Regioselective Iodoamination of Terminal Ynamides for the Synthesis of *α*-amino-*β*,*β*-diiodo-enamides

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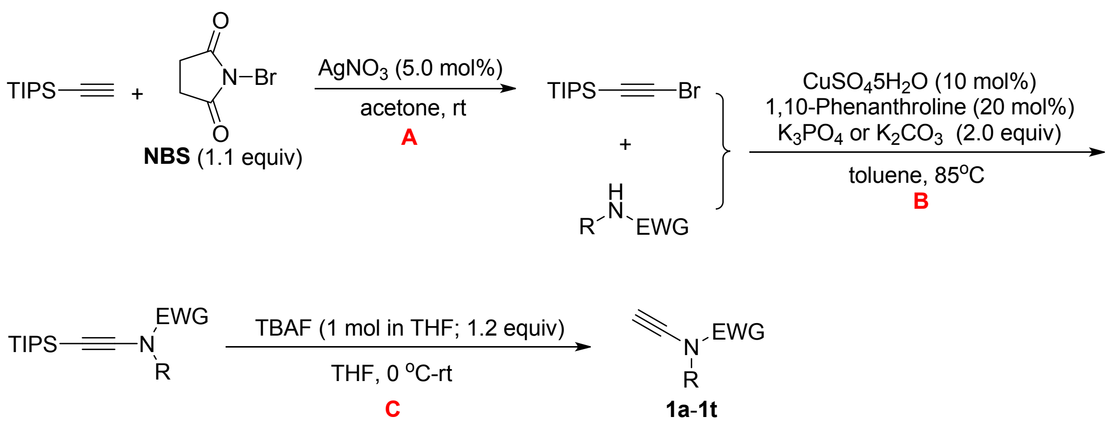
1. General Method

All reactions were performed in reaction tubes under air atmosphere. ^1H NMR and ^{13}C NMR were recorded at respectively 400 MHz and 100 MHz spectrometer using $CDCl_3$ as solvent. The following abbreviations are used to describe peak patterns where appropriate: br =broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets. Coupling constants are reported in Hertz (Hz). Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ = 0 ppm) for ^1H NMR and deuteriochloroform (δ = 77.00 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on an ESI-TOF (time-of-flight) mass spectrometer. Melting points were measured with micro melting point apparatus.

2. Preparation of terminal ynamides

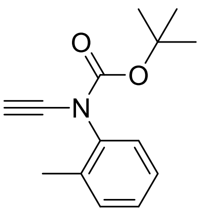


Procedure A: 1-bromo-2-triisopropylsilylacetylene was prepared according to Hofmeister's procedure:[1] A solution of ethynyltriisopropylsilane (50 mmol) in acetone (60 mL) is treated at rt with *N*-bromosuccinimide (NBS, 55 mmol) and $AgNO_3$ (2.5 mmol). After 2h, the reaction mixture is concentrated in vacuum. The crude products were purified by silica gel flash chromatography on a silica gel column with petroleum ether (PE) as eluent to afford the 1-bromo-2-triisopropylsilylacetylene.

Procedure B: TIPS-substituted ynamides were prepared according to a modified version of Hsung's procedure:[2] To a stirred solution of the appropriate amide (1.0 equiv, 1.0 M in toluene) were added K_2CO_3 or K_3PO_4 (2.0 equiv), $CuSO_4$•$5H_2O$ (10 mol%), 1,10-phenanthroline (20 mol% equiv) and 1-bromo-2-triisopropylsilylacetylene (1.25 equiv). The reaction was capped under a blanket of nitrogen and heated at 85 °C for 48 h while being monitored with TLC analysis. Upon completion, the reaction mixture was cooled to room temperature and diluted with EtOAc and filtered through Celite, and the filtrate was concentrated in vacuum. The crude products were purified by silica gel flash chromatography on a silica gel column with petroleum ether (PE) and ethyl acetate (EA) as eluent to afford directing products.

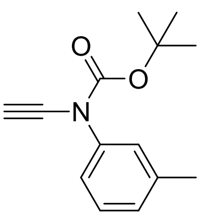
Procedure C: Terminal ynamides **1a-1t** were prepared by the modified version of Oestreich's procedure:[3] To a stirred solution of the appropriate TIPS-substituted ynamide (1.0 equiv, 0.2 M in THF) cooled to 0 °C was added a solution of TBAF (1.2 equiv, 1.0 M in THF). After 1h stirring at 0 °C, the reaction was allowed to warm to room temperature and then quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with Et_2O (x 3). The combined organics were washed with brine (x 2), dried (Na_2SO_4), filtered and the solvents were evaporated under reduced pressure to afford the crude product.

2.1. Characterization data for new compounds.



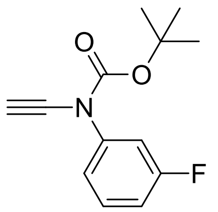
1b

***tert*-butyl ethynyl(*o*-tolyl)carbamate (1b)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1b** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 4 H), 2.79 (s, 1 H), 2.31 (s, 3 H), 1.49 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 137.9, 135.3, 131.0, 128.5, 127.3, 126.9, 83.2, 76.9, 57.3, 27.9, 17.4; **IR** ν (KBr, cm^{-1}) 2309, 2104, 1716, 1558, 1458, 1349, 1206, 968, 742; **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{17}NO_2$ ($[M+Na]^+$) 254.1157, Found: 245.1158.



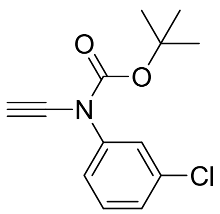
1c

***tert*-butyl ethynyl(*m*-tolyl)carbamate (1c)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1c** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 3 H), 7.09-7.04 (m, 1 H), 2.87 (s, 1 H), 2.36 (s, 3 H), 1.53 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 139.0, 138.8, 128.6, 127.7, 125.4, 121.9, 83.5, 58.0, 27.9, 21.3; **IR** ν (KBr, cm^{-1}) 2312, 2104, 1713, 1560, 1451, 1330, 1261, 954, 731; **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{17}NO_2$ ($[M+Na]^+$) 254.1157, Found: 245.1157.



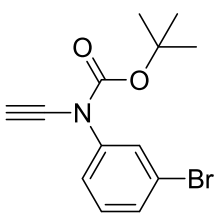
1d

***tert*-butyl ethynyl(3-fluorophenyl)carbamate (1d)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1d** as a yellow oil. R_f 0.20 (ν_{PE}/ν_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 3 H), 6.97-6.92 (m, 1 H), 2.93 (s, 1 H), 1.55 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5 (d, *J*= 244.2Hz), 152.6, 140.5 (d, *J* = 10.0 Hz), 129.8 (d, *J* = 9.0 Hz), 119.8 (d, *J* = 2.9 Hz), 113.5 (d, *J* = 20.8 Hz), 111.9 (d, J = 25.1 Hz), 84.1, 76.0, 59.1, 27.9; **IR** ν (KBr, cm^{-1}) 2302, 2118, 1721, 1531, 1446, 1325, 1277, 960, 728; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{14}FNO_2$ ($[M+H]^+$) 236.1087, Found: 236.1078.



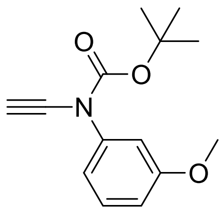
1e

***tert*-butyl (3-chlorophenyl)(ethynyl)carbamate (1e)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1e** as a yellow oil. R_f 0.20 (ν_{PE}/ν_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 2.0 Hz, 1 H), 7.41-7.37 (m, 1 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.24-7.20 (m, 1 H), 2.92 (s, 1 H), 1.54 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 140.2, 134.3, 129.6, 126.7, 124.7, 122.6, 84.2, 76.0, 59.0, 27.9; **IR** ν (KBr, cm^{-1}) 2298, 2076, 1736, 1520, 1429, 1311, 1289, 933, 754; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{14}ClNO_2$ ($[M+Na]^+$) 274.0611, Found: 274.0621.



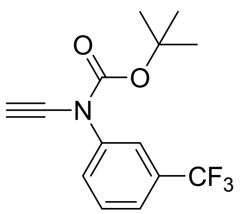
1f

***tert*-butyl (3-bromophenyl)(ethynyl)carbamate (1f)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1b** as a yellow oil. R_f 0.20 (ν_{PE}/ν_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 2.0 Hz, 1 H), 7.46-7.41 (m, 1 H), 7.39-7.35 (m, 1 H), 7.24 (t, *J* = 8.0 Hz, 1 H), 2.91 (s, 1 H), 1.54 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5, 140.3, 129.9, 129.7, 127.6, 123.1, 122.0, 84.2, 76.0, 59.1, 27.9; **IR** ν (KBr, cm^{-1}) 2301, 2133, 1703, 1558, 1431, 1321, 1299, 918, 733; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{14}BrNO_2$ ($[M+Na]^+$) 318.0106, Found: 318.0113.



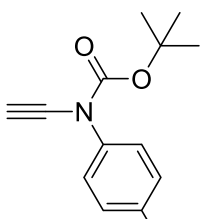
1g

***tert*-butyl ethynyl(3-methoxyphenyl)carbamate (1g)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1g** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, J = 8.0 Hz, 1 H), 7.08-7.04 (m, 1 H), 7.03 (t, J = 2.4 Hz, 1 H), 6.82-6.78 (m, 1 H), 3.81 (s, 3 H), 2.88 (s, 1 H), 1.53 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 152.9, 140.2, 129.4, 117.0, 112.5, 110.7, 83.7, 76.8, 58.4, 55.4, 27.9; **IR** ν (KBr, cm^{-1}) 2287, 2113, 1720, 1536, 1427, 1380, 1220, 886, 731; **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{17}NO_3$ ($[M+Na]^+$) 270.1106, Found: 270.1109.



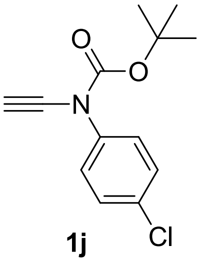
1h

***tert*-butyl ethynyl(3-(trifluoromethyl)phenyl)carbamate (1h)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 50:1) afforded analytically pure **1h** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 60:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1 H), 7.73-7.67 (m, 1 H), 7.50 (d, J = 4.8 Hz, 2 H), 2.94 (s, 1 H), 1.55 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5, 139.8, 131.3 (d), 129.3, 127.5, 125.0, 123.5 (m), 121.3 (m), 84.4, 75.8, 59.3, 27.9; **IR** ν (KBr, cm^{-1}) 2321, 2103, 1699, 1513, 1421, 1354, 1234, 957, 757; **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{14}F_3NO_2$ ($[M+Na]^+$) 308.0874, Found: 308.0880.



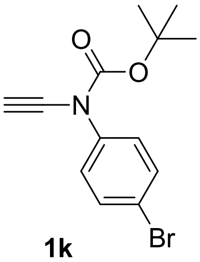
1i

***tert*-butyl ethynyl(*p*-tolyl)carbamate (1i)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1i** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2 H), 7.17 (d, J = 8.0 Hz, 1 H), 6.82-6.78 (m, 1 H), 2.85 (s, 1 H), 2.34 (s, 3 H), 1.52 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 136.8, 136.6, 129.4, 124.7, 83.5, 77.1, 57.9, 27.9, 21.0; **IR** ν (KBr, cm^{-1}) 2310, 2098, 1731, 1502, 1444, 1337, 1211, 932, 734; **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{17}NO_2$ ($[M+Na]^+$) 254.1157, Found: 245.1157.



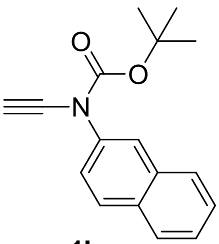
1j

***tert*-butyl (4-chlorophenyl)(ethynyl)carbamate (1j)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1j** as a yellow oil. R_f 0.20 (ν_{PE}/ν_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 2 H), 7.36-7.31 (m, 2 H), 2.89 (s, 1 H), 1.53 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 137.7, 132.2, 128.9, 125.9, 84.1, 76.3, 58.7, 27.9; **IR** ν (KBr, cm^{-1}) 2290, 2104, 1767, 1503, 1468, 1388, 1222, 912, 727; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{14}ClNO_2$ ($[M+Na]^+$) 274.0611, Found: 274.0623.



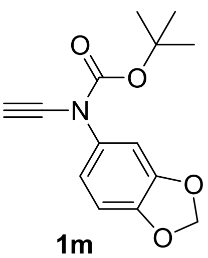
1k

***tert*-butyl (4-bromophenyl)(ethynyl)carbamate (1k)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1k** as a yellow oil. R_f 0.20 (ν_{PE}/ν_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 2 H), 7.38-7.34 (m, 2 H), 2.90 (s, 1 H), 1.53 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 138.3, 131.8, 126.2, 120.1, 84.1, 76.2, 58.8, 27.9; **IR** ν (KBr, cm^{-1}) 2306, 2098, 1741, 1487, 1455, 1338, 1204, 883, 756; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{14}BrNO_2$ ($[M+Na]^+$) 318.0106, Found: 318.0094.



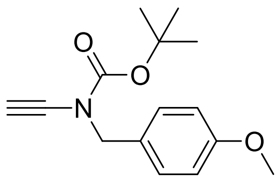
1l

***tert*-butyl ethynyl(naphthalen-2-yl)carbamate (1l)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 50:1) afforded analytically pure **1l** as a yellow oil. R_f 0.20 (ν_{PE}/ν_{EA}= 60:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 2.0 Hz, 1 H), 7.86-7.80 (m, 3 H), 7.57 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1 H), 7.52-7.45 (m, 2 H), 2.93 (s, 1 H), 1.55 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 136.6, 133.2, 131.9, 128.6, 127.9, 127.6, 126.5, 126.2, 123.3, 122.8, 83.8, 76.9, 58.3, 28.0; **IR** ν (KBr, cm^{-1}) 2305, 2122, 1732, 1498, 1453, 1230, 1210, 954, 727; **HRMS** (ESI^+): m/z calcd. for $C_{17}H_{17}NO_2$ ($[M+Na]^+$) 290.1157, Found: 290.1161.



1m

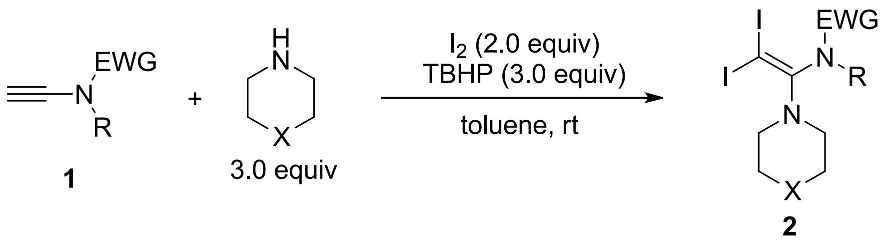
***tert*-butyl benzo[*d*][1,3]dioxol-5-yl(ethynyl)carbamate (1m)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 50:1) afforded analytically pure **1m** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 60:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.92-6.87 (m, 2 H), 6.78 (d, J = 8.0 Hz, 1 H), 5.98 (s, 2 H), 2.85 (s, 1 H), 1.52 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 147.7, 146.5, 133.1, 118.8, 107.9, 106.9, 101.6, 77.1, 57.9, 27.9; **IR** ν (KBr, cm^{-1}) 2298, 2132, 1741, 1501, 1466, 1277, 1248, 886, 731; **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{15}NO_4$ ($[M+Na]^+$) 284.0899, Found: 284.0898.



1o

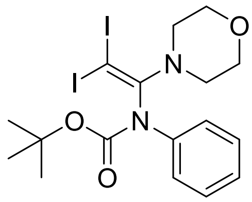
***tert*-butyl ethynyl(4-methoxybenzyl)carbamate (1o)**: Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1o** as a yellow oil. R_f 0.20 (v_{PE}/v_{EA}= 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8 Hz, 2 H), 6.89-6.84 (m, 2 H), 4.50 (s, 2 H), 3.80 (s, 3 H), 2.76 (m, 1 H), 1.49 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 154.1, 129.6, 128.5, 113.8, 82.8, 58.7, 55.2, 52.5, 28.0; **IR** ν (KBr, cm^{-1}) 2308, 2146, 1738, 1479, 1438, 1289, 1253, 911, 757; **HRMS** (ESI^+): m/z calcd. for $C_{15}H_{19}NO_3$ ($[M+Na]^+$) 284.1263, Found: 284.1265.

3. General Procedure for diiodo-enamides



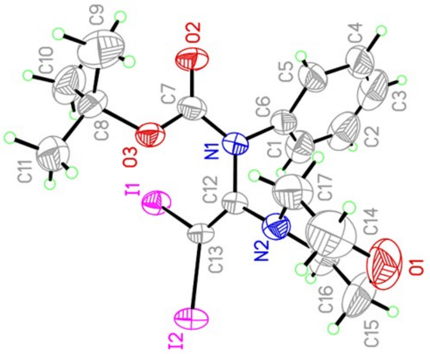
In a 10 mL flame-dried Schlenk tube under air condition, I_2 (0.6 mmol) and amines (0.9 mmol) were dissolved in toluene (2.0 mL) and stirred, then terminal ynamides **1** (0.3 mmol) and TBHP (70% in water, 0.9 mmol) were added successively. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford the corresponding diiodo-enamides**.**

3.1. Characterization data for New compounds.

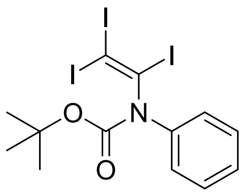


2a

***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(phenyl)carbamate (2a)**: yield 71% (118.7 mg); pale yellow solid; Mp 96-97 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.19 (t, J = 7.42 Hz, 1 H), 3.60-3.48 (m, 4 H), 3.11-3.03 (m, 2 H), 2.88-2.80 (m, 2 H), 1.57 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 150.3, 139.1, 128.7, 125.7, 124.0, 82.2, 66.6, 50.4, 28.3; **MS** (ESI) m/z (%) 579.0 (100) $[M+Na]^+$; **IR** ν (KBr, cm^{-1}) 1697, 1568, 1530, 1441, 1367, 1331, 1310, 1260, 1244, 1166, 1115, 1018, 887, 746, 701; **Anal. calcd** for $C_{17}H_{22}I_2N_2O_3$: C 36.71, H 3.99, N 5.04. Found: C 36.82, H 3.63, N 5.07.

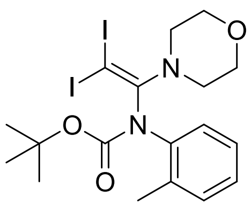


Crystal data for **2a**: $C_{17}H_{22}I_2N_2O_3$; M = 556.17; Orthorhombic; space group $P2_12_12_1$; final R indices [I>2σ(I)]: R_1=0.0202, wR_2 =0.0479, R indices(all data): R_1=0.0216, wR_2=0.0487, a = 9.1833(5) Å, b = 10.6603(6) Å, c = 20.8558(12) Å; V = 2041.7(2) Å^3; T = 296K; Z = 4; reflection measured/independent: 15181/3599 (R_{int} = 0.030), number of observations [I>2σ(I)]: 3451, parameters: 220. CCDC-1425989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

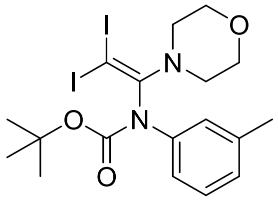


3a

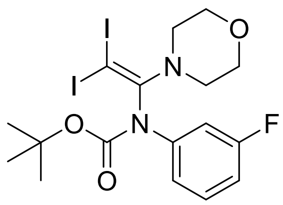
***tert*-butyl phenyl(1,2,2-triiodovinyl)carbamate (3a):** pale yellow solid; Mp 102-103 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 60:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 4 H), 7.31-7.25 (m, 1 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 138.5, 128.9, 126.6, 124.4, 110.5, 83.2, 32.1, 28.2; **MS** (ESI) m/z (%) 619.8 (100) $[M+Na]^+$; **IR** ν (KBr, cm^{-1}) 1651, 1598, 1552, 1466, 1338, 1321, 1299, 1236, 1112, 1003, 948, 767; **Anal. calcd** for $C_{13}H_{14}I_3NO_2$: C 26.16, H 2.36, N 2.35. Found: C 26.26, H 2.49, N 2.67.



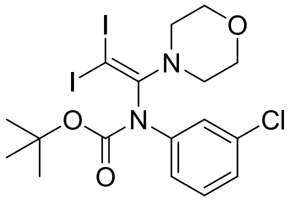
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(*o*-tolyl)carbamate (2b)**: yield 34% (58.2 mg); pale yellow solid; Mp 84-85 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 4 H), 3.57-3.40 (m, 4 H), 3.01 (br, 2 H), 2.73 (br, 2 H), 2.21 (s, 3 H), 1.60 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 134.4, 131.7, 131.6, 126.9, 126.3, 124.7, 81.9, 66.7, 50.4, 28.3, 19.2; **MS** (ESI) m/z (%) 571.3 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1689, 1648, 1602, 1588, 1561, 1466, 1352, 1318, 1288, 1224, 1153, 1101, 951, 757; **Anal. calcd** for $C_{18}H_{24}I_2N_2O_3$: C 37.91, H 4.24, N 4.91. Found: C 38.04, H 4.33, N 4.85.



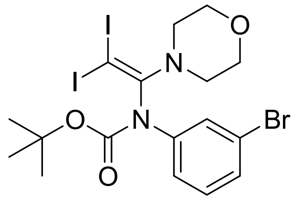
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(*m*-tolyl)carbamate (2c):** yield 65% (111.3 mg); pale yellow solid; Mp 111-112 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, J = 8.0 Hz, 1 H), 7.11 (s, 1 H), 7.05 (d, J = 8.0 Hz, 1 H), 7.00 (d, J = 7.6 Hz, 1 H), 3.60-3.48 (m, 4 H), 3.10-3.02 (m, 2 H), 2.86-2.79 (m, 2 H), 2.36 (s, 3 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 150.3, 139.0, 138.6, 128.5, 126.5, 124.6, 121.0, 82.1, 66.6, 50.4, 28.3, 21.5; **MS** (ESI) m/z (%) 571.6 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1727, 1692, 1650, 1650, 1575, 1558, 1488, 1369, 1323, 1301, 1252, 1153, 1114, 858, 734; **Anal. calcd** for $C_{18}H_{24}I_2N_2O_3$: C 37.91, H 4.24, N 4.91. Found: C 37.82, H 4.51, N 4.92.



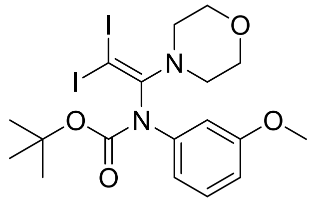
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(3-fluorophenyl)carbamate (2d)**: yield 69% (118.6 mg); pale yellow solid; Mp 121-123 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 1 H), 7.12-7.02 (m, 2 H), 6.90 (td, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H), 3.63-3.52 (m, 4 H), 3.11-3.08 (m, 2 H), 2.93-2.85 (m, 2 H), 1.58 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, J = 244.2 Hz), 151.6, 149.8, 140.7 (d, J = 9.7 Hz), 129.8 (d, J = 8.6 Hz), 119.0, 112.4 (d, J = 20.9 Hz), 111.2 (d, J = 24.2 Hz), 82.7, 66.6, 50.5, 28.3; **MS** (ESI) m/z (%) 575.3 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1698, 1615, 1488, 1370, 1319, 1265, 1220, 1152, 1117, 867, 771; **Anal. calcd** for $C_{17}H_{21}FI_2N_2O_3$: C 35.56, H 3.69, N 4.88. Found: C 35.63, H 3.58, N 4.68.



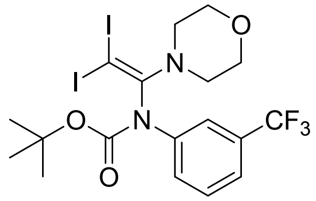
***tert*-butyl (3-chlorophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2j):** yield 70% (124.1 mg); pale yellow solid; Mp 124-125 °C (*n*-hexane/ethyl acetate); R_f 0.20 ($v_{\mathrm{PE}}/v_{\mathrm{EA}}$= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (s, 1 H), 7.27 (t, J = 8.0 Hz, 1 H), 7.19-7.13 (m, 2 H), 3.62-3.51 (m, 4 H), 3.11-3.03 (m, 2 H), 2.91-2.84 (m, 2 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.6, 149.7, 140.3, 134.4, 129.6, 125.7, 124.0, 121.7, 82.8, 66.6, 50.5, 28.3; **MS** (ESI) m/z (%) 591.0 (100) $[M+H]^+$; **IR** v (KBr, cm^{-1}) 1735, 1694, 1569, 1474, 1368, 1320, 1265, 1212, 1152, 1115, 1005, 891, 777, 668; **Anal. calcd** for $C_{17}H_{21}ClI_2N_2O_3$: C 34.57, H 3.58, N 4.74. Found: C 34.66, H 3.48, N 4.91.



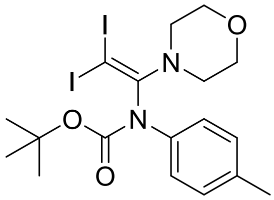
***tert*-butyl (3-bromophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2f):** yield 72% (136.9 mg); pale yellow solid; Mp 131-133 °C (*n*-hexane/ethyl acetate); R_f 0.20 ($v_{\mathrm{PE}}/v_{\mathrm{EA}}$= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (s, 1 H), 7.32 (dt, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1 H), 7.24-7.17 (m, 2 H), 3.62-3.51 (m, 4 H), 3.11-3.03 (m, 2 H), 2.91-2.83 (m, 2 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.6, 149.7, 140.5, 130.0, 128.6, 126.8, 122.2, 122.1, 82.8, 66.6, 50.5, 28.3; **MS** (ESI) m/z (%) 635.4 (100) $[M+H]^+$; **IR** v (KBr, cm^{-1}) 1719, 1577, 1475, 1369, 1309, 1265, 1230, 1154, 1140, 1114, 1001, 891, 759; **Anal. calcd** for $C_{17}H_{21}BrI_2N_2O_3$: C 32.15, H 3.33, N 4.41. Found: C 32.39, H 3.61, N 4.29.



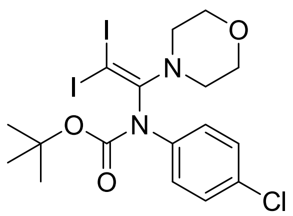
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(3-methoxyphenyl)carbamate:** yield 44% (77.4 mg); pale yellow solid; Mp 107-108 °C (*n*-hexane/ethyl acetate); R_f 0.20 ($v_{\mathrm{PE}}/v_{\mathrm{EA}}$= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 1 H), 6.90-6.85 (m, 2 H), 6.76-6.72 (m, 1 H), 3.81 (s, 3 H), 3.63-3.50 (m, 4 H) 3.11-3.04 (m, 2 H), 2.89-2.82 (m, 2 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 151.8, 150.2, 140.2, 129.3, 116.3, 110.7, 110.3, 82.3, 66.6, 55.4, 50.5, 28.3; **MS** (ESI) m/z (%) 587.1 (100) $[M+H]^+$; **IR** v (KBr, cm^{-1}) 1706, 1636, 1575, 1448, 1370, 1330, 1311, 1265, 1157, 1146, 1114, 1007, 848, 791; **Anal. calcd** for $C_{18}H_{24}I_2N_2O_4$: C 36.88, H 4.13, N 4.78. Found: C 36.73, H 4.28, N 4.87.



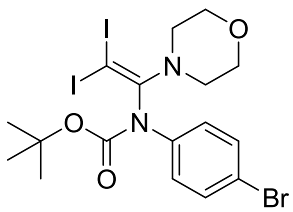
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(3-(trifluoromethyl)phenyl)carbamate:** yield 76% (142.1 mg); pale yellow solid; Mp 115-116 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1 H), 7.51-7.42 (m, 3 H), 3.61-3.49 (m, 4 H) 3.11-3.03 (m, 2 H), 2.91-2.89 (m, 2 H), 1.58 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.6, 149.5, 139.8, 131.3 (d, J = 32.8 Hz), 129.3, 126.5, 125.0, 122.3, 122.1 (q, J = 4.1 Hz), 120.6 (p), 83.0, 66.5, 50.4, 28.3; **MS** (ESI) m/z (%) 625.1 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1685, 1549, 1528, 1436, 1359, 1327, 1302, 1288, 1255, 1149, 1103, 1001, 976, 748; **Anal. calcd** for $C_{18}H_{21}F_3I_2N_2O_3$: C 34.64, H 3.39, N 4.49. Found: C 34.72, H 3.48, N 4.51.



***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(*m*-tolyl)carbamate:** yield 68% (116.5 mg); pale yellow solid; Mp 117-118 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.11 (m, 4 H), 3.61-3.49 (m, 4 H), 3.09-3.02 (m, 2 H), 2.85-2.78 (m, 2 H), 2.33 (s, 3 H), 1.56 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 150.4, 136.4, 135.5, 129.3, 123.9, 82.2, 66.6, 50.4, 28.3, 20.9; **MS** (ESI) m/z (%) 571.3 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1696, 1562, 1511, 1449, 1367, 1317, 1310, 1262, 1218, 1156, 1116, 1107, 887, 839, 771; **Anal. calcd** for $C_{18}H_{24}I_2N_2O_3$: C 37.91, H 4.24, N 4.91. Found: C 37.83, H 4.47, N 4.81.

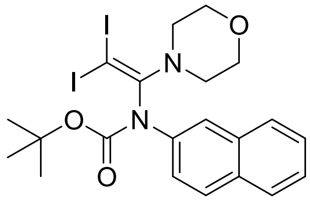


***tert*-butyl (4-chlorophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2j):** yield 63% (111.3 mg); pale yellow solid; Mp 123-124 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2 H), 7.23 (d, J = 8.8 Hz, 2 H), 3.62-3.51 (m, 4 H), 3.09-3.02 (m, 2 H), 2.90-2.82 (m, 2 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 149.8, 137.7, 130.9, 128.8, 125.1, 82.7, 66.6, 50.5, 28.3; **MS** (ESI) m/z (%) 591.1 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1716, 1563, 1490, 1366, 1313, 1300, 1239, 1213, 1155, 1108, 992, 882, 668; **Anal. calcd** for $C_{17}H_{21}ClI_2N_2O_3$: C 34.57, H 3.58, N 4.74. Found: C 34.65, H 3.53, N 4.90.

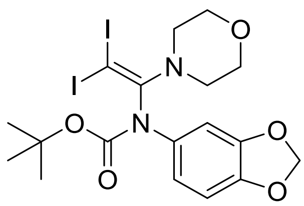


***tert*-butyl (4-bromophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2k):** yield 66% (125.1 mg); pale yellow solid; Mp 131-133 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20

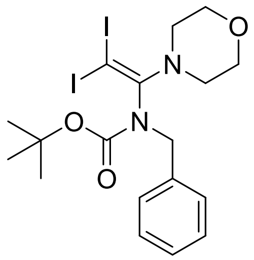
(ν_{PE}/ν_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2 H), 7.17 (d, *J* = 8.8 Hz, 2 H), 3.62-3.51 (m, 4 H), 3.09-3.02 (m, 2 H), 2.90-2.83 (m, 2 H), 1.56 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 149.8, 138.3, 131.8, 125.4, 118.7, 82.7, 66.6, 50.5, 28.3; **MS** (ESI) m/z (%) 635.4 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1716, 1652, 1633, 1558, 1488, 1311, 1154, 1108, 991, 668; **Anal. calcd** for $C_{17}H_{21}BrI_2N_2O_3$: C 32.15, H 3.33, N 4.41. Found: C 32.27, H 3.41, N 4.55.



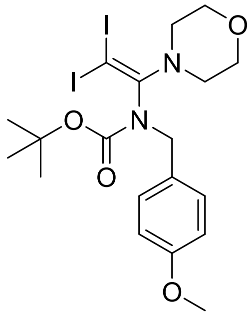
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(naphthalen-2-yl)carbamate (2l)**: yield 62% (112.6 mg); pale yellow solid; Mp 156-157 ^oC (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.77 (m, 3 H), 7.68 (b, 1 H), 7.52-7.42 (m, 3 H), 3.58-3.45 (m, 4 H), 3.13-3.05 (m, 2 H), 2.89-2.82 (m, 2 H), 1.60 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 150.4, 136.7, 133.4, 131.4, 128.5, 127.7, 127.6, 126.5, 125.8, 123.2, 121.3, 82.4, 66.6, 50.5, 28.4; **MS** (ESI) m/z (%) 607.1 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1695, 1652, 1635, 1575, 1558, 1507, 1370, 1317, 1253, 1153, 1113, 1008, 861, 755, 668; **Anal. calcd** for $C_{21}H_{24}I_2N_2O_3$: C 41.61, H 3.99, N 4.62. Found: C 41.59, H 3.88, N 4.79.



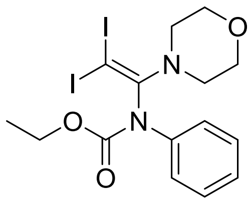
***tert*-butyl benzo[*d*][1,3]dioxol-5-yl(2,2-diiodo-1-morpholinovinyl)carbamate (2m):** yield 54% (96.9 mg); pale yellow solid; Mp 161-163 ^oC (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.86 (s, 1 H), 7.19-7.10 (m, 2 H), 6.41-6.37 (m, 2 H), 4.07-3.92 (m, 4 H), 3.52-3.40 (m, 2 H), 3.25-3.14 (m, 2 H), 1.56 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 150.4, 147.6, 145.5, 133.0, 117.4, 107.7, 106.2, 101.5, 82.1, 66.7, 50.4, 28.3; **MS** (ESI) m/z (%) 601.6 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1697, 1652, 1506, 1488, 1325, 1250, 1214, 1107, 1036; **Anal. calcd** for $C_{18}H_{22}I_2N_2O_5$: C 36.02, H 3.69, N 4.67. Found: C 36.17, H 3.57, N 4.39.



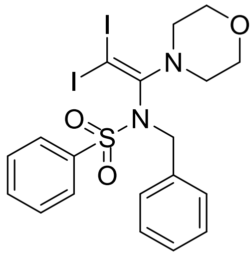
***tert*-butyl benzyl(2,2-diiodo-1-morpholinovinyl)carbamate (2n):** yield 52% (89.1 mg); pale yellow solid; Mp 81-82 ^oC (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5 H), 4.75 (d, *J* = 14.0 Hz, 1 H), , 4.38 (d, *J* = 14.4 Hz, 1 H), 3.59-3.41 (m, 4 H), 2.90-2.77 (m, 4 H), 1.53 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 150.8, 137.1, 129.7, 128.5, 127.9, 81.5, 66.6, 51.9, 50.1, 28.4; **MS** (ESI) m/z (%) 571.6 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1693, 1560, 1387, 1365, 1342, 1263, 1165, 1114, 1014, 946, 862, 761; **Anal. calcd** for $C_{18}H_{24}I_2N_2O_3$: C 37.91, H 4.24, N 4.91. Found: C 37.82, H 4.36, N 5.03.



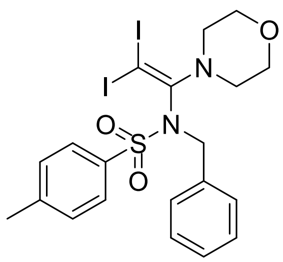
***tert*-butyl (2,2-diiodo-1-morpholinovinyl)(3-methoxyphenyl)carbamate:** yield 53% (95.4 mg); pale yellow solid; Mp 91-93 °C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.2 Hz, 2 H), 6. 85 (d, J = 8.4 Hz, 2 H), 4.66 (d, J = 14.4 Hz, 1 H), 4.36 (d, J = 14.8 Hz, 1 H), 3.80 (s, 3 H), 3.60-3.47 (m, 4 H), 2.92-2.78 (m, 4 H), 1.53 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 153.6, 131.0, 129.3, 113.8, 81.4, 66.6, 55.3, 51.3, 50.1, 28.4; **MS** (ESI) m/z (%) 601.6 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1706, 1636, 1616, 1558, 1511, 1370, 1337, 1301, 1246, 1159, 1106, 1030, 901, 668; **Anal. calcd** for $C_{19}H_{26}I_2N_2O_4$: C 38.02, H 4.37, N 4.67. Found: C 38.16, H 4.59, N 4.73.



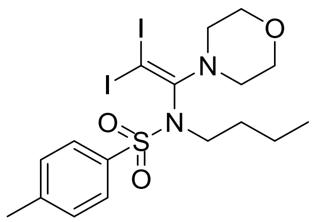
ethyl (2,2-diiodo-1-morpholinovinyl)(phenyl)carbamate (2p): yield 65% (103.2 mg); pale yellow solid; Mp 106-107 °C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2 H), 7.28 (d, J =7.6 Hz, 2 H), 7.25-7.20 (m, 1 H), 4.41-4.25 (m, 2 H), 3.60-3.49 (m, 4 H), 3.10-3.03 (m, 2 H), 2.87-2.80 (m, 2 H), 1.38 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 150.0, 138.9, 128.8, 126.1, 124.1, 66.6, 63.0, 50.4, 14.7; **MS** (ESI) m/z (%) 529.2 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1716, 1635, 1568, 1487, 1456, 1367, 1303, 1235, 1217, 1115, 1049, 888, 765; **Anal. calcd** for $C_{15}H_{18}I_2N_2O_3$: C 34.11, H 3.44, N 5.30. Found: C 34.23, H 3.67, N 5.09.



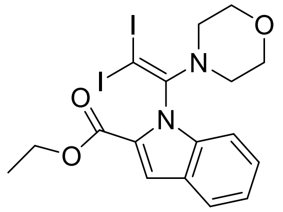
***N*-benzyl-*N*-(2,2-diiodo-1-morpholinovinyl)benzenesulfonamide (2q):** yield 61% (111.7 mg); pale yellow solid; Mp 171-172 °C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.95 (m, 2 H), 7.63 (tt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H), 7.58-7.52 (m, 2 H), 7.35 (m, 5 H), 4.74 (d, J = 14.4 Hz, 1 H), 4.64 (d, J = 14.4 Hz, 1 H), 3.62-3.55 (m, 2 H), 3.45-3.38 (m, 2 H), 3.10-3.03 (m, 2 H), 2.61-2.53 (m, 2 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.4, 139.9, 135.7, 133.4, 130.3, 129.3, 128.7, 128.3, 66.3, 53.7, 49.8; **MS** (ESI) m/z (%) 611.3 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1636, 1617, 1558, 1541, 1507, 1345, 1161, 1109, 854, 732; **Anal. calcd** for $C_{19}H_{20}I_2N_2O_3S$: C 37.40, H 3.30, N 4.59. Found: C 37.45, H 3.46, N 4.37.



***N*-benzyl-*N*-(2,2-diiodo-1-morpholinovinyl)-4-methylbenzenesulfonamide (2r):** yield 58% (108.5 mg); pale yellow solid; Mp 168-169 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2 H), 7.38-7.31 (m, 7 H), 4,69 (d, J = 14.4 Hz, 1 H), 4,62 (d, J = 14.4 Hz, 1 H), 3.61-3.54 (m, 2 H), 3.45-3.38 (m, 2 H), 3.10-3.02 (m, 2 H), 2.61-2.58 (m, 2 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 144.3, 137.0, 135.8, 130.3, 129.8, 128.7, 128.4, 66.3, 53.6, 49.9, 21.7; **MS** (ESI) m/z (%) 625.6 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1630, 1540, 1508, 1457, 1358, 1343, 1206, 1152, 1112, 1025, 827, 720; **Anal. calcd** for $C_{20}H_{22}I_2N_2O_3S$: C 38.48, H 3.55, N 4.49. Found: C 38.31, H 3.49, N 4.54.

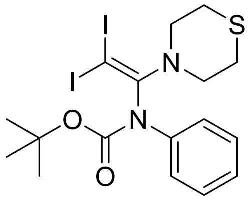


***N*-butyl-*N*-(2,2-diiodo-1-morpholinovinyl)-4-methylbenzenesulfonamide (2s):** yield 33% (58.1mg); pale yellow oil; R_f 0.20 (ν_{PE}/ν_{EA}= 25:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 3.86-3.79 (m, 2 H), 3.77-3.70 (m, 2 H), 3.48-3.32 (m, 4 H), 3.23-3.15 (m, 2 H), 2.43 (s, 3 H), 1.69-1.56 (m, 1 H), 1.54-1.43 (m, 1 H), 1.38-1.27 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 144.2, 136.3, 129.6, 128.5, 66.6, 50.6, 50.4, 31.2, 21.6, 20.2, 13.8; **IR** ν (KBr, cm^{-1}) 1641, 1538, 1503, 1486, 1366, 1329, 1213, 1149, 1106, 1008, 979, 737; **HRMS** (ESI$^+$): m/z calcd. for $C_{17}H_{24}I_2N_2O_2S$ ($[M+Na]^+$) 612.9495, Found: 612.9507.

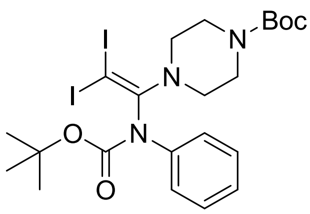


ethyl 1-(2,2-diiodo-1-morpholinovinyl)-1*H*-indole-2-carboxylate (2t): yield 78% (129.2 mg); pale yellow solid; Mp 141-142 ^{o}C (*n*-hexane/ethyl acetate); R_f 0.20 (ν_{PE}/ν_{EA}= 20:1); **^{1}H NMR** (400 MHz,

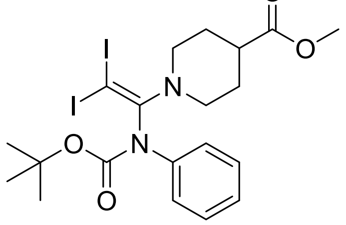
$CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 1 H), 7.47-7.41 (m, 1 H), 7.40 (d, J = 0.4 Hz, 1 H), 7.34 (dd, J_1 = 0.4 Hz, J_2 = 8.0 Hz, 1 H), 7.27-7.21 (m, 1 H), 4.48-4.32 (m, 2 H), 3.67-3.57 (m, 4 H), 3.11-3.04 (m, 2 H), 3.01-2.93 (m, 2 H), 1.44 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 146.3, 138.4, 128.3, 126.5, 126.3, 122.8, 122.2, 113.0, 111.9, 66.9, 61.1, 49.9, 14.4; **MS** (ESI) m/z (%) 553.5 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1711, 1564, 1538, 1443, 1396, 1306, 1260, 1205, 1114, 1004, 880, 747; **Anal. calcd** for $C_{17}H_{18}I_2N_2O_3$: C 36.98, H 3.29, N 5.07. Found: C 37.01, H 3.08, N 5.16.



