Supporting Information

Direct *gem*-Difluoromethylenation of sp^3-Hybridized Carbon Center through Copper-Mediated Radical/Radical Cross-Coupling for Construction of CH_2-CF_2 Linkage

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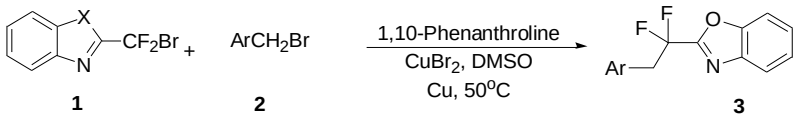
1. General Information.

General Comments： ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on 500 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported in ppm downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal chloroform (δ 77.2 ppm for ^{13}C), and chemical shifts for ^{19}F NMR spectra are reported in ppm downfield from internal fluorotrichloromethane ($CFCl_3$). Infrared spectra (IR) were recorded with KBr pellets. Silica gel (200−400 mesh) was used for flash column chromatography. Melting points are uncorrected. High-resolution mass spectrometry (HRMS) was conducted by TOF MS with electron impact (EI) ionization at 70 eV.

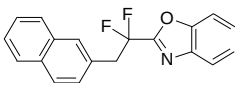
2. Typical procedure for cross-coupling reaction 1,3-azolic difluoromethyl bromides with benzyl/allyl halides.



1 **2** **3**

A 10 mL round-bottom flask was charged with **1** (0.6 mmol), **2** (0.4 mmol), Cu powder (88 mg, 1.4 mmol), $CuBr_2$ (4 mg, 0.02 mmol), 1,10-phenanthroline (14 mg, 0.08 mmol) and DMSO (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 50 ℃ for 4 h. After the reaction was completed, the crude product was directly purified by silica gel chromatography (petroleum ether/ethyl acetate, 50:1 v/v), to give **3**.

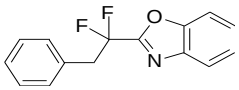
2-(1,1-Difluoro-2-naphthalen-2-yl-ethyl)-benzooxazole (3aa)



103 mg, 84% yield, white solid. Mp 74-75 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.82 (d, J = 16.0 Hz, 5H), 7.59 (d, 1H, J = 5.3 Hz, 1H), 7.47-7.43 (m, 5H), 3.97 (t, J = 16.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ: -97.02 (t, J = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.9 (t, $^{2}J_{C\text{-}F}$ = 34.2 Hz), 150.6, 140.0, 133.3, 132.8, 130.1, 128.3, 128.2, 127.9, 127.7, 126.8, 126.3, 126.2, 125.3, 121.3,

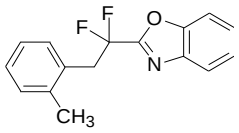
115.8 (t, $^{1}J_{C\text{-}F}$ = 242.6 Hz), 111.4, 42.4 (t, $^{2}J_{C\text{-}F}$ = 24.1 Hz); IR (KBr, cm^{-1}) *v*: 3027, 1615, 1600, 1451, 1356, 1038, 765, 748. Anal. Calcd for $C_{19}H_{13}F_2NO$ (309.10): calcd. C, 73.78; H, 4.24; N, 4.53; found C, 73.75; H, 4.22; N, 4.54

2-(1,1-Difluoro-2-phenylethyl)benzo[d]oxazole (3ab)



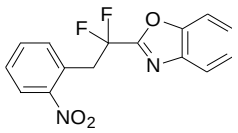
54 mg, 52% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.82 (d, *J* = 7.2 Hz, 1H), 7.61-7.59 (m, 1H), 7.47-7.44 (m, 1H), 7.43-7.40 (m, 1H), 7.33-7.29 (m, 5H), 3.77 (t, *J* = 16.7 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.54 (t, *J* = 16.7 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.2 (t, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 150.6, 140.0, 130.7, 128.6, 127.9, 126.8, 125.3, 121.3, 115.7 (t, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 111.4, 42.3 (t, $^{2}J_{C\text{-}F}$ = 24.2 Hz); IR (KBr, cm^{-1}) *v*: 3034, 1616, 1574, 1453, 1362, 1036, 749, 722. Anal. Calcd for $C_{15}H_{11}F_2NO$ (259.10): calcd. C, 69.49; H, 4.28; N, 5.40; found C, 69.51; H, 4.31; N, 5.36

2-(1,1-Difluoro-2-(o-tolyl)ethyl)benzo[d]oxazole (3ac)



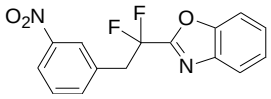
55 mg, 50% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.84 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.49-7.42 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 2H), 7.16-7.12 (m, 1H), 3.81 (t, *J* = 17.2 Hz, 2H), 2.40 (s, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.60 (t, *J* = 17.1 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 158.2 (t, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 150.6, 140.0, 138.1, 131.6, 130.7, 129.3, 128.0, 126.9, 126.0, 125.3, 121.3, 116.1 (t, $^{1}J_{C\text{-}F}$ = 243.7 Hz), 111.4, 39.0 (t, $^{2}J_{C\text{-}F}$ = 24.1 Hz), 19.9; IR (KBr, cm^{-1}) *v*: 3023, 1616, 1574, 1450, 1372, 1029, 748. HRMS (EI TOF) calcd for (M^{+}) $C_{16}H_{13}F_2NO$: 273.0965, found 273.0963

2-(1,1-Difluoro-2-(2-nitrophenyl)ethyl)benzo[d]oxazole (3ad)



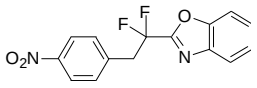
112 mg, 92% yield, yellow solid. Mp 81-82 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.93 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.58-7.52 (m, 3H), 7.47-7.38 (m, 3H), 4.29 (t, *J* = 16.6 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -96.81 (t, *J* = 16.5 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.1 (t, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 150.6, 150.5, 139.8, 134.0, 132.9, 129.2, 127.1, 125.4, 125.3, 125.2, 121.3, 115.0 (t, $^{1}J_{C\text{-}F}$ = 243.4 Hz), 111.4, 37.8 (t, $^{2}J_{C\text{-}F}$ = 24.0 Hz); IR (KBr, cm^{-1}) *v*: 3067, 1613, 1576, 1526, 1477, 1380, 1345, 1032, 750, 721. HRMS (EI TOF) calcd for (M^{+}) $C_{15}H_{10}F_2N_2O_3$: 304.0659, found 304.0662

2-(1,1-Difluoro-2-(3-nitrophenyl)ethyl)benzo[d]oxazole (3ae)



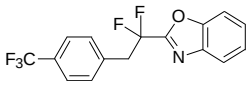
55 mg, 45% yield, yellow solid. Mp 103-104 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.25 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.49-7.39 (m, 3H), 3.88 (t, *J* = 16.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.22 (t, *J* = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.0 (t, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 150.6, 148.2, 139.8, 136.9, 132.8, 129.5, 127.2, 125.8, 125.5, 123.0, 121.3, 115.0 (t, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 111.4, 41.6 (t, $^{2}J_{C\text{-}F}$ = 24.4 Hz); IR (KBr, cm^{-1}) *v*: 3038, 1618, 1579, 1526, 1451, 1356, 1049, 749, 724. Anal. Calcd for $C_{15}H_{10}F_2N_2O_3$ (304.07): calcd. C, 59.21; H, 3.31; N, 9.21 found C, 59.14; H, 3.27; N, 9.23

2-(1,1-Difluoro-2-(4-nitrophenyl)ethyl)benzo[d]oxazole (3af)



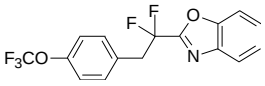
111 mg, 91% yield, yellow solid. Mp 190-191 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.18 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.49-7.42 (m, 2H), 3.89 (t, *J* = 16.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -96.86 (t, *J* = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.1 (t, $^{2}J_{C\text{-}F}$ = 33.1 Hz), 150.6, 147.8, 139.8, 138.1 (t, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 131.8, 127.2, 125.5, 123.6, 121.4, 115.0 (t, $^{1}J_{C\text{-}F}$ = 244.0 Hz), 111.5, 41.8 (t, $^{2}J_{C\text{-}F}$ = 24.1 Hz); IR (KBr, cm^{-1}) *v*: 3114, 1616, 1604, 1521, 1451, 1361, 1345, 1041, 749, 727. HRMS (EI TOF) calcd for (M^{+}) $C_{15}H_{10}F_2N_2O_3$: 304.0659, found 304.0651

2-(1,1-Difluoro-2-(4-(trifluoromethyl)phenyl)ethyl)benzo[d]oxazole (3ag)



101 mg, 77% yield, white solid. Mp 79-80 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.82 (d, *J* = 7.6 Hz, 1H), 7.61-7.57 (m, 3H), 7.48-7.41 (m, 4H), 3.84 (t, *J* = 16.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -62.68 (s, 3F), -97.22 (t, *J* = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.4 (t, $^{2}J_{C\text{-}F}$ = 33.5 Hz), 150.6, 139.9, 134.8, 131.2, 130.2 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 127.0, 125.6, 125.4, 124.0 (q, $^{1}J_{C\text{-}F}$ = 271.8 Hz), 121.3, 115.3 (t, $^{1}J_{C\text{-}F}$ = 244.1 Hz), 111.4, 41.9 (t, $^{2}J_{C\text{-}F}$ = 24.2 Hz); IR (KBr, cm^{-1}) *v*: 3052, 1620, 1571, 1452, 1325, 1031, 753, 718. Anal. Calcd for $C_{16}H_{10}F_5NO$ (327.07): calcd. C, 58.72; H, 3.08; N, 4.28. found C, 58.66; H, 3.12; N, 4.23

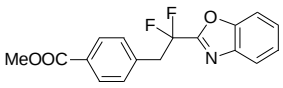
2-(1,1-Difluoro-2-(4-(trifluoromethoxy)phenyl)ethyl)benzo[d]oxazole (3ah)



67 mg, 49% yield, white solid. Mp 77-78 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.82 (d, *J* = 7.5 Hz, 1H), 7.59 (d, 1H, *J* = 8.3 Hz, 1H), 7.47-7.40 (m, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 3.78 (t, *J* = 16.6 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -57.9(s, 3F), -97.58 (t, *J* = 16.5 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.5 (t, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 150.6, 149.0 (q, $^{3}J_{C\text{-}F}$ = 1.7 Hz), 139.9, 132.2, 129.4 (t, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 127.0, 125.4, 121.3, 120.9, 120.4 (q, $^{1}J_{C\text{-}F}$ = 257.4 Hz), 115.4 (t, $^{1}J_{C\text{-}F}$

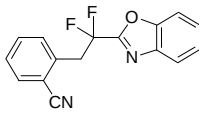
= 242.7 Hz), 111.4, 41.4 (t, $^{2}J_{C\text{-}F}$ = 24.2 Hz); IR (KBr, cm^{-1}) *v*: 3044, 1618, 1578, 1476, 1510, 1362, 1045, 748, 720. Anal. Calcd for $C_{16}H_{10}F_5NO_2$ (343.06): calcd. C, 55.99; H, 2.94; N, 4.08. found C, 56.02; H, 2.91; N, 4.10

Methyl 4-(2-(benzo[d]oxazol-2-yl)-2,2-difluoroethyl)benzoate (3ai)



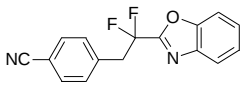
113 mg, 89% yield, white solid. Mp 93-94 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.96 (d, *J* = 7.9 Hz, 2H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.44-7.38 (m, 4H), 3.87 (s, 3H, OCH_3), 3.81 (t, *J* = 16.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.08 (t, *J* = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 166.7, 157.5 (t, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 150.6, 139.9, 135.9, 130.8, 129.8, 129.7, 126.9, 125.4, 121.3, 115.4 (t, $^{1}J_{C\text{-}F}$ = 242.4 Hz), 111.4, 52.1, 42.1 (t, $^{2}J_{C\text{-}F}$ = 24.2 Hz); IR (KBr, cm^{-1}) *v*: 3045, 1714, 1616, 1576, 1444, 1376, 1033, 750, 739. Anal. Calcd for $C_{17}H_{13}F_2NO_3$ (317.09): calcd. C, 64.35; H, 4.13; N, 4.41. found C, 64.40; H, 4.11; N, 4.40

2-(2-(Benzo[d]oxazol-2-yl)-2,2-difluoroethyl)benzonitrile (3aj)



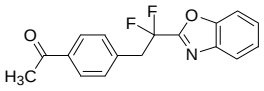
107 mg, 94% yield, white solid. Mp 103-104 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.79 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.55-7.51 (m, 2H), 7.46-7.39 (m, 3H), 3.87 (s, 3H), 4.03 (t, *J* = 16.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.16 (t, *J* = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.0 (t, $^{2}J_{C\text{-}F}$ = 33.1 Hz), 150.7, 139.8, 134.3, 133.1, 132.8, 132.0, 128.6, 127.1, 125.4, 121.3, 117.5, 114.9 (t, $^{1}J_{C\text{-}F}$ = 244.0 Hz), 114.8, 111.5, 40.2 (t, $^{2}J_{C\text{-}F}$ = 24.3 Hz); IR (KBr, cm^{-1}) *v*: 3068, 2230, 1617, 1602, 1453, 1382, 1031, 762, 749. Anal. Calcd for $C_{16}H_{10}F_2N_2O$ (284.08): calcd. C, 67.60; H, 3.55; N, 9.85. found C, 67.64; H, 3.50; N, 9.82

4-(2-(Benzo[d]oxazol-2-yl)-2,2-difluoroethyl)benzonitrile (3ak)



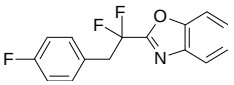
100 mg, 88% yield, yellow solid. Mp 148-149 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.79 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 3H), 7.46-7.39 (m, 4H), 3.82 (t, *J* = 16.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -96.96 (t, *J* = 16.3 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.1 (t, $^{2}J_{C\text{-}F}$ = 33.1 Hz), 150.6, 139.8, 136.2, 132.2, 131.6, 127.1, 125.5, 121.3, 118.5, 115.1 (t, $^{1}J_{C\text{-}F}$ = 243.6 Hz), 112.0, 111.5, 42.0 (t, $^{2}J_{C\text{-}F}$ = 24.2 Hz); IR (KBr, cm^{-1}) *v*: 3049, 2227, 1613, 1576, 1452, 1362, 1040, 747, 734. Anal. Calcd for $C_{16}H_{10}F_2N_2O$ (284.08): calcd. C, 67.60; H, 3.55; N, 9.85. found C, 67.58; H, 3.57; N, 9.81

1-(4-(2-(Benzo[d]oxazol-2-yl)-2,2-difluoroethyl)phenyl)ethanone (3al)



92 mg, 76% yield, white solid. Mp 85-86 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.87 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.45-7.38 (m, 4H), 3.81 (t, *J* = 16.5 Hz, 2H), 2.55 (s, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.09 (t, *J* = 16.4 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 197.6, 157.44 (t, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 150.6, 139.9, 136.6, 136.1, 131.0, 128.5, 127.0, 125.4, 121.3, 115.4 (t, $^{1}J_{C\text{-}F}$ = 243.2 Hz), 111.4, 111.5, 42.1 (t, $^{2}J_{C\text{-}F}$ = 24.4 Hz); IR (KBr, cm^{-1}) *v*: 3053, 1682, 1608, 1452, 1365, 1024, 768, 754. Anal. Calcd for $C_{17}H_{13}F_2NO_2$ (301.09): calcd. C, 67.77; H, 4.35; N, 4.65. found C, 67.78; H, 4.39; N, 4.66

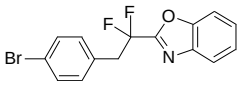
2-(1,1-Difluoro-2-(4-fluorophenyl)ethyl)benzo[d]oxazole (3am)



This compound has been reported in literature.[1] 51 mg, 46% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.81 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.47-7.40 (m, 2H), 7.29 (dd, ^{1}J = 8.4 Hz,

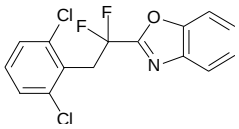
^{2}J = 5.4 Hz, 2H), 7.01-6.96 (m, 2H), 3.73 (t, J = 16.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ: -97.78 (t, J = 16.6 Hz, 2F), -114.46-114.52 (m, 1F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 162.5 (d, $^{1}J_{C\text{-}F}$ = 246.8 Hz), 157.7 (t, $^{2}J_{C\text{-}F}$ = 33.5 Hz), 150.6, 139.9, 132.3 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 126.9, 126.5, 125.3, 121.3, 115.5 (t, $^{1}J_{C\text{-}F}$ = 243.3 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 111.4, 41.4 (t, $^{2}J_{C\text{-}F}$ = 24.3 Hz). IR (KBr, cm^{-1}) v: 3018, 1617, 1604, 1452, 1250, 1046, 830, 743. HRMS (EI TOF) calcd for (M^{+}) $C_{15}H_{10}F_3NO$: 277.0714, found 277.0708

2-(2-(4-Bromophenyl)-1,1-difluoroethyl)benzo[d]oxazole (3an)



85 mg, 63% yield, white solid. Mp 93-94 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.81 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.47-7.40 (m, 4H), 7.20 (d, J = 8.2 Hz, 2H), 3.72 (t, J = 16.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ: -97.43 (t, J = 16.6 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.5 (t, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 150.6, 139.9, 132.4, 131.7, 129.7, 126.9, 125.4, 122.2, 121.3, 115.3 (t, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 111.4, 41.6 (t, $^{2}J_{C\text{-}F}$ = 24.3 Hz); IR (KBr, cm^{-1}) v: 3030, 1619, 1593, 1450, 1361, 1041, 760, 747. Anal. Calcd for $C_{15}H_{10}BrF_2NO$ (336.99): calcd. C, 53.28; H, 2.98; N, 4.14. found C, 53.21; H, 2.96; N, 4.07

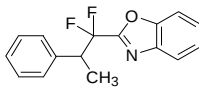
2-(2-(2,6-Dichlorophenyl)-1,1-difluoroethyl)benzo[d]oxazole (3ao)



115 mg, 88% yield, white solid. Mp 89-90 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.83-7.81 (m, 1H), 7.60-7.59 (m, 1H), 7.46-7.39 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.19-7.16 (m, 1H), 4.20 (t, J = 16.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ: -96.90 (t, J = 16.7 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.7 (t, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 150.7, 140.0, 137.4, 129.8, 128.5, 127.9, 126.9, 125.4, 121.3, 115.4 (t, $^{1}J_{C\text{-}F}$ = 246.3 Hz), 111.4, 37.2 (t, $^{2}J_{C\text{-}F}$ = 24.6 Hz); IR (KBr, cm^{-1}) v: 3080, 1615, 1578, 1435, 1377, 1036,

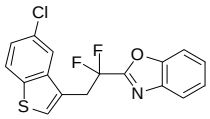
763, 750. Anal. Calcd for $C_{15}H_9Cl_2F_2NO$ (327.00): calcd. C, 54.90; H, 2.76; N, 4.27. found C, 54.85; H, 2.73; N, 4.21

2-(1,1-Difluoro-2-phenylpropyl)benzo[d]oxazole (3ap)



The title compound was prepared from (1-bromoethyl)benzene and **2a** according to general procedure except that 1 equiv of (1-bromoethyl)benzene, 4.5 equiv of copper powder, 2 equiv of **2**, 0.06 equiv of $CuBr_2$, and 0.3 equiv of 1,10-phenanthroline was used, 33 mg, 30% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.76 (d, 1H, *J* = 7.0 Hz), 7.53 (d, 1H, *J* = 7.9 Hz), 7.41-7.34 (m, 2H), 7.30-7.21 (m, 5H), 3.91-3.80 (m, 1H), 1.54 (d, *J* = 7.2 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -104.0 (t, *J* = 15.8 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 158.0 (t, $^2J_{C\text{-}F}$ = 34.0 Hz), 150.4, 140.0, 137.0, 129.0, 128.5, 127.9, 126.6, 125.2, 121.2, 117.4 (t, $^1J_{C\text{-}F}$ = 247.0 Hz), 111.3, 45.9 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 14.5 (t, $^3J_{C\text{-}F}$ = 3.8 Hz); IR (KBr, cm^{-1}) *v*: 3034, 1616, 1574, 1453, 1360, 1016, 749, 716. Anal. Calcd for $C_{16}H_{13}F_2NO$ (273.10): calcd. C, 70.32; H, 4.79; N, 5.13;. found C, 70.30; H, 4.81; N, 5.09

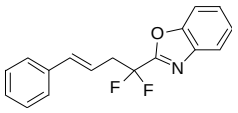
2-(2-(5-Chlorobenzo[b]thiophen-3-yl)-1,1-difluoroethyl)benzo[d]oxazole (3aq)



92 mg, 66% yield, yellow solid. Mp 89-90 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.76 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (s, 1H), 7.38-7.32 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 3.94 (t, *J* = 16.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -96.24 (t, *J* = 16.1 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.5 (t, $^2J_{C\text{-}F}$ = 33.1 Hz), 150.6, 140.2, 139.9, 138.1, 130.9, 129.0, 127.0, 125.4, 124.9, 124.8 (t, $^3J_{C\text{-}F}$ = 3.5 Hz), 123.7, 121.6, 121.3, 115.5 (t, $^1J_{C\text{-}F}$ = 243.2 Hz), 111.4, 34.9 (t, $^2J_{C\text{-}F}$ = 25.3 Hz); IR (KBr, cm^{-1}) *v*: 3053, 1617, 1579, 1452, 1355, 1045, 749, 723. Anal.

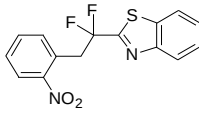
Calcd for $C_{17}H_{10}ClF_2NOS$ (349.01): calcd. C, 58.37; H, 2.88; N, 4.00;. found C, 58.41; H, 2.91; N, 4.02

(E)-2-(1,1-Difluoro-4-phenylbut-3-en-1-yl)benzo[d]oxazole (3ar)



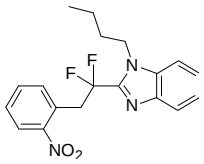
The title compound was prepared from (1-bromoethyl)benzene and **2a** according to general procedure except that 1 equiv of (1-bromoethyl)benzene, 6.9 equiv of copper powder and 3 equiv of **2a** was used, 23 mg, 20% yield, colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.82-7.80 (m, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.45-7.38 (m, 2H), 7.35-7.33 (m, 2H), 7.29- 7.26 (m, 2H), 7.23-7.20 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H) 6.23 (dt, *J* = 15.9 Hz, *J* = 7.2 Hz, 1H), 3.41-3.33 (m, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -97.42 (t, *J* = 16.5 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.8 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 150.6, 140.0, 136.7, 136.5, 128.6, 127.9, 126.9, 126.5, 125.3, 121.3, 118.1 (t, $^3J_{C\text{-}F}$ = 4.8 Hz), 115.8 (t, $^1J_{C\text{-}F}$ = 242.7 Hz), 111.4, 39.8 (t, $^2J_{C\text{-}F}$ = 24.1 Hz); IR (KBr, cm^{-1}) *v*:3028, 1616, 1576, 1451, 1364, 1057, 748. HRMS (EI TOF) calcd for (M^+) $C_{17}H_{13}F_2NO$: 285.0965, found 285.0955

2-(1,1-Difluoro-2-(2-nitrophenyl)ethyl)benzo[d]thiazole (3bd)



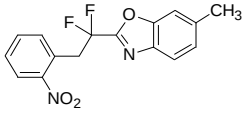
109 mg, 85% yield, yellow solid. Mp 77-78 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.13 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.58-7.44 (m, 5H), 4.34 (t, *J* = 16.6 Hz, 2H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ: -88.67 (t, *J* = 16.5 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.5 (t, $^2J_{C\text{-}F}$ = 33.6 Hz), 152.5, 150.8, 135.2, 134.2, 132.9, 129.1, 127.0, 127.9, 126.1, 125.1, 124.5, 122.2, 118.5 (t, $^1J_{C\text{-}F}$ = 243.5 Hz), 38.3 (t, $^2J_{C\text{-}F}$ = 24.8 Hz); IR (KBr, cm^{-1}) *v*: 3069, 1609, 1578, 1527, 1486 1362, 761, 727. HRMS (EI TOF) calcd for (M^+) $C_{15}H_{10}F_2N_2O_2S$: 320.0431, found 320.0426

1-Butyl-2-(1,1-difluoro-2-(2-nitrophenyl)ethyl)-1H-benzo[d]imidazole (3cd)



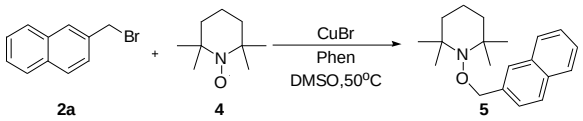
95 mg, 66% yield, yellow solid. Mp 91-92 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.87 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38-7.27 (m, 4H), 4.49 (t, *J* = 17.6 Hz, 2H), 4.22 (t, *J* = 7.9 Hz, 2H), 1.76-1.70 (m, 2H), 1.36-1.29 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -96.81 (t, *J* = 16.5 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 151.0, 145.5 (t, $^{2}J_{C\text{-}F}$ = 30.7 Hz), 141.3, 135.8, 134.4, 132.5, 128.8, 126.4, 124.9, 124.5, 122.9, 121.0, 118.1 (t, $^{1}J_{C\text{-}F}$ = 239.7 Hz), 110.5, 44.9, 37.8 (t, $^{2}J_{C\text{-}F}$ = 23.4 Hz), 32.0, 20.1, 13.6; IR (KBr, cm^{-1}) *v*: 3036, 1610, 1579, 1525, 1473,1340, 762, 725. Anal. Calcd for $C_{19}H_{19}F_2N_3O_2$ (359.14): calcd. C, 63.50; H, 5.33; N, 11.69. found C, 63.46; H, 5.37; N, 11.64

2-(1,1-Difluoro-2-(2-nitrophenyl)ethyl)-6-methylbenzo[d]oxazole (3a'd)



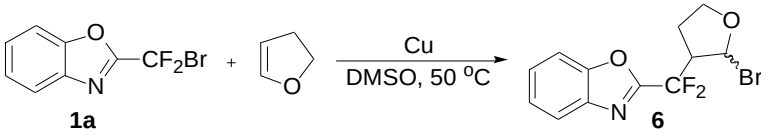
108 mg, 85% yield, yellow solid. Mp 91-92 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.89 (d, *J* = 8.1 Hz, 1H), 7.52-7.48 (m, 3H), 7.43-7.38 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 4.26 (t, *J* = 16.6 Hz, 2H), 2.43 (s, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -96.72 (t, *J* = 16.7 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 157.0 (t, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 150.5, 148.9, 140.0, 135.4, 134.0, 132.9, 129.2, 128.3, 125.3, 125.1, 121.0, 115.1 (t, $^{1}J_{C\text{-}F}$ = 243.1 Hz), 110.7, 37.8 (t, $^{2}J_{C\text{-}F}$ = 24.3 Hz), 21.4; IR (KBr, cm^{-1}) *v*: 3018, 1611, 1581, 1522, 1485, 1348, 1054, 786, 724. Anal. Calcd for $C_{16}H_{12}F_2N_2O_3$ (318.08): calcd. C, 60.38; H, 3.80; N, 8.80. found C, 60.41; H, 3.77; N, 8.76

3. Synthesis of benzyl-TEMPO adducts 5



A 10 mL round-bottom flask was charged with **2a** (110 mg, 0.5 mmol), **4** (94 mg, 0.6 mmol), CuBr (72 mg, 0.5 mmol), 1,10-phenanthroline (90 mg, 0.5 mmol) and DMSO (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 50 ℃ for 4 h. After the reaction was completed, the crude product was directly purified by flash chromatography (petroleum ether/ethyl acetate, 100:1 v/v), to give 83 mg (56% yield) of **5** as white solid. Mp 68-69 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.86-7.82 (m, 4H), 7.51-7.46 (m, 3H), 5.00 (s, 2H), 1.64-1.26 (m, 6H), 1.32 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 135.8, 133.4, 132.9, 127.9, 127.8, 127.7, 126.0, 125.9, 125.8, 125.7, 78.9, 60.1, 39.8, 33.2, 20.4, 17.2; IR (KBr, cm^{-1}) *v*: 3010, 2976, 2925, 2880, 1469, 1446, 1373, 1359, 1132.

4. The reaction of benzo-1,3-oxazolic difluoromethyl bromide with 2,3-Dihydrofuran.[S2]



A 10 mL round-bottom flask was charged with **1a** (124 mg, 0.5 mmol), 2,3-dihydrofuran (175 mg, 2.5 mmol) and copper powder (38 mg, 0.6 mmol) and DMSO (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 50 ℃ for 4 h. After the reaction was completed, the mixture was analyzed by ^{19}F NMR and the yield, 28%, based on **1a** using $PhCF_3$ as internal standard. ^{19}F NMR ($CDCl_3$, 470 MHz) *δ*: -101.64 (AB, *J* = 275.4 Hz, 1F), -104.22 (AB, *J* = 275.4 Hz, 1F). The compound **6,** MS (EI): *m/z* (%) 317 (M^+), 319 (M^++2), 149 (M^+- C4H6BrO), 151(M^++2- C4H6BrO)

5. Cross-coupling reaction of benzo-1,3-oxazolic difluoromethyl bromide with *o*-nitrobenzyl bromide

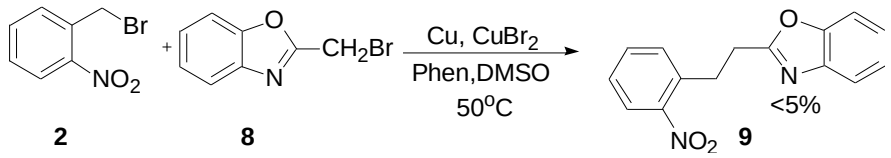


Figure S1. The reaction of benzo-1,3-oxazolic difluoromethyl bromide with *o*-nitrobenzyl bromide

A 10 mL round-bottom flask was charged with *o*-nitrobenzyl bromide (43 mg, 0.2 mmol), **8** (64 mg, 0.3 mmol), copper powder (45 mg, 0.7 mmol), $CuBr_2$ (2 mg, 0.01 mmol), 1,10-phenanthroline (7 mg, 0.04 mmol) and DMSO (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 50 ℃ for 8 h. After the reaction was completed, the crude product was analyzed by GC-MS, and the yield of **9** <5%, based on **1** using PPh_3 as internal standard.

6. Cross-coupling reaction of ethyl bromodifluoroacetate with 2-(bromomethyl)naphthalene.

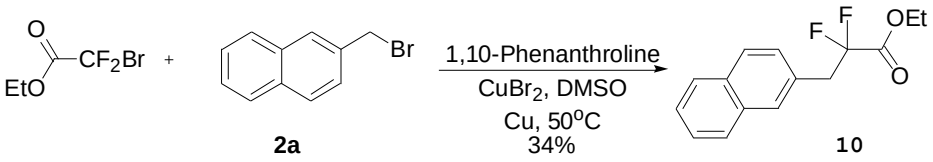


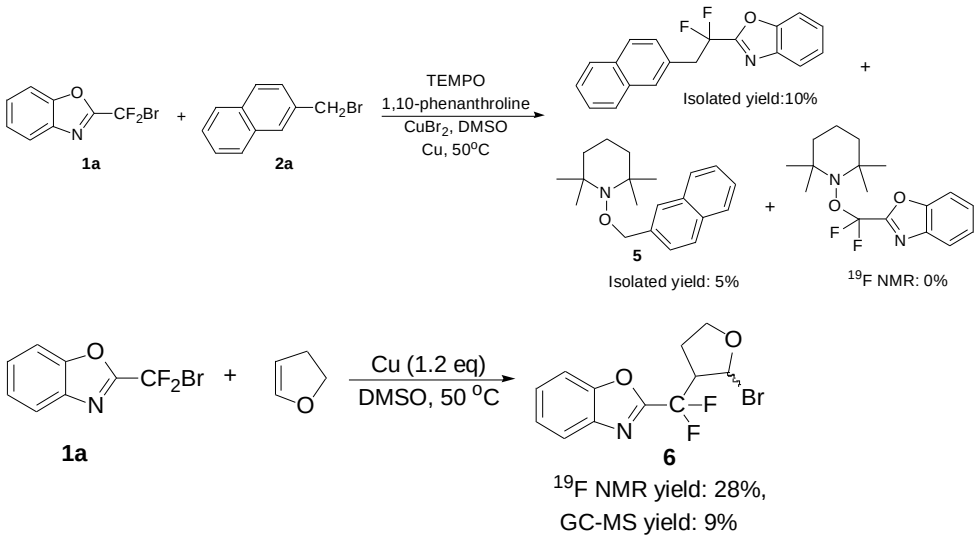
Figure S2. The reaction of ethyl bromodifluoroacetate with 2-(bromomethyl)naphthalene.

A 10 mL round-bottom flask was charged with 2-(bromomethyl)naphthalene (0.2 mmol), ethyl bromodifluoroacetate (0.3 mmol), copper powder (45 mg, 0.7 mmol), $CuBr_2$ (2 mg, 0.01 mmol), 1,10-phenanthroline (7 mg, 0.04 mmol) and DMSO (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 50 ℃ for 8 h, after the reaction was completed, the crude product was directly purified by flash chromatography (petroleum ether/ethyl acetate, 100:1 v/v), to give the desired compound **10**. 36 mg, 34% yield, colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.83(m, 3H), 7.77 (s, 1H), 7.52-7.50 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.59 (t, J = 16.4 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ: -104.12 (t, J = 16.1 Hz, 2F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.9 (t, $^2J_{C\text{-}F}$ = 32.8 Hz), 133.3, 132.8, 129.7, 128.3, 128.1, 127.8, 127.7,

126.3, 126.2, 115.5 (t, $^{1}J_{C\text{-}F}$ = 251.0 Hz), 62.9, 41.1 (t, $^{2}J_{C\text{-}F}$ = 23.8 Hz), 13.9; IR (KBr, cm^{-1}) *v*: 3059, 3023, 1724, 1260, 1216, 694, 662.

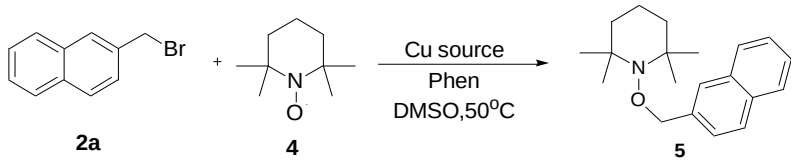
7. Capture the free radicals 1A and 2A

To prove the existence of radical intermediates, the TEMPO trapping reaction was carried out.[S3] One equiv of TEMPO was reacted with benzyl bromide (**2a**) in the presence of stoichiometric Cu^{0} and catalytic amount of $CuBr_2$ using 1,10-phenanthroline as ligand in DMSO. The TEMPO trapped complex **5** was isolated in 64% yield (Table 2, entry3). The other copper sources could also provide the complex **5** (Table 2, entries 1-2). The results supports the formation of benzylic radical species **2A**. Furthermore, when TEMPO was added in the standard reaction system (Table 1, entry 6), the *gem*-difluoromethylenation reaction was significantly suppressed (Scheme S1) and TEMPO trapped complex **5** was formed in 5% isolated yield. However, the adduct of TEMPO with **1a** was not detected on the basis of ^{19}F NMR analysis**.** Nevertheless, evidence of the formation of 1,3-azolic difluoromethyl radical **1A** was found by the observation of radical adduct **6** in the reaction of 2,3-dihydrofuran with substrate **1a** in the presence of copper (0) in DMSO by ^{19}F NMR and GC-MS analysis (Scheme 5).[S4] Thus, the *gem*-difluoromethylenation of sp3-hybirdized carbon center was demonstrated to be a radical process.



Scheme S1 The trapping reaction of radical **1A** and radical **2A**

Table S1 The reaction of **2a** with **4** in the presence of different copper sources



2a **4** **5**

Entry	Copper source (mol%)	Additive (mol%)[b]	Yield (%)[a] of **5**
1	Cu(0) (120), CuBr (10)	Phen (20)	65
2	CuBr (100)	Phen (100)	56
3	Cu(0) (120), $CuBr_2$ (5)	phen (20)	64
4	$CuBr_2$ (100)	Phen (100)	0

[a] Isolated yield; [b] Phen = 1,10-Phenanthroline.

8. Reference.

S1. M. Medebielle, S. Ait-Mohand, C. Vurkhloder, W. R. Dolbier, Jr., G. Laumond, A-M. Aubertin, *J. Fluorine Chem.***2005**, *126*, 535-542.

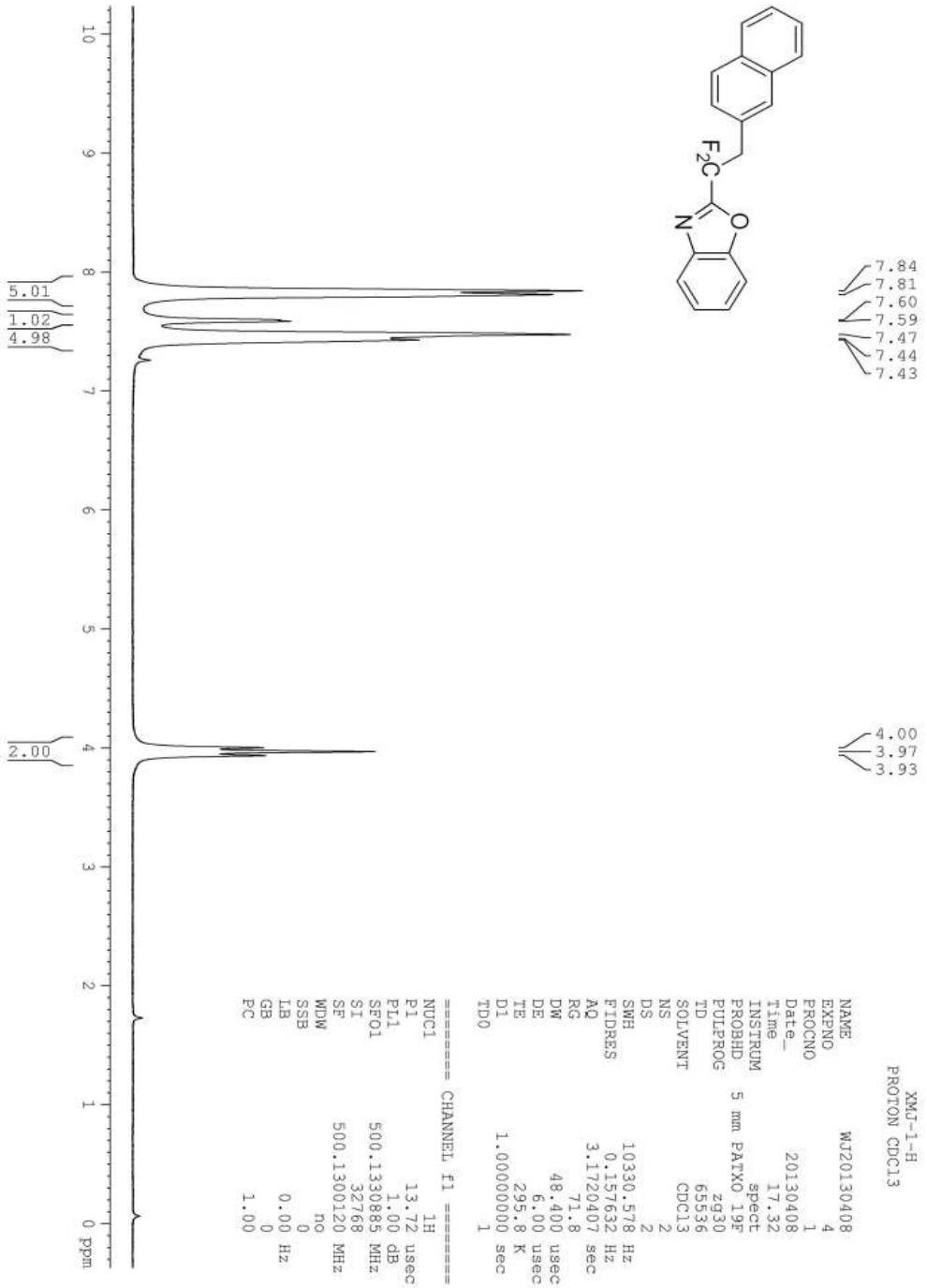
S2. C. Burkholder, W. R. Dolbier, Jr., *J. Org. Chem.* **1998**, *63*, 5385-5394.

