Electronic Supplementary Material (ESI) for RSC Advances.

Regioselective C(sp^2)-H Halogenation of Pyrazolo[1,5-*a*]pyrimidines Facilitated by Hypervalent Iodine(III) under Aqueous and Ambient Conditions

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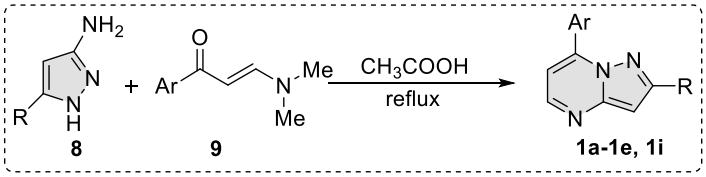
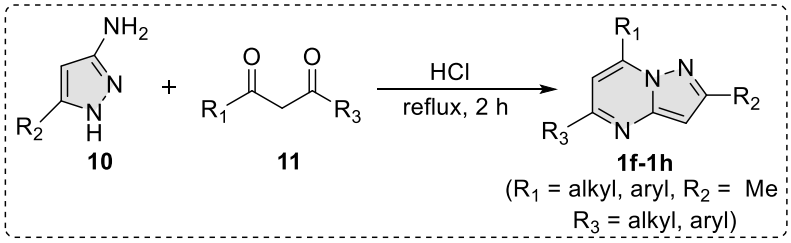
General Information

Commercial reagents, obtained from Spectrochem, Sigma-Aldrich, and TCI, were utilized without further purification. Organic solutions were concentrated under reduced pressure using a Heidolph rotary evaporator. All the reactions were carried out in borosilicate glass test tubes outfitted with glass stoppers. Thin layer chromatography was performed on pre-coated aluminum sheets with Merck silica gel $60F_{254}$, visualized under UV light (254 nm). Products isolation was carried out via silica gel column chromatography on silica gel possessing a mesh size of 60-120. Nuclear magnetic spectroscopic analyses, encompassing both ^{1}H and ^{13}C NMR, were conducted utilizing a Fourier transform nuclear magnetic resonance spectrometer, specifically the Bruker Avance 500 MHz model. $CDCl_3$ served as the solvent for spectroscopic acquisition, and the chemical shifts were indicated in δ values (parts per million), referenced relative to tetramethylsilane. High-resolution mass spectral analyses (HRMS) were performed utilizing Electrospray Ionization Time-of-Flight Mass Spectrometry (ESI-TOF-MS). Melting points were ascertained utilizing an electrothermal melting point apparatus, and the values reported remain uncorrected.

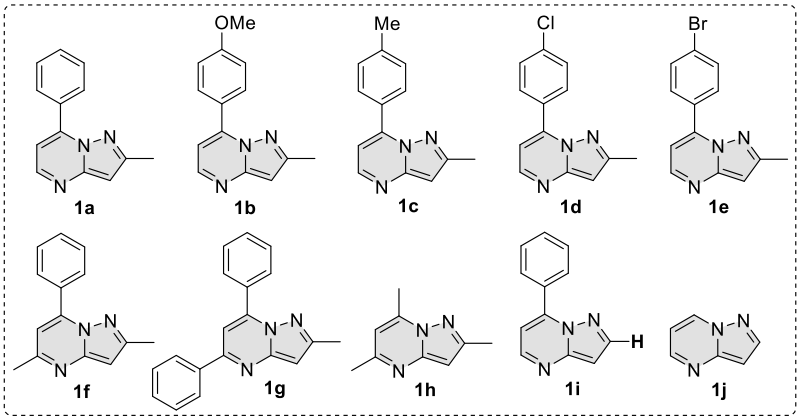
Preparation of starting materials



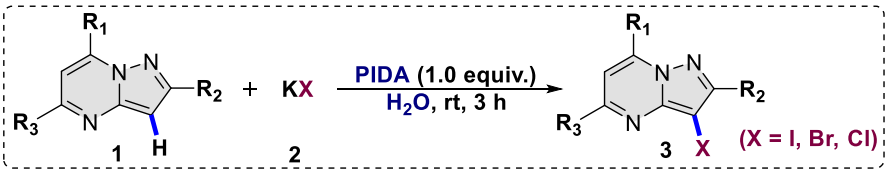
General procedure for the synthesis of substituted pyrazolo[1,5-*a*]pyrimidines:[1] A mixture of Substituted amino pyrazoles **8** (1.0 mmol, 1.0 equiv.) and enones **9** (1.0 mmol, 1.0 equiv.) was refluxed in acetic acid (1.0 mL) within an oven-dried round-bottom flask. The reaction was conducted using an oil bath with rigorous stirring. Progress of the reaction was checked by TLC analysis. Upon completion, the mixture underwent extraction with dichloromethane (DCM) and water. The organic layer was concentrated to obtain crude pyrazolo[1,5-*a*]pyrimidine derivatives **1a-1e**, **1i**. Purification was conducted through column chromatography utilizing 60-120 mesh silica gel, employing a gradient elution of ethyl acetate-hexane (1:9 to 1:4). Product confirmation was done with the aid of ^{1}H and ^{13}C NMR spectroscopic analysis.



General procedure for the synthesis of trisubstituted pyrazolo[1,5-*a*]pyrimidines:[2] Into an oven-dried round-bottom flask substituted amino pyrazoles **10** (1.0 mmol, 1.0 equiv.) and diketones **11** (1.0 mmol, 1.0 equiv.) were added along with 1.0 mL of hydrochloric acid (HCl). Reaction mixture was refluxed with intense stirring in an oil bath for duration of 2 hours. The reaction advancement was checked by TLC. After completion of the reaction, extraction was carried out using DCM and water. Organic layer was evaporated to get the crude pyrazolo[1,5-*a*]pyrimidine derivatives **1f-1h.** The crude products exhibited sufficient purity to proceed with subsequent halogenation reactions. Confirmation of the product's identity was established through ^{1}H and ^{13}C NMR spectroscopic analysis. Substrate **1j** was procured from commercial source.

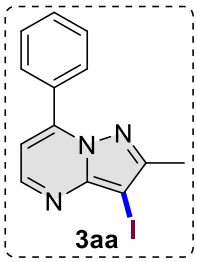


General procedure for the PIDA mediated halogenation of substituted pyrazolo[1,5-*a*]pyrimidines:

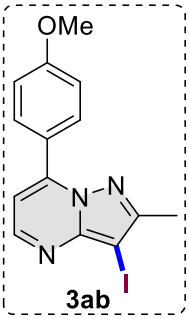


A mixture of various substituted pyrazolo[1,5-*a*]pyrimidines (1.0 equiv., 0.2 mmol), potassium halide salts (1.5 equiv., 0.3 mmol) and PIDA (1.0 equiv., 0.2 mmol) was added to a 25 mL screw capped test tube along with water (3.0 mL). Reaction was stirred for 3 hours at room temperature. Upon completion of the reaction (monitored by TLC), reaction mixture was diluted with brine solution (20 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by column chromatographic separation using silica gel (60-120 mesh size) and 2-8% ethyl acetate in hexane as the eluent to offer the desired products (**3aa-3cj**).

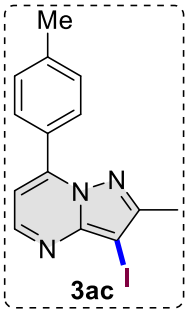
Characterisation data of compounds (3aa-3ao, 3ba-3bj, 3ca-3cj, 5, 7)



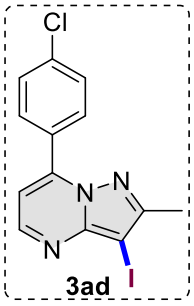
3-Iodo-2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine(3aa): Yellow solid; 87% (58.4 mg); m.p. 88-90 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 8.04-7.99 (m, 2H), 7.58-7.53 (m, 3H), 6.87 (d, *J* = 4.3 Hz, 1H), 2.53 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.6, 150.1, 149.7, 147.1, 131.4, 130.5, 129.4, 128.9, 107.8, 53.0, 15.4; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{11}IN_3$ $[M+H]^+$: 335.9992, found 335.9995.



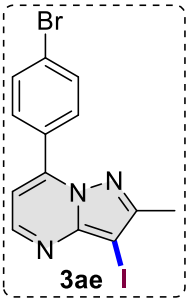
3-Iodo-7-(4-methoxyphenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine(3ab): Yellow solid; 90% (65.7 mg); m.p. 96-98 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 4.4 Hz, 1H), 3.90 (s, 3H), 2.53 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.1, 156.4, 150.0, 149.8, 146.8, 131.2, 122.7, 114.3, 106.9, 55.6, 52.7, 15.4; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}IN_3O$ $[M+H]^+$: 366.0098, found 366.0101.



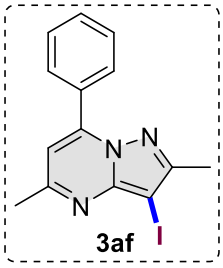
3-Iodo-2-methyl-7-(p-tolyl)pyrazolo[1,5-*a*]pyrimidine(3ac): Off white solid; 95% (66.5 mg); m.p. 94-96 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 4.4 Hz, 1H), 2.53 (s, 3H), 2.45 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.5, 150.0, 149.7, 147.2, 142.0, 129.6, 129.3, 127.6, 107.4, 52.8, 21.7, 15.4; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}IN_3$ $[M+H]^+$: 350.0149, found 350.0149.



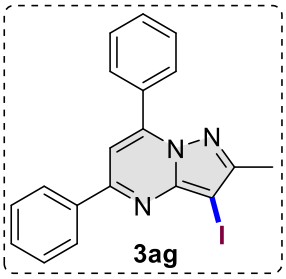
7-(4-Chlorophenyl)-3-iodo-2-methylpyrazolo[1,5-*a*]pyrimidine(3ad): Yellow solid; 85% (62.7 mg); m.p. 122-124 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 4.4 Hz, 1H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.8, 150.0, 149.7, 145.8, 137.7, 130.8, 129.2, 128.8, 107.6, 53.3, 15.3; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}ClIN_3$ $[M+H]^+$: 369.9602, found 369.9598.



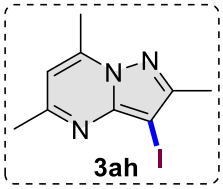
7-(4-Bromophenyl)-3-iodo-2-methylpyrazolo[1,5-*a*]pyrimidine(3ae): Yellow solid; 83% (68.7 mg); m.p. 172-174 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 4.3 Hz, 1H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.8, 150.0, 149.7, 145.9, 132.2, 130.9, 129.3, 126.1, 107.5, 53.3, 15.3; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}BrIN_3$ $[M+H]^+$: 413.9097, found 413.9079.



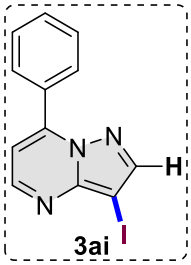
3-Iodo-2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine(3af): Yellow solid; 87% (61.4 mg); m.p. 92-94 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.56-7.51 (m, 3H), 6.73 (s, 1H), 2.67 (s, 3H), 2.49 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.2, 156.3, 149.4, 146.3, 131.2, 130.7, 129.4, 128.8, 108.8, 51.7, 25.0, 15.4; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}IN_3$ $[M+H]^+$: 350.0149, found 350.0153.



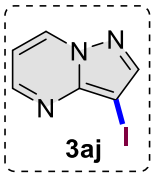
3-Iodo-2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine(3ag): Yellow solid; 91% (74.9 mg); m.p. 112-114 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 6.1 Hz, 2H), 8.05 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 3H), 7.32 (s, 1H), 2.54 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.9, 149.6, 147.0, 137.2, 131.3, 131.0, 130.6, 129.4, 129.0, 128.9, 127.5, 105.4, 53.4, 15.5; **HRMS** (ESI, *m/z*): Calculated for $C_{19}H_{15}IN_3$ $[M+H]^+$: 412.0305, found 412.0307.



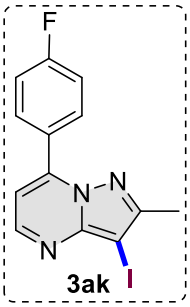
3-Iodo-2,5,7-trimethylpyrazolo[1,5-*a*]pyrimidine(3ah): Off white solid; 86% (49.4 mg); m.p. 102-104 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 (s, 1H), 2.69 (s, 3H), 2.59 (s, 3H), 2.50 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.9, 155.9, 148.6, 145.4, 108.9, 51.3, 24.9, 16.7, 15.2; **HRMS** (ESI, *m/z*): Calculated for $C_9H_{11}IN_3$ $[M+H]^+$: 287.9992, found 287.9990.



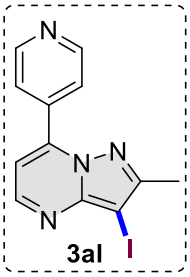
3-Iodo-7-phenylpyrazolo[1,5-*a*]pyrimidine(3ai): Yellow solid; 89% (56.9 mg); m.p. 136-138 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.3 Hz, 1H), 8.19 (s, 1H), 8.05 – 7.92 (m, 2H), 7.58 (d, *J* = 5.3 Hz, 3H), 6.95 (d, *J* = 4.3 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 150.5, 149.1, 148.9, 147.7, 131.6, 130.4, 129.4, 128.9, 108.2, 50.1; **HRMS** (ESI, *m/z*): Calculated for $C_{12}H_8IN_3Na$ $[M+Na]^+$: 343.9655, found 343.9655.



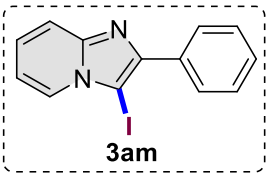
3-Iodopyrazolo[1,5-*a*]pyrimidine(3aj): White solid; 79% (37.4 mg); m.p. 104-106 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.9 Hz, 1H), 8.60 – 8.48 (m, 1H), 8.15 (s, 1H), 6.87 (dd, *J* = 7.0, 4.0 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 150.6, 149.4, 148.1, 135.9, 108.7, 49.7; **HRMS** (ESI, *m/z*): Calculated for $C_6H_5IN_3$ $[M+H]^+$: 245.9523, found 245.9508.



7-(4-Fluorophenyl)-3-iodo-2-methylpyrazolo[1,5-*a*]pyrimidine(3ak): Yellow solid; 84% (59.5 mg); m.p. 78-80 °C;**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.3 Hz, 1H), 8.11 – 8.02 (m, 2H), 7.27 – 7.22 (m, 2H), 6.84 (d, *J* = 4.4 Hz, 1H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.5, 163.5, 156.7, 150.0, 149.7, 146.0, 131.8, 131.7, 126.5, 116.2, 116.0, 107.5, 53.2, 15.4; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}FIN_3$ $[M+H]^+$: 353.9898, found 353.9895.

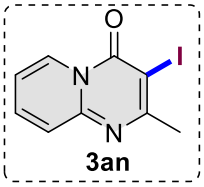


3-Iodo-2-methyl-7-(pyridin-4-yl)pyrazolo[1,5-*a*]pyrimidine(3al): Yellow solid; 92% (62.0 mg); m.p. 174-176 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 6.1 Hz, 2H), 8.57 (d, *J* = 4.3 Hz, 1H), 7.93 (d, *J* = 6.3 Hz, 2H), 6.93 (d, *J* = 4.4 Hz, 1H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 157.1, 150.6, 149.9, 149.6, 144.1, 137.9, 123.1, 107.9, 53.9, 15.3; **HRMS** (ESI, *m/z*): Calculated for $C_{12}H_{10}IN_4$ $[M+H]^+$: 336.9945, found 336.9952.



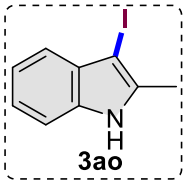
3-Iodo-2-phenylimidazo[1,2-*a*]pyridine: Off white solid; 86% (55.1 mg); m.p. 158-160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 6.9 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.94 (t, *J* = 6.9 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 148.2, 148.1, 133.6, 128.7, 128.5,

128.4, 126.7, 125.8, 117.7, 113.4, 59.7; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}IN_2$ $[M+H]^+$: 320.9883, found 320.9885.



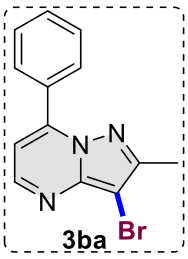
3an

3-Iodo-2-methyl-4H-pyrido[1,2-*a*]pyrimidin-4-one: Brown solid; 72% (41.1 mg); m.p. 160-162 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.03 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.83 – 7.72 (m, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.16 (t, *J* = 6.9 Hz, 1H), 2.75 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.3, 155.7, 149.6, 136.7, 128.0, 125.6, 116.2, 30.3; **HRMS** (ESI, *m/z*): Calculated for $C_9H_7IN_2ONa$ $[M+Na]^+$: 308.9495, found 308.9498.



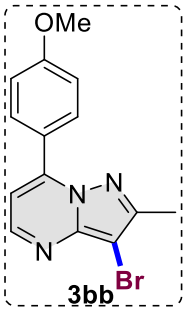
3ao

3-Iodo-2-methyl-1*H*-indole: Brown gummy mass; 78% (40.1 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.41 – 7.35 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 (dd, *J* = 6.6, 2.9 Hz, 2H), 2.46 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 136.5, 136.0, 131.0, 122.5, 120.7, 120.4, 110.7, 59.2, 14.6; **HRMS** (ESI, *m/z*): Calculated for C_9H_9IN $[M+H]^+$: 257.9774, found 257.9792.

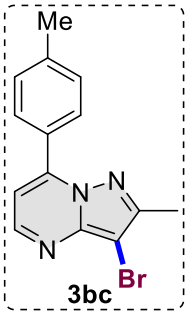


3ba

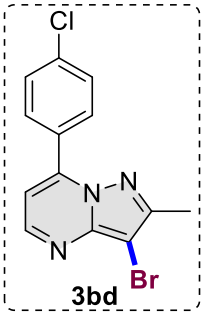
3-Bromo-2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine(3ba): Yellow solid; 88% (50.6 mg); m.p. 130-132 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.58-7.53 (m, 3H), 6.87 (d, *J* = 4.3 Hz, 1H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 153.4, 149.8, 147.0, 146.9, 131.5, 130.5, 129.4, 128.9, 107.6, 85.2, 13.6; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{11}BrN_3$ $[M+H]^+$: 288.0131, found 288.0129.



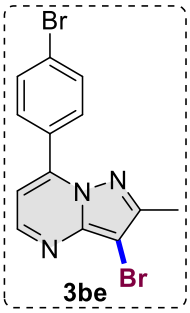
3-Bromo-7-(4-methoxyphenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine(3bb): Yellow solid; 91% (57.6 mg); m.p. 98-100 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.4 Hz, 1H), 8.06 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 4.4 Hz, 1H), 3.89 (s, 3H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.1, 153.2, 149.7, 147.1, 146.6, 131.2, 122.6, 114.3, 106.8, 84.9, 55.6, 13.6; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}BrN_3O$ $[M+H]^+$: 318.0237, found 318.0225.



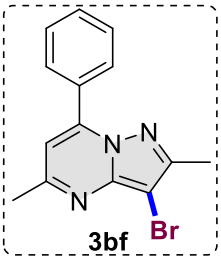
3-Bromo-2-methyl-7-(p-tolyl)pyrazolo[1,5-*a*]pyrimidine(3bc): Yellow solid; 92% (55.6 mg); m.p. 118-120 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 4.3 Hz, 1H), 2.51 (s, 3H), 2.45 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 153.3, 149.7, 147.0, 142.0, 129.5, 129.3, 127.5, 107.2, 85.0, 21.7, 13.6; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}BrN_3$ $[M+H]^+$: 302.0287, found 302.0282.



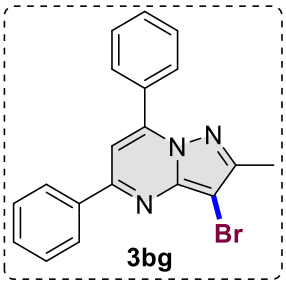
3-Bromo-7-(4-chlorophenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine(3bd): Pale yellow solid; 86% (55.0 mg); m.p. 164-166 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.0 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 5.0 Hz, 1H), 2.51 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 153.6, 149.7, 147.0, 145.7, 137.7, 130.8, 129.2, 128.8, 107.4, 85.5, 13.6; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}ClBrN_3$ $[M+H]^+$: 321.9741, found 321.9743.



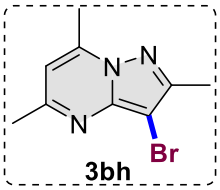
3-bromo-7-(4-bromophenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine(3be): Yellow solid; 87% (62.9 mg); m.p. 174-176 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 4.3 Hz, 1H), 2.51 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 153.6, 149.7, 147.0, 145.7, 132.2, 130.9, 129.3, 126.1, 107.4, 85.5, 13.6; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}Br_2N_3$ $[M+H]^+$: 365.9236, found 365.9242.



3-Bromo-2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine(3bf): Yellow solid, 88% (53.2 mg); m.p. 80-82 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 – 7.88 (m, 2H), 7.57-7.51 (m, 3H), 6.73 (s, 1H), 2.67 (s, 3H), 2.48 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.9, 153.0, 146.6, 146.0, 131.2, 130.5, 129.3, 128.7, 108.6, 83.8, 24.9, 13.5; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}BrN_3$ $[M+H]^+$: 302.0287, found 302.0272.

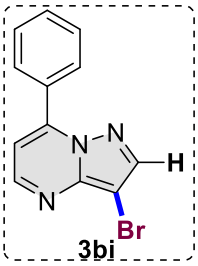


3-Bromo-2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine(3bg): Yellow solid; 87% (63.3 mg); m.p. 124-126 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.5 Hz, 2H), 8.06 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.51 (d, *J* = 7.6 Hz, 3H), 7.31 (s, 1H), 2.53 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.7, 153.7, 146.9, 146.8, 137.3, 131.3, 131.0, 130.6, 129.5, 129.0, 128.9, 127.5, 105.3, 85.4, 13.7; **HRMS** (ESI, *m/z*): Calculated for $C_{19}H_{15}BrN_3$ $[M+H]^+$: 364.0444, found 364.0435.



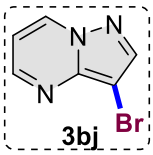
3bh

3-Bromo-2,5,7-trimethylpyrazolo[1,5-*a*]pyrimidine(3bh): Off white solid; 90% (43.2 mg); m.p. 100-102 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 (s, 1H), 2.68 (s, 3H), 2.58 (s, 3H), 2.48 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 152.8, 145.8, 145.3, 108.7, 83.6, 24.9, 16.7, 13.4; **HRMS** (ESI, *m/z*): Calculated for $C_9H_{10}BrN_3Na$ $[M+Na]^+$: 261.9950, found 261.9944.



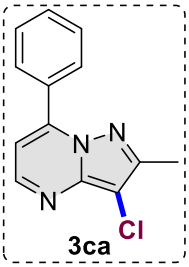
3bi

3-Bromo-7-phenylpyrazolo[1,5-*a*]pyrimidine(3bi): Yellow solid; 88% (48.4 mg); m.p. 158-160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.3 Hz, 1H), 8.16 (s, 1H), 8.07 – 7.84 (m, 2H), 7.57 (d, *J* = 5.3 Hz, 3H), 6.95 (d, *J* = 4.3 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 150.2, 147.5, 146.5, 144.6, 131.6, 130.3, 129.4, 128.9, 108.2, 84.9; **HRMS** (ESI, *m/z*): Calculated for $C_{12}H_8BrN_3Na$ $[M+Na]^+$: 295.9794, found 295.9805.

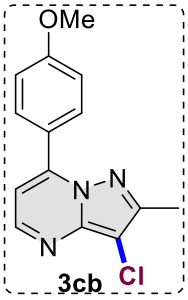


3bj

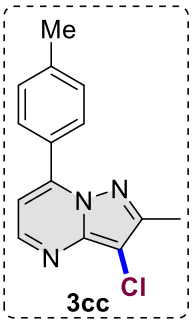
3-Bromopyrazolo[1,5-*a*]pyrimidine(3bj): White solid; 81% (30.7 mg); m.p. 118-120 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 7.0 Hz, 1H), 8.55 (d, *J* = 4.3 Hz, 1H), 8.12 (s, 1H), 6.87 (dd, *J* = 7.1, 4.0 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 150.2, 145.4, 145.1, 135.8, 108.6, 84.6; **HRMS** (ESI, *m/z*): Calculated for $C_6H_4BrN_3Na$ $[M+H]^+$: 219.9481, found 219.9477.



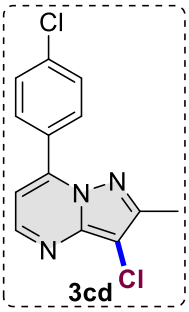
3-Chloro-2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine(3ca): Yellow solid; 86% (41.9 mg); m.p. 126-128 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.04-8.02 (m, 2H), 7.60-7.53 (m, 3H), 6.86 (dd, *J* = 4.4, 1.7 Hz, 1H), 2.51 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 151.9, 149.5, 146.8, 145.5, 131.5, 130.5, 129.4, 128.9, 107.5, 99.3, 12.6; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{11}ClN_3$ $[M+H]^+$: 244.0636, found 244.0636.



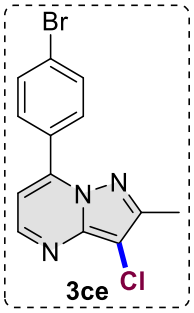
3-Chloro-7-(4-methoxyphenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine(3cb): Pale yellow solid; 89% (48.6 mg); m.p. 114-116 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.4 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 4.4 Hz, 1H), 3.89 (s, 3H), 2.51 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.1, 151.7, 149.4, 146.5, 145.7, 131.2, 122.6, 114.3, 106.6, 99.0, 55.6, 12.6; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}ClN_3O$ $[M+H]^+$: 274.0742, found 274.0742.



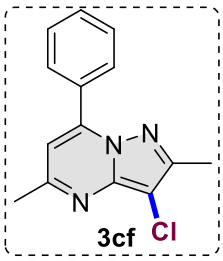
3-Chloro-2-methyl-7-(p-tolyl)pyrazolo[1,5-*a*]pyrimidine(3cc): Off white solid; 86% (44.4 mg); m.p. 160-162 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 4.3 Hz, 1H), 2.51 (s, 3H), 2.45 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 151.7, 149.4, 146.9, 145.6, 142.0, 129.6, 129.3, 127.5, 107.1, 99.1, 21.7, 12.6; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}ClN_3$ $[M+H]^+$: 258.0793, found 258.0790.



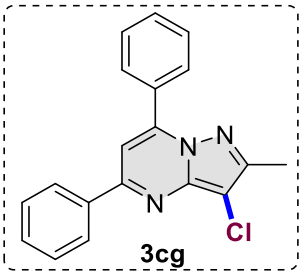
3-Chloro-7-(4-chlorophenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine(3cd): Off white solid; 92% (51.0 mg); m.p. 194-196 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.3 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 4.3 Hz, 1H), 2.51 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.0, 149.4, 145.5, 145.4, 137.7, 130.8, 129.2, 128.8, 107.3, 99.5, 12.5; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}Cl_2N_3$ $[M+H]^+$: 278.0246, found 278.0241.



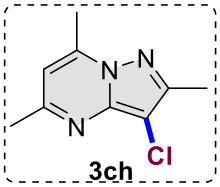
7-(4-bromophenyl)-3-chloro-2-methylpyrazolo[1,5-*a*]pyrimidine(3ce): Yellow solid; 90% (57.8 mg); m.p. 200-202 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 4.3 Hz, 1H), 2.50 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.0, 149.4, 145.6, 145.5, 132.2, 130.9, 129.3, 126.1, 107.2, 99.6, 12.5; **HRMS** (ESI, *m/z*): Calculated for $C_{13}H_{10}BrClN_3$ $[M+H]^+$: 321.9741, found 321.9735.



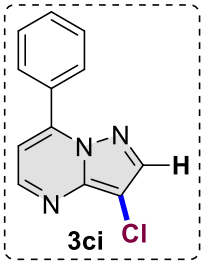
3-Chloro-2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine(3cf): Yellow solid; 88% (45.2 mg); m.p. 86-88 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.58 – 7.50 (m, 3H), 6.72 (s, 1H), 2.66 (s, 3H), 2.48 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 151.6, 146.1, 145.3, 131.3, 130.6, 129.4, 128.8, 108.5, 97.9, 25.0, 12.6; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{13}ClN_3$ $[M+H]^+$: 258.0793, found 258.0806.



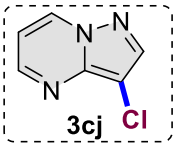
3-Chloro-2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine(3cg): Yellow solid; 88% (56.3 mg); m.p. 116-118 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 6.0 Hz, 2H), 8.06 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.63 – 7.56 (m, 3H), 7.51 (d, *J* = 7.6 Hz, 3H), 7.30 (s, 1H), 2.52 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 156.5, 152.2, 146.7, 145.5, 137.3, 131.3, 131.0, 130.6, 129.4, 129.0, 128.9, 127.5, 105.2, 99.4, 12.7; **HRMS** (ESI, *m/z*): Calculated for $C_{19}H_{15}ClN_3$ $[M+H]^+$: 320.0949, found 320.0942.



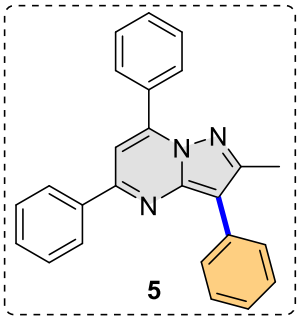
3-Chloro-2,5,7-trimethylpyrazolo[1,5-*a*]pyrimidine(3ch): Off white solid; 87% (33.7 mg); m.p. 98-100 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.50 (s, 1H), 2.67 (s, 3H), 2.57 (s, 3H), 2.48 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.23, 151.3, 145.2, 144.3, 108.6, 97.7, 24.8, 16.6, 12.4; **HRMS** (ESI, *m/z*): Calculated for $C_9H_{10}ClN_3Na$ $[M+Na]^+$: 218.0455, found 218.0437.



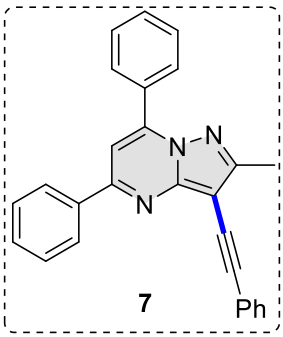
3-Chloro-7-phenylpyrazolo[1,5-*a*]pyrimidine(3ci): Yellow solid; 90% (41.2 mg); m.p. 140-142 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.3 Hz, 1H), 8.14 (s, 1H), 8.00 (dd, *J* = 7.4, 2.4 Hz, 2H), 7.71 – 7.47 (m, 3H), 6.95 (d, *J* = 4.3 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 149.8, 147.5, 145.2, 142.6, 131.6, 130.3, 129.4, 128.9, 108.1, 100.5; **HRMS** (ESI, *m/z*): Calculated for $C_{12}H_8ClN_3Na$ $[M+Na]^+$: 252.0299, found 252.0299.



3-Chloropyrazolo[1,5-*a*]pyrimidine(3cj): White solid; 75% (22.3 mg); m.p. 138-140 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.2 Hz, 1H), 8.53 (d, *J* = 4.4 Hz, 1H), 8.09 (s, 1H), 6.86 (dd, *J* = 7.2, 4.0 Hz, 1H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 149.8, 144.0, 143.1, 135.7, 108.6, 100.3; **HRMS** (ESI, *m/z*): Calculated for $C_6H_5ClN_3$ $[M+H]^+$: 154.0167, found 154.0155.

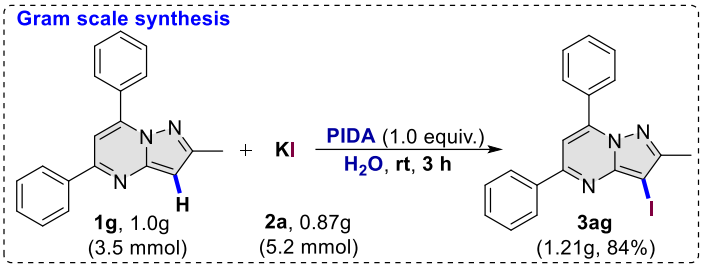


2-Methyl-3,5,7-triphenylpyrazolo[1,5-*a*]pyrimidine(5): Yellow solid; 85% (59.9 mg); mp 72-74 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.0 Hz, 2H), 8.13 (dd, *J* = 4.7, 2.9 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 3.2 Hz, 3H), 7.57 – 7.44 (m, 5H), 7.42 – 7.30 (m, 2H), 2.70 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 155.7, 152.9, 147.3, 146.2, 137.7, 133.0, 131.8, 131.0, 130.3, 129.5, 129.1, 129.0, 128.8, 128.6, 127.4, 126.2, 109.5, 104.8, 14.9; **HRMS** (ESI, *m/z*): Calculated for $C_{25}H_{20}N_3$ $[M+H]^+$: 362.1652, found 362.1643.



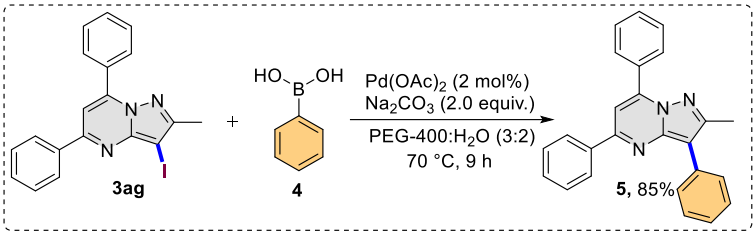
2-Methyl-5,7-diphenyl-3-(phenylethynyl)pyrazolo[1,5-*a*]pyrimidine(7): Orange solid; 73% (56.1 mg); m.p. 142-144 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.3 Hz, 2H), 8.09 (s, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.60 (s, 3H), 7.53 (d, *J* = 7.6 Hz, 3H), 7.40-7.30 (m, 4H), 2.65 (s, 3H); **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 157.8, 156.9, 150.4, 146.9, 137.3, 131.6, 131.3, 131.2, 130.7, 129.5, 129.0, 128.9, 128.4, 127.9, 127.6, 124.3, 105.5, 94.9, 93.6, 80.6, 14.0; **HRMS** (ESI, *m/z*): Calculated for $C_{27}H_{20}N_3$ $[M+H]^+$: 386.1652, found 386.1637.

Experimental procedure for gram scale synthesis of 3-iodo-2-methyl-5,7diphenylpyrazolo[1,5-*a*]pyrimidine (3ag):



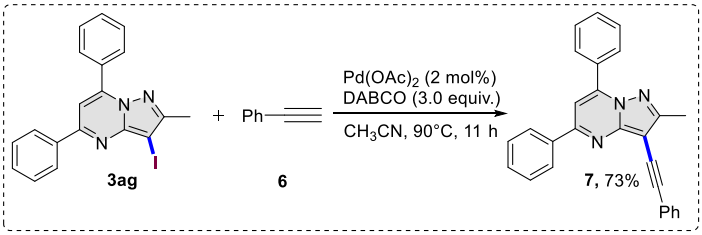
In a 50 mL round-bottom flask equipped with a magnetic stir bar, a mixture of 2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (**1g**) (1.0 g, 3.5 mmol), potassium iodide (**2a**) (0.87 g, 5.2 mmol), and PIDA (1.13 g, 3.5 mmol) was added. To this reaction mixture, 30 mL of water was added, and the reaction was stirred for 3 hours at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with a brine solution (60 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was then subjected to purification through column chromatography using silica gel (60-120 mesh size) and eluted with a gradient of 2-8% ethyl acetate in hexane. This process yielded the desired product, **3ag** in 84% yield (1.21g).