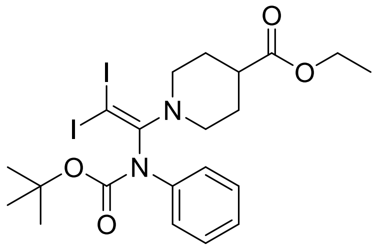
***tert*-butyl (2,2-diiodo-1-thiomorpholinovinyl)(phenyl)carbamate (2ab):** yield 74% (127.1 mg); pale yellow solid; Mp 125-127 °C (*n*-hexane/ethyl acetate); R_f 0.20 (v_{PE}/v_{EA}= 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 2 H), 7.27-7.23 (m, 2 H), 7.22-7.17 (m, 1 H), 3.28-3.20 (m, 2 H), 3.11-3.03 (m, 2 H), 2.61-2.58 (m, 2 H), 2.49-2.41 (m, 2 H), 1.57 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 151.5, 139.2, 128.7, 125.8, 124.2, 82.2, 52.8, 28.3, 27.4; **MS** (ESI) m/z (%) 573.2 (100) $[M+H]^+$; **IR** ν (KBr, cm^{-1}) 1695, 1566, 1496, 1371, 1319, 1309, 1283, 1248, 1157, 1122, 956, 873, 765; **Anal. calcd** for $C_{17}H_{22}I_2N_2O_2S$: C 35.68, H 3.88, N 4.90. Found: C 35.71, H 3.79, N 5.04.



***tert*-butyl 4-(1-((tert-butoxycarbonyl)(phenyl)amino)-2,2-diiodovinyl)piperazine-1-carboxylate (2ac):** yield 56% (110.1 mg); brown oil; R_f 0.20 (v_{PE}/v_{EA}= 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2 H), 7.26 (d, J =7.6 Hz, 2 H), 7.21-7.16 (m, 1 H), 3.35-3.20 (m, 4 H), 3.05-2.96 (m, 2 H), 2.82-2.74 (m, 2 H), 1.57 (s, 9 H), 1.40 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 152.0, 150.4, 139.1, 128.7, 125.7, 124.0, 82.2, 79.9, 50.0, 28.3; **IR** ν (KBr, cm^{-1}) 1695, 1597, 1529, 1421, 1367, 1312, 1250, 1162, 1047, 997, 880, 756; **HRMS** (ESI$^+$): m/z calcd. for $C_{22}H_{31}I_2N_3O_4$ ($[M+Na]^+$) 678.0302, Found: 678.0303.

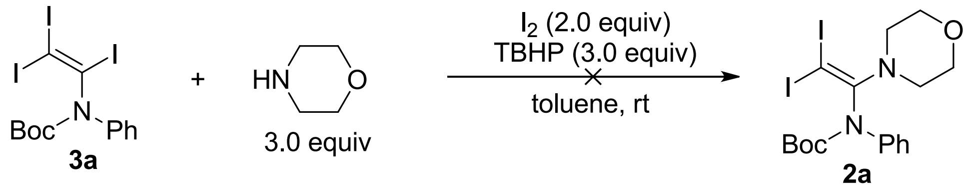


methyl 1-(1-((*tert*-butoxycarbonyl)(phenyl)amino)-2,2-diiodovinyl)piperidine-4-carboxylate (2ae): yield 34% (62.5 mg); brown oil; R_f 0.20 (v_{PE}/v_{EA}= 20:1); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.36-7.30 (m, 2 H), 7.29-7.24 (m, 2 H), 7.20-7.15 (m, 1 H), 7.24-7.17 (m, 2 H), 3.63 (s, 3 H), 3.43-3.36 (m, 1 H), 3.28-3.21 (m, 1 H), 2.69 (td, J_1 = 11.8 Hz, J_2 = 2.8 Hz, 1 H), 2.50-2.41 (m, 1 H), 2.24-2.15 (m, 1 H), 1.82-1.75 (m, 1 H), 1.74-1.67 (m, 1 H), 1.60-1.48 (m, 11 H), 1.20 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 175.0, 152.1, 151.0, 139.4, 128.6, 125.6, 124.0, 82.1, 51.7, 50.7, 49.3, 40.7, 28.4, 28.0, 27.9; **IR** ν (KBr, cm^{-1}) 1725, 1591, 1529, 1492, 1440, 1201, 1035, 747; **HRMS** (ESI$^+$): m/z calcd. for $C_{20}H_{26}I_2N_2O_4$ ([M+Na]$^+$) 634.9880, Found: 634.9891.

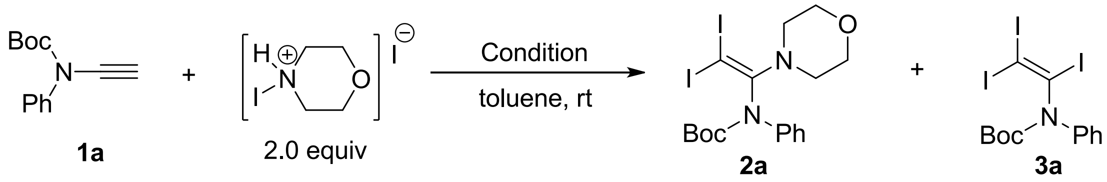


ethyl 1-(1-((tert-butoxycarbonyl)(phenyl)amino)-2,2-diiodovinyl)piperidine-4-carboxylate (2af): yield 36% (67.6 mg); brown oil; R_f 0.20 (ν_{PE}/ν_{EA}= 20:1); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.36-7.30 (m, 2 H), 7.29-7.25 (m, 2 H), 7.20-7.14 (m, 1 H), 4.07 (q, J = 7.2 Hz, 2 H), 3.42-3.35 (m, 1 H), 3.28-3.20 (m, 1 H), 2.69 (td, J_1 = 11.8 Hz, J_2 = 2.8 Hz, 1 H), 2.50-2.41 (m, 1 H), 2.24-2.13 (m, 1 H), 1.82-1.74 (m, 1 H), 1.74-1.67 (m, 1 H), 1.65-1.43 (m, 11 H), 1.20 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 174.5, 152.1, 150.9, 139.3, 128.6, 125.5, 123.9, 82.0, 60.3, 50.6, 49.4, 40.7, 28.3, 27.9, 27.9; **IR** ν (KBr, cm^{-1}) 1727, 1548, 1440, 1322, 1206, 1103, 1023, 767; **HRMS** (ESI$^+$): m/z calcd. for $C_{21}H_{28}I_2N_2O_4$ ([M+Na]$^+$) 649.0036, Found: 649.0048.

4 Experiment for Mechanistic Study



The reaction of 3a: In a 10 mL flame-dried Schlenk tutbe under air condition, I_2 (0.6 mmol) and amines (0.9 mmol) were dissolved in toluene (2.0 mL) and stirred, then **3a** (0.3 mmol) and TBHP (70% in water, 0.9 mmol) were added successively. And the resulting solution was stirred at room temperature for 12h and monitored by TLC.



Condition 1: In a 10 mL flame-dried Schlenk tube were placed terminal ynamide **1a** (0.3 mmol) and *N*-iodomorpholine-hydrogen iodide[4] (0.6 mmol) were dissolved in toluene (2.0 mL). Then The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **2a** (35.0 mg, 21%) and **3a** (78.7 mg, 44%).

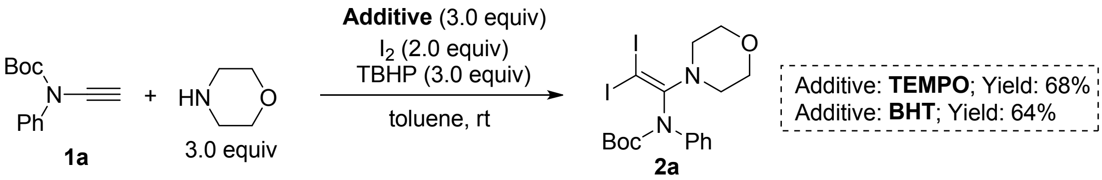
Condition 2: In a 10 mL flame-dried Schlenk tube were placed terminal ynamide **1a** (0.3 mmol) and *N*-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL) and stirred, then TBHP (70% in water, 0.9 mmol) were added. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **2a** (93.3 mg, 56%) and **3a** (33.9 mg, 19%).

Condition 3: In a 10 mL flame-dried Schlenk tube were placed terminal ynamide **1a** (0.3 mmol), morpholine (0.9 mmol) and *N*-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL). Then the reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **2a** (56.8 mg, 34%) and **3a** (66.4 mg, 37%).

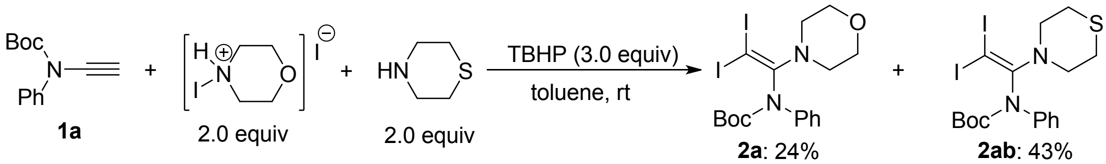
Condition 4: In a 10 mL flame-dried Schlenk tube were placed terminal ynamide **1a** (0.3 mmol), morpholine (0.9 mmol) and *N*-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL) and stirred, then TBHP (70% in water, 0.9 mmol) were added. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **2a** (125.2 mg, 75%).

Condition 5: In a 10 mL flame-dried Schlenk tube were placed terminal ynamide **1a** (0.3 mmol), I_2 (0.6 mmol) and *N*-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0

mL) and stirred, then TBHP (70% in water, 0.9 mmol) were added. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **3a** (120.1 mg, 67%).

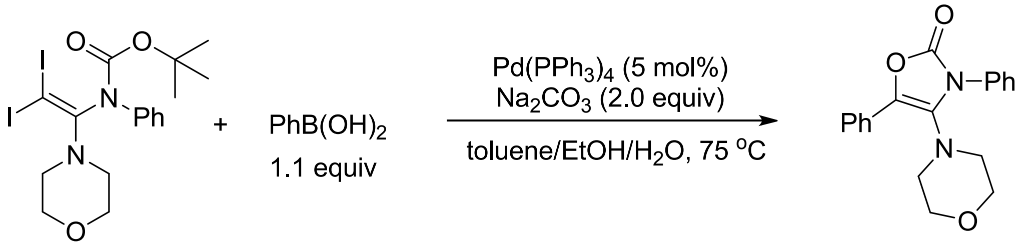


In a 10 mL flame-dried Schlenk tube under air condition, I_2 (0.6 mmol) and amines (0.9 mmol) were dissolved in toluene (2.0 mL) and stirred, then terminal ynamides **1a** (0.3 mmol), Additive (0.9 equiv) and TBHP (70% in water, 0.9 mmol) were added successively. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **2a**.



In a 10 mL flame-dried Schlenk tube were placed terminal ynamide **1a** (0.3 mmol), thiomorpholine (0.6 mmol) and *N*-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL). Then the reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford **2a** (40.0 mg, 24%) and **2ab** (73.8 mg, 43%).

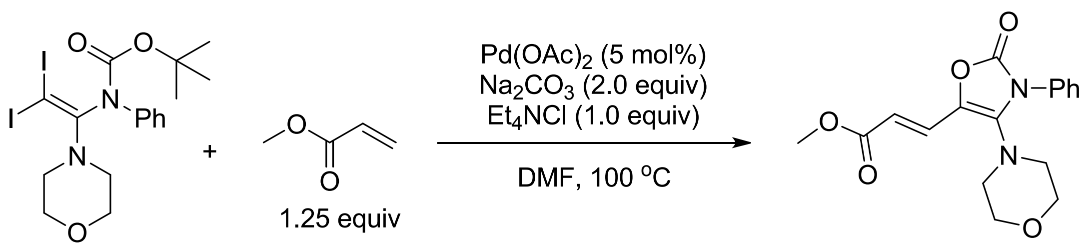
5. Suzuki-Miyaura coupling/cyclization of 2a.



2a **4a:** 62 % yield

A 10 mL flame-dried Schlenk tube was charged with $Pd(PPh_3)_4$ (5.0 mol%), *tert*-butyl (2,2-diiodo-1-morpholinovinyl)(phenyl)carbamate **2a** (0.3 mmol), and boronic acids (0.33 mmol). The flask was capped and then backfilled with nitrogen (this was repeated two additional times). Toluene (1.0 mL), ethanol (0.5 mL), Na_2CO_3 (0.6 mmol) in H_2O (0.5 mL) were added *via* syringe. The reaction solution was heated to 75 ^oC for 10 h under nitrogen while being stirred. After completion of the reaction, the reaction solution was neutralized by 5% aqueous HCl, then the aqueous phase was separated and further extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Then, the solution was concentrated to give a crude product, which was purified by silica gel column chromatography (PE/EA =8:1) to afford **4-morpholino-3,5-diphenyloxazol-2(3*H*)-one (4a)**: yield 62% (67.6 mg); yellow oil; R_f 0.20 (v_{PE}/v_{EA}= 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 2 H), 7.55-7.491 (m, 2 H), 7.48-7.40 (m, 5 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 3.58 (t, *J* = 4.4 Hz, 4 H), 2.89 (t, *J* = 4.8 Hz, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 133.8, 131.2, 130.7, 129.5, 129.0, 128.6, 128.0, 127.9, 127.6, 125.6, 66.9, 49.9; **IR** *v* (KBr, cm^{-1}) 1758, 1677, 1532, 1460, 1400, 1373, 1240, 1136, 1102, 1039, 998, 902, 743; **HRMS** (ESI^+): m/z calcd. for $C_{19}H_{18}N_2O_3$ ($[M+Na]^+$) 345.1215, Found: 345.1223.

6. Heck coupling/cyclization of 2a.



2a **4b:** 46% yield

A 10 mL flame-dried Schlenk tube was charged with $Pd(OAc)_2$ (5.0 mol %), Na_2CO_3 (2.0 equiv),

n-Bu_4NCl (1.0 equiv) and **2a** (0.3 mmol). The flask was capped and then backfilled with nitrogen (this was repeated two additional times). DMF (2.00 mL) was added *via* syringe, followed by the addition of methyl acrylate (0.375 mmol). The reaction solution was heated to 100 ^{o}C for 5 h under nitrogen while being stirred. After completion of the reaction, the reaction solution was neutralized by H_2O, then the aqueous phase was separated and further extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Then, the solution was concentrated to give a crude product, which was purified by silica gel column chromatography (PE/EA = 4:1) to afford **(*E*)-methyl 3-(4-morpholino-2-oxo-3-phenyl-2,3-dihydrooxazol-5-yl)acrylate (4b)**: yield 46% (45.4 mg); yellow oil; R_f 0.20 (v_{PE}/v_{EA}= 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54-7.39 (m, 6 H), 6.08 (d, J = 14.8 Hz, 1 H), 3.78 (s, 3 H), 3.56 (t, J = 4.4 Hz, 4 H), 3.00 (t, J = 4.8 Hz, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 151.4, 137.9, 133.0, 129.5, 128.9, 127.1, 126.4, 124.2, 112.8, 66.2, 51.6, 50.4; **IR** v (KBr, cm^{-1}) 1747, 1612, 1488, 1402, 1388, 1302, 1277, 1154, 1103, 1049, 1003, 913, 757; **HRMS** (ESI^+): m/z calcd. for $C_{17}H_{18}N_2O_5$ ($[M+Na]^+$) 353.1113, Found: 353.1126.

Reference

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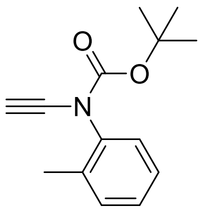
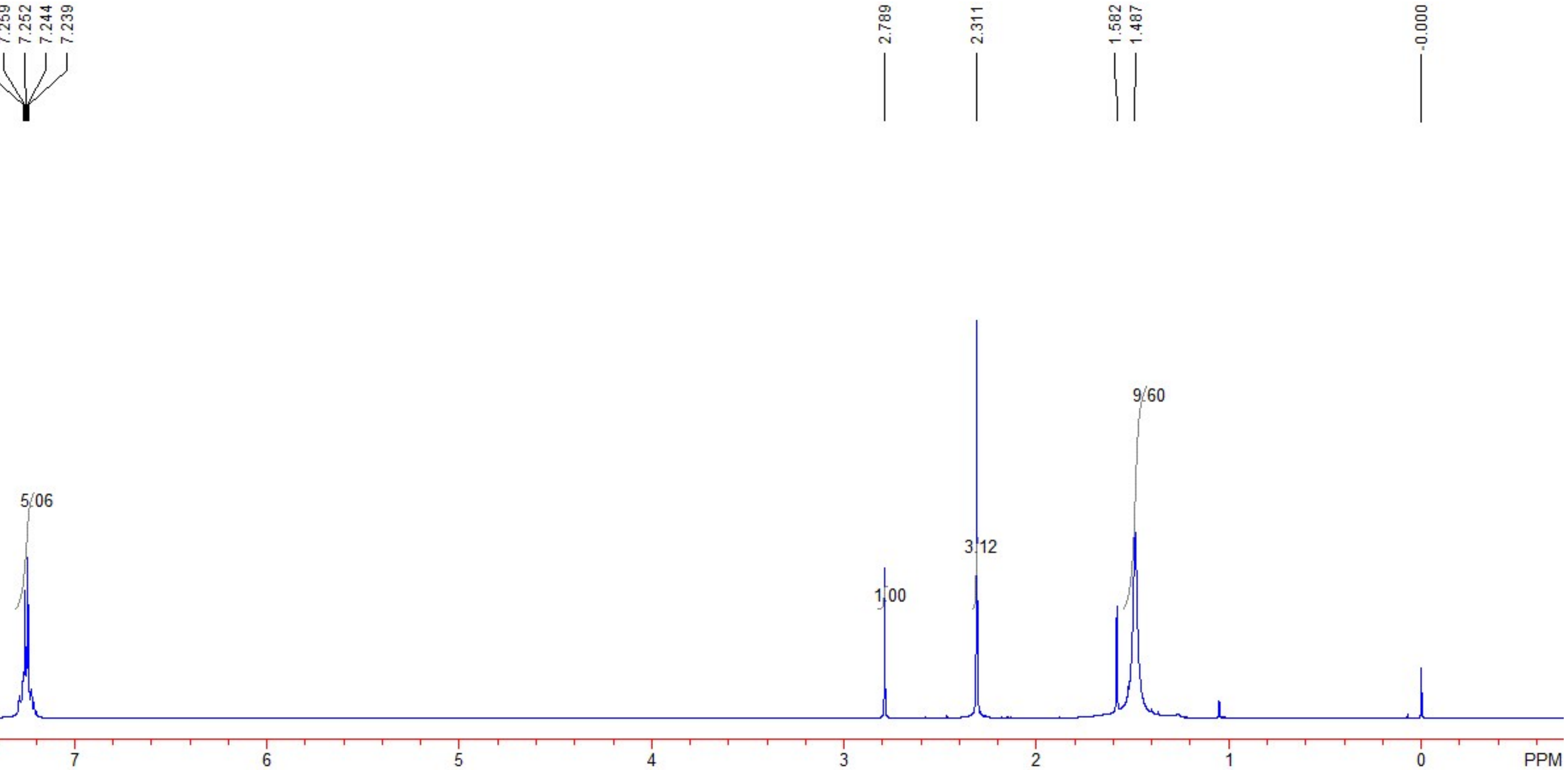
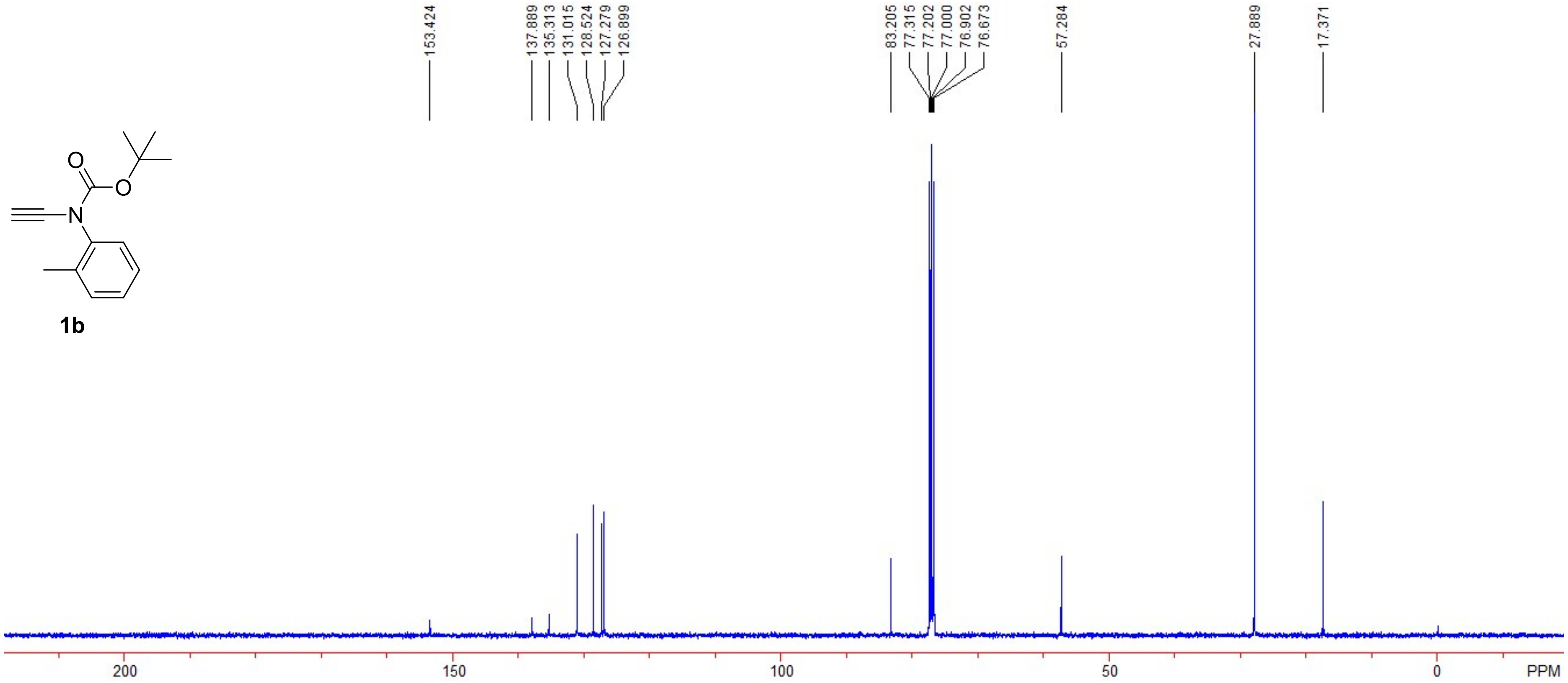
NMR spectra



1b





1b
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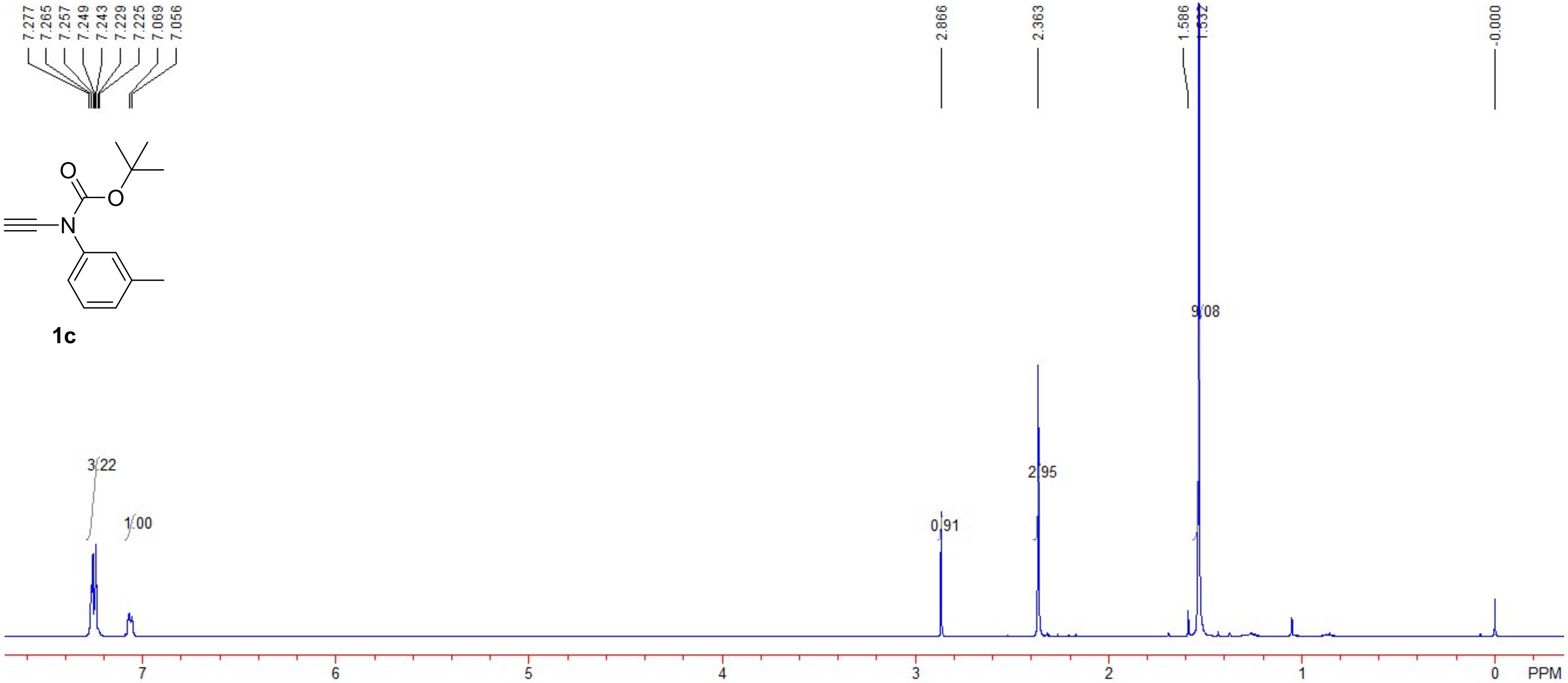

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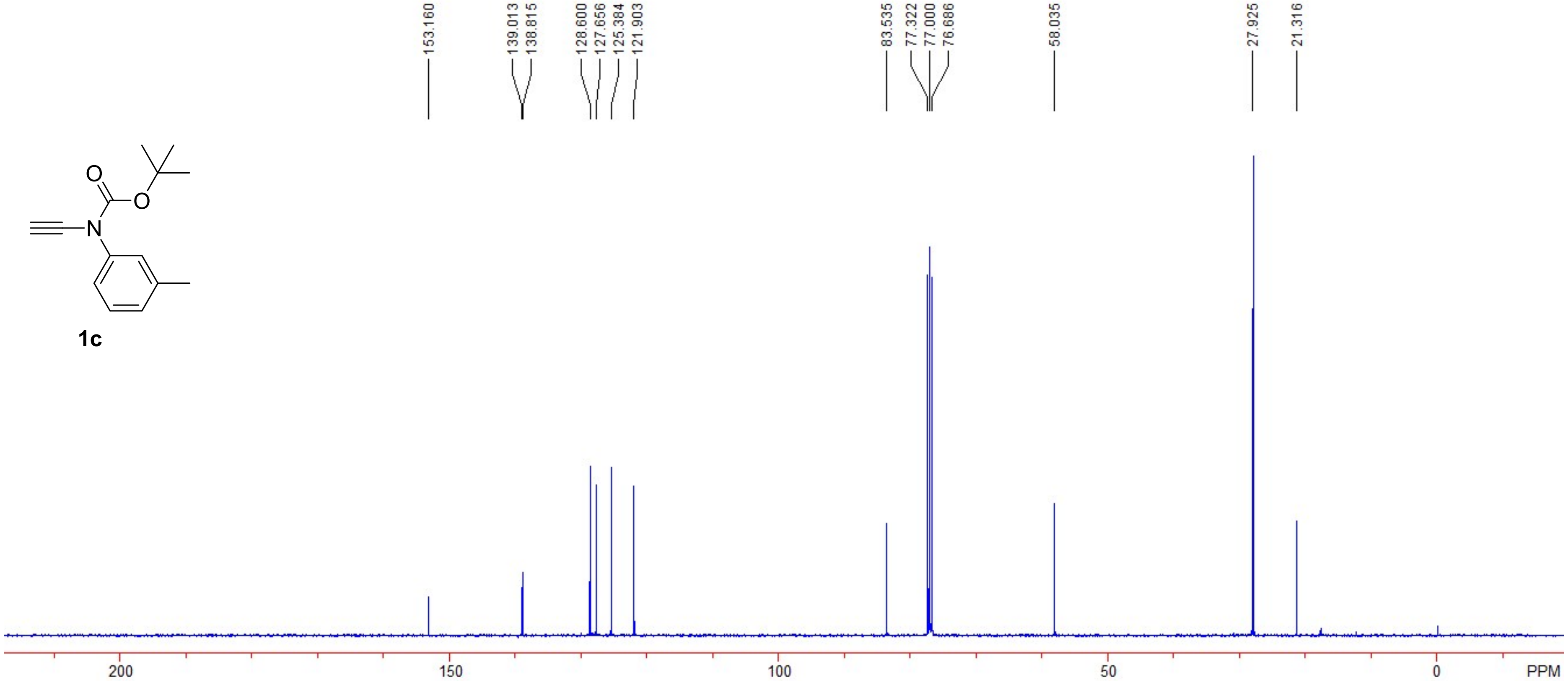

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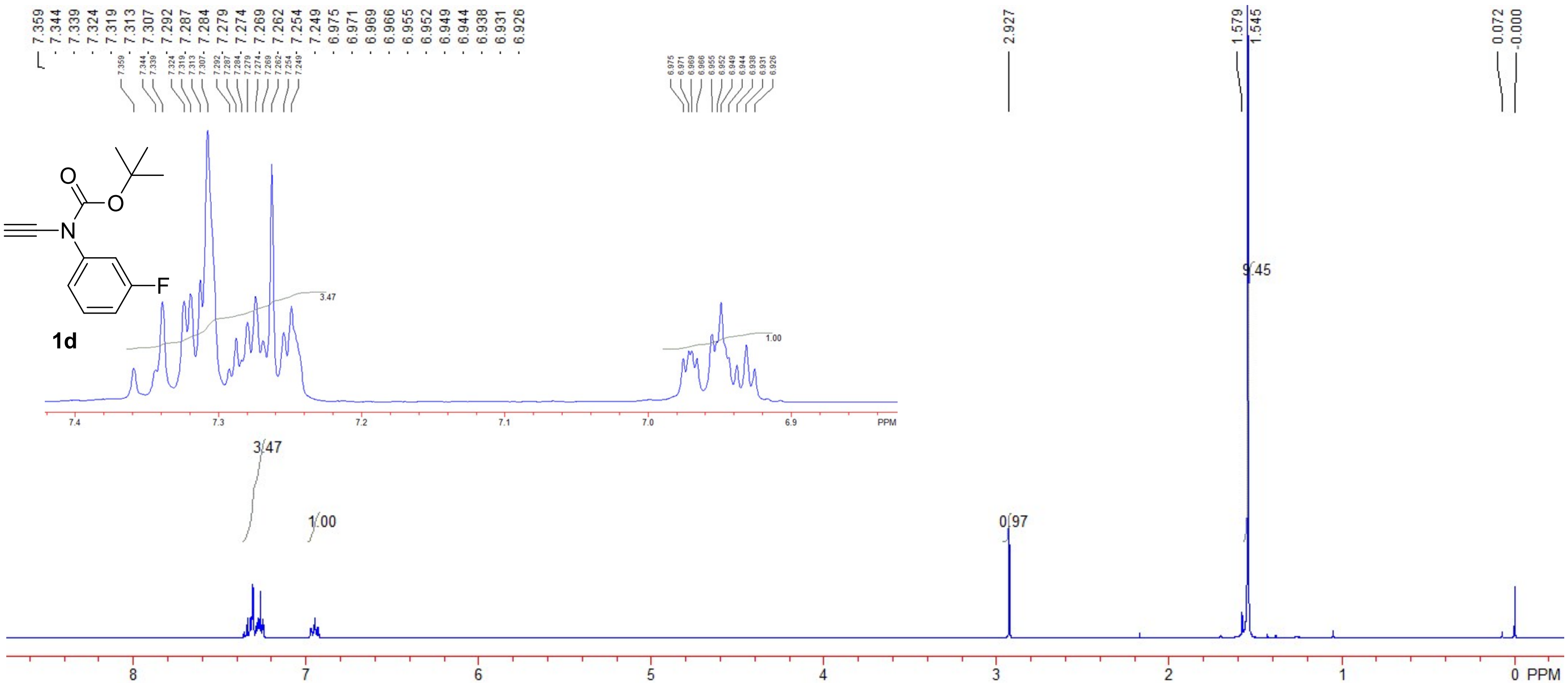

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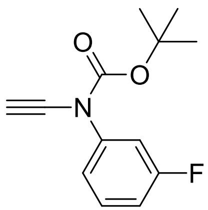

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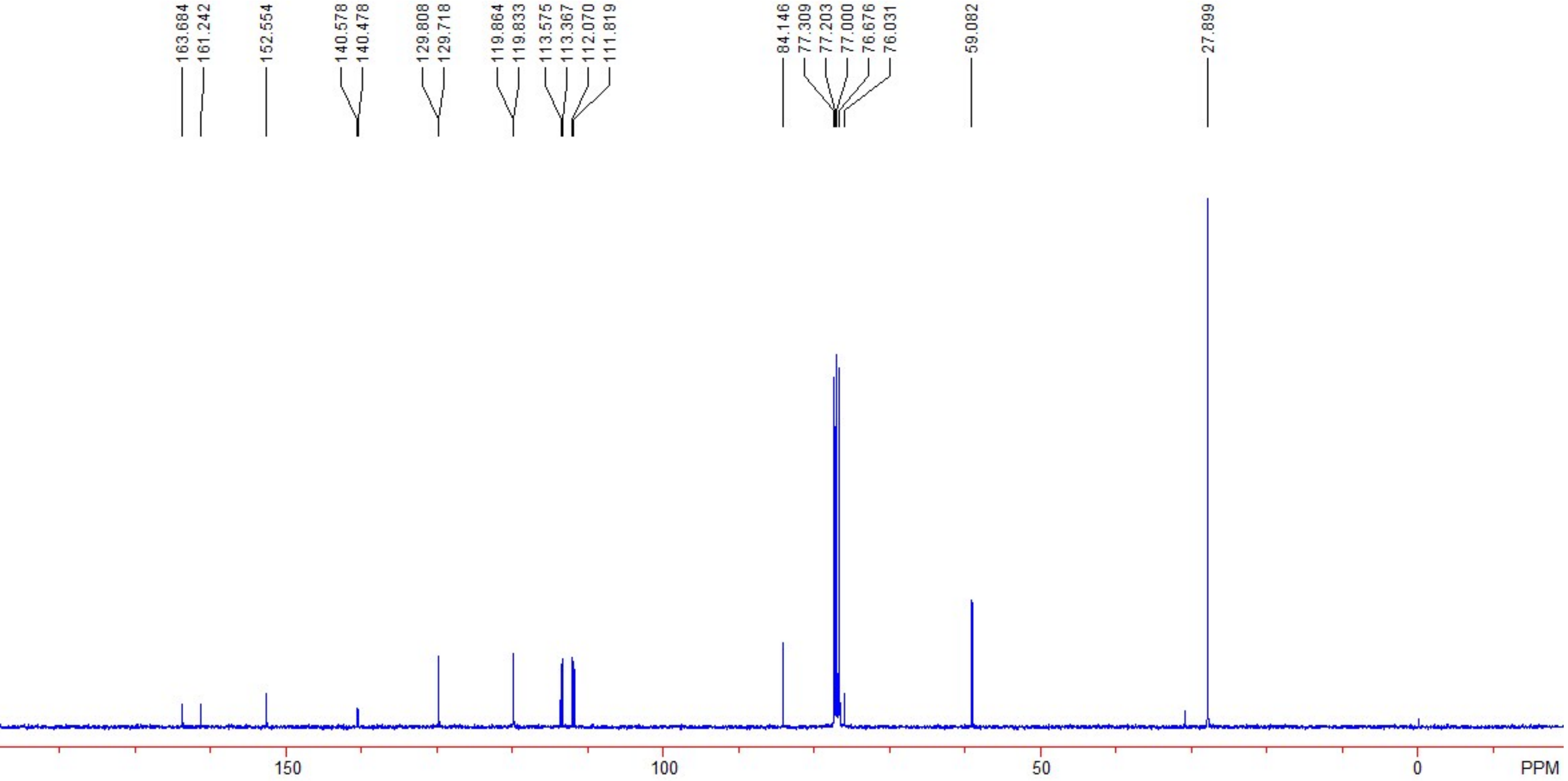

