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Supplementary Information

Base-mediated direct fluoroalkenylation of 2-phenyl-1,3,4-oxadiazole, benzothiazole and benzoxazole with *gem*-difluoroalkenes

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General experimental procedures

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. DMSO and other solvents were dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR, respectively) using TMS as internal standard. The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz). $CDCl_3$ was used as the NMR solvent in all cases. High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer. Silica gel (300−400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

Preparation of 1, 1-difluoroalkenes 1a–g and 2-phenyl-1,3,4-oxadiazole 2a

The 1,1-difluoroalkenes (**1a–g**) were prepared according to the the Hu's reported procedure.[1] The 2-phenyl-1,3,4-oxadiazole (**2a**) was prepared according to the Miura's reported procedure.[2]

General procedure for synthesis of 3aa–ga

A solution of **1a–g** (1.0 mmol) in DMSO (0.2 mL) was added dropwise to a mixture of **2a** (584 mg, 4.0 mmol) and a THF solution of KHMDS (4.0 mmol, 4.0 mL, 1.0 M) in DMSO (5 mL) via syringe and then stirred at room temperature for 12 h (monitored by TLC). After the consumption of the 1,1-difluoroalkenes (**1a–g)**, the reaction mixture was quenched with H_2O (20 mL), and subsequently extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using a hexane/EtOAc (30:1) mixture as eluent to afford the pure target compounds **3aa–ga**.

General procedure for synthesis of 3ab–gb

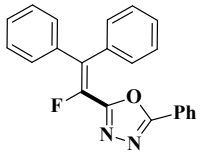
A solution of **1a–g** (1.0 mmol) in DMSO (0.2 mL) was added dropwise to a mixture of **2b** (270 mg, 2.0 mmol) and a THF solution of KHMDS (2.0 mmol, 2.0 mL, 1.0 M) in DMSO (5 mL) via syringe and then stirred at room temperature for 2 h (monitored by TLC). After the consumption of the 1,1-difluoroalkenes (**1a–g**), the reaction mixture was quenched with H_2O (20 mL), and subsequently extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using a hexane/EtOAc (30:1) mixture as eluent to afford the pure target compounds **3ab–gb**.

General procedure for synthesis of 3ac–cc, 3gc

A solution of **1a–c**, **1g** (1.0 mmol) in DMSO (0.2 mL) was added dropwise to a mixture of **2c** (476 mg, 4.0 mmol) and NaH (96 mg, 4.0 mmol) in DMSO (5 mL) via syringe and then stirred at room temperature for 2 h (monitored by TLC). After the consumption of the 1,1-difluoroalkenes (**1a–c**, **1g**), the reaction mixture was quenched with H_2O (20 mL), and subsequently extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using a hexane/EtOAc (30:1) mixture as eluent to afford the pure target compounds **3ac–cc**, **3gc**.

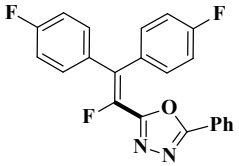
Spectral and analytical data of 3

2-(2,2-Diphenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3aa**): White solid. Yield: 75%, mp 157.0−158.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.62 (m, 2H), 7.54–7.38 (m, 11H), 7.35–7.32 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 159.4 (d, $^{2}J_{CF}$ = 40.1 Hz), 140.5 (d, $^{1}J_{CF}$ = 248.3 Hz), 136.1 (d, $^{3}J_{CF}$ = 5.0 Hz), 135.6 (d, $^{4}J_{CF}$ = 2.7 Hz), 132.0, 130.9 (d, $^{2}J_{CF}$ = 11.0 Hz), 130.2 (d, $^{3}J_{CF}$ = 3.0 Hz), 130.1, 130.0, 129.1, 129.0, 128.7, 128.4, 126.9, 123.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −123.0 (s, 1F) ppm; HRMS (EI): calcd for $C_{22}H_{15}FN_2O$ $[M-H]^+$: 341.1090, found: 341.1100.



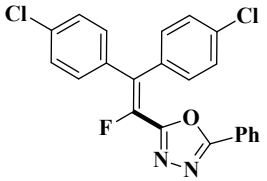
3aa

2-(2,2-Di-4-fluorophenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3ba**): White solid. Yield: 78%, mp 153.7−154.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (m, 2H), 7.53–7.43 (m, 5H), 7.32–7.29 (m, 2H), 7.20–7.08 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 163.2 (d, $^{1}J_{CF}$ = 247.8 Hz), 162.9 (d, $^{1}J_{CF}$ = 249.4 Hz), 140.5 (d, $^{1}J_{CF}$ = 249.0 Hz), 132.2–132.1 (m), 132.1–132.0 (m), 131.8–131.7 (m), 131.6–131.5 (m), 129.1, 128.9 (d, $^{2}J_{CF}$ = 14.6 Hz), 128.8, 128.7 (d, $^{2}J_{CF}$ = 41.1 Hz), 126.9, 123.0, 115.9 (d, $^{2}J_{CF}$ = 21.6 Hz), 115.6 (d, $^{2}J_{CF}$ = 21.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.7 to −110.8 (m, 1F), −112.0 to −112.1 (m, 1F), −122.2 (s, 1F) ppm; HRMS (EI): calcd for $C_{22}H_{13}F_3N_2O$ $[M-H]^+$: 377.0902, found: 377.0919.



3ba

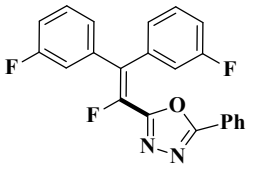
2-(2,2-Di-4-chlorophenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3ca**): White solid. Yield: 78%, mp 129.6−130.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.2 Hz, 2H), 7.53–7.39 (m, 9H), 7.26 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR(100 MHz, $CDCl_3$): δ 164.6, 158.8 (d, $^{2}J_{CF}$ = 39.3 Hz), 140.9 (d, $^{1}J_{CF}$ = 250.6 Hz), 135.4 (d, $^{4}J_{CF}$ = 1.8 Hz), 135.3, 134.0 (d, $^{3}J_{CF}$ = 5.2 Hz), 133.6 (d, $^{4}J_{CF}$ = 2.9 Hz), 132.2, 131.6 (d, $^{3}J_{CF}$ = 3.1 Hz), 131.4, 131.3, 129.2, 128.8, 128.5 (d, $^{2}J_{CF}$ = 11.5 Hz), 126.9, 122.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −121.4 (s, 1F) ppm; HRMS (EI): calcd for $C_{22}H_{13}Cl_2FN_2O$ $[M-H]^+$: 409.0311, found: 409.0310.



3ca

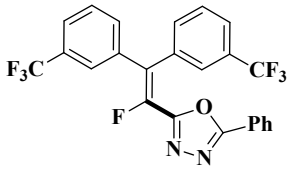
2-(2,2-Di-3-fluorophenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3da**): White solid. Yield: 80%, mp 120.2−121.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.59 (s, 1H), 7.44–7.27 (m, 5H), 7.17–6.93 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 162.9 (d, $^{1}J_{CF}$ = 246.6 Hz), 162.6 (d, $^{1}J_{CF}$ = 245.0 Hz), 158.7 (d, $^{2}J_{CF}$ = 39.1 Hz), 141.3 (d, $^{1}J_{CF}$ = 251.7 Hz), 137.4 (dd, $^{3}J_{CF}$ = 8.0 Hz, $^{3}J_{CF}$ = 5.2 Hz), 137.0 (dd, $^{3}J_{CF}$ = 7.9 Hz, $^{3}J_{CF}$ = 2.7 Hz), 132.2, 130.5 (d, $^{3}J_{CF}$ = 8.3 Hz), 130.0 (d, $^{3}J_{CF}$ = 8.2 Hz), 129.1, 126.9, 126.0–125.9 (m), 125.8–125.7 (m), 123.0, 117.3 (dd, $^{2}J_{CF}$ = 22.1 Hz, $^{4}J_{CF}$ = 3.4 Hz), 116.9 (d, $^{2}J_{CF}$ = 23.0 Hz), 116.8 (d, $^{2}J_{CF}$ = 23.0 Hz), 116.3 (d,

$^{2}J_{CF}$ = 21.1 Hz), 116.1 (d, $^{2}J_{CF}$ = 20.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.9 to −112.0 (m, 1F), −112.1 to −112.2 (m, 1F), −120.2 (s, 1F); HRMS (EI): calcd for $C_{22}H_{13}F_3N_2O$ [M−H]$^+$: 377.0902, found: 377.0900.



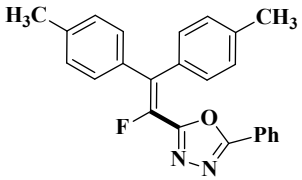
3da

2-(2,2-Di-3-(trifluoromethyl)phenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3ea**): White solid. Yield: 60%, mp 98.7−99.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.67–7.40 (m, 11H) ppm; ^{13}C NMR (100 Hz, $CDCl_3$): δ 164.8, 158.4 (d, $^{2}J_{CF}$ = 38.8 Hz), 141.8 (d, $^{1}J_{CF}$ = 252.4 Hz), 136.0 (d, $^{3}J_{CF}$ = 5.1 Hz), 135.7 (d, $^{3}J_{CF}$ = 2.5 Hz), 133.6 (d, $^{3}J_{CF}$ = 1.3 Hz), 133.1 (d, $^{3}J_{CF}$ = 4.6 Hz), 132.4, 131.6 (q, $^{2}J_{CF}$ = 32.6 Hz), 131.2 (q, $^{2}J_{CF}$ = 32.4 Hz), 129.7, 129.3, 129.1, 127.8 (d, $^{2}J_{CF}$ = 12.3 Hz), 127.0, 126.9, 126.8, 126.6–126.4 (m), 126.2–126.0 (m), 123.7 (q, $^{1}J_{CF}$ = 270.9 Hz), 123.6 (q, $^{1}J_{CF}$ = 270.9 Hz), 122.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.6 (s, 3F), −62.8 (s, 3F), −119.6 (s, 1F) ppm; HRMS (EI): calcd for $C_{24}H_{13}F_7N_2O$ [M−H]$^+$: 477.0838, found: 477.0848.



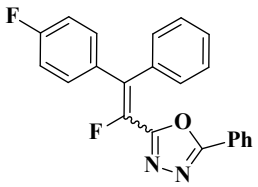
3ea

2-(2,2-Di-4-methylphenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3fa**): White solid. Yield: 15%, mp 138.9–139.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.59 (m, 2H), 7.50–7.45 (m, 1H), 7.41–7.35 (m, 4H), 7.25–7.15 (m, 6H), 2.45 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 159.6 (d, $^{2}J_{CF}$ = 40.2 Hz), 140.1 (d, $^{1}J_{CF}$ = 247.4 Hz), 139.3, 138.6, 133.2 (d, $^{3}J_{CF}$ = 5.3 Hz), 132.9 (d, $^{3}J_{CF}$ = 3.0 Hz), 131.9, 130.9 (d, $^{2}J_{CF}$ = 10.7 Hz), 130.1 (d, $^{4}J_{CF}$ = 1.7 Hz), 130.0 (d, $^{4}J_{CF}$ = 2.8 Hz), 129.3, 129.1, 128.9, 126.9, 123.3, 21.4, 21.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −123.9 (s, 1F); HRMS (EI): calcd for $C_{24}H_{19}FN_2O$ [M−H]$^+$: 369.1403, found: 369.1413.



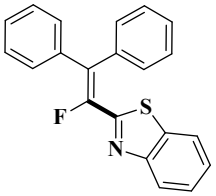
3fa

(*E/Z*)-2-(2-(4-Fluorophenyl)-2-phenyl-1-fluorovinyl)-5-phenyl-1,3,4-oxadiazole (**3ga**): White solid. Yield: 85%. A mixture of *E*- and *Z*-isomers (4:3, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.67 (m, 1H), 7.60–7.58 (m, 1H), 7.51–7.37 (m, 8H), 7.30–7.27 (m, 2H), 7.16–7.12 (m, 1H), 7.10–7.06 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 164.4, 163.1 (d, $^{1}J_{CF}$ = 247.6 Hz), 162.9 (d, $^{1}J_{CF}$ = 247.4 Hz), 159.3 (d, $^{2}J_{CF}$ = 40.0 Hz), 159.2 (d, $^{2}J_{CF}$ = 39.3 Hz), 140.5 (d, $^{1}J_{CF}$ = 249.4 Hz), 140.4 (d, $^{1}J_{CF}$ = 246.9 Hz), 135.9, 135.8, 135.5, 135.4, 132.1–132.0 (m), 131.7–131.6 (m), 130.1 (d, $^{3}J_{CF}$ = 3.0 Hz), 130.0 (d, $^{3}J_{CF}$ = 5.8 Hz), 129.9 (d, $^{2}J_{CF}$ = 13.5 Hz), 129.7 (d, $^{2}J_{CF}$ = 10.9 Hz), 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 126.9, 126.8, 123.2, 123.1, 115.8 (d, $^{2}J_{CF}$ = 21.6 Hz), 115.5 (d, $^{2}J_{CF}$ = 21.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.0 to −111.1 (m), −112.3 to −112.4 (m), −122.0 (s), −123.2 (s) ppm; HRMS (EI): calcd for $C_{22}H_{14}F_2N_2O$ [M−H]$^+$: 359.0996, found: 359.1010.



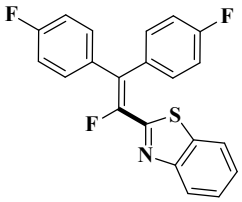
3ga

2-(2,2-Diphenyl-1-fluorovinyl)benzo[*d*]thiazole (**3ab**): White solid. Yield: 88%, mp 148.2−150.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.55−7.46 (m, 6H), 7.42−7.34 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5 (d, $^{2}J_{CF}$ = 27.7 Hz), 151.6, 148.5 (d, $^{1}J_{CF}$ = 254.4 Hz), 136.5 (d, $^{4}J_{CF}$ = 2.3 Hz), 136.2 (d, $^{3}J_{CF}$ = 6.2 Hz), 135.6 (d, $^{4}J_{CF}$ = 1.6 Hz), 131.1 (d, $^{4}J_{CF}$ = 3.0 Hz), 130.0 (d, $^{3}J_{CF}$ = 6.3 Hz), 129.5, 129.4, 129.2 (d, $^{2}J_{CF}$ = 13.9 Hz), 128.6, 128.3, 126.5, 126.0, 123.7, 121.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.8 (s, 1F); HRMS (EI): calcd for $C_{21}H_{14}FNS$ $[M-H]^+$: 330.0753, found: 330.0749.



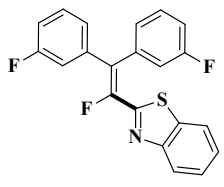
3ab

2-(2,2-Di-4-fluorophenyl-1-fluorovinyl)benzo[*d*]thiazole (**3bb**): White solid. Yield: 89%, mp 163.0−164.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.49−7.43 (m, 3H), 7.38−7.32 (m, 3H), 7.22−7.17 (m, 2H), 7.10−7.06 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5 (d, $^{1}J_{CF}$ = 248.1 Hz), 162.6 (d, $^{1}J_{CF}$ = 248.6 Hz), 159.0 (d, $^{2}J_{CF}$ = 28.8 Hz), 152.2, 148.7 (d, $^{1}J_{CF}$ = 253.4 Hz), 135.6 (d, $^{4}J_{CF}$ = 1.6 Hz), 133.0 (dd, $^{3}J_{CF}$ = 8.4 Hz, $^{4}J_{CF}$ = 3.1 Hz), 132.5−132.4 (m), 132.1−132.0 (m), 131.8 (dd, $^{3}J_{CF}$ = 8.1 Hz, $^{4}J_{CF}$ = 6.6 Hz), 126.6 (d, $^{2}J_{CF}$= 14.5 Hz), 126.5, 126.0, 123.9, 121.1, 116.6 (d, $^{2}J_{CF}$ = 21.6 Hz), 115.4 (d, $^{2}J_{CF}$ = 21.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.8 (s, 1F), −111.2 to −111.3 (m, 1F), −111.6 to −111.7 (m, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{12}F_3NS$ $[M-H]^+$: 366.0564, found: 366.0559.



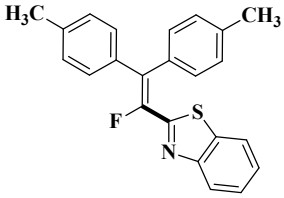
3bb

2-(2,2-Di-3-fluorophenyl-1-fluorovinyl)benzo[*d*]thiazole (**3db**): White solid. Yield: 90%, mp 114.3−115.4°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.65 (s, 1H), 7.37–6.98 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (d, $^{1}J_{CF}$ = 246.9 Hz), 162.6 (d, $^{1}J_{CF}$ = 244.4 Hz), 158.6 (d, $^{2}J_{CF}$ = 29.2 Hz), 152.2, 149.3 (d, $^{1}J_{CF}$ = 255.4 Hz), 138.0 (dd, $^{3}J_{CF}$ = 8.0 Hz, $^{3}J_{CF}$ = 2.3 Hz), 137.8 (dd, $^{3}J_{CF}$ = 7.8 Hz, $^{3}J_{CF}$ = 6.4 Hz), 135.6, 131.1 (d, $^{3}J_{CF}$ = 8.3 Hz), 129.8 (d, $^{3}J_{CF}$ = 8.2 Hz), 126.9–126.8 (m), 126.6, 126.2, 125.6–125.5 (m), 124.1, 121.1, 118.1 (dd, $^{2}J_{CF}$ = 21.7 Hz, $^{4}J_{CF}$ = 3.3 Hz), 116.8 (d, $^{2}J_{CF}$ = 22.9 Hz), 116.7 (d, $^{2}J_{CF}$ = 23.0 Hz), 116.5 (d, $^{2}J_{CF}$ = 20.8 Hz), 115.7 (d, $^{2}J_{CF}$ = 20.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −107.9 (s, 1F), −111.2 to −111.3 (m, 1F), −112.5 to −112.6 (m, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{12}F_3NS$ $[M-H]^+$: 366.0564, found: 366.0576.



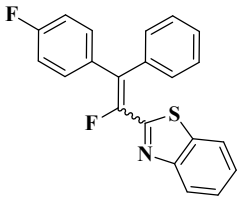
3db

2-(2,2-Di-4-methylphenyl-1-fluorovinyl)benzo[*d*]thiazole (**3fb**): White solid. Yield: 70%, mp 138.7–140.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.42–7.38 (m, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.30–7.20 (m, 5H), 7.14 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (d, $^2J_{CF}$ = 27.1 Hz), 152.1, 148.4 (d, $^1J_{CF}$ = 253.4 Hz), 139.4, 138.6 (d, $^5J_{CF}$ = 1.0 Hz), 135.8 (d, $^4J_{CF}$ = 1.8 Hz), 134.0 (d, $^4J_{CF}$ = 2.5 Hz), 133.3 (d, $^3J_{CF}$ = 6.4 Hz), 131.0 (d, $^4J_{CF}$ = 3.0 Hz), 130.2, 130.0 (d, $^3J_{CF}$ = 6.5 Hz), 129.1 (d, $^2J_{CF}$ = 13.8 Hz), 129.0, 126.3, 125.7, 123.7, 121.0, 121.6, 121.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.6 (s, 1F); HRMS (EI): calcd for $C_{23}H_{18}FNS$ [M−H]$^+$: 358.1066, found: 358.1069.



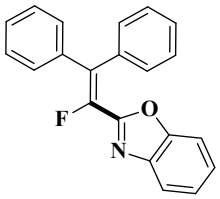
3fb

(***E/Z***)**-2-(2-(4-Fluorophenyl)-2-phenyl-1-fluorovinyl)benzo[*d*]thiazole** (**3gb**): White solid. Yield: 92%. A mixture of *E*- and *Z*-isomers (4:3, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–8.00 (m, 1H), 7.72–7.65 (m, 1H), 7.50–7.30 (m, 9H), 7.18–7.02 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5 (d, $^1J_{CF}$ = 247.7 Hz), 162.5 (d, $^1J_{CF}$ = 250.2 Hz), 159.2 (d, $^2J_{CF}$ = 27.6 Hz), 159.1 (d, $^2J_{CF}$ = 29.2 Hz), 152.2, 152.1, 148.8 (d, $^1J_{CF}$ = 253.2 Hz), 148.6 (d, $^1J_{CF}$ = 253.9 Hz), 136.1, 136.0, 135.7 (d, $^4J_{CF}$ = 1.7 Hz), 135.1 (d, $^4J_{CF}$ = 1.7 Hz), 133.6 (dd, $^3J_{CF}$ = 8.3Hz, $^4J_{CF}$ = 3.1 Hz), 131.9 (dd, $^3J_{CF}$ = 8.2 Hz, $^4J_{CF}$ = 6.7 Hz), 132.7–132.6 (m), 132.4–132.3 (m), 131.1 (d, $^3J_{CF}$ = 3.0 Hz), 129.5 (d, $^3J_{CF}$ = 6.2 Hz), 129.5, 129.4, 128.7, 128.4, 127.7 (d, $^2J_{CF}$ = 12.9 Hz), 127.6 (d, $^2J_{CF}$ = 14.8 Hz), 126.5, 126.4, 126.0, 125.9, 123.9, 123.8, 121.1, 121.0, 116.5 (d, $^2J_{CF}$ = 21.5 Hz), 115.4 (d, $^2J_{CF}$ = 21.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.7 (s), −111.0 (s), −111.6 to −111.7 (m), −112.0 to −112.1 (m); HRMS (EI): calcd for $C_{21}H_{13}F_2NS$ [M−H]$^+$: 348.0659, found: 348.0660.



3gb

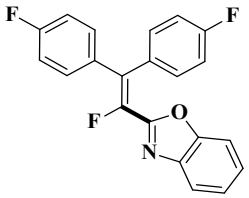
2-(2,2-Diphenyl-1-fluorovinyl)benzo[*d*]oxazole (**3ac**): White solid. Yield: 57%, mp 111.2−112.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.74 (m, 1H), 7.47–7.36 (m, 8H), 7.35–7.27 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 (d, $^2J_{CF}$ = 37.6 Hz), 150.1 (d, $^4J_{CF}$ = 1.0 Hz), 142.7 (d, $^1J_{CF}$ = 246.8 Hz), 140.9, 136.6 (d, $^3J_{CF}$ = 5.0 Hz), 136.5 (d, $^4J_{CF}$ = 1.9 Hz), 131.1 (d, $^2J_{CF}$ = 12.7 Hz), 130.5 (d, $^4J_{CF}$ = 3.0 Hz), 130.2 (d, $^3J_{CF}$ = 5.3 Hz), 128.8, 128.5, 128.4, 128.3, 126.0, 124.9, 120.7, 110.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.3 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{14}FNO$ [M−H]$^+$: 314.0981, found: 314.0985.



3ac

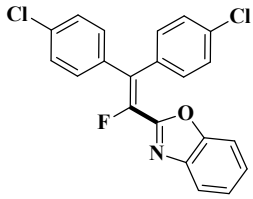
2-(2,2-Di-4-fluorophenyl-1-fluorovinyl)benzo[*d*]oxazole (**3bc**): White solid. Yield: 58%, mp 106.3−107.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75−7.73 (m, 1H), 7.44−7.41 (m, 2H), 7.36−7.33 (m, 3H), 7.27−7.24 (m, 2H), 7.13−7.08 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{CF}$ = 247.0 Hz), 162.8 (d, $^1J_{CF}$ = 248.8 Hz),

156.6 (d, $^2J_{CF}$ = 37.4 Hz), 150.1, 142.8 (d, $^1J_{CF}$ = 247.3 Hz), 140.8, 132.3 (dd, $^3J_{CF}$ = 8.2 Hz, $^4J_{CF}$ = 3.1 Hz), 132.1 (dd, $^3J_{CF}$ = 8.3 Hz, $^4J_{CF}$ = 5.6 Hz), 130.5−130.1 (m), 128.9 (d, $^2J_{CF}$ = 13.1 Hz), 128.5−128.4 (m), 126.2, 125.0, 120.7, 115.6 (d, $^2J_{CF}$ = 21.6 Hz), 115.5 (d, $^2J_{CF}$ = 21.5 Hz), 110.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.3 to −111.4 (m, 1F), −112.4 to −112.5 (m, 1F), −120.0 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{12}F_3NO$ $[M-H]^+$: 350.0793, found: 350.0798.



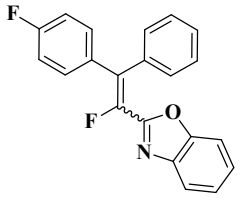
3bc

2-(2,2-Di-4-chlorophenyl-1-fluorovinyl)benzo[*d*]oxazole (**3cc**): White solid. Yield: 54%, mp 158.5−159.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.73 (m, 1H), 7.40–7.35 (m, 9H), 7.22–7.20 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4 (d, $^2J_{CF}$ = 37.2 Hz), 150.1, 143.1 (d, $^1J_{CF}$ = 248.8 Hz), 140.8, 135.1, 134.9, 134.7 (d, $^3J_{CF}$ = 5.2 Hz), 134.5 (d, $^4J_{CF}$ = 1.9 Hz), 131.8 (d, $^4J_{CF}$ = 3.0 Hz), 131.4 (d, $^3J_{CF}$ = 5.6 Hz), 128.8, 128.7, 128.6 (d, $^2J_{CF}$ = 11.7 Hz), 126.4, 125.1, 120.8, 110.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −118.7 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{12}Cl_2FNO$ $[M-H]^+$: 382.0202, found: 382.0208.