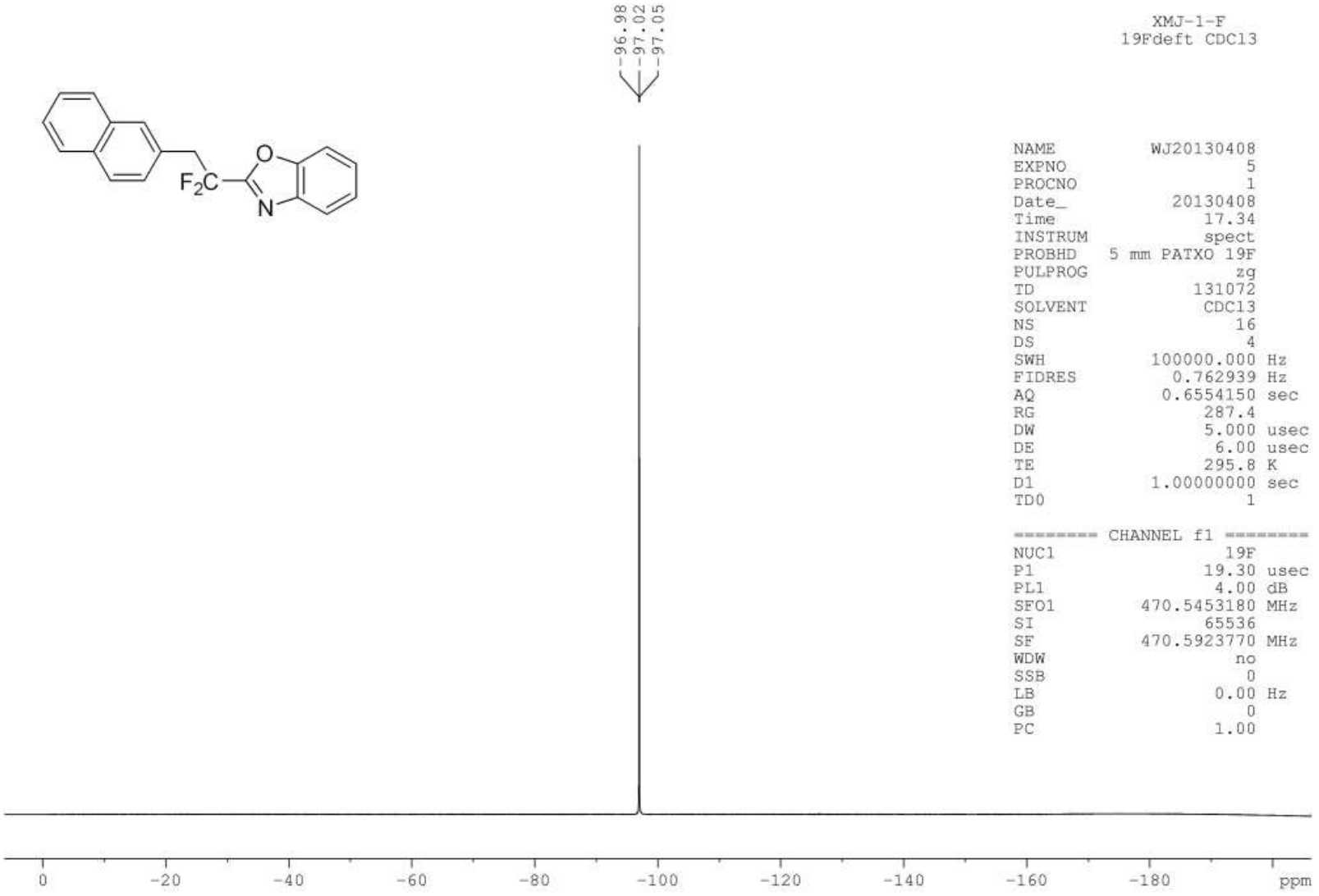
S3. a) For a review on the use of TEMPO, see: Vogler, T.; Studer, A. *Synthesis*, **2008**, 1979 -1993. b) Gildner, P. G.; Gietter, A. A. S.; Cui, D.; Watson, D. A. *J. Am. Chem. Soc.* **2012**, *134*, 9942-9945. c) Sorin, G.; Mallorquin, R. M.; Contie, Y.; Baralle, A.; Malacria, M.; Goddard, J. P.; Fensterbank, L.; *Angew. Chem. Int. Ed*. **2010**, *49*, 8721-8723.

S4. Burkholder, C.; Dolbier, Jr., W. R. *J. Org. Chem.* **1998**, *63*, 5385

9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectrums for all compounds

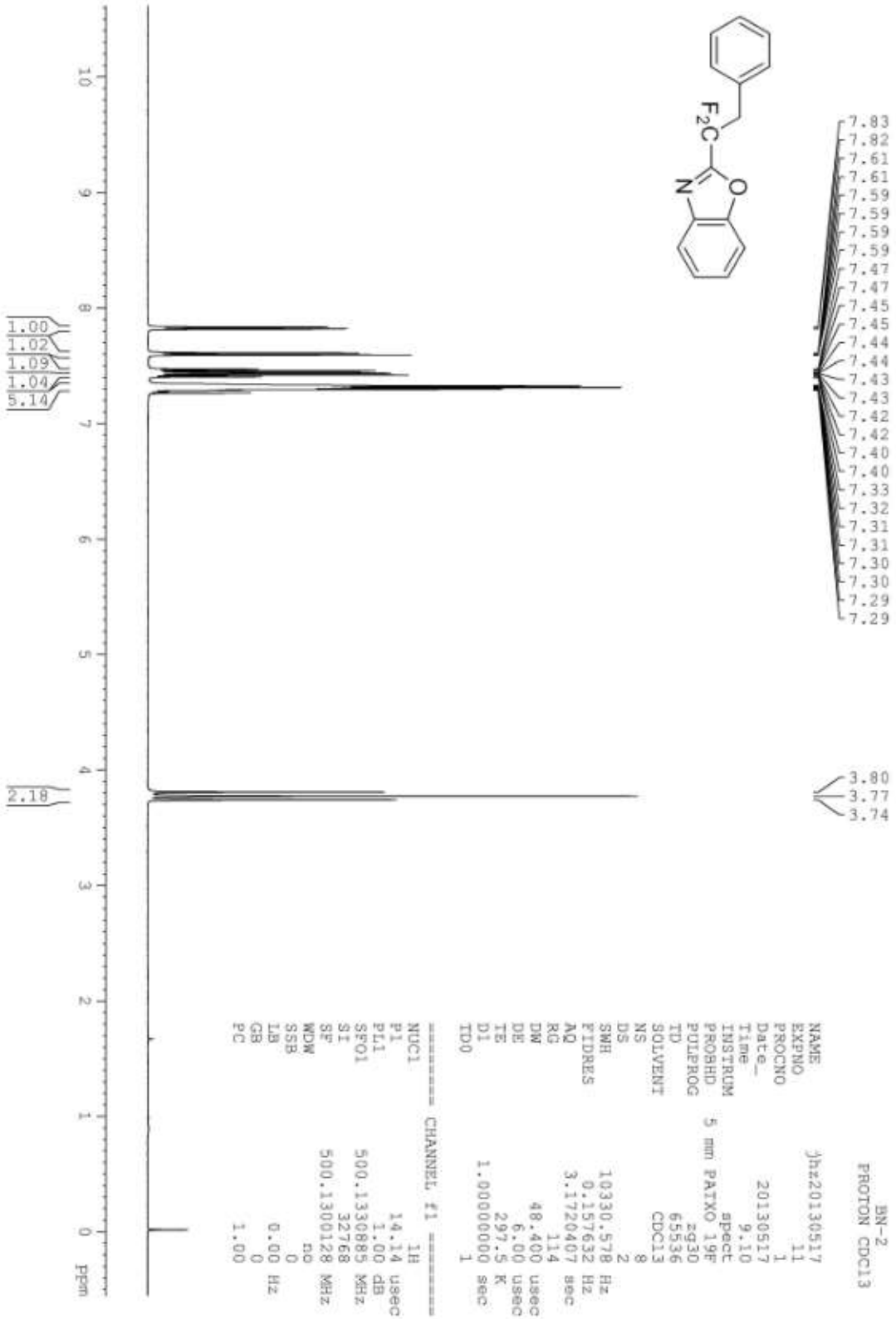
2-(1,1-Difluoro-2-naphthalen-2-yl-ethyl)-benzooxazole (3aa)



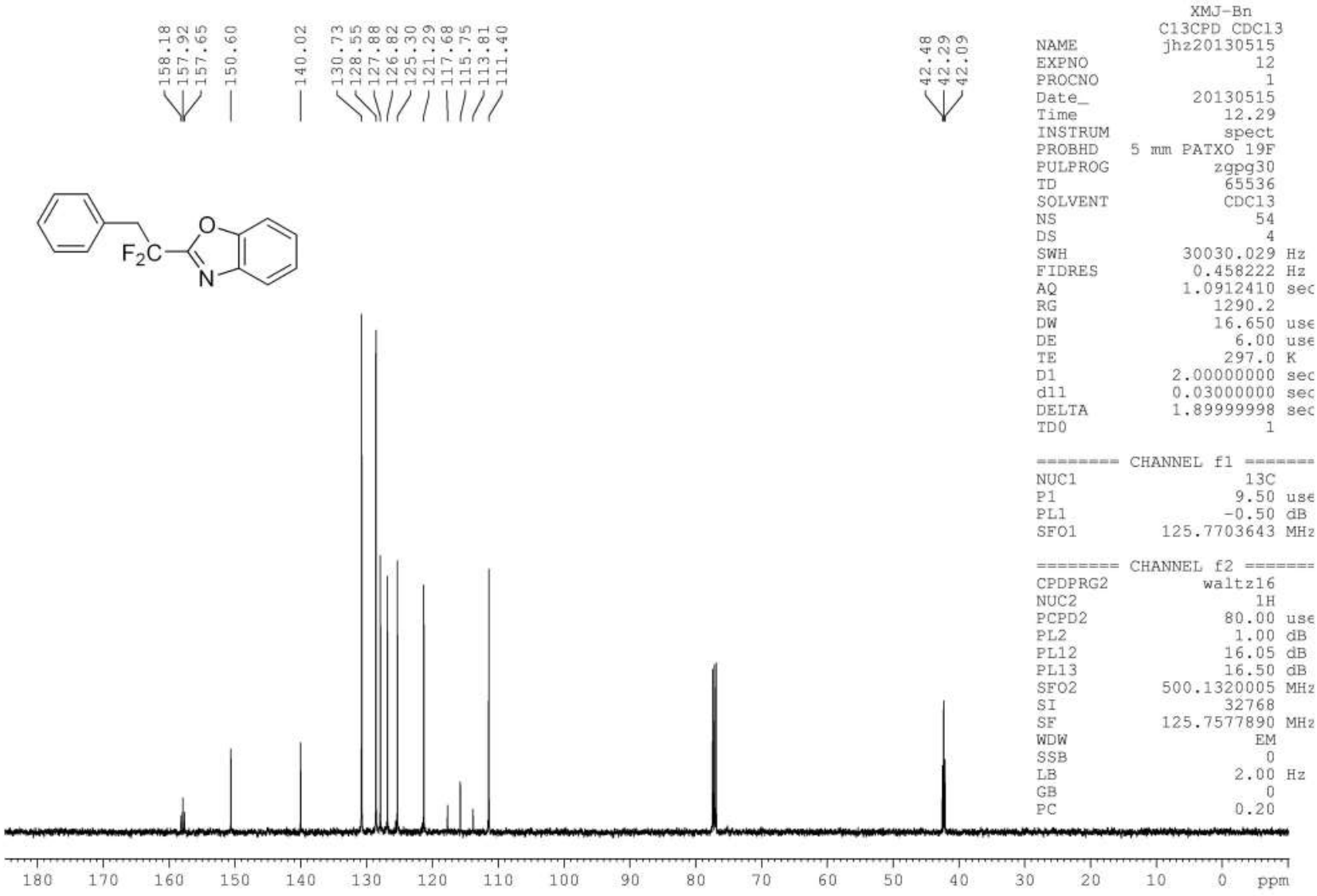

-96.98
-97.02
-97.05
XMJ-1-F
19Fdeft CDCl3
NAME WJ20130408
EXPNO 5
PROCNO 1
Date_ 20130408
Time 17.34
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 287.4
DW 5.000 usec
DE 6.00 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
O
F2C
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

158.20
157.93
157.67
150.63
140.04
133.31
132.83
130.07
128.30
128.21
127.87
127.67
126.86
126.24
126.20
125.33
121.31
117.78
115.84
113.91
111.42
42.60
42.41
42.22
F2C
O
N
XMJ-1-C
C13CPD CDC13
NAME WJ20130408
EXPNO 6
PROCNO 1
Date_ 20130408
Time 17.38
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 81
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 512
DW 16.650 usec
DE 6.00 usec
TE 296.5 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2-(1,1-Difluoro-2-phenylethyl)benzo[d]oxazole (3ab)



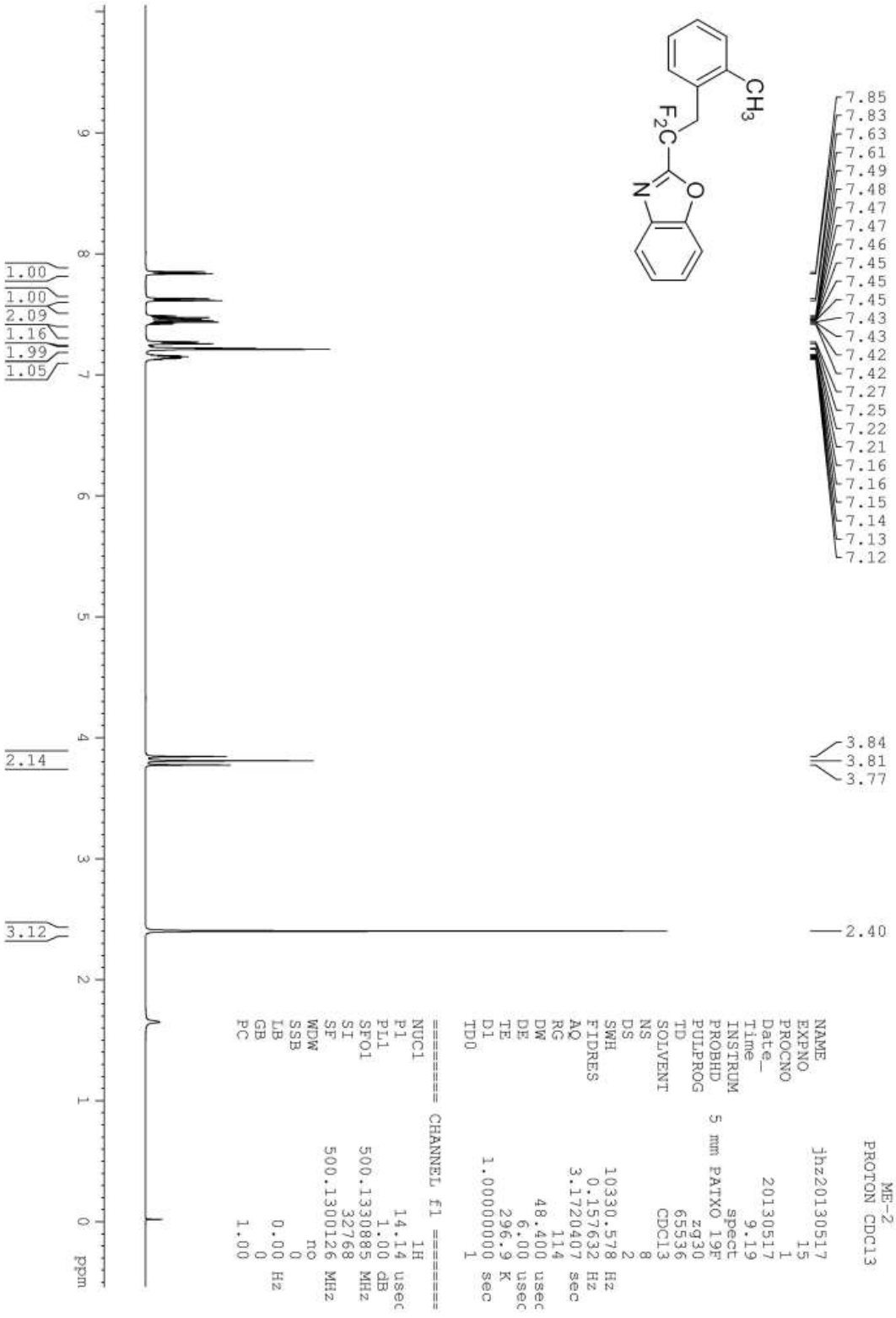
BN-2
19Fdeft CDCl3
NAME jhz20130517
EXPNO 12
PROCNO 1
Date_ 20130517
Time_ 9.11
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 8
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 645.1
DW 5.000 usec
DE 6.00 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
-97.50
-97.54
-97.57
F2C
N
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

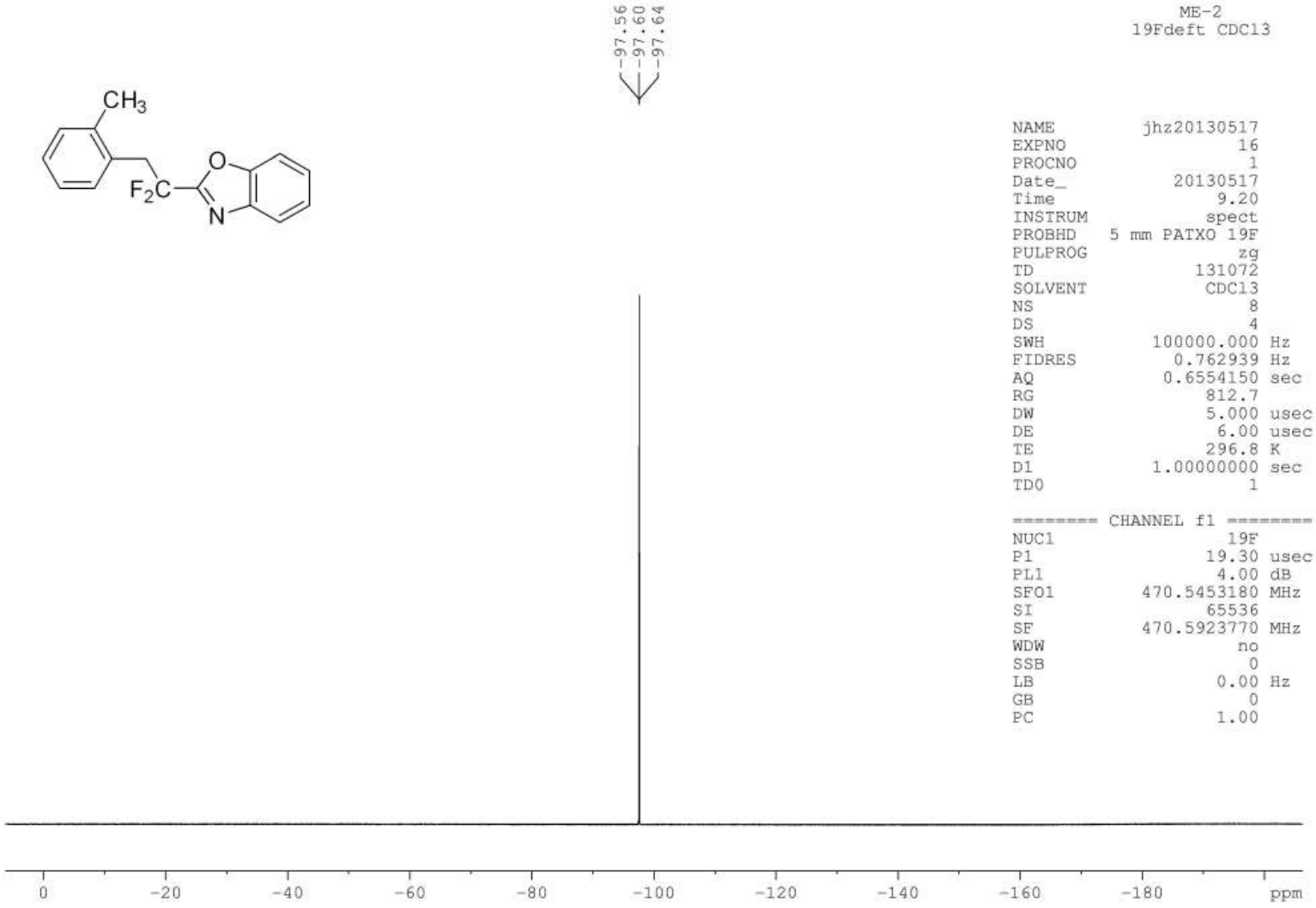


XMJ-Bn
C13CPD CDCl3

NAME	jhz20130515
EXPNO	12
PROCNO	1
Date_	20130515
Time	12.29
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	54
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912410 sec
RG	1290.2
DW	16.650 use
DE	6.00 use
TE	297.0 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 =======	
NUC1	13C
P1	9.50 use
PL1	-0.50 dB
SFO1	125.7703643 MHz
======== CHANNEL f2 =======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 use
PL2	1.00 dB
PL12	16.05 dB
PL13	16.50 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	0.20

2-(1,1-Difluoro-2-(o-tolyl)ethyl)benzo[d]oxazole (3ac)



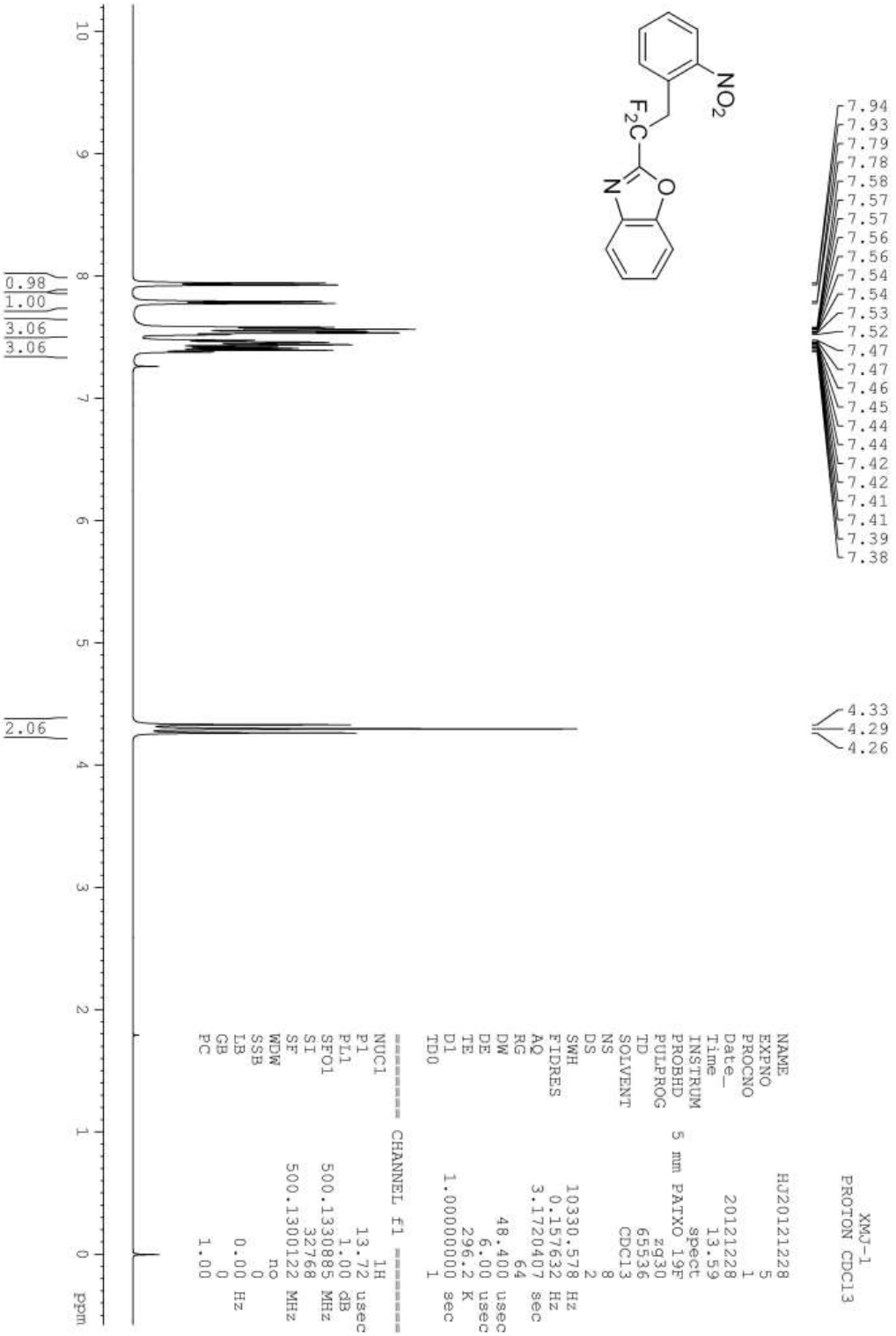


ME-2
19Fdeft CDCl3

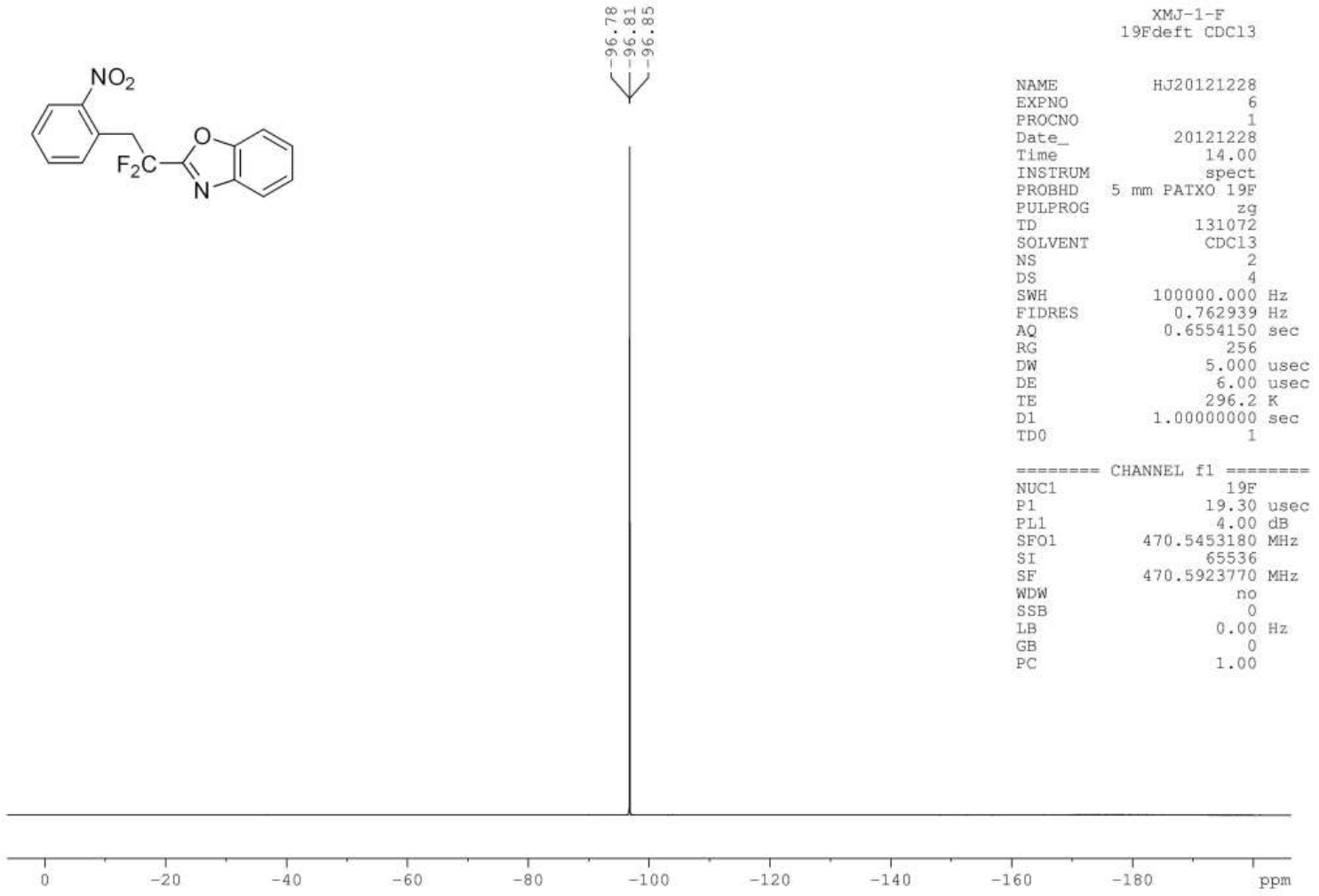
NAME	jhz20130517	
EXPNO	16	
PROCNO	1	
Date_	20130517	
Time	9.20	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	zg	
TD	131072	
SOLVENT	CDCl3	
NS	8	
DS	4	
SWH	100000.000	Hz
FIDRES	0.762939	Hz
AQ	0.6554150	sec
RG	812.7	
DW	5.000	usec
DE	6.00	usec
TE	296.8	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	19F	
P1	19.30	usec
PL1	4.00	dB
SFO1	470.5453180	MHz
SI	65536	
SF	470.5923770	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	

158.47
158.20
157.94
150.65
140.02
138.09
131.58
130.67
129.27
128.06
126.87
126.01
125.35
121.30
118.05
116.11
114.18
111.42
39.21
39.02
38.83
19.91
CH3
F2C
N
O
XMJ-2-CH3
C13CPD CDC13
jhz20130515
NAME
EXPNO 15
PROCNO 1
Date_ 20130515
Time 12.40
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 64
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 362
DW 16.650 use
DE 6.00 use
TE 296.7 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 use
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.20
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2-(1,1-Difluoro-2-(2-nitrophenyl)ethyl)benzo[d]oxazole (3ad)

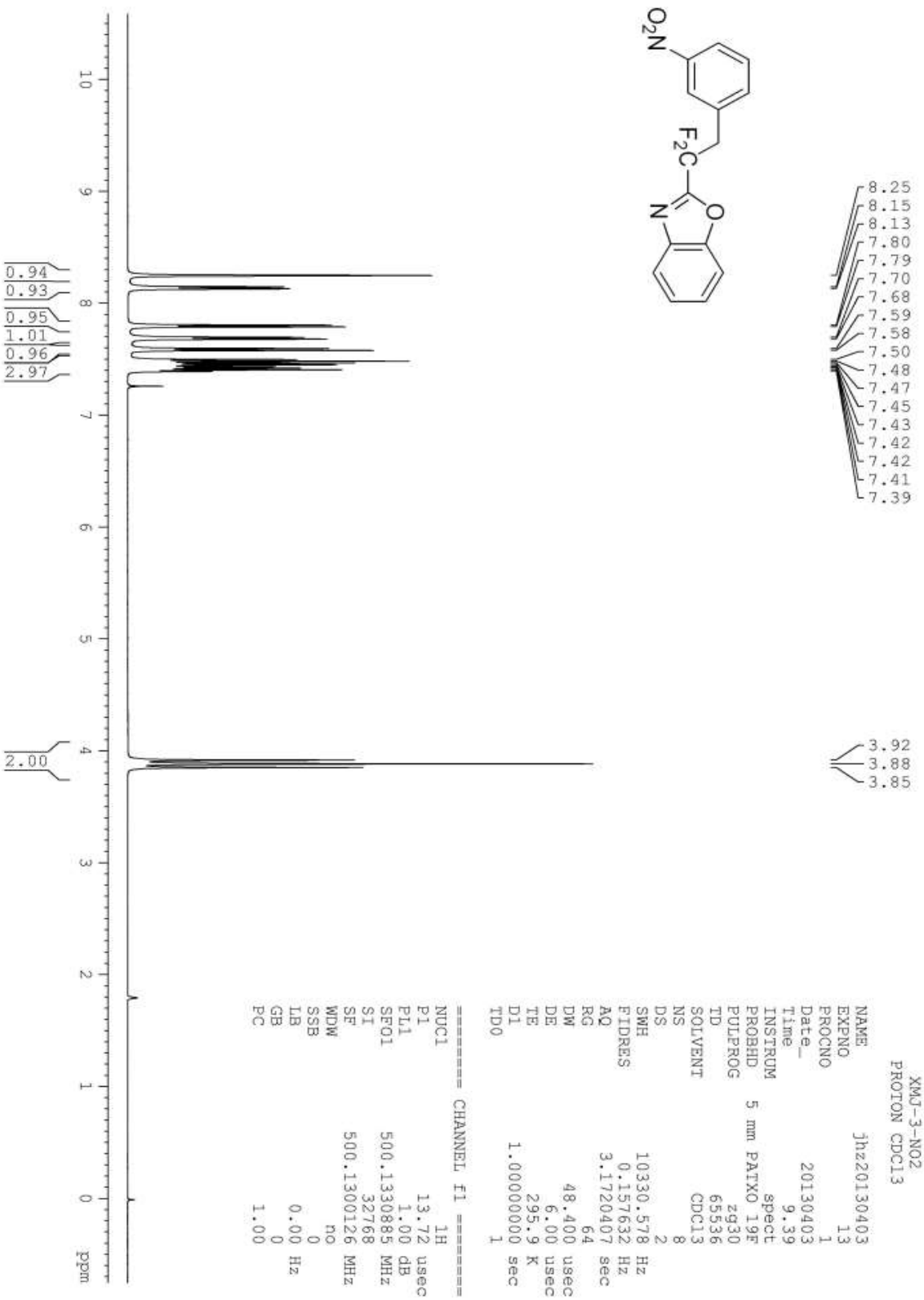


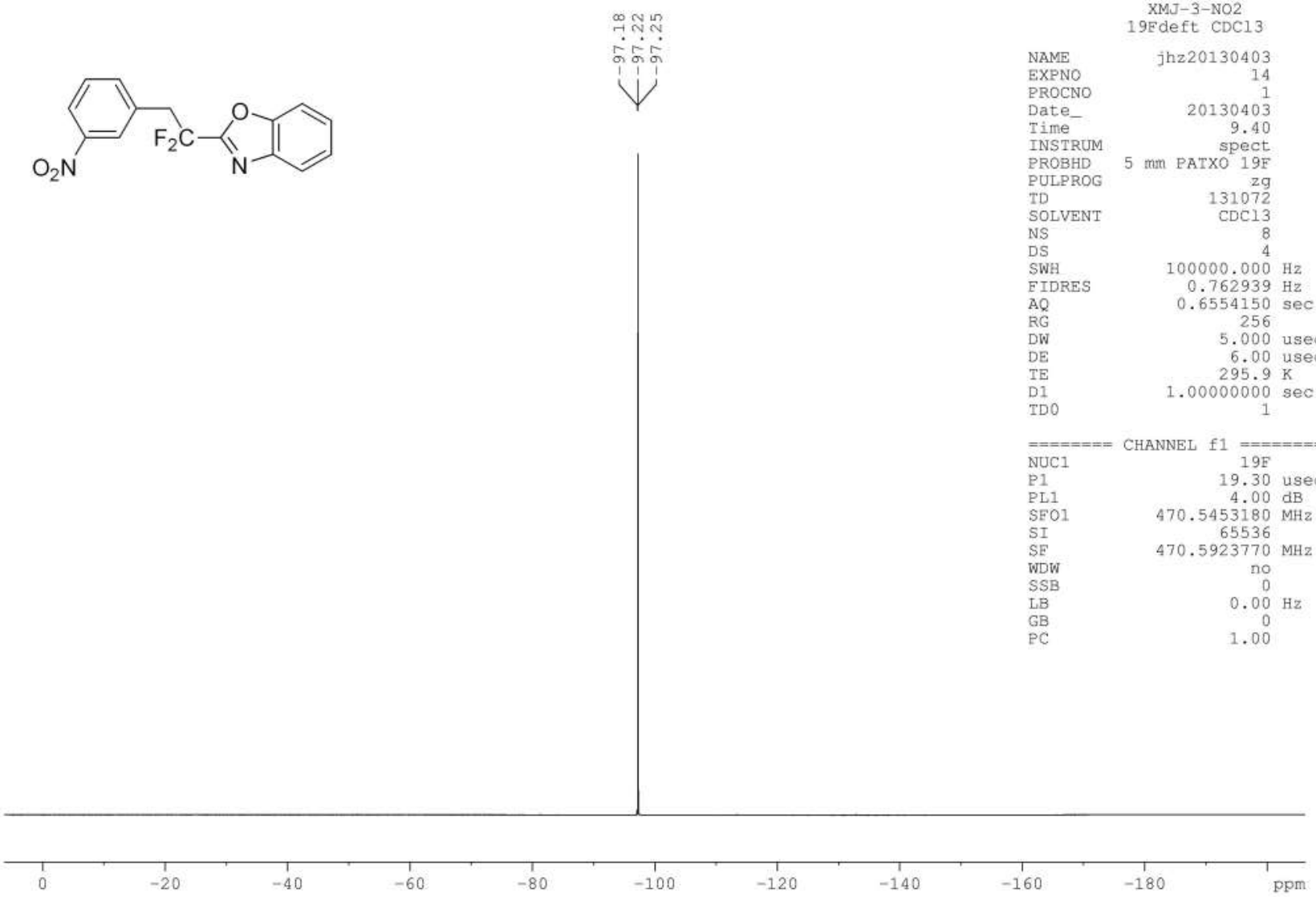
NAME HJ20121228
EXPNO 5
PROCNO 1
Date_ 20121228
Time 13.59
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 64
DW 48.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.72 usec
PL1 1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300122 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


NO2
O
F2C
N
-96.78
-96.81
-96.85
XMJ-1-F
19Fdeft CDCl3
NAME HJ20121228
EXPNO 6
PROCNO 1
Date_ 20121228
Time 14.00
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 2
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 256
DW 5.000 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

157.33
157.06
156.80
150.62
150.53
139.80
134.06
132.90
129.23
127.07
125.40
125.34
125.18
121.32
116.95
115.02
113.08
111.44
38.01
37.82
37.63
XMJ-1
C13CPD CDC13
NAME HJ20121228
EXPNO 7
PROCNO 1
Date_ 20121228
Time 14.05
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 69
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 181
DW 16.650 usec
DE 6.00 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

