Supplementary Information

Synthesis of monofluoroalkenes through selective hydrodefluorination of *gem*-difluoroalkenes with Red-Al®

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General experimental procedures

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. 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–n and symmetrical *gem*-difluoroalkene 1o–q

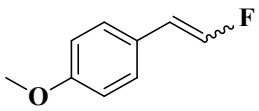
The 1,1-difluoroalkenes (**1a**–**n**) were prepared according to the reported procedure.[1] The symmetrical *gem*-difluoroalkene (**1o–q**) was prepared according to the Hu's reported procedure.[2]

General procedure for the synthesis of 2a–q

To a solution of *gem*-difluoroalkenes **1a**–**q** (1.0 mmol) in CH_2Cl_2 (8 mL) was added dropwise sodium bis(2-methoxyethoxy)aluminumhydride (Red-Al®, a 70% w/w in toluene) (0.8 mL) at room temperature. The mixture was stirred at room temperature for 1 h under argon atmosphere (TLC). After the completion of reaction, the reaction was quenched with saturated ammonium chloride solution. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography using *n*-hexane as eluent to afford the corresponding monofluoro reduction products **2a–q**.

Spectral and analytical data of compounds 2a-q

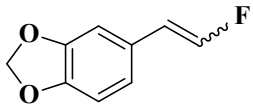
(*E*/*Z*)-1-(2-Fluorovinyl)-4-methoxybenzene (**2a, CAS: 26946-13-4**) [3]:



2a

Colorless liquid. Yield of *E*/*Z*-**2a**: 80%, *E*/*Z* ratio: 93/7. The *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy and the same below. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.7 Hz, 2H, *Z*-isomer), 7.18−7.14 (m, 2H, both *E*- and *Z*-isomers), 7.09 (dd, $^{2}J_{H\text{-}F}$ = 84.0 Hz, $^{3}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomer), 6.84 (d, J = 8.7 Hz, 2H, *E*-isomer), 6.58 (dd, $^{2}J_{H\text{-}F}$ = 80.5 Hz, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 1H, *Z*-isomer), 6.34 (dd, $^{3}J_{H\text{-}F}$ = 19.6 Hz, $^{3}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomer), 5.54 (dd, $^{3}J_{H\text{-}F}$ = 45.2 Hz, $^{3}J_{H\text{-}H}$ = 5.3 Hz, 1H, *Z*-isomer), 3.80 (s, 3H, *Z*-isomer), 3.79 (s, 3H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 159.3 (d, $^{5}J_{C\text{-}F}$ = 1.8 Hz), 149.2 (d, $^{1}J_{C\text{-}F}$ = 256.3 Hz), 127.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.3 (d, $^{3}J_{C\text{-}F}$ = 11.7 Hz), 114.5, 113.5 (d, $^{2}J_{C\text{-}F}$ = 16.0 Hz), 55.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −125.4 (dd, $^{2}J_{F\text{-}H}$ = 83.1 Hz, $^{3}J_{F\text{-}H}$ = 45.3 Hz, 1F, *Z*-isomer), −132.7 (dd, $^{2}J_{F\text{-}H}$ = 83.8 Hz, $^{3}J_{F\text{-}H}$ = 19.6 Hz, 1F, *E*-isomer) ppm.

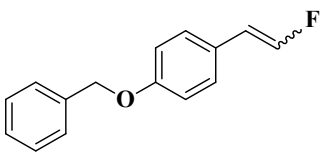
(*E*/*Z*)-5-(2-Fluorovinyl)benzo[d][1,3]dioxole (**2b, CAS: 276244-89-4**) [4]**:**



2b

Light yellow liquid. Yield of *E*/*Z*-**2b**: 77%, *E*/*Z* ratio: 94/6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (dd, $^{2}J_{H\text{-}F}$ = 83.4 Hz, $^{3}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomer), 6.81−6.77 (m, 2H, both *E*- and *Z*-isomers), 6.73−6.70 (m, 1H, both *E*- and *Z*-isomers), 6.61 (dd, $^{2}J_{H\text{-}F}$ = 83.4 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomer), 6.35 (dd, $^{3}J_{H\text{-}F}$ = 19.3 Hz, $^{2}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomer), 5.98 (s, 2H, *Z*-isomer) 5.97 (s, 2H, *E*-isomer), 5.55 (dd, $^{3}J_{H\text{-}F}$ = 44.5 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 149.3 (d, $^{1}J_{C\text{-}F}$ = 255.7 Hz), 148.1, 147.1 (d, $^{5}J_{C\text{-}F}$ = 2.0 Hz), 126.6 (d, $^{3}J_{C\text{-}F}$ = 11.8 Hz), 120.4 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 113.7 (d, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 108.6, 105.8 (d, $^{5'}J_{C\text{-}F}$ = 2.2 Hz), 101.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −124.5 (dd, $^{2}J_{F\text{-}H}$ = 83.0 Hz, $^{3}J_{F\text{-}H}$ = 44.4 Hz, 1F, *Z*-isomer), −132.3 (dd, $^{2}J_{F\text{-}H}$ = 83.4 Hz, $^{3}J_{F\text{-}H}$ = 19.3 Hz, 1F, *E*-isomer) ppm.

(*E*/*Z*)-1-(Benzyloxy)-4-(2-fluorovinyl)benzene (**2c**):

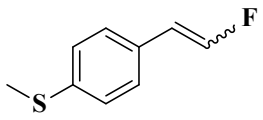


2c

White solid. Yield of *E*/*Z*-**2c**: 85%, *E*/*Z* ratio: 95/5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.38 (m, 5H, both *E*- and *Z*-isomers), 7.25−7.22 (m, 2H, both *E*- and *Z*-isomers), 7.15 (dd, $^{2}J_{H\text{-}F}$ = 83.6 Hz, $^{3}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomer), 7.01−6.98 (m, 2H, both *E*- and *Z*-isomers), 6.66 (dd,$^{2}J_{H\text{-}F}$ = 83.1 Hz, $^{3}J_{H\text{-}H}$ = 5.3 Hz, 1H, *Z*-isomer), 6.42 (dd, $^{3}J_{H\text{-}F}$

= 19.6 Hz, $^{3}J_{H-H}$ = 11.3 Hz, 1H, *E*-isomer), 5.61 (dd, $^{3}J_{H-F}$ = 45.2 Hz, $^{3}J_{H-H}$ = 5.3 Hz, 1H, *Z*-isomer), 5.13 (s, 2H, *Z*-isomer), 5.12(s, 2H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 158.4 (d, $^{5}J_{C-F}$ = 1.9 Hz), 149.1 (d, $^{1}J_{C-F}$ = 256.6 Hz), 136.9, 128.7, 128.1, 127.5, 127.4 (d, $^{4}J_{C-F}$ = 3.0 Hz), 125.4 (d,$^{3}J_{C-F}$ = 11.7 Hz), 115.3, 113.3 (d,$^{2}J_{C-F}$ = 16.1 Hz), 70.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −125.0 (dd, $^{2}J_{F-H}$ = 83.1 Hz, $^{3}J_{F-H}$ = 45.2 Hz,1F, *Z*-isomer), −132.3 (dd, $^{2}J_{F-H}$ = 83.7 Hz, $^{3}J_{F-H}$ = 19.6 Hz, 1F, *E*-isomer) ppm. HRMS (EI): calc. for $C_{15}H_{13}FO$ $[M]^+$ 228.0950, found 228.0949.

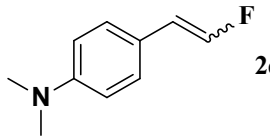
(*E*/*Z*)-(4-(2-Fluorovinyl)phenyl)(methyl)sulfane (**2d**):



2d

Colorless oily liquid. Yield of *E*/*Z*-**2d**: 79%, *E*/*Z* ratio: 93/7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, $^{2}J_{H-F}$ = 83.2 Hz, $^{3}J_{H-H}$ = 11.4 Hz, 1H, *E*-isomer), 7.22−7.13 (m, 4H, both *E*- and *Z*-isomers), 6.62 (dd, $^{2}J_{H-F}$ = 82.1 Hz, $^{3}J_{H-H}$ = 5.4 Hz, 1H, *Z*-isomer), 6.34 (dd, $^{3}J_{H-F}$ = 19.3 Hz, $^{3}J_{H-H}$ = 11.4 Hz,1H, *E*-isomer), 5.55 (dd, $^{3}J_{H-F}$ = 44.8 Hz, $^{3}J_{H-H}$ = 5.3 Hz, 1H, *Z*-isomer), 2.47 (s, 3H, *Z*-isomer), 2.46 (s, 3H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 149.9 (d, $^{1}J_{C-F}$= 258.9 Hz), 137.8 (d, $^{5}J_{C-F}$ = 2.2 Hz), 129.5 (d, $^{3}J_{C-F}$ = 11.9 Hz), 126.9, 126.5 (d, $^{4}J_{C-F}$= 3.1 Hz), 113.4 (d,$^{2}J_{C-F}$ = 16.3 Hz), 15.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −122.3 (dd, $^{2}J_{F-H}$ = 82.7 Hz, $^{3}J_{F-H}$ = 44.8 Hz, 1F, *Z*-isomer), −130.4 (dd, $^{2}J_{F-H}$ = 83.2 Hz, $^{3}J_{F-H}$ = 19.2 Hz, 1F, *E*-isomer) ppm. HRMS (*E*-isomerI): calc. for C_9H_9FS $[M]^+$ 168.0409, found 168.0411.

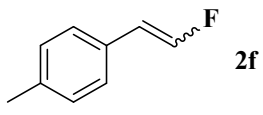
(*E*/*Z*)-4-(2-Fluorovinyl)-*N*,*N*-dimethylaniline (**2e, CAS: 1259106-87-0**) [5]:



2e

Light yellow solid. Yield of *E*/*Z*-**2e**: 85%, *E*/*Z* ratio: 89/11, mp 65.2–66.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13−7.11 (m, 2H, both *E*- and *Z*-isomers), 7.07 (dd, $^{2}J_{H-F}$= 84.5 Hz, $^{3}J_{H-H}$ = 11.3 Hz, 1H, *E*-isomers), 6.67−6.65 (m, 2H, both *E*- and *Z*-isomers), 6.31 (dd, $^{3}J_{H-F}$ = 20.1 Hz, $^{3}J_{H-H}$ = 11.3 Hz, 1H, *E*-isomers), 5.49 (dd, $^{3}J_{H-F}$ = 46.2 Hz, $^{3}J_{H-H}$ = 5.2 Hz, 1H, *Z*-isomers), 2.95 (s, 6H, *Z*-isomers), 2.94 (s, 6H, *E*-isomers)ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 150.0, 148.1 (d, $^{1}J_{C-F}$ = 253.8 Hz), 129.9 (d,$^{3}J_{C-F}$ = 7.0 Hz), 127.0 (d, $^{4}J_{C-F}$ = 2.9 Hz), 113.6 (d, $^{2}J_{C-F}$ = 15.8 Hz), 112.7, 40.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −127.2 (dd, $^{2}J_{F-H}$ = 83.3 Hz, $^{3}J_{F-H}$= 46.1 Hz, 1F, *Z*-isomers), −135.4 (dd, $^{2}J_{F-H}$ = 84.5 Hz, $^{3}J_{F-H}$ = 20.1 Hz, 1F, *E*-isomers) ppm.

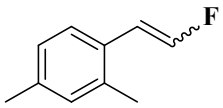
(*E*/*Z*)-1-(2-Fluorovinyl)-4-methylbenzene (**2f, CAS: 26928-21-2**) [3]:



2f

Colorless oily liquid. Yield of *E*/*Z*-**2f**: 55%, *E*/*Z* ratio: 93/7. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.19－7.14 (m, 4H, both *E*- and *Z*-isomers), δ 7.18 (dd, $^{2}J_{H\text{-}F}$ = 83.6 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomer), 6.66 (dd, $^{2}J_{H\text{-}F}$ = 82.9 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomer), 6.41 (dd, $^{3}J_{H\text{-}F}$ = 19.5 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomer), 5.62 (dd, $^{3}J_{H\text{-}F}$ = 45.1 Hz,$^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomer), 2.39 (s, 3H, *Z*-isomer), 2.37 (s, 3H, *E*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 149.7 (d, $^{1}J_{C\text{-}F}$ = 257.7 Hz), 137.3 (d, $^{5}J_{C\text{-}F}$ = 2.1 Hz), 129.8 (d,$^{3}J_{C\text{-}F}$ = 11.7 Hz), 129.5, 126.1 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 113.7 (d, $^{2}J_{C\text{-}F}$ = 15.8 Hz), 21.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −123.3 (dd, $^{2}J_{F\text{-}H}$ = 82.9, $^{3}J_{F\text{-}H}$ = 45.2 Hz, 1F, *Z*-isomer), −131.3 (dd,$^{2}J_{F\text{-}H}$ = 83.6 Hz, $^{3}J_{F\text{-}H}$ = 19.5 Hz, 1F, *E*-isomer) ppm.

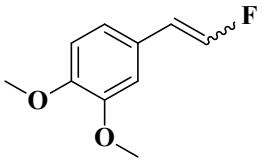
(*E*/*Z*)-1-(2-Fluorovinyl)-2,4-dimethylbenzene (**2g**):



2g

Colorless oily liquid. Yield of *E*/*Z*-**2g**: 70%, *E*/*Z* ratio: 95/5. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.19−7.17 (m, 1H, both *E*- and *Z*-isomers), 7.05−7.00 (m, 2H, both *E*- and *Z*-isomers), 7.02 (dd, $^{2}J_{H\text{-}F}$ = 84.5 Hz, $^{3}J_{H\text{-}H}$ = 11.2 Hz, 1H, *E*-isomers), 6.57 (dd, $^{3}J_{H\text{-}F}$ = 19.6 Hz, $^{3}J_{H\text{-}H}$ = 11.2 Hz, 1H, *E*- isomers), 5.78 (dd, $^{3}J_{H\text{-}F}$ = 44.5 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomers), 2.36(s, 3H, both *E*- and *Z*-isomers), 2.32 (s, 3H, both *E*- and *Z*-isomers) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 149.9 (d, $^{1}J_{C\text{-}F}$ = 258.6 Hz), 137.5 (d, $^{5}J_{C\text{-}F}$ = 1.4 Hz), 135.7 (d, $^{4}J_{C\text{-}F}$ = 4.3 Hz), 131.2, 128.5 (d,$^{3}J_{C\text{-}F}$ = 11.2 Hz), 126.9, 126.0 (d, $^{5'}J_{C\text{-}F}$ = 1.0 Hz), 111.9 (d, $^{2}J_{C\text{-}F}$ = 15.2 Hz), 21.0, 19.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −124.8 (dd, $^{2}J_{F\text{-}H}$ = 83.8 Hz, $^{3}J_{F\text{-}H}$ = 44.6 Hz, 1F, *Z*-isomers), −127.8 (dd, $^{2}J_{F\text{-}H}$ = 84.5 Hz, $^{3}J_{F\text{-}H}$= 19.6 Hz, 1F, *E*-isomers) ppm. HRMS (EI): calc. for $C_{10}H_{11}F$ $[M]^{+}$ 150.0845, found 150.0846.

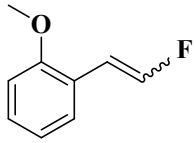
(*E*/*Z*)-4-(2-Fluorovinyl)-1,2-dimethoxybenzene (**2h**):



2h

Light yellow oily liquid. Yield of *E*/*Z*-**2h**: 80%, *E*/*Z* ratio: 93/7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, $^{2}J_{H\text{-}F}$ = 83.6 Hz, $^{3}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomers), 6.86−6.77 (m, 3H, both *E*- and *Z*-isomers), 6.62 (dd, $^{2}J_{H\text{-}F}$ = 83.1 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomers) , 6.36 (dd, $^{3}J_{H\text{-}F}$ = 19.5 Hz, $^{3}J_{H\text{-}H}$ = 11.3 Hz, 1H, *E*-isomers), 5.56 (dd, $^{3}J_{H\text{-}F}$ = 45.0 Hz, $^{3}J_{H\text{-}H}$ = 5.3Hz, 1H, *Z*-isomers), 3.90 (s, 6H, *E*-isomers), 3.89 (s, 6H, *E*-isomers) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 149.2, 149.1 (d, $^{1}J_{C\text{-}F}$ = 257.0 Hz), 148.7 (d, $^{5}J_{C\text{-}F}$ = 1.9 Hz), 125.4 (d, $^{3}J_{C\text{-}F}$ = 11.8 Hz), 119.0 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 113.6 (d, $^{2}J_{C\text{-}F}$ = 16.2 Hz), 111.5, 109.0 (d, $^{4'}J_{C\text{-}F}$ = 2.4 Hz), 55.9, 55.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −125.1 (dd, $^{2}J_{F\text{-}H}$ = 83.1 Hz, $^{3}J_{F\text{-}H}$ = 45.0 Hz, 1F, *Z*-isomers), −132.3 (dd, $^{2}J_{F\text{-}H}$ = 83.6 Hz, $^{3}J_{F\text{-}H}$ = 19.5 Hz, 1F, *E*-isomers) ppm. HRMS (EI): calc. for $C_{10}H_{11}FO_2$ $[M]^{+}$ 182.0743, found 182.0744.

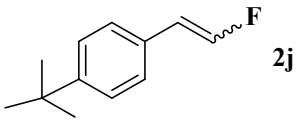
(*E*/*Z*)-1-(2-Fluorovinyl)-2-methoxybenzene (**2i, CAS: 95799-46-5**) [3]:



2i

Colorless oily liquid. Yield of *E*/*Z*-**2i**: 81%, *E*/*Z* ratio: 93/7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, $^{2}J_{H\text{-}F}$ = 86.3 Hz, $^{3}J_{H\text{-}H}$ = 11.2 Hz, 1H, *E*-isomers), 7.28－7.22 (m, 2H, both *E*- and *Z*-isomers), 6.98－6.92 (m, 2H, both *E*- and *Z*-isomers), 6.72 (dd, $^{2}J_{H\text{-}F}$ = 83.8 Hz, $^{3}J_{H\text{-}H}$ = 5.5 Hz, 1H, *Z*-isomers), 6.55 (dd,$^{3}J_{H\text{-}F}$ = 22.3 Hz, $^{3}J_{H\text{-}H}$ = 11.2 Hz, 1H, *E*-isomers), 6.11 (dd, $^{3}J_{H\text{-}F}$ = 46.4 Hz, $^{3}J_{H\text{-}H}$ = 5.5 Hz, 1H, *Z*-isomers), 3.91 (s, 3H, *E*-isomers), 3.88 (s, 3H, *Z*-isomers) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 156.8 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 151.6 (d, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 128.5 (d, $^{4'}J_{C\text{-}F}$ = 2.7 Hz), 128.3 (d, $^{5}J_{C\text{-}F}$ = 2.1 Hz), 121.6 (d, $^{3}J_{C\text{-}F}$ = 11.2 Hz), 120.7, 110.8, 110.5 (d, $^{2}J_{C\text{-}F}$ = 18.3 Hz), 55.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −123.9 (dd, $^{2}J_{F\text{-}H}$ = 83.8 Hz, $^{3}J_{F\text{-}H}$ = 46.4 Hz, 1F, *Z*-isomers), −125.0 (dd,$^{2}J_{F\text{-}H}$ = 86.3 Hz, $^{3}J_{F\text{-}H}$ = 22.3 Hz, 1F, *E*-isomers) ppm.

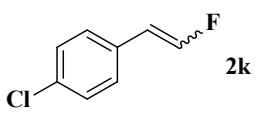
(*E*/*Z*)-1-(*tert*-Butyl)-4-(2-fluorovinyl)benzene (**2j**):



2j

Colorless oily liquid. Yield of *E*/*Z*-**2j**: 84%, *E*/*Z* ratio: 90/10. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.32 (m, 2H, both *E*- and *Z*-isomers), 7.14 (dd, $^{2}J_{H\text{-}F}$= 83.8 Hz, $^{3}J_{H\text{-}H}$ = 11.2 Hz, 1H, *E*-isomers), 7.19−7.17 (m, 2H, both *E*- and *Z*-isomers), 6.62 (dd, $^{2}J_{H\text{-}F}$ = 82.9 Hz, $^{3}J_{H\text{-}H}$ = 5.3 Hz, 1H, *Z*-isomers), 6.37 (dd, $^{3}J_{H\text{-}F}$ = 19.5 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomers), 5.58 (dd, $^{3}J_{H\text{-}F}$ = 45.1 Hz, $^{3}J_{H\text{-}H}$ = 5.3 Hz, 1H, *Z*-isomers), 1.32−1.31 (m, 9H, both *E*- and *Z*-isomers) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 150.6 (d, $^{5}J_{C\text{-}F}$ = 2.1 Hz), 149.8 (d, $^{1}J_{C\text{-}F}$ = 257.9 Hz), 129.8 (d,$^{3}J_{C\text{-}F}$ = 11.8 Hz), 125.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.7, 113.6 (d, $^{2}J_{C\text{-}F}$ = 15.7 Hz), 34.6, 31.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −123.2 (dd, $^{2}J_{F\text{-}H}$ = 82.9 Hz, $^{3}J_{F\text{-}H}$ = 45.1 Hz, 1F, *Z*-isomers), −140.0 (dd, $^{2}J_{F\text{-}H}$ = 83.6 Hz, $^{3}J_{F\text{-}H}$ = 19.5 Hz, 1F, *E*-isomers) ppm. HRMS (EI): calc. for $C_{12}H_{15}F$ $[M]^{+}$ 178.1158, found 178.1159.

(*E*/*Z*)-1-Chloro-4-(2-fluorovinyl)benzene (**2k, CAS: 26928-23-4**) [5]:

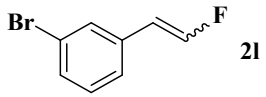


2k

Colorless oily liquid. Yield of *E*/*Z*-**2k**: 70%, *E*/*Z* ratio: 95/5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.25 (m, 2H, both *E*- and *Z*-isomers), 7.17−7.15 (m, 2H, both *E*- and *Z*-isomers), 7.14 (dd, $^{2}J_{H\text{-}F}$ = 82.4 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomers), 6.65 (dd, $^{2}J_{H\text{-}F}$ = 82.5 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomers), 6.34 (dd, $^{3}J_{H\text{-}F}$ = 19.0 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomers), 5.57 (dd, $^{3}J_{H\text{-}F}$ = 44.2 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomers) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 150.4 (d, $^{1}J_{C\text{-}F}$ = 260.4 Hz), 133.2 (d, $^{5}J_{C\text{-}F}$ = 2.2 Hz), 129.0, 131.2 (d, $^{3}J_{C\text{-}F}$ = 12.1 Hz), 127.4 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 113.0 (d, $^{2}J_{C\text{-}F}$ = 16.6 Hz) ppm;^{19}F NMR (376 MHz, $CDCl_3$): δ −121.3 (dd, $^{2}J_{F\text{-}H}$ = 82.4

Hz, $^{3}J_{F\text{-}H}$= 44.2 Hz, 1F, *Z*-isomers), −128.6 (dd, $^{2}J_{F\text{-}H}$ = 82.6 Hz, $^{3}J_{F\text{-}H}$ = 19.0 Hz, 1F, *E*-isomers) ppm.

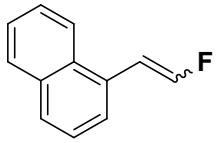
(*E*/*Z*)-1-Bromo-3-(2-fluorovinyl)benzene (**2l**):



2l

Colorless oily liquid. Yield of *E*/*Z*-**2l**: 65%, *E*/*Z* ratio: 92/8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.40 (m, 2H, both *E*- and *Z*-isomers), 7.21−7.19 (m, 2H, both *E*- and *Z*-isomers), 7.18 (dd, $^{1}J_{H\text{-}F}$ = 82.4 Hz, $^{2}J_{H\text{-}H}$ =11.4 Hz, 1H, *E*-isomer), 6.70 (dd, $^{2}J_{H\text{-}F}$ = 82.2 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomer), 6.36 (dd, $^{2}J_{H\text{-}F}$ = 18.7 Hz, $^{2}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomer), 5.59 (dd, $^{3}J_{H\text{-}F}$ = 43.8 Hz, $^{3}J_{H\text{-}H}$ = 5.4 Hz, 1H, *Z*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 150.9 (d, $^{1}J_{C\text{-}F}$ = 261.7 Hz), 134.9 (d,$^{3}J_{C\text{-}F}$ = 12.2 Hz), 130.5 (d,$^{5}J_{C\text{-}F}$ = 2.0 Hz), 130.4, 129.1 (d,$^{4}J_{C\text{-}F}$ = 3.0 Hz), 124.8, 122.9, 112.9 (d,$^{2}J_{C\text{-}F}$ = 16.8 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.90 (dd, $^{2}J_{F\text{-}H}$ = 82.2 Hz, $^{3}J_{F\text{-}H}$ = 43.8 Hz, 1F, *Z*-isomer), −127.24 (dd, $^{2}J_{F\text{-}H}$ = 82.7 Hz, $^{3}J_{F\text{-}H}$ = 18.8 Hz, 1F, *E*-isomer) ppm. HRMS (EI): calc. for C_8H_6BrF $[M]^+$ 201.9616, found 201.9615.

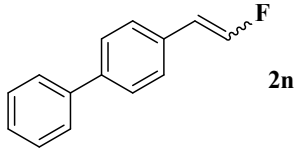
(*E*/*Z*)-1-(2-fluorovinyl)naphthalene (**2m, CAS: 1236300-50-7**) [3]:



2m

Colorless oily liquid. Yield of *E*/*Z*-**2m**: 83%, *E*/*Z* ratio: 90/10. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−7.97 (m, 1H, both *E*- and *Z*-isomers), 7.85−7.77 (m, 2H, both *E*- and *Z*-isomers), 7.54−7.48 (m, 2H, both *E*- and *Z*-isomers), 7.43−7.38 (m, 2H, both *E*- and *Z*-isomers), 7.07 (dd, $^{2}J_{H\text{-}F}$ = 86.0 Hz, $^{3}J_{H\text{-}H}$ = 11.1 Hz, 1H, *E*-isomer), 7.05 (dd, $^{3}J_{H\text{-}F}$ = 15.9 Hz, $^{3}J_{H\text{-}H}$ = 11.1Hz, 1H, *E*-isomer), 6.87 (dd, $^{1}J_{H\text{-}F}$ = 83.2 Hz, $^{2}J_{H\text{-}H}$ = 5.5 Hz, 1H, *Z*-isomer), 6.29 (dd, $^{3}J_{H\text{-}F}$ = 42.6 Hz,$^{3}J_{H\text{-}H}$ = 5.5 Hz, 1H, *Z*-isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 151.0 (d, $^{1}J_{C\text{-}F}$ = 262.1 Hz), 134.0, 131.9 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 129.9 (d, $^{3}J_{C\text{-}F}$ = 11.6 Hz), 128.8, 128.6, 126.6, 126.4, 125.8, 124.7 (d, $^{5}J_{C\text{-}F}$ = 1.5 Hz), 124.3, 111.7 (d, $^{2}J_{C\text{-}F}$ = 15.3 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −123.2 (dd, $^{2}J_{F\text{-}H}$ = 83.4 Hz, $^{3}J_{F\text{-}H}$ = 42.5 Hz, 1F, *Z*-isomer), −123.6 (dd, $^{2}J_{F\text{-}H}$ = 85.1 Hz, $^{3}J_{F\text{-}H}$ = 16.0 Hz, 1F, *E*-isomer) ppm.

(*E*/*Z*)-4-(2-Fluorovinyl)-1,1'-biphenyl (**2n, CAS: 123133-22-2**) [6]:

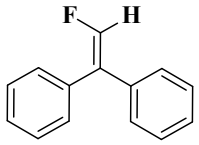


2n

White solid. Yield of *E*/*Z*-**2n**: 91%, *E*/*Z* ratio: 92/8, mp 113.8–117.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.52 (m, 4H, both *E*- and *Z*-isomers), 7.44−7.41 (m, 2H, both *E*- and *Z*-isomers), 7.35−7.29 (m, 3H, both *E*- and *Z*-isomers), 7.20 (dd, $^{2}J_{H\text{-}F}$ = 82.4 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomers), 6.66 (dd, $^{2}J_{H\text{-}F}$ = 82.6 Hz, $^{3}J_{H\text{-}H}$ = 5.3 Hz, 1H, *Z*-isomers), 6.41 (dd, $^{3}J_{H\text{-}F}$ = 19.3 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, 1H, *E*-isomers), 5.64 (dd, $^{3}J_{H\text{-}F}$ = 44.8 Hz, $^{3}J_{H\text{-}H}$ = 5.3

Hz, 1H, *Z*-isomers) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) for the major *E*-isomer: δ 150.3 (d, $^1J_{C\text{-}F}$ = 259.4 Hz), 140.6, 140.4 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 131.7 (d,$^3J_{C\text{-}F}$ = 11.8 Hz), 128.9, 127.5, 127.4, 127.0, 126.6 (d, $^5J_{C\text{-}F}$ = 3.0 Hz), 113.6 (d, $^2J_{C\text{-}F}$ = 16.1 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −121.6 (dd, $^2J_{F\text{-}H}$ = 82.7 Hz, $^3J_{F\text{-}H}$ = 44.9 Hz, 1F, *Z*-isomers), −129.4 (dd, $^2J_{F\text{-}H}$ = 83.2 Hz, $^3J_{F\text{-}H}$ = 19.3 Hz, 1F, *E*-isomers) ppm.