3cc

(*E/Z*)-2-(2-(4-Fluorophenyl)-2-phenyl-1-fluorovinyl)benzo[*d*]oxazole (**3gc**): White solid. Yield: 70%. A mixture of *E*- and *Z*-isomers (4:3, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.73 (m, 1H), 7.46–7.32 (m, 8H), 7.28–7.25 (m, 2H), 7.12–7.07 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{CF}$ = 246.7 Hz), 162.7 (d, $^1J_{CF}$ = 250.0 Hz), 156.9 (d, $^2J_{CF}$ = 37.6 Hz), 156.8 (d, $^2J_{CF}$ = 37.4 Hz), 150.1, 140.9, 142.8 (d, $^1J_{CF}$ = 248.0 Hz), 142.7 ($^1J_{CF}$ = 246.8 Hz), 136.4, 136.3, 136.2, 136.1, 132.6–132.5 (m), 132.5–132.4 (m), 132.3 (dd, $^3J_{CF}$ = 8.3 Hz, $^4J_{CF}$ = 3.2 Hz), 132.1 (dd, $^3J_{CF}$ = 8.3 Hz, $^4J_{CF}$ = 5.7 Hz), 130.4 (d, $^3J_{CF}$ = 3.0 Hz), 130.2 (d, $^3J_{CF}$ = 5.3 Hz), 130.1 (d, $^2J_{CF}$ = 13.3 Hz), 130.0 (d, $^2J_{CF}$ = 12.4 Hz), 128.9, 128.7, 128.5, 128.4, 126.1, 126.0, 125.0, 124.9, 120.8, 120.7, 115.5 (d, $^2J_{CF}$ = 21.6 Hz), 115.4 (d, $^2J_{CF}$ = 21.5 Hz), 110.7, 110.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.6 to −111.7 (m), −112.8 to −112.9 (m), −119.9 (s), −120.6 (s) ppm; HRMS (EI): calcd for $C_{21}H_{13}F_2NO$ $[M-H]^+$: 332.0887, found: 332.0891.



3gc

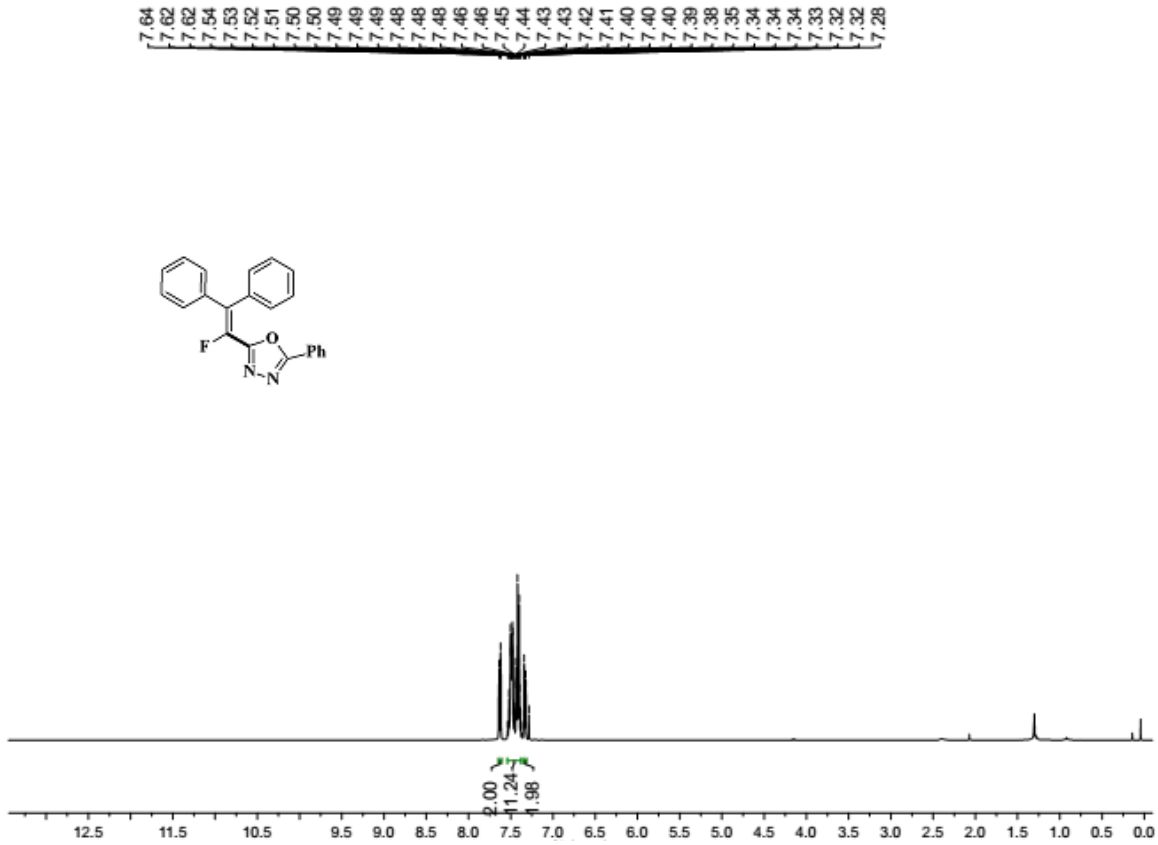
References

1 M. Hu, Z. He, B. Gao, L. Li, C. Ni and J. Hu, *J. Am. Chem. Soc.*, 2013, **135**, 17302.

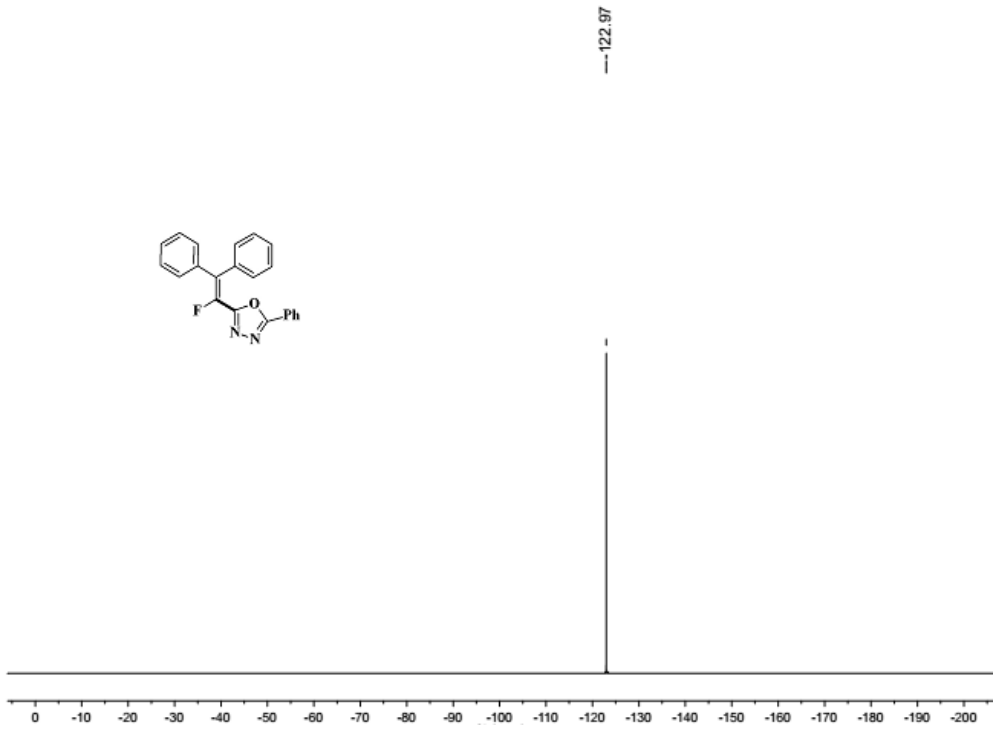
2 T. Kawano, K. Hirano, T. Satoh and M. Miura, *J. Am. Chem. Soc.*, 2010, **132**, 6900.

