Supporting Online Material for

Organocatalytic C–H bond arylation of aldehydes to bis-heteroaryl ketones.

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1. General information

2. Preparation of iodonium salts

3. Experimental procedures and data

4. Further derivatisations of ketone 4t

5. ^{1}H and ^{13}C NMR spectra

1. General information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker AM 400 (400 MHz) or an Avance 500 (500 MHz) spectrometer. Carbon nuclear magnetic resonance (^{13}C NMR) were recorded using a Bruker AM 400 (101 MHz) or an Avance 500 (126 MHz) spectrometer. All spectra were recorded at ambient temperature (298 K). Chemical shifts (δ) are quoted in ppm relative to residual solvent ($CHCl_3$: δ = 7.26 ppm for ^{1}H and δ = 77.0 for ^{13}C; $(CD_3)_2SO$: δ = 2.50 ppm for ^{1}H and δ = 39.52 for ^{13}C; CD_3CN: δ = 1.94 ppm for ^{1}H and δ = 118.26 for ^{13}C; MeOD: δ = 3.31 ppm for ^{1}H and δ = 49.0 for ^{13}C). Coupling constants (*J*) are corrected and quoted to the nearest 0.1 Hz. The following abbreviations are used to indicate the multiplicity of the signals: s = singlet; d = doublet; t = triplet; q = quartet; qn = quintet; st = sextet, sp = septet; m = multiplet; br = broad; app = apparent; and associated combinations, e.g. dd = doublet of doublets. NMR yields were determined with trimethyl1,3,5-benzenetricarboxylate or 1,3,5-trimethoxybenzene as NMR standards.

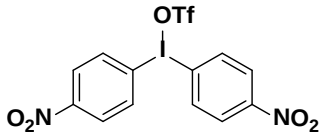
High resolution mass spectra (HRMS) were measured on a Micromass Q-TOF spectrometer using EI (electron impact) or ES (electrospray ionization) techniques at the Department of Chemistry, University of Cambridge or at the EPSRC Mass Spectrometry Service at the University of Swansea. Infared (IR) spectra were recorded on a Perkin Elmer OneFT-IR Spectrometer fitted with an ATR sampling accessory as either solids or neat films through direct application or deposited in CH_2Cl_2, with absorptions reported in wavenumbers (cm^{-1}). Optical rotations were measured in $CHCl_3$ on a Perkin Elmer 343 Polarimeter using a sodium lamp (λ 589 nm, D-line). $[\alpha]_D$ values are reported in 10^{-1} degrees $cm^2\ g^{-1}$ and concentration in mg /0.1 mL. Melting points (m.p.) were recorded using a Gallenkamp melting point apparatus and are reported uncorrected. All flash chromatography was carried out using dry packed Merck 9385 Kieselgel 60 silica gel or Material Harvest silica gel (230-400 mesh) under a positive pressure of nitrogen and thin layer chromatography was carried out on Merck Kieselgel 60 PF254 0.2 mm plates. Visualization was accomplished using ultraviolet light (254 nm) and chemical staining with acidic potassium permanganate solution.

All reactions were carried out using oven dried glassware and under an atmosphere of nitrogen unless otherwise stated. Tetrahydrofuran (THF), toluene, diethyl ether and dichloromethane were dried and distilled using standard methods. Isopropanol was purchased in anhydrous form. All reagents were purified by standard procedures or used as obtained

from commercial sources. Iodonium salts **2a**, **2b** and **2f** were prepared according to literature procedures.[1,2]

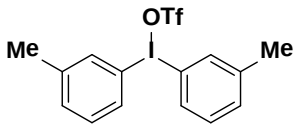
2. Preparation of iodonium salts

Di-(4-nitrophenyl)iodonium triflate (2c)



Prepared according to the method of Olofsson on a 2.00 mmol scale to provide the title compound as a grey solid (569 mg, 1.06 mmol, 53%).[3] m.p. 170 °C; IR ν max (solid, cm^{-1}): 1533, 1359, 1287, 1230 1163, 1149, 1024, 853, 740, 734; ^{1}H NMR (400 MHz, MeOD) δ 8.49 (d, *J* = 9.1 Hz, 4H), 8.35 (d, *J* = 9.1 Hz, 4H); ^{13}C NMR (101 MHz, MeOD) δ 151.8, 138.1, 127.8, 121.9; ^{19}F NMR (376 MHz, MeOD) δ –79.6; HRMS (ESI) calculated for $C_{12}H_8O_4N_2I$ $[M – OTf]^+$ m/z 370.9523, found 370.9528.

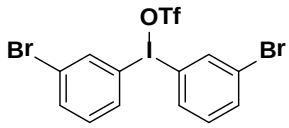
Di-(3-tolyl)iodonium triflate (2d)



Prepared according to the method of Olofsson on a 3.60 mmol scale to provide the title compound as a grey solid (680 mg, 1.48 mmol, 41%).[3] m.p. 138 °C; IR ν max (solid, cm^{-1}): 1740, 1598, 1472, 1276, 1241, 1168, 1026, 985, 814, 773; ^{1}H NMR (400 MHz, MeOD) δ 8.02 (s, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.41 (app t, *J* = 7.9 Hz, 2H), 2.40 (s, 6H); ^{13}C NMR (101 MHz, MeOD) δ 144.2, 136.6, 134.4, 133.4, 132.8, 115.7, 21.2; ^{19}F NMR (376 MHz, MeOD) δ –80.5; HRMS (ESI) calculated for $C_{14}H_{14}I$ $[M – OTf]^+$ m/z 309.0135, found 309.0133.

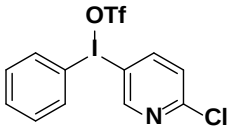
[1] Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* **2007**, *349*, 2610.
[2] Kuriyama, M.; Hamaguchi, N.; Onomura, O. *Chem. Eur. J.* **2012**, *18*, 1591.
[3] Bielawski, M.; Aili, D.; Olofsson, B. *J. Org. Chem.* **2008**, *73*, 4602.

Di-(3-bromophenyl)iodonium triflate (2e)



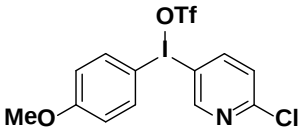
Prepared according to the method of Olofsson on a 2.50 mmol scale to provide the title compound as a grey solid (815 mg, 1.39 mmol, 56%).[3] m.p. 144 °C; IR ν max (solid, cm^{-1}): 3455, 1570, 1553, 1455, 1238, 1165, 1025, 983, 778, 704; ^{1}H NMR (400 MHz, MeOD) δ 8.50 (app t, *J* = 1.7 Hz, 2H), 8.21 (ddd, *J* = 8.1, 1.7, 0.8 Hz, 2H), 7.89 (dd, *J* = 8.1, 0.8 Hz, 2H), 7.48 (app t, *J* = 8.1 Hz, 2H); ^{13}C NMR (101 MHz, MeOD) δ 138.6, 137.1, 135.2, 134.6, 125.5, 116.5; ^{19}F NMR (376 MHz, MeOD) δ –79.6; HRMS (ESI) calculated for $C_{12}H_8Br_2I$ $[M – OTf]^+$ m/z 436.8032, found 436.8037.

(6-Chloropyridin-3-yl)(phenyl)iodonium triflate (2g)



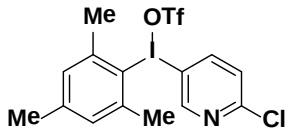
Prepared according to the method of Olofsson on a 0.46 mmol scale to provide the title compound as an off-white solid (120 mg, 0.26 mmol, 56%).[1] The physical data was consistent with that reported previously.[1] ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.17 (d, *J* = 2.3 Hz, 1H), 8.70 (dd, *J* = 8.5, 2.4 Hz, 1H), 8.28 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.56 (app t, *J* = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.3, 153.4, 145.6, 135.2, 132.4, 132.0, 127.7, 120.7 (q, *J* = 328 Hz), 117.0, 114.2; HRMS (ESI) calculated for $C_{11}H_8NClI$ $[M – OTf]^+$ m/z: 315.9384, found: 315.9380.

(6-Chloropyridin-3-yl)(4-methoxyphenyl)iodonium triflate (2h)



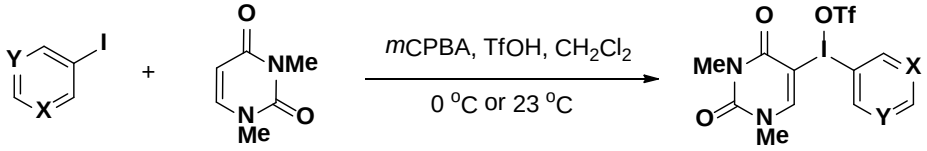
Prepared according to the method of Olofsson on a 2.30 mmol scale to provide the title compound as an off-white solid (697 mg, 1.41 mmol, 61%).[1] The physical data was consistent with that reported previously.[1] ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (d, *J* = 2.4 Hz, 1H), 8.64 (dd, *J* = 8.5, 2.4 Hz, 1H), 8.20 (d, *J* = 9.1 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.2, 154.0, 153.2, 145.3, 137.3, 127.6, 120.7 (q, *J* = 324 Hz), 117.7, 114.6, 105.7, 55.8; HRMS (ESI) calculated for $C_{12}H_{10}ONClI$ $[M – OTf]^+$ m/z 345.9490, found 345.9495.

(6-Chloropyridin-3-yl)(mesityl)iodonium triflate (2i)



Prepared according to the method of MacMillan on a 2.20 mmol scale to provide the title compound as an off-white solid (520 mg, 1.03 mmol, 46%).[4] m.p. 166 °C (decomposed); IR ν max (solid, cm^{-1}): 1448, 1241, 1219, 1172, 1104, 1022, 995, 846; ^{1}H NMR (400 MHz, CD_3CN): δ 8.74 (d, *J* = 2.2 Hz, 1H), 8.18 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.55 (dd, *J* = 8.7, 0.5 Hz, 1H), 7.23 (d, *J* = 0.4 Hz, 2H), 2.61 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN): δ 155.3, 153.7, 146.3, 145.8, 143.7, 131.5, 129.4, 121.6 (q, *J* = 321 Hz), 121.5, 109.8, 27.2, 21.0; ^{19}F NMR (376 MHz, CD_3CN): δ −78.8; HRMS (ESI) calculated for $C_{14}H_{14}NClI$ $[M - OTf]^+$ m/z 357.9854, found 357.9853.

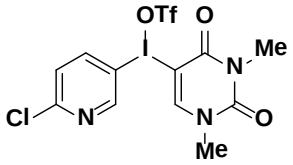
General Procedure A: Preparation of heteroaryl-uracil iodonium salts.



To heteroaryl iodide (1 equiv) in CH_2Cl_2 (0.3 M) at 23 °C or 0 °C was added *m*CPBA[5] (75% active oxidant, 1.09 equiv) followed by TfOH (3 equiv) dropwise. The reaction mixture was warmed to 23 °C before a solution of 1,3-dimethylpyrimidine-2,4-dione (1 equiv) in CH_2Cl_2 (1.2 M) was added. The reaction mixture was further stirred for 18 hours before it was concentrated *in vacuo*. Et_2O was added to the residue and the resultant heterogeneous mixture was cooled to 4 °C for 2 hours. If the suspension failed to form, Et_2O was removed under reduced pressure and the residue was disolved in minimum EtOAc to which Et_2O was added till precipitation occurred. The resultant mixture was then cooled to 4 °C for 16 hours. The solid was collected via filtration over a sintered glass funnel and further triturated with the indicated solvent system provided the desired heteroaryl-uracil iodonium salt.[6]

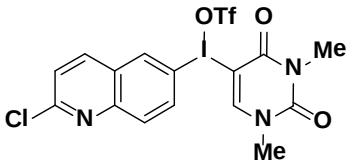
[4] Allen, A. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2011**, *133*, 4260.
[5] *m*CPBA was dried under high vacuum at 23 °C for 1 h before it was titrated and found to contain 75% active oxidant. Vogel, A. I.; Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: UK, 1989; pp 456.
[6] These iodonium salts have been observed to be slightly hygroscopic and should be filtered quickly and dried under high vacuum promptly. Occassionally yields were measured slightly above 100% due to the incorporation of minor amounts of water.

[5-(2-Chloropyridyl)]{5-[1,3-dimethylpyrimidine-2,4-dionyl]}iodonium triflate (2j)



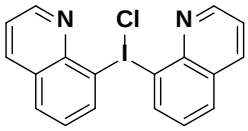
Prepared according to the General Procedure A on a 4.60 mmol scale at 23 °C. The filtered white solids were purified by trituration with vigourous stirring in diethyl ether/ethyl acetate (10:1, 22 mL) for 1 hour before filtering again to obtain the title compound as a white solid (2.30 g, 4.36 mmol, 95%). m.p. 162 °C (decomposed); IR ν max (film, cm^{-1}): 1710, 1651, 1612, 1431, 1215, 1156, 1021, 759; ^{1}H NMR (400 MHz, CD_3CN): δ 8.93 (d, *J* = 2.4 Hz, 1H), 8.56 (s, 1H), 8.48–8.36 (m, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 3.42 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (126 MHz, CD_3CN): δ 160.0, 156.6, 153.4, 152.6, 151.7, 150.1, 130.0, 121.4 (q, *J* = 320.0 Hz), 111.4, 87.3, 38.7, 29.9; ^{19}F NMR (376 MHz, CD_3CN): δ −79.4; HRMS (ESI) calculated for $C_{11}H_{10}O_2N_3ClI$ $[M - OTf]^+$ m/z 377.9501, found 377.9501.

6-(2-chloroquinolinyl){5-[1,3-dimethylpyrimidine-2,4-dionyl]}iodonium triflate (2k)



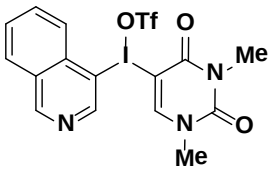
Prepared according to the General Procedure A on a 0.92 mmol scale at 23 °C. The filtered white solids were purified by trituration with vigourous stirring in diethyl ether (5 mL) for 15 mins before filtering again to obtain the title compound as a white solid (610 mg, 1.05 mmol, quant.). m.p. 220 °C (decomposed); IR ν max (solid, cm^{-1}): 1702, 1659, 1619, 1345, 1276, 1233, 1218, 1149, 1024; ^{1}H NMR (500 MHz, CD_3CN): δ 8.92 (d, *J* = 2.0 Hz, 1H), 8.85 (d, *J* = 8.8 Hz, 1H), 8.68 (s, 1H), 8.52 (dd, *J* = 9.2, 2.1 Hz, 1H), 8.24 (d, *J* = 9.2 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 3.45 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (126 MHz, CD_3CN): δ 160.0, 153.7, 153.7, 151.8, 147.1, 146.4, 143.9, 138.4, 129.3, 127.5, 127.0, 121.7 (q, *J* = 320.0 Hz), 113.8, 87.0, 38.7, 30.0; ^{19}F NMR (376 MHz, CD_3CN): δ −79.8; HRMS (ESI) calculated for $C_{15}H_{12}O_2N_3ClI$ $[M - OTf]^+$ m/z 427.9657, found 427.9651.

Di-(8-quinolinyl)iodonium chloride (2l)



Prepared according to the method of Stang on a 1.50 mmol scale to provide the title compound as a white solid (169 mg, 0.41 mmol, 27%).[7] m.p. 168 °C (decomposed); IR ν max (solid, cm^{-1}): 1483, 1447, 1376, 1306, 1204, 1106, 945, 820, 783; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.10 (dd, J = 4.3, 1.6 Hz, 2H), 8.56 (dd, J = 8.3, 1.5 Hz, 2H), 8.31–8.29 (m, 4H), 7.78 (dd, J = 8.3, 4.3 Hz, 2H), 7.66 (app t, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 152.8, 143.7, 137.6, 137.3, 132.5, 129.0, 128.8, 123.7, 122.1; HRMS (ESI) calculated for $C_{18}H_{12}N_2I$ $[M – Cl]^+$ m/z 383.0040, found 383.0046.

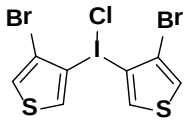
4-Isoquinolinyl{5-[1,3-dimethylpyrimidine-2,4-dionyl]}iodonium triflate (2m)



Prepared according to the General Procedure A on a 0.46 mmol scale at 0 °C. The filtered white solids were purified by trituration with vigourous stirring in diethyl ether/ethyl acetate (9:1, 5 mL) for 15 mins before filtering again to obtain the title compound as a white solid (isolated as 85% purity, 252 mg, 0.46 mmol, quant.). m.p. 196 °C (decomposed); IR ν max (solid, cm^{-1}): 1720, 1660, 1609, 1339, 1276, 1221, 1164, 1019, 762; ^{1}H NMR (500 MHz, CD_3CN): δ 9.84 (s, 1H), 9.36 (s, 1H), 8.77 (s, 1H), 8.61 (d, J = 8.3 Hz, 1H), 8.56–8.50 (m, 2H), 8.22 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 3.41 (s, 3H), 3.18 (s, 3H); ^{13}C NMR (126 MHz, CD_3CN): δ 160.1, 156.6, 152.8, 151.6, 141.8, 140.6, 138.0, 134.0, 133.8, 130.4, 128.7, 121.7 (q, J = 320.7 Hz), 115.8, 88.5, 38.7, 29.9; ^{19}F NMR (376 MHz, CD_3CN): δ −79.3; HRMS (ESI) calculated for $C_{15}H_{13}O_2N_3I$ $[M − OTf]^+$ m/z 394.0047, found 394.0041.

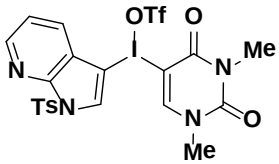
[7] Stang, P. J.; Olenyuk, B.; Chen, K. *Synthesis* **1995**, 937.

Di-4-(3-bromothiophenyl)iodonium chloride (2n)



Prepared according to the method of Gronowitz with modifications.[8] To 3,4-dibromothiophene (970 mg, 4.0 mmol) in Et_2O (2 mL) at –78 °C was added n-BuLi (2.65 mL, 8.4 mmol, 1.6 M in hexanes) and stirred at that temperature for 30 mins. *trans*-Chlorovinyliodonium dichloride (500 mg, 1.9 mmol) was added as a suspension in toluene (4 mL) and further stirred at –78 °C for 2 hours. The reaction mixture was warmed to 0 °C, poured onto water and filtered. The solids obtained were washed sequentially with water (4 mL), acetone (10 mL) and Et_2O (20 mL), and dried under vacuum overnight to give the title compound as an off-white solid (584 mg, 1.2 mmol, 60%). m.p. 218 °C (decomposed); IR ν max (solid, cm^{-1}): 1457, 1319, 888, 824, 790; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.61 (d, J = 3.3 Hz, 2H), 7.86 (d, J = 3.3 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 137.6, 126.1, 115.3, 114.2; HRMS (ESI) calculated for $C_8H_4Br_2IS_2$ $[M – Cl]^+$ m/z 448.7160, found 448.7162.

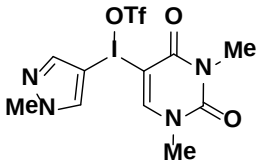
3-(1-Tosyl-azaindolyl){5-[1,3-dimethylpyrimidine-2,4-dionyl]}iodonium triflate (2o)



Prepared according to the General Procedure A on a 0.69 mmol scale at 0 °C. The filtered white solids were purified by trituration with vigourous stirring in diethyl ether/ethyl acetate (3:1, 4 mL) for 1 hour before filtering again to obtain the title compound as a white solid (529 mg, 0.77 mmol, quant.). m.p. 186 °C (decomposed); IR ν max (solid, cm^{-1}): 1724, 1660, 1226, 1145, 1025, 761; ^{1}H NMR (400 MHz, CD_3CN): δ 8.88 (d, J = 8.2 Hz, 1H), 8.79–8.72 (m, 2H), 8.64 (s, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.99 (dd, J = 8.1, 5.9 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 3.40 (s, 3H), 3.19 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CD_3CN): δ 159.9, 155.9, 151.7, 149.8, 141.7, 139.8, 139.6, 138.4, 133.2, 131.7, 129.7, 126.6, 122.2, 121.7 (q, J = 320.7 Hz), 88.8, 84.3, 38.6, 29.9, 21.8; ^{19}F NMR (376 MHz, CD_3CN): δ −78.7; HRMS (ESI) calculated for $C_{20}H_{18}O_4N_4IS$ $[M − OTf]^+$ m/z 537.0088, found 537.0075.

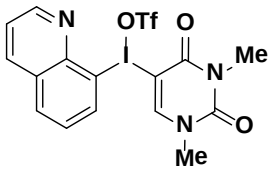
[8] Gronowitz, S.; Holm, B. *J. Heterocycl. Chem.* **1977**, *14*, 281.

[4-(1-Methylpyrazolyl)]{5-[1,3-dimethylpyrimidine-2,4-dionyl]}iodonium triflate (2p)



Prepared according to the General Procedure A on a 2.30 mmol scale at 23 °C. The filtered white solids were purified by trituration with vigourous stirring in diethyl ether/ethyl acetate (10:1, 22 mL) for 1 hour before filtering again to obtain the title compound as a white solid (1.27 g, 2.5 mmol, quant.) m.p. 204 °C (decomposed); IR ν max (solid, cm^{-1}):1725, 1675, 1610, 1283, 1212, 1160, 1022; ^{1}H NMR (400 MHz, CD_3CN): δ 8.56 (s, 1H), 8.44 (s, 1H), 8.39 (s, 1H), 4.09 (s, 3H), 3.42 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN): δ 159.7, 155.8, 151.7, 142.2, 141.1, 121.6 (q, *J* = 319.6 Hz), 88.5, 80.6, 40.5, 38.6, 29.9; ^{19}F NMR (376 MHz, CD_3CN): δ −78.8; HRMS (ESI) calculated for $C_{10}H_{12}O_2N_4I$ $[M - OTf]^+$ m/z 346.9999, found 347.0001.

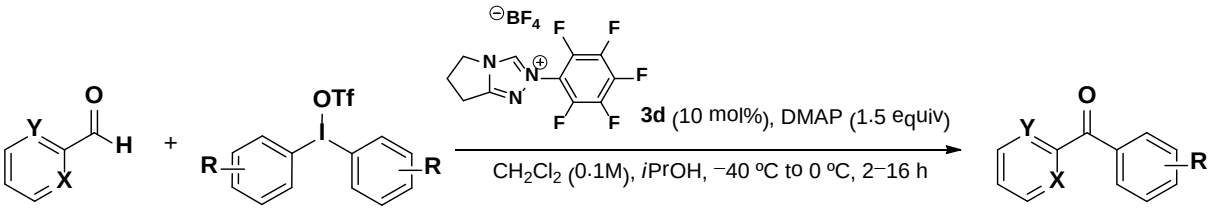
8-quinolyl{5-[1,3-dimethylpyrimidine-2,4-dionyl]}iodonium triflate (2q)



Prepared according to the General Procedure A on a 5.00 mmol scale at 0 °C. The filtered white solids were purified by washing with CH_2Cl_2 (250 mL) to obtain the title compound as a white solid (1.8 g, 3.3 mmol, 66%) m.p. 201 °C; IR ν max (solid, cm^{-1}):1722, 1651, 1610, 1549, 1487, 1441, 1338, 1280, 1210, 1164; ^{1}H NMR (400 MHz, CD_3CN): δ 9.32 (dd, *J* = 5.4, 1.4 Hz, 1H), 9.19 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.97 (dd, *J* = 7.7, 0.8 Hz, 1H), 8.79 (s, 1H), 8.59 (dd, *J* = 8.3, 0.8 Hz, 1H), 8.23 (dd, *J* = 8.4, 5.5 Hz, 1H), 8.00 (t, *J* = 8.0 Hz, 1H), 3.44 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN): δ 160.8, 156.5, 151.6, 149.4, 149.2, 145.9, 137.4, 135.9, 132.4, 131.4, 125.1, 121.6 (q, *J* = 321.2 Hz), 108.4, 87.3, 38.7, 30.0 ; ^{19}F NMR (376 MHz, CD_3CN): δ −78.7.

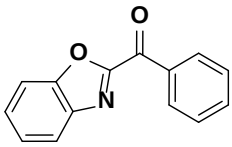
3. Experimental procedures and data

General Procedure B: Arylation of heteroaryl aldehydes with diaryliodonium triflates.



To the heteroaryl aldehyde (0.25 mmol, 1 equiv) and catalyst **3d** (9 mg, 0.025mmol, 0.1 equiv) in CH_2Cl_2 (1 mL) at the indicated temperature was added a solution of the diaryliodonium triflate (0.25 mmol, 1 equiv), DMAP (46 mg, 0.38 mmol, 1.5 eq.) and *i*PrOH (125 µL) in CH_2Cl_2 (1.5 mL). If the mixture of reagents (iodonium salt and DMAP) was not homogeneous (prior to addition), it was sonicated until all components dissolved. The reaction mixture was stirred at the indicated temperature and for the stated time before it was concentrated *in vacuo*. Flash column chromatography of the resulting residue provided the desired product.

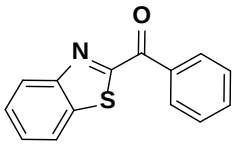
Benzoxazol-2-yl(phenyl)methanone (4a)



Prepared according to the General Procedure B using benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at –40 °C for 2.5 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/diethylether 20:1) provided **4a** (52 mg, 93%) as a white solid. The physical data was consistent with that reported previously.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.75–7.65 (m, 2H), 7.61–7.51 (m, 3H), 7.51–7.43 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.7, 157.3, 150.6, 140.9, 135.2, 134.5, 131.2, 128.8, 128.6, 125.9, 122.6, 112.0; HRMS (ESI) calculated for $C_{14}H_{10}O_2N$ $[M + H]^+$ m/z 224.0706, found 224.0707.

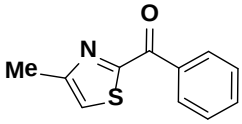
Benzothiazol-2-yl(phenyl)methanone (4b)

[9] Wu, X.-F.; Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 7316.



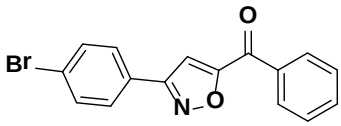
Prepared according to the General Procedure B using benzothiazole-2-carbaldehyde (41 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 4 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 9:1) provided **4b** (72 mg, 88%) as a white solid. The physical data was consistent with that reported previously.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.29–8.21 (m, 1H), 8.07–7.99 (m, 1H), 7.72–7.64 (m, 1H), 7.64–7.50 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.4, 167.1, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.6, 126.9, 125.7, 122.2; HRMS (ESI) calculated for $C_{14}H_{10}NOS$ $[M + H]^+$ m/z 240.0478, found 240.0481.

(4-Methylthiazol-2-yl)(phenyl)methanone (4c)



Prepared according to the General Procedure B using 4-methyl-4,5-dihydrothiazole-2-carbaldehyde (33 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 2 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 4:1) provided **4c** (42 mg, 83%) as a yellow oil. R_f 0.41 (40-60° petroleum ether/ethyl acetate 4:1); IR ν max (film, cm^{-1}): 2970, 2924, 1738, 1642, 1450, 1430, 1290; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.29 (d, *J* = 0.8 Hz, 1H), 2.59 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 184.1, 166.8, 155.5, 135.3, 133.5, 131.2, 128.4, 121.4, 17.5; HRMS (ESI) calculated $C_{11}H_{10}NOS$ $[M + H]^+$ m/z 204.0478, found 204.0478.

(3-(4-Bromophenyl)isoxazol-5-yl)(phenyl)methanone (4d)

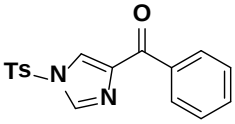


Prepared according to the General Procedure B using 3-(4-bromophenyl)isoxazole-5-carbaldehyde (63 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 2 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 9:1) provided **4d** (77 mg, 94%) as a white solid. R_f 0.41 (40-60° petroleum

[10] Boga, C.; Micheletti, G. *Eur. J. Org. Chem.* **2010**, 5659.

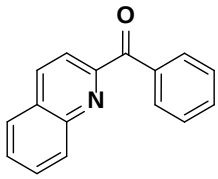
ether/ethyl acetate 4:1); m.p. 100–108 °C; IR ν max (film, cm^{-1}): 3065, 1654, 1430, 1270; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 2H) 7.73–7.62 (m, 3H), 7.57 (app t, *J* = 7.8 Hz, 2H), 7.32 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.2, 167.7, 161.9, 135.4, 134.2, 132.4, 130.0, 128.8, 128.4, 126.9, 125.0, 107.9; HRMS (ESI) calculated for $C_{16}H_{11}BrNO_2$ $[M + H]^+$ m/z 327.9968, found 327.9974.

Phenyl(1-tosylimidazol-4-yl)methanone (4e)



Prepared according to the General Procedure B using 1-tosylimidazole-4-carbaldehyde (63 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 4:1) provided **4e** (58 mg, 71%) as a white solid. R_f 0.27 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 158–160 °C; IR ν max (film, cm^{-1}): 2970, 1738, 1365, 1217; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.06 (d, *J* = 1.4 Hz, 1H), 7.98 (d, *J* = 1.4 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.61–7.54 (m, 1H), 7.51–7.44 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.0, 147.2, 143.0, 136.9, 136.2, 134.1, 133.0, 130.7, 130.1, 128.3, 127.7, 123.4, 21.8; HRMS (ESI) calculated $C_{17}H_{15}O_3N_2S$ $[M + H]^+$ mz 327.0798, found 327.0800.

Phenyl(quinolin-2-yl)methanone (4f)

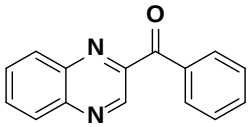


Prepared according to the General Procedure B using quinoline-2-carbaldehyde (39 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at –10 °C for 3 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 15:1) provided **4f** (51 mg, 87%) as a white solid. The physical data was consistent with that reported previously.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.27–8.19 (m, 3H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.79 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.69–7.59 (m, 2H), 7.56–7.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.0, 154.8, 146.9, 137.3,

[11] Sliwa, H.; Quattara, L. *J. Heterocycl. Chem.* **1987**, *24*, 1617.

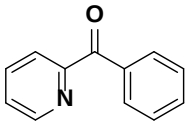
136.3, 133.2, 131.6, 130.7, 130.2, 129.1, 128.6, 128.3, 127.8, 121.0; HRMS (ESI) calculated for $C_{13}H_{12}ON$ $[M + H]^+$ m/z 234.0913, found 234.0916.

Phenyl(quinoxalin-2-yl)methanone (4g)



Prepared according to the General Procedure B using quinoxaline-2-carbaldehyde (40 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 4:1) provided **4g** (57 mg, 97%) as a yellow solid. The physical data was consistent with that reported previously.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 8.30–8.15 (m, 4H), 7.96–7.81 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (app t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3, 148.6, 145.3, 143.1, 140.4, 135.5, 133.6, 132.0, 131.2, 130.8, 130.4, 129.4, 128.4; HRMS (ESI) calculated $C_{15}H_{11}ON_2$ $[M + H]^+$ m/z 235.0866, found 235.0870.

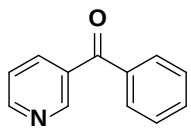
Phenyl(pyridin-2-yl)methanone (4h)



Prepared according to the General Procedure B using picolinaldehyde (27 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 4 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 4:1) provided **4h** (36 mg, 79%) as a yellow oil. The physical data was consistent with that reported previously.[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.8 Hz, 1H), 8.08–8.03 (m, 3H), 7.91 (app td, *J* = 7.7, 1.7 Hz, 1H), 7.64–7.55 (m, 1H), 7.51–7.47 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.9, 155.1, 148.5, 137.0, 136.2, 132.9, 131.0, 128.2, 126.2, 124.6; HRMS (ESI) calculated for $C_{12}H_{10}ON$ $[M + H]^+$ m/z 184.0757, found 184.0758.

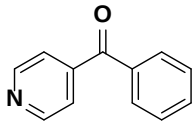
Phenyl(pyridin-3-yl)methanone (4i)

[12] Yin, Z.; Zhang, Z.; Kadow, J. F.; Meanwell, N. A.; Wang, T. *J. Org. Chem.* **2004**, *69*, 1364.
[13] Mamane, V.; Fort, Y.; Aubert, E. *J. Org. Chem.* **2007**, *72*, 7294.



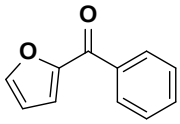
Prepared according to the General Procedure B using nicotinaldehyde (27 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 1:1) provided **4i** (22 mg, 48%) as a yellow solid. The physical data was consistent with that reported previously.[14] ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.00 (d, *J* = 1.4 Hz, 1H), 8.82 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.16 (app dt, *J* = 7.9, 2.0 Hz, 1H), 7.87–7.76 (m, 2H), 7.69–7.61 (m, 1H), 7.58–7.42 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.7, 152.4, 150.6, 137.6, 136.6, 133.3, 133.2, 130.0, 128.7, 123.5. HRMS (ESI) calculated for $C_{12}H_{10}ON$ $[M + H]^+$ m/z 184.0757, found 184.0756.

Phenyl(pyridin-4-yl)methanone (4j)



Prepared according to the General Procedure B using isonicotinaldehyde (27 mg, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 1:1) provided **4j** (33 mg, 72%) as an off-white solid. The physical data is consistent with that reported previously.[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 5.8 Hz, 2H), 7.82 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 6.0 Hz, 2H), 7.55–7.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.1, 150.3, 144.4, 135.9, 133.6, 130.2, 128.7, 123.0; HRMS (ESI) calculated for $C_{12}H_{10}ON$ $[M + H]^+$ m/z 184.0757, found 184.0756.

Furan-2-yl(phenyl)methanone (4k)

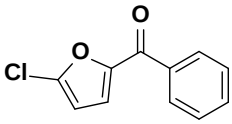


Prepared according to the General Procedure B except using 20 mol% of catalyst **3d**. To 2-furfural (21 μL, 0.25 mmol) and catalyst **3d** (18 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added a solution of iodonium triflate **2a** (108 mg, 0.25 mmol), DMAP (46 mg, 0.38 mmol, 1.5 eq.) and *i*PrOH (125 μL) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at 0

[14] Tambade, P. J.; Patil, Y. P.; Panda, A. G.; Bhanage, B. M. *Eur. J. Org. Chem.* **2009**, *18*, 3022.
[15] Couve-Bonnaire, S.; Carpentier, J.-F.; Mortreux, A.; Castanet, Y. *Tetrahedron* **2003**, 2793.

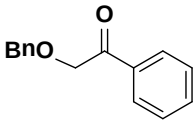
°C for 14 hours. Purification by flash chromatography on silica gel (hexanes/ethyl acetate 97:3) provided **4k** (22 mg, 51%) as a yellow oil. The physical data was consistent with that reported previously.[16] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.71 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 10.8, 4.5 Hz, 2H), 7.24 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.60 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.6, 152.3, 147.1, 137.2, 132.6, 129.3, 128.4, 120.5, 112.2.

(5-Chlorofuran-2-yl)(phenyl)methanone (4l)



Prepared according to the General Procedure B except that 15 mol% of catalyst was used. To a solution of 5-chloro-2-furfural (33 mg, 0.25 mmol) and catalyst **3d** (13.5 mg, 0.038 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added a solution of iodonium triflate **2a** (108 mg, 0.25 mmol), DMAP (46 mg, 0.38 mmol, 1.5 eq.) and *i*PrOH (125 µL) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at 0 °C for 16 hours. Purification by flash chromatography on silica gel: first column (hexanes/ethyl acetate 97:3), second column (hexanes/toluene 8:2 to 9:1) provided **4l** (32 mg, 62%) as a yellow oil. R_f 0.48 (40-60° petroleum ether/ethyl acetate 4:1); IR ν max (film, cm^{-1}) 1644, 1598, 1567, 1465, 1361, 1286, 1207, 1174, 1151; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (app t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 3.6 Hz, 1H), 6.41 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.1, 151.5, 142.6, 136.6, 132.8, 129.2, 128.5, 122.4, 109.3.

2-(Benzyloxy)-1-phenylethanone (4m)

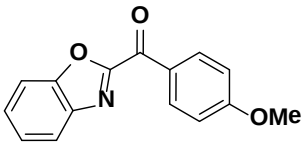


Prepared according to the General Procedure B using 2-(benyzloxy)acetaldehyde (35 µL, 0.25 mmol) and iodonium triflate **2a** (108 mg, 0.25 mmol) at 0 °C for 16 hours. Purification by flash chromatography on silica gel: first column (hexanes/ethyl acetate 95:5) provided **4m** (29 mg, 52%) as a yellow oil. The physical data was consistent with that reported previously.[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (app

[16] Crawford, J. J.; Henderson, K. W.; Kerr, W. J. *Org. Lett.* **2006**, *8*, 5073.
[17] Aikawa, K.; Okamoto, T.; Mikami, K. *J. Am. Chem. Soc.* **2012**, *134*, 10329

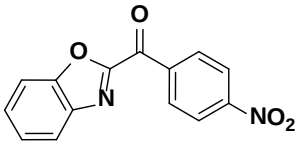
t, J = 7.7 Hz, 2H), 7.41–7.28 (m, 5H), 4.76 (s, 2H), 4.70 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.3, 137.3, 134.9, 133.6, 128.7, 128.6, 128.1, 128.0 (2C), 73.4, 72.6.

Benzoxazol-2-yl(4-methoxyphenyl)methanone (4n)



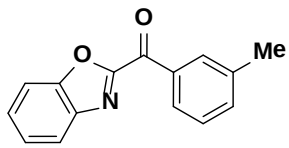
Prepared according to the General Procedure B using benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and iodonium triflate **2b** (123 mg, 0.25 mmol) at –40 °C for 2.5 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/diethylether 10:1) provided **4k** (51 mg, 81%) as a white solid. The physical data was consistent with that reported previously.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 9.0 Hz, 2H), 7.93 (dd, J = 8.0, 0.6 Hz, 1H), 7.70 (dd, J = 8.2, 0.6 Hz, 1H), 7.56–7.50 (m, 1H), 7.46 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 164.8, 157.6, 150.5, 140.9, 133.7 (2C), 128.2, 128.1, 125.7, 122.3, 114.1 (2C), 111.9, 55.7; HRMS (ESI) calculated for $C_{15}H_{12}O_3N$ $[M + H]^+$ m/z 254.0815, found 254.0812.

Benzoxazol-2-yl(4-nitrophenyl)methanone (4o)



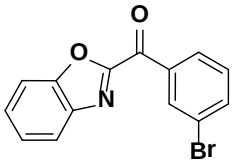
Prepared according to the General Procedure B using benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and iodonium triflate **2c** (130 mg, 0.25 mmol) at –40 °C for 2.5 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/diethylether 10:1) provided **4l** (49 mg, 73%) as a white solid. The physical data was consistent with that reported previously.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, J = 8.9 Hz, 2H), 8.41 (d, J = 8.9 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.64–7.58 (m, 1H), 7.55–7.49 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 156.6, 151.0, 150.7, 140.8, 139.6, 132.3, 129.4, 126.3, 123.8, 122.8, 112.2; HRMS (ESI) calculated for $C_{14}H_9O_4N_2$ $[M + H]^+$ m/z 269.0557, found 269.0557.

Benzoxazol-2-yl(4-methoxyphenyl)methanone (4p)



Prepared according to the General Procedure B using benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and iodonium triflate **2d** (123 mg, 0.25 mmol) at –40 °C for 2.5 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/diethylether 20:1) provided **4m** (51 mg, 81%) as a white solid. R_f 0.52 (40-60° petroleum ether/diethylether 10:1); m.p. 73 °C; IR ν max (solid, cm^{-1}): 1663, 1603, 1528, 1306, 1147, 1136, 971, 828, 744, 688, 676; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 7.5 Hz, 1H), 8.29 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.59–7.52 (m, 1H), 7.52–7.43 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 157.4, 150.6, 140.9, 138.6, 135.3, 135.2, 131.4, 128.7, 128.6, 128.5, 125.8, 122.6, 112.0, 21.6; HRMS (ESI) calculated for $C_{15}H_{12}O_2N$ $[M + H]^+$ m/z 238.0863, found 238.0865.

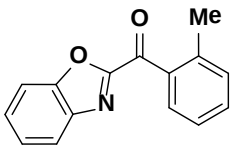
Benzoxazol-2-yl(3-bromophenyl)methanone (4q)



Prepared according to the General Procedure B using benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and iodonium triflate **2e** (147 mg, 0.25 mmol) at –40 °C for 2.5 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/diethylether 20:1) provided **4n** (68 mg, 90%) as a white solid. The physical data was consistent with that reported previously.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.54 (d, *J* = 7.3 Hz, 1H), 7.95 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 6.5 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.61–7.52 (m, 1H), 7.52–7.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.1, 156.8, 150.6, 140.8, 137.2, 136.8, 133.9, 130.3, 129.8, 128.9, 126.0, 122.9, 122.7, 112.0; HRMS (ESI) calculated for $C_{14}H_9O_2NBr$ $[M + H]^+$ m/z 301.9811, found 301.9818.

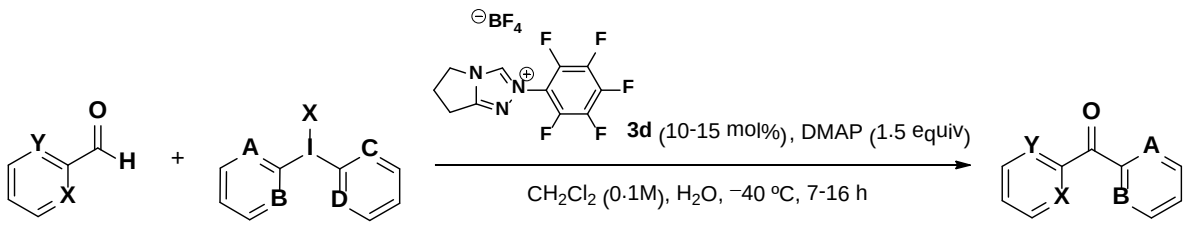
Benzoxazol-2-yl(2-tolyl)methanone (4r)

[18] Fan, X.; He, Y.; Zhang, X.; Guo, S.; Wang, Y. *Tetrahedron* **2011**, *67*, 6369.



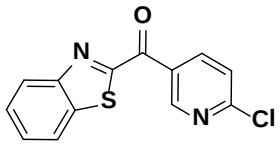
Prepared according to the General Procedure B using benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and iodonium triflate **2f** (115 mg, 0.25 mmol) at –40 °C for 2.5 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/diethylether 20:1) provided **4o** (47 mg, 79%) as a white solid. The physical data was consistent with that reported previously.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.59–7.44 (m, 3H), 7.40–7.33 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 183.9, 158.0, 150.8, 141.0, 139.7, 135.1, 132.7, 131.9, 131.5, 128.6, 125.9, 125.6, 122.6, 112.0, 20.8; HRMS (ESI) calculated for $C_{15}H_{12}O_2N$ $[M + H]^+$ m/z 238.0863, found 238.0865.

General Procedure C: Arylation of heteroaryl aldehydes with diheteroaryliodonium salts.



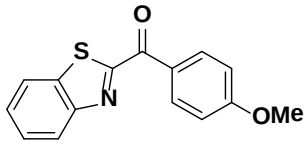
To heteroaryl aldehyde (0.25 mmol, 1 equiv) and catalyst **3d** in CH_2Cl_2 (1 mL) at –40 °C was added a solution of the iodonium salt (0.25 mmol, 1 equiv), DMAP (46 mg, 0.38 mmol, 1.5 equiv) and H_2O (10 µL) in CH_2Cl_2 (1.5 mL). If the mixture of reagents (iodonium salt and DMAP) was not homogeneous prior to addition, it was sonicated until all components dissolved. The reaction mixture was stirred at the indicated temperature and for the stated time. After completion of the reaction, NH_4Cl (sat. aq.) was added and the reaction extracted with CH_2Cl_2. The combined organic extracts was dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the resulting residue provided the desired product.

Benzothiazol-2-yl(6-chloropyridin-3-yl)methanone (4s)



Prepared according to the General Procedure C using iodonium triflate **2j** (124 mg, 0.25 mmol), benzothiazole-2-carbaldehyde (41 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 10:1) provided **4s** (51 mg, 75%) as a yellow solid. R_f 0.50 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 110 ºC; IR ν max (film, cm^{-1}) 1649, 1574, 1487, 1455, 1298, 1100, 892; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (dd, *J* = 2.4, 0.6 Hz, 1H), 8.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.21 (d, *J* = 7.5Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.64–7.54 (m, 2H), 7.52 (dd, *J* = 8.4, 0.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 182.9, 165.8, 156.1, 153.7, 152.8, 140.8, 137.0, 129.5, 128.2, 127.3, 125.9, 124.2, 122.2; HRMS (ESI) calculated for $C_{13}H_8ON_2ClS$ $[M + H]^+$ m/z 275.0040, found 275.0045.

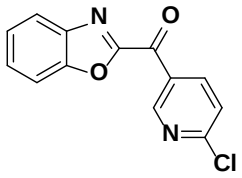
Benzothiazol-2-yl(4-methoxyphenyl)methanone (5b)



Prepared according to General Procedure B using iodonium triflate **2h** at 0 °C with yield determined from the crude ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as the internal standard (50%). The physical data was consistent with that reported previously.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 9.1 Hz, 2H), 8.28–8.21 (m, 1H), 8.06–7.99 (m, 1H), 7.63–7.49 (m, 2H), 7.05 (d, *J* = 9.1 Hz, 2H), 3.93 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 183.4, 167.9, 164.4, 153.9, 136.9, 133.9, 127.8, 127.4, 126.8, 125.5, 122.1, 113.9, 55.6; HRMS (ESI) calculated $C_{15}H_{12}O_2NS$ $[M + H]^+$ 270.0583, found 270.0585.

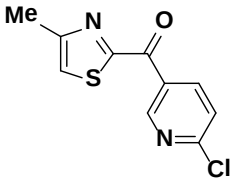
Benzoxazol-2-yl(6-chloropyridin-3-yl)methanone (4t)

[19] Boga, C.; Stengel, R.; Abdayem, R.; Del Vecchio, E.; Forlani, L.; Todesco, P. E. *J. Org. Chem.* **2004**, *69*, 8903.



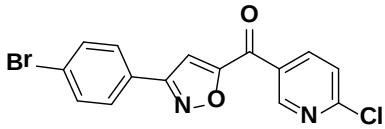
Prepared according to the General Procedure C using iodonium triflate **2j** (133 mg, 0.25 mmol), benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 7 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 10:1) provided **4t** (60 mg, 93%) as a white solid; R_f 0.42 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 138 ºC; IR ν max (solid, cm^{-1}) 1662, 1572, 1458, 1361, 1093, 958, 739; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (dd, *J* = 2.4, 0.6 Hz, 1H), 8.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.55 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.3, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.0, 156.7, 156.4, 152.6, 150.5, 140.6, 140.6, 129.5, 129.2, 126.1, 124.3, 122.7, 112.0; HRMS (ESI) calculated for $C_{13}H_8O_2N_2Cl$ $[M + H]^+$ m/z 259.0269, found 259.0272.

(6-Chloropyridin-3-yl)(4-methylthiazol-2-yl)methanone (4u)



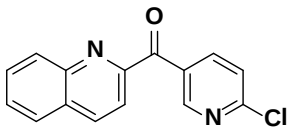
Prepared according to the General Procedure C using iodonium triflate **2j** (133 mg, 0.25 mmol), 4-methylthiazole-2-carbaldehyde (32 mg, 0.25 mmol) and catalyst **3d** (13.5 mg, 0.038 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 7:3) provided **4u** (42 mg, 70%) as an off-white solid; R_f 0.20 (40-60° petroleum ether/ethyl acetate 5:1); m.p. 86 ºC; IR ν max (solid, cm^{-1}) 1643, 1570, 1424, 1294, 1100, 971, 877, 782; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (d, *J* = 2.4 Hz, 1H), 8.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 0.8 Hz, 1H), 2.58 (d, *J* = 0.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.5, 165.5, 156.0, 155.8, 152.8, 140.8, 129.9, 124.1, 122.4, 17.3; HRMS (ESI) calculated for $C_{10}H_8ON_2ClS$ $[M + H]^+$ m/z 239.0040, found 239.0044.

(3-(4-Bromophenyl)isoxazol-5-yl)(6-chloropyridin-3-yl)methanone (4v)



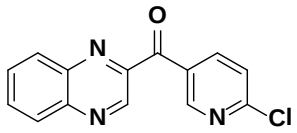
Prepared according to the General Procedure C using iodonium triflate **2j** (133 mg, 0.25 mmol), 3-(4-bromophenyl)isoxazole-5-carbaldehyde (63 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 10:1) provided **4v** (79 mg, 87%) as a white solid; R_f 0.46 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 154 ºC; IR ν max (solid, cm^{-1}) 1652, 1575, 1424, 1361, 1276, 1104, 1073, 891, 825, 760; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.23 (d, *J* = 2.2 Hz, 1H), 8.47 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.56 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.43 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.4, 167.0, 162.2, 156.8, 151.5, 139.7, 132.5, 129.8, 128.4, 126.4, 125.4, 124.7, 108.5; HRMS (ESI) calculated for $C_{15}H_9O_2N_2BrCl$ $[M + H]^+$ m/z 362.9530, found 362.9535.

(6-Chloropyridin-3-yl)(quinolin-2-yl)methanone (4w)



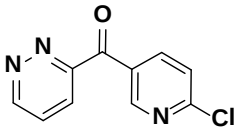
Prepared according to the General Procedure C iodonium triflate **2j** (133 mg, 0.25 mmol), quinoline-2-carbaldehyde (40 mg, 0.25 mmol) and catalyst **3d** (13.5 mg, 0.038 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 10:1) provided **4w** (42 mg, 63%) as a white solid. R_f 0.40 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 128 ºC; IR ν max (solid, cm^{-1}) 1664, 1576, 1453, 1315, 1095, 924, 843, 768; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (d, *J* = 2.4, 0.5 Hz, 1H), 8.58 (dd, *J* = 8.3, 2.4 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.82 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.51 (dd, *J* = 8.3, 0.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 190.7, 155.1, 153.2, 153.1, 146.7, 141.2, 137.5, 130.9, 130.6, 130.5, 129.3, 129.1, 127.7, 123.9, 120.3; HRMS (ESI) calculated for $C_{15}H_{10}ON_2Cl$ $[M + H]^+$ m/z 269.0476, found 269.0481.

(6-Chloropyridin-3-yl)(quinoxalin-2-yl)methanone (4x)



Prepared according to the General Procedure C using iodonium triflate **2j** (133 mg, 0.25 mmol), quinoxaline-2-carbaldehyde (40 mg, 0.25 mmol) and catalyst **3d** (13.5 mg, 0.038 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 3:2) provided **4x** (43 mg, 64%) as an off-white solid. R_f 0.45 (40-60° petroleum ether/ethyl acetate 3:2); m.p. 122 ºC; IR ν max (solid, cm^{-1}) 1665, 1569, 1362, 1316, 1104, 917, 864, 766, 752; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 9.43 (dd, *J* = 2.4, 0.6 Hz, 1H), 8.57 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.29–8.14 (m, 2H), 7.93 (m, 2H), 7.54 (dd, *J* = 8.4, 0.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.0, 155.8, 152.9, 147.0, 145.0, 143.6, 140.8, 140.4, 132.8, 131.3, 130.5, 130.2, 129.5, 124.3; HRMS (ESI) calculated for $C_{14}H_9ON_3Cl$ $[M + H]^+$ m/z 270.0429, found 270.0433.

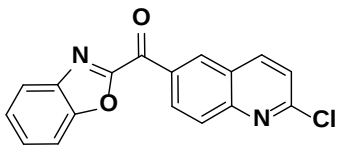
(6-Chloropyridin-3-yl)(pyridazin-3-yl)methanone (4y)



Prepared according to the General Procedure C using iodonium triflate **2j** (133 mg, 0.25 mmol), pyridazin-3-carbaldehyde[20] (28 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (dichloromethane/diethyl ether 1:0 to 4:1) provided **4y** (35 mg, 63%) as an off-white solid. R_f 0.26 (dichloromethane/diethyl ether 4:1); m.p. 115 ºC; IR ν max (film, cm^{-1}) 1676, 1584, 1308, 1290, 1112, 1013, 924, 759; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (d, *J* = 3.6 Hz, 1H), 9.20 (dd, *J* = 2.4, 0.5 Hz, 1H), 8.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.21 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.70 (dd, *J* = 8.5, 5.0 Hz, 1H), 7.43 (dd, *J* = 8.4, 0.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 189.2, 156.8, 156.0, 153.0, 152.8, 141.3, 130.0, 127.7, 127.4, 124.0; HRMS (ESI) calculated for $C_{10}H_7ON_3Cl$ $[M + H]^+$ m/z 220.0272, found 220.0274.

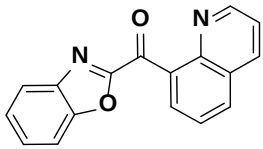
Benzoxazol-2-yl(2-chloroquinolin-6-yl)methanone (4z)

[20] Pyridazine-3-carbaldehyde was prepared according to the following procedure: Tsukamoto, I.; Koshio, H.; Kuramochi, T.; Saitoh, C.; Yanai-Inamura, H.; Kitada-Nozawa, C.; Yamamoto, E.; Yatsu, T.; Shimada, Y.; Sakamoto, S.; Tsukamoto, S. *Bioorg. Med. Chem.* **2009**, *17*, 3130.



Prepared according to the General Procedure C using iodonium triflate **2k** (145 mg, 0.25 mmol), benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 4:1) provided **4z** (54 mg, 70%) as an off-white solid. R_f 0.35 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 170 ºC; IR ν max (solid, cm^{-1}) 1660, 1610, 1529, 1443, 1288, 1128, 931, 851, 739; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.35 (d, *J* = 1.8 Hz, 1H), 8.78 (dd, *J* = 8.9, 1.9 Hz, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.4, 8.2, 1.2 Hz, 1H), 7.57–7.50 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.3, 156.9, 153.9, 150.5, 150.2, 140.7, 140.6, 133.4, 133.1, 130.6, 129.2, 128.8, 126.0, 126.0, 123.6, 122.5, 112.0; HRMS (ESI) calculated for $C_{17}H_{10}O_2N_2Cl$ $[M + H]^+$ m/z 309.0425, found 309.0428.

Benzoxazol-2-yl(quinolin-8-yl)methanone (4aa)



<u>With symmetrical iodonium chloride **2l**</u>

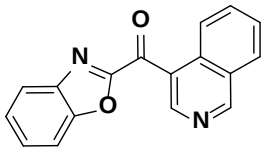
Prepared according to the General Procedure C with *i*PrOH used in place of H_2O. To benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) in CH_2Cl_2 at –40 °C was added a solution of iodonium chloride **2l** (105 mg, 0.25 mmol), DMAP (45 mg, 0.38 mmol) and *i*PrOH (125 μL) in CH_2Cl_2 (2.5 mL). The reaction mixture was stirred for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 5:1) provided **4aa** (51 mg, 73%) as a white solid.

<u>With non-symmetrical uracil iodonium triflate **2q**</u>

Prepared according to the General Procedure C using the uracil iodonium triflate **2q** (136 mg, 0.25 mmol), benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 12 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 7:3) provided **4aa** (42 mg, 62%) as a white solid.

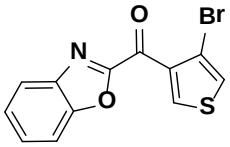
R_f 0.47 (40-60° petroleum ether/ethyl acetate 7:3); m.p. 126 ºC; IR ν max (solid, cm^{-1}) 1678, 1532, 1496, 1321, 1297, 1053, 957, 912, 830, 799, 744; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.24 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.13–8.04 (m, 2H), 7.81 (ddd, *J* = 8.0, 1.2, 0.7 Hz, 1H), 7.71 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.69–7.65 (m, 1H), 7.52 (ddd, *J* = 8.4, 7.4, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.5, 6.6, 2.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.7, 158.9, 150.9, 150.7, 140.9, 136.3, 136.1, 132.0, 130.2, 128.2, 128.1, 125.9, 125.5, 122.3, 121.9, 111.9; HRMS (ESI) calculated for $C_{17}H_{11}O_2N_2$ $[M + H]^+$ m/z 275.0815, found 275.0817.