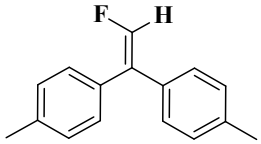
(2-Fluoroethene-1,1-diyl)dibenzene (**2o, CAS: 390-75-0**) [6]:



2o

Colorless oily liquid. Yield of **2o**: 80%.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42－7.29 (m, 10H), 7.02 (d,$^2J_{H\text{-}F}$ =83.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9 (d, $^1J_{C\text{-}F}$ = 268.6 Hz), 137.0 (d,$^3J_{C\text{-}F}$ =8.1 Hz), 135.2, 129.8 (d, $^4J_{C\text{-}F}$ = 4.0 Hz), 128.7 (d, $^6J_{C\text{-}F}$ = 3.2 Hz), 128.4 (d, $^2J_{C\text{-}F}$ = 29.4 Hz), 127.8 (d, $^5J_{C\text{-}F}$ = 3.9 Hz), 126.3 (d, $^{4'}J_{C\text{-}F}$ = 5.6 Hz) ppm; ^{19}F NMR (376 M Hz, $CDCl_3$): δ -128.0 (d,$^2J_{F\text{-}H}$ = 83.4 Hz) ppm.

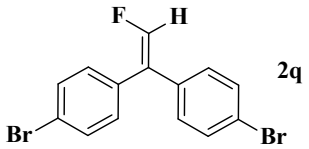
4,4'-(2-Fluoroethene-1,1-diyl)bis(methylbenzene) (**2p, CAS: 26551-47-3**) [5]:



2p

White solid. Yield of **2p**: 78%, mp 89.4–91.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.12 (m, 8H), 6.90 (d, $^2J_{H\text{-}F}$ = 83.9 Hz, 1H), 2.35 (s, 6H) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3 (d, $^1J_{C\text{-}F}$ = 267.3 Hz), 137.6 (d, $^4J_{C\text{-}F}$ = 5.5 Hz), 134.3 (d,$^3J_{C\text{-}F}$ = 8.1 Hz), 129.7 (d, $^5J_{C\text{-}F}$ = 4.3 Hz), 129.1 (d, $^2J_{C\text{-}F}$ = 28.5 Hz), 128.6 (d, $^6J_{C\text{-}F}$ = 3.1 Hz), 125.9 (d, $^{4'}J_{C\text{-}F}$ = 5.5 Hz), 21.3 (d, $J_{C\text{-}F}$ = 11.3 Hz) ppm; ^{19}F NMR (376 M Hz, $CDCl_3$): δ –129.3 (d, $^2J_{F\text{-}H}$ = 83.9 Hz) ppm.

4,4'-(2-Fluoroethene-1,1-diyl)bis(bromobenzene) (**2q, CAS: 1427-99-2**) [7]:



2q

White solid. Yield of **2q**: 83%, mp 77.7–79.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.06 (m, 8H), 6.92 (d, $^2J_{H\text{-}F}$ = 82.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1 (d, $^1J_{C\text{-}F}$ = 271.1 Hz), 135.4 (d,$^3J_{C\text{-}F}$ = 8.1 Hz), 133.5, 131.8 (d, $J_{C\text{-}F}$ = 29.2 Hz), 131.4 (d, $^4J_{C\text{-}F}$ = 4.4 Hz), 130.3 (d, $^5J_{C\text{-}F}$ = 3.1 Hz), 124.6 (d, $^{4'}J_{C\text{-}F}$ = 6.0 Hz), 122.2 (d, $^2J_{C\text{-}F}$ = 11.9 Hz) ppm; ^{19}F NMR (376 M Hz, $CDCl_3$): δ –125.6 (d, $^2J_{F\text{-}H}$ = 82.4 Hz) ppm.

References

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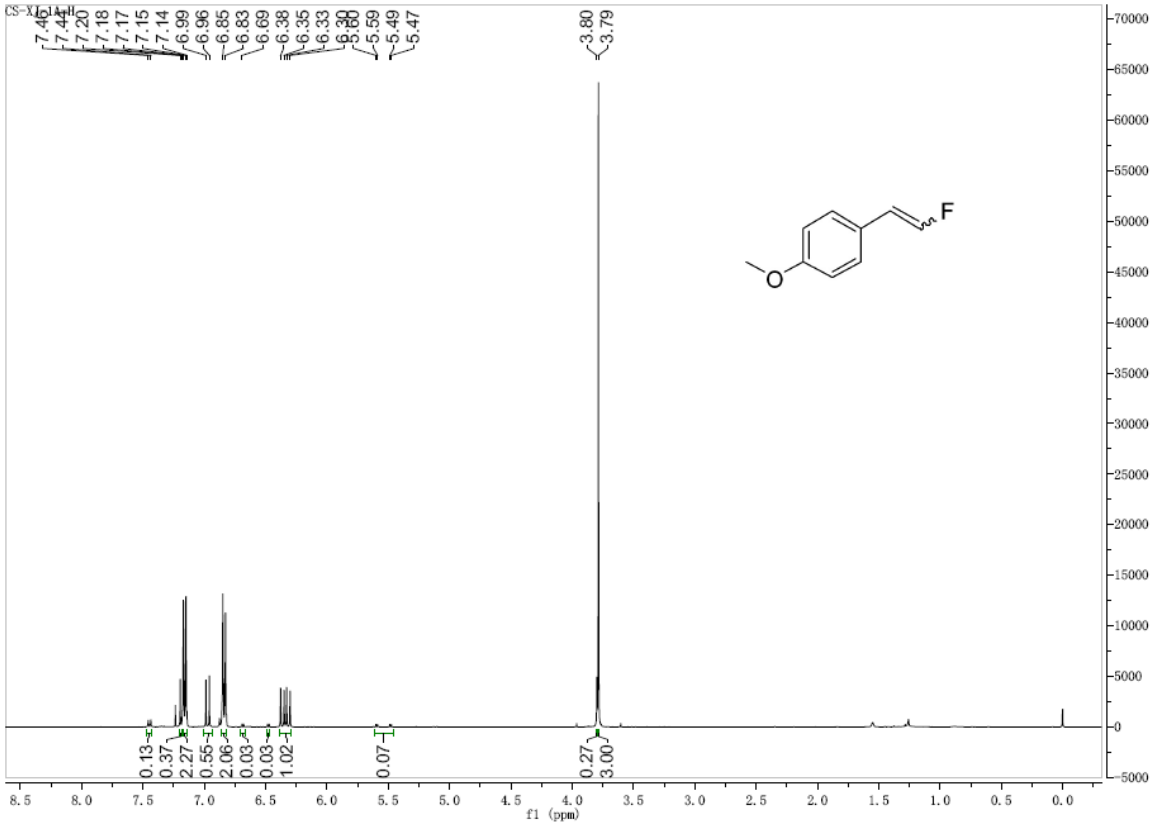
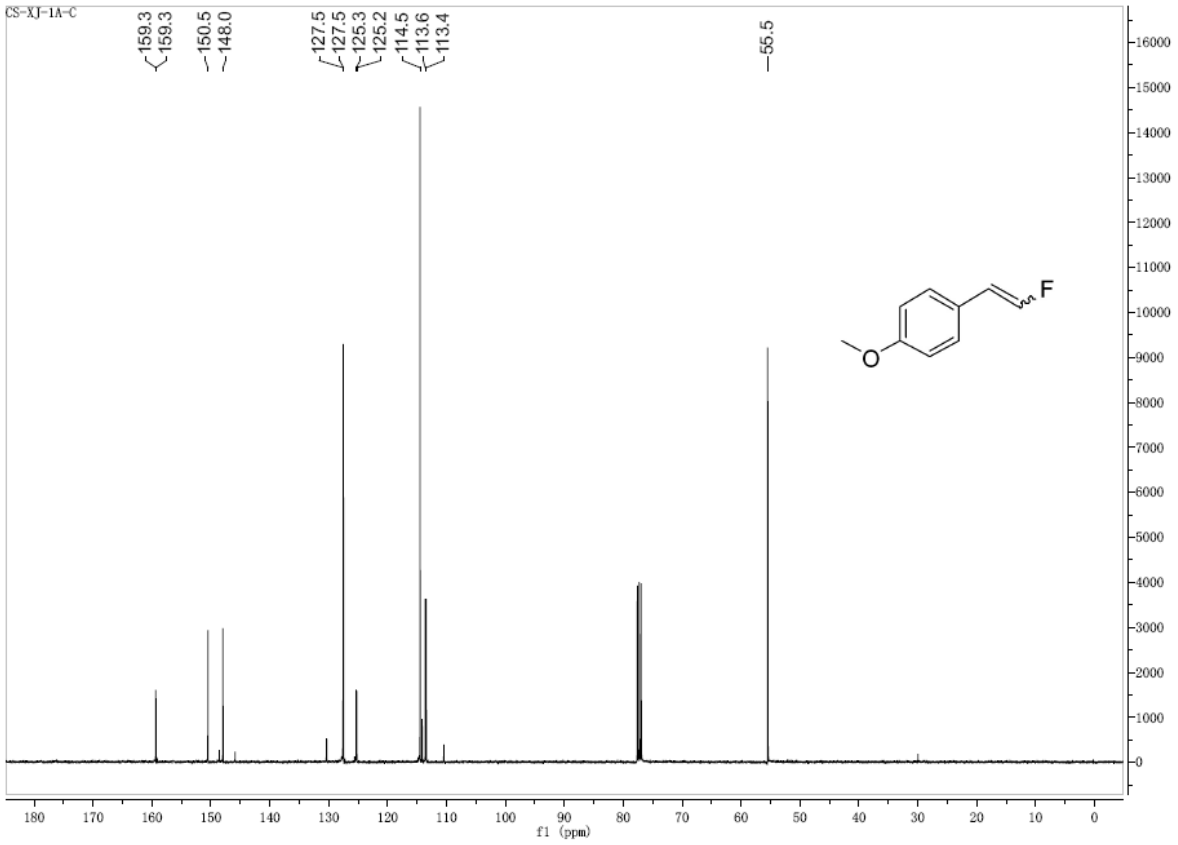
^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of compounds 2a-q

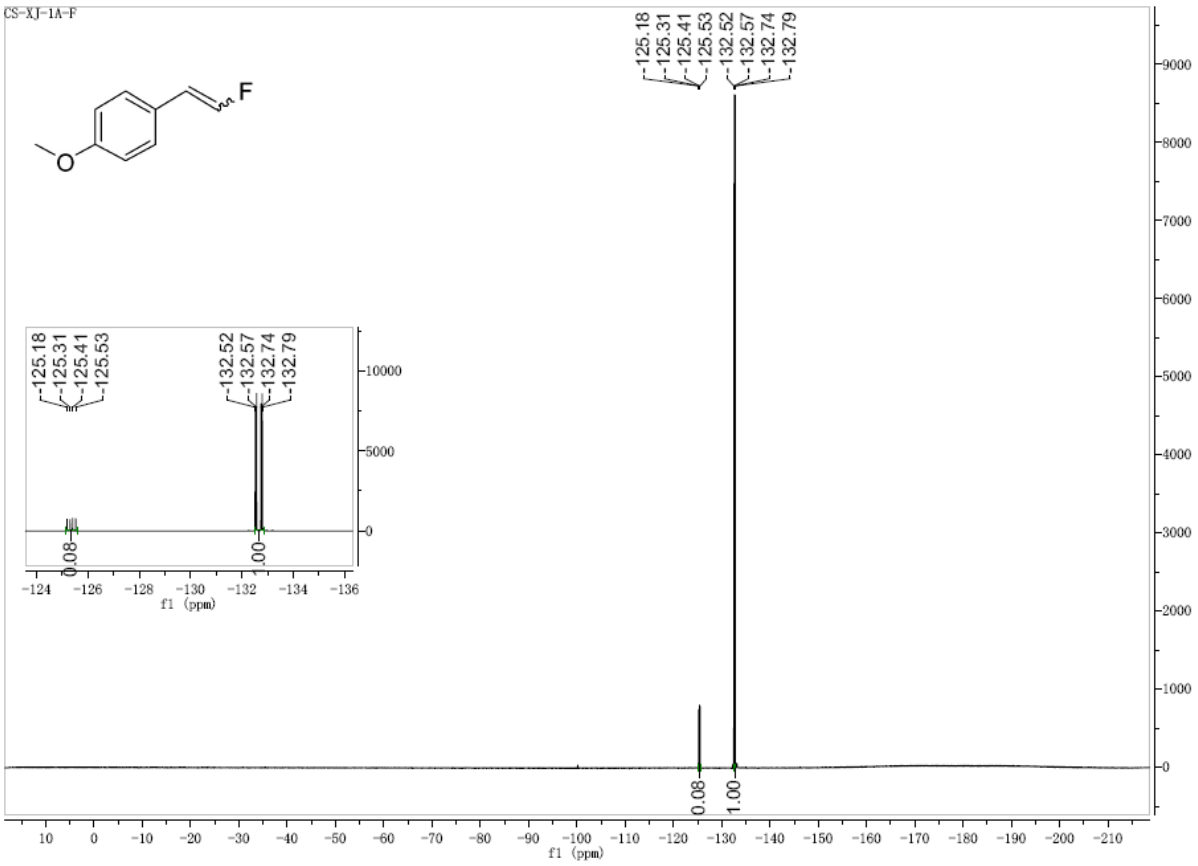
^{1}H NMR spectra of ***E***/***Z***-**2a**



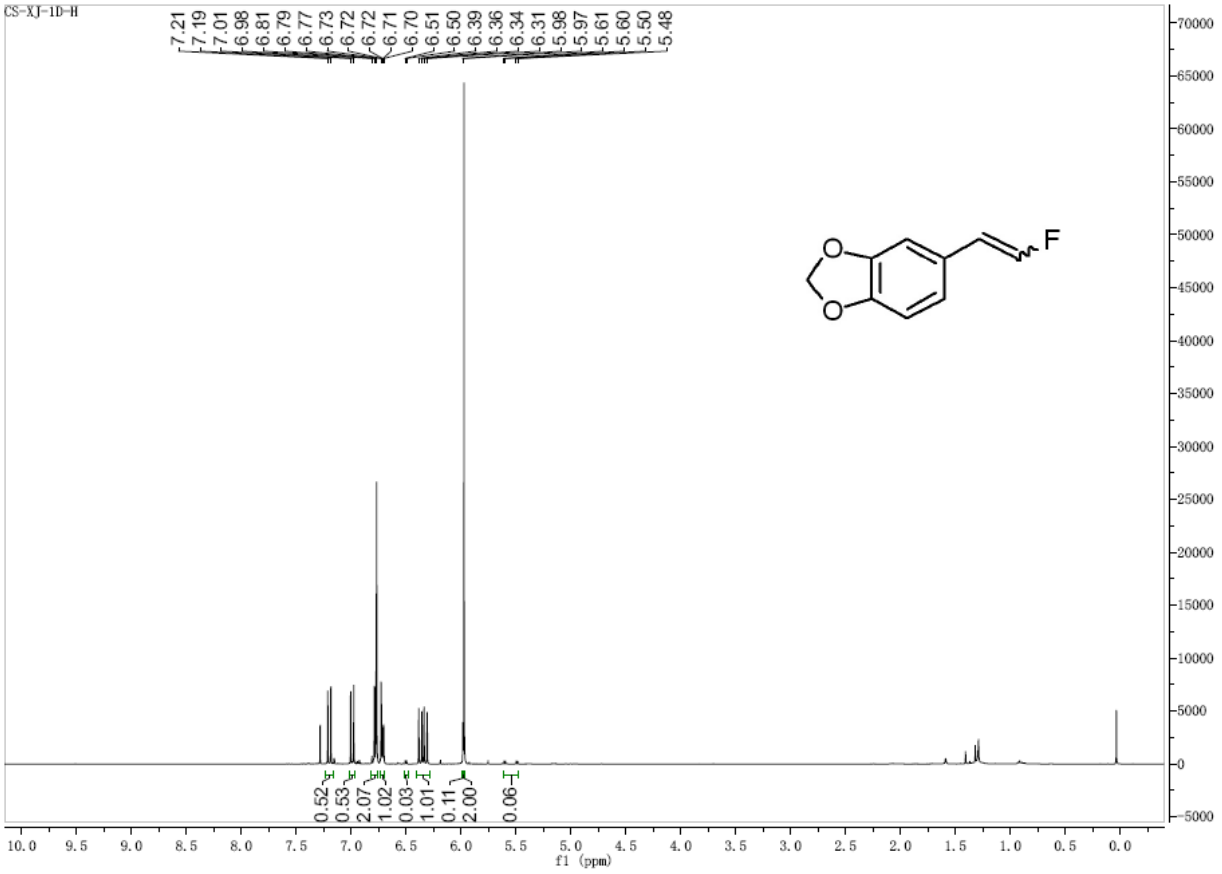
^{13}C NMR spectra of ***E***/***Z***-**2a**



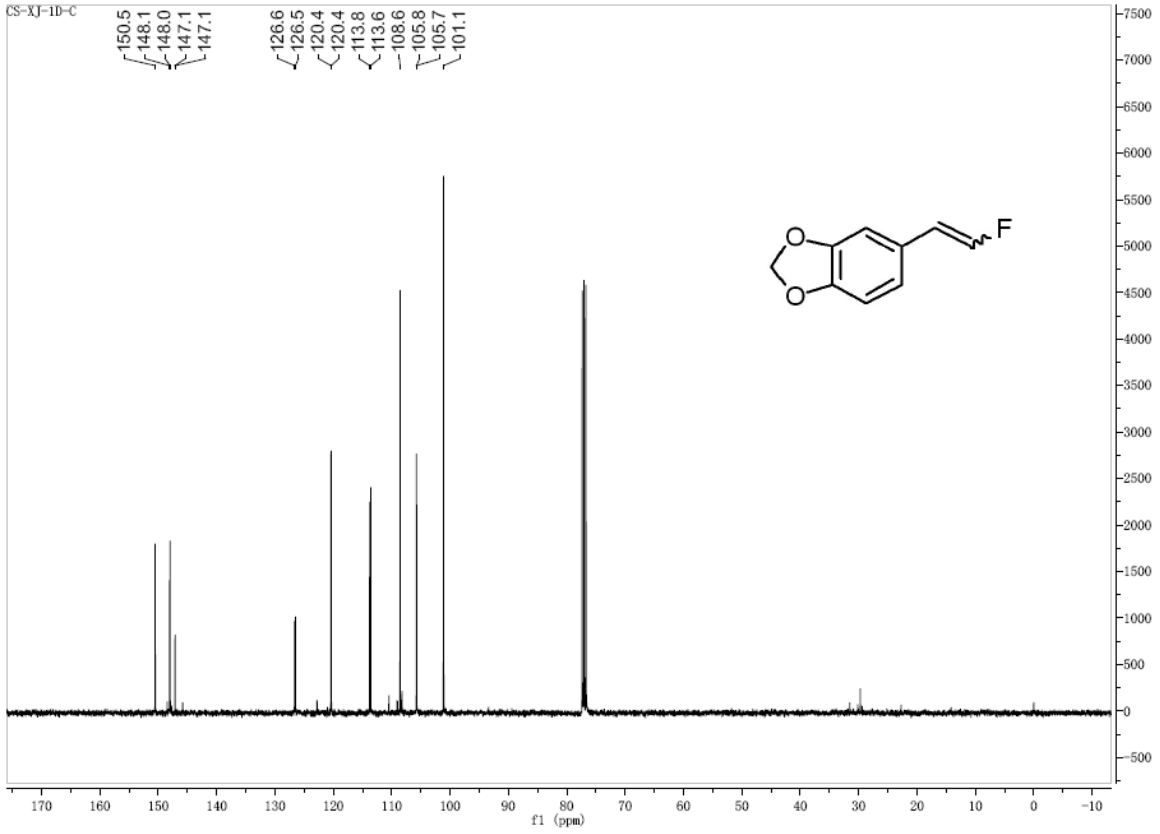
^{19}F NMR spectra of ***E*/*Z*-2a**



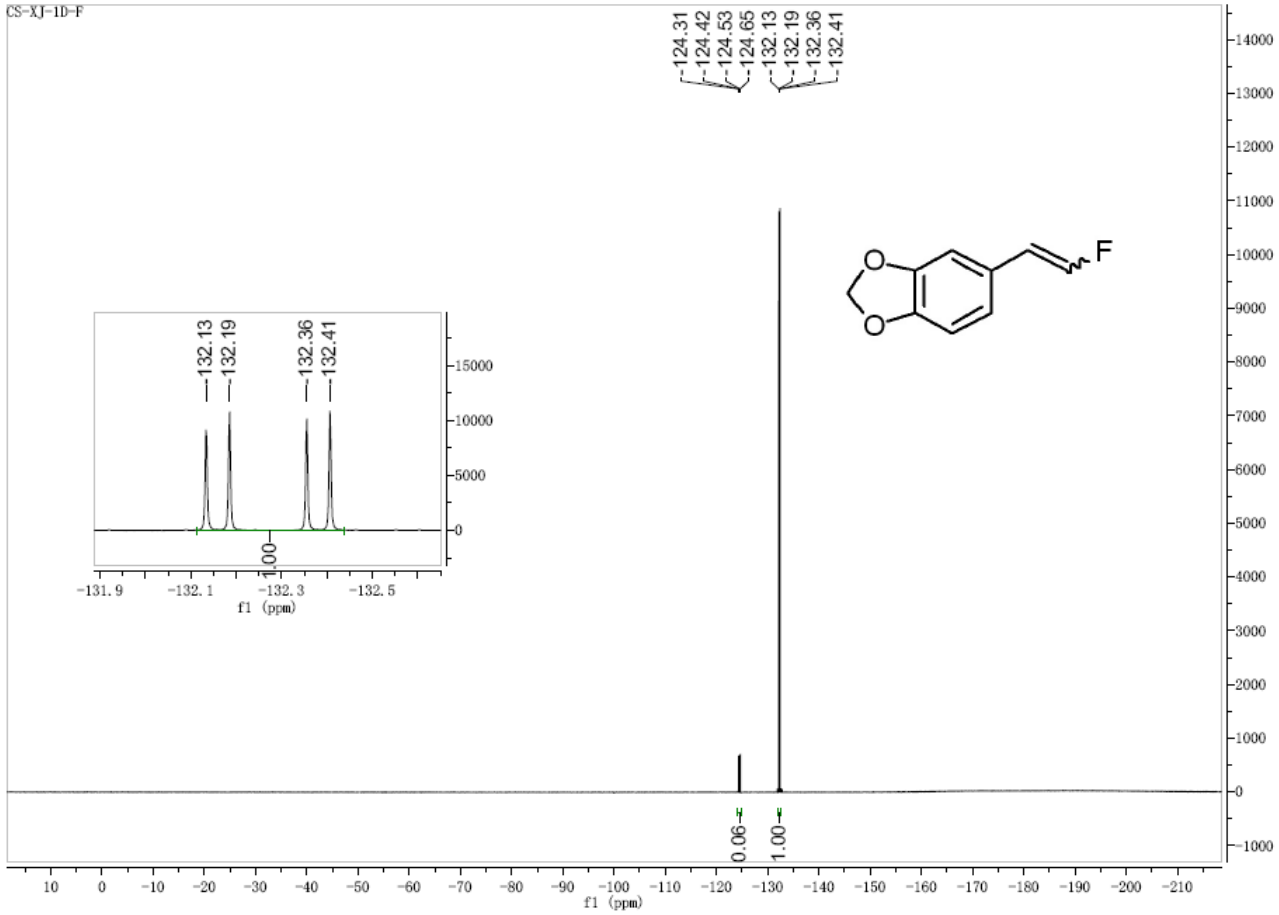
^{1}H NMR spectra of ***E***/***Z*-2b**



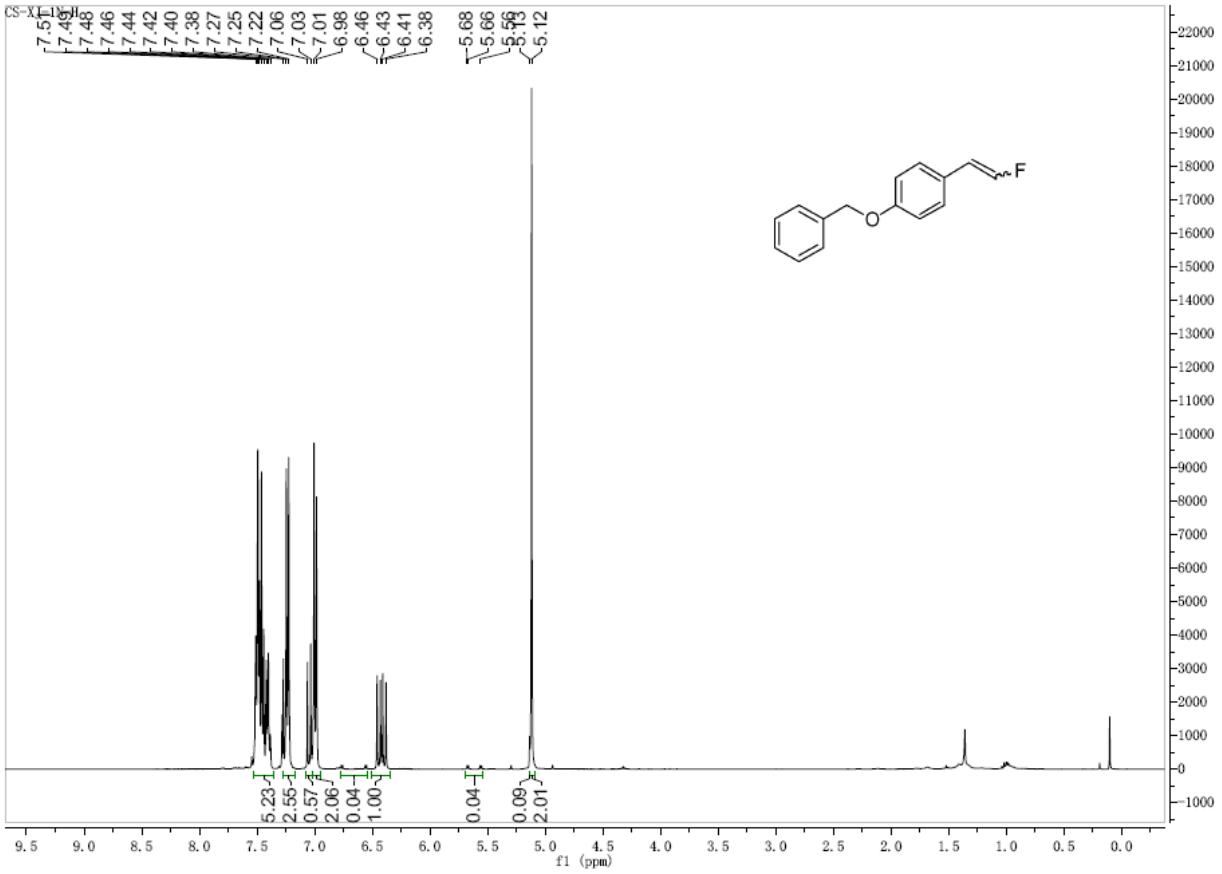
^{13}C NMR spectra of ***E***/***Z*-2b**