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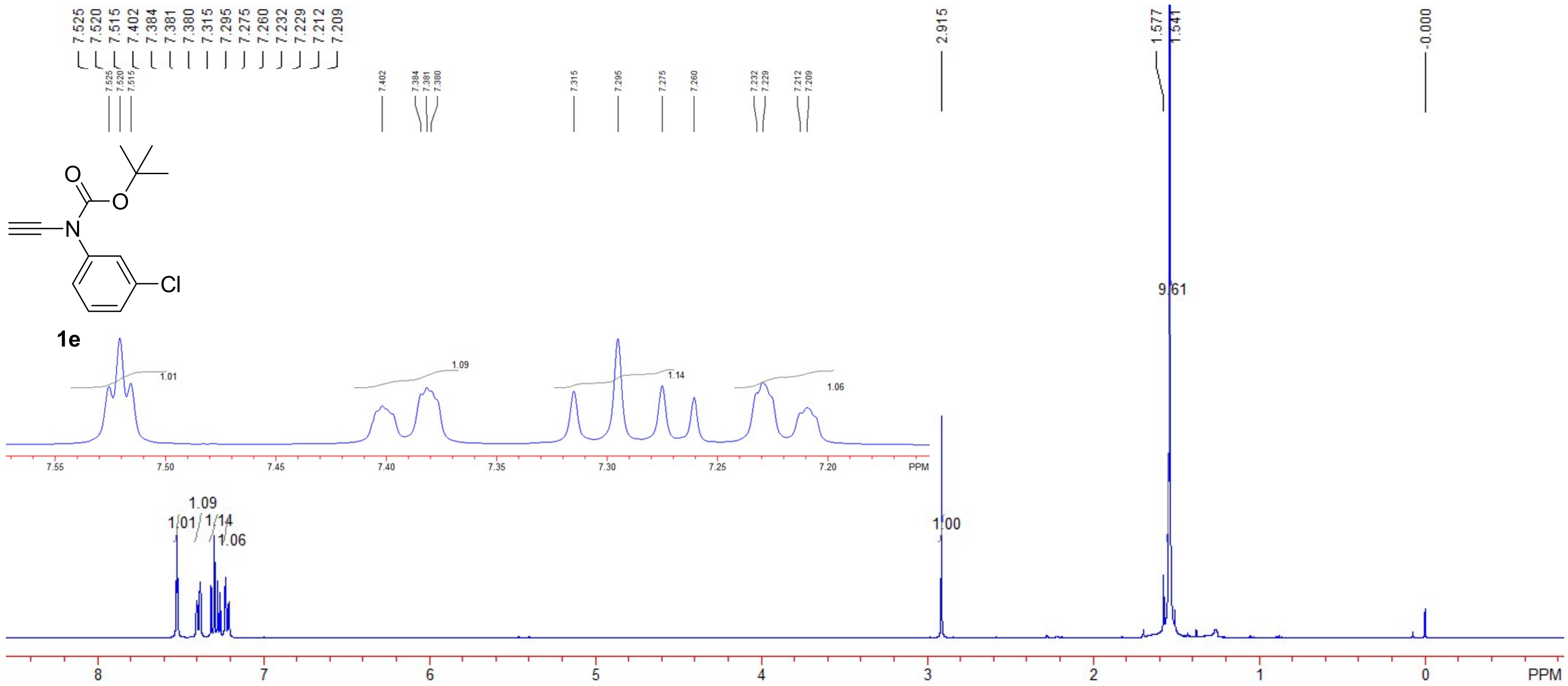
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1.541
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O
N
Cl
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1.06
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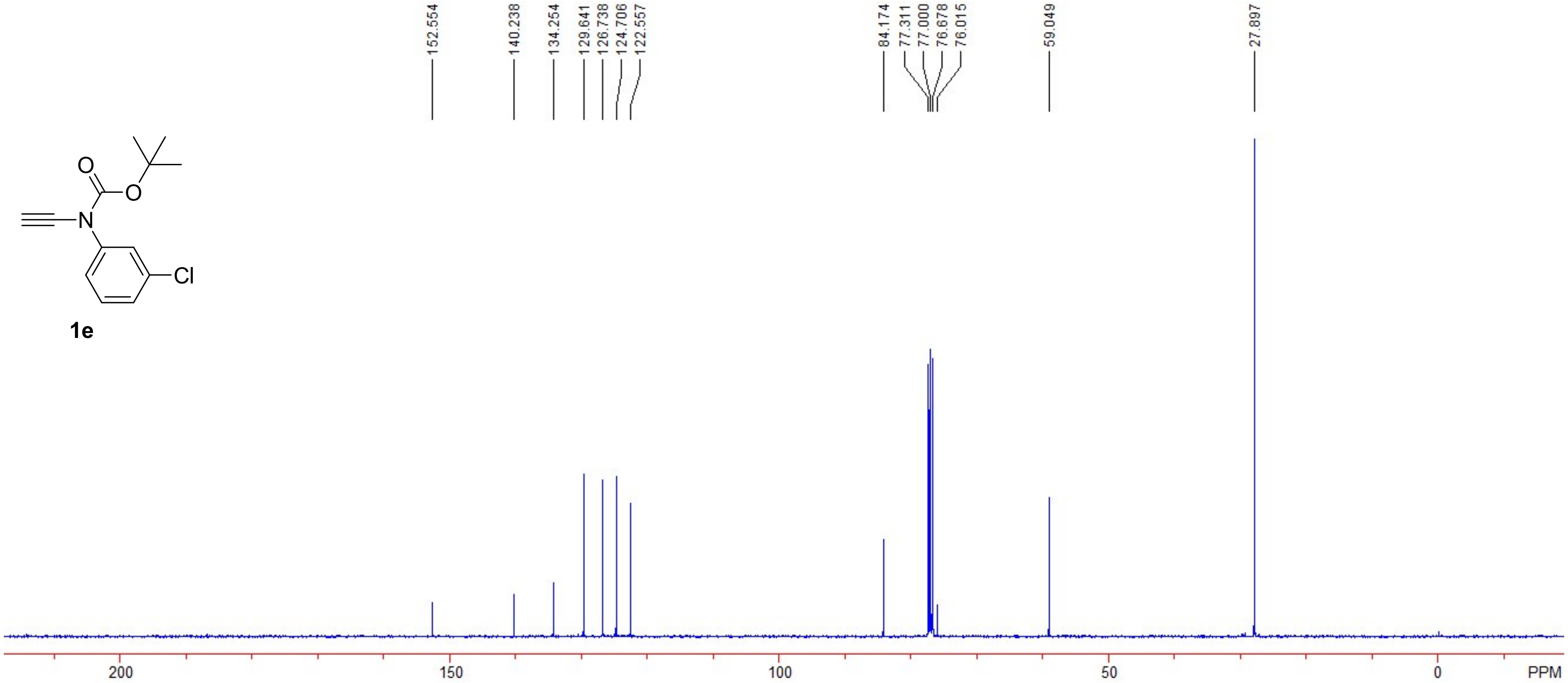
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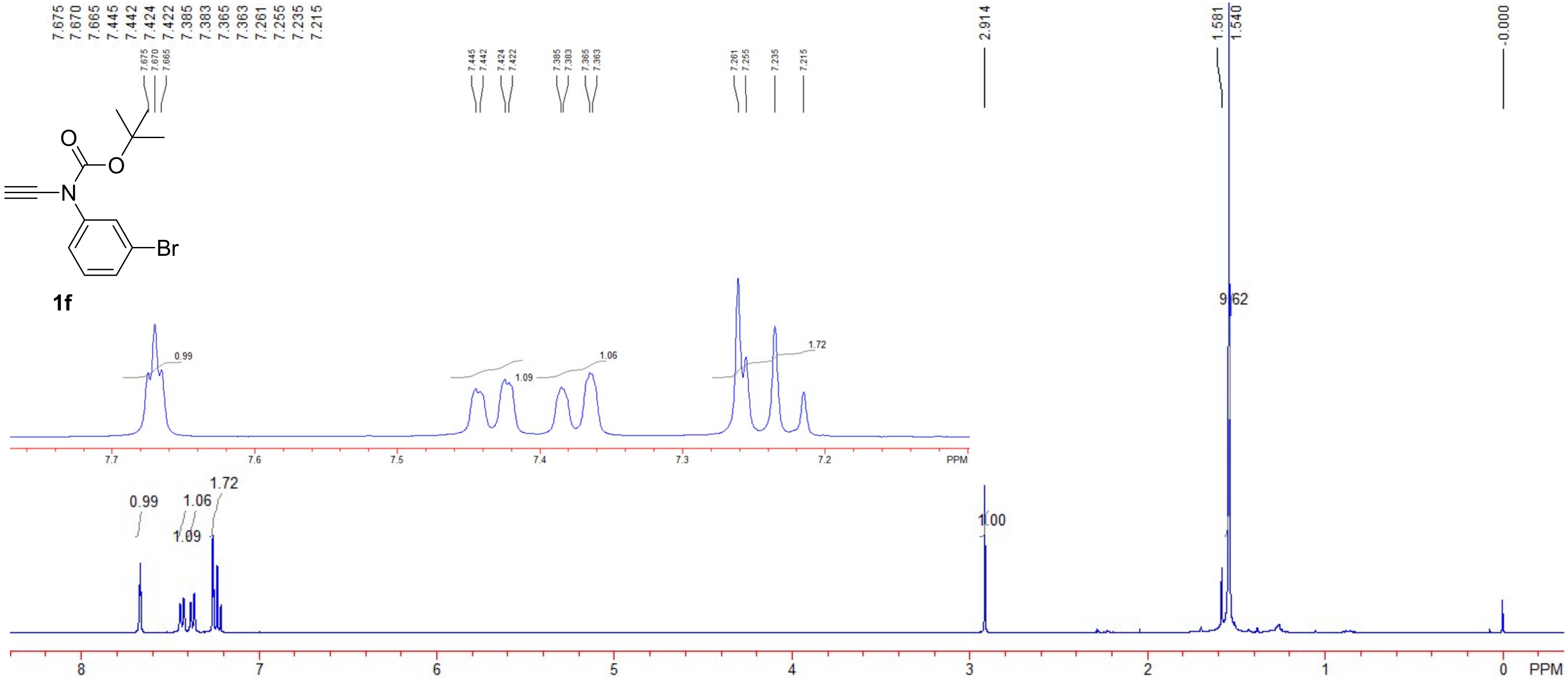

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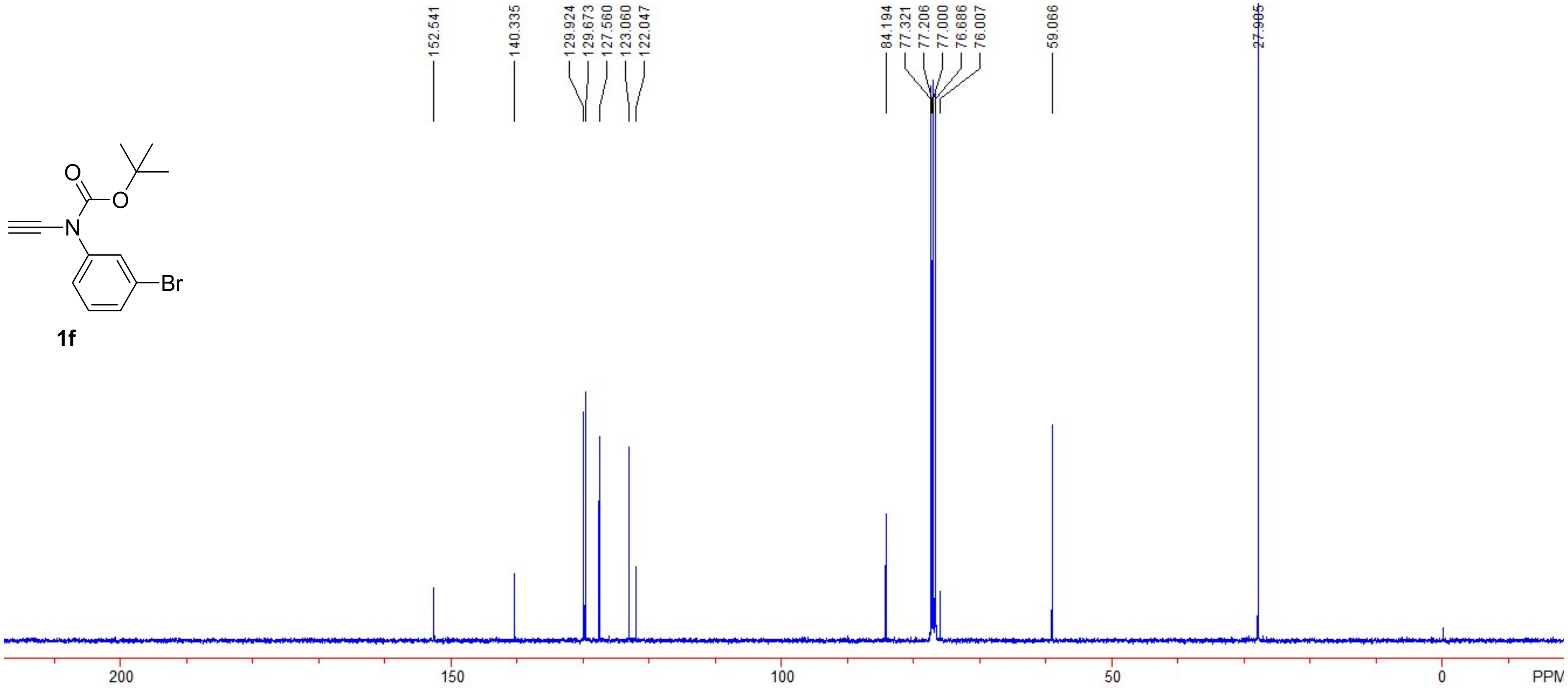
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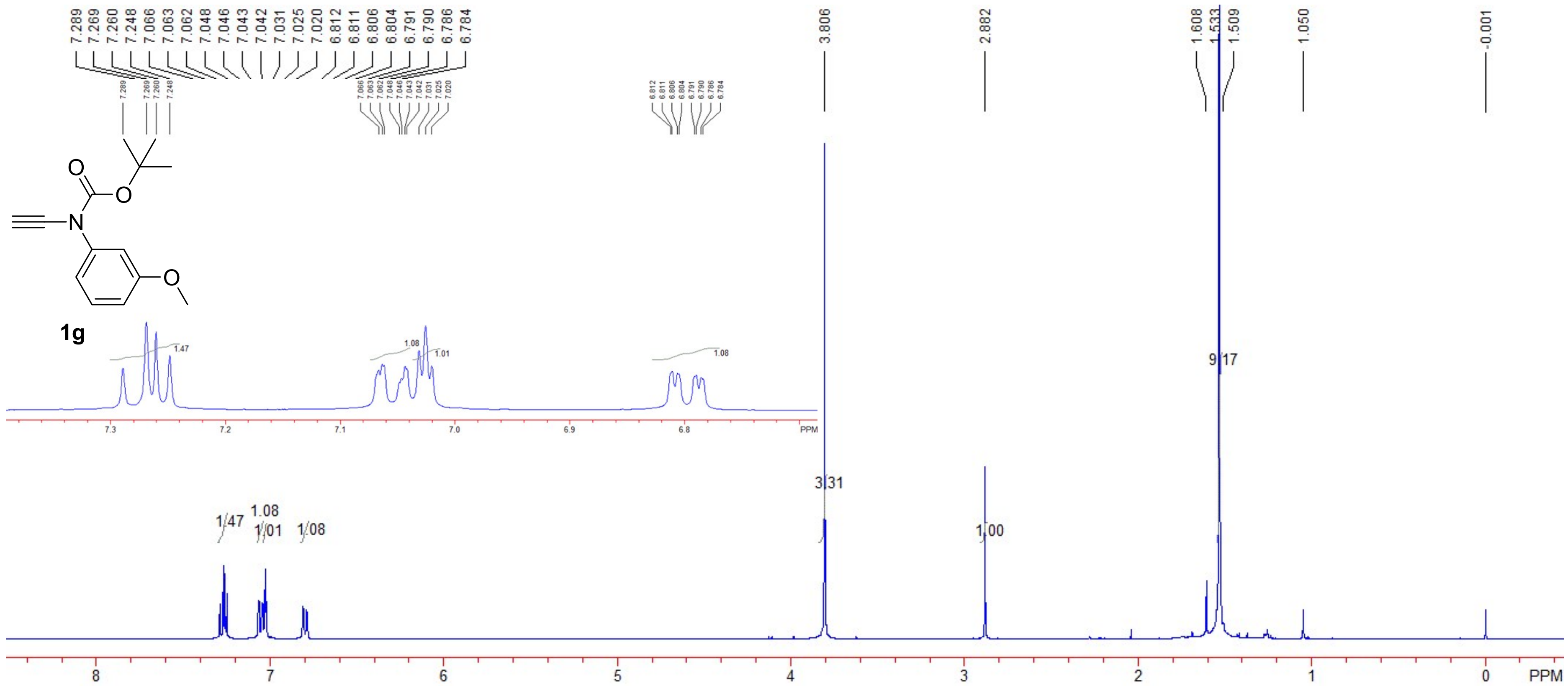

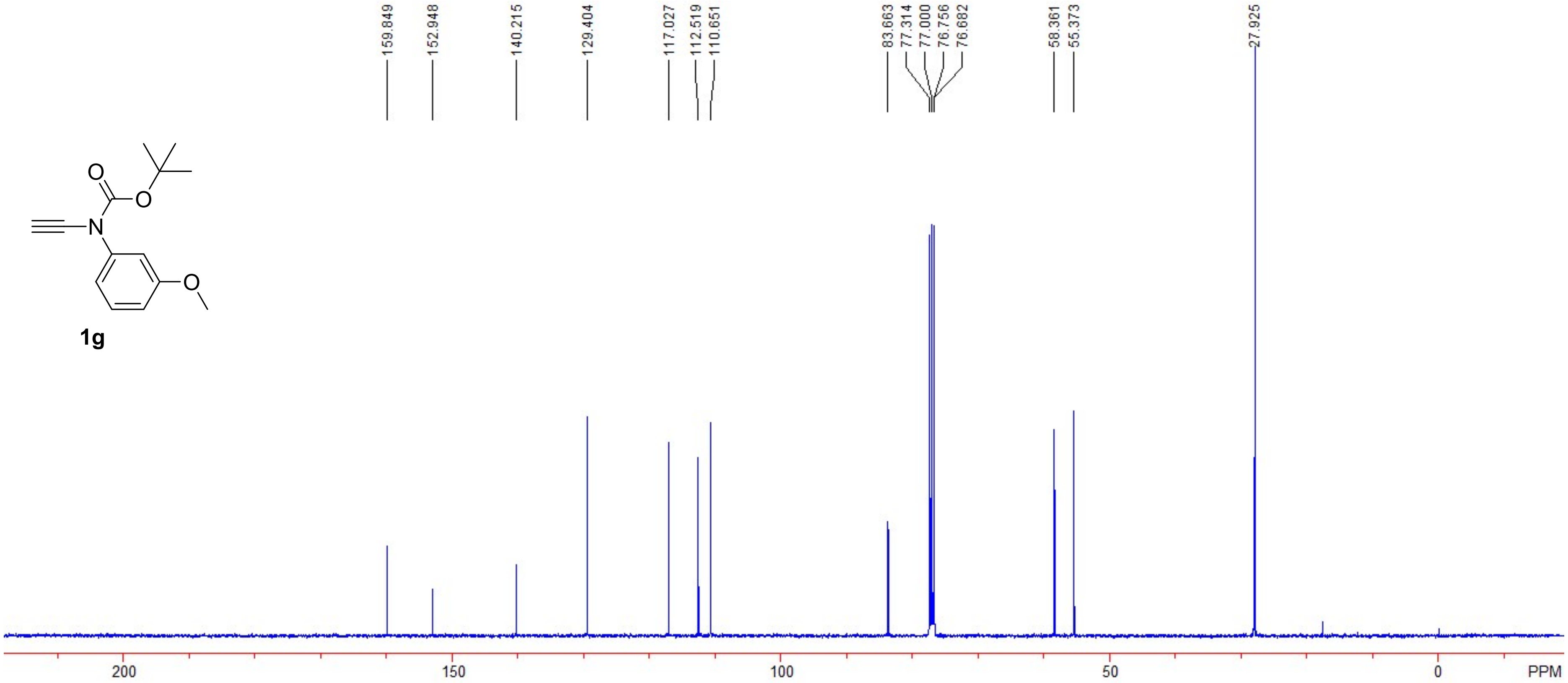
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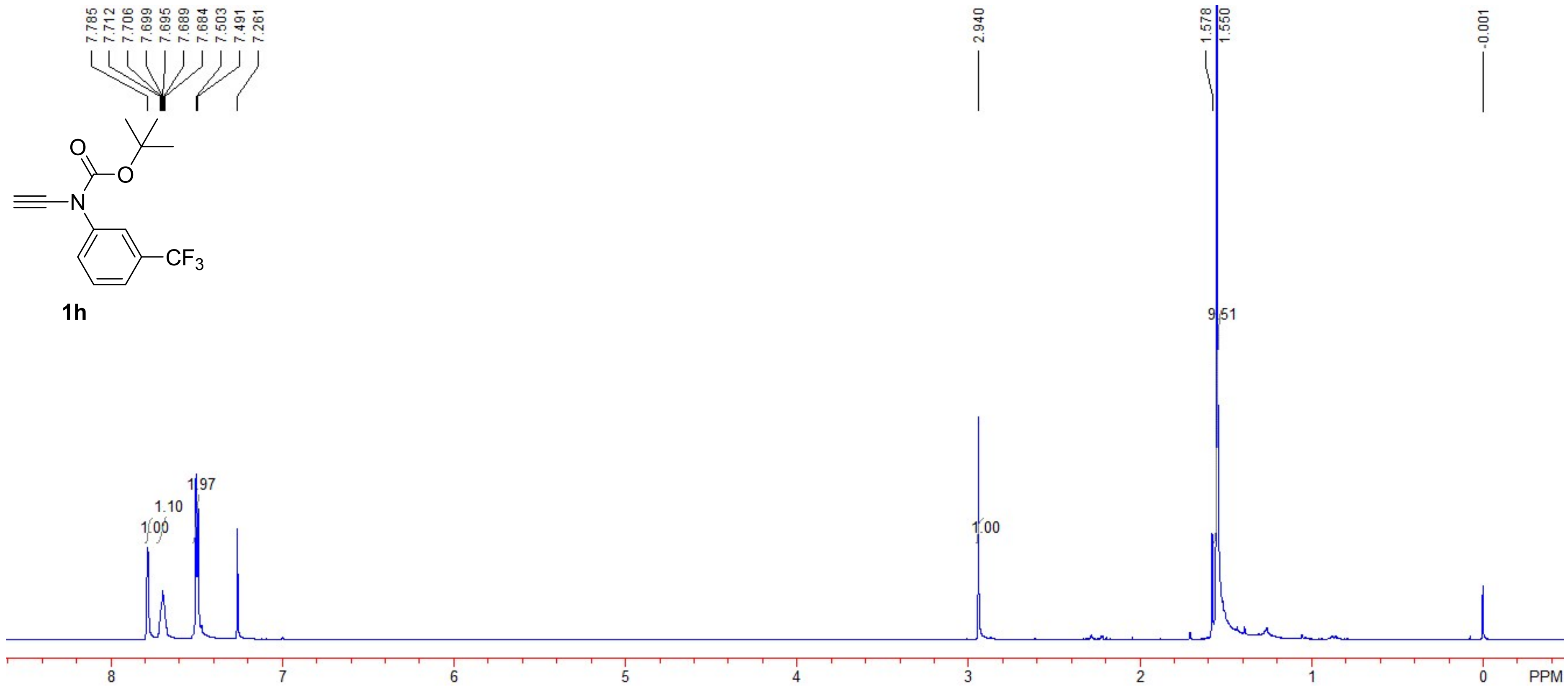
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7.503
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7.261
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1.550
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O
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CF3
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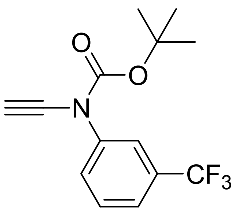

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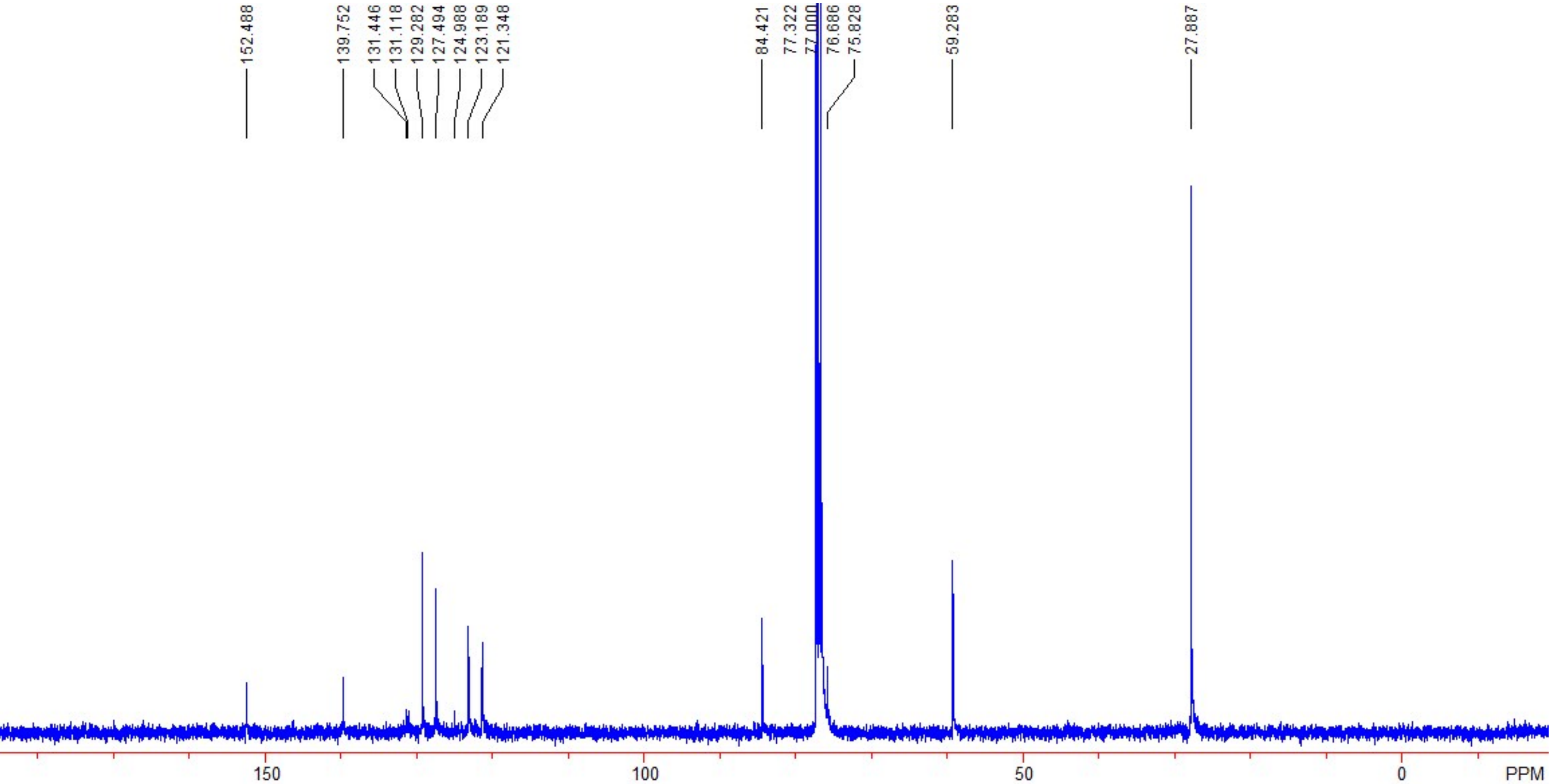
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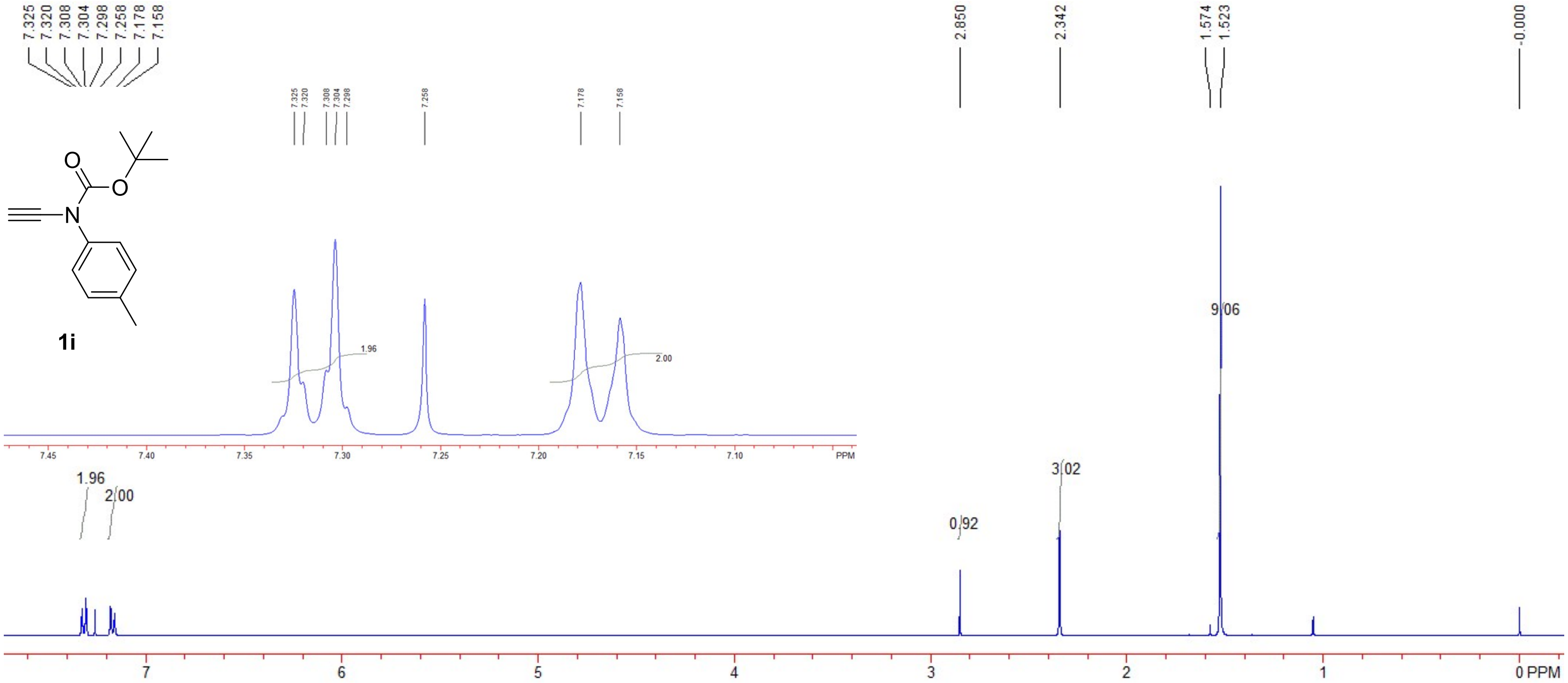
0
PPM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1.96
2.00
0.92
3.02
9.06
7.45
7.40
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7.25
7.20
7.15
7.10
PPM
7
6
5
4
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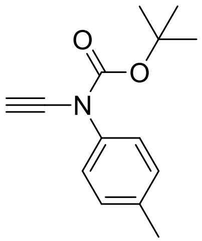
2
1
0 PPM



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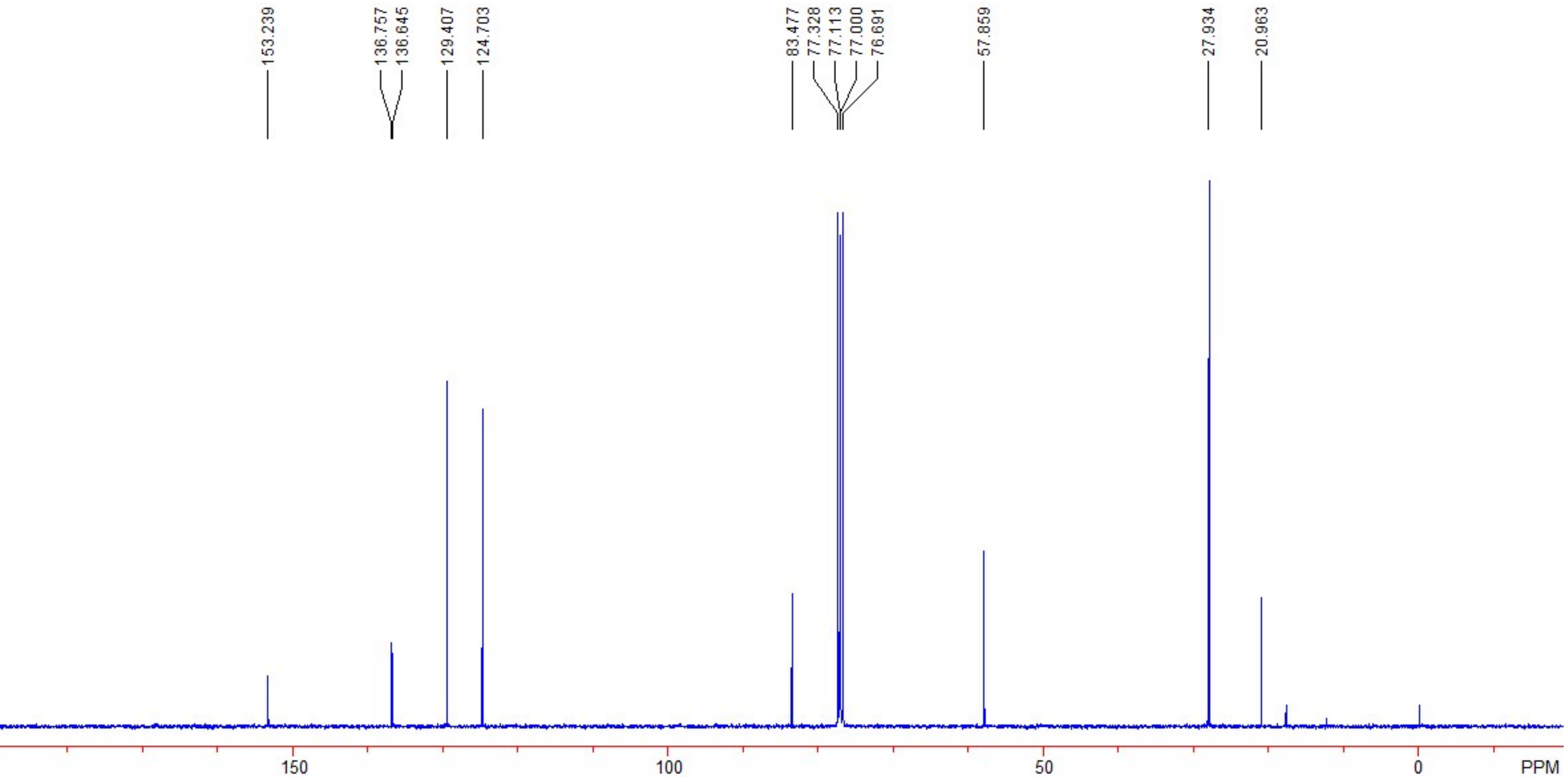
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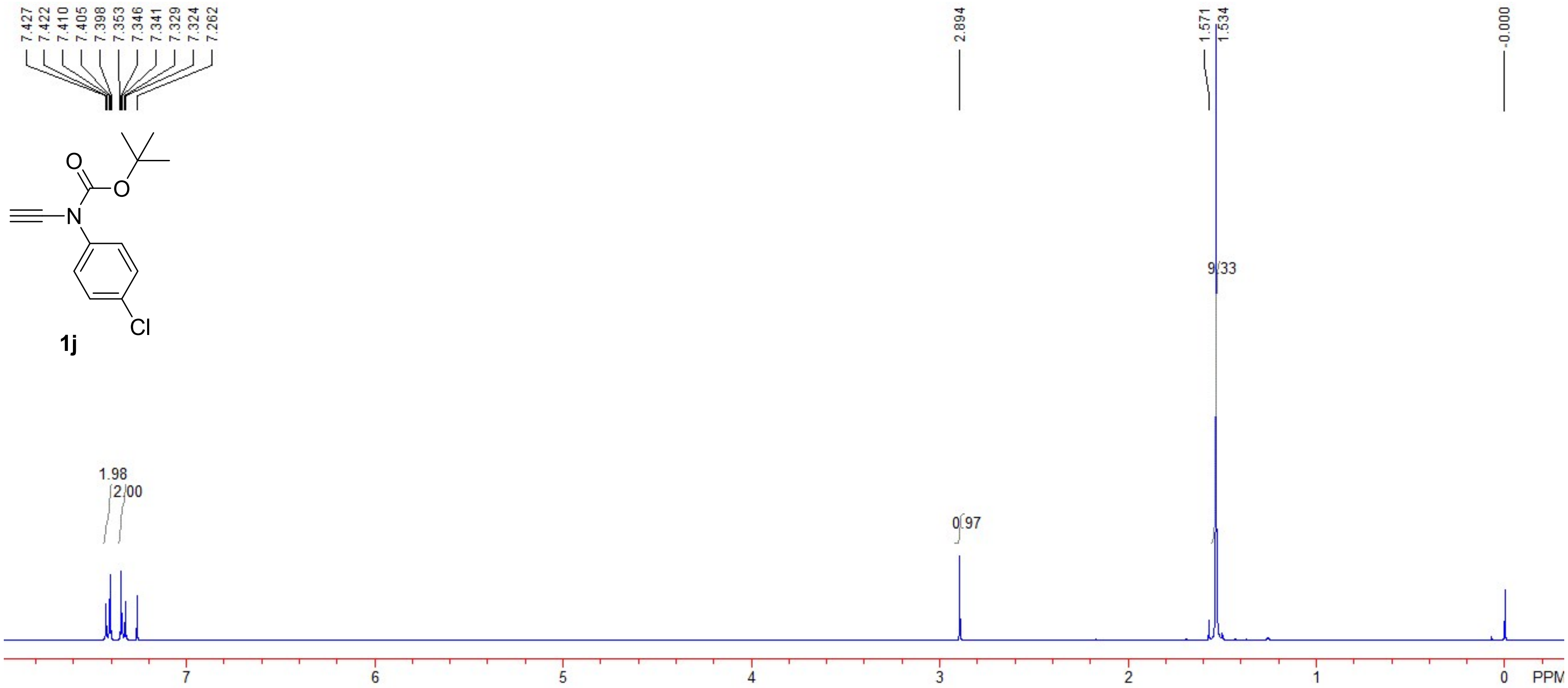
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7.341
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1.534
-0.000
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4
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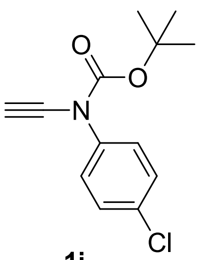

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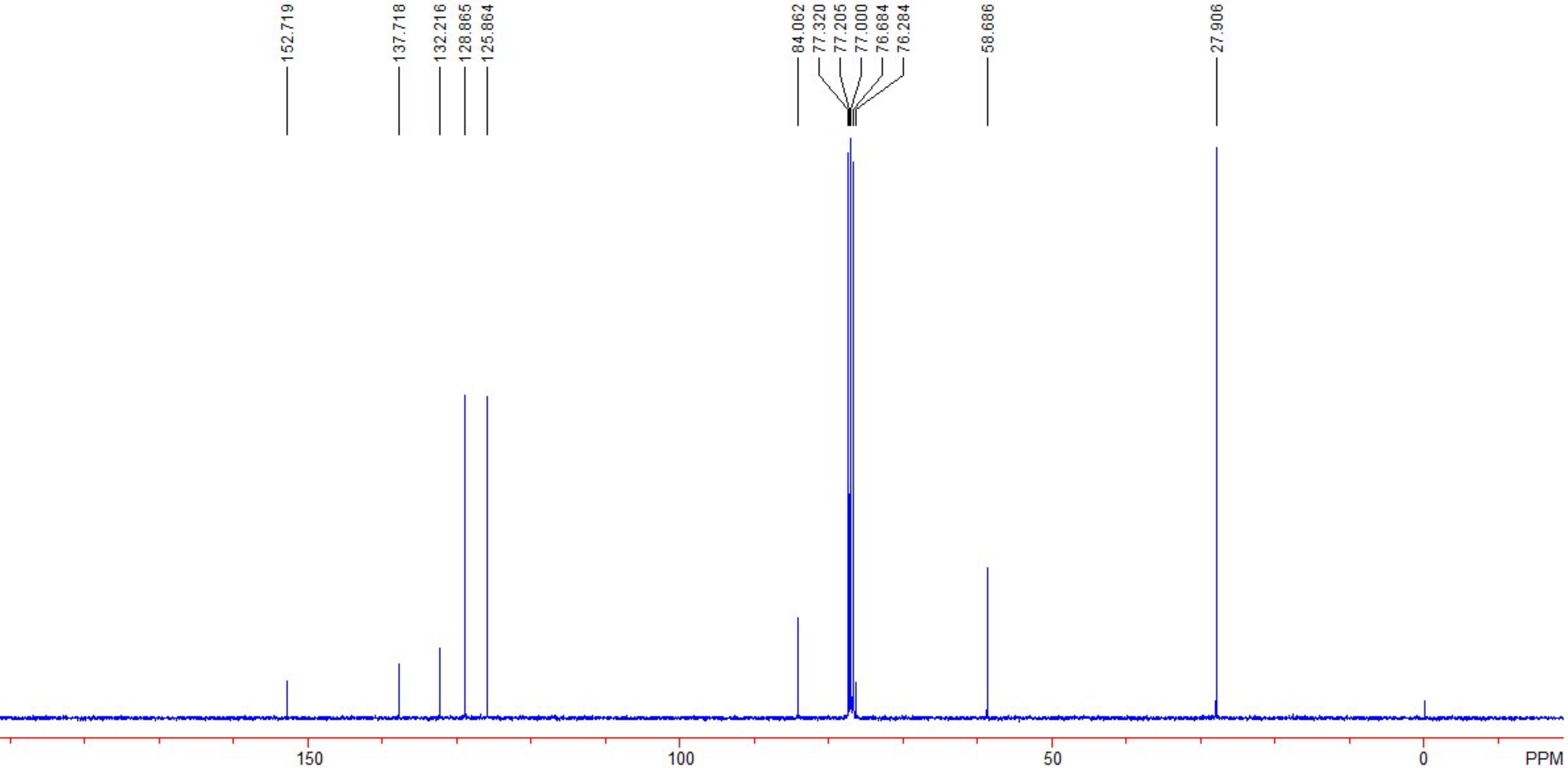
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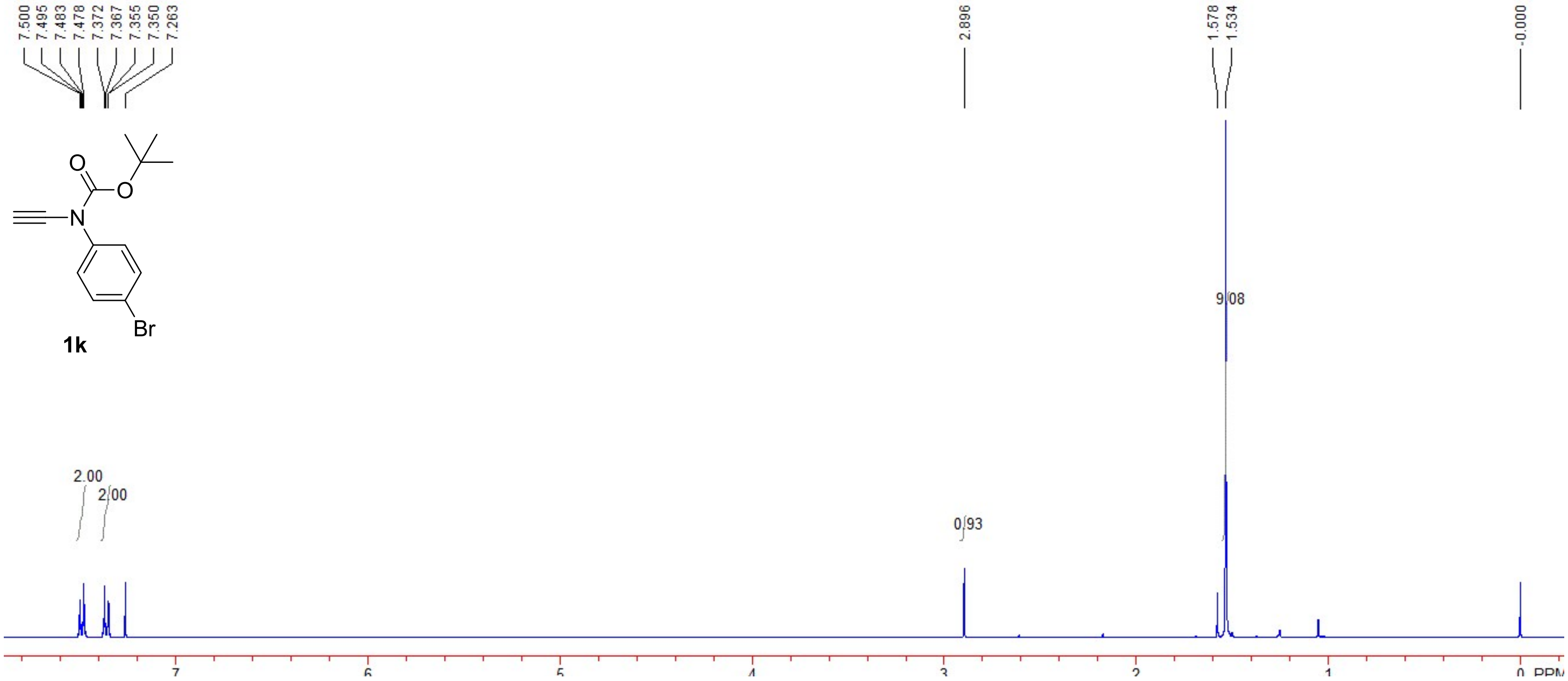