Benzoxazol-2-yl(isoquinolin-4-yl)methanone (4ab)



Prepared according to the General Procedure C using iodonium triflate **2m** (136 mg, 0.25 mmol), benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 7:3) provided **4ab** (47 mg, 69%) as a light yellow solid. R_f 0.29 (40-60° petroleum ether/ethyl acetate 3:2); m.p. 146 ºC; IR ν max (solid, cm^{-1}) 1664, 1524, 1503, 1309, 1075, 956, 918, 831, 749; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.51 (br s, 2H), 8.64 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.76–7.73 (m, 2H), 7.60 (ddd, *J* = 7.8, 7.4, 1.2 Hz, 1H), 7.50 (ddd, *J* = 7.7, 7.6, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 181.9, 157.6, 157.2, 150.9, 148.2, 140.8, 133.5, 133.0, 128.9, 128.6, 128.3, 126.0, 124.5, 122.7, 112.0; HRMS (ESI) calculated for $C_{17}H_{11}O_2N_2$ $[M + H]^+$ m/z 275.0815, found 275.0817.

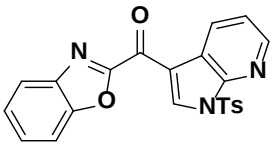
Benzoxazol-2-yl(4-bromothiophen-3-yl)methanone (4ac)



Prepared according to the General Procedure C except that *i*PrOH was used instead of H_2O. To benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) in CH_2Cl_2 at –40 °C was added a solution of iodonium chloride **2n** (122 mg, 0.25 mmol), DMAP (45 mg, 0.38 mmol) and *i*PrOH (125 μL) in CH_2Cl_2 (2.5 mL). The reaction mixture

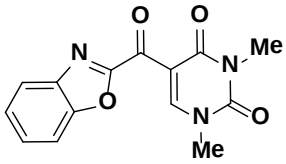
was stirred for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether/ethyl acetate 1:0 to 4:1) provided **4ac** (56 mg, 73%) as an off-white solid. R_f 0.37 (40-60° petroleum ether/ethyl acetate 4:1); m.p. 182 ºC; IR ν max (solid, cm^{-1}) 1646, 1528, 1489, 1422, 1369, 1148, 1027, 867, 751; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, *J* = 3.5 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.61–7.53 (m, 1H), 7.52–7.45 (m, 1H), 7.42 (d, *J* = 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.1, 157.1, 150.6, 140.6, 139.2, 134.8, 128.5, 125.8, 125.4, 122.3, 112.0, 111.4; HRMS (ESI) calculated for $C_{12}H_7NO_2BrS$ $[M + H]^+$ m/z 307.9375, found 307.9382.

Benzoxazol-2-yl(1-tosyl-1H-indol-3-yl)methanone (4ad)



Prepared according to the General Procedure C using iodonium triflate **2o** (172 mg, 0.25 mmol), benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum ether followed by dichloromethane followed by dichloromethane/diethyl ether 96:4) provided **4ad** (53 mg, 51%) as a white solid. R_f 0.43 (dichloromethane); m.p. 220 ºC (decomposed); IR ν max (film, cm^{-1}) 1644, 1532, 1519, 1374, 1268, 1174, 1154, 986, 742, 665; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 8.76 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.51 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 2H), 8.07–8.00 (m, 1H), 7.77–7.70 (m, 1H), 7.59–7.50 (m, 2H), 7.38–7.31 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 156.9, 150.5, 147.0, 146.4, 146.2, 140.7, 136.8, 134.4, 131.8, 129.9, 128.9, 128.3, 125.8, 122.4, 121.0, 120.8, 115.4, 111.9, 21.7; HRMS (ESI) calculated for $C_{22}H_{16}O_4N_3S$ $[M + H]^+$ m/z 418.0856, found 418.0857.

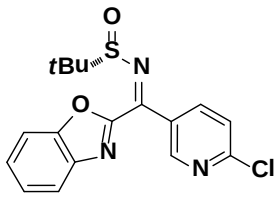
5-(Benzoxazole-2-carbonyl)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4ae)



Prepared according to the General Procedure C using iodonium triflate **2p** (124 mg, 0.25 mmol), benzoxazole-2-carbaldehyde (37 mg, 0.25 mmol) and catalyst **3d** (9 mg, 0.025 mmol) at –40 °C for 16 hours. Purification by flash chromatography on silica gel (40-60° petroleum

ether followed by dichloromethane followed by dichloromethane/diethyl ether 4:1) provided **4ae** (45 mg, 64%) as a light yellow solid. R_f 0.10 (dichloromethane/diethyl ether 18:1); m.p. 196 ºC; IR ν max (solid, cm^{-1}) 1717, 1667, 1615, 1437, 1360, 1317, 1164, 940, 754; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.53 (ddd, *J* = 8.3, 7.4, 1.3 Hz, 1H), 7.45 (ddd, *J* = 8.4, 7.4, 1.1 Hz, 1H), 3.61 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.4, 159.4, 157.0, 151.6, 150.6, 150.5, 140.2, 128.3, 125.8, 122.0, 111.9, 110.3, 38.3, 28.2; HRMS (ESI) calculated for $C_{14}H_{12}O_4N_3$ $[M + H]^+$ m/z 286.0822, found 286.0826.

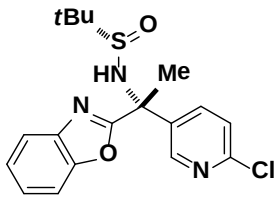
(*S*)-(+)-*N*-(Benzoxazol-2-yl(6-chloropyridin-3-yl)methylene)-2-methylpropane-2-sulfinamide



Ketone **4t** (323 mg, 1.25 mmol) and (*S*)-(–)-2-methyl-2-propanesulfinamide (137 mg, 1.13 mmol) were dissolved in THF (5.7 mL). Titanium ethoxide (1.19 mL, 5.65 mmol) was added and the resulting mixture was placed in a preheated oil bath at 60°C and stirred for 5 hours. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was dissolved in EtOAc (100 mL) and poured into a conical flask containing $NaHCO_3$ (50 mL, sat. aq.) and vigorously stirred for 20 minutes. The mixture was filtered over celite. The organic layer was separated, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel (dichloromethane/diethyl ether 1:0 to 95:5) provided the title compound (347 mg, 86%) as a yellow solid. R_f 0.24 (40-60° petroleum ether/diethy lether 3:1); m.p. 141 °C; $[\alpha]_D^{26}$ = +111.3 (*c*=1, $CHCl_3$); IR ν max (solid, cm^{-1}): 1578, 1452, 1363, 1309, 1104, 914, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (br s, 1H), 7.97 (br s, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53–7.46 (m, 1H), 7.46–7.40 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 150.5 (br), 149.8, 140.6 (br), 138.5 (br), 129.1, 127.4 (br), 125.5, 124.3, 123.9 (br), 122.6, 121.6, 111.4, 60.4, 23.0; HRMS (ESI) calculated for $C_{17}H_{17}N_3O_2ClS$ $[M + H]^+$ m/z 362.0725, found 362.0729.[21]

[21] The ^{13}C NMR spectrum gave broad peaks despite that a well resolved ^{1}H NMR spectrum was obtained. Attempts to obtain the ^{13}C NMR spectrum at higher temperatures in DMSO-d_6 resulted in decomposition of the sample.

(+)-*N*-(1-(Benzoxazol-2-yl)-1-(6-chloropyridin-3-yl)ethyl)-2-methylpropane-2-sulfinamide



To (*S*)-(+)-*N*-(Benzoxazol-2-yl(6-chloropyridin-3-yl)methylene)-2-methylpropane-2-sulfinamide (91 mg, 0.25 mmol) in THF (2.5 mL) was added MeMgBr (750 μL, 0.75 mmol, 1.0 M in THF) dropwise over 7 minutes at –5°C and the resulting mixture was stirred for a further 5 minutes.[22] The reaction mixture was quenched with NH_4Cl (4 mL, sat. aq.) and stirred for 5 minutes. The aqueous layer was separated and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. A 21:1 mixture of diastereomers was observed from the ^{1}H NMR spectrum of the crude oil. Flash chromatography on silica gel (hexanes/ethyl acetate 1:1 to 1:4) provided the title compound (87 mg, 92%, an improved diastereomeric ratio of 31:1 was observed by ^{1}H NMR analysis of the purified product) as a clear oil. R_f 0.45 (40-60° petroleum ether/ethyl acetate 1:4); $[\alpha]_D^{26}$ = +23.2 (*c*=1, $CHCl_3$); IR ν max (solid, cm^{-1}): 1561, 1454, 1366, 1241, 1180, 111, 1055, 1018, 909, 833, 729; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.4 Hz, 1H), 7.92 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.79–7.71 (m, 1H), 7.49–7.46 (m, 1H), 7.39–7.33 (m, 2H), 7.31 (dd, *J* = 8.5, 0.6 Hz, 1H), 4.66 (s, 1H), 2.28 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 151.6, 151.1, 148.1, 140.5, 138.0, 137.2, 126.0, 125.1, 124.31, 120.7, 111.0, 60.1, 57.2, 26.9, 22.7; HRMS (ESI) calculated for $C_{18}H_{21}N_3O_2ClS$ $[M + H]^+$ m/z 378.1038 , found 378.1037. The X-Ray crystal structure is deposited in the Cambridge Crystallographic Data Centre CCDC 915797.[23]

[22] Slow addition of the Grignard reagent at –5 °C is important to obtain the described level of diastereoselectivity. Addition at lower temperatures resulted in lower levels of diastereoselectivity.
[23] Absolute configuration of the sulfinamide was determined from the X-ray crystal structure.

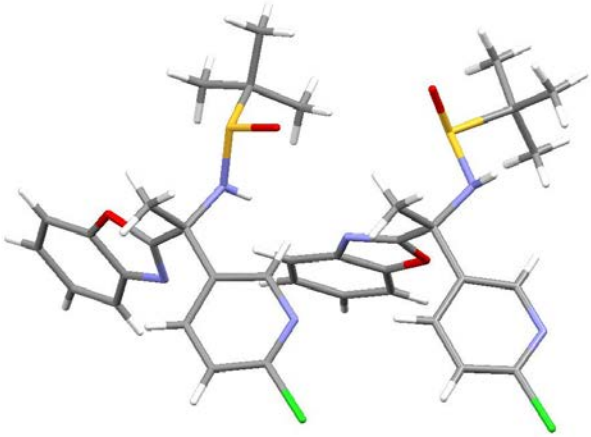
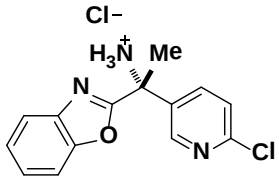


Figure 1: X-ray crystal structure of the sulfinamide adduct.

(*R*)-(+)-1-(Benzoxazol-2-yl)-1-(6-chloropyridin-3-yl)ethylammonium chloride (6)

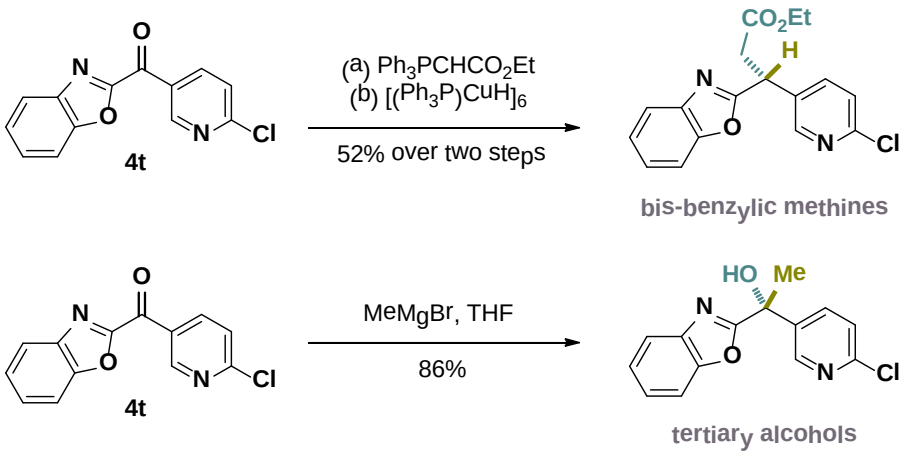


(+)-*N*-(1-(Benzoxazol-2-yl)-1-(6-chloropyridin-3-yl)ethyl)-2-methylpropane-2-sulfinamide (86 mg, 0.23 mmol) was dissolved in MeOH (2.3 mL) and cooled to 0 °C. A solution of HCl in dioxane (173 µL, 0.69 mmol, 4.0 M in dioxane) was added and the reaction was stirred at 0 °C for 6 hours. The reaction mixture was concentrated *in vacuo*. Et_2O was added, followed by concentration *in vacuo.* This procedure was repeated until a white precipitate persisted. The precipitate was rinsed with Et_2O and concentrated *in vacuo* to give a white solid. The solid was dissolved in a minimum amount of dichloromethane and subjected to flash chromatography on silica gel (dichloromethane/methanol 1:0 to 95:5). The fractions containing the product were concentrated to approximately 10 mL and cooled to 0 °C.[24] A solution of HCl in dioxane (173 µL, 0.69 mmol, 4.0 M in dioxane) was added to the concentrated fractions and further concentrated *in vacuo* to give HCl salt **6** (61 mg, 86%) as a white solid. m.p. 120–124 °C (decomposed); $[\alpha]_D^{26}$ = +6.2 (*c*=1, MeOH); IR ν max (film, cm^{-}

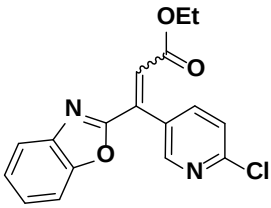
[24] Subjection of the crude HCl salt to column chromatography resulted in the corresponding free base material. We found the free base to be unstable upon concentration so the material was reacidified to the more stable HCl salt.

[1]): 3396, 2733, 1564, 1454, 1379, 1239, 1103, 745; ^{1}H NMR (500 MHz, MeOD) δ 8.54 (dd, *J* = 2.8, 0.5 Hz, 1H), 7.99 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.87–7.81 (m, 1H), 7.70–7.65 (m, 1H), 7.61 (dd, *J* = 8.6, 0.6 Hz, 1H), 7.52–7.46 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, MeOD) δ 164.1, 154.0, 152.7, 148.7, 141.3, 138.9, 133.5, 127.9, 126.7, 126.2, 121.7, 112.3, 57.8, 24.0; HRMS (ESI) calculated for $C_{14}H_{13}N_3OCl$ $[M – Cl]^+$ m/z 274.0747 , found 274.0751.

4. Further derivatisations of ketone 4t



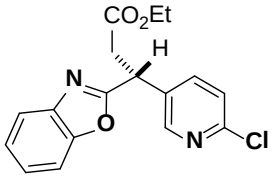
Ethyl-3-(benzoxazol-2-yl)-3-(6-chloropyridin-3-yl)acrylate



A solution of ethyl 2-(triphenylphosphoranylidene)acetate (136 mg, 0.39 mmol) in THF (1 mL) was added dropwise to a solution of ketone **4t** (78 mg, 0.3 mmol) dissolved in THF (2 mL) at 23 °C. The reaction mixture was stirred for 4 hours before it was quenched with NH_4Cl (4 mL, sat. aq.). The aqueous layer was separated and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Flash chromatography on silica gel (hexanes/ethyl acetate 4:1) provided the title compound (98 mg, 99%, 4.3:1 mixture of olefin isomers as judged by ^{1}H NMR spectroscopy) as a white solid. R_f 0.21 (minor isomer) and 0.33 (major isomer) (40-60° petroleum ether/ethyl acetate 4:1); IR ν max (film, cm^{-1}): 1721, 1583, 1462, 1288, 1213, 1179, 1105, 1026, 750; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.3 Hz, 0.2H), 8.42 (d, *J* = 2.2 Hz, 0.8H), 7.81–7.72 (m, 2H), 7.61–7.52 (m, 1H), 7.46–7.34 (m, 3H), 7.29 (s, 0.8H), 6.68

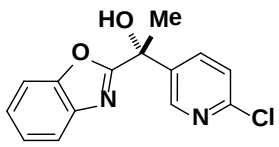
(s, 0.2H), 4.22 (q, J = 7.1 Hz, 0.4H), 4.15 (q, J = 7.1 Hz, 1.6H), 1.20 (t, J = 7.1 Hz, 2.4H), 1.17 (t, 7.1 Hz, 0.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 164.4, 161.3, 159.2, 152.9, 151.8, 150.7, 150.6, 149.8, 148.6, 141.8, 141.2, 139.7, 138.1, 137.1, 135.4, 131.0, 128.9, 127.0 (2C), 126.9, 126.3, 126.1, 125.2, 125.0, 123.5, 121.1, 120.8, 110.8, 61.5, 61.2, 14.0; HRMS (ESI) calculated for $C_{17}H_{14}N_2O_3Cl$ $[M + H]^+$ m/z 329.0693 , found 329.0694.

Ethyl 3-(benzoxazol-2-yl)-3-(6-chloropyridin-3-yl)propanoate



A vial was charged with ethyl-3-(benzoxazol-2-yl)-3-(6-chloropyridin-3-yl)acrylate (71 mg, 0.22 mmol) and $[(Ph_3P)CuH]_6$ (130 mg, 0.07 mmol) under a N_2 atmosphere and sealed with a septum. A solution of benzene and H_2O (500:1 benzene/H_2O, previously degassed by purging with N_2 for 10 minutes) was added and the resulting mixture was stirred for 36 hours at room temperature. The vial was then opened and stirred for 1 hour before filtering over celite and concentrated *in vacuo*. Flash chromatography on silica gel: first column (dichloromethane/diethyl ether 1:0 to 95:5), second column (hexanes/ethyl acetate 9:1 to 85:15) provided the title compound (38 mg, 53%) as a clear oil. R_f 0.52 (dichloromethane/diethyl ether 9:1); IR ν max (film, cm^{-1}): 1732, 1567, 1456, 1392, 1241, 1144, 1106, 1024, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 2.5 Hz, 1H), 7.71–7.66 (m, 2H), 7.49–7.42 (m, 1H), 7.35–7.27 (m, 3H), 4.82 (t, J = 7.7 Hz, 1H), 4.11 (app qd, J = 7.1, 1.1 Hz, 2H), 3.48 (dd, J = 16.7, 7.8 Hz, 1H), 3.05 (dd, J = 16.7, 7.7 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 165.3, 151.0, 150.9, 149.4, 140.8, 138.2, 133.2, 125.3, 124.5, 120.1, 110.6, 61.2, 38.7, 38.6, 14.0; HRMS (ESI) calculated for $C_{17}H_{16}N_2O_3Cl$ $[M + H]^+$ m/z 331.0849 , found 331.0847.

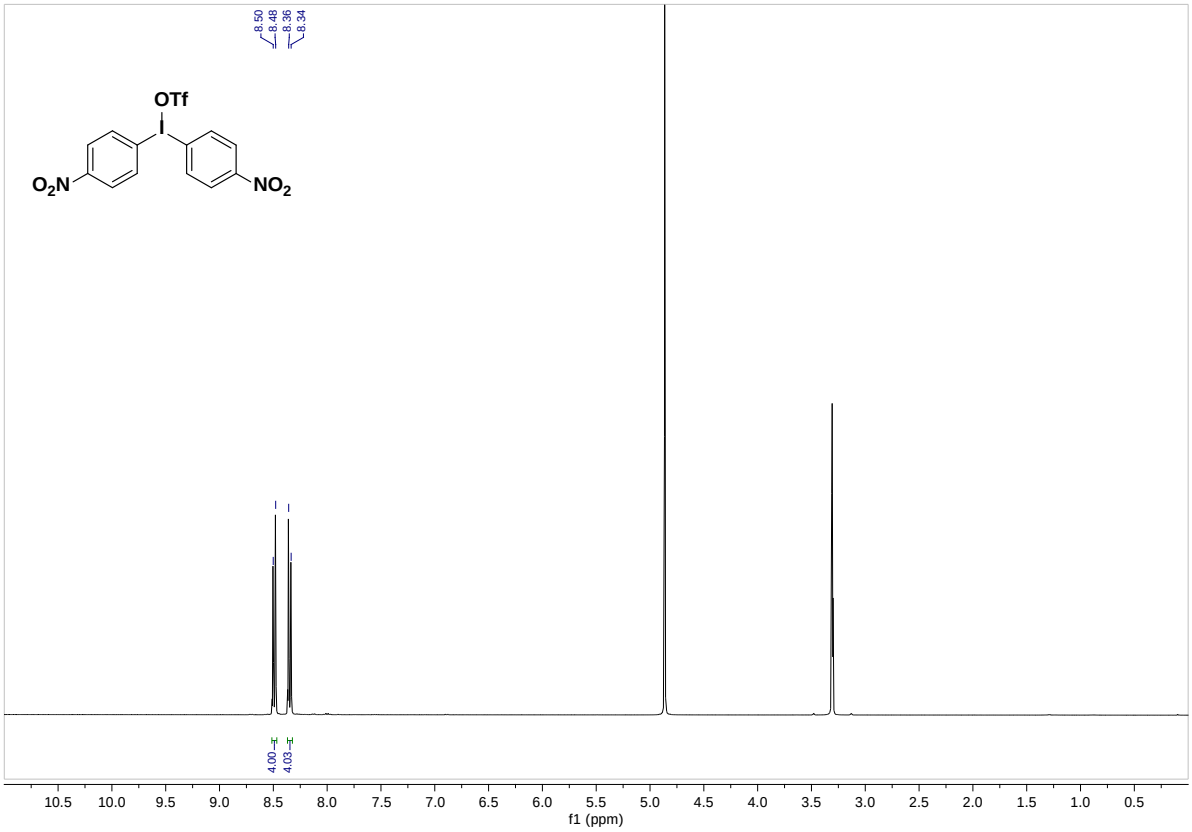
1-(Benzoxazol-2-yl)-1-(6-chloropyridin-3-yl)ethanol

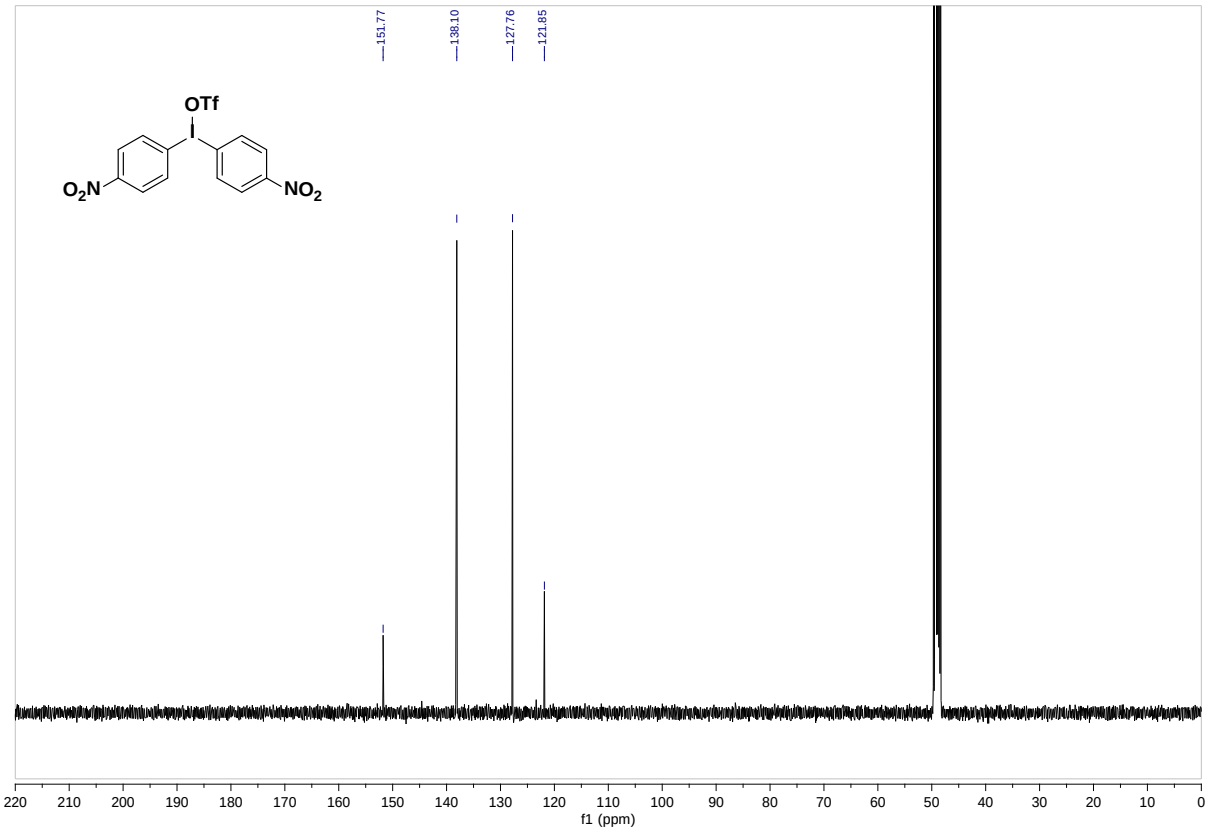


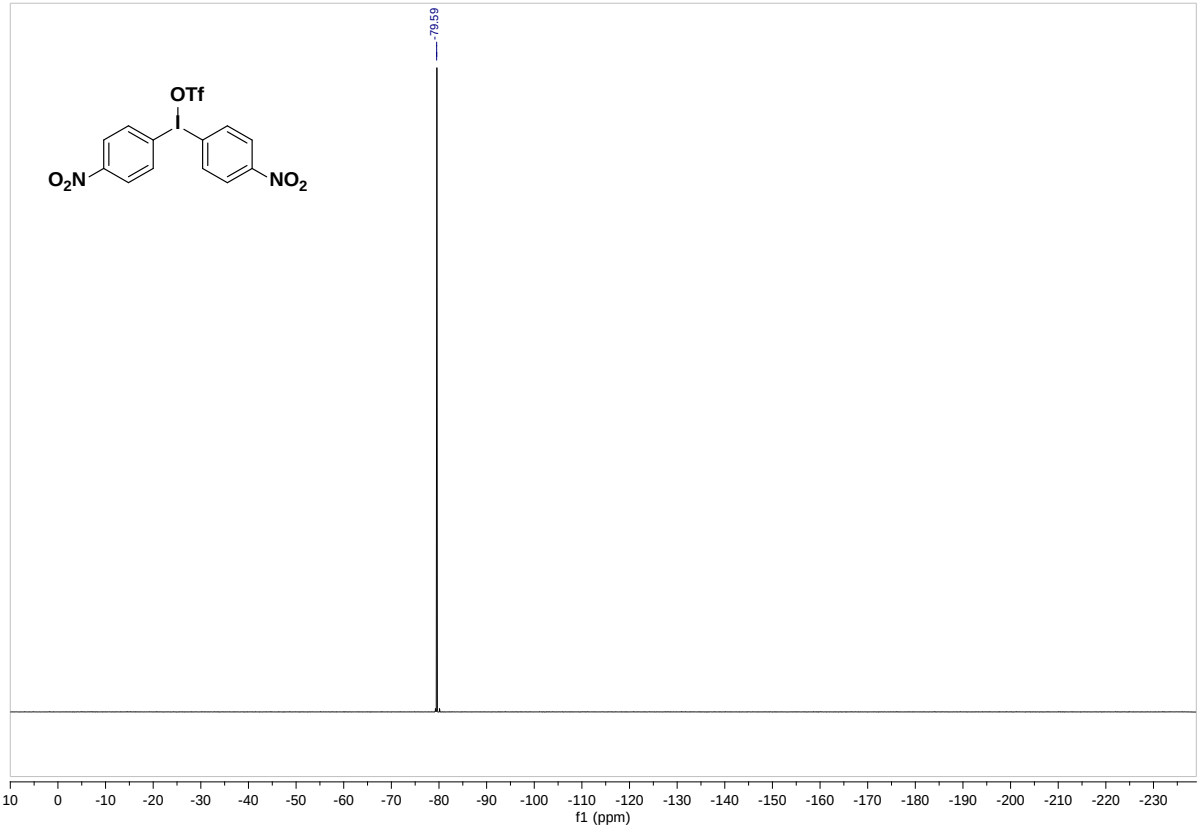
To ketone **4t** (52 mg, 0.2 mmol) in THF (1.0 mL) at 0 °C was added MeMgBr (373 μL, 0.22 mmol, 0.59 M in THF) and the mixture was stirred for 2 hours. The reaction mixture was quenched with NH_4Cl (4 mL, sat. aq.). The organic layer was separated and the aqueous layer

was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water (5 mL) and concentrated *in vacuo*. Flash chromatography on silica gel (40-60° petroleum ether/diethyl ether 3:1) provided the title compound (47 mg, 86%) as a colorless oil. R_f 0.21 (40-60° petroleum ether/diethyl ether 3:1); IR ν max (solid, cm^{-1}): 3292, 1564, 1455, 1367, 1242, 1131, 1107, 1087, 835, 766, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.73–7.68 (m, 1H), 7.53–7.47 (m, 1H), 7.38–7.32 (m, 2H), 7.30 (dd, *J* = 8.4, 0.5 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 151.3, 151.2, 147.3, 140.2, 138.3, 136.4, 125.9, 125.1, 124.1, 120.4, 111.1, 72.1, 29.0; HRMS (ESI) calculated for $C_{14}H_{12}N_2O_2Cl$ $[M + H]^+$ m/z 275.0582, found 275.0587.