^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of compounds 3

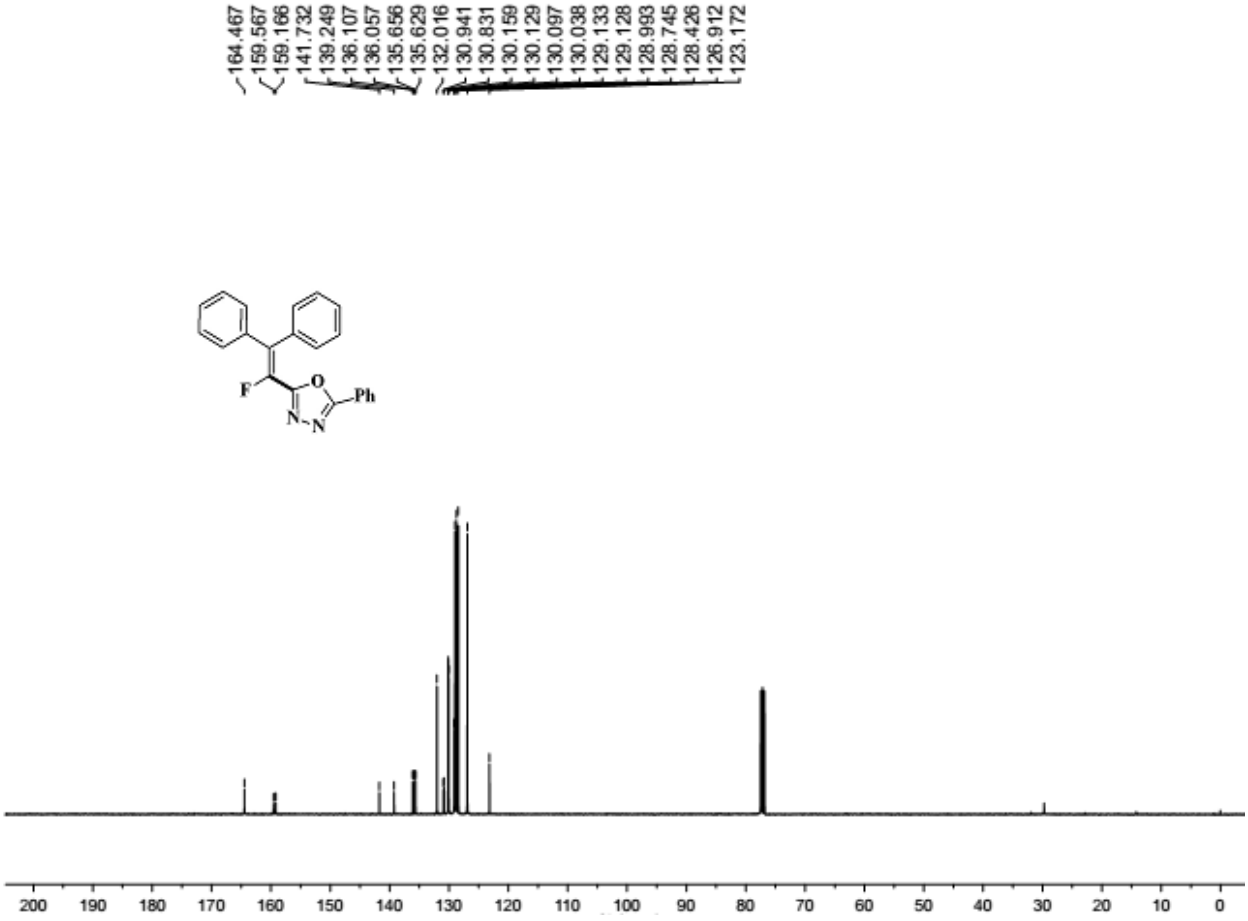
^{1}H NMR Spectrum of 3aa



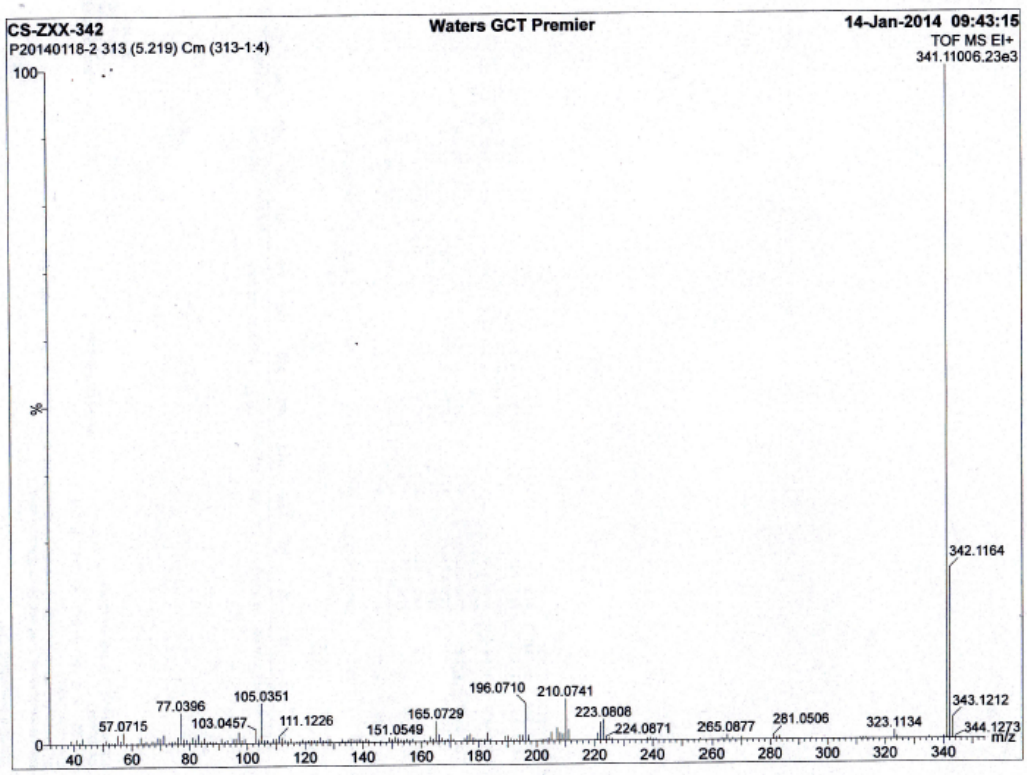
^{19}F NMR Spectrum of 3aa



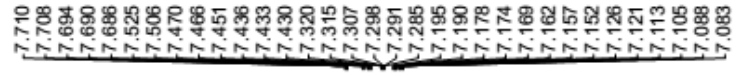
^{13}C NMR Spectrum of 3aa

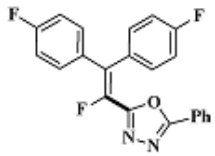


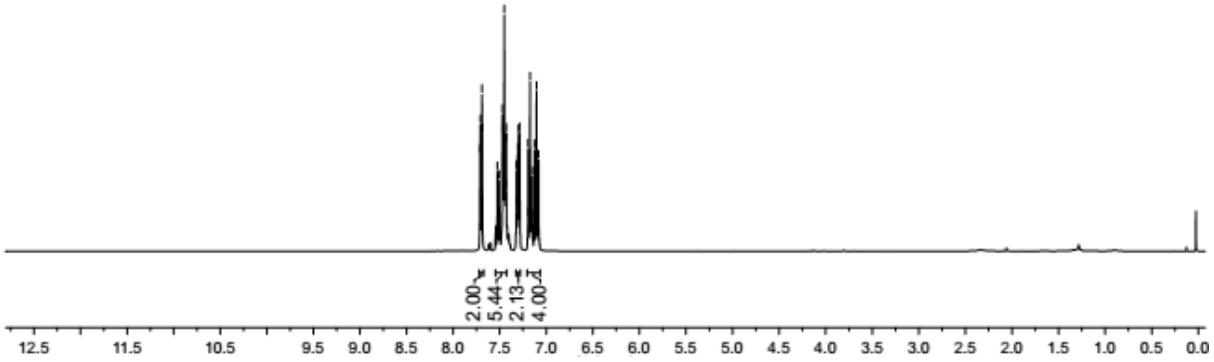
HRMS (EI) of 3aa



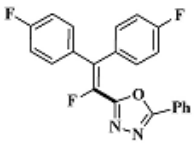
[1]H NMR Spectrum of 3ba

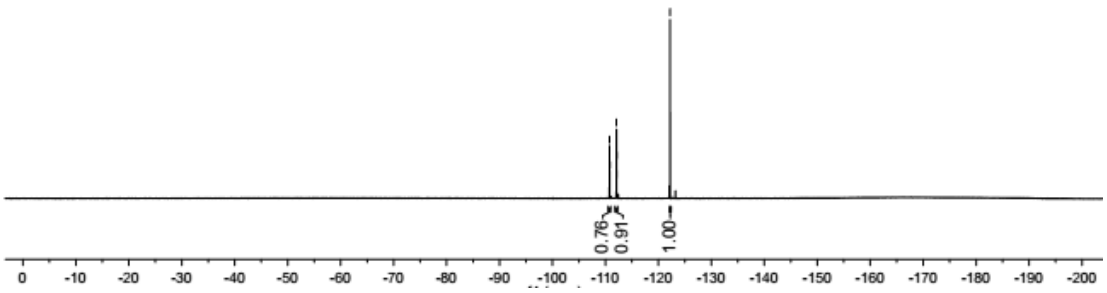




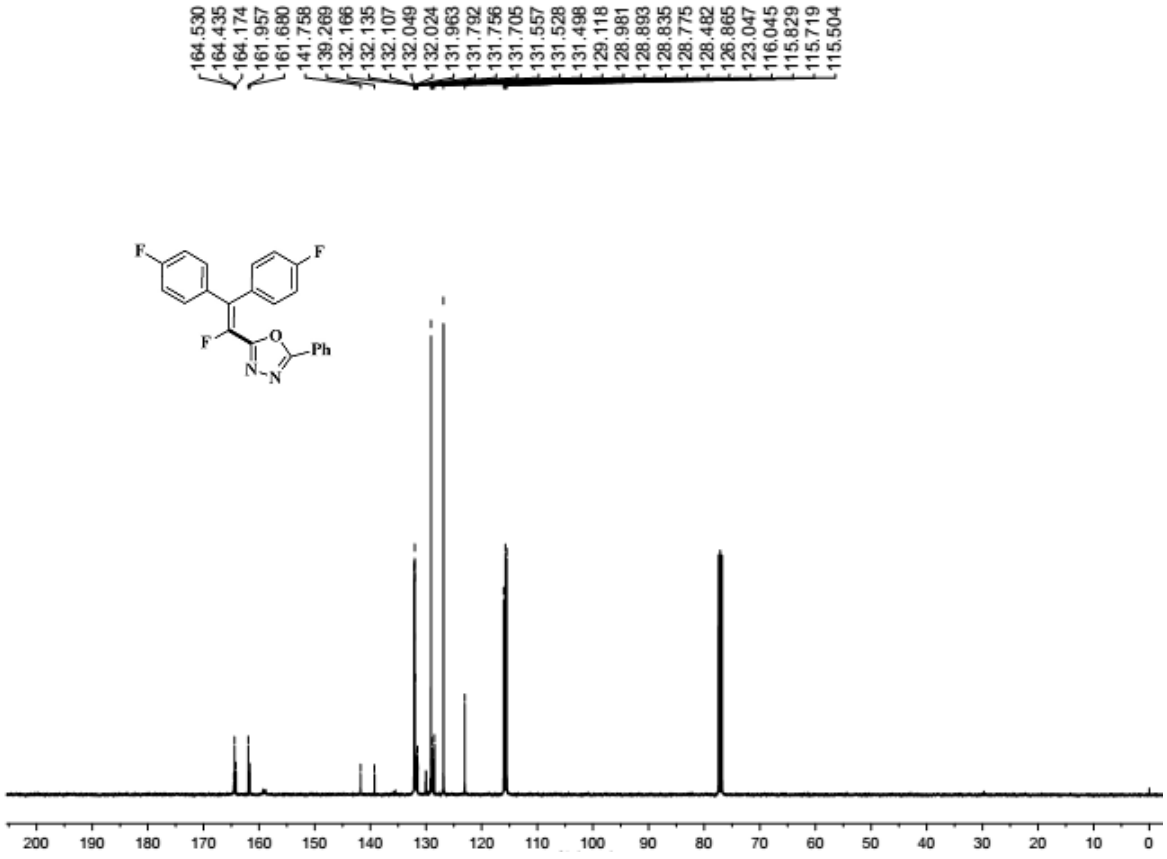


[19]F NMR Spectrum of 3ba

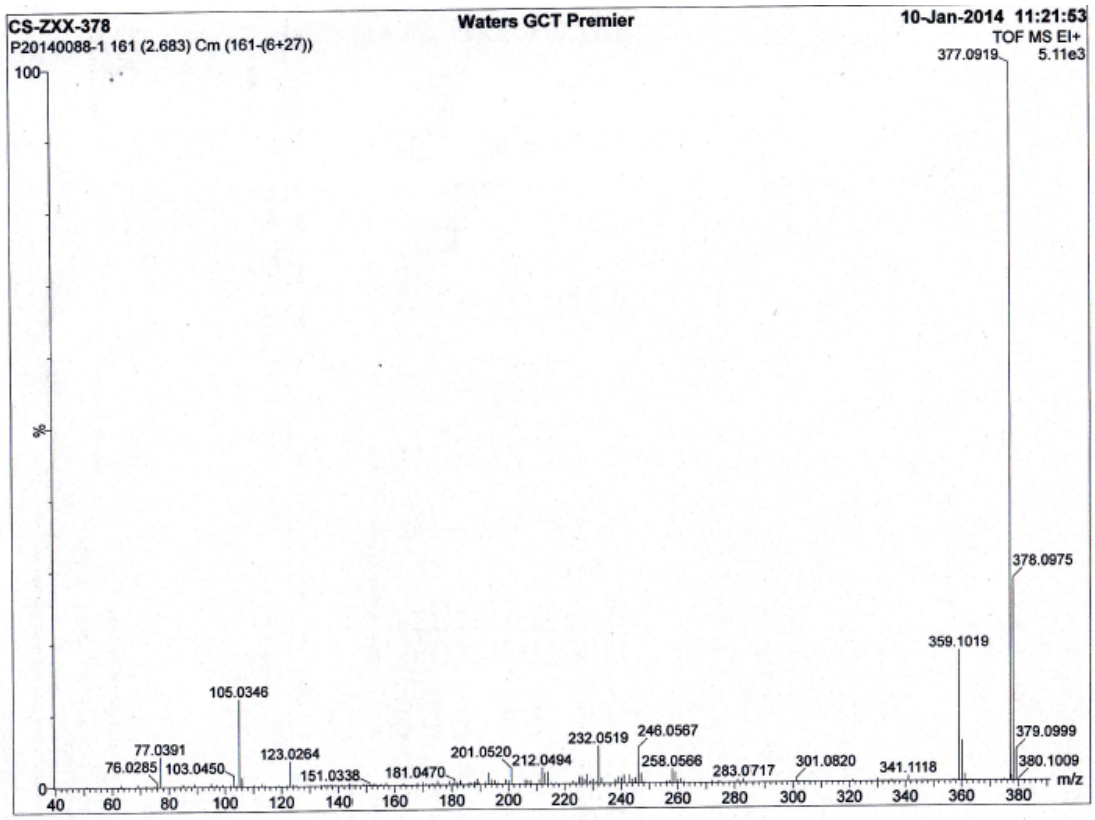




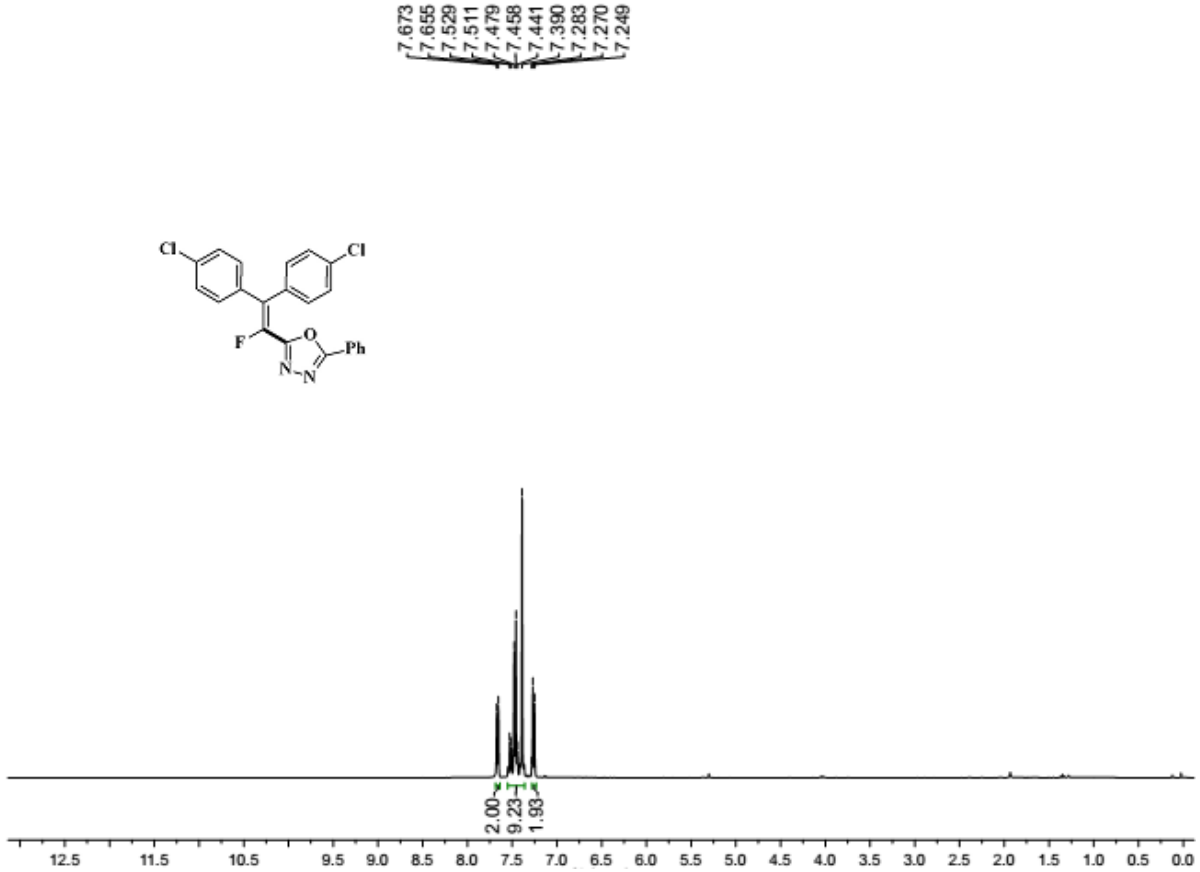
^{13}C NMR Spectrum of 3ba



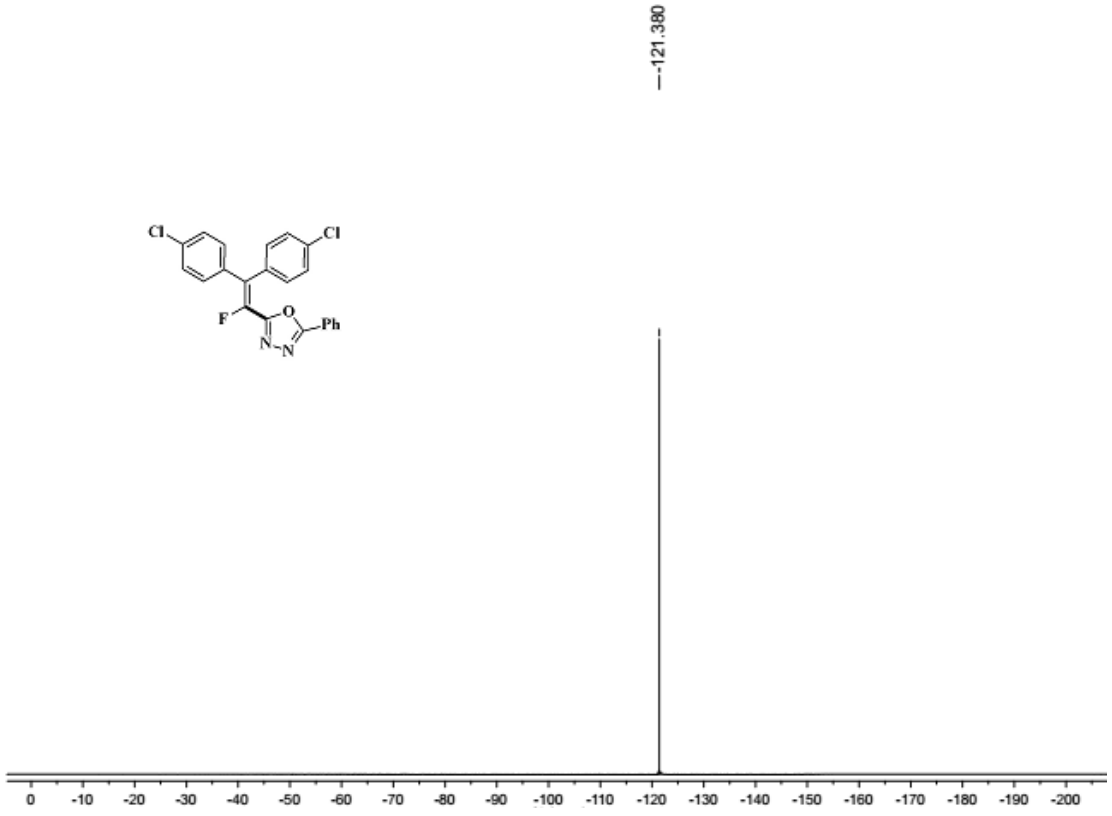
HRMS (EI) of 3ba



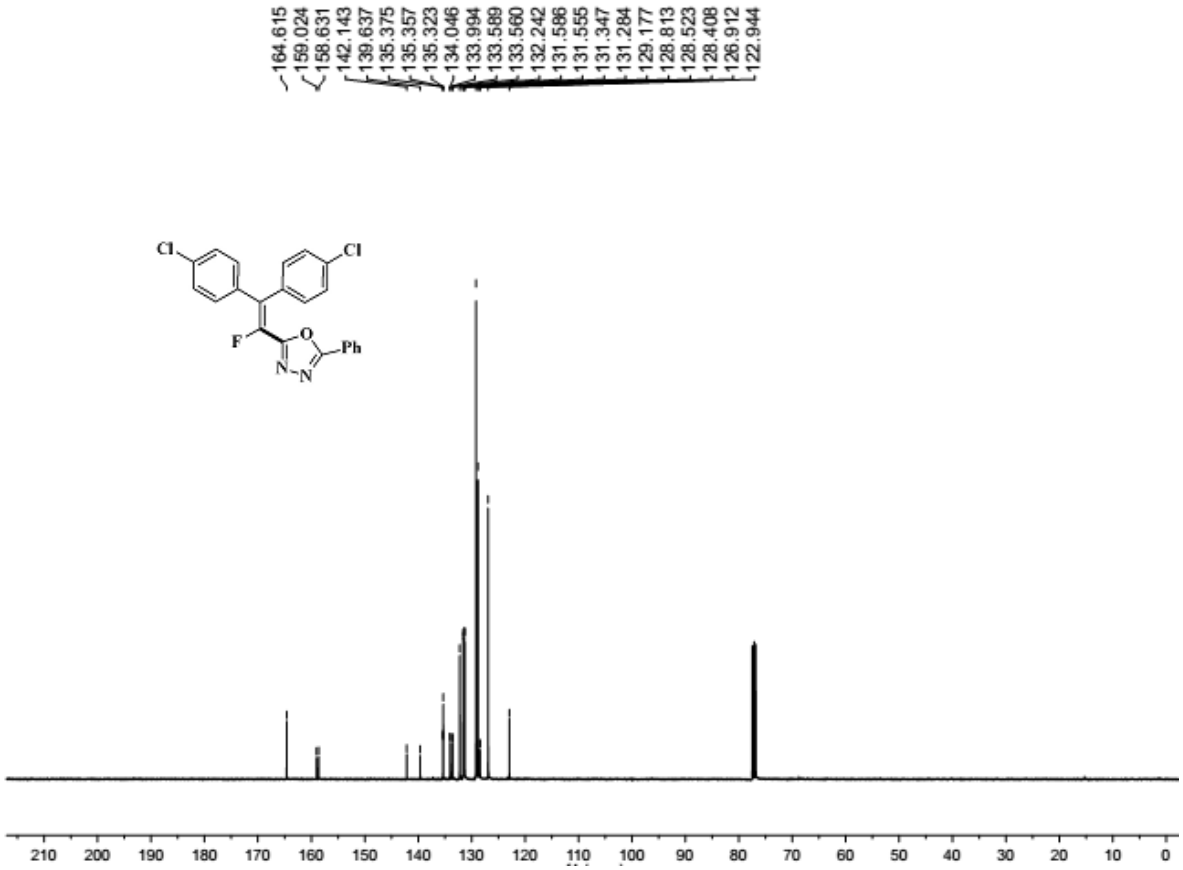