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-0.000
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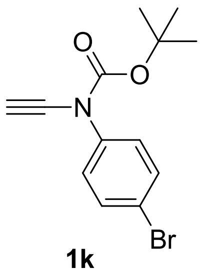
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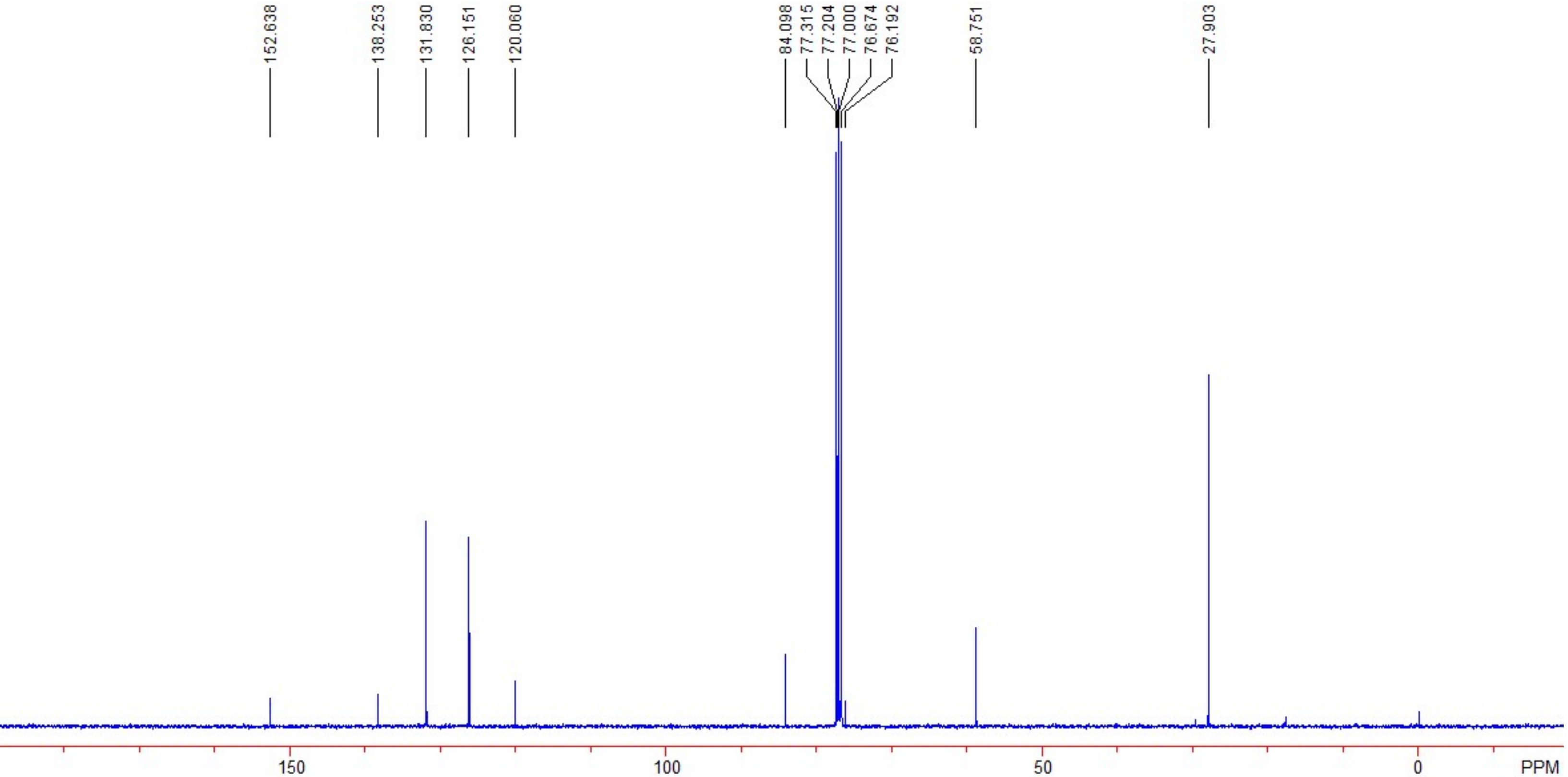
1k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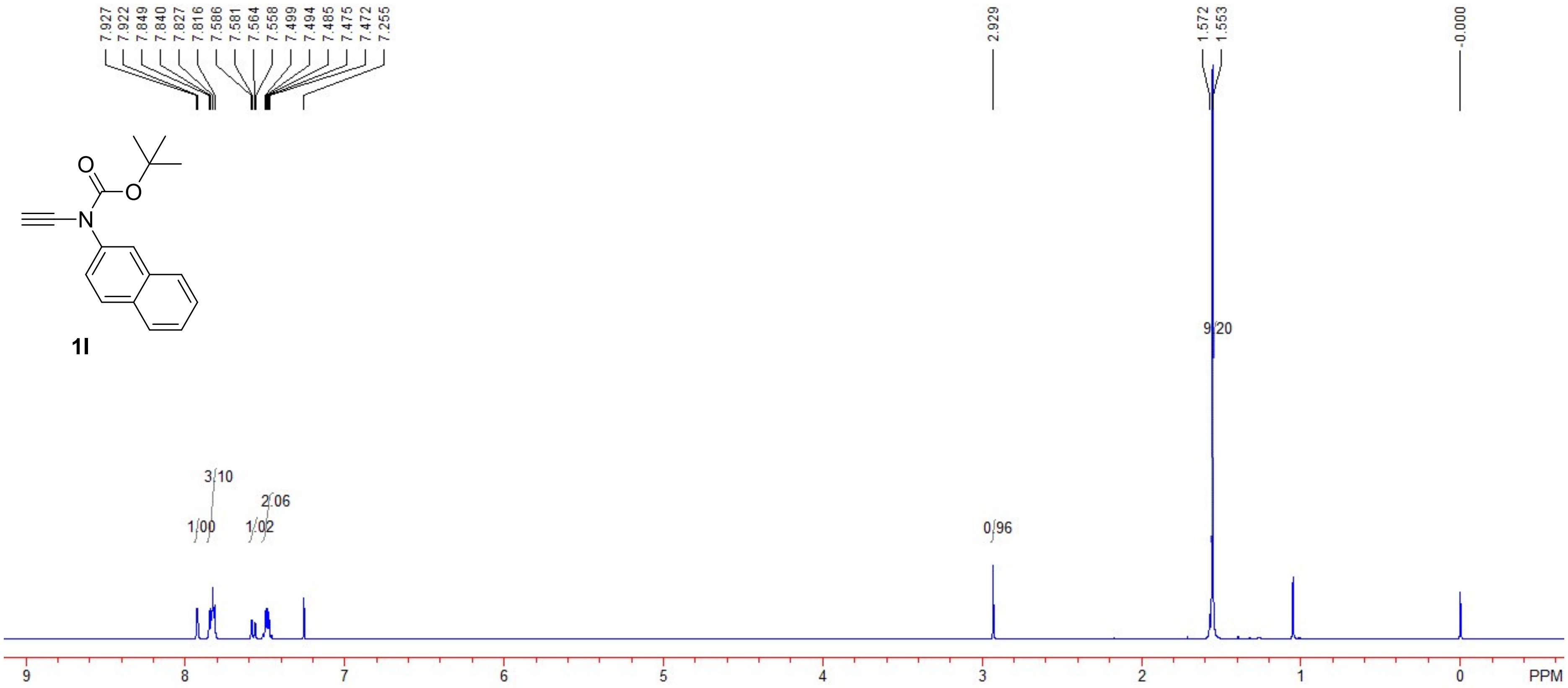

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7.485
7.475
7.472
7.255
2.929
1.572
1.553
-0.000
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O
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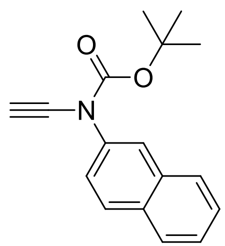

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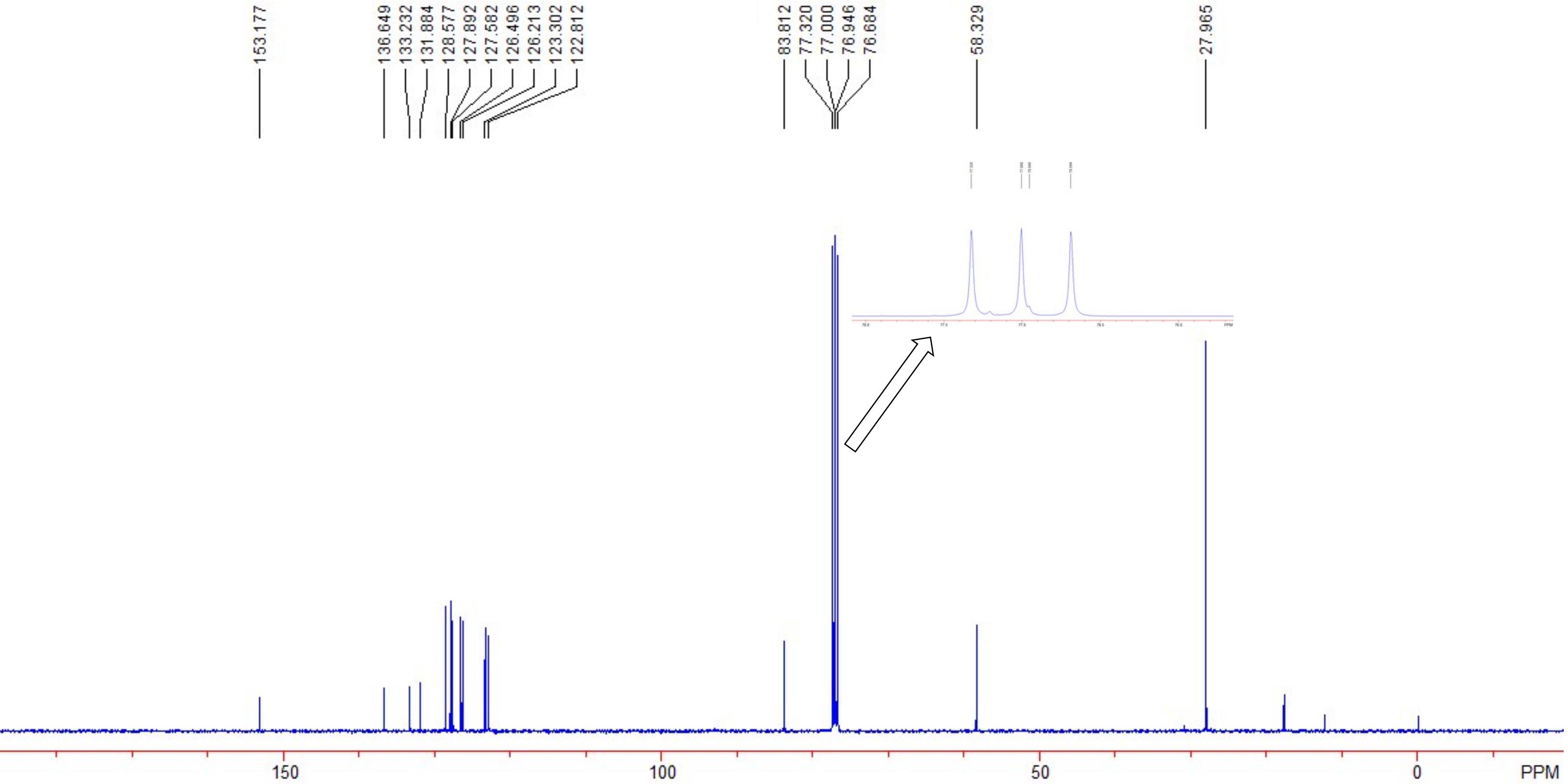

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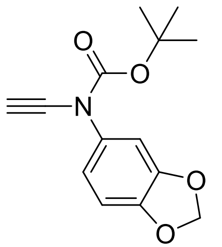

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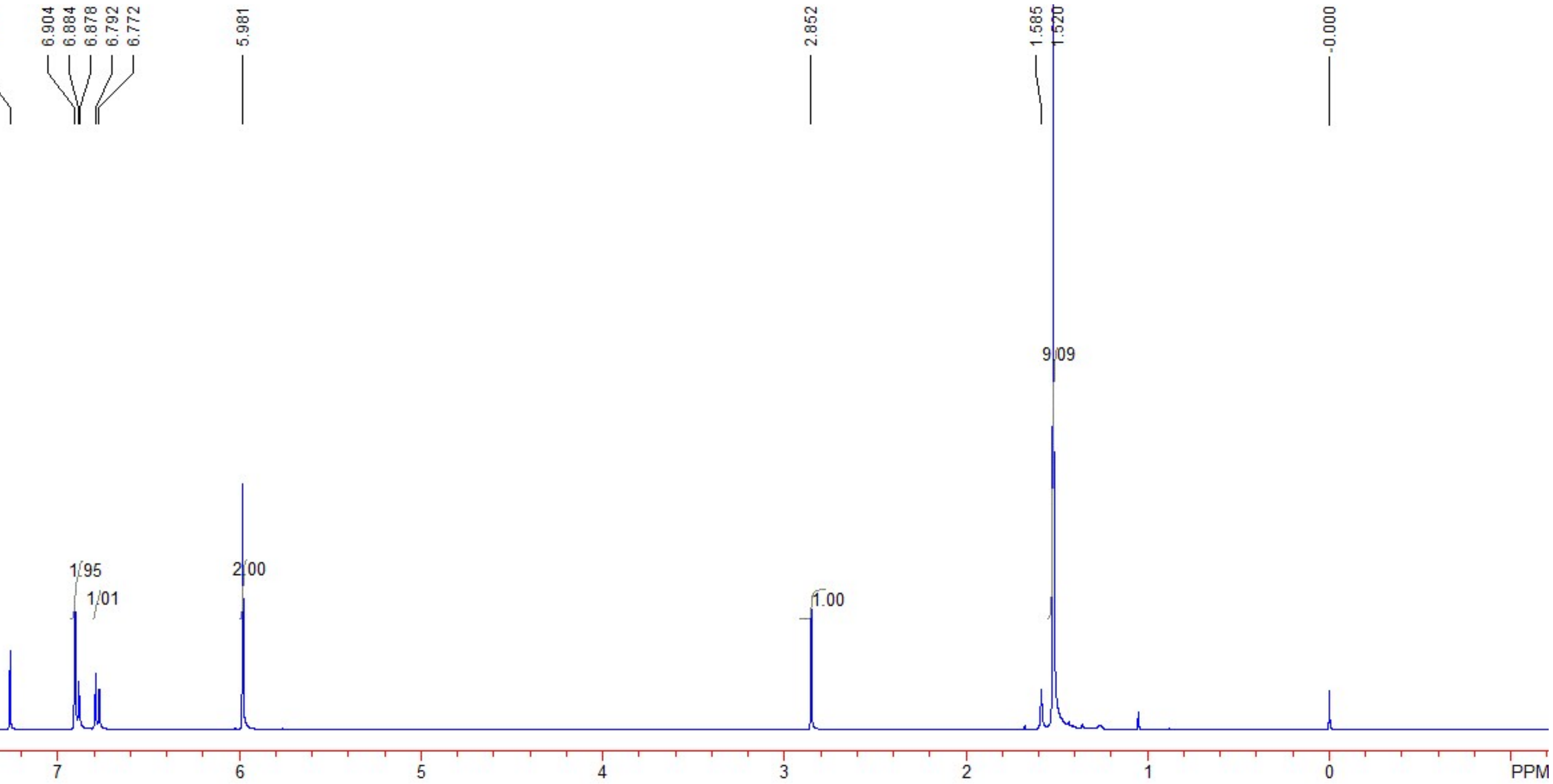
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1.520
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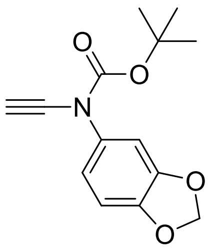

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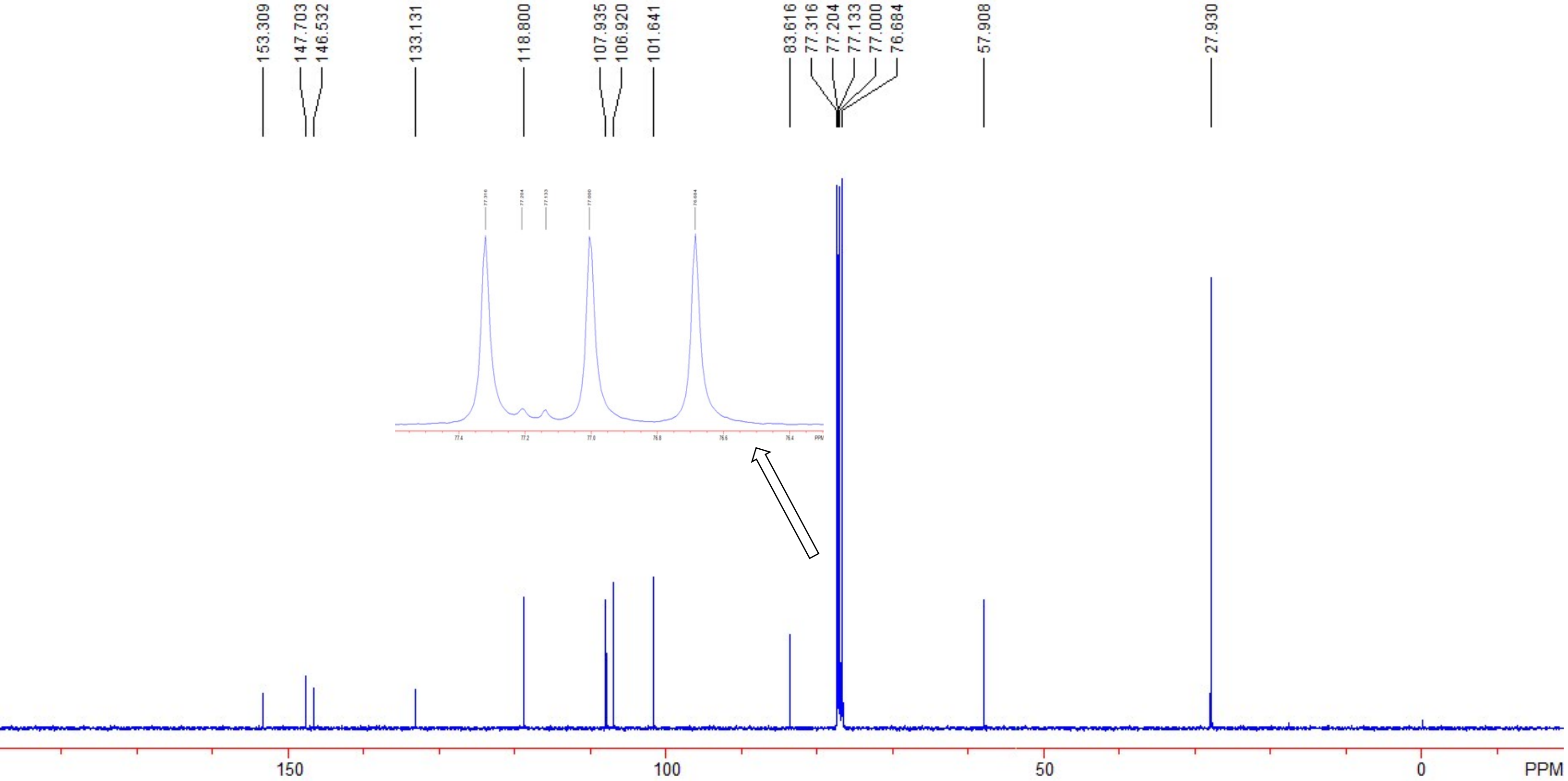

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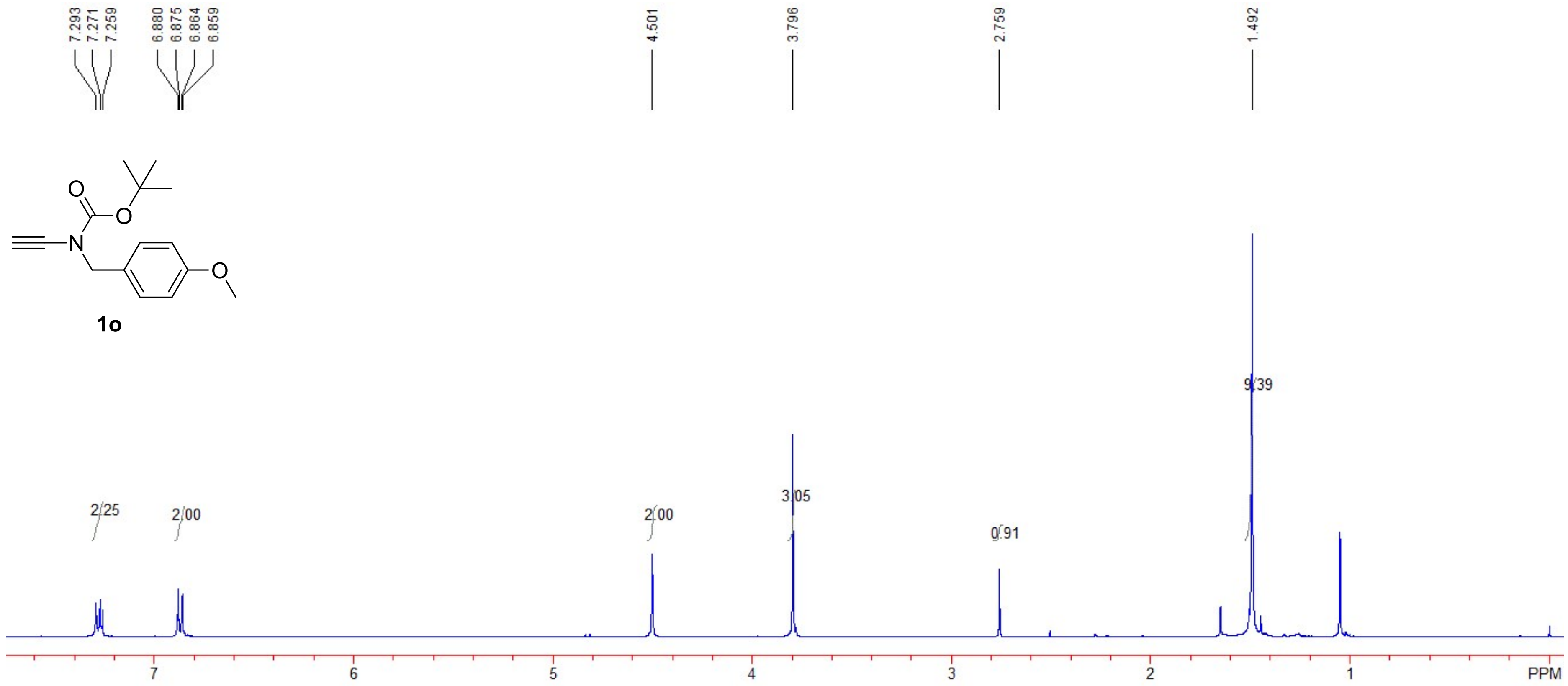
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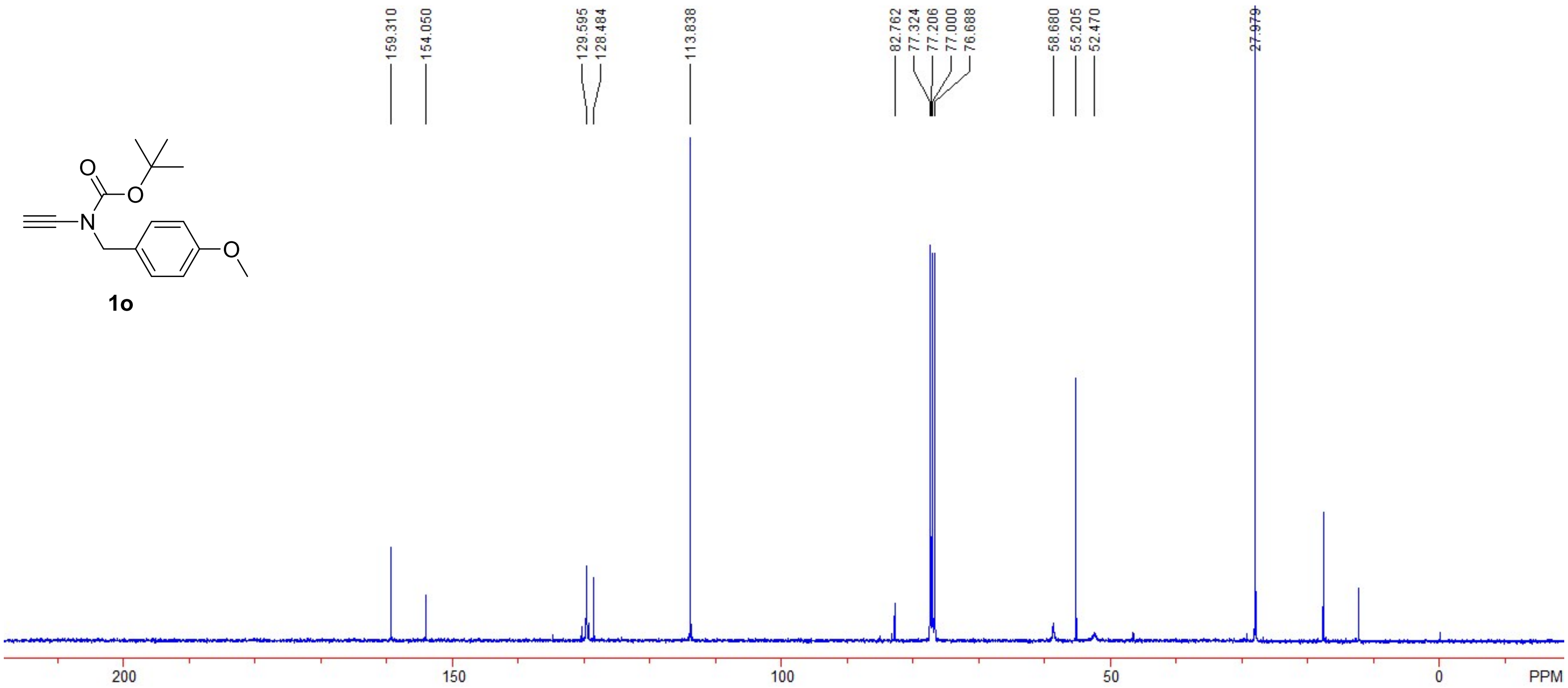

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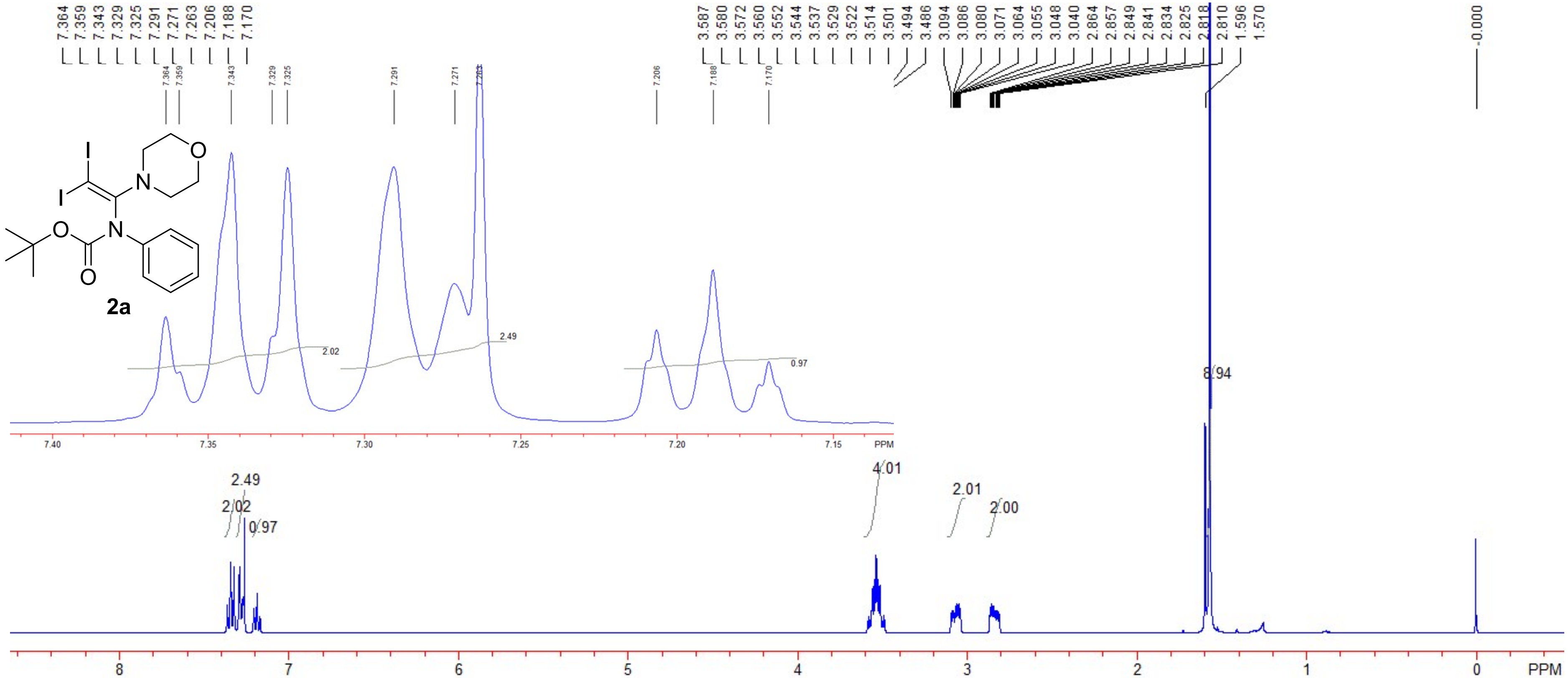

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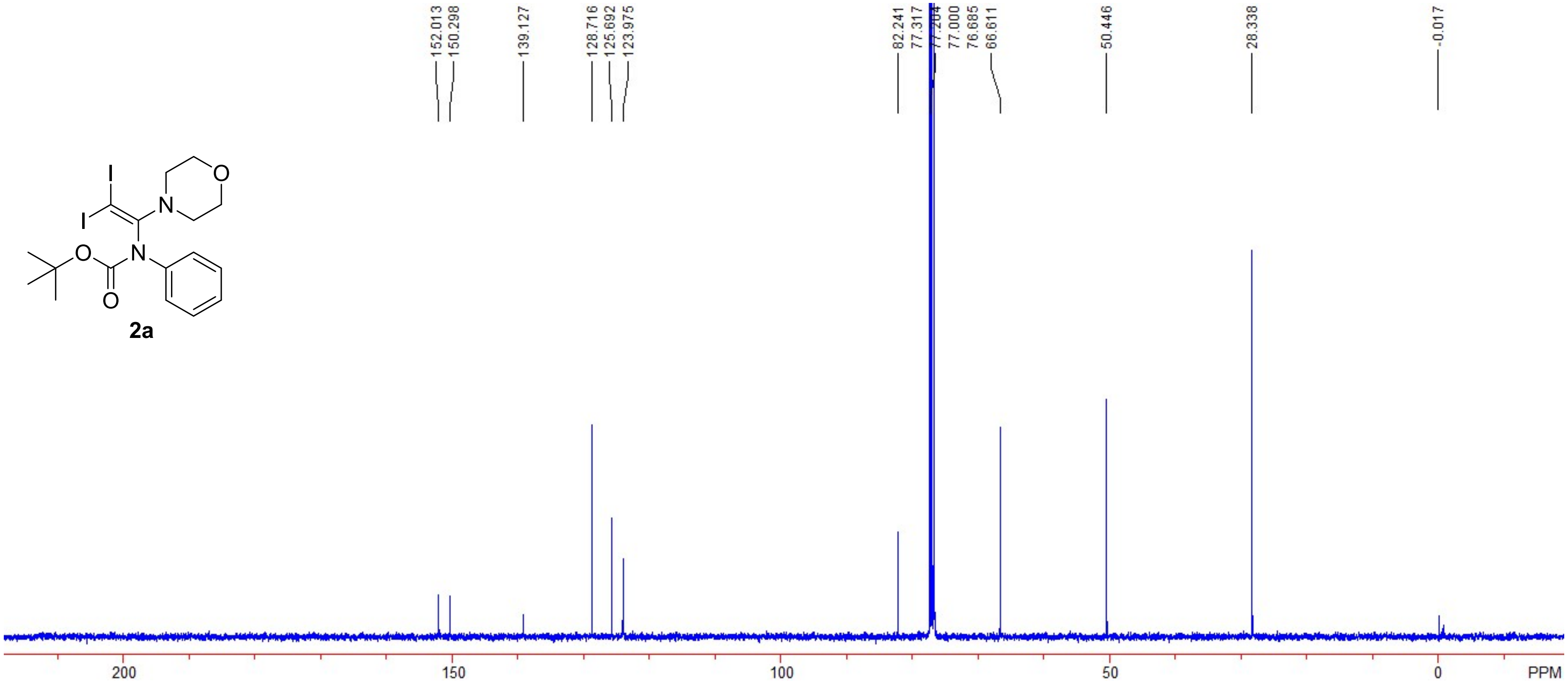
I
I
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O
N
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123.975
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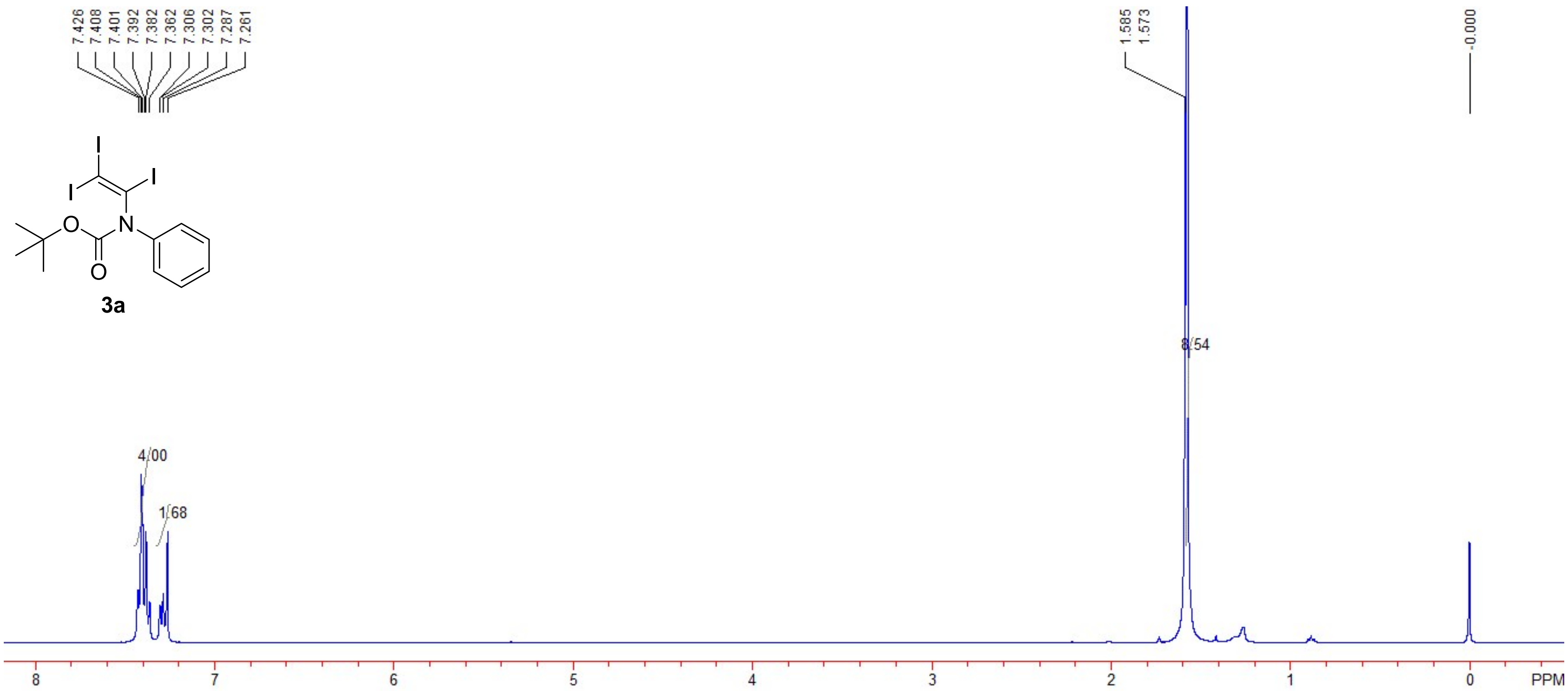
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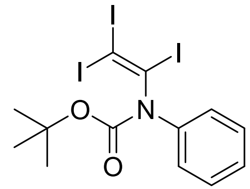

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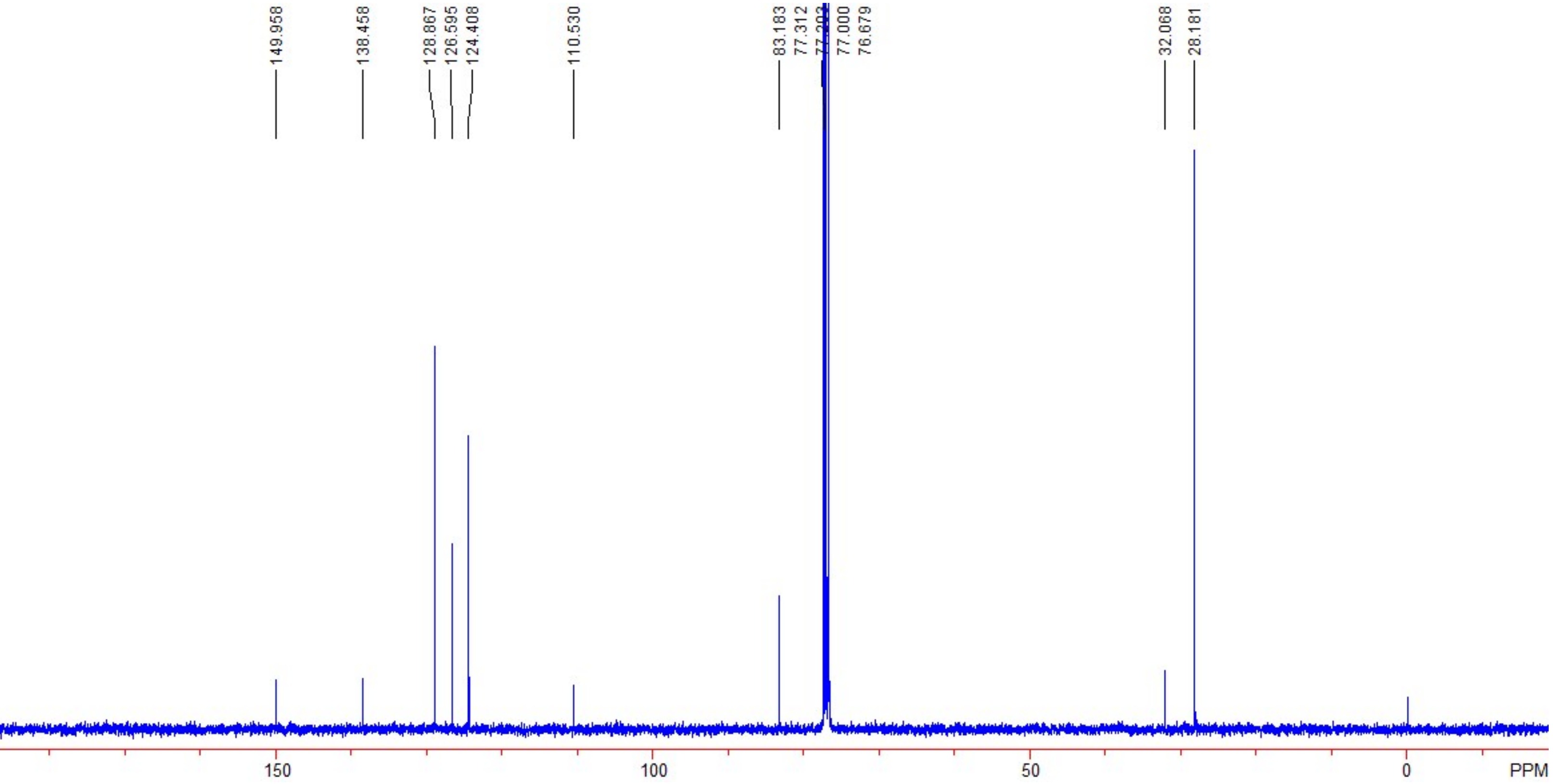

