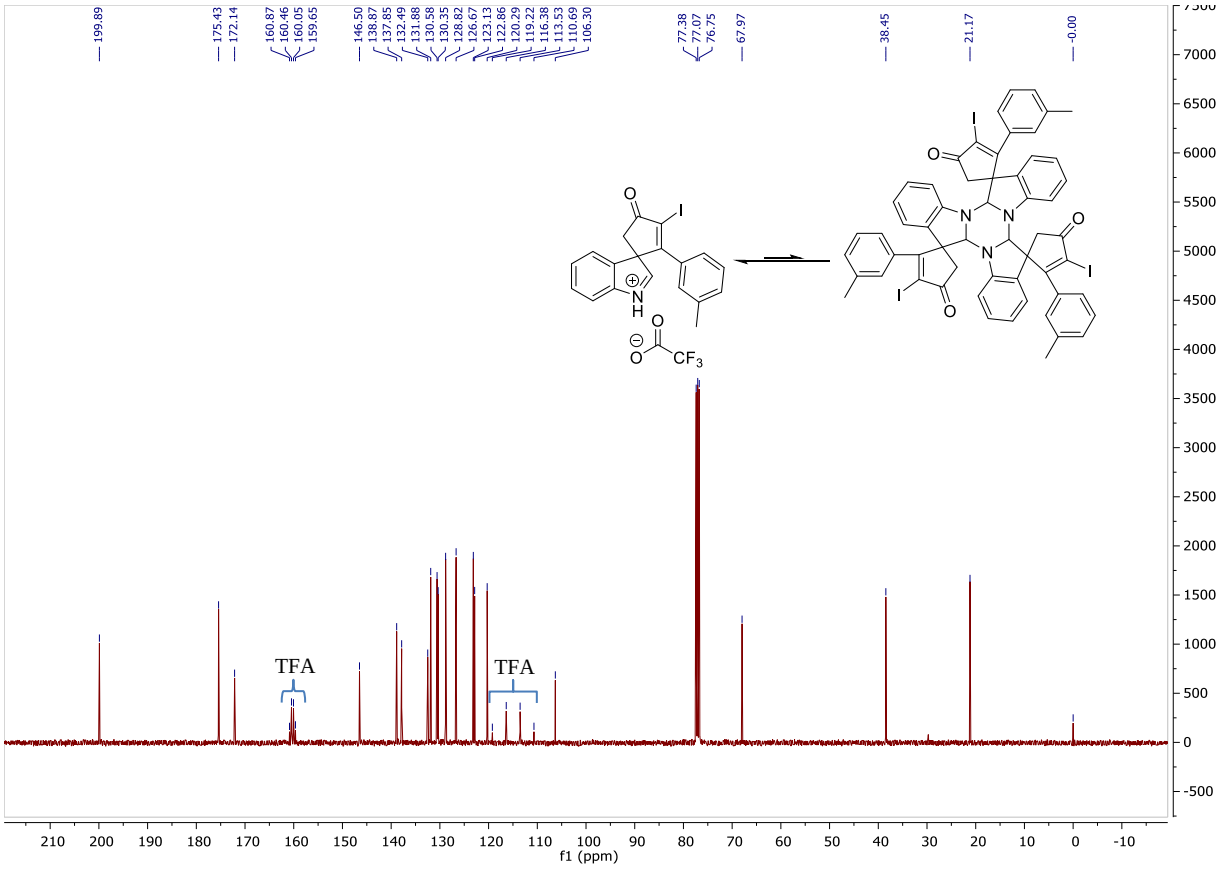
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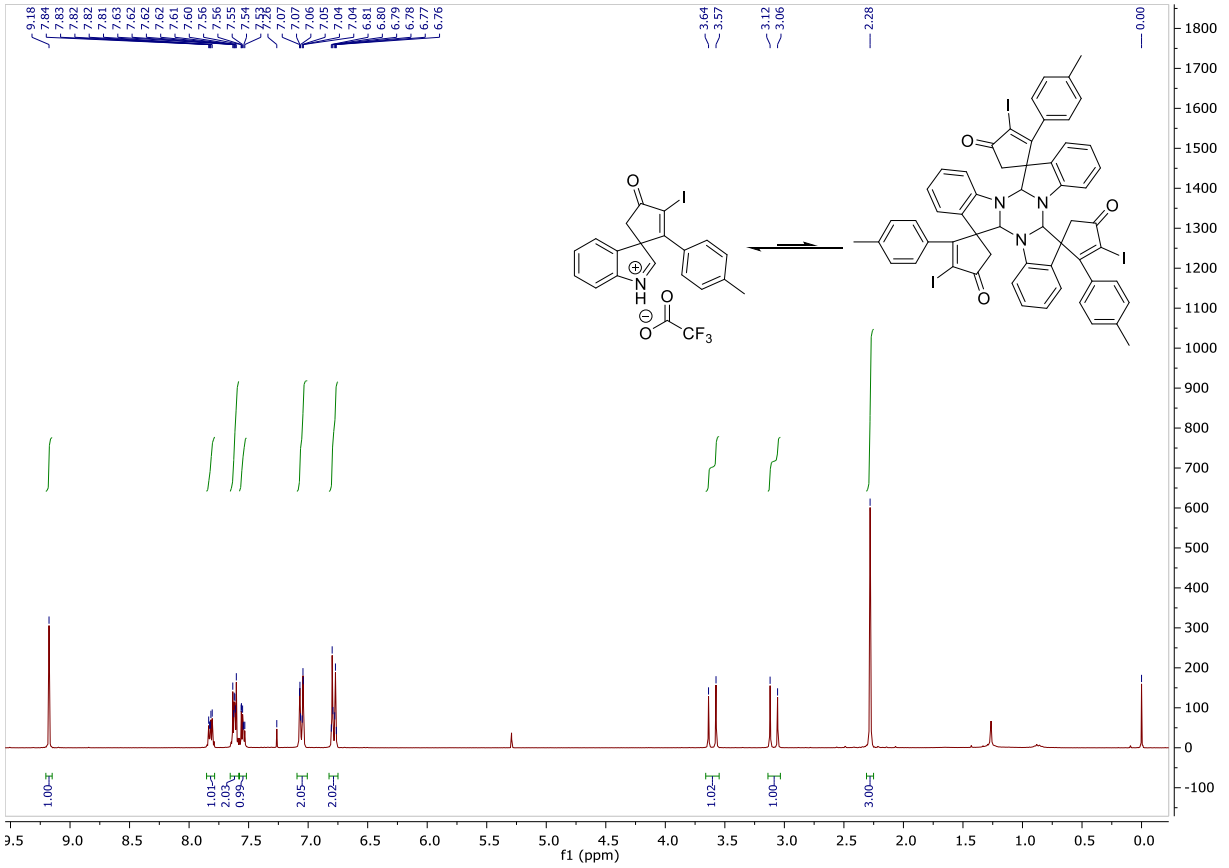
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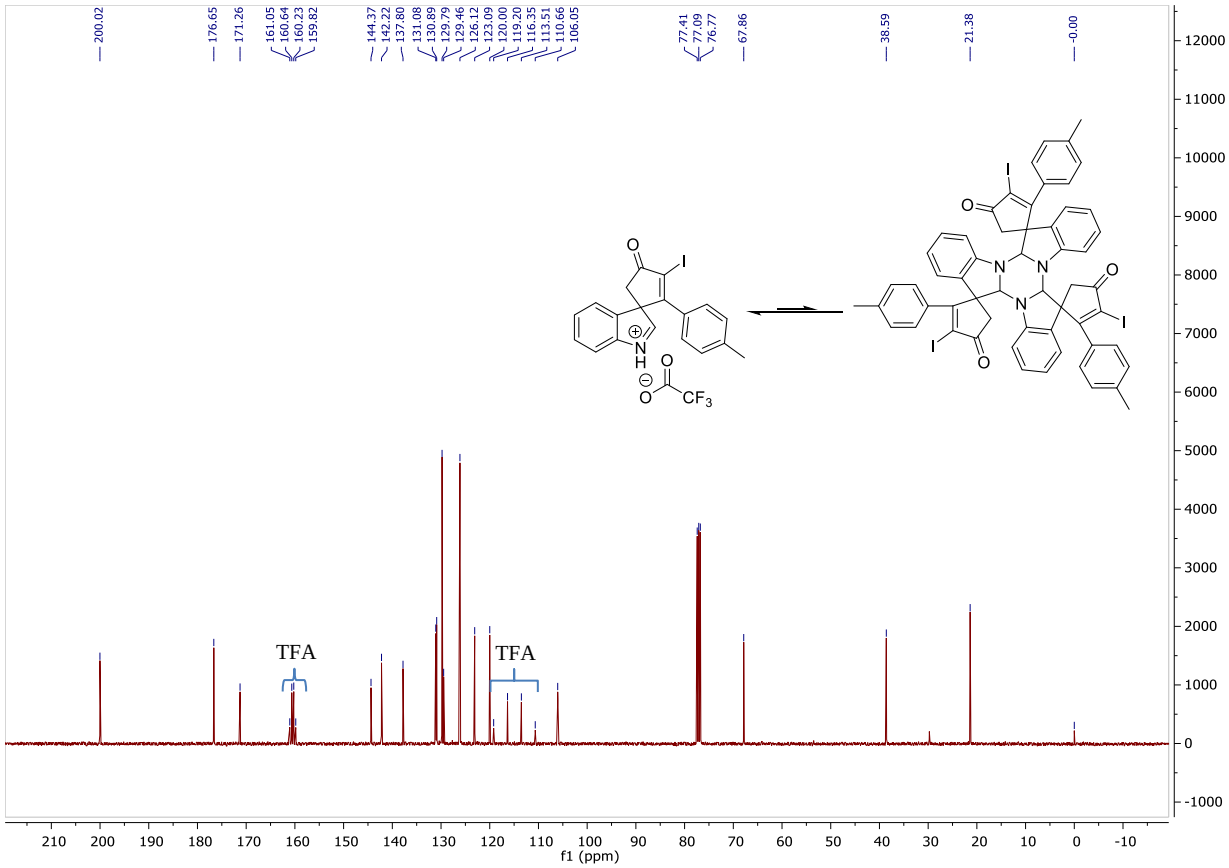
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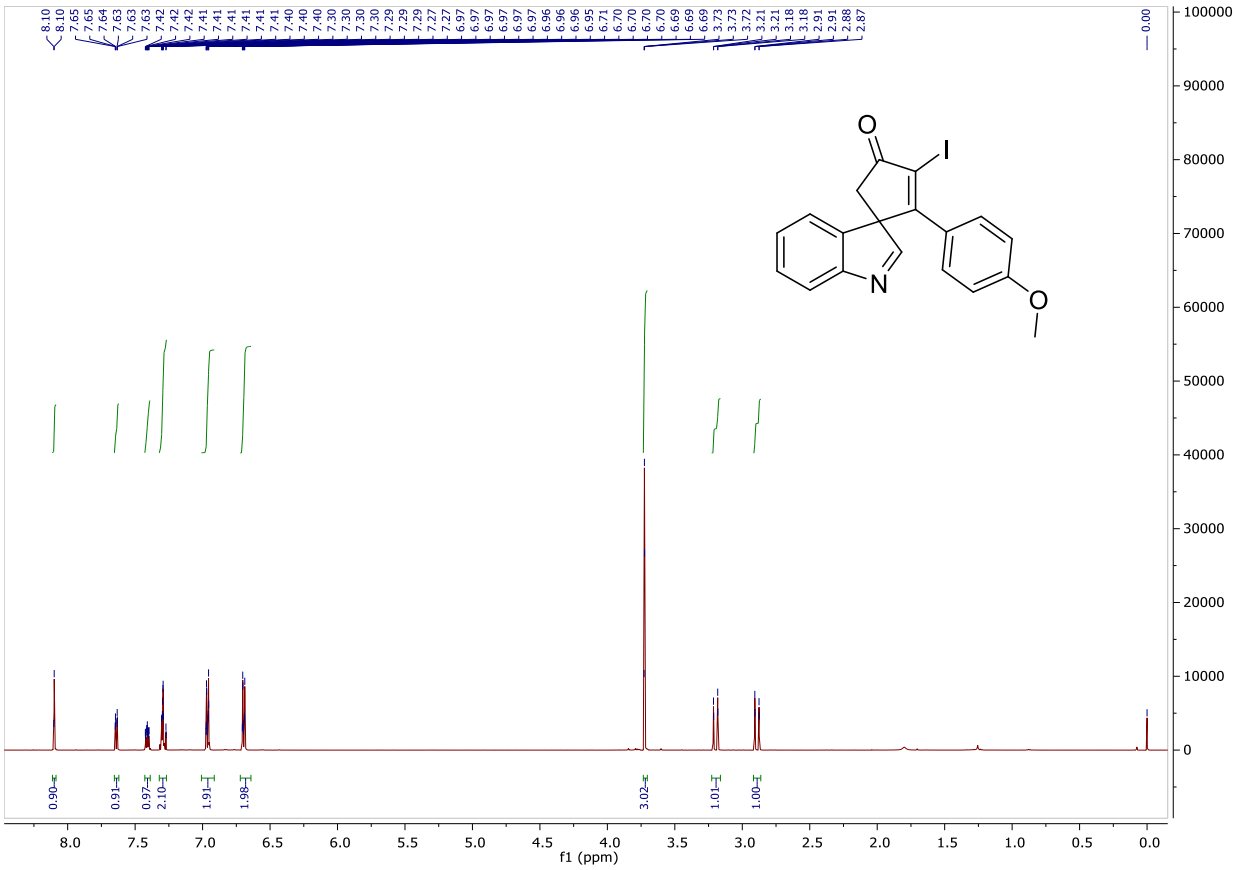
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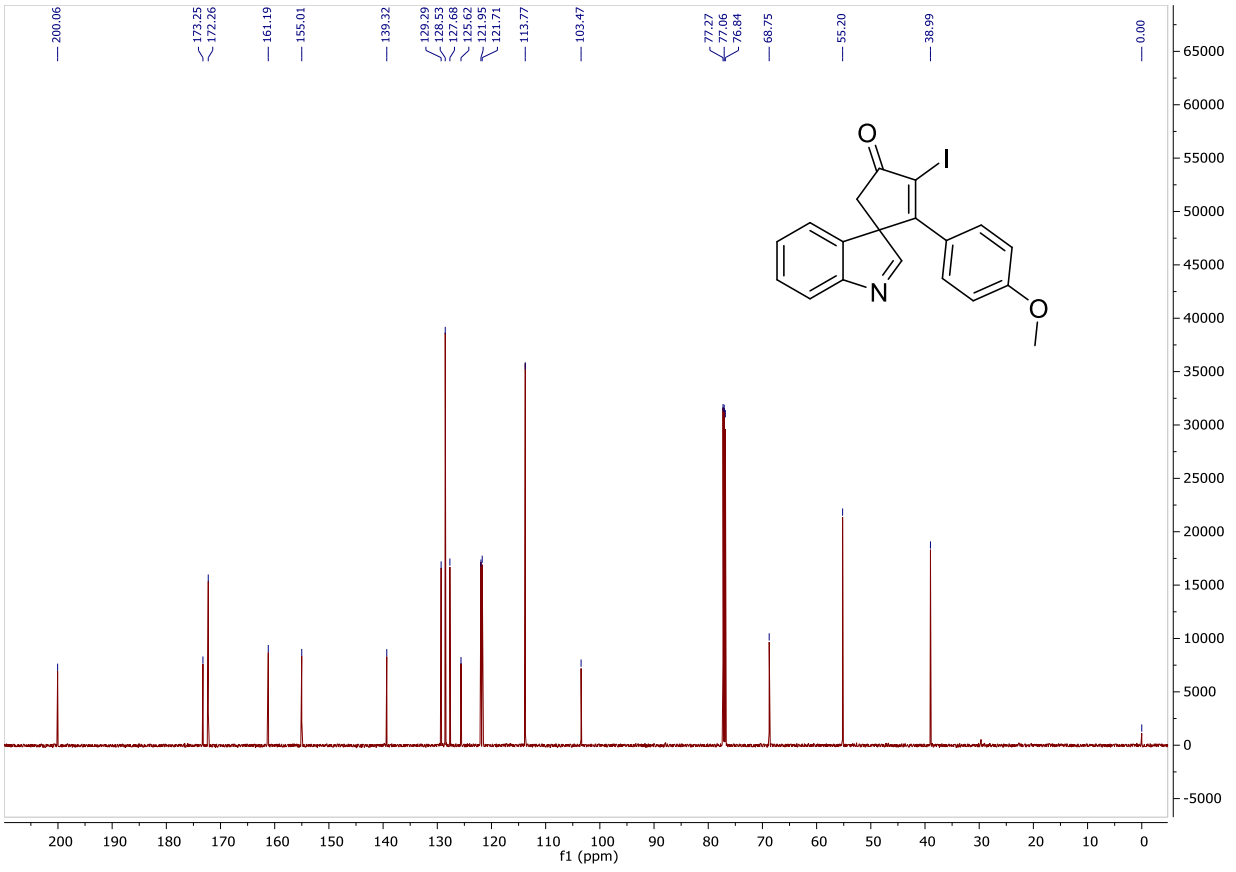
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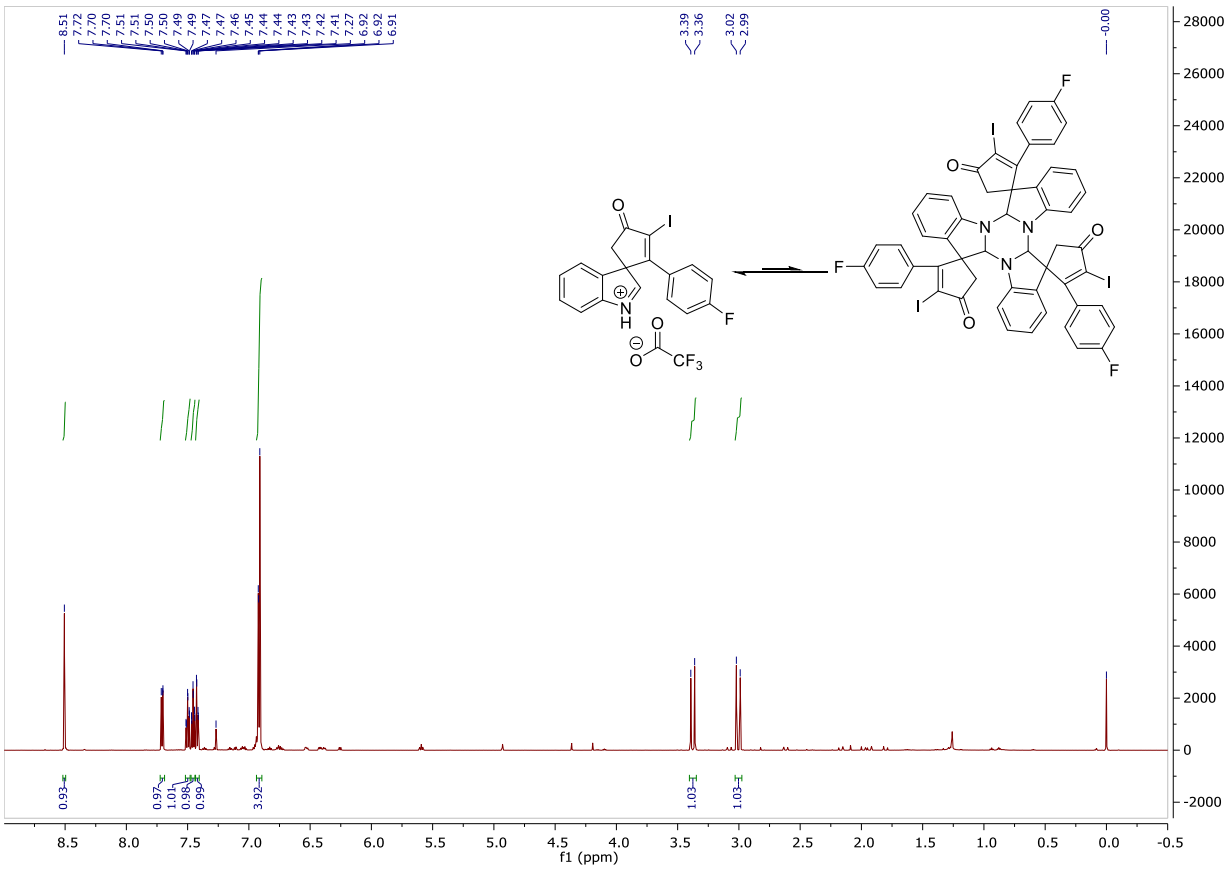
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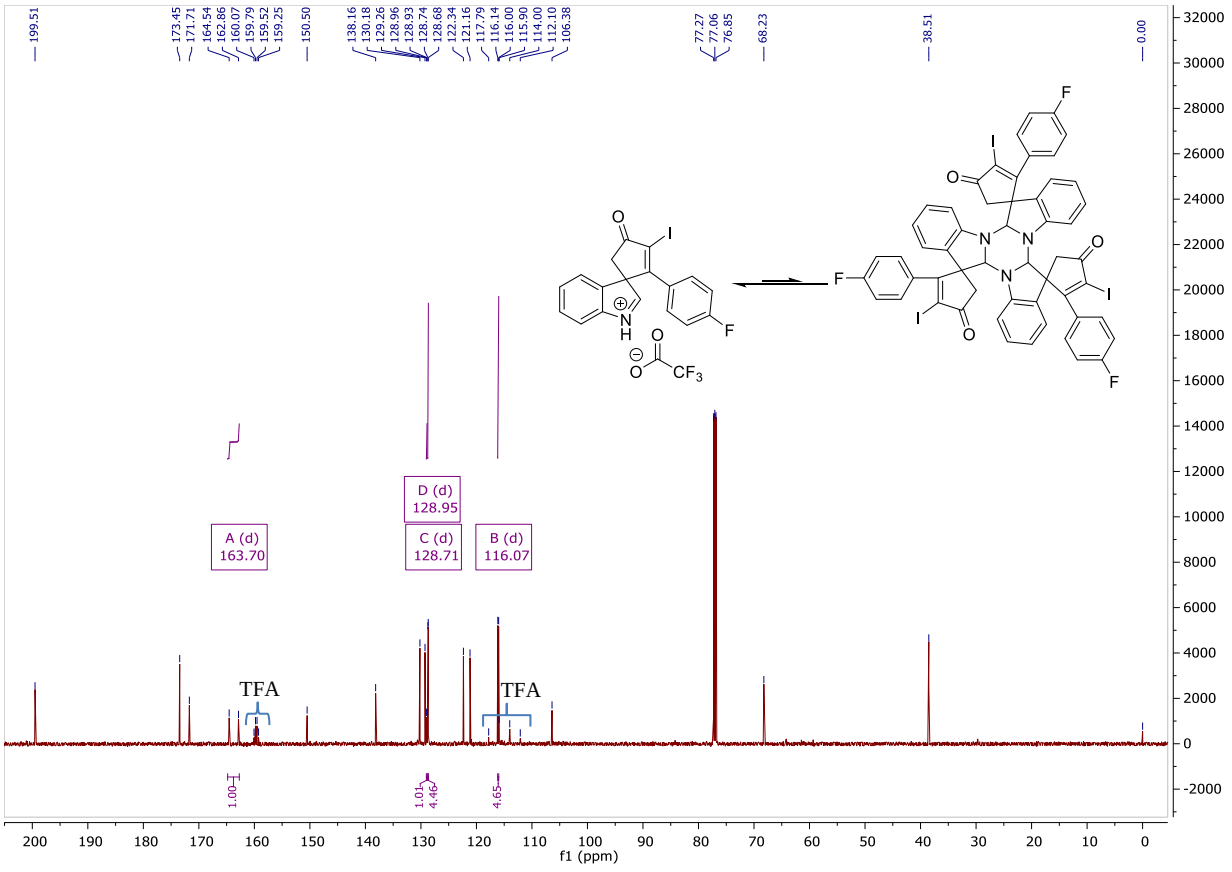
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D (d)
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C (d)