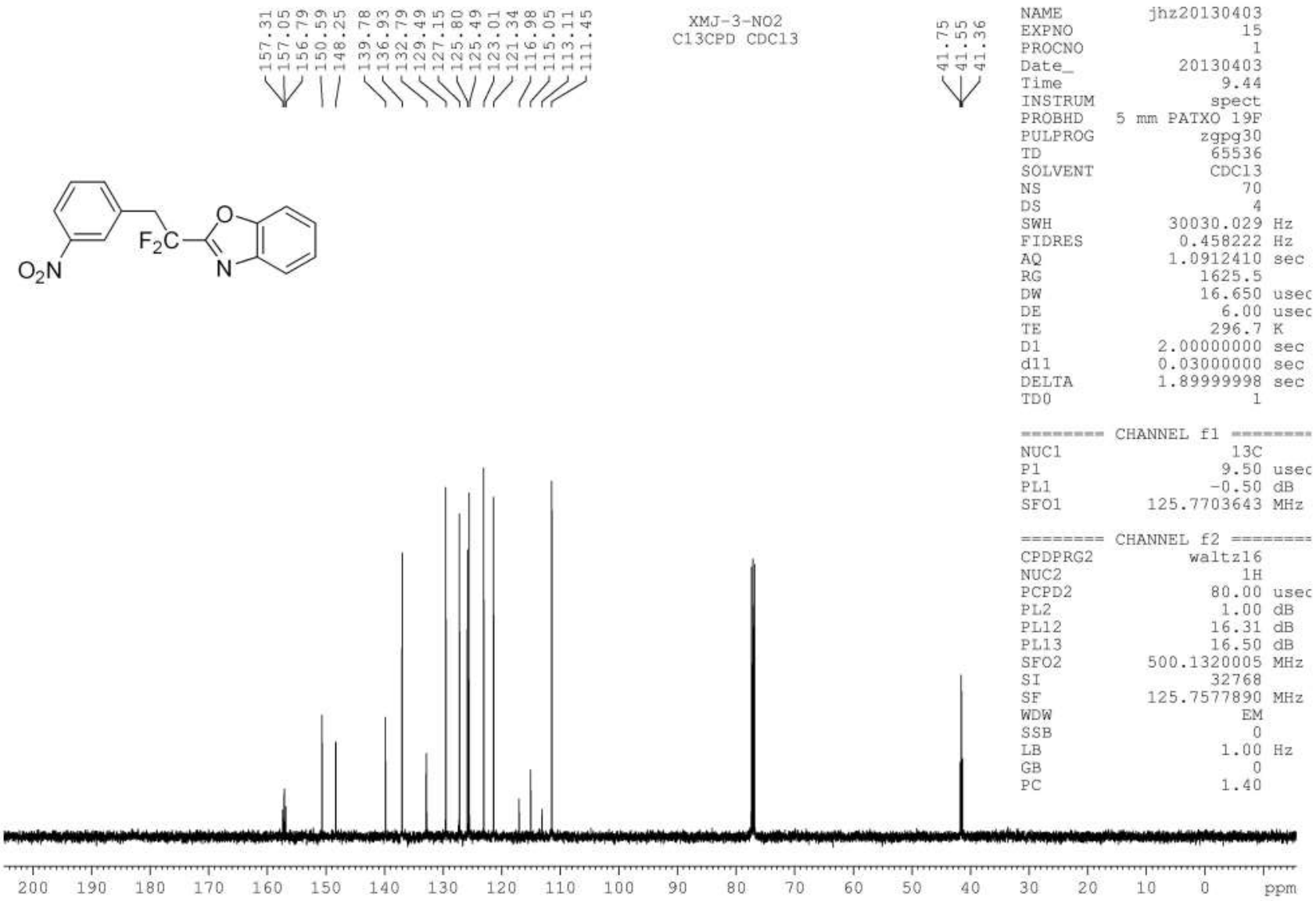
2-(1,1-Difluoro-2-(3-nitrophenyl)ethyl)benzo[d]oxazole (3ae)



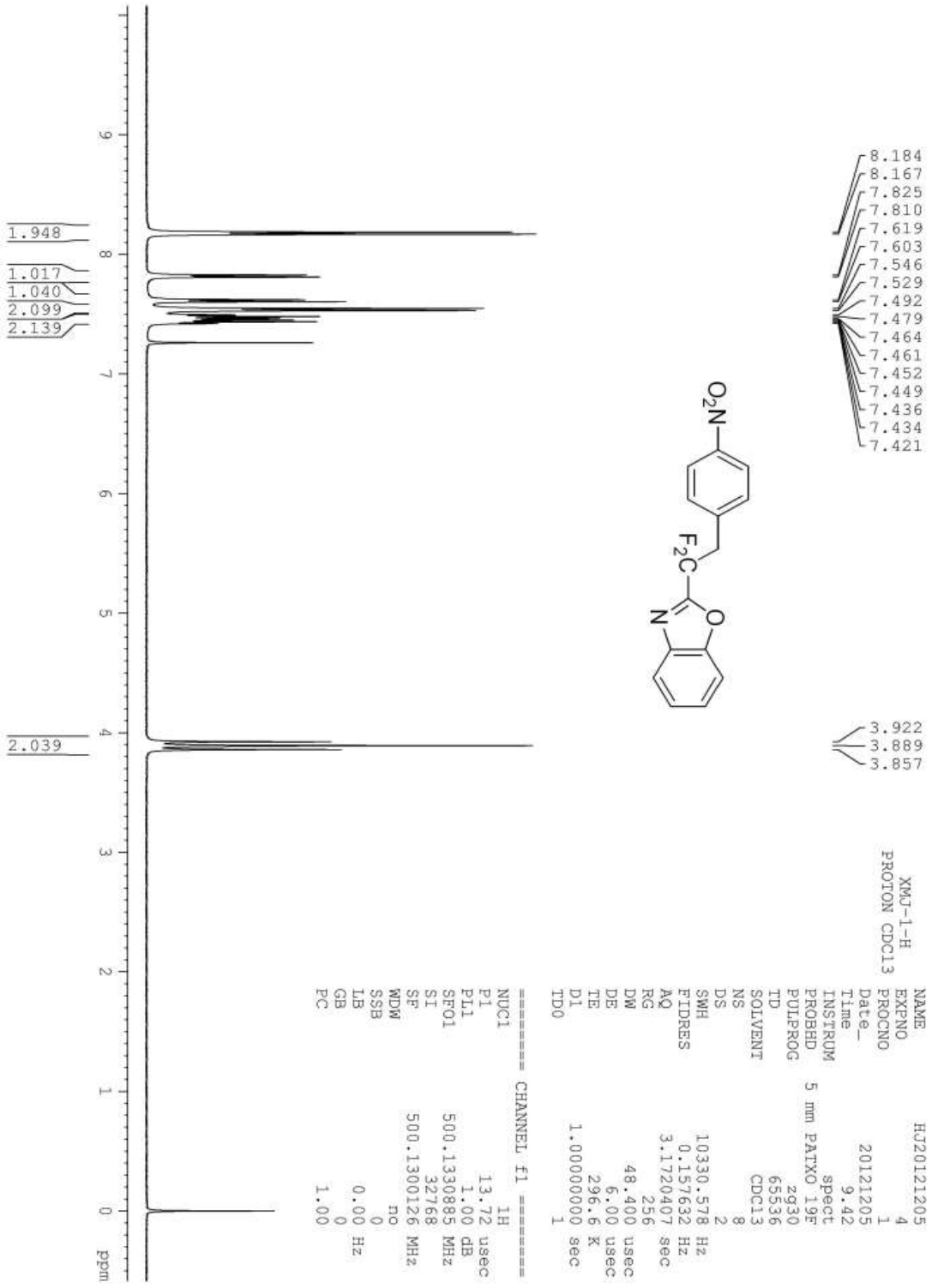


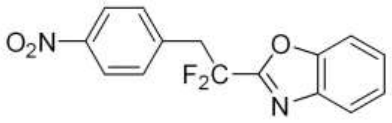
XMJ-3-NO2
19Fdeft CDCl3

NAME	jhz20130403	
EXPNO	14	
PROCNO	1	
Date_	20130403	
Time	9.40	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	zg	
TD	131072	
SOLVENT	CDCl3	
NS	8	
DS	4	
SWH	100000.000	Hz
FIDRES	0.762939	Hz
AQ	0.6554150	sec
RG	256	
DW	5.000	usec
DE	6.00	usec
TE	295.9	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	19F	
P1	19.30	usec
PL1	4.00	dB
SFO1	470.5453180	MHz
SI	65536	
SF	470.5923770	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	


157.31
157.05
156.79
150.59
148.25
139.78
136.93
132.79
129.49
127.15
125.80
125.49
123.01
121.34
116.98
115.05
113.11
111.45
XMJ-3-NO2
C13CPD CDC13
41.75
41.55
41.36
O2N
F2C
O
N
NAME jhz20130403
EXPNO 15
PROCNO 1
Date_ 20130403
Time 9.44
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 70
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 1625.5
DW 16.650 usec
DE 6.00 usec
TE 296.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

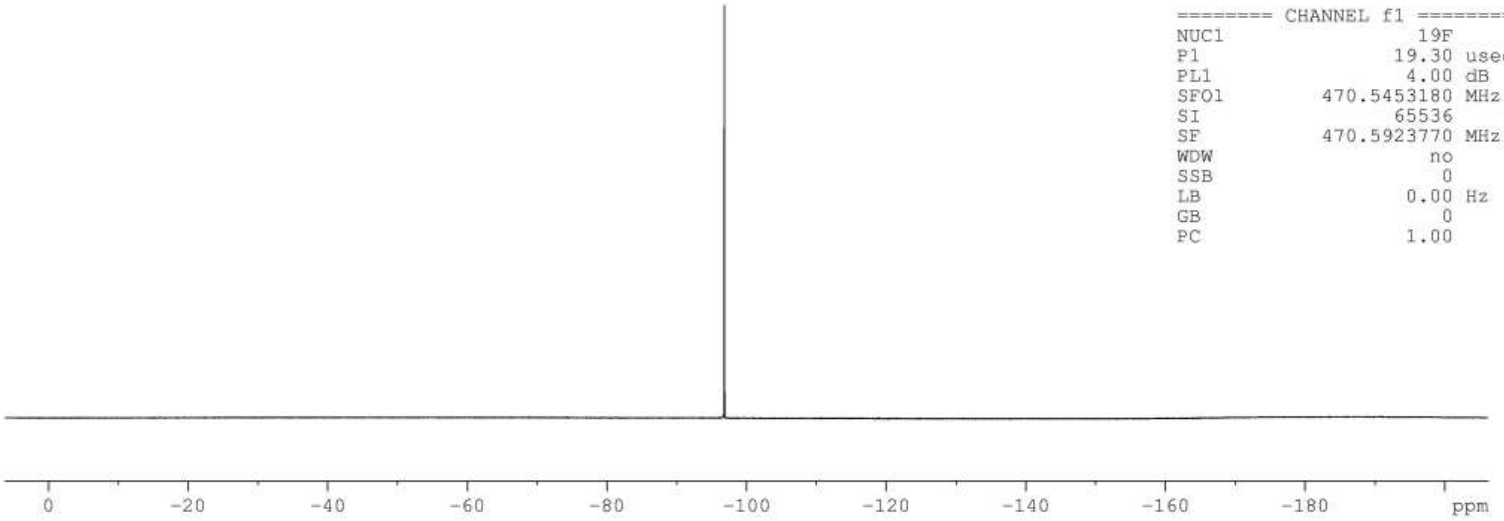
2-(1,1-Difluoro-2-(4-nitrophenyl)ethyl)benzo[d]oxazole (3af)

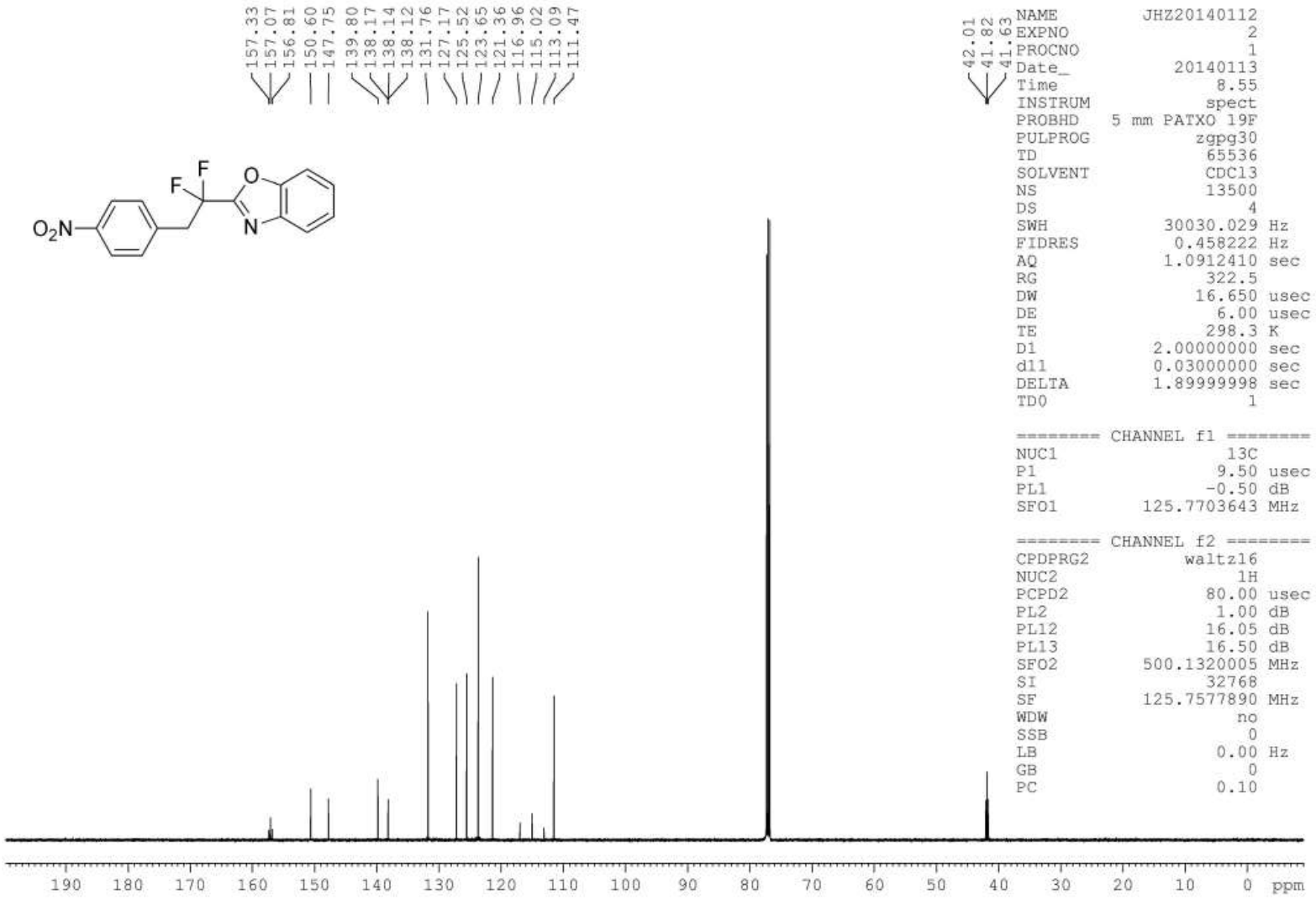




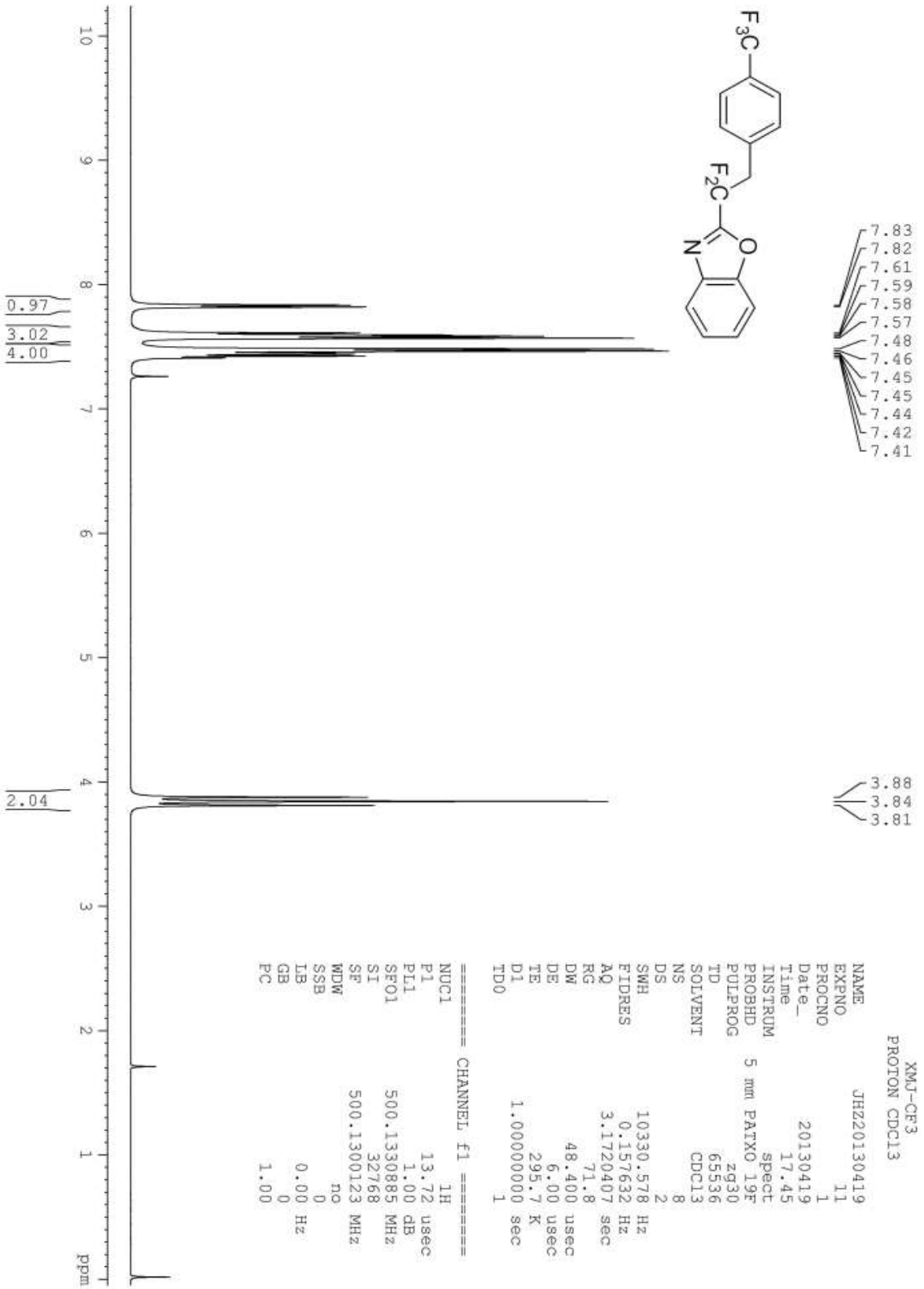
XMJ-1-F
19Fdeft CDCl3

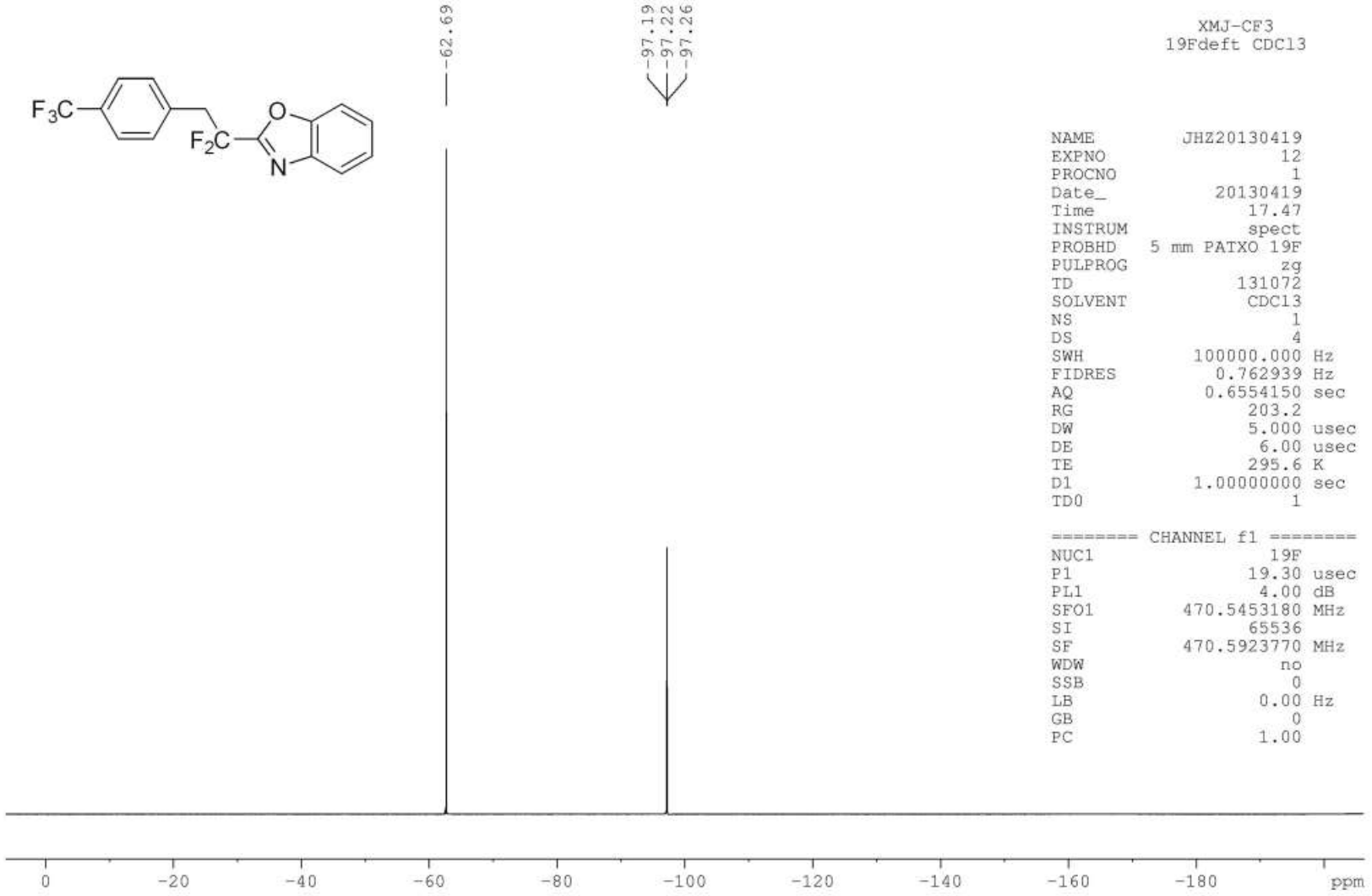
NAME	HJ20121205
EXPNO	5
PROCNO	1
Date_	20121205
Time	9.43
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg
TD	131072
SOLVENT	CDCl3
NS	8
DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554150 sec
RG	362
DW	5.000 usec
DE	6.00 usec
TE	296.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	19.30 usec
PL1	4.00 dB
SFO1	470.5453180 MHz
SI	65536
SF	470.5923770 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

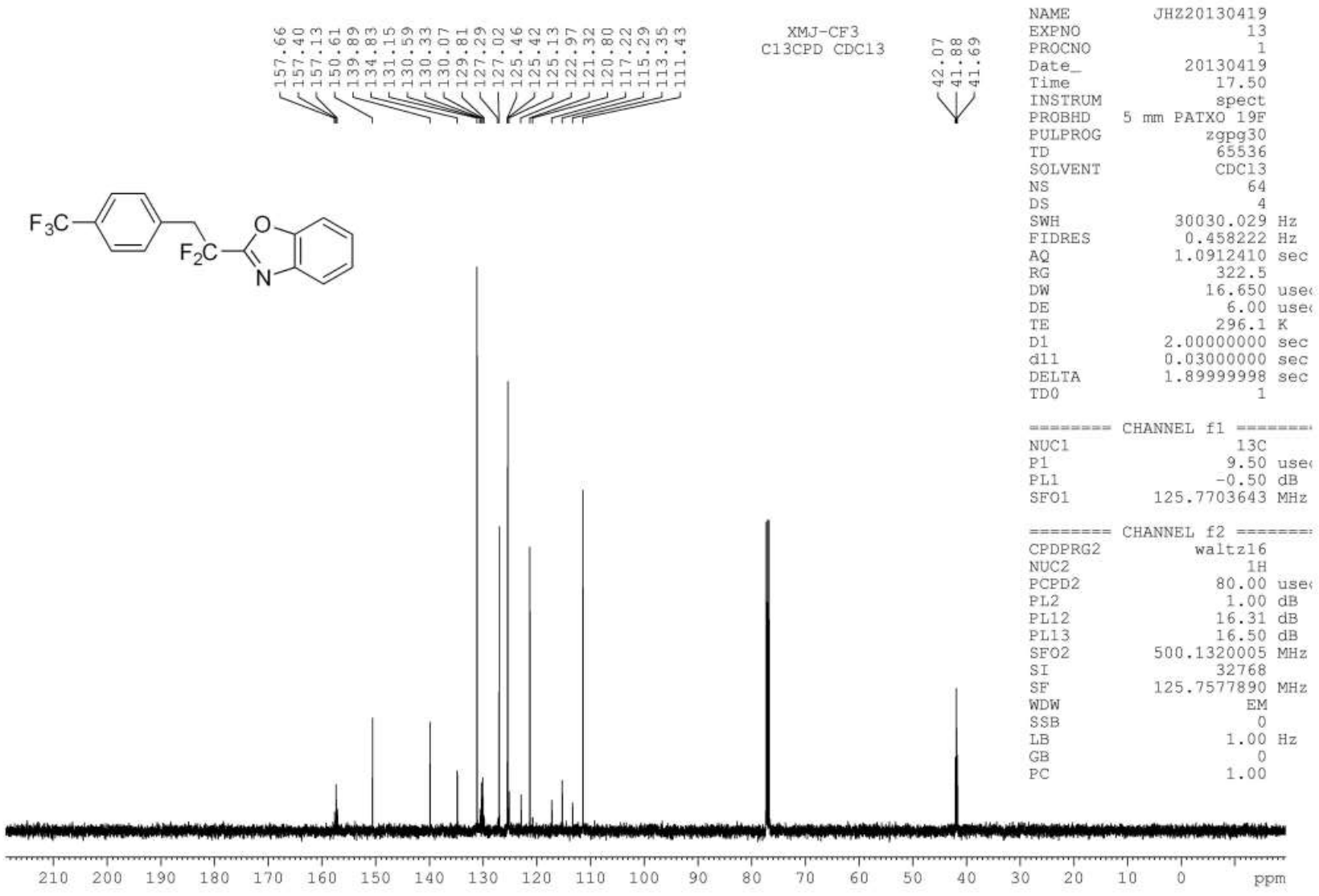



157.33
157.07
156.81
150.60
147.75
139.80
138.17
138.14
138.12
131.76
127.17
125.52
123.65
121.36
116.96
115.02
113.09
111.47
42.01
41.82
41.63
F
F
O
N
O2N
NAME JHZ20140112
EXPNO 2
PROCNO 1
Date_ 20140113
Time 8.55
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13500
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 322.5
DW 16.650 usec
DE 6.00 usec
TE 298.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

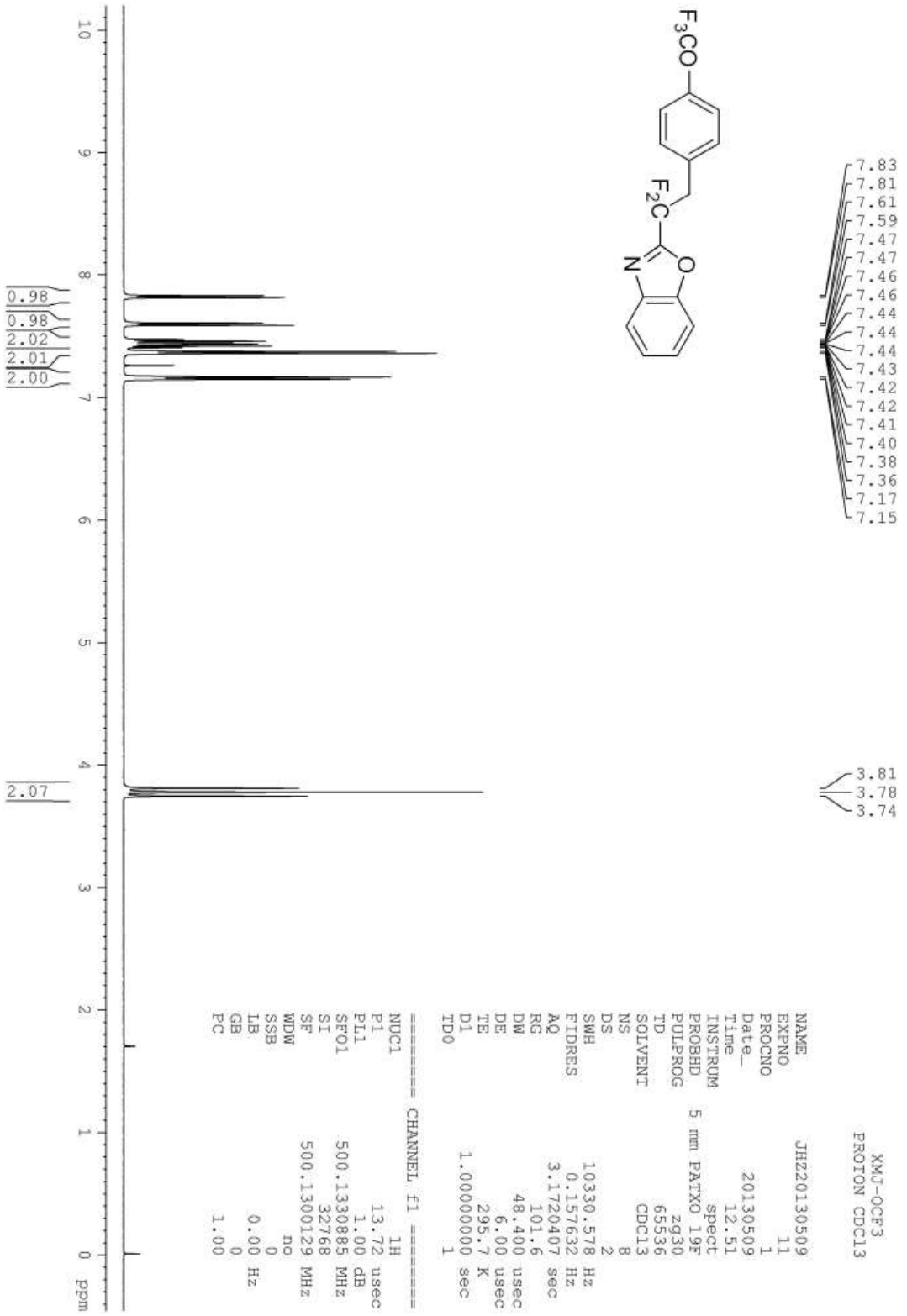
2-(1,1-Difluoro-2-(4-(trifluoromethyl)phenyl)ethyl)benzo[d]oxazole (3ag)

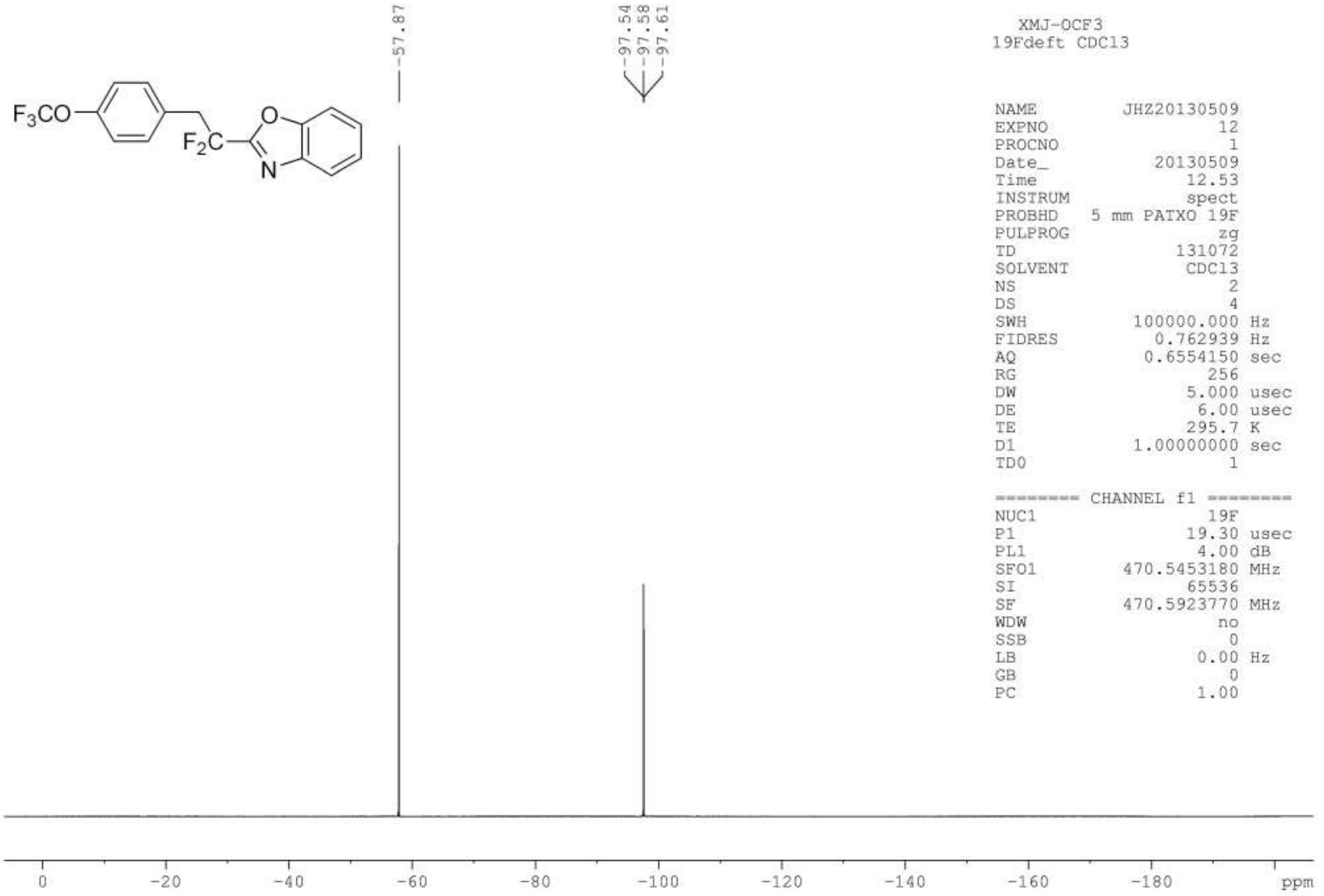



F3C
F2C
O
N
-62.69
-97.19
-97.22
-97.26
XMJ-CF3
19Fdeft CDCl3
NAME JHZ20130419
EXPNO 12
PROCNO 1
Date_ 20130419
Time 17.47
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 1
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 203.2
DW 5.000 usec
DE 6.00 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


157.66
157.40
157.13
150.61
139.89
134.83
131.15
130.59
130.33
130.07
129.81
127.29
127.02
125.46
125.42
125.13
122.97
121.32
120.80
117.22
115.29
113.35
111.43
XMJ-CF3
C13CPD CDC13
42.07
41.88
41.69
F3C
F2C
O
N
NAME JHZ20130419
EXPNO 13
PROCNO 1
Date_ 20130419
Time 17.50
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 64
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 322.5
DW 16.650 use
DE 6.00 use
TE 296.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 use
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2-(1,1-Difluoro-2-(4-(trifluoromethoxy)phenyl)ethyl)benzo[d]oxazole (3ah)



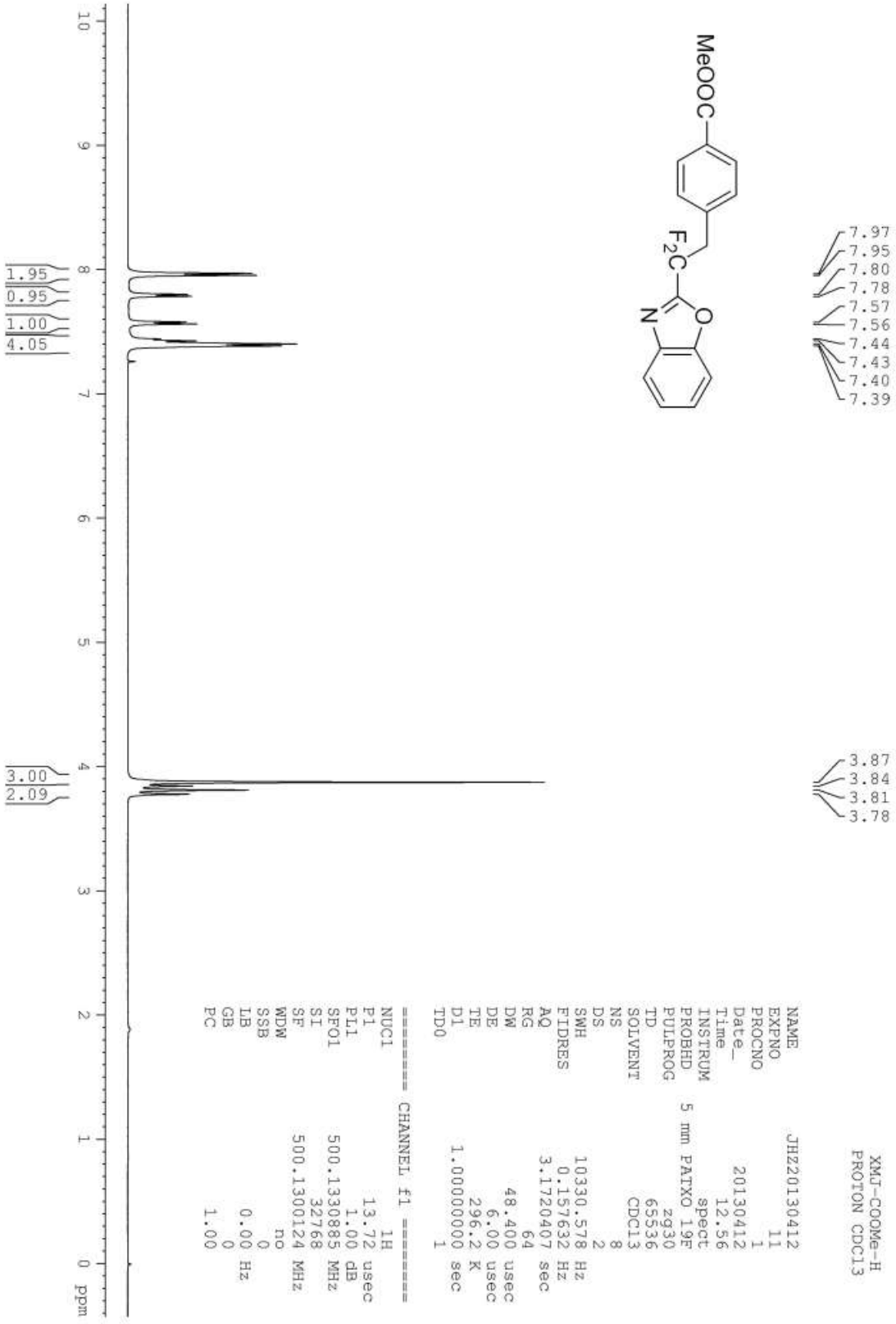


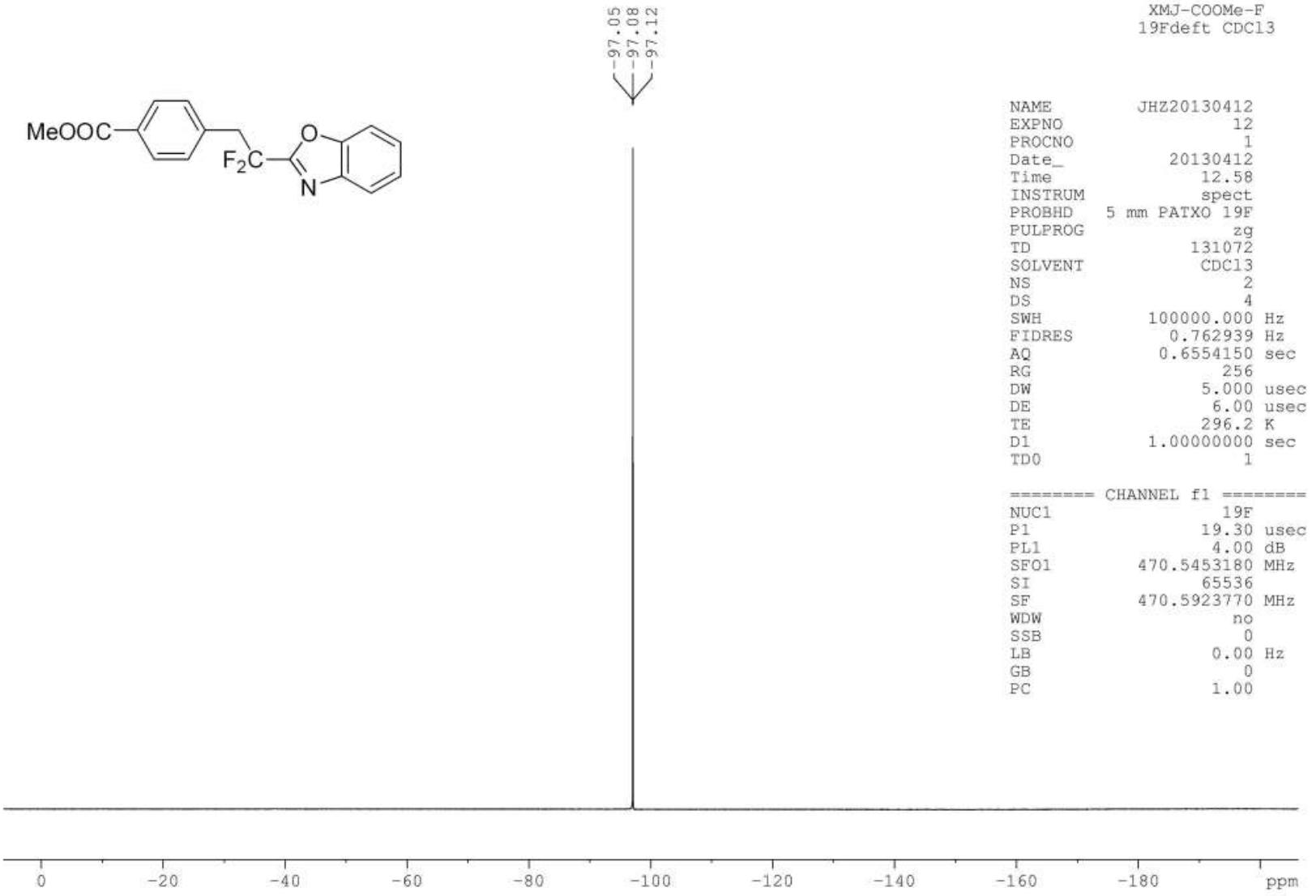
XMJ-OCF3
19Fdeft CDCl3

NAME	JHZ20130509	
EXPNO	12	
PROCNO	1	
Date_	20130509	
Time	12.53	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	zg	
TD	131072	
SOLVENT	CDCl3	
NS	2	
DS	4	
SWH	100000.000	Hz
FIDRES	0.762939	Hz
AQ	0.6554150	sec
RG	256	
DW	5.000	usec
DE	6.00	usec
TE	295.7	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	19F	
P1	19.30	usec
PL1	4.00	dB
SFO1	470.5453180	MHz
SI	65536	
SF	470.5923770	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	