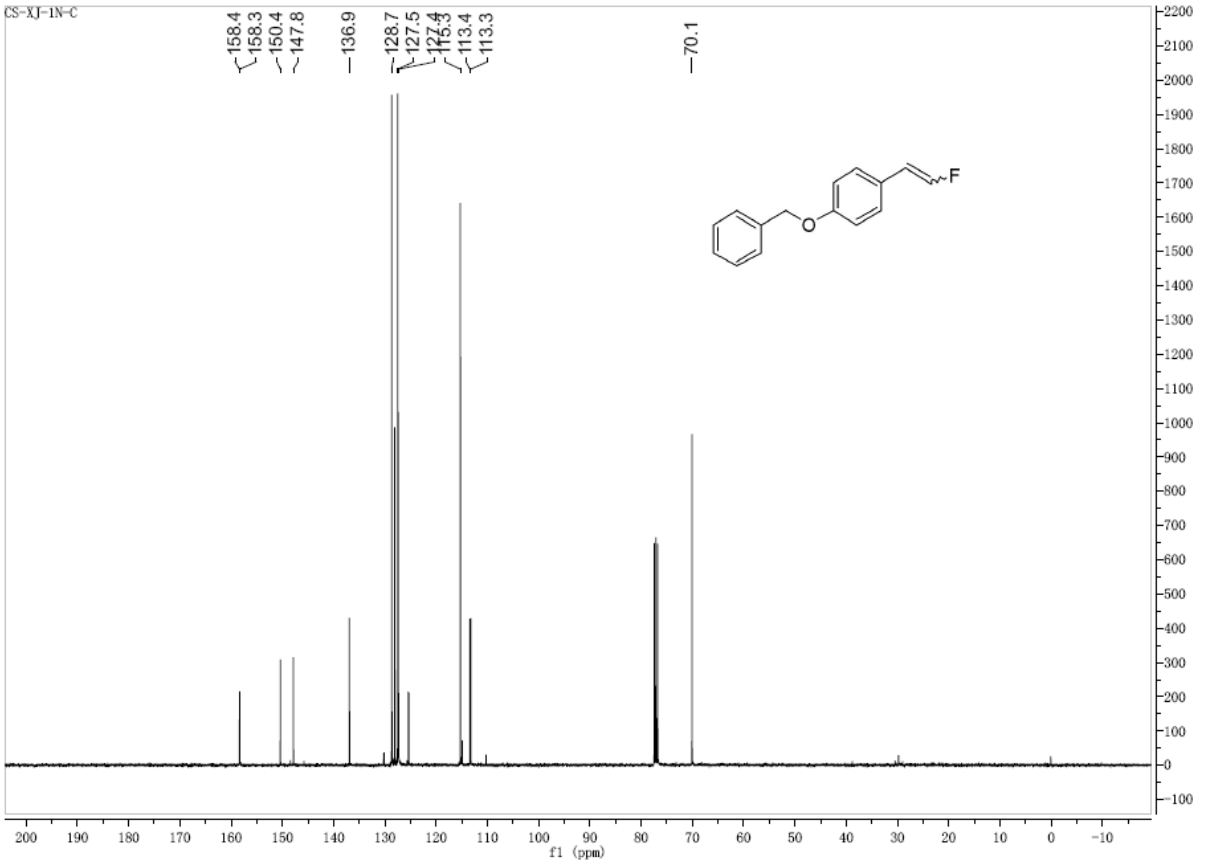
^{19}F NMR spectra of ***E***/***Z***-**2b**



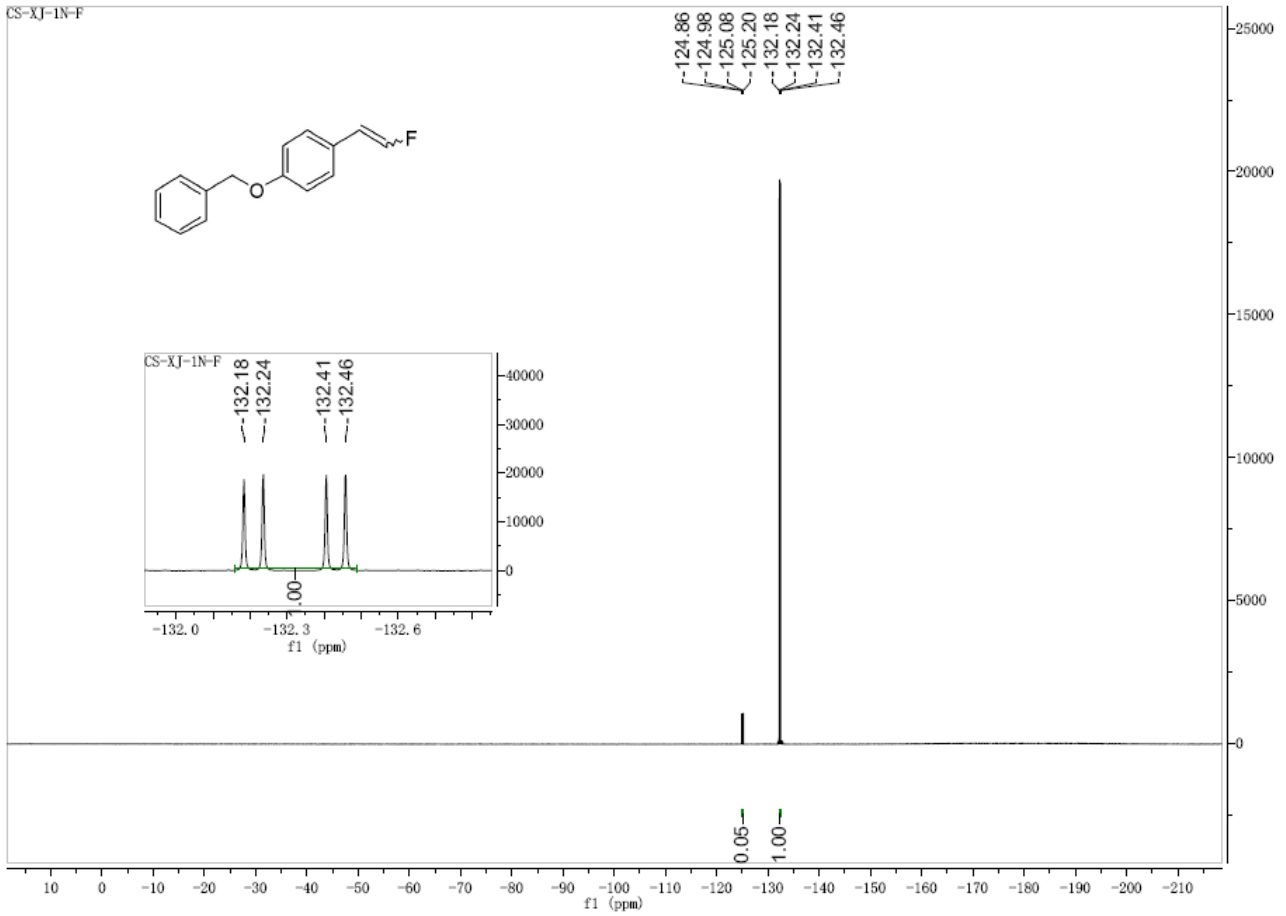
^{1}H NMR spectra of ***E***/***Z*-2c**



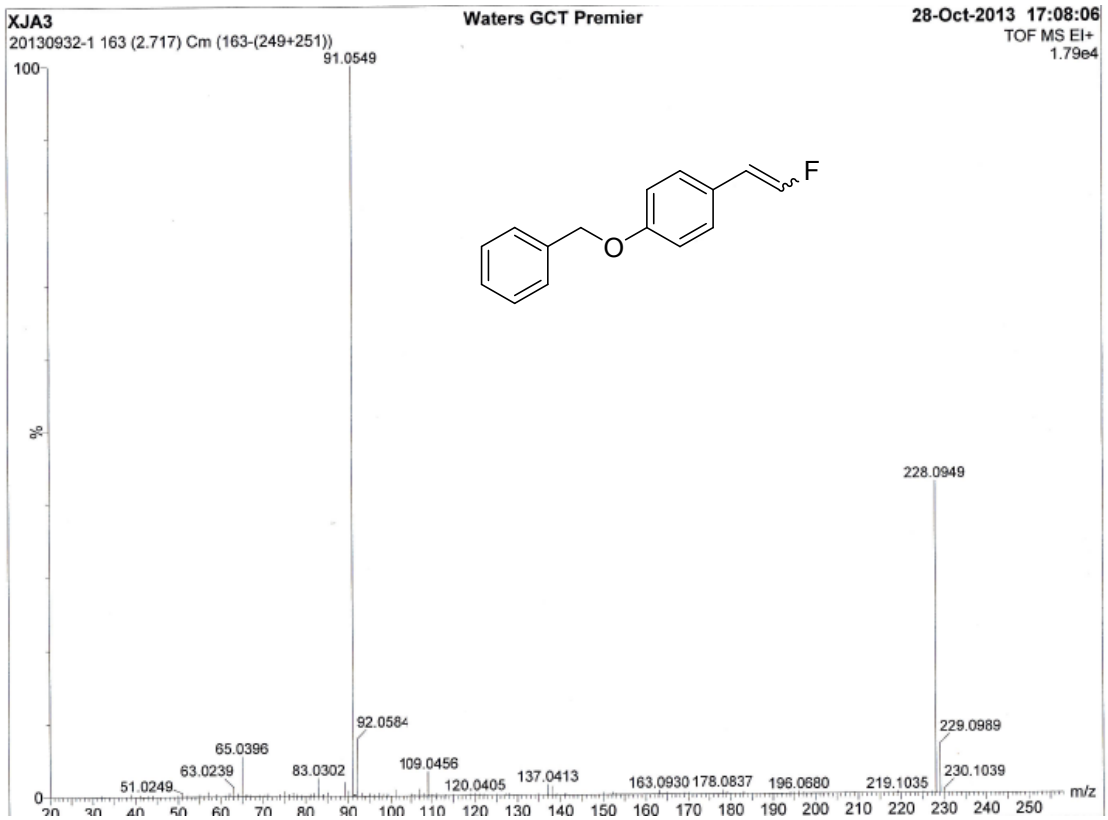
^{13}C NMR spectra of ***E***/***Z*-2c**