^{1}H NMR Spectrum of 3ca



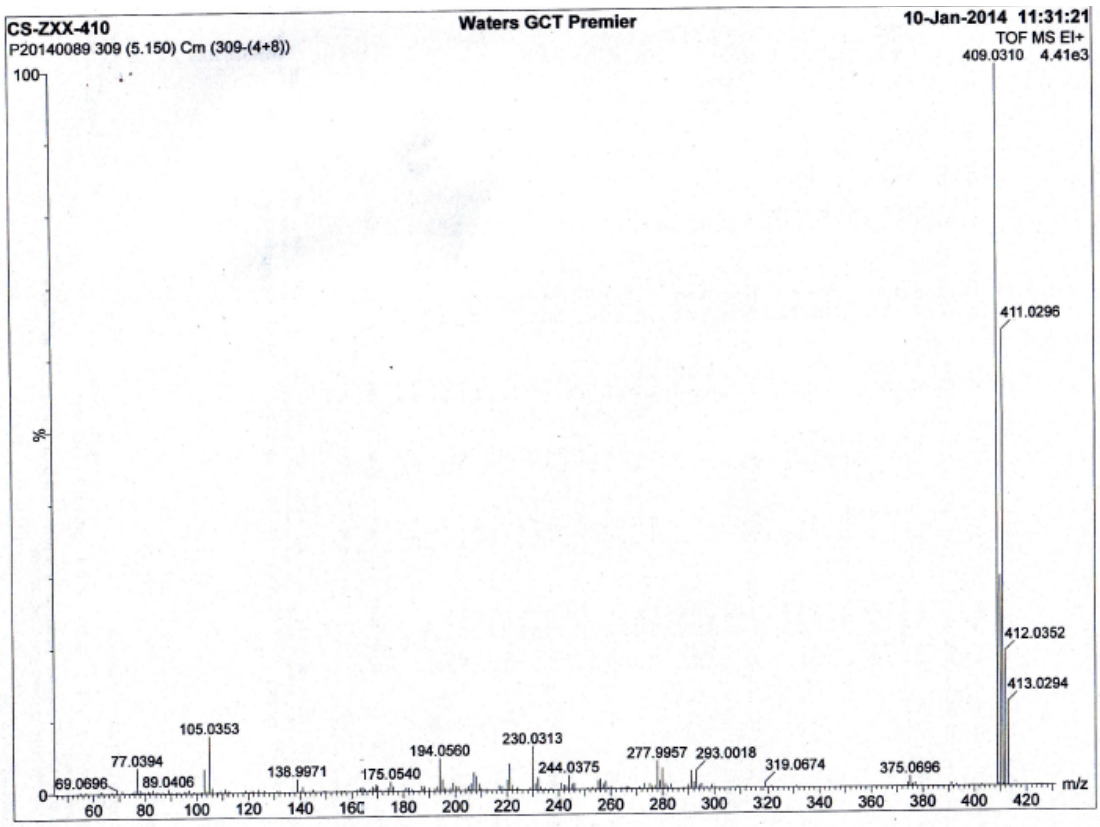
^{19}F NMR Spectrum of 3ca



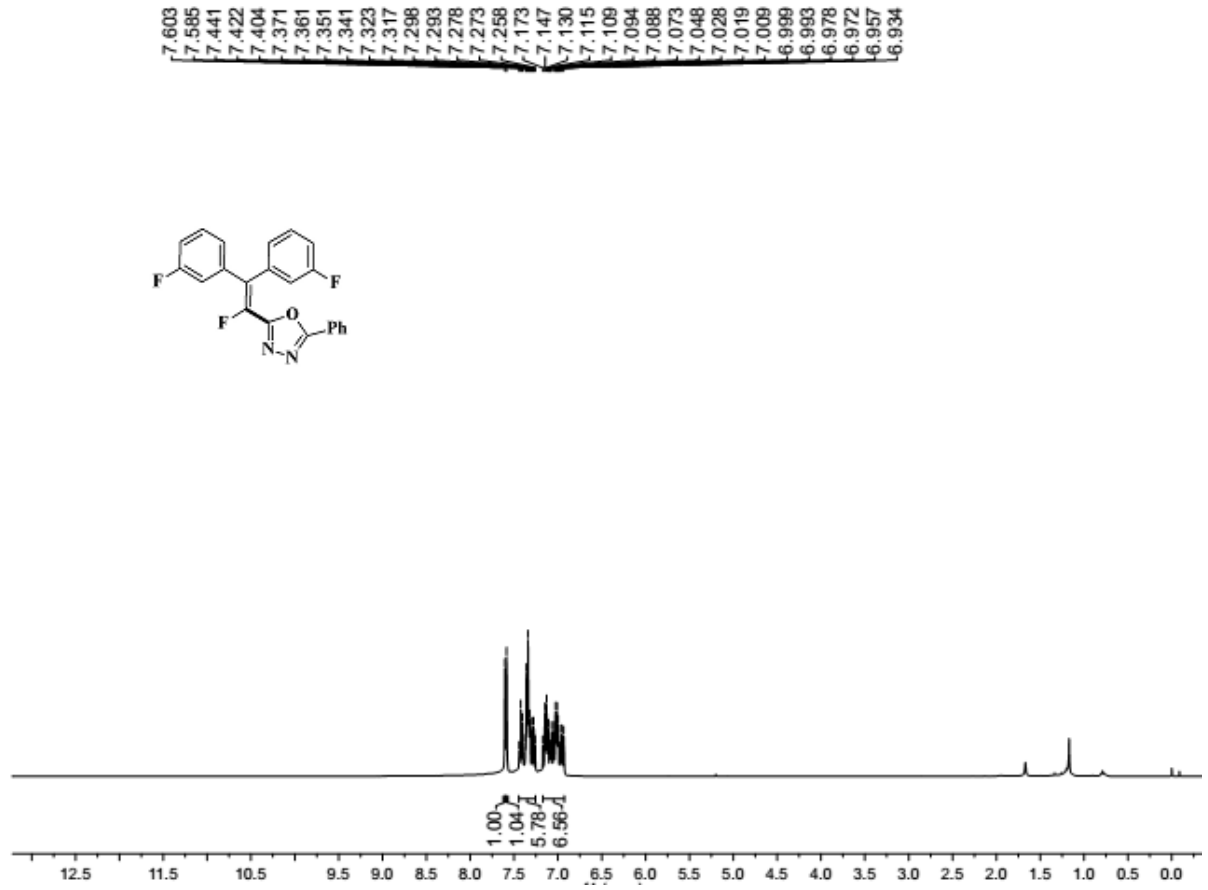
^{13}C NMR Spectrum of 3ca



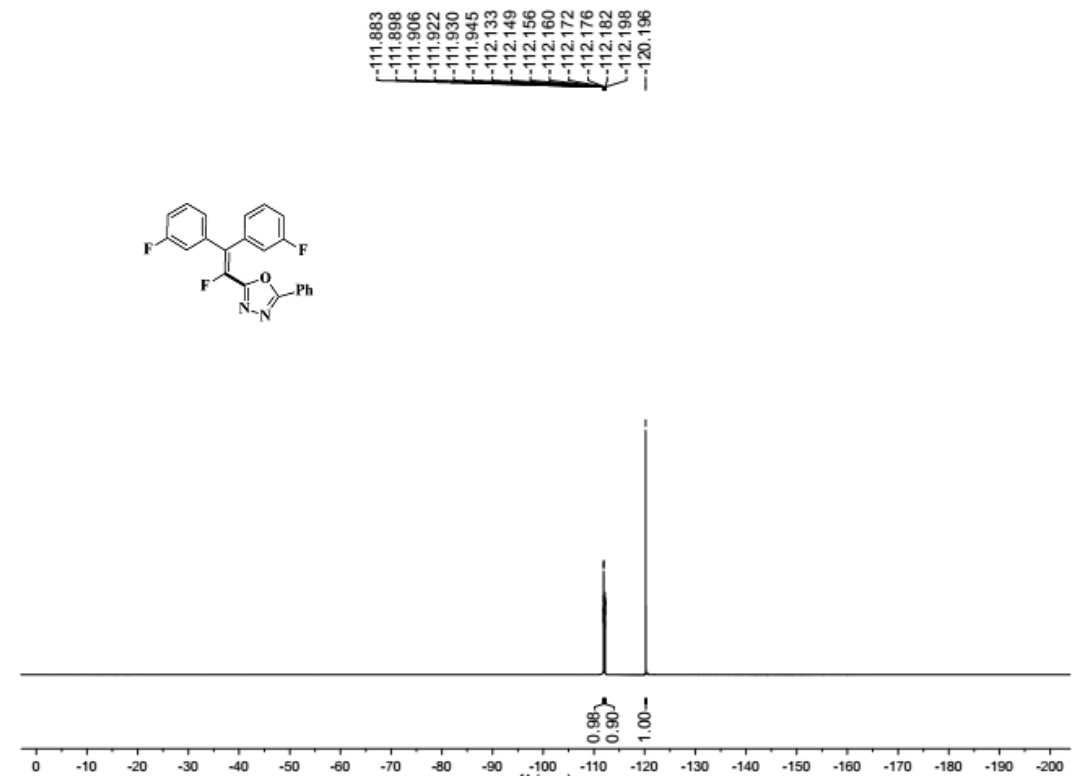
HRMS (EI) of 3ca



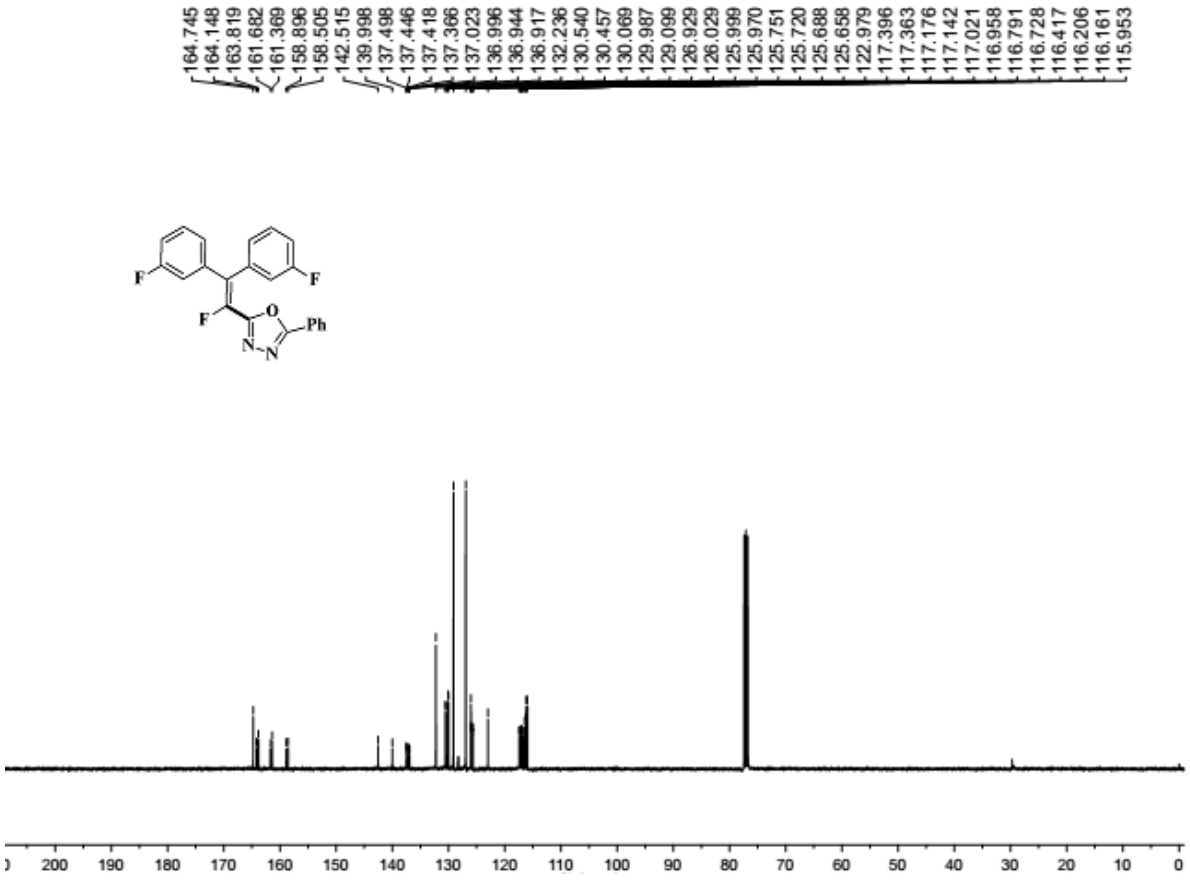
^{1}H NMR Spectrum of 3da



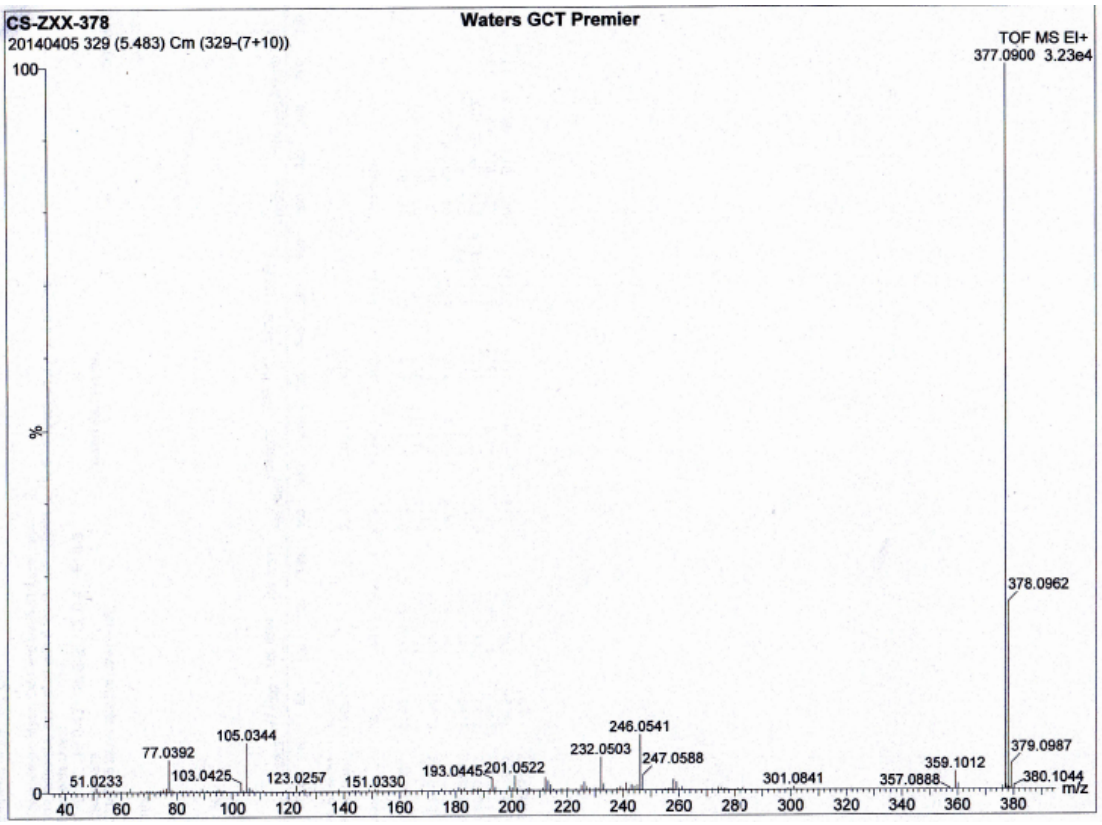
^{19}F NMR Spectrum of 3da



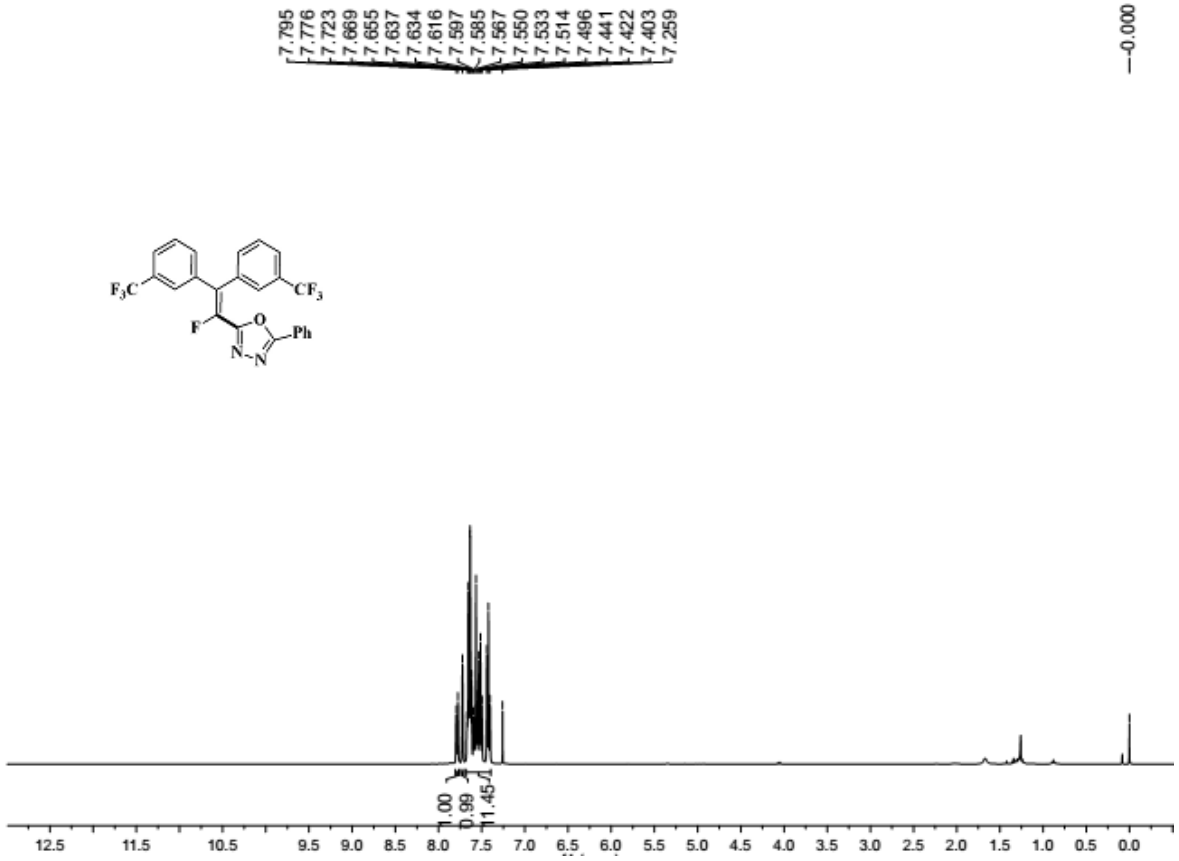
^{13}C NMR Spectrum of 3da



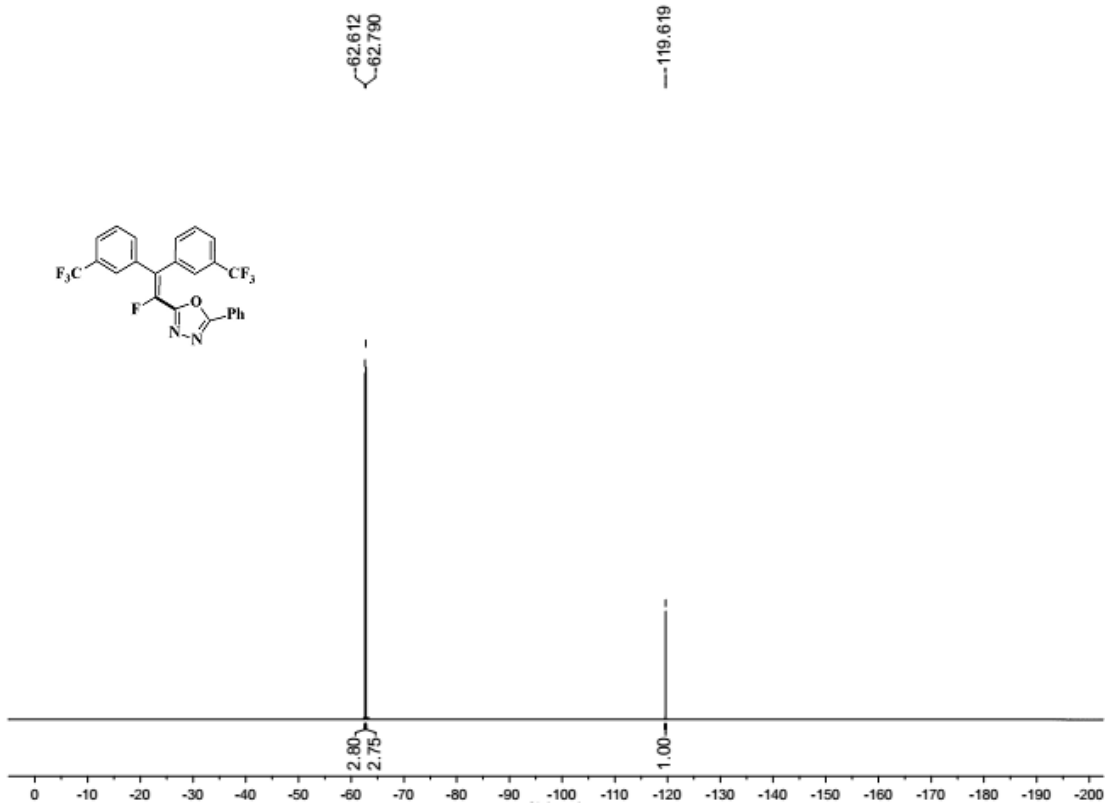
HRMS (EI) of 3da



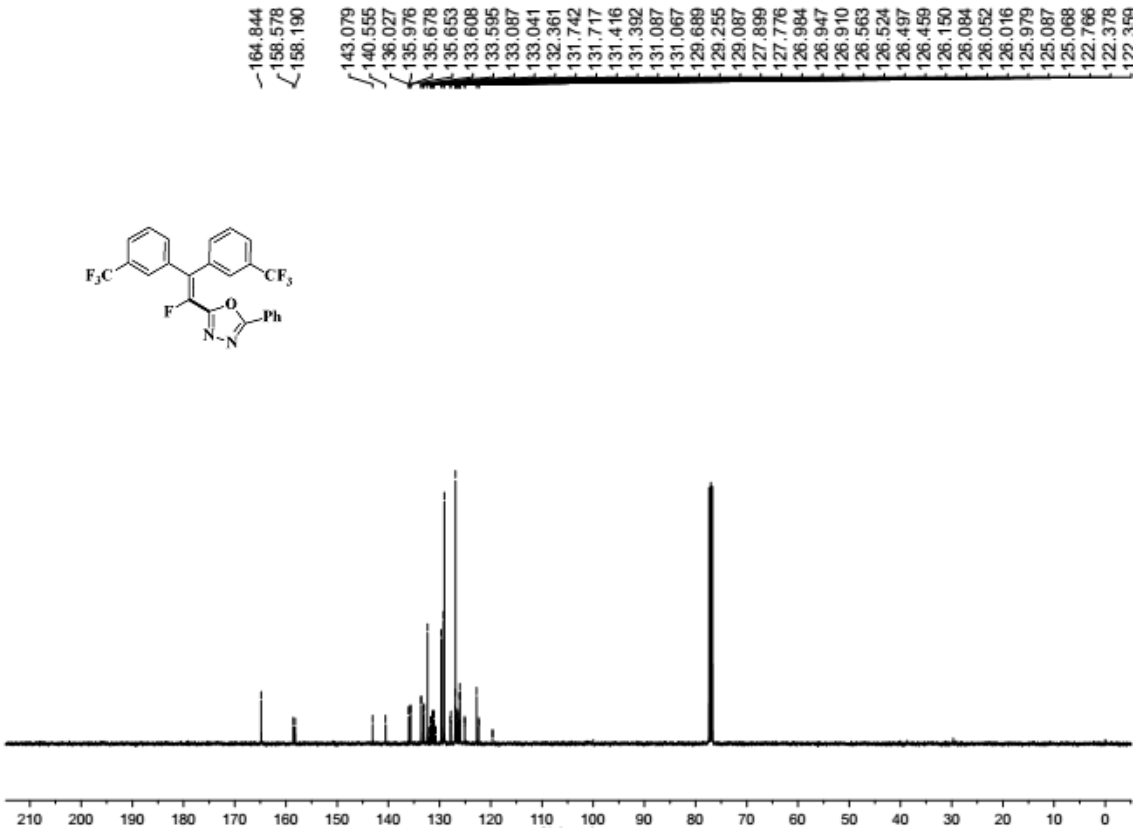
^{1}H NMR Spectrum of 3ea



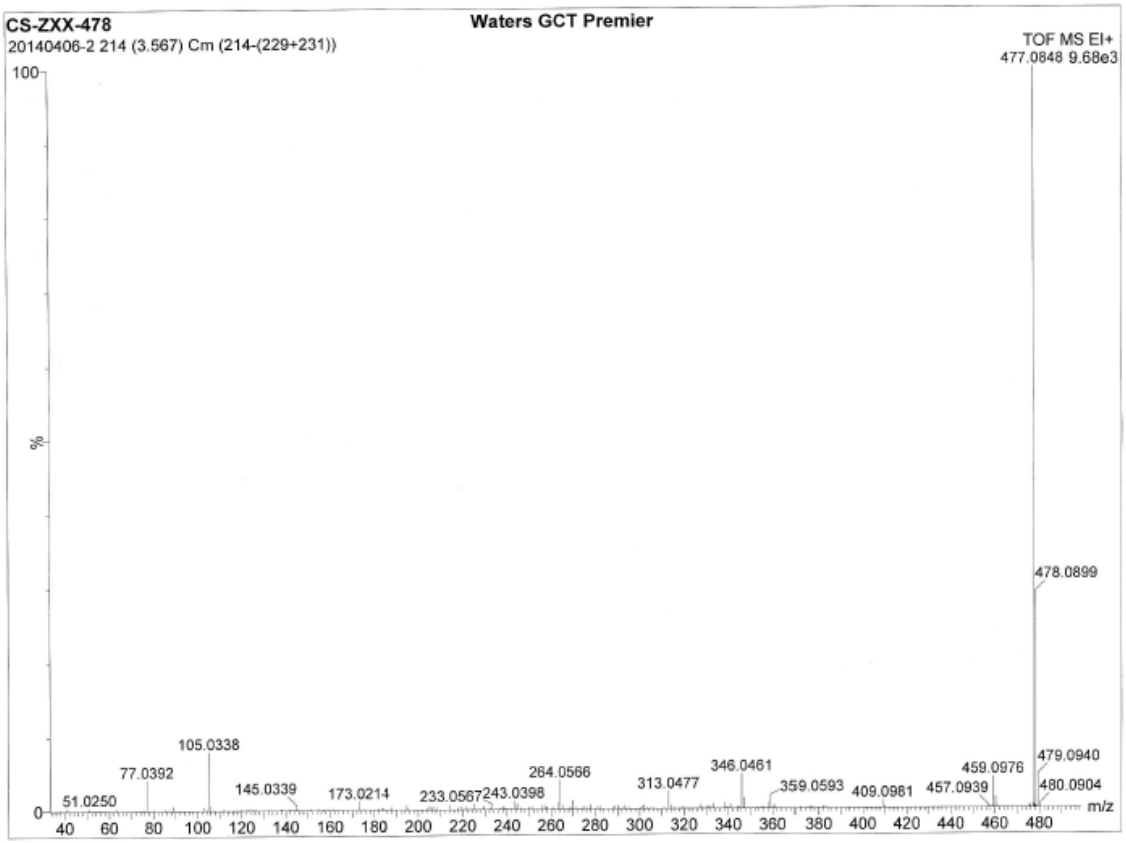
^{19}F NMR Spectrum of 3ea



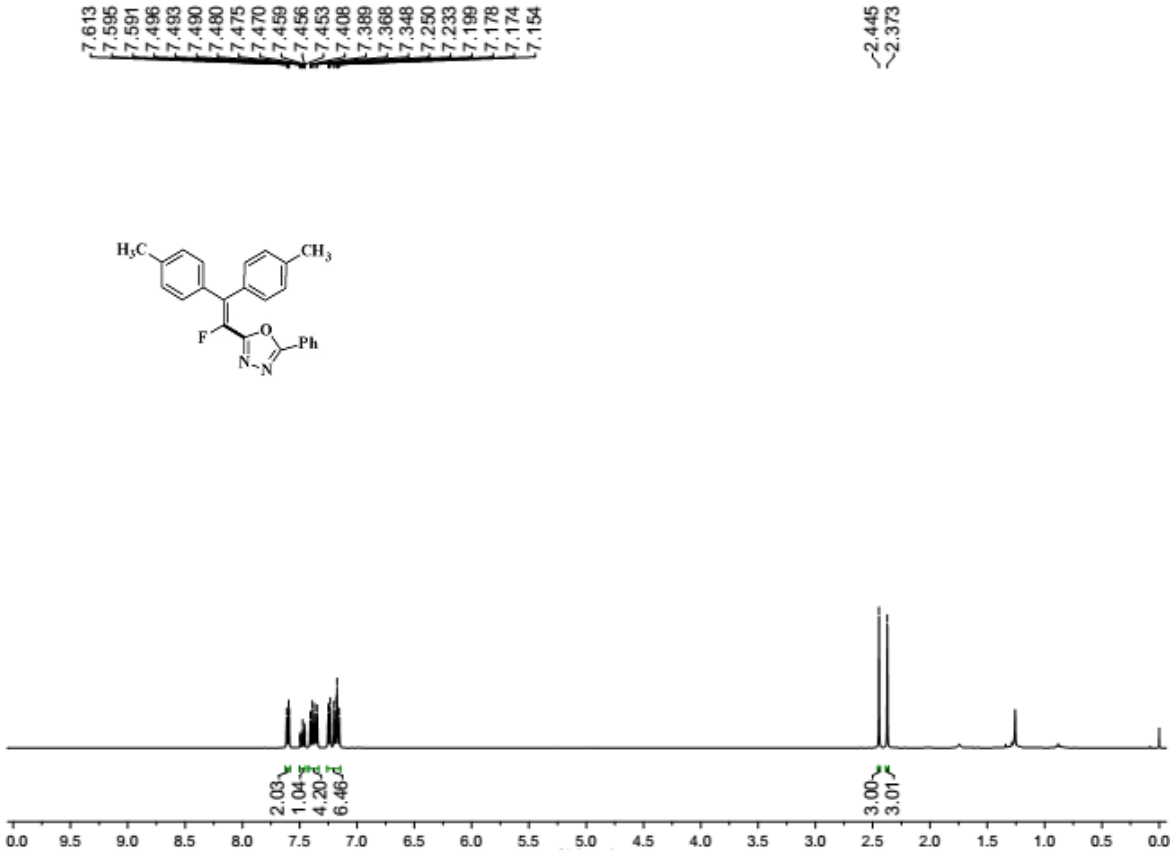
^{13}C NMR Spectrum of 3ea



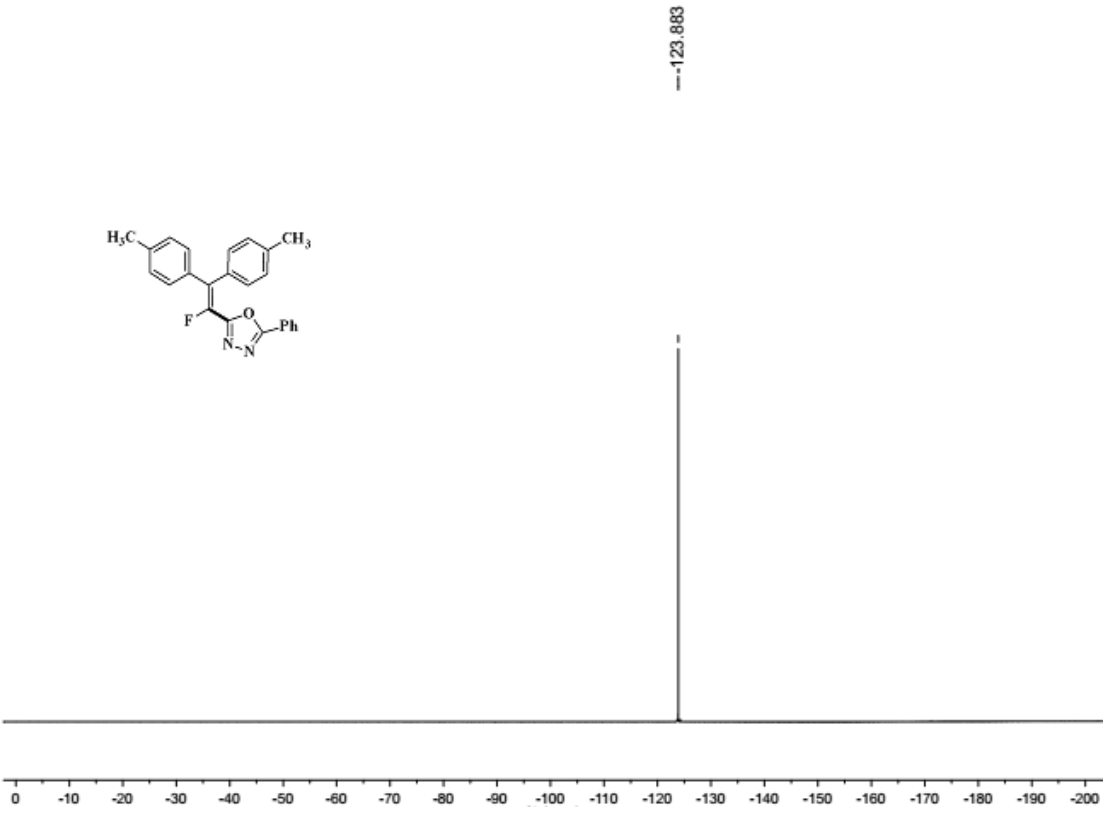
HRMS (EI) of 3ea



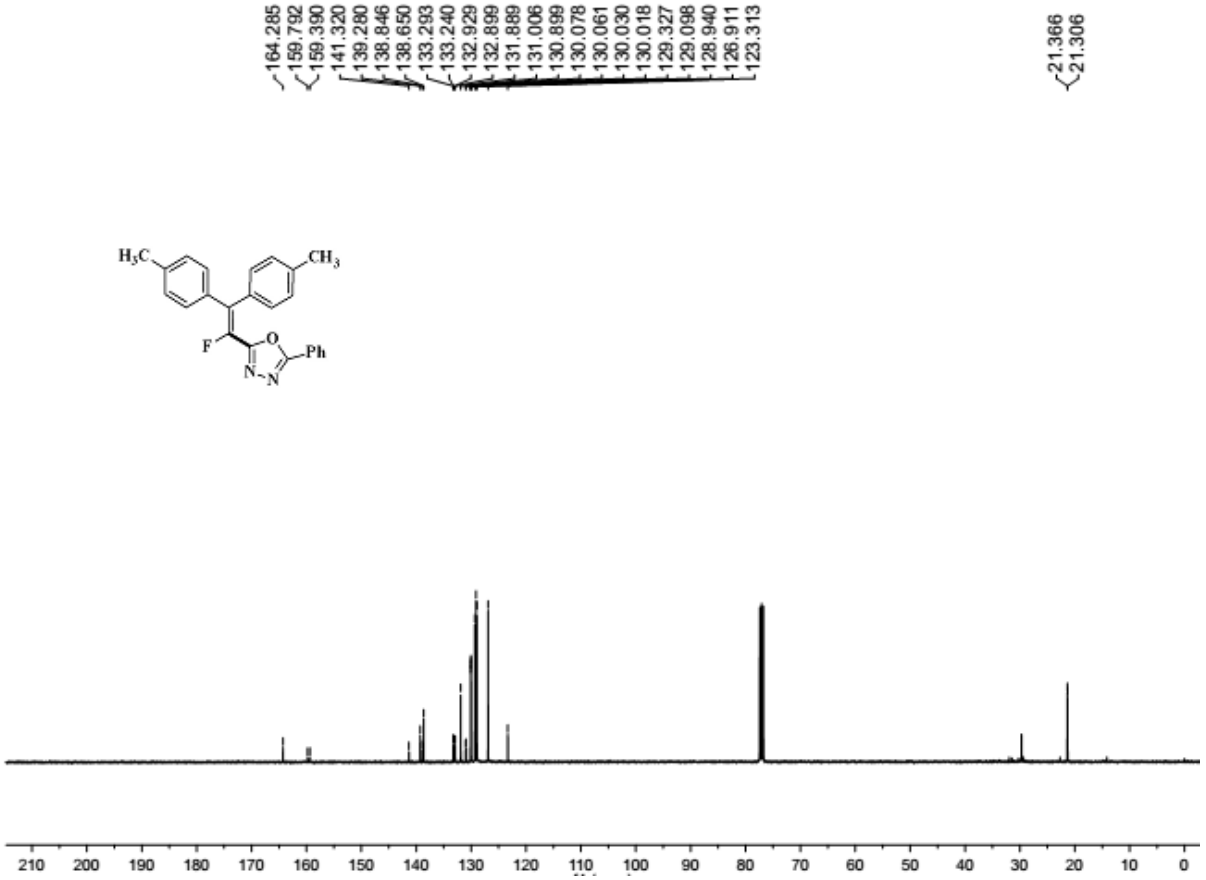
