Electronic Supplementary Information

Synthesis of Di/trifluoromethyl Cyanocyclopropane-dicarbonitriles via [2+1] Annulation of Fluoro-based Diazoethanes with (Alkylidene)malononitriles

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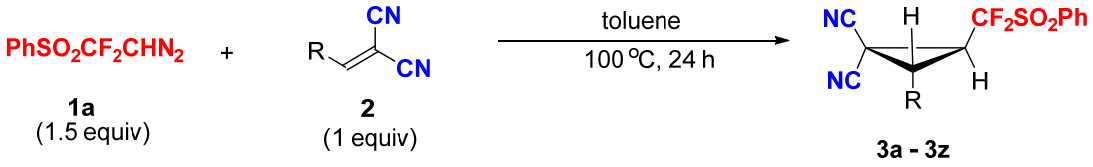
General Considerations

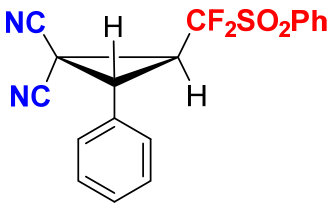
General Analytical Information. ^{1}H, ^{13}C and ^{19}F were recorded on JEOL AV 400 MHz instrument at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), and 376 MHz (^{19}F NMR). ^{1}H, ^{13}C and ^{19}F were recorded on Bruker AV 500 MHz instrument at 500 MHz (^{1}H NMR), 126 MHz (^{13}C NMR), and 470 MHz (^{19}F NMR).All ^{1}H NMR spectra were measured in parts per million (ppm) downfield from tetramethylsilane (TMS, 0 ppm) as internal standard or were measured relative to the residual proton signals of chloroform-*d* ($CDCl_3$, 7.26 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual carbon signals of $CHCl_3$ (77.16 ppm) and were obtained with ^{1}H decoupling. All ^{19}F NMR spectra were measured in parts per million (ppm) from trichlorofluoromethane (CCl_3F, 0 ppm) as external standard and were obtained with ^{1}H decoupling. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker micrOTOF-QII instrument. X-ray crystallographic analysis was conducted on a Bruker APEX-II CCD instrument.

General Reagents Information. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone prior to use. Dicloromethane (CH_2Cl_2) was distilled from CaH_2. Dried acetonitrile (MeCN), 1,4-dioxane, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were commercially available and used without further purifications. All reagents were commercially available and used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. The $PhSO_2CF_2CHN_2$ (**1a**) and a stock solution of CF_3CHN_2 (**1b**) in toluene were prepared according to the known procedures.[1,2] (**Cautions**: **1a** and **1b** are potentially explosive compound! They should be handled with care when synthesizing them or transferring them into the reaction tubes.) Dihydropyrazole **4a'** was prepared according to the literature procedure.[3]

General Procedure for the Preparation of Difluoromethyl Cyclopropane-1,1-dicarbonitrile 3



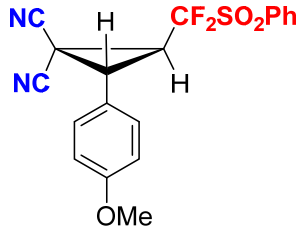
To a Teflon screw-capped Schlenk tube with a magnetic stirring bar, benzylidenemalononitrile (**2**, 0.2 mmol), $PhSO_2CF_2CHN_2$ (**1a**, 69.6 mg, 0.3 mmol, 1.5 equiv), and dry toluene (2 mL) were added. The tube was heated at 100 °C under an air atmosphere in a preheated heat block for 24 hours. At this point, the reaction was completed as monitored by TLC analysis. The reaction mixture was concentrated *in vacuo* with the aid of rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10/1) to give the product **3**.



3a

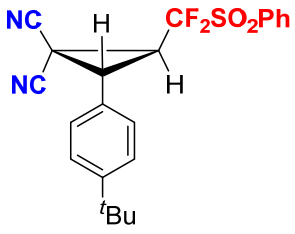
2-(Difluoro(phenylsulfonyl)methyl)-3-phenylcyclopropane-1,1-dicarbonitrile (3a): white solid; 65.2 mg; 91% yield; **M.p.**: 157-158 °C; R_f = 0.20 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.95 - 7.81 (m, 1H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 2.3 Hz, 3H), 7.44 (dd, *J* = 6.8, 2.9 Hz, 2H), 3.67 (d, *J* = 8.5 Hz, 1H), 3.37 (ddd, *J* = 17.1, 8.5, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.5, 131.1, 130.9, 130.2, 129.9, 129.5, 128.6, 128.2, 119.2 (dd, *J* = 290.6, 288.4 Hz), 110.9, 110.8, 36.6 (dd, *J* = 5.3, 2.7 Hz), 31.1 (t, *J* = 23.5 Hz), 10.3 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.63 (dd, *J* = 234.3, 5.2 Hz, 1F), -108.07 (dd, *J* = 234.3, 17.1 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{12}N_2O_2F_2NaS$ 381.0485, found

381.0484.



3b

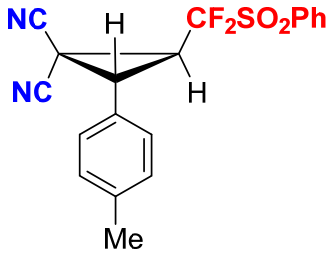
2-(Difluoro(phenylsulfonyl)methyl)-3-(4-methoxyphenyl)cyclopropane-1,1-dicarbonitrile (3b): white solid; 75.2 mg; 97% yield; **M.p.**: 149-150 °C; R_f = 0.10 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.59 (d, *J* = 8.4 Hz, 1H), 3.28 (ddd, *J* = 17.4, 8.5, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 136.6, 131.2, 130.8, 130.0, 129.9, 120.0, 119.2 (dd, *J* = 290.7, 288.3 Hz), 115.0, 111.2, 111.1, 55.5, 36.6 (dd, *J* = 5.4, 2.8 Hz), 31.3 (dd, *J* = 24.1, 22.5 Hz), 10.4 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.45 (dd, *J* = 234.1, 6.3 Hz, 1F), -108.07 (dd, *J* = 234.0, 17.6 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{19}H_{14}N_2O_3F_2NaS$ 411.0591, found 411.0590.



3c

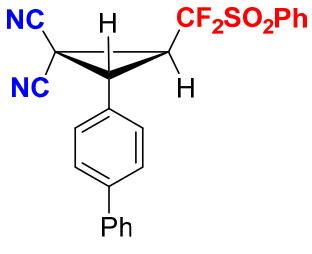
2-(4-(*Tert*-butyl)phenyl)-3(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3c): white solid; 60.4 mg; 73% yield; **M.p.**: 153-154 °C; R_f = 0.30 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 3.60 (d, *J* = 8.5 Hz, 1H), 3.32 (ddd, *J* = 17.0, 8.5, 5.6 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.6, 136.6, 131.2, 130.9, 129.9, 128.3, 126.6, 125.1, 119.2 (dd, *J* = 290.6, 288.2 Hz), 111.1, 111.1, 36.6 (dd, *J* = 5.3, 2.8 Hz), 34.9, 31.2, 31.2 (dd, *J* =

24.0, 22.8 Hz), 10.4 (t, J = 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.58 (dd, J = 234.2, 4.7 Hz, 1F), -107.95 (dd, J = 234.2, 17.0 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{22}H_{20}N_2O_2F_2NaS$ 437.1111, found 437.1108.



3d

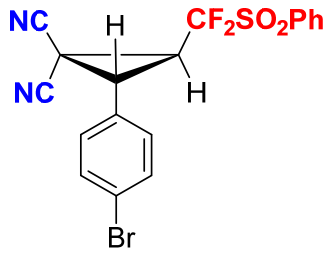
2-(Difluoro(phenylsulfonyl)methyl)-3-(*p*-tolyl)cyclopropane-1,1-dicarbonitrile (3d): white solid; 61.0 mg; 82% yield; **M.p.**: 171-172 °C; R_f = 0.20 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.9 Hz, 2H), 7.84 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 9.0 Hz, 4H), 3.60 (d, J = 8 .5 Hz, 1H), 3.31 (ddd, J = 17.0, 8.4, 5.5 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 136.6, 131.2, 130.9, 130.3, 130.0, 128.5, 125.2, 119.2 (dd, J = 290.6, 288.2 Hz), 111.1, 111.1, 36.7 (dd, J = 5.3, 2.8 Hz), 31.1 (dd, J = 24.1, 22.7 Hz), 21.4, 10.4 (t, J = 2.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.56 (dd, J = 234.3, 5.2 Hz, 1F), -107.93 (dd, J = 234.2, 17.1 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{19}H_{14}N_2O_2F_2NaS$ 395.0642, found 395.0649.



3e

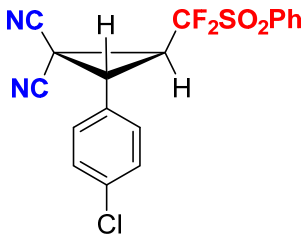
2-([1,1'-Biphenyl]-4-yl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3e): white solid; 80.4 mg; 88% yield; **M.p.**: 189-190 °C; R_f = 0.26 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 2H), 7.84 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 8.0 Hz, 4H), 7.59 (d, J = 7.3 Hz, 2H), 7.51 - 7.43 (m, 4H), 7.39 (t,

J = 7.3 Hz, 1H), 3.69 (d, *J* = 8.5 Hz, 1H), 3.39 (ddd, *J* = 17.1, 8.4, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 139.8, 136.7, 131.2, 130.8, 130.0, 129.1, 129.0, 128.2, 128.1, 127.3, 127.1, 119.2 (dd, *J* = 290.8, 288.4 Hz), 111.1, 111.0, 36.6 (dd, *J* = 5.4, 2.7 Hz), 31.2 (dd, *J* = 24.2, 22.6 Hz), 10.5 (t, *J* = 2.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.45 (dd, *J* = 234.1, 4.8 Hz, 1F), -108.04 (dd, *J* = 234.1, 17.1 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{24}H_{16}N_2O_2F_2NaS$ 457.0798, found 457.0799.



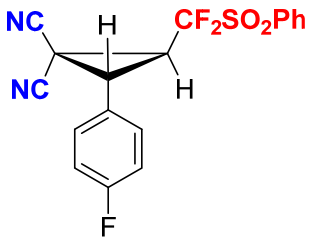
3f

2-(4-Bromophenyl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3f): white solid; 76.6 mg; 88% yield; **M.p.**: 167-168 ºC; R_f = 0.28 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.59 (d, *J* = 8.5 Hz, 1H), 3.28 (ddd, *J* = 17.5, 8.4, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 132.9, 131.2, 130.6, 130.3, 130.0, 127.4, 124.8, 119.1 (dd, *J* = 291.0, 288.5 Hz), 110.8, 110.7, 36.1 (dd, *J* = 5.5, 2.8 Hz), 31.2 (dd, *J* = 24.6, 22.2 Hz), 10.1 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.31 (dd, *J* = 233.7, 4.5 Hz, 1F), -108.54 (dd, *J* = 233.7, 17.6 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{12}N_2O_2F_2SBr$ 436.9771, found 436.9769.



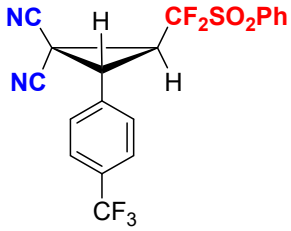
3g

2-(4-Chlorophenyl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3g): white solid; 66.6 mg; 85% yield; **M.p.**: 168-170 ºC; R_f = 0.20 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 3.62 (d, *J* = 8.5 Hz, 1H), 3.29 (ddd, *J* = 17.5, 8.4, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 136.6, 131.2, 130.6, 130.1, 130.0, 129.9, 126.8, 119.1 (dd, *J* = 291.7, 289.0 Hz), 110.8, 110.7, 36.0 (dd, *J* = 5.5, 2.9 Hz), 31.3 (dd, *J* = 24.6, 22.2 Hz), 10.2 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.28 (dd, *J* = 233.7, 4.0 Hz, 1F), -108.57 (dd, *J* = 233.5, 17.6 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{12}N_2O_2F_2SCl$ 393.0276, found 393.0282.



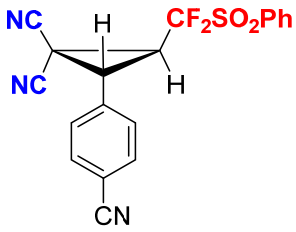
3h

2-(Difluoro(phenylsulfonyl)methyl)-3-(4-fluorophenyl)cyclopropane-1,1-dicarbonitrile (3h): white solid; 69.9 mg; 93% yield; **M.p.**: 187-189 ºC; R_f = 0.20 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.86 (t, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 2H), 7.42 (dd, *J* = 8.5, 5.0 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 3.63 (d, *J* = 8.4 Hz, 1H), 3.29 (ddd, *J* = 17.7, 8.4, 4.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7 (d, *J* = 251.2 Hz), 136.7, 131.2, 130.8 (d, *J* = 8.7 Hz), 130.6, 130.0, 124.2 (d, *J* = 3.3 Hz), 119.1 (dd, *J* = 291.0, 288.5 Hz), 116.9 (d, *J* = 22.2 Hz), 110.9, 110.8, 36.1 (dd, *J* = 5.5, 2.8 Hz), 31.4 (dd, *J* = 24.4, 22.1 Hz), 10.2 (t, *J* = 1.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.21 (dd, *J* = 233.6, 4.4 Hz, 1F), -108.55 (dd, *J* = 233.7, 17.6 Hz, 1F), -109.28 - 109.71 (m, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{12}N_2O_2F_3S$ 377.0572, found 377.0584.



3i

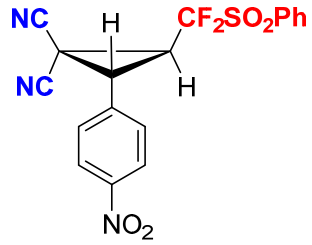
2-(Difluoro(phenylsulfonyl)methyl)-3-(4-(trifluoromethyl)phenyl) cyclopropane-1,1-dicarbonitrile (3i): white solid; 72.4 mg; 85% yield; **M.p.**: 166-167 ºC; R_f = 0.30 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.69 (t, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 3.71 (d, *J* = 8.5 Hz, 1H), 3.36 (ddd, *J* = 17.6, 8.5, 4.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 132.7, 132.3, 131.2, 130.5, 130.0, 129.4, 126.7 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.6 Hz), 119.0 (dd, *J* = 291.2, 288.7 Hz), 110.7, 110.6, 35.9 (dd, *J* = 5.5, 2.8 Hz), 31.2 (dd, *J* = 24.8, 22.1 Hz), 10.1 (t, *J* = 2.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.85 (s, 3F) -102.29 (dd, *J* = 233.3, 3.9 Hz, 1F), -108.77 (dd, *J* = 233.4, 17.6 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{19}H_{12}N_2O_2F_5S$ 427.0540, found 427.0538.



3j

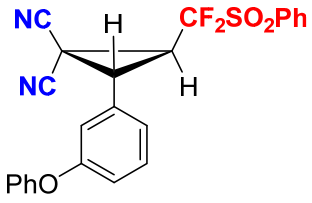
2-(4-Cyanophenyl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3j): white solid; 68.4 mg; 89% yield; **M.p.**: 186-188 ºC; R_f = 0.10 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (t, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 3.71 (d, *J* = 8.5 Hz, 1H), 3.34 (ddd, *J* = 17.8, 8.5, 4.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 133.4, 133.3, 131.2, 130.4, 130.1, 129.7, 118.9 (dd, *J* = 291.5, 288.7 Hz), 117.7, 114.5, 110.6, 110.3, 35.9 (dd, *J* = 5.7, 2.9 Hz), 31.2 (dd, *J* = 25.1, 21.9 Hz),

10.1 (t, J = 2.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.19 (dd, J = 233.1, 3.7 Hz, 1F), -109.04 (dd, J = 233.2, 17.8 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{19}H_{12}N_3O_2F_2S$ 384.0618, found 384.0614.



3k

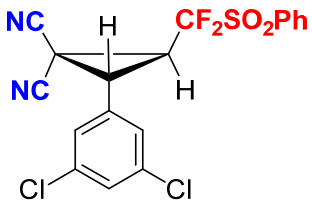
2-(Difluoro(phenylsulfonyl)methyl)-3-(4-nitrophenyl)cyclopropane-1,1-dicarbonitrile (3k): white solid; 70.1 mg; 87% yield; **M.p.**: 194-196 °C; R_f = 0.20 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.8 Hz, 2H), 8.03 (d, J = 7.2 Hz, 2H), 7.95 - 7.81 (m, 1H), 7.69 (dd, J = 18.3, 7.5 Hz, 4H), 3.74 (d, J = 7.9 Hz, 1H), 3.36 (ddd, J = 11.4, 6.2, 2.1 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 148.6, 137.6, 137.0, 131.1, 131.1, 131.0, 130.9, 124.2, 120.0 (dd, J = 289.3, 288.2 Hz), 111.9, 111.6, 35.0 (dd, J = 5.5, 2.4 Hz), 30.4 (t, J = 22.9 Hz), 11.9 (t, J = 2.8 Hz). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -103.54 (dd, J = 233.5, 6.5 Hz, 1F), -105.18 (dd, J = 233.6, 16.7 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{11}N_3O_4SF_2Na$ 426.0336, found 426.0338.