Experimental procedure for arylation of 3-iodo-2-methyl-5,7diphenylpyrazolo[1,5-*a*]pyrimidine (3ag):[3]



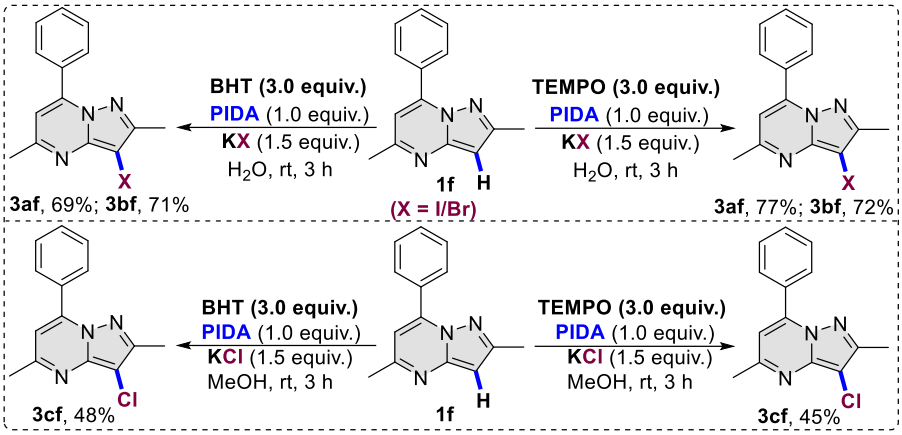
Mixture of $Pd(OAc)_2$ (1 mg, 2 mol %), Na_2CO_3 (42 mg, 2.0 equiv.), PEG-400 (0.6 mL), and water (0.5 mL) was taken in an oven dried seal tube. This mixture was heated at 70 °C for 10 minutes with constant stirring in an oil bath, following this, 3-iodo-2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (**3ag**) (82 mg, 0.2 mmol) and phenylboronic acid (**4**) (36 mg, 0.3 mmol) were introduced in the sealed tube and allowed to react at 70 °C for 9 hours. After confirming completion of the reaction via TLC, the resulting mixture underwent extraction with ethyl acetate; organic layer was dried over anhydrous Na_2SO_4. Subsequent evaporation of ethyl acetate yielded the crude product. The obtained crude product was purified through column chromatography using 100–200 mesh silica gel and eluted with a mixture of ethyl acetate and petroleum ether (1:13) to get arylated product **5** in 85% yield.

Experimental procedure for alkynylation of 3-iodo-2-methyl-5,7diphenylpyrazolo[1,5-*a*]pyrimidine (3ag):[3]



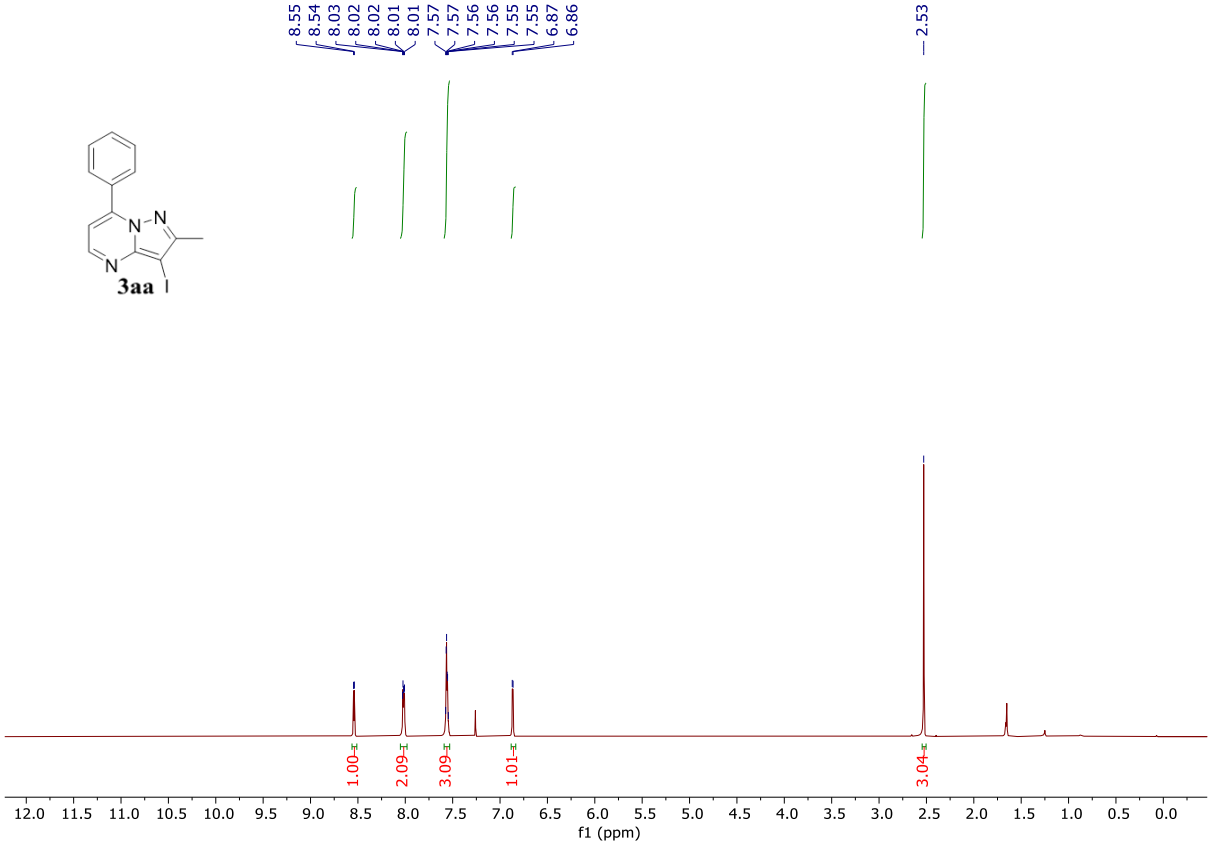
In an oven-dried sealed tube, a mixture of 3-iodo-2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (**3ag**) (82 mg, 0.2 mmol), phenyl acetylene (**6**) (20 µL, 0.2 mmol), $Pd(OAc)_2$ (1 mg, 2 mol %), DABCO (67 mg, 0.6 mmol), and CH_3CN (1 mL) was stirred at 90 °C for 11 hours in an oil bath. Progress of the reaction was checked by TLC analysis. After completion of the reaction, the mixture was extracted with dichloromethane, dried over anhydrous Na_2SO_4, and evaporated to get the crude product. The crude product was purified by column chromatography (100−200 mesh silica gel, eluent: ethyl acetate/petroleum ether 1:10), yielding the alkynylated product 7 in a 73% yield.

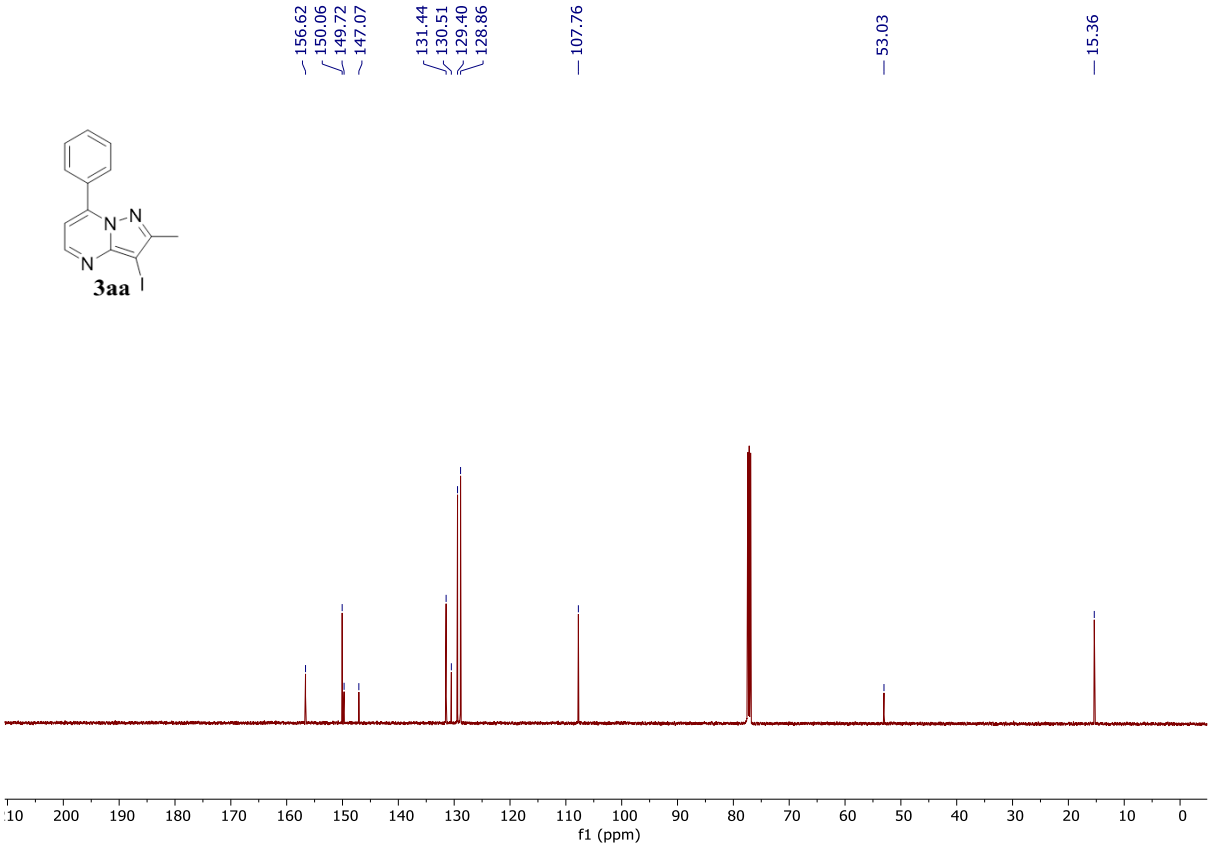
Control experiments

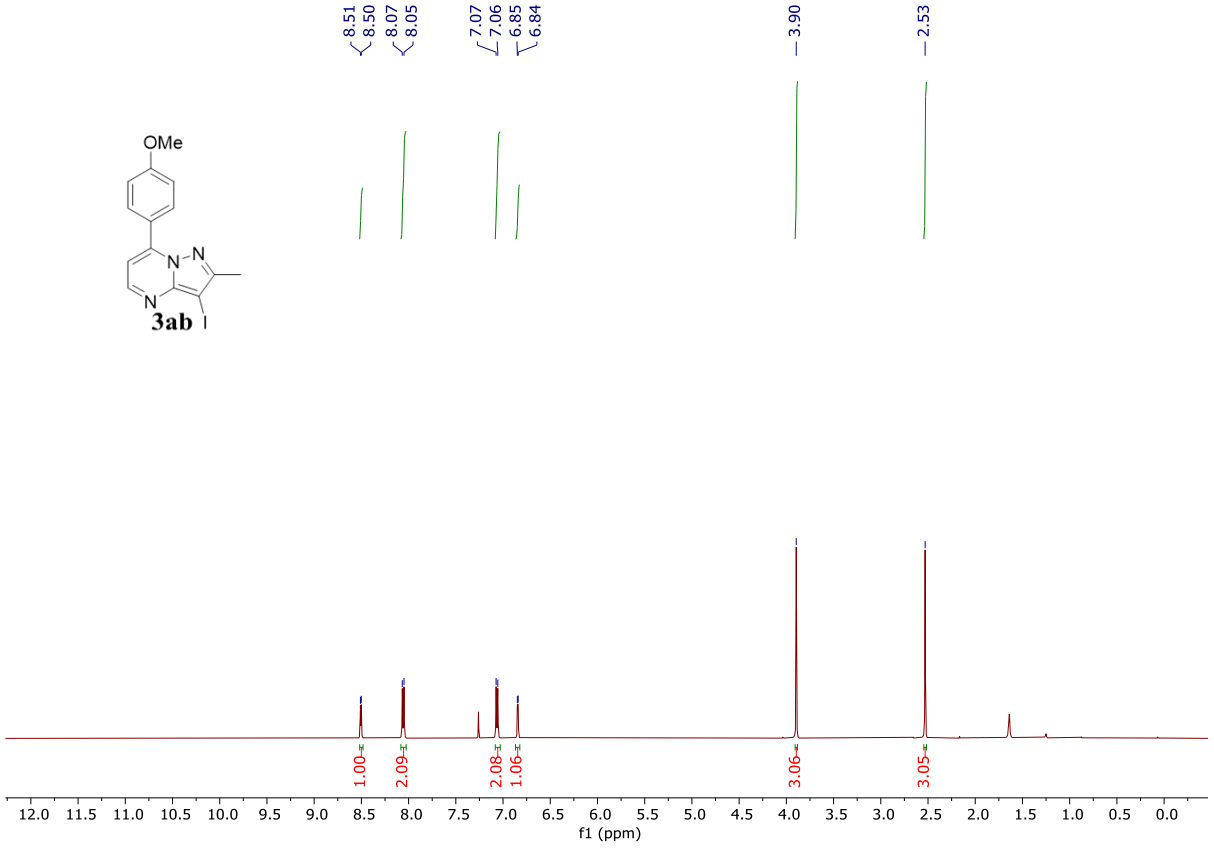


A mixture of 2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine (**1f**) (1.0 equiv., 0.2 mmol), potassium halide salts (1.5 equiv., 0.3 mmol), PIDA (1.0 equiv., 0.2 mmol) and radical scavengers (TEMPO or BHT, 0.6 mmol, 3.0 equiv.) was added to a 25 mL screw capped test tube along with water or methanol (3.0 mL). Reaction was stirred for 3 hours at room temperature. Upon completion of the reaction (monitored by TLC), reaction mixture was diluted with brine solution (20 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then isolated by column chromatographic separation using silica gel (60-120 mesh size) and 2-8% ethyl acetate in hexane as the eluent.

NMR spectra of compounds (3aa-3aj, 3ba-5bj, 3ca-3cj, 5, 7)



