Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Metal-Free, Efficient Hydrazination of Imidazo[1,2-a]pyridine with Diethyl Azodicarboxylate in Neutral Media

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Table of Contents

General Information

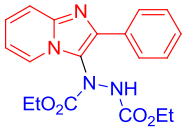
Solvents were purchased from Aldrich or Acros and used without further purification. Other reagents were used as obtained from commercial providers except when otherwise noted. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel plates available from EMD. Visualization was accomplished with UV light. Column chromatography was performed using Biotage chromatographic systems. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Inova instrument (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the residual undeuterated solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Low and high resolution mass spectra were obtained using ESI methods.

General procedure for the preparation of compounds 3 and 5

In a 25 mL tube imidazo[1,2-a]pyridines (**1**, 1 mmol), and diethyl azodicarboxylate (DEAD, 2 mmol) were taken in 5 mL MeCN. The tube was sealed with a pressure cap and heated to 80 ^{o}C for 6 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (20 mL) and washed with water, brine, and dried over anhydrous Na_2SO_4. The organic solvent was removed under vacuum to get the crude product, which is purified using Biotage chromatographic systems.

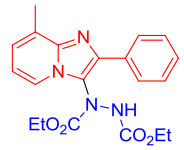
Characterization of 3 and 6

Diethyl 1-(2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3a)



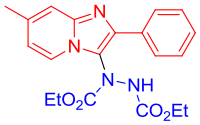
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.79 (d, *J* = 7.3 Hz, 3H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.39 (t, *J* = 7.5, 7.5 Hz, 2H), 7.33 – 7.24 (m, 2H), 6.89 (t, *J* = 6.8, 6.8 Hz, 1H), 4.21 – 4.15 (m, 4H), 1.22 – 1.06 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 155.2, 142.8, 139.2, 132.5, 128.5, 128.1, 126.9, 125.8, 124.6, 118.4, 117.1, 112.4, 63.8, 62.3, 14.2; HRMS (ESI+, *m/z*) calculated for $C_{19}H_{21}N_4O_4$ $[M + H]^+$ 369.1557; found 369.1561.

Diethyl 1-(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3b)



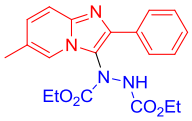
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.5, 7.5 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 3H), 6.72 (d, *J* = 7.0 Hz, 1H), 4.22 – 4.11 (m, 4H), 2.42 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.3, 143.3, 139.0, 136.7, 132.7, 128.5, 127.9, 126.8, 123.8, 117.9, 115.5, 114.9, 63.7, 62.2, 21.2, 14.2; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{23}N_4O_4$ $[M + H]^+$ 383.1714; found 383.1718.

Diethyl 1-(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3c)



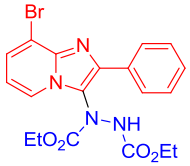
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.48 (s, 1H), 7.41 (t, *J* = 7.5, 7.5 Hz, 2H), 7.33 (dd, *J* = 13.6, 6.0 Hz, 2H), 6.72 (dd, *J* = 7.0, 1.6 Hz, 1H), 4.19 (dt, *J* = 14.3, 6.9, 6.9 Hz, 4H), 2.41 (s, 3H), 1.22 (t, *J* = 7.1, 7.1 Hz, 3H), 1.09 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 154.9, 143.4, 139.1, 136.8, 132.9, 128.8, 128.2, 127.6, 126.7, 123.8, 115.6, 115.0, 63.93, 62.53, 21.36, 14.31; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{23}N_4O_4$ $[M + H]^+$ 383.1714; found 383.1712.

Diethyl 1-(6-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3d)



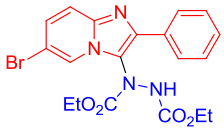
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 9.2 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.34 – 7.30 (m, 1H), 7.11 (d, *J* = 11.9 Hz, 1H), 4.26 – 4.13 (m, 4H), 2.37 (s, 3H), 1.23 (t, *J* = 7.1, 7.1 Hz, 3H), 1.08 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 155.2, 142.0, 139.0, 133.1, 128.9, 128.7, 128.1, 126.7, 122.6, 122.1, 118.1, 116.6, 63.8, 62.4, 18.4, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{23}N_4O_4$ $[M + H]^+$ 383.1714; found 383.1715.

Diethyl 1-(8-bromo-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3e)



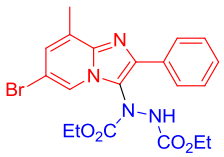
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.59 (s, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5, 7.5 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 6.76 (t, *J* = 7.1, 7.1 Hz, 1H), 4.34 – 4.08 (m, 4H), 1.22 (t, *J* = 7.1, 7.1 Hz, 3H), 1.05 (t, *J* = 7.1, 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 154.9, 140.7, 140.3, 132.2, 128.7, 128.5, 128.1, 127.0, 124.0, 119.6, 112.7, 111.4, 64.0, 62.6, 14.2; $[M+H]^+$ = 447; HRMS (ESI+, *m/z*) calculated for $C_{19}H_{20}BrN_4O_4$ $[M + H]^+$ 447.0662; found 447.0665.

Diethyl 1-(6-bromo-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3f)



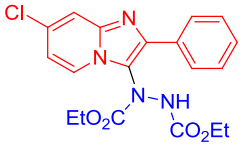
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.39 (d, *J* = 6.1 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.19 (s, 1H), 4.24 (dd, *J* = 12.3, 5.4 Hz, 4H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.11 (t, *J* = 7.0, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.9, 141.4, 140.1, 132.3, 129.3, 129.0, 128.6, 126.9, 124.8, 118.7, 117.9, 107.3, 64.2, 62.7, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{19}H_{20}BrN_4O_4$ $[M + H]^+$ 447.0662; found 447.0667.

Diethyl 1-(6-bromo-8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3g)



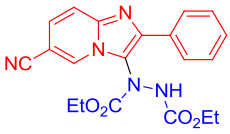
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.15 (m, 3H), 7.13 (s, 1H), 4.34 – 3.95 (m, 64H), 2.61 (s, 3H), 1.24 (t, *J* = 7.1, 7.1 Hz, 3H), 1.04 (t, *J* = 7.1, 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 154.9, 146.5, 141.6, 139.5, 132.4, 128.6, 128.2, 127.8, 126.9, 122.5, 118.8, 107.1, 64.0, 62.5, 16.4, 14.3, 14.2; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{22}BrN_4O_4$ $[M + H]^+$ 461.0819; found 416.0812.

Diethyl 1-(7-chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3h)



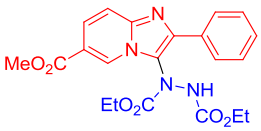
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 3H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.36 (dt, *J* = 19.7, 4.3, 4.3 Hz, 3H), 6.87 (dd, *J* = 7.3, 2.0 Hz, 1H), 4.26 – 4.12 (m, 4H), 1.21 (t, *J* = 7.1, 7.1 Hz, 3H), 1.08 (t, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.0, 142.8, 140.2, 132.6, 128.8, 128.5, 128.0, 126.8, 125.2, 118.6, 116.1, 114.1, 64.1, 62.6, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{19}H_{20}ClN_4O_4$ $[M + H]^+$ 403.1168; found 403.1166.

Diethyl 1-(6-cyano-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3i)



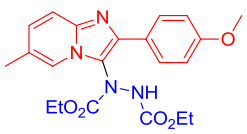
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.62 – 7.27 (m, 5H), 4.43 – 4.13 (m, 4H), 1.26 (t, *J* = 7.1, 7.1 Hz, 3H), 1.11 (t, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 154.6, 142.2, 131.7, 131.0, 129.2, 129.1, 127.1, 125.8, 119.5, 118.3, 116.6, 110.0, 64.5, 63.1, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{20}N_5O_4$ $[M + H]^+$ 394.1510; found 394.1515.

Diethyl 1-(6-(methoxycarbonyl)-2-phenylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3j)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.83 (t, *J* = 9.1, 9.1 Hz, 3H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.44 (t, *J* = 7.5, 7.5 Hz, 2H), 7.37 (dd, *J* = 8.4, 6.2 Hz, 1H), 6.85 (s, 1H), 4.24 – 4.17 (m, 4H), 3.97 (s, 3H), 1.25 (t, *J* = 7.1, 7.1 Hz, 3H), 1.09 (t, *J* = 7.0, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 156.7, 154.9, 143.6, 140.9, 132.2, 128.9, 128.8, 126.9, 125.5, 119.4, 116.7, 116.5, 64.2, 62.1, 52.5, 14.3, 14.2; HRMS (ESI+, *m/z*) calculated for $C_{21}H_{23}N_4O_6$ $[M + H]^+$ 427.1612; found 427.1615.

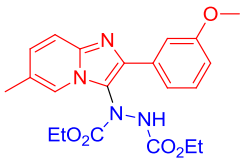
Diethyl 1-(2-(4-methoxyphenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3k)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.70 (d, *J* = 10.6 Hz, 2H), 7.49 (d, *J* = 5.7 Hz, 1H), 7.10 (d, *J* = 9.6 Hz, 1H), 7.02 – 6.81 (m, 3H), 4.22 (dq, *J* = 14.0, 7.0, 7.0, 6.9 Hz, 4H), 3.83 (s, 3H), 2.37 (s, 3H), 1.24 (t, *J* = 6.8, 6.8 Hz, 3H), 1.09 (t, *J* = 6.9, 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 156.6, 155.4, 142.0, 139.1, 129.7, 128.9, 127.9, 125.5, 122.2, 116.4, 114.3, 113.9, 63.9, 62.4, 55.2, 18.4, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{21}H_{25}N_4O_5$ $[M + H]^+$

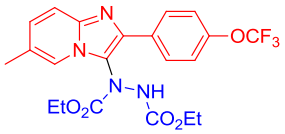
413.1819; found 413.1814.

Diethyl 1-(2-(3-methoxyphenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3l)



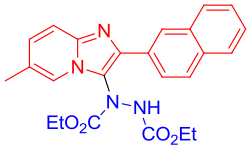
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.66 (s, 1H), 7.52 (d, *J* = 9.1 Hz, 1H), 7.39 (s, 1H), 7.33 – 7.21 (m, 2H), 7.11 (d, *J* = 9.2 Hz, 1H), 6.86 (dt, *J* = 6.5, 2.9, 2.9 Hz, 1H), 4.23 – 4.17 (m, 4H), 3.81 (s, 3H), 2.37 (s, 3H), 1.22 (t, *J* = 7.1, 7.1 Hz, 3H), 1.09 (t, *J* = 7.0, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.9, 155.2, 141.8, 138.9, 134.1, 129.6, 128.9, 122.2, 119.0, 118.2, 116.5, 114.4, 111.8, 63.8, 62.3, 55.1, 18.3, 14.2; HRMS (ESI+, *m/z*) calculated for $C_{21}H_{25}N_4O_5$ $[M + H]^+$ 413.1819; found 413.1823.

Diethyl 1-(6-methyl-2-(4-(trifluoromethoxy)phenyl)imidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3m)



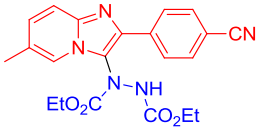
Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.83 (s, 1H), 7.74 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.12 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.05 (t, *J* = 8.7, 8.7 Hz, 2H), 4.21 – 4.17 (m, 4H), 2.37 (s, 3H), 1.23 (t, *J* = 7.2, 7.2 Hz, 3H), 1.08 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246 Hz), 156.9, 155.3, 142.0, 138.4, 129.1, 128.6 (d, *J* = 7.0 Hz), 122.3, 122.1, 117.9, 116.5, 115.7 (d, *J* = 21 Hz), 64.0, 62.5, 18.4, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{21}H_{22}F_3N_4O_5$ $[M + H]^+$ 467.1537; found 467.1539.

Diethyl 1-(6-methyl-2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3n)



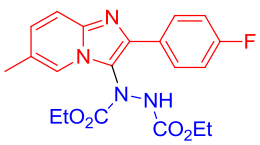
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.44 (s, 1H), 8.28 (s, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.78 – 7.67 (m, 3H), 7.48 – 7.39 (m, 3H), 6.99 (d, *J* = 11.0 Hz, 1H), 4.12 (dt, *J* = 22.9, 7.4, 7.4 Hz, 4H), 2.28 (s, 3H), 1.16 (t, *J* = 7.2, 7.2 Hz, 3H), 0.97 (t, *J* = 7.1, 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.2, 142.1, 138.8, 133.3, 132.8, 130.0, 129.0, 128.3, 128.1, 127.4, 126.1, 124.4, 122.2, 118.3, 116.3, 63.8, 62.3, 18.3, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{24}H_{25}N_4O_4$ $[M + H]^+$ 433.1870; found 433.1876.

Diethyl 1-(2-(4-cyanophenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3o)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.90 – 7.78 (m, 3H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 6.80 – 6.73 (m, 1H), 4.31 – 4.07 (m, 4H), 2.44 (s, 3H), 1.24 (t, *J* = 7.2, 7.2 Hz, 3H), 1.08 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.0, 143.6, 137.9, 137.2, 132.3, 132.0, 130.4, 128.4, 127.2, 124.2, 118.7, 115.6, 111.2, 64.1, 62.6, 21.4, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{21}H_{22}N_5O_4$ $[M + H]^+$ 408.1666; found 408.1666.

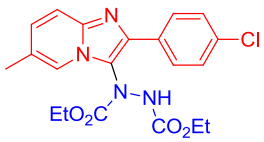
Diethyl 1-(2-(4-fluorophenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3p)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.83 (s, 1H), 7.74

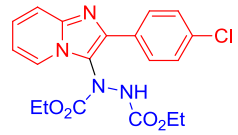
(dd, *J* = 8.4, 5.5 Hz, 2H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.12 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.05 (t, *J* = 8.7, 8.7 Hz, 2H), 4.21 – 4.17 (m, 4H), 2.37 (s, 3H), 1.23 (t, *J* = 7.2, 7.2 Hz, 3H), 1.08 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246 Hz), 156.9, 155.3, 142.0, 138.4, 129.1, 128.6 (d, *J* = 7.0 Hz), 122.3, 122.1, 117.9, 116.5, 115.7 (d, *J* = 21 Hz), 64.0, 62.5, 18.4, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{22}FN_4O_4$ $[M + H]^+$ 401.1620; found 401.1625.

Diethyl 1-(2-(4-chlorophenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3q)



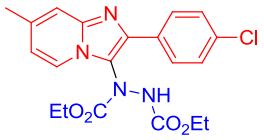
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.11 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.31 – 7.28 (m, 3H), 6.90 (t, *J* = 6.8, 6.8 Hz, 1H), 4.22 – 4.16 (m, 4H), 1.20 (t, *J* = 7.2, 7.2 Hz, 3H), 1.07 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.1, 143.0, 138.3, 134.1, 131.2, 128.9, 128.1, 126.1, 124.6, 118.5, 117.2, 112.6, 64.0, 62.5, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{22}ClN_4O_4$ $[M + H]^+$ 417.1324; found 417.1327.

Diethyl 1-(2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3r)



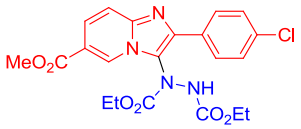
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 3H), 6.73 – 6.71 (m, 1H), 4.22 – 4.16 (m, 4H), 2.41 (s, 3H), 1.22 (t, *J* = 7.2, 7.2 Hz, 3H), 1.07 (t, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.1, 143.5, 138.0, 137.2, 133.9, 131.3, 128.8, 128.0, 123.9, 118.0, 115.6, 115.2, 64.0, 62.5, 21.3, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{19}H_{20}ClN_4O_4$ $[M + H]^+$ 403.1168; found 403.1166.

Diethyl 1-(2-(4-chlorophenyl)-7-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3s)



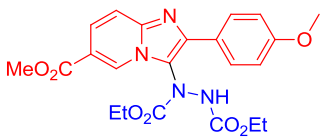
White solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.49 (s, 1H), 8.47 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 17.1, 8.7 Hz, 3H), 7.24 (d, *J* = 9.2 Hz, 1H), 4.19 – 4.05 (m, 4H), 2.33 (s, 3H), 1.22 (t, *J* = 7.2, 7.2 Hz, 3H), 0.88 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) δ 157.5, 154.4, 141.4, 137.1, 133.0, 132.1, 129.4, 129.2, 128.8, 122.5, 122.2, 118.4, 116.8, 63.7, 61.9, 18.2, 14.7, 14.4; HRMS (ESI+, *m/z*) calculated for $C_{20}H_{22}ClN_4O_4$ $[M + H]^+$ 417.1324; found 417.1325.

Diethyl 1-(2-(4-chlorophenyl)-6-(methoxycarbonyl)imidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3t)



Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$ + CD_3OD) δ 9.43 (s, 1H), 7.88 (d, *J* = 9.4 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 2H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 3H), 4.21 (dd, *J* = 15.6, 8.1 Hz, 4H), 3.99 (s, 3H), 1.27 (t, *J* = 7.1, 7.1 Hz, 3H), 1.07 (d, *J* = 7.1, 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) δ 165.2, 156.9, 154.6, 143.4, 139.7, 134.8, 130.3, 129.0, 128.4, 125.9, 119.7, 116.8, 116.4, 64.1, 62.5, 52.5, 14.1; HRMS (ESI+, *m/z*) calculated for $C_{21}H_{22}ClN_4O_6$ $[M + H]^+$ 461.1222; found 461.1227.

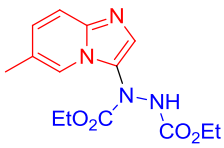
Diethyl 1-(6-(methoxycarbonyl)-2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (3u)



Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.82 (d, *J*

= 9.5 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 9.4 Hz, 1H), 7.32 (s, 1H), 7.02 – 6.96 (m, 2H), 4.23 (tt, *J* = 10.0, 10.0, 5.3, 5.3 Hz, 4H), 3.97 (s, 3H), 3.86 (s, 3H), 1.28 – 1.22 (m, 3H), 1.22 – 1.03 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 160.0, 156.6, 155.0, 143.4, 140.8, 129.7, 128.4, 125.4, 124.7, 118.5, 116.4, 116.3, 114.4, 64.18, 62.6, 55.2, 52.4, 14.2; HRMS (ESI+, *m/z*) calculated for $C_{22}H_{25}N_4O_7$ $[M + H]^+$ 457.1718; found 457.1714.