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B (d)
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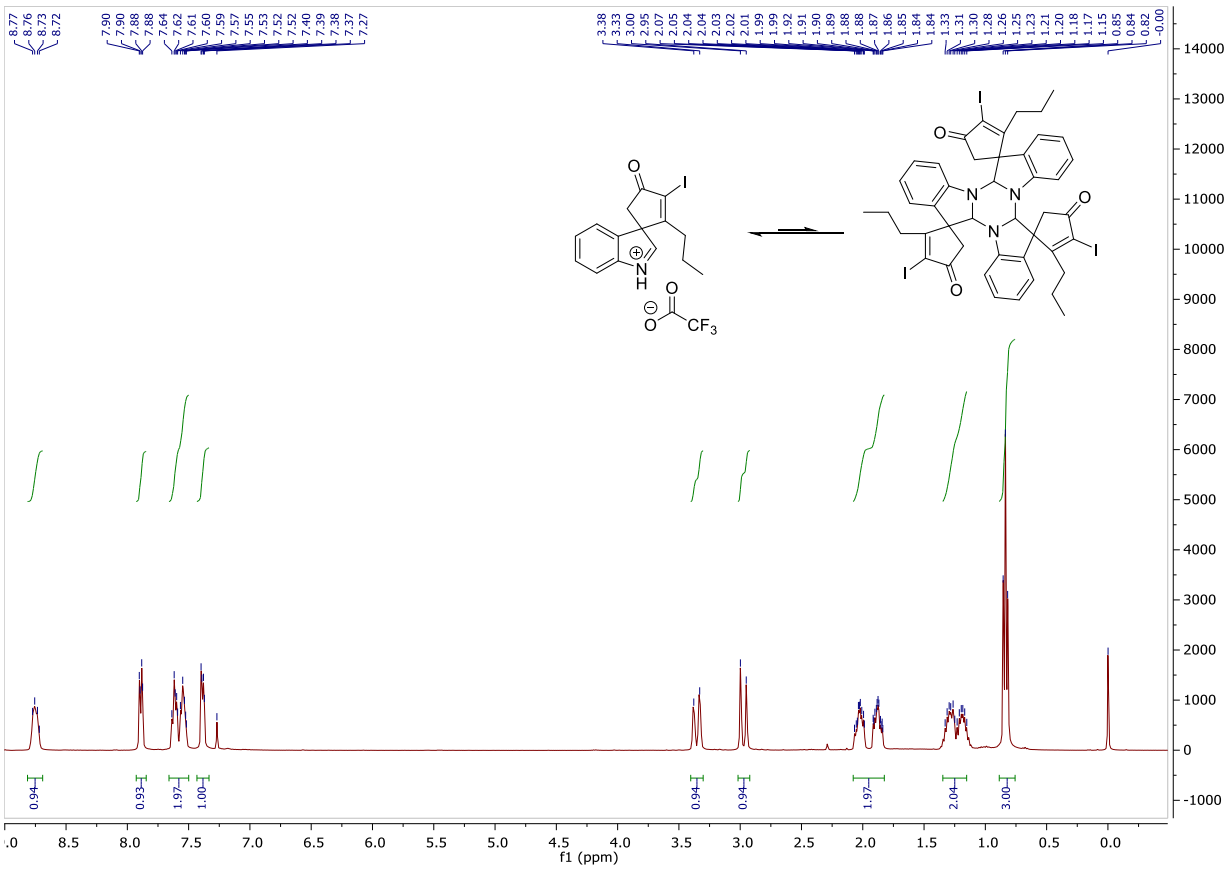
TFA
TFA
f1 (ppm)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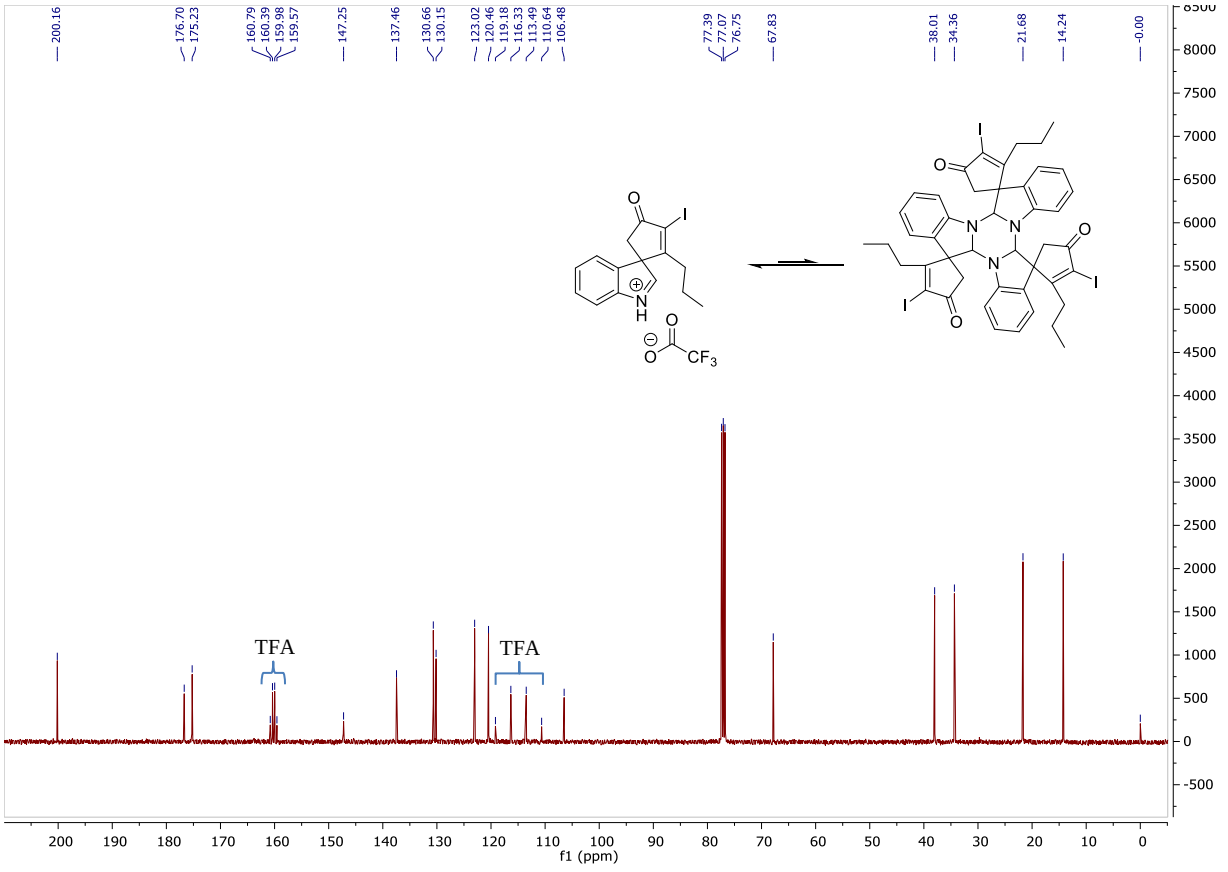
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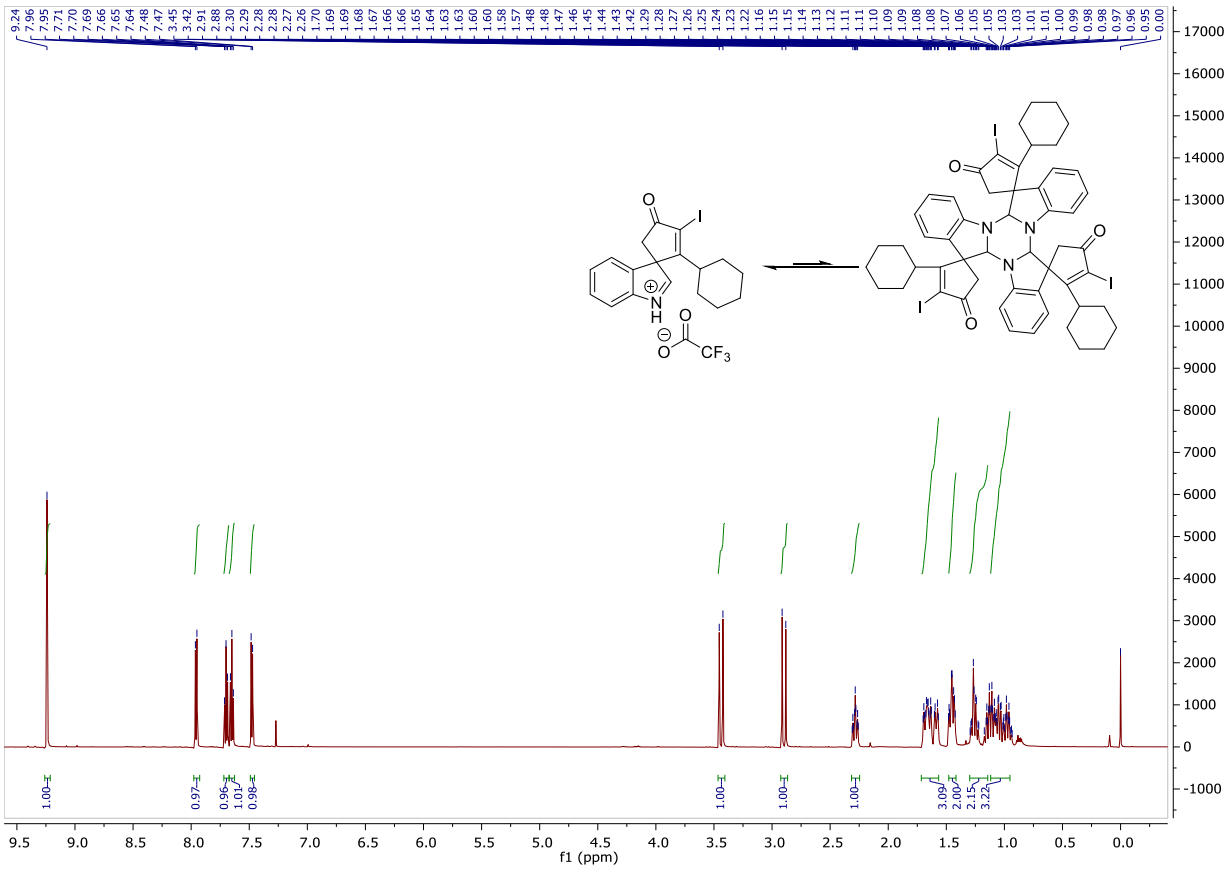
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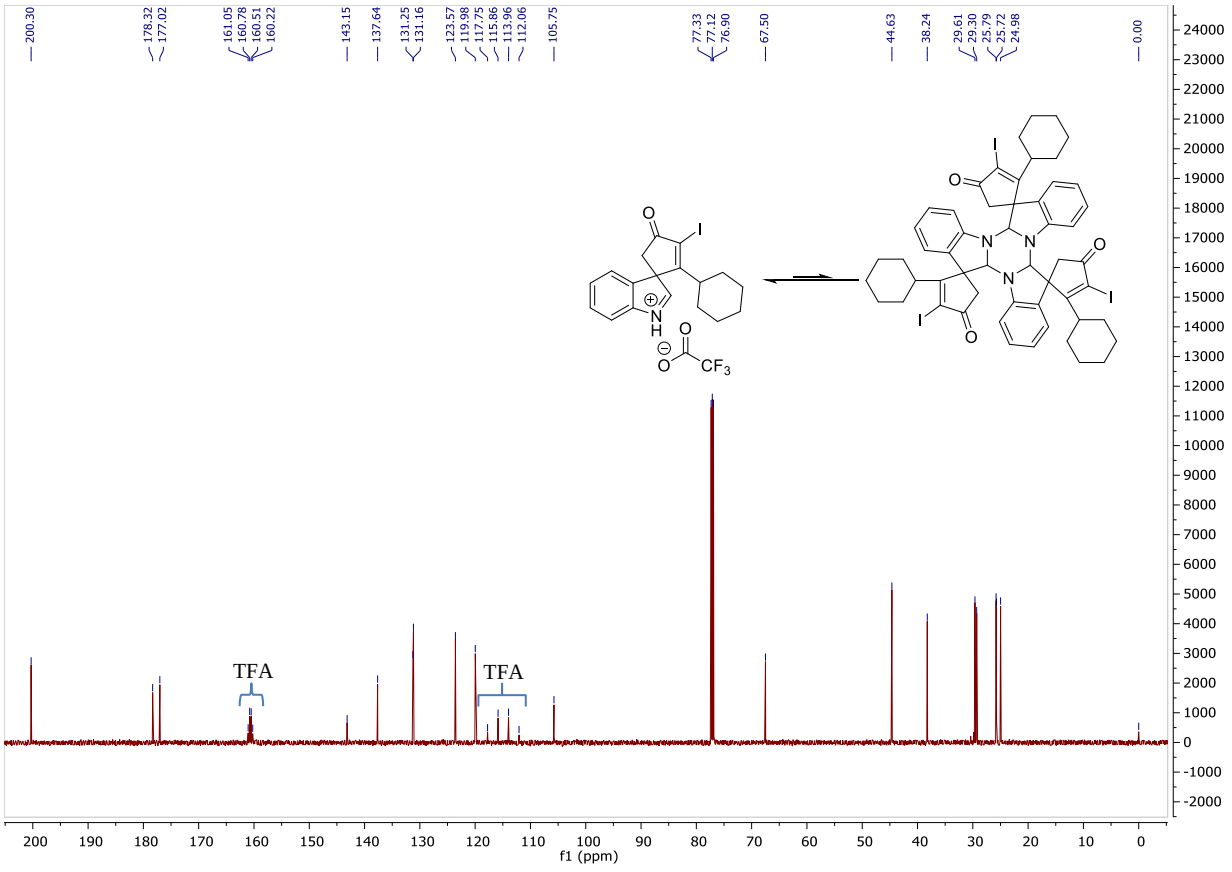
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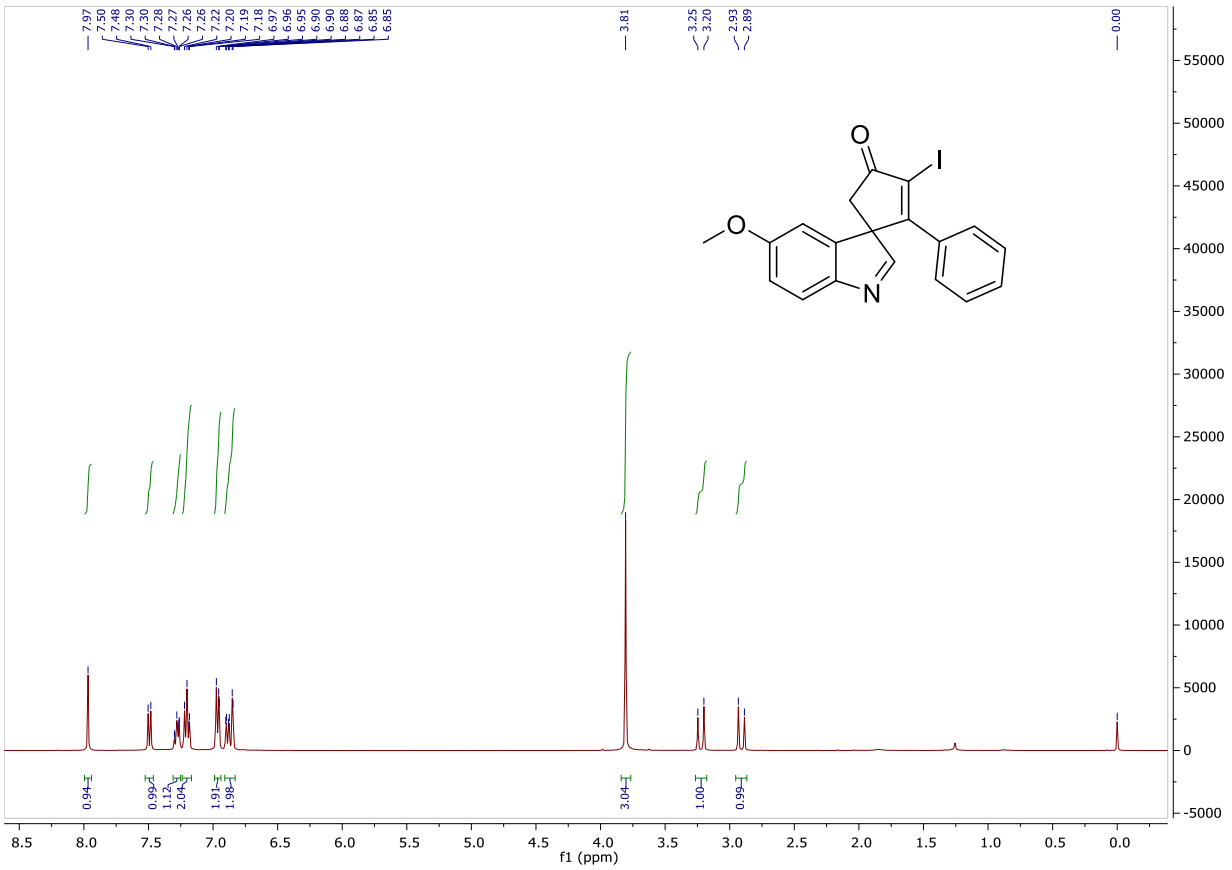
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7.30
7.28
7.27
7.26
7.26
7.22
7.20
7.19
7.18
6.97
6.96
6.95
6.90
6.90
6.88
6.87
6.85
6.85
3.81
3.25
3.20
2.93
2.89
0.00
O
I
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1.98