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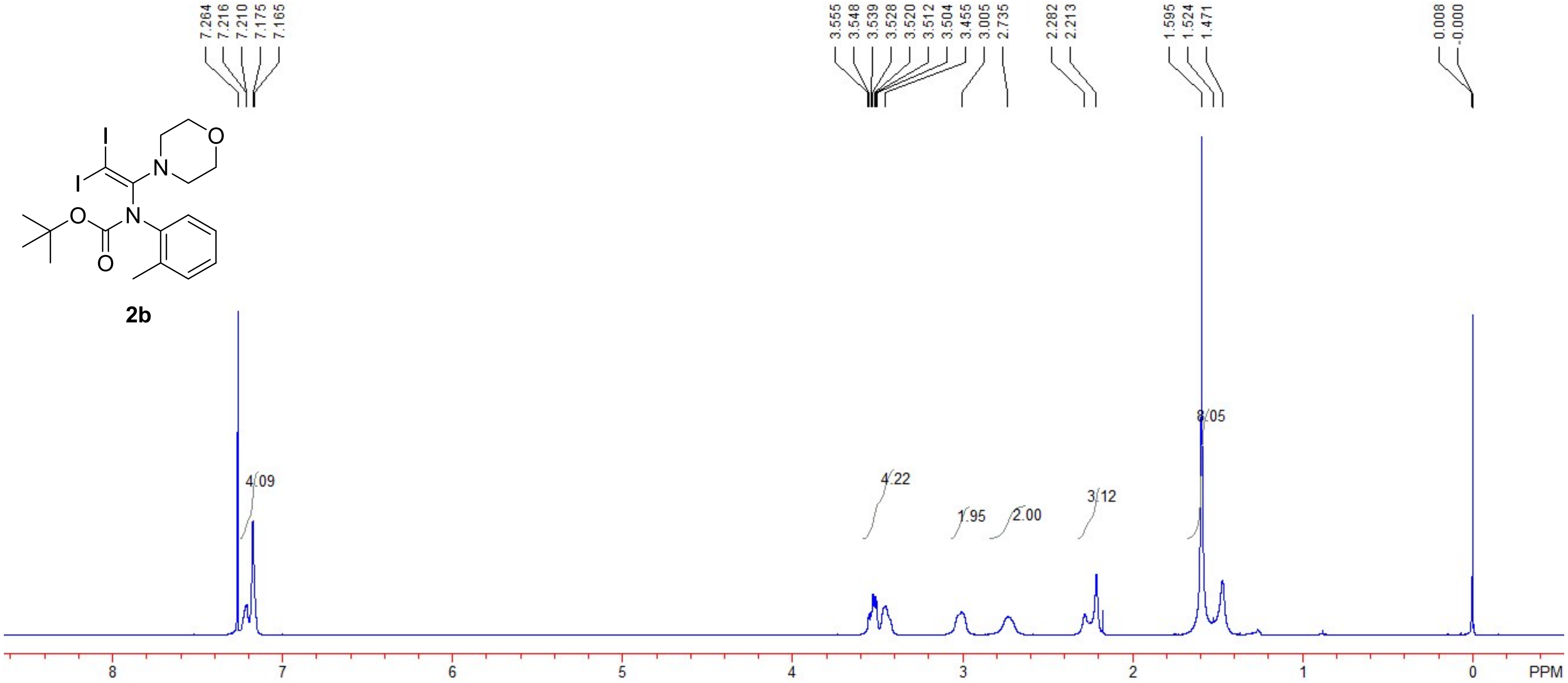
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1.524
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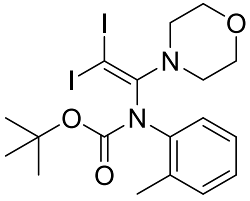
2b



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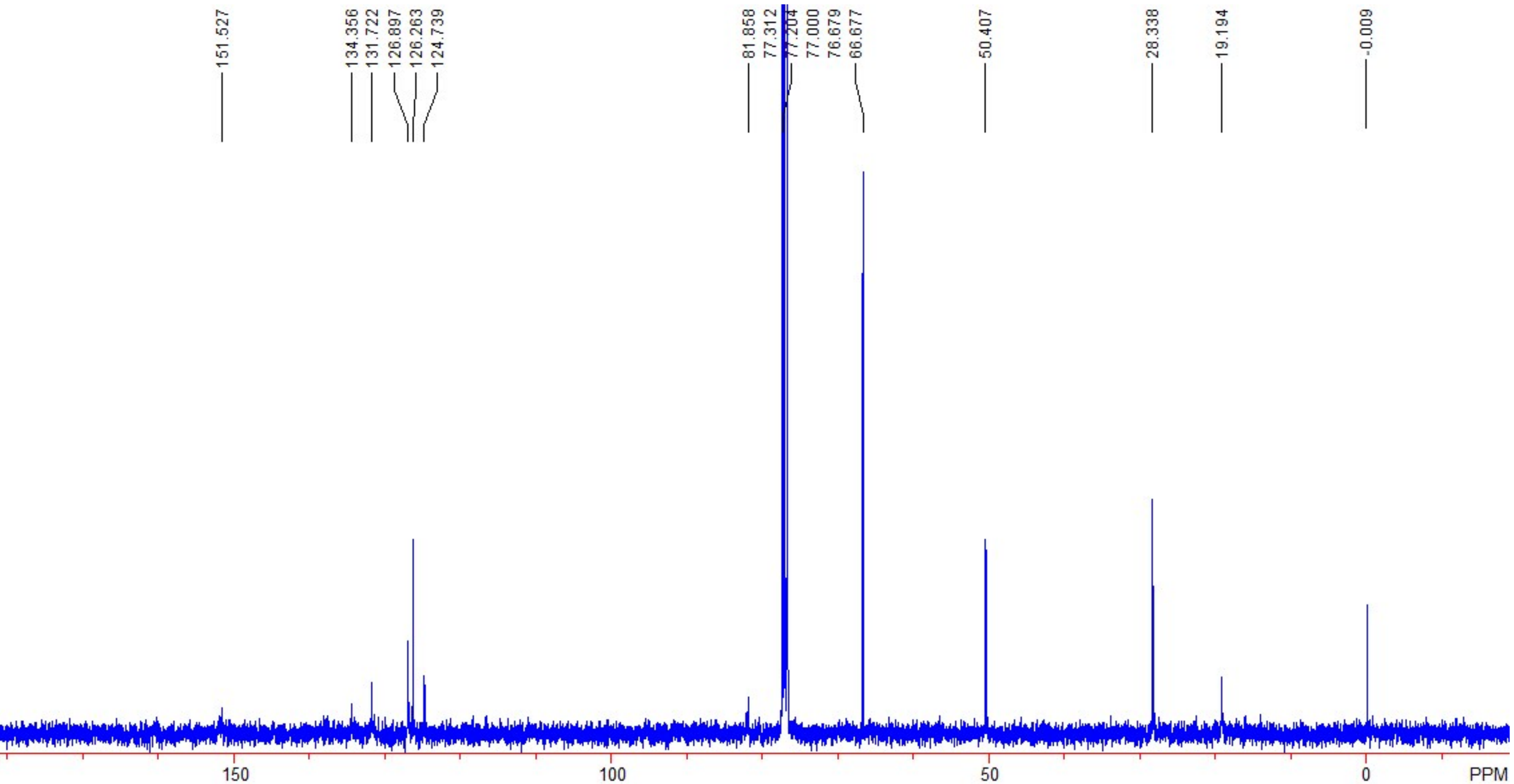

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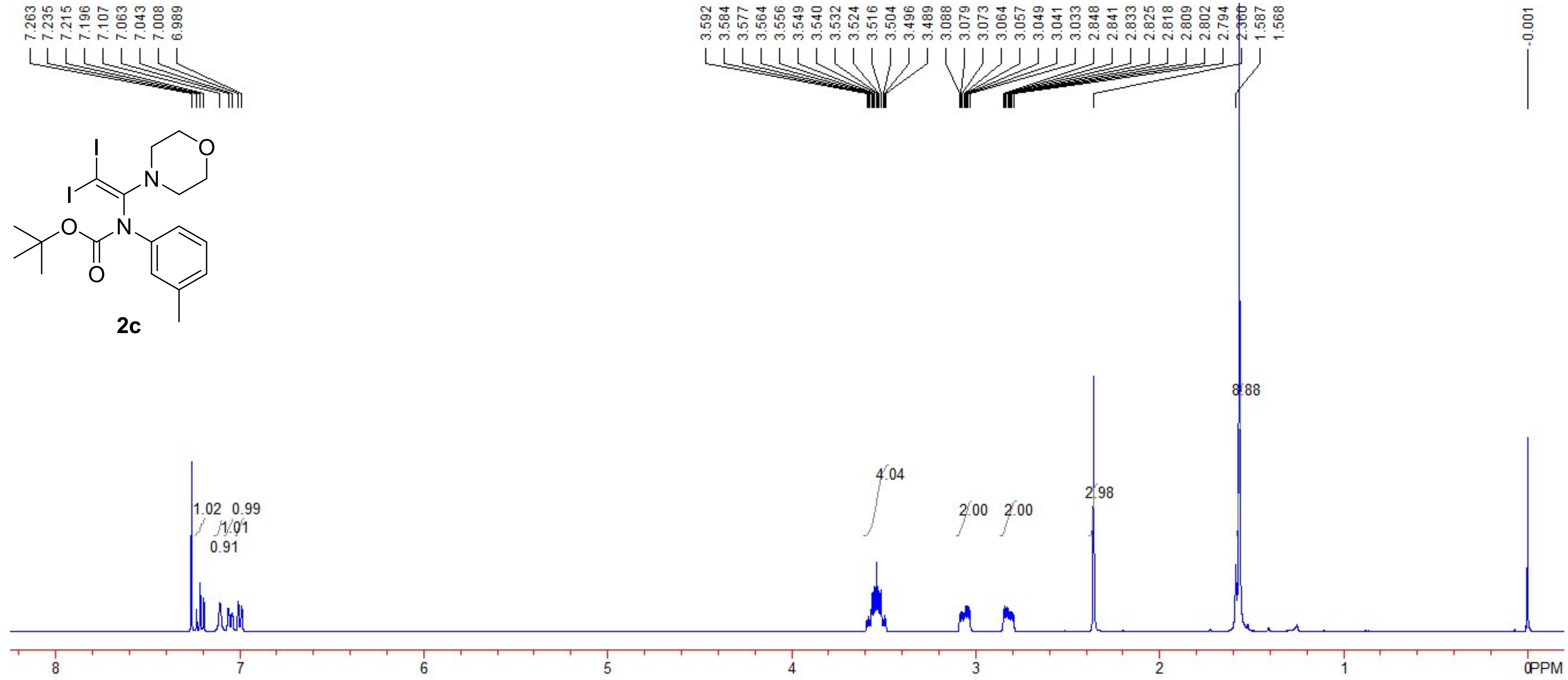

2c

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2.00
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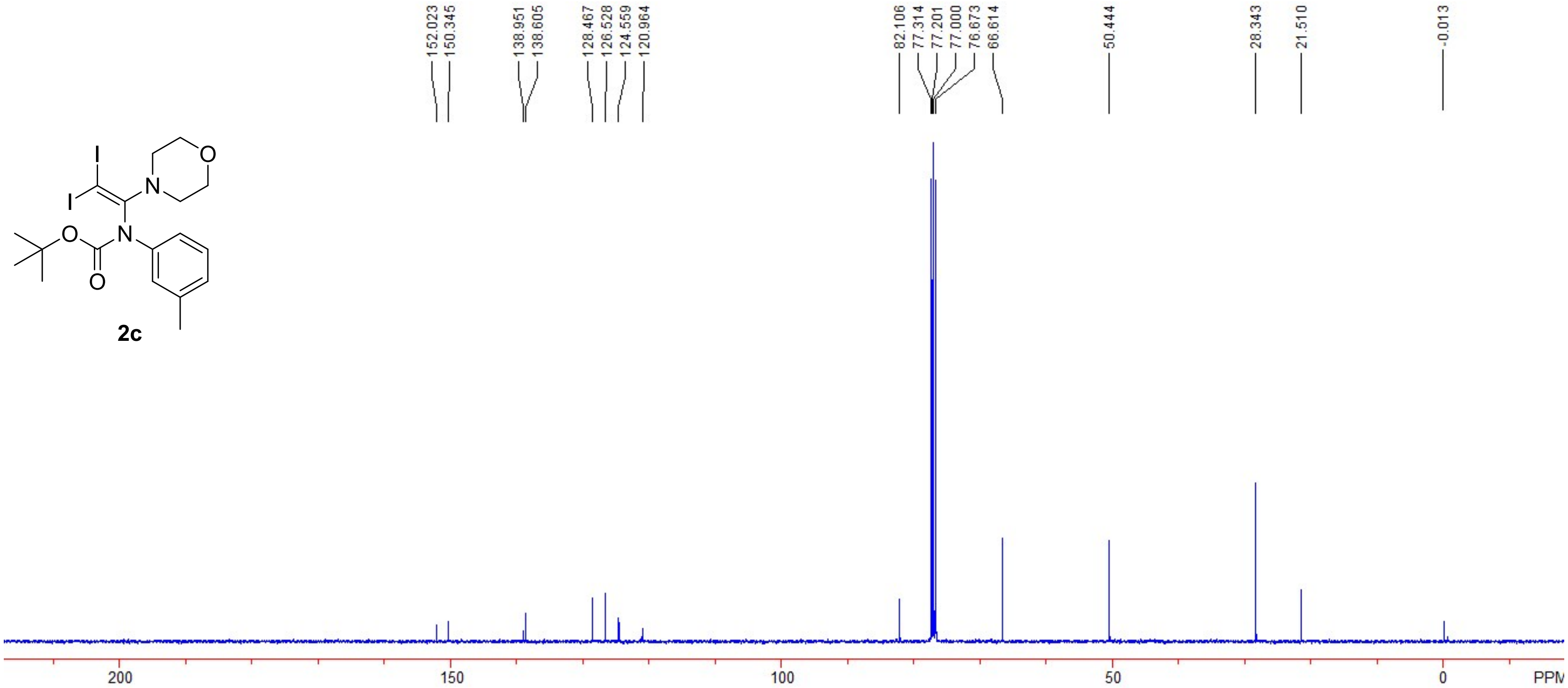

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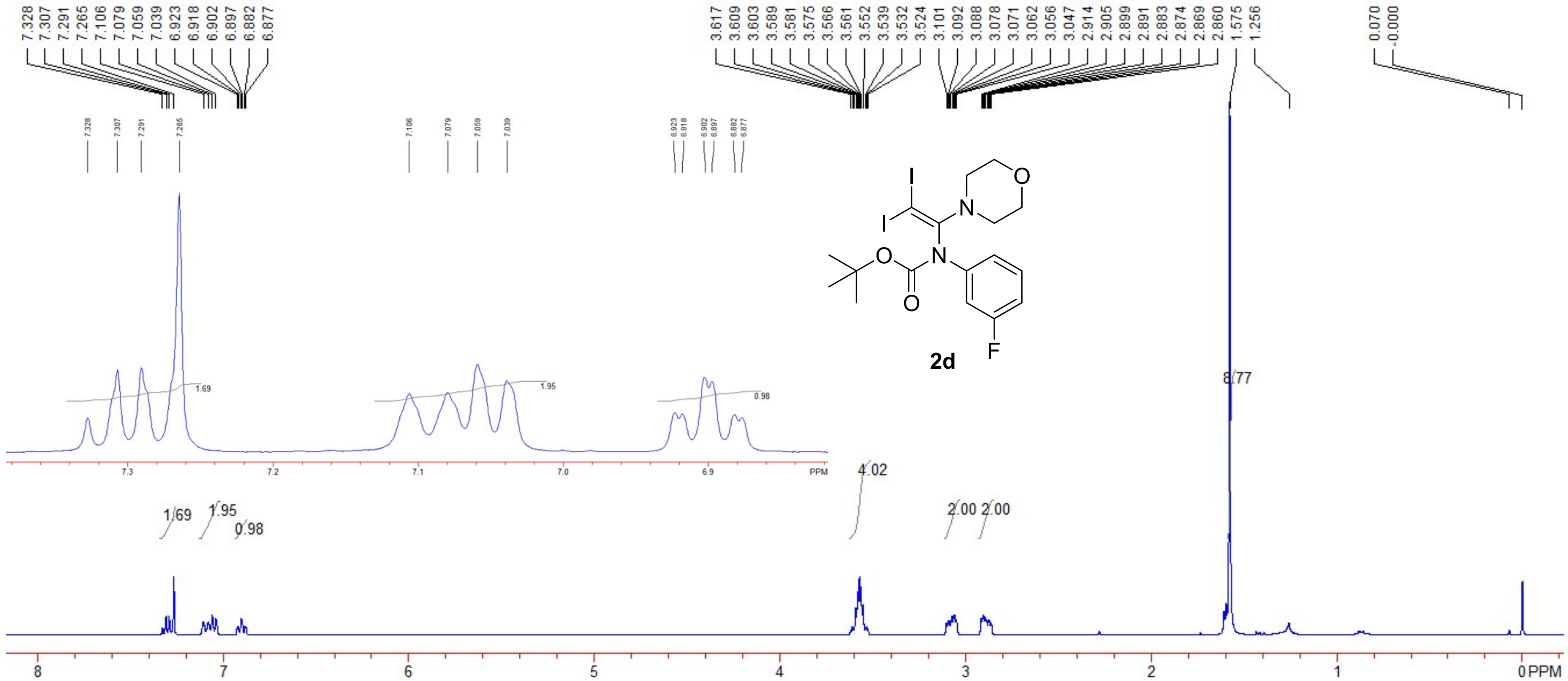
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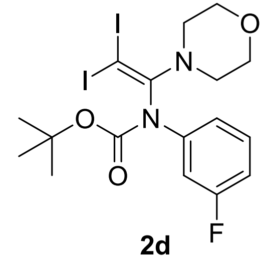
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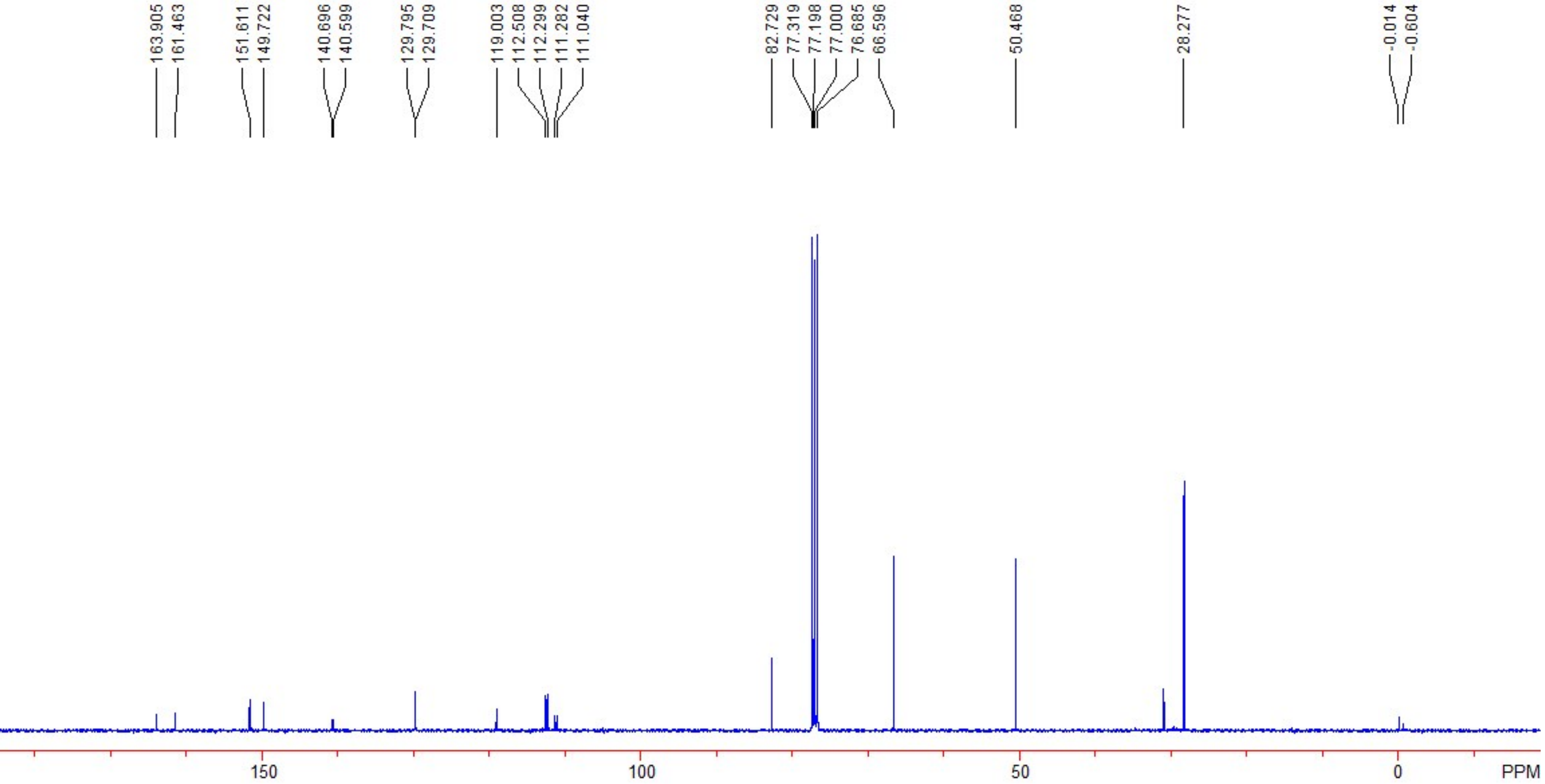
O
N
O
N
O
F

2d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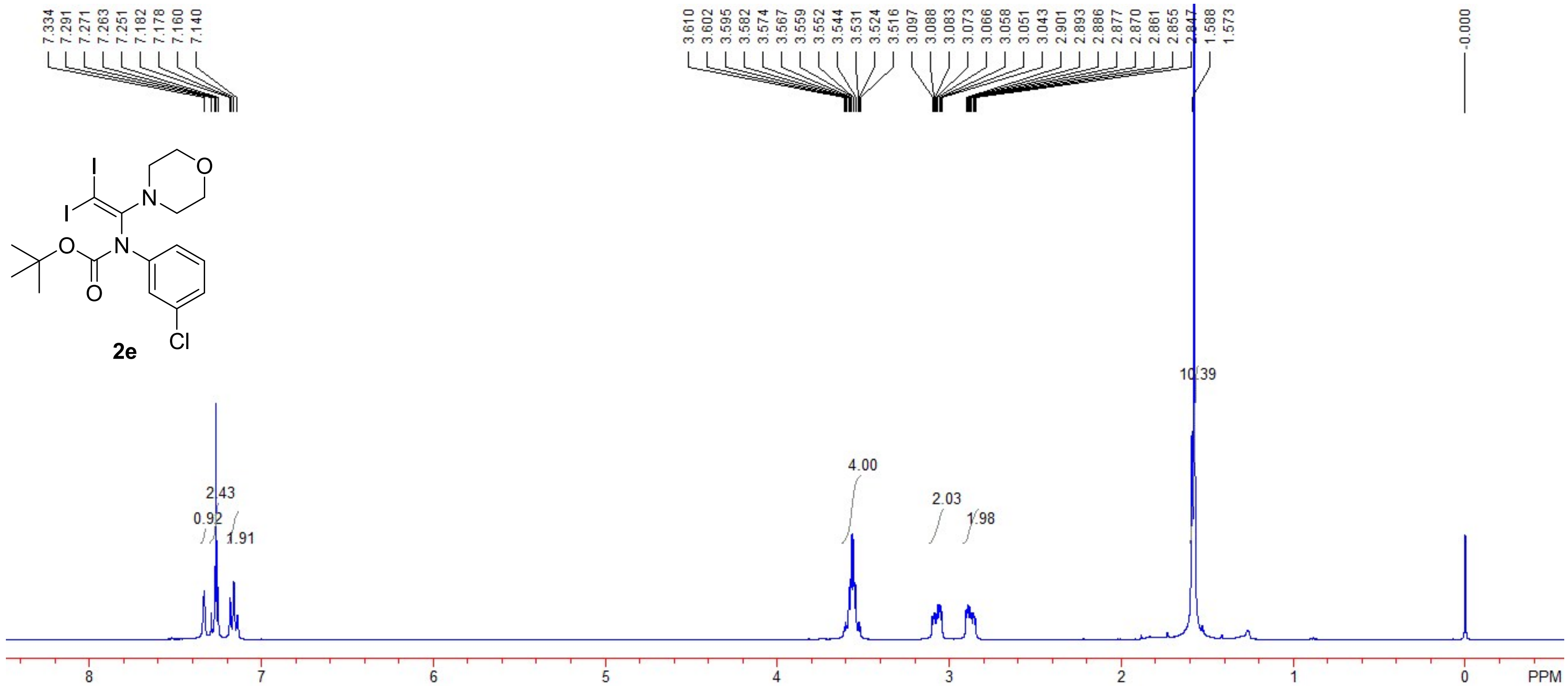

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2.870
2.861
2.855
2.847
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1.573
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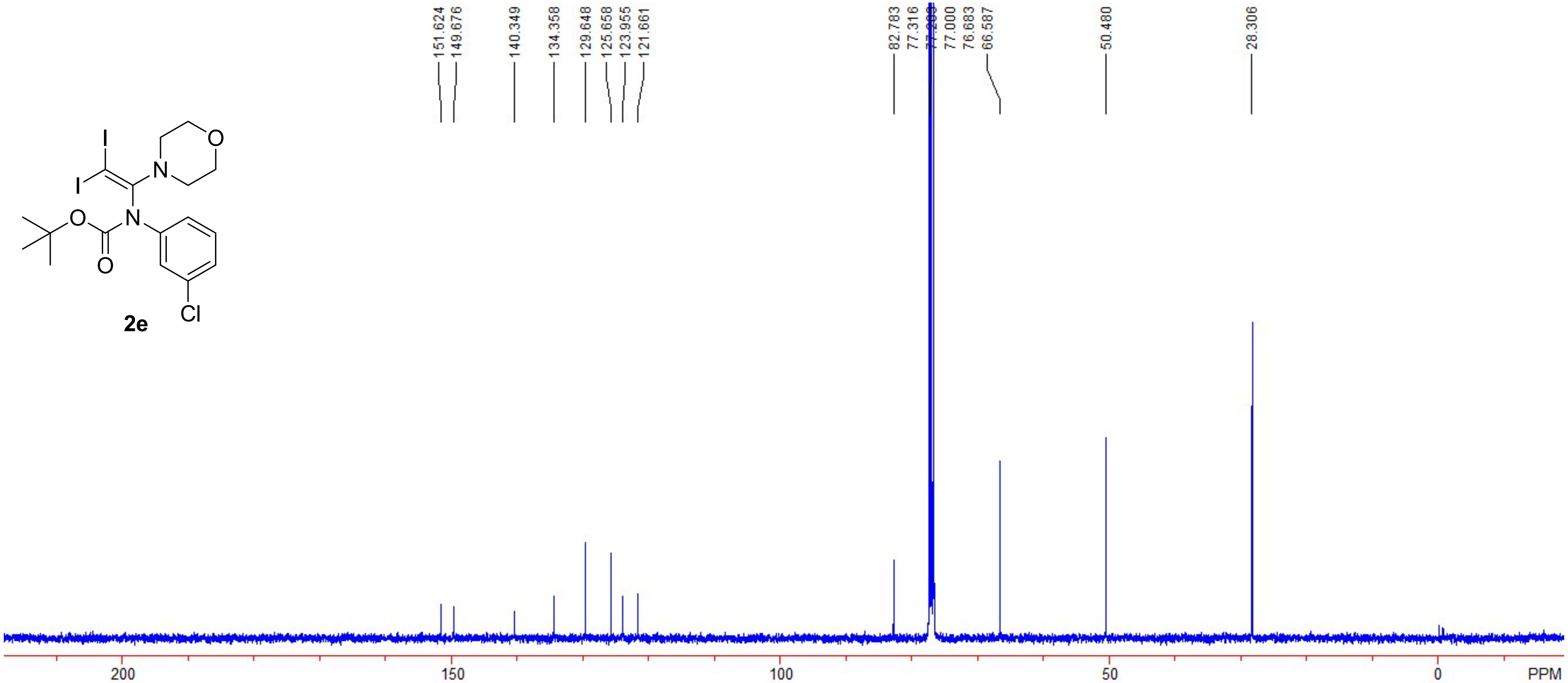

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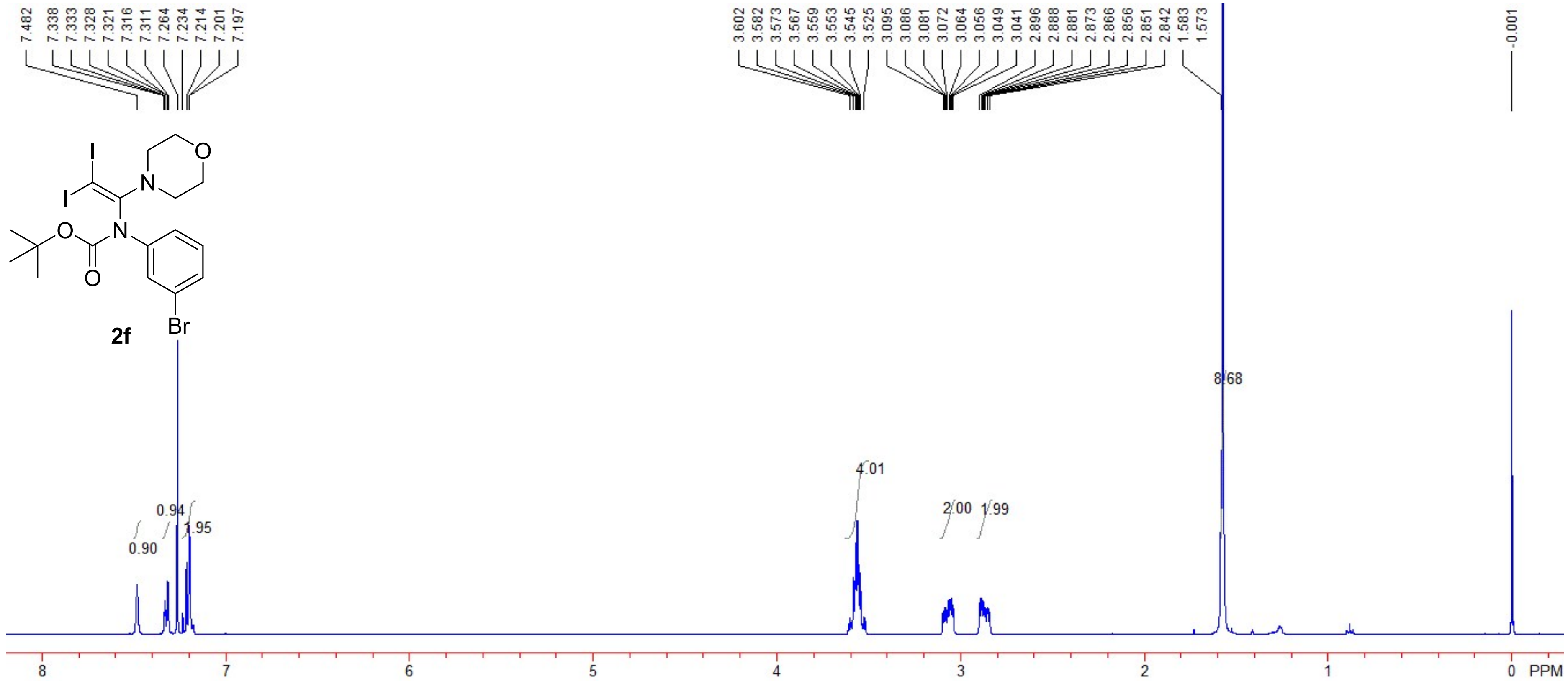
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7.264
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3.573
3.567
3.559
3.553
3.545
3.525
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3.072
3.064
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3.049
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2.851
2.842
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1.573
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I
N
O
O
N
O
Br
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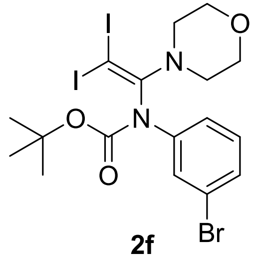

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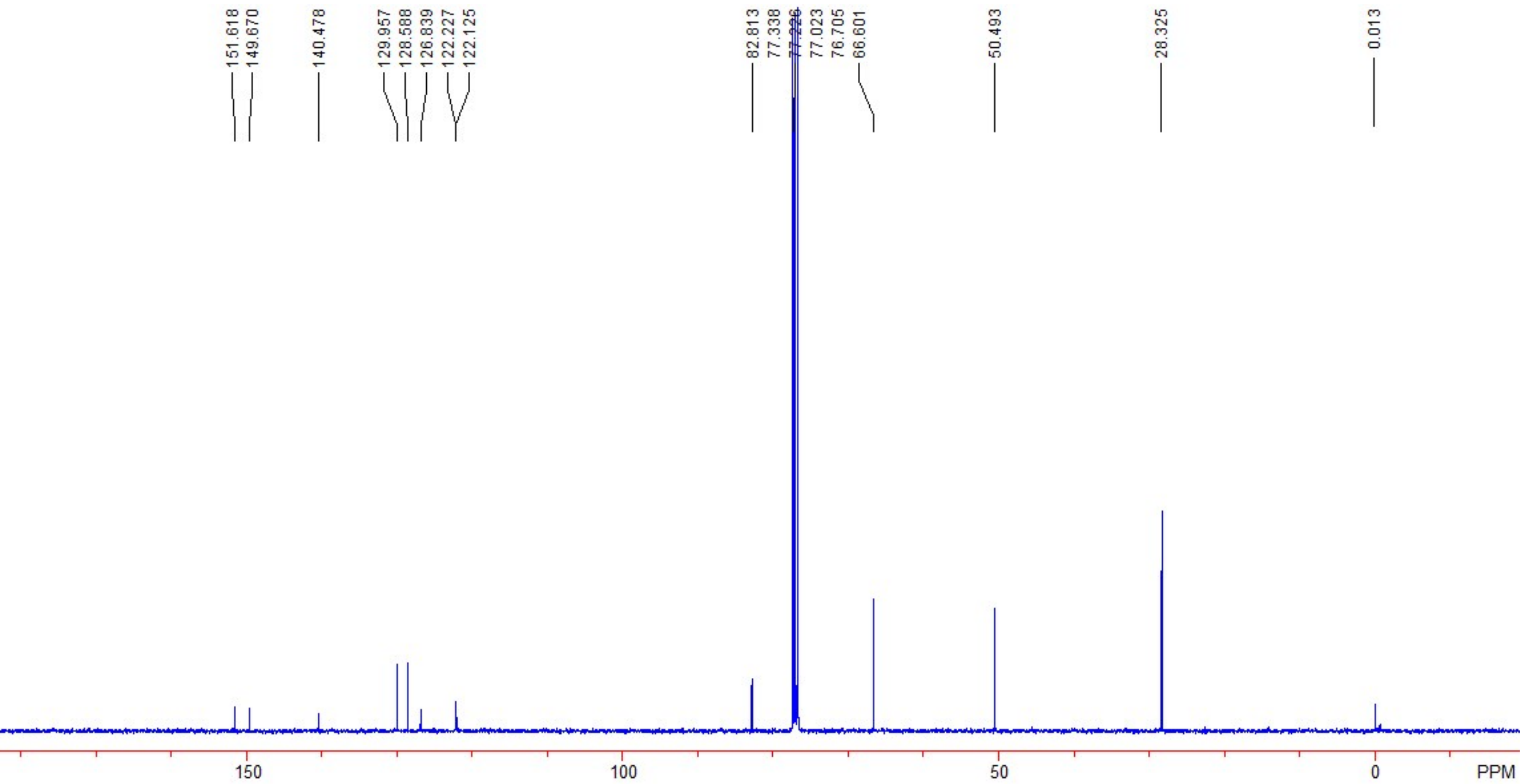
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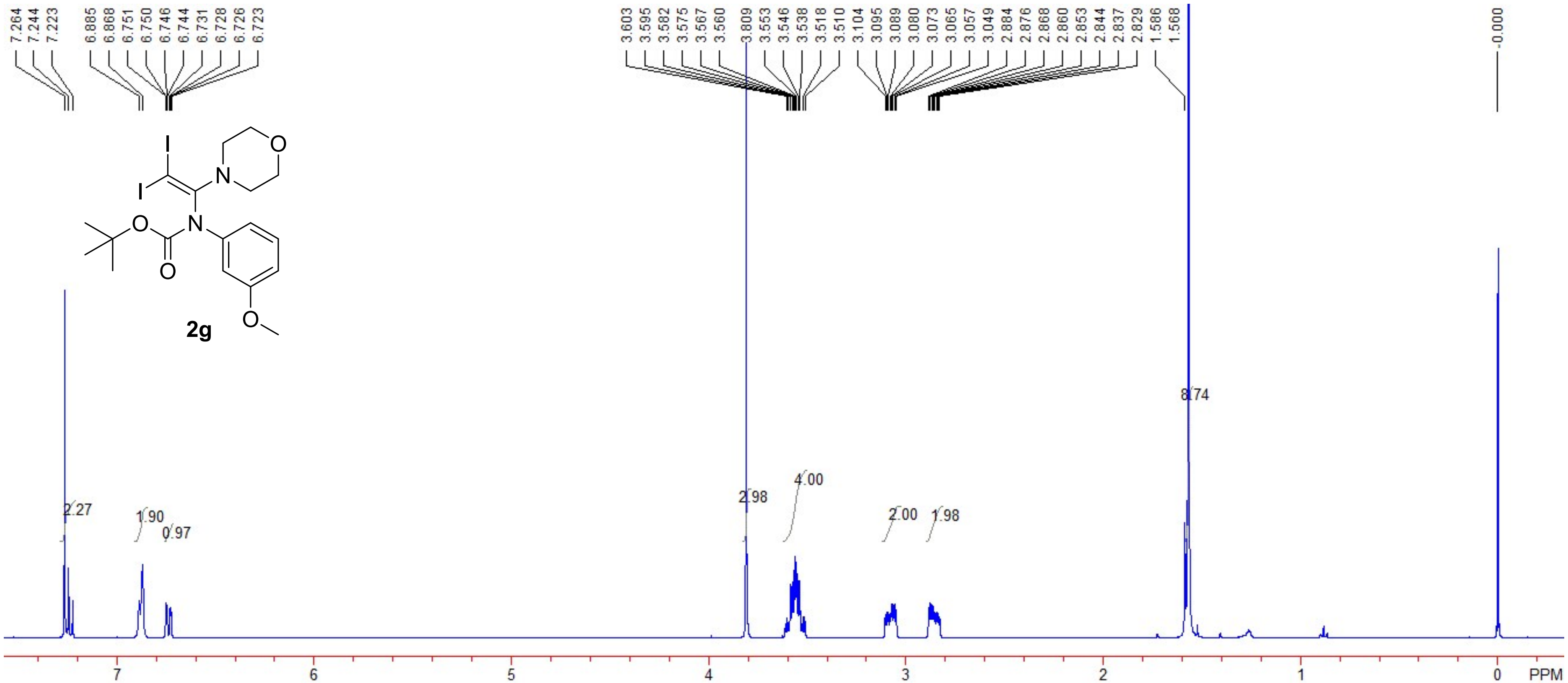
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3.595
3.582
3.575
3.567
3.560
3.809
3.553
3.546
3.538
3.518
3.510
3.104
3.095
3.089
3.080
3.073
3.065
3.057
3.049
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2.868
2.860
2.853
2.844
2.837
2.829
1.586
1.568
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2.27
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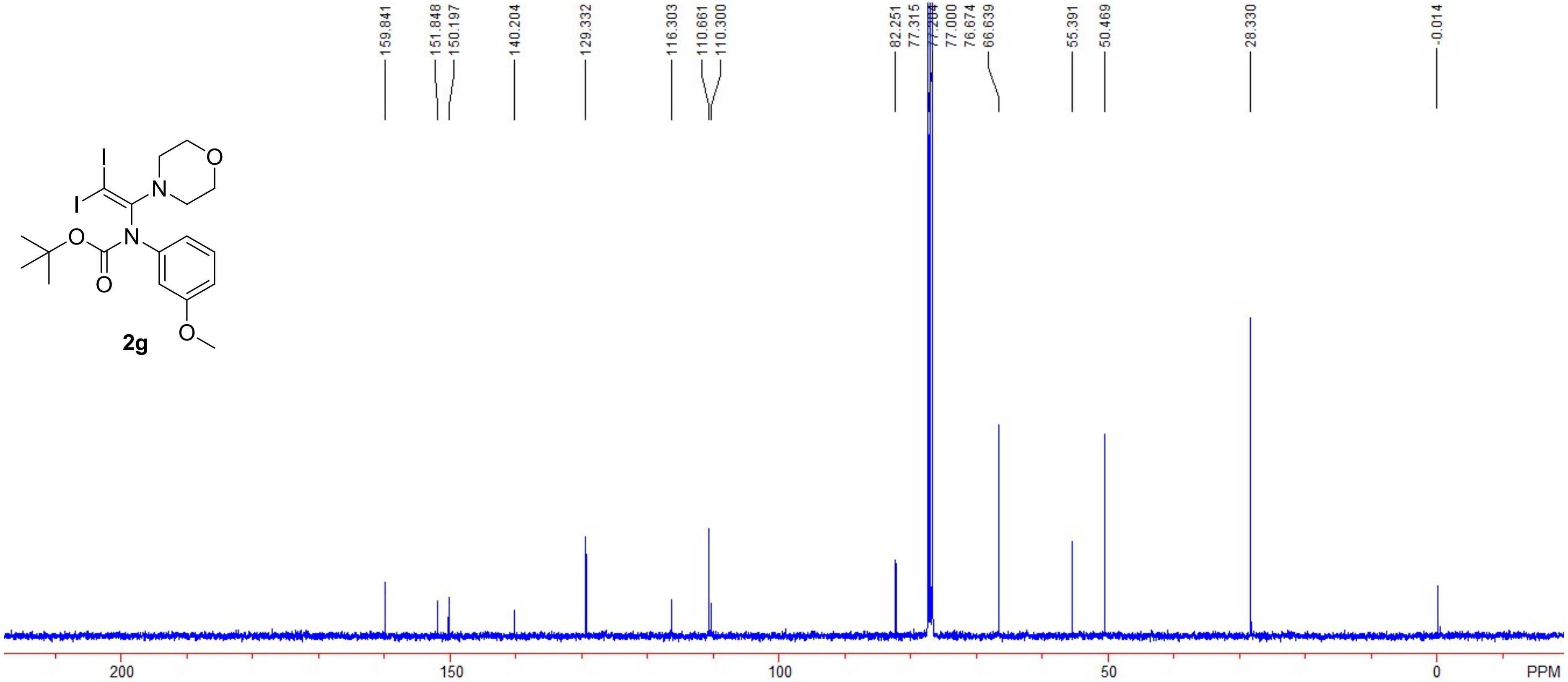