5. ^{1}H and ^{13}C NMR spectra



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NO2
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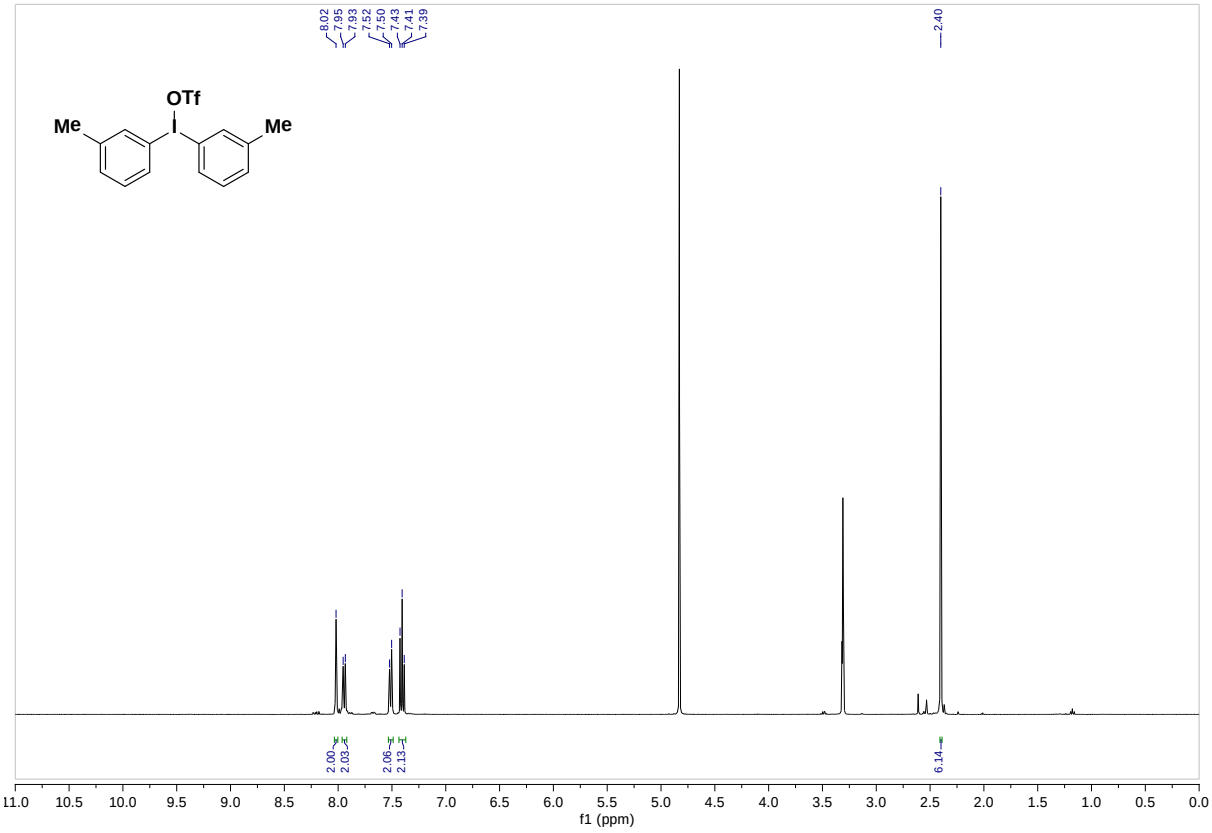
f1 (ppm)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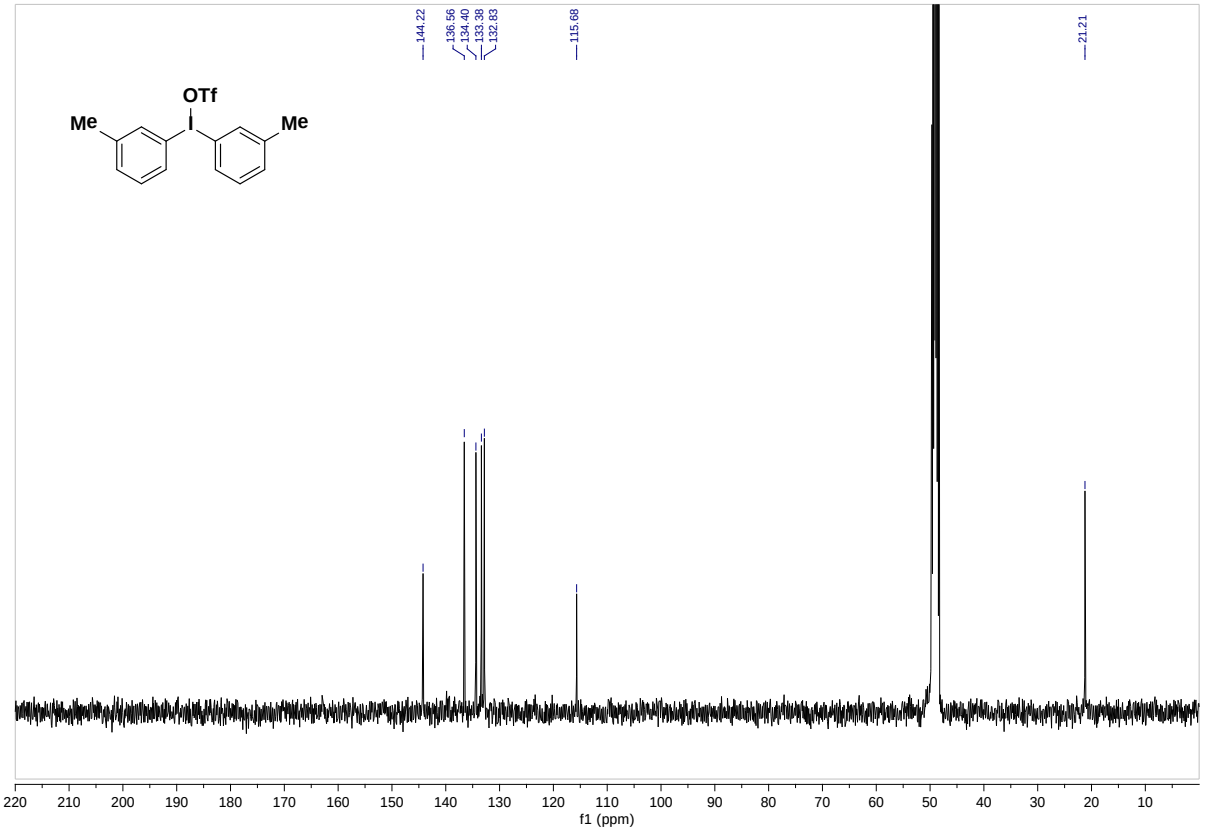
f1 (ppm)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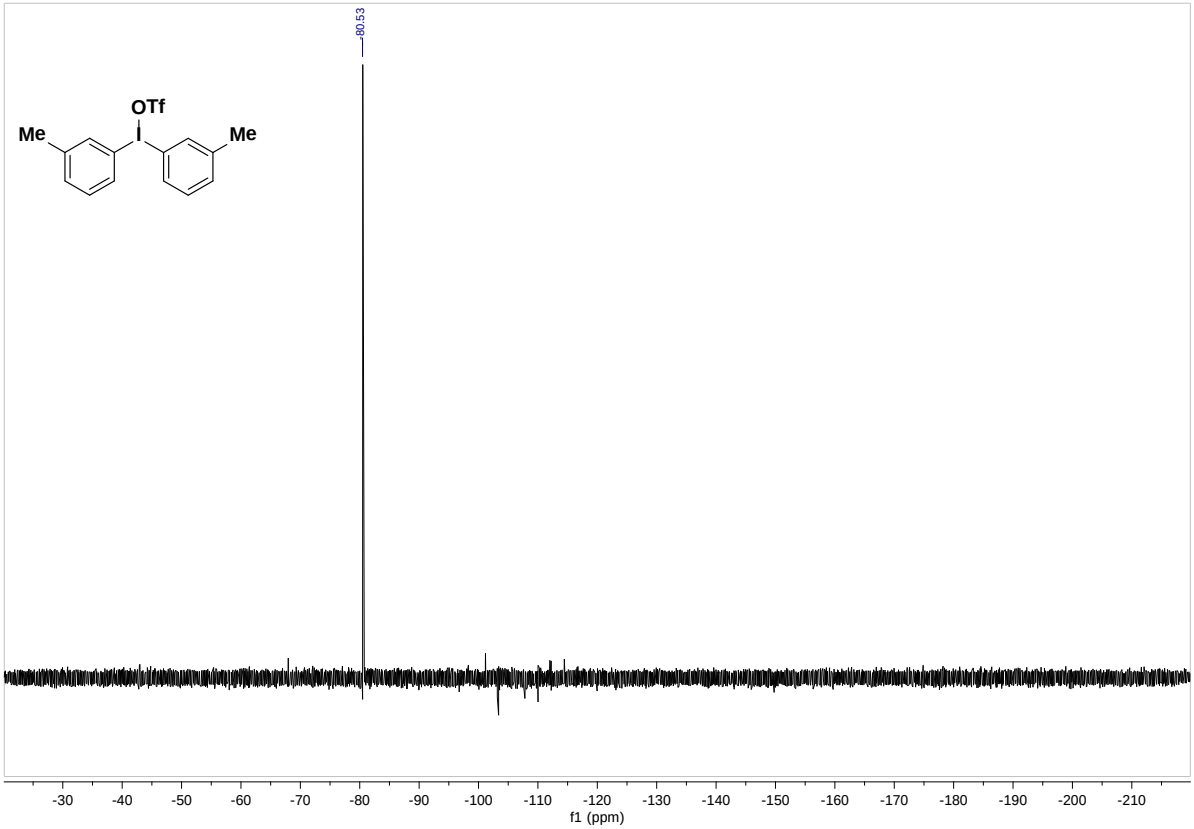
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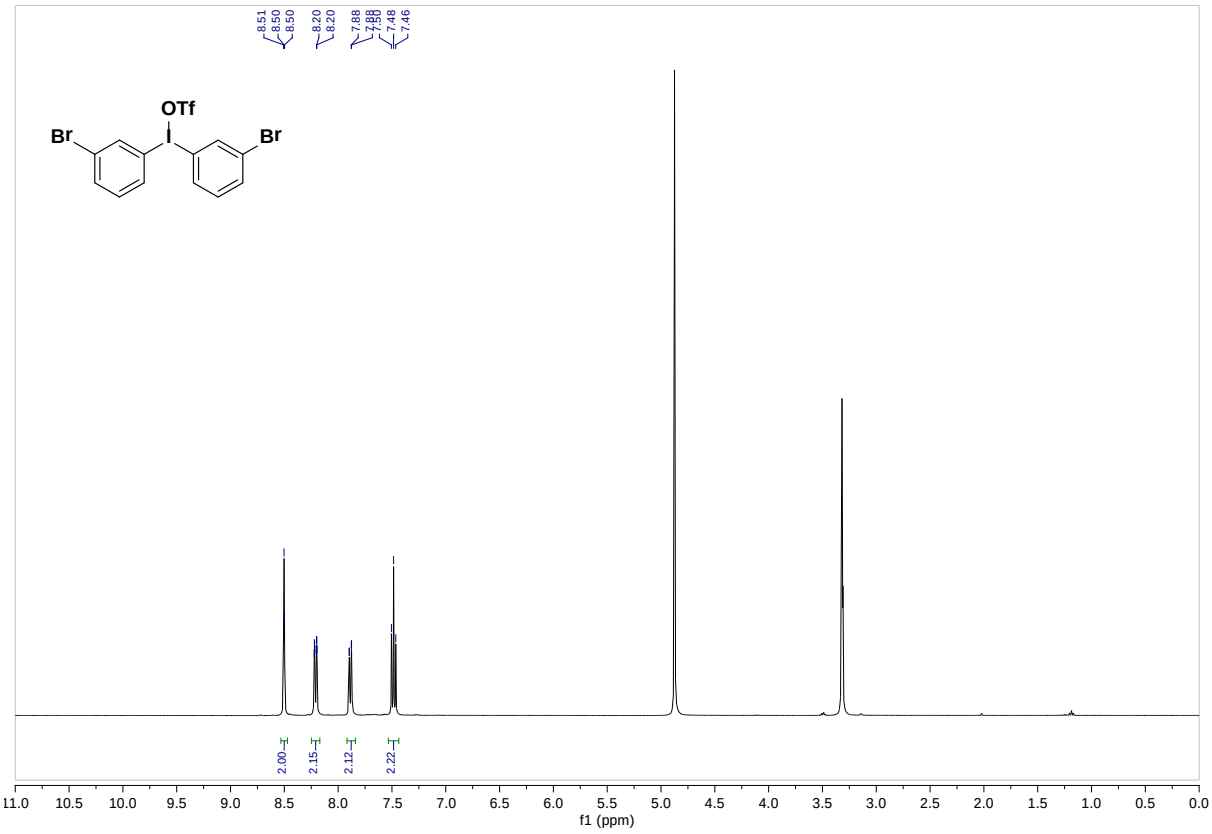
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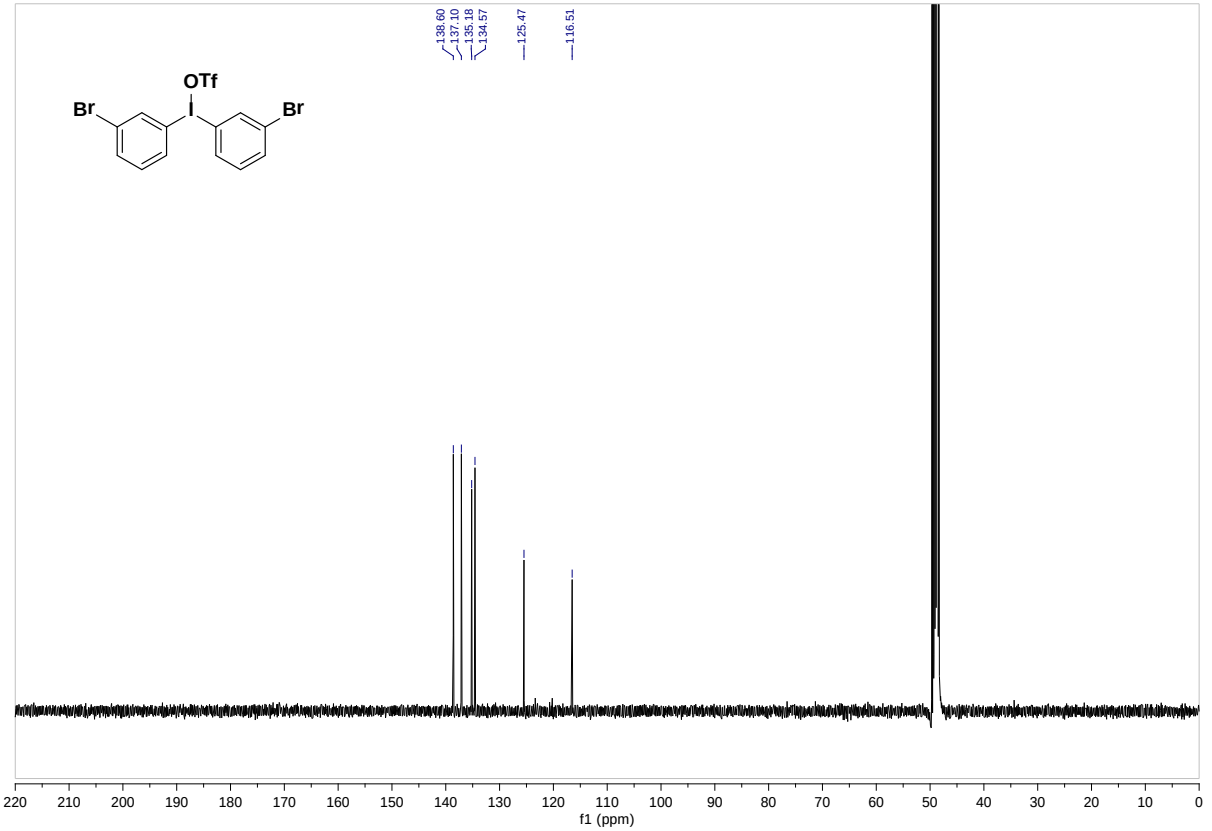
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137.10
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116.51
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Br
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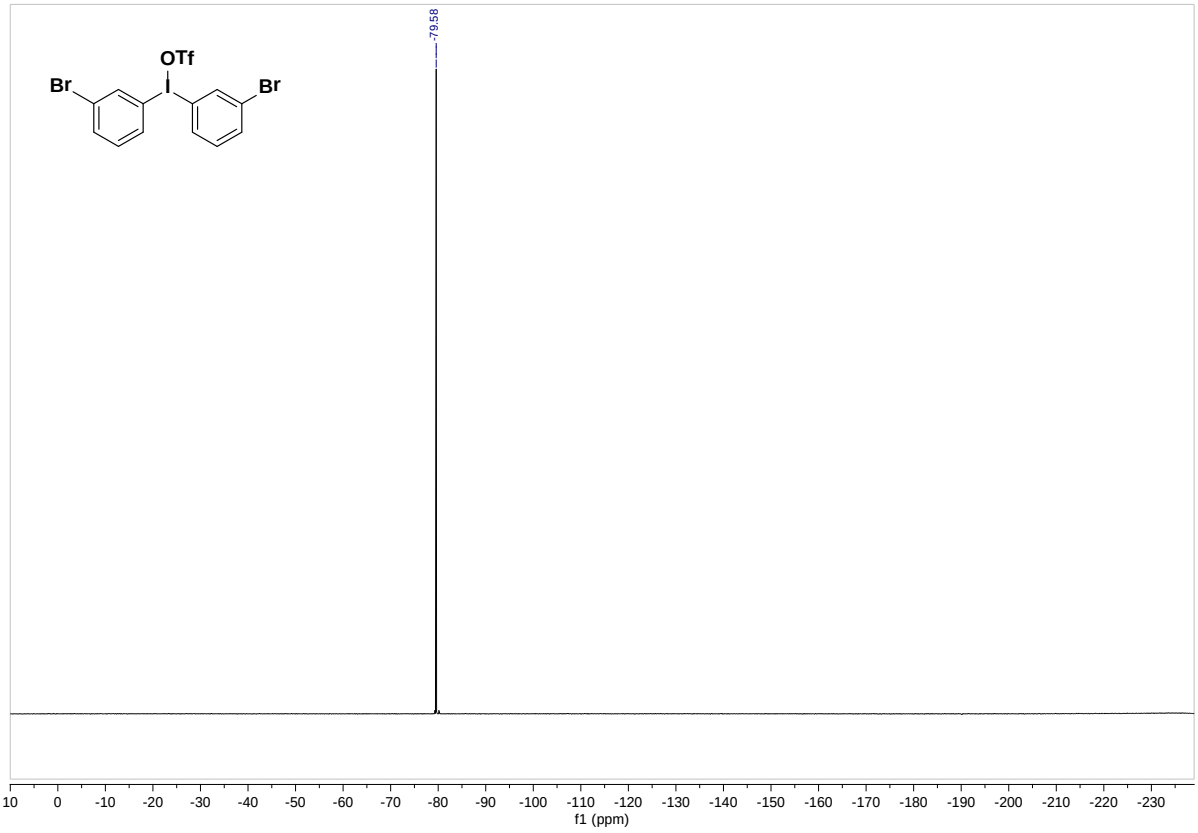
f1 (ppm)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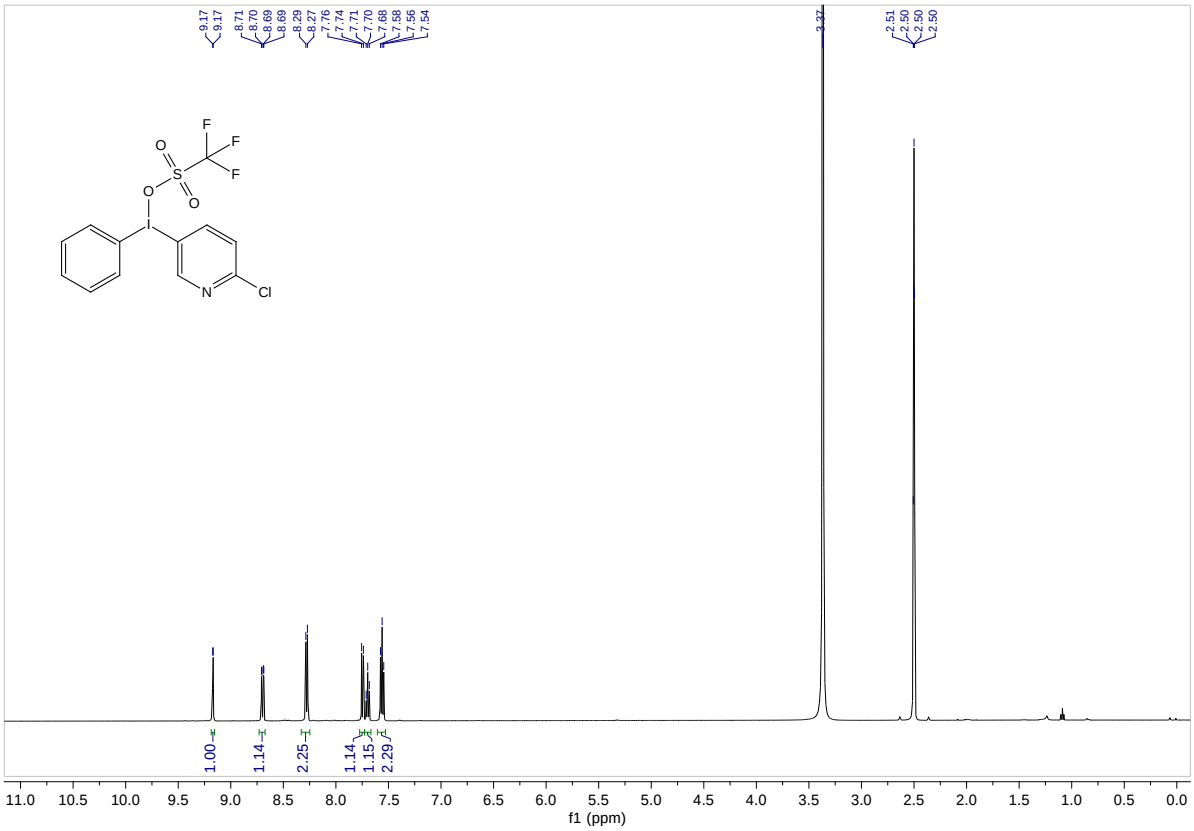
f1 (ppm)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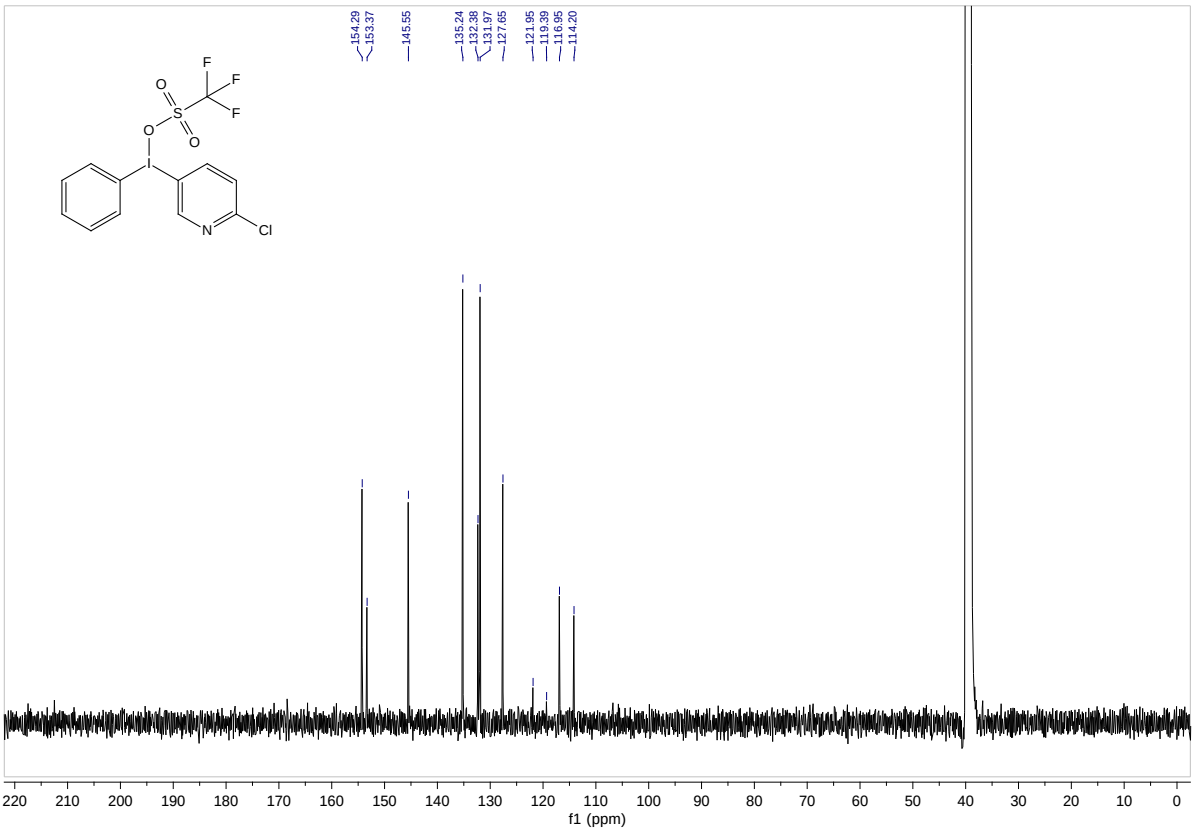
f1 (ppm)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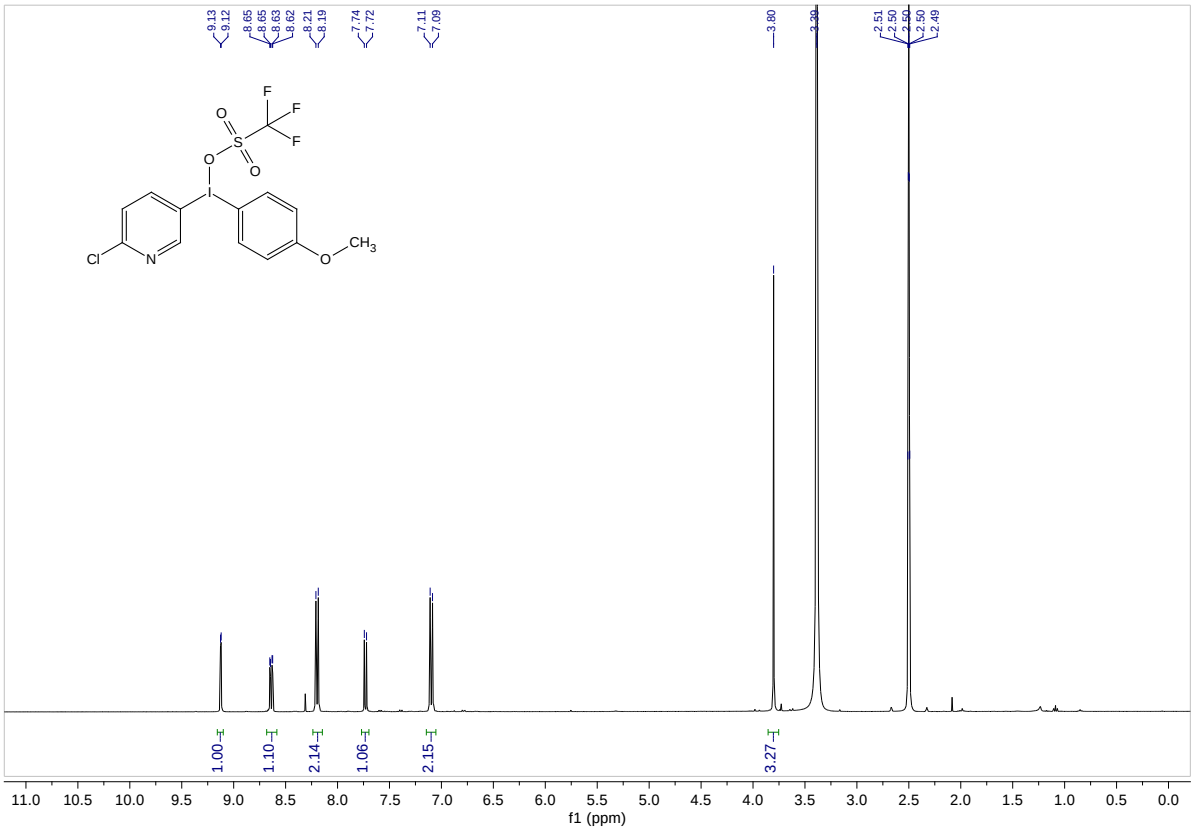
f1 (ppm)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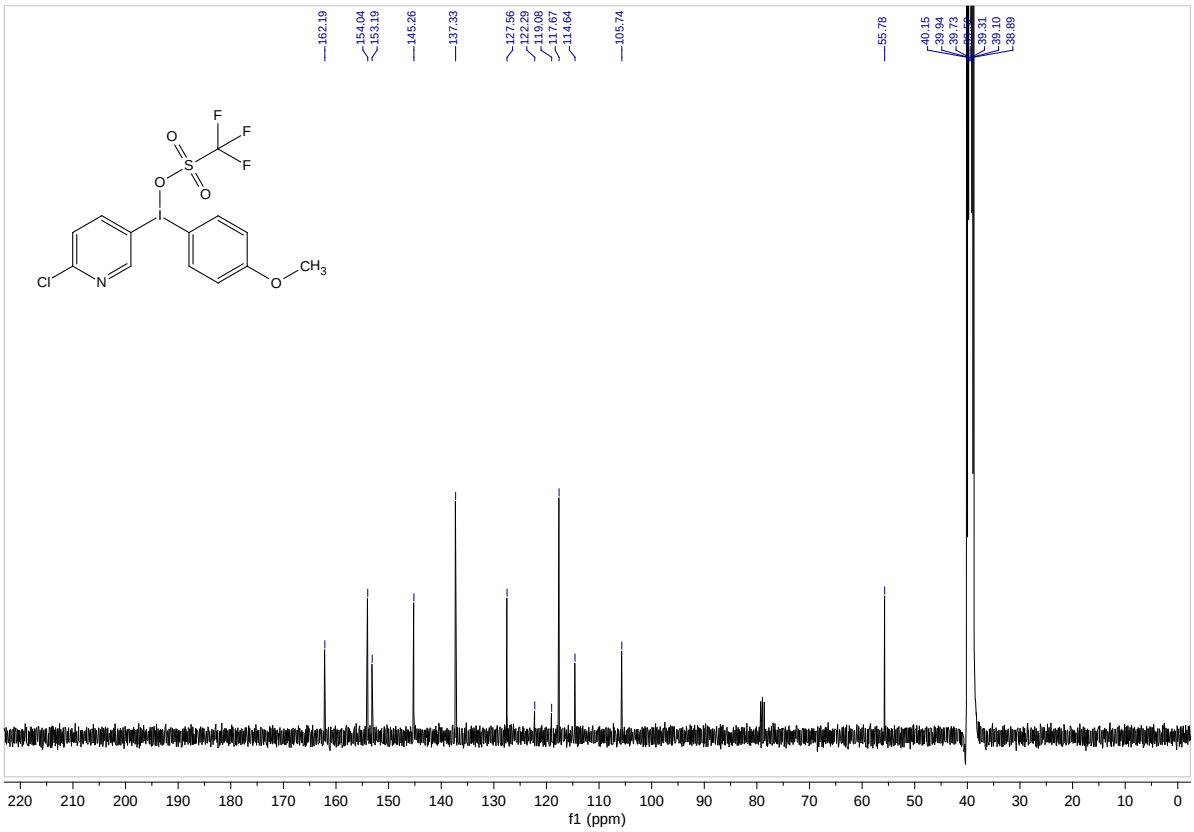
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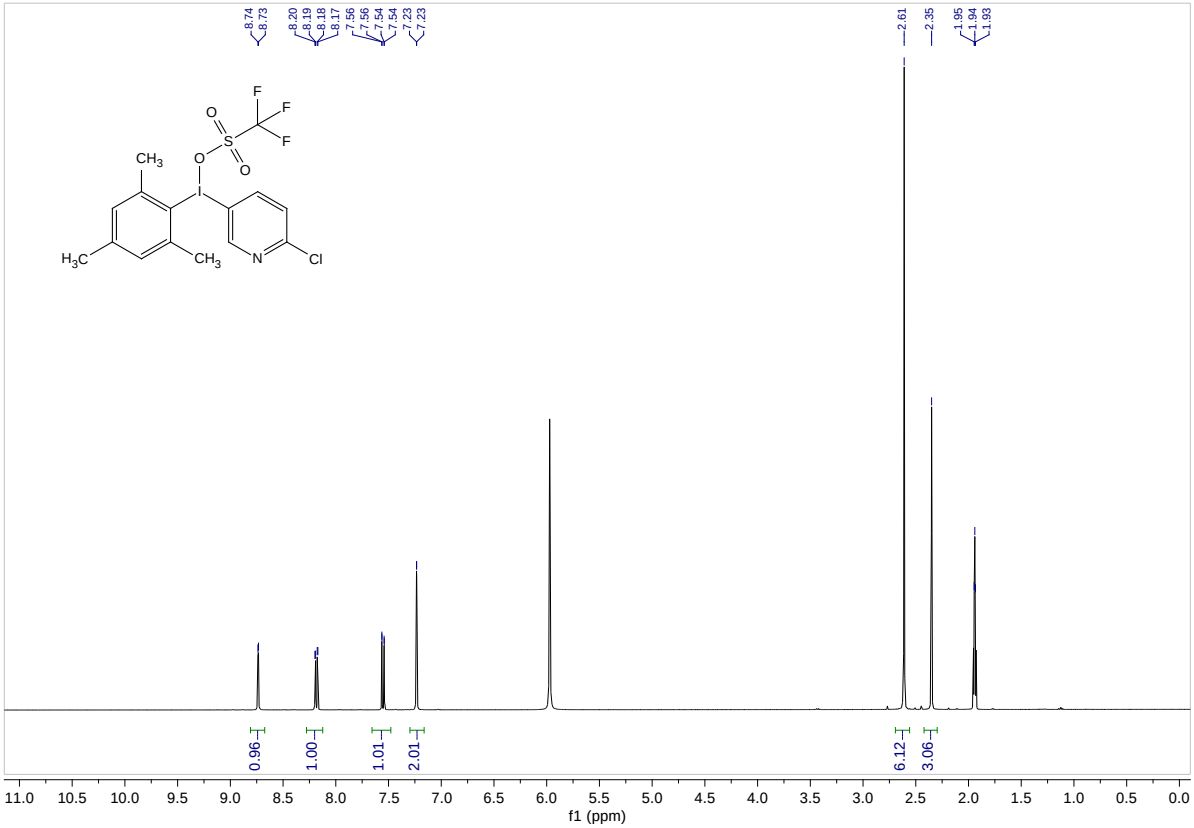
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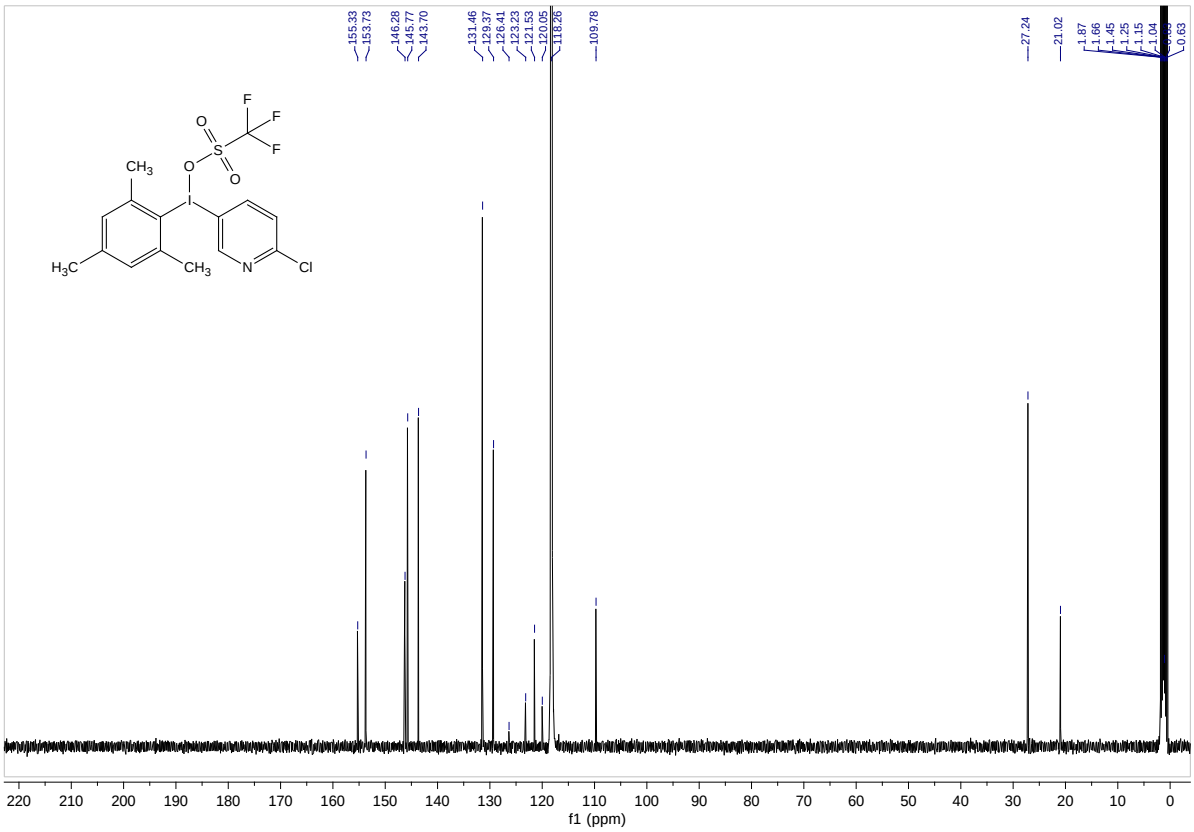
2.35
1.95
1.94
1.93
0.96
1.00
1.01
2.01
6.12
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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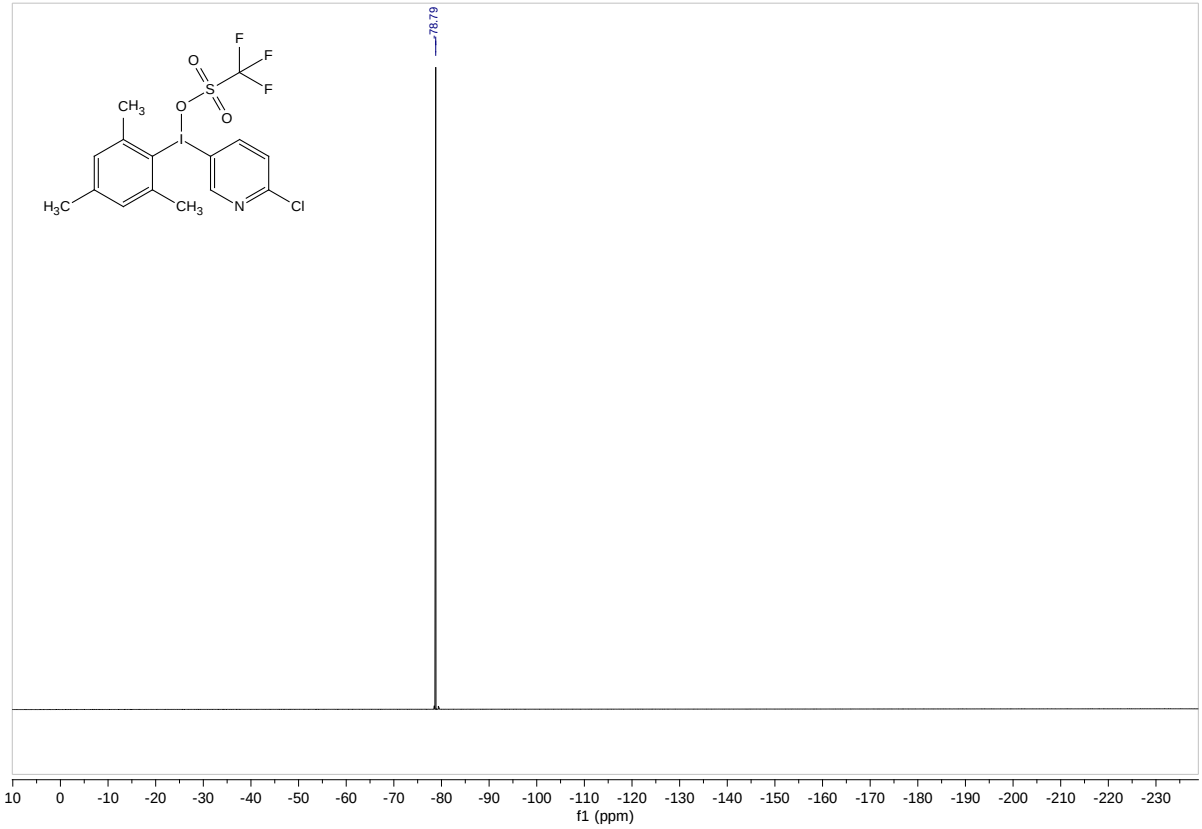
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S
O
O
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H3C
CH3
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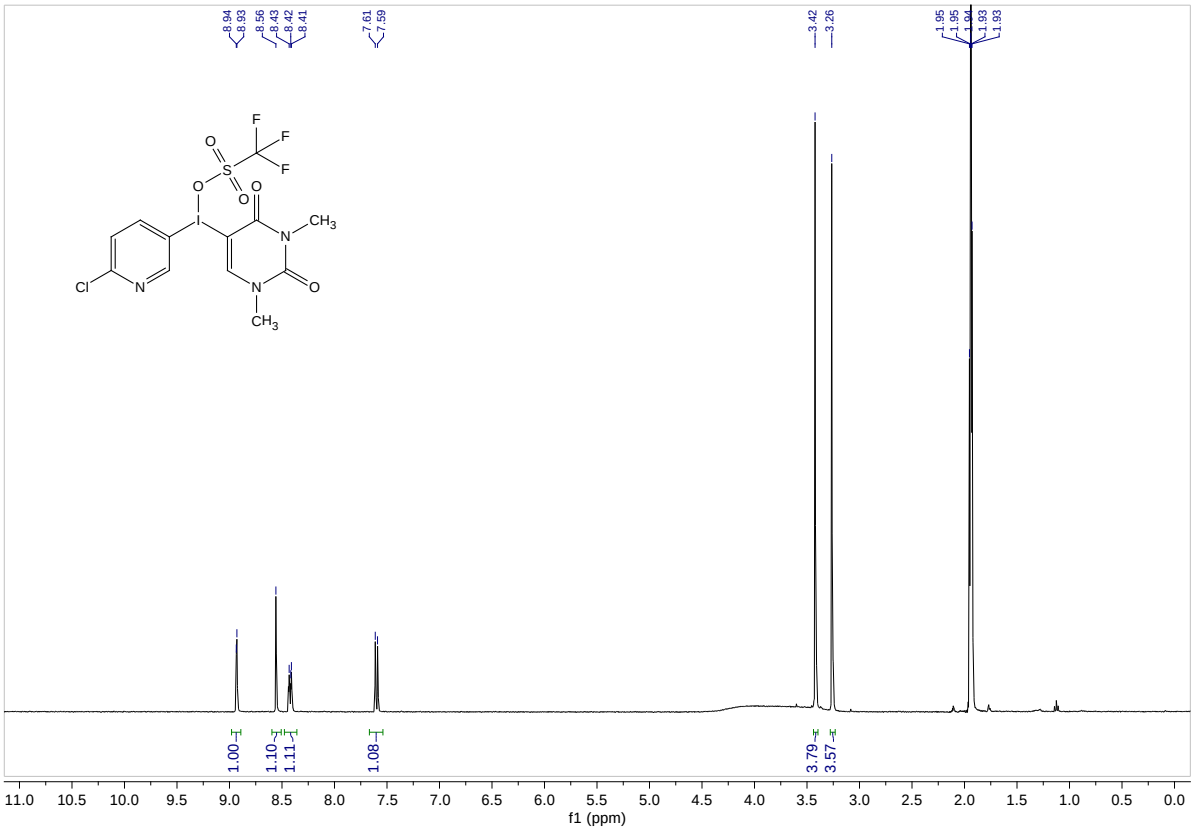
f1 (ppm)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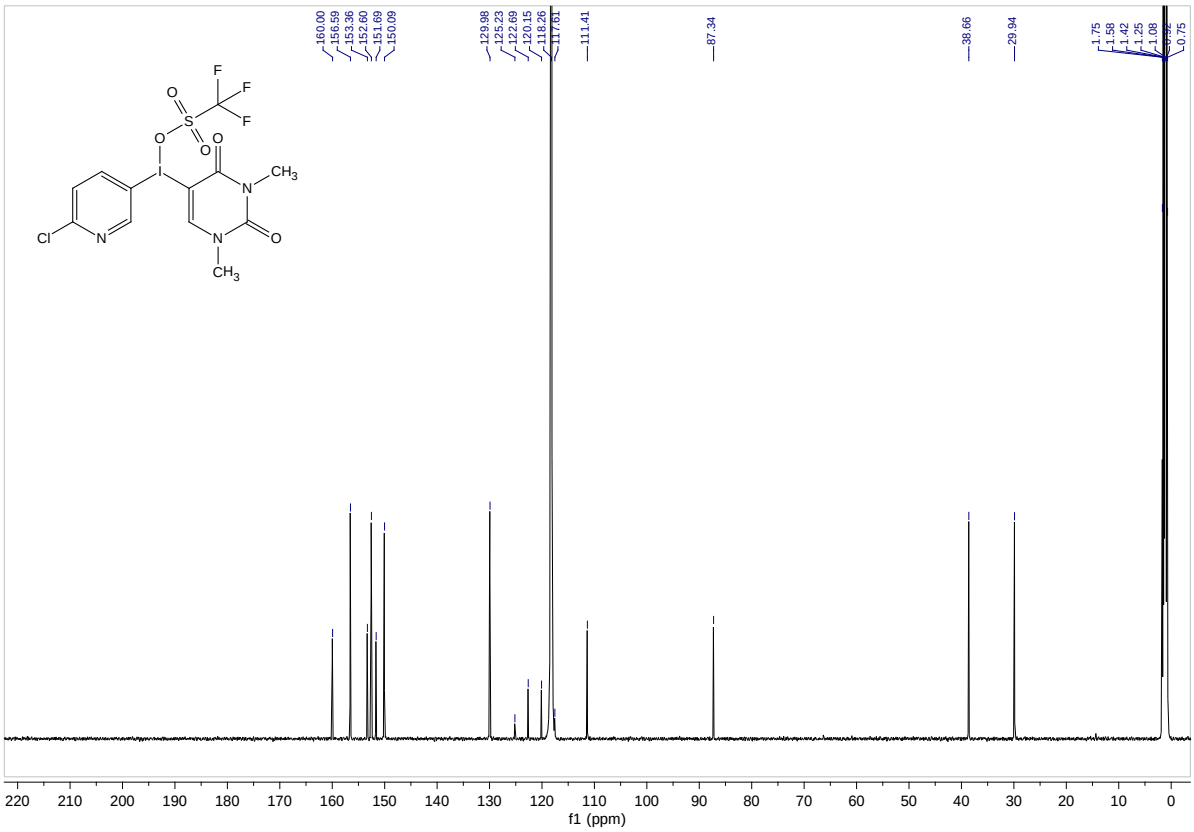
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38.66
29.94
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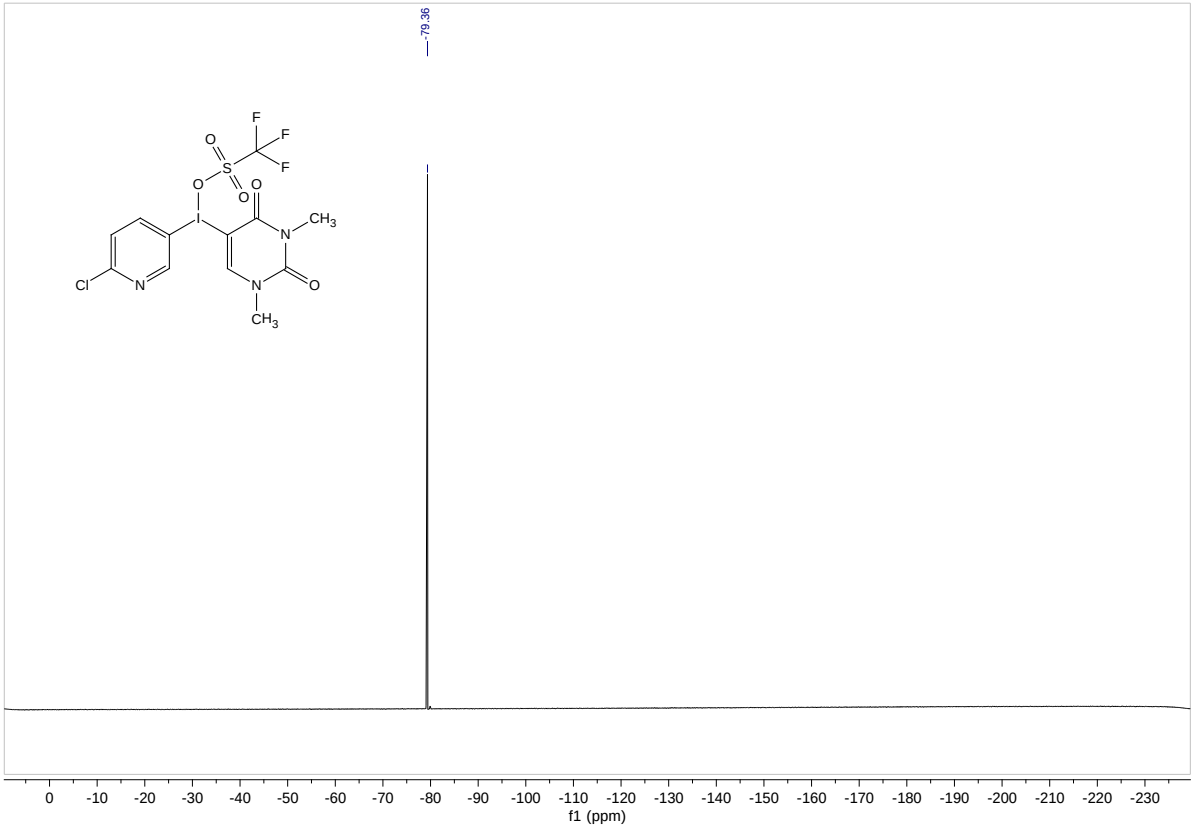
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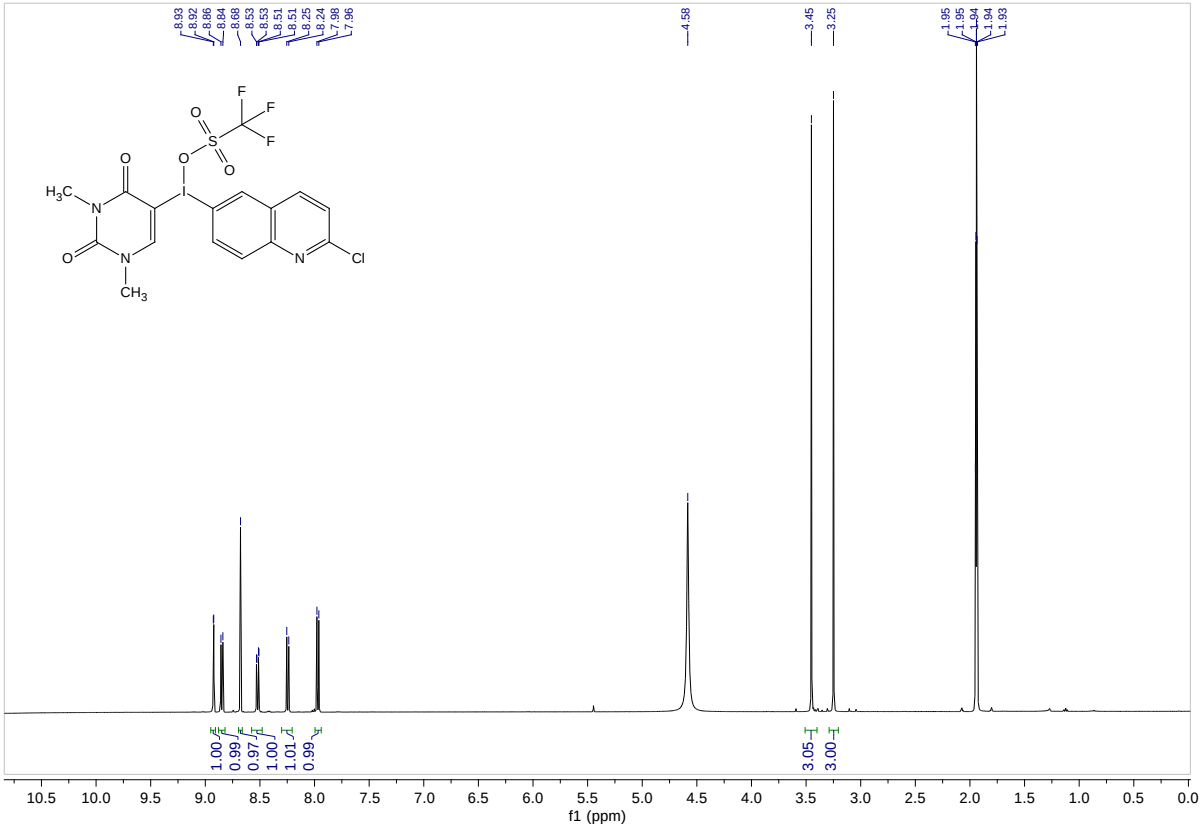
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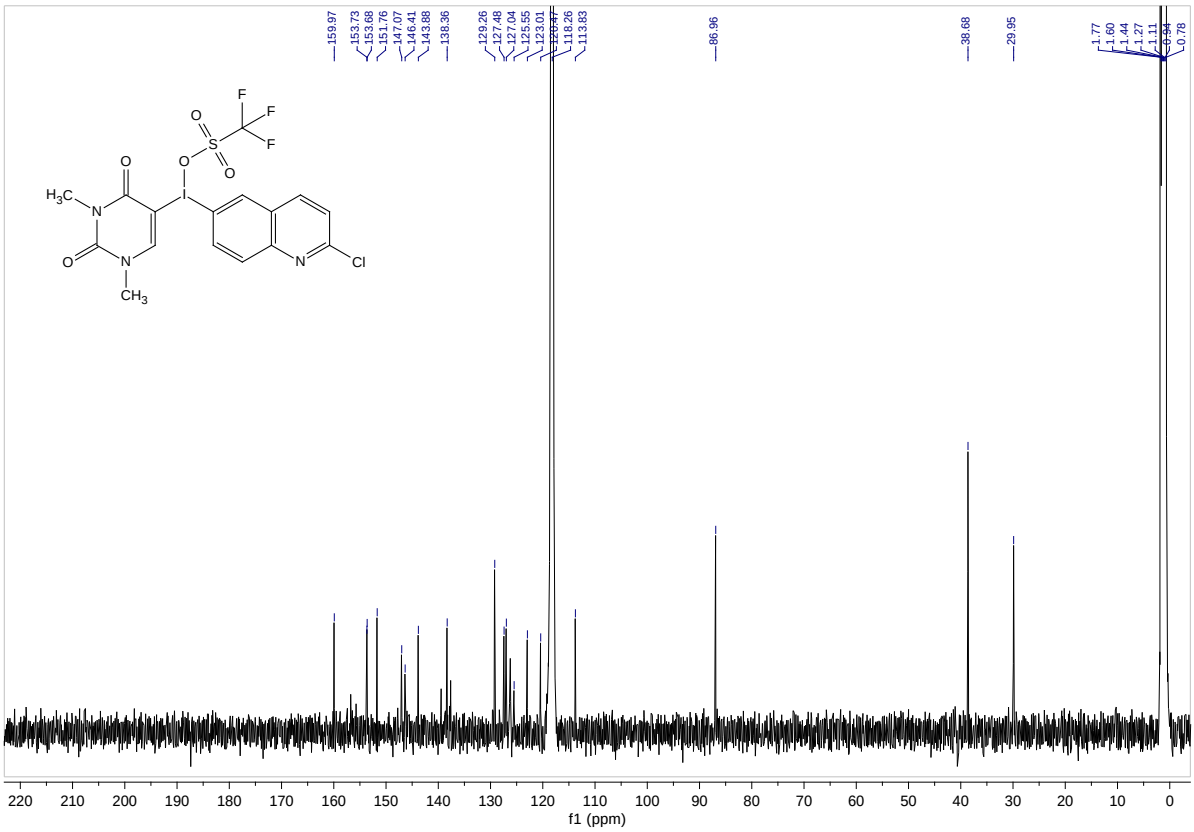
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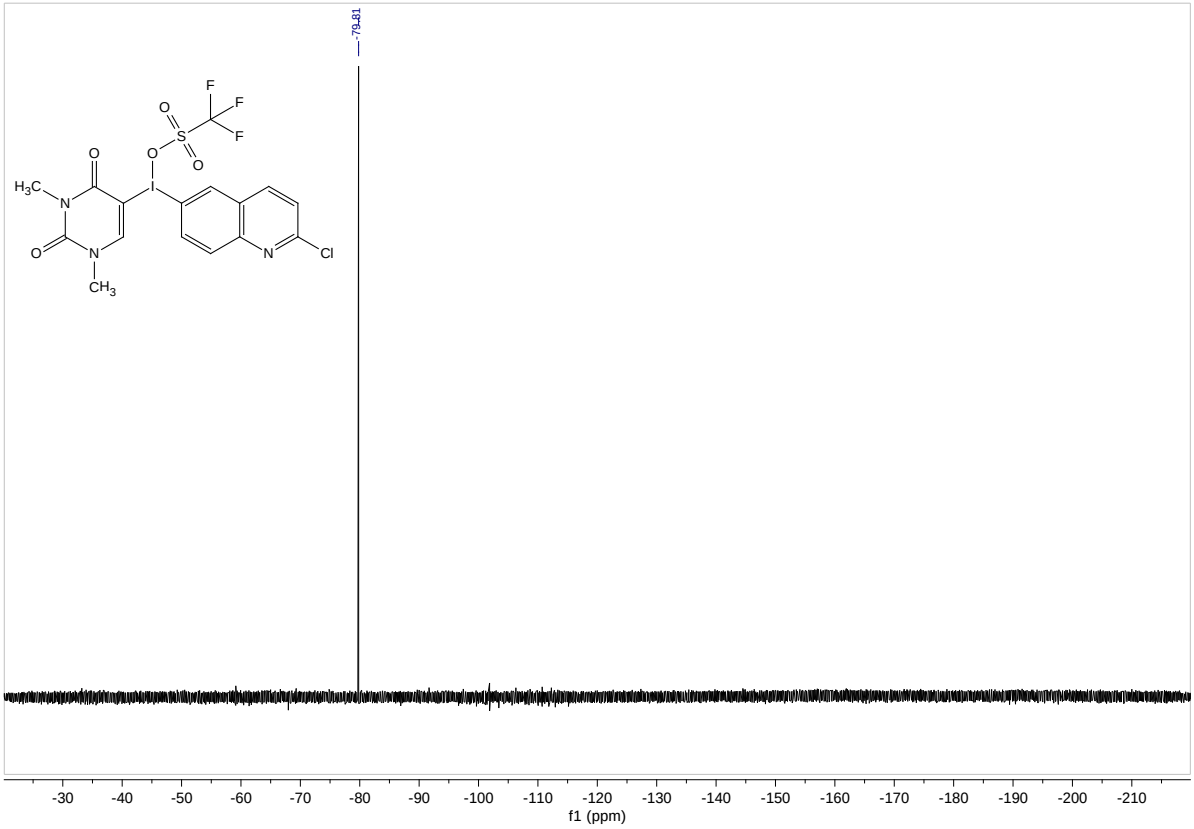
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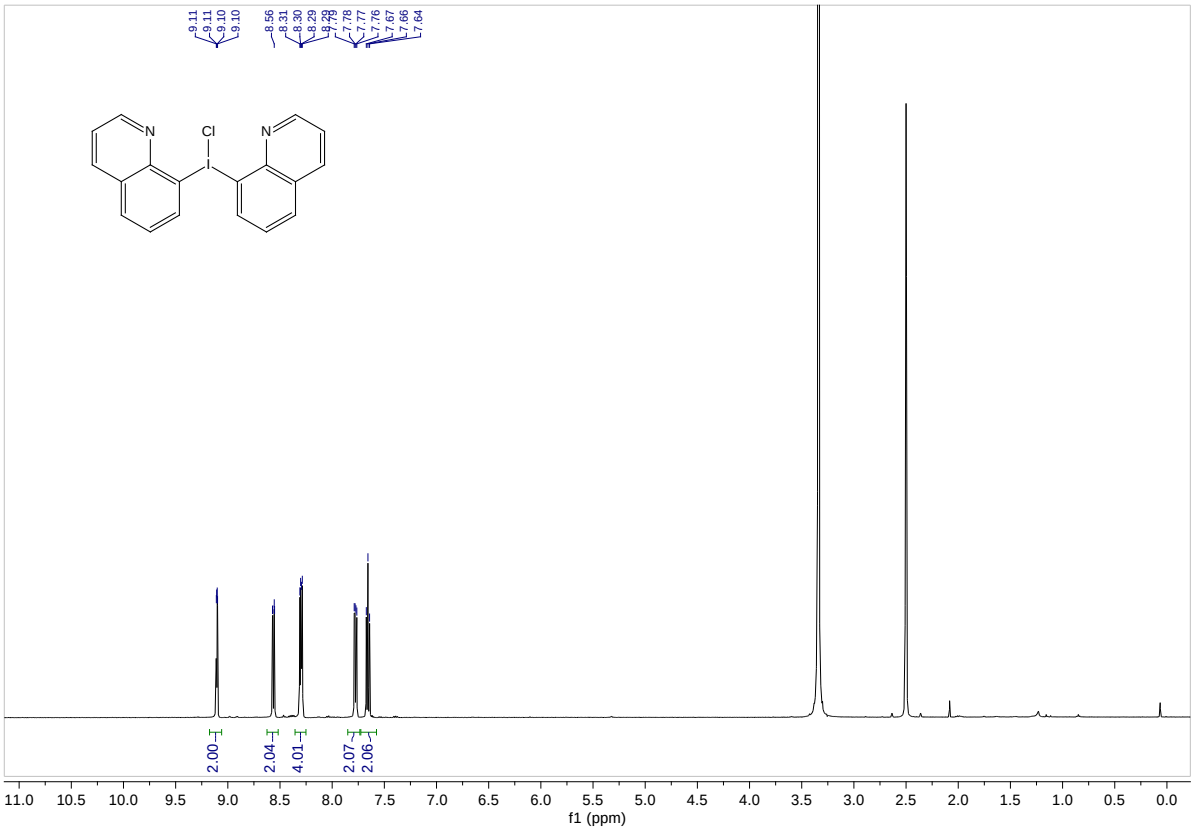
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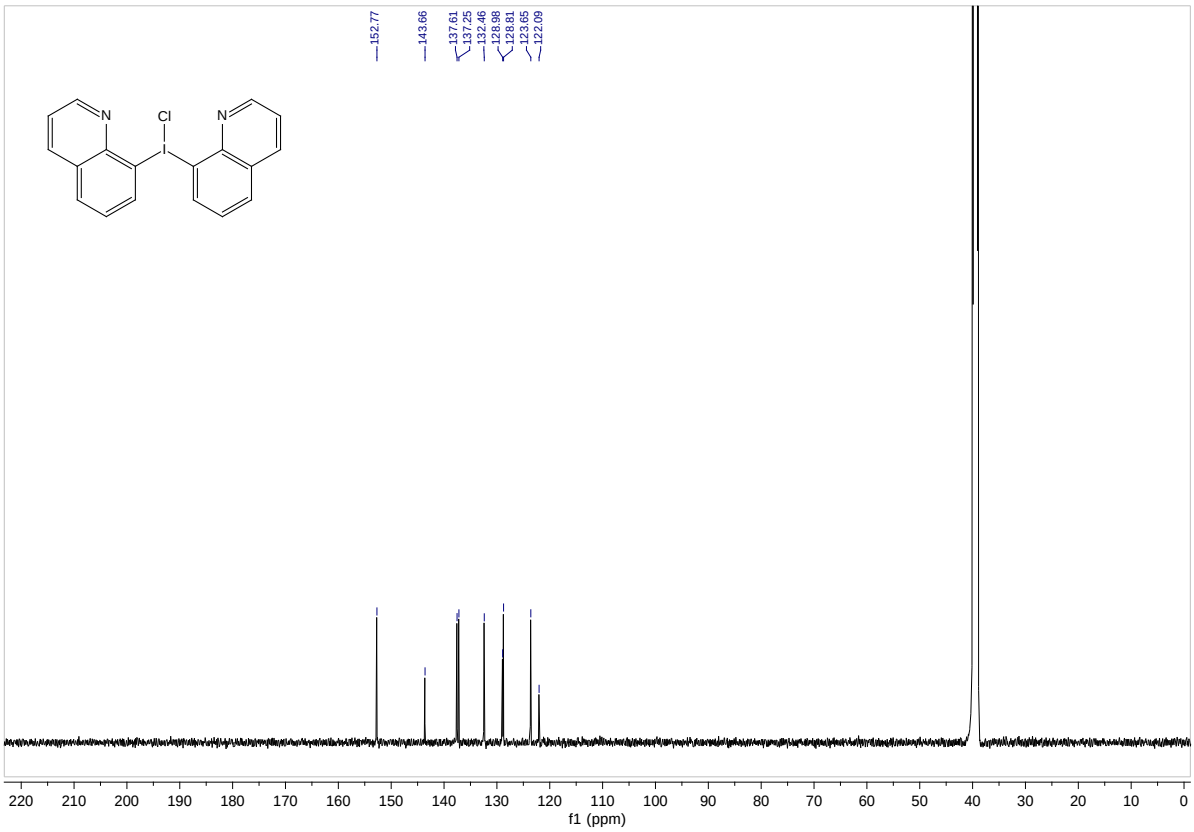
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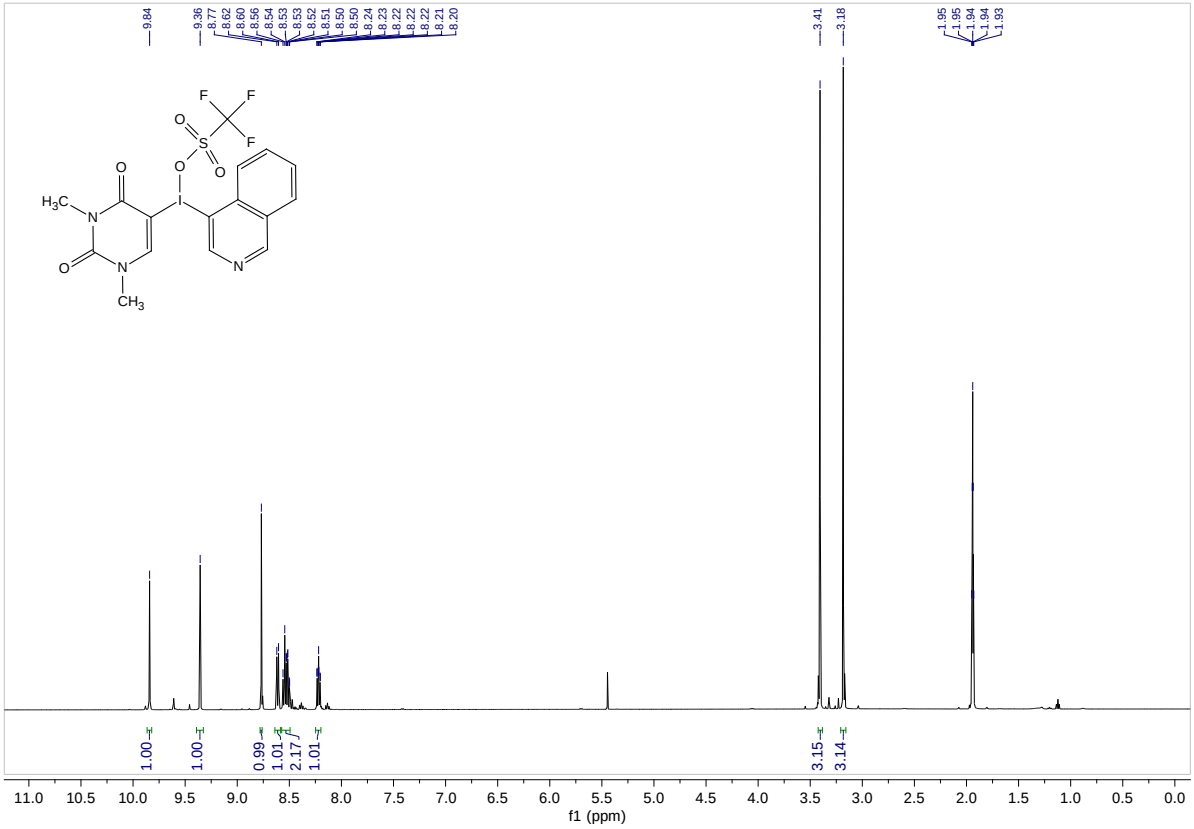
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1.94
1.94
1.93
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1.00
0.99
1.01
2.17
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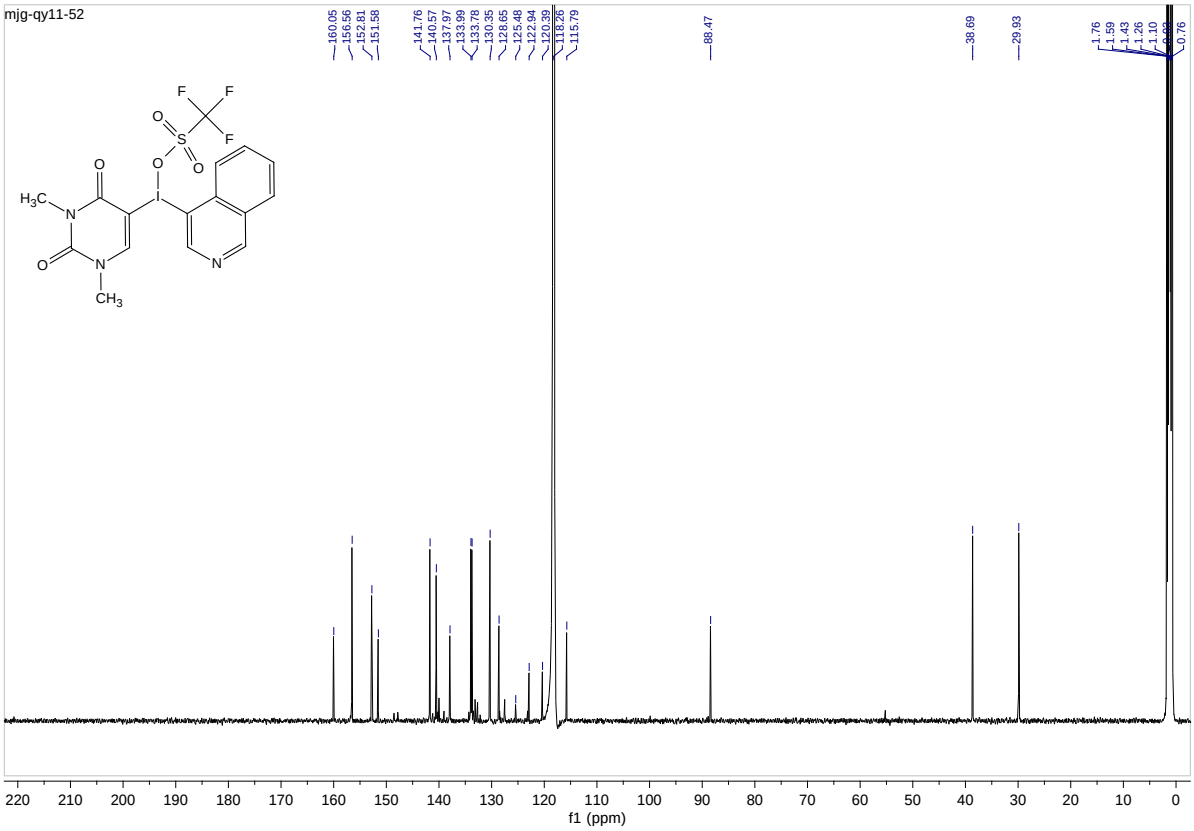
f1 (ppm)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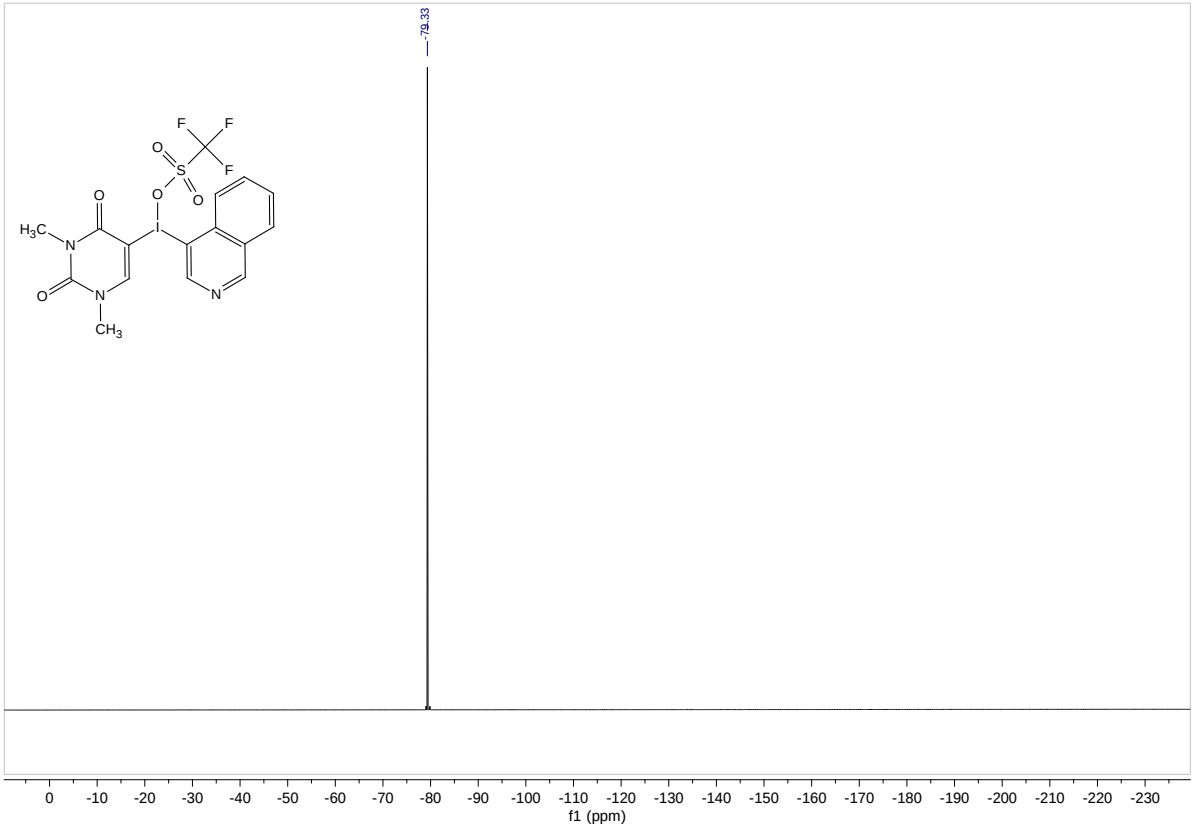
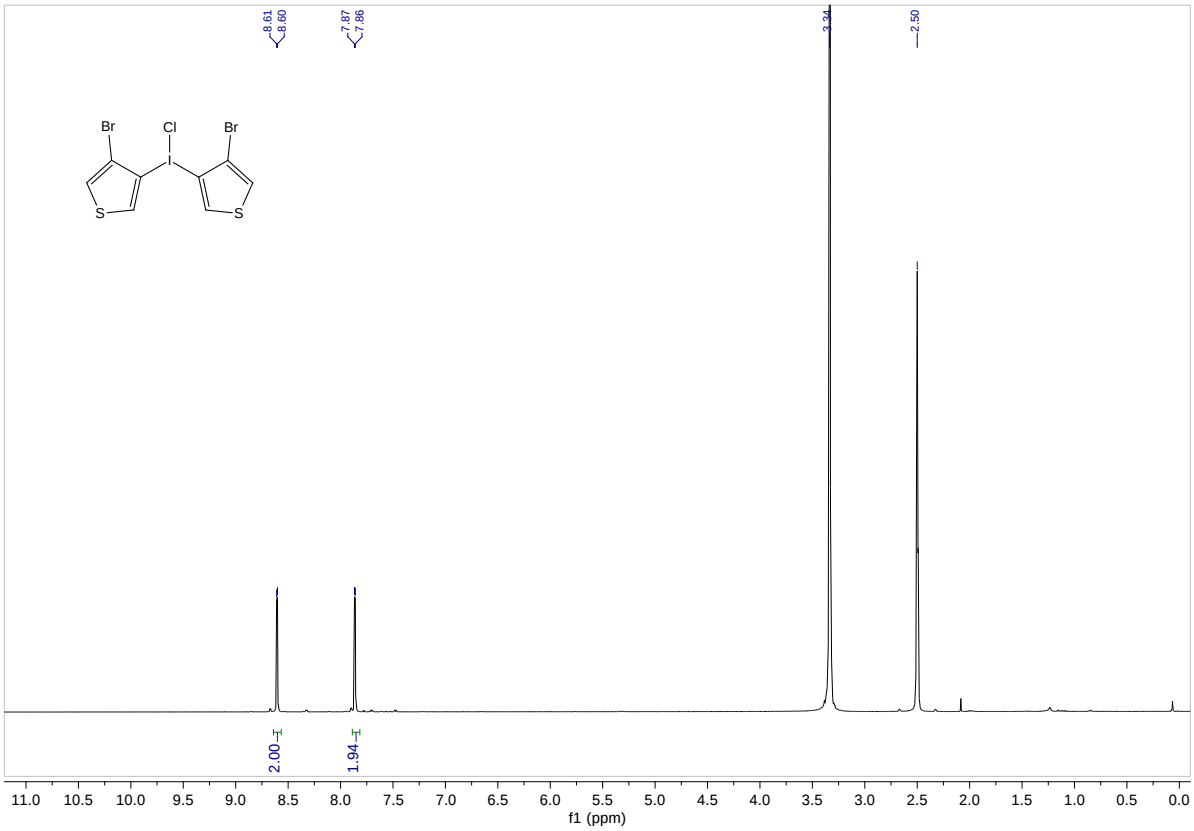
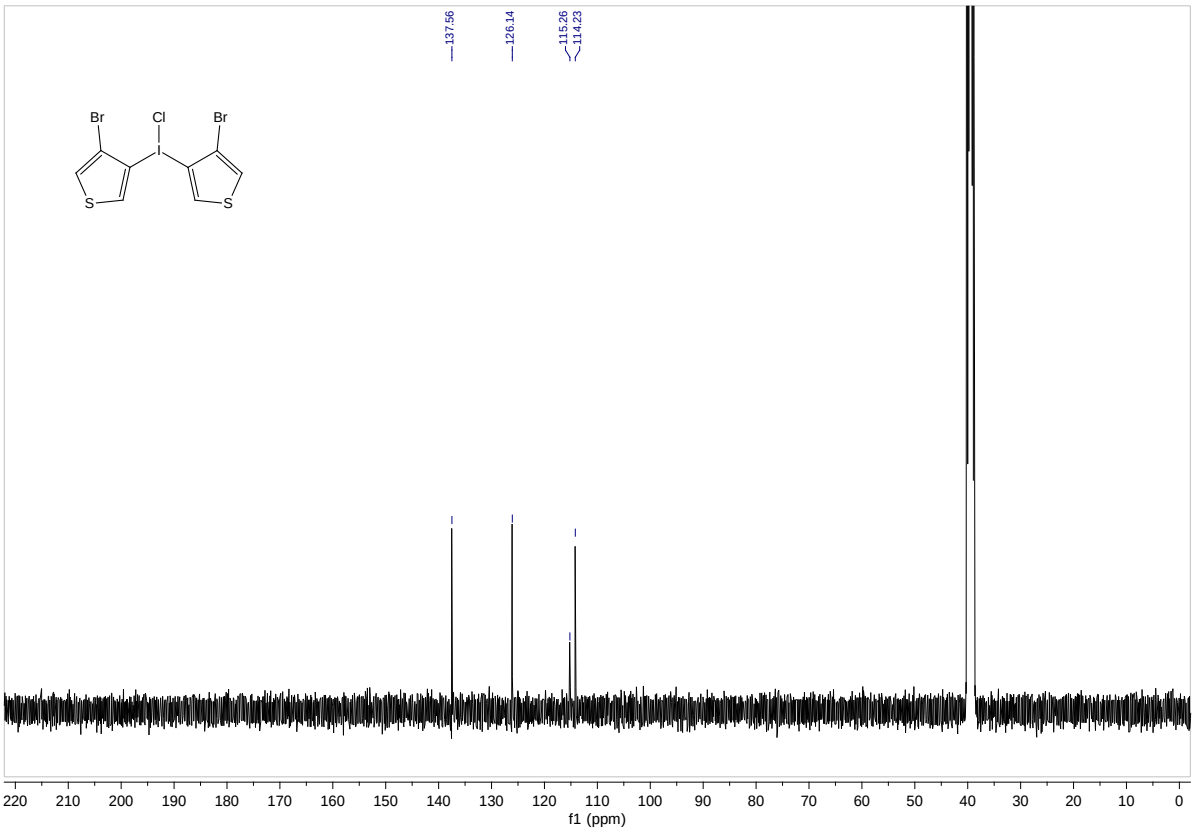
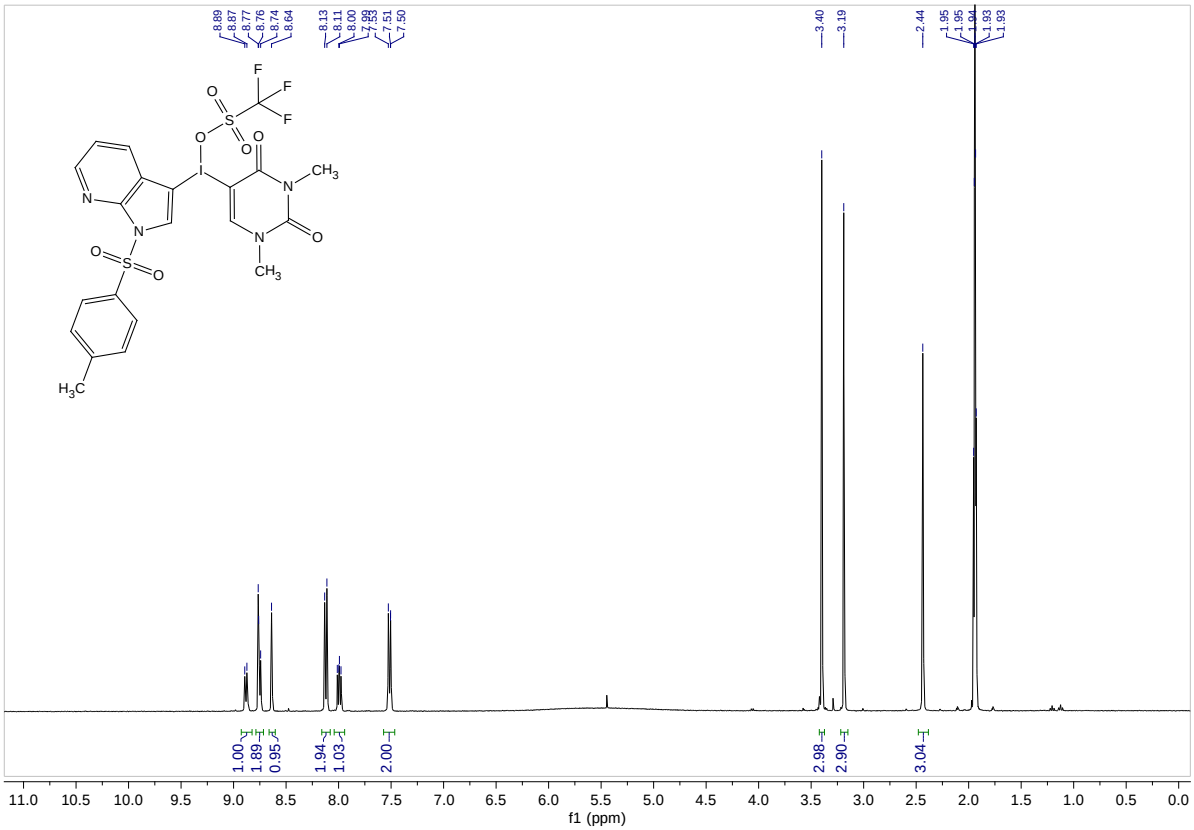
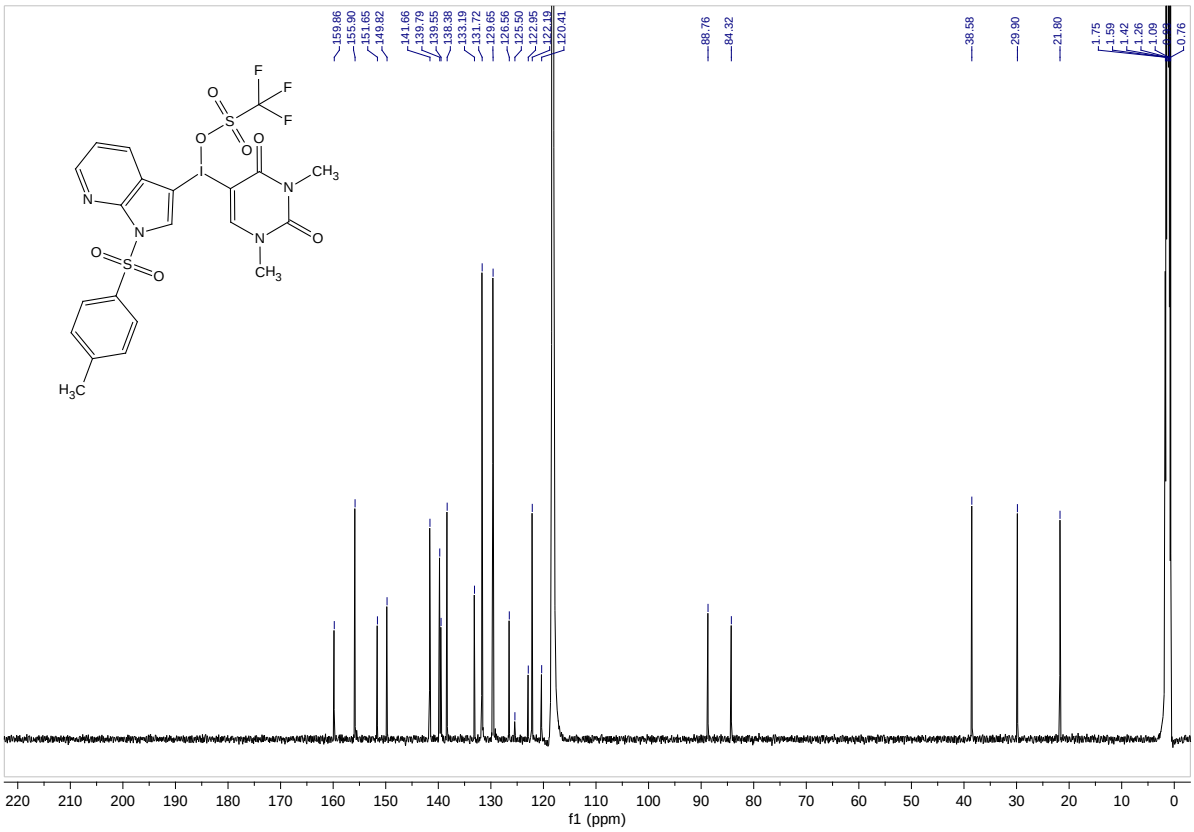
118.26
115.79
88.47
38.69
29.93
1.76
1.59
1.43
1.26
1.10
0.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