3.04
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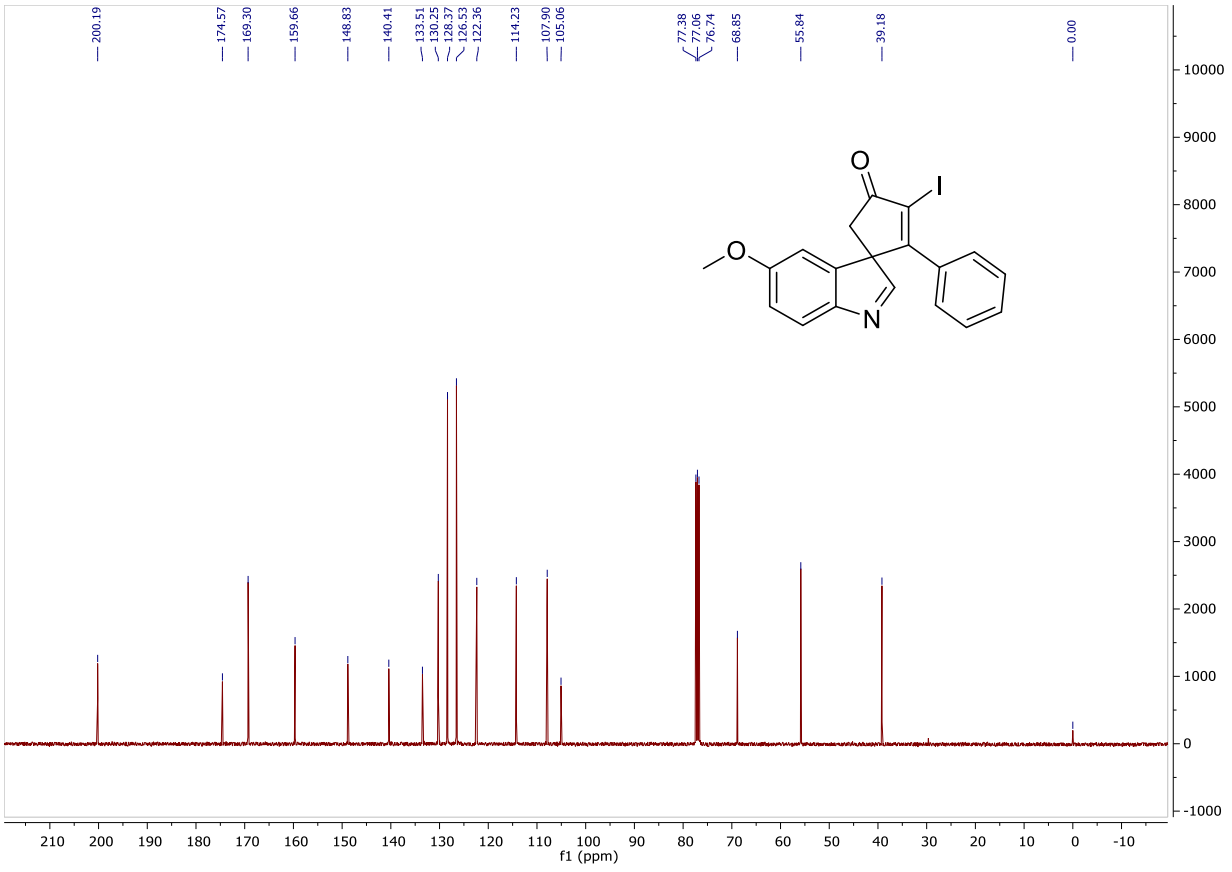
0.99
f1 (ppm)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130.25
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126.53
122.36
114.23
107.90
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77.06
76.74
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55.84
39.18
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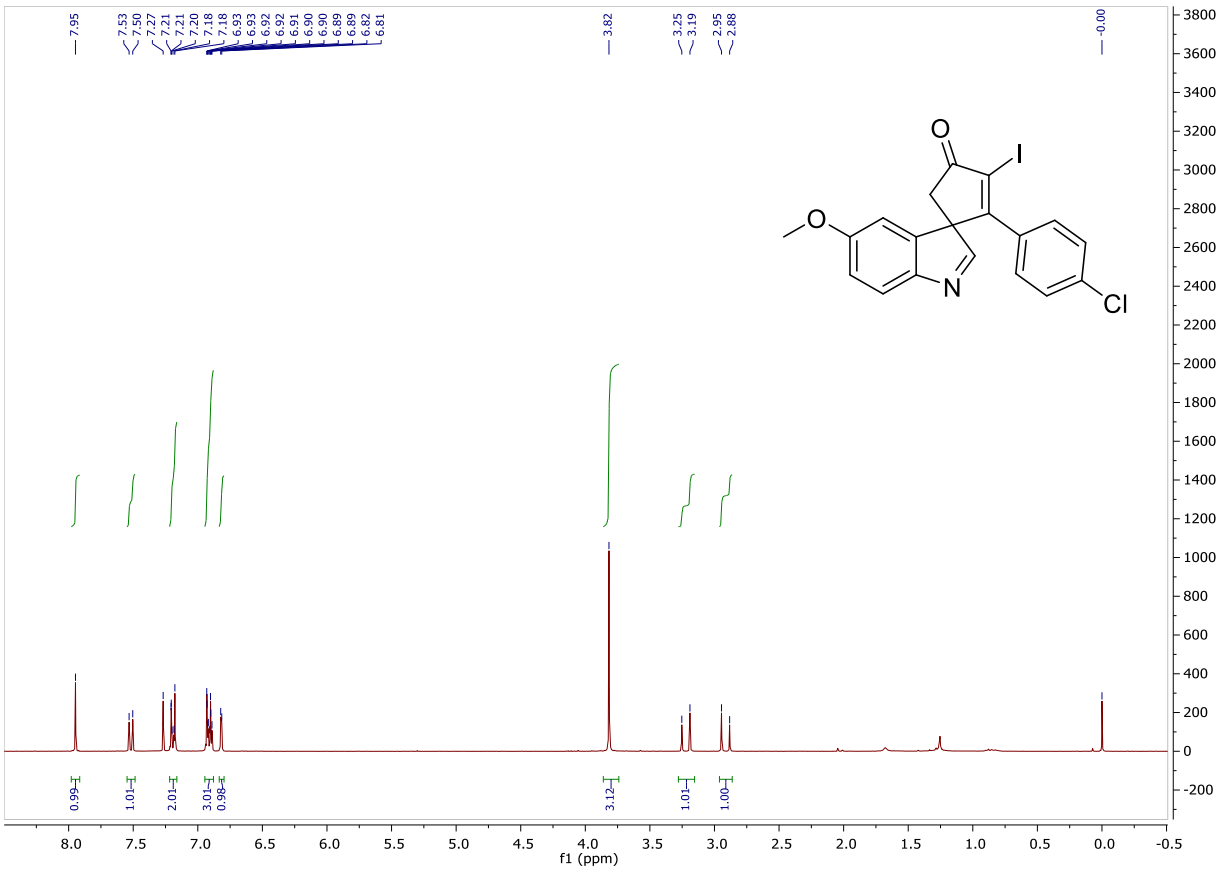
O
N
f1 (ppm)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7.18
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6.93
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6.91
6.90
6.90
6.89
6.89
6.82
6.81
3.82
3.25
3.19
2.95