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100
50
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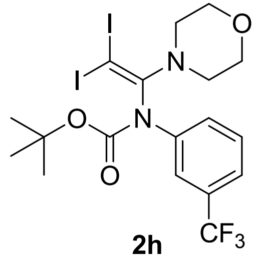
PPM



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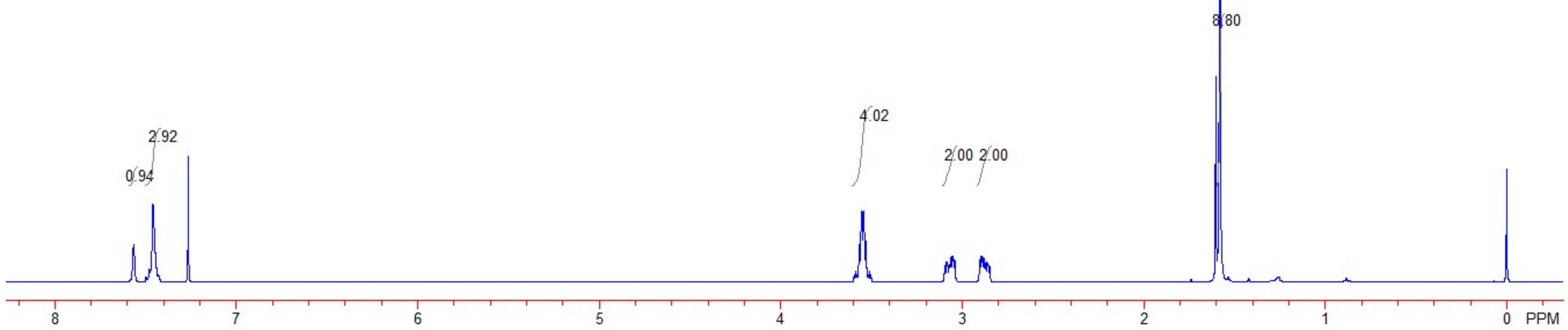

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3.545
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3.096
3.087
3.082
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1.582
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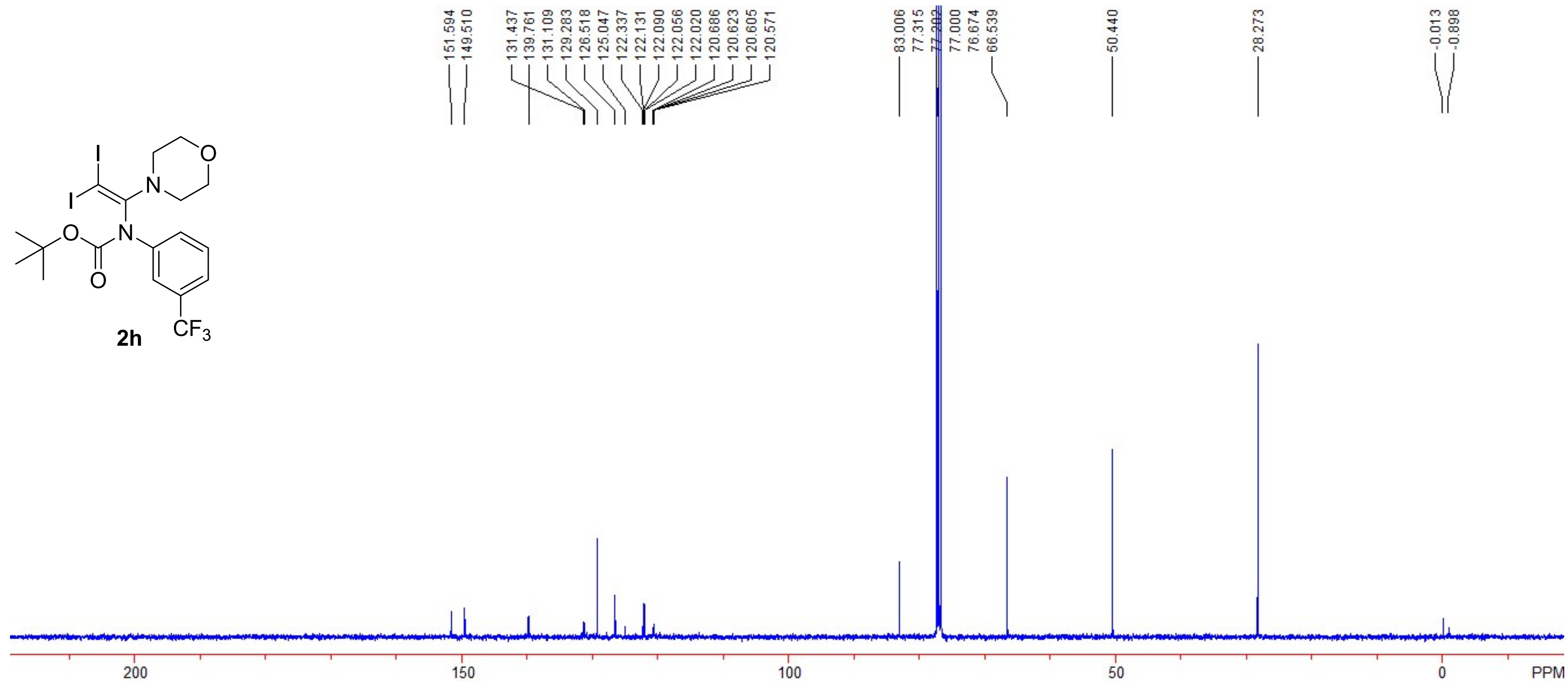

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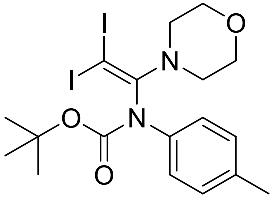

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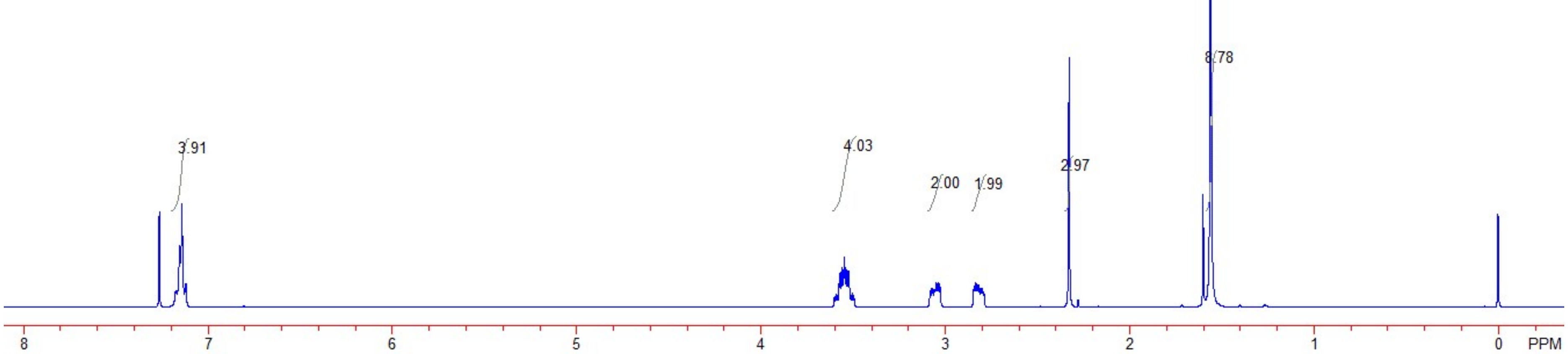

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3.539
3.531
3.523
3.503
3.081
3.074
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3.051
3.043
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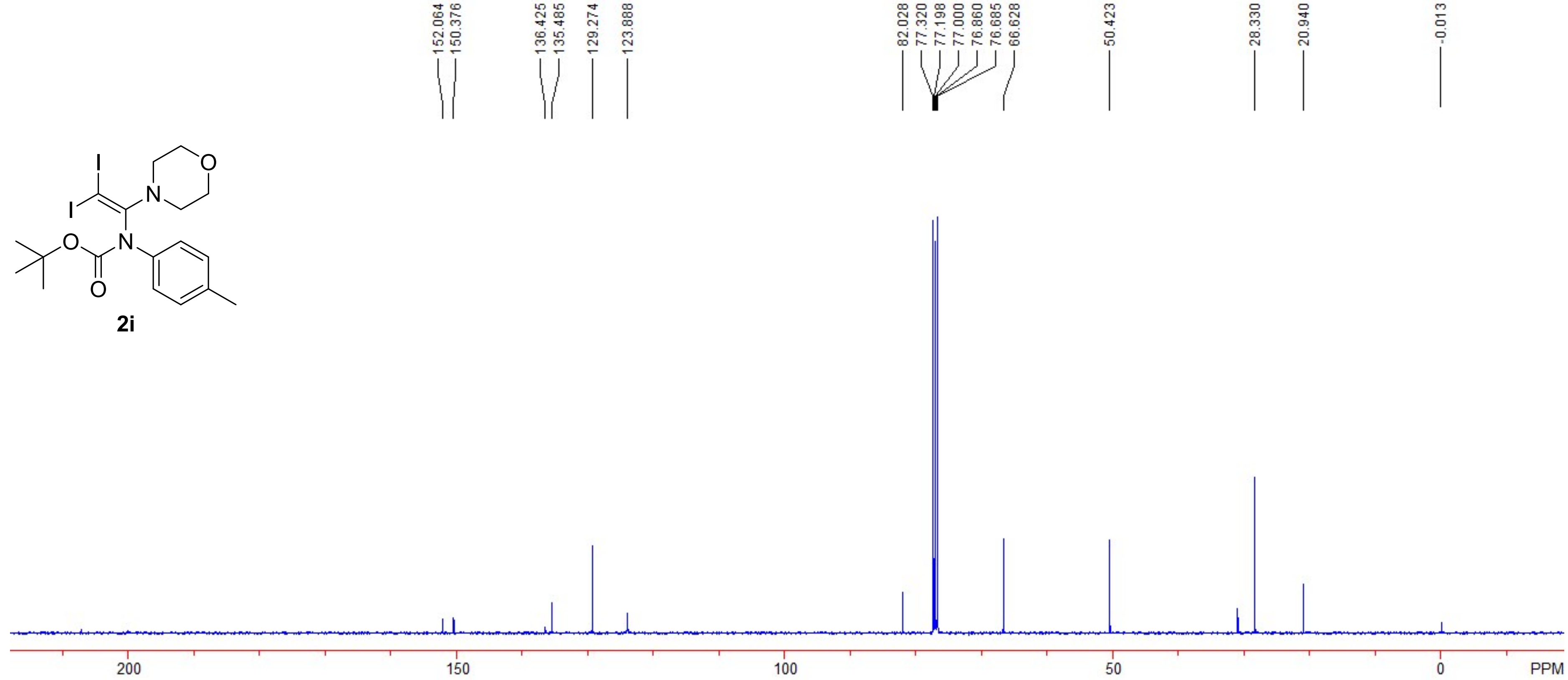

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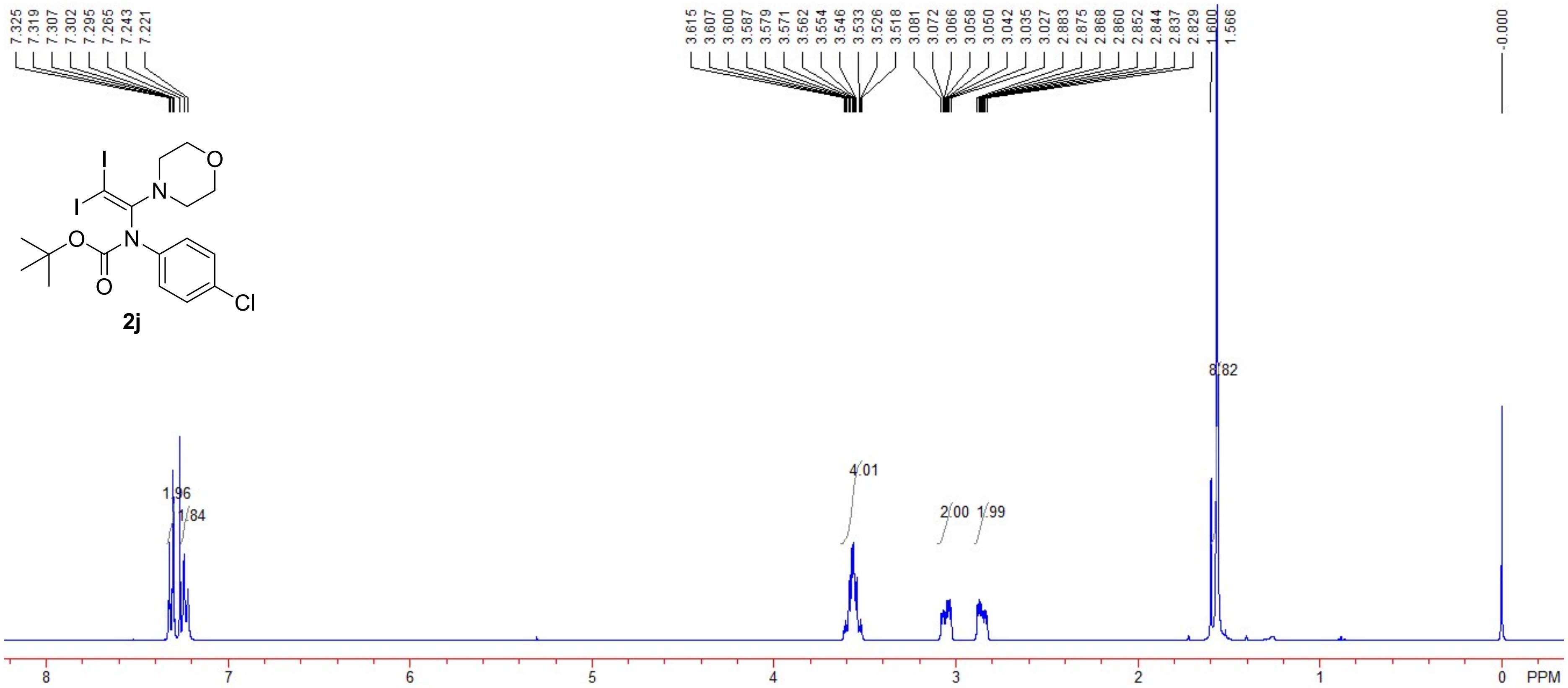
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3.571
3.562
3.554
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3.526
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3.072
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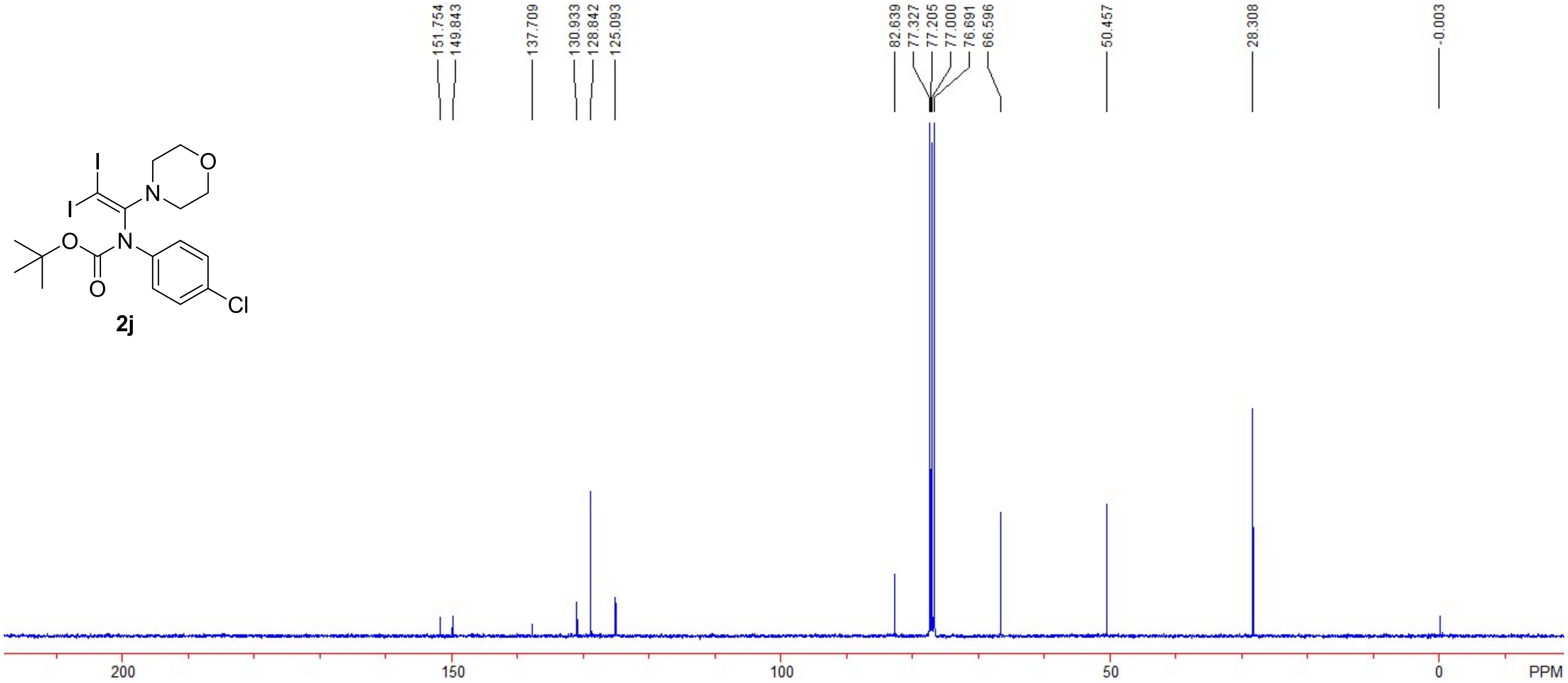
2j

2j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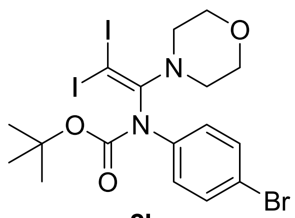

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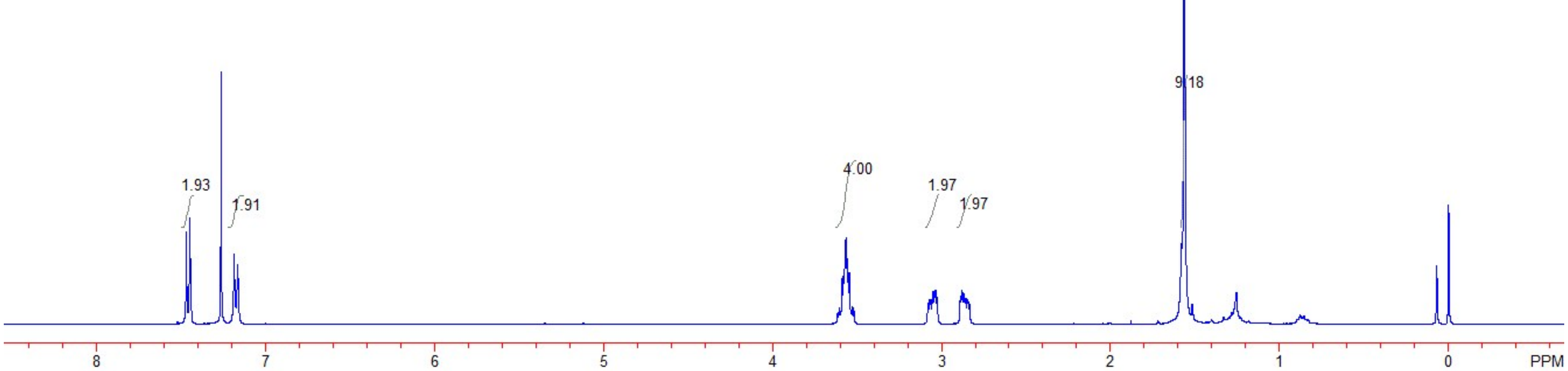
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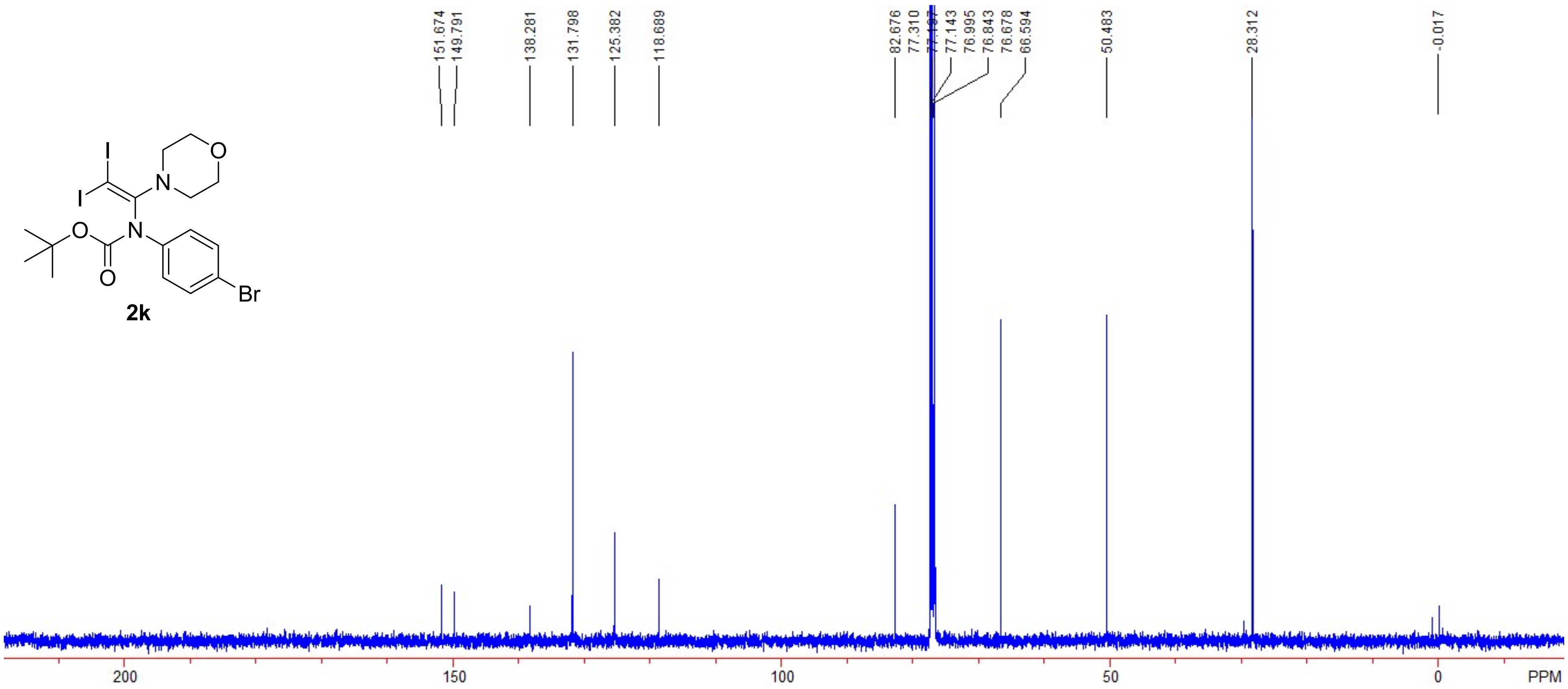

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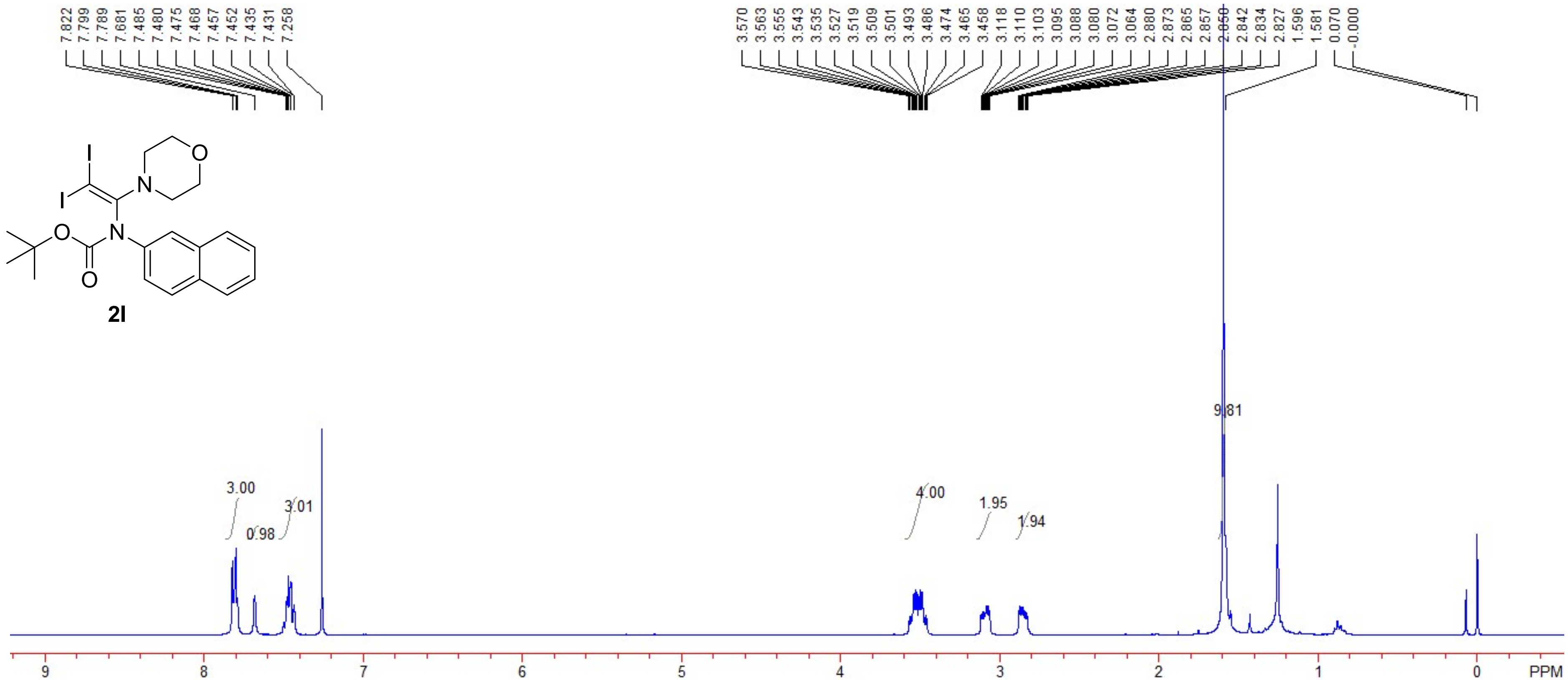
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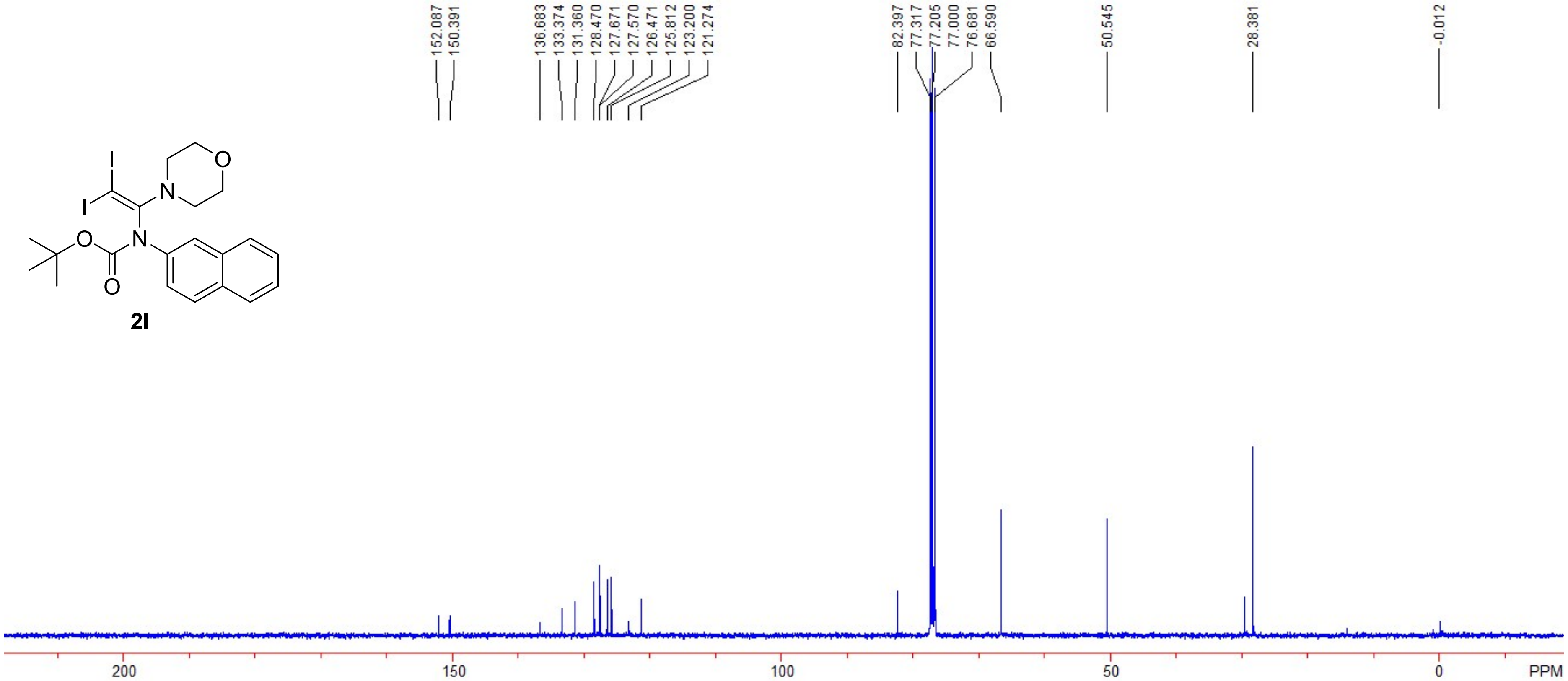
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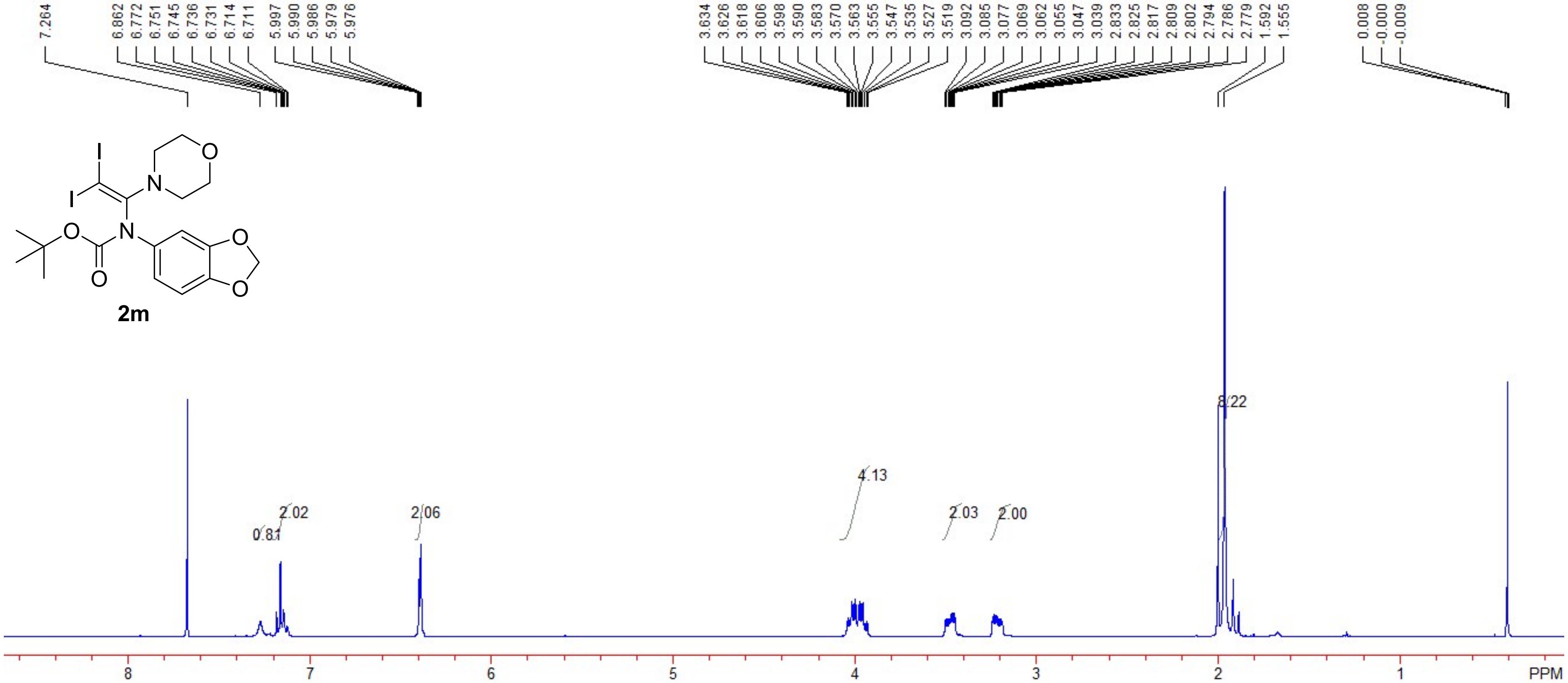

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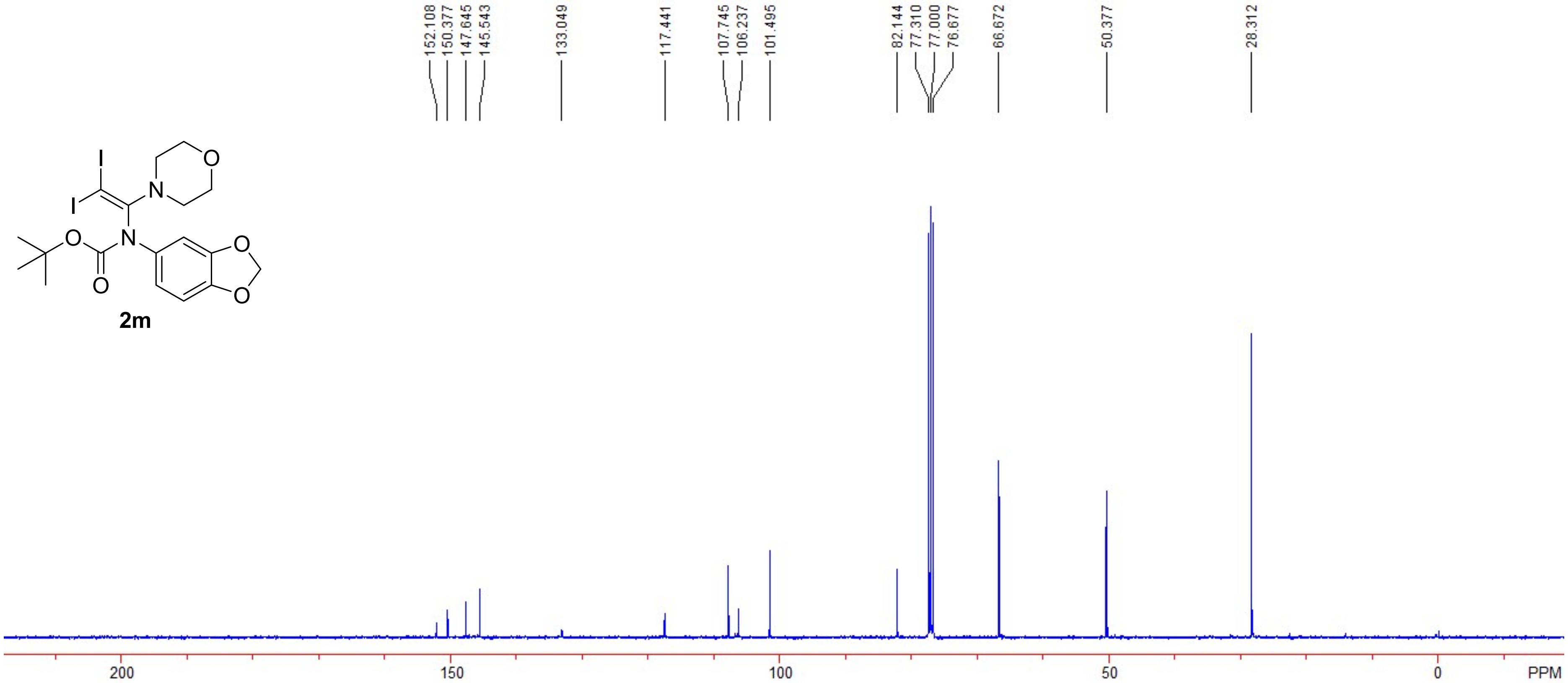
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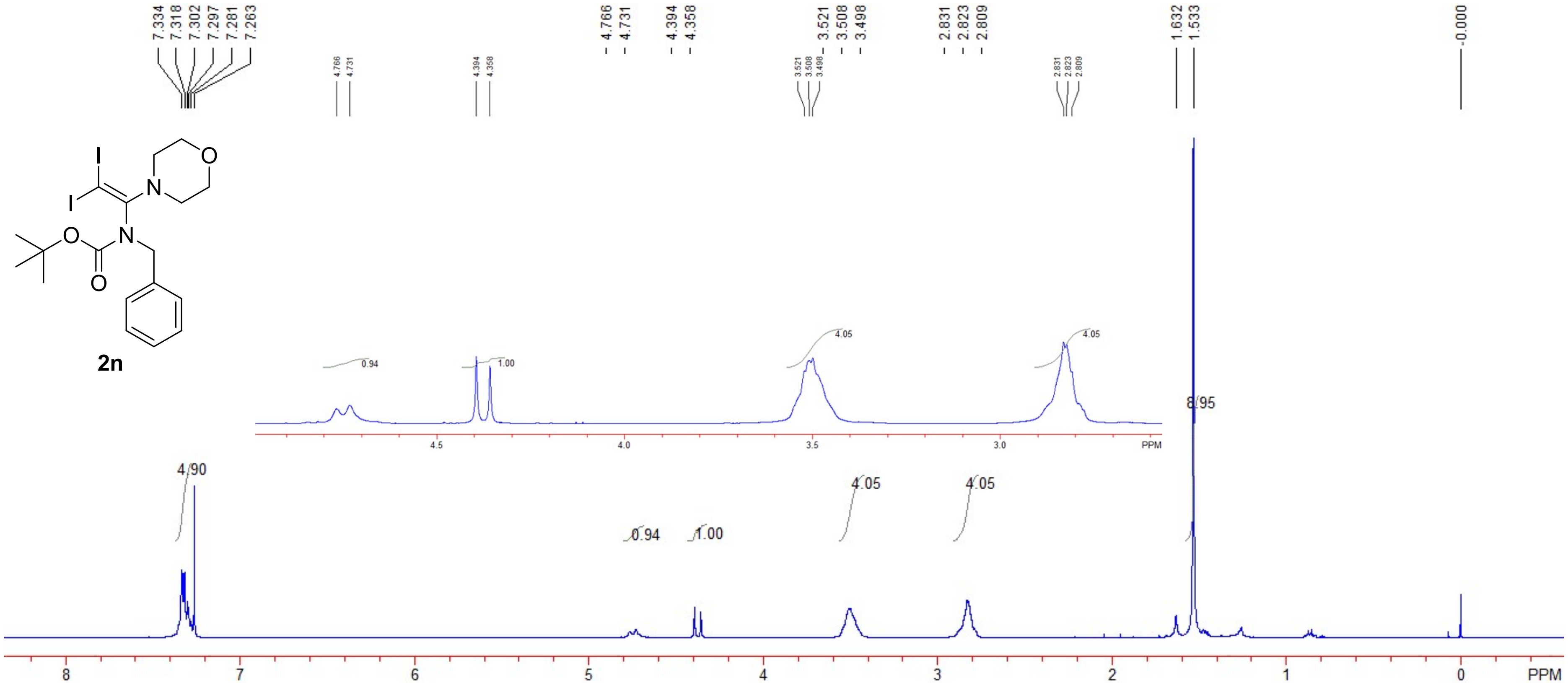
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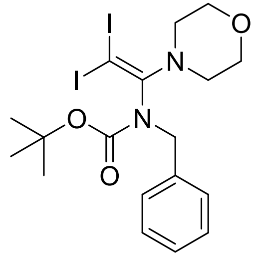

