Supplementary Information

Synthesis of fluorovinyl aryl ethers by a three-component reaction of *gem*-difluoroalkenes with arylboronic acids and oxygen

Mingjin Wang, Fang Liang, Yang Xiong and Song Cao*

Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (ECUST), Shanghai 200237, China

**Corresponding author: Tel: +86-21-64253452; fax: +86-21-64252603, E-mail address: scao@ecust.edu.cn*

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General experimental procedures

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. NMP 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 1-aryl-2,2-difluoroethenes 1h–k

The 1,1-difluoroalkenes (**1a–g**) were prepared according to the Hu's reported procedure.[1] The 1-aryl-2,2-difluoroethenes (**1h–k**) was prepared according to the reported procedure.[2]

General procedure for the synthesis of 3aa–df and 3ha–kl

To a solution of *gem*-difluoroalkenes (**1a**–**d**, **1h**–**k**, 1.0 mmol) in NMP (2 mL) was added arylboronic acids (2.0 mmol) and K_3PO_4 (2.0 mmol, 424 mg) at room temperature. The mixture was stirred at 100 °C for 24 h under air atmosphere (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using *n*-hexane/EtOAc (100/1) as eluent to afford the pure target compounds **3aa**–**df** and **3ha**–**kl**.

General procedure for the synthesis of 3ea–ga

To a solution of *gem*-difluoroalkenes (**1e**–**g**, 1.0 mmol) in toluene (2 mL) was added phenylboronic acid **2a** (2.0 mmol), Cs_2CO_3 (2.0 mmol, 652 mg), and $Ni(acac)_2$ (0.05 mmol, 13 mg) at room temperature. The mixture was stirred at 100 °C for 24 h under an oxygen atmosphere (balloon). After the completion of reaction, the reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using *n*-hexane/EtOAc (100/1) as eluent to afford the pure target compounds **3ea**–**ga**.

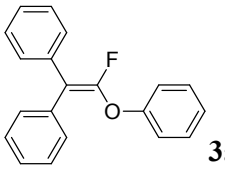
References

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

2. C. S. Thomoson, H. Martinez, W. R. Dolbier Jr., *J. Fluorine Chem.*, 2013, **150**, 53.

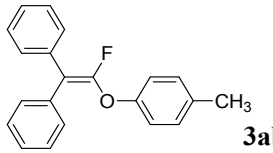
Spectral and analytical data of compounds 3

(2-Fluoro-2-phenoxyethene-1,1-diyl)dibenzene (3aa): White solid. Yield: 81%, mp 77.9−79.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.19 (m, 12H), 7.11−7.08 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9 (d, $^3J_{CF}$ = 2.7 Hz), 151.0 (d, $^1J_{CF}$ = 286.8 Hz), 136.3 (d, $^3J_{CF}$ = 4.1 Hz), 136.2 (d, $^4J_{CF}$ = 3.7 Hz), 129.9 (d, $^3J_{CF}$ = 4.0 Hz), 129.8, 129.6 (d, $^4J_{CF}$ = 3.2 Hz), 128.3, 128.2, 127.3, 127.2, 124.1, 116.5, 106.1 (d, $^2J_{CF}$ = 25.0 Hz) ppm; ^{19}F NMR (376M Hz, $CDCl_3$) δ −87.1 (s, 1F) ppm; HRMS (EI): calcd for $C_{20}H_{15}FO$ $[M]^+$: 290.1107, found: 290.1108.



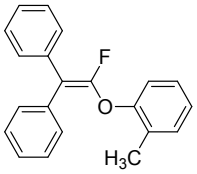
3aa

(2-Fluoro-2-(*p*-tolyloxy)ethene-1,1-diyl)dibenzene (3ab): White solid. Yield: 69%, mp 70.8−72.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.21 (m, 10H), 7.11 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 7.6 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (d, $^3J_{CF}$ = 2.5 Hz), 151.2 (d, $^1J_{CF}$ = 286.9 Hz), 136.4 (d, $^3J_{CF}$ = 4.2 Hz), 136.3 (d, $^4J_{CF}$ = 3.8 Hz), 133.6, 130.3, 130.0 (d, $^3J_{CF}$ = 4.0 Hz), 129.6 (d, $^4J_{CF}$ = 3.2 Hz), 128.3, 128.2, 127.3, 127.2, 116.4, 105.7 (d, $^2J_{CF}$ = 25.3 Hz), 20.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −87.0 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{17}FO$ $[M]^+$: 304.1263, found: 304.1262.



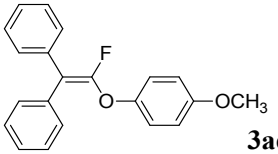
3ab

(2-Fluoro-2-(*o*-tolyloxy)ethene-1,1-diyl)dibenzene (3ac): White solid. Yield: 73%, mp 68.8–70.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m, 10H), 7.15–7.10 (m, 3H), 7.01–6.97 (m, 1H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (d, $^3J_{CF}$ = 2.3 Hz), 151.3 (d, $^1J_{CF}$ = 286.4 Hz), 136.4 (d, $^3J_{CF}$ = 4.1 Hz), 136.3 (d, $^4J_{CF}$ = 3.6 Hz), 131.5, 130.0 (d, $^3J_{CF}$ = 4.0 Hz), 129.6 (d, $^4J_{CF}$ = 3.1 Hz), 128.3, 128.2, 127.5, 127.3, 127.1, 127.0, 124.0, 115.0, 105.5 (d, $^2J_{CF}$ = 25.3 Hz), 16.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −85.9 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{17}FO$ $[M]^+$: 304.1263, found: 304.1262.



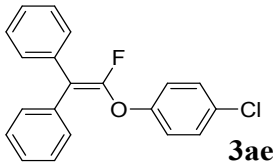
3ac

(2-Fluoro-2-(4-methoxyphenoxy)ethene-1,1-diyl)dibenzene (3ad): White solid. Yield: 65%, mp 67.6–69.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 10H), 7.03–7.01 (m, , 2H), 6.85–6.81 (m, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 151.5 (d, $^1J_{CF}$ = 286.9 Hz), 148.6 (d, $^3J_{CF}$ = 2.3 Hz), 136.4 (d, $^3J_{CF}$ = 4.1 Hz), 136.3 (d, $^4J_{CF}$ = 3.7 Hz), 130.0 (d, $^3J_{CF}$ = 4.0 Hz), 129.7 (d, $^4J_{CF}$ = 3.2 Hz), 128.3, 128.2, 127.2, 127.1, 117.7, 114.9, 105.3 (d, $^2J_{CF}$ = 25.5 Hz), 55.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –87.0 ppm; HRMS (EI): calcd for $C_{21}H_{17}FO_2$ $[M]^+$: 320.1213, found: 320.1214.



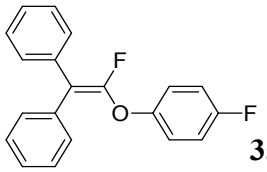
3ad

(2-(4-Chlorophenoxy)-2-fluoroethene-1,1-diyl)dibenzene (3ae): White solid. Yield: 76%, mp 67.4–68.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.33 (m, 4H), 7.27–7.19 (m, 8H), 7.03–7.00 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 (d, $^3J_{CF}$ = 2.8 Hz), 150.7 (d, $^1J_{CF}$ = 287.2 Hz), 136.0 (d, $^3J_{CF}$ = 4.0 Hz), 135.8 (d, $^3J_{CF}$ = 3.9 Hz), 129.9, 129.8, 129.6 (d, $^4J_{CF}$ = 3.1 Hz), 129.3, 128.4, 128.3, 127.5, 127.4, 117.8, 106.5 (d, $^2J_{CF}$ = 24.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –88.0 (s, 1F) ppm; HRMS (EI): calcd for $C_{20}H_{14}ClFO$ $[M]^+$: 324.0717, found: 324.0722.



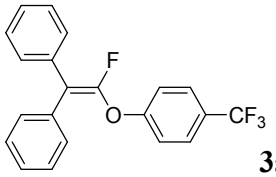
3ae

(2-Fluoro-2-(4-fluorophenoxy)ethene-1,1-diyl)dibenzene (3af): White solid. Yield: 78%, mp 93.8–94.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 4H), 7.30–7.23 (m, 6H), 7.07–6.98 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, $^1J_{CF}$ = 240.8 Hz), 151.0 (d, $^1J_{CF}$ = 286.9 Hz), 150.8–150.7 (m), 136.1 (d, $^3J_{CF}$ = 4.0 Hz), 135.9 (d, $^4J_{CF}$ = 3.8 Hz), 129.8 (d, $^3J_{CF}$ = 4.1 Hz), 129.6 (d, $^4J_{CF}$ = 3.2 Hz), 128.3, 128.2, 127.4, 127.3, 117.9 (d, $^3J_{CF}$ = 8.0 Hz), 116.3 (d, $^2J_{CF}$ = 23.5 Hz), 106.0 (d, $^2J_{CF}$ = 24.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –87.8 (s, 1F), –119.2 to –119.3 (m, 1F) ppm; HRMS (EI): calcd for $C_{20}H_{14}F_2O$ $[M]^+$: 308.1013, found: 308.1014.



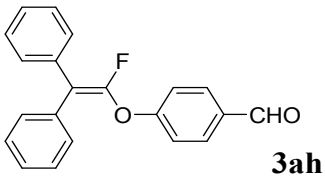
3af

(2-Fluoro-2-(4-(trifluoromethyl)phenoxy)ethene-1,1-diyl)dibenzene (3ag): Colorless liquid. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.8 Hz, 2H), 7.37–7.34 (m, 4H), 7.33–7.17 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 150.2 (d, $^1J_{CF}$ = 287.3 Hz), 135.7 (d, $^3J_{CF}$ = 3.9 Hz), 135.6 (d, $^4J_{CF}$ = 3.8 Hz), 129.8 (d, $^3J_{CF}$ = 4.2 Hz), 129.5 (d, $^4J_{CF}$ = 3.1 Hz), 128.4, 128.3, 127.6, 127.5, 127.3 (q, $^3J_{CF}$ = 3.7 Hz), 126.3 (q, $^2J_{CF}$ = 32.8 Hz), 124.0 (q, $^1J_{CF}$ = 269.9 Hz), 116.5, 107.2 (d, $^2J_{CF}$ = 23.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.9 (s, 3F), –88.6 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{14}F_4O$ $[M]^+$: 358.0981, found: 358.0986.



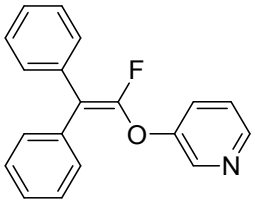
3ag

4-((1-Fluoro-2,2-diphenylvinyl)oxy)benzaldehyde (3ah): Colorless oil. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.36–7.20 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 159.5 (d, $^3J_{CF}$ = 3.3 Hz), 150.1 (d, $^1J_{CF}$ = 287.3 Hz), 135.7 (d, $^4J_{CF}$ = 3.8 Hz), 135.6 (d, $^3J_{CF}$ = 3.9 Hz), 132.7, 132.0, 129.8 (d, $^3J_{CF}$ = 4.4 Hz), 129.5 (d, $^4J_{CF}$ = 3.2 Hz), 128.4, 128.3, 127.7, 127.6, 116.7, 107.5 (d, $^2J_{CF}$ = 23.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –88.2 (s, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{15}FO_2$ $[M]^+$: 318.1056, found: 318.1055.



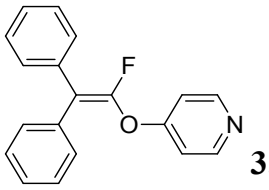
3ah

3-((1-Fluoro-2,2-diphenylvinyl)oxy)pyridine (3ai): Yellow oil. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 2.4 Hz, 1H), 8.37–8.36 (m, 1H), 7.41–7.21 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5 (d, $^{3}J_{CF}$ = 2.8 Hz), 150.6 (d, $^{1}J_{CF}$ = 287.6 Hz), 145.4, 139.4 (d, $^{4}J_{CF}$ = 0.9 Hz), 135.7 (d, $^{3}J_{CF}$ = 3.9 Hz), 135.6 (d, $^{3}J_{CF}$ = 3.9 Hz), 129.8, 129.7, 129.6 (d, $^{4}J_{CF}$ = 3.2 Hz), 128.4, 128.3, 127.6, 124.2, 123.6, 106.8 (d, $^{2}J_{CF}$ = 23.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −88.6 ppm; HRMS (EI): calcd for $C_{19}H_{14}FNO$ $[M]^+$: 291.1059, found: 291.1058.



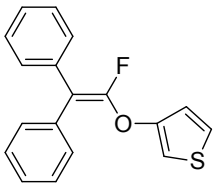
3ai

4-((1-Fluoro-2,2-diphenylvinyl)oxy)pyridine (3aj): White solid. Yield: 91%, mp 144.6−146.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.27 (m, 10H), 7.05−7.03 (m, 2H), 6.27−6.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 146.3 (d, $^{1}J_{CF}$ = 269.3 Hz), 138.5 (d, $^{3}J_{CF}$ = 1.7 Hz), 134.9 (d, $^{3}J_{CF}$ = 3.8 Hz), 134.8 (d, $^{4}J_{CF}$ = 3.2 Hz), 129.7 (d, $^{3}J_{CF}$ = 4.5 Hz), 129.5 (d, $^{4}J_{CF}$ = 3.2 Hz), 129.1, 128.7, 128.6, 128.5, 118.8, 117.4 (d, $^{2}J_{CF}$ = 20.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −95.0 (s, 1F) ppm; HRMS (EI): calcd for $C_{19}H_{14}FNO$ $[M]^+$: 291.1059, found: 291.1060.



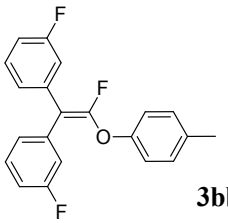
3aj

3-((1-Fluoro-2,2-diphenylvinyl)oxy)thiophene (3ak): Colorless oil. Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.23 (m, 10H), 7.18 (dd, J = 5.2, 3.2 Hz, 1H), 6.85–6.83 (m, 1H), 6.74−6,72 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (d, $^{1}J_{CF}$ = 287.9 Hz), 151.7 (d, $^{3}J_{CF}$ = 2.3 Hz), 136.2 (d, $^{3}J_{CF}$ = 4.0 Hz), 136.0 (d, $^{3}J_{CF}$ = 3.8 Hz), 129.9 (d, $^{4}J_{CF}$ = 4.1 Hz), 129.7 (d, $^{4}J_{CF}$ = 3.2 Hz), 128.3, 128.2, 127.3, 127.2, 125.4, 119.0 (d, $^{4}J_{CF}$ = 0.5 Hz), 105.4 (d, $^{4}J_{CF}$ = 1.5 Hz), 104.7 (d, $^{2}J_{CF}$ = 24.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −88.3 ppm; HRMS (EI): calcd for $C_{18}H_{13}FOS$ $[M]^+$: 296.0671, found: 296.0674.



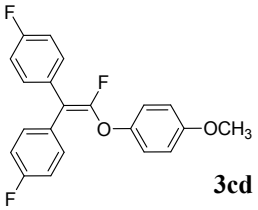
3ak

3,3'-(2-Fluoro-2-(*p*-tolyloxy)ethene-1,1-diyl)bis(fluorobenzene) (3bb): Yellow solid. Yield: 75%, mp 80.4−81.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.27 (m, 1H), 7.24−7.19 (m, 1H), 7.13−6.90 (m, 10H), 2.30(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, $^{1}J_{CF}$ = 244.2 Hz), 162.6 (d, $^{1}J_{CF}$ = 244.1 Hz), 152.2 (d, $^{3}J_{CF}$ = 2.2 Hz), 151.8 (d, $^{1}J_{CF}$ = 289.0 Hz), 138.0 (dd, $^{3}J_{CF}$ = 8.1 Hz, $^{3}J_{CF}$ = 4.3 Hz), 137.8 (dd, $^{3}J_{CF}$ = 8.0 Hz, $^{3}J_{CF}$ = 3.8 Hz), 134.1, 130.4, 129.8 (d, $^{3}J_{CF}$ = 8.2 Hz), 129.7 (d, $^{3}J_{CF}$ = 8.1 Hz), 125.6 (dd, $^{4}J_{CF}$ = 4.0 Hz, $^{4}J_{CF}$ = 3.6 Hz), 125.3−125.2 (m), 116.8 (dd, $^{2}J_{CF}$ = 22.2 Hz, $^{4}J_{CF}$ = 4.4 Hz), 116.5 (dd, $^{2}J_{CF}$ = 22.2 Hz, $^{4}J_{CF}$ = 3.4 Hz), 116.5, 114.4 (d, $^{2}J_{CF}$ = 21.0 Hz), 114.3 (d, $^{2}J_{CF}$ = 21.0 Hz), 103.9–103.6 (m), 20.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −84.1 (s, 1F), −113.0 to −113.1 (m, 2F) ppm; HRMS(EI): calcd for $C_{21}H_{15}F_3O$ $[M]^+$: 340.1075, found: 340.1076.



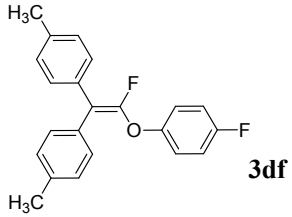
3bb

4,4'-(2-Fluoro-2-(4-methoxyphenoxy)ethene-1,1-diyl)bis(fluorobenzene) (3cd): Yellow solid. Yield: 76%, mp 79.6–81.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.21 (m, 4H), 7.05−6.94 (m, 6H), 6.87–6.82 (m, 2H), 3.76 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $^{1}J_{CF}$ = 245.5 Hz), 156.3, 151.5 (d, $^{1}J_{CF}$ = 286.7 Hz), 148.4 (d, $^{3}J_{CF}$ = 2.3 Hz), 132.2−132.1 (m), 132.0−131.9 (m), 131.5 (dd, $^{3}J_{CF}$ = 8.0 Hz, $^{4}J_{CF}$ = 3.9 Hz), 131.2 (dd, $^{3}J_{CF}$ = 7.9 Hz, $^{4}J_{CF}$ = 3.2 Hz), 117.7, 115.3 (d, $^{2}J_{CF}$ = 21.4 Hz), 115.2 (d, $^{2}J_{CF}$ = 21.3 Hz), 114.9, 103.4 (d, $^{2}J_{CF}$ = 26.3 Hz), 55.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −87.0 (s, 1F), −114.4 to −114.5 (m, 1F), −114.6 to −114.7 (m, 1F) ppm; HRMS (EI): calcd for $C_{21}H_{15}F_3O_2$ $[M]^+$:356.1024, found: 356.1025.



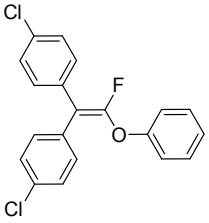
3cd

4,4'-(2-Fluoro-2-(4-fluorophenoxy)ethene-1,1-diyl)bis(methylbenzene) (3df): Colorless liquid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.22 (m, 2H), 7.14 (d, J = 8.4 Hz, 4H), 7.06−7.00 (m, 4H), 6.98−6.94 (m, 2H), 2.34 (s, 3H), 2.28 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, $^{1}J_{CF}$ = 240.7 Hz), 150.8 (d, $^{1}J_{CF}$ = 285.9 Hz), 151.0−150.9 (m), 137.1, 137.0, 133.4 (d, $^{3}J_{CF}$ = 4.0 Hz), 133.2 (d, $^{4}J_{CF}$ = 3.8 Hz), 129.8 (d, $^{3}J_{CF}$ = 4.1 Hz), 129.5 (d, $^{4}J_{CF}$ = 3.2 Hz), 129.0, 128.9, 117.9 (d, $^{3}J_{CF}$ = 8.1 Hz), 116.4 (d, $^{2}J_{CF}$ = 23.5 Hz), 105.9 (d, $^{2}J_{CF}$ = 24.7 Hz), 21.3, 21.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −88.7 (s, 1F), −119.3 to −119.4 (m, 1F) ppm; HRMS (EI): calcd for $C_{22}H_{18}F_2O$ $[M]^+$: 336.1326, found: 336.1327.



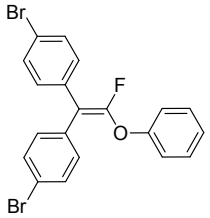
3df

4,4'-(2-Fluoro-2-phenoxyethene-1,1-diyl)bis(chlorobenzene) (3ea): Colorless liquid. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 4H), 7.26–7.16 (m, 6H), 7.14–7.06 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 (d, $^{3}J_{CF}$ = 2.5 Hz), 151.2 (d, $^{1}J_{CF}$ = 288.4 Hz), 134.3 (d, $^{3}J_{CF}$ = 4.1 Hz), 134.2 (d, $^{4}J_{CF}$ = 4.0 Hz), 133.4, 133.3, 131.2 (d, $^{3}J_{CF}$ = 4.2 Hz), 130.9 (d, $^{4}J_{CF}$ = 3.2 Hz), 130.0, 128.6, 128.5, 124.4, 116.5, 104.1 (d, $^{2}J_{CF}$ = 25.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –85.5 (s, 1F) ppm; HRMS (EI): calcd for $C_{20}H_{13}Cl_2FO$ $[M]^+$: 358.0327, found: 358.0326.



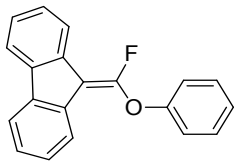
3ea

4,4'-(2-Fluoro-2-phenoxyethene-1,1-diyl)bis(bromobenzene) (3fa): White solid. Yield: 47%, mp 96.8–98.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.40–7.31 (m, 4H), 7.23–7.06 (m, 7H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4 (d, $^{3}J_{CF}$ = 2.4 Hz), 151.1 (d, $^{1}J_{CF}$ = 288.7 Hz), 134.7 (d, $^{3}J_{CF}$ = 4.2 Hz), 134.5 (d, $^{4}J_{CF}$ = 3.8 Hz), 131.6 (d, $^{3}J_{CF}$ = 6.3 Hz), 131.5 (d, $^{4}J_{CF}$ = 4.1 Hz), 131.2, 131.1, 130.0, 124.4, 121.6, 121.5, 116.5, 104.2 (d, $^{2}J_{CF}$ = 25.8 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –85.3 (s, 1F) ppm; HRMS (EI): calcd for $C_{20}H_{13}Br_2FO$ $[M]^+$: 447.9297, found: 447.9304.



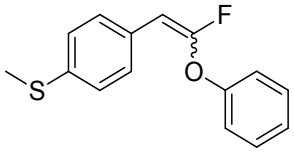
3fa

9-(Fluoro(phenoxy)methylene)-9*H*-fluorene (3ga): Yellow solid. Yield: 73%, mp 76.9–78.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 1H), 7.80–7.76 (m, 3H), 7.40–7.31 (m, 5H), 7.23–7.17 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (d, $^{3}J_{CF}$ = 2.0 Hz), 152.4 (d, $^{1}J_{CF}$ = 299.6 Hz), 139.1, 138.8, 135.3 (d, $^{3}J_{CF}$ = 7.6 Hz), 135.2 (d, $^{3}J_{CF}$ = 6.5 Hz), 130.1, 127.4, 127.3, 127.3, 127.2, 125.1, 124.3, 124.2, 123.6, 120.0, 117.4, 103.1 (d, $^{2}J_{CF}$ = 25.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –72.9 (s, 1F) ppm; HRMS (EI): calcd for $C_{20}H_{13}FO$ $[M]^+$: 288.0950, found: 288.0949.



3ga

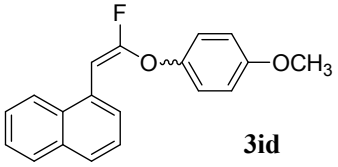
(*E*/*Z*)-(4-(2-Fluoro-2-phenoxyvinyl)phenyl)(methyl)sulfane (3ha): Colorless liquid. Yield: 86%. A mixture of *E*- and *Z*-isomers (47:53, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 4H, both *E*- and *Z*-isomer), 7.21–7.12 (m, 5H, both *E*- and *Z*-isomer), 5.64 (d, *J* = 5.6 Hz, 1H, *E*-isomer), 5.26 (d, *J* = 28.8 Hz, 1H, *Z*-isomer), 2.45 (s, 3H, *Z*-isomer), 2.41 (s, 3H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (d, $^{1}J_{CF}$ = 286.0 Hz), 154.8 (d, $^{3}J_{CF}$ = 0.9 Hz), 153.7 (d, $^{3}J_{CF}$ = 2.6 Hz), 153.5 (d, $^{1}J_{CF}$ = 282.1 Hz), 136.9, 136.8, 130.0, 129.9, 129.2 (d, $^{3}J_{CF}$ = 6.5 Hz), 128.9 (d, $^{3}J_{CF}$ = 8.1 Hz), 128.2, 128.1, 128.0 (d, $^{4}J_{CF}$ = 3.6 Hz), 126.8 (d, $^{4}J_{CF}$ = 4.6 Hz), 124.6, 124.5, 117.4, 116.6, 91.9 (d, $^{2}J_{CF}$ = 37.9 Hz), 90.0 (d, $^{2}J_{CF}$ = 19.4 Hz), 15.9, 15.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –82.1 (d, *J* = 28.6 Hz, 1F, *Z*-isomer), –82.5 (d, *J* = 5.6 Hz, 1F, *E*-isomer) ppm; HRMS (EI): calcd for $C_{15}H_{13}FOS$ $[M]^+$: 260.0671, found: 260.0673.



3ha

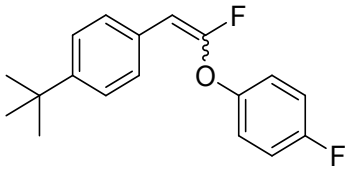
(*E*/*Z*)-1-(2-Fluoro-2-(4-methoxyphenoxy)vinyl)naphthalene (3id): Yellow solid. Yield: 81%. A mixture of *E*- and *Z*-isomers (65:35, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H, *E*-isomer), 8.10–8.08 (m, 1H, *Z*-isomer), 7.98–7.85 (m, 3H, both *E*- and *Z*-isomer), 7.68–7.53 (m, 3H, both *E*- and *Z*-isomer), 7.34 (d, *J* = 8.8 Hz, 2H, *Z*-isomer), 7.20 (d, *J* = 8.8 Hz, 2H, *E*-isomer), 7.05 (d, *J* = 9.2 Hz, 2H, *Z*-isomer), 6.94 (d, *J* = 8.8 Hz, 2H, *E*-isomer), 6.42 (d, *J* = 5.6 Hz, 1H, *E*-isomer), 5.95 (d, *J* = 27.2 Hz, 1H, *Z*-isomer), 3.88 (s, 3H, *Z*-isomer), 3.82 (s, 3H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4

(d, $^{1}J_{CF}$ = 280.3 Hz), 157.0, 156.6, 155.3 (d, $^{1}J_{CF}$ = 282.0 Hz), 148.2, 147.9, 134.0, 133.9, 131.9 (d, $^{3}J_{CF}$ = 3.6 Hz), 131.7, 129.0, 128.9, 128.8, 128.7, 127.7, 127.5, 126.8, 126.7, 126.4, 126.3, 126.1 (d, $^{4}J_{CF}$ = 2.0 Hz), 126.0, 125.9, 125.8, 124.1, 124.0, 119.5, 118.2, 115.2, 115.0, 87.8 (d, $^{2}J_{CF}$ = 38.2 Hz), 84.7 (d, $^{2}J_{CF}$ = 20.6 Hz), 55.7, 55.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –81.1 (d, *J* = 5.6 Hz, 1F, *E*-isomer), –85.1 (d, *J* = 27.1 Hz, 1F, *Z*-isomer) ppm; HRMS(EI): calcd for $C_{19}H_{15}FO_2$ $[M]^+$: 294.1056, found: 294.1058.



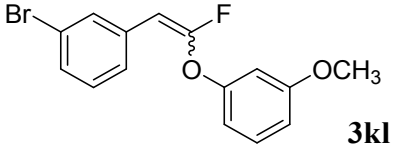
3id

(*E*/*Z*)-1-(*tert*-Butyl)-4-(2-fluoro-2-(4-fluorophenoxy)vinyl)benzene (3jf): Colorless liquid. Yield: 88%. A mixture of *E*- and *Z*-isomers (74:26, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4H, both *E*- and *Z*-isomer), 7.11–7.08 (m, 2H, both *E*- and *Z*-isomer), 7.04–6.99 (m, 2H, both *E*- and *Z*-isomer), 5.66 (d, *J* = 5.6 Hz, 1H, *E*-isomer), 5.27 (d, *J* = 28.8 Hz, 1H, *Z*-isomer), 1.31 (s, 9H, *Z*-isomer), 1.28 (s, 9H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $^{1}J_{CF}$ = 241.5 Hz), 159.3 (d, $^{1}J_{CF}$ = 241.1 Hz), 155.0 (d, $^{1}J_{CF}$ = 285.7 Hz), 153.4 (d, $^{1}J_{CF}$ = 281.6 Hz), 150.8, 150.7, 149.9 (d, $^{3}J_{CF}$ = 2.0 Hz), 149.8 (d, $^{3}J_{CF}$ = 2.1 Hz), 149.7–149.6 (m), 129.2 (d, $^{3}J_{CF}$ = 6.4 Hz), 128.9 (d, $^{3}J_{CF}$ = 7.9 Hz), 127.5 (d, $^{4}J_{CF}$ = 6.9 Hz), 127.3 (d, $^{4}J_{CF}$ = 3.6 Hz), 125.6, 118.8 (d, $^{3}J_{CF}$ = 8.4 Hz), 118.0 (d, $^{3}J_{CF}$ = 8.2 Hz), 116.5 (d, $^{2}J_{CF}$ = 23.5 Hz), 116.4 (d, $^{2}J_{CF}$ = 23.5 Hz), 92.0 (d, $^{2}J_{CF}$ = 37.0 Hz), 90.0 (d, $^{2}J_{CF}$ = 19.4 Hz), 34.6, 34.5, 31.3, 31.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –83.6 (d, *J* = 29.0 Hz, 1F, *Z*-isomer), –84.0 (d, *J* = 5.6 Hz, 1F, *E*-isomer), –118.5 to –118.6 (m, 1F, *Z*-isomer), –118.9 to –119.0 (m, 1F, *E*-isomer) ppm; HRMS (EI): calcd for $C_{18}H_{18}F_2O$ $[M]^+$: 288.1326, found: 288.1327.



3jf

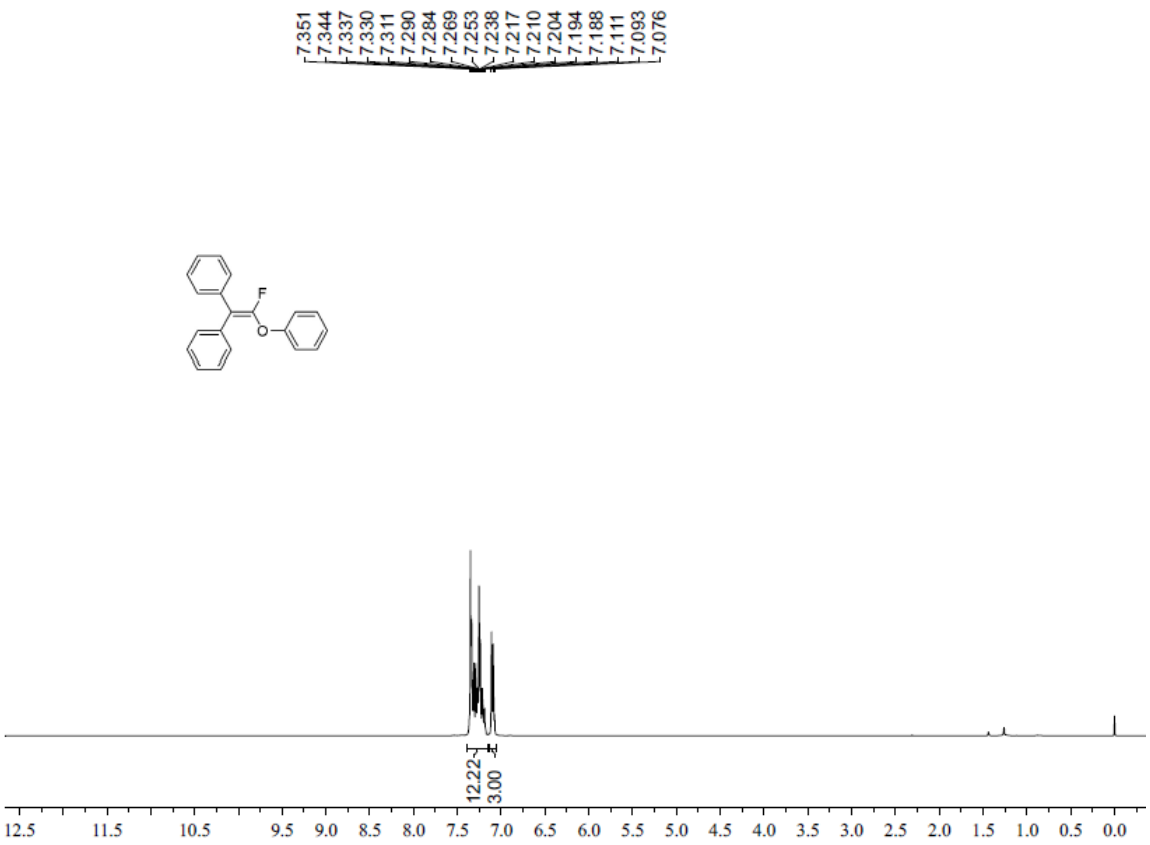
(*E*/*Z*)-1-Bromo-3-(2-fluoro-2-(3-methoxyphenoxy)vinyl)benzene (3kl): Yellow oil. Yield: 80%. A mixture of *E*- and *Z*-isomers (44:56, the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H, both *E*- and *Z*-isomer), 7.25–7.14 (m, 3H, both *E*- and *Z*-isomer), 7.10–7.01 (m, 1H, both *E*- and *Z*-isomer), 6.65–6.60 (m, 3H, both *E*- and *Z*-isomer), 5.50 (d, *J* = 5.6 Hz, 1H, *E*-isomer), 5.12 (d, *J* = 28.4 Hz, 1H, *Z*-isomer), 3.70 (s, 3H, both *E*- and *Z*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.9, 154.7 (d, $^{1}J_{CF}$ = 286.2 Hz), 154.3, 153.3 (d, $^{3}J_{CF}$ = 2.1 Hz), 153.1 (d, $^{1}J_{CF}$ = 284.1 Hz), 133.4 (d, $^{3}J_{CF}$ = 6.5 Hz), 133.2 (d, $^{3}J_{CF}$ = 8.6 Hz), 129.5, 129.4, 129.3, 129.0, 128.6 (d, $^{4}J_{CF}$ = 1.9 Hz), 128.4 (d, $^{4}J_{CF}$ = 2.0 Hz), 125.2 (d, $^{4}J_{CF}$ = 7.1 Hz), 125.0 (d, $^{4}J_{CF}$ = 3.5 Hz), 121.6, 121.5, 109.4, 109.3, 108.6, 107.7, 102.9, 102.1, 90.0 (d, $^{2}J_{CF}$ = 38.4 Hz), 87.7 (d, $^{2}J_{CF}$ = 28.9 Hz), 54.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ –80.1 (d, *J* = 5.6 Hz, 1F, *E*-isomer), –80.3 (d, *J* = 28.2 Hz, 1F, *Z*-isomer) ppm; HRMS (EI): calcd for $C_{15}H_{12}BrFO_2$ $[M]^+$: 322.0005, found: 322.0007.



