Electronic Supplementary Material (ESI) for Chemical Communications.

Palladium-Catalyzed Regioselective C-2 Arylation of 7-Azaindoles, Indoles, and Pyrroles with Arenes

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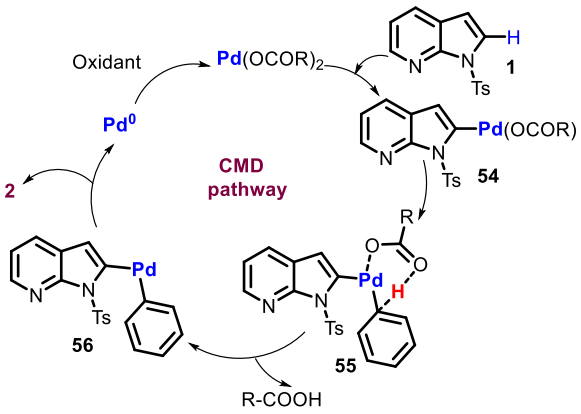
Supporting Information

I. Plausible Mechanism of C-2 arylation



Scheme 1: Plausible Mechanism

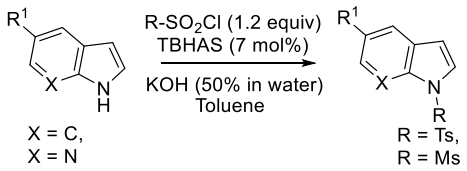
In line with the previous mechanism,[1] we also propose a mechanism based on concerted metlation-deprotonation pathway (Scheme 1). As a C-3 substituted 7-azaindole formed the C-2 arylated product **12**, the first palladation of **1** could occur at the C-2 position to form **54**, largely via CMD pathway. Then, second palladation could occur with arenes also by CMD pathway to form **56**, which upon reductive elimination could give **2** with a concomitant release of Pd(0). The active Pd(II) could be regenerated upon oxidation.

II. General Considerations

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All palladium-catalyzed reactions were performed in a screw-cap sealed tube. The ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ as solvent using a 400 MHz and 100 MHz spectrometer respectively with Me_4Si as an internal standard. Coupling constants (*J* values) are reported in Hz. Column chromatography was performed using silica gel (100-200 mesh). High resolution mass spectra (HRMS) were obtained using electron spray ionisation (ESI) technique and as TOF mass analyser. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer and are uncorrected. New compounds were characterized by melting point, ^{1}H NMR, ^{13}C NMR, IR, and HRMS data. Substrates **20**, **38**, **39**, **40** were purchased from chemical vendors.

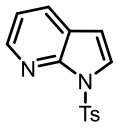
III. Experimental section

1. Typical Procedure for *N*-sulfonylation of Heterocycles (1, 21 – 26, 41)[2]



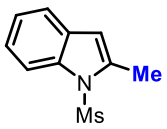
Following a literature procedure, a solution of aryl/alkyl sulfonyl chloride (1.2 equiv) in toluene (mL), Tetrabutylammonium hydrogensulfate (7 mol%) and potassium hydroxide (KOH; 50% aqueous solution, 2.5 mL), were added to a solution of indole/pyrrole (1 equiv) in toluene (2 mL) and stirred at room temperature. After completion of reaction, H_2O (10 mL) was added, and the layers were separated. The organic layer was washed with H_2O (2 x 10 mL) and brine (1 x 10 mL), dried over sodium sulfate, and concentrated under reduced pressure followed by chromatography [silica, EtOAc-hexanes = 1:9 ~ 2:8] gave corresponding *N*-sulfonylated heterocycle.

1-Tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (1)



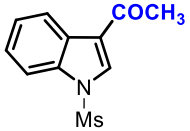
White solid, (209 mg, 77%); R_f (15% EtOAc/Hexane): 0.5; mp 89-95 ^oC; IR (KBr, cm^{-1}): 2919, 1579, 1268, 768; ^1H NMR($CDCl_3$): δ 8.45 – 8.43 (m, 1H), 8.08 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.86 – 7.83 (m, 1H), 7.74(dd, *J* = 3.9, 2.2 Hz, 2H), 7.29-7.27(m, 2H), 7.20-7.16(m, 1H), 6.60(dd, *J* = 4.0, 2.0 Hz, 1H), 2.38(s, 3H); ^{13}C NMR($CDCl_3$): δ 147.2, 145.1, 144.8, 135.4, 129.6, 129.5, 128.0, 126.4, 122.8, 118.8, 105.2, 21.6; HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2O_2S$ $[M+H]^+$ 273.0698, found 273.0688.

2-Methyl-1-(methylsulfonyl)-1*H*-indole (23)



Brown liquid, (119 mg, 57%); R_f (10% EtOAc/Hexane): 0.3; IR (ATR, cm^{-1}): 2925, 1734, 1455, 1365, 1172; ^1H NMR($CDCl_3$): δ 8.04-7.99 (m, 1H), 7.53-7.49 (m, 1H), 7.33-7.26 (m, 2H), 6.45 (s, 1H), 3.05 (s, 3H), 2.62 (s, 3H); ^{13}C NMR($CDCl_3$): δ 137.3, 136.6, 129.7, 123.9, 123.6, 120.2, 113.9, 109.4, 40.7, 15.5; HRMS (ESI) m/z calcd for $C_{10}H_{12}NO_2S$ $[M+H]^+$ 210.0589, found 210.0583.

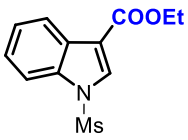
1-(1-(Methylsulfonyl)-1*H*-indol-3-*yl*) ethanone (24)



White crystalline solid, (206 mg, 87%); R_f (10% EtOAc/Hexane): 0.1; mp 288-290 °C; IR (KBr, cm^{-1}): 2923, 1664, 1541, 1385, 971; ^1H NMR($CDCl_3$): δ 8.45-8.43 (m, 1H), 8.11 (s, 1H), 7.91-7.88 (m, 1H), 7.48-7.43 (m, 2H), 3.28 (s, 3H),

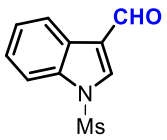
2.59 (s, 3H); ^{13}C NMR($CDCl_3$): δ 193.4, 134.9, 132.0, 127.5, 126.1, 125.1, 123.5, 121.5, 112.5, 41.6, 27.7; HRMS (ESI) m/z calcd for $C_{11}H_{12}NO_3S$ $[M+H]^+$ 238.0538, found 238.0530.

Ethyl 1-(methylsulfonyl)-1*H*-indole-3-carboxylate (25)



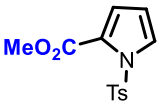
Colorless solid (240 mg, 90%); R_f (10% EtOAc/Hexane): 0.2; mp 137-139 °C; IR (KBr, cm^{-1}): 2978, 1721, 1553, 1361, 1169; ^{1}H NMR($CDCl_3$): δ 8.21(m, 1H), 8.15(s, 1H), 7.89-7.88 (m, 1H), 7.44-7.41 (m, 2H), 4.43 (q, *J* =7.1 Hz, 2H), 3.23 (s, 3H), 1.45 (t, *J* =7.1 Hz, 3H); ^{13}C NMR($CDCl_3$): δ 163.5, 134.8, 131.7, 127.8, 125.6, 124.6, 122.4, 113.7, 112.7, 60.6, 41.5, 14.4; HRMS (ESI) m/z calcd for $C_{12}H_{14}NO_4S$ $[M+H]^+$ 268.0644, found 268.0635.

1-(Methylsulfonyl)-1*H*-indole 3-carbaldehyde (26)



Off-white solid, (178 mg, 80%); R_f (10% EtOAc/Hexane): 0.1; mp 164-166 °C. IR (KBr, cm^{-1}): 2923, 1676, 1541, 1367, 1128; ^{1}H NMR($CDCl_3$): δ 10.12(s, 1H), 8.36(d, *J* = 4 Hz, 1H), 8.13 (s, 1H), 7.90(d, *J* = 7.4 Hz, 1H), 7.50-7.46 (m, 2H), 3.31(s, 3H); ^{13}C NMR($CDCl_3$): δ 185.3, 135.9, 135.2, 126.6, 126.2, 125.3, 122.9, 122.2, 112.7, 41.8; HRMS (ESI) m/z calcd for $C_{10}H_{10}NO_3S$ $[M+H]^+$ 224.0381, found 224.0375.

Methyl 1-(methylsulfonyl)-1*H*-pyrrole-2-carboxylate (41)



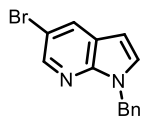
White solid; (285 mg, 77%); R_f (10% EtOAc/Hexane): 0.4; mp 107-110 °C IR (ATR, cm^{-1}): 2931, 1735, 1147, 780; ^{1}H NMR ($CDCl_3$): δ 7.89 (d, *J* = 8.4, 1.9 Hz, 2H), 7.74-7.73 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.07 -7.05 (m, 1H), 6.32 (t, *J* = 3.5 Hz, 1H), 3.74(s, 3H), 2.44(s, 3H); ^{13}C NMR($CDCl_3$): δ 159.1, 144.9, 135.8, 129.4, 129.1, 128.2, 124.8, 123.3, 110.3, 51.7, 21.7; HRMS (ESI) m/z calcd for $C_{13}H_{14}NO_4S$ $[M+H]^+$ 280.0644 found 280.0637.

2. Procedure for the *N*-alkylation of 7-azaindoles (3-5, 8)[2]

A dried round bottom flask equipped with a magnetic stirrer bar was charged with 7-azaindoles and THF (5 mL) under nitrogen atmosphere. The reaction mixture was cool down to 0 °C and NaH (1.2 equiv) was added and stirred for 1 h. After 1 h stirring alkyl halide(1.1 equiv) was added and continued the stirring for another 1 h. After completion of the reaction it was quenched with water (10 mL) and was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried

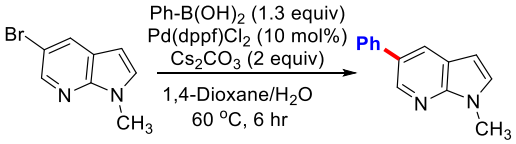
over Na_2SO_4 and the solvent was removed under reduced pressure to give *N*-alkyl-7-azaindoles in quantitative yield.

1-Benzyl-5-bromo-1*H*-pyrrolo[2,3-*b*] pyridine (8)



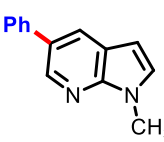
Colorless liquid, (140 mg, 49%); R_f (10% EtOAc/Hexane): 0.7; IR(ATR, cm^{-1}): 2923, 2850, 1455, 838, 740; ^1H NMR($CDCl_3$): δ 8.38 (d, *J* = 2.1 Hz, 1H), 8.05 (d, *J* = 2.1 Hz, 1H); 7.35-7.29 (m, 3H), 7.28-7.21 (m, 2H), 6.44(d, *J* = 3.5 Hz, 1H), 5.48 (s, 2H); ^{13}C NMR($CDCl_3$): δ 146.6, 143.5, 137.3, 130.8, 129.3, 128.7, 128.5, 127.7, 127.4, 122.0, 111.7, 99.6, 48.0; HRMS (ESI) m/z calcd for $C_{14}H_{12}BrN_2$ $[M+H]^+$ 287.0184 found 287.0179.

3. Procedure for Suzuki coupling of 5-Bromo-1-methyl-7-azaindole[2]



A solution of 5-bromo-1-methyl-1*H*-pyrrolo[2,3-b]pyridine (0.5 mmol), phenylboronic acid (1.3 equiv), $Pd(dppf)_2Cl_2$-DCM complex (10 mol%) and Cs_2CO_3 (2 equiv) in 1,4-dioxane:water (4 mL, 3:1 mixture) was heated at 60 °C for 6 h. The reaction mixture was allowed to cool to room temperature, diluted with EtOAc (5 mL) and was concentrated under vacuum. The residue product was purified by silica gel column chromatography (hexane/EtOAc, 96:4) to give product **(6)** in 94% (97 mg) yield.

1-methyl-5-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (6)

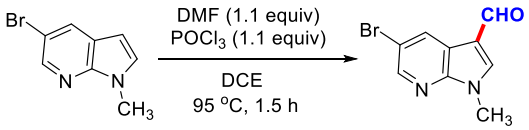


Yellow viscous liquid; (97 mg, 94%); IR(ATR, cm^{-1}): 2924, 2853, 1634, 730; ^1H NMR($CDCl_3$): δ 8.60 (d, *J* = 2.1 Hz, 1H); 8.11 (d, *J* = 2.1 Hz, 1H), 7.65(dd, *J* = 8.4, 1.4 Hz, 2H), 7.49 (t, *J* = 7.44 Hz, 2H), 7.38 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.23 (d, *J* = 3.4 Hz, 1H), 6.52 (d, *J* = 3.4 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR($CDCl_3$): δ 147.3, 142.2, 139.7, 129.8, 129.3, 128.9, 127.4, 127.3, 126.9, 120.5, 99.6, 31.4; HRMS(ESI) m/z calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1079 found 209.1068.

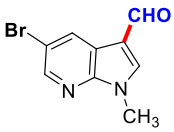
3. Procedure for C-3 formylation of 5-Bromo-1-methyl-7-azaindole(5)

To the cooled solution of DMF (1.1 equiv), $POCl_3$ (1.1 equiv) was added slowly and reaction is allowed to stir at room temperature for 5 min. Then, 1,2-dichloroethane (4 mL) was added and mixture was cooled again to which solution of 5-Bromo-1-methyl-7-azaindole **(5)** (2 equiv) in

DCE (10 mL) was added. Reaction mixture was refluxed for 1.5 h following which cooled satd. solution of sodium bicarbonate (20 mL) was added slowly until effervescence ceases. Then, it was diluted with dichloromethane (30 mL), layers were separated. Organic layer was washed with water (10 mL), brine (10 mL). Then, organic layer was evaporated to dryness and washed with hexane, decanted and dried under reduced pressure to give yellow solid (**7**) in quantitative yield.

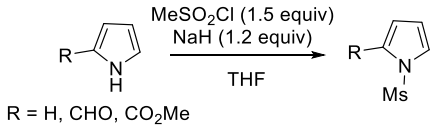


5-Bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbaldehyde (7)



Yellow solid; IR(KBr, cm^{-1}): 3087, 2923, 2807, 1650, 725; ^1H NMR($CDCl_3$): δ 9.96(s, 1H), 8.73(d, *J* = 2.2 Hz, 1H), 8.48(d, *J* = 2.2 Hz, 1H), 7.86(s, 1H), 3.94(s, 3H); ^{13}C NMR ($CDCl_3$): δ 184.2, 147.0, 145.8, 139.5, 132.7, 118.9, 115.6, 115.2, 32.3; HRMS(ESI) m/z calcd for $C_9H_8BrN_2O[M+H]^+$ 238.9820 found 238.9815.

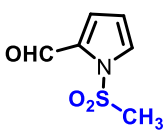
4. Procedure for *N*-mesylation of pyrrole (35-37)



To the cooled solution of pyrrole (2 mmol) in THF, NaH (1.2 equiv) was added slowly with vigorous stirring. After 10 min methane sulfonyl chloride (1.5 equiv) was added dropwise to the reaction mixture. Upon completion of reaction, H_2O (10 mL) was added and extracted with ethyl acetate (2 x 10 mL). Then, organic layer was dried over sodium sulphate and concentrated under reduced pressure followed by chromatography [silica, EtOAc-hexanes = 0.5:9.5 ~ 2:8] gave corresponding *N*-mesylated pyrroles (**35-37**).

Note: Special care has to be taken in case of mesylation of unsubstituted pyrrole that temperature has to be kept 0 °C while addition of NaH and mesyl chloride. Also, mesyl chloride has to be added over period of 10 min. *N*-mesyl pyrrole(**37**) is only iodine active so TLC monitoring has to be done that way, followed by purification.

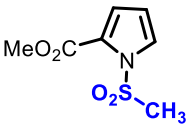
1-(Methylsulfonyl)-1*H*-pyrrole-2-carbaldehyde (35)



Brown solid; (283 mg, 82%); R_f (20% EtOAc/Hexane): 0.4; mp 45-48 °C; IR (KBr, cm^{-1}): 3017, 2933, 2843 2793, 1674, 1362, 743; ^1H NMR($CDCl_3$): δ 9.69 (d, *J* = 0.84 Hz, 1H), 7.62-7.61 (m, 1H), 7.23-7.22 (m, 1H), 6.42(t, *J* = 3.3 Hz, 1H), 3.64(s,

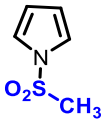
3H); ^{13}C NMR ($CDCl_3$): δ 178.1, 133.0, 130.5, 129.2, 111.4, 42.8; HRMS (ESI) m/z calcd for $C_6H_8NO_3S$ $[M+H]^+$ 174.0225 found 174.0219.

Methyl 1-(methylsulfonyl)-1*H*-pyrrole-2-carboxylate (36)



Colorless liquid; (285 mg, 77%); R_f (10% EtOAc/Hexane): 0.2; IR(ATR, cm^{-1}): 2924, 2853, 1722, 1150, 757;^{1}H NMR ($CDCl_3$): δ 7.53-7.52 (m, 1H), 7.12-7.11 (m, 1H), 6.29 (t, *J* = 3.4 Hz, 1H), 3.89(s, 3H), 3.73(s, 3H); ^{13}C NMR($CDCl_3$): δ 160.1, 128.7, 124.5, 123.5, 110.1, 52.0, 43.0; HRMS (ESI) m/z calcd for $C_7H_{10}NO_4S$ $[M+H]^+$ 204.331 found 204.324.

1-(Methylsulfonyl)-1*H*-pyrrole (37)



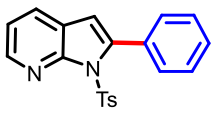
Brown liquid; (128 mg, 44%); R_f (10% EtOAc/Hexane): 0.3; IR (ATR, cm^{-1}): 3025, 2933, 1730, 1456, 739; ^{1}H NMR($CDCl_3$): δ 7.15(t, *J* = 2.3 Hz, 2H), 6.39(t, *J* = 2.3 Hz, 2H), 3.16(s, 3H); ^{13}C NMR ($CDCl_3$): δ 120.4, 113.5, 42.8; HRMS (ESI) m/z calcd for $C_5H_8NO_2S$ $[M+H]^+$ 146.0276 found 146.0269.

III. Synthesis of C2-arylated compounds and characterization data

1. General procedure for the 2-aryl 7-azaindoles (2, 9-19)

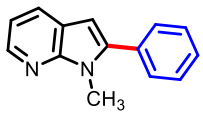
In an oven-dried screw cap vial equipped with a magnetic stir bar, 7-azaindole substrate (0.5 mmol), $Pd(TFA)_2$ (10 mol%), AgOAc (1.5 mmol), CsOPiv (40 mol%), 2.5 mL arene and 2 mL pivalic acid as solvent was heated at 130 ºC for 12 h. The reaction mixture was allowed to cool to room temperature and neutralized by the addtion of saturated solution of Na_2CO_3 (10 mL). Then, it was extracted with ethyl acetate (2 x 10 mL). The organic layer was dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography on silica using (ethyl acetate/ hexane) as an eluent to give the desired product.

2-Phenyl-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (2)



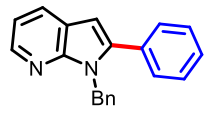
Off-white solid; (113 mg, 65%); R_f (15% EtOAc/Hexane): 0.6; mp 108-110 °C; IR (KBr, cm^{-1}): 3406, 2928, 1367, 1185; ^{1}H NMR($CDCl_3$): δ 8.51 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.80-7.77 (m, 3H), 7.58-7.55 (m, 2H), 7.49-7.47 (m, 3H), 7.22-7.17 (m, 3H), 6.51 (s, 1H), 2.35 (s, 3H); ^{13}C NMR($CDCl_3$): δ 150.1, 144.7, 144.6, 142.2, 135.7, 132.6, 129.9, 129.2, 128.8, 128.7, 127.7, 127.6, 122.3, 119.5, 109.0, 21.6; HRMS(ESI) m/z calcd for $C_{20}H_{17}N_2O_2S$ $[M+H]^+$349.1011, found 349.1004.

1-Methyl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (9)[3]



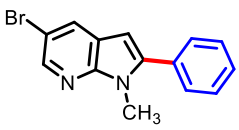
As previously reported[2], yellowish liquid; (88 mg, 85%); R_f (10% EtOAc/Hexane): 0.3; ^{1}H NMR($CDCl_3$): δ 8.37(dd, *J* = 4.8, 1.5 Hz, 1H); 7.93(dd, *J* = 7.8, 1.6 Hz, 1H), 7.58(dd, *J* = 8.5, 1.6 Hz, 2H), 7.51(dt, *J* = 7.1, 1.2 Hz, 2H), 7.45(tt, *J* = 7.2, 1.5 Hz, 1H), 7.13-7.09(m, 1H), 6.54(s, 1H), 3.91 (s, 3H); ^{13}C NMR($CDCl_3$): δ 149.2, 142.6, 141.8, 132.3, 129.1, 128.6, 128.3, 128.1, 120.6, 116.1, 99.4, 29.9.

1-Benzyl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (10)



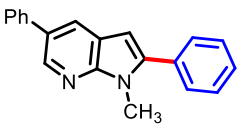
Off-white solid, (100 mg, 71%); R_f (10% EtOAc/Hexane): 0.5; mp 114-116 ^{o}C; IR(KBr, cm^{-1}): 2924, 2854, 1593, 1417, 729; ^{1}H NMR ($CDCl_3$): δ 8.36 (dd, *J* = 4.7, 1.4 Hz, 1H); 7.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.43-7.39 (m, 5H), 7.24-7.18 (m, 3H), 7.15-7.12 (m, 1H), 6.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.58 (s, 1H), *5*.59 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 143.0, 141.9, 138.5, 132.3, 129.2, 128.5, 128.4, 128.4, 128.2, 127.0, 126.5, 120.6, 116.4, 100.3, 45.9; HRMS (ESI) m/z calcd for $C_{20}H_{16}N_2Na$ $[M+Na]^+$ 307.1211 found 307.1214.

5-Bromo-1-methyl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (11)[3]



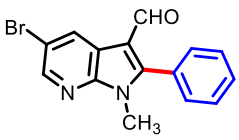
As previously reported, Colorless solid; (101 mg, 71%); R_f (10% EtOAc/Hexane): 0.6; ^{1}H NMR($CDCl_3$): δ 8.37 (d, *J* = 2.2 Hz, 1H); 8.04 (d, *J* = 2.2 Hz, 1H), 7.57-7.47 (m, 5H), 6.48 (s, 1H), 3.87 (s, 3H); ^{13}C NMR($CDCl_3$): δ 147.6, 143.3, 143.0, 131.8, 130.0, 129.1,128.7,128.6, 122.0, 111.8, 98.8, 30.0.

1-Methyl-2,5-diphenyl-1*H*-pyrrolo[2,3-*b*]pyridine (12)



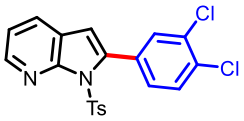
Yellowish solid; (99 mg, 70%); R_f (10% EtOAc/Hexane): 0.4; mp 112-116 ^{o}C; IR(KBr, cm^{-1}): 2917, 1593, 1480, 886, 757; ^{1}H NMR ($CDCl_3$): δ 8.61 (d, *J* = 2.1 Hz, 1H); 8.11 (d, *J* = 2.1 Hz, 1H), 7.67(dd, *J* = 8.4, 1.4 Hz, 2H), 7.6 (dd, *J* = 8.5 ,1.6 Hz, 2H), 7.55-7.47 (m, 5H), 7.39 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.59 (s, 1H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 148.9, 142.6, 142.0, 139.7, 132.3, 129.9, 129.1, 128.9, 128.6, 128.4, 127.4, 126.9, 126.6, 120.5, 99.6, 30.0; HRMS (ESI) m/z calcd for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392 found 285.1401.

5-Bromo-1-methyl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (13)[3]



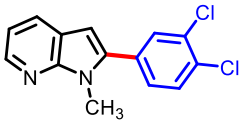
Yellow solid; (101 mg, 66%); R_f (10% EtOAc/Hexane): 0.3; mp 138-140 ^oC IR(KBr, cm^{-1}): 2923, 1649, 742; ^1H NMR($CDCl_3$): δ 9.75(s, 1H), 8.82 (d, *J* = 2.2 Hz, 1H), 8.50 (d, *J* = 2.2 Hz, 1H), 7.63-7.60 (m, 3H), 7.56-7.64 (m, 2H), 3.80 (s, 3H);^{13}C NMR($CDCl_3$): δ 186.1, 152.0, 146.9, 132.5, 130.6, 130.4, 128.9, 127.7, 119.2, 115.4, 113.3, 29.9; HRMS (ESI) m/z calcd for $C_{15}H_{12}BrN_2O$ $[M+H]^+$ 315.0133 found 315.0126.

2-(3,4-Dichlorophenyl)-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (14)



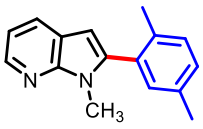
Colorless solid, (93 mg, 45%); R_f (10% EtOAc/Hexane): 0.2; mp 162-168 ^oC; IR(KBr, cm^{-1}): 2917, 1593, 1372, 1172, 815, 768; ^1H NMR($CDCl_3$): δ 8.52 (dd, *J* = 4.8, 1.5 Hz, 1H); 7.83-7.79 (m, 3H), 7.60(d, *J* = 1.9 Hz, 1H), 7.55(d, *J* = 8.3 Hz, 1H), 7.43(dd, *J* = 8.3, 1.9 Hz, 1H), 7.25-7.20 (m, 3H), 6.54 (s, 1H), 2.37 (s, 3H); ^{13}C NMR($CDCl_3$): δ 150.0, 145.2, 145.1, 139.4, 135.4, 133.1, 132.5, 131.9, 131.2, 129.7, 129.4, 129.2, 129.1, 127.7, 122.0, 119.7, 109.7, 21.6; HRMS (ESI) m/z calcd for $C_{20}H_{15}Cl_2N_2O_2S$ $[M+H]^+$ 417.0231 found 417.0239.

2-(3,4-Dichlorophenyl)-1-methyl-5-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (15)[3]



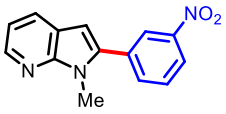
As previously reported[2], colorless solid; (120 mg, 87%); R_f (10% EtOAc/Hexane): 0.3; ^1H NMR($CDCl_3$): δ 8.37 (dd, *J* = 4.7, 1.4 Hz, 1H); 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.65(d, *J* = 2 Hz, 1H), 7.56(d, *J* = 8.3 Hz, 1H), 7.38 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.12-7.09 (m, 1H), 6.54 (s, 1H), 3.88 (s, 3H); ^{13}C NMR($CDCl_3$): δ 149.3, 143.3, 139.1, 132.9, 132.6, 132.3, 130.7, 130.6, 128.5, 128.1, 120.3, 116.4, 100.4, 29.9.

2-(2,5-Dimethylphenyl)-1-methyl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (16)



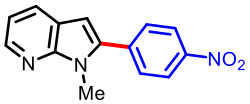
Yellowish liquid, (38 mg, 32%); R_f (10% EtOAc/Hexane): 0.6; IR(ATR, cm^{-1}): 2924, 2853, 1455, 771; ^1H NMR($CDCl_3$): δ 8.36 (dd, *J* = 4.8, 1.5 Hz, 1H); 7.93 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.25-7.19 (m, 2H), 7.14-7.10(m, 2H), 6.39 (s, 1H), 3.65(s, 3H), 2.39(s, 3H), 2.18(s, 3H); ^{13}C NMR($CDCl_3$): δ 148.3, 142.1, 141.2, 135.1, 134.6, 131.8, 131.4, 130.0, 129.7, 128.0, 120.6, 115.8, 99.3, 29.7, 20.9, 19.4; HRMS (ESI) m/z calcd for $C_{16}H_{17}N_2$ $[M+H]^+$ 237.1392 found 237.1399.

1-Methyl-2-(3-nitrophenyl)-1*H*-pyrrolo[2,3-*b*] pyridine (17a)



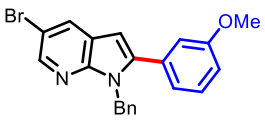
Colorless liquid, (39 mg, 31%); R_f (20% EtOAc/Hexane): 0.3; IR(ATR, cm^{-1}): 2930, 1598, 1438, 856; ^{1}H NMR($CDCl_3$): δ 8.46 (s, 1H), 8.43 (d, *J* = 4.7 Hz, 1H), 8.32 (d, *J* = 8 Hz, 1H), 8.0 (d, *J* = 7.8 Hz, 1H); 7.91 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.19 - 7.15(m, 1H), 6.67(s, 1H), 3.96(s, 3H); ^{13}C NMR($CDCl_3$): δ 143.7, 138.8, 134.6, 134.2, 129.6, 129.4, 128.6, 123.9, 123.7, 122.8, 120.3, 116.5, 101.0, 29.8; HRMS (ESI) m/z calcd for $C_{14}H_{12}N_3O_2$ $[M+H]^+$ 254.0930 found 254.0921.

1-Methyl-2-(4-nitrophenyl)-1*H*-pyrrolo[2,3-*b*] pyridine (17b)



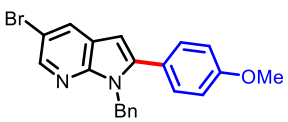
Yellow semisolid, (18 mg, 14%); R_f (20% EtOAc/Hexane): 0.3; IR(ATR, cm^{-1}): 2912, 1438, 856, 778; ^{1}H NMR($CDCl_3$): δ 8.43 (d, *J* = 4.7, 1.5 Hz, 1H), 8.38 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.17 - 7.14(m, 1H), 6.69(s, 1H), 3.96(s, 3H); ^{13}C NMR($CDCl_3$): δ 149.7, 147.3, 144.0, 139.0, 138.7, 129.4, 128.9, 124.0, 120.3, 116.7, 101.7, 30.2; HRMS (ESI) m/z calcd for $C_{14}H_{12}N_3O_2$ $[M+H]^+$ 254.0930 found 254.0928.

1-Benzyl-5-bromo-2-(3-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (18a)



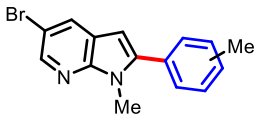
Whitish semisolid, (41 mg, 21%); R_f (10% EtOAc/Hexane): 0.68; IR(ATR, cm^{-1}): 2924, 1605, 1453, 1143 771; ^{1}H NMR($CDCl_3$): δ 8.37 (d, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 2.1 Hz, 1H); 7.33 (t, *J* = 7.9 Hz, 1H), 7.24-7.20 (m, 3H), 7.02- 6.94(m, 4H), 6.88(t, *J* = 1.7 Hz, 1H) 6.53 (s, 1H), 5.55(s, 2H), 3.65(s, 3H); ^{1}H NMR(d_6-DMSO): δ 8.31 (d, *J* = 2.2 Hz, 1H), 8.28 (d, *J* = 2.1 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.23-7.16 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.01- 6.97(m, 2H), 6.83(d, *J* = 6.6 Hz, 2H), 6.70 (s, 1H), 5.55 (s, 2H); ^{13}C NMR($CDCl_3$): δ 159.7, 147.6, 143.5, 143.2, 138.1, 133.0, 130.2, 129.7, 128.5, 127.1, 126.3, 122.0, 121.6, 114.9, 114.1, 112.2, 99.7, 55.0, 46.2; HRS (ESI) m/z calcd for $C_{21}H_{17}BrN_2O$ $[M+H]^+$ 393.0603 found 393.0601.

1-Benzyl-5-bromo-2-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*] pyridine (18b)



Creamish semisolid, (82 mg, 42%); R_f (10% EtOAc/Hexane): 0.7; IR(ATR, cm^{-1}): 2923, 2850, 1455, 740; ^{1}H NMR($CDCl_3$): δ 8.34 (d, *J* = 1.9 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H); 7.32 (d, *J* = 8.6 Hz, 1H), 7.24-7.22 (m, 3H), 6.97- 6.92(m, 4H), 6.46(s, 1H), 5.54(s, 2H), 3.86(s, 3H); ^{13}C NMR($CDCl_3$): δ 160.0, 147.5, 143.3, 143.1, 138.1, 130.5, 129.8, 128.5, 127.1, 126.4, 124.2, 122.2, 114.0, 112.1, 99.1, 55.3, 46.3; HRMS (ESI) m/z calcd for $C_{21}H_{17}BrN_2O$ $[M+H]^+$ 393.0603 found 393.0597.

1-Methyl-2-(methylphenyl)-1*H*-pyrrolo[2,3-*b*] pyridine (19)

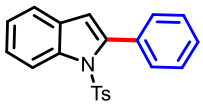


Colorless liquid, (114 mg, 76%); R_f (10% EtOAc/Hexane): 0.7; IR(ATR, cm^{-1}): 2921, 1679, 735; ^1H NMR($CDCl_3$): δ 8.37 – 8.35 (m, 1.5 H), 8.03-8.01 (m ,1.5 H), 7.44 (d, *J* = 8.1 Hz, 0.8 H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.36 - 7.28(m, 4H), 6.46(s, 1H), 6.44(s, 0.4H), 3.86(s, 4H), 2.46(s, 4H); ^{13}C NMR($CDCl_3$): δ 147.6, 143.5, 142.9, 142.8, 138.7, 138.4, 131.7, 129.9, 129.9, 129.8, 129.4, 129.0, 128.5, 126.2, 122.1, 111.8, 98.7, 98.5, 30.0, 29.9, 21.5, 21.3; LCMS (ESI) m/z calcd for $C_{15}H_{13}BrN_2$ $[M+H]^+$ 301.0.

2. General procedure for the 2-aryl indoles (27-33)

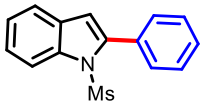
In an oven-dried screw cap vial equipped with a magnetic stir bar, indole substrate (0.5 mmol), $Pd(OAc)_2$ (10 mol%), AgOAc (1.5 mmol), CsOPiv (20 mol%), 2.5 mL arene and 2 mL pivalic acid as solvent was heated at 130 ºC for 12 h. The reaction mixture was allowed to cool to room temperature and neutralized by the addtion of saturated solution of Na_2CO_3 (10 mL). Then, it was extracted with ethyl acetate (2 x 10 mL). The organic layer was dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography on silica using (ethyl acetate/ hexane) as an eluent to give the desired product.

2-Phenyl-1-tosyl-1H-indole (27)[4]



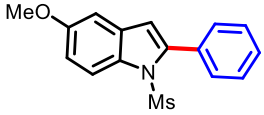
Colorless solid; (87 mg, 50%); R_f (10% EtOAc/Hexane): 0.5; ^1H NMR($CDCl_3$): δ 8.35 (d, *J* = 8.3 Hz, 1H), 7.52-7.51 (m, 2H), 7.48-7.43 (m, 4H), 7.40 (dt, *J* = 7.3, 1.1 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 3H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.57 (s, 1H), 2.31 (s, 3H); ^{13}C NMR($CDCl_3$): δ 144.5, 142.1, 138.2, 134.6, 132.4, 130.5, 130.3, 129.2, 128.6, 127.5, 126.8, 124.7, 124.3, 120.6, 116.6, 113.6, 21.5.

1-(Methylsulfonyl)-2-phenyl-1*H*-indole (28)[5]



Colorless crystals; (119 mg, 88%); R_f (10% EtOAc/Hexane): 0.4; ^1H NMR($CDCl_3$): δ 8.16(d, *J* =7, 0.96 Hz, 1H), 7.64-7.58 (m, 3H), 7.47-7.46 (m, 3H), 7.45-7.35 (m, 2H), 6.74 (s, 1H), 2.77 (s, 3H); ^{13}C NMR($CDCl_3$): δ 142.0, 138.0, 132.0, 130.3, 130.1, 128.9, 127.7, 125.1, 124.6, 121.0, 115.8, 113.1, 39.4.

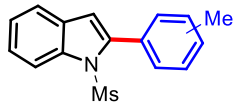
5-Methoxy-1-(methylsulfonyl)-2-phenyl-1*H*-indole (29)



Off-white solid (130 mg, 86%); R_f (10% EtOAc/Hexane): 0.3; mp 130-132 °C; IR (KBr, cm^{-1}): 2840, 1605, 1471, 1359, 1143; ^1H NMR($CDCl_3$): δ 8.04 (d, *J* = 9.1 Hz, 1H), 7.60-7.57 (m, 2H), 7.45-7.44 (m, 3H), 7.08 (d, *J* =2.6

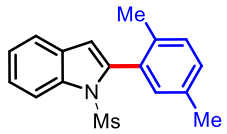
Hz, 1H), 7.01 (dd, *J* =9.1, 2.6 Hz, 1H), 6.69 (s, 1H), 3.90 (s, 3H), 2.70 (s, 3H); ^{13}C NMR($CDCl_3$): δ 157.3, 142.9, 132.6, 131.9, 131.4, 130.0, 128.9, 127.7, 116.9, 113.7, 113.3, 103.5, 55.7, 38.8; HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0851, found 302.0843.

1-(Methylsulfonyl)-2-(tolyl)-1*H*-indole (mixture) (30)



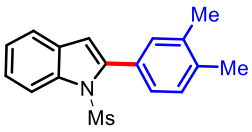
Yellowish liquid; (120 mg, 80%); R_f (10% EtOAc/Hexane): 0.3; ^{1}H NMR($CDCl_3$): δ 8.15 (td, *J* = 8.3, 1 Hz, 1.5 H), 7.62-7.60 (m, 1.5 H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.40-7.34 (m, 7H), 7.28-7.25 (m, 3H), 6.72 (s, 1H), 6.71 (d, *J* = 0.2 Hz, 0.5H), 2.76 (s, 3H), 2.75 (s, 1.5H), 2.44 (s, 5H).

2-(2,5-Dimethylphenyl)-1-(methylsulfonyl)-1*H*-indole (31)



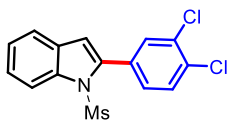
Colorless solid; (99 mg, 66%); R_f (10% EtOAc/Hexane): 0.4; mp 118-120 °C; IR (KBr, cm^{-1}): 2917, 1437, 1355, 1171, 1036; ^{1}H NMR($CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.46-7.36 (m, 2H), 7.20 (s, 2H), 7.15 (s, 1H), 6.62 (s, 1H), 2.89 (s, 3H), 2.39 (s, 3H), 2.29 (s, 3H); ^{13}C NMR($CDCl_3$): δ 140.6, 136.9, 136.0, 134.5, 131.8, 130.7, 130.1, 130.0, 129.7, 124.8, 124.0, 120.9, 115.0, 111.8, 40.5, 20.9, 20.0; HRMS (ESI) m/z calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$ 300.1058, found 300.1054.

2-(3,4-Dimethylphenyl)-1-(methylsulfonyl)-1*H*-indole (32)



Colorless solid; (109 mg, 73%); R_f (10% EtOAc/Hexane): 0.4; mp 157-159 °C; IR (KBr, cm^{-1}): 2929, 1450, 1365, 1172; ^{1}H NMR($CDCl_3$): δ 8.15 (dd, *J* = 8, 0.7 Hz, 1H), 7.61 (dd, *J* = 6.9, 2.6 Hz, 1H), 7.42-7.33 (m, 3H), 7.23(d, *J* =7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 2.76 (s, 3H), 2.36 (s, 6H); ^{13}C NMR($CDCl_3$): δ 142.3, 137.9, 137.6, 135.9, 131.2, 130.4, 129.4, 129.0, 127.7, 124.9, 124.4, 120.8, 115.9, 112.6, 39.4, 19.8, 19.7; HRMS (ESI) m/z calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$ 300.1058, found 300.1054.

2-(3,4-Dichlorophenyl)-1-(methylsulfonyl)-1*H*-indole (33)

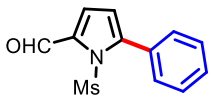


Off-white solid; (127 mg, 75%); R_f (10% EtOAc/Hexane): 0.3; mp 105-107 °C; IR (KBr, cm^{-1}): 3406, 2928, 1544, 1447, 1362, 1176, 957, 829; ^{1}H NMR($CDCl_3$): δ 8.13 (d, *J* =8.4 Hz, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 6.8, 1.2, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.45-7.40 (m, 3H),6.79 (s, 1H), 2.76 (s, 3H); ^{13}C NMR($CDCl_3$): δ 139.4, 138.1, 133.1, 132.0, 131.9, 131.2, 130.0, 129.7, 129.5, 125.8, 124.9, 121.3, 115.8, 114.1, 39.2; HRMS (ESI) m/z calcd for $C_{15}H_{11}Cl_2NO_2SNa$ $[M+Na]^+$ 361.9785, found 361.9779

3. General procedure for the 2-aryl pyrroles (42-52)

In an oven-dried screw cap vial equipped with a magnetic stir bar, pyrrole substrate (0.5 mmol), $Pd(TFA)_2$ (10 mol%), AgOAc (1.5 mmol), PivOH (5 equiv), 1.5 mL arene as solvent was heated at 80 ºC for 12 h. The reaction mixture was allowed to cool to room temperature and neutralized by the addtion of saturated solution of Na_2CO_3 (10 mL). Then, it was extracted with ethyl acetate (2 x 10 mL). The organic layer was dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography on silica using (ethyl acetate/ hexane) as an eluent to give the desired product.

1-(Methylsulfonyl)-5-phenyl-1*H*-pyrrole-2-carbaldehyde (42)

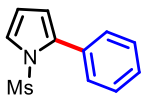


Brown Solid, (93 mg, 75%); R_f (20% EtOAc/Hexane): 0.45; mp 150-154 ºC; IR(KBr, cm^{-1}): 1663, 1377, 752; ^1H NMR ($CDCl_3$): δ 9.88 (s, 1H), 7.48-7.45(m, 5H), 7.25(d, *J* = 3.7 Hz, 1H), 6.39(d, *J* = 3.7 Hz, 1H), 3.46(s, 3H); ^{13}C NMR ($CDCl_3$): δ 179.8, 145.6, 136.9, 131.2, 129.5, 129.4, 128.1, 126.5, 115.4, 43.7; HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_3S$ $[M+H]^+$ 250.0538 found 250.0530.

Methyl 1-(methylsulfonyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (43)

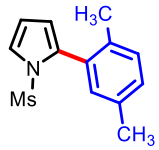
White Solid, (96 mg, 69%); R_f (10% EtOAc/Hexane): 0.3; mp 183-187 ºC; IR(KBr, cm^{-1}): 3017, 2938, 1723, 1472, 753; ^1H NMR($CDCl_3$): δ 7.44-7.41(m, 5H), 7.04(d, *J* = 3.6 Hz, 1H), 6.23(d, *J* = 3.6 Hz, 1H), 3.92(s, 3H), 3.78(s, 3H); ^{13}C NMR ($CDCl_3$): δ 161.0, 144.3, 132.6, 128.8, 128.7, 128.1, 122.2, 113.5, 52.2, 44.6; HRMS (ESI) m/z calcd for $C_{13}H_{14}NO_4S$ $[M+H]^+$ 280.0644 found 280.0637.

1-(Methylsulfonyl)-2-phenyl-1*H*-pyrrole (44)



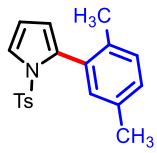
Colorless solid; (77 mg, 70%); R_f (10% EtOAc/Hexane): 0.4; mp 56-58 ºC; IR(KBr, cm^{-1}): 2922, 1738, 1360, 764; ^1H NMR ($CDCl_3$): δ 7.51-7.48(m, 2H), 7.40-7.38(m, 3H), 7.30(dd, *J* = 3.3, 1.7 Hz, 1H), 6.36(t, *J* = 3.3 Hz, 1H), 6.31(dd, *J* = 3.3, 1.8 Hz, 1H), 2.83(s, 3H); ^{13}C NMR($CDCl_3$): δ 135.4, 131.1, 130.8, 128.7, 127.8, 123.6, 115.9, 111.8, 42.2; HRMS(ESI) m/z calcd for $C_{11}H_{12}NO_2S$ $[M+H]^+$ 222.0589 found 222.0588.

2-(2,5-dimethylphenyl)-1-mesyl-1*H*-pyrrole (45)



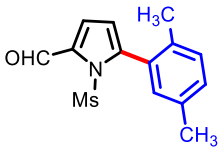
Colorless crystalline solid; (77 mg, 70%); R_f (10% EtOAc/Hexane): 0.4; mp 114-116 °C; IR(KBr, cm^{-1}): 2927, 1473, 1352, 743; ^{1}H NMR ($CDCl_3$): 7.29(dd, *J* = 3.3, 1.7 Hz, 1H), 7.17(m, 2H), 7.11(s, 1H), 6.38(t, *J* = 3.3 Hz, 1H), 6.22(dd, *J* = 3.3, 1.7 Hz, 1H), 2.94(s, 3H), 2.35(s, 3H), 2.18(s, 3H); ^{13}C NMR ($CDCl_3$): 136.7, 134.4, 133.8, 131.8, 130.9, 130.0, 129.7, 122.3, 115.2, 111.6, 42.6, 20.8, 19.8; HRMS (ESI) m/z calcd for $C_{13}H_{16}NO_2S$ $[M+H]^+$ 250.0902 found 250.0895.

2-(2,5-Dimethylphenyl)-1-tosyl-1*H*-pyrrole (46)



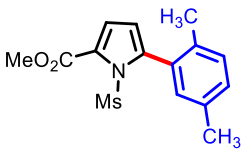
Colourless liquid; (56 mg, 35%); R_f (10% EtOAc/Hexane): 0.7; IR(ATR, cm^{-1}): 2924, 2854, 1367, 812, 669; ^{1}H NMR ($CDCl_3$): 7.48(dd, *J* = 3.3, 1.8 Hz, 1H), 7.28(d, *J* = 8.3 Hz, 2H), 7.16(d, *J* = 8.2 Hz, 2H), 7.10-7.08(m, 2H), 6.56 (s, 1H), 6.34(t, *J* = 3.3 Hz, 1H), 6.08(dd, *J* = 3.2, 1.8 Hz, 1H), 2.41(s, 3H), 2.22(s, 3H), 1.93(s, 3H); ^{13}C NMR($CDCl_3$): 144.6, 136.6, 135.8, 133.8, 133.6, 132.7, 130.7, 129.5, 129.3, 129.2, 127.6, 122.5, 114.8, 111.2, 21.6, 20.7, 19.5; HRMS (ESI) m/z calcd for $C_{19}H_{19}NNaO_2S$ $[M+Na]^+$ 348.1034 found 348.1037

5-(2,5-Dimethylphenyl)-1-(methylsulfonyl)-1*H*-pyrrole-2-carbaldehyde (47)



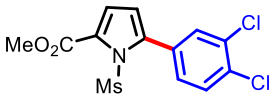
Pale yellow solid, (106 mg, 72%); R_f (10% EtOAc/Hexane): 0.2; m.p. 112-114 °C; IR(KBr, cm^{-1}): 2925, 1662, 1474, 756; ^{1}H NMR ($CDCl_3$): δ 9.91 (s, 1H), 7.28(d, *J* = 3.7 Hz, 1H), 7.19(m, 2H), 7.05(s, 1H), 6.29(d, *J* = 3.8 Hz, 1H), 3.41(s, 3H), 2.36(s, 3H), 2.22(s, 3H); ^{13}C NMR ($CDCl_3$): δ 179.6, 144.0, 135.6, 135.0, 134.7, 131.0, 130.4, 130.3, 129.8, 125.9, 115.1, 43.6, 20.8, 19.8; HRMS (ESI) m/z calcd for $C_{14}H_{16}NO_3S$ $[M+H]^+$ 278.0851 found 278.0841.

Methyl 5-(2,5-dimethylphenyl)-1-(methylsulfonyl)-1*H*-pyrrole-2-carboxylate (48)



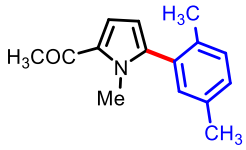
White Solid, (83 mg, 54%); R_f (10% EtOAc/Hexane): 0.3; mp 107-109 °C; IR(KBr, cm^{-1}): 2928, 1740, 1484, 754; ^{1}H NMR($CDCl_3$): δ 7.17-7.16 (m, 2H), 7.04-7.03 (m, 2H); 6.13 (d, *J* =3.6 Hz, 1H); 3.92 (s, 3H); 3.64 (s, 3H), 2.35 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 161.0, 142.4, 134.5, 132.2, 130.3, 129.8, 129.8, 127.2, 121.5, 113.3, 52.2, 44.1, 20.8, 19.7; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO_4S$ $[M+H]^+$ 308.0957 found 308.0955.

Methyl 5-(3,4-dichlorophenyl)-1-(methylsulfonyl)-1*H*-pyrrole-2-carboxylate (49)



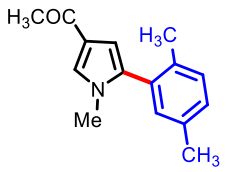
White Solid, (131 mg, 76%); R_f (10% EtOAc/Hexane): 0.2; mp 159-162 ^oC; IR(KBr, cm^{-1}): 2928, 1718, 1459, 804, 756; ^1H NMR ($CDCl_3$): δ 7.49-7.47(m, 2H), 7.21(dd, J = 8.2, 2 Hz, 1H), 7.01(d, J = 3.6 Hz, 1H), 6.22 (d, J = 3.6 Hz, 1H), 3.90(s, 3H), 3.77(s, 3H); ^{13}C NMR ($CDCl_3$): δ 160.7, 141.3, 133.0, 132.5, 132.4, 130.4, 130.1, 129.3, 128.0, 122.1, 114.2, 52.3, 44.8; HRMS (ESI) m/z calcd for $C_{13}H_{12}Cl_2NO_4S$ $[M+H]^+$ 347.9864 found 347.9861.

1-(5-(2,5-Dimethylphenyl)-1-methyl-1*H*-pyrrol-2-yl)ethan-1-one (50)



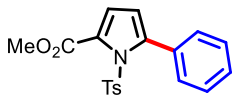
White viscous liquid; (73 mg, 65%); R_f (10% EtOAc/Hexane): 0.5; IR(KBr, cm^{-1}): 2924, 1650, 1370, 773; ^1H NMR ($CDCl_3$): 7.21-7.15(m, 2H), 7.05(d, J = 4.0 Hz, 1H), 7.03(s, 1H), 6.10(d, J = 4.0 Hz, 1H), 3.68(s, 3H), 2.49(s, 3H), 2.36(s, 3H), 2.11(s, 3H); ^{13}C NMR ($CDCl_3$): 188.4, 142.4, 135.2, 134.7, 131.4, 131.2, 130.9, 130.0, 129.7, 119.4, 109.0, 34.3, 27.2, 20.8, 19.2; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388 found 228.1395.

1-(5-(2,5-Dimethylphenyl)-1-methyl-1*H*-pyrrol-2-yl)ethan-1-one (51)



White viscous liquid; (73 mg, 65%); R_f (10% EtOAc/Hexane): 0.15; IR(KBr, cm^{-1}): 2924, 1650, 1370, 773; ^1H NMR ($CDCl_3$): 7.35(d, J = 1.9 Hz, 1H), 7.20-7.13(m, 2H), 7.04(s, 1H), 6.49(d, J = 1.9 Hz, 1H), 3.42(s, 3H), 2.44(s, 3H), 2.35(s, 3H), 2.14(s, 3H); ^{13}C NMR ($CDCl_3$): 193.5, 135.1, 135.1, 134.9, 131.7, 131.4, 130.0, 129.4, 126.7, 125.0, 108.8, 34.6, 26.9, 20.8, 19.4; HRMS (ESI) m/z calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388 found 228.1380.

Methyl 5-phenyl-1-tosyl-1*H*-pyrrole-2-carboxylate (52)

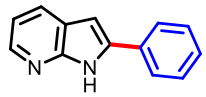


Colorless solid; (115 mg, 65%); R_f (10% EtOAc/Hexane): 0.3; mp 130-131 ^oC; IR(KBr, cm^{-1}): 2922, 1706, 1478, 1371, 763; ^1H NMR ($CDCl_3$): 7.41-7.37(m, 3H), 7.31(dt, J = 8.5, 1.4 Hz, 2H), 7.21(dd, J = 8.0, 1.0 Hz, 2H), 7.14(d, J = 8.0 Hz, 2H), 6.92(d, J = 3.5 Hz, 1H), 6.12(d, J = 3.5 Hz, 1H), 3.96(s, 3H), 2.40(s, 3H); ^{13}C NMR ($CDCl_3$): 161.8, 144.9, 143.8, 135.6, 131.3, 130.6, 130.1, 129.1, 128.8, 127.6, 127.6, 121.8, 114.4, 52.5, 21.6; HRMS (ESI) m/z calcd for $C_{19}H_{18}NO_4S$ $[M+H]^+$ 356.0957 found 356.0951.

4. General procedure for the *deprotection* of *N*-sulfonyl group (53, 54)

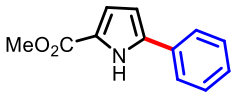
To the solution of *N*-sulfonyl heterocycles **(1**,**43)** (0.1 mmol) in acetontrile, TBAF.3H_2O (4 equiv) was added and then, reaction was heated at 80 ^oC for 6 h. The reaction mixture was allowed to cool to room temperature and solvent was evaporated. It was diluted with ethyl acetate (2 mL) and then, washed with water and brine. The organic layer was dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography on silica using (ethyl acetate/ hexane) as an eluent to give the desired product.

2-Phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (53)



Yellowish solid; (16 mg, 82%), R_f (10% EtOAc/Hexane): 0.2, mp 202-203 ^oC; IR(KBr, cm^{-1}): 3163, 1588, 1281, 74; ^1H NMR ($CDCl_3$): δ 12.13(bs, 1H), 8.33 (d, *J* = 3.8 Hz, 1H); 7.98 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.90(d, *J* = 8 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.43(tt, *J* = 7.4, 1.1 Hz, 1H), 7.15-7.12 (m, 1H), 6.82 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 149.9, 142.1, 139.5, 132.4, 129.0, 128.7, 128.2, 125.9, 122.3, 116.1, 97.4; HRMS (ESI) m/z calcd for $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0922 found 195.0918.

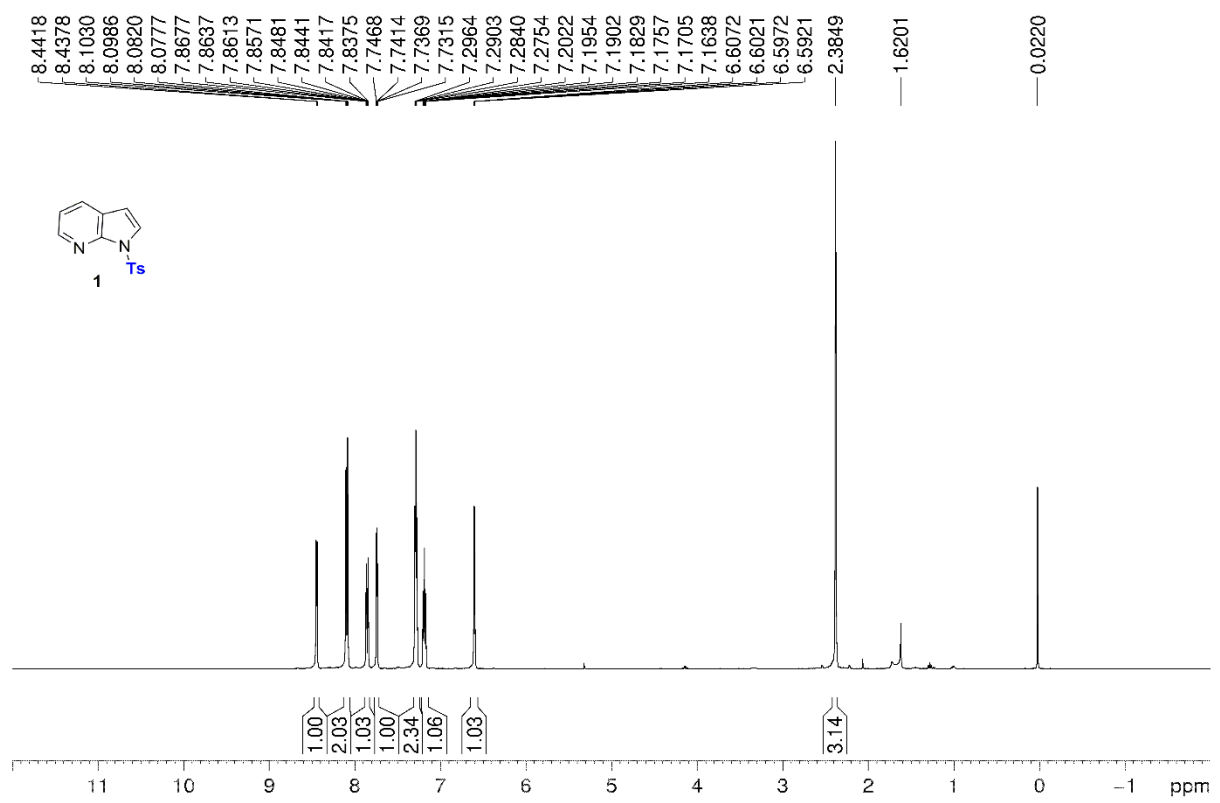
Methyl 5-phenyl-1*H*-pyrrole-2-carboxylate (54)



White Solid, (18 mg, 91%); R_f (10% EtOAc/Hexane): 0.4, mp 148-149 ^oC; IR(KBr, cm^{-1}): 3292, 1682, 1468, 764; ^1H NMR ($CDCl_3$): 9.47(s, 1H), 7.6(d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.33(tt, *J* = 7.4, 1.1 Hz, 1H), 6.99-6.97 (m, 1H), 6.57-6.56 (m, 1H), 3.90(s, 3H); ^{13}C NMR ($CDCl_3$): 161.7, 136.8, 131.2, 129.0, 127.8, 124.7, 123.0, 116.8, 108, 51.6; HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_2$ $[M+H]^+$ 202.0868 found 202.0859.

IV. References

1. D. R. Stuart, E. Villemure and K. Fagnou, *J. Am. Chem. Soc.*, 2007, **129**, 12072.
2. K. Wang and Z. Liu, *Synth. Commun.*, 2010, **40**, 144.
3. P. Kannaboina, K. Anilkumar, S. Aravinda, R. A. Vishwakarma and P. Das, *Org. Lett.*, 2013, **15**, 5718.
4. S. Potavathri, K. C. Pereira, S. I. Gorelsky, A. Pike, A. P. Lebris and B. Deboef, *J. Am. Chem. Soc.*, 2010, **132**, 14676.
5. K. Hiroya, S., Itoh and T. Sakamoto, *Tetrahedron*, 2005, **61**, 10958.