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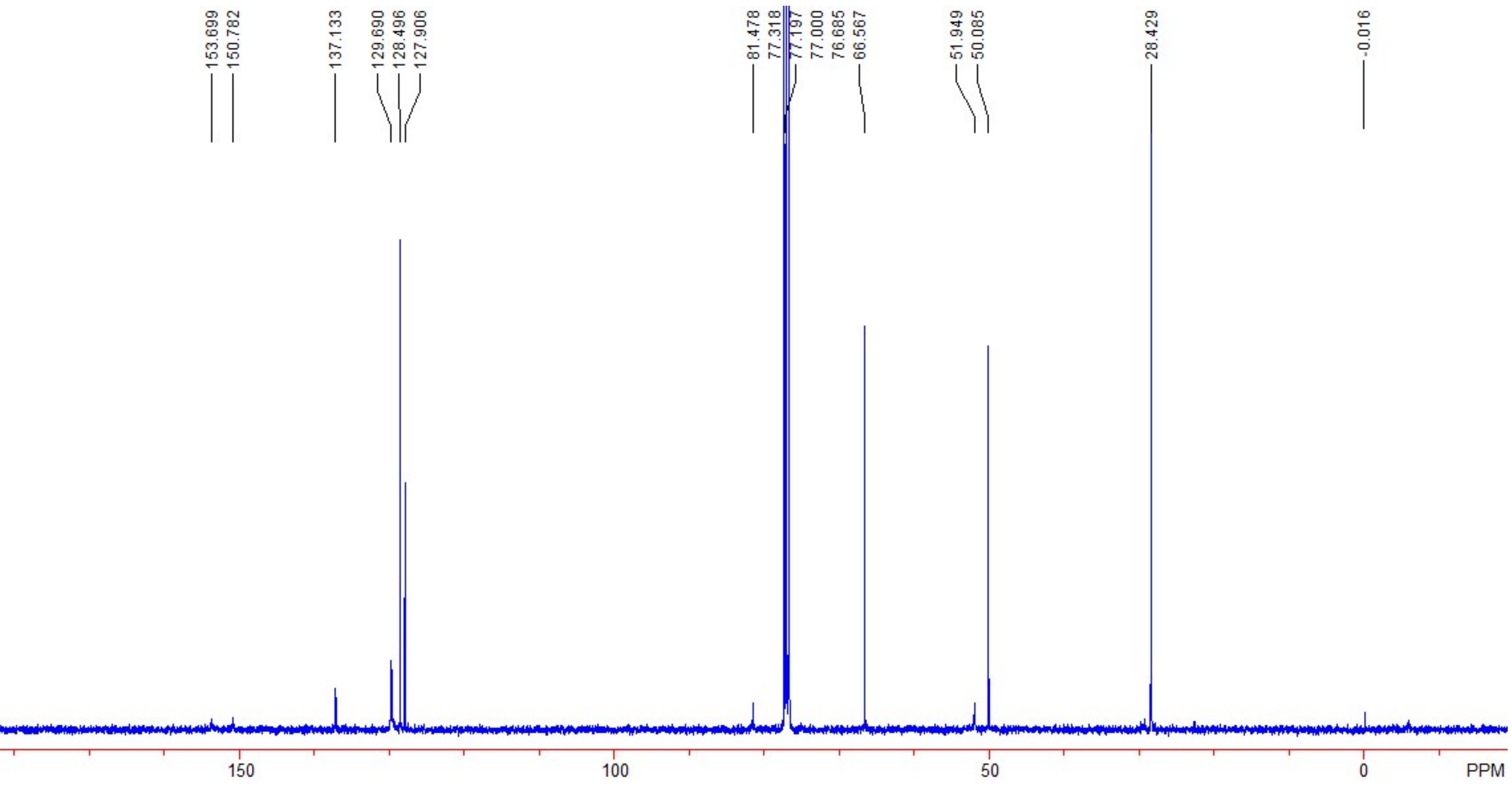
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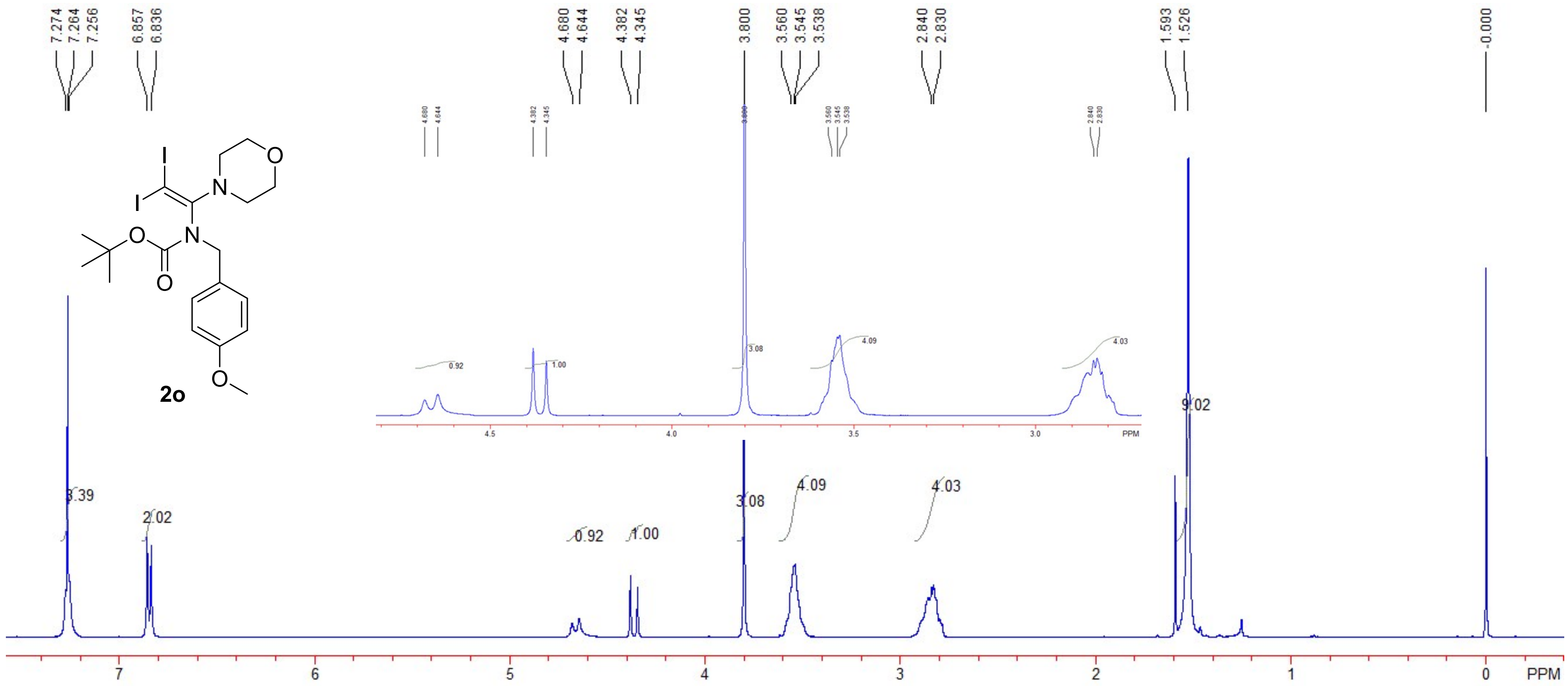
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2.830
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1.526
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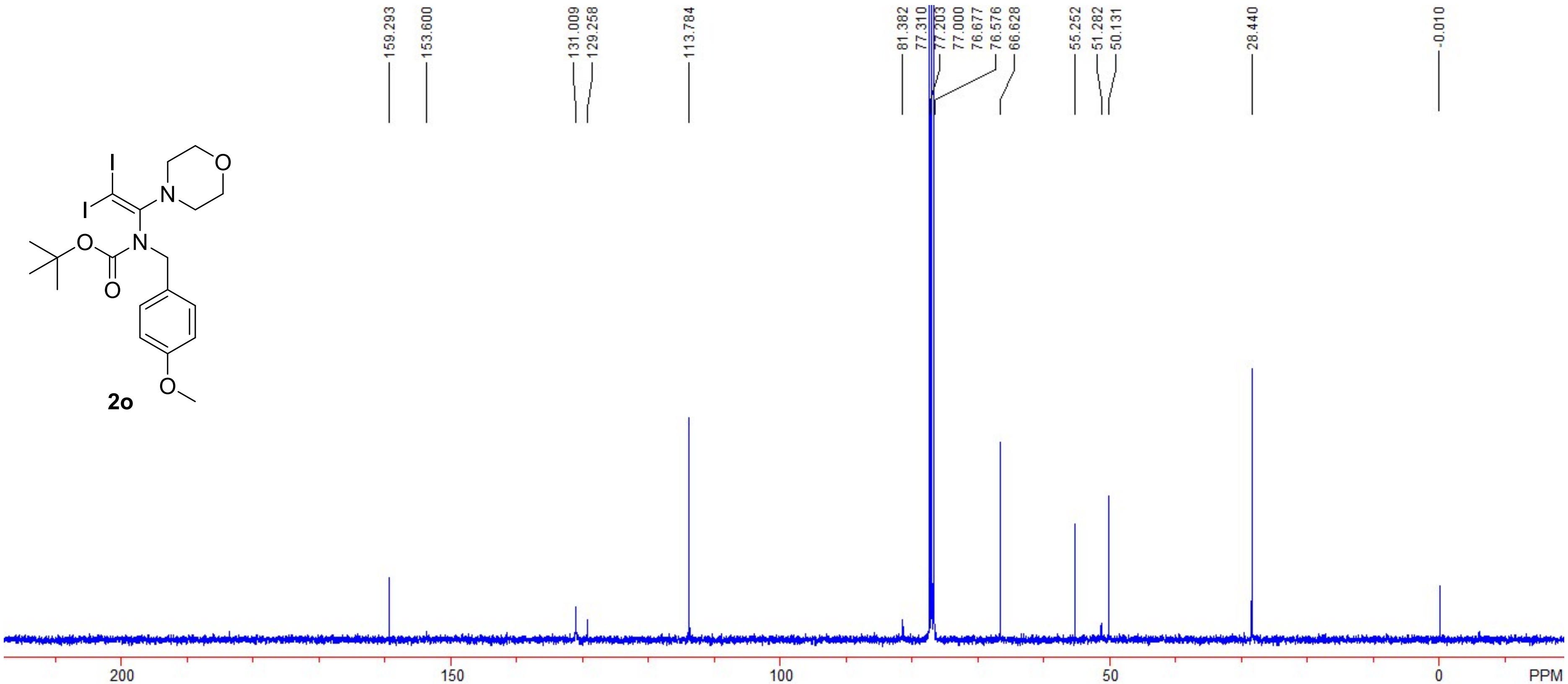

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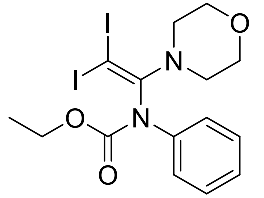

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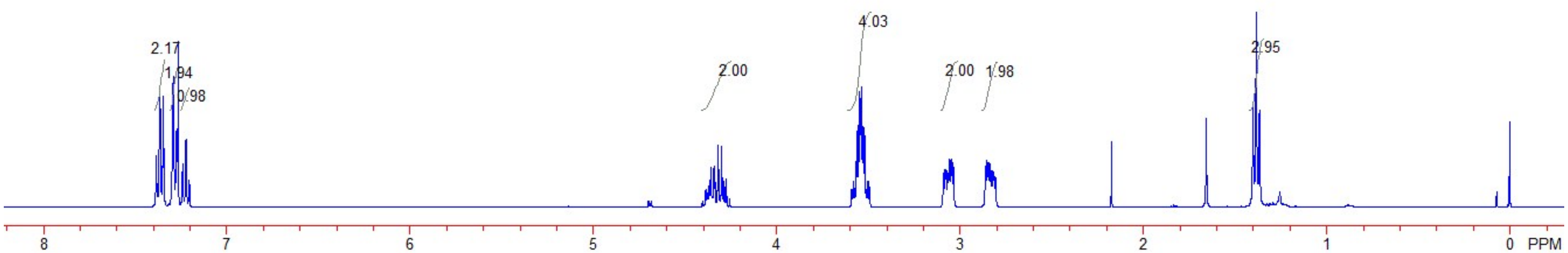

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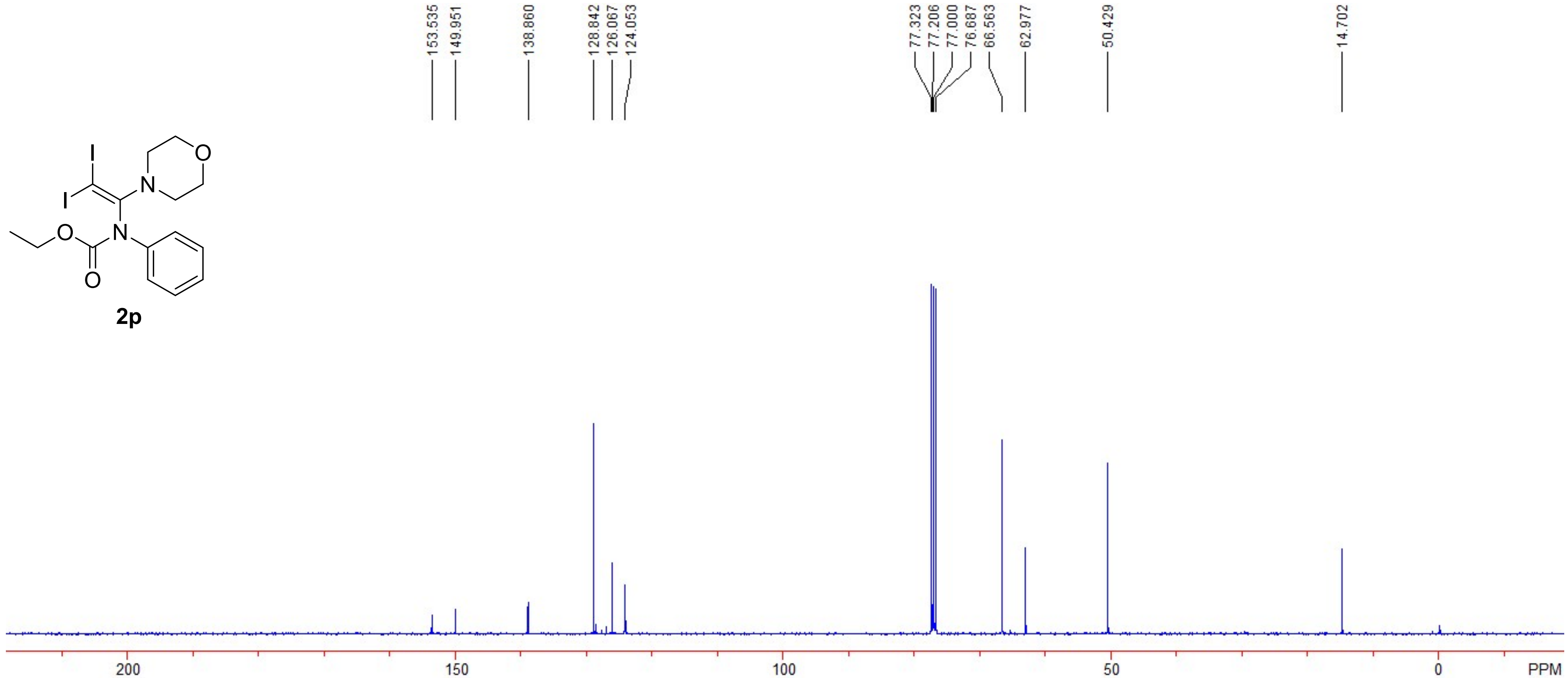
2
1
0 PPM


I
I
N
O
O
N
O
2p
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126.067
124.053
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76.687
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62.977
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14.702
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100
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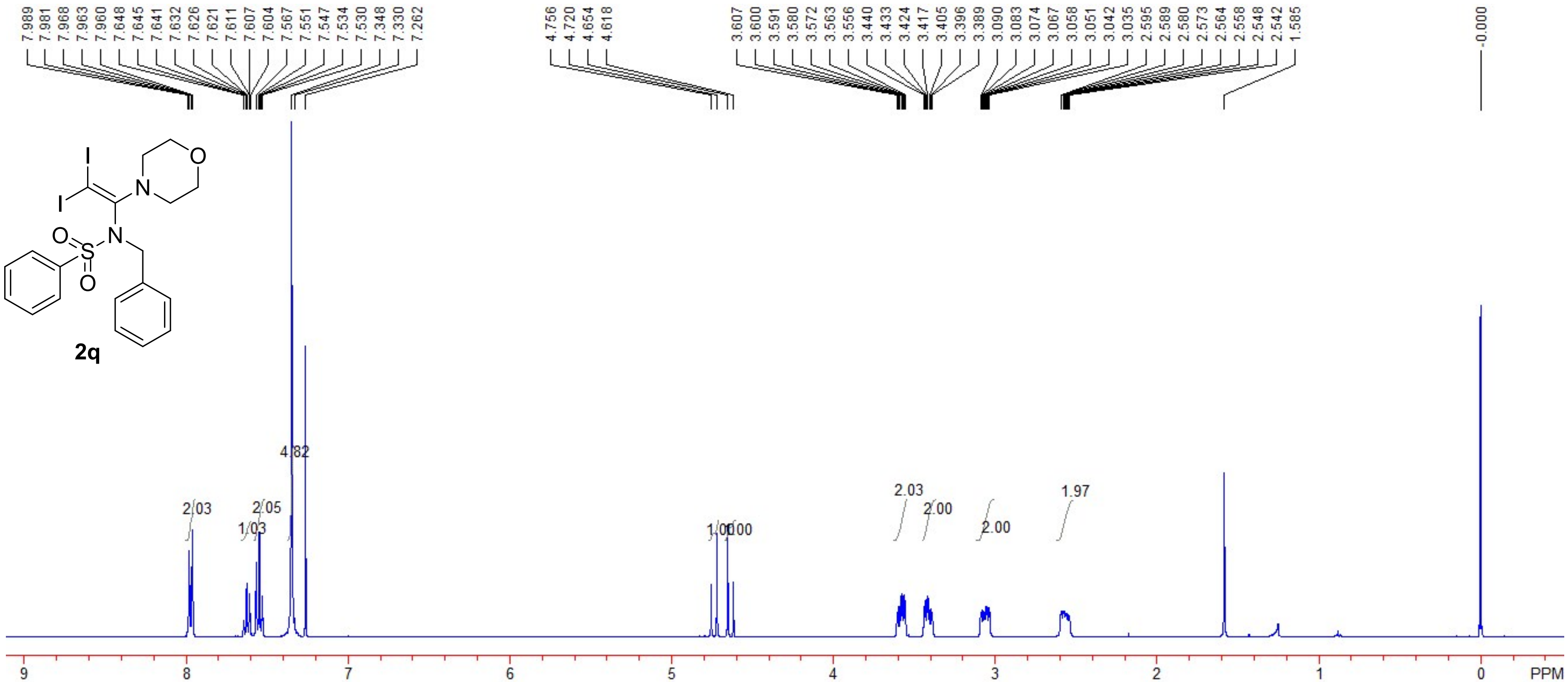
PPM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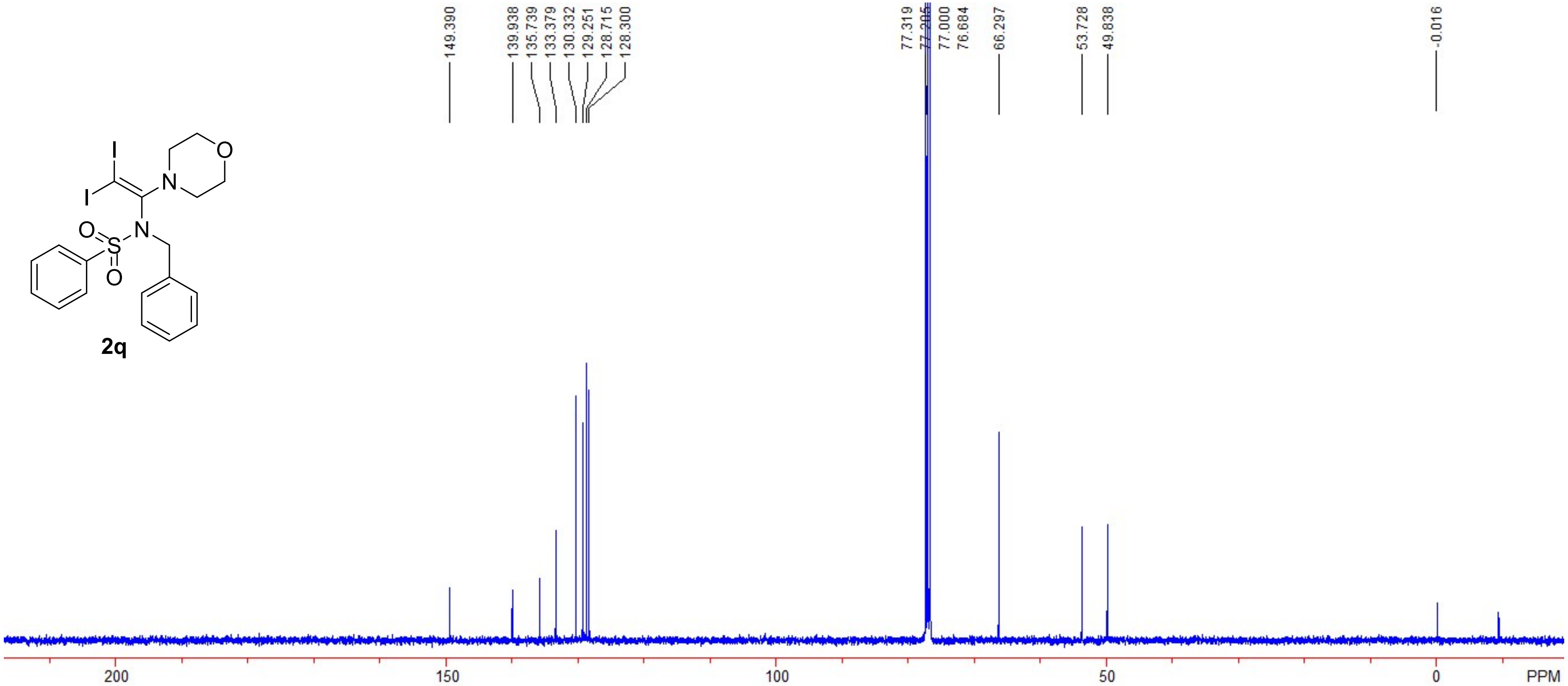
4.756 4.720 4.654 4.618
3.607 3.600 3.591 3.580 3.572 3.563 3.556 3.440 3.433 3.424 3.417 3.405 3.396 3.389 3.090 3.083 3.074 3.067 3.058 3.051 3.042 3.035 2.595 2.589 2.580 2.573 2.564 2.558 2.548 2.542 1.585
-0.000
2.03
1.03
2.05
4.82
1.00
1.00
2.03
2.00
2.00
1.97
2q
9 8 7 6 5 4 3 2 1 0 PPM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53.728
49.838
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200
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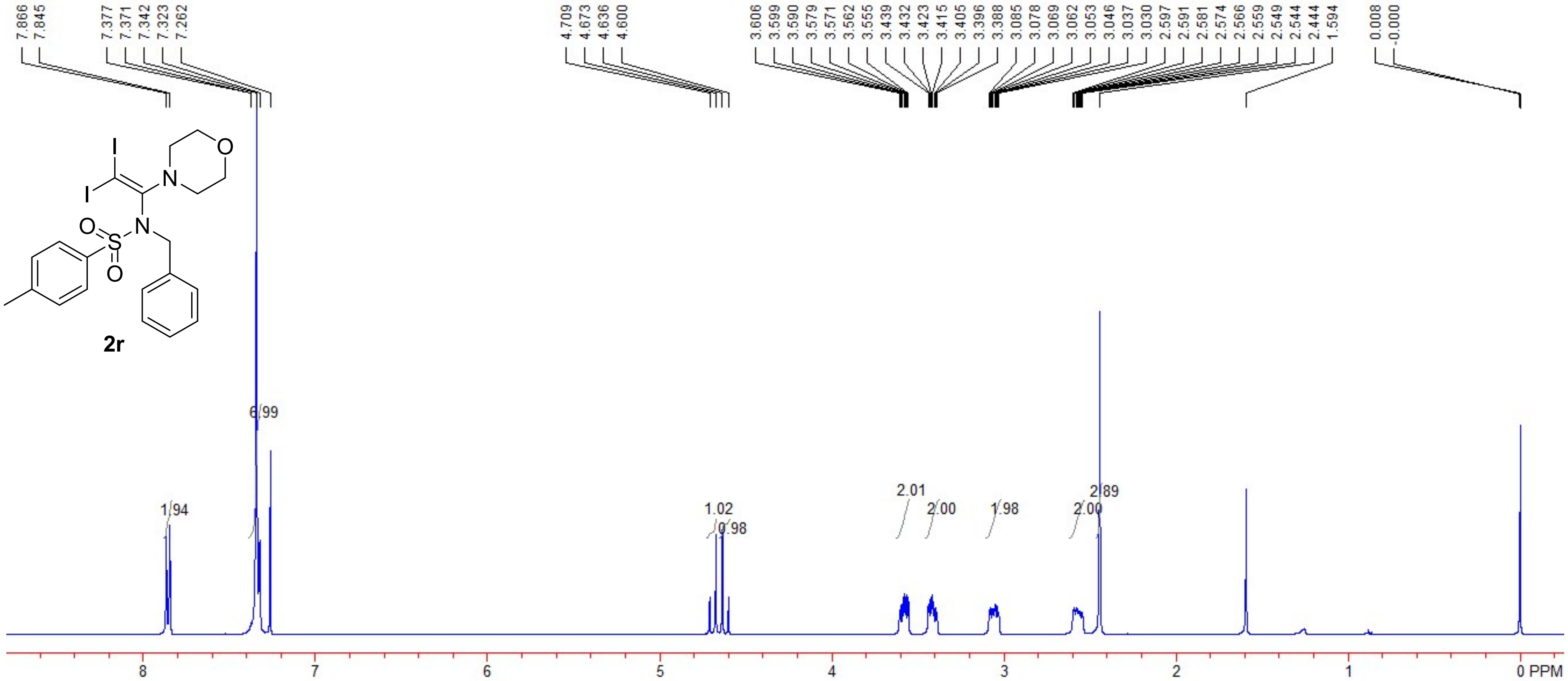
50
0
PPM

2q



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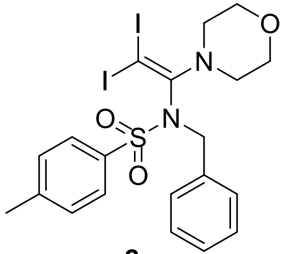

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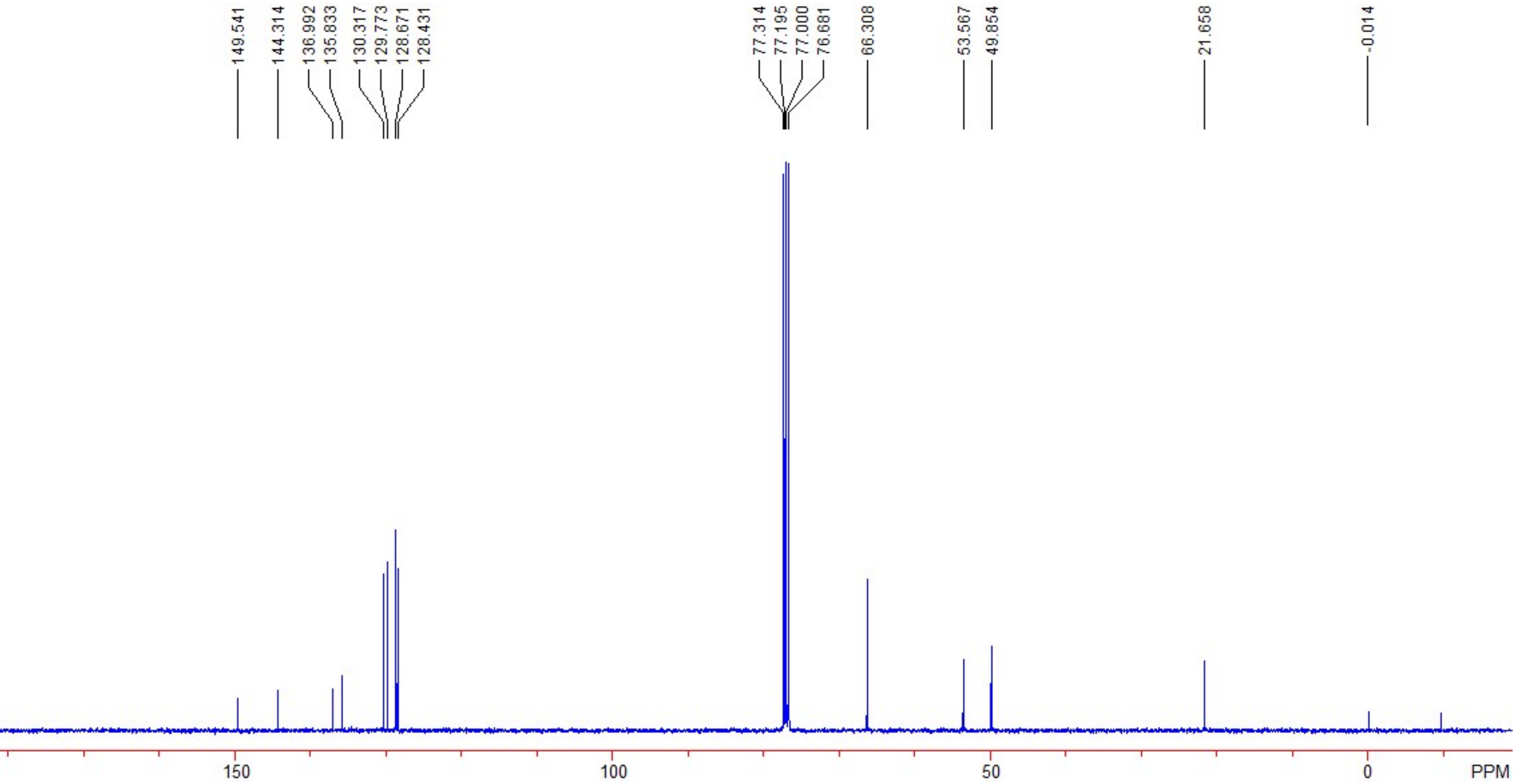
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144.314
136.992
135.833
130.317
129.773
128.671
128.431
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77.000
76.681
66.308
53.567
49.854
21.658
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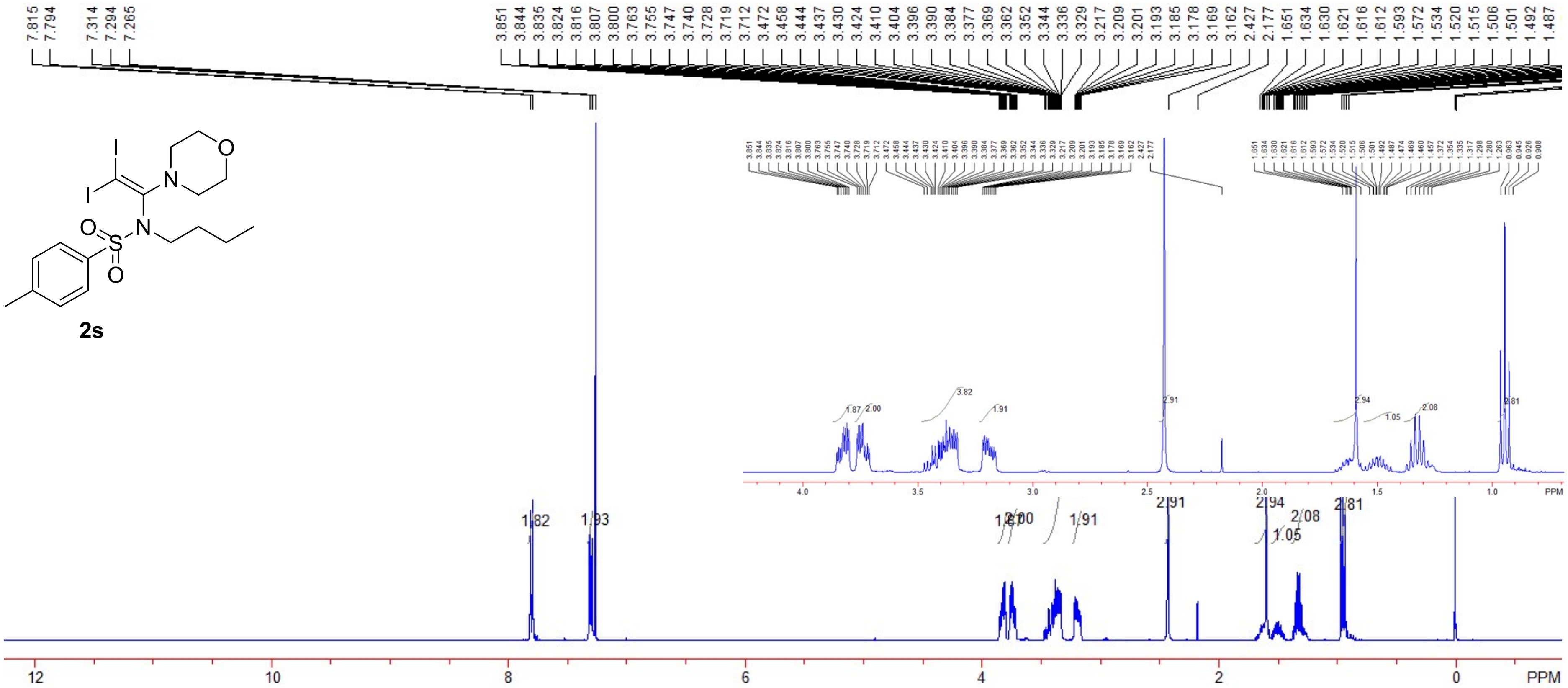
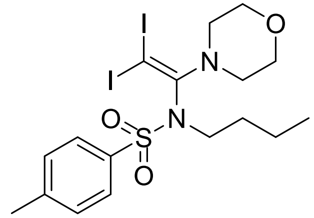
150
100
50
0
PPM



2s
7.815 7.794 7.314 7.294 7.265
3.851 3.844 3.835 3.824 3.816 3.807 3.800 3.763 3.755 3.747 3.740 3.728 3.719 3.712 3.472 3.458 3.444 3.437 3.430 3.424 3.410 3.404 3.396 3.390 3.384 3.377 3.369 3.362 3.352 3.344 3.336 3.329 3.217 3.209 3.201 3.193 3.185 3.178 3.169 3.162 2.427 2.177 1.651 1.634 1.630 1.621 1.616 1.612 1.593 1.572 1.534 1.520 1.515 1.506 1.501 1.492 1.487
1.82
1.93
1.87
2.00
1.91
2.91
2.94
1.05
2.08
2.81
3.82
12
10
8
6
4
2
0
PPM



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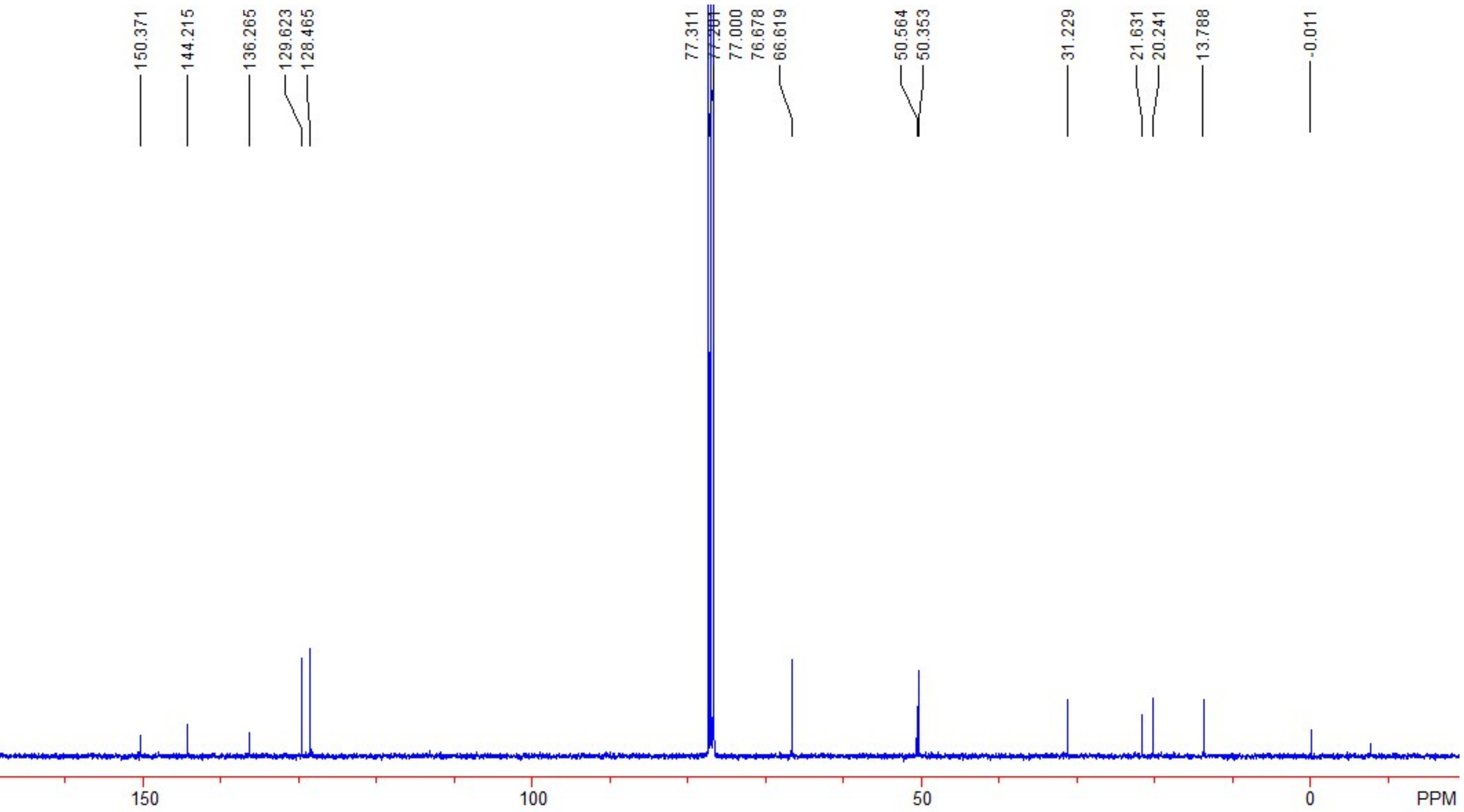
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77.000
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31.229
21.631
20.241
13.788
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200
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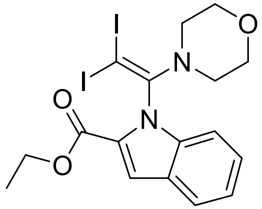
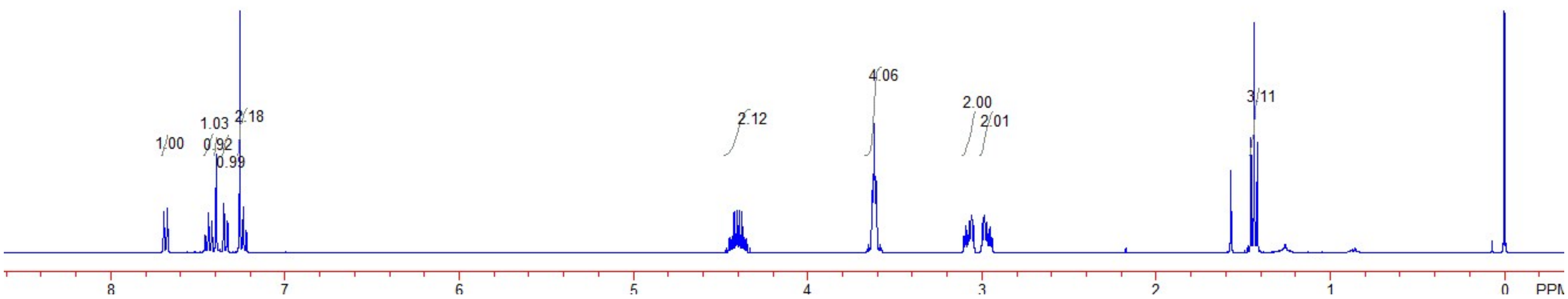
100
50
0
PPM



2t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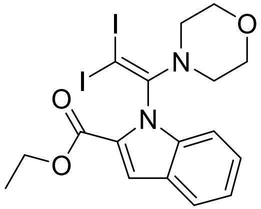
4.449 4.440 4.431 4.422 4.412 4.404 4.394 4.386 4.376 4.367 4.358 4.349 3.630 3.626 3.621 3.616 3.612 3.606 3.603 3.102 3.090 3.078 3.070 3.059 3.057 3.046 2.996 2.987 2.983 2.973 2.965 2.953 2.941 1.569 1.453 1.435 1.418
0.070 -0.000
1.00
1.03
0.92
0.99
2.18
2.12
4.06
2.00
2.01
3.11
8 7 6 5 4 3 2 1 0 PPM