157.80
157.53
157.26
150.60
149.00
148.99
148.97
148.96
139.91
132.18
129.48
129.45
129.43
126.96
125.38
123.50
121.45
121.30
120.94
119.41
117.36
117.30
115.37
113.44
111.40
41.63
41.44
41.25
F3CO
F2C
N
O
XMJ-OCF3
C13CPD CDC13
NAME JH220130509
EXPNO 13
PROCNO 1
Date_ 20130509
Time 12.56
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 113
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 2048
DW 16.650 usec
DE 6.00 usec
TE 296.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

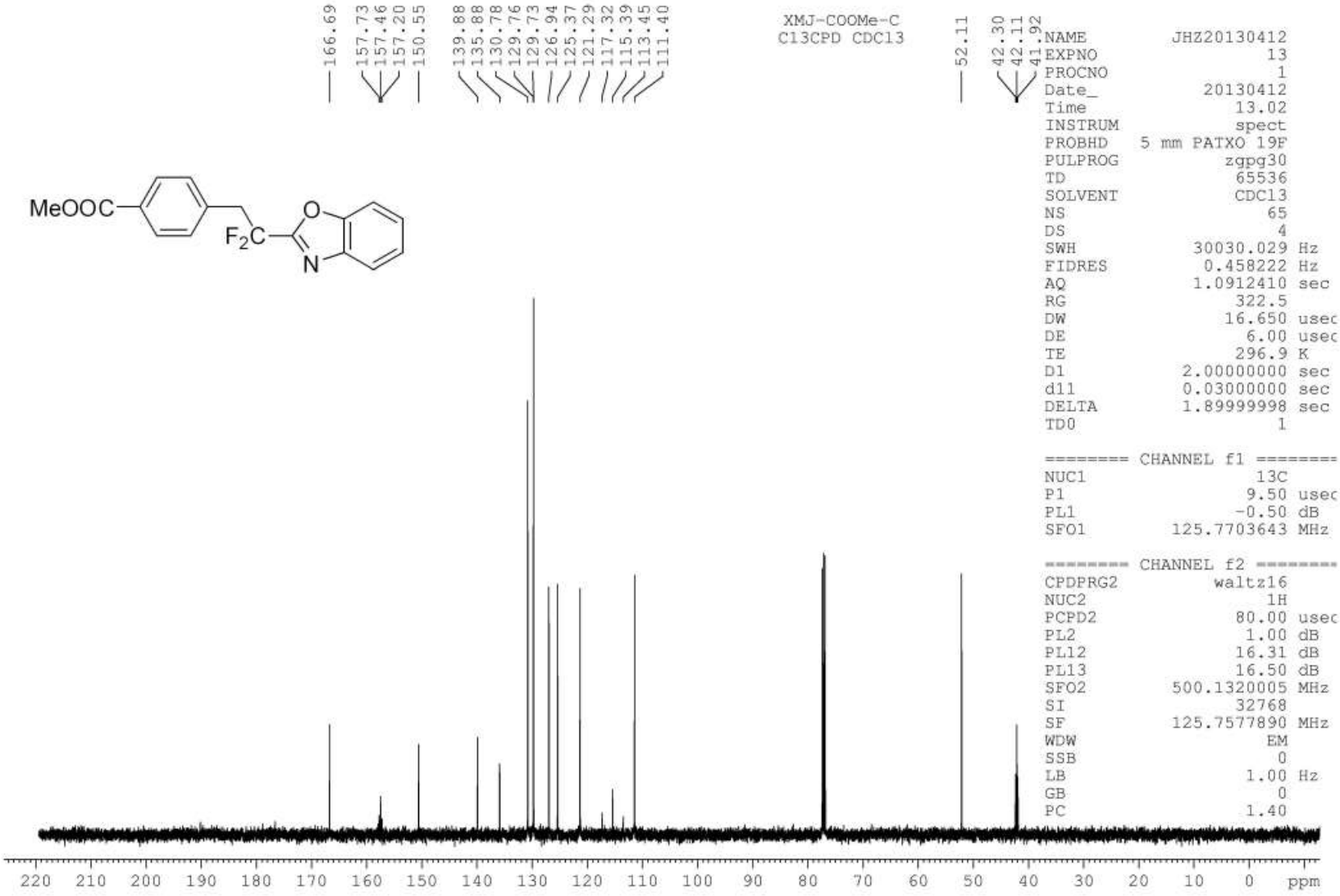
Methyl 4-(2-(benzo[d]oxazol-2-yl)-2,2-difluoroethyl)benzoate (3ai)



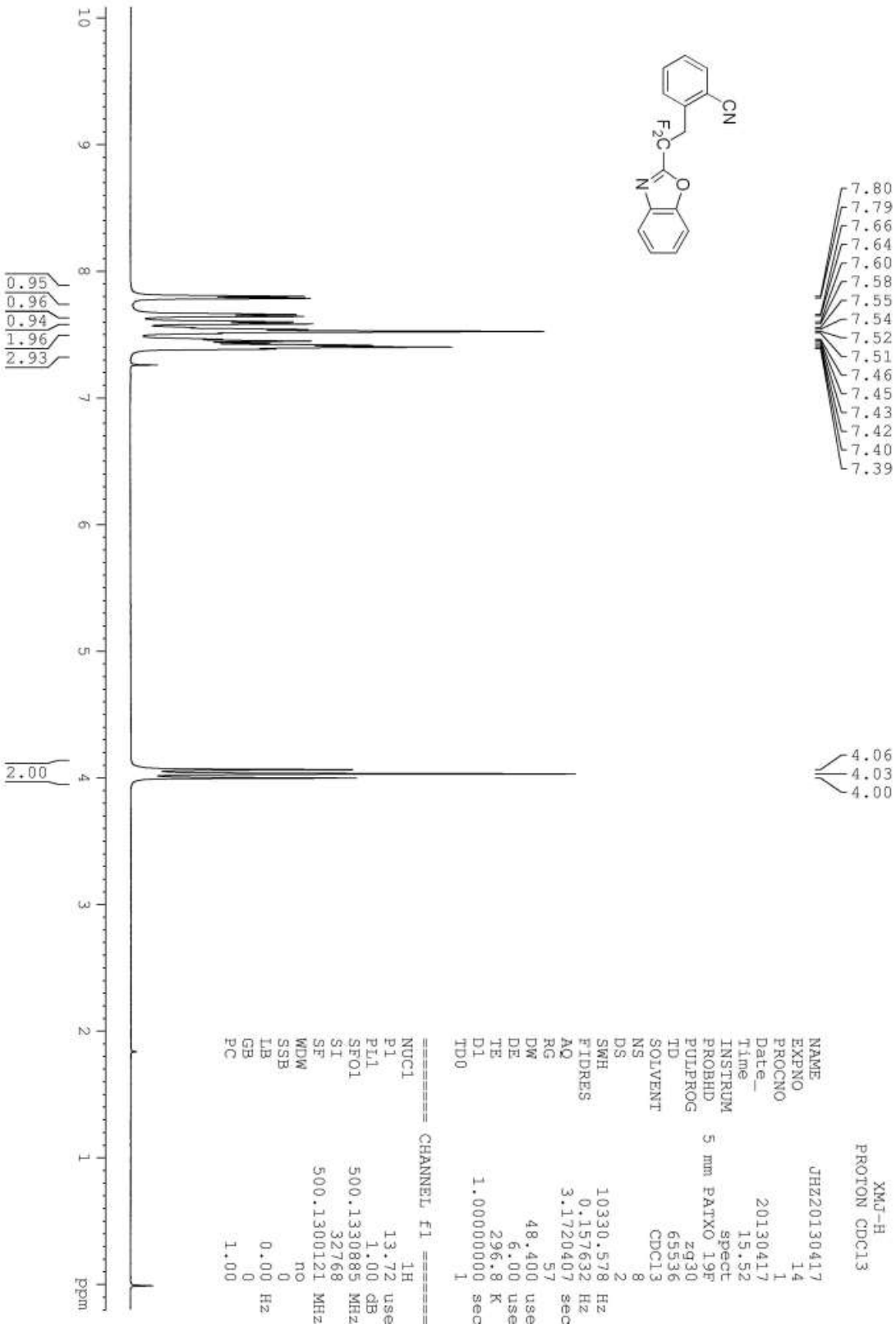


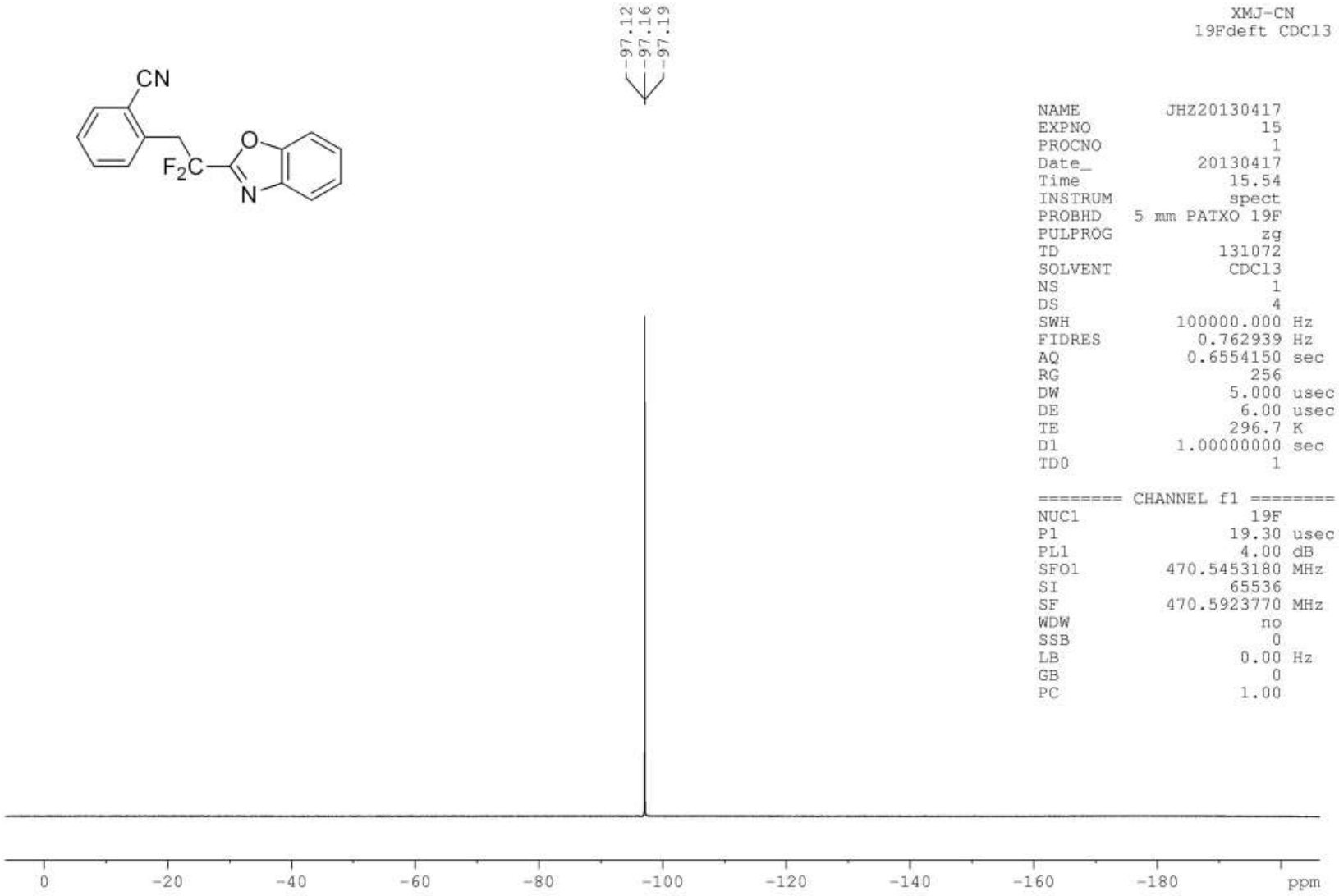
XMJ-COOMe-F
19Fdeft CDCl3

NAME	JHZ20130412
EXPNO	12
PROCNO	1
Date_	20130412
Time	12.58
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg
TD	131072
SOLVENT	CDCl3
NS	2
DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554150 sec
RG	256
DW	5.000 usec
DE	6.00 usec
TE	296.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	19.30 usec
PL1	4.00 dB
SFO1	470.5453180 MHz
SI	65536
SF	470.5923770 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00


166.69
157.73
157.46
157.20
150.55
139.88
135.88
130.78
129.76
129.73
126.94
125.37
121.29
117.32
115.39
113.45
111.40
XMJ-COOMe-C
C13CPD CDC13
52.11
42.30
42.11
41.92
MeOOC
O
F2C
N
NAME JHZ20130412
EXPNO 13
PROCNO 1
Date_ 20130412
Time 13.02
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 65
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 322.5
DW 16.650 usec
DE 6.00 usec
TE 296.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

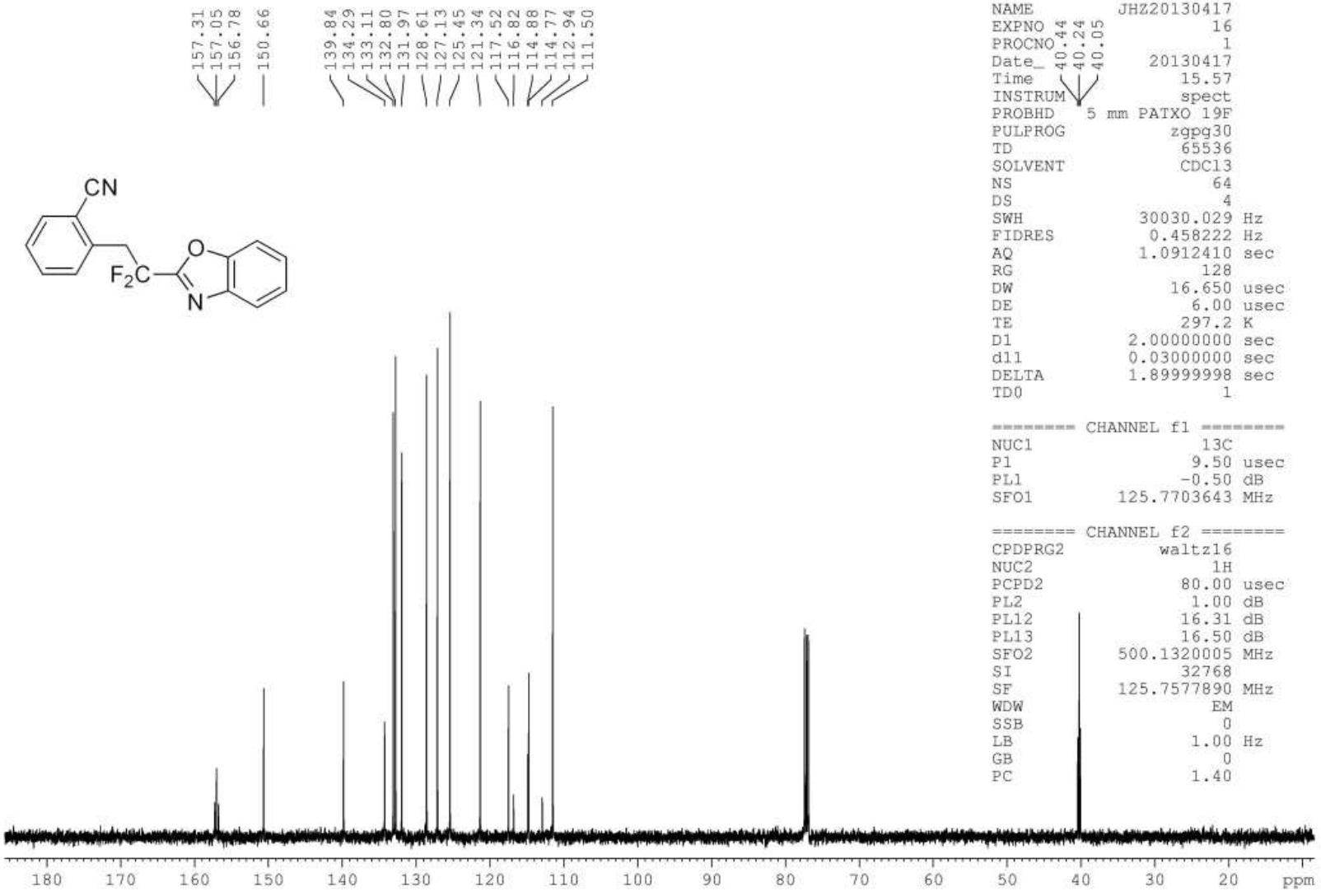
2-(2-(Benzo[d]oxazol-2-yl)-2,2-difluoroethyl)benzonitrile (3aj)





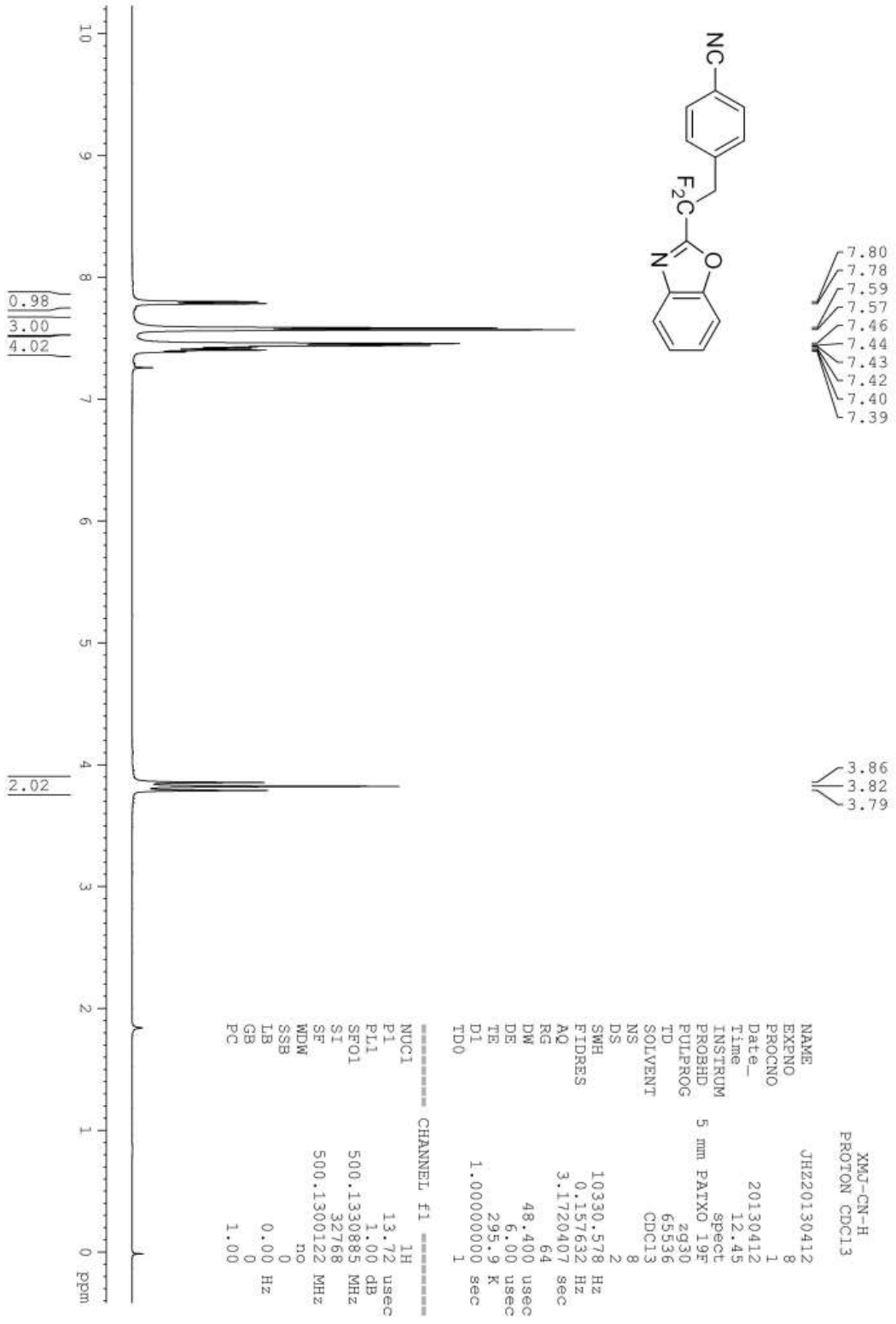
XMJ-CN
19Fdeft CDCl3

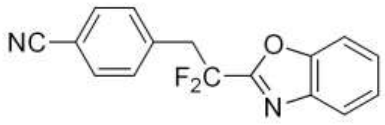
NAME	JHZ20130417	
EXPNO	15	
PROCNO	1	
Date_	20130417	
Time	15.54	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	zg	
TD	131072	
SOLVENT	CDCl3	
NS	1	
DS	4	
SWH	100000.000	Hz
FIDRES	0.762939	Hz
AQ	0.6554150	sec
RG	256	
DW	5.000	usec
DE	6.00	usec
TE	296.7	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	19F	
P1	19.30	usec
PL1	4.00	dB
SFO1	470.5453180	MHz
SI	65536	
SF	470.5923770	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	



NAME	JHZ20130417
EXPNO	16
PROCNO	1
Date_	20130417
Time	15.57
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	64
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912410 sec
RG	128
DW	16.650 usec
DE	6.00 usec
TE	297.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-0.50 dB
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	16.31 dB
PL13	16.50 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

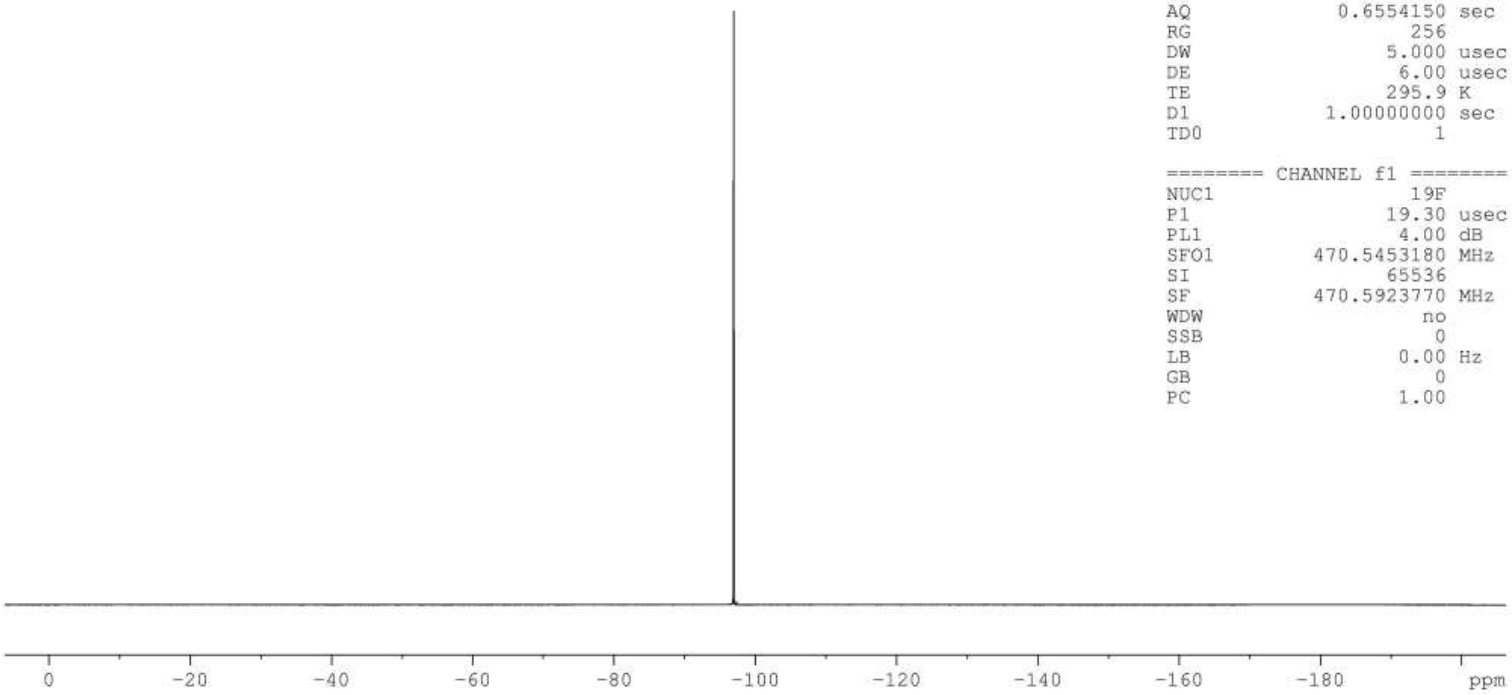
4-(2-(Benzo[d]oxazol-2-yl)-2,2-difluoroethyl)benzonitrile (3ak)





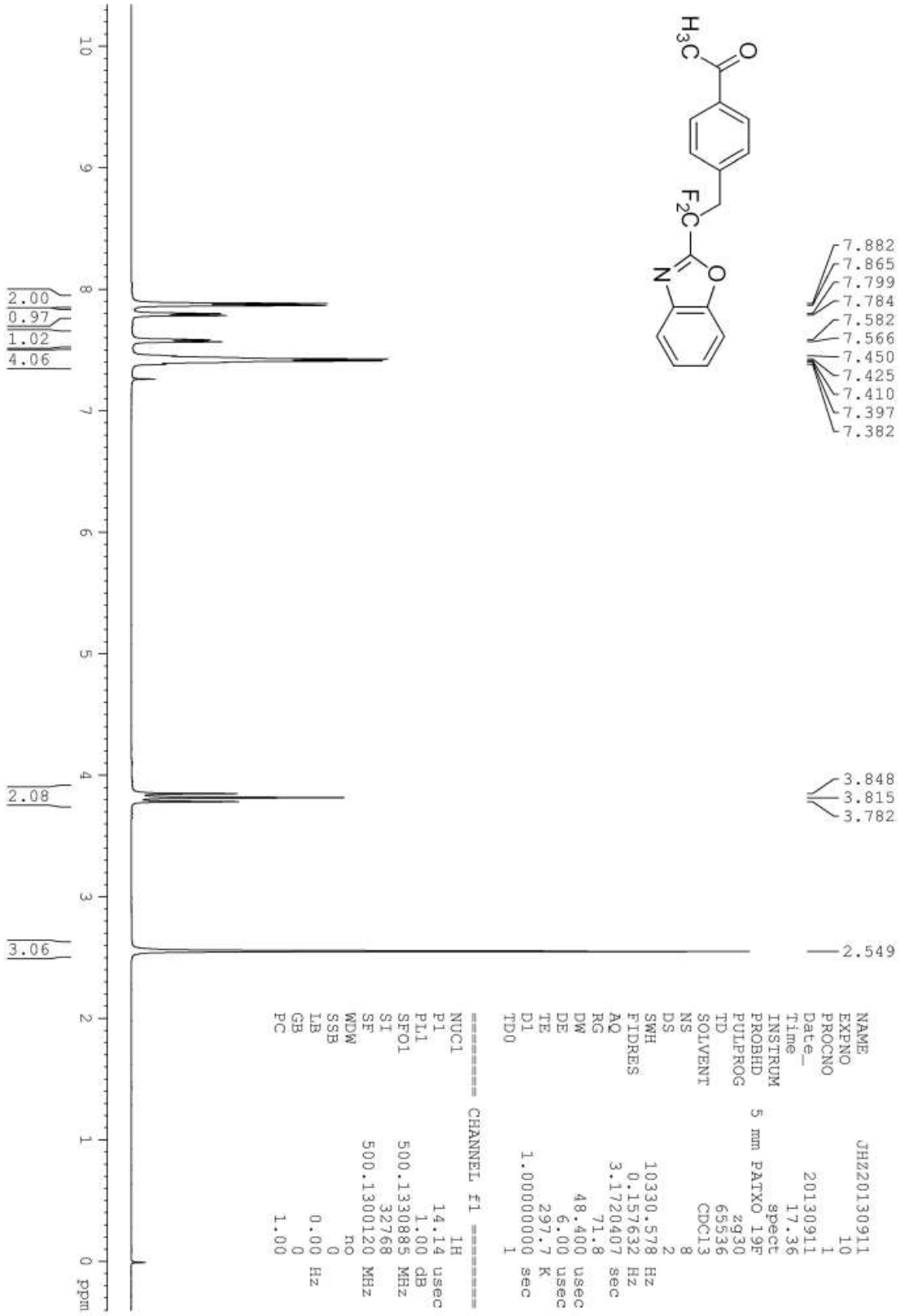
XMJ-CN
19Fdeft CDCl3

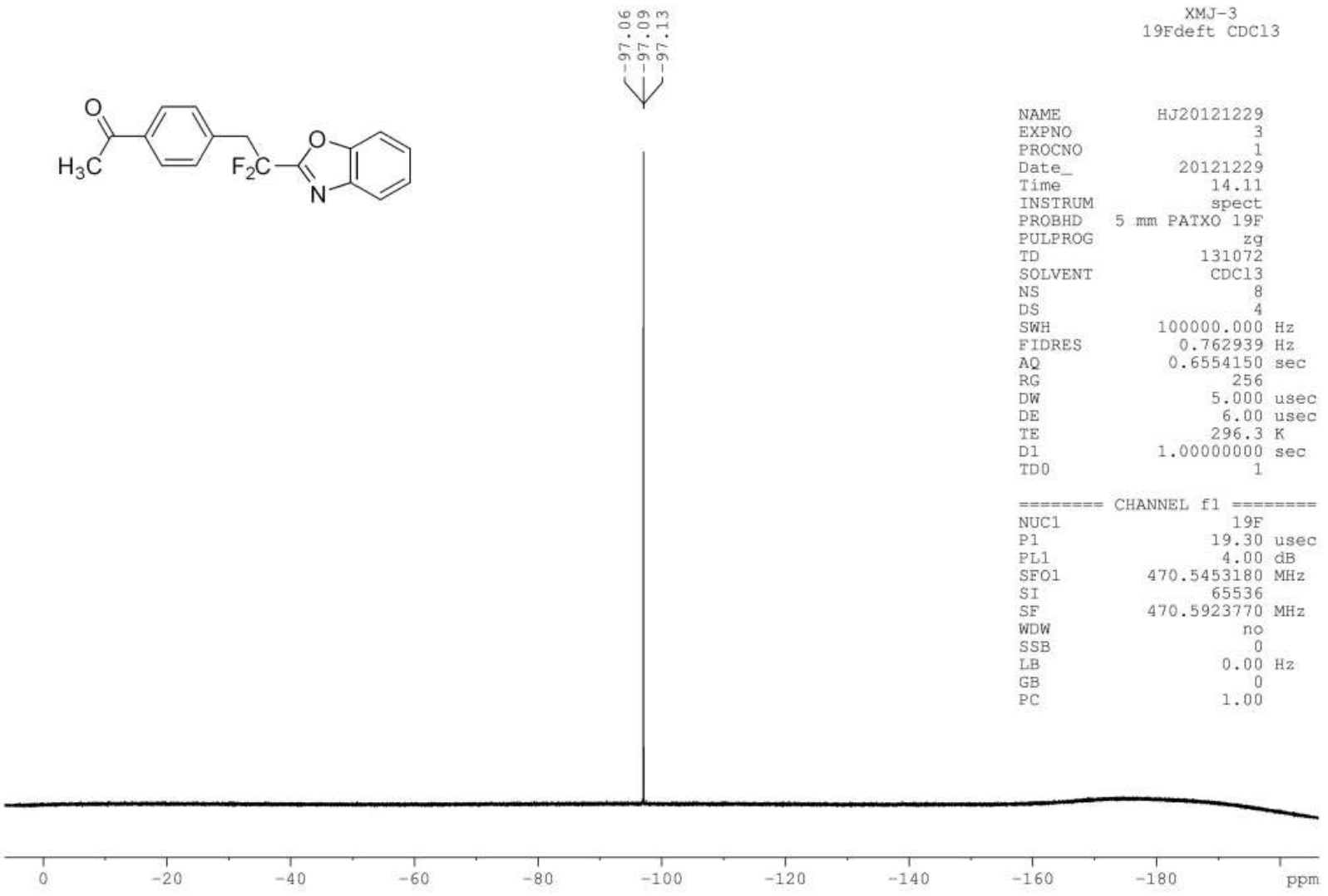
NAME	JHZ20130412
EXPNO	9
PROCNO	1
Date_	20130412
Time	12.46
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg
TD	131072
SOLVENT	CDCl3
NS	2
DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554150 sec
RG	256
DW	5.000 usec
DE	6.00 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	19.30 usec
PL1	4.00 dB
SFO1	470.5453180 MHz
SI	65536
SF	470.5923770 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



NC
F2C
N
O
157.39
157.13
156.86
150.57
139.79
136.19
132.24
131.58
127.13
125.49
121.32
118.50
117.05
115.11
113.18
111.99
111.45
42.24
42.04
41.85
XMJ-CN-C
C13CPD CDC13
NAME JH220130412
EXPNO 10
PROCNO 1
Date_ 20130412
Time 12.50
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 65
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 128
DW 16.650 usec
DE 6.00 usec
TE 296.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.31 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

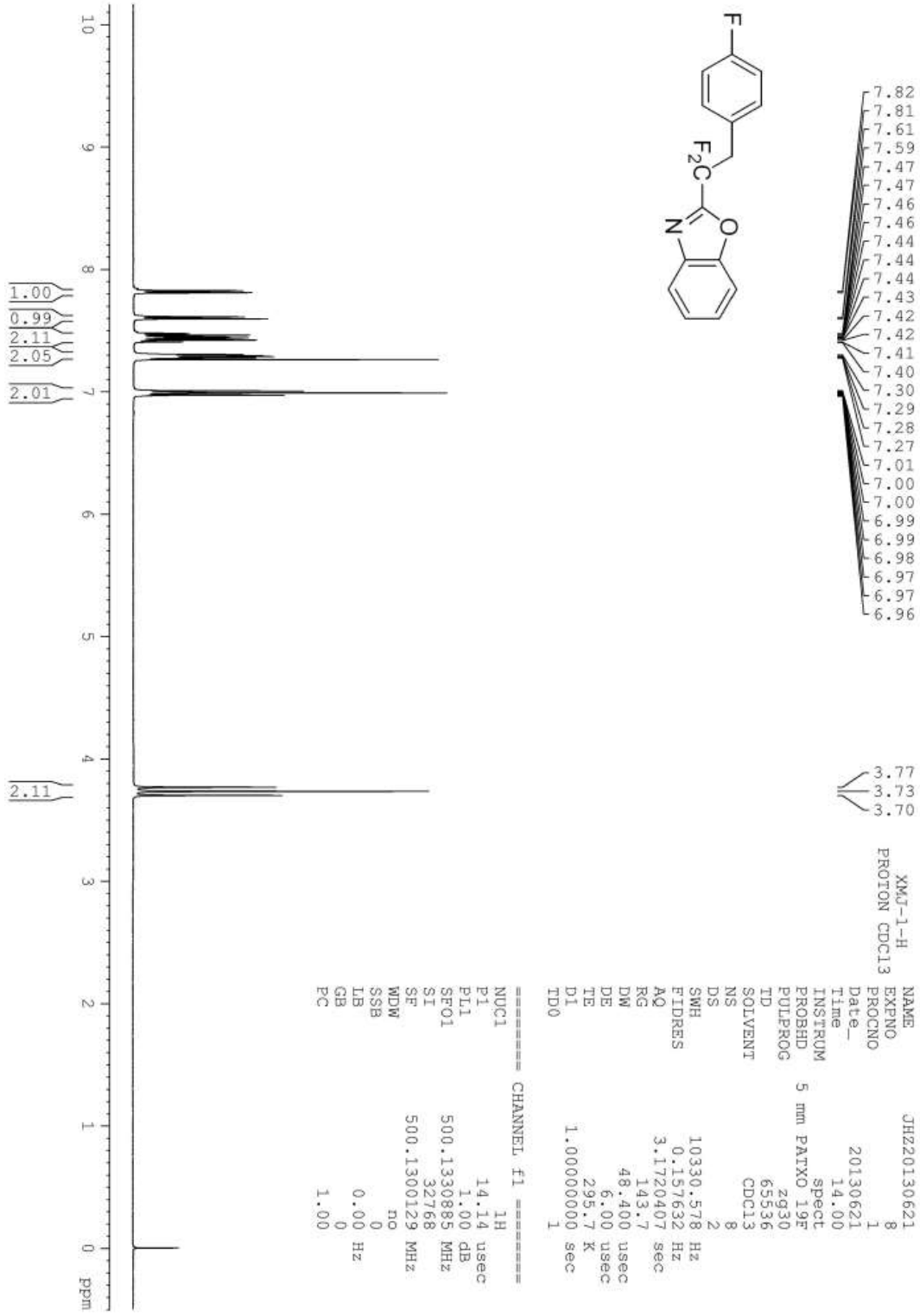
1-(4-(2-(Benzo[d]oxazol-2-yl)-2,2-difluoroethyl)phenyl)ethanone (3al)