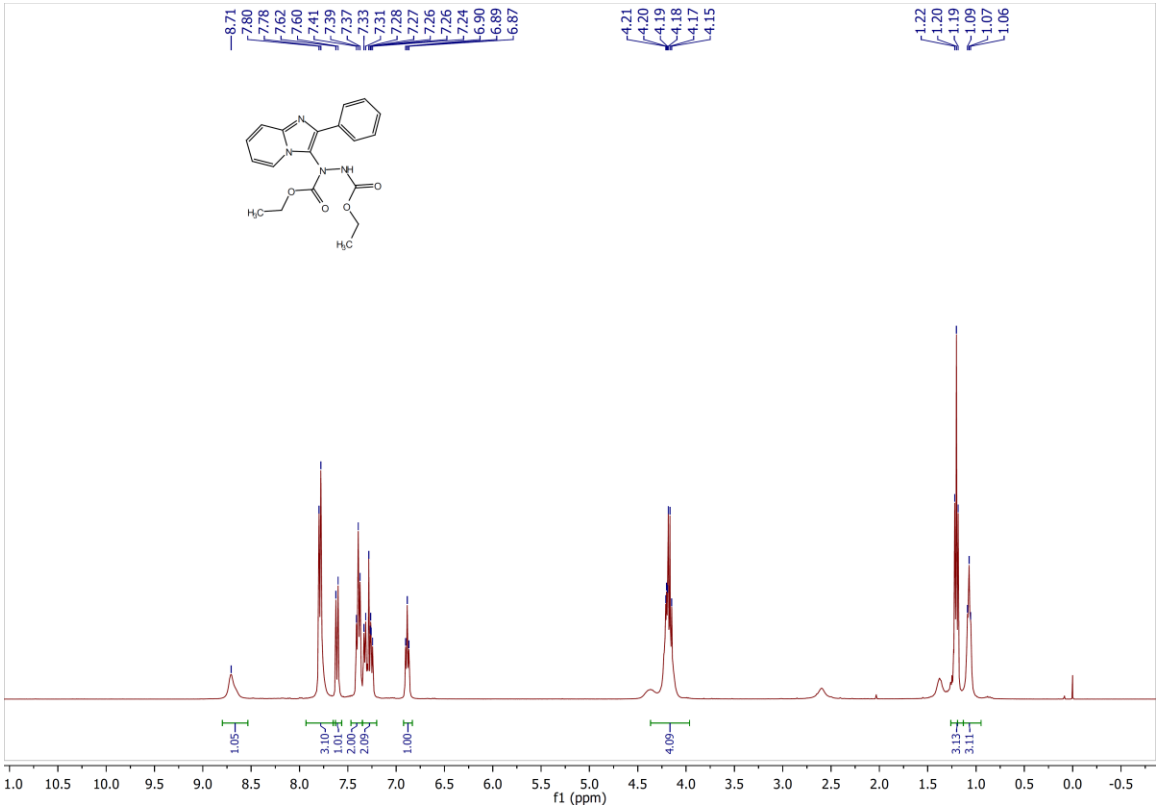
Diethyl 1-(6-methylimidazo[1,2-a]pyridin-3-yl)hydrazine-1,2-dicarboxylate (6)



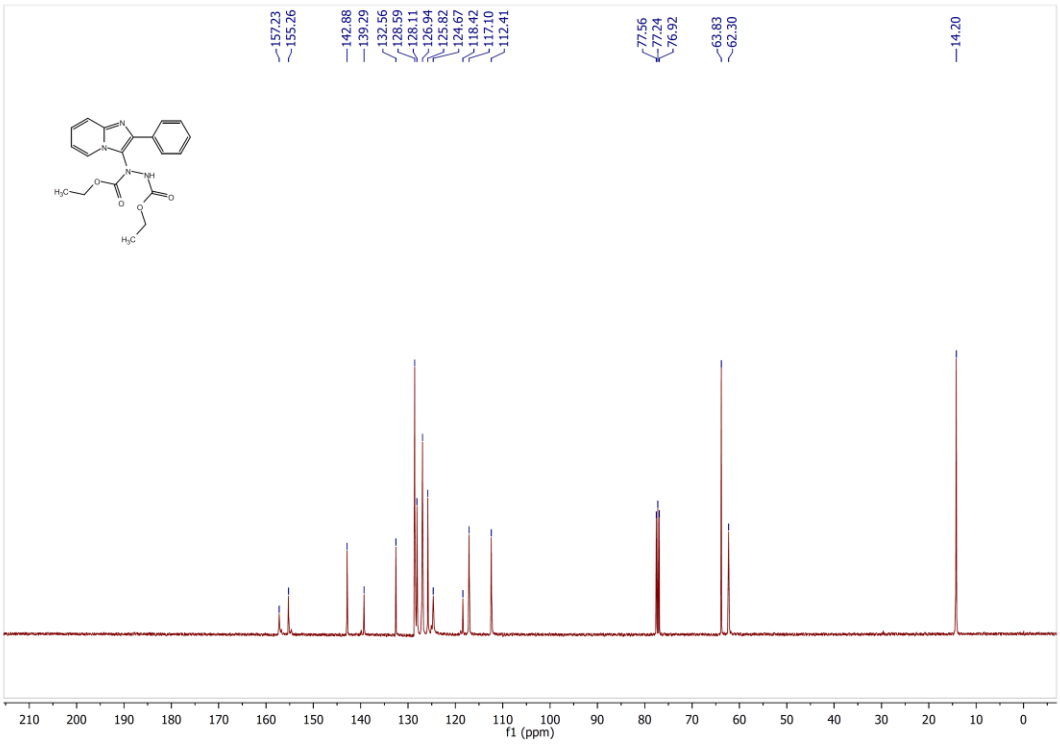
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.23 (s, 1H), 7.55 (s, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.08 (dd, *J* = 9.2, 1.7 Hz, 1H), 4.22 (t, *J* = 7.3, 7.3 Hz, 4H), 2.32 (s, 3H), 1.37 – 1.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.6, 155.2, 142.8, 129.7, 128.5, 122.9, 122.4, 121.6, 116.9, 63.6, 62.1, 18.2, 14.4, 14.3; HRMS (ESI+, *m/z*) calculated for $C_{14}H_{19}N_4O_4$ $[M + H]^+$ 307.1401; found 307.1404.

Copies of NMR Spectra

^{1}H-NMR of 3a



^{13}C-NMR of 3a



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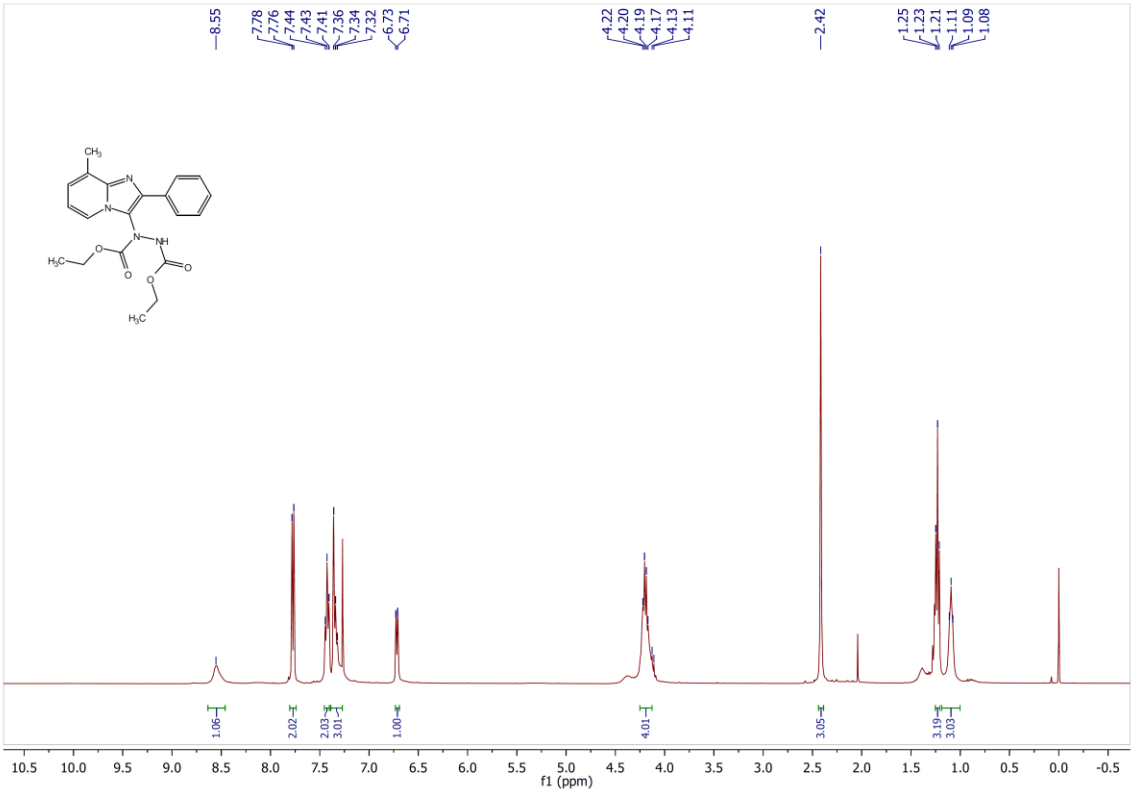

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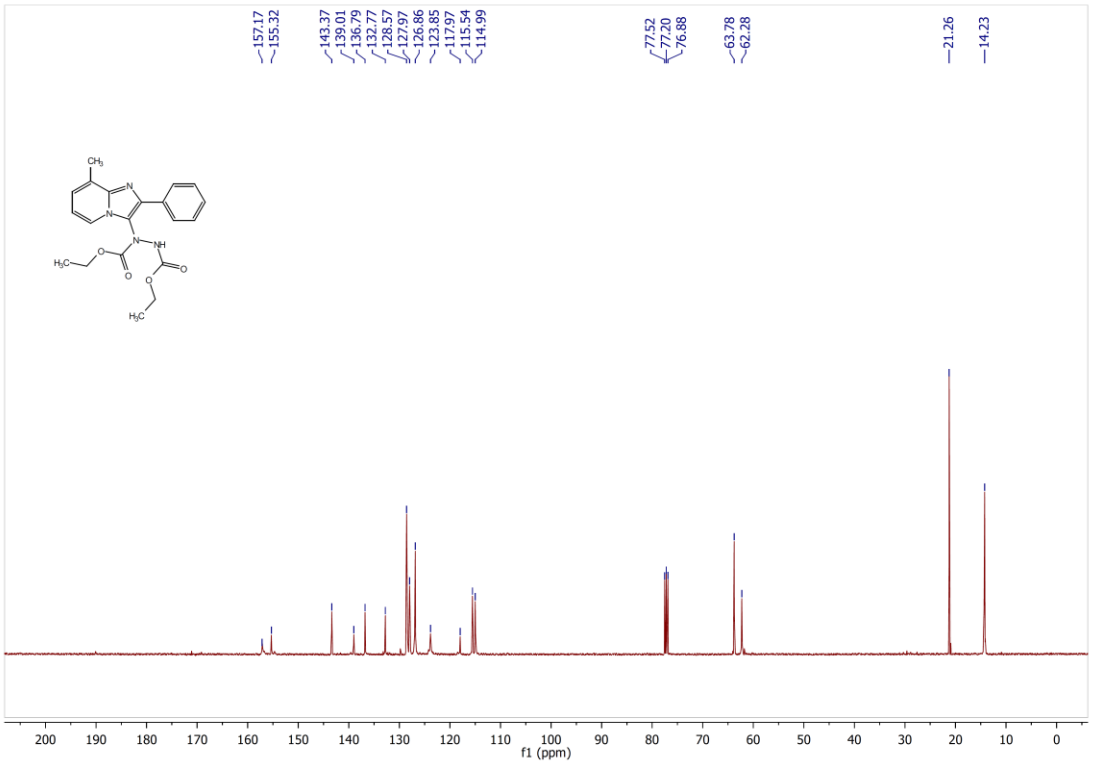

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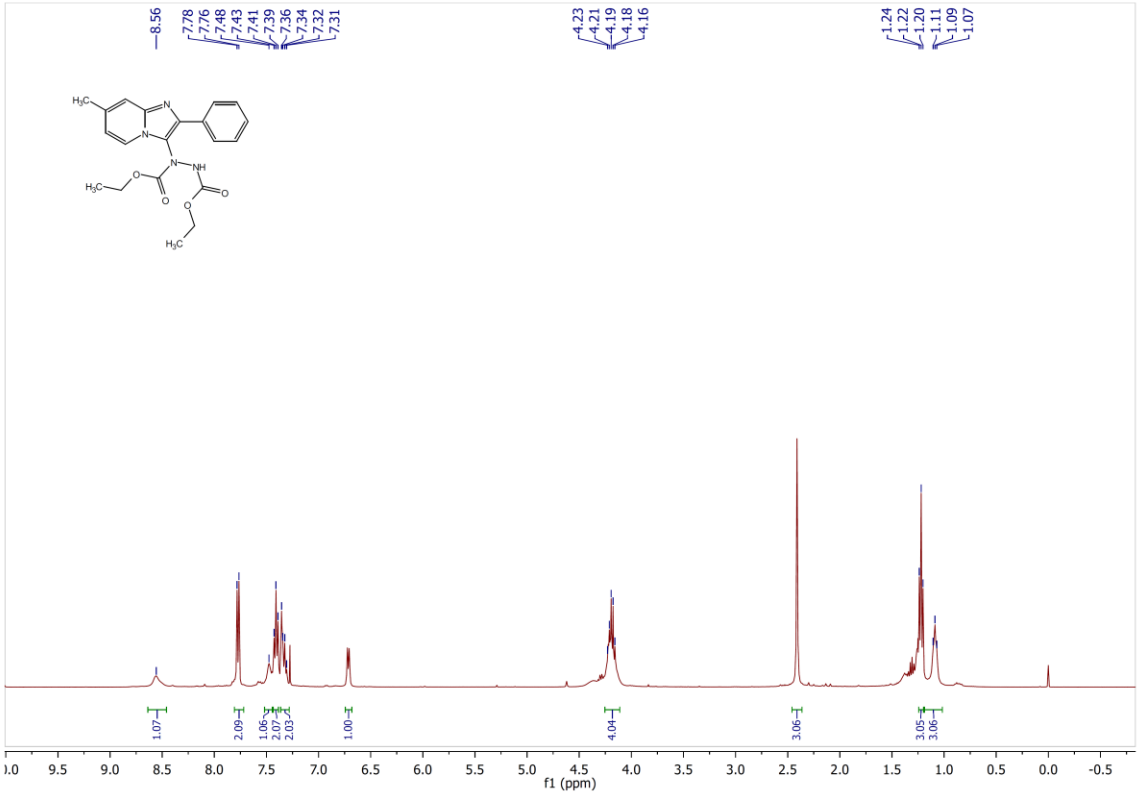

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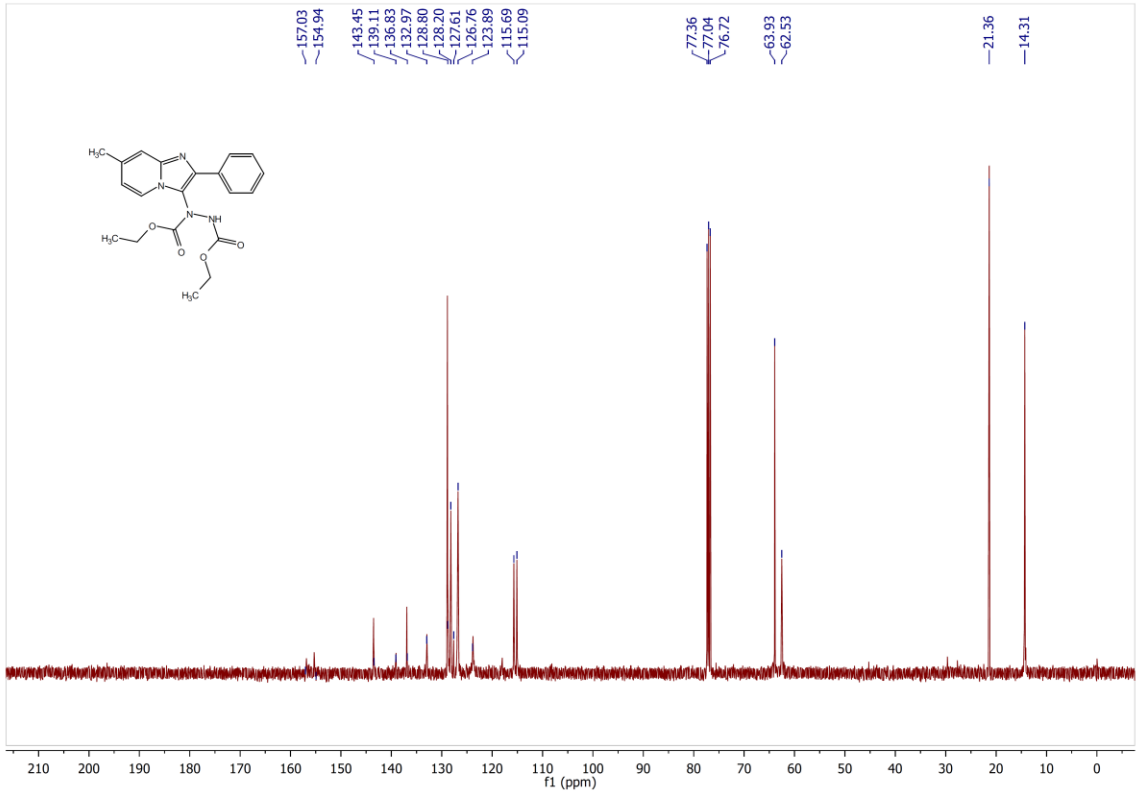