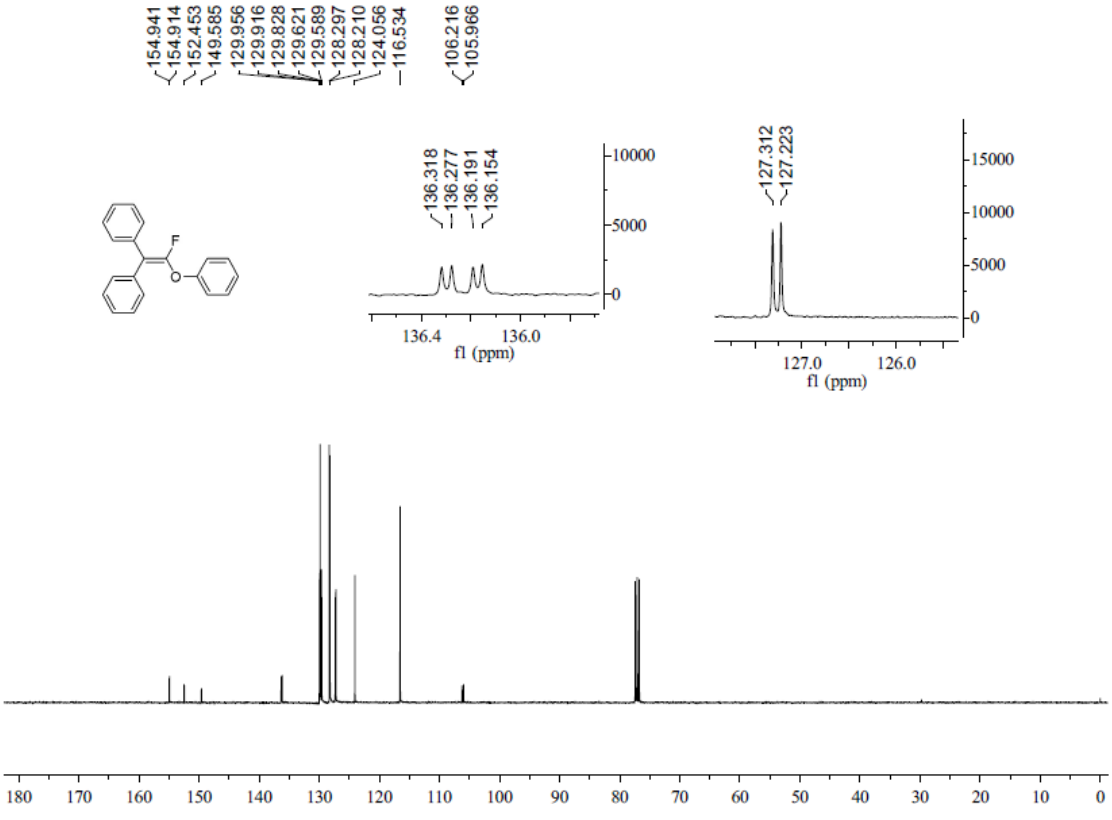
3kl

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

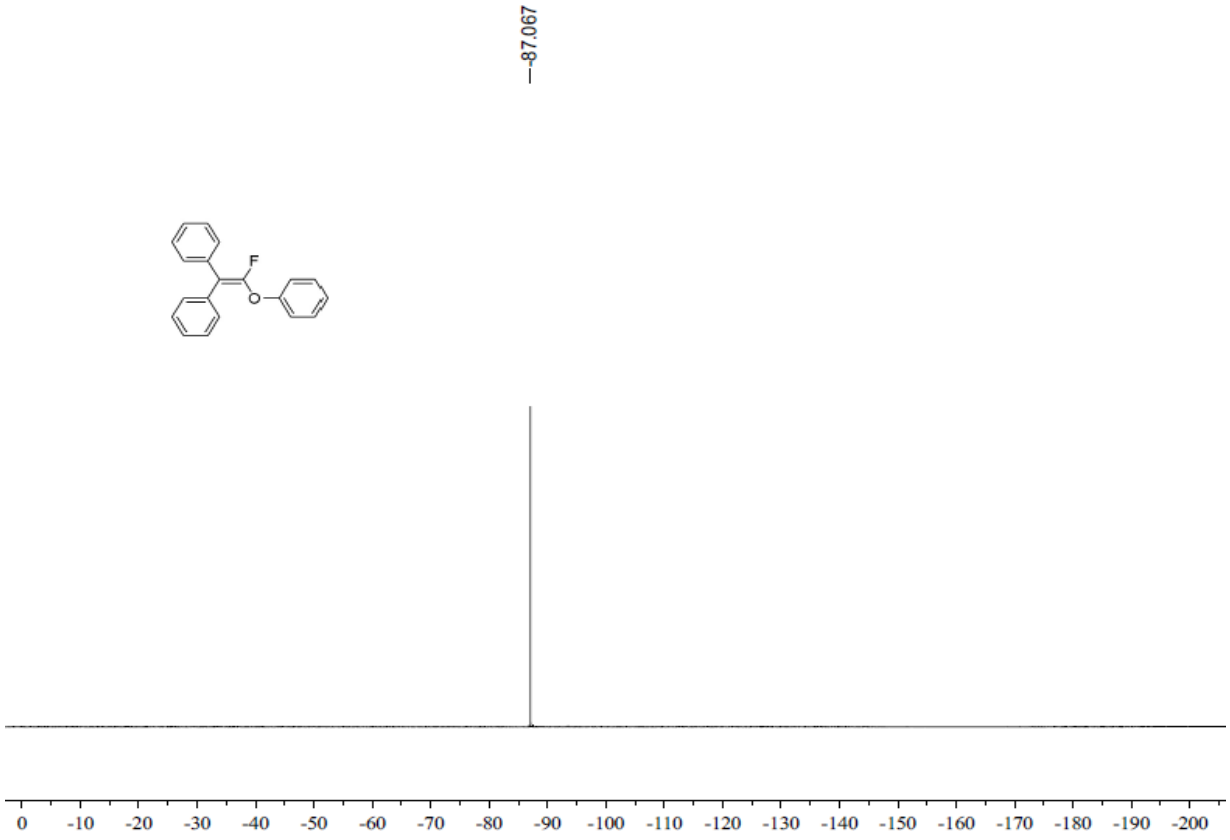
^{1}H NMR Spectrum of 3aa



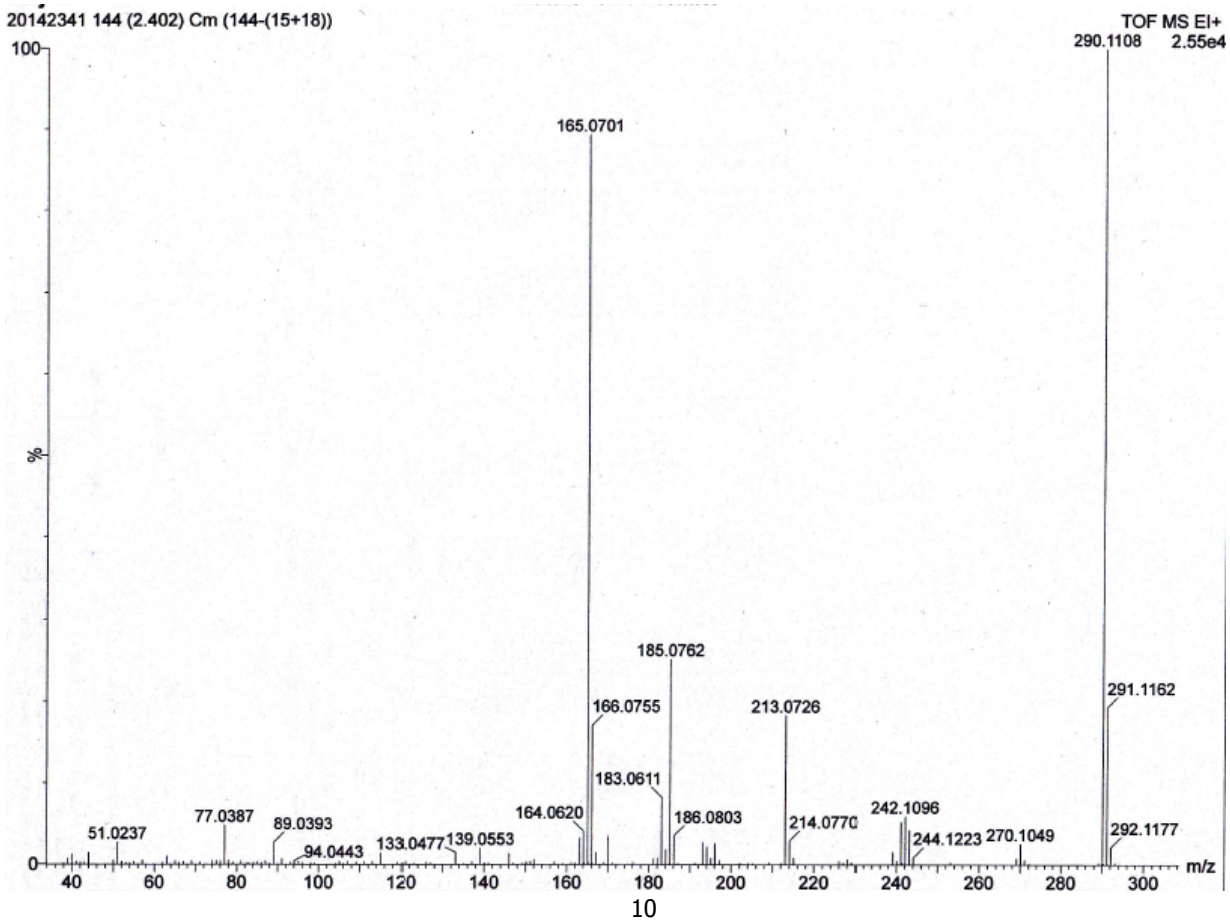
^{13}C NMR Spectrum of 3aa



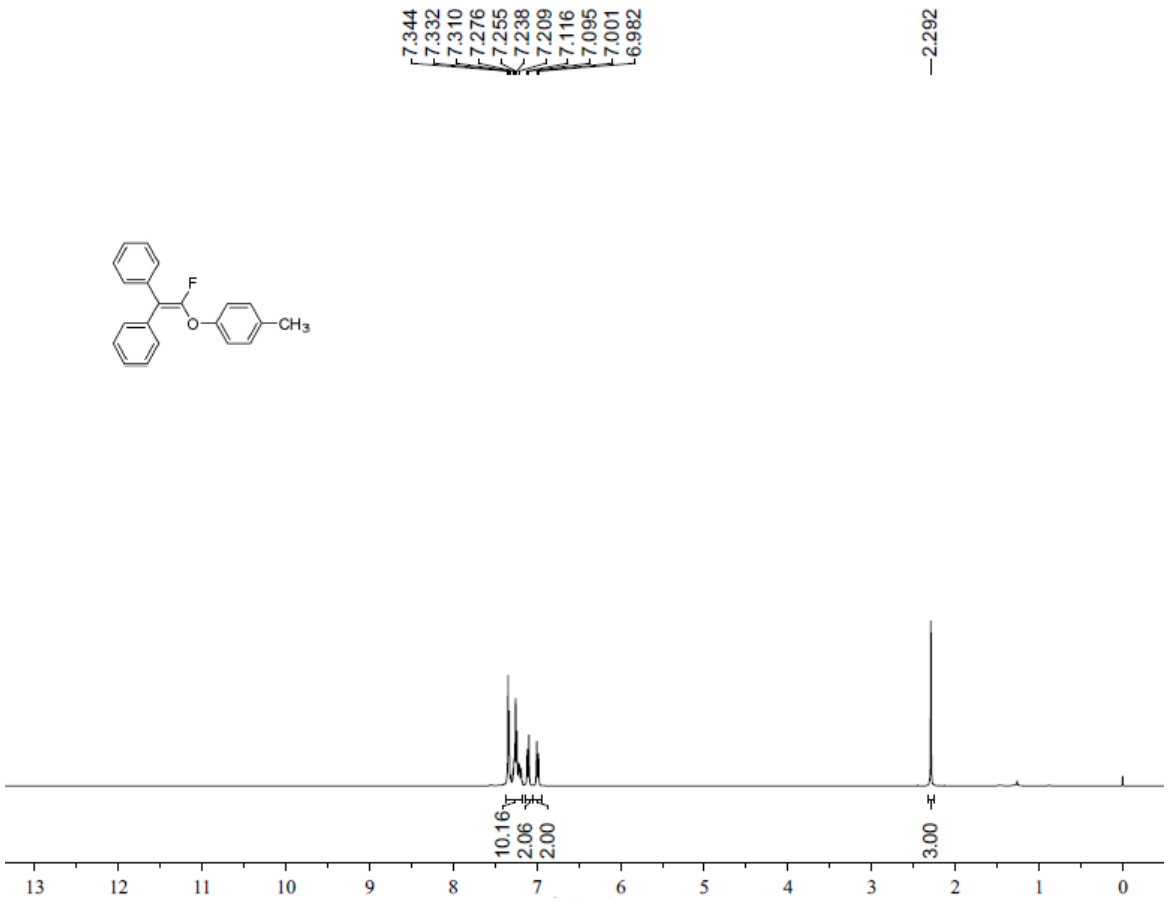
^{19}F NMR Spectrum of 3aa



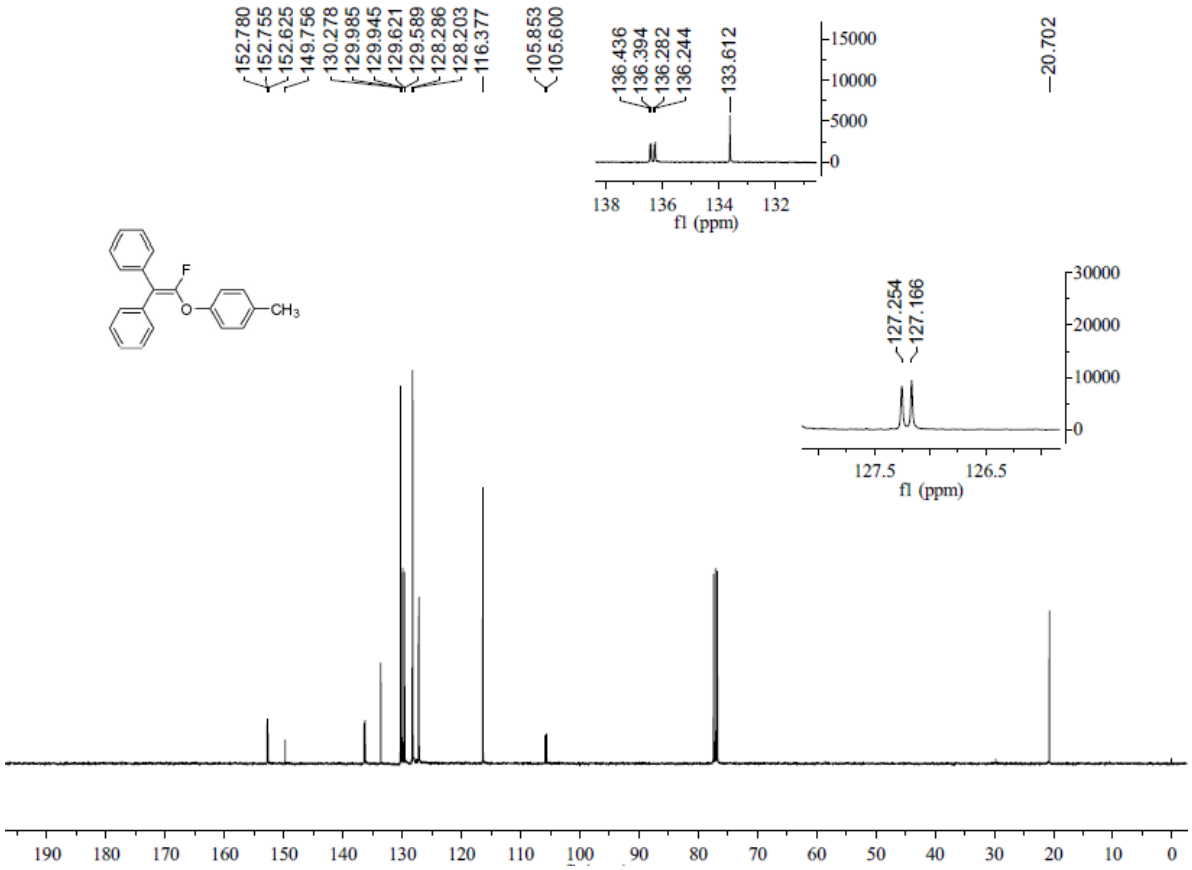
HRMS (EI) of 3aa



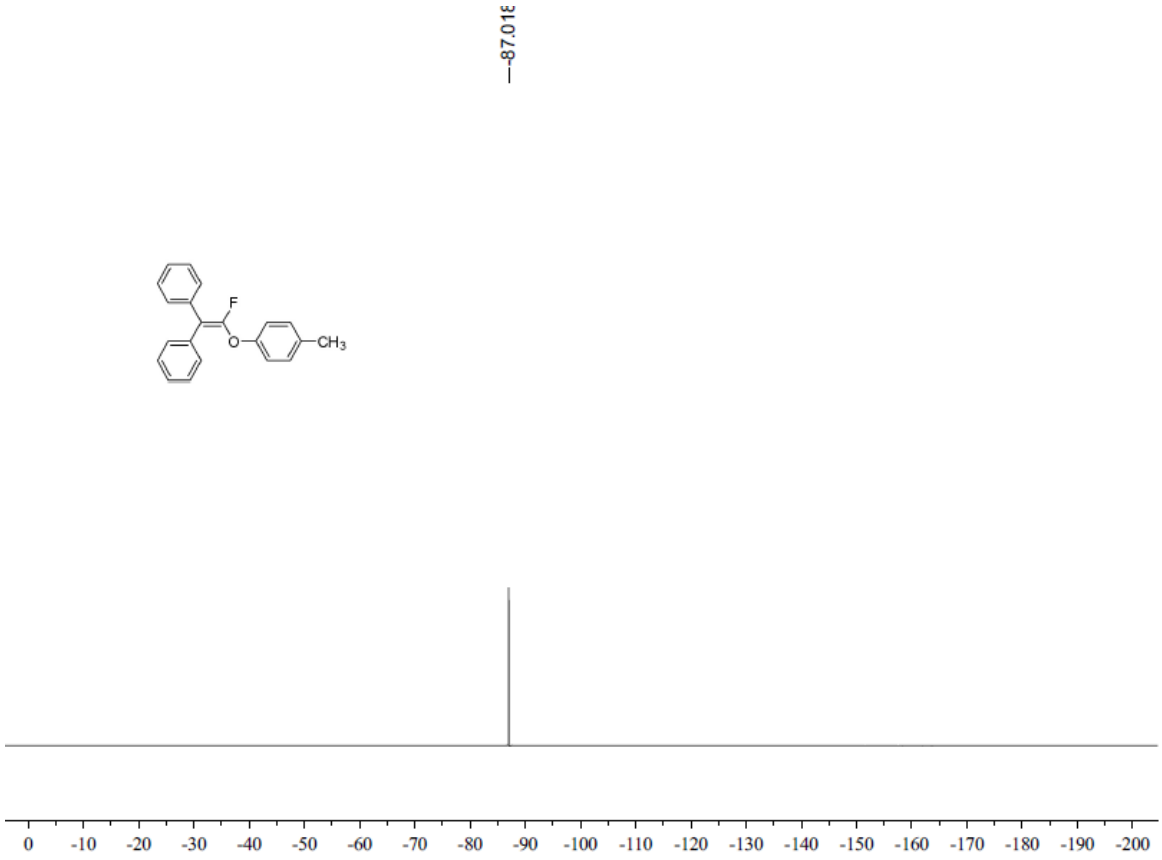
^{1}H NMR Spectrum of 3ab



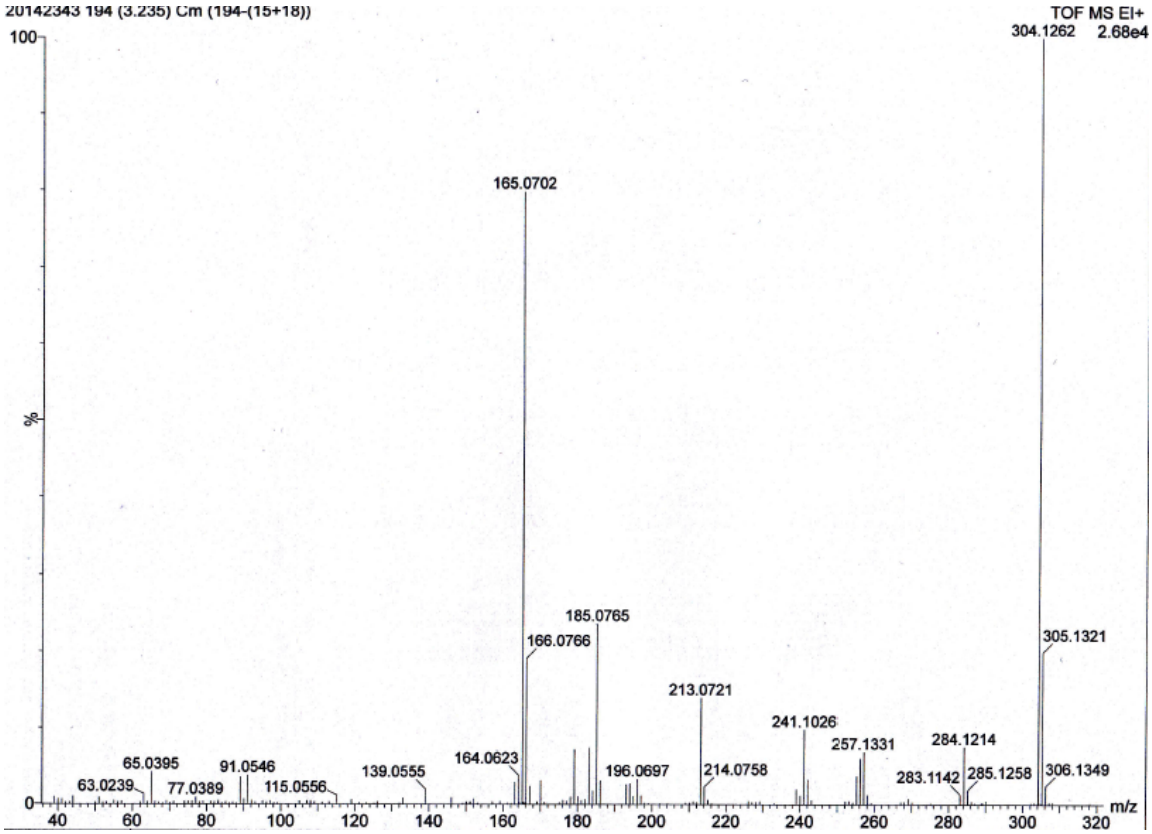
^{13}C NMR Spectrum of 3ab



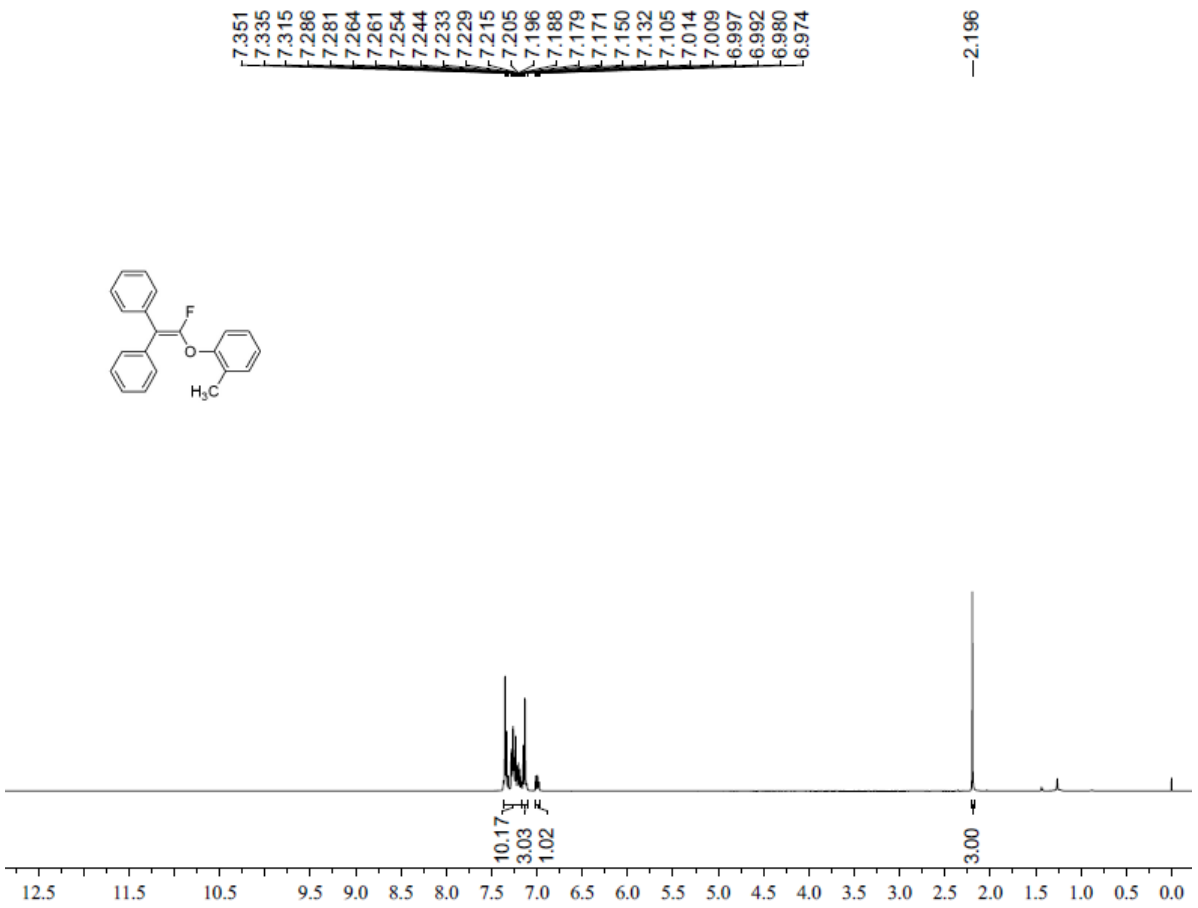
^{19}F NMR Spectrum of 3ab



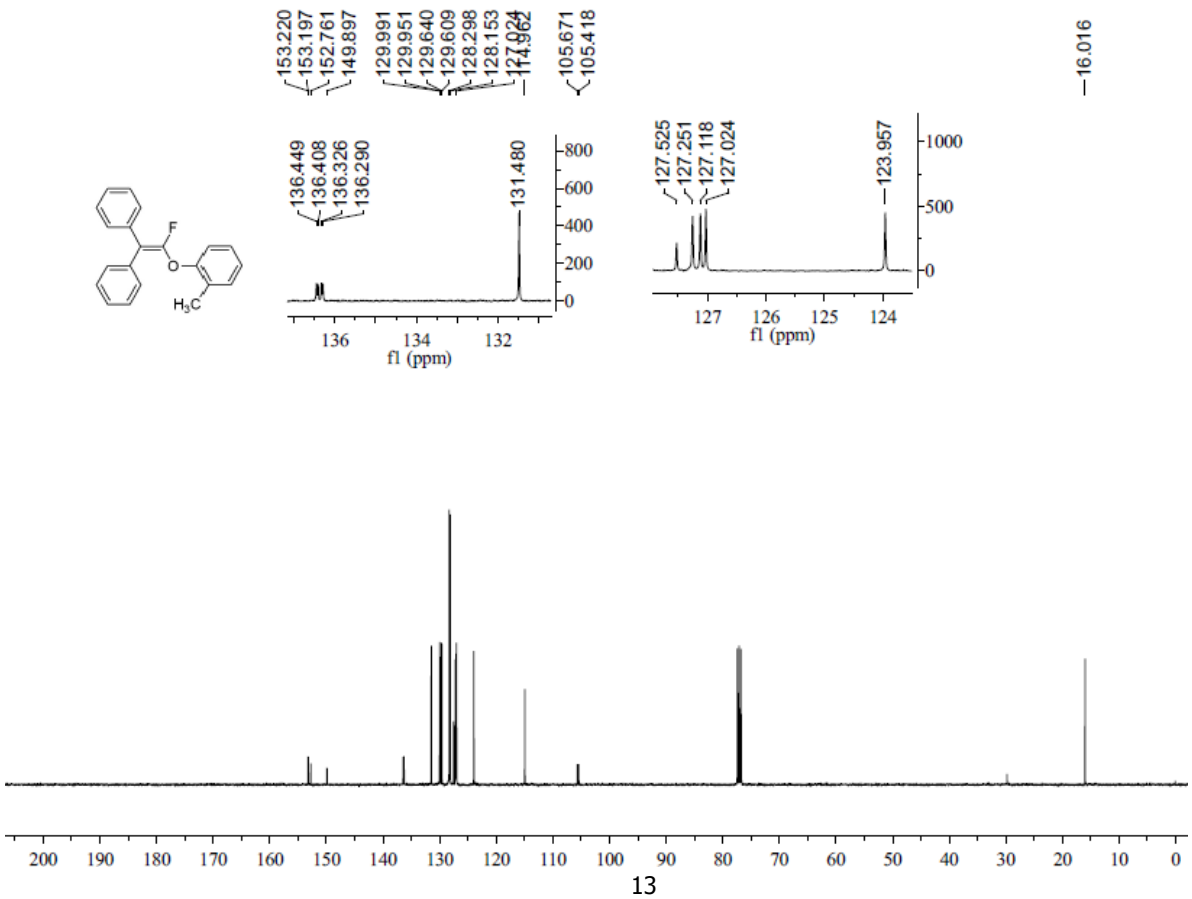
HRMS (EI) of 3ab



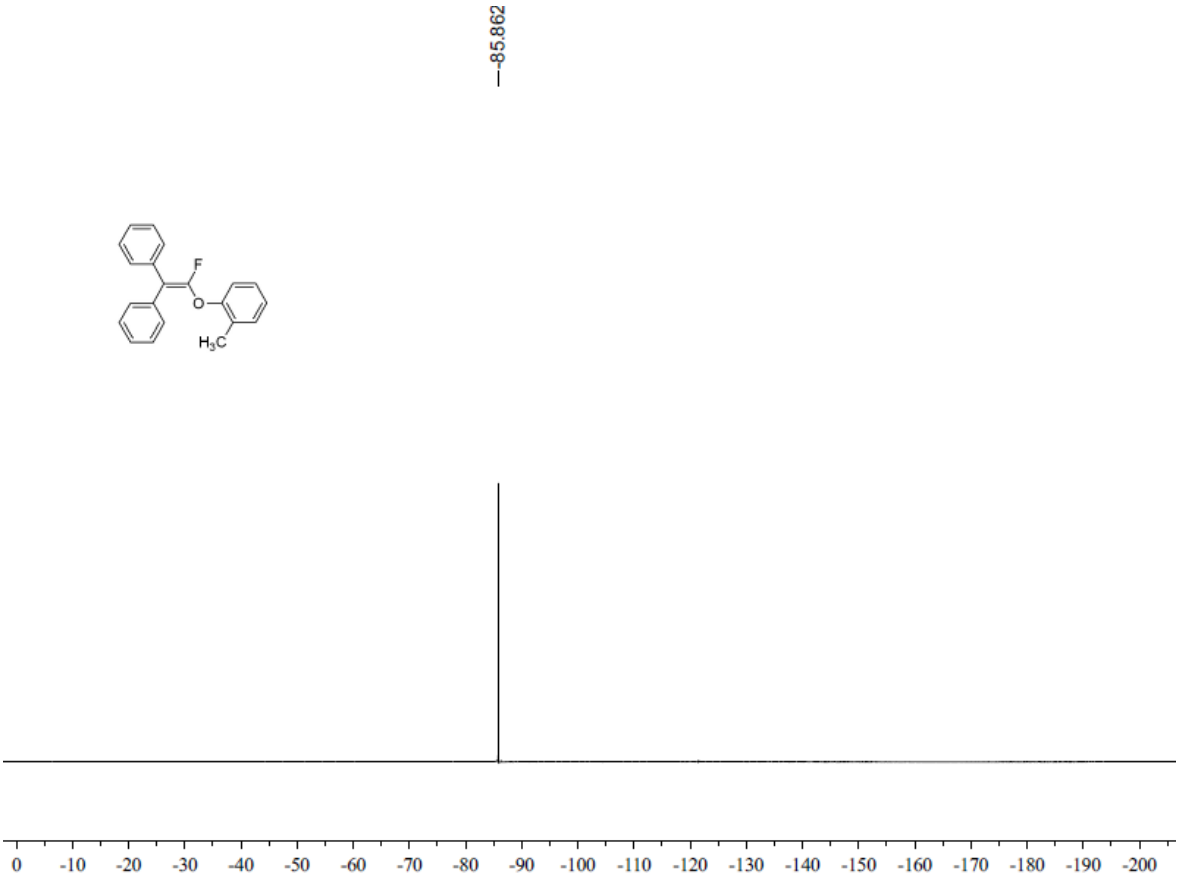
[1]H NMR Spectrum of 3ac



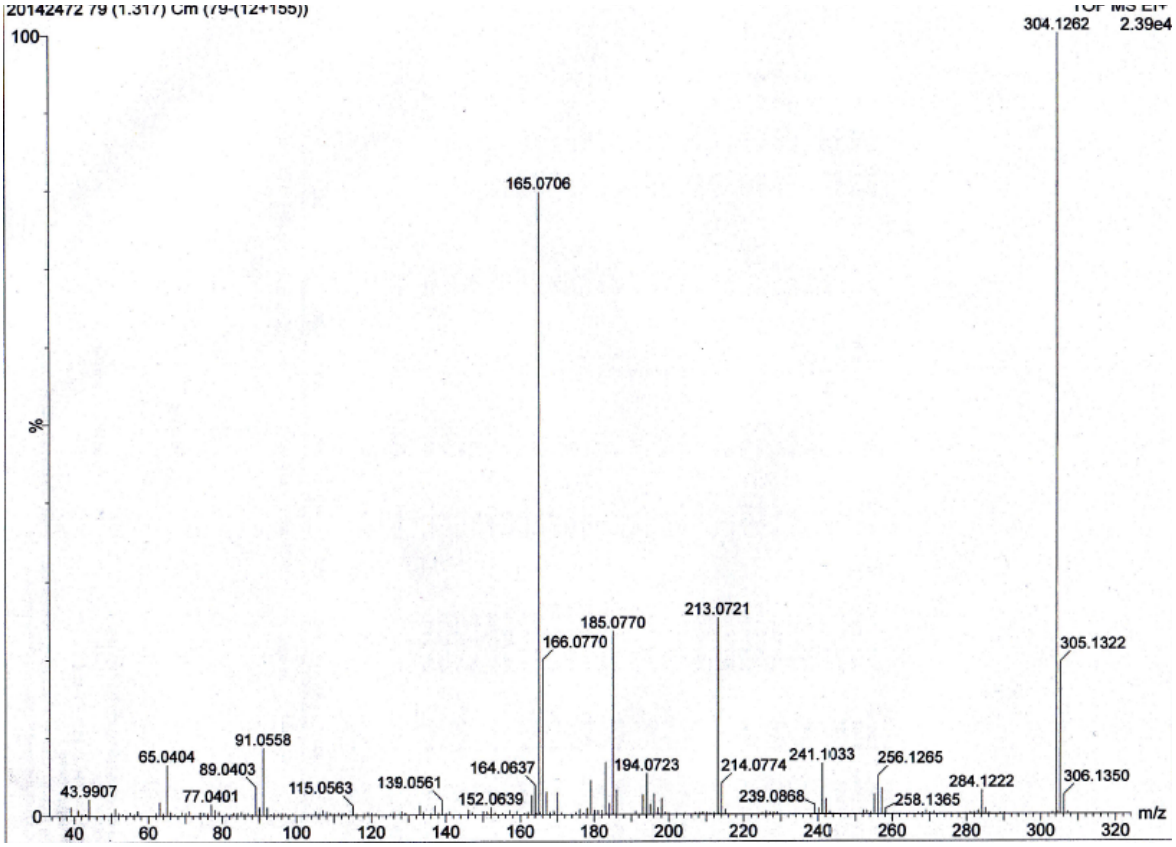
[13]C NMR Spectrum of 3ac



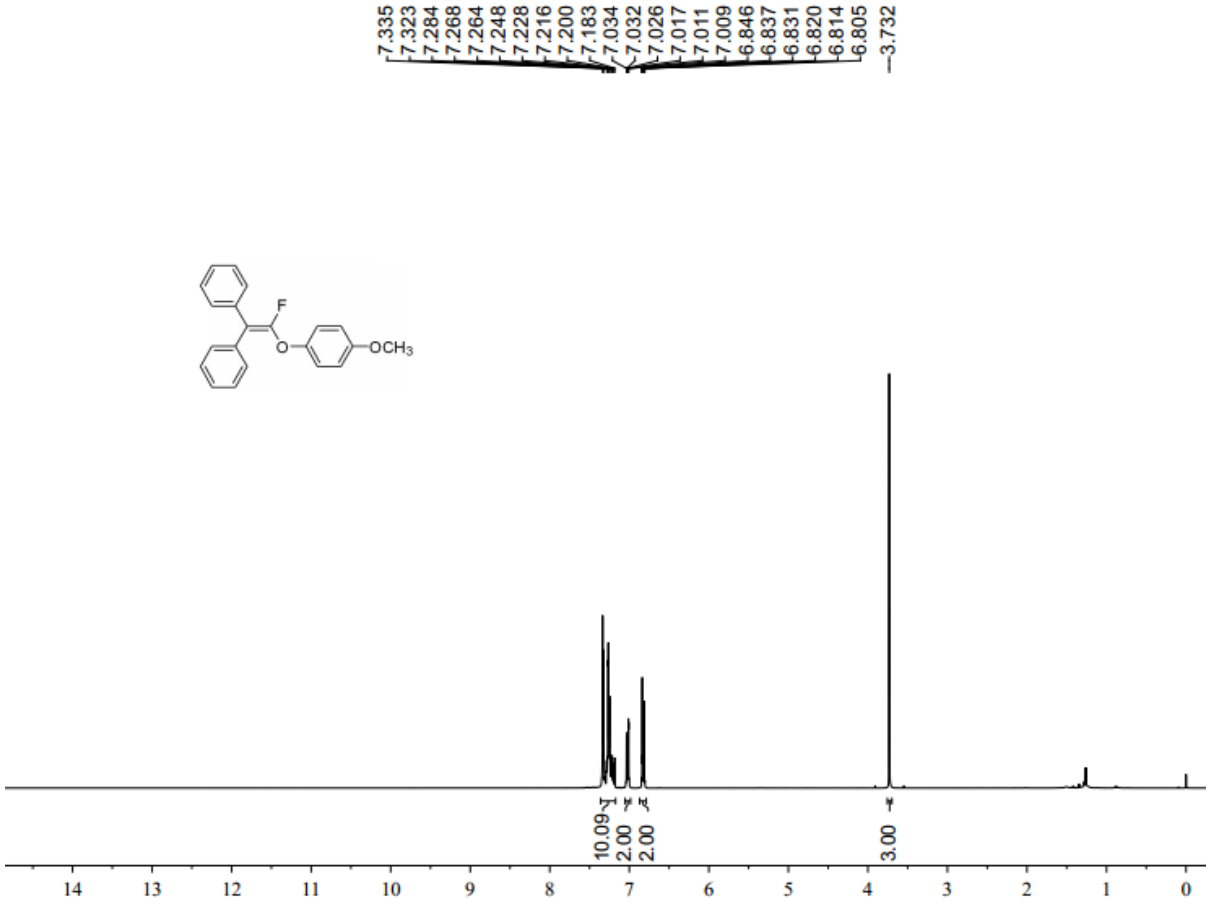
^{19}F NMR Spectrum of 3ac



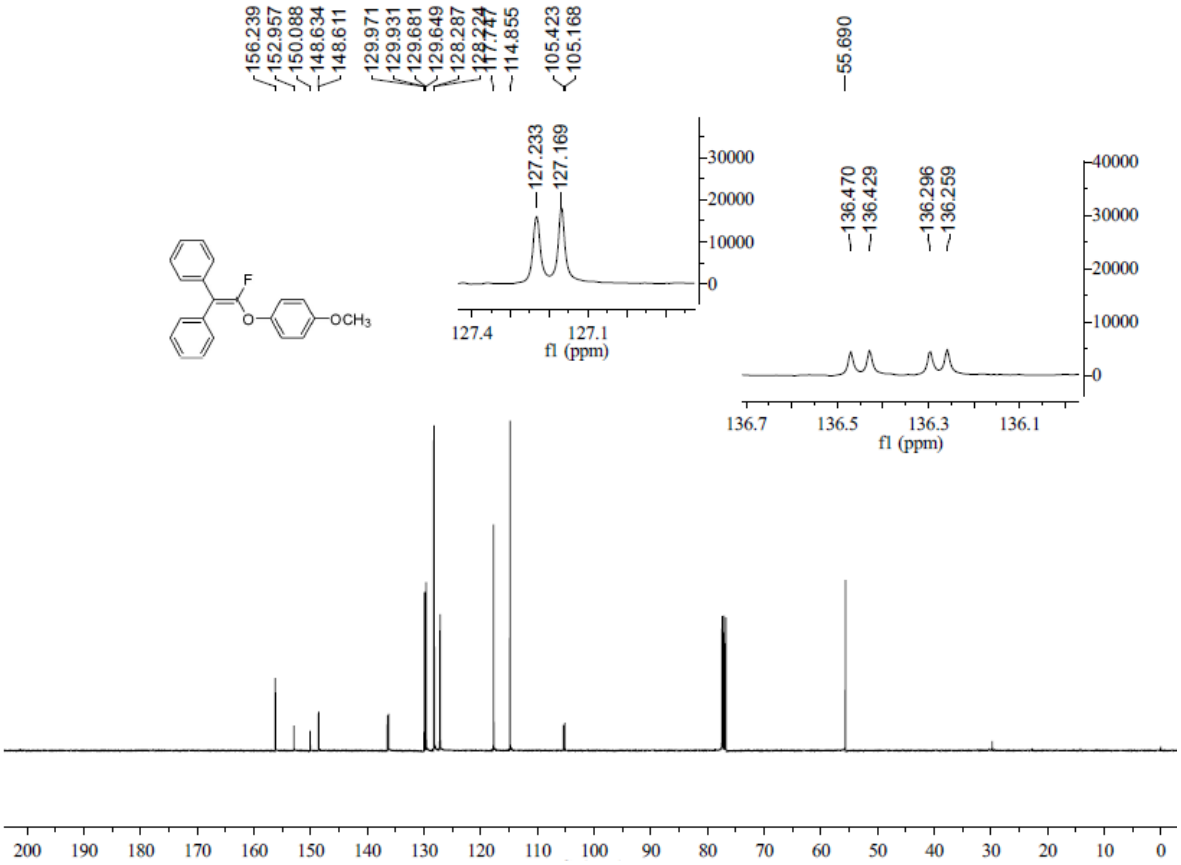
HRMS (EI) of 3ac