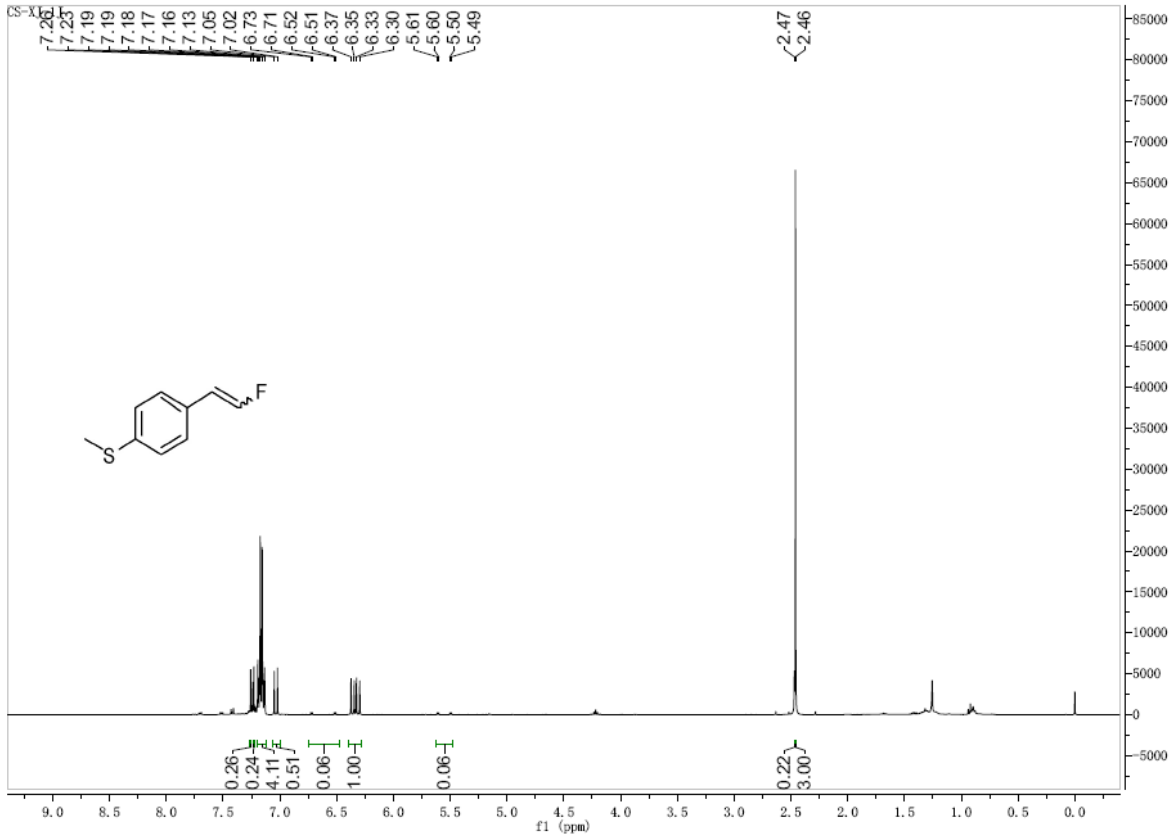
^{19}F NMR spectra of ***E*/*Z*-2c**



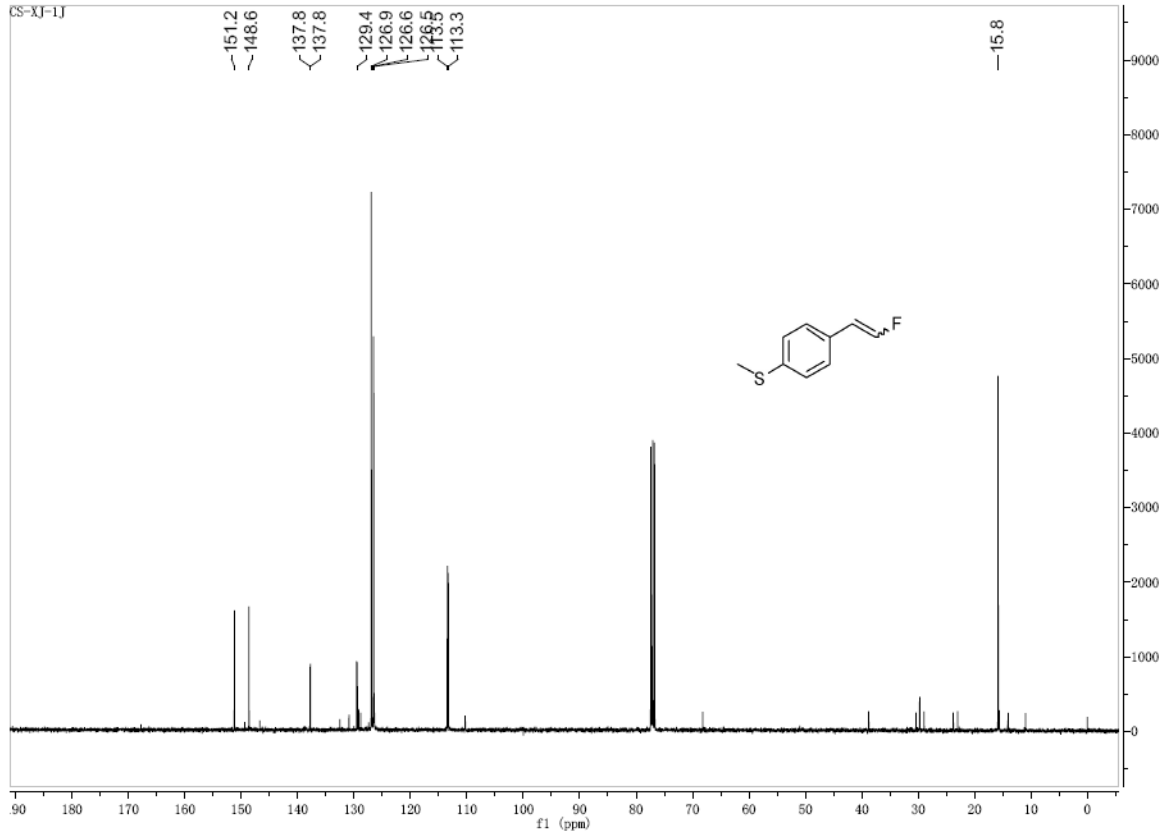
HRMS (EI) spectra of ***E*/*Z*-2c**



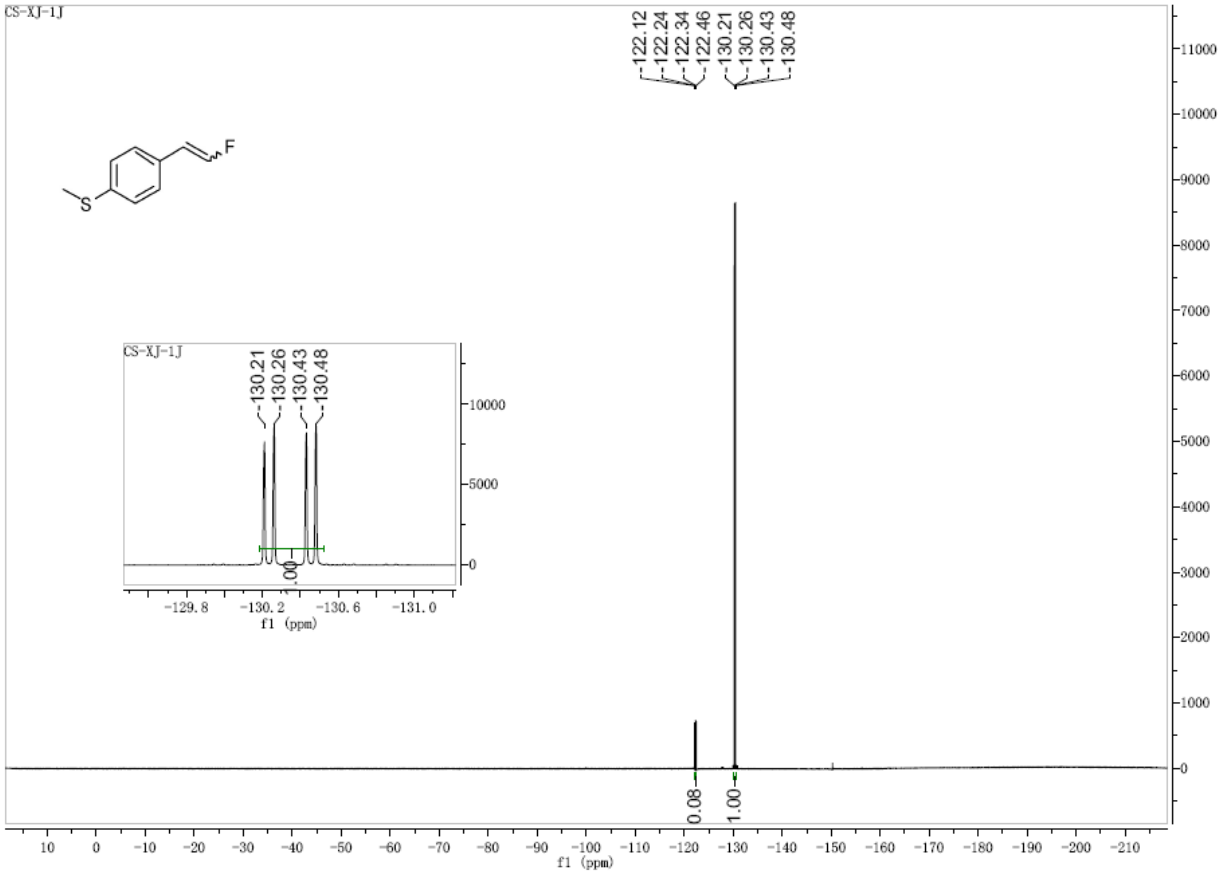
^{1}H NMR spectra of ***E*/*Z*-2d**



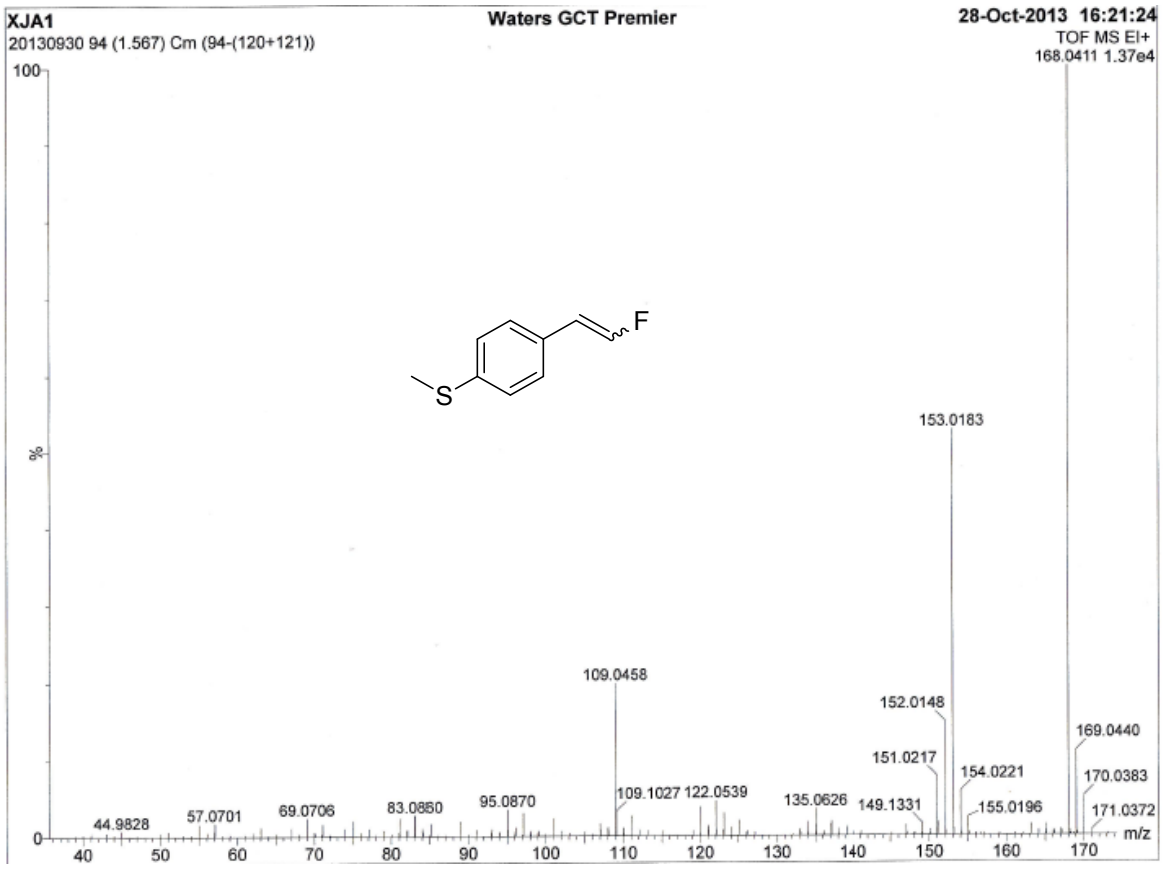
^{13}C NMR spectra of ***E*/*Z*-2d**



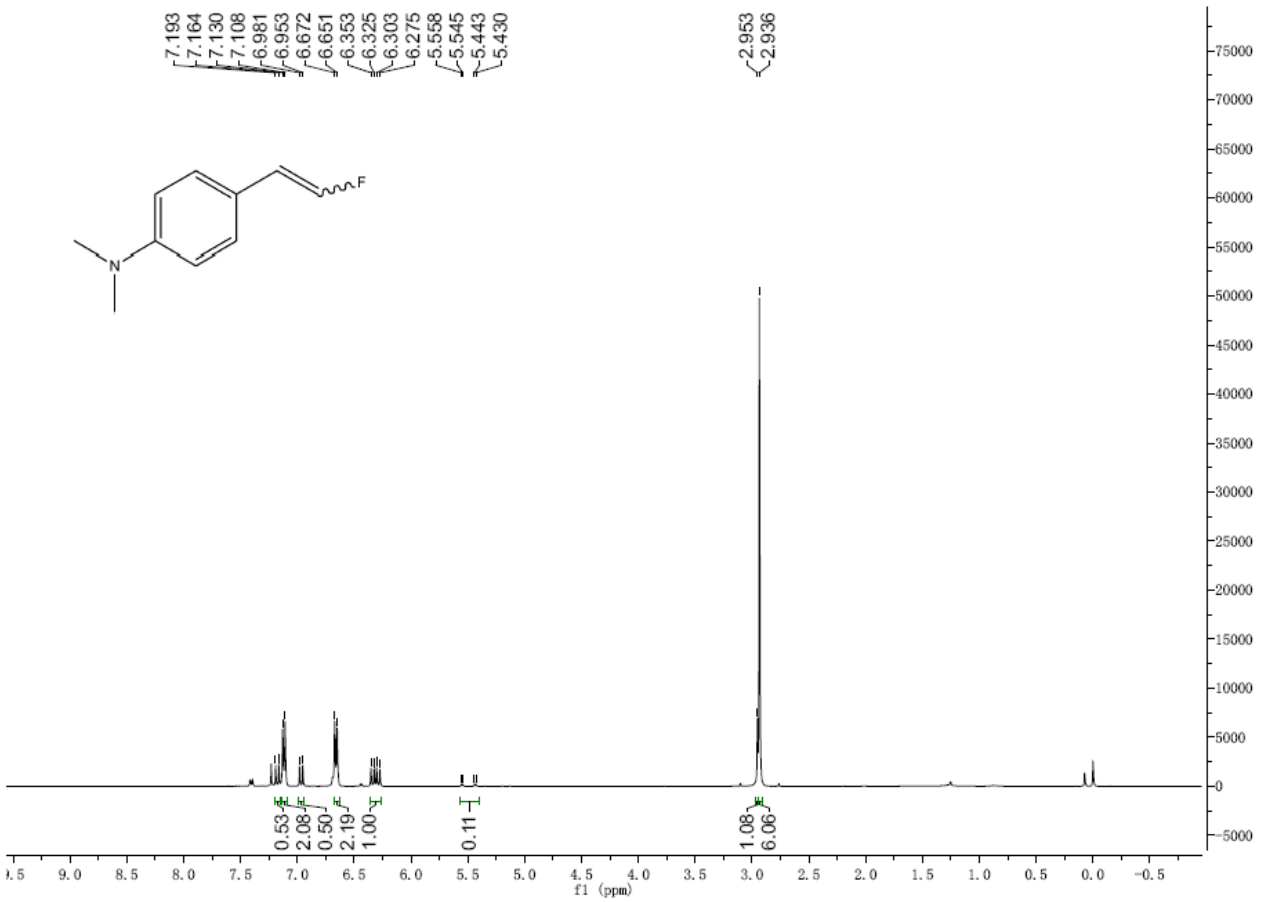
^{19}F NMR spectra of ***E*/*Z*-2d**



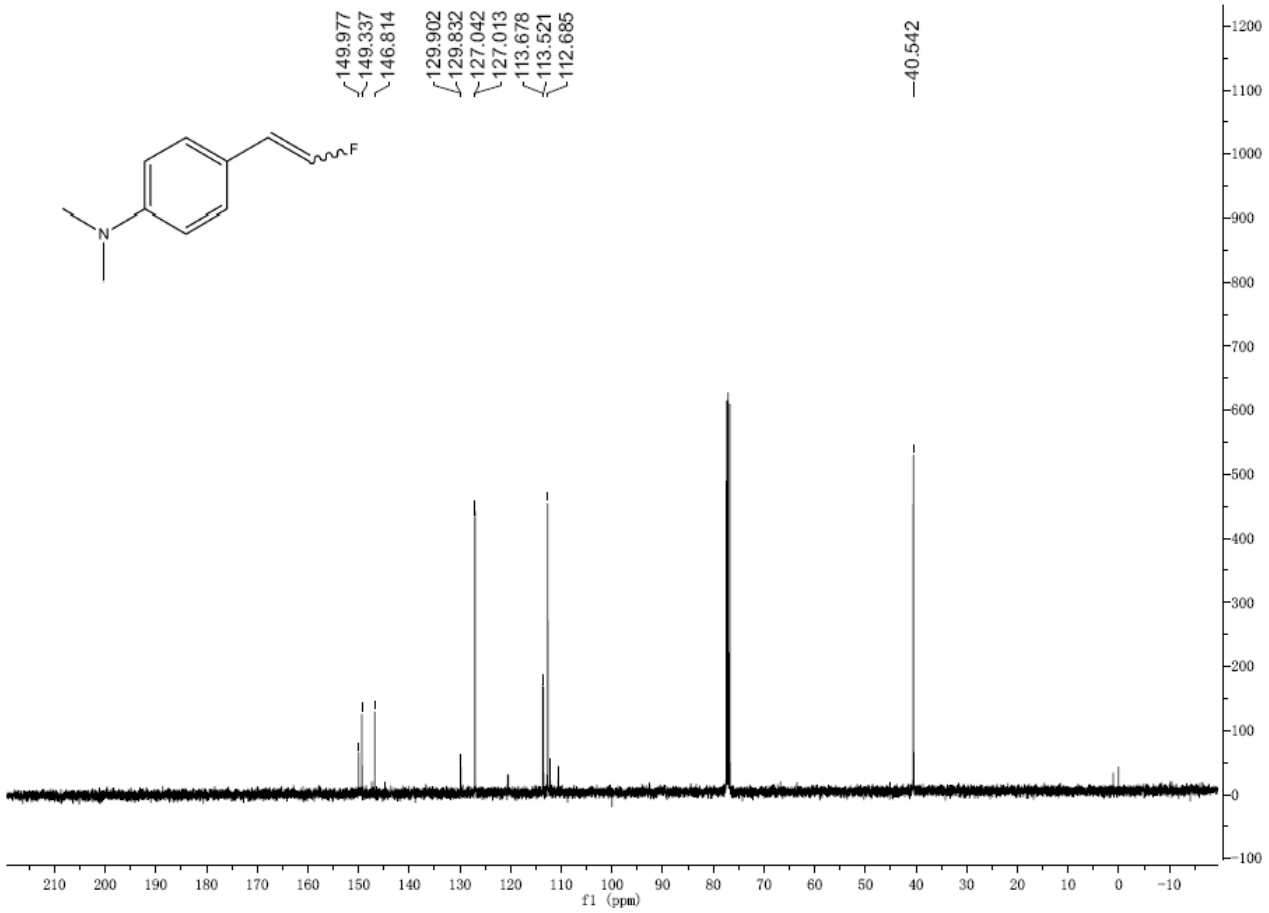
HRMS (EI) spectra of ***E*/*Z*-2d**



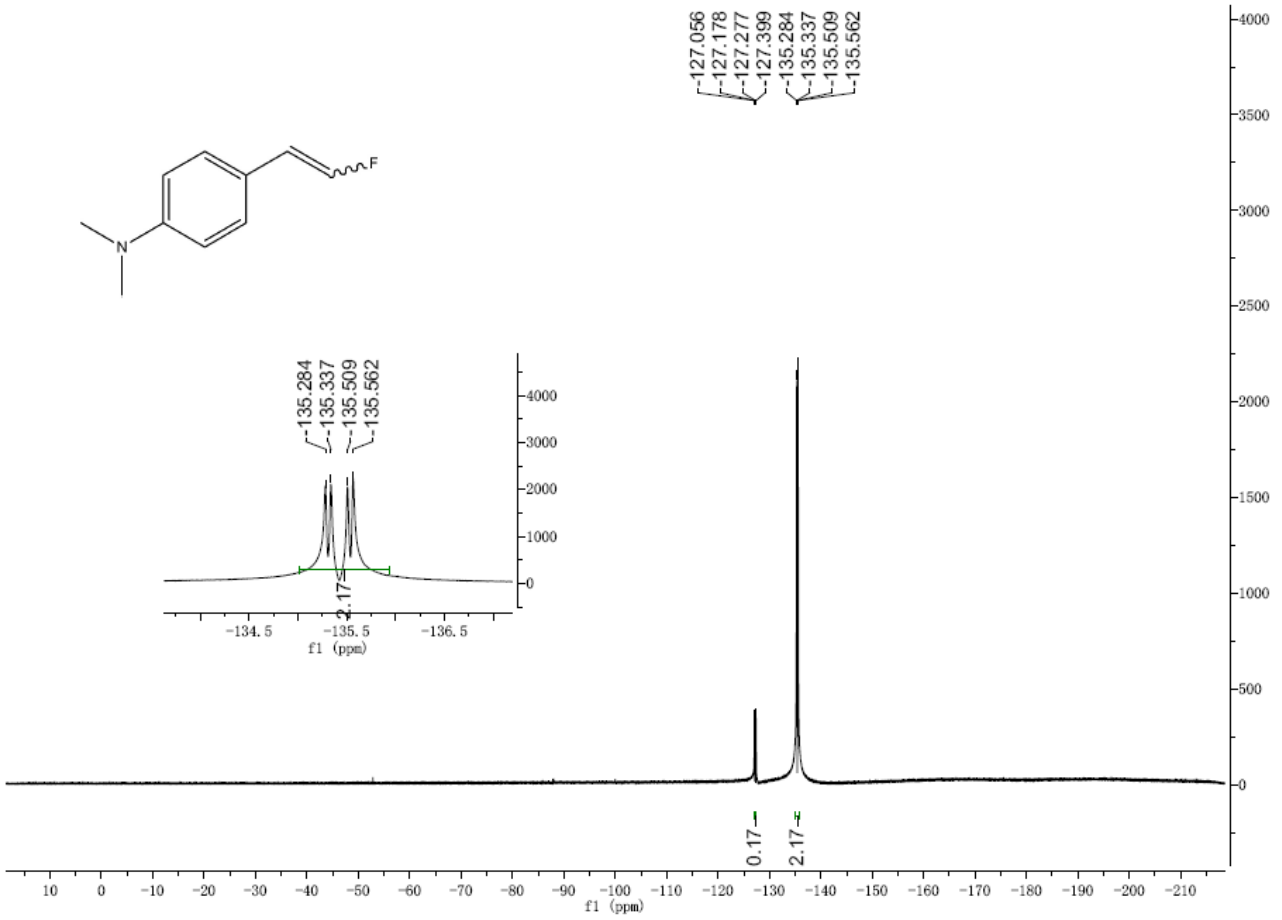
^{1}H NMR spectra of ***E***/***Z*-2e**



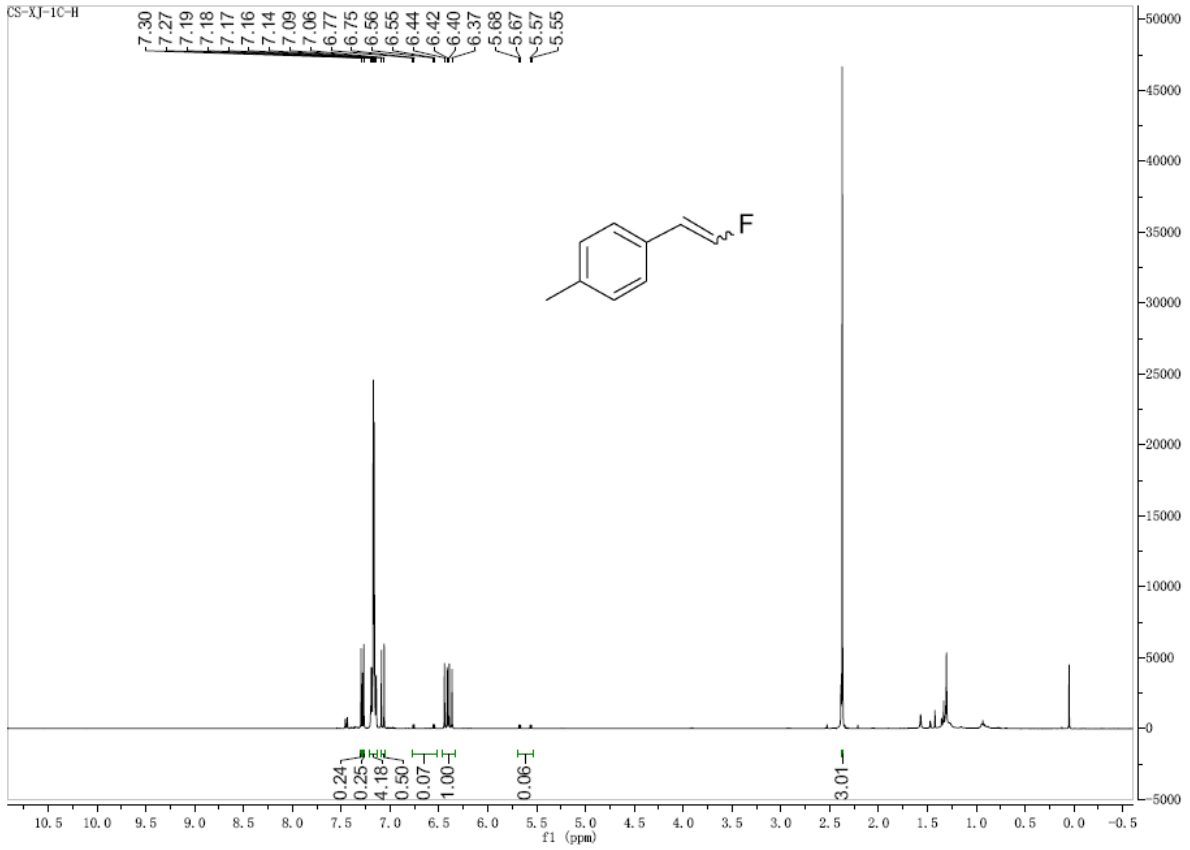
^{13}C NMR spectra of ***E***/***Z*-2e**



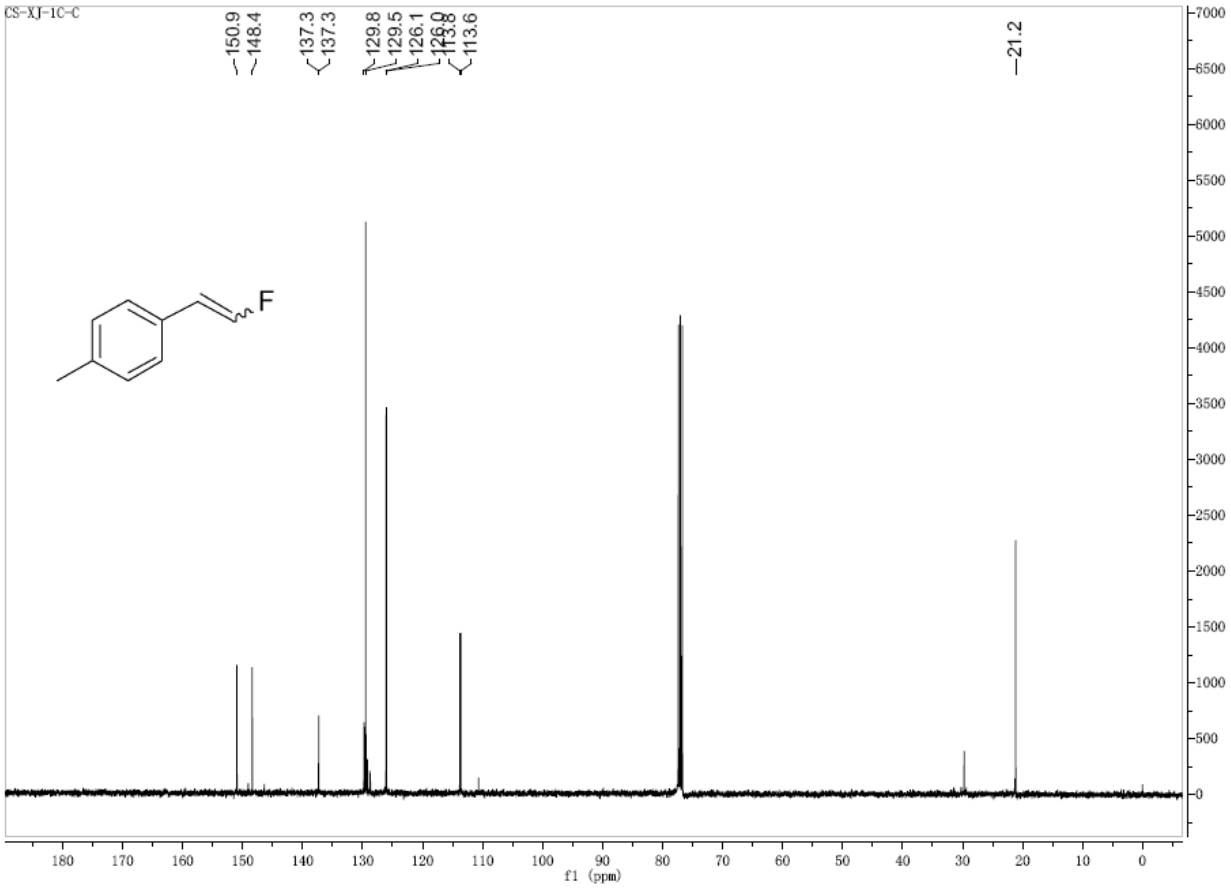
^{19}F NMR spectra of ***E***/***Z*-2e**