3l

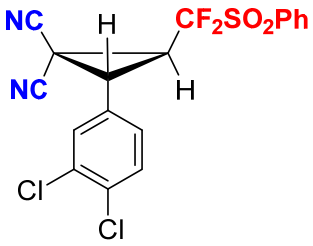
2-(Difluoro(phenylsulfonyl)methyl)-3-(3-phenoxyphenyl)cyclopropane-1,1-dicarbonitrile (3l): white solid; 88.2 mg; 98% yield; **M.p.**: 131-132 °C; R_f = 0.31 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 2H), 7.84 (t, J = 7.8 Hz, 1H), 7.66 (t, J = 7.8 Hz, 2H), 7.40 (dd, J = 15.3, 11.7 Hz, 3H), 7.17 (t, J = 7.8 Hz,

1H), 7.11 (d, *J* = 6.9 Hz, 1H), 7.09 - 7.01 (m, 4H), 3.60 (d, *J* = 8.5 Hz, 1H), 3.30 (ddd, *J* = 17.1, 8.4, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 156.2, 136.7, 131.2, 131.1, 130.8, 130.2, 130.0, 130.0, 124.3, 122.8, 120.2, 119.6, 119.1 (dd, *J* = 290.8, 288.4 Hz), 118.6, 111.0, 110.9, 36.4 (dd, *J* = 5.4, 2.8 Hz), 31.1 (dd, *J* = 24.3, 22.6 Hz), 10.4 (t, *J* = 2.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.79 (d, *J* = 17.2 Hz, 1F), -108.41 (d, *J* = 17.1 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{24}H_{16}N_2O_3SF_2Na$ 473.0747, found 473.0750



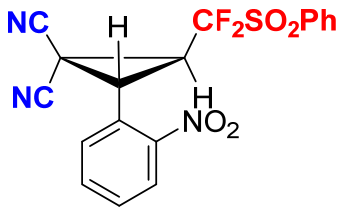
3m

2-(3,5-Dichlorophenyl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3m): white solid; 74.1 mg; 87% yield; **M.p.**: 169-170 °C; R_f = 0.34 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 2H), 3.60 (d, *J* = 8.4 Hz, 1H), 3.31 (ddd, *J* = 17.1, 8.4, 5.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 136.4, 131.5, 131.2, 131.1, 130.5, 130.0, 127.3, 118.9 (dd, *J* = 291.5, 288.7 Hz), 110.5, 110.4, 35.2 (dd, *J* = 5.9, 3.0 Hz), 31.0 (dd, *J* = 25.1, 22.3 Hz), 10.3 (t, *J* = 2.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.59 (dd, *J* = 233.9, 4.9 Hz, 1F), -108.43 (dd, *J* = 233.9, 17.0 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{10}N_2O_2F_2NaSCl_2$ 448.9706, found 448.9706.



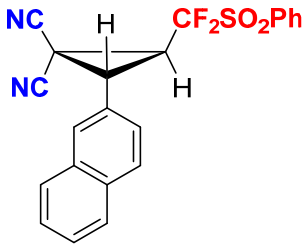
3n

2-(3,4-Dichlorophenyl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3n): white solid; 73.4 mg; 86% yield; **M.p.**: 160-162 ºC; R_f = 0.28 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.33 - 7.19 (m, 1H), 3.61 (d, *J* = 8.4 Hz, 1H), 3.30 (ddd, *J* = 17.2, 8.2, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 135.1, 134.0, 131.7, 131.2, 130.9, 130.5, 130.0, 128.4, 127.8, 119.0 (dd, *J* = 291.4, 288.8 Hz), 110.7, 110.5, 35.3 (dd, *J* = 5.7, 2.9 Hz), 31.2 (dd, *J* = 24.9, 22.2 Hz), 10.2 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.42 (dd, *J* = 233.6, 4.3 Hz, 1F), -108.59 (dd, *J* = 233.6, 17.4 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{10}N_2O_2F_2NaSCl_2$ 448.9706, found 448.9701.



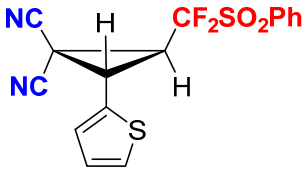
3o

2-(Difluoro(phenylsulfonyl)methyl)-3-(2-nitrophenyl)cyclopropane-1,1-dicarbonitrile (3o): white solid; 65.3 mg; 81% yield; **M.p.**: 158-160 ºC; R_f = 0.17 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 9.1 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.70 (dt, *J* = 11.3, 7.2 Hz, 4H), 4.10 (d, *J* = 8.6 Hz, 1H), 3.44 (ddd, *J* = 18.8, 8.6, 3.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 136.9, 135.3, 131.8, 131.2, 131.2, 130.4, 130.0, 126.5, 125.1, 119.2 (dd, *J* = 291.2, 289.0 Hz), 111.0, 110.4, 35.8 (dd, *J* = 6.1, 3.0 Hz), 32.2 (dd, *J* = 25.3, 21.1 Hz), 10.9 (dd, *J* = 2.7, 1.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.39 (d, *J* = 232.7 Hz, 1F), -109.13 (dd, *J* = 232.7, 18.7 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{11}N_3O_4SF_2Na$ 426.0336, found 426.0343.



3p

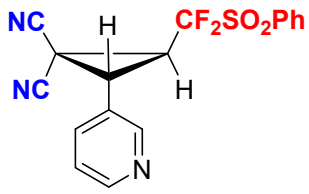
2-(Difluoro(phenylsulfonyl)methyl)-3-(naphthalen-2-yl)cyclopropane-1,1-dicarbonitrile (3p): white solid; 70.2 mg; 86% yield; **M.p.**: 142-144 °C; R_f = 0.20 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.87 (ddd, *J* = 22.1, 15.8, 8.0 Hz, 5H), 7.65 (t, *J* = 7.9 Hz, 2H), 7.56 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.47 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.81 (d, *J* = 8.5 Hz, 1H), 3.51 (ddd, *J* = 16.9, 8.4, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.6, 133.8, 133.1, 131.2, 130.8, 130.0, 129.8, 128.5, 128.3, 128.0, 127.6, 127.3, 125.6, 125.2, 119.3 (dd, *J* = 290.7, 288.3 Hz), 111.1, 111.1, 37.0 (dd, *J* = 5.3, 2.8 Hz), 31.3 (dd, *J* = 24.1, 22.8 Hz), 10.5 (t, *J* = 2.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.5 (dd, *J* = 234.3, 4.6 Hz, 1F), -107.77 (dd, *J* = 234.3, 17.1 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{22}H_{14}N_2O_2SF_2Na$ 431.0642 found 431.0648.



3q

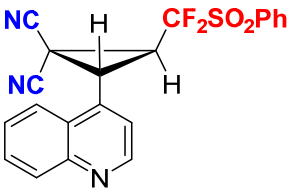
2-(Difluoro(phenylsulfonyl)methyl)-3-(thiophen-2-yl)cyclopropane-1,1-dicarbonitrile (3q): white solid; 65.5 mg; 90% yield; **M.p.**: 123-124 °C; R_f = 0.28 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.90 - 7.80 (m, 1H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 7.14 - 7.02 (m, 1H), 3.71 (d, *J* = 8.2 Hz, 1H), 3.32 (ddd, *J* = 16.2, 7.8, 6.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 131.2, 130.7, 130.4, 130.0, 129.2, 128.7, 127.9, 118.9 (dd, *J* = 291.0, 288.6 Hz), 110.8, 110.5, 32.2 (dd, *J* = 5.8, 3.1 Hz), 11.7 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.26 (dd, *J* = 235.0, 5.4 Hz, 1F), -107.80 (dd, *J* = 235.0,

16.7 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{16}H_{10}N_2O_2S_2F_2Na$ 387.0049, found 387.0045.



3r

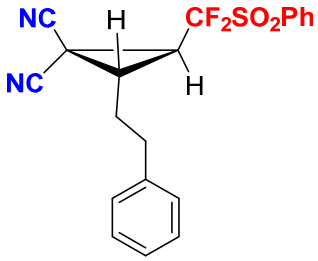
2-(Difluoro(phenylsulfonyl)methyl)-3-(pyridin-3-yl)cyclopropane-1,1-dicarbonitrile (3r): white solid; 46.0 mg; 64% yield; **M.p.**: 126-127 ºC; R_f = 0.12 (PE/EA = 2/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 16.8 Hz, 2H), 8.01 (d, *J* = 5.9 Hz, 2H), 7.83 (d, *J* = 6.4 Hz, 1H), 7.77 - 7.55 (m, 3H), 7.41 (d, *J* = 3.4 Hz, 1H), 3.65 (d, *J* = 7.6 Hz, 1H), 3.37 (ddd, *J* = 24.5, 12.0, 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 150.3, 136.8, 135.9, 131.2, 130.5, 130.0, 124.8, 124.1, 119.0 (dd, *J* = 291.3, 288.6 Hz), 110.7, 110.5, 34.1 (dd, *J* = 5.6, 2.9 Hz), 30.8 (dd, *J* = 24.8, 22.3 Hz), 10.1 (t, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.55 (d, *J* = 233.9 Hz, 1F), -108.58 (dd, *J* = 233.5, 17.0 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{17}H_{12}N_3O_2SF_2$ 360.0618, found 360.0620.



3s

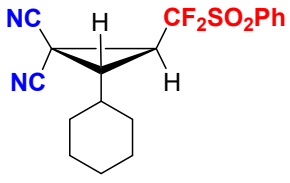
2-(Difluoro(phenylsulfonyl)methyl)-3-(quinolin-4-yl)cyclopropane-1,1-dicarbonitrile (3s): white solid; 62.2 mg; 76% yield; **M.p.**: 207-209 ºC; R_f = 0.14 (PE/EA = 2/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.03 (dd, *J* = 18.9, 7.7 Hz, 3H), 7.79 (ddd, *J* = 39.4, 14.1, 6.8 Hz, 5H), 7.45 (s, 1H), 4.04 (d, *J* = 8.1 Hz, 1H), 3.55 (ddd, *J* = 10.7, 7.2, 3.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 148.4, 136.9, 134.2, 131.2, 131.1, 130.8, 130.4, 130.1, 128.9, 126.5, 123.5 (dd, *J* = 159.6, 158.9 Hz), 122.1, 120.7, 110.6, 110.3, 34.1 (dd, *J* = 5.7, 2.5 Hz),

30.6 (dd, *J* = 25.2, 21.8 Hz), 10.1 (t, *J* = 3.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.77 (d, *J* = 233.0 Hz, 1F), -108.66 (dd, *J* = 233.0, 17.7 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{21}H_{14}N_3O_2SF_2$ 410.0775, found 410.0776.



3t

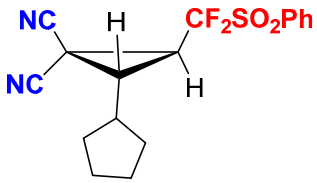
2-(difluoro(phenylsulfonyl)methyl)-3-phenethylcyclopropane-1,1-dicarbonitrile (3t) colourless liquid; 61.8mg; 80% yield; R_f = 0.61 (PE/EA = 10/1)**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 6.2 Hz, 3H), 2.94 (h, *J* = 7.0 Hz, 2H), 2.70 (ddd, *J* = 17.1, 8.2, 5.9 Hz, 1H), 2.35 (q, *J* = 7.2 Hz, 1H), 2.17 (dq, *J* = 14.5, 6.6 Hz, 1H), 2.04 (dq, *J* = 15.0, 7.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.9, 136.5, 131.1, 130.8, 129.8, 129.0, 128.5, 120.2 (d, *J* = 287.7 Hz), 111.4, 110.9, 33.6, 32.7, 32.5, 32.4 (dd, *J* = 5.1, 2.8 Hz), 31.1, 8.2 (t, *J* = 2.8 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -102.40 (dd, *J* = 234.1, 6.1 Hz), -107.82 (dd, *J* = 234.5, 16.9 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{20}H_{17}F_2N_2O_2S$ 387.0979, found 387.1806.



3u

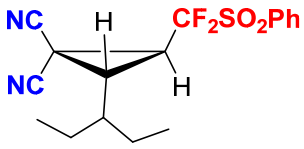
2-Cyclohexyl-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3u): white solid; 71.3 mg; 98% yield; **M.p.**: 129-130 ºC; R_f = 0.43 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 2H), 2.72 (ddd, *J* = 17.3, 8.1, 5.5 Hz, 1H), 2.20 (t, *J* = 8.3 Hz, 1H), 1.97 (d, *J* = 11.4 Hz, 2H), 1.82 (d, *J* = 9.7 Hz, 2H), 1.70 (d, *J* = 10.1 Hz, 1H), 1.42 - 1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 131.2, 131.0, 129.9, 119.1 (dd, *J* = 290.1, 287.6 Hz), 111.8, 111.2, 39.2, 38.5 (dd, *J* = 4.3, 2.0 Hz), 32.1 (t, *J* = 23.2 Hz), 31.5, 31.3, 25.7, 25.5, 25.3, 7.5 (t, *J* = 2.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.16 (dd, *J* = 234.6, 5.3 Hz, 1F), -107.88 (dd, *J* = 234.8, 17.4 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{18}N_2O_2SF_2Na$ 387.0955, found 387.0959.



3v

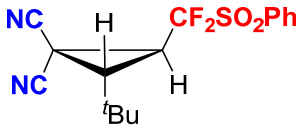
2-cyclopentyl-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3v) white solid; 60.9mg; 87% yield; **M.p.**: 116-118 ºC; R_f = 0.65 (PE/EA = 10/1)**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.2 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 2H), 2.75 (ddd, *J* = 17.7, 8.1, 5.3 Hz, 1H), 2.29 (t, *J* = 8.3 Hz, 1H), 2.17 – 2.05 (m, 1H), 2.05 – 1.93 (m, 1H), 1.90 – 1.72 (m, 3H), 1.74 – 1.63 (m, 3H), 1.62 – 1.49 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.4, 131.1, 130.9, 129.8, 120.2 (d, *J* = 287.7 Hz), 116.8, 111.9, 111.2, 40.8, 38.1 (dd, *J* = 4.6, 2.3 Hz), 32.66 (t, *J* = 23.0 Hz), 31.4, 31.2, 25.1 (d, *J* = 6.4 Hz), 7.9 (t, *J* = 2.8 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -101.43 (dd, *J* = 234.1, 6.1 Hz), -108.27 (dd, *J* = 234.3, 17.7 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{17}H_{17}F_2N_2O_2S$ 351.0979, found 351.0977.



3w

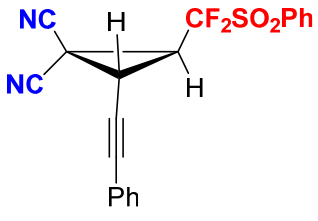
2-(difluoro(phenylsulfonyl)methyl)-3-(pentan-3-yl)cyclopropane-1,1-dicarbonitrile (3w) white solid; 59.8mg; 85% yield; **M.p.**: 64-67 ºC; R_f = 0.63 (PE/EA = 10/1)**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.96 – 7.77 (m, 1H), 7.68 (t, *J* = 7.9 Hz, 2H), 2.82 – 2.66 (m, 1H), 2.23 (t, *J* = 8.9 Hz, 1H), 1.85 – 1.66 (m,

2H), 1.66 – 1.54 (m, 2H), 1.34 (dq, J = 11.7, 6.0 Hz, 1H), 1.06 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.4, 131.1, 131.0, 129.8, 120.2 (d, J = 287.7 Hz), 112.0, 111.1, 41.6, 37.2 (dd, J = 4.1, 2.3 Hz), 31.8 (t, J = 23.0 Hz), 24.8, 24.6, 10.3 (d, J = 17.0 Hz), 8.6 (t, J = 3.2 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -102.30 (dd, J = 236.7, 7.8 Hz), -106.04 (dd, J = 235.8, 14.7 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{17}H_{19}F_2N_2O_2S$ 353.1135, found 353.1127.



3x

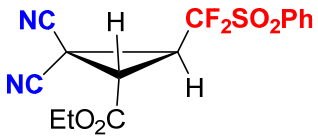
2-(*Tert*-butyl)-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1,1-dicarbonitrile (3x): white solid; 67.1 mg; 99% yield; **M.p.**: 92-94 ºC; R_f = 0.31 (PE/EA = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 2H), 7.83 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.9 Hz, 2H), 2.92 (ddd, J = 16.8, 9.2, 5.5 Hz, 1H), 2.26 (dd, J = 9.2, 1.4 Hz, 1H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.5, 131.1, 130.9, 129.9, 119.2 (dd, J = 290.0, 287.9 Hz), 112.2, 111.7, 43.6 (dd, J = 4.1, 1.9 Hz), 30.8, 30.25 (t, J = 23.4 Hz), 27.9, 5.5 (t, J = 2.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.35 (dd, J = 233.4, 5.2 Hz), -107.94 (dd, J = 233.5, 16.9 Hz). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{16}H_{16}N_2O_2SF_2Na$ 361.0798, found 361.0801.



3y

2-(difluoro(phenylsulfonyl)methyl)-3-(phenylethynyl)cyclopropane-1,1-dicarbonitrile (3y) yellow solid; 53.5mg; 70% yield; **M.p.**: 133-135 ºC; R_f = 0.53 (PE/EA = 10/1)**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.86 (t, J = 7.4 Hz, 1H), 7.70 (t, J = 7.9 Hz, 2H), 7.56 – 7.45 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 3.22 – 3.09 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.7, 132.3,

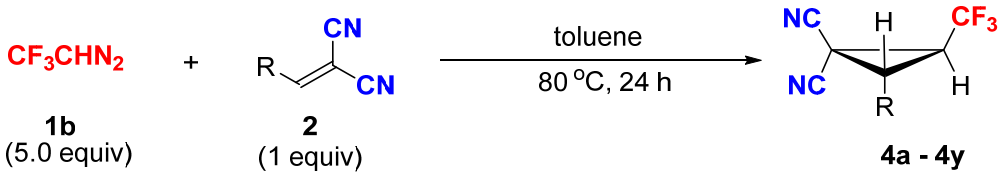
131.1, 130.8, 130.0, 129.9, 128.6, 120.3, 119.4 (d, J = 289.1 Hz), 110.7, 109.7, 87.2, 77.8, 33.4 (t, J = 23.9 Hz), 23.4 (dd, J = 6.4, 3.7 Hz), 11.2 (t, J = 2.8 Hz)..**^{19}F NMR** (470 MHz, $CDCl_3$) δ -104.98 (dd, J = 238.0, 6.5 Hz), -106.60 (dd, J = 238.4, 14.7 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{20}H_{13}F_2N_2O_2S$ 383.0666, found 383.0670.