2.88
-0.00
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O
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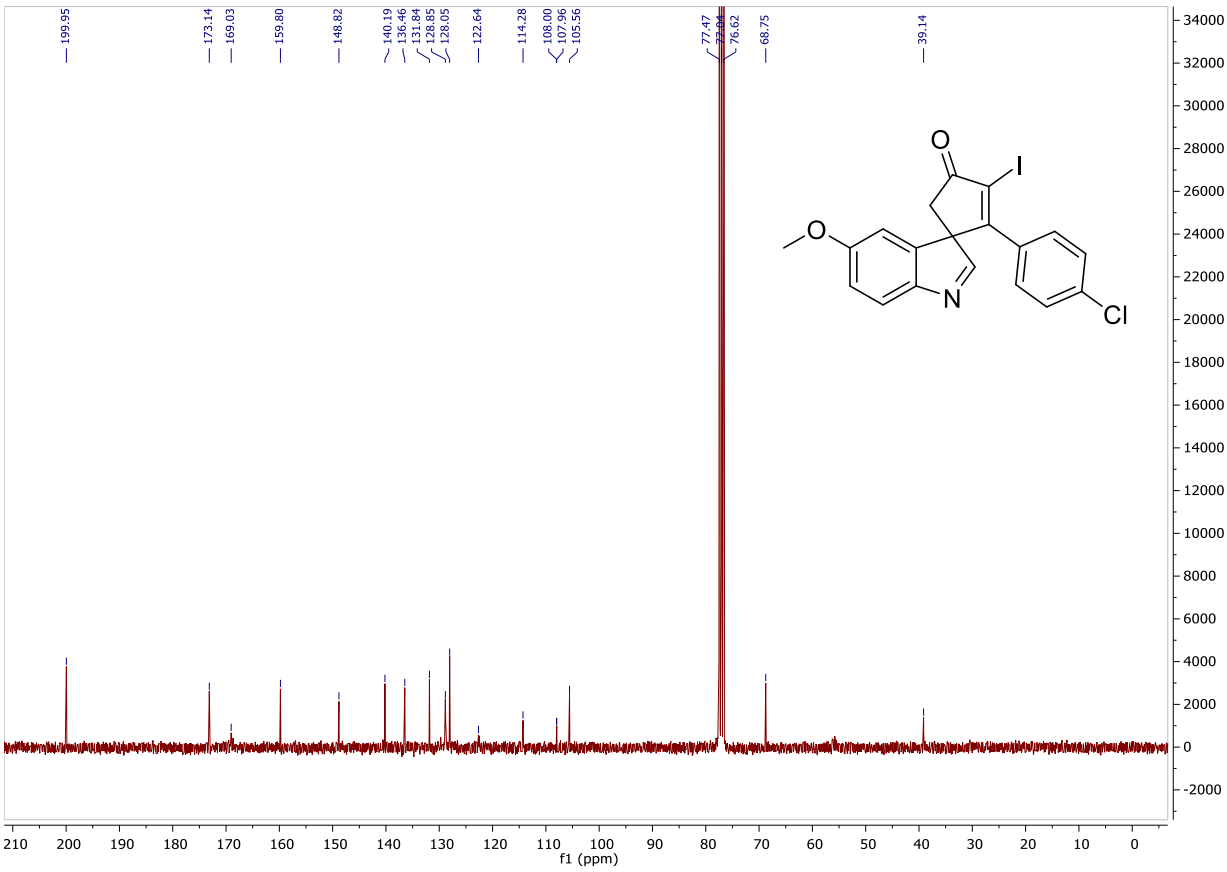
Cl
0.99
1.01
2.01
3.01
0.98
3.12
1.01
1.00
f1 (ppm)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140.19
136.46
131.84
128.85
128.05
122.64
114.28
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77.47
77.04
76.62
68.75
39.14
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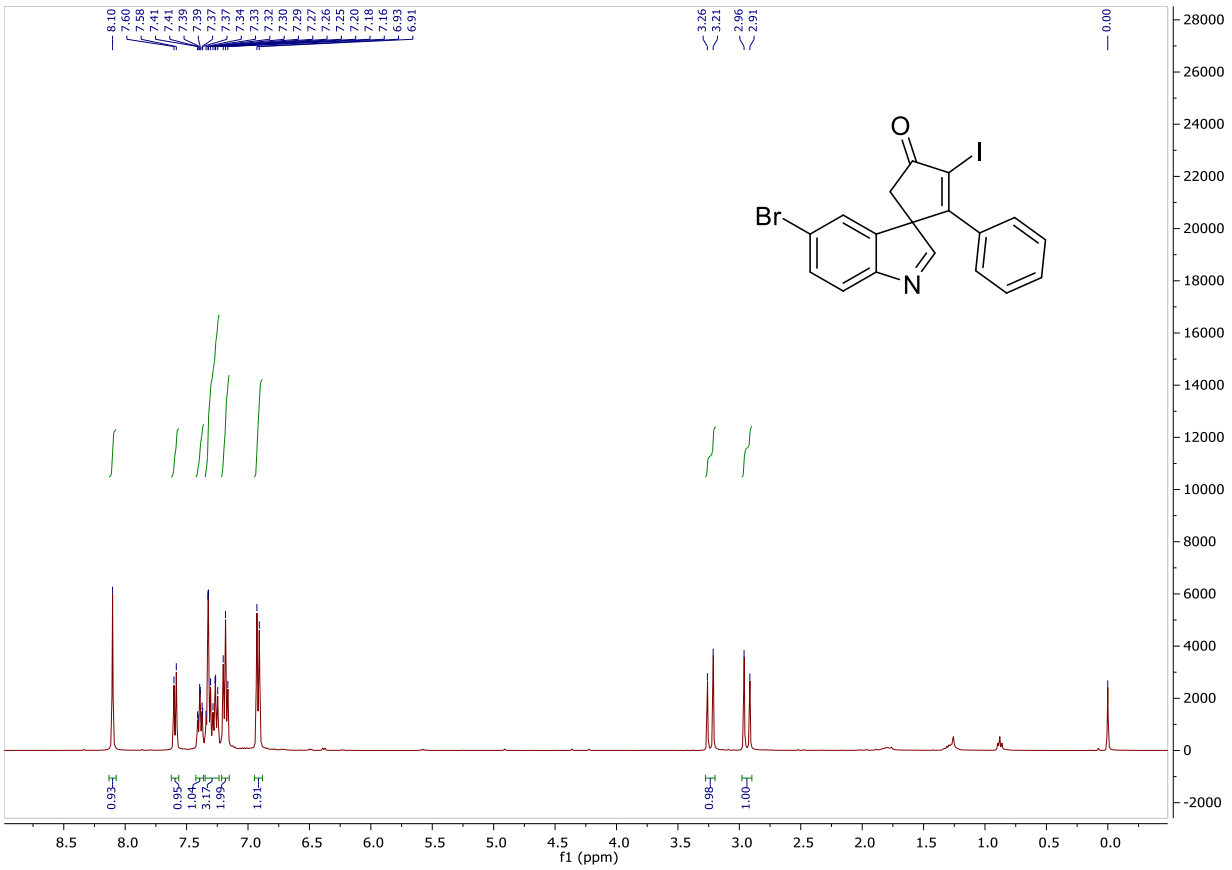
I
O
N
Cl
f1 (ppm)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7.32
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7.29
7.27
7.26
7.25
7.20
7.18
7.16
6.93
6.91
3.26
3.21
2.96
2.91
0.00
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1.04