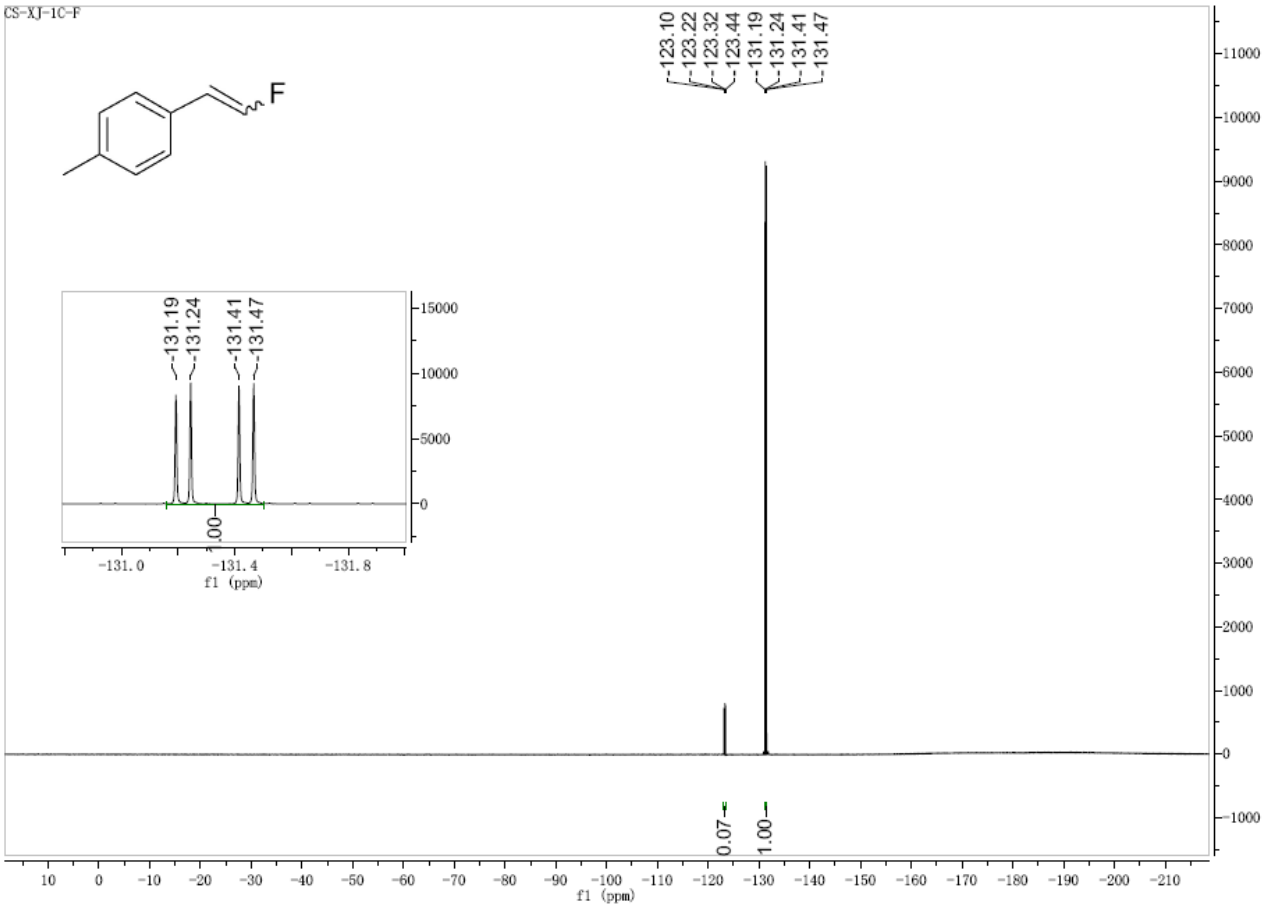
^{1}H NMR spectra of ***E*/*Z*-2f**



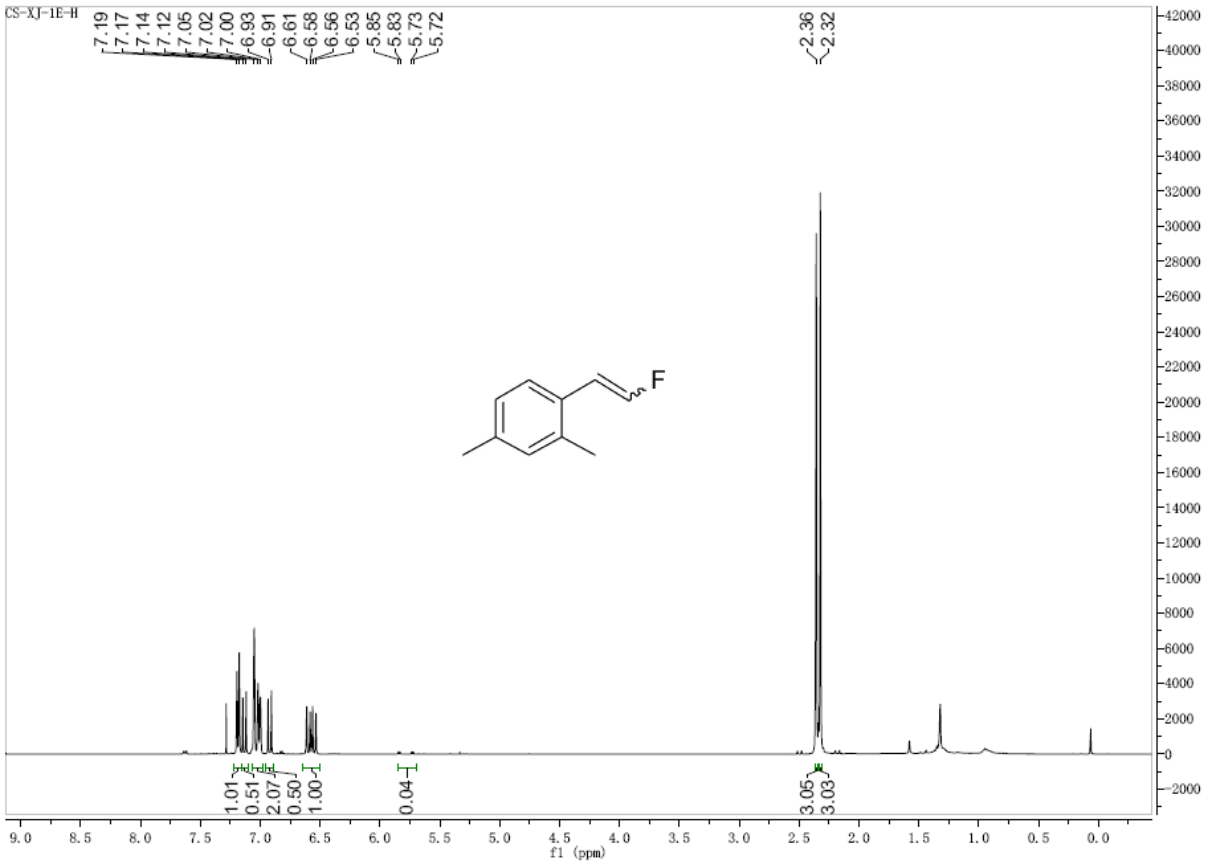
^{13}C NMR spectra of *E*/*Z*-**2f**



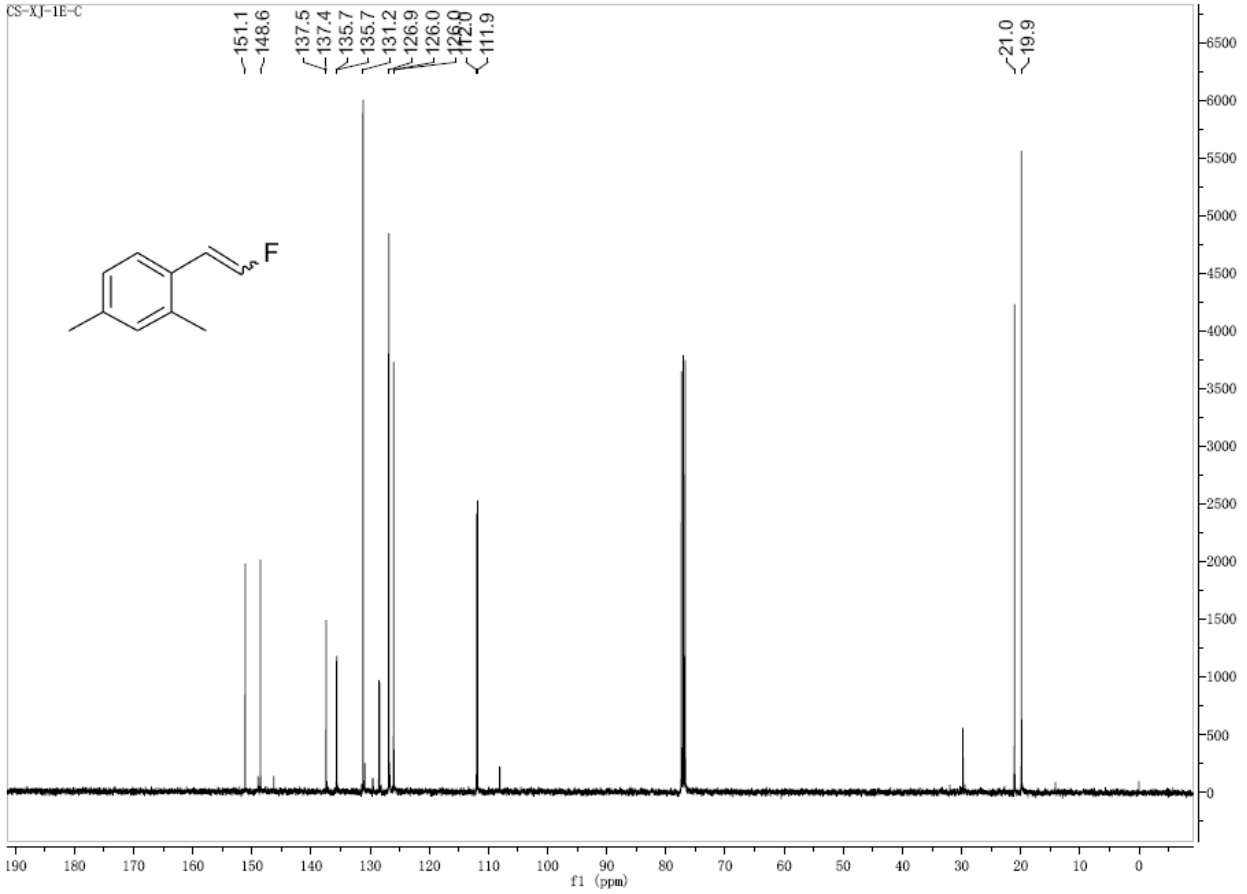
^{19}F NMR spectra of *E*/*Z*-**2f**



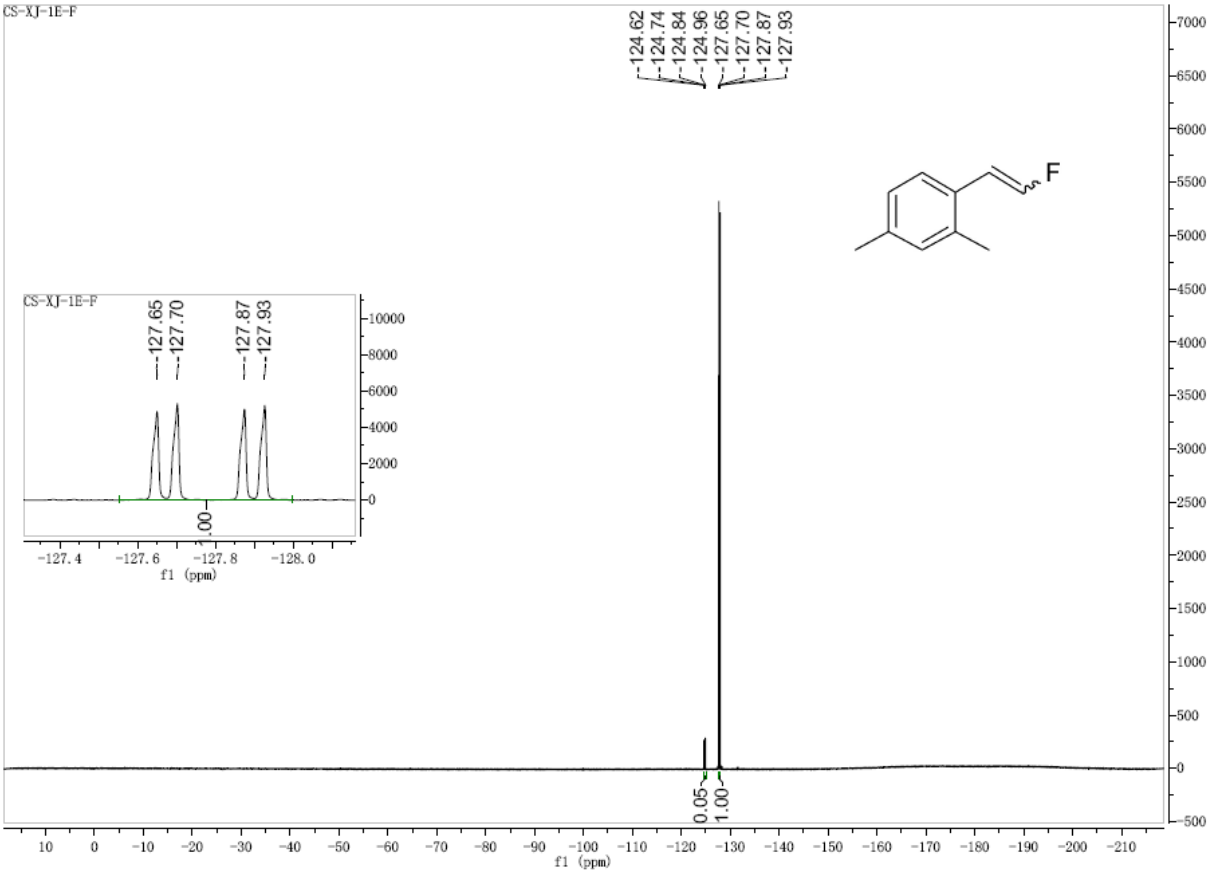
^{1}H NMR spectra of *E*/*Z*-**2g**



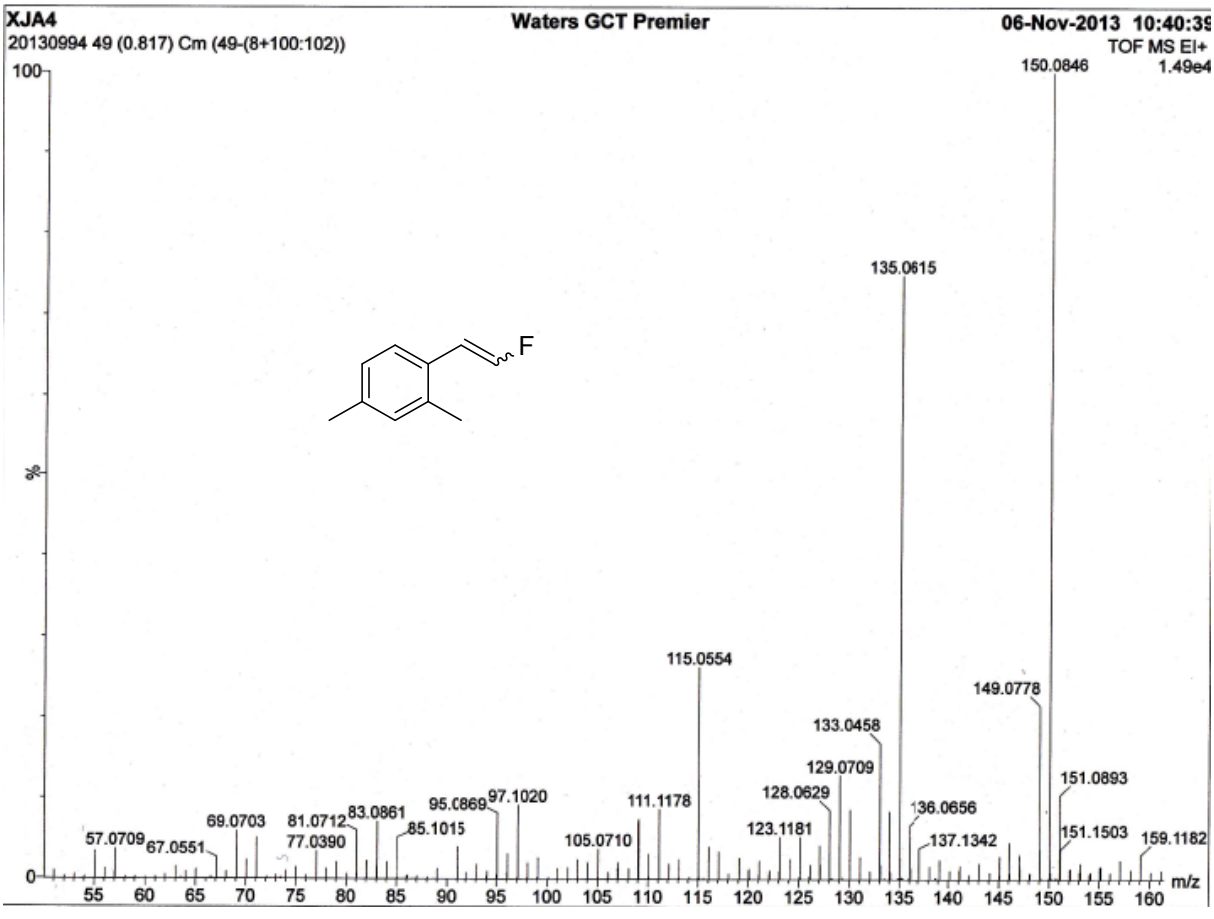
^{13}C NMR spectra of *E*/*Z*-**2g**



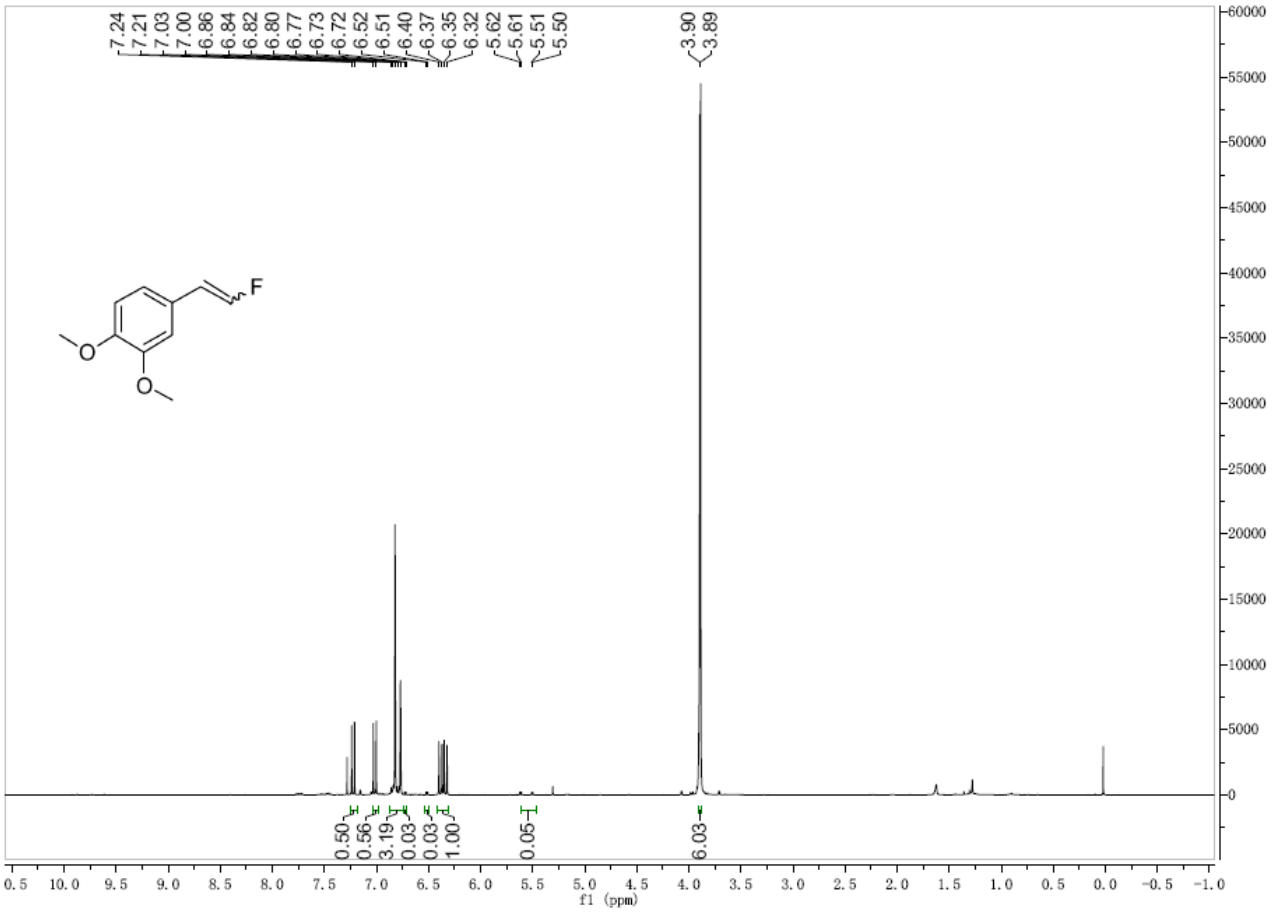
^{19}F NMR spectra of *E*/*Z*-**2g**



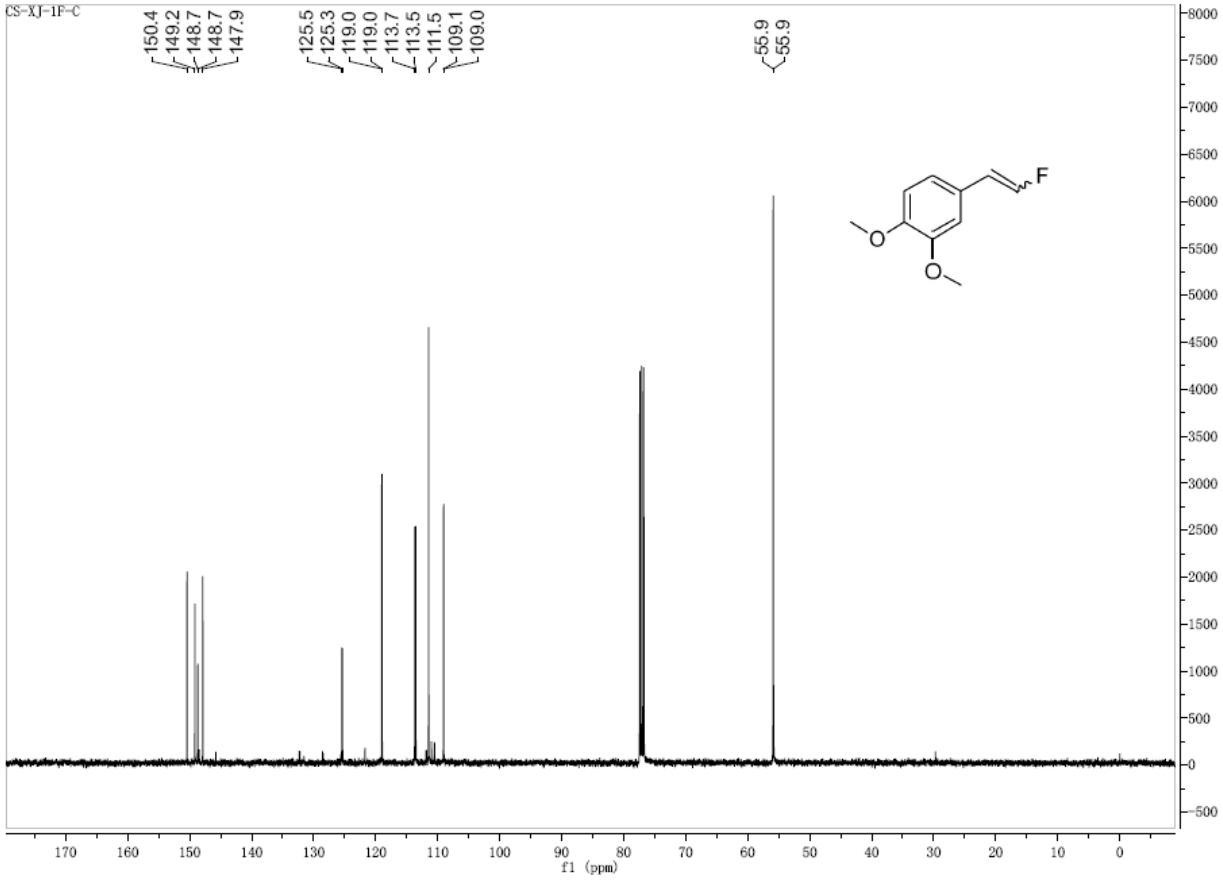
HRMS (EI) spectra of *E*/*Z*-**2g**



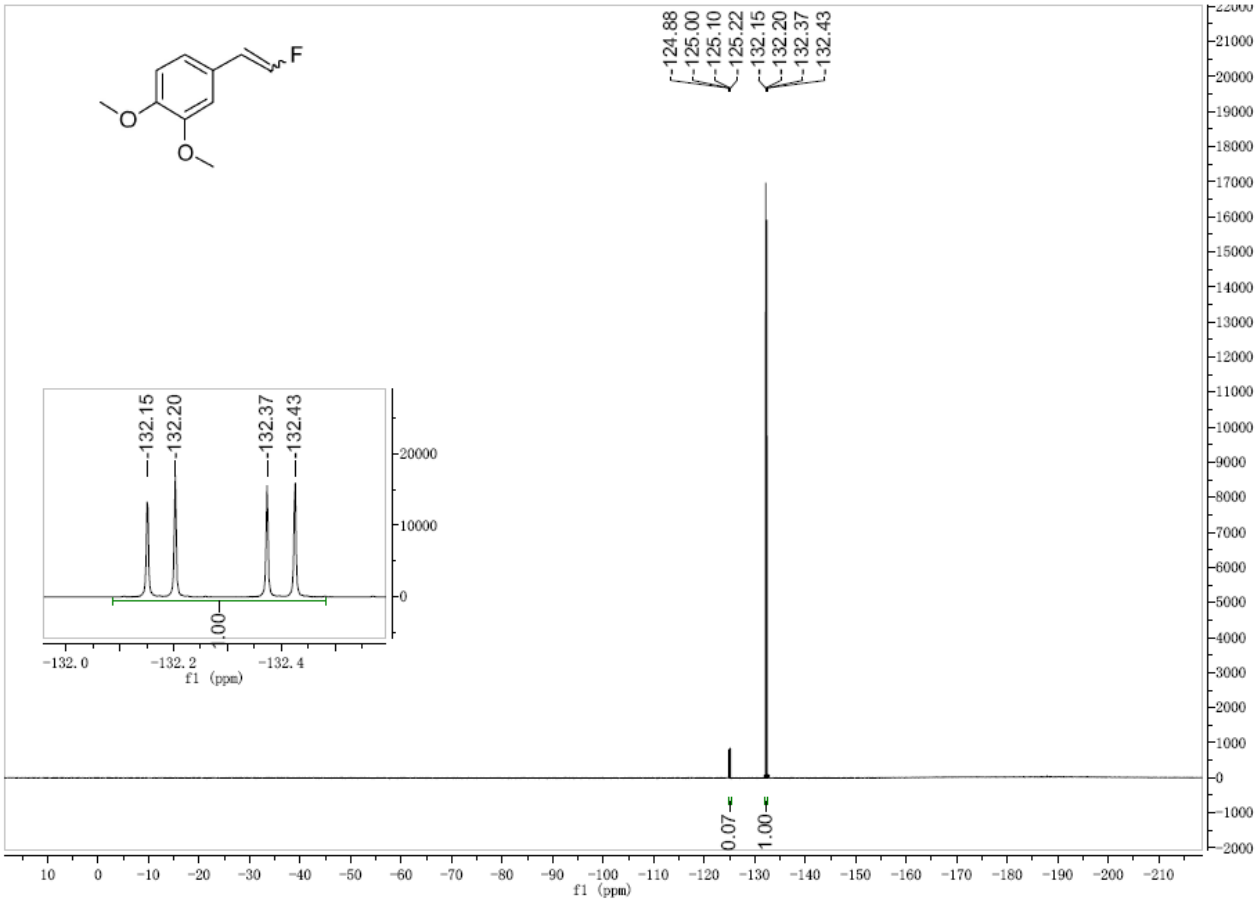
^{1}H NMR spectra of *E*/*Z*-**2h**



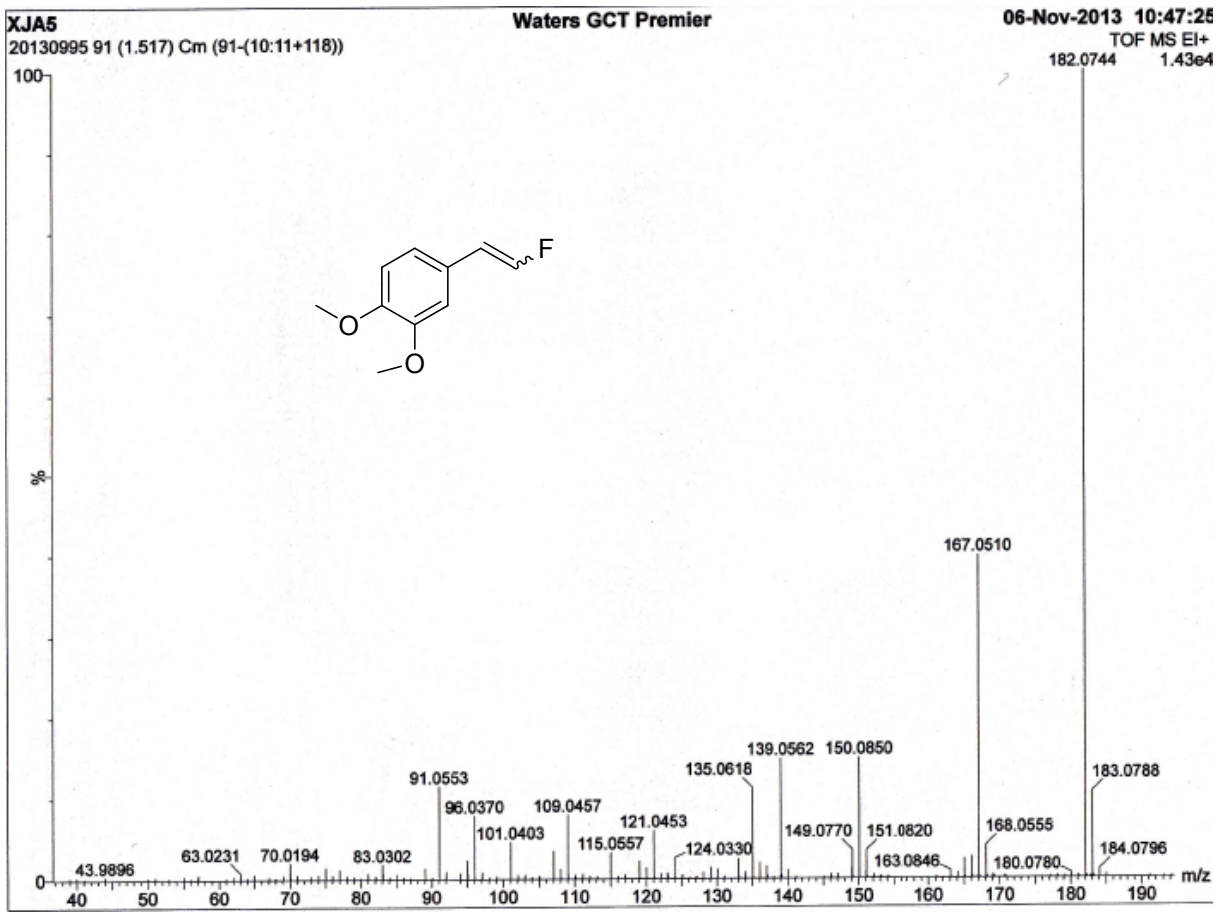
^{13}C NMR spectra of *E*/*Z*-**2h**



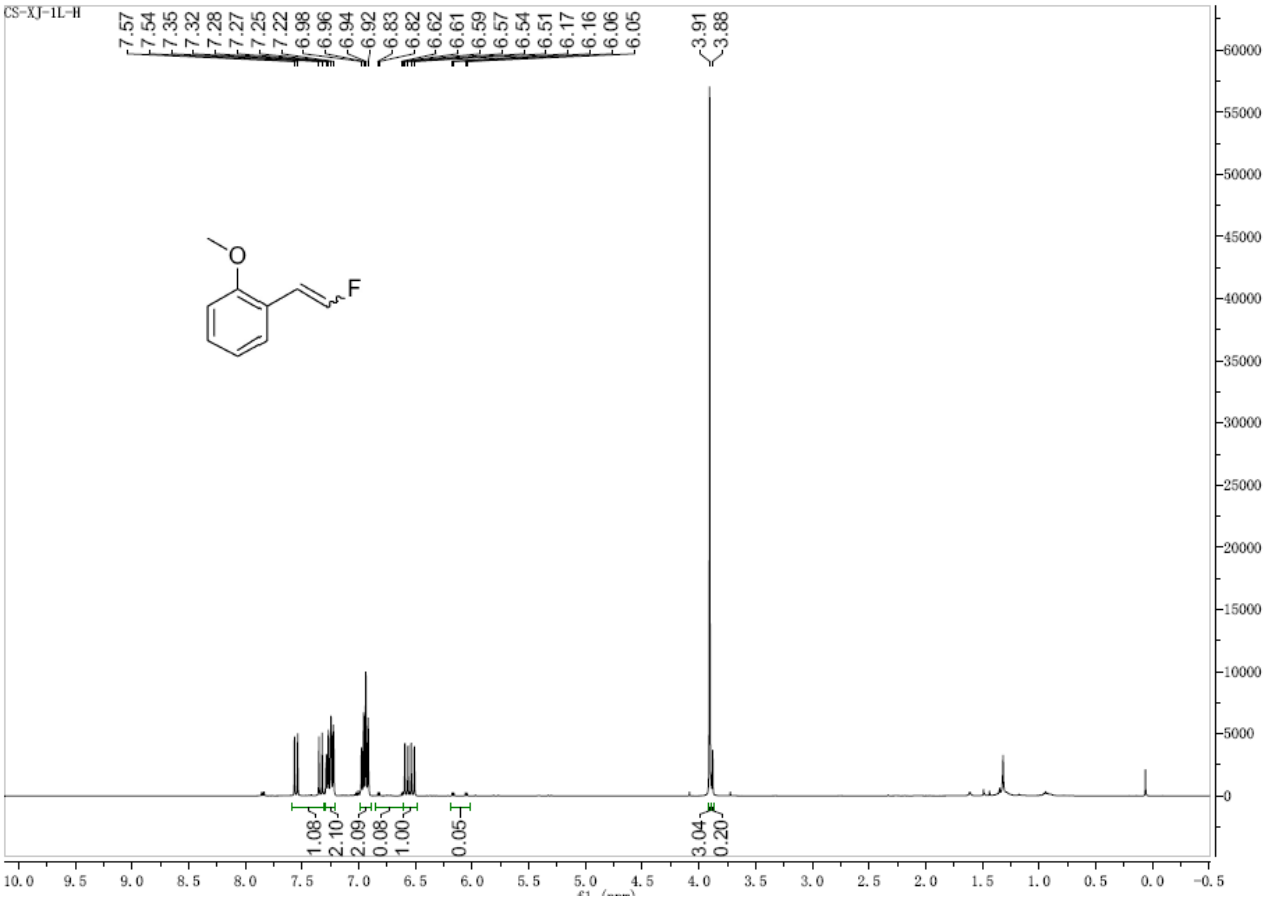
^{19}F NMR spectra of *E*/*Z*-**2h**



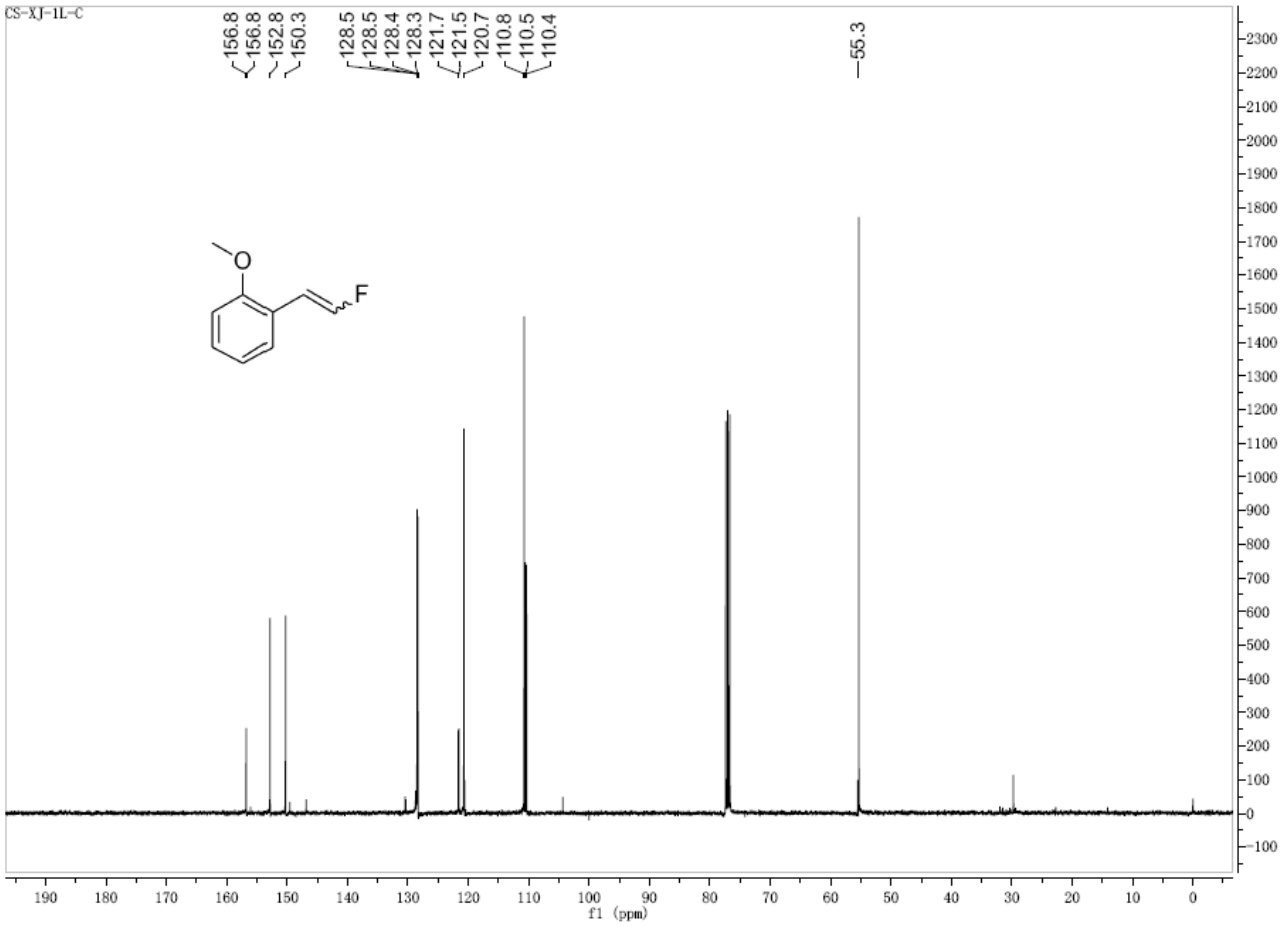
HRMS (EI) spectra of ***E***/***Z***-**2h**