3z

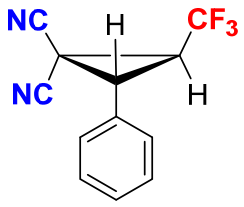
ethyl 2,2-dicyano-3-(difluoro(phenylsulfonyl)methyl)cyclopropane-1-carboxylate (3z) white solid; 53.1mg; 75% yield; **M.p.**: 129-131 ºC; R_f = 0.57 (PE/EA = 10/1)**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 2H), 7.87 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 8.0 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 3.82 – 3.16 (m, 1H), 3.07 (dd, J = 7.9, 1.3 Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.7, 136.7, 131.1, 130.6, 130.0, 119.6 (d, J = 288.6 Hz), 115.9, 109.5, 64.2, 31.1 (dd, J = 4.6, 1.8 Hz), 30.4, (t, J = 23.0 Hz), 14.0, 9.0 (t, J = 3.2 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -104.71 (dd, J = 238.0, 8.2 Hz), -106.37 (dd, J = 237.6, 14.7 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{15}H_{13}F_2N_2O_4S$ 355.0564, found 355.0563.

General Procedure for the Preparation of Trifluoromethyl Cyclopropane-1,1-dicarbonitrile 4



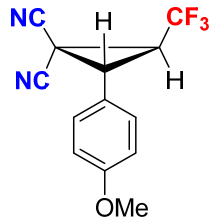
1b (5.0 equiv) **2** (1 equiv) **4a - 4y**

To a Teflon screw-capped Schlenk tube with a magnetic stirring bar, (alkylidene)malononitrile (**2**, 0.2 mmol) and a stock solution of CF_3CHN_2 (**1b,** 1.0 mmol) in toluene were added. The tube was heated at 80 °C under an air atmosphere in a preheated heat block for 24 hours. At this point, the reaction was completed as monitored by TLC analysis. The reaction mixture was concentrated *in vacuo* with the aid of rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 15/1) to give the product **4**.



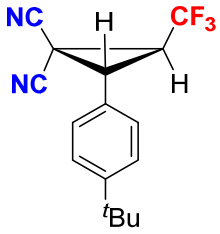
4a

2-Phenyl-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4a): white solid; 46.2 mg; 96% yield; **M.p.**: 100-102 °C; R_f = 0.31 (PE/EA = 4/1); **^{1}H NMR** (500 MHz, CDCl3) δ 7.53 – 7.44 (m, 3H), 7.37 – 7.29 (m, 2H), 3.63 (d, *J* = 8.4 Hz,1H), 3.11 (dq, *J* = 8.4, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 124.6, 123.8, 122.5, 122.0, 116.0 (q, *J* = 274.6 Hz), 104.9, 104.9, 30.4 (dd, *J* = 5.9, 3.0 Hz), 27.9 (dd, *J* = 38.8, 1.3 Hz), 5.1 (dd, *J* = 6.0, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.39 (d, *J* = 5.0 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_8N_2F_3$ 237.0640, found 237.0647.



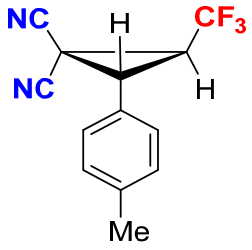
4b

2-(4-Methoxyphenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4b): white solid; 52.1 mg; 98% yield; **M.p.**: 102-104 °C; R_f = 0.14 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.58 (d, *J* = 8.3 Hz, 1H), 3.03 (dq, *J* = 11.5, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 129.7, 121.9 (q, *J* = 274.7 Hz), 119.5, 115.0, 111.0, 110.8, 55.5 (t, *J* = 4.2 Hz), 36.2 (dd, *J* = 4.1, 1.6 Hz), 33.9 (dd, *J* = 39.4, 1.3 Hz), 11.1 (dd, *J* = 5.4, 2.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.26 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{13}H_{10}N_2OF_3$ 267.0745, found 267.0749.



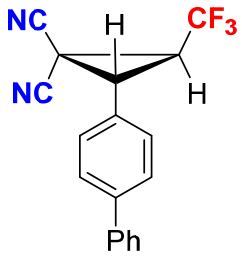
4c

2-(4-(*Tert*-butyl)phenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4c): white solid; 57.8 mg; 99% yield; **M.p.**: 90-91 °C; R_f = 0.43 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.58 (d, *J* = 8.4 Hz, 1H), 3.08 (dq, *J* = 8.3, 5.7 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.9, 128.0, 126.6, 124.7, 122.0 (q, *J* = 274.6 Hz), 111.0, 110.9, 36.1 (dd, *J* = 5.1, 2.2 Hz), 34.9, 33.8 (qd, *J* = 39.5, 1.4 Hz), 31.2, 11.0 (dd, *J* = 6.0, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.30 (d, *J* = 6.6 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{16}H_{16}N_2F_3$ 293.1266, found 293.1274.



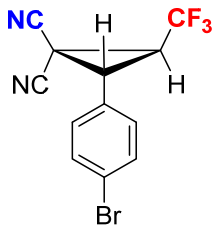
4d

2-(*p*-Tolyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4d): white solid; 40.5 mg; 81% yield; **M.p.**: 103-105 °C; R_f = 0.40 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.59 (d, *J* = 8.3 Hz, 1H), 3.07 (dq, *J* = 11.5, 5.7 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 130.3 (dd, *J* = 5.0, 3.2 Hz), 128.2, 124.8, 122.0 (q, *J* = 274.7 Hz), 110.9, 110.8, 36.2 (dd, *J* = 5.3, 2.7 Hz), 33.8 (q, *J* = 39.7 Hz), 21.4 (dd, *J* = 5.7, 2.8 Hz), 11.0 (dd, *J* = 5.9, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.28 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{13}H_{10}N_2F_3$ 251.0796, found 251.0789.



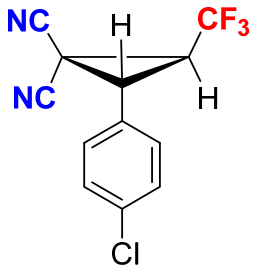
4e

2-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4e): white solid; 51.8 mg; 83% yield; **M.p.**: 130-131 °C; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 - 7.66 (m, 2H), 7.62 - 7.56 (m, 2H), 7.50 - 7.44 (m, 2H), 7.44 - 7.35 (m, 3H), 3.66 (d, *J* = 8.3 Hz, 1H), 3.13 (dq, *J* = 8.3, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 139.6, 129.1, 128.8, 128.3, 127.3, 126.6, 121.9 (q, *J* = 274.9 Hz), 110.9, 110.8, 36.1 (dd, *J* = 5.9, 2.9 Hz), 33.9 (q, *J* = 39.6 Hz), 11.1 (dd, *J* = 5.8, 2.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.22 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{12}N_2F_3$ 313.0953, found 313.0949.



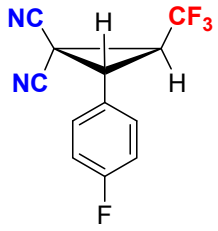
4f

2-(4-Bromophenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4f): white solid; 60.7 mg; 96% yield; **M.p.**: 87-89 ºC; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 3.57 (d, *J* = 8.3 Hz, 1H), 3.06 (dq, *J* = 8.2, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.9, 129.9, 126.9, 125.0, 121.8 (q, *J* = 274.9 Hz), 110.6, 110.5, 35.5 (dd, *J* = 5.2, 2.2 Hz), 33.8 (q, *J* = 39.7 Hz), 10.9 (dd, *J* = 6.0, 3.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.25 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_7N_2F_3Br$ 314.9745, found 314.9735.



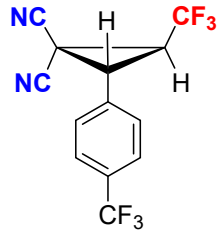
4g

2-(4-Chlorophenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4g): white solid; 47.0 mg; 87% yield; **M.p.**: 102-104 ºC; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 3.59 (d, *J* = 8.3 Hz, 1H), 3.06 (dq, *J* = 8.5, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 130.0, 129.7, 126.4, 121.8 (q, *J* = 274.9 Hz), 110.6, 110.4, 35.5 (dd, *J* = 5.9, 3.0 Hz), 33.9 (q, *J* = 39.6 Hz), 11.0 (dd, *J* = 5.9, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.25 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_7N_2F_3Cl$ 271.0250, found 271.0252.



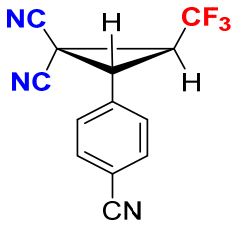
4h

2-(4-Fluorophenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4h): white solid; 41.1 mg; 81% yield; **M.p.**: 95-97 ºC; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.2, 5.1 Hz, 2H), 7.17 (dd, *J* = 14.0, 5.7 Hz, 2H), 3.60 (d, *J* = 8.3 Hz, 1H), 3.06 (ddd, *J* = 8.2, 5.6, 2.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7 (d, *J* = 251.6 Hz), 130.3 (d, *J* = 8.7 Hz), 123.7 (d, *J* = 2.3 Hz), 121.7 (q, *J* = 275.2 Hz), 116.9 (d, *J* = 22.2 Hz), 110.6, 110.5, 35.4, 33.9 (q, *J* = 39.7 Hz), 10.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.28 (d, *J* = 5.5 Hz, 3F), -109.06 - 109.21 (m, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_7N_2F_4$ 255.0545, found 255.0549.



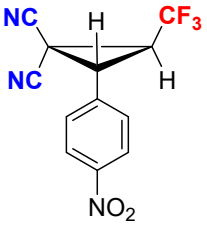
4i

2-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarbonitrile (4i): white solid; 59.6 mg; 98% yield; **M.p.**: 103-105 ºC; R_f = 0.29 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 3.66 (d, *J* = 8.3 Hz, 1H), 3.13 (dq, *J* = 8.4, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.7 (q, *J* = 33.2 Hz), 131.8, 129.0, 126.7 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.6 Hz), 121.7 (q, *J* = 274.9 Hz), 110.4, 110.3, 35.3 (dd, *J* = 7.6, 5.1 Hz), 33.8 (q, *J* = 39.6 Hz), 11.0 (dd, *J* = 6.2, 3.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.93 (s, 3F), -64.30 (d, *J* = 5.6 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{13}H_7N_2F_6$ 305.0513, found 305.0511.



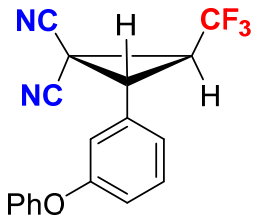
4j

2-(4-Cyanophenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4j): white solid; 50.6 mg; 97% yield; **M.p.**: 160-161 °C; R_f = 0.20 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 9.5 Hz, 2H), 3.66 (d, *J* = 8.2 Hz, 1H), 3.13 (ddd, *J* = 5.4, 4.6, 3.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 133.4, 132.9, 129.3, 121.6 (q, *J* = 275.0 Hz), 117.6, 114.7, 110.3, 110.0, 35.2 (dd, *J* = 6.1, 3.1 Hz), 33.8 (q, *J* = 39.9 Hz), 11.1 (dd, *J* = 6.0, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.21 (d, *J* = 5.4 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{13}H_7N_3F_3$ 262.0592, found 262.0597.



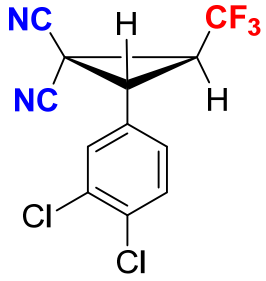
4k

2-(4-Nitrophenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4k): white solid; 50.0 mg; 89% yield; **M.p.**: 83-85 °C; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 3.72 (d, *J* = 8.3 Hz, 1H), 3.19 (dq, *J* = 8.2, 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0, 134.6, 129.6, 124.7, 121.5 (q, *J* = 275.1 Hz), 110.2, 109.9, 34.9 (q, *J* = 2.7 Hz), 33.9 (q, *J* = 39.8 Hz), 11.1 (q, *J* = 2.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.22 (d, *J* = 5.6 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_7N_3O_2F_3$ 282.0490, found 282.0488.



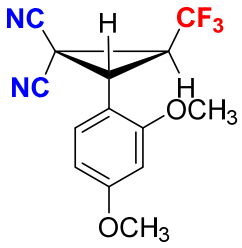
4l

2-(3-Phenoxyphenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4l): white solid; 61.7 mg; 94% yield; **M.p.**: 142-145 °C; R_f = 0.30 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 - 7.34 (m, 3H), 7.22 - 7.14 (m, 1H), 7.12 - 6.98 (m, 4H), 6.94 (t, *J* = 2.0 Hz, 1H), 3.58 (d, *J* = 8.3 Hz, 1H), 3.06 (dq, *J* = 8.3, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 156.1, 131.1, 130.2, 129.7, 124.4, 122.6, 121.8 (q, *J* = 275.1 Hz), 120.3, 119.6, 118.2, 110.7, 110.6, 35.9 (dd, *J* = 5.8, 2.9 Hz), 33.7 (q, *J* = 39.6 Hz), 11.0 (dd, *J* = 5.9, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.26 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{12}N_2OF_3$ 329.0902, found 329.0900.



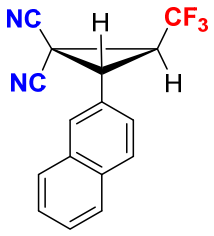
4m

2-(3,4-Dichlorophenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4m): white solid; 55.7 mg; 91% yield; **M.p.**: 76-78 °C; R_f = 0.26 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.16 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.57 (d, *J* = 8.3 Hz, 1H), 3.07 (dq, *J* = 11.2, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.3, 134.2, 131.7, 130.5, 128.0, 127.5, 121.6 (q, *J* = 275.0 Hz), 110.4, 110.2, 34.8 (dd, *J* = 5.5, 2.8 Hz), 33.8 (q, *J* = 39.7 Hz), 11.0 (dd, *J* = 5.2, 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.24 (d, *J* = 5.6 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_6N_2F_3Cl_2$ 304.9860, found 304.9864.



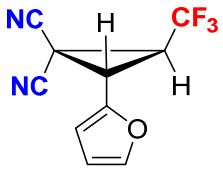
4n

2-(2,4-Dimethoxyphenyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4n): white solid; 50.9 mg; 86% yield; **M.p.**: 109-110 °C; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.52 (d, *J* = 8.4 Hz, 1H), 3.00 (dq, *J* = 8.4, 5.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.7, 159.8, 129.3, 122.2 (q, *J* = 274.4 Hz), 111.5, 111.3, 109.3, 104.8, 99.0, 55.9, 55.6, 34.1 (q, *J* = 39.2 Hz), 32.7 (q, *J* = 2.8 Hz), 10.4 (q, *J* = 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.29 (d, *J* = 6.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{14}H_{12}N_2O_2F_3$ 297.0851, found 297.0849.



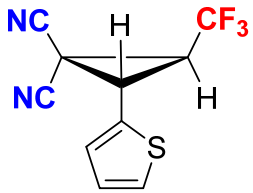
4o

(Naphthalen-2-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4o): white solid; 52.1 mg; 91% yield; **M.p.**: 209-211 °C; R_f = 0.30 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.91 - 7.83 (m, 2H), 7.75 (s, 1H), 7.63 - 7.52 (m, 2H), 7.42 - 7.33 (m, 1H), 3.78 (d, *J* = 8.3 Hz, 1H), 3.25 (dq, *J* = 8.3, 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.9, 133.0, 129.9, 128.2, 128.1, 128.0, 127.8, 127.5, 125.2, 124.8, 122.0 (q, *J* = 274.8 Hz), 110.9, 110.8, 36.5 (dd, *J* = 5.8, 2.9 Hz), 33.9 (q, *J* = 39.5 Hz), 11.1 (dd, *J* = 5.9, 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.15 (d, *J* = 5.4 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{16}H_{10}N_2F_3$ 287.0796, found 287.0795.



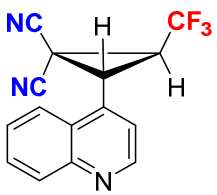
4p

(Furan-2-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4p): white solid; 37.5 mg; 83% yield; **M.p.**: 83-85 ºC; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 1.9, 0.7 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.9 Hz, 1H), 3.62 (d, *J* = 8.1 Hz, 1H), 3.27 (dq, *J* = 8.1, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 141.5, 121.6 (q, *J* = 274.8 Hz), 112.9, 111.8, 110.7, 110.2, 33.0 (q, *J* = 39.9 Hz), 30.1 (dd, *J* = 6.5, 3.3 Hz), 10.6 (dd, *J* = 6.1, 3.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.45 (d, *J* = 6.4 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{10}H_6N_2OF_3$ 227.0432, found 227.0435.