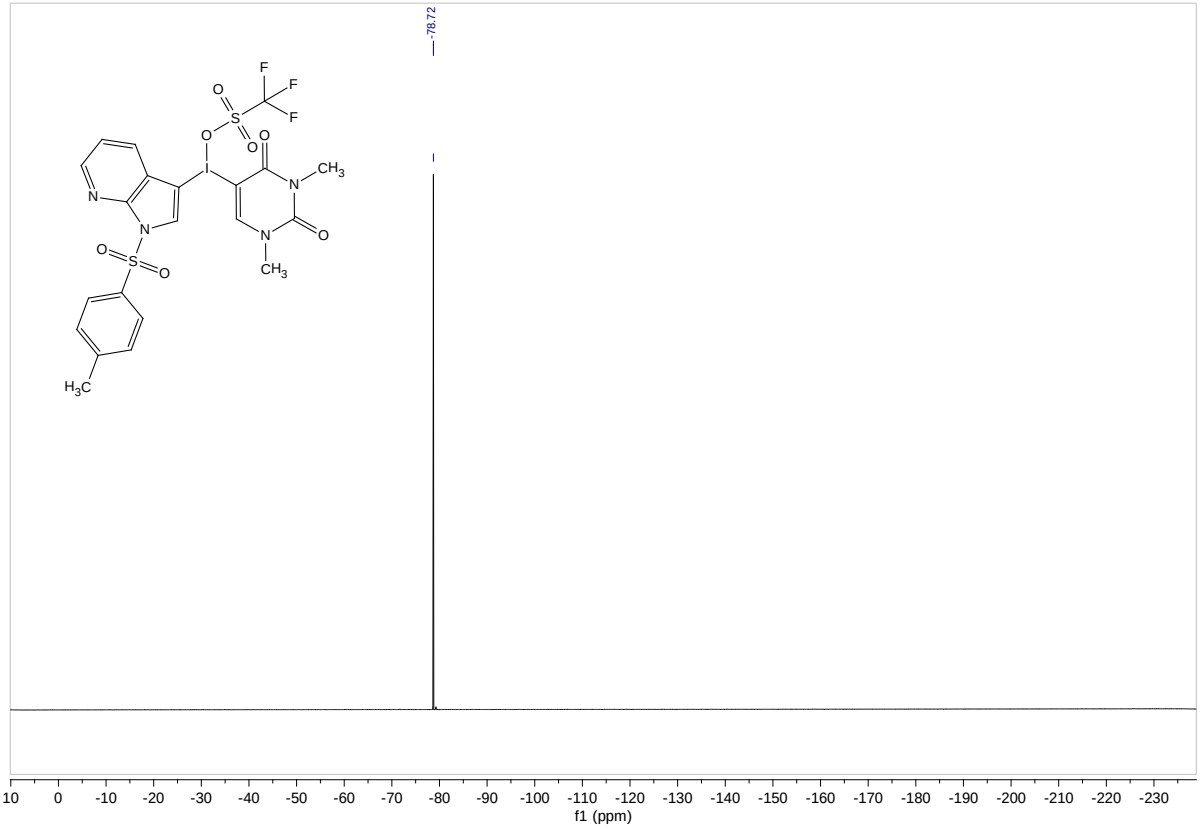

-79.33
F
F
F
O
S
O
O
O
I
H3C
N
O
N
CH3
N
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

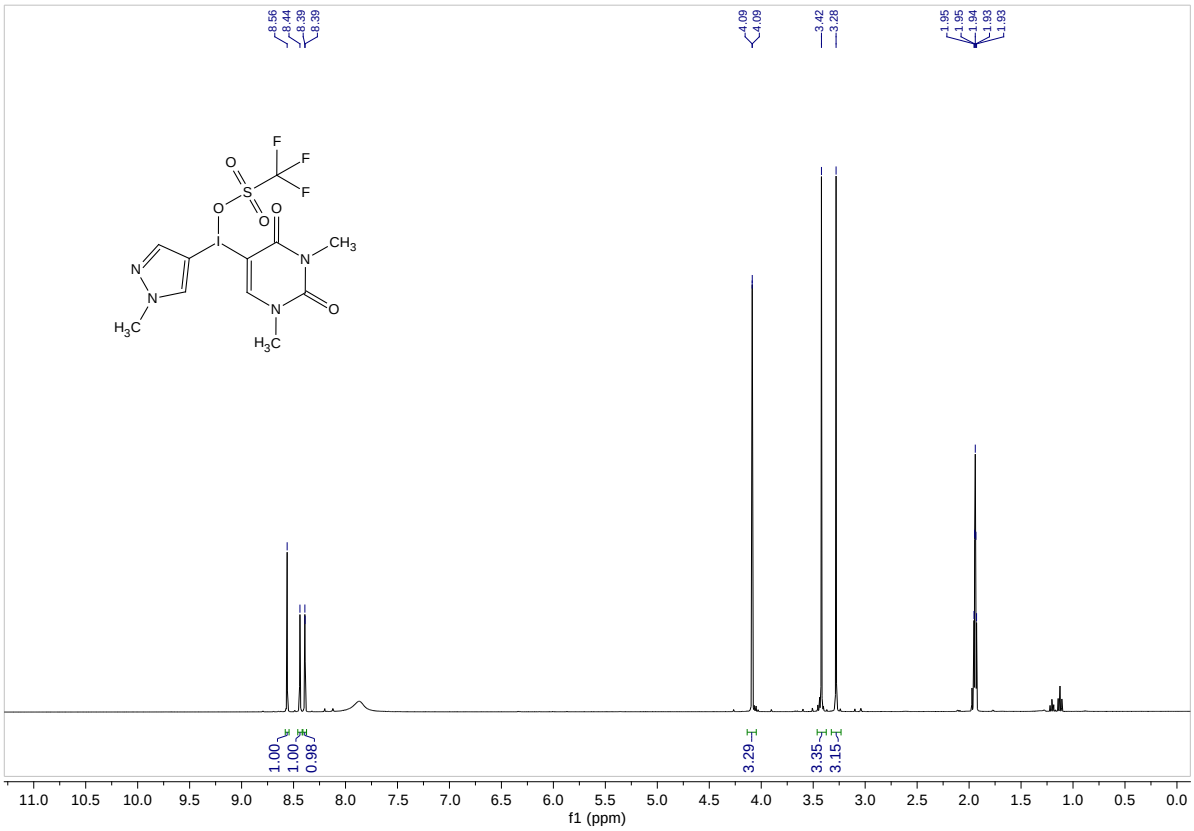

8.61
8.60
7.87
7.86
3.34
2.50
Br
Cl
Br
S
S
2.00
1.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

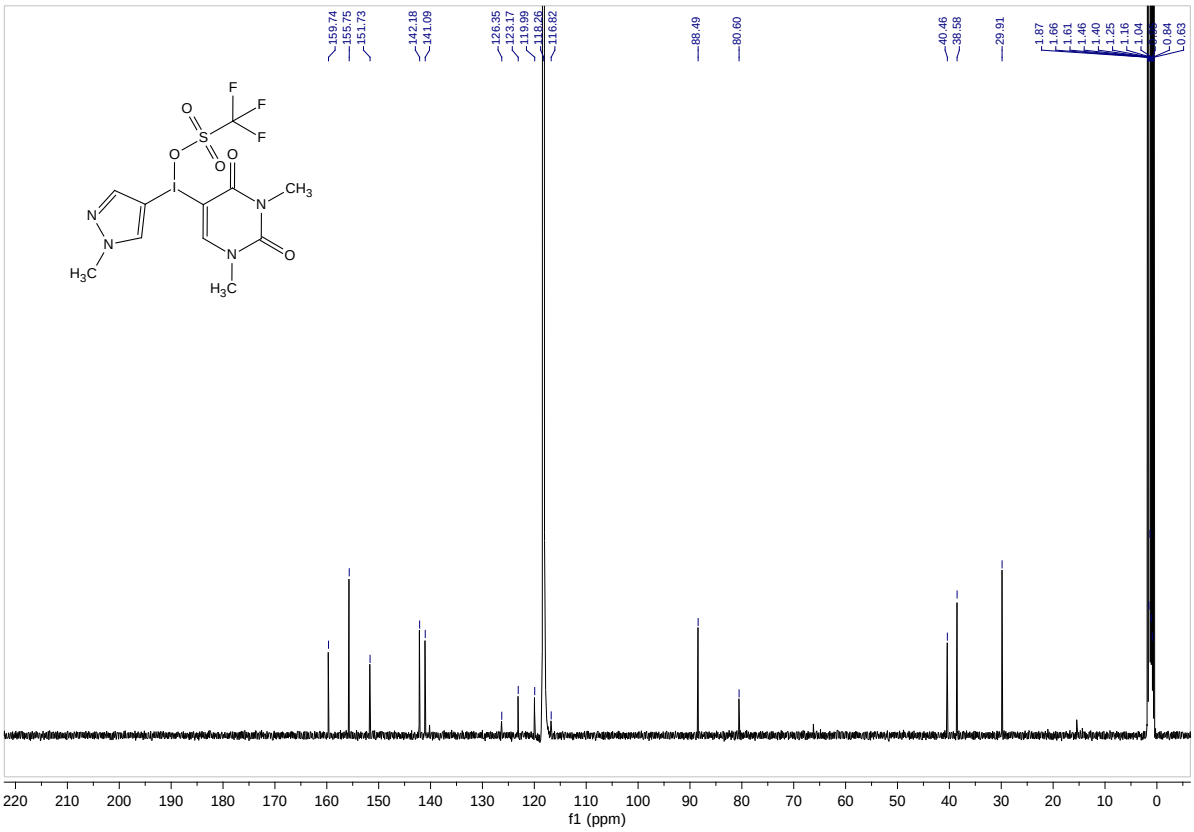

137.56
126.14
115.26
114.23
Br
Cl
Br
S
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

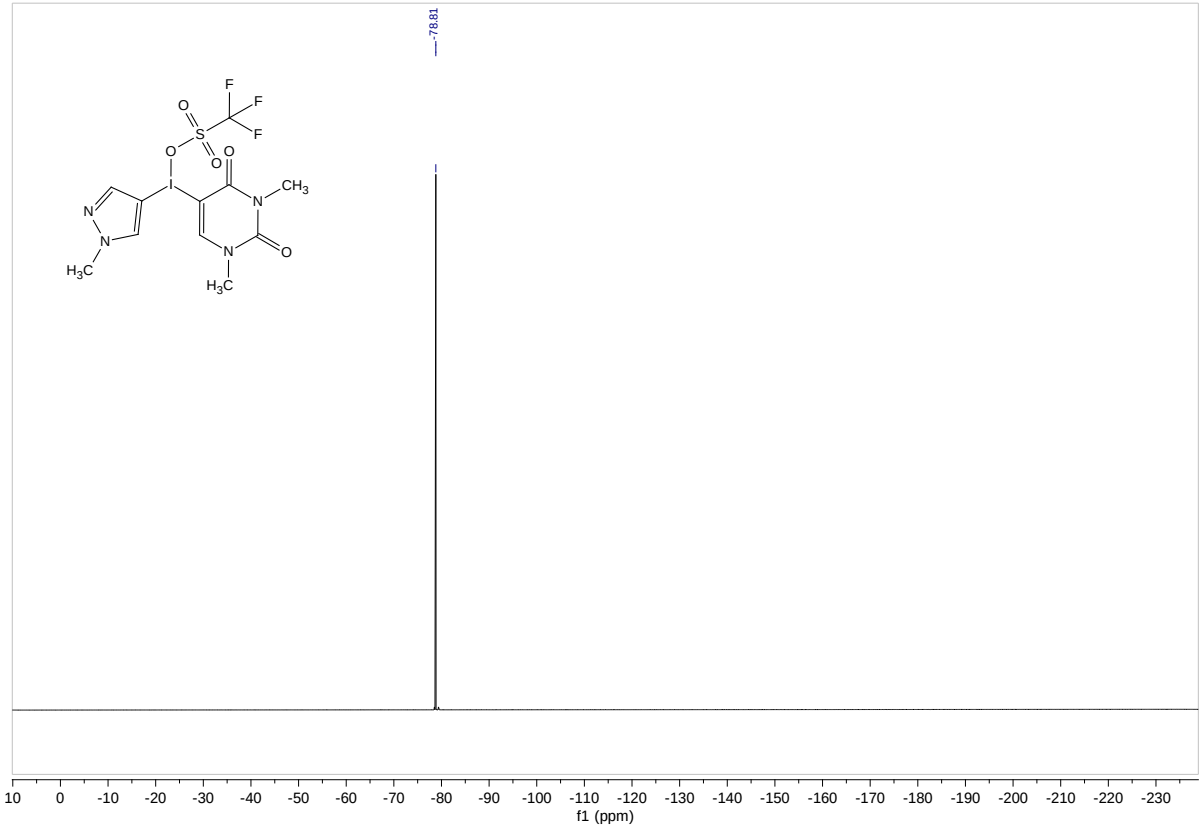

8.89
8.87
8.77
8.76
8.74
8.64
8.13
8.11
8.00
7.53
7.51
7.50
3.40
3.19
2.44
1.95
1.95
1.94
1.93
1.93
1.00
1.89
0.95
1.94
1.03
2.00
2.98
2.90
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

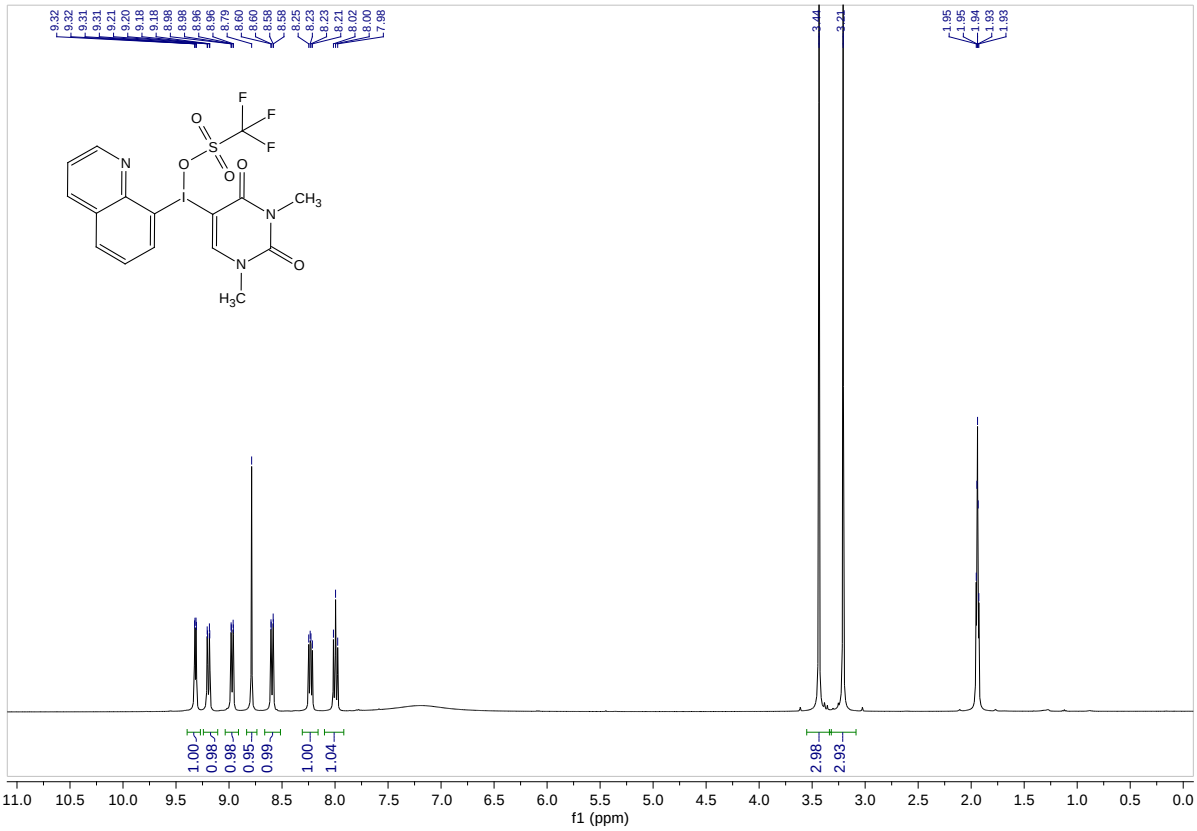

159.86
155.90
151.65
149.82
141.66
139.79
139.55
138.38
133.19
131.72
129.65
126.56
125.50
122.95
122.19
120.41
88.76
84.32
38.58
29.90
21.80
1.75
1.59
1.42
1.26
1.09
0.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

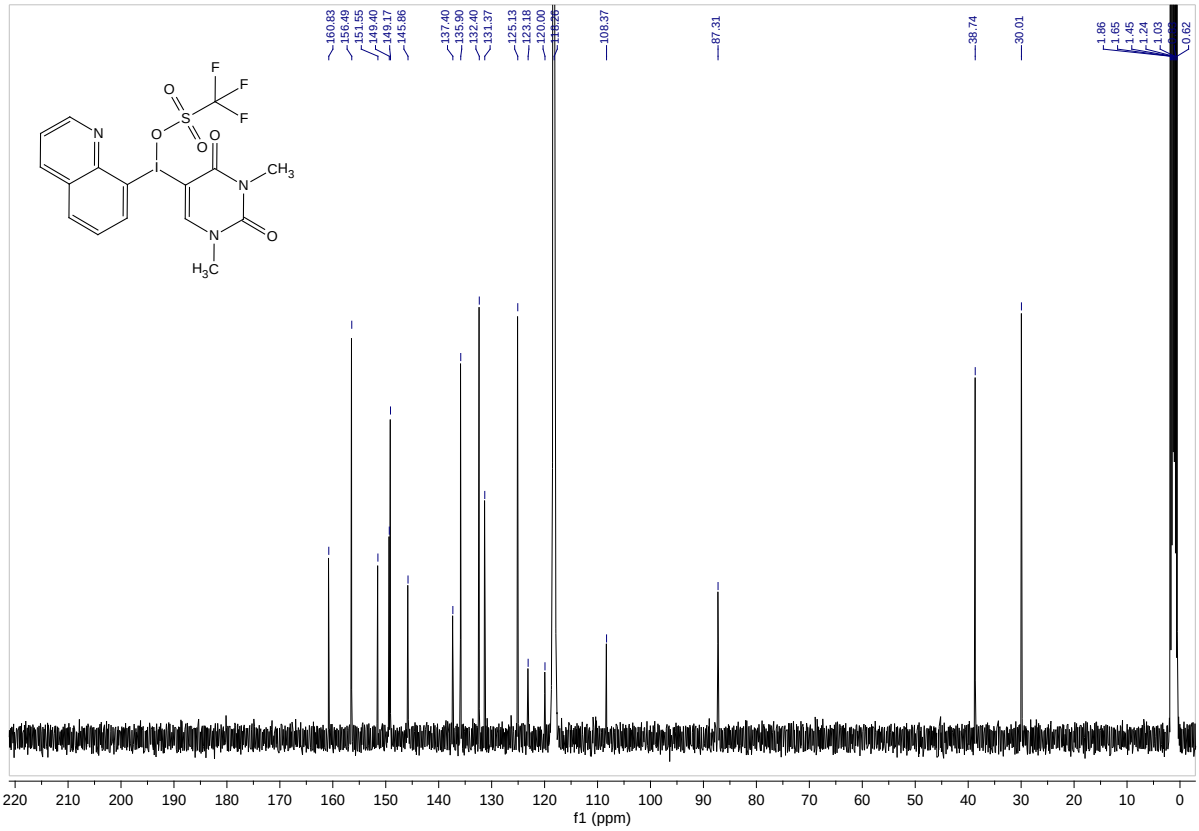

-78.72
F
F
F
O
S
O
O
O
I
N
CH3
N
N
O
O
S
O
N
CH3
H3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

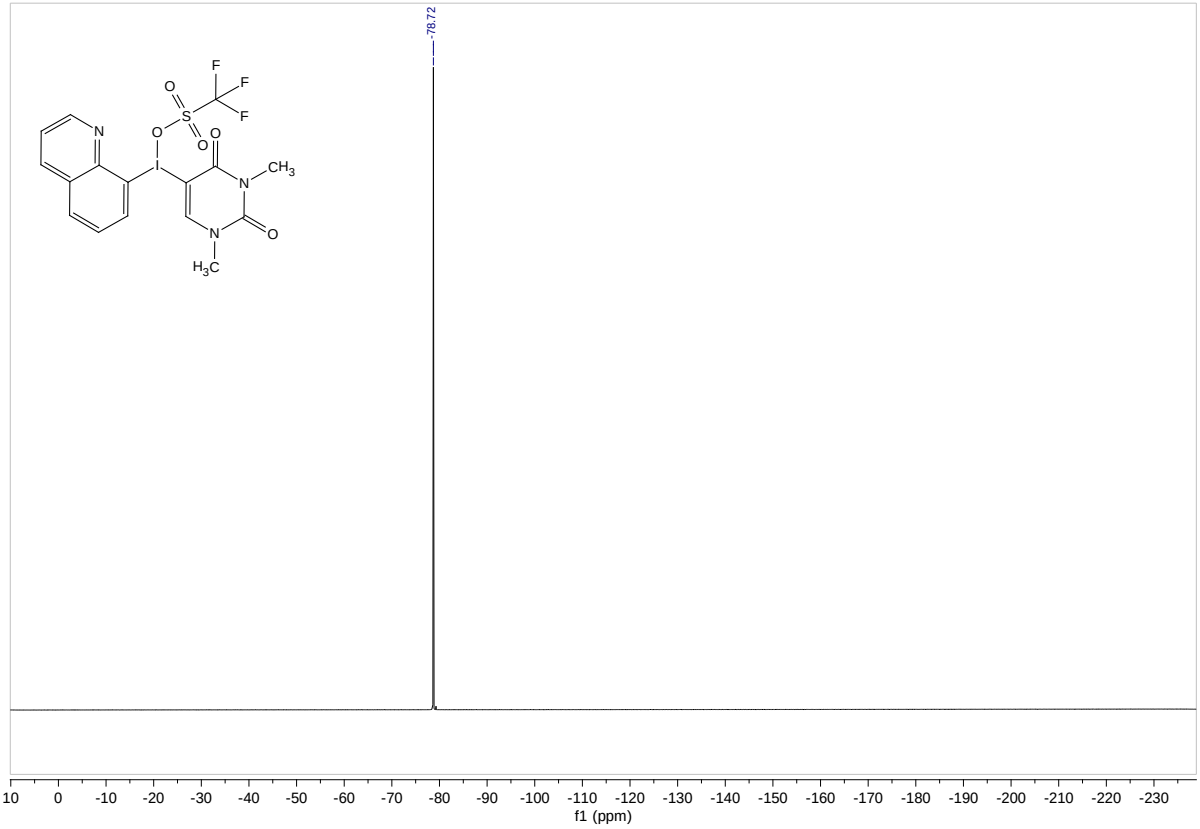

8.56
8.44
8.39
8.39
4.09
4.09
3.42
3.28
1.95
1.95
1.94
1.93
1.93
1.00
1.00
0.98
3.29
3.35
3.15
f1 (ppm)

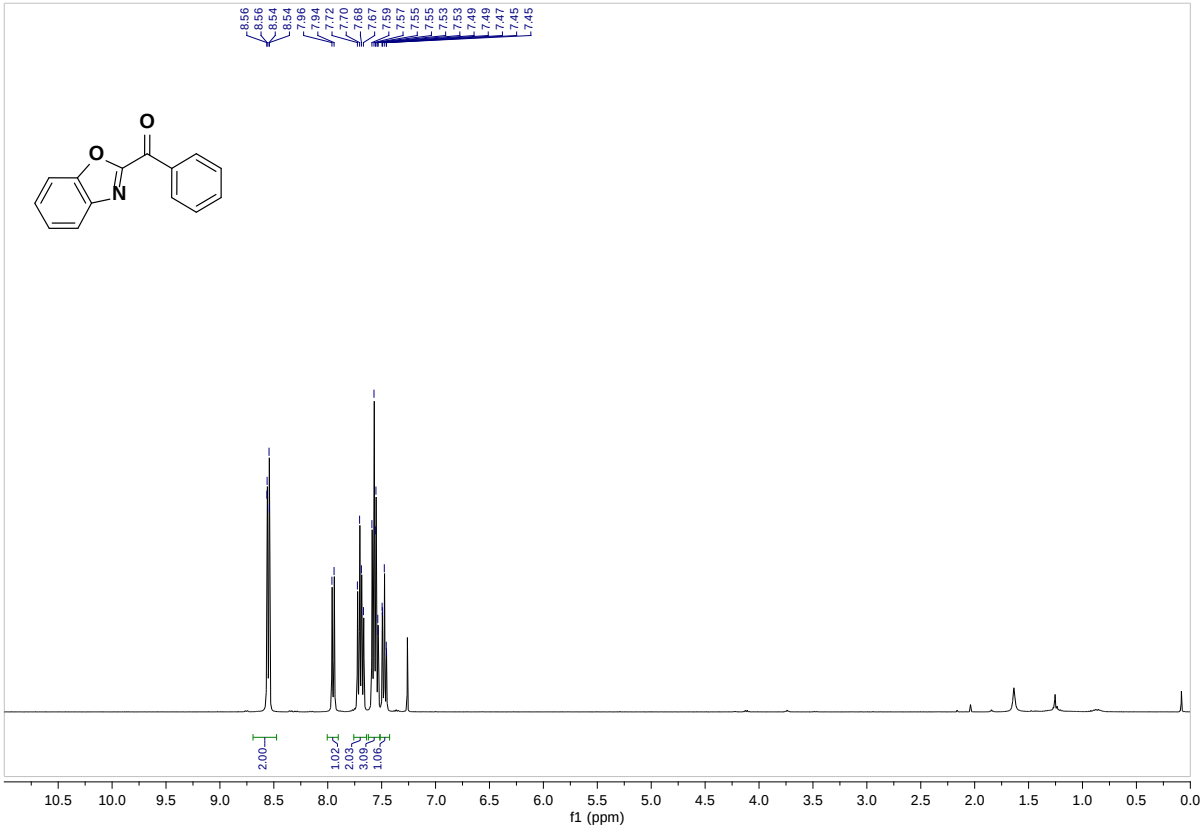

159.74
155.75
151.73
142.18
141.09
126.35
123.17
119.99
118.26
116.82
88.49
80.60
40.46
38.58
29.91
1.87
1.66
1.61
1.46
1.40
1.25
1.16
1.04
0.84
0.63
f1 (ppm)

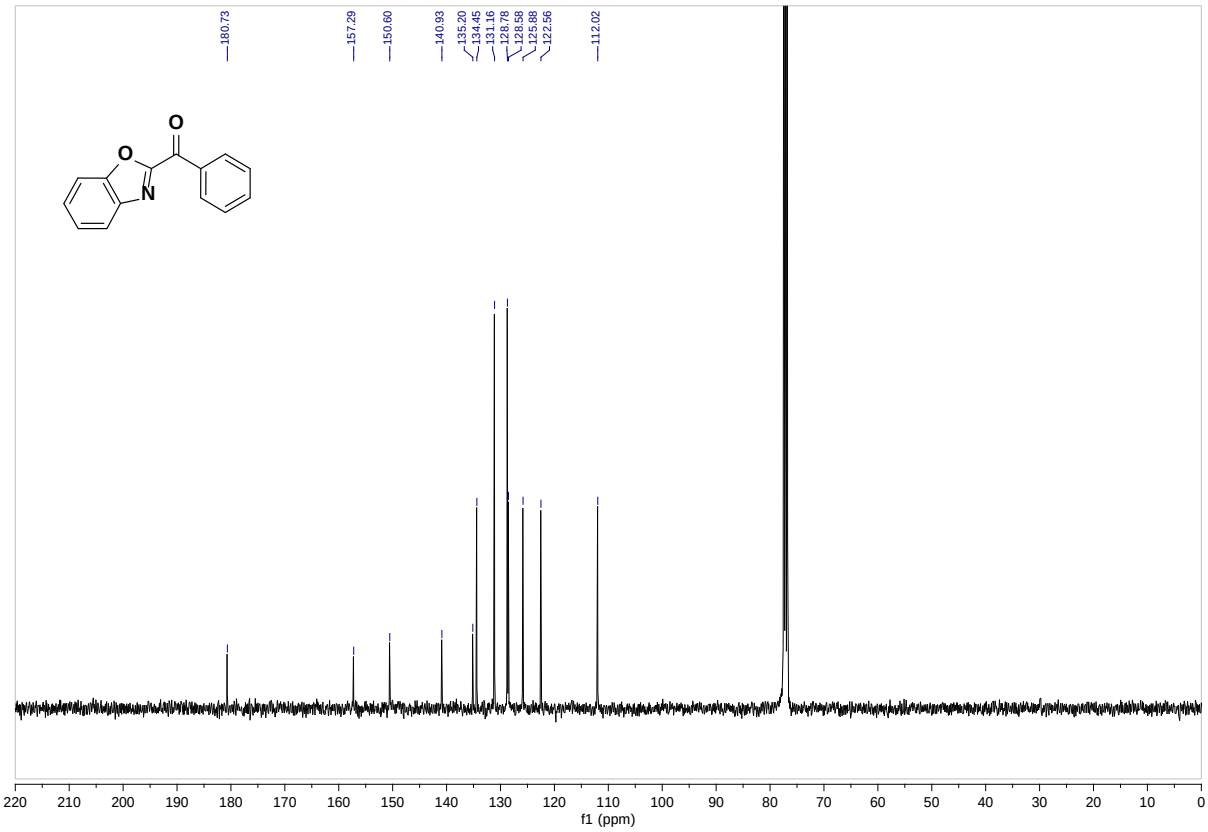

-78.81
F
F
F
O
S
O
O
O
I
N
CH3
N
N
O
H3C
H3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

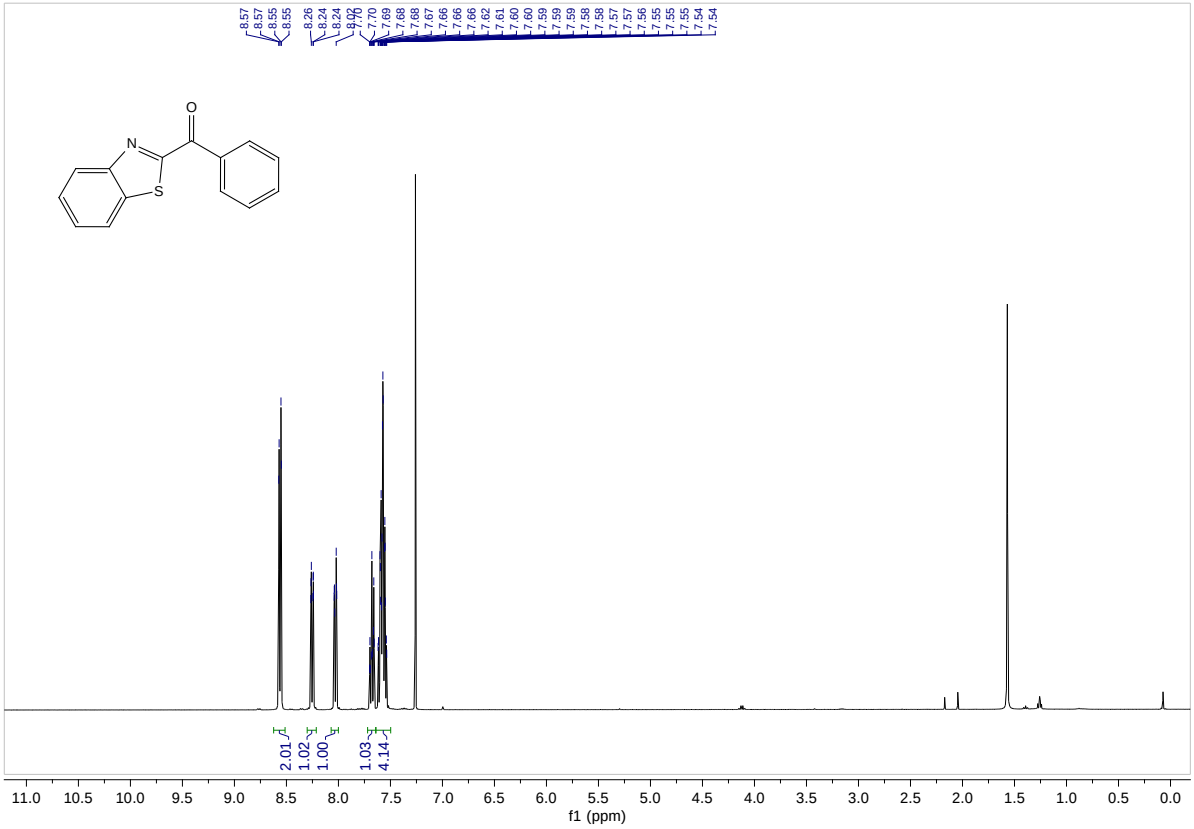

9.32
9.32
9.31
9.31
9.21
9.20
9.18
9.18
8.98
8.98
8.96
8.96
8.79
8.60
8.60
8.58
8.58
8.25
8.23
8.23
8.21
8.02
8.00
7.98
3.44
3.21
1.95
1.95
1.94
1.94
1.93
1.93
1.00
0.98
0.98
0.95
0.99
1.00
1.04
2.98
2.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

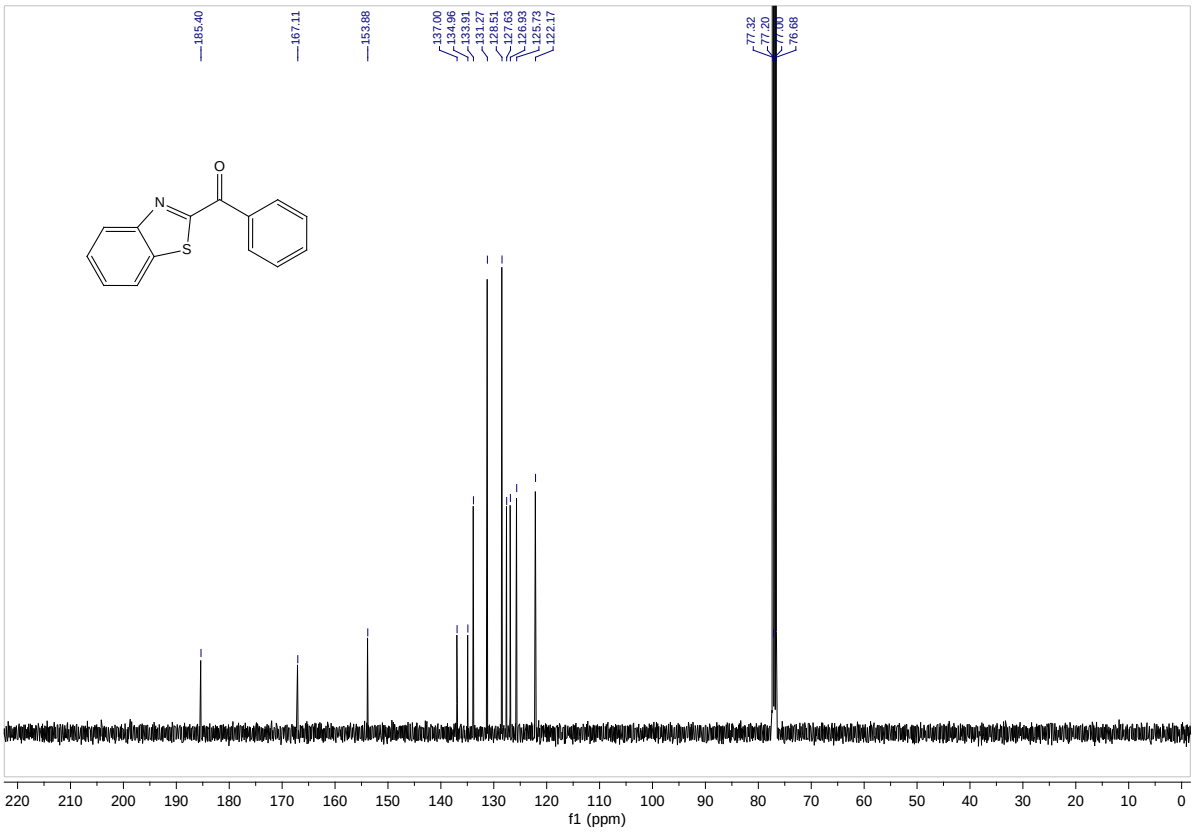

160.83
156.49
151.55
149.40
149.17
145.86
137.40
135.90
132.40
131.37
125.13
123.18
120.00
118.26
108.37
87.31
38.74
30.01
1.86
1.65
1.45
1.24
1.03
0.62
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

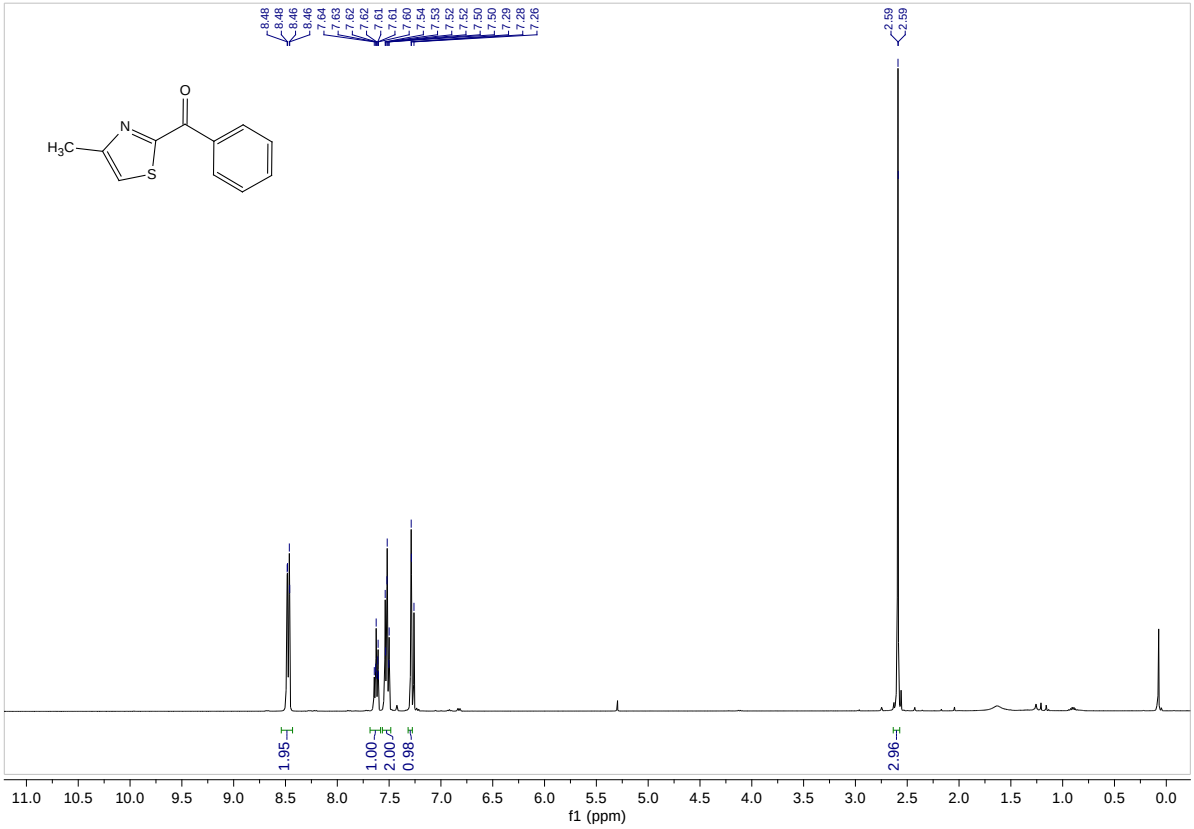

-78.72
F
F
F
O
S
O
O
N
O
I
O
N
CH3
N
O
H3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

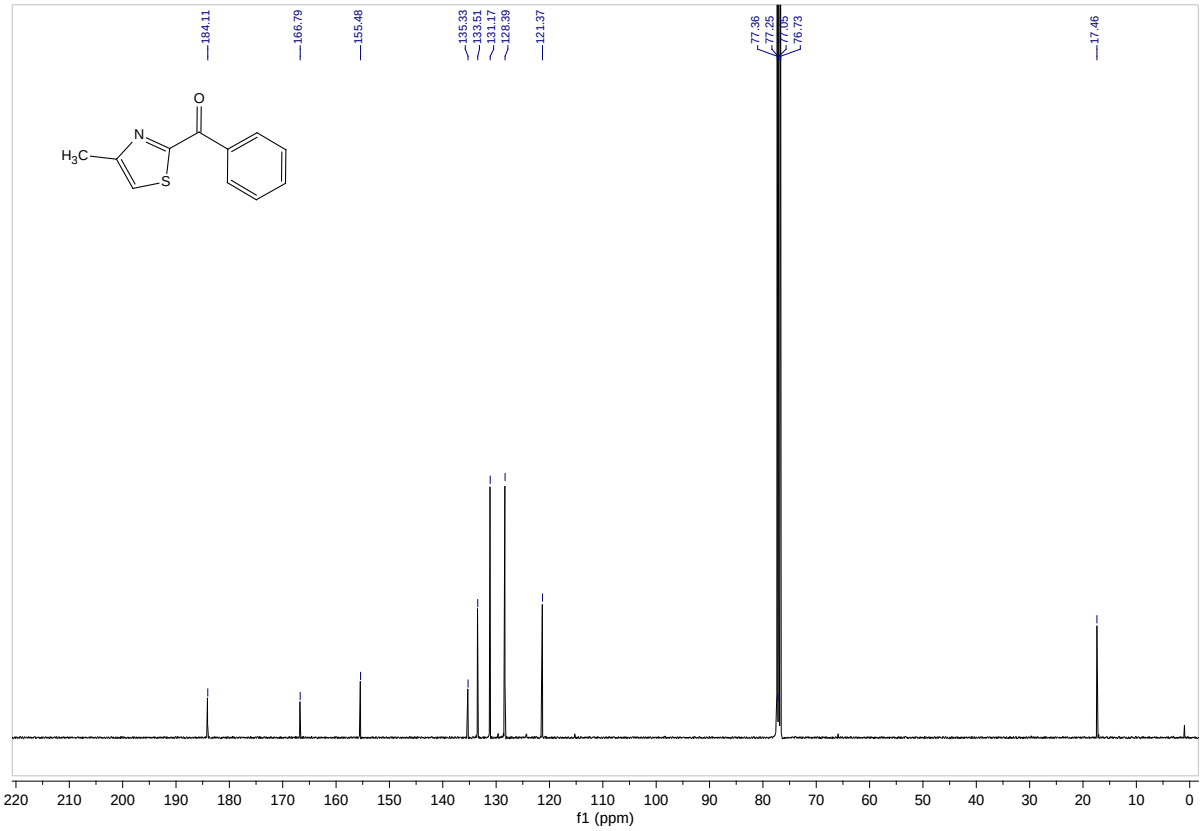

8.56
8.56
8.54
8.54
7.96
7.94
7.72
7.70
7.68
7.67
7.59
7.57
7.55
7.55
7.53
7.53
7.49
7.49
7.47
7.45
7.45
O
O
N
2.00
1.02
2.03
3.08
1.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

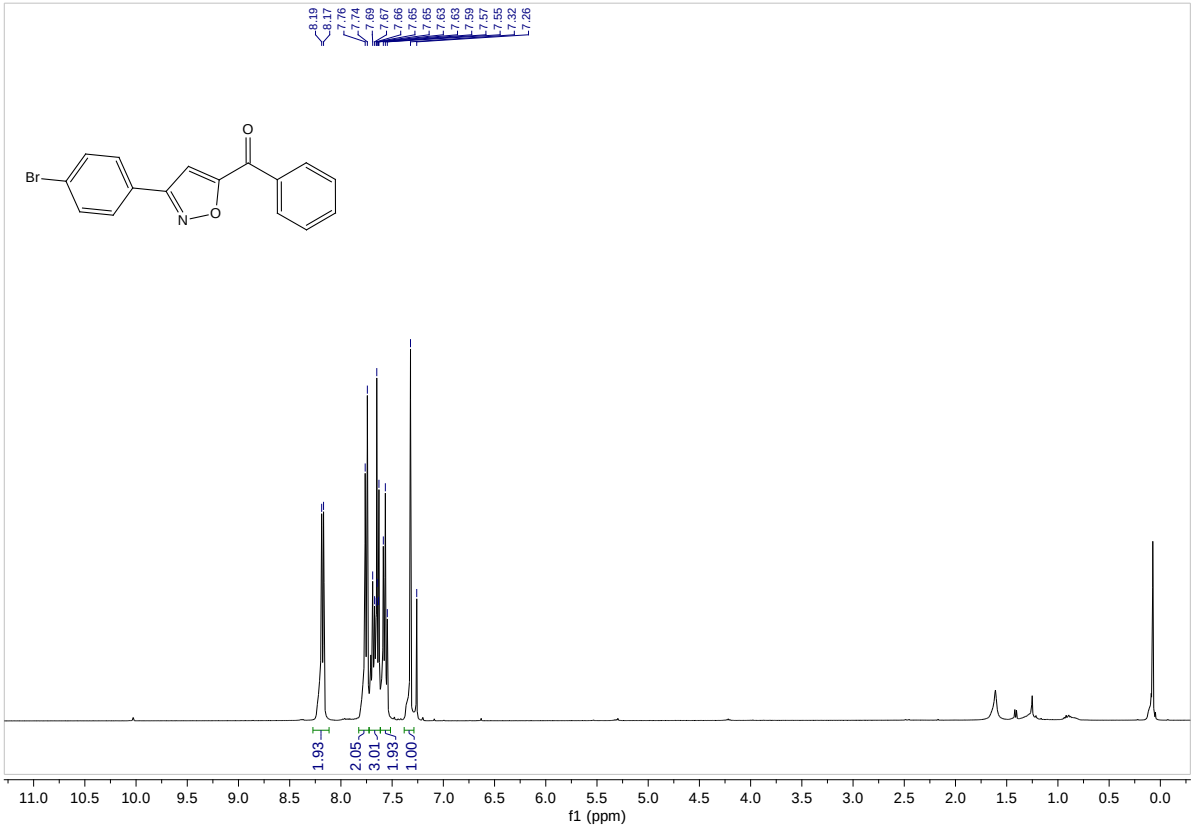

180.73
157.29
150.60
140.93
135.20
134.45
131.16
128.78
128.58
125.88
122.56
112.02
O
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

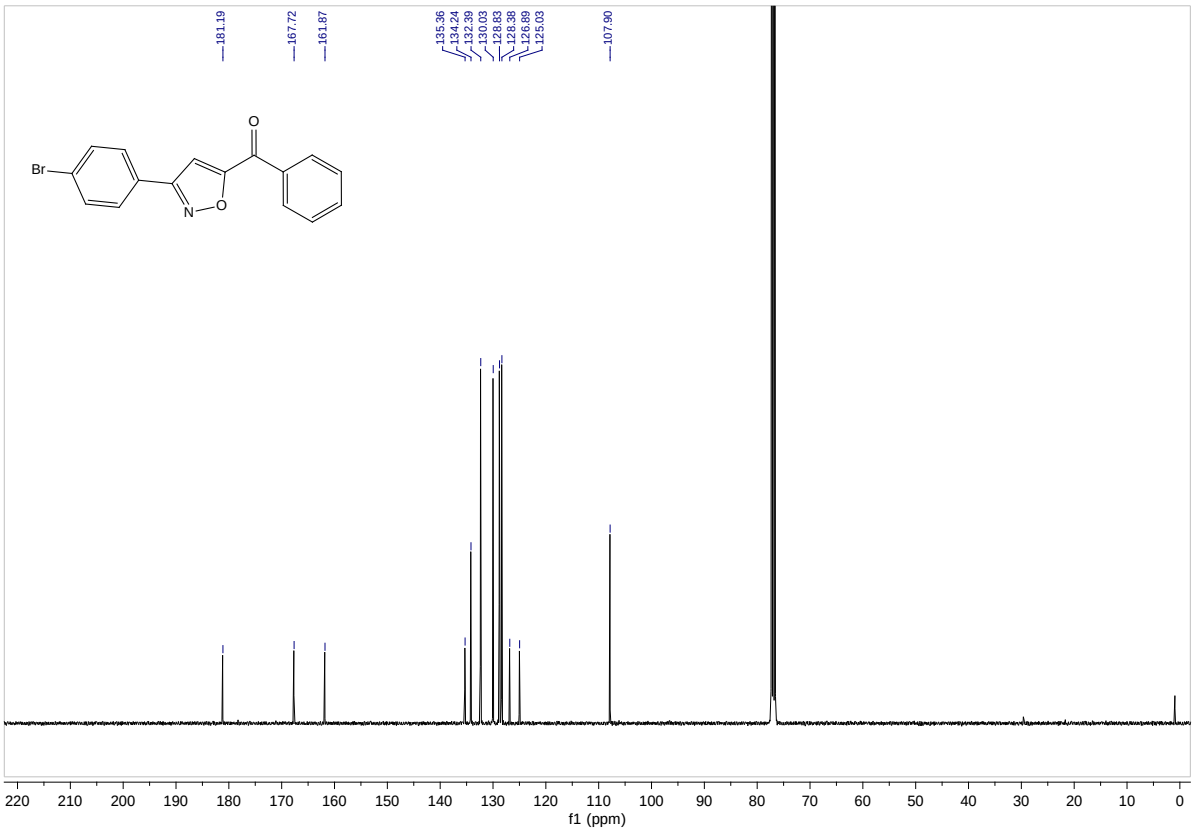

8.57
8.57
8.55
8.55
8.26
8.24
8.24
8.24
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.66
7.62
7.61
7.60
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.55
7.55
7.55
7.55
7.54
7.54
O
N
S
2.01
1.02
1.00
1.03
4.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

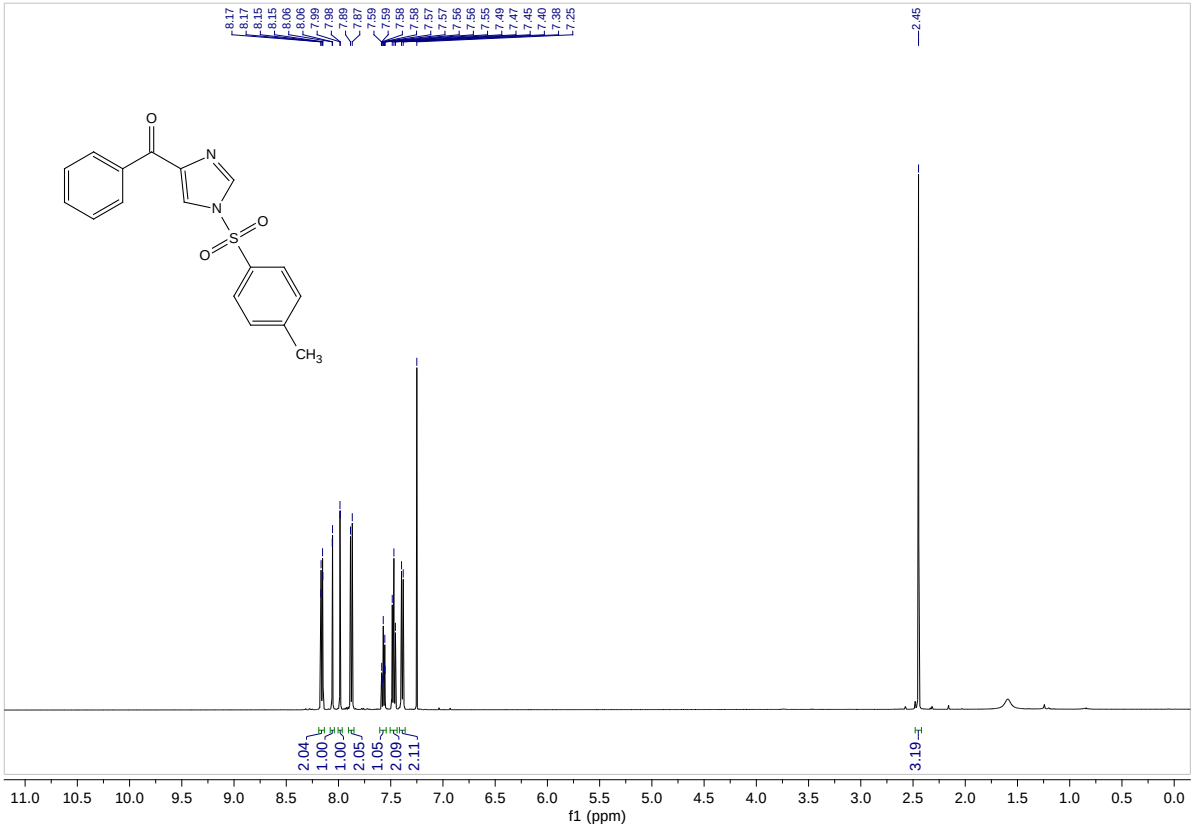

185.40
167.11
153.88
137.00
134.96
133.91
131.27
128.51
127.63
126.93
125.73
122.17
77.32
77.20
77.00
76.68
O
N
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