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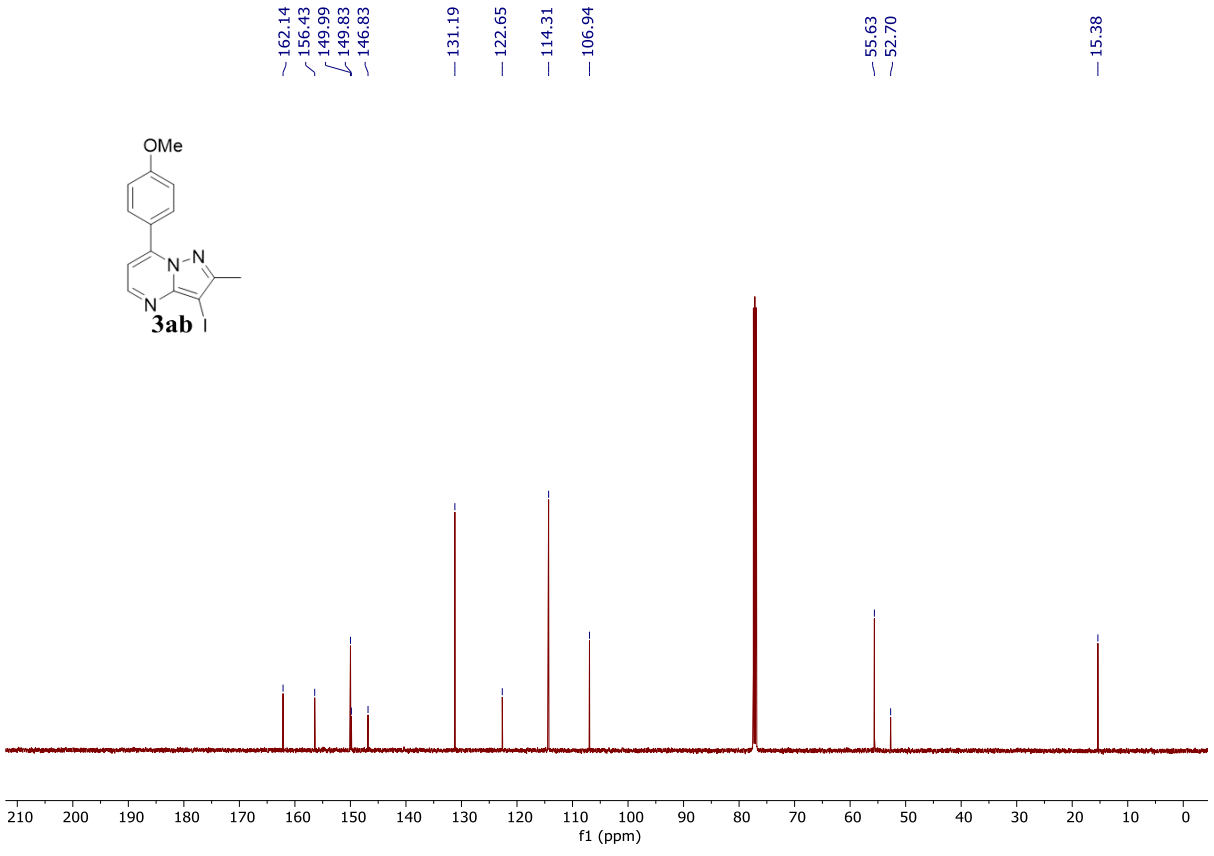
8.50
8.07
8.05
7.07
7.06
6.85
6.84
3.90
2.53
OMe
N
N
N
3ab
I
1.00
2.09
2.08
1.06
3.06
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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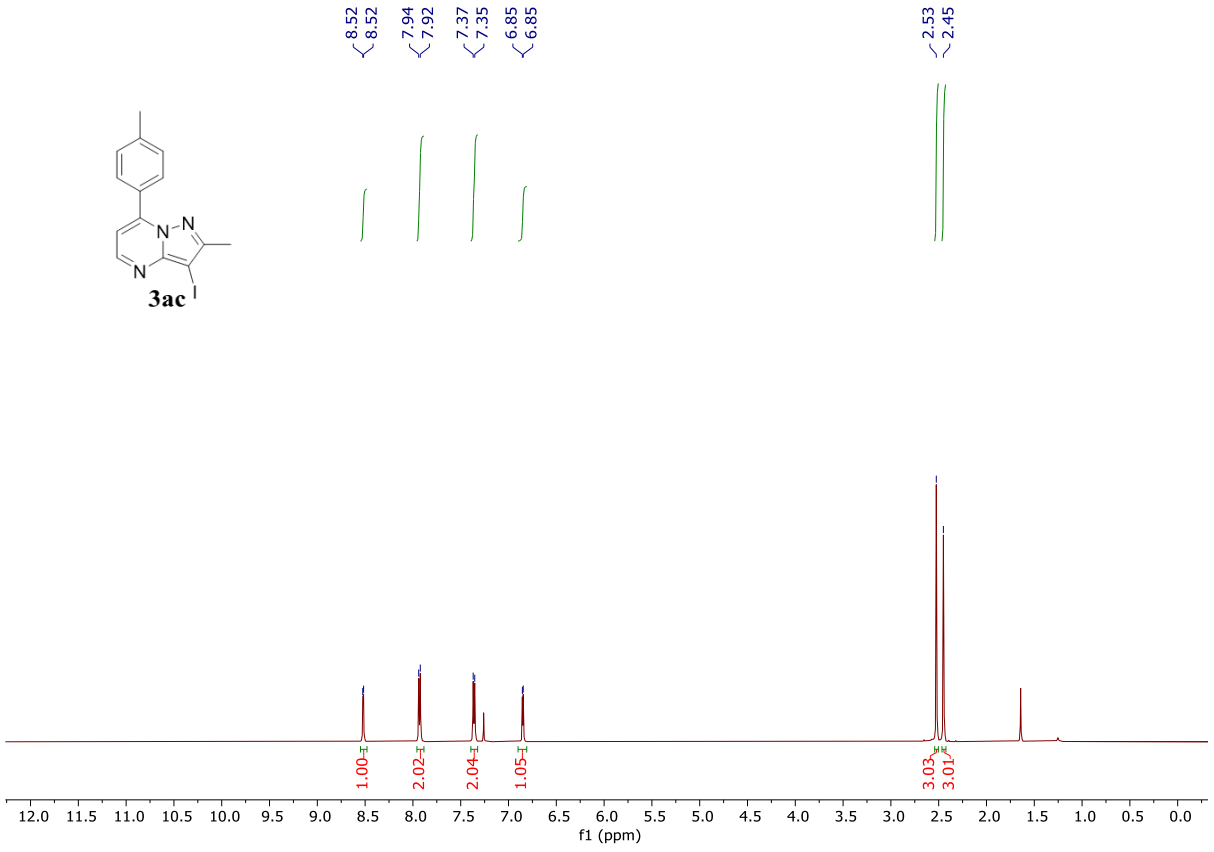
156.43
149.99
149.83
146.83
131.19
122.65
114.31
106.94
55.63
52.70
15.38
OMe
N
N
N
3ab
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.92
7.37
7.35
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6.85
2.53
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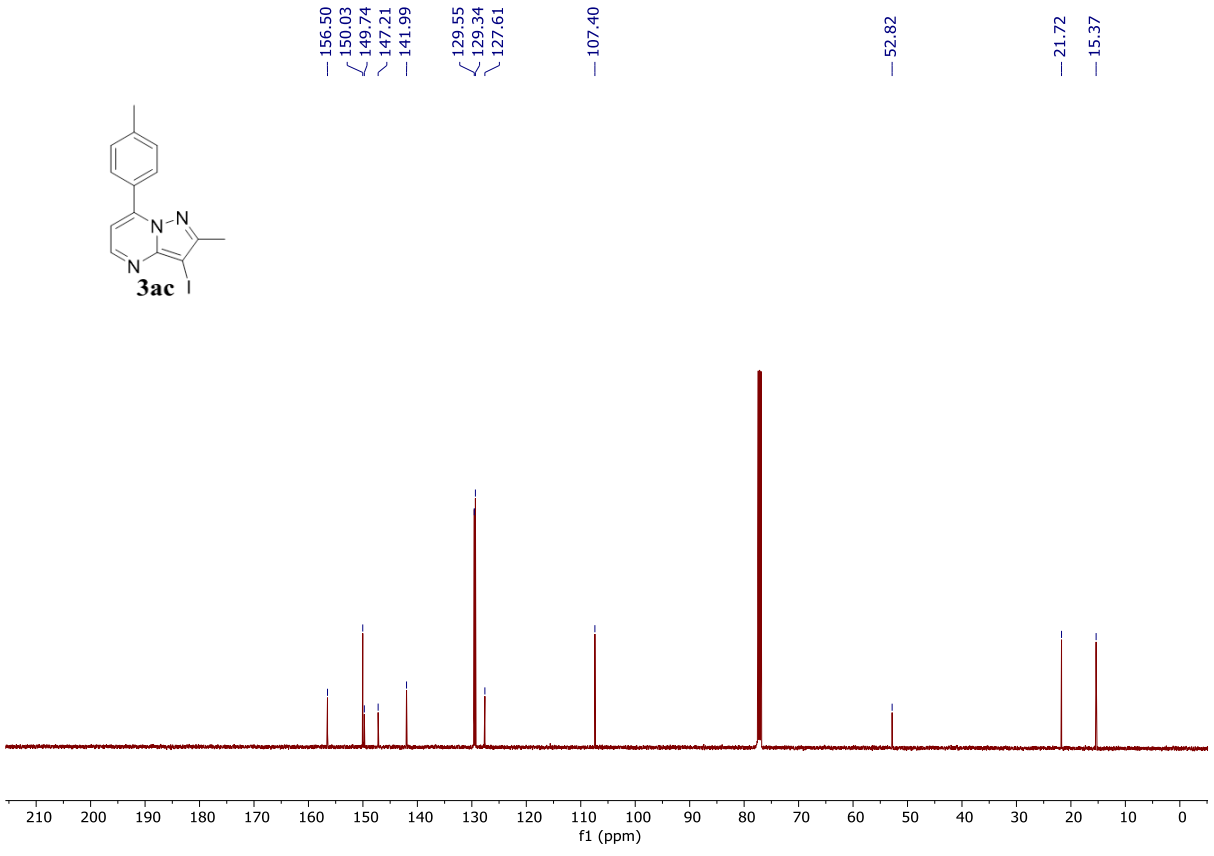
2.04
1.05
3.03
3.01
f1 (ppm)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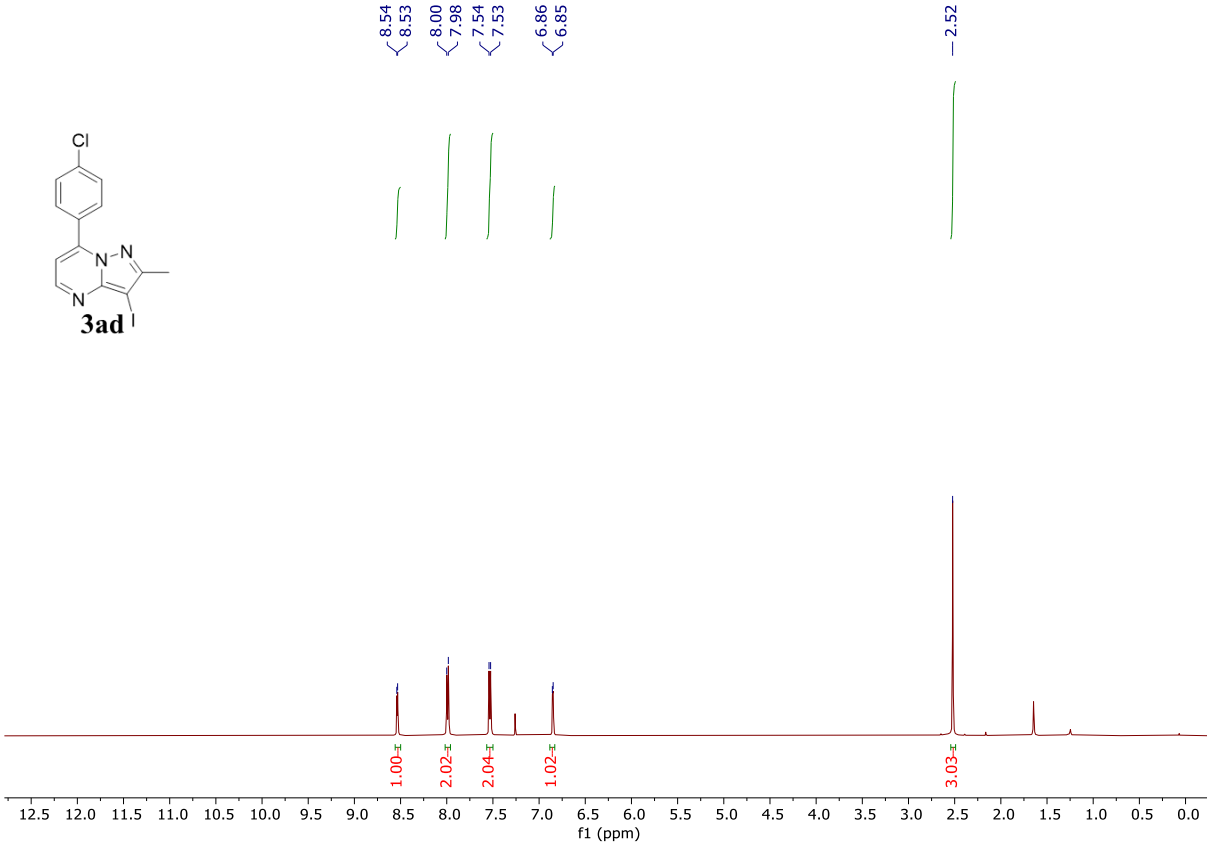
141.99
129.55
129.34
127.61
107.40
52.82
21.72
15.37
3ac
f1 (ppm)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8.00
7.98
7.54
7.53
6.86
6.85
2.52
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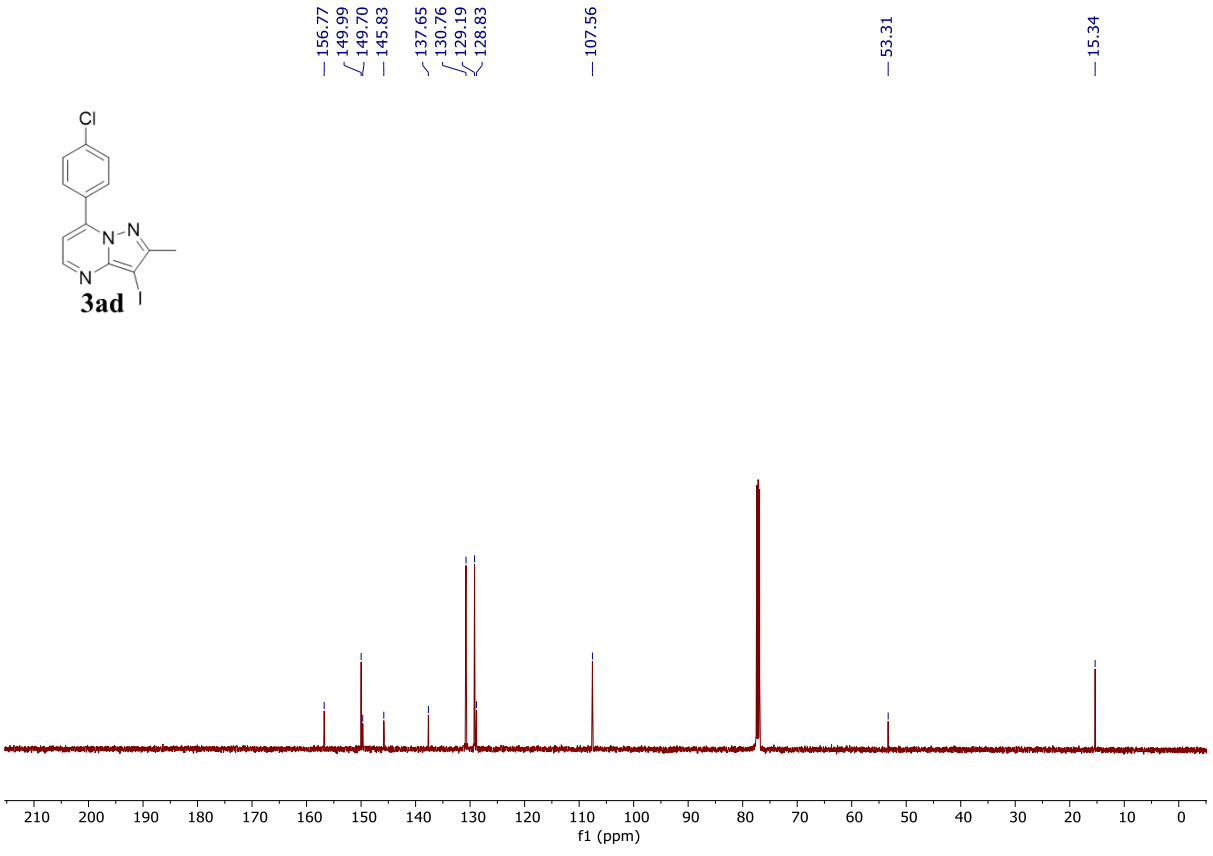
N
N
I
3ad
1.00
2.02
2.04
1.02
3.03
f1 (ppm)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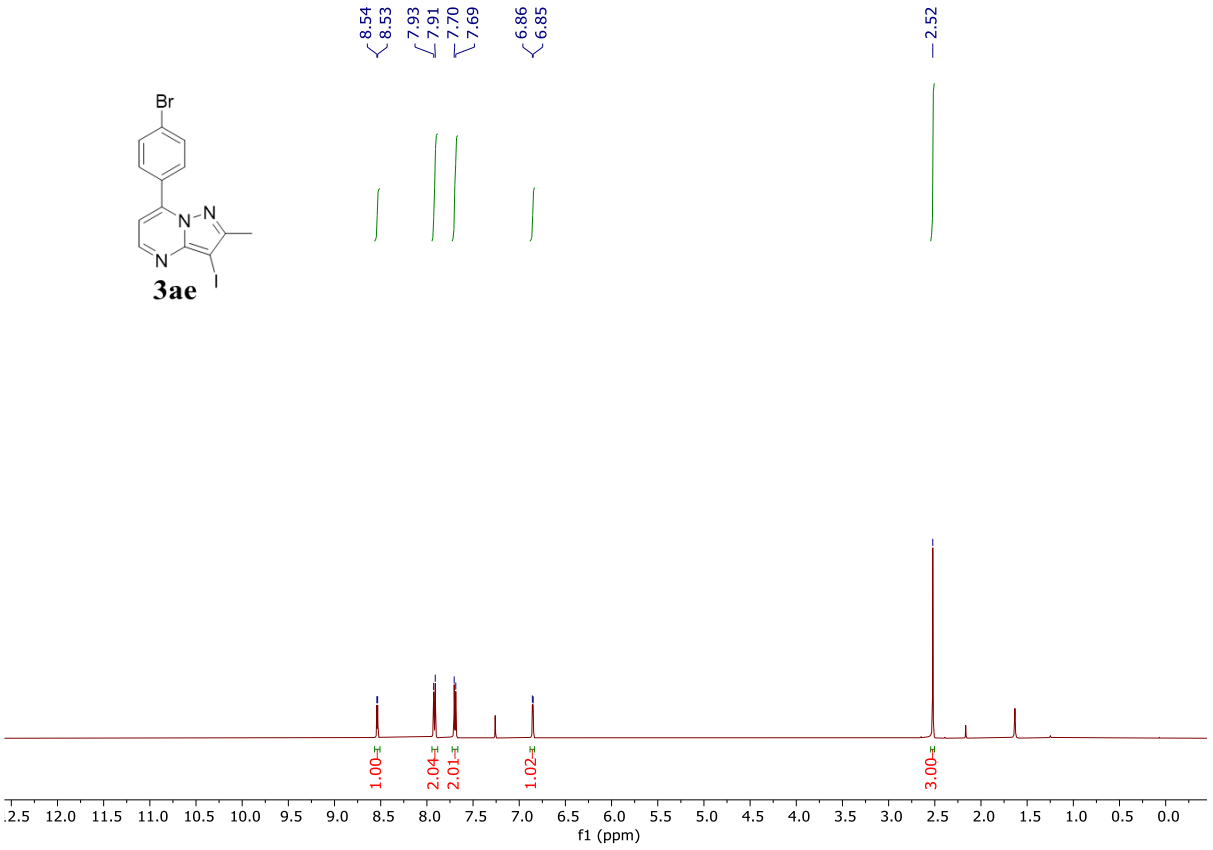
145.83
137.65
130.76
129.19
128.83
107.56
53.31
15.34
Cl
N
N
N
I
3ad
f1 (ppm)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7.69
6.86
6.85
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N
N
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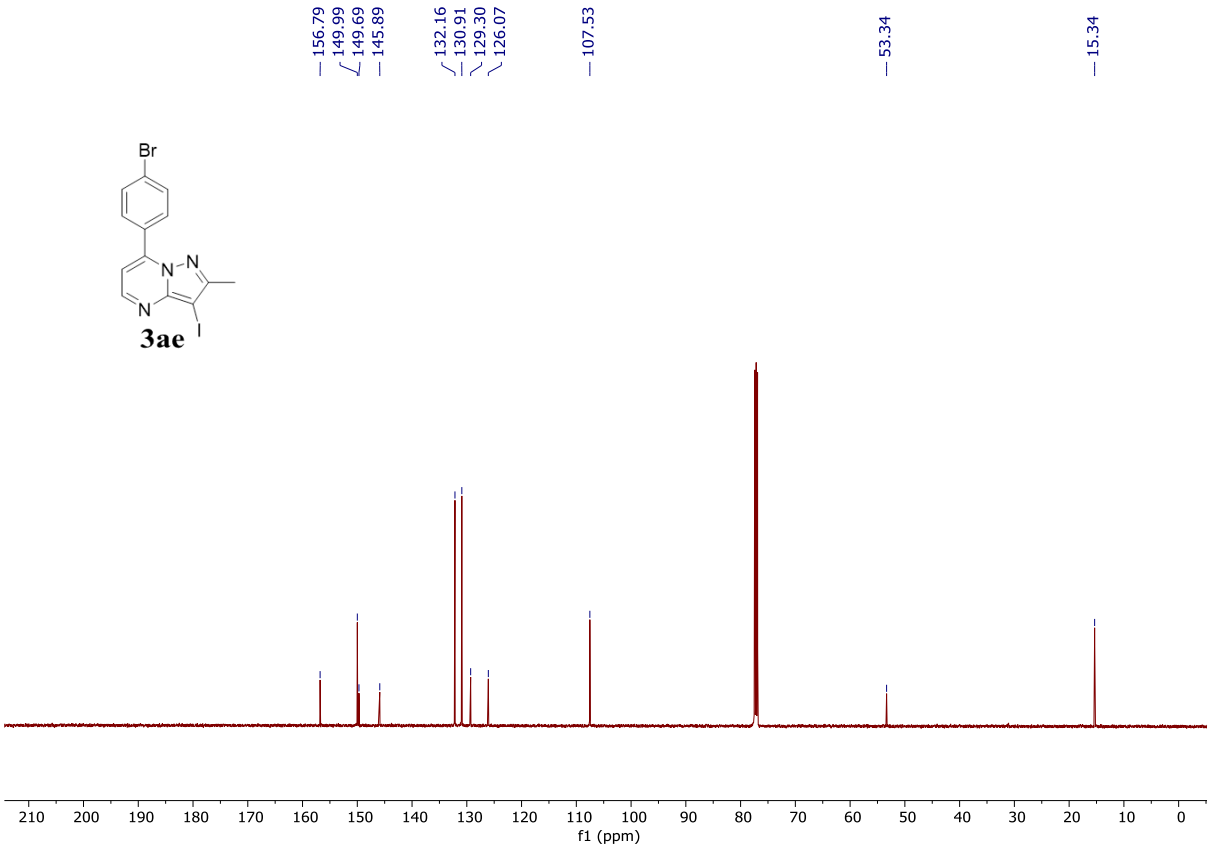
1.00
2.04
2.01
1.02
3.00
f1 (ppm)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126.07
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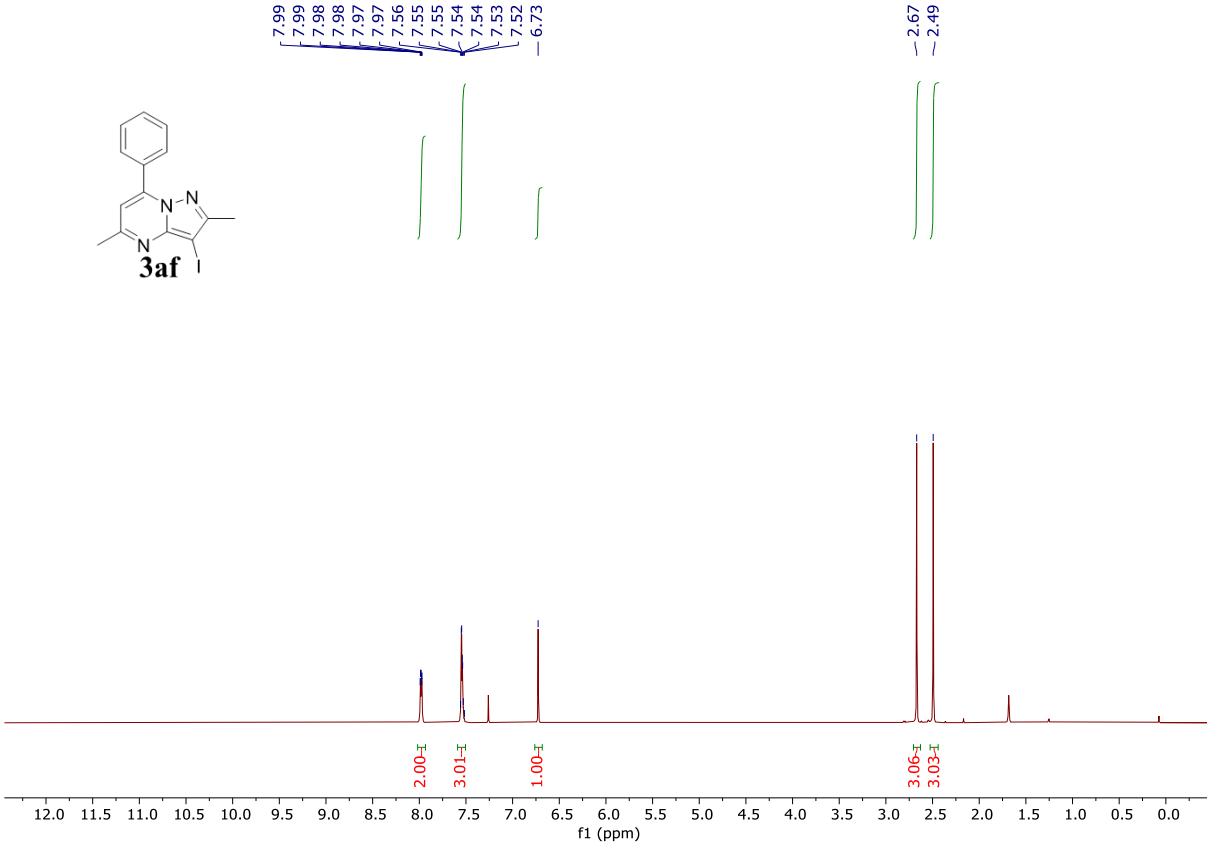
53.34
15.34
Br
N
N
N
I
3ae
f1 (ppm)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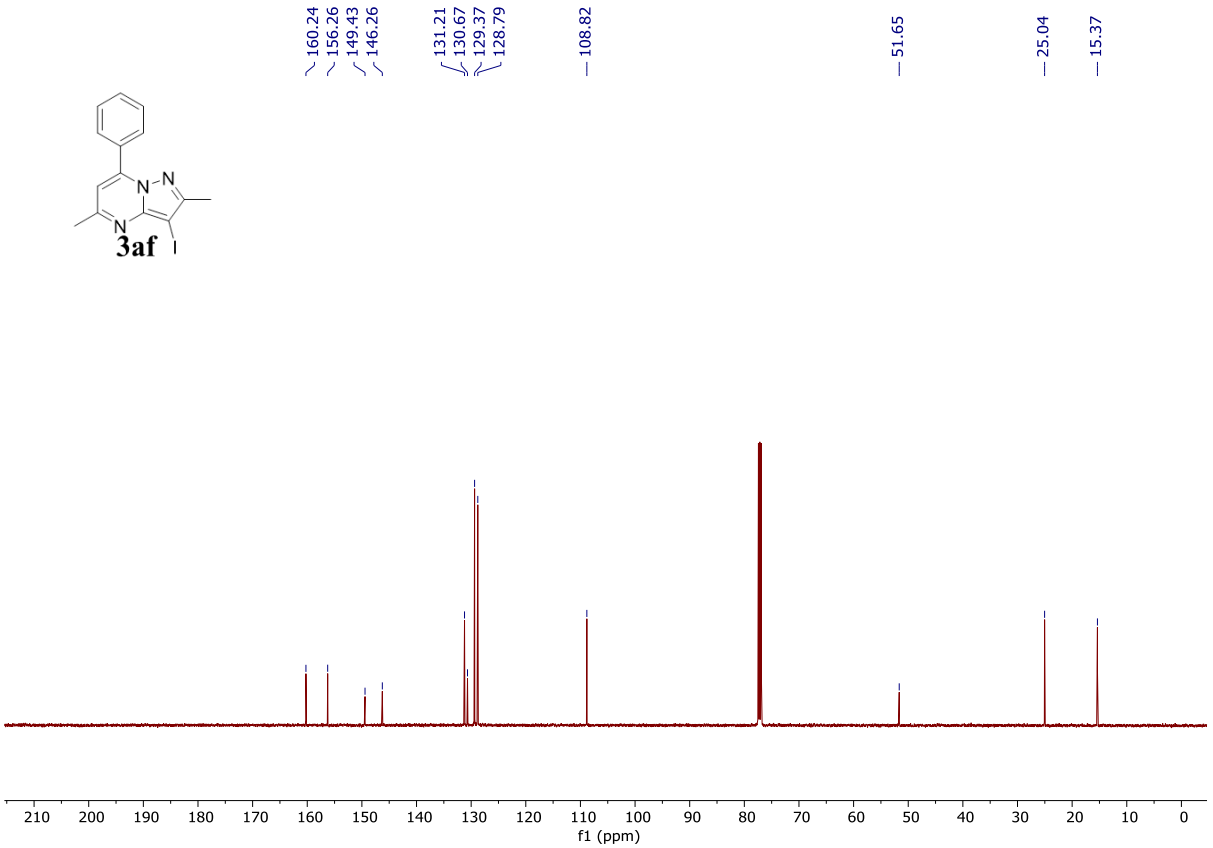
7.98
7.98
7.97
7.97
7.56
7.55
7.55
7.54
7.54
7.53
7.52
6.73
2.67
2.49
3af
2.00
3.01
1.00
3.06
3.03
f1 (ppm)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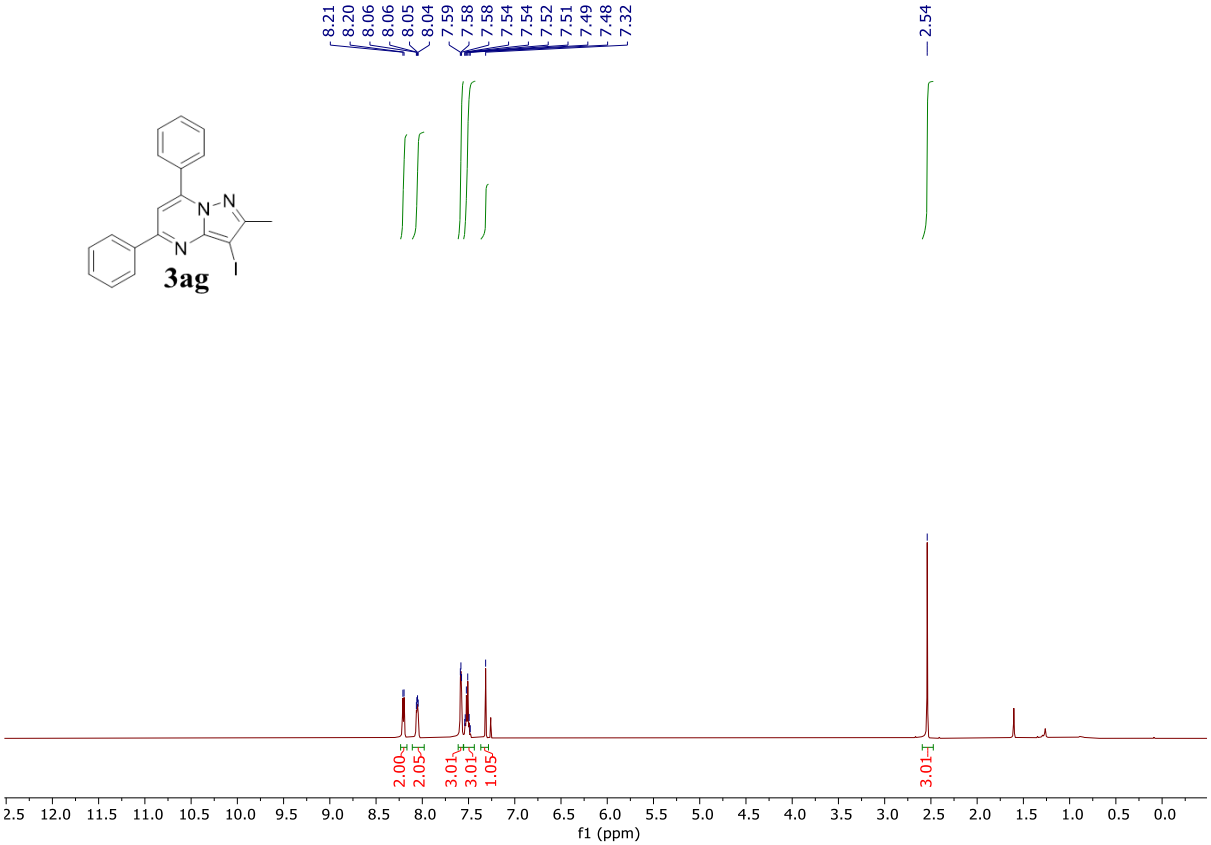
f1 (ppm)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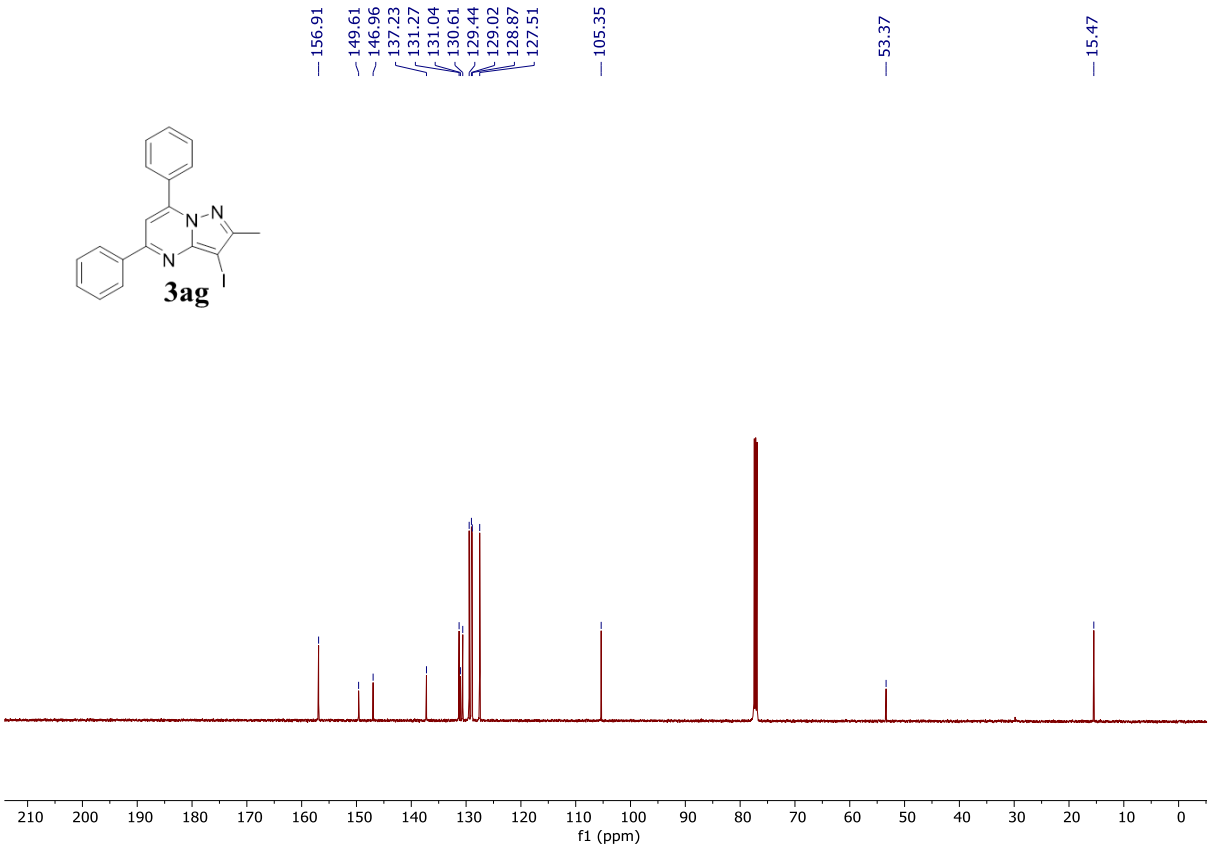
7.51
7.49
7.48
7.32
2.54
N
N
N
I
3ag
2.00
2.05
3.01
3.01
1.05
3.01
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.44
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128.87
127.51
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N
N
I
3ag
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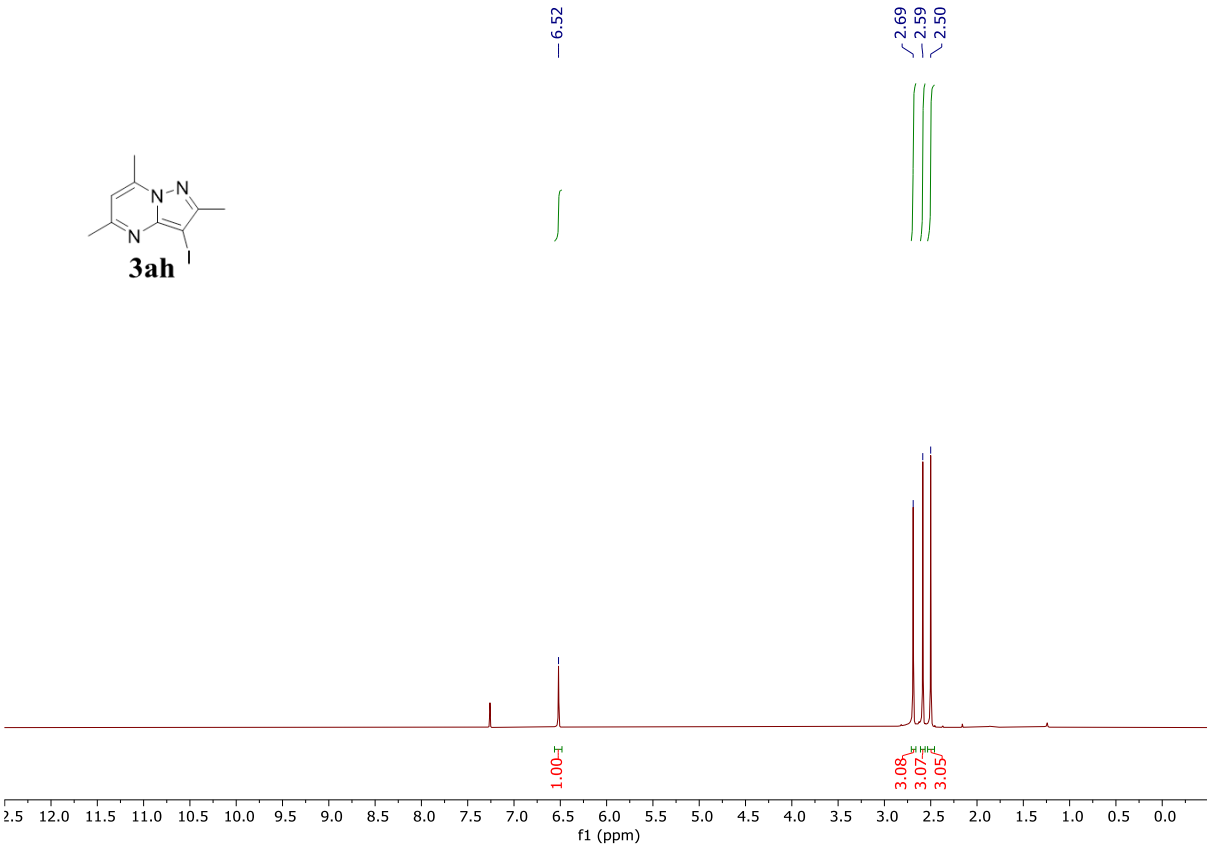
f1 (ppm)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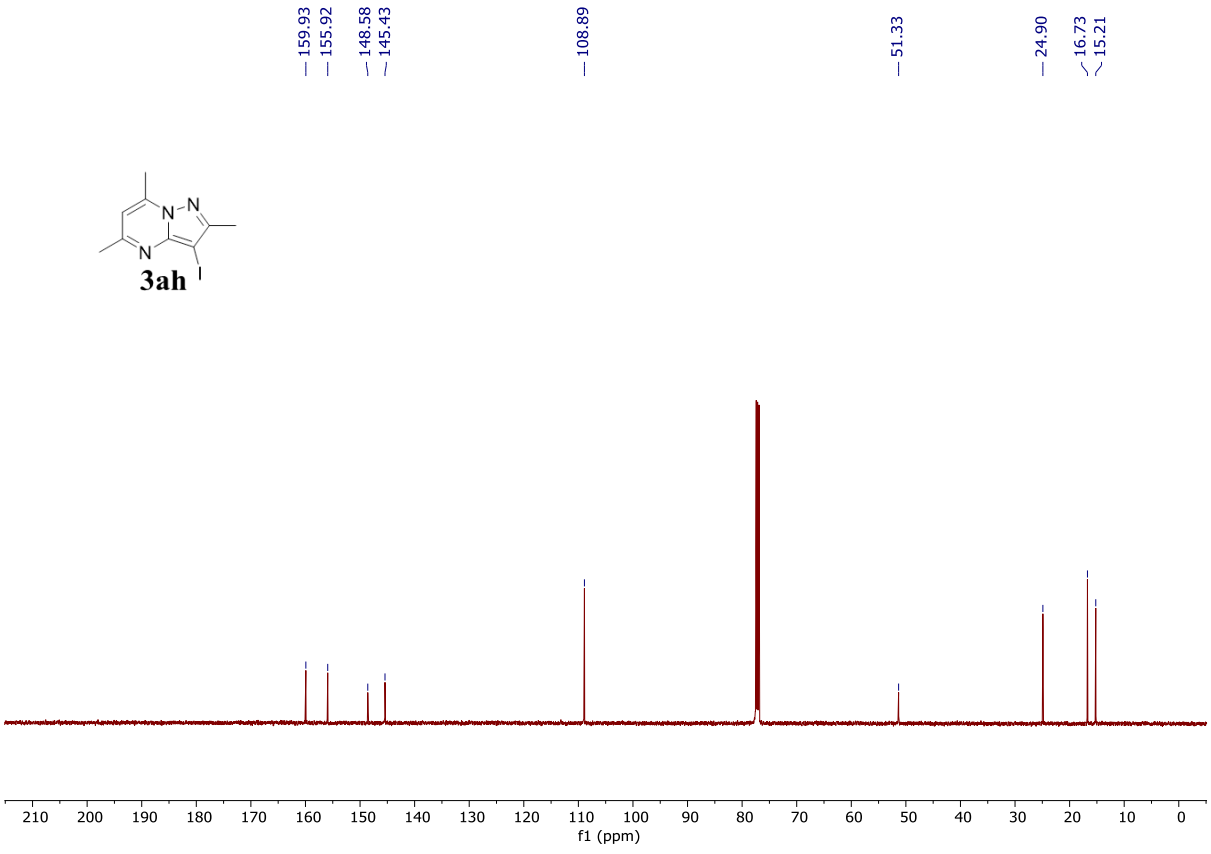
f1 (ppm)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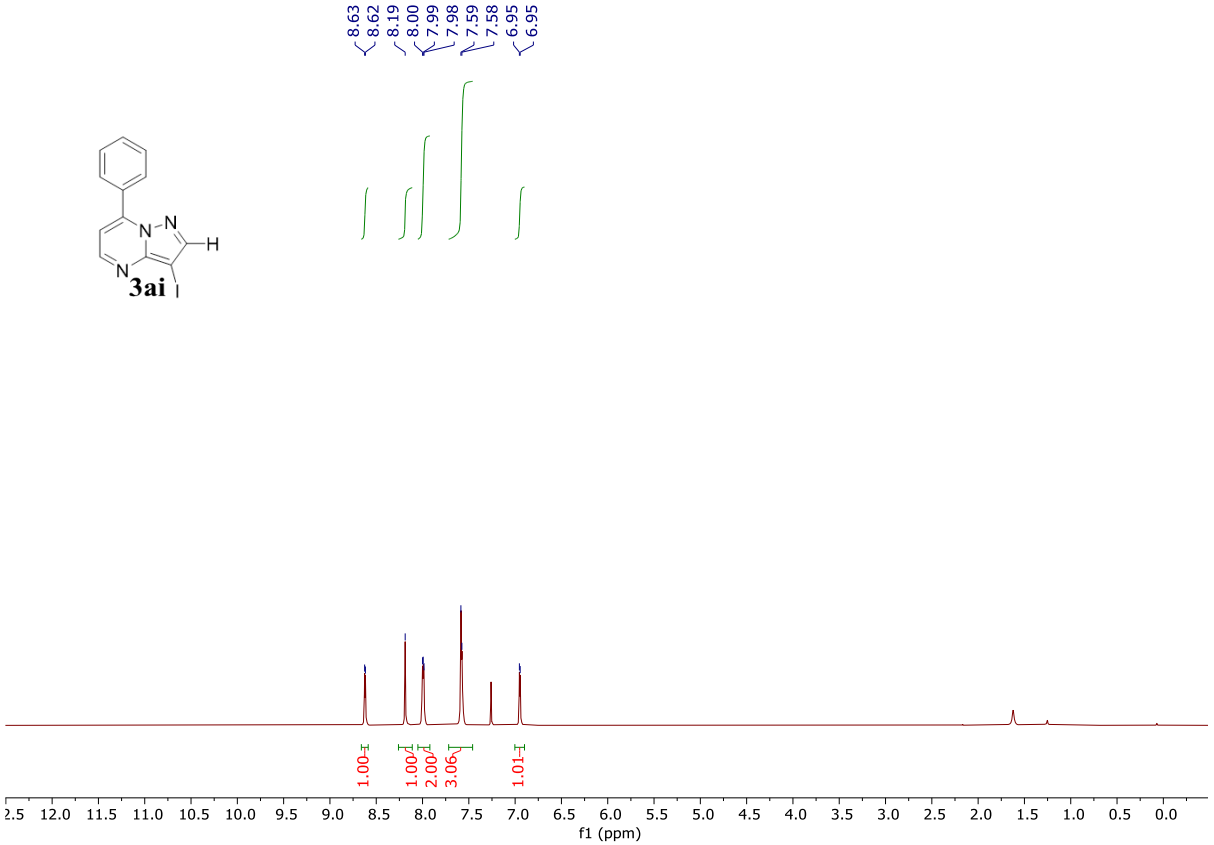
f1 (ppm)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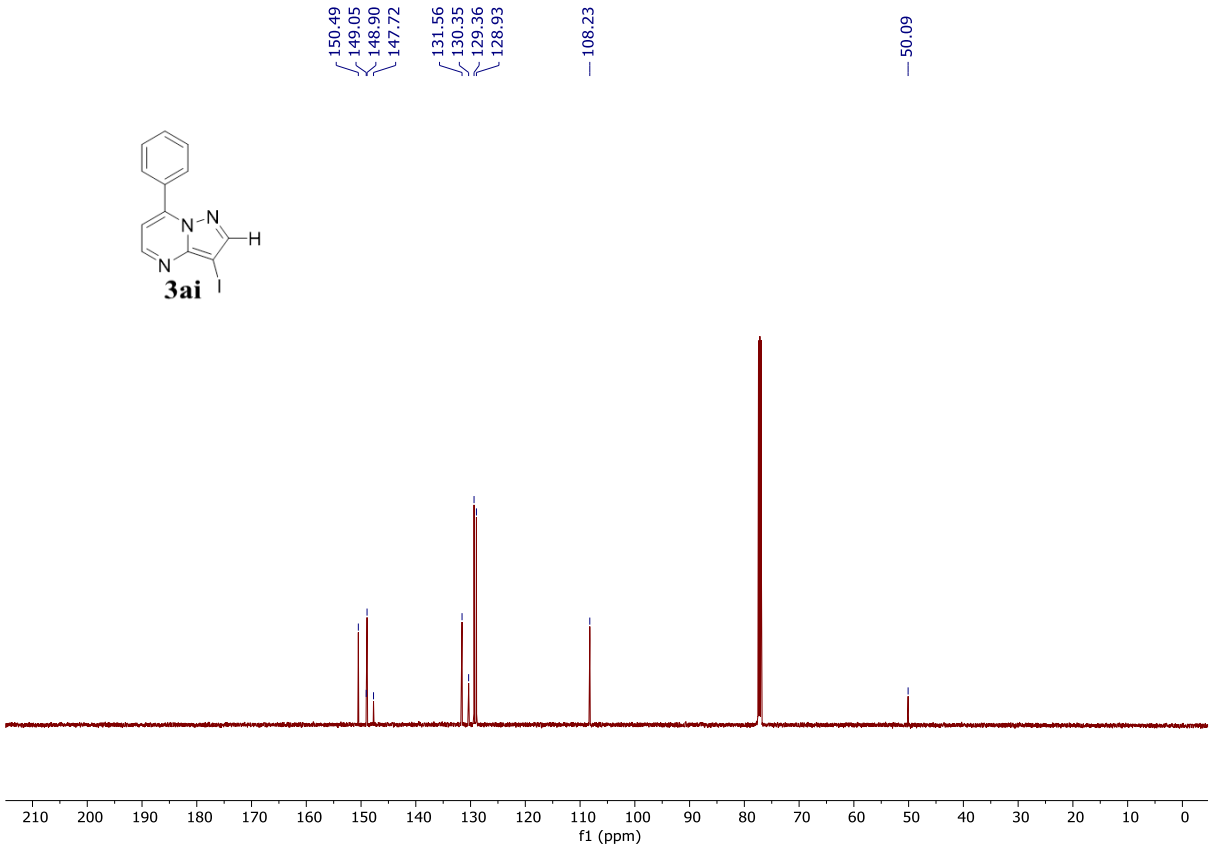
1.01
f1 (ppm)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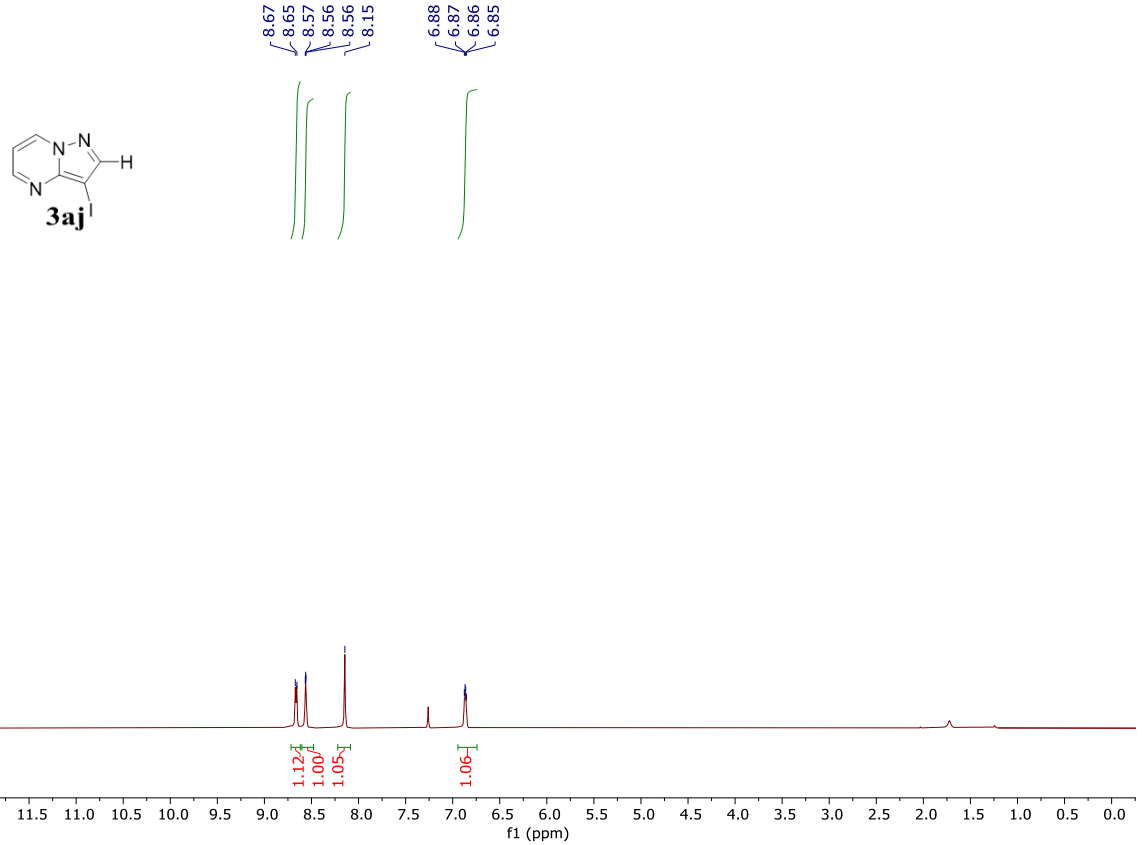
f1 (ppm)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1.06
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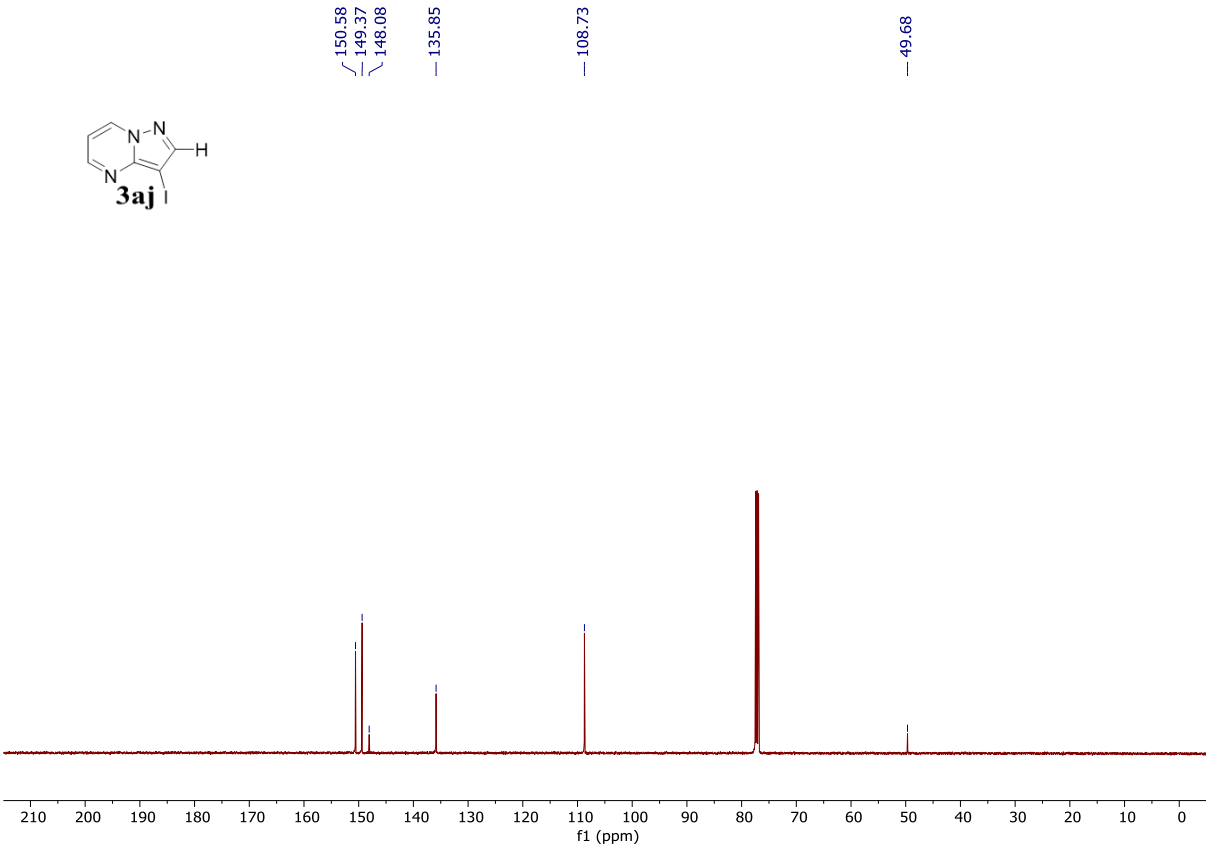
f1 (ppm)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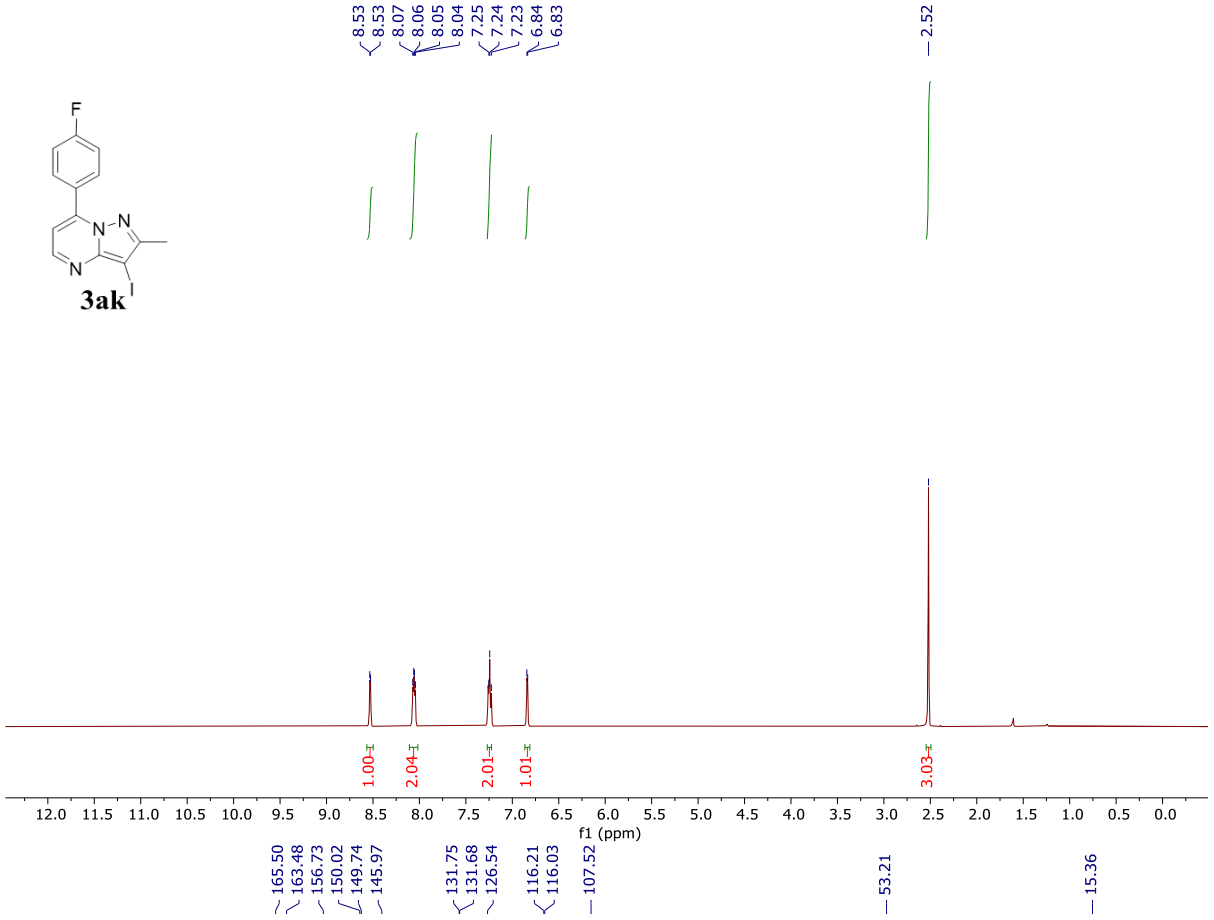
f1 (ppm)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8.05
8.04
7.25
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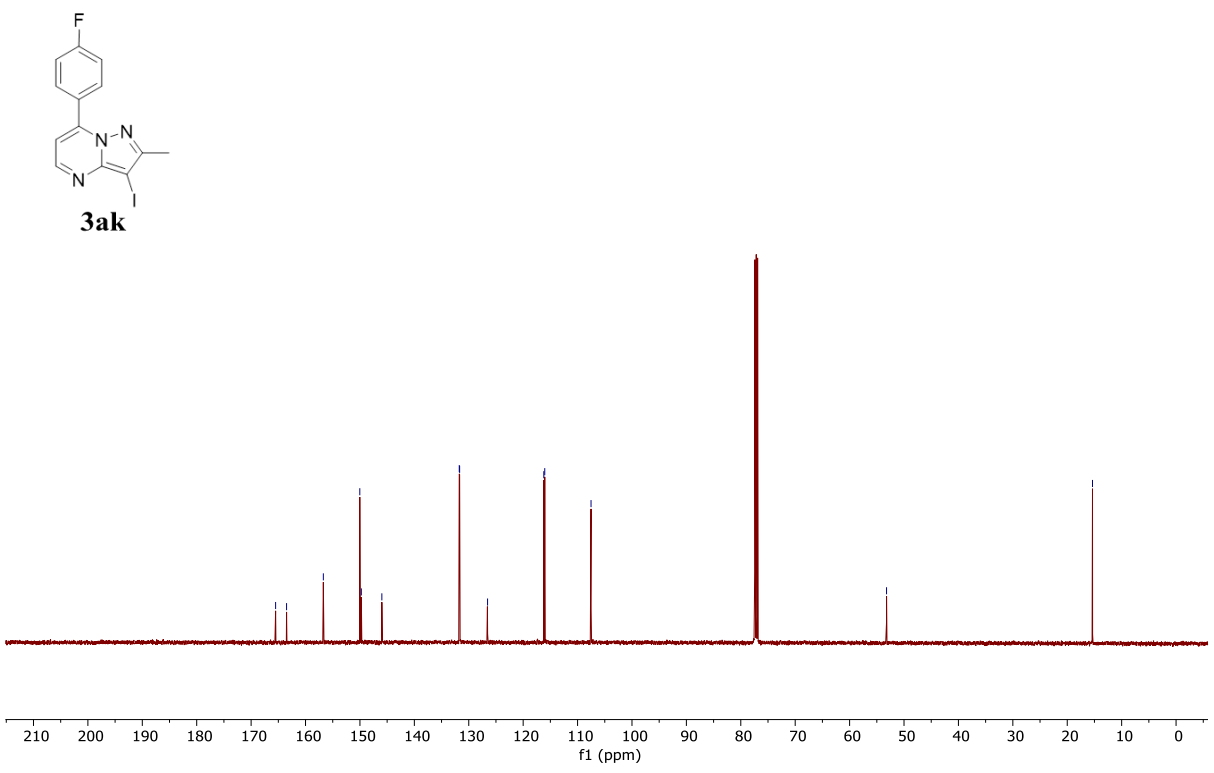
2.04
2.01
1.01
3.03
f1 (ppm)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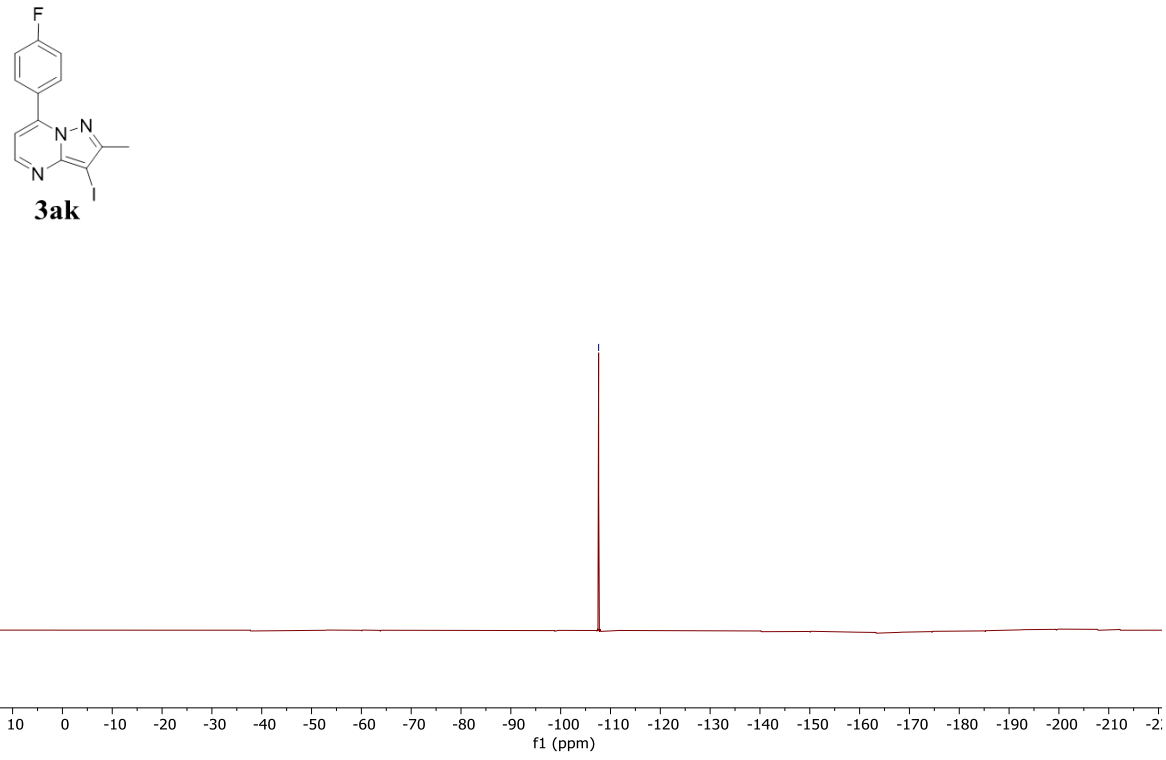
F
N
N
N
I
3ak
f1 (ppm)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F
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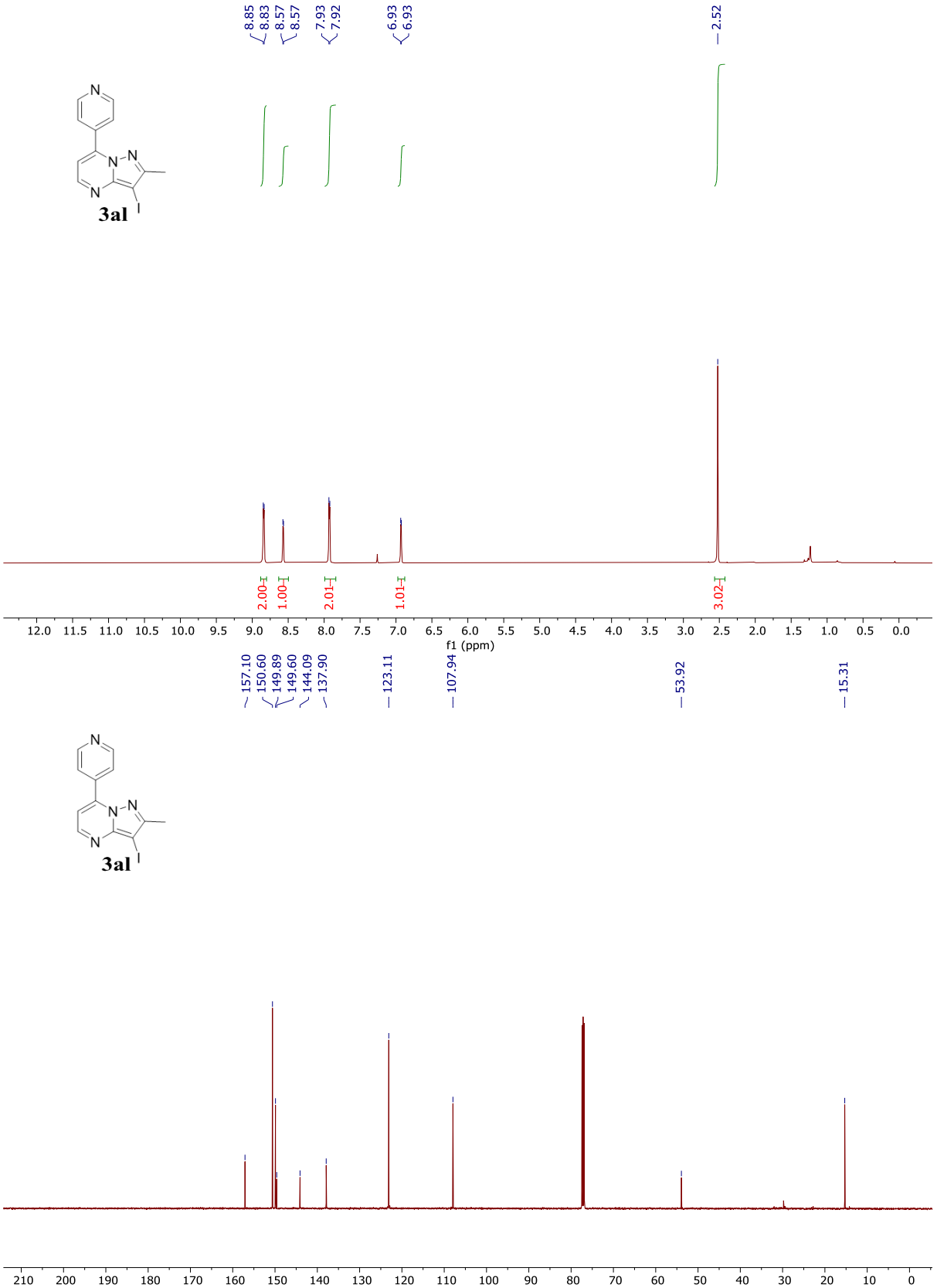
N
N
I
3ak
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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f1 (ppm)
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149.60
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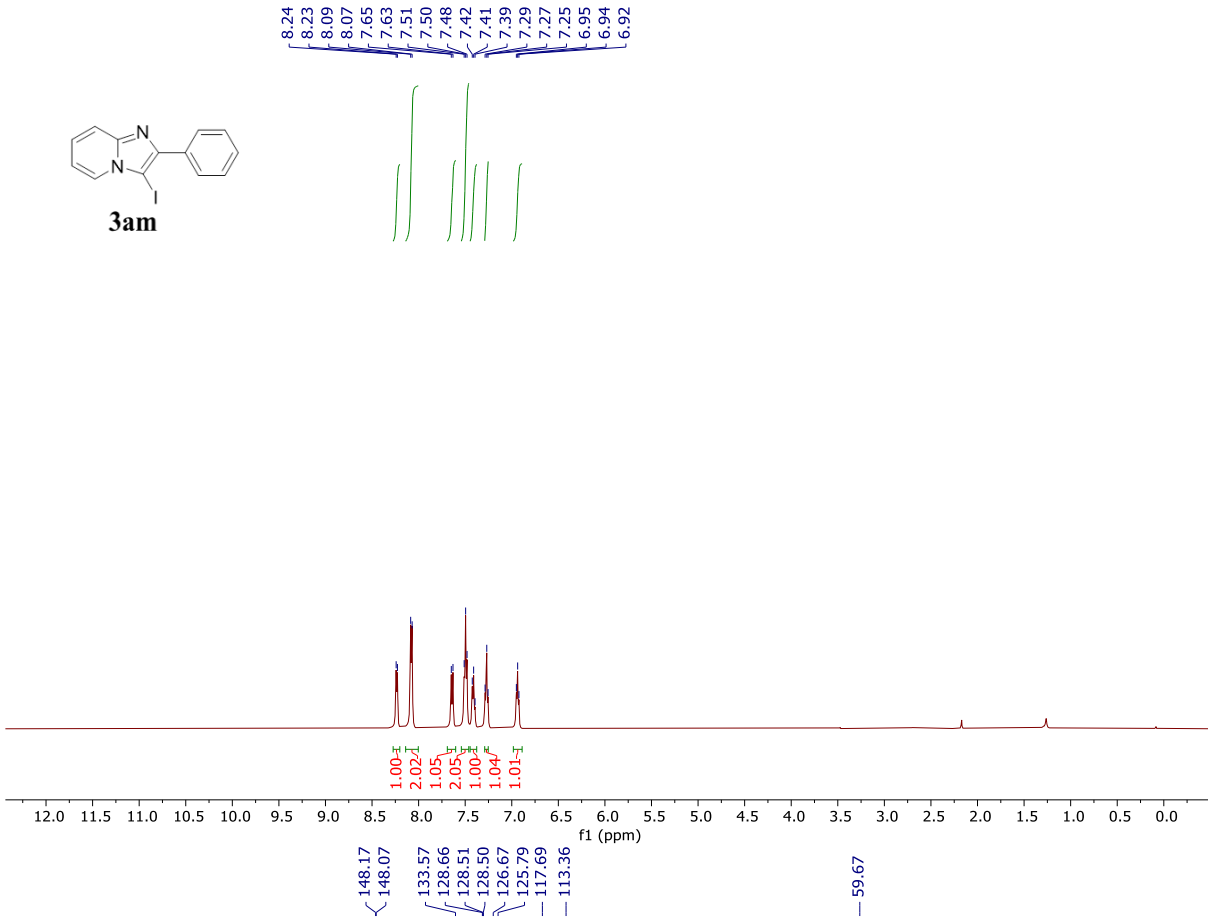
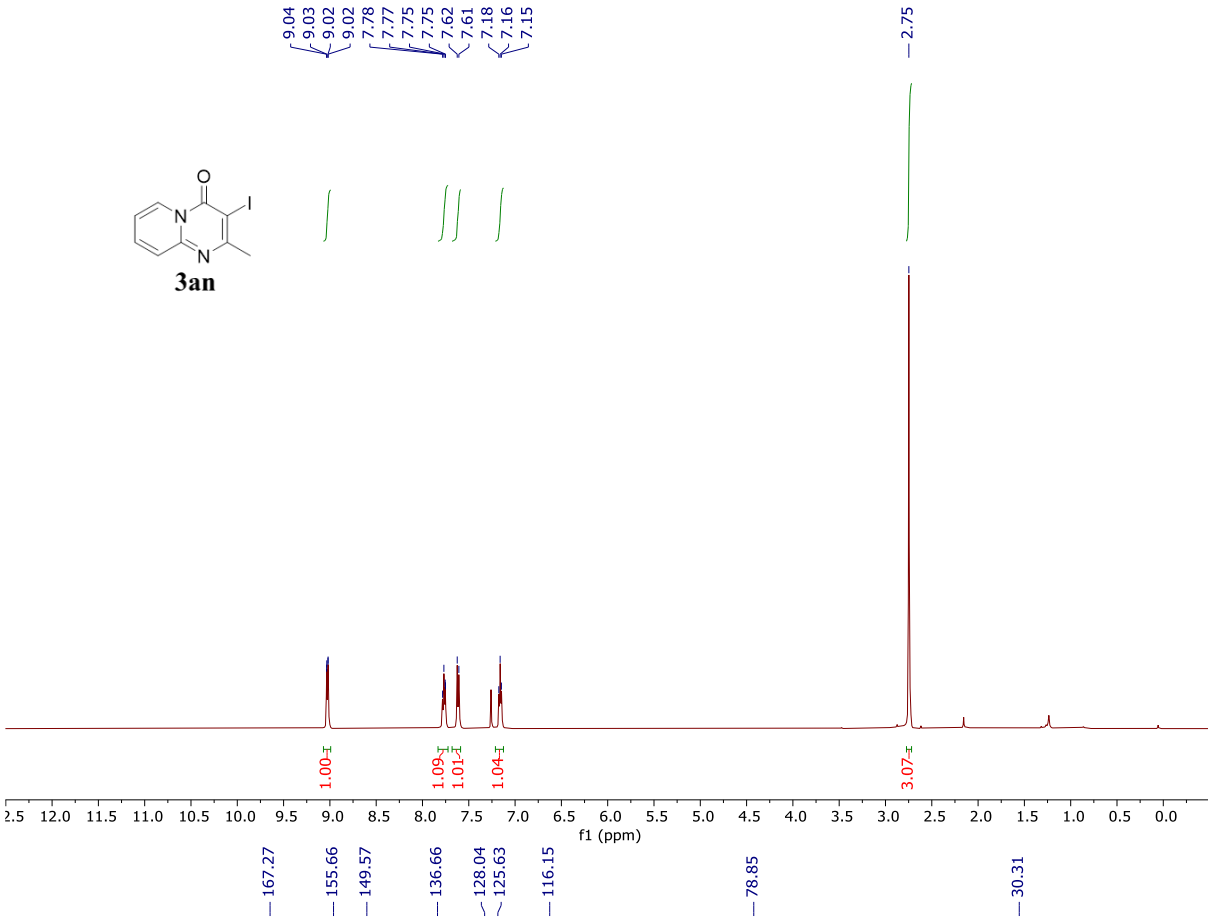
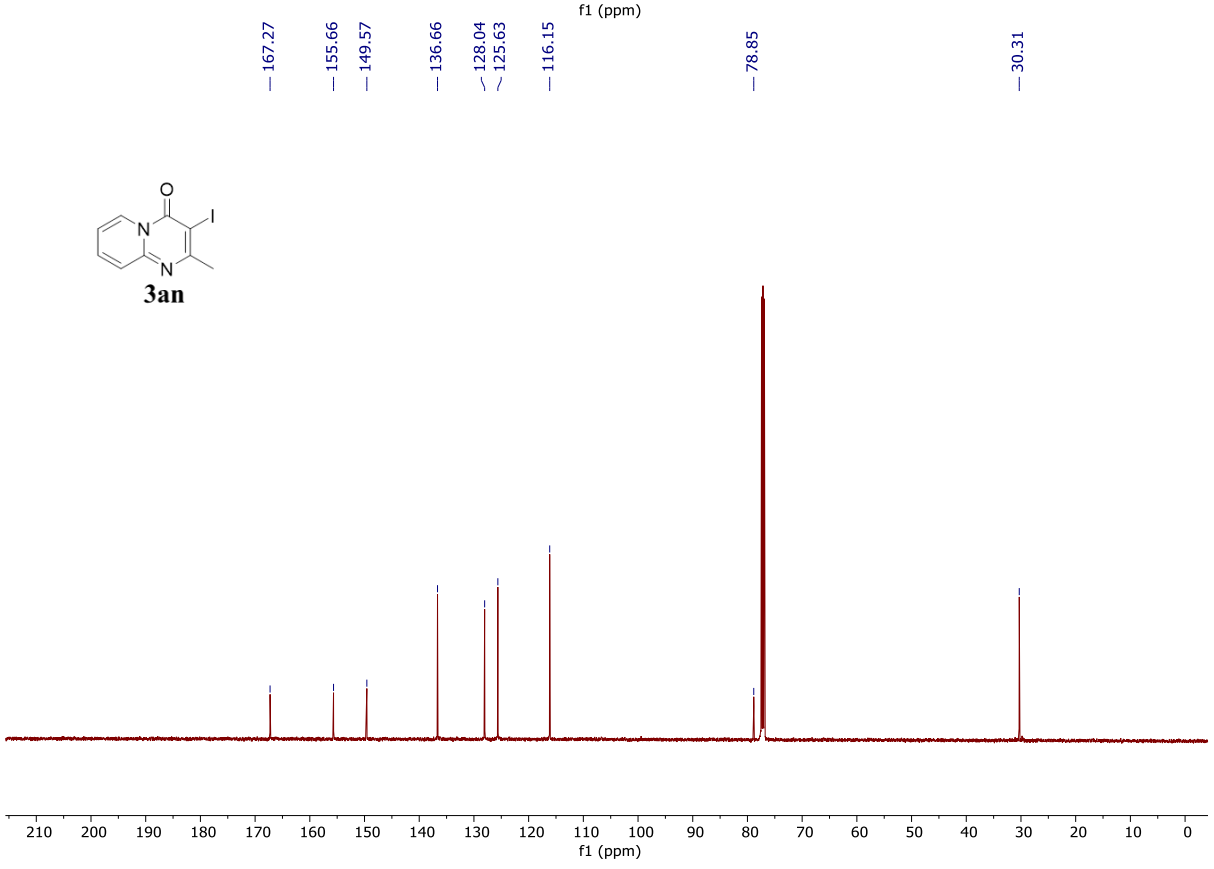
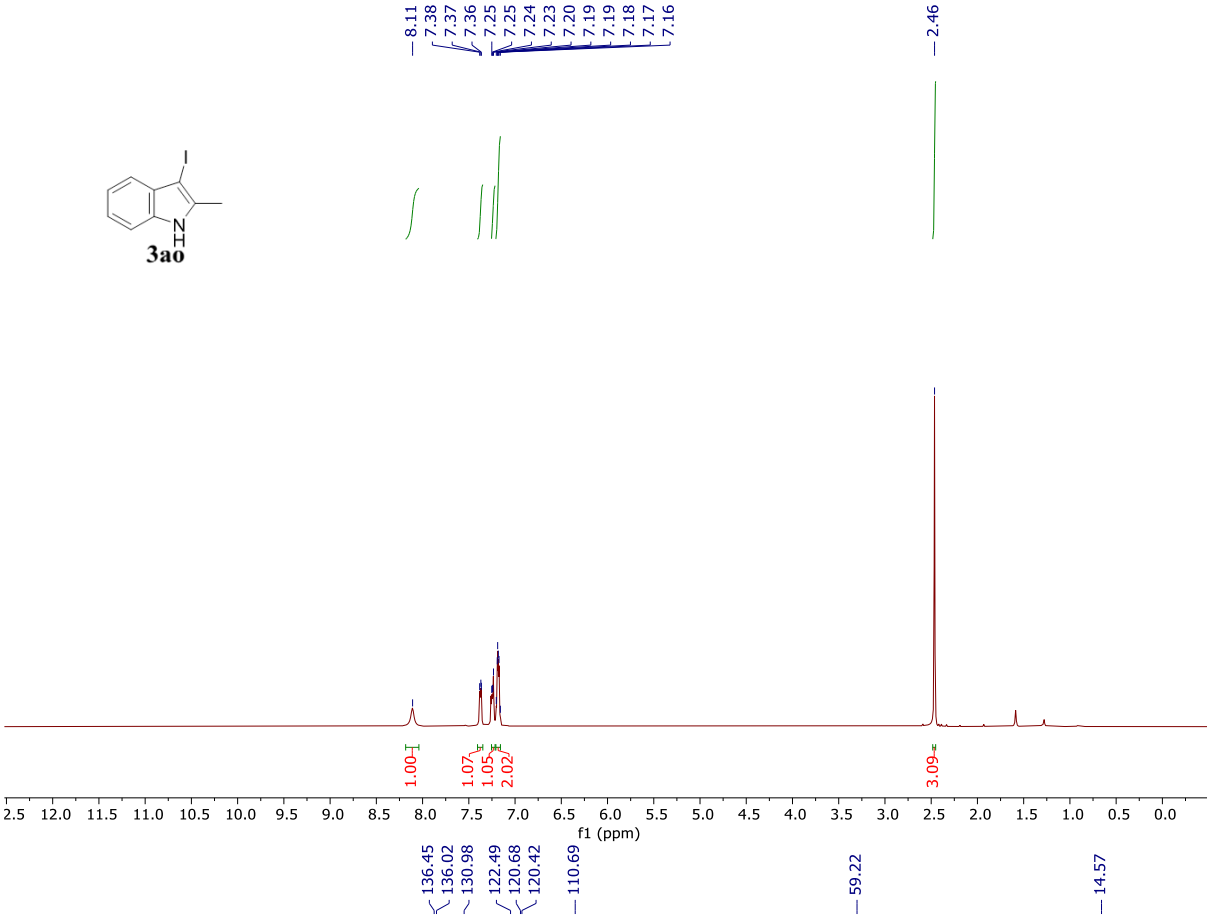
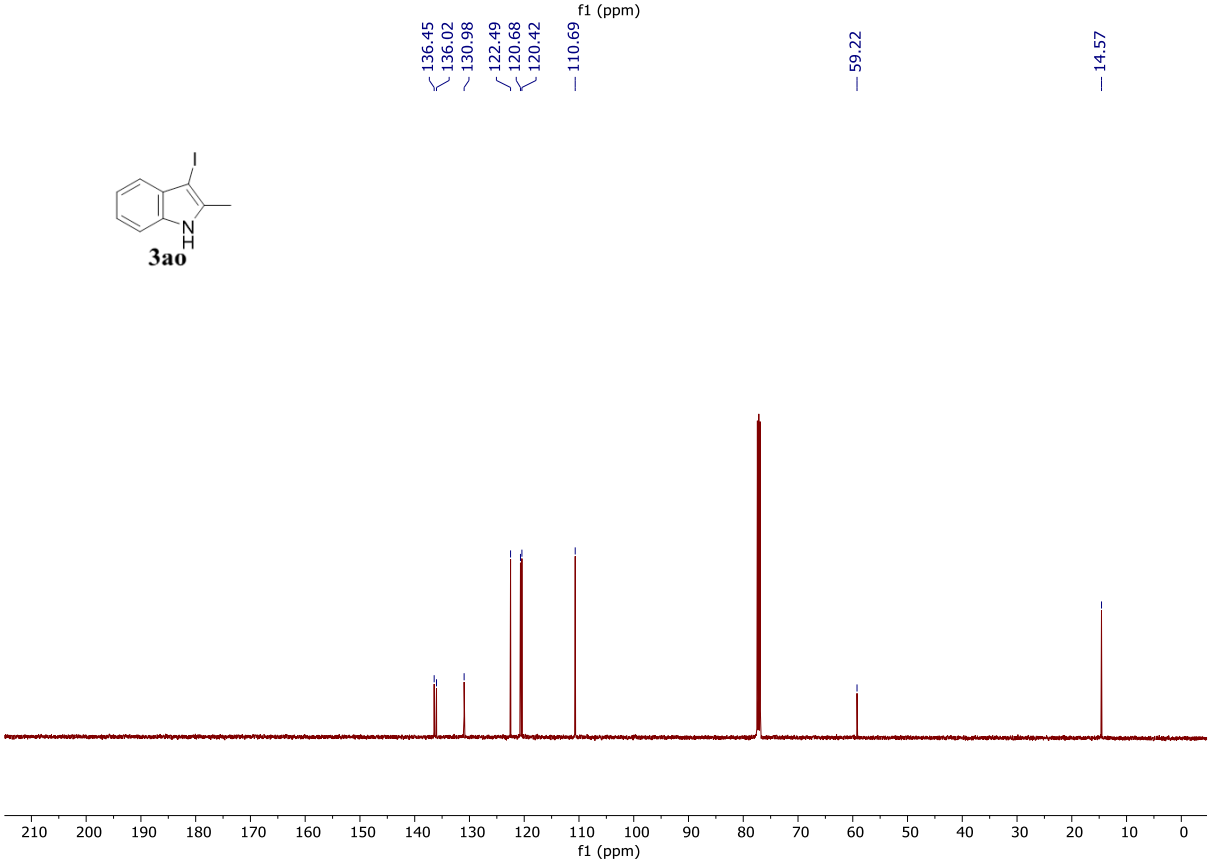
137.90
123.11
107.94
53.92
15.31
3al
f1 (ppm)