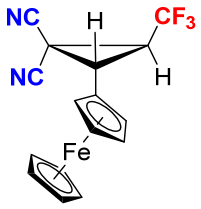
4q

(Thiophen-2-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4q): white solid; 33.9 mg; 70% yield; **M.p.**: 147-149 ºC; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 - 7.42 (m, 1H), 7.13 - 7.10 (m, 1H), 7.10 - 7.06 (m, 1H), 3.75 (d, *J* = 8.1 Hz, 1H), 3.09 (dq, *J* = 8.1, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 130.1, 128.9, 128.6, 128.0, 121.6 (q, *J* = 275.0 Hz), 110.6, 110.3, 35.2 (q, *J* = 39.7 Hz), 31.8 (dd, *J* = 6.4, 3.2 Hz), 12.2 (q, *J* = 2.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.28 (d, *J* = 5.7 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{10}H_6N_2F_3S$ 243.0204, found 243.0206.



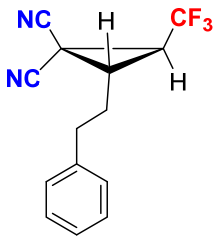
4r

(Quinolin-4-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4r): white solid; 51.7 mg; 90% yield; **M.p.**: 194-195 °C; R_f = 0.20 (PE/EA = 2/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 4.4 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.93 - 7.85 (m, 1H), 7.85 - 7.75 (m, 1H), 7.24 (d, *J* = 0.9 Hz, 1H), 4.00 (d, *J* = 8.3 Hz, 1H), 3.29 (dq, *J* = 8.2, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 148.5, 133.9, 131.1, 131.0, 129.1, 126.4, 121.9, 121.8 (q, *J* = 275.0 Hz), 120.0, 110.2, 110.1, 33.5 (q, *J* = 39.6 Hz), 33.21 (q, *J* = 2.7 Hz), 10.7 (q, *J* = 2.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.97 (d, *J* = 5.6 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{15}H_9N_3F_3$ 288.0749, found 288.0746.



4s

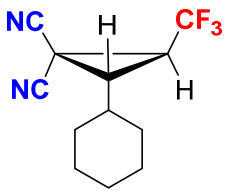
(Ferrocenyl-2-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4s): White solid; 46.1 mg; 67% yield; **M.p.**: 165-167 °C; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.47 (s, 1H), 4.35 (s, 1H), 4.31 (s, 1H), 4.23 (d, *J* = 0.6 Hz, 5H), 4.11 (s, 1H), 3.38 (d, *J* = 8.3 Hz, 1H), 2.77 (dq, *J* = 8.2, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 121.9 (dd, *J* = 549.2, 275.1 Hz), 111.4, 110.6, 74.7, 70.6, 69.9, 69.5, 69.3, 66.2, 35.0 (d, *J* = 3.0 Hz), 34.6 (q, *J* = 39.4 Hz), 12.4 (dd, *J* = 6.4, 4.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.35 (d, *J* = 5.8 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{16}H_{12}N_2F_3Fe$ 345.0302, found 345.0306.



4t

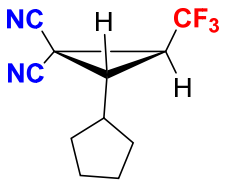
2-phenethyl-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4t) colourless

liquid; 44.4 mg; 84% yield; R_f = 0.73 (PE/EA = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.36 (q, *J* = 5.6 Hz, 1H), 2.28 (q, *J* = 7.3 Hz, 1H), 2.06 (tp, *J* = 14.5, 7.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.4, 129.1, 128.4, 127.1, 121.6 (q, *J* = 274.4 Hz), 111.3, 110.7, 35.4 (q, *J* = 39.5 Hz), 33.7, 31.7 (q, *J* = 2.5 Hz), 30.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.38 (d, *J* = 6.1 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{14}H_{12}F_3N_2$ 265.0952, found 265.0946.



4u

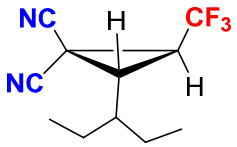
Cyclohexyl-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4u): white solid; 47.9 mg; 99% yield; **M.p.**: 130-132 °C; R_f = 0.28 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.41 (dq, *J* = 11.8, 5.9 Hz, 1H), 2.10 (dd, *J* = 9.6, 8.3 Hz, 1H), 1.99 (d, *J* = 8.0 Hz, 1H), 1.75 (dd, *J* = 27.1, 12.9 Hz, 4H), 1.23 (dd, *J* = 32.4, 20.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 121.8 (q, *J* = 274.3 Hz), 111.6, 111.0, 38.8, 37.8 (dd, *J* = 4.7, 2.3 Hz), 34.9 (q, *J* = 39.5 Hz), 31.4, 31.3, 25.6, 25.4, 25.2, 7.8 (dd, *J* = 6.2, 3.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.64 (d, *J* = 5.8 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{12}H_{14}N_2F_3$ 243.1109, found 243.1112.



4v

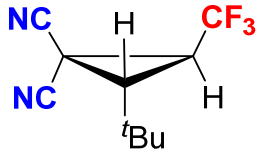
2-cyclopentyl-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4v) colourless liquid; 40.6 mg; 89% yield; R_f = 0.71 (PE/EA = 10/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.52 – 2.37 (m, 1H), 2.30 – 2.15 (m, 1H), 2.14 – 2.04 (m, 1H), 2.02 – 1.88 (m, 1H),

1.84 – 1.62 (m, 5H), 1.61 – 1.40 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 121.9 (q, *J* = 274.4 Hz), 111.8, 111.0, 40.5, 37.6, 35.6 (q, *J* = 39.3 Hz), 31.6, 31.3, 25.2, 25.1, 8.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.64 (d, *J* = 6.1 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{11}H_{12}F_3N_2$ 229.0952, found 229.0945.



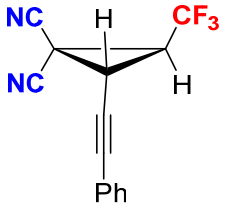
4w

2-(pentan-3-yl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4w) white solid; 38.6mg; 84% yield; **M.p.**: 113-115 ºC; R_f = 0.70 (PE/EA = 10/1)**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.43 (dq, *J* = 8.1, 5.7 Hz, 1H), 2.12 (dd, *J* = 10.8, 8.2 Hz, 1H), 1.74 – 1.46 (m, 5H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 120.8 (q, *J* = 274.4 Hz), 110.7, 109.9, 39.4, 36.5 (d, *J* = 2.3 Hz), 34.5 (q, *J* = 39.3 Hz), 30.5, 30.2, 24.2, 24.1, 7.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.46 (d, *J* = 6.1 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{11}H_{14}F_3N_2$ 231.1109, found 231.1099.



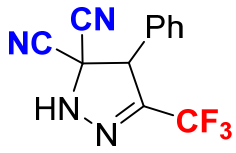
4x

(*Tert*-butyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4x): white solid; 27.2 mg; 63% yield; **M.p.**: 69-70 ºC; R_f = 0.30 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.62 (dq, *J* = 9.2, 5.7 Hz, 1H), 2.17 (d, *J* = 9.0 Hz, 1H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 122.0 (q, *J* = 274.5 Hz), 111.9, 111.4, 43.0 (q, *J* = 2.0 Hz), 32.7 (q, *J* = 39.6 Hz), 30.6, 27.8, 5.9 (q, *J* = 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.67 (d, *J* = 5.8 Hz, 3F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{10}H_{12}N_2F_3$ 217.0953, found 217.0946.



4y

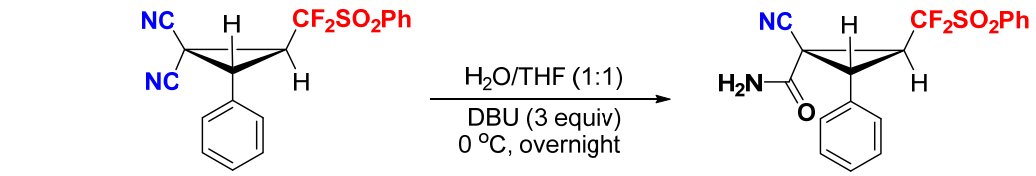
2-(phenylethynyl)-3-(trifluoromethyl)cyclopropane-1,1-dicarbonitrile (4y) yellow liquid; 32.8 mg; 63% yield; R_f = 0.67 (PE/EA = 10/1)**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.38 – 7.30 (m, 2H), 3.20 (d, *J* = 7.5 Hz, 1H), 2.92 (dq, *J* = 7.5, 5.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.2, 130.0, 128.6, 121.0 (q, *J* = 275.3 Hz), 120.1, 110.6, 109.5, 87.2, 36.2 (q, *J* = 39.1 Hz), 31.5, 30.2, 29.7, 23.2, 11.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.57 (d, *J* = 6.1 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{14}H_8F_3N_2$ 261.0639, found 261.0632.



4a'

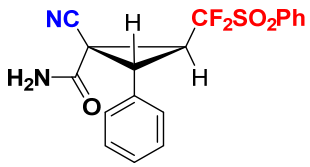
4-phenyl-5-(trifluoromethyl)-2,4-dihydro-3*H*-pyrazole-3,3-dicarbonitrile (4a')[3]**:** white solid; 42.2 mg; 80% yield **M.p.**:117-119 °C; R_f = 0.71 (PE/EA = 3/1), purified by column chromatography on silical gel (PE/EtOAc = 20/1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.56 – 7.39 (m, 3H), 7.41 – 7.22 (m, 2H), 5.67 (s, 1H). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -62.72. **^{13}C NMR** (101 MHz, DMSO-d_6) δ 143.8 (q, *J* = 37.1 Hz), 130.7, 130.3, 129.9, 129.1, 120.1 (q, *J* = 271.3 Hz), 114.2, 111.4, 59.9, 59.2. **HRMS** (ESI) m/z calcd. for $C_{12}H_8F_3N_4^+$([M+H]$^+$): 265.0701, found 265.0698.

Procedure for the Preparation of Compound 5a



3a **5a**, 80%

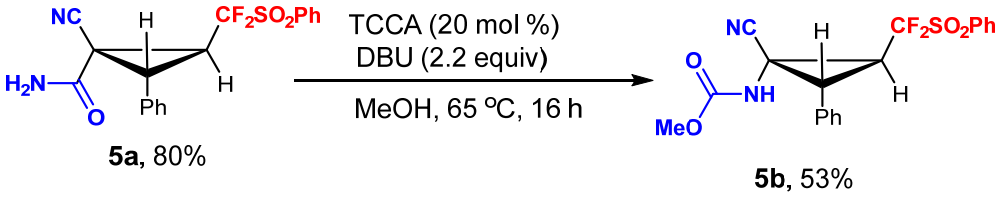
To a Schlenk tube equipped with a magnetic stirring bar, **3a** (0.1 mmol), THF (1 mL), and H_2O (1 mL) were added. The reaction mixture was cooled to 0 °C. DBU (37.5 mg, 3.0 equiv) was then added, and the mixture was stirred at 0 °C in an air atmosphere for overnight. After the reaction was completed as monitored by TLC, the resulting mixture was extracted with ethyl acetate (3× 10 mL). The combined organic fraction was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 5/1 → 2/1) to afford the product **5a**.



5a

1-Cyano-2-(difluoro(phenylsulfonyl)methyl)-3-phenylcyclopropane-1-carboxamide (5a): white solid; 30.1 mg; 80% yield; **M.p.**: 163-165 °C; R_f = 0.30 (PE/EA = 1/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.33 (s, 5H), 6.32 (s, 1H), 5.68 (s, 1H), 3.82 – 3.64 (m, 1H), 3.55 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 136.1, 131.6, 131.1, 129.7, 129.5, 129.1, 129.0, 128.8, 120.4 (dd, *J* = 288.8, 286.3 Hz), 116.3, 37.4 (dd, *J* = 5.8, 2.8 Hz), 28.3 (dd, *J* = 23.7, 22.4 Hz), 24.0 (t, *J* = 1.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.43 (dd, *J* = 233.5, 7.1 Hz, 1F), -106.72 (dd, *J* = 233.2, 17.5 Hz, 1F). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{15}N_2O_3F_2S$ 377.0771, found 377.0775.

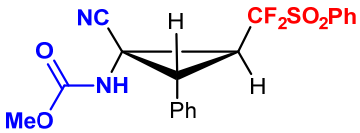
Procedure for the Preparation of Compound 5b



5a, 80%

5b, 53%

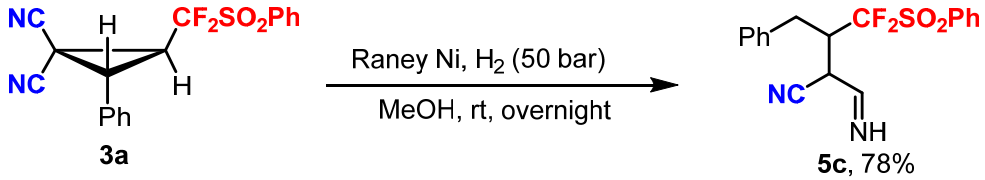
To a flask equipped with magnetic stirring, external heating, external temperature probe, reflux condenser, and N_2 inlet was added **5** (75.2 mg, 0.2 mmol), MeOH (2 mL), and 1,8-diazabicyclo[5.4.0]undec-7-ene (67 mg, 0.44 mmol). To the reaction was added trichloroisocyanuric acid (TCCA) (23.2 mg, 0.1 mmol). The reaction was allowed to stir for 15 min. at which time additional TCCA (23.2 mg, 0.1 mmol) was added. The reaction temperature was increased to 65 ºC and was stirred for 16 h. The reaction was judged complete by disappearance of the starting material using TLC. The reaction was concentrated on rotary evaporator at 40 ºC. The oil was dissolved in a minimal amount of EtOAc and the solvent was concentrated. Compound **5b** was purified by chromatography to give 43.0 mg (53%) of a colourless liquid.



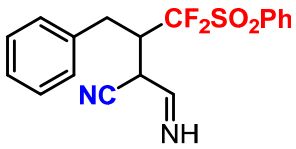
5b

methyl-1-cyano-2-(difluoro(phenylsulfonyl)methyl)-3-phenylcyclopropyl) carbamate (5b) colourless liquid; 43.0mg; 53% yield; R_f = 0.40 (PE/EA = 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 1H), 7.93 – 7.78 (m, 1H), 7.75 – 7.60 (m, 2H), 7.54 – 7.31 (m, 5H), 3.66 (d, *J* = 8.4 Hz, 1H), 3.63 (s, 3H), 3.61 – 3.56 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5, 135.1, 130.4, 130.0, 128.6, 128.1, 127.9, 127.82, 120.3 (d, *J* = 286.8 Hz), 113.4, 53.1, 36.7 (dd, *J* = 6.0, 2.8 Hz), 28.0 (dd, *J* = 24.4, 21.6 Hz), 22.8, 13.2. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -101.79 (dd, *J* = 232.8, 6.5 Hz), -107.44 (dd, *J* = 233.2, 18.2 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{19}H_{17}F_2N_2O_4S$ 407.0877, no found.

Procedure for the Preparation of Compound 5c



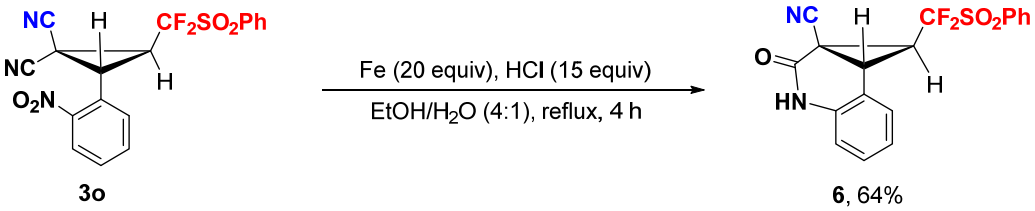
Freshly prepared Raney-Ni (ca. 0.1 g/mmol) was added to a soln. of 0.2 g and **3a** (71.6 mg, 0.2 mmol) in MeOH (3 mL). Resulting mixture was stirred under H_2 atmosphere (50 bar) at r.t. overnight. After the reaction was complete, the suspension was filtered through Celite pad and organic solvents were evaporated under reduced pressure to give crude product. Purification with flash column chromatography results in pure product **5c**.



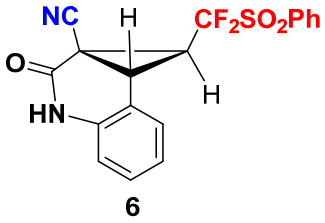
5c

3-benzyl-4,4-difluoro-2-(iminomethyl)-4-(phenylsulfonyl)butanenitrile (5c) white solid; 56.5mg; 78% yield; **M.p.**: 155.1-156.7 °C; R_f = 0.3 (PE/EA = 3/1)**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 2H), 7.50 – 7.28 (m, 2H), 7.29 – 7.05 (m, 3H), 6.55 (t, *J* = 10.7 Hz, 1H), 4.65 (d, *J* = 10.7 Hz, 2H), 3.83 – 3.13 (m, 2H), 2.92 (dd, *J* = 13.6, 11.6 Hz, 1H), 1.27 (d, *J* = 13.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.7, 137.1, 135.3, 133.3, 130.7, 129.3, 129.3, 128.6, 126.8, 121.8 (q, *J* = 292.8 Hz), 117.1, 73.2 (d, *J* = 6.0 Hz), 45.1 (dd, *J* = 21.1, 18.4 Hz), 32.9 (t, *J* = 2.8 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -101.51 (dd, *J* = 232.3, 11.3 Hz), -105.03 (dd, *J* = 232.8, 18.6 Hz). **HRMS** (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{17}F_2N2O_2S$ 363.0979, found 363.0977.

General Procedure for the Preparation of Compound 6



To a Schlenk tube equipped with a magnetic stirring bar, **3o** (0.2 mmol, 1.0 equiv) and EtOH/H_2O (4:1, 4.0 mL) were added. Iron powder (224.0 mg, 4.0 mmol, 20 equiv) and 12M HCl (0.26 mL, 3.0 mmol, 15.0 equiv) were then transferred into the reaction mixture. The reaction mixture was heated in oil bath in an air atmosphere under reflux for 4 h. After cooling to room temperature, saturated $NaHCO_3$ was added and the mixture was stirred for additional 30 min.[4] The reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic fraction was dried over dry anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 → 2/1) to afford the product **6**.