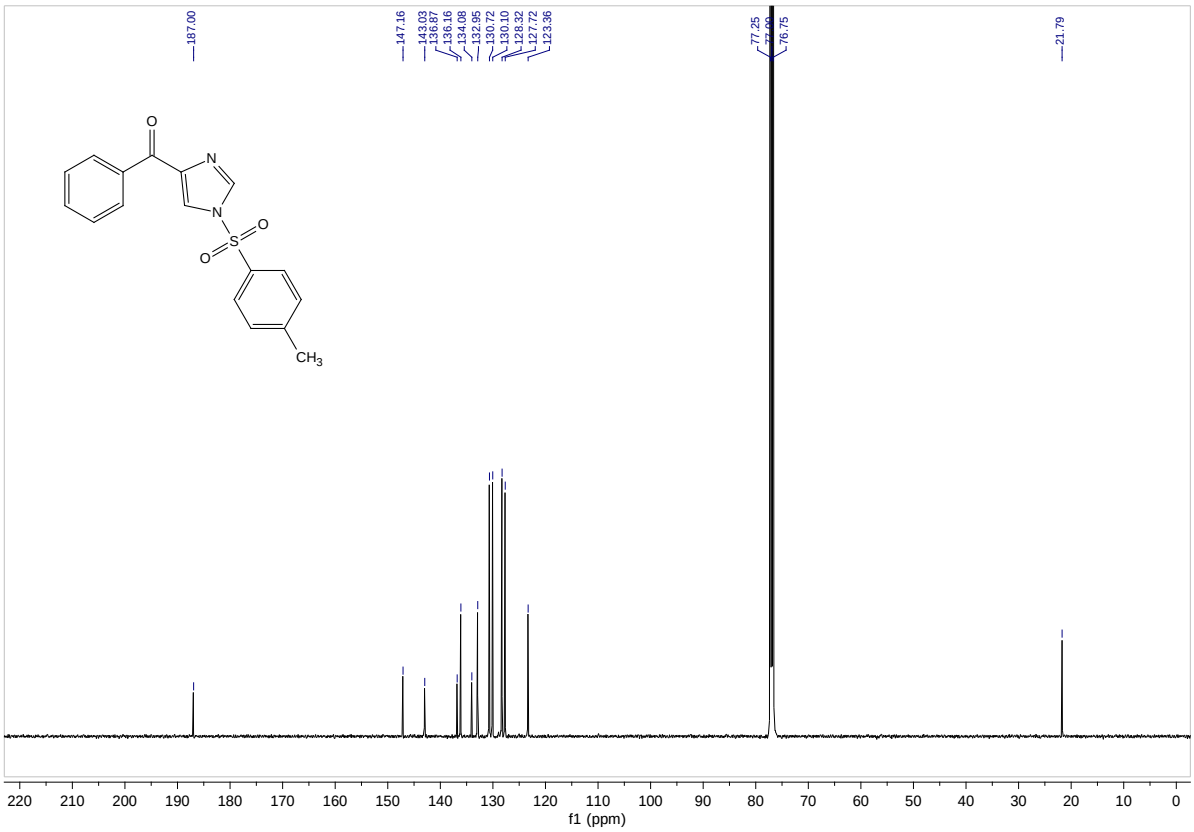

8.48
8.48
8.46
8.46
7.64
7.63
7.62
7.62
7.61
7.61
7.60
7.54
7.53
7.52
7.52
7.50
7.50
7.29
7.28
7.26
2.59
2.59
O
N
H_3C
S
1.95
1.00
2.00
0.98
2.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

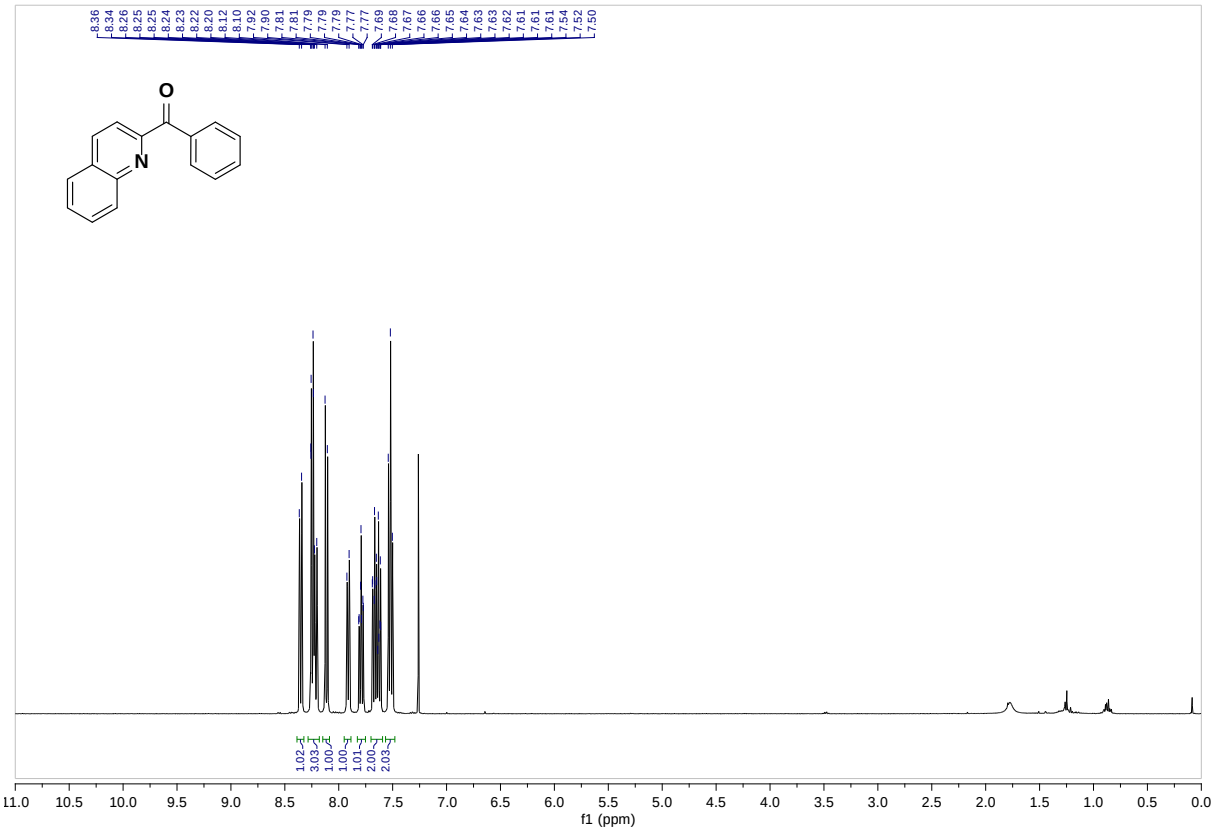

184.11
166.79
155.48
135.33
133.51
131.17
128.39
121.37
77.36
77.25
77.05
76.73
17.46
O
N
H_3C
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

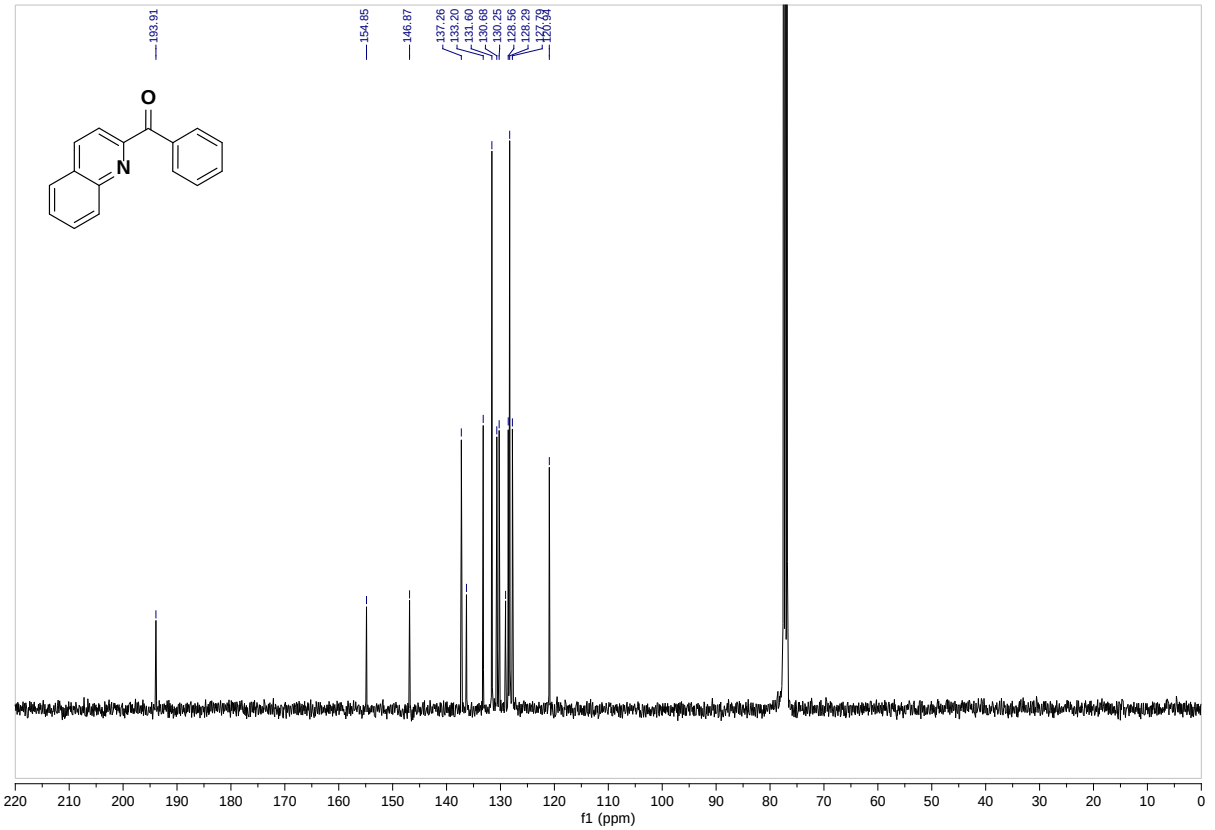

8.19
8.17
7.76
7.74
7.69
7.67
7.66
7.65
7.65
7.63
7.63
7.59
7.57
7.55
7.32
7.26
Br
O
N
O
1.93
2.05
3.01
1.93
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

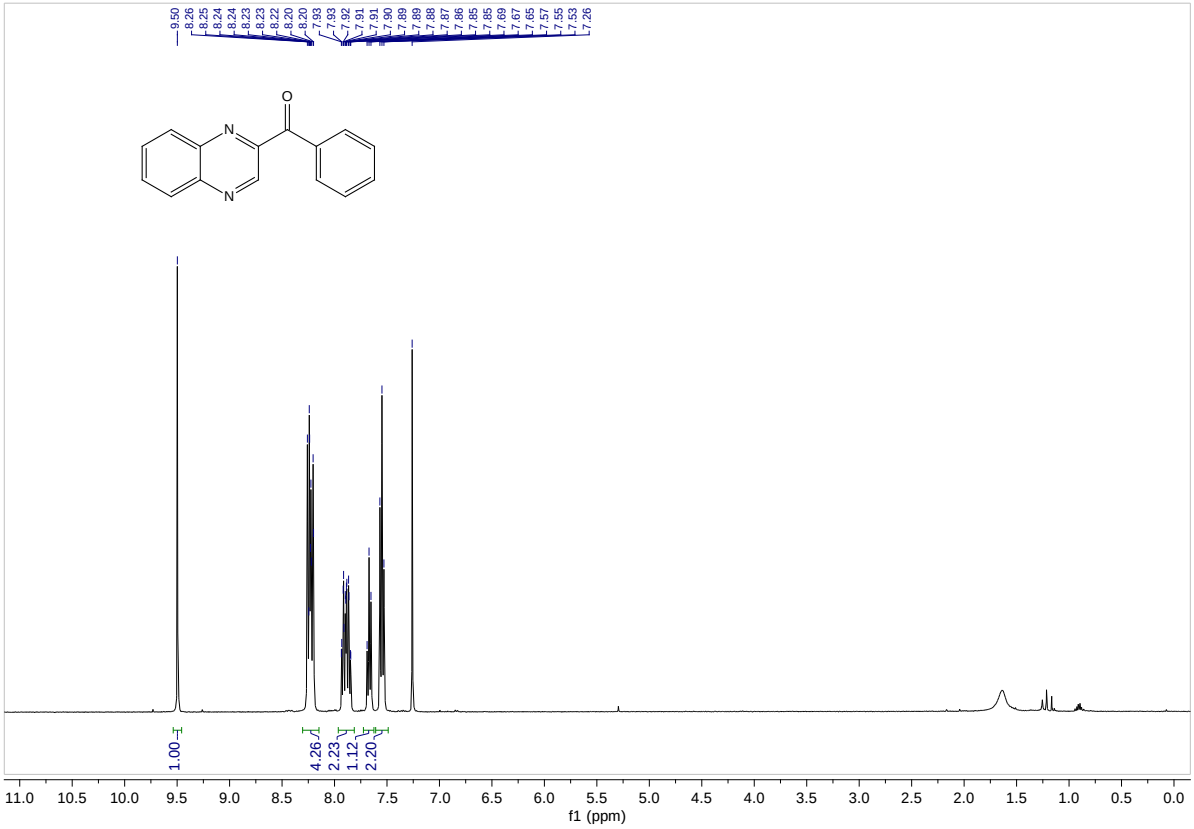

181.19
167.72
161.87
135.36
134.24
132.39
130.03
128.83
128.38
126.89
125.03
107.90
Br
O
N
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

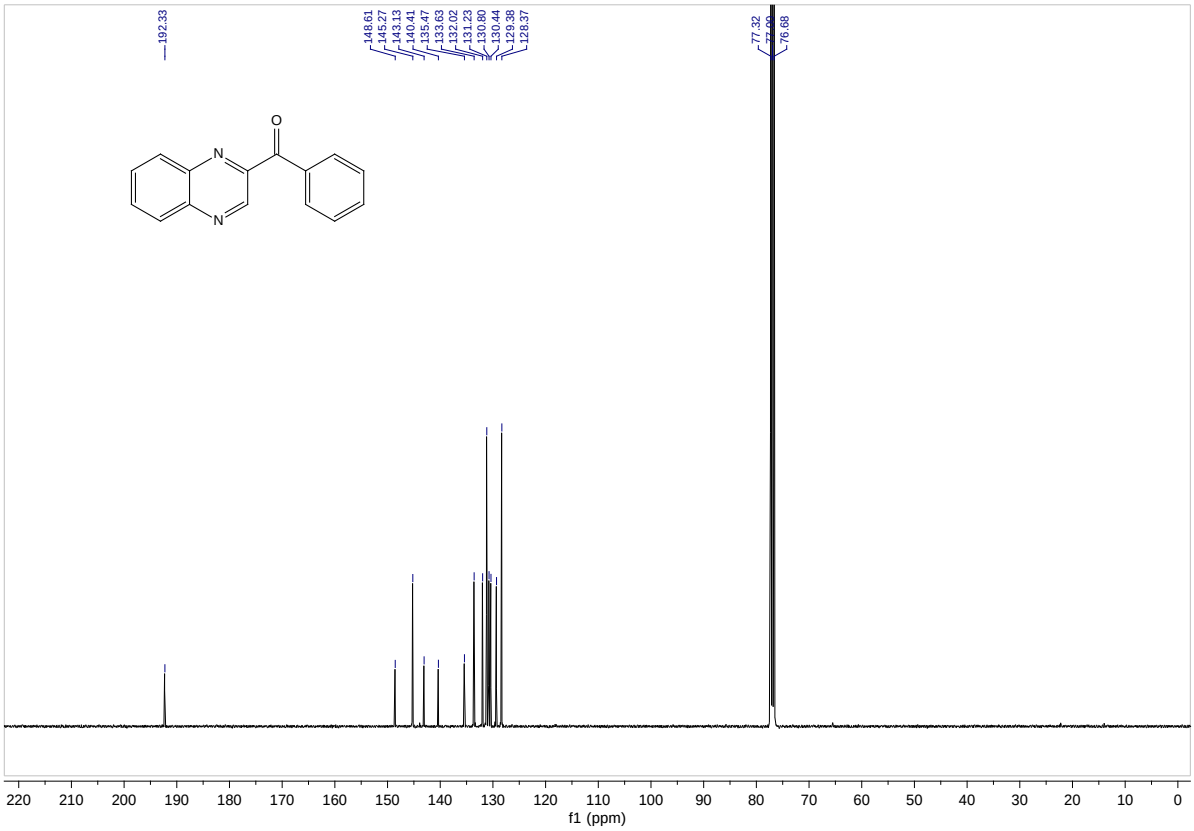

8.17
8.17
8.15
8.15
8.06
8.06
7.99
7.98
7.89
7.87
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.49
7.47
7.45
7.40
7.38
7.25
2.45
O
N
N
S
O
O
CH3
2.04
1.00
1.00
2.05
1.05
2.09
2.11
3.19
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

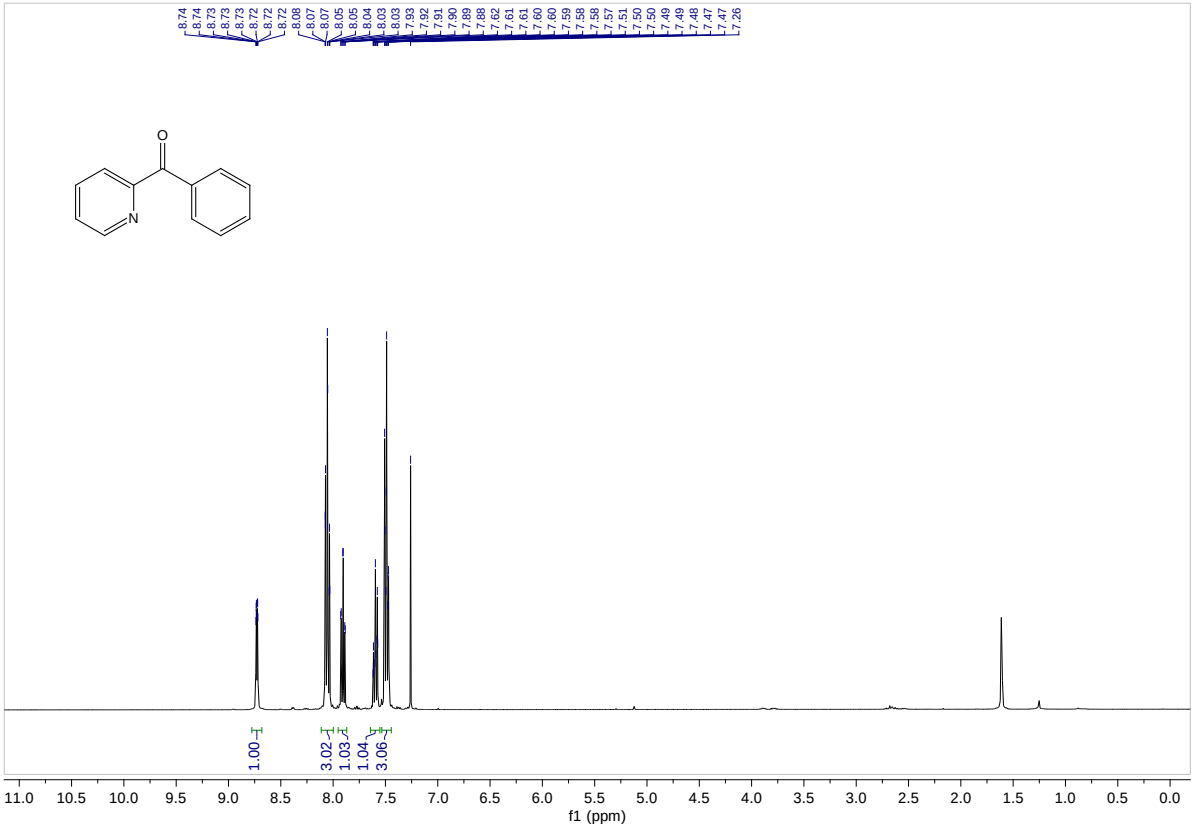

187.00
147.16
143.03
136.37
136.16
134.08
132.95
130.72
130.10
128.32
127.72
123.36
77.25
77.00
76.75
21.79
O
N
N
S
O
O
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.36
8.34
8.26
8.25
8.25
8.24
8.23
8.22
8.20
8.12
8.10
7.92
7.90
7.81
7.81
7.79
7.79
7.79
7.79
7.77
7.77
7.77
7.69
7.68
7.67
7.66
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.61
7.54
7.52
7.50
O
N
1.02
3.03
1.00
1.00
1.01
2.00
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.91
154.85
146.87
137.26
133.20
131.60
130.68
130.25
128.56
128.29
127.79
120.94
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.50
8.26
8.25
8.24
8.24
8.23
8.23
8.22
8.20
8.20
7.93
7.93
7.92
7.91
7.91
7.90
7.89
7.89
7.88
7.87
7.86
7.85
7.85
7.69
7.67
7.65
7.57
7.55
7.53
7.26
O
N
N
1.00
4.26
2.23
1.12
2.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