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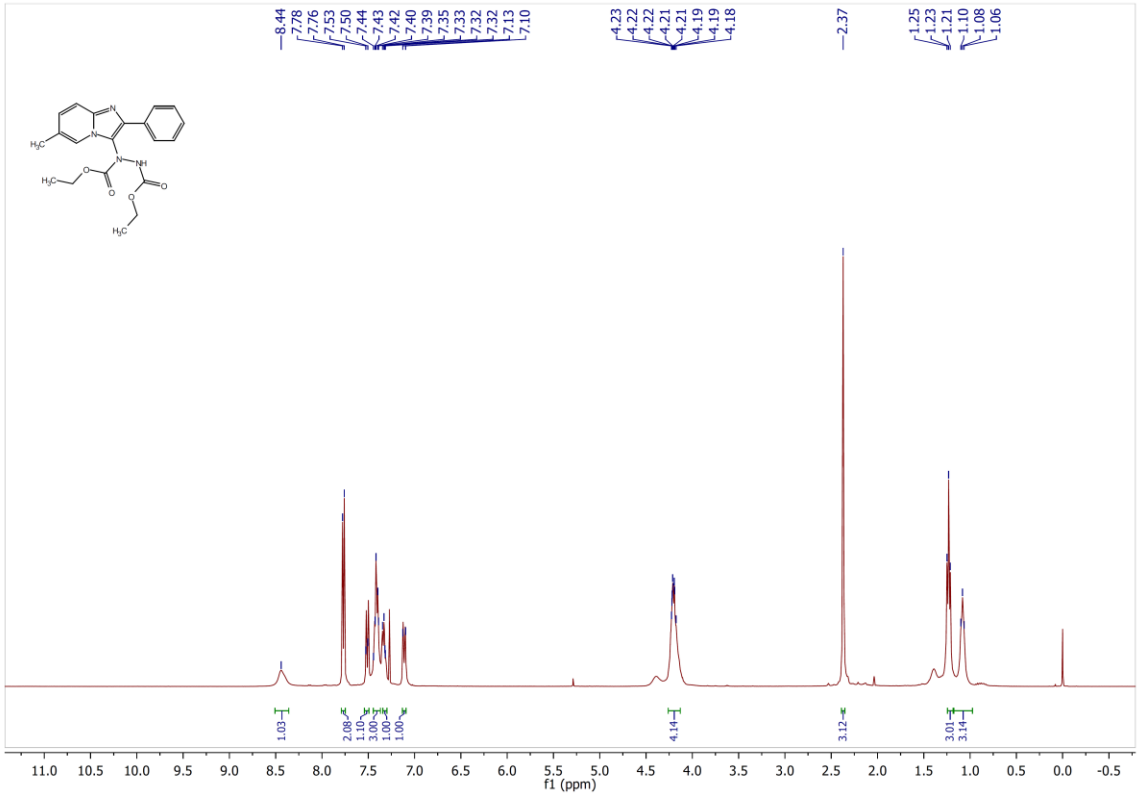

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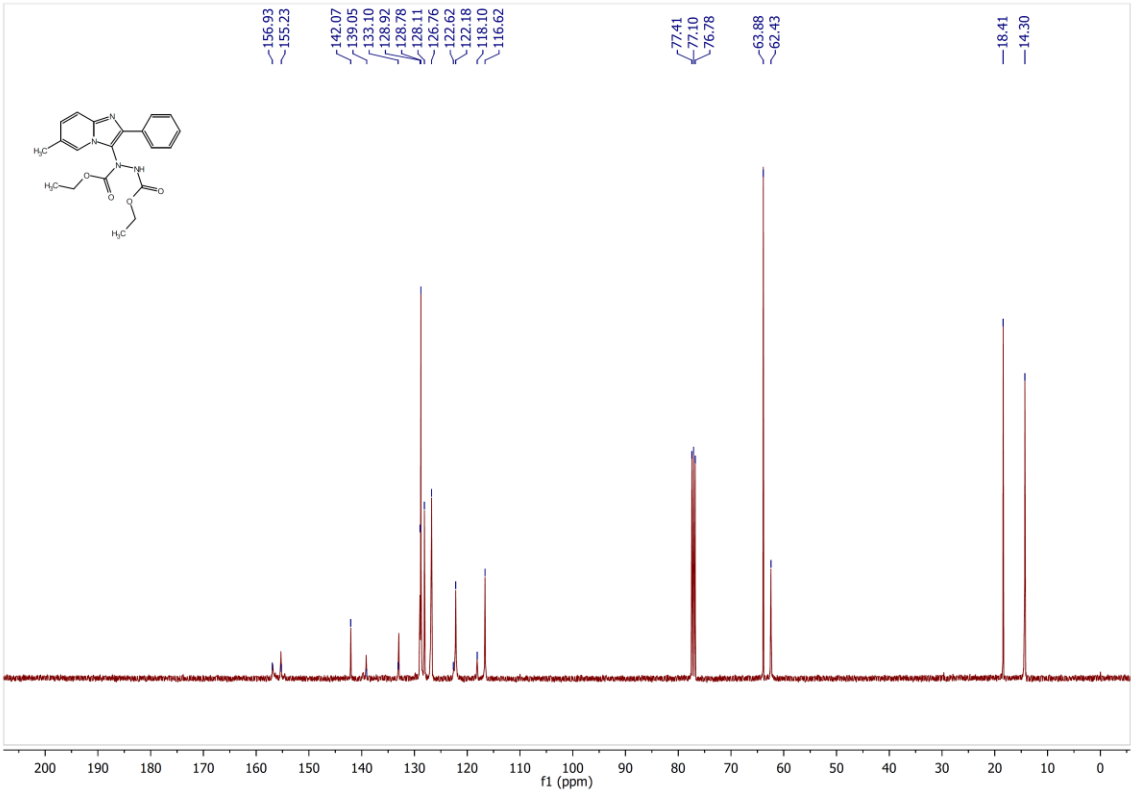

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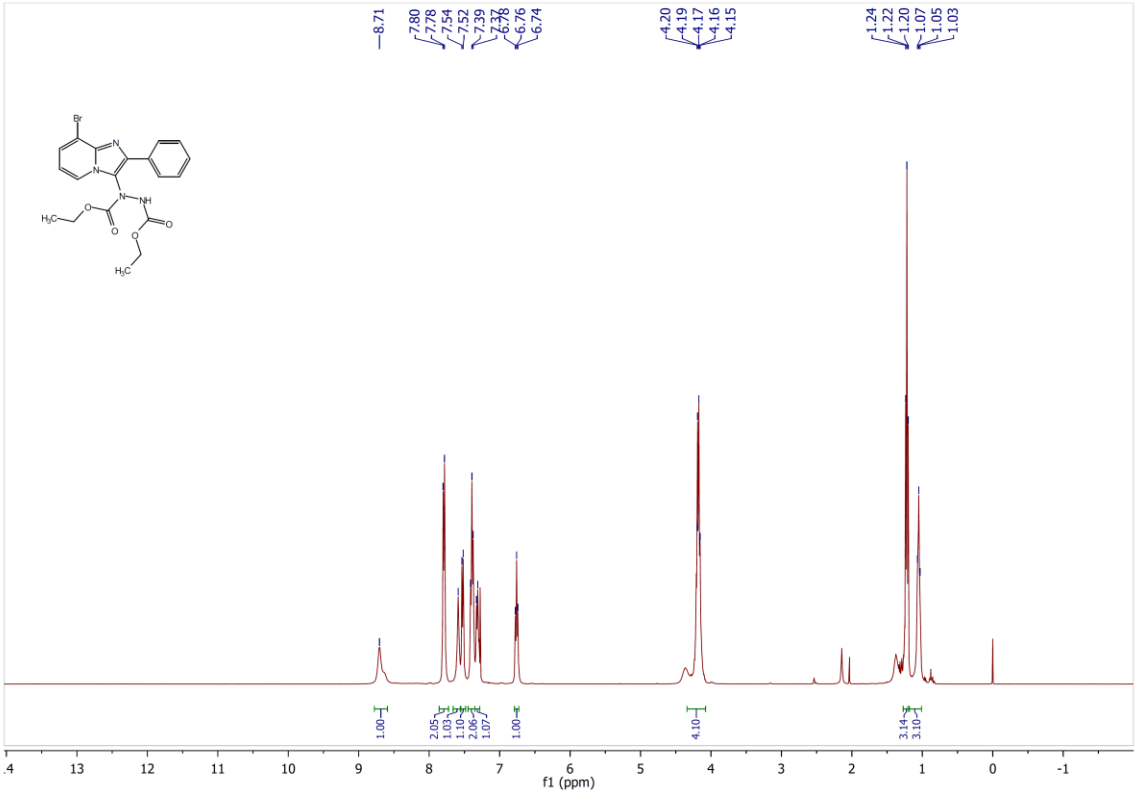

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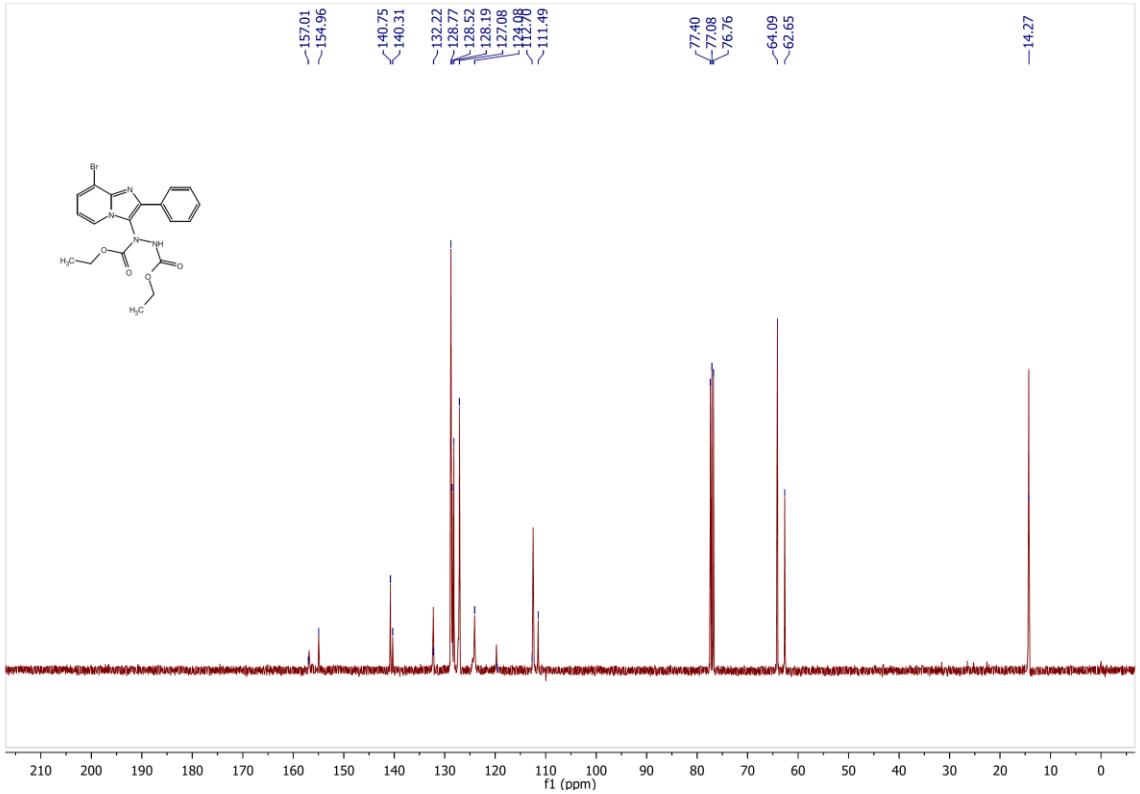

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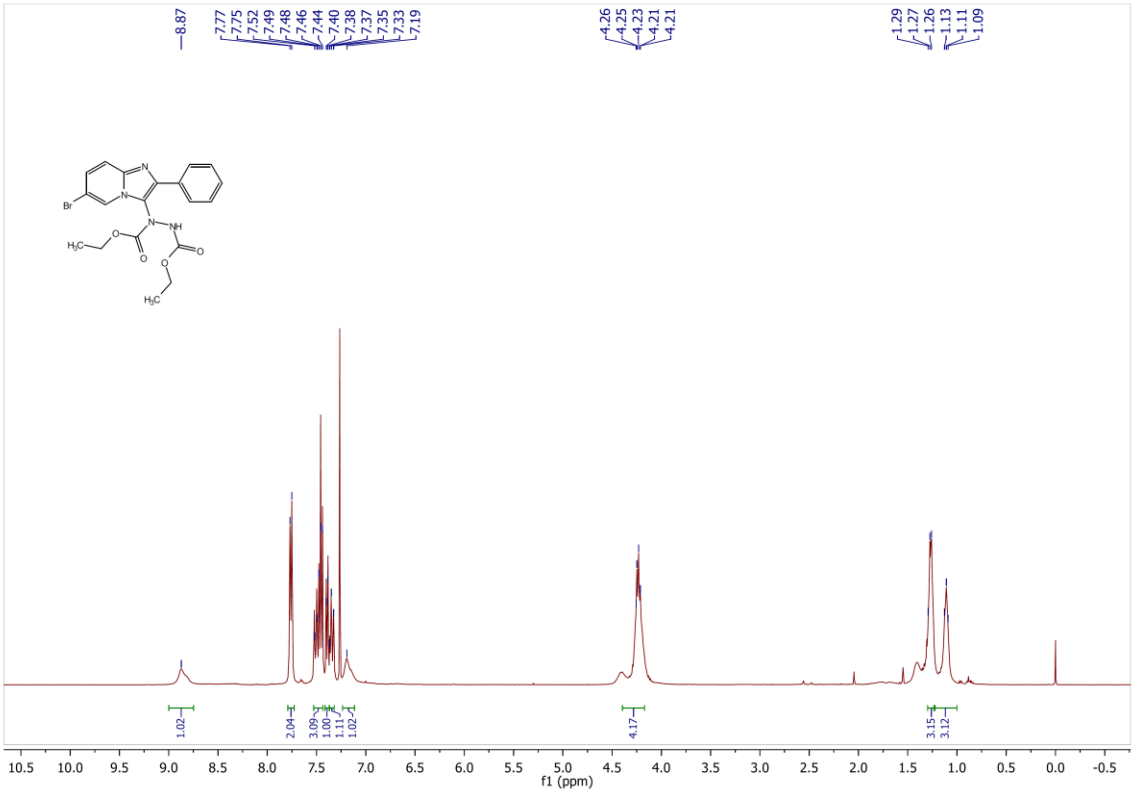
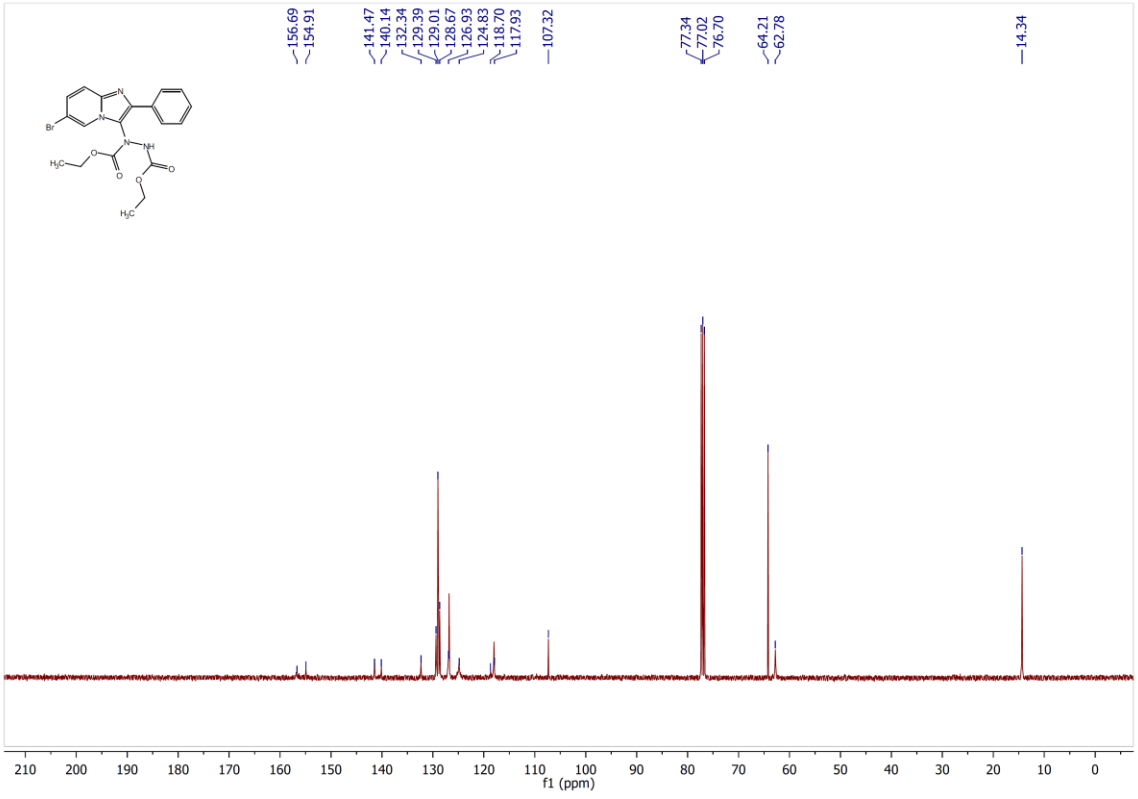
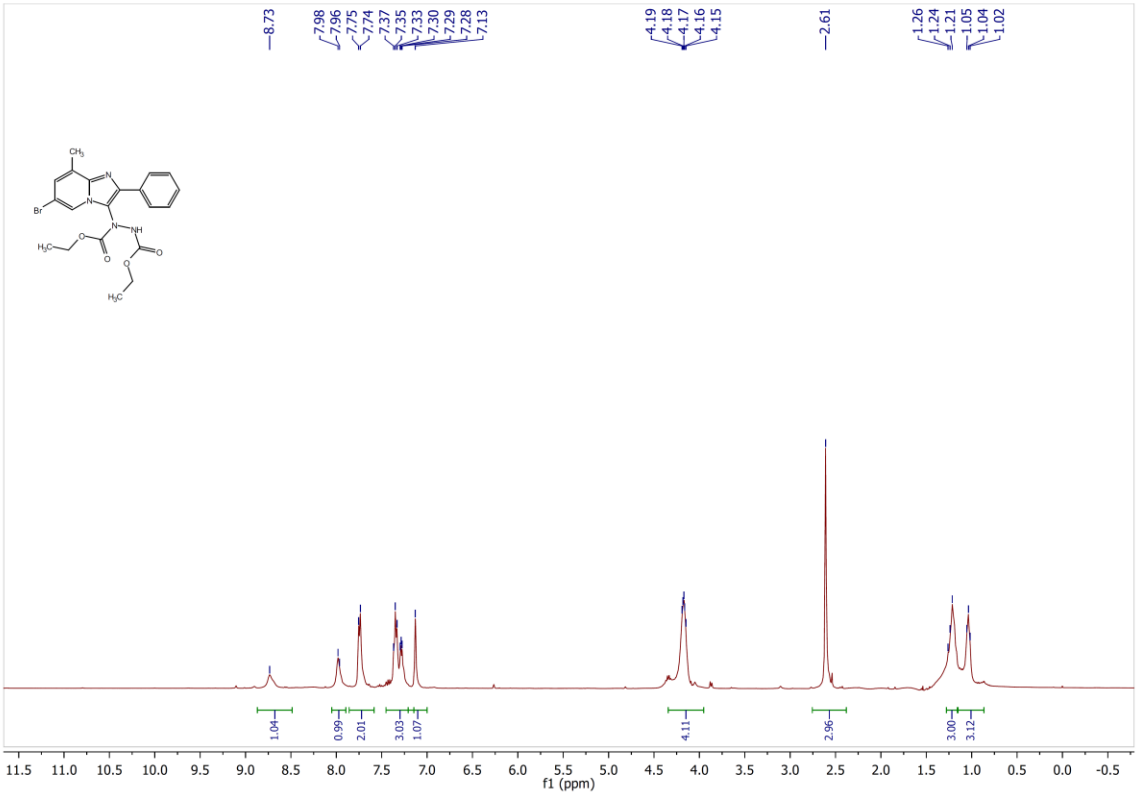


^{13}C-NMR of 3f



^{1}H-NMR of 3g



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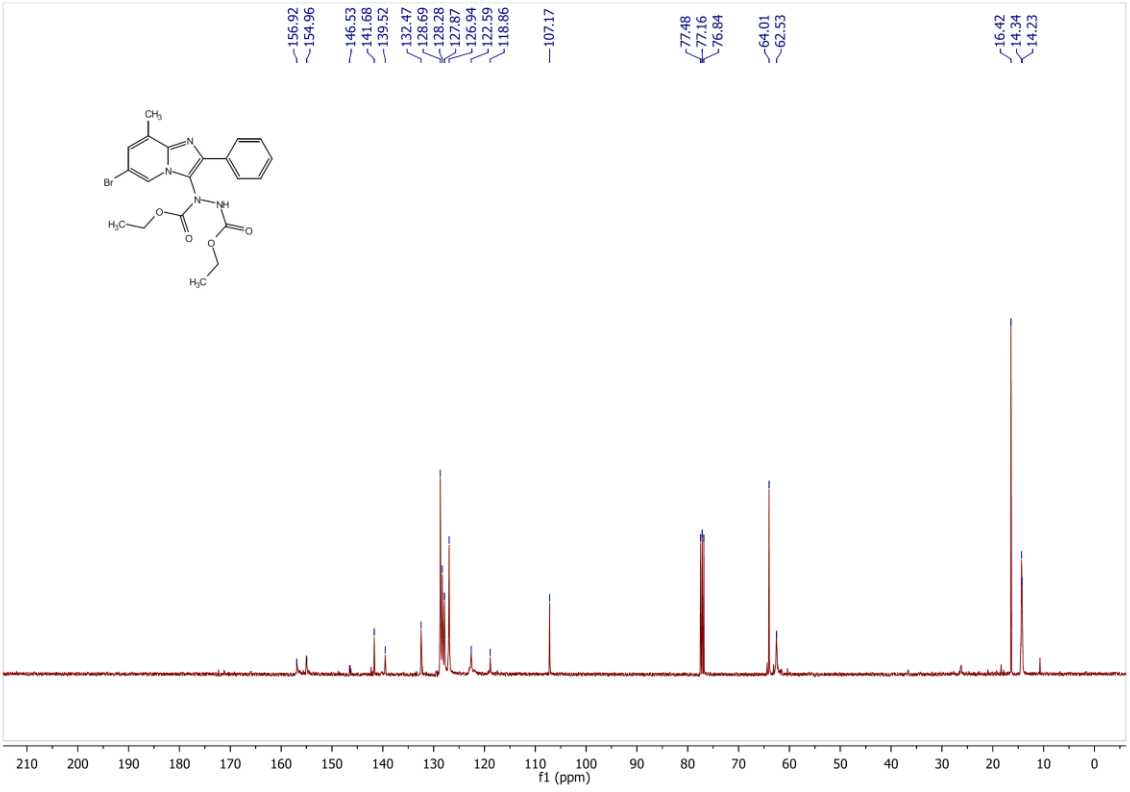

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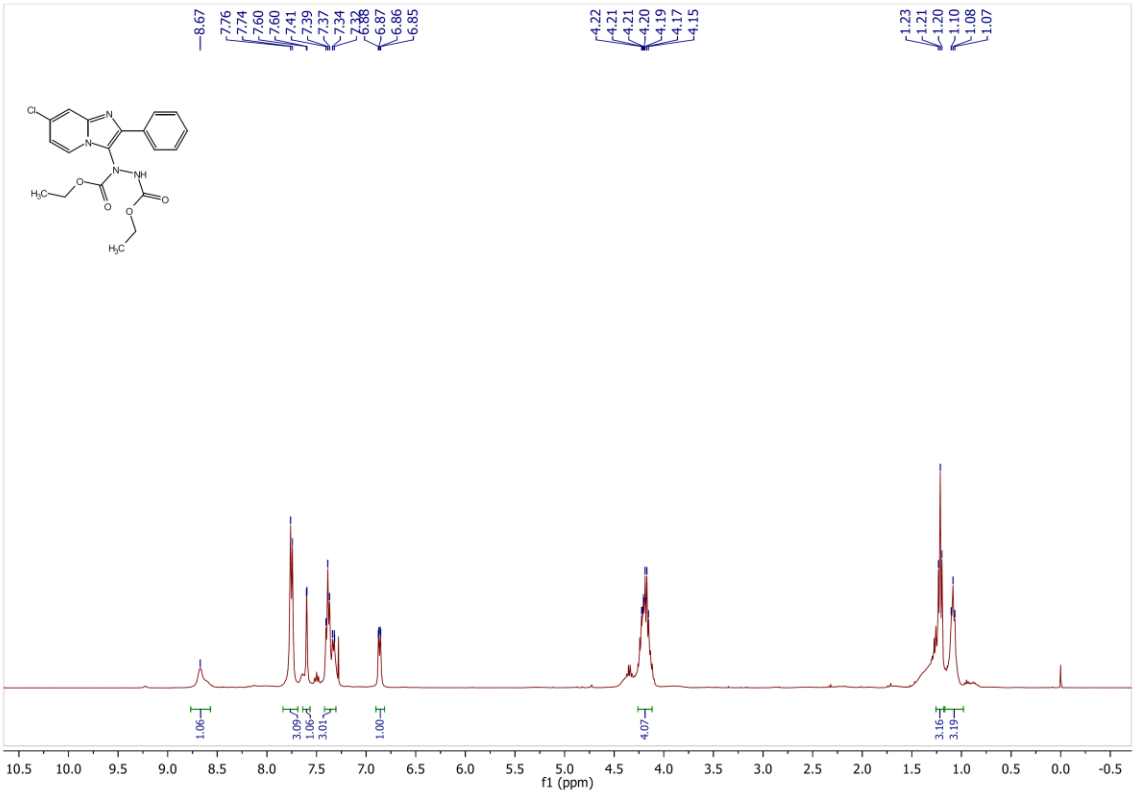

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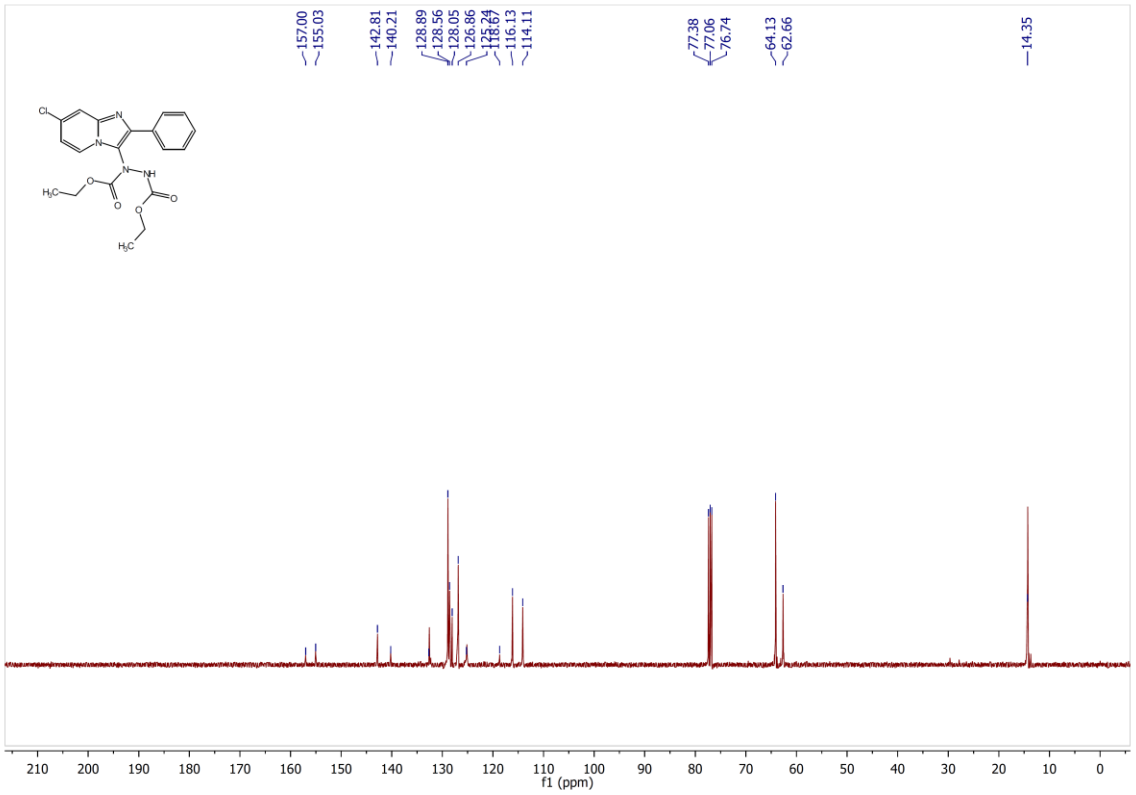
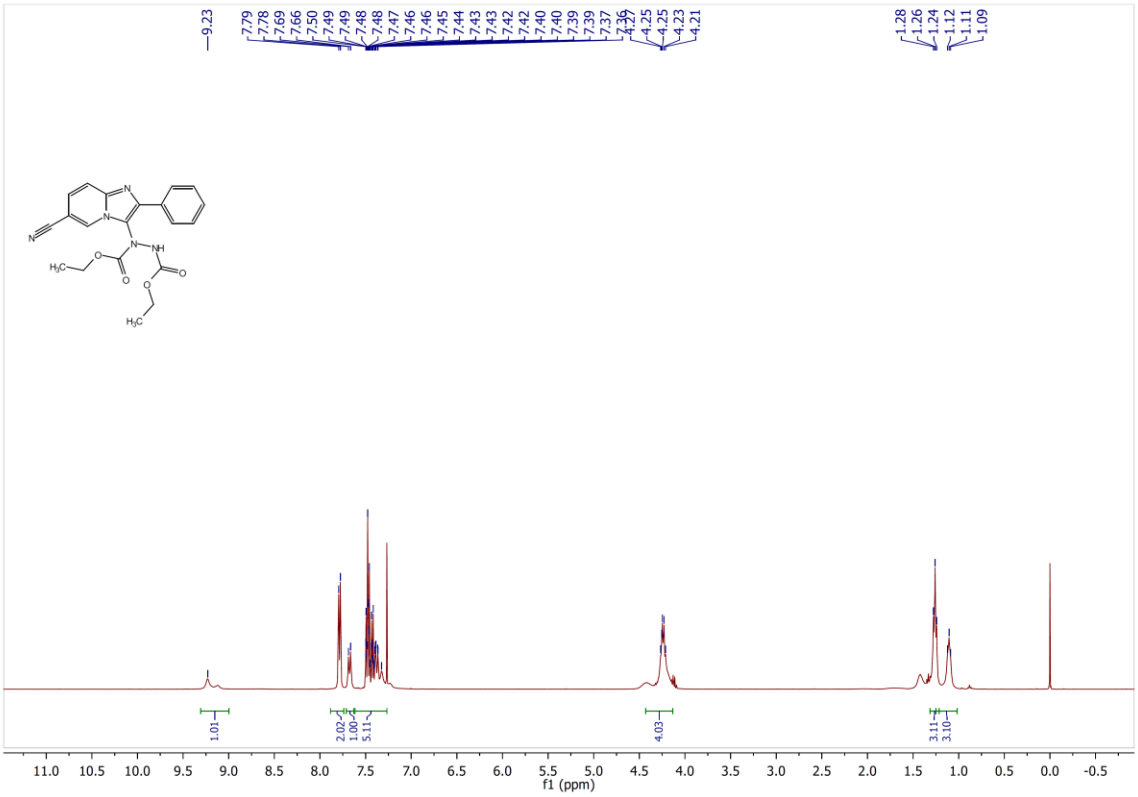


^{1}H-NMR of 3i



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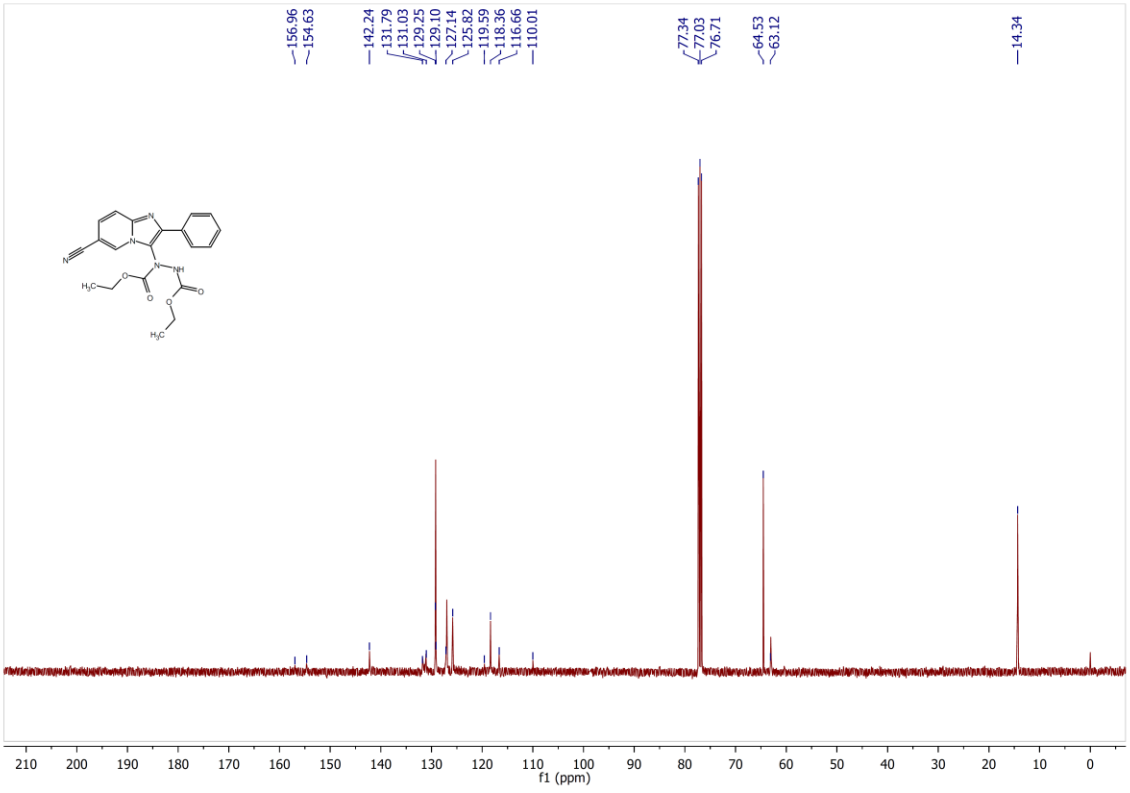

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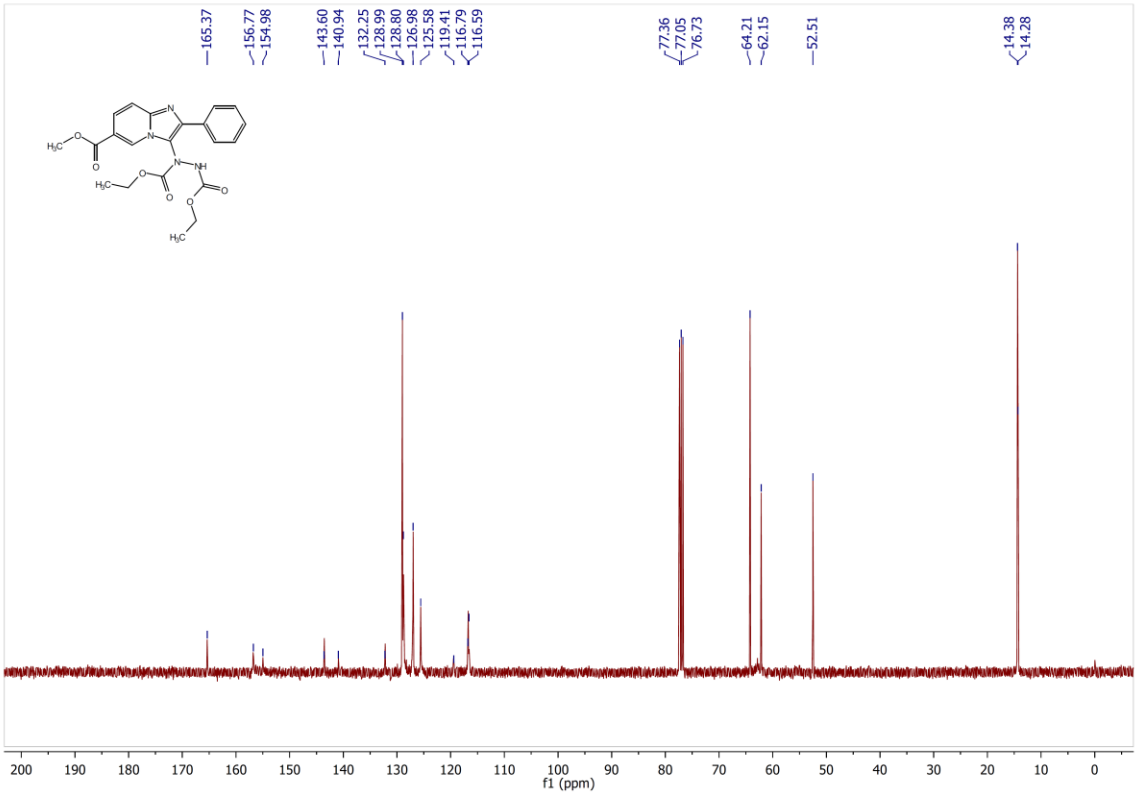

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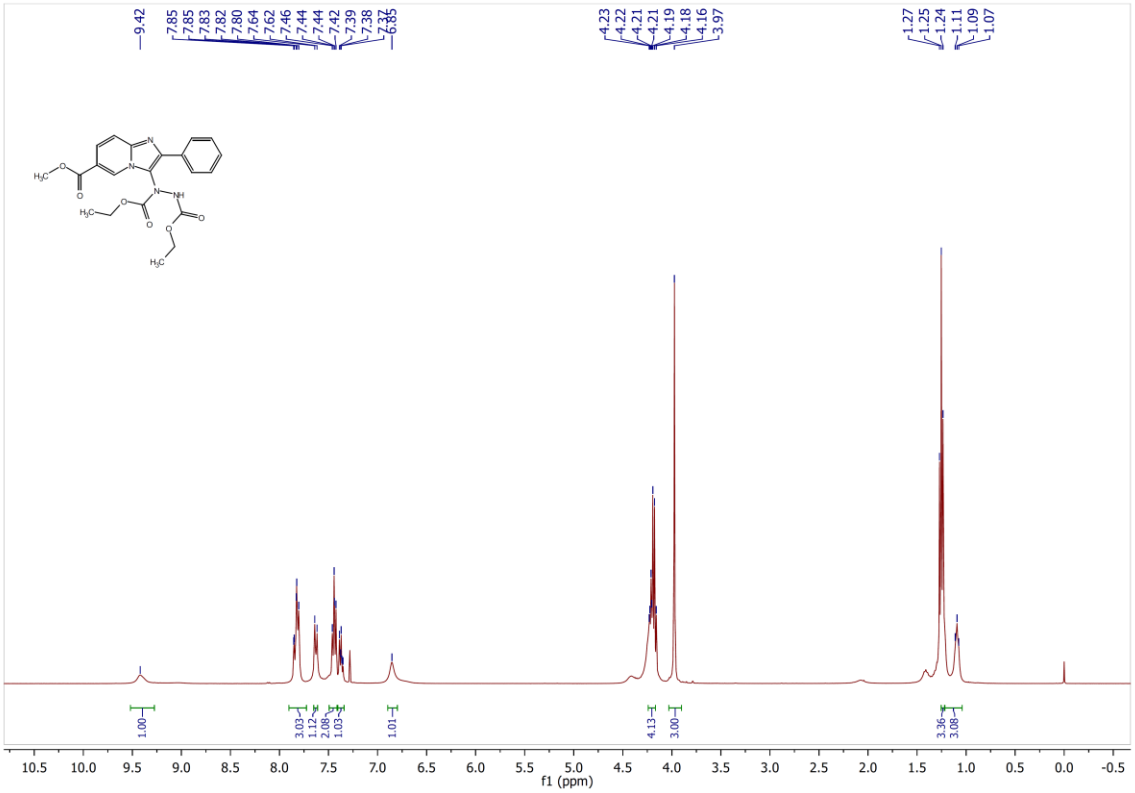
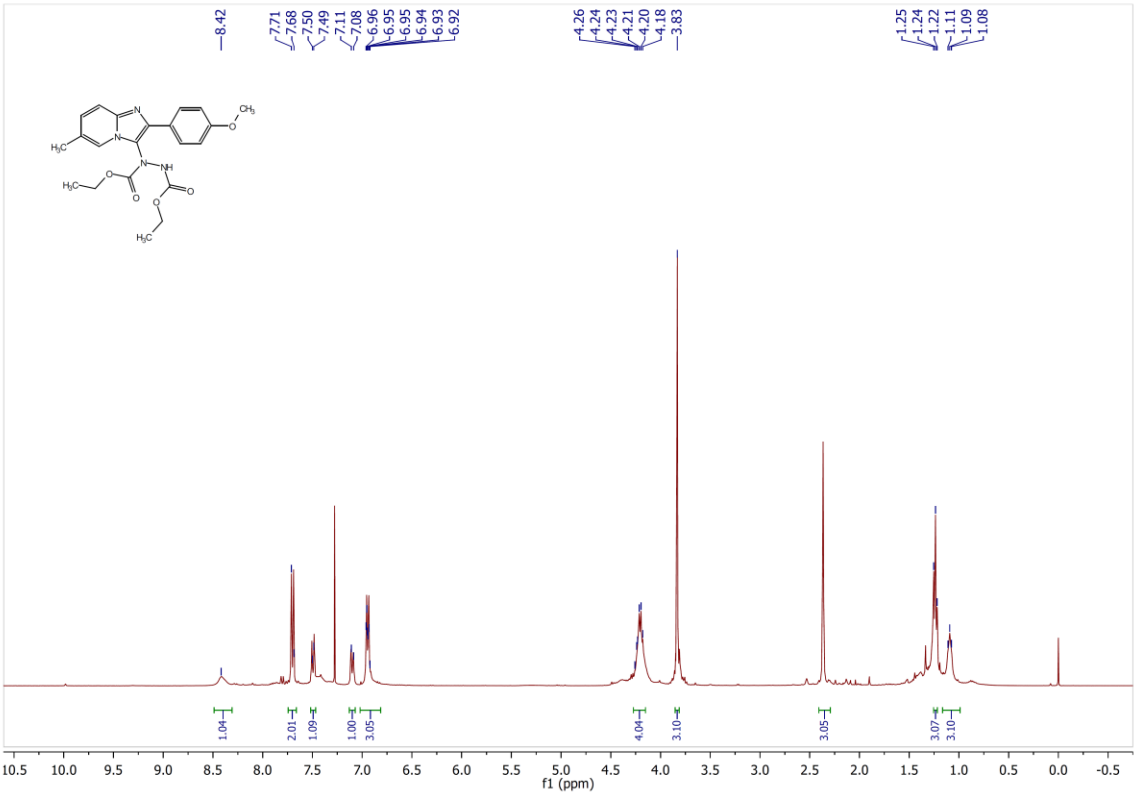


^{1}H-NMR of 3k



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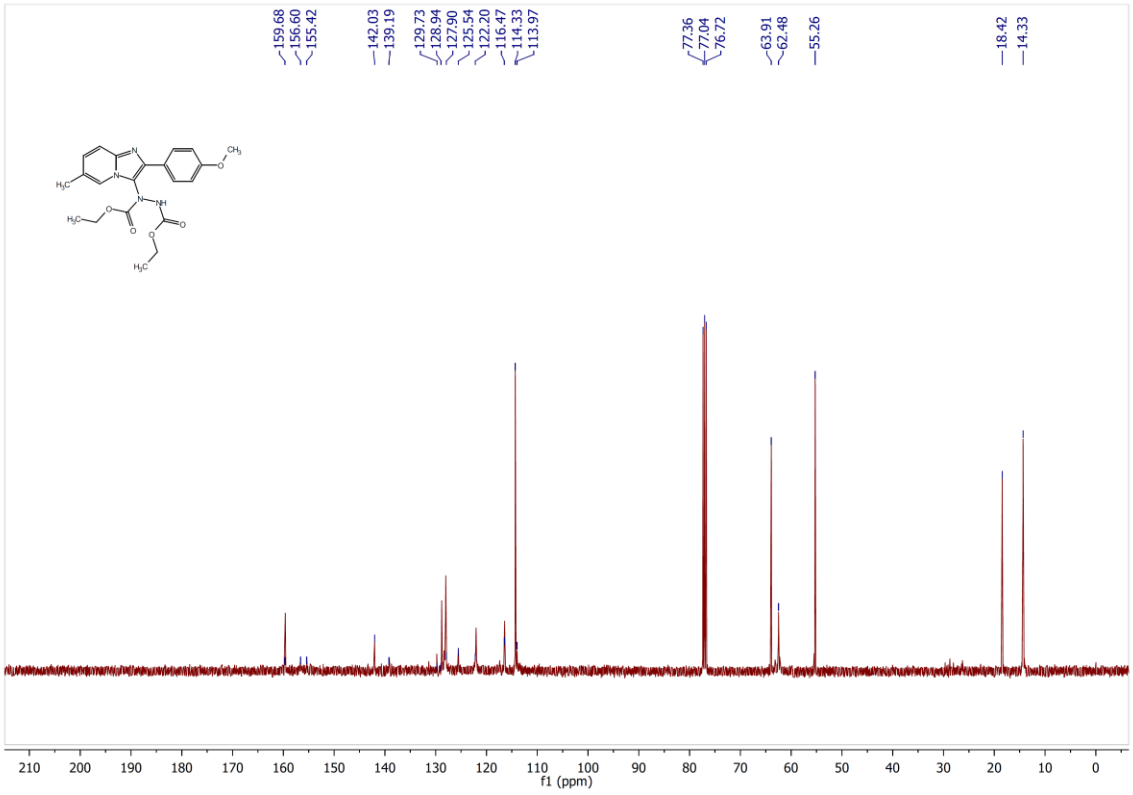

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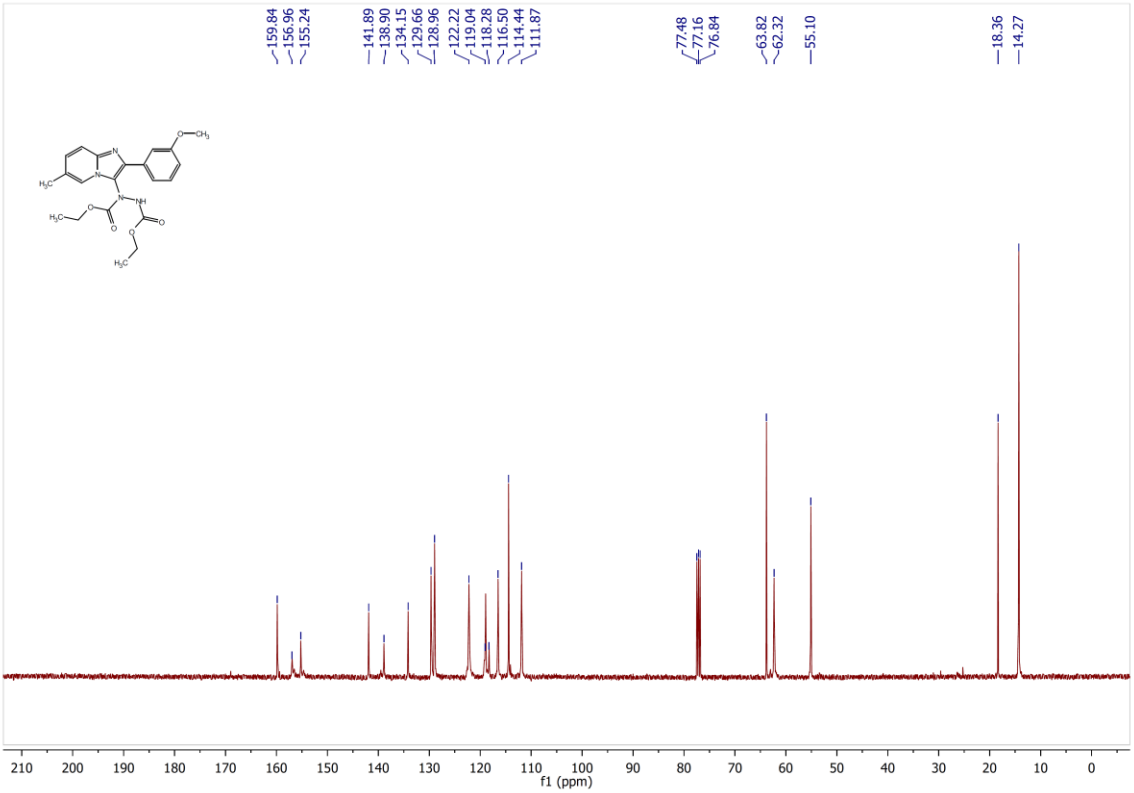

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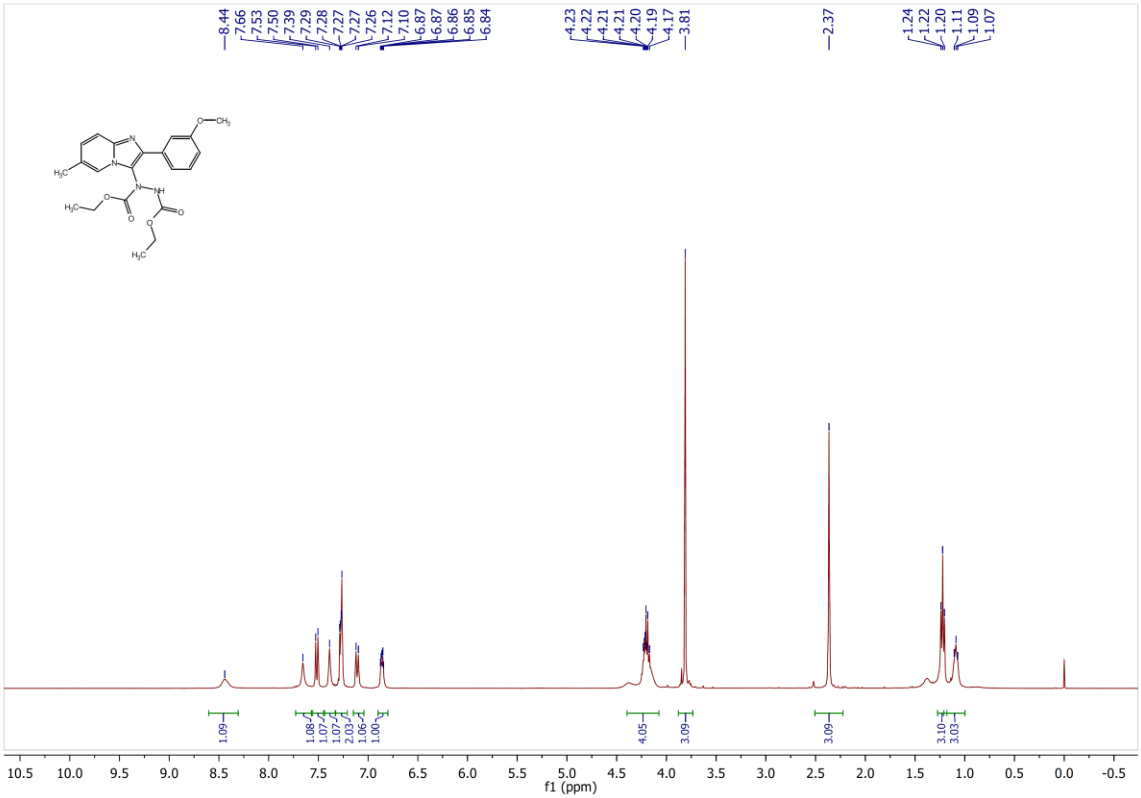

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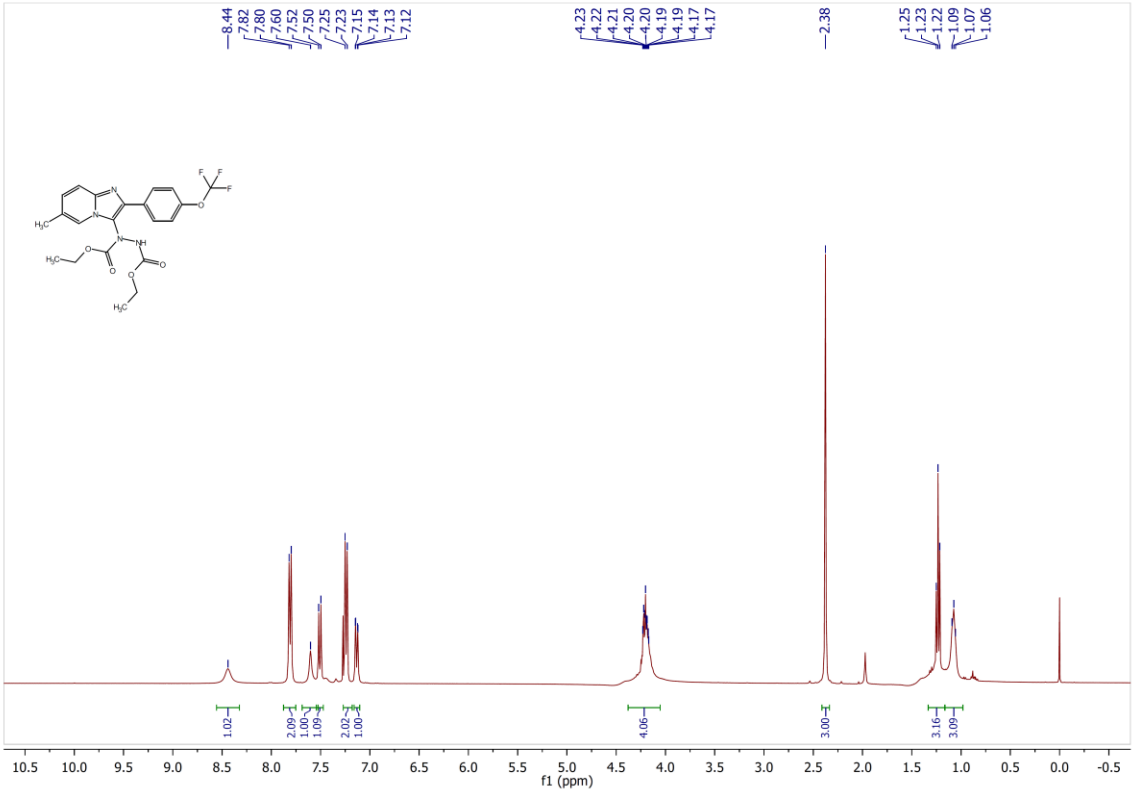

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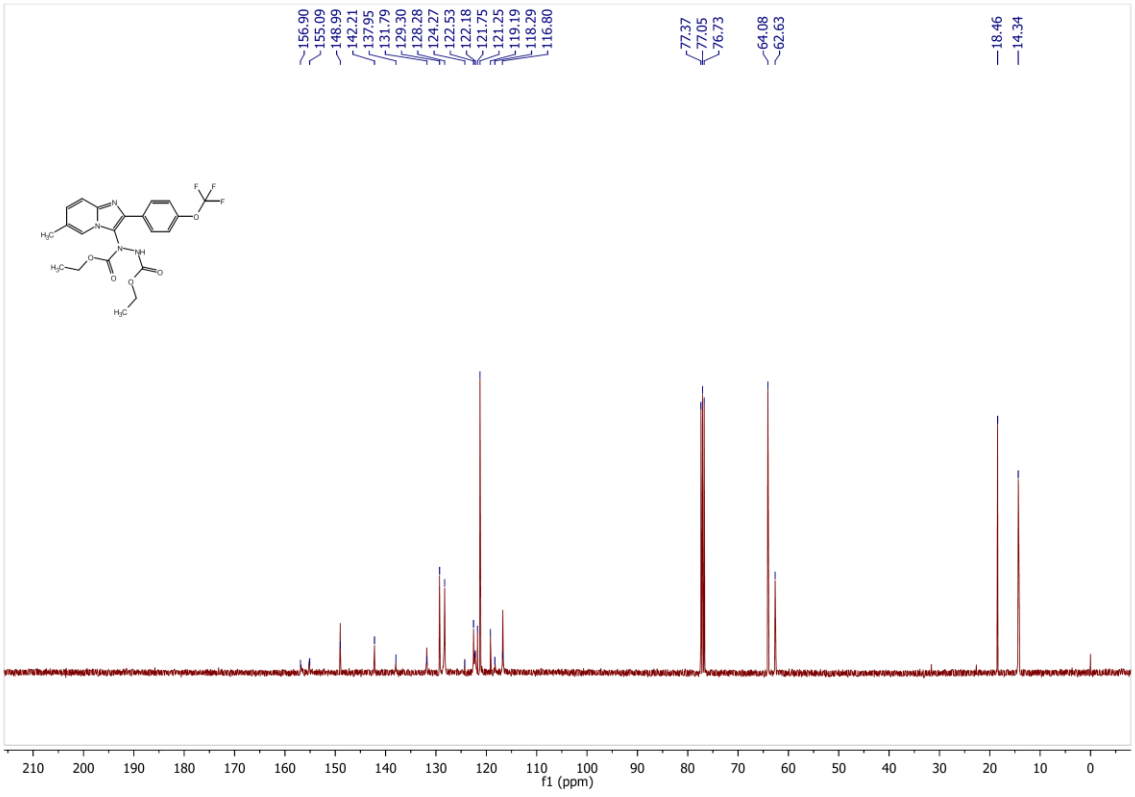

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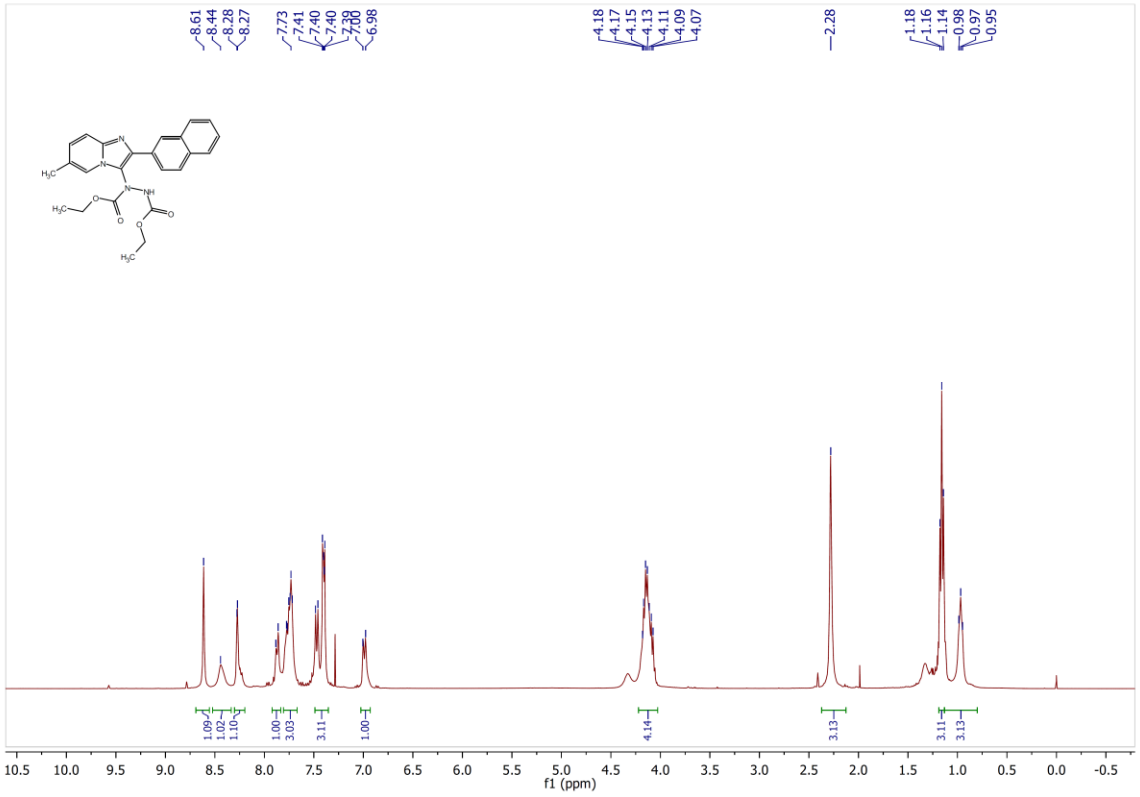

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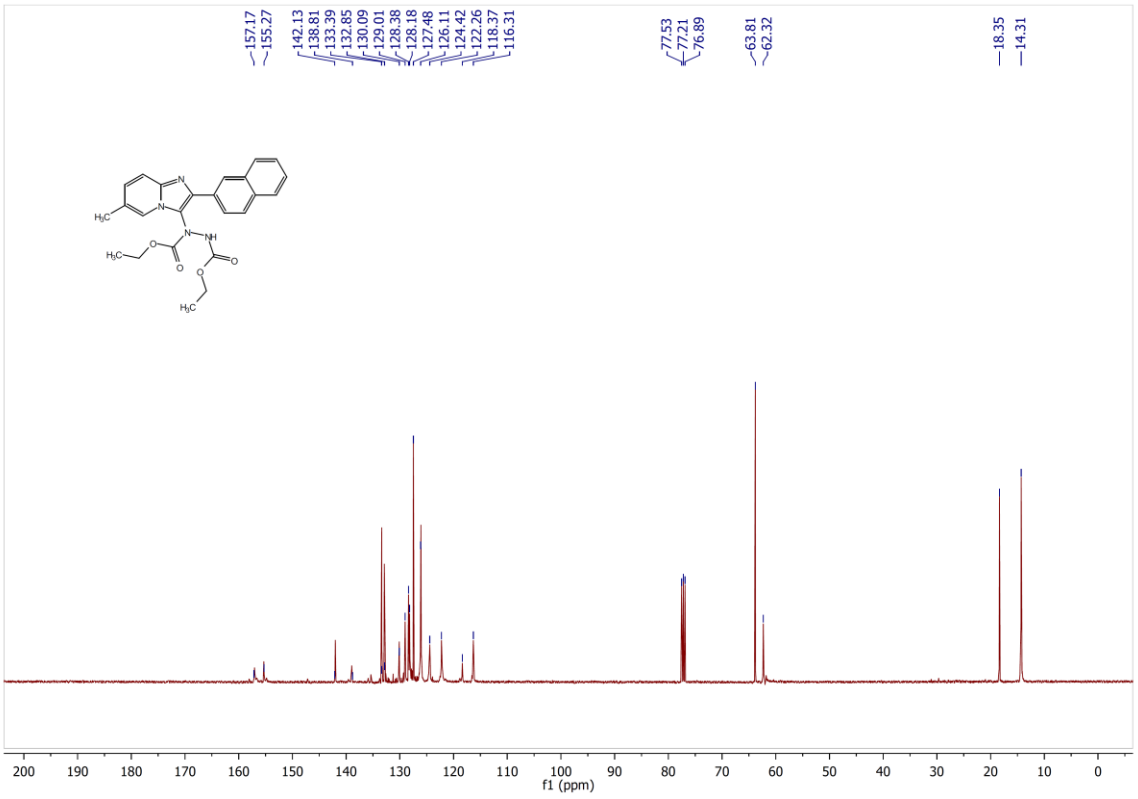
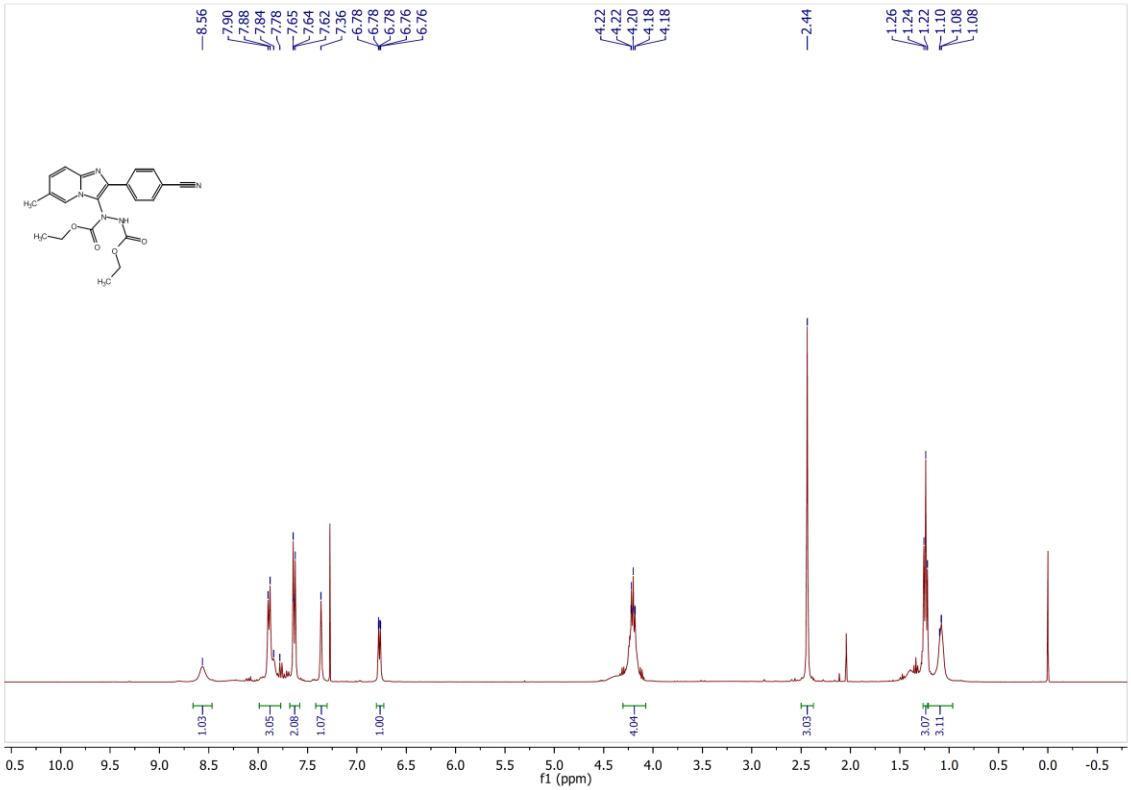
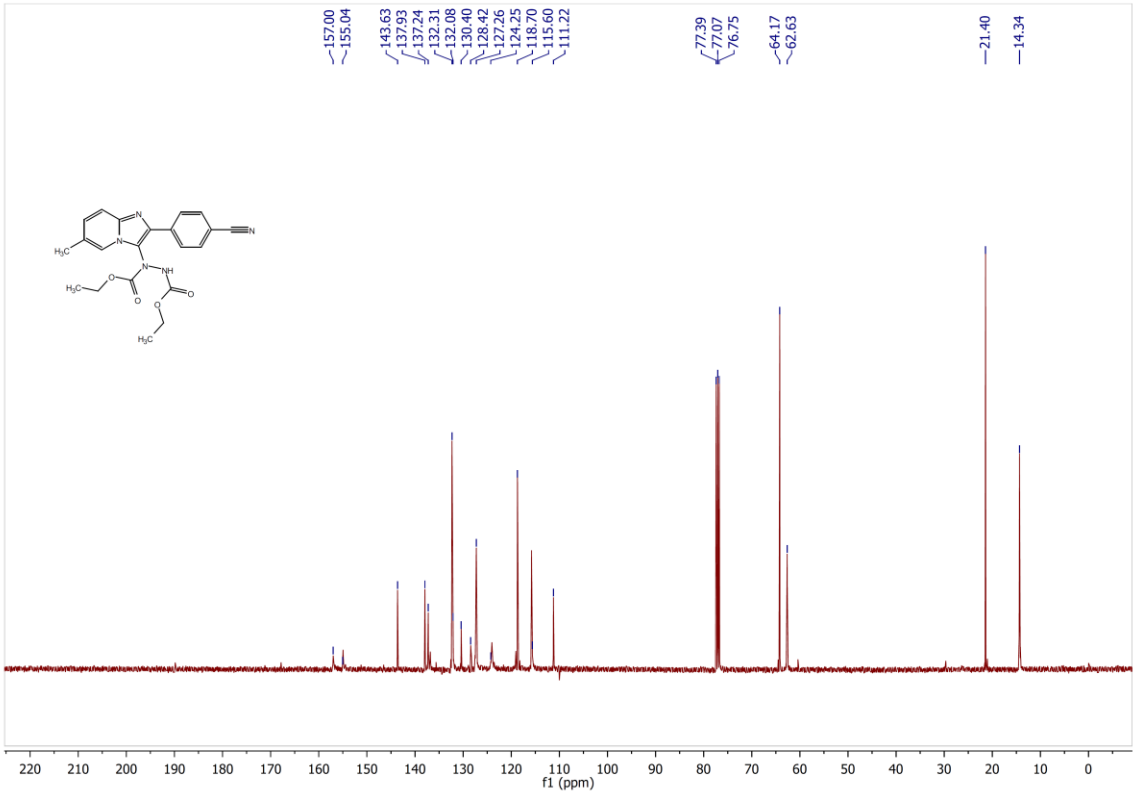


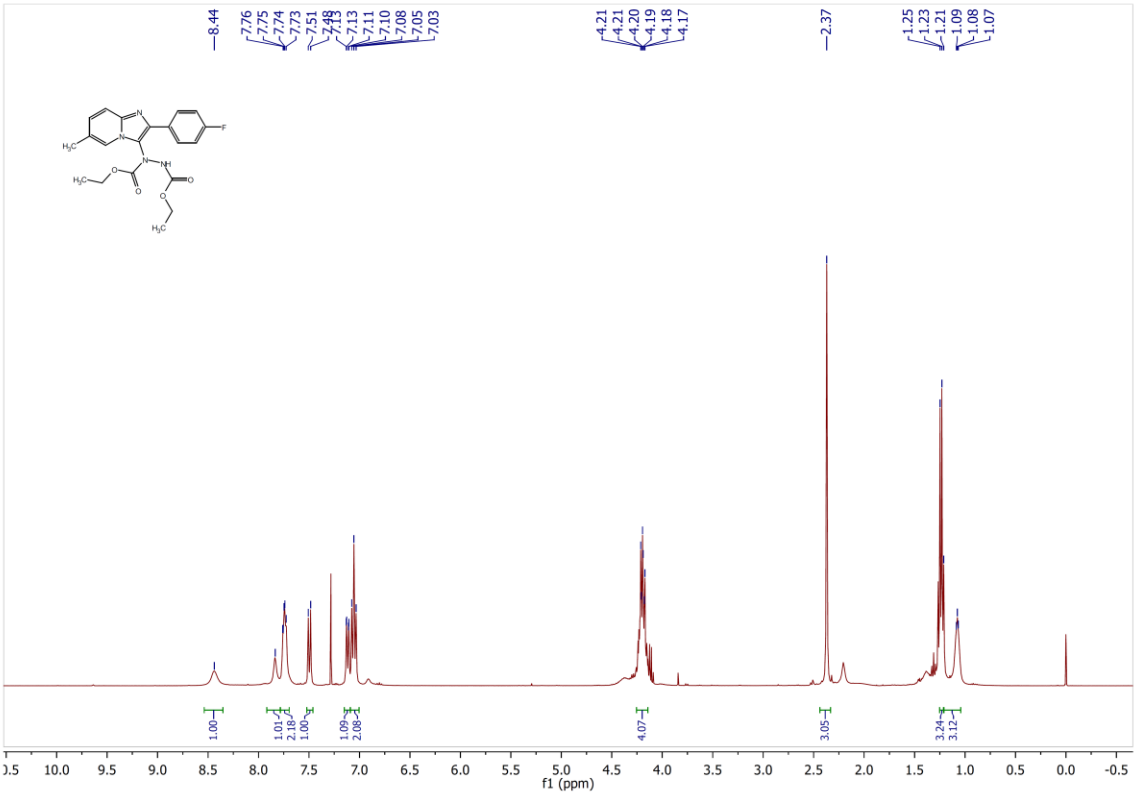
^{1}H-NMR of 3o



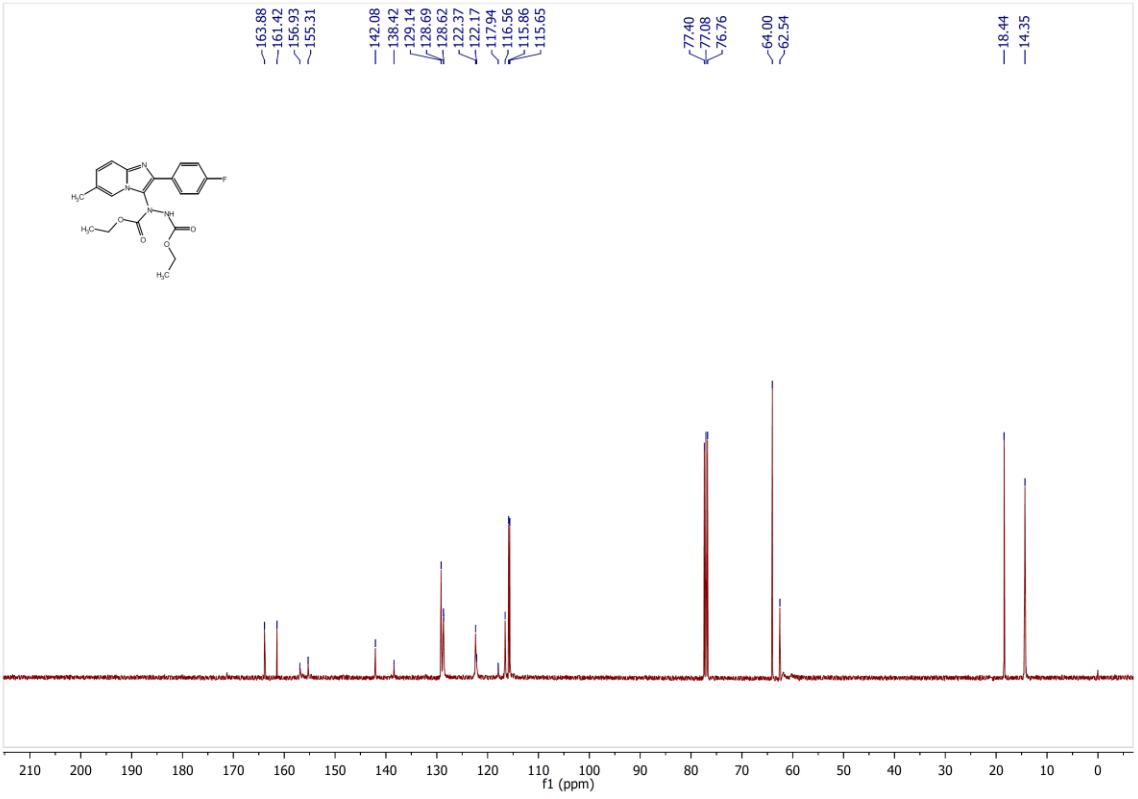
^{13}C-NMR of 3o



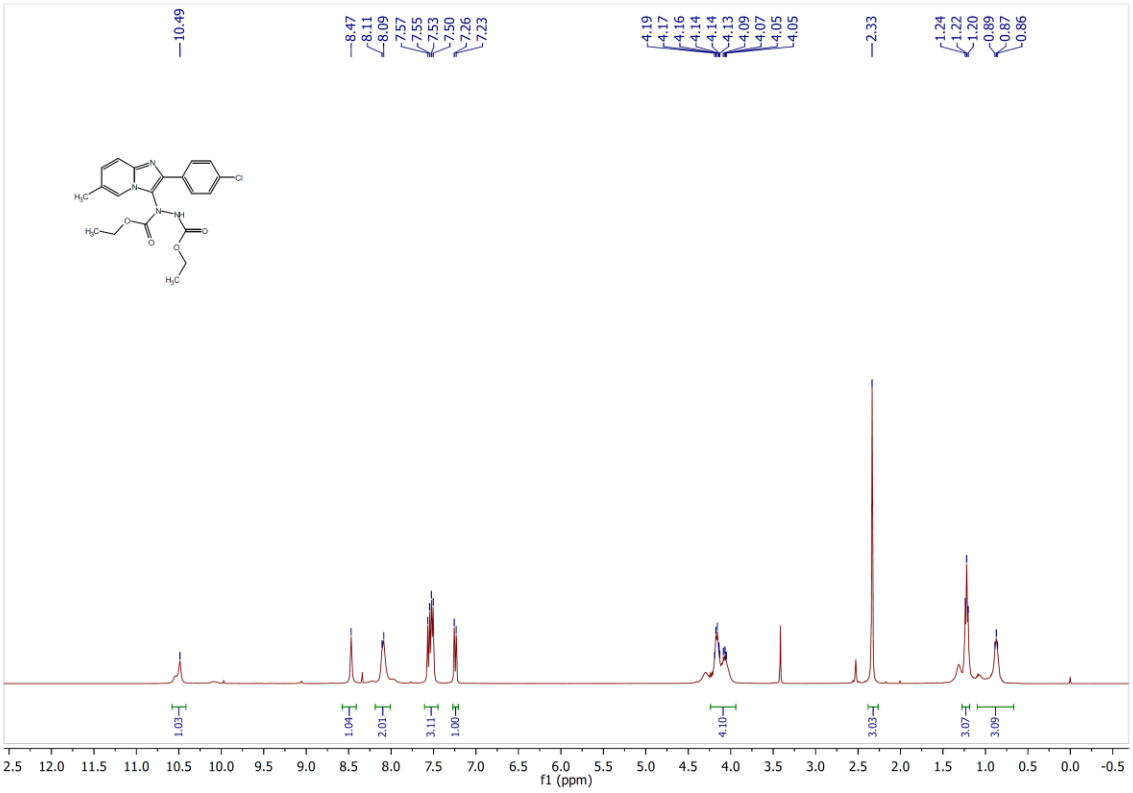
^{1}H-NMR of 3p



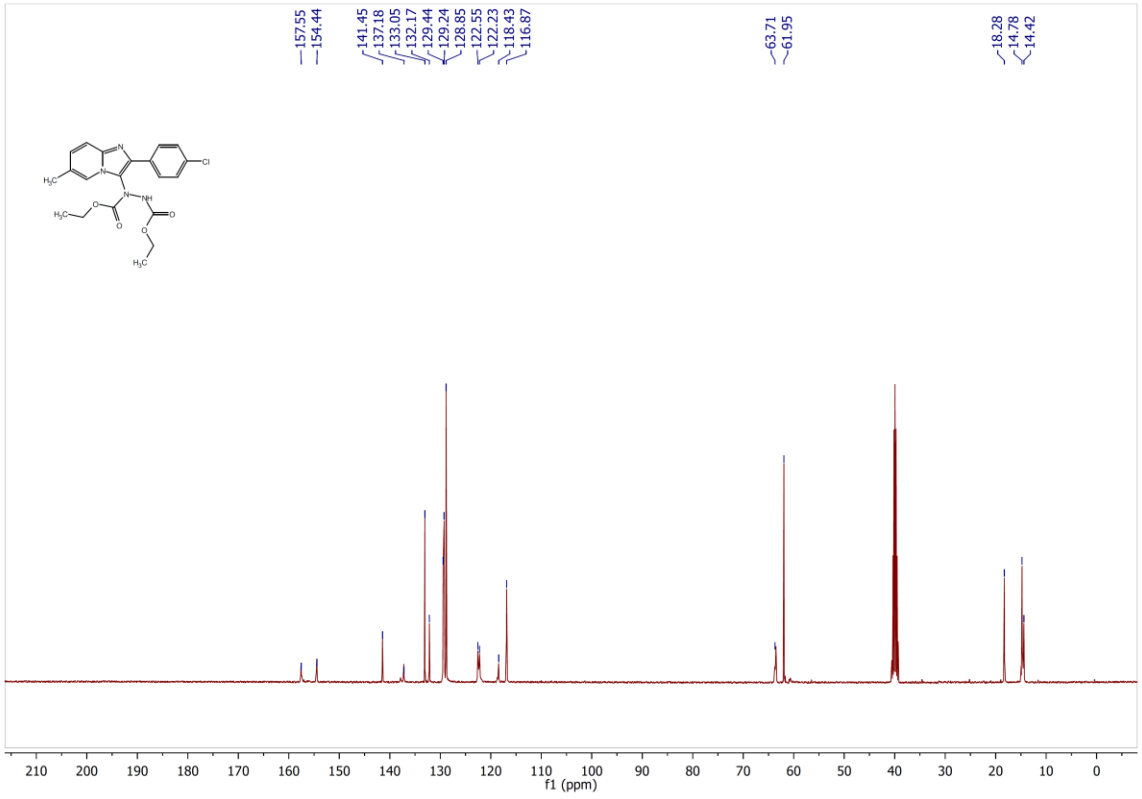
^{13}C-NMR of 3p



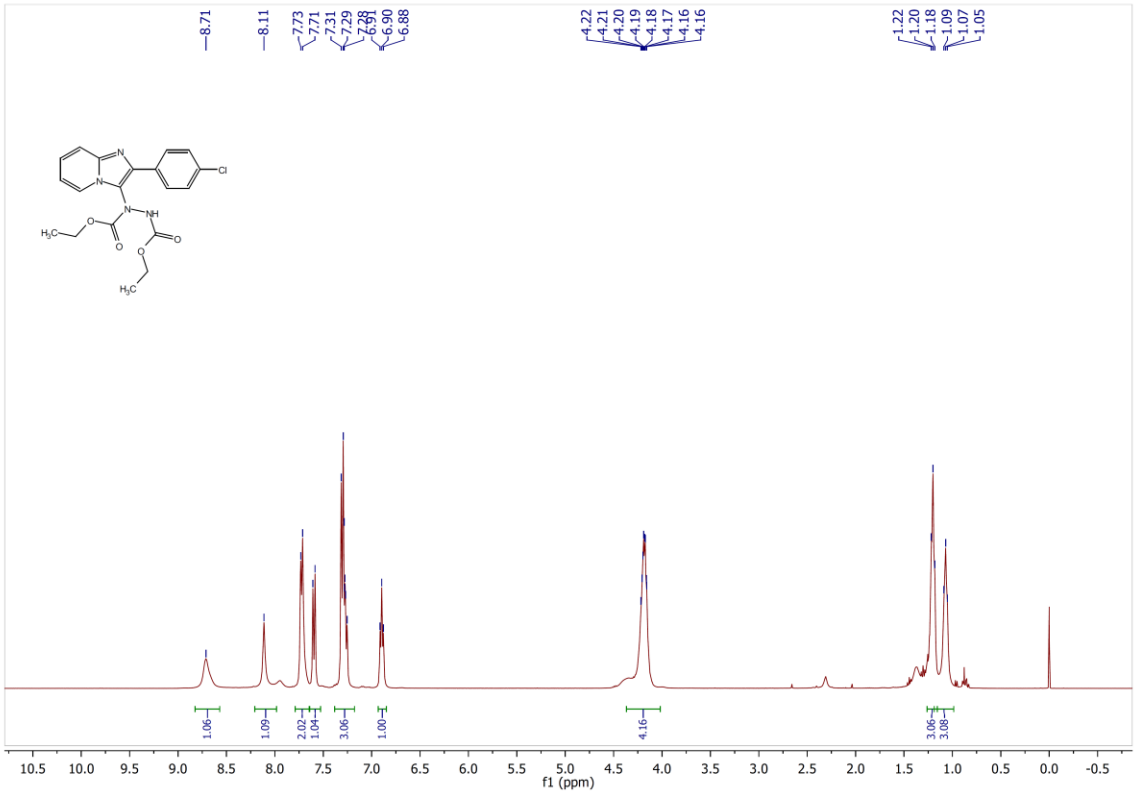
^{1}H-NMR of 3q



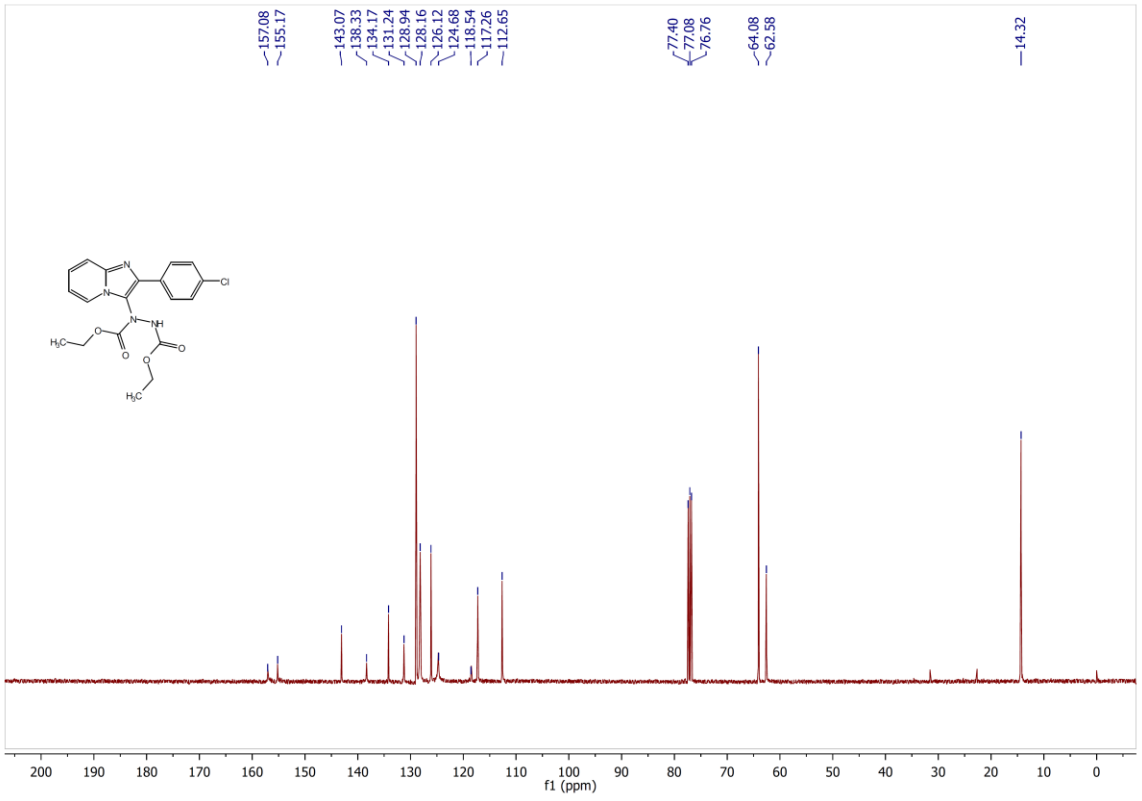
^{13}C-NMR of 3q



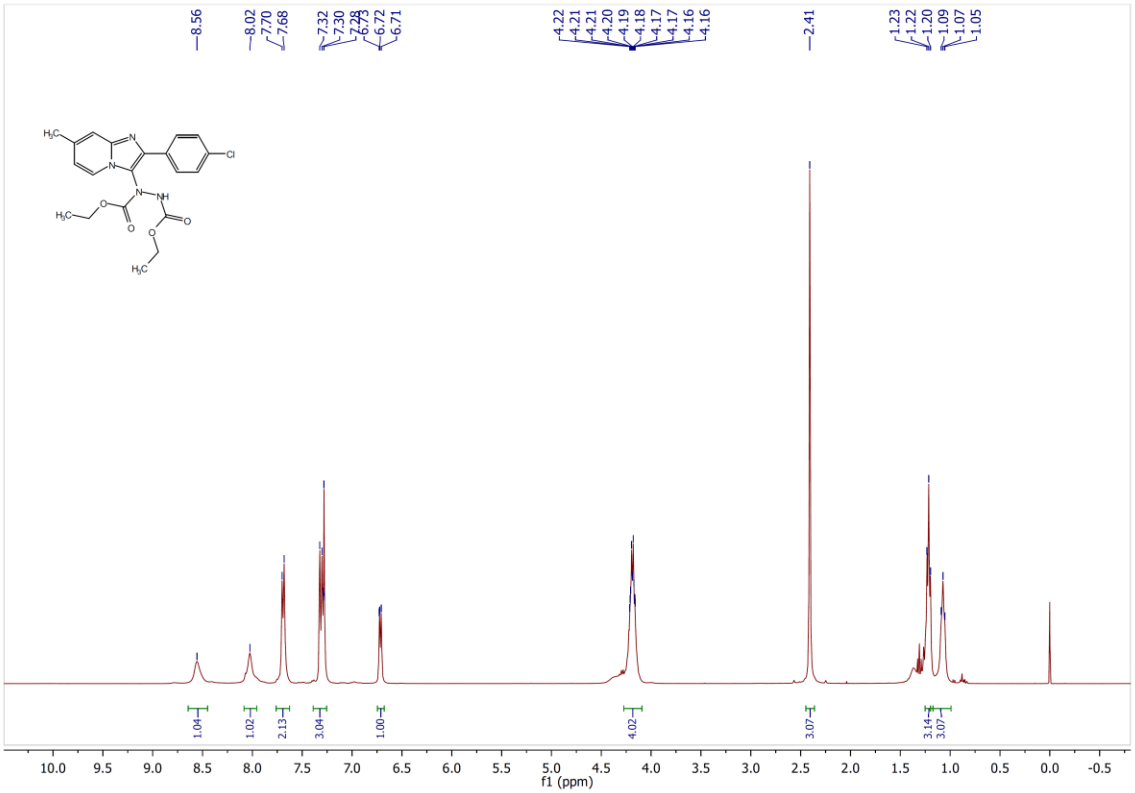
^{1}H-NMR of 3r



^{13}C-NMR of 3r



^{1}H-NMR of 3s