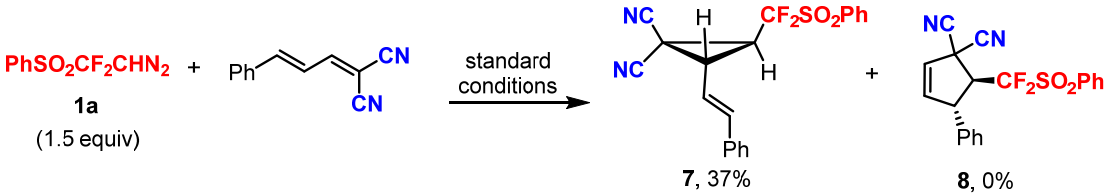
6

1-(Difluoro(phenylsulfonyl)methyl)-2-oxo-1,2,3,7b-tetrahydro-1aH-cyclopropa [c]quinoline-1a-carbonitrile (6): white solid; 60 mg; 64% yield; **M.p.**: 229-231 °C; R_f = 0.23 (PE/EA = 1/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.59 (d, *J* = 7.5 Hz, 1H), 2.55 (ddd, *J* = 19.0, 6.1, 4.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 136.2, 133.6, 131.3, 131.1, 129.8, 129.8, 128.7, 124.7, 120.3 (dd, *J* = 291.2, 287.3 Hz), 116.7, 115.5, 113.0, 31.2 (dd, *J* = 5.6, 2.8 Hz), 26.8 (dd, *J* = 48.3, 26.6 Hz), 20.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -101.63 (d, *J* = 235.1 Hz, 1F), -109.25 (dd, *J* = 233.3, 19.0 Hz, 1F). HRMS (ESI-TOF) *m/z*: [M+H] calcd for $C_{18}H_{13}N_2O_3F_2S$ 375.0615, found

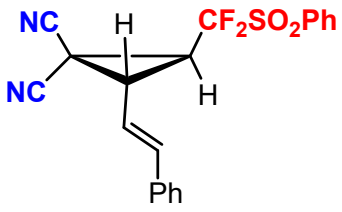
375.0620.

Control experiments

(i) Mechanistic scenario 2:



To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added (*E*)-2-(3-phenylallylidene)malononitrile[3] (36 mg, 1.0 equiv). $PhSO_2CF_2CHN_2$ (**1a**, 69.6 mg, 1.5 equiv) and toluene (2 mL) were added and stirred at 100 °C for 12 h. Then the reaction mixture evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (PE/EA = 20/1) to afford the 2-(difluoro(phenylsulfonyl) methyl)-3-((*E*)-styryl)cyclopropane-1,1-dicarbonitrile (**7**, 37%, 28.4 mg).

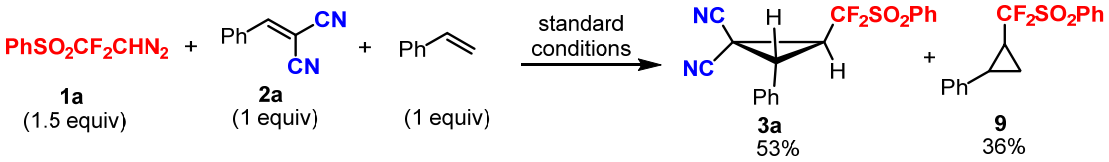


7

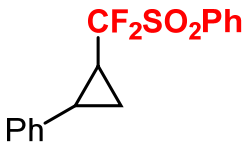
2-(difluoro(phenylsulfonyl)methyl)-3-((*E*)-styryl)cyclopropane-1,1-dicarbonitrile (7): Colorless liquid; 28.4 mg; 37% yield; R_f = 0.31 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.95 (m, 2H), 7.88 – 7.77 (m, 1H), 7.69 (t, *J* = 7.9 Hz, 2H), 7.48 – 7.30 (m, 5H), 6.94 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.7, 7.7 Hz, 1H), 3.16 (t, *J* = 8.0 Hz, 1H), 3.10 – 2.98 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.6, 136.2, 134.7, 131.2, 130.0, 129.6, 129.0, 128.3, 127.1, 120.5 (d, *J* = 288.0 Hz), 116.8, 111.4, 110.7, 35.3 (dd, *J* = 5.4, 2.7 Hz), 32.2 (t, *J* = 23.5 Hz), 9.7 (t, *J* = 2.9 Hz). **^{19}F NMR** (376 MHz,

$CDCl_3$) δ -103.47 (dd, *J* = 235.6, 6.3 Hz, 1F), -107.65 (dd, *J* = 235.5, 16.1 Hz 1F). **HRMS** (ESI-TOF) *m/z*: [M+Na] calcd for $C_{20}H_{14}F_2O_2N_2SNa$ 407.0642, found 407.0648.

(ii) Mechanistic scenario 3:



To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added 2-benzylidenemalononitrile (**2a**, 30.8 mg, 1.0 equiv) and styrene (20.8 mg, 1.0 equiv). $PhSO_2CF_2CHN_2$ (**1a**, 69.6 mg, 1.5 equiv) and toluene (2 mL) were added and stirred at 100 °C for 12 h. Then the reaction mixture evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (PE/EA = 20/1) to afford the 2-(difluoro (phenylsulfonyl)methyl)-3-phenylcyclopropane-1,1-dicarbonitrile (**3a**,53%, 37.9 mg) and ((difluoro(2-phenylcyclopropyl)methyl)sulfonyl)benzene (**9**, 36%, 22.2 mg).



9

((difluoro(2-phenylcyclopropyl)methyl)sulfonyl)benzene (9): Colorless liquid; 28.4 mg; 37% yield; R_f = 0.35 (PE/EA = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, 2H), 7.79 – 7.71 (m, 1H), 7.60 (t, J = 7.8 Hz, 2H), 7.35 – 7.20 (m, 3H), 7.16 (d, J = 8.7 Hz, 2H), 2.55 – 2.33 (m, 1H), 2.06 – 1.85 (m, 1H), 1.49 – 1.39 (m, 1H), 1.38 – 1.22 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.8, 135.3, 133.3, 130.8, 129.4, 128.7, 127.0, 126.9, 121.5 (d, *J* = 283.8 Hz), 20.1 (t, *J* = 3.6 Hz), 19.6 (t, *J* = 23.9 Hz), 10.7 (t, *J* = 3.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.75 (d, *J* = 13.1 Hz, 1F). **HRMS** (ESI-TOF)

m/z: [M+Na] calcd for $C_{16}H_{14}F_2O_2SNa$ 331.0581, found 331.0590.

References

(1) F.-G. Zhang, Y. Wei, Y.-P. Yi, J. Nie and J.-A. Ma, *Org. Lett*. 2014, **16**, 3122–3125.

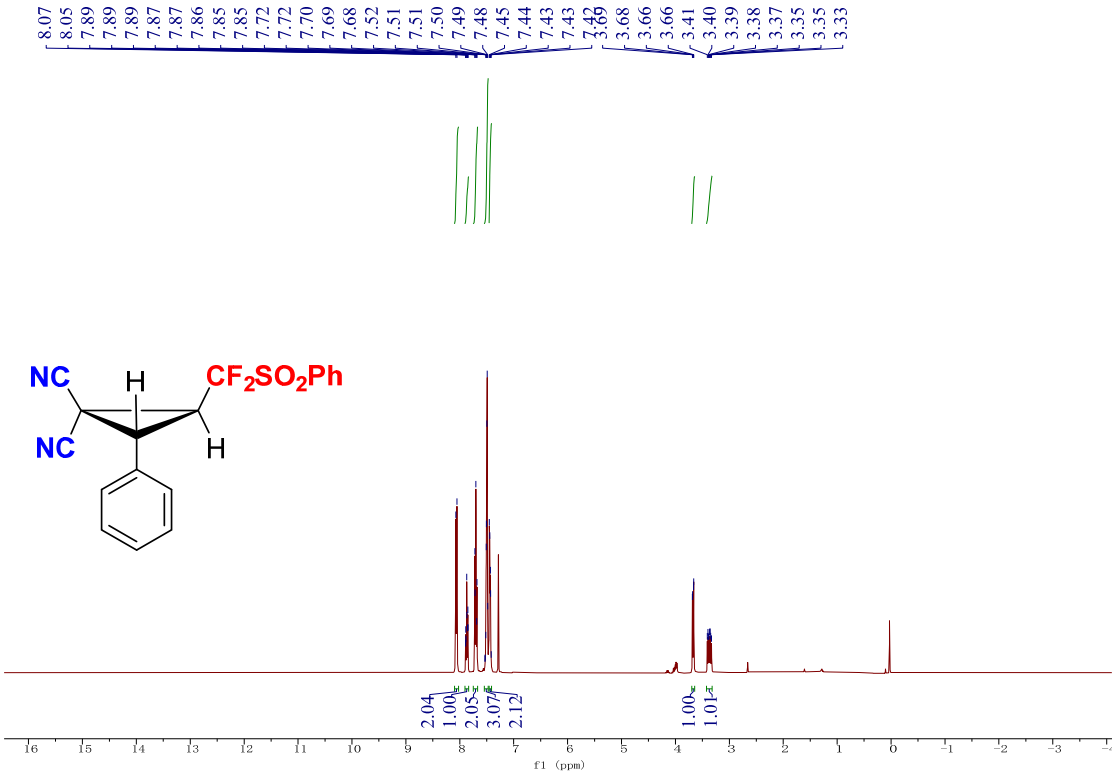
(2) J.-L. Zeng, Z. Chen, F.-G. Zhang and J.-A. Ma, *Org. Lett.* 2018, **20**, 4562–4565.

(3) C.-F. Gao, Y. Zhou, Y., H. Ma, Y. Zhang, J. Nie, F.-G. Zhang and J.-A. Ma, *CCS Chem.* 2022, **4**, 3693–3704.

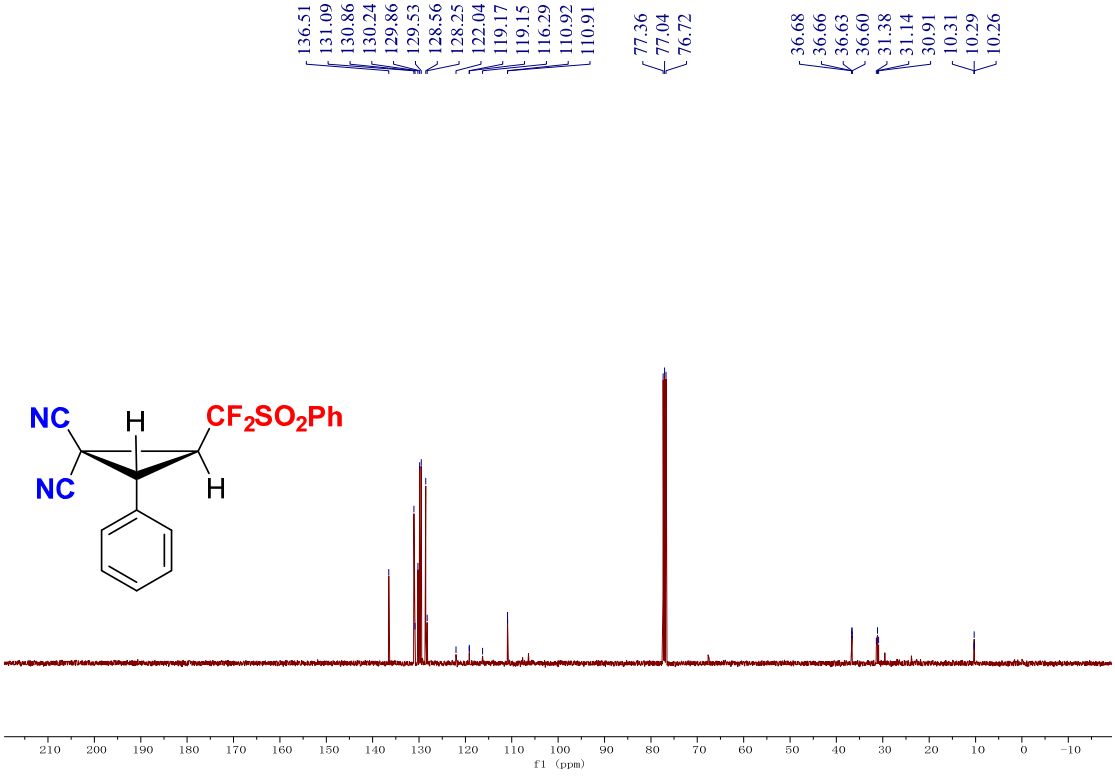
(4) N.-Z. Wang, Y.-M. Lang, J.-J. Wang, Z.-G. Wu and Y.-X. Lu, *Org. Lett*. 2022, **24**, 3712–3716.

NMR Spectra

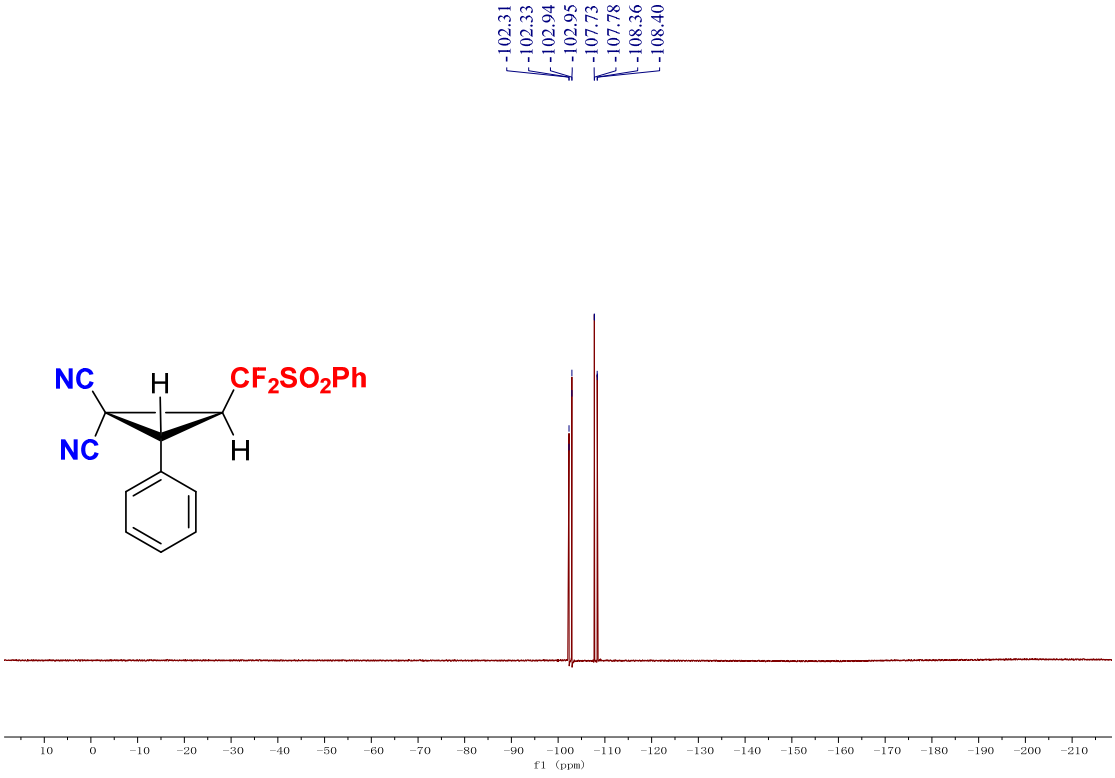
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



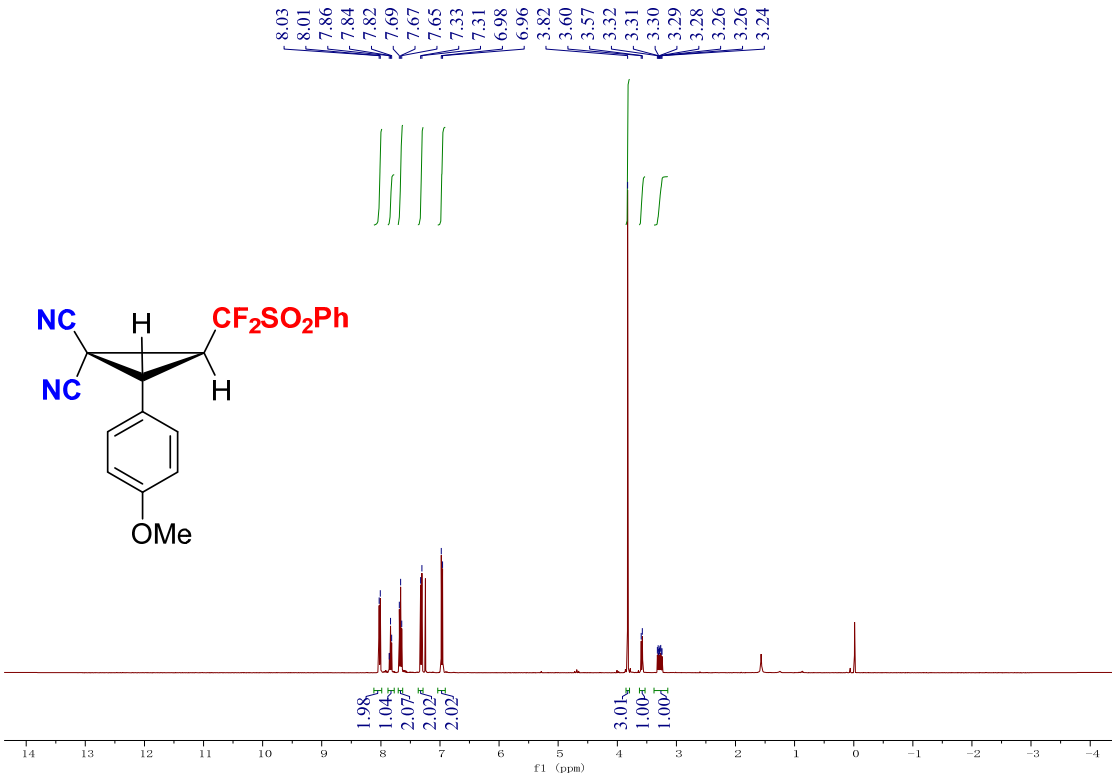
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a**