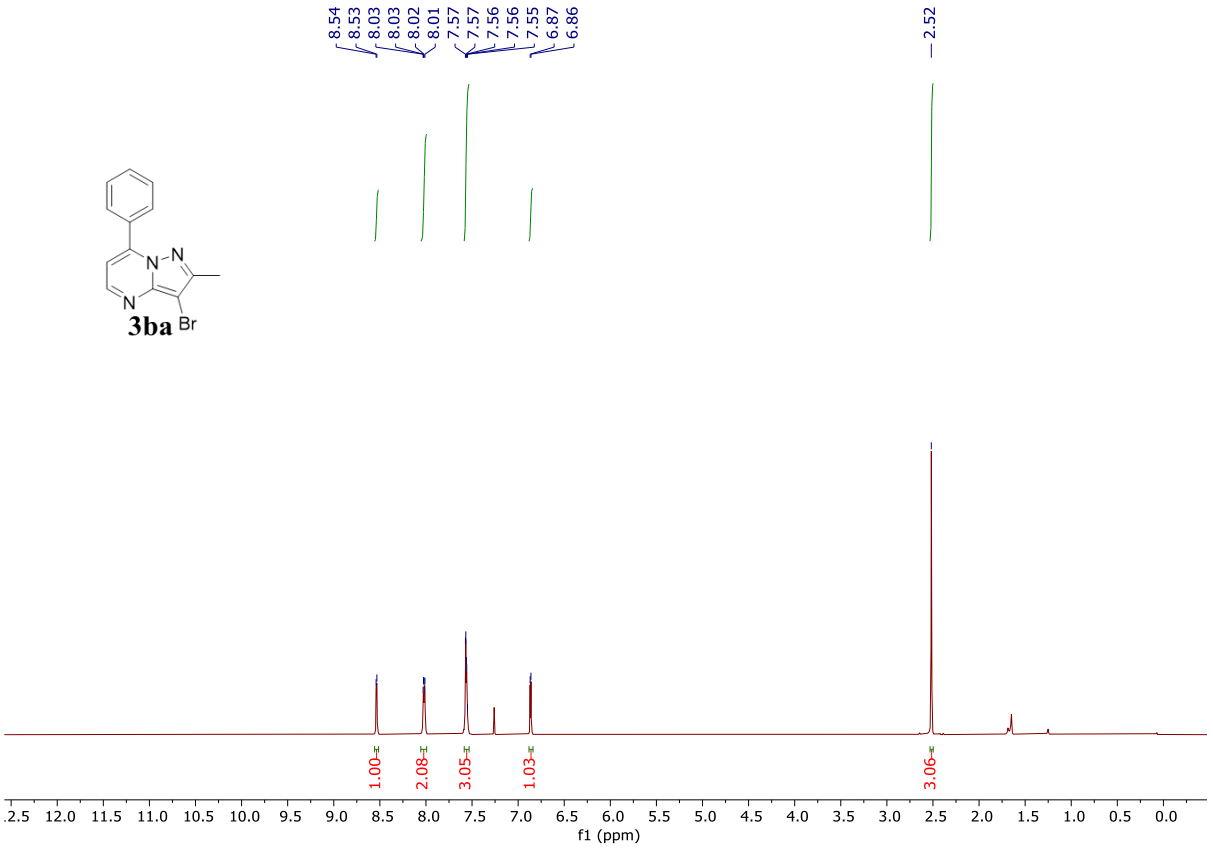

8.24
8.23
8.09
8.07
7.65
7.63
7.51
7.50
7.48
7.42
7.41
7.39
7.29
7.27
7.25
6.95
6.94
6.92
3am
1.00
2.02
1.05
2.05
1.00
1.04
1.01
f1 (ppm)
148.17
148.07
133.57
128.66
128.51
128.50
126.67
125.79
117.69
113.36
59.67
3am
f1 (ppm)


9.04
9.03
9.02
9.02
7.78
7.77
7.75
7.75
7.62
7.61
7.18
7.16
7.15
2.75
3an
1.00
1.09
1.01
1.04
3.07
f1 (ppm)


167.27
155.66
149.57
136.66
128.04
125.63
116.15
78.85
30.31
3an
f1 (ppm)


8.11
7.38
7.37
7.36
7.25
7.25
7.24
7.23
7.20
7.19
7.19
7.18
7.17
7.16
2.46
3ao
1.00
1.07
1.05
2.02
3.09
f1 (ppm)


136.45
136.02
130.98
122.49
120.68
120.42
110.69
59.22
14.57
3ao
f1 (ppm)