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1.91
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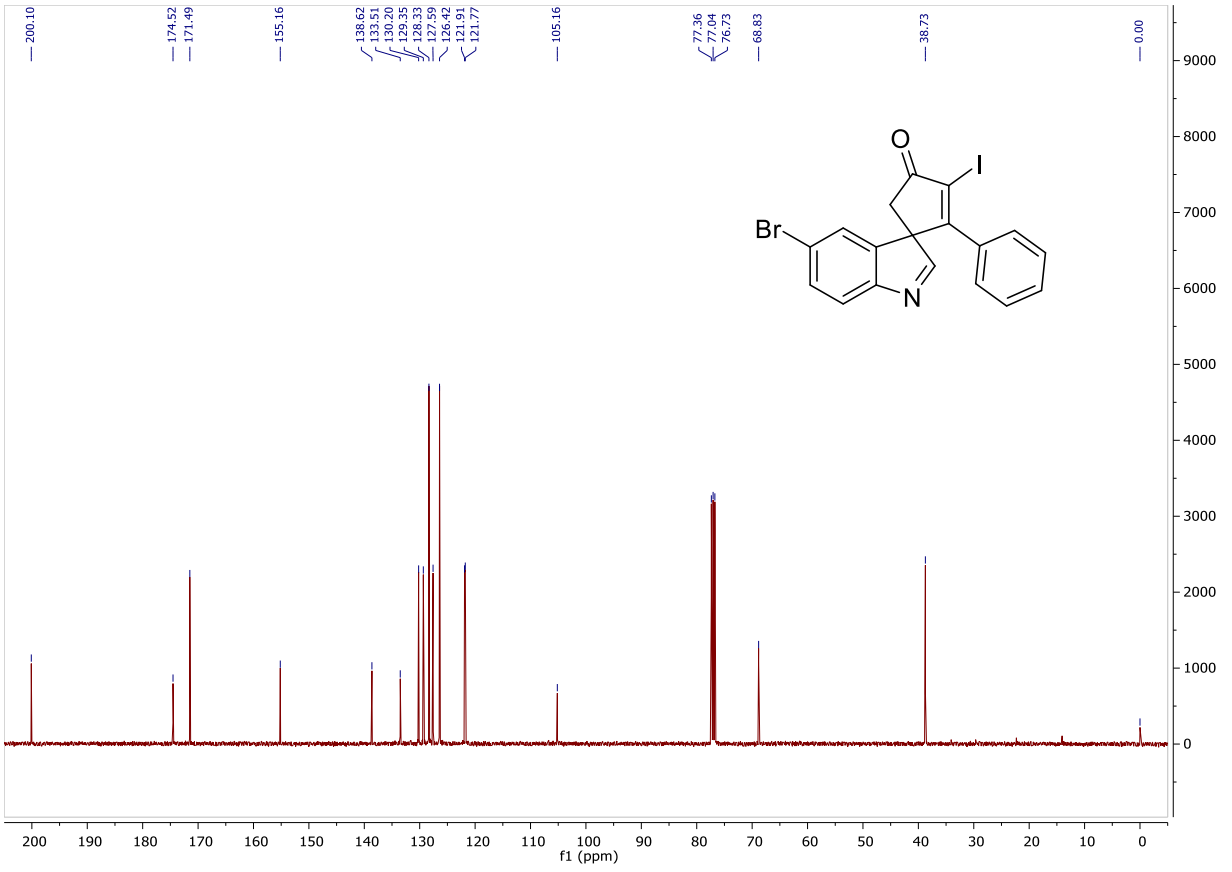
1.00
f1 (ppm)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121.91
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77.04
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68.83
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0.00
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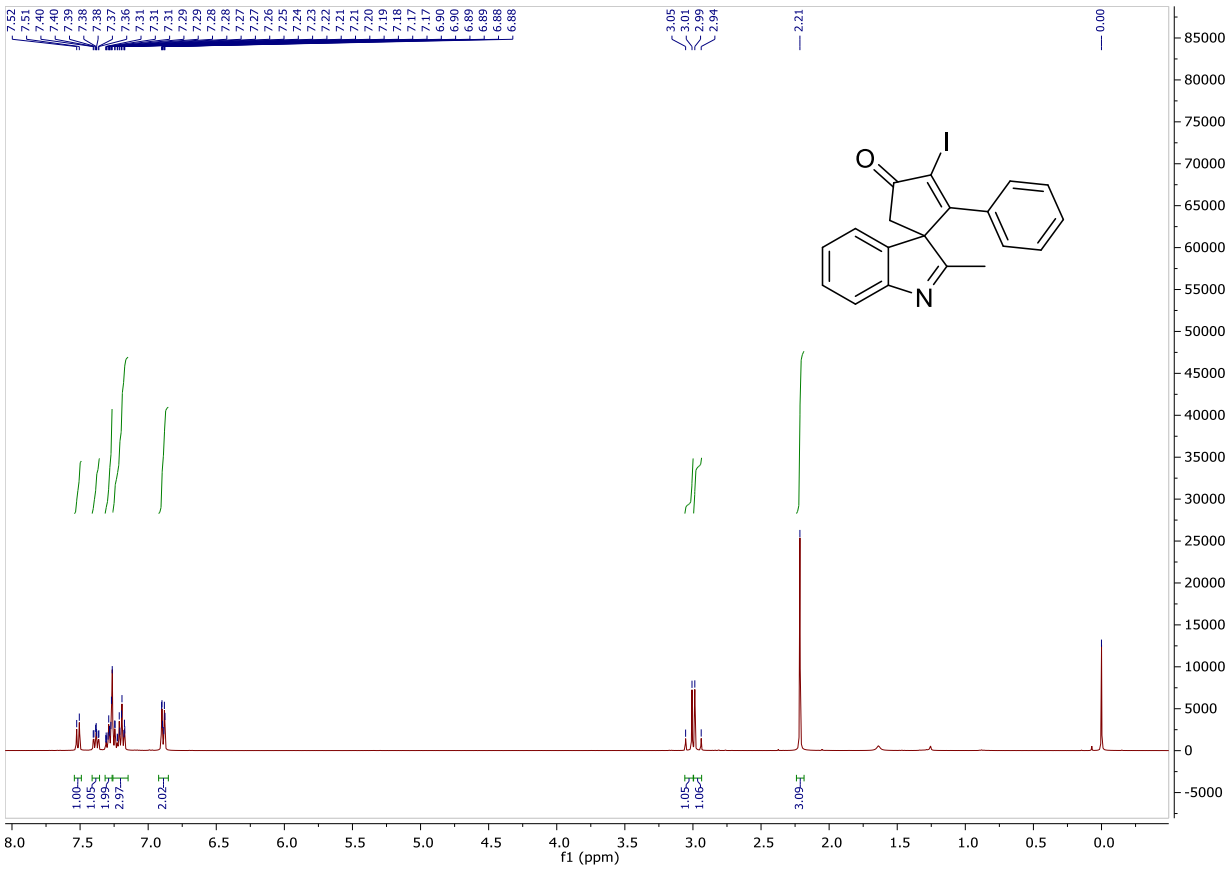
Br
N
f1 (ppm)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7.28
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.17
7.17
6.90
6.90
6.89
6.89
6.88
6.88
3.05
3.01
2.99
2.94
2.21
0.00
O
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N