^{1}H NMR Spectrum of 3fa



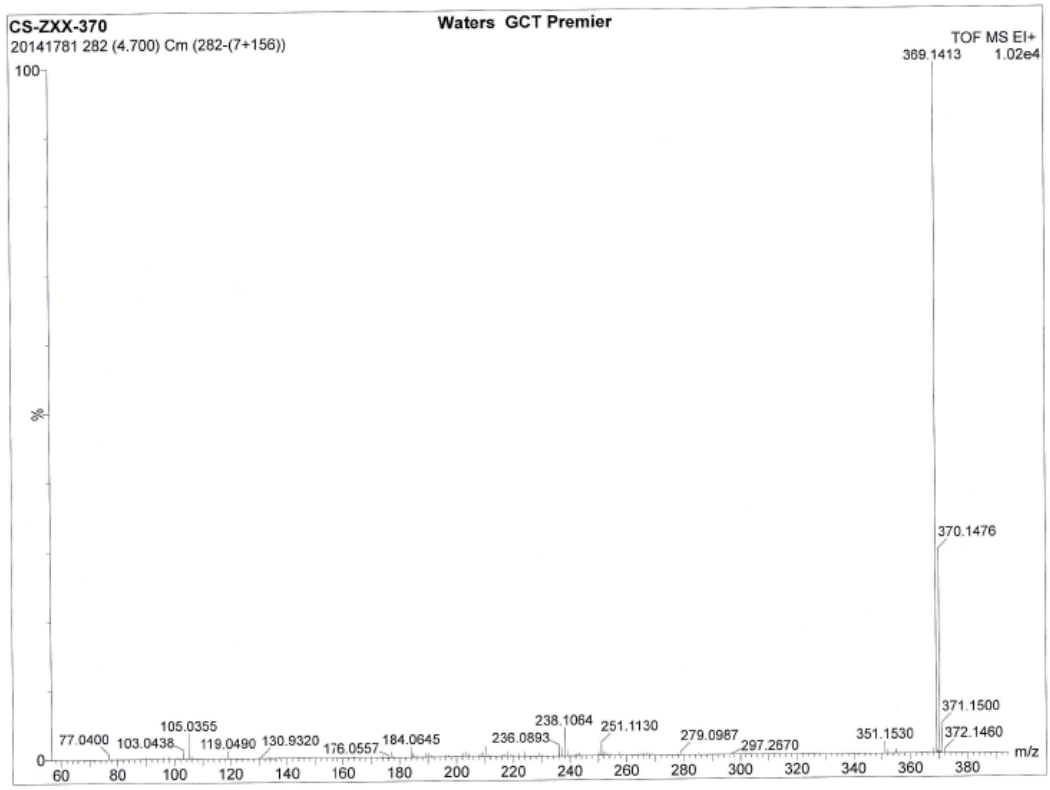
^{19}F NMR Spectrum of 3fa



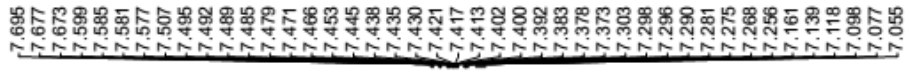
^{13}C NMR Spectrum of 3fa

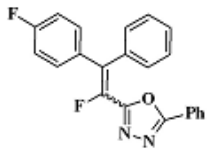


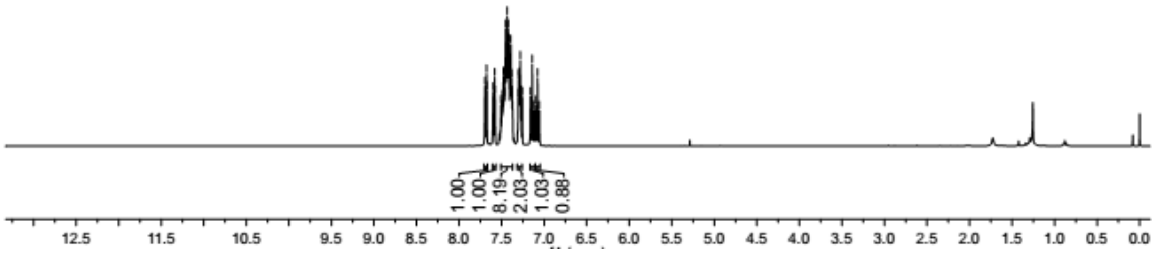
HRMS (EI) of 3fa



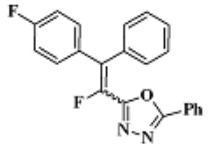
^{1}H NMR Spectrum of 3ga

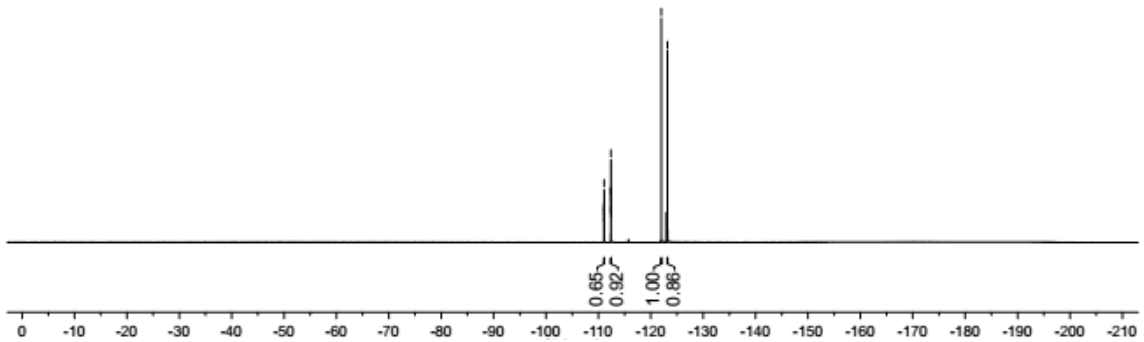




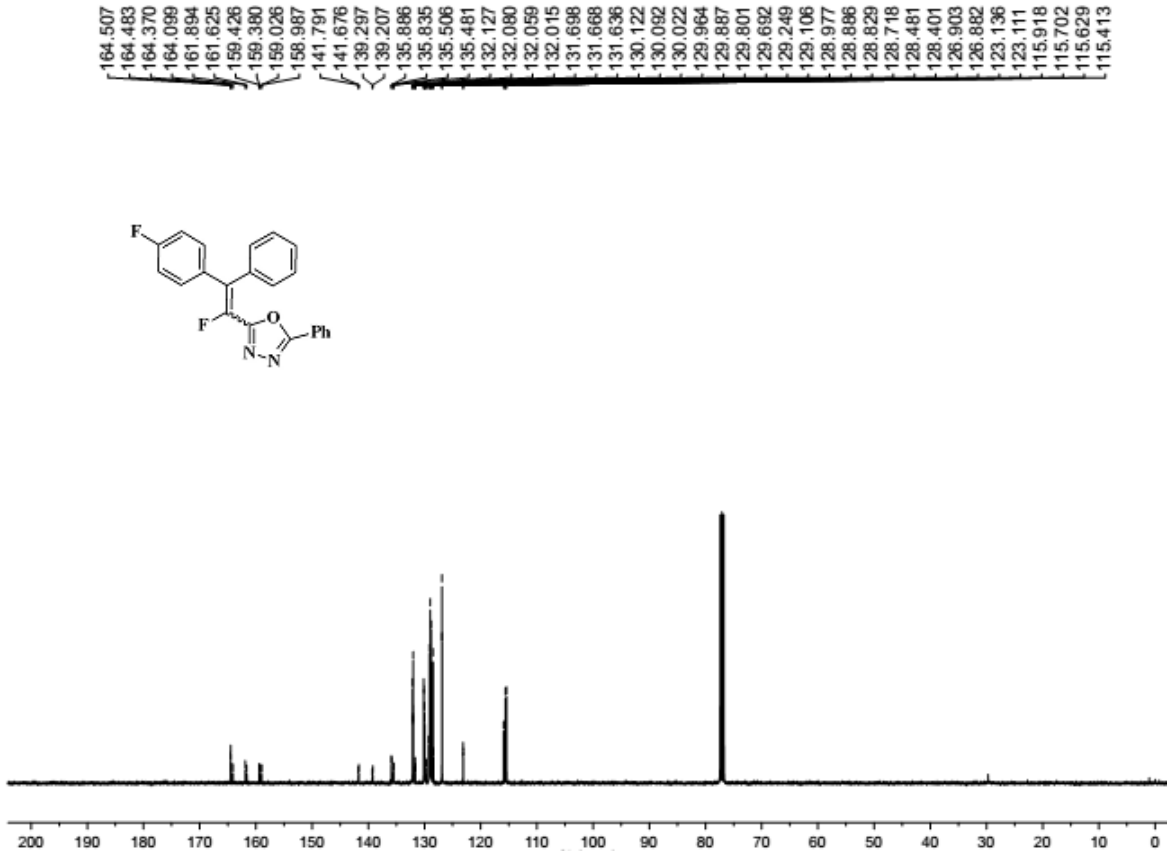


^{19}F NMR Spectrum of 3ga

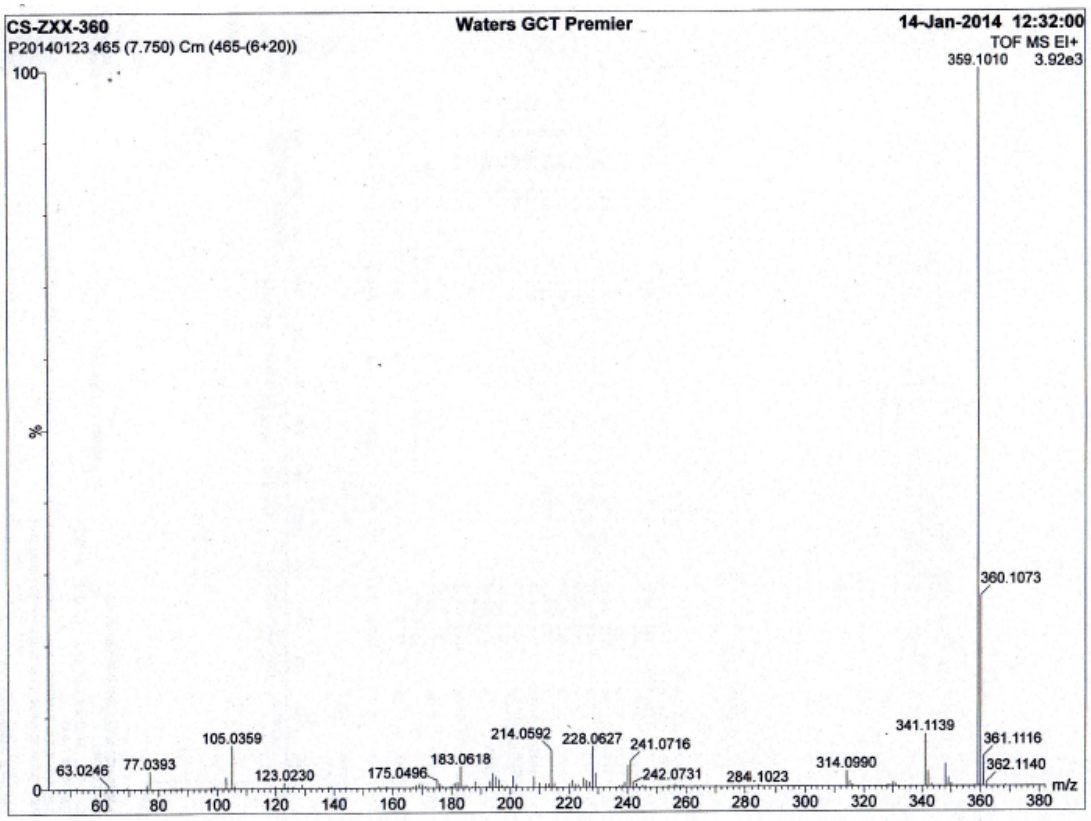




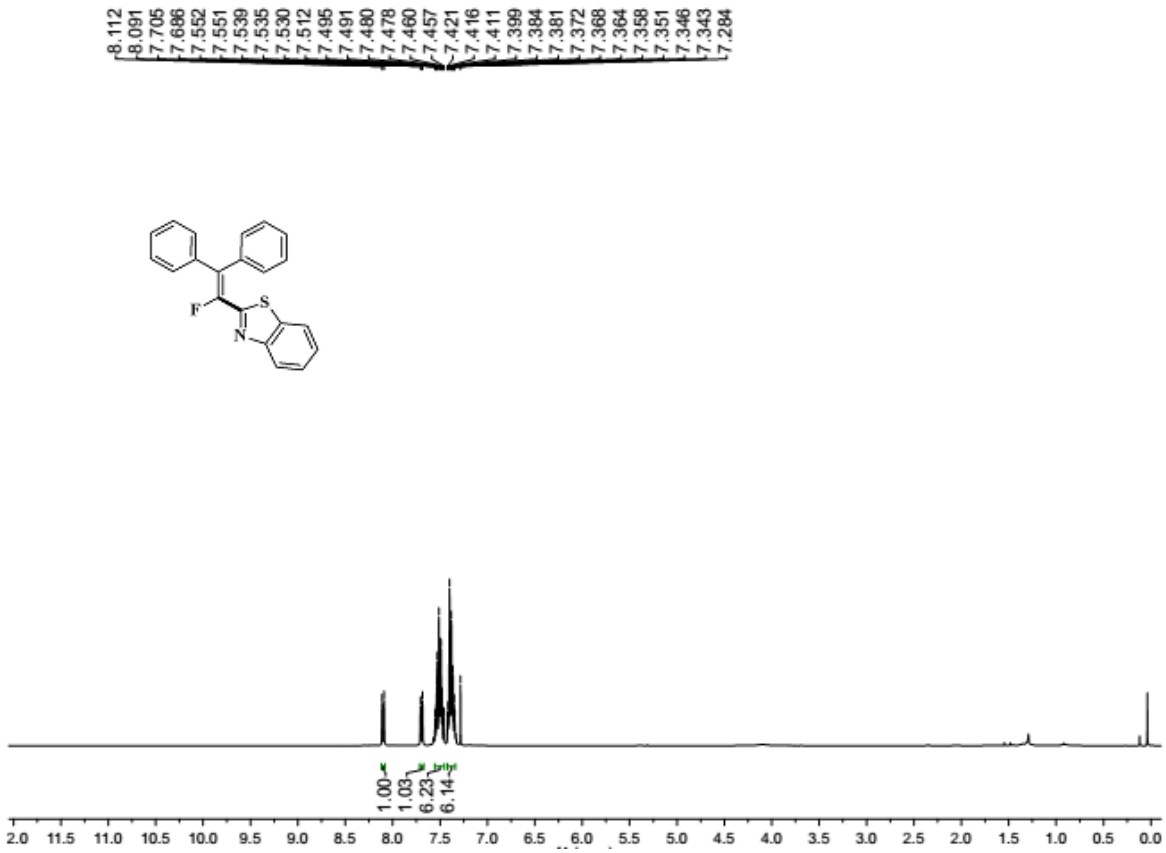
^{13}C NMR Spectrum of 3ga



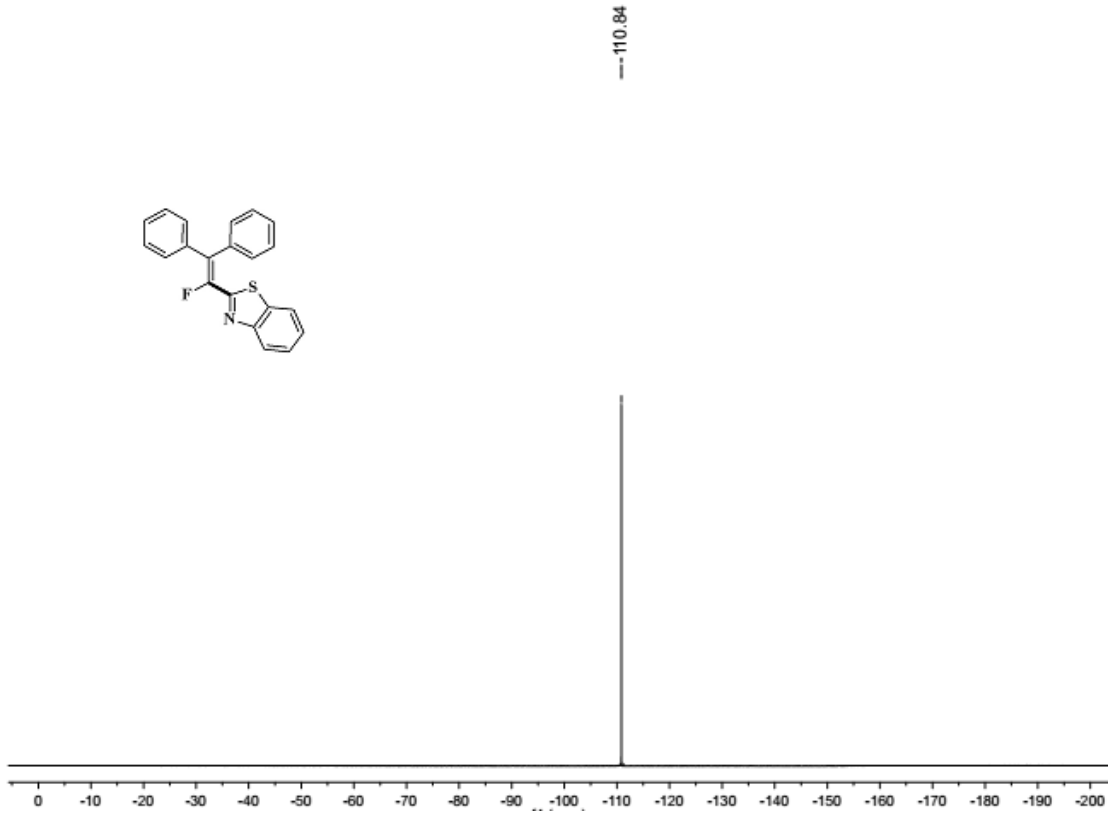
HRMS (EI) of 3ga



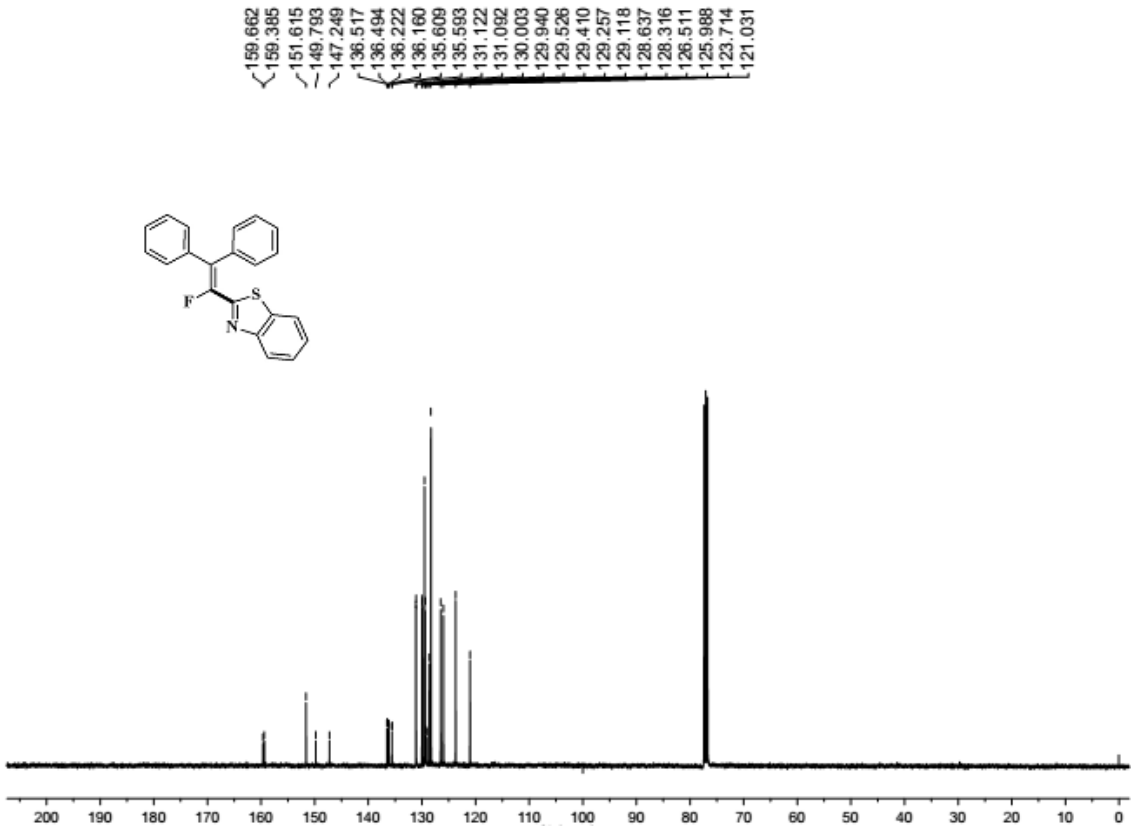
[1]H NMR Spectrum of 3ab



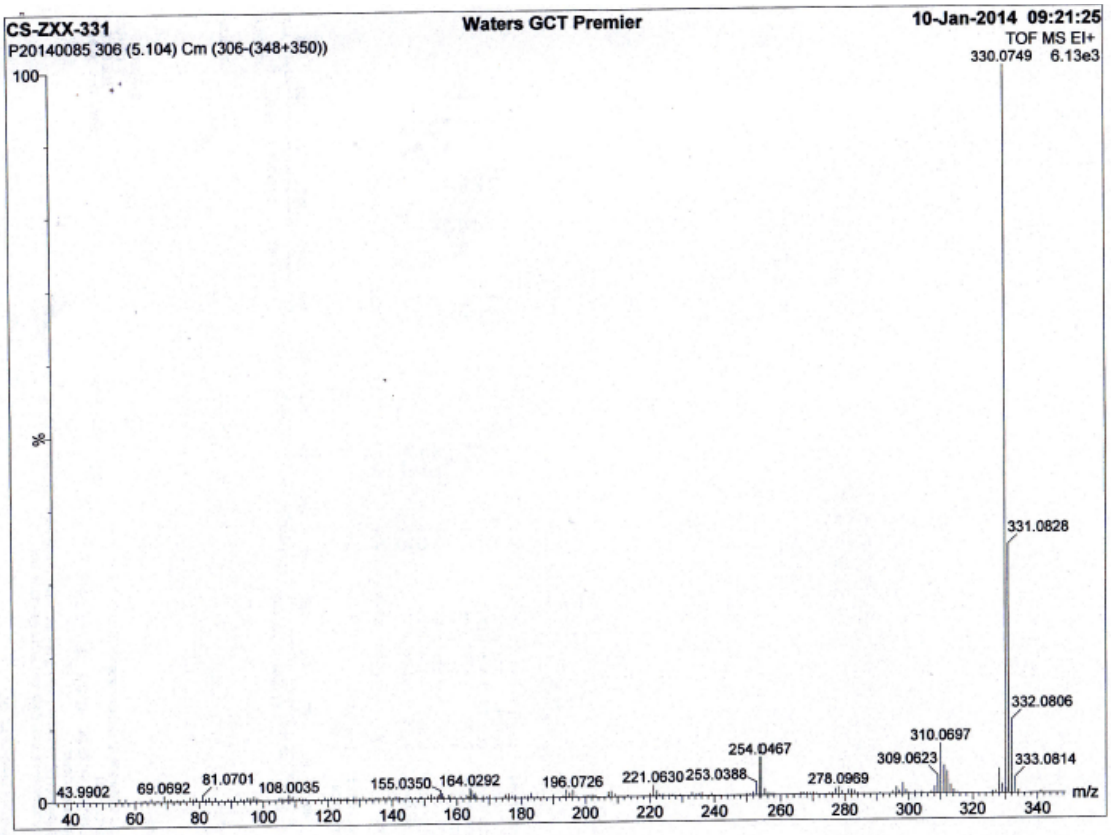
[19]F NMR Spectrum ofb3ab