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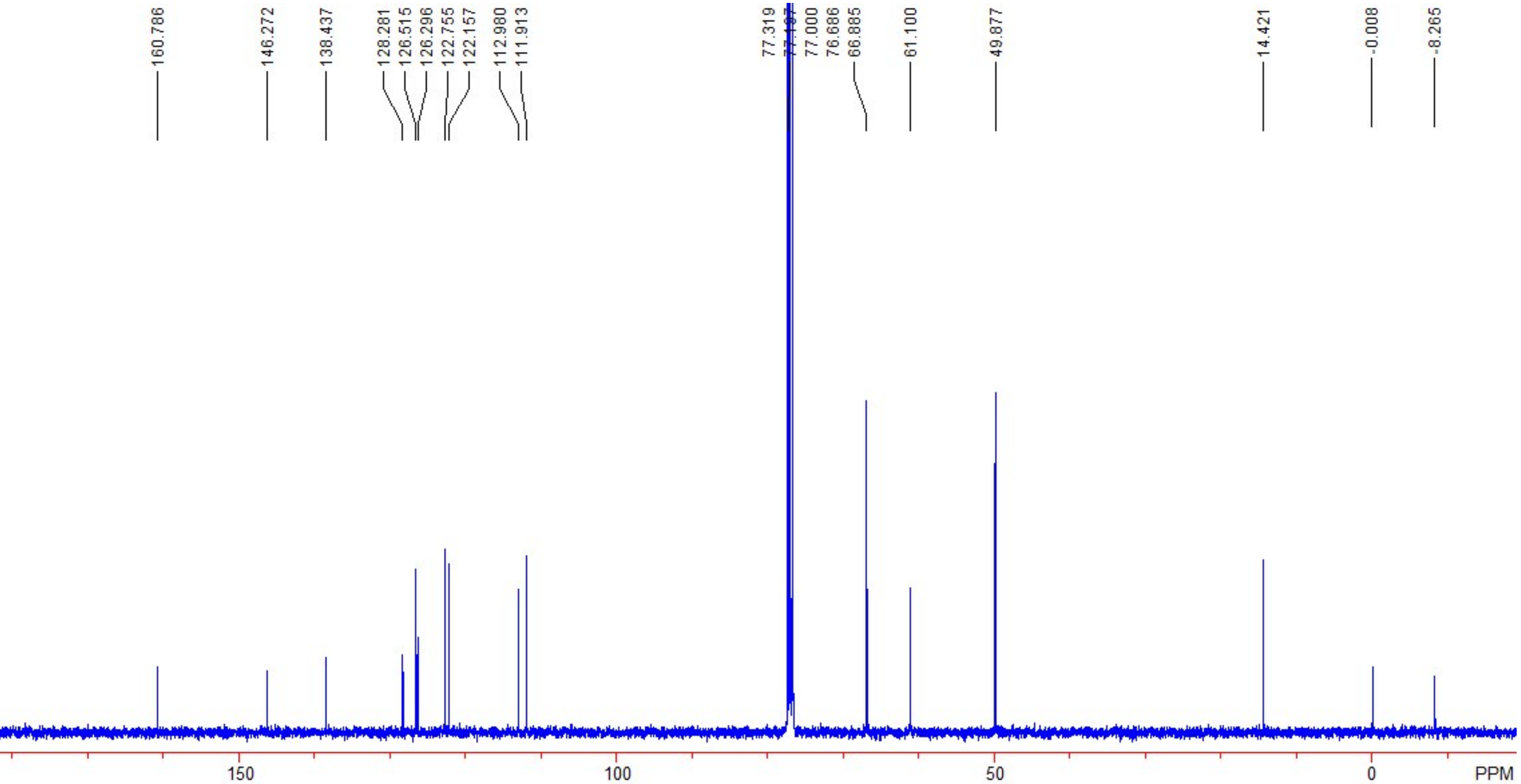
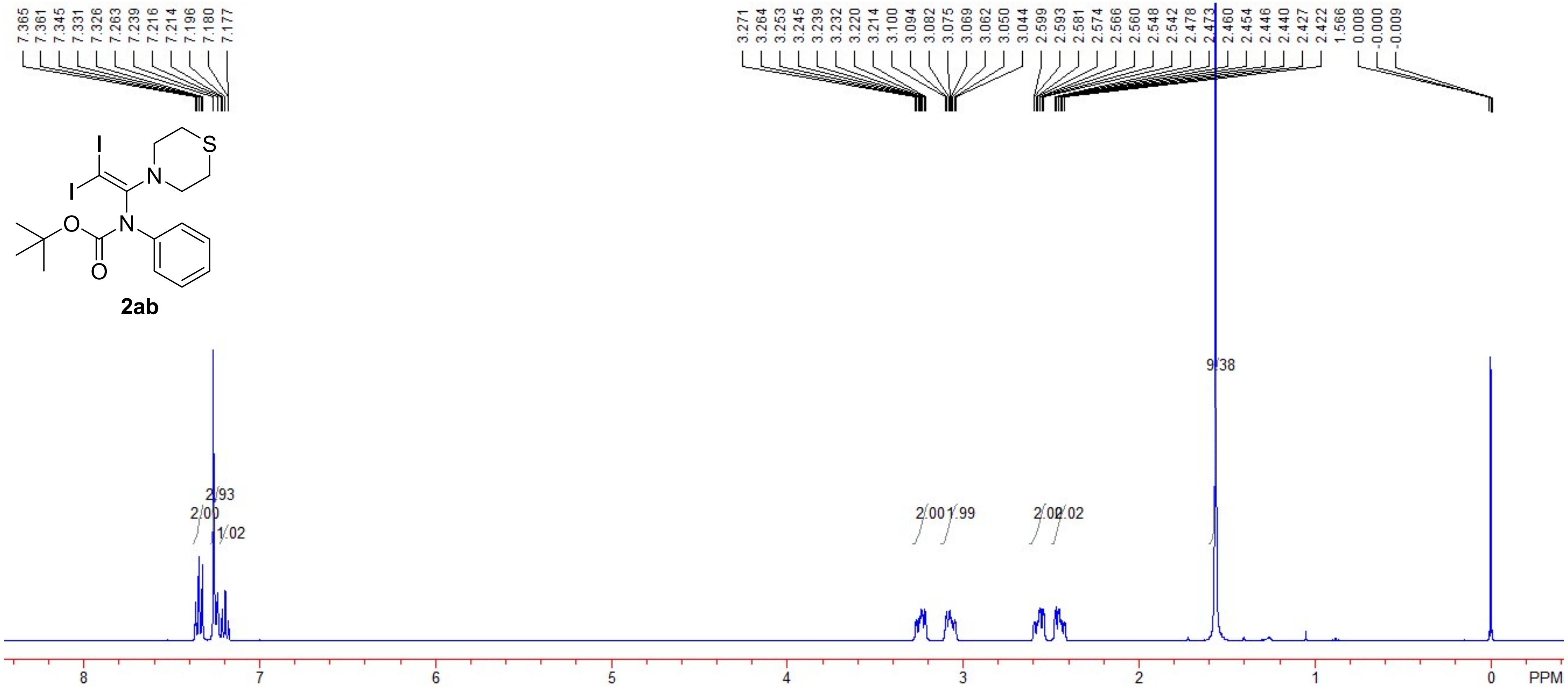


160.786
146.272
138.437
128.281
126.515
126.296
122.755
122.157
112.980
111.913
77.319
77.000
76.686
66.885
61.100
49.877
14.421
-0.008
-8.265
200
150
100
50
0
PPM



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7.361
7.345
7.331
7.326
7.263
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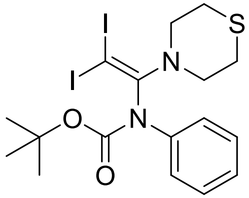
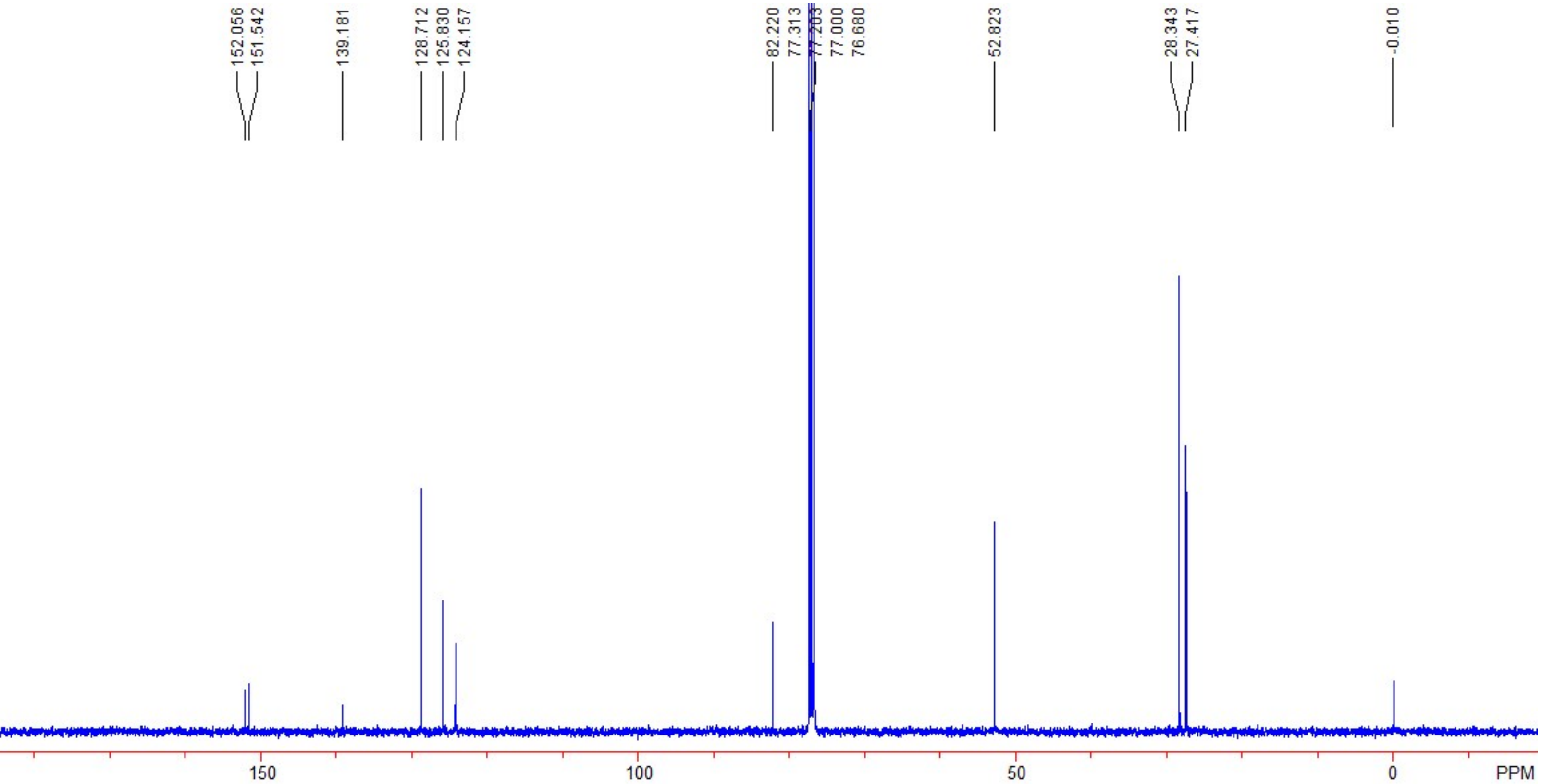
7.216
7.214
7.196
7.180
7.177
3.271
3.264
3.253
3.245
3.239
3.232
3.220
3.214
3.100
3.094
3.082
3.075
3.069
3.062
3.050
3.044
2.599
2.593
2.581
2.574
2.566
2.560
2.548
2.542
2.478
2.473
2.460
2.454
2.446
2.440
2.427
2.422
1.566
0.008
-0.000
-0.009
2ab
2.00
2.93
1.02
2.00
1.99
2.02
2.02
9.38
8
7
6
5
4
3
2
1
0
PPM


I
I
N
S
O
N
O

2ab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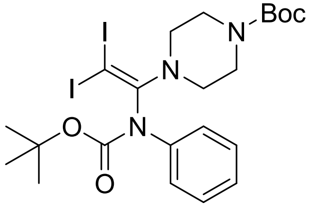
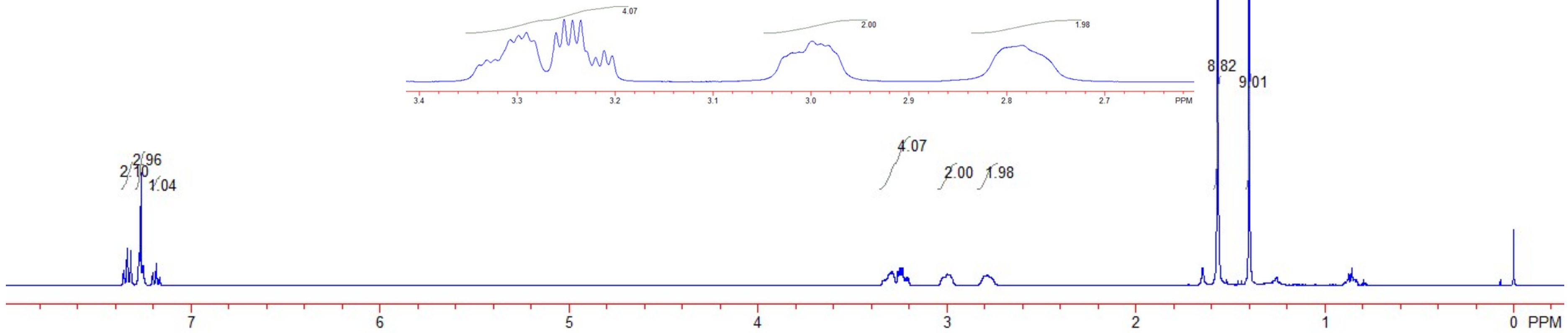
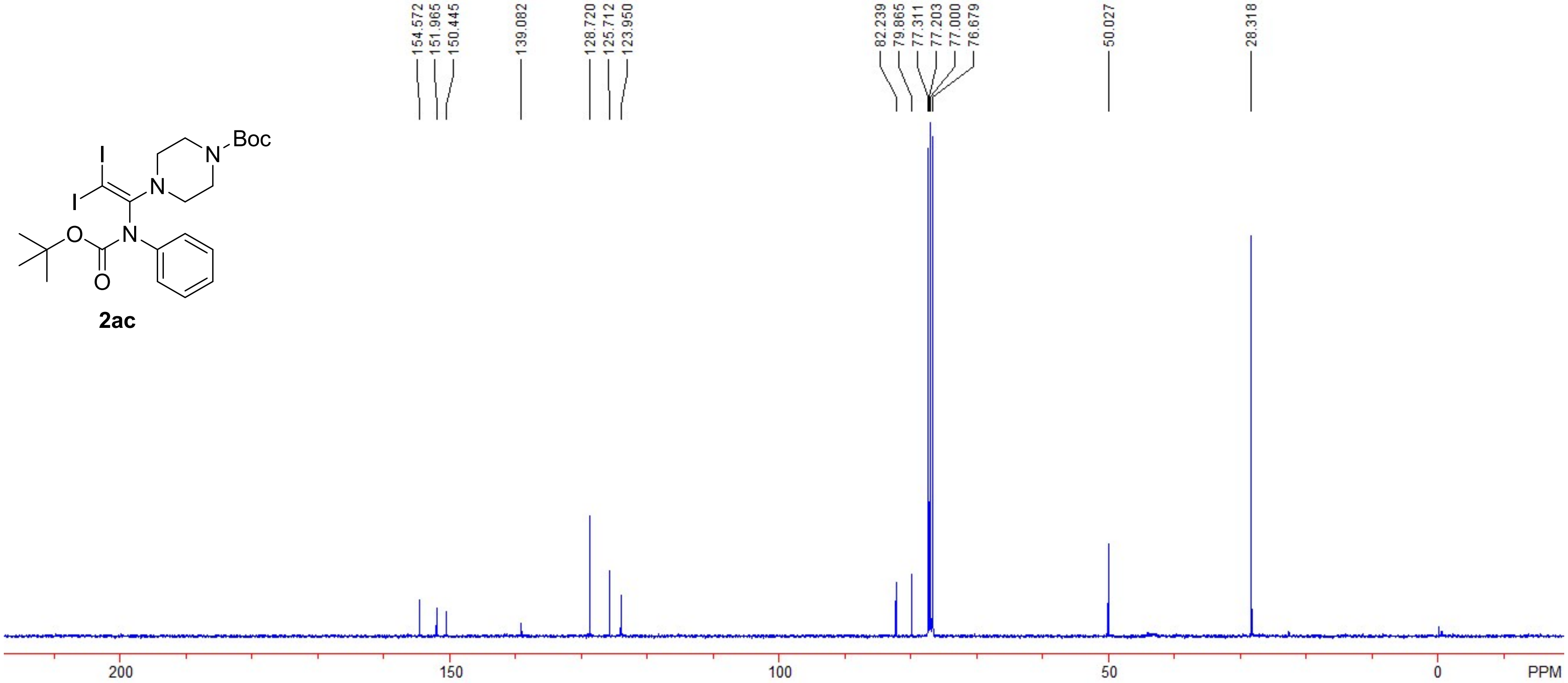
125.830
124.157
82.220
77.313
77.203
77.000
76.680
52.823
28.343
27.417
-0.010
200
150
100
50
0
PPM



2ac





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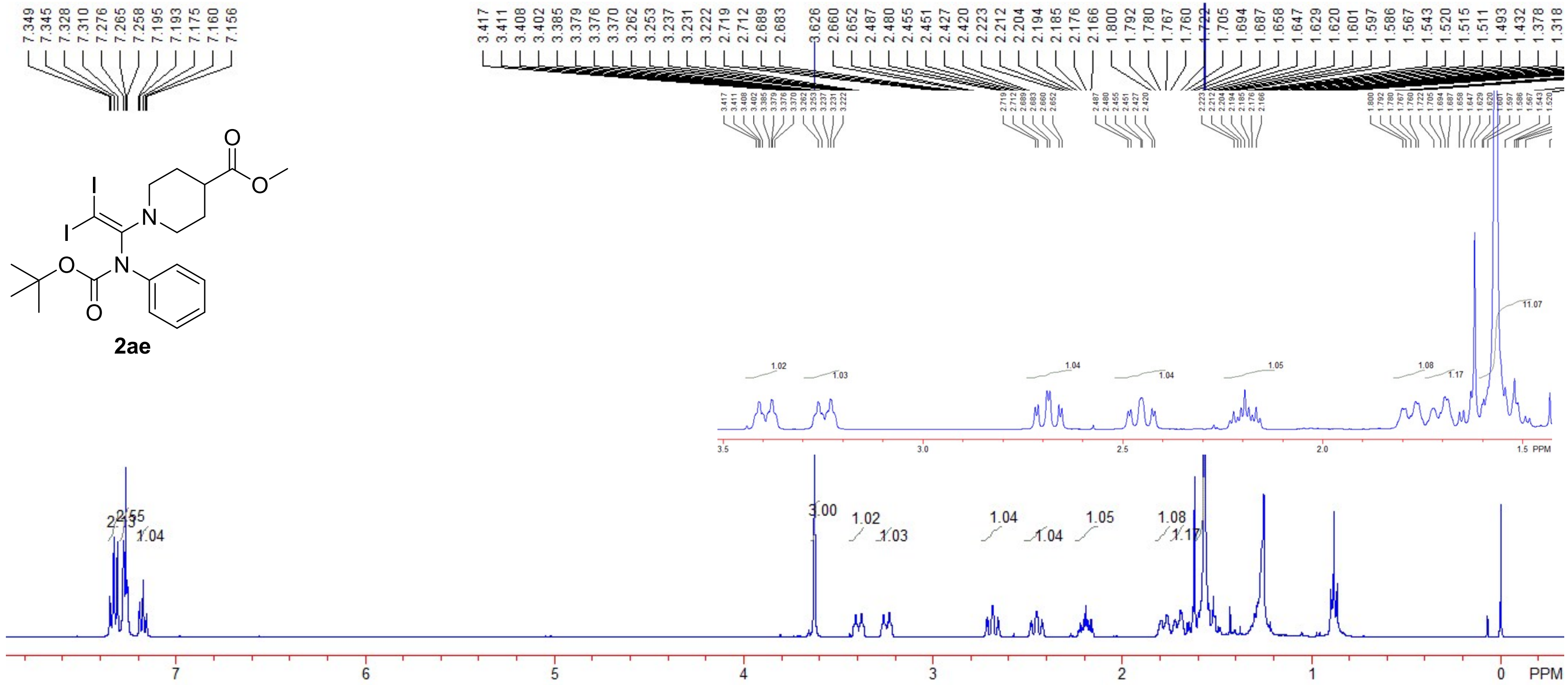
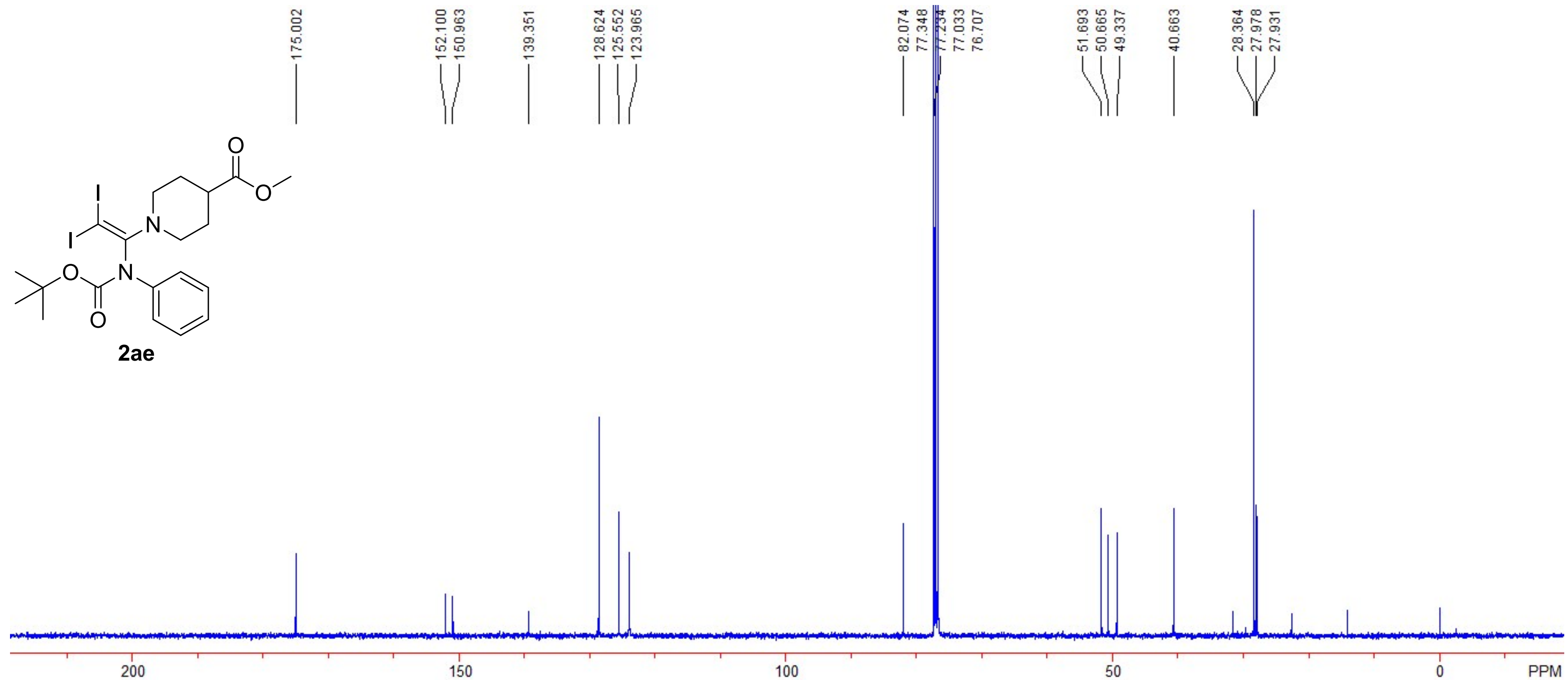
150.445
139.082
128.720
125.712
123.950
82.239
79.865
77.311
77.203
77.000
76.679
50.027
28.318
200
150
100
50
0
PPM

2ac



2ae



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125.552
123.965
82.074
77.348
77.234
77.033
76.707
51.693
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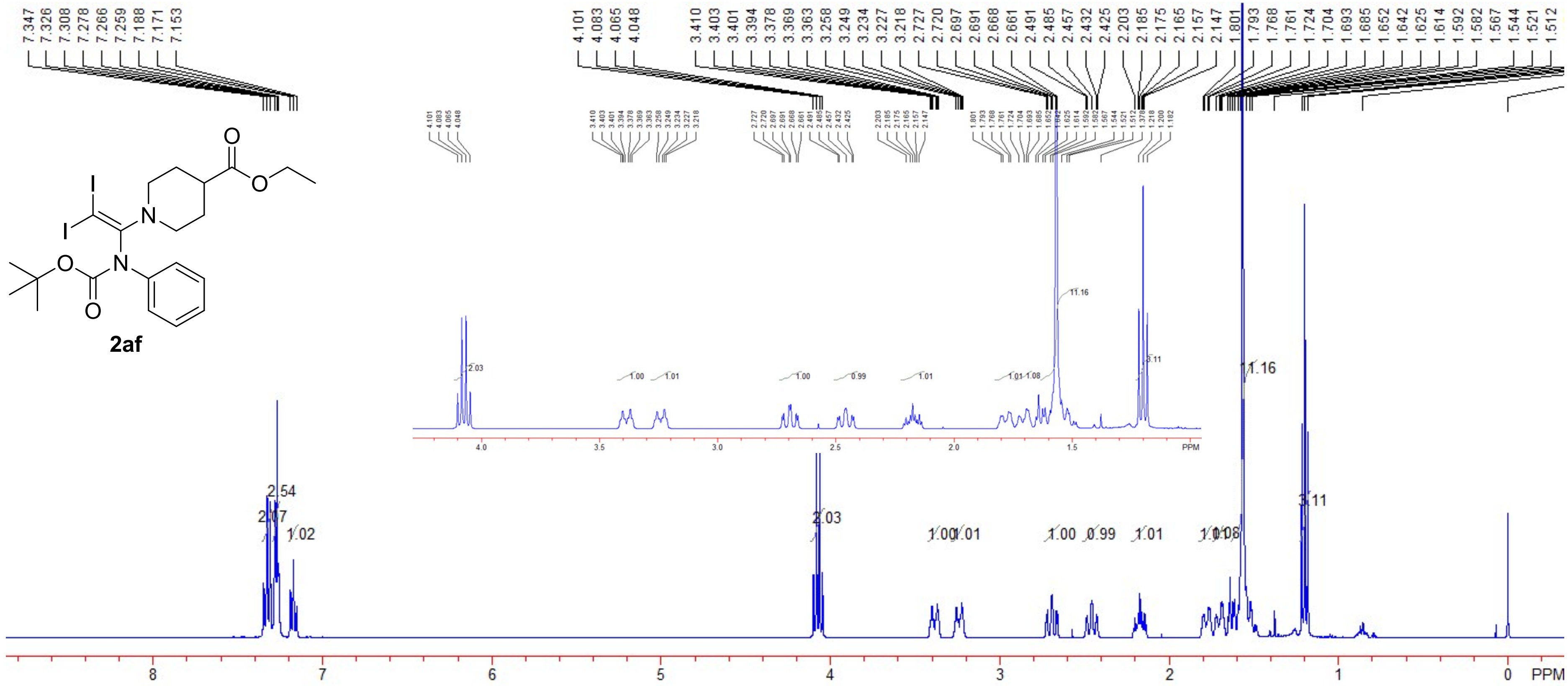
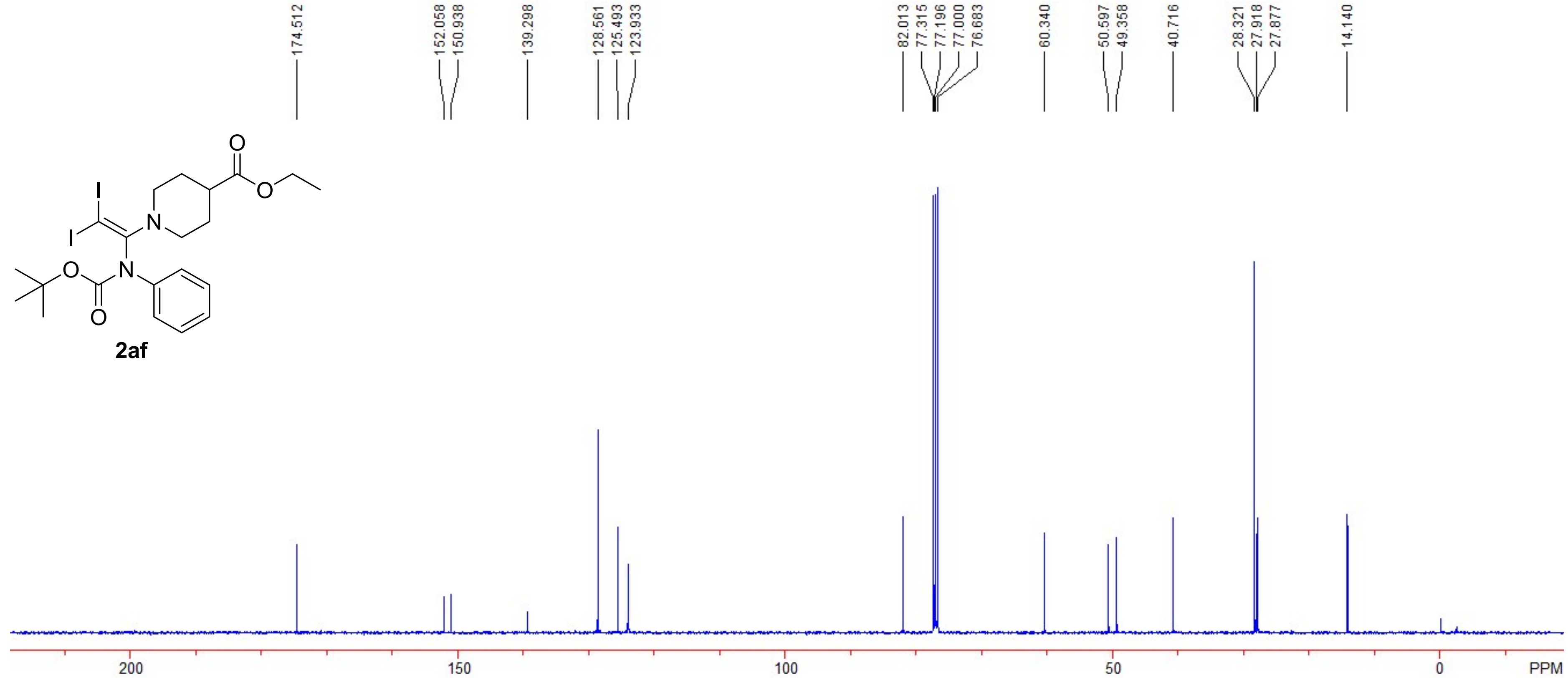
49.337
40.663
28.364
27.978
27.931
200
150
100
50
0
PPM

2ae



2af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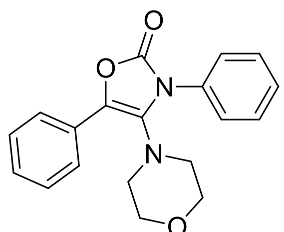
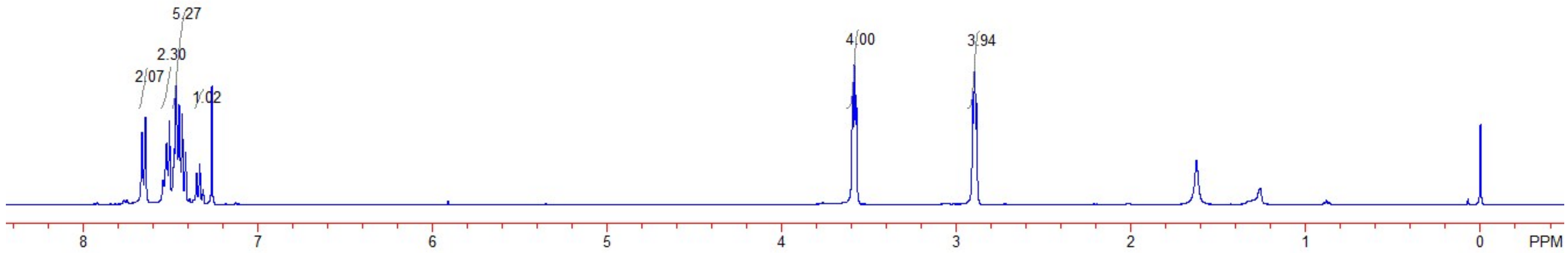
128.561
125.493
123.933
82.013
77.315
77.196
77.000
76.683
60.340
50.597
49.358
40.716
28.321
27.918
27.877
14.140
2af
200
150
100
50
0
PPM



4a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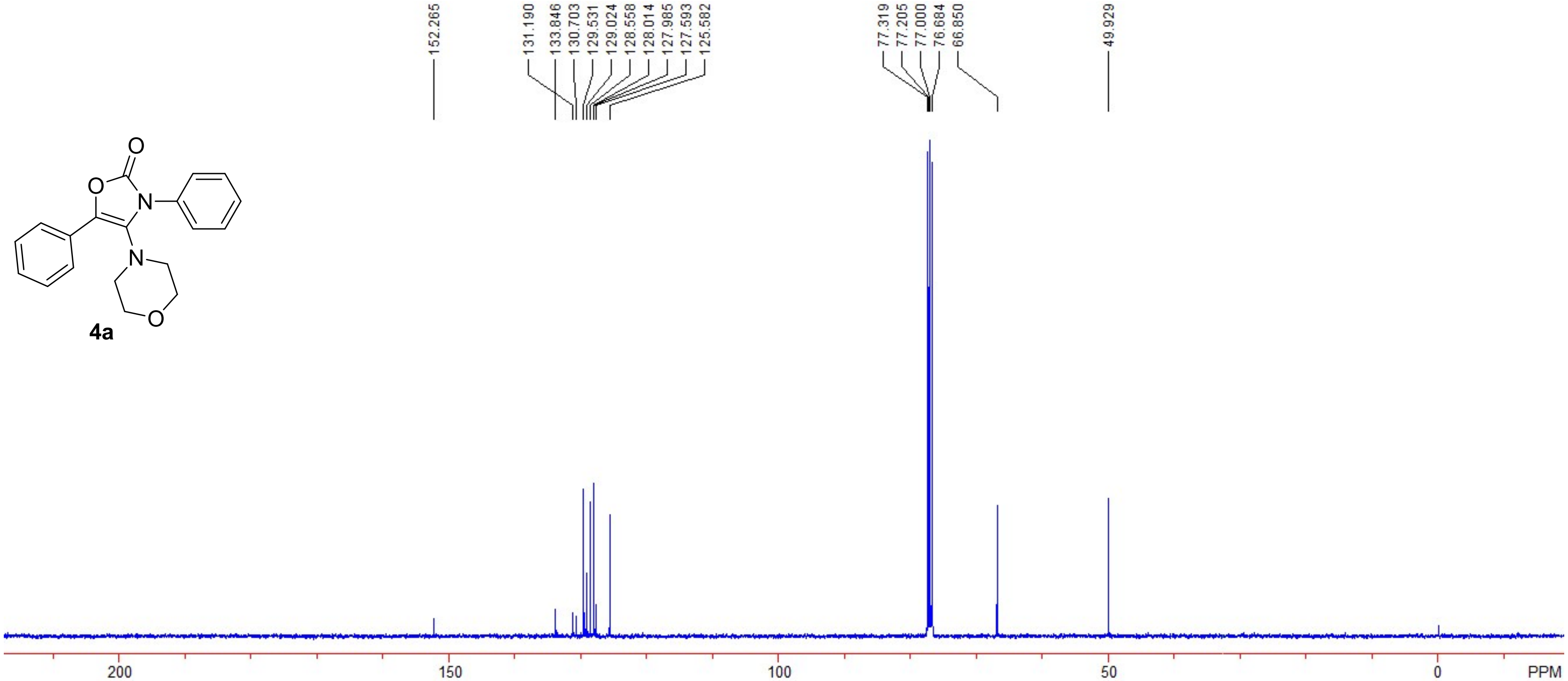
7.448
7.431
7.411
7.349
7.330
7.312
7.261
3.594
3.583
3.571
2.905
2.893
2.882
1.624
-0.001
5.27
2.30
2.07
1.02
4.00
3.94
8
7
6
5
4
3
2
1
0
PPM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127.985
127.593
125.582
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77.205
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76.684
66.850
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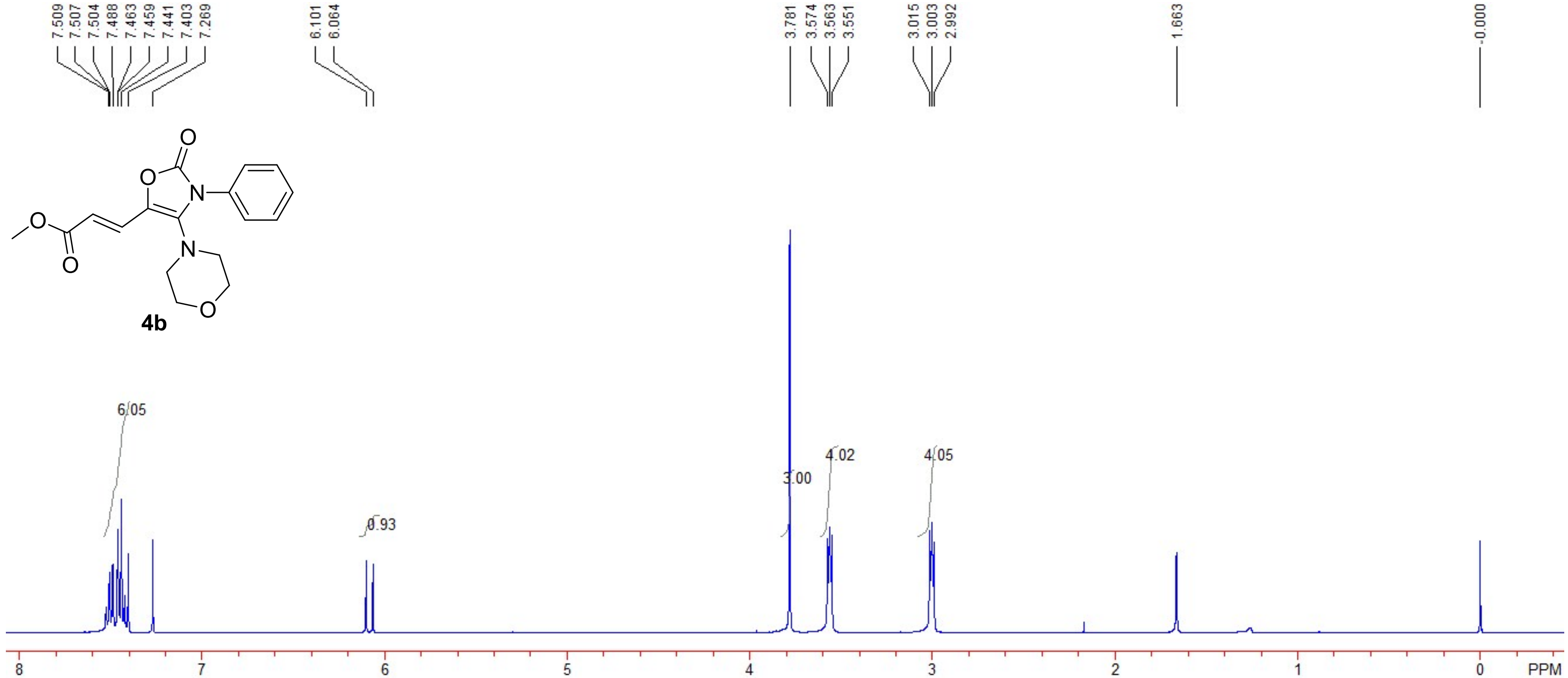
200
150
100
50
0
PPM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7.441
7.403
7.269
6.101
6.064
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3.574
3.563
3.551
3.015
3.003
2.992
1.663
-0.000
O
O
N
O
O
N
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4.05
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5
4
3
2
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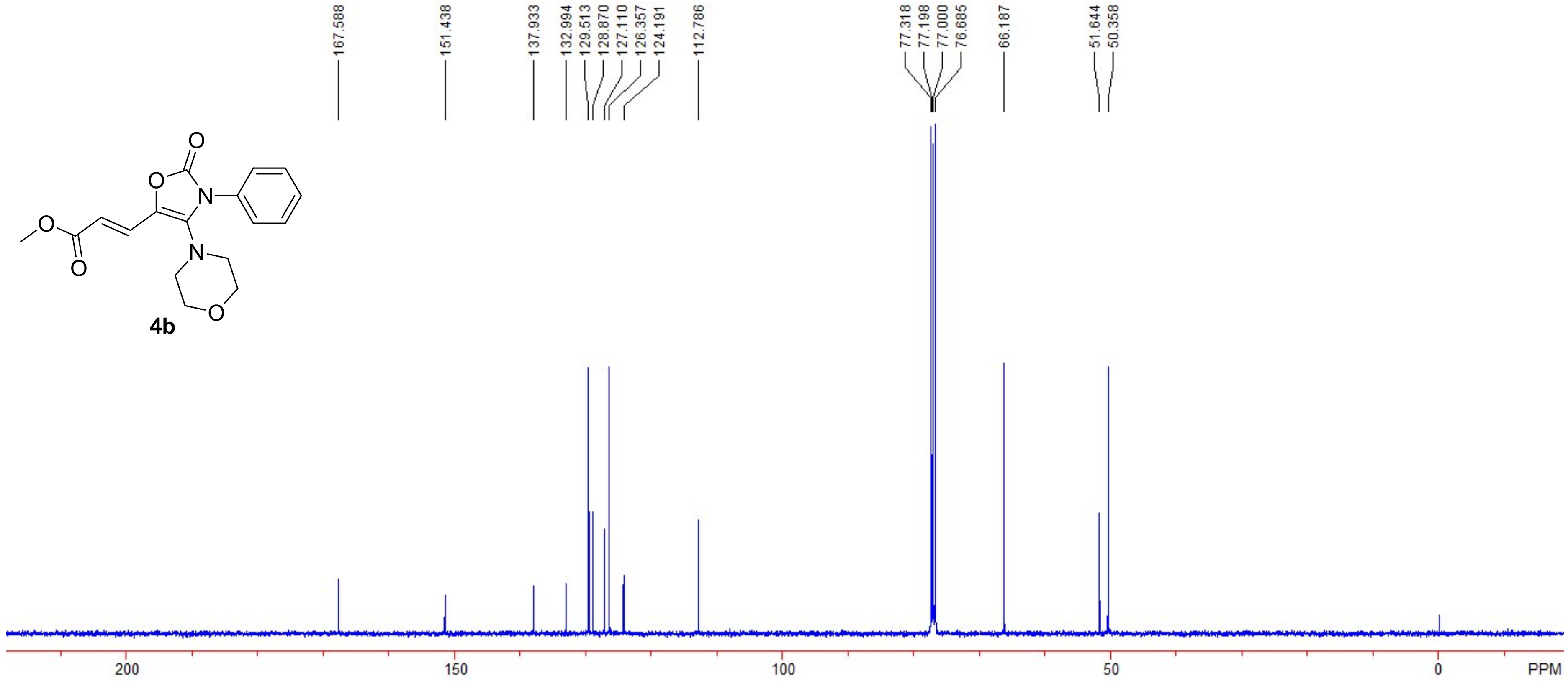
0
PPM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127.110
126.357
124.191
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77.198
77.000
76.685
66.187
51.644
50.358
200
150
100
50
0
PPM