8.4418
8.4378
8.1030
8.0986
8.0820
8.0777
7.8677
7.8637
7.8613
7.8571
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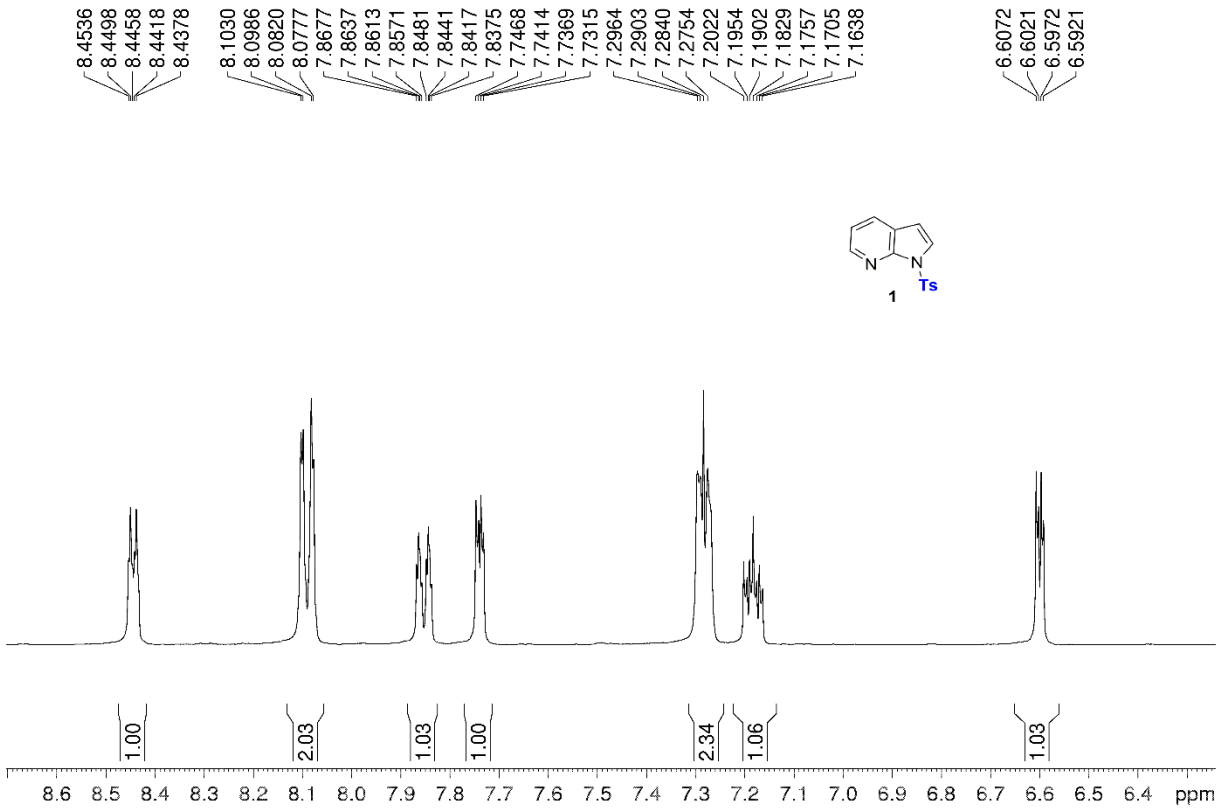
7.8441
7.8417
7.8375
7.7468
7.7414
7.7369
7.7315
7.2964
7.2903
7.2840
7.2754
7.2022
7.1954
7.1902
7.1829
7.1757
7.1705
7.1638
6.6072
6.6021
6.5972
6.5921
2.3849
1.6201
0.0220
Ts
1
1.00
2.03
1.03
1.00
2.34
1.06
1.03
3.14
ppm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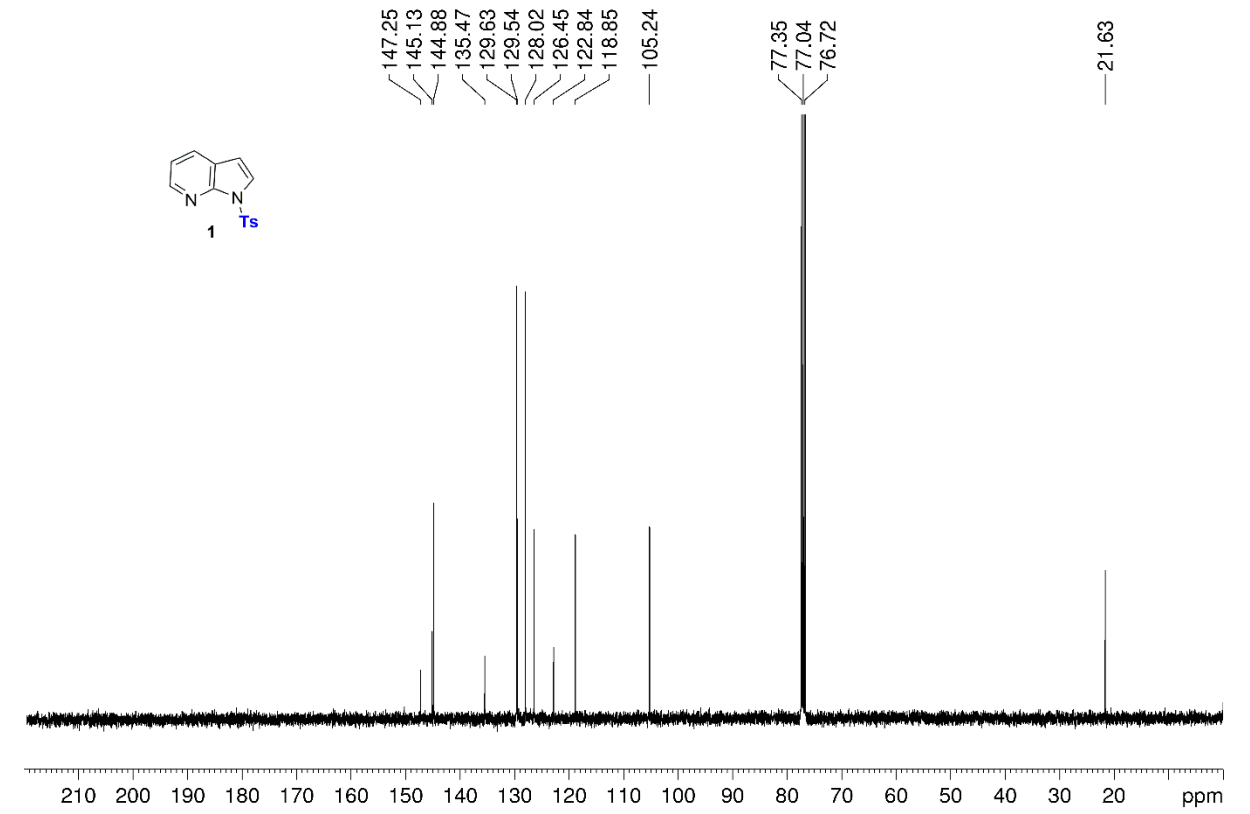
7.8417
7.8375
7.7468
7.7414
7.7369
7.7315
7.2964
7.2903
7.2840
7.2754
7.2022
7.1954
7.1902
7.1829
7.1757
7.1705
7.1638
6.6072
6.6021
6.5972
6.5921
Ts
1
1.00
2.03
1.03
1.00
2.34
1.06
1.03
ppm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126.45
122.84
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77.04
76.72
21.63
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Ts
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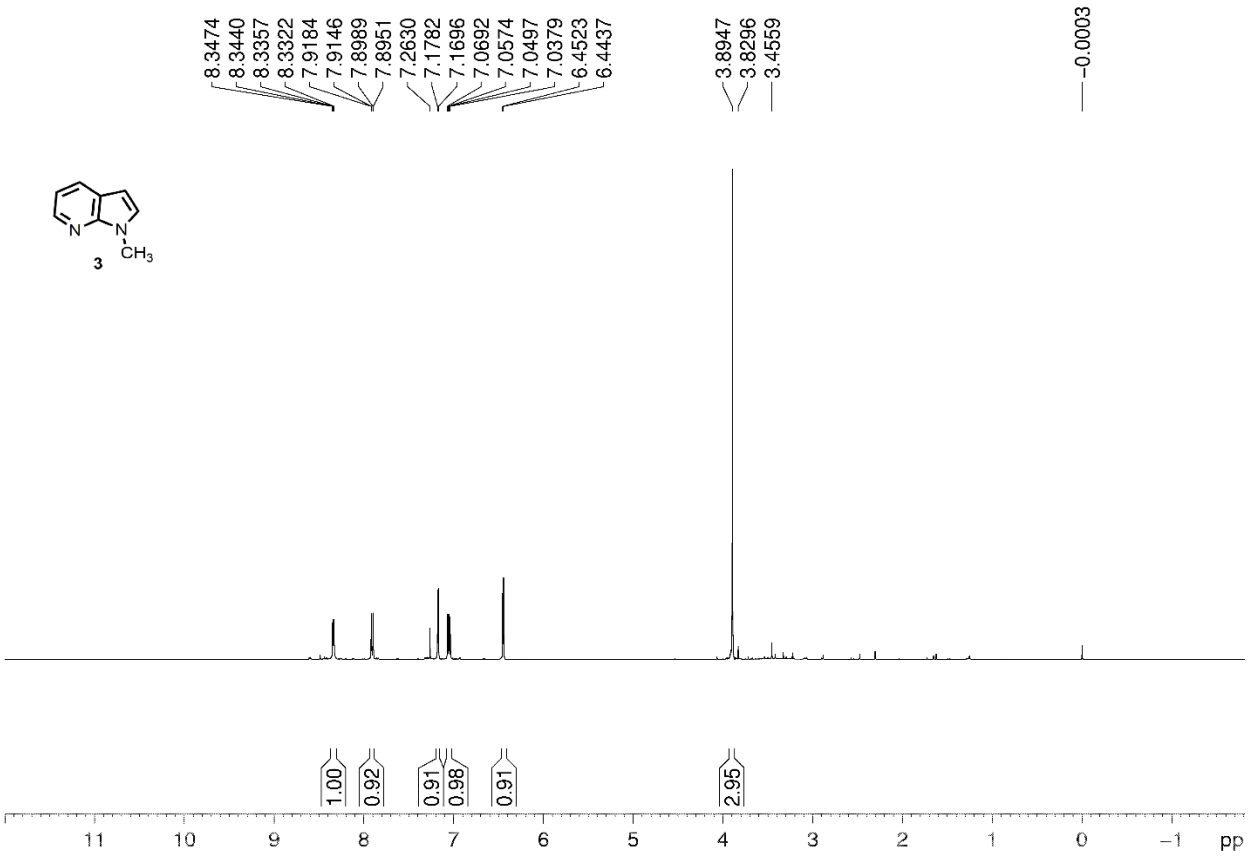
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7.8989
7.8951
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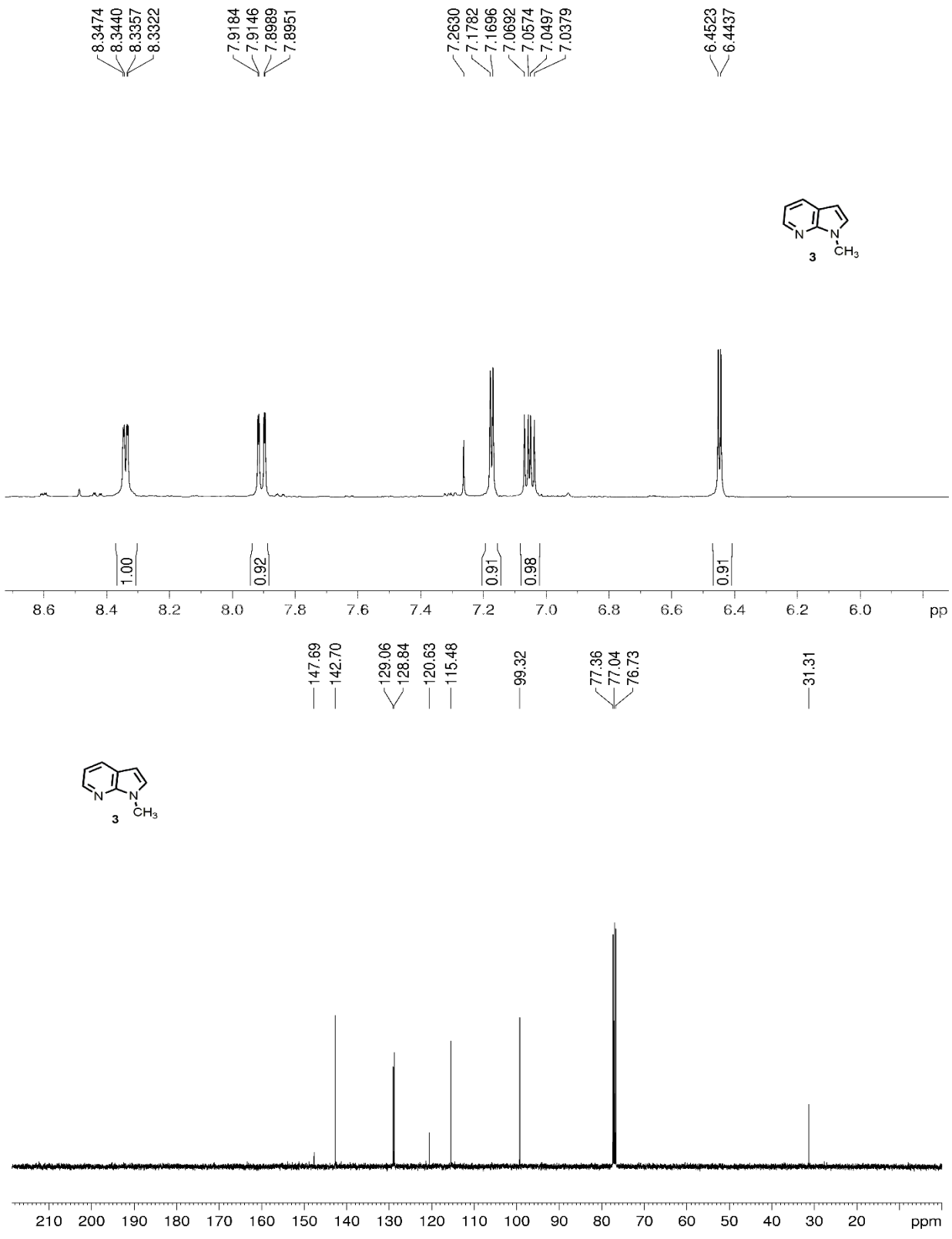
7.1782
7.1696
7.0692
7.0574
7.0497
7.0379
6.4523
6.4437
3.8947
3.8296
3.4559
-0.0003
3
CH3
1.00
0.92
0.91
0.98
0.91
2.95
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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7.1696
7.0692
7.0574
7.0497
7.0379
6.4523
6.4437
3
1.00
0.92
0.91
0.98
0.91
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
pp
147.69
142.70
129.06
128.84
120.63
115.48
99.32
77.36
77.04
76.73
31.31
3
210
200
190
180
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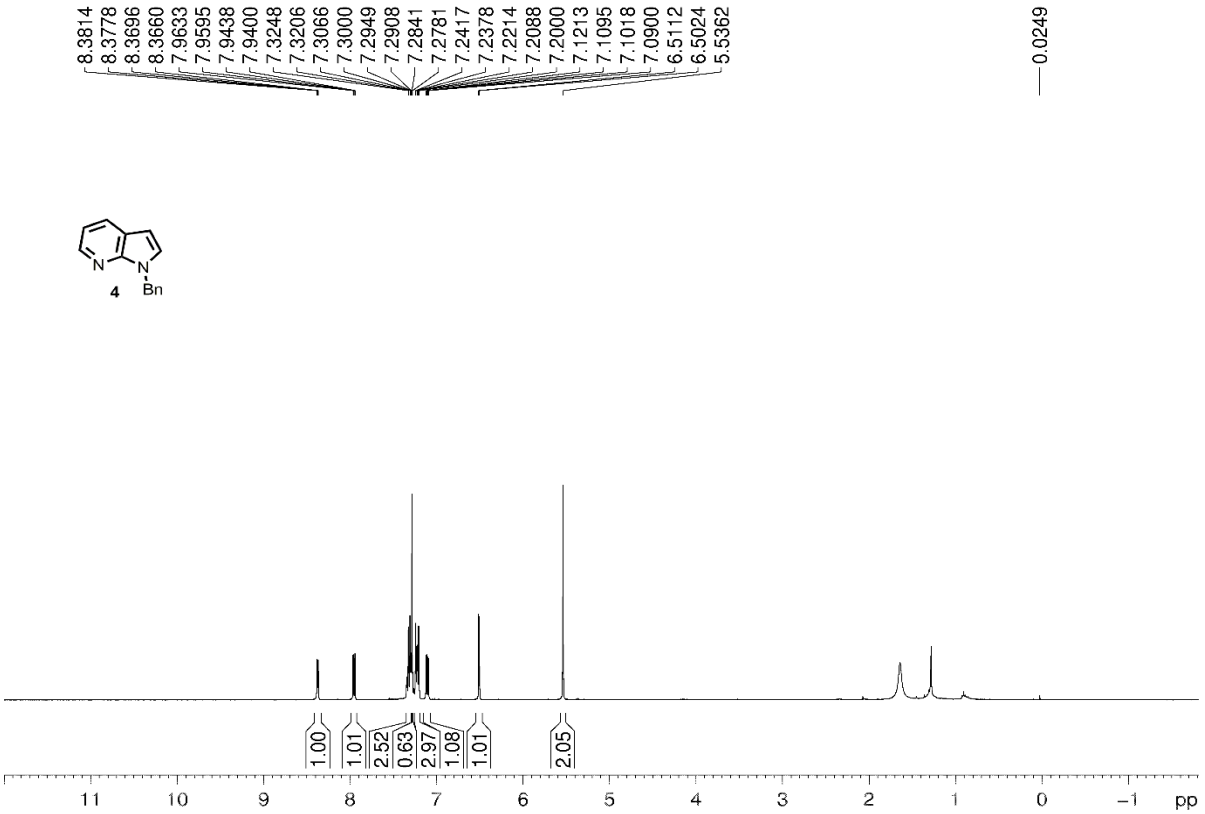
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.3066
7.3000
7.2949
7.2908
7.2841
7.2781
7.2417
7.2378
7.2214
7.2088
7.2000
7.1213
7.1095
7.1018
7.0900
6.5112
6.5024
5.5362
0.0249
4
Bn
1.00
1.01
2.52
0.63
2.97
1.08
1.01
2.05
pp
4
Bn
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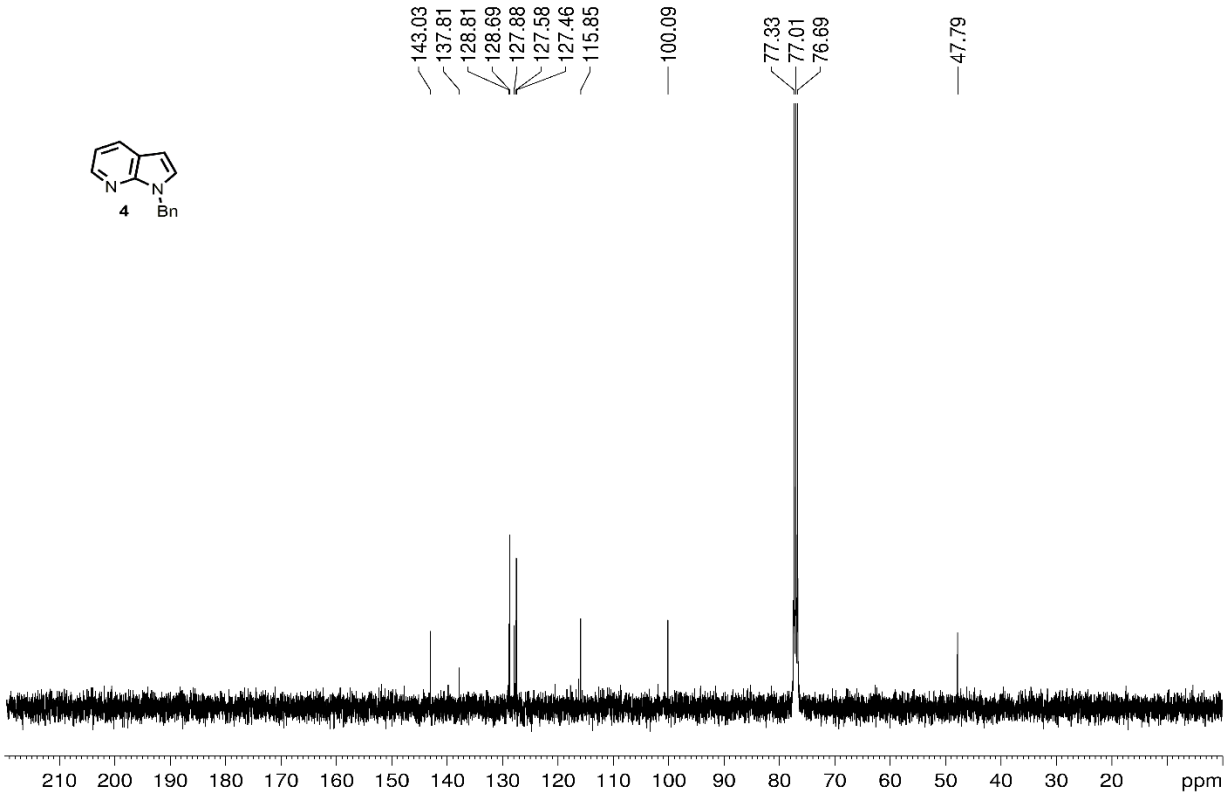
2.52
0.63
2.97
1.08
1.01
pp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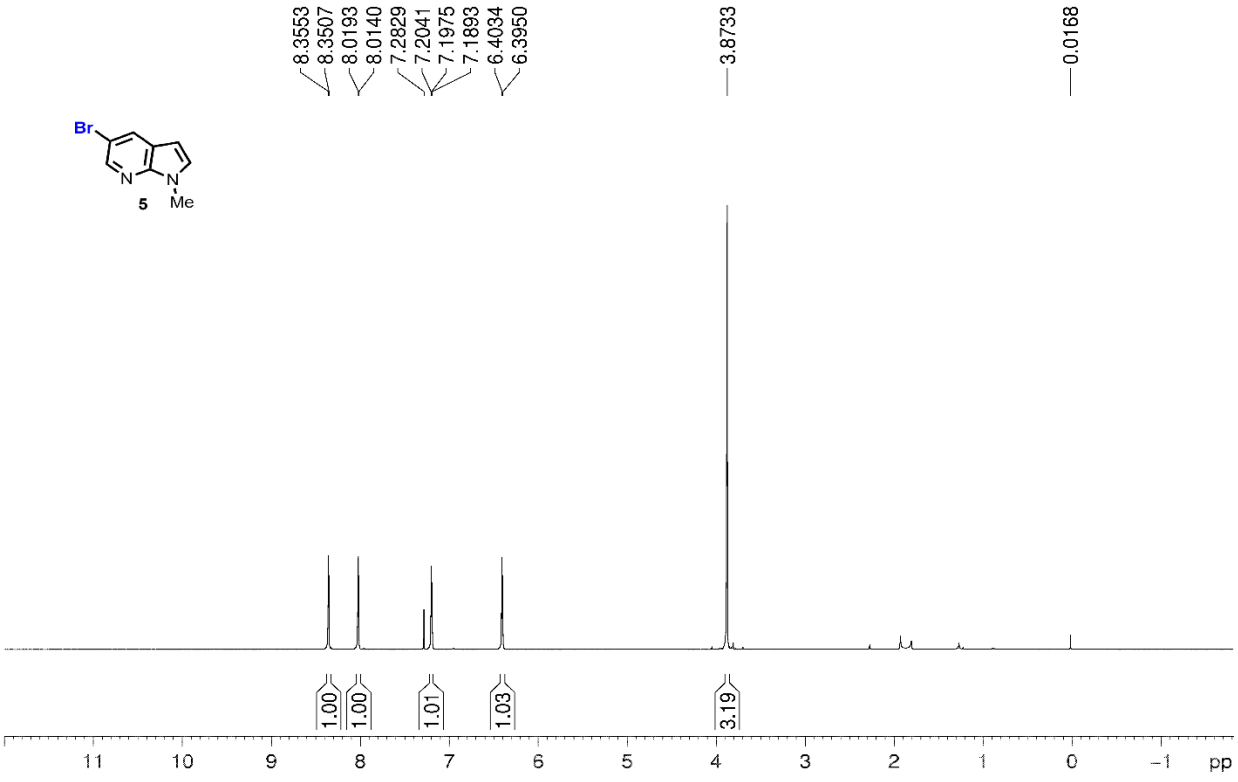
137.81
128.81
128.69
127.88
127.58
127.46
115.85
100.09
77.33
77.01
76.69
47.79
4
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.0140
7.2829
7.2041
7.1975
7.1893
6.4034
6.3950
3.8733
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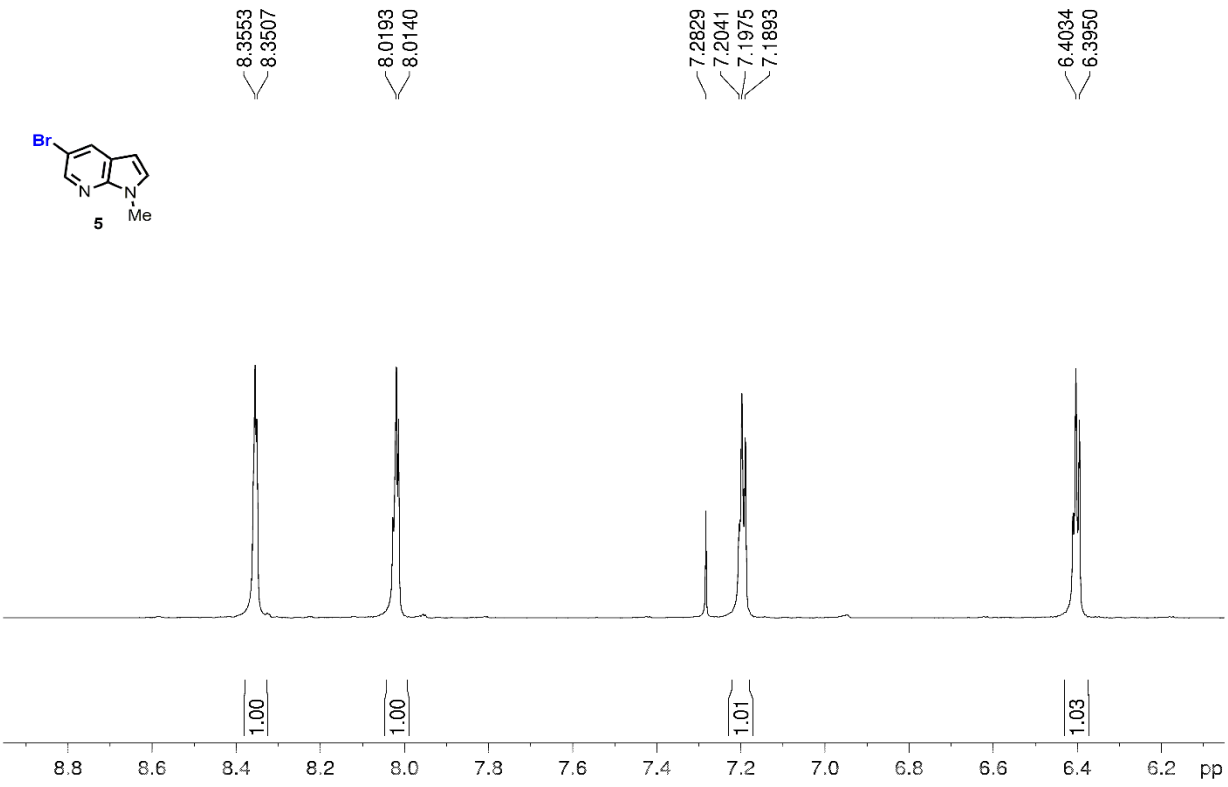
Br
5
Me
1.00
1.00
1.01
1.03
3.19
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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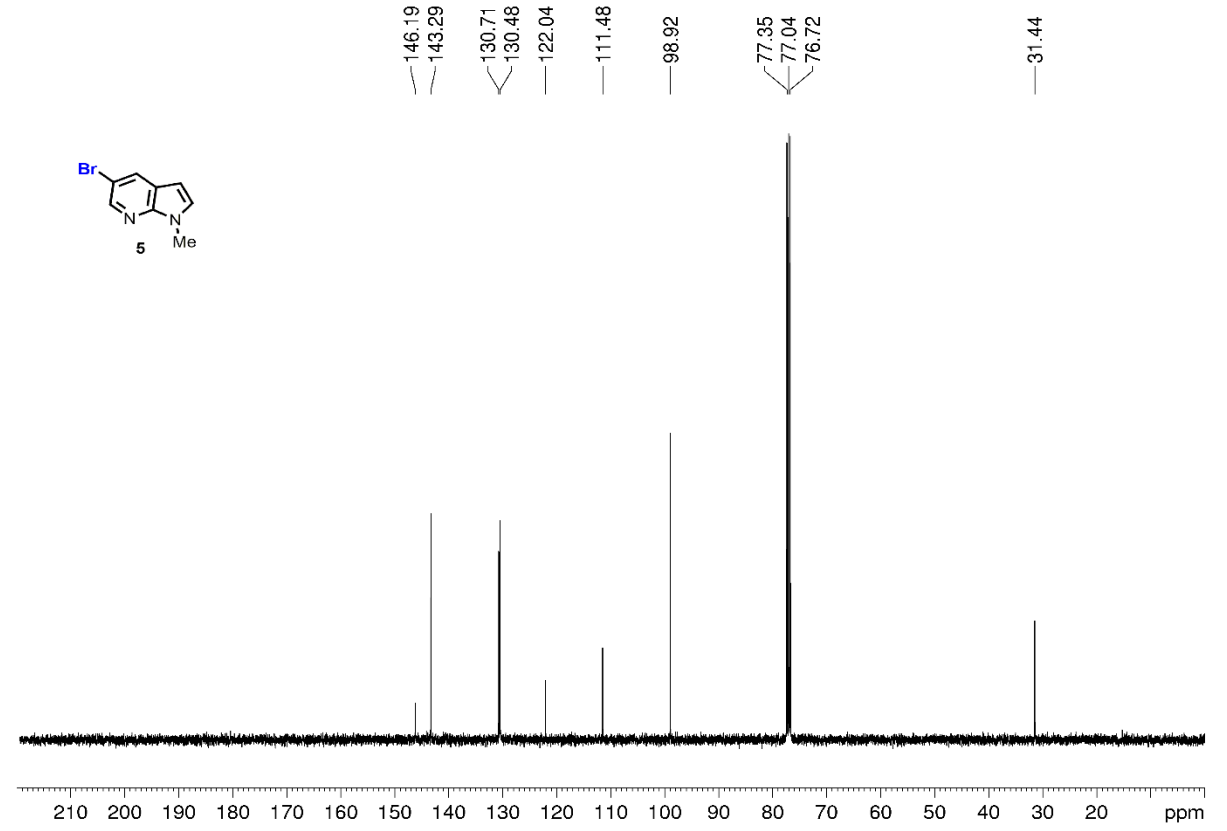
8.0140
7.2829
7.2041
7.1975
7.1893
6.4034
6.3950
Br
N
N
Me
5
1.00
1.00
1.01
1.03
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
pp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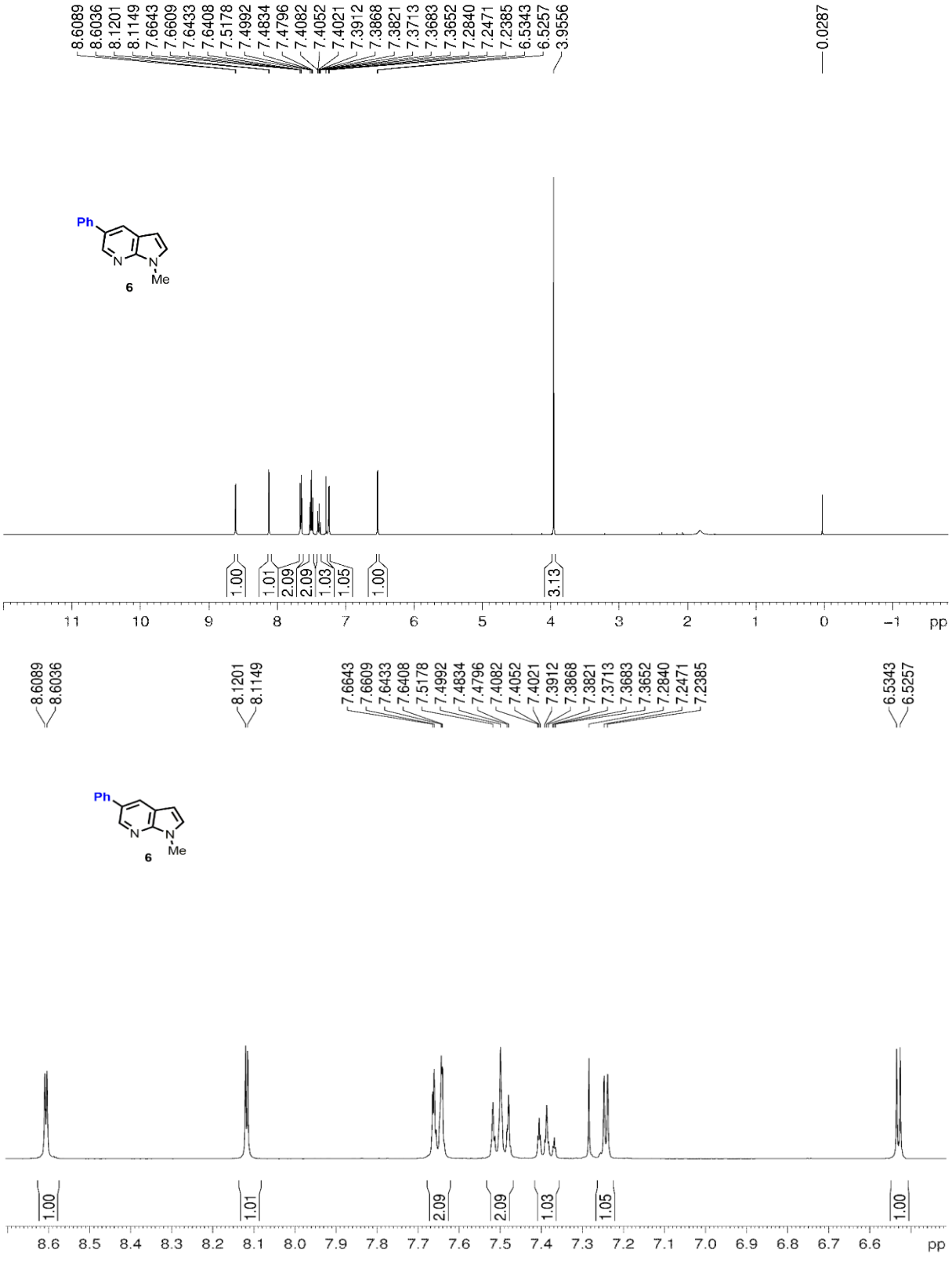
143.29
130.71
130.48
122.04
111.48
98.92
77.35
77.04
76.72
31.44
Br
N
N
Me
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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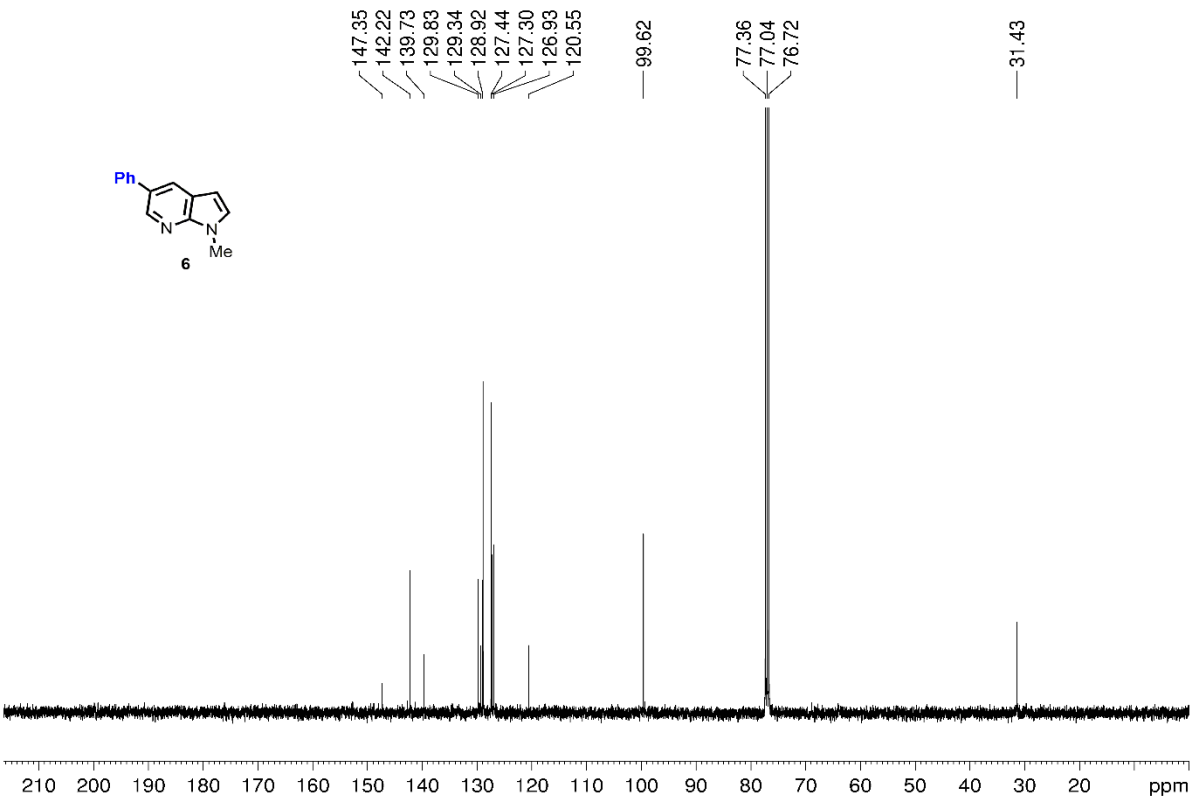
8.1201
8.1149
7.6643
7.6609
7.6433
7.6408
7.5178
7.4992
7.4834
7.4796
7.4082
7.4052
7.4021
7.3912
7.3868
7.3821
7.3713
7.3683
7.3652
7.2840
7.2471
7.2385
6.5343
6.5257
3.9556
0.0287
Ph
N
N
Me
6
1.00
1.01
2.09
2.09
1.03
1.05
1.00
3.13
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp
8.6089
8.6036
8.1201
8.1149
7.6643
7.6609
7.6433
7.6408
7.5178
7.4992
7.4834
7.4796
7.4082
7.4052
7.4021
7.3912
7.3868
7.3821
7.3713
7.3683
7.3652
7.2840
7.2471
7.2385
6.5343
6.5257
Ph
N
N
Me
6
1.00
1.01
2.09
2.09
1.03
1.05
1.00
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
pp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139.73
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129.34
128.92
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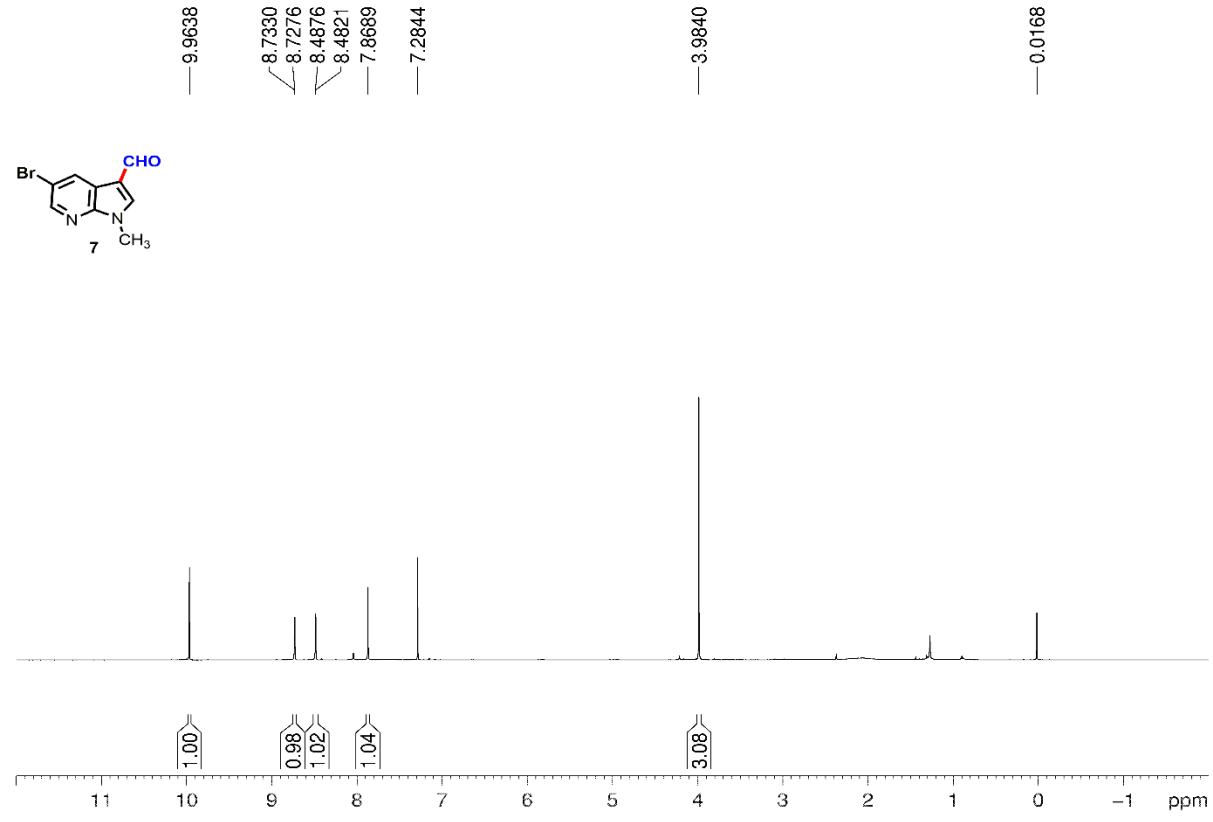
127.30
126.93
120.55
99.62
77.36
77.04
76.72
31.43
Ph
N
N
Me
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.7330
8.7276
8.4876
8.4821
7.8689
7.2844
3.9840
0.0168
Br
CHO
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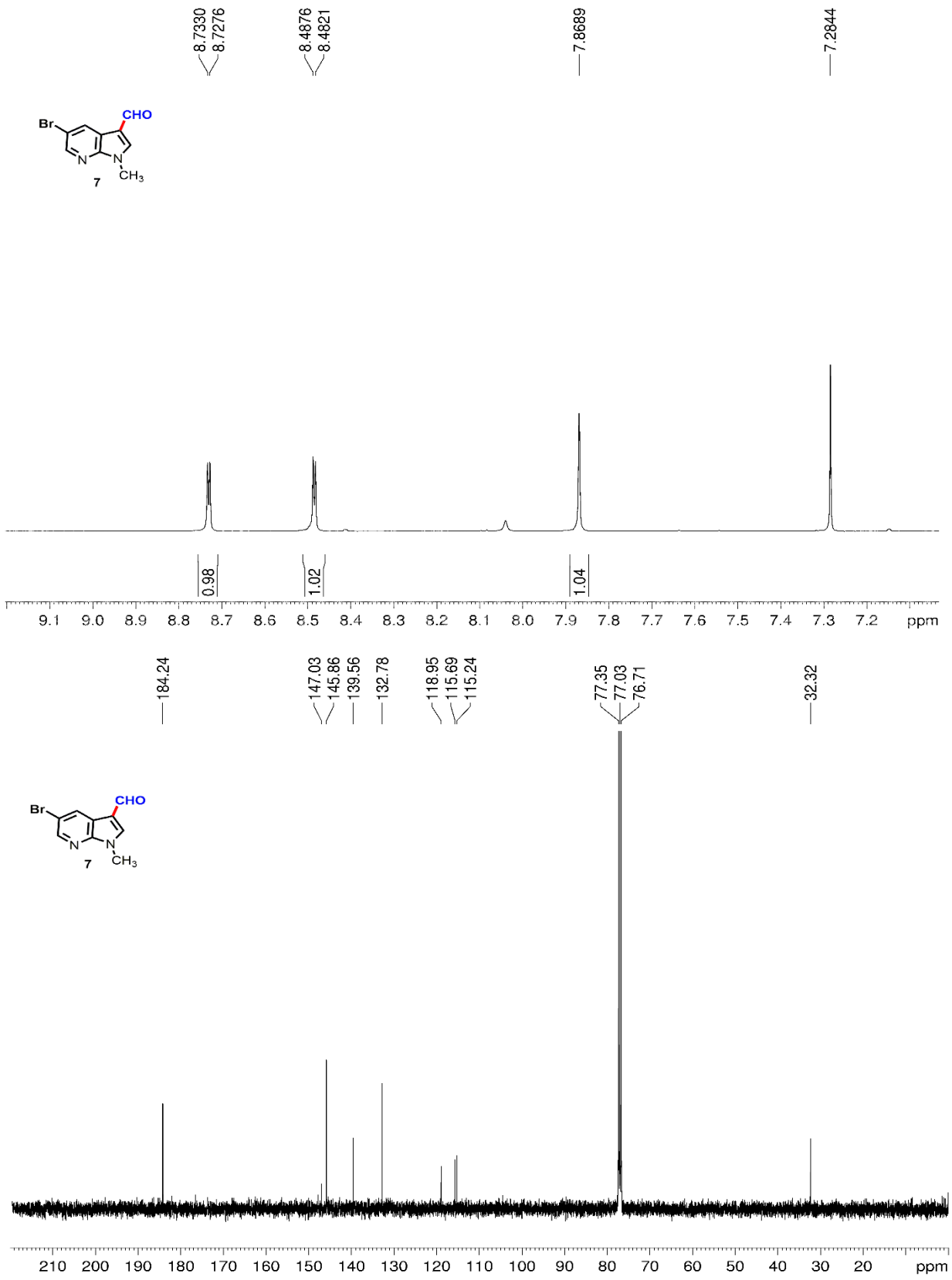
N
CH3
7
1.00
0.98
1.02
1.04
3.08
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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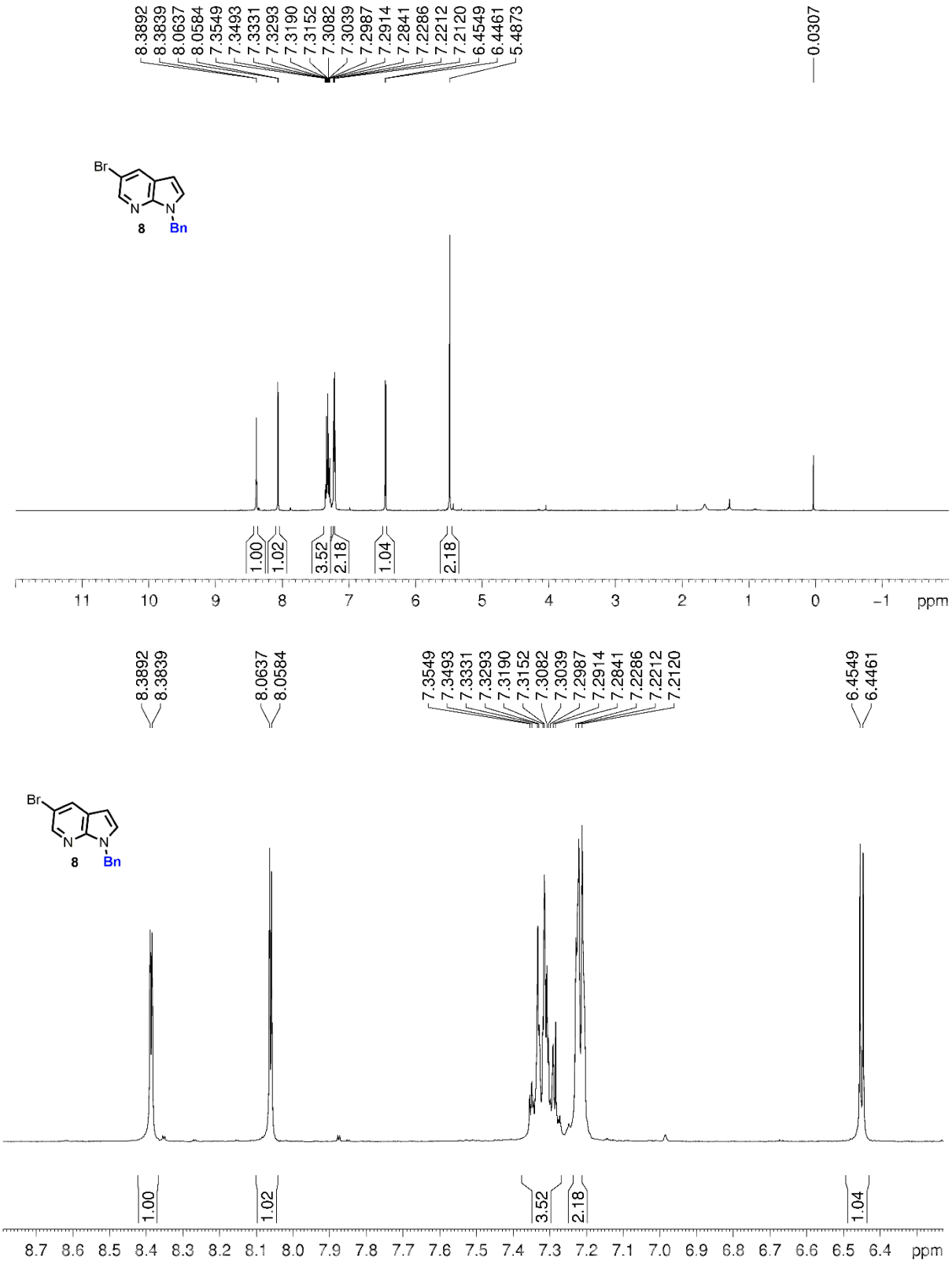
8.7276
8.4876
8.4821
7.8689
7.2844
Br
CHO
N
N
CH3
7
0.98
1.02
1.04
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
184.24
147.03
145.86
139.56
132.78
118.95
115.69
115.24
77.35
77.03
76.71
32.32
Br
CHO
N
N
CH3
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.0584
7.3549
7.3493
7.3331
7.3293
7.3190
7.3152
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7.3039
7.2987
7.2914
7.2841
7.2286
7.2212
7.2120
6.4549
6.4461
5.4873
0.0307
Br
N
N
8
Bn
1.00
1.02
3.52
2.18
1.04
2.18
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
8.3892
8.3839
8.0637
8.0584
7.3549
7.3493
7.3331
7.3293
7.3190
7.3152
7.3082
7.3039
7.2987
7.2914
7.2841
7.2286
7.2212
7.2120
6.4549
6.4461
Br
N
N
8
Bn
1.00
1.02
3.52
2.18
1.04
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
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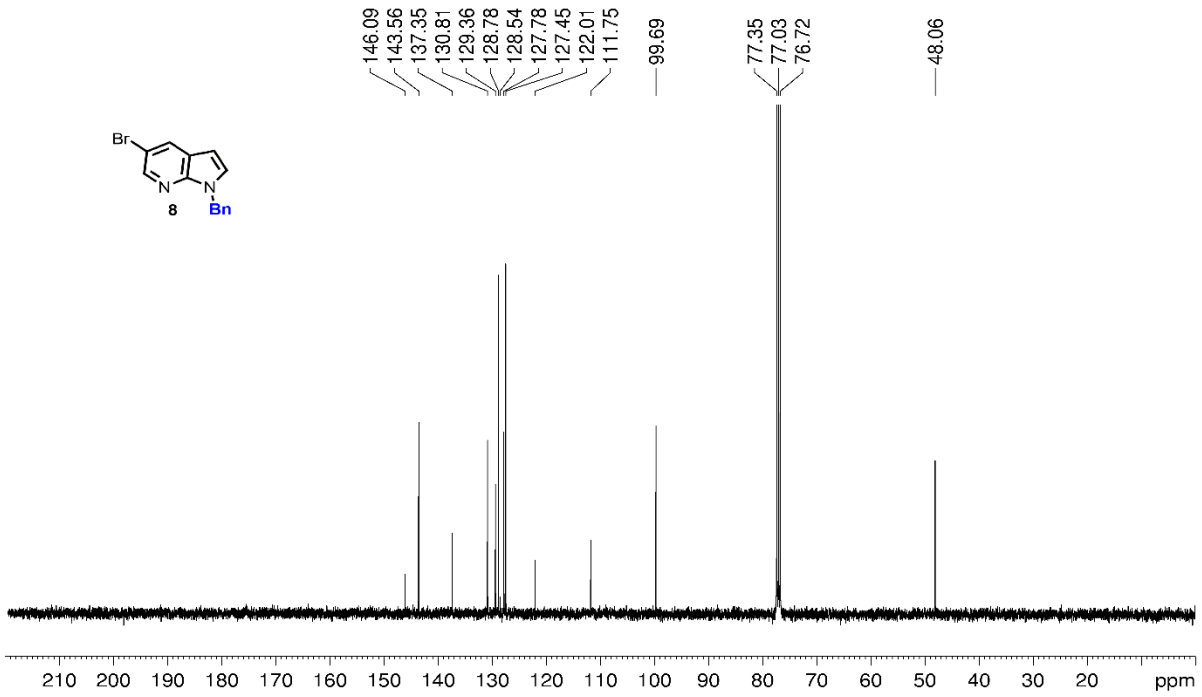
6.8
6.7
6.6
6.5
6.4
ppm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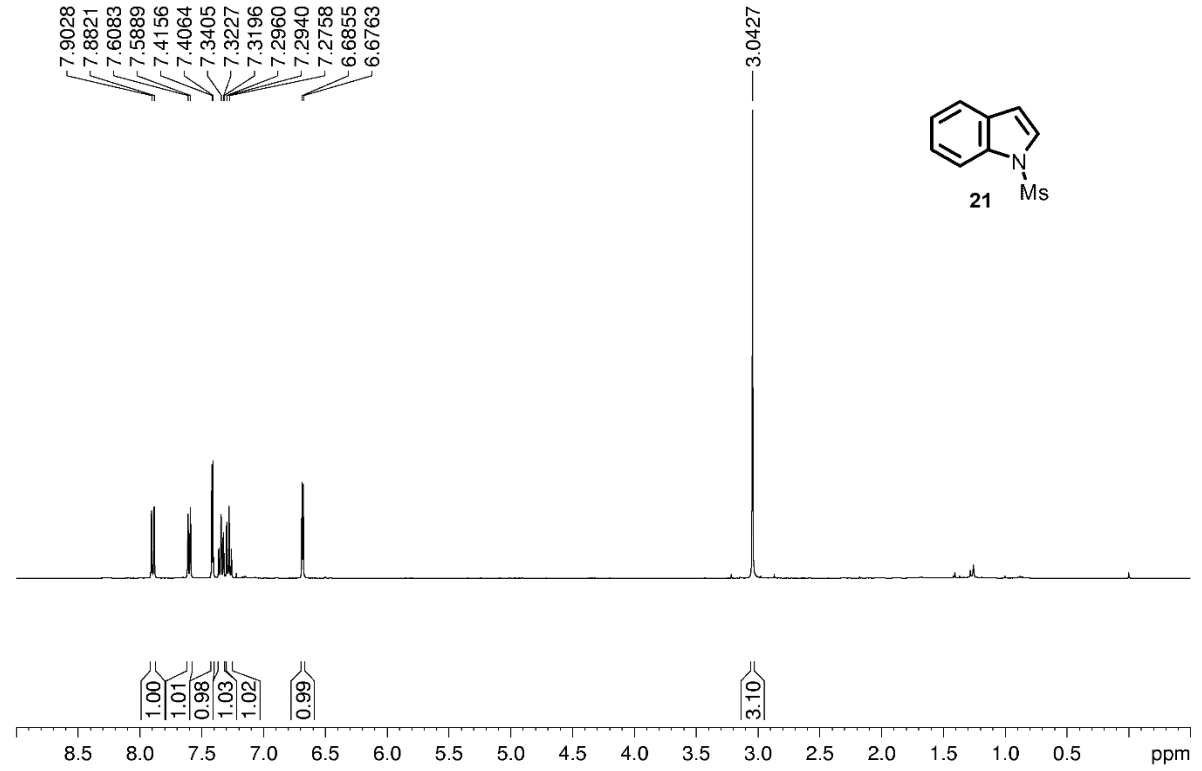
129.36
128.78
128.54
127.78
127.45
122.01
111.75
99.69
77.35
77.03
76.72
48.06
Br
N
N
Bn
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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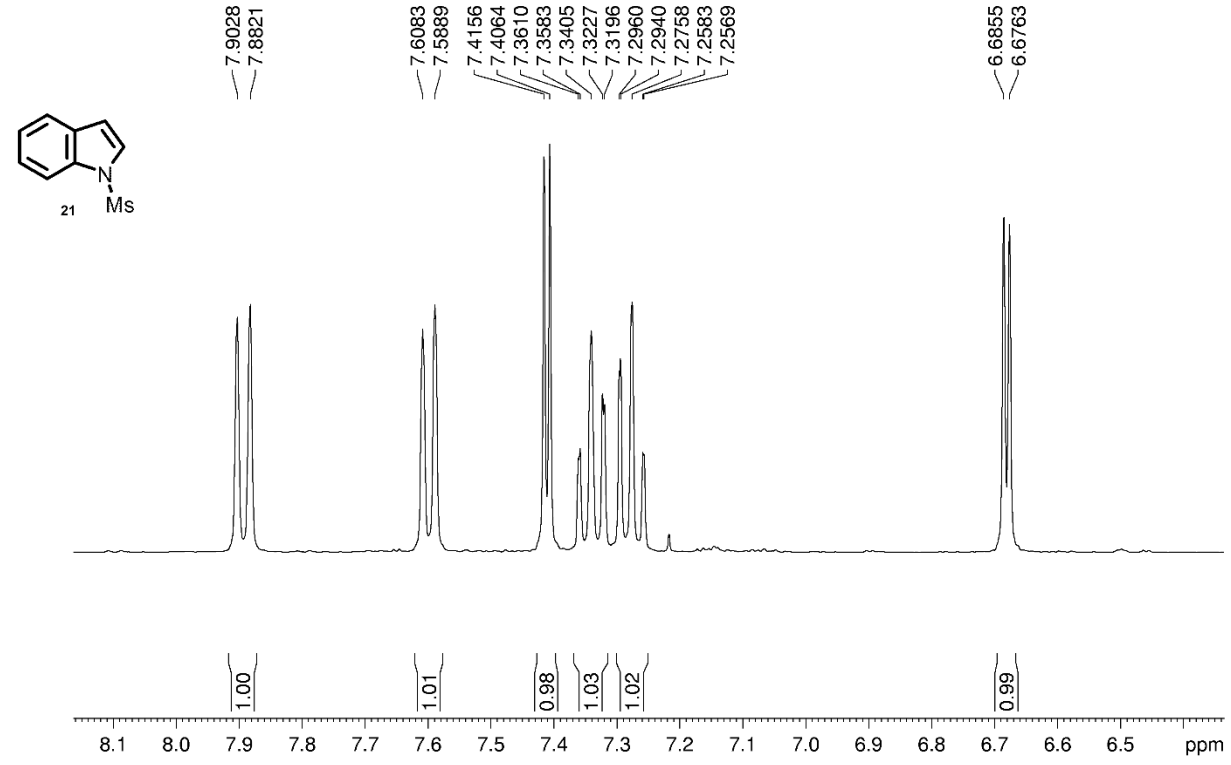
7.6083
7.5889
7.4156
7.4064
7.3405
7.3227
7.3196
7.2960
7.2940
7.2758
6.6855
6.6763
3.0427
N
Ms
21
1.00
1.01
0.98
1.03
1.02
0.99
3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm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7.8821
7.6083
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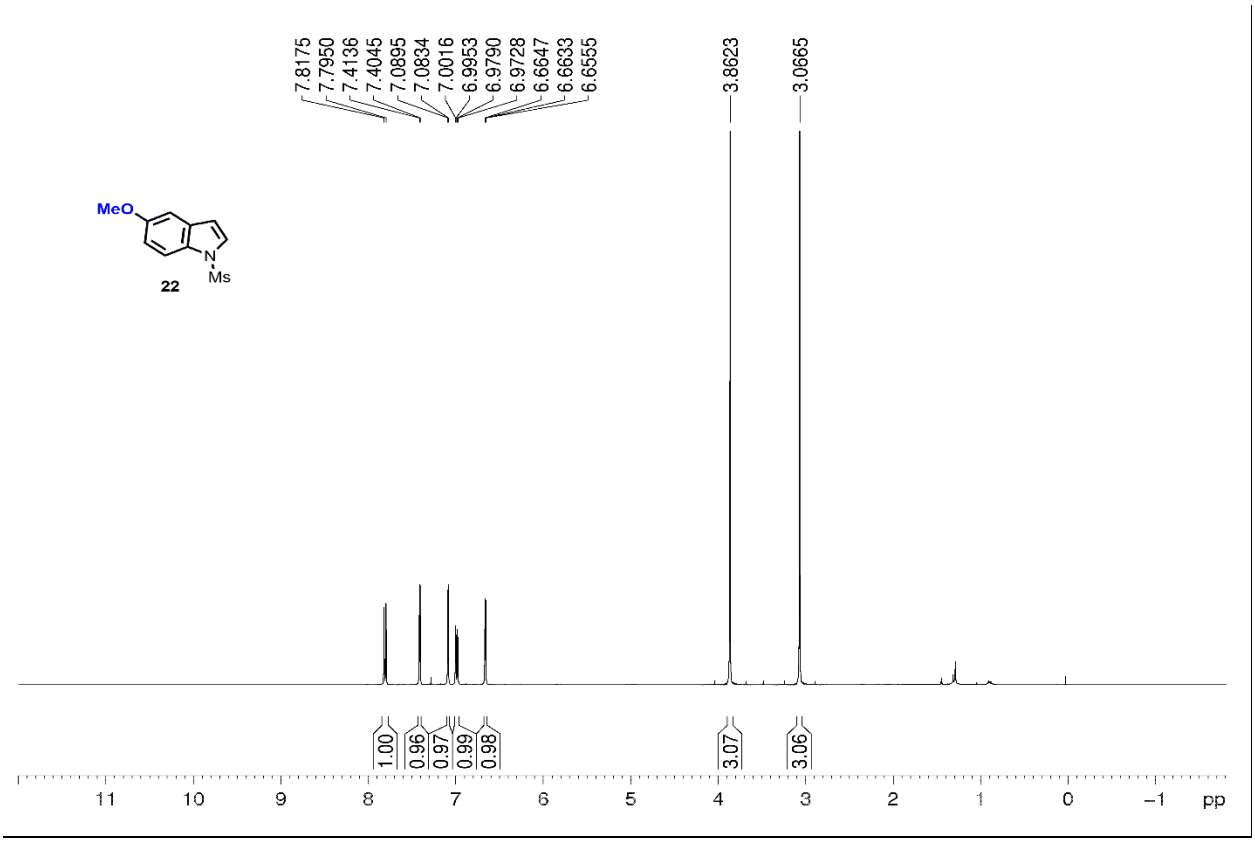
7.3405
7.3227
7.3196
7.2960
7.2940
7.2758
7.2583
7.2569
6.6855
6.6763
N
Ms
21
1.00
1.01
0.98
1.03
1.02
0.99
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
ppm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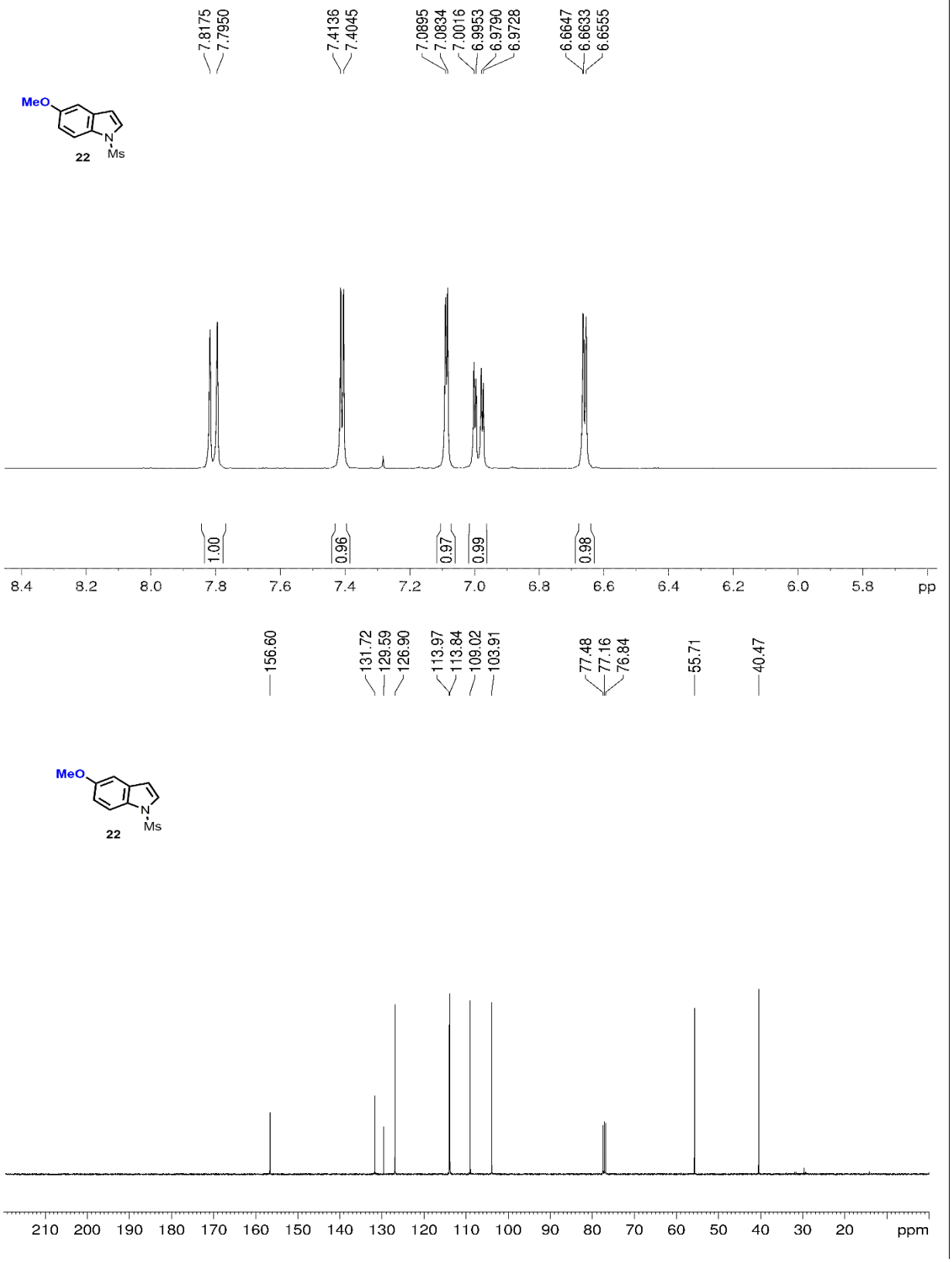
7.4136
7.4045
7.0895
7.0834
7.0016
6.9953
6.9790
6.9728
6.6647
6.6633
6.6555
3.8623
3.0665
MeO
N
Ms
22
1.00
0.96
0.97
0.99
0.98
3.07
3.06
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp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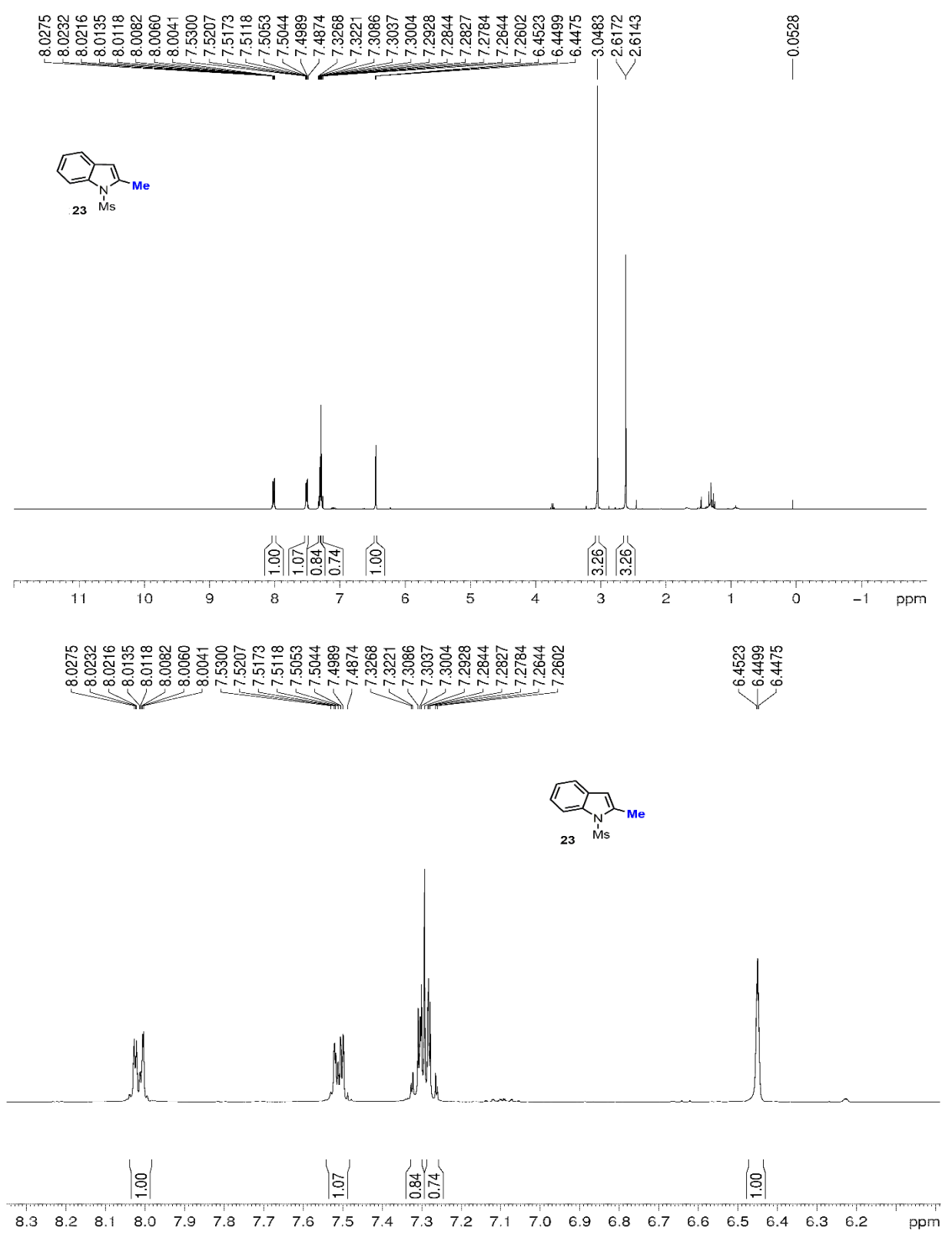
7.7950
7.4136
7.4045
7.0895
7.0834
7.0016
6.9953
6.9790
6.9728
6.6647
6.6633
6.6555
MeO
N
Ms
22
1.00
0.96
0.97
0.99
0.98
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
pp
156.60
131.72
129.59
126.90
113.97
113.84
109.02
103.91
77.48
77.16
76.84
55.71
40.47
MeO
N
Ms
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.0135
8.0118
8.0082
8.0060
8.0041
7.5300
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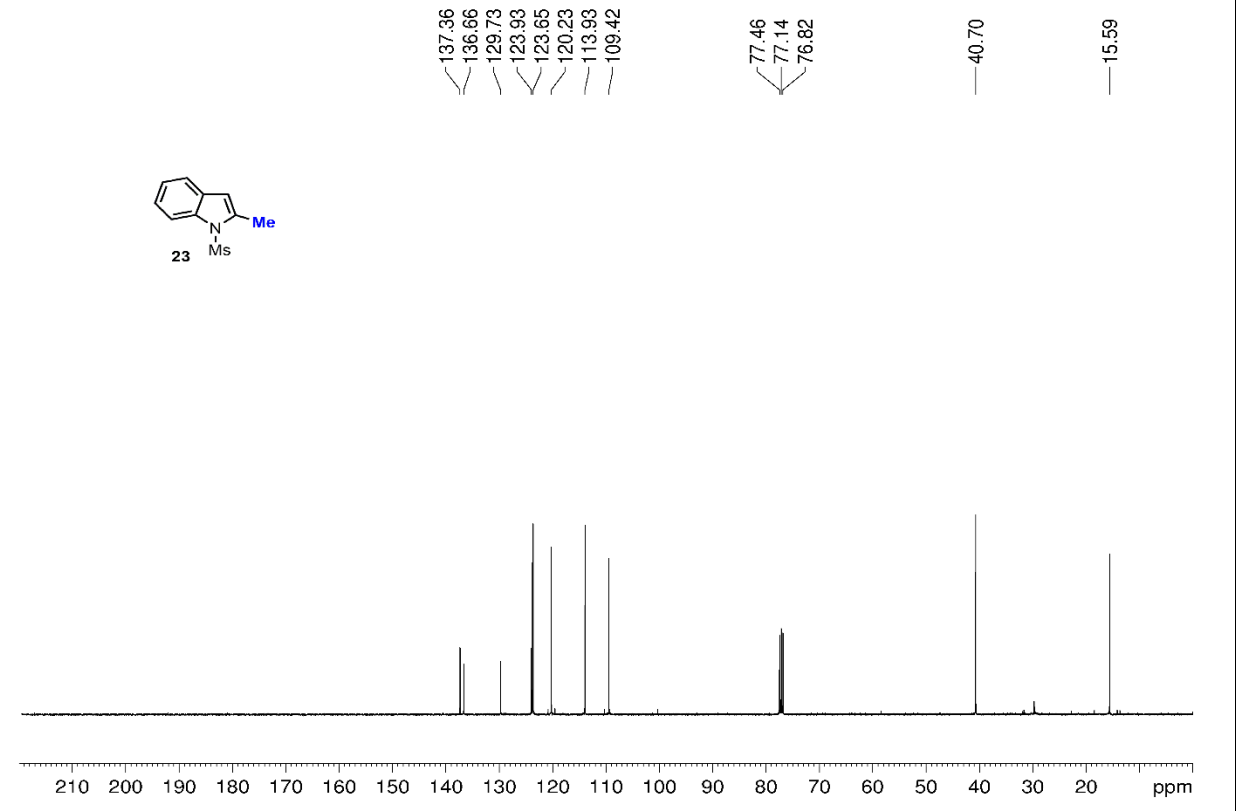
7.5173
7.5118
7.5053
7.5044
7.4989
7.4874
7.3268
7.3221
7.3086
7.3037
7.3004
7.2928
7.2844
7.2827
7.2784
7.2644
7.2602
6.4523
6.4499
6.4475
3.0483
2.6172
2.6143
0.0528
Me
N
Ms
23
1.00
1.07
0.84
0.74
1.00
3.26
3.26
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 ppm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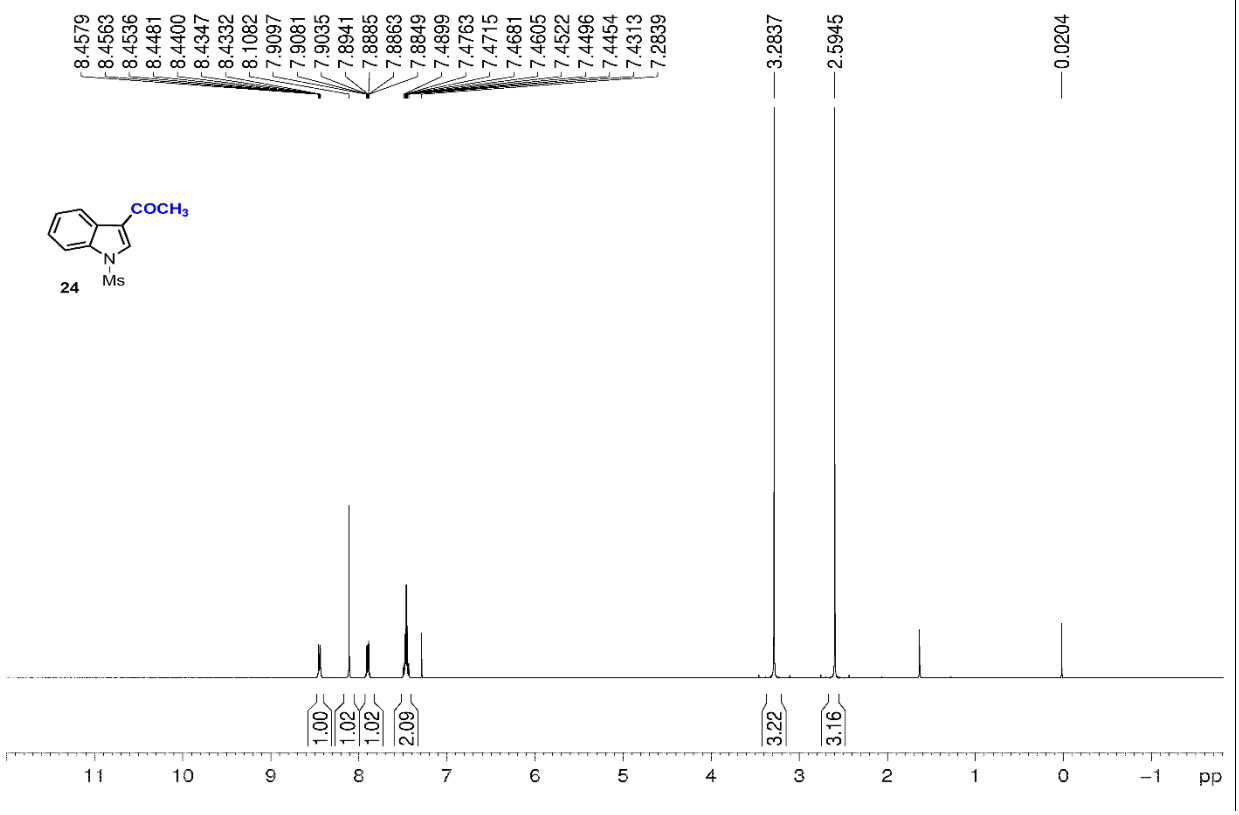
129.73
123.93
123.65
120.23
113.93
109.42
77.46
77.14
76.82
40.70
15.59
Me
N
Ms
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.4400
8.4347
8.4332
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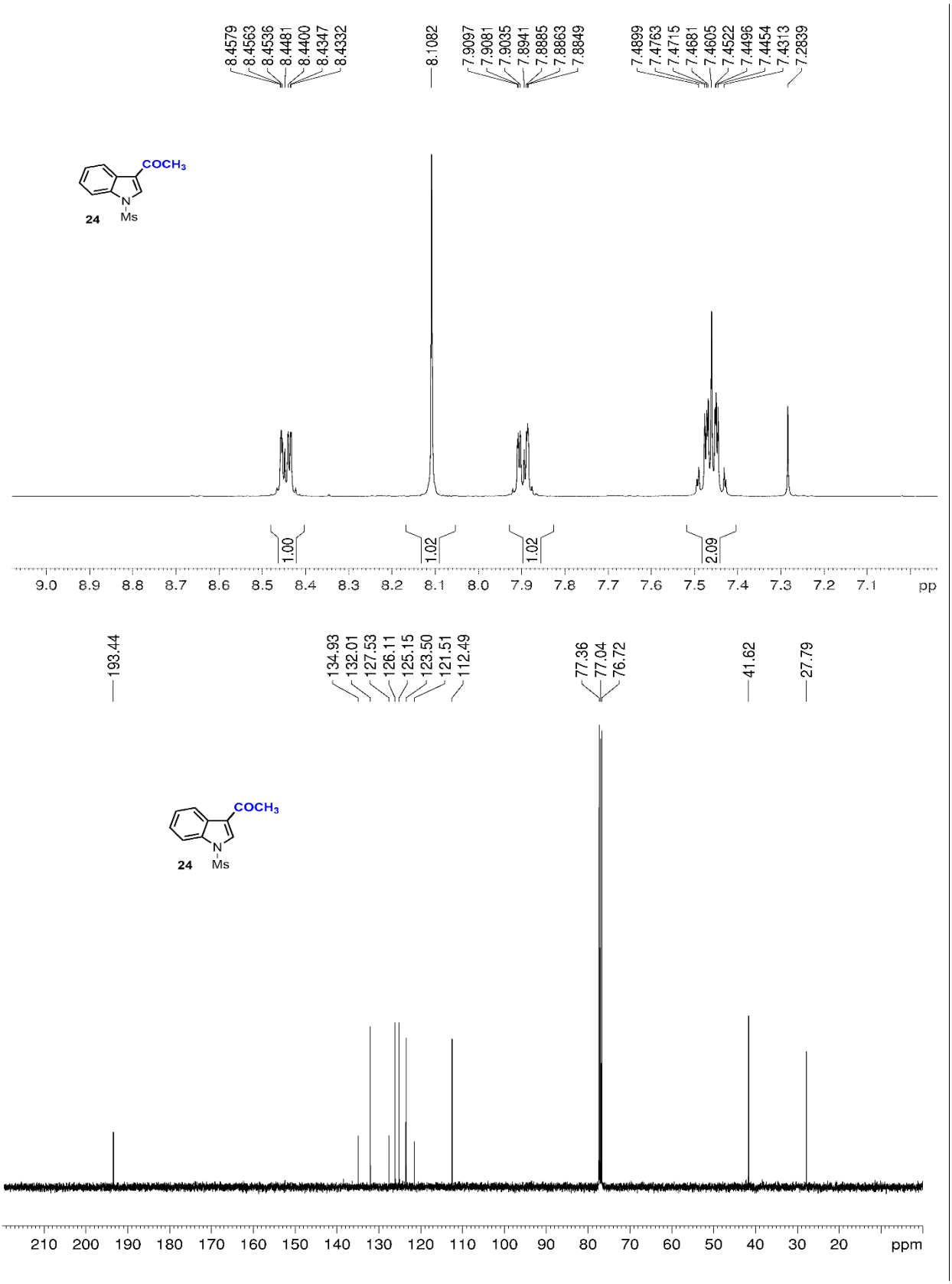
7.9097
7.9081
7.9035
7.8941
7.8885
7.8863
7.8849
7.4899
7.4763
7.4715
7.4681
7.4605
7.4522
7.4496
7.4454
7.4313
7.2839
3.2837
2.5945
0.0204
COCH3
N
Ms
24
1.00
1.02
1.02
2.09
3.22
3.16
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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8.4347
8.4332
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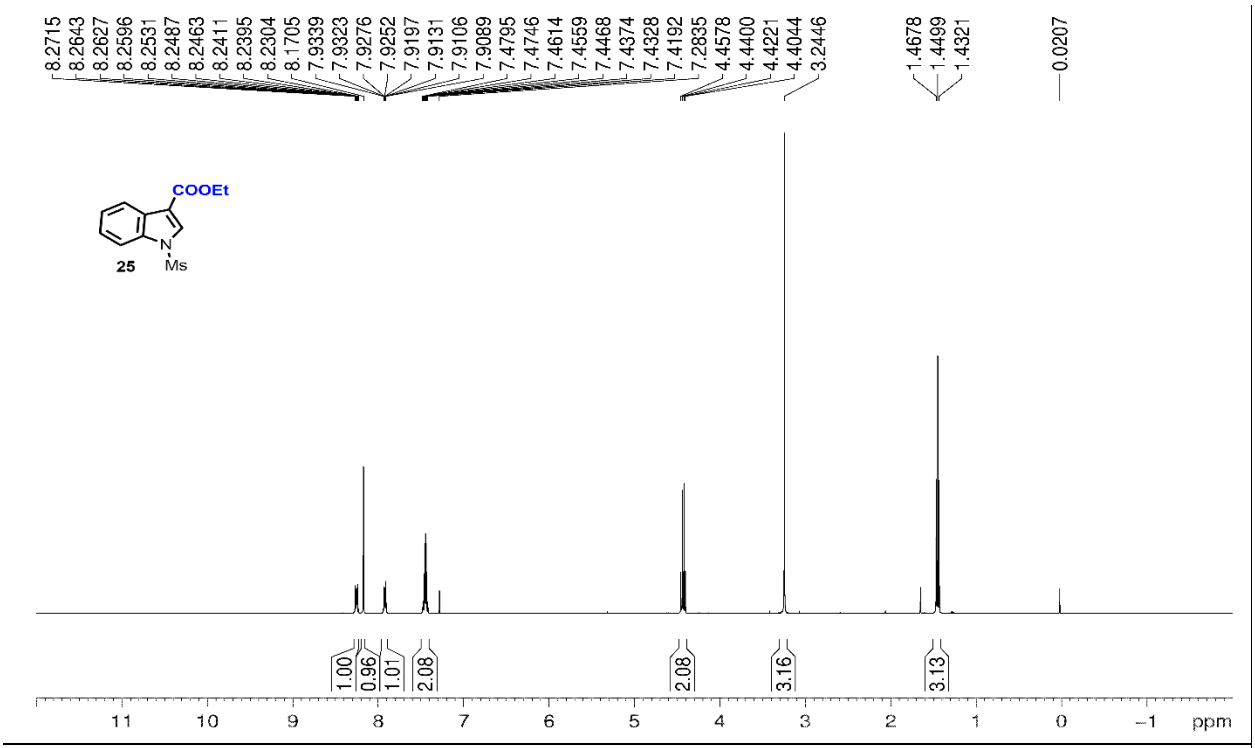
7.9097
7.9081
7.9035
7.8941
7.8885
7.8863
7.8849
7.4899
7.4763
7.4715
7.4681
7.4605
7.4522
7.4496
7.4454
7.4313
7.2839
COCH3
N
Ms
24
1.00
1.02
1.02
2.09
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 pp
193.44
134.93
132.01
127.53
126.11
125.15
123.50
121.51
112.49
77.36
77.04
76.72
41.62
27.79
COCH3
N
Ms
24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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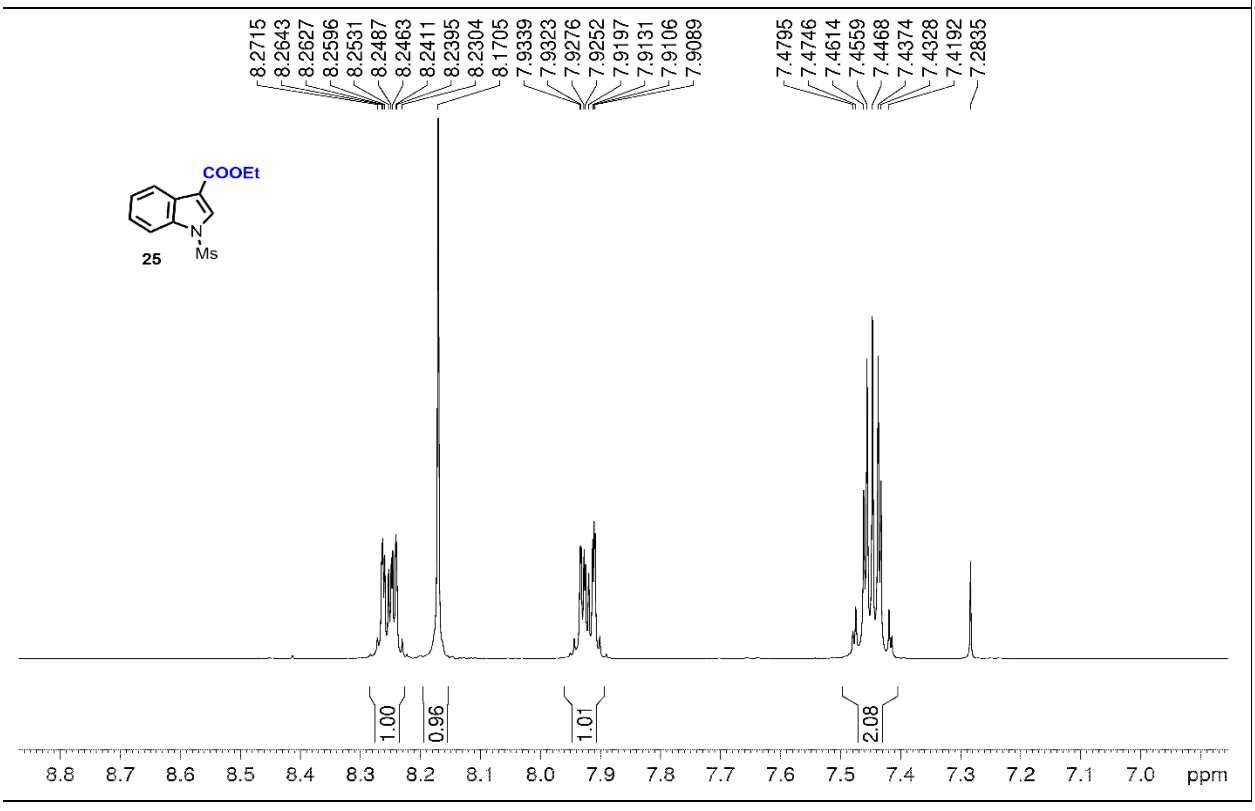
8.1705
7.9339
7.9323
7.9276
7.9252
7.9197
7.9131
7.9106
7.9089
7.4795
7.4746
7.4614
7.4559
7.4468
7.4374
7.4328
7.4192
7.2835
4.4578
4.4400
4.4221
4.4044
3.2446
1.4678
1.4499
1.4321
0.0207
COOEt
N
Ms
25
1.00
0.96
1.01
2.08
2.08
3.16
3.13
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm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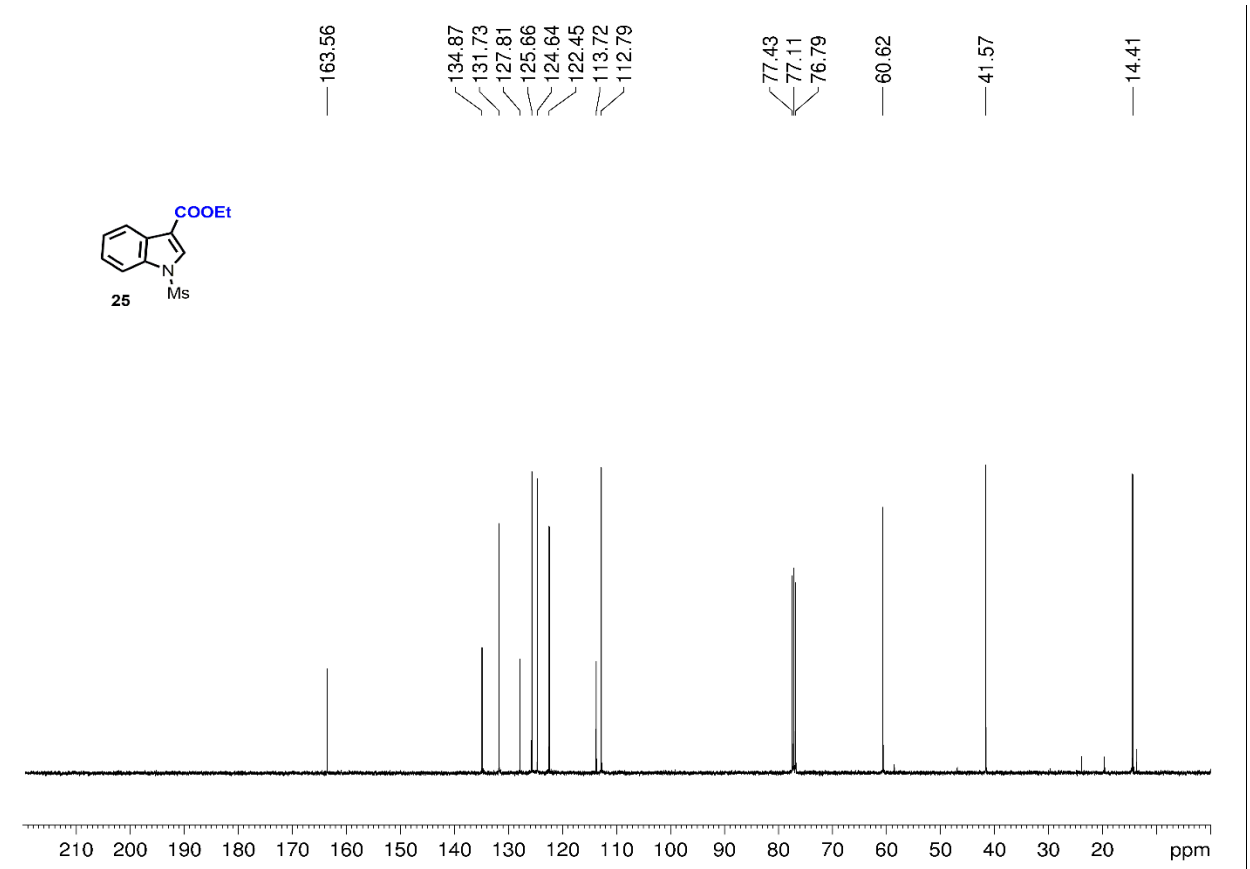
8.2531
8.2487
8.2463
8.2411
8.2395
8.2304
8.1705
7.9339
7.9323
7.9276
7.9252
7.9197
7.9131
7.9106
7.9089
7.4795
7.4746
7.4614
7.4559
7.4468
7.4374
7.4328
7.4192
7.2835
COOEt
N
Ms
25
1.00
0.96
1.01
2.08
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm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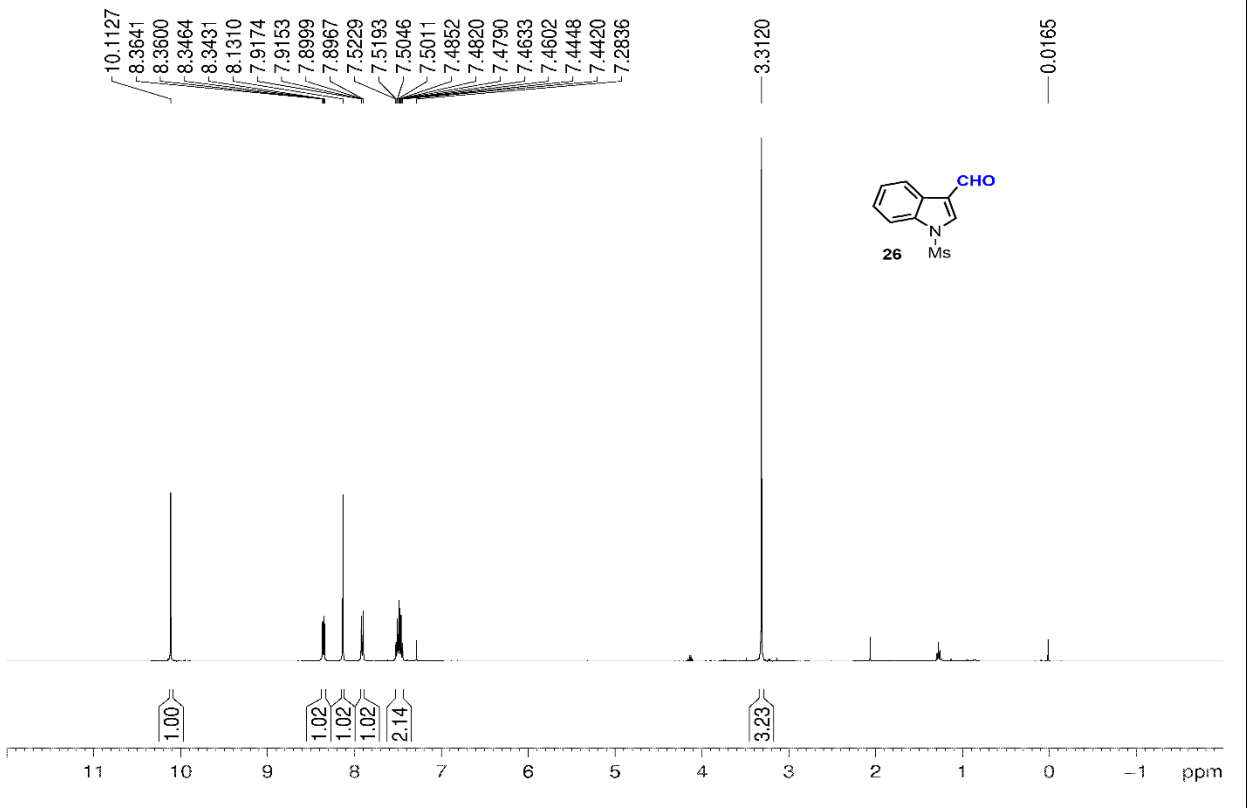
134.87
131.73
127.81
125.66
124.64
122.45
113.72
112.79
77.43
77.11
76.79
60.62
41.57
14.41
COOEt
N
Ms
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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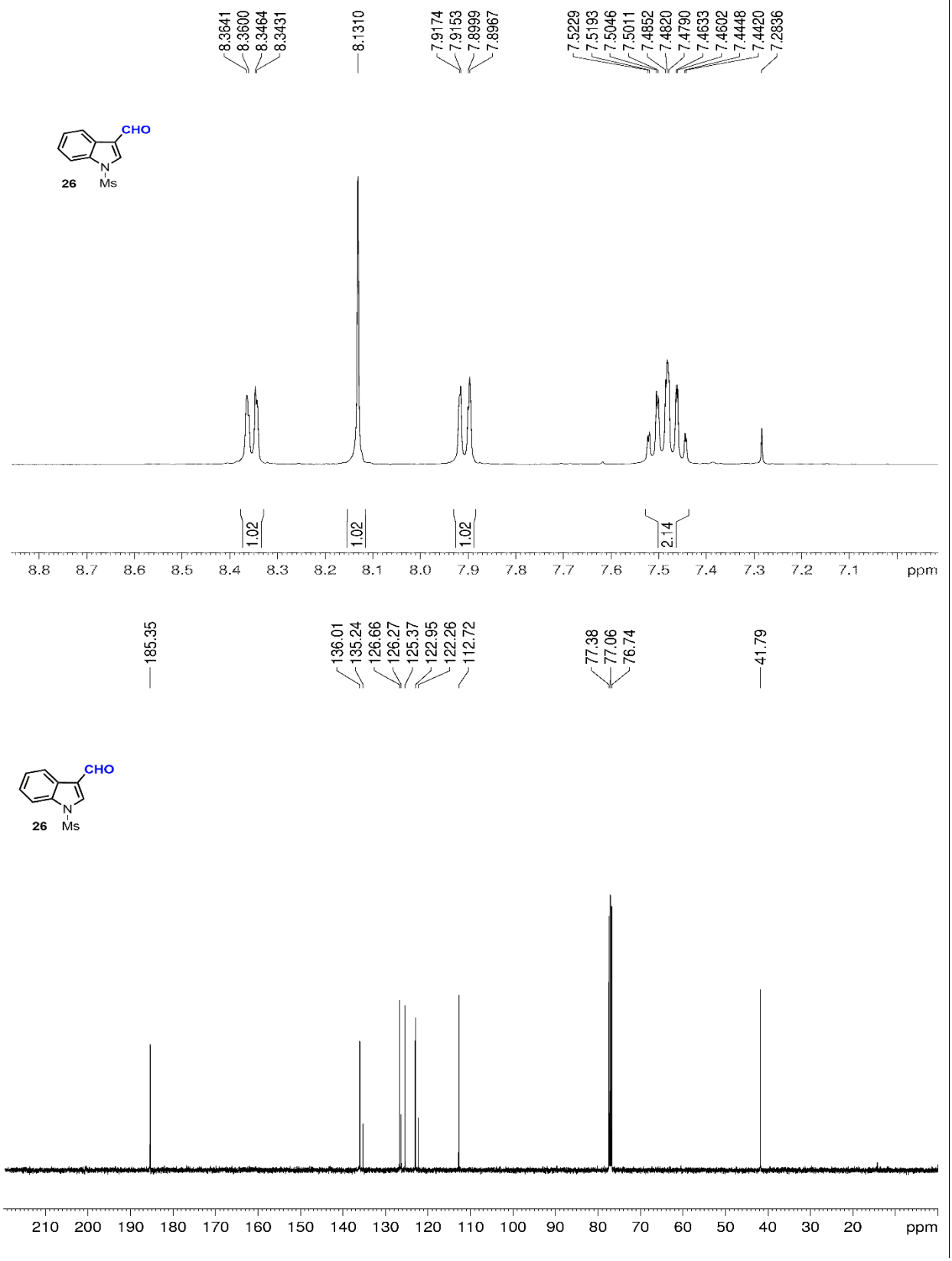
8.3600
8.3464
8.3431
8.1310
7.9174
7.9153
7.8999
7.8967
7.5229
7.5193
7.5046
7.5011
7.4852
7.4820
7.4790
7.4633
7.4602
7.4448
7.4420
7.2836
3.3120
0.0165
CHO
N
Ms
26
1.00
1.02
1.02
1.02
2.14
3.23
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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8.3600
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7.9174
7.9153
7.8999
7.8967
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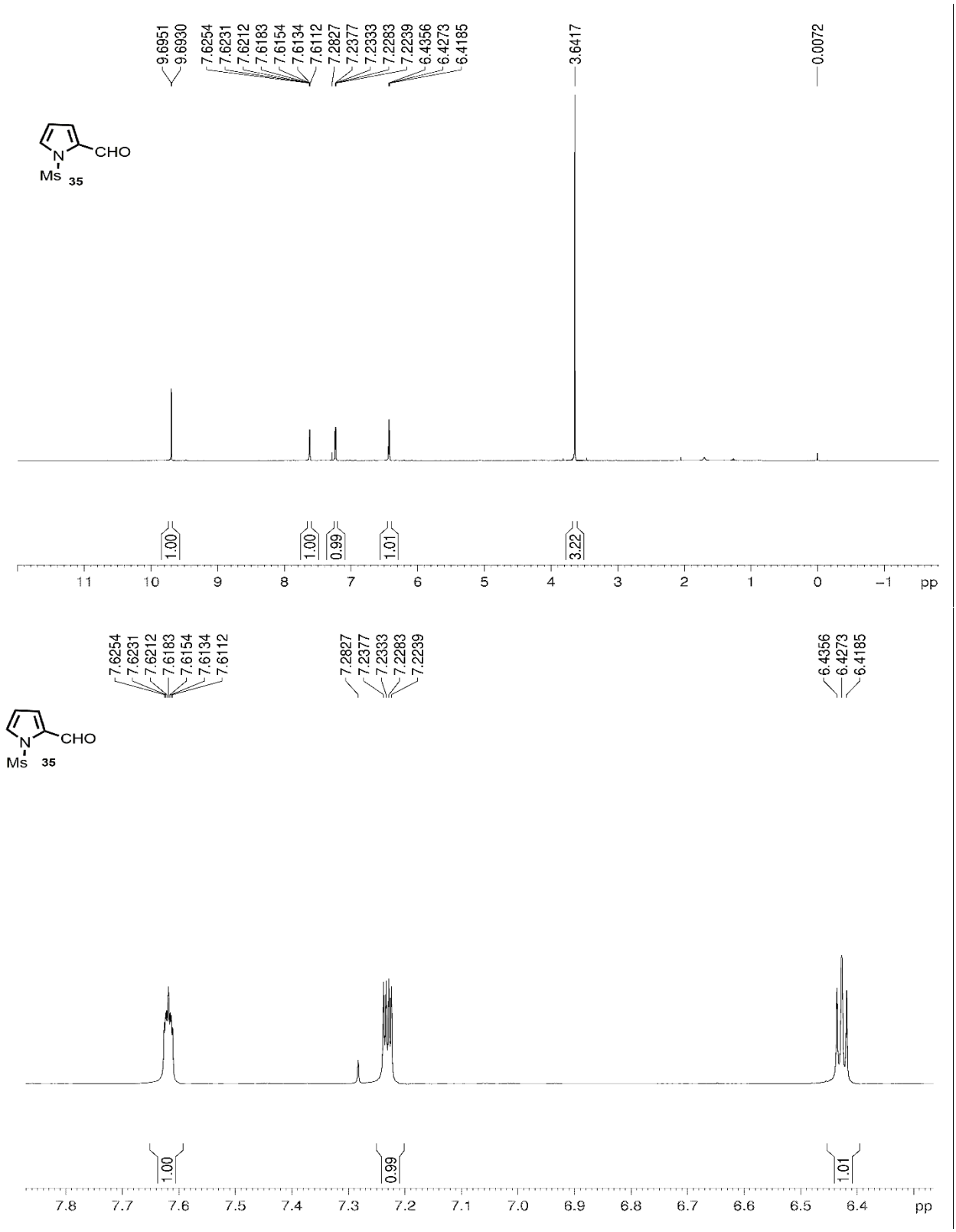
7.5193
7.5046
7.5011
7.4852
7.4820
7.4790
7.4633
7.4602
7.4448
7.4420
7.2836
CHO
N
Ms
26
1.02
1.02
1.02
2.14
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
185.35
136.01
135.24
126.66
126.27
125.37
122.95
122.26
112.72
77.38
77.06
76.74
41.79
CHO
N
Ms
26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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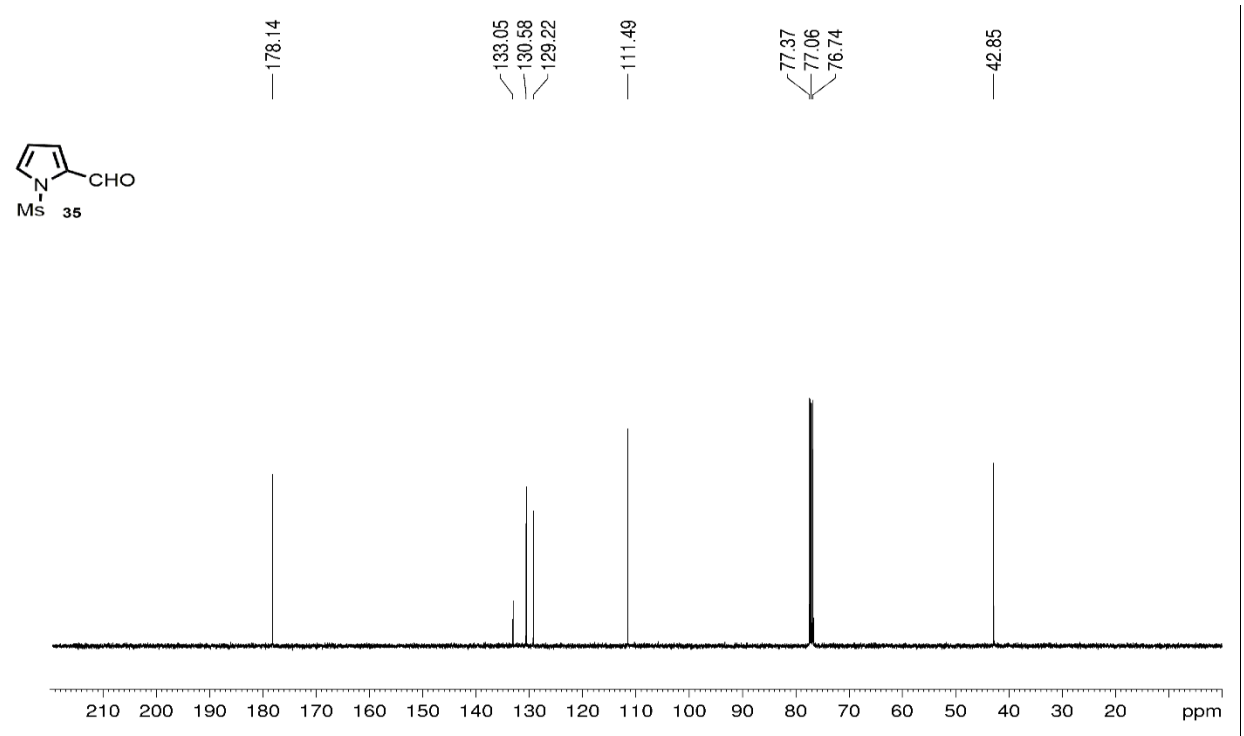
9.6930
7.6254
7.6231
7.6212
7.6183
7.6154
7.6134
7.6112
7.2827
7.2377
7.2333
7.2283
7.2239
6.4356
6.4273
6.4185
3.6417
0.0072
CHO
N
Ms
35
1.00
1.00
0.99
1.01
3.22
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp
7.6254
7.6231
7.6212
7.6183
7.6154
7.6134
7.6112
7.2827
7.2377
7.2333
7.2283
7.2239
6.4356
6.4273
6.4185
CHO
N
Ms
35
1.00
0.99
1.01
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
pp