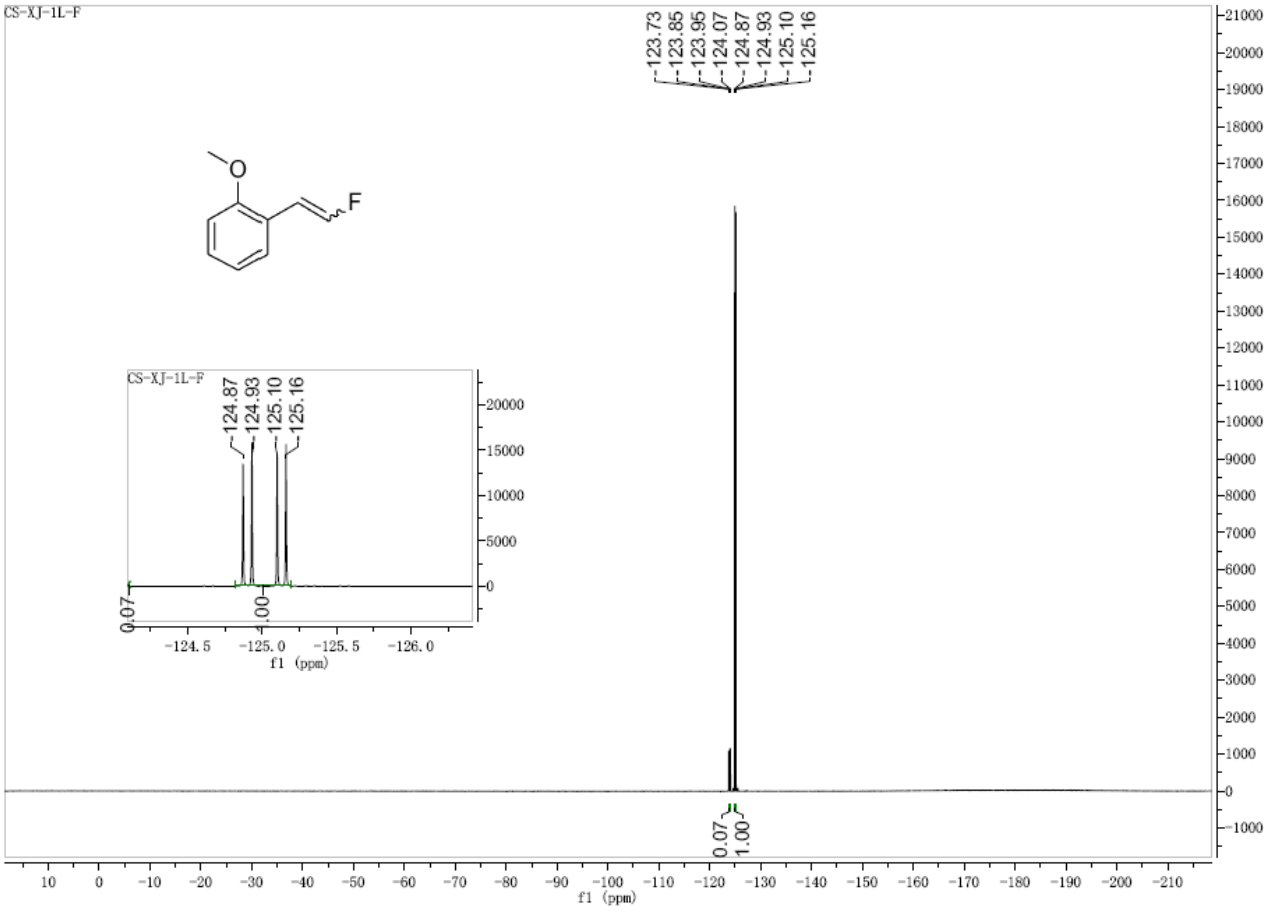
^{1}H NMR spectra of *E*/*Z*-**2i**



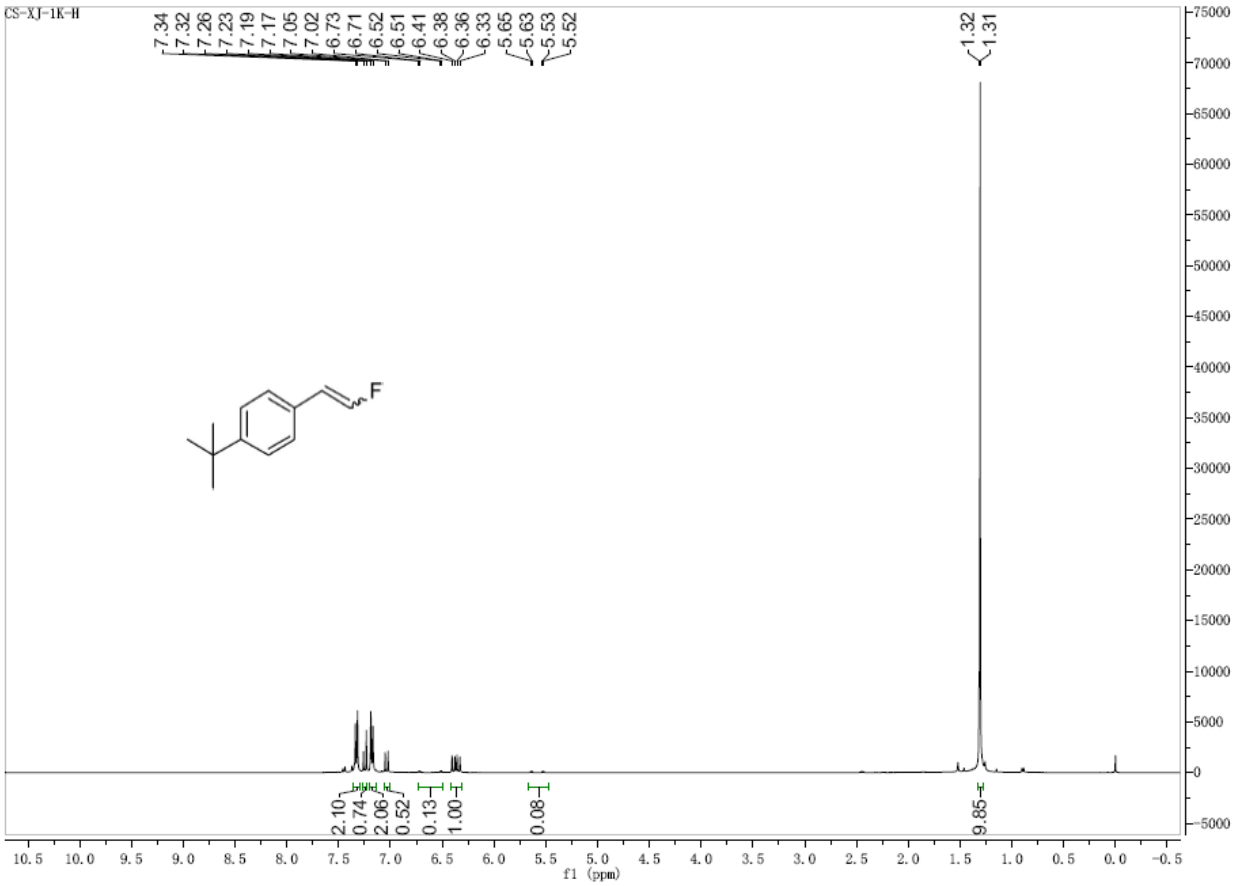
^{13}C NMR spectra of *E*/*Z*-**2i**



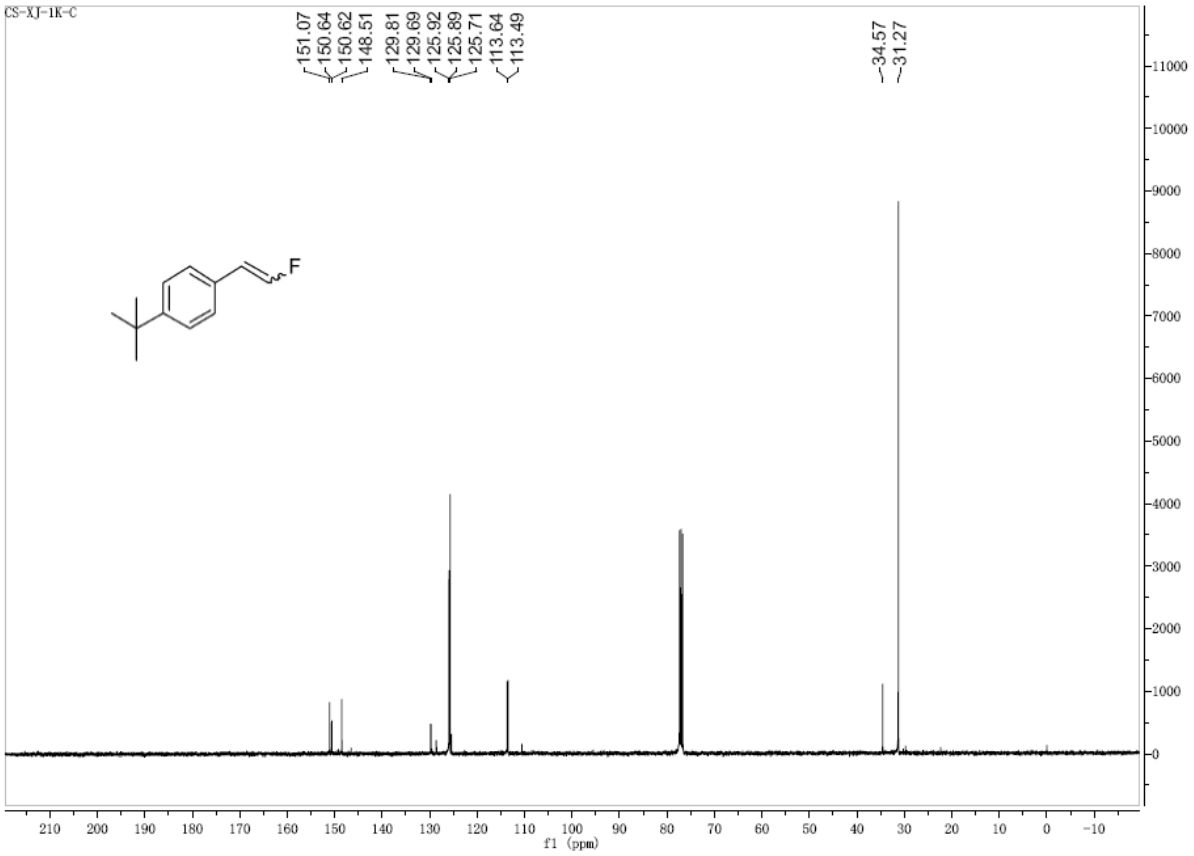
^{19}F NMR spectra of *E*/*Z*-**2i**



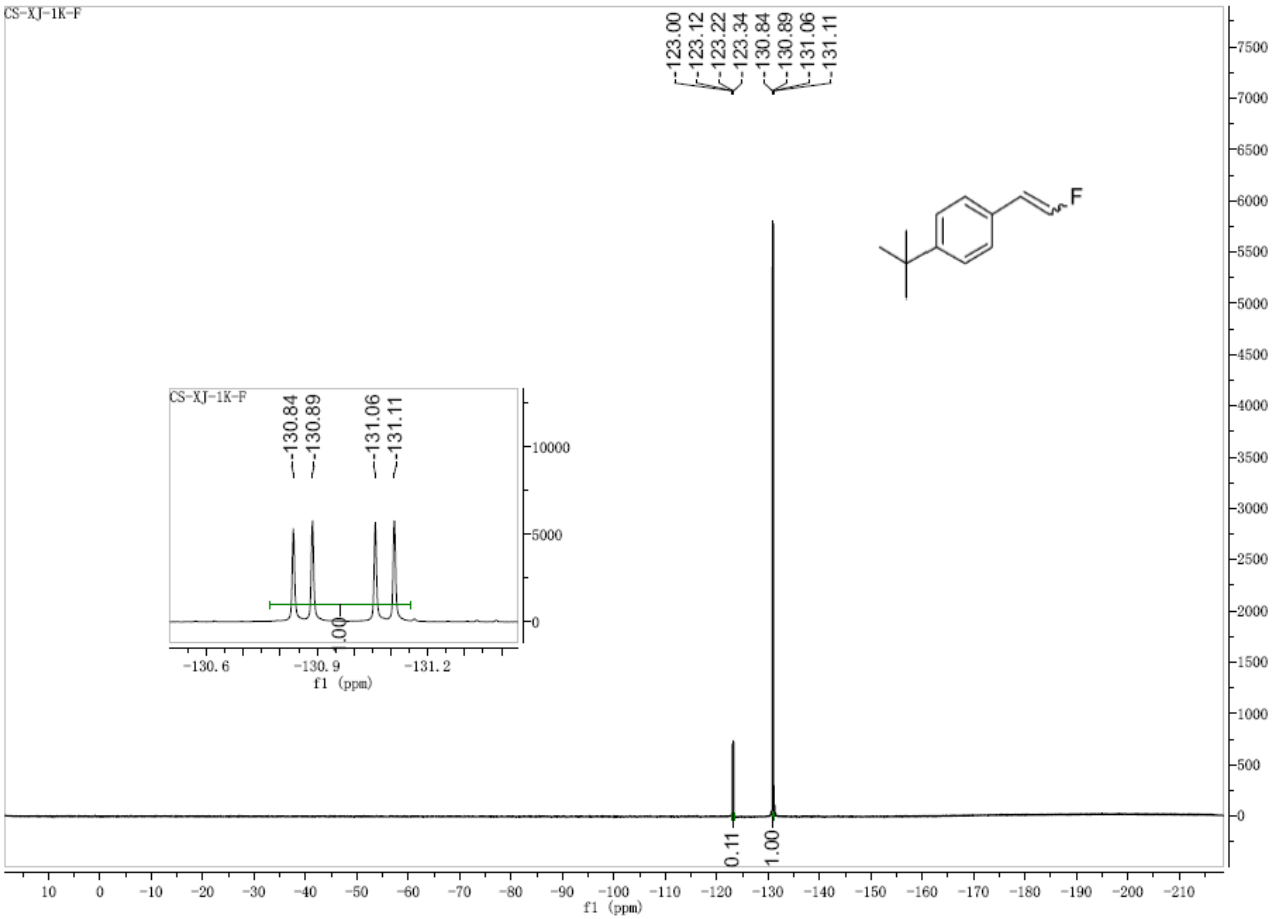
^{1}H NMR spectra of *E*/*Z*-**2j**



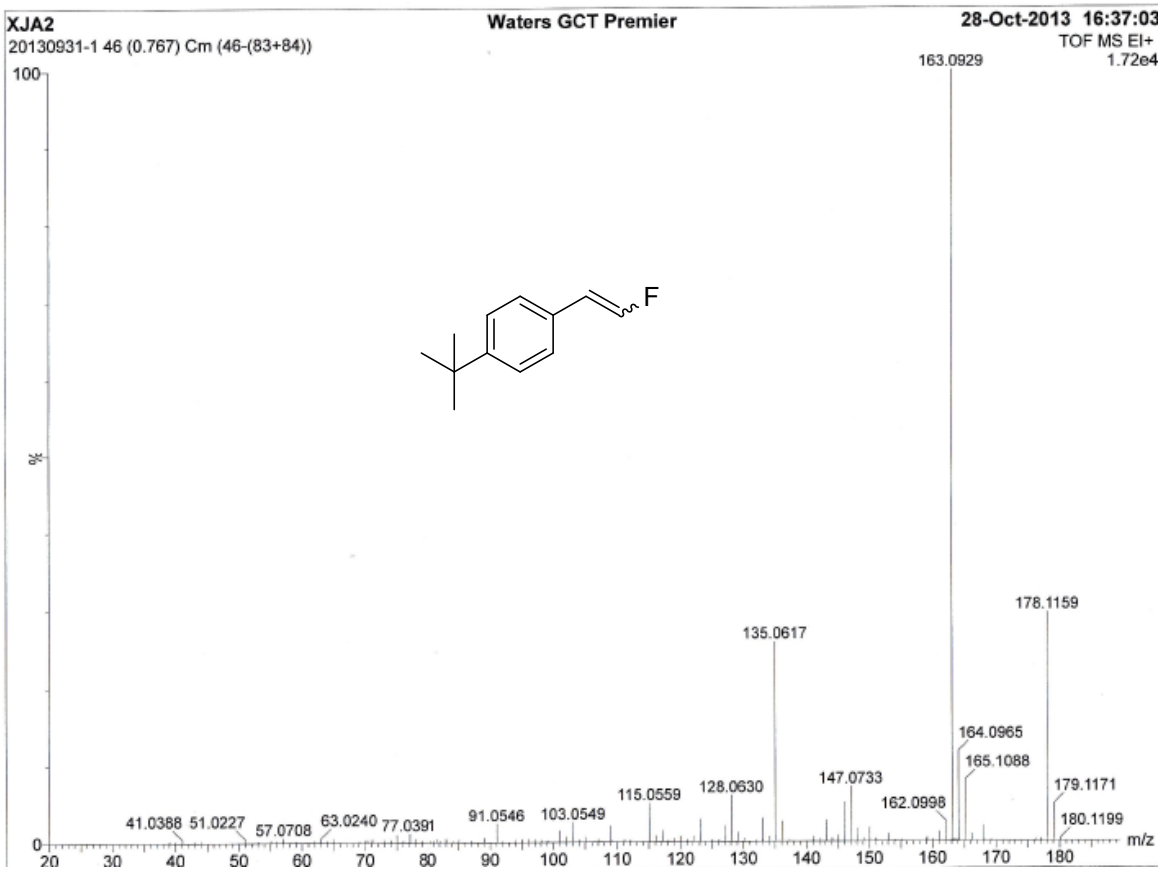
^{13}C NMR spectra of *E*/*Z*-**2j**



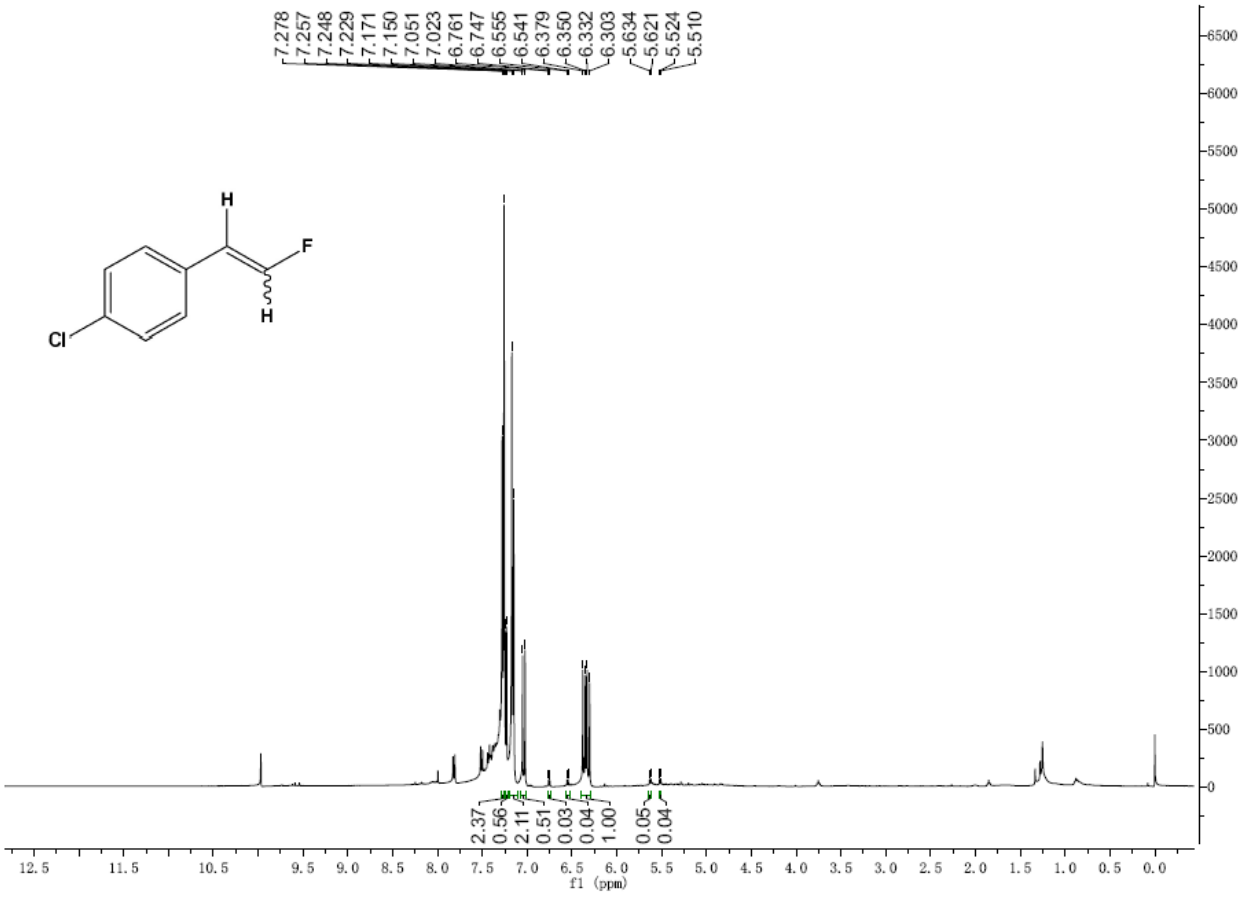
^{19}F NMR spectra of ***E*/*Z*-2j**



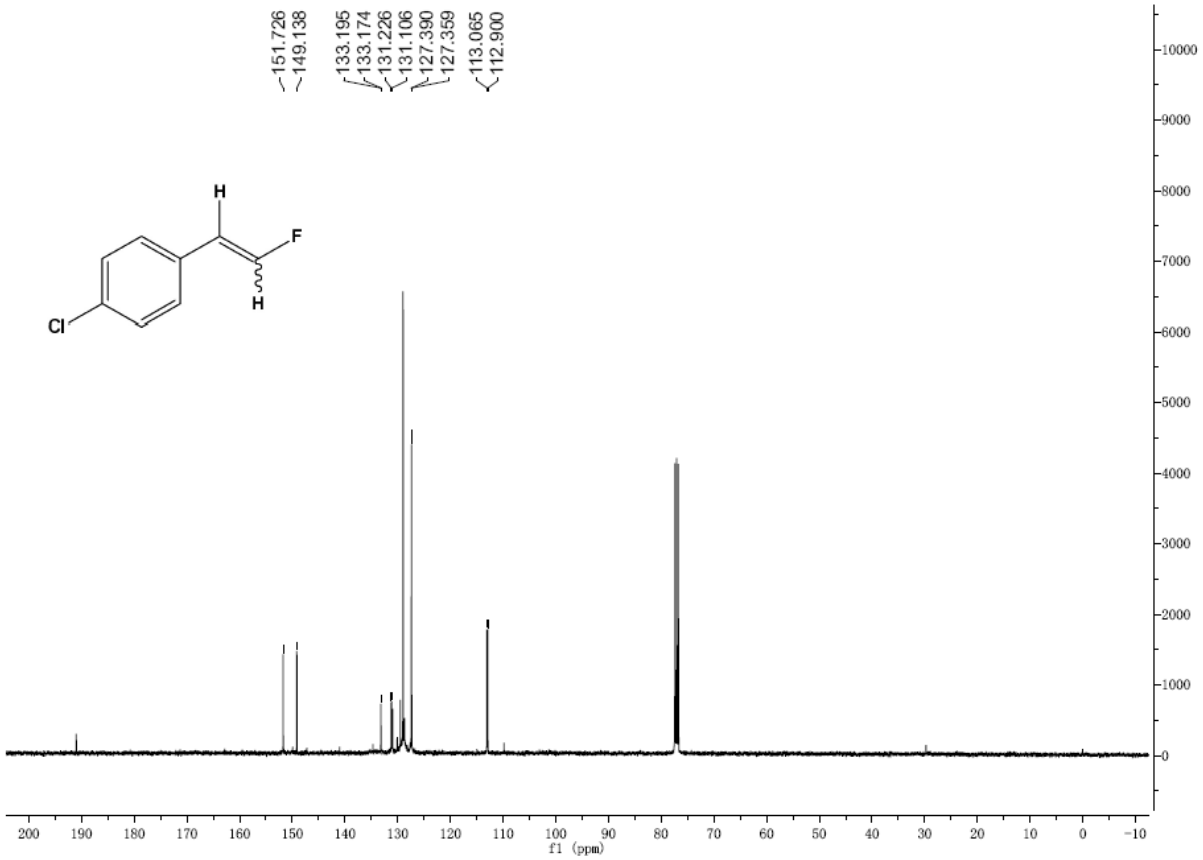
HRMS (EI) spectra of ***E*/*Z*-2j**



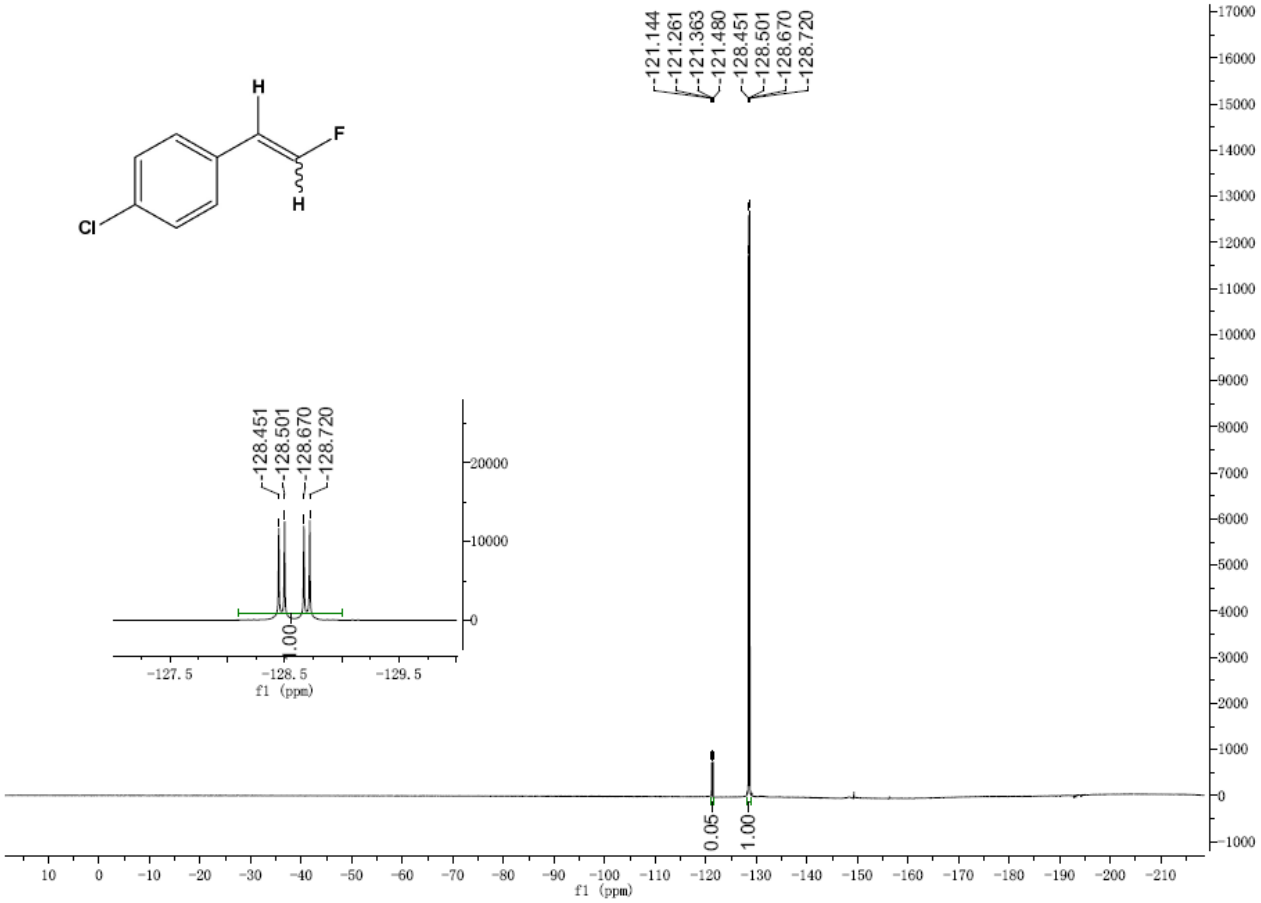
^{1}H NMR spectra of ***E***/***Z*-2k**



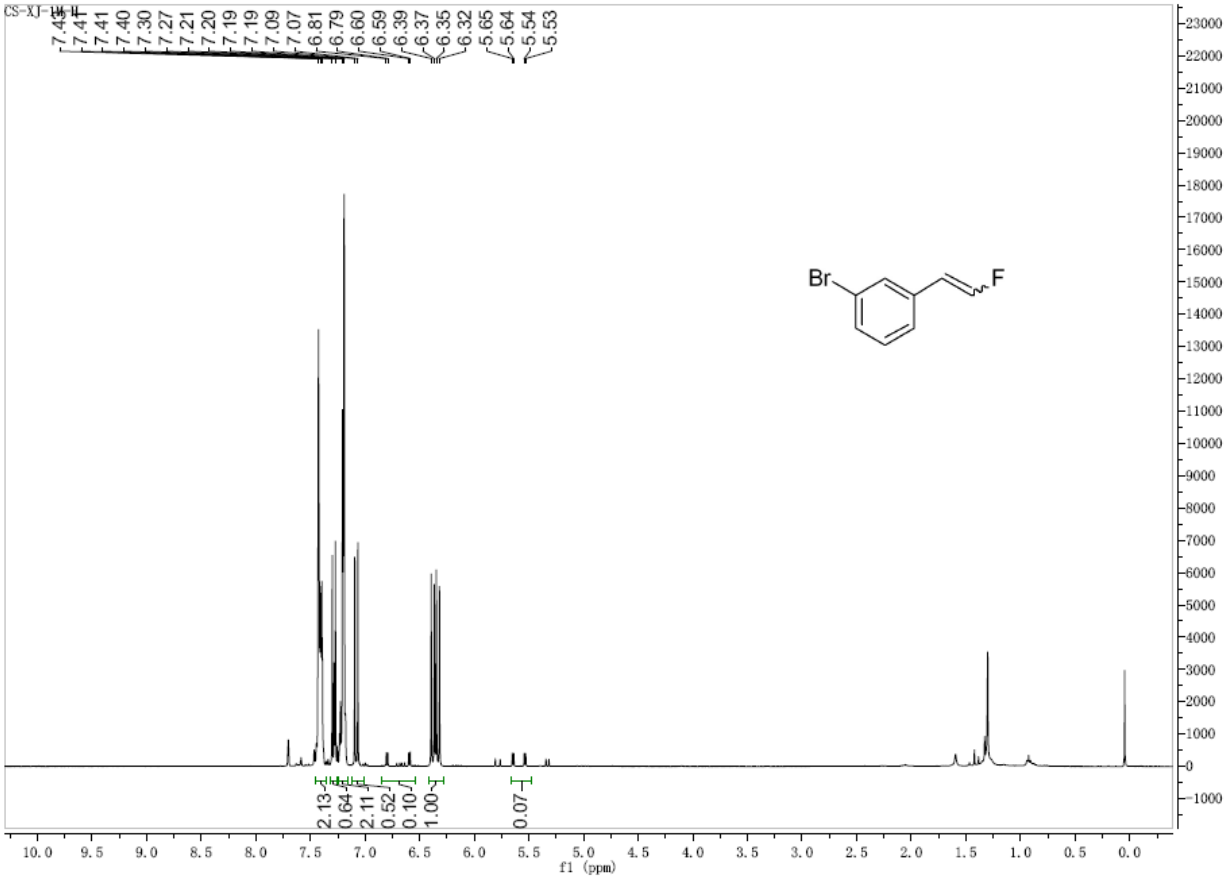
^{13}C NMR spectra of ***E***/***Z*-2k**