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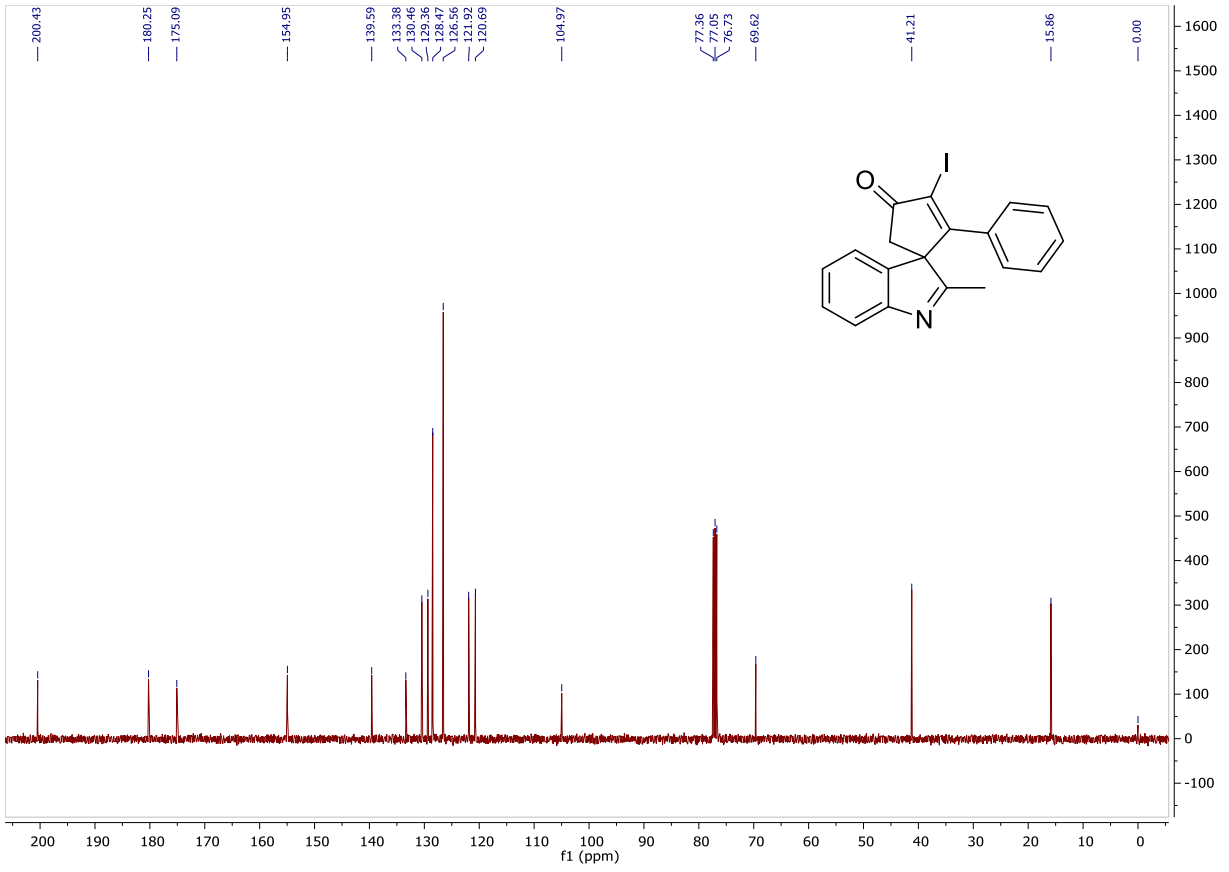
1.05
1.99
2.97
2.02
1.05
1.06
3.09
f1 (ppm)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175.09
154.95
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133.38
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129.36
128.47
126.56
121.92
120.69
104.97
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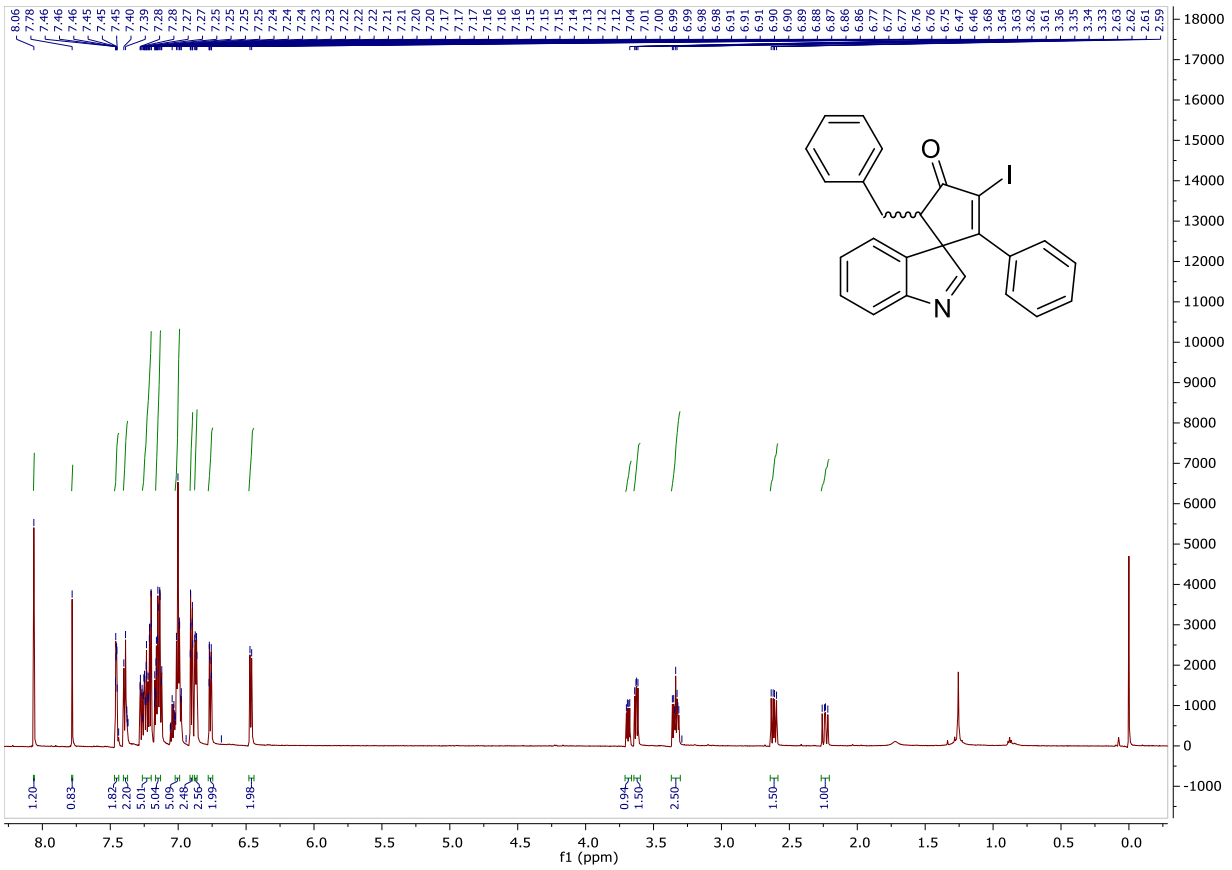
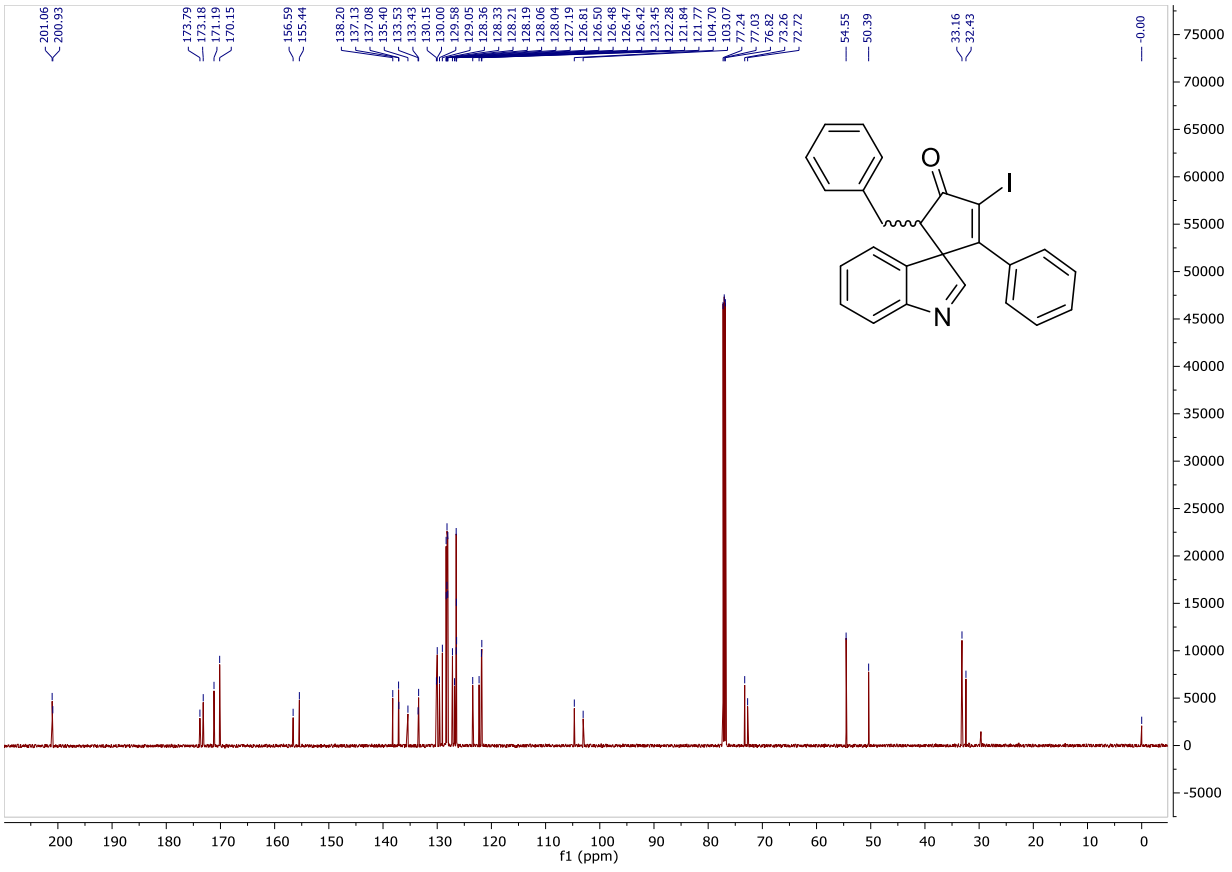
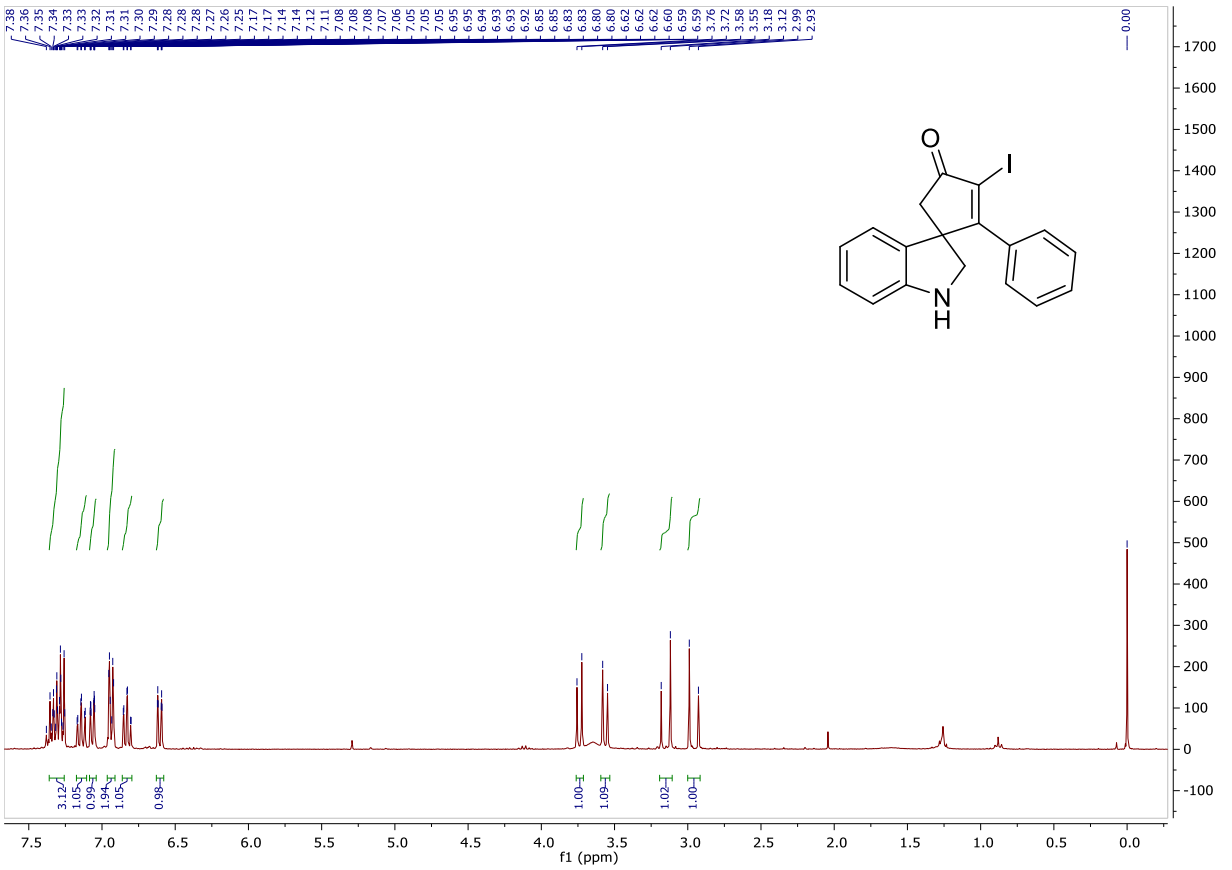
77.05
76.73
69.62
41.21
15.86
0.00
O
I
N
f1 (ppm)


O
I
N
f1 (ppm)


O
I
N
f1 (ppm)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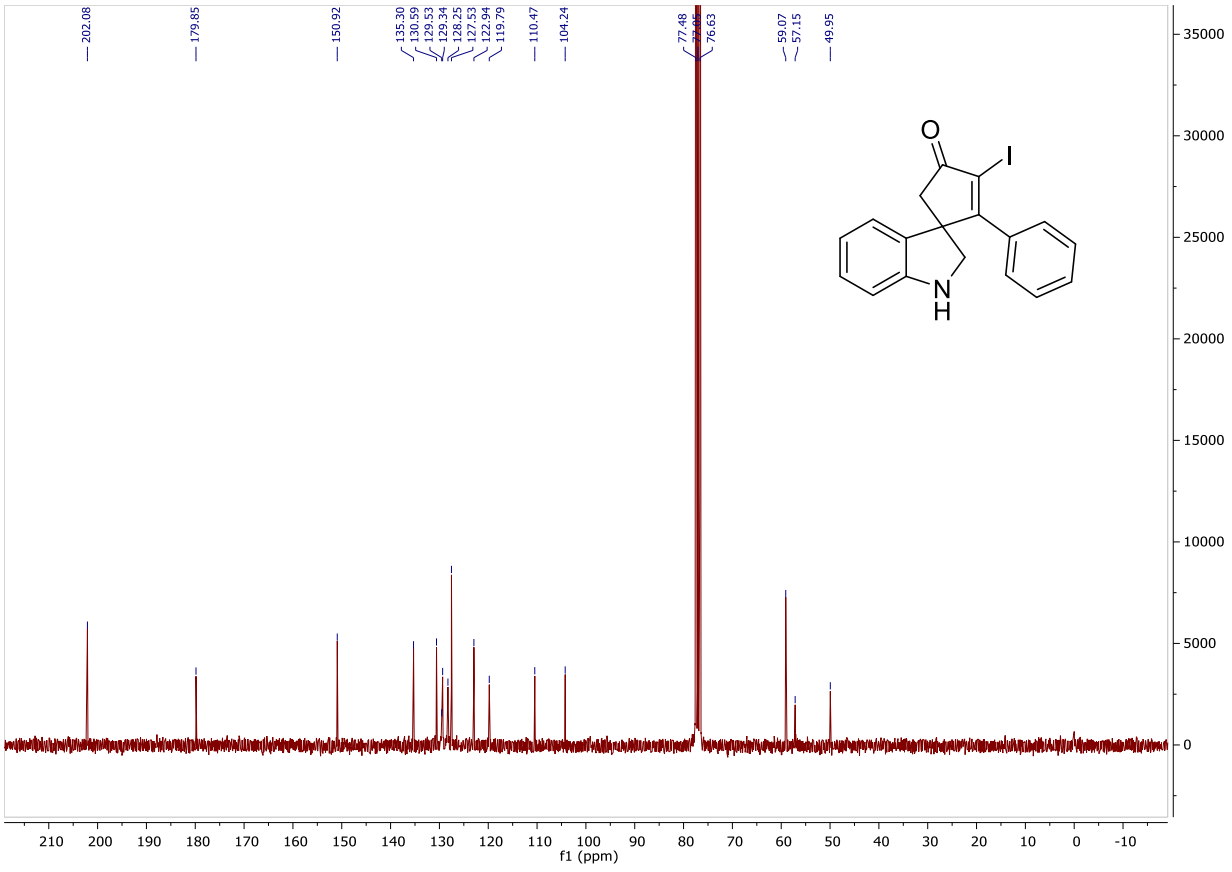