178.14
133.05
130.58
129.22
111.49
77.37
77.06
76.74
42.85
CHO
N
Ms
35
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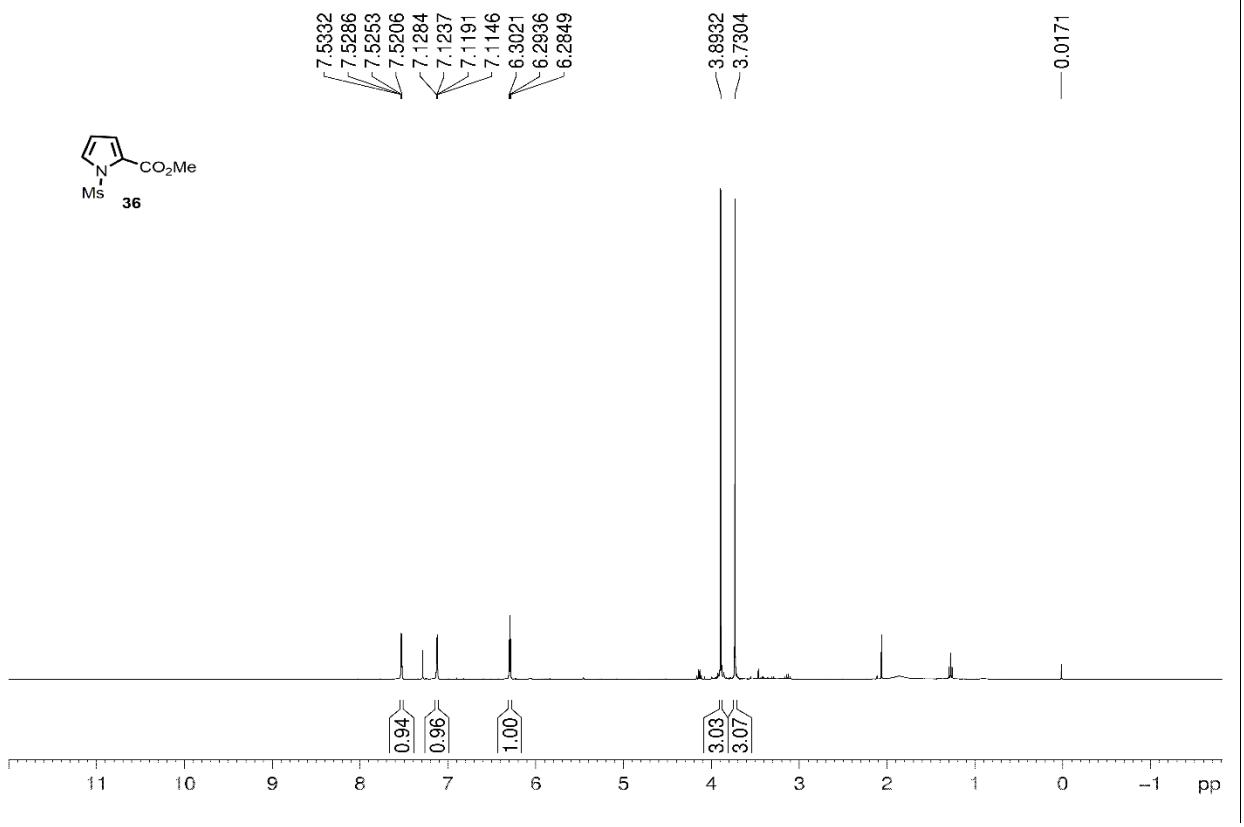
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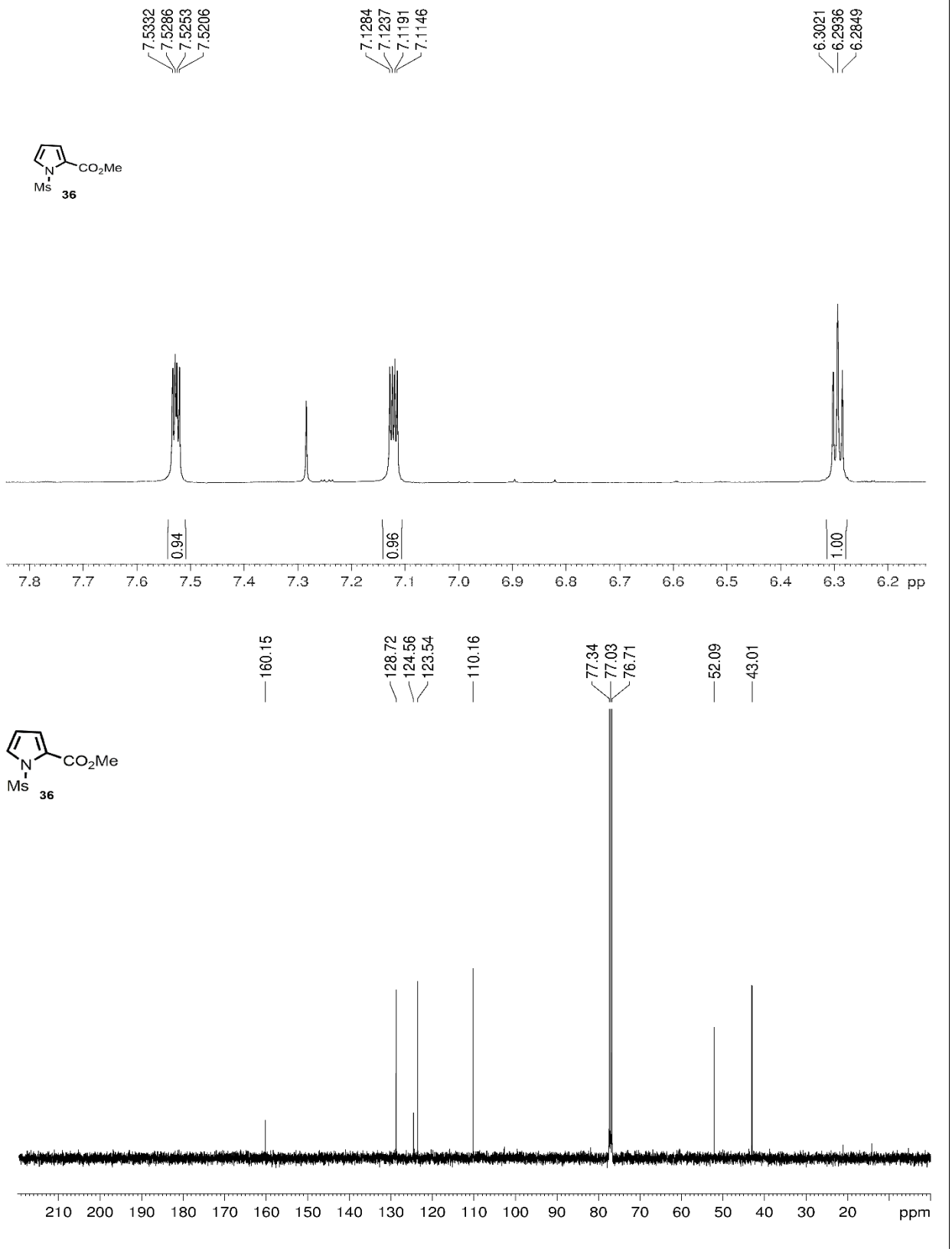
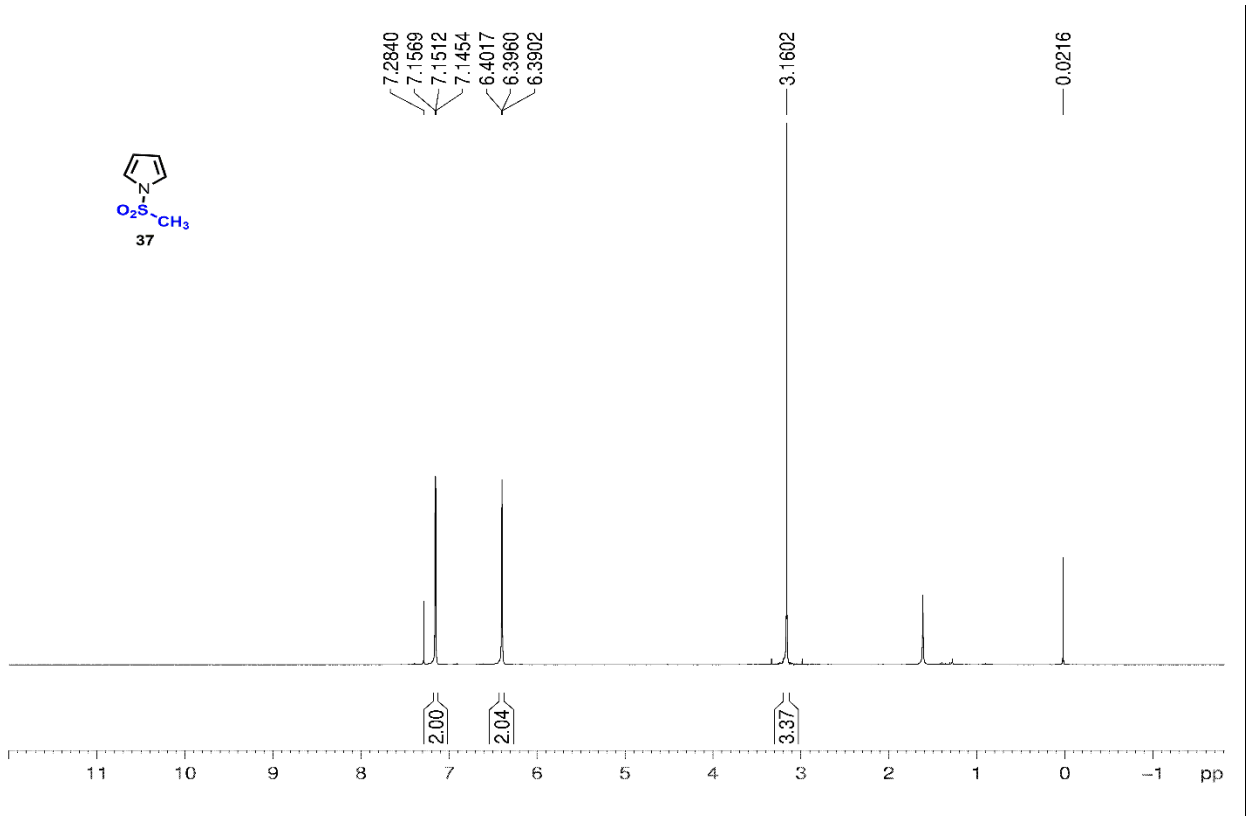
7.5286
7.5253
7.5206
7.1284
7.1237
7.1191
7.1146
6.3021
6.2936
6.2849
3.8932
3.7304
0.0171
CO2Me
N
Ms
36
0.94
0.96
1.00
3.03
3.07
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp


7.5332
7.5286
7.5253
7.5206
7.1284
7.1237
7.1191
7.1146
6.3021
6.2936
6.2849
CO2Me
N
Ms
36
0.94
0.96
1.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 pp
160.15
128.72
124.56
123.54
110.16
77.34
77.03
76.71
52.09
43.01
CO2Me
N
Ms
36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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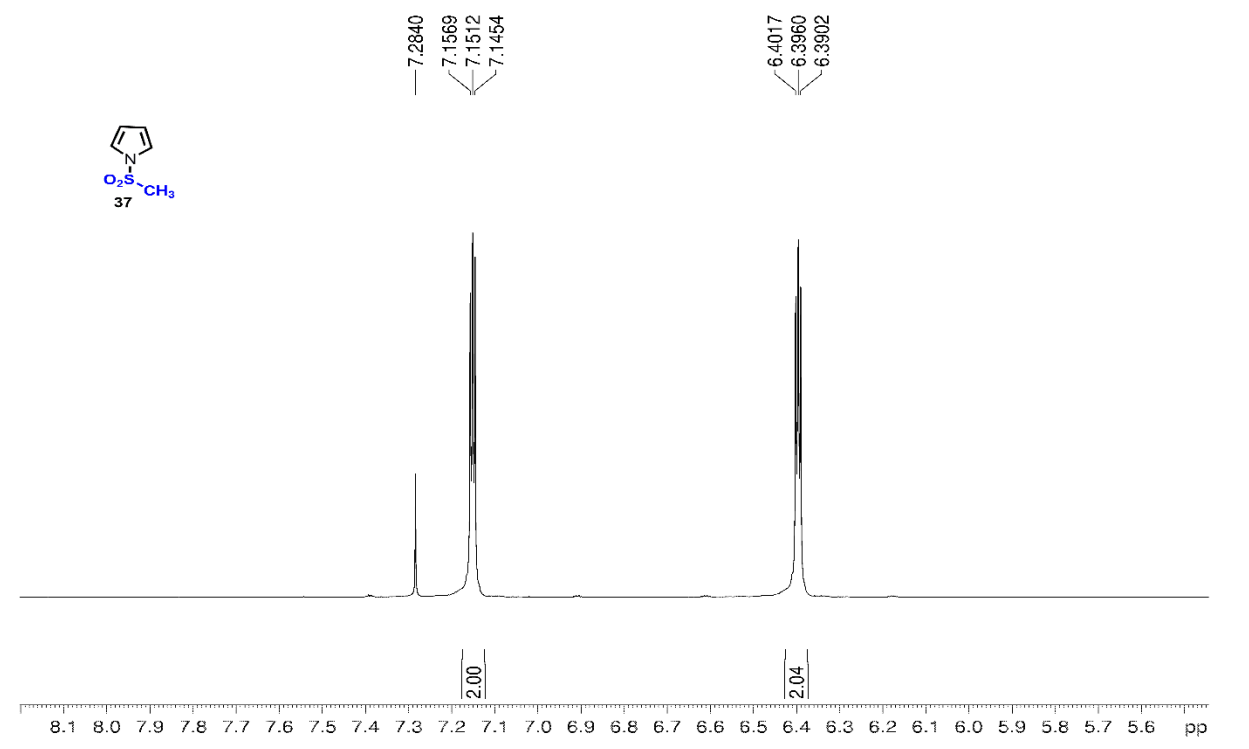
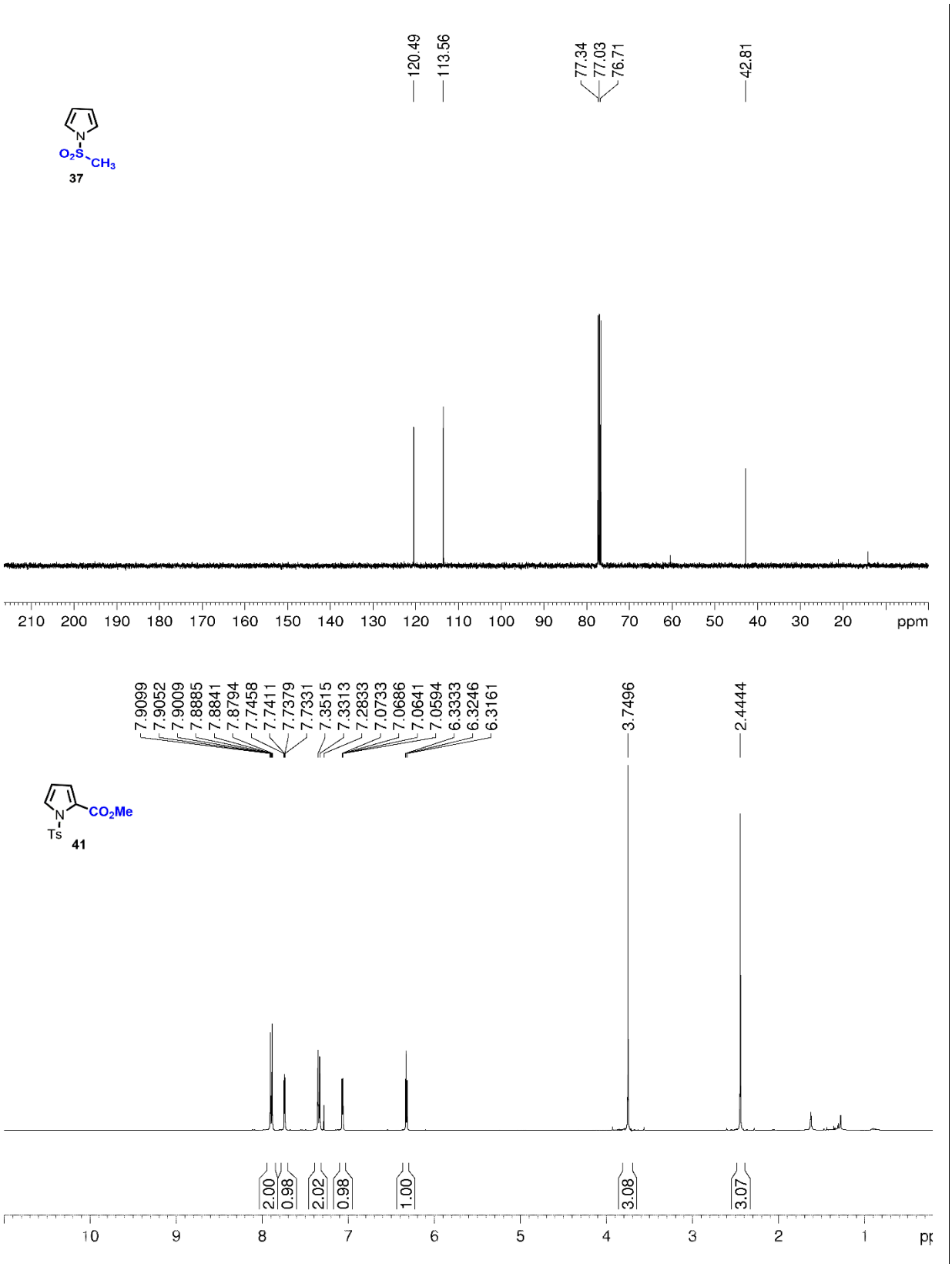
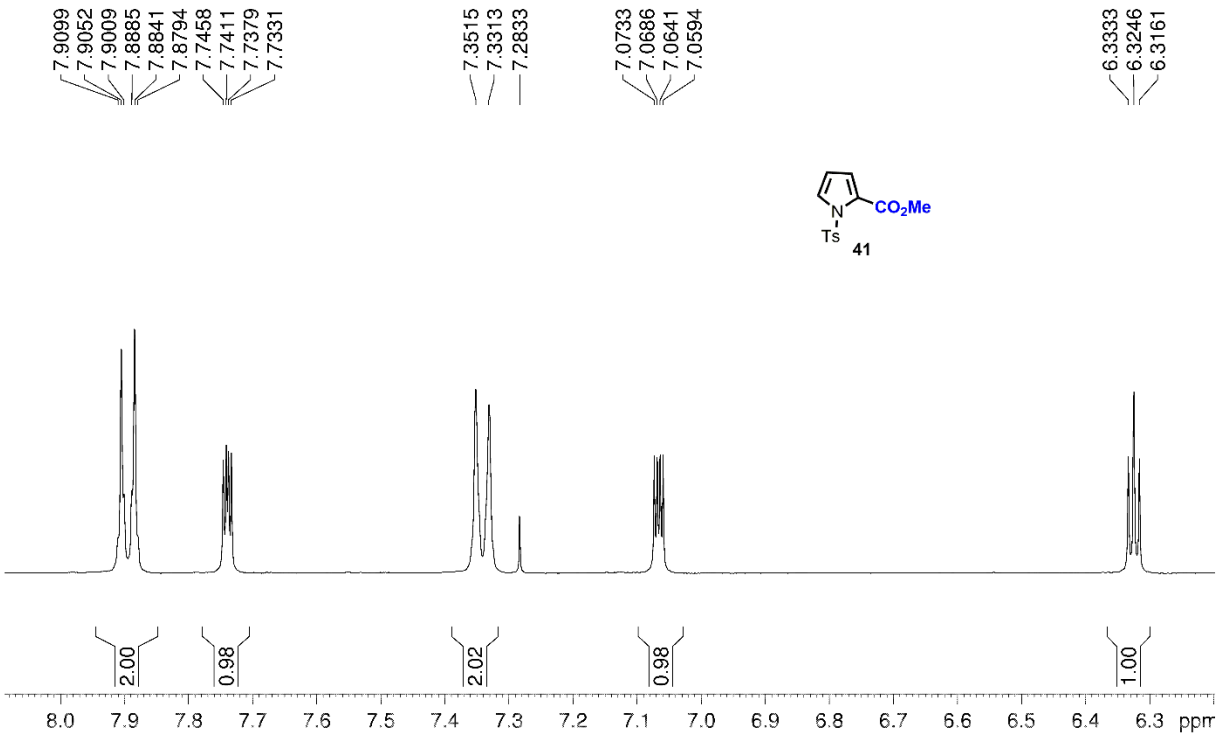
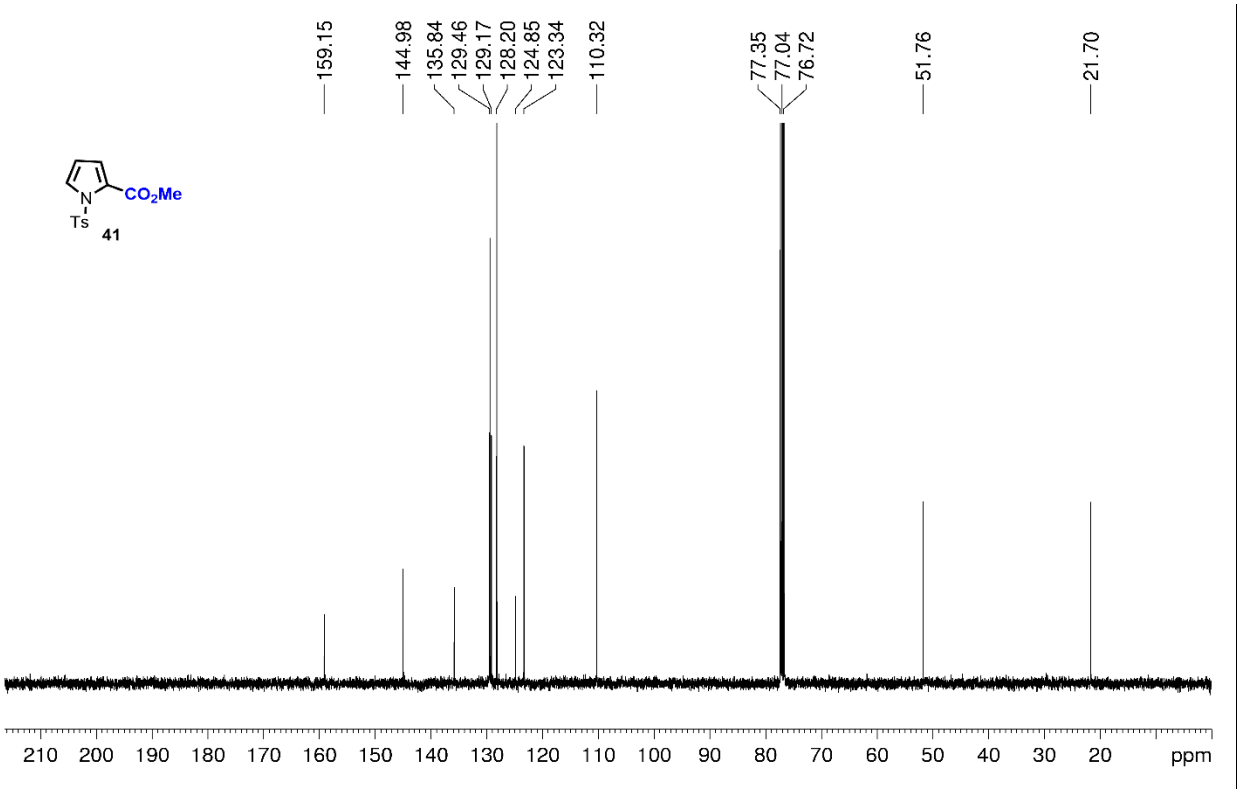
7.1569
7.1512
7.1454
6.4017
6.3960
6.3902
3.1602
0.0216
37
2.00
2.04
3.37
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp


7.2840
7.1569
7.1512
7.1454
6.4017
6.3960
6.3902
37
2.00
2.04
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 pp


120.49
113.56
77.34
77.03
76.71
42.81
37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
7.9099
7.9052
7.9009
7.8885
7.8841
7.8794
7.7458
7.7411
7.7379
7.7331
7.3515
7.3313
7.2833
7.0733
7.0686
7.0641
7.0594
6.3333
6.3246
6.3161
3.7496
2.4444
CO2Me
Ts
41
2.00
0.98
2.02
0.98
1.00
3.08
3.07
10 9 8 7 6 5 4 3 2 1 pp


7.9099
7.9052
7.9009
7.8885
7.8841
7.8794
7.7458
7.7411
7.7379
7.7331
7.3515
7.3313
7.2833
7.0733
7.0686
7.0641
7.0594
6.3333
6.3246
6.3161
CO2Me
N
Ts
41
2.00
0.98
2.02
0.98
1.00
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 ppm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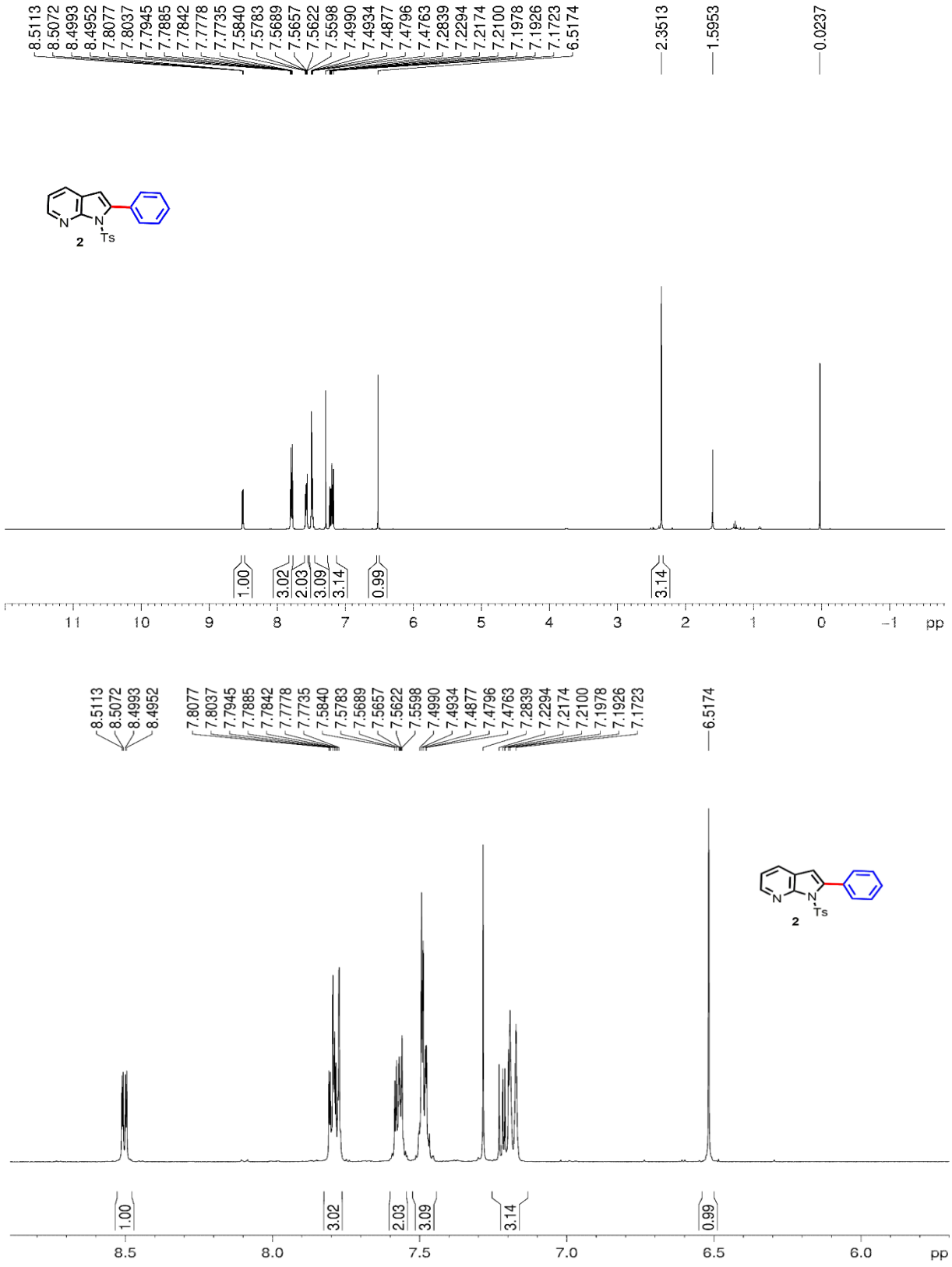
144.98
135.84
129.46
129.17
128.20
124.85
123.34
110.32
77.35
77.04
76.72
51.76
21.70
CO2Me
N
Ts
41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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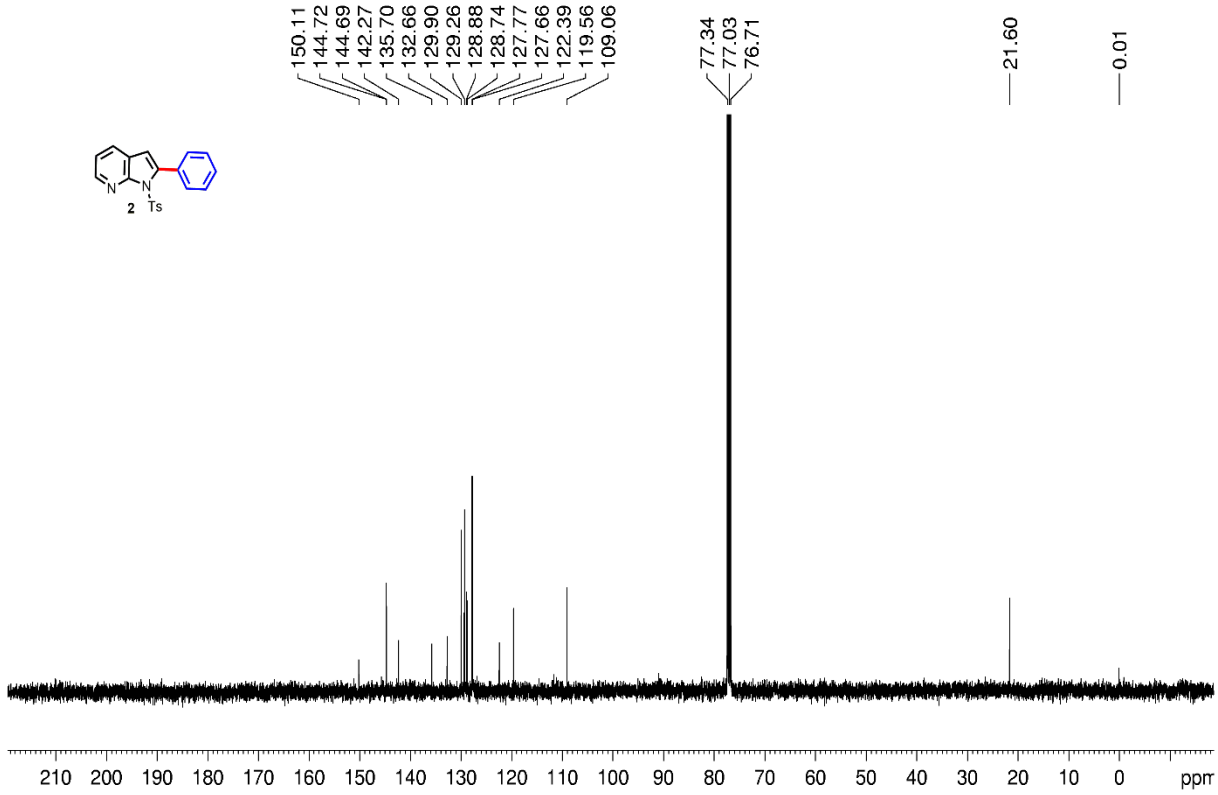
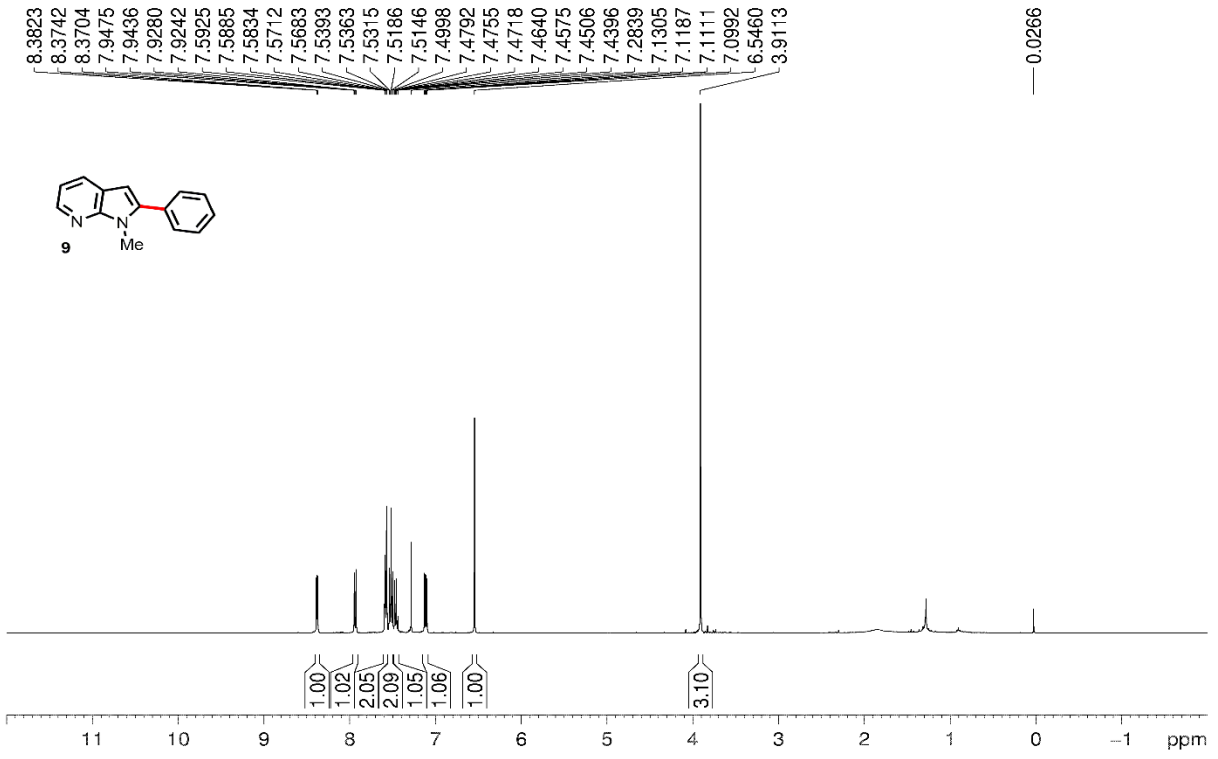
8.5072
8.4993
8.4952
7.8077
7.8037
7.7945
7.7885
7.7842
7.7778
7.7735
7.5840
7.5783
7.5689
7.5657
7.5622
7.5598
7.4990
7.4934
7.4877
7.4796
7.4763
7.2839
7.2294
7.2174
7.2100
7.1978
7.1926
7.1723
6.5174
2.3513
1.5953
0.0237
N
N
Ts
2
1.00
3.02
2.03
3.09
3.14
0.99
3.14
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp
8.5113
8.5072
8.4993
8.4952
7.8077
7.8037
7.7945
7.7885
7.7842
7.7778
7.7735
7.5840
7.5783
7.5689
7.5657
7.5622
7.5598
7.4990
7.4934
7.4877
7.4796
7.4763
7.2839
7.2294
7.2174
7.2100
7.1978
7.1926
7.1723
6.5174
N
N
Ts
2
1.00
3.02
2.03
3.09
3.14
0.99
8.5
8.0
7.5
7.0
6.5
6.0
pp


150.11
144.72
144.69
142.27
135.70
132.66
129.90
129.26
128.88
128.74
127.77
127.66
122.39
119.56
109.06
77.34
77.03
76.71
21.60
0.01
2
Ts
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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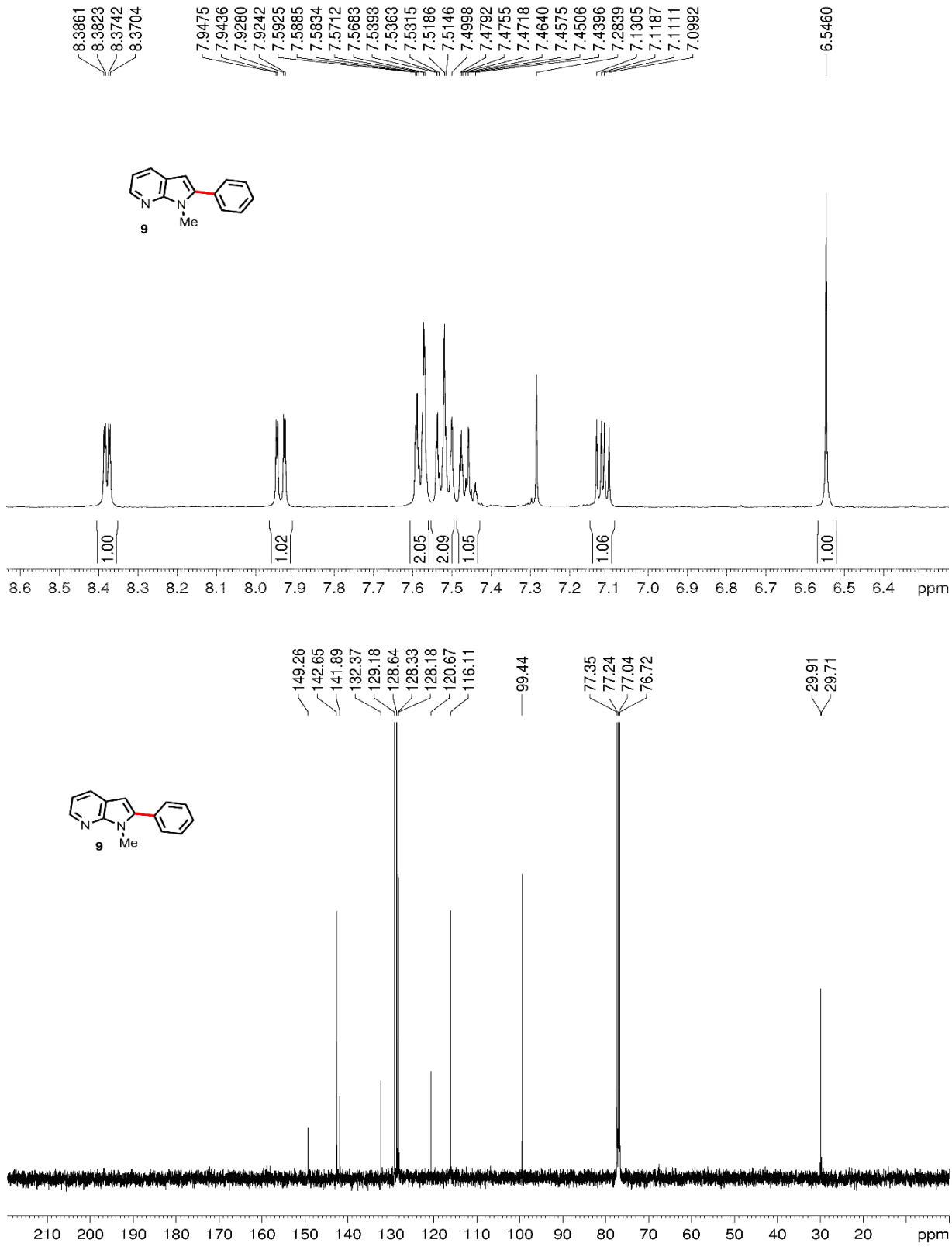
8.3704
7.9475
7.9436
7.9280
7.9242
7.5925
7.5885
7.5834
7.5712
7.5683
7.5393
7.5363
7.5315
7.5186
7.5146
7.4998
7.4792
7.4755
7.4718
7.4640
7.4575
7.4506
7.4396
7.2839
7.1305
7.1187
7.1111
7.0992
6.5460
3.9113
0.0266
9
Me
1.00
1.02
2.05
2.09
1.05
1.06
1.00
3.10
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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8.3742
8.3704
7.9475
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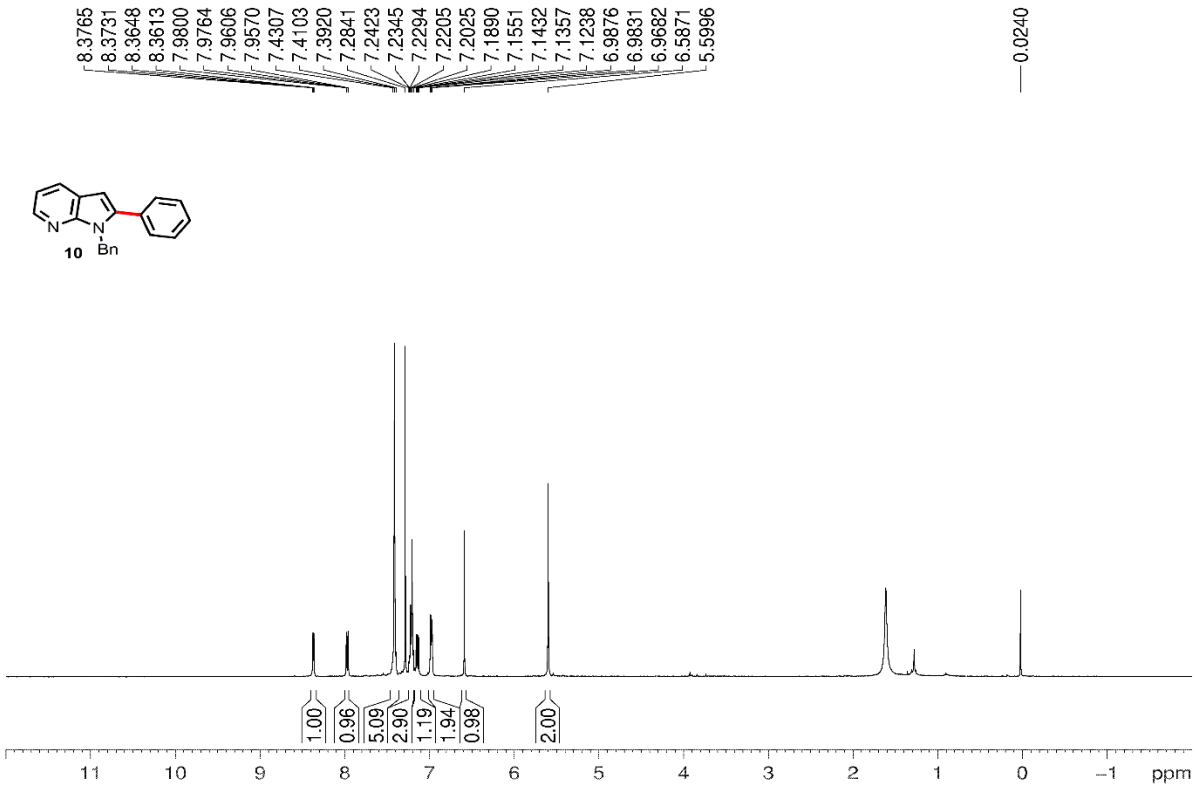
7.9280
7.9242
7.5925
7.5885
7.5834
7.5712
7.5683
7.5393
7.5363
7.5315
7.5186
7.5146
7.4998
7.4792
7.4755
7.4718
7.4640
7.4575
7.4506
7.4396
7.2839
7.1305
7.1187
7.1111
7.0992
6.5460
N
N
Me
9
1.00
1.02
2.05
2.09
1.05
1.06
1.00
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 ppm
149.26
142.65
141.89
132.37
129.18
128.64
128.33
128.18
120.67
116.11
99.44
77.35
77.24
77.04
76.72
29.91
29.71
N
N
Me
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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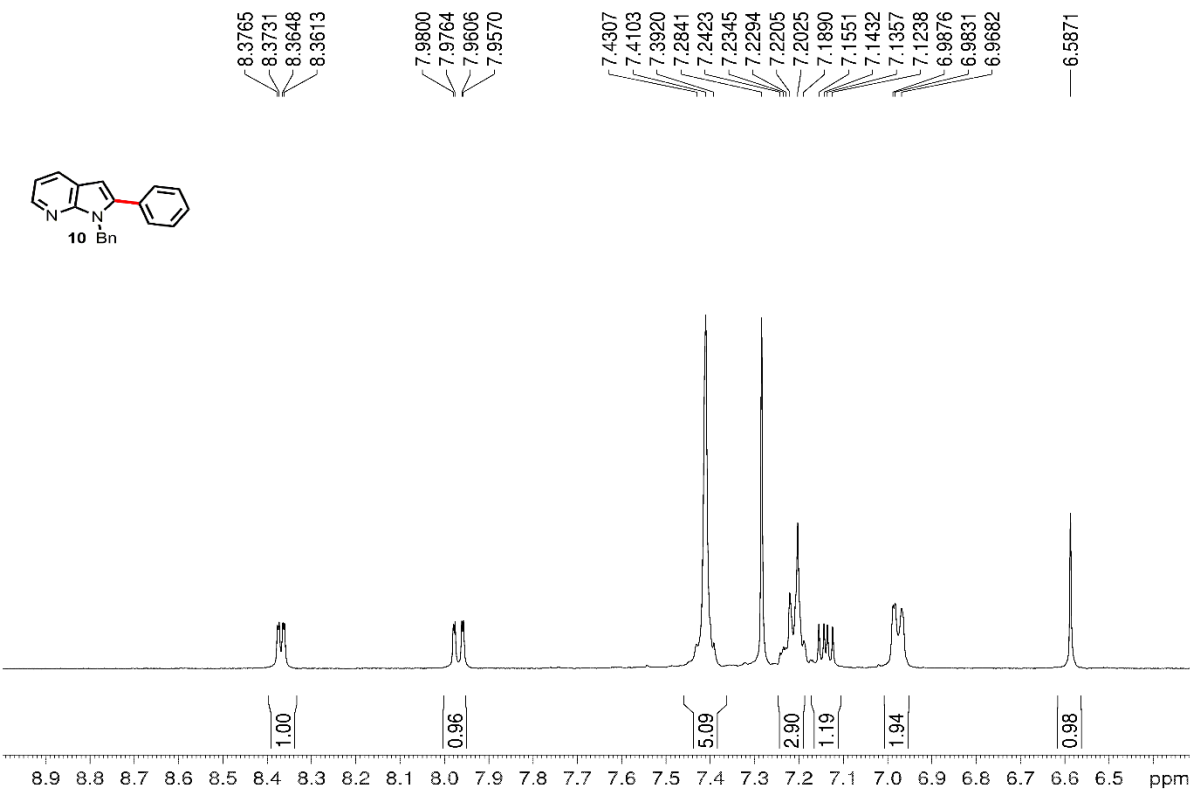
8.3648
8.3613
7.9800
7.9764
7.9606
7.9570
7.4307
7.4103
7.3920
7.2841
7.2423
7.2345
7.2294
7.2205
7.2025
7.1890
7.1551
7.1432
7.1357
7.1238
6.9876
6.9831
6.9682
6.5871
5.5996
0.0240
10 Bn
1.00
0.96
5.09
2.90
1.19
1.94
0.98
2.00
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm


8.3765
8.3731
8.3648
8.3613
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7.9606
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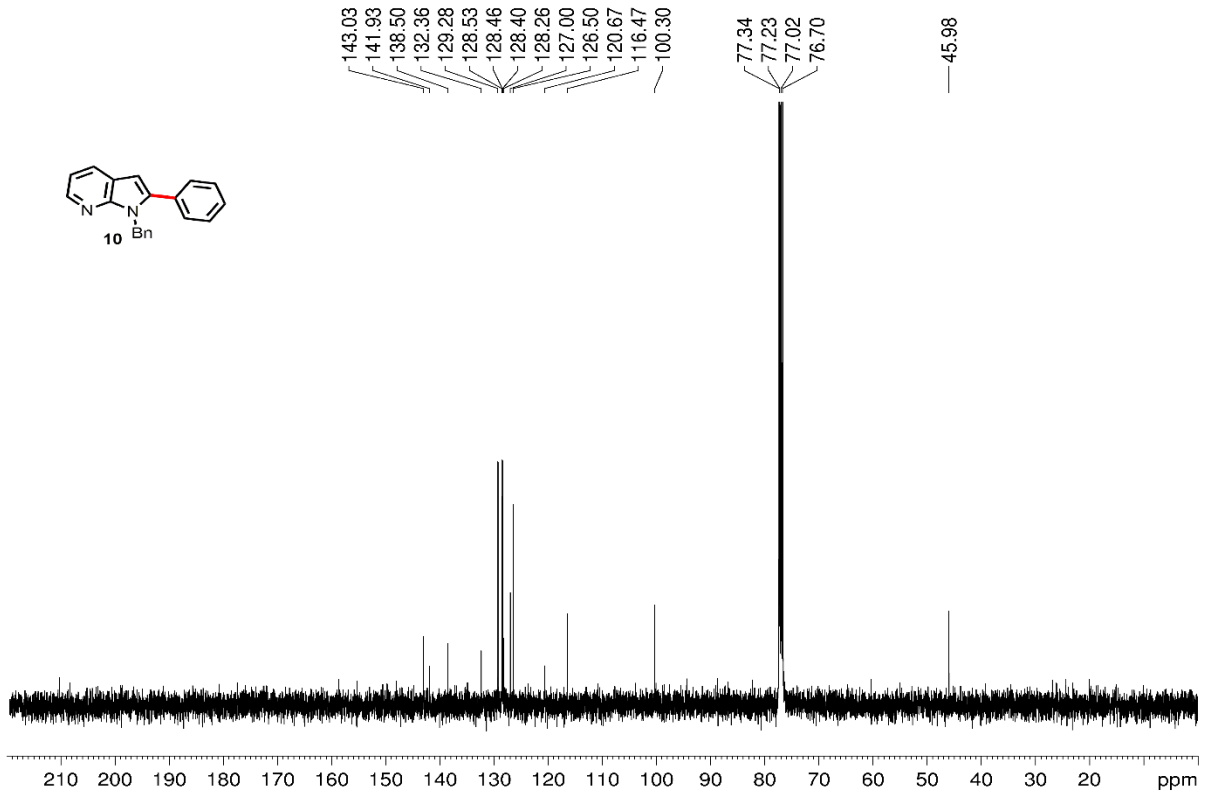
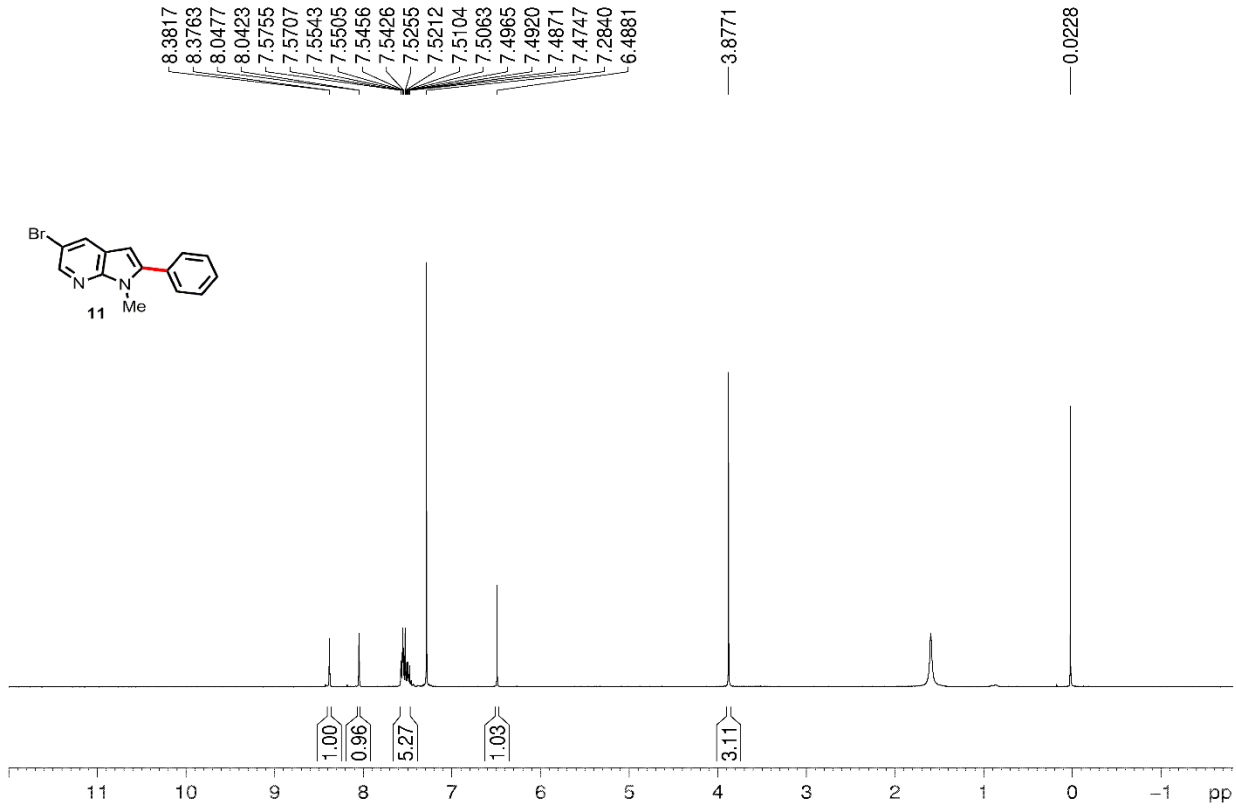
7.4307
7.4103
7.3920
7.2841
7.2423
7.2345
7.2294
7.2205
7.2025
7.1890
7.1551
7.1432
7.1357
7.1238
6.9876
6.9831
6.9682
6.5871
10 Bn
1.00
0.96
5.09
2.90
1.19
1.94
0.98
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm


143.03
141.93
138.50
132.36
129.28
128.53
128.46
128.40
128.26
127.00
126.50
120.67
116.47
100.30
77.34
77.23
77.02
76.70
45.98
10
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.0477
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7.5212
7.5104
7.5063
7.4965
7.4920
7.4871
7.4747
7.2840
6.4881
3.8771
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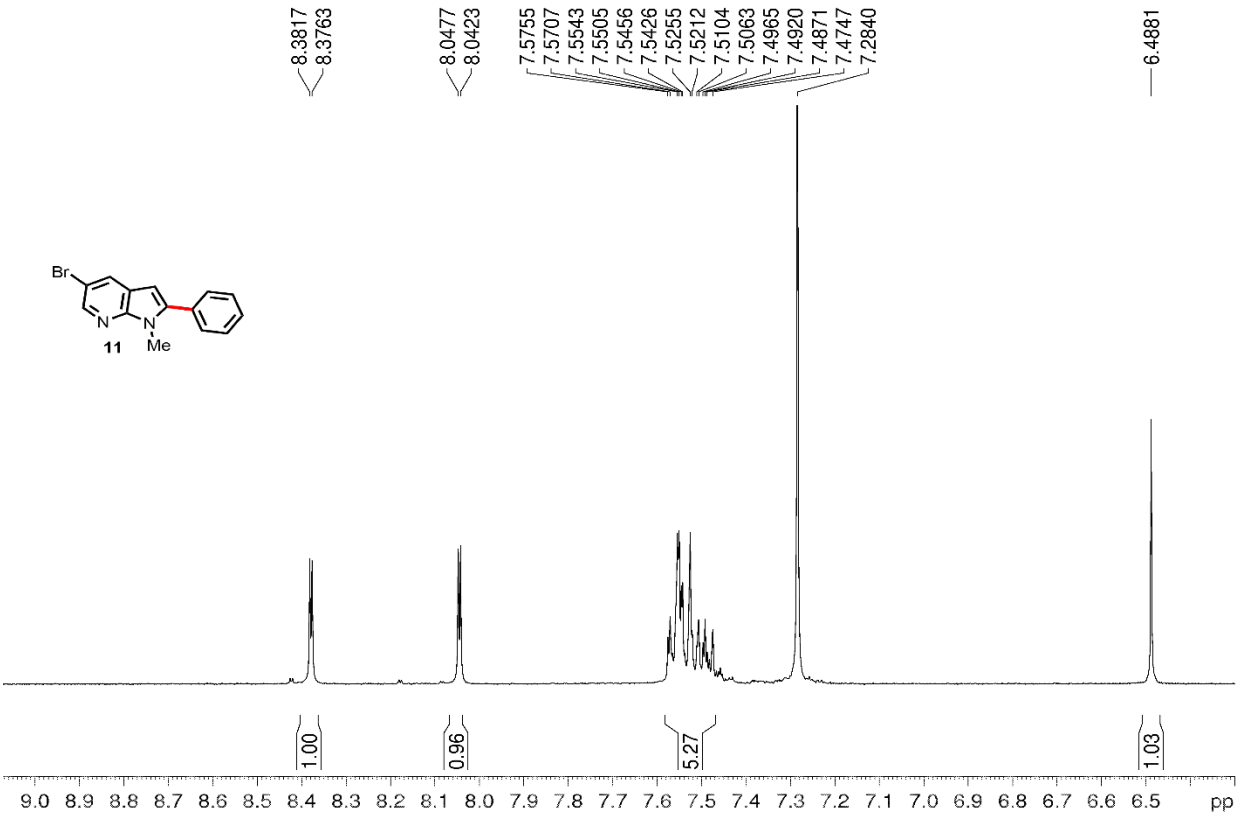
Br
11
Me
1.00
0.96
5.27
1.03
3.11
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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8.3763
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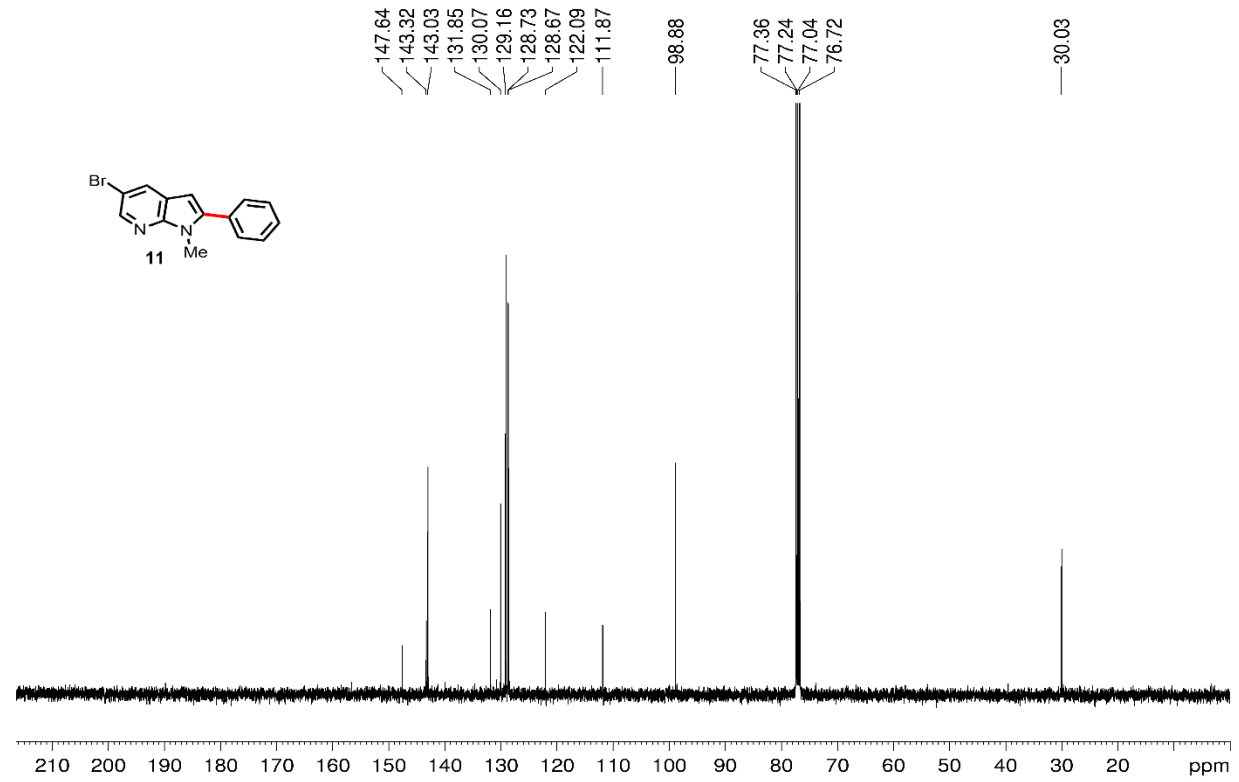
7.5212
7.5104
7.5063
7.4965
7.4920
7.4871
7.4747
7.2840
6.4881
Br
N
N
Me
11
1.00
0.96
5.27
1.03
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
pp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128.67
122.09
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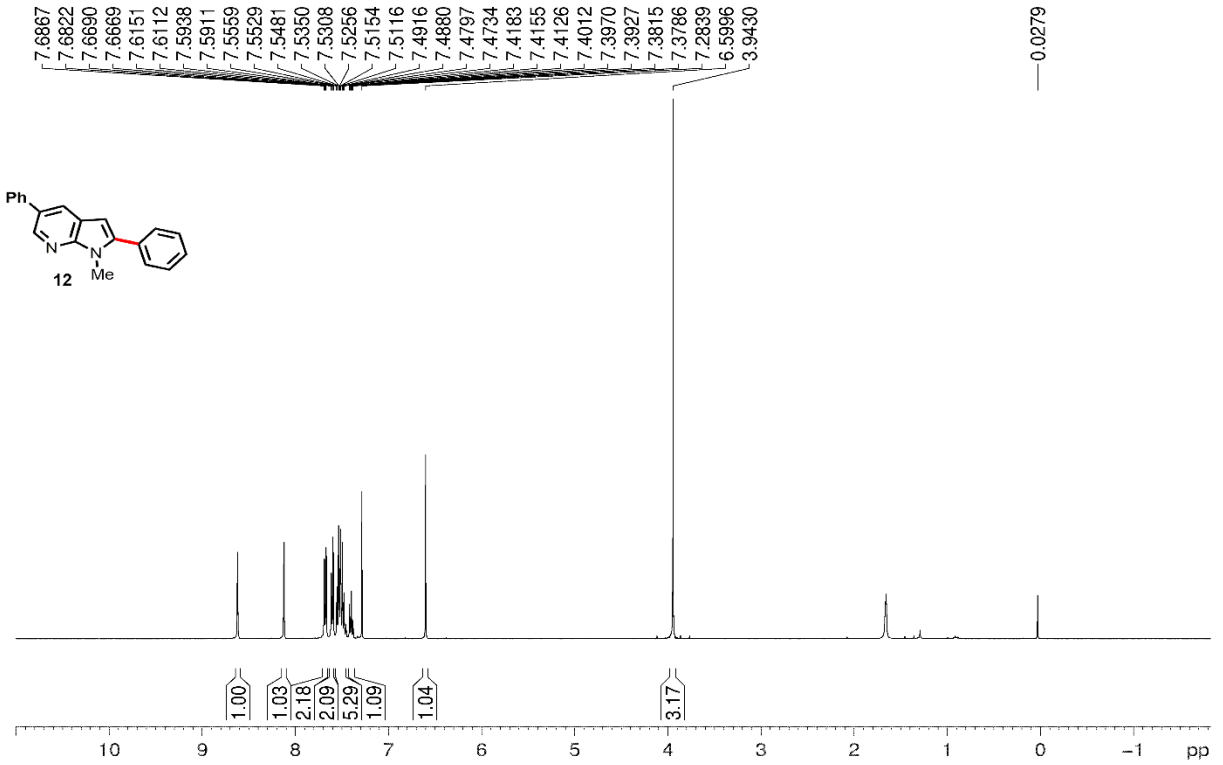
98.88
77.36
77.24
77.04
76.72
30.03
Br
N
N
Me
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm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7.5938
7.5911
7.5559
7.5529
7.5481
7.5350
7.5308
7.5256
7.5154
7.5116
7.4916
7.4880
7.4797
7.4734
7.4183
7.4155
7.4126
7.4012
7.3970
7.3927
7.3815
7.3786
7.2839
6.5996
3.9430
0.0279
Ph
N
N
Me
12
1.00
1.03
2.18
2.09
5.29
1.09
1.04
3.17
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9
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5
4
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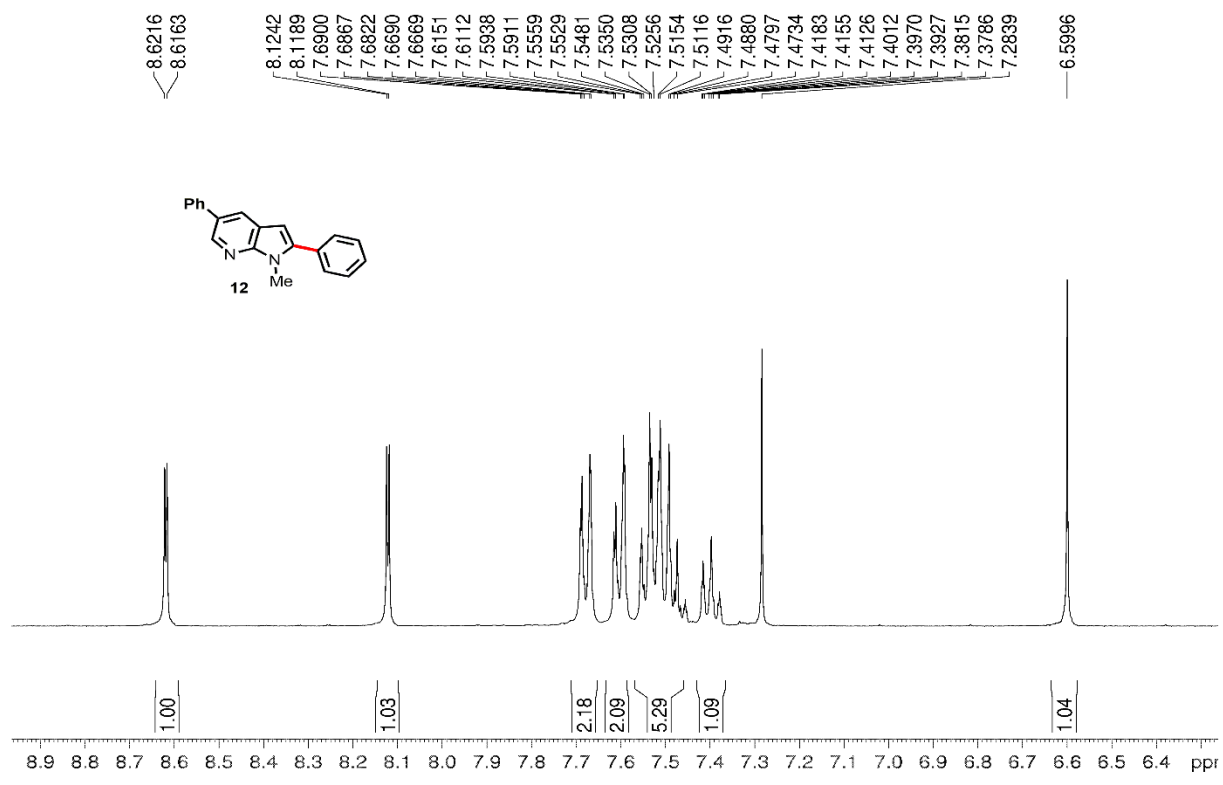
1
0
−1
pp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7.6822
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7.5938
7.5911
7.5559
7.5529
7.5481
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7.5308
7.5256
7.5154
7.5116
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7.4880
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7.4734
7.4183
7.4155
7.4126
7.4012
7.3970
7.3927
7.3815
7.3786
7.2839
6.5996
Ph
N
N
Me
12
1.00
1.03
2.18
2.09
5.29
1.09
1.04
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
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7.1
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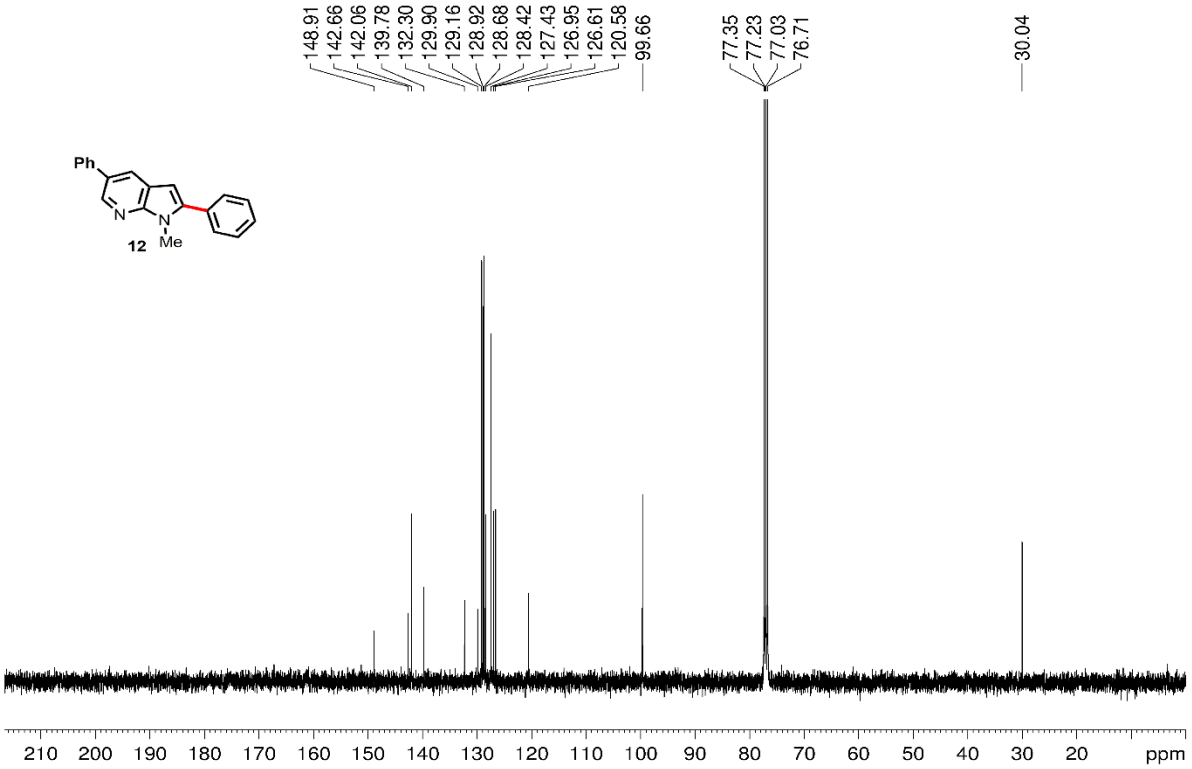
6.8
6.7
6.6
6.5
6.4
ppr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142.06
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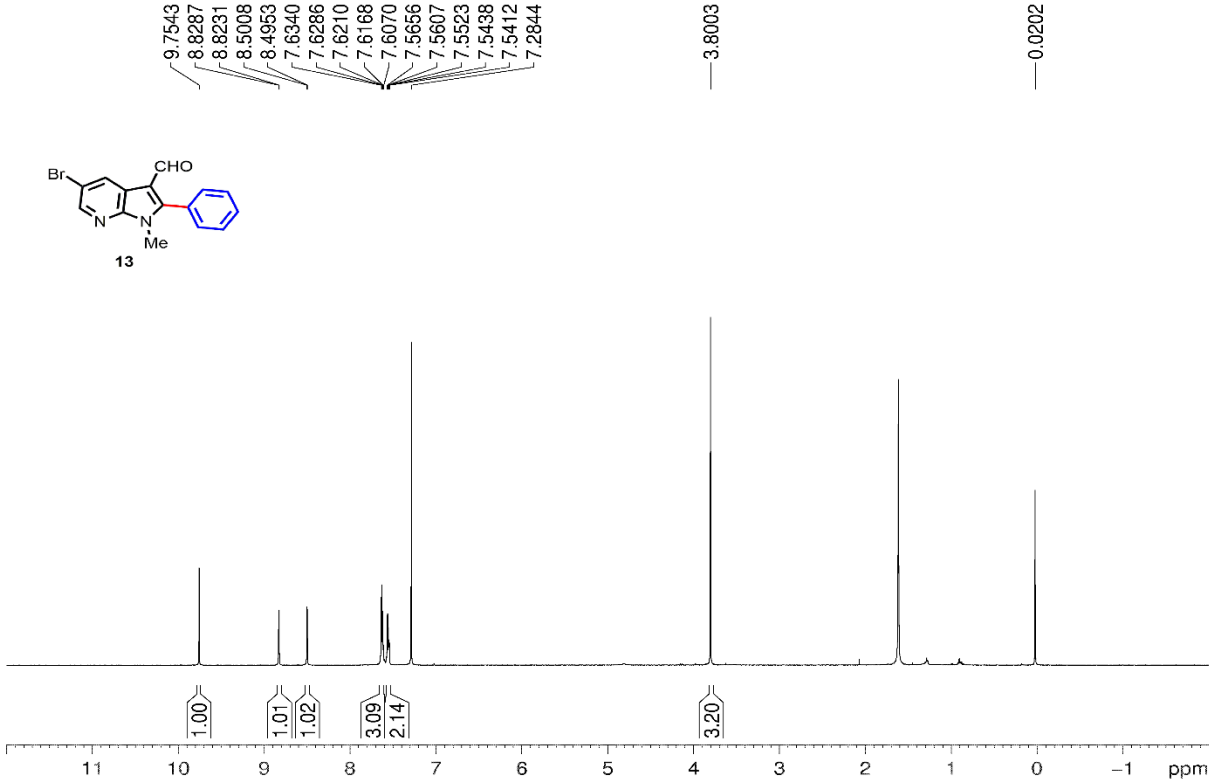
132.30
129.90
129.16
128.92
128.68
128.42
127.43
126.95
126.61
120.58
99.66
77.35
77.23
77.03
76.71
30.04
Ph
N
N
Me
12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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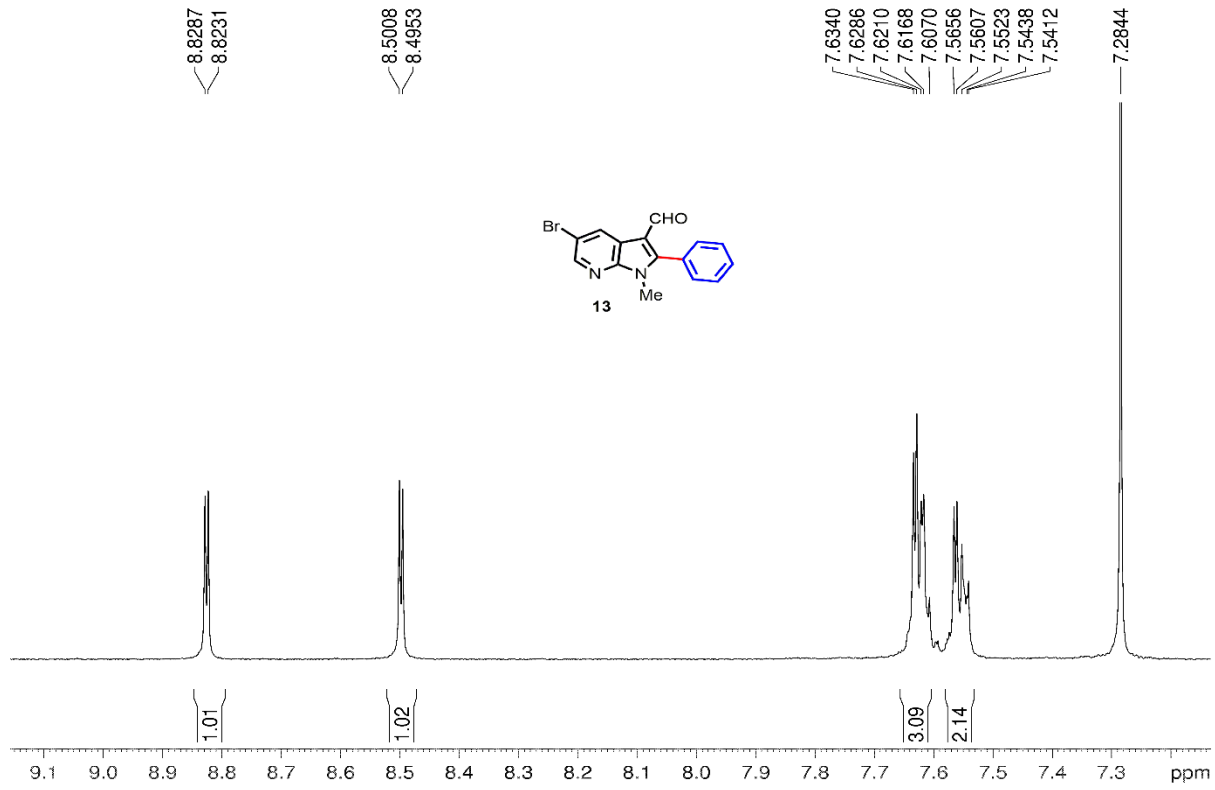
8.8231
8.5008
8.4953
7.6340
7.6286
7.6210
7.6168
7.6070
7.5656
7.5607
7.5523
7.5438
7.5412
7.2844
3.8003
0.0202
Br
CHO
N
N
Me
13
1.00
1.01
1.02
3.09
2.14
3.20
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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8.8231
8.5008
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7.6340
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7.6210
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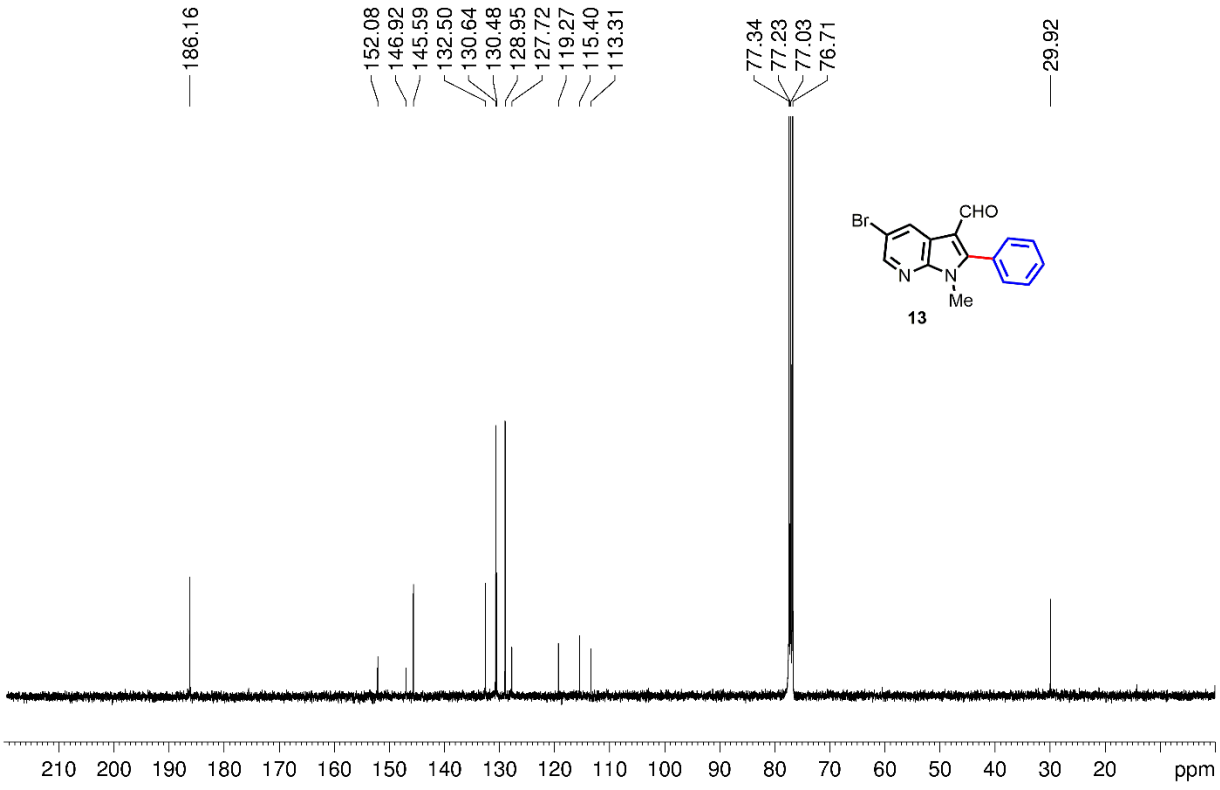
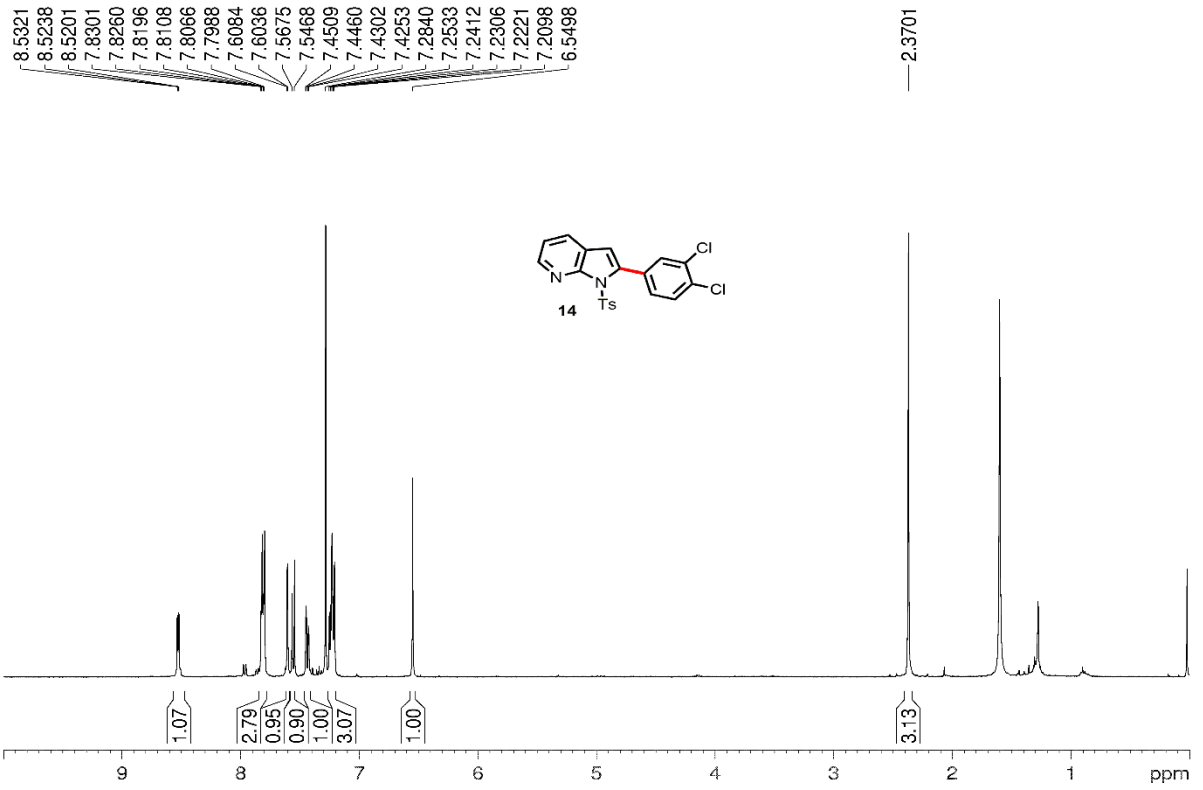
7.5656
7.5607
7.5523
7.5438
7.5412
7.2844
Br
CHO
N
N
Me
13
1.01
1.02
3.09
2.14
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm


186.16
152.08
146.92
145.59
132.50
130.64
130.48
128.95
127.72
119.27
115.40
113.31
77.34
77.23
77.03
76.71
29.92
Br
CHO
N
N
Me
13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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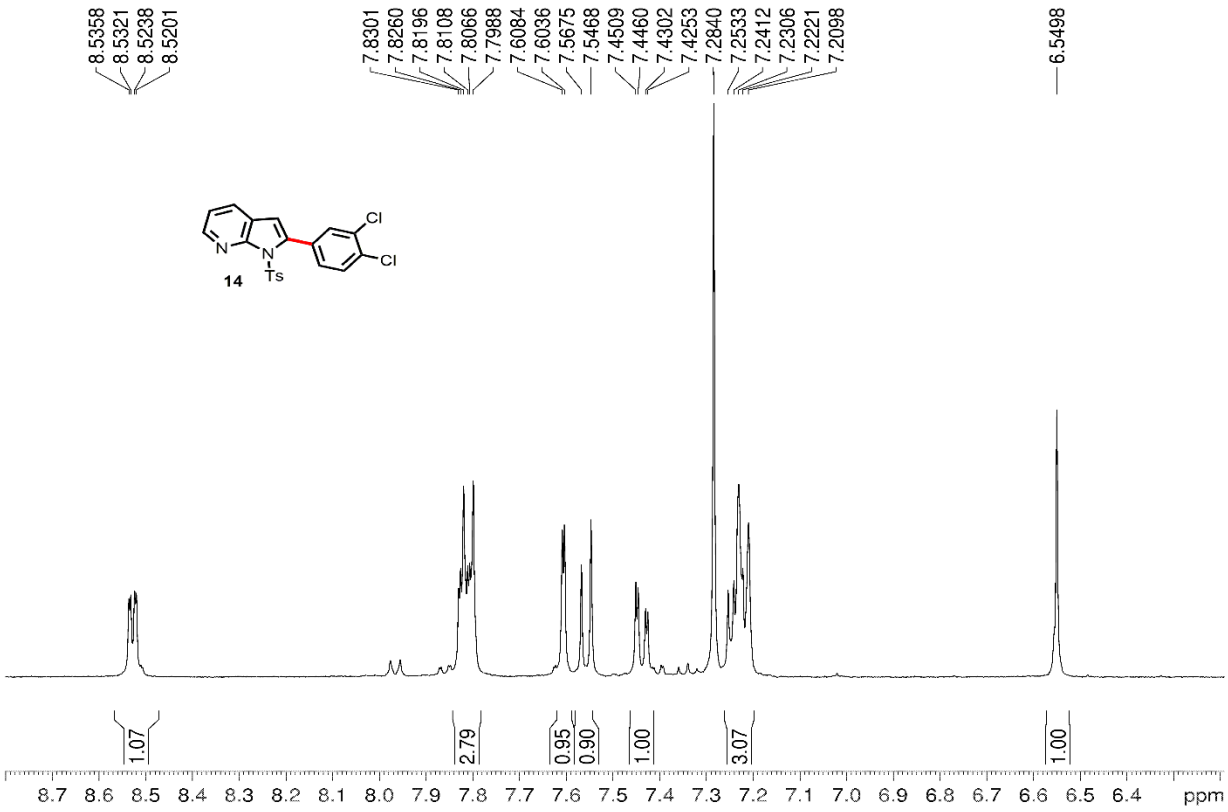
8.5238
8.5201
7.8301
7.8260
7.8196
7.8108
7.8066
7.7988
7.6084
7.6036
7.5675
7.5468
7.4509
7.4460
7.4302
7.4253
7.2840
7.2533
7.2412
7.2306
7.2221
7.2098
6.5498
2.3701
Cl
Cl
N
N
Ts
14
1.07
2.79
0.95
0.90
1.00
3.07
1.00
3.13
9
8
7
6
5
4
3
2
1
ppm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8.5238
8.5201
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7.8196
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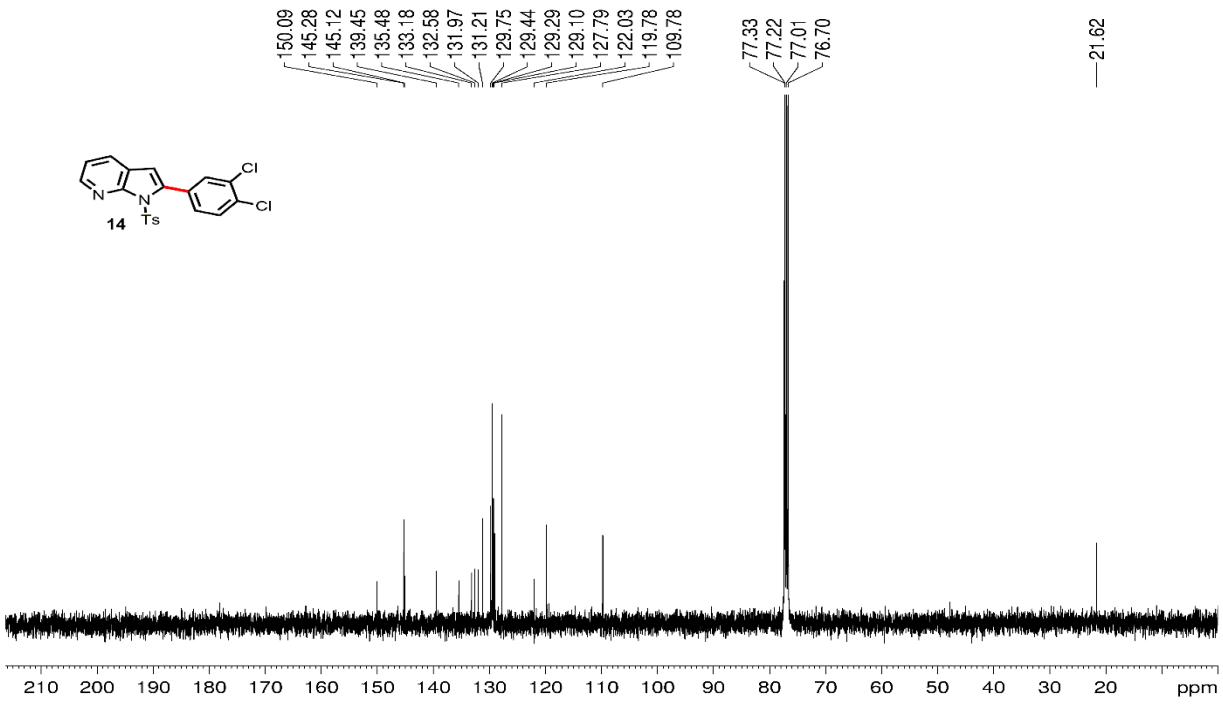
7.8066
7.7988
7.6084
7.6036
7.5675
7.5468
7.4509
7.4460
7.4302
7.4253
7.2840
7.2533
7.2412
7.2306
7.2221
7.2098
6.5498
Cl
Cl
N
N
Ts
14
1.07
2.79
0.95
0.90
1.00
3.07
1.00
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
ppm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145.12
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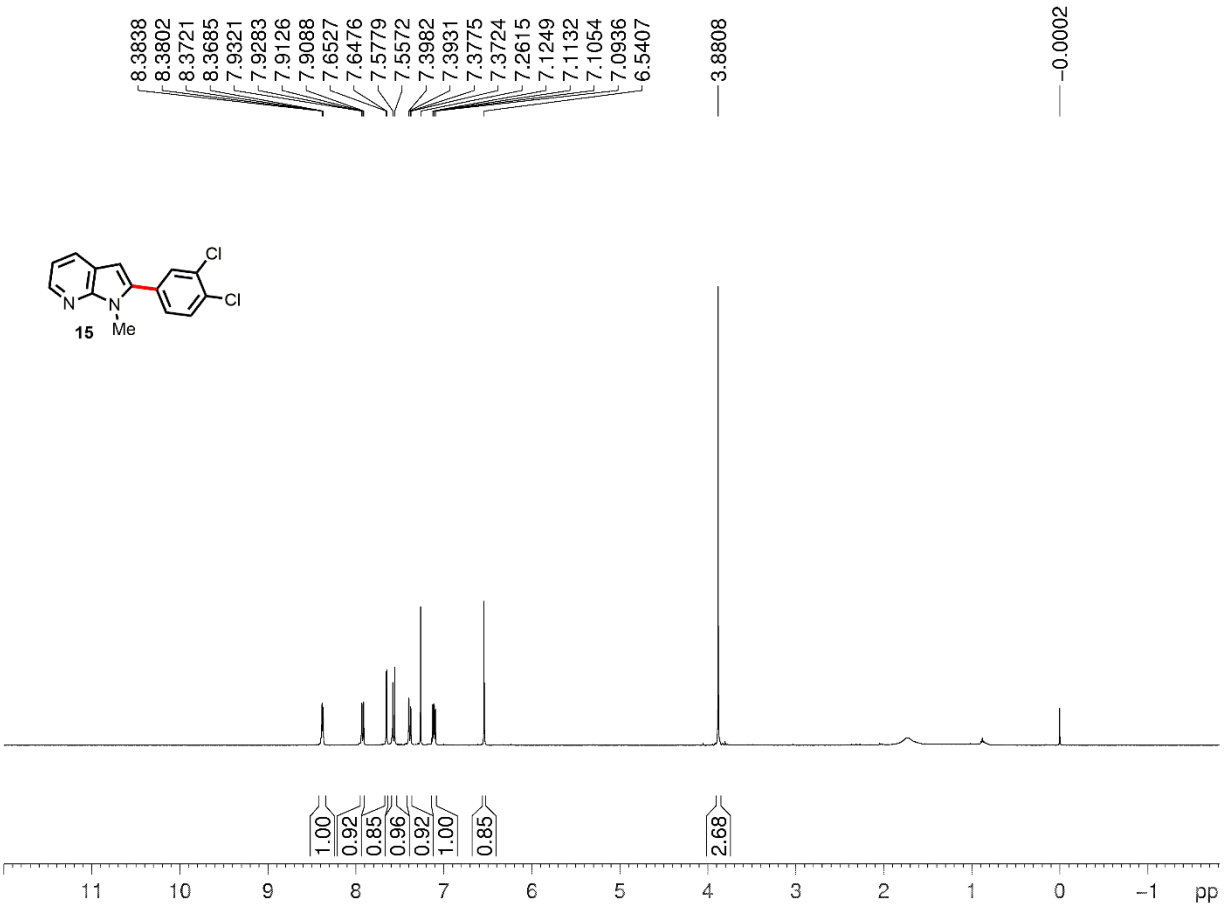
135.48
133.18
132.58
131.97
131.21
129.75
129.44
129.29
129.10
127.79
122.03
119.78
109.78
77.33
77.22
77.01
76.70
21.62
Cl
Cl
N
N
Ts
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.3721
8.3685
7.9321
7.9283
7.9126
7.9088
7.6527
7.6476
7.5779
7.5572
7.3982
7.3931
7.3775
7.3724
7.2615
7.1249
7.1132
7.1054
7.0936
6.5407
3.8808
0.0002
Cl
Cl
N
N
Me
15
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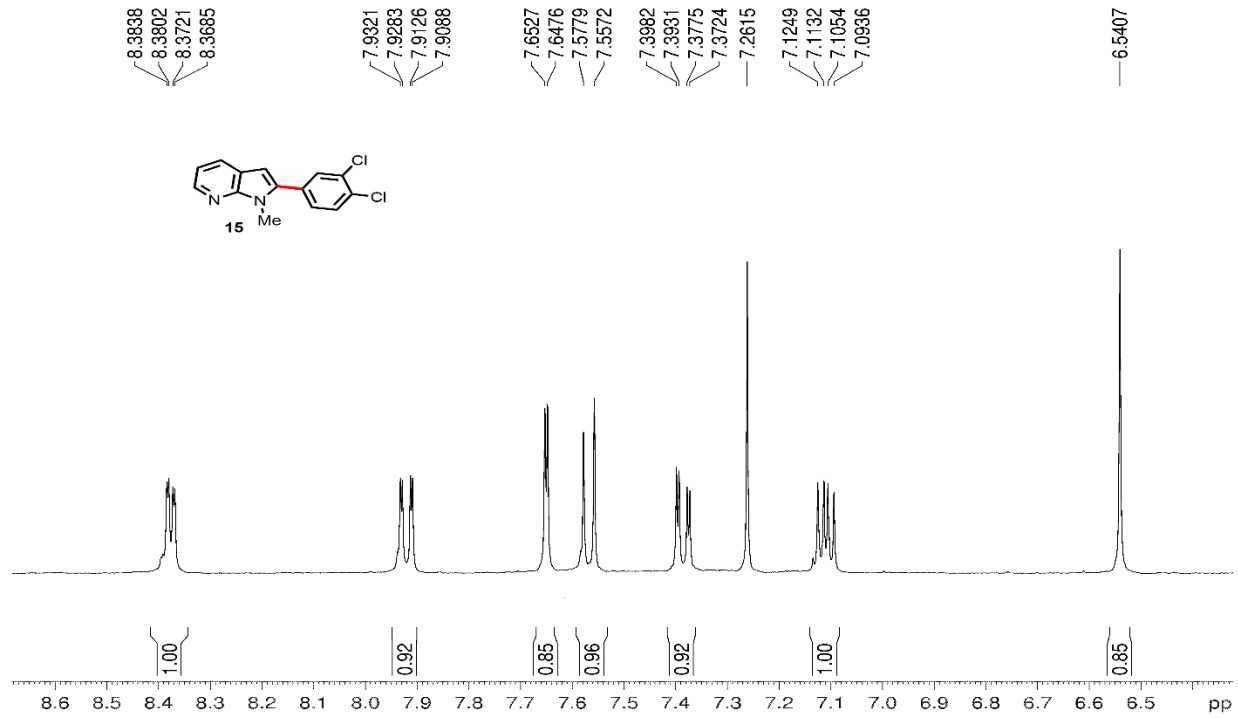
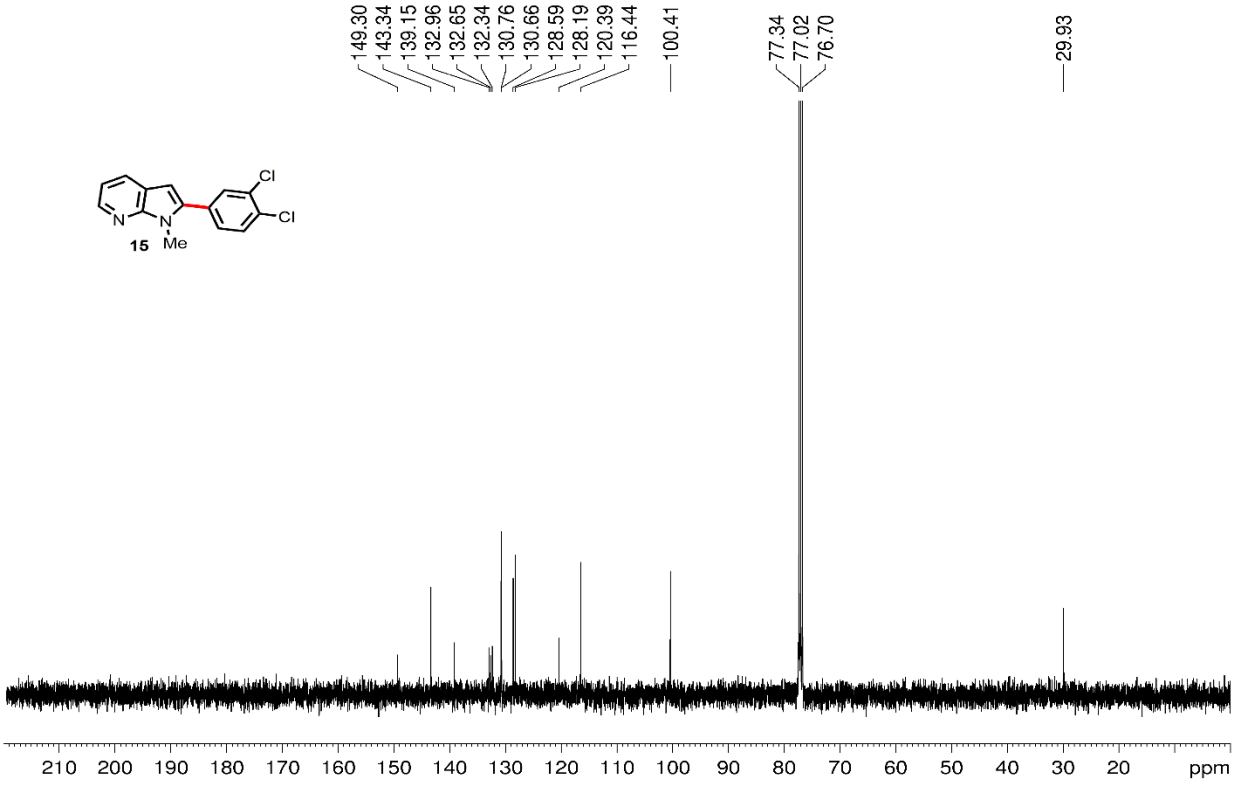
0.92
0.85
0.96
0.92
1.00
0.85
2.68
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp


8.3838
8.3802
8.3721
8.3685
7.9321
7.9283
7.9126
7.9088
7.6527
7.6476
7.5779
7.5572
7.3982
7.3931
7.3775
7.3724
7.2615
7.1249
7.1132
7.1054
7.0936
6.5407
Cl
Cl
N
N
Me
15
1.00
0.92
0.85
0.96
0.92
1.00
0.85
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 pp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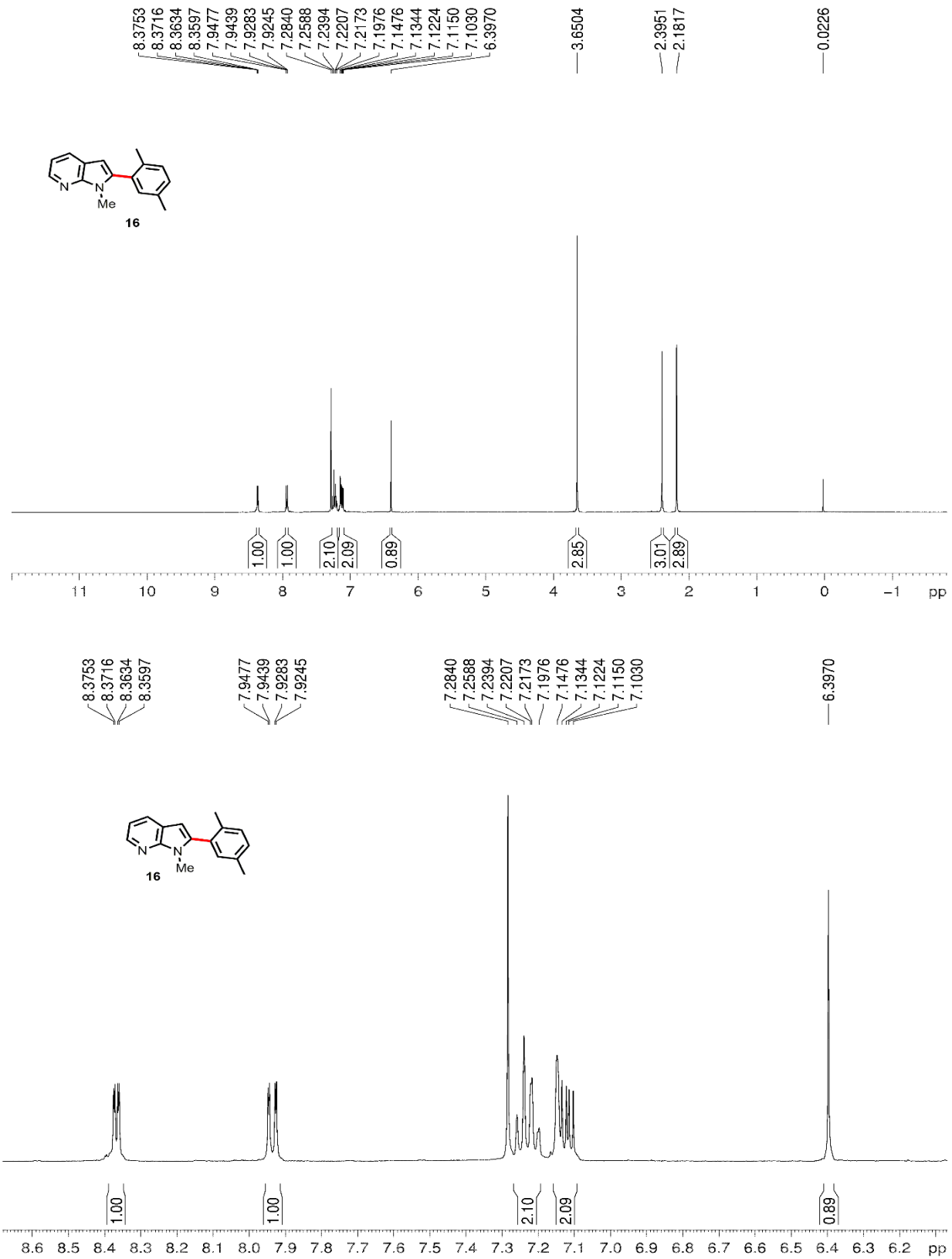
143.34
139.15
132.96
132.65
132.34
130.76
130.66
128.59
128.19
120.39
116.44
100.41
77.34
77.02
76.70
29.93
Cl
Cl
N
N
Me
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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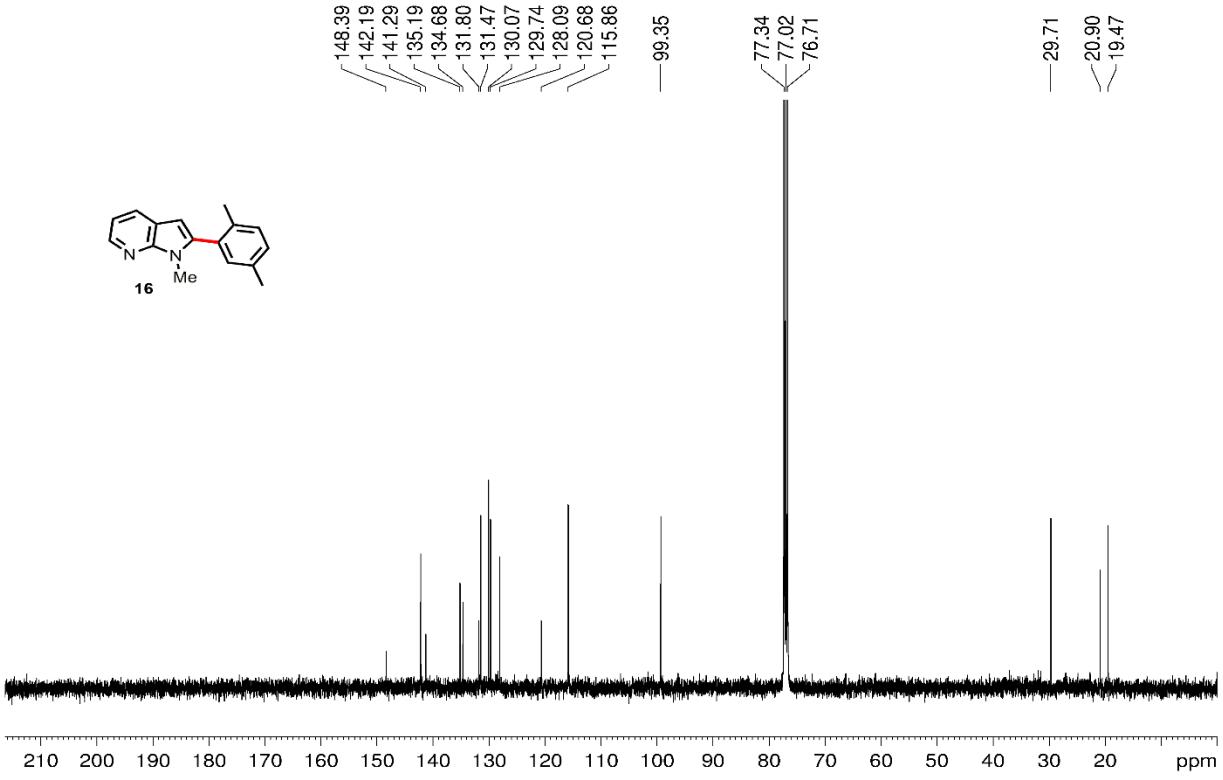
8.3597
7.9477
7.9439
7.9283
7.9245
7.2840
7.2588
7.2394
7.2207
7.2173
7.1976
7.1476
7.1344
7.1224
7.1150
7.1030
6.3970
3.6504
2.3951
2.1817
0.0226
N
N
Me
16
1.00
1.00
2.10
2.09
0.89
2.85
3.01
2.89
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp
8.3753
8.3716
8.3634
8.3597
7.9477
7.9439
7.9283
7.9245
7.2840
7.2588
7.2394
7.2207
7.2173
7.1976
7.1476
7.1344
7.1224
7.1150
7.1030
6.3970
N
N
Me
16
1.00
1.00
2.10
2.09
0.89
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 pp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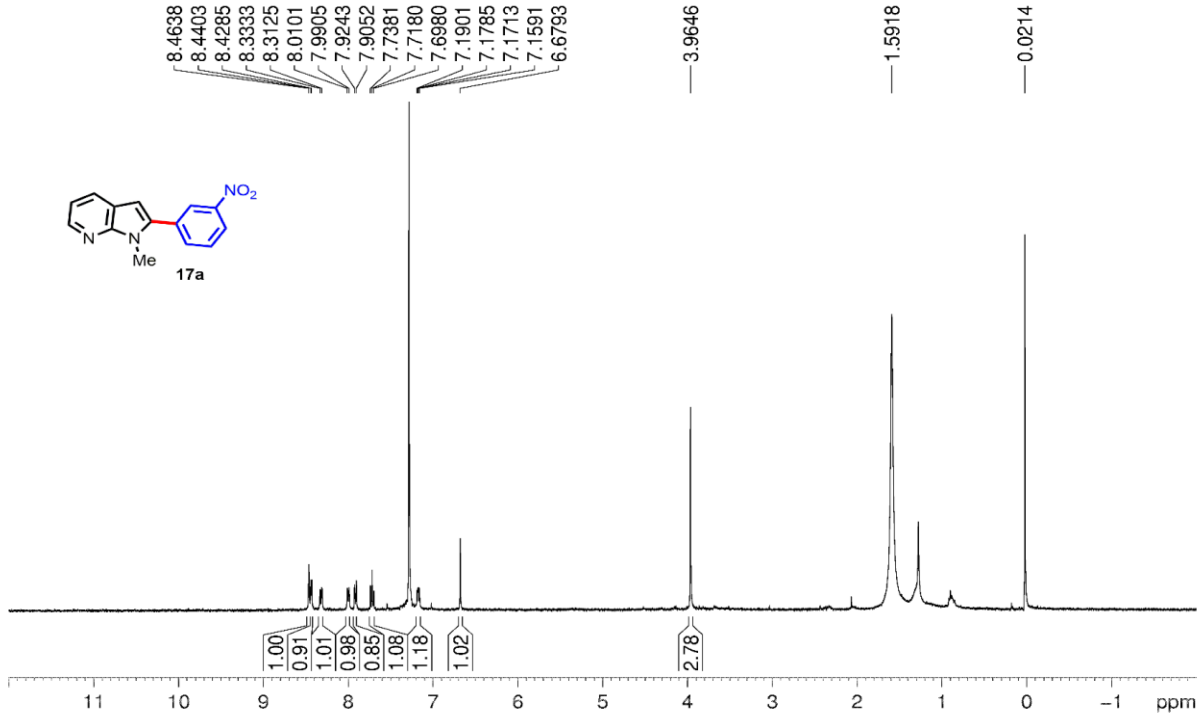
131.80
131.47
130.07
129.74
128.09
120.68
115.86
99.35
77.34
77.02
76.71
29.71
20.90
19.47
Me
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.3333
8.3125
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7.9905
7.9243
7.9052
7.7381
7.7180
7.6980
7.1901
7.1785
7.1713
7.1591
6.6793
3.9646
1.5918
0.0214
NO2
Me
17a
1.00
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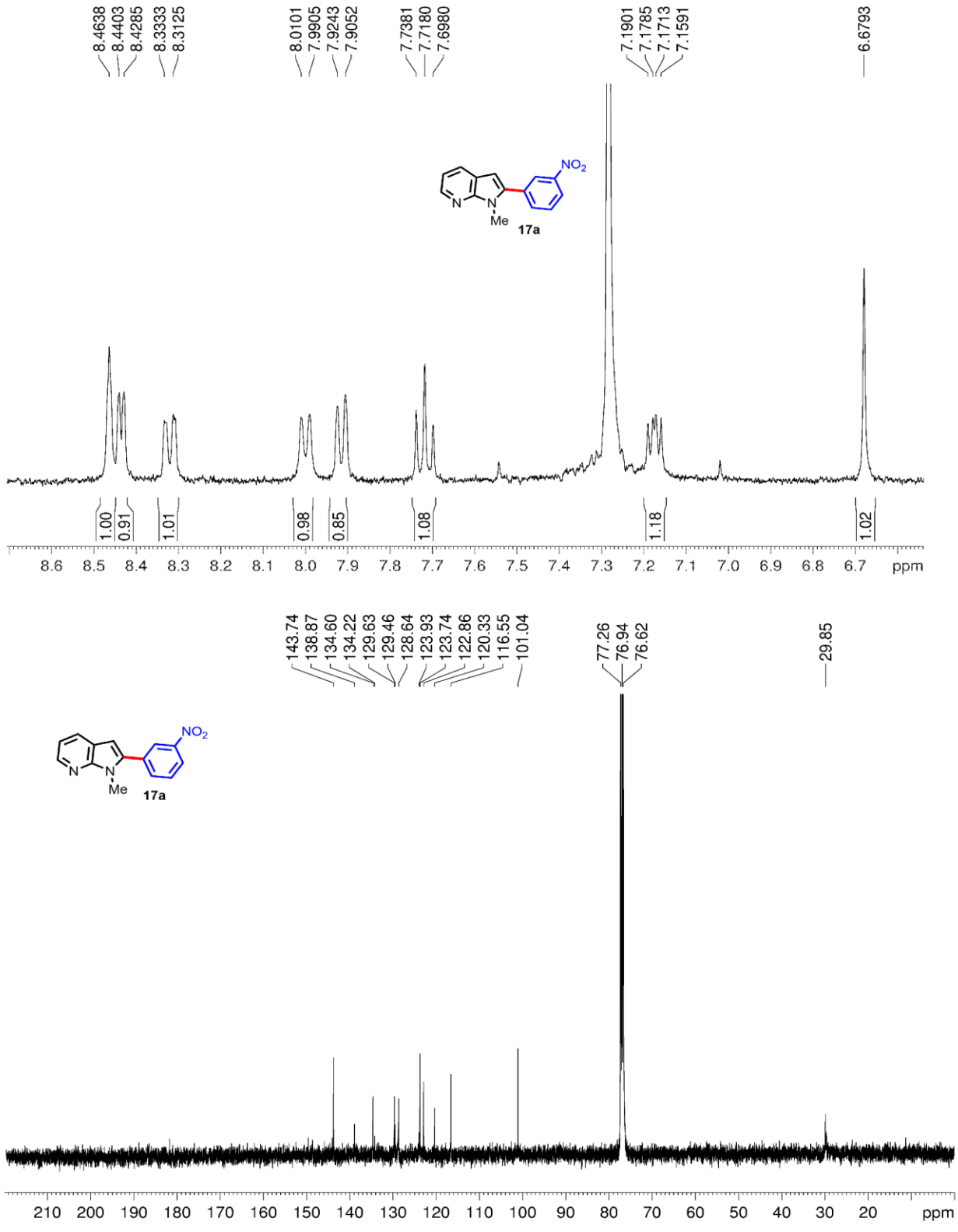
1.01
0.98
0.85
1.08
1.18
1.02
2.78
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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8.4285
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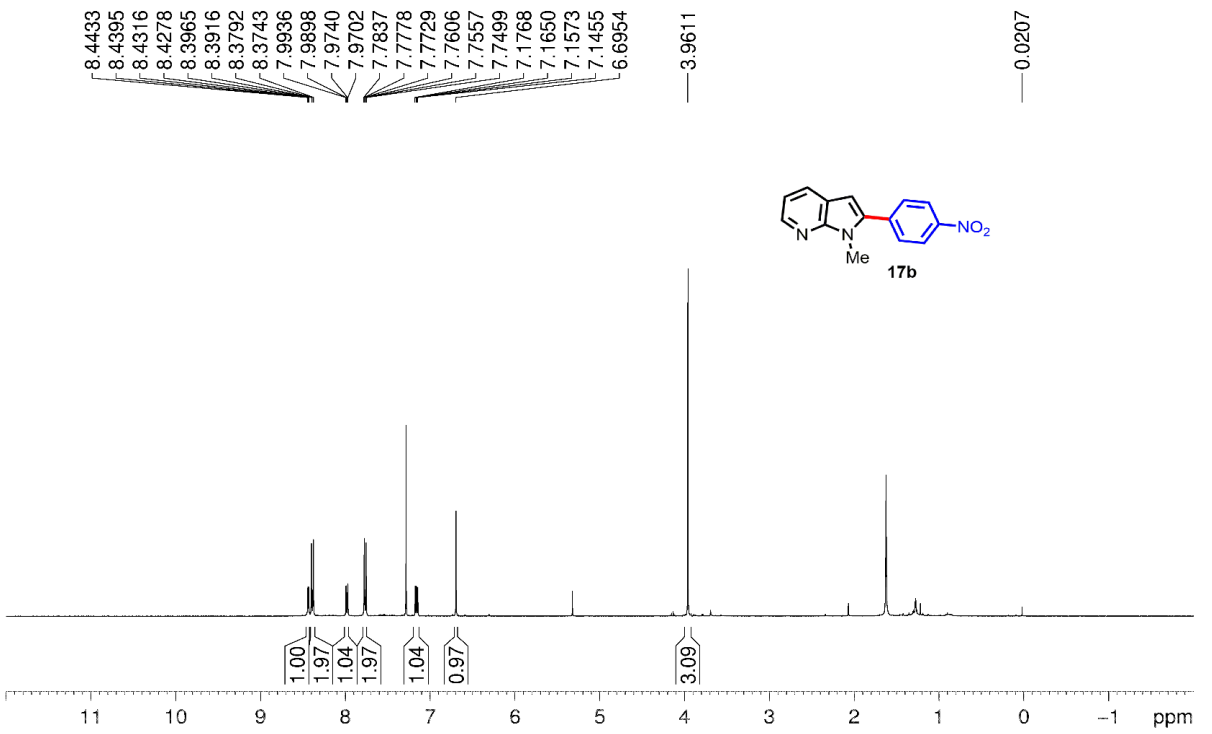
7.6980
7.1901
7.1785
7.1713
7.1591
6.6793
NO2
N
N
Me
17a
1.00
0.91
1.01
0.98
0.85
1.08
1.18
1.02
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
143.74
138.87
134.60
134.22
129.63
129.46
128.64
123.93
123.74
122.86
120.33
116.55
101.04
77.26
76.94
76.62
29.85
NO2
N
N
Me
17a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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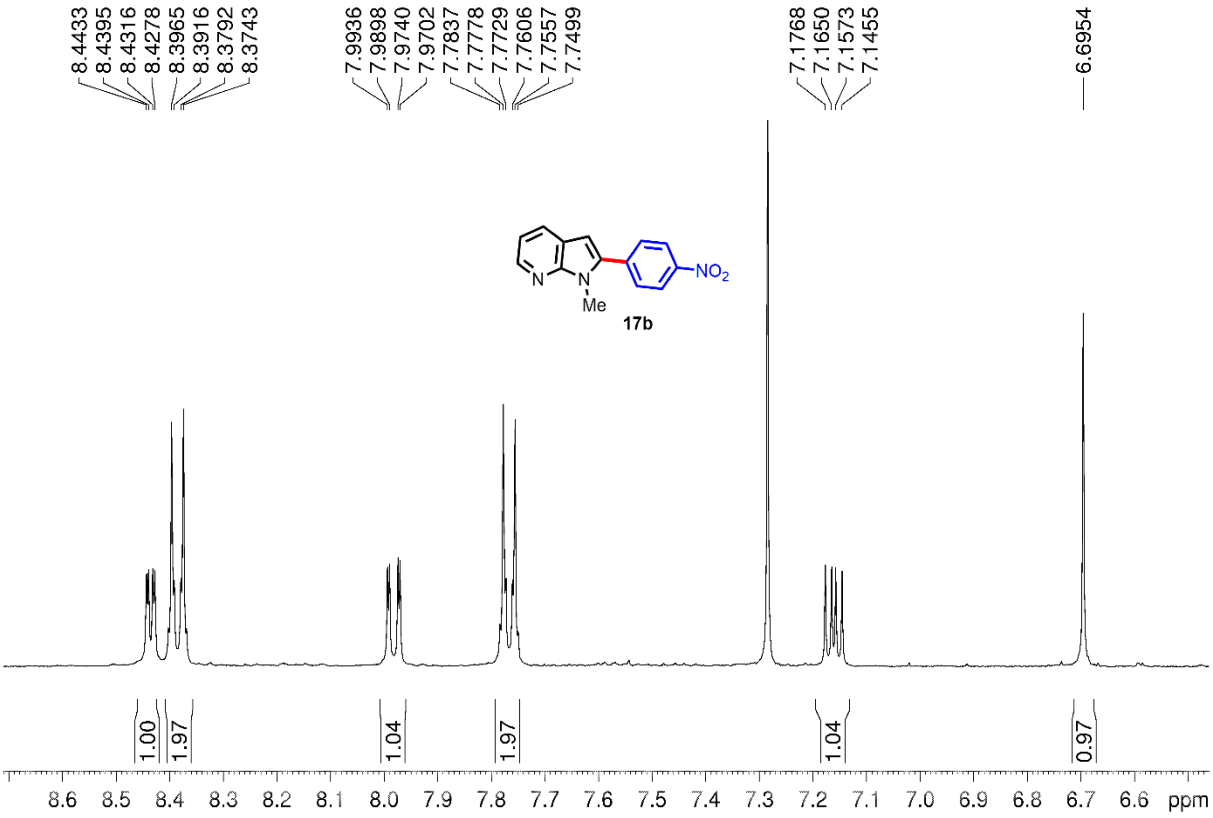
8.3792
8.3743
7.9936
7.9898
7.9740
7.9702
7.7837
7.7778
7.7729
7.7606
7.7557
7.7499
7.1768
7.1650
7.1573
7.1455
6.6954
3.9611
0.0207
NO2
N
N
Me
17b
1.00
1.97
1.04
1.97
1.04
0.97
3.09
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm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7.7837
7.7778
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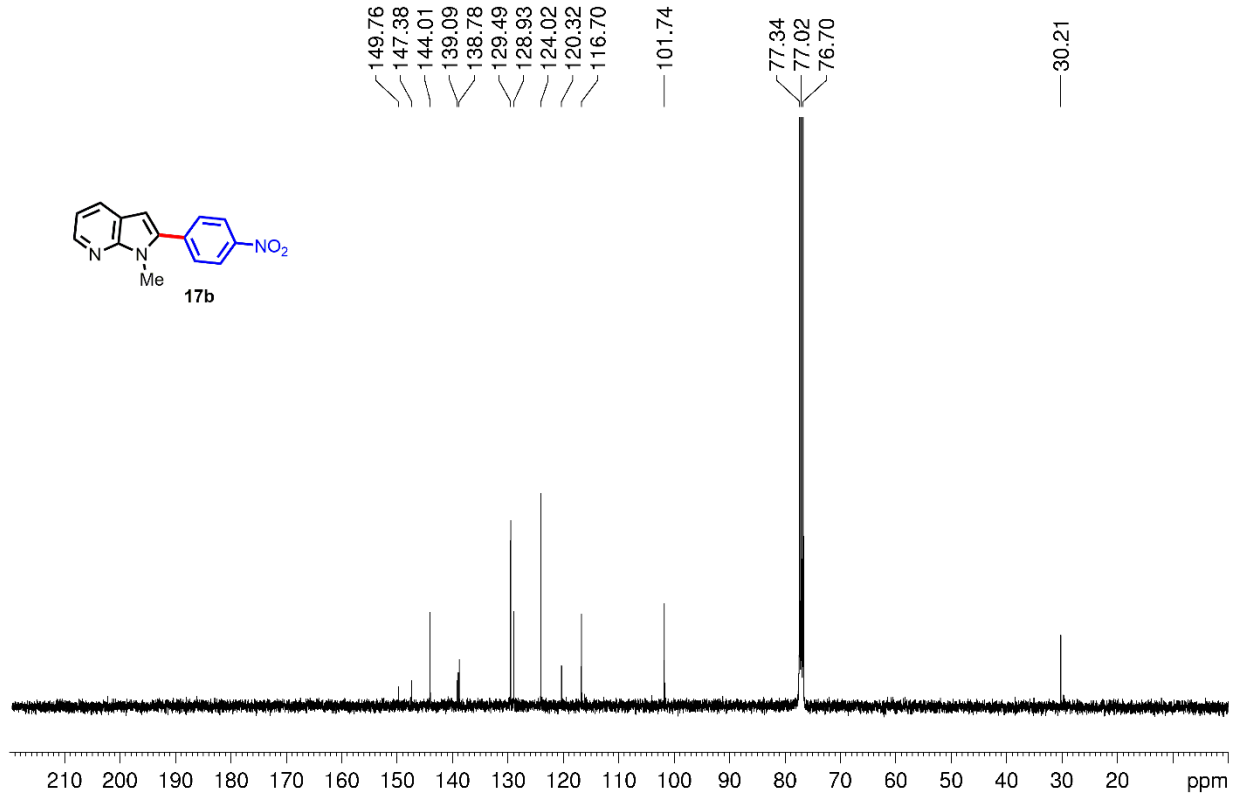
7.7606
7.7557
7.7499
7.1768
7.1650
7.1573
7.1455
6.6954
NO2
N
N
Me
17b
1.00
1.97
1.04
1.97
1.04
0.97
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm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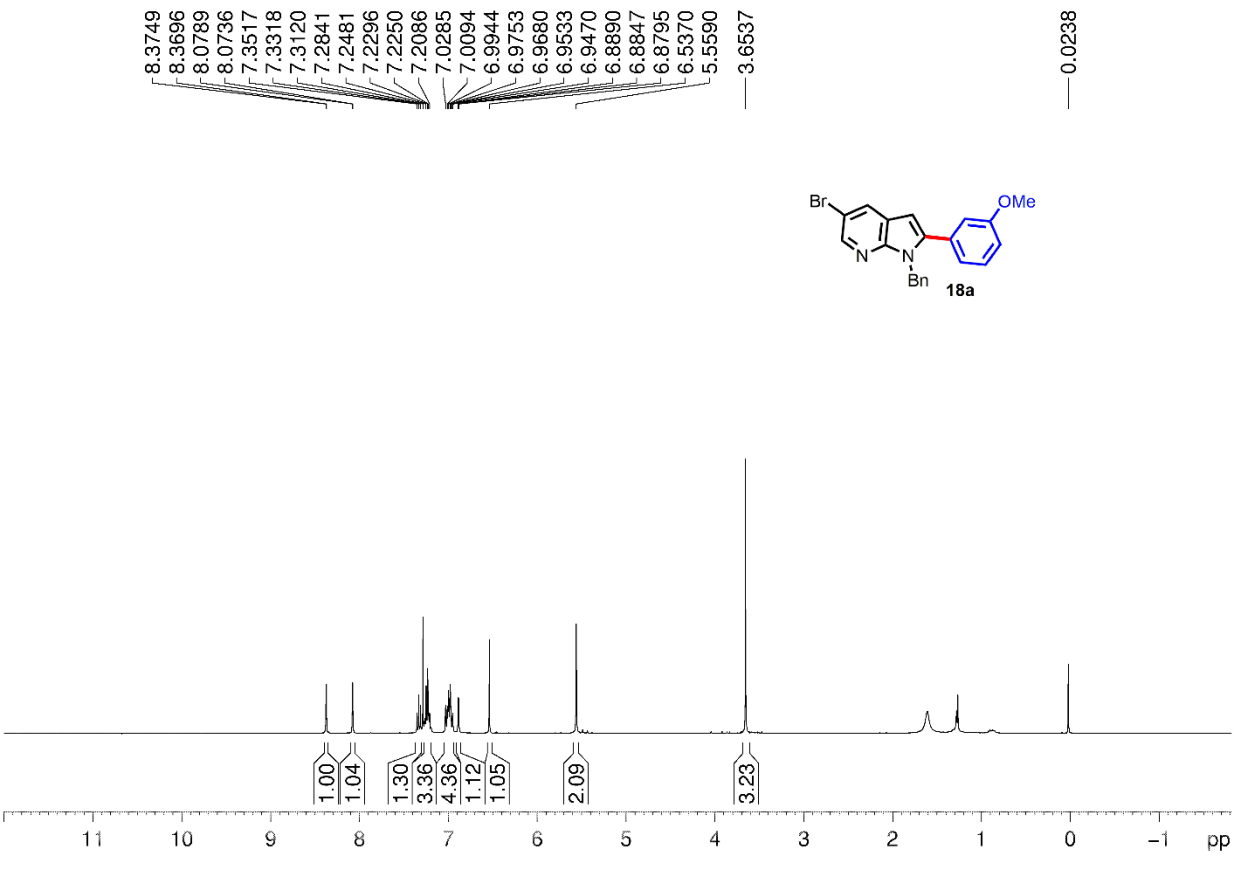
138.78
129.49
128.93
124.02
120.32
116.70
101.74
77.34
77.02
76.70
30.21
NO2
N
Me
17b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.0736
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7.2841
7.2481
7.2296
7.2250
7.2086
7.0285
7.0094
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6.9753
6.9680
6.9533
6.9470
6.8890
6.8847
6.8795
6.5370
5.5590
3.6537
0.0238
Br
OMe
N
N
Bn
18a
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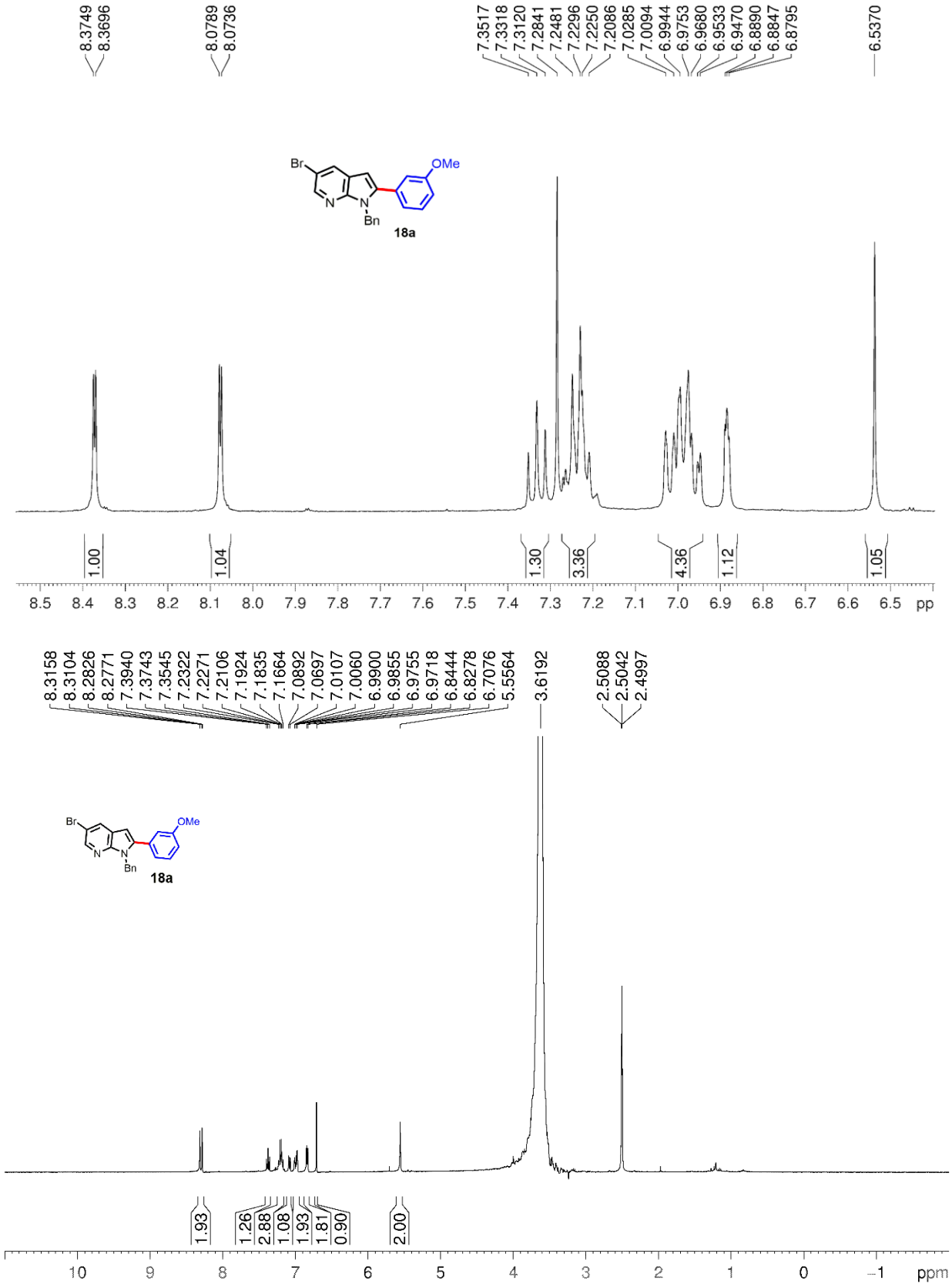
1.04
1.30
3.36
4.36
1.12
1.05
2.09
3.23
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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6.5370
Br
OMe
N
N
Bn
18a
1.00
1.04
1.30
3.36
4.36
1.12
1.05
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 pp
8.3158
8.3104
8.2826
8.2771
7.3940
7.3743
7.3545
7.2322
7.2271
7.2106
7.1924
7.1835
7.1664
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7.0697
7.0107
7.0060
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6.9718
6.8444
6.8278
6.7076
5.5564
3.6192
2.5088
2.5042
2.4997
Br
OMe
N
N
Bn
18a
1.93
1.26
2.88
1.08
1.93
1.81
0.90
2.00
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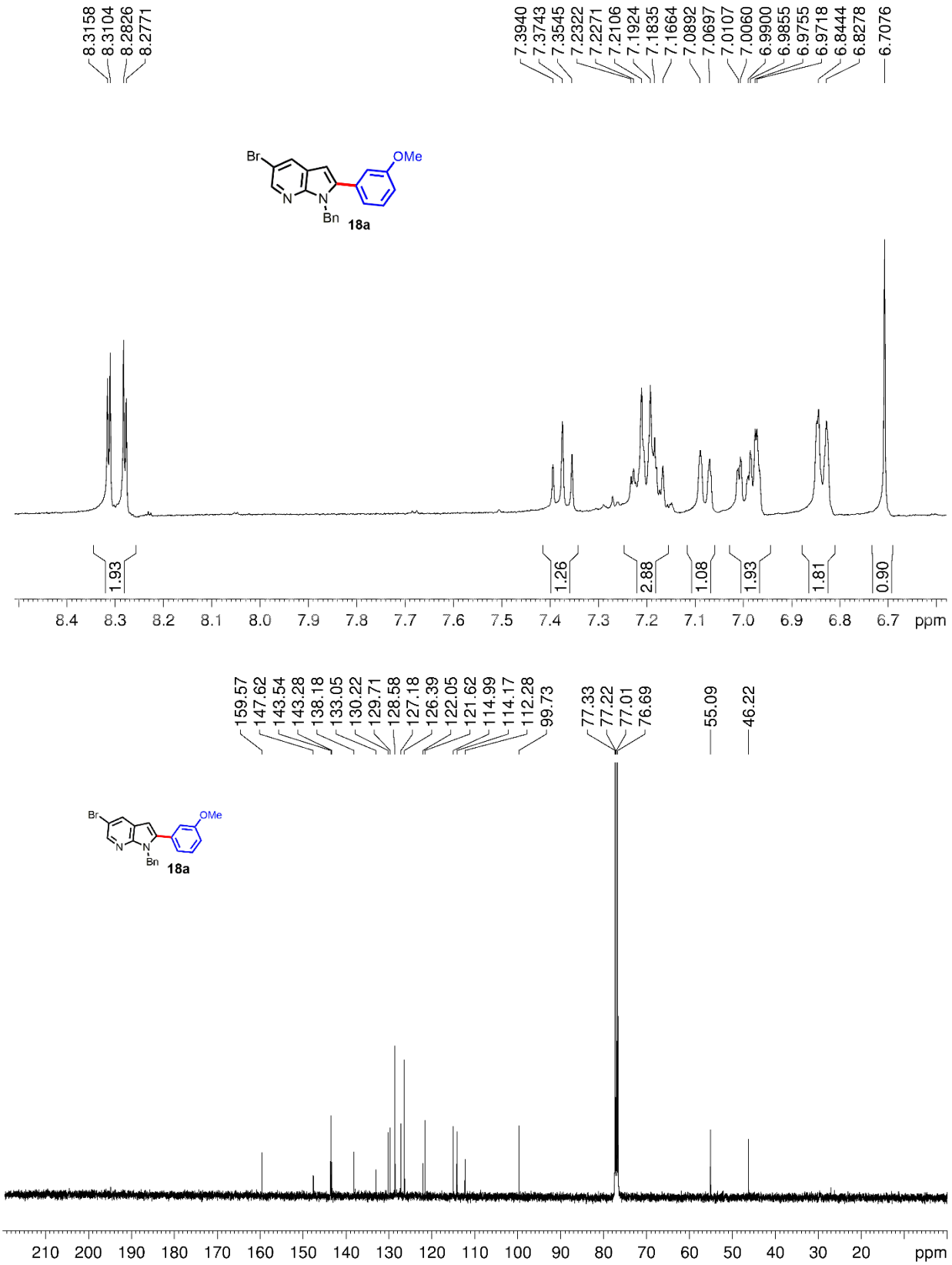
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7.1924
7.1835
7.1664
7.0892
7.0697
7.0107
7.0060
6.9900
6.9855
6.9755
6.9718
6.8444
6.8278
6.7076
Br
OMe
N
N
Bn
18a
1.93
1.26
2.88
1.08
1.93
1.81
0.90
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
159.57
147.62
143.54
143.28
138.18
133.05
130.22
129.71
128.58
127.18
126.39
122.05
121.62
114.99
114.17
112.28
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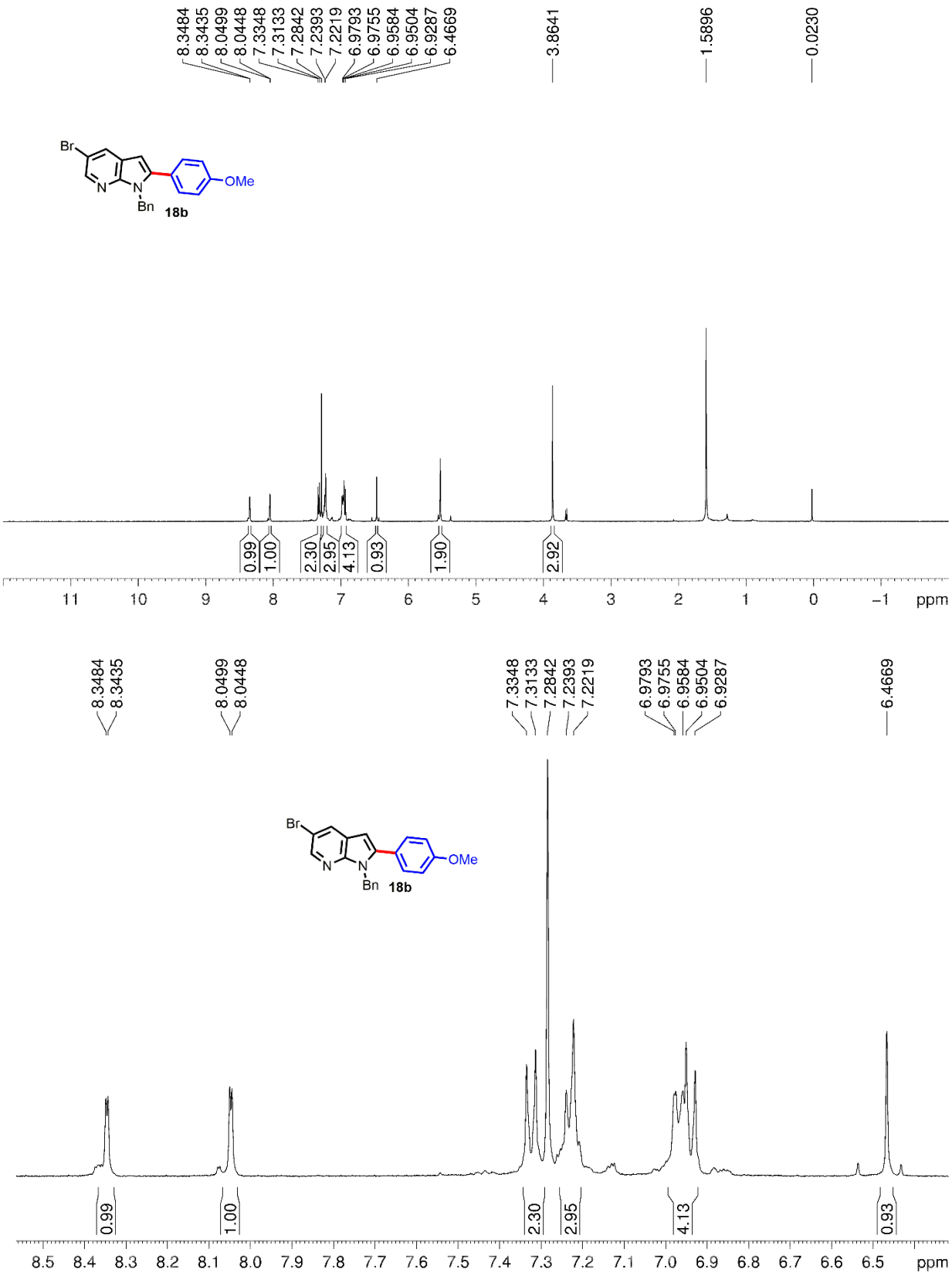
77.22
77.01
76.69
55.09
46.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.3133
7.2842
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7.2219
6.9793
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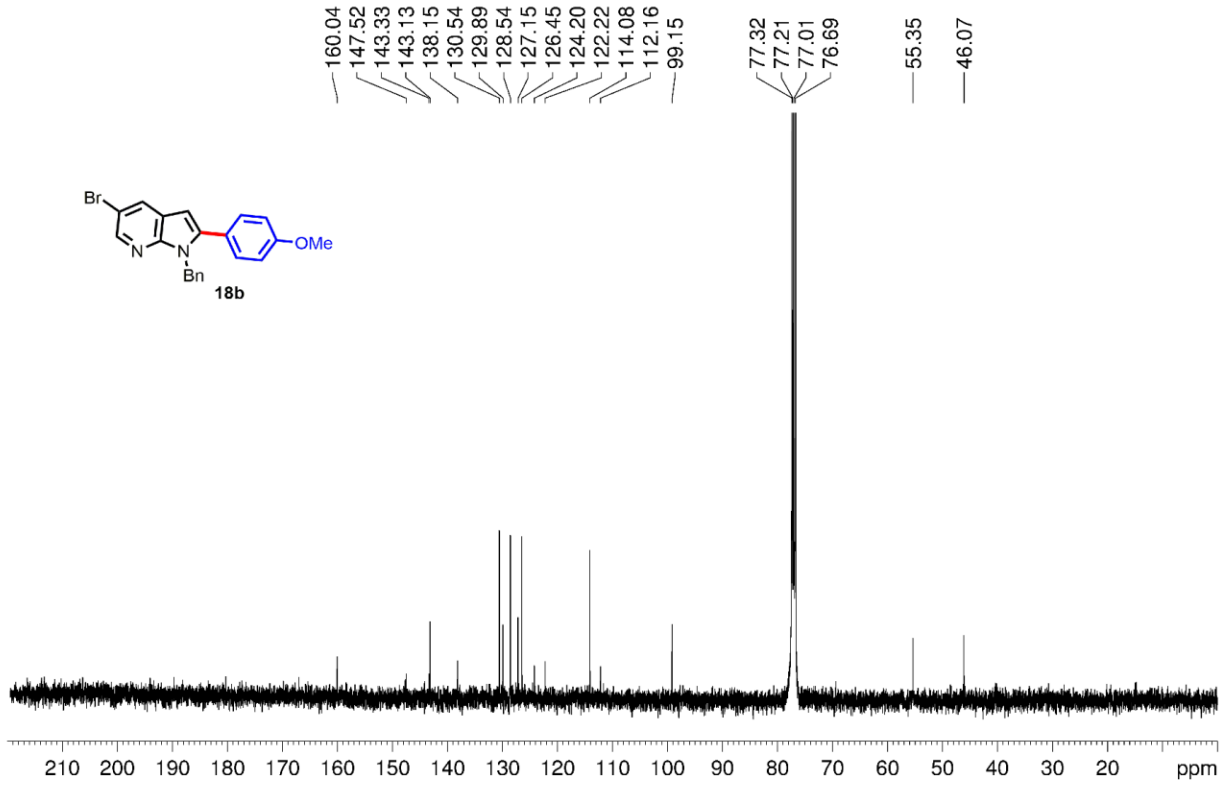
6.9584
6.9504
6.9287
6.4669
3.8641
1.5896
0.0230
Br
N
N
Bn
OMe
18b
0.99
1.00
2.30
2.95
4.13
0.93
1.90
2.92
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
8.3484
8.3435
8.0499
8.0448
7.3348
7.3133
7.2842
7.2393
7.2219
6.9793
6.9755
6.9584
6.9504
6.9287
6.4669
Br
N
N
Bn
OMe
18b
0.99
1.00
2.30
2.95
4.13
0.93
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
ppm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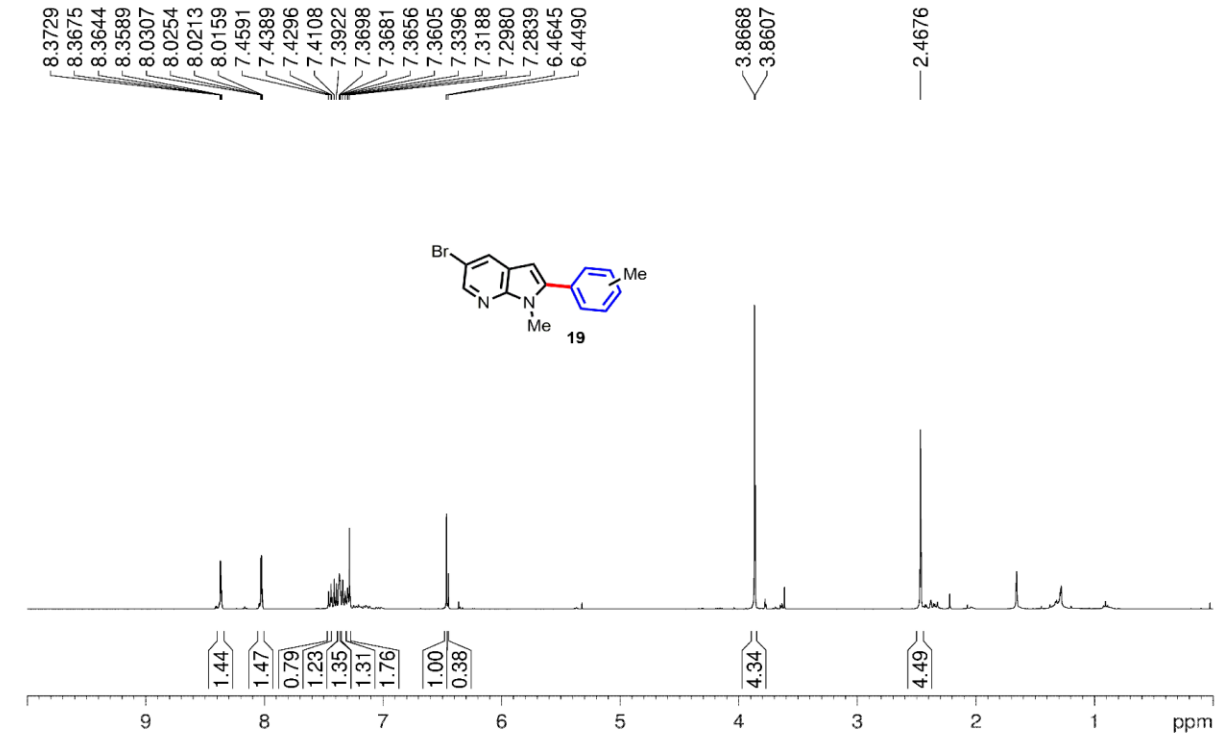
130.54
129.89
128.54
127.15
126.45
124.20
122.22
114.08
112.16
99.15
77.32
77.21
77.01
76.69
55.35
46.07
Br
N
N
Bn
OMe
18b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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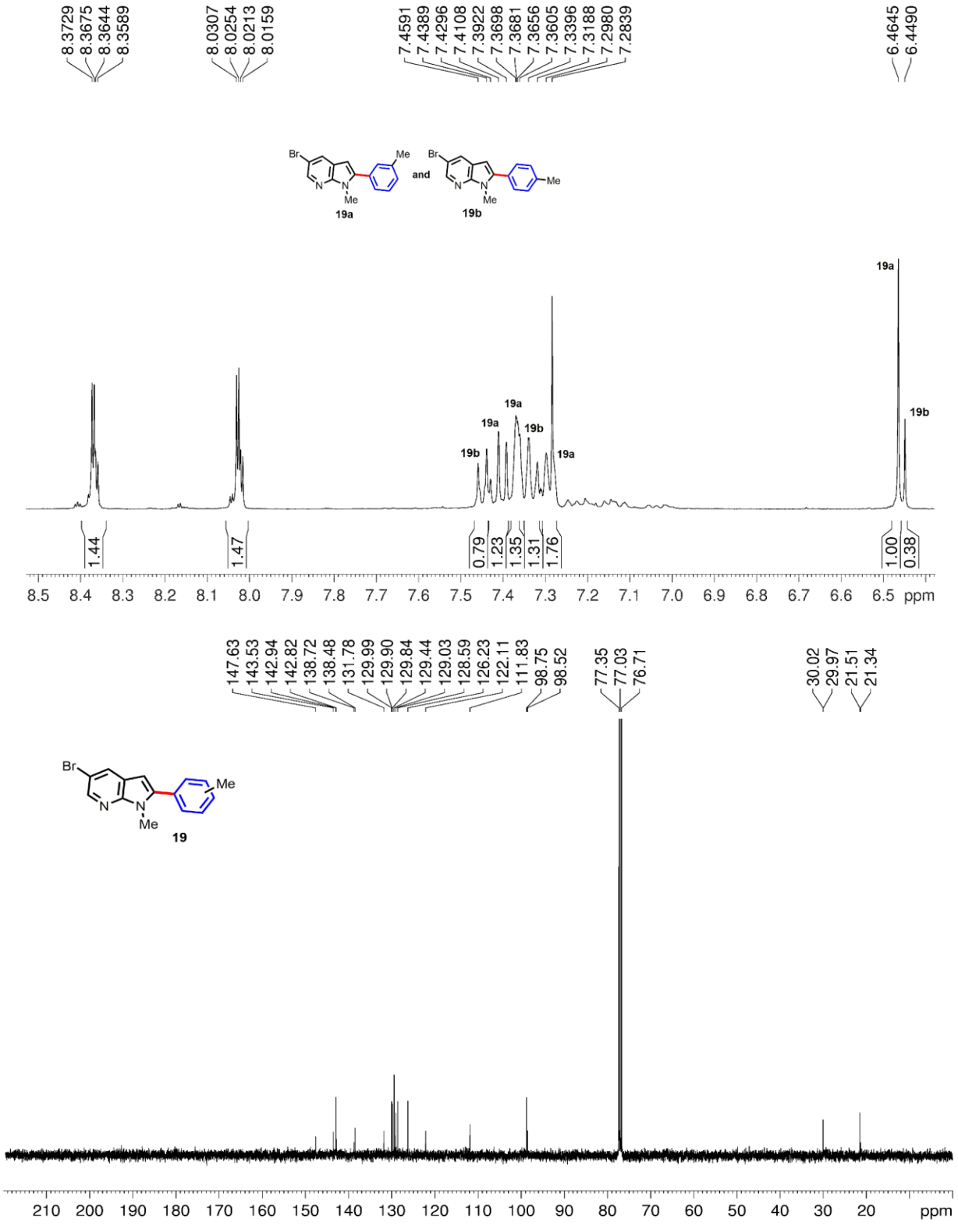
8.3644
8.3589
8.0307
8.0254
8.0213
8.0159
7.4591
7.4389
7.4296
7.4108
7.3922
7.3698
7.3681
7.3656
7.3605
7.3396
7.3188
7.2980
7.2839
6.4645
6.4490
3.8668
3.8607
2.4676
Br
N
N
Me
Me
19
1.44
1.47
0.79
1.23
1.35
1.31
1.76
1.00
0.38
4.34
4.49
9 8 7 6 5 4 3 2 1 ppm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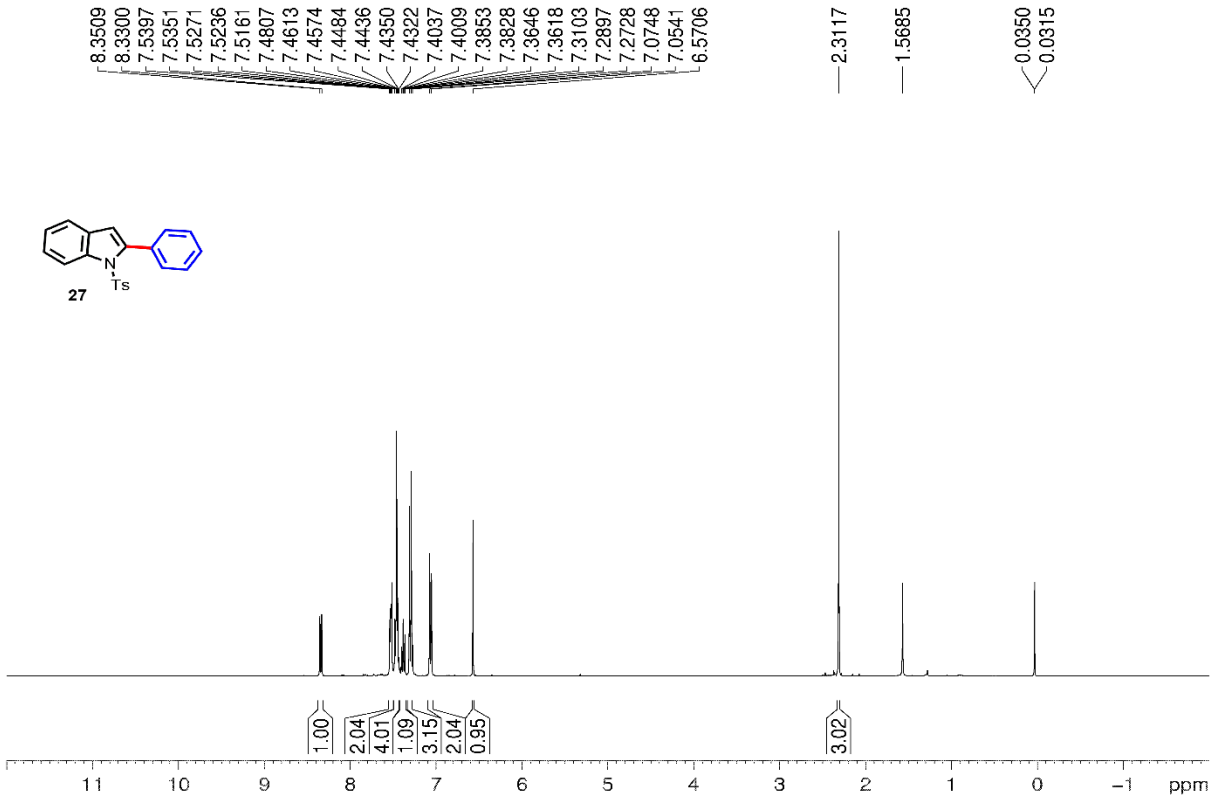
8.3675
8.3644
8.3589
8.0307
8.0254
8.0213
8.0159
7.4591
7.4389
7.4296
7.4108
7.3922
7.3698
7.3681
7.3656
7.3605
7.3396
7.3188
7.2980
7.2839
6.4645
6.4490
Br
Me
N
Me
19a
and
Br
N
Me
Me
19b
19a
19a
19a
19b
19b
19a
19b
1.44
1.47
0.79
1.23
1.35
1.31
1.76
1.00
0.38
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm
147.63
143.53
142.94
142.82
138.72
138.48
131.78
129.99
129.90
129.84
129.44
129.03
128.59
126.23
122.11
111.83
98.75
98.52
77.35
77.03
76.71
30.02
29.97
21.51
21.34
Br
N
Me
Me
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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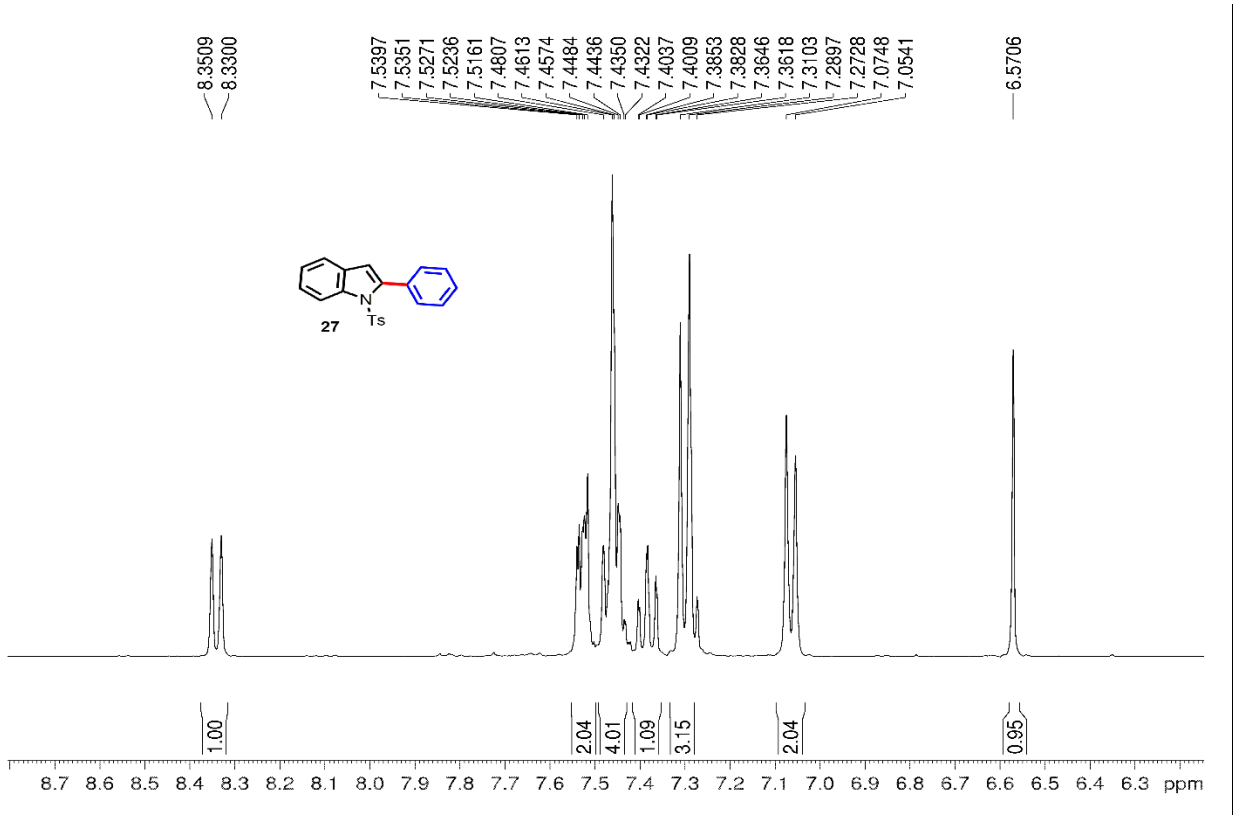
8.3300
7.5397
7.5351
7.5271
7.5236
7.5161
7.4807
7.4613
7.4574
7.4484
7.4436
7.4350
7.4322
7.4037
7.4009
7.3853
7.3828
7.3646
7.3618
7.3103
7.2897
7.2728
7.0748
7.0541
6.5706
2.3117
1.5685
0.0350
0.0315
27
Ts
1.00
2.04
4.01
1.09
3.15
2.04
0.95
3.02
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm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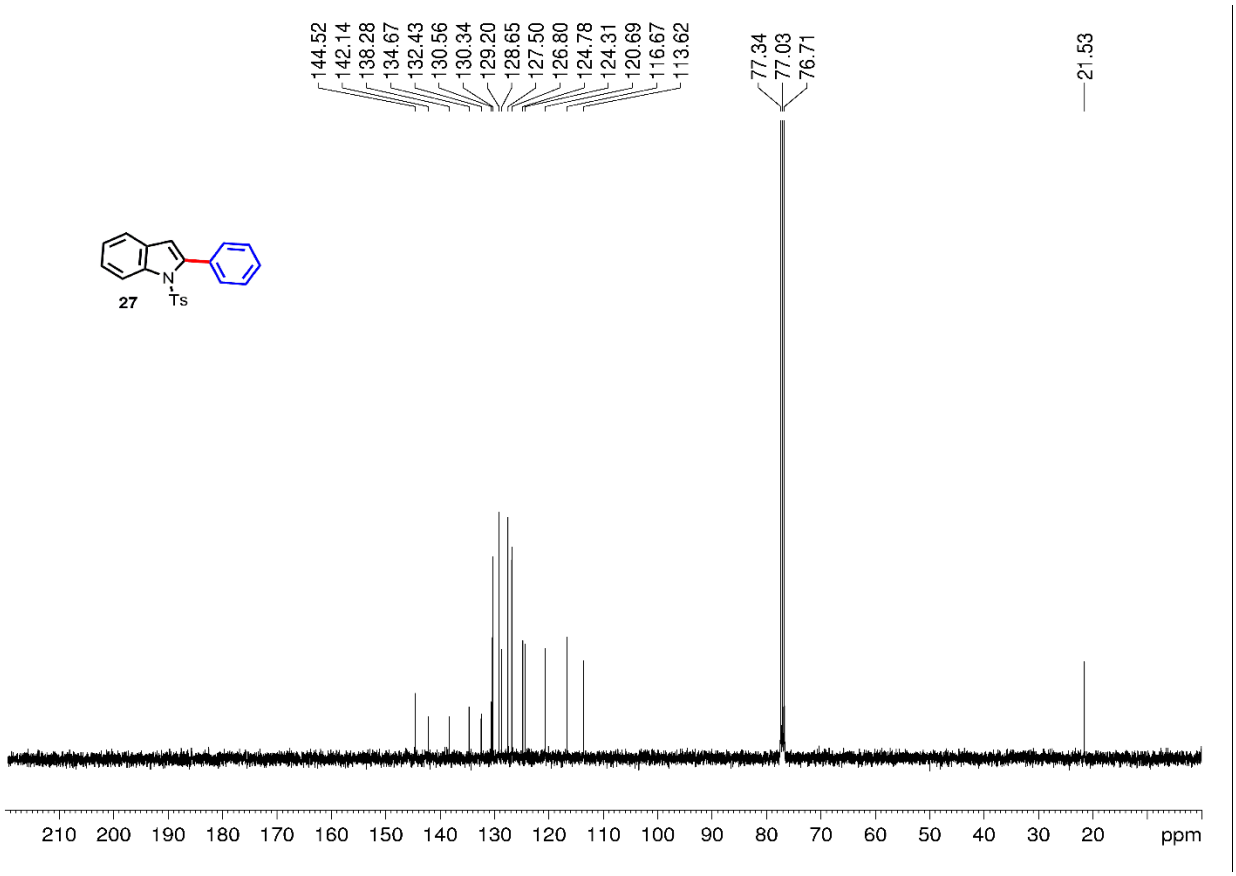
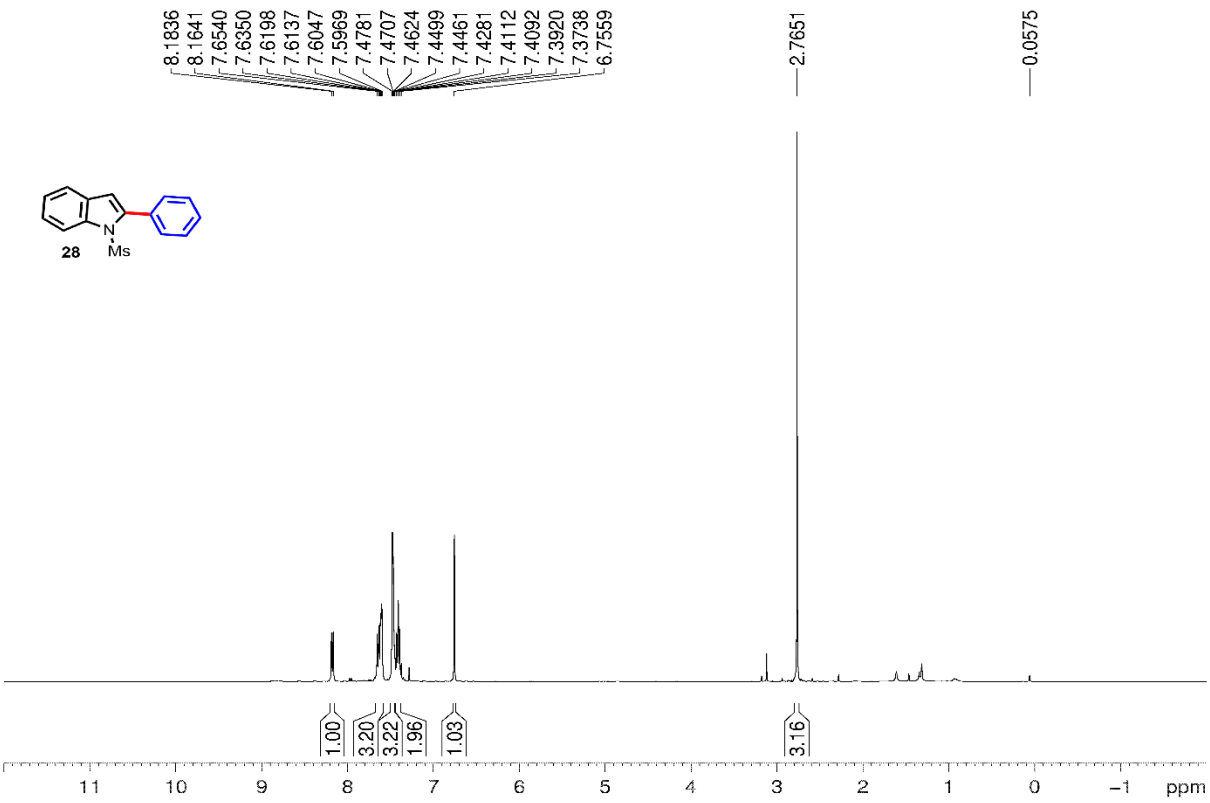
8.3300
7.5397
7.5351
7.5271
7.5236
7.5161
7.4807
7.4613
7.4574
7.4484
7.4436
7.4350
7.4322
7.4037
7.4009
7.3853
7.3828
7.3646
7.3618
7.3103
7.2897
7.2728
7.0748
7.0541
6.5706
27
Ts
1.00
2.04
4.01
1.09
3.15
2.04
0.95
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
ppm