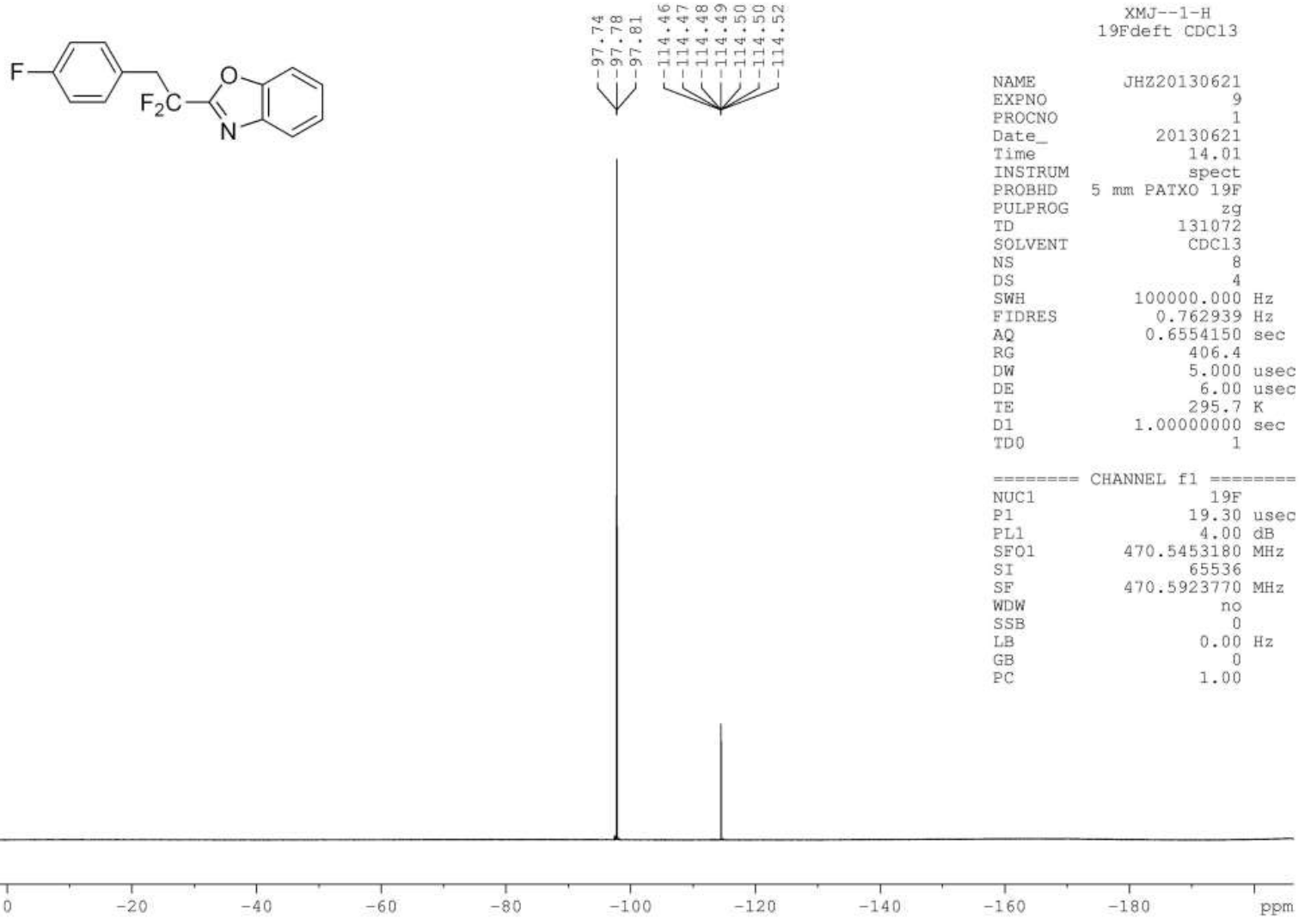



XMJ-3
19Fdeft CDCl3
-97.06
-97.09
-97.13
NAME HJ20121229
EXPNO 3
PROCNO 1
Date_ 20121229
Time 14.11
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 8
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 256
DW 5.000 usec
DE 6.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
O
H3C
F2C
O
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

197.64
157.71
157.44
157.18
150.57
139.87
136.61
136.07
130.99
128.48
126.98
125.40
121.30
117.29
115.35
113.42
111.41
42.26
42.07
41.88
26.59
NAME JHZ20130911
EXPNO 12
PROCNO 1
Date_ 20130911
Time 17.43
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 57
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 322.5
DW 16.650 usec
DE 6.00 usec
TE 298.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

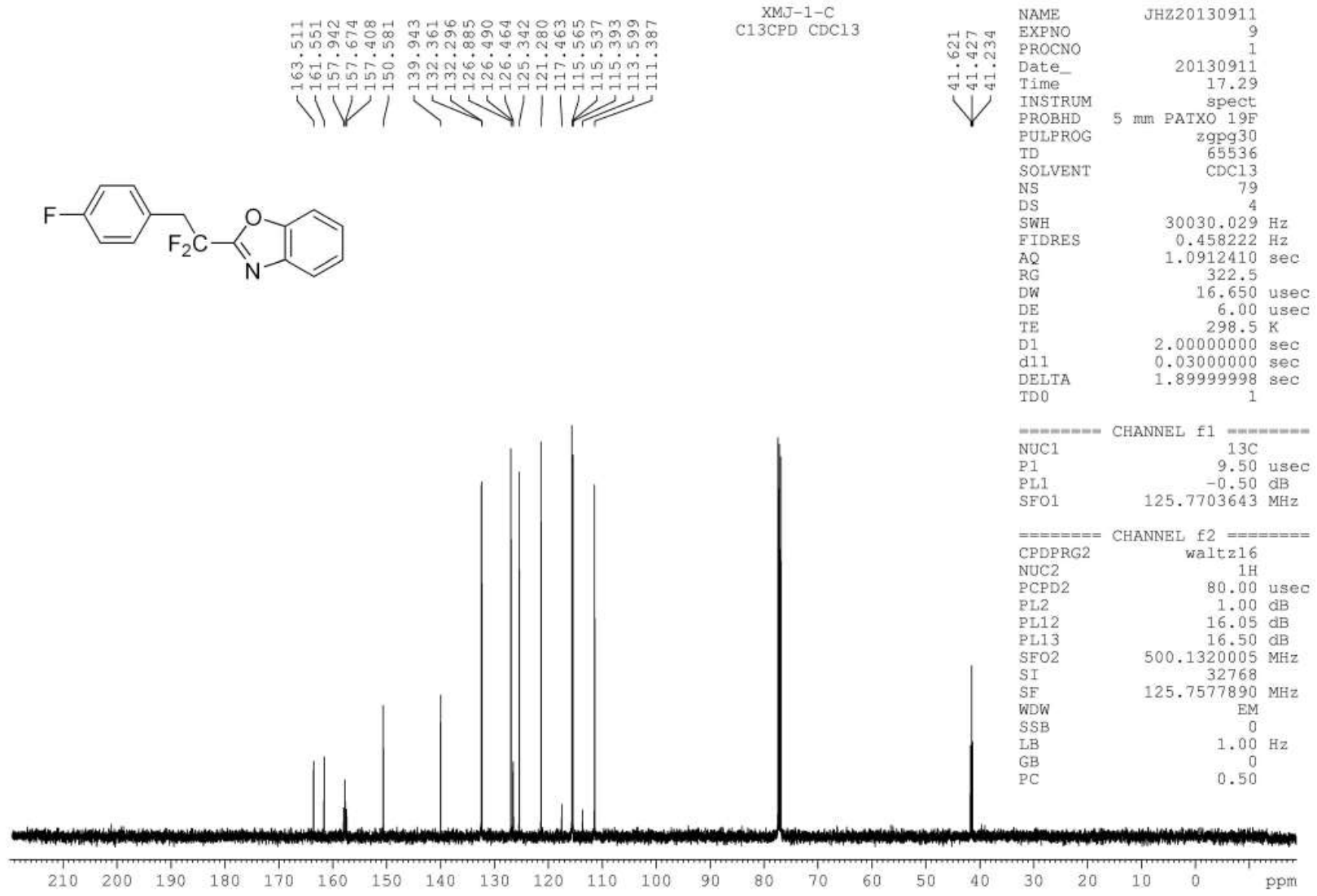
2-(1,1-Difluoro-2-(4-fluorophenyl)ethyl)benzo[d]oxazole (3am)



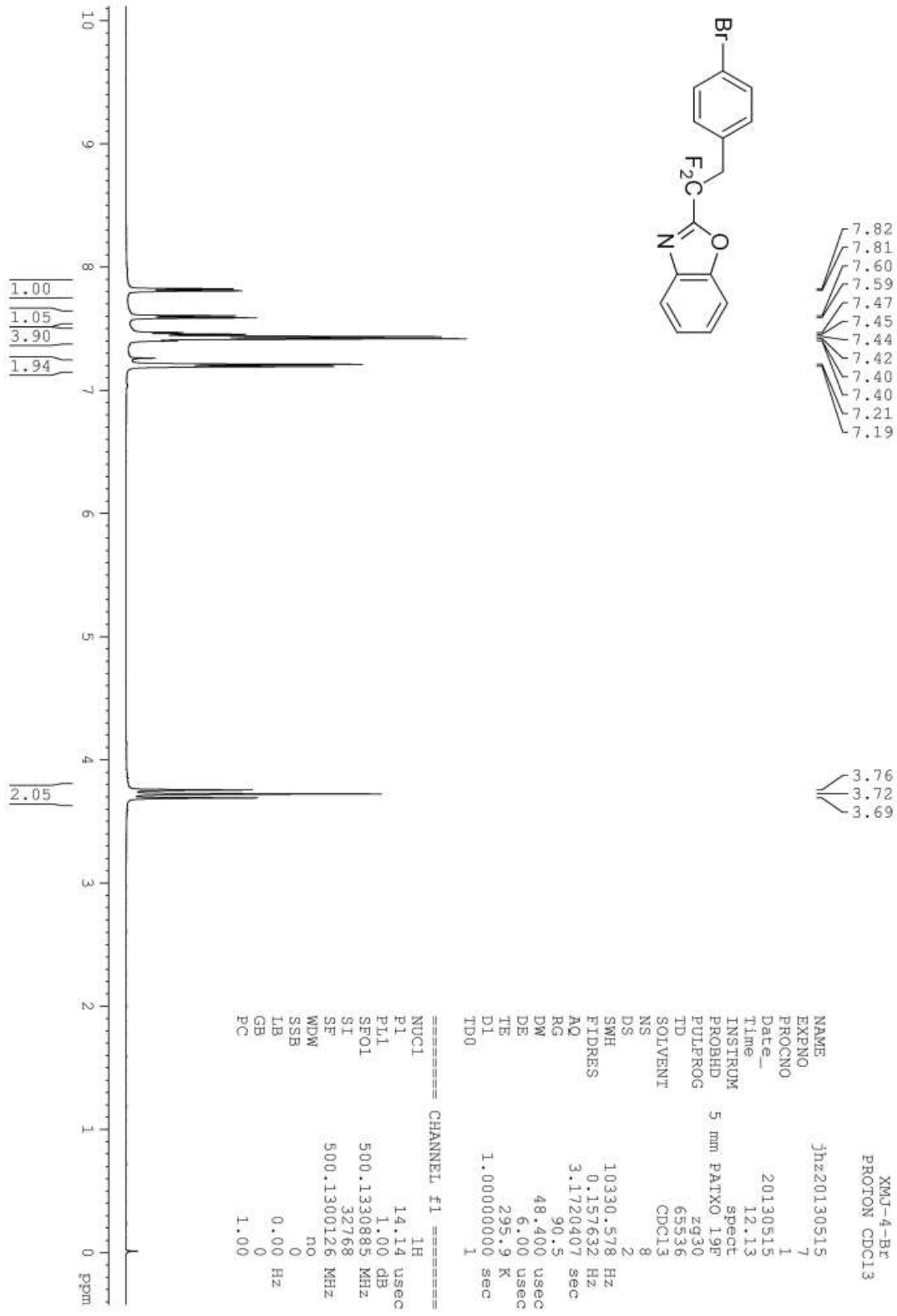


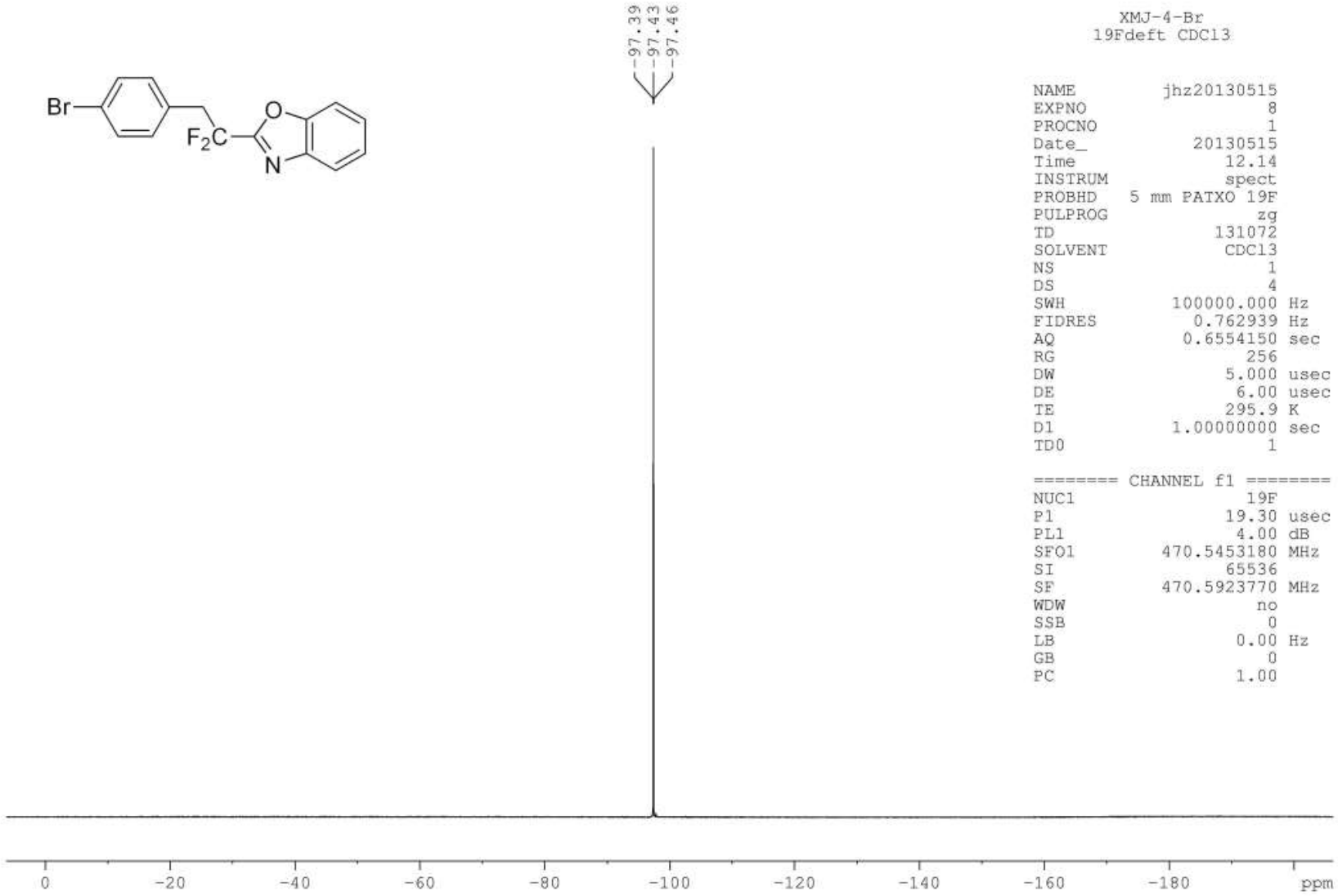
XMJ--1-H
19Fdeft CDCl3

NAME	JHZ20130621
EXPNO	9
PROCNO	1
Date_	20130621
Time	14.01
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg
TD	131072
SOLVENT	CDCl3
NS	8
DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554150 sec
RG	406.4
DW	5.000 usec
DE	6.00 usec
TE	295.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	19.30 usec
PL1	4.00 dB
SFO1	470.5453180 MHz
SI	65536
SF	470.5923770 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00


163.511
161.551
157.942
157.674
157.408
150.581
139.943
132.361
132.296
126.885
126.490
126.464
125.342
121.280
117.463
115.565
115.537
115.393
113.599
111.387
41.621
41.427
41.234
XMJ-1-C
C13CPD CDCl3
F
F2C
O
N
NAME JHZ20130911
EXPNO 9
PROCNO 1
Date_ 20130911
Time 17.29
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 79
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 322.5
DW 16.650 usec
DE 6.00 usec
TE 298.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

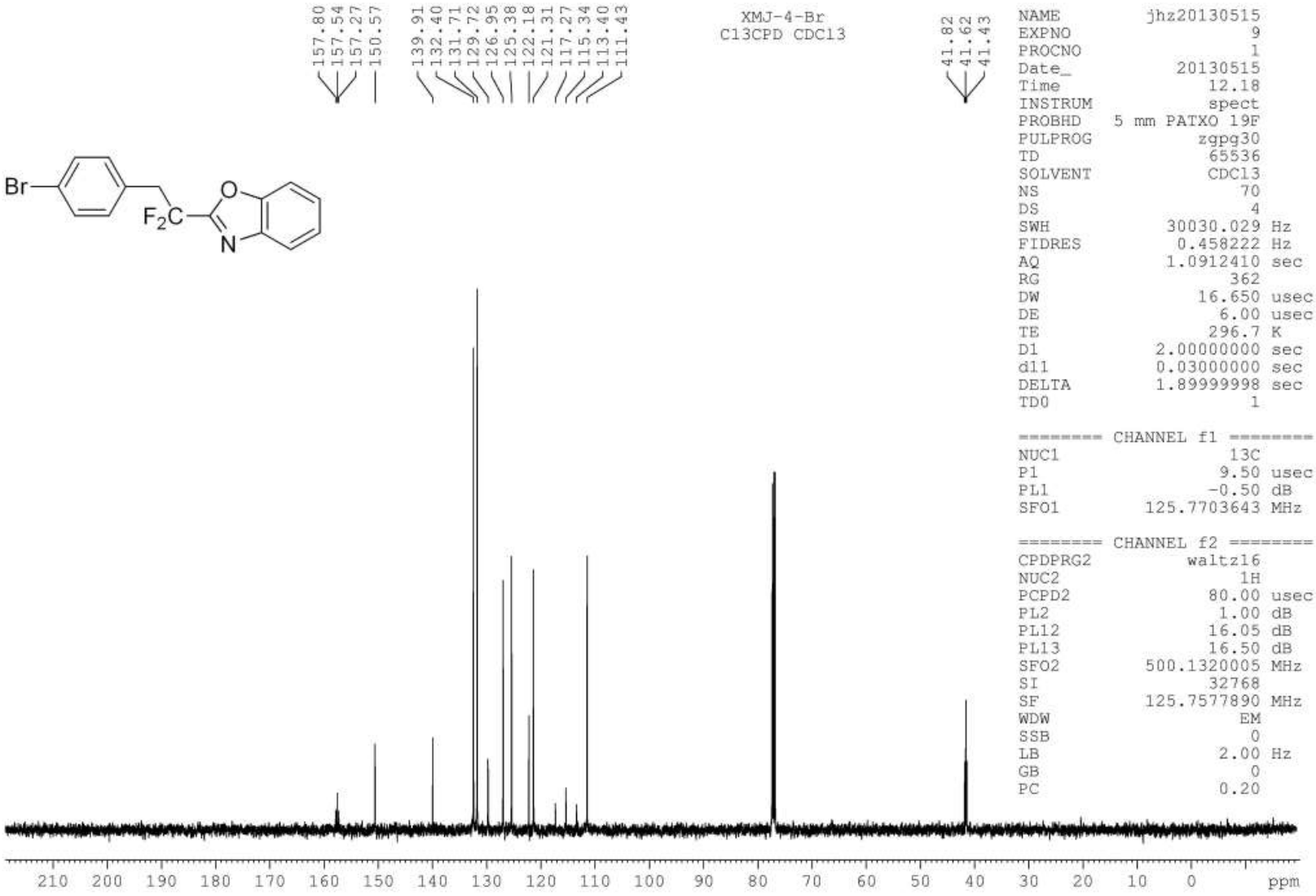
2-(2-(4-Bromophenyl)-1,1-difluoroethyl)benzo[d]oxazole (3an)



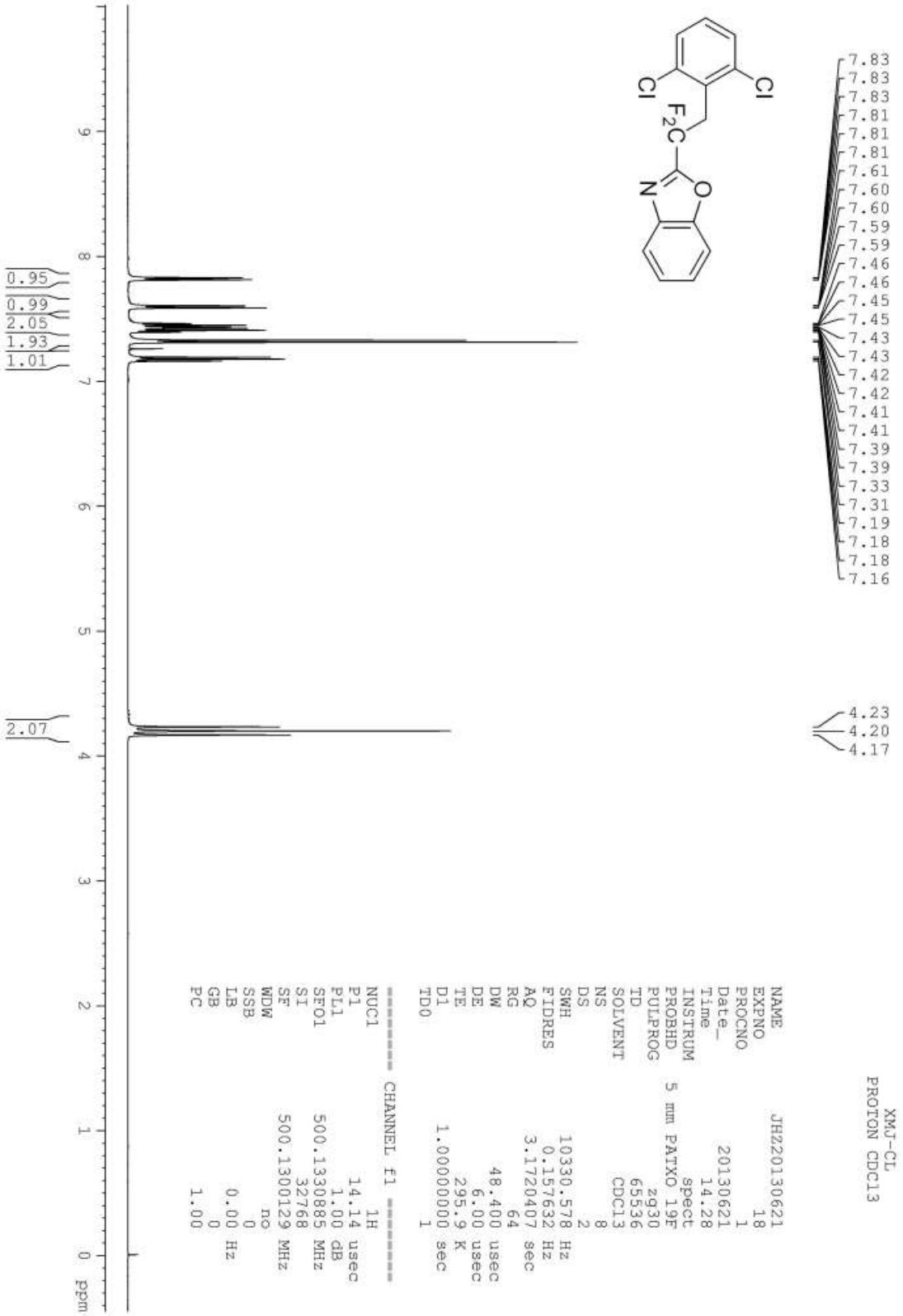


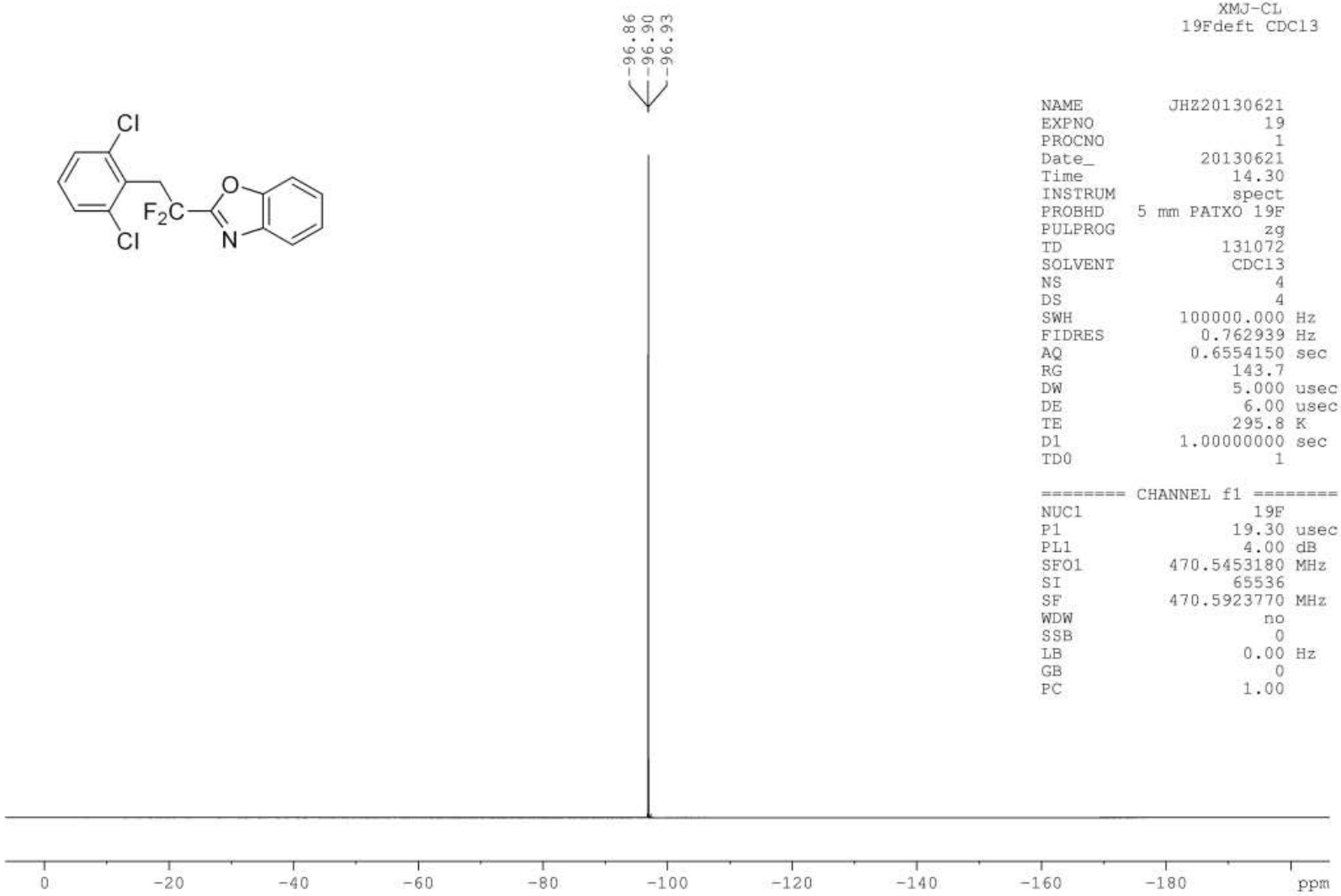
XMJ-4-Br
19Fdeft CDCl3

NAME	jhz20130515	
EXPNO	8	
PROCNO	1	
Date_	20130515	
Time	12.14	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	zg	
TD	131072	
SOLVENT	CDCl3	
NS	1	
DS	4	
SWH	100000.000	Hz
FIDRES	0.762939	Hz
AQ	0.6554150	sec
RG	256	
DW	5.000	usec
DE	6.00	usec
TE	295.9	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	19F	
P1	19.30	usec
PL1	4.00	dB
SFO1	470.5453180	MHz
SI	65536	
SF	470.5923770	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	


157.80
157.54
157.27
150.57
139.91
132.40
131.71
129.72
126.95
125.38
122.18
121.31
117.27
115.34
113.40
111.43
XMJ-4-Br
C13CPD CDC13
41.82
41.62
41.43
Br
O
F2C
N
NAME jhz20130515
EXPNO 9
PROCNO 1
Date_ 20130515
Time 12.18
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 70
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 362
DW 16.650 usec
DE 6.00 usec
TE 296.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2-(2-(2,6-Dichlorophenyl)-1,1-difluoroethyl)benzo[d]oxazole (3ao)



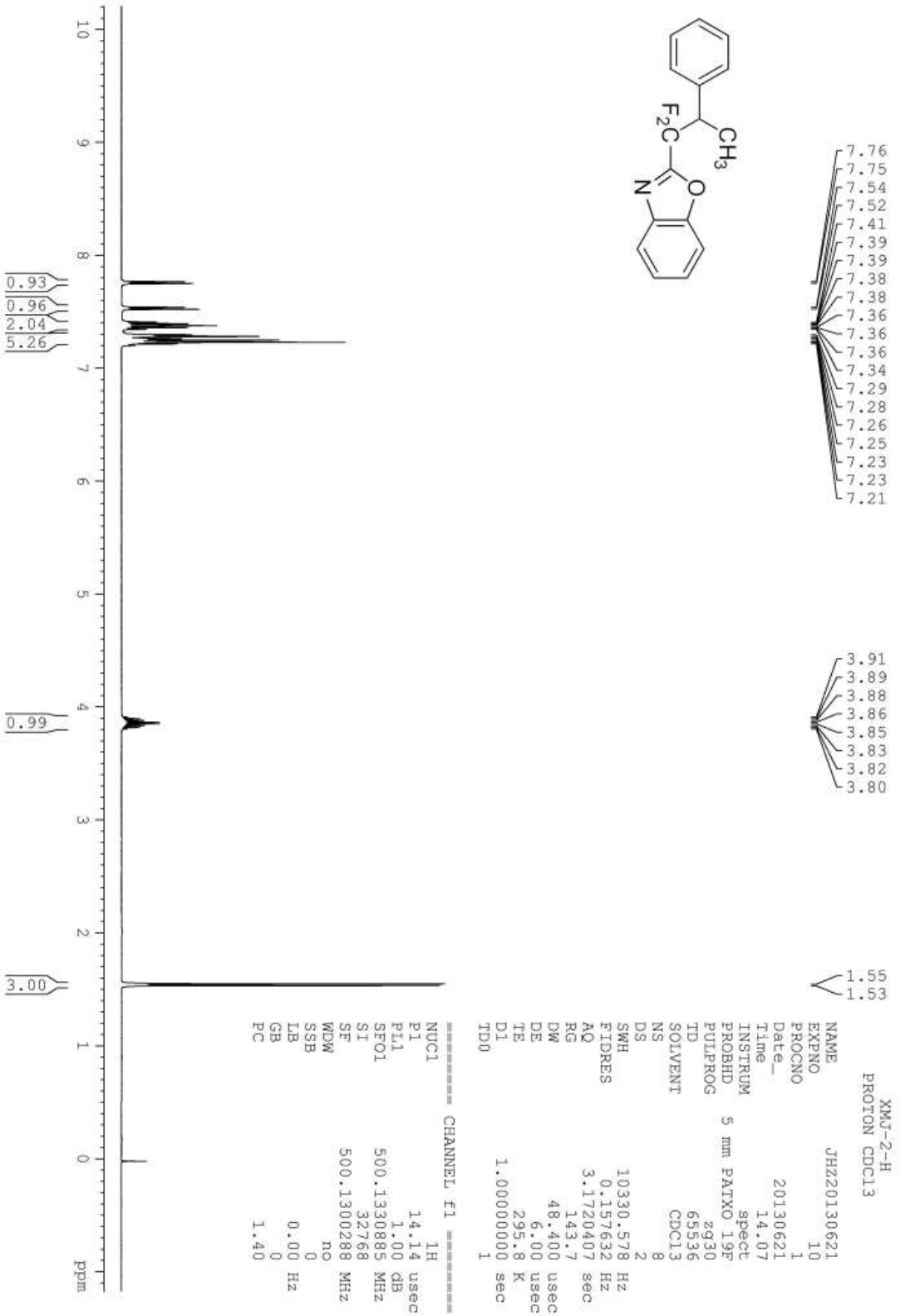


XMJ-CL
19Fdeft CDCl3

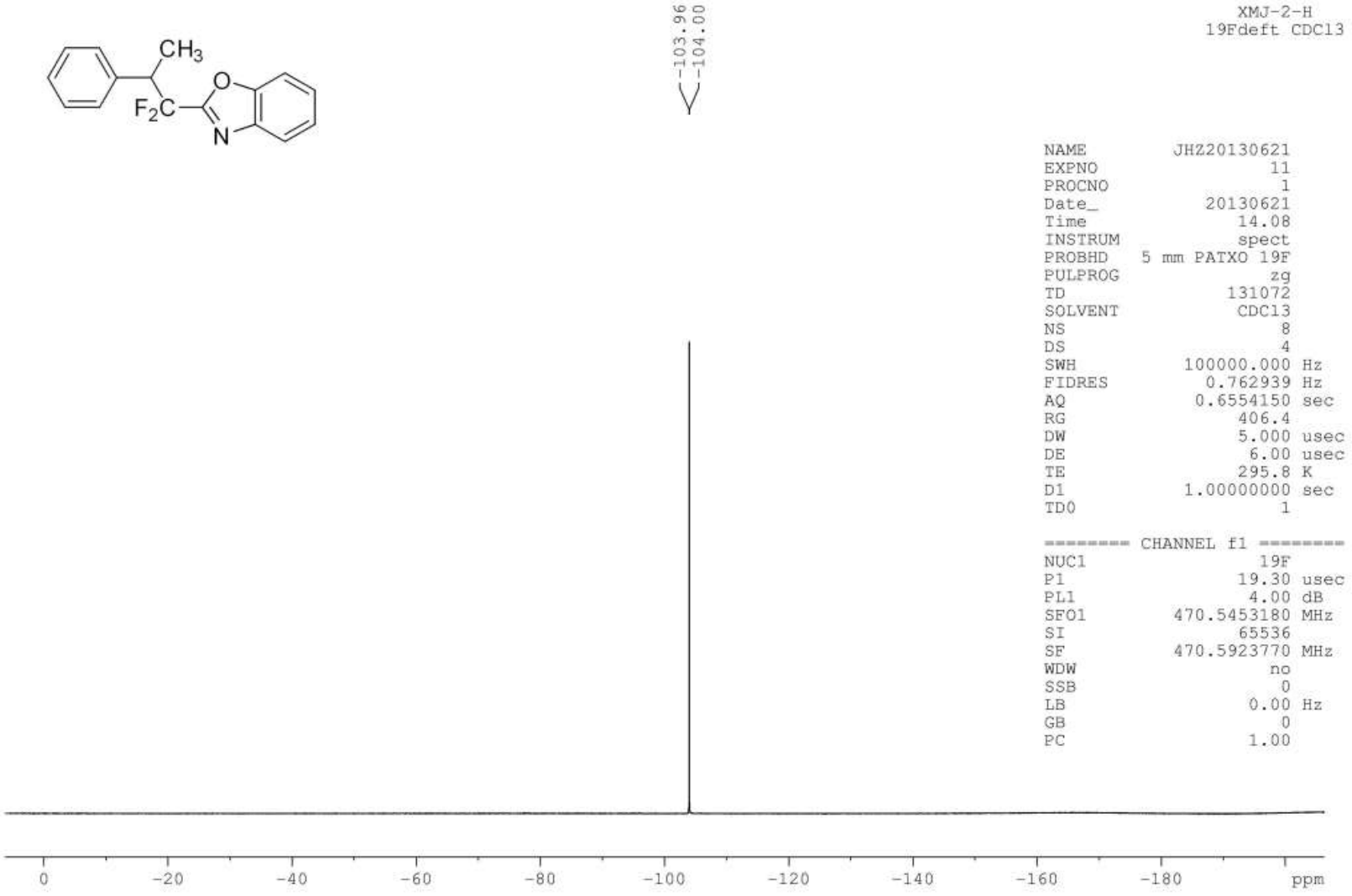
NAME	JHZ20130621
EXPNO	19
PROCNO	1
Date_	20130621
Time	14.30
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg
TD	131072
SOLVENT	CDCl3
NS	4
DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554150 sec
RG	143.7
DW	5.000 usec
DE	6.00 usec
TE	295.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	19.30 usec
PL1	4.00 dB
SFO1	470.5453180 MHz
SI	65536
SF	470.5923770 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

157.93
157.66
157.40
150.72
140.03
137.37
129.76
128.48
127.91
126.94
125.35
121.31
117.31
115.35
113.40
111.41
37.38
37.18
36.99
XMJ-CL
C13CPD CDC13
NAME JHZ20130621
EXPNO 20
PROCNO 1
Date_ 20130621
Time 14.33
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 33
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 406.4
DW 16.650 use
DE 6.00 use
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 use
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2-(1,1-Difluoro-2-phenylpropyl)benzo[d]oxazole (3ap)

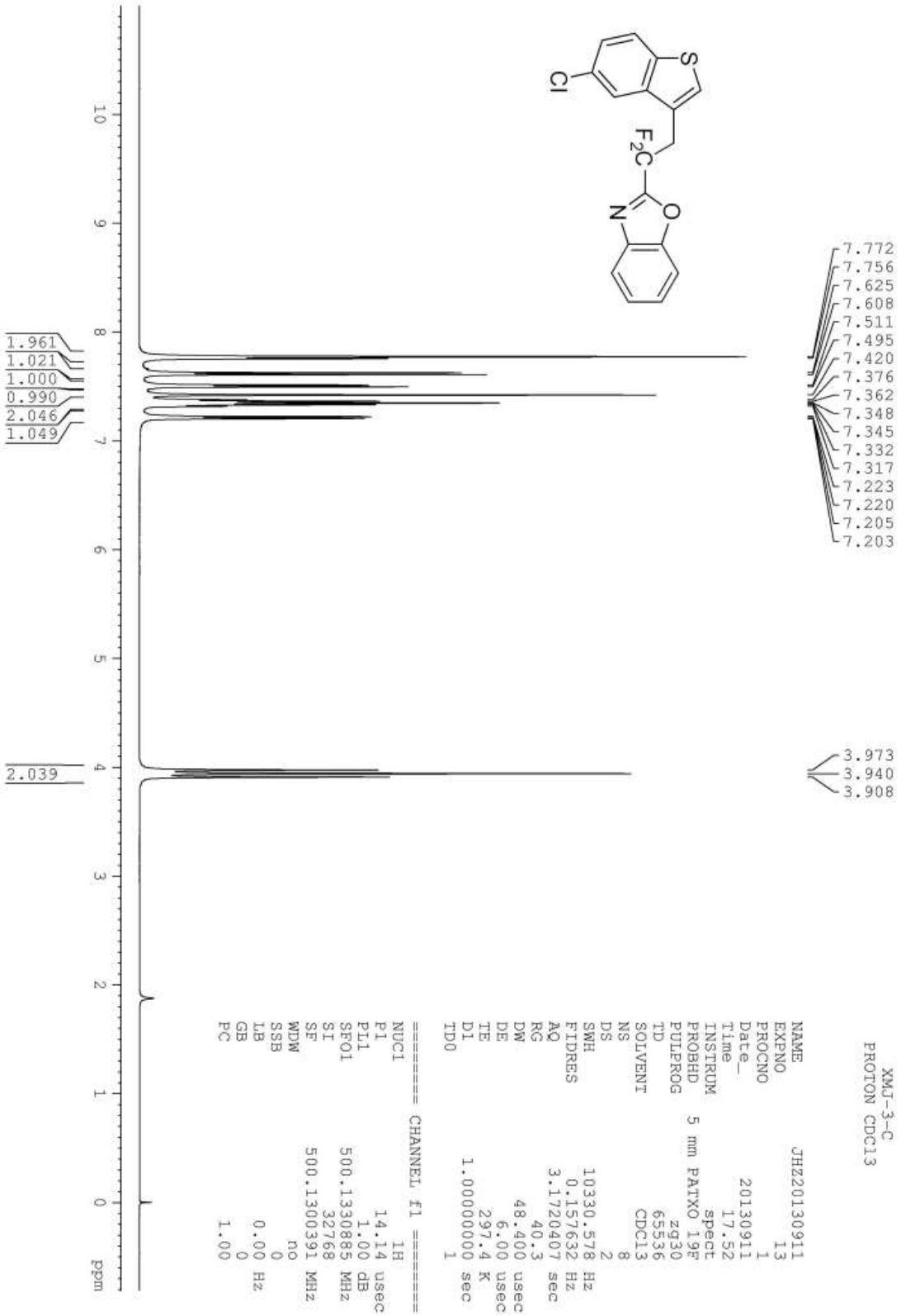


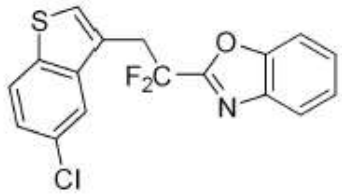
CH3
O
F2C
N


-103.96
-104.00
XMJ-2-H
19Fdeft CDCl3
NAME JHZ20130621
EXPNO 11
PROCNO 1
Date_ 20130621
Time 14.08
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 8
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 406.4
DW 5.000 usec
DE 6.00 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