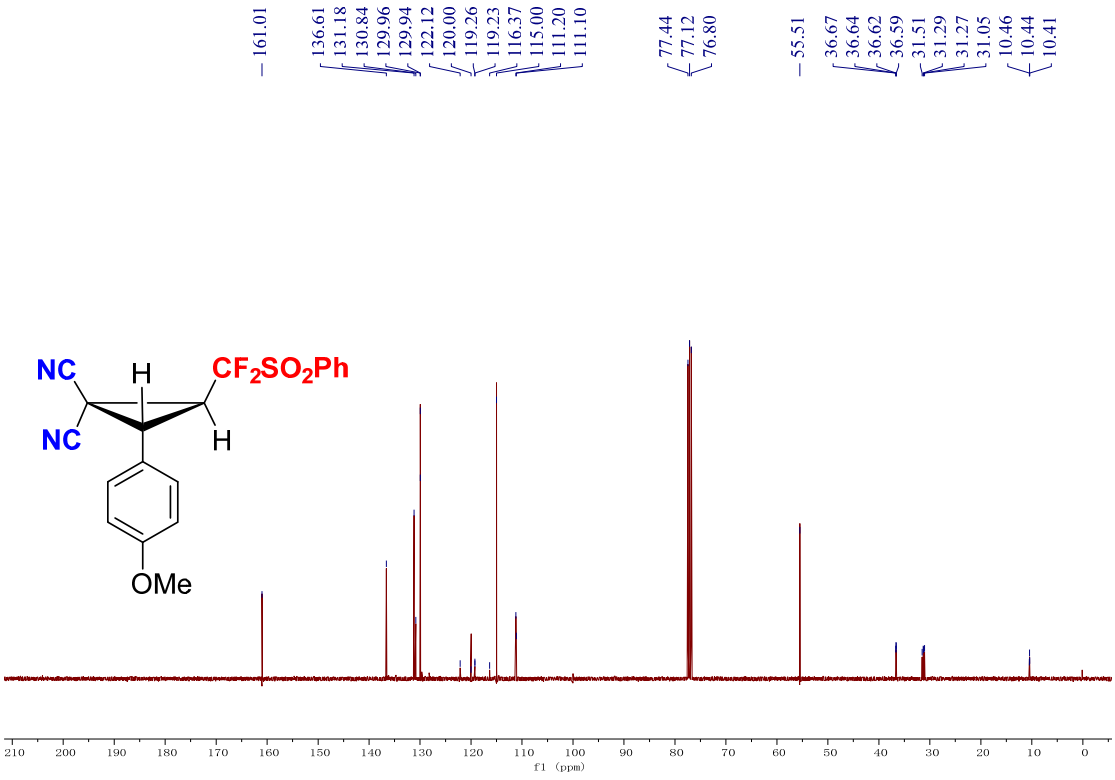
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3a**



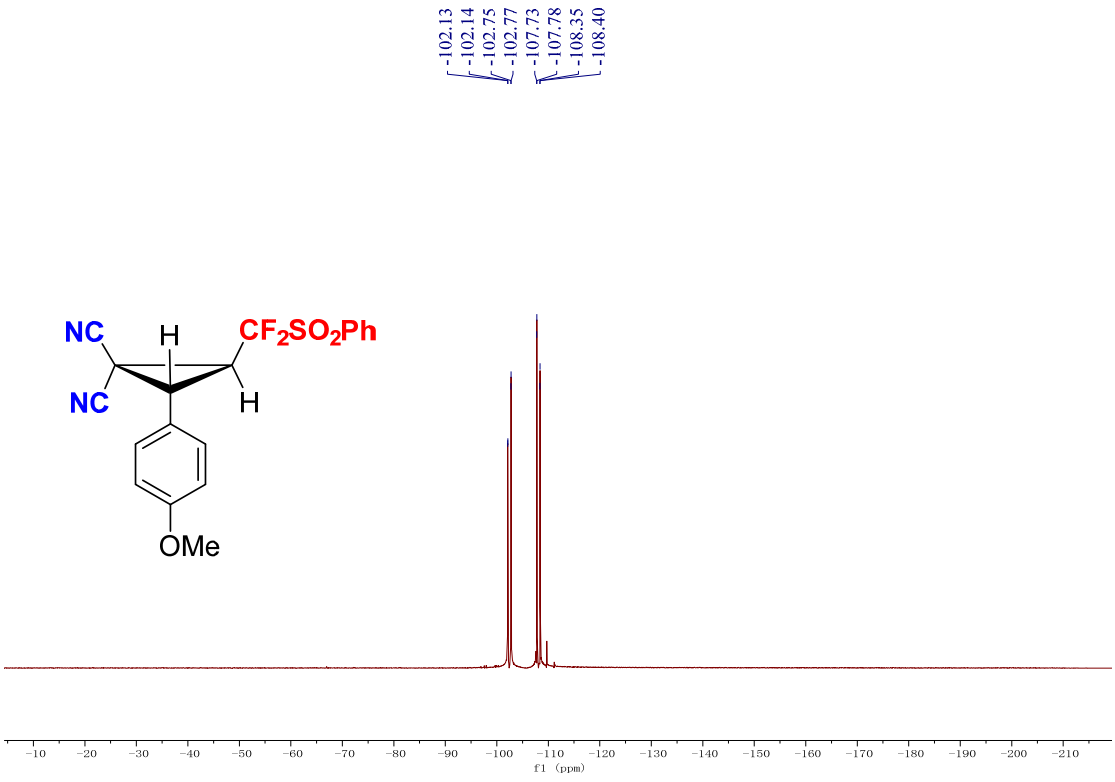
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



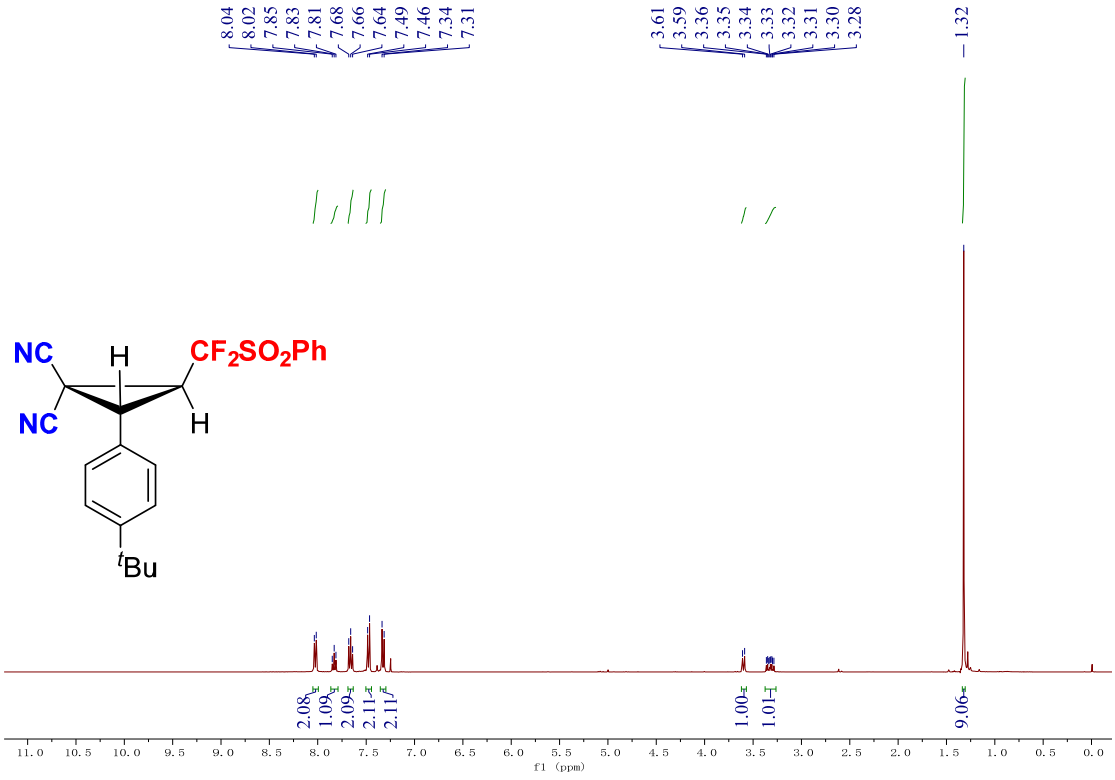
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3b**



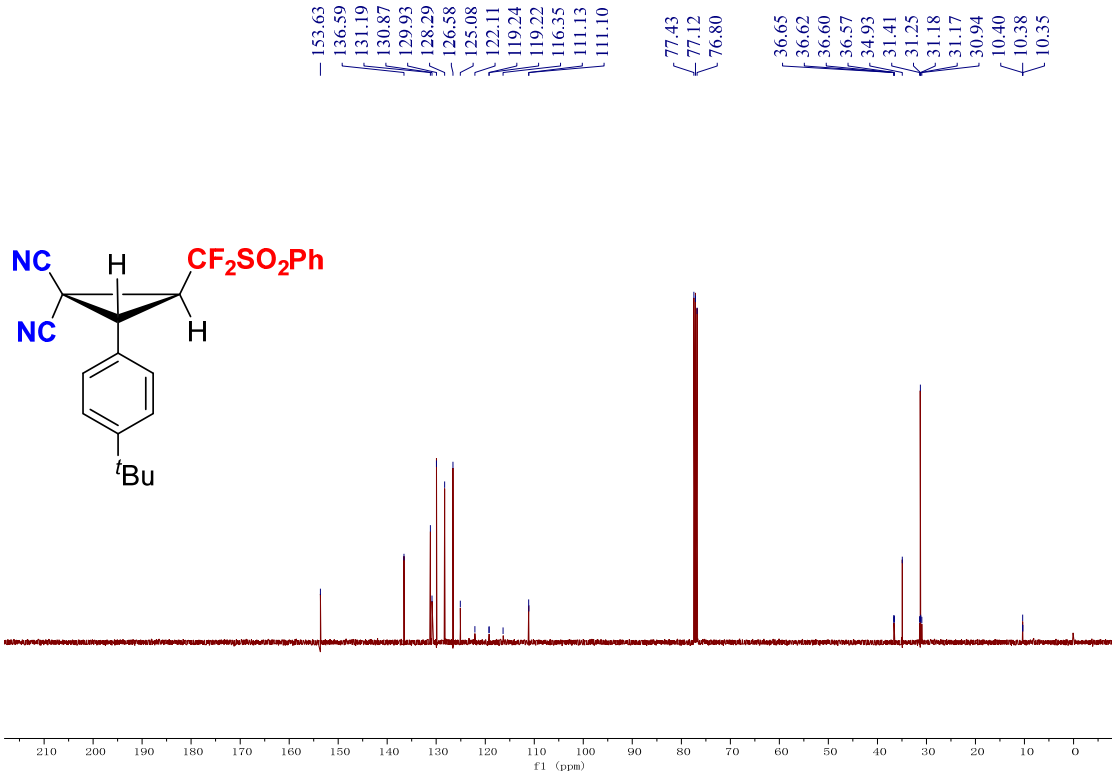
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3b**



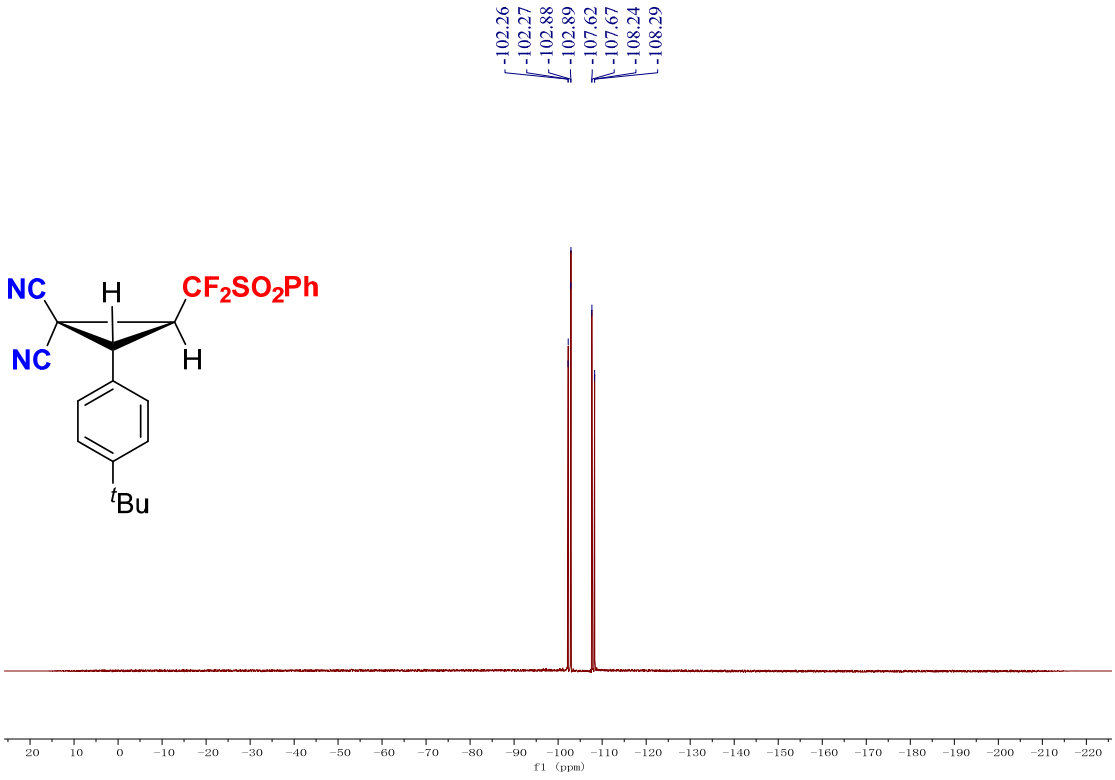
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



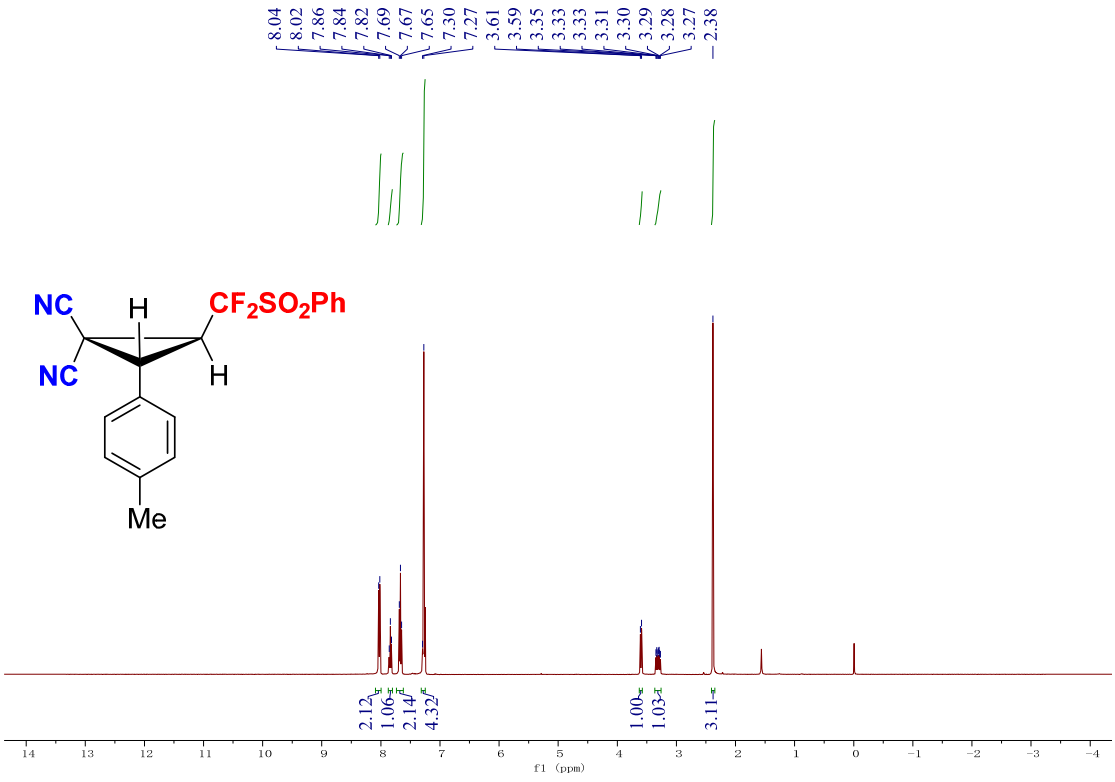
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3c**