144.52
142.14
138.28
134.67
132.43
130.56
130.34
129.20
128.65
127.50
126.80
124.78
124.31
120.69
116.67
113.62
77.34
77.03
76.71
21.53
27
Ts
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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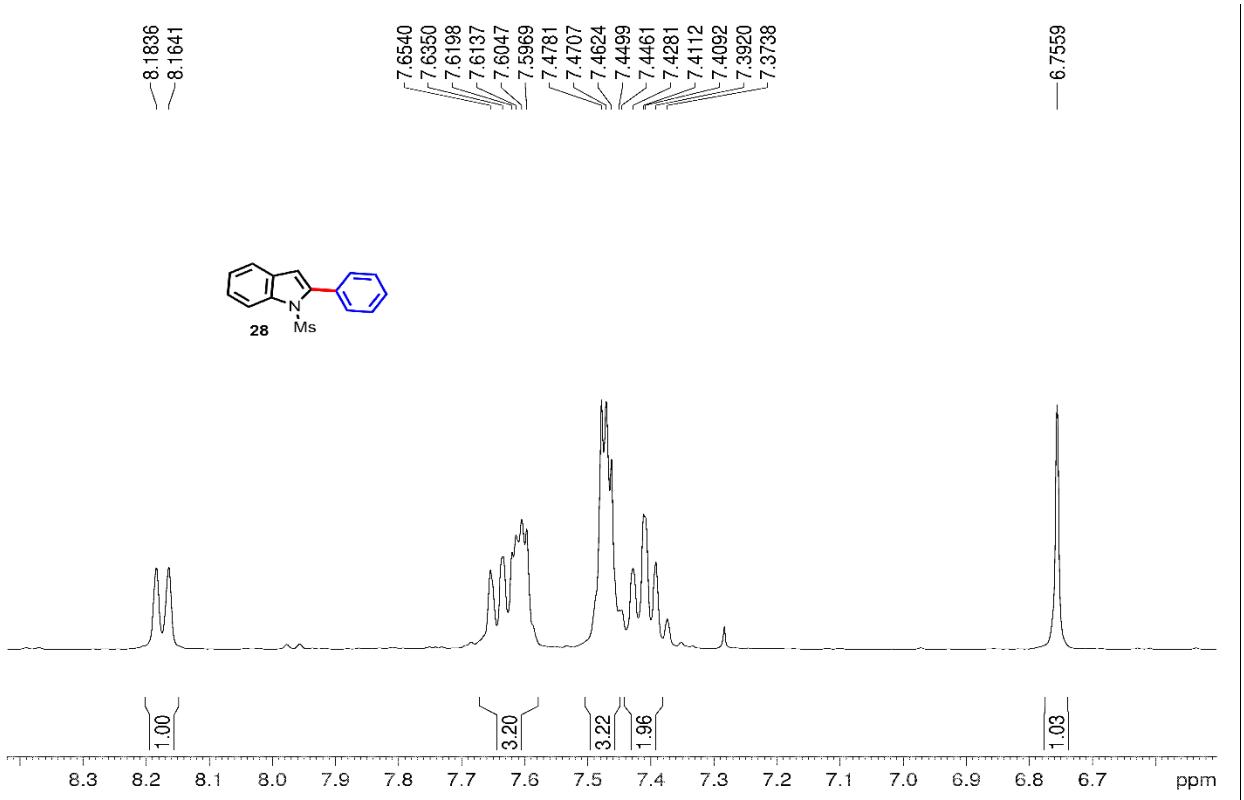
8.1641
7.6540
7.6350
7.6198
7.6137
7.6047
7.5969
7.4781
7.4707
7.4624
7.4499
7.4461
7.4281
7.4112
7.4092
7.3920
7.3738
6.7559
2.7651
0.0575
28
Ms
1.00
3.20
3.22
1.96
1.03
3.16
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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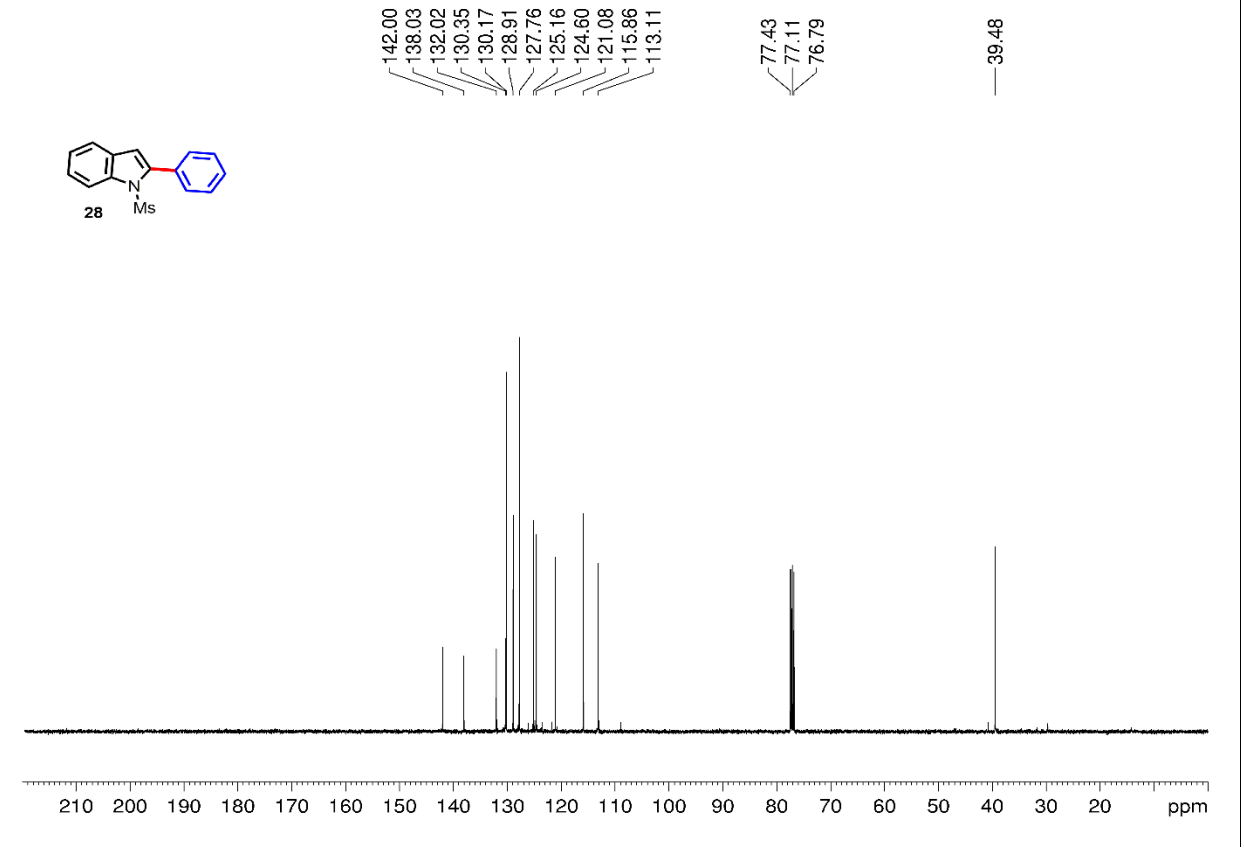
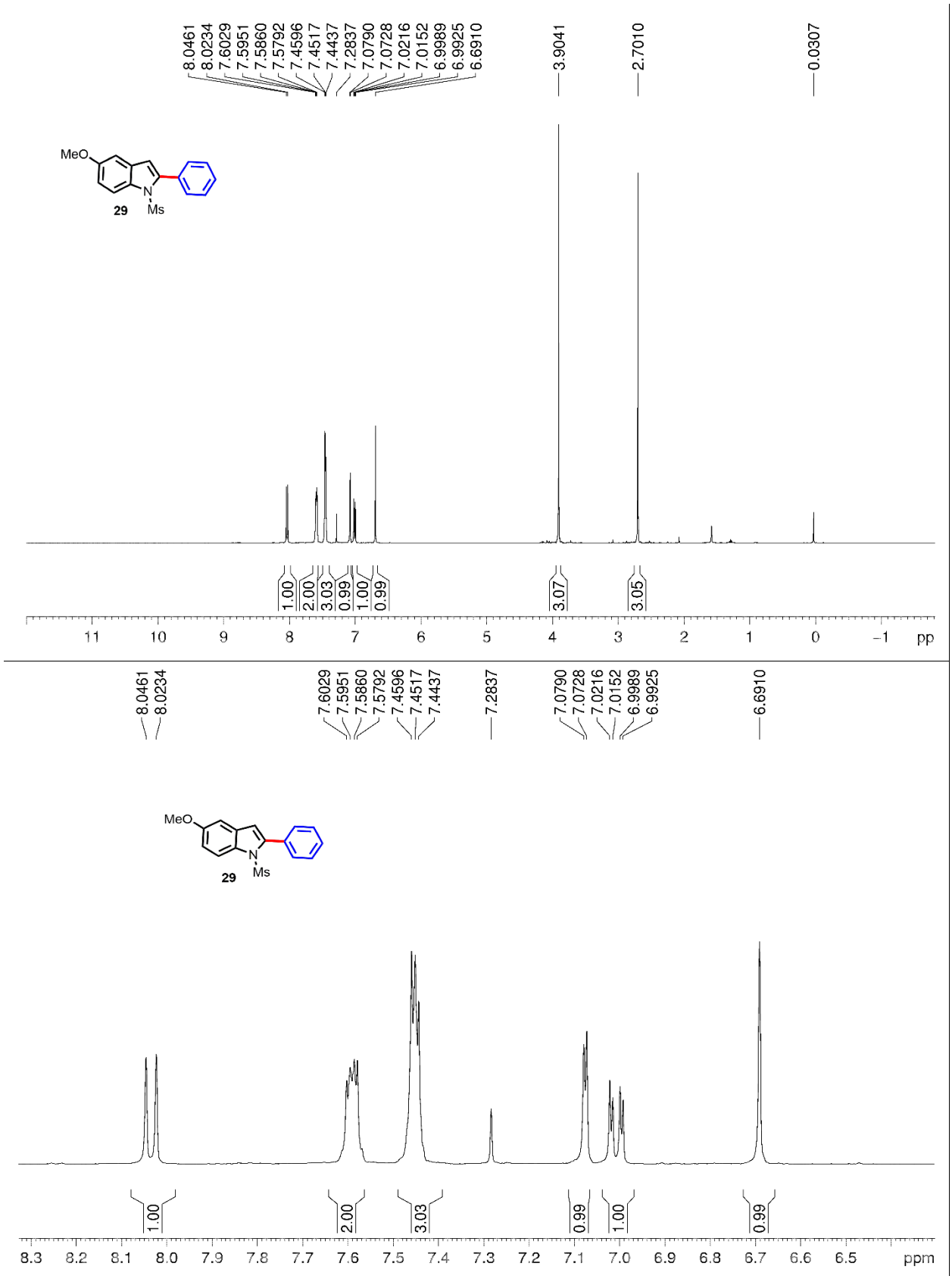
8.1641
7.6540
7.6350
7.6198
7.6137
7.6047
7.5969
7.4781
7.4707
7.4624
7.4499
7.4461
7.4281
7.4112
7.4092
7.3920
7.3738
6.7559
28
Ms
1.00
3.20
3.22
1.96
1.03
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
ppm