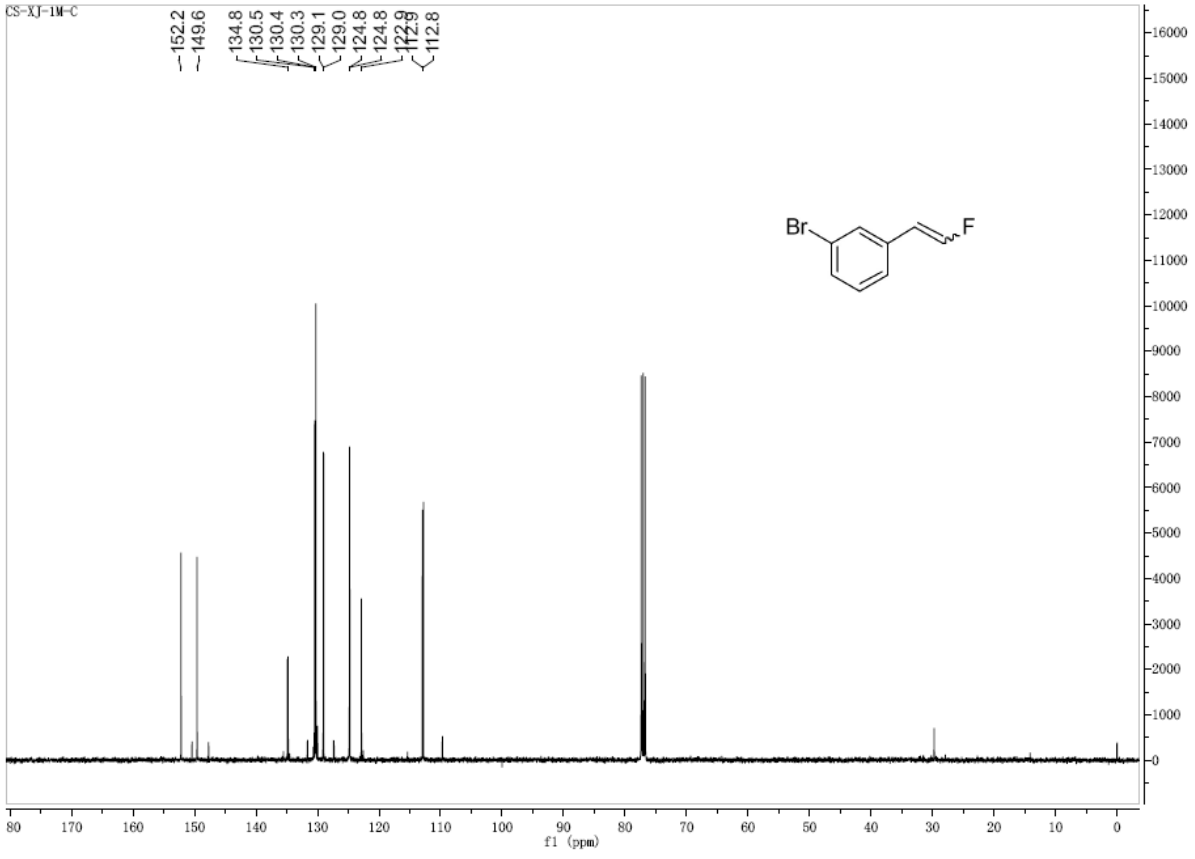
^{19}F NMR spectra of ***E*/*Z*-2k**



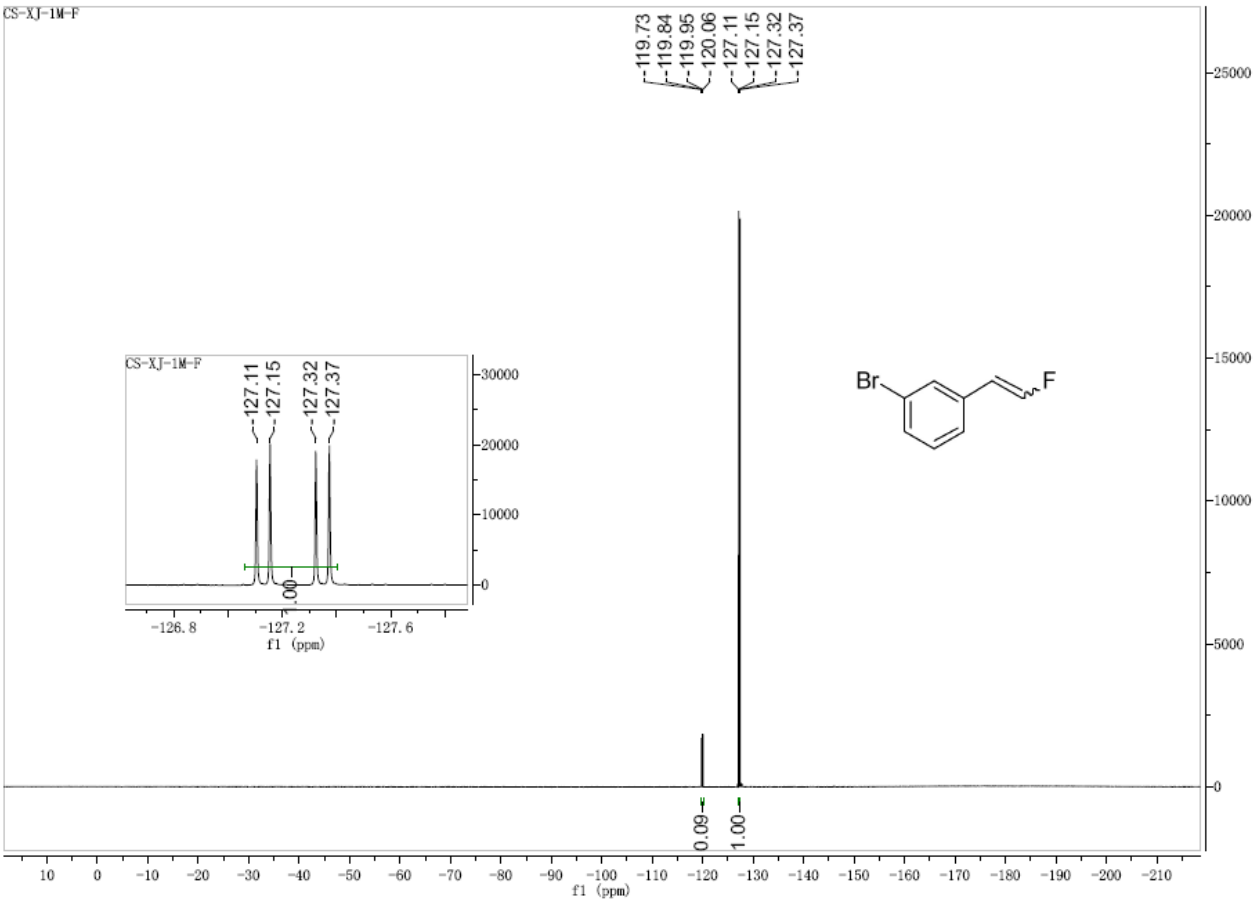
^{1}H NMR spectra of *E*/*Z*-**2l**



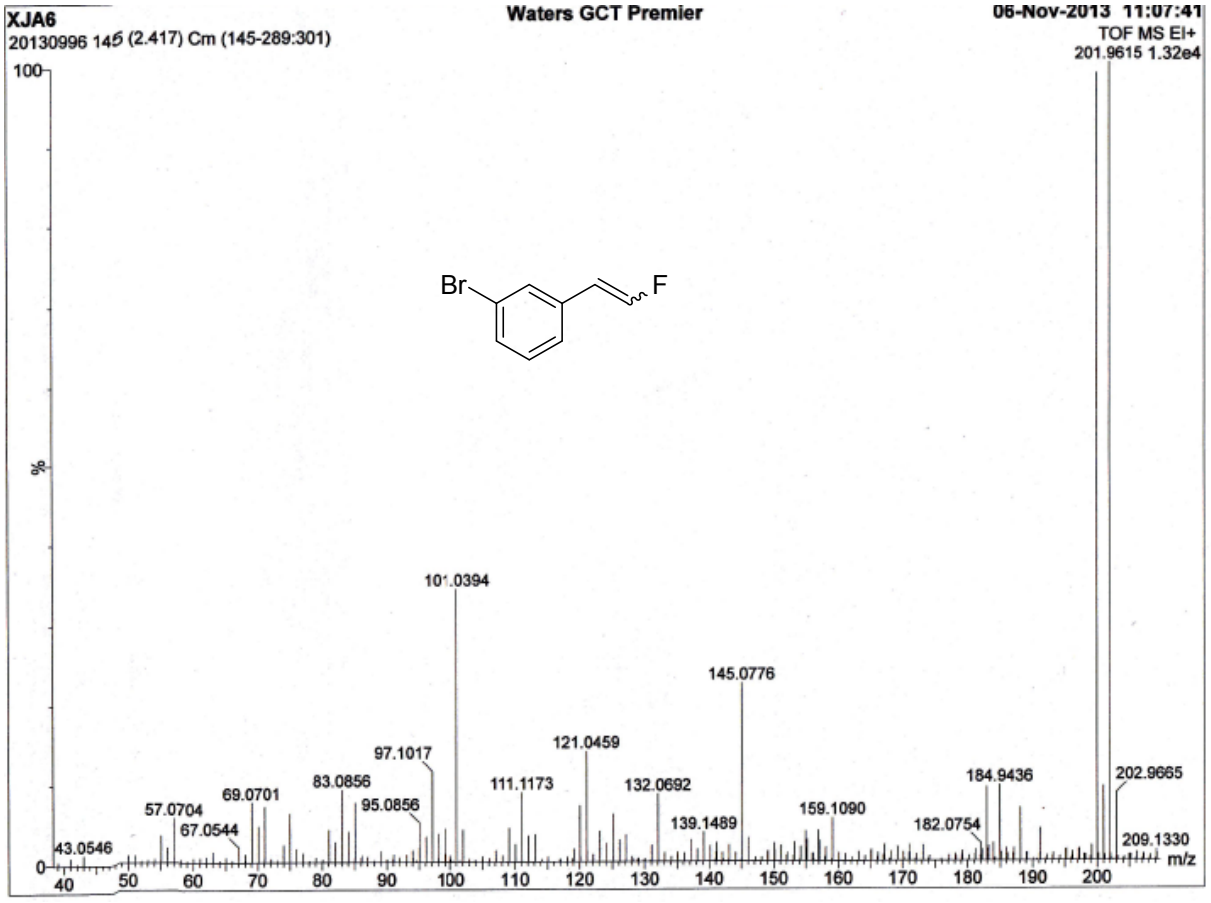
^{13}C NMR spectra of *E*/*Z*-**2l**



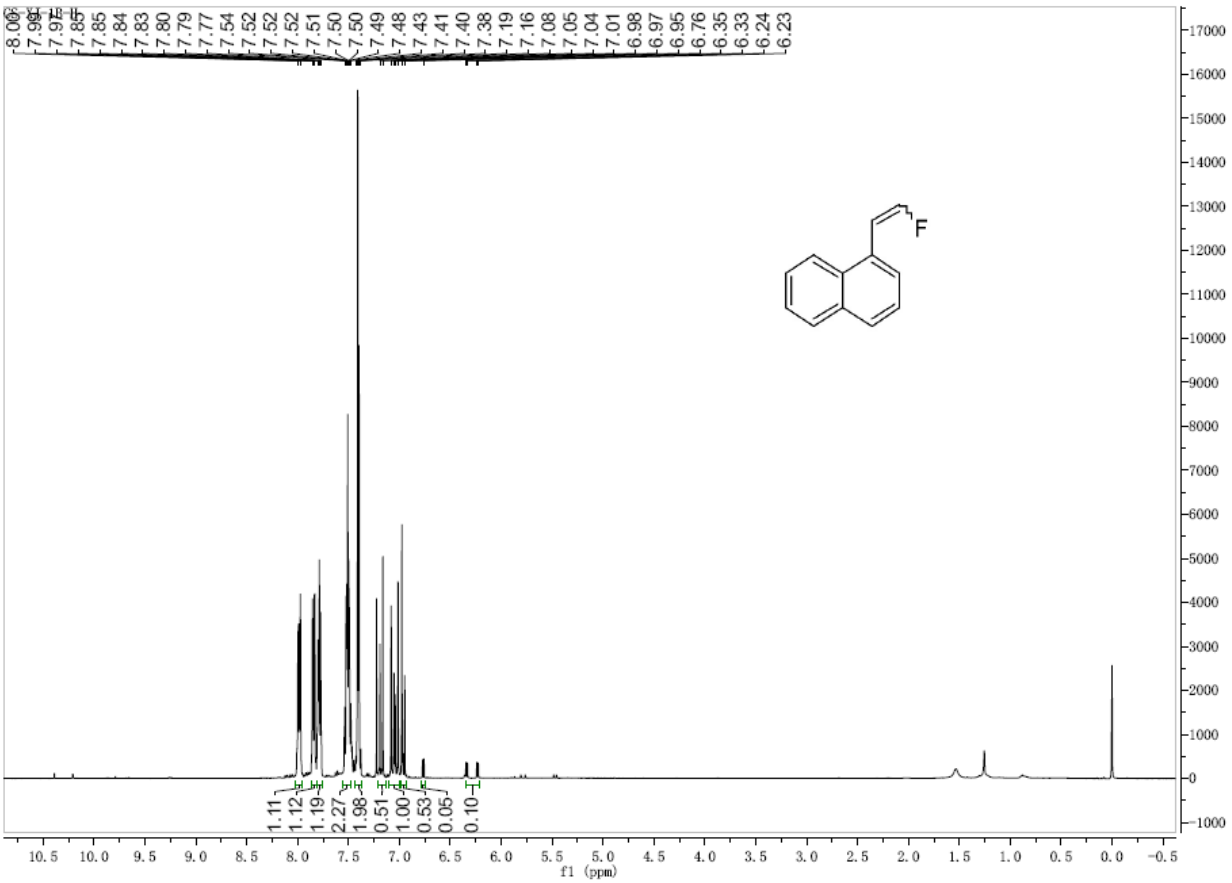
^{19}F NMR spectra of *E*/*Z*-**2l**



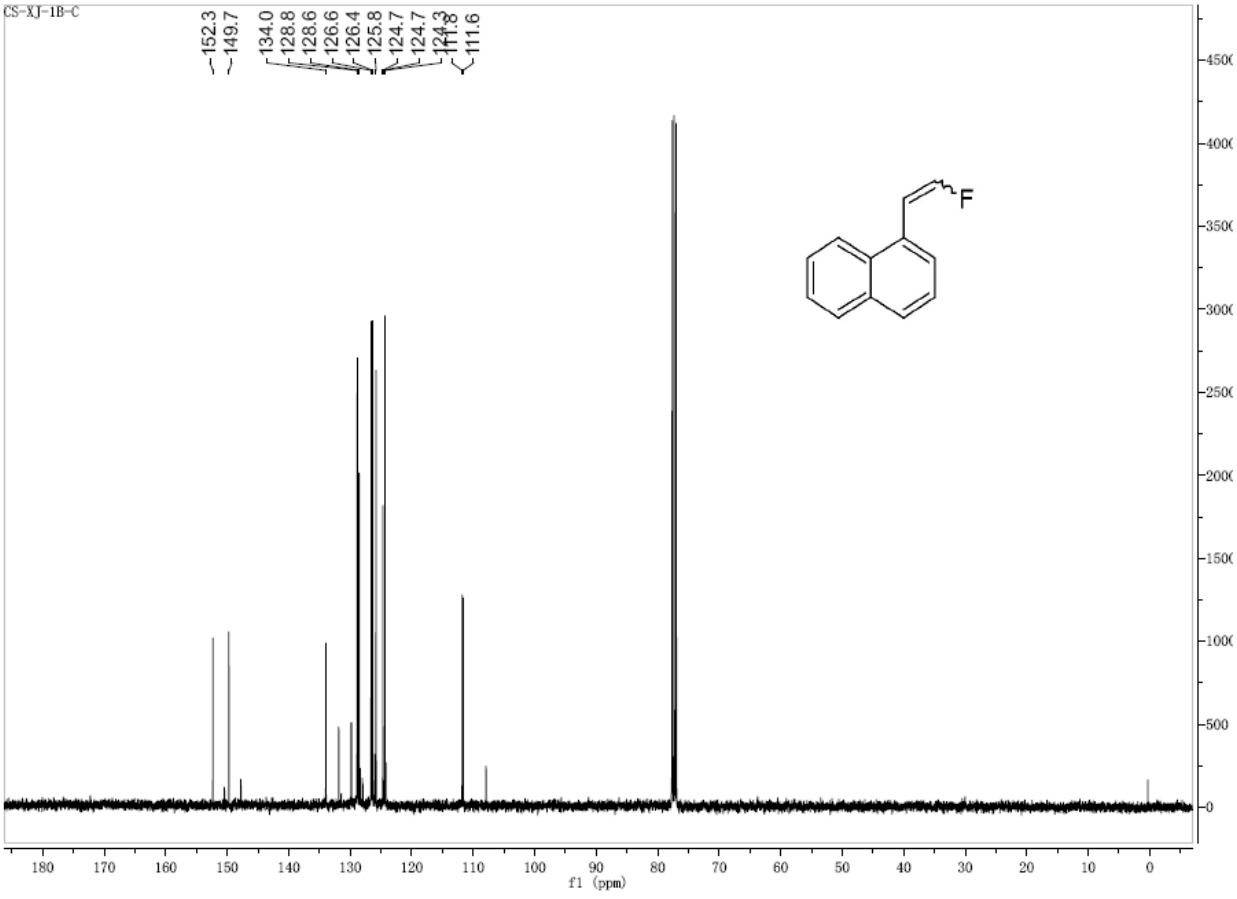
HRMS (EI) spectra of *E*/*Z*-**2l**



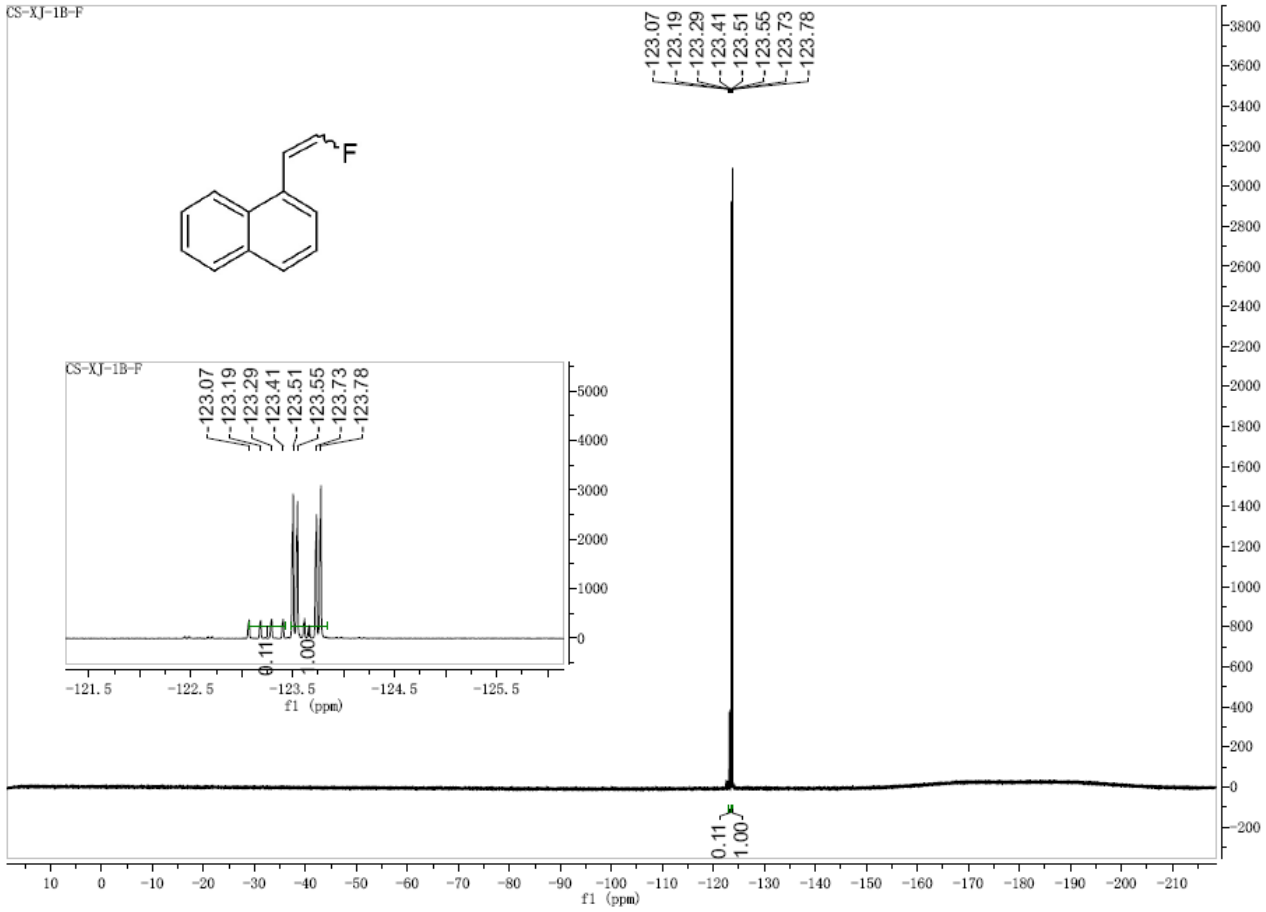
^{1}H NMR spectra of ***E*/*Z*-2m**



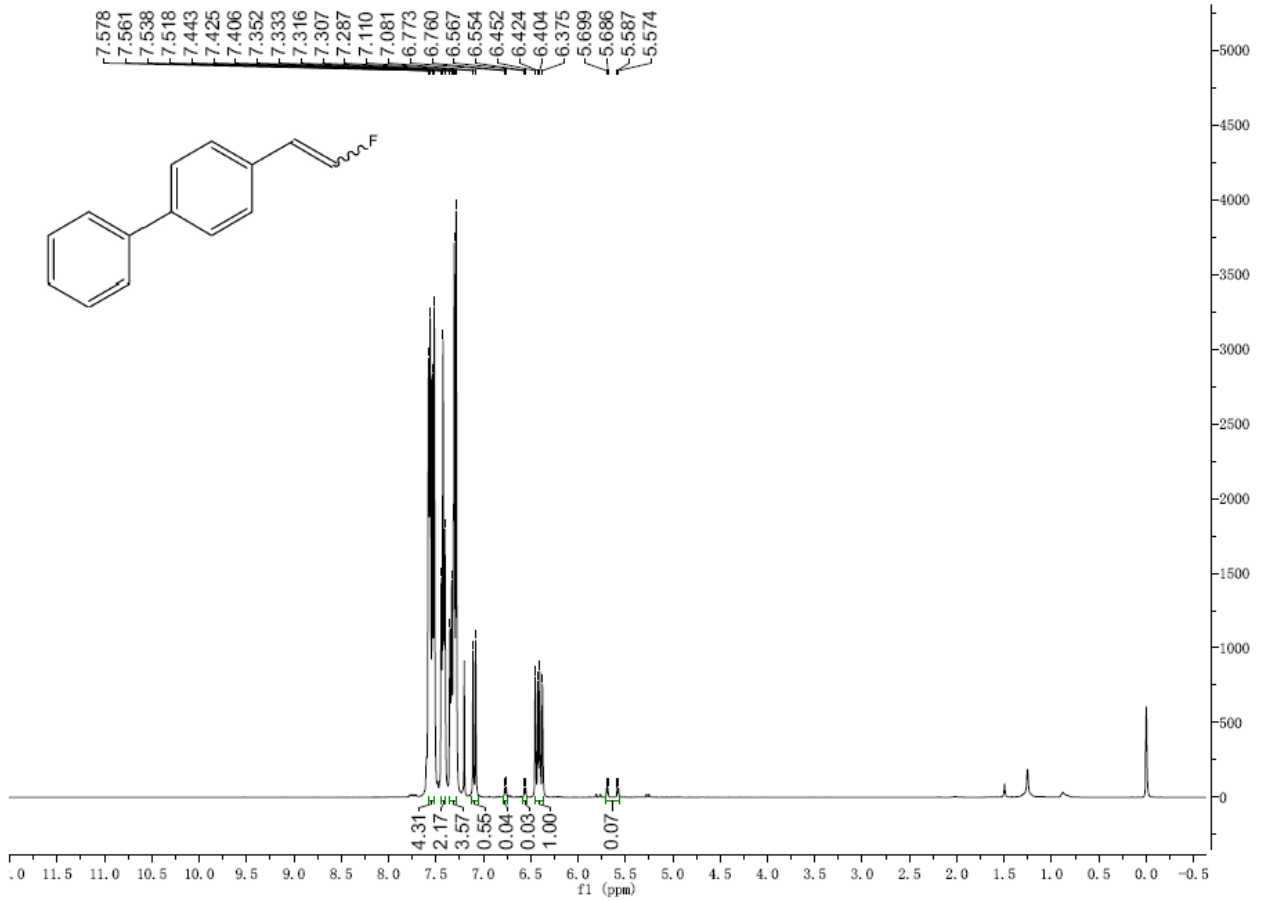
^{13}C NMR spectra of ***E*/*Z*-2m**



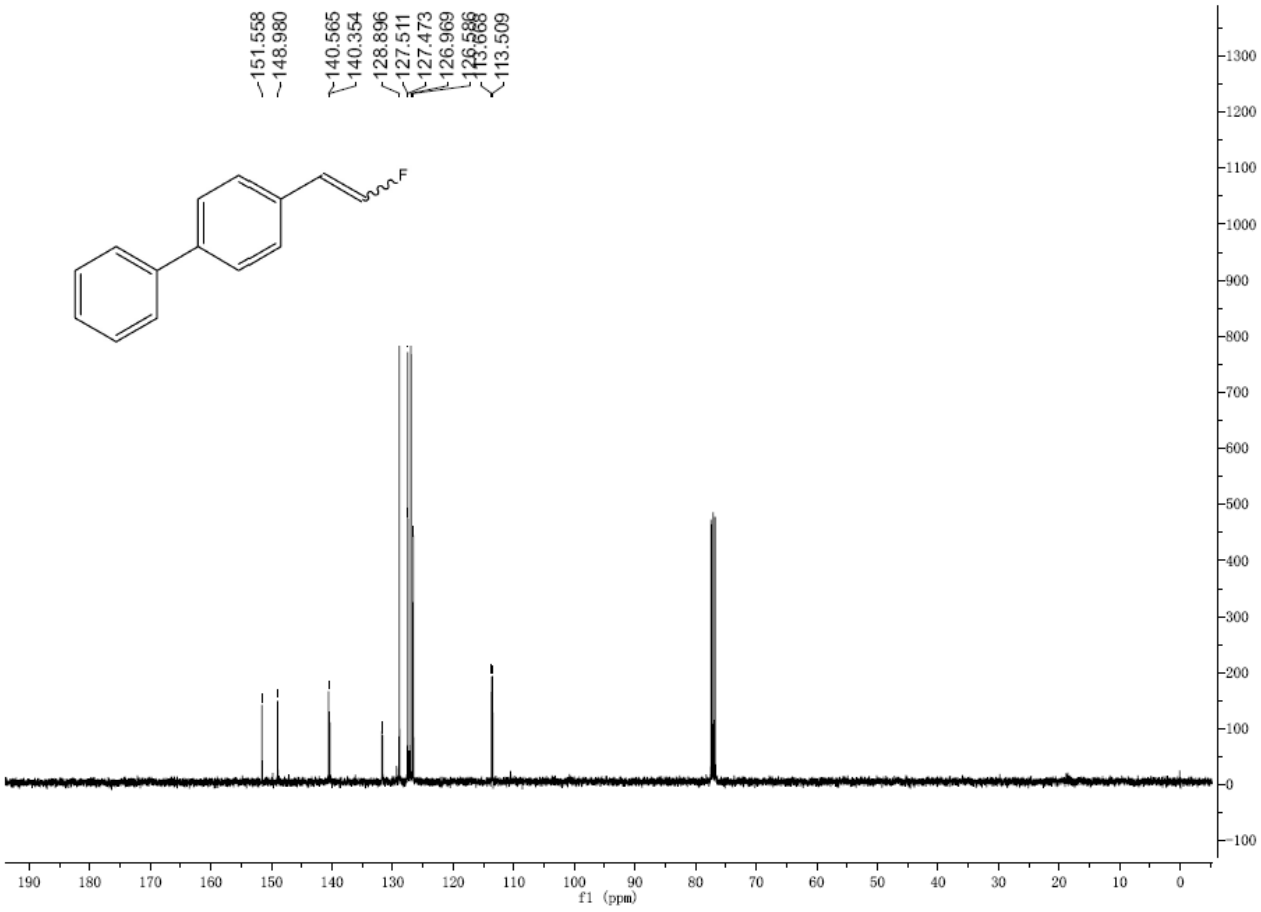
^{19}F NMR spectra of ***E***/***Z*-2m**