8.54
8.53
8.03
8.03
8.02
8.01
7.57
7.57
7.56
7.56
7.55
6.87
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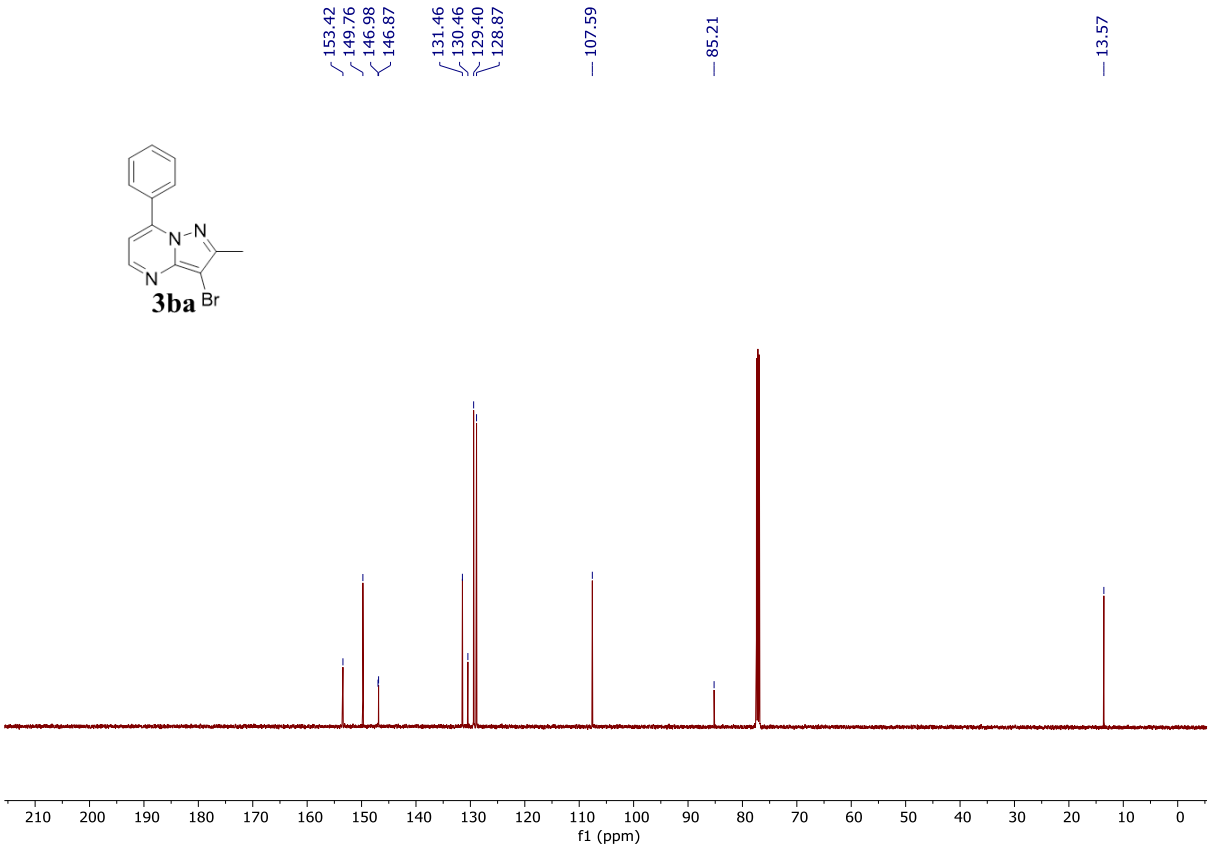
2.08
3.05
1.03
3.06
f1 (ppm)


153.42
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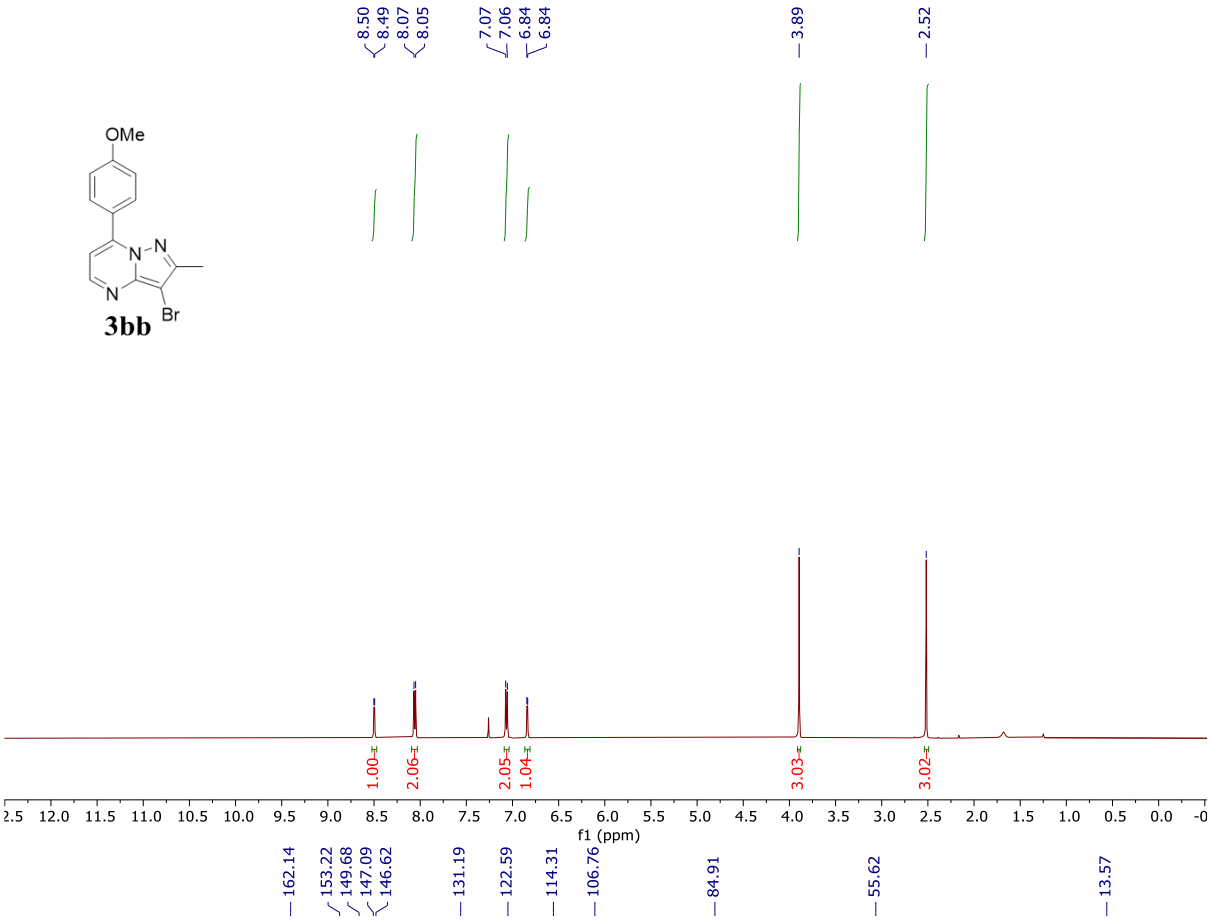
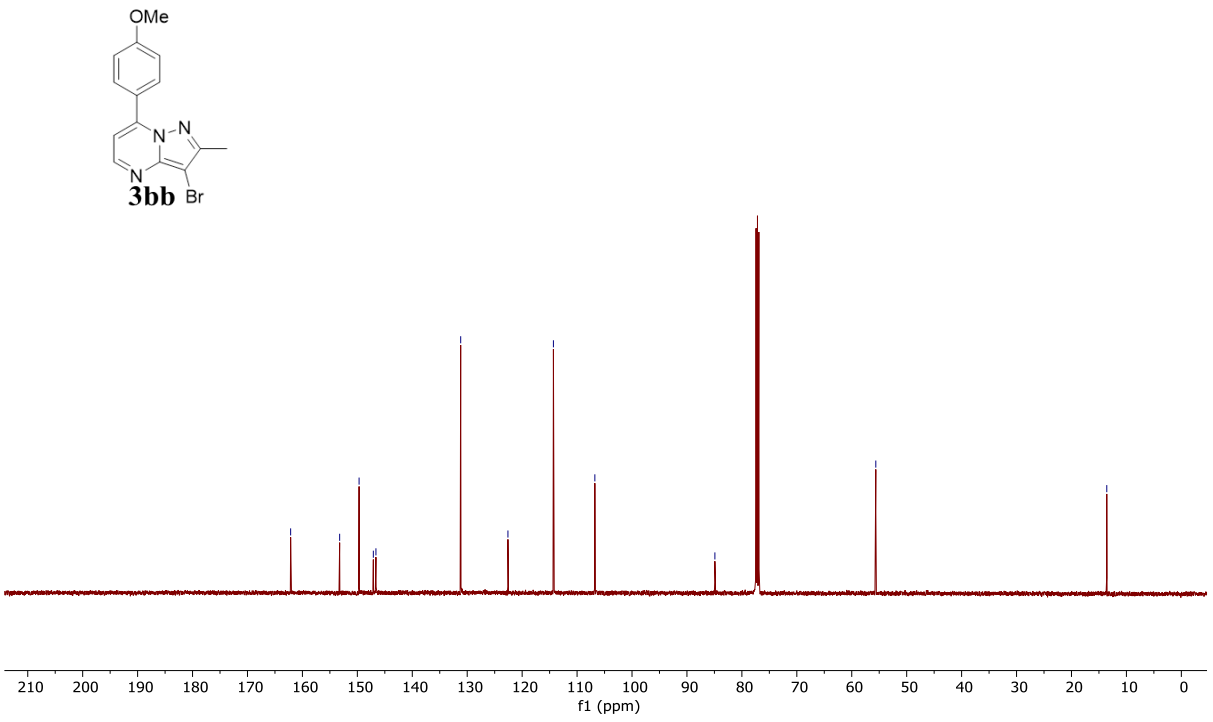
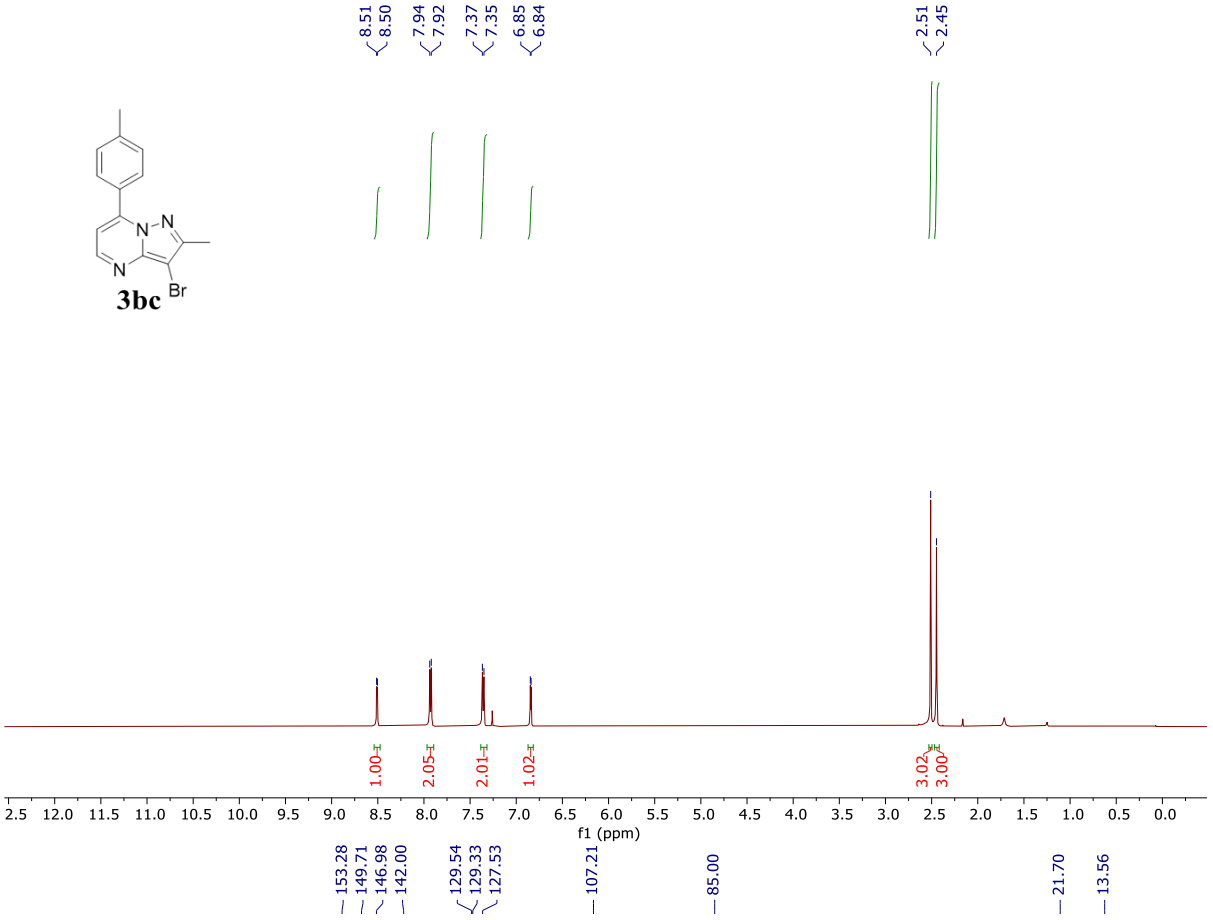
146.98
146.87
131.46
130.46
129.40
128.87
107.59
85.21
13.57
3ba Br
f1 (ppm)


8.50
8.49
8.07
8.05
7.07
7.06
6.84
6.84
3.89
2.52
OMe
N
N
N
Br
3bb
1.00
2.06
2.05
1.04
3.03
3.02
f1 (ppm)


162.14
153.22
149.68
147.09
146.62
131.19
122.59
114.31
106.76
84.91
55.62
13.57
OMe
N
N
N
3bb
Br
f1 (ppm)


8.51
8.50
7.94
7.92
7.37
7.35
6.85
6.84
2.51
2.45
3bc
Br
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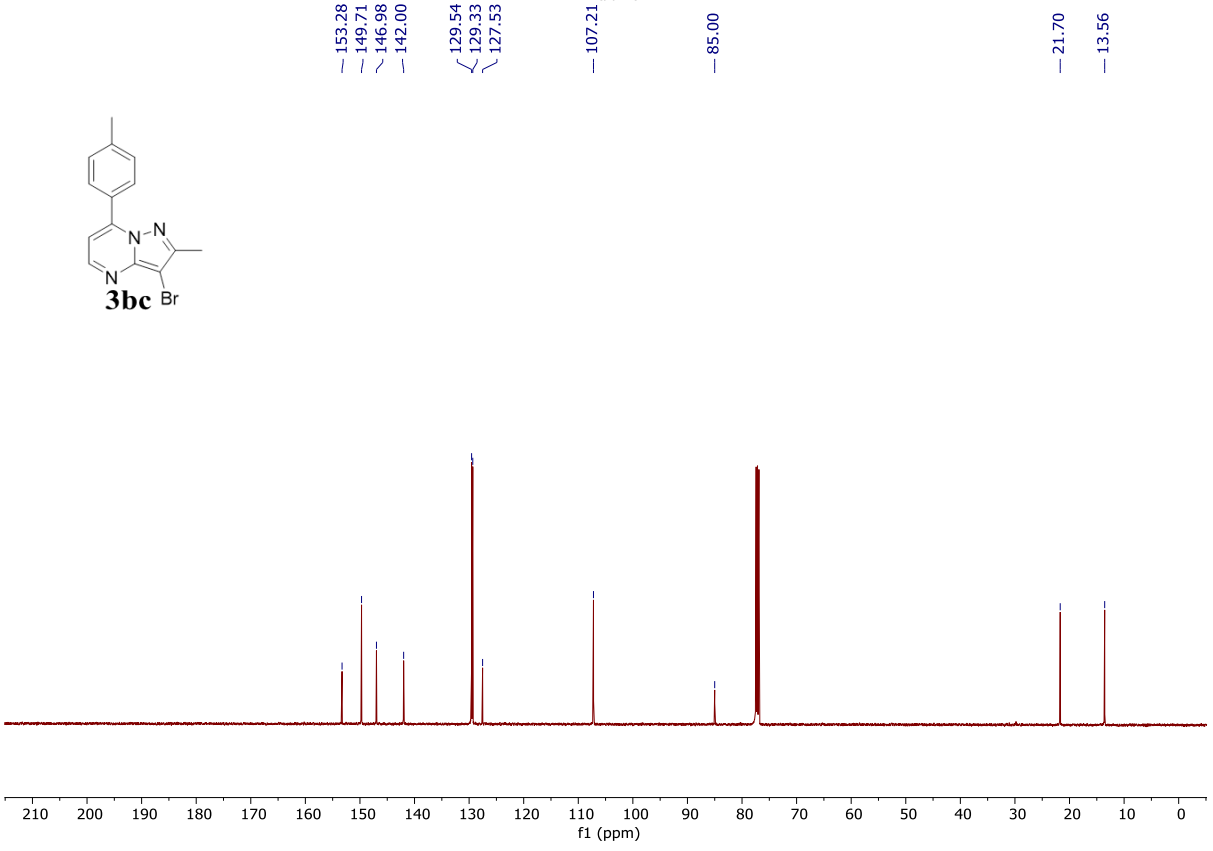
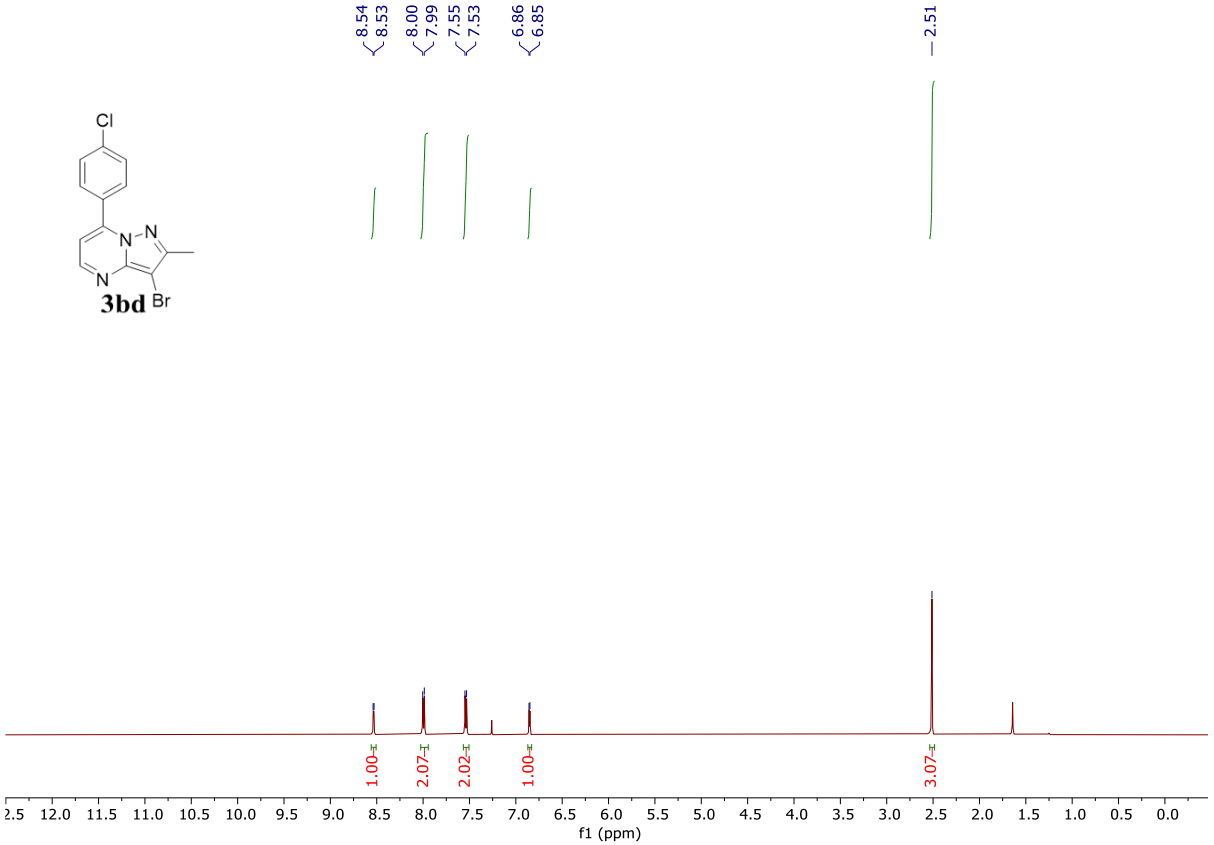
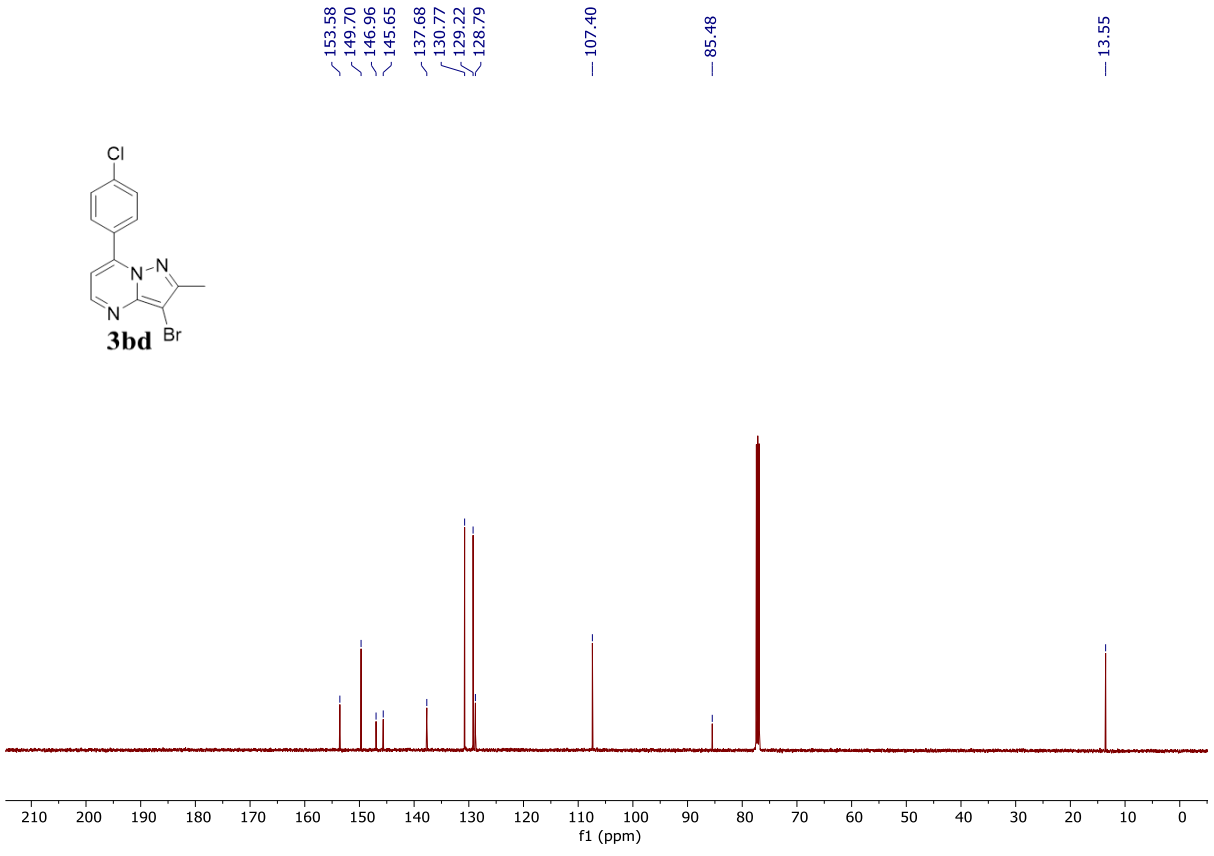
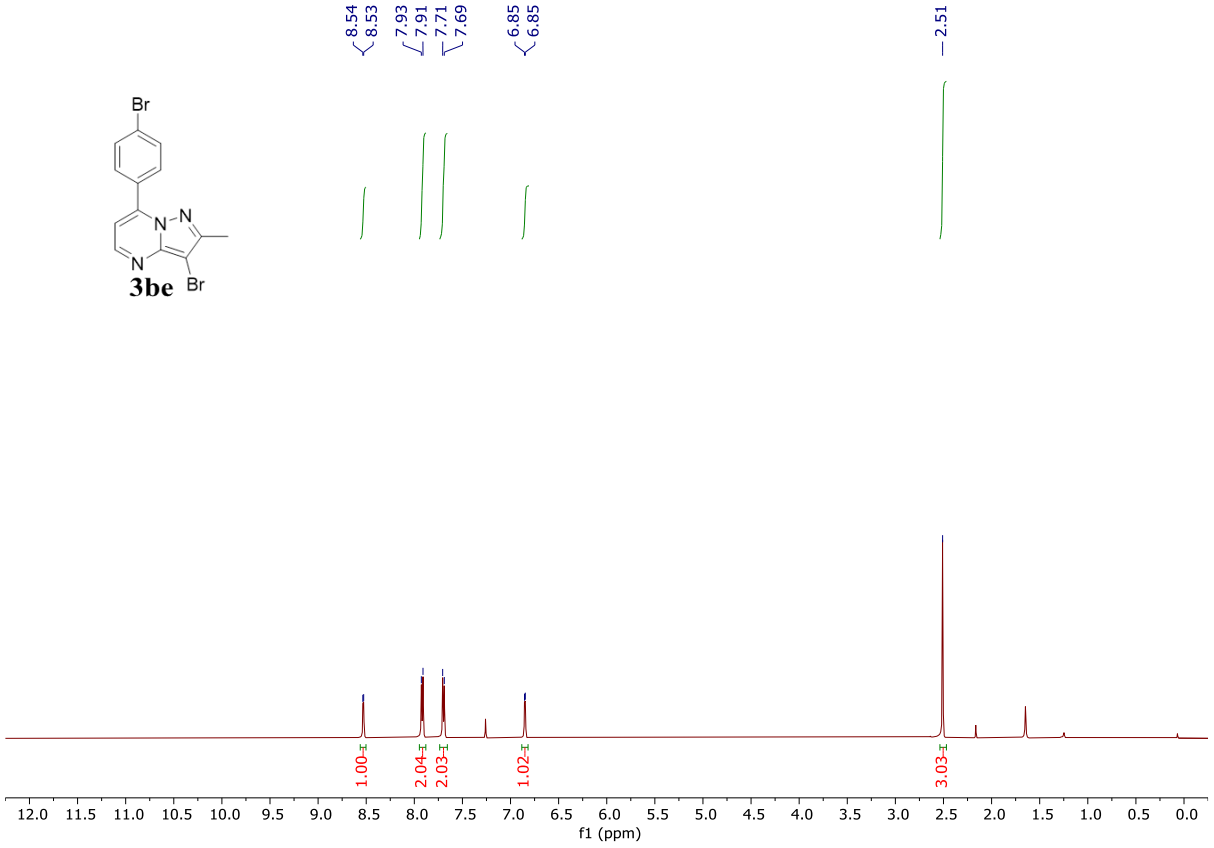
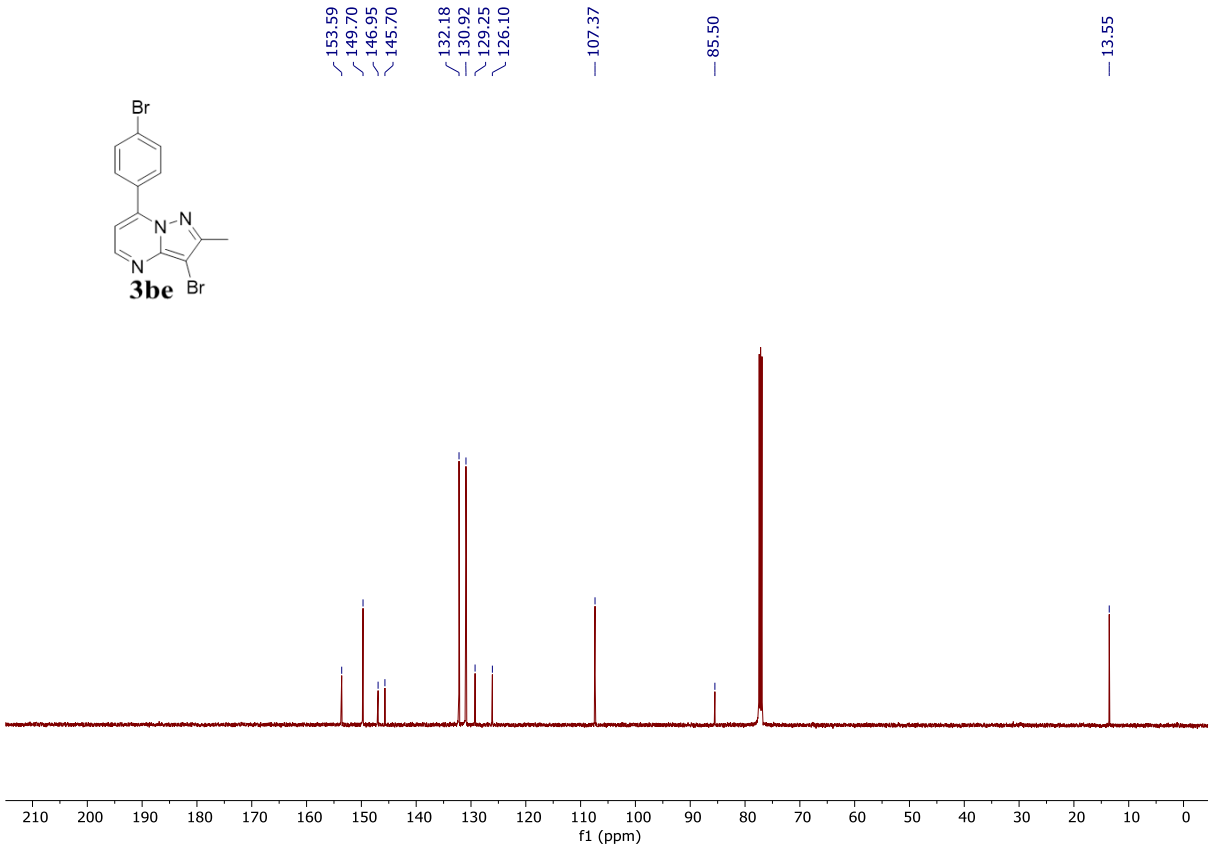
2.05
2.01
1.02
3.02
3.00
f1 (ppm)

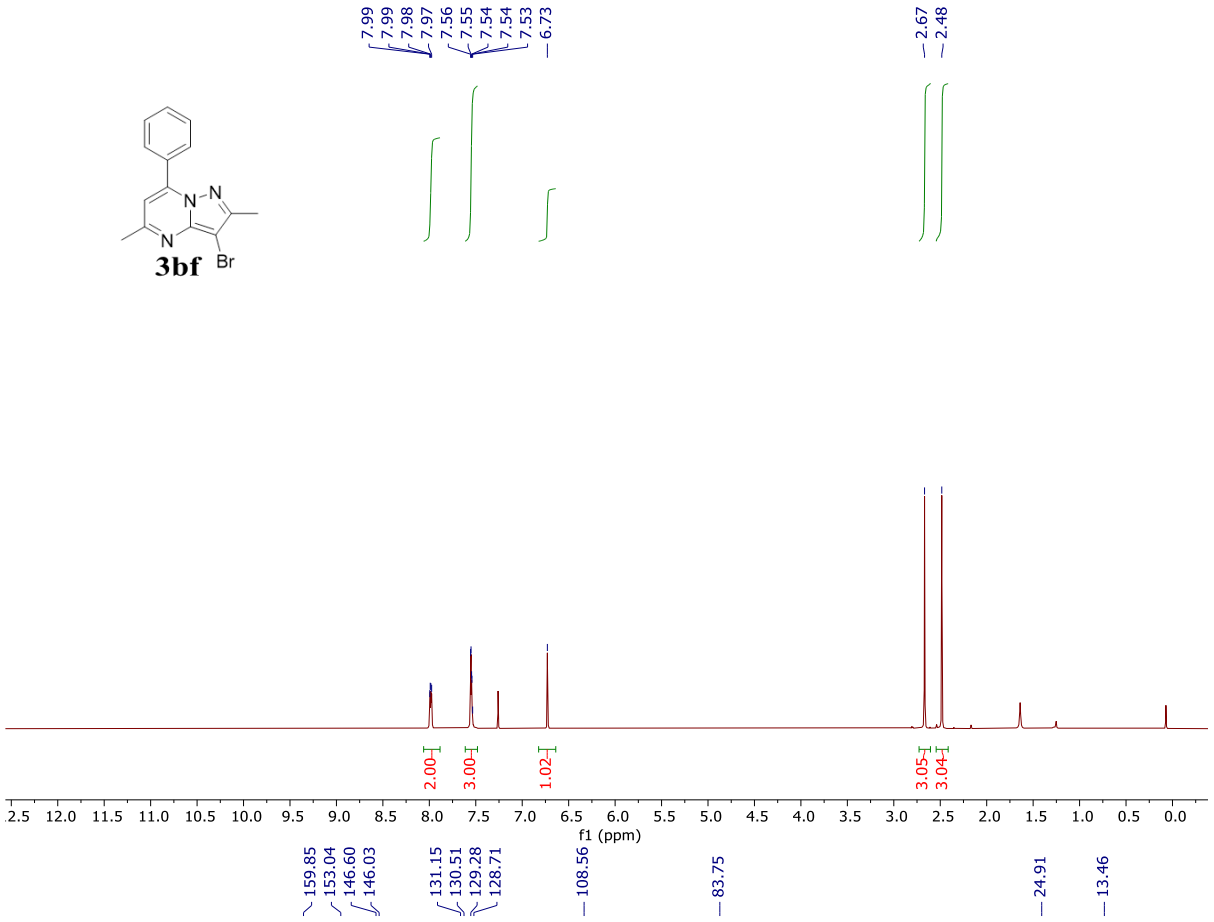

153.28
149.71
146.98
142.00
129.54
129.33
127.53
107.21
85.00
21.70
13.56
3bc
Br
f1 (ppm)

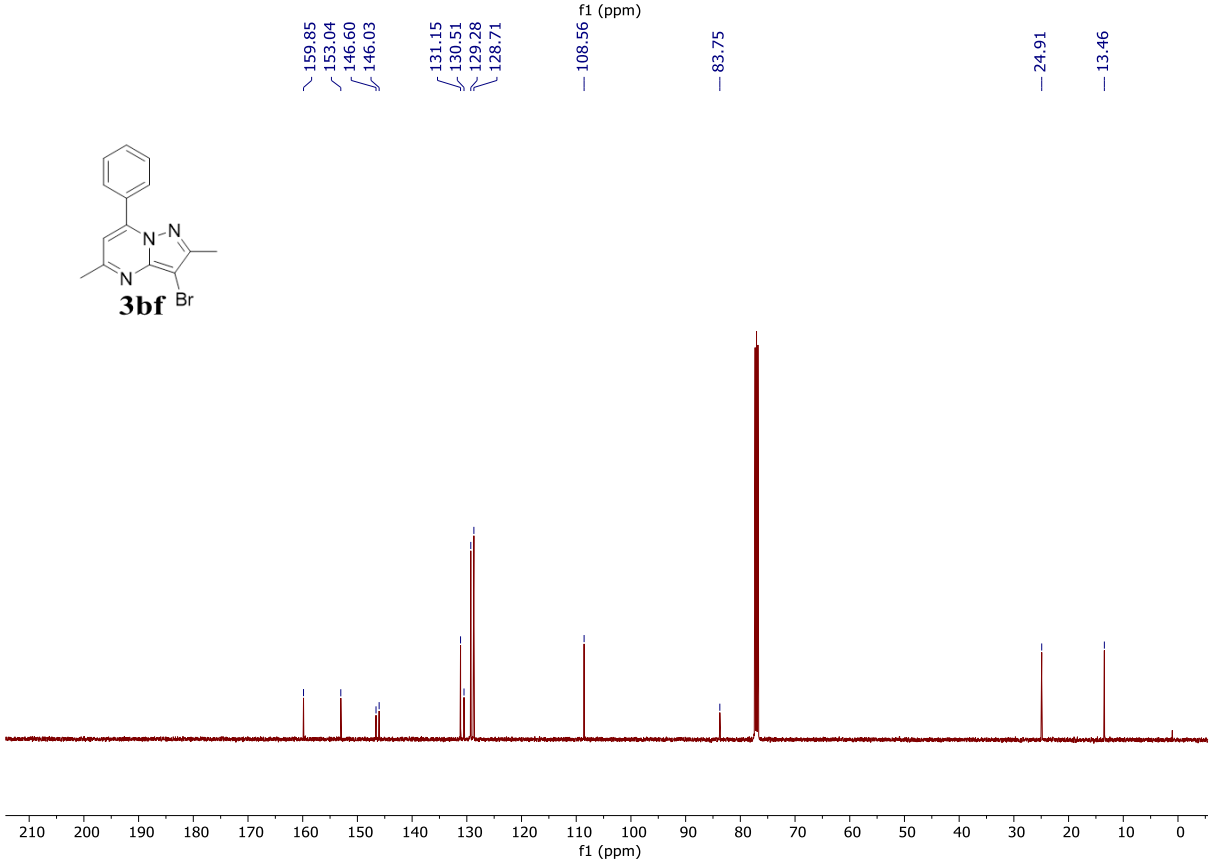

8.54
8.53
8.00
7.99
7.55
7.53
6.86
6.85
2.51
Cl
N
N
N
Br
3bd
1.00
2.07
2.02
1.00
3.07
f1 (ppm)