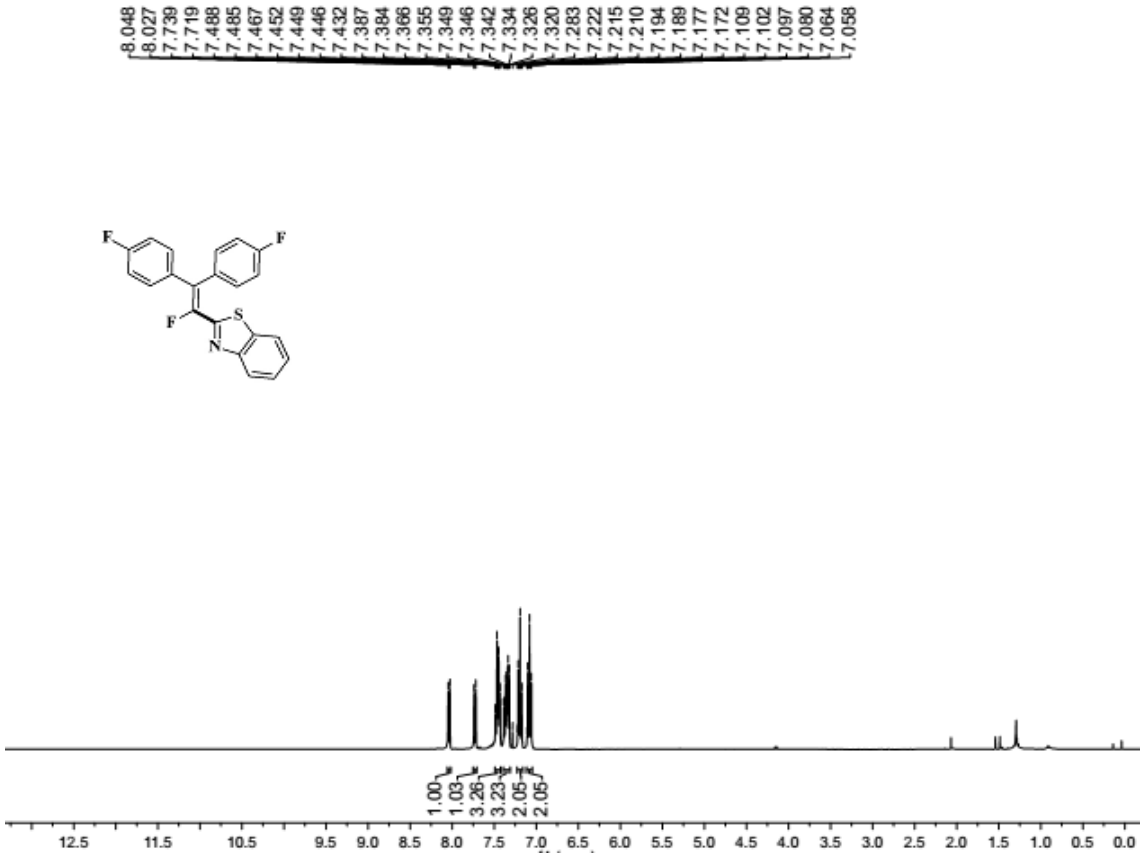
^{13}C NMR Spectrum of 3ab



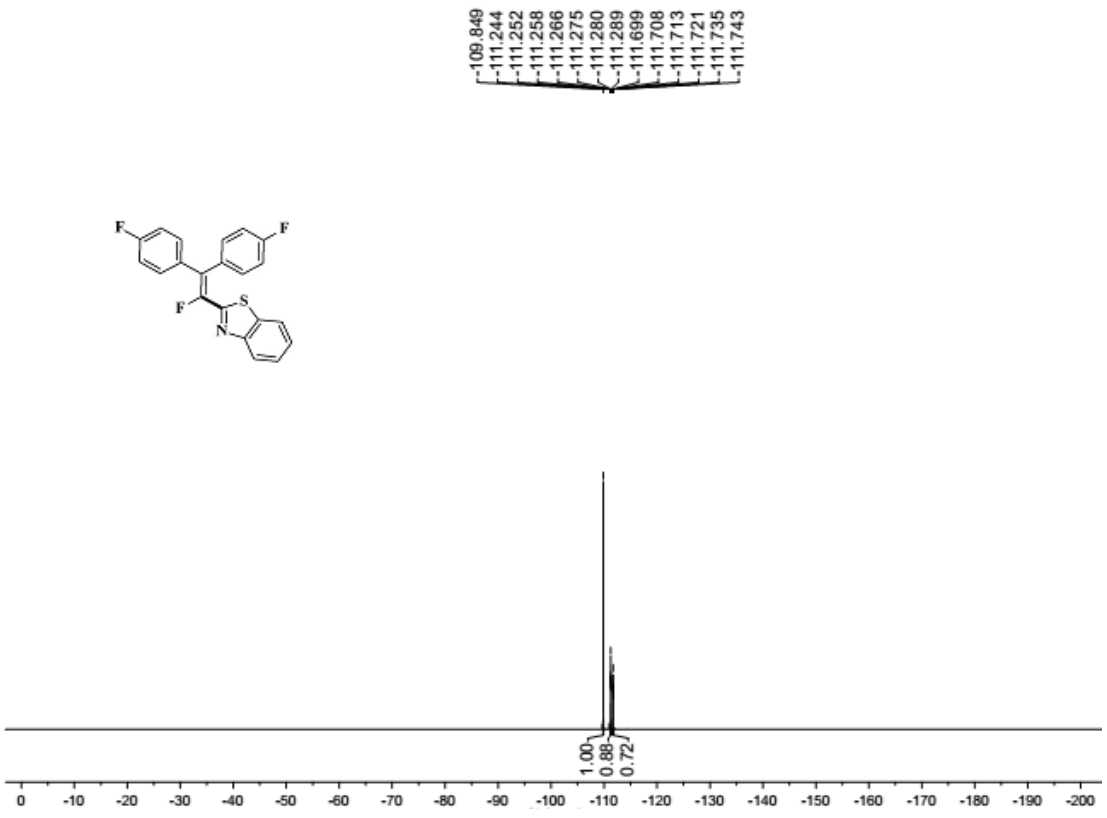
HRMS (EI) of 3ab



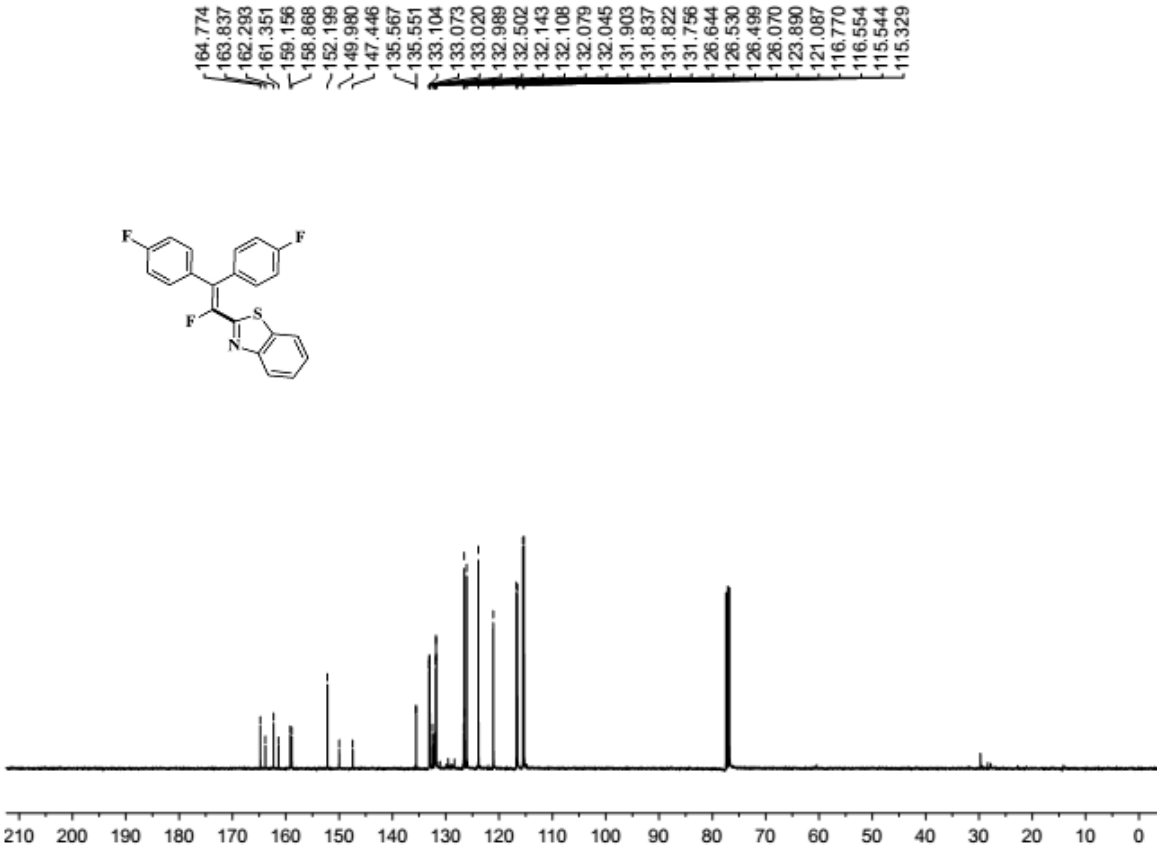
^{1}H NMR Spectrum of 3bb



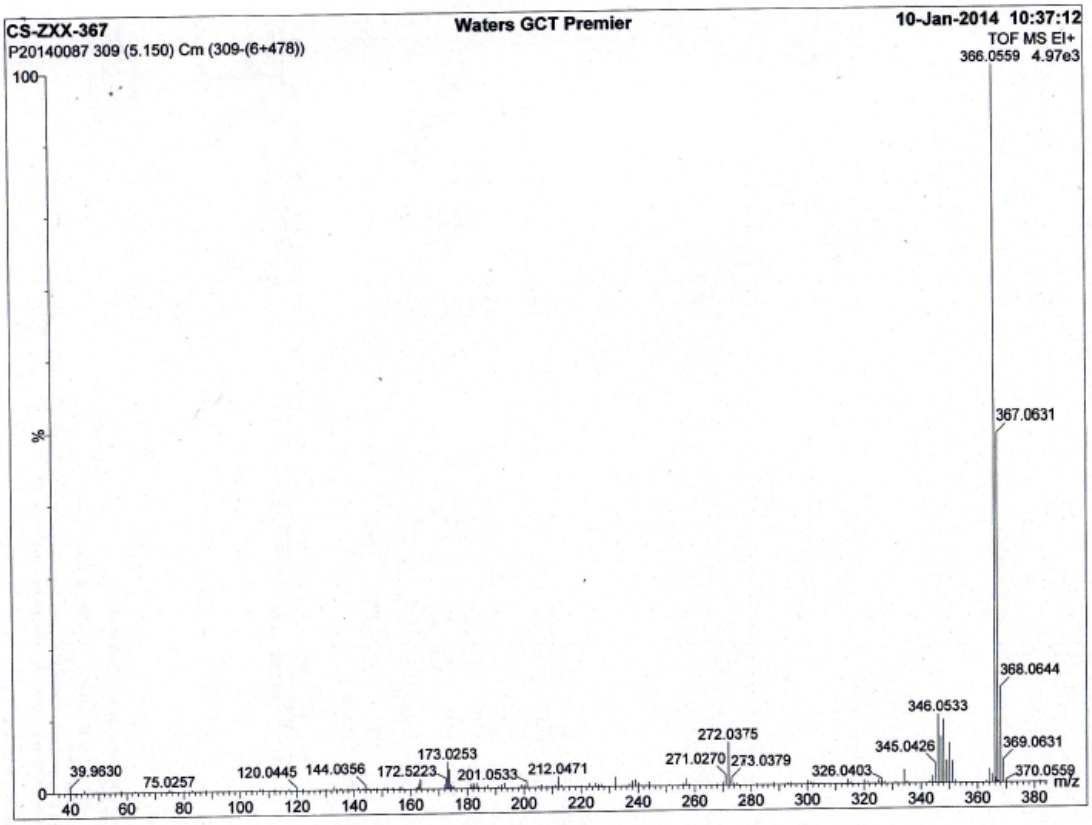
^{19}F NMR Spectrum of 3bb



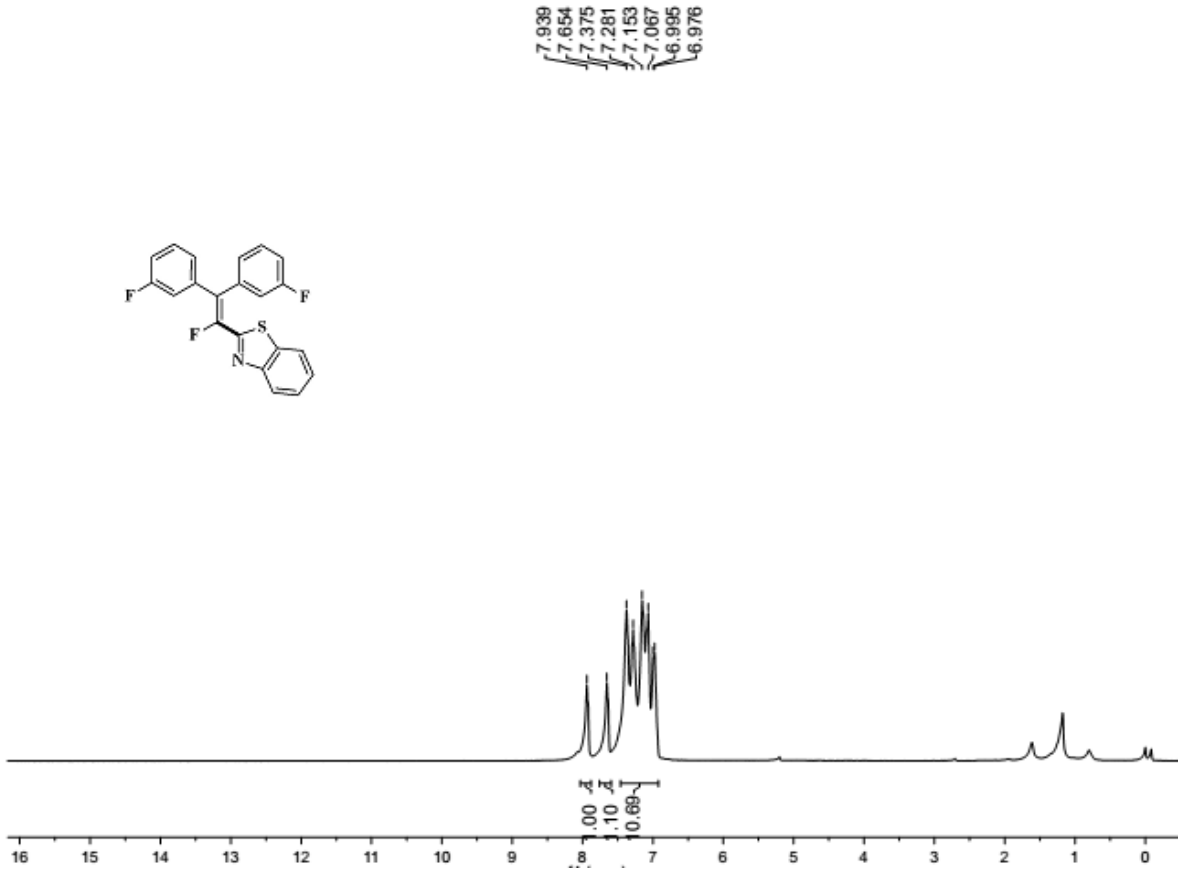
^{13}C NMR Spectrum of 3bb



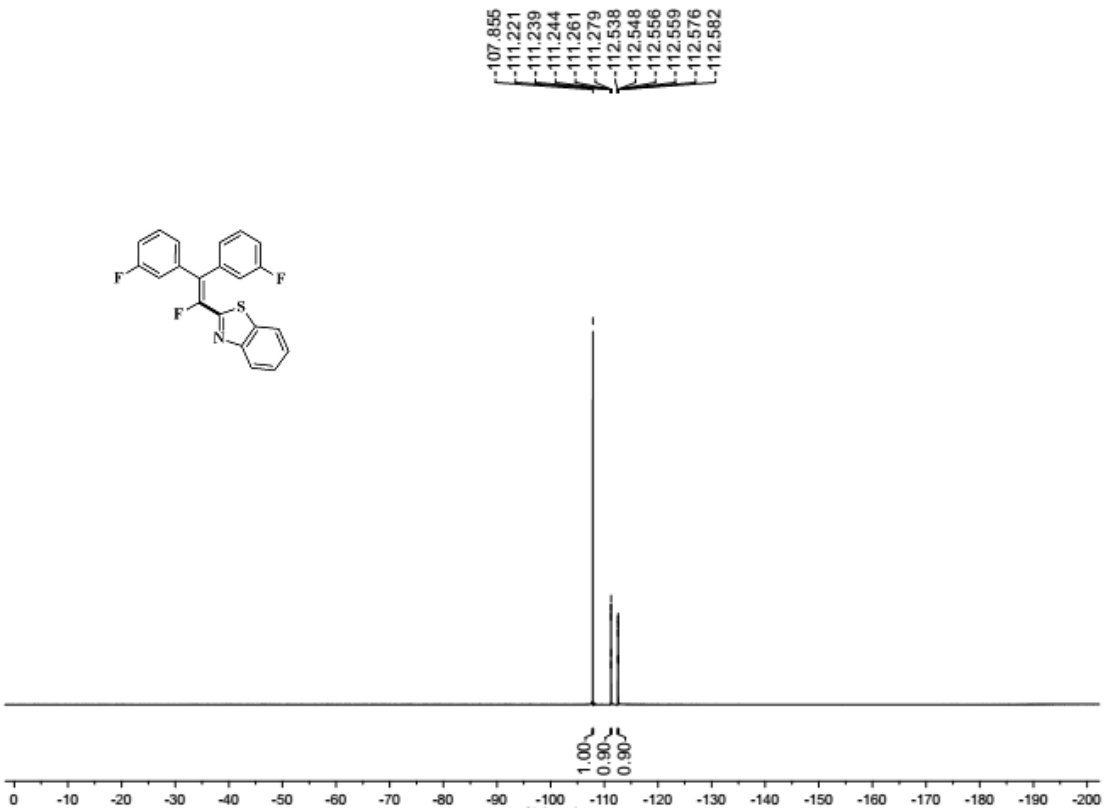
HRMS (EI) of 3bb



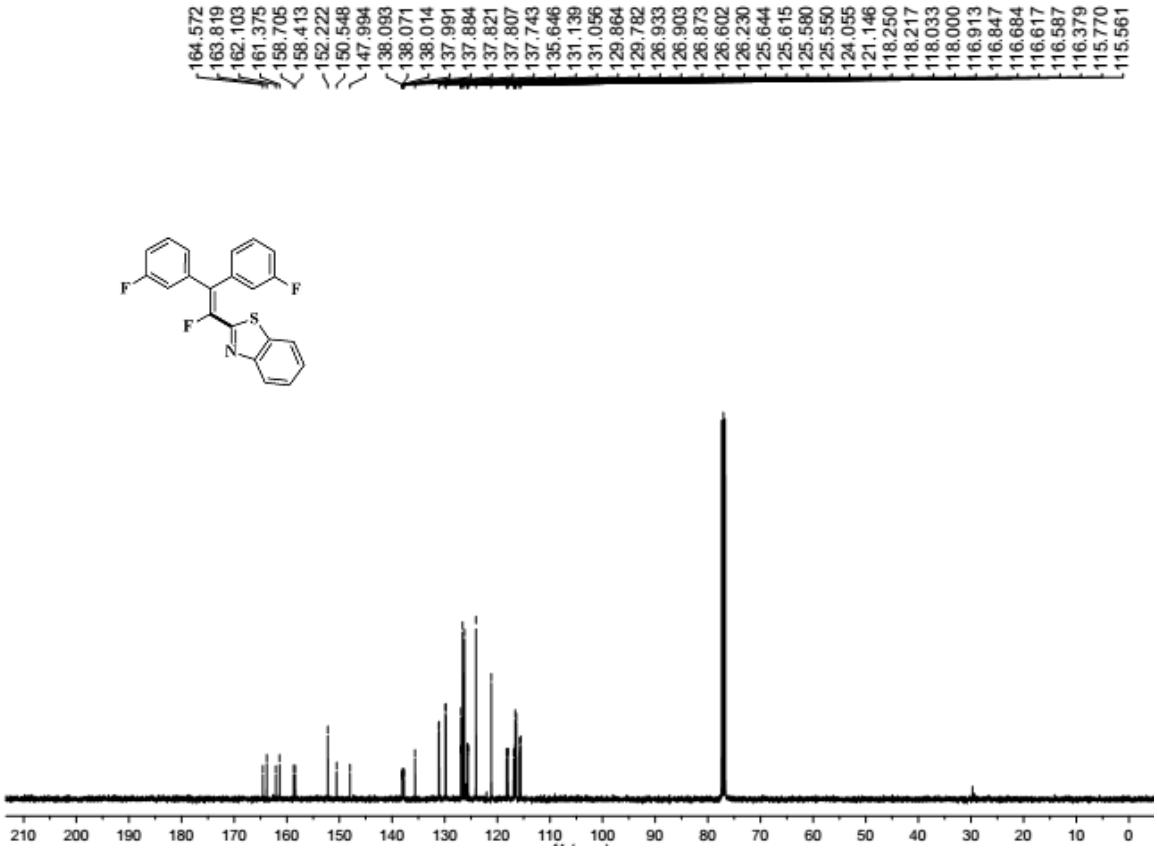
^{1}H NMR Spectrum of 3db



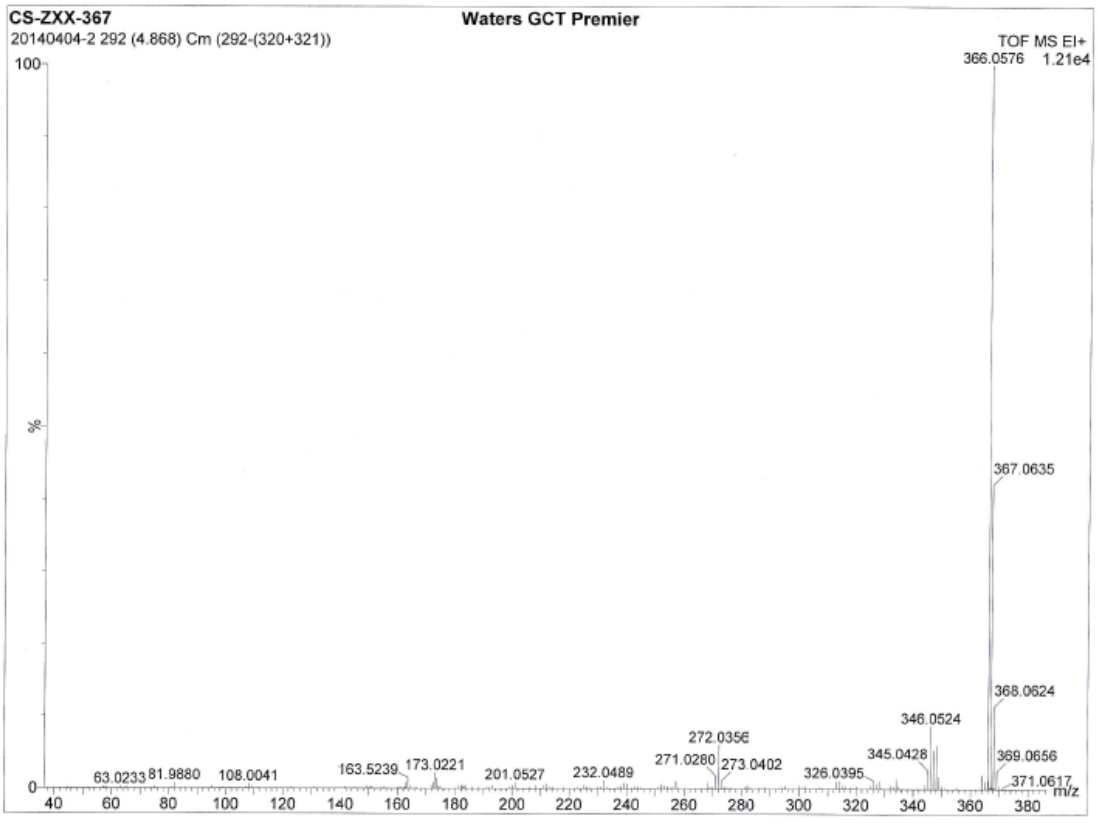
^{19}F NMR Spectrum of 3db



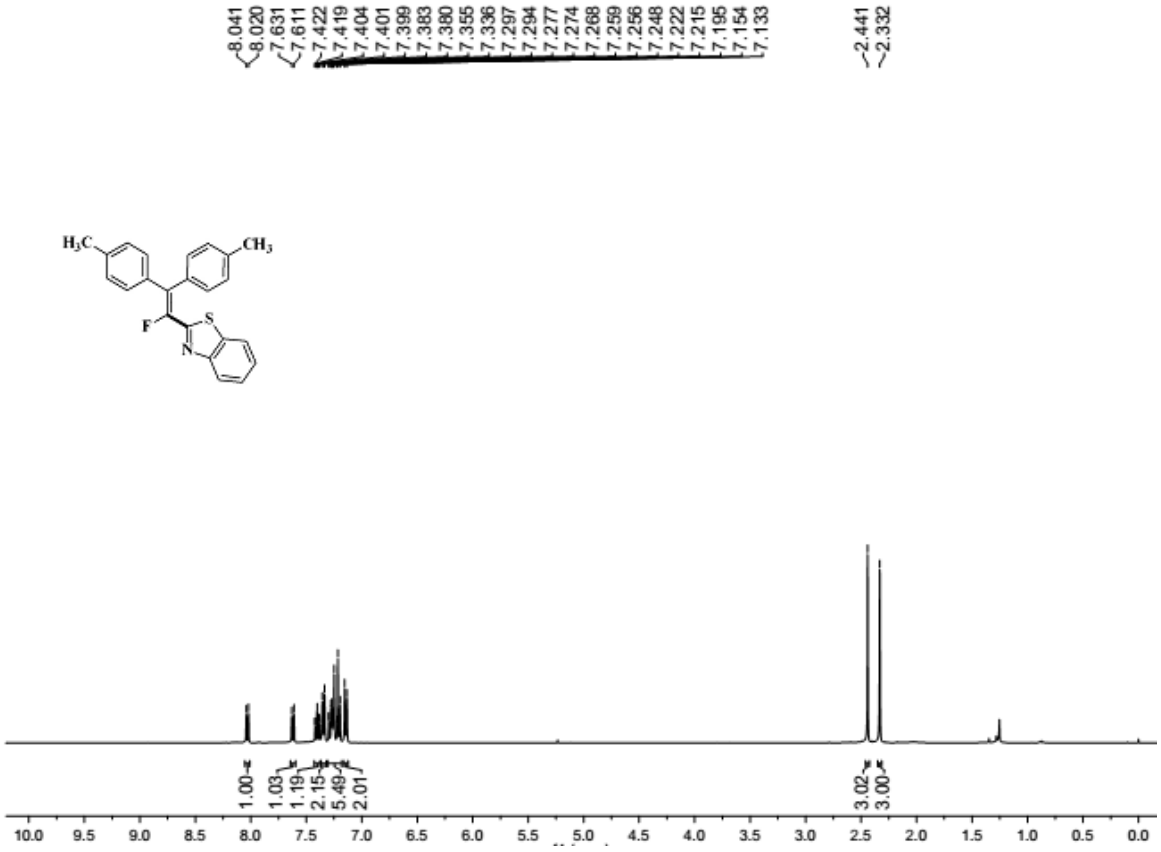
^{13}C NMR Spectrum of 3db



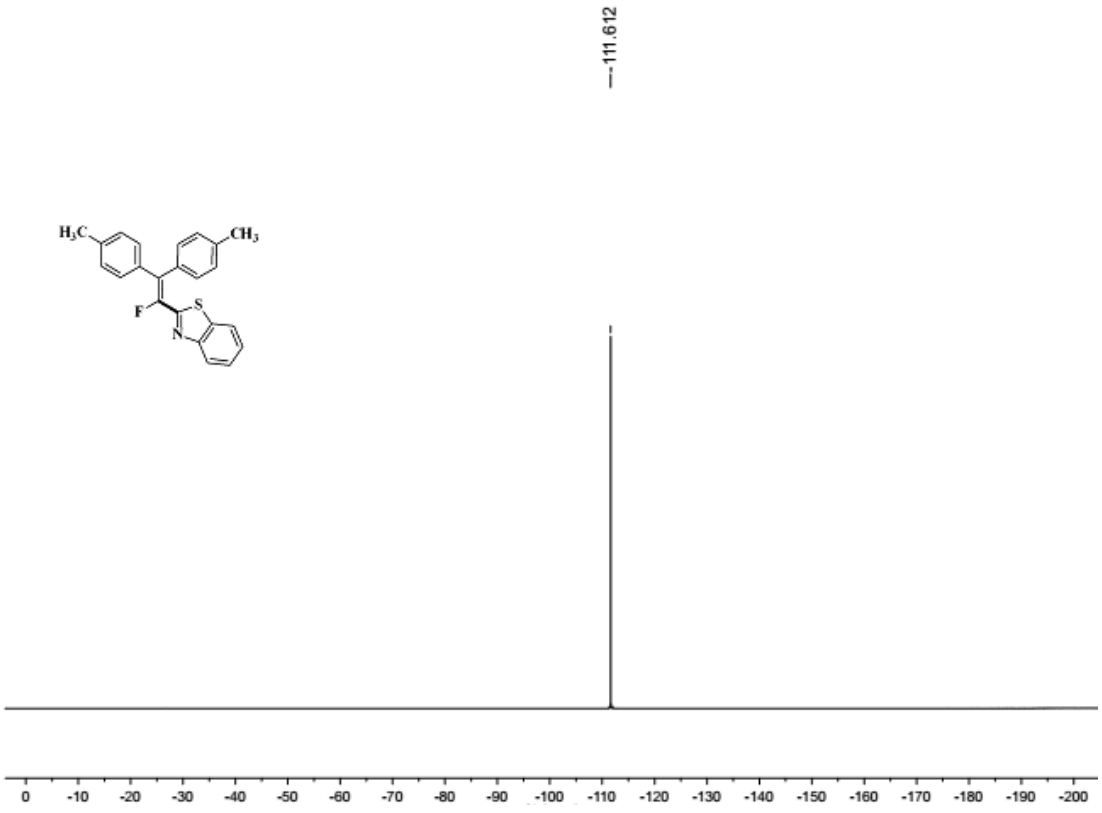
HRMS (EI) of 3db



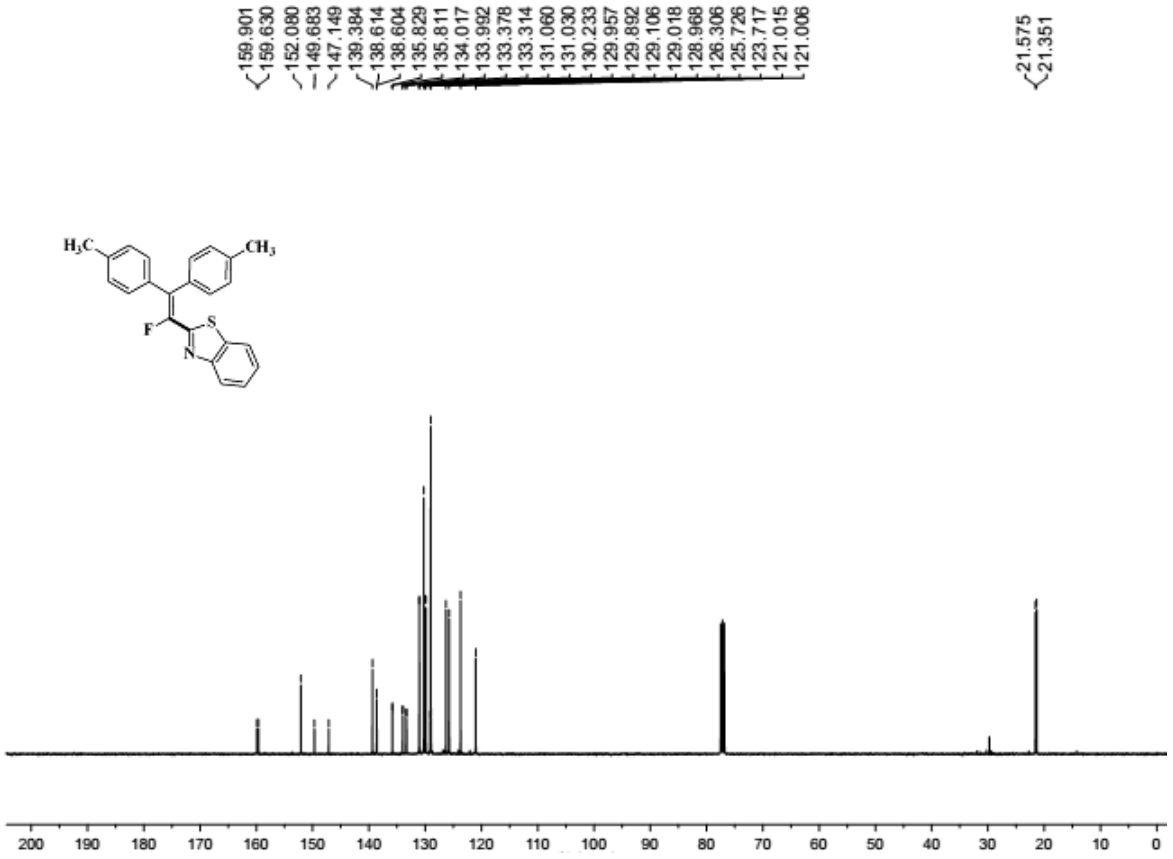
^{1}H NMR Spectrum of 3fb



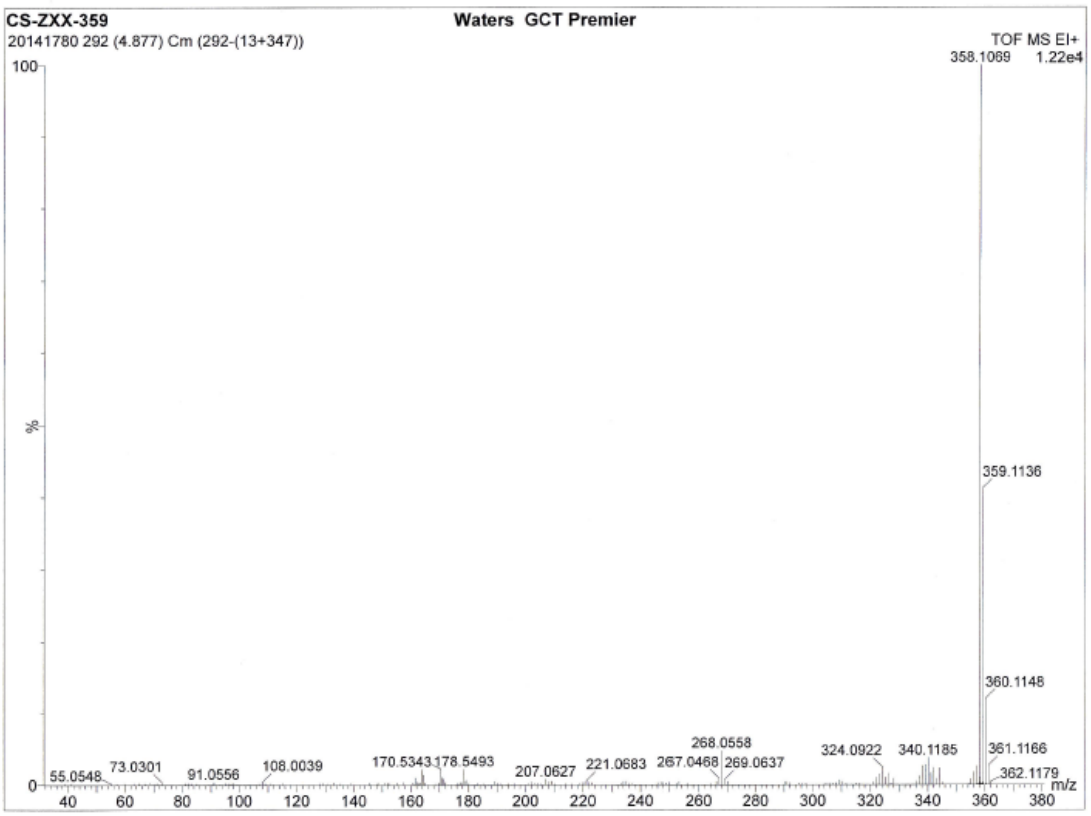
^{19}F NMR Spectrum of 3fb