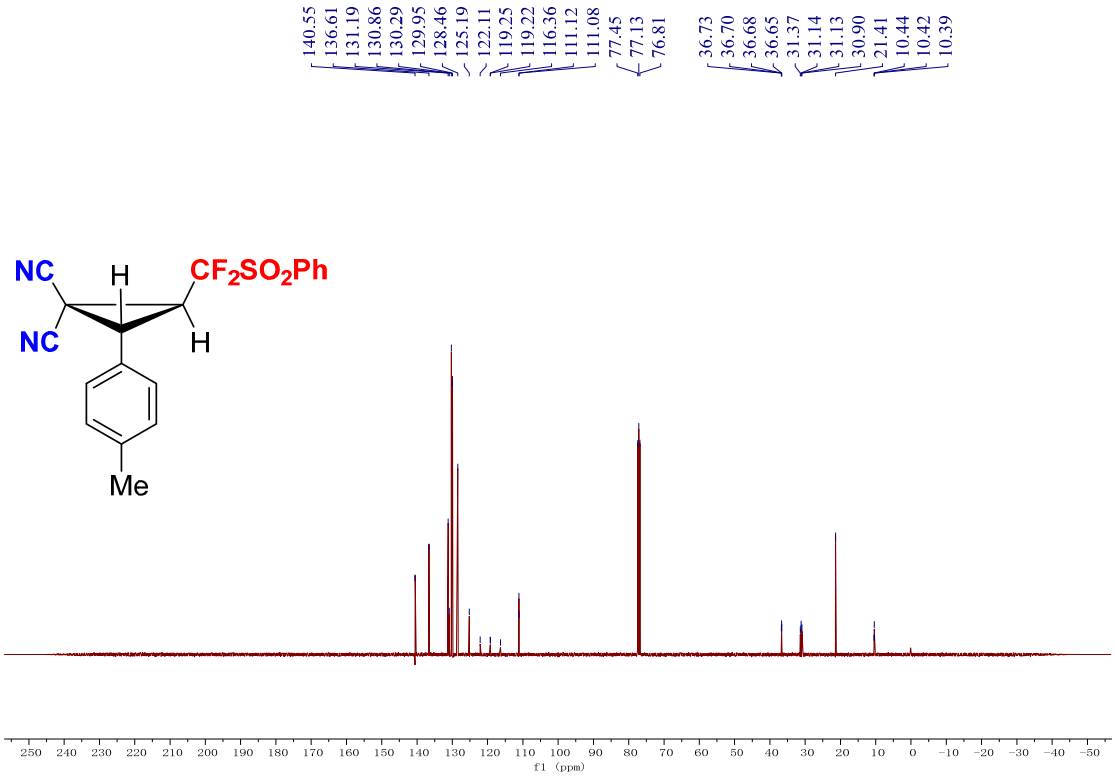
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3c**



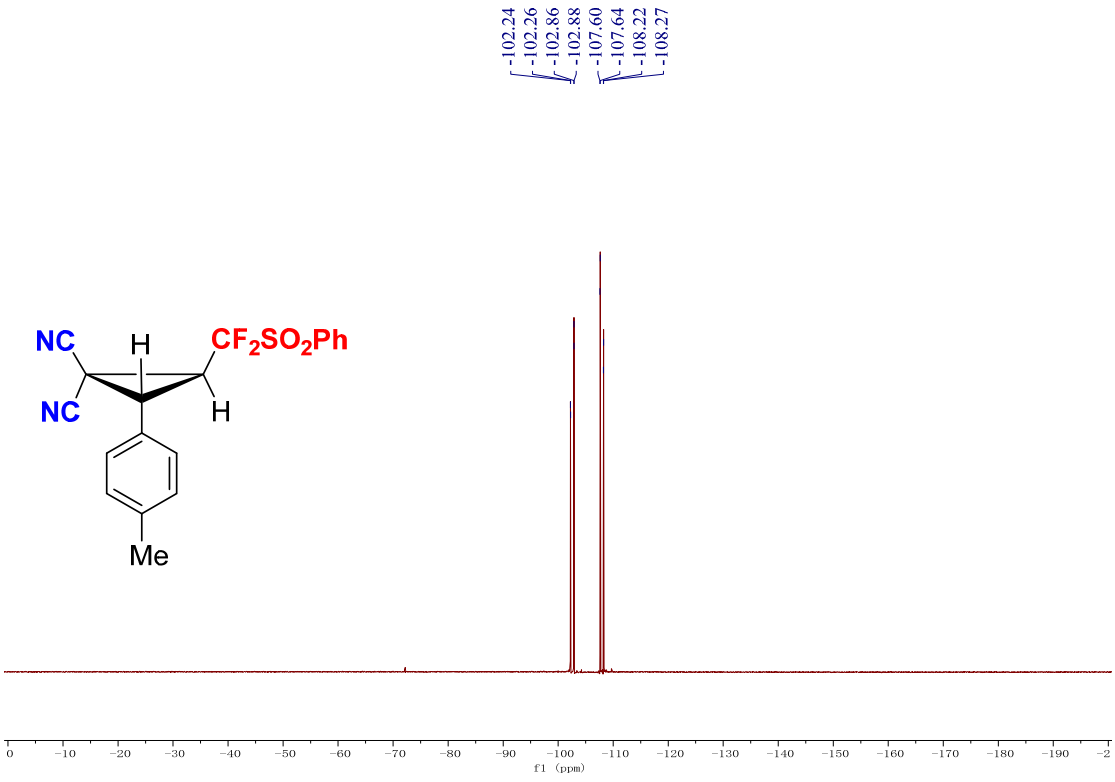
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**



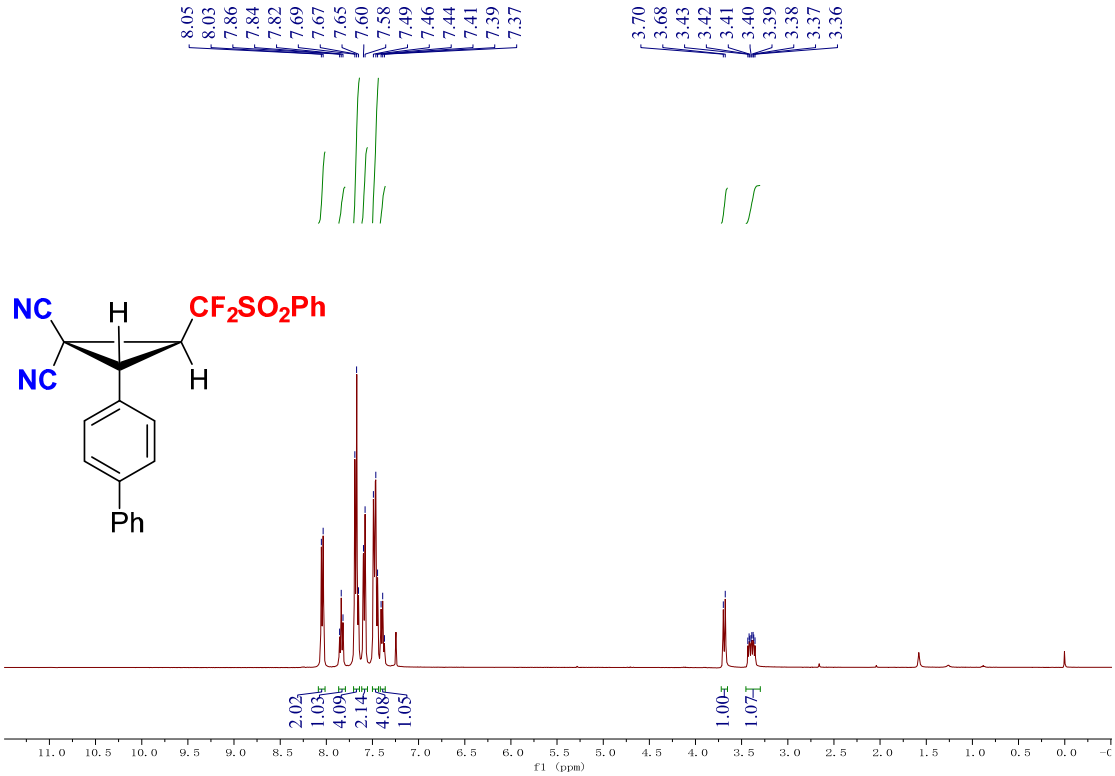
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3d**



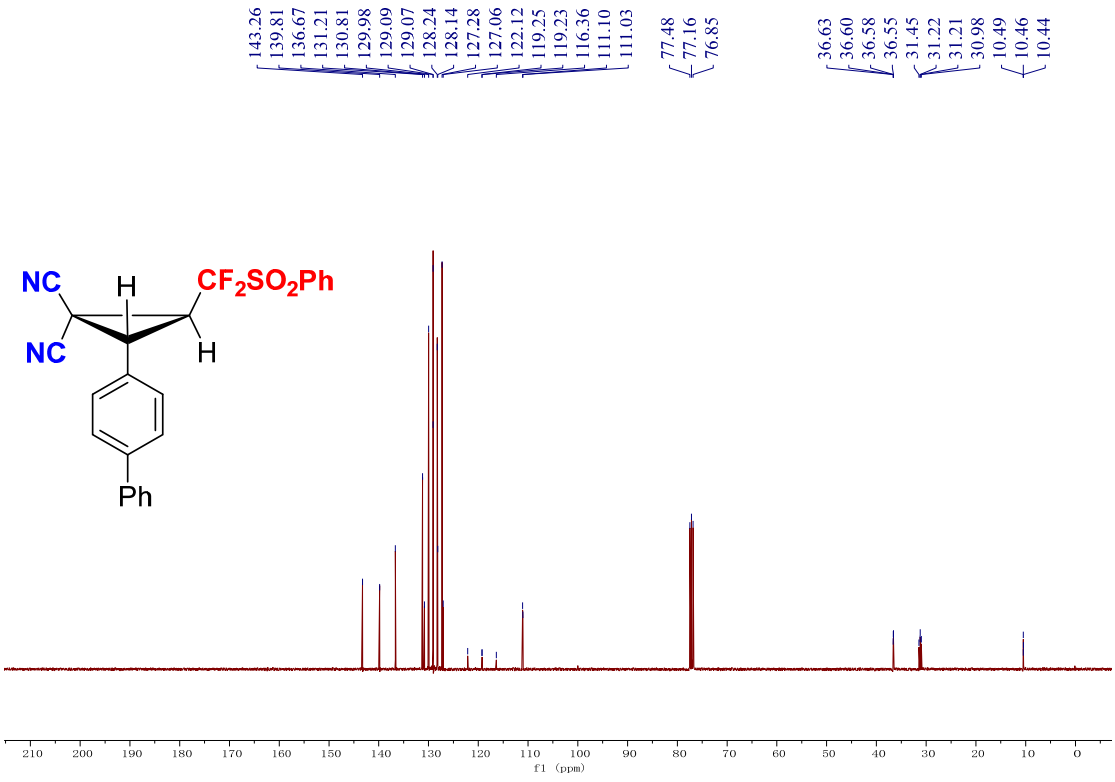
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3d**



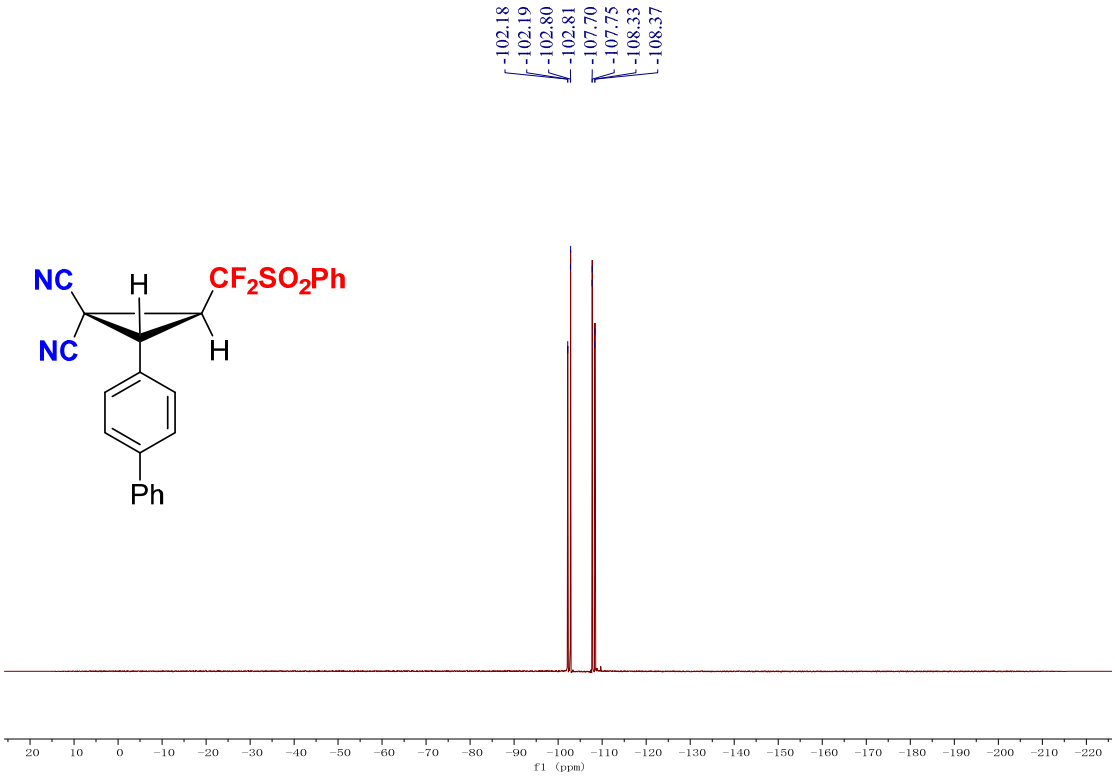
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



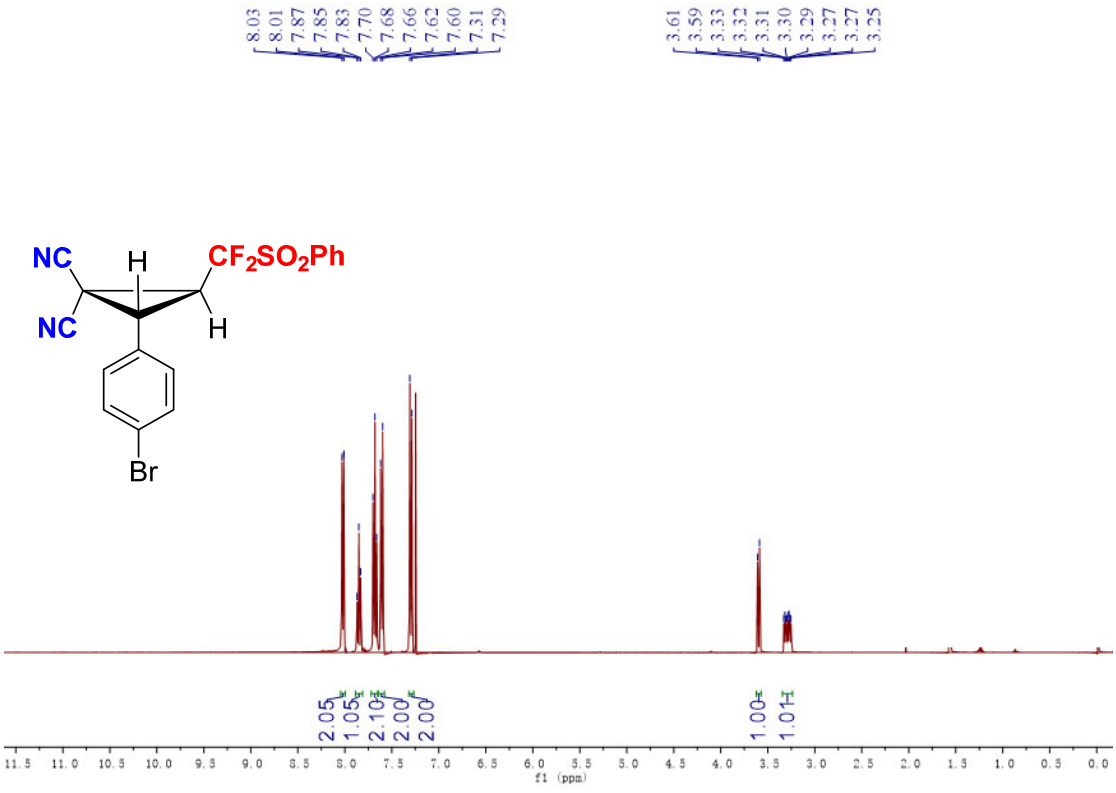
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3e**



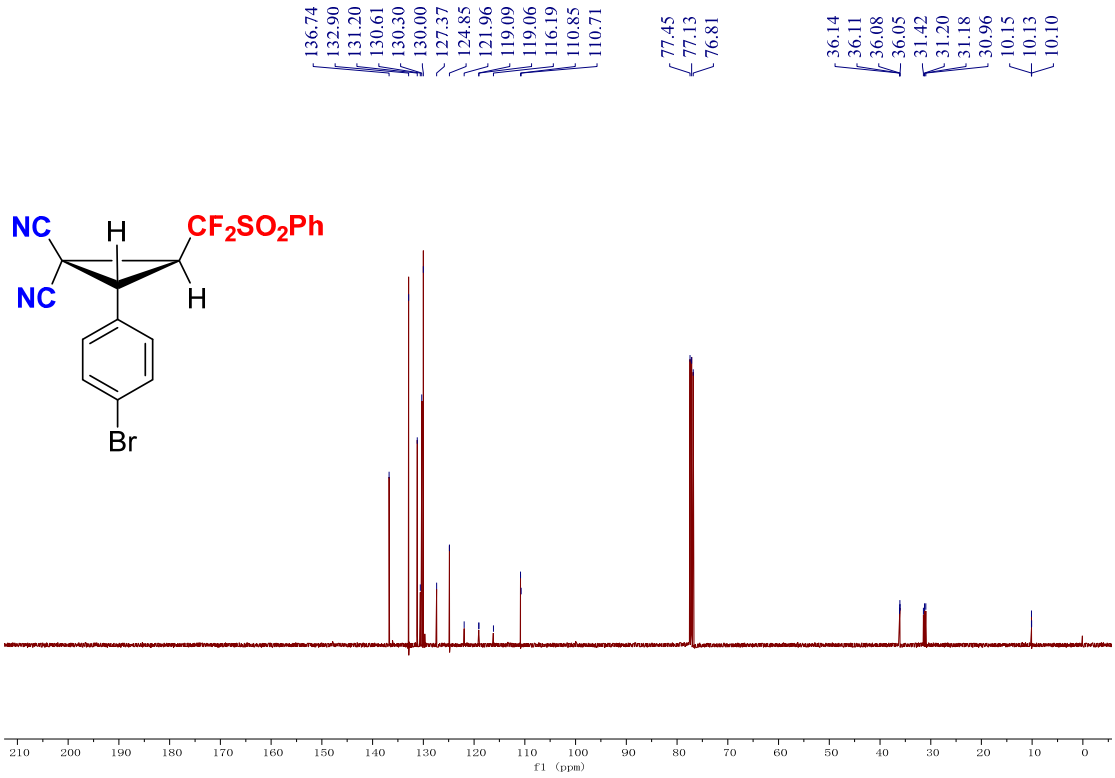
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3e**



