Supporting Information

Scope of Successive C–H Functionalizations of the Methyl Group in 3-Picolines: Intramolecular Carbonylation of Arenes to the Metal-Free Synthesis of 4-Azafluorenones

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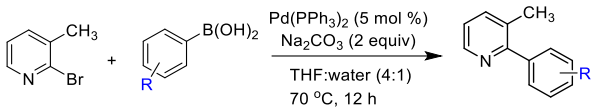
General considerations

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All reactions were performed in a screw-capped vial. The proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained using a 400 MHz using Me_4Si as an internal standard and are reported in δ units. Coupling constants (J values) are reported in Hz. Column chromatography was performed on silica gel (60-120#, 100-200#). High Resolution Mass Spectra (HRMS) were obtained using electron spray ionisation (ESI) technique and as TOF mass analyser. IR spectra are reported in cm^{-1} units. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer and are uncorrected. 2-Bromo-3-methyl pyridine, arylboronic acid derivatives, TBHP (5.0 – 6.0 M in decane) and 3-picoline (**35**) were purchased used as received.

Experimental section

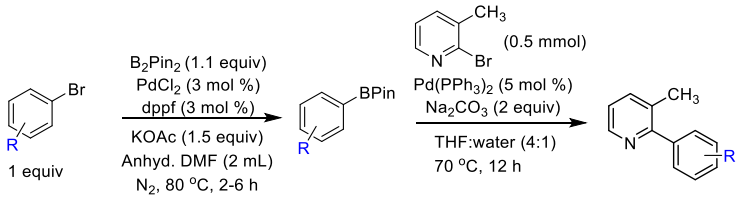
General procedure for the synthesis of starting materials

General procedure-A (GP-A) (3, 6-8, 10-17)



Following a modified literature procedure,[1] a solution of 2-bromo-3-methyl pyridine (0.5 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL), was heated at 70 °C for 12 h. THF was evaporated *in vacuuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography (100-200# silica, ethyl acetate/hexane = 0.5:9.5 ~ 2:8) to give the desired product.

General procedure-B (GP-B) (5, 9, 18)



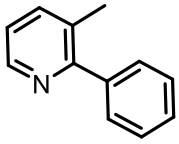
Following a modified literature procedure,[2] a suspension of arylbromide (0.7 mmol), bispinacolato diboron (1.1 equiv, 0.77 mmol), $PdCl_2$ (3 mol %), 1,1'-Bis(diphenylphosphino)ferrocene (dppf, 3 mol %), and KOAc (3 equiv, 2.1 mmol) in anhydrous DMF (2 mL) was heated at 80 ^oC for 2-6 h under nitrogen atmosphere. After complete consumption of arylbromide (monitored by TLC), the reaction mixture was extracted with ethyl acetate (2×10 mL) and the organic layer was washed with water (2×20 mL), dried (Na_2SO_4), and concentrated *in vacuuo*. The crude was directly used for the next step without purification. A stirred solution of the crude product, 2-bromo-3-methyl pyridine (0.5 mmol), $Pd(PPh_3)_4$ (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL) was stirred at 70 ^oC for 12 h. THF was evaporated *in vacuuo.* Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography (100-200# silica, ethyl acetate /hexane = 0.5:9.5 ~ 2:8) to give the desired product.

General procedure for the synthesis of 4-azafluorenones (4, 20-33, 36)

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of 3-methyl-4-aryl pyridine (0.15 mmol), TBHP (8 equiv) and DCE (0.5 mL) was heated at 100 ^oC for 24-42 h. Silica gel was added to the reaction mixture and the excess solvent was evaporated. The silica gel mixed with the crude product was loaded on the column, which upon chromatography (ethyl acetate /hexane = 1:9 ~ 3:7) afforded desired product.

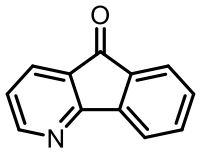
Characterization of synthesized compounds

3-Methyl-2-phenylpyridine (3)



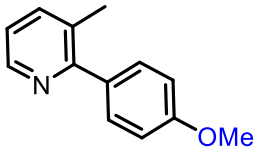
Following the general procedure-A, **3** was obtained as pale yellow oil; Yield 76% (65 mg); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.54 (dd, J = 4.7, 1.1 Hz, 1H), 7.59 (d, J = 7.64 Hz, 1H), 7.53-7.55 (m, 2H), 7.44-7.48 (m, 2H), 7.40 (tt, J = 7.2, 2.8, 1.4 Hz, 1H), 7.19 (dd, J = 7.7, 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 146.9, 140.5, 138.6, 130.9, 128.9, 128.3, 128.2, 128.0, 128.0, 106.4, 20.0; HRMS-ESI m/z calcd for $C_{12}H_{12}N$ $[M+H]^+$ 170.0970, found 170.0972.

5*H*-Indeno[1,2-*b*]pyridin-5-one (4)[3]



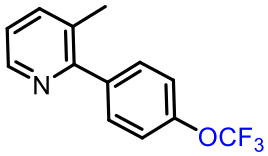
Yellow solid; Yield 70% (19 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (dd, J = 5.1, 1.6 Hz, 1H), 7.93 (dd, J = 7.4, 1.6 Hz, 1H), 7.89 (d, J = 7.4, 1H), 7.76 (d, J = 7.4 Hz, 1H), 7.63 (td, J = 7.5, 1.1 Hz, 1H), 7.48 (td, J = 7.4, 1.0 Hz, 1H), 7.24 (dd, J = 7.4, 5.1 Hz, 1H); HRMS-ESI m/z calcd for $C_{12}H_8NO$ $[M+H]^+$ 182.0606, found 182.0609.

2-(4-Methoxyphenyl)-3-methylpyridine (5)



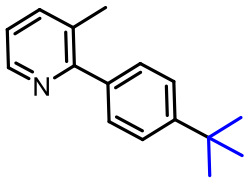
Following the general procedure-B (6 h reaction time for the first step), **5** was obtained as yellow oil; Yield 65% (65 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (dt, J = 4.8, 0.8 Hz, 1H), 7.52-7.57 (m, 1H), 7.45-7.51 (m, 2H), 7.13 (dd, J = 7.8, 4.8 Hz, 1H), 6.94-7.01 (m, 2H), 3.84 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 158.3, 146.9, 138.5, 133.2, 130.7, 130.3, 121.7, 113.5, 55.3, 20.3; HRMS-ESI m/z calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1075, found 200.1084.

3-Methyl-2-(4-(trifluoromethoxy)phenyl)pyridine (6)



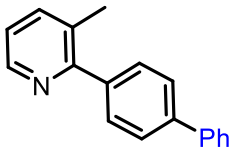
Following the general procedure-A, **6** was obtained as pale yellow oil; Yield 72% (91 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (dd, J = 4.8, 1.0 Hz, 1H), 7.62 (dd, J = 7.6, 0.8, 1H), 7.56-7.60 (m, 2H), 7.32 (dd, J = 8.8, 0.8 Hz, 2H), 7.23 (dd, J = 7.8, 4.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.3, 149.0, 147.1, 139.2, 138.7, 130.9, 122.5, 121.8, 120.6, 119.2, 116.2, 20.0; HRMS-ESI m/z calcd for $C_{13}H_{11}F_3NO$ $[M+H]^+$ 254.0793, found 254.0800.

2-(4-(*tert*-Butyl)phenyl)-3-methylpyridine (7)



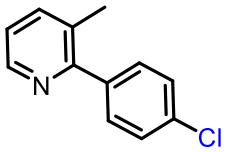
Following the general procedure-A, **7** was obtained as pale yellow oil; Yield 78% (88 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (dd, J = 4.7, 1.6 Hz, 1H), 7.58 (dd, J = 7.6, 1.5 Hz, 1H), 7.49 (s, 4H), 7.17 (dd, J = 7.5, 4.8 Hz, 1H), 2.40 (s, 3H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 150.8, 146.9, 138.4, 137.7, 130.8, 128.6, 126.0, 121.8, 34.6, 31.6, 20.2; HRMS-ESI m/z calcd for $C_{16}H_{20}N$ $[M+H]^+$ 226.1596, found 226.1595.

2-([1,1'-Biphenyl]-4-yl)-3-methylpyridine (8)



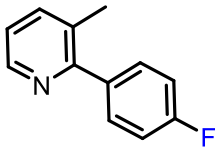
Following the general procedure-A, **8** was obtained as light yellow oil; Yield 68% (84 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (dd, J = 4.8, 1.0 Hz, 1H), 7.65-7.70 (m, 3H), 7.60-7.65 (m, 3H), 7.57-7.60 (m, 1H), 7.43-7.48 (m, 2H), 7.33-7.38 (m, 1H), 7.18 (dd, J = 7.7, 4.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 147.1, 140.8, 140.7, 139.6, 138.6, 130.9, 129.5, 128.8, 127.4, 127.2, 126.9, 126.6, 122.1, 20.2; HRMS-ESI m/z calcd for $C_{18}H_{16}N$ $[M+H]^+$ 246.1283, found 246.1285.

2-(4-Chlorophenyl)-3-methylpyridine (9)



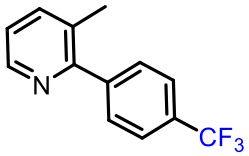
Following the general procedure-B (5 h reaction time for the first step), **9** was obtained as off-white solid; mp 65-67 ^{o}C; Yield 76% (77 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (dd, J = 4.7, 1.0 Hz, 1H), 7.57-7.62 (m, 1H), 7.47-7.50 (m, 2H), 7.41-7.45 (m, 2H), 7.20 (dd, J = 7.8, 4.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 147.1, 138.9, 138.7, 134.0, 130.8, 130.4, 128.4, 122.4, 20.0; HRMS-ESI m/z calcd for $C_{12}H_{11}ClN$ $[M+H]^+$ 204.0580, found 204.0578.

2-(4-Fluorophenyl)-3-methylpyridine (10)



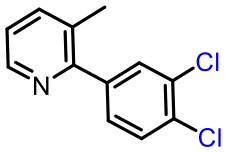
Following the general procedure-A, **10** was obtained as pale yellow oil; Yield 70% (66 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, J = 4.4, 1H), 7.57 (d, J = 7.5, 1H), 7.46-7.55 (m, 2H), 7.08-7.21 (m, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.8, 161.3, 157.6, 147.0, 138.6, 136.6, 130.8, 130.7, 122.2, 115.0, 20.0; HRMS-ESI m/z calcd for $C_{12}H_{11}FN$ $[M+H]^+$ 188.0876, found 188.0880.

3-Methyl-2-(4-(trifluoromethyl)phenyl)pyridine (11)



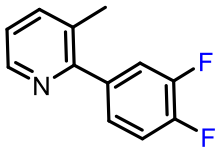
Following the general procedure-A, **11** was obtained as pale yellow oil; Yield 72% (85 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (dd, J = 4.7, 1.0 Hz, 1H), 7.70-7.76 (m, 2H), 7.65-7.69 (m, 2H), 7.63 (dd, J = 7.8, 1.5 Hz, 1H), 7.25 (dd, J = 7.8, 4.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.2, 147.2, 138.8, 131.0, 130.2, 129.4, 128.3, 125.2, 122.7, 120.2, 115.5, 19.9; HRMS-ESI m/z calcd for $C_{13}H_{11}F_3N$ $[M+H]^+$ 238.0844, found 238.0852.

2-(3,4-Dichlorophenyl)-3-methylpyridine (12)



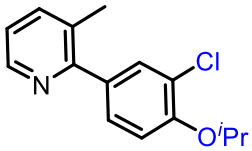
Following the general procedure-A, **12** was obtained as off-white solid; mp 56-58 °C; Yield 64% (76 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, J = 4.6 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.2 Hz, 1H), 7.38 (dd, J = 8.2, 1.6 Hz, 1H), 7.22 (dd, J = 7.7, 4.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.0, 147.4, 147.1, 146.8, 140.4, 138.9, 132.4, 131.1, 130.9, 130.1, 128.4, 122.8, 19.9; HRMS-ESI m/z calcd for $C_{12}H_{10}Cl_2N$ $[M+H]^+$ 238.0190, found 238.0193.

2-(3,4-Difluorophenyl)-3-methylpyridine (13)



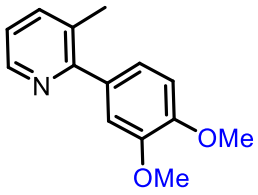
Following the general procedure-A, **13** was obtained as off-white solid; mp 62-63 °C; Yield 60% (62 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, J = 4.5 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.36-7.43 (m, 1H), 7.25-7.31 (m, 2H), 7.20-7.25 (m, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.4, 156.4, 151.3, 148.9, 147.1, 138.8, 137.5, 137.5, 130.8, 125.3, 122.6, 118.2, 116.9, 19.8; HRMS-ESI m/z calcd for $C_{12}H_{10}F_2N$ $[M+H]^+$ 206.0781, found 206.0790.

2-(3-Chloro-4-isopropoxyphenyl)-3-methylpyridine (14)



Following the general procedure-A, **14** was obtained as yellow oil; Yield 75% (98 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (dd, J = 4.8, 1.0 Hz, 1H), 7.58 (d, J = 2.3 Hz, 2H), 7.39 (dd, J = 8.5, 2.3 Hz, 1H), 7.17 (dd, J = 7.5, 4.8 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 4.62 (dt, J = 12.1, 6.1 Hz, 1H), 2.38 (s, 3H), 1.41 (d, J = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.0, 153.4, 147.0, 138.7, 134.0, 131.0, 128.4, 123.9, 122.1, 115.4, 72.1, 22.0, 20.0; HRMS-ESI m/z calcd for $C_{15}H_{17}ClNO$ $[M+H]^+$ 262.0999, found 262.0994.

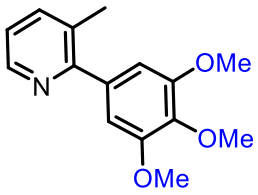
2-(3,4-Dimethoxyphenyl)-3-methylpyridine (15)



Following the general procedure-A, **15** was obtained as yellow oil; Yield 80% (92 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.48 (dd, J = 4.4, 1.1 Hz, 1H), 7.54 (ddd, J = 7.7, 1.6, 0.8 Hz, 1H), 7.13 (dd, J = 7.7, 4.9 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.06 (d, J = 8.2, 1.9 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.91 (s, 6H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 148.9, 148.7, 146.8, 138.6, 133.3,

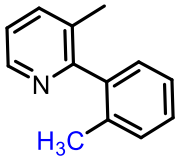
130.7, 121.8, 121.5, 112.4, 110.6, 55.9, 20.3; HRMS-ESI m/z calcd for $C_{14}H_{16}NO_2$ $[M+H]^+$ 230.1181, found 230.1185.

3-Methyl-2-(3,4,5-trimethoxyphenyl)pyridine (16)



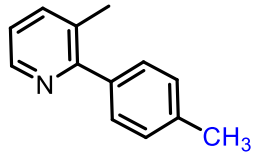
Following the general procedure-A, **16** was obtained as yellow oil; Yield 74% (96 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (dd, J = 4.8, 1.0 Hz, 1H), 7.58 (dd, J = 7.7, 0.8 Hz, 1H), 7.19 (dd, J = 7.8, 4.8 Hz, 1H), 6.73 (s, 2H), 3.89 (s, 9H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 152.9, 146.7, 138.6, 137.9, 136.2, 130.7, 122.1, 106.3, 60.8, 56.1, 55.7, 20.1; HRMS-ESI m/z calcd for $C_{15}H_{18}NO_3$ $[M+H]^+$ 260.1287, found 260.1296.

3-Methyl-2-(*o*-tolyl)pyridine (17)



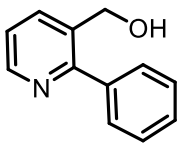
Following the general procedure-A, **17** was obtained as pale yellow oil; Yield 71% (65 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (dd, J = 4.8, 1.0 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.24-7.34 (m, 3H), 7.17-7.24 (m, 2H), 2.13 (s, 3H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 146.7, 140.2, 137.8, 135.5, 131.5, 130.2, 128.5, 127.9, 125.7, 122.2, 19.4, 19.0; HRMS-ESI m/z calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1126, found 184.1125.

3-Methyl-2-(*p*-tolyl)pyridine (18)



Following the general procedure-B (2 h reaction time for the first step), **18** was obtained as pale yellow oil; Yield 70% (64 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (dd, J = 4.8, 1.0 Hz, 1H), 7.56-7.61 (m, 1H), 7.42-7.47 (m, 2 H), 7.26-7.30 (m, 2H), 7.17 (dd, J = 7.8, 4.8 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 146.9, 138.5, 137.7, 130.8, 128.9, 128.8, 121.9, 21.3, 20.2; HRMS-ESI m/z calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1126, found 184.1128.

(2-Phenylpyridin-3-yl)methanol (19)

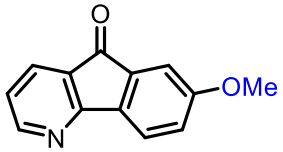


In oven dried screw capped vial, 2-bromonicotinic acid (1 mmol), methanol (1 mL) and catalytic H_2SO_4 was heated at 80 ^{o}C overnight. The reaction was monitored by using TLC. After complete consumption of substrate, reaction mixture was diluted with ethyl acetate (2×10 mL) and water (20 mL). The organic layers were combined, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column

chromatography (100-200# silica, ethyl acetate/hexane) to give the desired product methyl 2-bromonicotinate [^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49 (dd, J = 4.8, 2.0 Hz, 1H), 8.09 (dd, J = 7.8, 2.0 Hz, 1H), 7.36 (dd, J = 7.8, 4.8 Hz, 1H), 3.97 (s, 3H)]. Methyl 2-phenylnicotinate was prepared by GP-A using Methyl 2-bromonicotinate (0.5 mmol) and phenylboronic acid (0.6 mmol) [^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (dd, J = 5.0, 1.8 Hz, 1H), 8.12 (dd, J = 7.8, 1.8 Hz, 1H), 7.55-7.59 (m, 2H), 7.43-7.50 (m, 3 H), 7.36 (dd, J = 7.9, 4.9 Hz, 1H), 3.72 (s, 3H)].

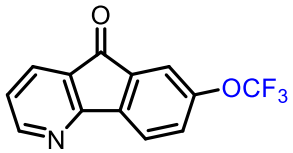
Following standard procedure for the preparation of alcohol from ester by using sodium borohydride, **19** was prepared. A suspension of methyl 2-phenylnicotinate (0.25 mmol), sodium borohydride (20 equiv), MeOH (1 mL) in THF (2 mL) heated at 70 ^{o}C and reaction was monitored by TLC. After complete consumption of substrate, reaction mixture was diluted with ethyl acetate (2×5 mL) and water (10 mL). The organic layers were combined, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography (60-120# silica, ethyl acetate/hexane) to give the desired product 2-(Phenylpyridin-3-yl)methanol as off-white solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (dd, J = 4.8, 1.8 Hz, 1H), 7.94-7.99 (m, 1H), 7.55-7.59 (m, 2H), 7.44-7.52 (m, 3H), 7.35 (dd, J = 7.8, 4.8 Hz, 1H), 4.74 (d, J = 4.3 Hz, 2H), 1.85 (br. s., 1H); HRMS-ESI m/z calcd for $C_{12}H_{11}NO$ $[M]^+$ 185.0841, found 185.0840.

7-Methoxy-5*H*-indeno[1,2-*b*]pyridin-5-one (20)[3a]



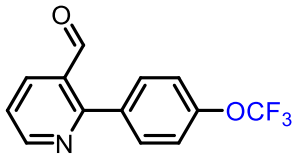
Yellow solid; Yield 70% (22 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (dd, J = 5.1, 1.6 Hz, 1H), 7.85 (dd, J = 7.4, 1.6 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.28 (s, 1H), 7.10-7.17 (m, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7, 165.4, 162.4, 153.9, 136.8, 136.0, 131.4, 128.5, 122.3, 122.2, 120.9, 109.3, 55.9; HRMS-ESI m/z calcd for $C_{13}H_{10}NO_2$ $[M+H]^+$ 212.0712, found 212.0705.

7-(Trifluoromethoxy)-5*H*-indeno[1,2-*b*]pyridin-5-one (21)



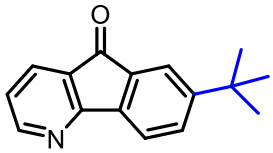
Light yellow solid; mp. 159-161 ^{o}C; Yield 24% (9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (dd, J = 5.1, 1.6 Hz, 1H), 7.95 (dd, J = 7.5, 1.6 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.60 (s, 1H), 7.45-7.48 (m, 1H), 7.26-7.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3, 166.2, 160.2, 156.2, 150.8, 148.7, 147.7, 142.6, 140.3, 139.4, 138.8, 137.2, 127.0, 114.0; HRMS-ESI m/z calcd for $C_{13}H_7F_3NO_2$ $[M+H]^+$ 266.0429, found 266.0420; IR (KBr): 3045, 2960, 1269, 1719, 789 cm^{-1}.

2-(4-(Trifluoromethoxy)phenyl)nicotinaldehyde (22)



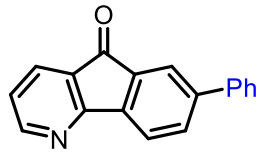
Off-white solid; Yield <10%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.1 (s, 1H), 8.88 (dd, J = 4.7, 1.7 Hz, 1H), 8.33 (dd, J = 7.8, 1.8 Hz, 1H), 7.64-7.66 (m, 2H), 7.24 (dd, J = 7.4, 5.1 Hz, 1H), 7.39 (d, J = 7.9 Hz, 2H); HRMS-ESI m/z calcd for $C_{13}H_9F_3NO_2$ $[M+H]^+$ 267.0507, found 267.0520.

7-(Tert-butyl)-5*H*-indeno[1,2-*b*]pyridin-5-one (23)



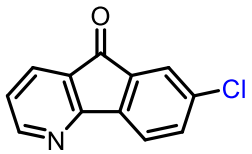
Light yellow solid; Yield 55% (19 mg); mp 160-162 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (dd, J = 5.2, 1.6 Hz, 1H), 7.90 (dd, J = 7.5, 1.6 Hz, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.66 (dd, J = 7.8, 1.8 Hz, 1H), 7.28 (s, 1H) 7.21 (dd, J = 7.4, 5.1 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.2, 165.1, 155.2, 153.7, 140.8, 132.4, 131.4, 128.8, 125.1, 123.0, 122.0, 121.5, 120.9, 34.0, 31.3; HRMS-ESI m/z calcd for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1232, found 238.1224; IR (KBr): 3067, 2054, 1720 cm^{-1}.

7-Phenyl-5*H*-indeno[1,2-*b*]pyridin-5-one (24)[4]



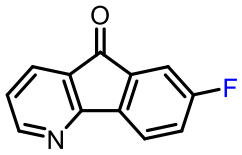
Yellow solid; Yield 78% (30 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (dd, J = 5.2, 1.6 Hz, 1H), 8.00 (dd, J = 1.6, 0.6 Hz, 1H), 7.95 (ddd, J = 7.6, 4.7, 1.0 Hz, 2H), 7.87 (dd, J = 7.8, 1.5 Hz, 1H), 7.64-7.68 (m, 2H), 7.48-7.53 (m, 2H), 7.41-7.45 (m, 1H), 7.25 (dd, J = 7.5, 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7, 165.0, 154.1, 144.3, 142.2, 139.6, 135.6, 133.9, 131.5, 129.0, 128.8, 128.4, 128.3, 126.9, 123.2, 122.9, 121.4; HRMS-ESI m/z calcd for $C_{18}H_{12}NO$ $[M+H]^+$ 258.0919, found 258.0915.

7-Chloro-5*H*-indeno[1,2-*b*]pyridin-5-one (25)[5]



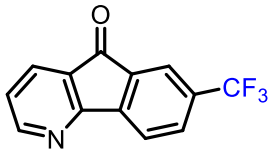
Light yellow solid; Yield 60% (19 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (dd, J = 5.1, 1.5 Hz, 1H), 8.03 (dd, J = 7.5, 1.4 Hz, 1H), 7.87-7.89 (m, 1H), 7.70-7.72 (m, 2H), 7.42 (dd, J = 7.5, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.3, 164.3, 154.3, 153.5, 141.7, 136.2, 135.0, 131.8, 124.6, 123.2, 122.2; HRMS-ESI m/z calcd for $C_{12}H_7ClNO$ $[M+H]^+$ 216.0216, found 216.0210.

7-Fluoro-5*H*-indeno[1,2-*b*]pyridin-5-one (26)[5]



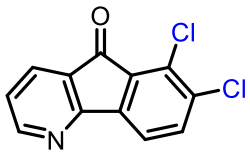
Light yellow solid; Yield 46% (14 mg); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.91 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.86 (dd, *J* = 8.2, 4.5 Hz, 1H), 7.43 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.31 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.23 (dd, *J* = 7.4, 5.2 Hz, 1H); HRMS-ESI m/z calcd for $C_{12}H_7FNO$ $[M+H]^+$ 200.0512, found 200.0503.

7-(Trifluoromethyl)-5*H*-indeno[1,2-*b*]pyridin-5-one (27)



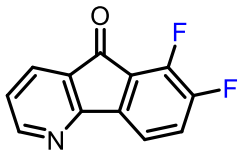
Yellow solid; Yield 43% (16 mg); mp 145-146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.73 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.98-8.02 (m, 2H), 7.92 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.75 (s, 1H), 7.34 (dd, *J* = 7.5, 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.2, 163.7, 162.3, 154.6, 152.0, 138.2, 135.1, 132.3, 132.0, 129.1, 128.7, 125.6, 124.3, 121.4, 121.2; HRMS-ESI m/z calcd for $C_{13}H_7F_3NO$ $[M+H]^+$ 250.0480, found 250.0488; IR (KBr): 3049, 2963, 1720, 1256 cm^{-1}.

6,7-Dichloro-5*H*-indeno[1,2-*b*]pyridin-5-one (28)



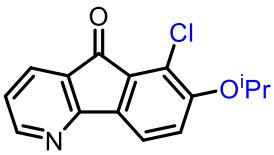
Light yellow solid; Yield 58% (21 mg); mp 173-174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.98 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 7.4, 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.8, 162.5, 154.5, 143.6, 136.6, 136.2, 132.0, 131.6, 128.0, 124.0, 119.8, 114.0; HRMS-ESI m/z calcd for $C_{12}H_6Cl_2NO$ $[M+H]^+$ 249.9826, found 249.9830; IR (KBr): 3065, 2923, 1727, 1260, 686 cm^{-1}.

6,7-Difluoro-5*H*-indeno[1,2-*b*]pyridin-5-one (29)



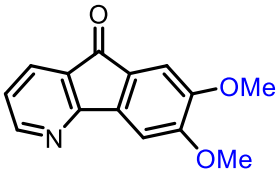
Light yellow solid; Yield 47% (15 mg); mp 179-180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.96 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.34-7.44 (m, 1H), 7.26-7.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.8, 164.9, 153.5, 138.1, 136.3, 129.6, 127.0, 123.1, 122.2, 119.5, 117.7; HRMS-ESI m/z calcd for $C_{12}H_6F_2NO$ $[M+H]^+$ 218.0417, found 218.0410; IR (KBr): 3045, 2937, 1715, 1271 cm^{-1}

6-Chloro-7-isopropoxy-5*H*-indeno[1,2-*b*]pyridin-5-one (30)



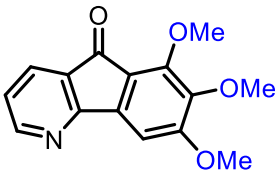
Yellow solid; Yield 66% (27 mg); mp 194-196 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (dd, J = 5.1, 1.6 Hz, 1H), 7.89 (dd, J = 7.4, 1.6 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.18 (dd, J = 7.4, 5.1 Hz, 1H), 7.10 (d, J = 7.1 Hz, 1H), 4.61-4.67 (m, 1H), 0.98 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.9, 163.5, 156.8, 154.1,141.0, 136.7, 131.6, 128.6, 127.0, 122.6, 119.8 , 114.0, 73.0, 21.9; HRMS-ESI m/z calcd for $C_{15}H_{13}ClNO_2$ $[M+H]^+$ 274.0635, found 274.0630; IR (KBr): 3072, 2954, 1728, 797 cm^{-1}.

7,8-Dimethoxy-5*H*-indeno[1,2-*b*]pyridin-5-one (31)



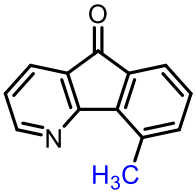
Yellow solid; Yield 68% (24 mg); mp >200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (dd, J = 5.1, 1.6 Hz, 1H), 7.77-7.81 (m, 1H), 7.38 (s, 1H), 7.27 (s, 1H), 7.13 (dd, J = 7.3, 5.3 Hz, 1H), 4.06 (s, 3H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.9, 165.0, 155.3, 153.1, 151.4, 138.6, 130.6, 129.0, 127.9, 122.4, 106.7, 103.7, 56.6, 56.4; HRMS-ESI m/z calcd for $C_{14}H_{12}NO_3$ $[M+H]^+$ 242.0817, found 242.0816; IR (KBr): 3063, 2942, 1729 cm^{-1}.

6,7,8-Trimethoxy-5*H*-indeno[1,2-*b*]pyridin-5-one (32)



Yellow solid; Yield 62% (25 mg); mp >200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (dd, J = 5.1, 1.6 Hz, 1H), 7.85 (dd, J = 7.4, 1.6 Hz, 1H), 7.25 (s, 1H), 7.19 (dd, J = 7.4, 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.3, 163.4, 159.4, 153.4, 153.2, 143.6, 140.9, 130.8, 129.4, 123.1, 118.8, 100.4, 62.2, 61.4, 56.7; HRMS-ESI m/z calcd for $C_{15}H_{14}NO_4$ $[M+H]^+$ 272.0923, found 272.0913; IR (KBr): 3069, 2936, 1732 cm^{-1}.

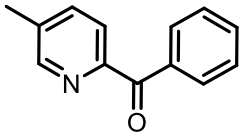
9-Methyl-5*H*-indeno[1,2-*b*]pyridin-5-one (33)



Yellow solid; Yield 53% (16 mg); mp 147-148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (dd, J = 5.1, 1.6 Hz, 1H), 7.90 (dd, J = 7.4, 1.7 Hz, 1H), 7.60 (d, J = 7.0, Hz, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.19 (dd, J = 7.4, 5.1 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.3, 167.1, 153.7, 140.4,

138.0, 135.7, 135.2, 131.0, 130.2, 128.6, 122.3, 121.7, 18.9; HRMS-ESI m/z calcd for $C_{13}H_{10}NO$ $[M+H]^+$ 196.0762, found 196.0751; IR (KBr): 3065, 2924, 1710 cm^{-1}.

(5-Methylpyridin-2-yl)(phenyl)methanone (36)



Light yellow oil; Yield 18% (5 mg); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.57 (dd, J = 1.4, 0.8 Hz, 1H), 8.05-8.09 (m, 2H), 7.99 (d, J = 7.9 Hz, 1H), 7.71-7.74 (m, 1H), 7.58-7.63 (m, 1H), 7.47-7.53 (m, 2H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 137.4, 132.7, 130.9, 128.1, 124.4, 18.7; IR 3045, 2959, 1722 cm^{-1}. HRMS-ESI m/z calcd for $C_{13}H_{12}NNaO$ $[M+H]^+$ 198.0919, found 198.0919; IR (neat): 3065, 2924, 1733 cm^{-1}.

References

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2. Modified procedure from: Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508-7510.
3. a) Marquise, N.; Harford, P. J.; Chevallier, F.; Roisnel, T.; Dorcet, V.; Gagez, A.-L.; Sable, S.; Picot, L.; Thiery, V.; Wheatley, A. E. H.; Gros, P. C.; Mongin, F. *Tetrahedron* **2013**, *69*, 10123-10133; b) Rebstock, A.-S.; Mongin, F.; Trécourt, F.; Quéguiner, G. *Tetrahedron*, **2003**, *59*, 4973-4977.
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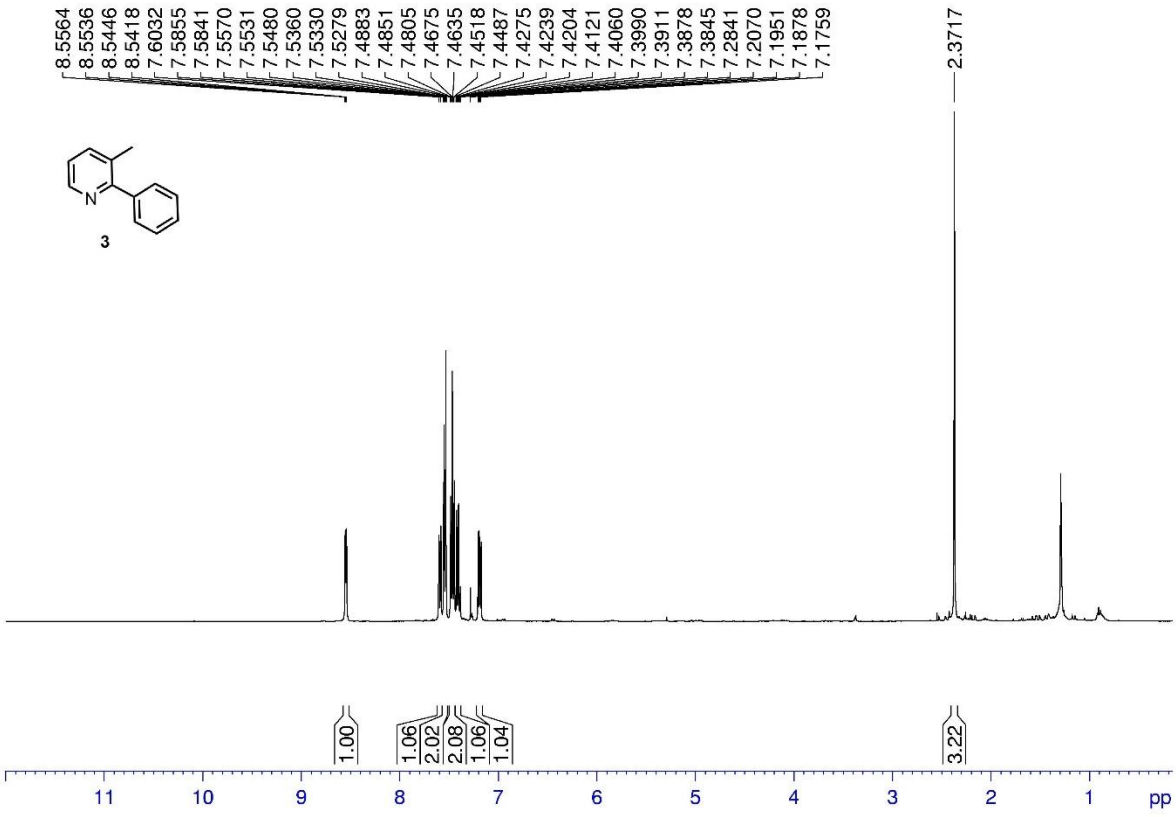
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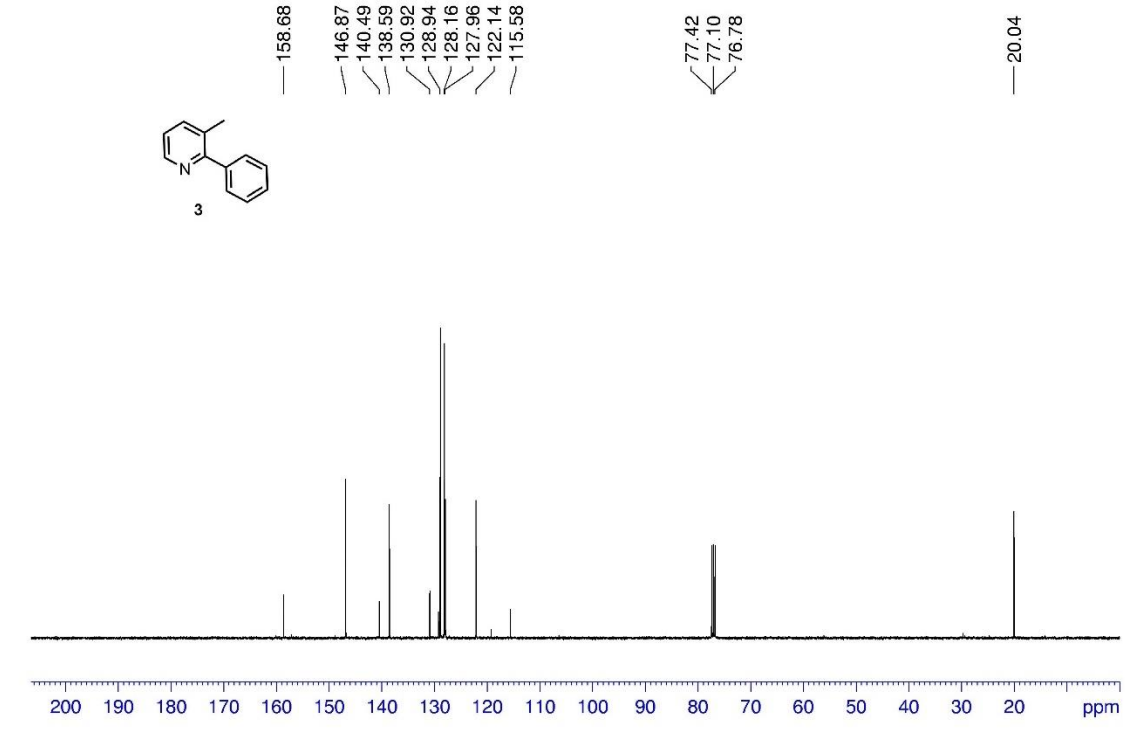
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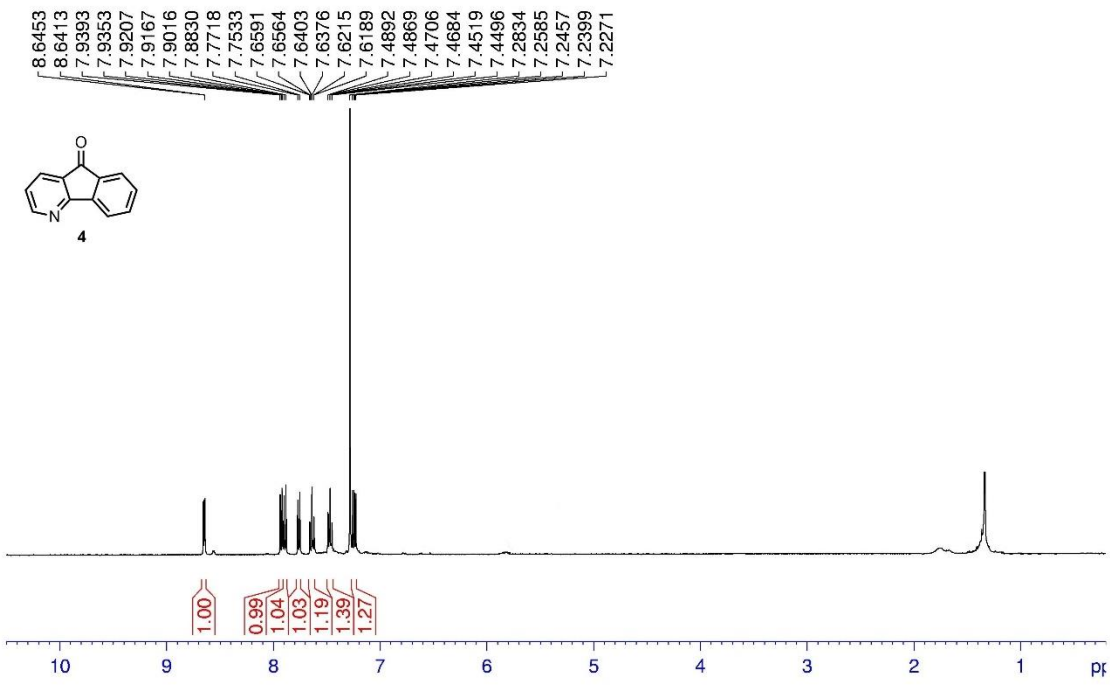
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7.4869
7.4706
7.4684
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7.2457
7.2399
7.2271
O
N
4
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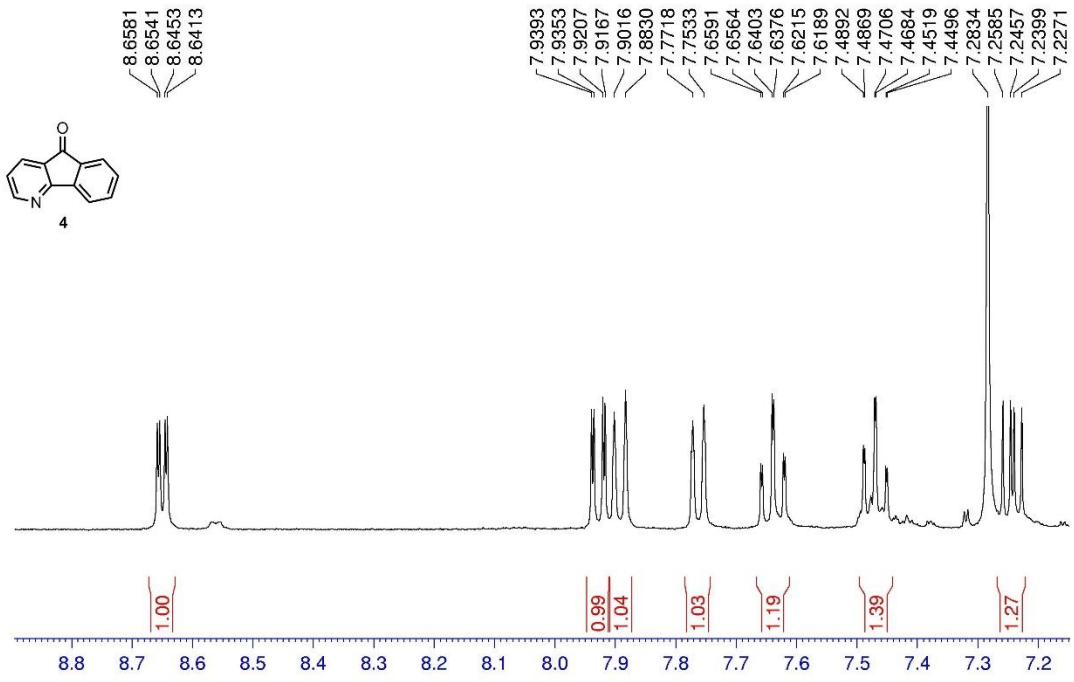
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7.2271
O
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4
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1.39
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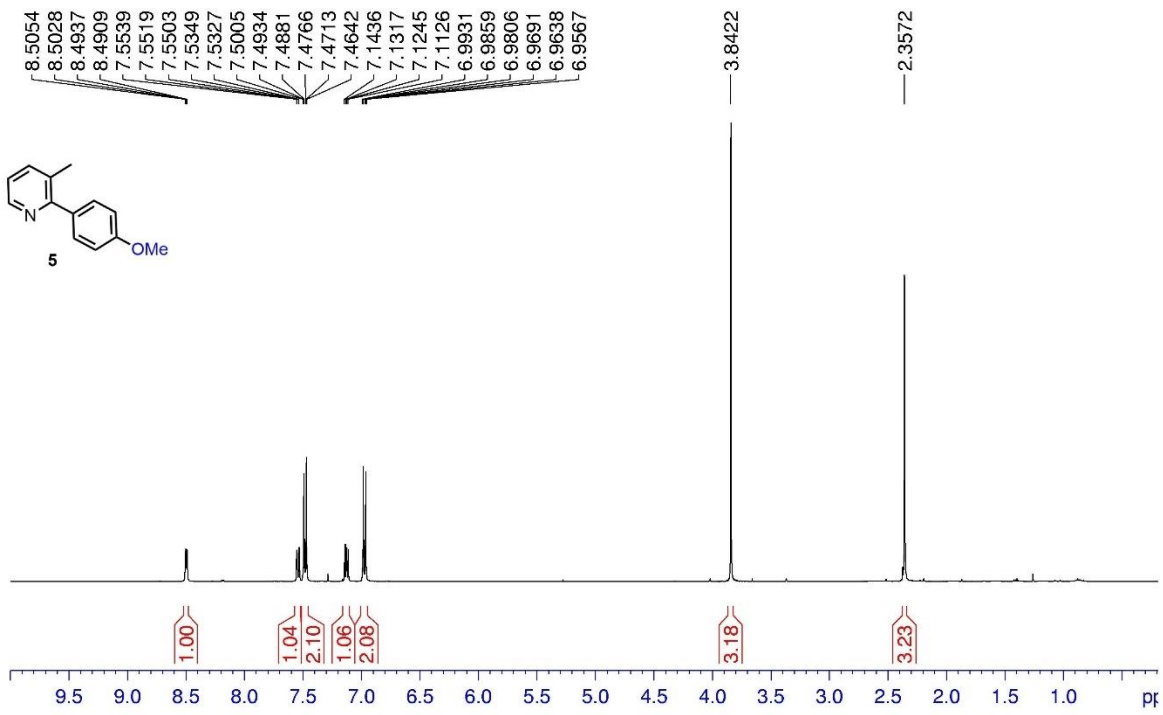
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OMe
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1.04
2.10
1.06
2.08
3.18
3.23
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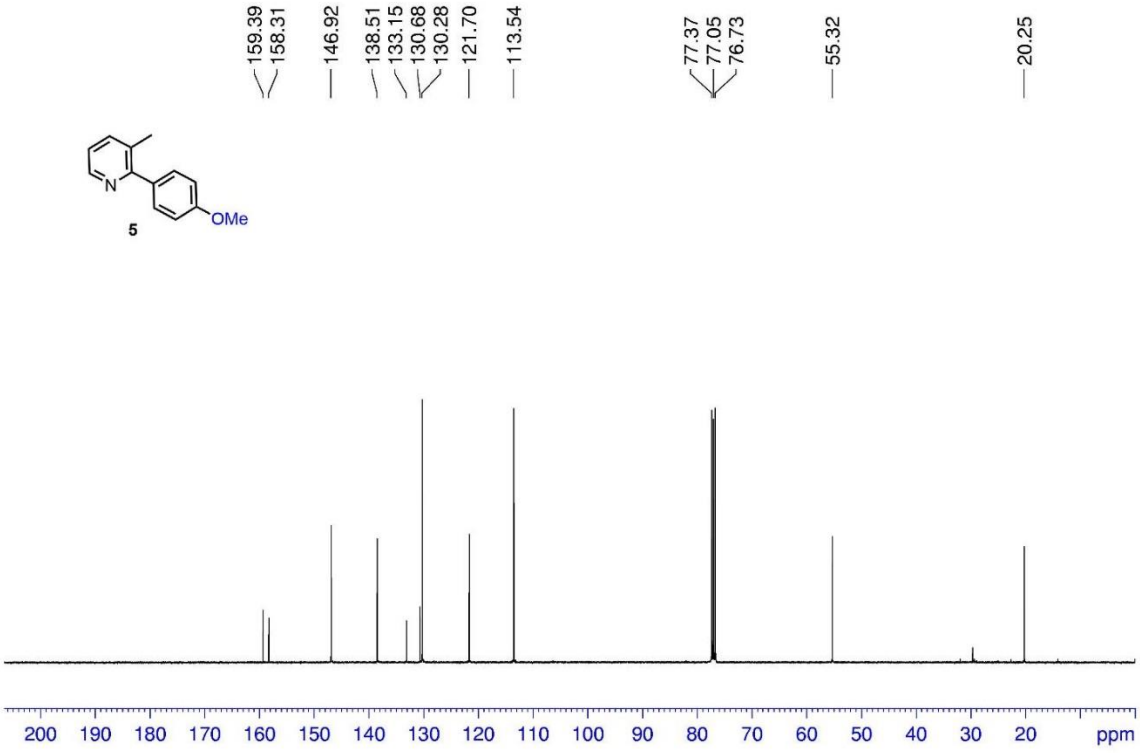
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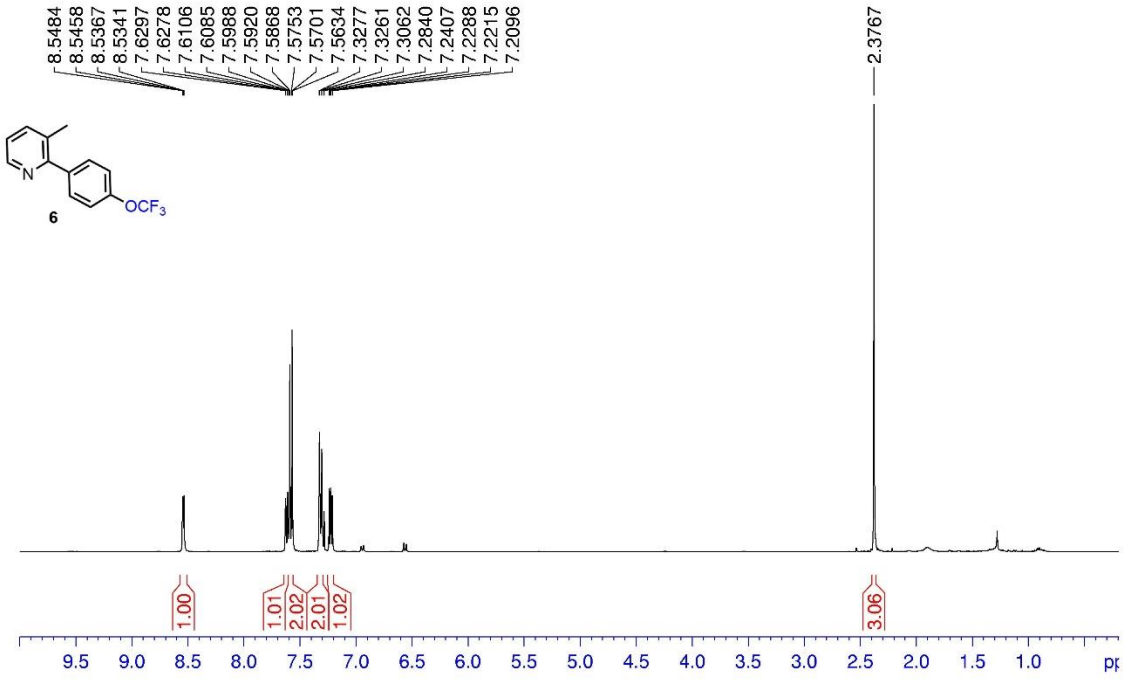
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7.2215
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OCF3
6
1.00
1.01
2.02
2.01
1.02
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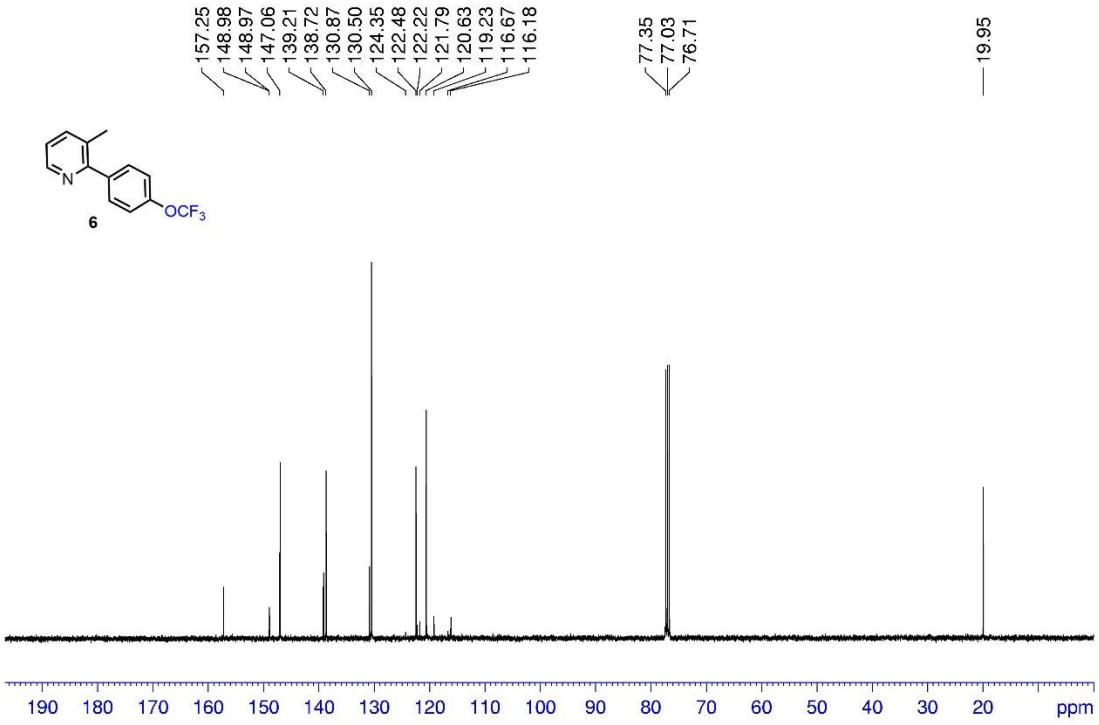
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OCF3
6
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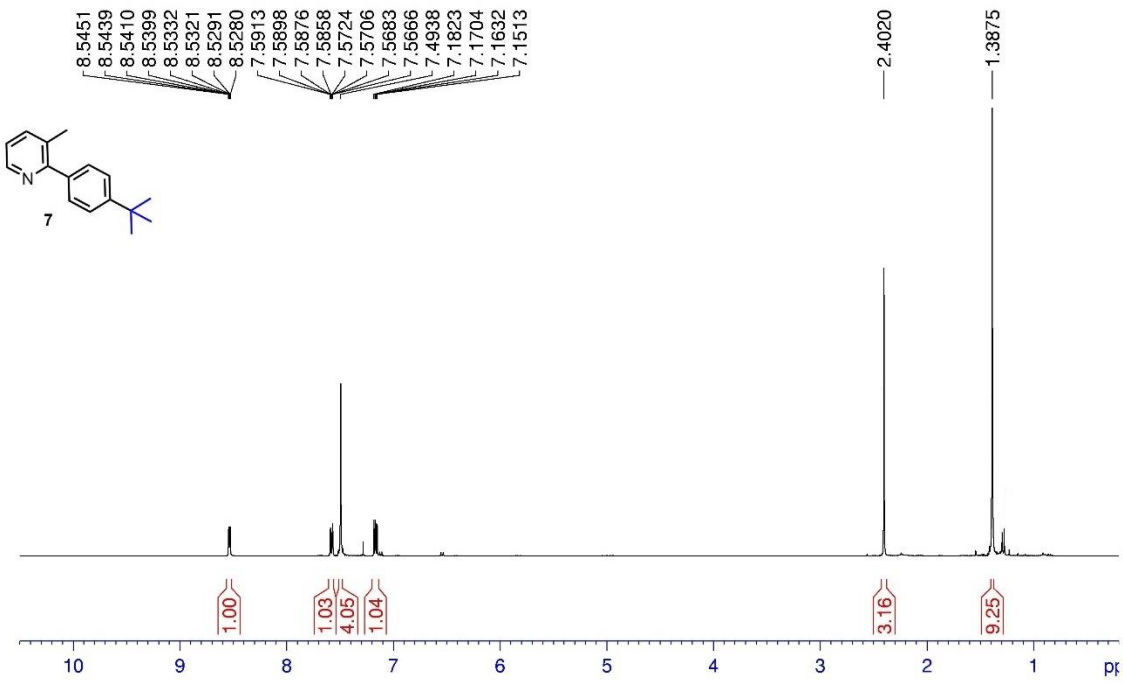
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7.5706
7.5683
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7.1632
7.1513
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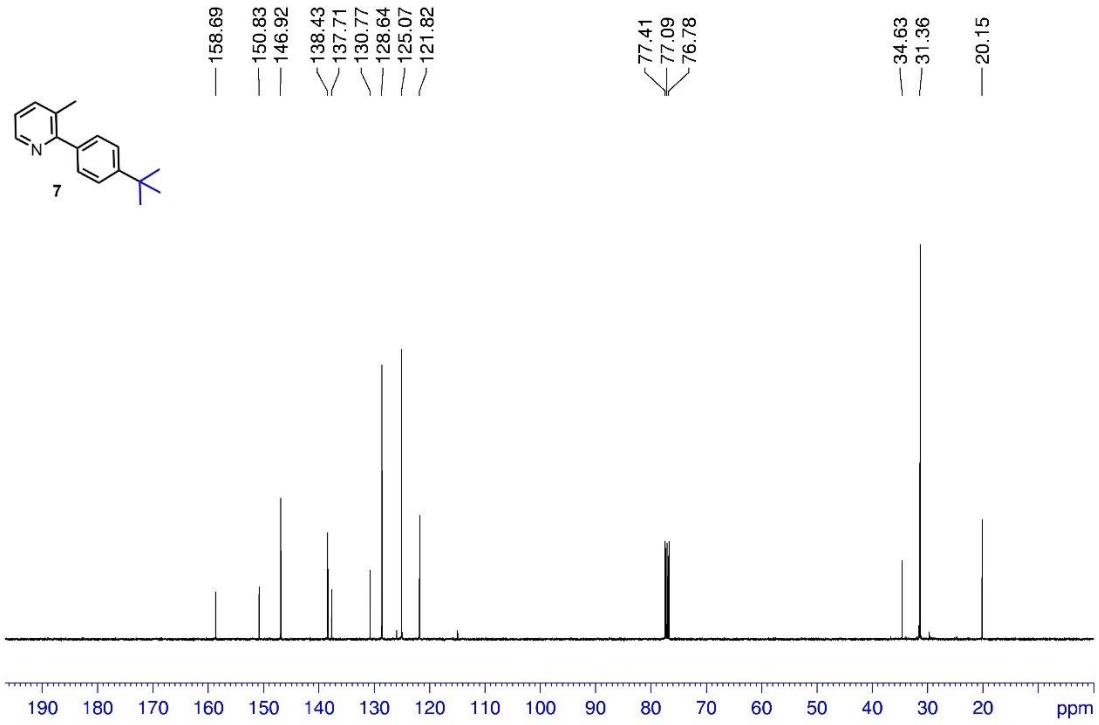
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20.15
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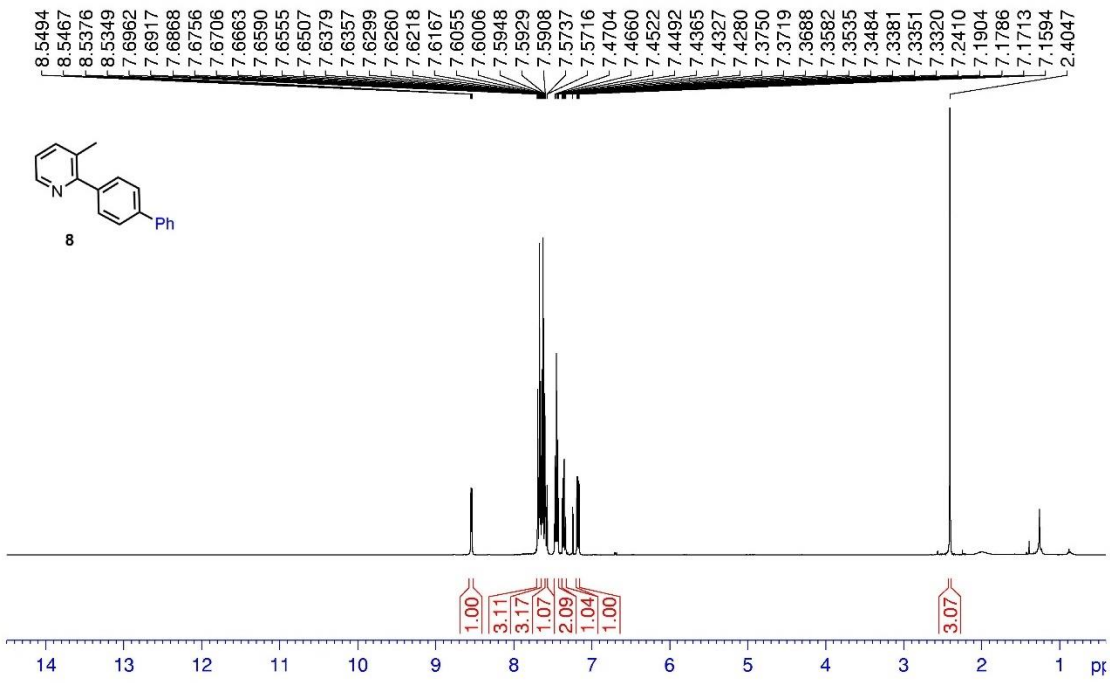
20
ppm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Ph
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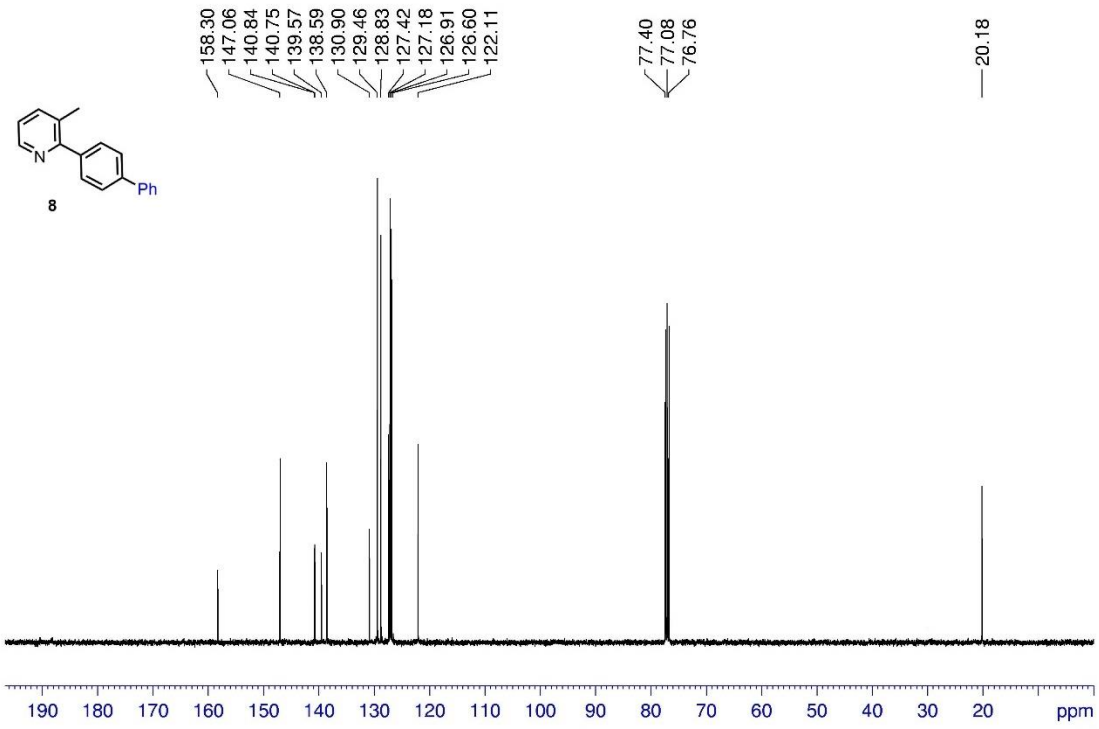
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77.40
77.08
76.76
20.18
N
Ph
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150
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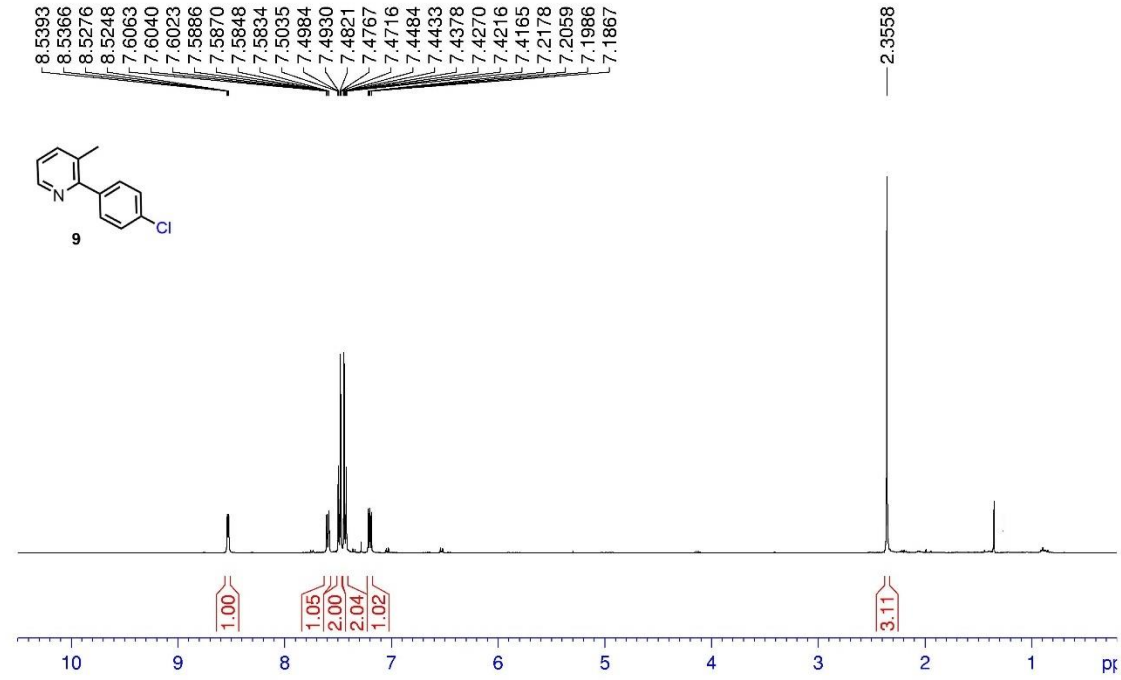
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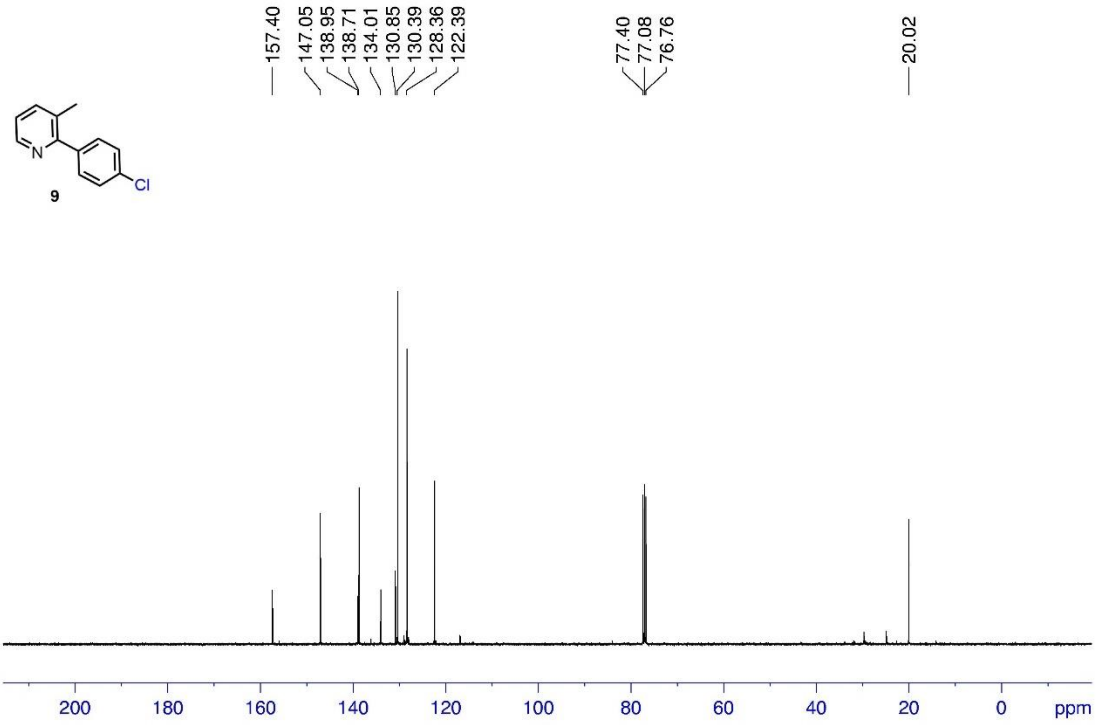
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Cl
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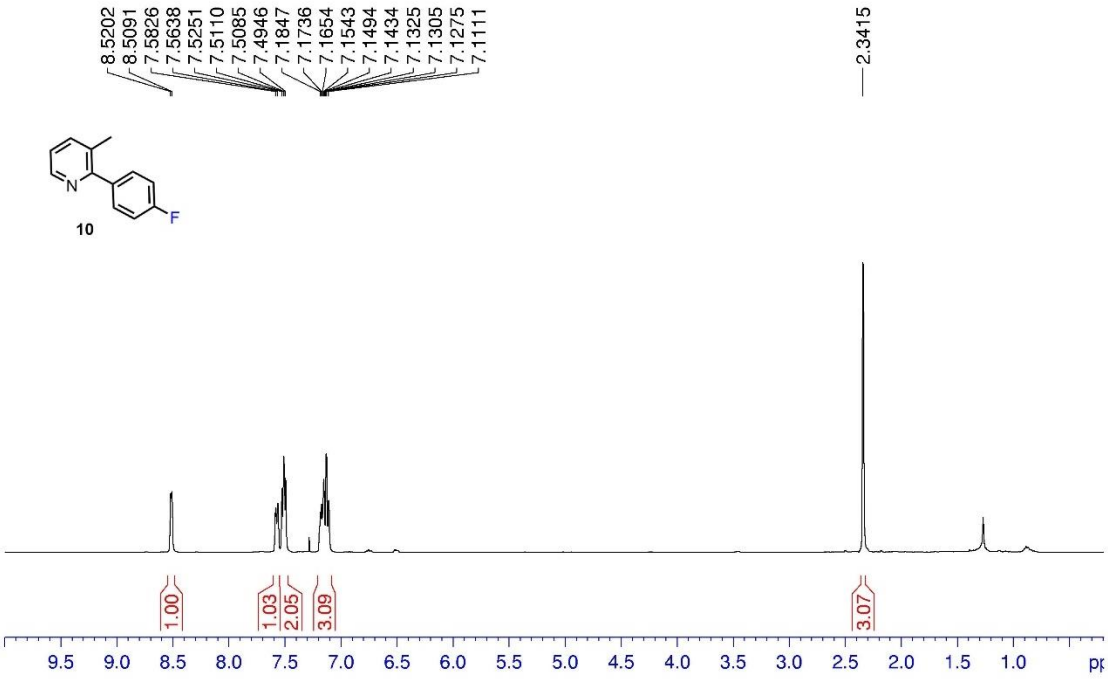
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10
1.00
1.03
2.05
3.09
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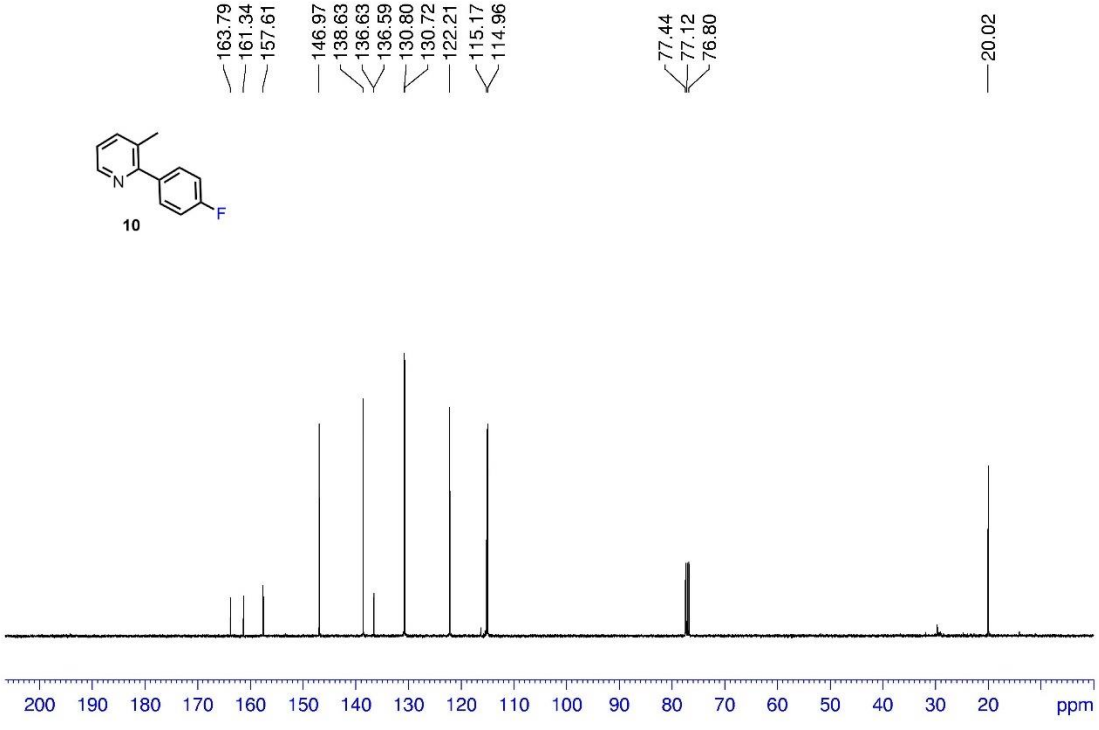
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10
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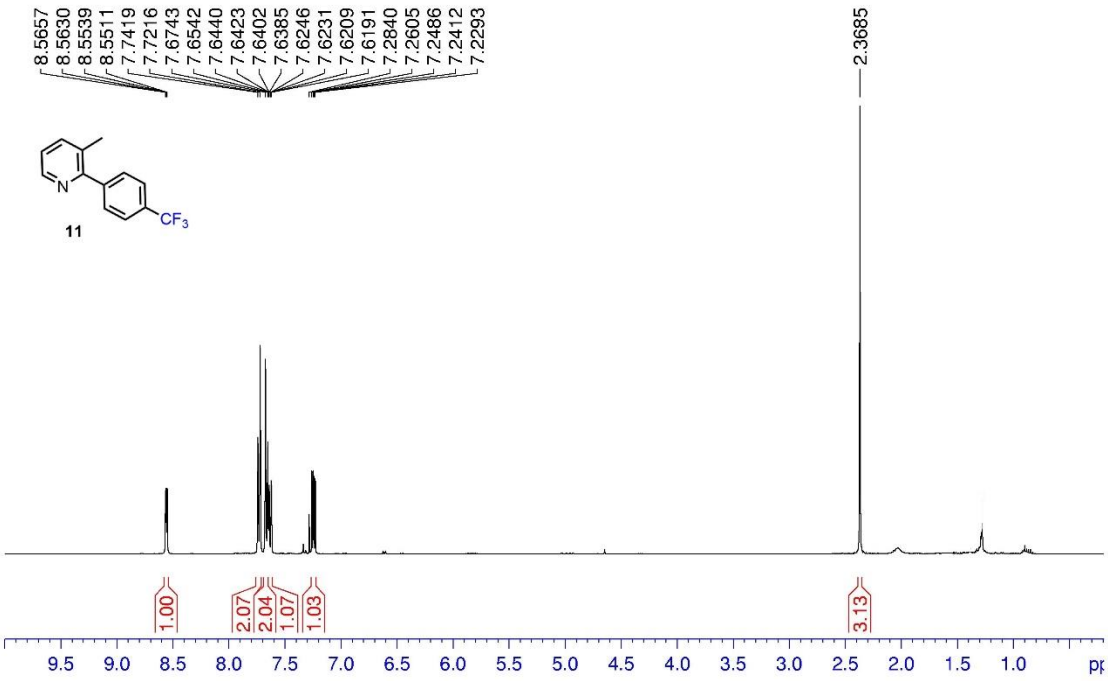
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7.2412
7.2293
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11
CF3
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2.07
2.04
1.07
1.03
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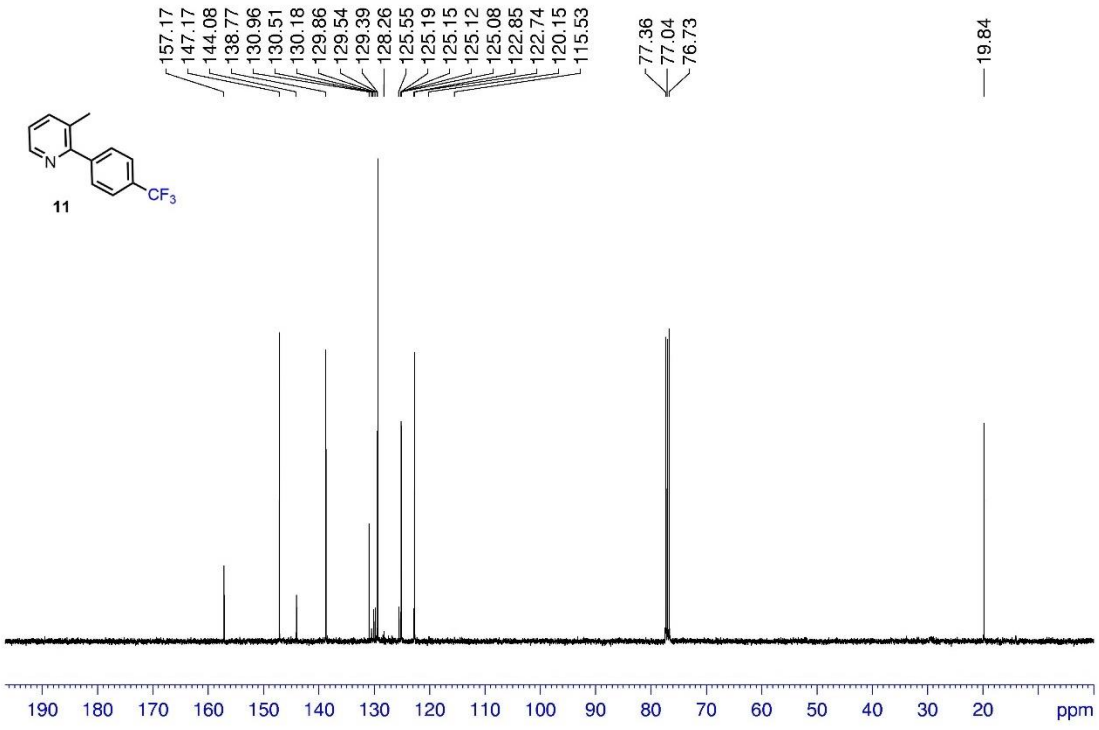
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125.12
125.08
122.85
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77.04
76.73
19.84
11
CF3
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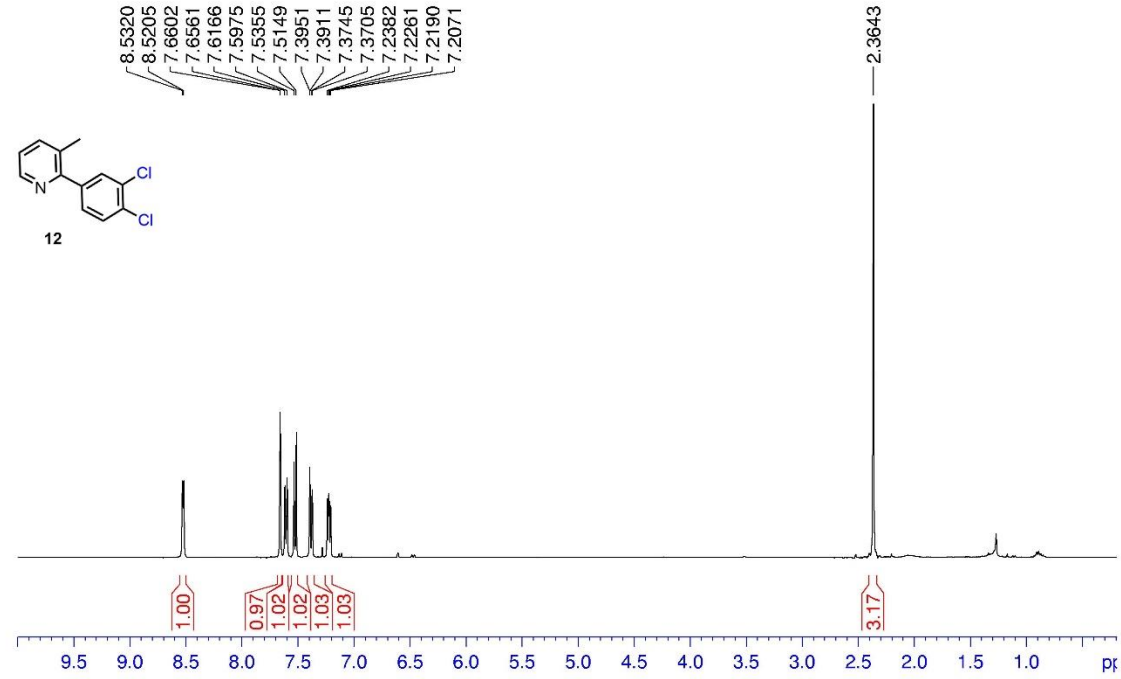
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7.3705
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7.2261
7.2190
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Cl
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1.02
1.03
1.03
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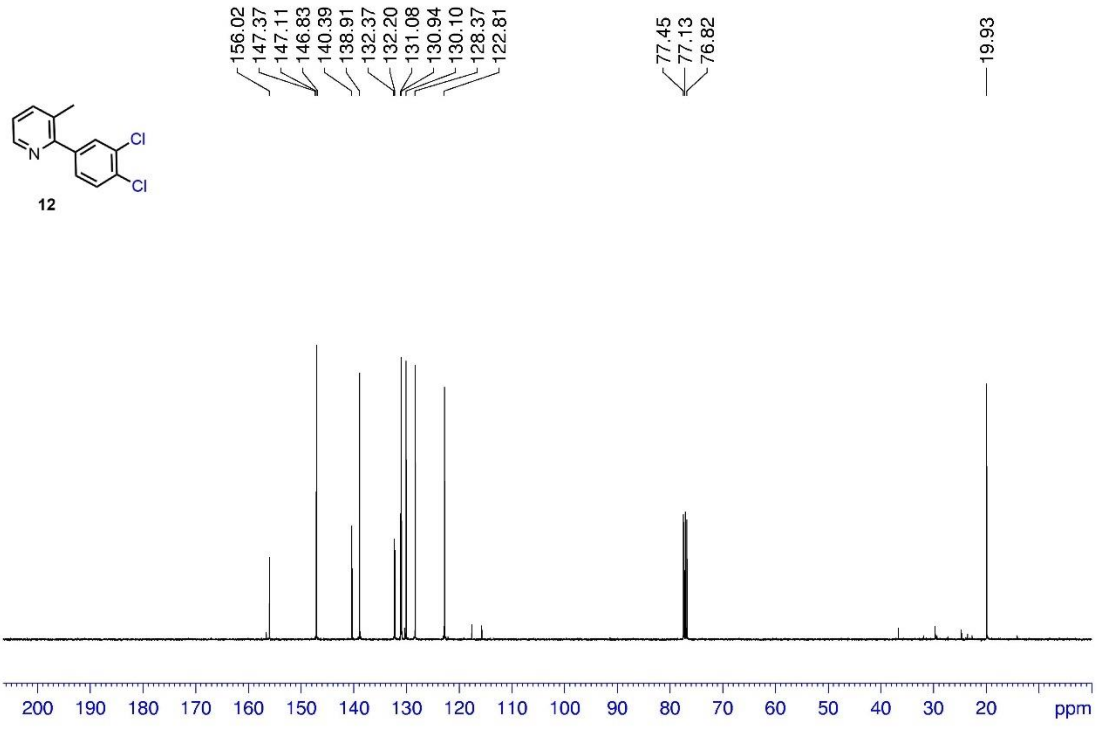
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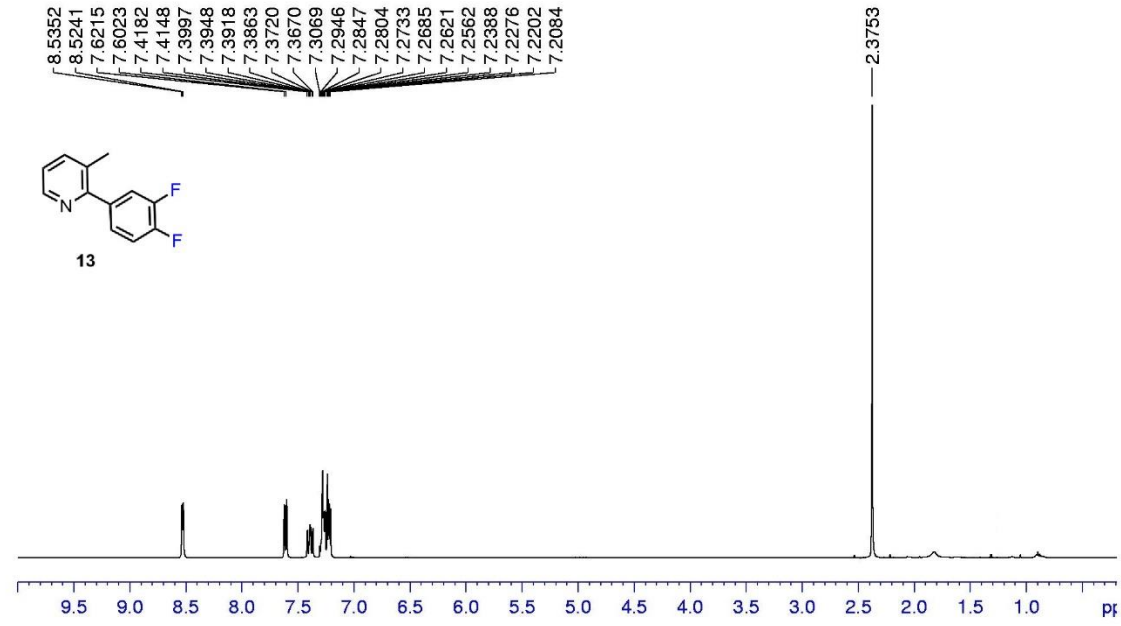
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7.2084
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F
F
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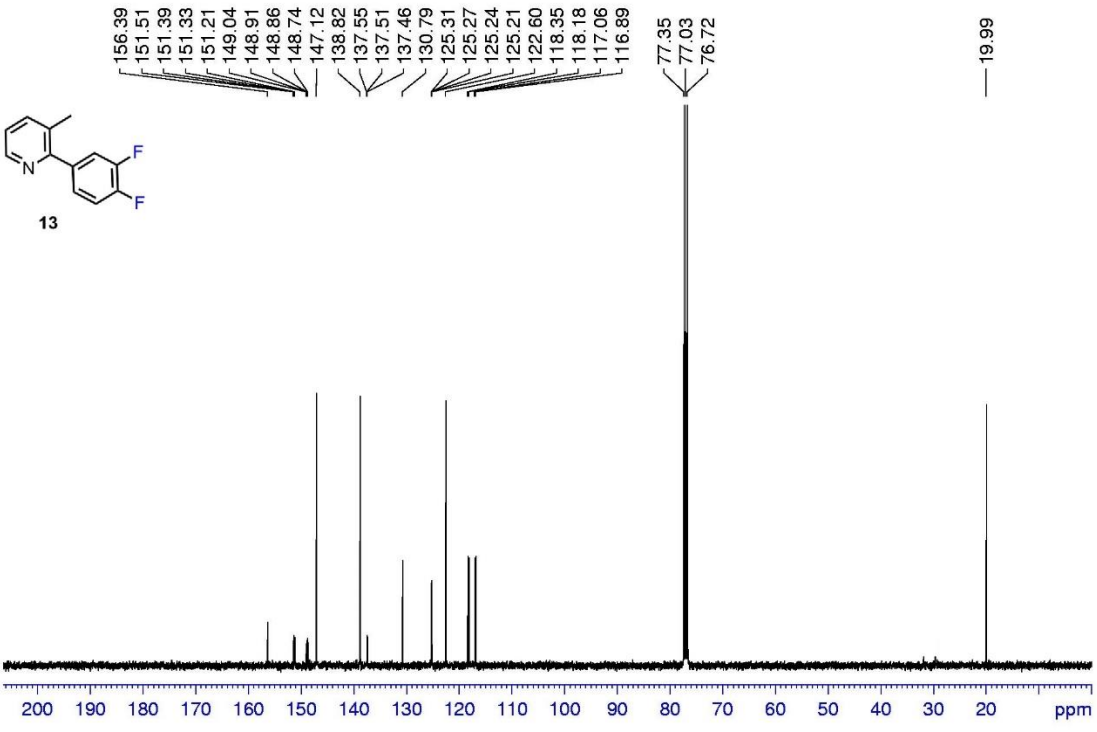
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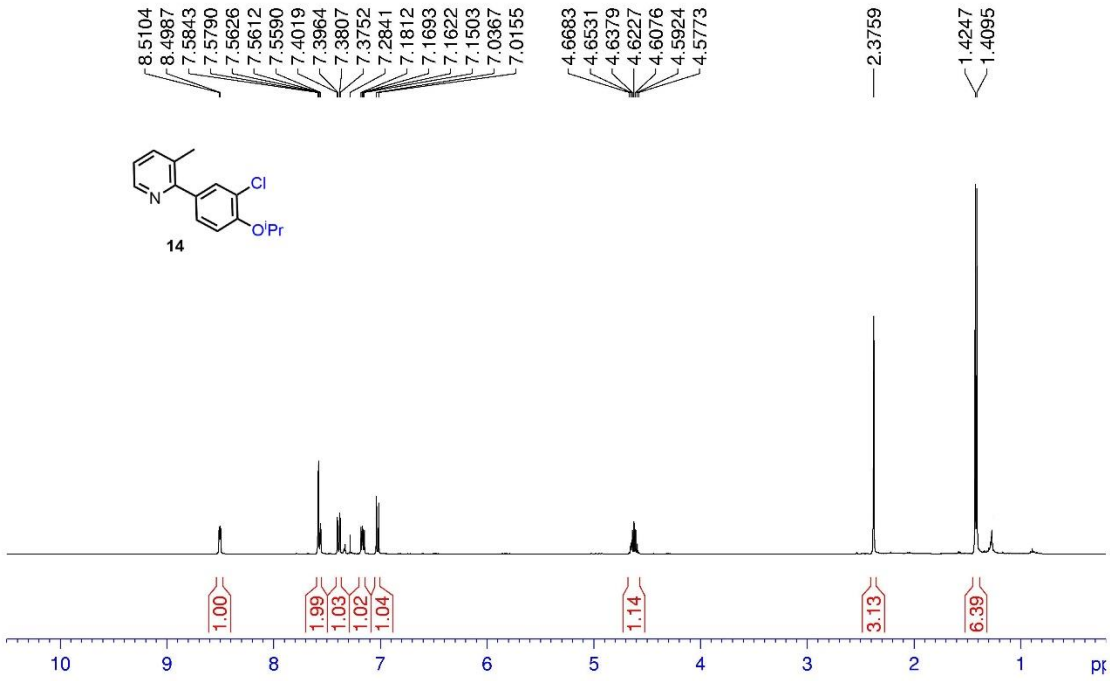
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4.6227
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Cl
OiPr
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1.99
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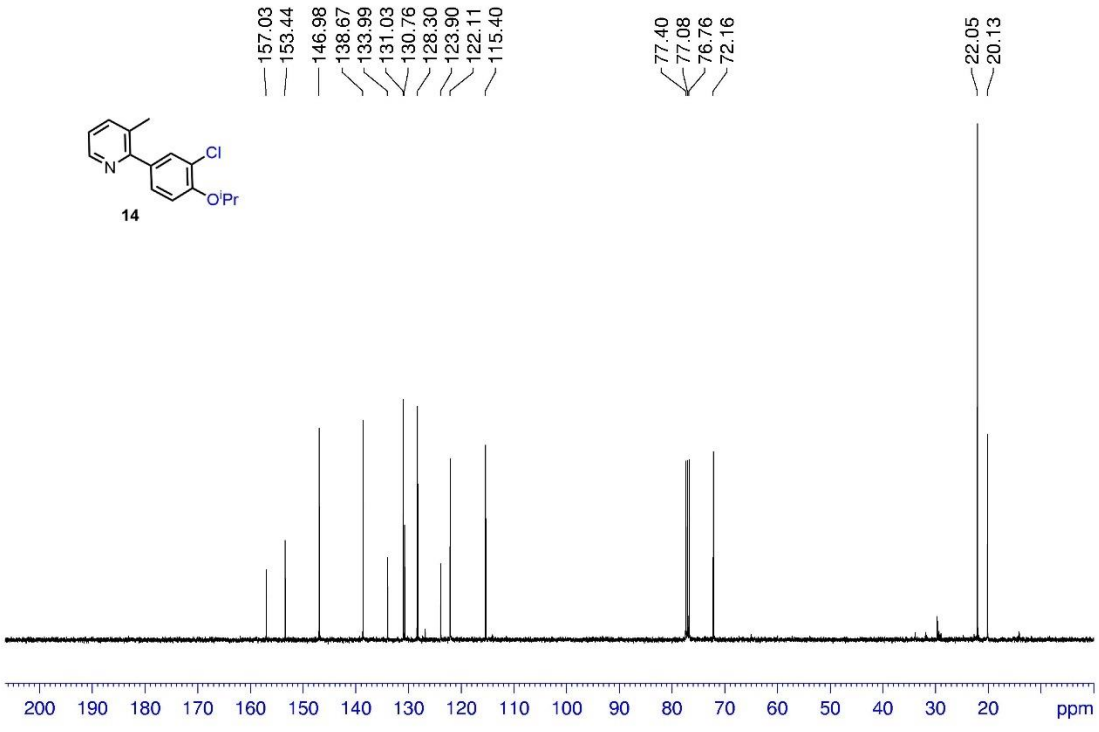
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76.76
72.16
22.05
20.13
Cl
OiPr
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120
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80
70
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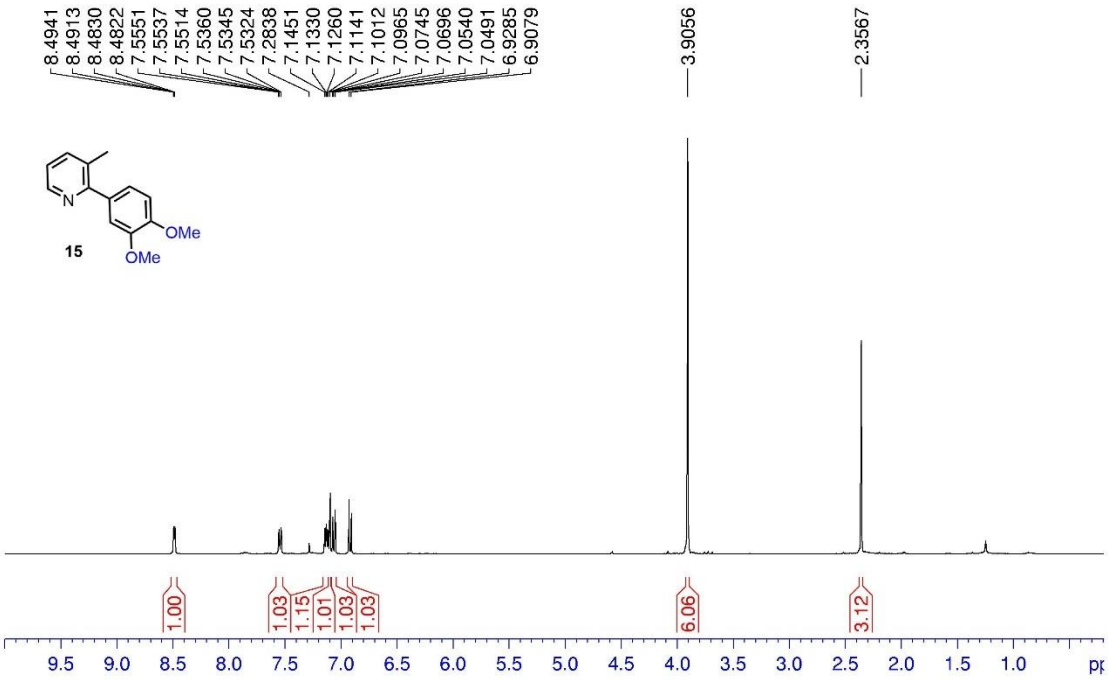
30
20
ppm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6.9079
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OMe
OMe
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1.00
1.03
1.15
1.01
1.03
1.03
6.06
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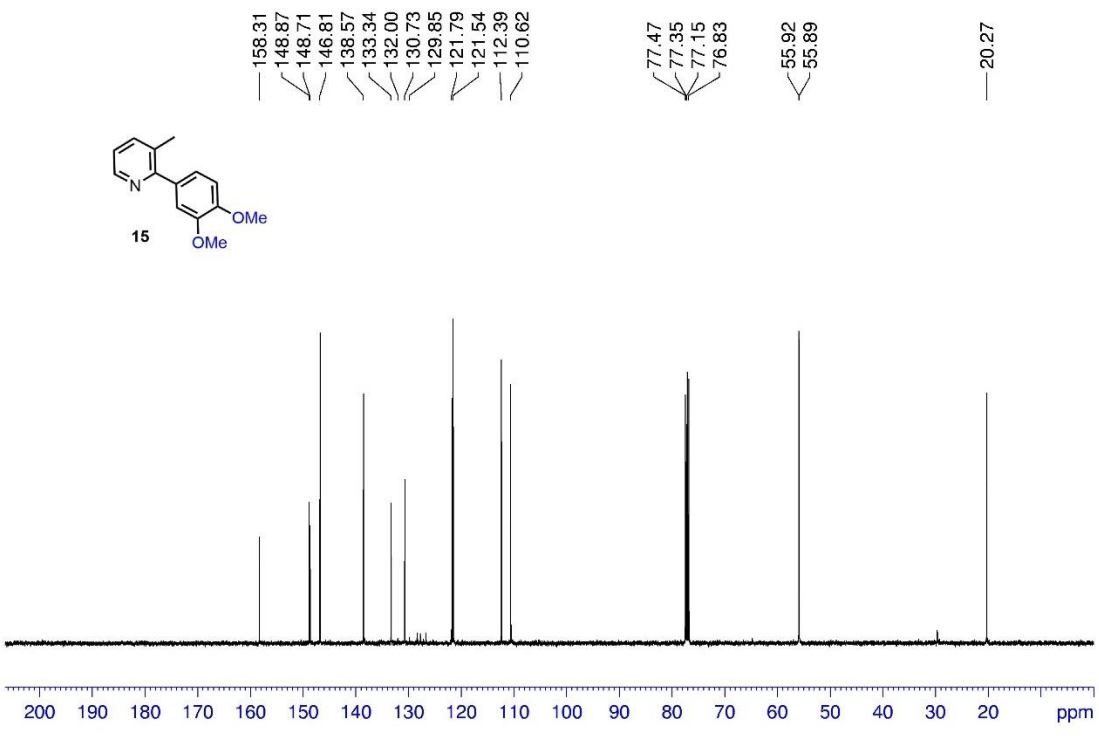
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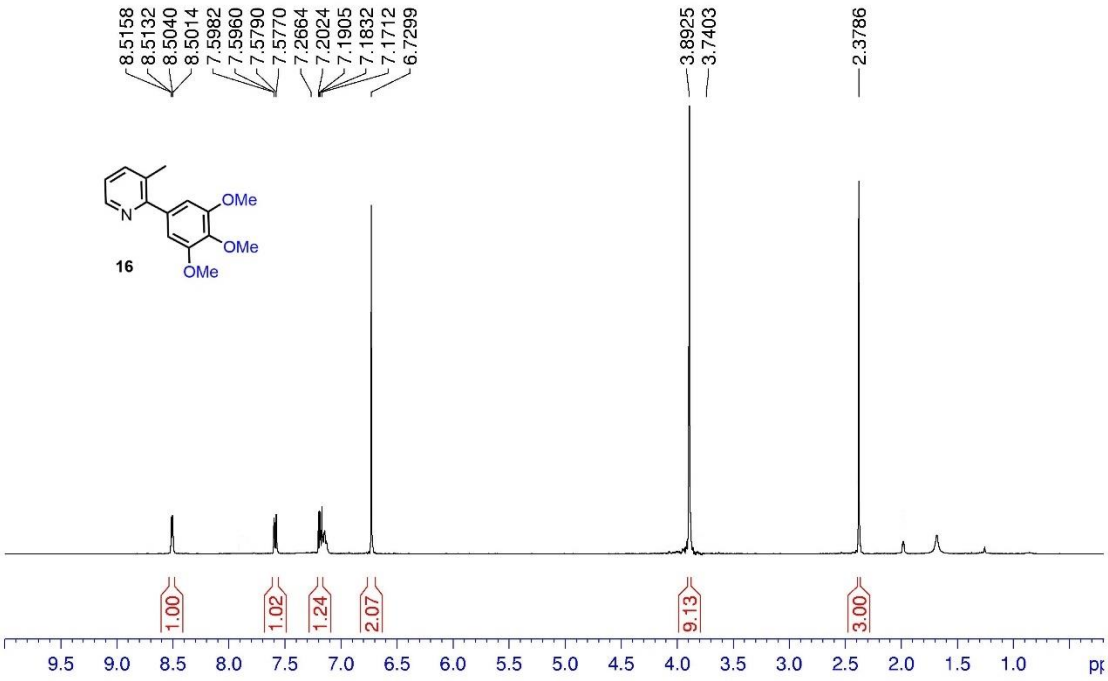
20.27
OMe
OMe
15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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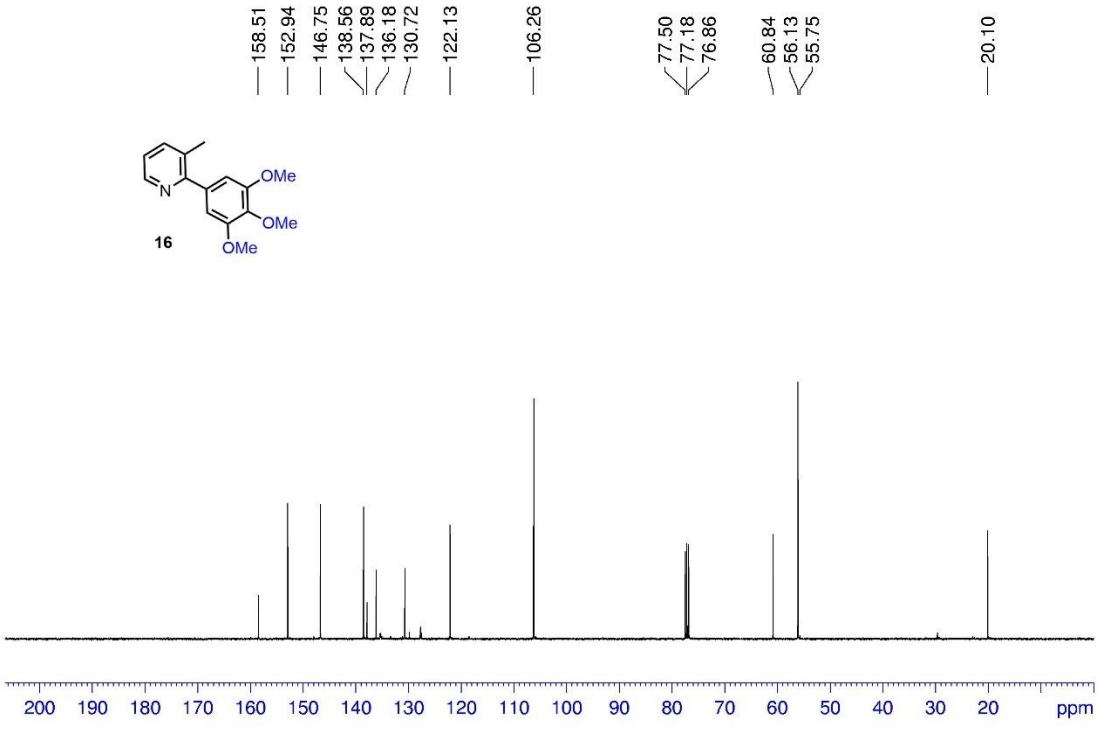
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OMe
OMe
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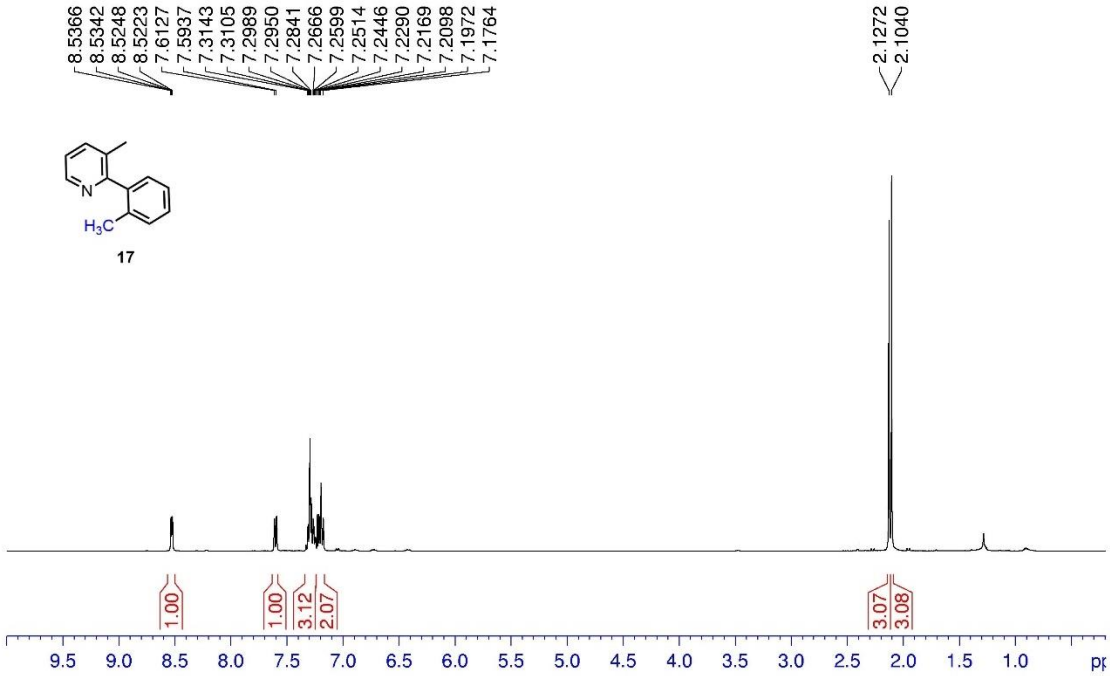
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1.00
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2.07
3.07
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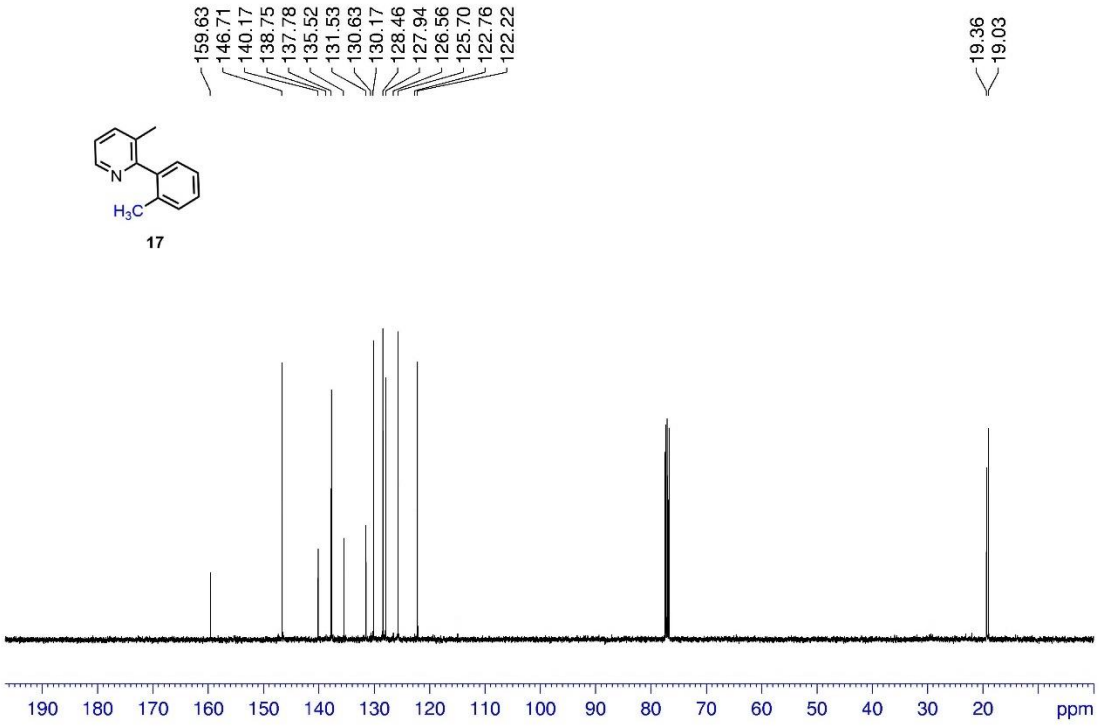
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17
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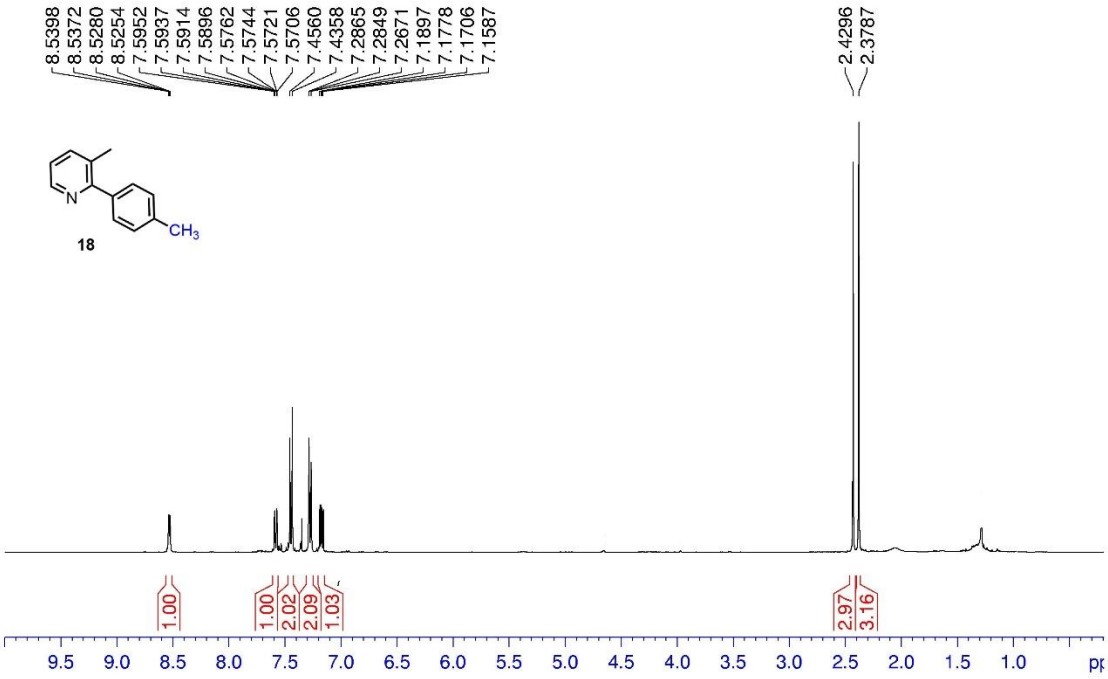
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2.09
1.03
2.97
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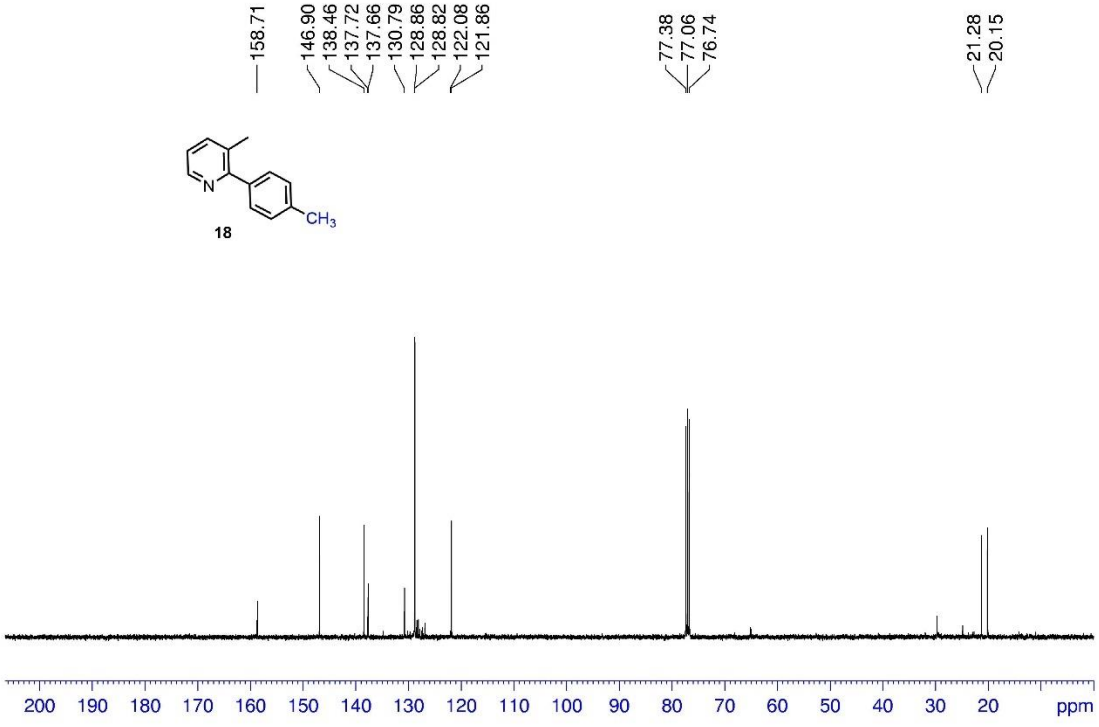
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CH3
18
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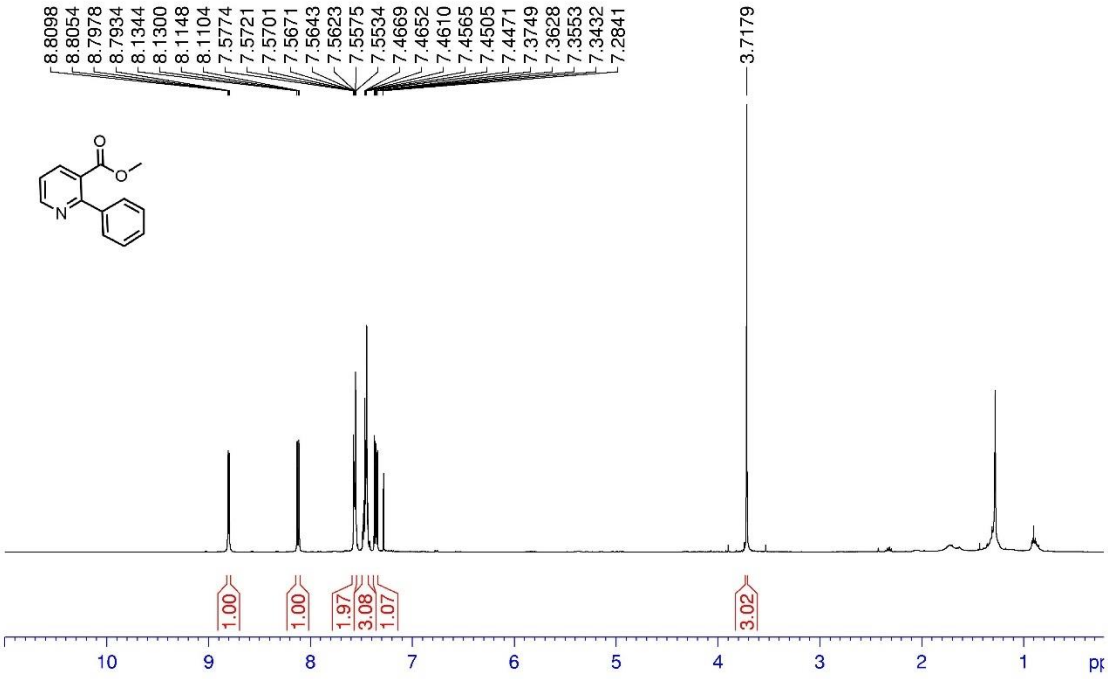
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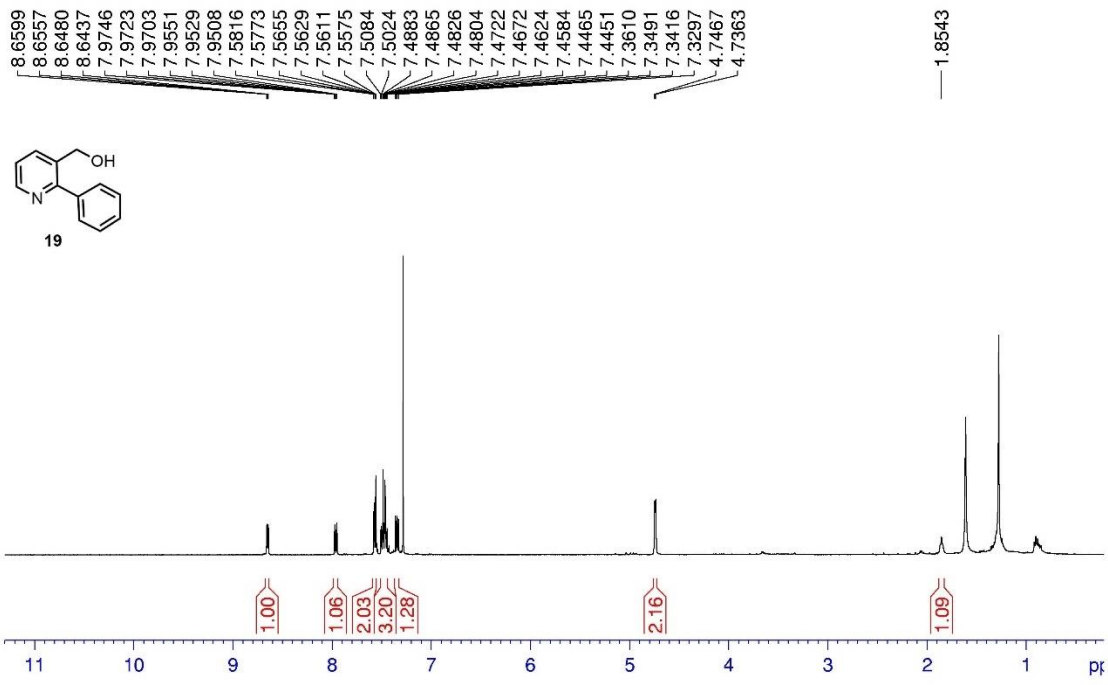
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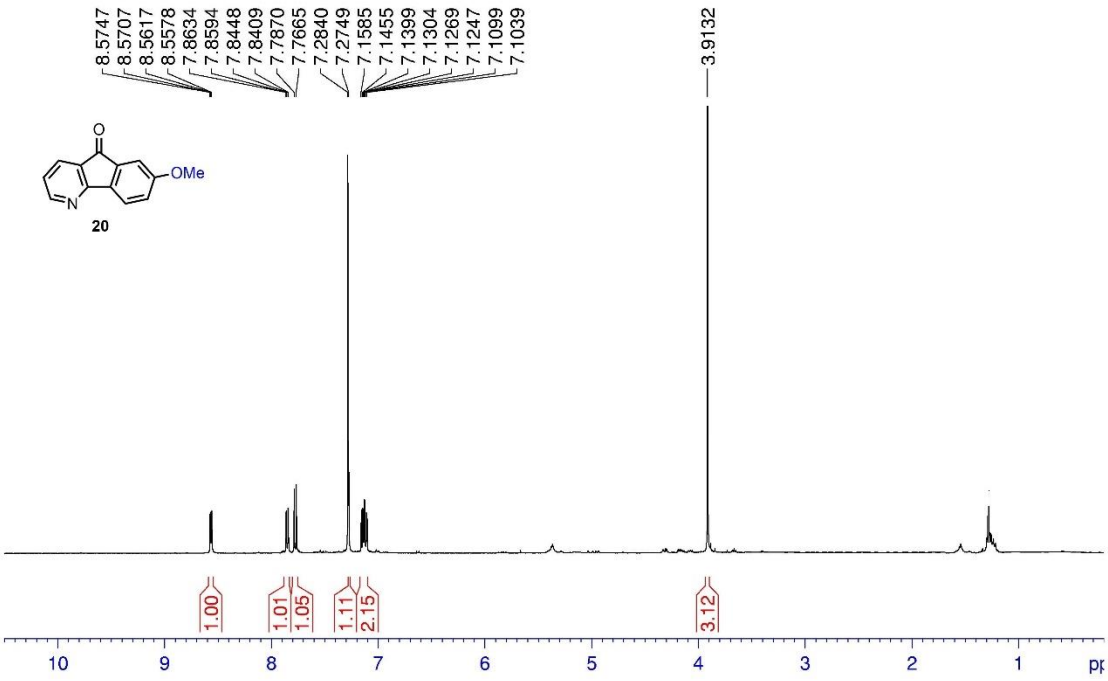
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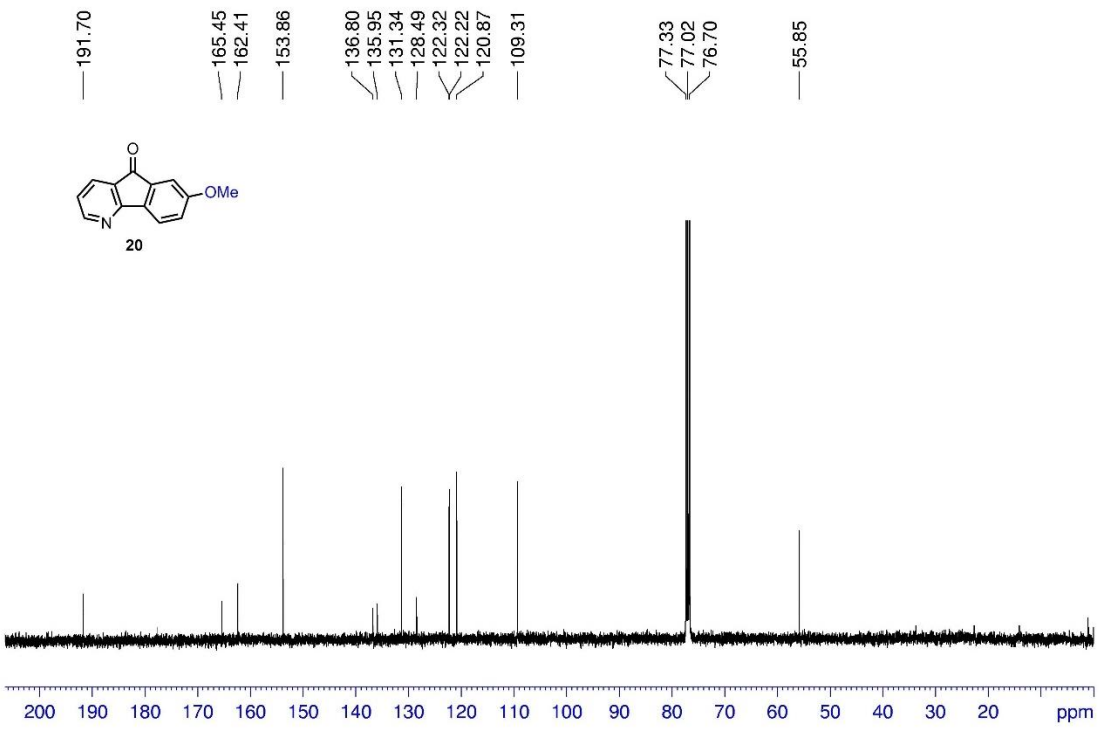
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OMe
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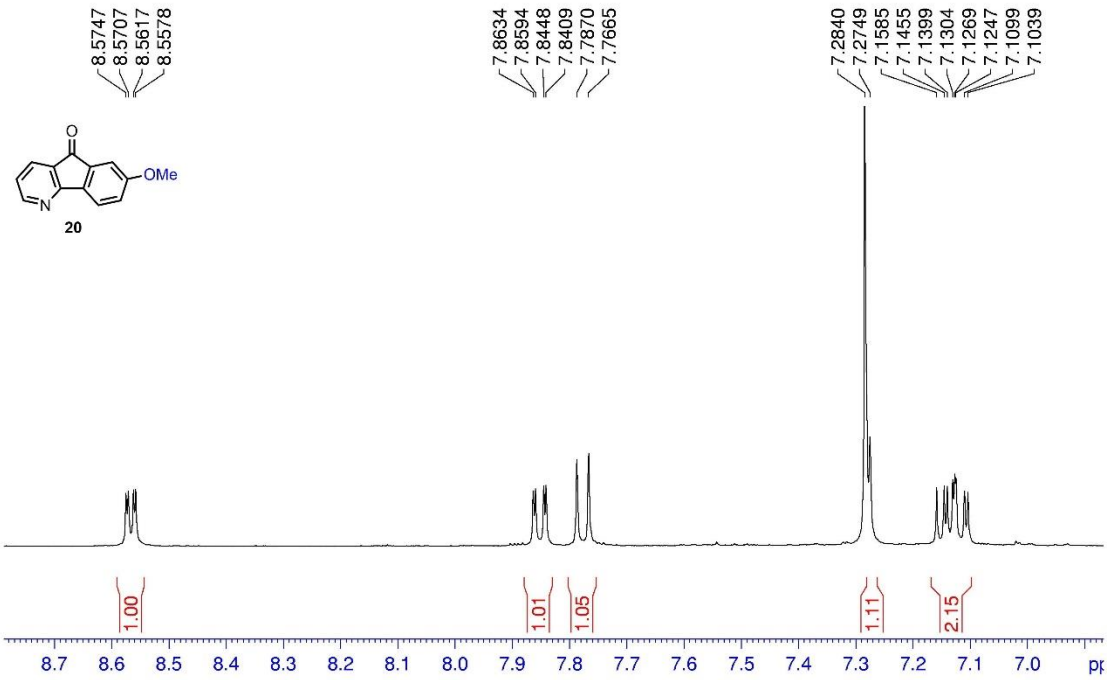
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OMe
N
20
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1.01
1.05
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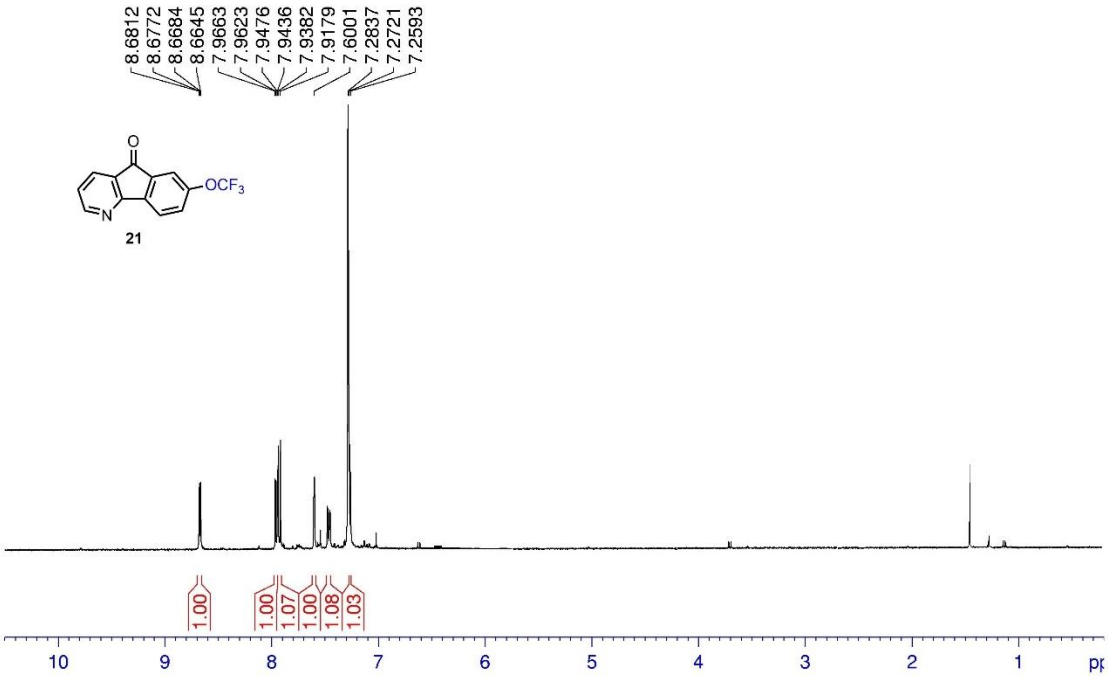
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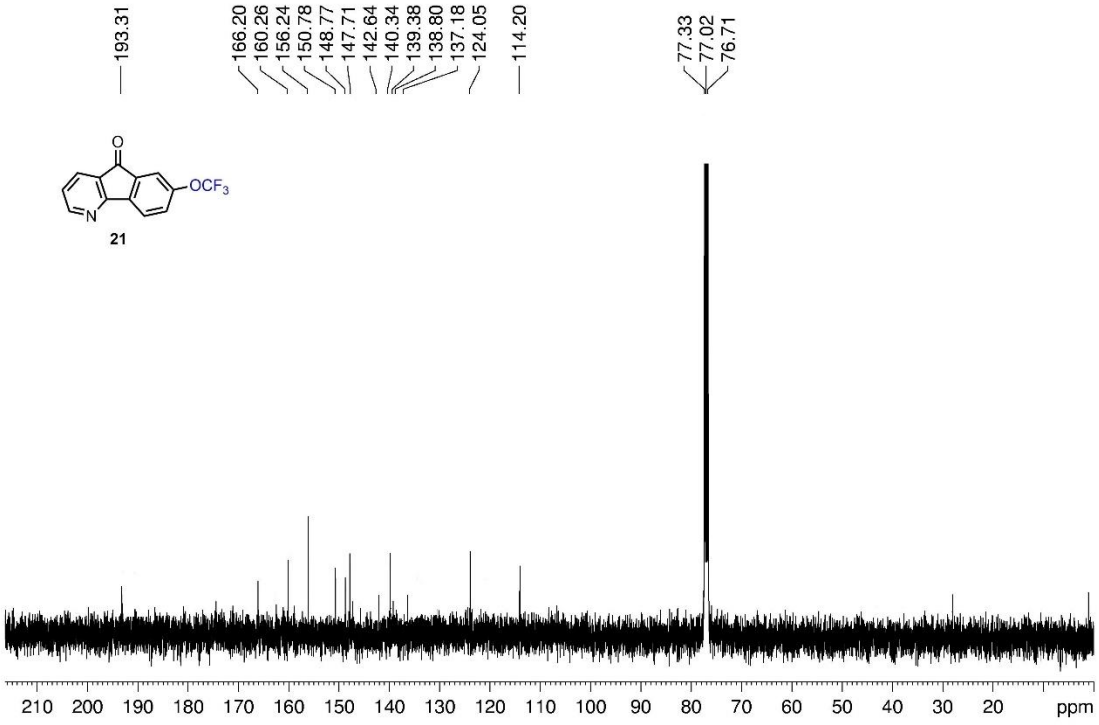
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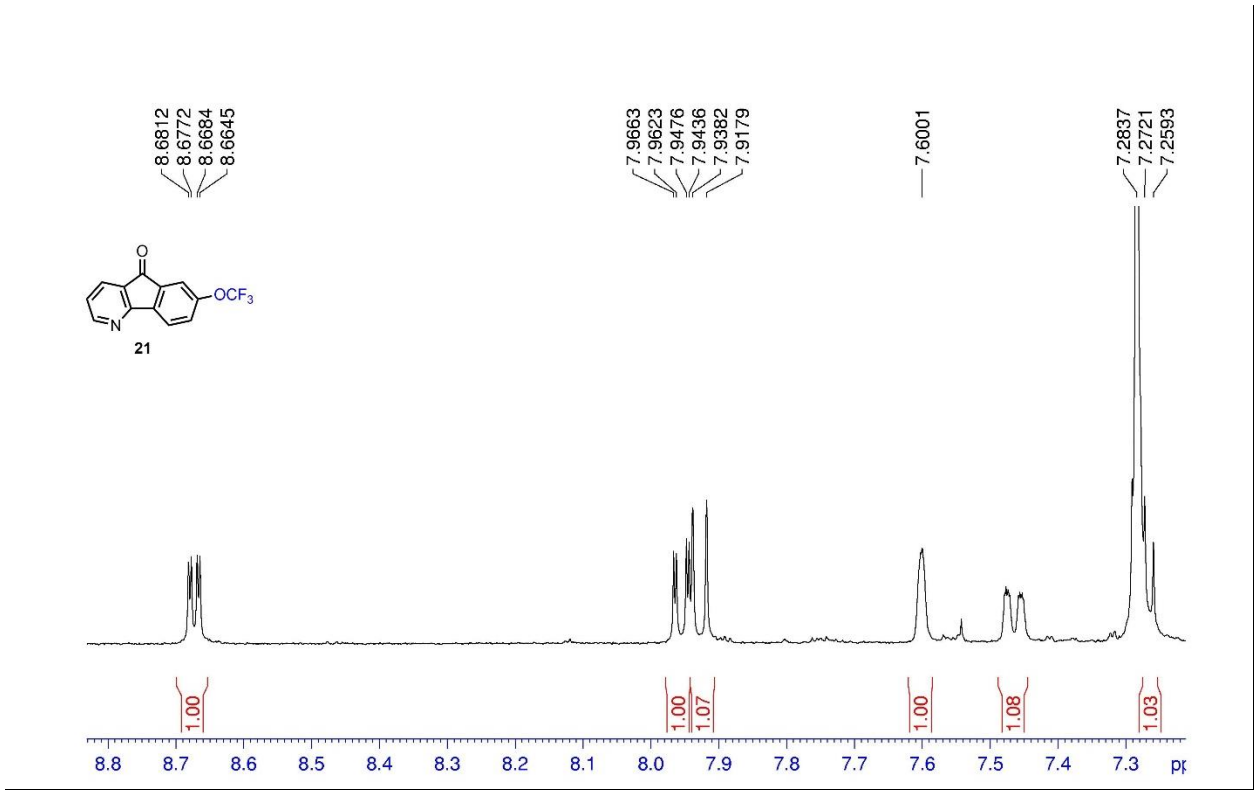
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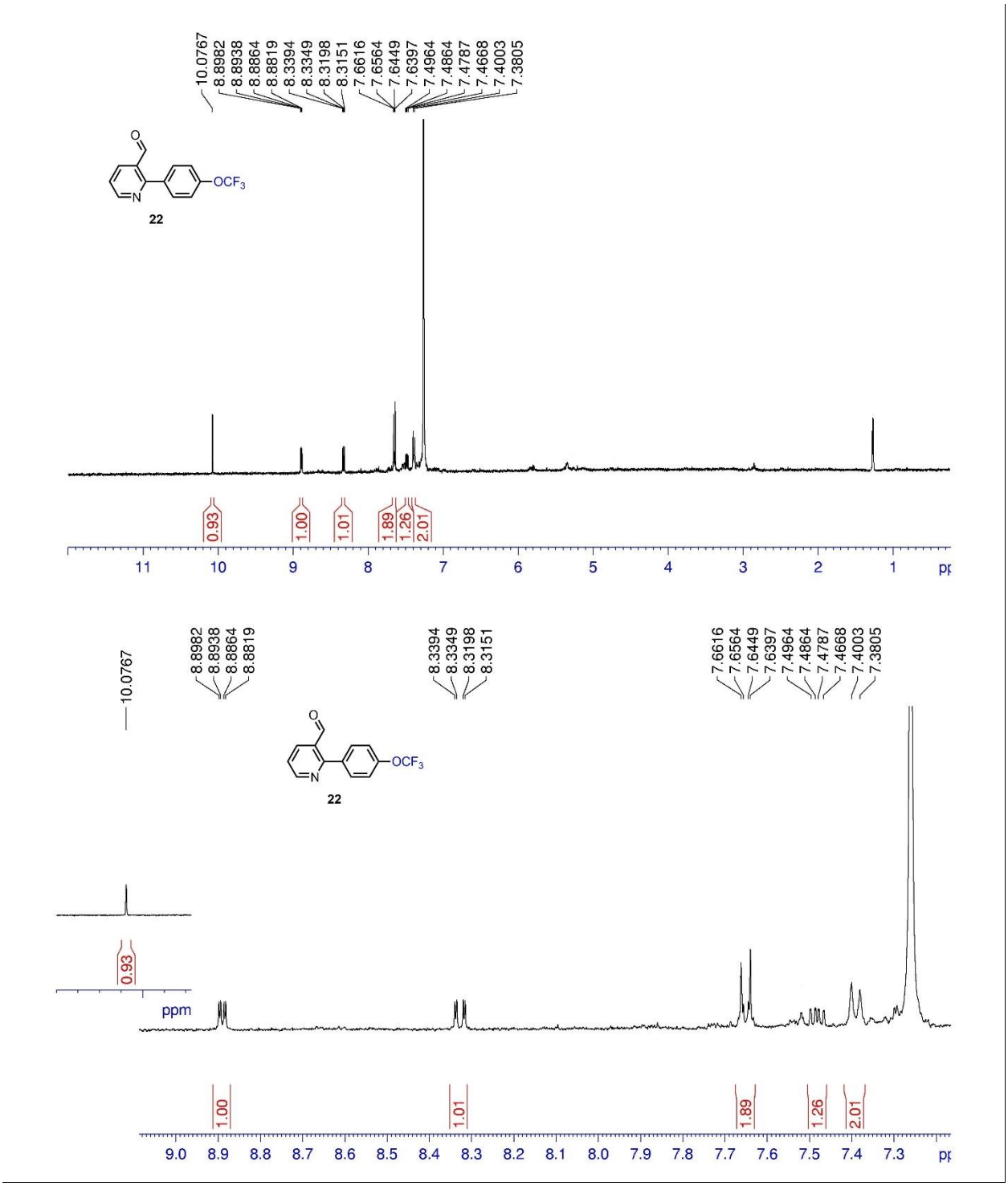
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ppm
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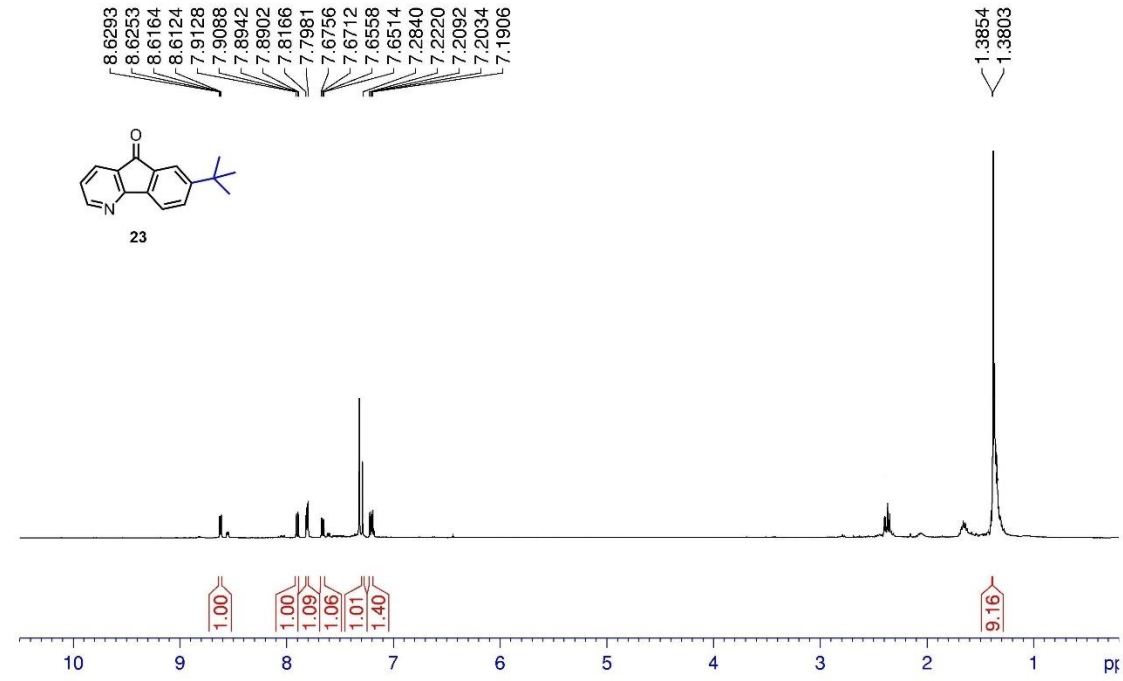
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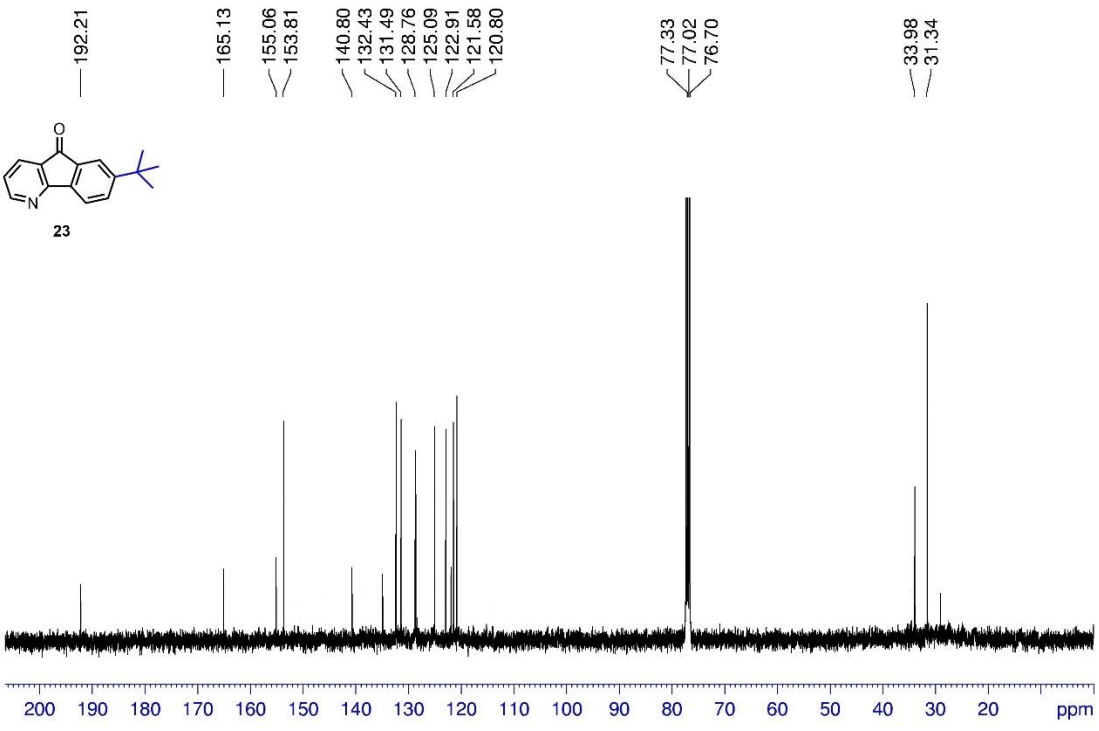
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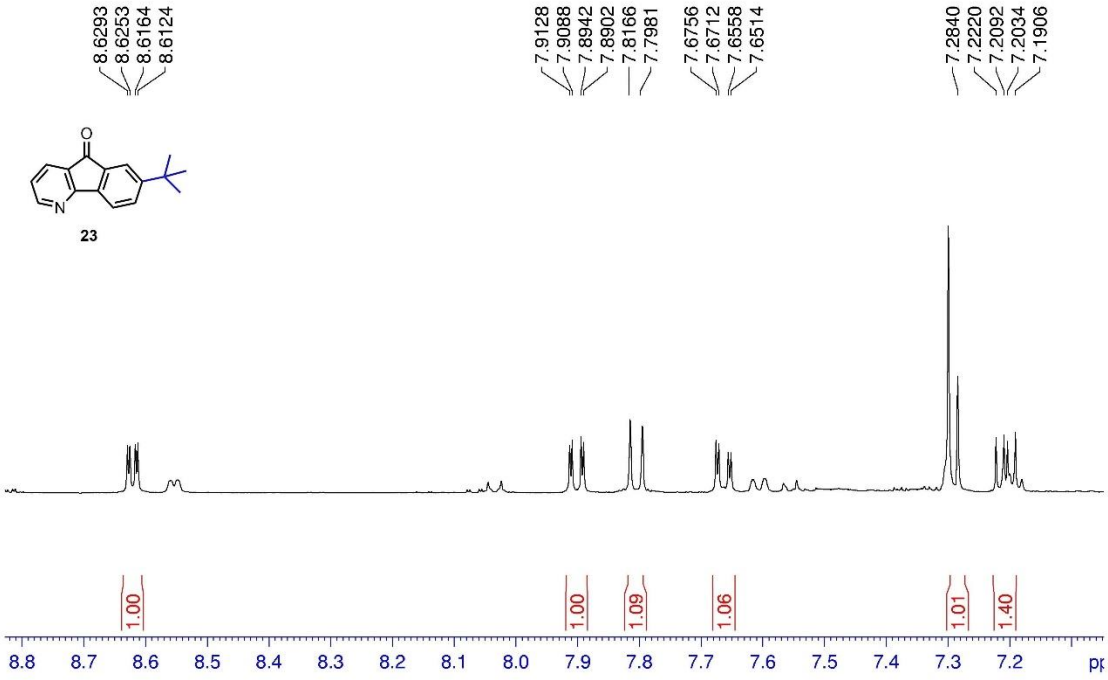
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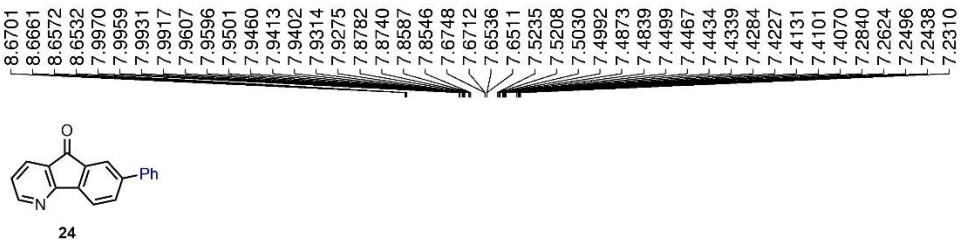
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N

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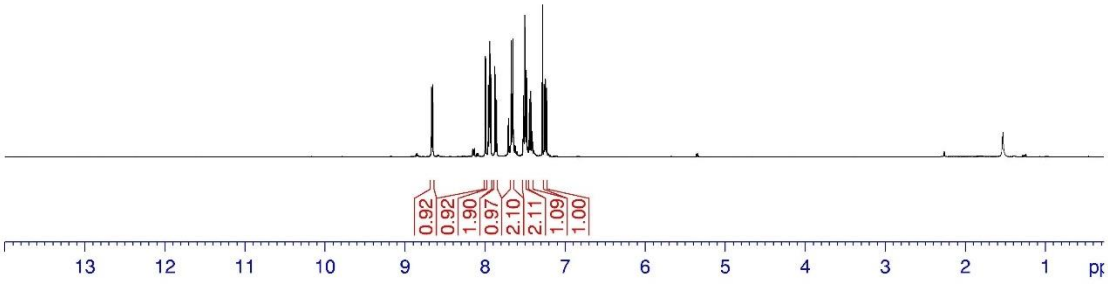
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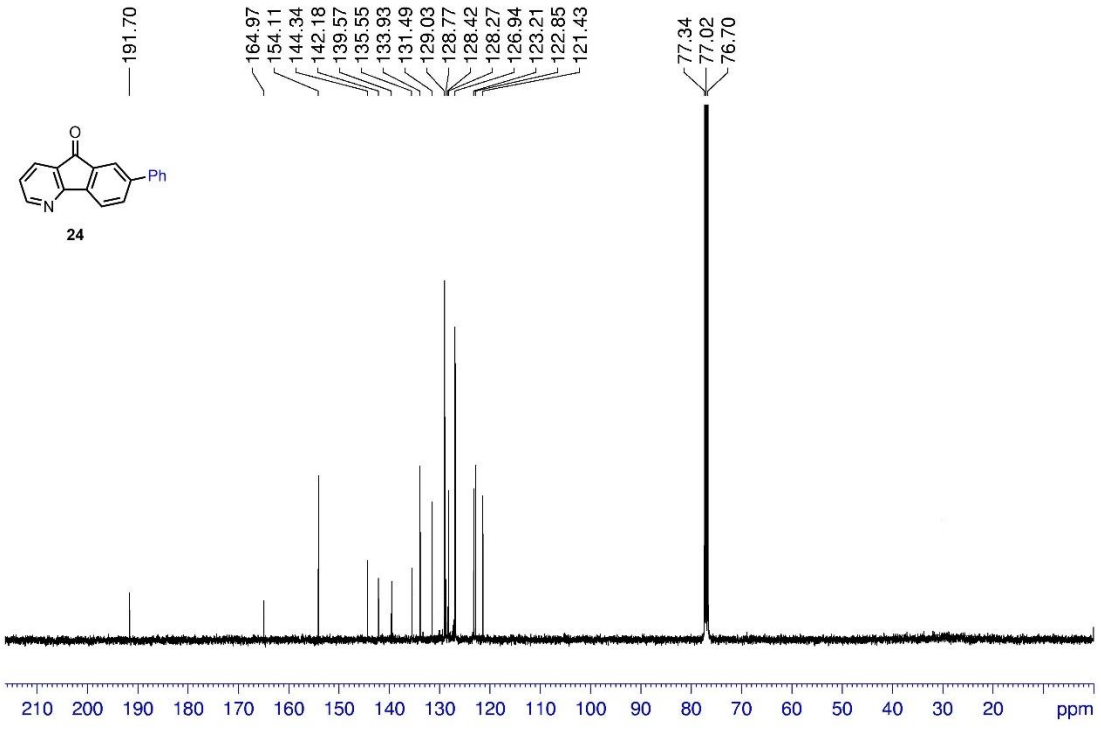
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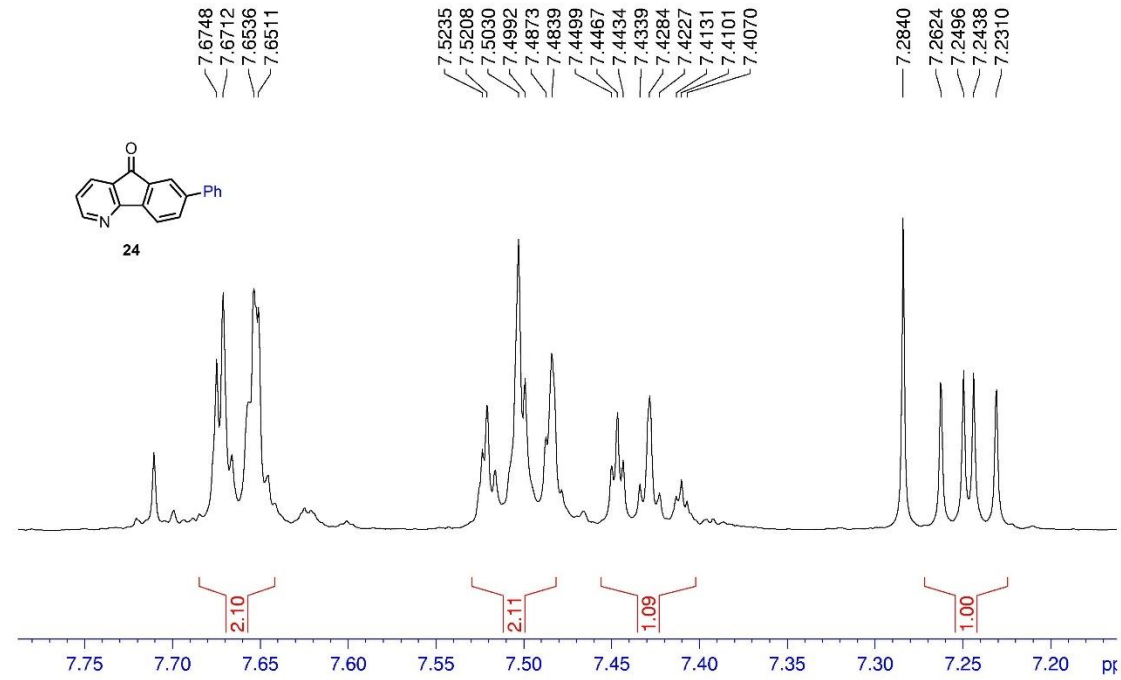
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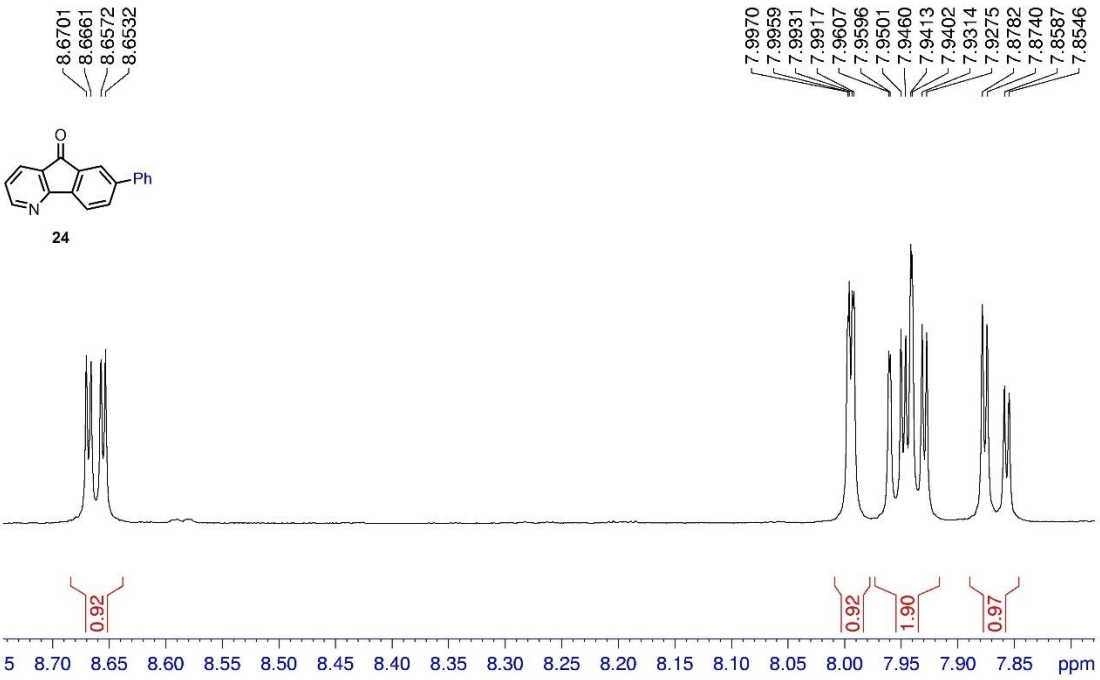
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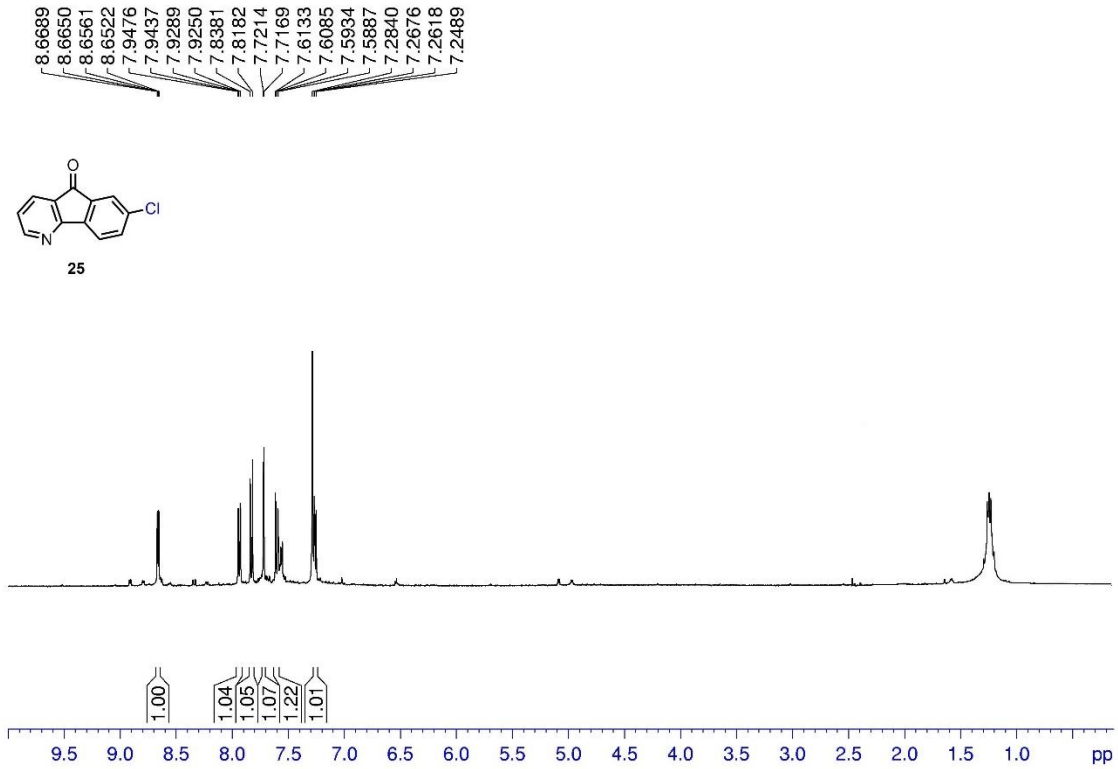
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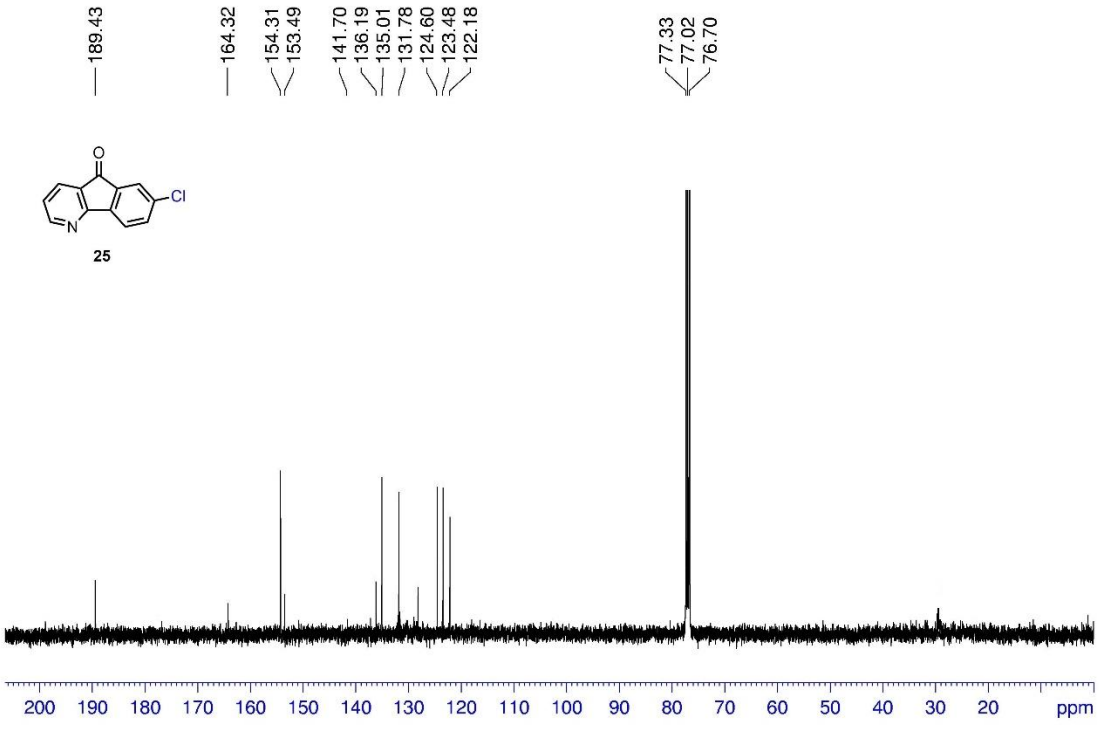
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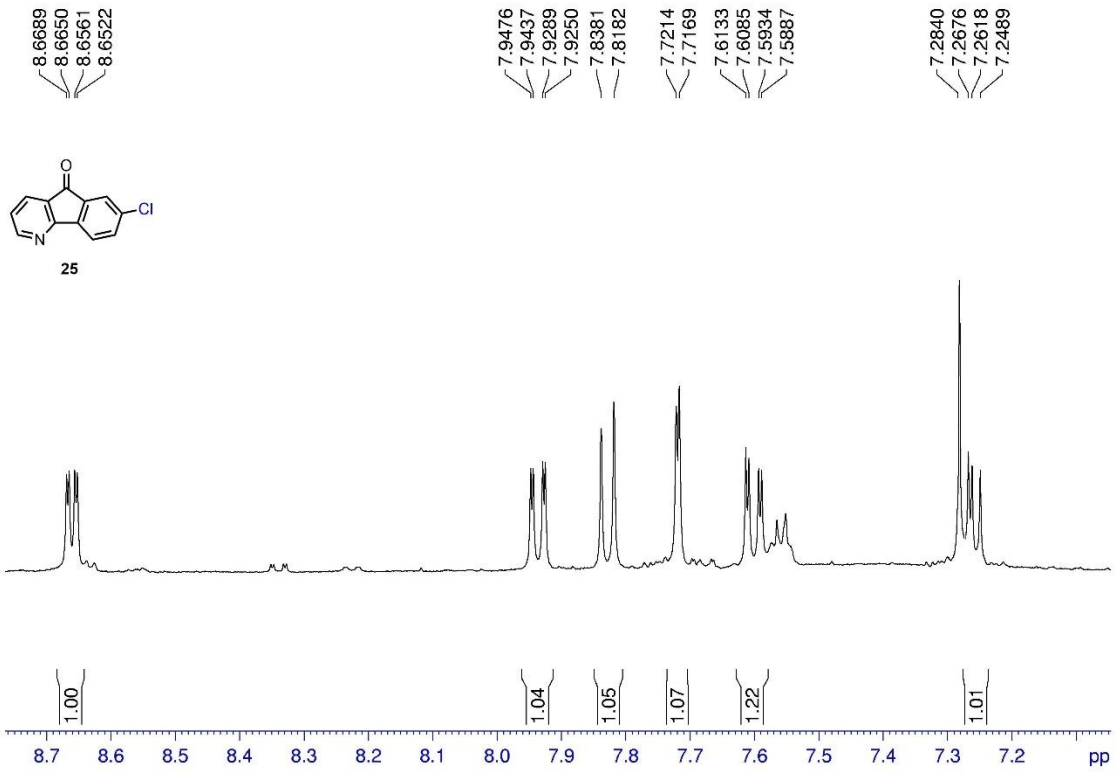
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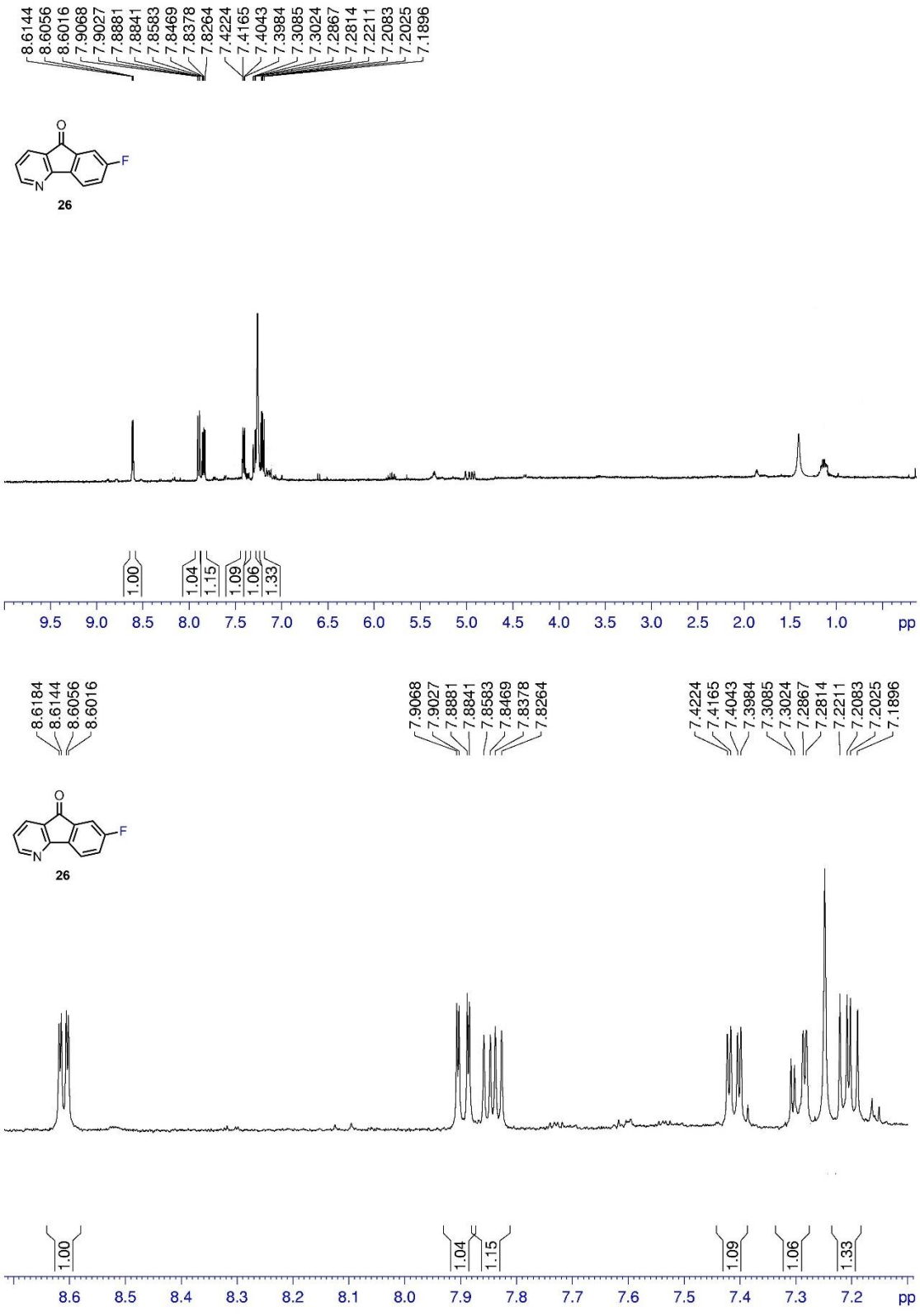
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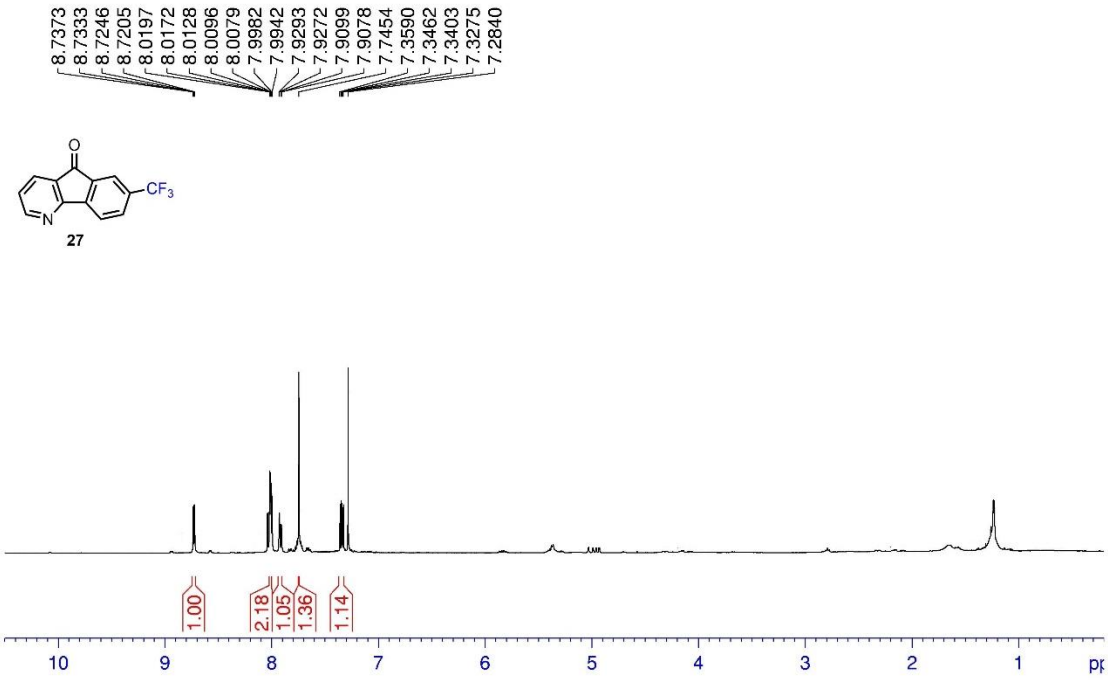
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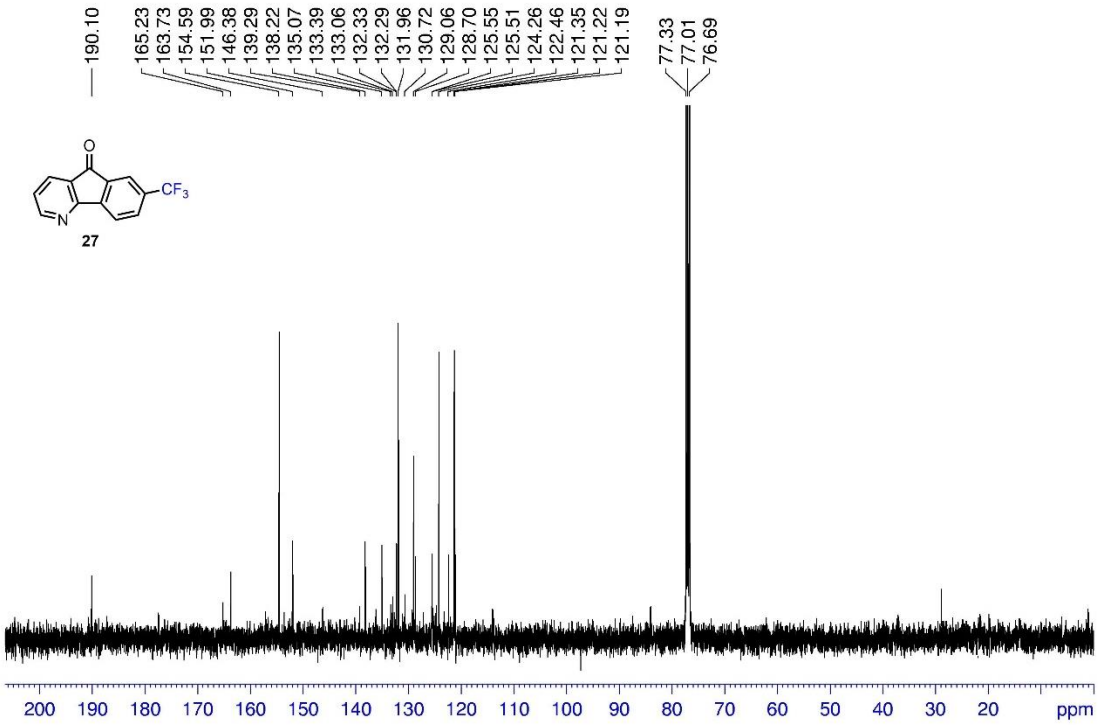
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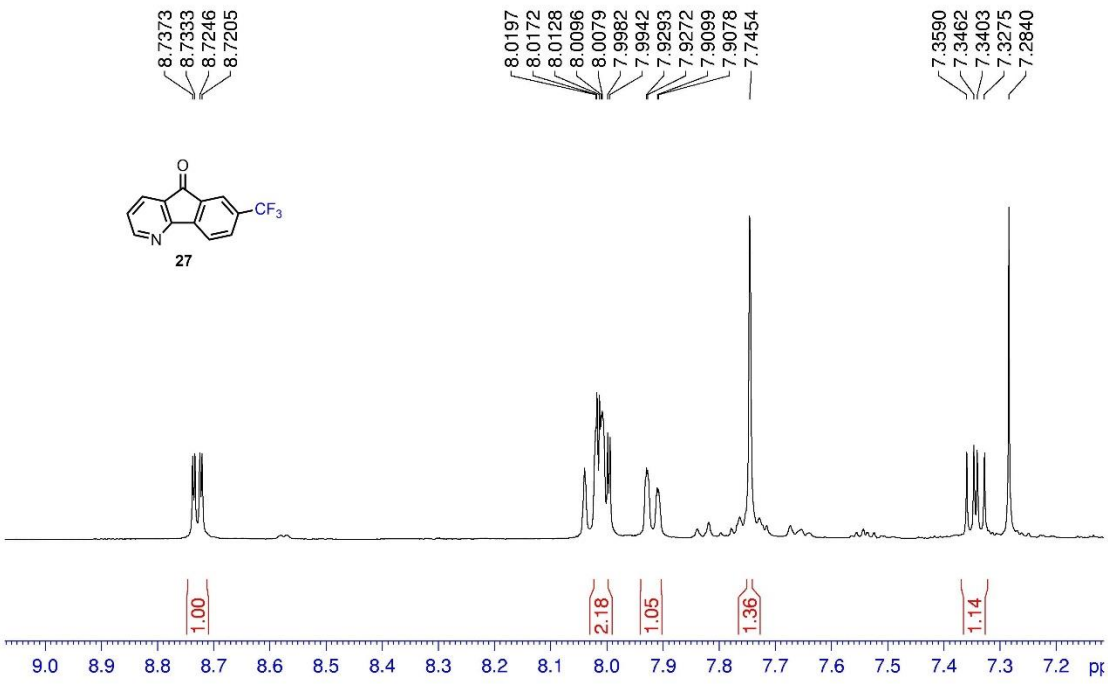
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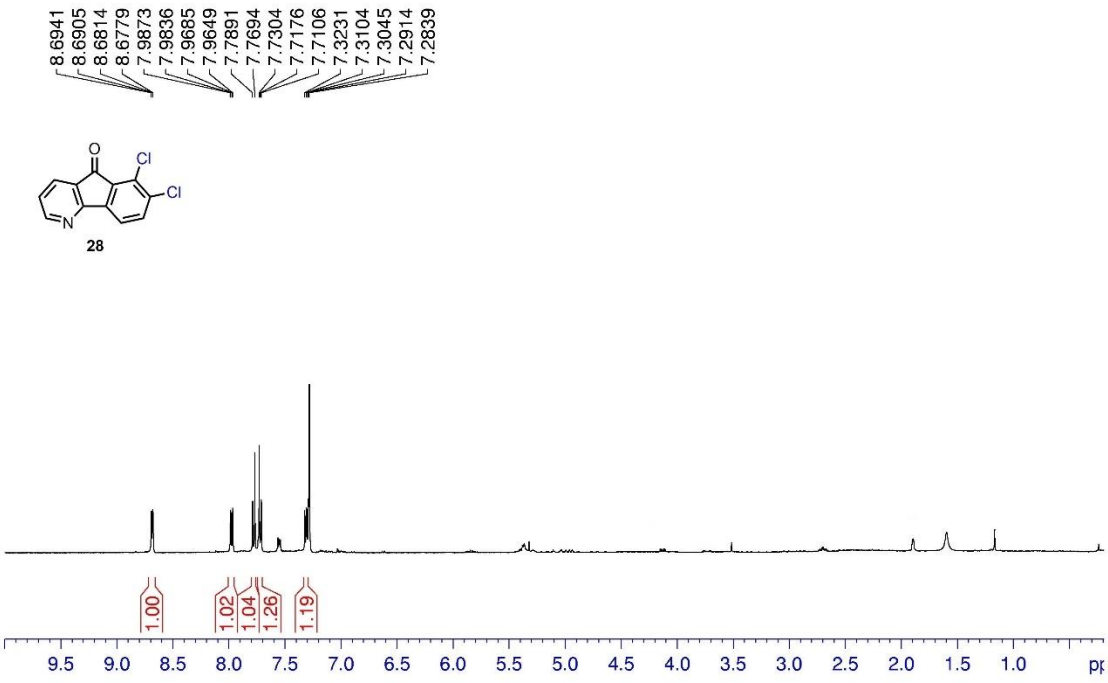
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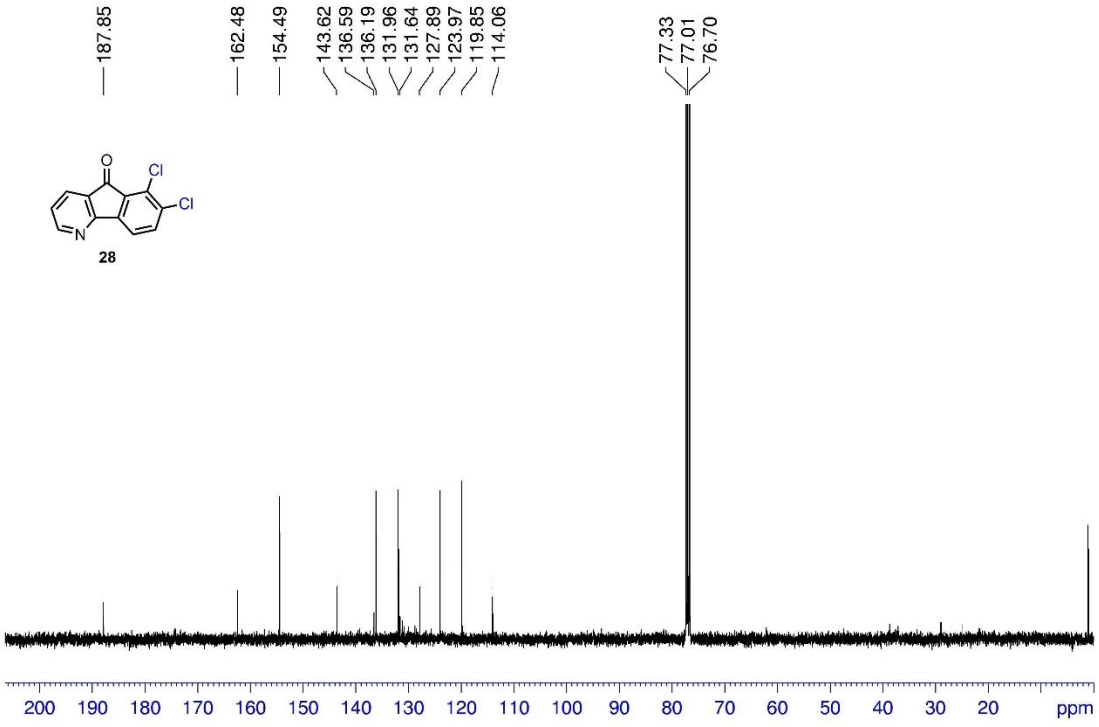
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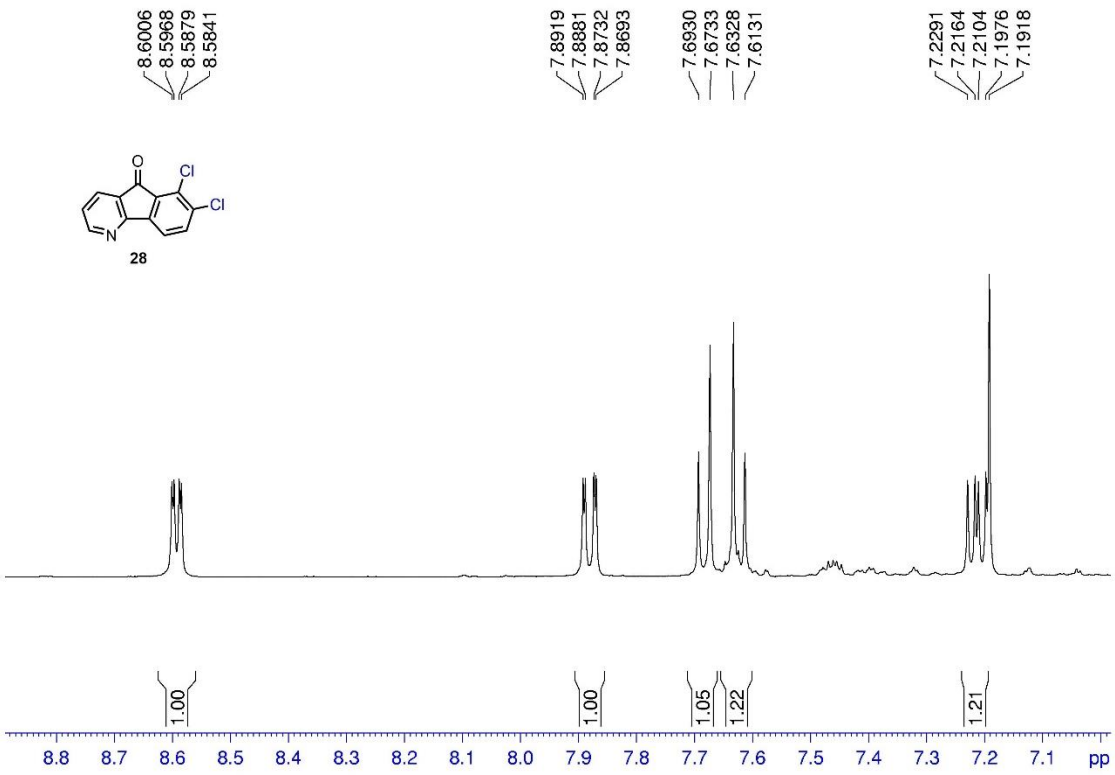
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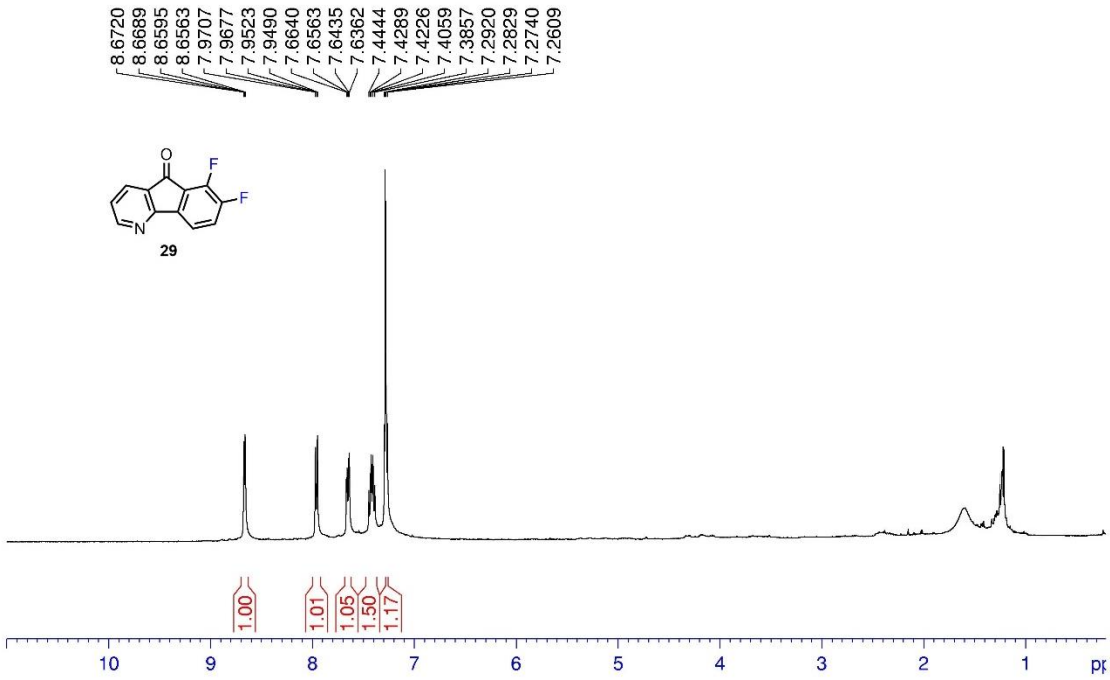
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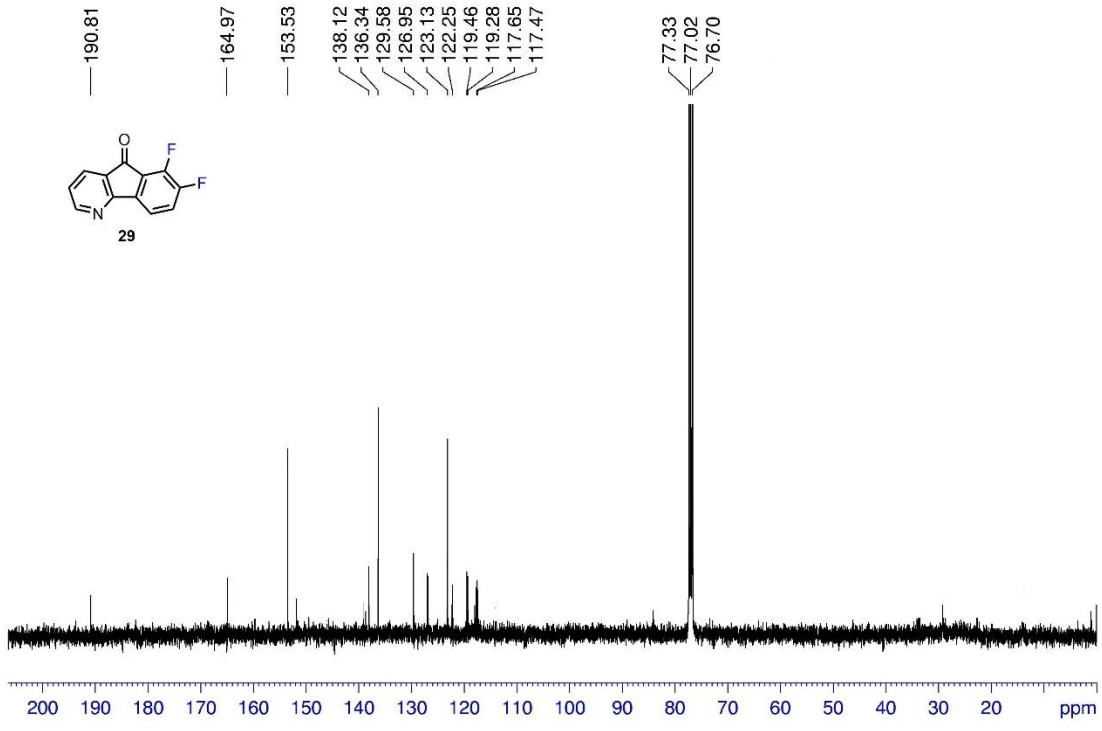
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N
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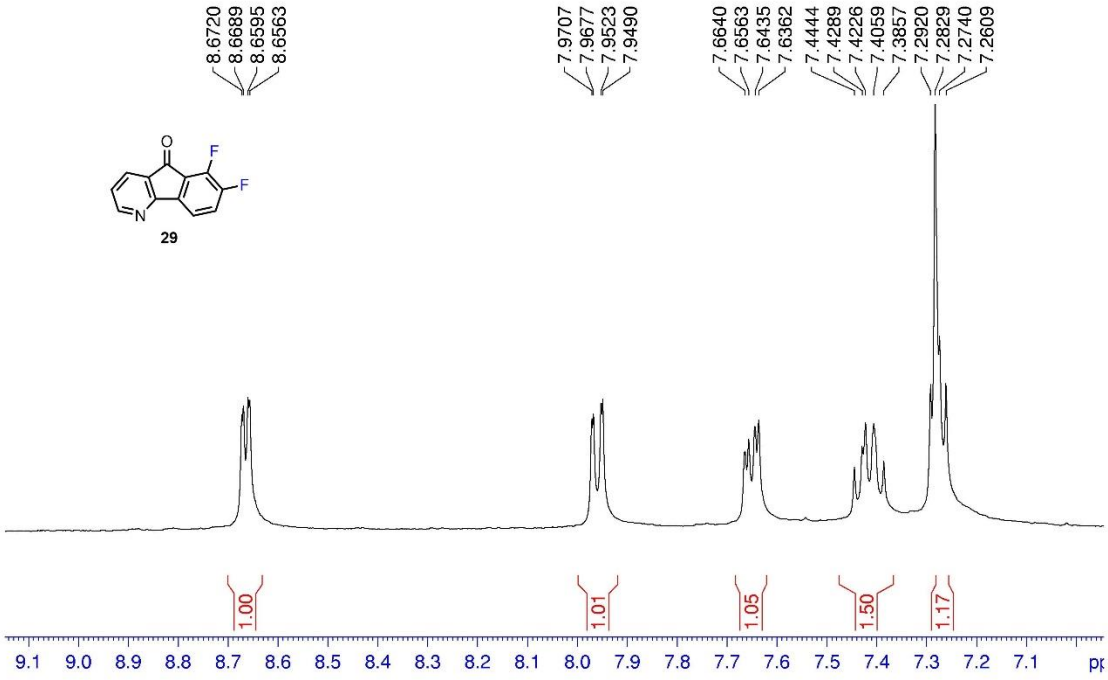
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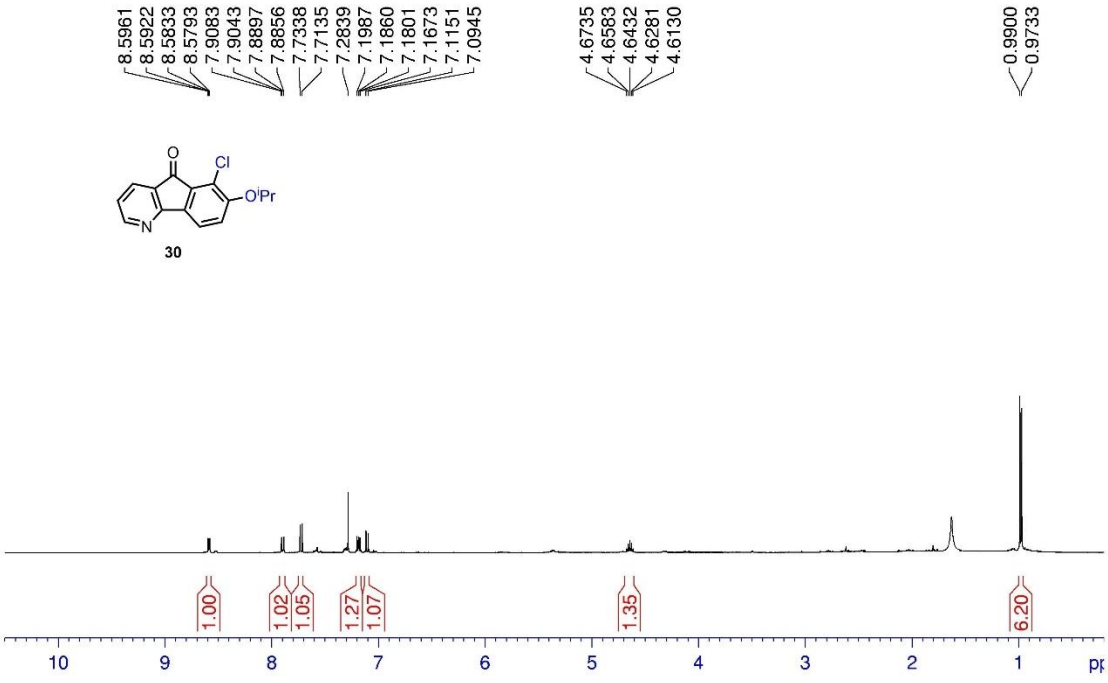
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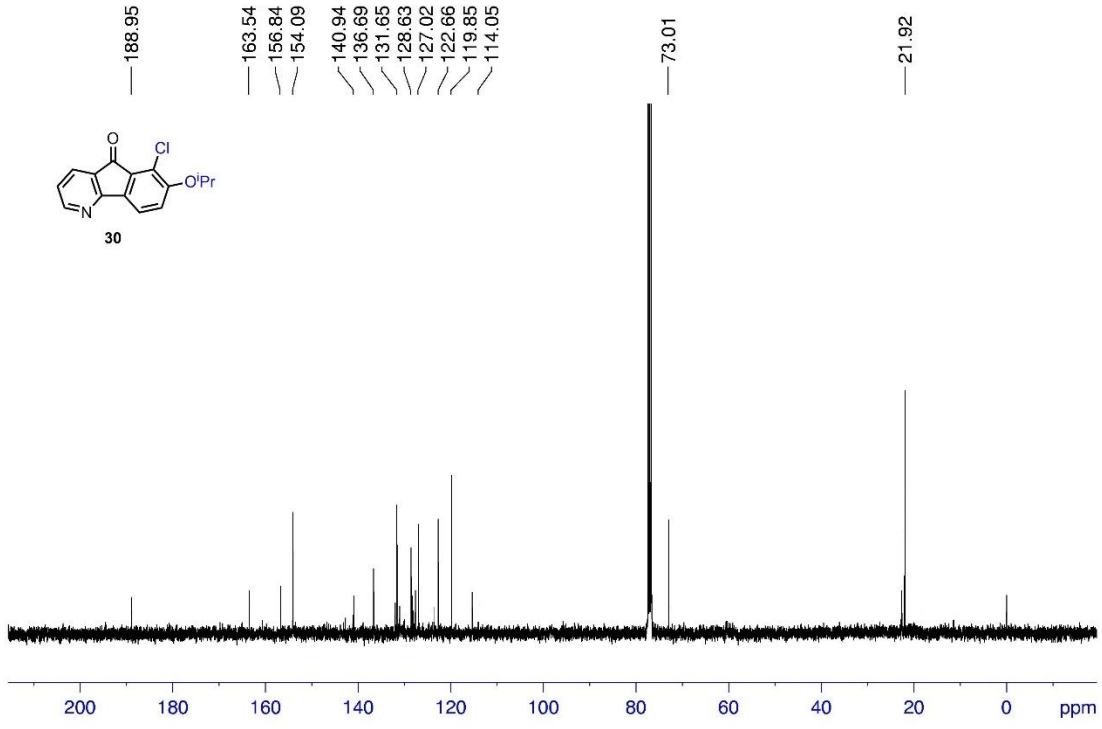
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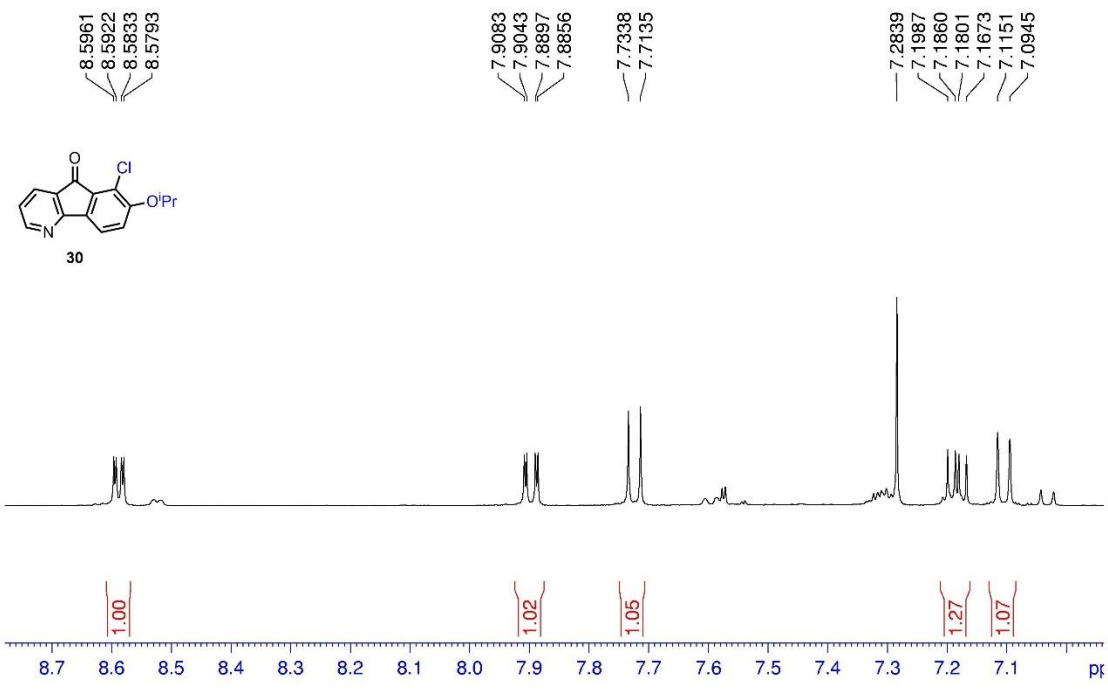
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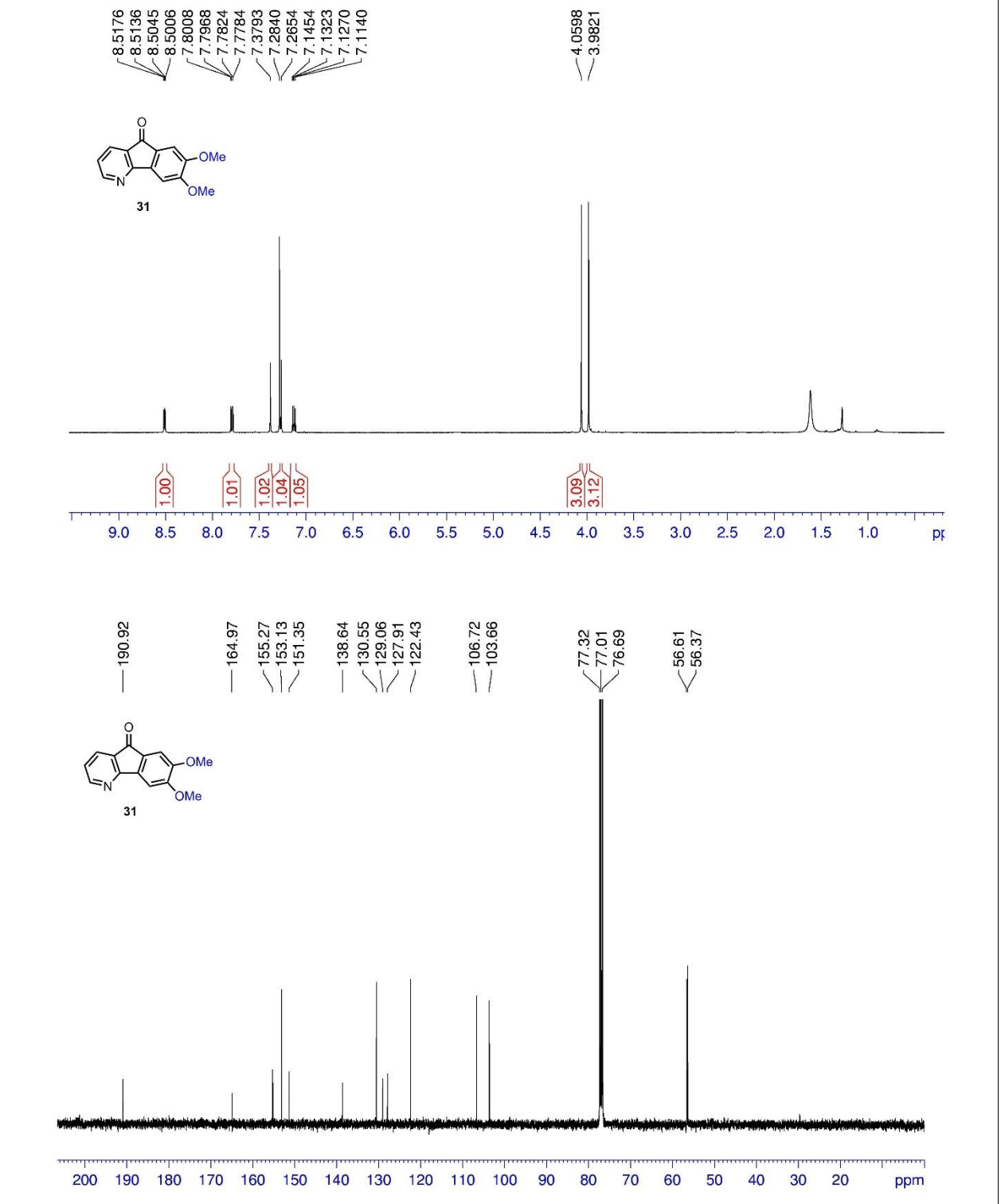
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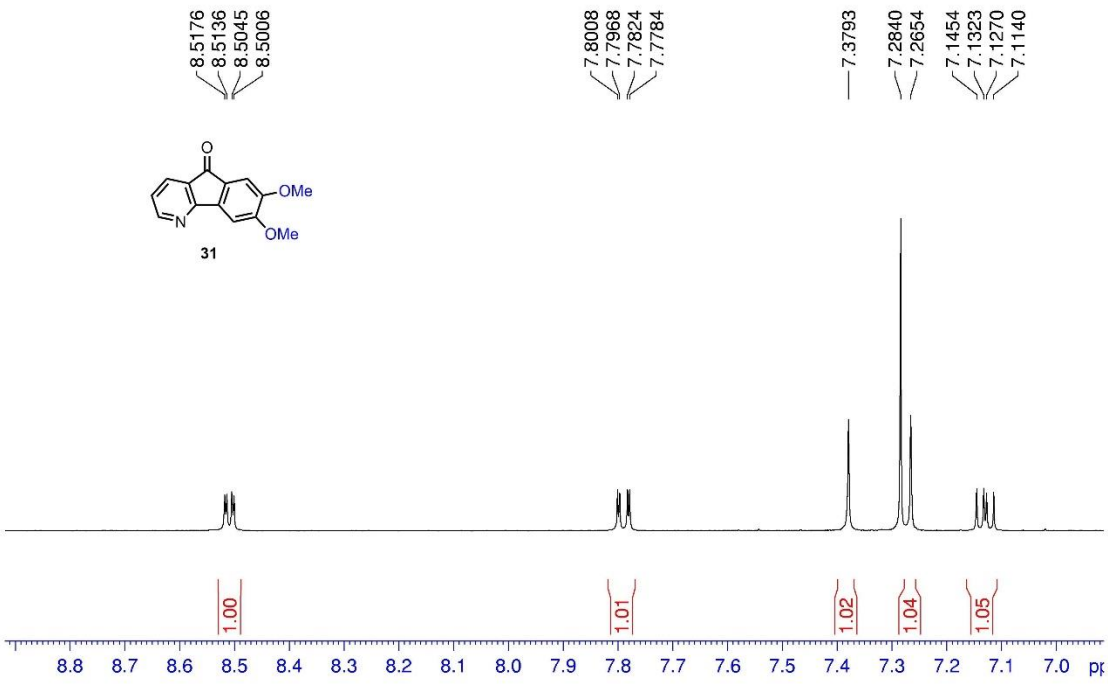
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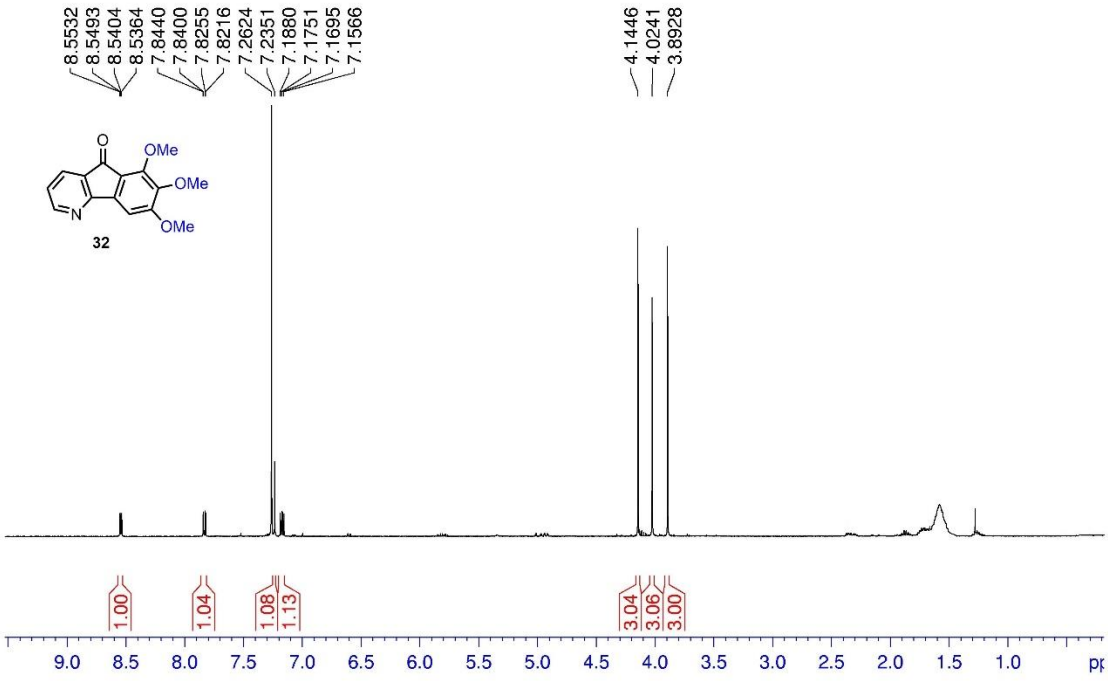
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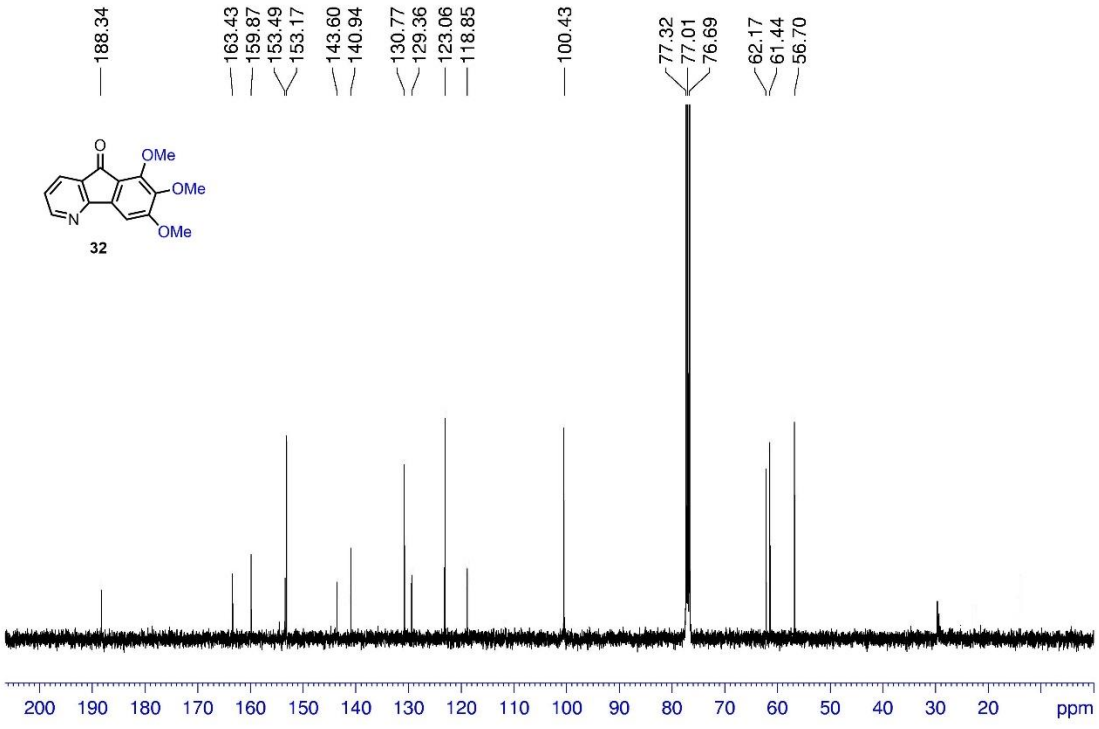
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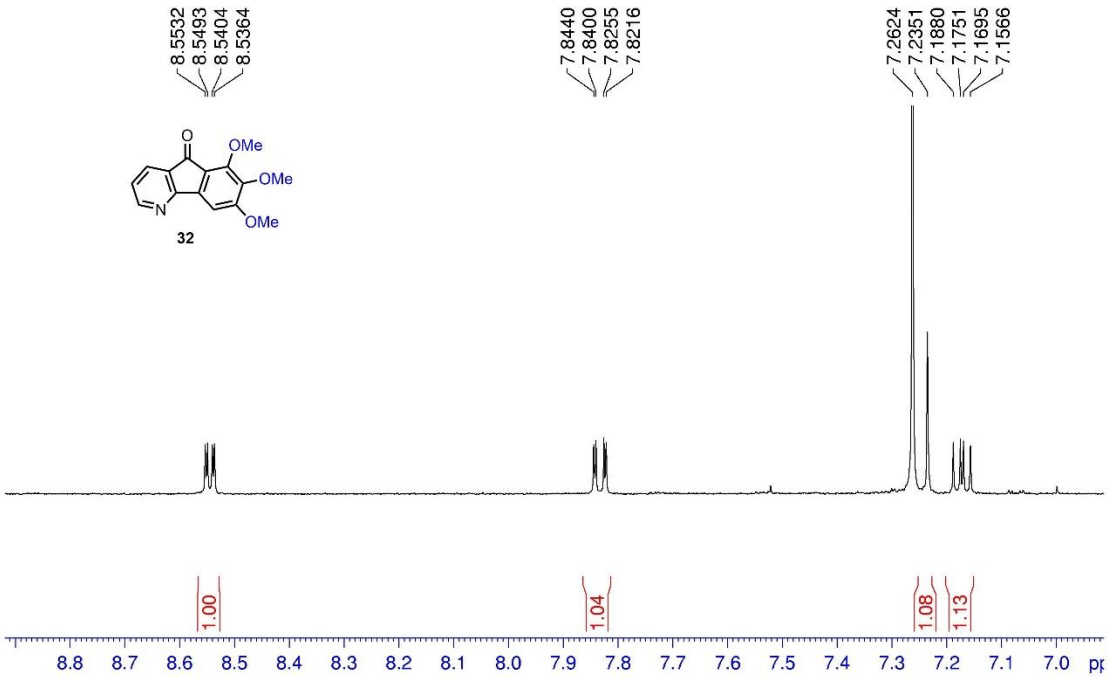
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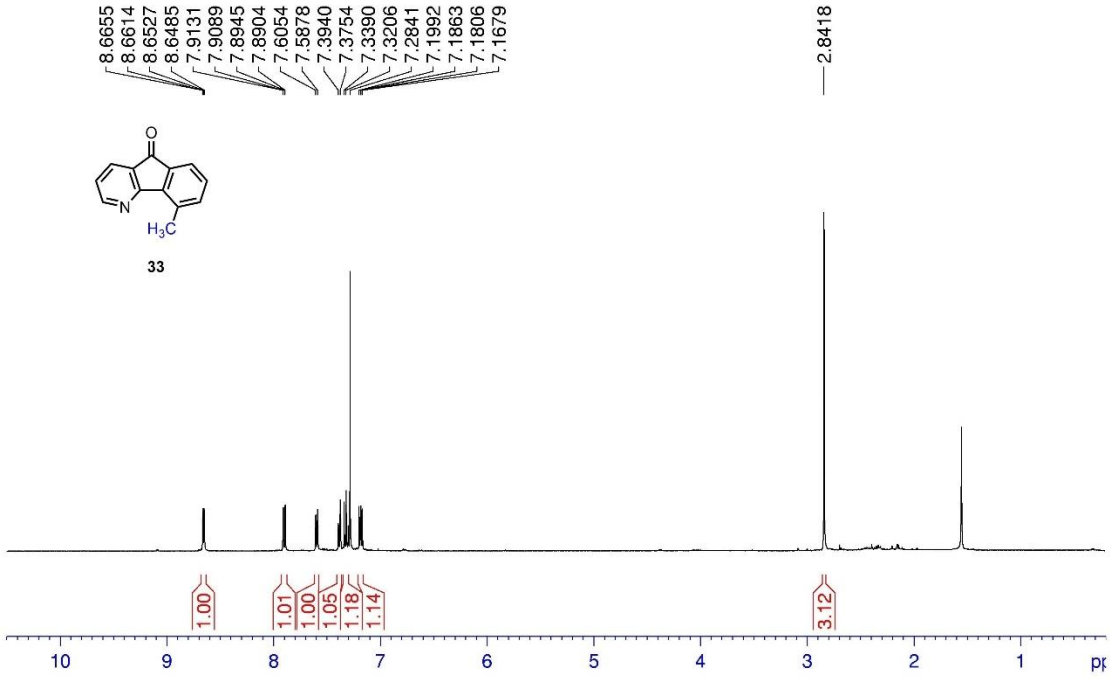
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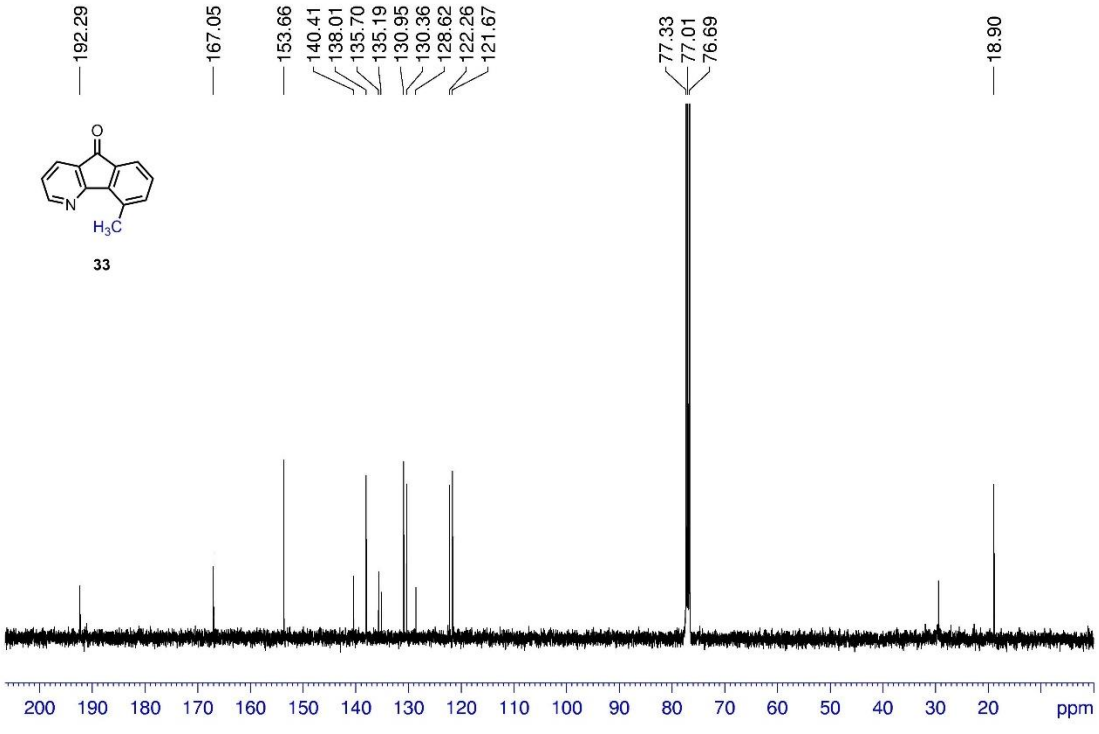
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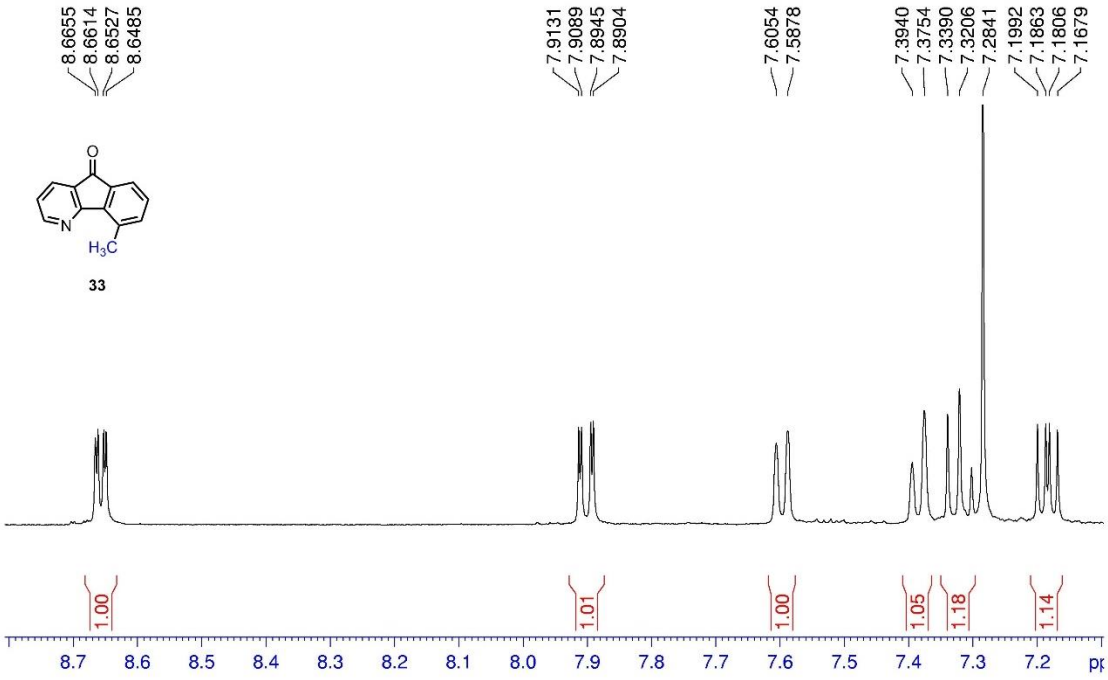
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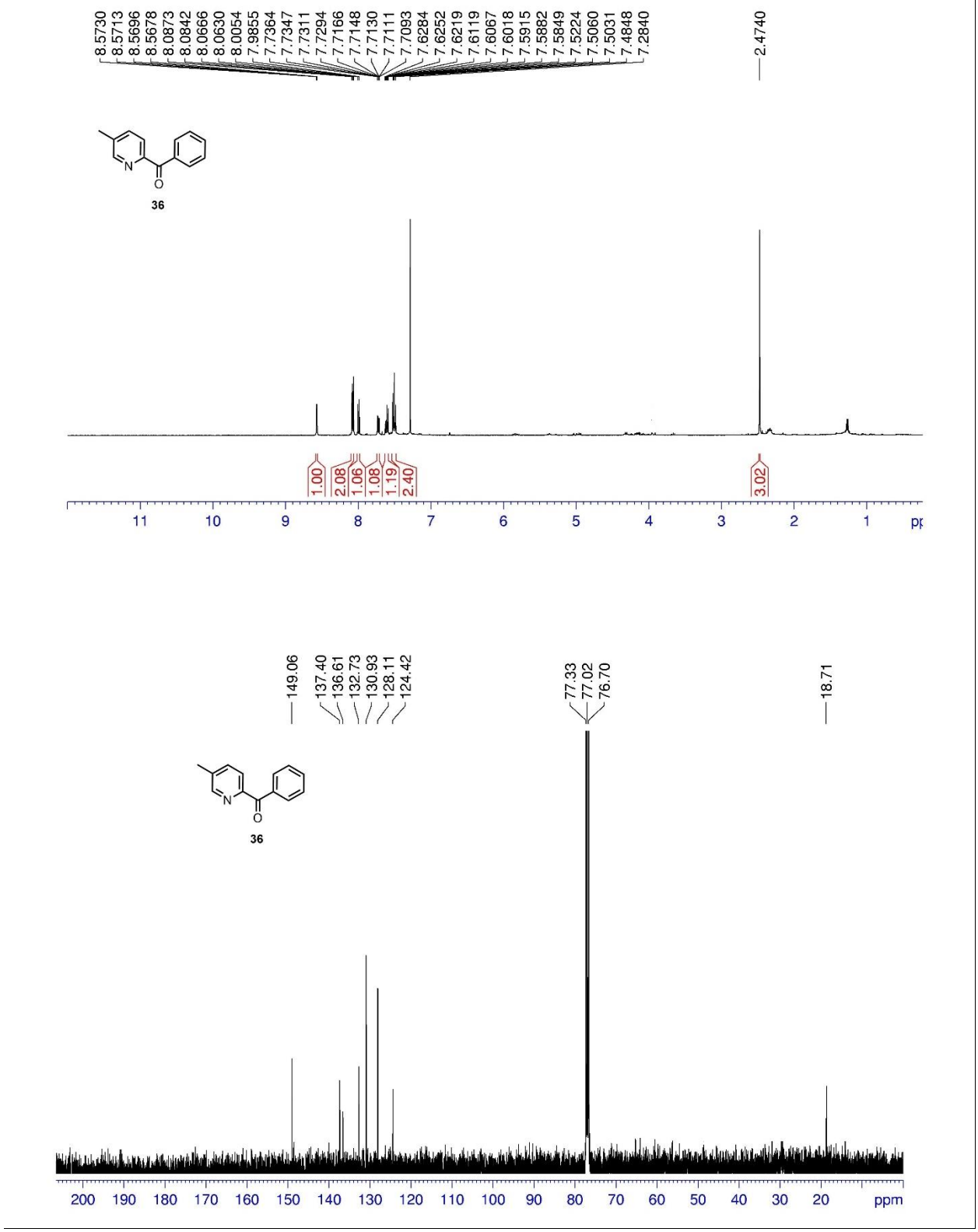
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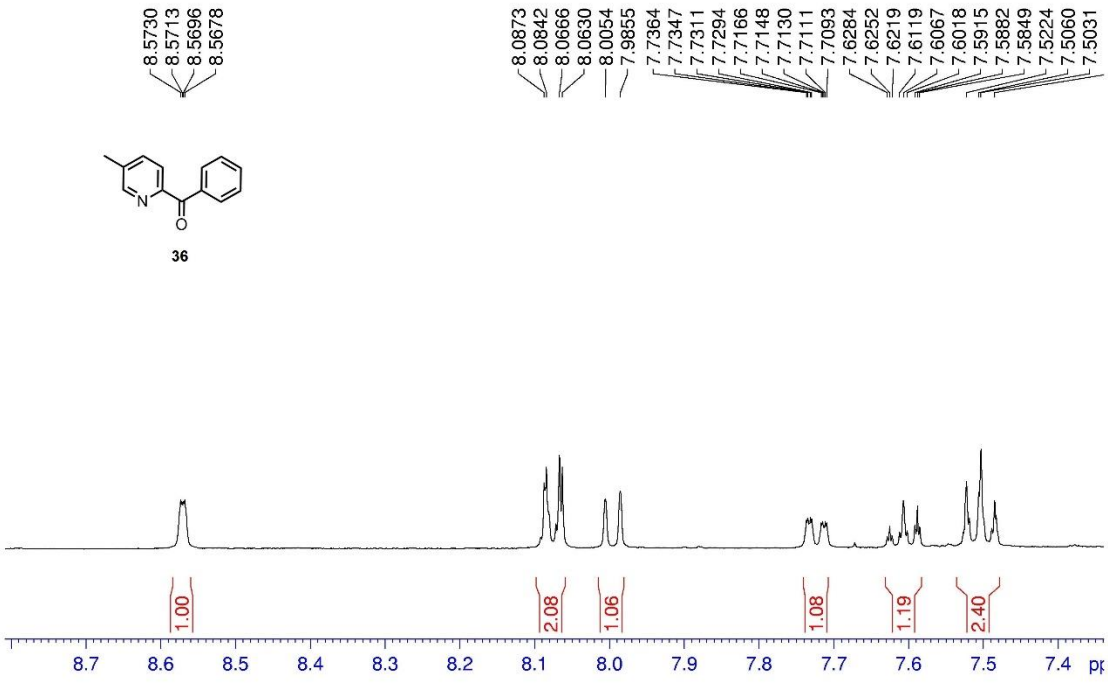
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