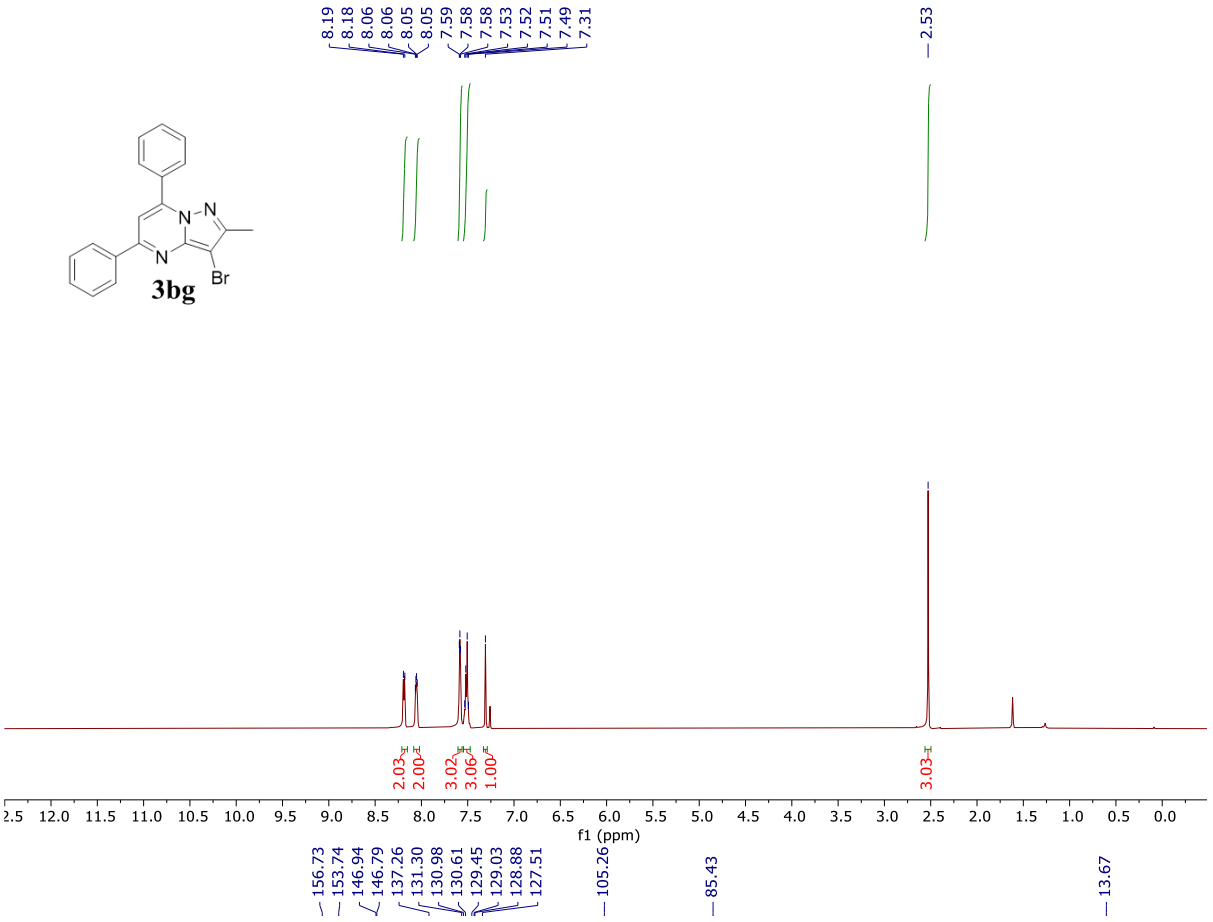

153.58
149.70
146.96
145.65
137.68
130.77
129.22
128.79
107.40
85.48
13.55
Cl
N
N
N
Br
3bd
f1 (ppm)

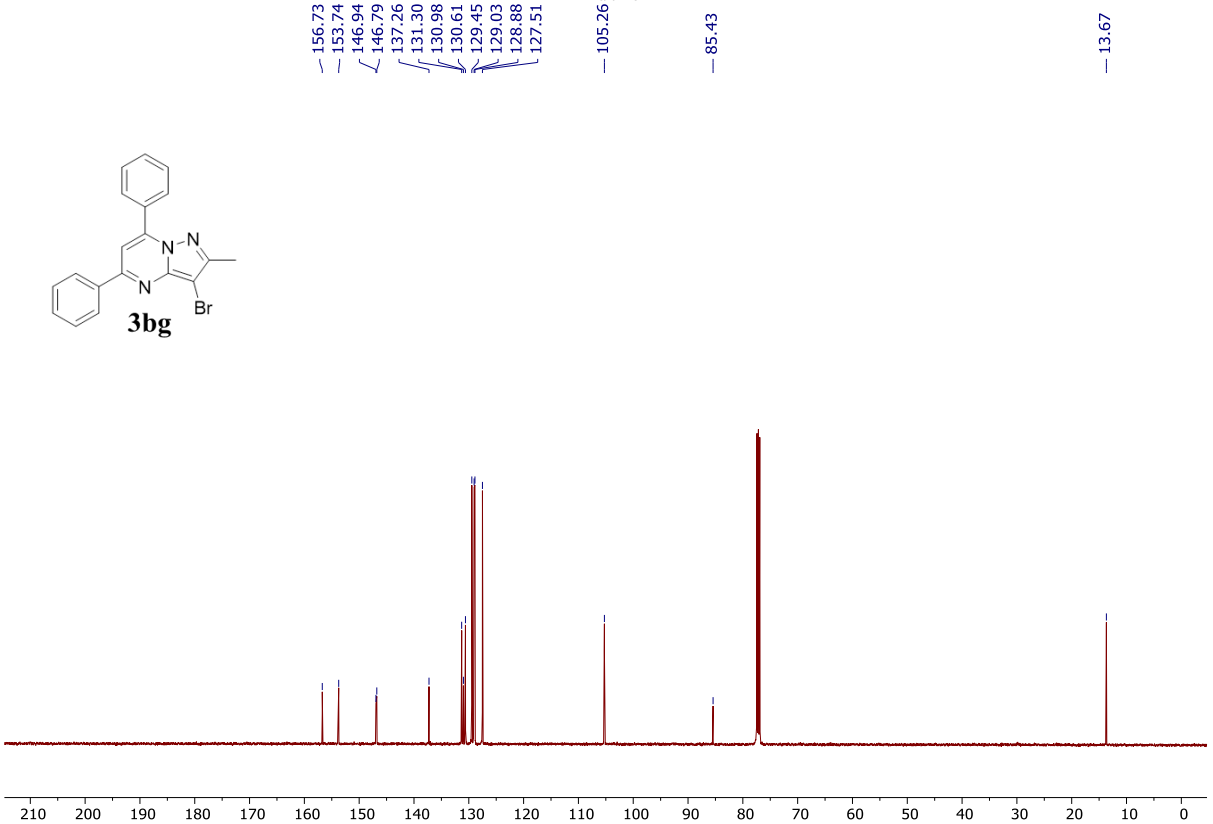

8.54
8.53
7.93
7.91
7.71
7.69
6.85
6.85
2.51
Br
N
N
N
Br
3be
1.00
2.04
2.03
1.02
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

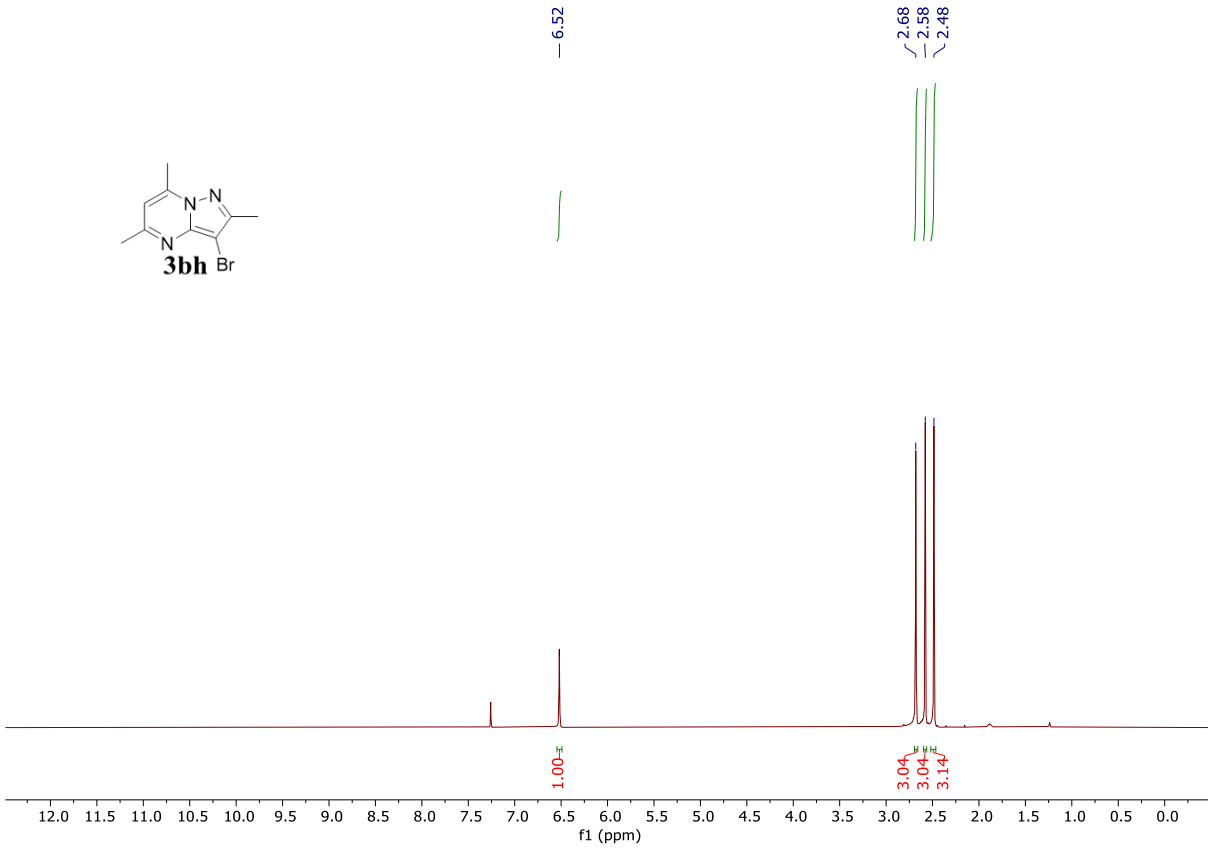

153.59
149.70
146.95
145.70
132.18
130.92
129.25
126.10
107.37
85.50
13.55
Br
N
N
N
Br
3be
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

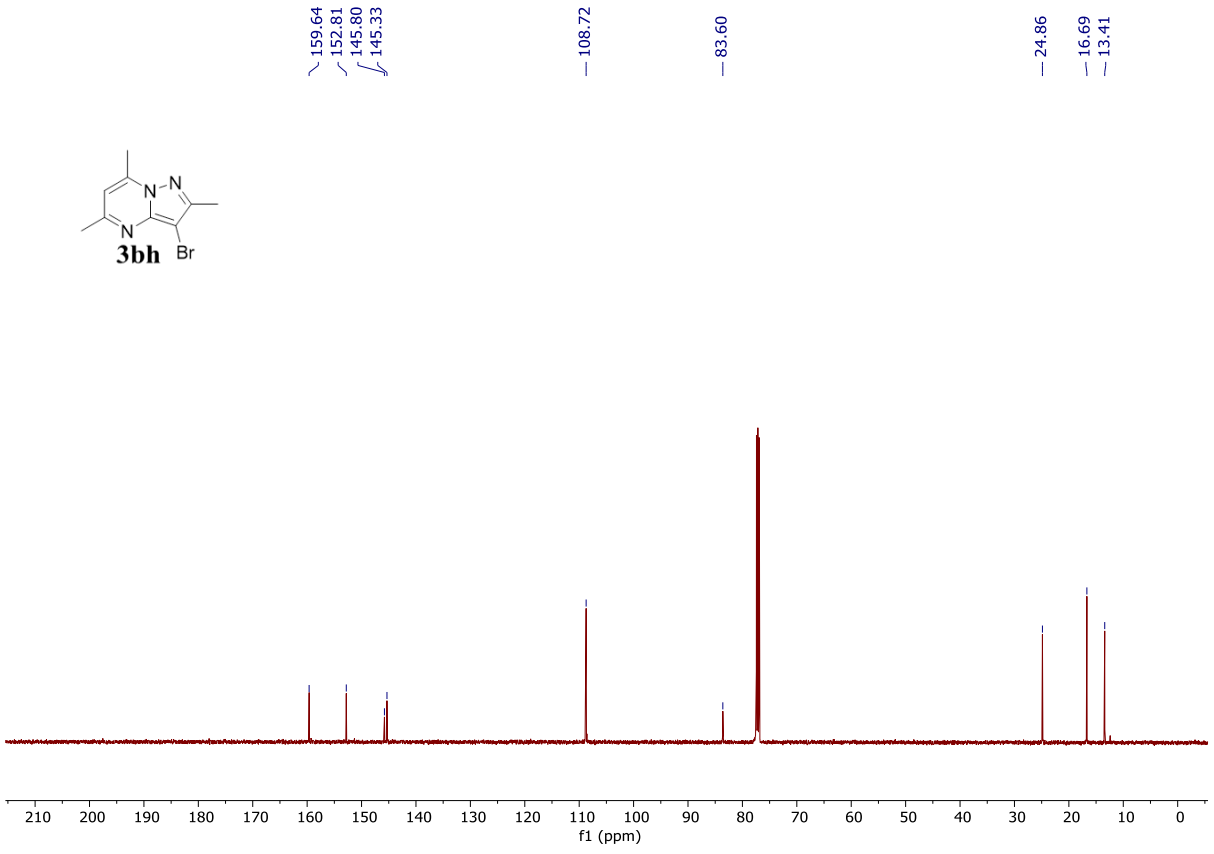

7.99
7.99
7.98
7.97
7.56
7.55
7.54
7.54
7.53
6.73
2.67
2.48
3bf
Br
2.00
3.00
1.02
3.05
3.04
f1 (ppm)


159.85
153.04
146.60
146.03
131.15
130.51
129.28
128.71
108.56
83.75
24.91
13.46
3bf
Br
f1 (ppm)


8.19
8.18
8.06
8.06
8.05
8.05
7.59
7.58
7.58
7.53
7.52
7.51
7.49
7.31
2.53
N
N
N
Br
3bg
2.03
2.00
3.02
3.06
1.00
3.03
f1 (ppm)


156.73
153.74
146.94
146.79
137.26
131.30
130.98
130.61
129.45
129.03
128.88
127.51
105.26
85.43
13.67
N
N
N
Br
3bg
f1 (ppm)


6.52
2.68
2.58
2.48
3bh Br
1.00
3.04
3.04
3.14
f1 (ppm)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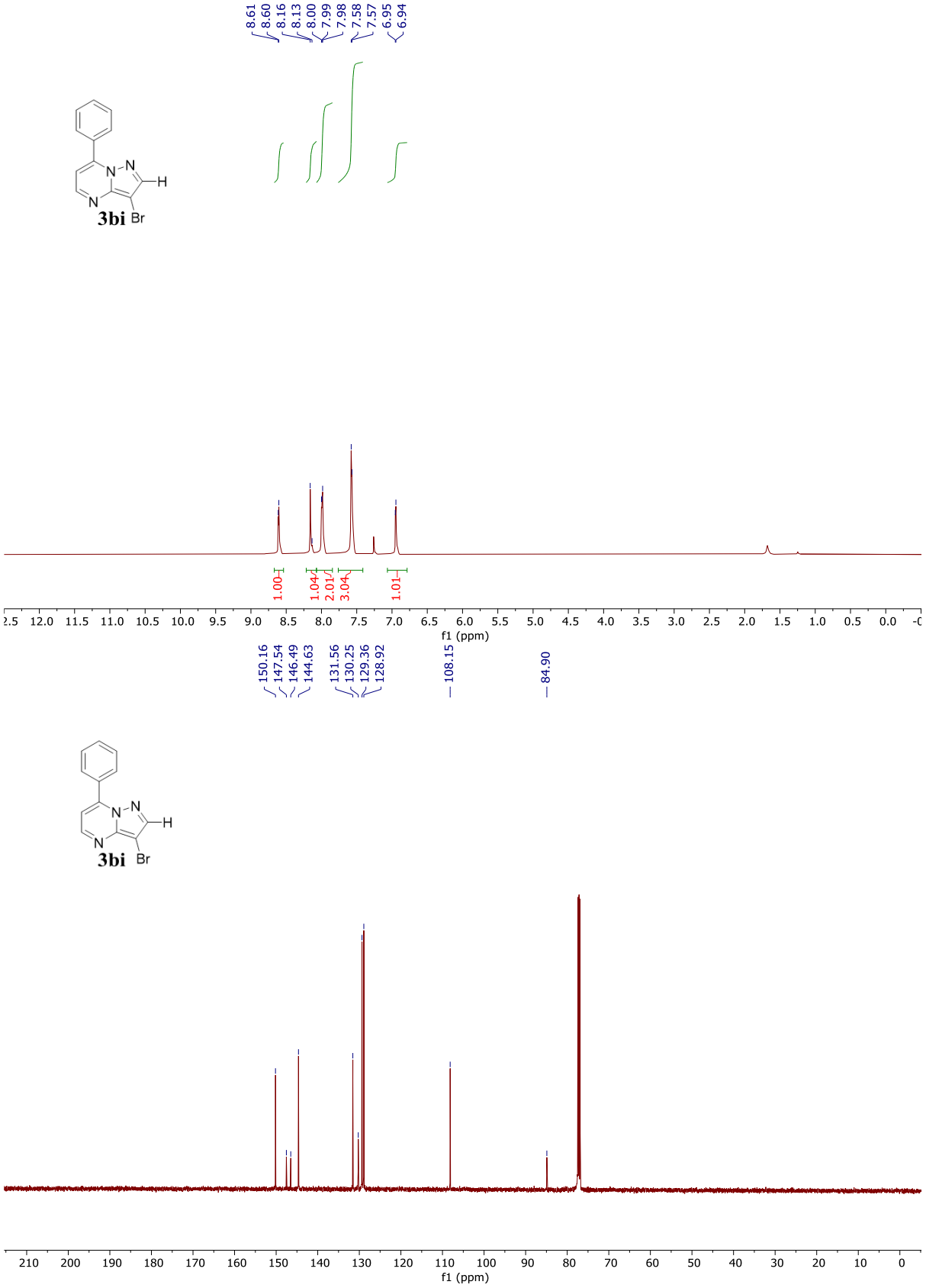
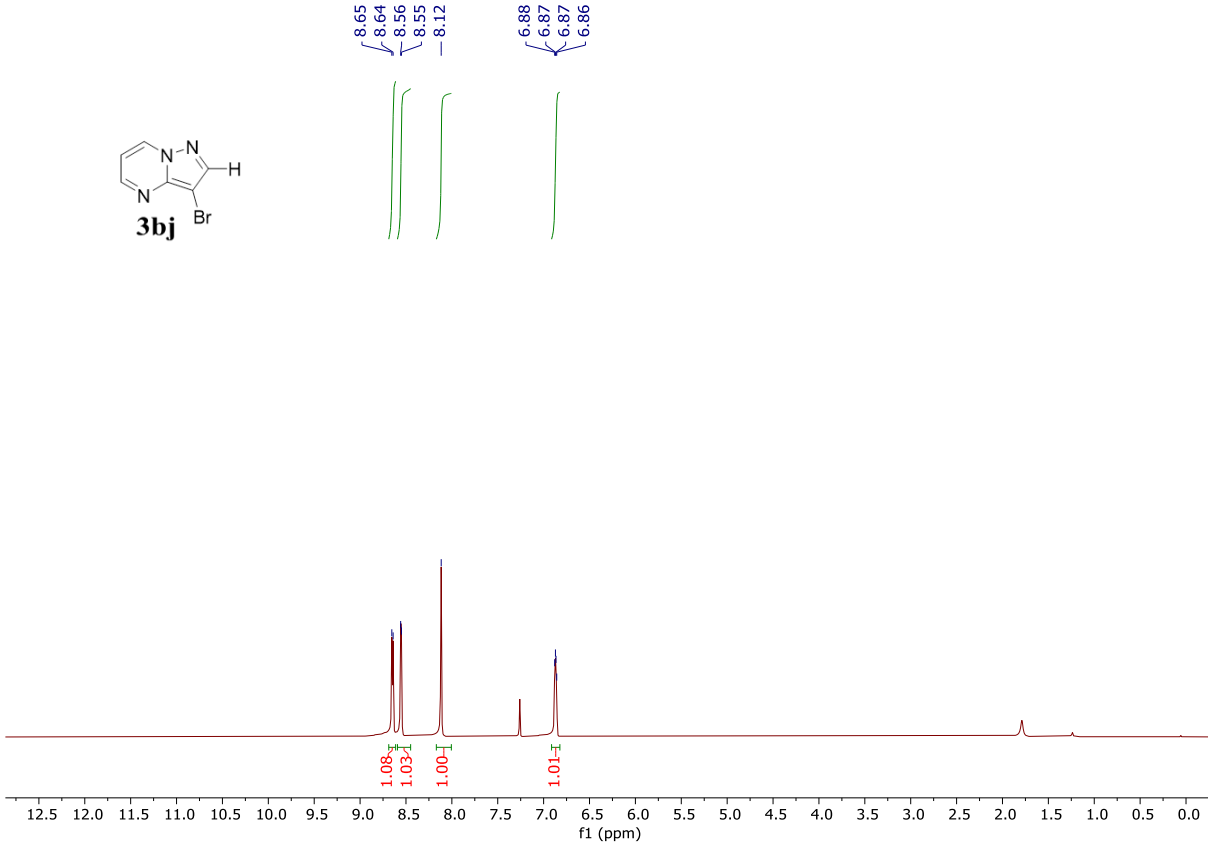
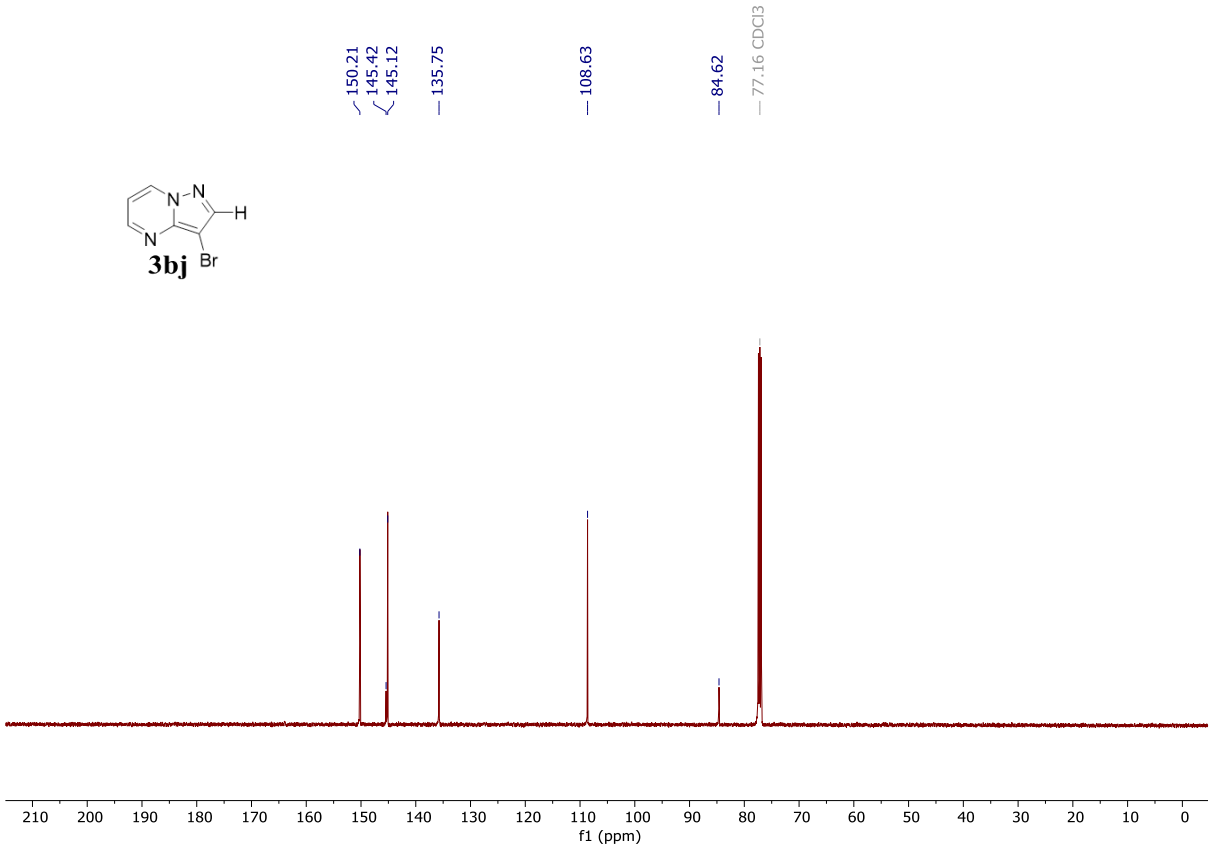
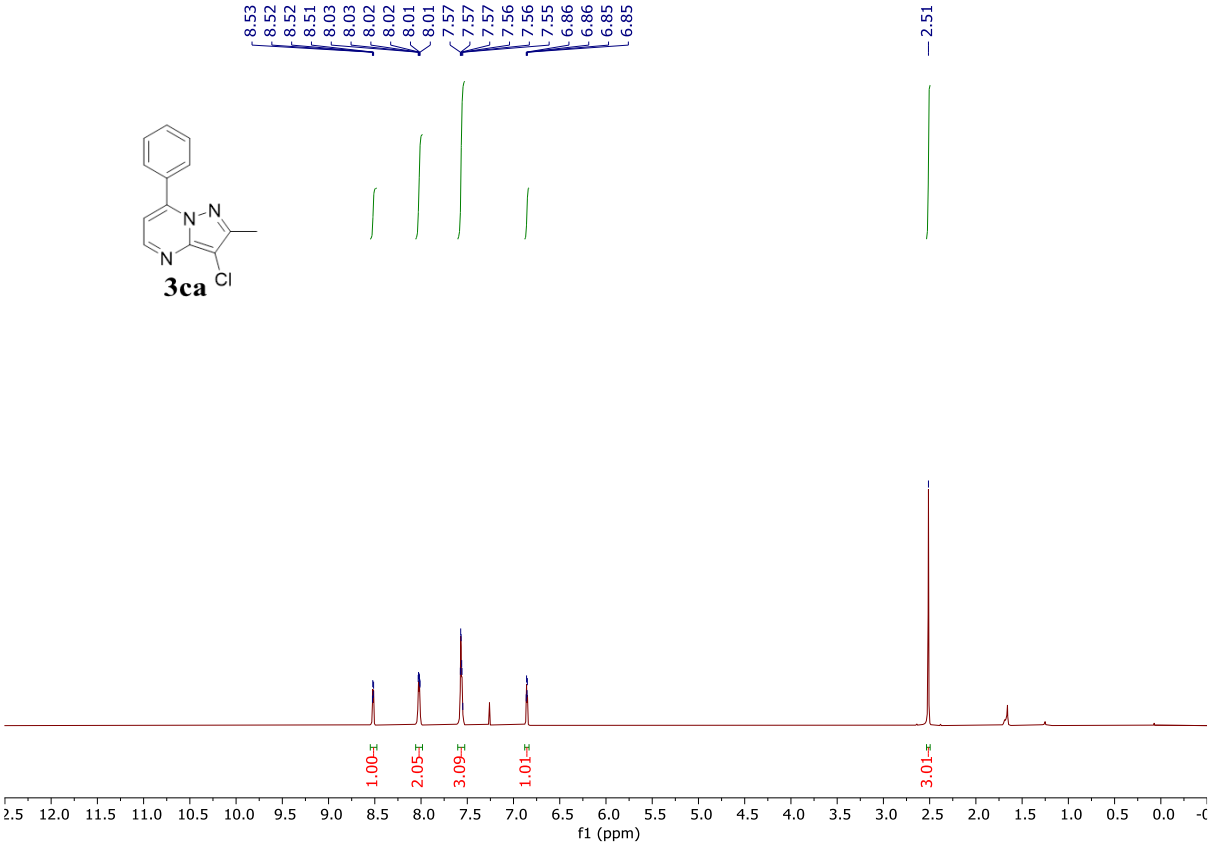
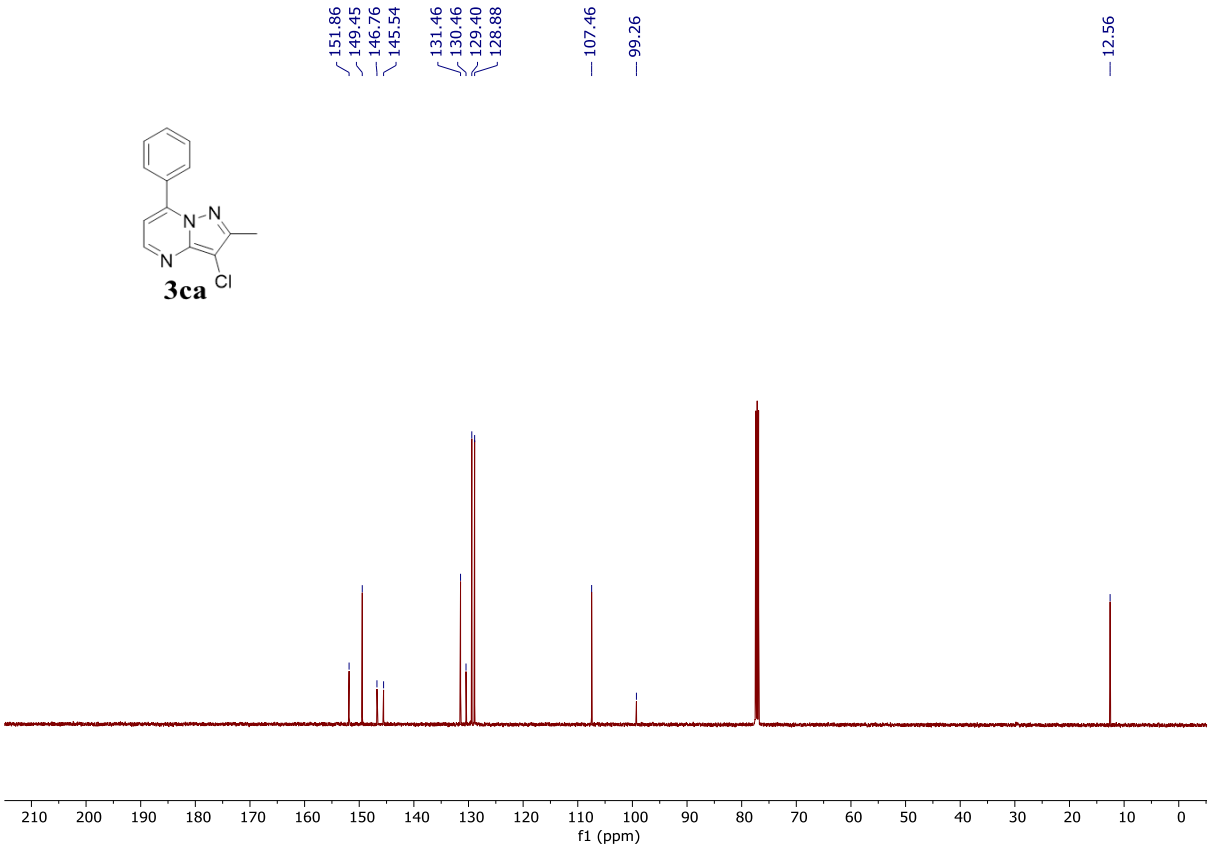
145.33
108.72
83.60
24.86
16.69
13.41
3bh Br
f1 (ppm)


8.61
8.60
8.16
8.13
8.00
7.99
7.98
7.58
7.57
6.95
6.94
3bi Br
1.00
1.04
2.01
3.04
1.01
f1 (ppm)
150.16
147.54
146.49
144.63
131.56
130.25
129.36
128.92
108.15
84.90
3bi Br
f1 (ppm)


8.65
8.64
8.56
8.55
8.12
6.88
6.87
6.87
6.86
3bj
Br
1.08
1.03
1.00
1.01
12.5 12.0 11.5 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)