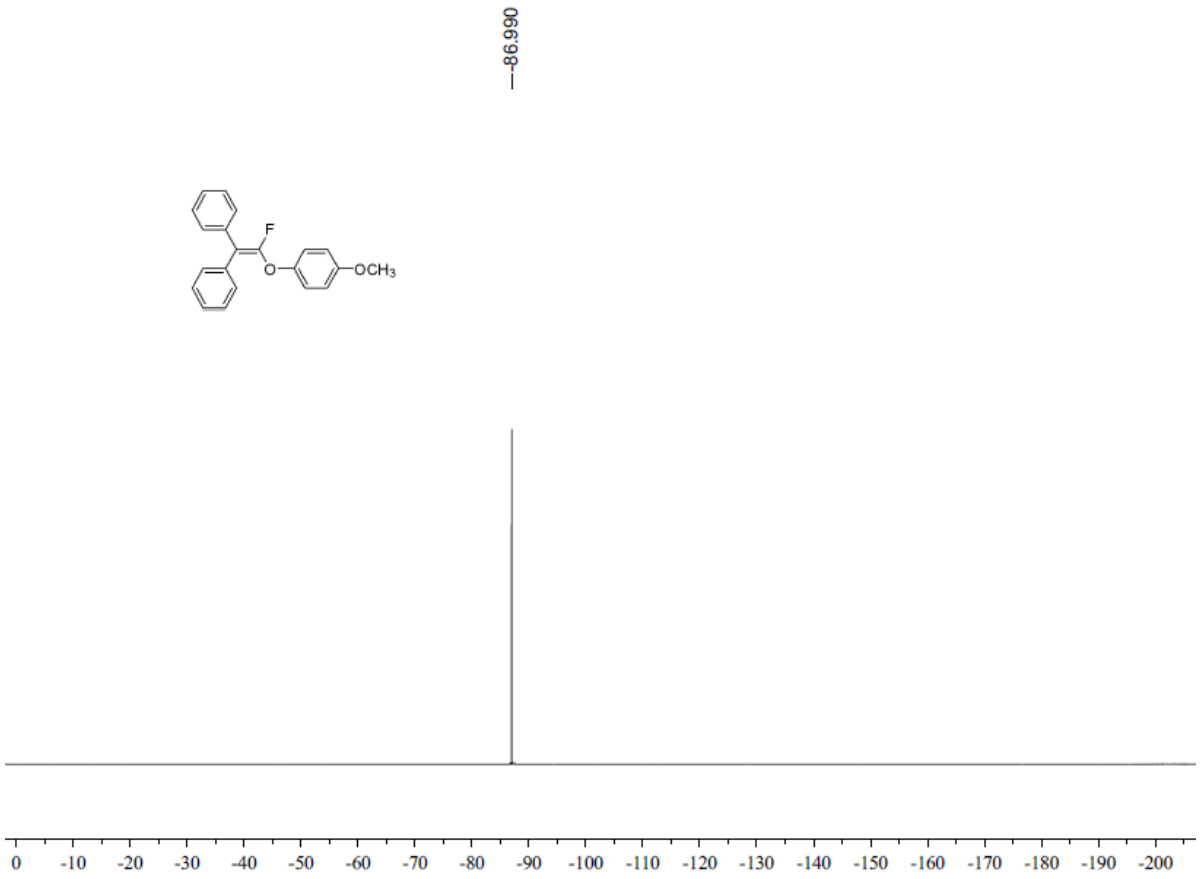
^{1}H NMR Spectrum of 3ad



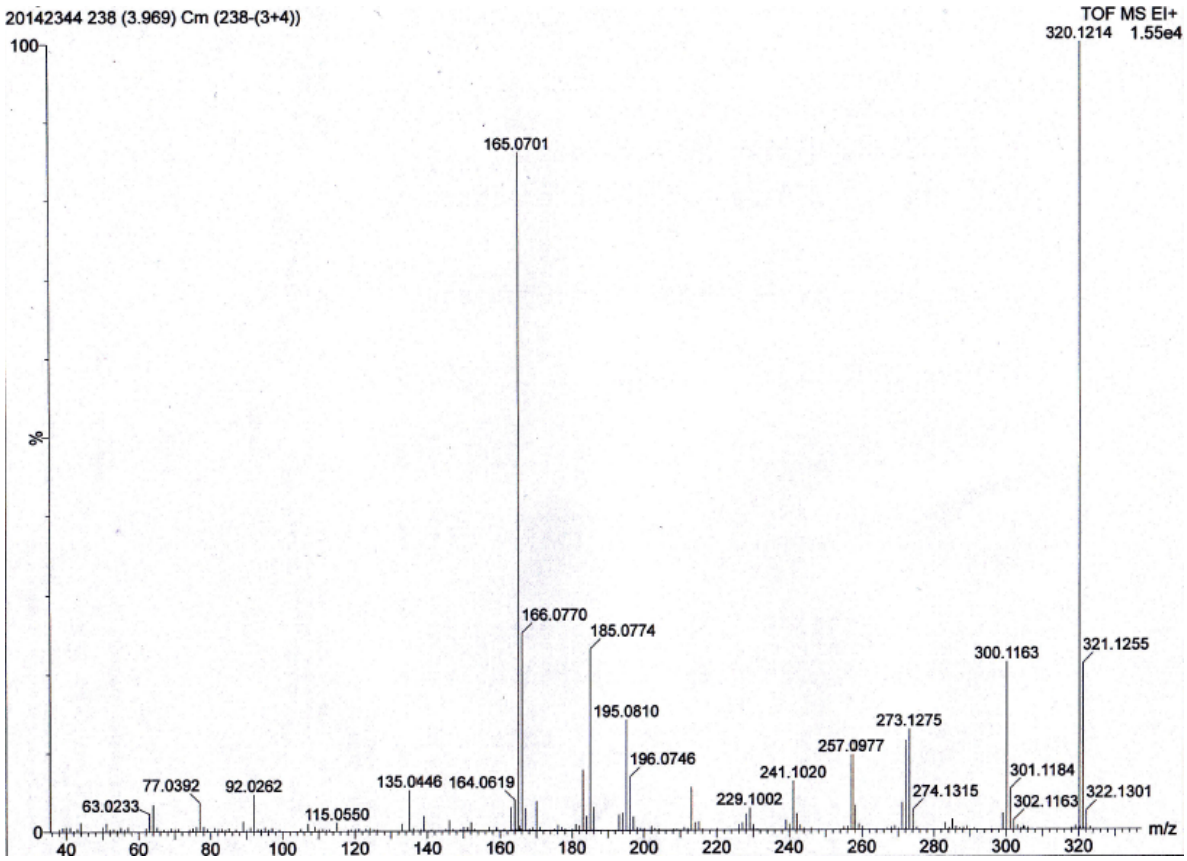
^{13}C NMR Spectrum of 3ad



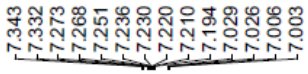
^{19}F NMR Spectrum of 3ad

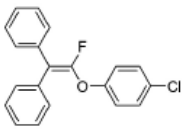


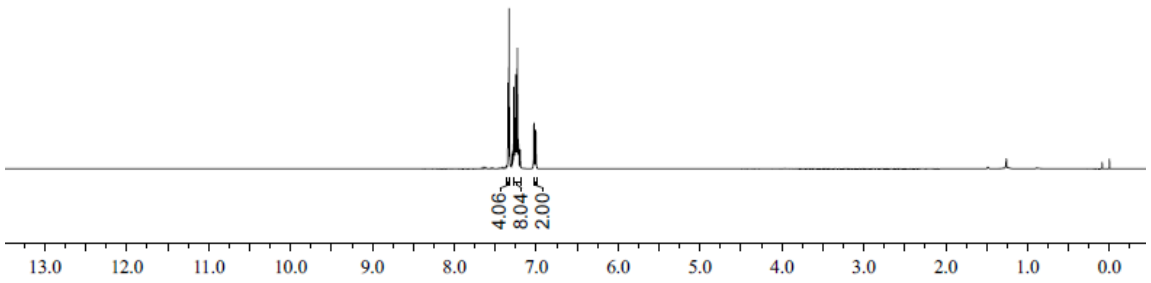
HRMS (EI) of 3ad



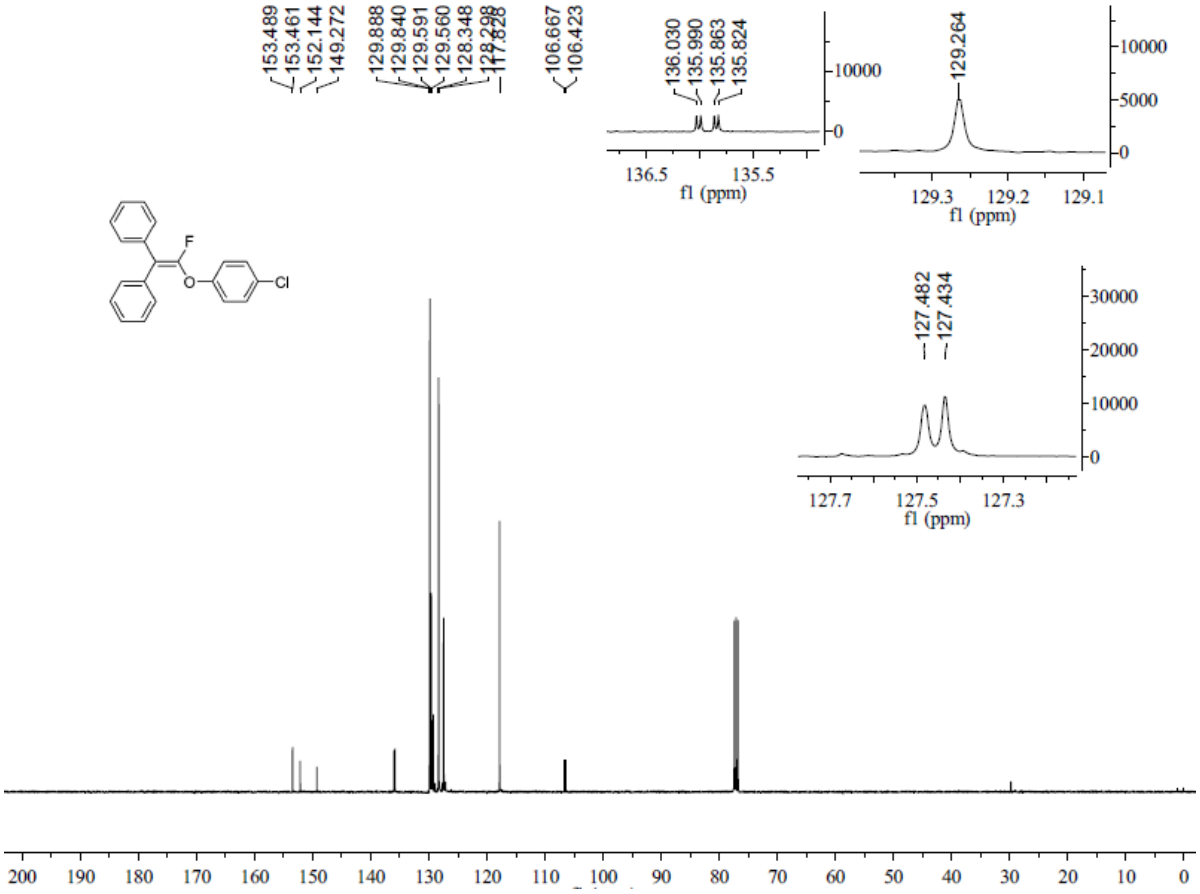
[1]H NMR Spectrum of 3ae



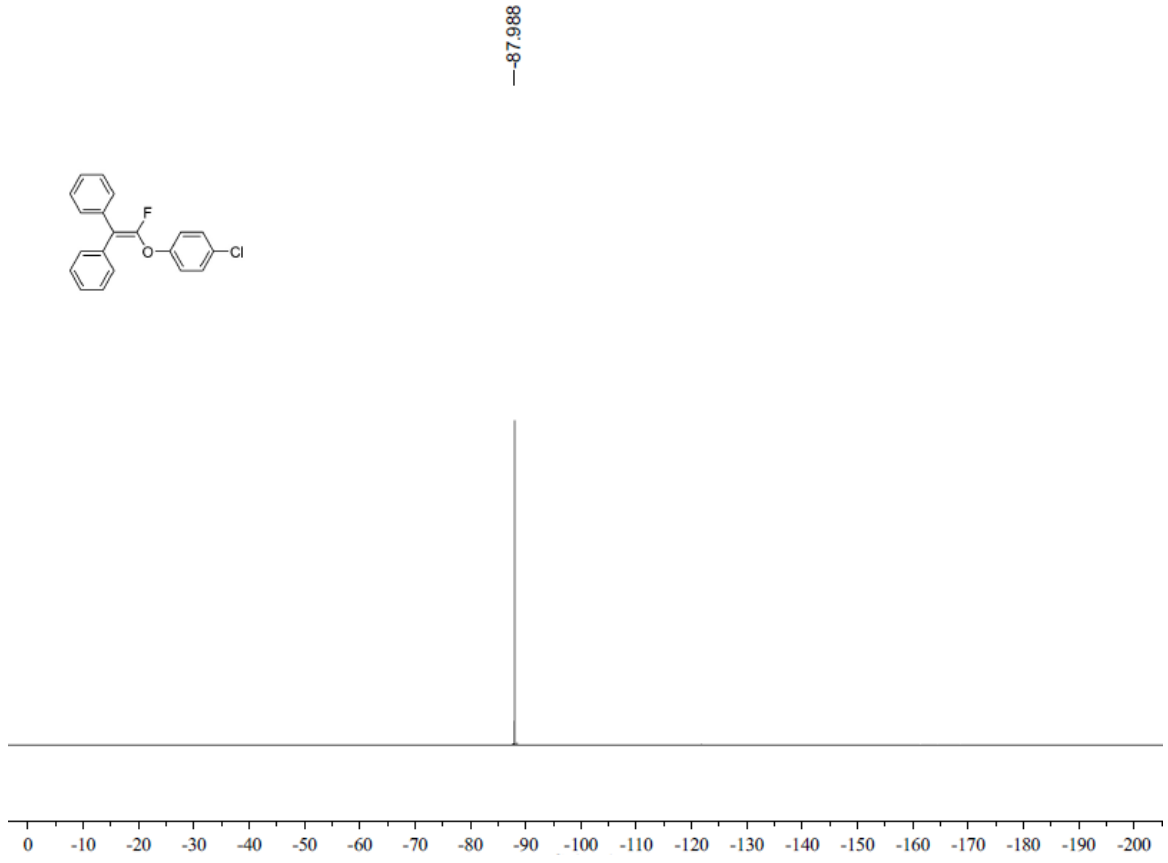




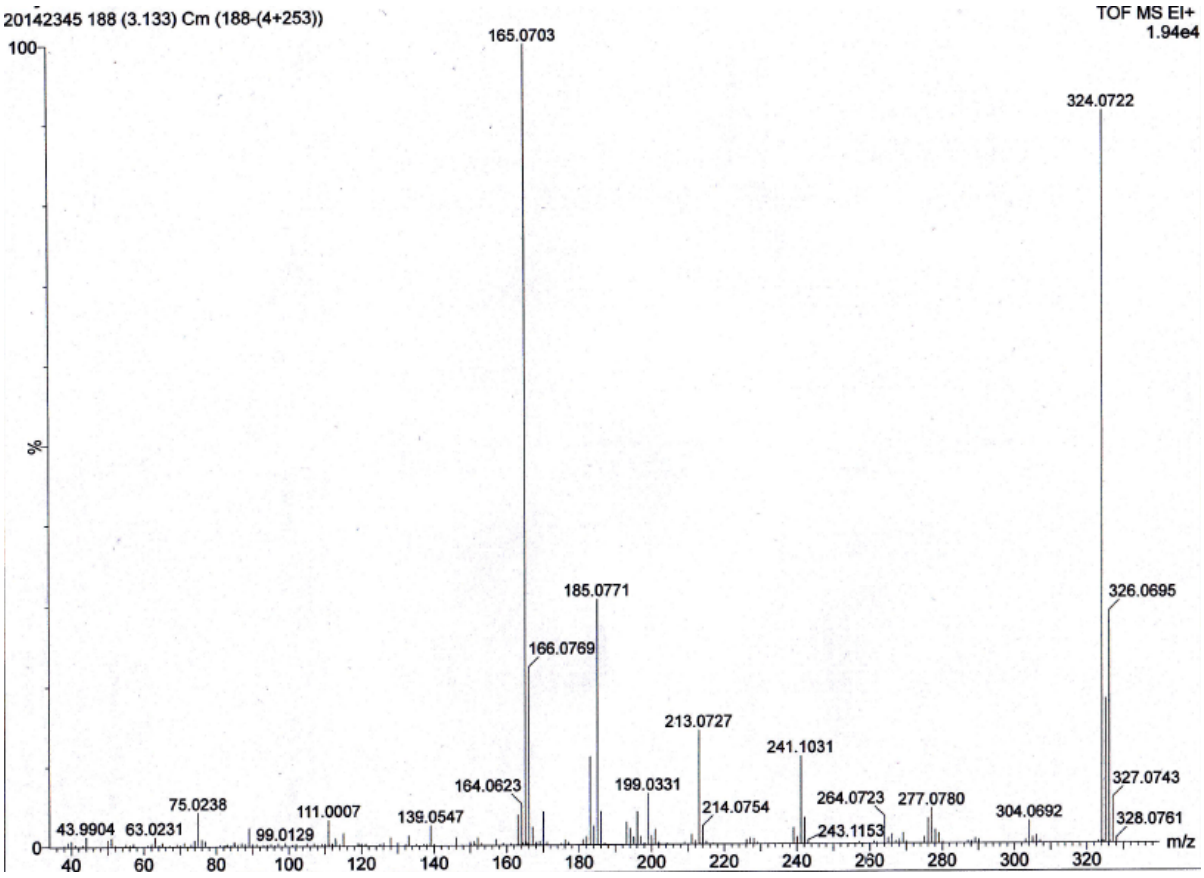
[13]C NMR Spectrum of 3ae



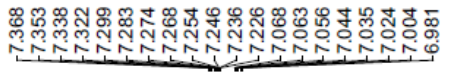
^{19}F NMR Spectrum of 3ae

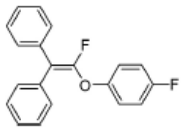


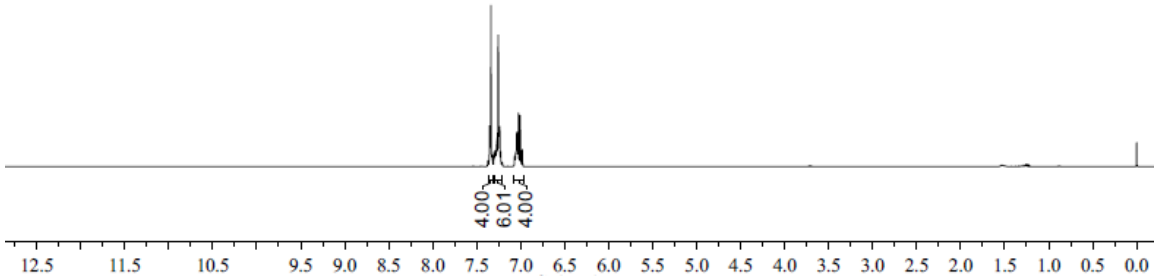
HRMS (EI) of 3ae



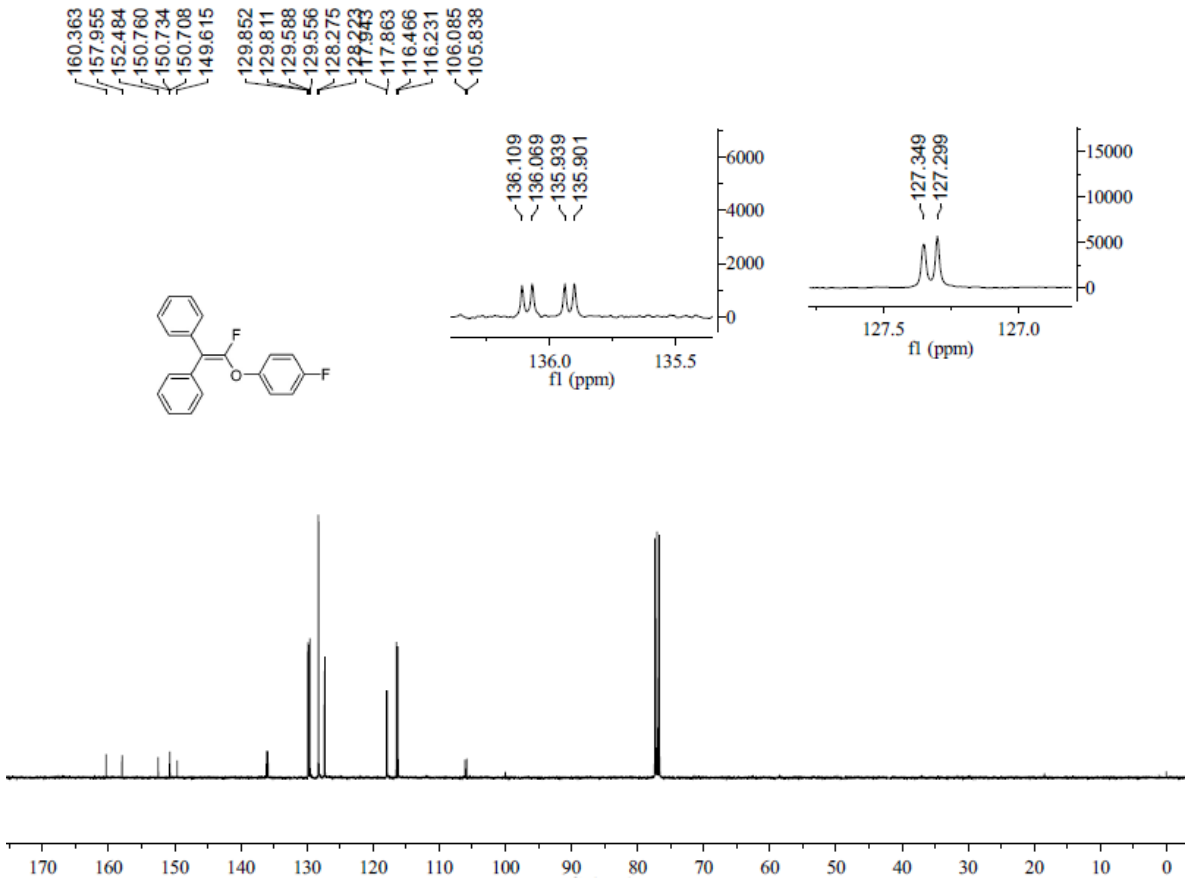
^{1}H NMR Spectrum of 3af



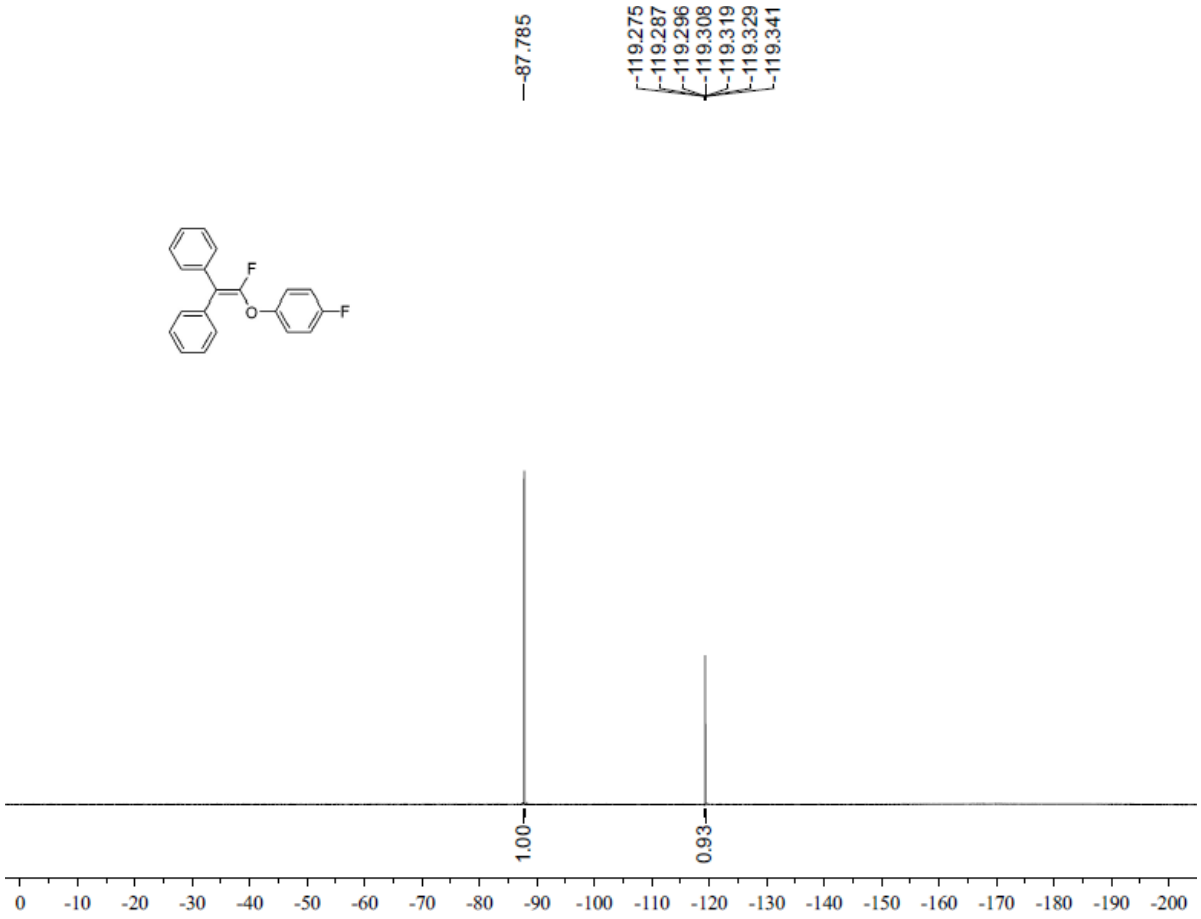




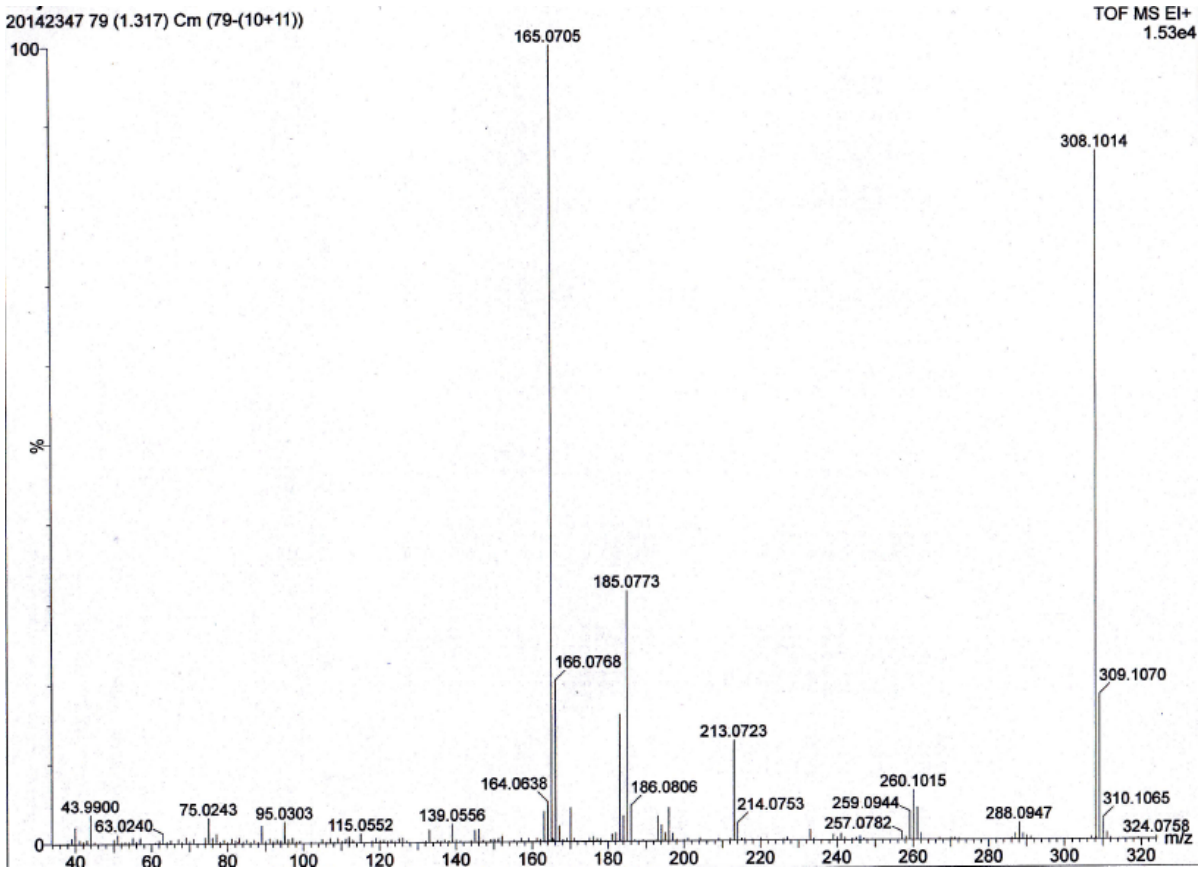
^{13}C NMR Spectrum of 3af



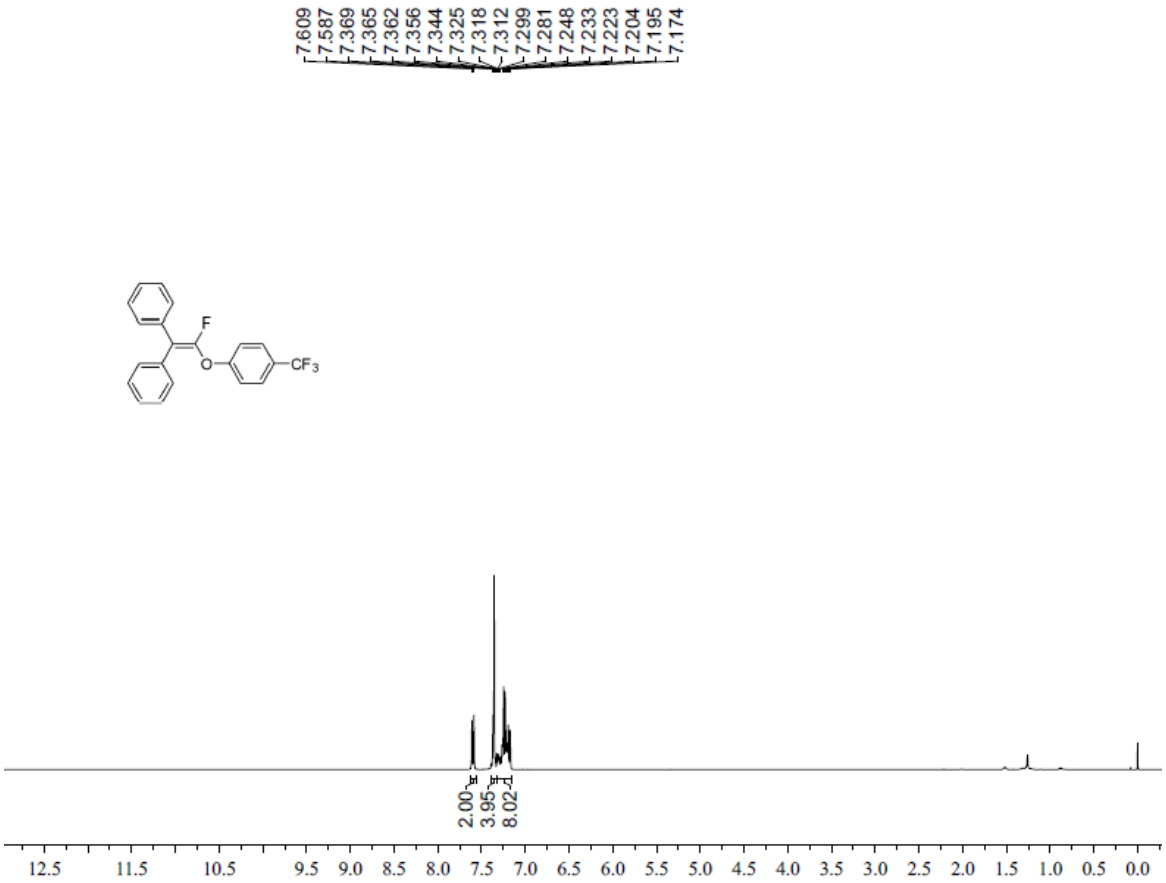
^{19}F NMR Spectrum of 3af



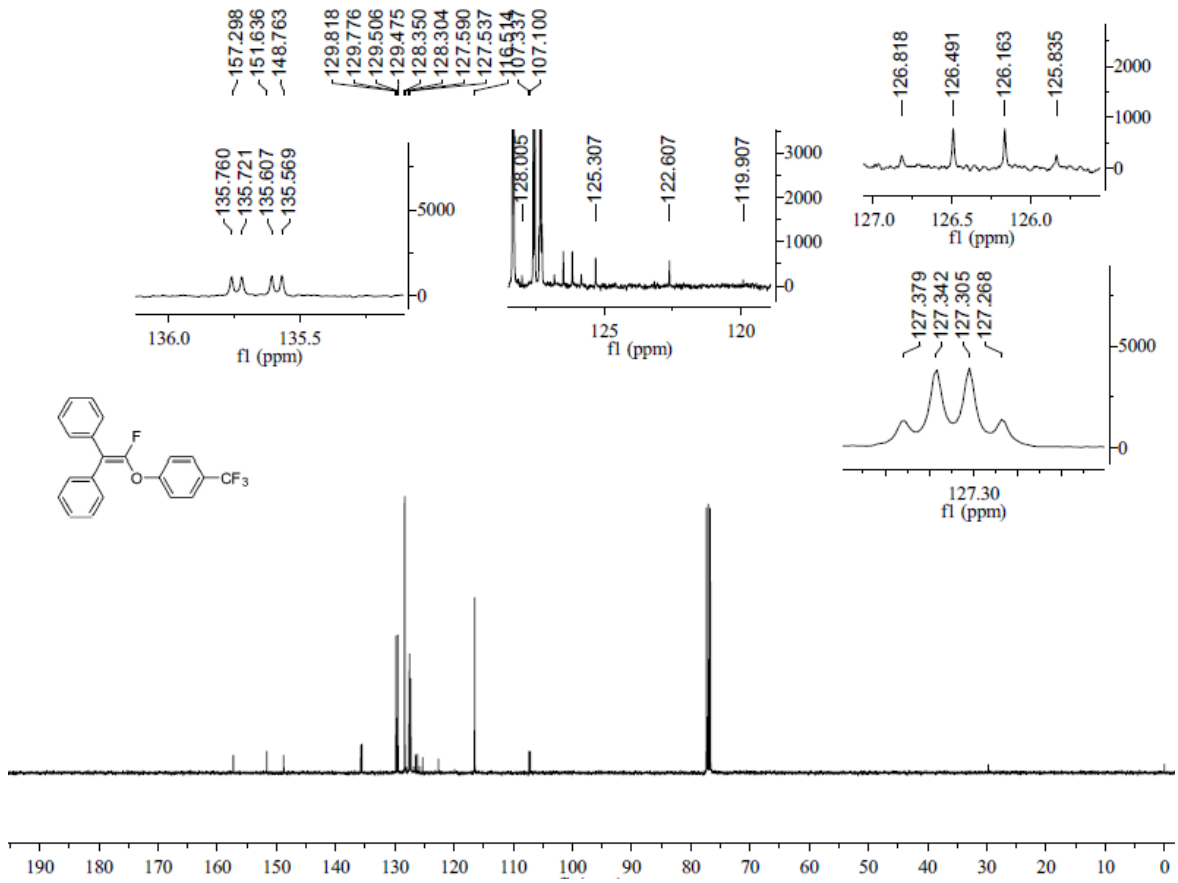
HRMS (EI) of 3af



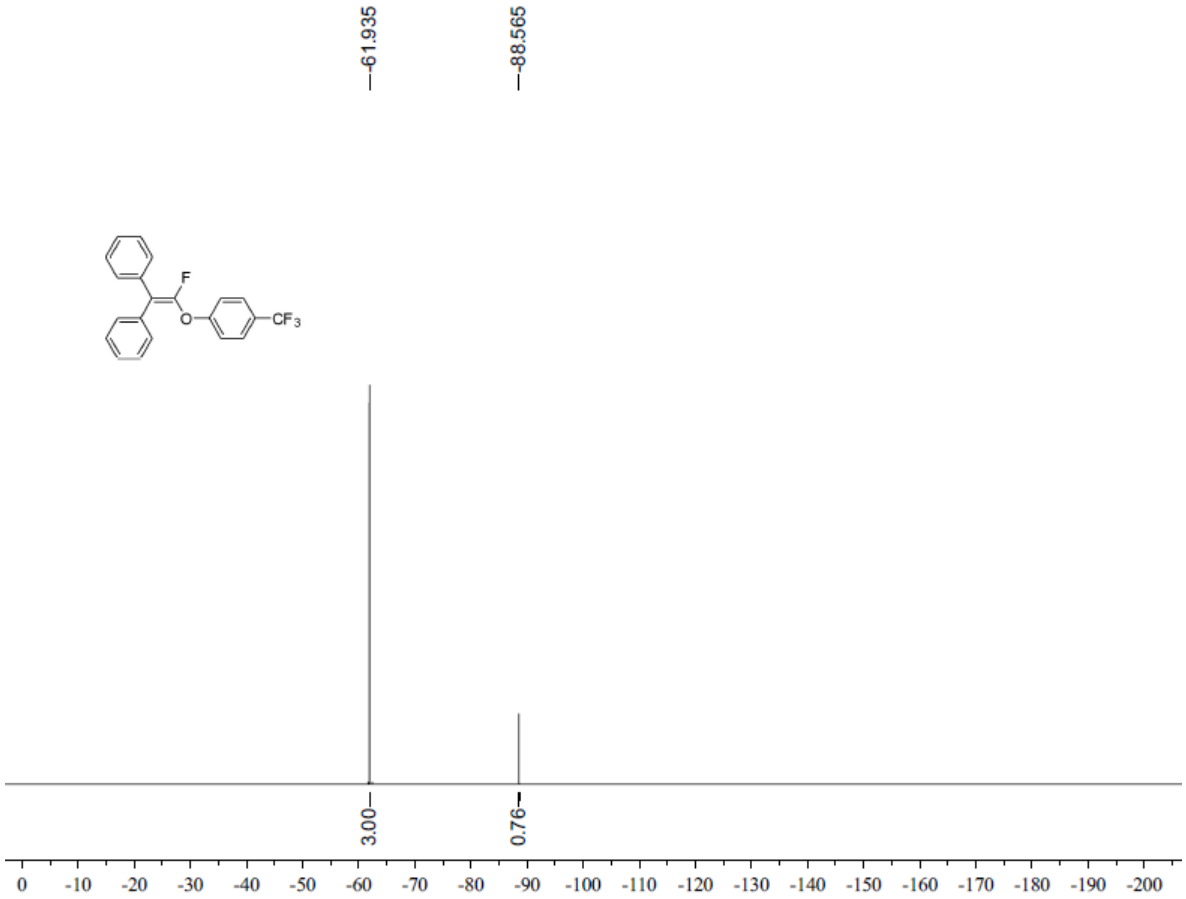
^{1}H NMR Spectrum of 3ag



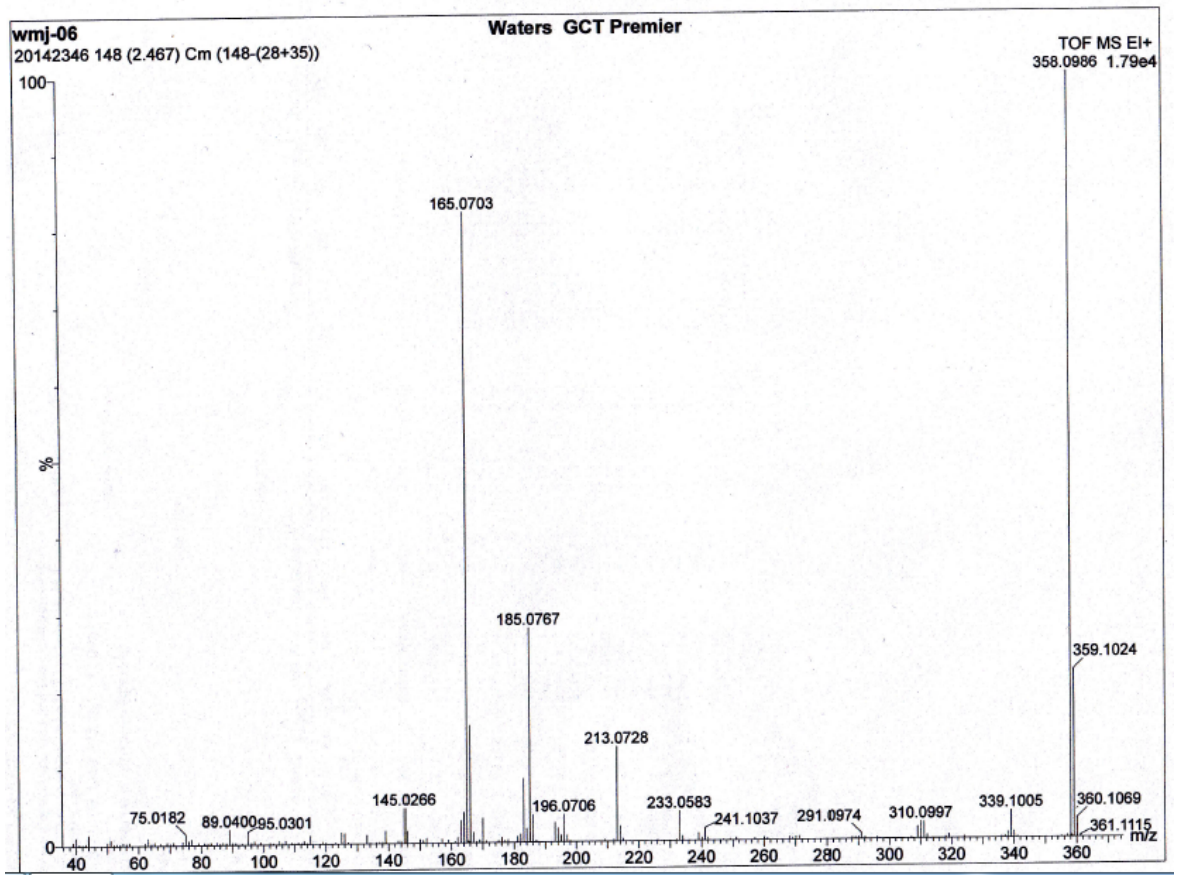
^{13}C NMR Spectrum of 3ag



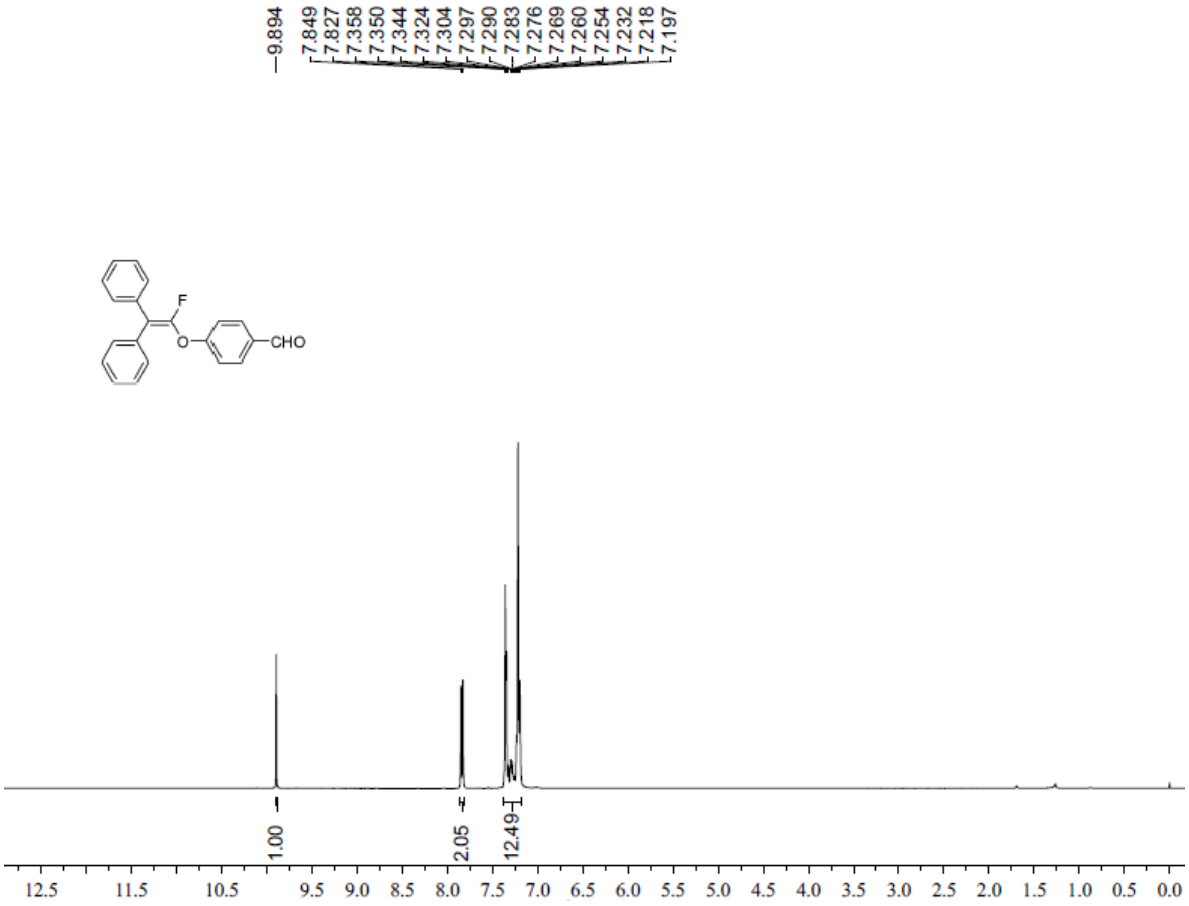
^{19}F NMR Spectrum of 3ag



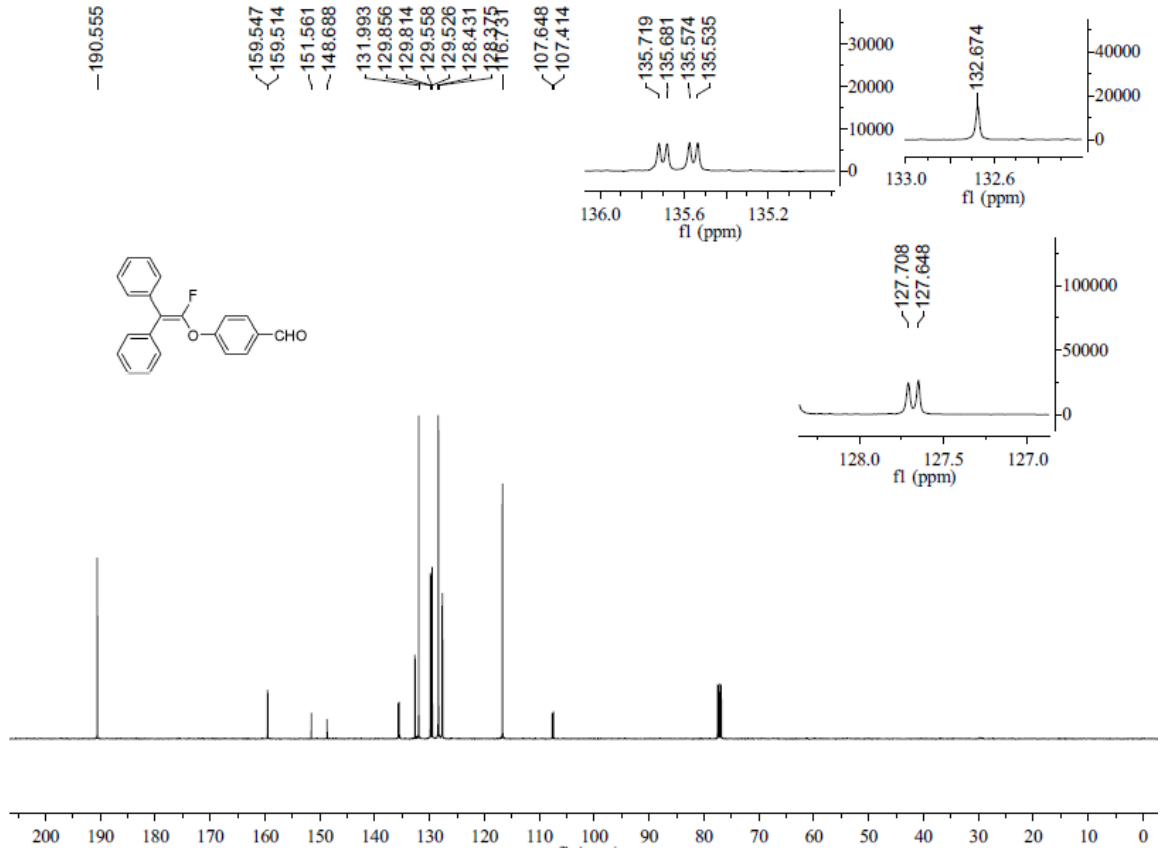
HRMS (EI) of 3ag



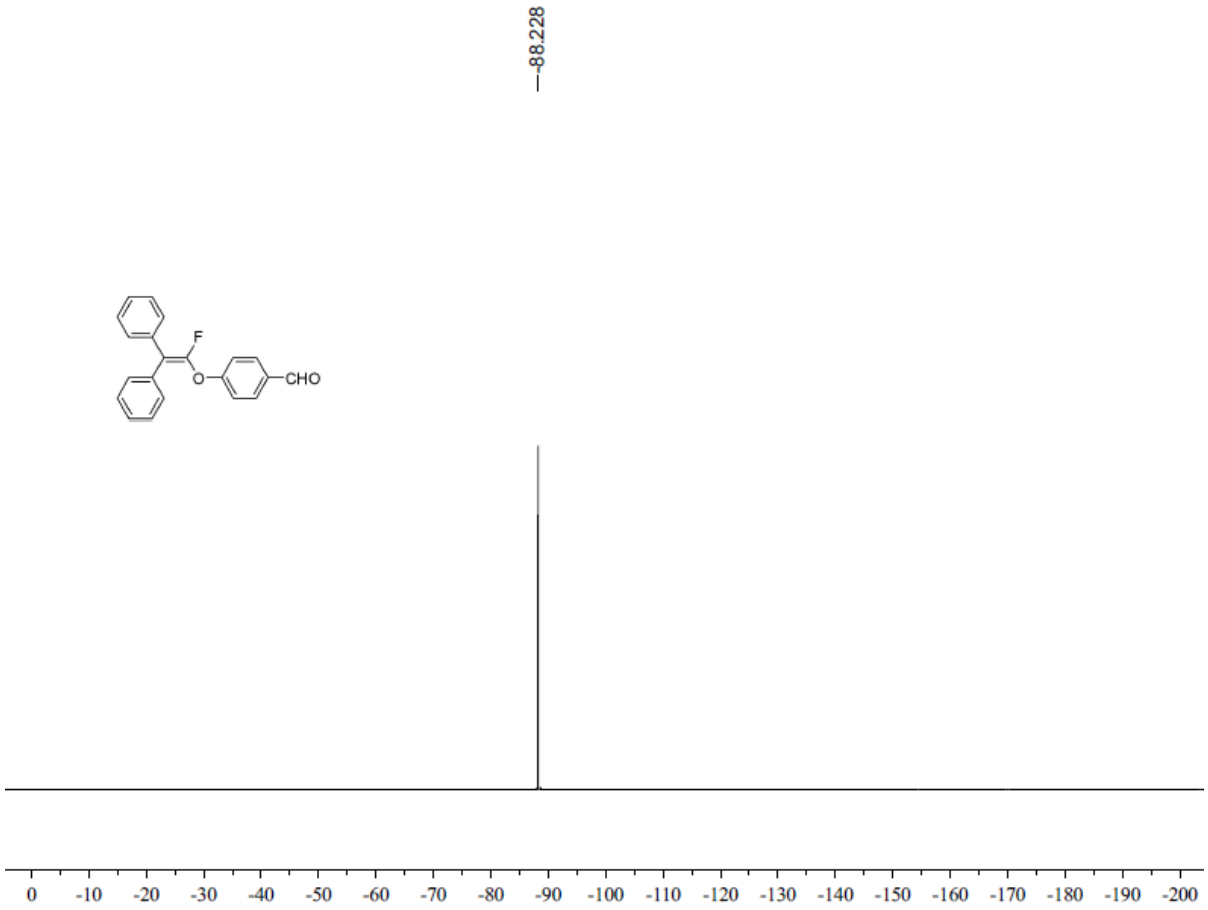
^{1}H NMR Spectrum of 3ah



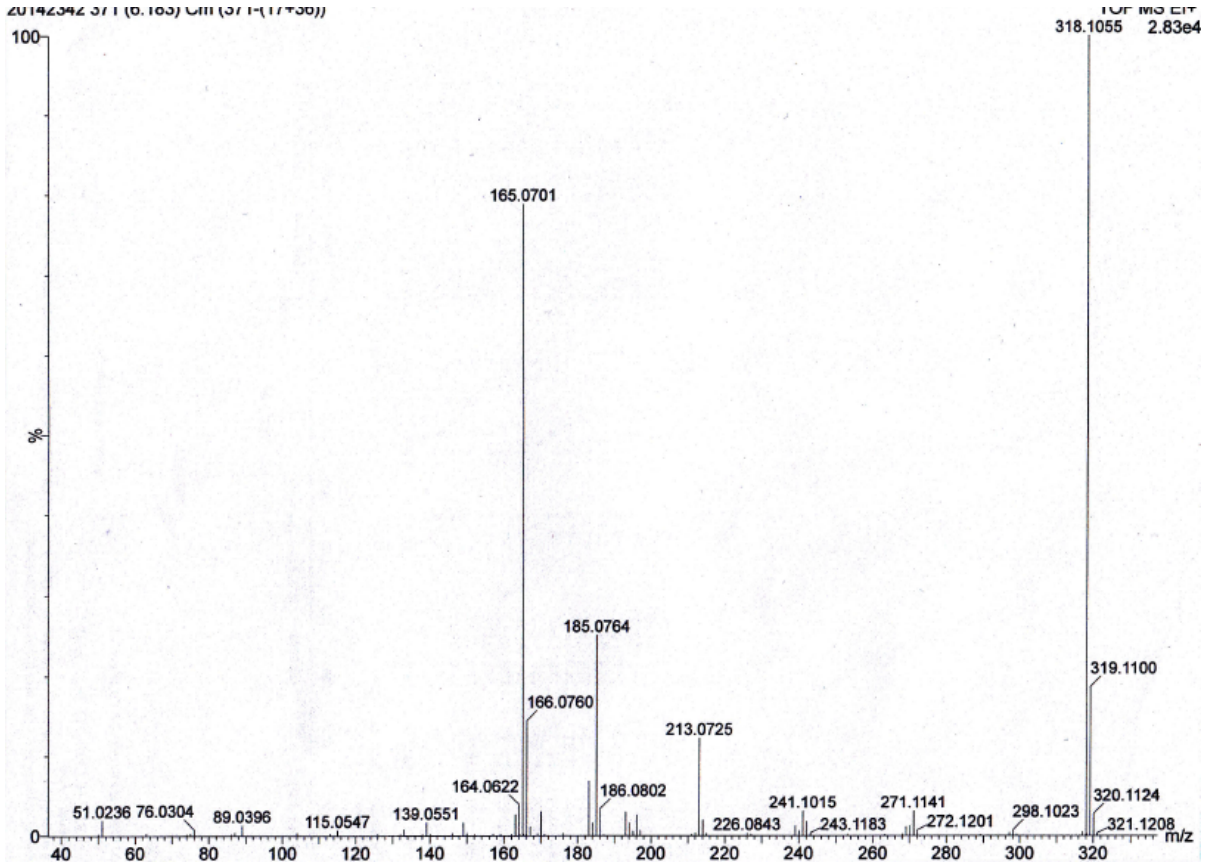
^{13}C NMR Spectrum of 3ah



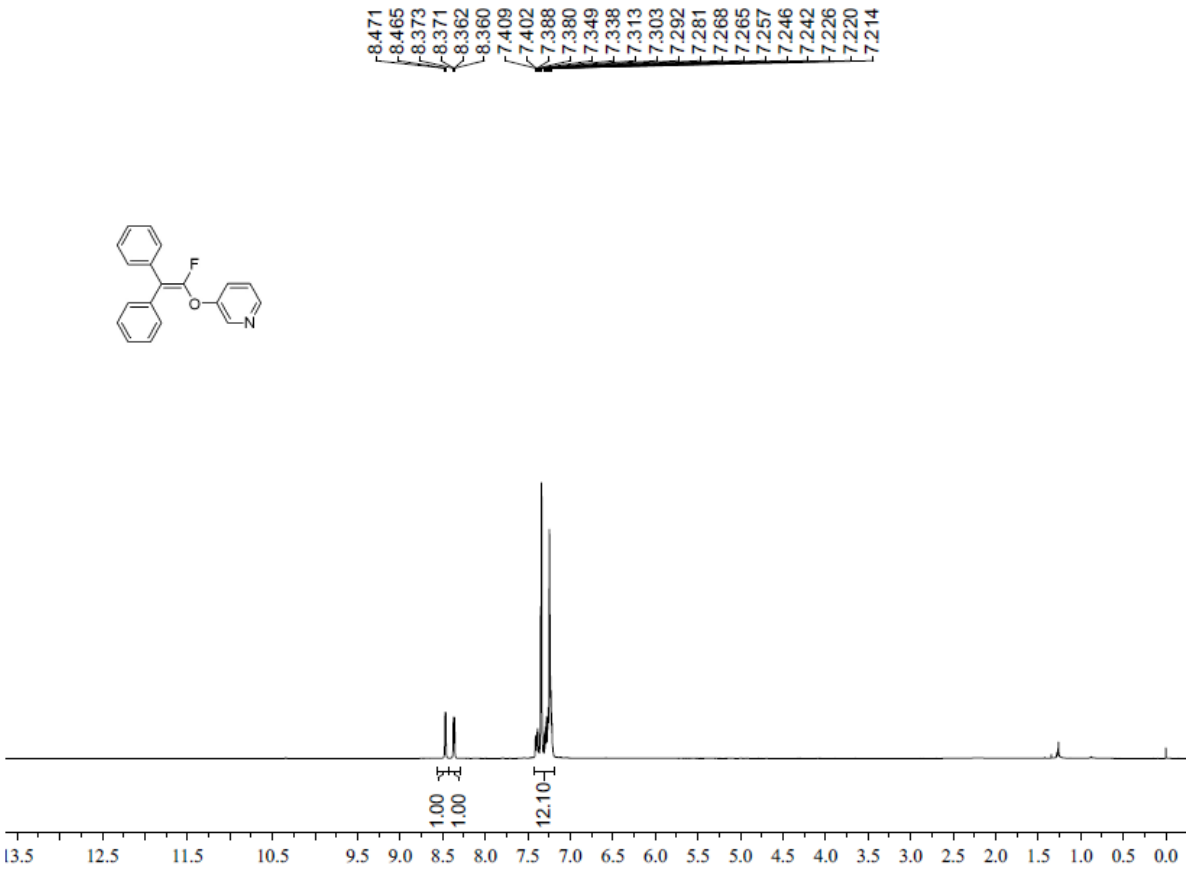
^{19}F NMR Spectrum ofb3ah



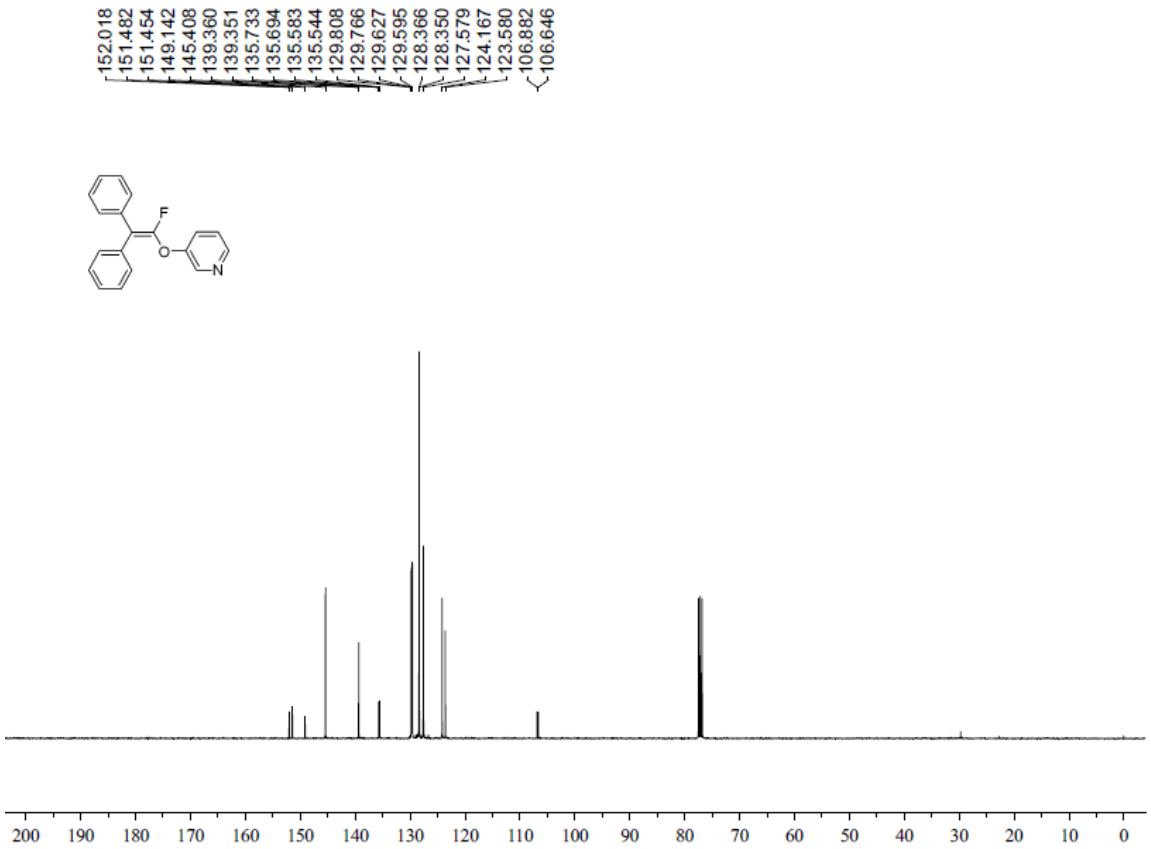
HRMS (EI) of 3ah



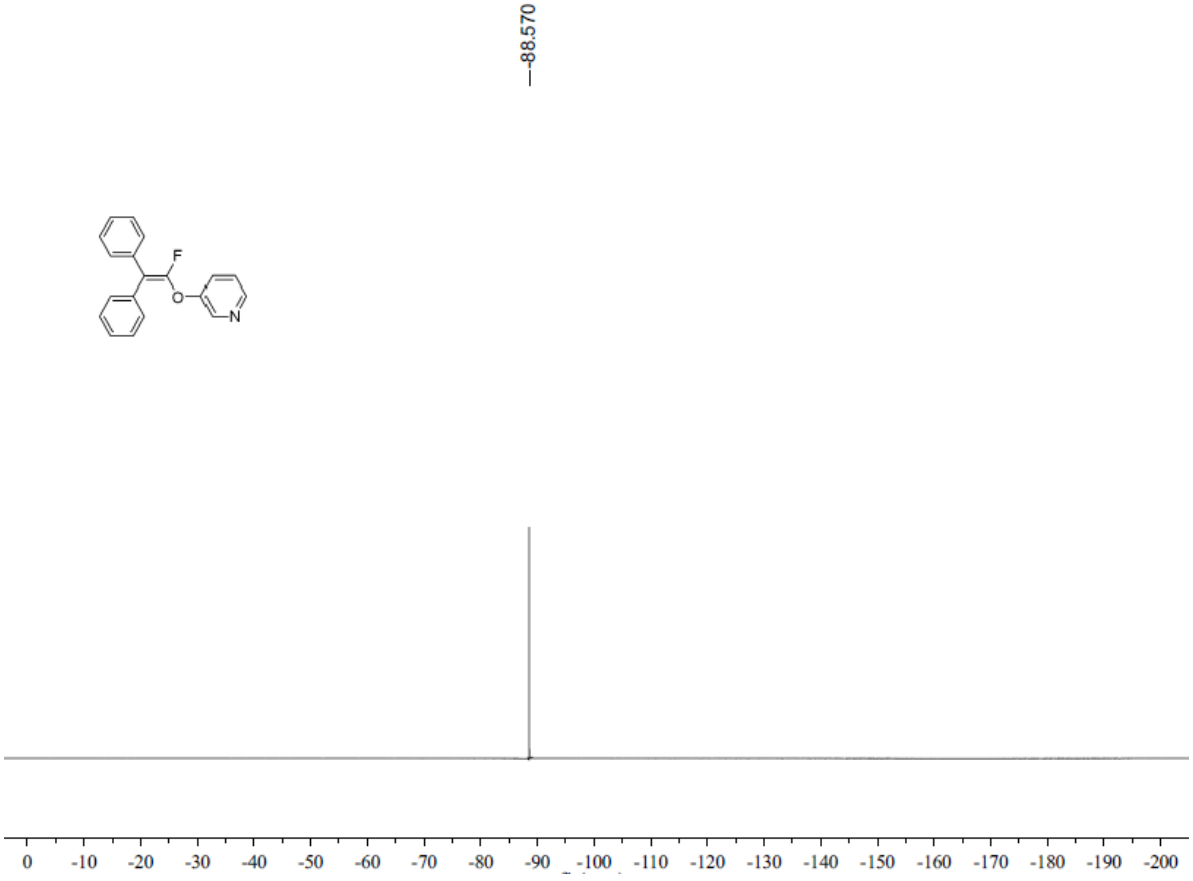
^{1}H NMR Spectrum of 3ai



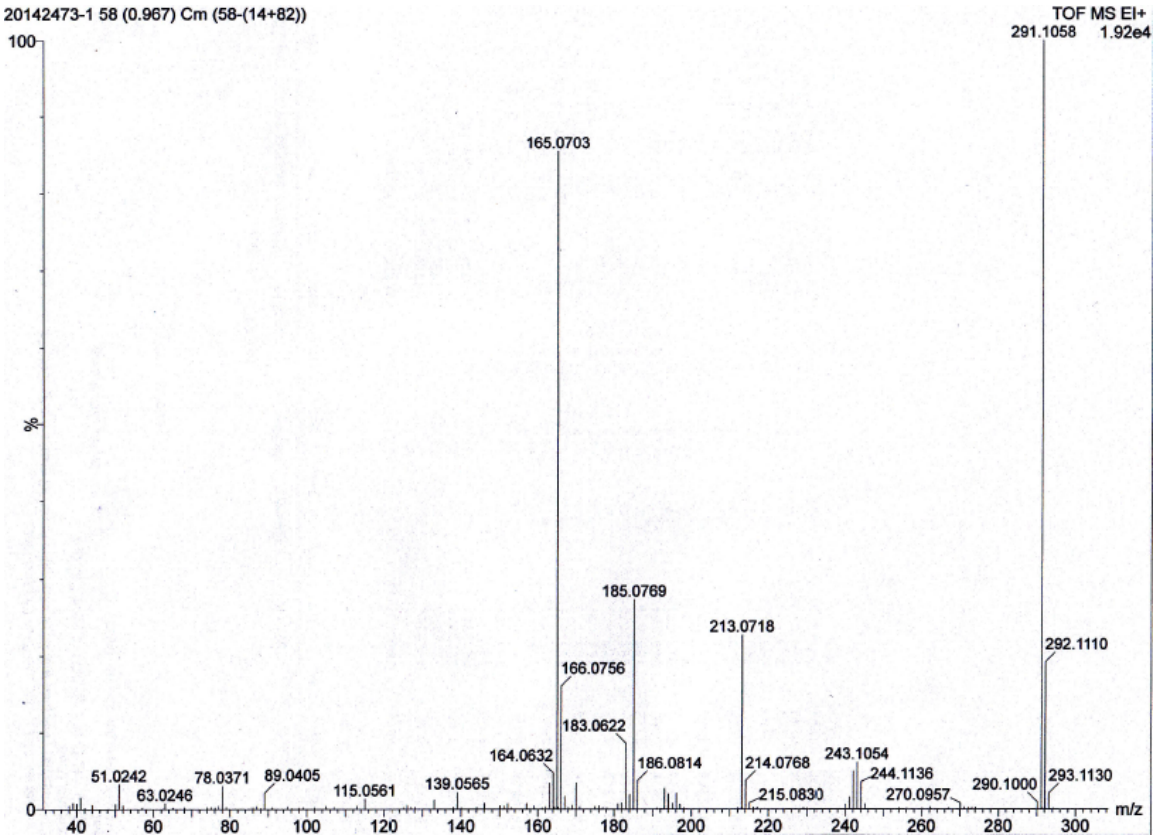
^{13}C NMR Spectrum of 3ai



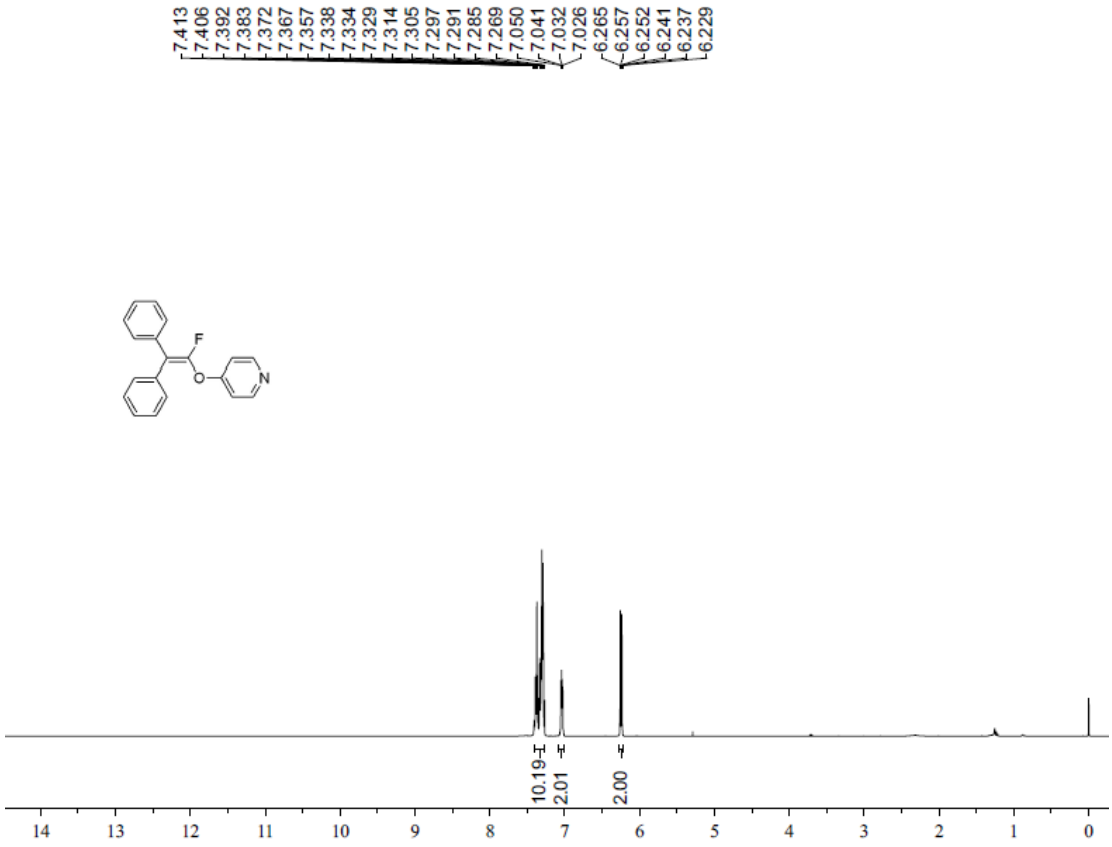
^{19}F NMR Spectrum of 3ai



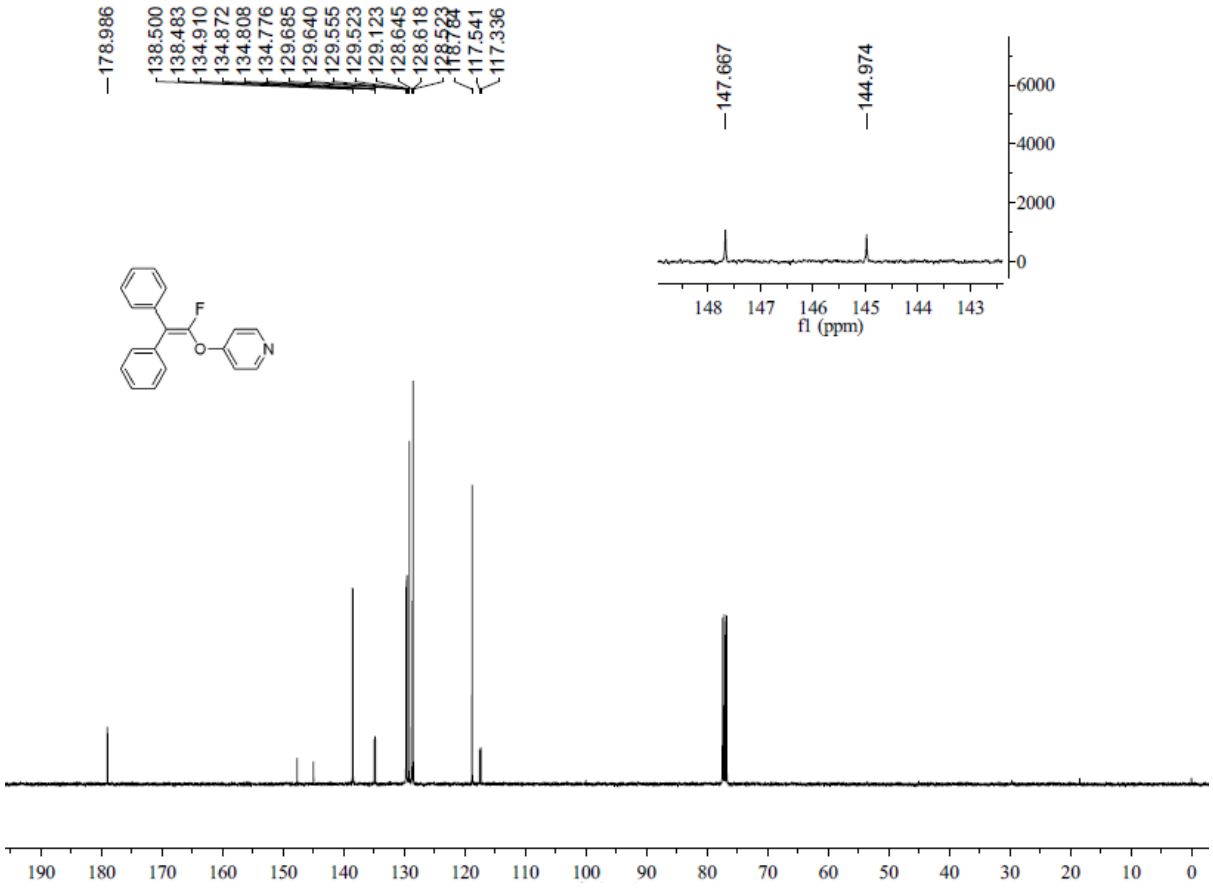
HRMS (EI) of 3ai



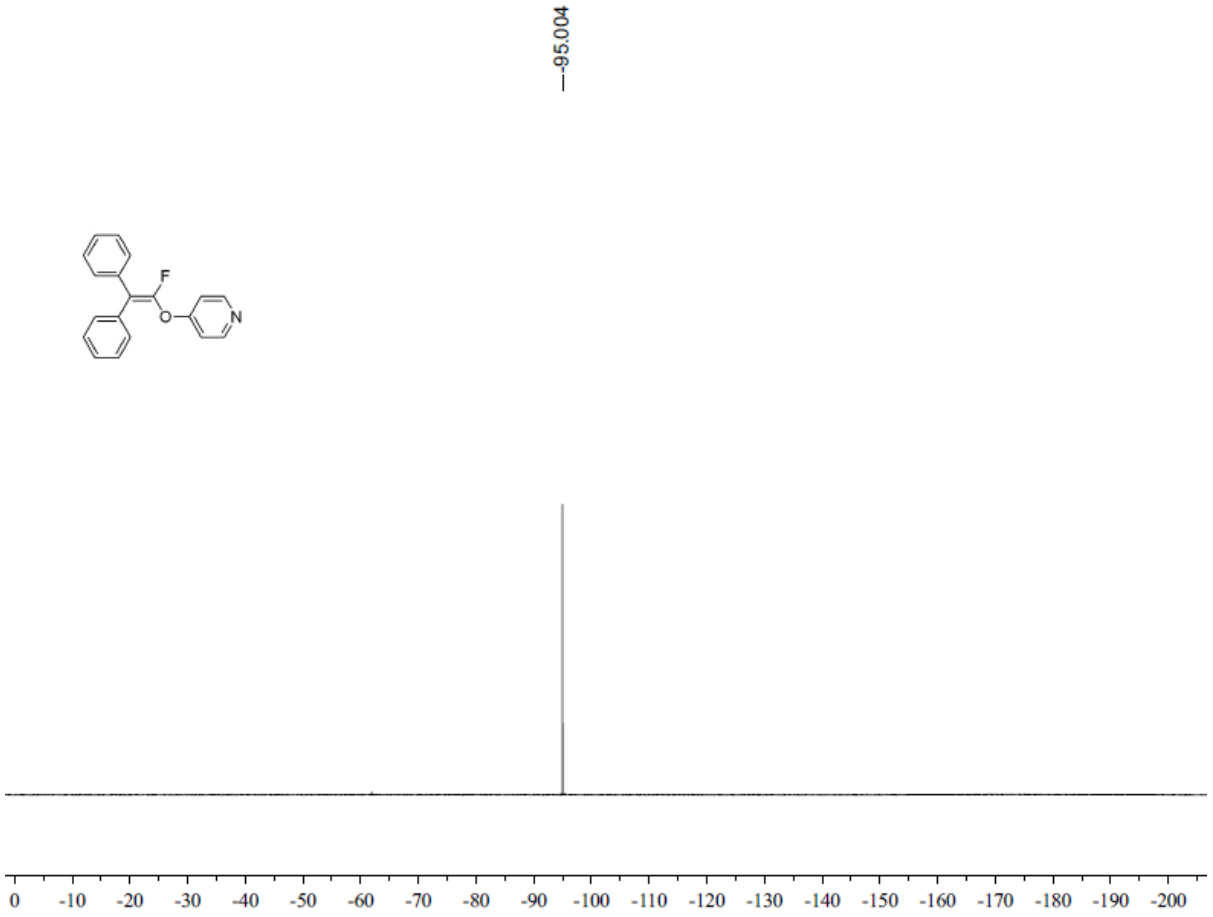
^{1}H NMR Spectrum of 3aj



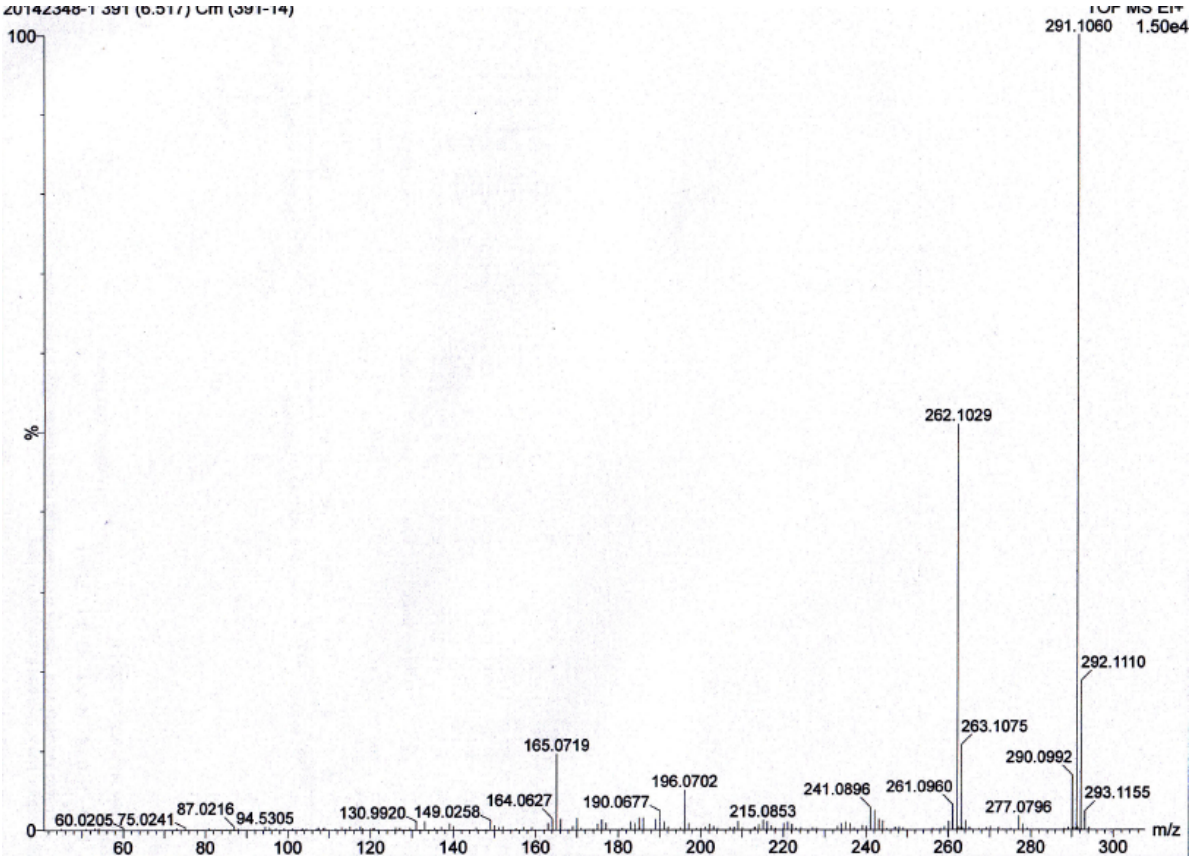
^{13}C NMR Spectrum of 3aj



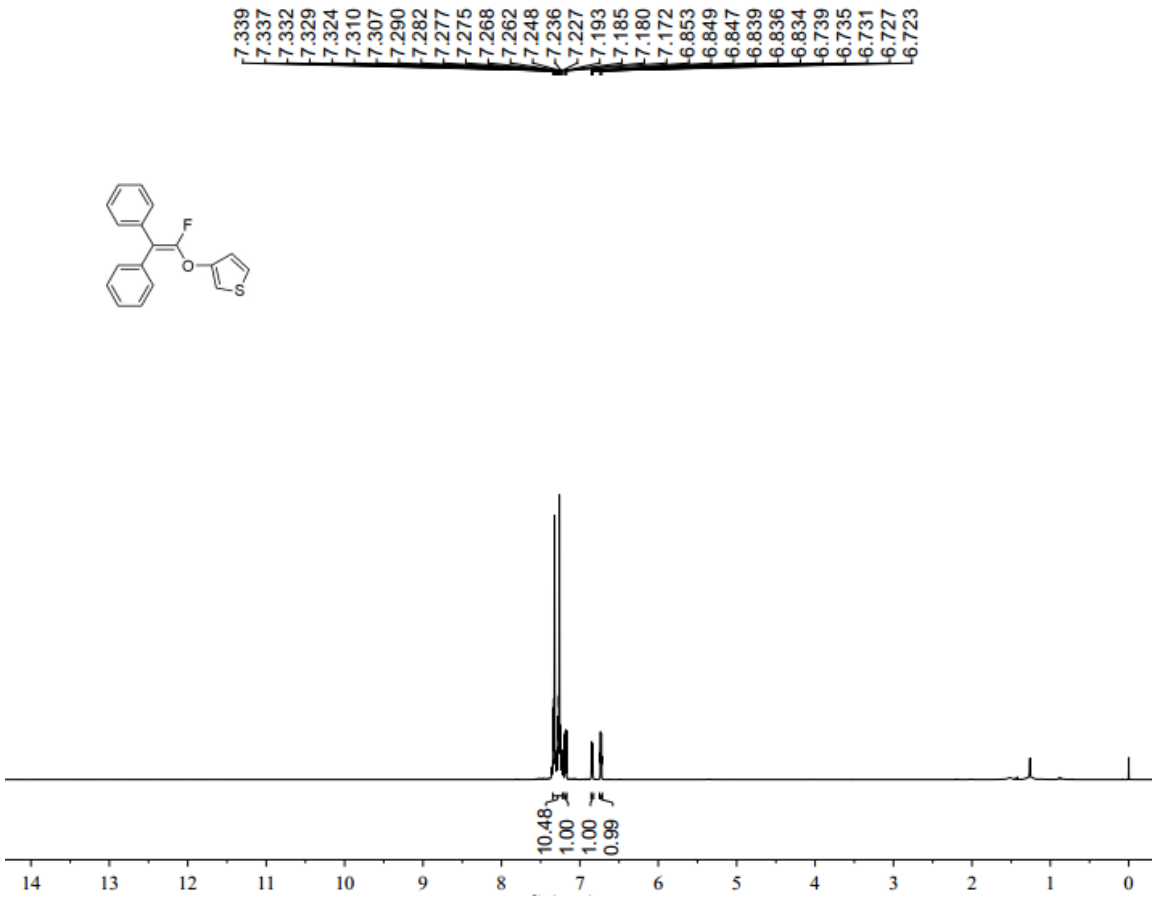
^{19}F NMR Spectrum of 3aj



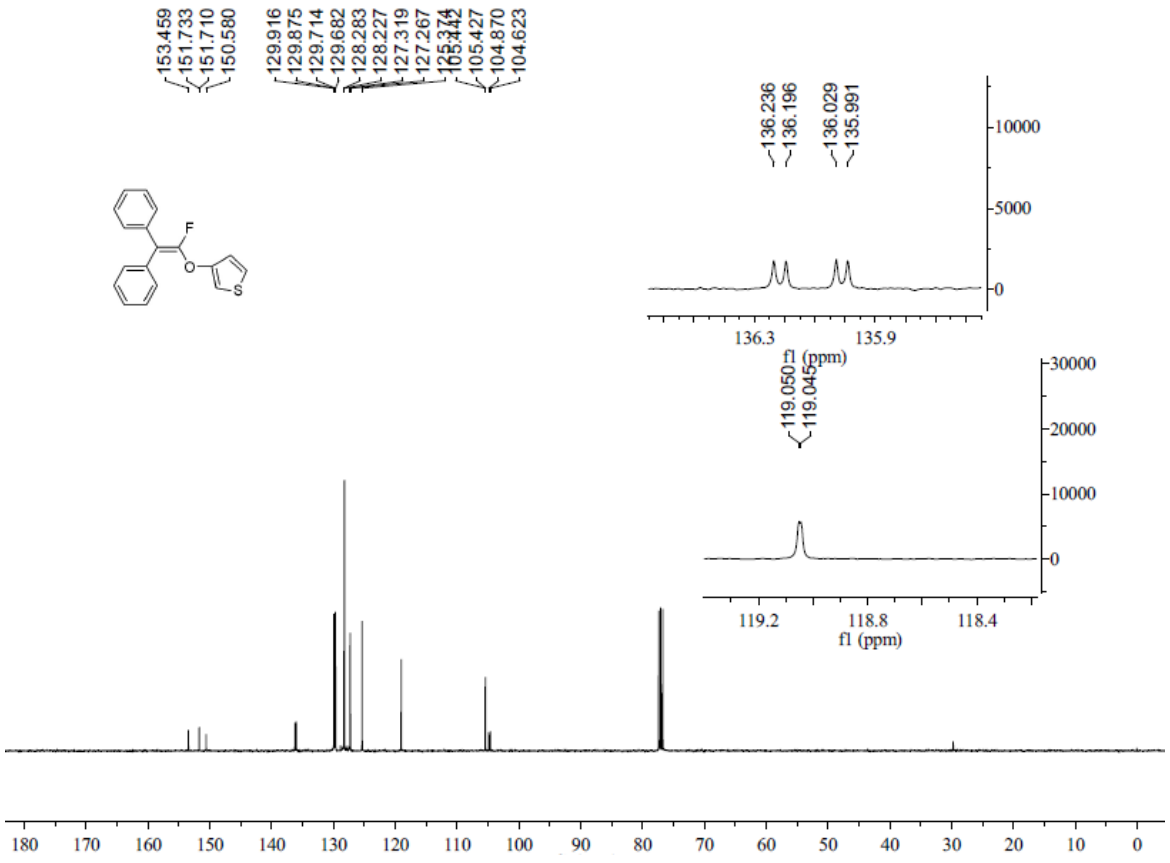
HRMS (EI) of 3aj



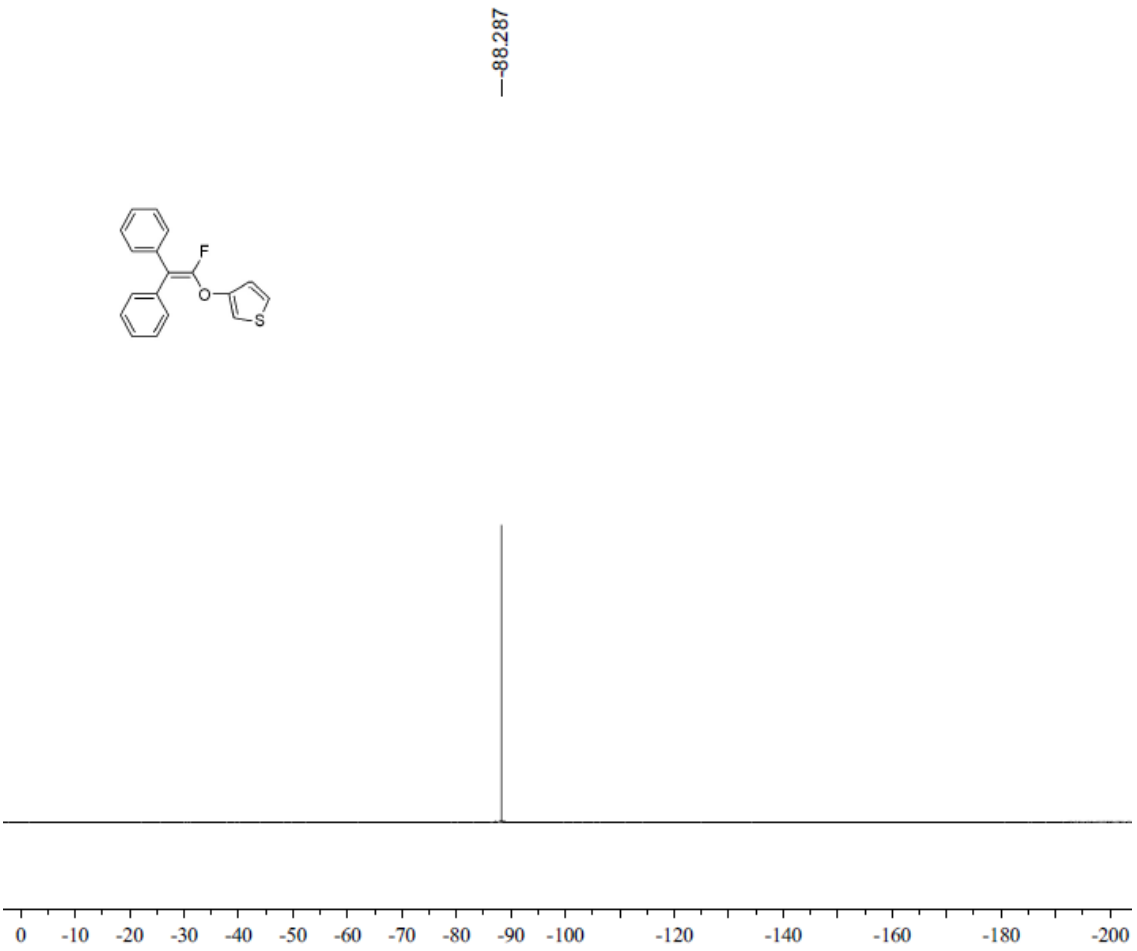
^{1}H NMR Spectrum of 3ak



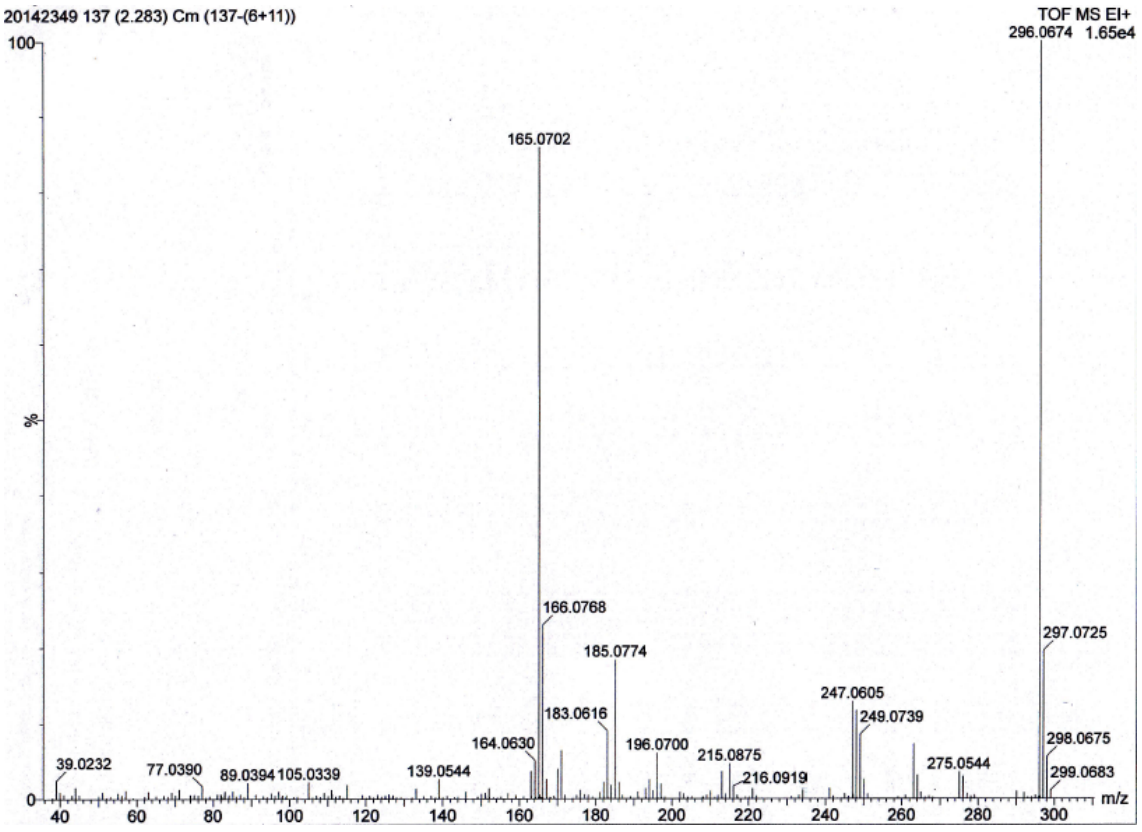
^{13}C NMR Spectrum of 3ak



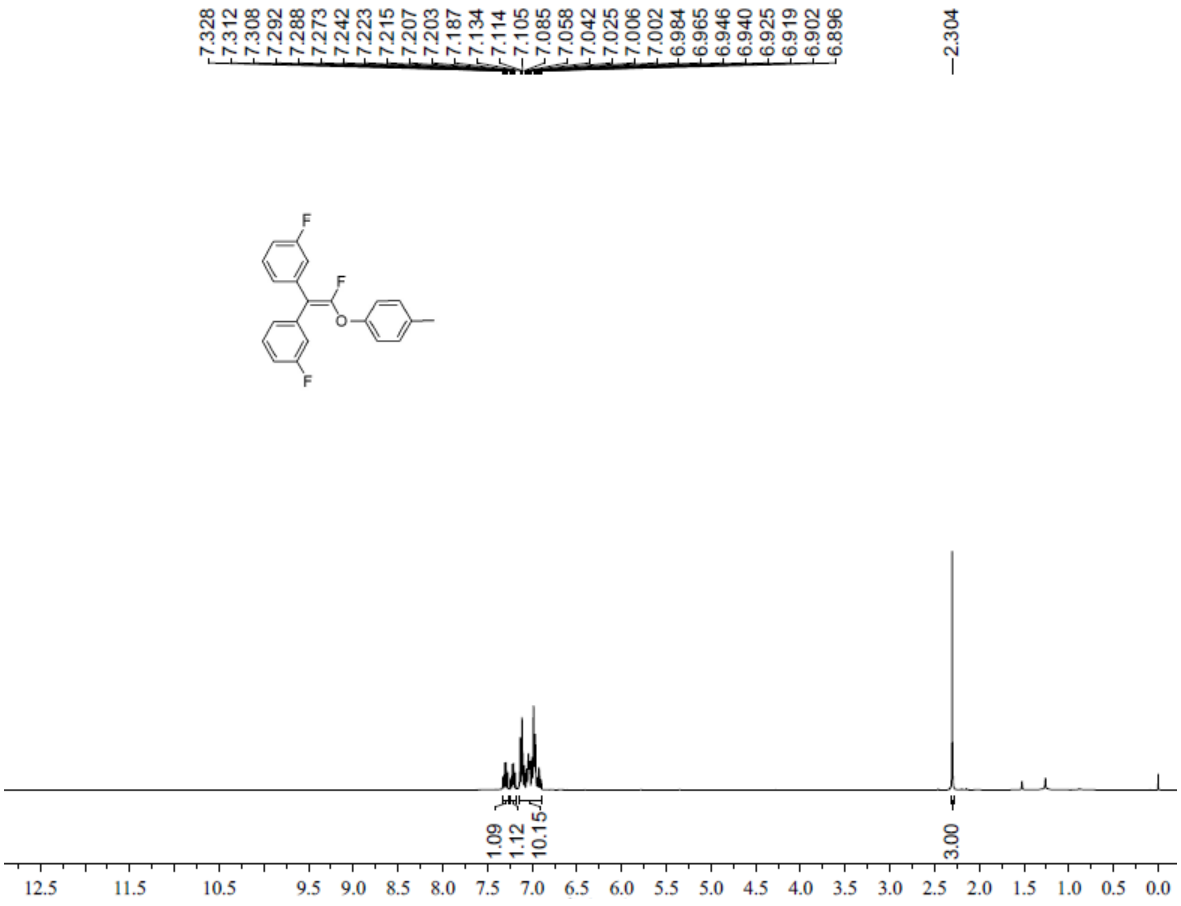
^{19}F NMR Spectrum of 3ak



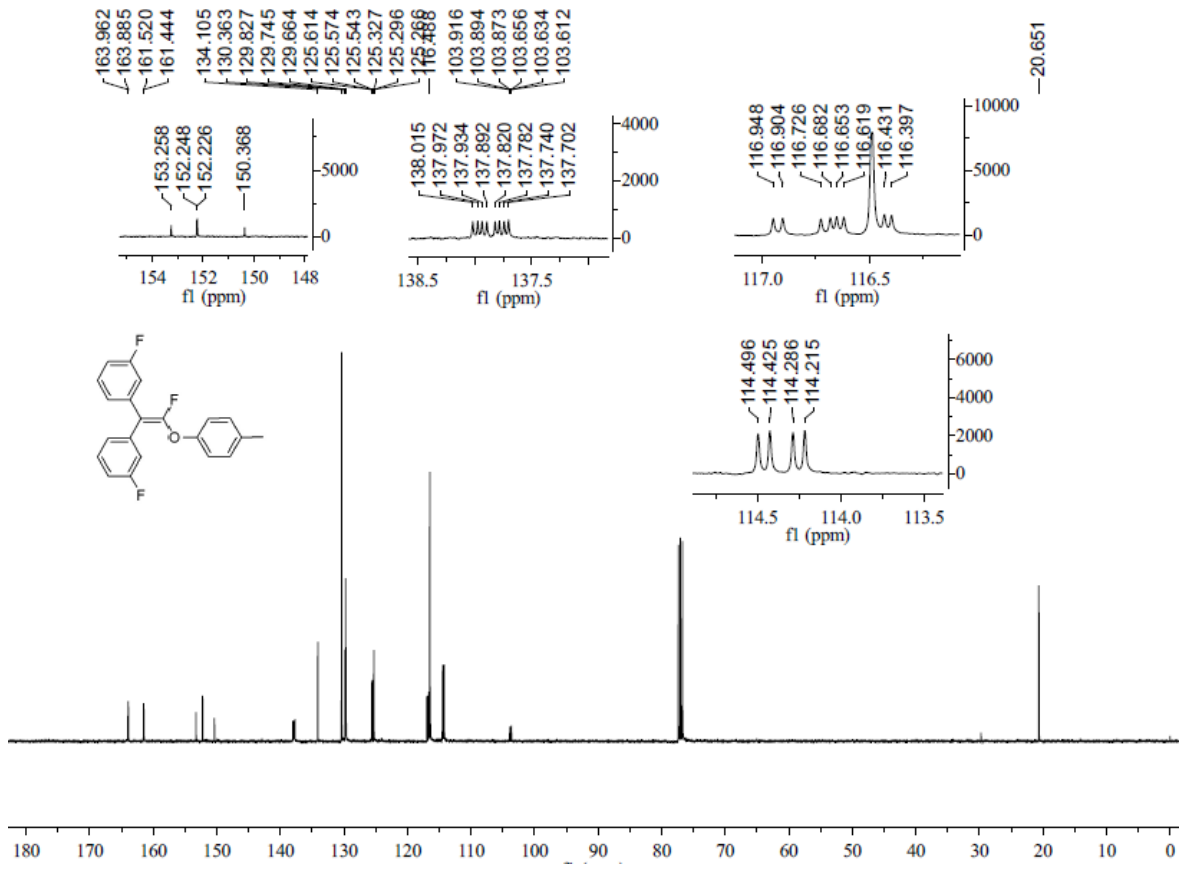
HRMS (EI) of 3ak



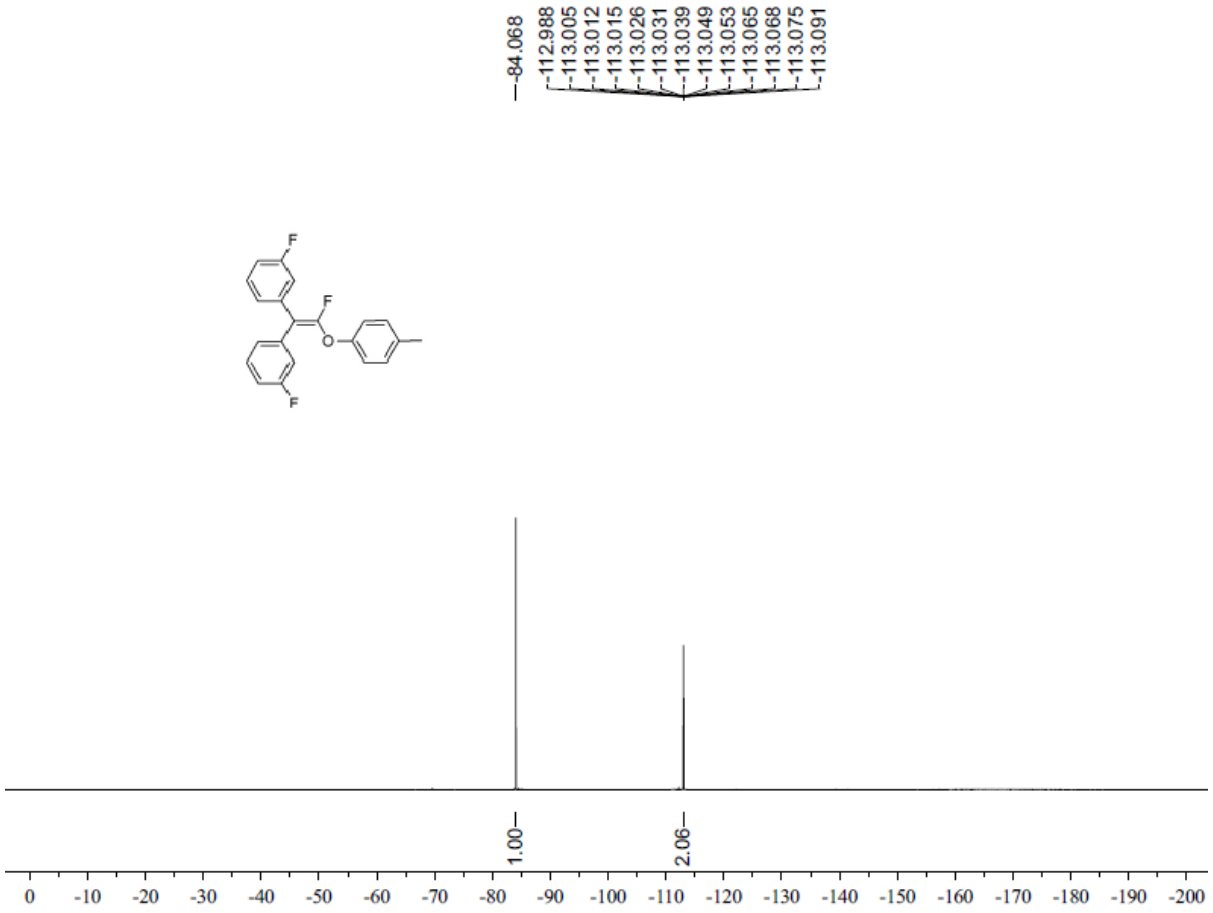
[1]H NMR Spectrum of 3bb



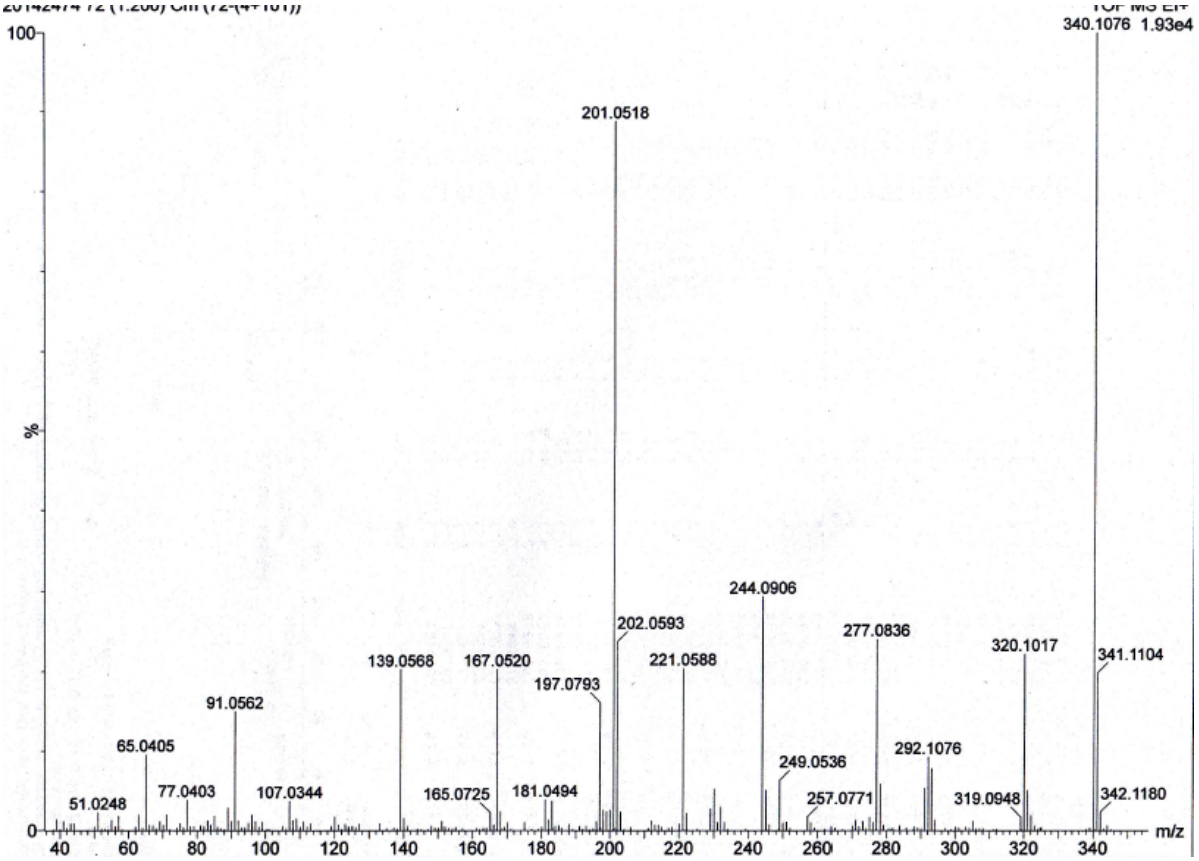
[13]C NMR Spectrum of 3bb



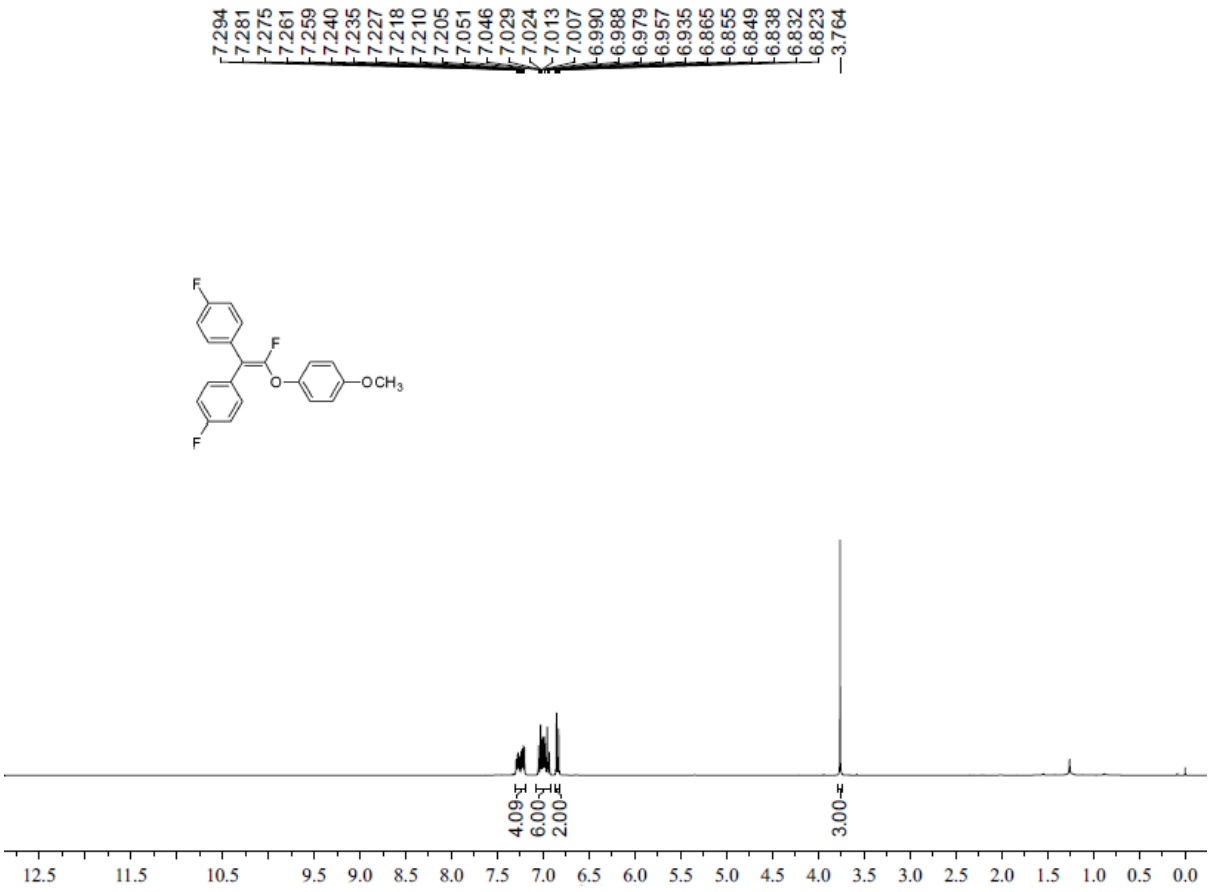
^{19}F NMR Spectrum of 3bb



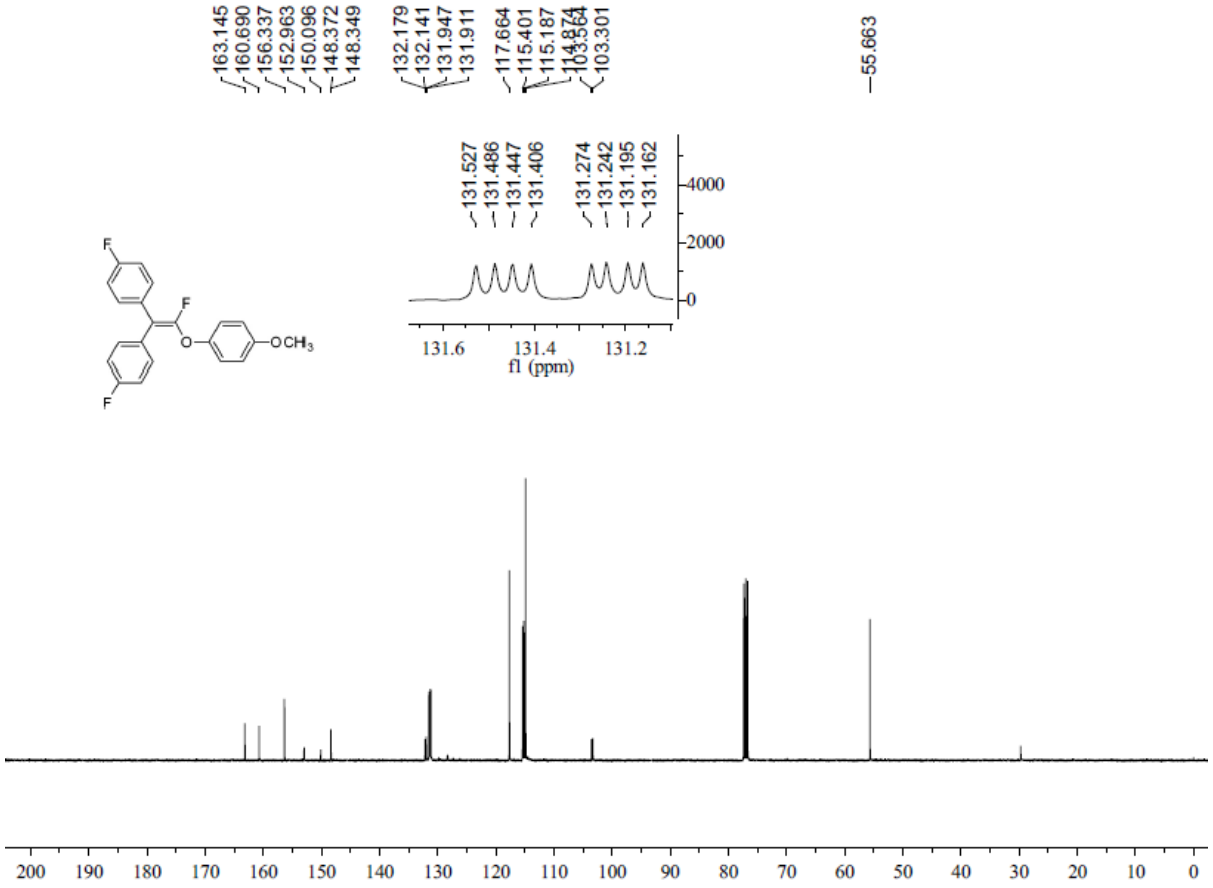
HRMS (EI) of 3bb



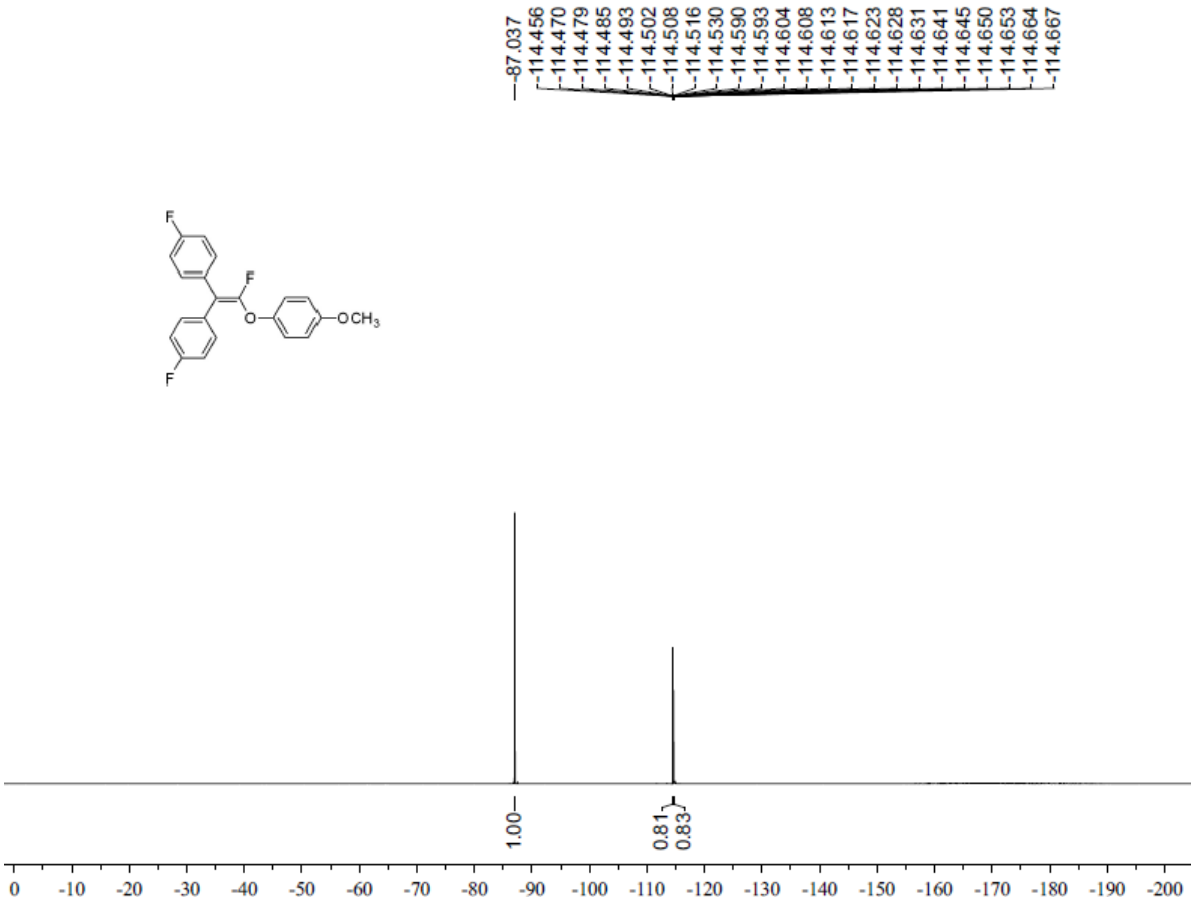
[1]H NMR Spectrum of 3cd



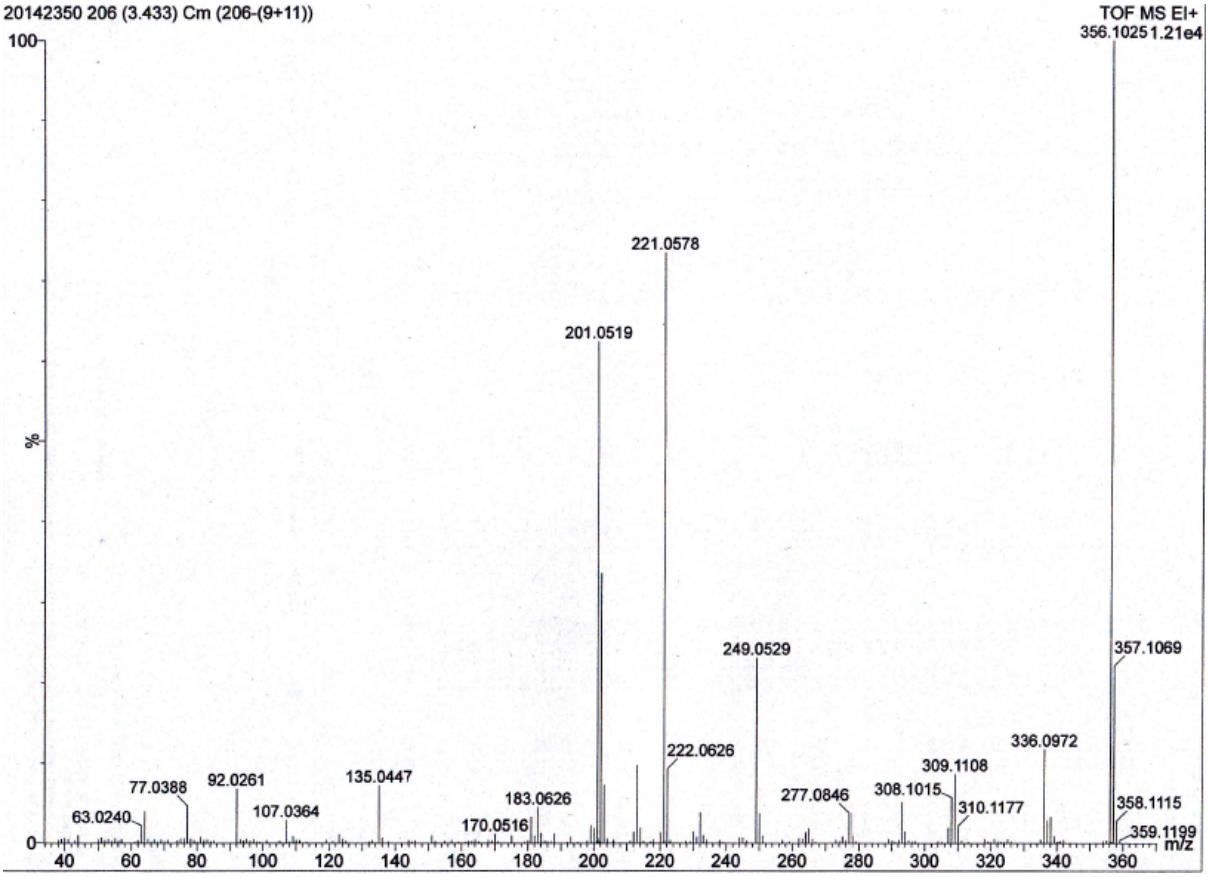
[13]C NMR Spectrum of 3cd



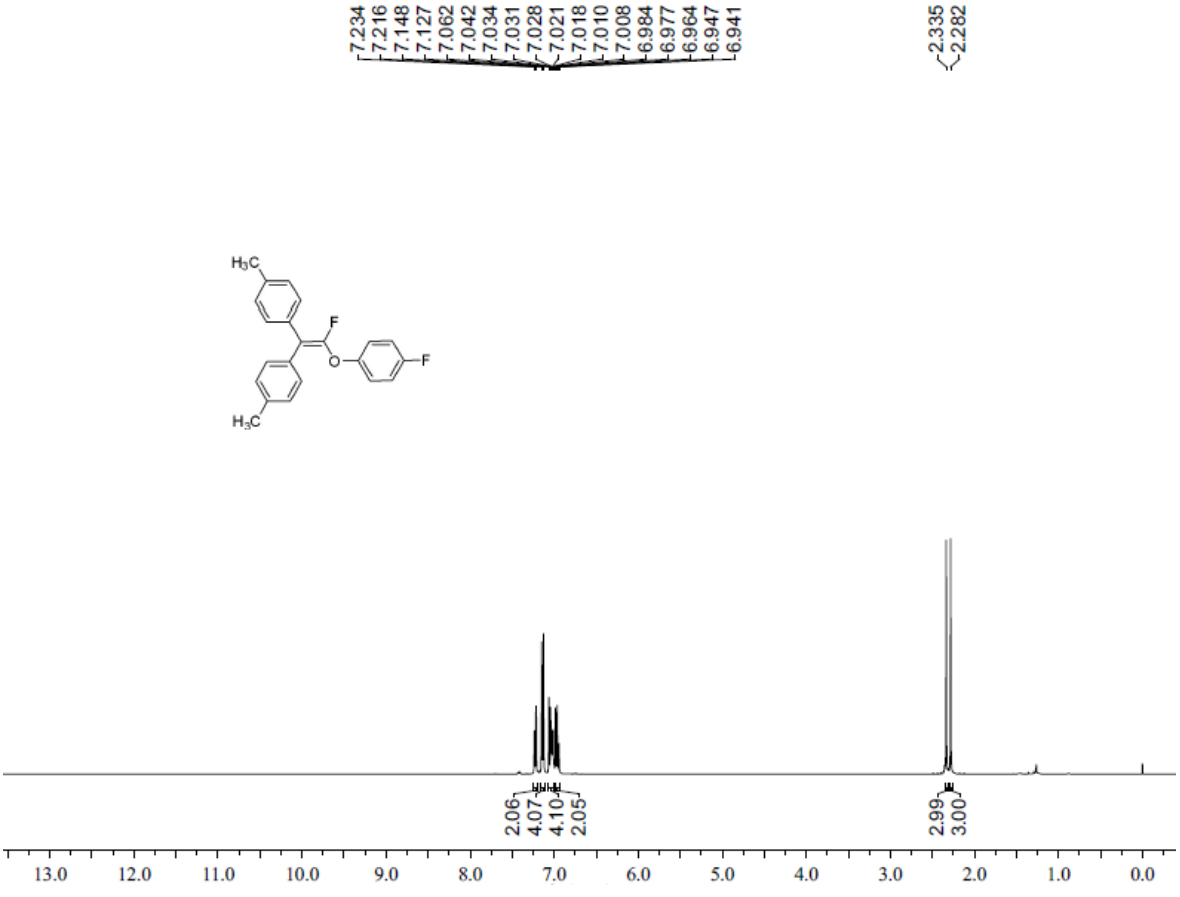
^{19}F NMR Spectrum of 3cd



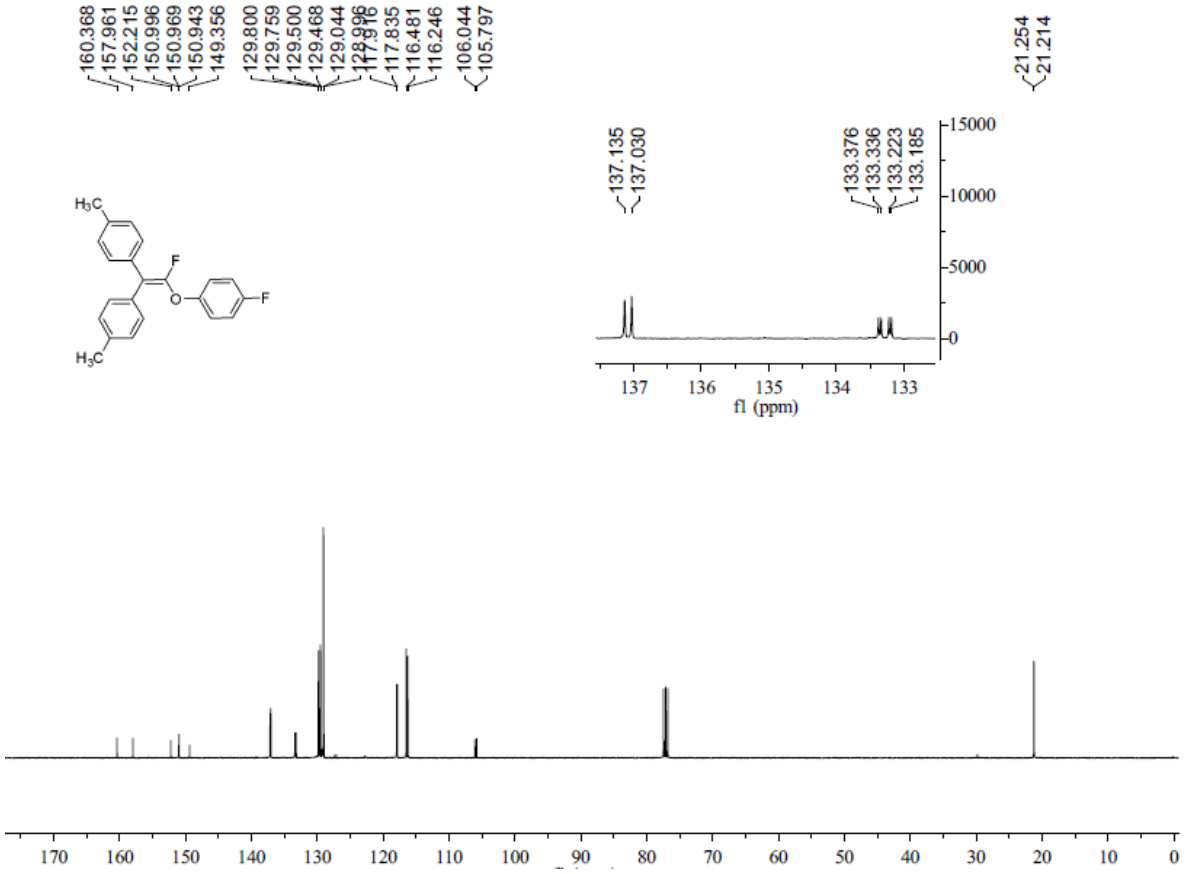
HRMS (EI) of 3cd



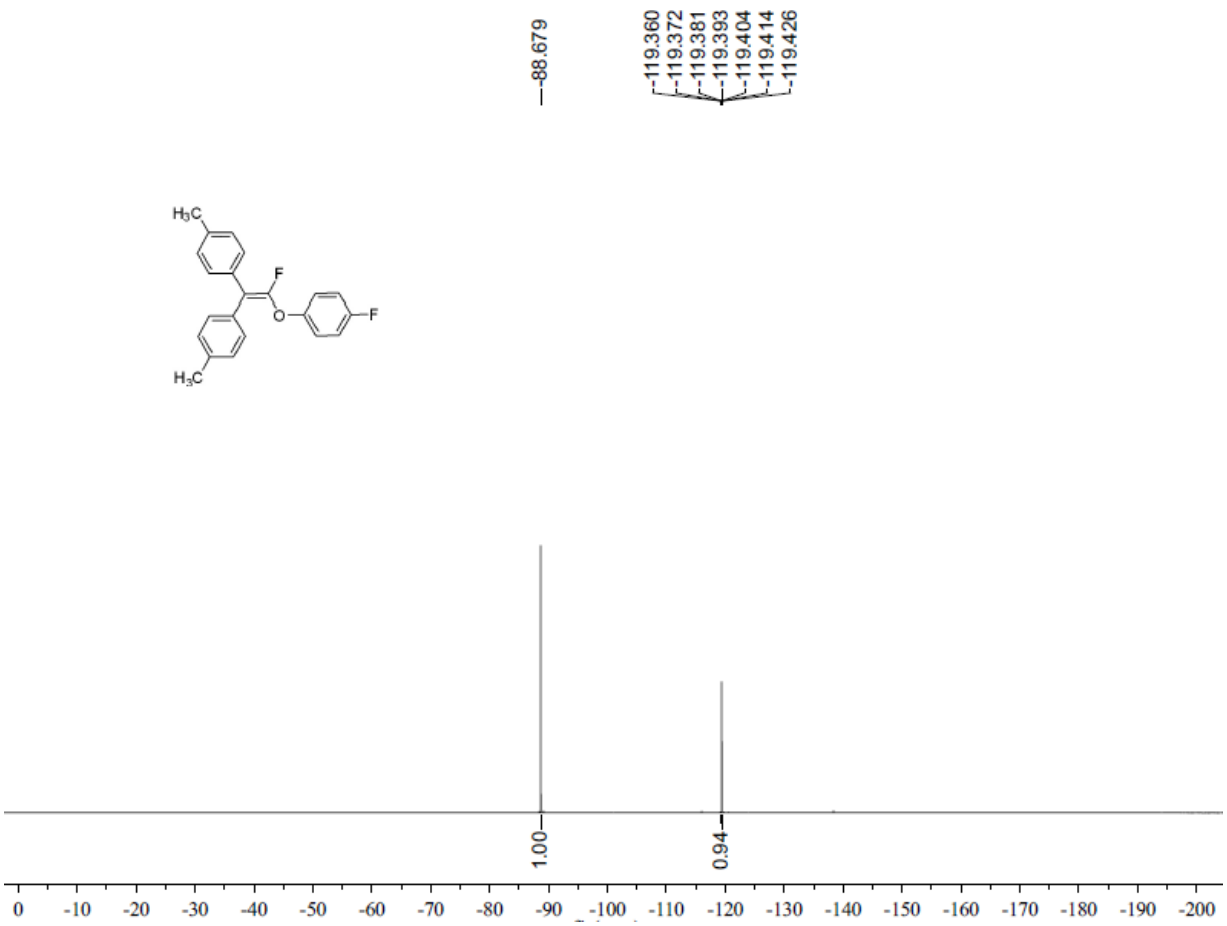
^{1}H NMR Spectrum of 3df



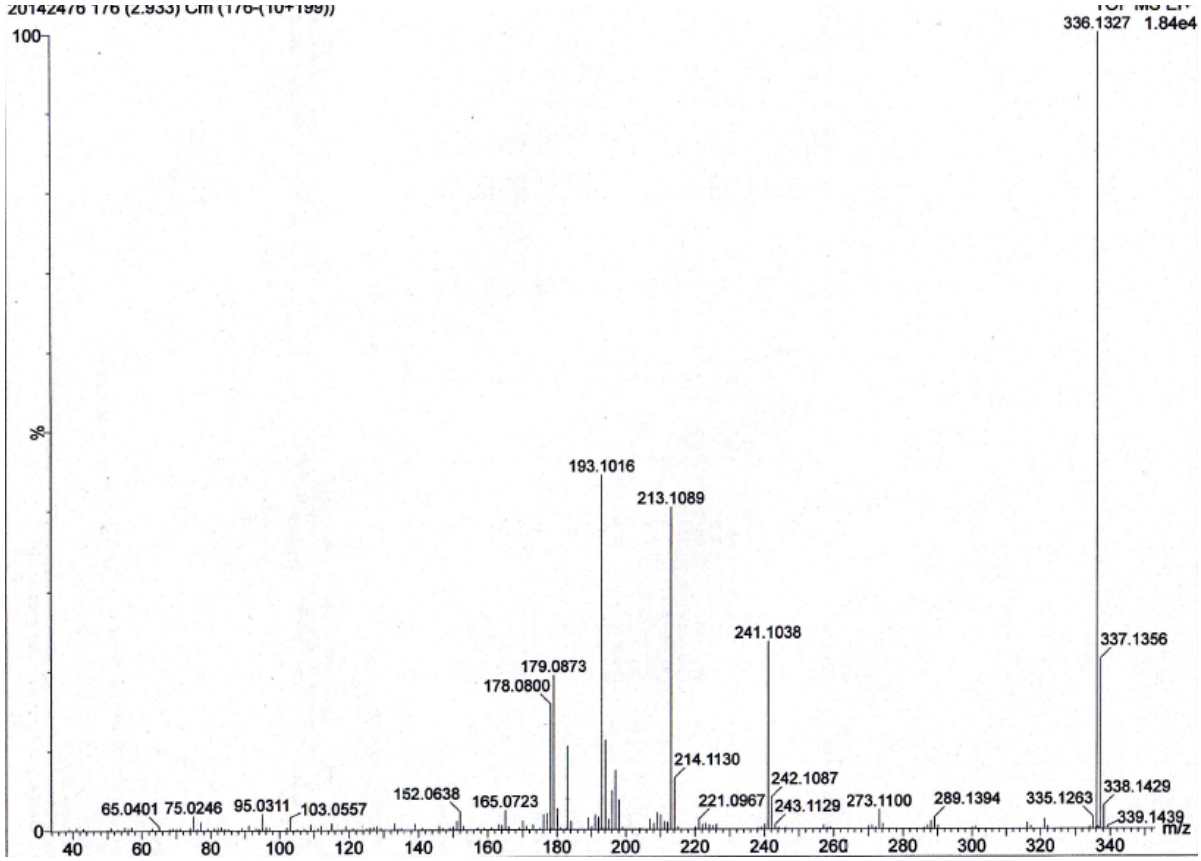
^{13}C NMR Spectrum of 3df



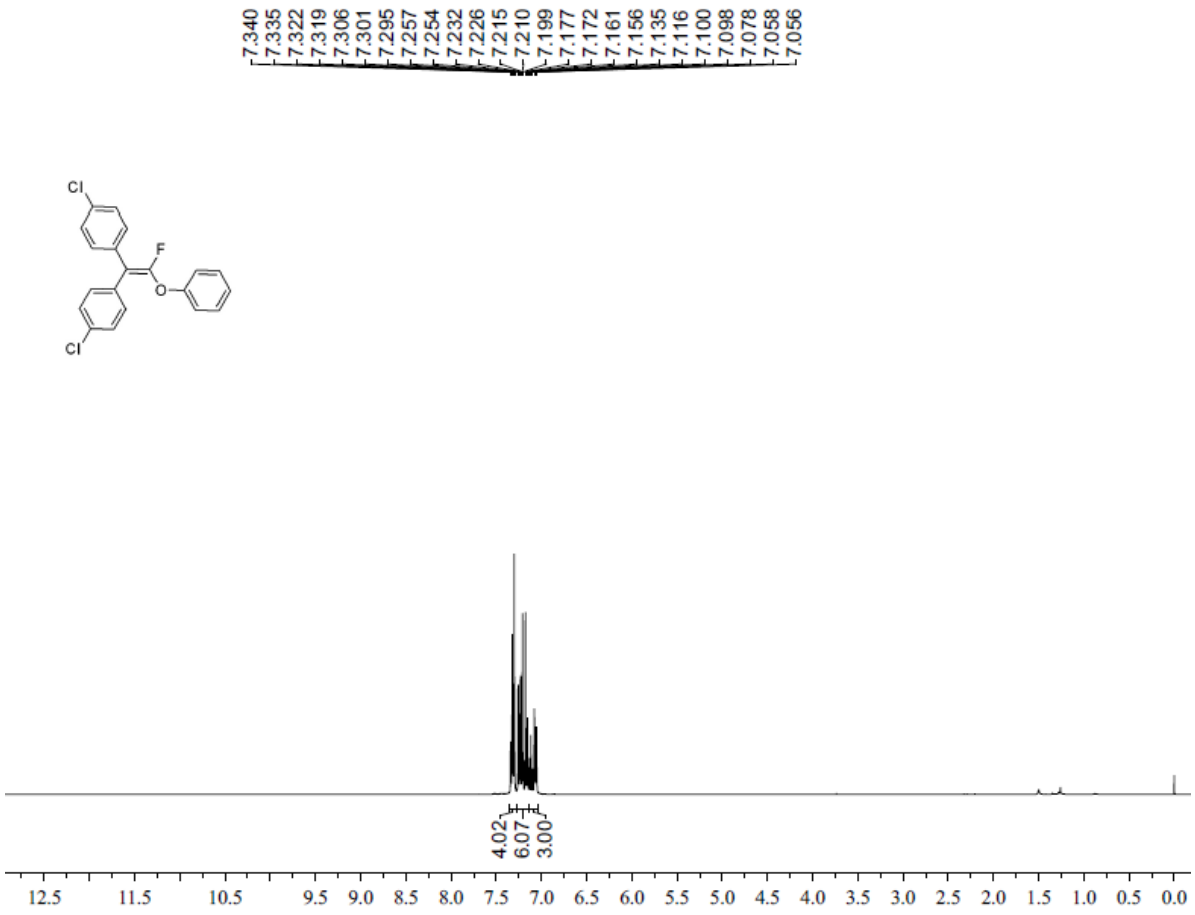
^{19}F NMR Spectrum of 3df



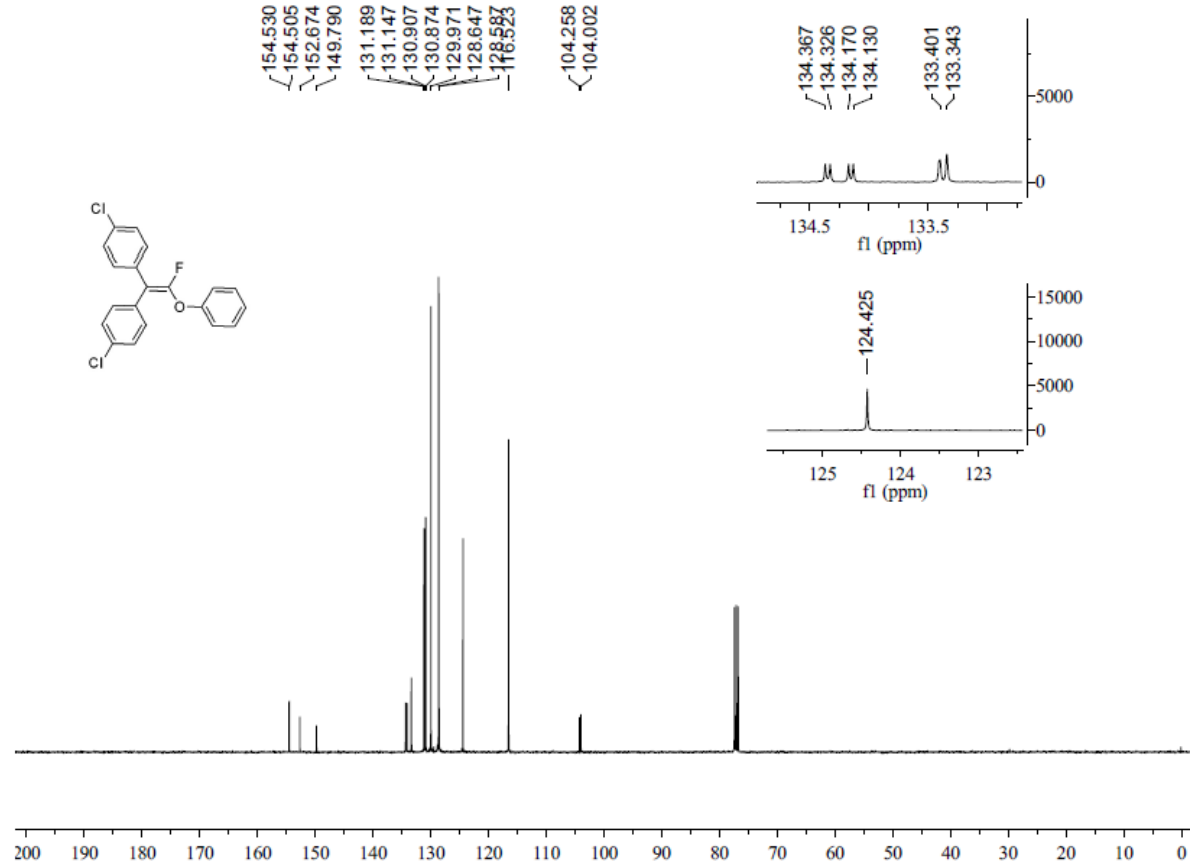
HRMS (EI) of 3df



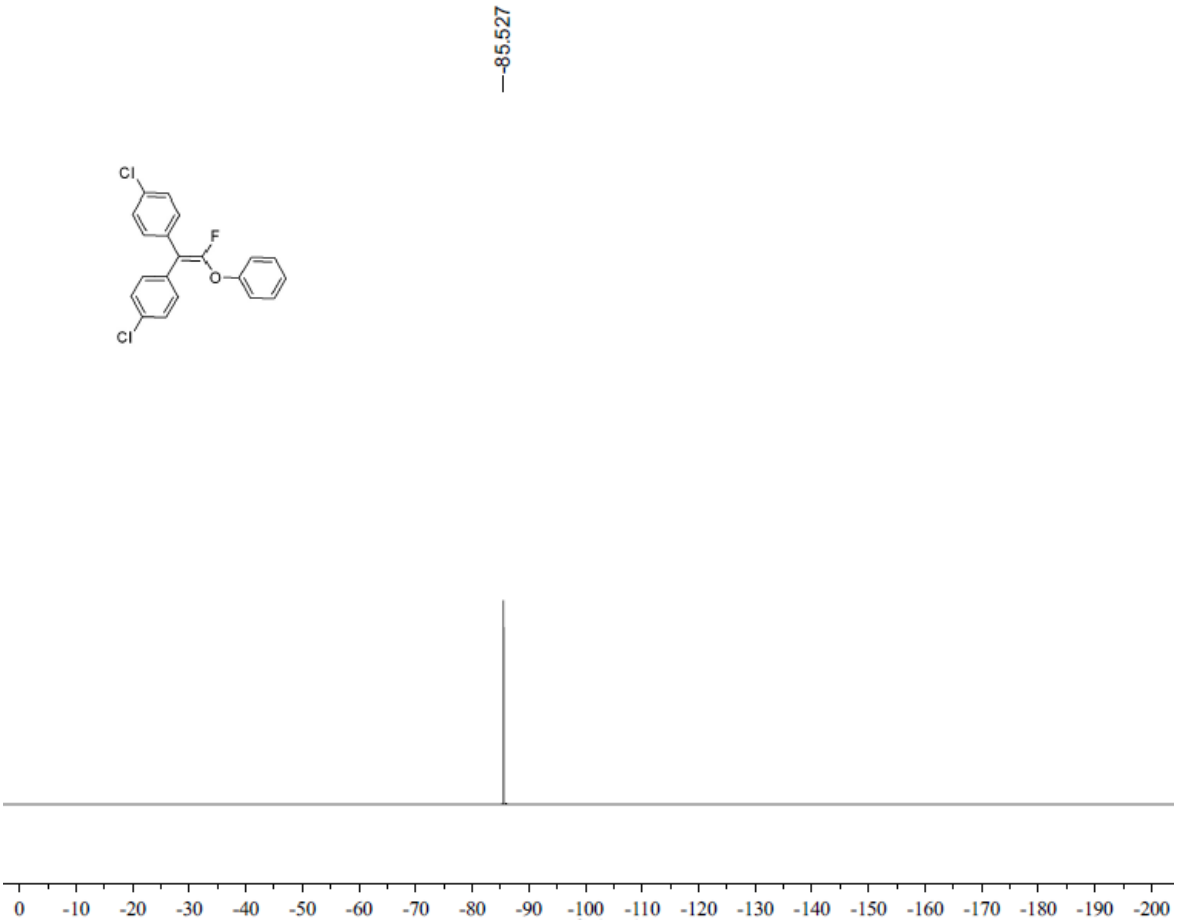
^{1}H NMR Spectrum of 3ea



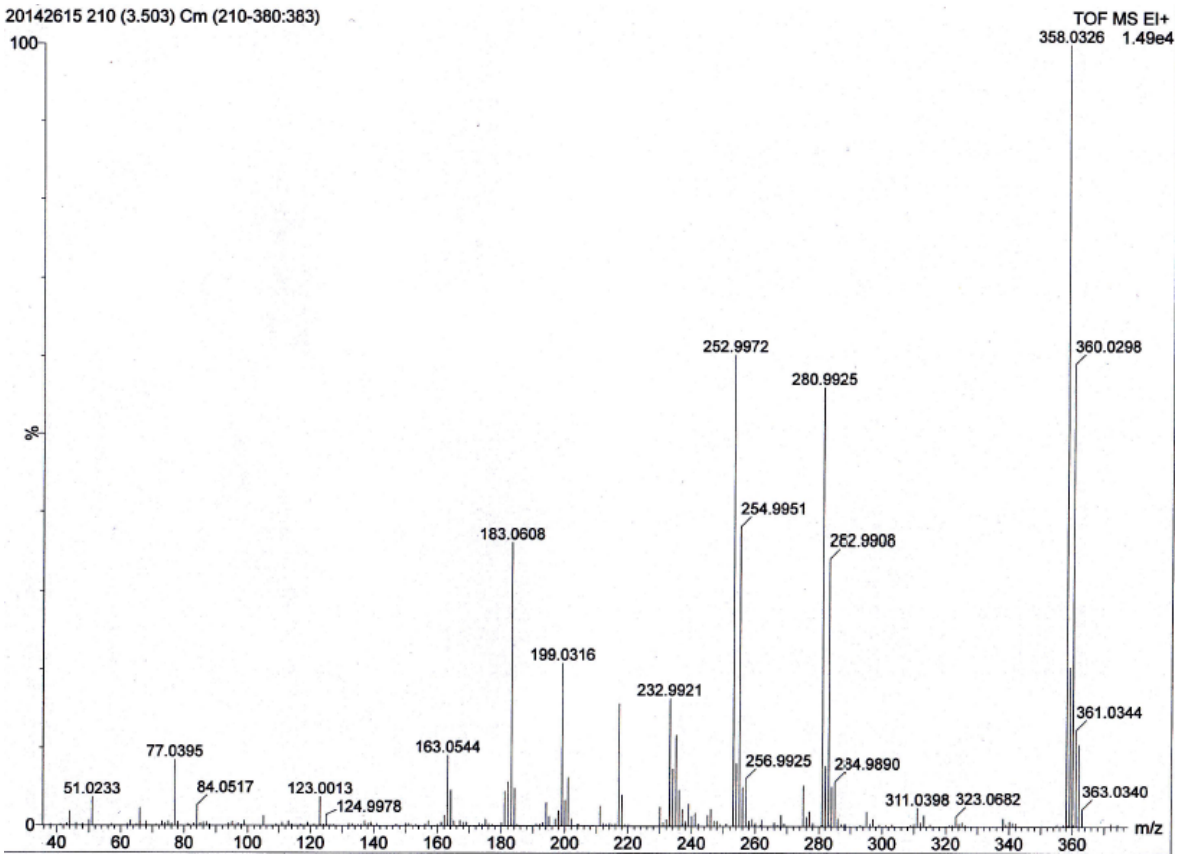
^{13}C NMR Spectrum of 3ea



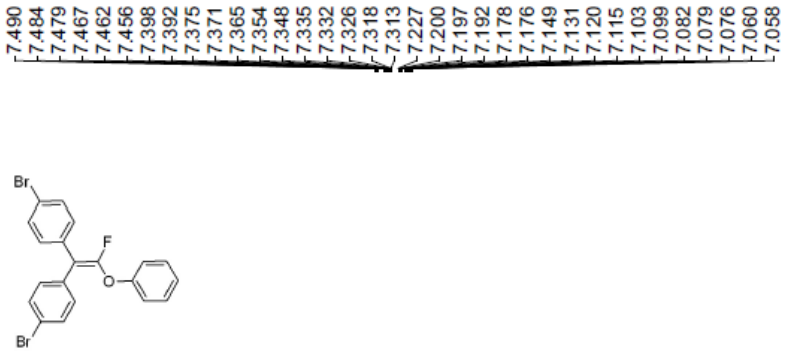
^{19}F NMR Spectrum of 3ea

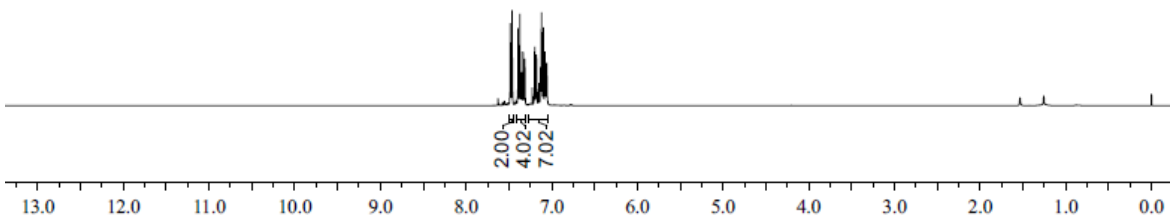


HRMS (EI) of 3ea

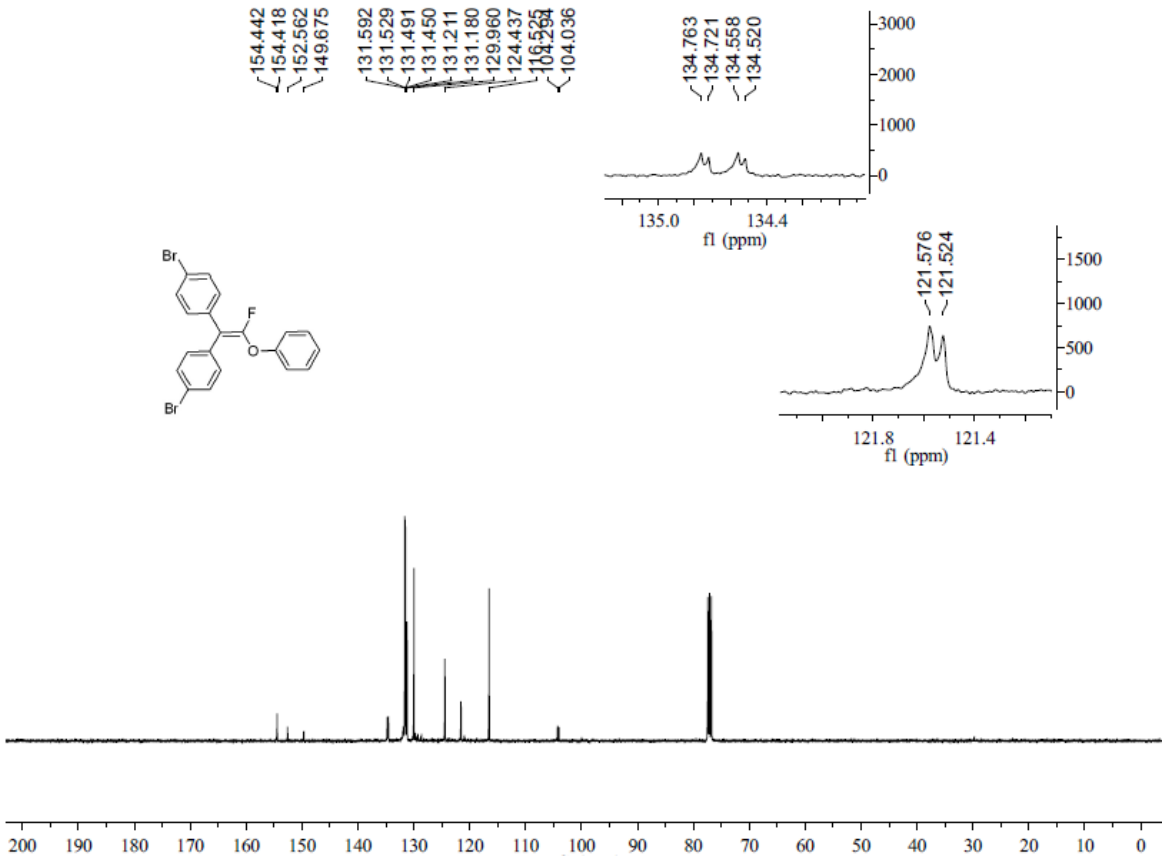


[1]H NMR Spectrum of 3fa

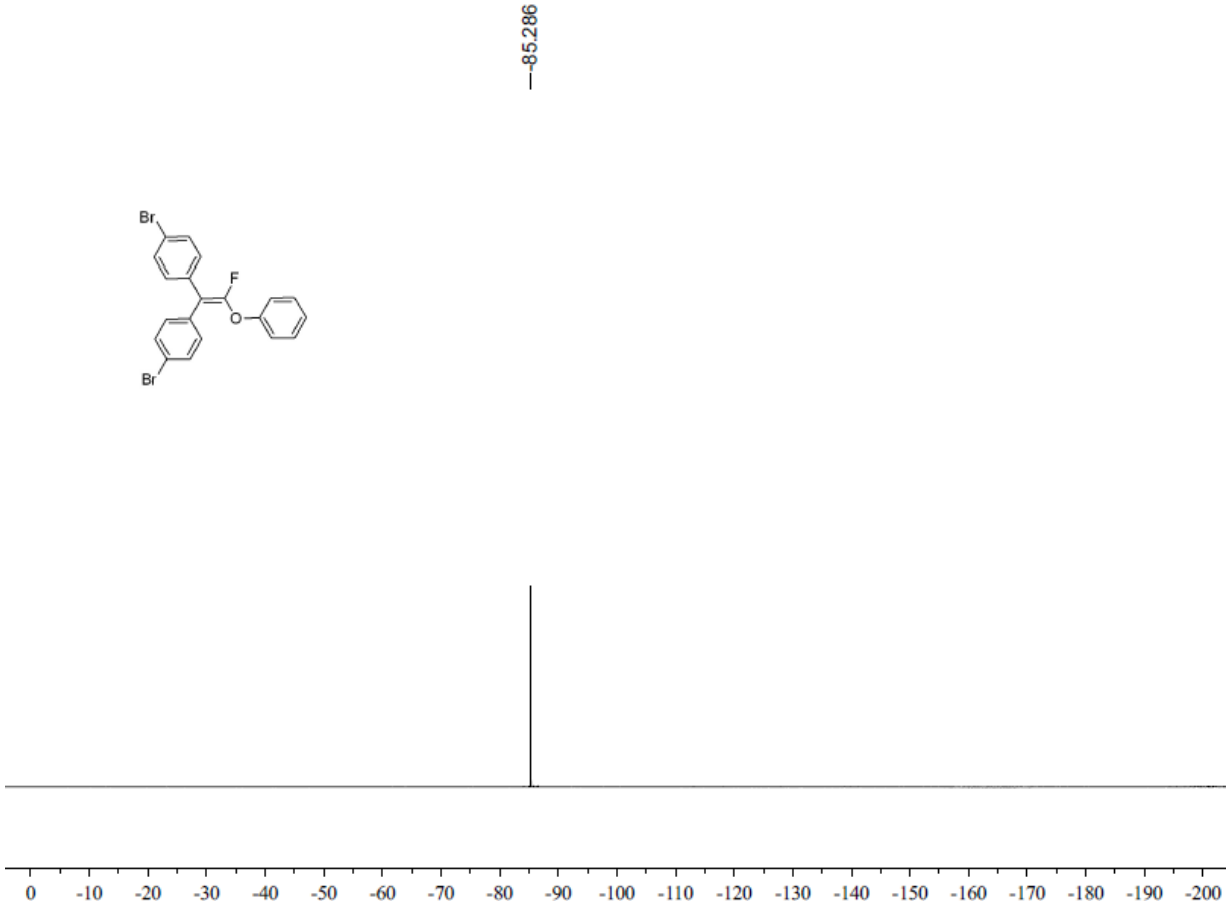




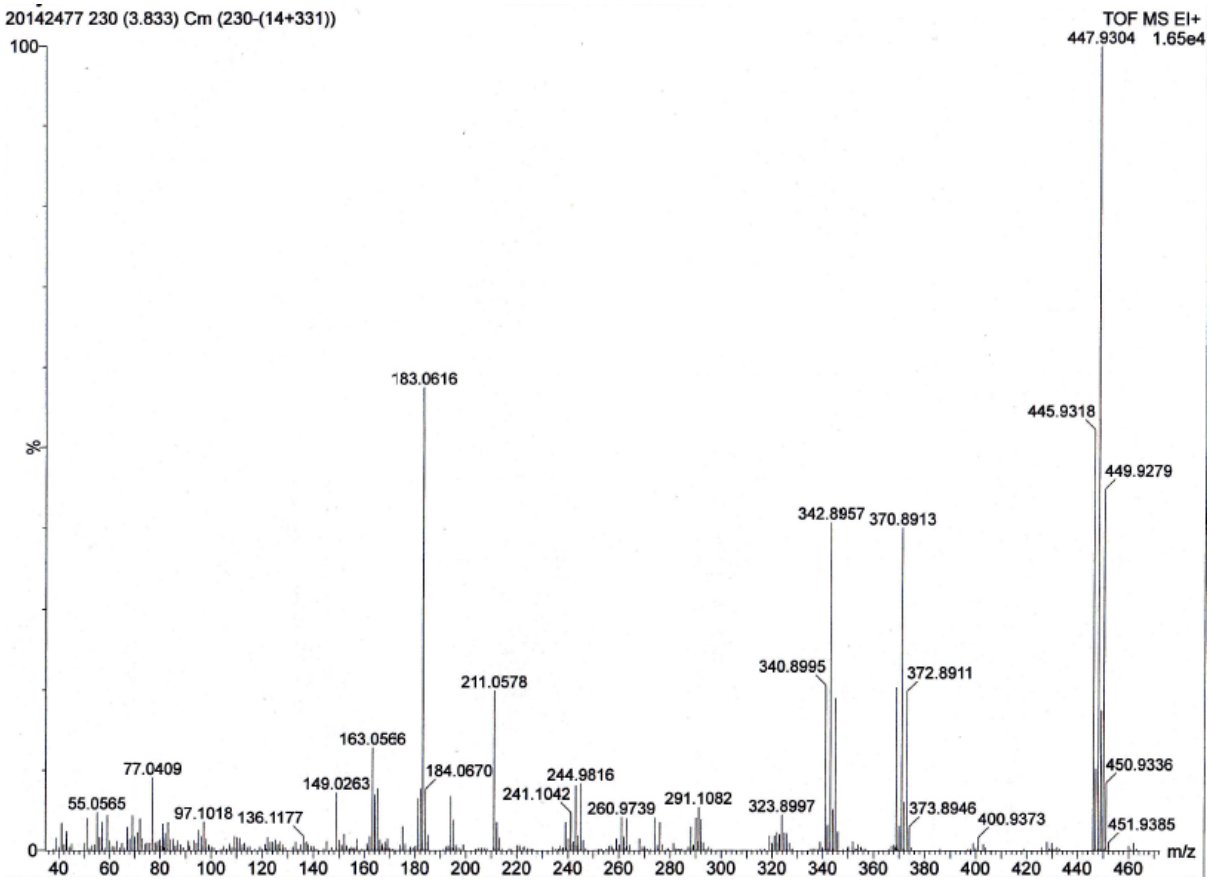
[13]C NMR Spectrum of 3fa



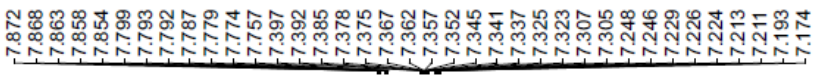
^{19}F NMR Spectrum of 3fa

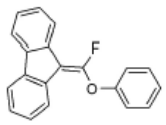


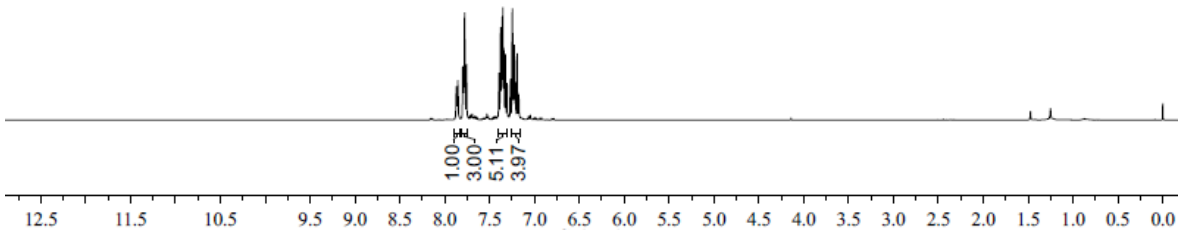
HRMS (EI) of 3fa



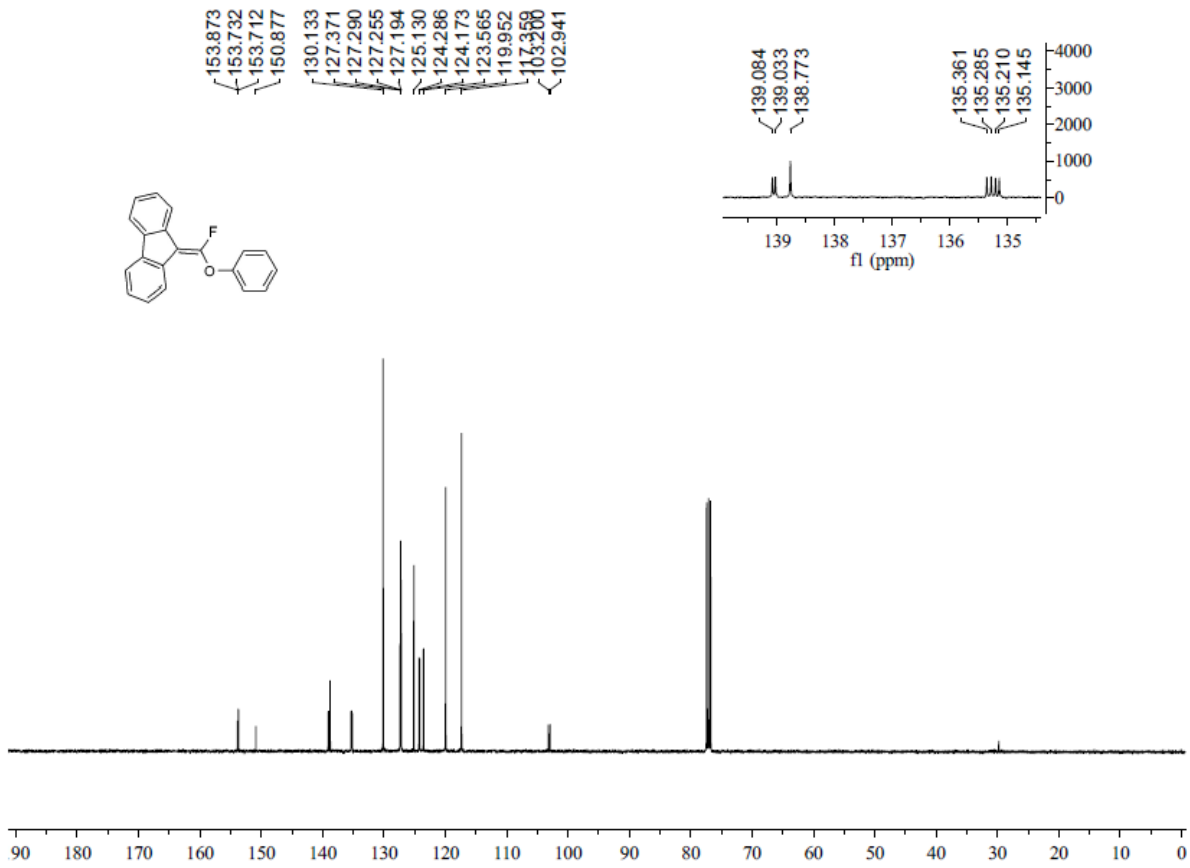
[1]H NMR Spectrum of 3ga



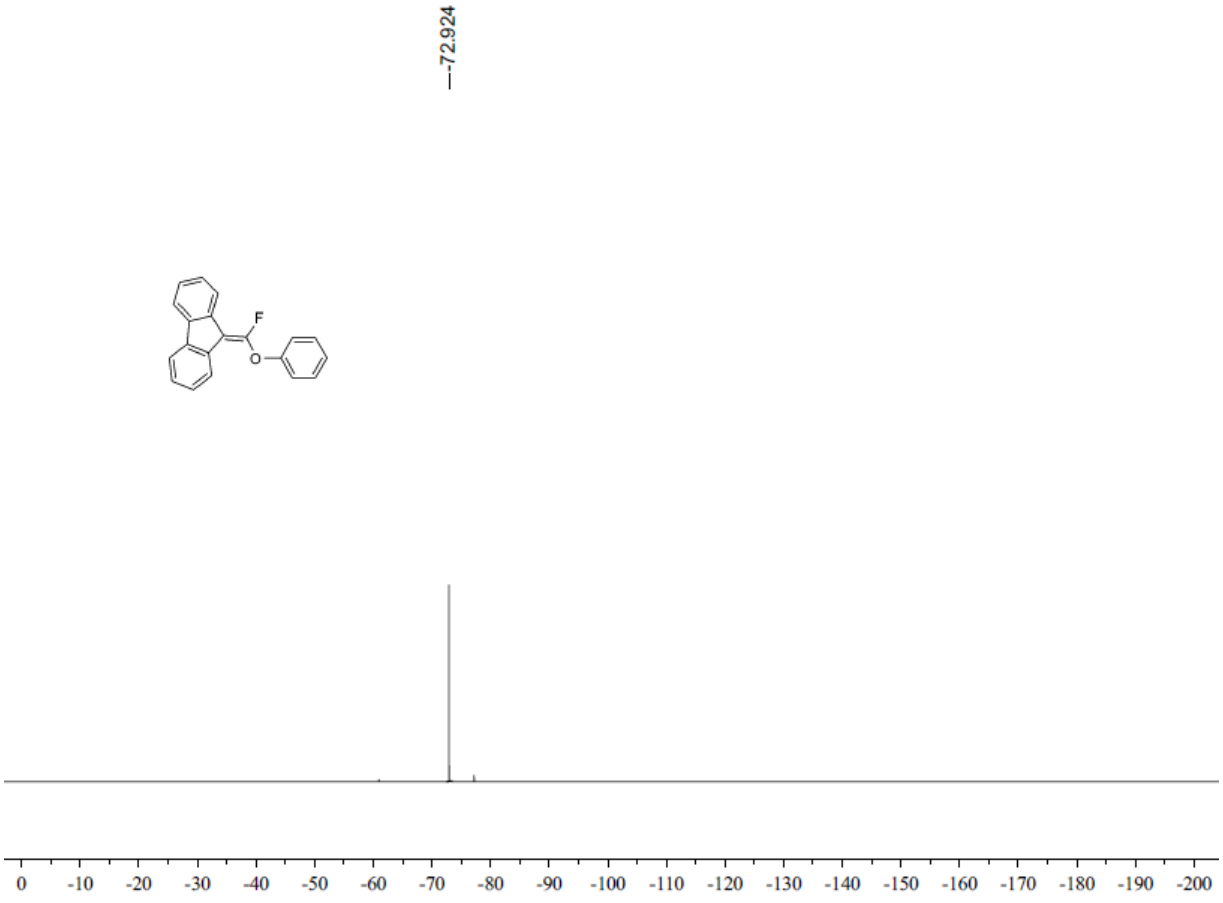




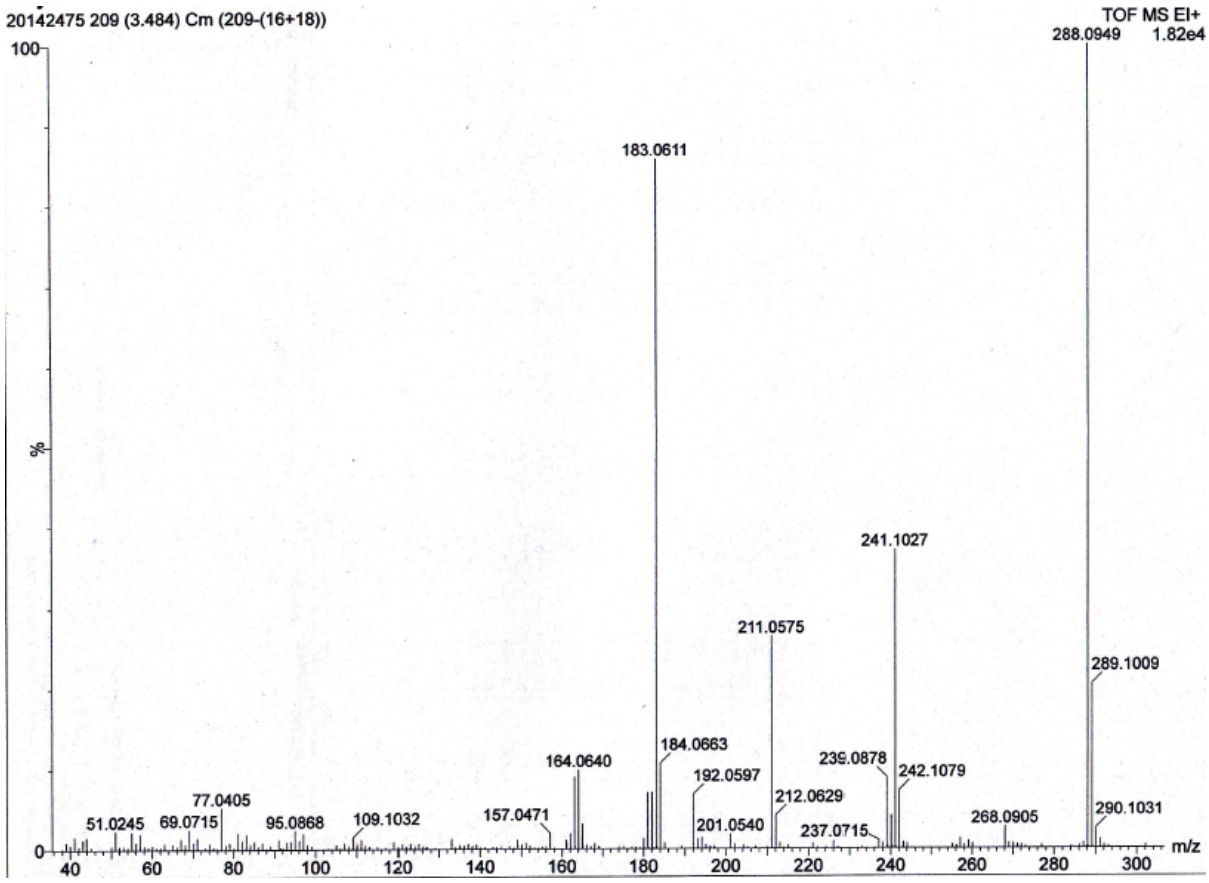
[13]C NMR Spectrum of 3ga



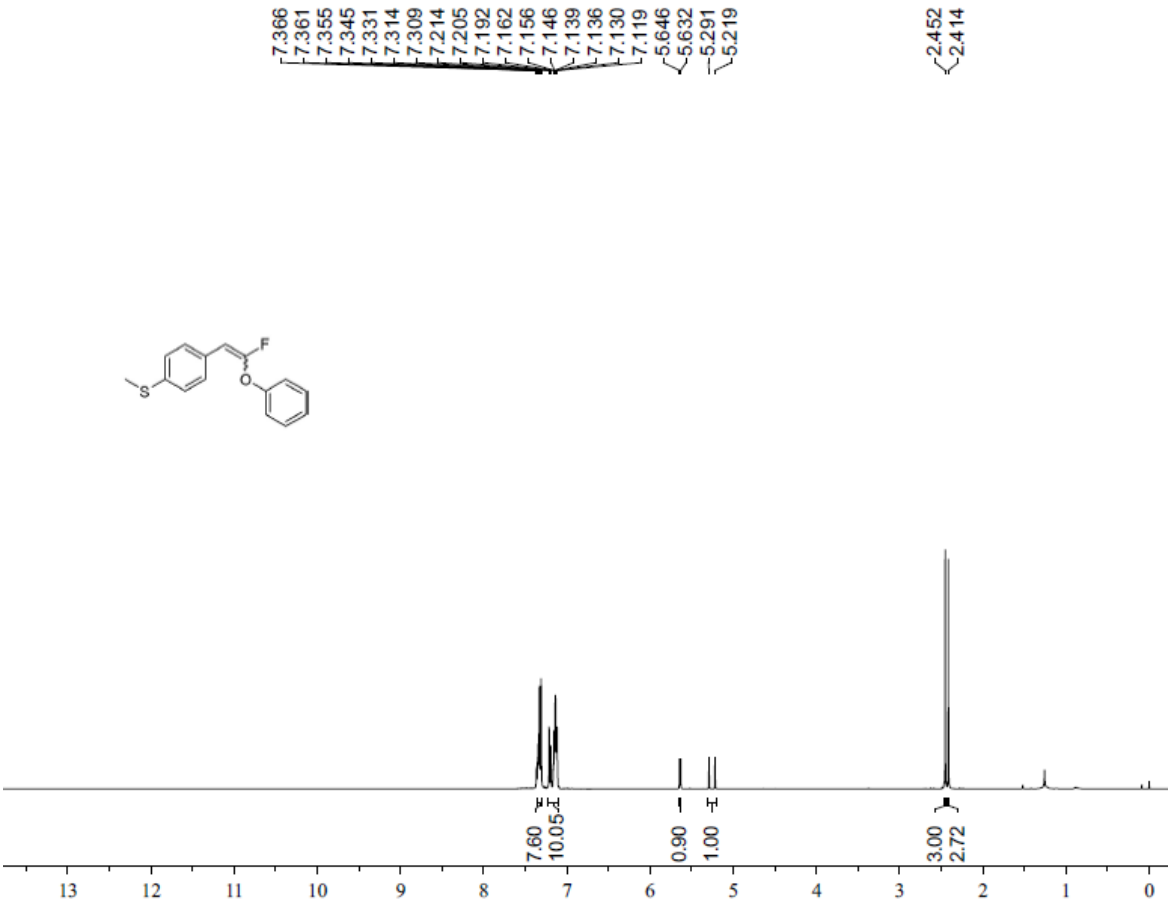
^{19}F NMR Spectrum of 3ga



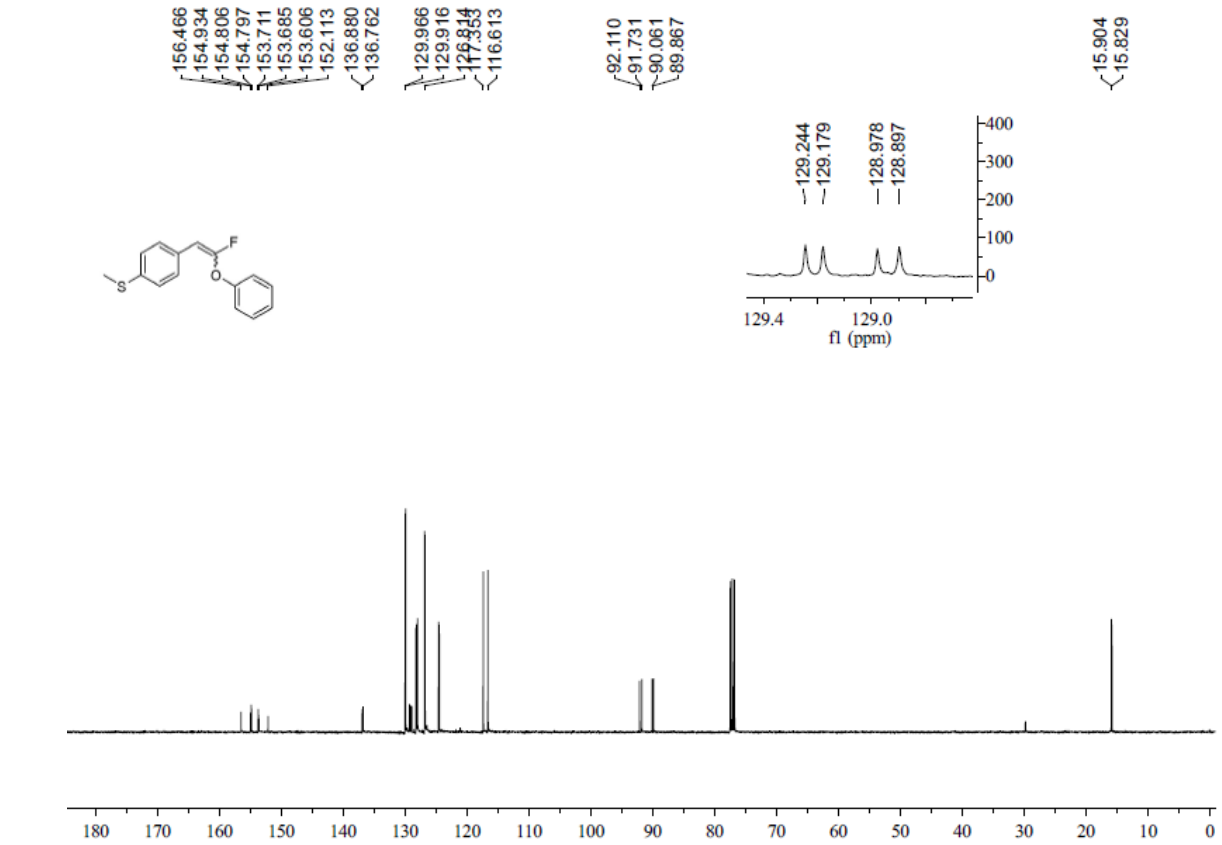
HRMS (EI) of 3ga



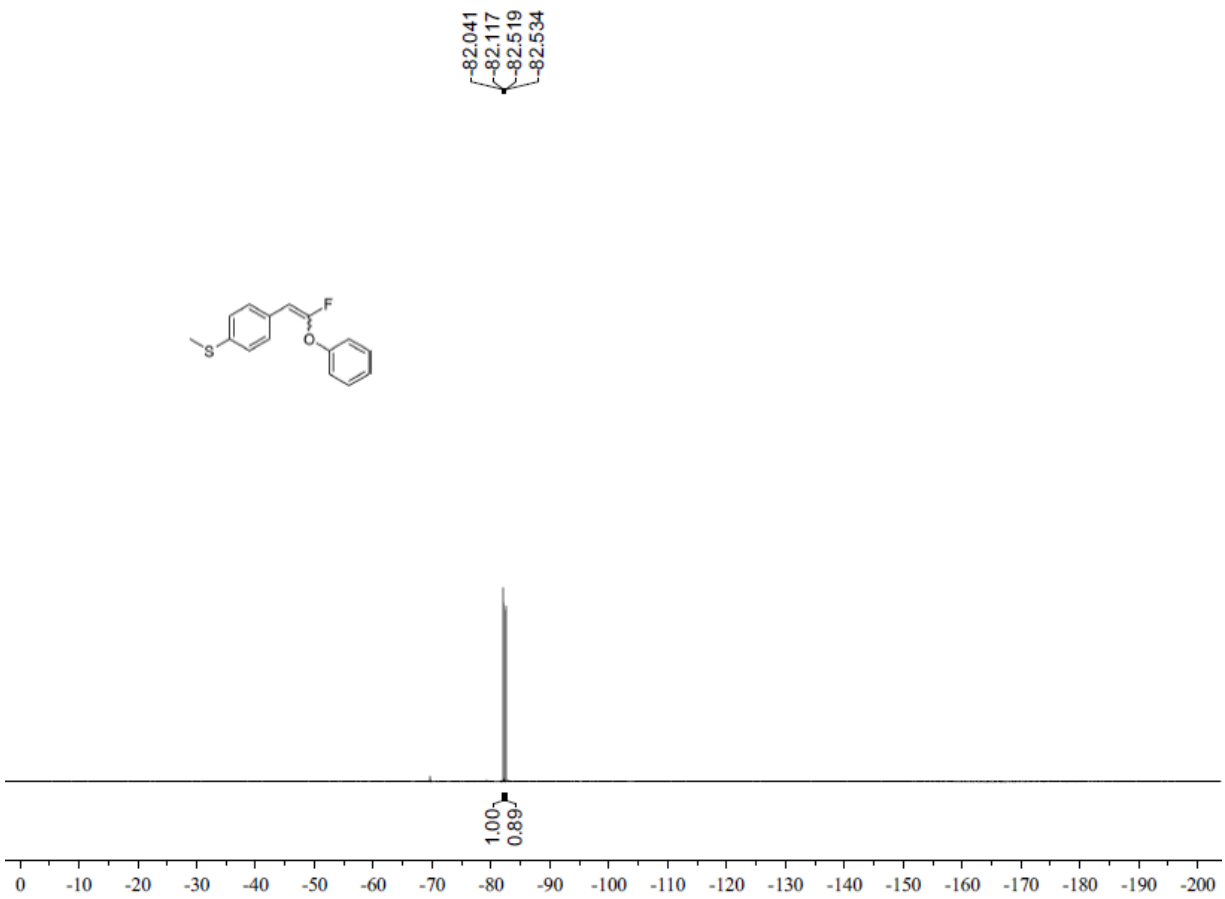
^{1}H NMR Spectrum of 3ha



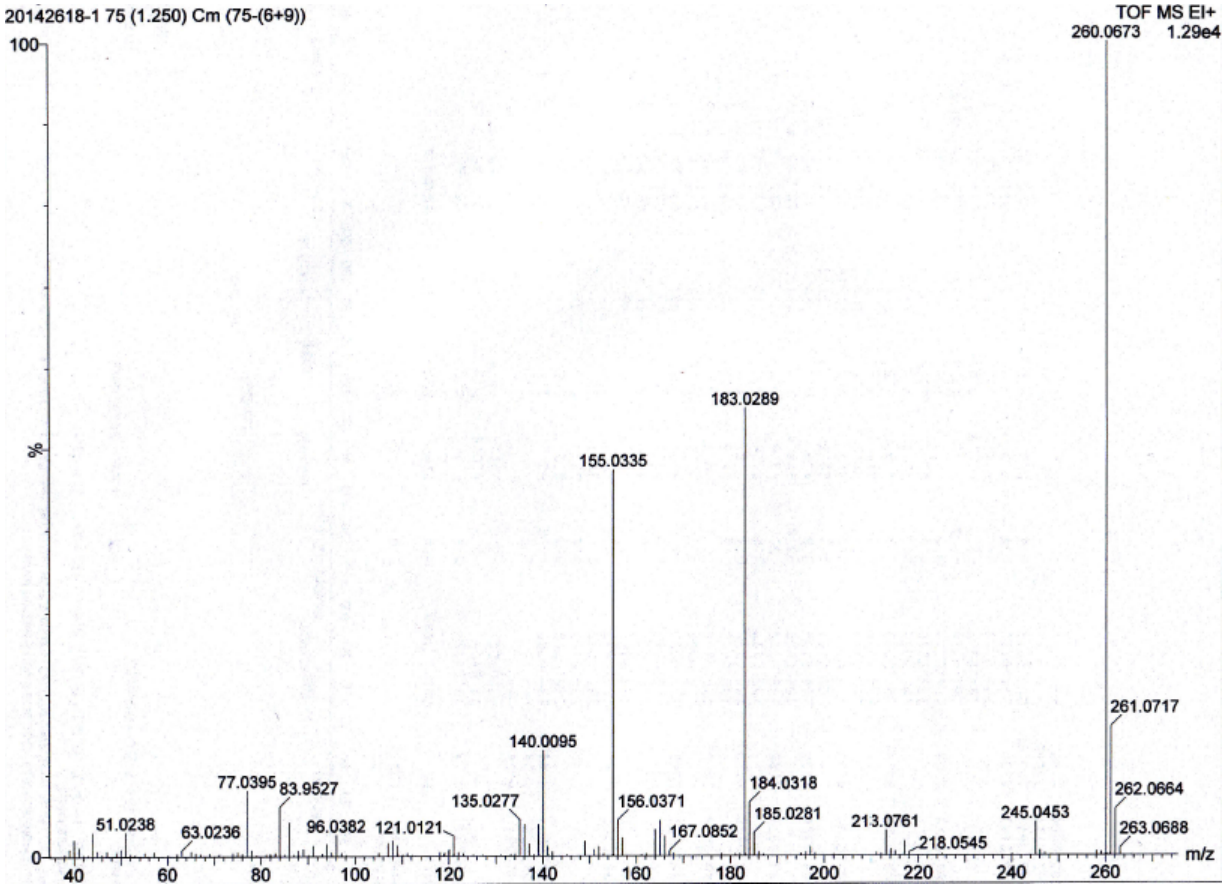
^{13}C NMR Spectrum of 3ha



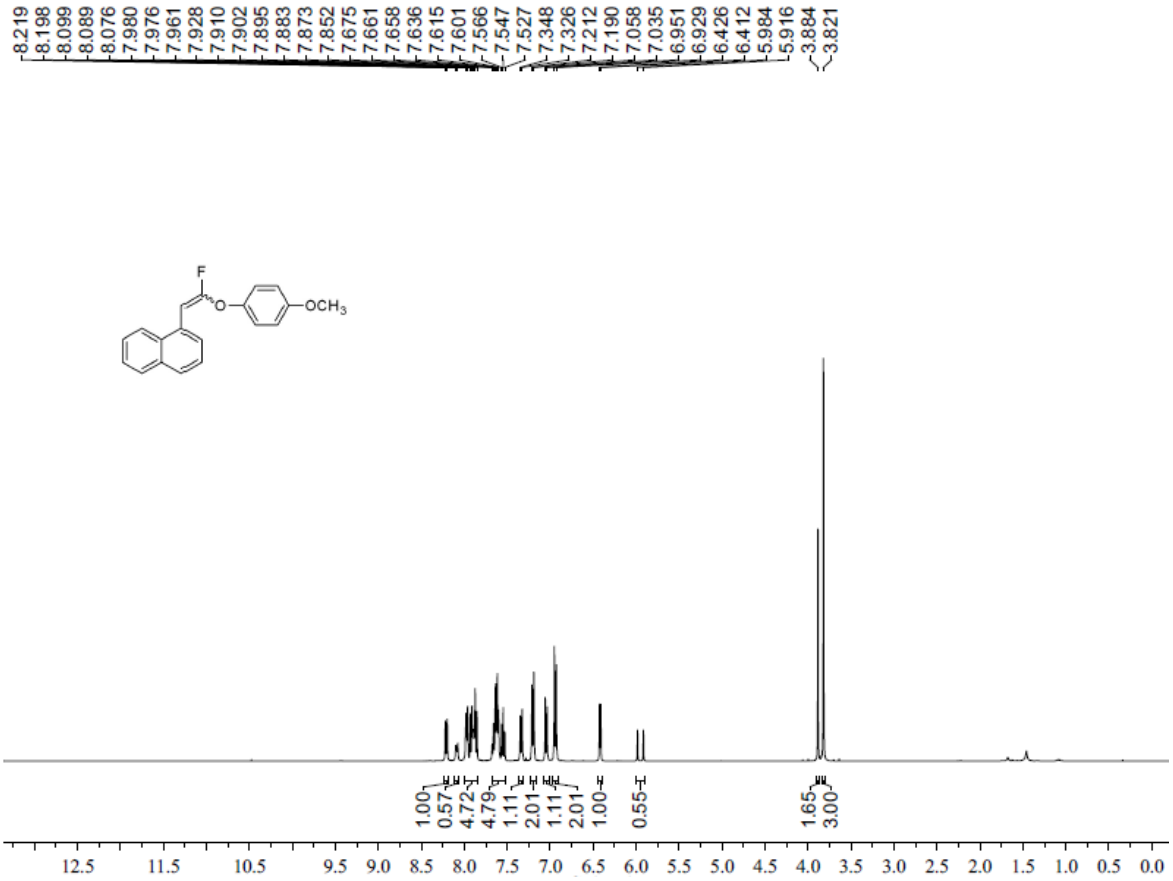
^{19}F NMR Spectrum of 3ha



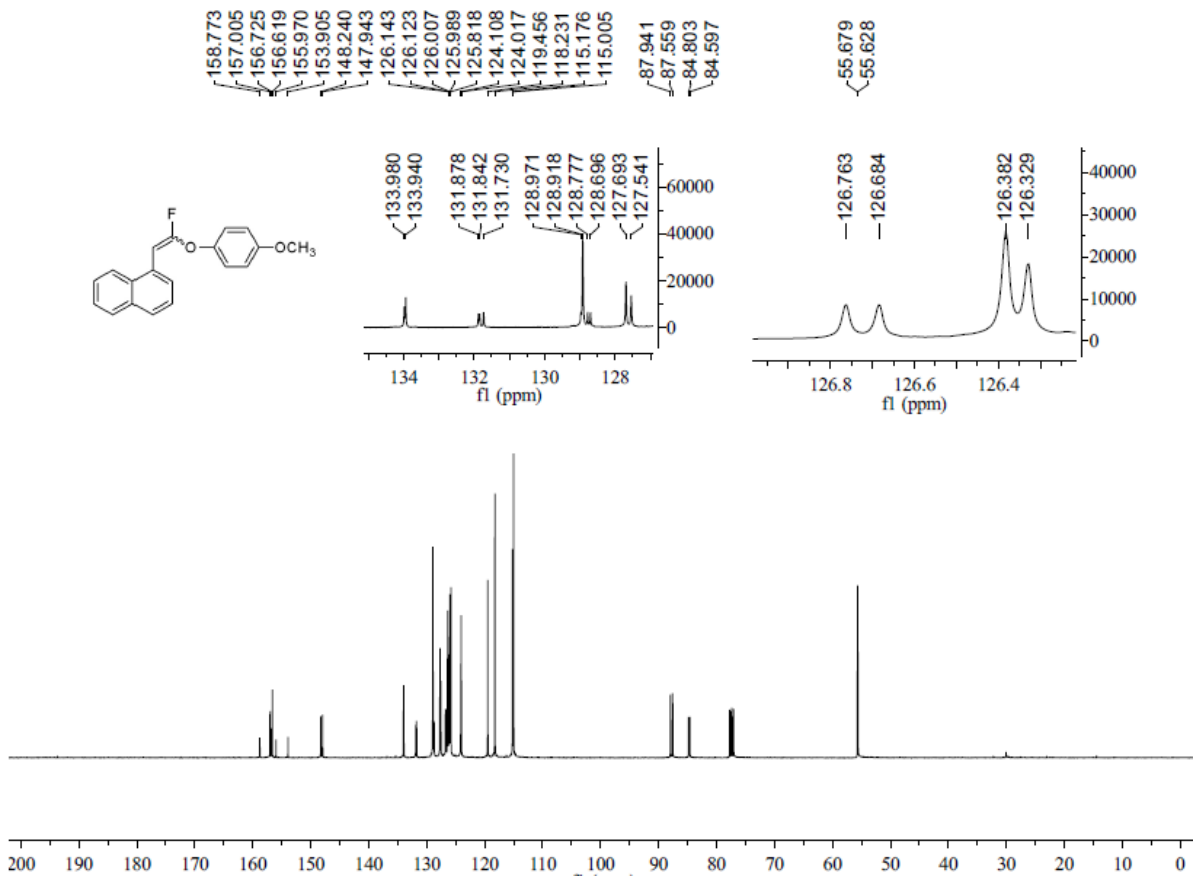
HRMS (EI) of 3ha



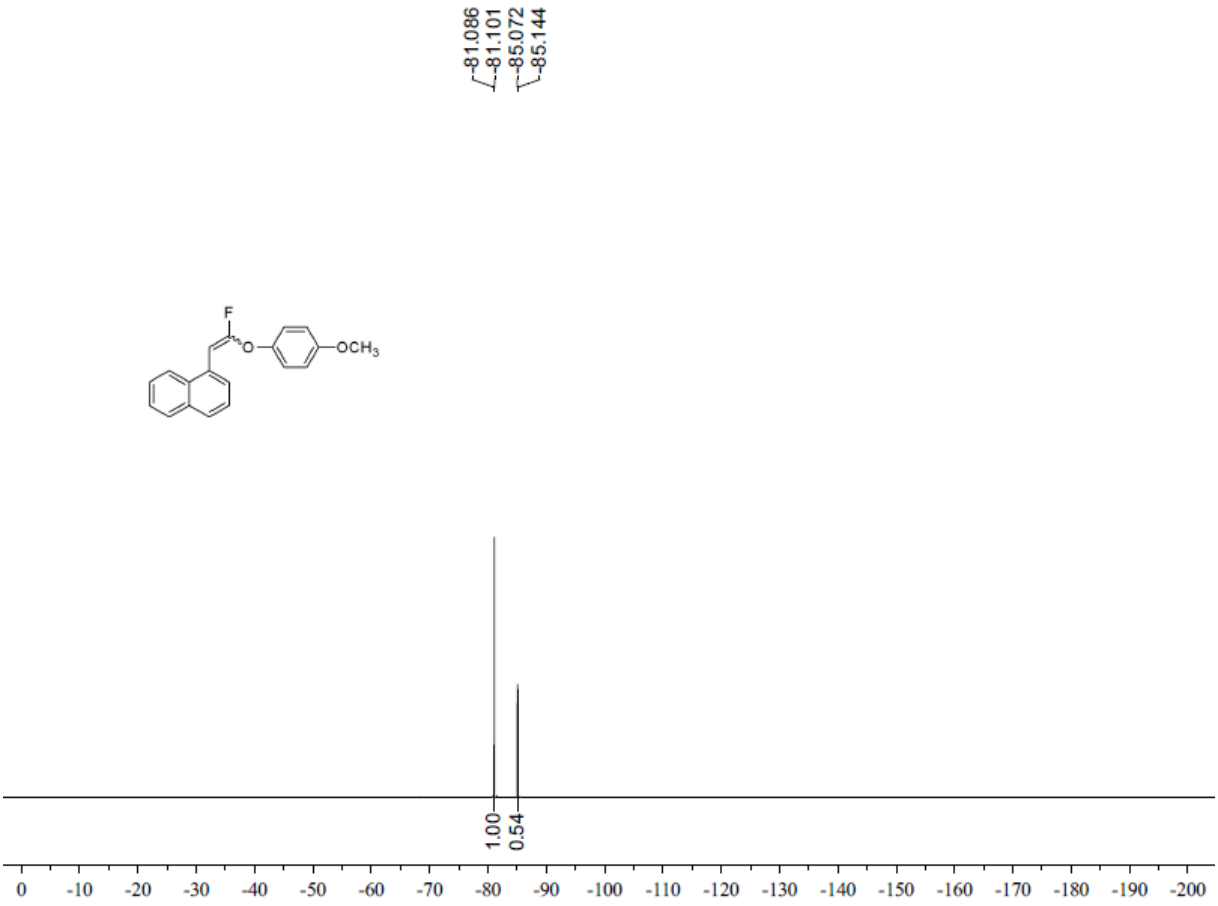
^{1}H NMR Spectrum of 3id



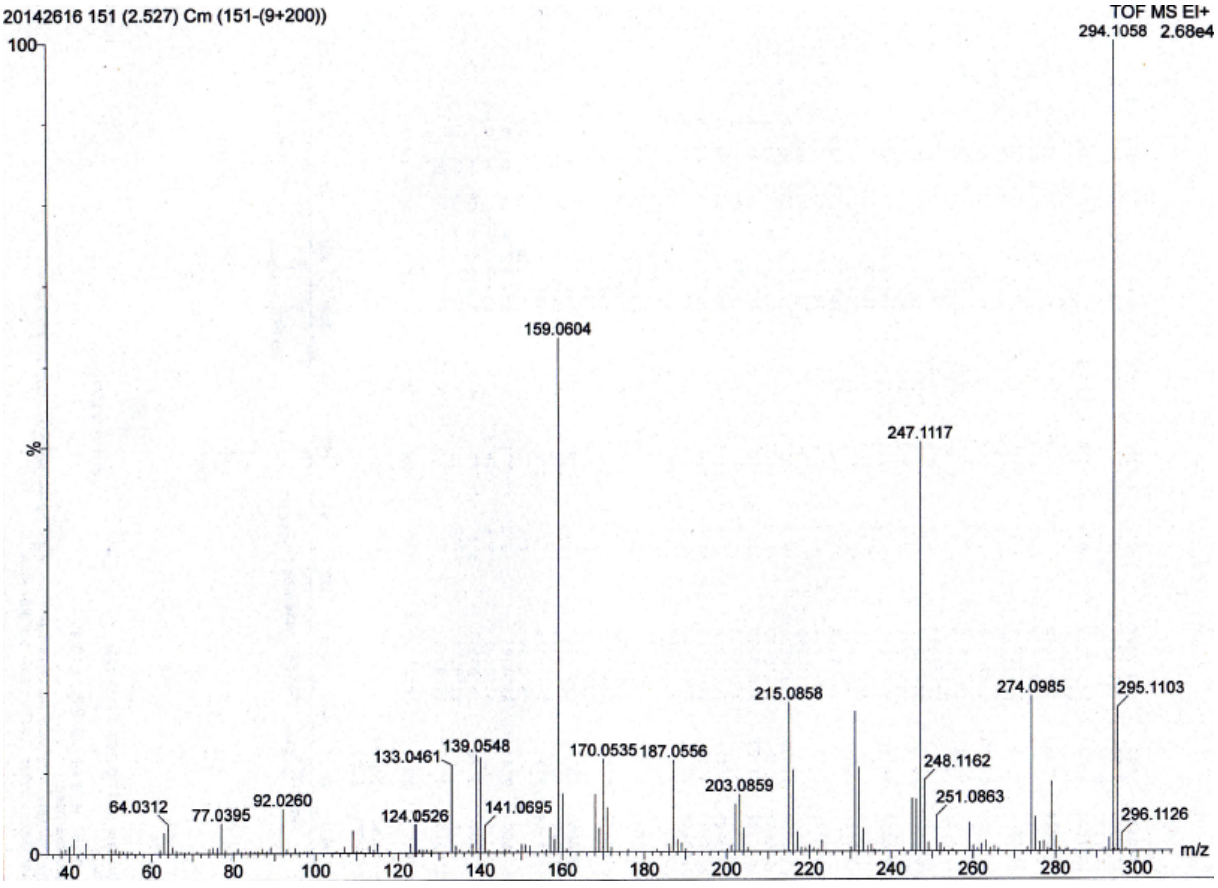
^{13}C NMR Spectrum of 3id



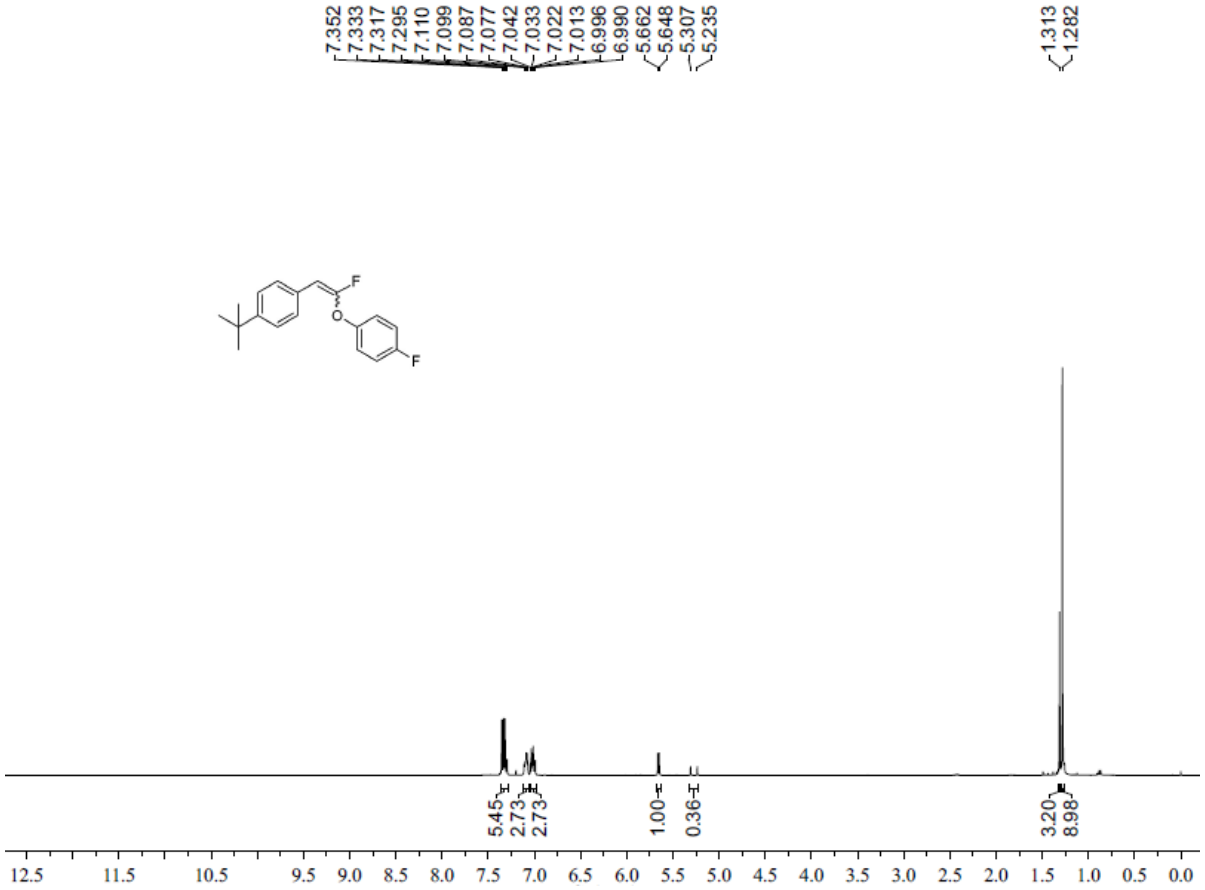