192.33
148.61
145.27
143.13
140.41
135.47
133.63
132.02
131.23
130.80
130.44
129.38
128.37
77.32
77.00
76.68
O
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.74
8.74
8.73
8.73
8.73
8.72
8.72
8.72
8.08
8.07
8.07
8.05
8.05
8.04
8.03
8.03
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7.92
7.91
7.90
7.89
7.88
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7.61
7.60
7.60
7.59
7.58
7.58
7.57
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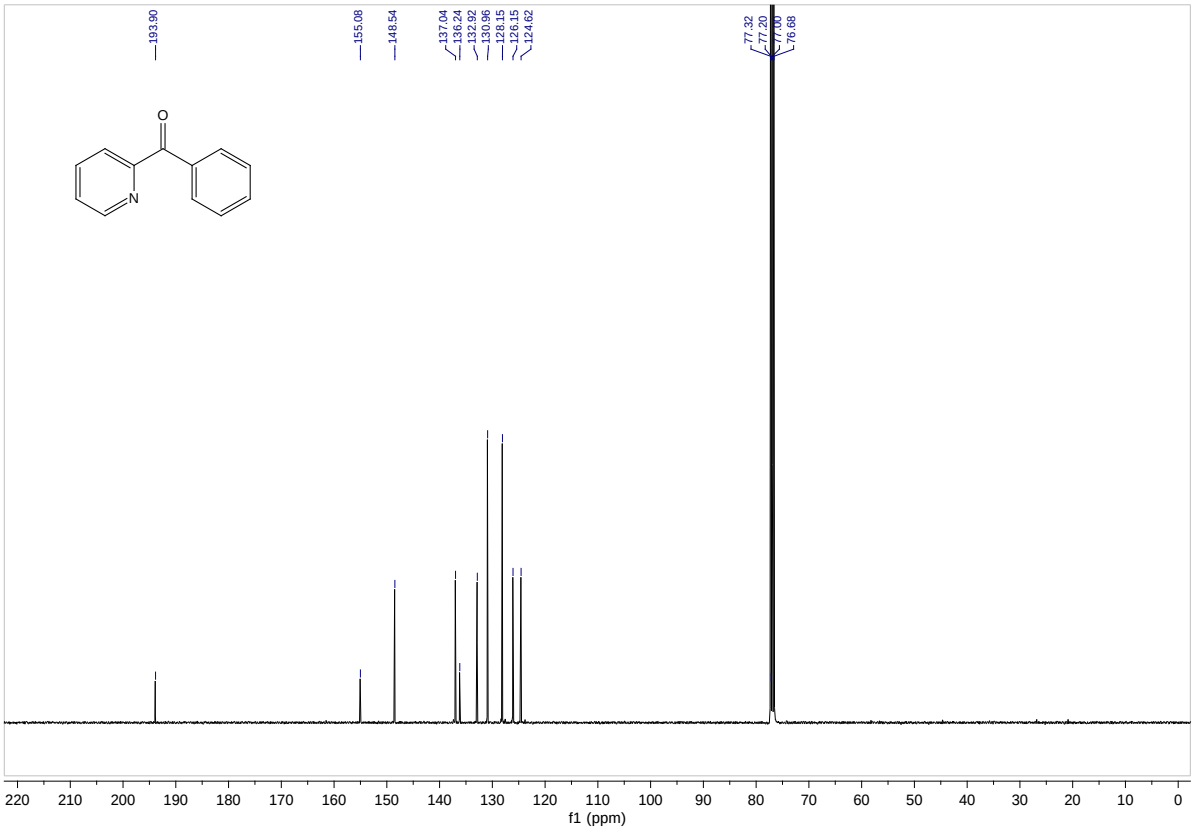
7.50
7.49
7.49
7.48
7.47
7.47
7.26
O
N
1.00
3.02
1.03
1.04
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.92
130.96
128.15
126.15
124.62
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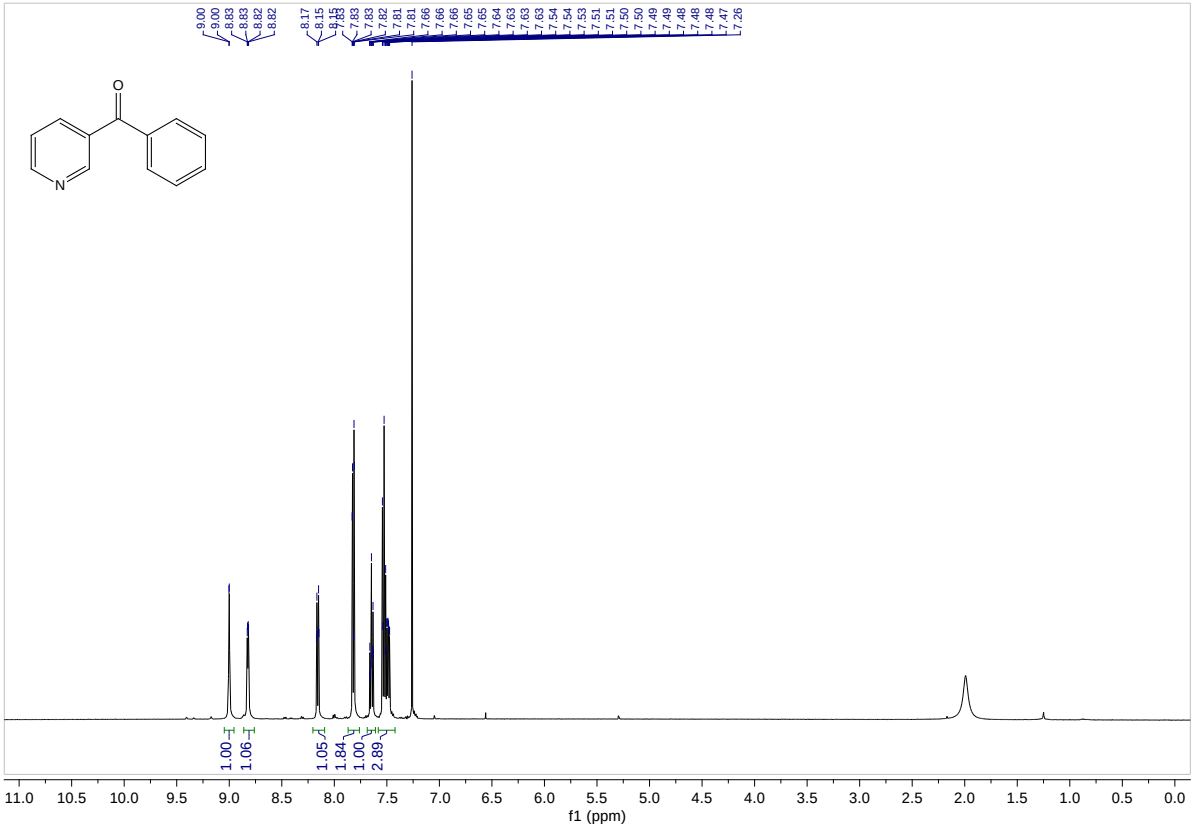
77.00
76.68
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.15
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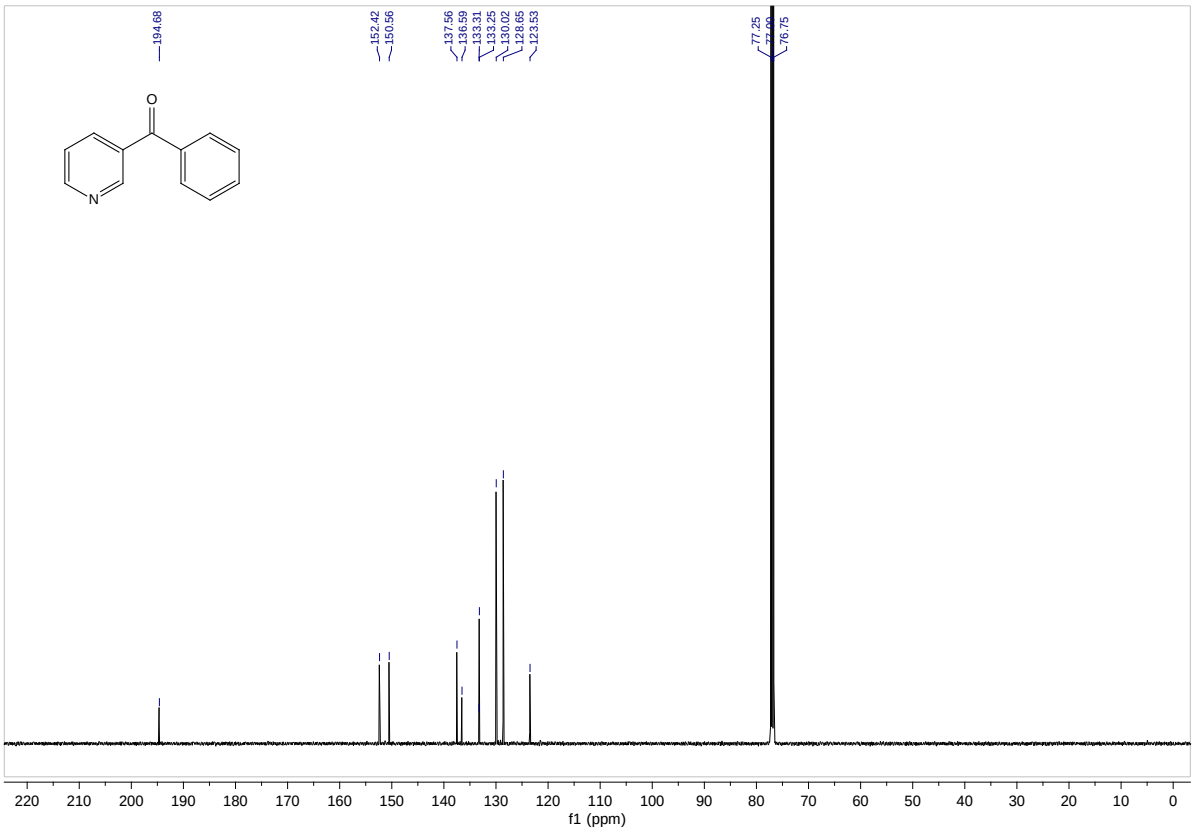
7.81
7.81
7.66
7.66
7.66
7.65
7.65
7.65
7.64
7.63
7.63
7.63
7.54
7.54
7.53
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.48
7.47
7.26
O
N
1.00
1.06
1.05
1.84
1.00
2.89
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.25
130.02
128.65
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77.00
76.75
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N
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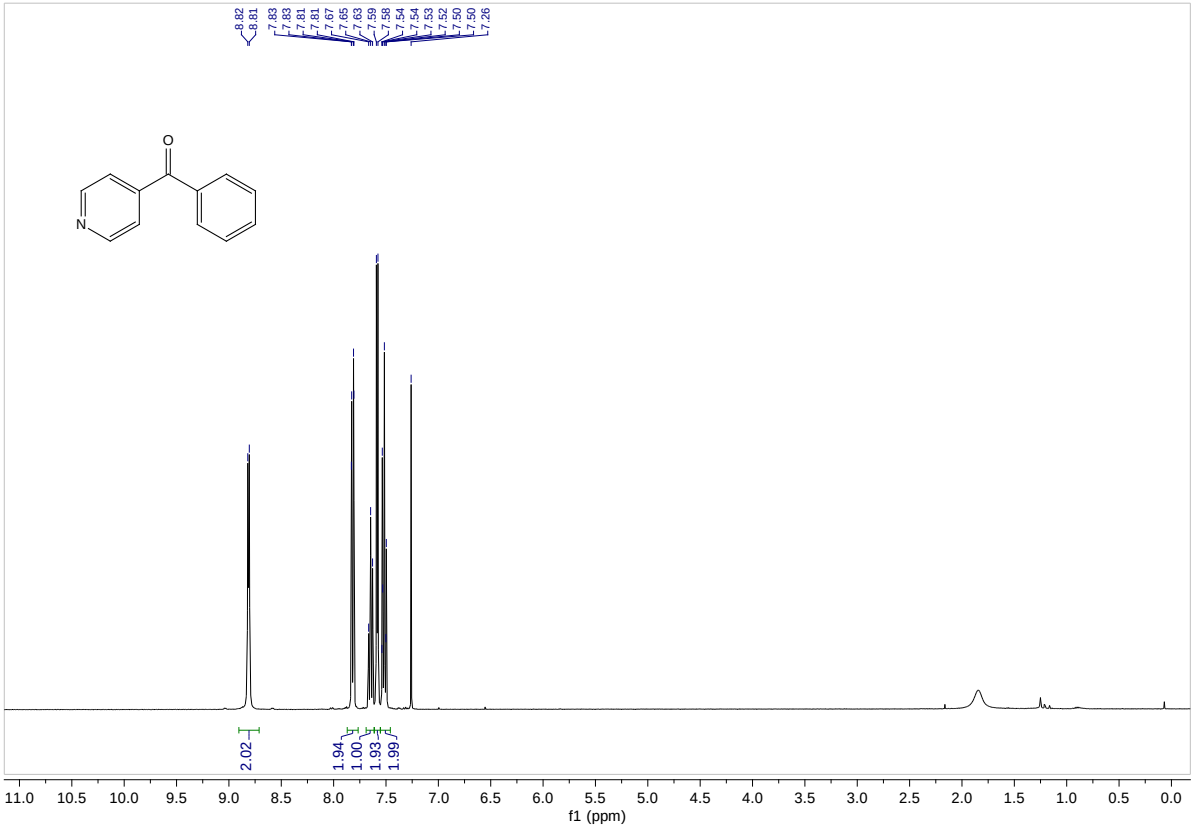
f1 (ppm)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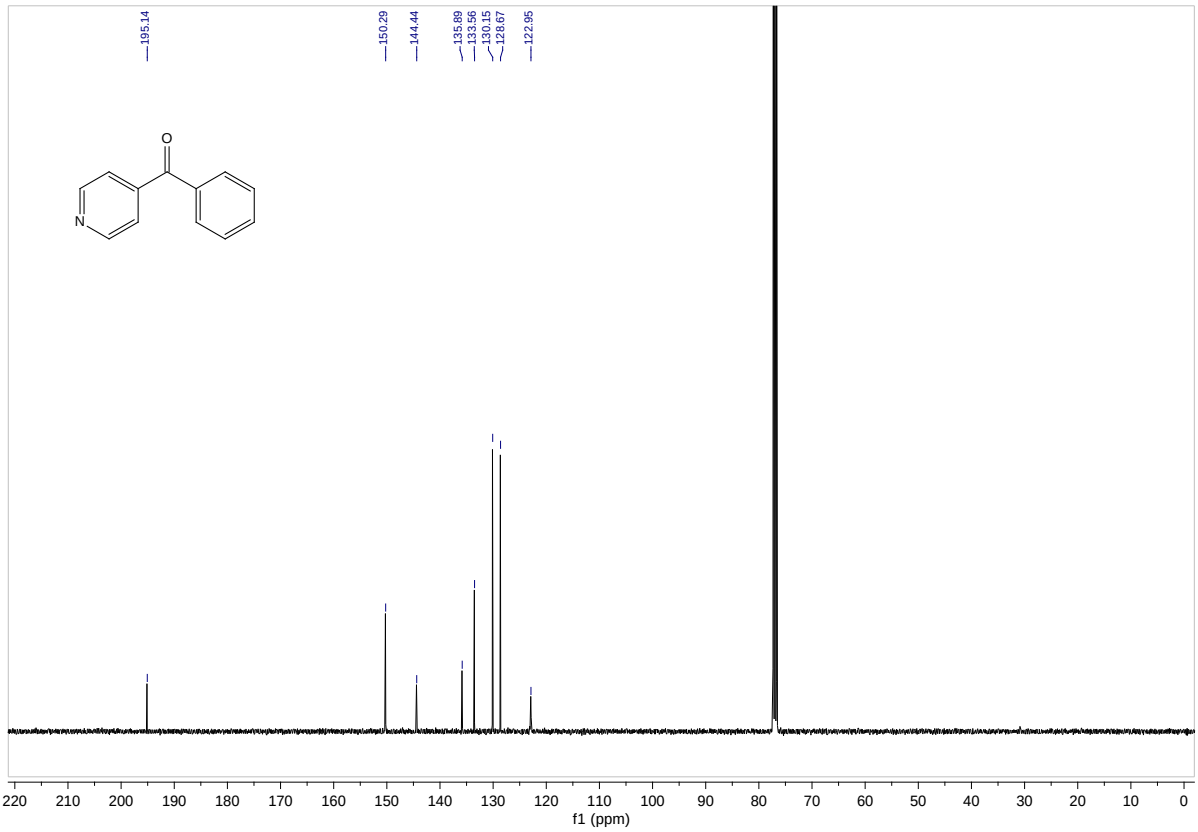
7.83
7.81
7.81
7.67
7.65
7.63
7.59
7.58
7.54
7.54
7.53
7.52
7.50
7.50
7.26
O
N
2.02
1.94
1.00
1.93
1.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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150.29
144.44
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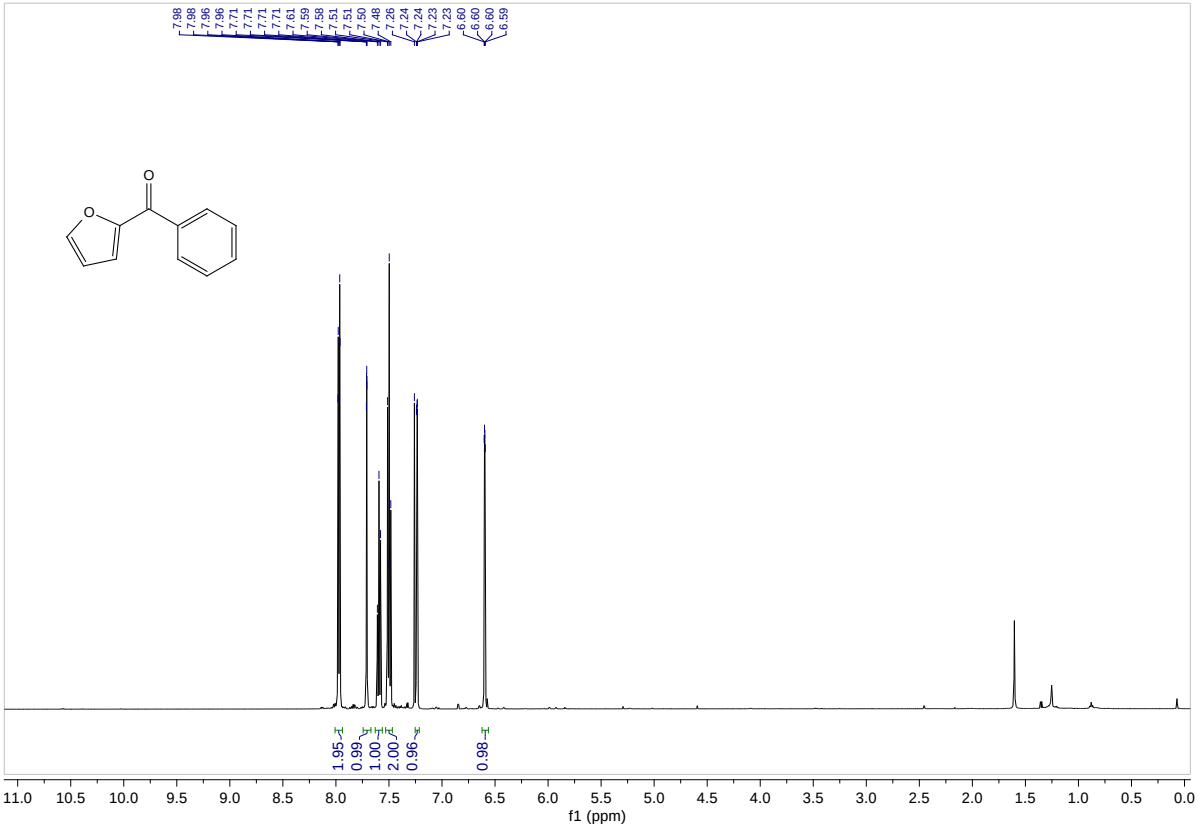
130.15
128.67
122.95
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.98
7.96
7.96
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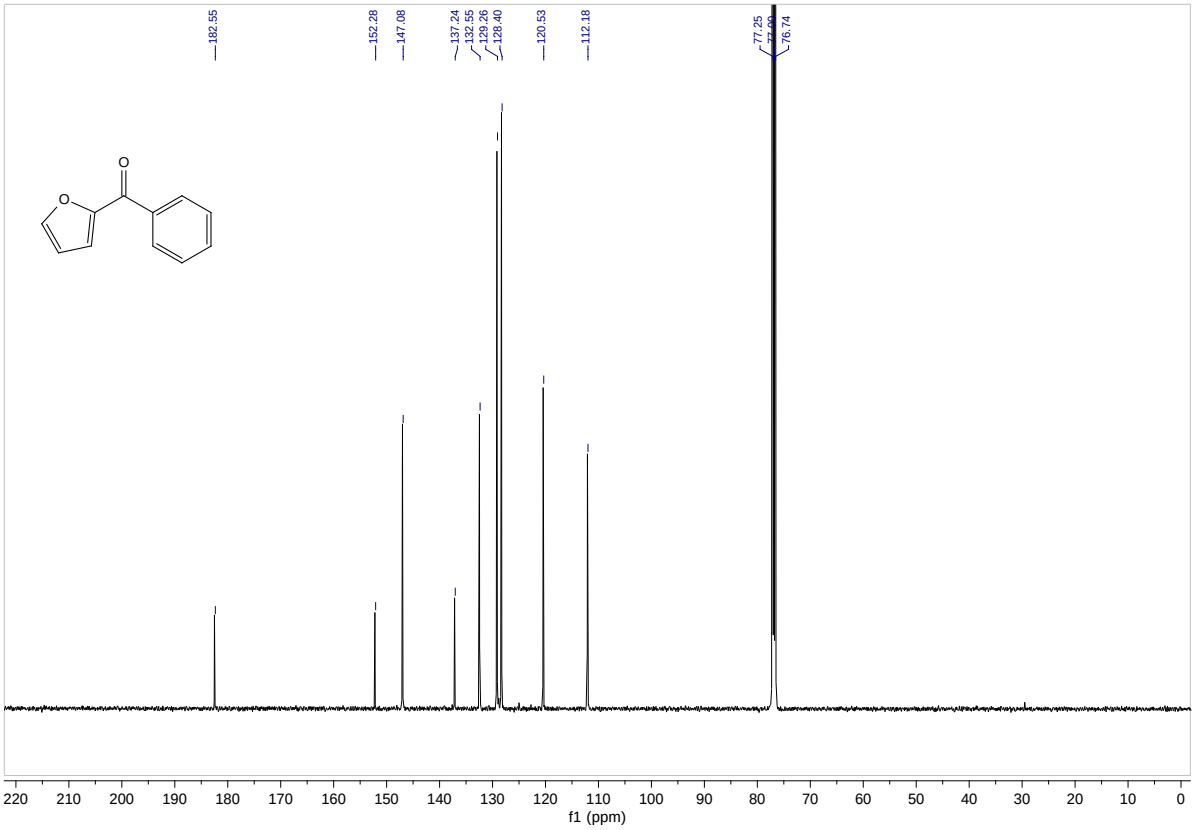
7.71
7.71
7.71
7.61
7.59
7.58
7.51
7.51
7.50
7.48
7.26
7.24
7.24
7.23
6.60
6.60
6.59
O
O
1.95
0.99
1.00
2.00
0.96
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.55
129.26
128.40
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77.00
76.74
O
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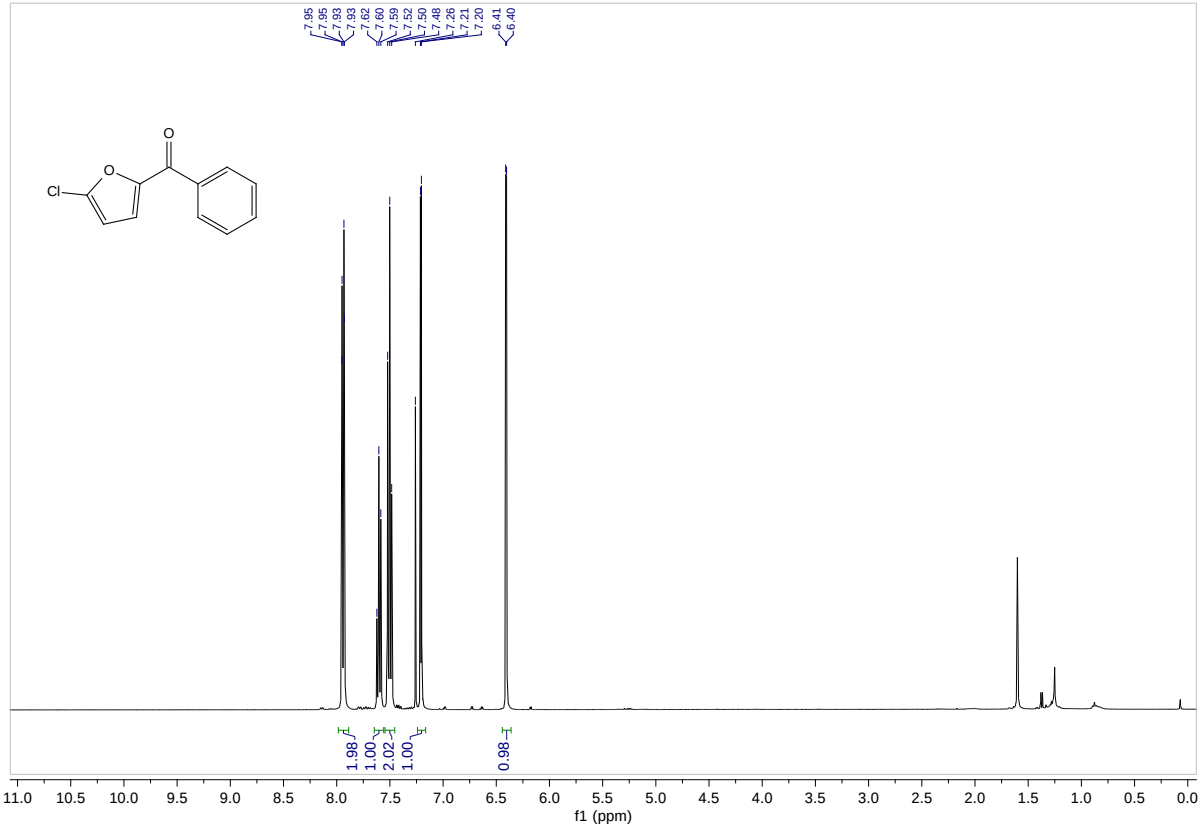
f1 (ppm)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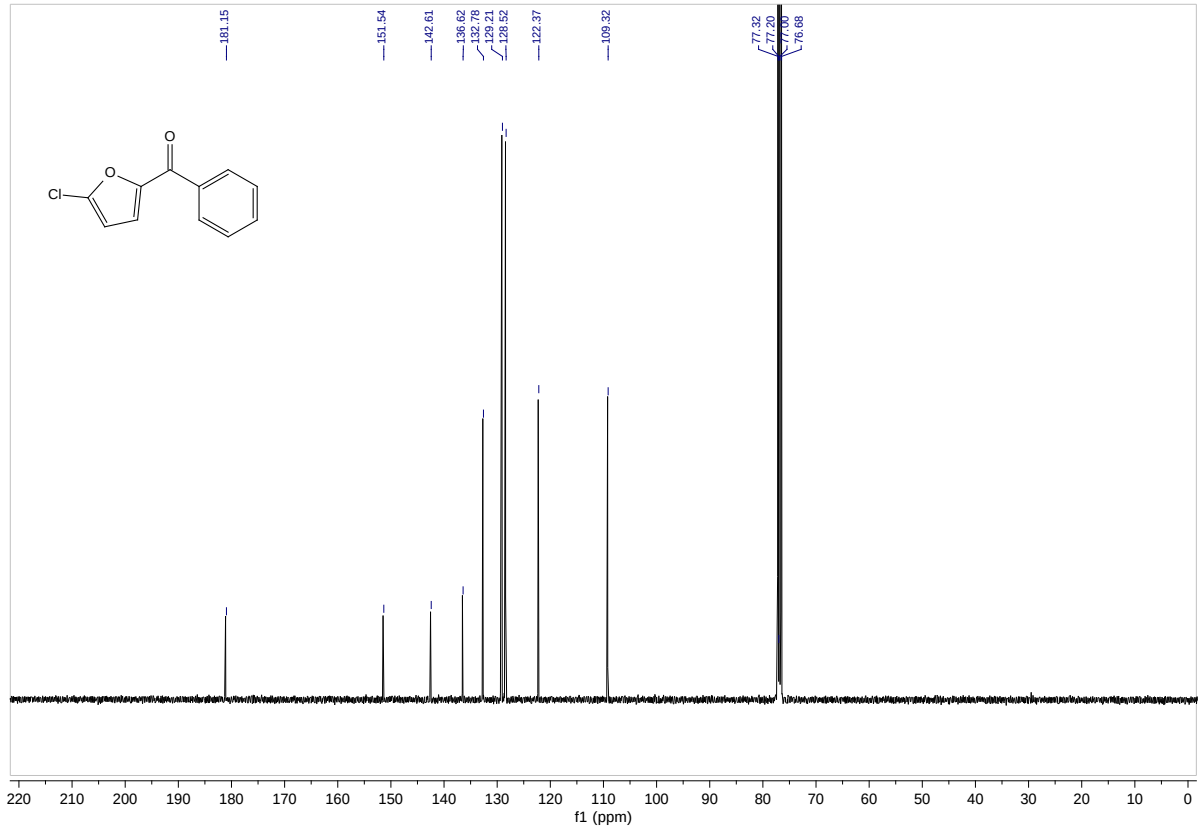
7.95
7.93
7.93
7.62
7.60
7.59
7.52
7.50
7.48
7.26
7.21
7.20
6.41
6.40
O
O
Cl
1.98
1.00
2.02
1.00
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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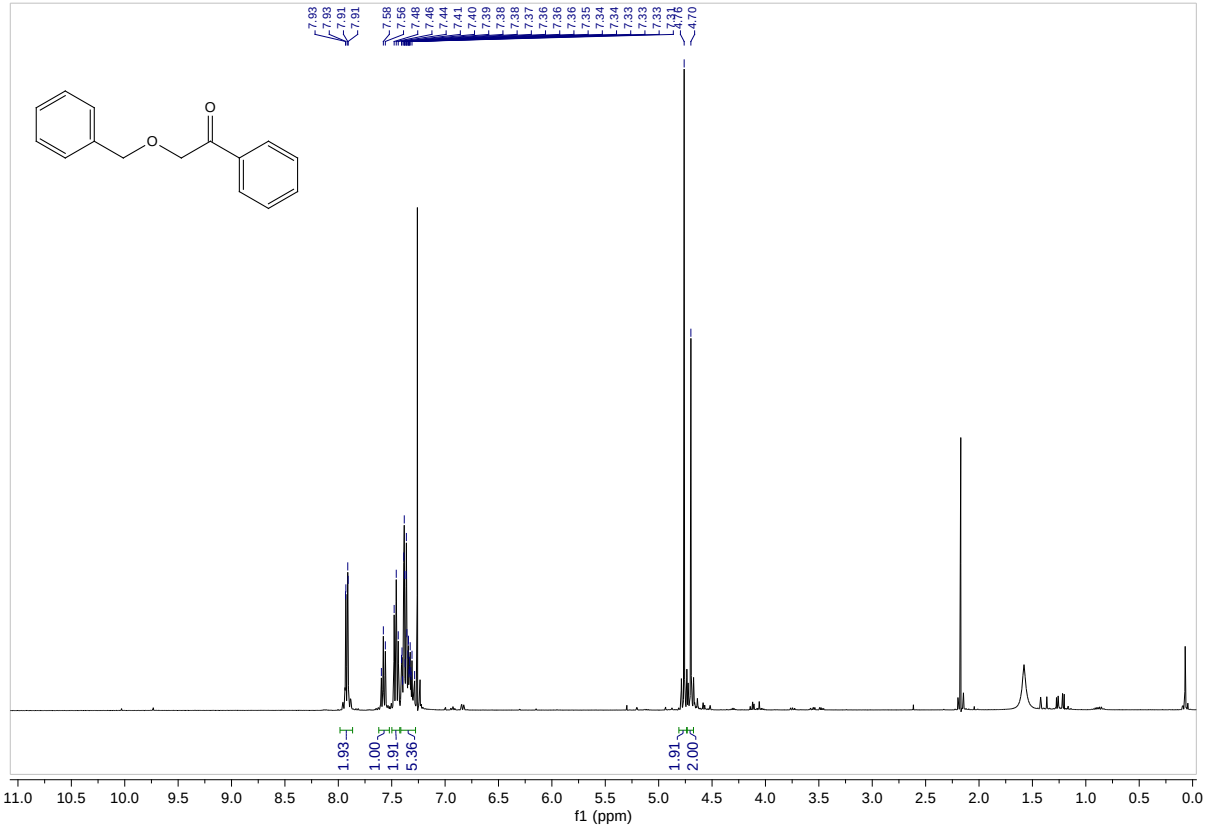
151.54
142.61
136.62
132.78
129.21
128.52
122.37
109.32
77.32
77.20
77.00
76.68
O
O
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.91
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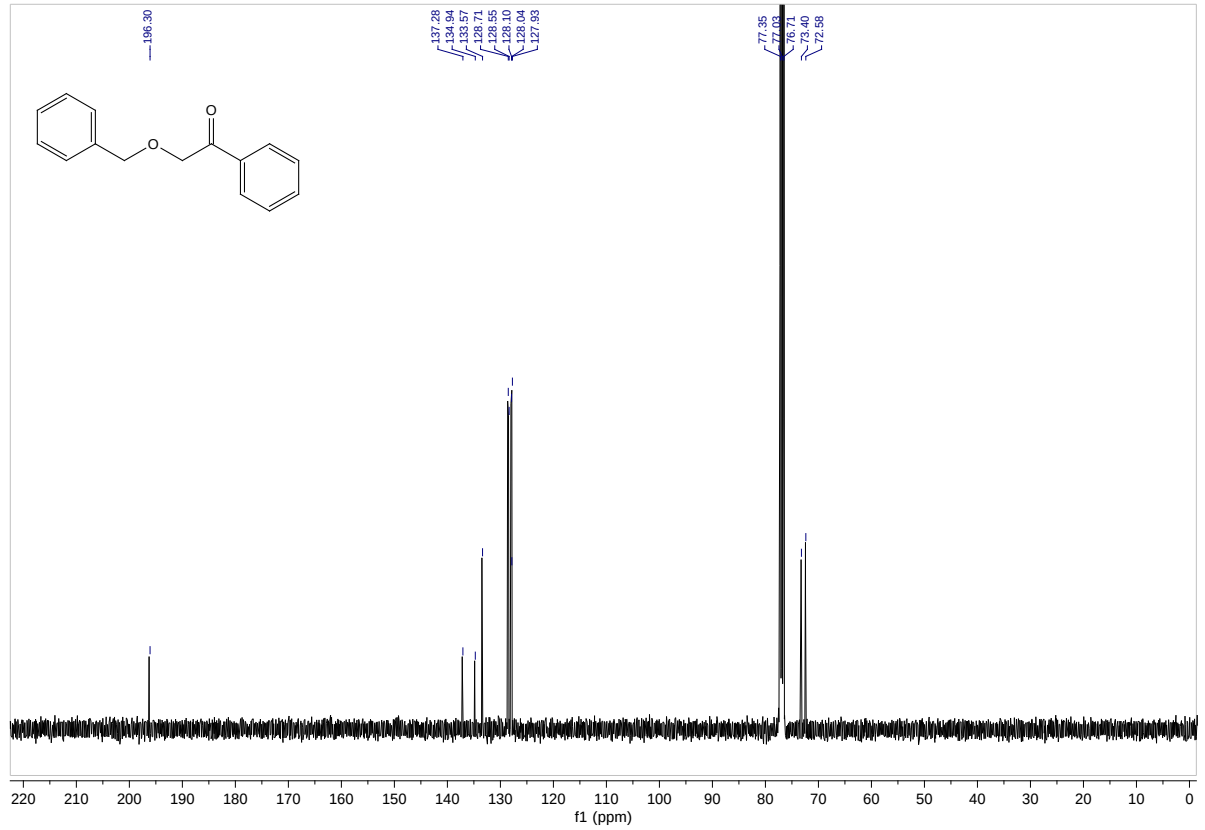
7.56
7.48
7.46
7.44
7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.33
4.76
4.70
O
O
1.93
1.00
1.91
5.36
1.91
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.94
133.57
128.71
128.55
128.10
128.04
127.93
77.35
77.03
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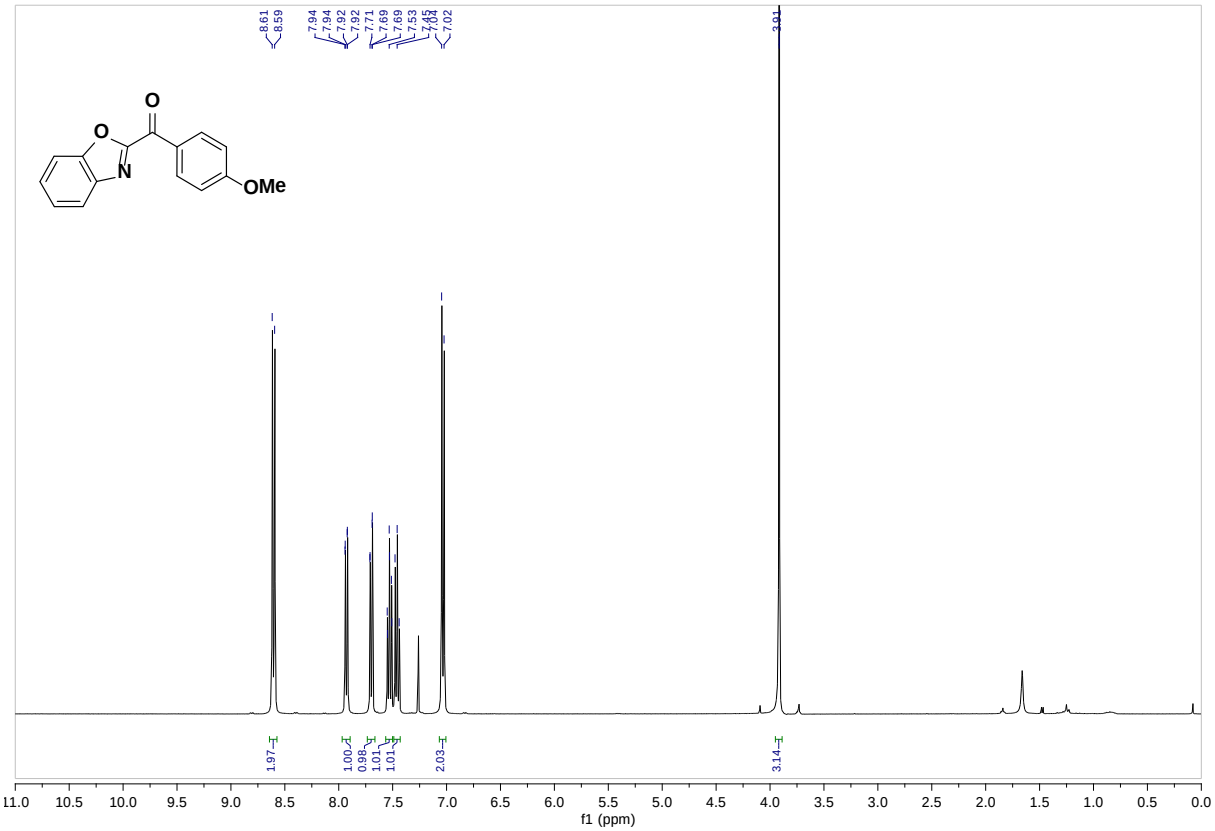
73.40
72.58
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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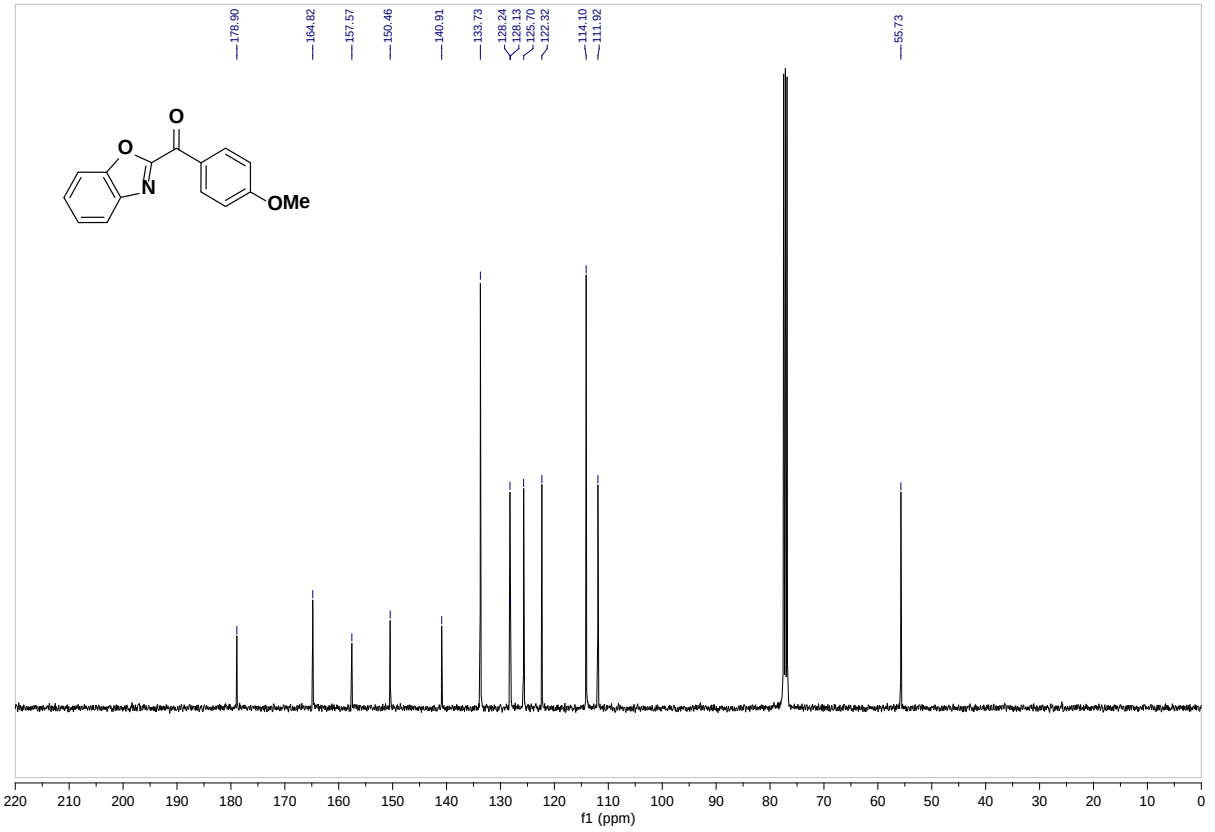
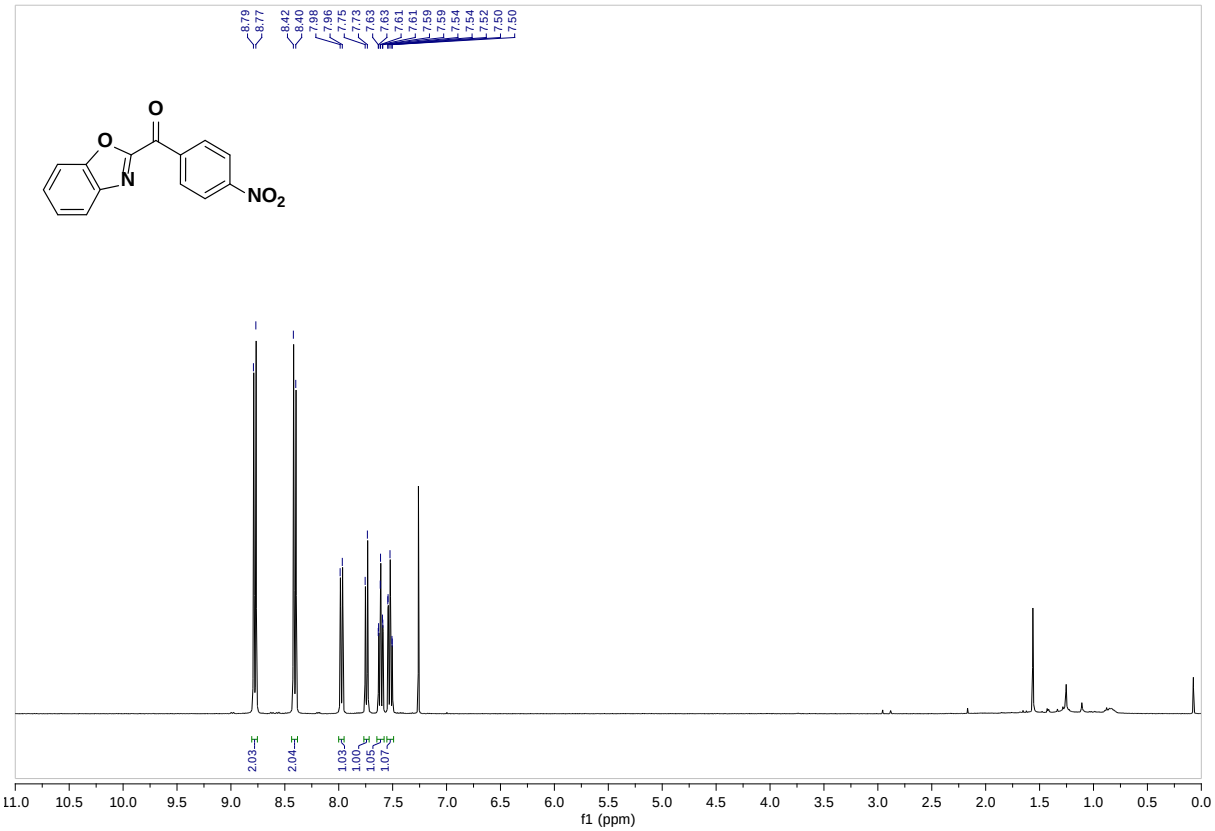
8.59
7.94
7.94
7.92
7.92
7.71
7.69
7.69
7.53
7.45
7.04
7.02
3.91
O
O
N
OMe
1.97
1.00
0.98
1.01
1.01
2.03
3.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.90
164.82
157.57
150.46
140.91
133.73
128.24
128.13
125.70
122.32
114.10
111.92
55.73
O
O
N
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.75
7.73
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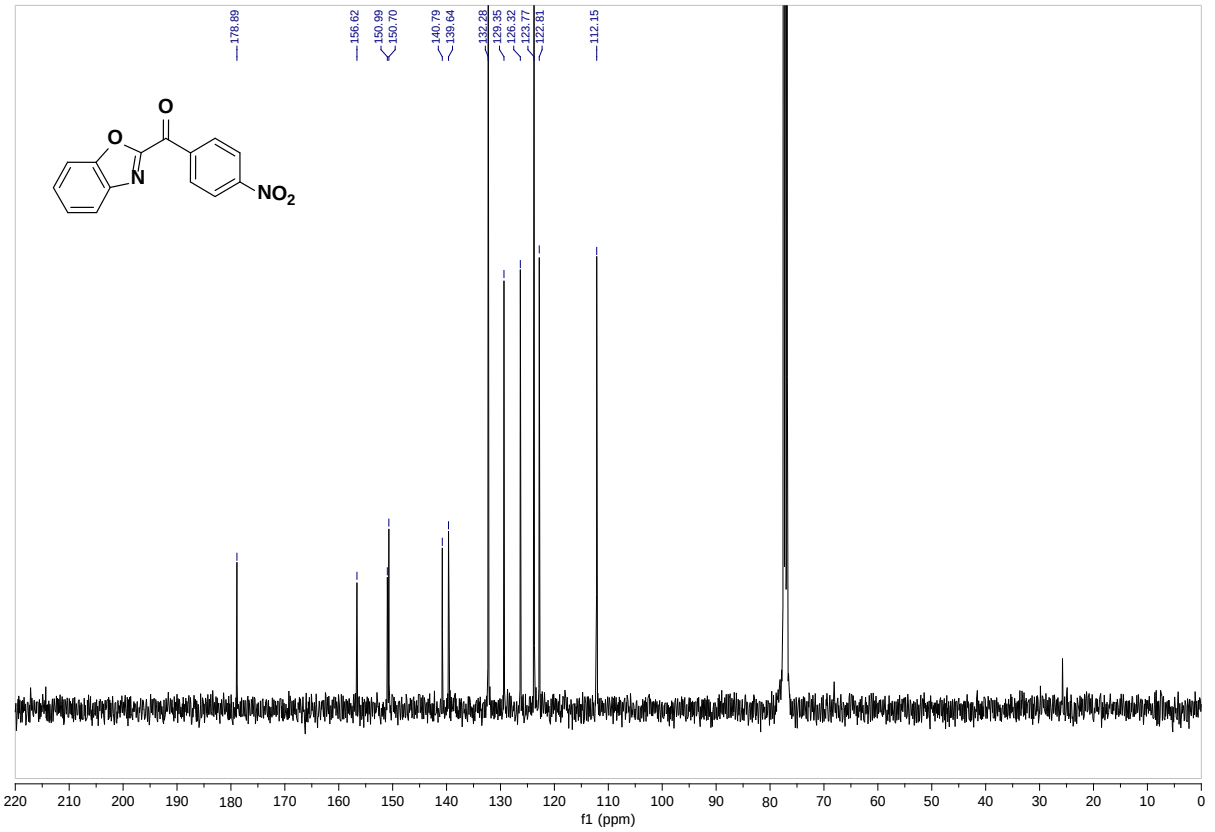
7.61
7.61
7.59
7.59
7.54
7.54
7.52
7.50
7.50
O
O
N
NO2
2.03
2.04
1.03
1.00
1.05
1.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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139.64
132.28
129.35
126.32
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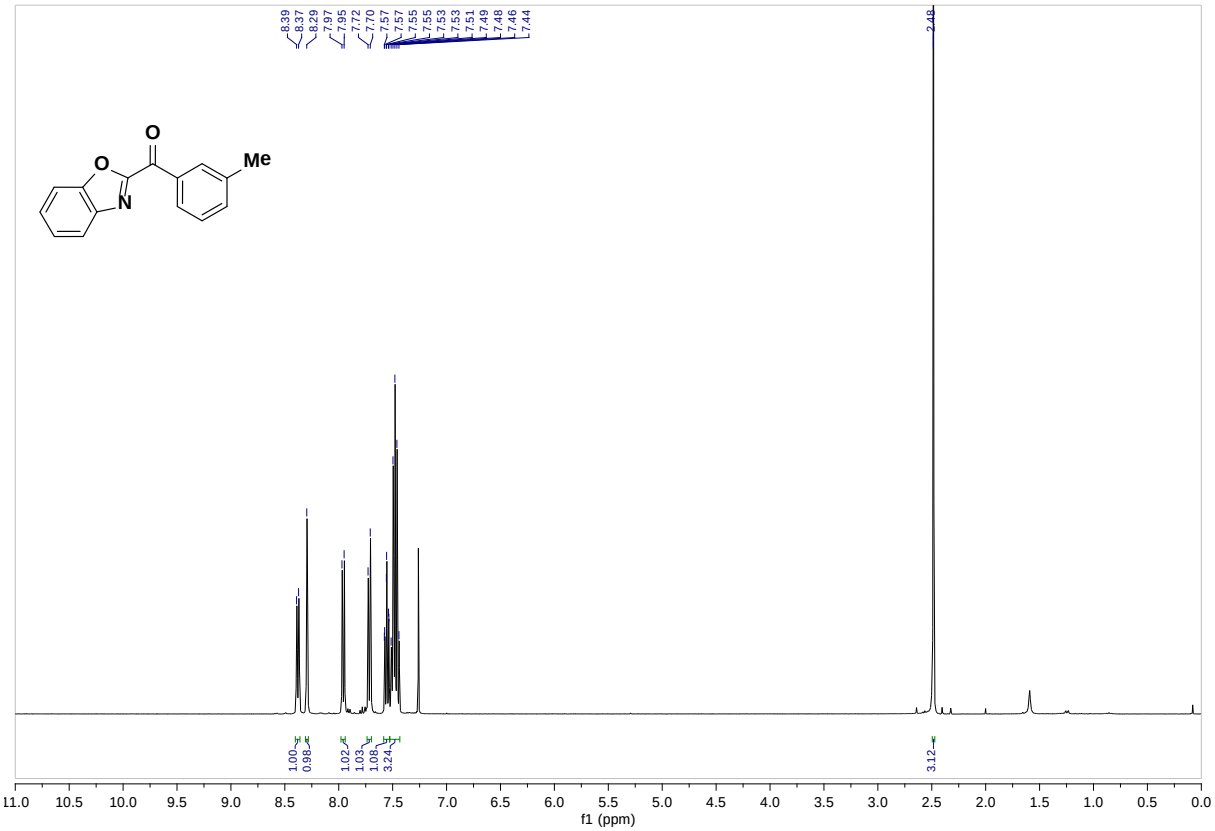
122.81
112.15
O
O
N
NO2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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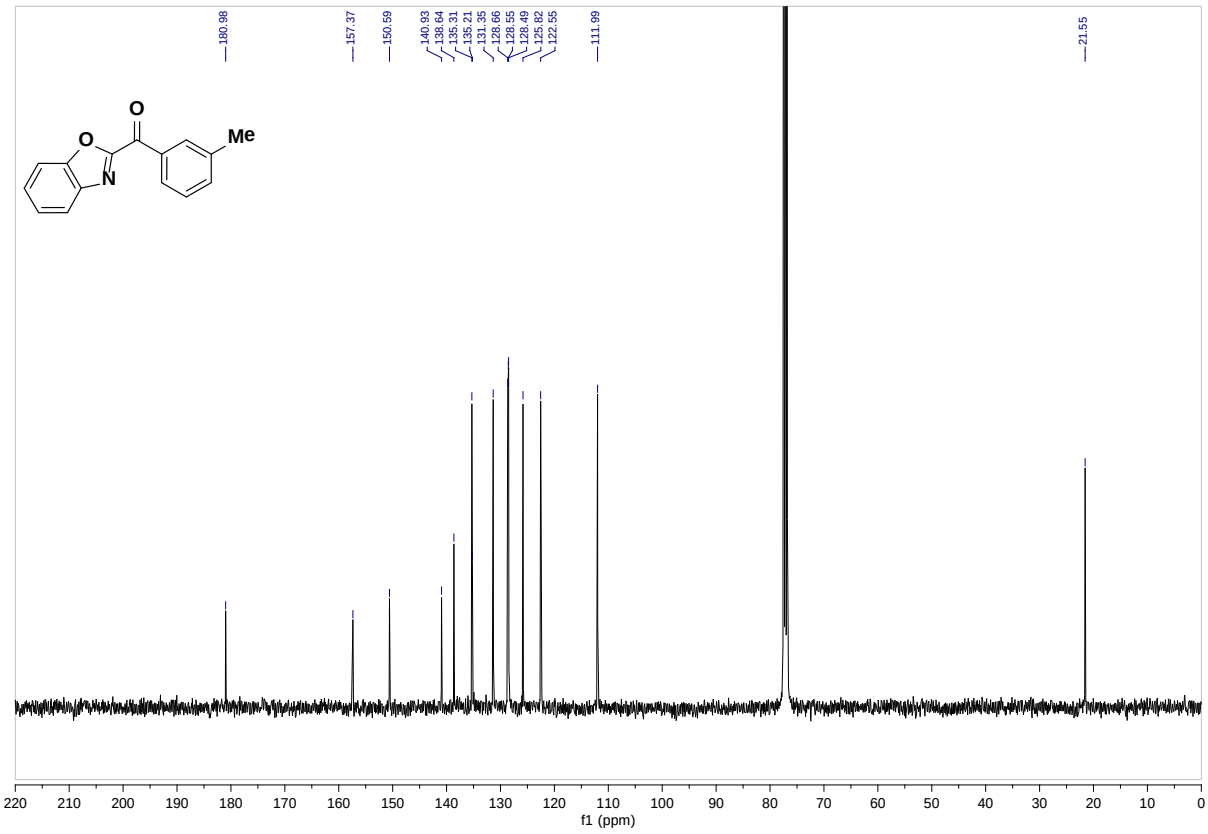
7.55
7.55
7.53
7.53
7.51
7.49
7.48
7.46
7.44
2.48
O
O
N
Me
1.00
0.98
1.02
1.03
1.08
3.24
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.31
135.21
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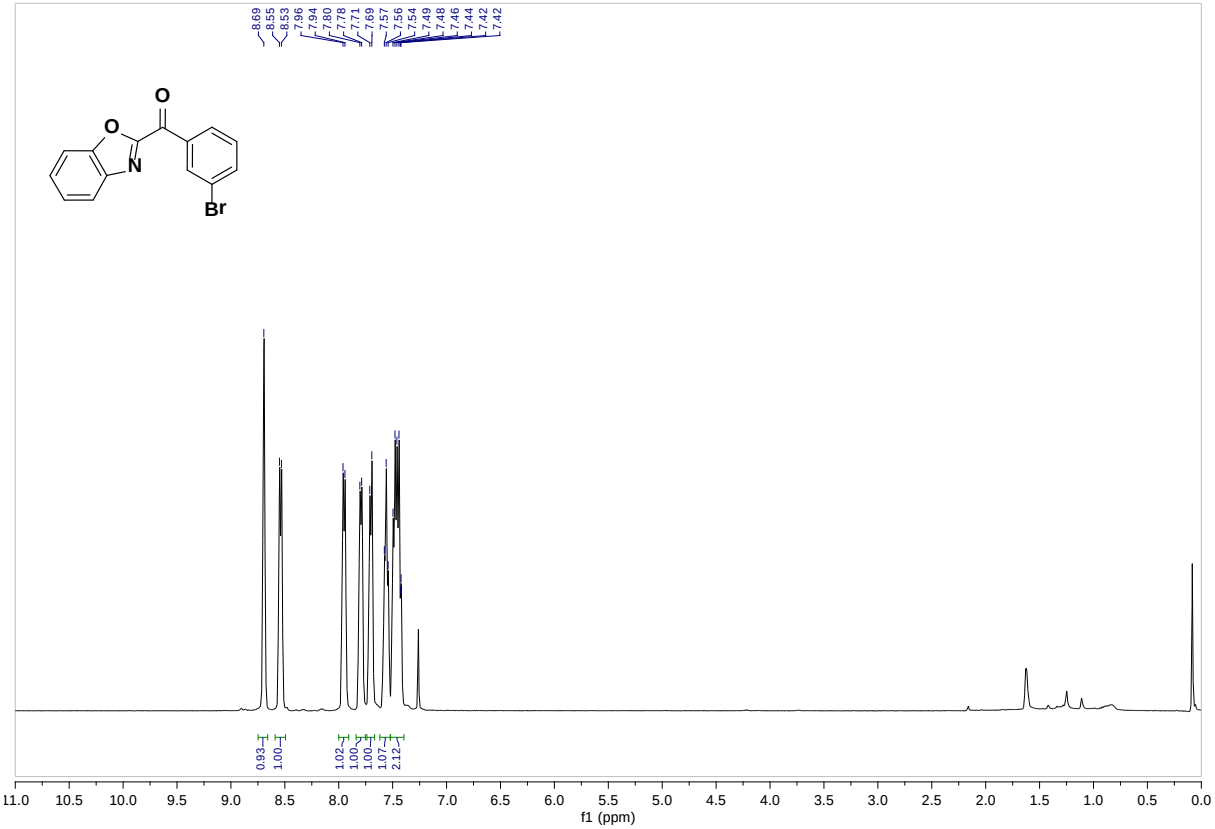
128.66
128.55
128.49
125.82
122.55
111.99
21.55
O
O
N
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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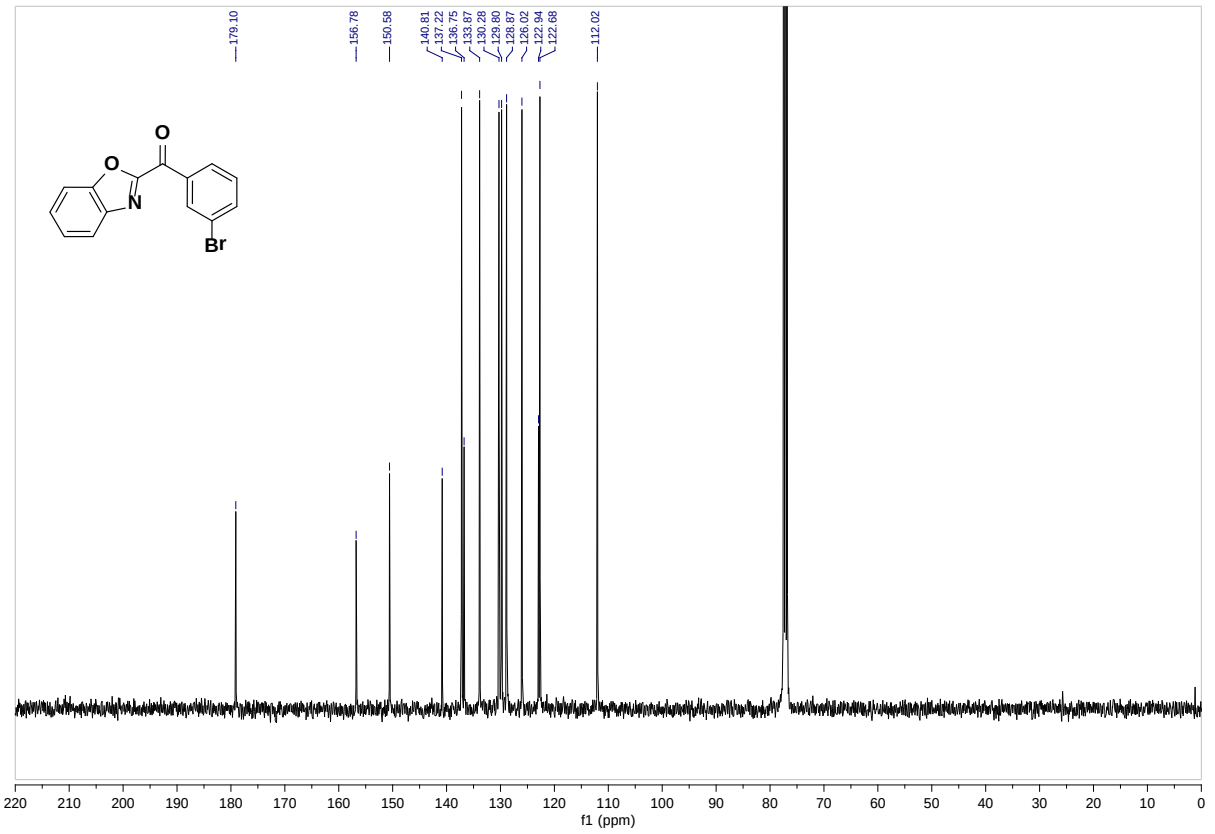
7.94
7.80
7.78
7.71
7.69
7.57
7.56
7.54
7.49
7.48
7.46
7.44
7.42
7.42
O
O
N
Br
0.93
1.00
1.02
1.00
1.00
1.07
2.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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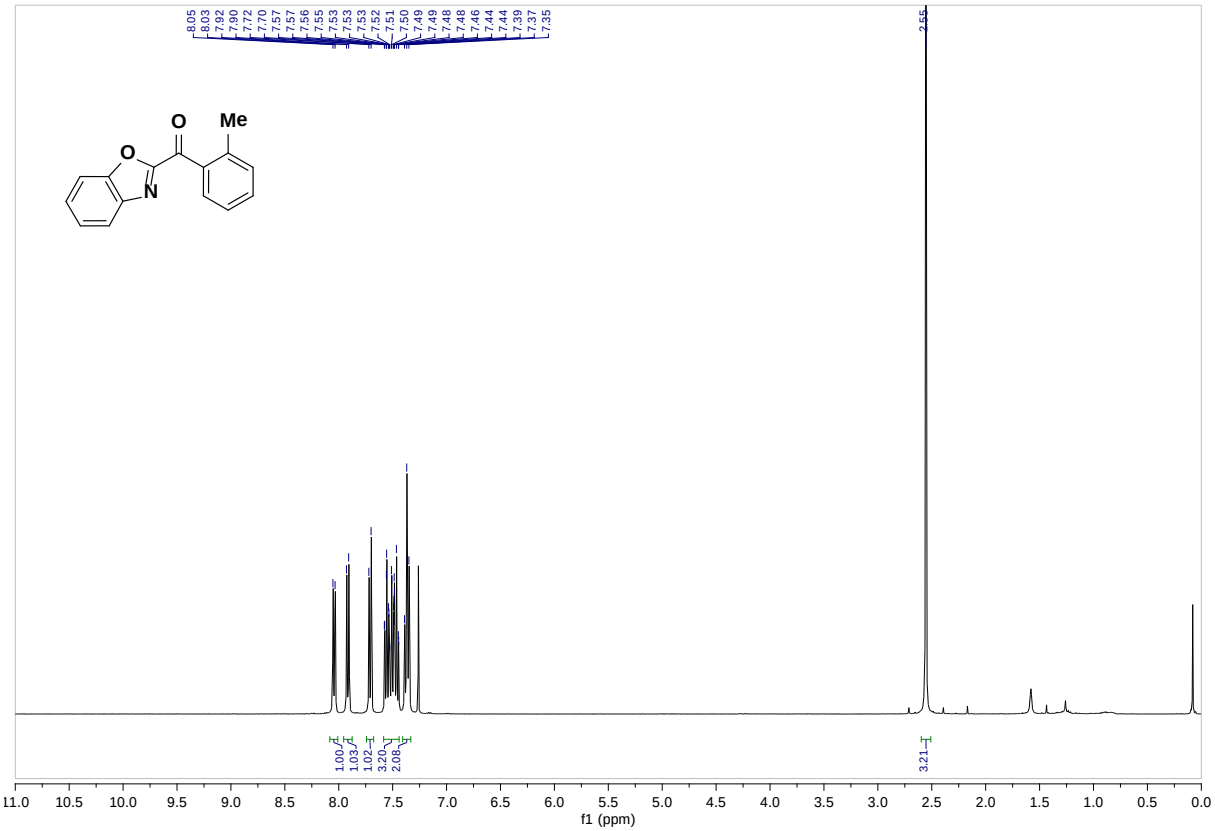
136.75
133.87
130.28
129.80
128.87
126.02
122.94
122.68
112.02
O
O
N
Br
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.53
7.53
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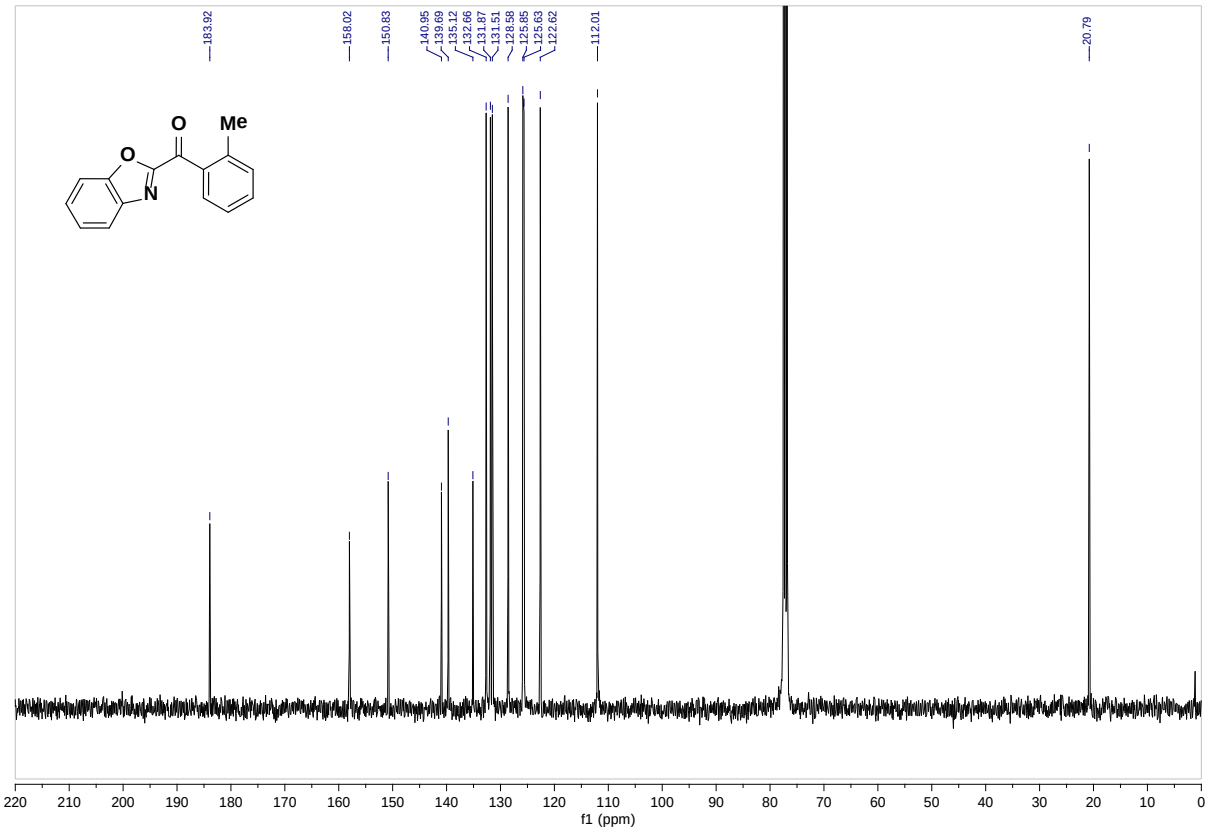
7.52
7.51
7.50
7.49
7.49
7.48
7.48
7.46
7.44
7.44
7.39
7.37
7.35
2.55
O
Me
O
N
1.00
1.03
1.02
3.20
2.08
3.21
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.12
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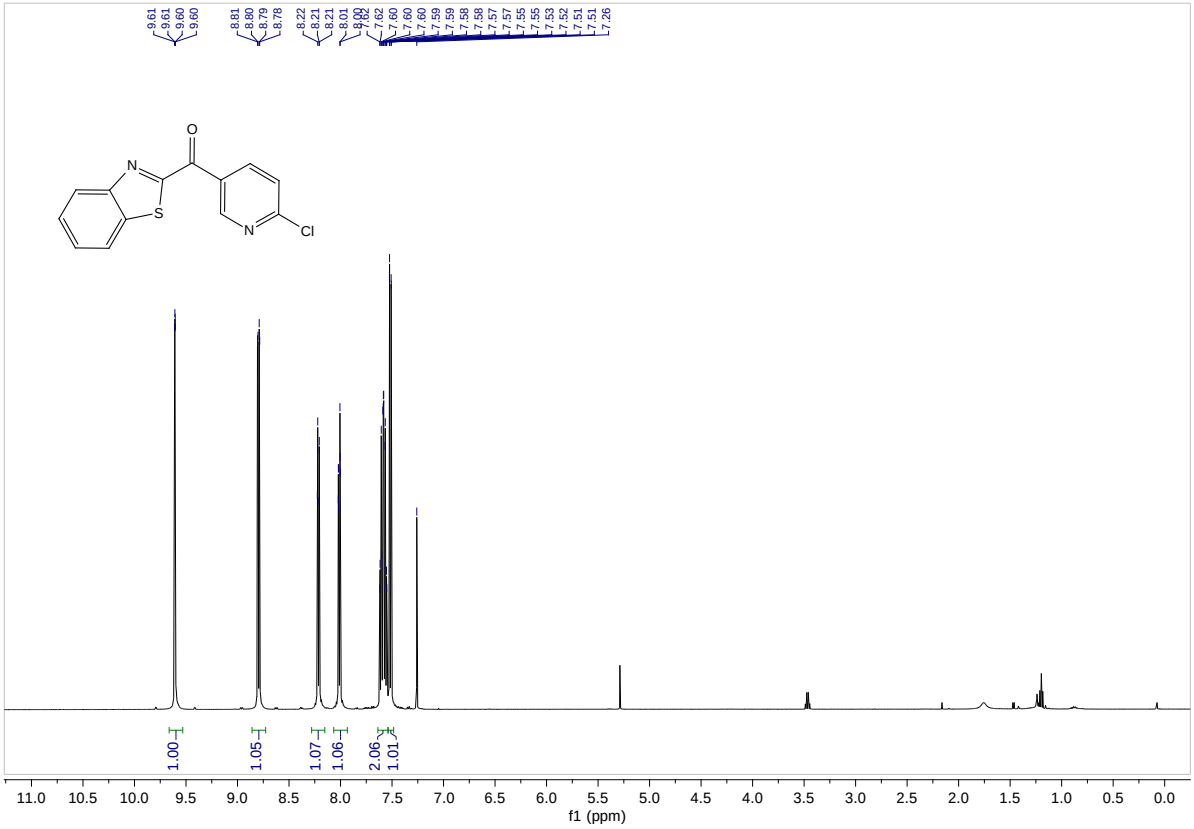
131.87
131.51
128.58
125.85
125.63
122.62
112.01
20.79
O
Me
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.53
7.52
7.51
7.51
7.26
O
N
S
N
Cl
1.00
1.05
1.07
1.06
2.06
1.01
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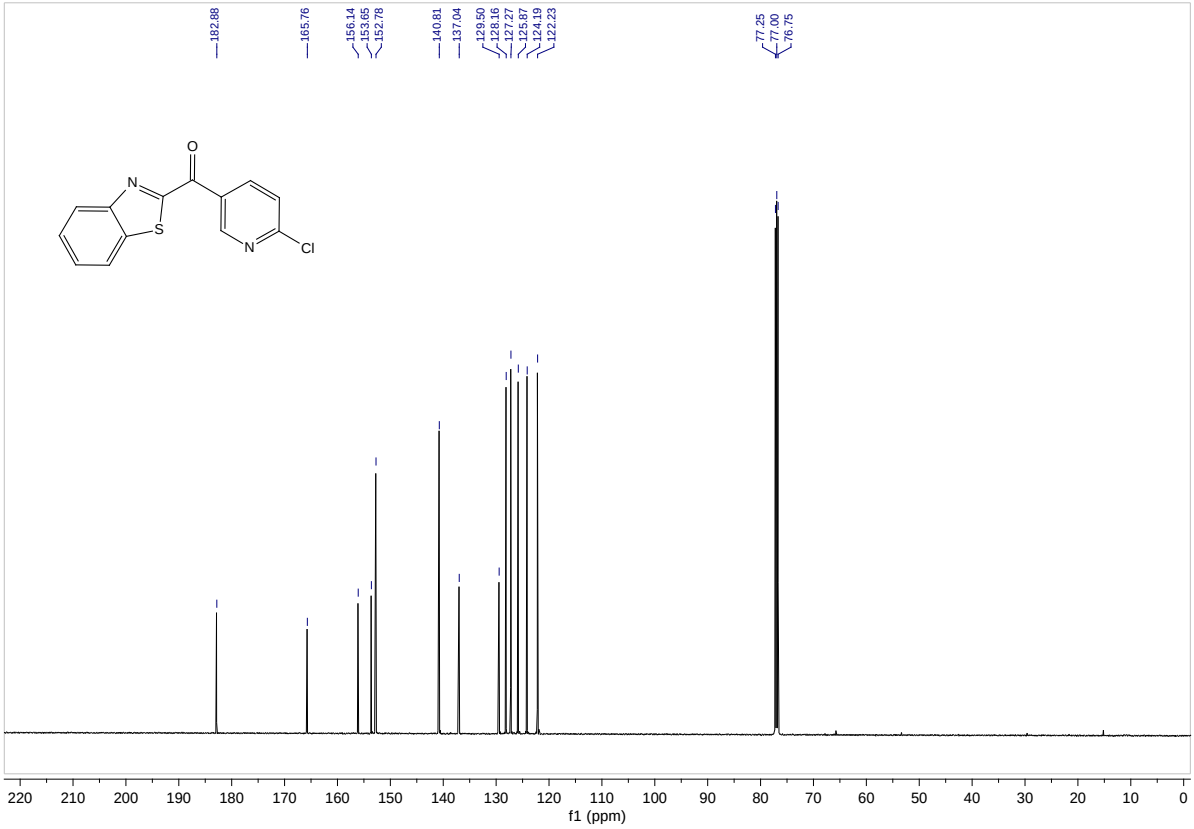
f1 (ppm)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140.81
137.04
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128.16
127.27
125.87
124.19
122.23
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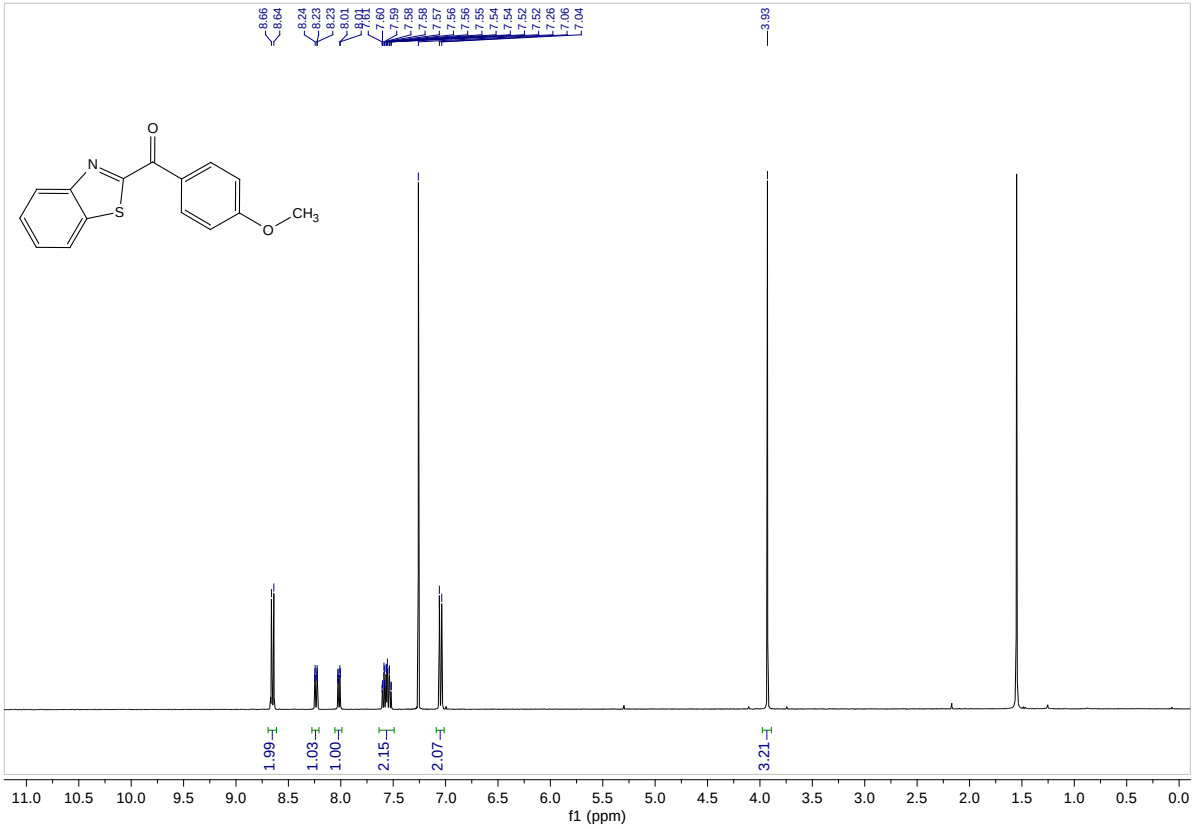
77.00
76.75
O
N
S
N
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.01
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7.58
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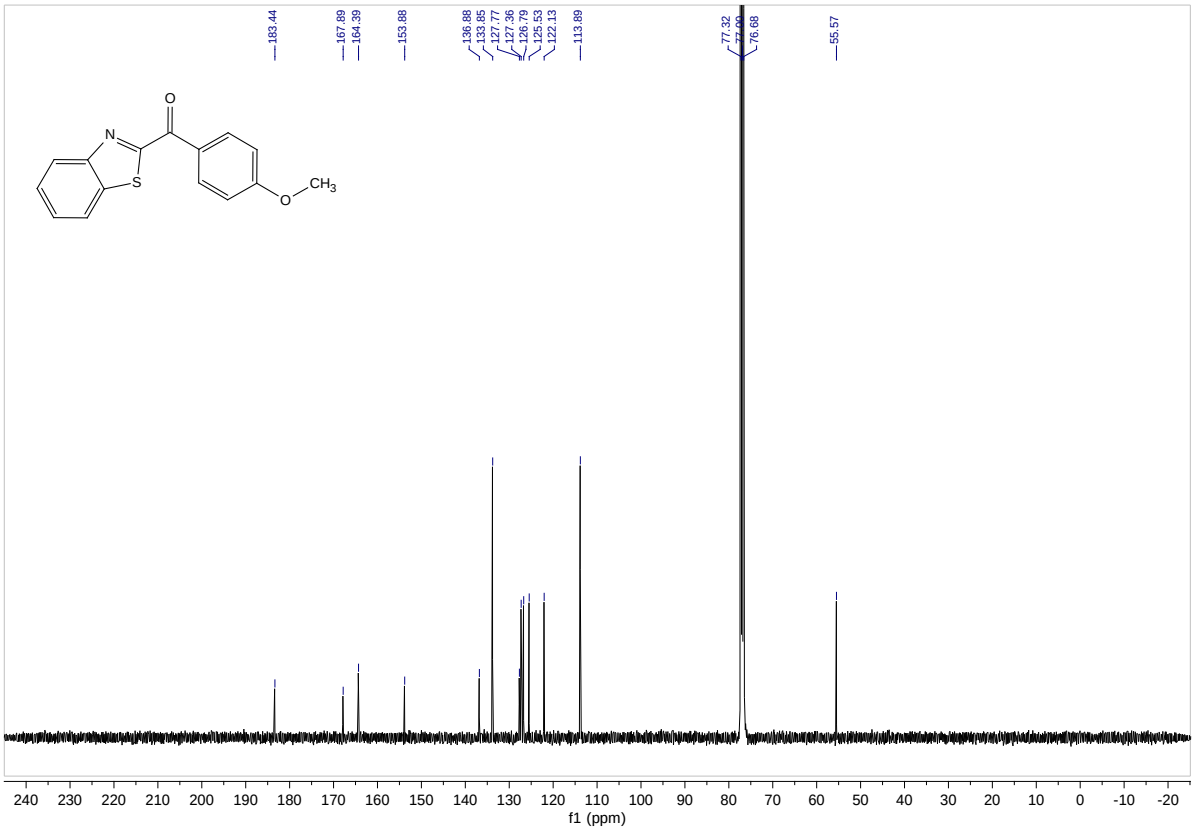
7.54
7.54
7.52
7.52
7.26
7.06
7.04
3.93
1.99
1.03
1.00
2.15
2.07
3.21
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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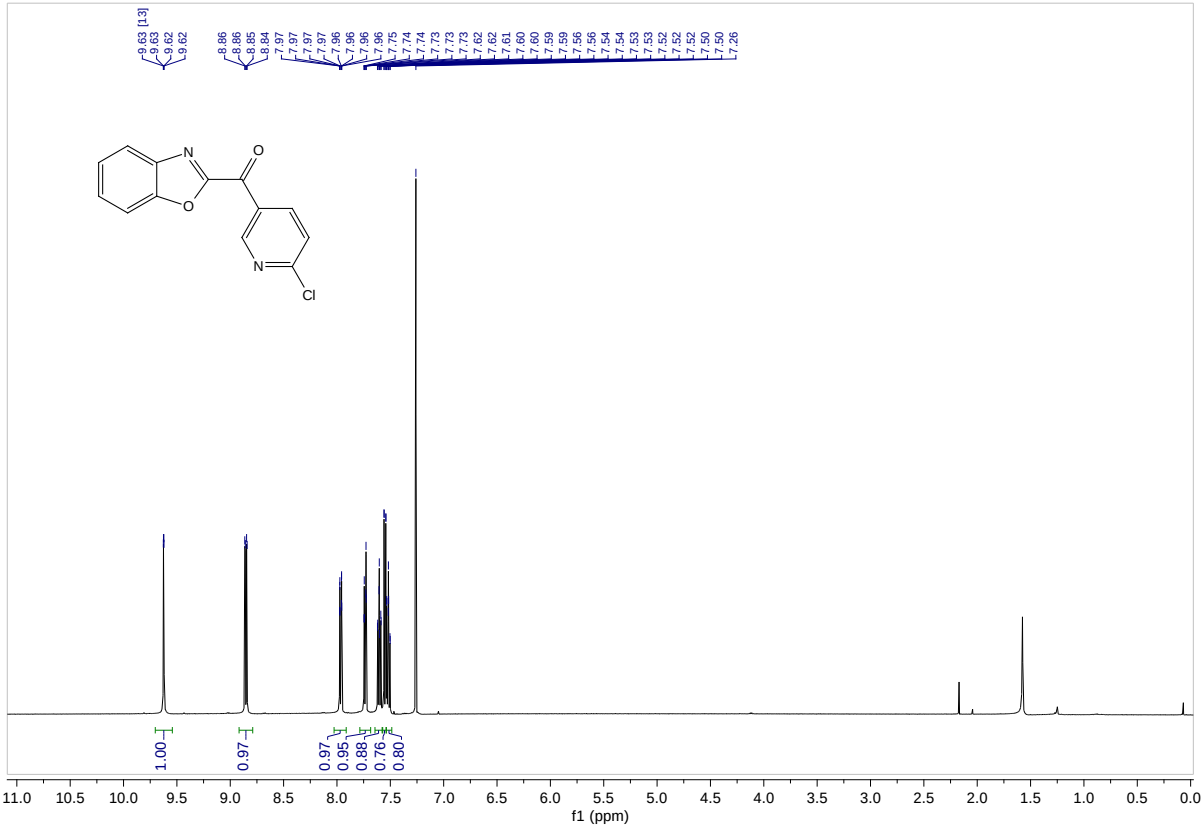
127.36