150.21
145.42
145.12
135.75
108.63
84.62
77.16 CDCl3
3bj
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.53
8.52
8.52
8.51
8.03
8.03
8.02
8.02
8.01
8.01
7.57
7.57
7.57
7.56
7.56
7.55
6.86
6.86
6.85
6.85
2.51
N
N
N
Cl
3ca
1.00
2.05
3.09
1.01
3.01
f1 (ppm)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149.45
146.76
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131.46
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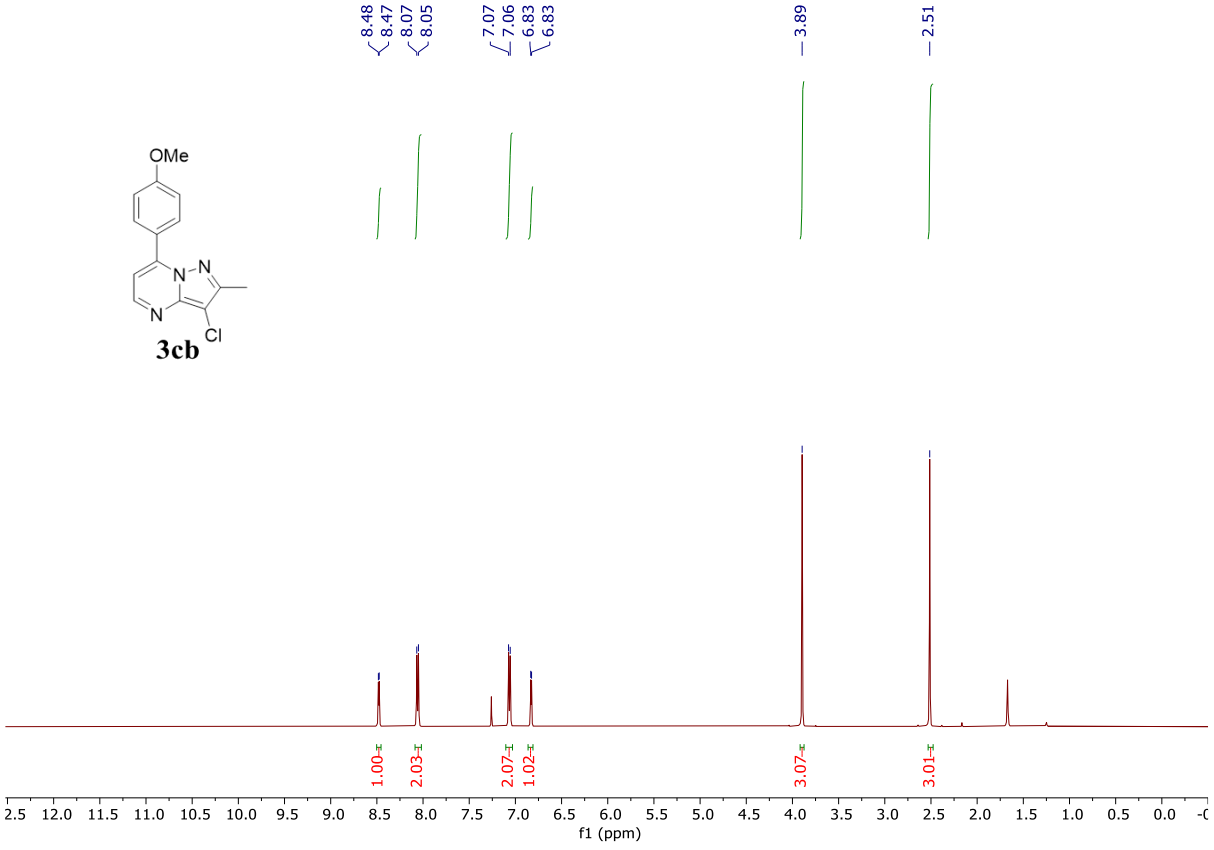
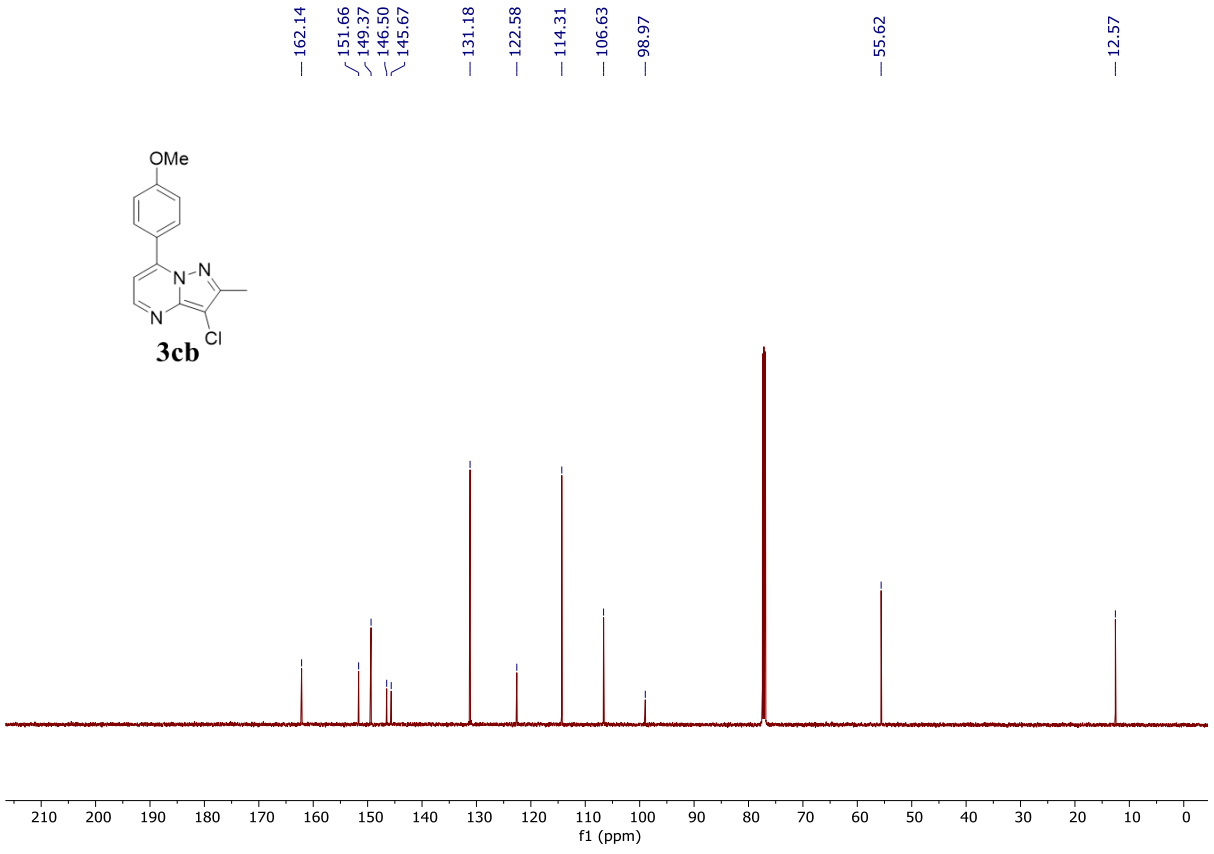
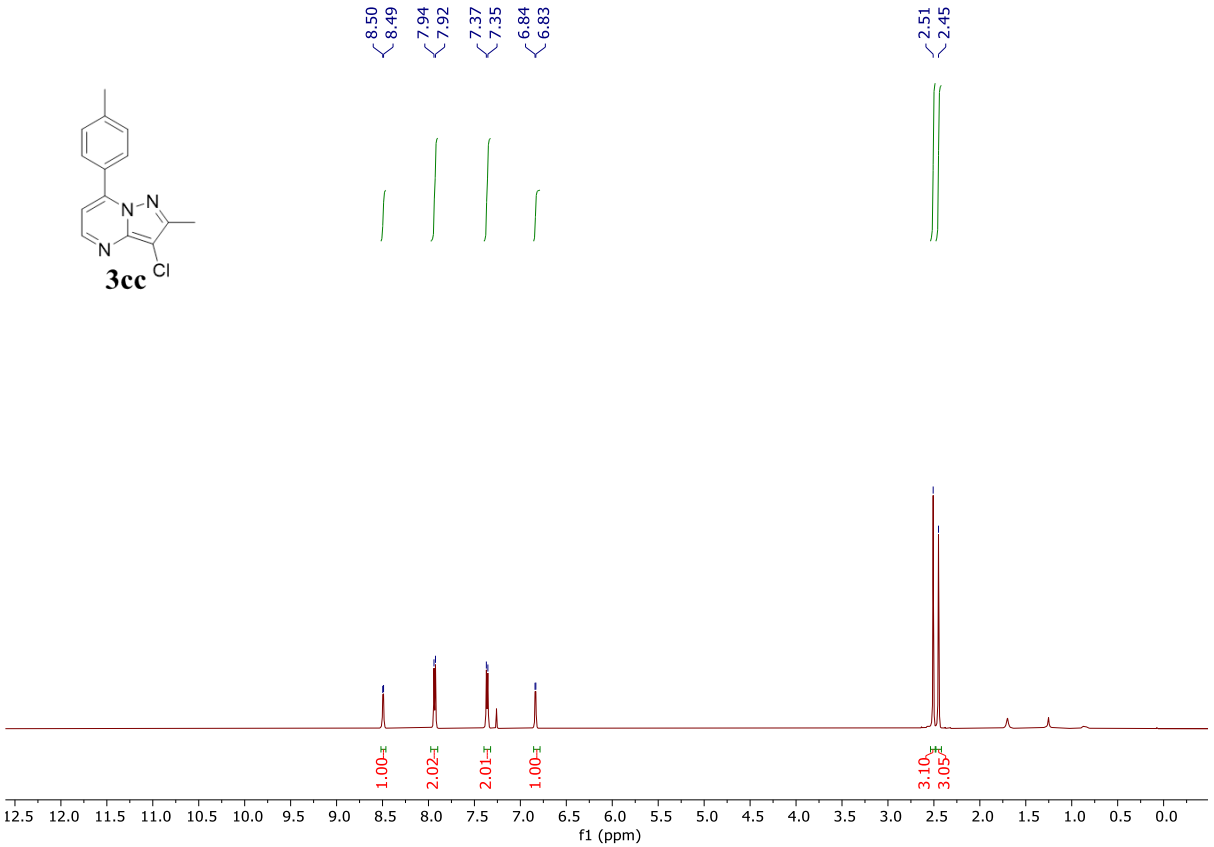
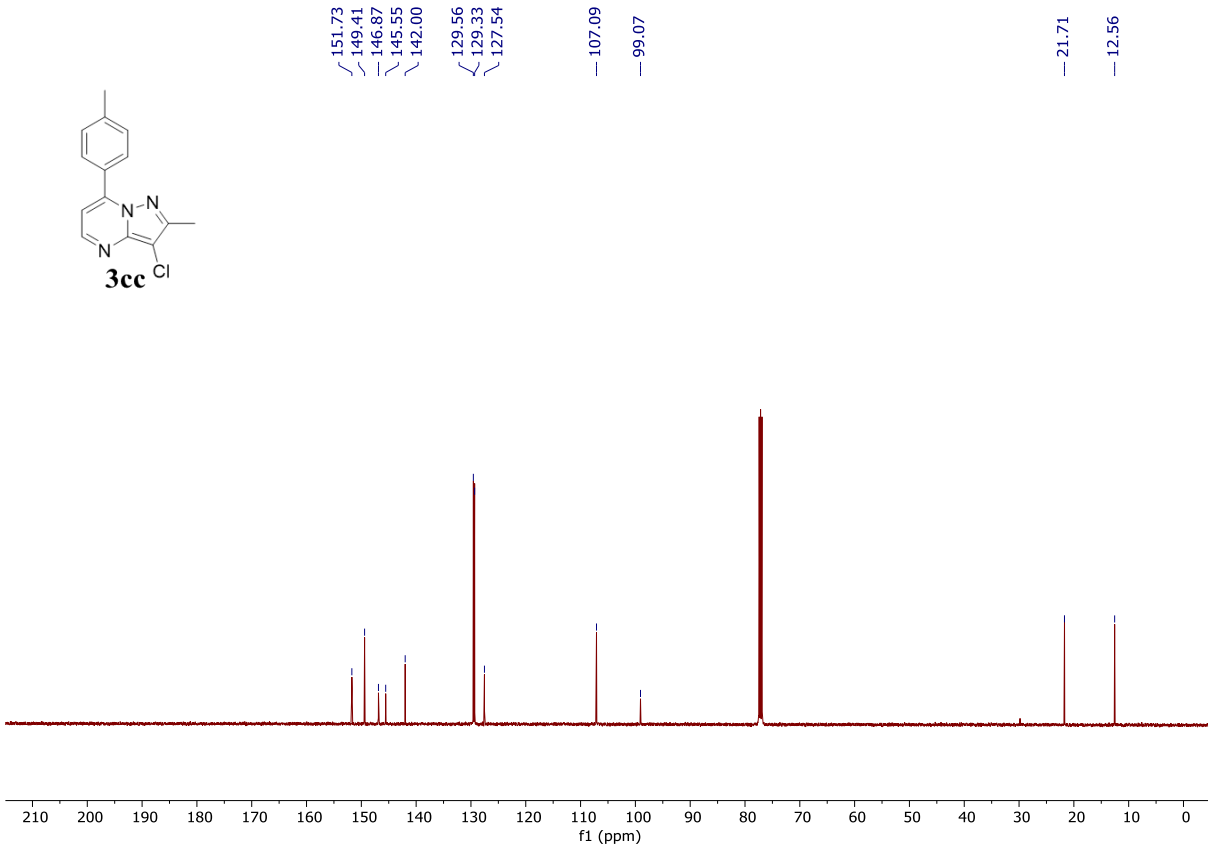
129.40
128.88
107.46
99.26
12.56
N
N
N
Cl
3ca
f1 (ppm)


8.48
8.47
8.07
8.05
7.07
7.06
6.83
6.83
3.89
2.51
OMe
N
N
N
Cl
3cb
1.00
2.03
2.07
1.02
3.07
3.01
f1 (ppm)


162.14
151.66
149.37
146.50
145.67
131.18
122.58
114.31
106.63
98.97
55.62
12.57
OMe
N
N
N
Cl
3cb
f1 (ppm)


8.50
8.49
7.94
7.92
7.37
7.35
6.84
6.83
2.51
2.45
3cc
Cl
1.00
2.02
2.01
1.00
3.10
3.05
f1 (ppm)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146.87
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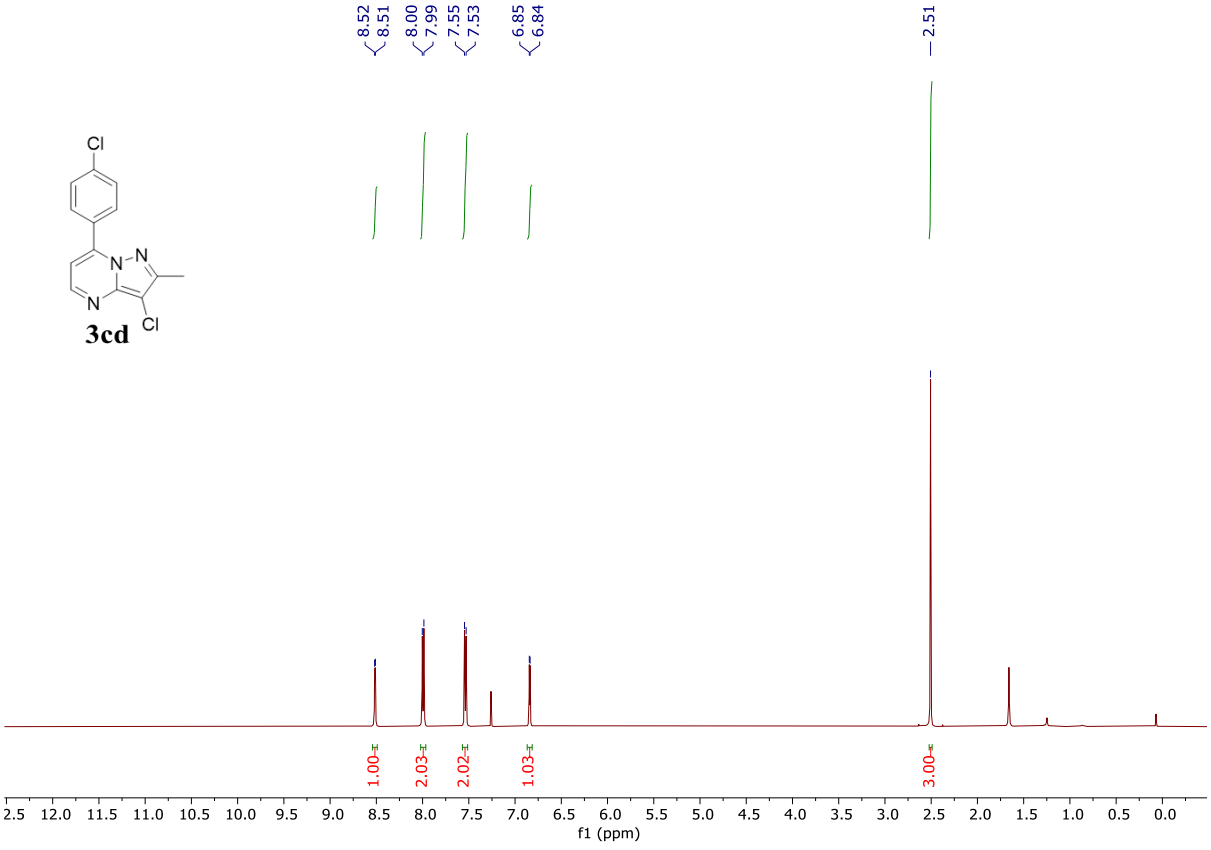
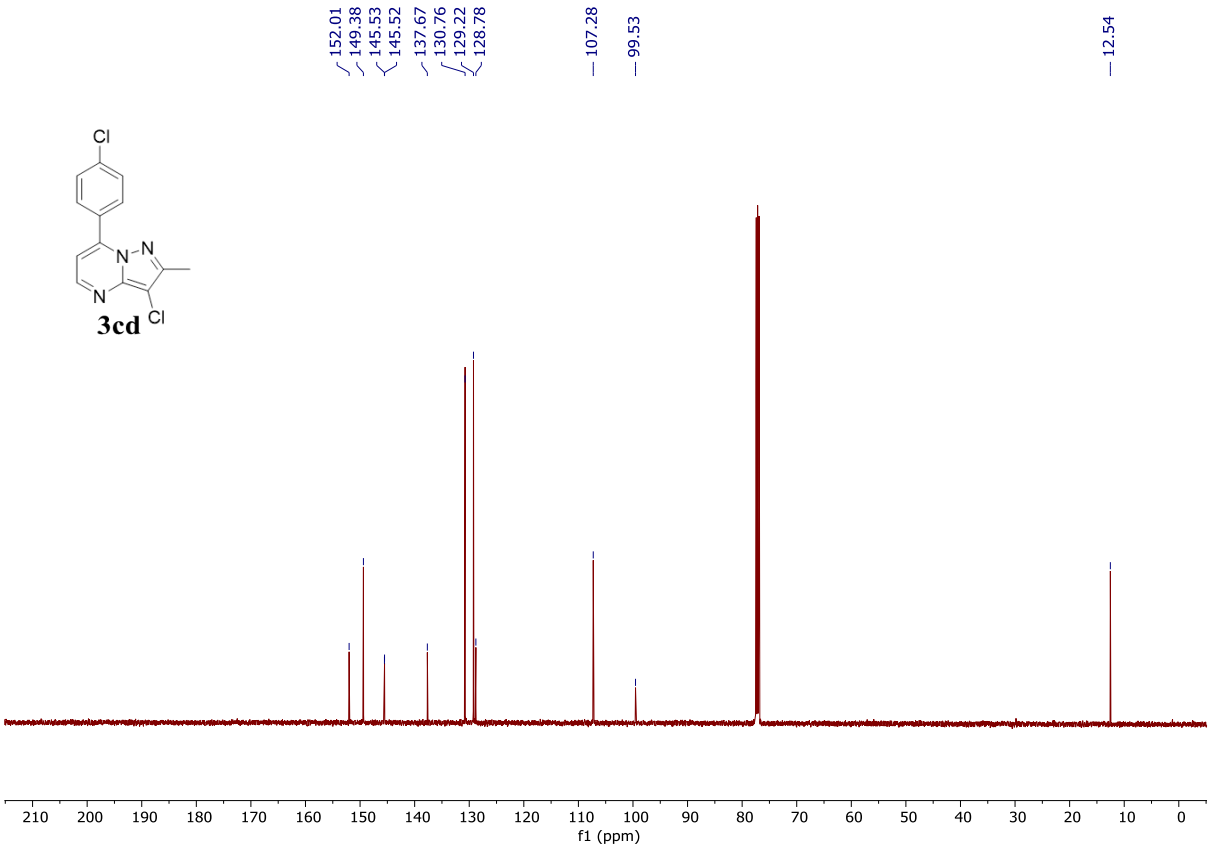
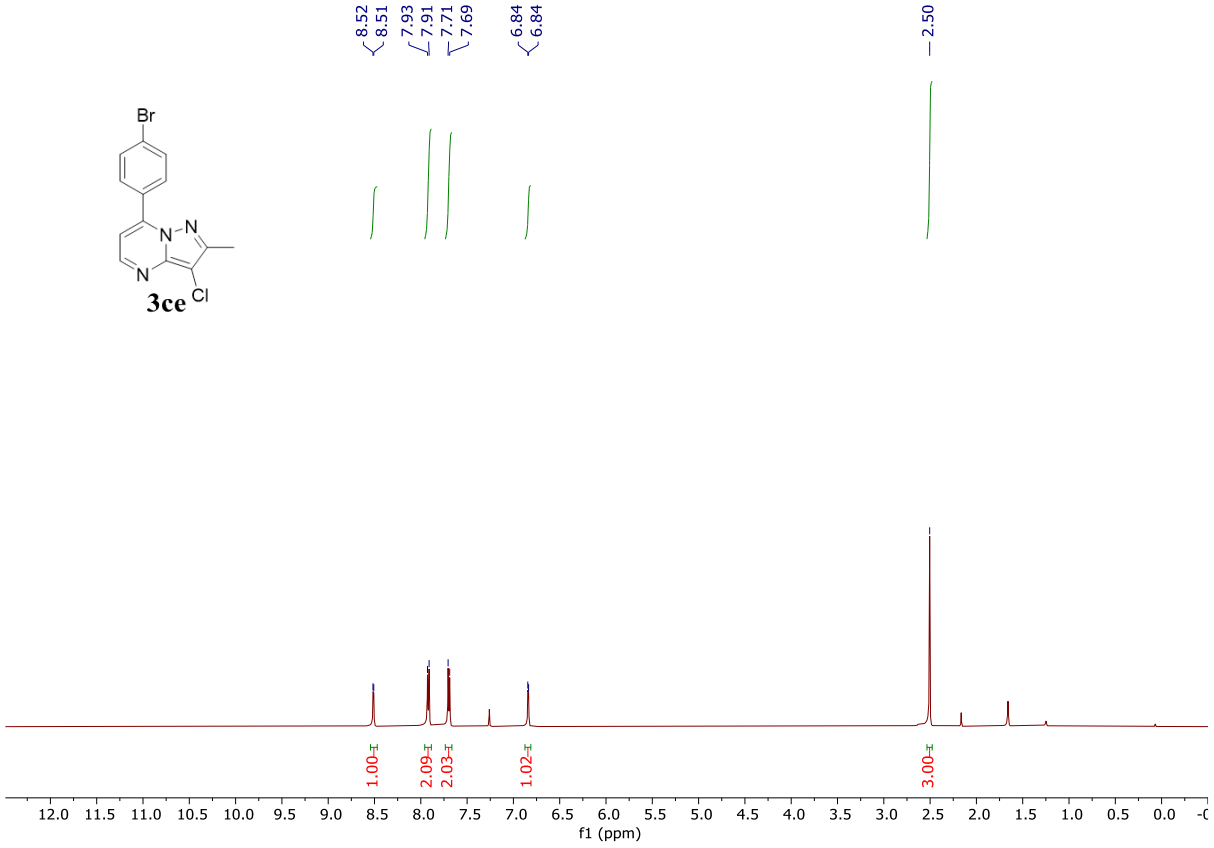
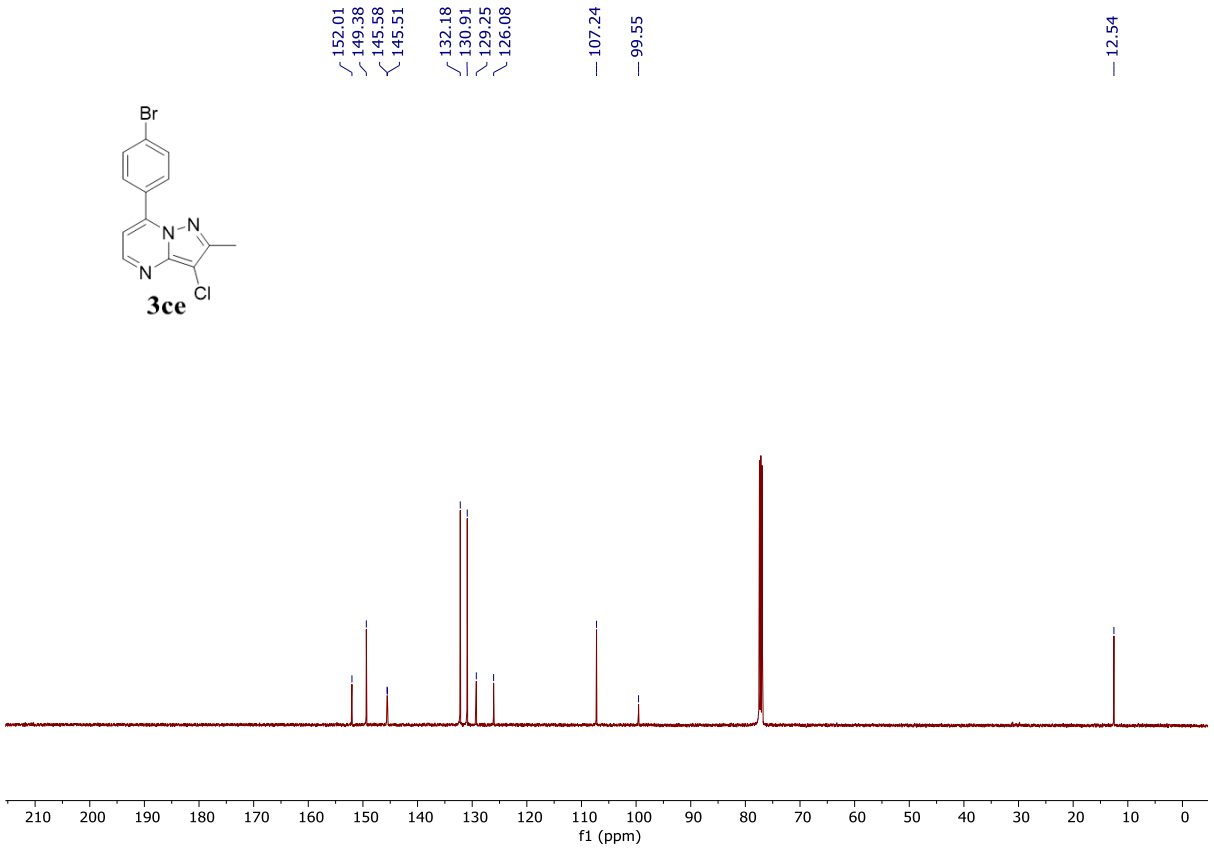
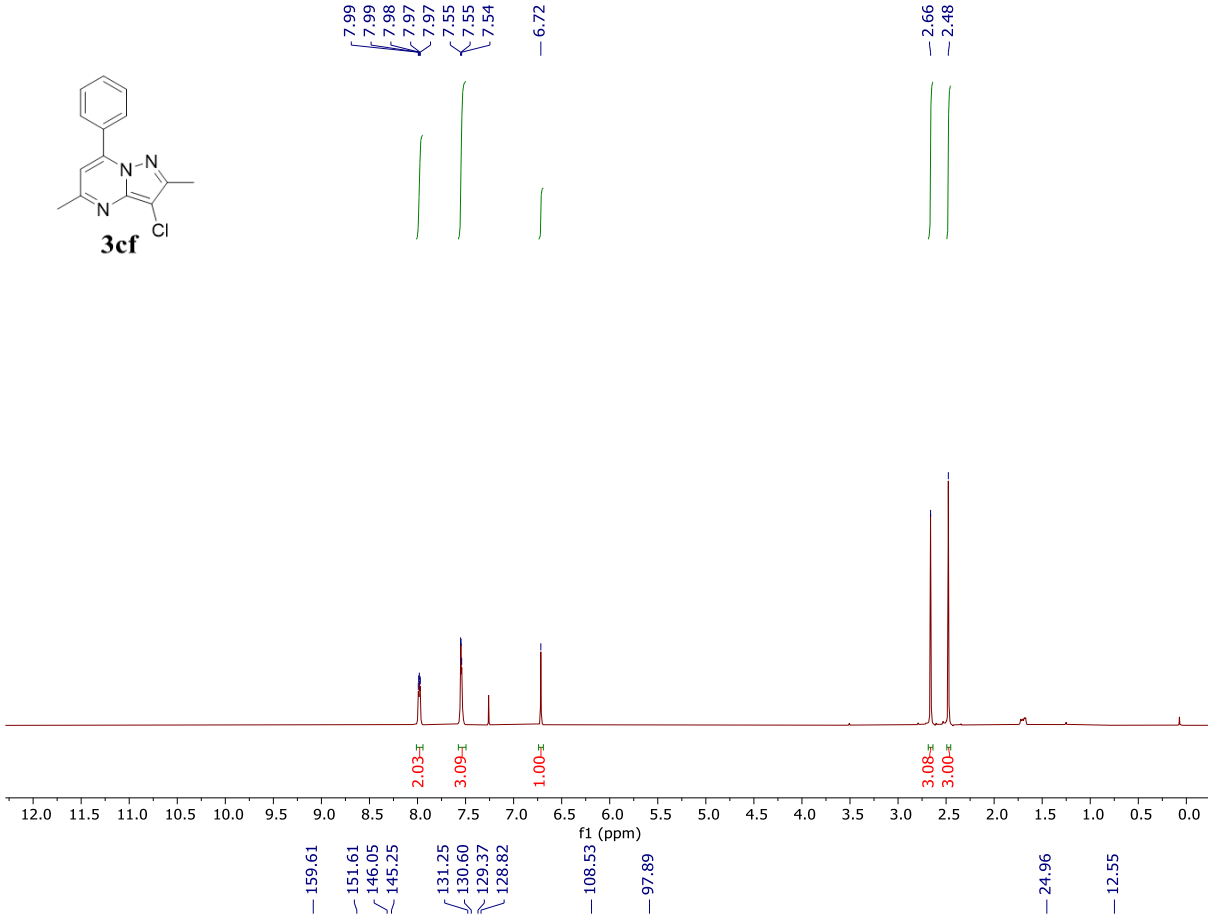
142.00
129.56
129.33
127.54
107.09
99.07
21.71
12.56
3cc
Cl
f1 (ppm)

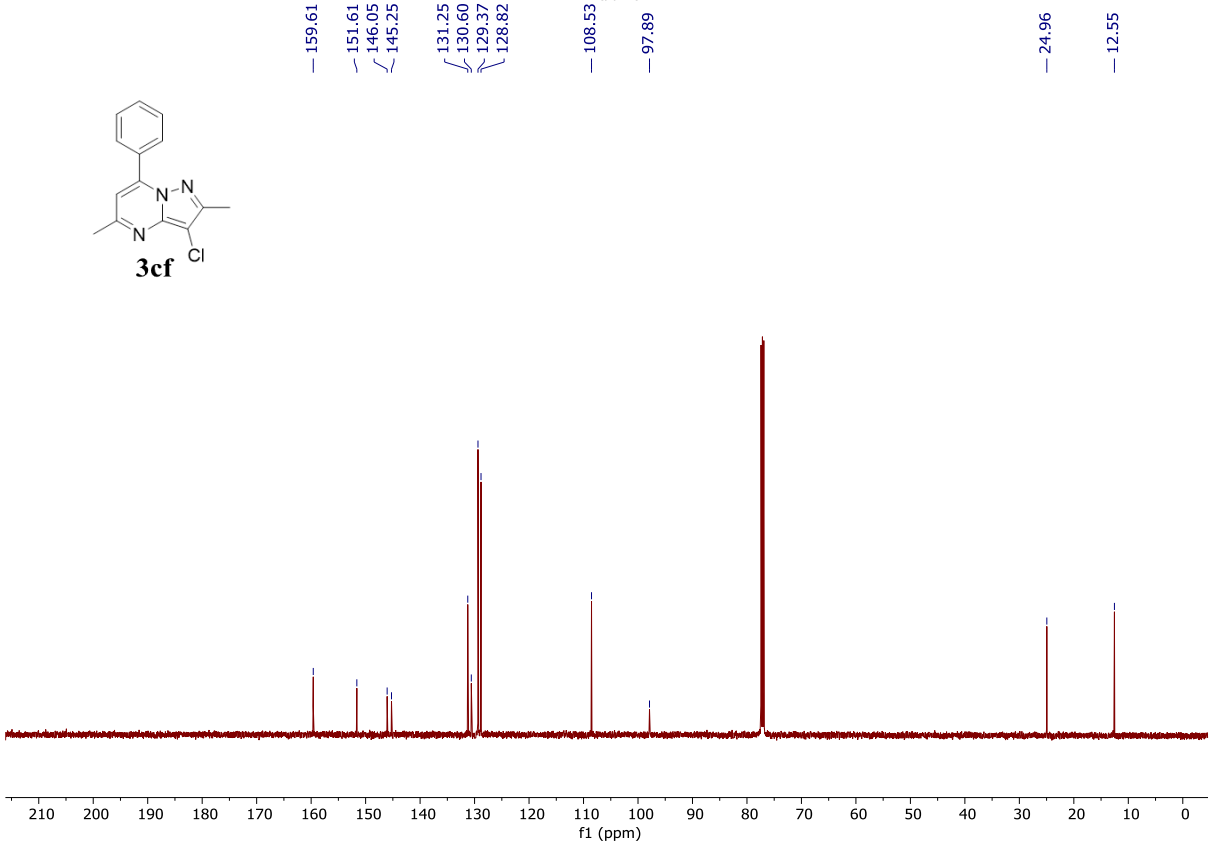

8.52
8.51
8.00
7.99
7.55
7.53
6.85
6.84
2.51
Cl
N
N
N
Cl
3cd
1.00
2.03
2.02
1.03
3.00
f1 (ppm)

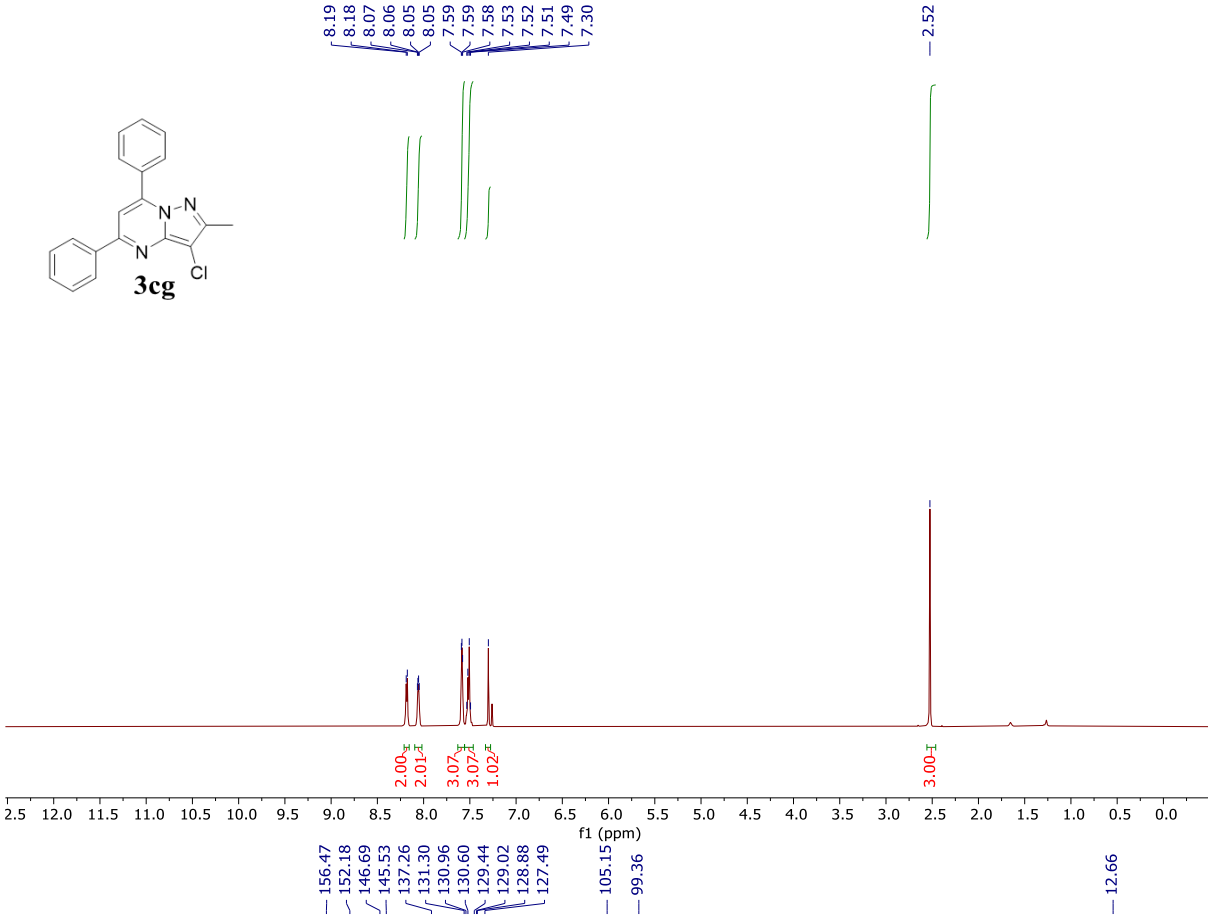

152.01
149.38
145.53
145.52
137.67
130.76
129.22
128.78
107.28
99.53
12.54
Cl
N
N
N
Cl
3cd
f1 (ppm)