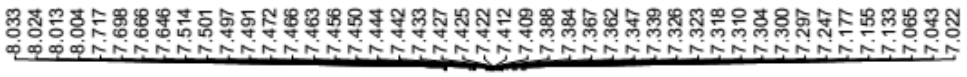
^{13}C NMR Spectrum of 3fb

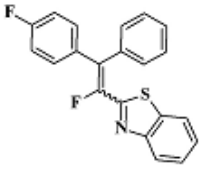


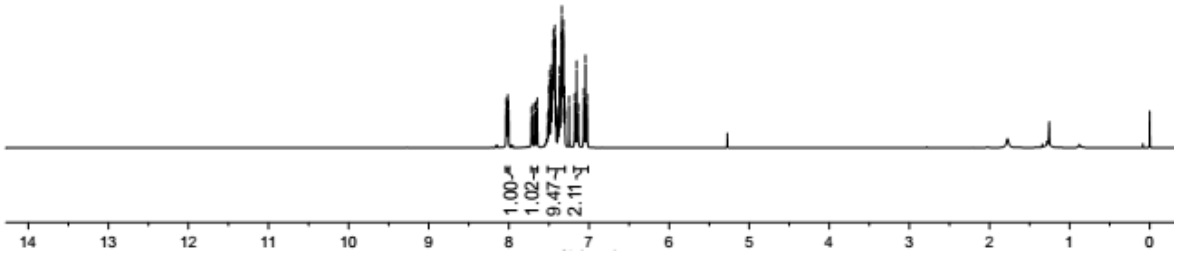
HRMS (EI) of 3fb



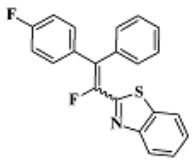
^{1}H NMR Spectrum of 3gb

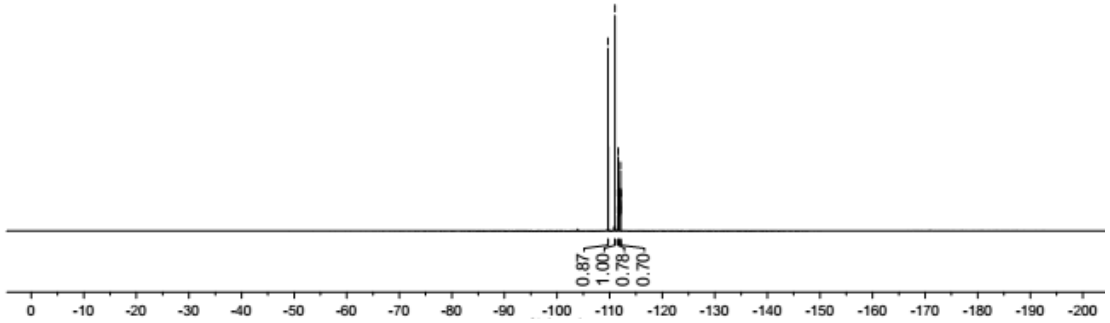




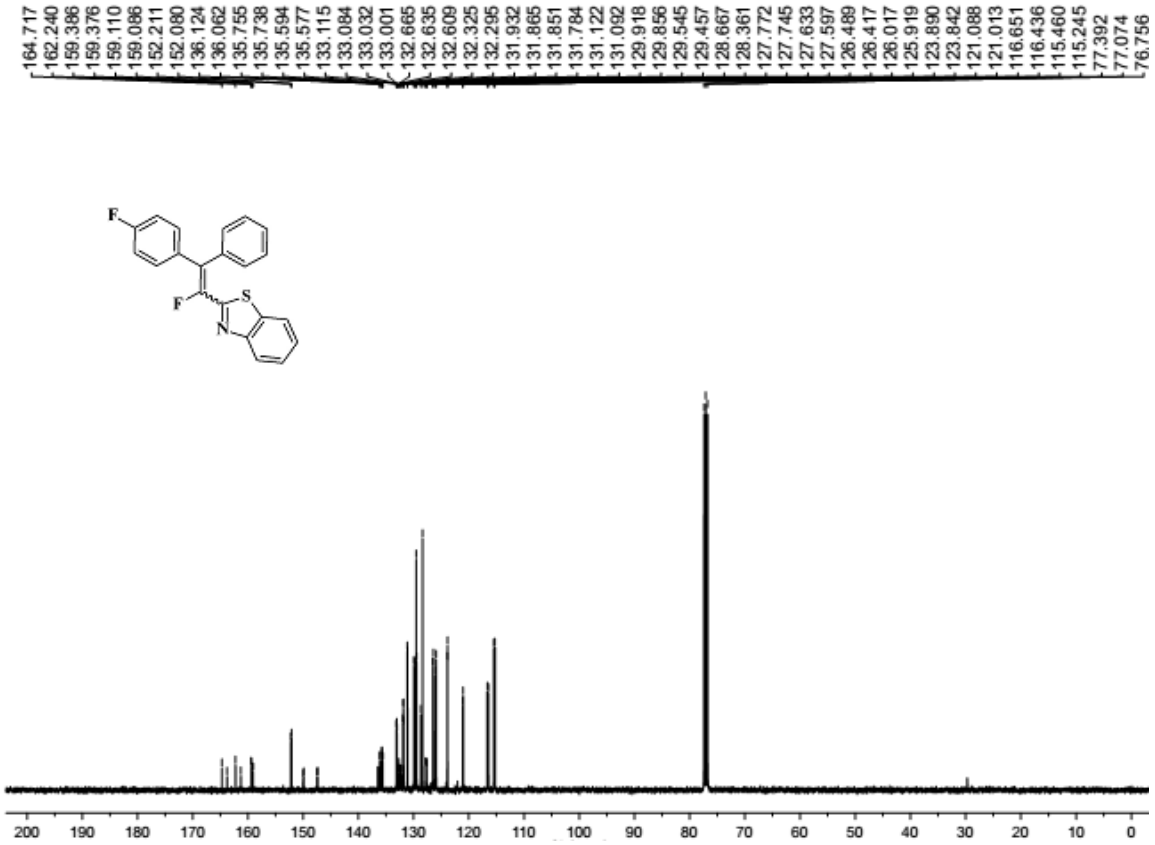


^{19}F NMR Spectrum of 3gb

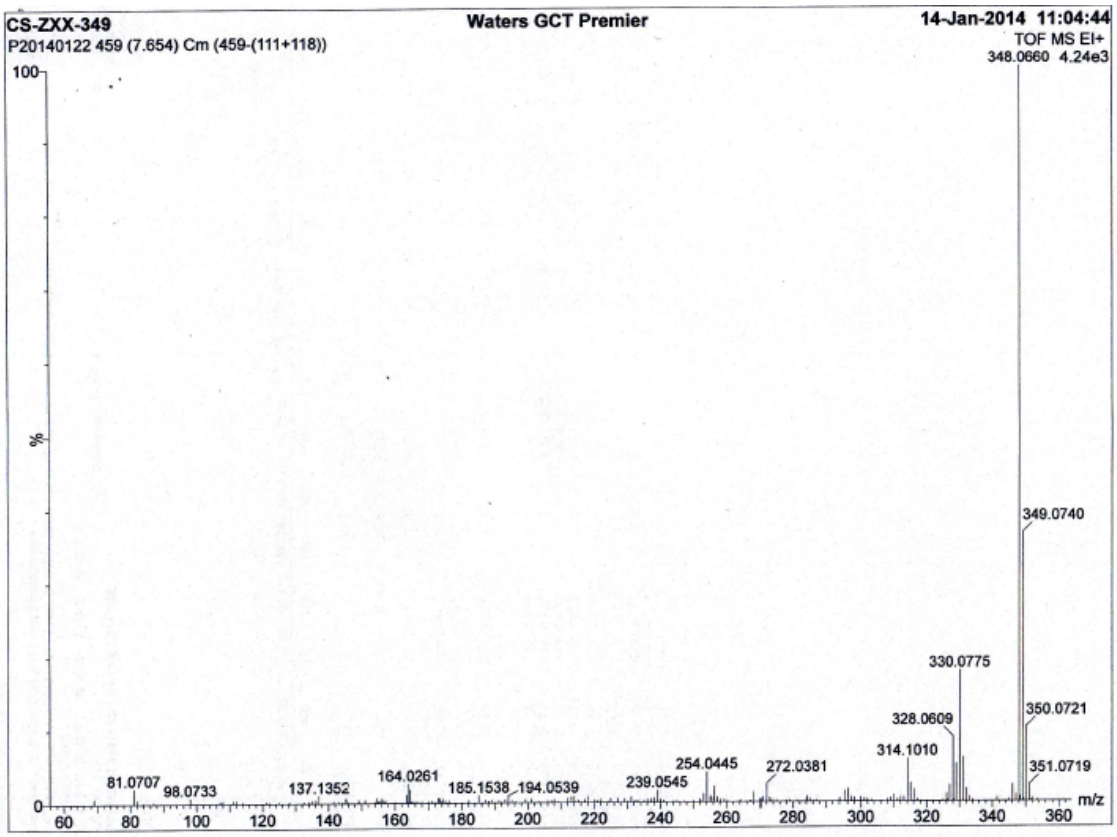




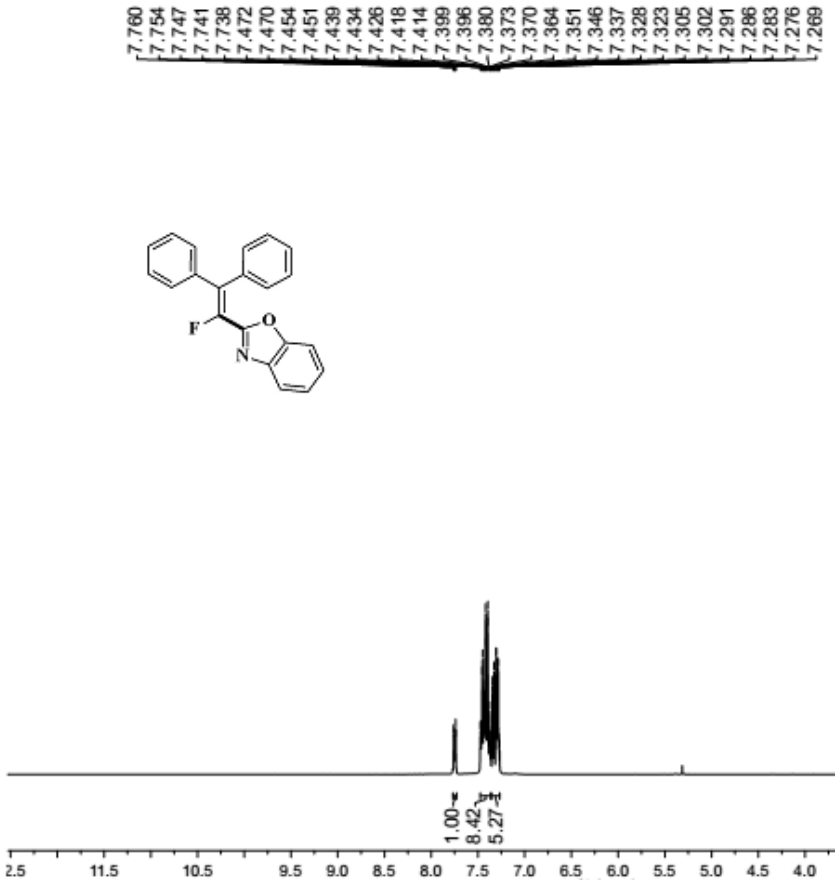
^{13}C NMR Spectrum of 3gb



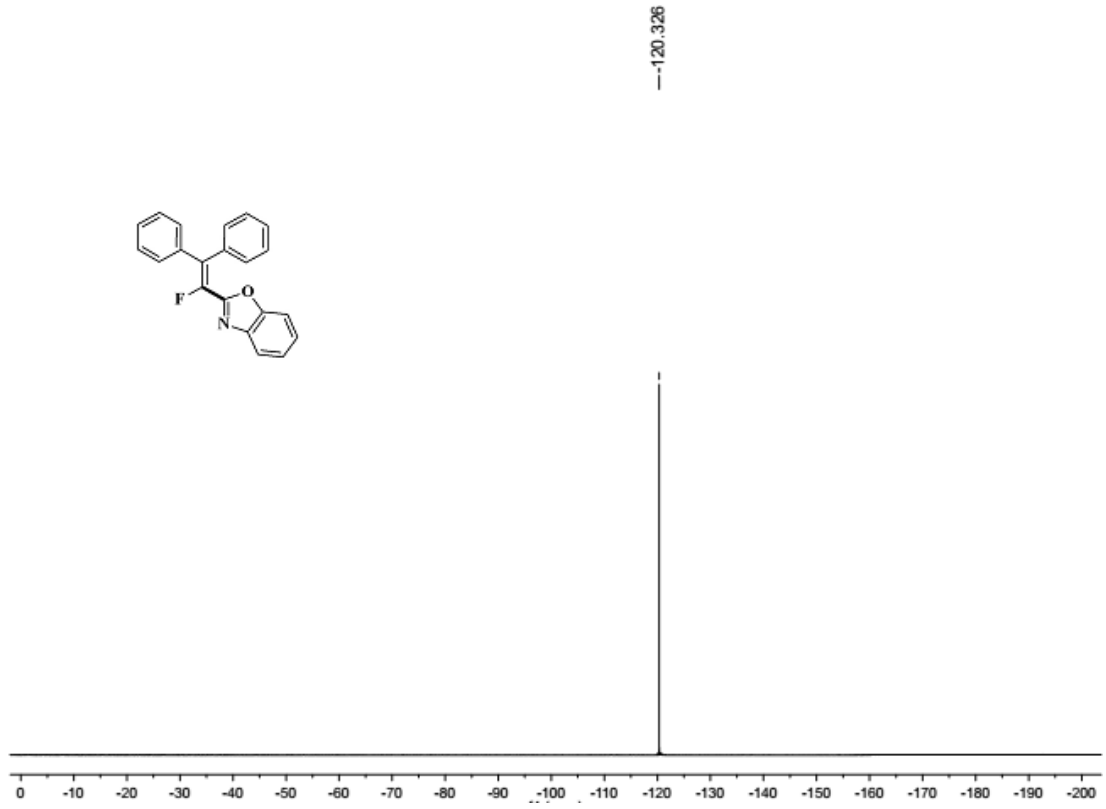
HRMS (EI) of 3gb



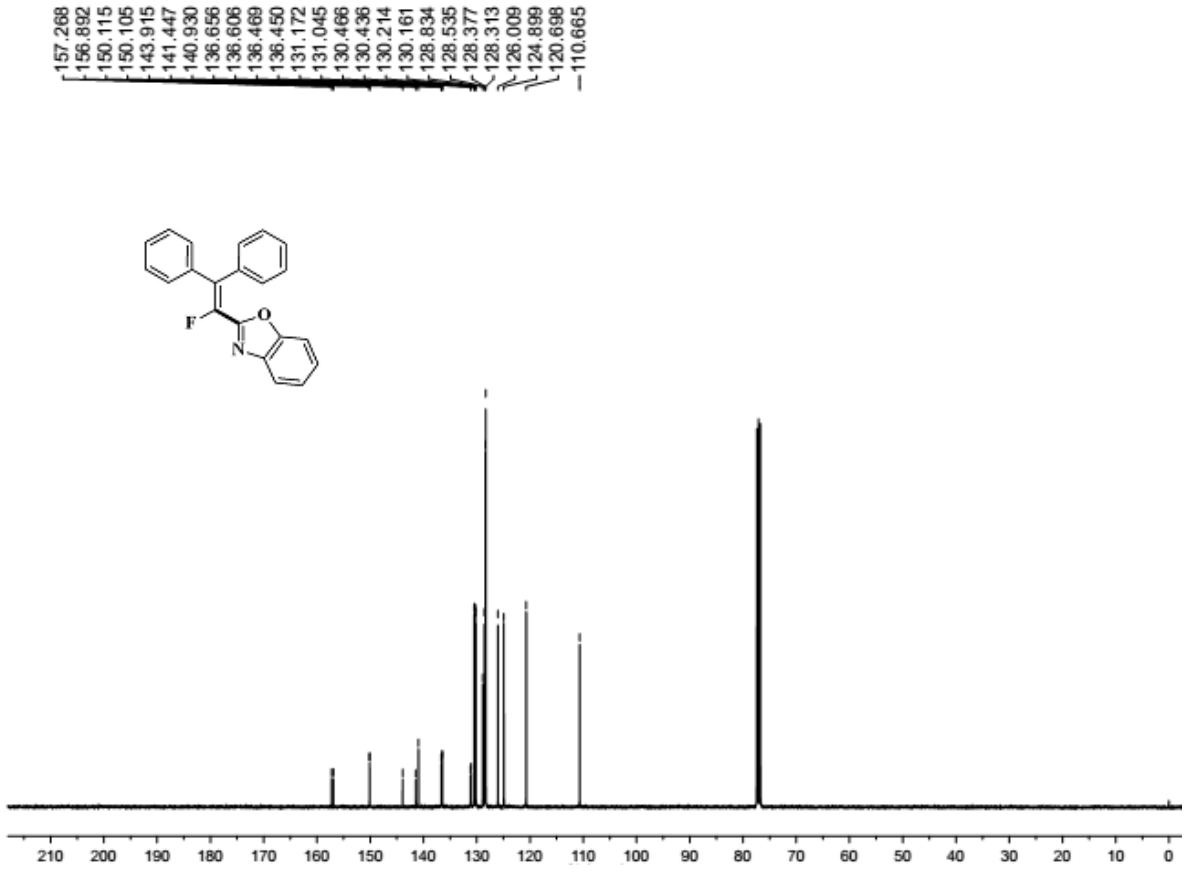
[1]H NMR Spectrum of 3ac



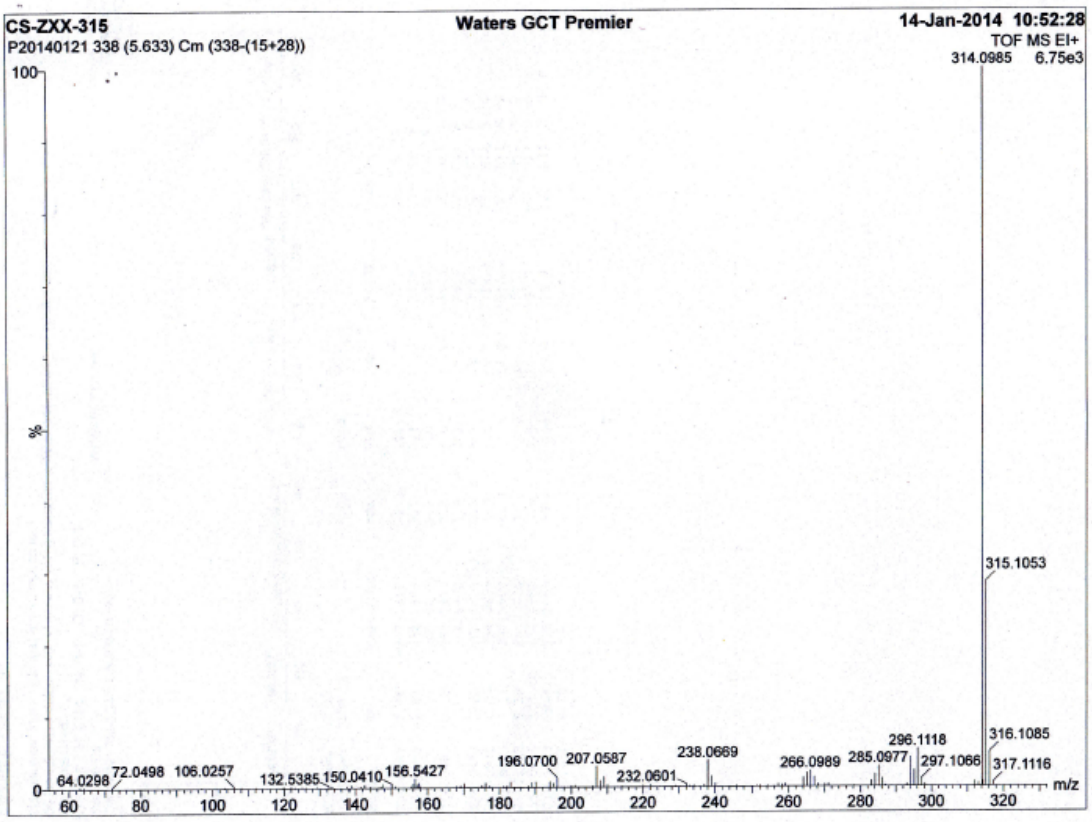
[19]F NMR Spectrum of 3ac



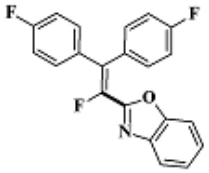
^{13}C NMR Spectrum of 3ac

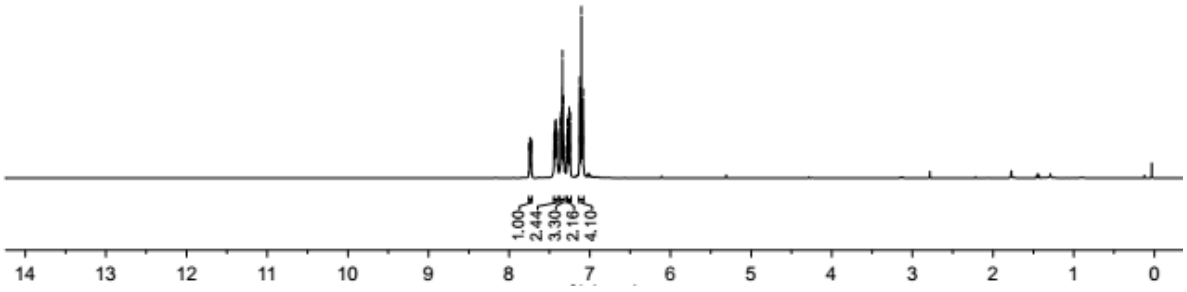