142.00
138.03
132.02
130.35
130.17
128.91
127.76
125.16
124.60
121.08
115.86
113.11
77.43
77.11
76.79
39.48
28
Ms
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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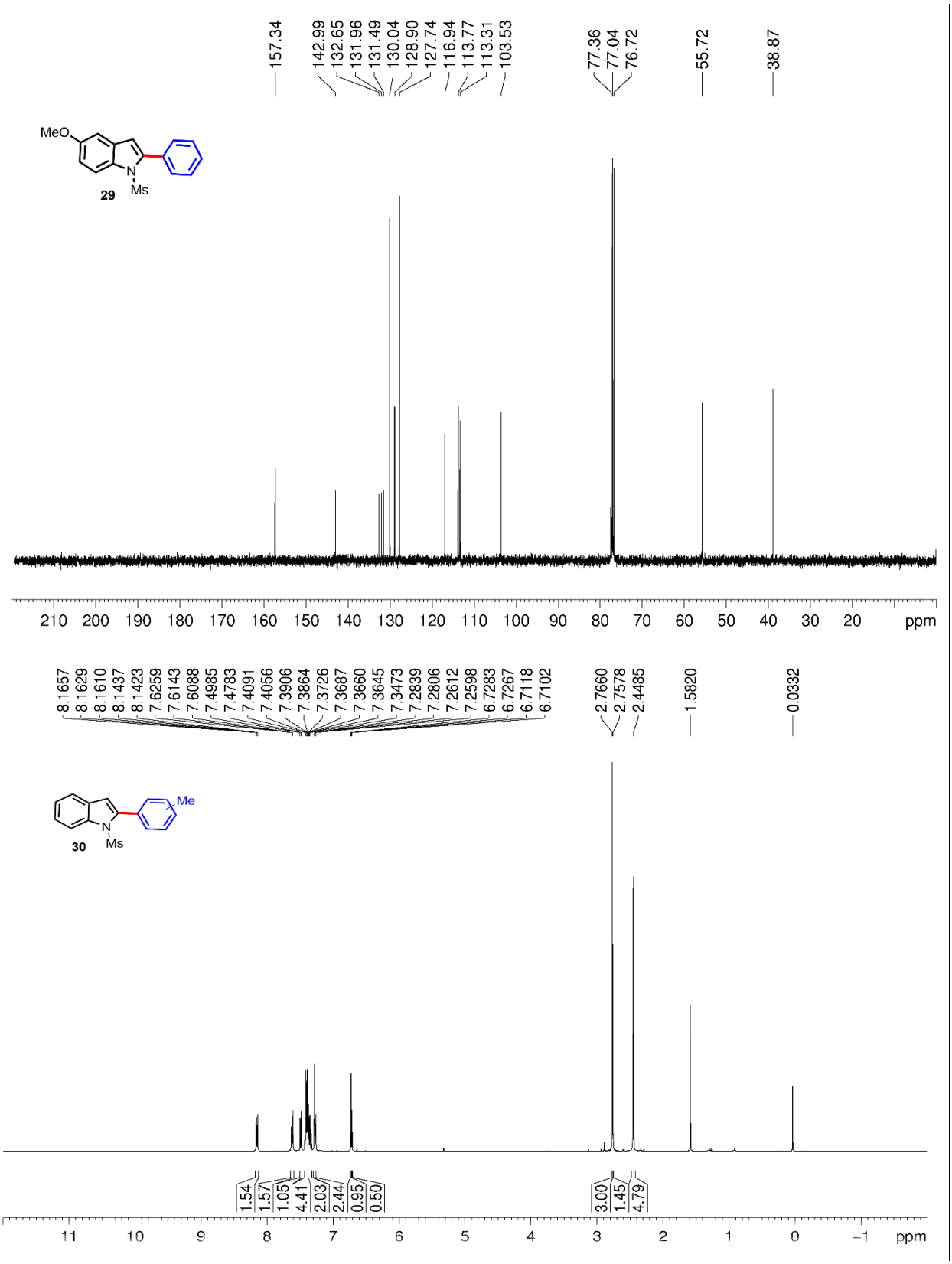
7.4437
7.2837
7.0790
7.0728
7.0216
7.0152
6.9989
6.9925
6.6910
3.9041
2.7010
0.0307
MeO
N
Ms
29
1.00
2.00
3.03
0.99
1.00
0.99
3.07
3.05
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp
8.0461
8.0234
7.6029
7.5951
7.5860
7.5792
7.4596
7.4517
7.4437
7.2837
7.0790
7.0728
7.0216
7.0152
6.9989
6.9925
6.6910
MeO
N
Ms
29
1.00
2.00
3.03
0.99
1.00
0.99
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
ppm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131.49
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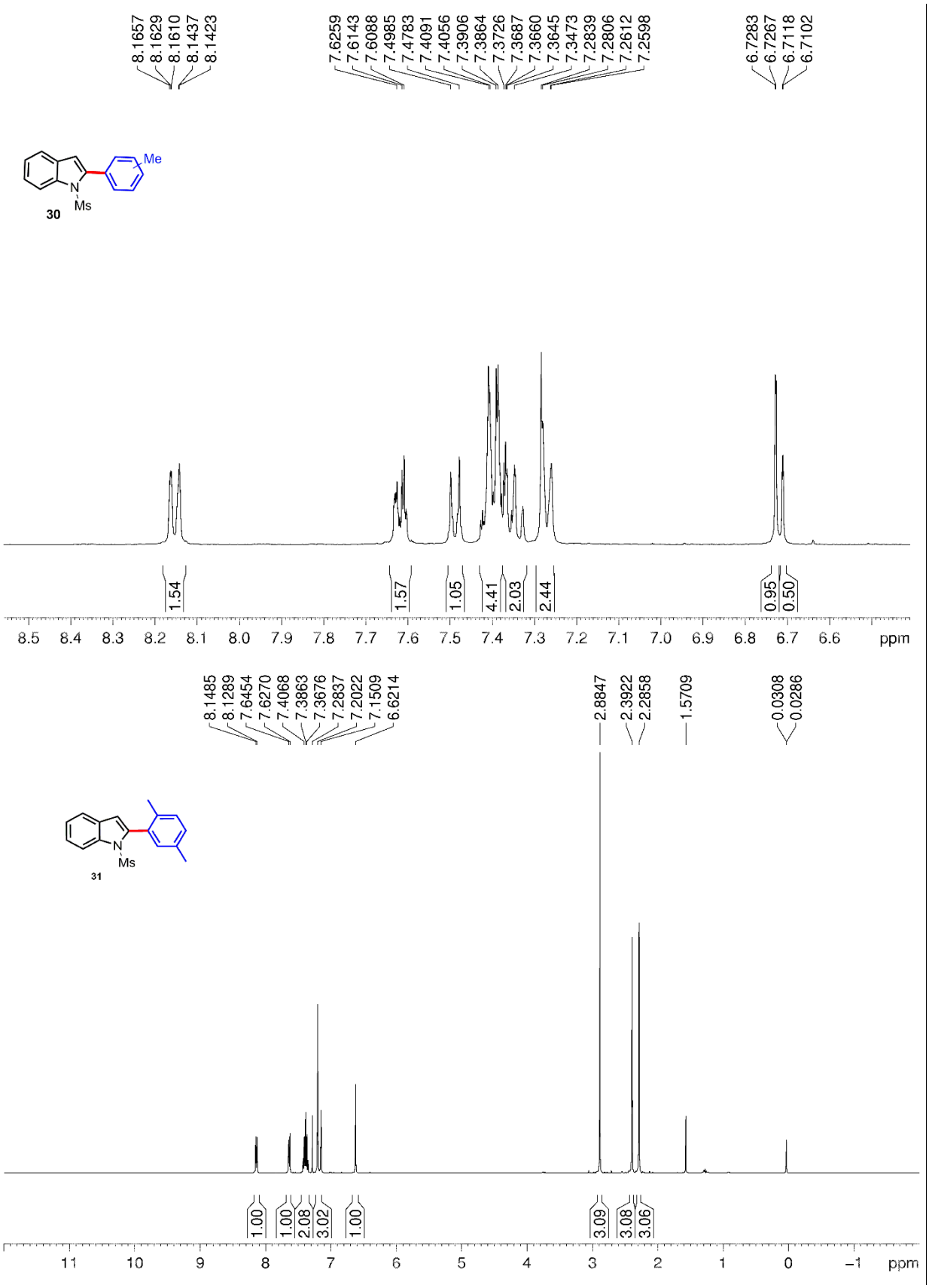
128.90
127.74
116.94
113.77
113.31
103.53
77.36
77.04
76.72
55.72
38.87
MeO
N
Ms
29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
8.1657
8.1629
8.1610
8.1437
8.1423
7.6259
7.6143
7.6088
7.4985
7.4783
7.4091
7.4056
7.3906
7.3864
7.3726
7.3687
7.3660
7.3645
7.3473
7.2839
7.2806
7.2612
7.2598
6.7283
6.7267
6.7118
6.7102
2.7660
2.7578
2.4485
1.5820
0.0332
Me
N
Ms
30
1.54
1.57
1.05
4.41
2.03
2.44
0.95
0.50
3.00
1.45
4.79
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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8.1629
8.1610
8.1437
8.1423
7.6259
7.6143
7.6088
7.4985
7.4783
7.4091
7.4056
7.3906
7.3864
7.3726
7.3687
7.3660
7.3645
7.3473
7.2839
7.2806
7.2612
7.2598
6.7283
6.7267
6.7118
6.7102
Me
N
Ms
30
1.54
1.57
1.05
4.41
2.03
2.44
0.95
0.50
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 ppm
8.1485
8.1289
7.6454
7.6270
7.4068
7.3863
7.3676
7.2837
7.2022
7.1509
6.6214
2.8847
2.3922
2.2858
1.5709
0.0308
0.0286
N
Ms
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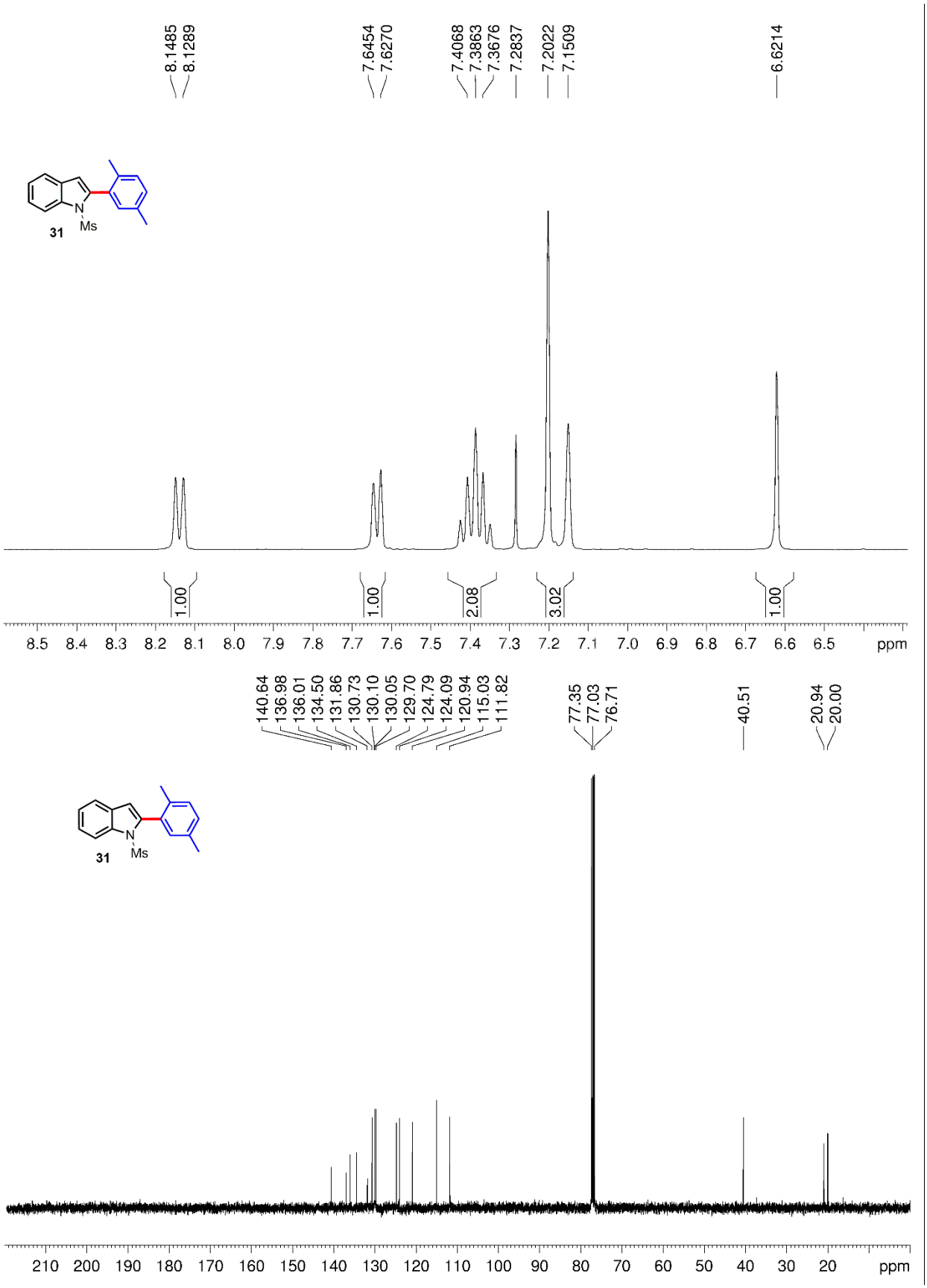
1.00
2.08
3.02
1.00
3.09
3.08
3.06
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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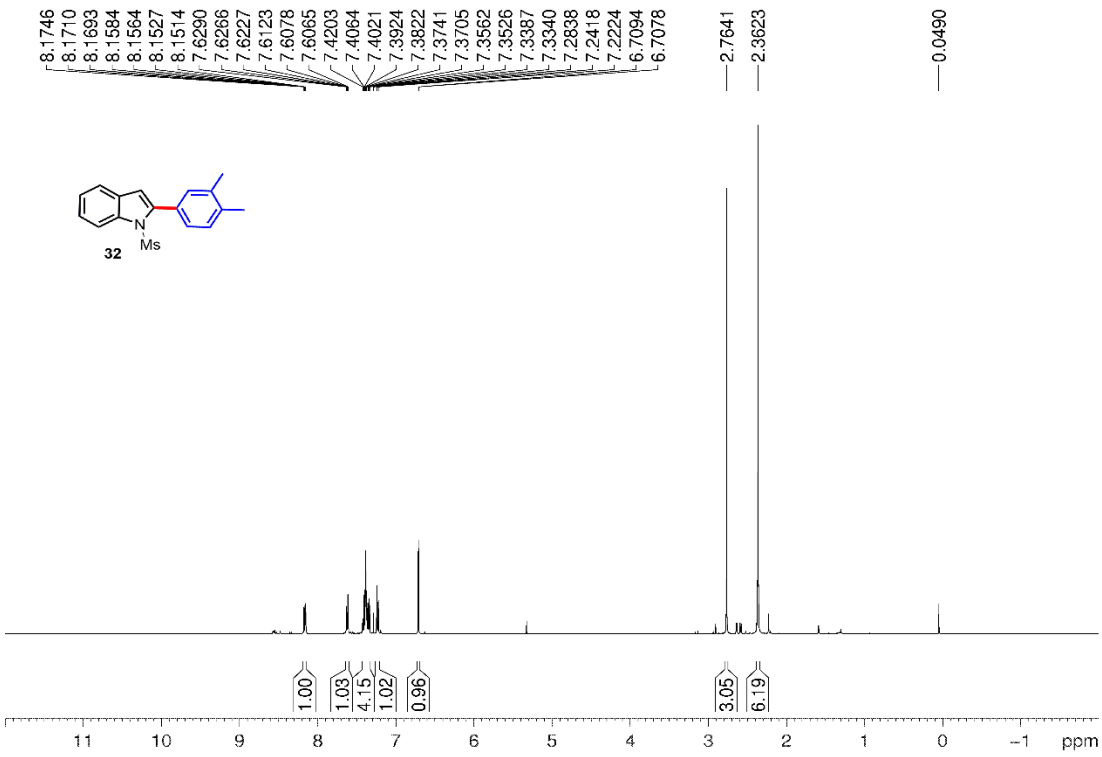
7.4068
7.3863
7.3676
7.2837
7.2022
7.1509
6.6214
N
Ms
31
1.00
1.00
2.08
3.02
1.00
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm
140.64
136.98
136.01
134.50
131.86
130.73
130.10
130.05
129.70
124.79
124.09
120.94
115.03
111.82
77.35
77.03
76.71
40.51
20.94
20.00
N
Ms
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.6065
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7.4021
7.3924
7.3822
7.3741
7.3705
7.3562
7.3526
7.3387
7.3340
7.2838
7.2418
7.2224
6.7094
6.7078
2.7641
2.3623
0.0490
N
Ms
32
1.00
1.03
4.15
1.02
0.96
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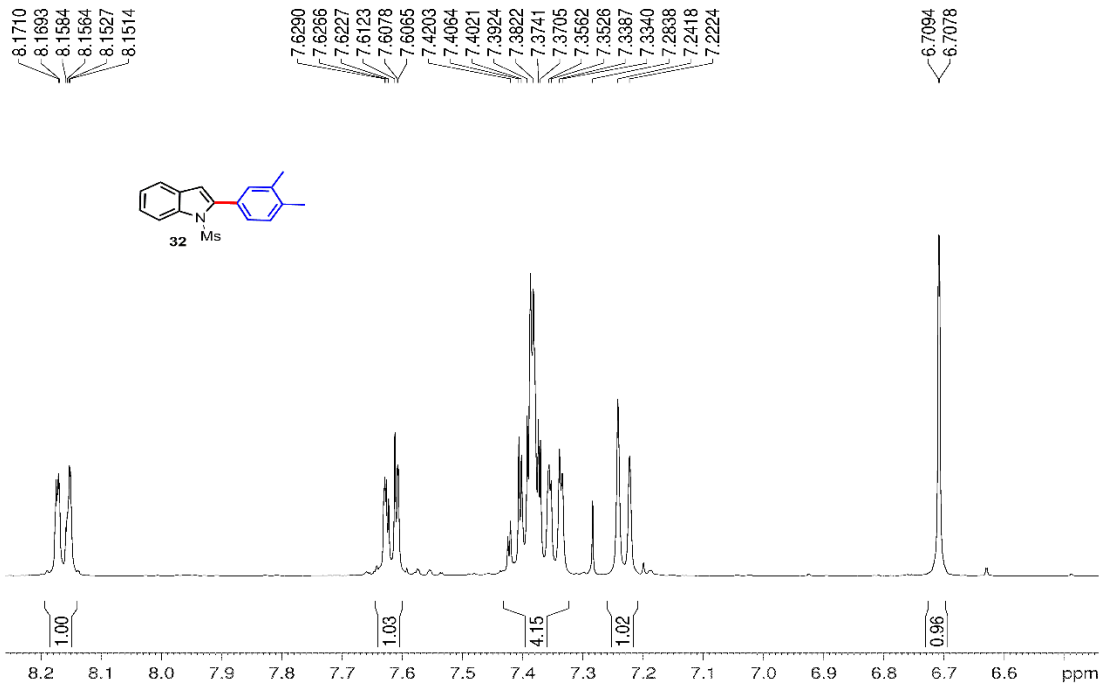
6.19
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm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8.1693
8.1584
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8.1527
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7.6227
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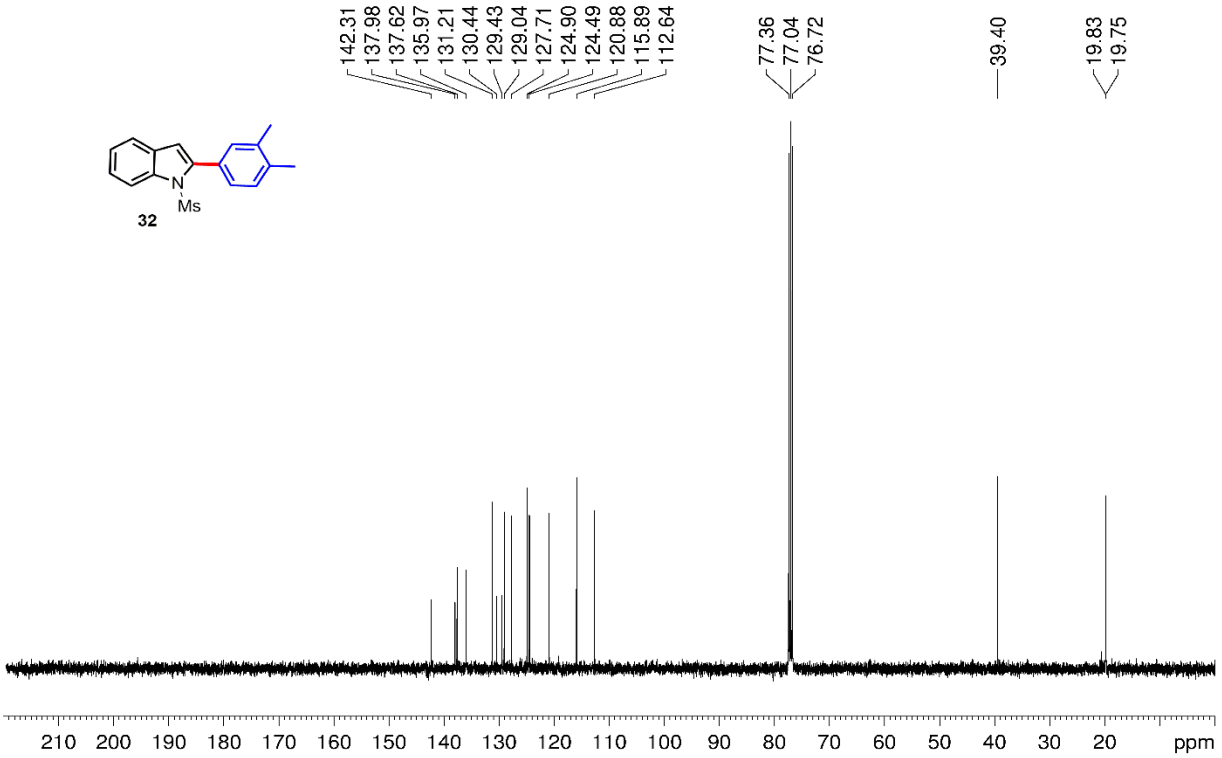
7.6078
7.6065
7.4203
7.4064
7.4021
7.3924
7.3822
7.3741
7.3705
7.3562
7.3526
7.3387
7.3340
7.2838
7.2418
7.2224
6.7094
6.7078
N
Ms
32
1.00
1.03
4.15
1.02
0.96
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm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137.62
135.97
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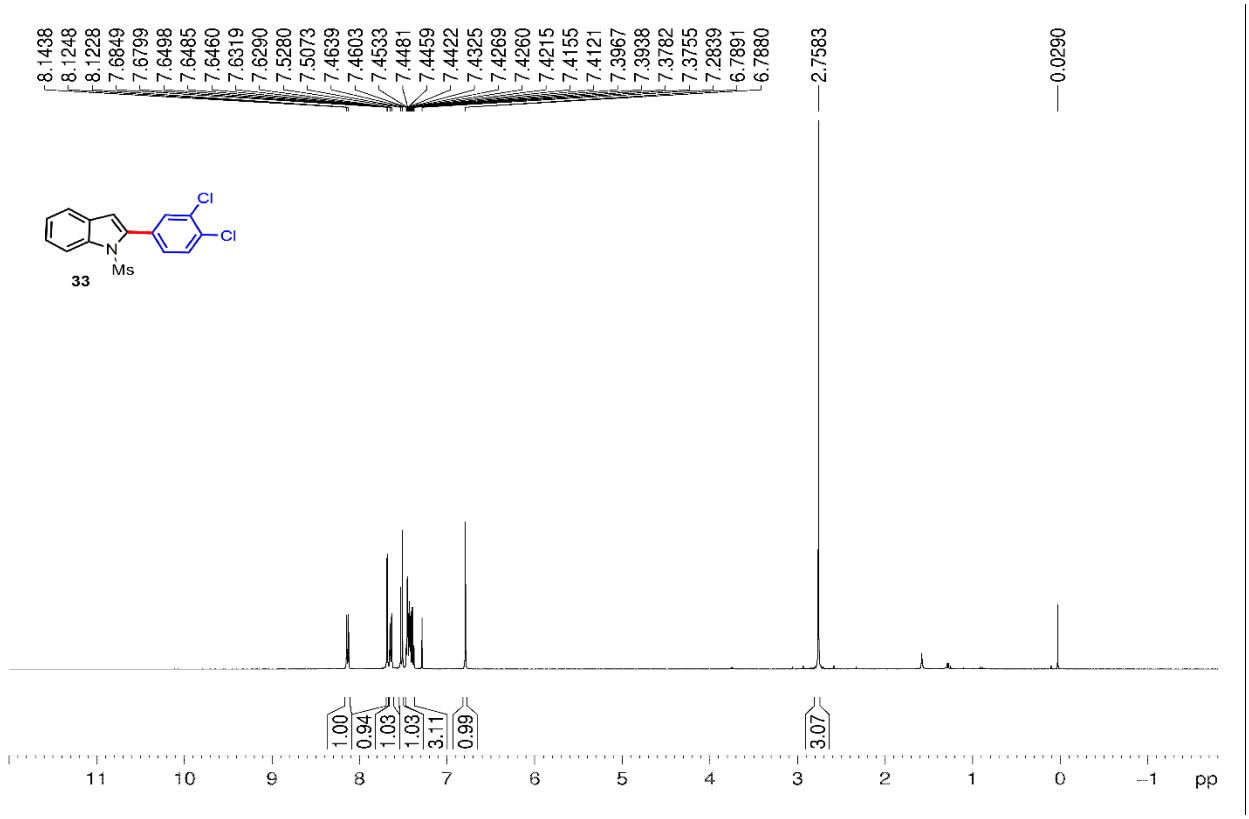
130.44
129.43
129.04
127.71
124.90
124.49
120.88
115.89
112.64
77.36
77.04
76.72
39.40
19.83
19.75
N
Ms
32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.1228
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7.6799
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7.6485
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7.6319
7.6290
7.5280
7.5073
7.4639
7.4603
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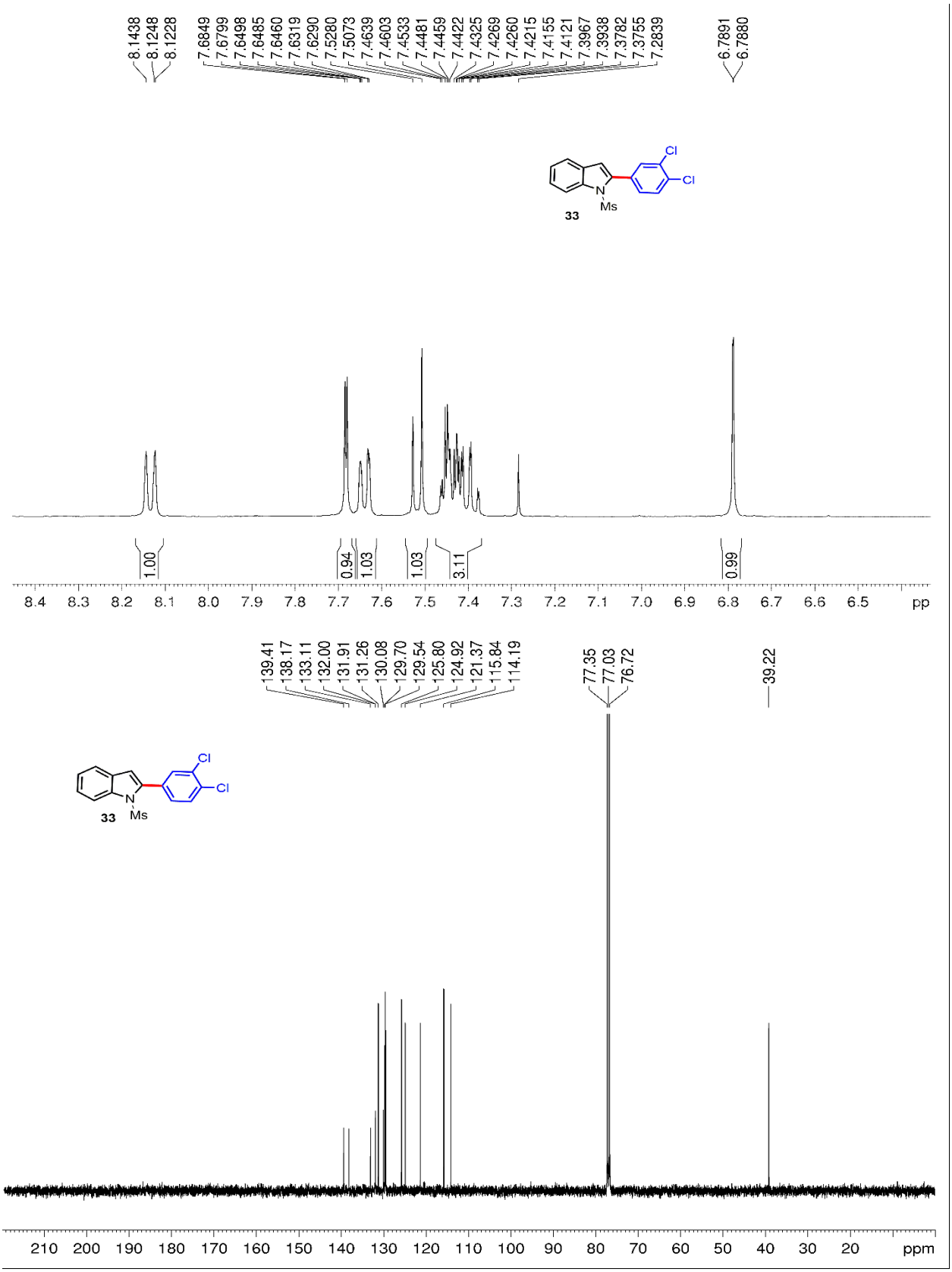
7.4459
7.4422
7.4325
7.4269
7.4260
7.4215
7.4155
7.4121
7.3967
7.3938
7.3782
7.3755
7.2839
6.7891
6.7880
2.7583
0.0290
Cl
Cl
N
Ms
33
1.00
0.94
1.03
1.03
3.11
0.99
3.07
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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7.5073
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7.4459
7.4422
7.4325
7.4269
7.4260
7.4215
7.4155
7.4121
7.3967
7.3938
7.3782
7.3755
7.2839
6.7891
6.7880
Cl
Cl
N
Ms
33
1.00
0.94
1.03
1.03
3.11
0.99
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 pp
139.41
138.17
133.11
132.00
131.91
131.26
130.08
129.70
129.54
125.80
124.92
121.37
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114.19
77.35
77.03
76.72
39.22
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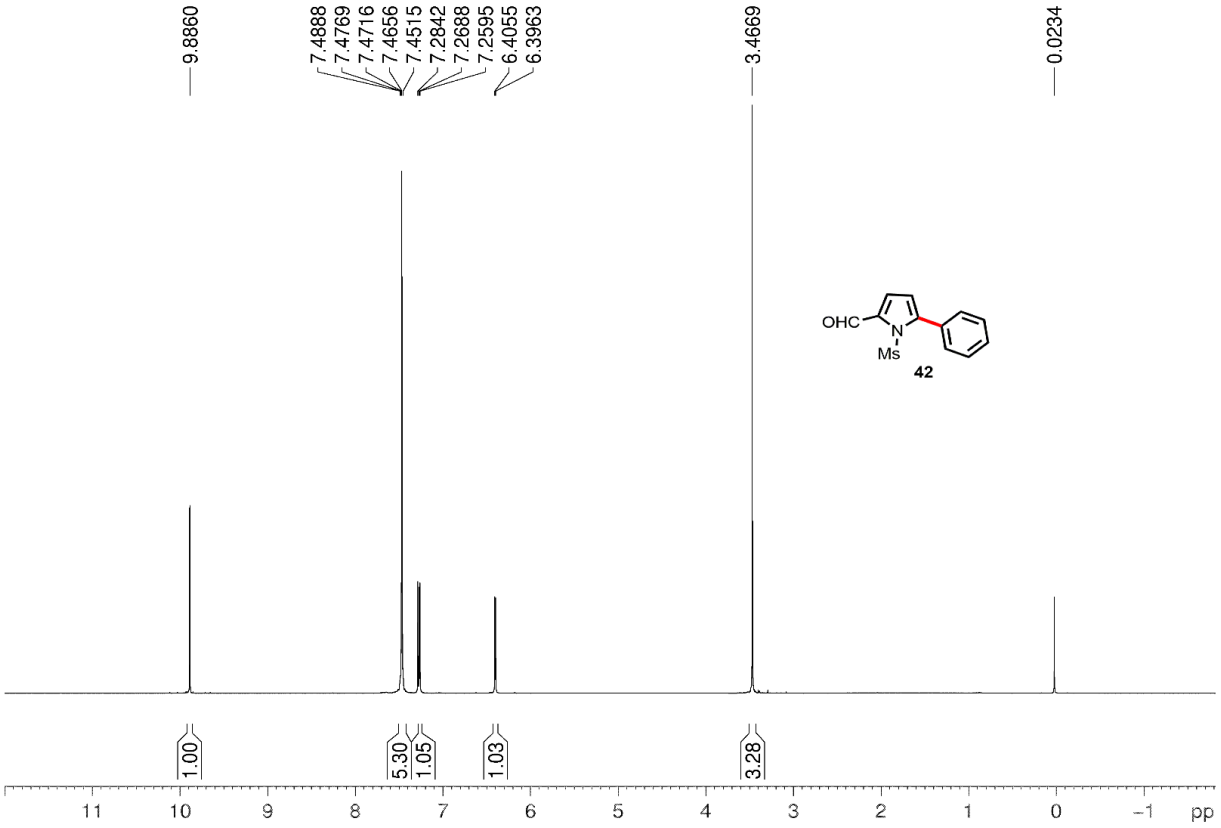
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7.2842
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7.2595
6.4055
6.3963
3.4669
0.0234
OHC
N
Ms
42
1.00
5.30
1.05
1.03
3.28
11
10
9
8
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6
5
4
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2
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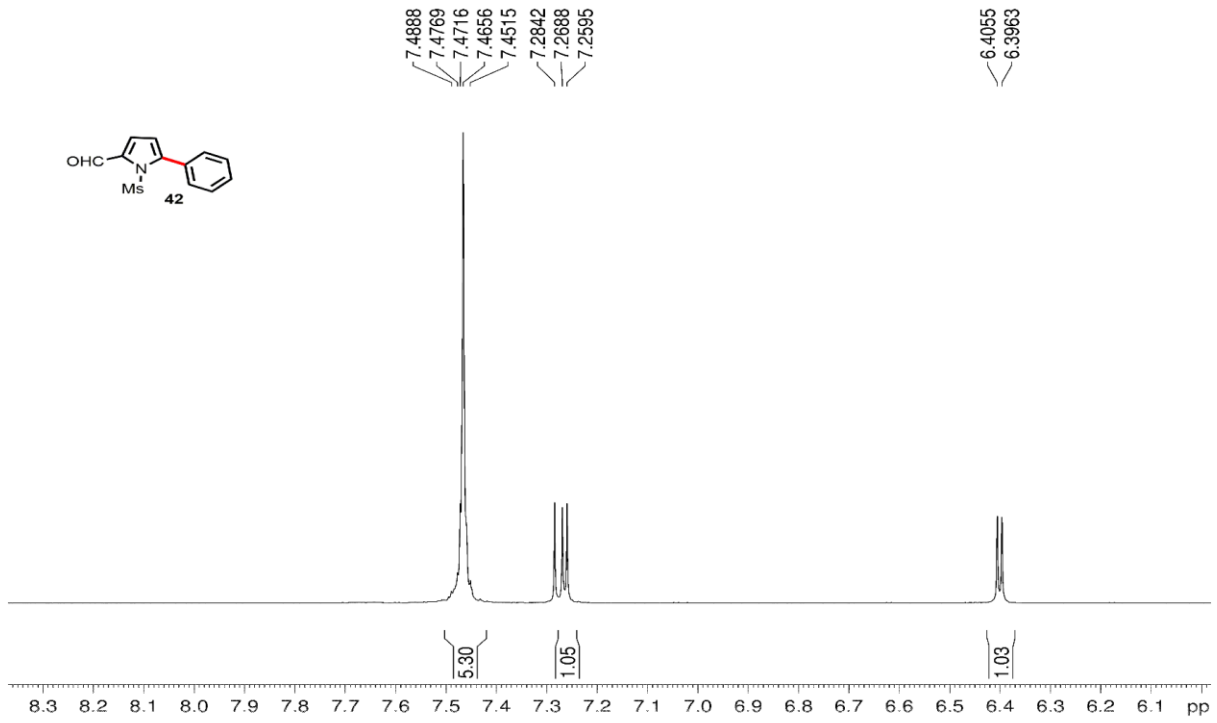
0
−1
pp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6.3963
OHC
N
Ms
42
5.30
1.05
1.03
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
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6.8
6.7
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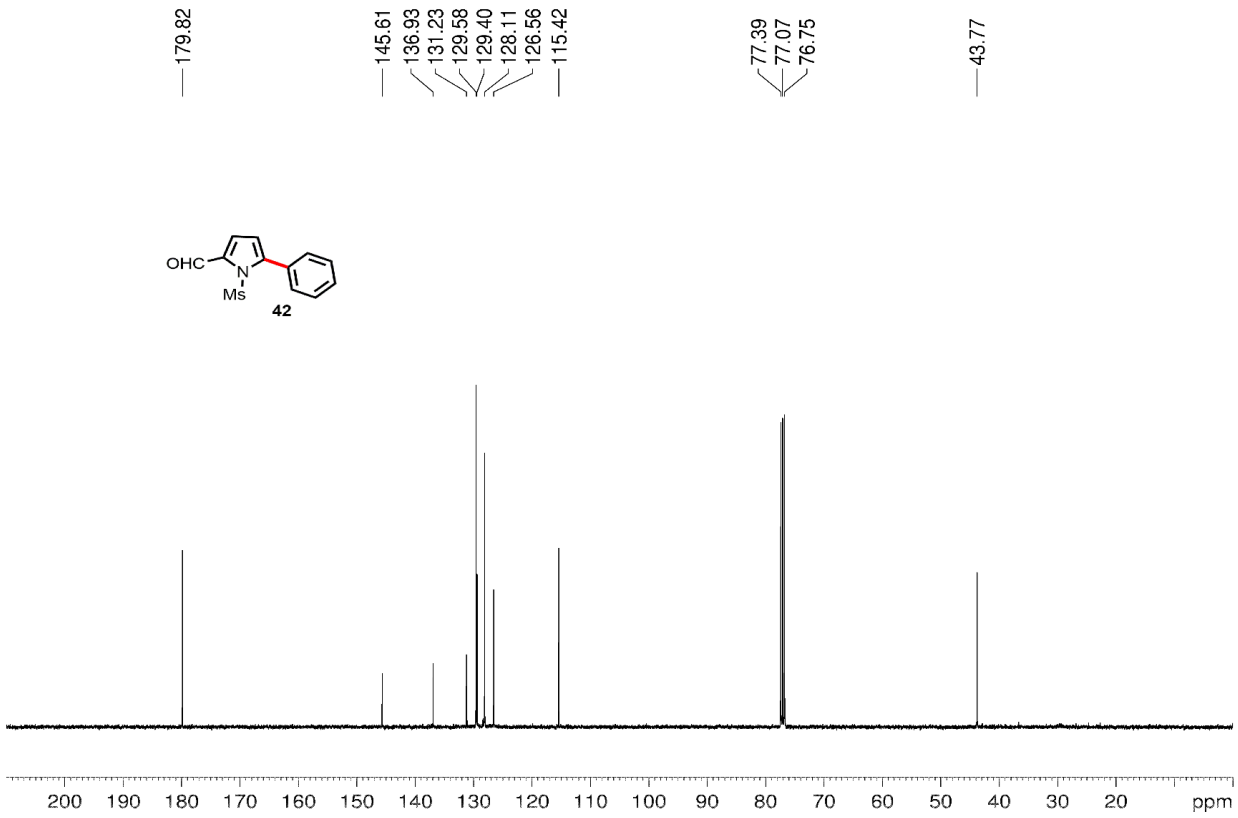
6.4
6.3
6.2
6.1
pp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131.23
129.58
129.40
128.11
126.56
115.42
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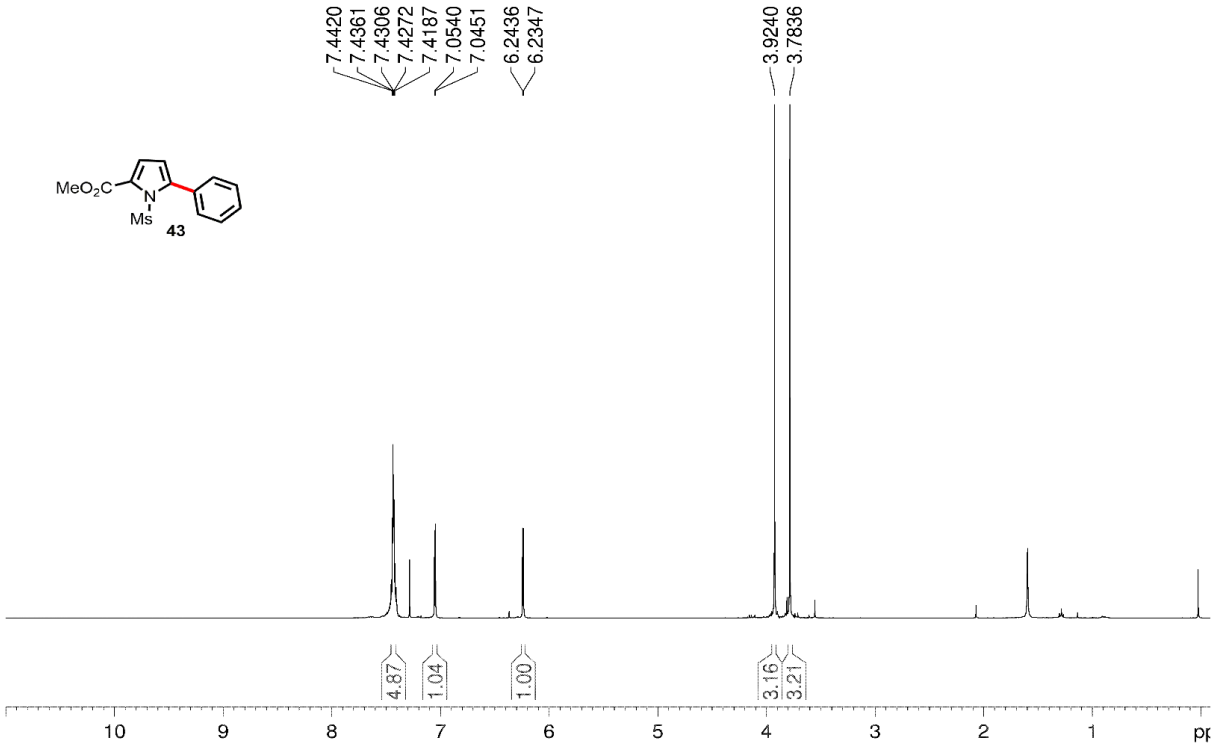
77.07
76.75
43.77
OHC
N
Ms
42
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.4306
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7.4187
7.0540
7.0451
6.2436
6.2347
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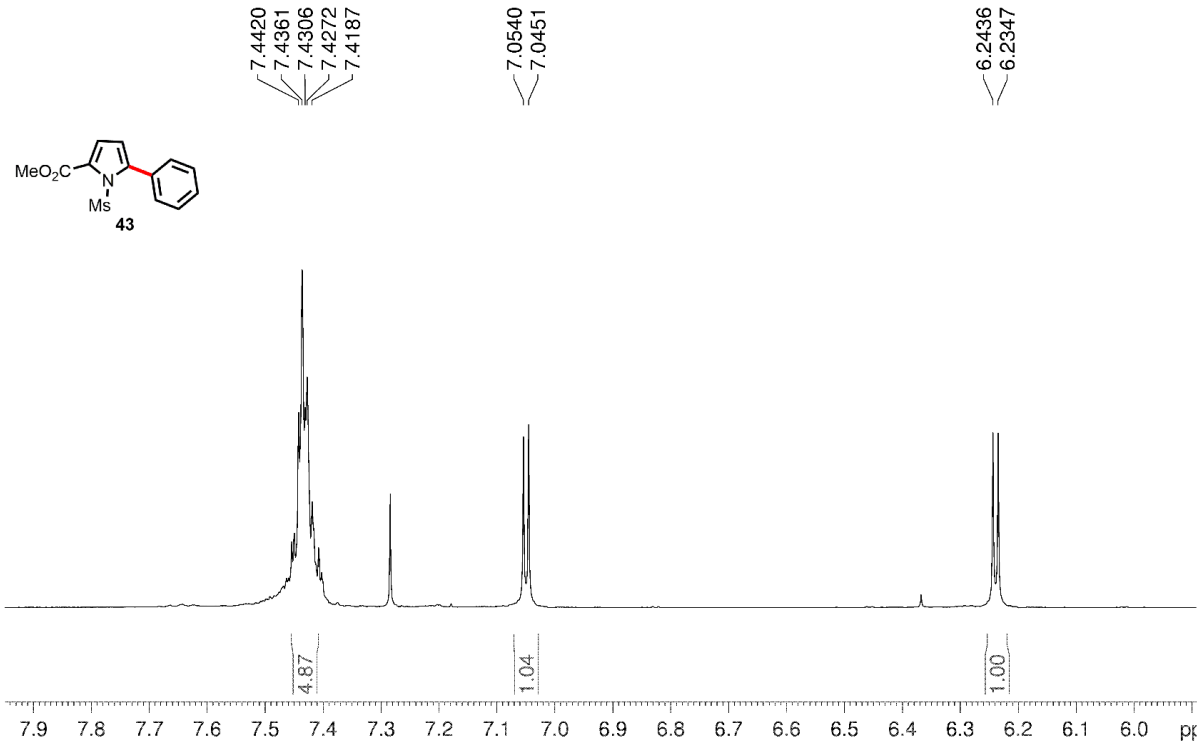
MeO2C
N
Ms
43
4.87
1.04
1.00
3.16
3.21
10 9 8 7 6 5 4 3 2 1 pp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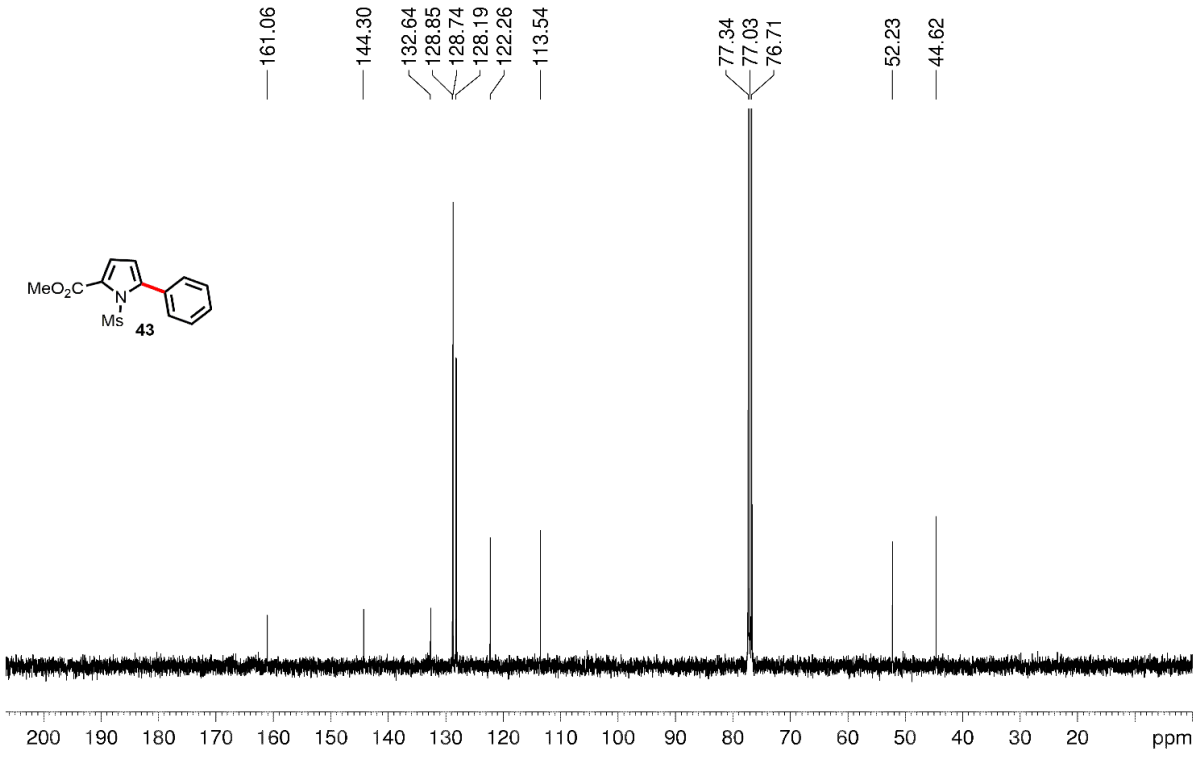
N
Ms
43
4.87
1.04
1.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0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113.54
77.34
77.03
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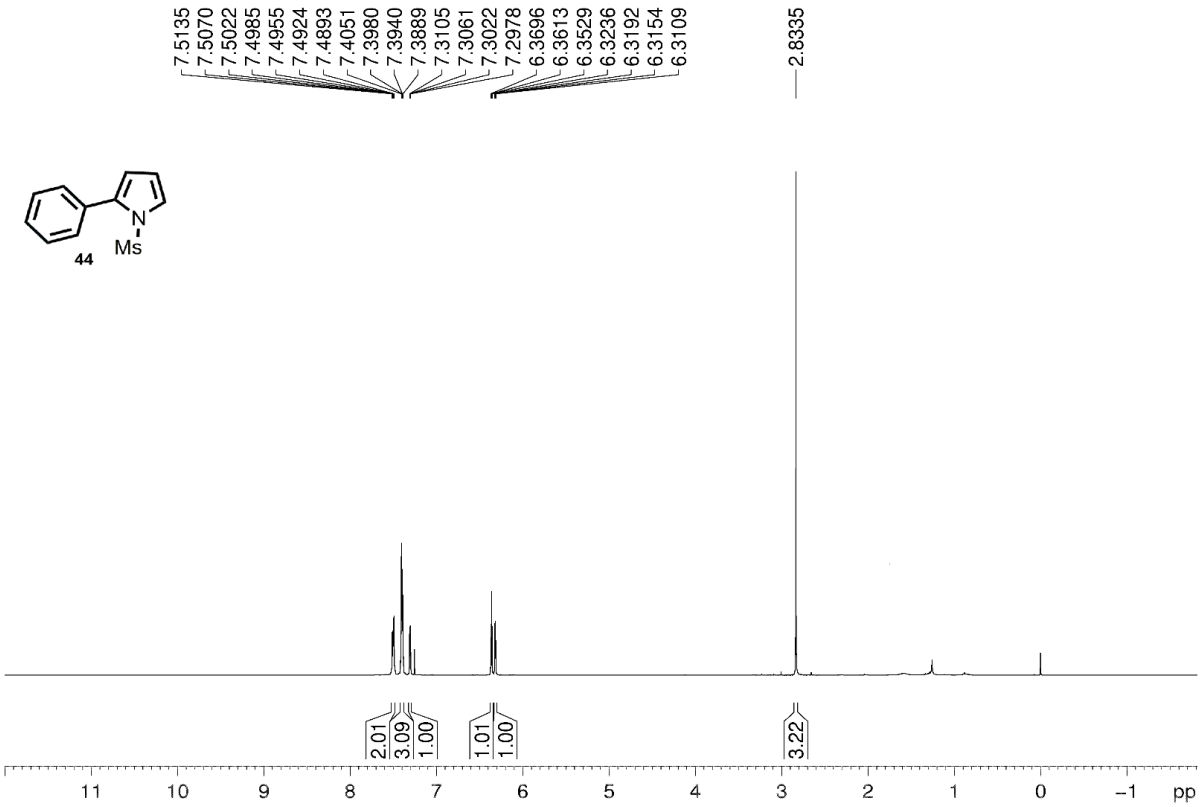
52.23
44.62
MeO2C
N
Ms
43
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm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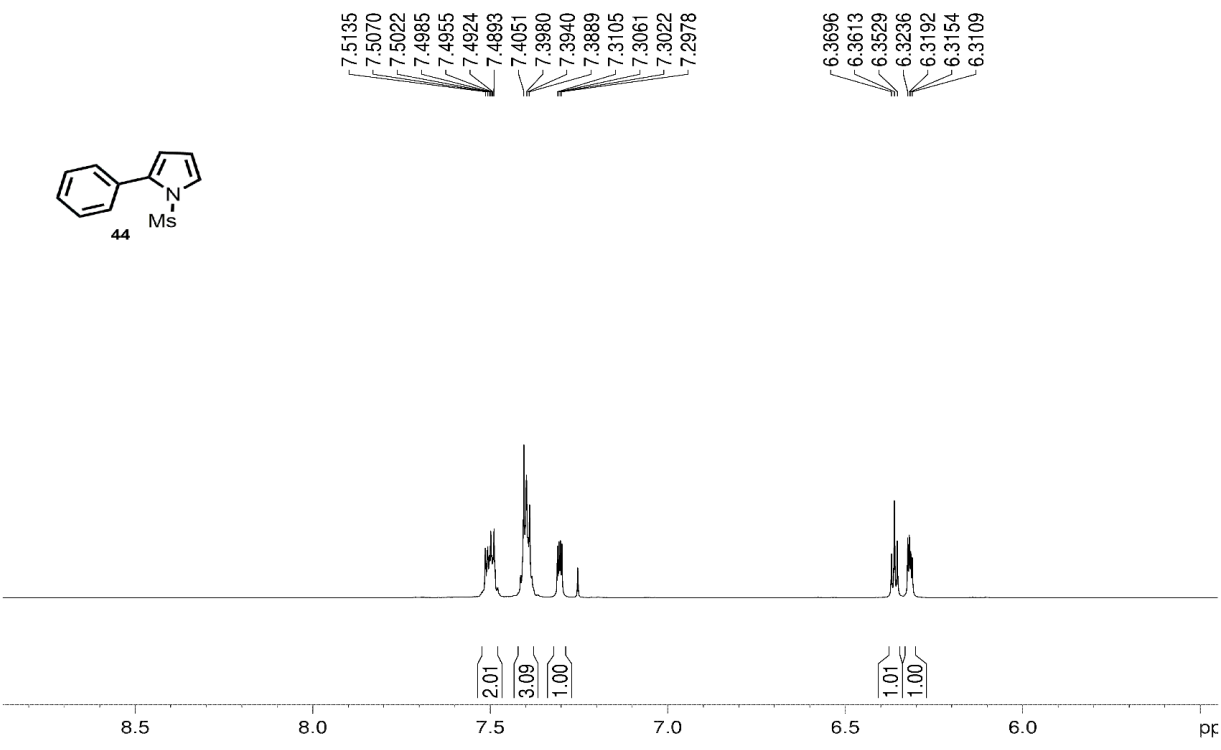
7.5022
7.4985
7.4955
7.4924
7.4893
7.4051
7.3980
7.3940
7.3889
7.3105
7.3061
7.3022
7.2978
6.3696
6.3613
6.3529
6.3236
6.3192
6.3154
6.3109
2.8335
N
Ms
44
2.01
3.09
1.00
1.01
1.00
3.22
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp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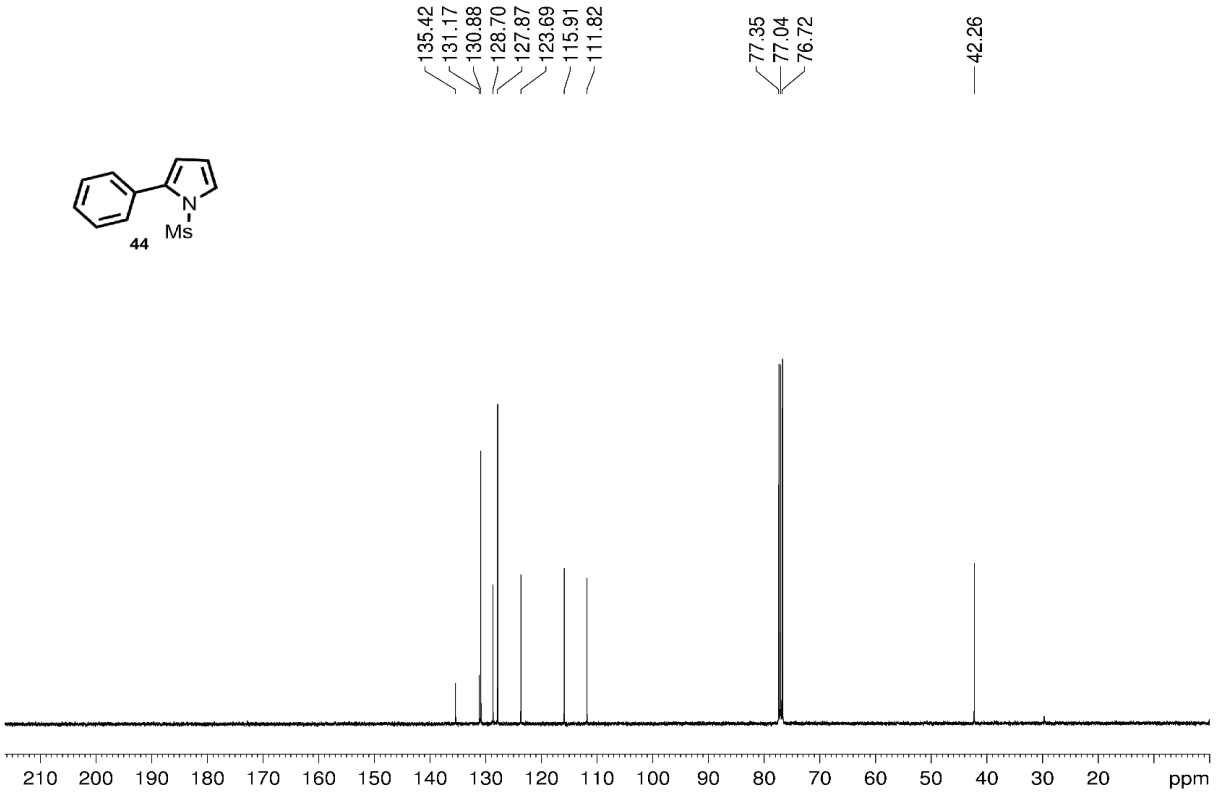
7.3105
7.3061
7.3022
7.2978
6.3696
6.3613
6.3529
6.3236
6.3192
6.3154
6.3109
N
Ms
44
2.01
3.09
1.00
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
pp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127.87
123.69
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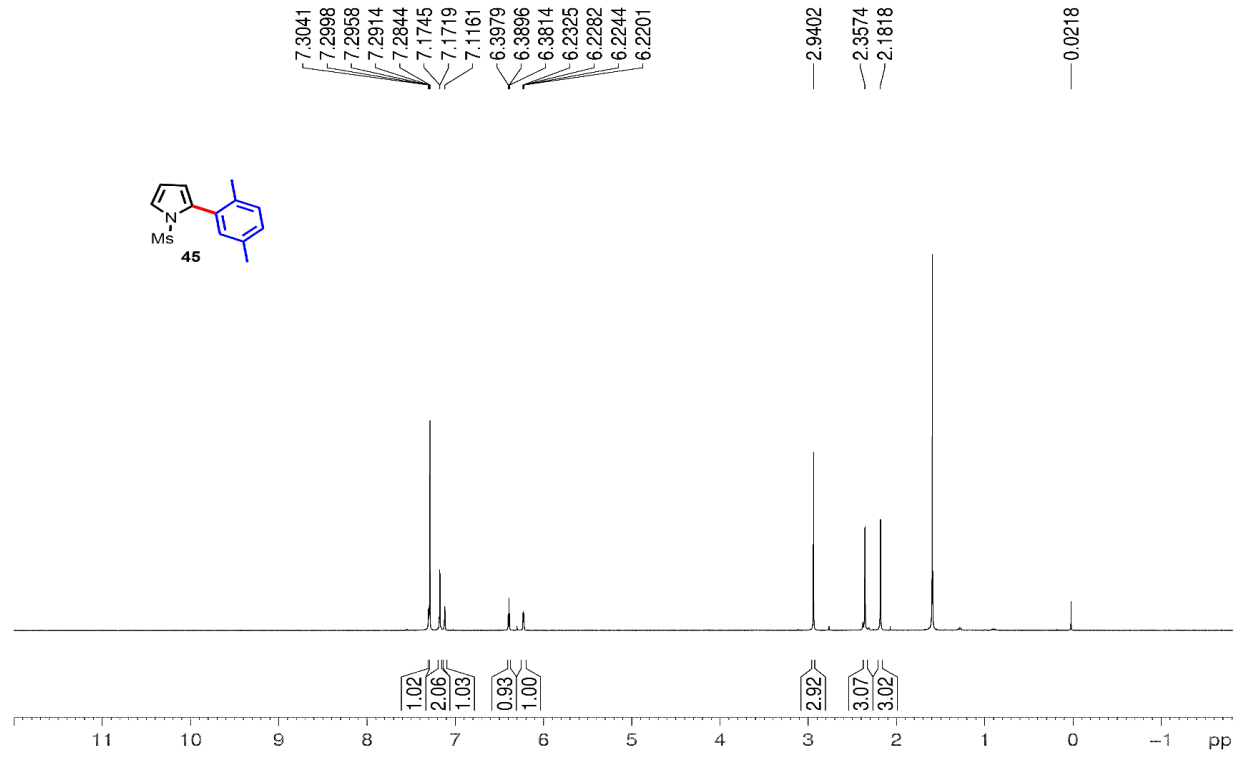
111.82
77.35
77.04
76.72
42.26
N
Ms
44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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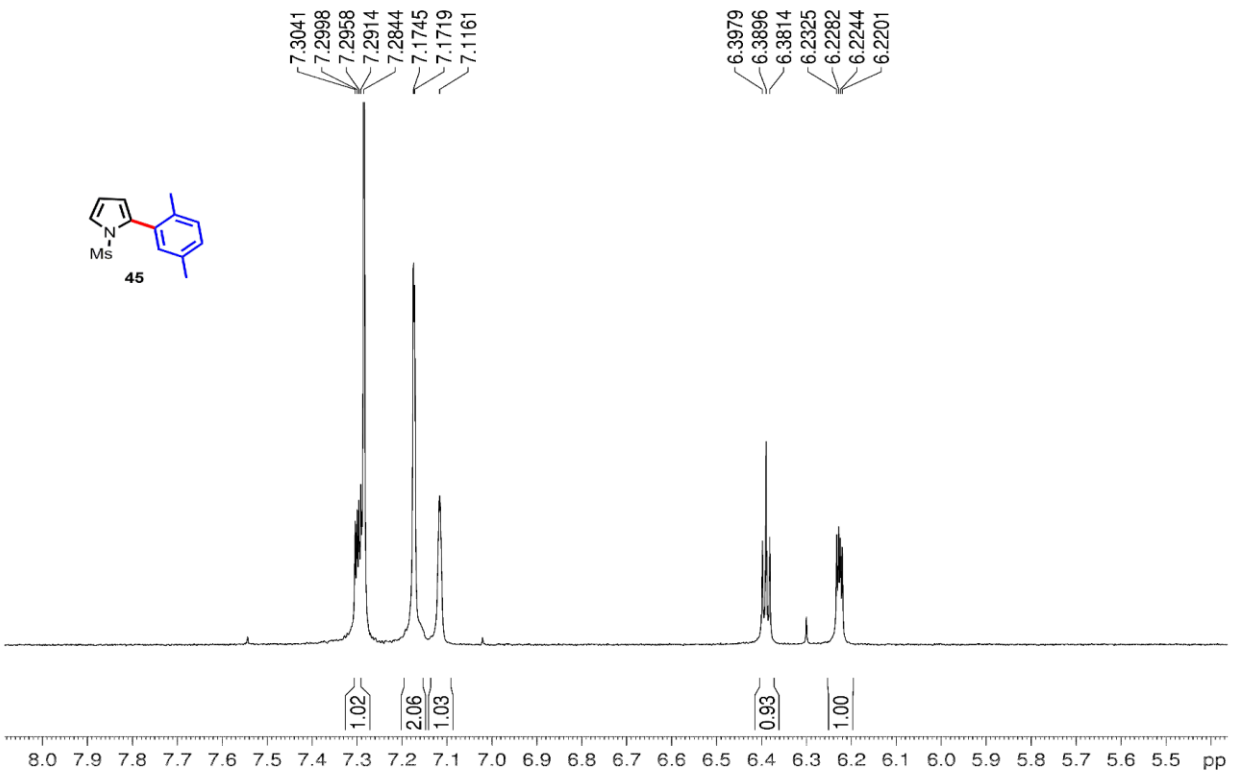
7.2958
7.2914
7.2844
7.1745
7.1719
7.1161
6.3979
6.3896
6.3814
6.2325
6.2282
6.2244
6.2201
2.9402
2.3574
2.1818
0.0218
N
Ms
45
1.02
2.06
1.03
0.93
1.00
2.92
3.07
3.02
11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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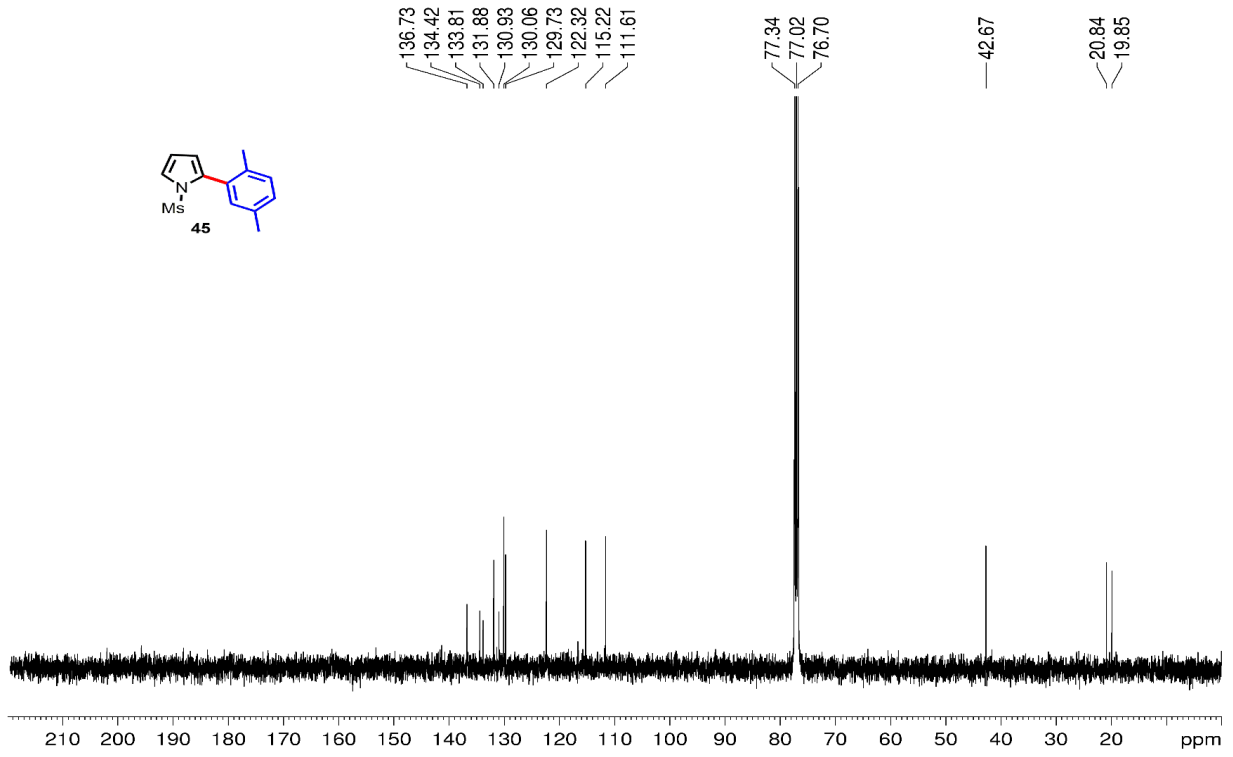
6.3814
6.2325
6.2282
6.2244
6.2201
Ms
45
1.02
2.06
1.03
0.93
1.00
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 pp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130.93
130.06
129.73
122.32
115.22
111.61
77.34
77.02
76.70
42.67
20.84
19.85
Ms
45