126.79
125.53
122.13
113.89
77.32
77.00
76.68
55.57
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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9.63
9.62
9.62
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8.86
8.85
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7.97
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7.56
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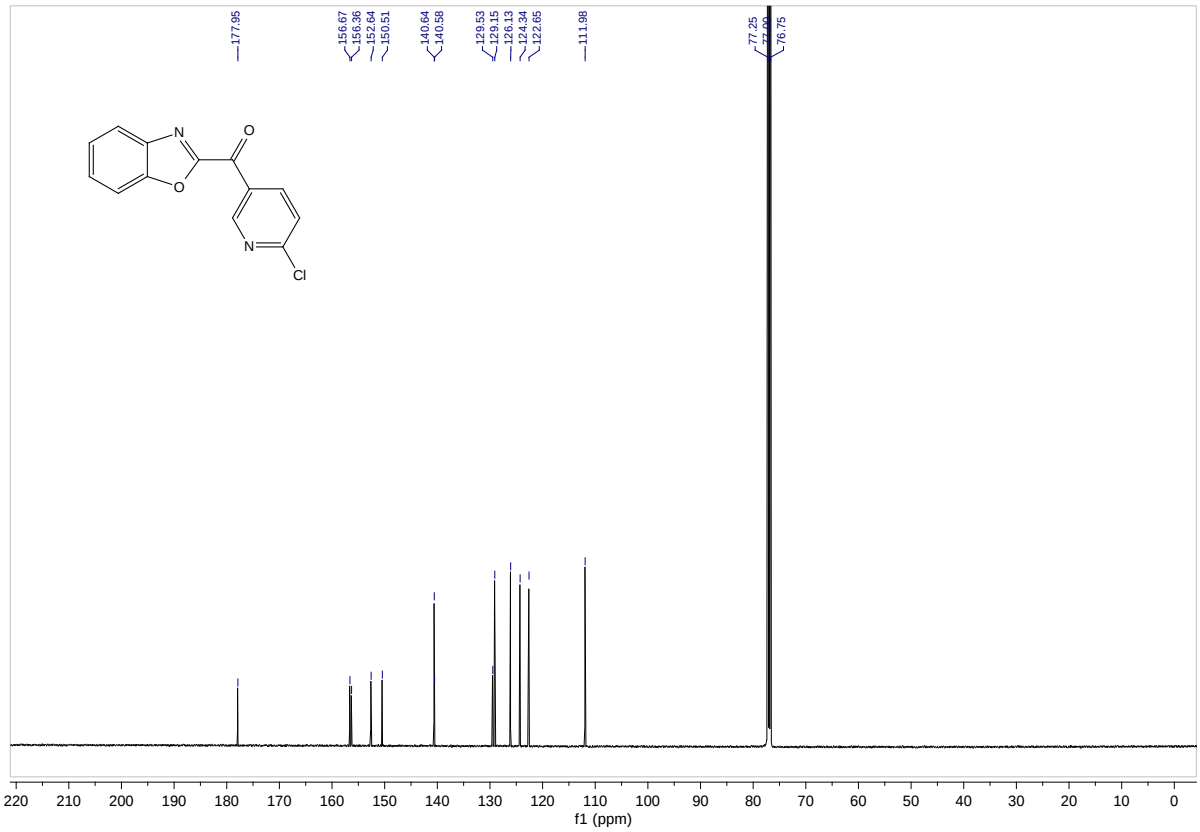
7.53
7.52
7.52
7.52
7.50
7.50
7.26
N
O
O
N
Cl
1.00
0.97
0.97
0.95
0.88
0.76
0.80
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.34
122.65
111.98
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O
O
N
Cl
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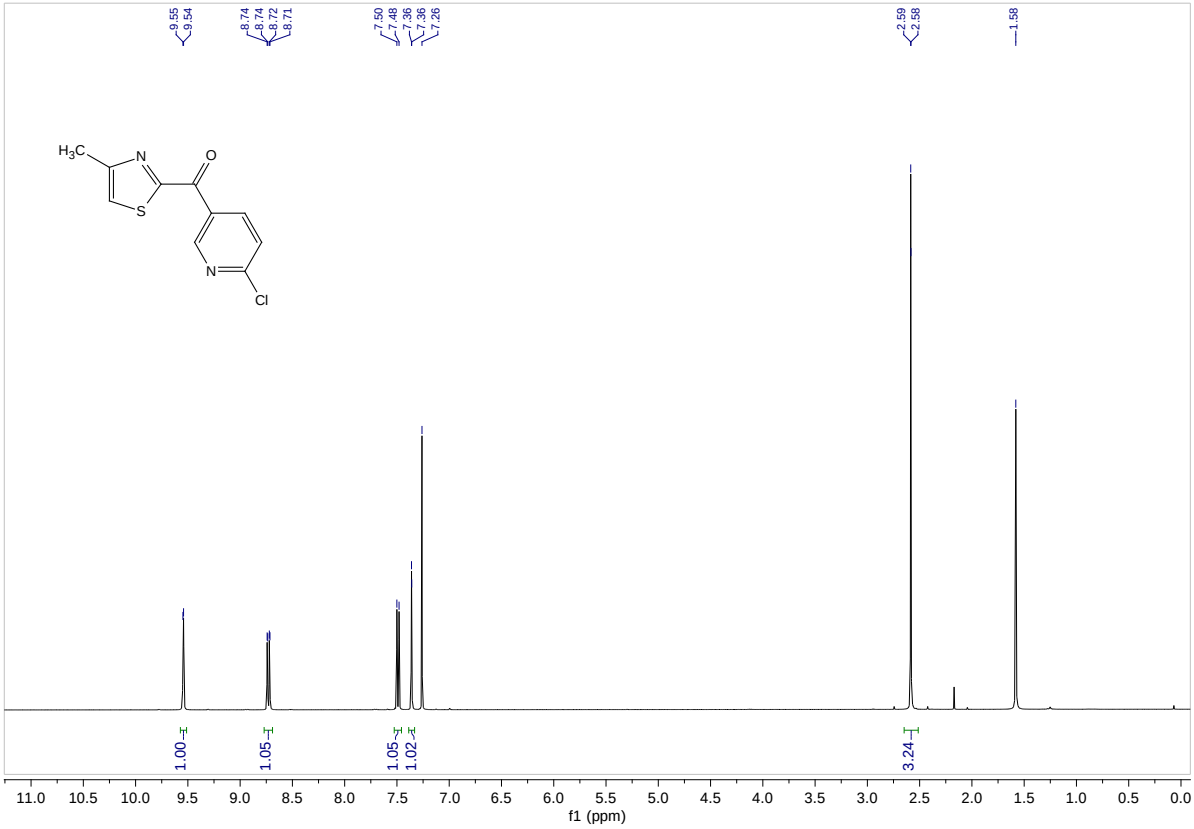
f1 (ppm)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7.36
7.26
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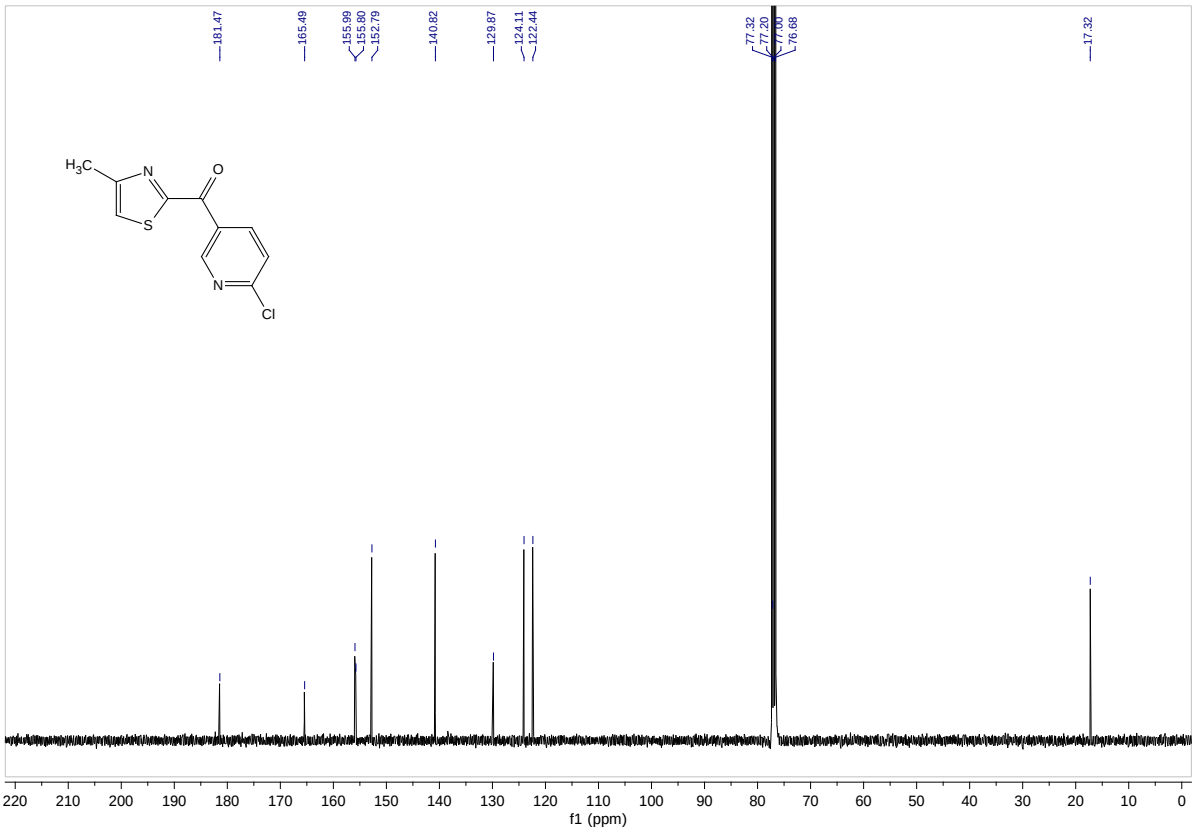
2.58
1.58
H3C
N
O
S
N
Cl
1.00
1.05
1.05
1.02
3.24
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.87
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77.32
77.20
77.00
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N
O
S
N
Cl
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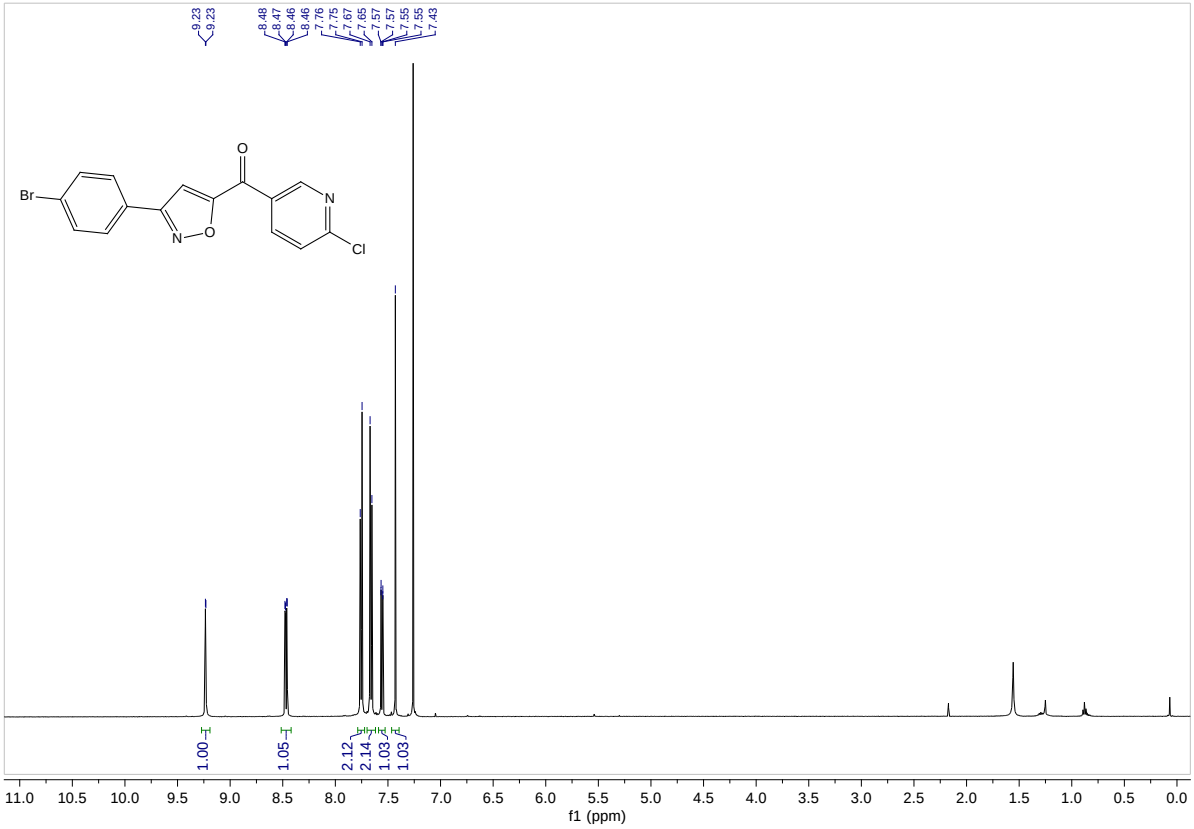
f1 (ppm)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7.57
7.57
7.55
7.55
7.43
Br
O
N
N
O
Cl
1.00
1.05
2.12
2.14
1.03
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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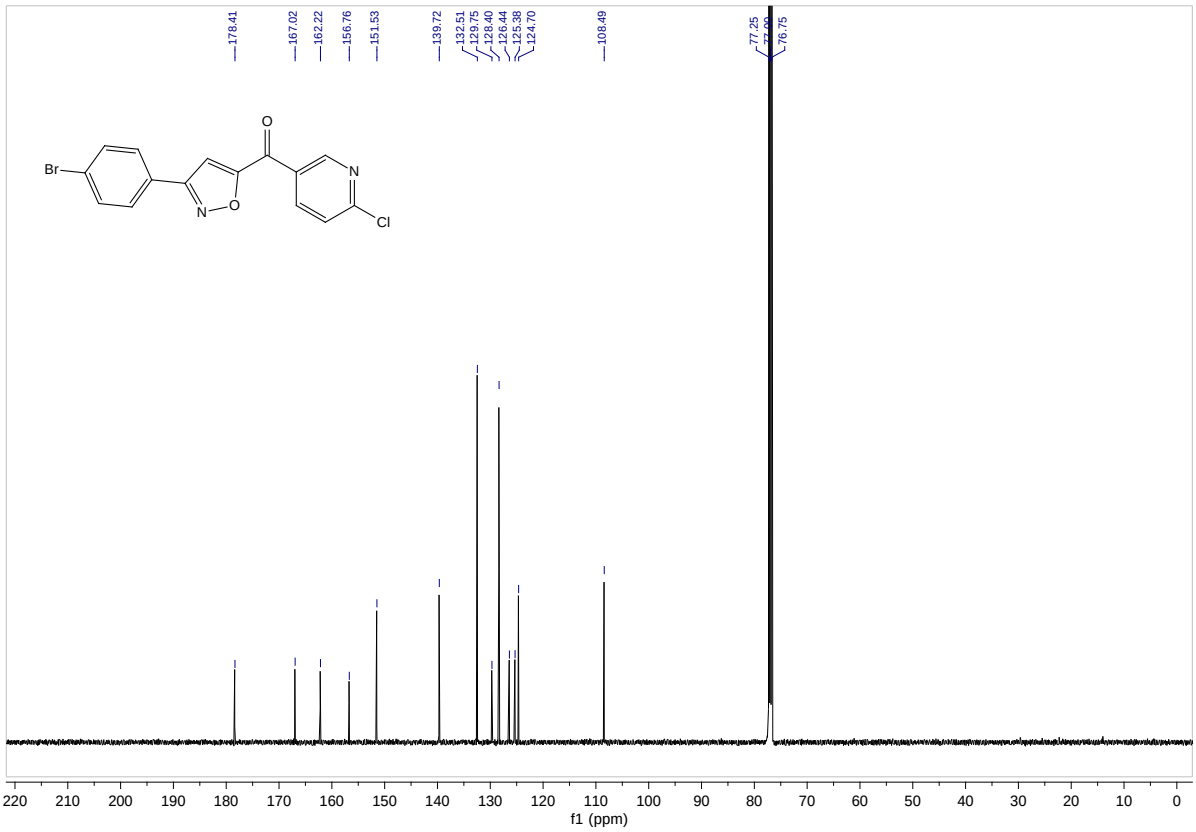
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124.70
108.49
77.25
77.00
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Br
O
N
N
O
Cl
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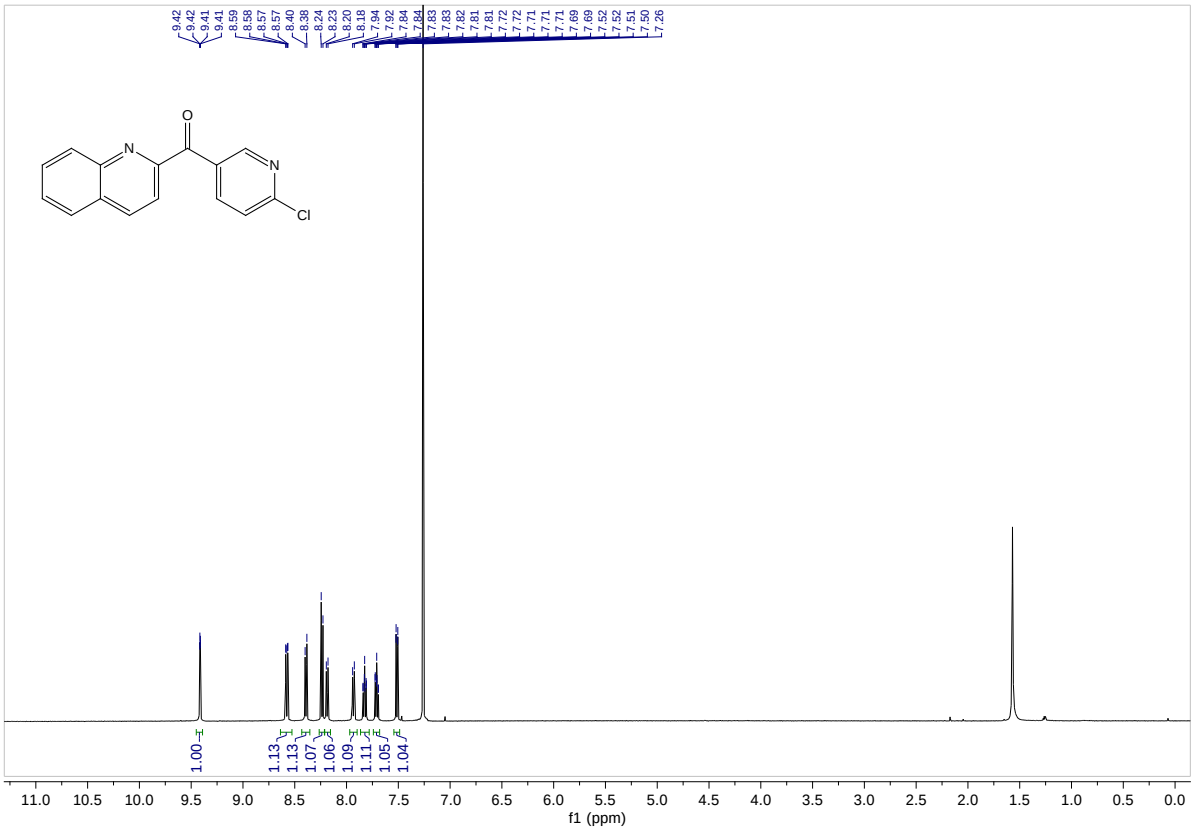
f1 (ppm)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7.84
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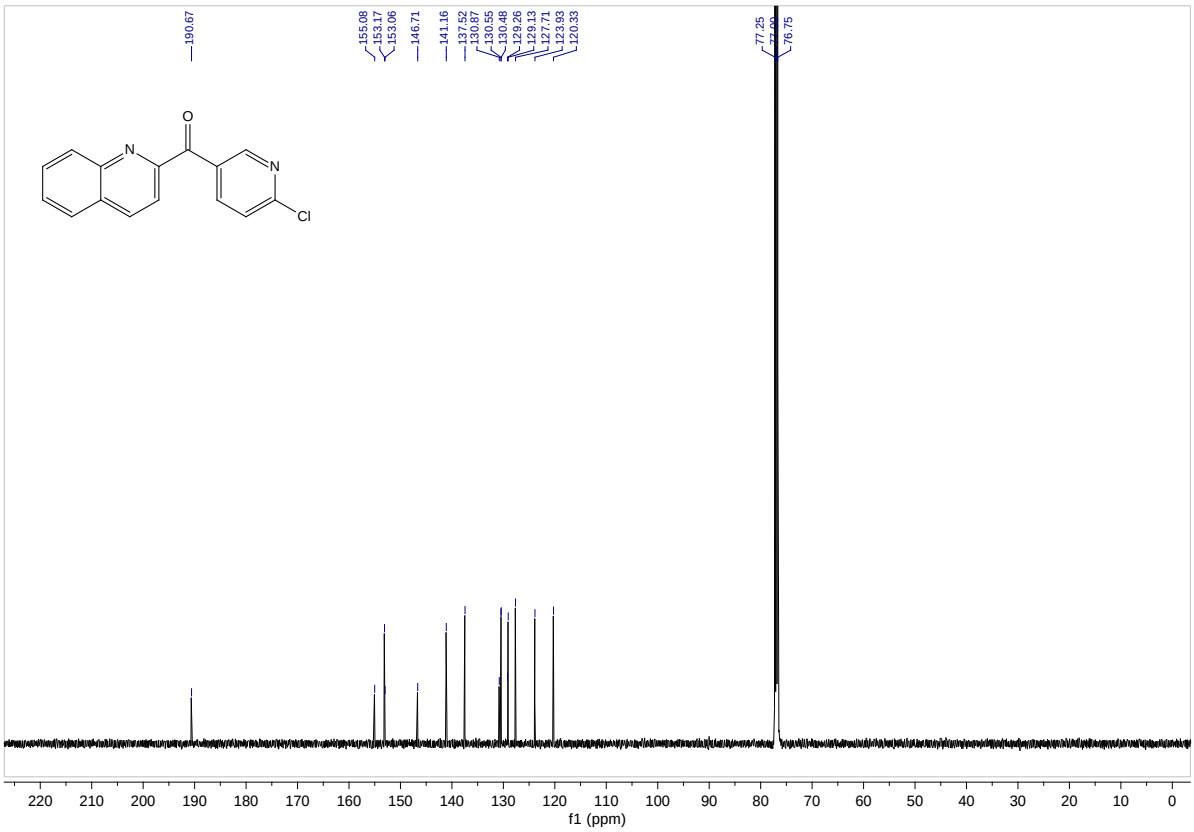
7.83
7.82
7.81
7.81
7.72
7.72
7.71
7.71
7.71
7.69
7.69
7.52
7.52
7.51
7.50
7.26
O
N
N
Cl
1.00
1.13
1.13
1.07
1.06
1.09
1.11
1.05
1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.26
129.13
127.71
123.93
120.33
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76.75
O
N
N
Cl
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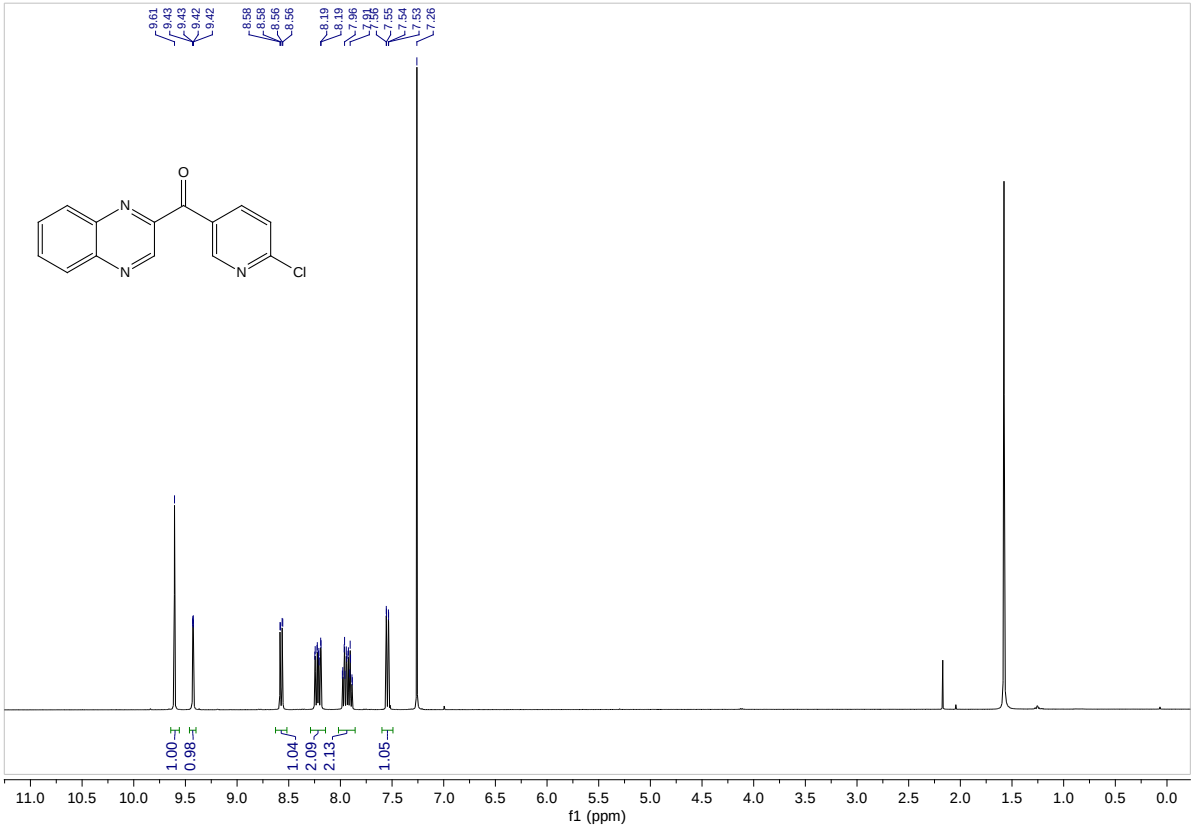
f1 (ppm)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9.43
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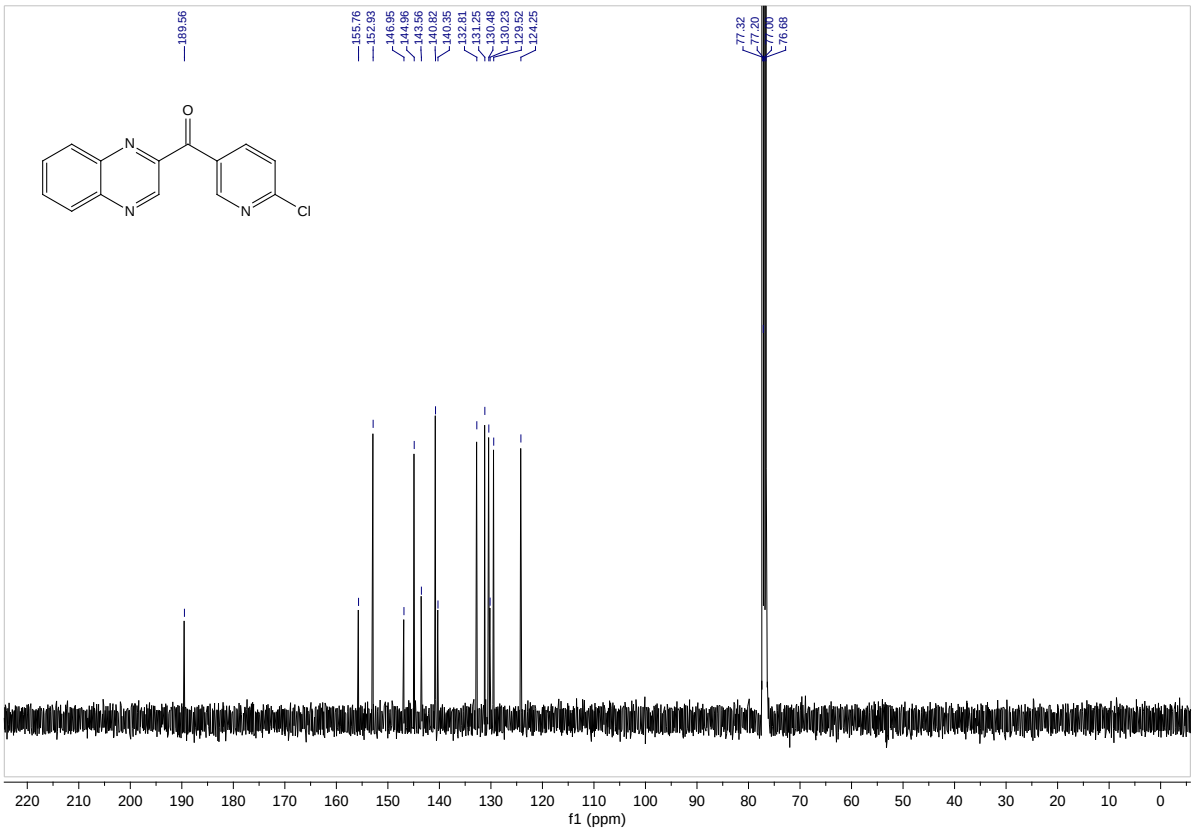
9.42
8.58
8.58
8.56
8.56
8.19
8.19
7.96
7.91
7.90
7.55
7.54
7.53
7.26
O
N
N
N
Cl
1.00
0.98
1.04
2.09
2.13
1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.25
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130.23
129.52
124.25
77.32
77.20
77.00
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O
N
N
N
Cl
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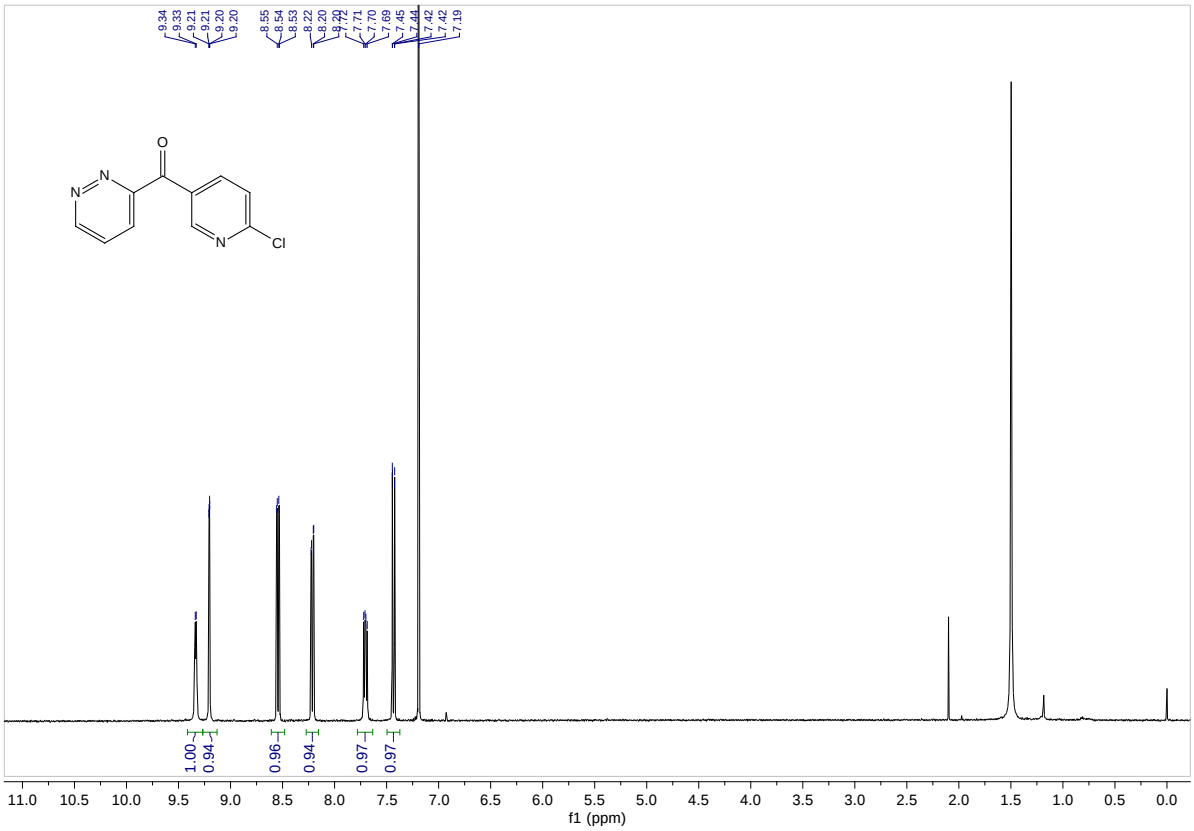
f1 (ppm)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9.20
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8.54
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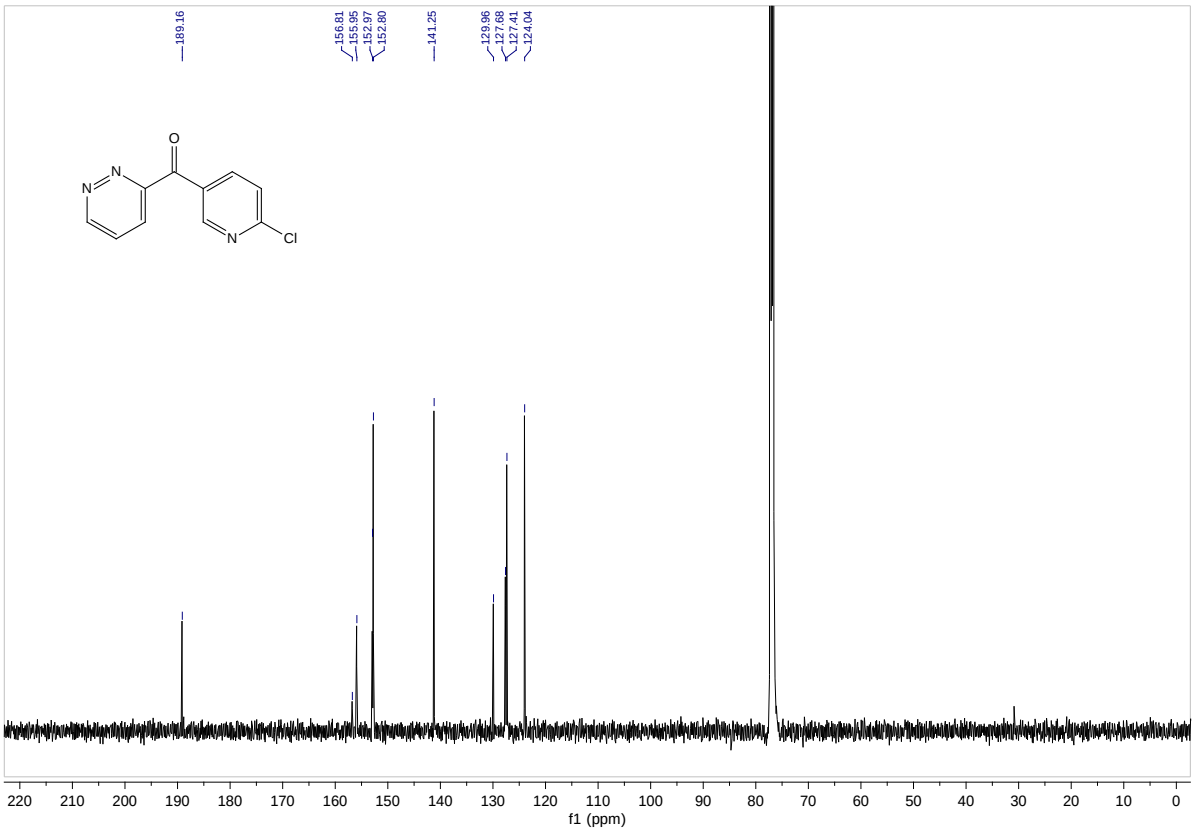
8.22
8.20
7.71
7.70
7.69
7.45
7.44
7.42
7.42
7.19
O
N
N
N
Cl
1.00
0.94
0.96
0.94
0.97
0.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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N
Cl
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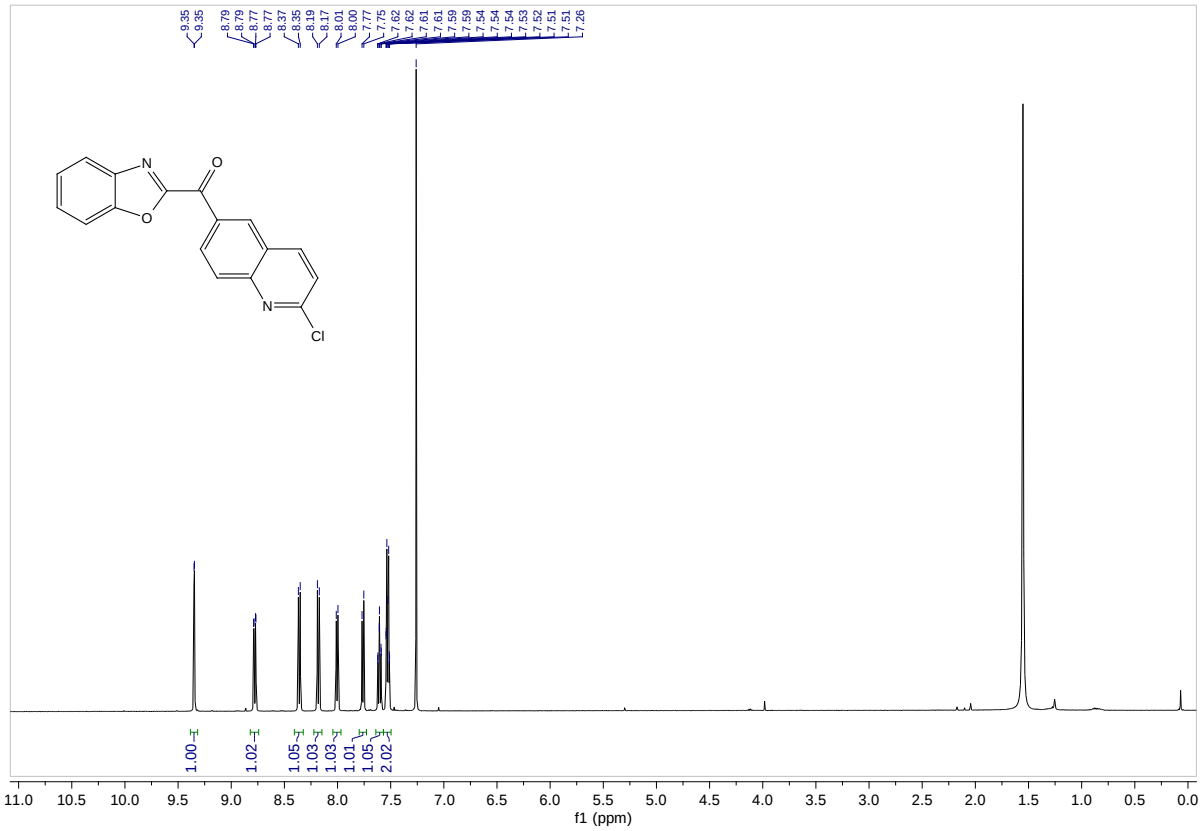
f1 (ppm)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1.03
1.03
1.01
1.05
2.02
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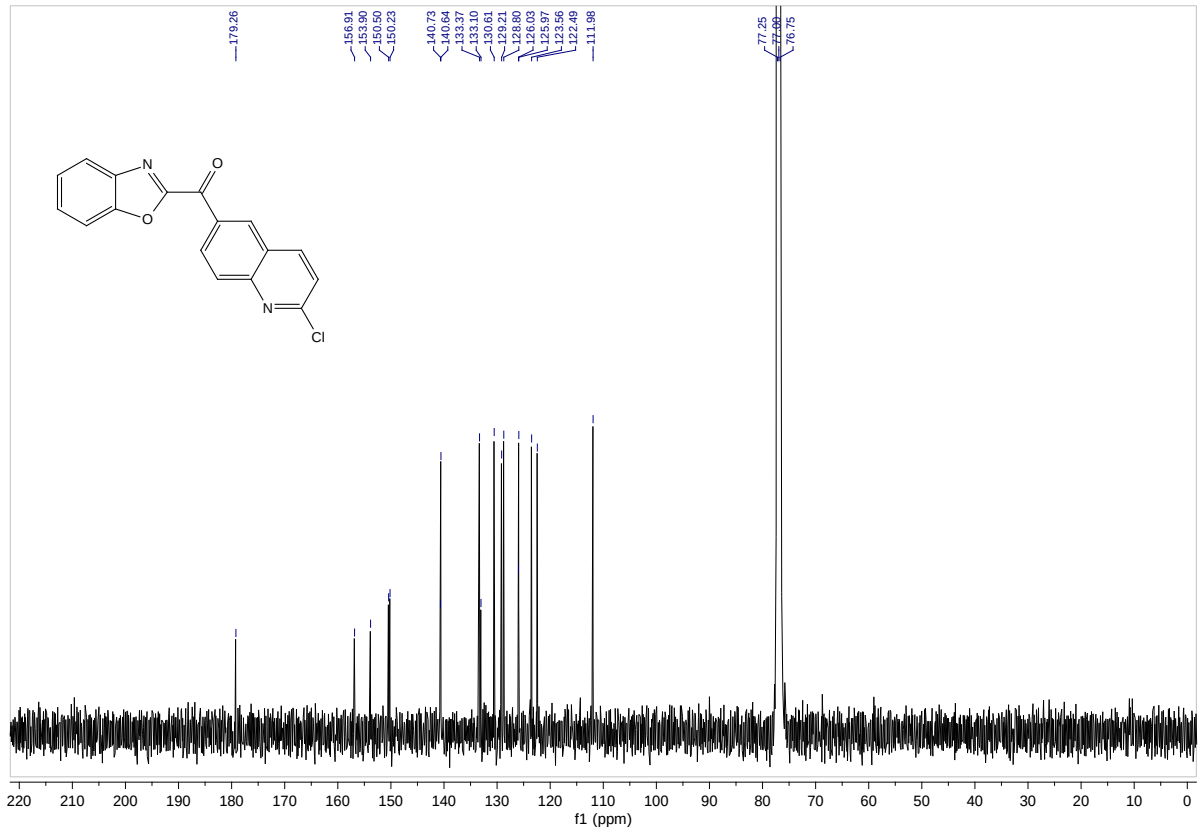
f1 (ppm)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133.10
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129.21
128.80
126.03
125.97
123.56
122.49
111.98
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O
O
N
Cl
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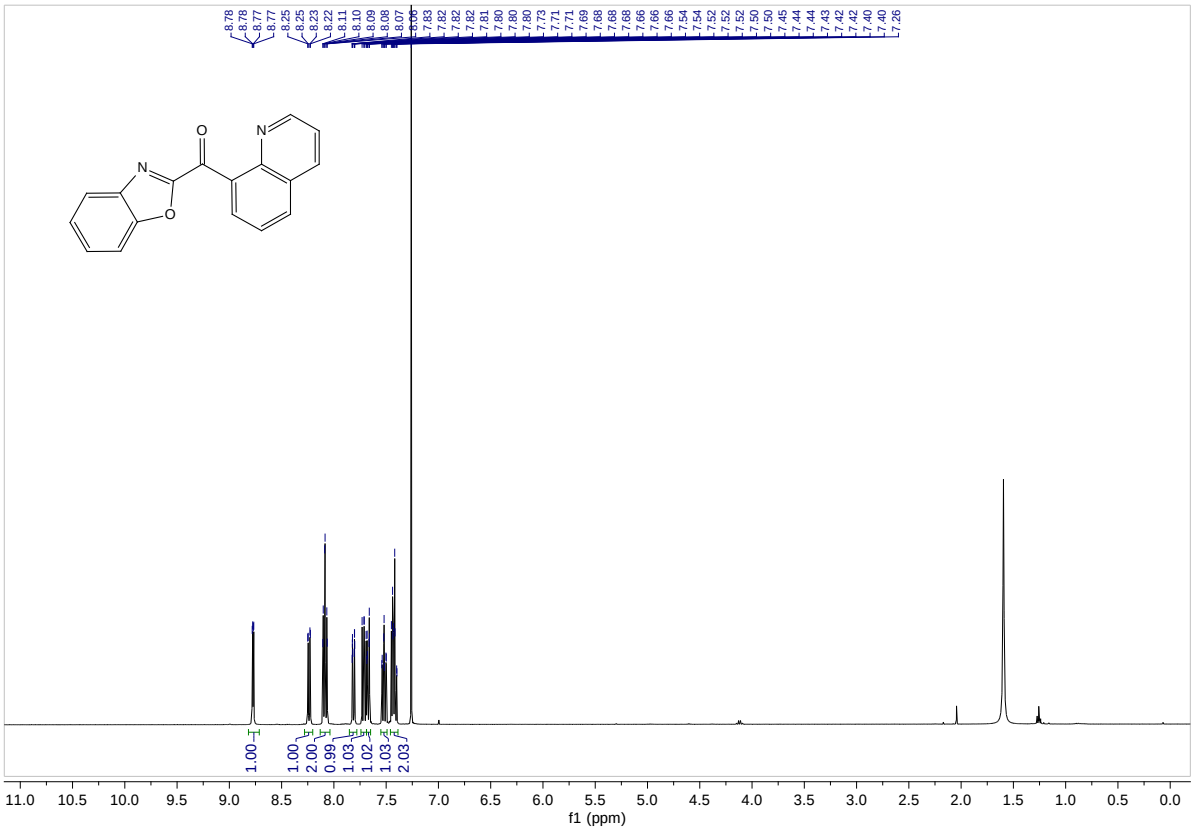
f1 (ppm)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O
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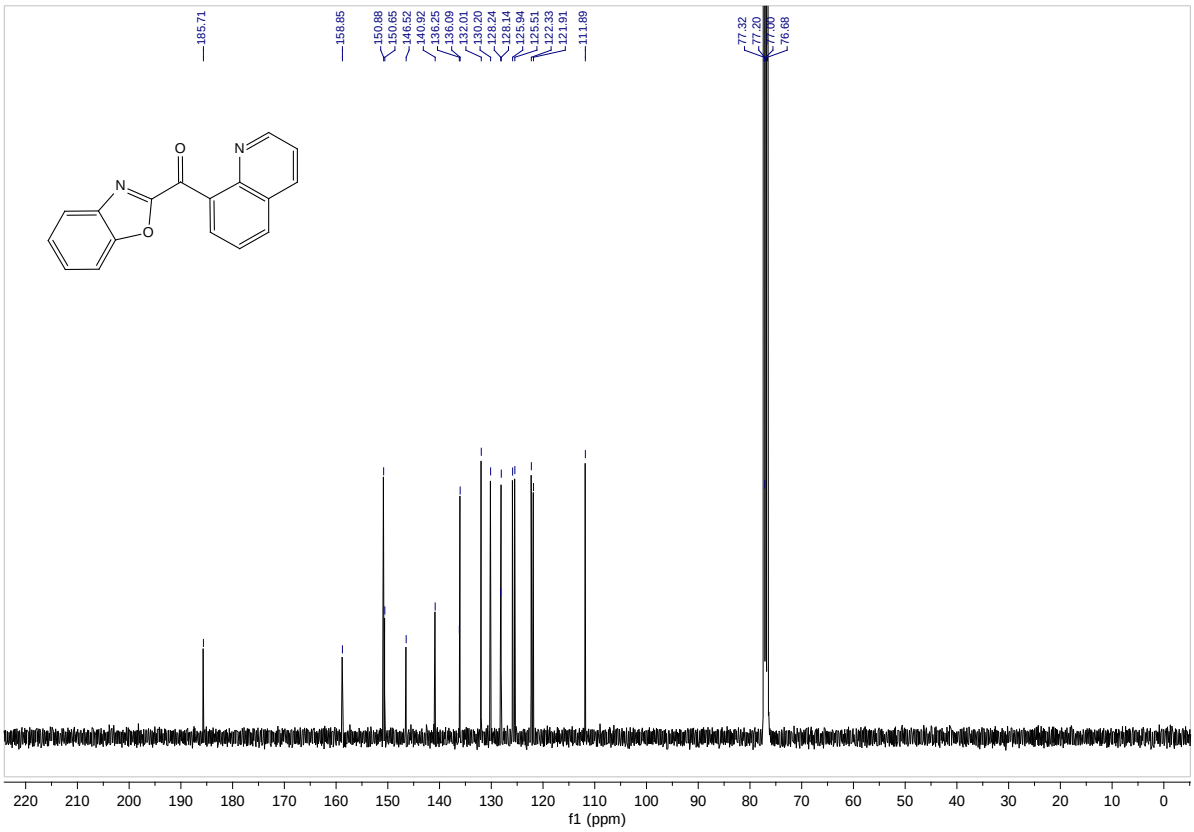
1.00
2.00
0.99
1.03
1.02
1.03
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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121.91
111.89
77.32
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N
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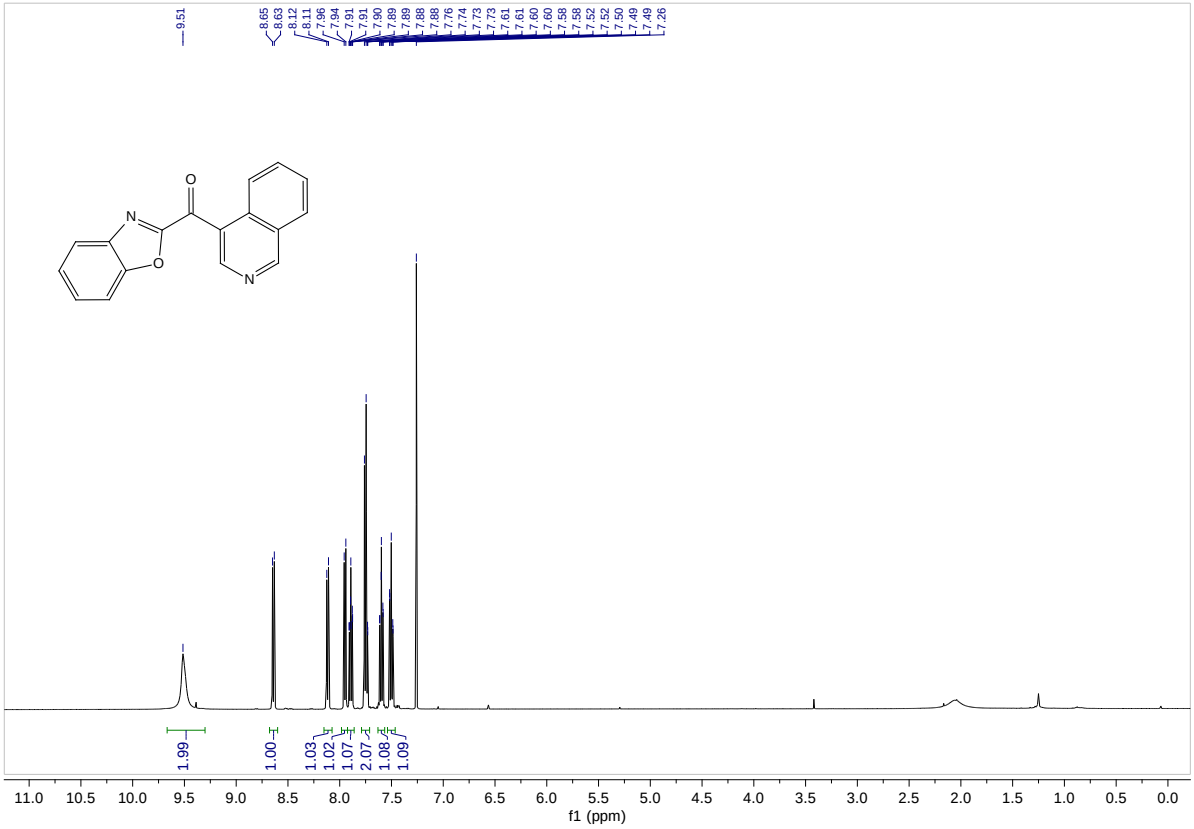
f1 (ppm)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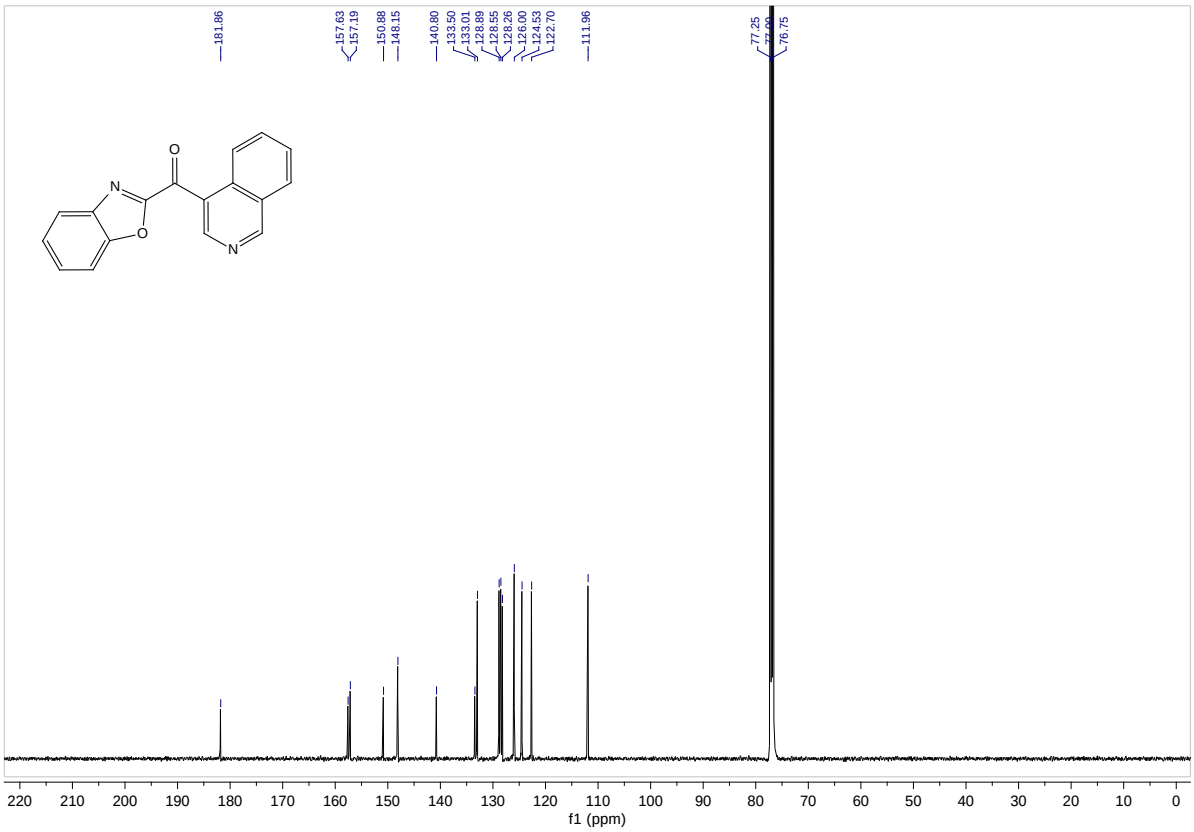
f1 (ppm)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128.55
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126.00
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122.70
111.96
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76.75
O
N
O
N
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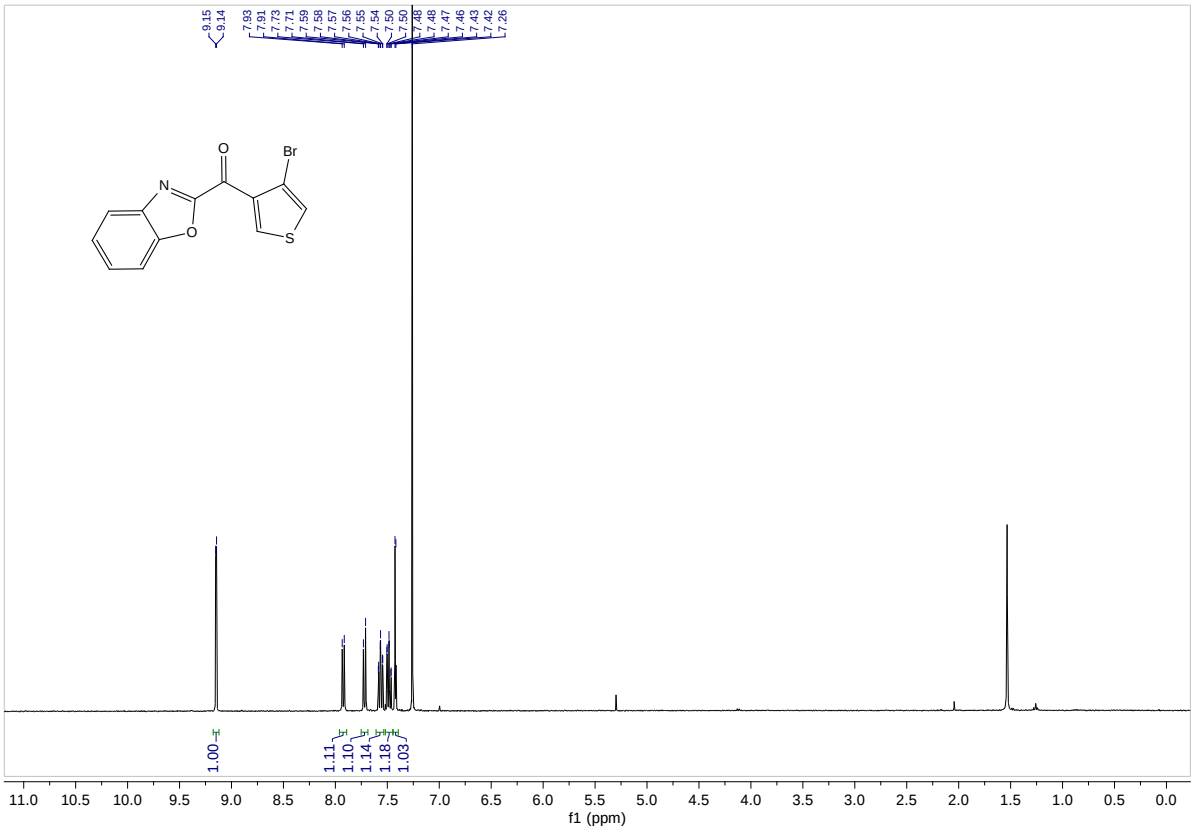
f1 (ppm)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7.48
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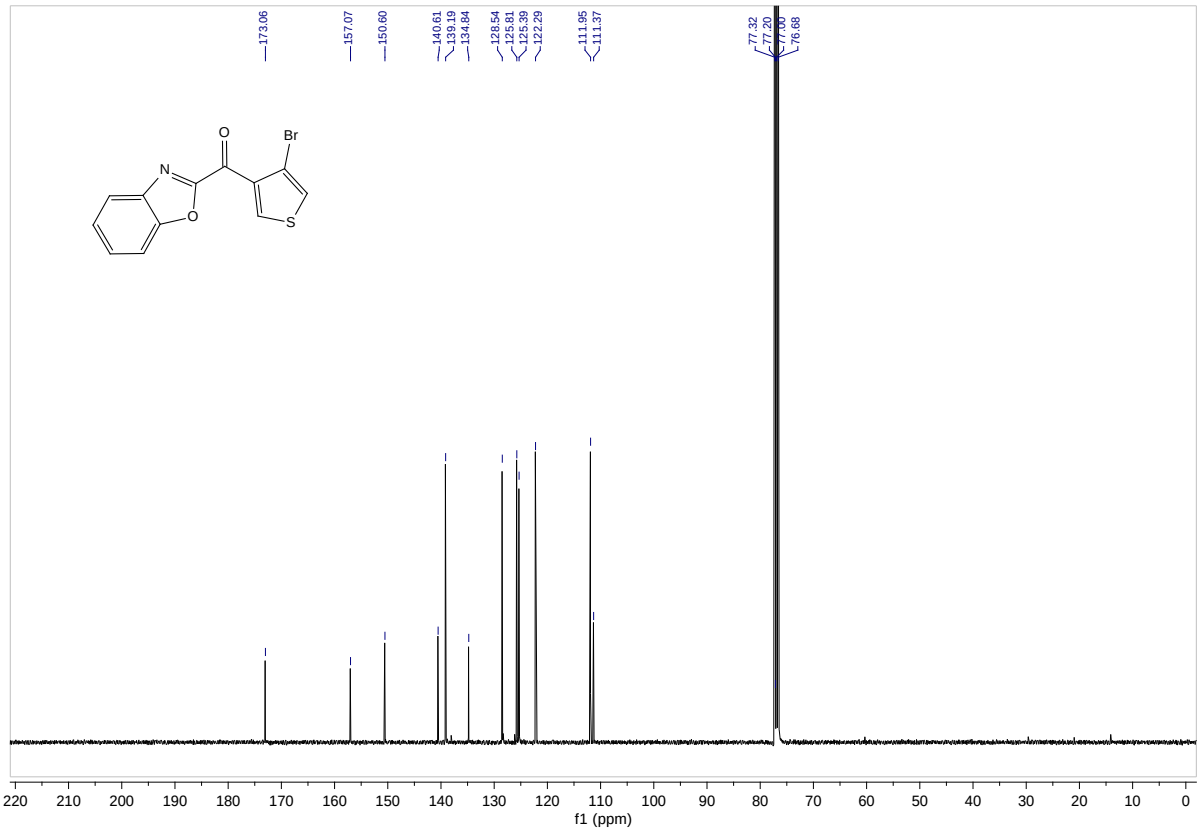
7.47
7.46
7.43
7.42
7.26
O
Br
N
O
S
1.00
1.11
1.10
1.14
1.18
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.32
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77.00
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O
Br
N
O
S
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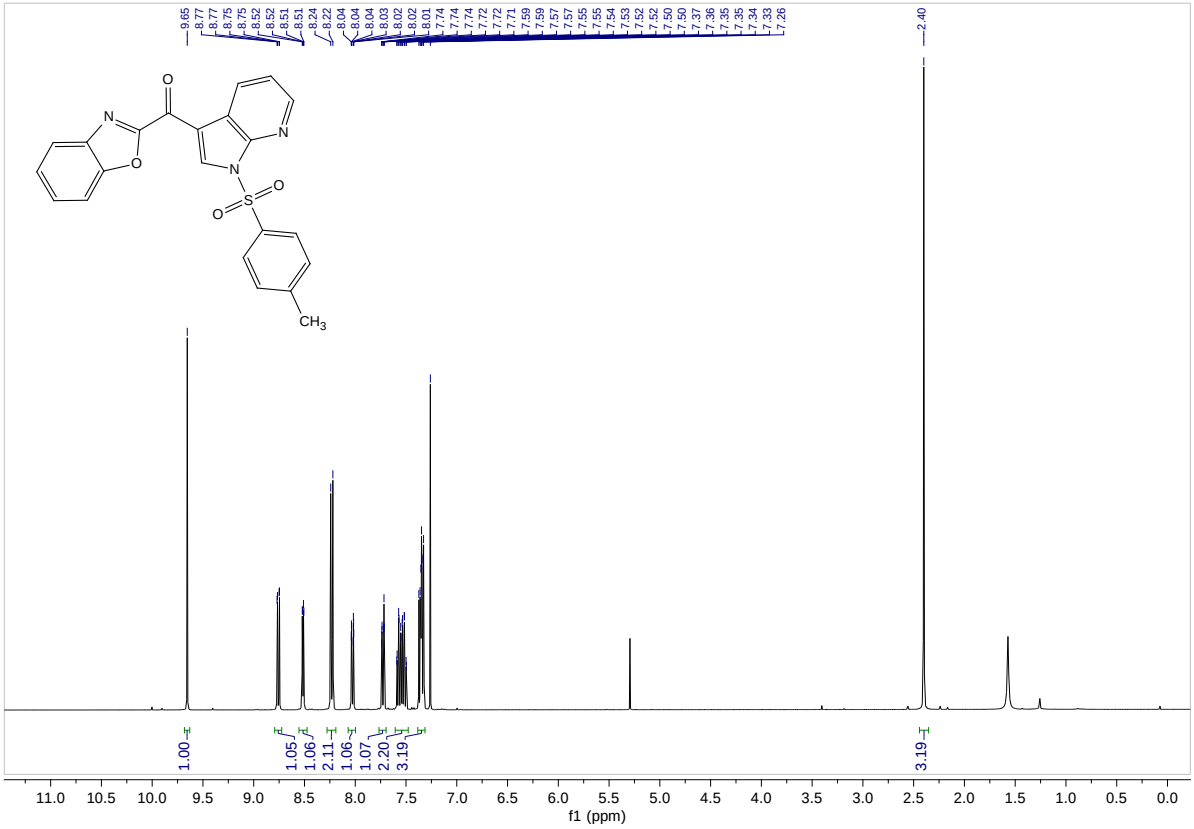
f1 (ppm)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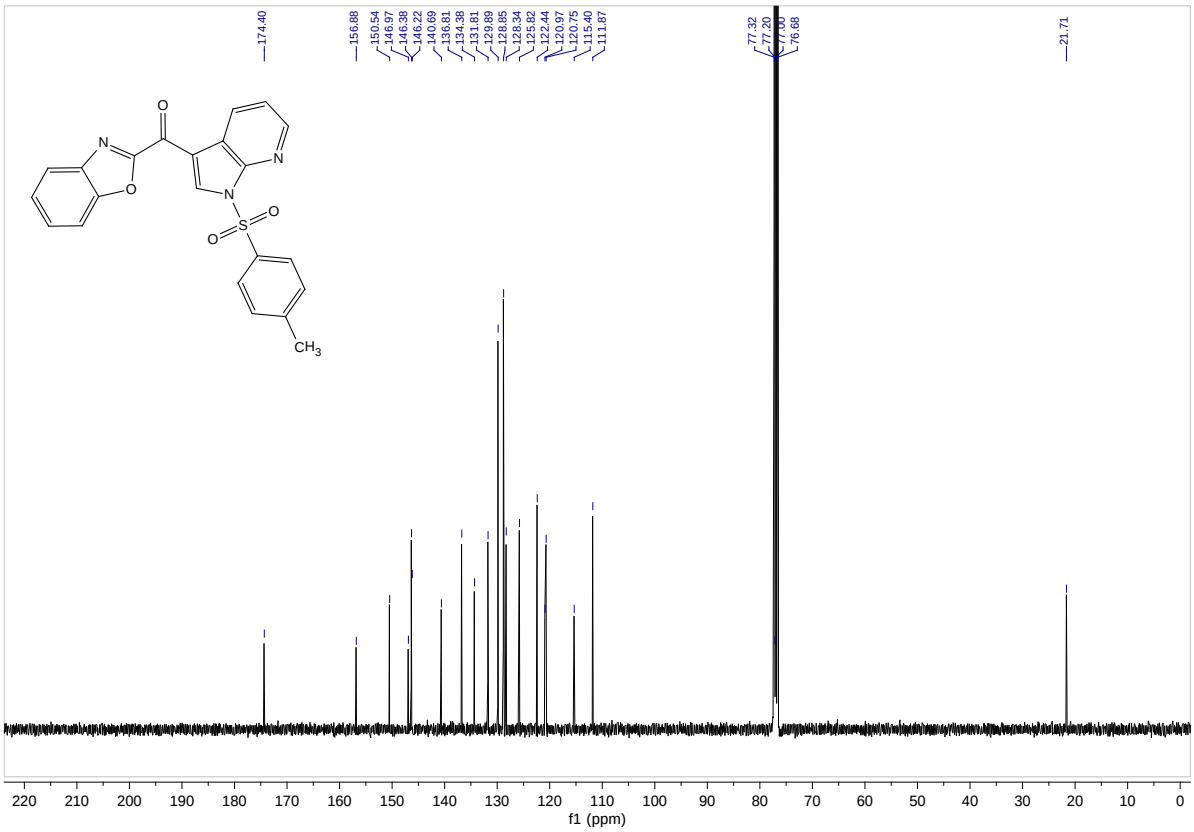
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128.34
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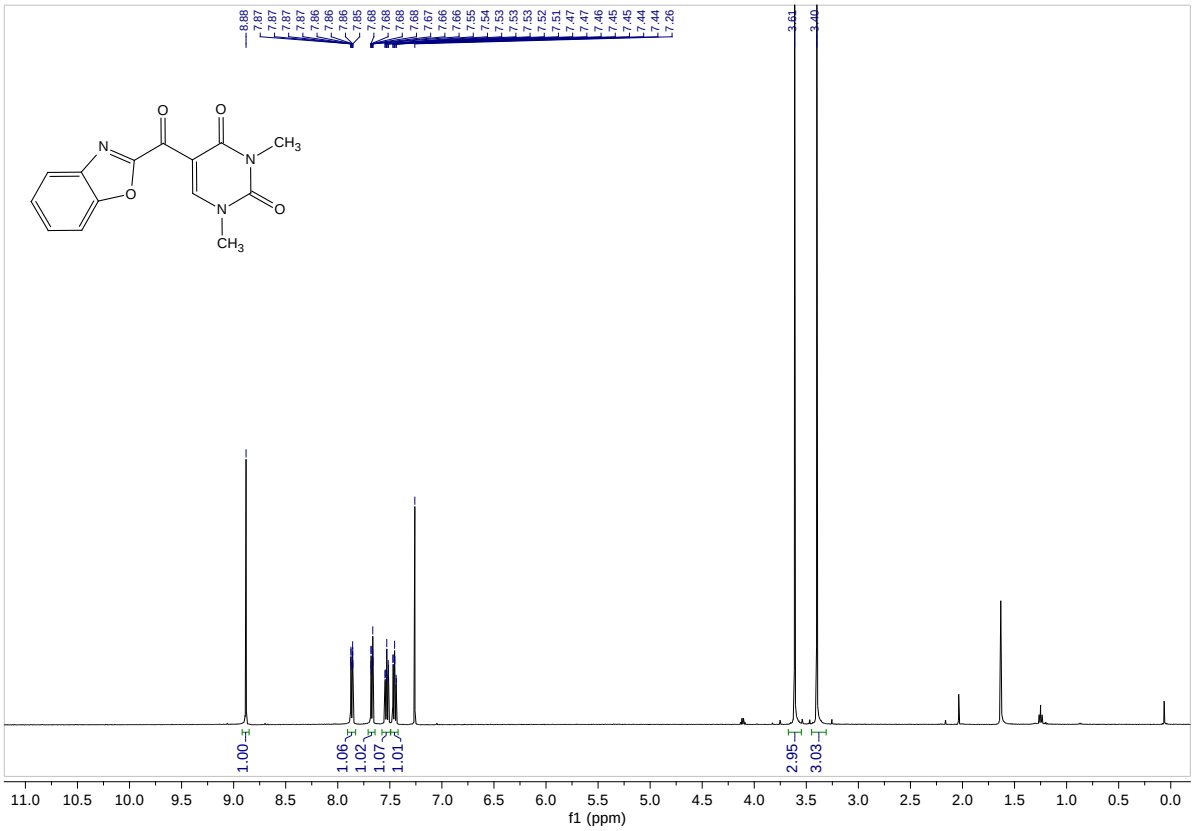
77.00
76.68
21.71
f1 (ppm)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1.01
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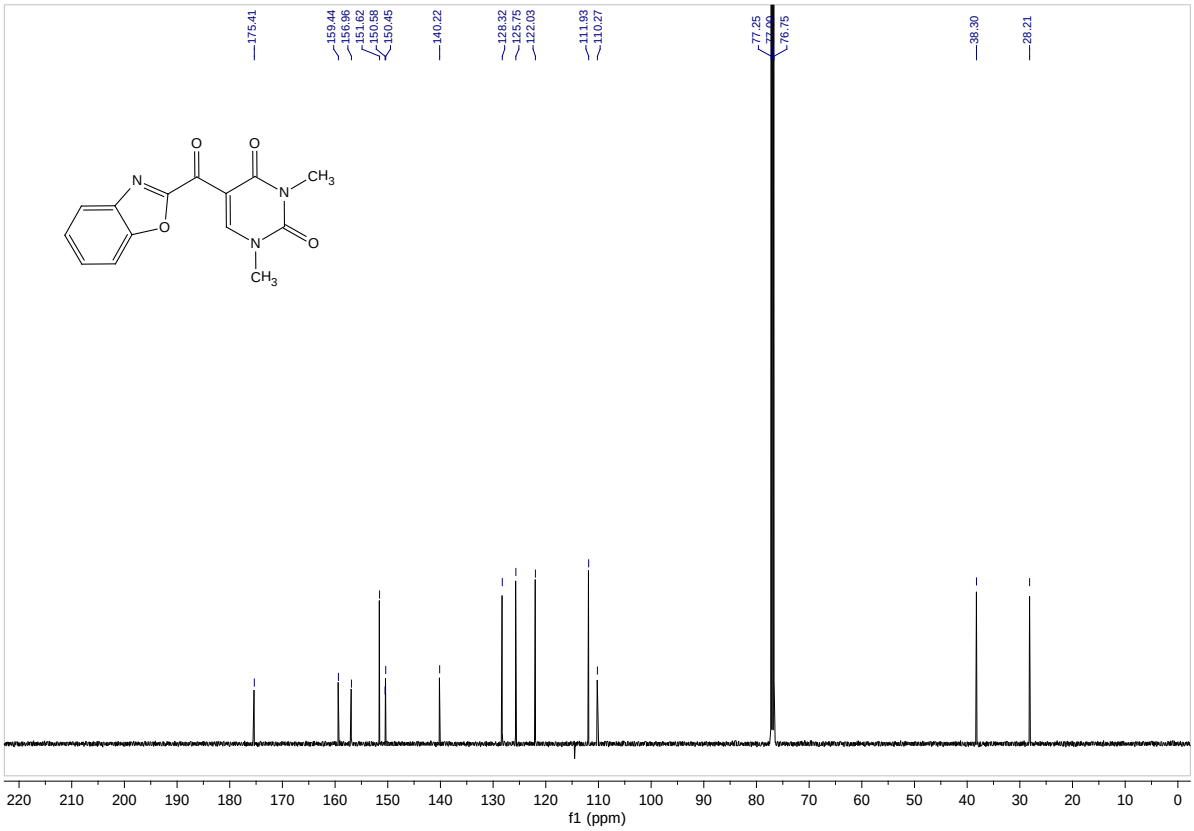
f1 (ppm)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125.75
122.03
111.93
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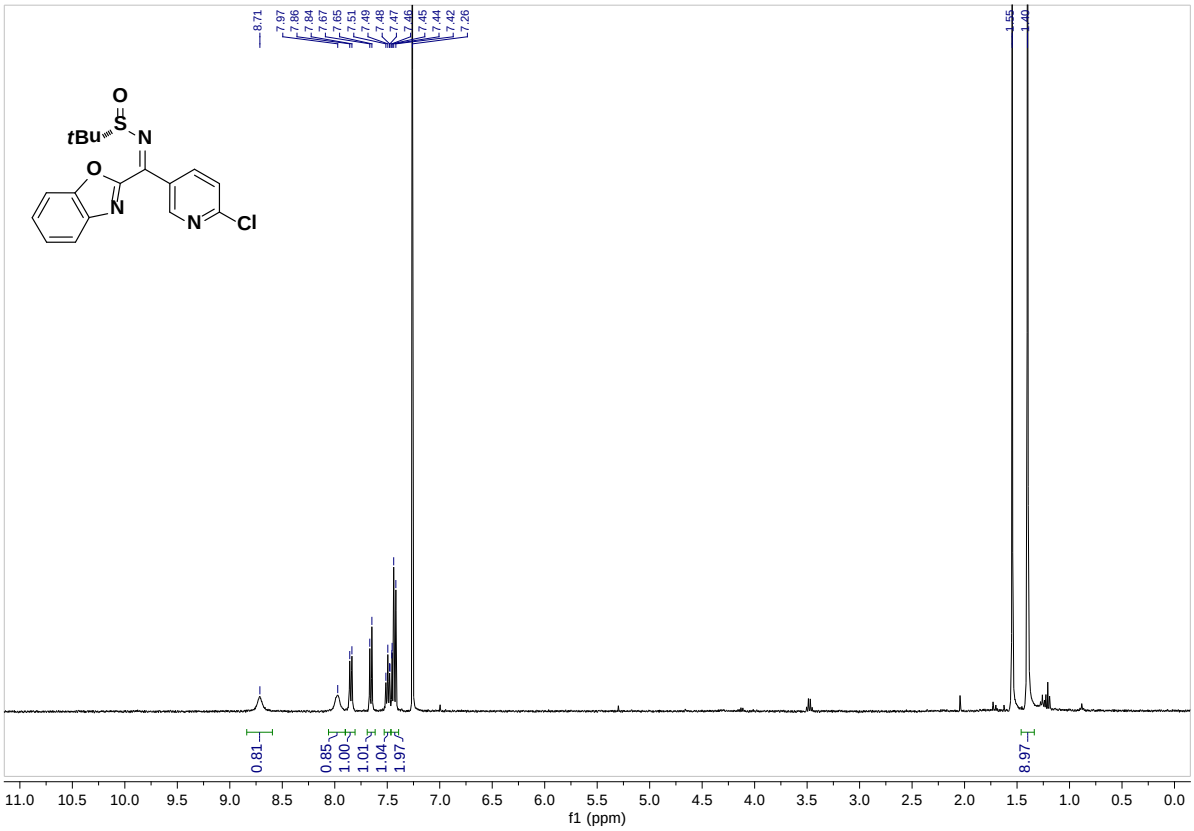
77.25
77.00
76.75
38.30
28.21
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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1.04
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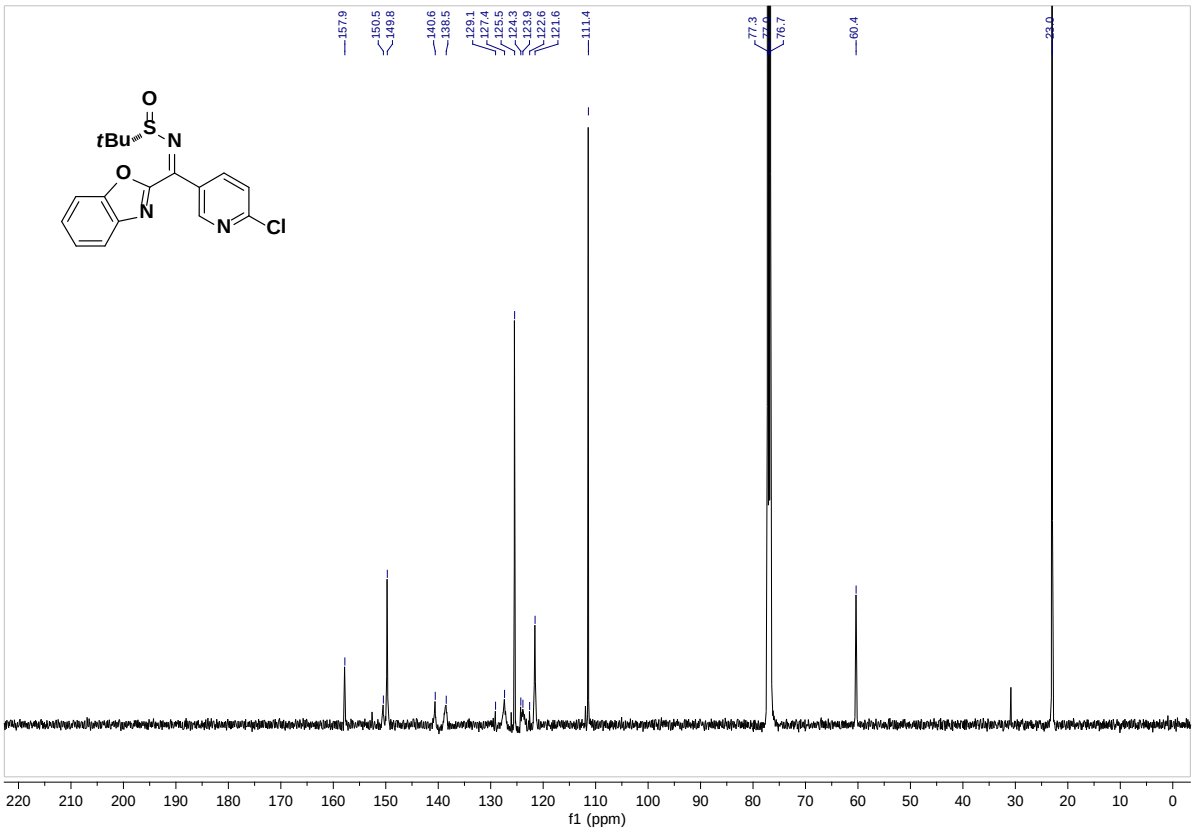
f1 (ppm)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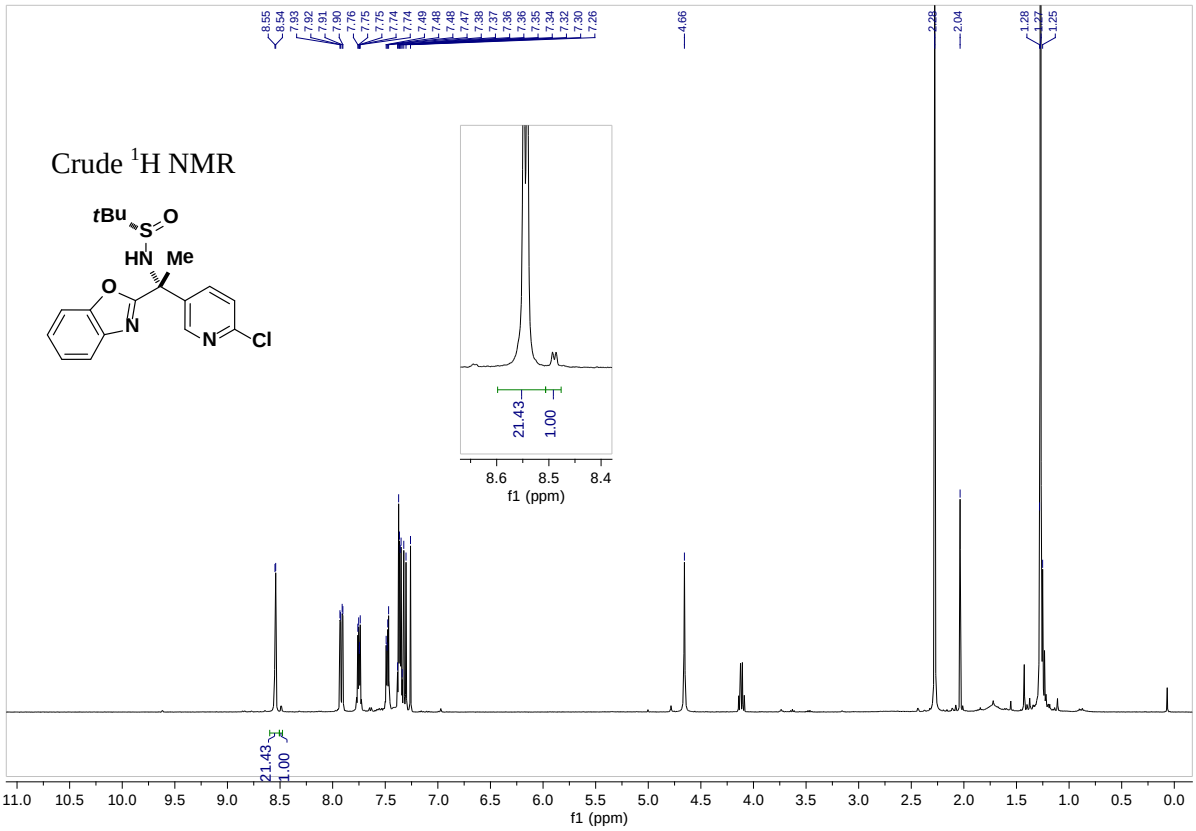
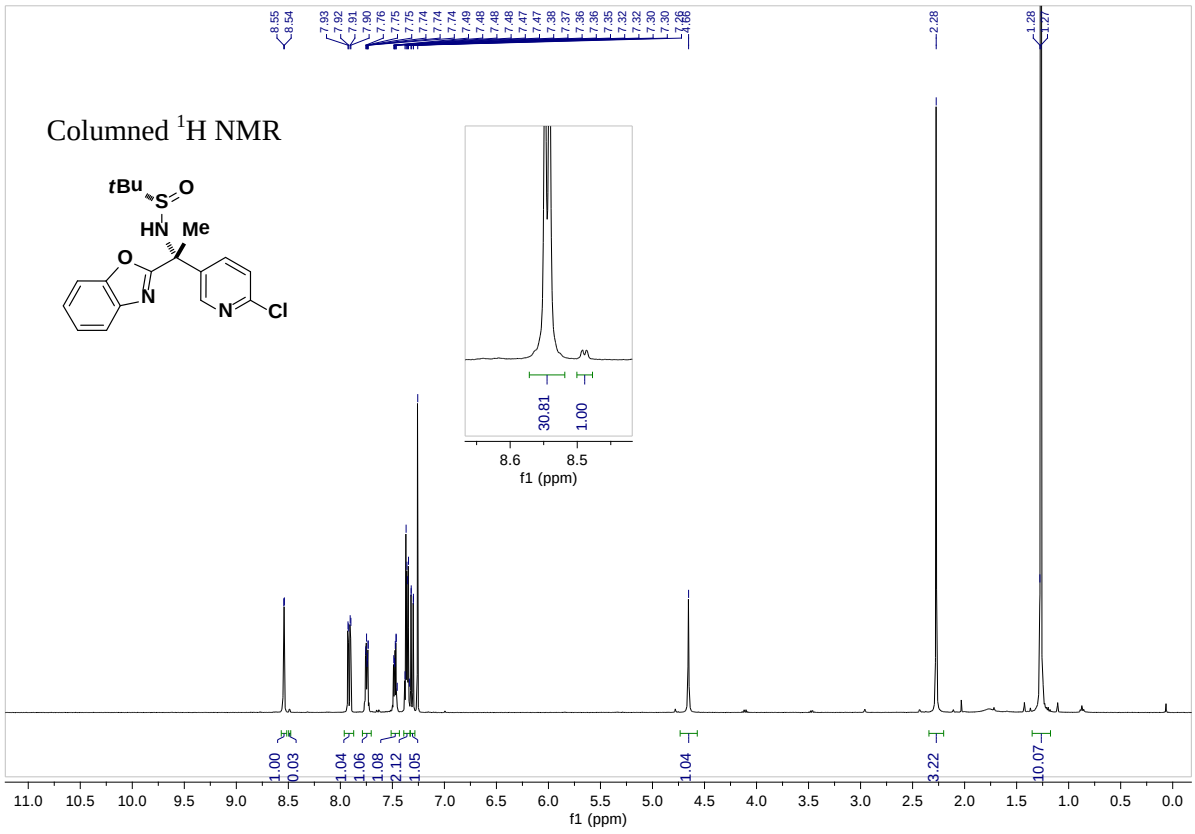
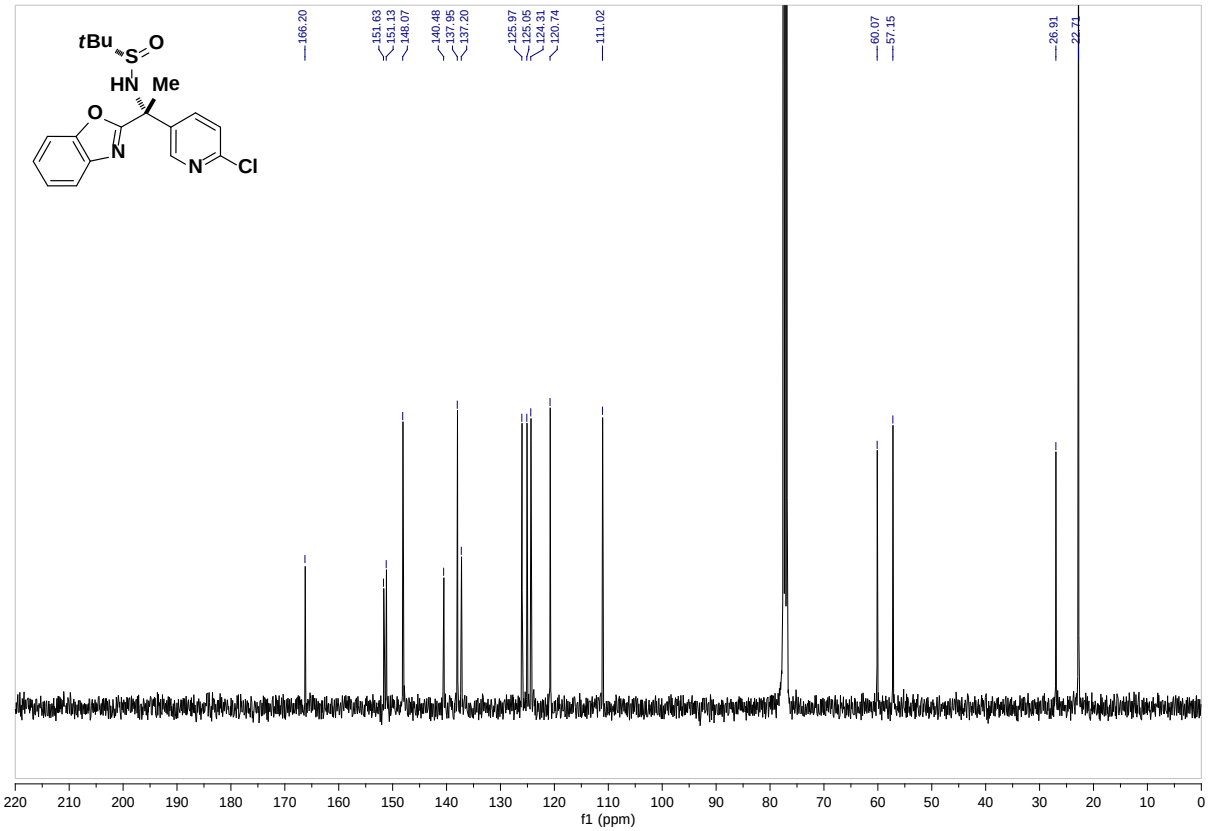
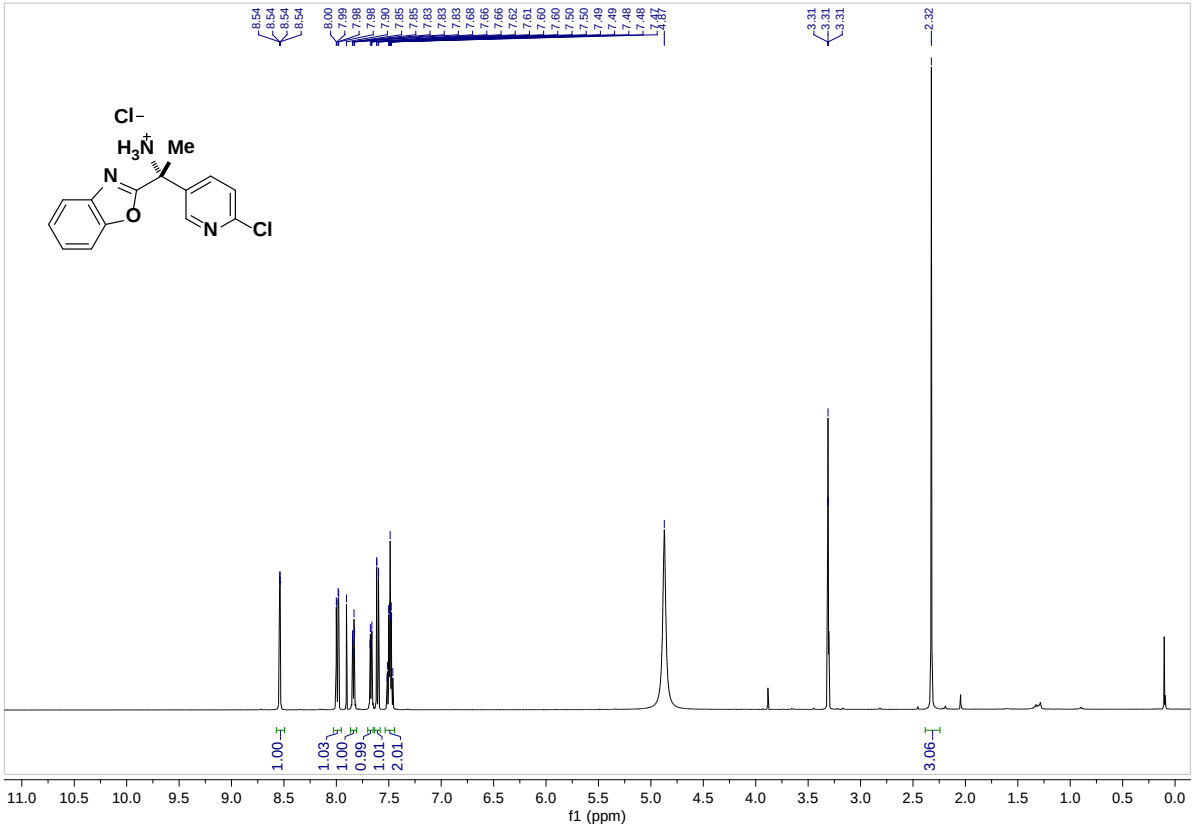
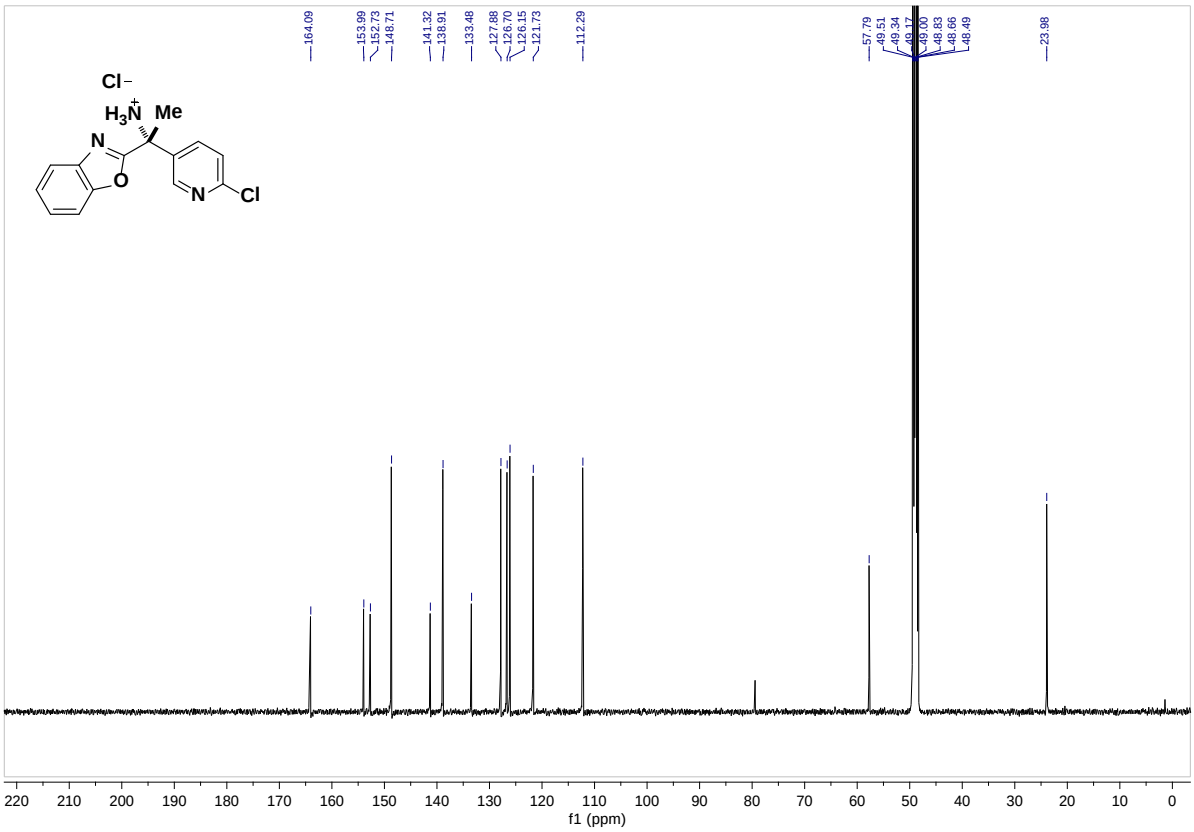
122.6
121.6
111.4
77.3
77.0
76.7
60.4
23.0
f1 (ppm)