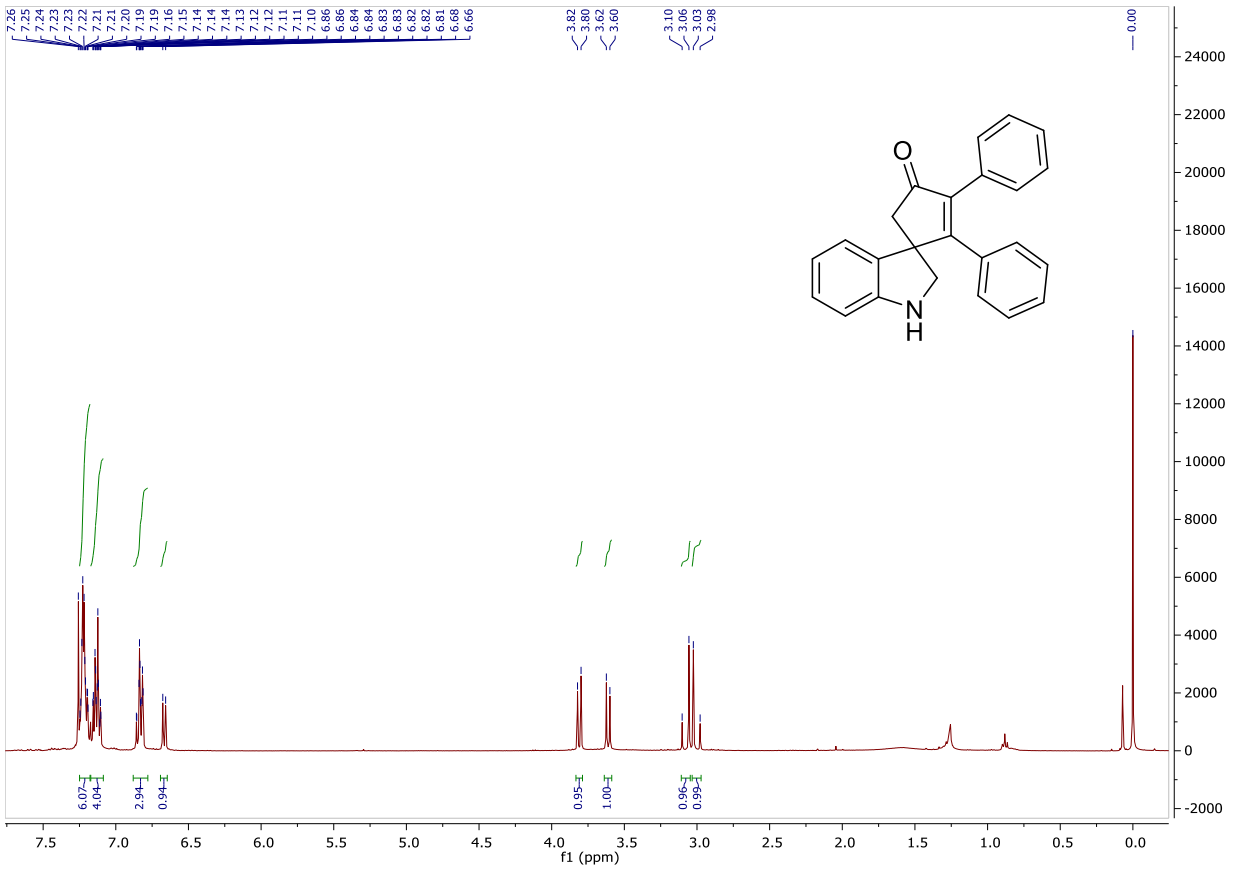
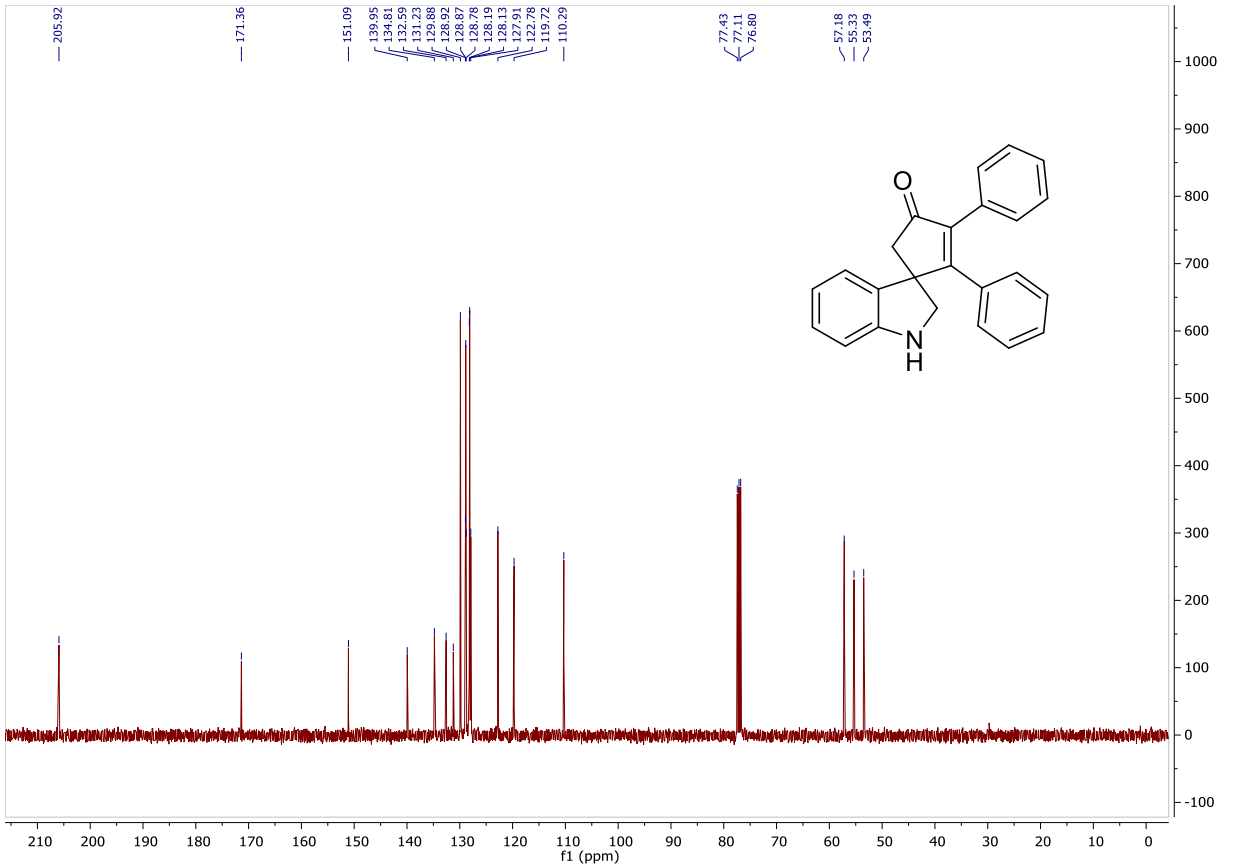
0.00
O
I
N
H
3.12 1.05 0.99 1.94 1.05 0.98 1.00 1.09 1.02 1.00
f1 (ppm)


202.08 179.85 150.92 135.30 130.59 129.53 129.34 128.25 127.53 122.94 119.79 110.47 104.24 77.48 77.05 76.63 59.07 57.15 49.95
O
I
N
H
f1 (ppm)


7.26 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.16 7.15 7.14 7.14 7.14 7.13 7.12 7.12 7.11 7.11 7.10 6.86 6.86 6.84 6.84 6.83 6.83 6.82 6.82 6.81 6.68 6.66
3.82 3.80 3.62 3.60
3.10 3.06 3.03 2.98
0.00
O
N
H
6.07 4.04 2.94 0.94 0.95 1.00 0.96 0.99
f1 (ppm)


205.92
171.36
151.09
139.95 134.81 132.59 131.23 129.88 128.92 128.87 128.78 128.19 128.13 127.91 122.78 119.72
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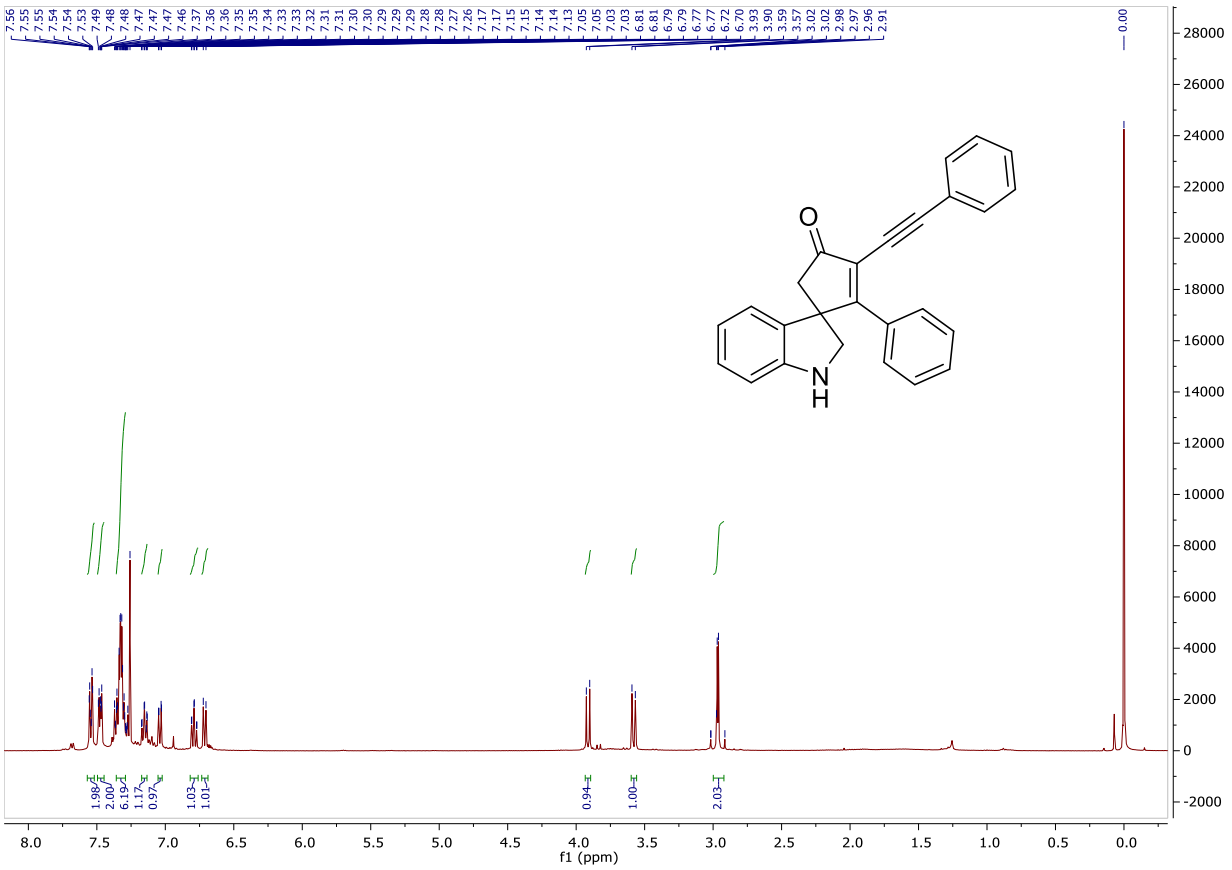