158.28
158.01
157.74
150.42
140.04
136.98
128.99
128.51
127.88
126.62
125.21
121.19
119.39
117.42
115.46
111.27
46.10
45.92
45.73
14.49
14.46
14.43
XMJ-20-1
C13CPD CDC13
NAME JHZ20130618
EXPNO 15
PROCNO 1
Date_ 20130618
Time 14.16
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 36
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.091410 sec
RG 128
DW 16.650 use
DE 6.00 use
TE 296.5 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 use
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

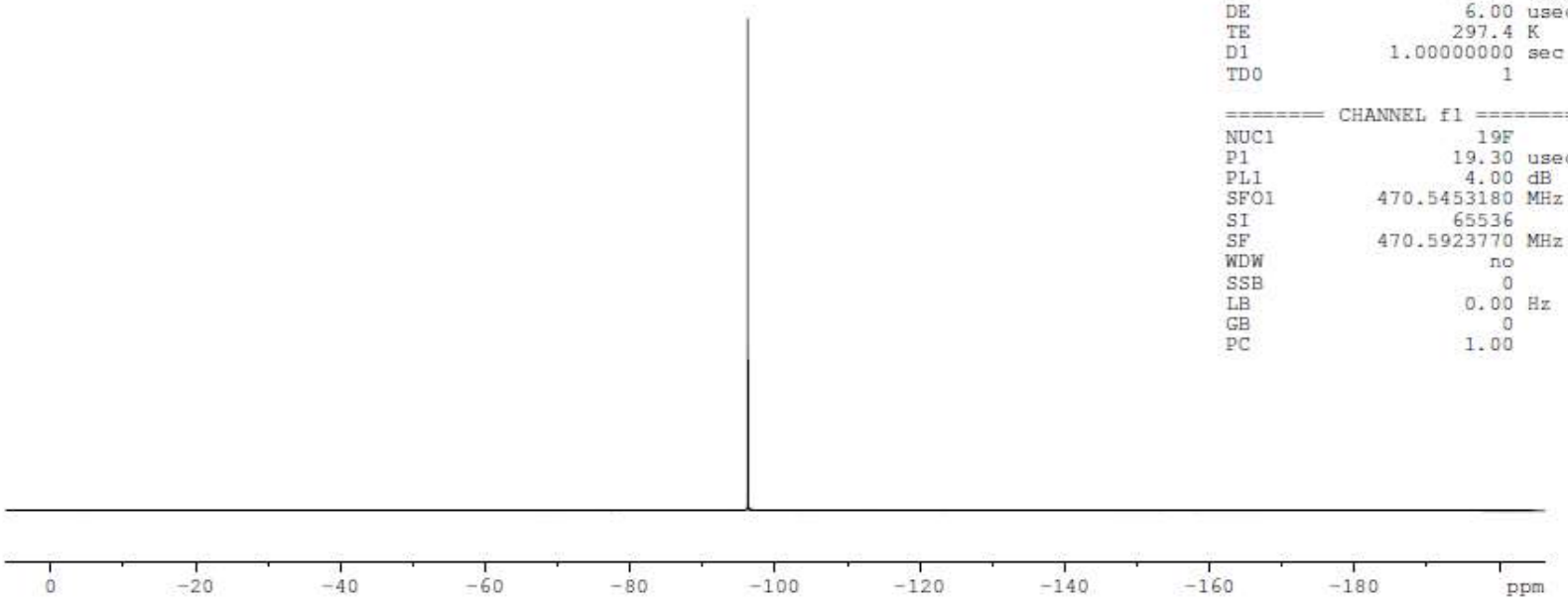
2-(2-(5-Chlorobenzo[b]thiophen-3-yl)-1,1-difluoroethyl)benzo[d]oxazole (3aq)





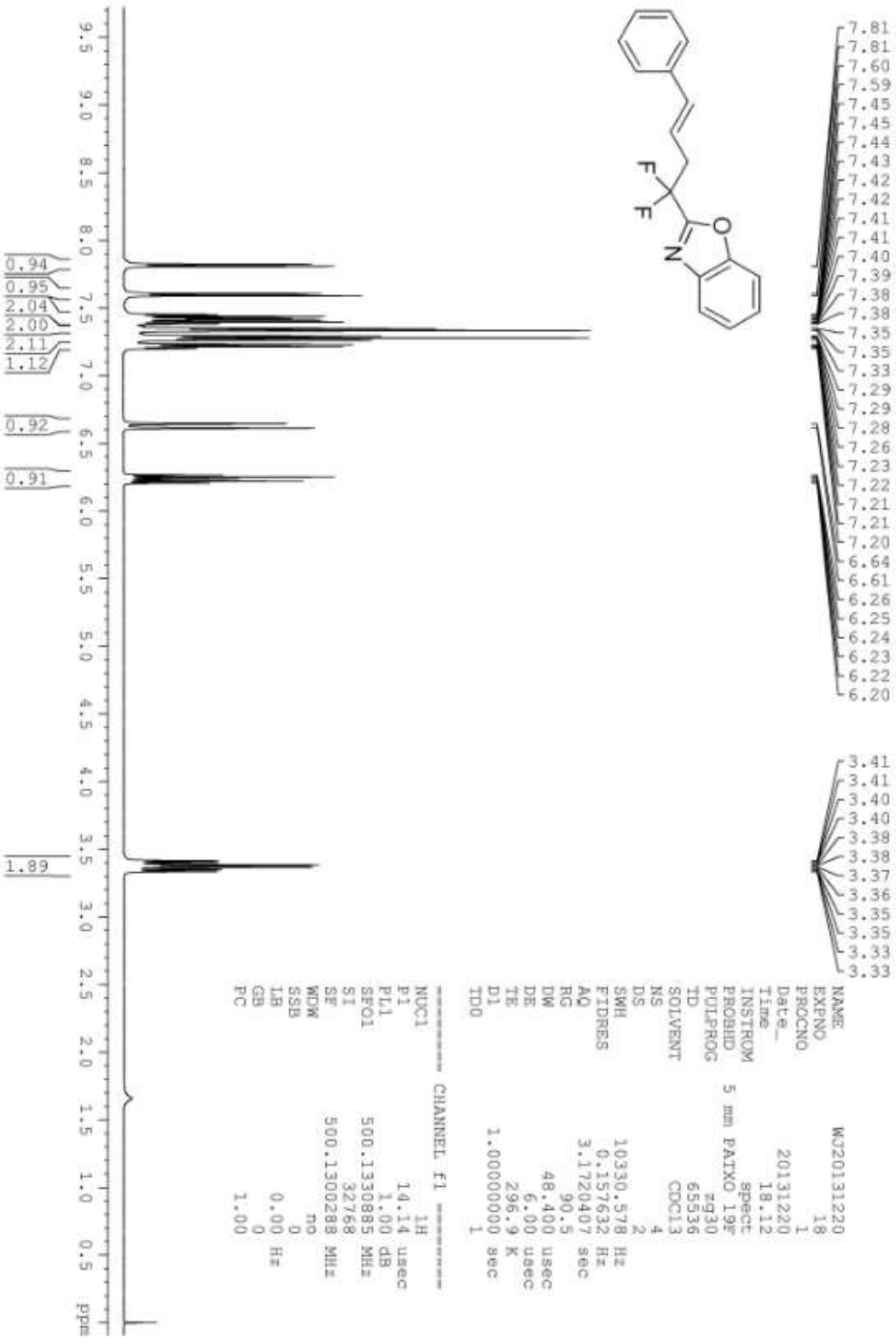
XMJ-3-C
19Fdeft CDC13

NAME	JHZ20130911	
EXPNO	14	
PROCNO	1	
Date_	20130911	
Time	17.54	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	zg	
TD	131072	
SOLVENT	CDC13	
NS	2	
DS	4	
SWH	100000.000	Hz
FIDRES	0.762939	Hz
AQ	0.6554150	sec
RG	128	
DW	5.000	use
DE	6.00	use
TE	297.4	K
D1	1.00000000	sec
TD0	1	
=======	CHANNEL f1 =======	
NUC1	19F	
P1	19.30	use
PL1	4.00	dB
SFO1	470.5453180	MHz
SI	65536	
SF	470.5923770	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	



157.730
157.463
157.198
150.605
140.234
139.913
138.143
130.862
129.021
127.013
125.418
124.930
124.842
124.814
124.787
123.704
121.653
121.295
117.408
115.471
113.534
111.402
35.119
34.916
34.715
XMJ-3-C
C13CPD CDCl3
NAME JHZ20130911
EXPNO 15
PROCNO 1
Date_ 20130911
Time_ 17.57
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 41
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 322.5
DW 16.650 use
DE 6.00 use
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 use
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
S
Cl
F2C
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

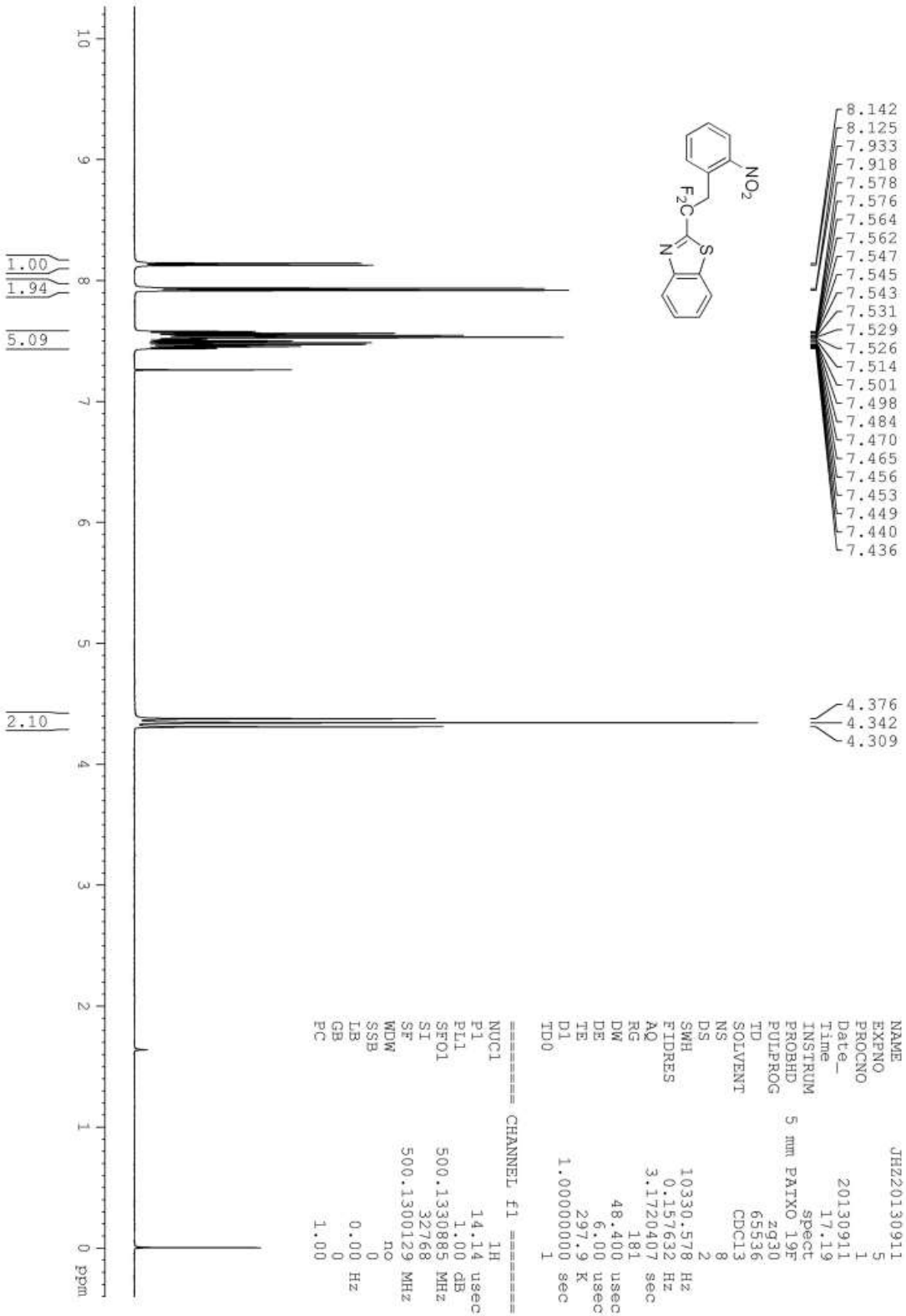
(E)-2-(1,1-Difluoro-4-phenylbut-3-en-1-yl)benzo[d]oxazole (3ar)

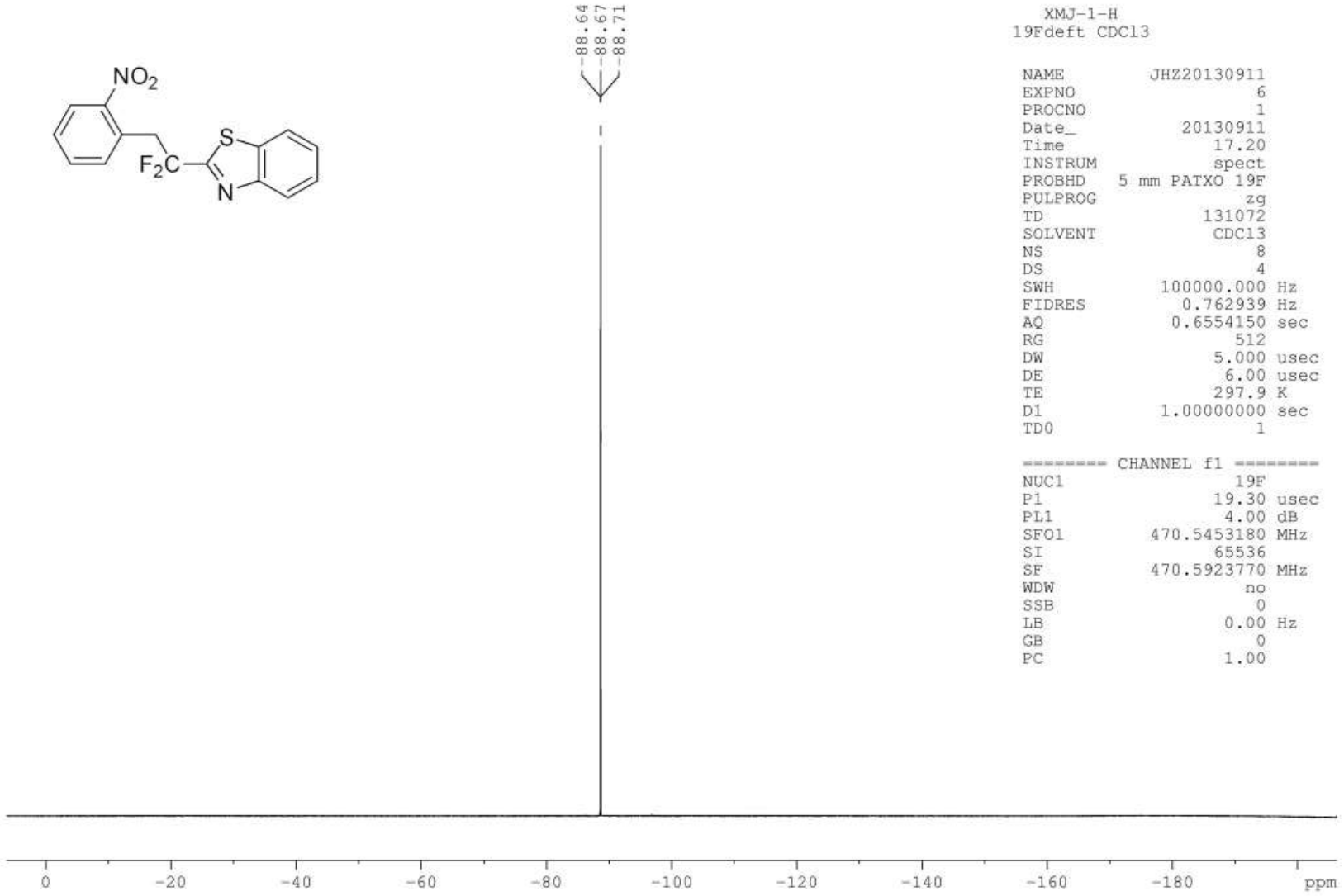


-97.39
-97.42
-97.46
F
F
O
N
NAME WJ20131220
EXPNO 19
PROCNO 1
Date_ 20131220
Time 18.12
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 4
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 362
DW 5.000 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

158.11
157.84
157.57
150.66
140.02
136.70
136.50
128.58
127.94
126.88
126.47
125.32
121.33
118.18
118.15
118.11
117.74
115.81
113.88
111.44
39.98
39.78
39.59
F
F
O
N
NAME WU20140108
EXPNO 11
PROCNO 1
Date_ 20140108
Time 17.35
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 96
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 128
DW 16.650 usec
DE 6.00 usec
TE 297.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

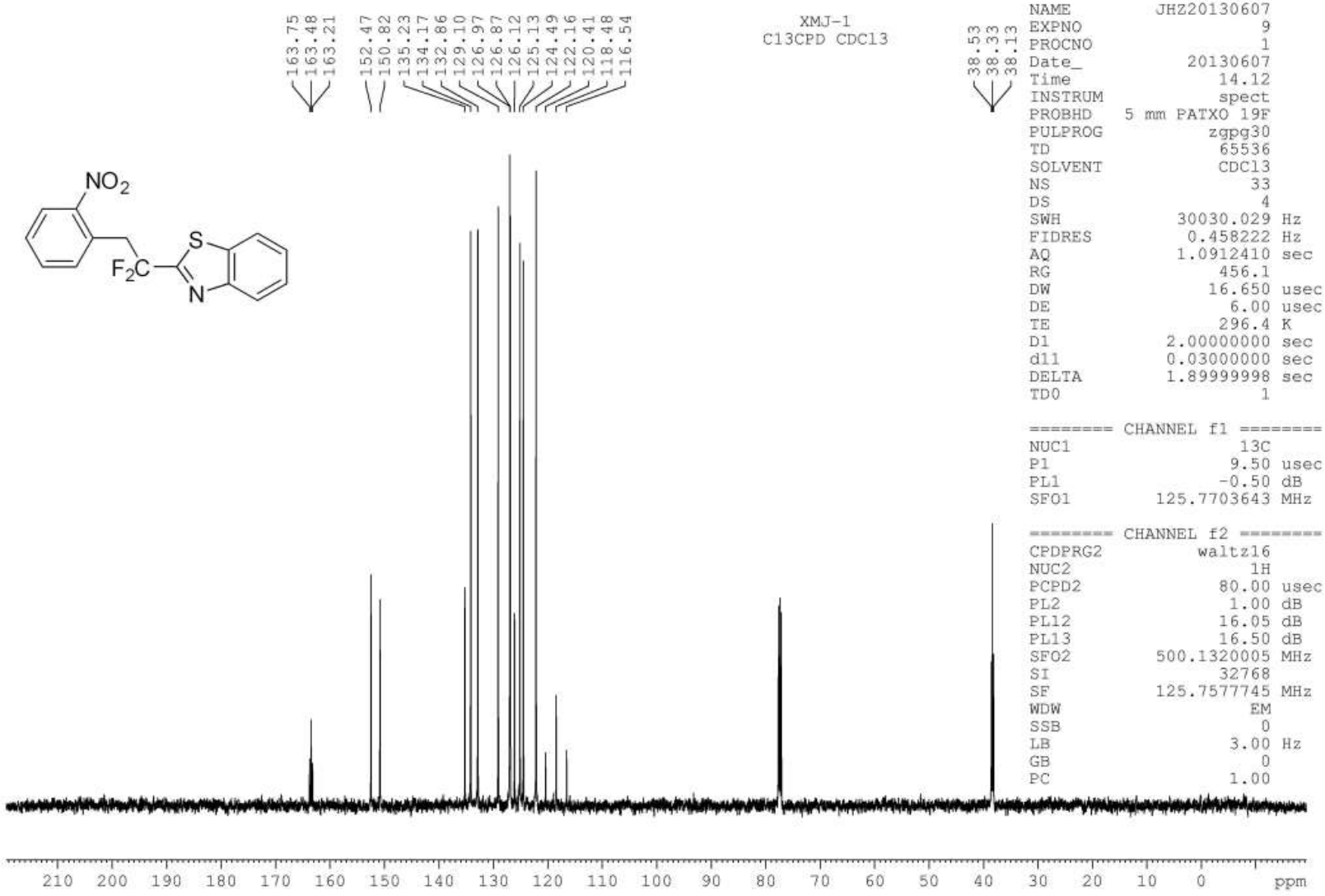
2-(1,1-Difluoro-2-(2-nitrophenyl)ethyl)benzo[d]thiazole (3bd)



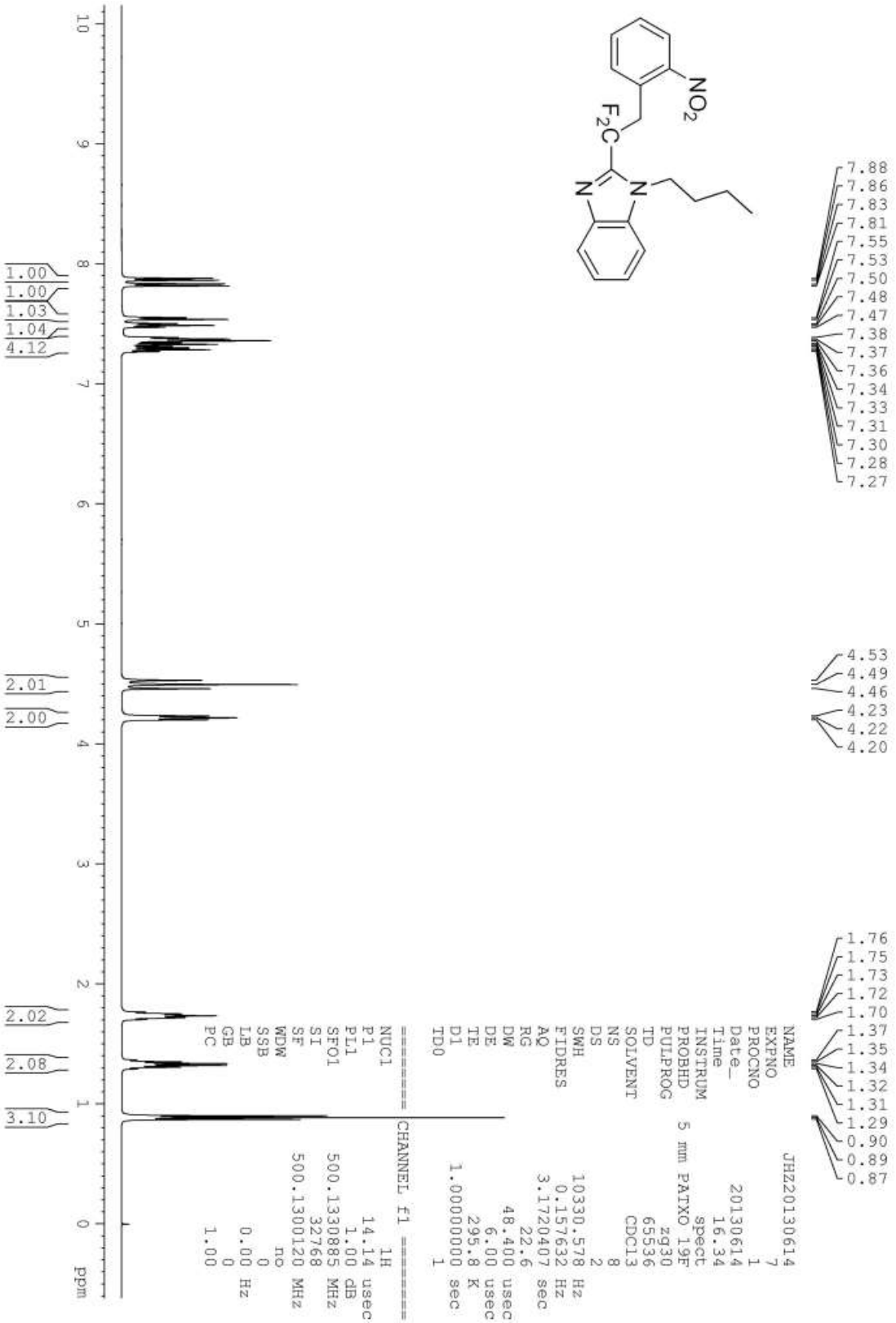


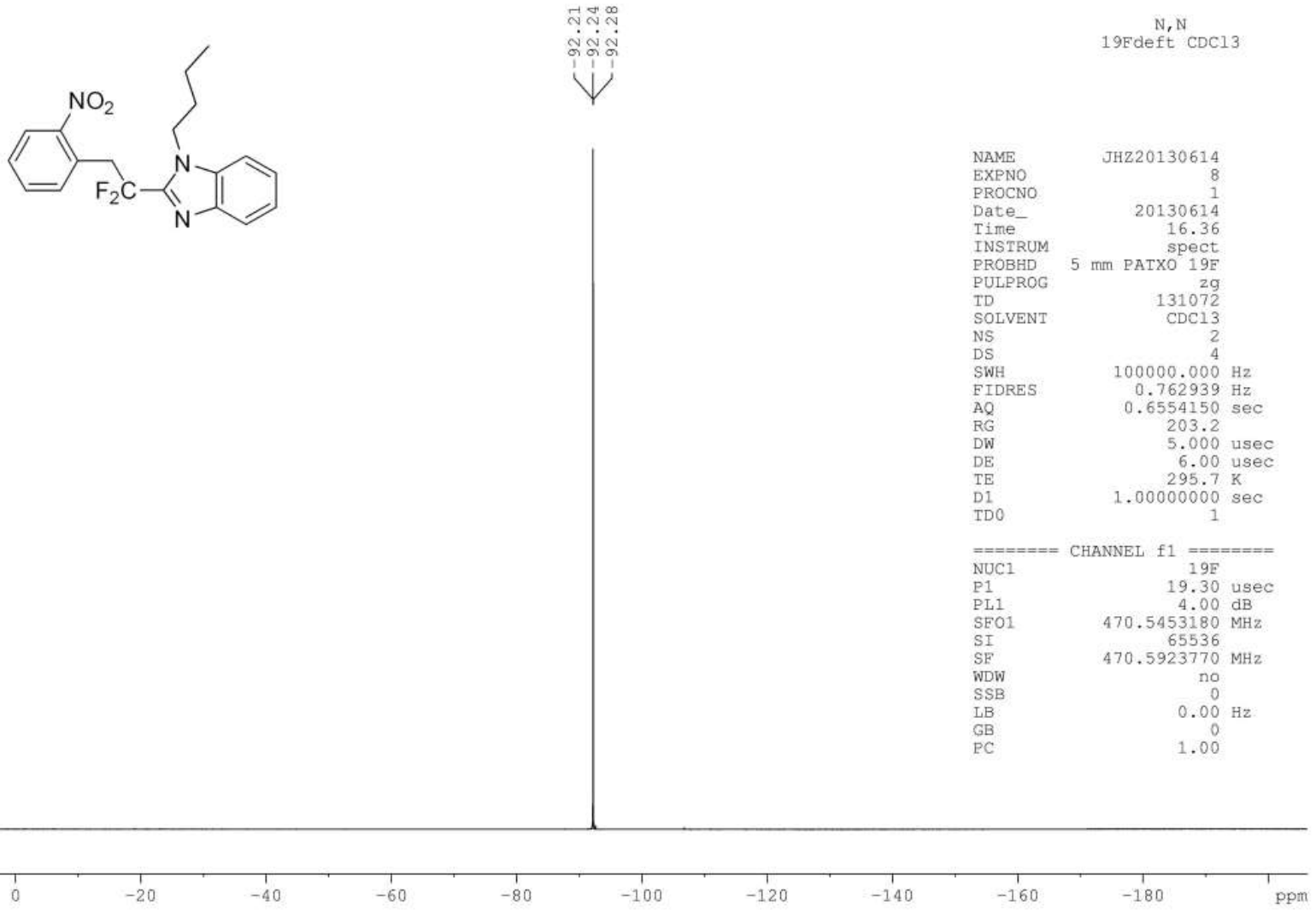
XMJ-1-H
19Fdeft CDCl3

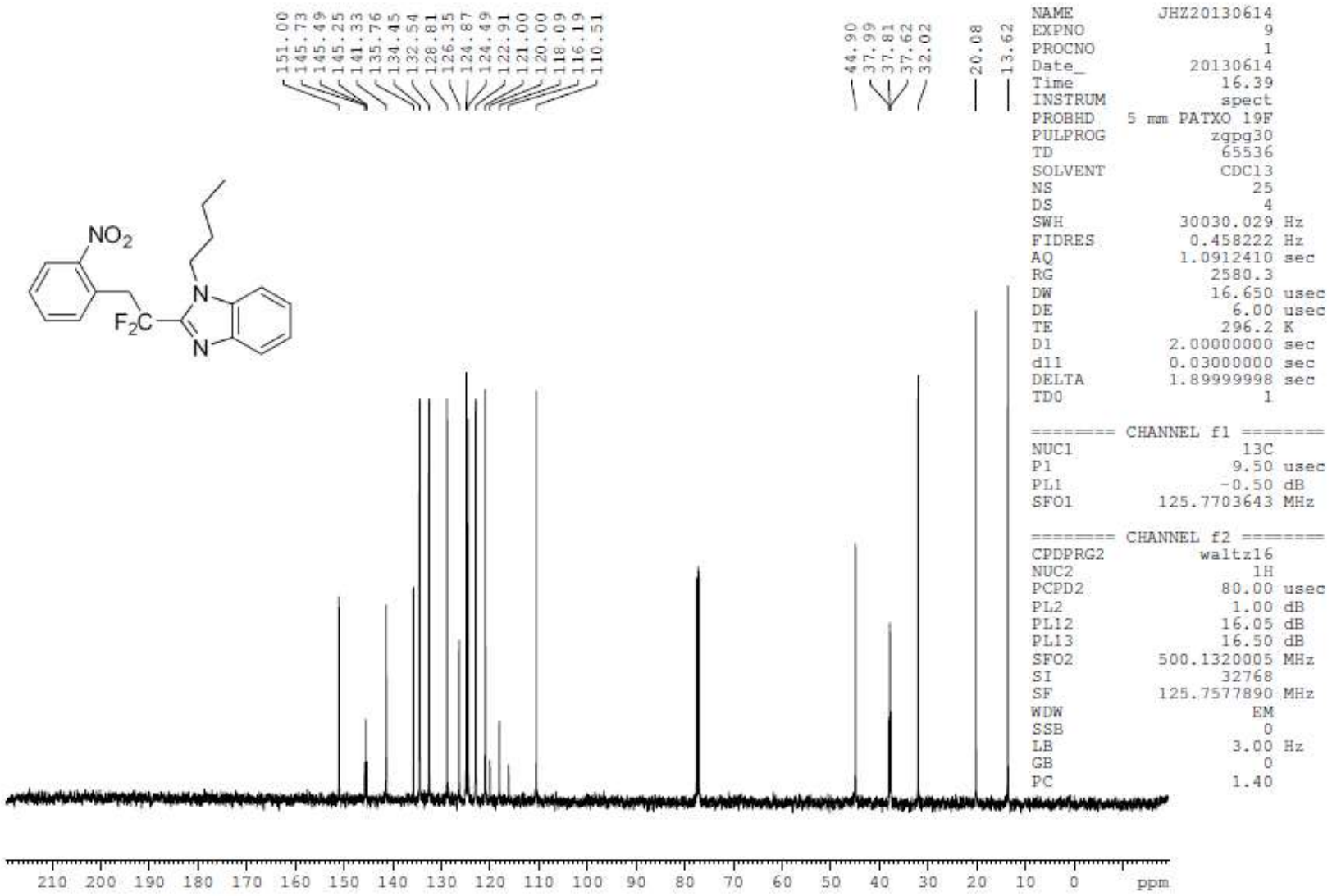
NAME	JHZ20130911
EXPNO	6
PROCNO	1
Date_	20130911
Time	17.20
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg
TD	131072
SOLVENT	CDCl3
NS	8
DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554150 sec
RG	512
DW	5.000 usec
DE	6.00 usec
TE	297.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	19.30 usec
PL1	4.00 dB
SFO1	470.5453180 MHz
SI	65536
SF	470.5923770 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00


163.75
163.48
163.21
152.47
150.82
135.23
134.17
132.86
129.10
126.97
126.87
126.12
125.13
124.49
122.16
120.41
118.48
116.54
XMJ-1
C13CPD CDCl3
38.53
38.33
38.13
NO2
S
F2C
N
NAME JHZ20130607
EXPNO 9
PROCNO 1
Date_ 20130607
Time 14.12
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 33
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 456.1
DW 16.650 usec
DE 6.00 usec
TE 296.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577745 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

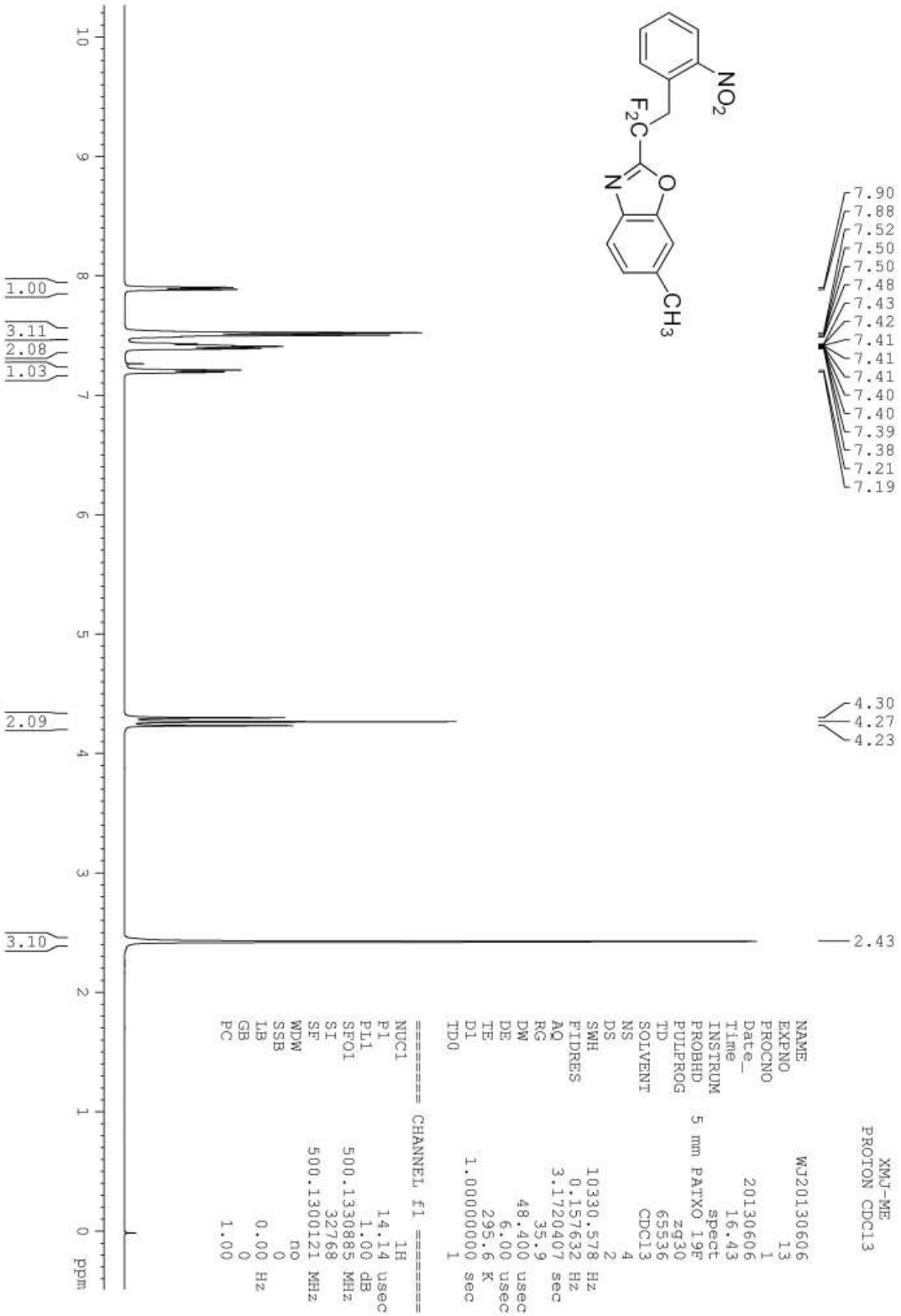
1-*n*-Butyl-2-(1,1-difluoro-2-(2-nitrophenyl)ethyl)-1H-benzo[d]imidazole (3cd)

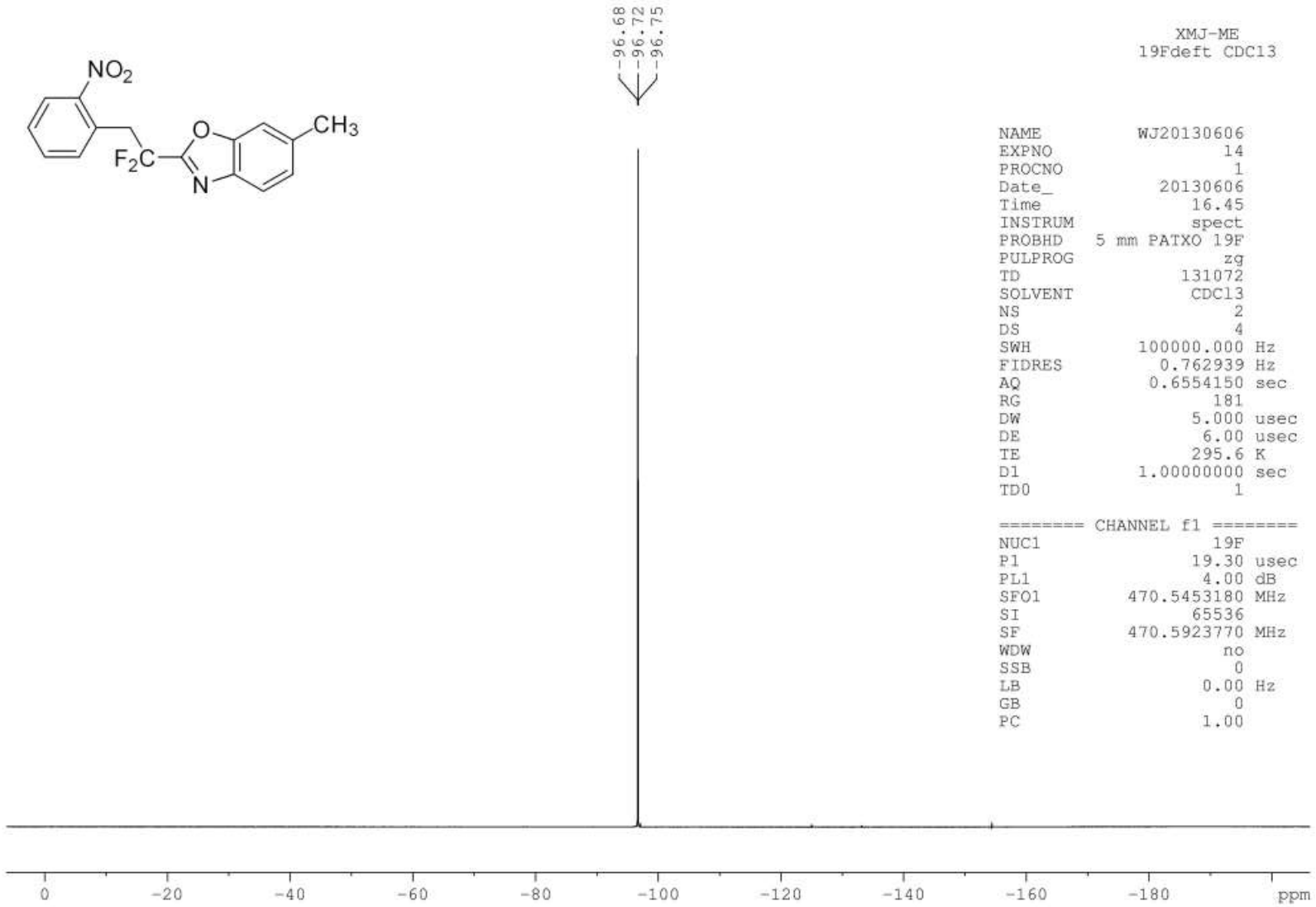



NO2
F2C
N
N
-92.21
-92.24
-92.28
N,N
19Fdeft CDCl3
NAME JHZ20130614
EXPNO 8
PROCNO 1
Date_ 20130614
Time 16.36
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 2
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 203.2
DW 5.000 usec
DE 6.00 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