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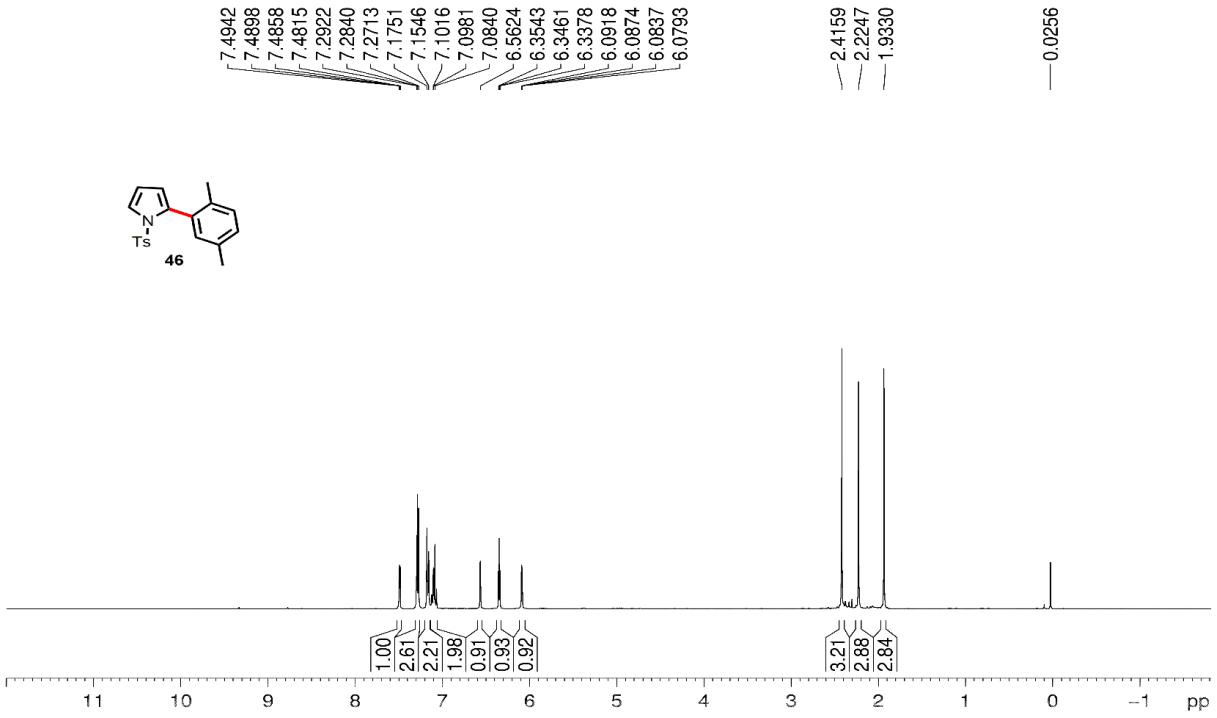
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7.2922
7.2840
7.2713
7.1751
7.1546
7.1016
7.0981
7.0840
6.5624
6.3543
6.3461
6.3378
6.0918
6.0874
6.0837
6.0793
2.4159
2.2247
1.9330
0.0256
Ts
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2.61
2.21
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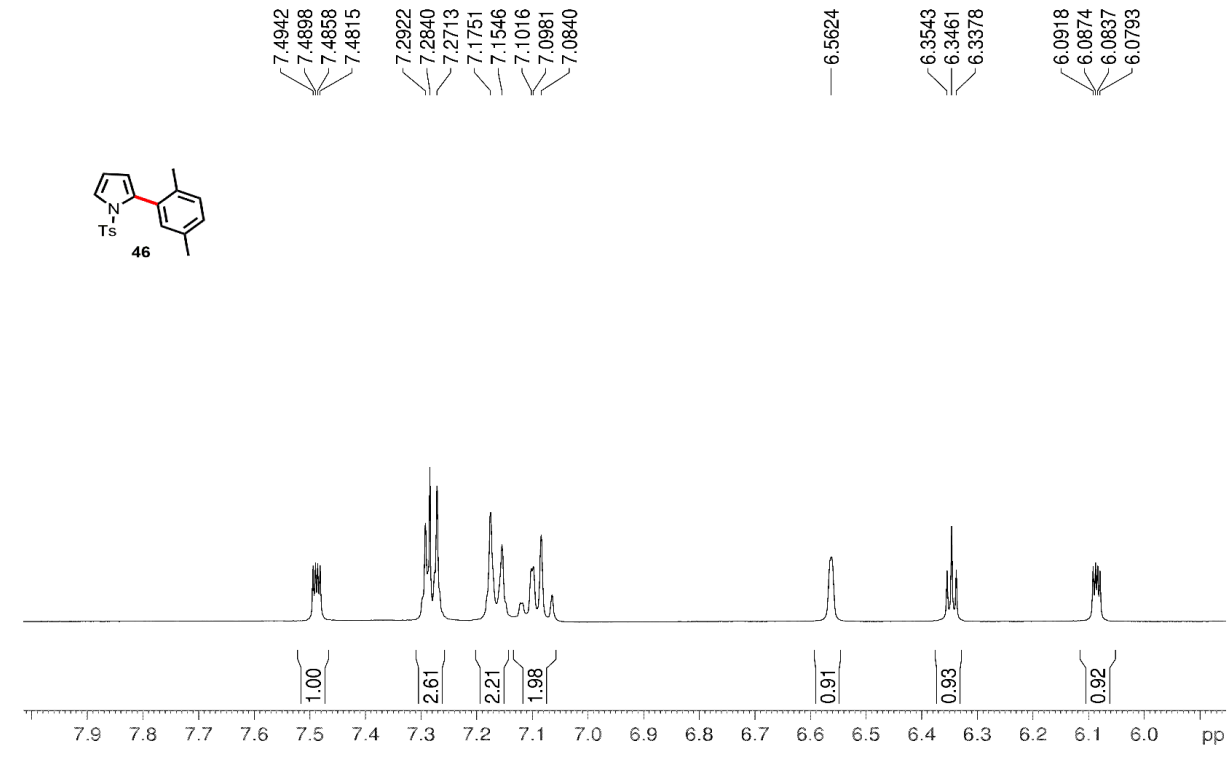
0.91
0.93
0.92
3.21
2.88
2.84
pp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7.2713
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7.1546
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7.0981
7.0840
6.5624
6.3543
6.3461
6.3378
6.0918
6.0874
6.0837
6.0793
Ts
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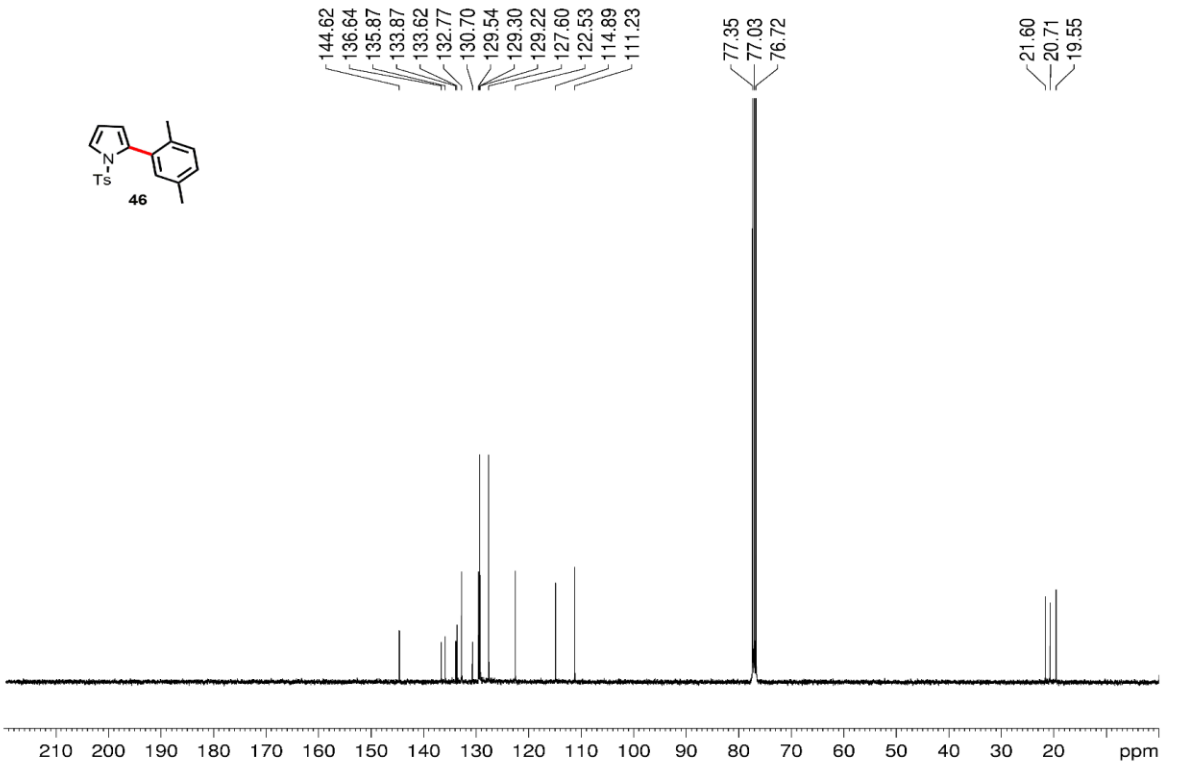
1.00
2.61
2.21
1.98
0.91
0.93
0.92
pp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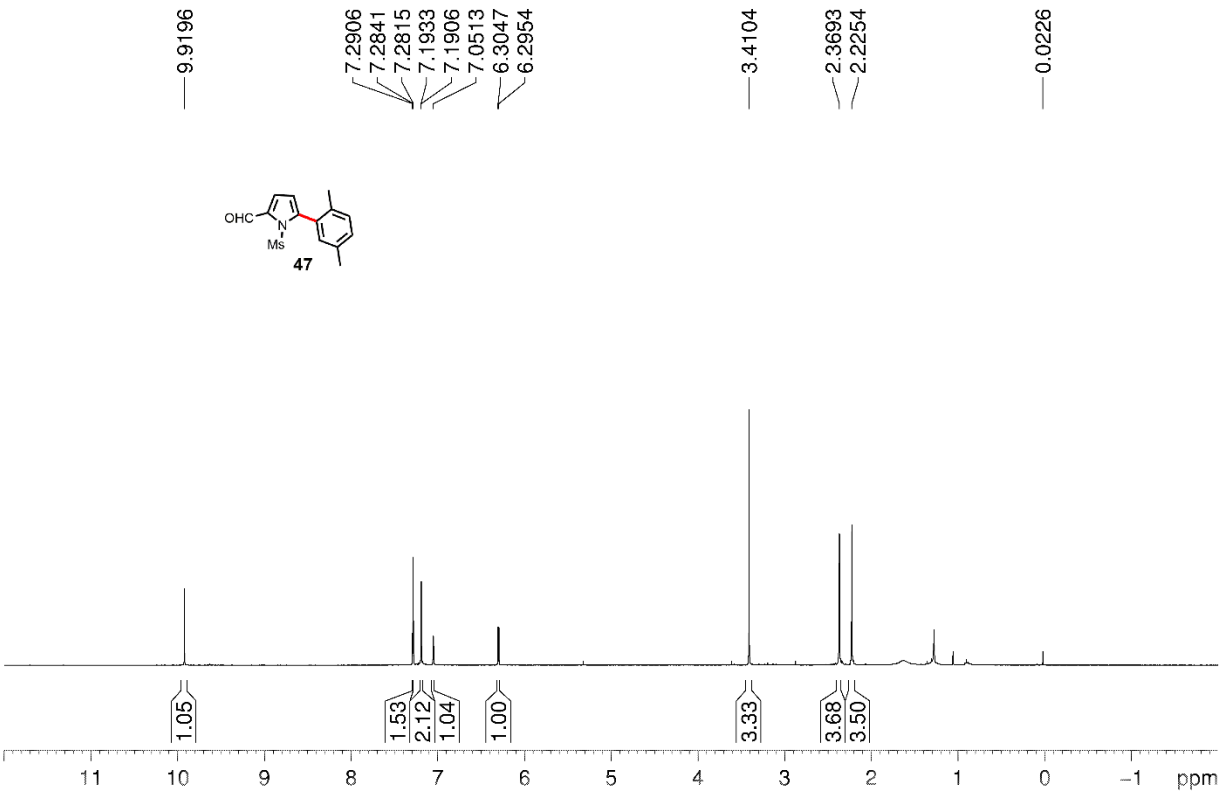
129.54
129.30
129.22
127.60
122.53
114.89
111.23
77.35
77.03
76.72
21.60
20.71
19.55
Ts
46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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2.3693
2.2254
0.0226
OHC
Ms
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1.04
1.00
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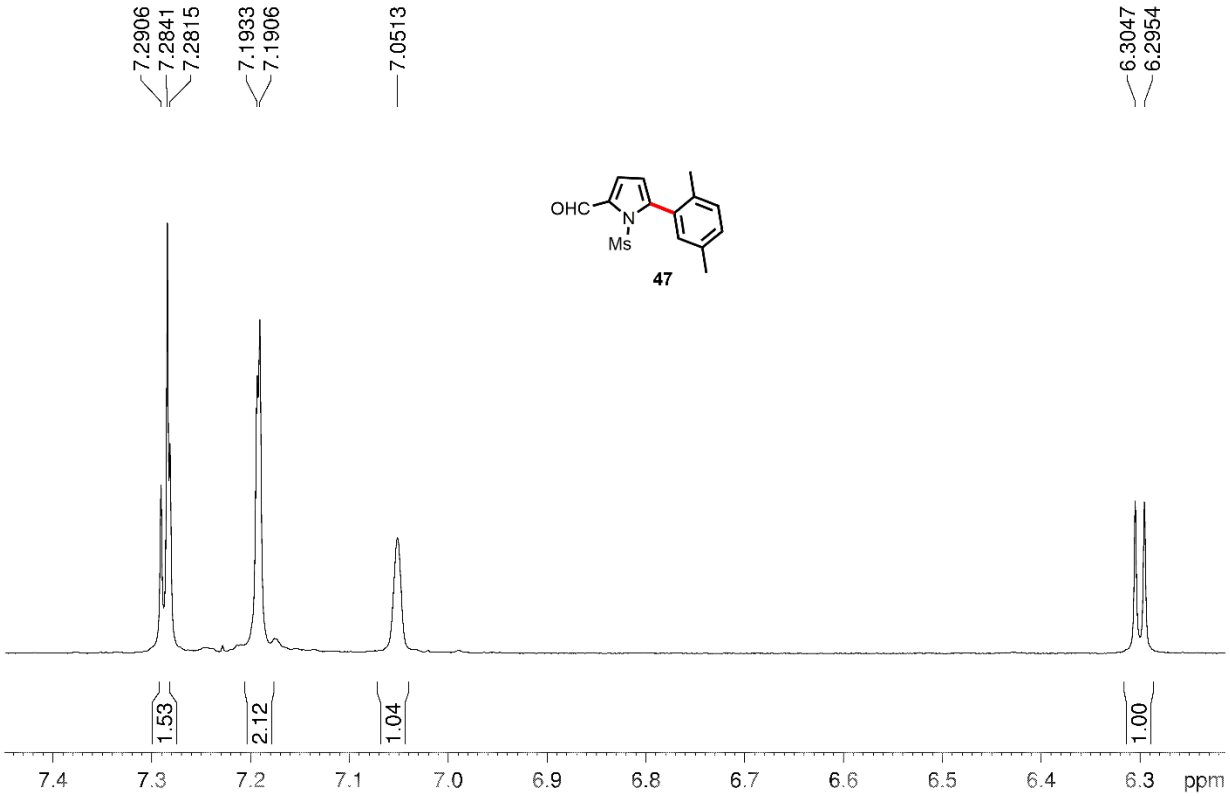
3.50
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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6.2954
OHC
N
Ms
47
1.53
2.12
1.04
1.00
7.4
7.3
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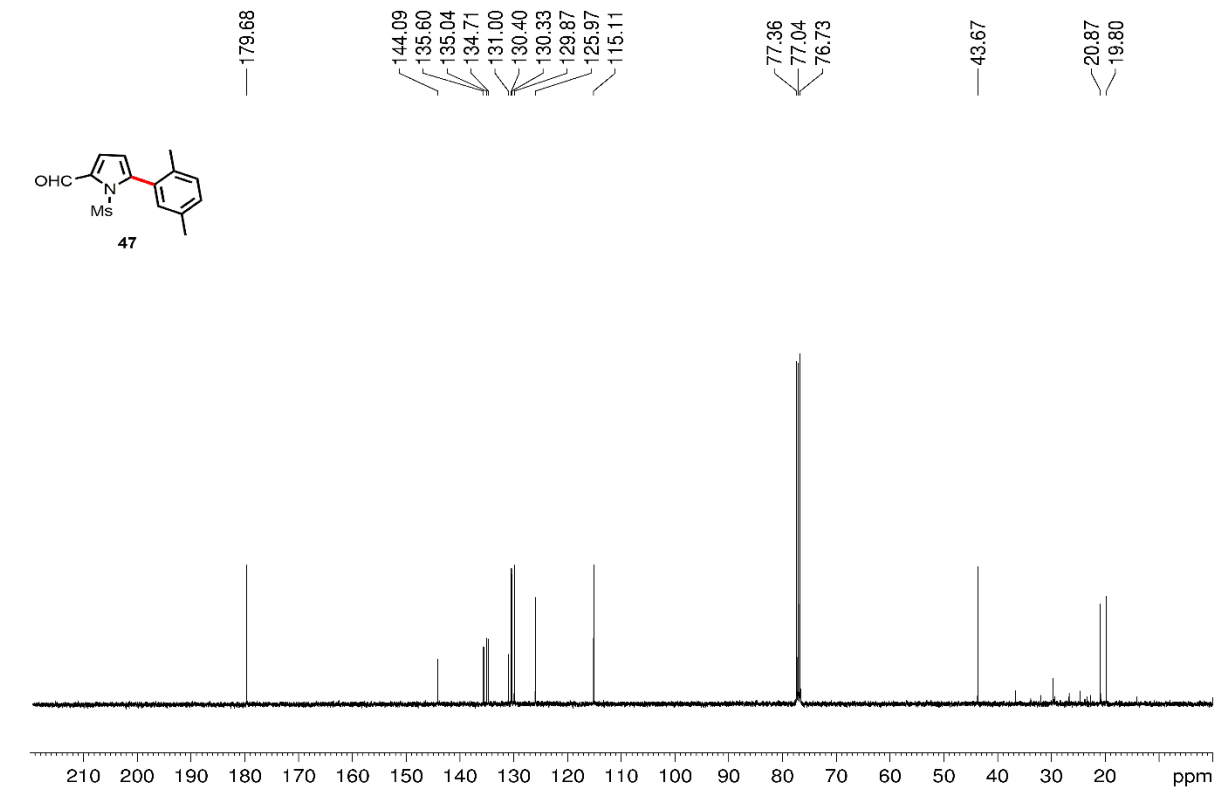
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
ppm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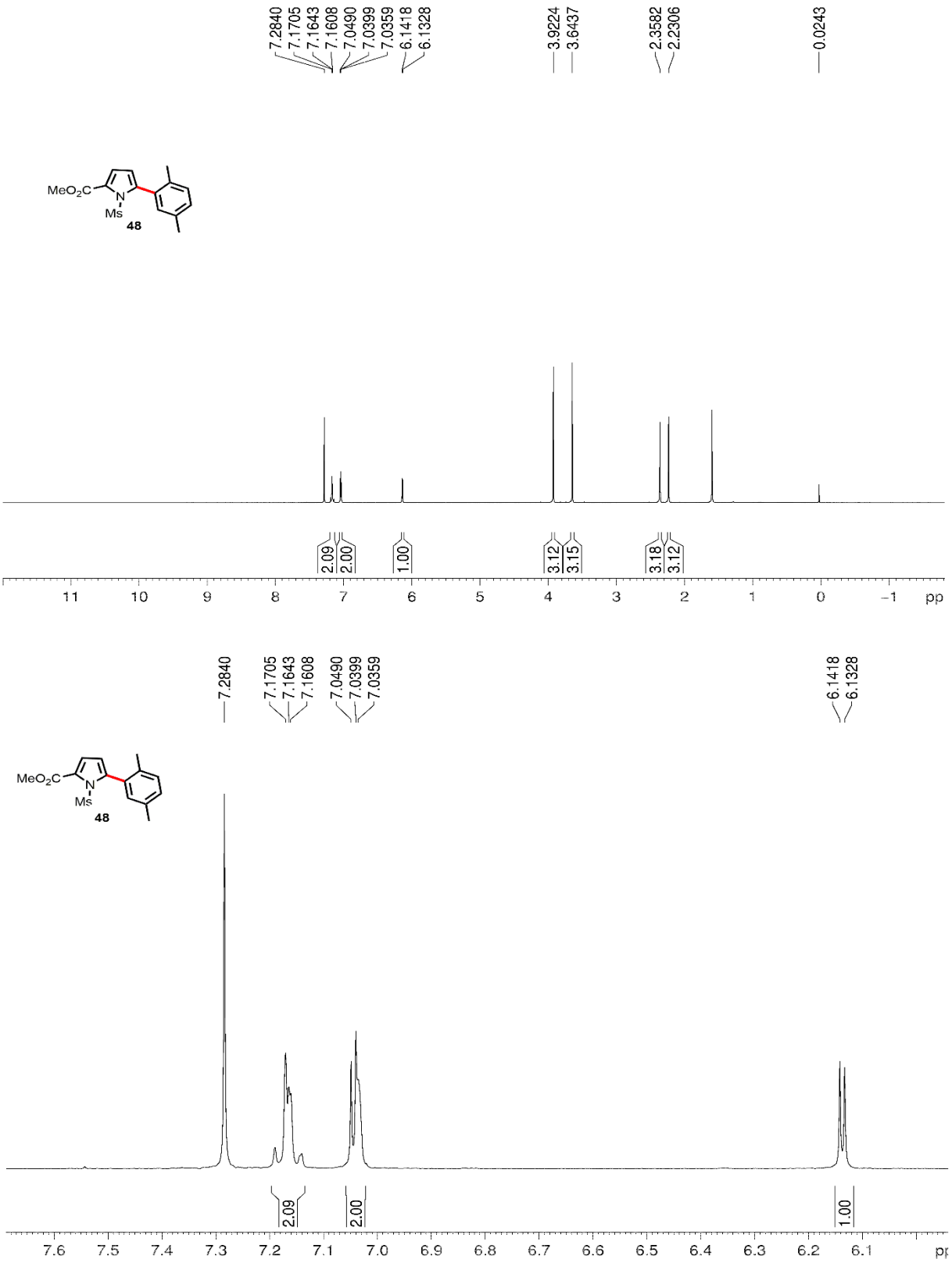
130.33
129.87
125.97
115.11
77.36
77.04
76.73
43.67
20.87
19.80
OHC
N
Ms
47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.1328
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2.3582
2.2306
0.0243
MeO2C
N
Ms
48
2.09
2.00
1.00
3.12
3.15
3.18
3.12
11
10
9
8
7
6
5
4
3
2
1
0
−1
pp
7.2840
7.1705
7.1643
7.1608
7.0490
7.0399
7.0359
6.1418
6.1328
MeO2C
N
Ms
48
2.09
2.00
1.00
7.6
7.5
7.4
7.3
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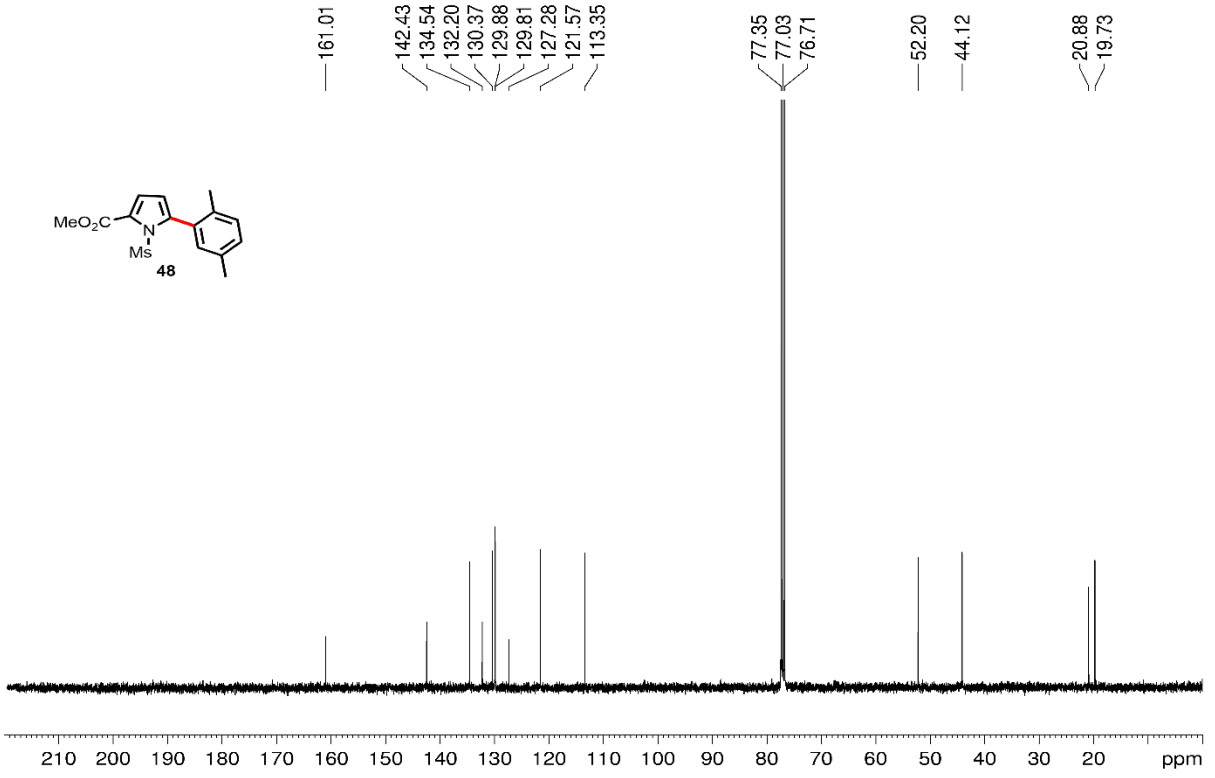
6.1
pp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77.03
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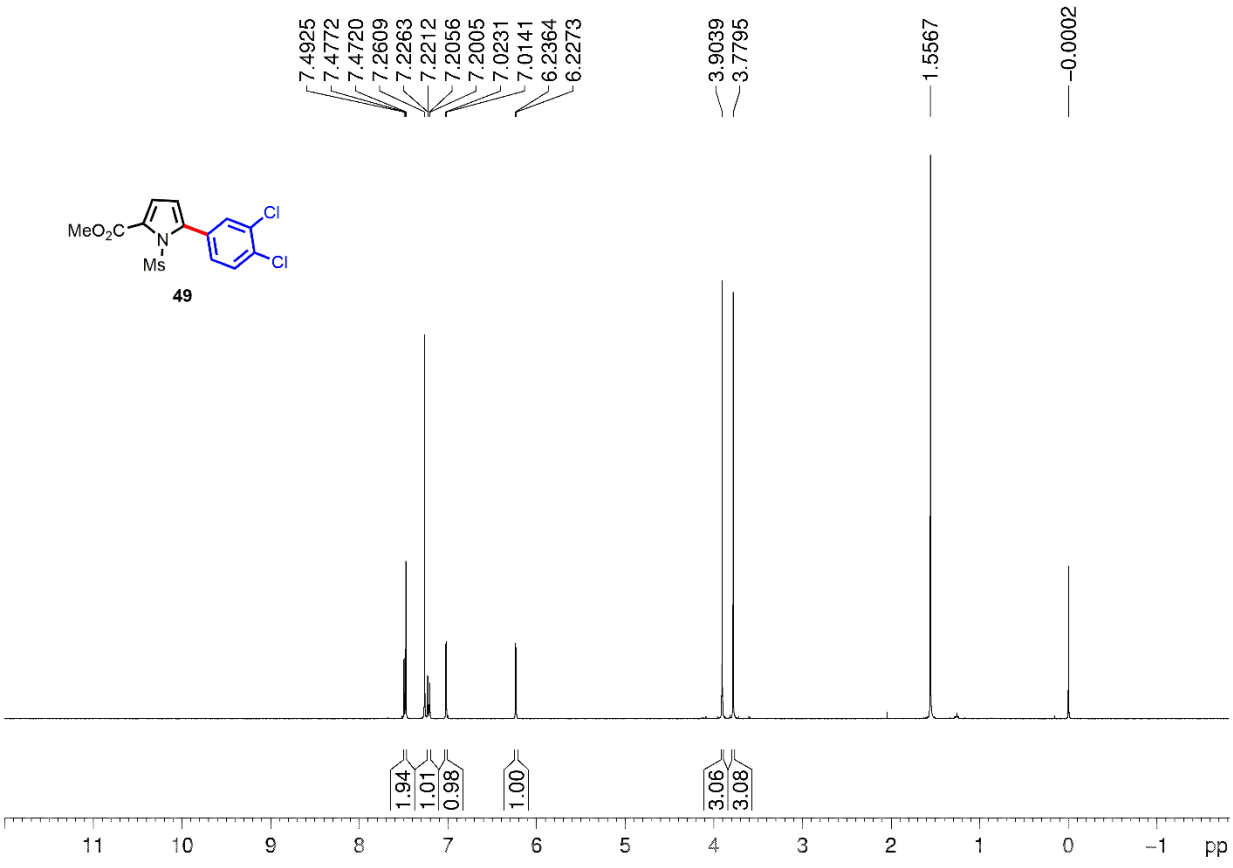
20.88
19.73
MeO2C
N
Ms
48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.0141
6.2364
6.2273
3.9039
3.7795
1.5567
-0.0002
MeO2C
N
Ms
Cl
Cl
49
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1.01
0.98
1.00
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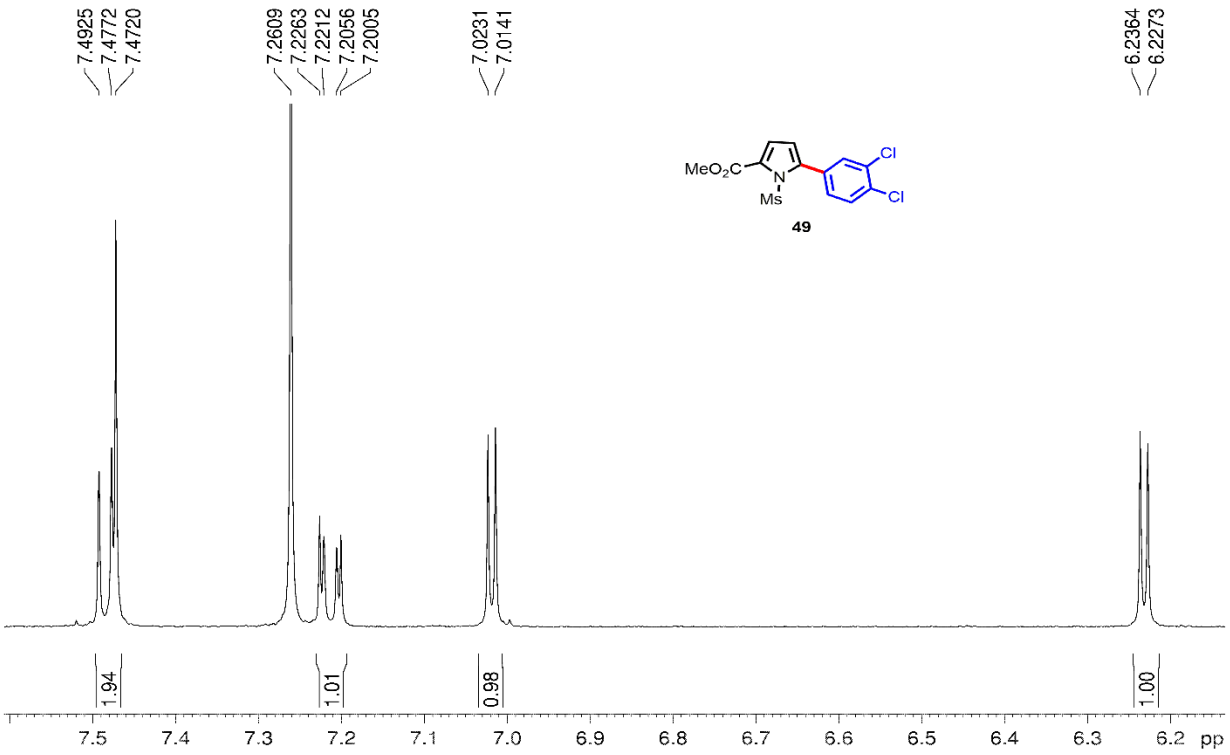
3.08
11 10 9 8 7 6 5 4 3 2 1 0 -1 pp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6.2364
6.2273
MeO2C
N
Ms
Cl
Cl
49
1.94
1.01
0.98
1.00
7.5
7.4
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6.5
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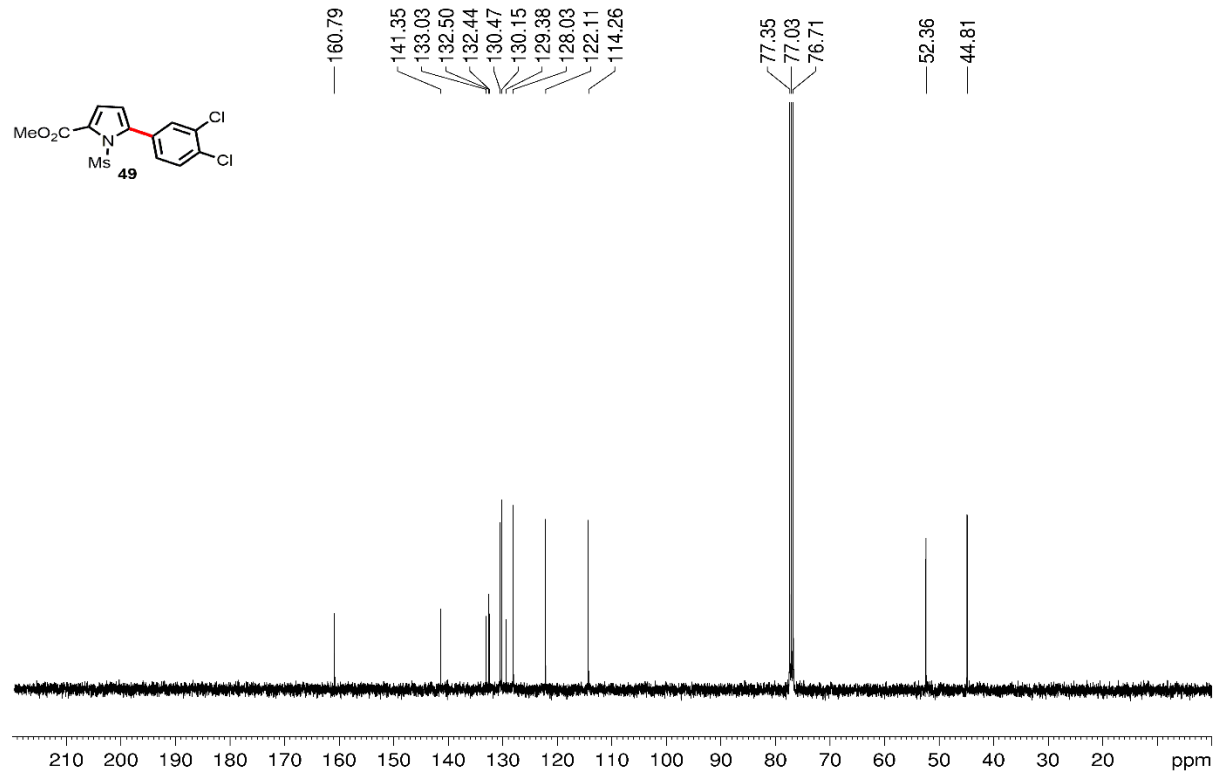
6.3
6.2
pp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129.38
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122.11
114.26
77.35
77.03
76.71
52.36
44.81
MeO2C
N
Ms
Cl
Cl
49
210
200
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180
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160
150
140
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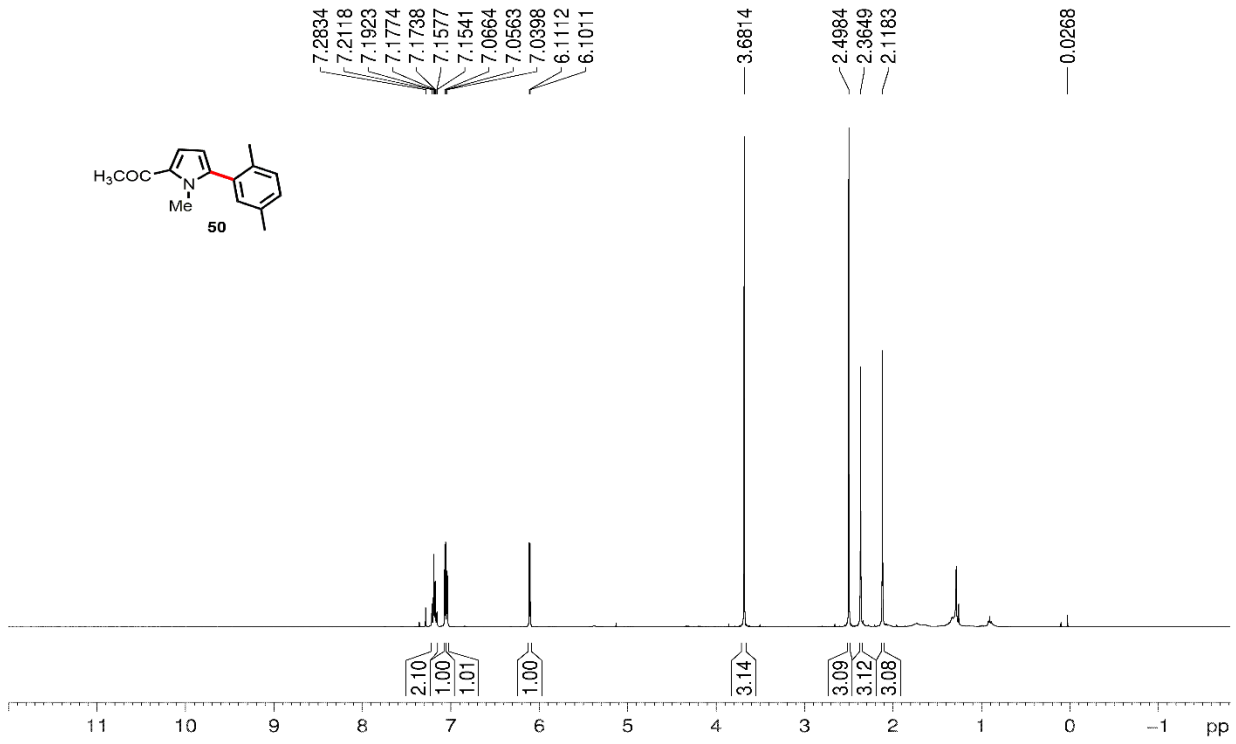
120
110
100
90
80
70
60
50
40
30
20
ppm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6.1011
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2.1183
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Me
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1.00
1.01
1.00
3.14
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3.08
11
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4
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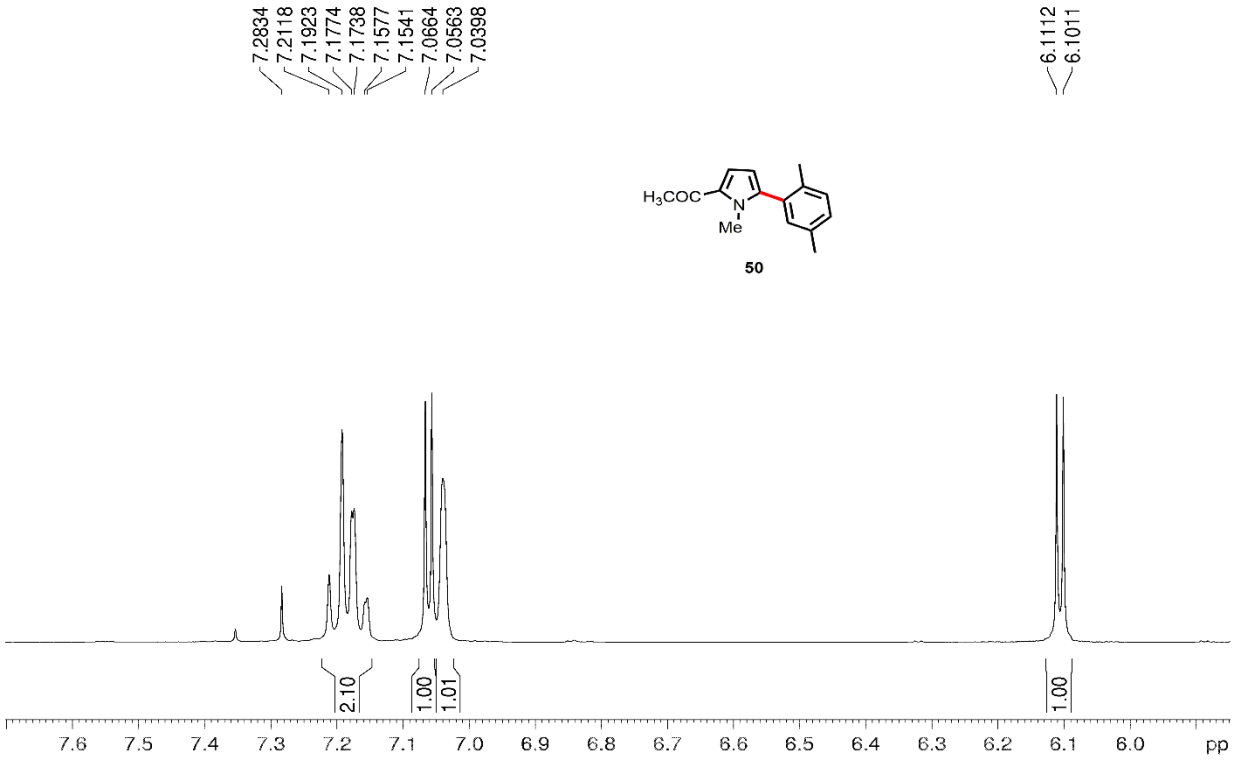
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6.1011
H3COC
N
Me
50
2.10
1.00
1.01
1.00
7.6
7.5
7.4
7.3
7.2
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6.7
6.6
6.5
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6.3
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6.1
6.0
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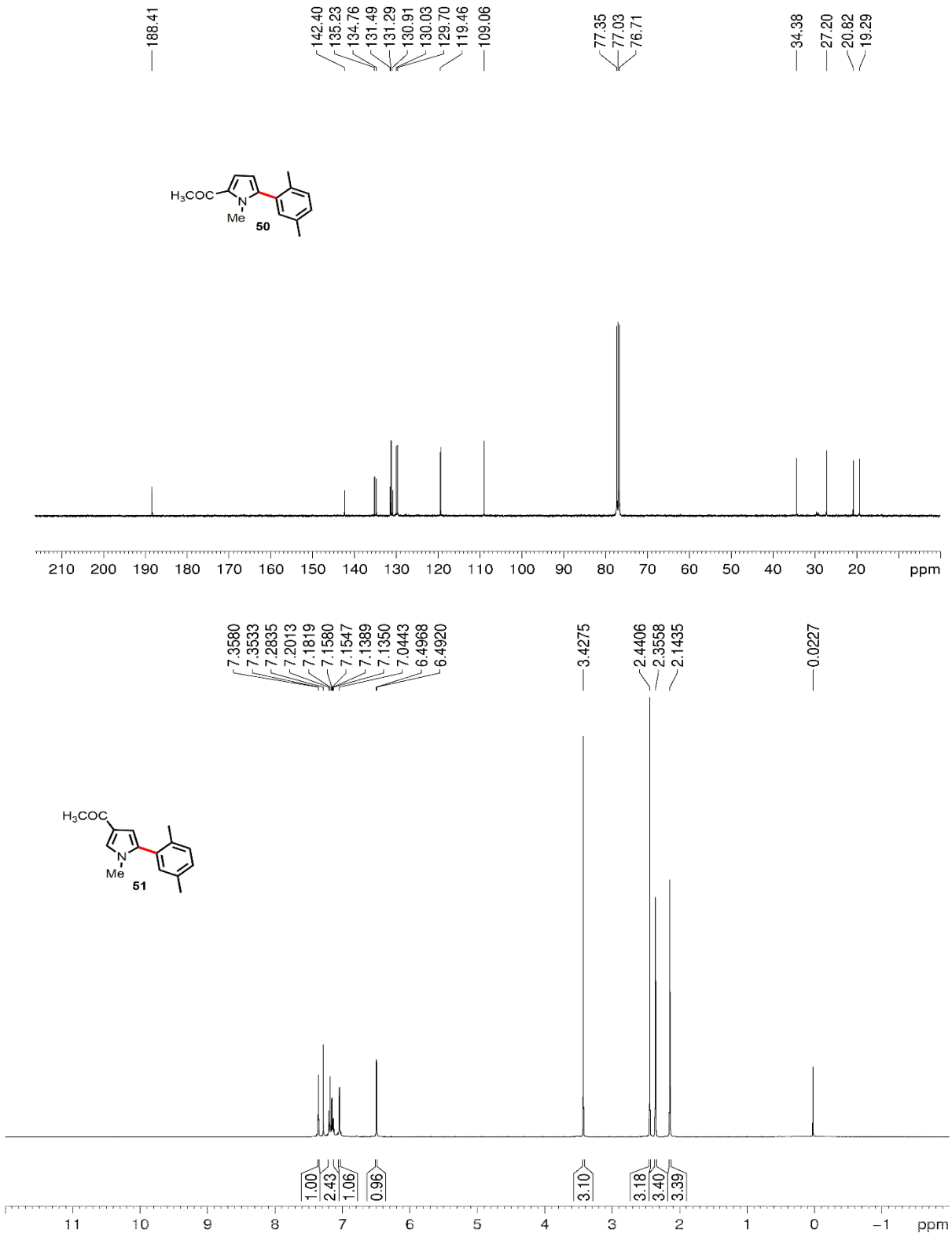
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129.70
119.46
109.06
77.35
77.03
76.71
34.38
27.20
20.82
19.29
H3COC
N
Me
50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
7.3580
7.3533
7.2835
7.2013
7.1819
7.1580
7.1547
7.1389
7.1350
7.0443
6.4968
6.4920
3.4275
2.4406
2.3558
2.1435
0.0227
H3COC
N
Me
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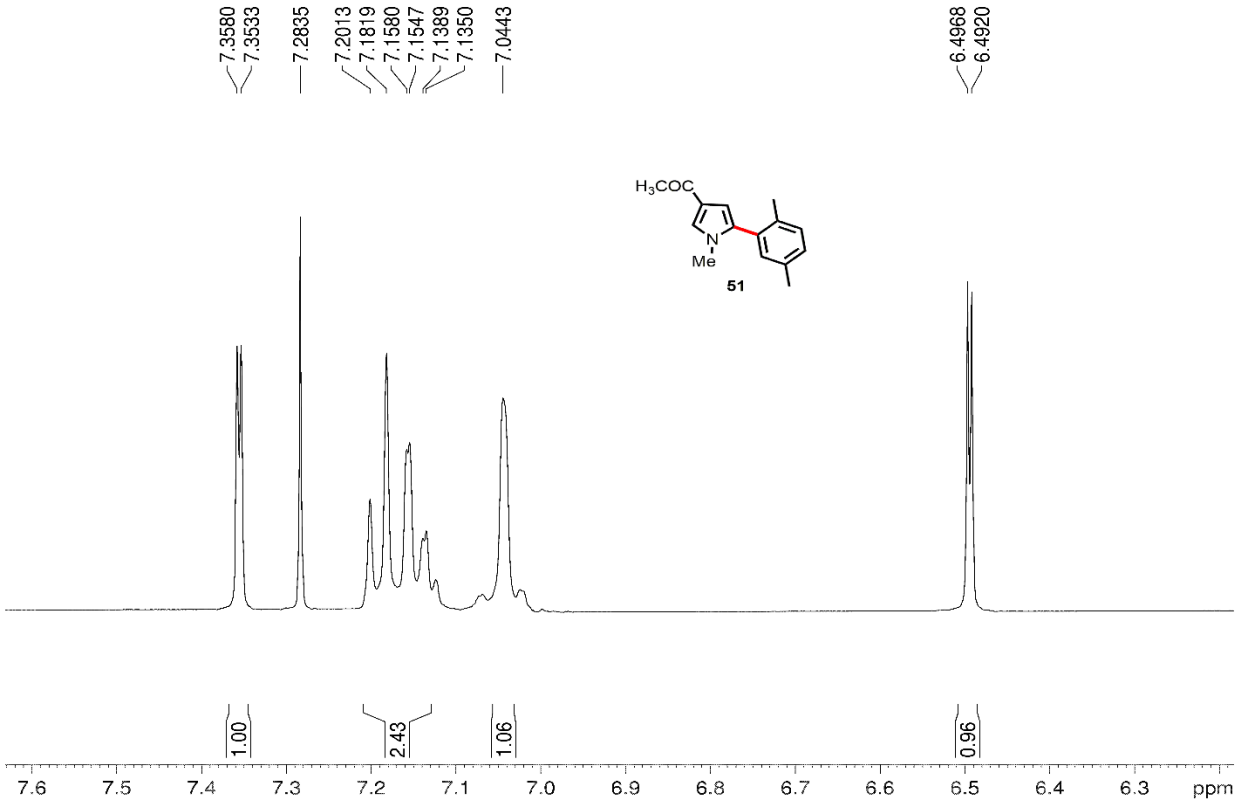
2.43
1.06
0.96
3.10
3.18
3.40
3.39
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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7.1547
7.1389
7.1350
7.0443
6.4968
6.4920
H3COC
N
Me
51
1.00
2.43
1.06
0.96
7.6
7.5
7.4
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6.9
6.8
6.7
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6.3
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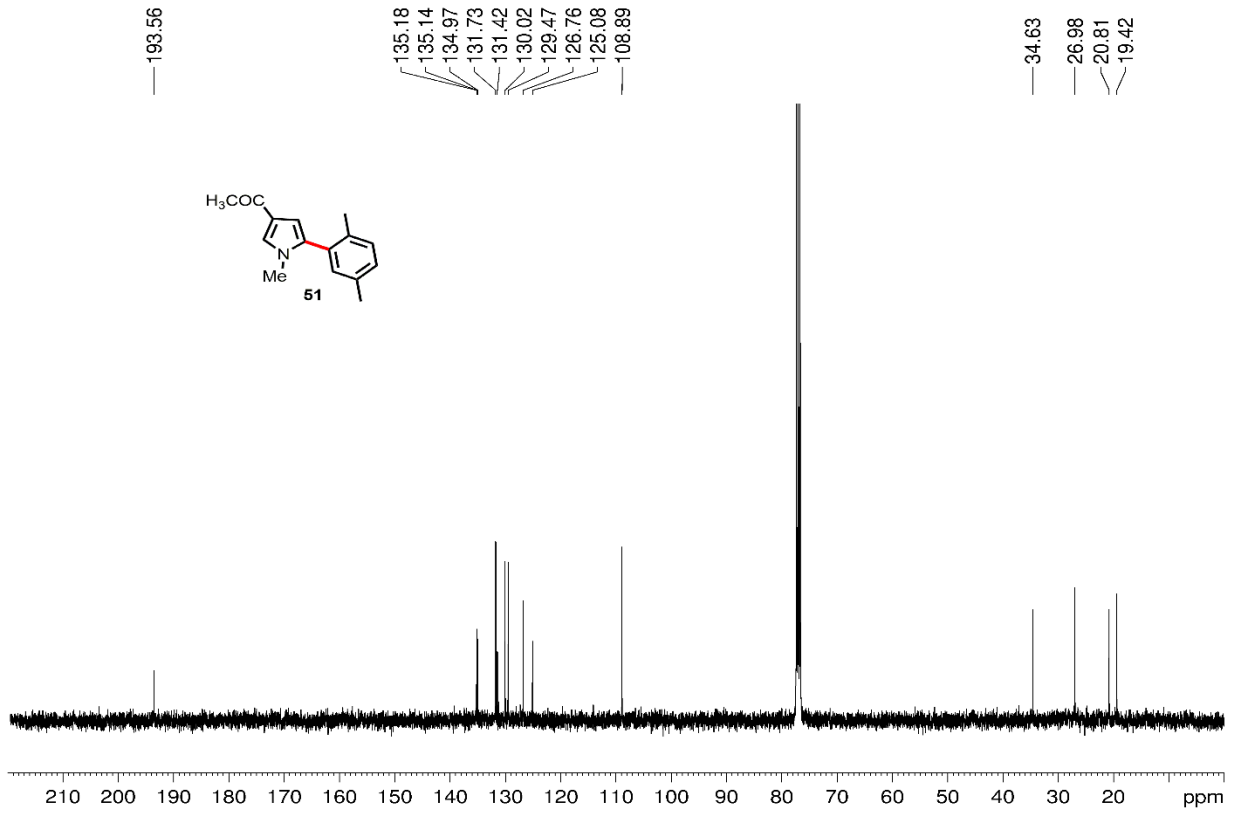
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135.14
134.97
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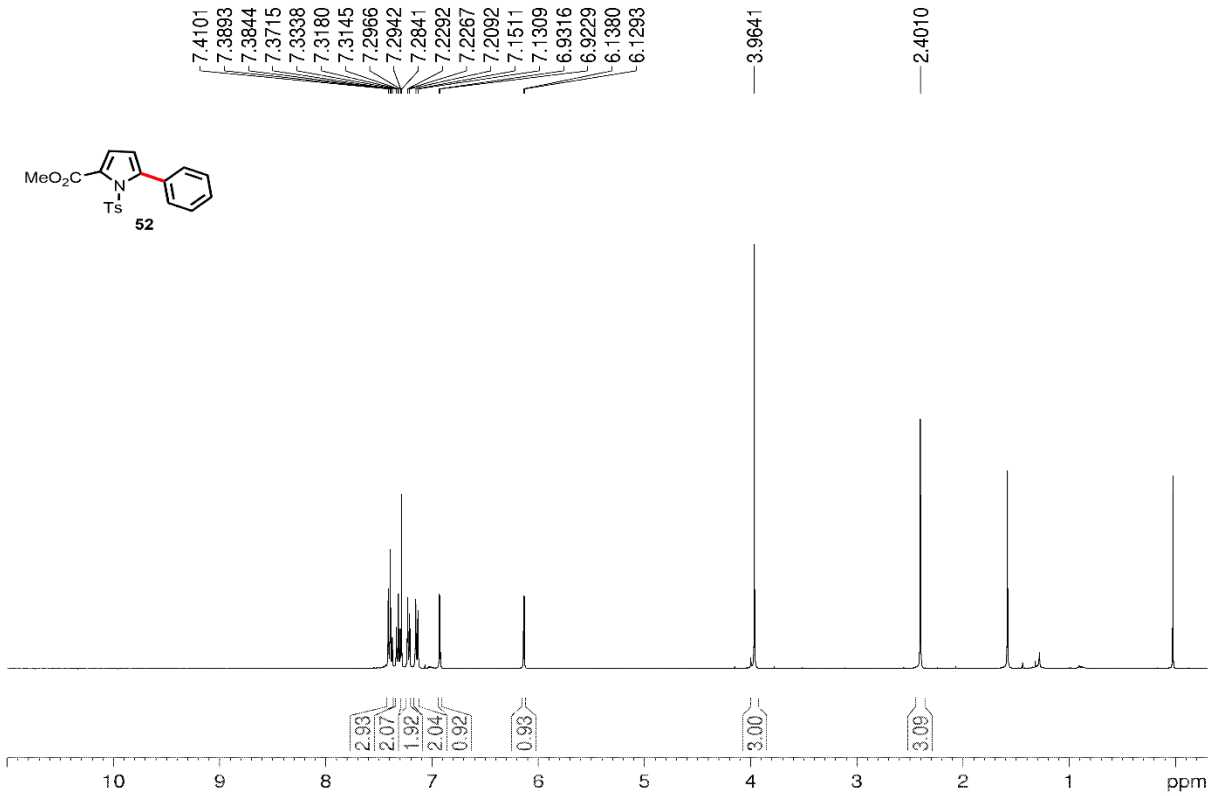
131.42
130.02
129.47
126.76
125.08
108.89
34.63
26.98
20.81
19.42
H3COC
N
Me
51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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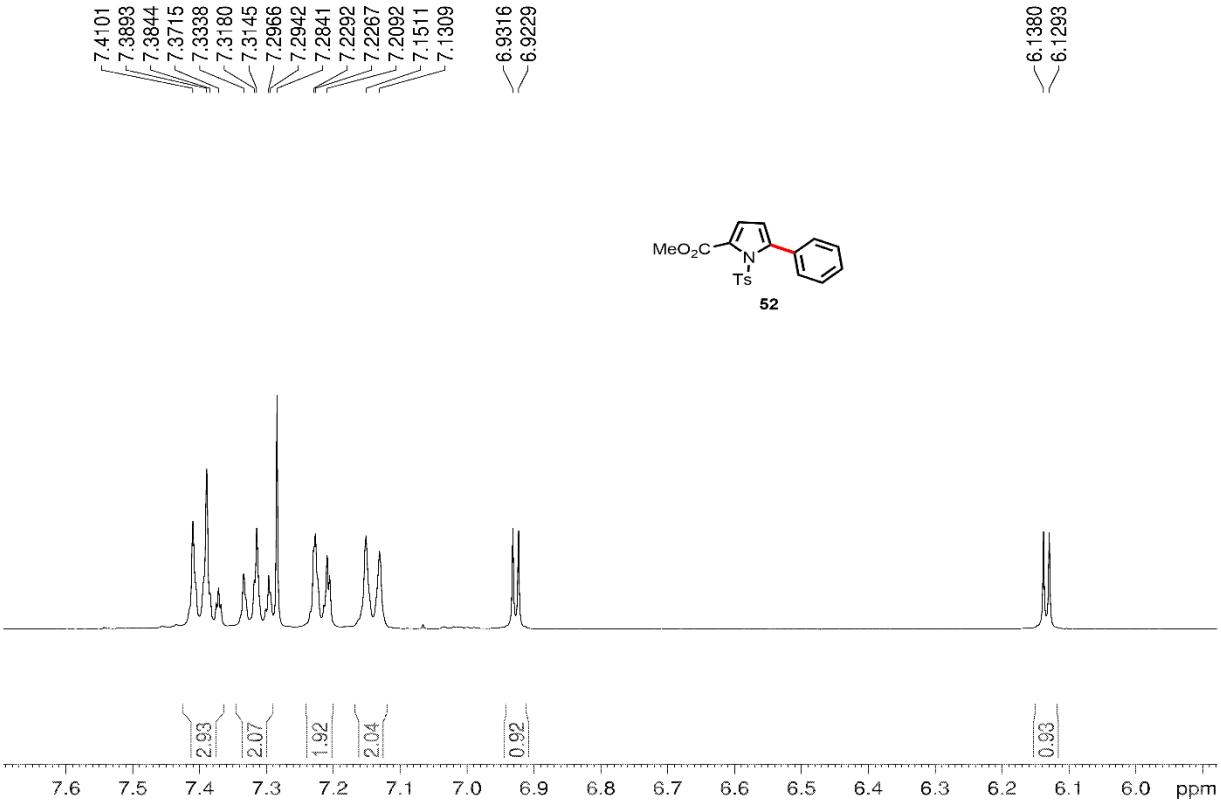
7.3844
7.3715
7.3338
7.3180
7.3145
7.2966
7.2942
7.2841
7.2292
7.2267
7.2092
7.1511
7.1309
6.9316
6.9229
6.1380
6.1293
3.9641
2.4010
MeO2C
N
Ts
52
2.93
2.07
1.92
2.04
0.92
0.93
3.00
3.09
10
9
8
7
6
5
4
3
2
1
ppm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7.3844
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7.3145
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7.2942
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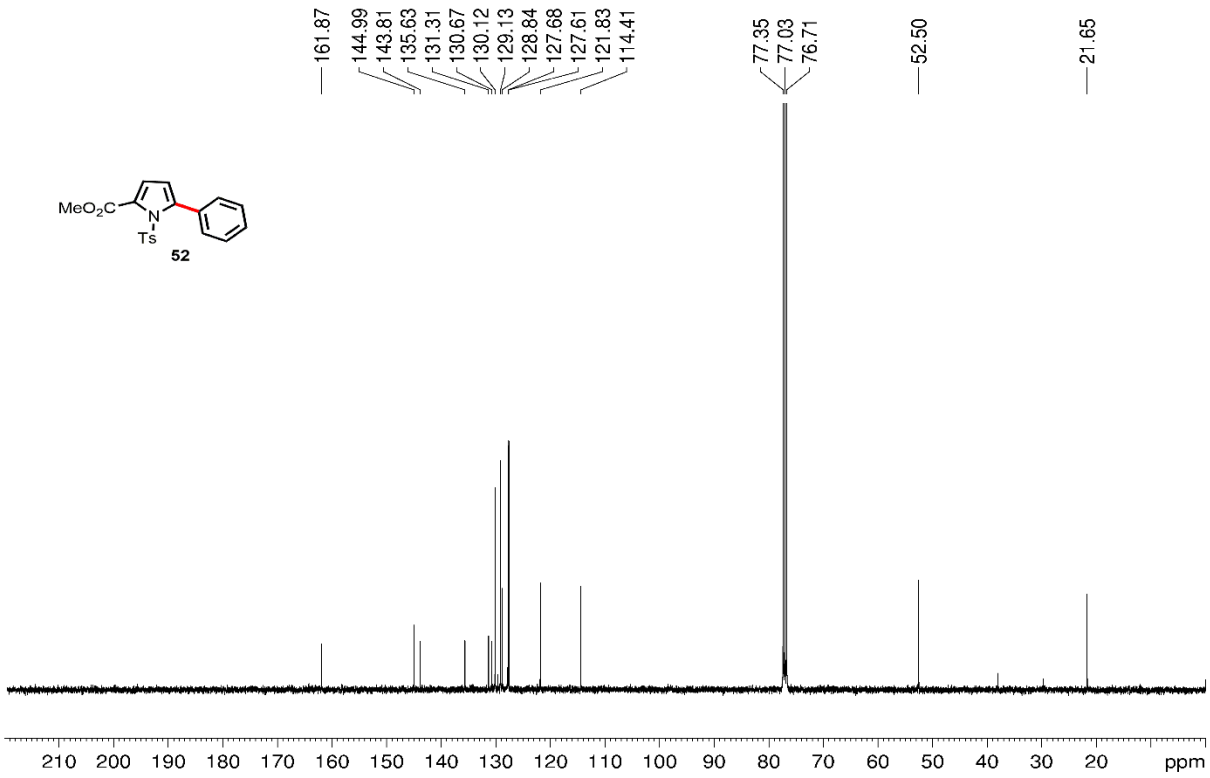
7.2292
7.2267
7.2092
7.1511
7.1309
6.9316
6.9229
6.1380
6.1293
MeO2C
N
Ts
52
2.93
2.07
1.92
2.04
0.92
0.93
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
ppm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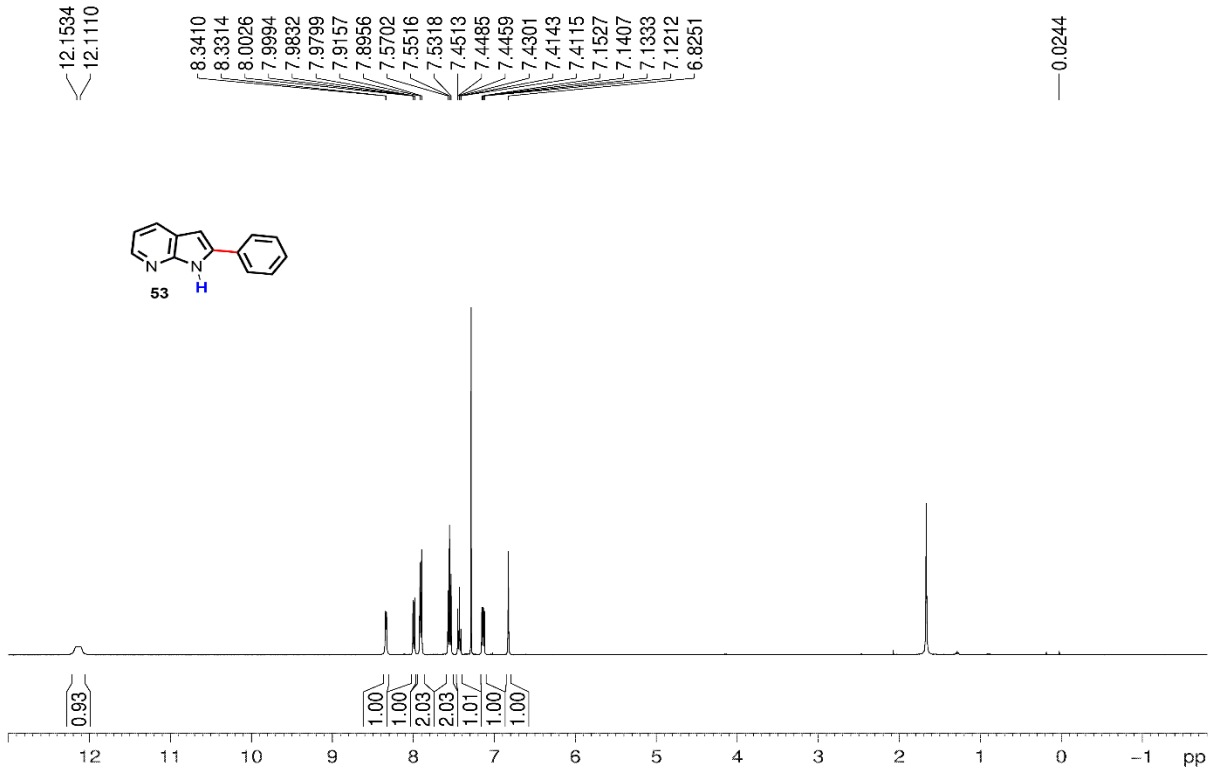
143.81
135.63
131.31
130.67
130.12
129.13
128.84
127.68
127.61
121.83
114.41
77.35
77.03
76.71
52.50
21.65
MeO2C
N
Ts
52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.3314
8.0026
7.9994
7.9832
7.9799
7.9157
7.8956
7.5702
7.5516
7.5318
7.4513
7.4485
7.4459
7.4301
7.4143
7.4115
7.1527
7.1407
7.1333
7.1212
6.8251
0.0244
N
H
53
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1.00
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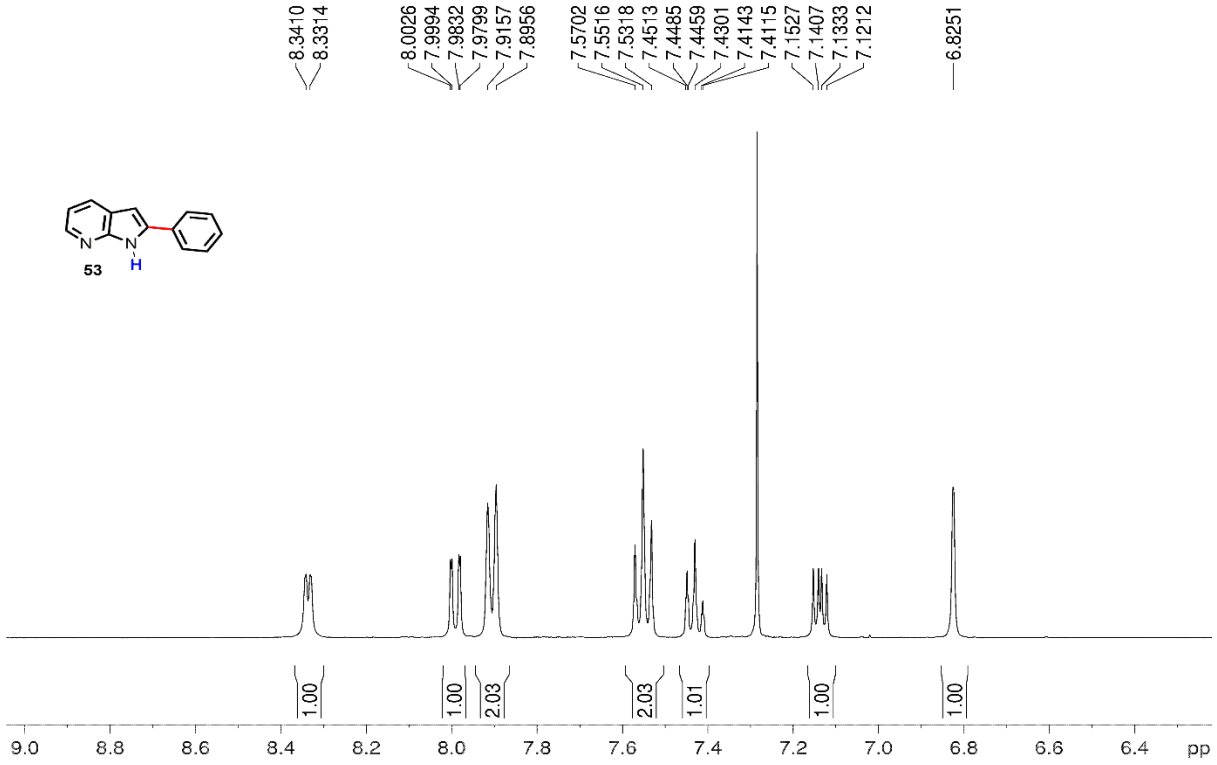
2.03
1.01
1.00
1.00
12 11 10 9 8 7 6 5 4 3 2 1 0 −1 pp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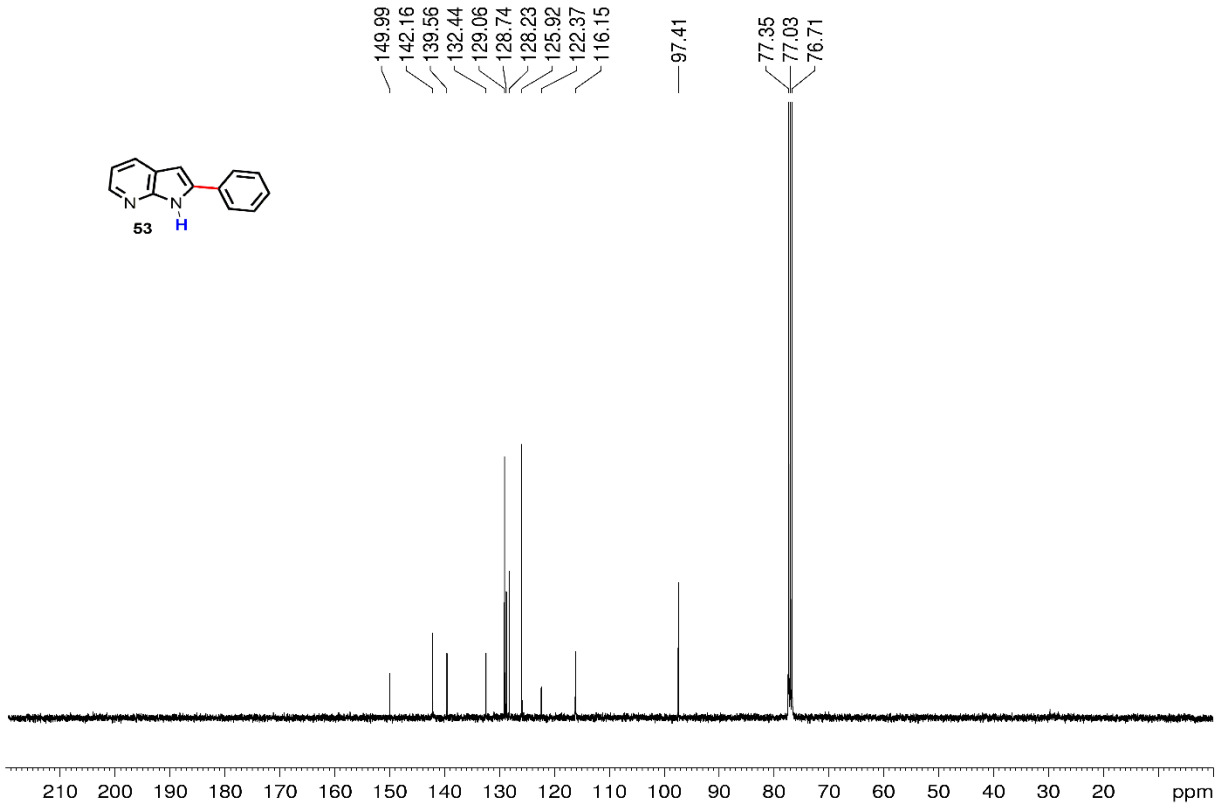
8.3314
8.0026
7.9994
7.9832
7.9799
7.9157
7.8956
7.5702
7.5516
7.5318
7.4513
7.4485
7.4459
7.4301
7.4143
7.4115
7.1527
7.1407
7.1333
7.1212
6.8251
53
1.00
1.00
2.03
2.03
1.01
1.00
1.00
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
pp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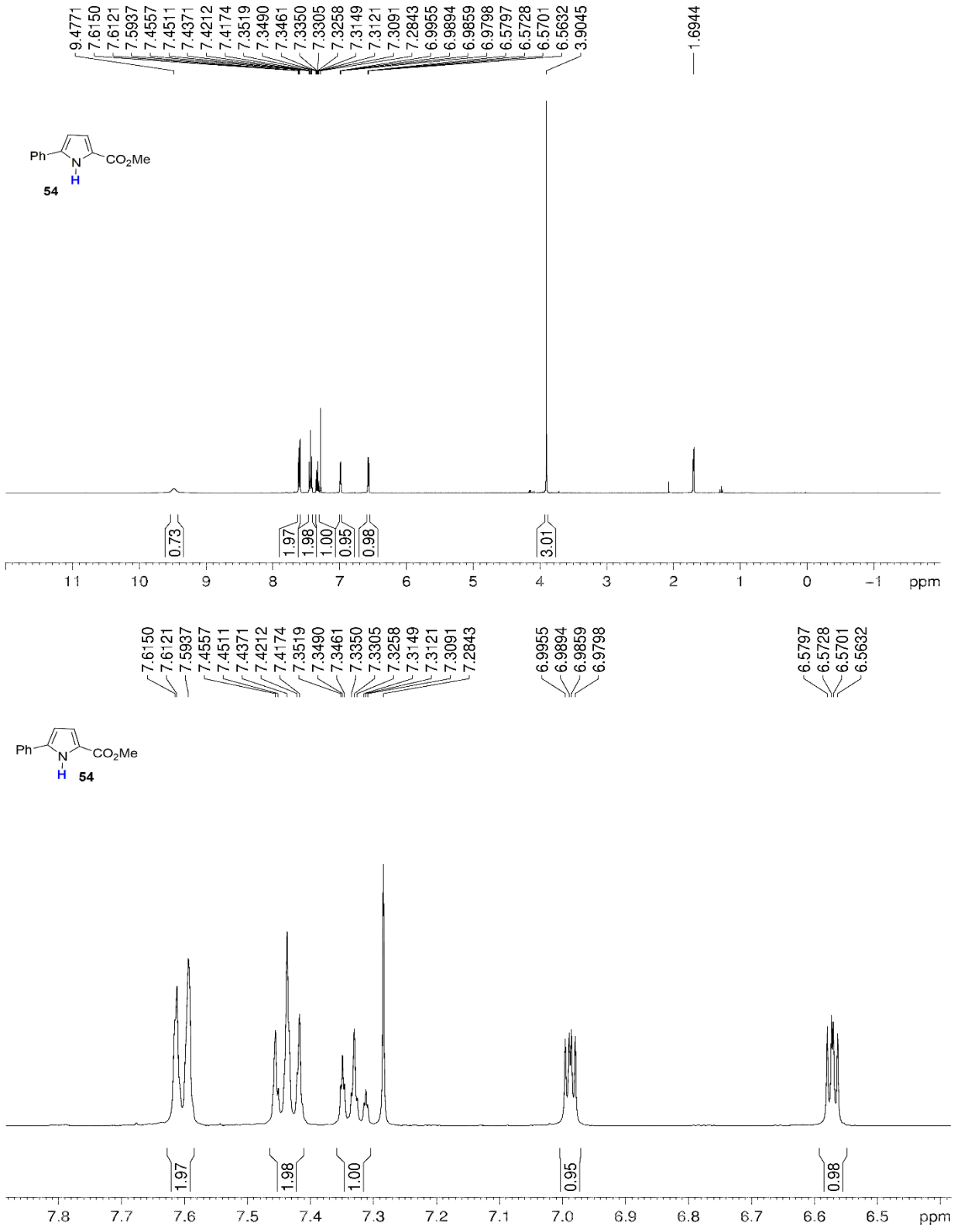
132.44
129.06
128.74
128.23
125.92
122.37
116.15
97.41
77.35
77.03
76.71
53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.3461
7.3350
7.3305
7.3258
7.3149
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7.2843
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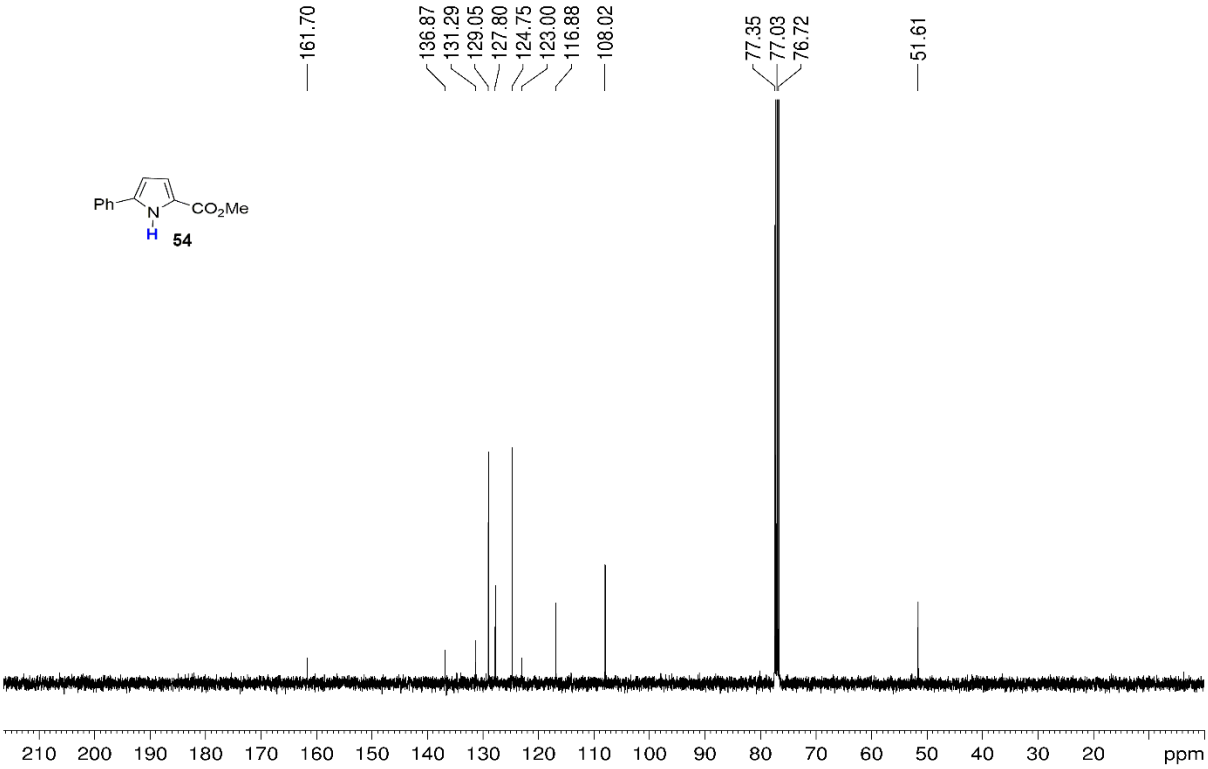
6.9894
6.9859
6.9798
6.5797
6.5728
6.5701
6.5632
3.9045
1.6944
Ph
N
H
CO2Me
54
0.73
1.97
1.98
1.00
0.95
0.98
3.01
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5


161.70
136.87
131.29
129.05
127.80
124.75
123.00
116.88
108.02
77.35
77.03
76.72
51.61
Ph
N
H
CO2Me
54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm