

Copper-catalyzed C-H ethoxycarbonyldifluoromethylation of imidazoheterocycles

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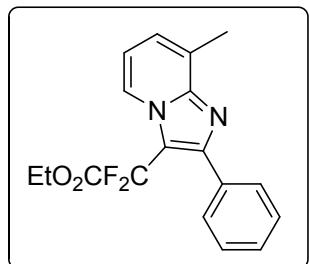
1. General Information:

¹H NMR spectra were determined on a 400 MHz (Bruker Avance) spectrometer using solutions in CDCl₃. Chemical shifts (δ) are expressed in parts per million and are referenced to tetramethylsilane (TMS) as an internal standard. The multiplicities of the signals are reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), or m (multiplet), and coupling constants (J) are given in hertz. Proton-decoupled ¹³C{¹H} NMR spectra were recorded at 100 MHz (Bruker Avance). Proton-decoupled ¹⁹F NMR spectra were recorded at 376.5 MHz (Bruker Avance). HRMS analysis was performed on a Q-TOF mass analyzer (Agilent Accurate-Mass Q-TOF LC/MS-6520 using the ESI ionization method. Elemental analyses were performed by a PerkinElmer, Series II, CHNS/O analyser-2400. TLC was done on silica gel 60 F₂₅₄ coated on aluminum sheets (Merck). Silica gel (60-120 mesh) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C unless otherwise mentioned. All of the solvents were dried and distilled before use. All of the reactions involving moisture-sensitive reactants were executed using oven-dried glassware.

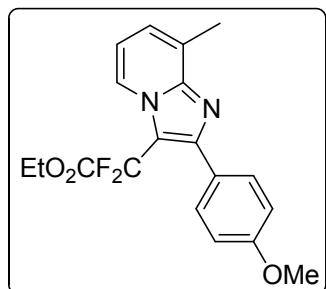
2. Typical experimental procedure for the compound (3a**):**

The mixture of 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (**1a**, 41 mg, 0.20 mmol), ethyl-2-bromo-2,2-difluoroacetate (**2**, 51 μ L, 2 equiv), Cu₂O (3 mg, 10 mol%), 1,10-phenanthroline (4.4 mg, 12 mol%) and K₂CO₃ (55 mg, 2 equiv) in CH₃CN (1 mL) was stirred at 80 °C under air in the sealed tube for 10 h. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature and extracted with ethylacetate/water. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporation of the solvent in vacuum and purified by column chromatography on silica gel (60-120 mesh) using *n*-hexane/EtOAc (9:1) as the eluent to afford pure **3a** as colorless oil (55 mg, 84% yield).

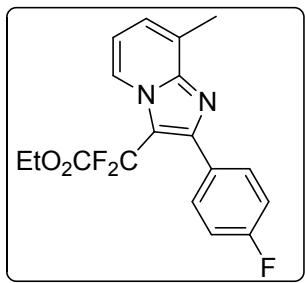
3. Characterization data for the synthesized products:



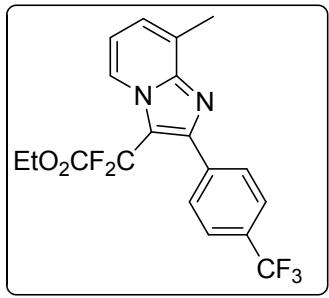
Ethyl-2,2-difluoro-2-(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3a): Colourless oil (84%, 55 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 9.2$ Hz, 2H), 7.37-7.32 (m, 3H), 7.07 (d, $J = 6.8$ Hz, 1H), 6.78 (t, $J = 7.2$ Hz, 1H), 3.86 (q, $J = 7.2$ Hz, 2H), 2.58 (s, 3H), 1.06 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.5 (t, $J_{\text{C}-\text{F}} = 32$ Hz), 147.6, 146.7, 133.7, 129.9, 128.8, 128.2, 128.0, 125.5, 124.4 (t, $J_{\text{C}-\text{F}} = 16$ Hz), 113.6, 112.0, 111.6 (t, $J_{\text{C}-\text{F}} = 242$ Hz), 63.6, 17.3, 13.7; ^{19}F NMR (376.5 MHz, CDCl_3): δ -98.3; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_2$: 331.1258; found: 331.1264.



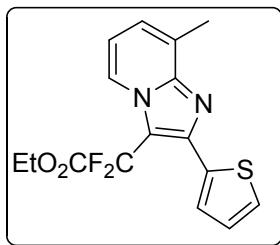
Ethyl-2,2-difluoro-2-(2-(4-methoxyphenyl)-8-methylimidazo[1,2-a]pyridin-3-yl)acetate (3b): Colourless oil (85%, 61 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.36 (d, $J = 7.2$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 2H), 6.83 (t, $J = 6.8$ Hz, 1H), 3.99 (q, $J = 7.2$ Hz, 2H), 3.84 (s, 3H), 2.64 (s, 3H), 1.15 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6 (t, $J_{\text{C}-\text{F}} = 35$ Hz), 160.1, 147.5, 147.5, 146.6, 131.1, 127.8, 126.1, 125.4, 124.3 (t, $J_{\text{C}-\text{F}} = 6$ Hz), 113.7, 113.4, 111.9, 111.7 (t, $J_{\text{C}-\text{F}} = 246$ Hz), 111.6, 63.6, 55.4, 17.3, 13.7; ^{19}F NMR (376.5 MHz, CDCl_3): δ -98.6; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_3$: 361.1364; found: 361.1384.



Ethyl-2,2-difluoro-2-(2-(4-fluorophenyl)-8-methylimidazo[1,2-*a*]pyridin-3-yl)acetate (3c): Colourless oil (83%, 57 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.37 (d, $J = 6.8$ Hz, 1H), 7.65-7.62 (m, 2H), 7.15-7.10 (m, 3H), 6.86 (t, $J = 7.2$ Hz, 1H), 4.05 (q, $J = 7.2$ Hz, 2H), 2.64 (s, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.2 (d, $J_{\text{C}-\text{F}} = 247$ Hz), 162.6 (t, $J_{\text{C}-\text{F}} = 36$ Hz), 146.7, 146.6, 131.7 (d, $J_{\text{C}-\text{F}} = 9$ Hz), 129.8 (d, $J_{\text{C}-\text{F}} = 3$ Hz), 128.0, 125.6, 124.3 (t, $J_{\text{C}-\text{F}} = 6$ Hz), 115.2 (d, $J_{\text{C}-\text{F}} = 21$ Hz), 113.7, 111.9, 111.5 (t, $J_{\text{C}-\text{F}} = 247$ Hz), 63.8, 17.3, 13.8; ^{19}F NMR (376.5 MHz, CDCl_3): δ -99.1, -113.0; Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_2$: C, 62.07; H, 4.34; N, 8.04%; Found: C, 61.92; H, 4.20; N, 7.92%.

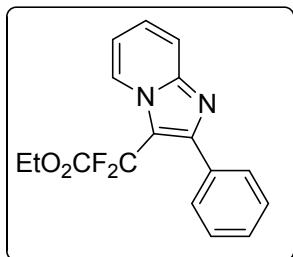


Ethyl-2,2-difluoro-2-(8-methyl-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridin-3-yl)acetate (3d): Colourless oil (75%, 59 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.38 (d, $J = 6.8$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 6.8$ Hz, 1H), 6.88 (t, $J = 7.2$ Hz, 1H), 4.10 (q, $J = 7.2$ Hz, 2H), 2.65 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6 (t, $J_{\text{C}-\text{F}} = 35$ Hz), 146.9, 145.9, 137.5, 130.7 (q, $J_{\text{C}-\text{F}} = 32$ Hz), 130.3, 128.2, 125.8, 125.1 (q, $J_{\text{C}-\text{F}} = 4$ Hz), 124.3 (t, $J_{\text{C}-\text{F}} = 5$ Hz), 124.2 (q, $J_{\text{C}-\text{F}} = 270$ Hz), 113.9, 112.3 (t, $J_{\text{C}-\text{F}} = 33$ Hz), 111.3 (t, $J_{\text{C}-\text{F}} = 249$ Hz), 63.9, 17.2, 13.8; ^{19}F NMR (376.5 MHz, CDCl_3): δ -62.6, -99.7; Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_5\text{N}_2\text{O}_2$: C, 57.29; H, 3.80; N, 7.03%; Found: C, 57.04; H, 3.91; N, 6.94%.

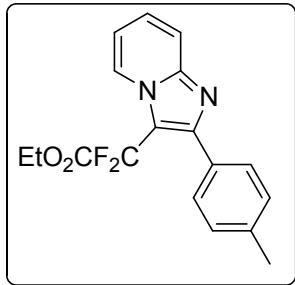


Ethyl-2,2-difluoro-2-(8-methyl-2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl)acetate (3e):

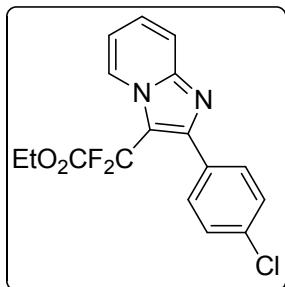
Brown oil (78%, 52 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 6.8 Hz, 1H), 7.43-7.40 (m, 2H), 7.12-7.07 (m, 2H), 6.82 (t, *J* = 7.2 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.64 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.5 (t, *J*_{C-F} = 35 Hz), 146.6, 140.9, 135.3, 128.5 (t, *J*_{C-F} = 4 Hz), 127.9, 127.6, 127.4, 125.6, 124.3 (t, *J*_{C-F} = 7 Hz), 113.7, 111.5 (t, *J*_{C-F} = 248 Hz), 109.0, 63.8, 17.2, 13.8; ¹⁹F NMR (376.5 MHz, CDCl₃): δ -99.8; Anal. Calcd for C₁₆H₁₄F₂N₂O₂S: C, 57.13; H, 4.20; N, 8.33%; Found: C, 56.97; H, 4.12; N, 8.21%.



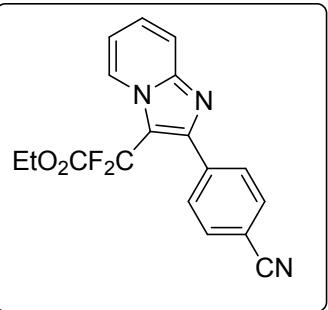
Ethyl-2,2-difluoro-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3f): Colourless oil (75%, 47 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.53 (d, *J* = 6.8 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.45-7.41 (m, 3H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 6.8 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.5, 159.1, 148.3, 146.3, 133.5, 129.7, 128.9, 128.2, 126.8, 126.7 (t, *J*_{C-F} = 6 Hz), 118.0, 113.6, 111.7 (t, *J*_{C-F} = 258 Hz), 63.7, 13.7; ¹⁹F NMR (376.5 MHz, CDCl₃): δ -98.5. Anal. Calcd for C₁₇H₁₄F₂N₂O₂: C, 64.55; H, 4.46; N, 8.86%; Found: C, 64.32; H, 4.32; N, 8.78%.



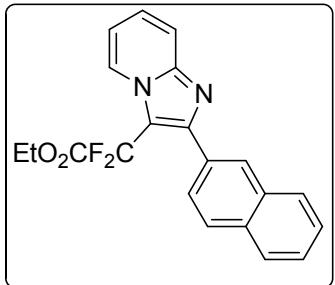
Ethyl-2,2-difluoro-2-(2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)acetate (3g): Colourless oil (80%, 52 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.45 (d, $J = 7.2$ Hz, 1H), 7.63 (d, $J = 9.2$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.30-7.26 (m, 1H), 7.19-7.16 (m, 2H), 6.89-6.87 (m, 1H), 3.92 (q, $J = 7.2$ Hz, 2H), 2.33 (s, 3H), 1.08 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.5, 148.3, 146.2, 138.8, 130.4, 129.6, 128.9, 126.7 ($t, J_{\text{C}-\text{F}} = 6$ Hz), 126.3, 117.9, 113.5, 111.6 ($t, J_{\text{C}-\text{F}} = 246$ Hz), 111.4, 63.7, 21.4, 13.7; ^{19}F NMR (376.5 MHz, CDCl_3): δ -98.6; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_2$: 331.1258; found: 331.1269.



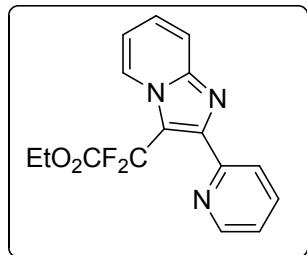
Ethyl-2-(2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)-2,2-difluoroacetate (3h): Colourless oil (67%, 47 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.52 (d, $J = 7.2$ Hz, 1H), 7.70 (d, $J = 9.2$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.43-7.40 (m, 2H), 7.39-7.34 (m, 1H), 6.96 (t, $J = 7.2$ Hz, 1H), 4.12 (q, $J = 7.2$ Hz, 2H), 1.21 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6 ($t, J_{\text{C}-\text{F}} = 39$ Hz), 146.9, 146.4, 135.0, 132.0, 131.1, 128.4, 127.6, 127.0, 126.7 ($t, J_{\text{C}-\text{F}} = 5$ Hz), 118.0, 113.7, 111.4 ($t, J_{\text{C}-\text{F}} = 248$ Hz), 63.9, 13.8; ^{19}F NMR (376.5 MHz, CDCl_3): δ -99.5; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{17}\text{H}_{13}\text{ClF}_2\text{N}_2\text{O}_2$: 351.0712; found: 351.0740.



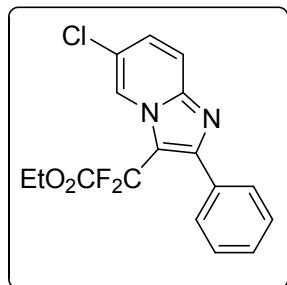
Ethyl-2-(2-(4-cyanophenyl)imidazo[1,2-*a*]pyridin-3-yl)-2,2-difluoroacetate (3i): Yellow oil (58%, 39 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.53 (d, $J = 7.2$ Hz, 1H), 7.84 (d, $J = 8.8$ Hz, 2H), 7.75-7.70 (m, 2H), 7.42-7.38 (m, 1H), 7.01-6.98 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6, 146.6, 145.9, 138.2, 132.0, 130.5, 127.4, 126.7 (t, $J_{\text{C}-\text{F}} = 6$ Hz), 125.9, 118.8, 118.2, 114.1, 112.5, 111.2 (t, $J_{\text{C}-\text{F}} = 249$ Hz), 64.1, 13.9; ^{19}F NMR (376.5 MHz, CDCl_3): δ -100.3; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{18}\text{H}_{13}\text{F}_2\text{N}_3\text{O}_2$: 342.1054; found: 342.1067.



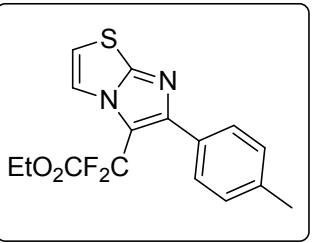
Ethyl-2,2-difluoro-2-(2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridin-3-yl)acetate (3j): Brown oil (42%, 30 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.57 (d, $J = 7.2$ Hz, 1H), 8.11 (s, 1H), 7.93-7.86 (m, 3H), 7.81-7.79 (m, 1H), 7.74 (d, $J = 9.2$ Hz, 1H), 7.53-7.50 (m, 2H), 7.38 (t, $J = 8.0$ Hz, 1H), 6.97 (t, $J = 6.8$ Hz, 1H), 3.89 (q, $J = 7.2$ Hz, 2H), 1.08 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6, 148.2, 146.5, 133.4, 133.0, 130.8, 129.3, 128.5, 127.9, 127.8, 127.1, 126.9, 126.8 (t, $J_{\text{C}-\text{F}} = 5$ Hz), 126.4, 125.3, 124.3, 118.0, 113.6, 111.6 (t, $J_{\text{C}-\text{F}} = 249$ Hz), 63.7, 13.6; ^{19}F NMR (376.5 MHz, CDCl_3): δ -98.5; Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_2$: C, 68.85; H, 4.40; N, 7.65%; Found: C, 68.69; H, 4.29; N, 7.52%.



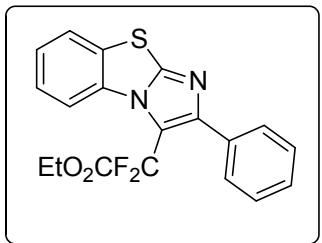
Ethyl-2,2-difluoro-2-(2-(pyridin-2-yl)imidazo[1,2-*a*]pyridin-3-yl)acetate (3k): Colourless oil (70%, 44 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, $J = 7.2$ Hz, 1H), 8.52 (d, $J = 4.4$ Hz, 1H), 8.20 (d, $J = 7.6$ Hz, 1H), 7.83-7.78 (m, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.36 (t, $J = 8.8$ Hz, 1H), 7.27-7.24 (m, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 4.08 (q, $J = 7.2$ Hz, 2H), 1.04 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.2 (t, $J_{\text{C}-\text{F}} = 34$ Hz), 151.7, 147.9, 145.9, 145.3, 137.0, 127.3 (t, $J_{\text{C}-\text{F}} = 10$ Hz), 126.9, 123.3, 122.3, 118.1, 114.1, 113.8, 112.5 (t, $J_{\text{C}-\text{F}} = 243$ Hz), 62.8, 13.6; ^{19}F NMR (376.5 MHz, CDCl_3): δ -96.4; Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_2\text{N}_3\text{O}_2$: C, 60.57; H, 4.13; N, 13.24%; Found: C, 60.39; H, 3.98; N, 13.16%.



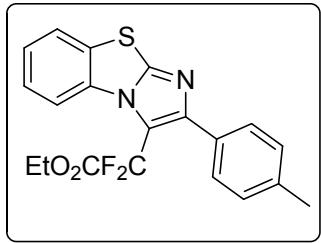
Ethyl-2-(6-chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)-2,2-difluoroacetate (3l): Colourless oil (72%, 50 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.58 (s, 1H), 7.66-7.60 (m, 3H), 7.46-7.42 (m, 3H), 7.35-7.32 (m, 1H), 4.00 (q, $J = 7.2$ Hz, 2H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.2 (t, $J_{\text{C}-\text{F}} = 34$ Hz), 148.9, 144.7, 132.9, 129.6, 129.1, 128.9, 128.3, 124.6 (t, $J_{\text{C}-\text{F}} = 6$ Hz), 121.9, 118.3, 112.2 (t, $J_{\text{C}-\text{F}} = 31$ Hz), 111.2 (t, $J_{\text{C}-\text{F}} = 248$ Hz), 63.9, 13.7; ^{19}F NMR (376.5 MHz, CDCl_3): δ -98.8; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{17}\text{H}_{13}\text{ClF}_2\text{N}_2\text{O}_2$: 351.0712; found: 351.0700.



Ethyl-2,2-difluoro-2-(6-(*p*-tolyl)imidazo[2,1-*b*]thiazol-5-yl)acetate (5a): Yellow oil (85%, 57 mg); ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 4.4$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 4.8$ Hz, 1H), 4.05 (q, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.12 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.4 (t, $J_{\text{C}-\text{F}} = 35$ Hz), 151.4, 148.8, 138.8, 129.8, 129.0, 129.0, 119.9 (t, $J_{\text{C}-\text{F}} = 5$ Hz), 113.7, 113.6 (t, $J_{\text{C}-\text{F}} = 31$ Hz), 110.9 (t, $J_{\text{C}-\text{F}} = 247$ Hz), 63.7, 21.4, 13.6; ^{19}F NMR (376.5 MHz, CDCl_3): δ -97.2; Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_2\text{S}$: C, 57.13; H, 4.20; N, 8.33%; Found: C, 56.95; H, 4.09; N, 8.20%.

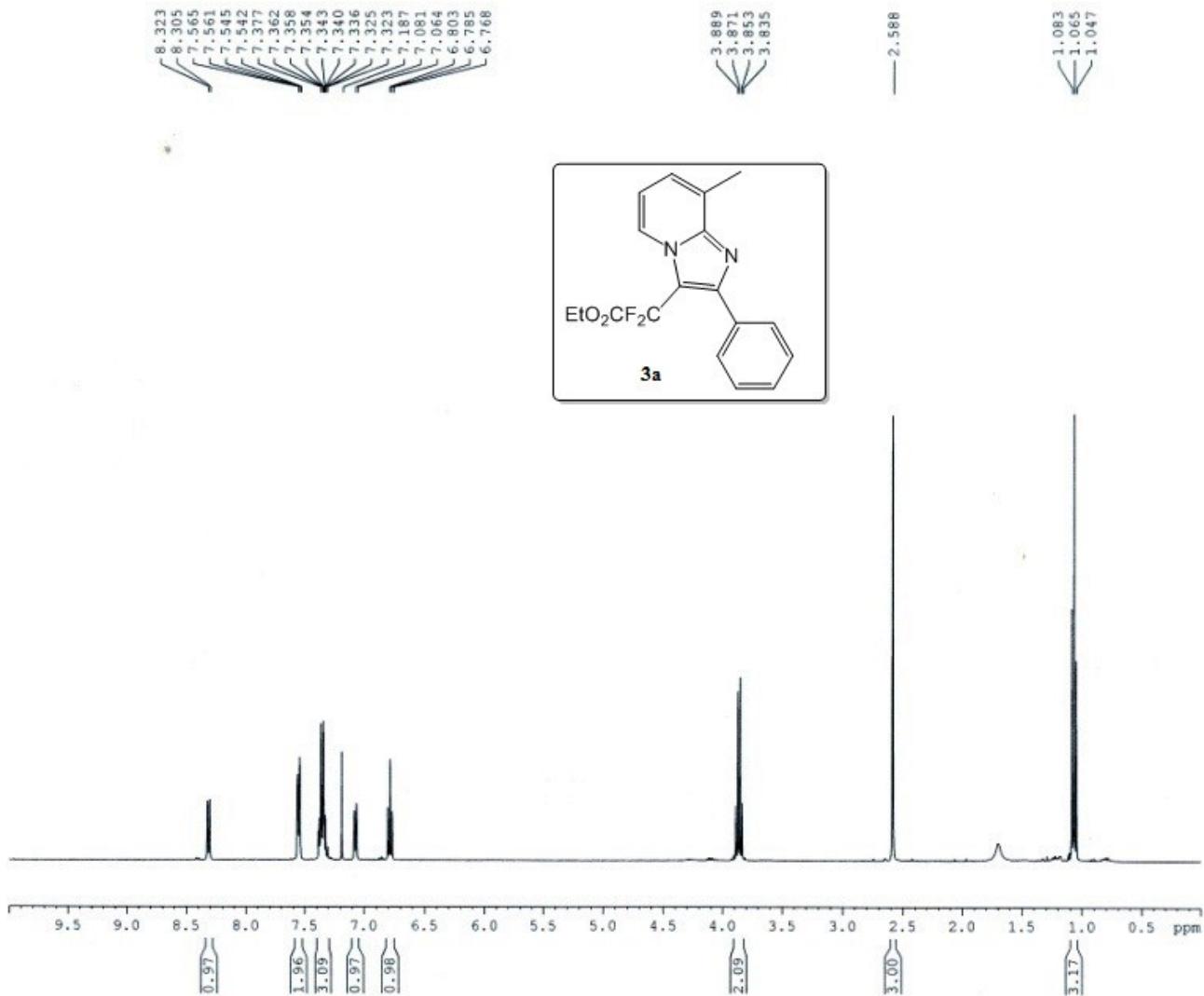


Ethyl-2,2-difluoro-2-(2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)acetate (5b): Brown oil (82%, 61 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.57-7.55 (m, 2H), 7.52-7.48 (m, 1H), 7.46-7.38 (m, 4H), 3.73 (q, $J = 7.2$ Hz, 2H), 1.05 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.1 (t, $J_{\text{C}-\text{F}} = 33$ Hz), 150.9, 150.2 (t, $J_{\text{C}-\text{F}} = 6$ Hz), 133.3, 132.8, 130.1, 129.7, 129.0, 128.2, 126.7, 125.5, 124.2, 116.0 (t, $J_{\text{C}-\text{F}} = 8$ Hz), 115.5 (t, $J_{\text{C}-\text{F}} = 30$ Hz), 110.8 (t, $J_{\text{C}-\text{F}} = 243$ Hz), 63.7, 13.5; ^{19}F NMR (376.5 MHz, CDCl_3): δ -90.1; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{19}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_2\text{S}$: 373.0822; found: 373.0822.



Ethyl-2,2-difluoro-2-(2-(*p*-tolyl)benzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)acetate (5c): Brown oil (80%, 61 mg); ^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.52-7.48 (m, 1H), 7.45-7.38 (m, 3H), 7.23 (d, $J = 7.6$ Hz, 2H), 3.76 (q, $J = 7.2$ Hz, 2H), 2.39 (s, 3H), 1.07 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.2 (t, $J_{\text{C}-\text{F}} = 35$ Hz), 150.8, 150.4, 138.9, 132.9, 130.4, 130.1, 129.6, 128.9, 126.7, 125.4, 124.2, 116.0 (t, $J_{\text{C}-\text{F}} = 8$ Hz), 115.3, 110.9 (t, $J_{\text{C}-\text{F}} = 245$ Hz), 63.7, 21.8, 13.6; ^{19}F NMR (376.5 MHz, CDCl_3): δ -90.1; HRMS (ESI-TOF) m/z : [M+ H] $^+$ Calcd for $\text{C}_{20}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_2\text{S}$: 387.0979; found: 387.0979.

NMR spectra for the synthesized products



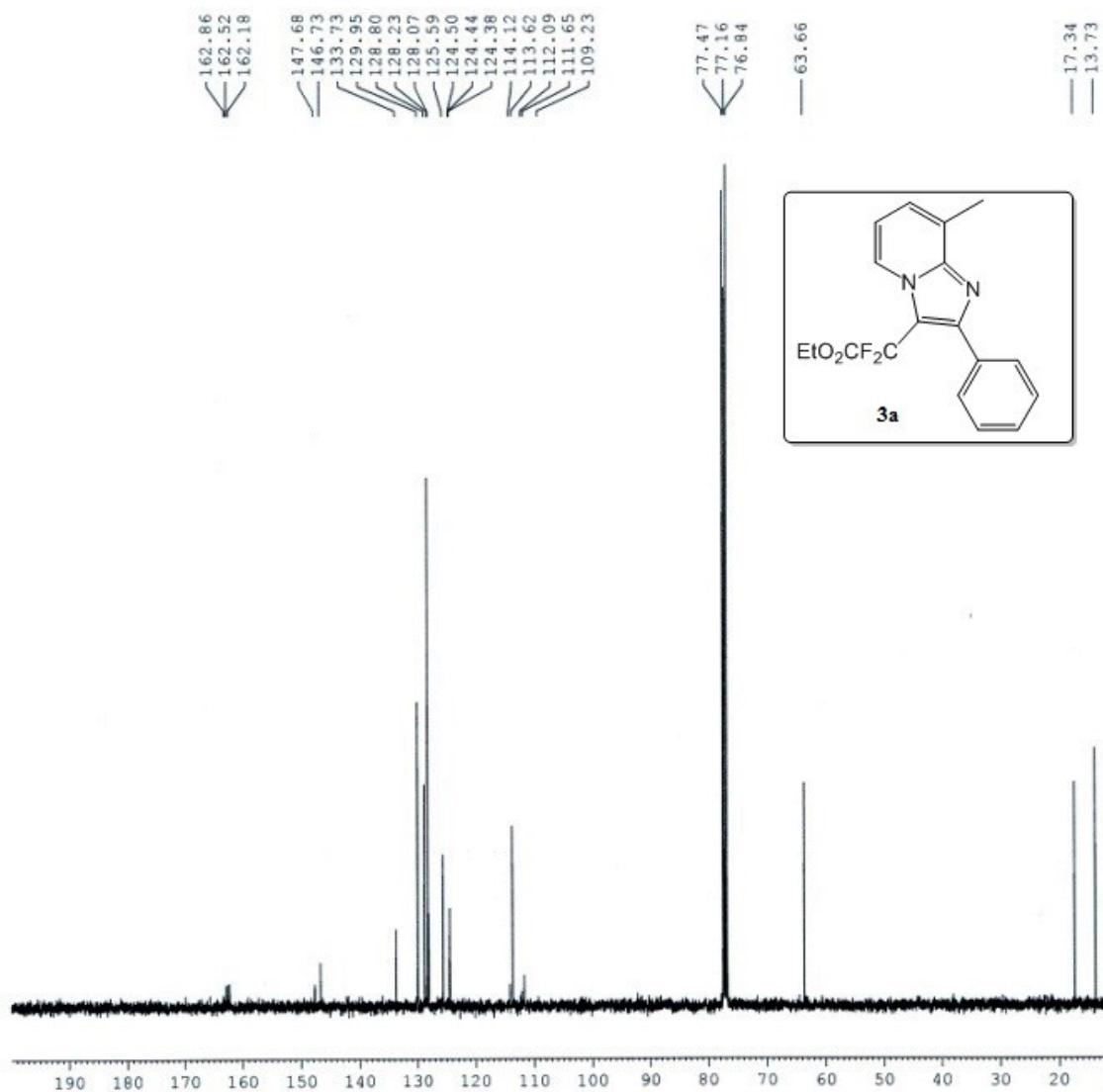
BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 232
PROCNO 1

F2 - Acquisition Parameters
Date 20150527
Time 19.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 24
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 106.66
DW 60.800 usec
DE 6.50 usec
TE 299.9 K
D1 1.0000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 1H
P1 14.75 usec
PLW1 11.99499989 W
SFO1 400.1524711 MHz

F2 - Processing parameters
SI 16384
SF 400.1500382 MHz
WDW EM
SSB 0
LB 0 , 0.30 Hz
GB 0
PC 1.00



BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 234
PROCNO 1

F2 - Acquisition Parameters
Date 20150527
Time 20.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 500
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6916244 sec
RG 106.66
DW 20.800 usec
DE 6.50 usec
TE 301.1 K
D1 2.0000000 sec
D11 0.03000000 sec
TDO 1

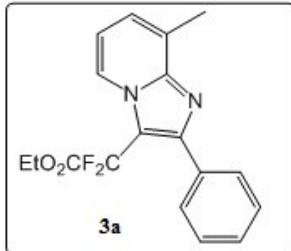
----- CHANNEL f1 -----
NUC1 13C
P1 8.90 usec
PLW1 54.0000000 W
SFO1 100.6278588 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 12.0000000 W
PLW12 0.40792999 W
PLW13 0.26107001 W
SFO2 400.1516006 MHz

F2 - Processing parameters
SI 16384
SF 100.6177830 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

BRUKER

-98.39



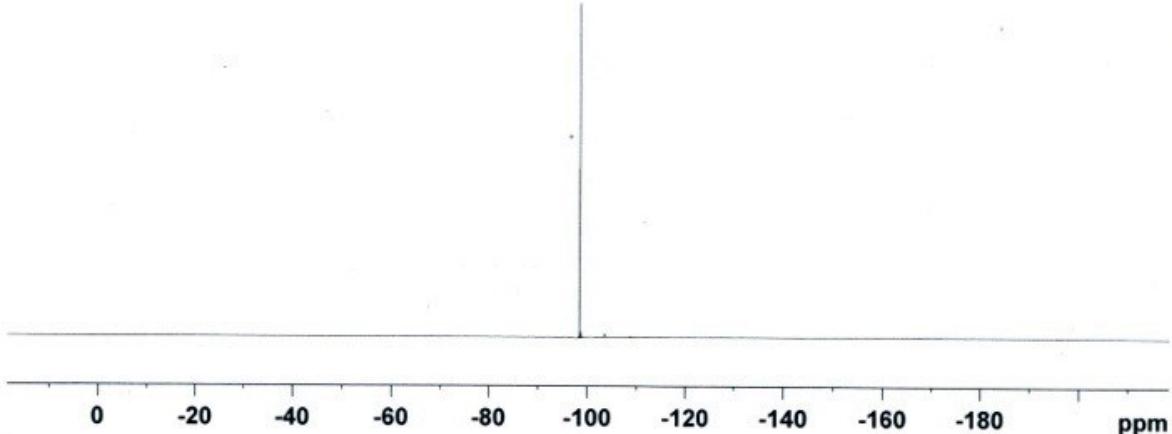
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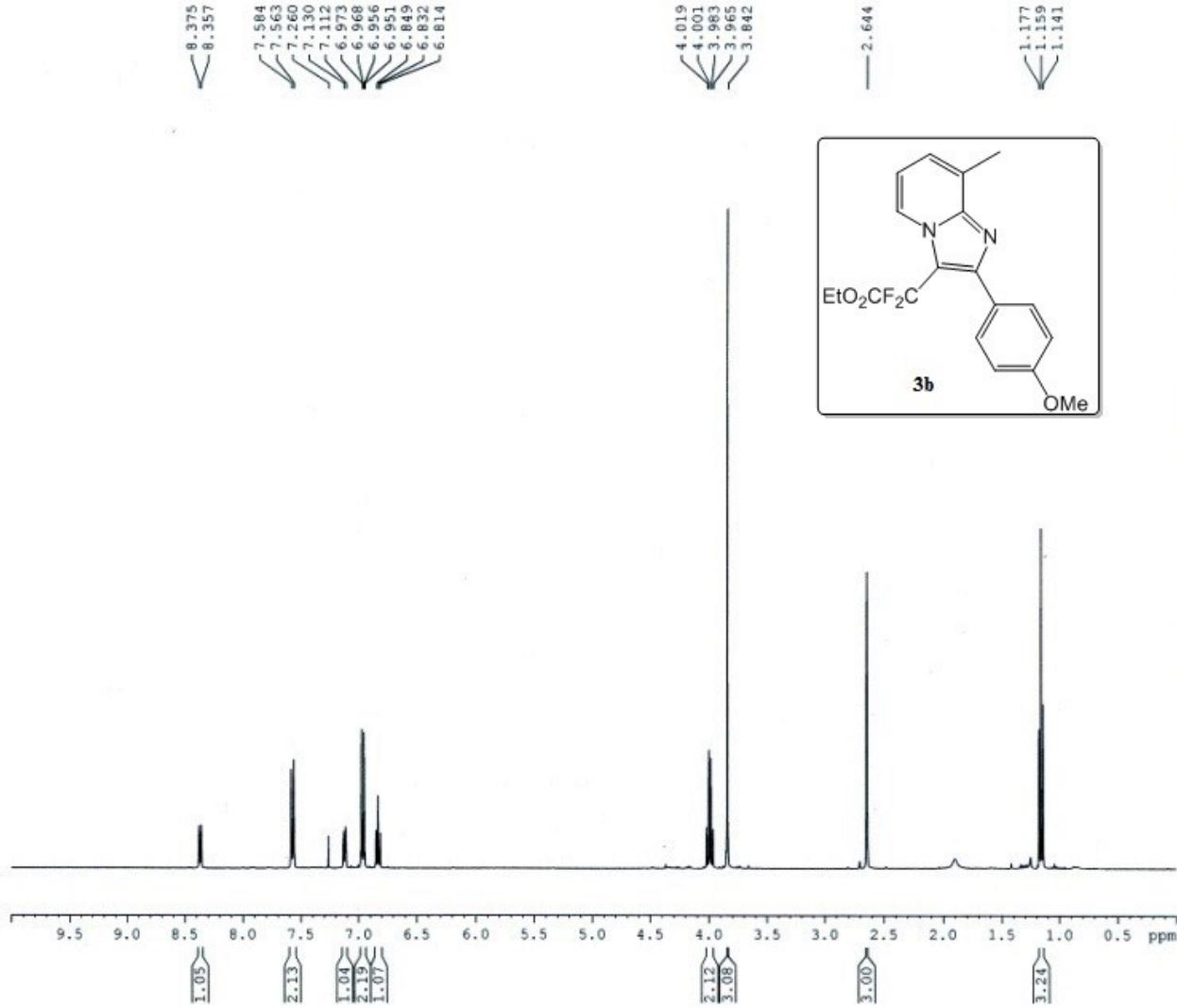
Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 233
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150527
Time 20.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 32768
SOLVENT CDCl₃
NS 16
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 106.66
DW 5.600 usec
DE 6.50 usec
TE 299.9 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 19F
PI 12.50 usec
PLW1 20.0000000 W
SFOL 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171850 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





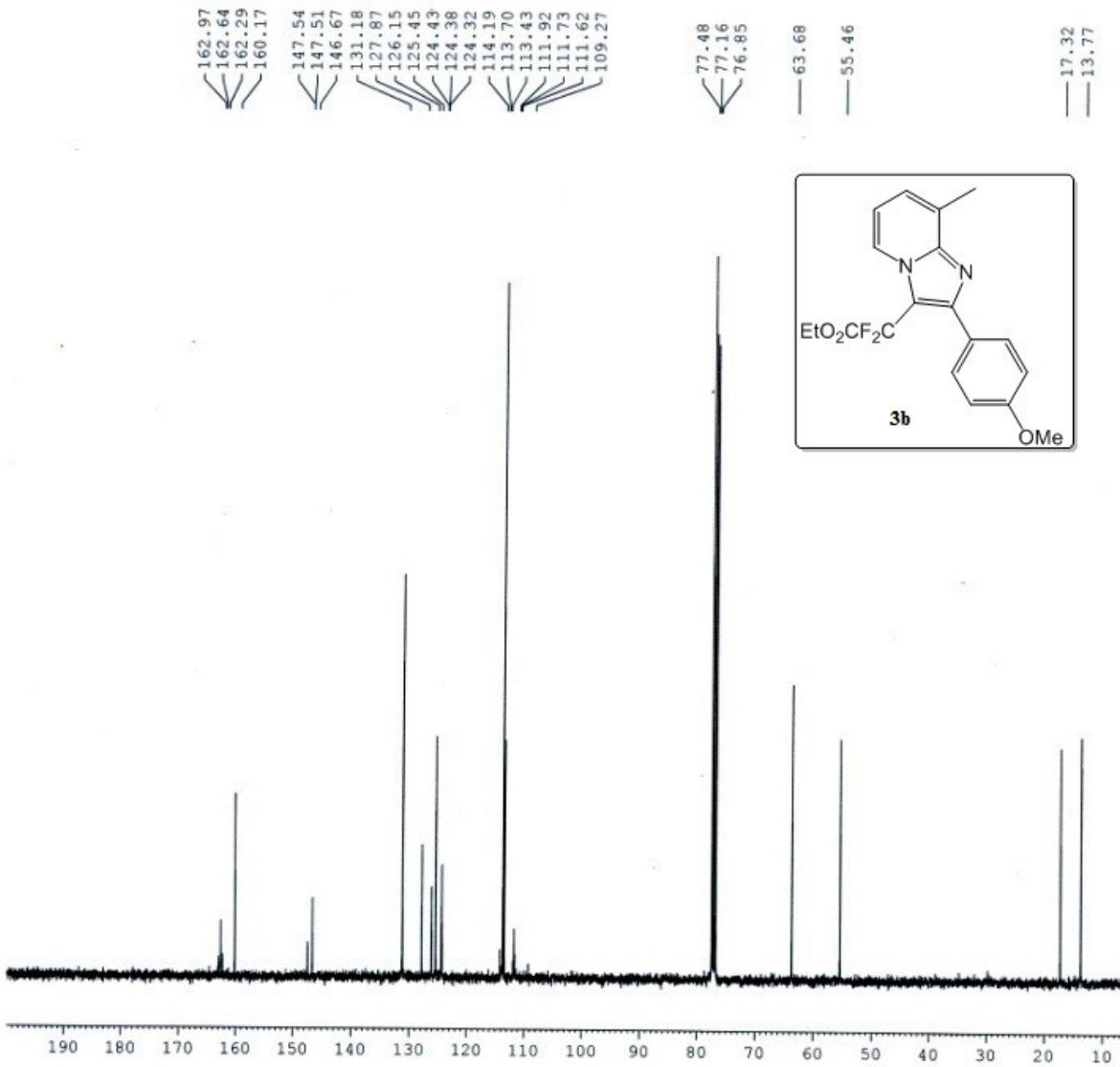
BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 418
PROCNO 1

F2 - Acquisition Parameters
Date 20150722
Time 12.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 1
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.992344 sec
RG 67.81
DW 60.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.0000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 1H
P1 14.75 usec
PLW1 11.99499989 W
SF01 400.1524711 MHz

F2 - Processing parameters
SI 16384
SF 400.1500090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

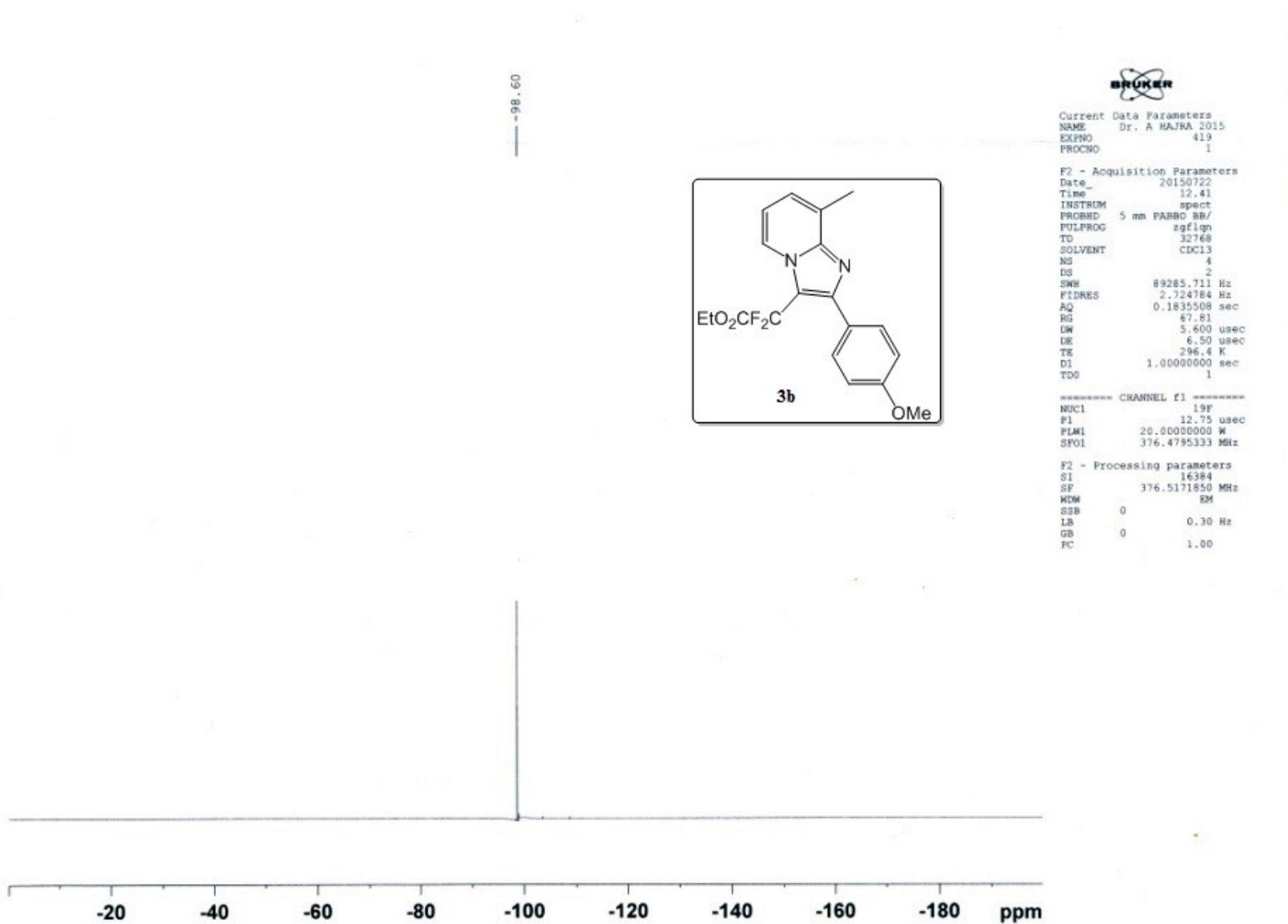
Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 420
PROCNO 1

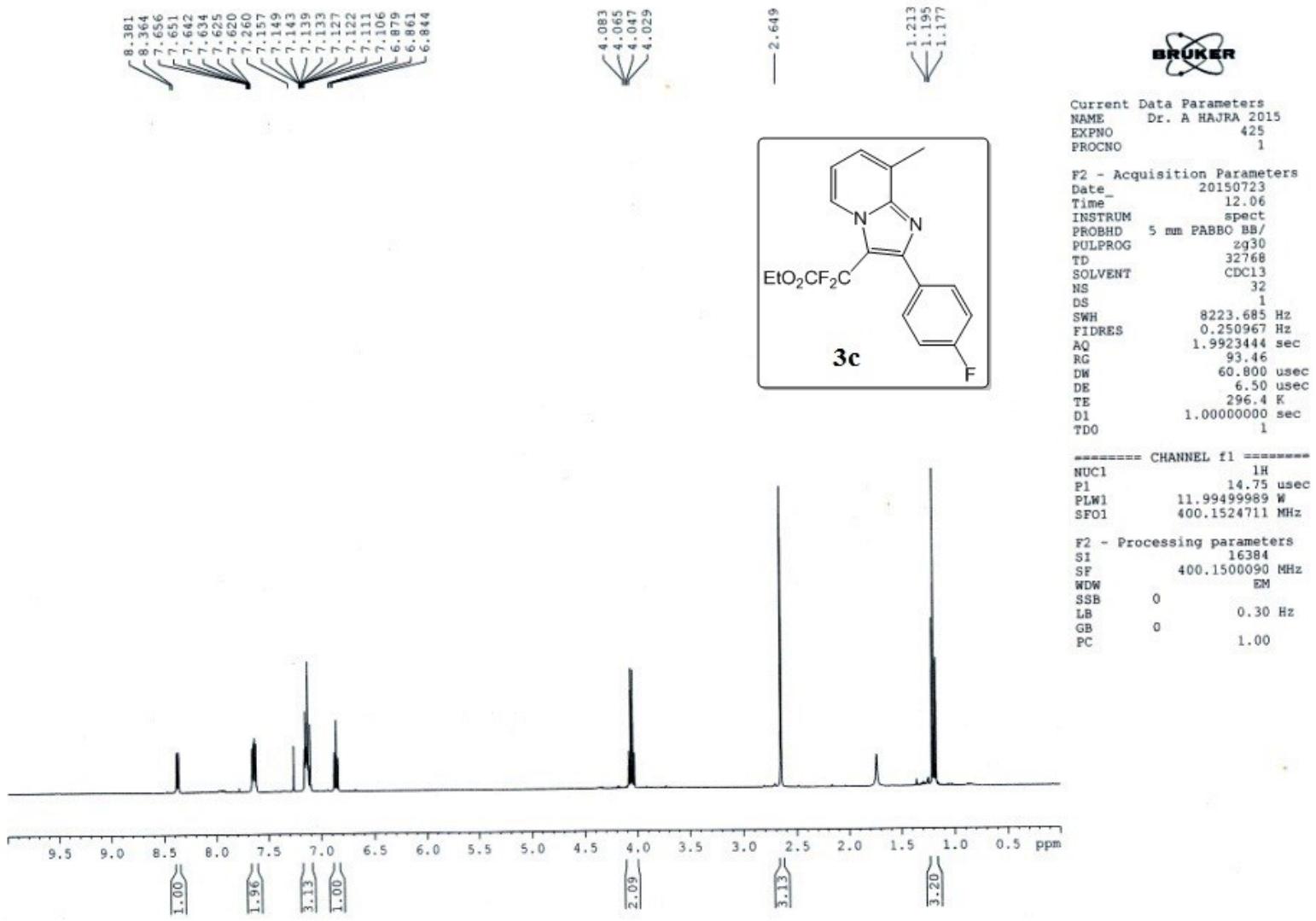
F2 - Acquisition Parameters
Date_ 20150722
Time_ 13.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 512
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 67.81
DW 20.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.0000000 sec
D11 0.03000000 sec
TD0 1

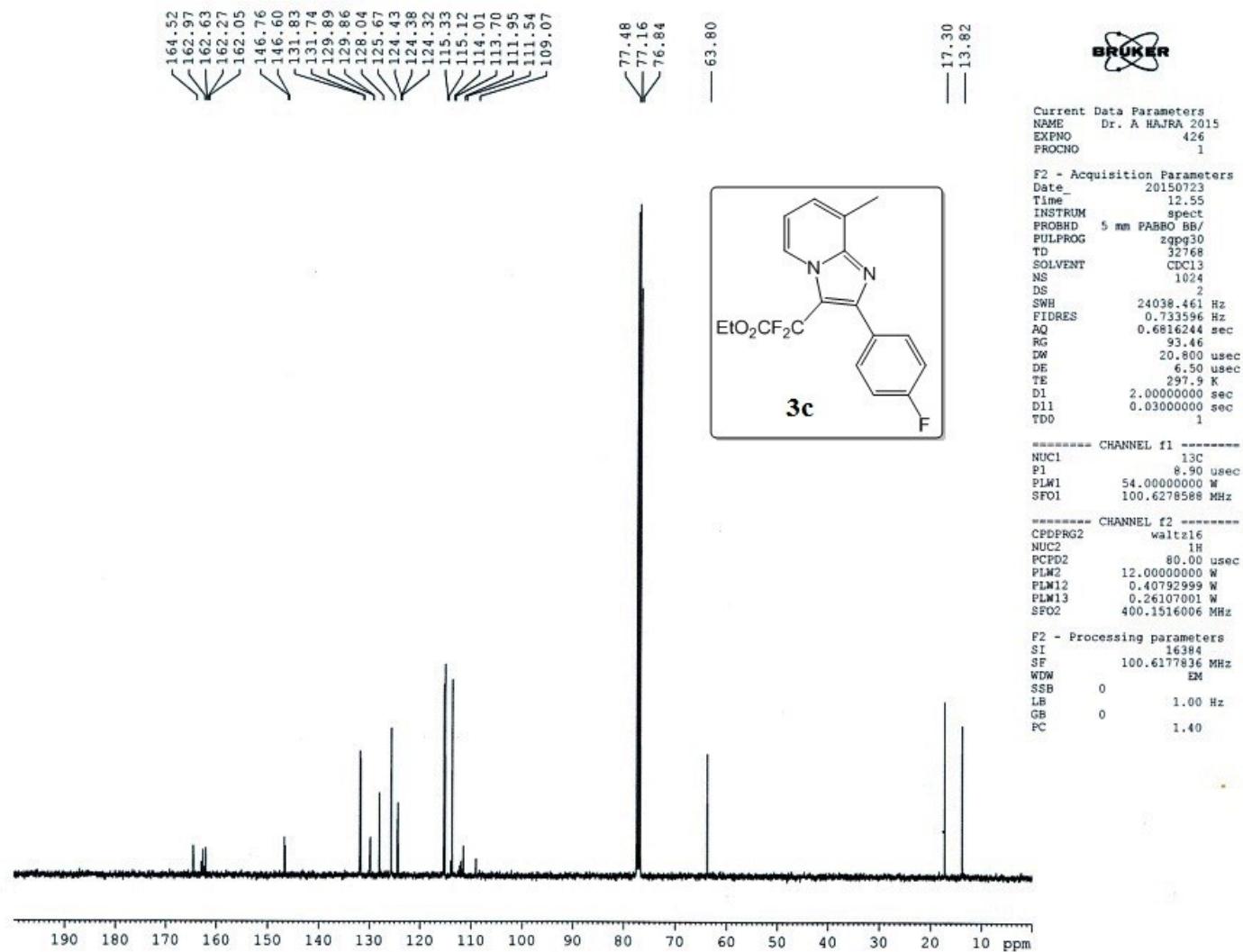
----- CHANNEL f1 -----
NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W
SF01 100.6278588 MHz

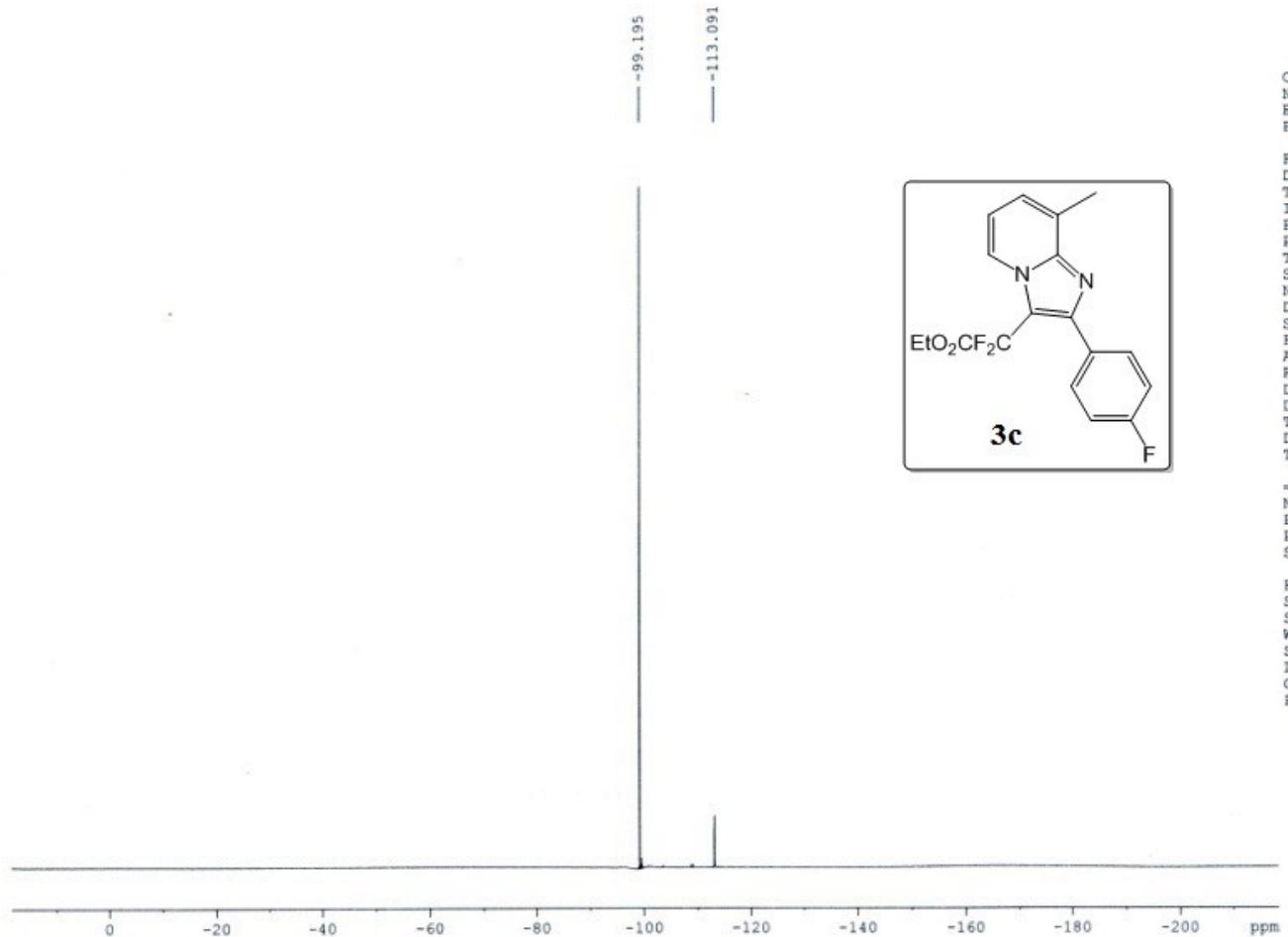
----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 12.00000000 W
PLW12 0.40792999 W
PLW13 0.26107001 W
SFQ2 400.1516006 MHz

F2 - Processing parameters
SI 16384
SF 100.6177854 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40









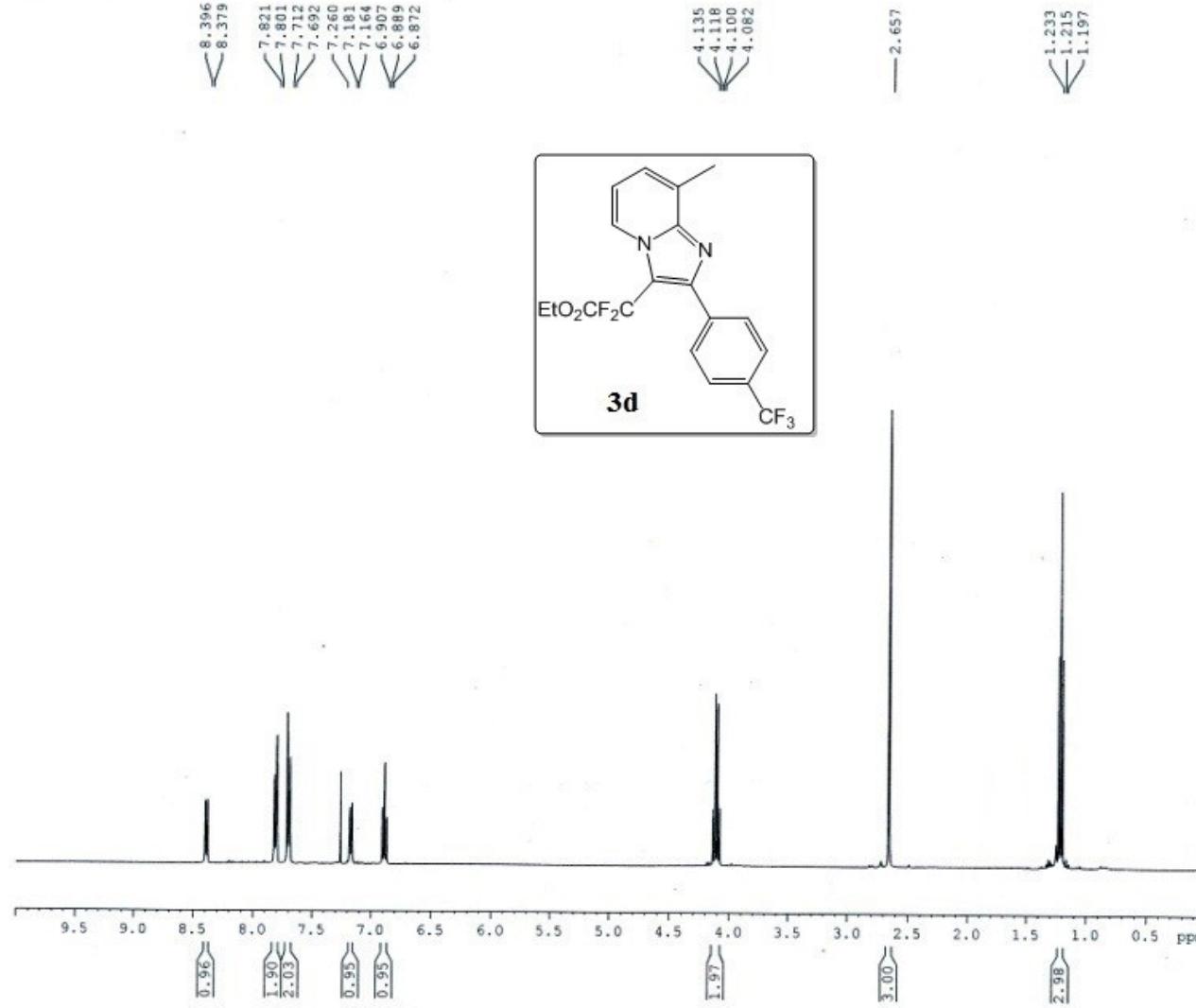
BRUKER

Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 427
 PROCNO 1

F2 - Acquisition Parameters
 Date 20150723
 Time 12.58
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgfgqn
 TD 32768
 SOLVENT CDCl3
 NS 4
 DS 2
 SWH 89285.711 Hz
 FIDRES 2.724784 Hz
 AQ 0.1835508 sec
 RG 87.66
 DW 5.600 usec
 DE 6.50 usec
 TE 297.1 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 19F
 P1 12.75 usec
 PLW1 20.0000000 W
 SFOL 376.4795333 MHz

F2 - Processing parameters
 SI 16384
 SF 376.5171850 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 454
PROCNO 1

```

F2 - Acquisition Parameters
Date_          20150729
Time           12.19
INSTRUM        spect
PROBHD      5 mm PABBO BB/
PULPROG       zg30
TD             32768
SOLVENT        CDCl3
NS              24
DS               1
SWH            8223.685 Hz
FIDRES        0.250967 Hz
AQ            1.9923444 sec
RG              106.66
DW             60.800 usec
DE               6.50 usec
TE              293.8 K
D1         1.00000000 sec
TD0                  1

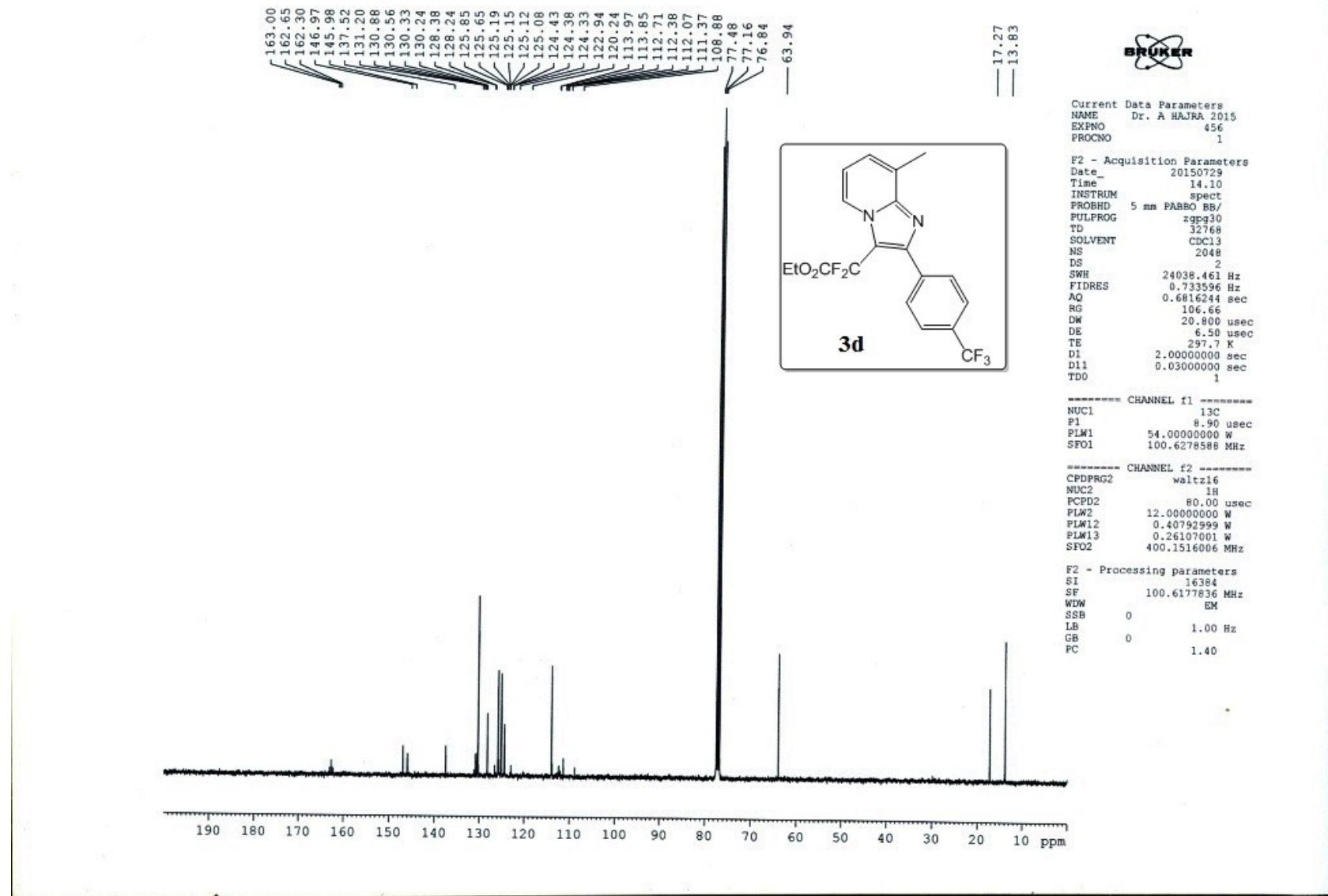
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===== CHANNEL f1 =====
NUC1 1H
P1 14.75 usec
PLW1 11.99499989 W
SFO1 400.1524711 MHz

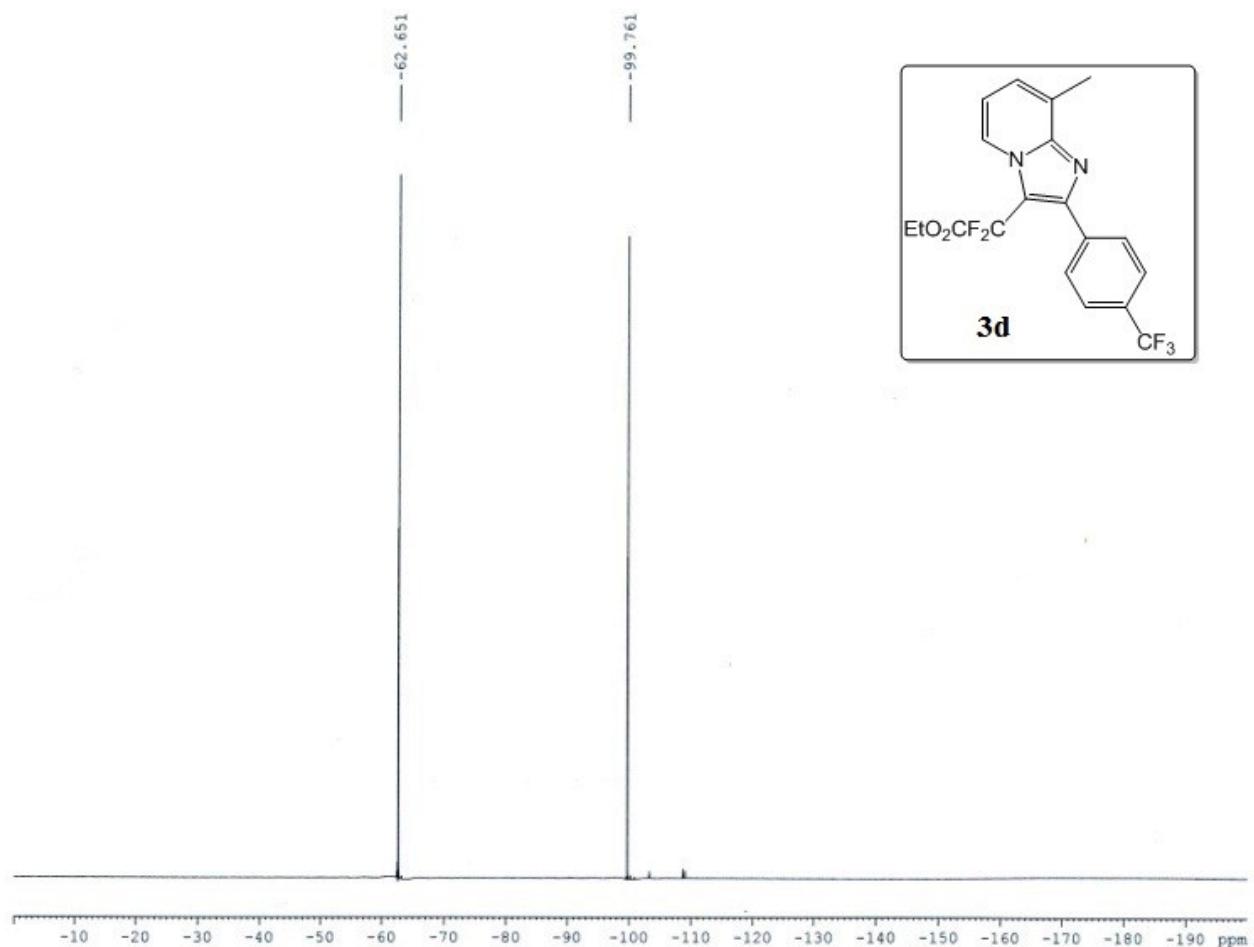
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F2 - Processing parameters
SI          16384
SF        400.1500090 MHz
NDW           EM
SSB          0
LB          0.30 Hz
GB          0
PC          1.00

```



F19 1H coupled VBPM-459 I

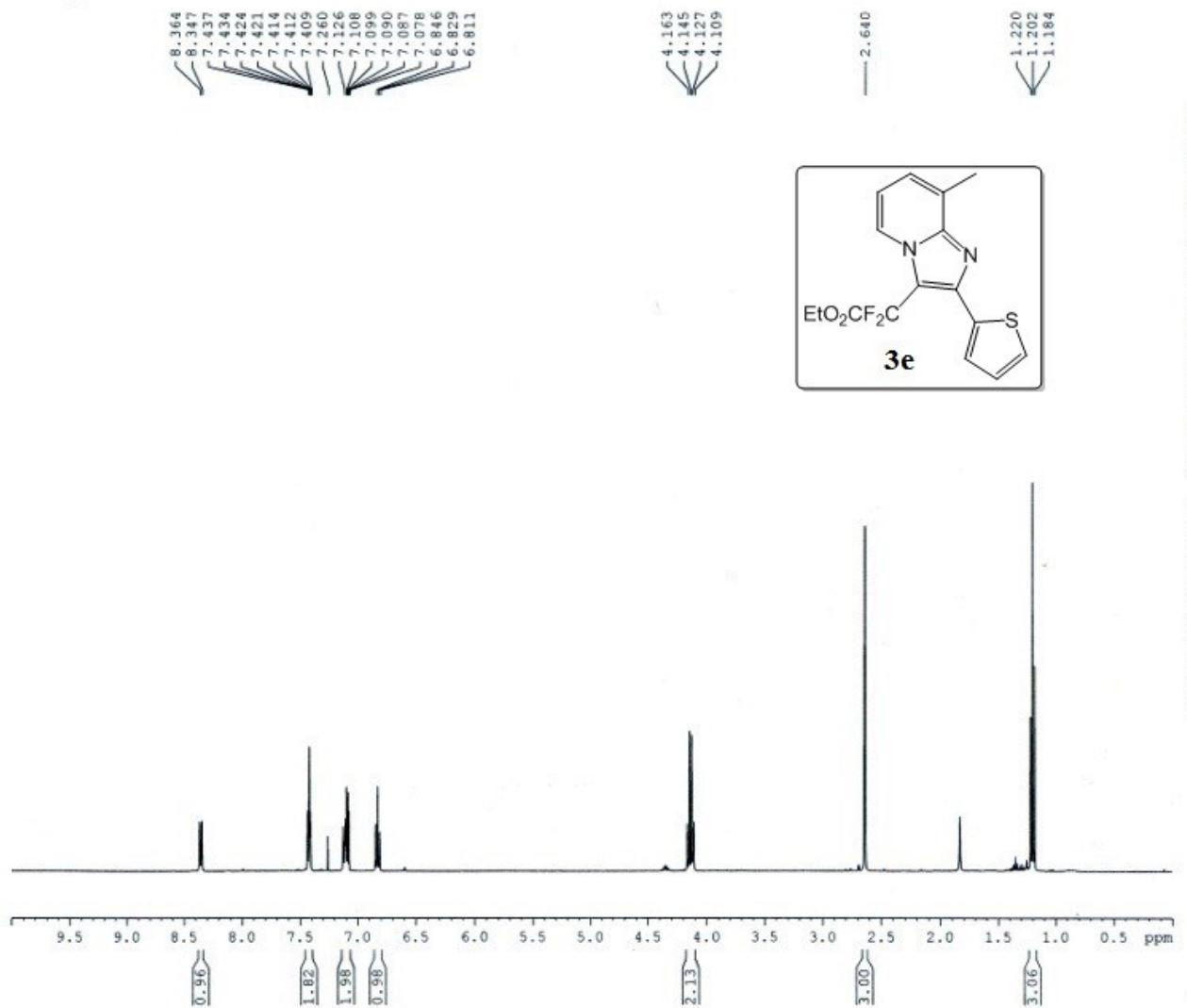


Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 455
PROCNO 1

F2 - Acquisition Parameters
Date 20150729
Time 12.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgfgn
TD 32768
SOLVENT CDCl₃
NS 16
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 106.66
DW 5.600 usec
DE 6.50 usec
TE 294.2 K
D1 1.0000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 ¹⁹F
P1 12.50 usec
PLW1 20.0000000 W
SFO1 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171850 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



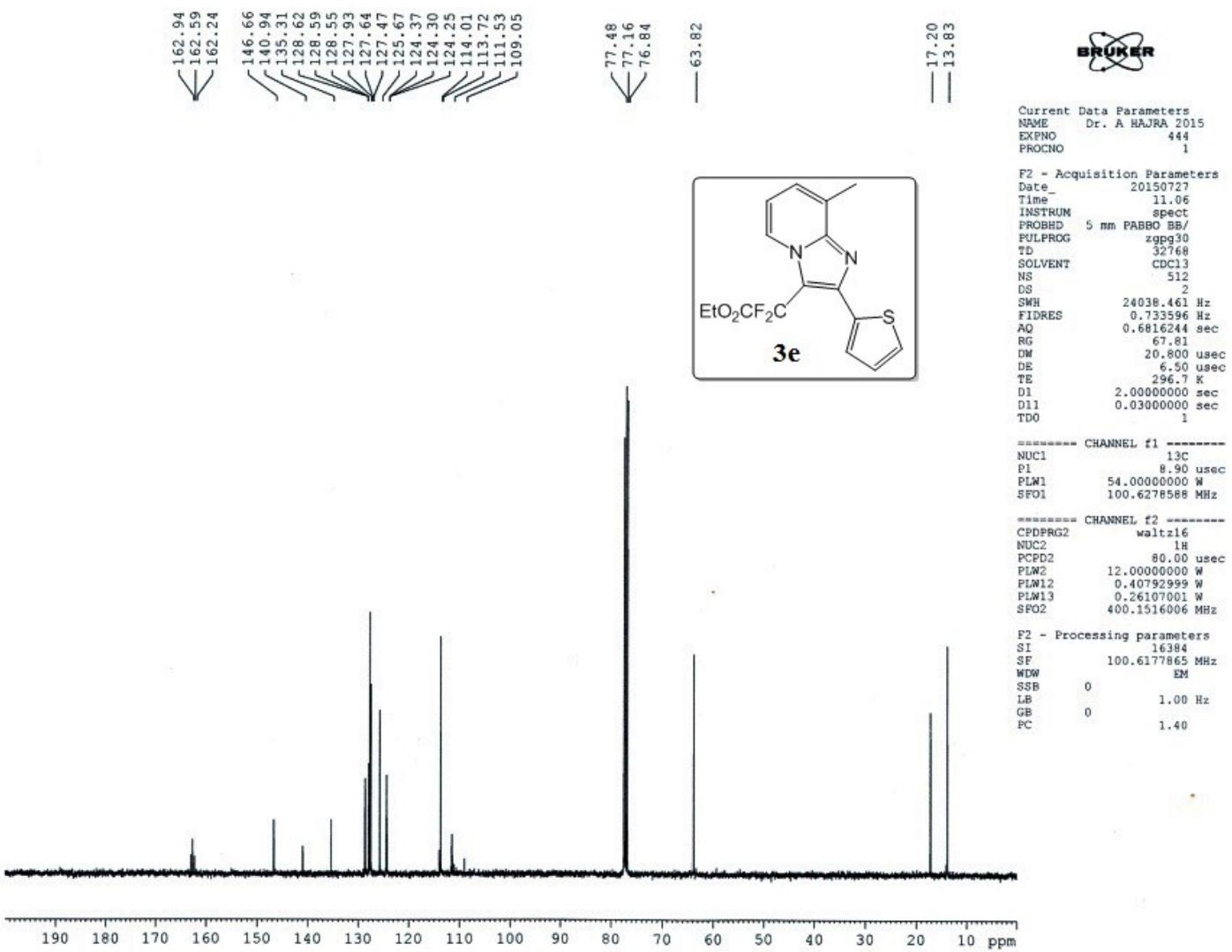
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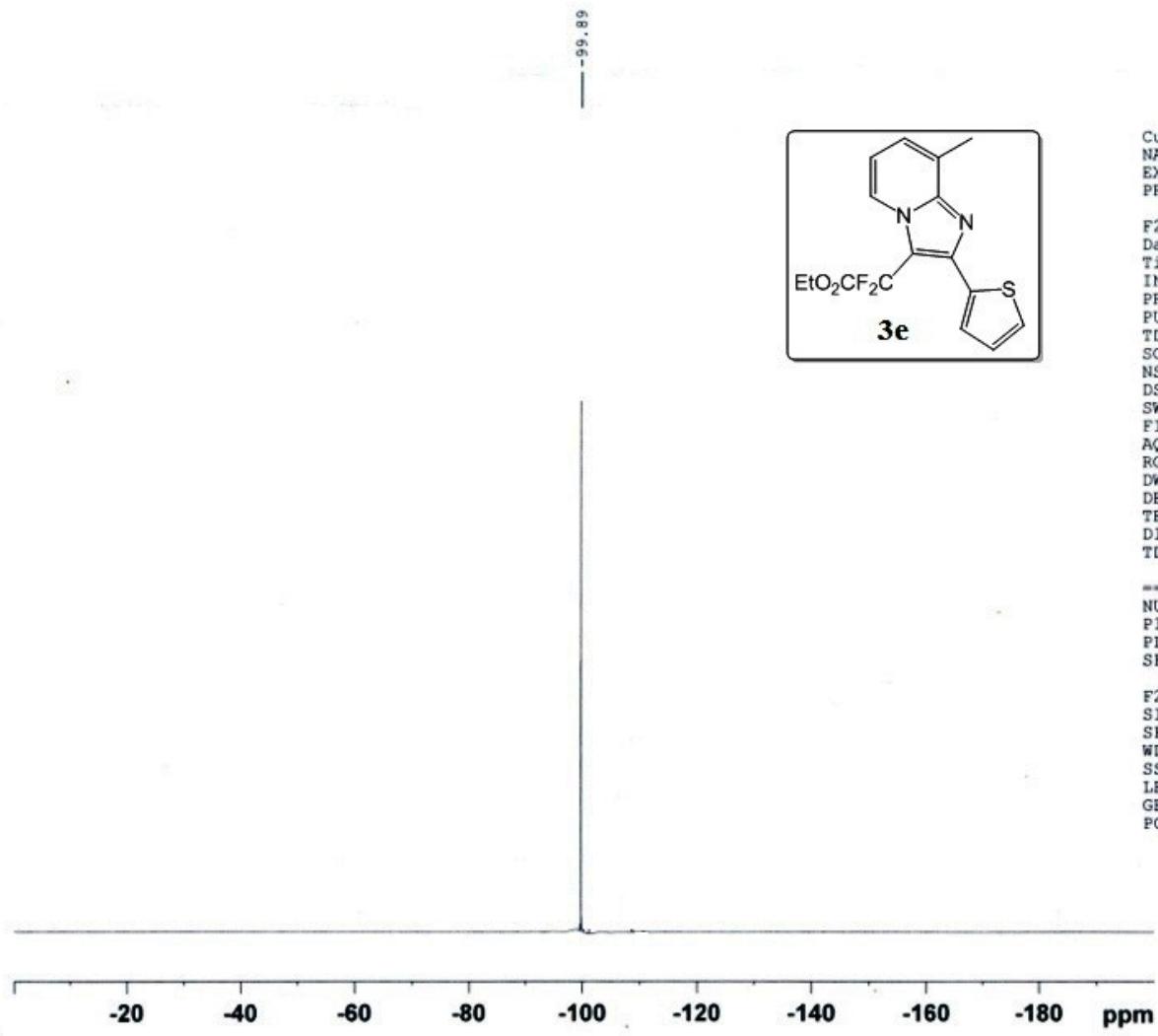
Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 442
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20150727
 Time 10.38
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 24
 DS 1
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9923444 sec
 RG 67.81
 DW 60.800 usec
 DE 6.50 usec
 TE 295.5 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.75 usec
 PLWI 11.99499989 W
 SF01 400.1524711 MHz

F2 - Processing parameters
 SI 16384
 SF 400.1500090 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





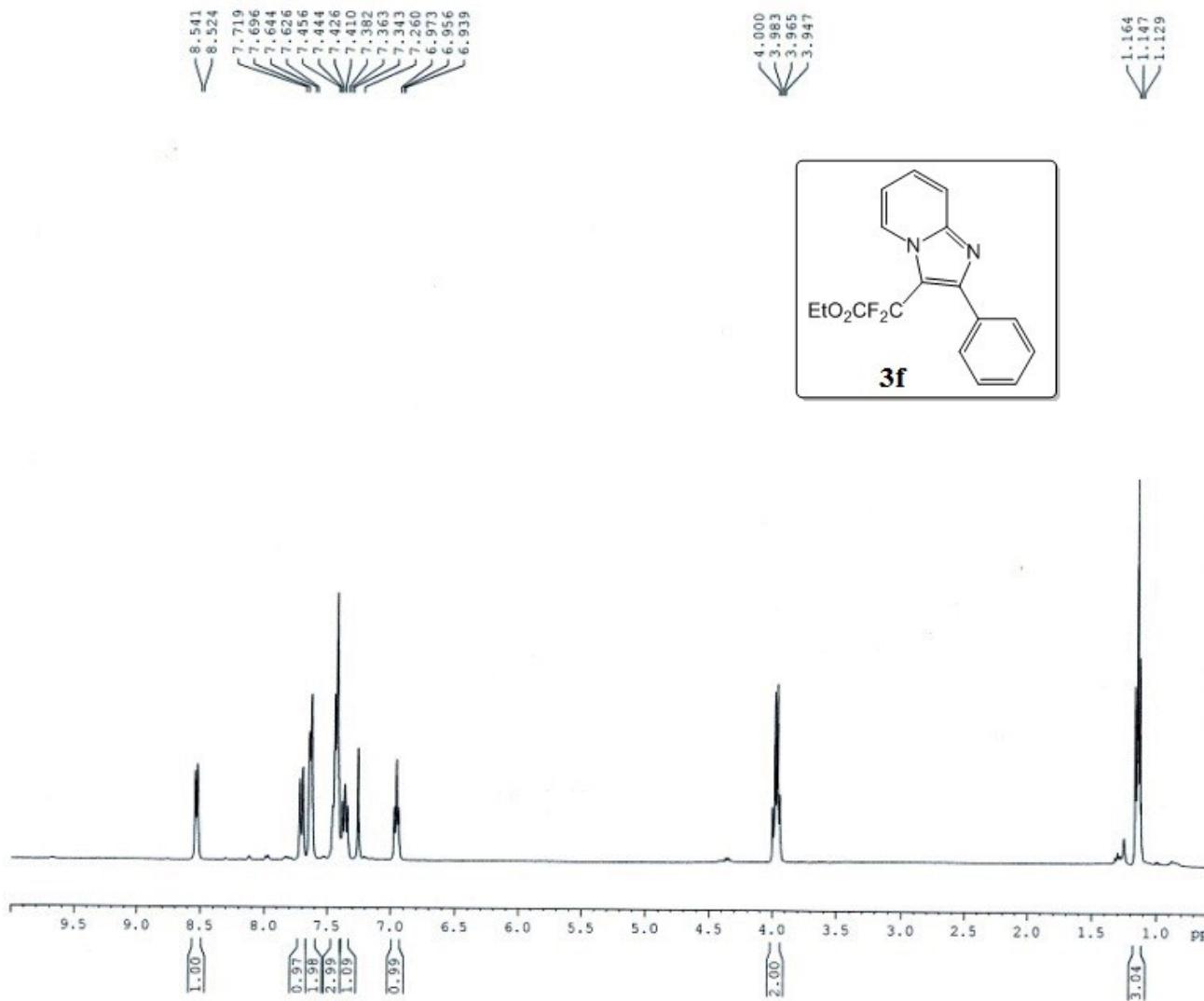
BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 443
PROCNO 1

F2 - Acquisition Parameters
Date 20150727
Time 10.40
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 32768
SOLVENT CDCl₃
NS 4
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 67.81
DW 5.600 usec
DE 6.50 usec
TE 295.4 K
D1 1.0000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 19F
P1 12.75 usec
PLW1 20.0000000 W
SFO1 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171850 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



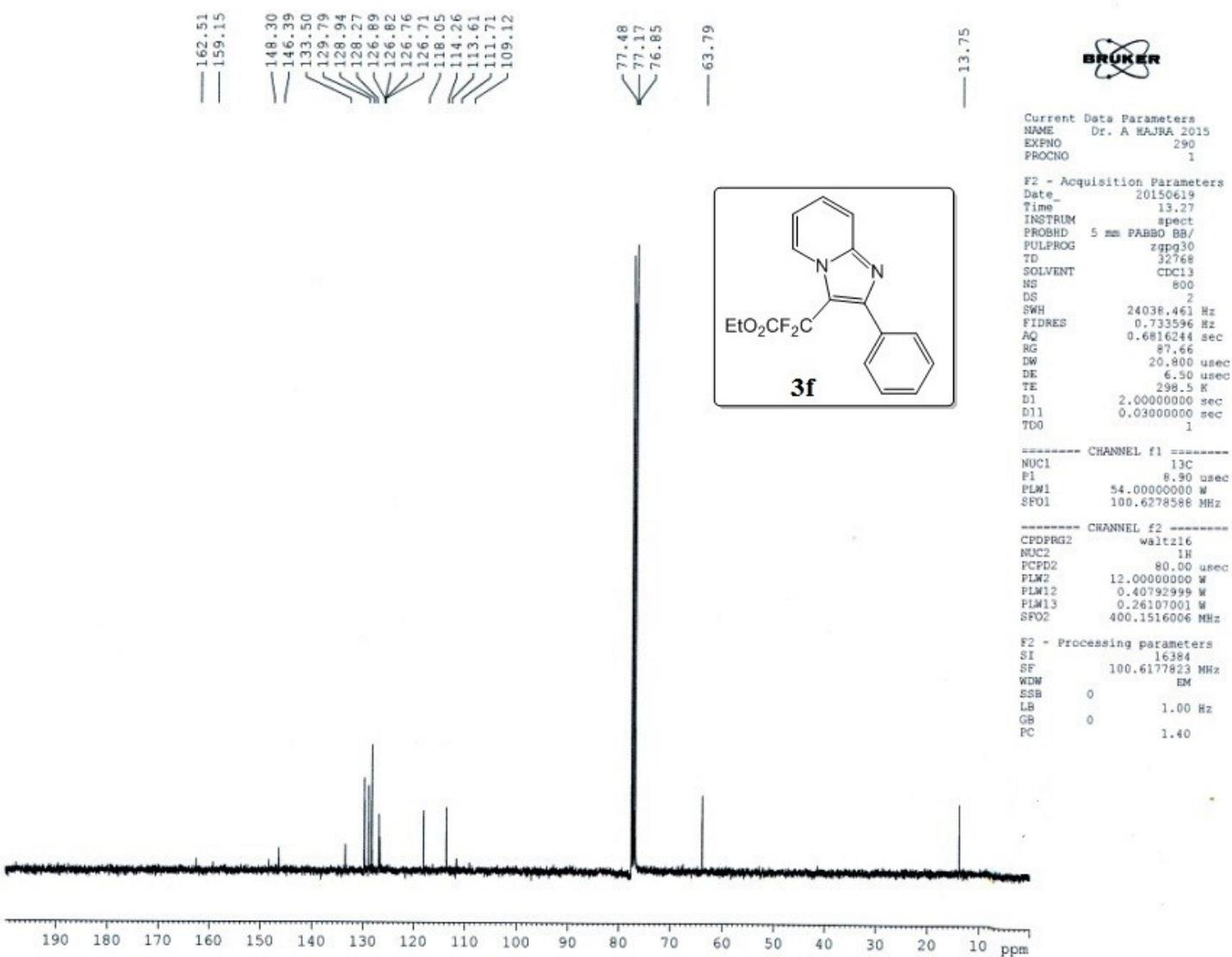
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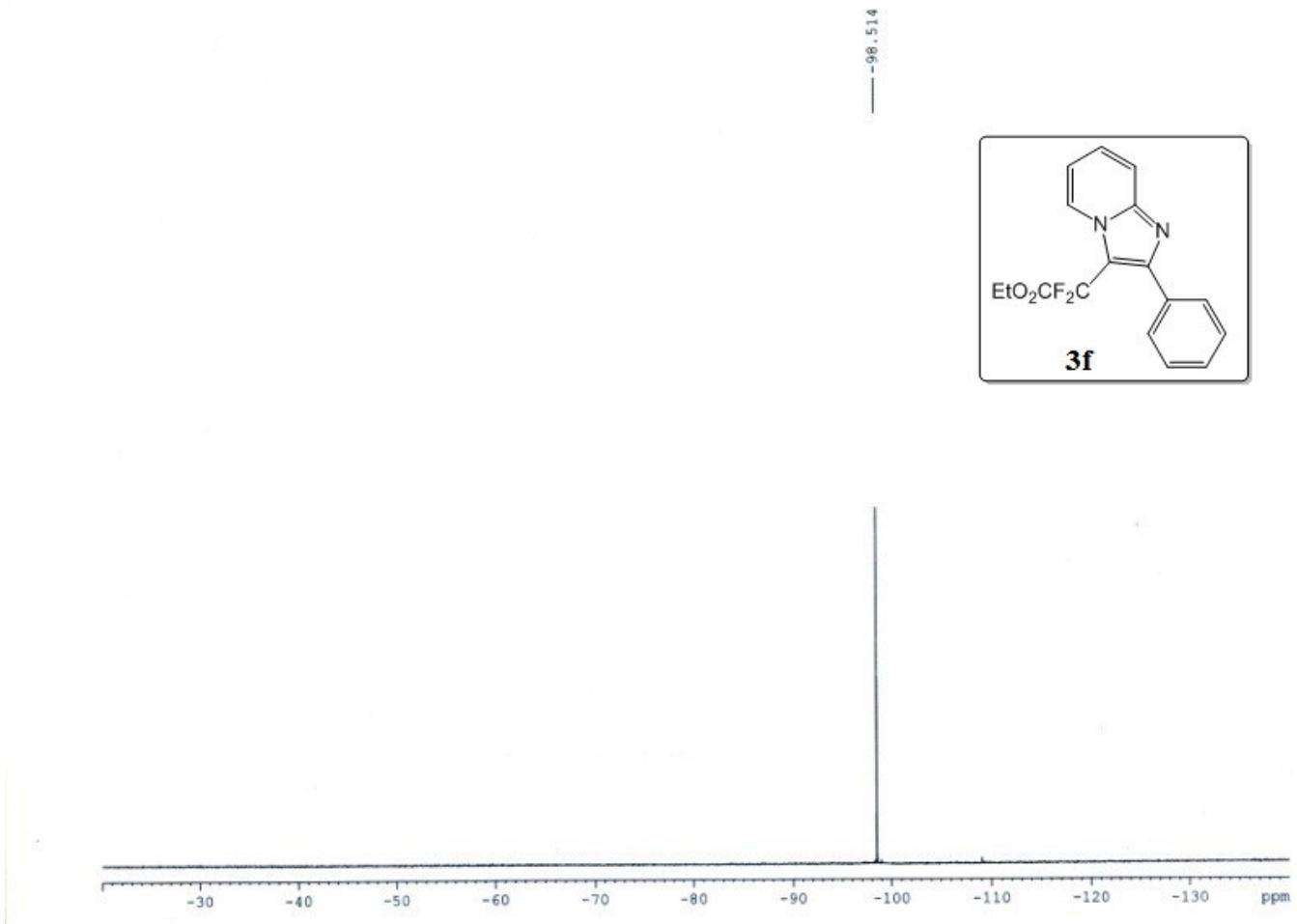
Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 289
 PROCNO 1

F2 - Acquisition Parameters
 Date 20150619
 Time 12.46
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 1
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9923444 sec
 RG 135.7
 DW 60.800 usec
 DE 6.50 usec
 TE 297.1 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 PI 14.75 usec
 PLW1 11.99499989 W
 SFO1 400.1524711 MHz

F2 - Processing parameters
 SI 16384
 SF 400.1500097 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





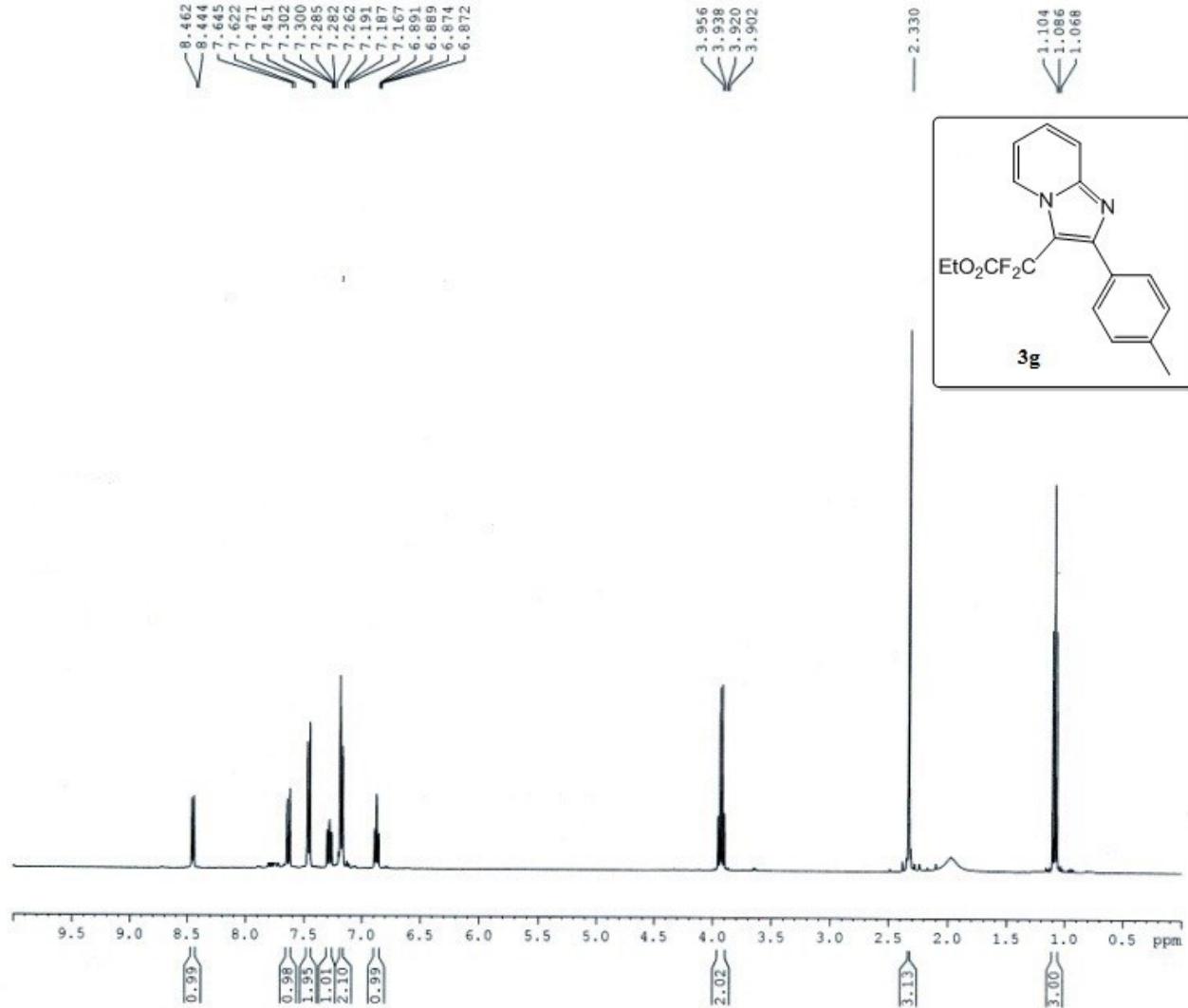
BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 291
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150619
Time 12.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 32768
SOLVENT CDCl₃
NS 2
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 87.66
DW 5.600 usec
DE 6.50 usec
TE 297.1 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 19F
P1 12.50 usec
PLW1 20.00000000 W
SFO1 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171050 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

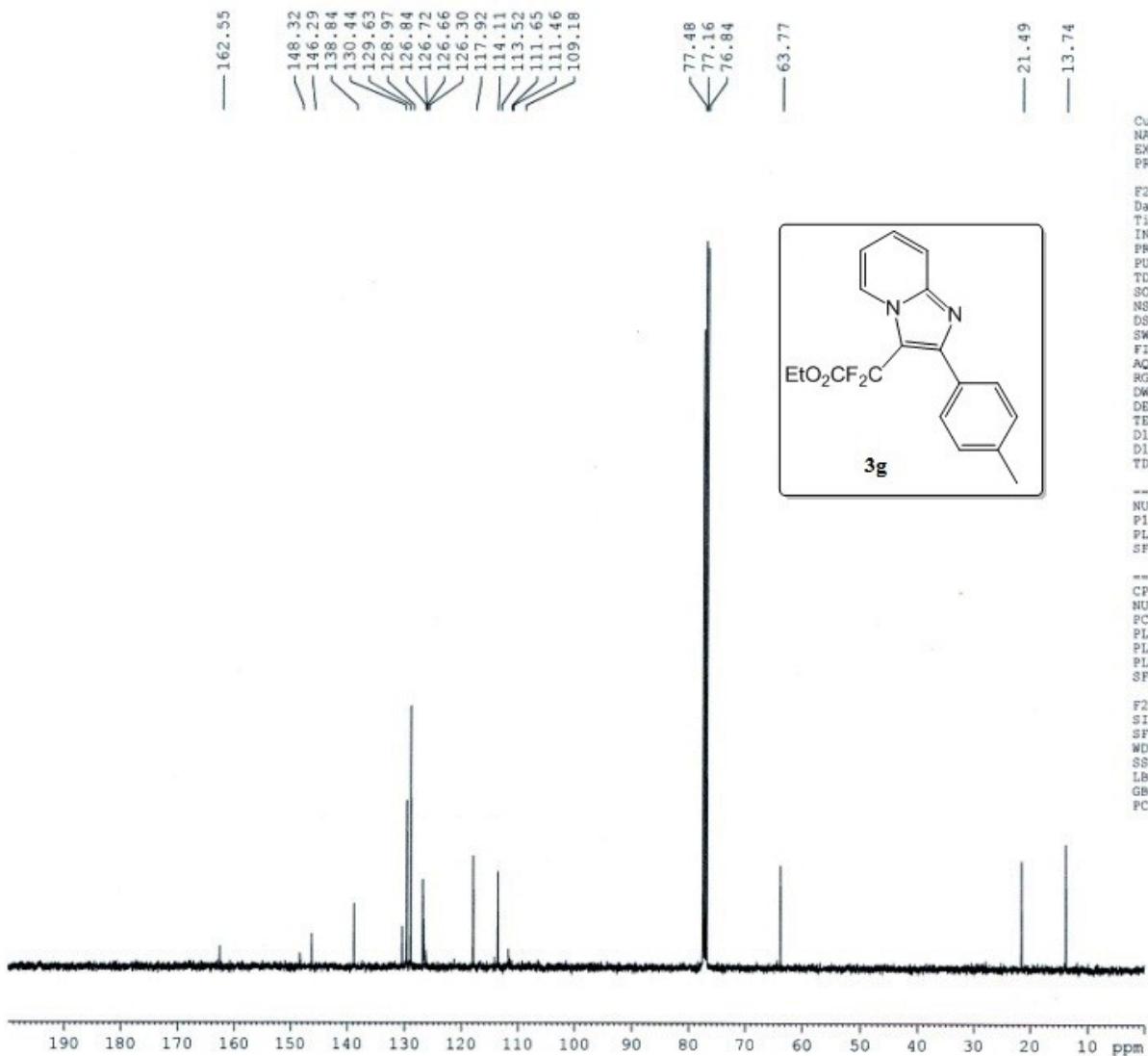


Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 247
 PROCNO 1

F2 - Acquisition Parameters
 Date 20150529
 Time 20.12
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 24
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9923444 sec
 RG 120.16
 DW 60.800 usec
 DE 6.50 usec
 TE 295.4 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.75 usec
 PLW1 11.99499989 W
 SFO1 400.1524711 MHz

F2 - Processing parameters
 SI 16384
 SF 400.1500364 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



BRUKER

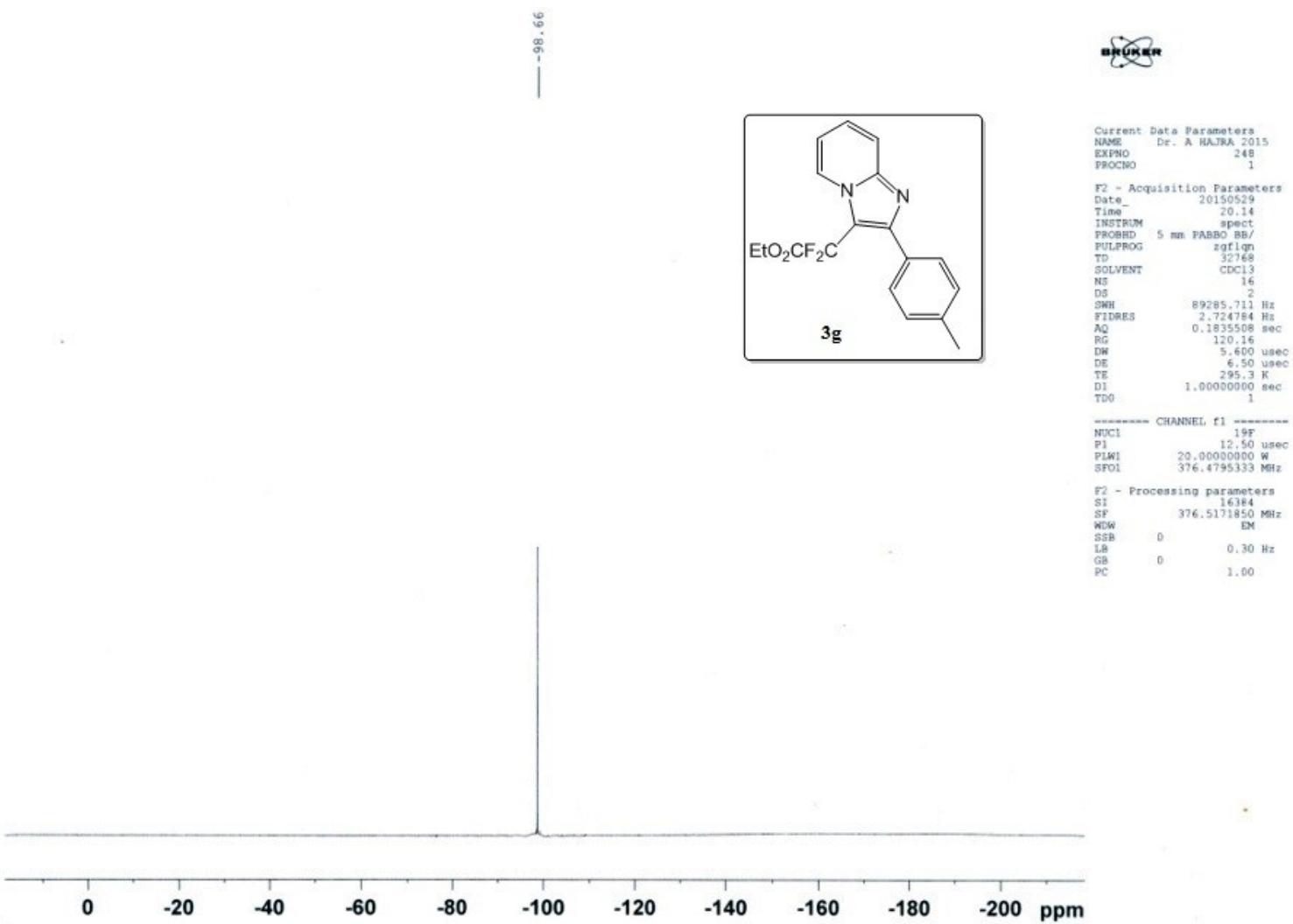
Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 249
 PROCNO 1

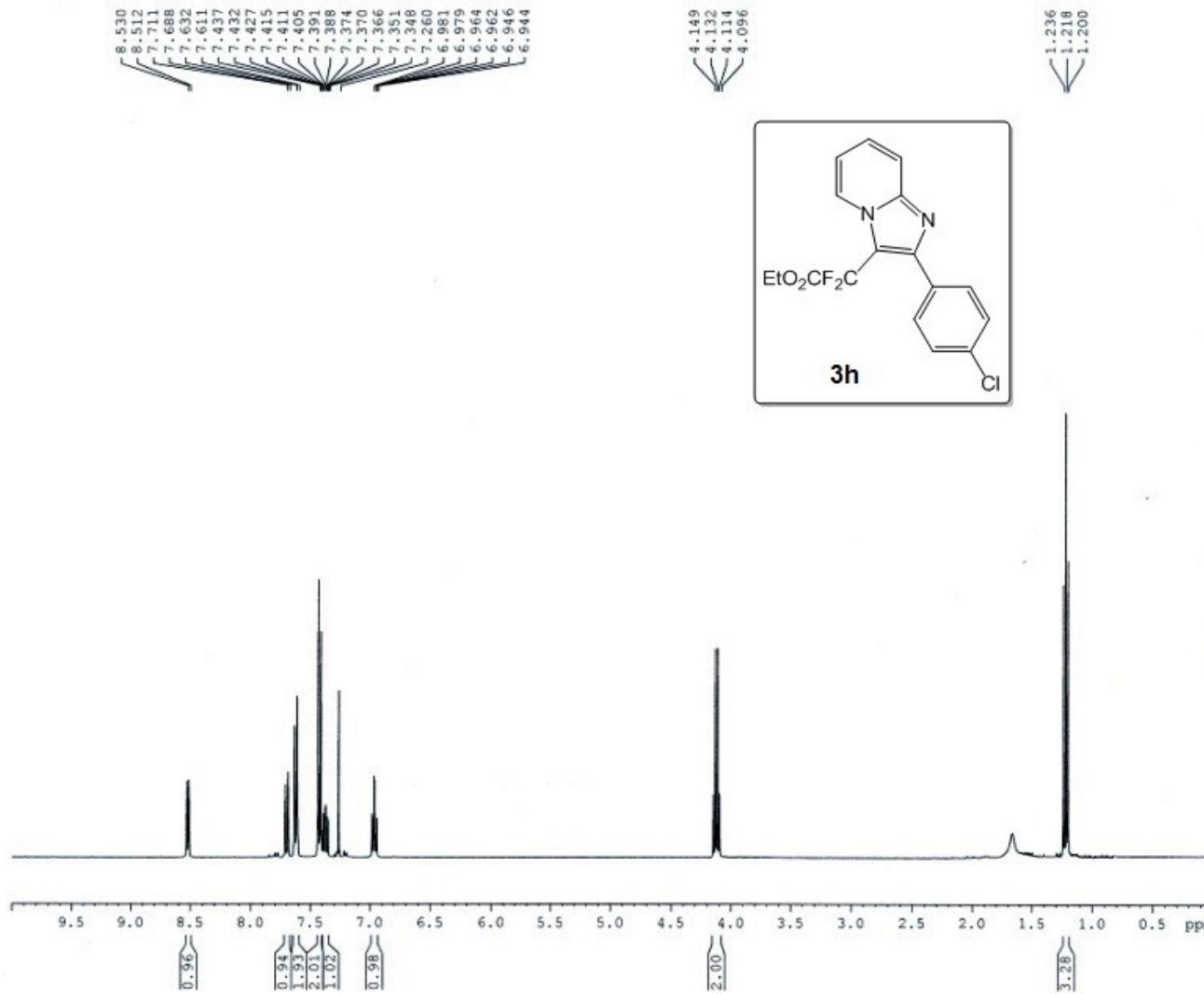
F2 - Acquisition Parameters
 Date_ 20150530
 Time 11.57
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 800
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6816244 sec
 RG 87.66
 DW 20.800 usec
 DE 6.50 usec
 TE 295.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO i

----- CHANNEL f1 -----
 NUC1 13C
 P1 8.90 usec
 PLW1 54.0000000 W
 SFO1 100.6278568 MHz

----- CHANNEL f2 -----
 CPDPBG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PLW2 12.0000000 W
 PLW12 0.40792999 W
 PLW13 0.26107001 W
 SFO2 400.1516006 MHz

F2 - Processing parameters
 SI 16384
 SF 100.6177851 MHz
 WDM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





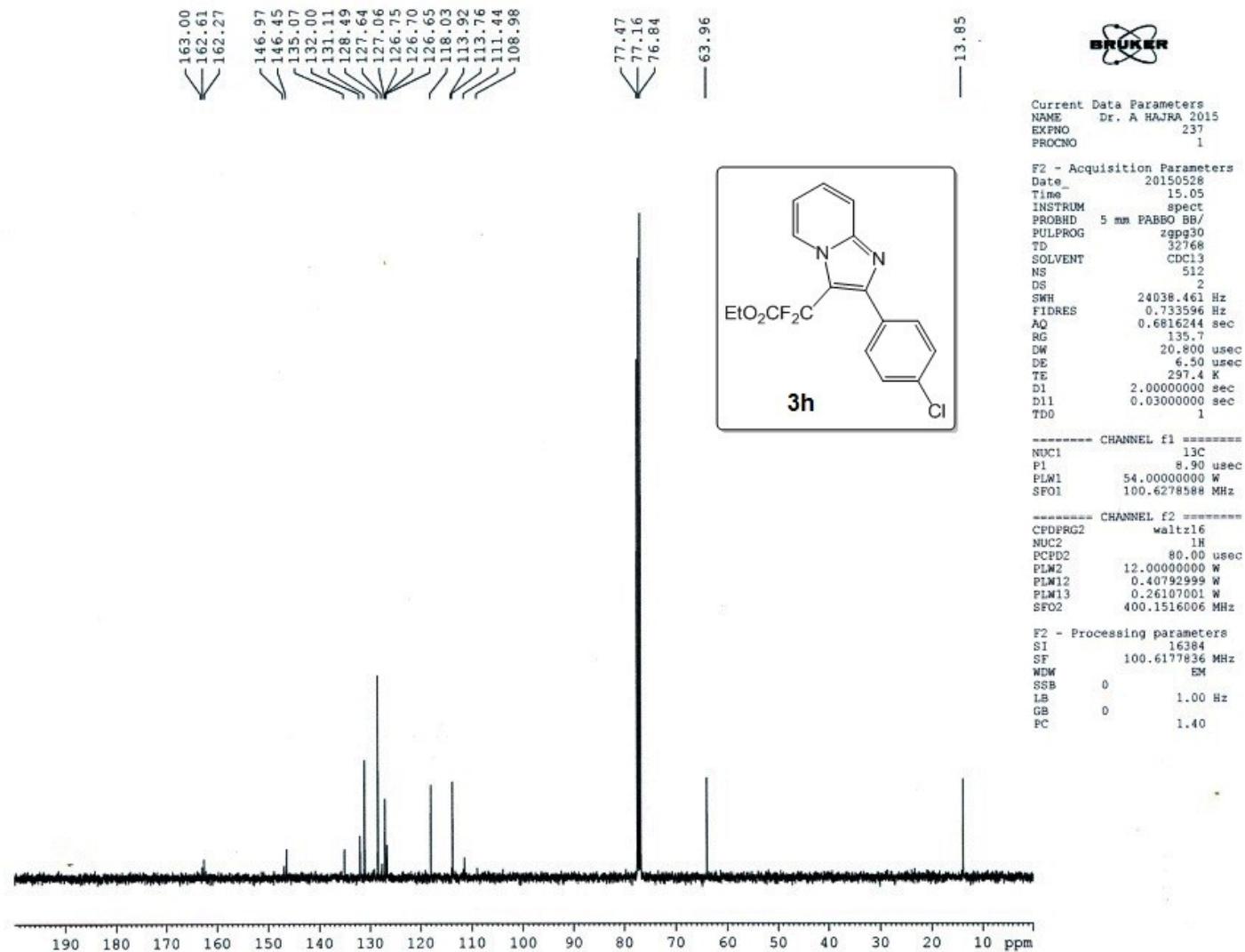
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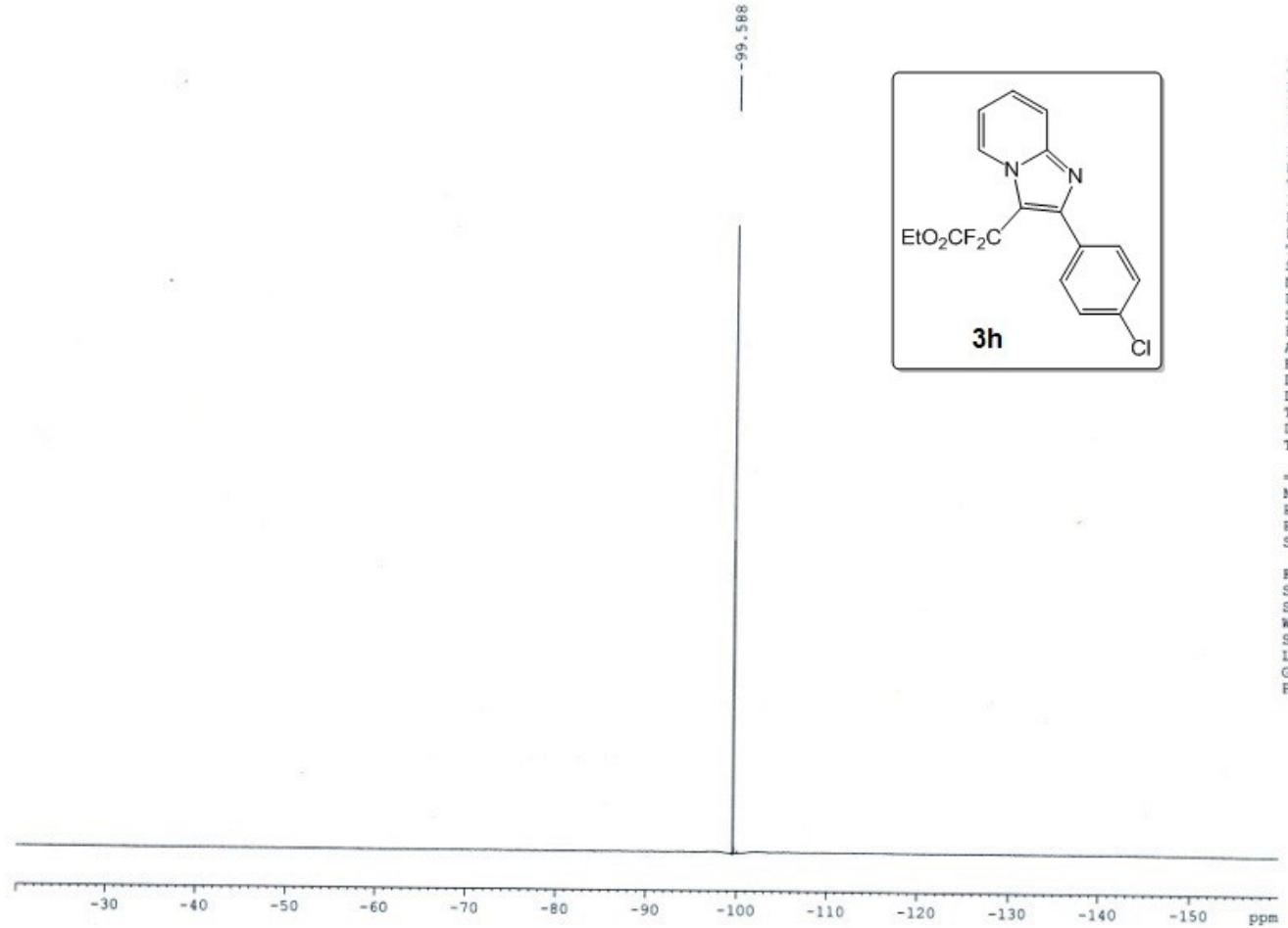
Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 236
 PROCNO 1

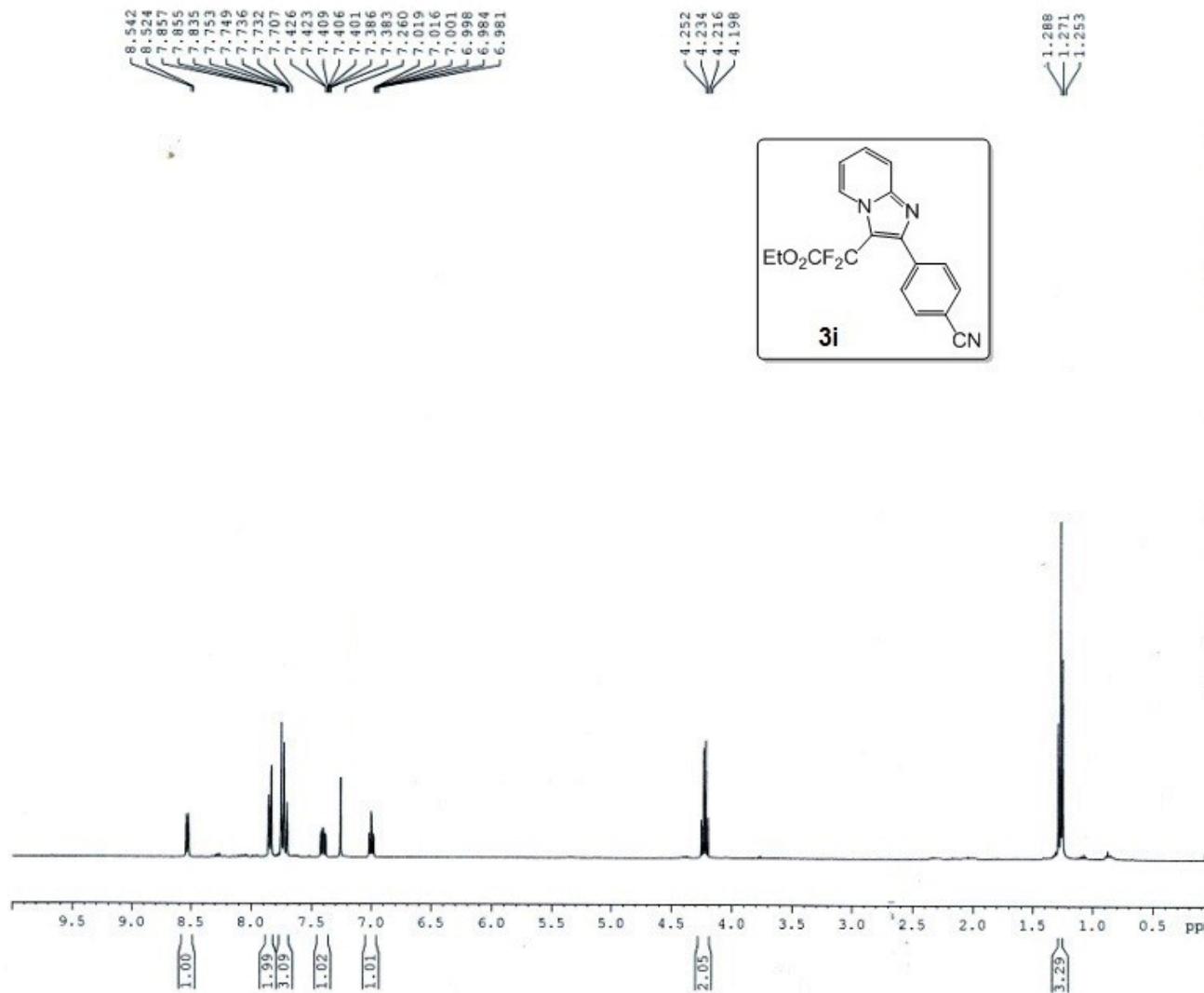
F2 - Acquisition Parameters
 Date 20150528
 Time 14.35
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9923444 sec
 RG 135.7
 DW 60.800 usec
 DE 6.50 usec
 TE 296.7 K
 D1 1.0000000 sec
 TDO 1

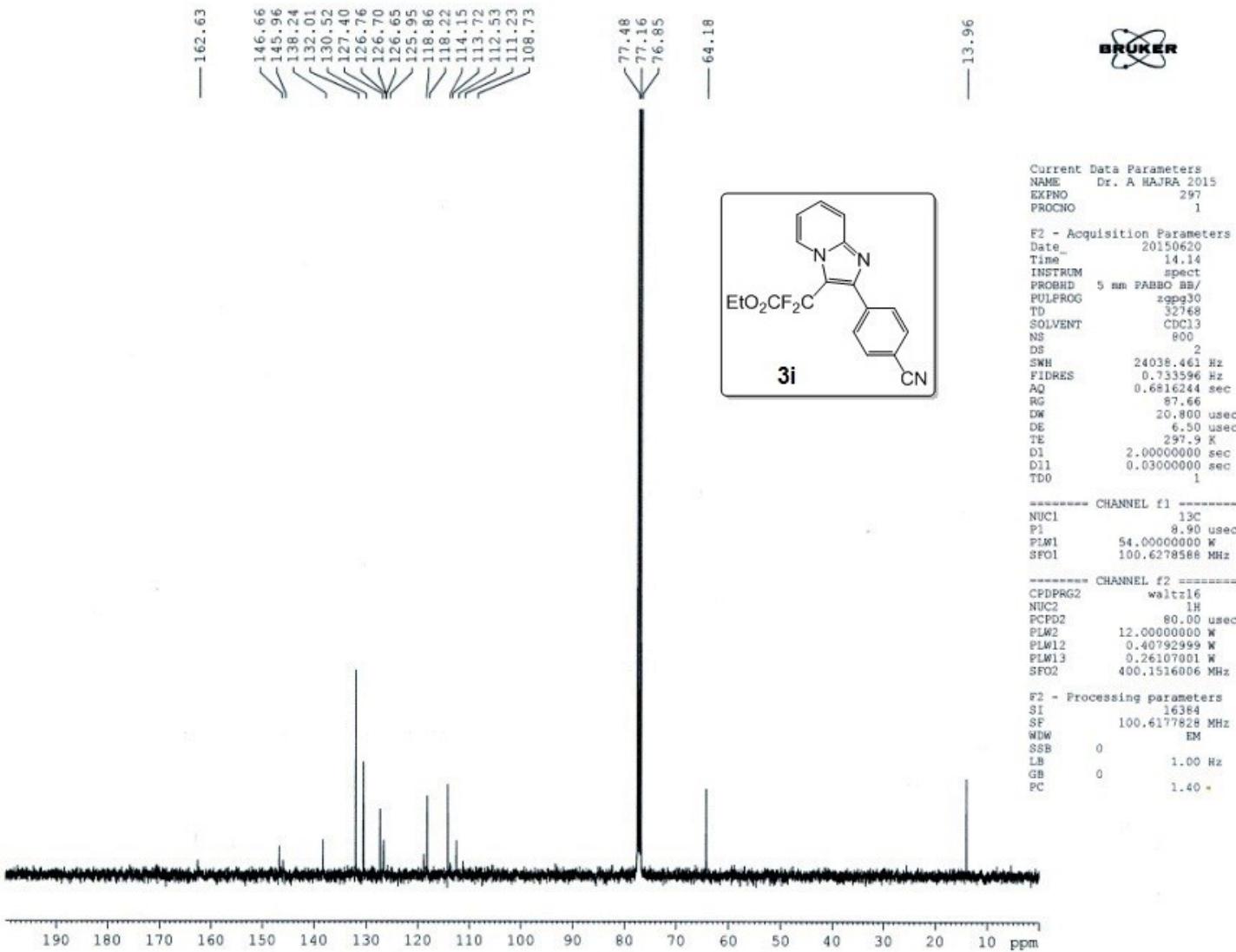
===== CHANNEL f1 =====
 NUC1 1H
 P1 14.75 usec
 PLW1 11.99499989 W
 SFO1 400.1524711 MHz

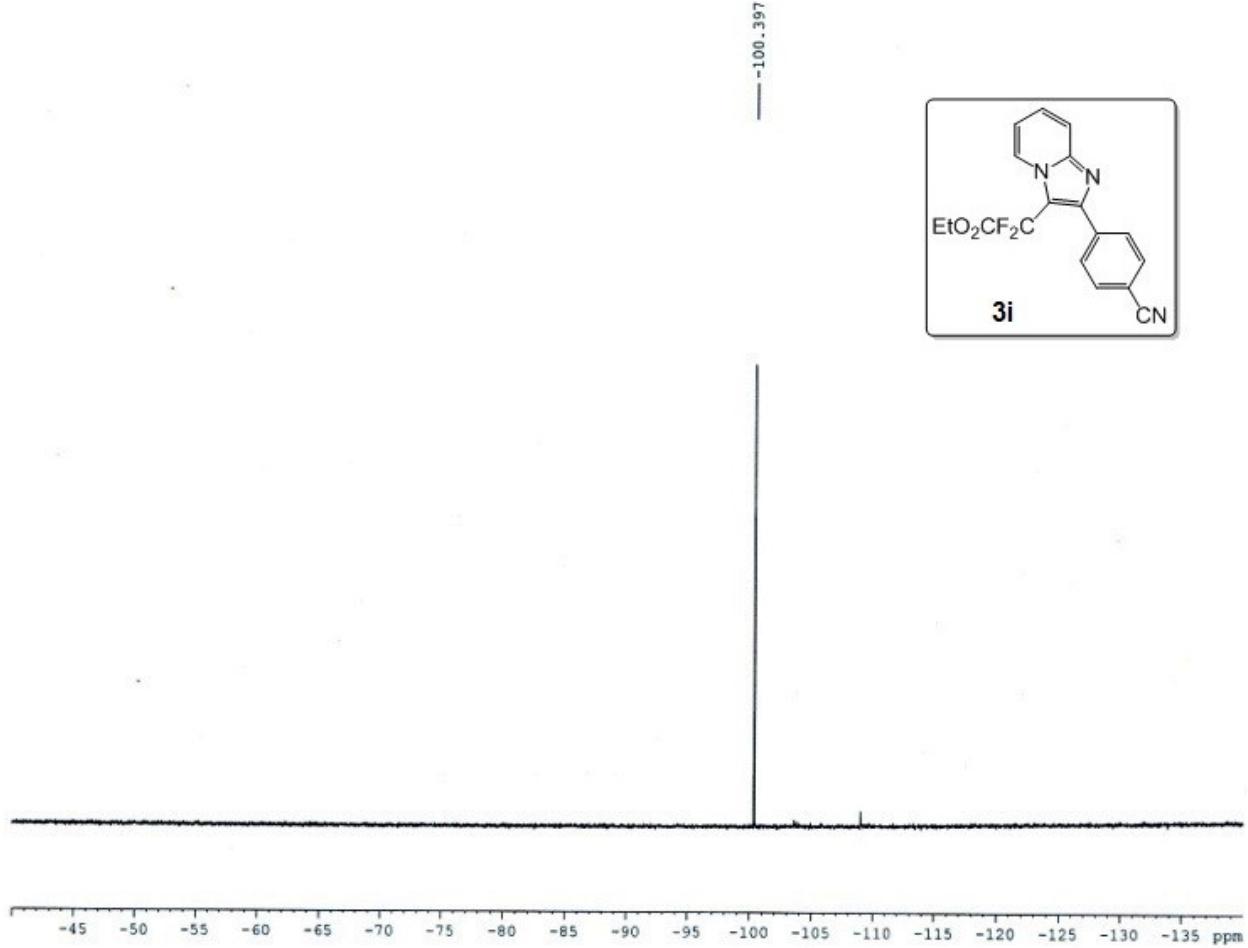
F2 - Processing parameters
 SI 16384
 SF 400.1500090 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00











BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 293
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150619
Time 18.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgfgqn
TD 32768
SOLVENT CDCl₃
NS 4
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 87.66
DW 5.600 usec
DE 6.50 usec
TE 297.7 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 19F
P1 12.50 usec
PLW1 20.0000000 W
SF01 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171850 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



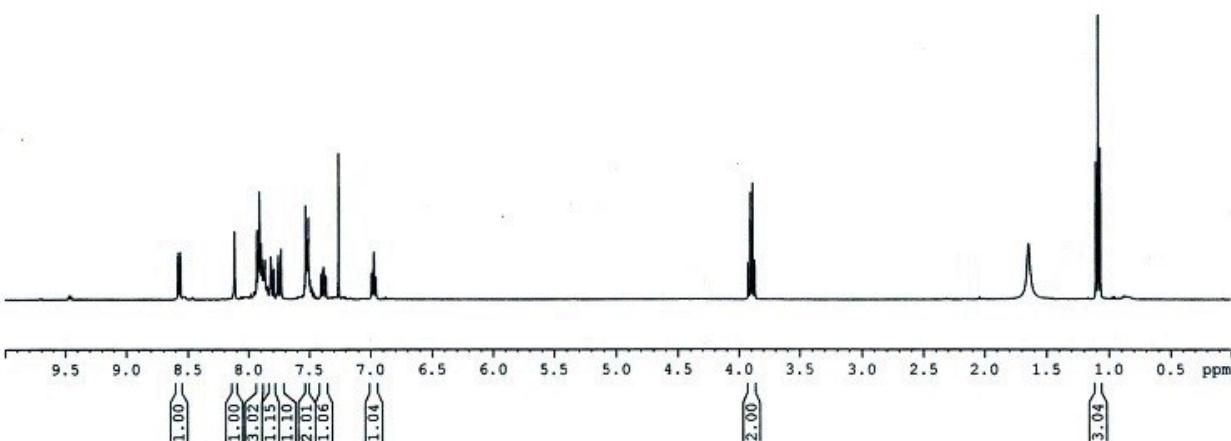
BRUKER

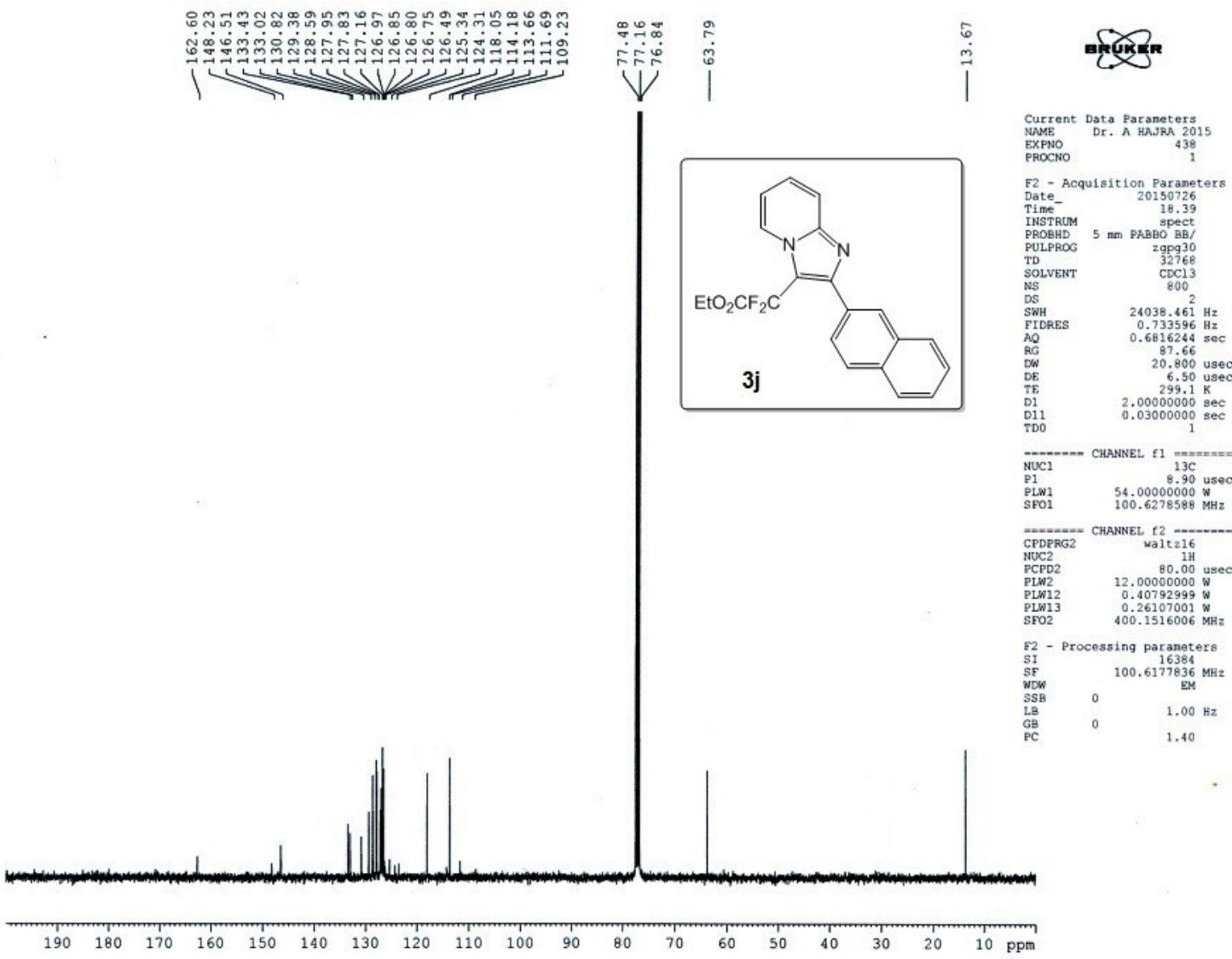
Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 433
 PROCNO 1

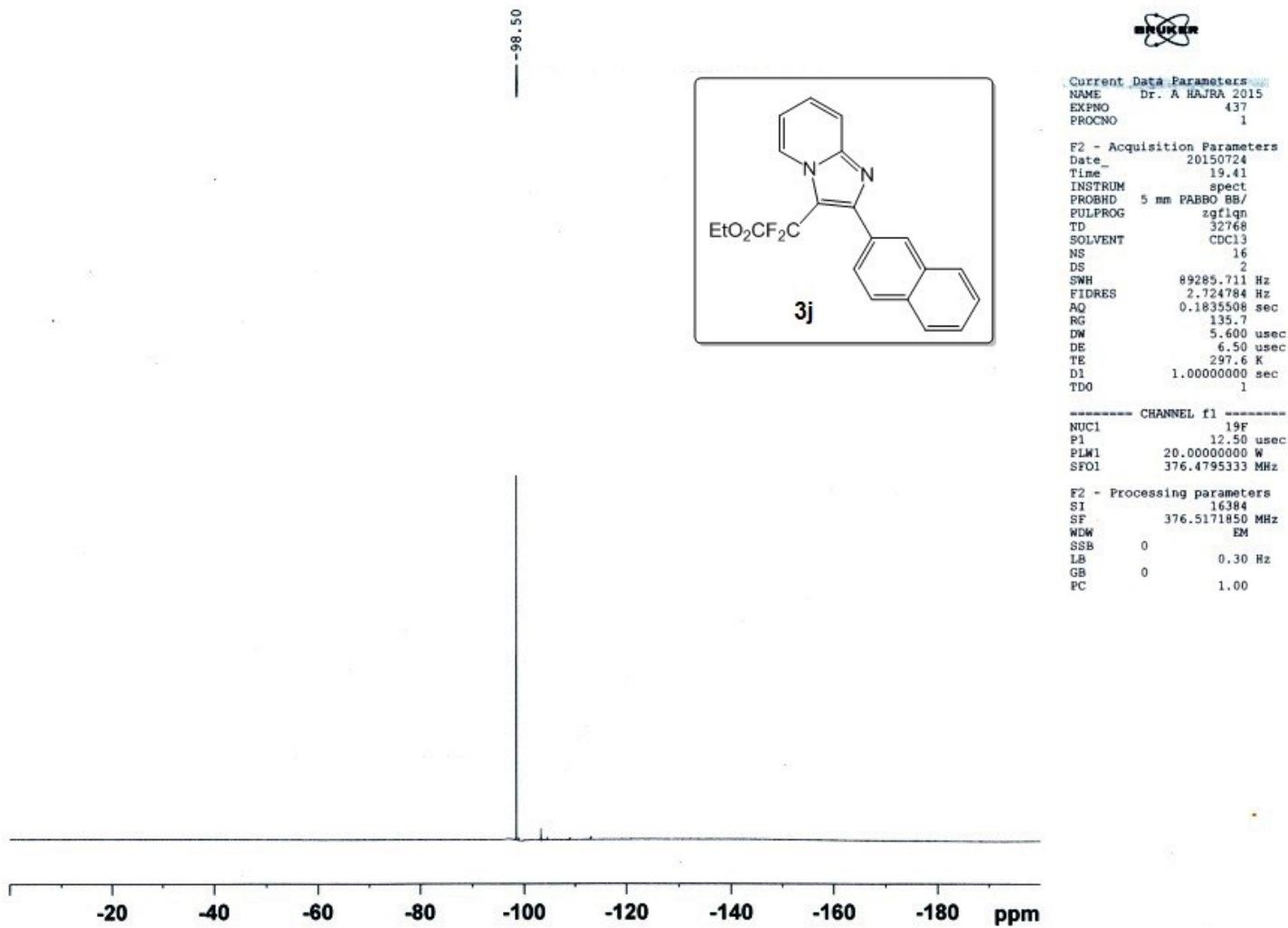
F2 - Acquisition Parameters
 Date_ 20150724
 Time 11.58
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 1
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9923444 sec
 RG 135.7
 DW 60.800 usec
 DE 6.50 usec
 TE 299.9 K
 D1 1.0000000 sec
 TDO 1

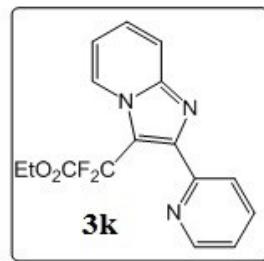
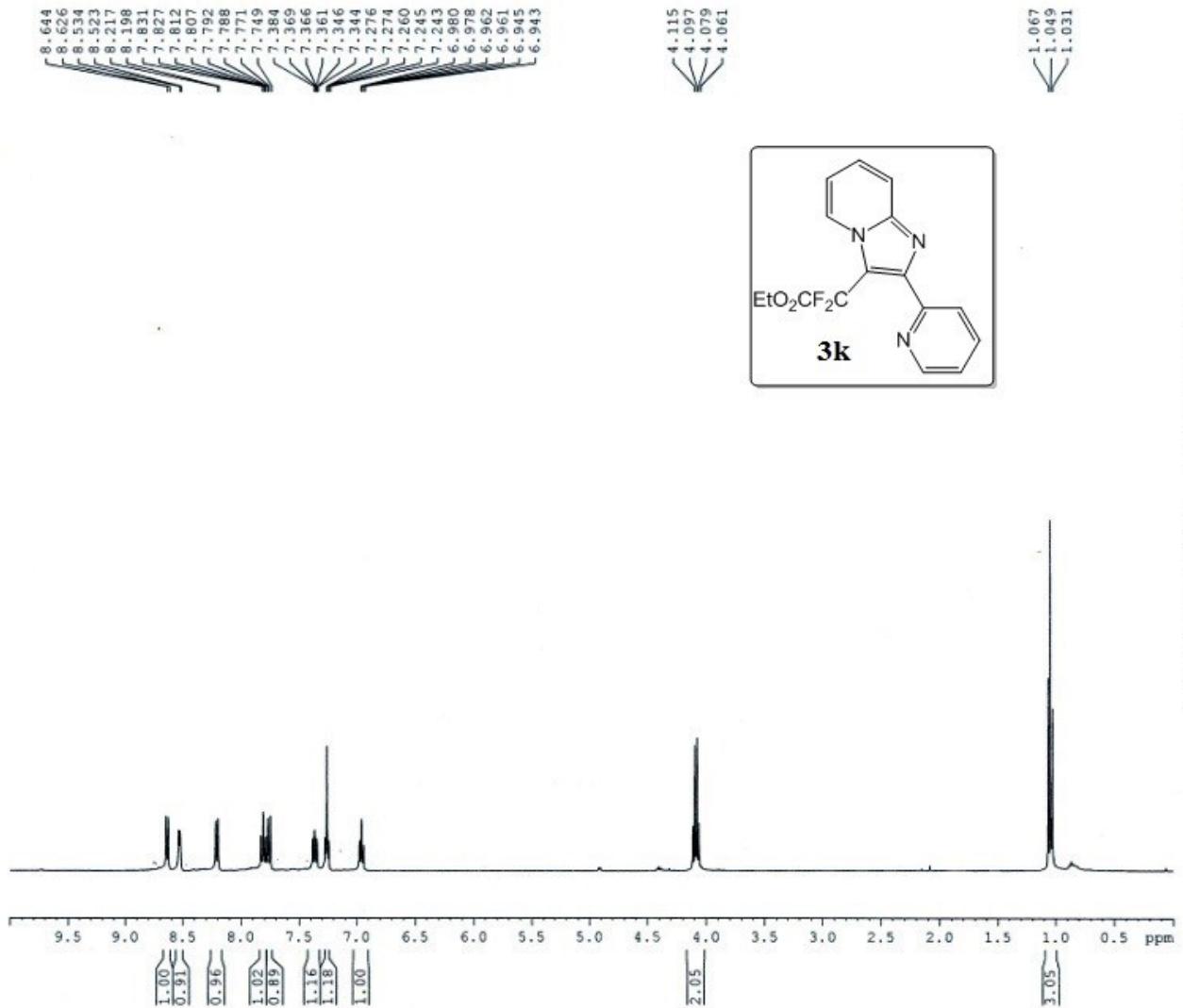
----- CHANNEL f1 -----
 NUC1 1H
 P1 14.75 usec
 PLW1 11.99499989 W
 SF01 400.1524711 MHz

F2 - Processing parameters
 SI 16384
 SF 400.1500089 MHz
 WDW EM
 SSB 0 0.30 Hz
 LB 0
 GB 0 1.00
 PC









Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 567
PROCNO 1

```

F2 - Acquisition Parameters
Date_      20150831
Time       11.27
INSTRUM   spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD        32768
SOLVENT    CDC13
NS         32
DS          1
SWH       8223.685 Hz
FIDRES   0.250967 Hz
AQ        1.9923444 sec
RG        93.46
DW        60.800 usec
DE        6.50  usec
TE        296.8 K
D1        1.0000000 sec
TDO       1

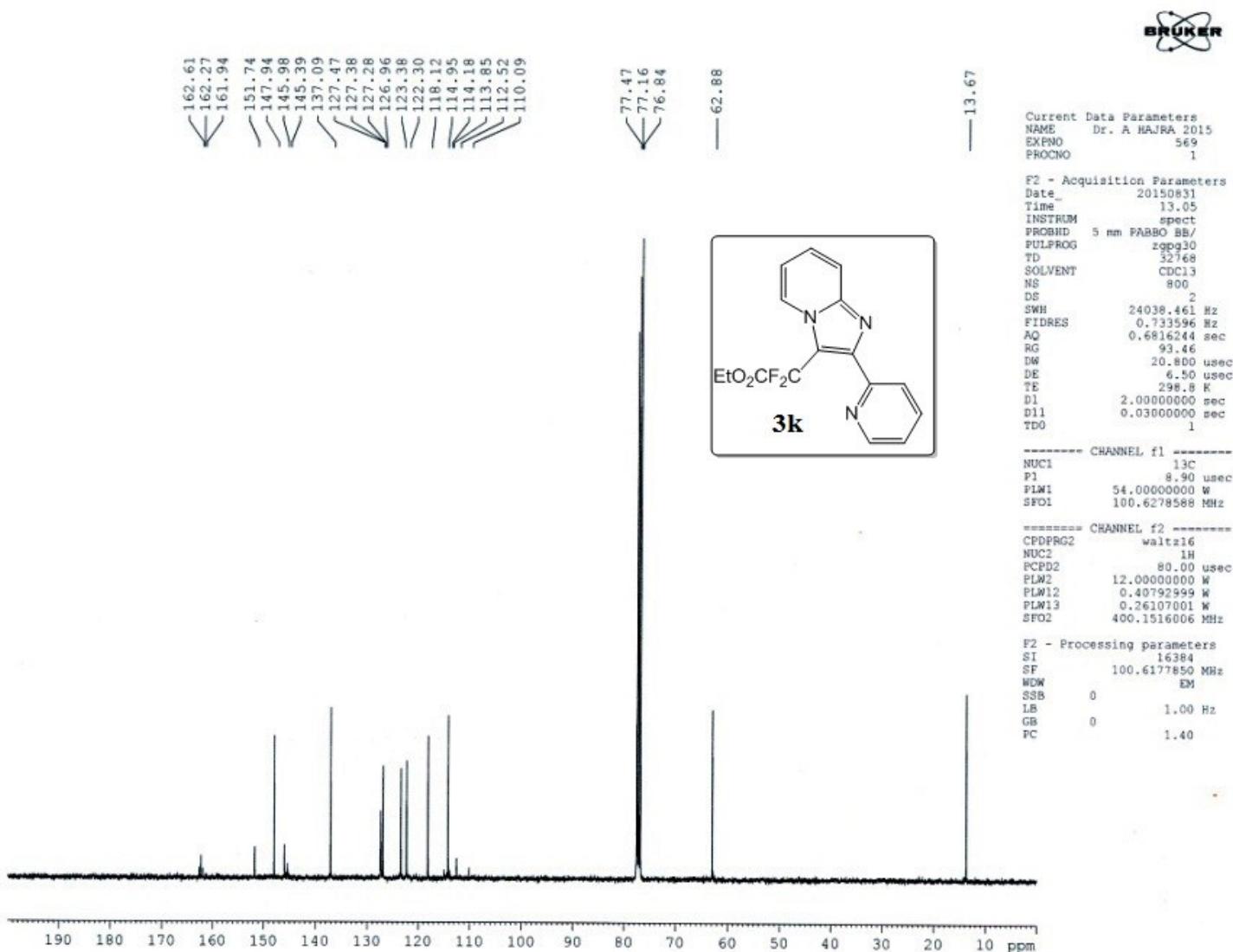
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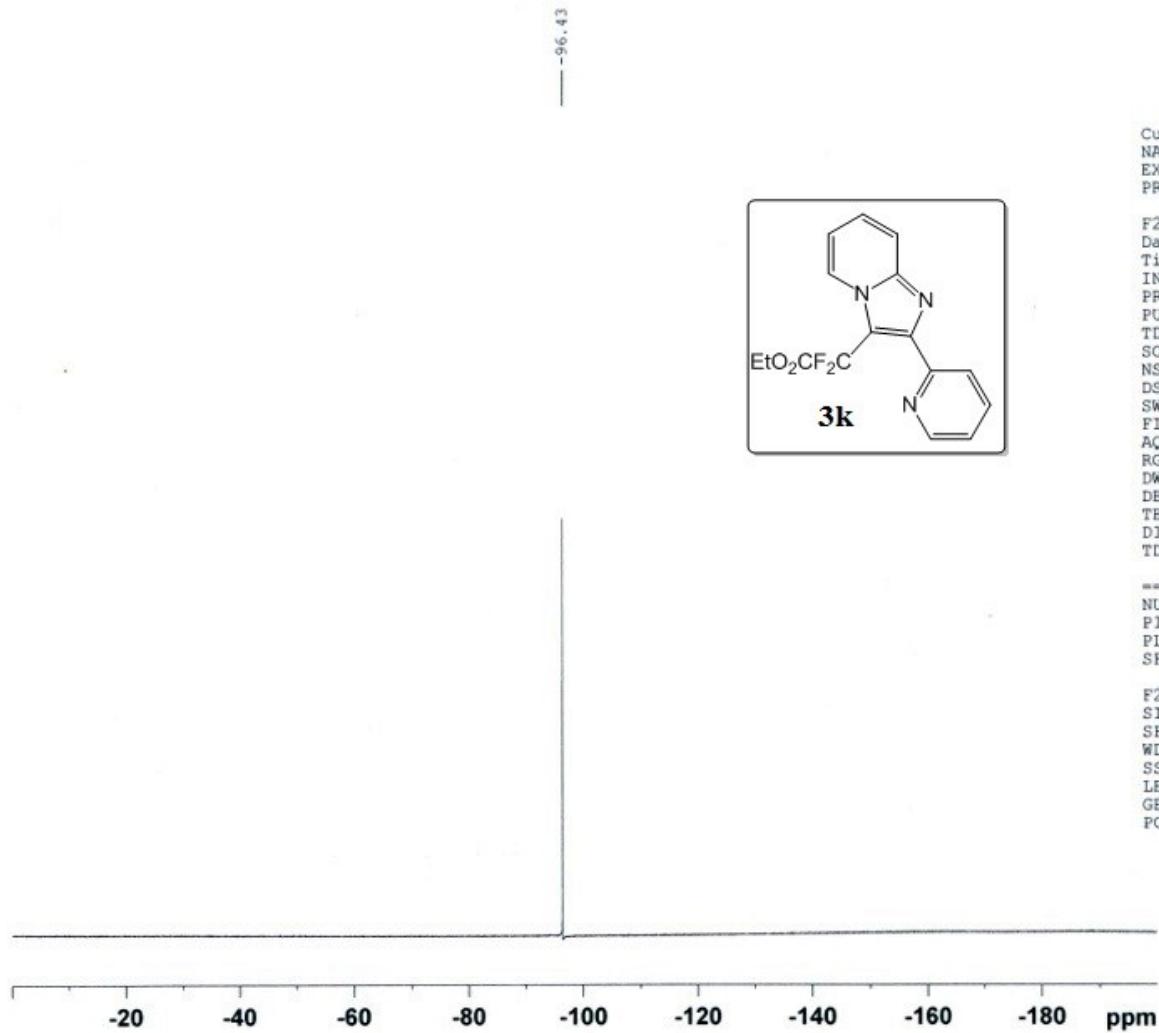
----- CHANNEL f1 -----
NUC1 1H
P1 14.75 usec
PLW1 11.99499989 W
SFO1 400.1524711 MHz

```

P2 - Processing parameters
SI          16384
SF        400.1500090 MHz
WDW           EM
SSB          0
LB            0.30 Hz
GB          0
PC          1.00

```





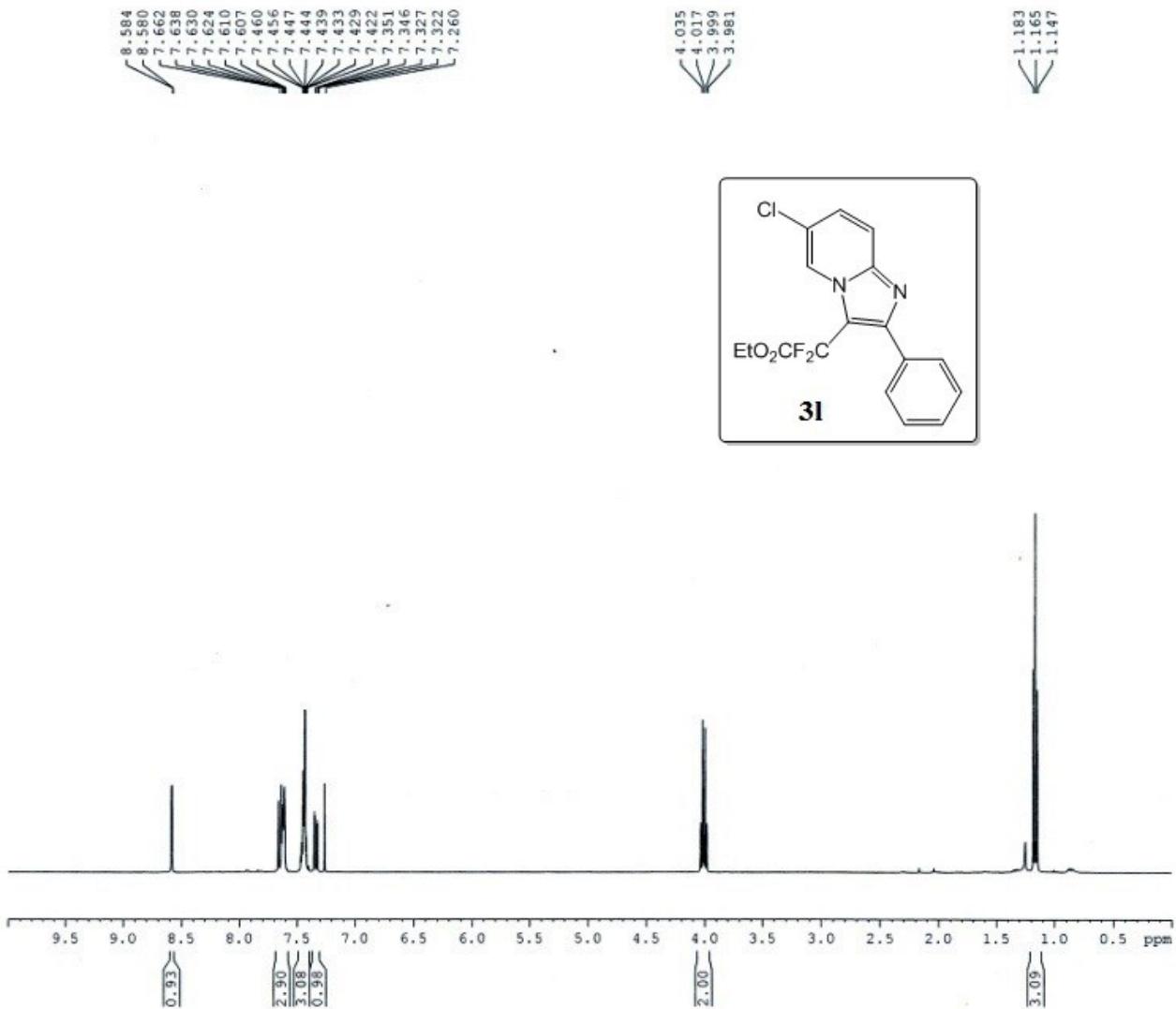
BRUKER

Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 565
PROCNO 1

F2 - Acquisition Parameters
Date 20150829
Time 12.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqnm
TD 32768
SOLVENT CDCl₃
NS 4
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 135.7
DW 5.600 usec
DE 6.50 usec
TE 296.8 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 19F
P1 12.75 usec
PLW1 20.0000000 W
SF01 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171850 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



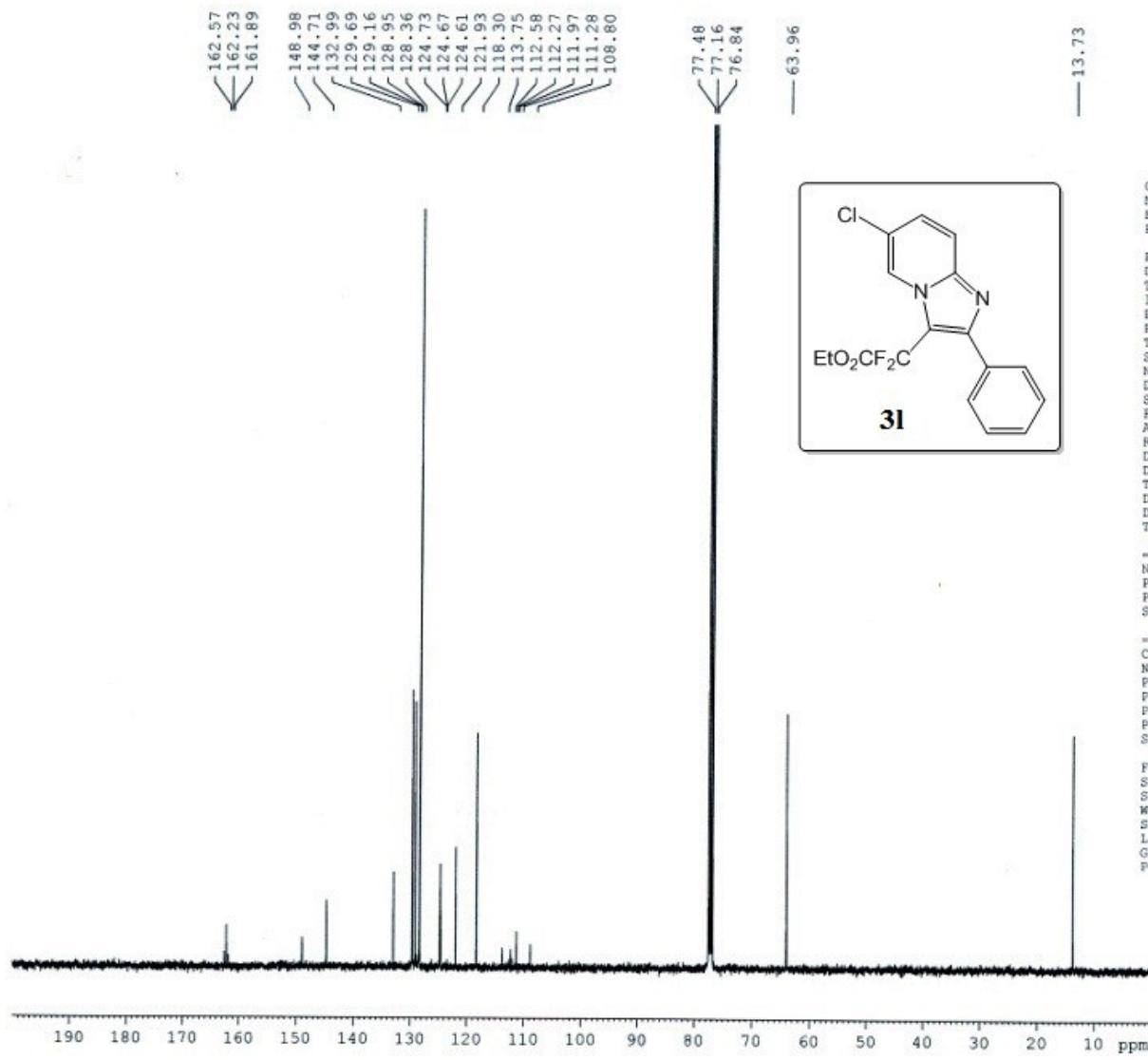
BRUKER

Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 514
 PROCNO 1

F2 - Acquisition Parameters
 Date 20150809
 Time 10.10
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 1
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.992344 sec
 RG 120.16
 DW 60.800 usec
 DE 6.50 usec
 TE 296.1 K
 D1 1.0000000 sec
 T00 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.75 usec
 PLW1 11.99499989 W
 SF01 400.1524711 MHz

F2 - Processing parameters
 SI 16384
 SF 400.1500090 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



BRUKER

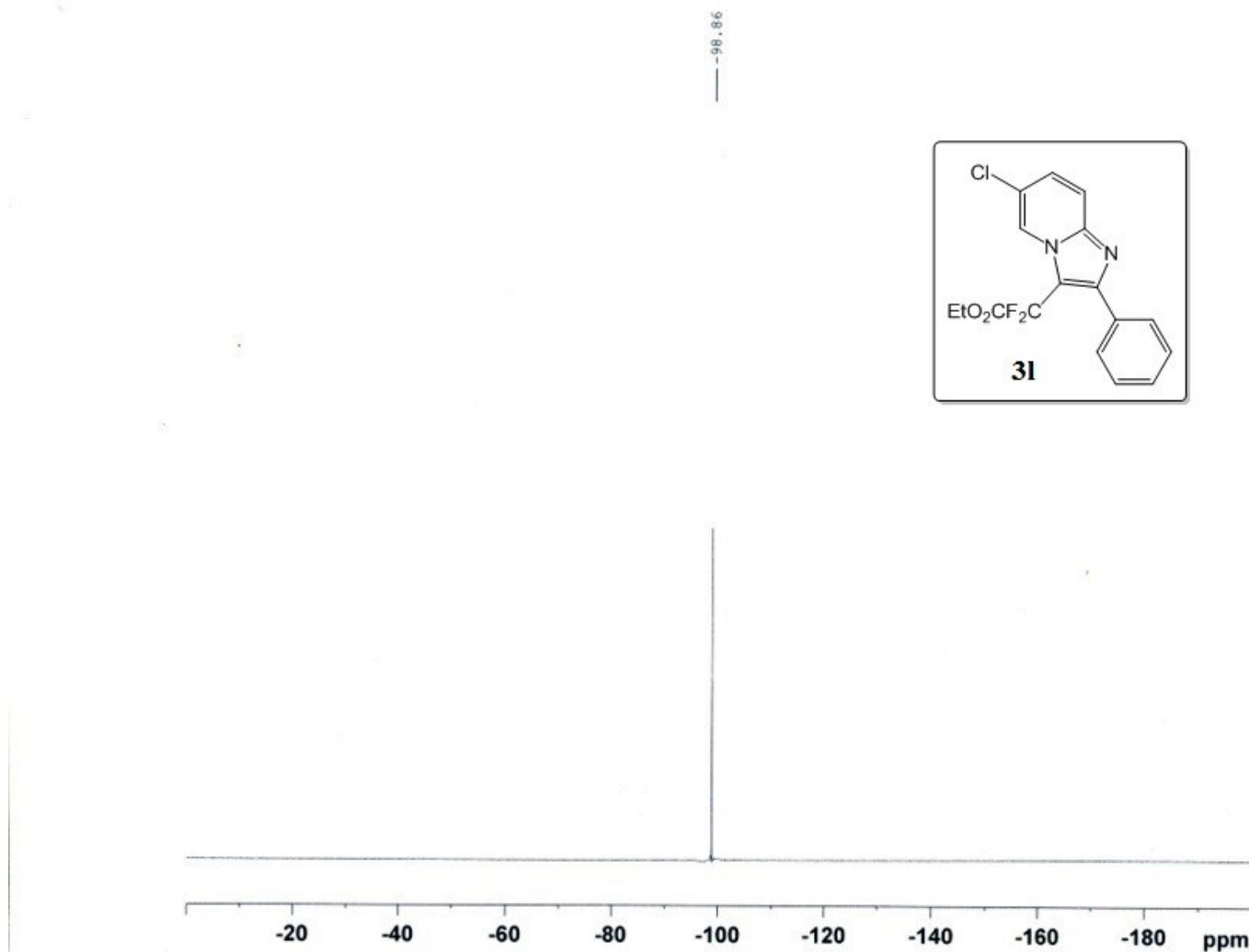
Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 516
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150809
Time 12.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 800
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 120.16
DW 20.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.0000000 sec
D11 0.03000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W
SFO1 100.6278588 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 12.00000000 W
PLW3 0.40792999 W
PLW13 0.26107001 W
SFO2 400.1516006 MHz

F2 - Processing parameters
SI 16384
SF 100.6177836 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

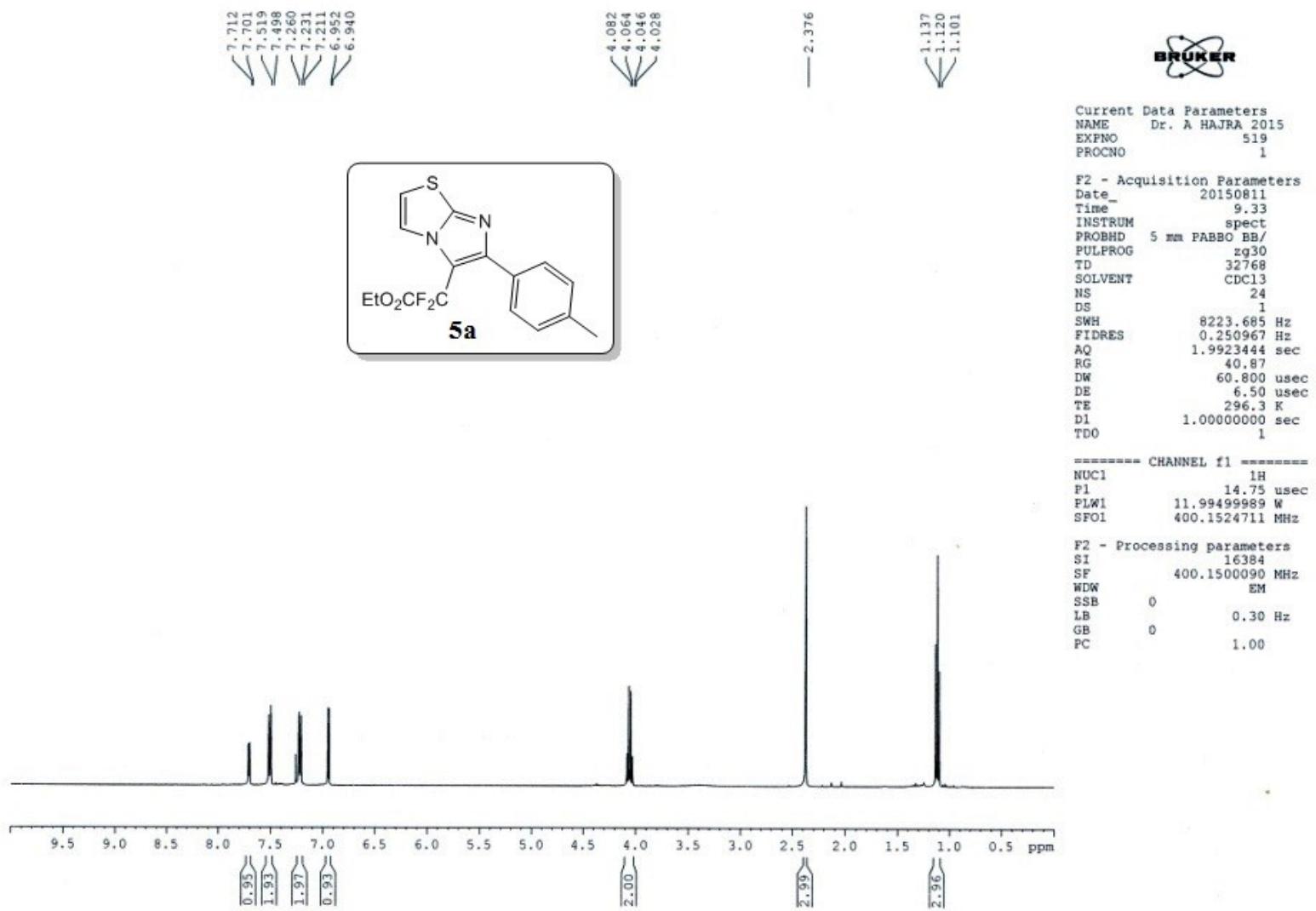


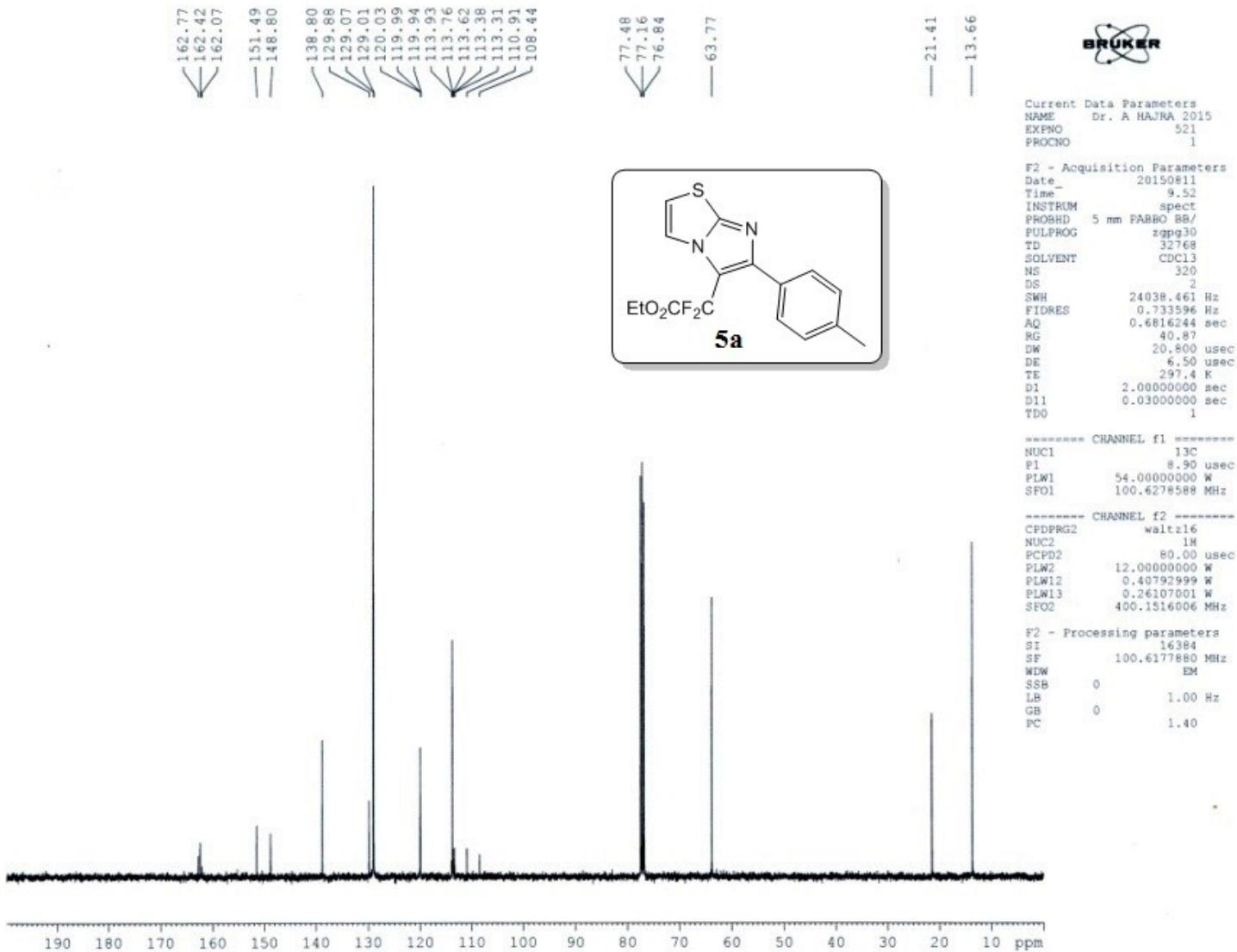
Current Data Parameters
 NAME Dr. A HAJRA 2015
 EXPNO 515
 PROCHNO 1

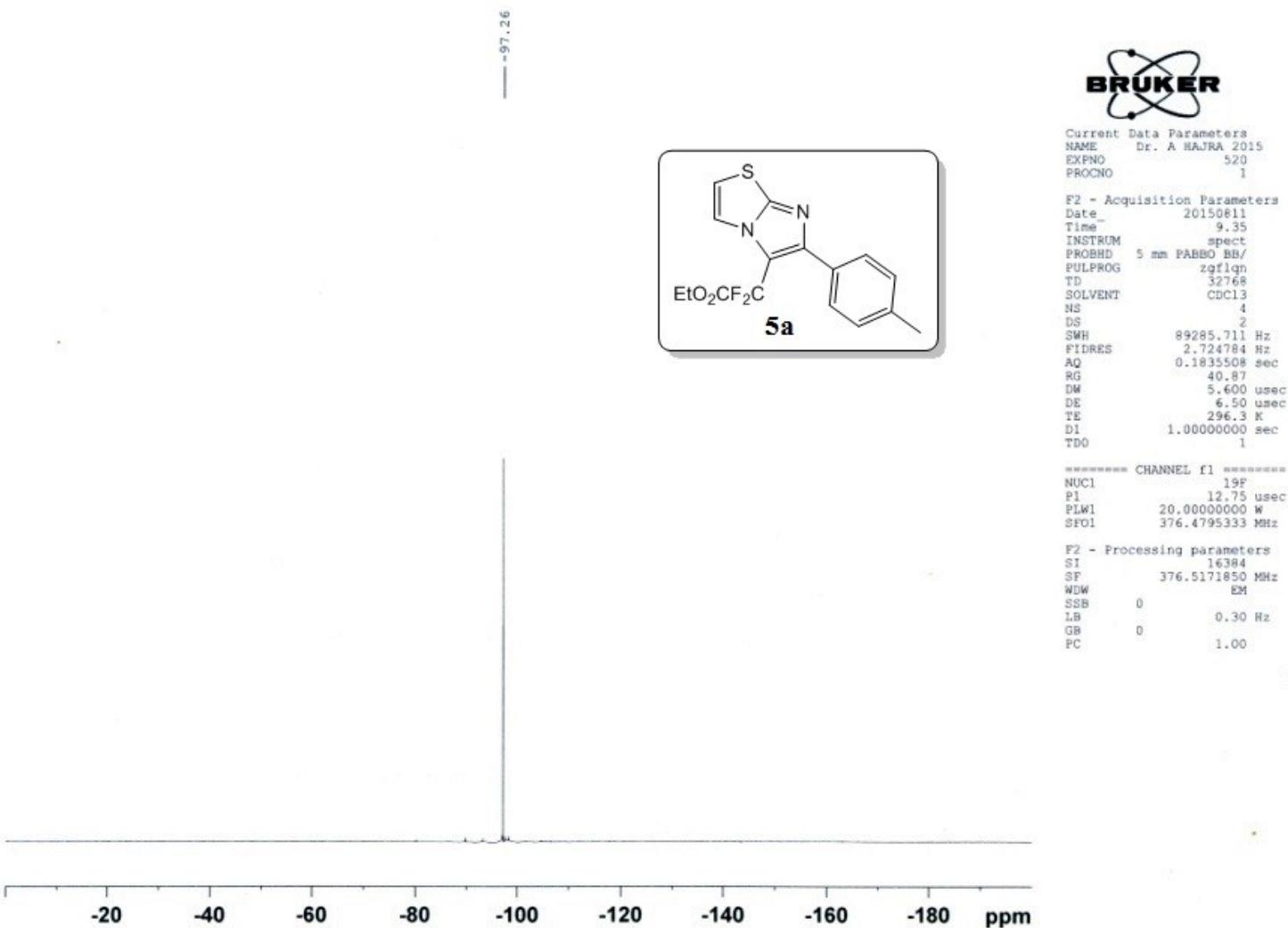
F2 - Acquisition Parameters
 Date 20150809
 Time 10.12
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgfgn
 TD 32768
 SOLVENT CDCl3
 NS 4
 DS 2
 SWH 89285.711 Hz
 FIDRES 2.724784 Hz
 AQ 0.1835508 sec
 RG 120.16
 DW 5.600 usec
 DE 6.50 usec
 TE 296.1 K
 D1 1.0000000 sec
 TDO 1

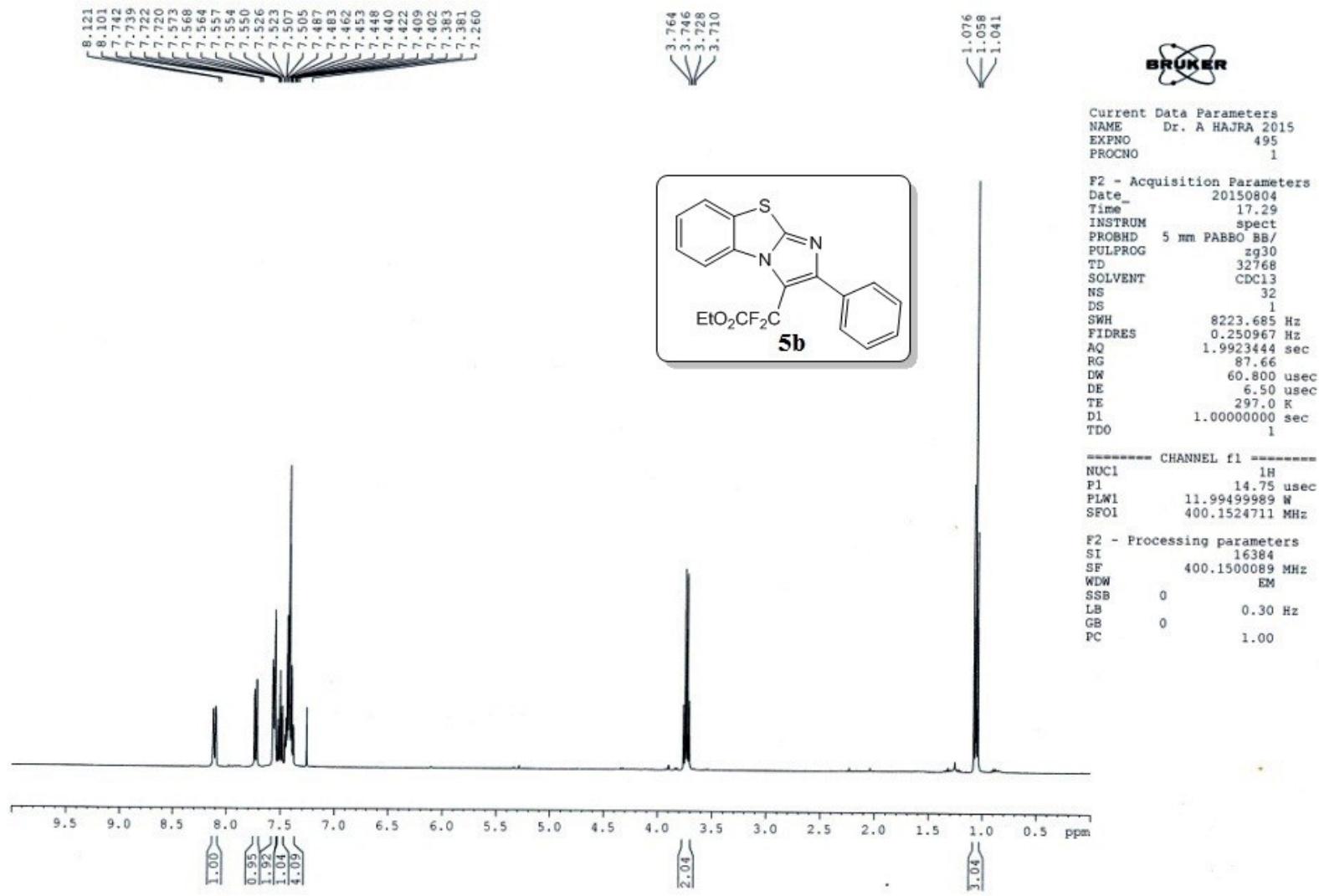
===== CHANNEL f1 =====
 NUC1 19F
 PI 12.75 usec
 PLW1 20.0000000 W
 SPO1 376.4795333 MHz

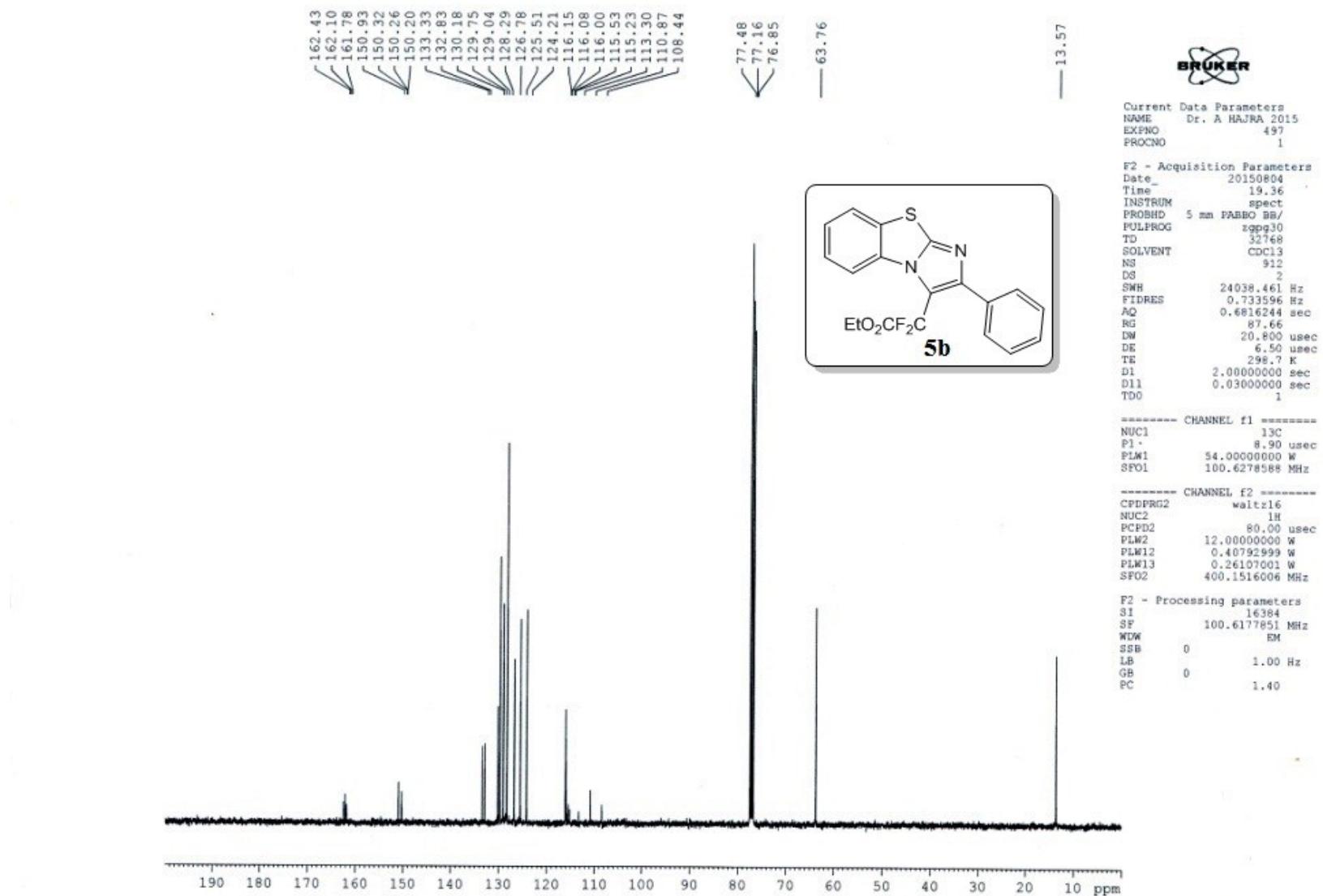
F2 - Processing parameters
 SI 16384
 SF 376.5171850 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

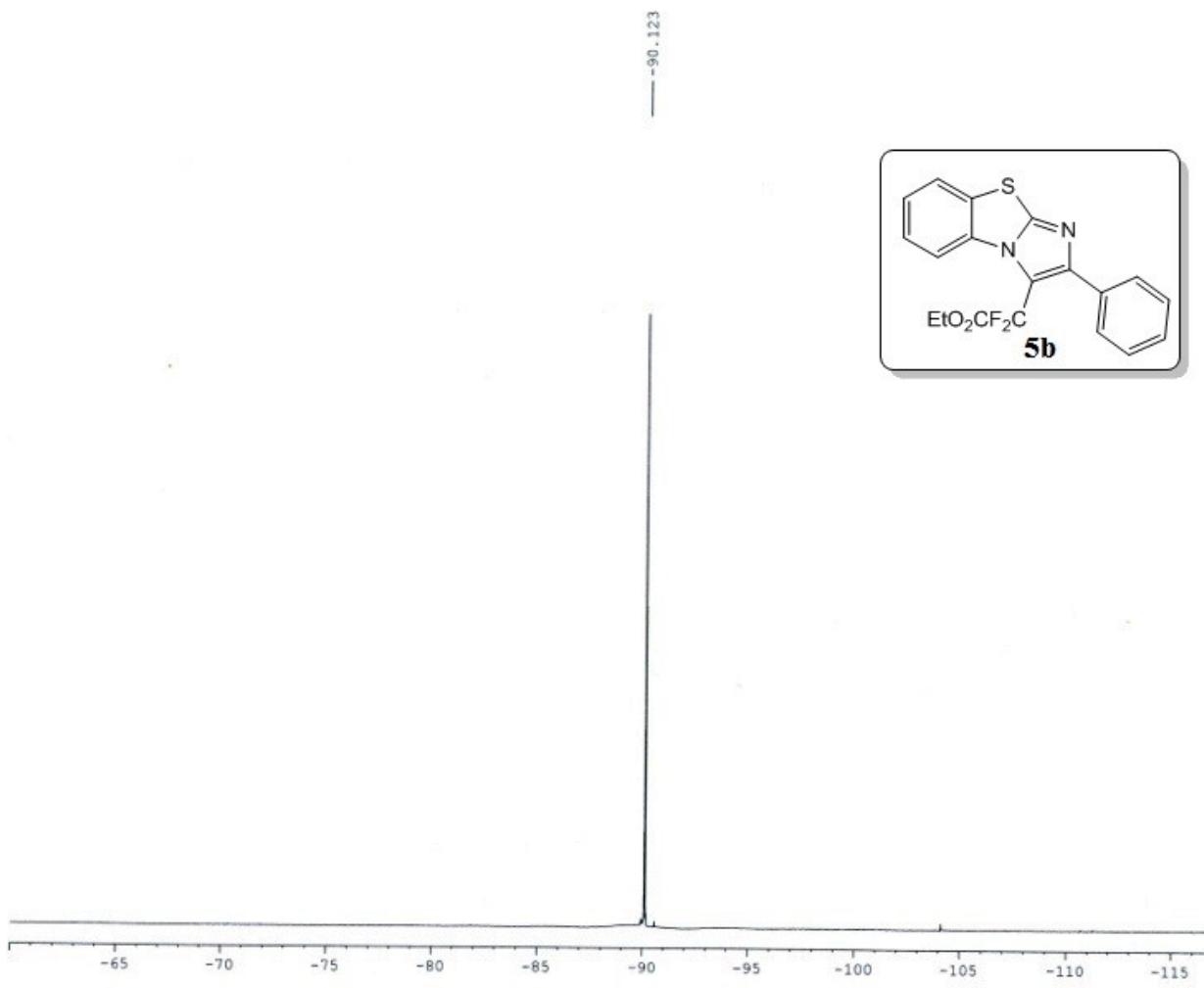












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Current Data Parameters
NAME Dr. A HAJRA 2015
EXPNO 496
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150804
Time 17.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgfgn
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 89285.711 Hz
FIDRES 2.724784 Hz
AQ 0.1835508 sec
RG 87.66
DW 5.600 usec
DE 6.50 usec
TE 297.0 K
DI 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 19F
P1 12.50 usec
PLW1 20.0000000 W
SF01 376.4795333 MHz

F2 - Processing parameters
SI 16384
SF 376.5171850 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