151.00
145.73
145.49
145.25
141.33
135.76
134.45
132.54
128.81
126.35
124.87
124.49
122.91
121.00
120.00
118.09
116.19
110.51
44.90
37.99
37.81
37.62
32.02
20.08
13.62
NO2
F2C
N
N
NAME JHZ20130614
EXPNO 9
PROCNO 1
Date_ 20130614
Time 16.39
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 25
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 2580.3
DW 16.650 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

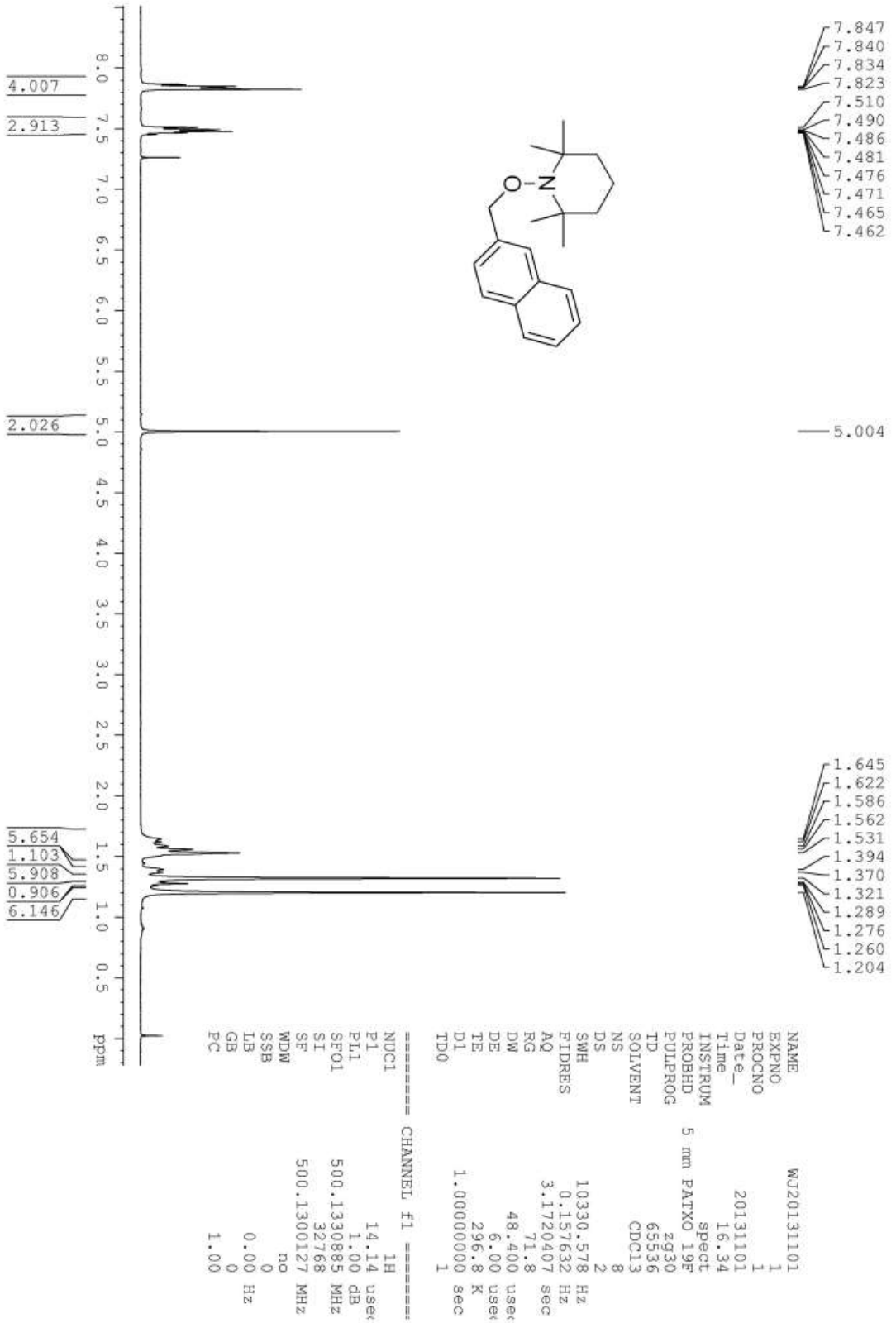
2-(1,1-Difluoro-2-(2-nitrophenyl)ethyl)-6-methylbenzo[d]oxazole (3a'd)




NO2
O
CH3
F2C
N
-96.68
-96.72
-96.75
XMJ-ME
19Fdeft CDC13
NAME WJ20130606
EXPNO 14
PROCNO 1
Date_ 20130606
Time 16.45
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 2
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 181
DW 5.000 usec
DE 6.00 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

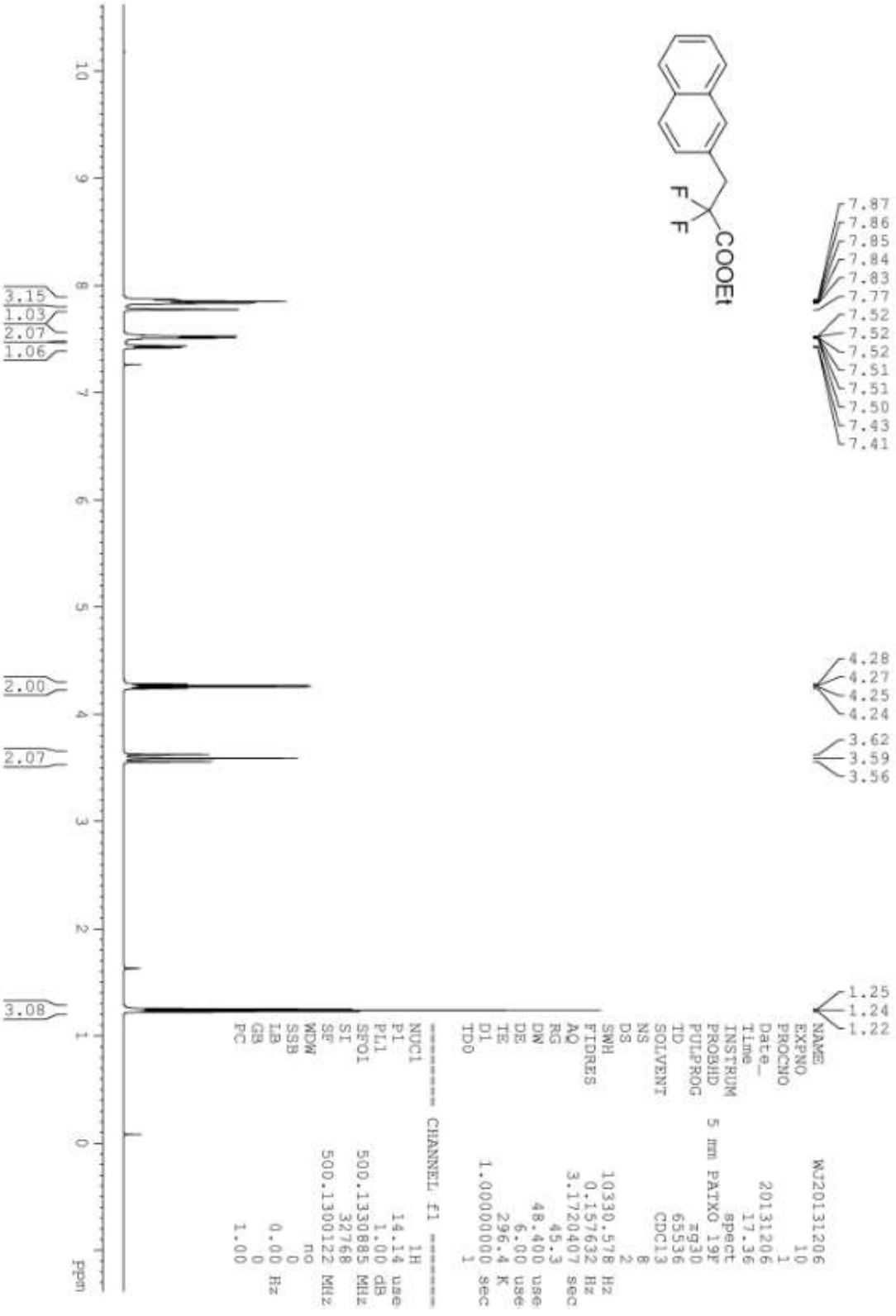
NAME	WJ20130606
EXPNO	15
PROCNO	1
Date_	20130606
Time	16.48
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	33
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912410 sec
RG	362
DW	16.650 use
DE	6.00 use
TE	296.3 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
==========	CHANNEL f1 ==========
NUC1	13C
P1	9.50 use
PL1	-0.50 dB
SFO1	125.7703643 MHz
==========	CHANNEL f2 ==========
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 use
PL2	1.00 dB
PL12	16.05 dB
PL13	16.50 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Benzyl-TEMPO adducts 5



135.834
133.387
132.877
127.918
127.846
127.691
126.020
125.962
125.858
125.661
78.912
60.103
39.773
33.188
20.374
17.174
NAME WJ20131101
EXPNO 3
PROCNO 1
Date_ 20131101
Time 16.40
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 42
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 128
DW 16.650 usec
DE 6.00 usec
TE 297.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Ethyl 2,2-difluoro-3-(naphthalen-2-yl)propanoate

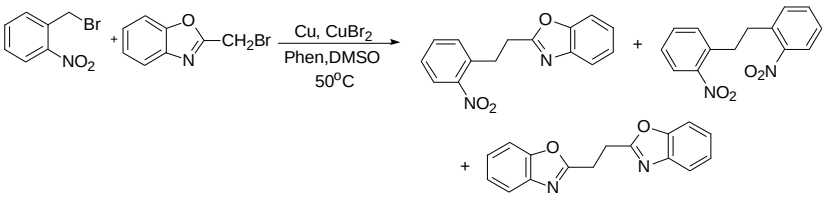


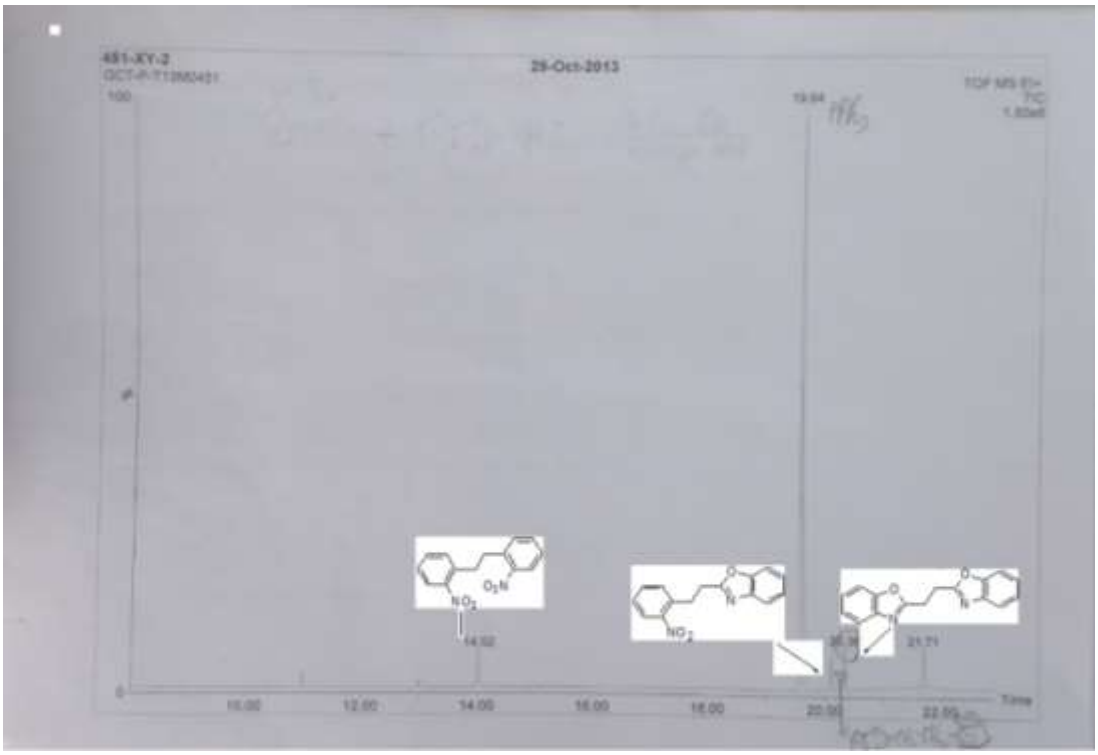
COOEt
F
F
-104.09
-104.12
-104.16
NAME WJ20131206
EXPNO 11
PROCNO 1
Date_ 20131206
Time 17.38
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg
TD 131072
SOLVENT CDCl3
NS 8
DS 4
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6554150 sec
RG 228.1
DW 5.000 usec
DE 6.00 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 19.30 usec
PL1 4.00 dB
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
ppm

164.19
163.93
163.67
133.33
132.86
129.70
128.28
128.08
127.80
127.71
126.33
126.23
117.54
115.54
113.53
62.89
41.32
41.13
40.94
13.87
F
F
COOEt
NAME WJ20131206
EXPNO 12
PROCNO 1
Date_ 20131206
Time 17.41
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 63
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 128
DW 16.650 usec
DE 6.00 usec
TE 297.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

10. GC-MS Spectra and ^{19}F NMR

1) Cross-coupling reaction of benzo-1,3-oxazolic difluoromethyl bromide with *o*-nitrobenzyl bromide (2d)





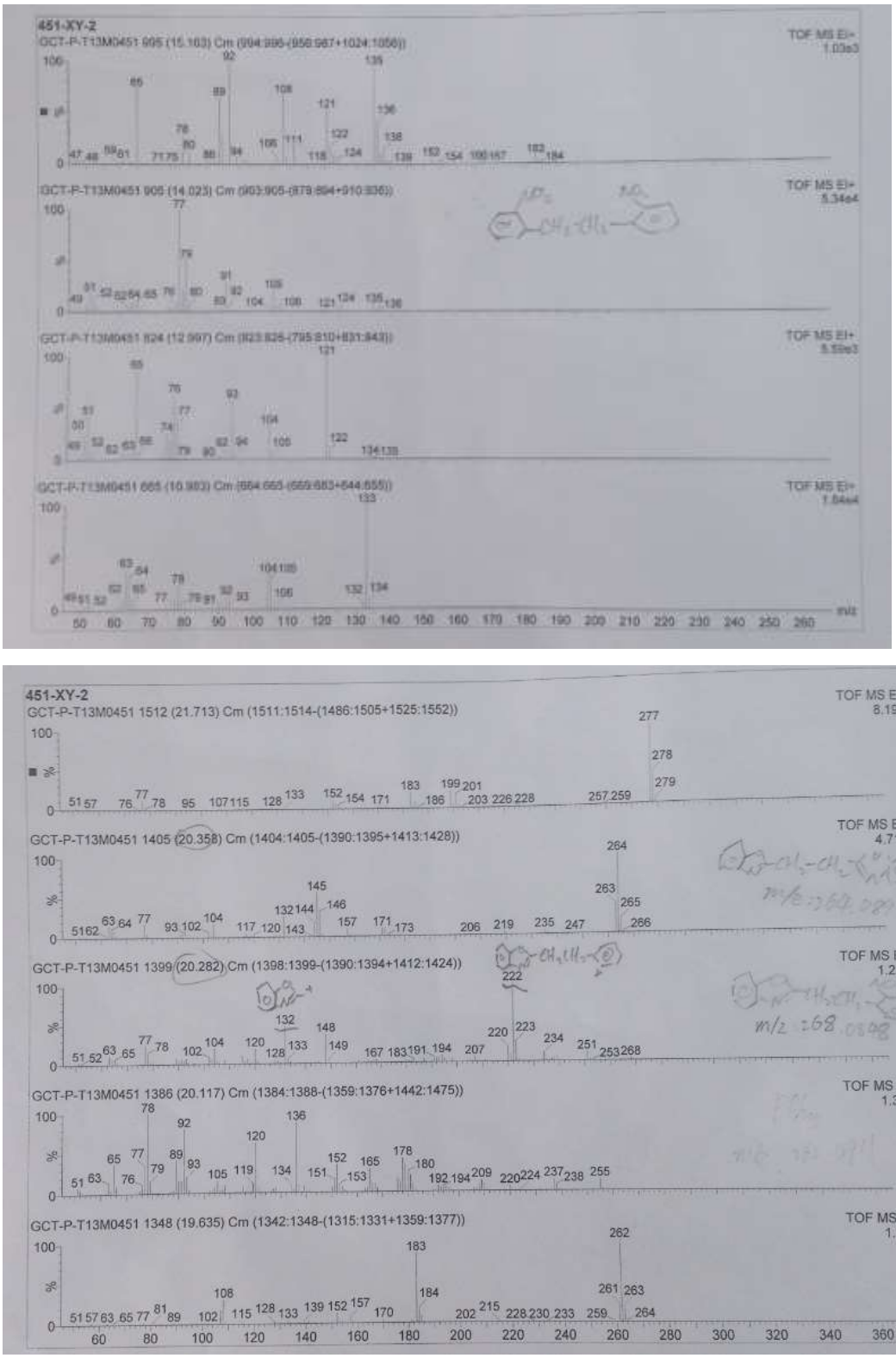
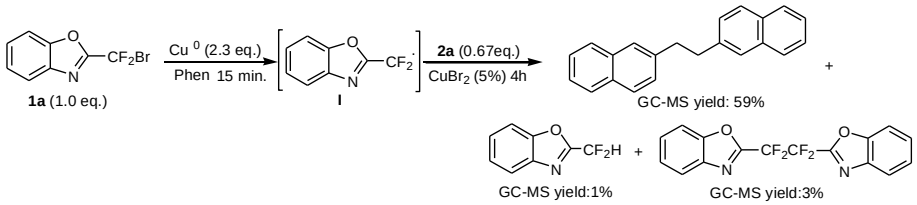


Figure S1 GC-MS of Reaction of 2-bromomethyl-benzooxazole with *o*-nitrobenzyl bromide (**2d**)

2) a) GC-MS for step by step reaction of addition of 2a to mixture of 1a with copper powder



Data path: C:\data\2014\2014-7\
Data file: 2.D
Date: 4 Jul 2014 14:32
Operator:
Sample: Sample 1
Others:
ALS number: 6 product factor: 1

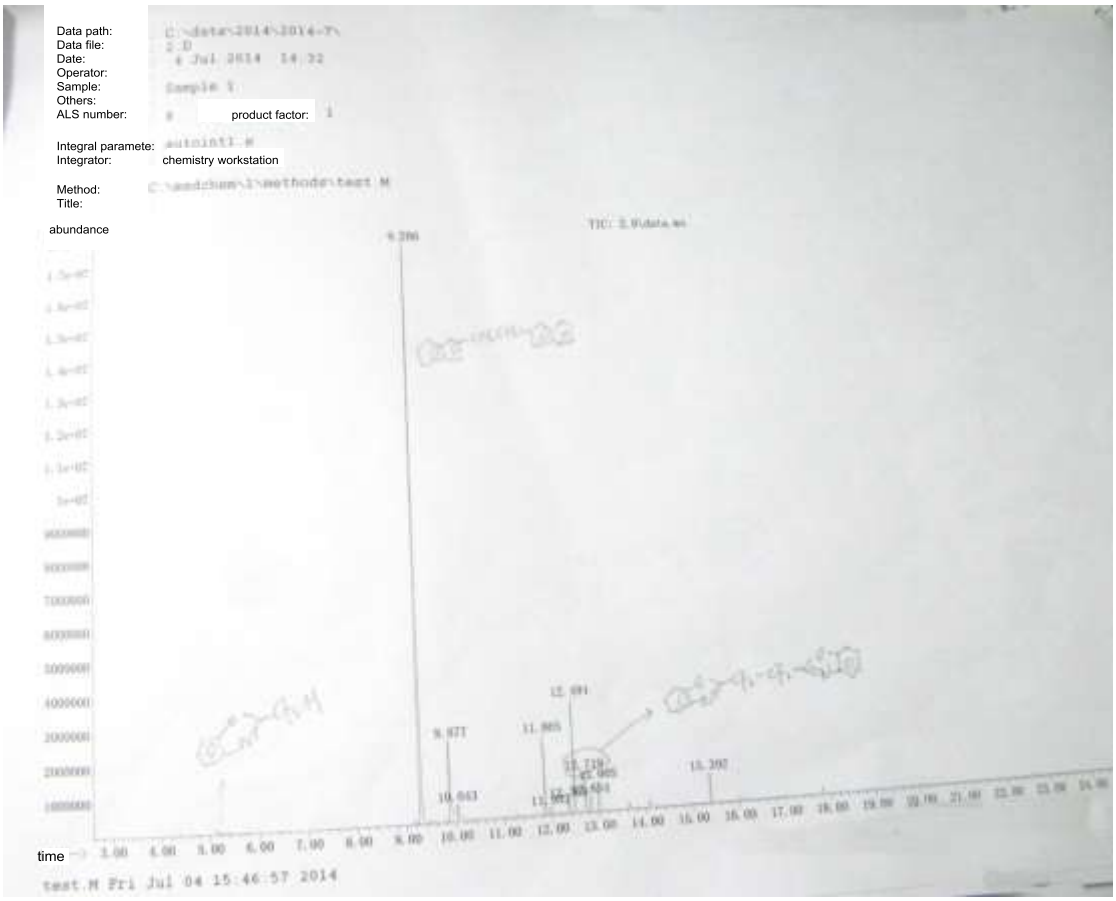
Integral paramete: autoint1.e
Integrator: chemistry workstation

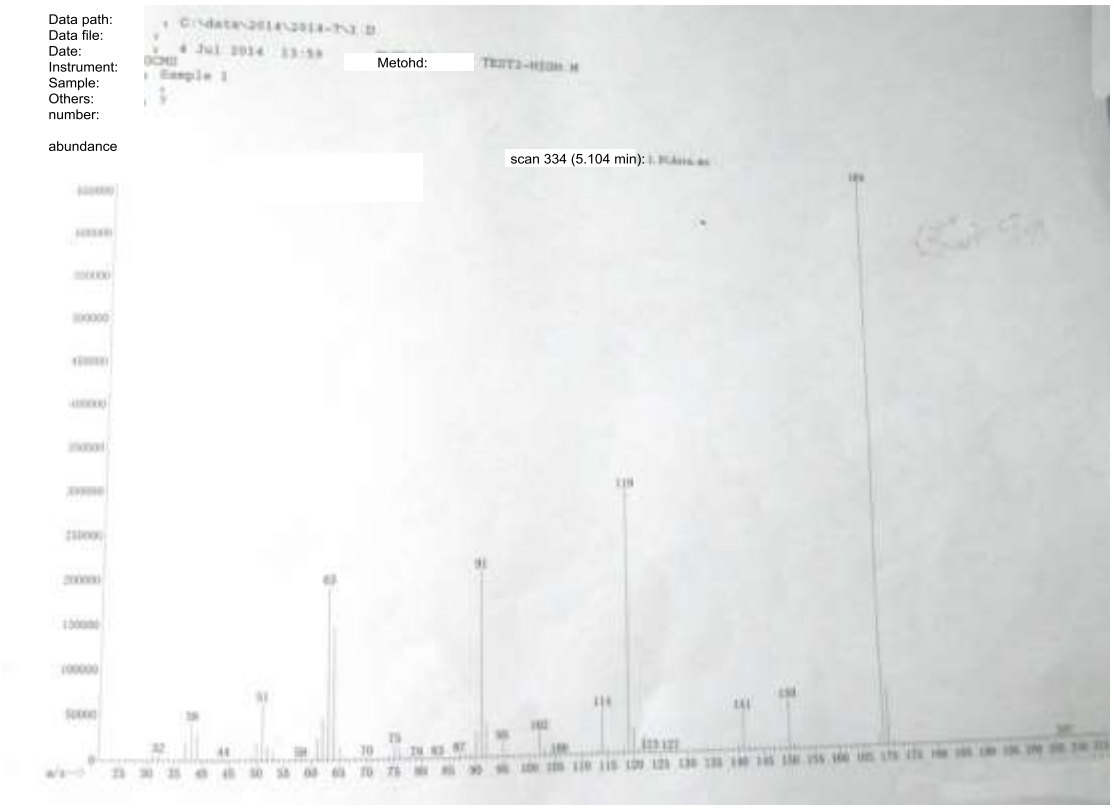
Method: C:\msdchem\1\methods\test.M
Title:

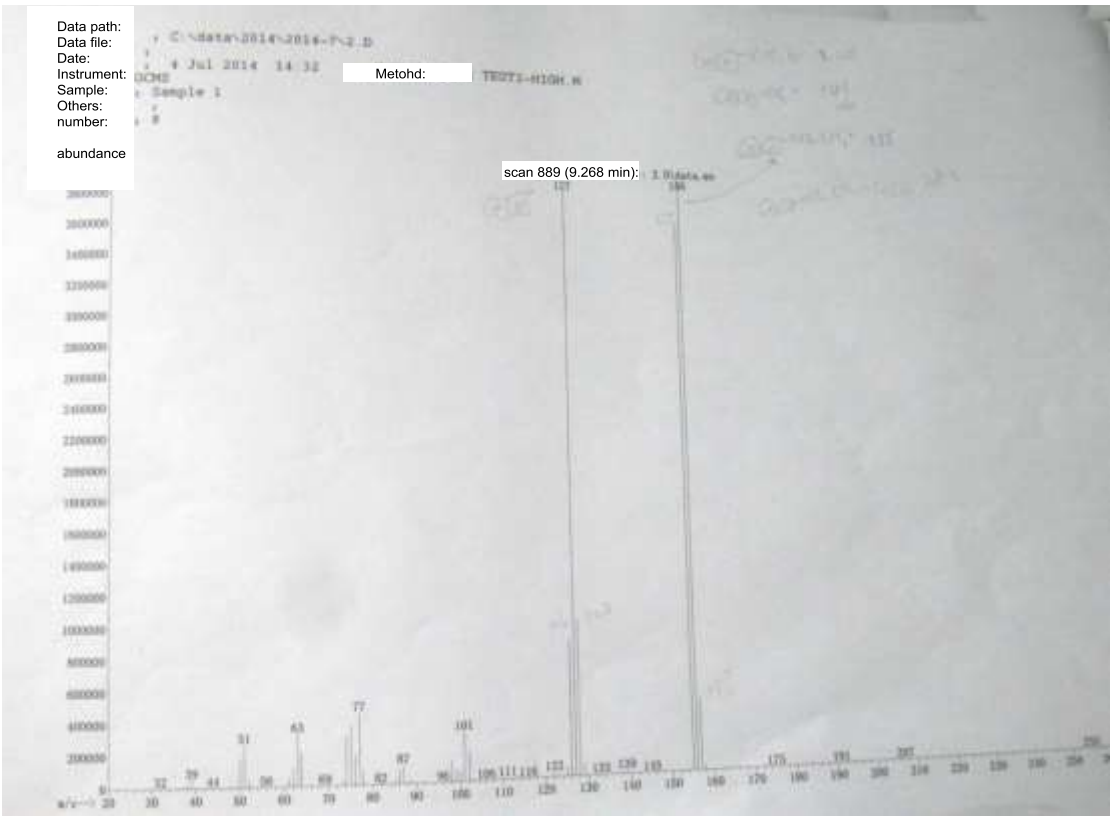
Signal: TIC 2.D\data.ms

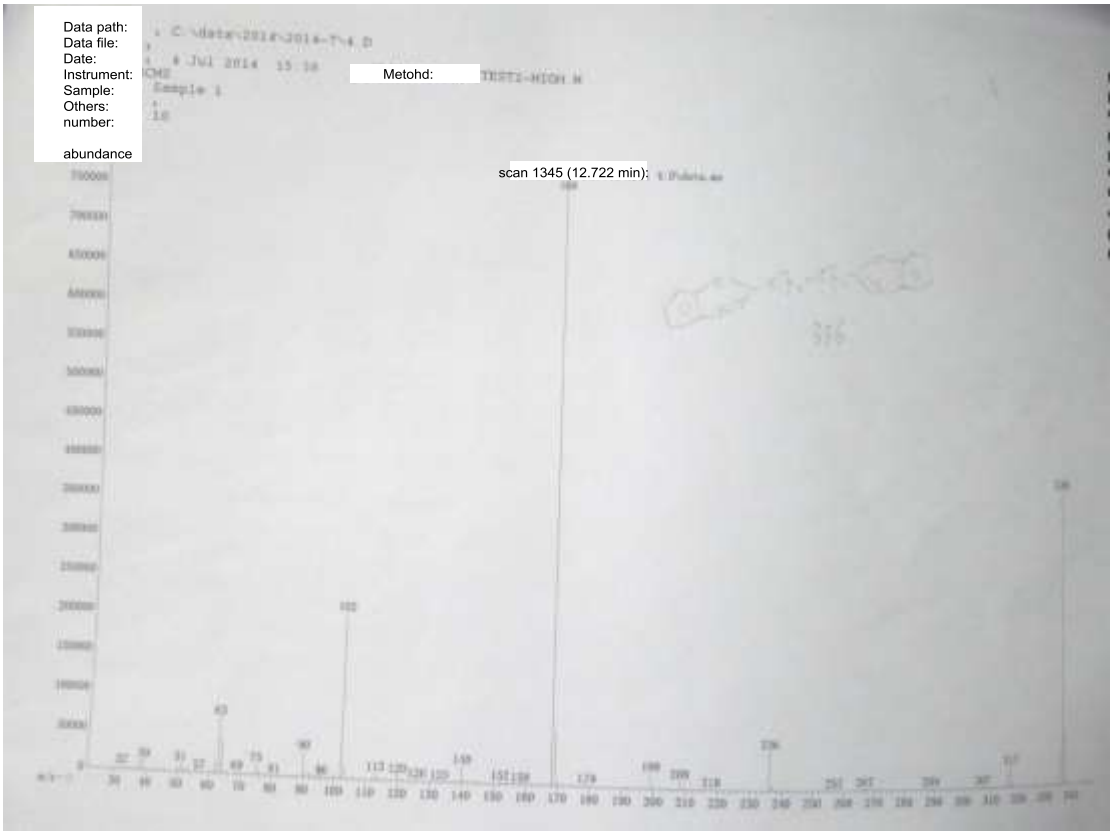
peaks	time/min	scan from scan	top scan	end at	type of peaks	peak height	revised area total area	revised area relative area	area proportion
1	9.206	878	889	920	PV	17421801	294978698	100.00%	58.956%
2	9.877	957	967	986	PV	2319784	56143385	19.03%	11.221%
3	10.043	986	990	998	VB 2	450437	7681685	2.60%	1.535%
4	11.865	1223	1231	1243	BV	2167903	29148105	9.88%	5.826%
5	11.983	1243	1247	1257	VV	333916	3429564	1.16%	0.685%
6	12.368	1289	1298	1310	BV	418408	8373360	2.84%	1.674%
7	12.494	1310	1315	1324	VB	3312113	44281140	15.01%	8.850%
8	12.719	1339	1345	1352	BV	1162561	16174641	5.48%	3.233%
9	12.834	1352	1360	1371	VB	480532	7866500	2.67%	1.572%
10	13.005	1374	1383	1396	BV 2	952271	15414096	5.23%	3.081%
11	15.392	1693	1699	1715	BB	893624	16845303	5.71%	3.367%

total revised area: 500316377

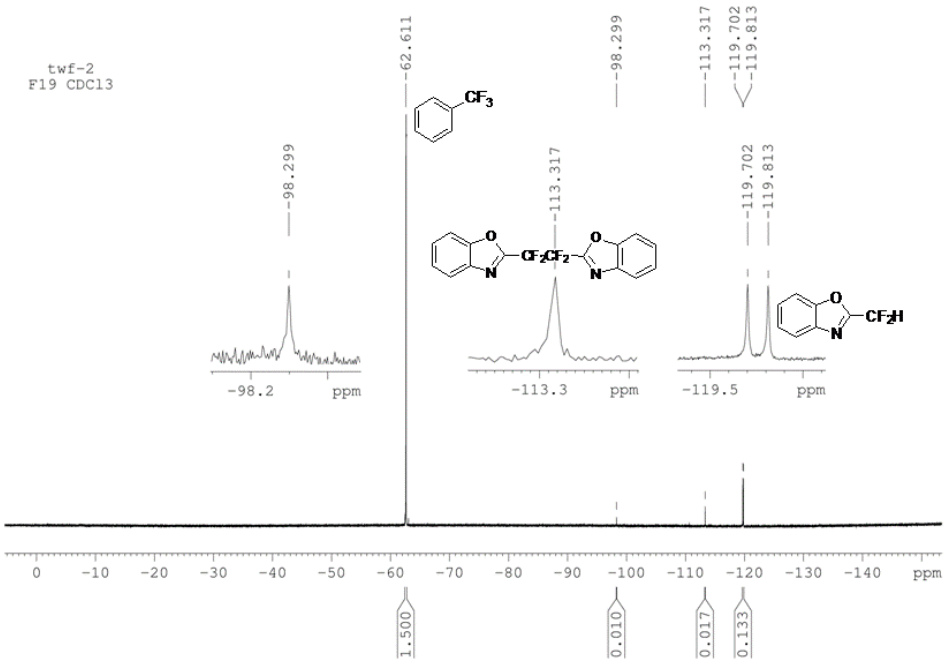

Data path:
Data file:
Date:
Operator:
Sample:
Others:
ALS number:
product factor:
Integral paramete:
Integrator:
chemistry workstation
Method:
Title:
abundance
time
test.M Fri Jul 04 15:46:57 2014


Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Metohd:
abundance
scan 334 (5.104 min):

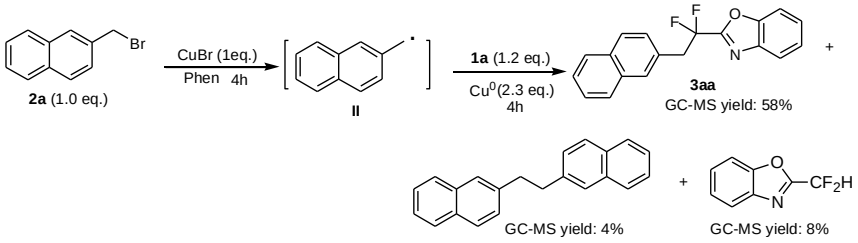

Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
abundance
Metohd:
scan 889 (9.268 min):


Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
abundance
Metohd:
scan 1345 (12.722 min):

b) ^{19} F NMR for step by step reaction of addition of 2a to mixture of 1a with copper powder



3) a) GC-MS for step by step reaction of addition of 1a to mixture of 2a with CuBr



Data path: C:\data\2014\2014-7\
Data file: 1.D
Date: 4 Jul 2014 13:59
Operator:
Sample: Sample 1
Others:
ALS number: 7 product factor: 1

Integral paramete: autoint1.e
Integrator: chemistry workstation

Method: C:\mndchem\1\methods\test.M
Title:

Signal: TIC: 1.D\data.ms

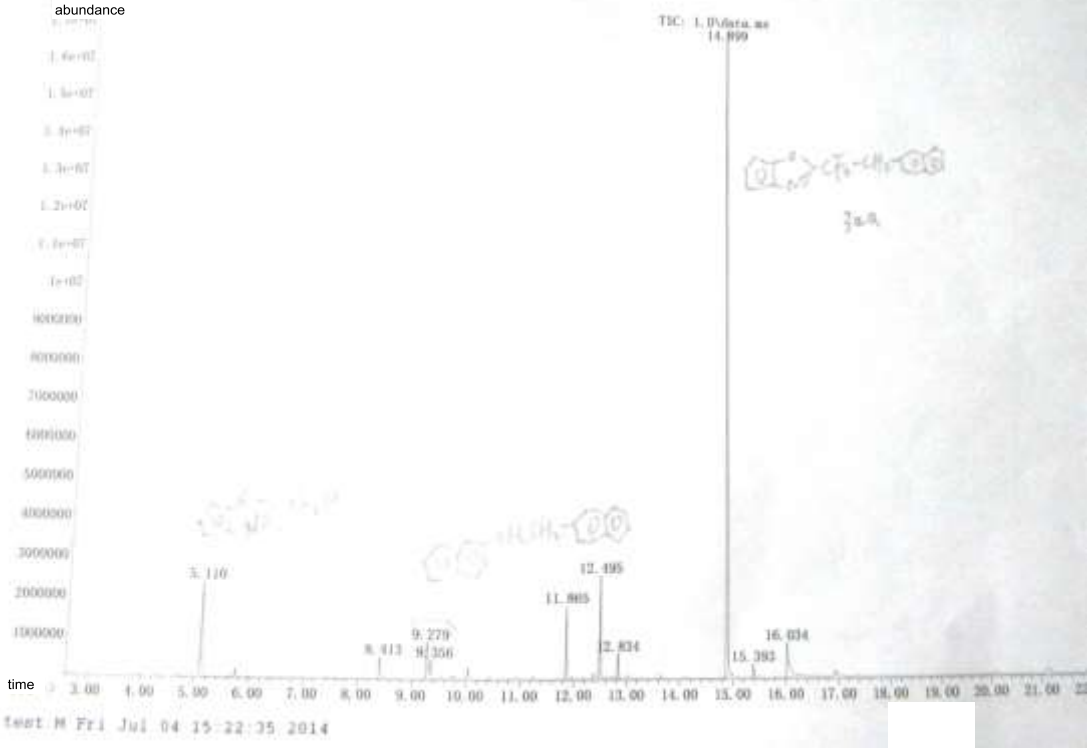
peaks	time/min	scan from	top scan	scan end at	type of peaks	peak height	revised area total area	revised area relative area	area proportion
1	5.110	328	335	358	BV	2269065	38735860	14.89%	8.680%
2	8.413	769	773	786	BB	554794	10233365	3.93%	2.293%
3	9.279	884	888	895	BV	931482	19465893	7.48%	4.362%
4	9.356	895	898	913	VB	467933	9726968	3.74%	2.180%
5	11.865	1225	1231	1239	BB	1717234	23389200	8.99%	5.241%
6	12.495	1310	1315	1325	VV	2630618	36257477	13.94%	8.124%
7	12.834	1352	1360	1371	BB	650313	9651390	3.71%	2.163%
8	14.899	1623	1634	1644	BV	16999114	260126374	100.00%	58.288%
9	15.393	1685	1700	1712	BB	351464	6742402	2.59%	1.511%
10	16.034	1775	1785	1817	BB	876075	31945265	12.28%	7.158%

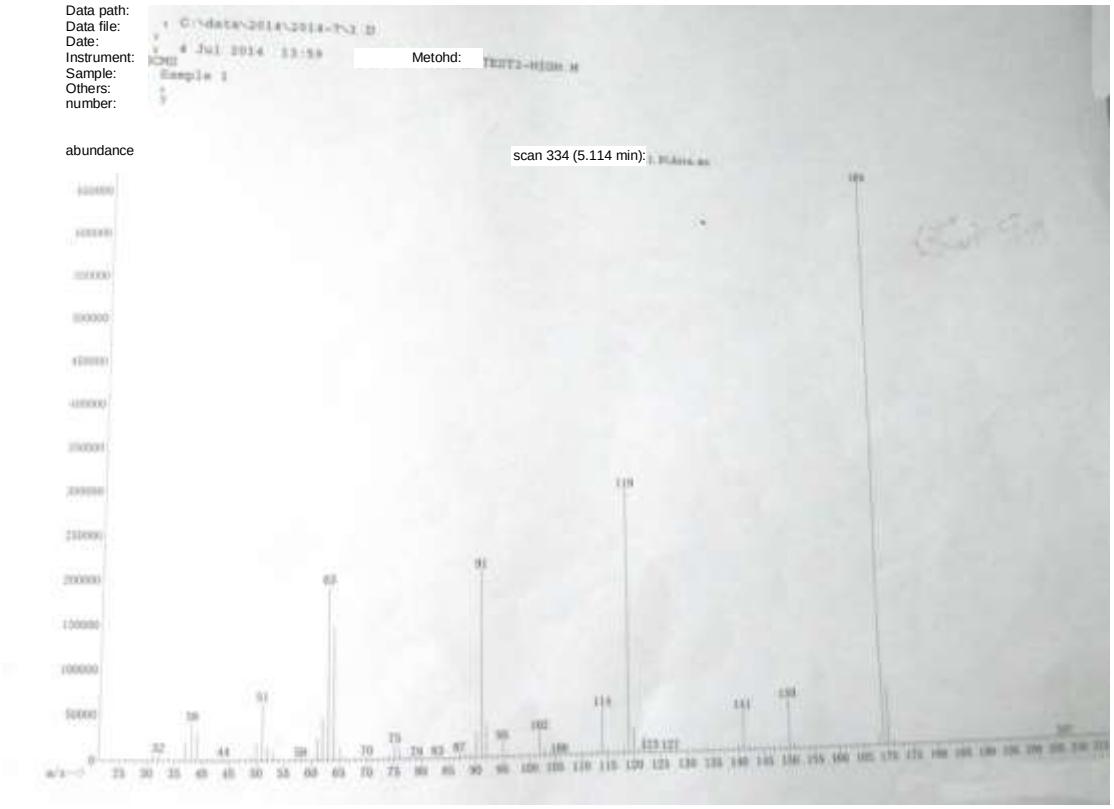
total revised area: 446274202

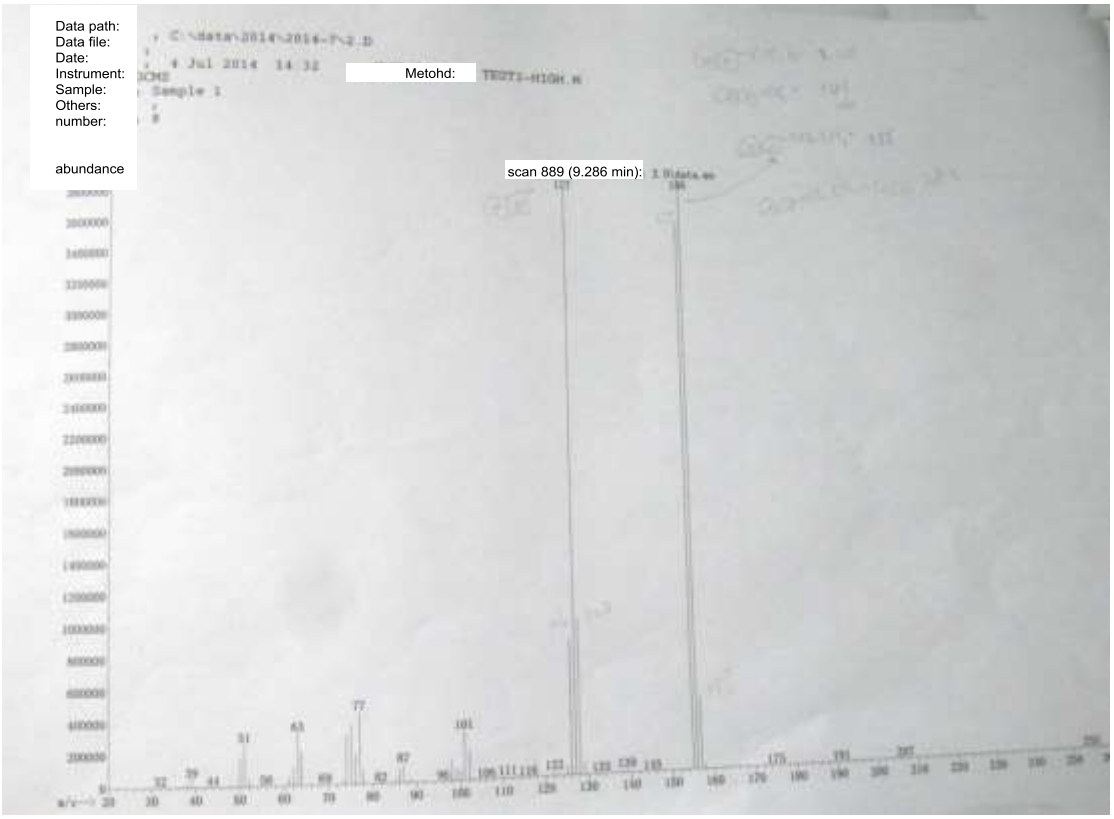
Data path: C:\data\2014\2014-7\
Data file: 1.D
Date: 4 Jul 2014 13:59
Operator:
Sample: Sample 1
Others:
ALS number: 7 product factor: 1

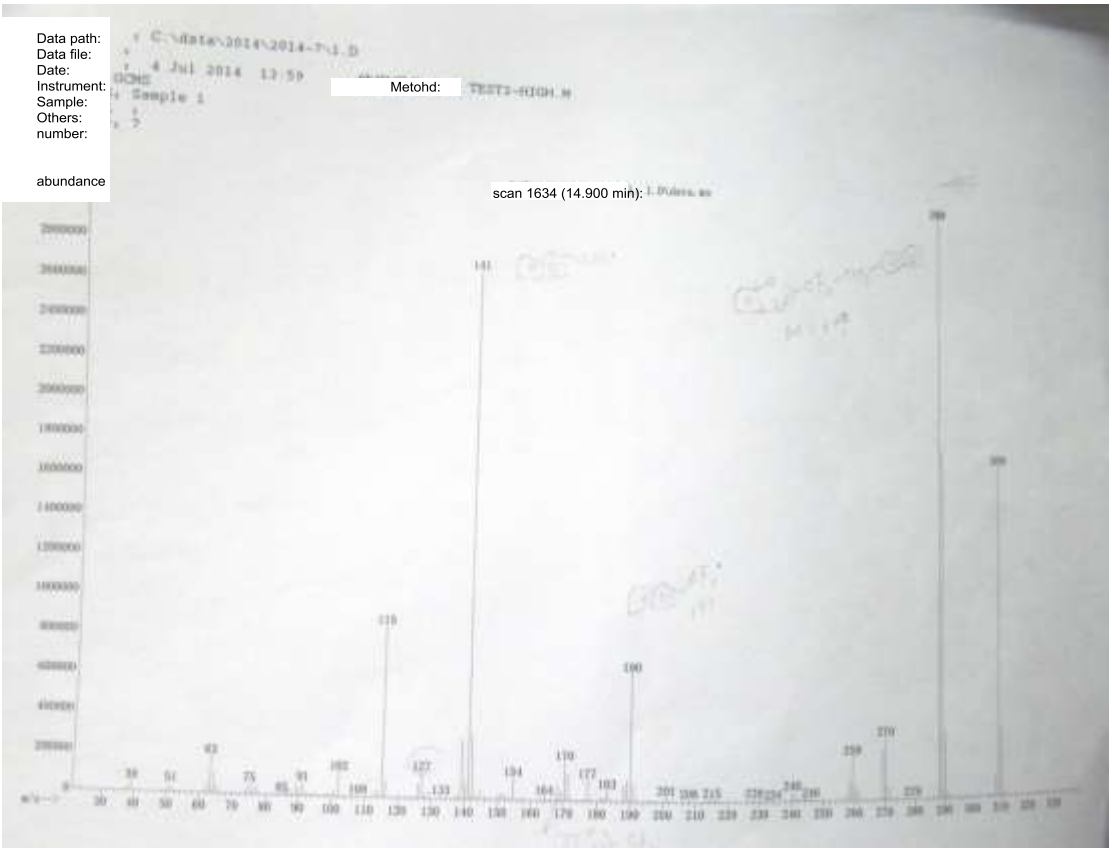
Integral paramete: autoint1.e
Integrator: chemistry workstation

Method: \mndchem\1\methods\test.M
Title:

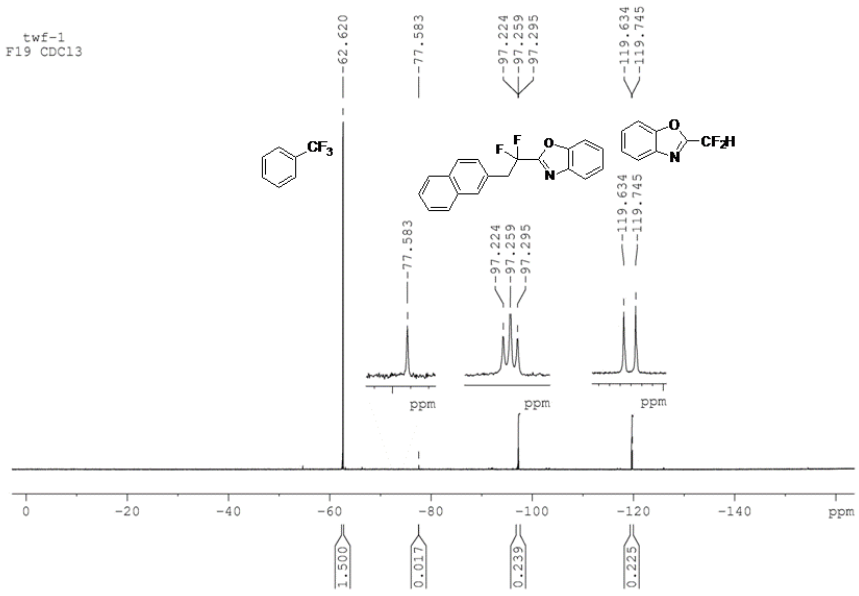



Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Metohd:
abundance
scan 334 (5.114 min):


Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Metohd:
abundance
scan 889 (9.286 min):



b) ^{19} F NMR for step by step reaction of addition of 2a to mixture of 1a with copper powder



4) a) GC-MS for one-pot reaction of 1a and 2a under Cu-mediated

Data path: C:\data\2014\2014-7\
Data file: 3.D
Date: 4 Jul 2014 15:05
Operator:
Sample: Sample 1
Others:
ALS number: 3 product factor: 1

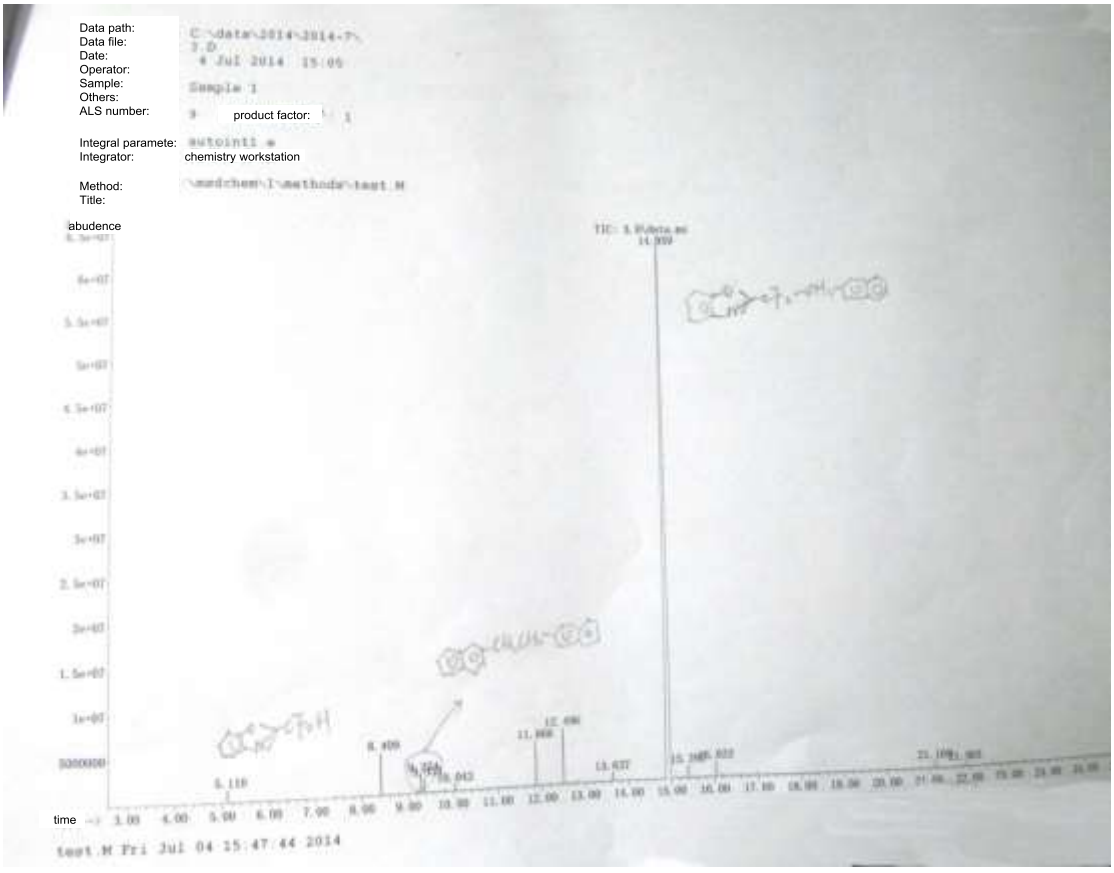
Integral paramete: autoint1.e
Integrator: chemistry workstation

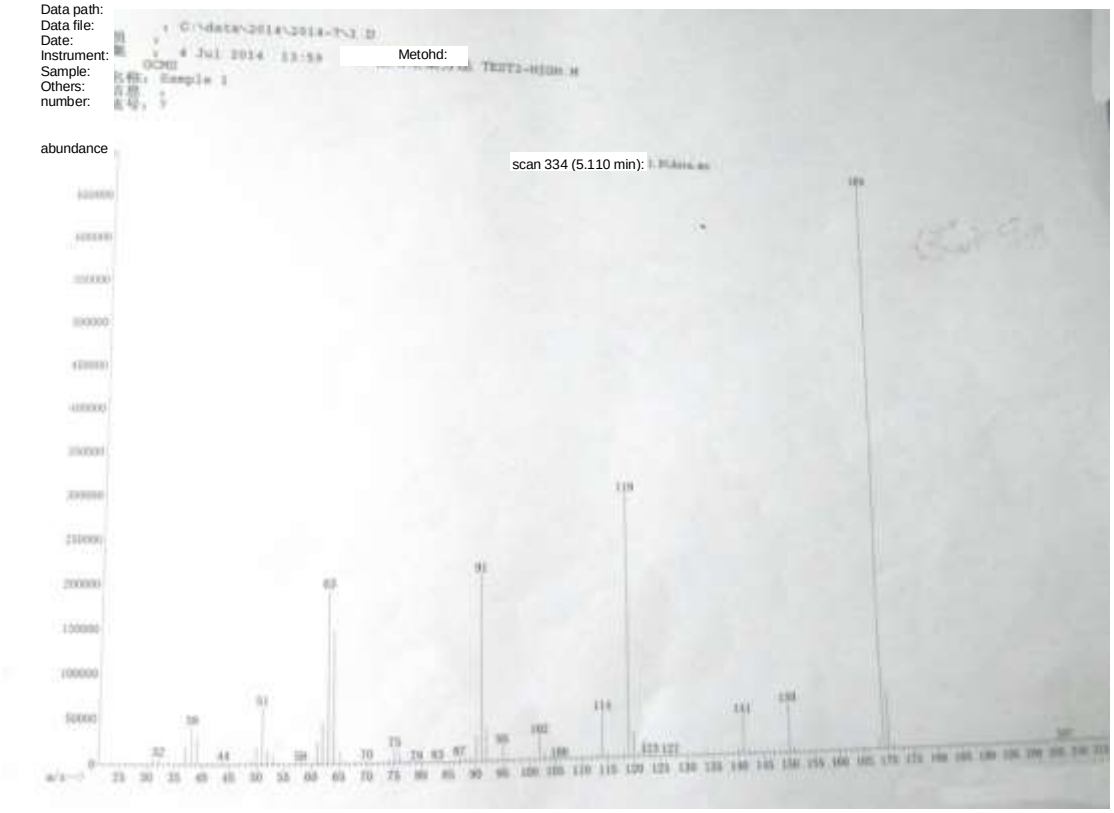
Method: C:\medchem\1\methods\test.M
Title:

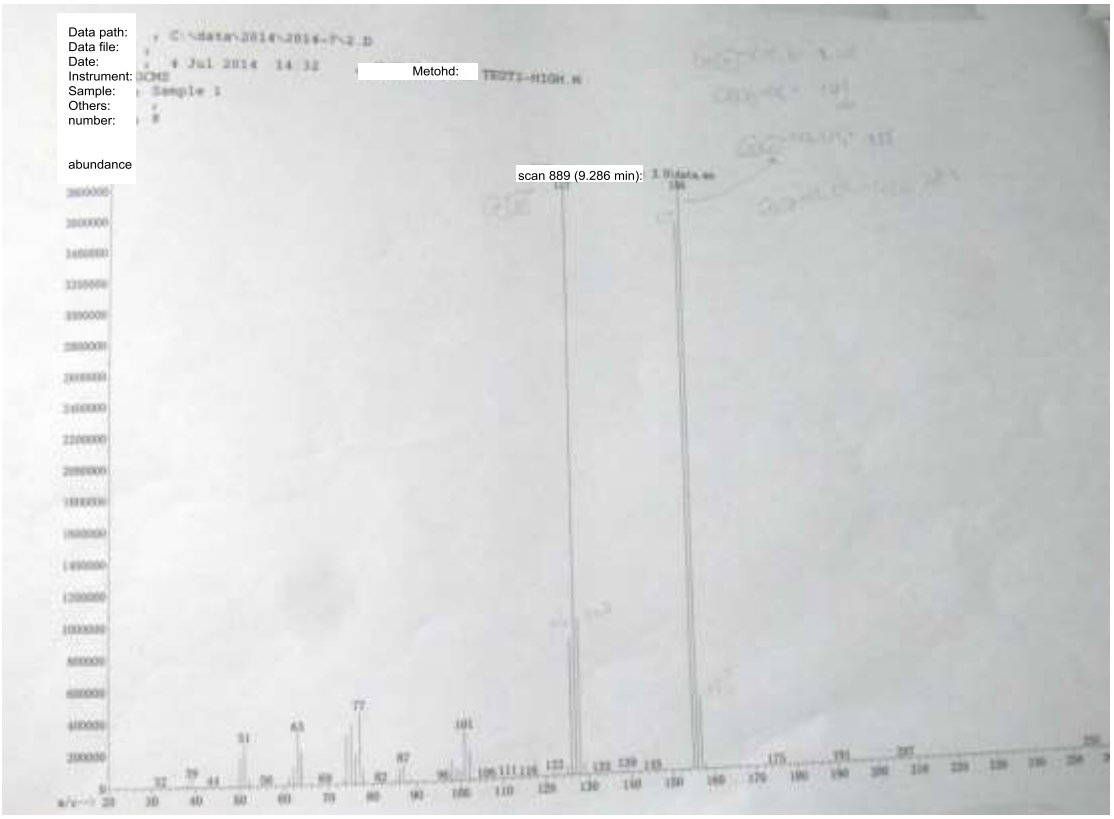
Signal: 1: TIC 3.D\data.ms

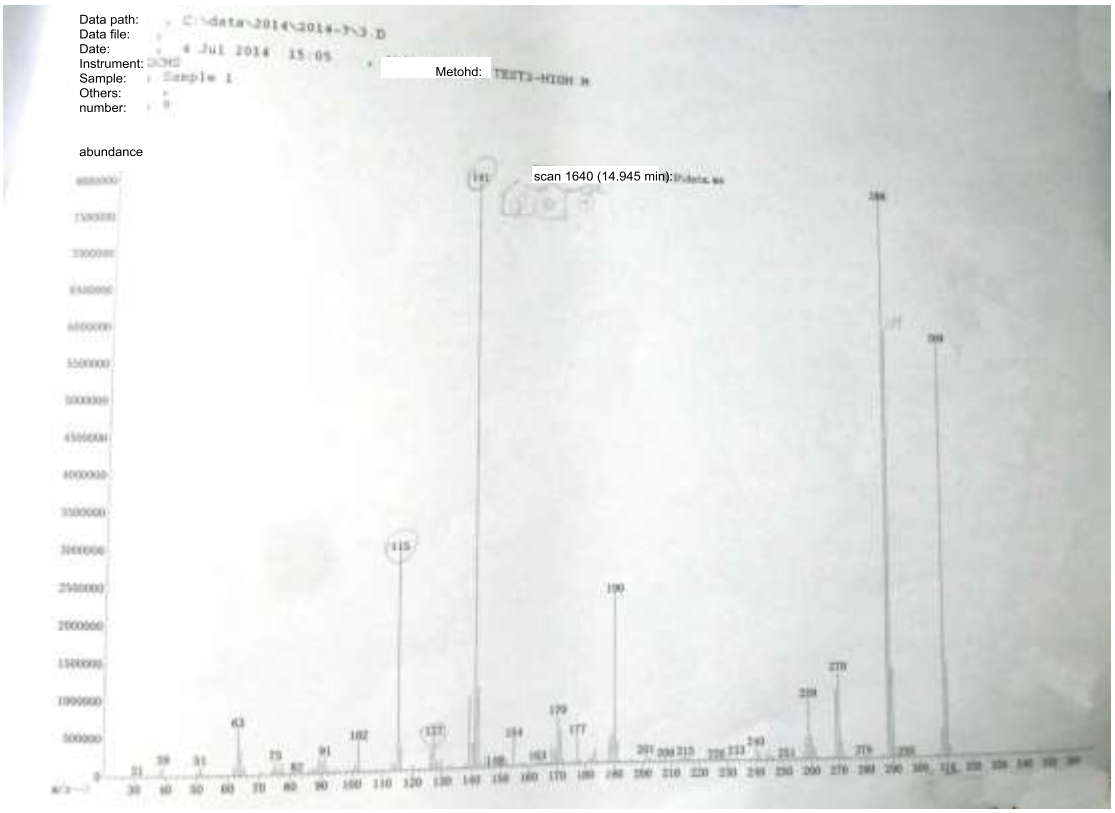
peaks	time/min	scan from	top scan	scan end at	type of peaks	peak height	revised area total area	revised area relative area	area proportion
1	5.110	339	345	350	BB	14866362	24038078	1.00%	0.634%
2	8.409	767	773	785	BV	4746515	67091609	2.74%	2.329%
3	9.274	883	887	894	VV	2131756	37130993	1.55%	1.294%
4	9.753	894	898	912	VB	1708322	26859911	1.11%	0.932%
5	10.043	982	990	997	BB	905203	12831268	0.53%	0.445%
6	11.066	1219	1231	1239	BB	4140040	64766114	2.69%	2.248%
7	12.496	1389	1315	1320	BV	6546111	94260261	3.50%	2.925%
8	13.637	1462	1466	1477	BB	1038407	15665035	0.65%	0.544%
9	14.959	1625	1642	1645	BB	2 65632772	2409224783	100.00%	83.627%
10	15.392	1695	1699	1712	BB	1496522	24224146	1.01%	0.841%
11	18.032	1776	1784	1812	BB	1441589	51506494	2.14%	1.788%
12	21.169	2440	2465	2487	BB	941518	41251356	1.71%	1.432%
13	21.903	2538	2565	2583	BB	2 541650	21863574	0.91%	0.759%

total revised area: 2880913619

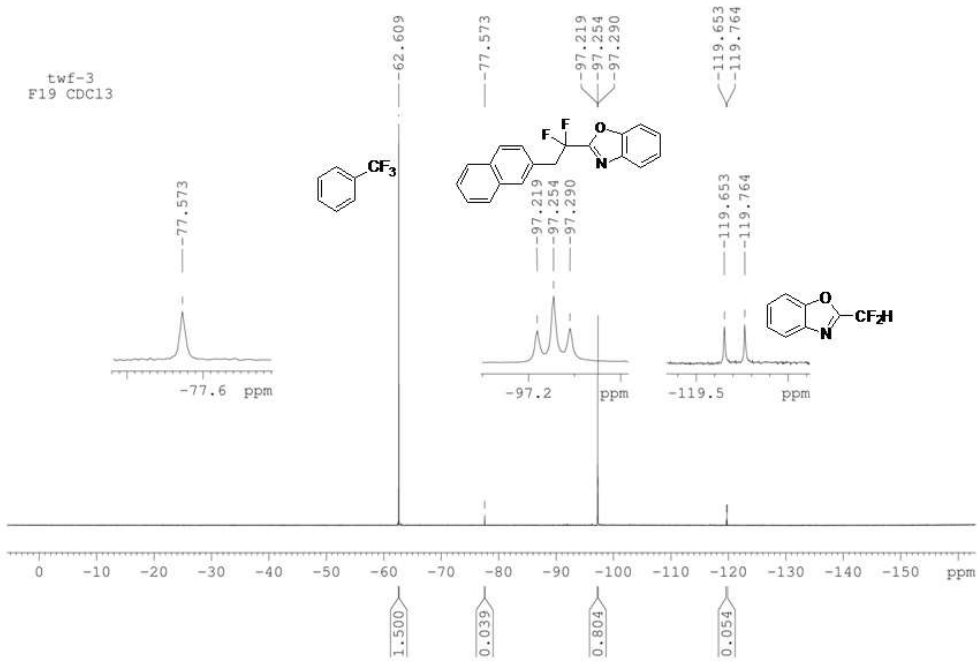



Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Metohd:
abundance
scan 334 (5.110 min):

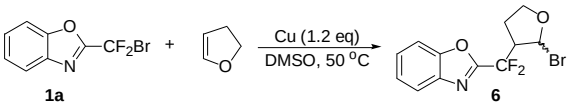

Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Metohd:
abundance
scan 889 (9.286 min):



b) ^{19}F NMR for one-pot reaction of 1a and 2a under Cu-mediated



5) a) GC-MS for the reaction of 1a with 2,3-Dihydrofuran[S2]



1a **6**

^{19}F NMR yield: 29%,
GC-MS yield: 9%

Data path: C:\data\2014\2014-7\
Data file: 6.D
Date: 6 Jul 2014 15:38
Operator:
Sample: Sample 1
Others:
ALS number: 10 product factor: 1

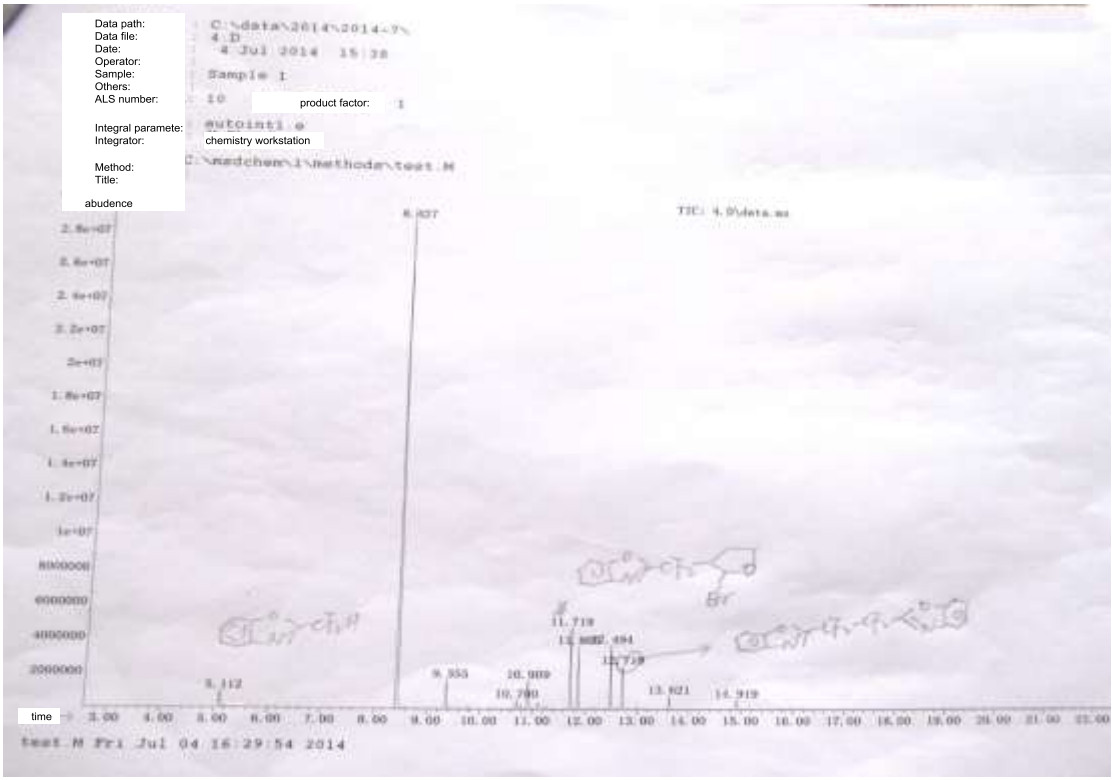
Integral paramete: autoint1.e
Integrator: chemistry workstation

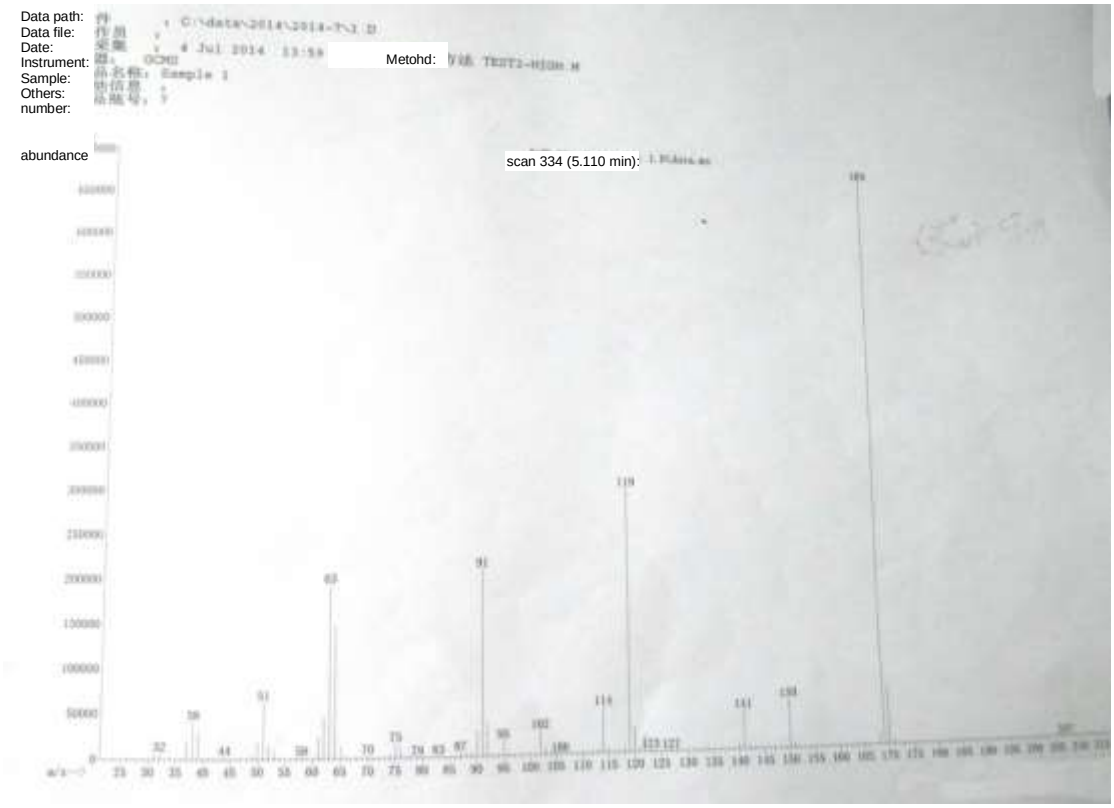
Method: C:\msdchem\1\methods\test.M
Title:

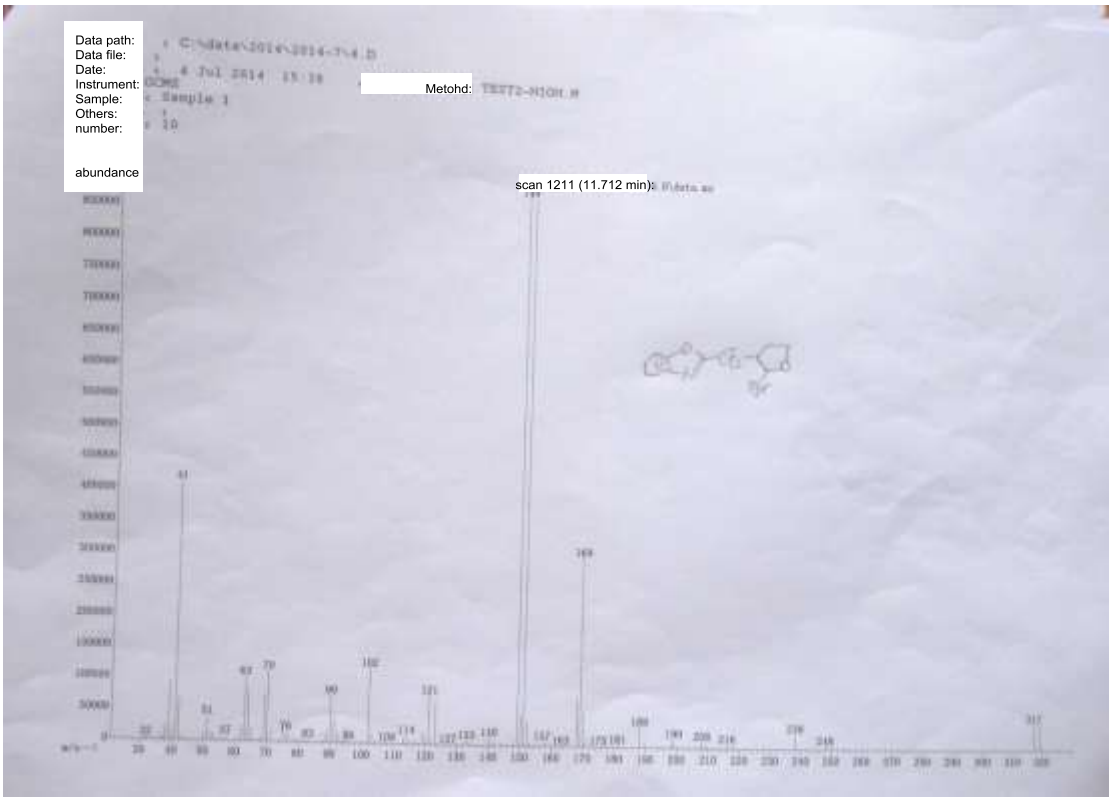
Signal: TIC: 6 D\data.ms

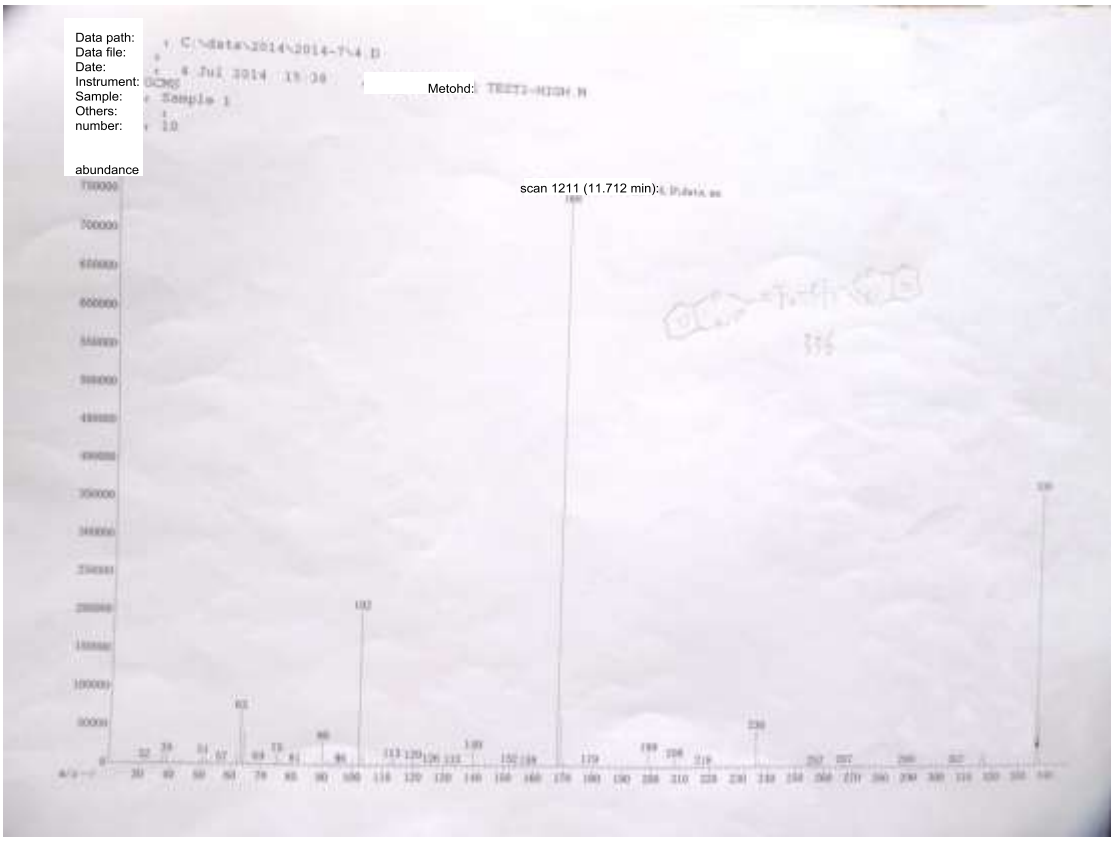
peaks	time/min	scan from	top scan	scan end at	type of peaks	peak height	revised area total area	revised area relative area	area proportion
1	5.112	330	335	351	BB	972201	16971652	3.66%	2.345%
2	8.427	767	775	791	BB	27317047	463602226	100.00%	61.312%
3	9.355	892	898	908	BV	1640968	25181113	5.43%	3.330%
4	10.700	1059	1077	1082	BV	530578	8586416	1.85%	1.136%
5	10.909	1088	1104	1119	BB	1590034	27391368	5.91%	3.623%
6	11.719	1207	1212	1225	BB	4756296	46346082	14.31%	8.774%
7	11.865	1226	1231	1241	BB	2327094	44455809	9.59%	5.879%
8	12.494	1305	1315	1324	BB	3664533	49963643	10.78%	6.608%
9	12.719	1334	1345	1354	VB	2440089	33821334	7.30%	4.472%
10	13.421	1459	1464	1473	BB	771529	11467017	2.47%	1.517%
11	14.919	1625	1637	1642	BV	545550	8353778	1.80%	1.105%

total revised area: 756140637


Data path:
Data file:
Date:
Operator:
Sample:
Others:
ALS number:
Integral paramete:
Integrator:
Method:
Title:
abudence
C:\data\2014\2014-7\
4 Jul 2014 15:38
Sample 1
10
product factor: 1
autoint1.e
chemistry workstation
C:\msdchem\1\methods\test.M
TIC: 4.D\data.ms
8.037
11.719
12.494
9.355
10.909
10.700
13.921
14.919
9.112
time
test.M Fri Jul 04 16:29:54 2014


Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
C:\data\2014\2014-7\1.D
4 Jul 2014 13:59
Metohd:
Sample 1
abundance
scan 334 (5.110 min):
119
91
63
m/z


Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Sample 1
10
Metohd:
abundance
scan 1211 (11.712 min):


Data path:
Data file:
Date:
Instrument:
Sample:
Others:
number:
Sample 1
10
Metohd:
abundance
scan 1211 (11.712 min):

b) ^{19}F NMR for the reaction of 1a with 2,3-Dihydrofuran[S2]