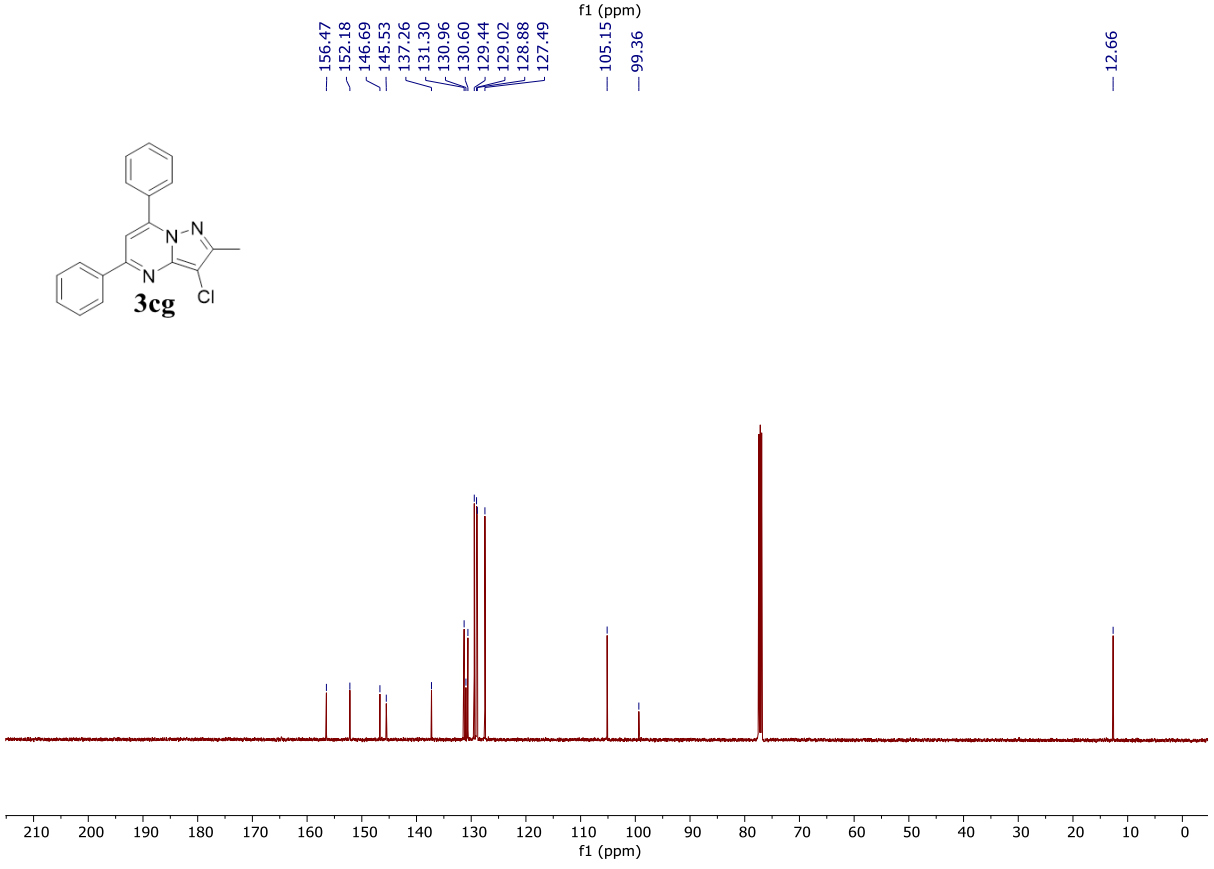

8.52
8.51
7.93
7.91
7.71
7.69
6.84
6.84
2.50
Br
N
N
N
Cl
3ce
1.00
2.09
2.03
1.02
3.00
f1 (ppm)

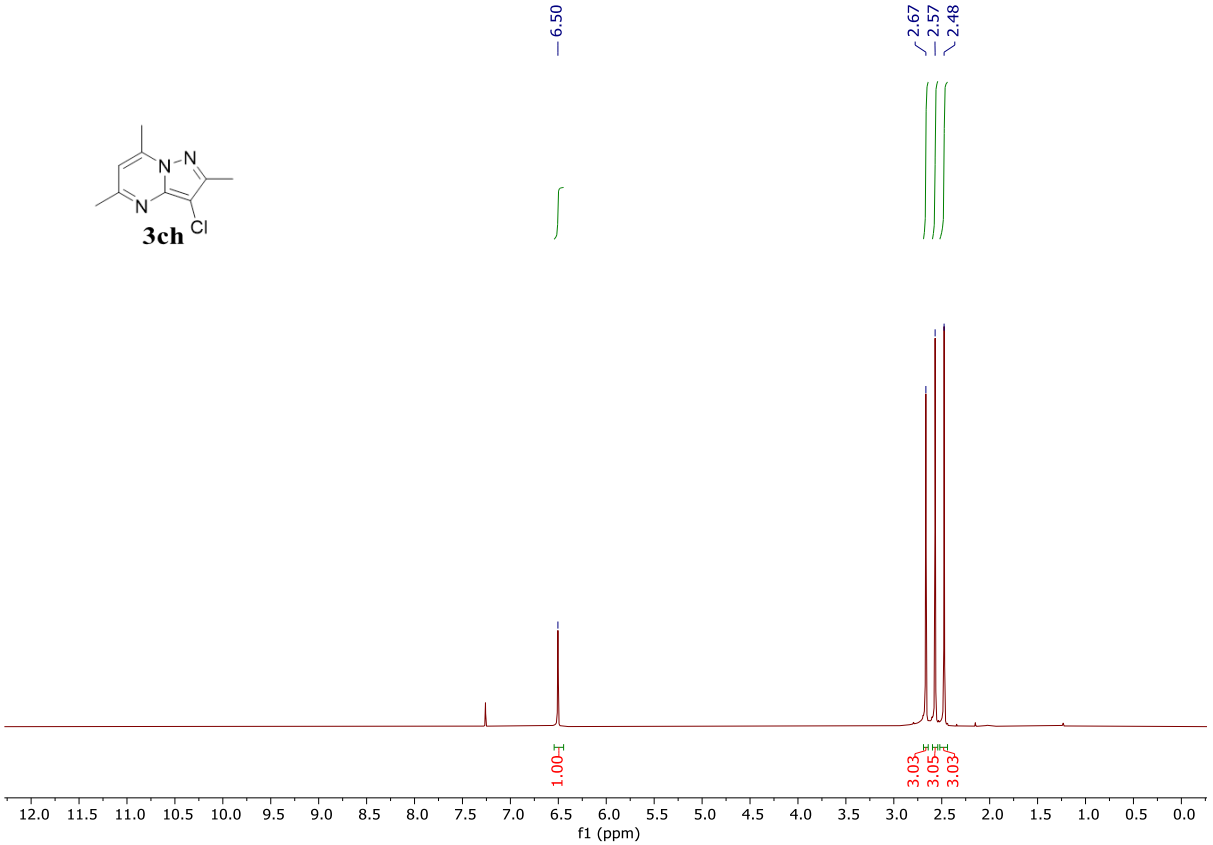

152.01
149.38
145.58
145.51
132.18
130.91
129.25
126.08
107.24
99.55
12.54
Br
N
N
N
Cl
3ce
f1 (ppm)

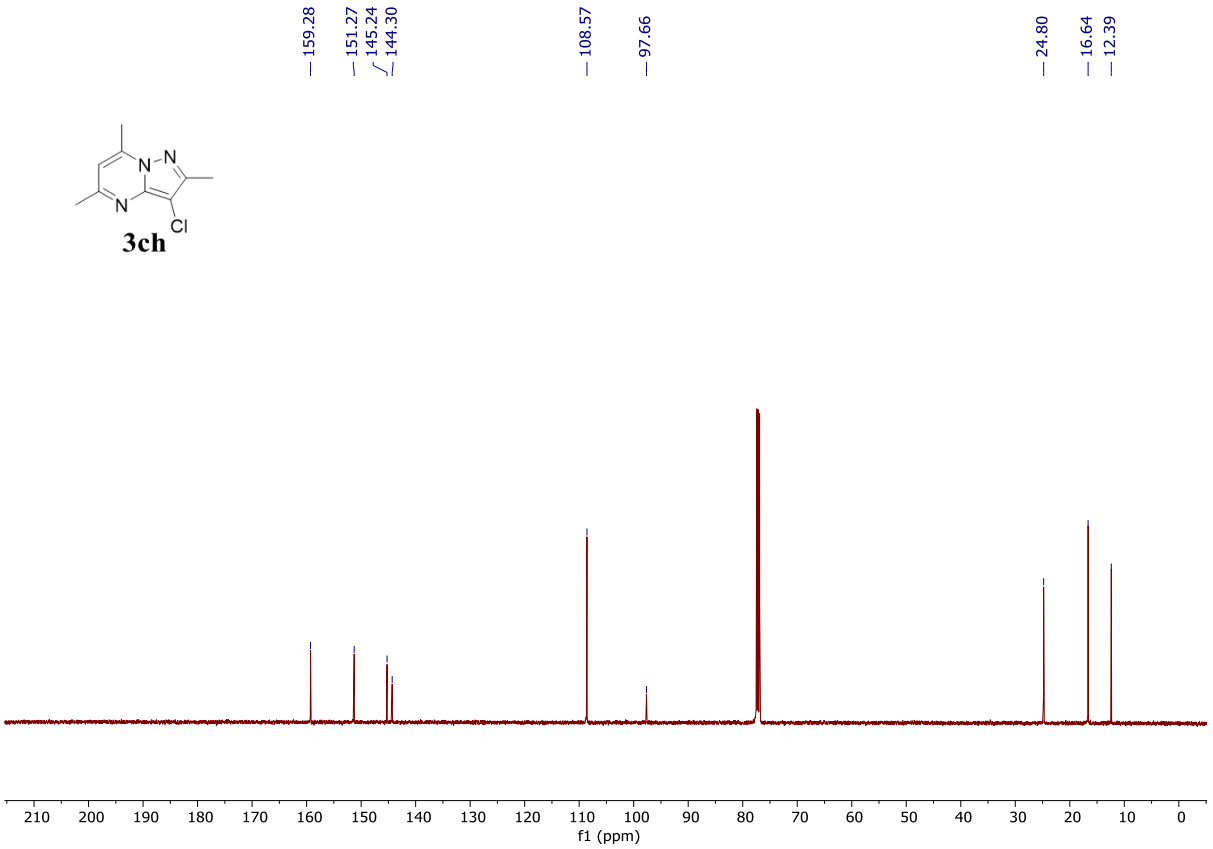

7.99
7.99
7.98
7.97
7.97
7.55
7.55
7.54
6.72
2.66
2.48
3cf
Cl
2.03
3.09
1.00
3.08
3.00
f1 (ppm)

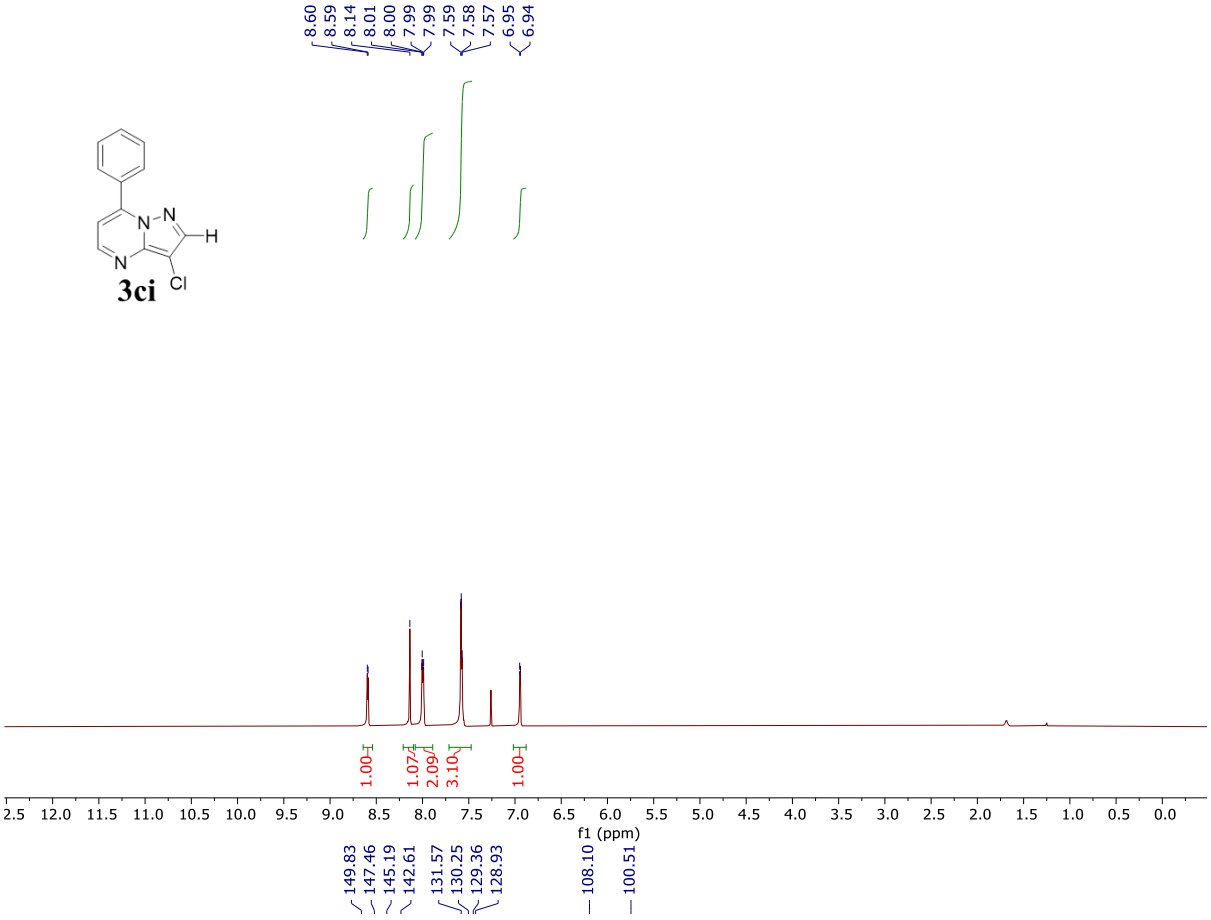

159.61
151.61
146.05
145.25
131.25
130.60
129.37
128.82
108.53
97.89
24.96
12.55
3cf
Cl
f1 (ppm)

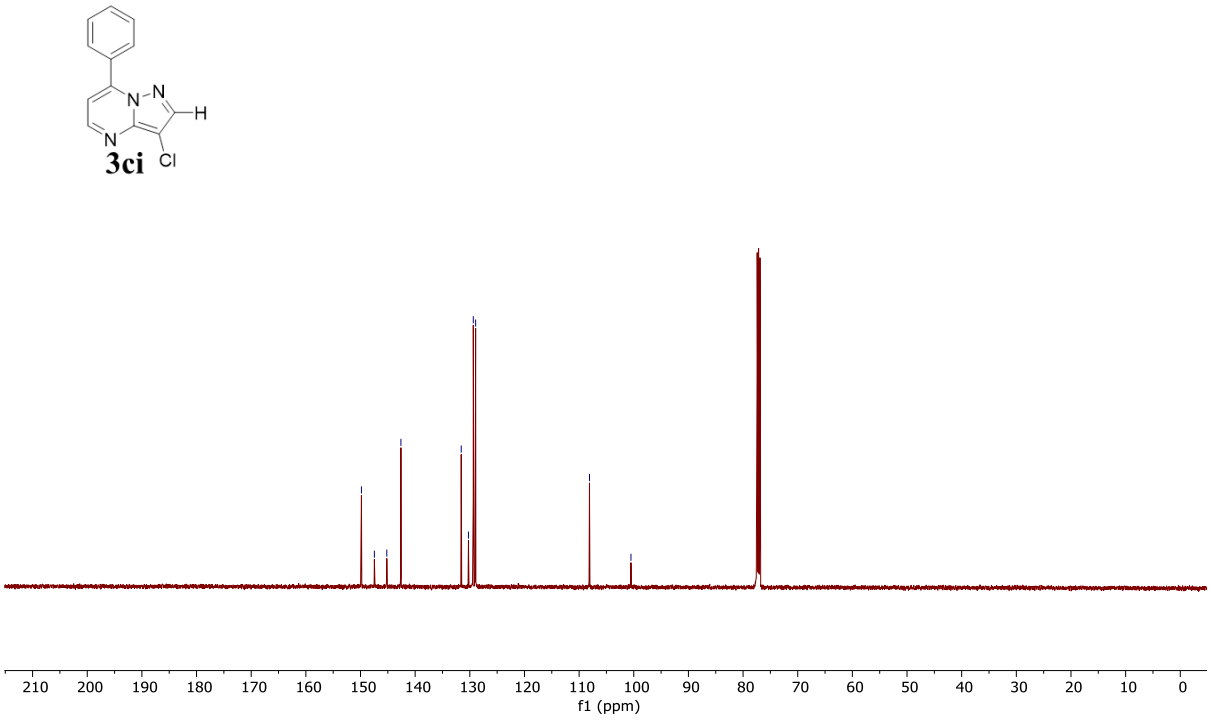

8.19
8.18
8.07
8.06
8.05
8.05
7.59
7.59
7.58
7.53
7.52
7.51
7.49
7.30
2.52
N
N
N
Cl
3cg
2.00
2.01
3.07
3.07
1.02
3.00
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

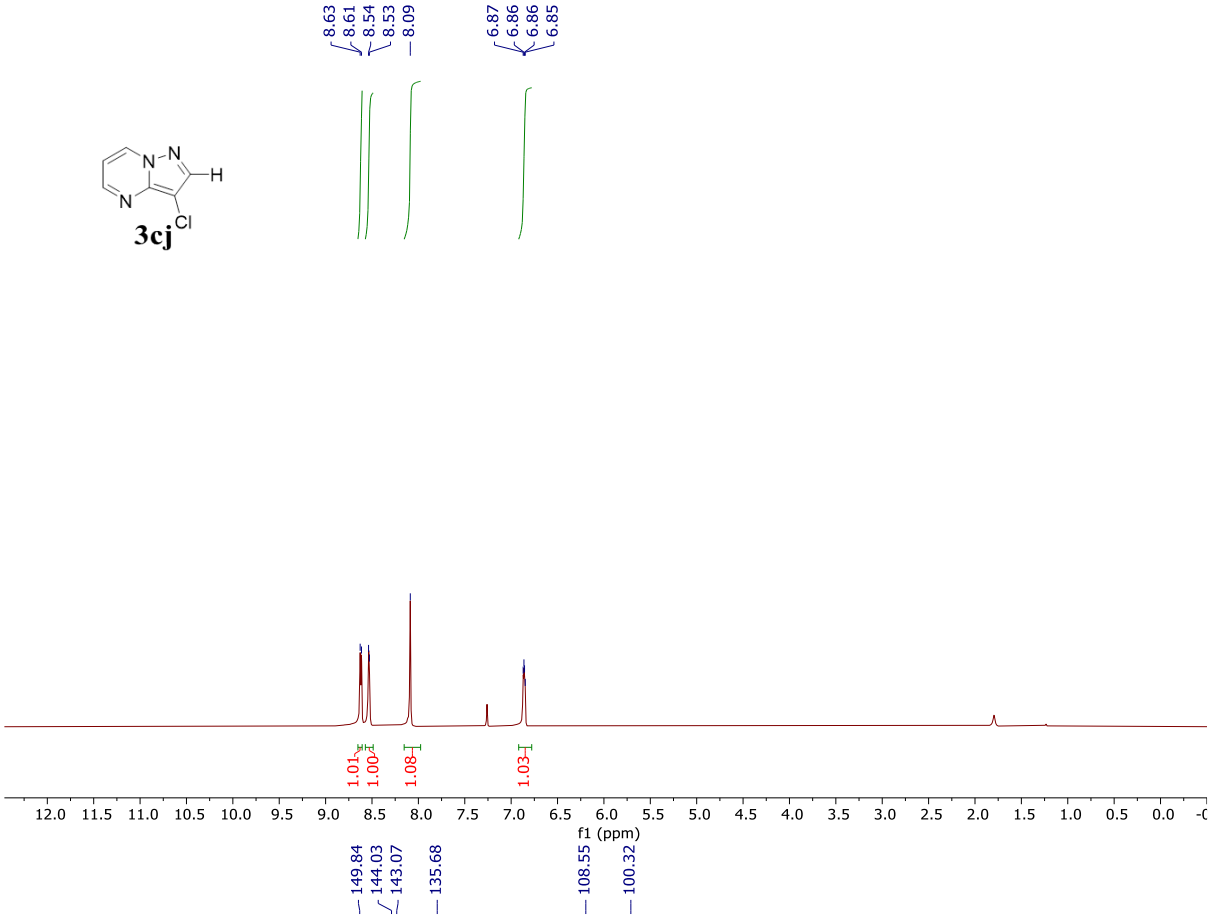

156.47
152.18
146.69
145.53
137.26
131.30
130.96
130.60
129.44
129.02
128.88
127.49
105.15
99.36
12.66
N
N
N
Cl
3cg
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

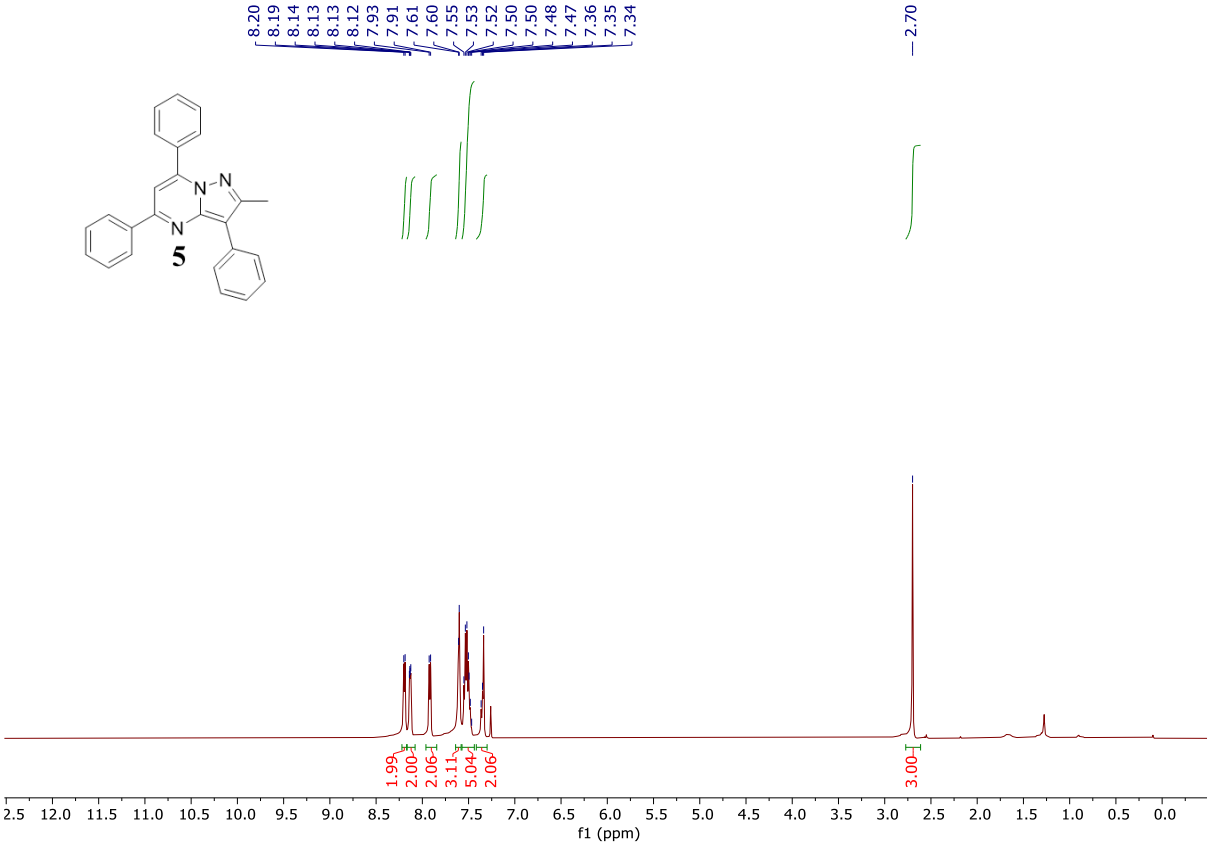

6.50
2.67
2.57
2.48
3ch
Cl
1.00
3.03
3.05
3.03
f1 (ppm)

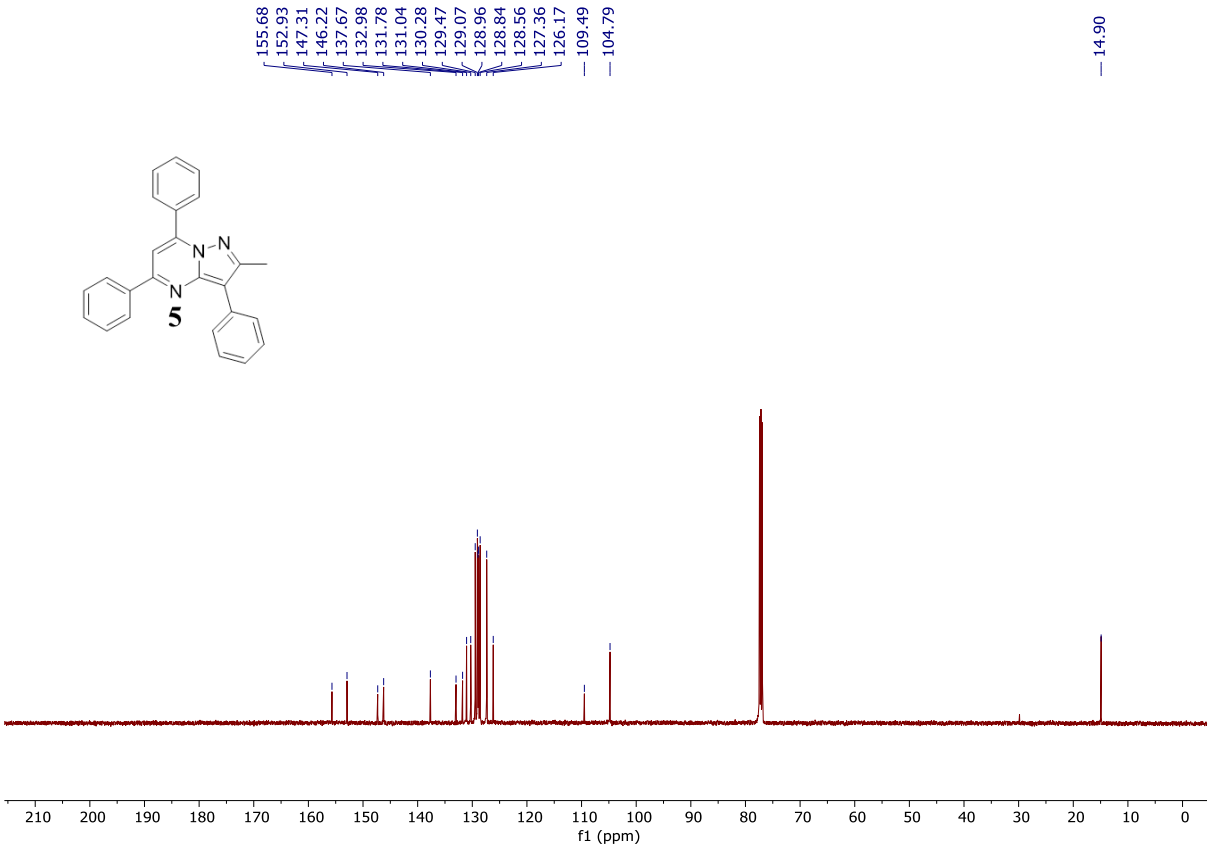

159.28
151.27
145.24
144.30
108.57
97.66
24.80
16.64
12.39
3ch
Cl
f1 (ppm)

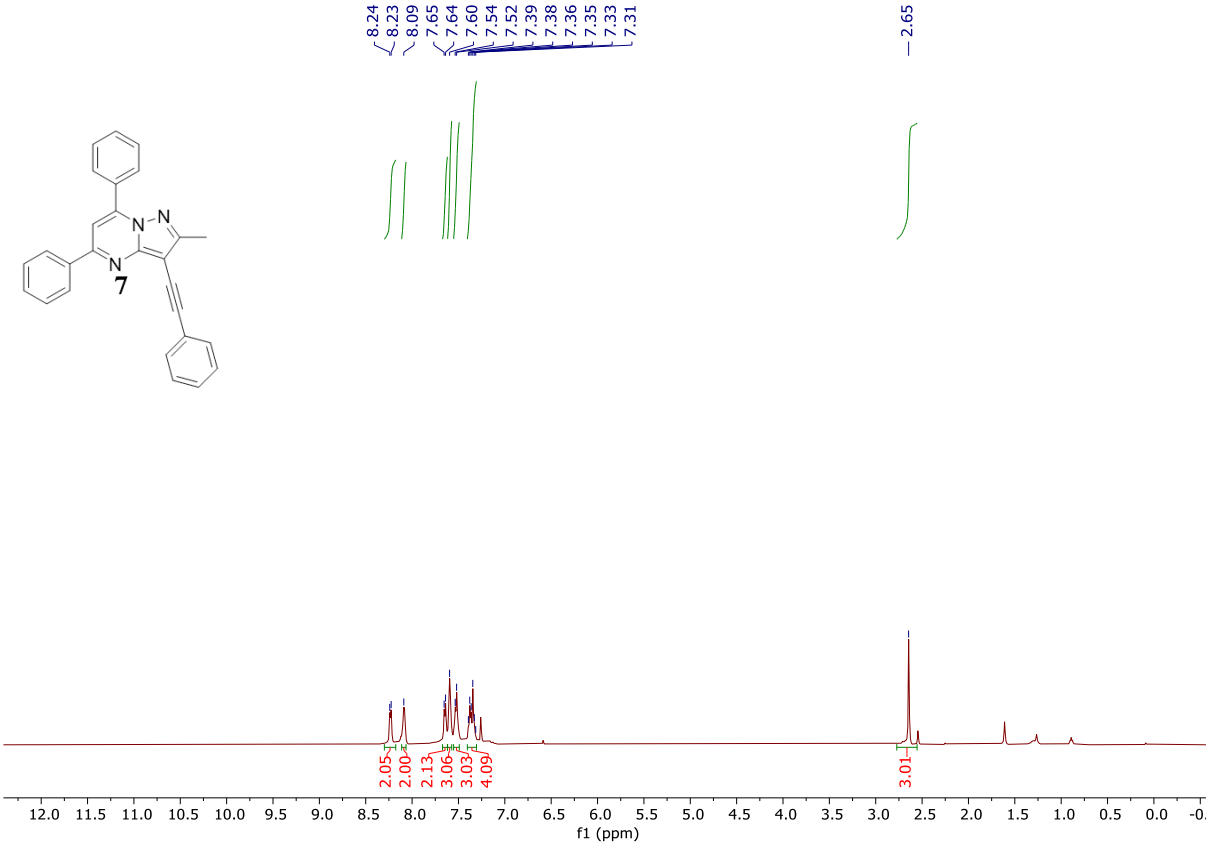

8.60
8.59
8.14
8.01
8.00
7.99
7.99
7.59
7.58
7.57
6.95
6.94
N
N
H
N
Cl
3ci
1.00
1.07
2.09
3.10
1.00
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

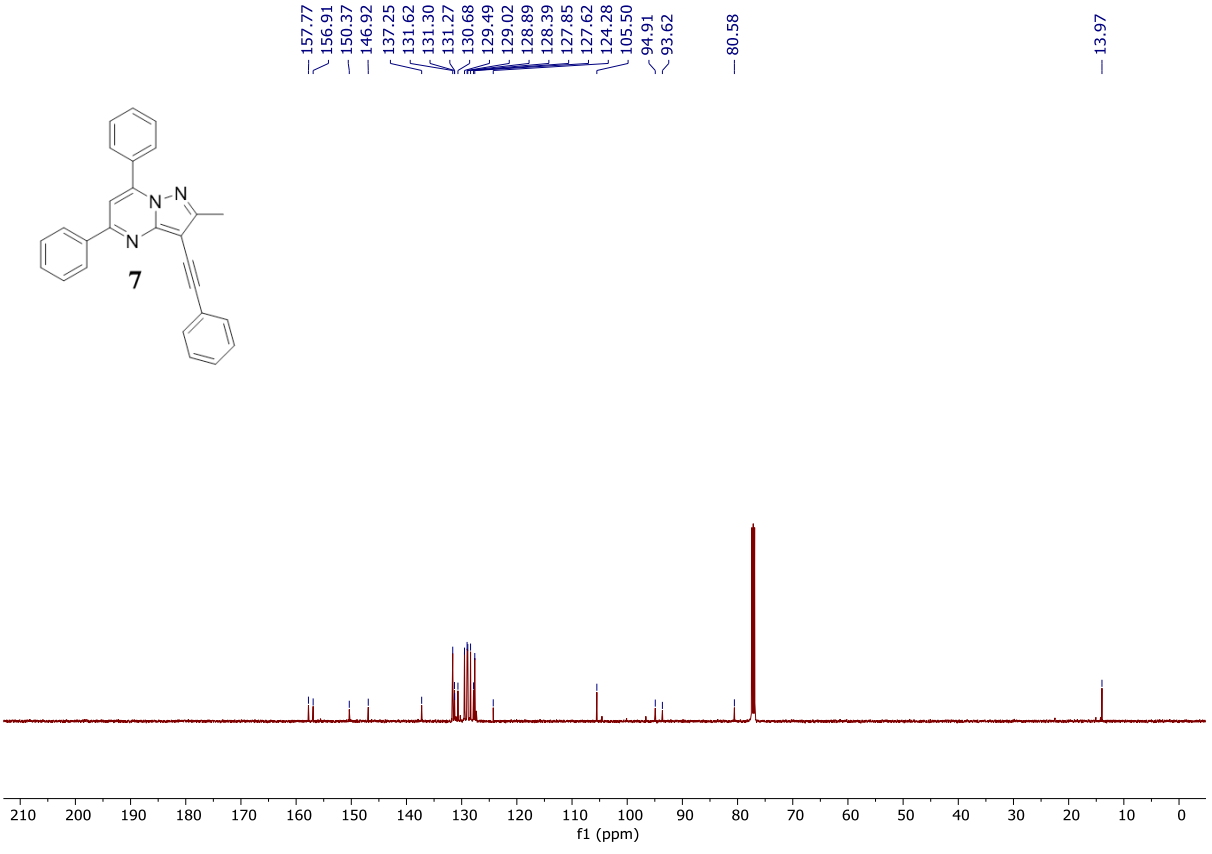

149.83
147.46
145.19
142.61
131.57
130.25
129.36
128.93
108.10
100.51
N
N
H
N
Cl
3ci
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.63
8.61
8.54
8.53
8.09
6.87
6.86
6.86
6.85
3cj
Cl
1.01
1.00
1.08
1.03
f1 (ppm)
149.84
144.03
143.07
135.68
108.55
100.32
3cj
Cl
f1 (ppm)


8.20
8.19
8.14
8.13
8.13
8.12
7.93
7.91
7.61
7.60
7.55
7.53
7.52
7.50
7.50
7.48
7.47
7.36
7.35
7.34
2.70
5
1.99
2.00
2.06
3.11
5.04
2.06
3.00
f1 (ppm)


155.68
152.93
147.31
146.22
137.67
132.98
131.78
131.04
130.28
129.47
129.07
128.96
128.84
128.56
127.36
126.17
109.49
104.79
14.90
5
f1 (ppm)


8.24
8.23
8.09
7.65
7.64
7.60
7.54
7.52
7.39
7.38
7.36
7.35
7.33
7.31
2.65
N
N
N
7
2.05
2.00
2.13
3.06
3.03
4.09
3.01
12.0 11.5 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)


157.77
156.91
150.37
146.92
137.25
131.62
131.30
131.27
130.68
129.49
129.02
128.89
128.39
127.85
127.62
124.28
105.50
94.91
93.62
80.58
13.97
N
N
N
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

References

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