HRMS (EI) of 3ac

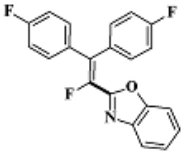


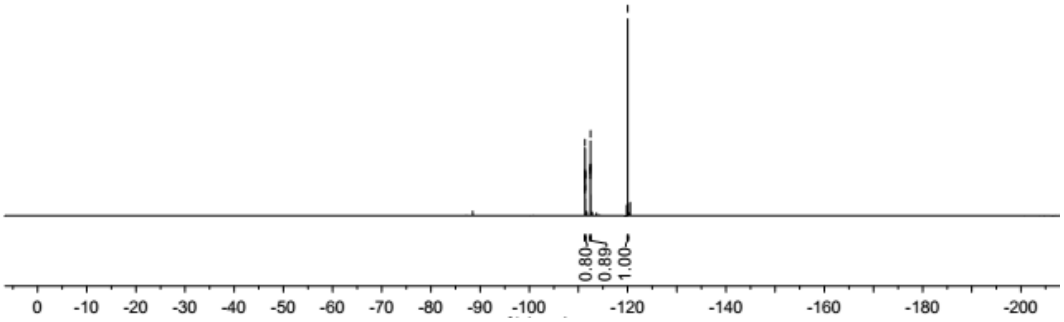
[1]H NMR Spectrum of 3bc



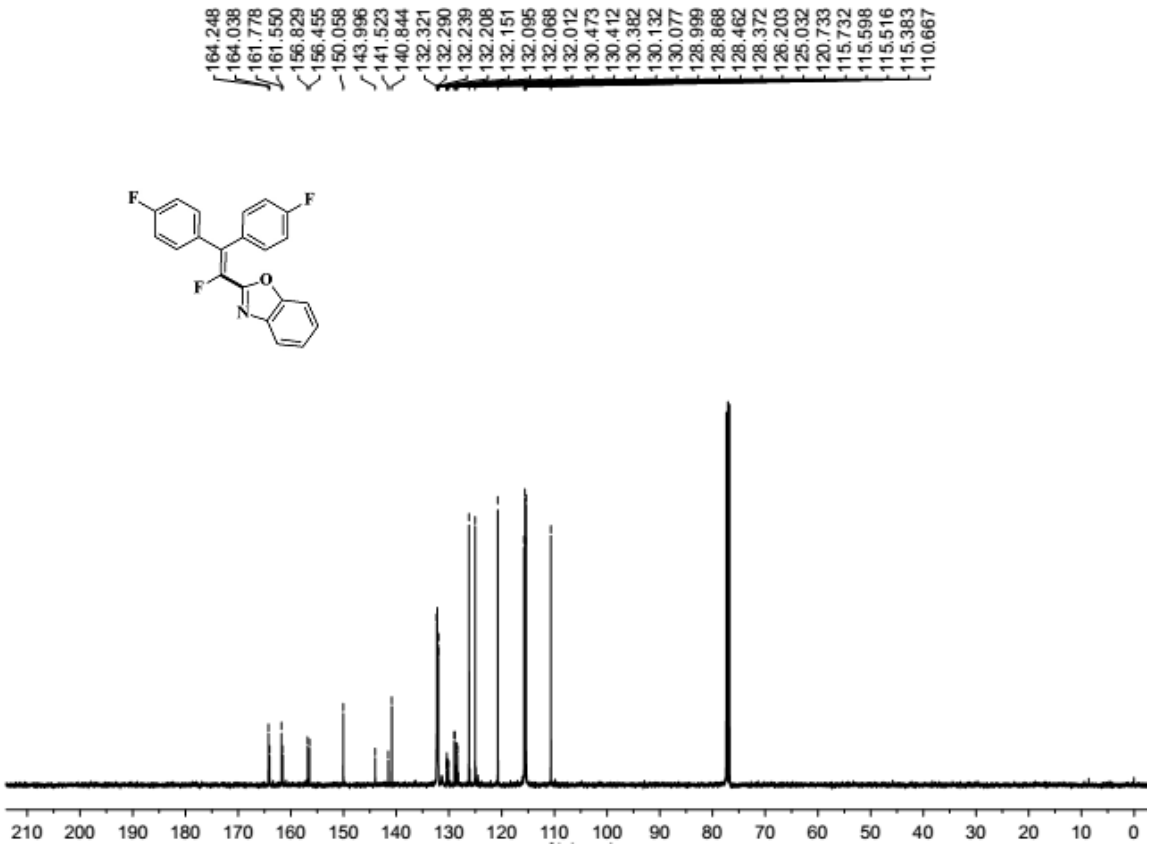


[19]F NMR Spectrum of 3bc

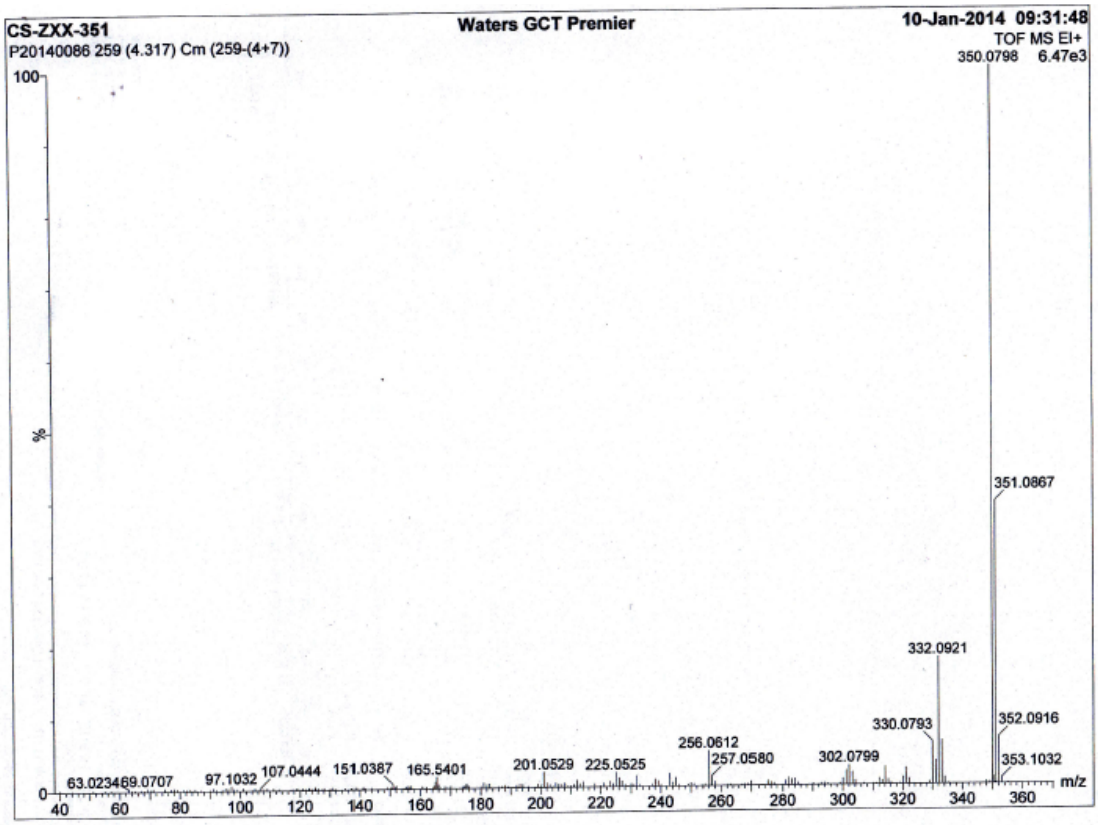




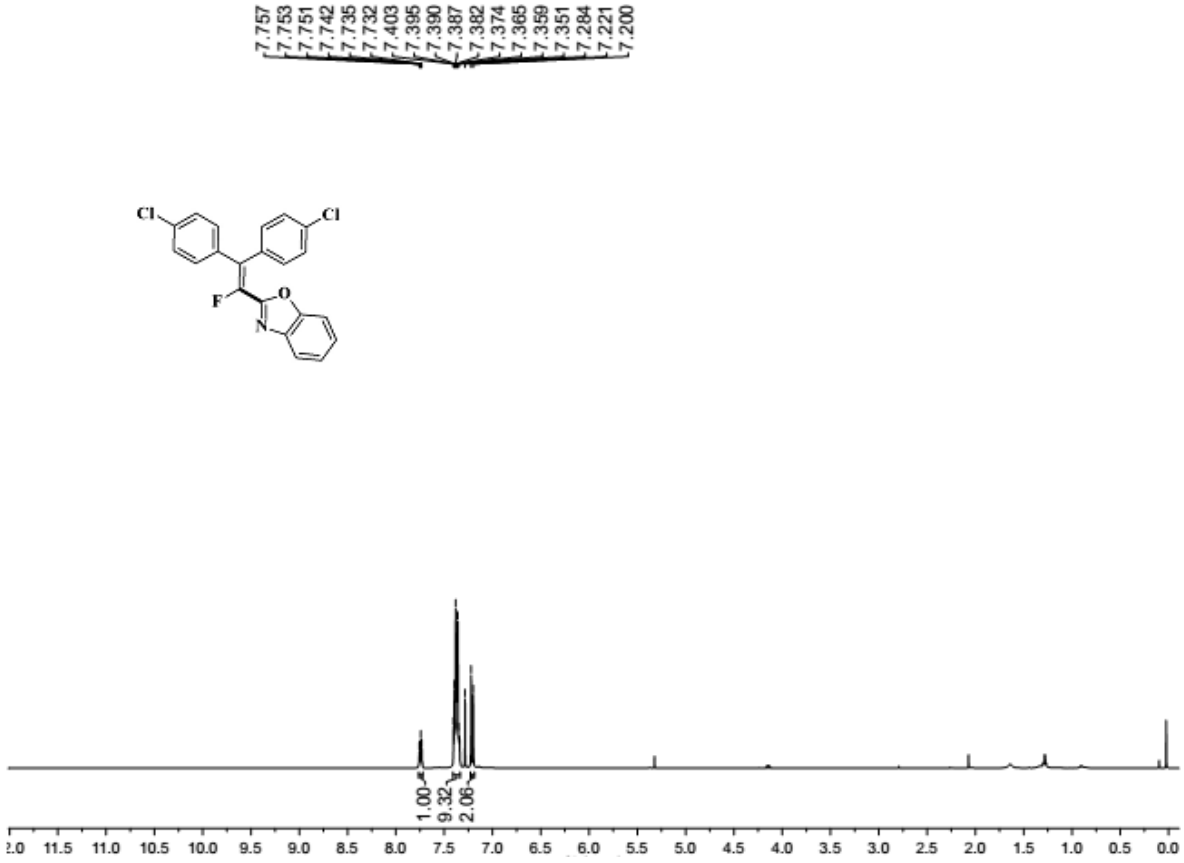
^{13}C NMR Spectrum of 3bc



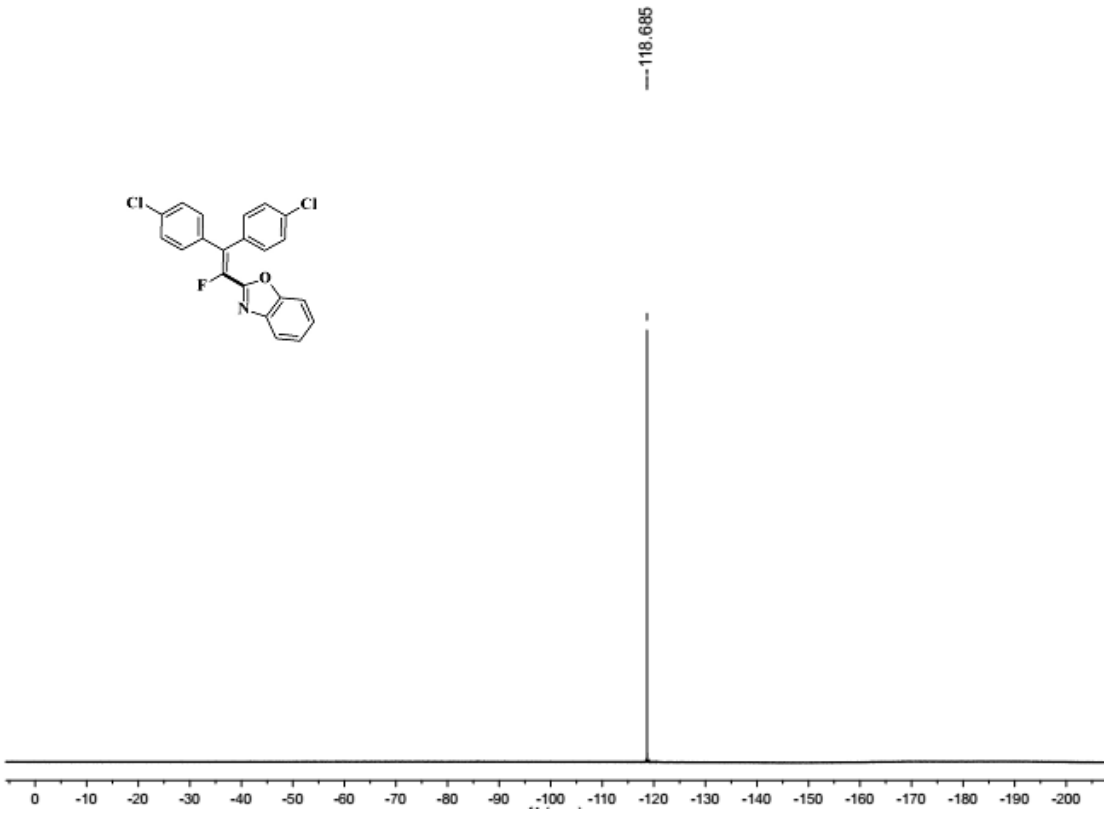
HRMS (EI) of 3bc



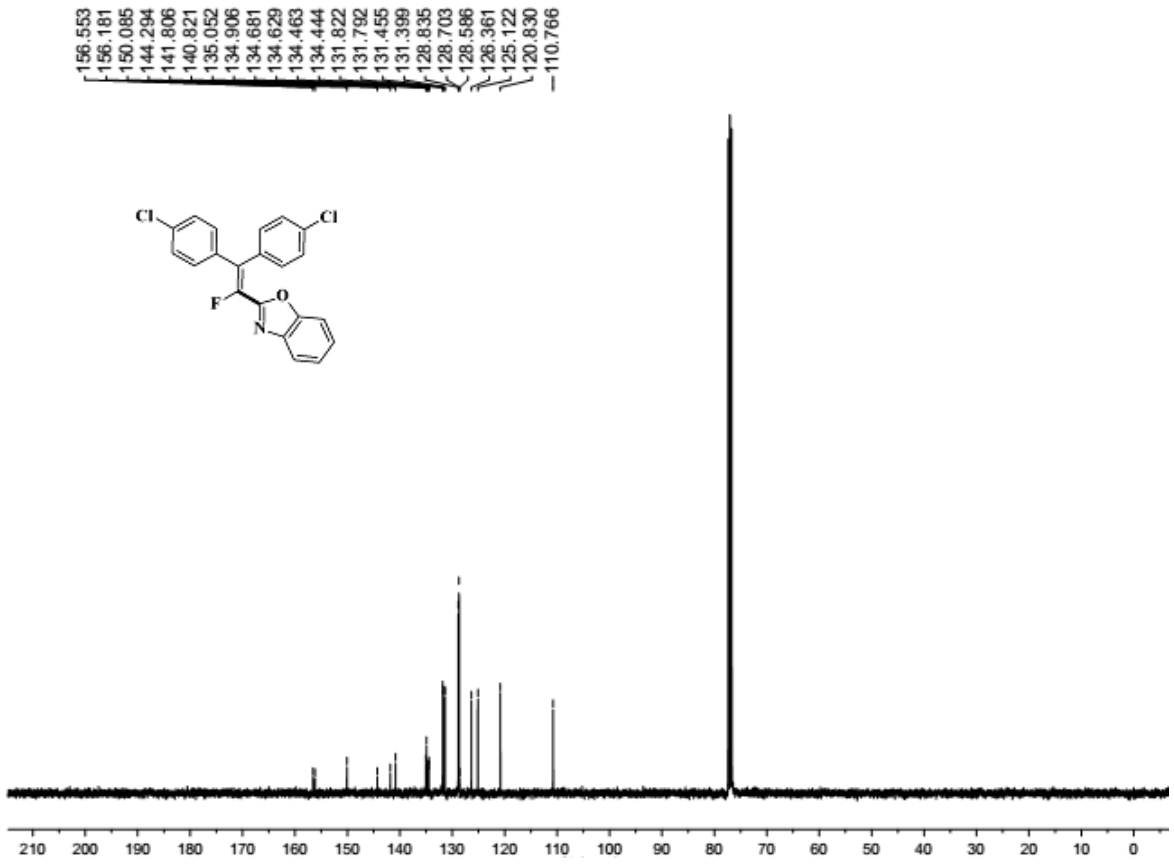
[1]H NMR Spectrum of 3cc



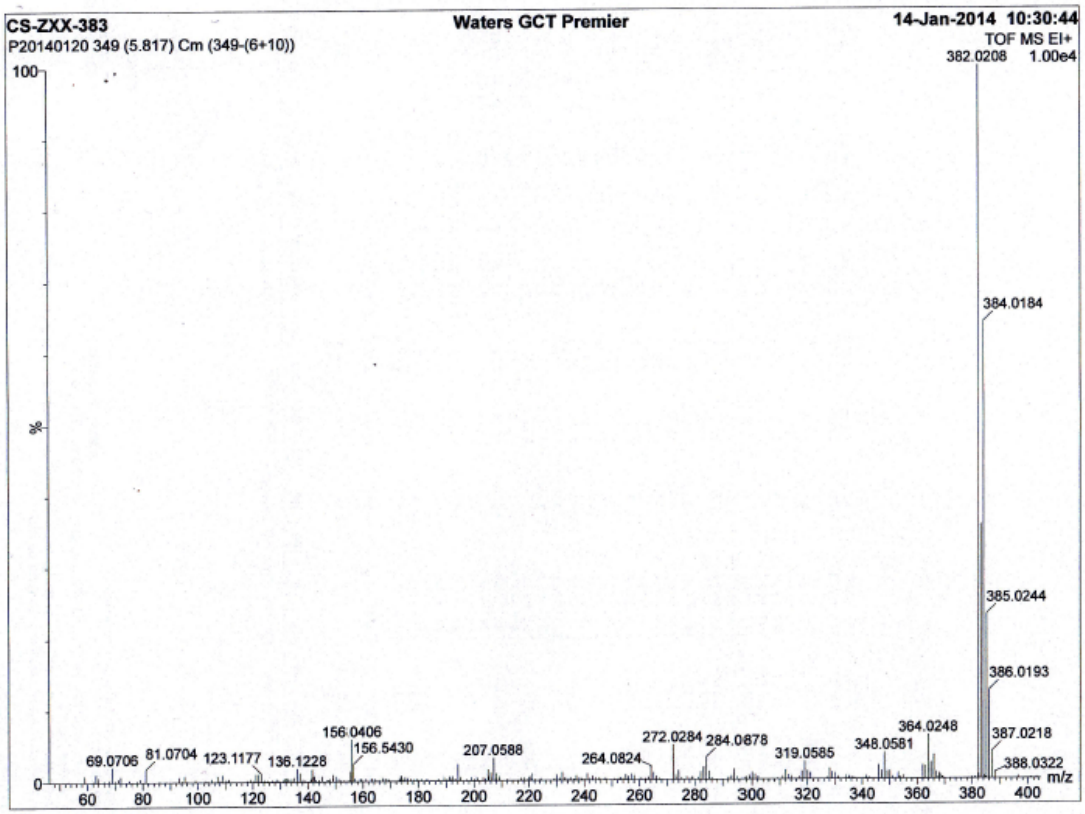
[19]F NMR Spectrum of 3cc



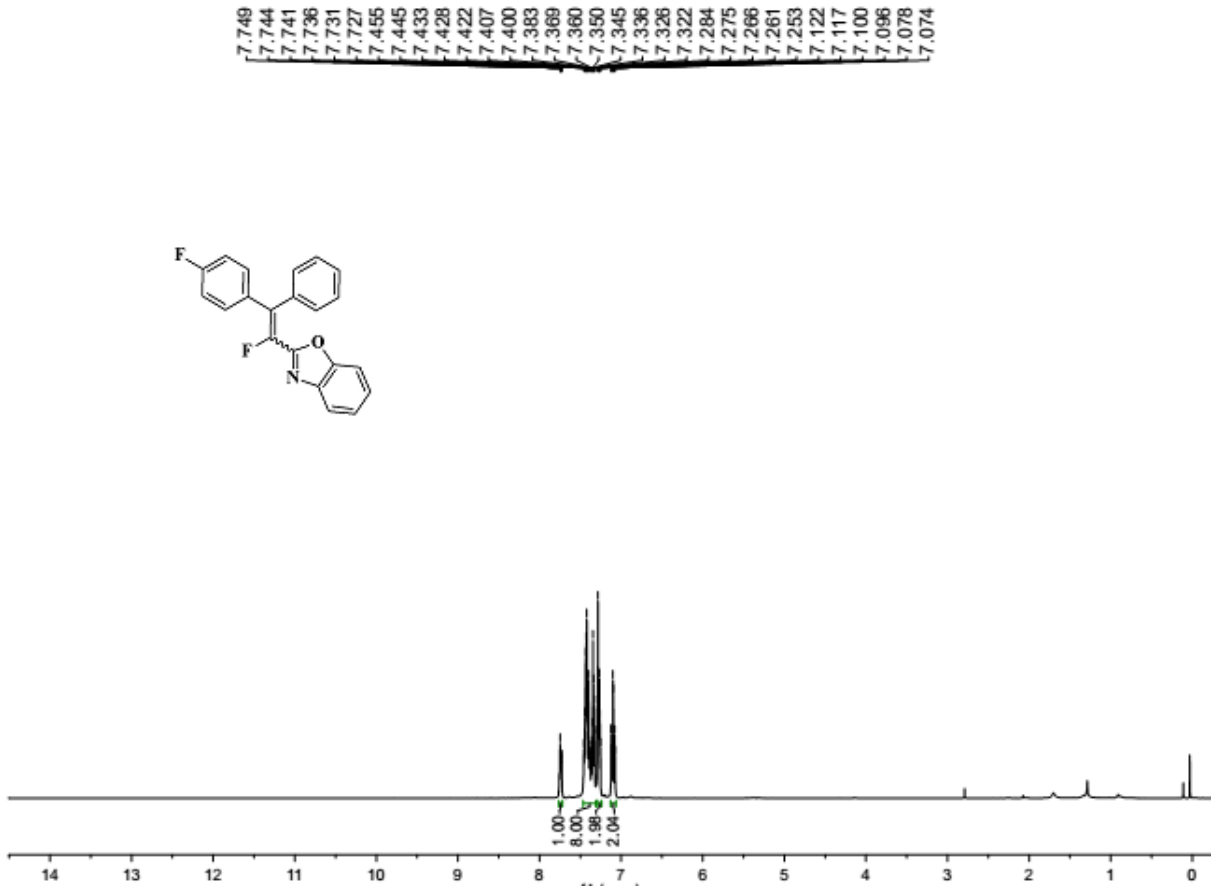
^{13}C NMR Spectrum of 3cc



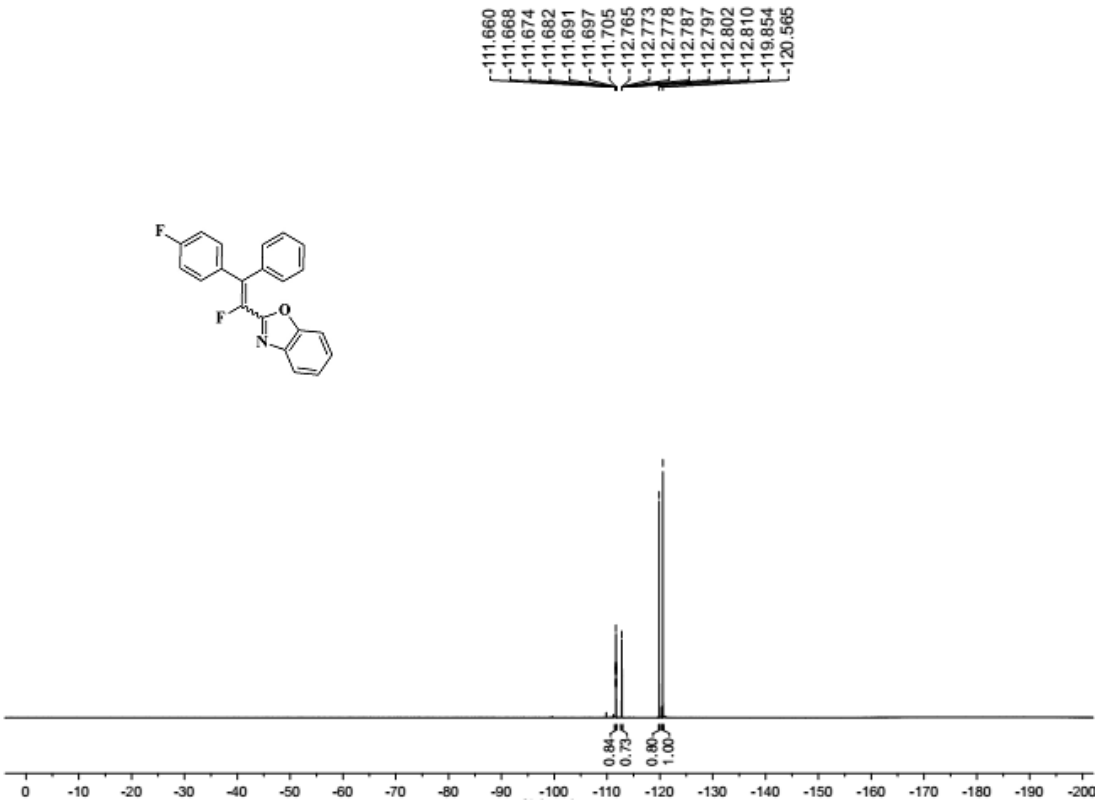
HRMS (EI) of 3cc



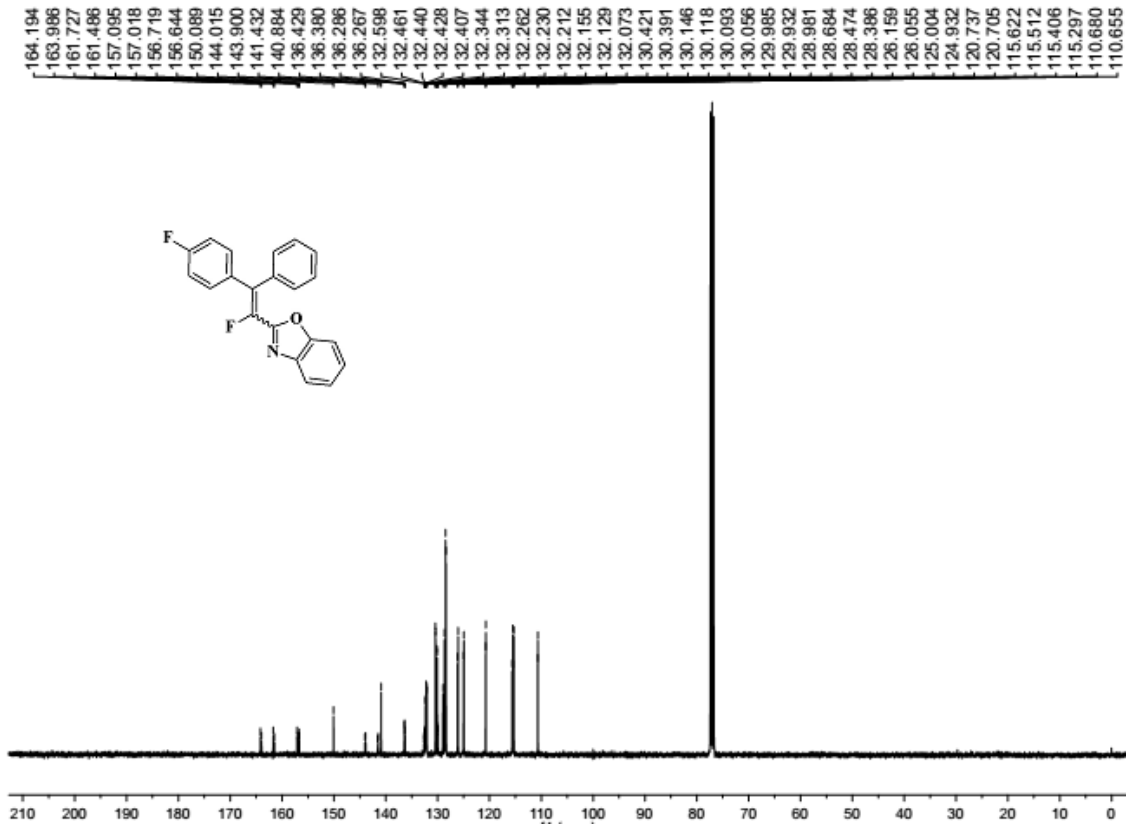
^{1}H NMR Spectrum of 3gc



^{19}F NMR Spectrum of 3gc



^{13}C NMR Spectrum of 3gc



HRMS (EI) of 3gc