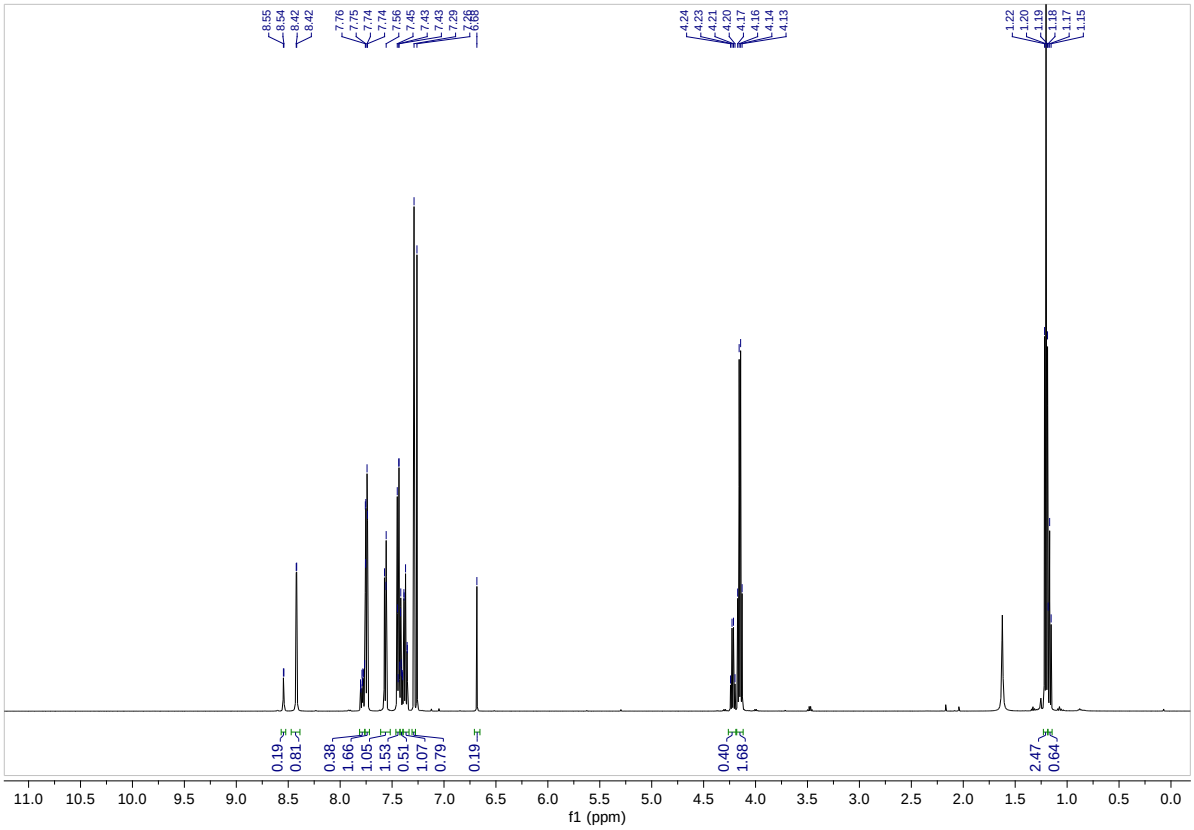

Crude 1H NMR
tBu
S
O
HN
Me
O
N
N
Cl
21.43
1.00
8.6
8.5
8.4
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

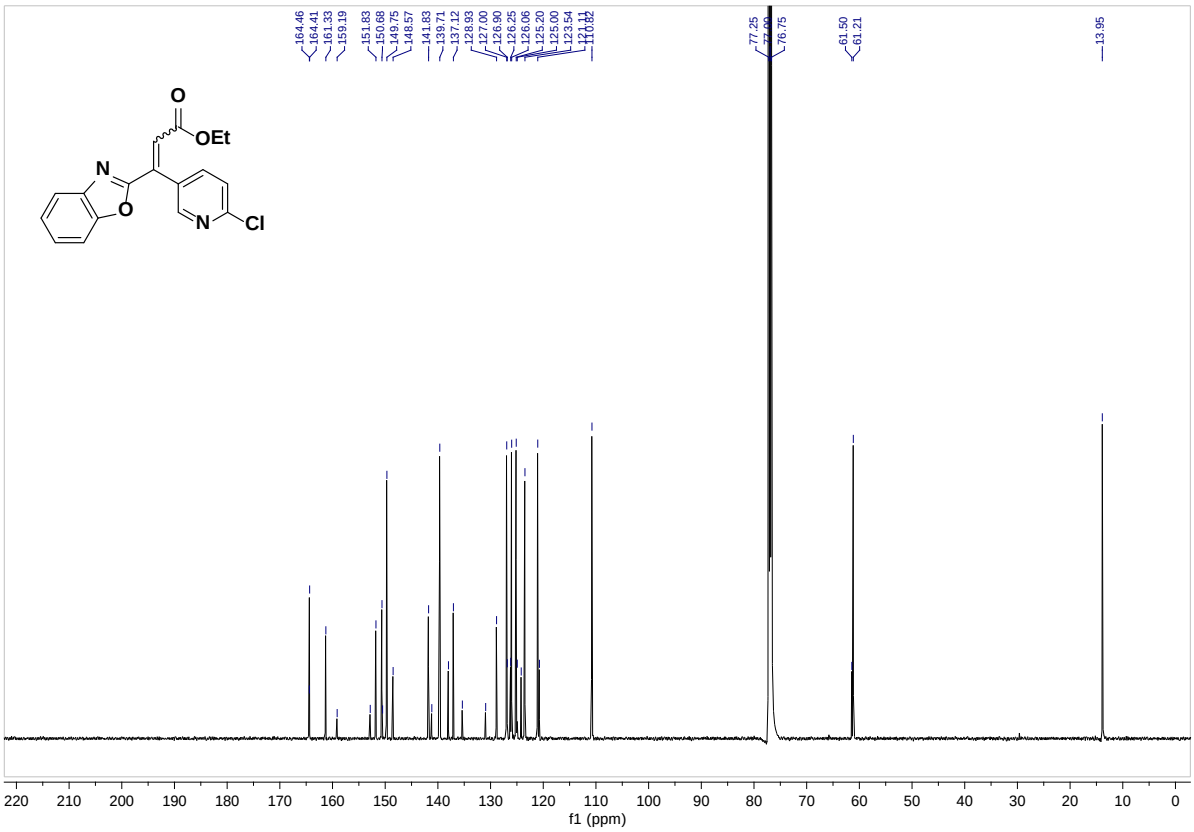

Columned 1H NMR
tBu
S
O
HN
Me
O
N
N
Cl
30.81
1.00
8.6
8.5
f1 (ppm)
1.00
0.03
1.04
1.06
1.08
2.12
1.05
1.04
3.22
10.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

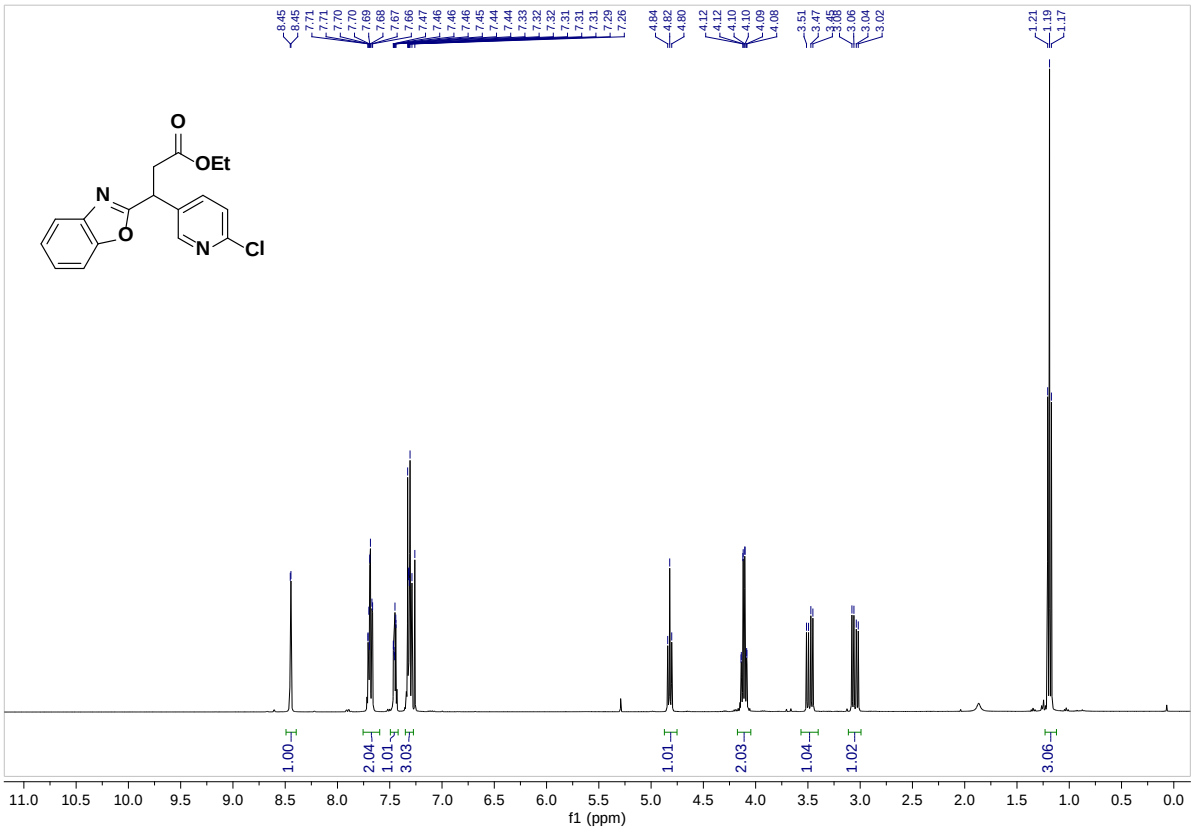

tBu
S
O
HN
Me
O
N
N
Cl
166.20
151.63
151.13
148.07
140.48
137.95
137.20
125.97
125.05
124.31
120.74
111.02
60.07
57.15
26.91
22.71
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

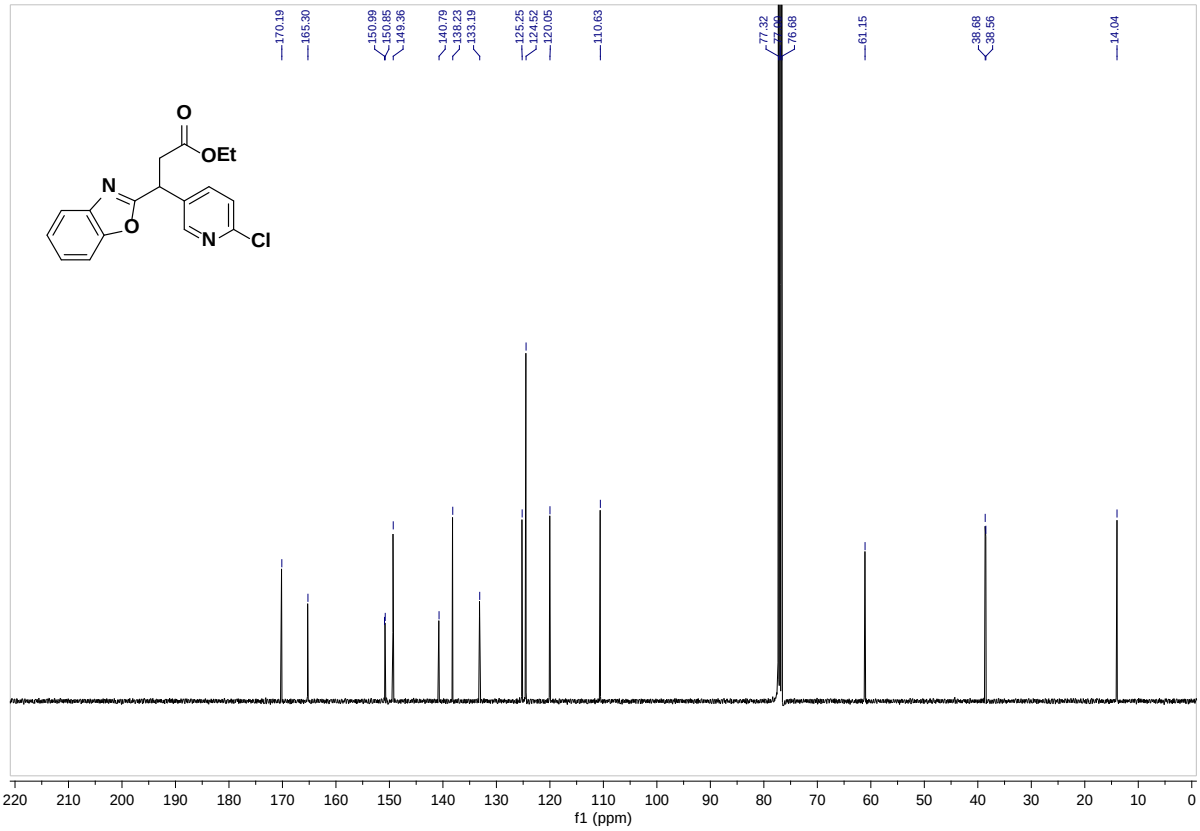

8.54
8.54
8.54
8.54
8.00
7.99
7.98
7.98
7.90
7.85
7.85
7.83
7.83
7.83
7.68
7.66
7.66
7.62
7.61
7.60
7.60
7.50
7.50
7.49
7.49
7.48
7.48
4.87
3.31
3.31
3.31
2.32
Cl−
H3N+ Me
N
O
N
Cl
1.00
1.03
1.00
0.99
1.01
2.01
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

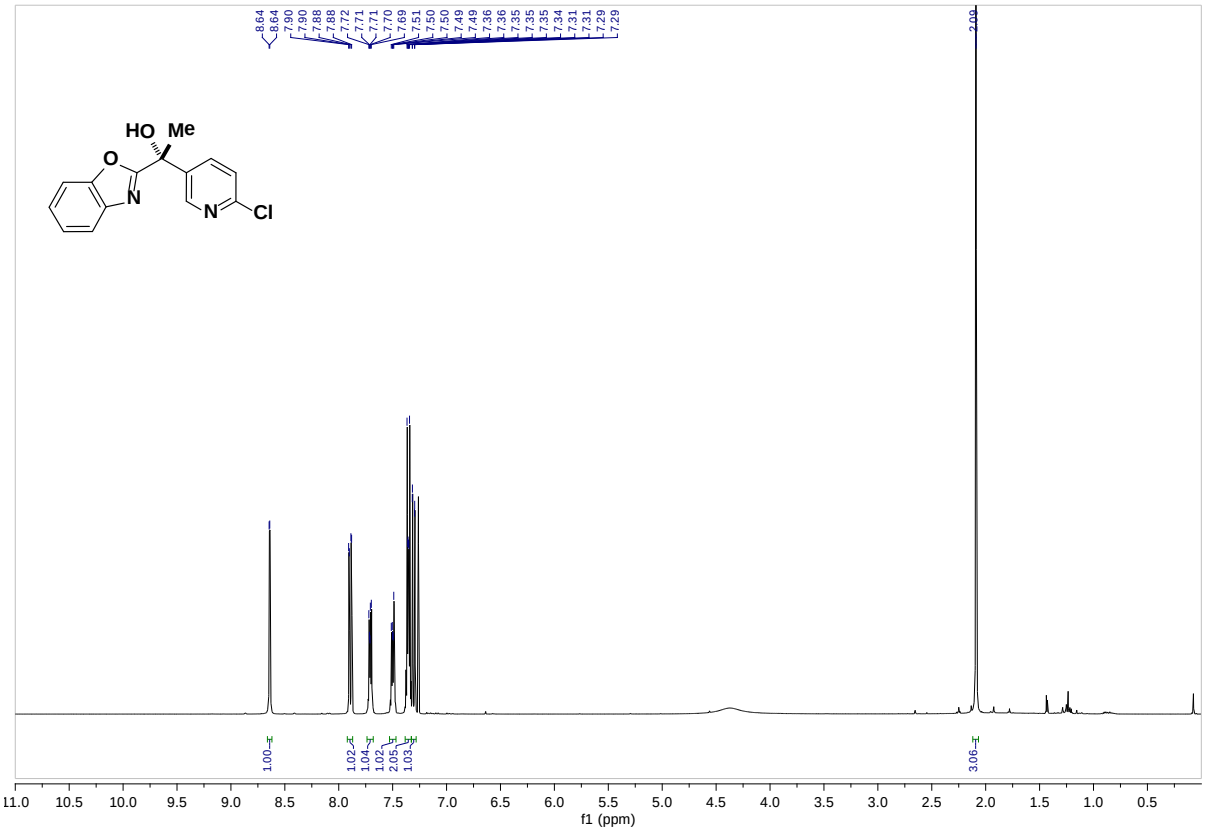

164.09
153.99
152.73
148.71
141.32
138.91
133.48
127.88
126.70
126.15
121.73
112.29
57.79
49.51
49.34
49.17
49.00
48.83
48.66
48.49
23.98
Cl−
H3N+ Me
N
O
N
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

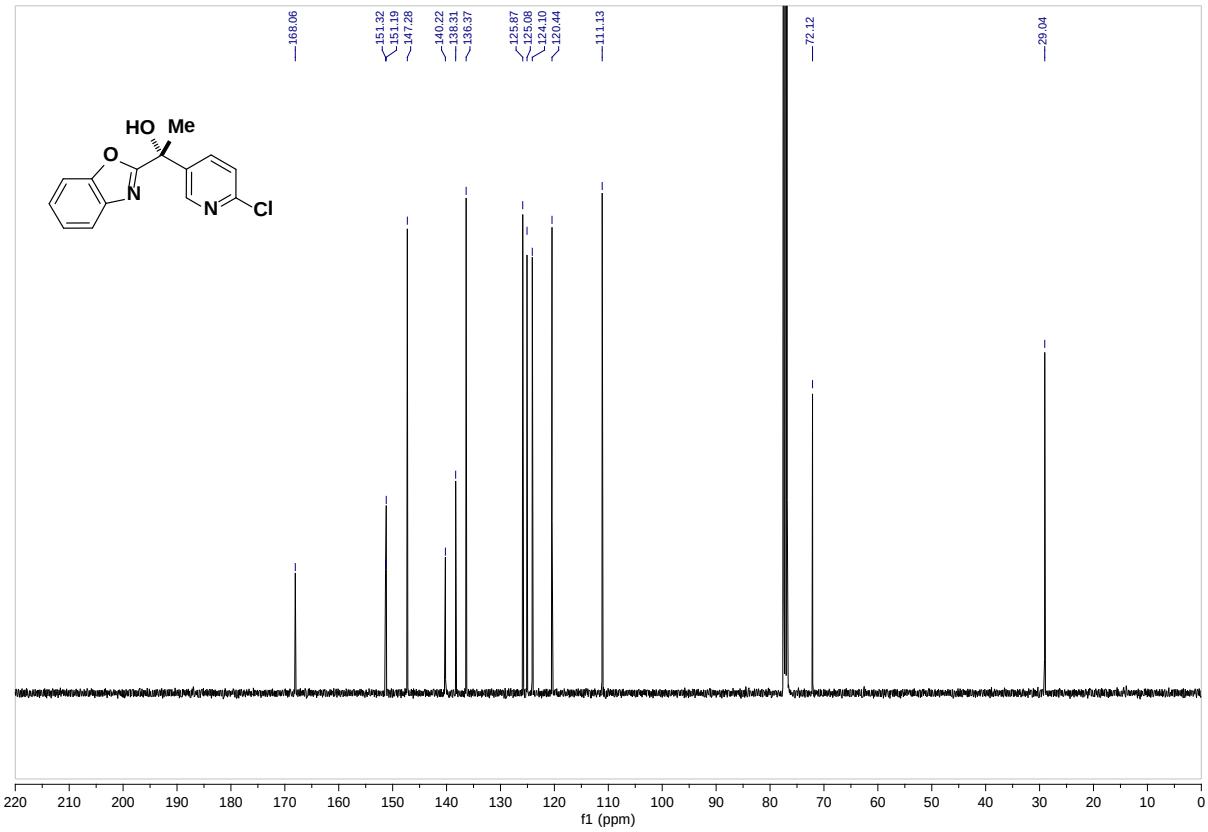

8.55
8.54
8.42
8.42
7.76
7.75
7.74
7.74
7.56
7.45
7.43
7.43
7.29
6.88
4.24
4.23
4.21
4.20
4.17
4.16
4.14
4.13
1.22
1.20
1.19
1.18
1.17
1.15
0.19
0.81
0.38
1.66
1.05
1.53
0.51
1.07
0.79
0.19
0.40
1.68
2.47
0.64
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.46
164.41
161.33
159.19
151.83
150.68
149.75
148.57
141.83
139.71
137.12
128.93
127.00
126.90
126.25
126.06
125.20
125.00
123.54
77.25
76.75
61.50
61.21
13.95
O
OEt
N
O
N
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.45
8.45
7.71
7.71
7.71
7.70
7.70
7.70
7.69
7.68
7.67
7.66
7.47
7.46
7.46
7.46
7.45
7.44
7.44
7.33
7.32
7.32
7.31
7.31
7.31
7.29
7.26
4.84
4.82
4.80
4.12
4.12
4.10
4.10
4.09
4.08
3.51
3.47
3.06
3.06
3.04
3.02
1.21
1.19
1.17
O
OEt
N
O
N
Cl
1.00
2.04
1.01
3.03
1.01
2.03
1.04
1.02
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.19
165.30
150.99
150.85
149.36
140.79
138.23
133.19
125.25
124.52
120.05
110.63
77.32
77.00
76.68
61.15
38.68
38.56
14.04
O
OEt
N
O
N
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.64
8.64
7.90
7.90
7.88
7.88
7.72
7.71
7.71
7.70
7.69
7.51
7.50
7.50
7.49
7.49
7.36
7.36
7.35
7.35
7.35
7.34
7.31
7.31
7.29
7.29
2.09
HO
Me
O
N
N
Cl
1.00
1.02
1.04
1.02
2.05
1.03
3.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


168.06
151.32
151.19
147.28
140.22
138.31
136.37
125.87
125.08
124.10
120.44
111.13
72.12
29.04
HO
Me
O
N
N
Cl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)