^{19}F NMR Spectrum of 3id



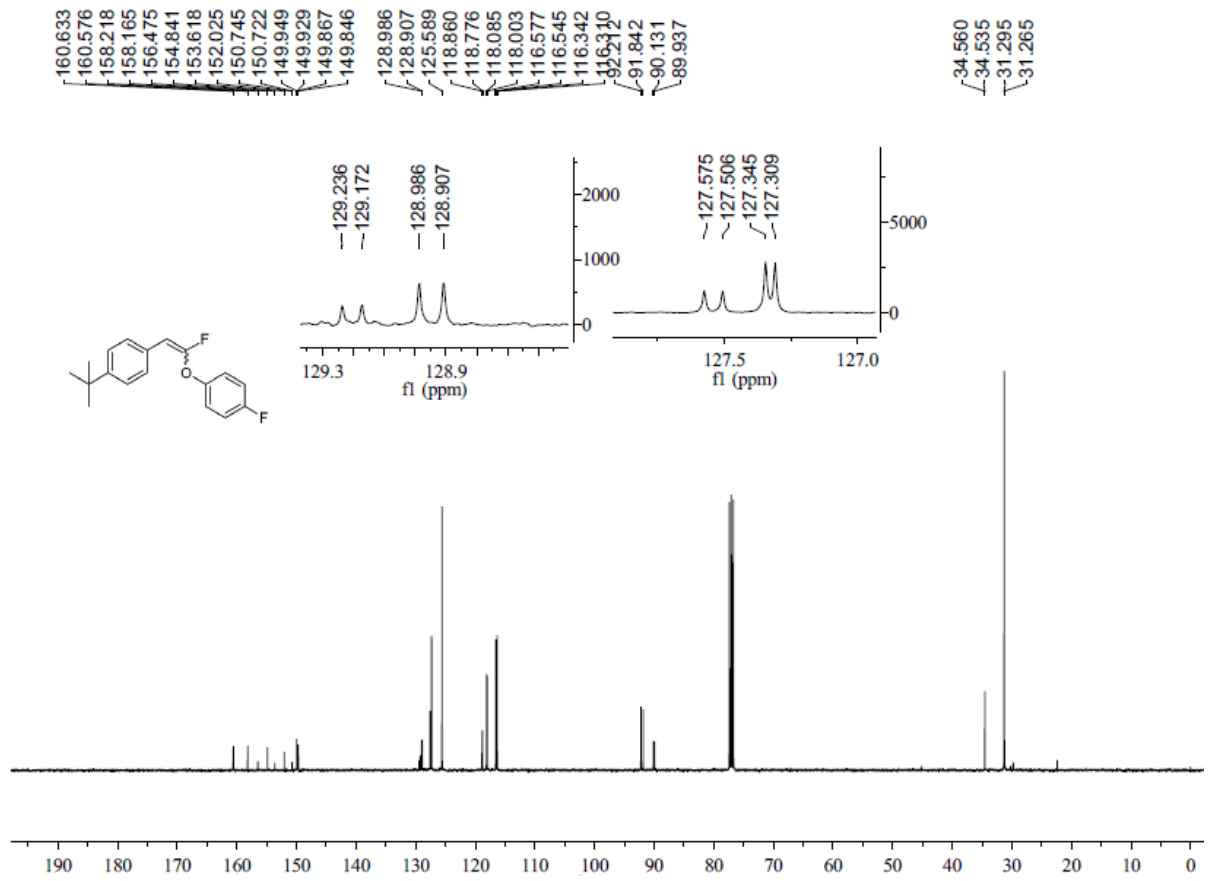
HRMS (EI) of 3id



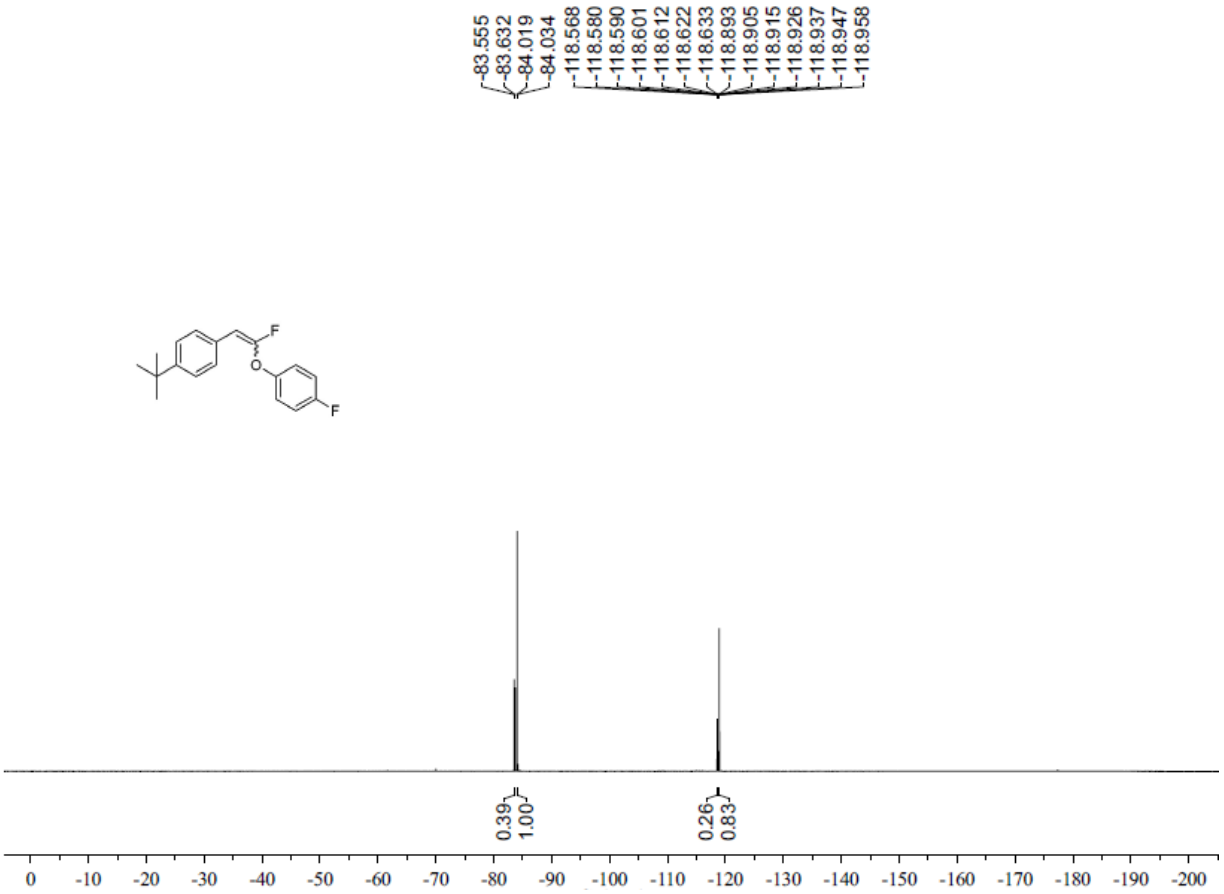
^{1}H NMR Spectrum of 3jf



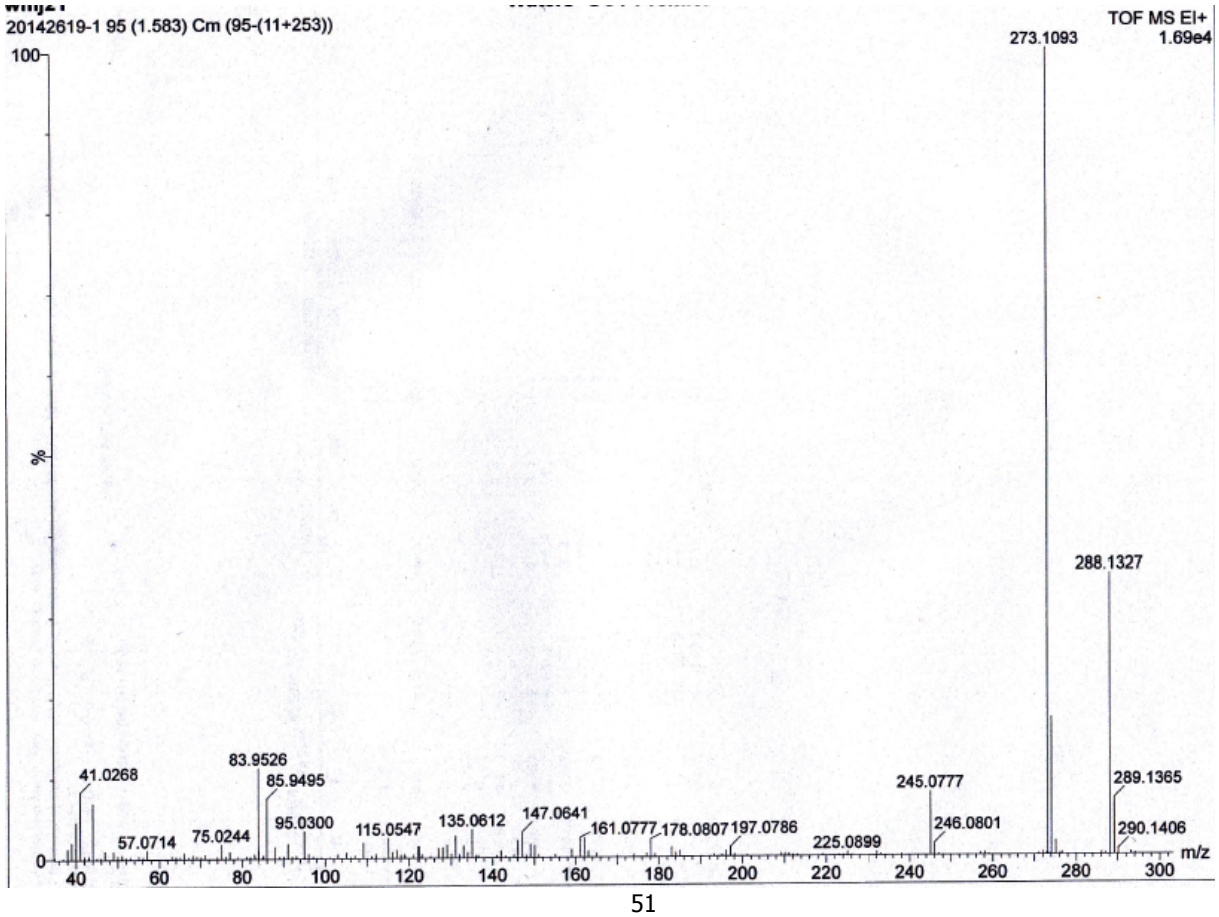
^{13}C NMR Spectrum of 3jf



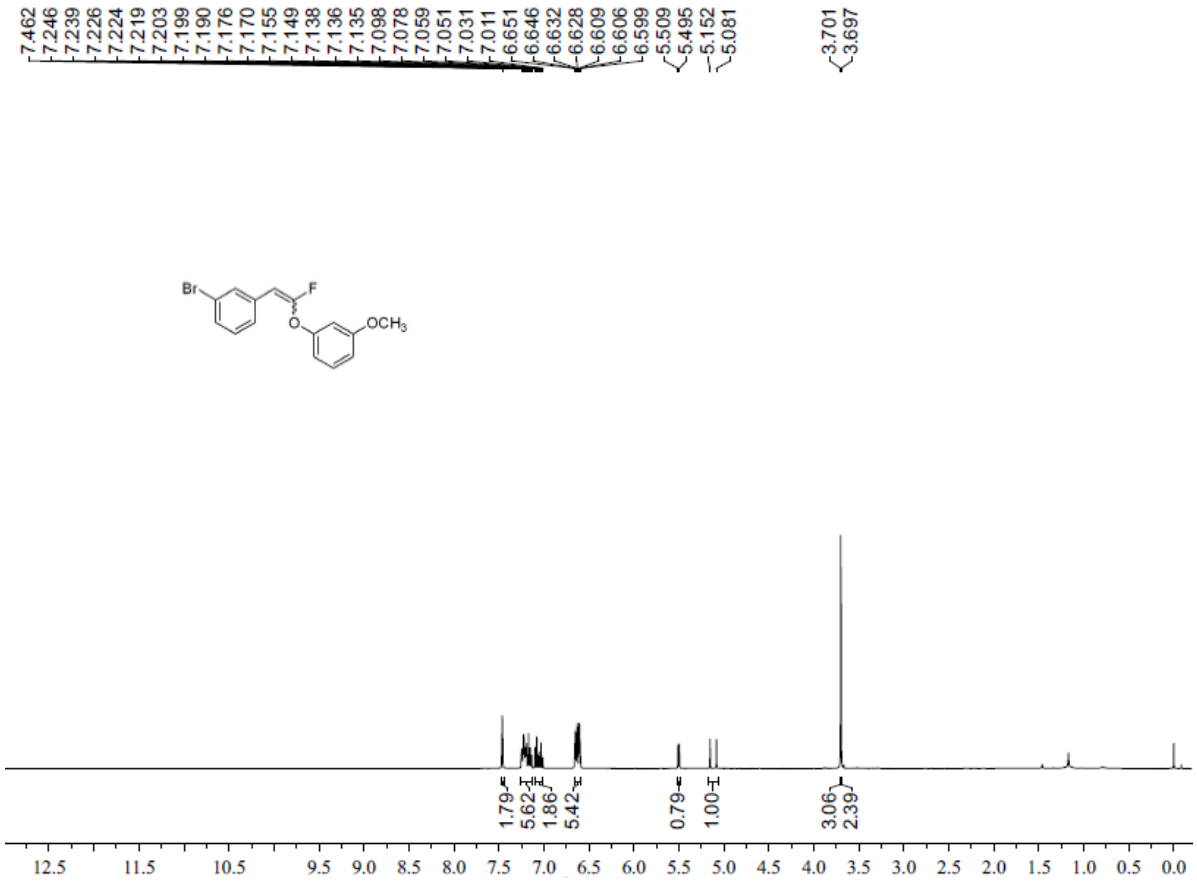
^{19}F NMR Spectrum of 3jf



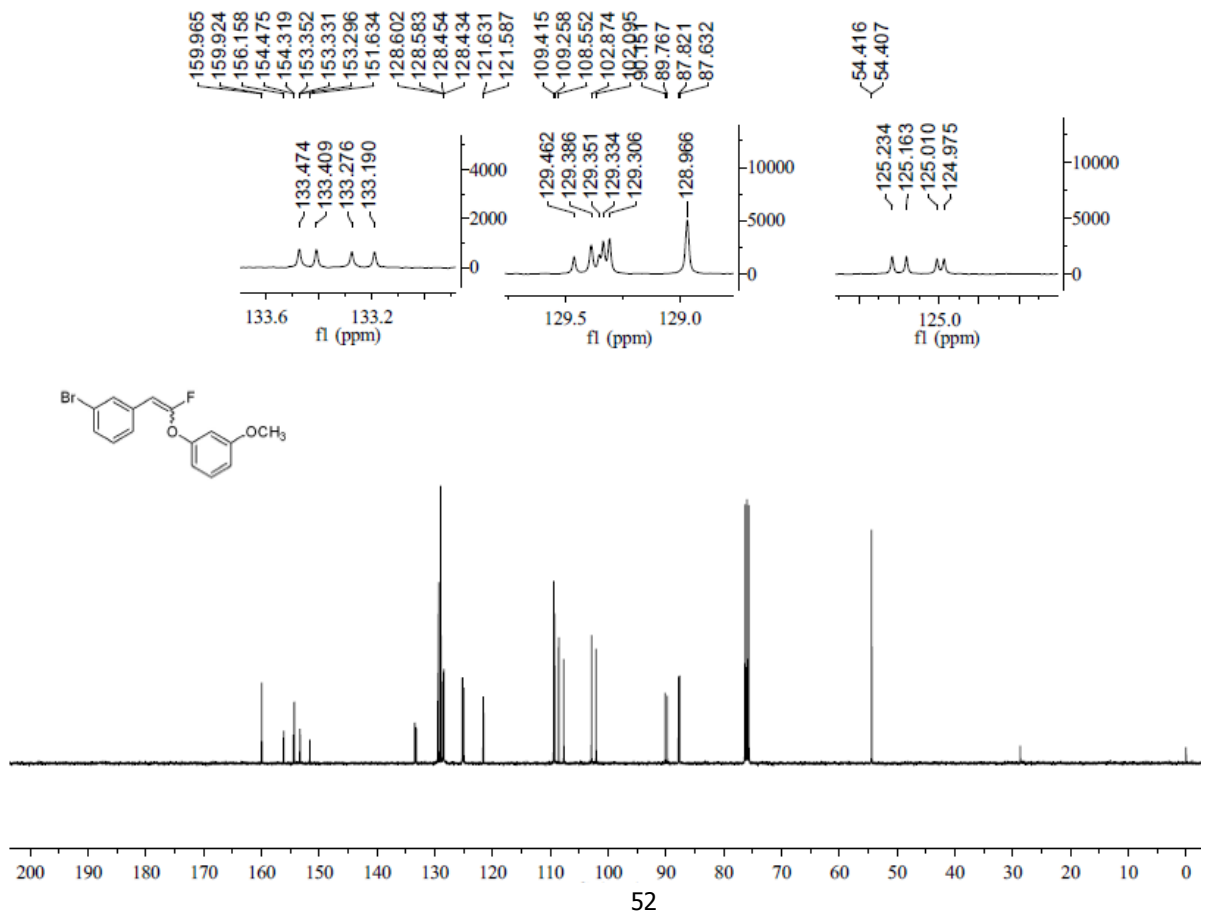
HRMS (EI) of 3jf



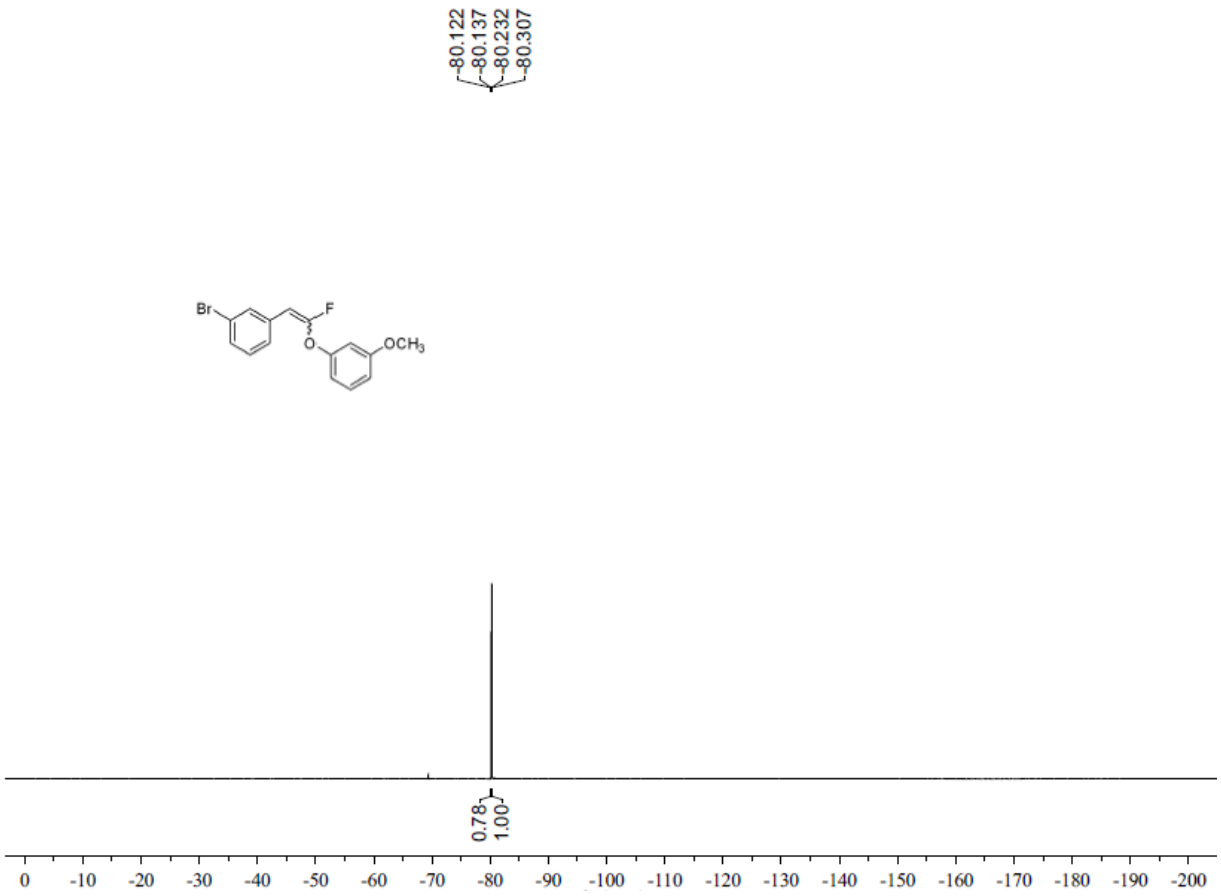
[1]H NMR Spectrum of 3kl



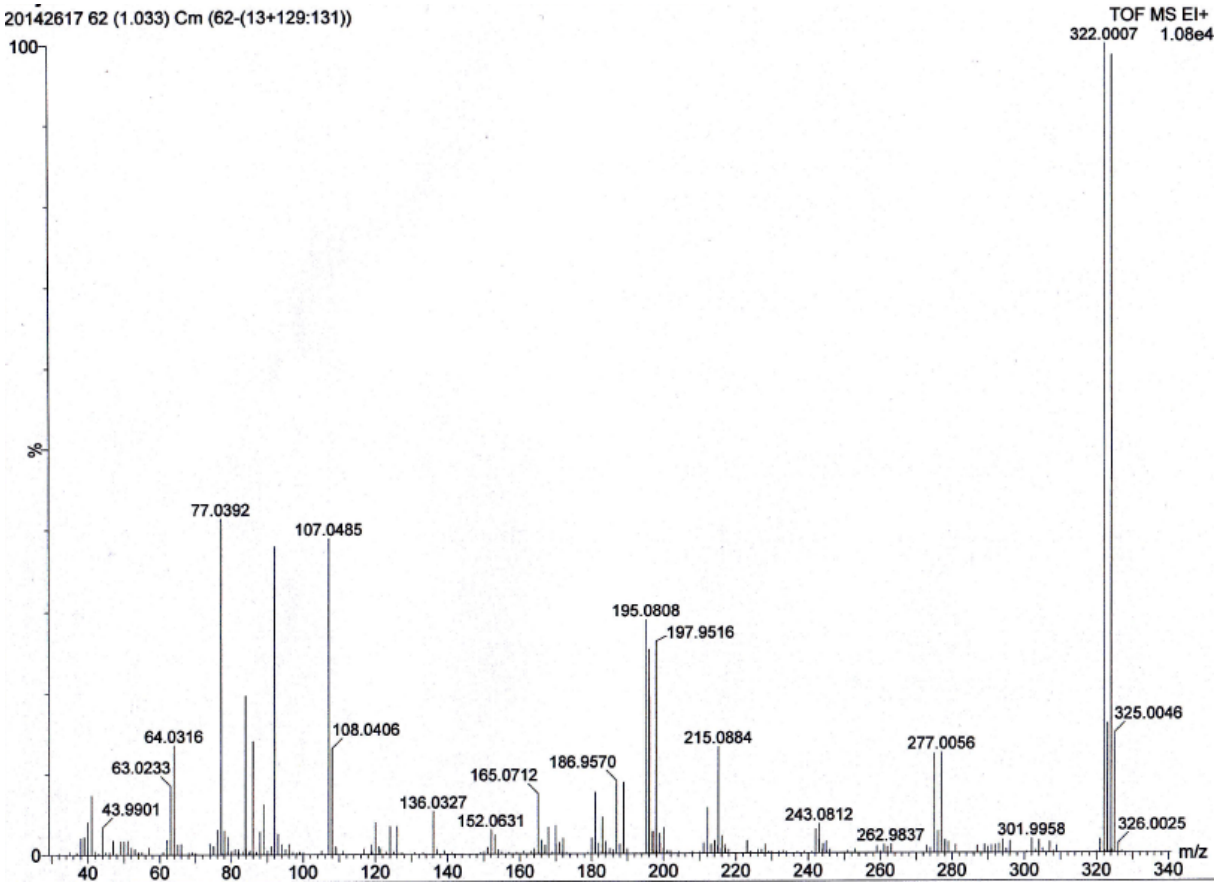
[13]C NMR Spectrum of 3kl



^{19}F NMR Spectrum of 3kl



HRMS (EI) of 3kl


20142617 62 (1.033) Cm (62-(13+129:131))
TOF MS EI+
322.0007 1.08e4
100
%
0
77.0392
107.0485
195.0808
197.9516
325.0046
64.0316
108.0406
215.0884
277.0056
63.0233
186.9570
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136.0327
43.9901
152.0631
243.0812
262.9837
301.9958
326.0025
m/z
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340