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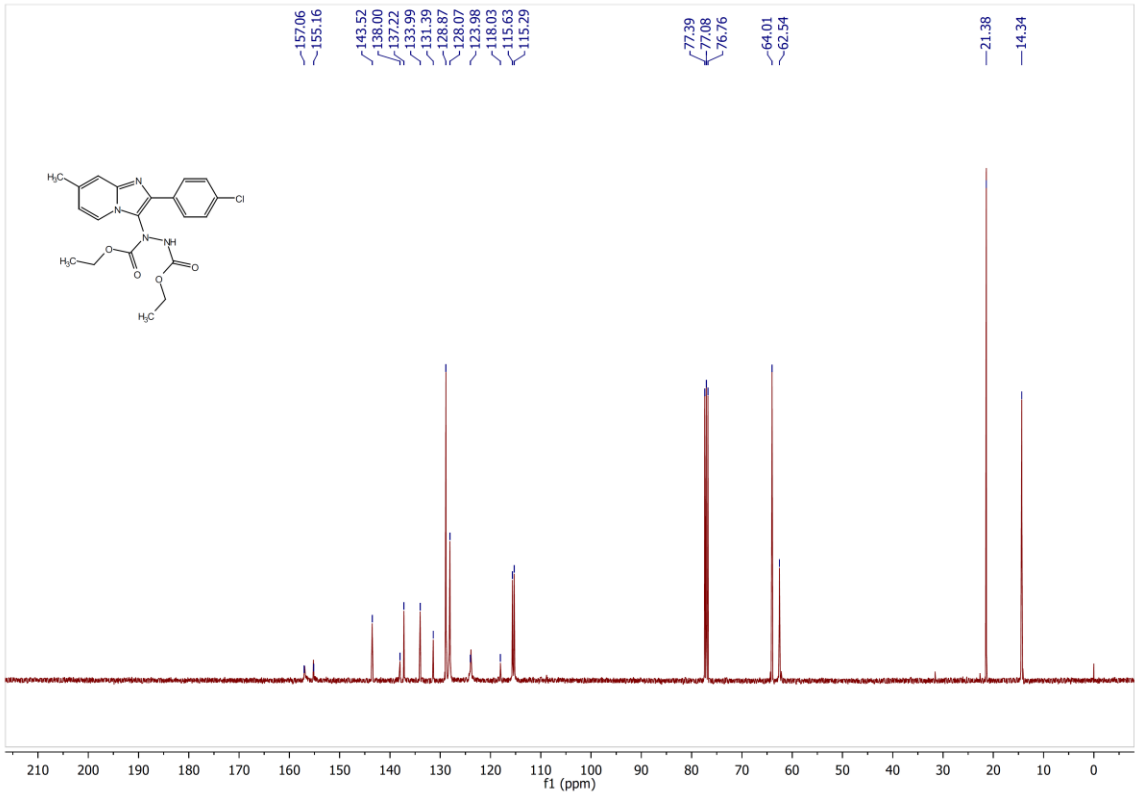
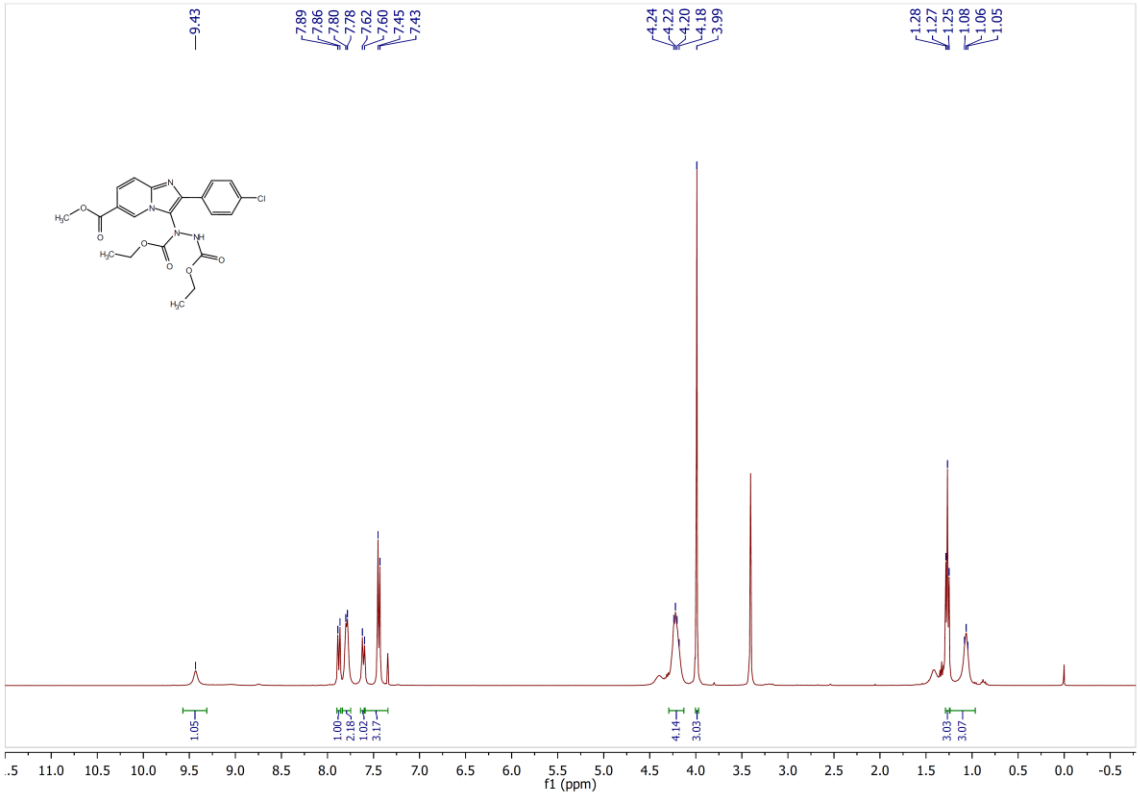


^{1}H-NMR of 3t



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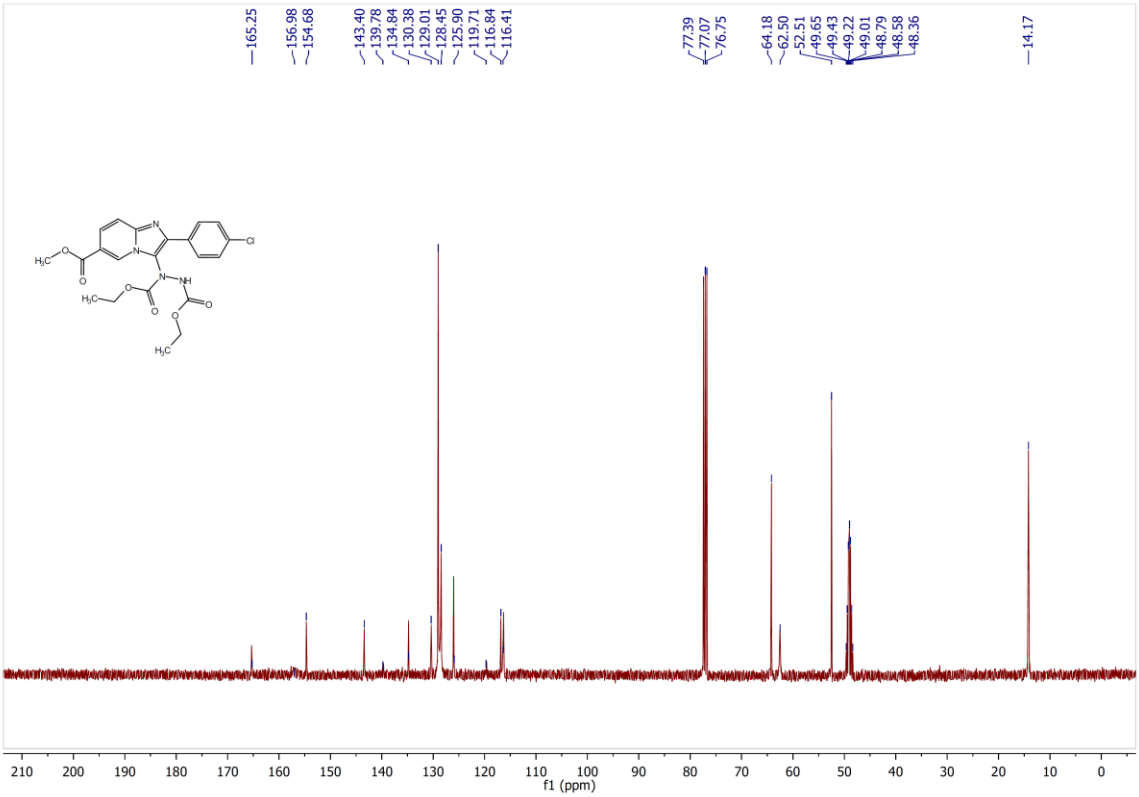
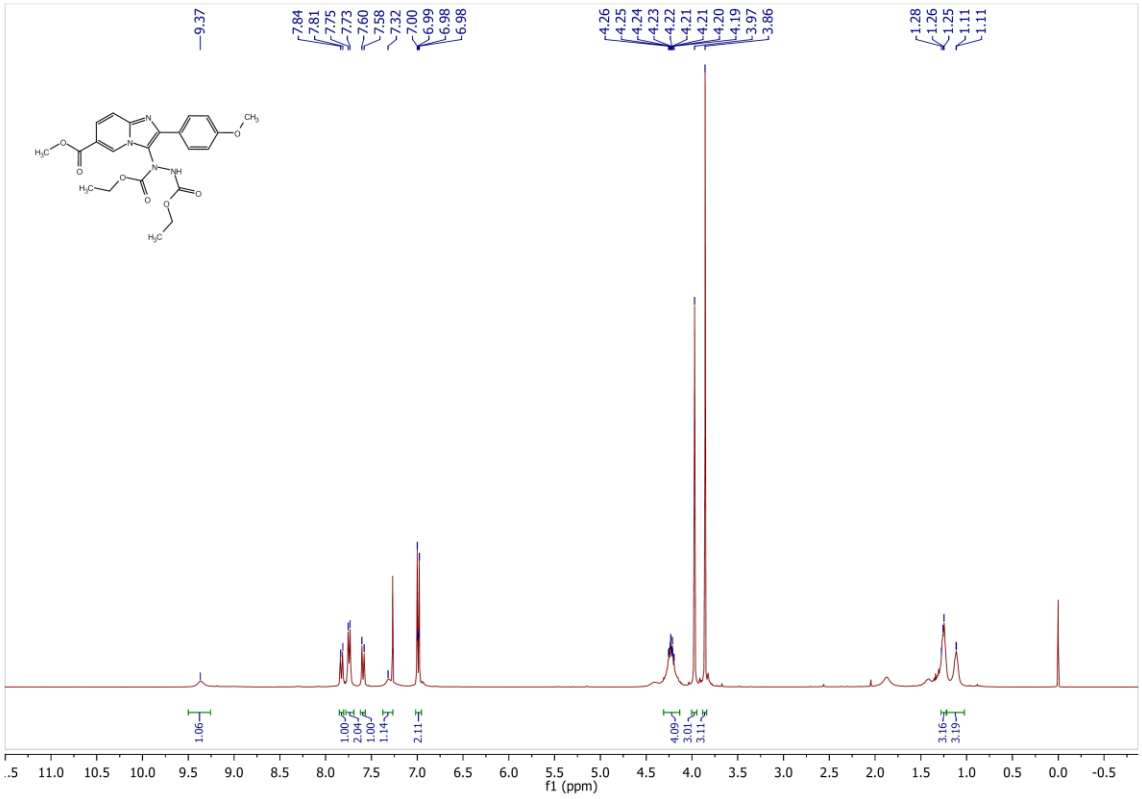
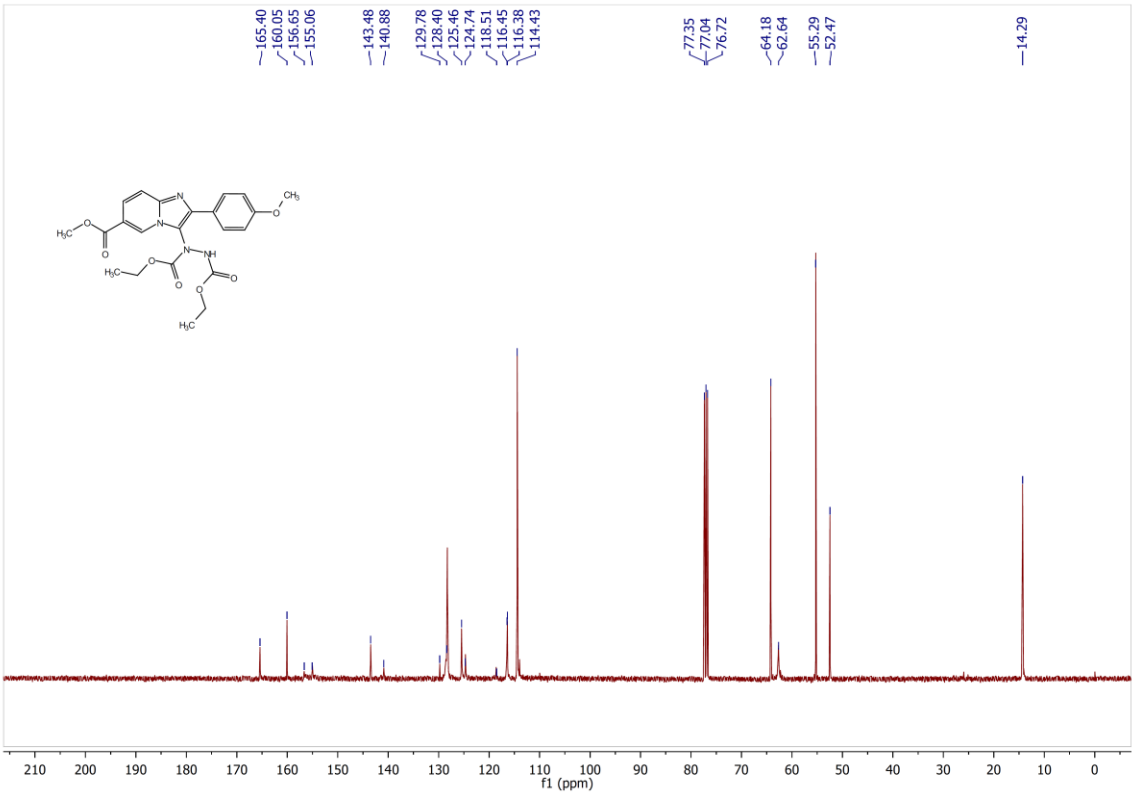


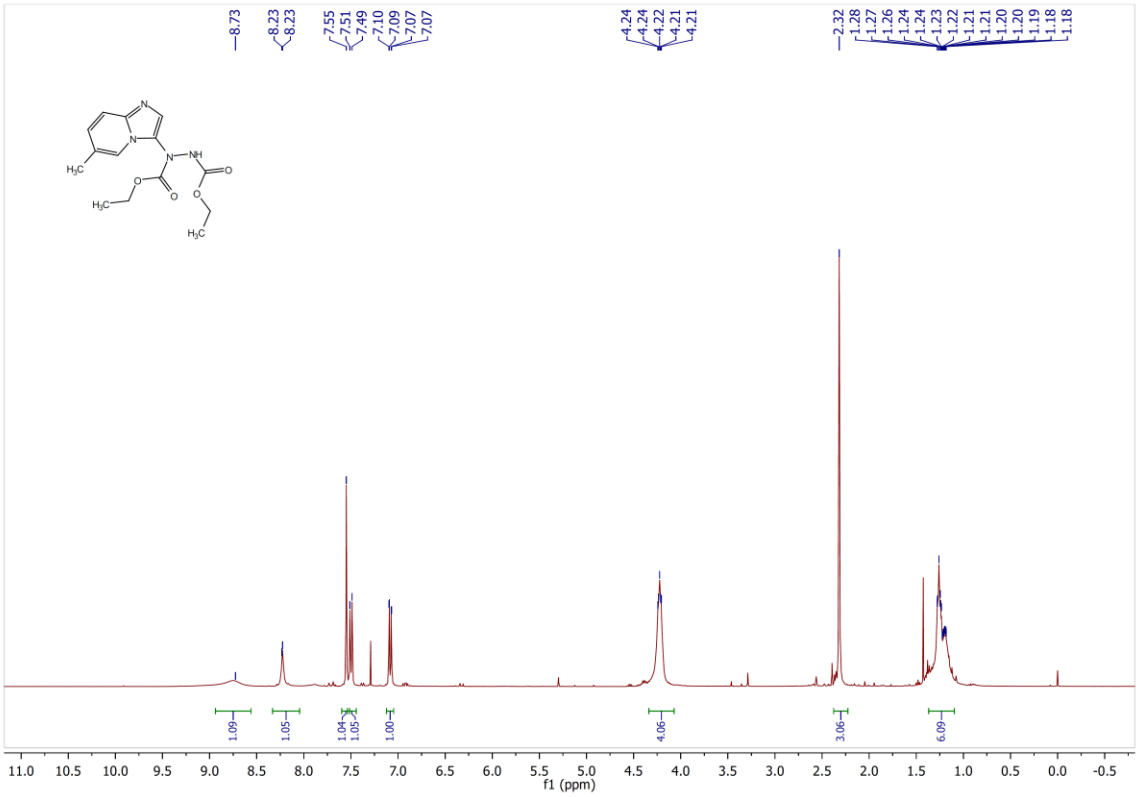
^{1}H-NMR of 3u



^{13}C-NMR of 3u



^{1}H-NMR of 6



^{13}C-NMR of 6