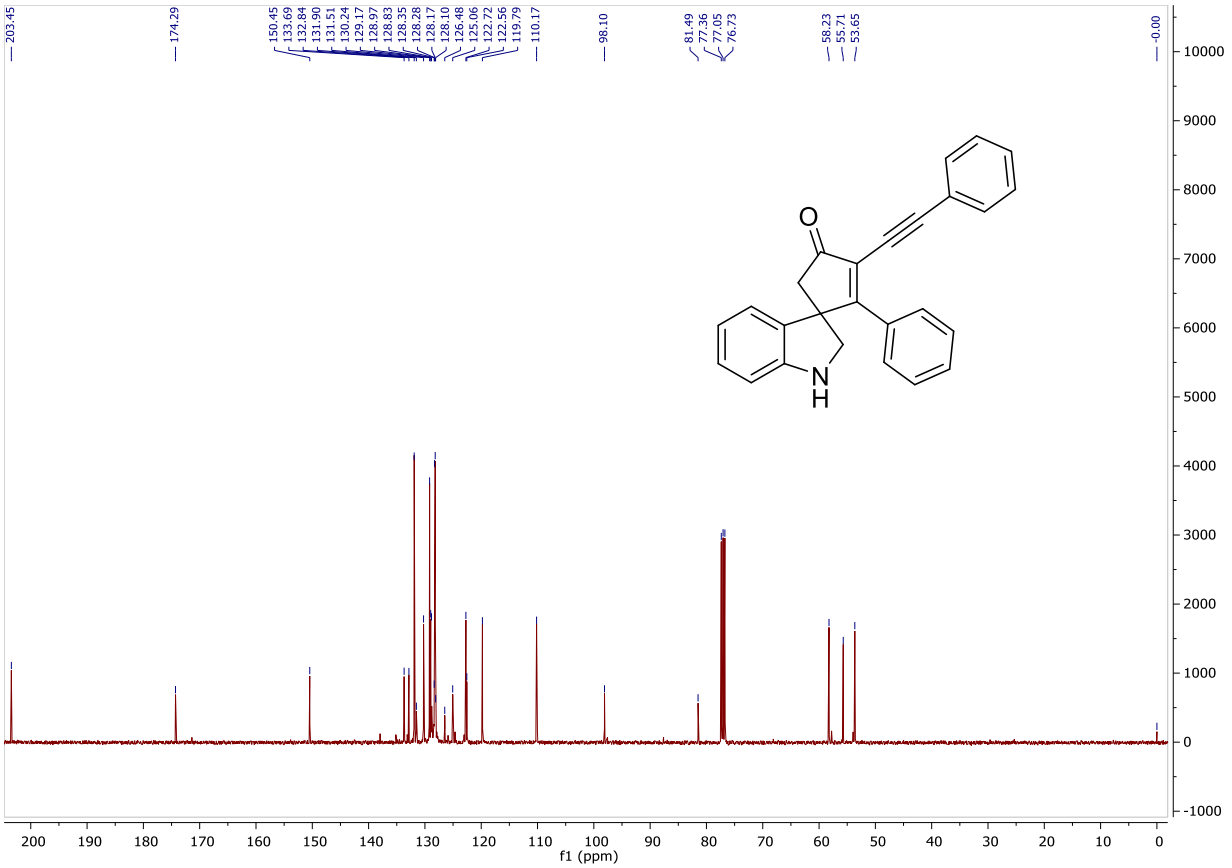
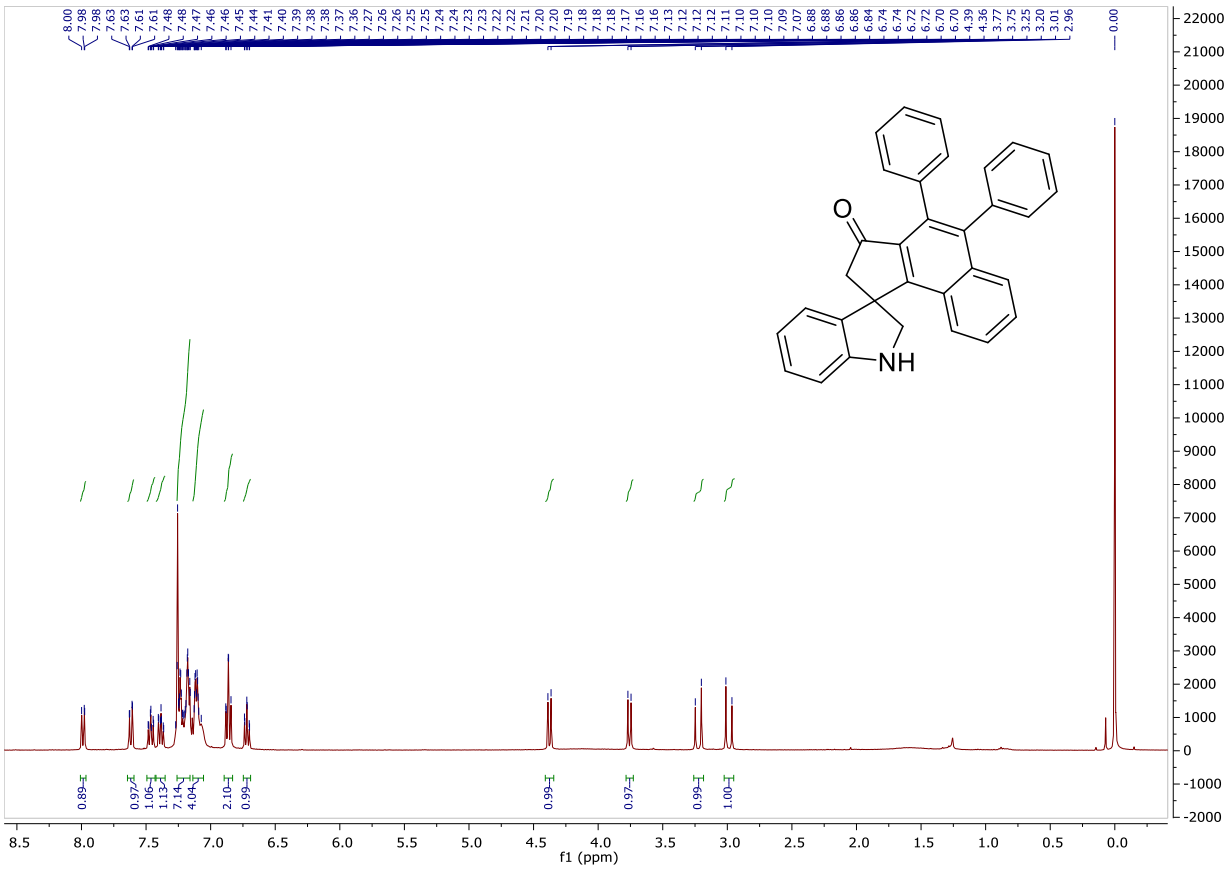
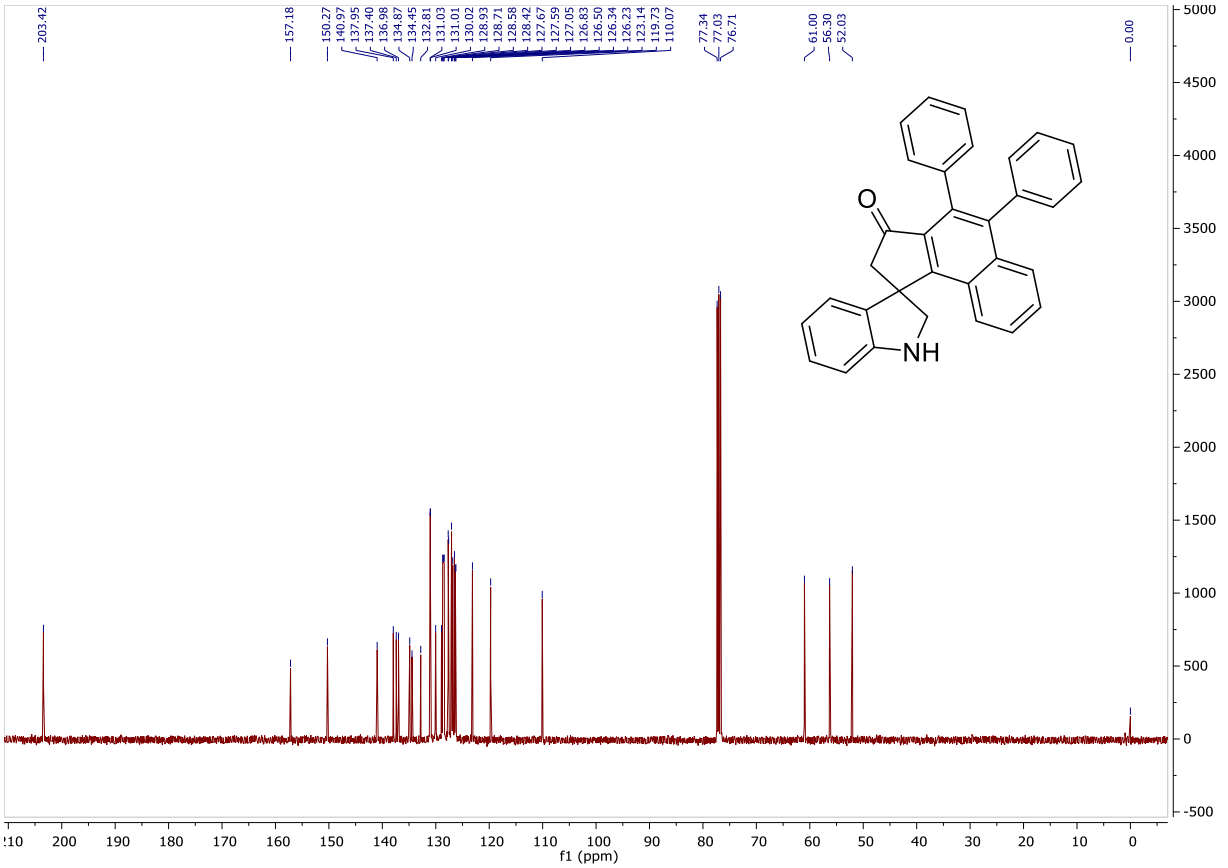
57.18 55.33 53.49
O
N
H
f1 (ppm)


7.56 7.55 7.55 7.54 7.54 7.53 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.26 7.17 7.17 7.15 7.15 7.14 7.14 7.13 7.05 7.05 7.03 7.03 6.81 6.81 6.79 6.79 6.77 6.77 6.72 6.70 3.93 3.90 3.59 3.57 3.02 3.02 2.98 2.97 2.96 2.91
0.00
O
N
H
1.98 2.00 6.19 1.17 0.97 1.03 1.01 0.94 1.00 2.03
f1 (ppm)


203.45 174.29 150.45 133.69 132.84 131.90 131.51 130.24 129.17 128.97 128.83 128.35 128.28 128.17 128.10 126.48 125.06 122.72 122.56 119.79 110.17 98.10 81.49 77.36 77.05 76.73 58.23 55.71 53.65 -0.00
O
N
H
f1 (ppm)


O
NH
f1 (ppm)


O
NH
f1 (ppm)