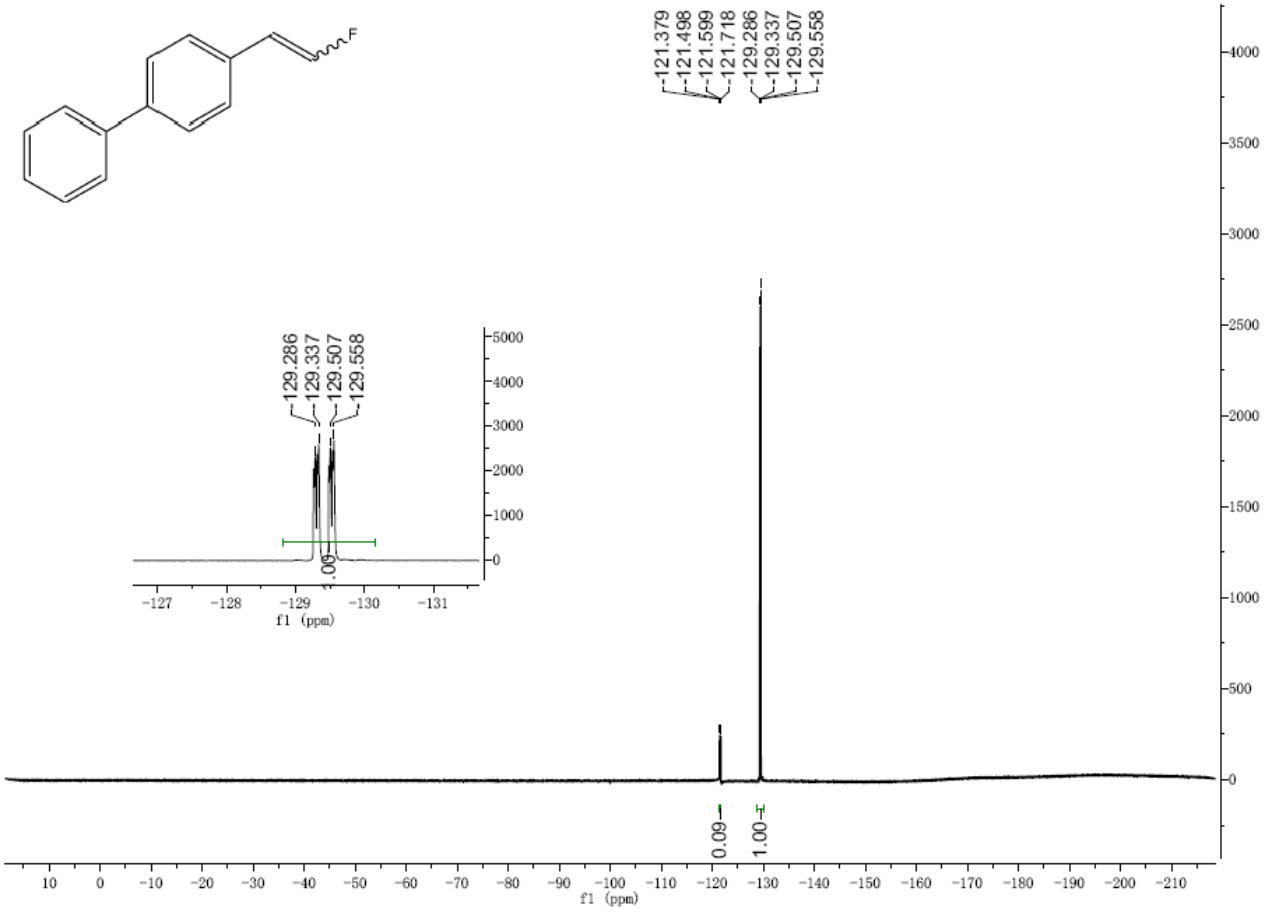
^{1}H NMR spectra of ***E*/*Z*-2n**



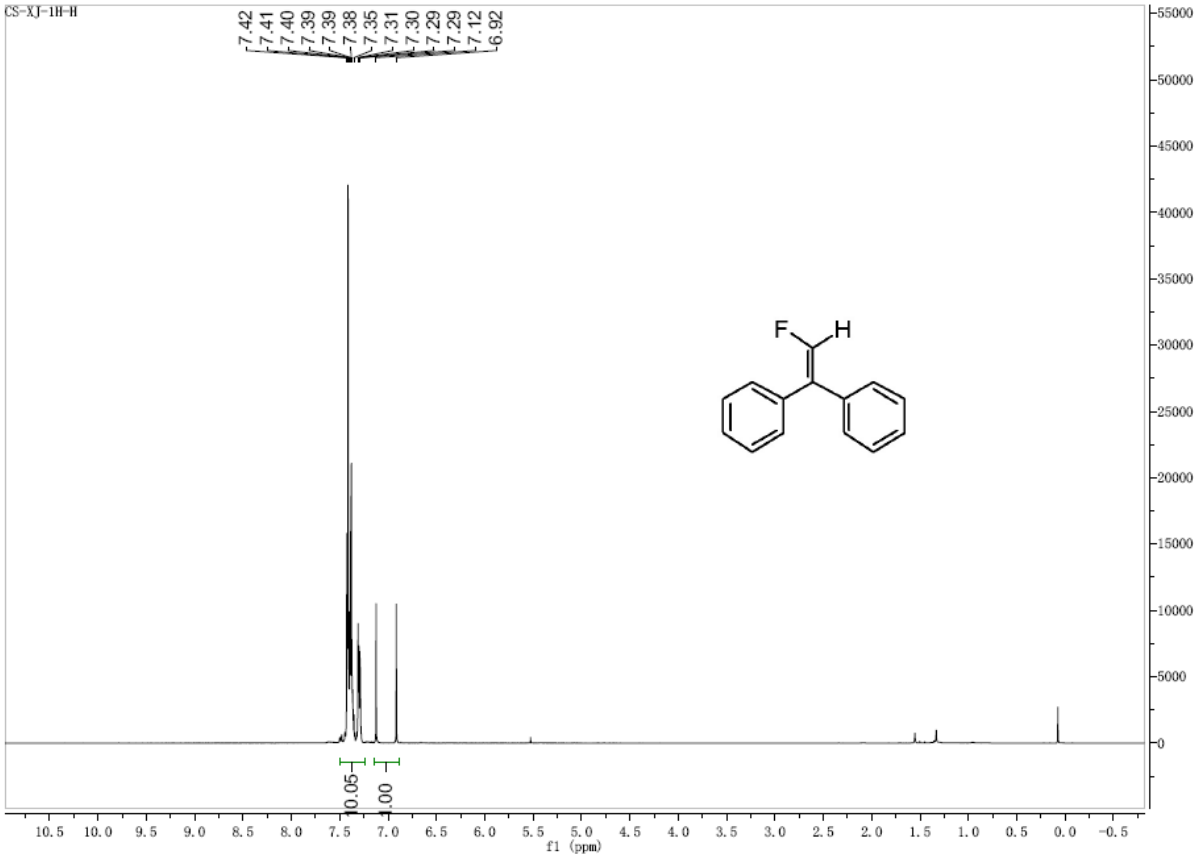
^{13}C NMR spectra of ***E*/*Z*-2n**



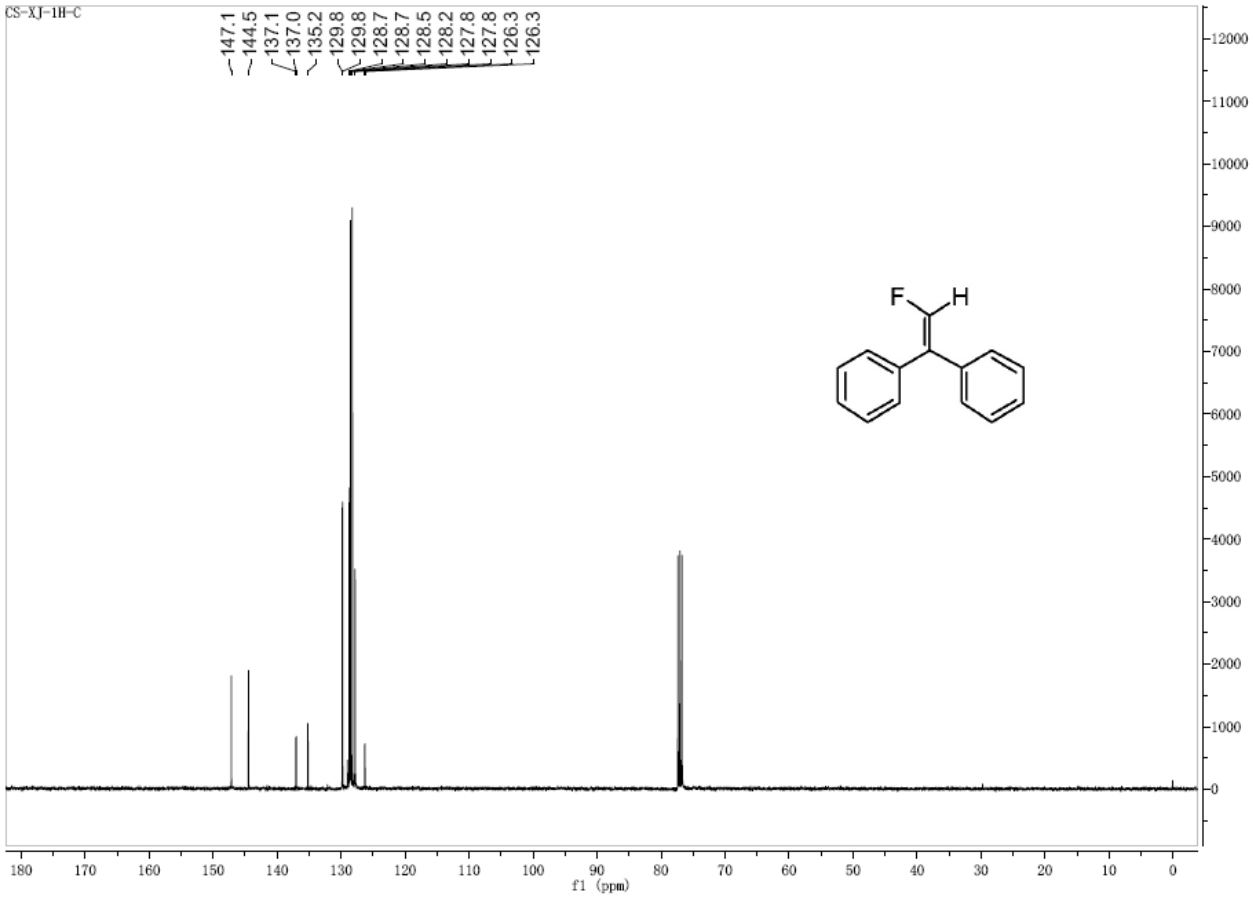
^{19}F NMR spectra of ***E***/***Z***-**2n**



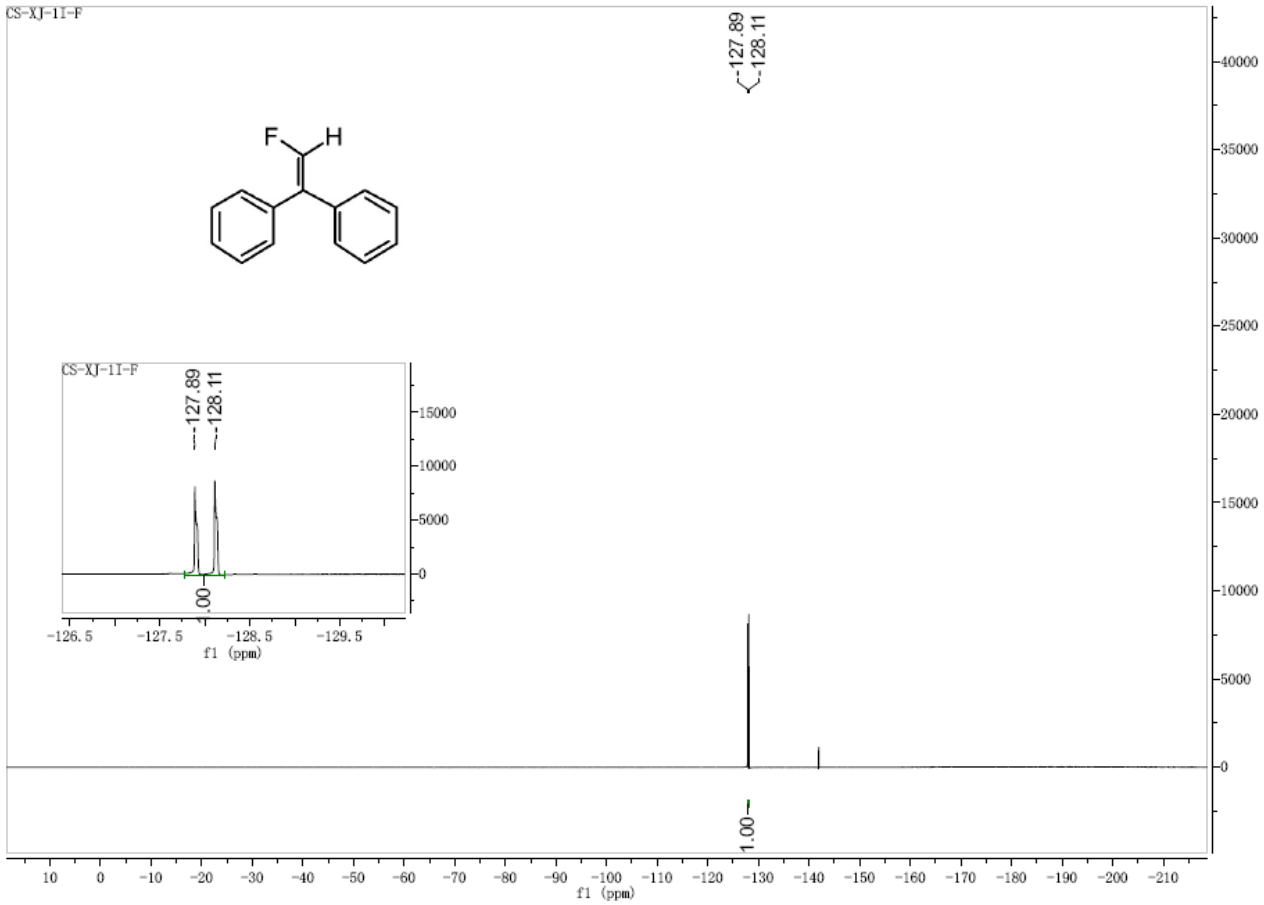
^{1}H NMR spectra of ***E*/*Z*-2o**



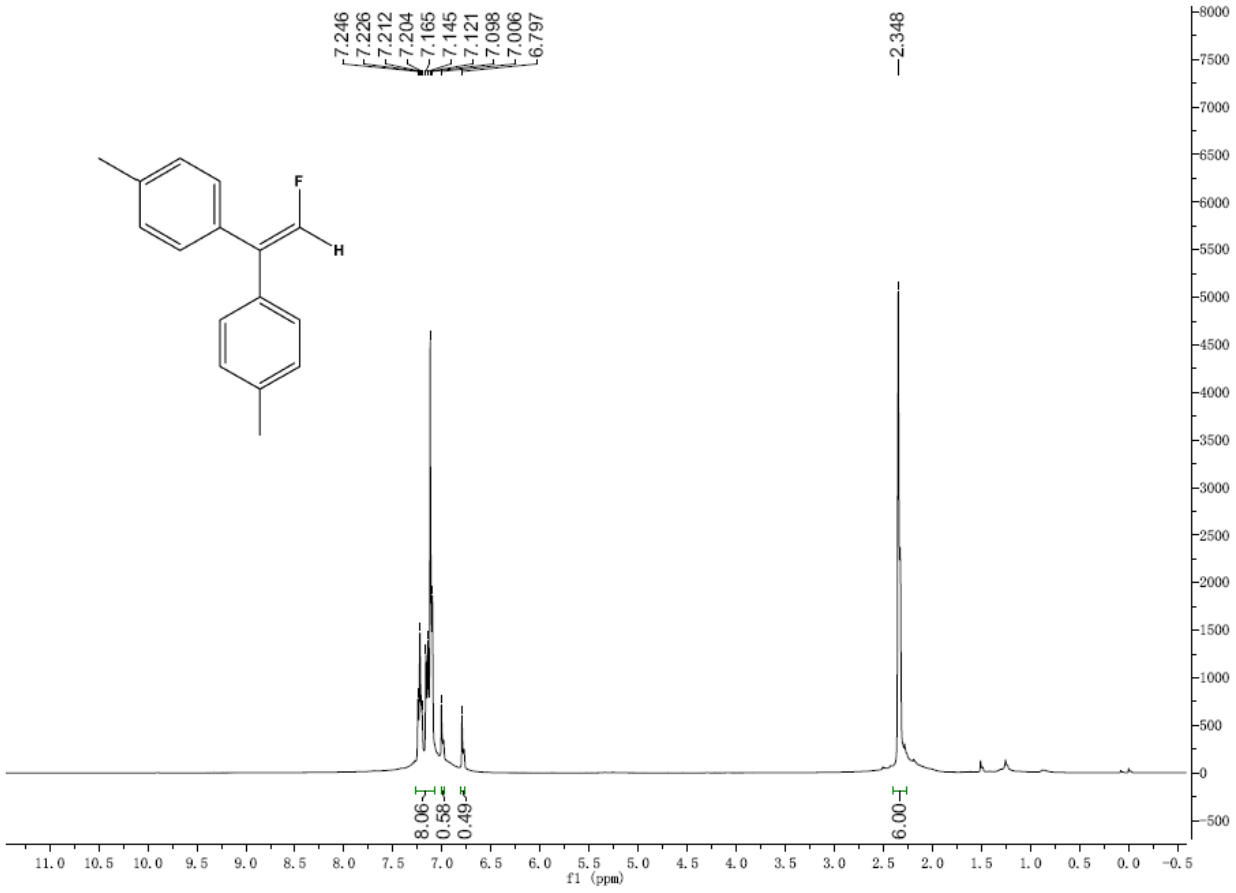
^{13}C NMR spectra of ***E*/*Z*-2o**



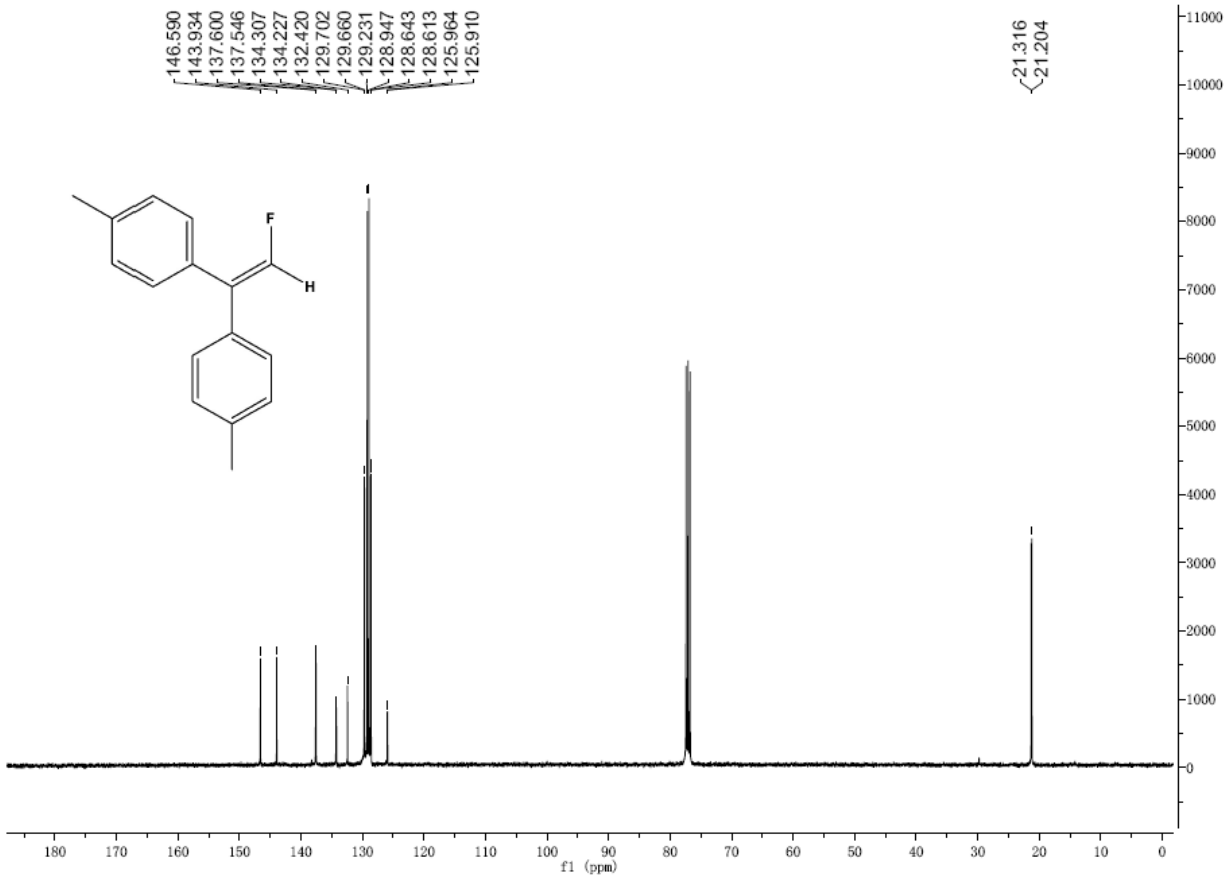
^{19}F NMR spectra of ***E*/*Z*-2o**



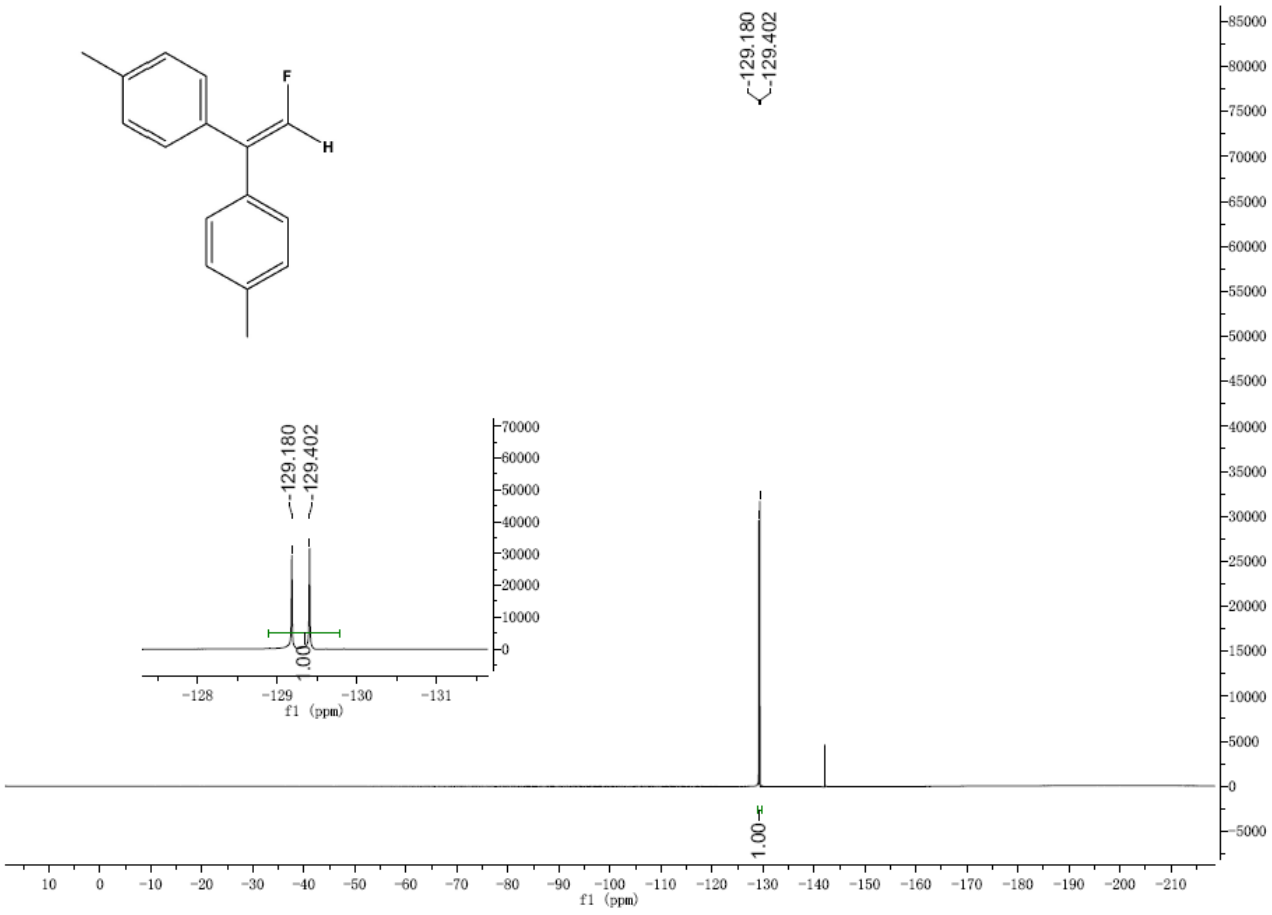
^{1}H NMR spectra of ***E*/*Z*-2p**



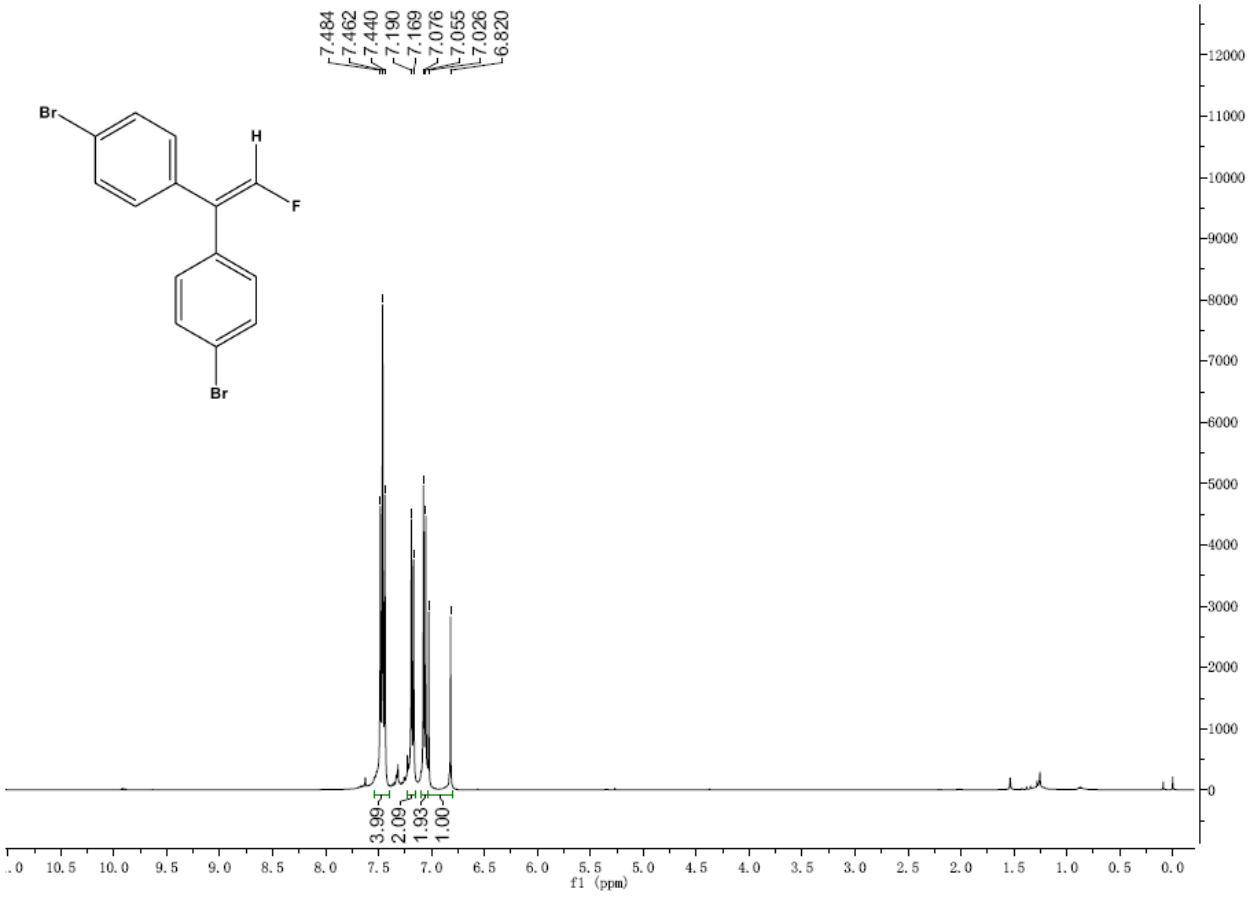
^{13}C NMR spectra of ***E*/*Z*-2p**



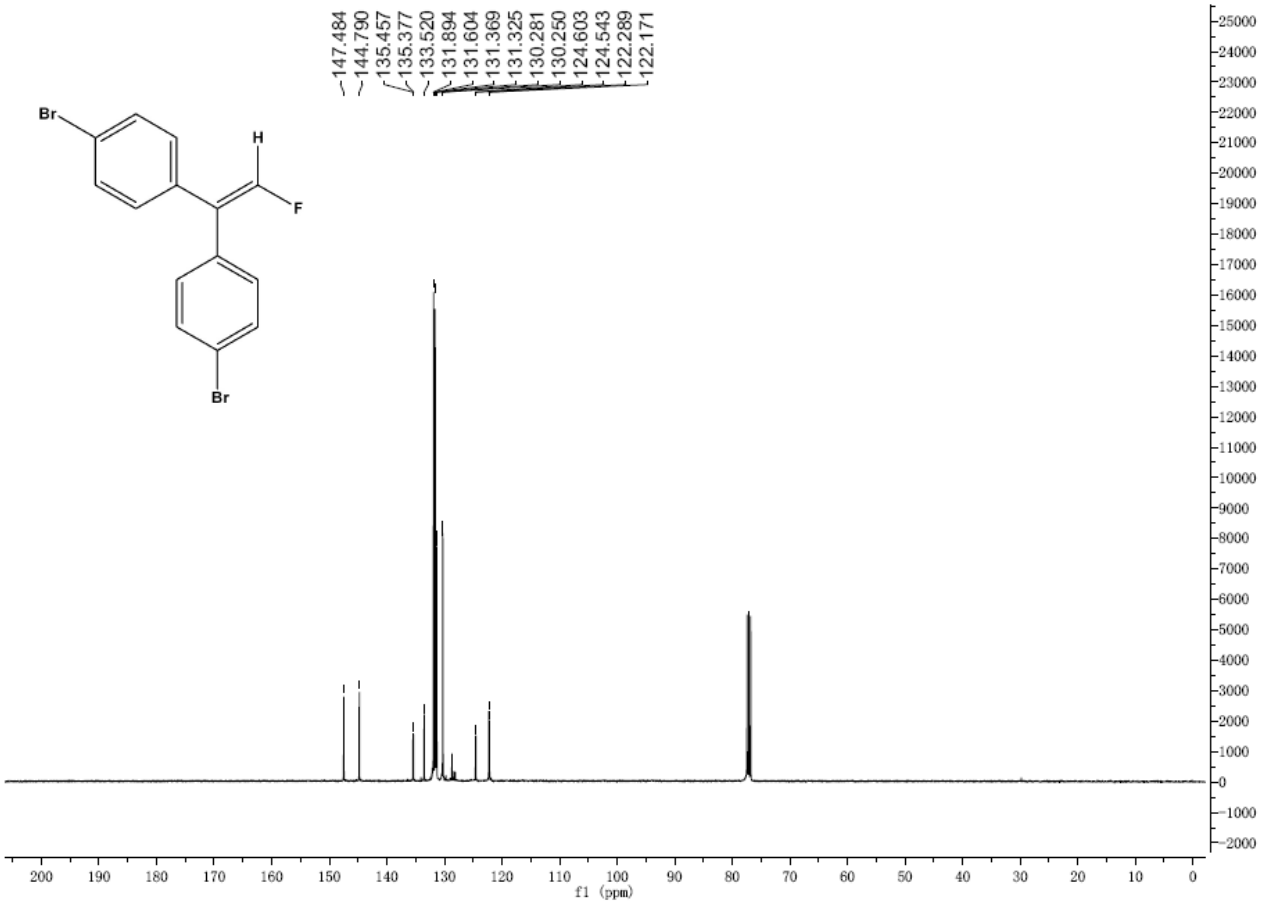
^{19}F NMR spectra of ***E*/*Z*-2p**



[1]H NMR spectra of ***E*/*Z*-2q**



[13]C NMR spectra of ***E*/*Z*-2q**



^{19}F NMR spectra of ***E***/***Z*-2q**