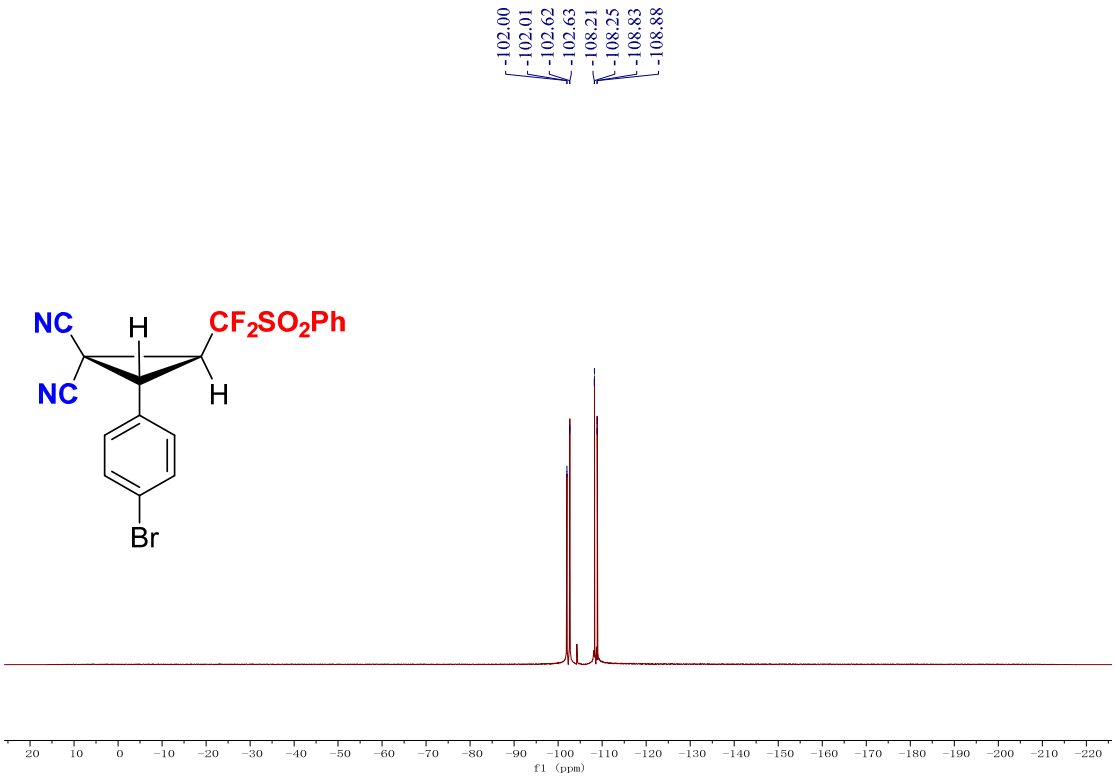
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



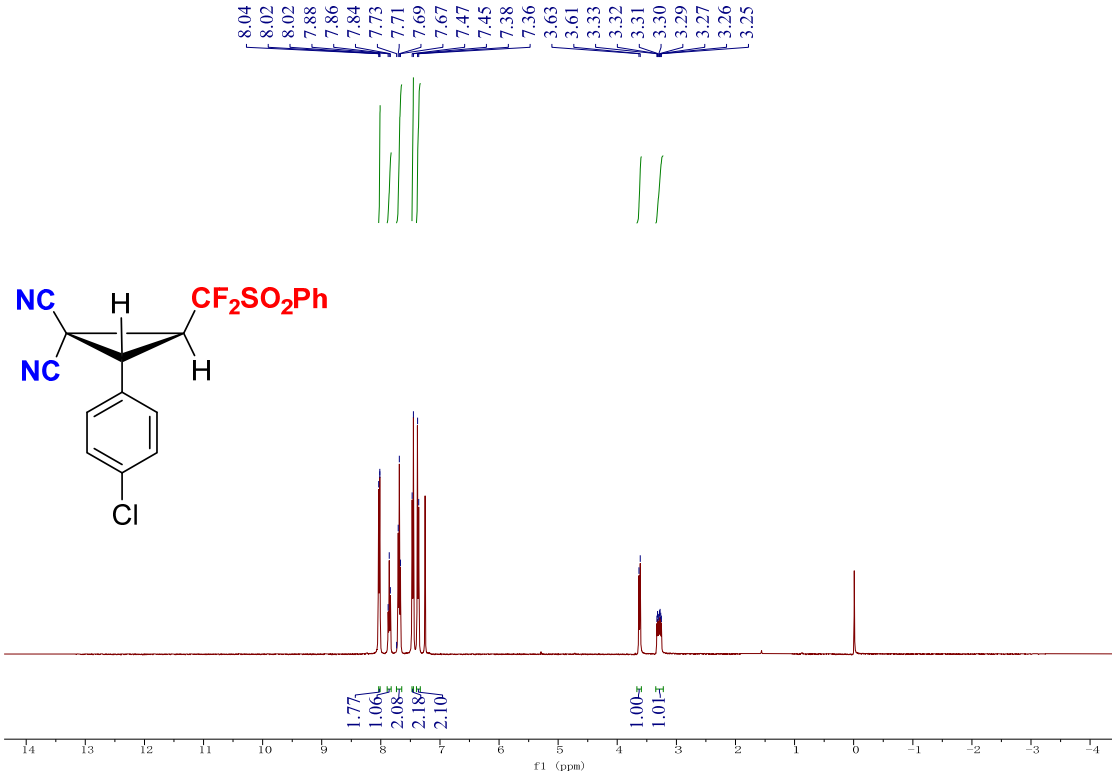
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3f**



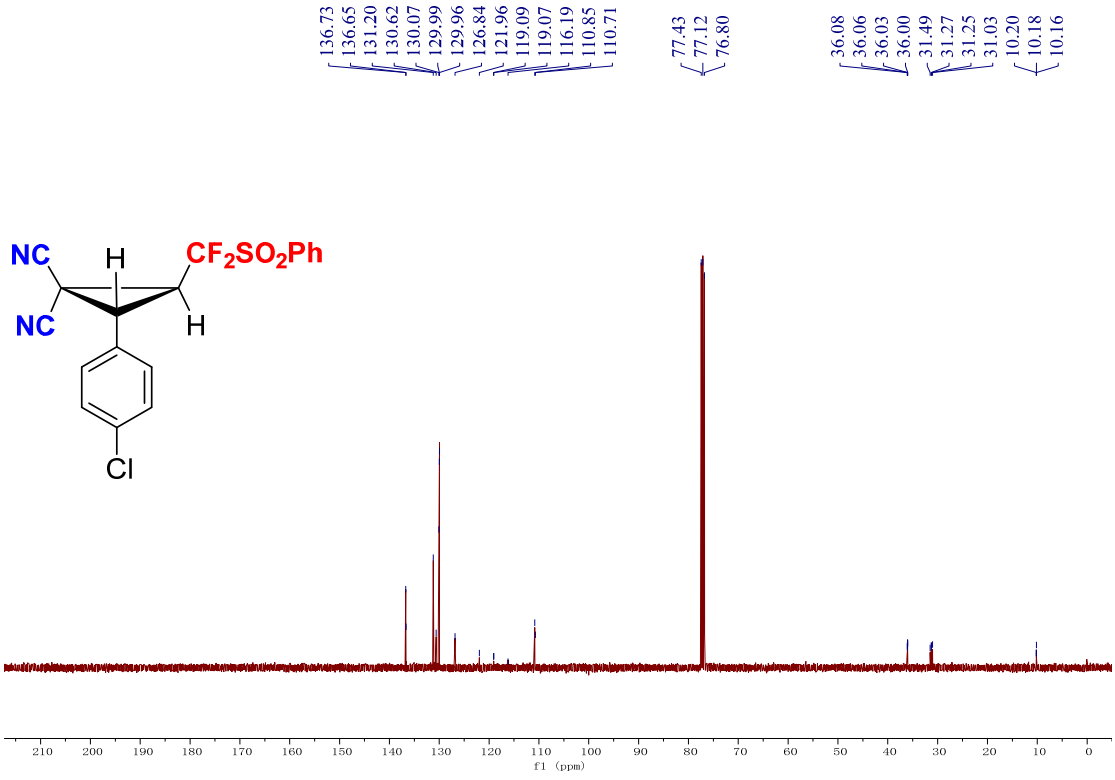
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3f**



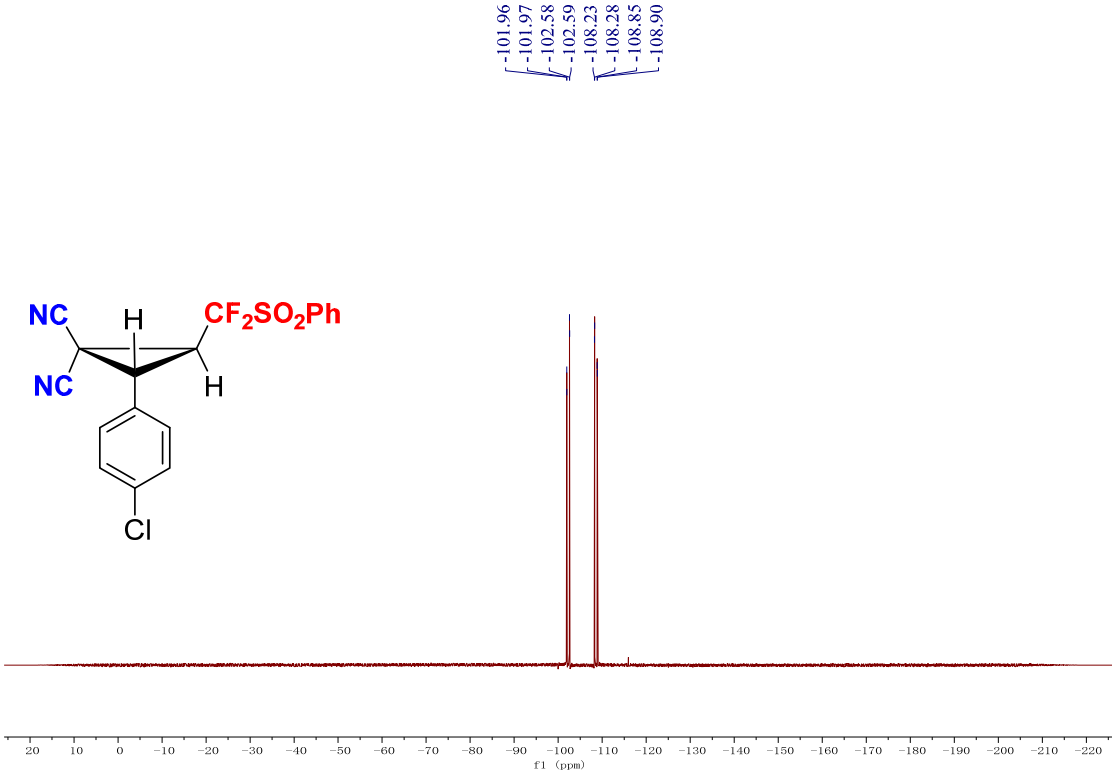
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**



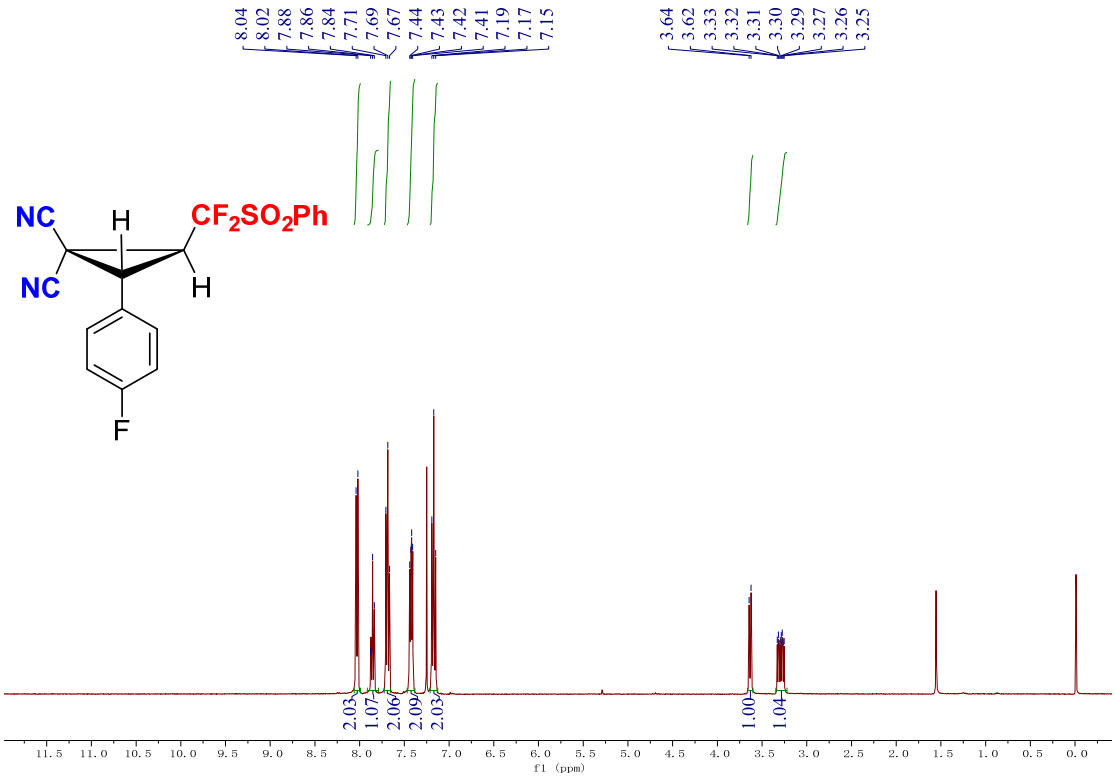
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3g**



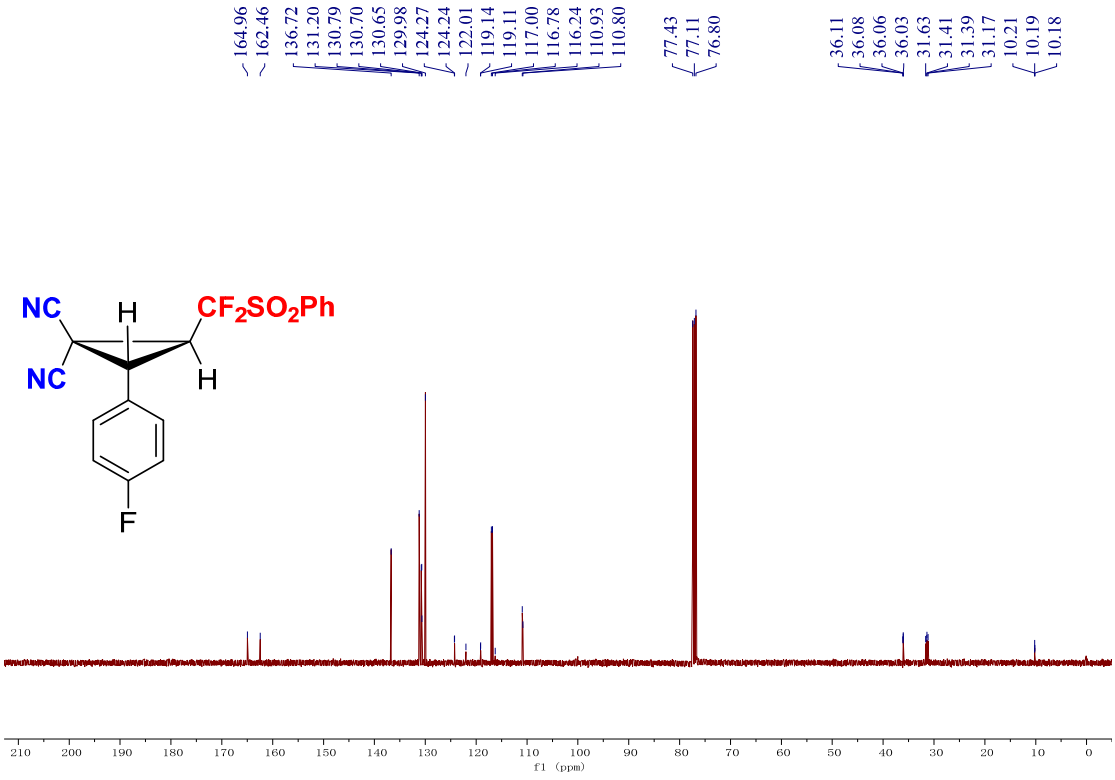
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3g**



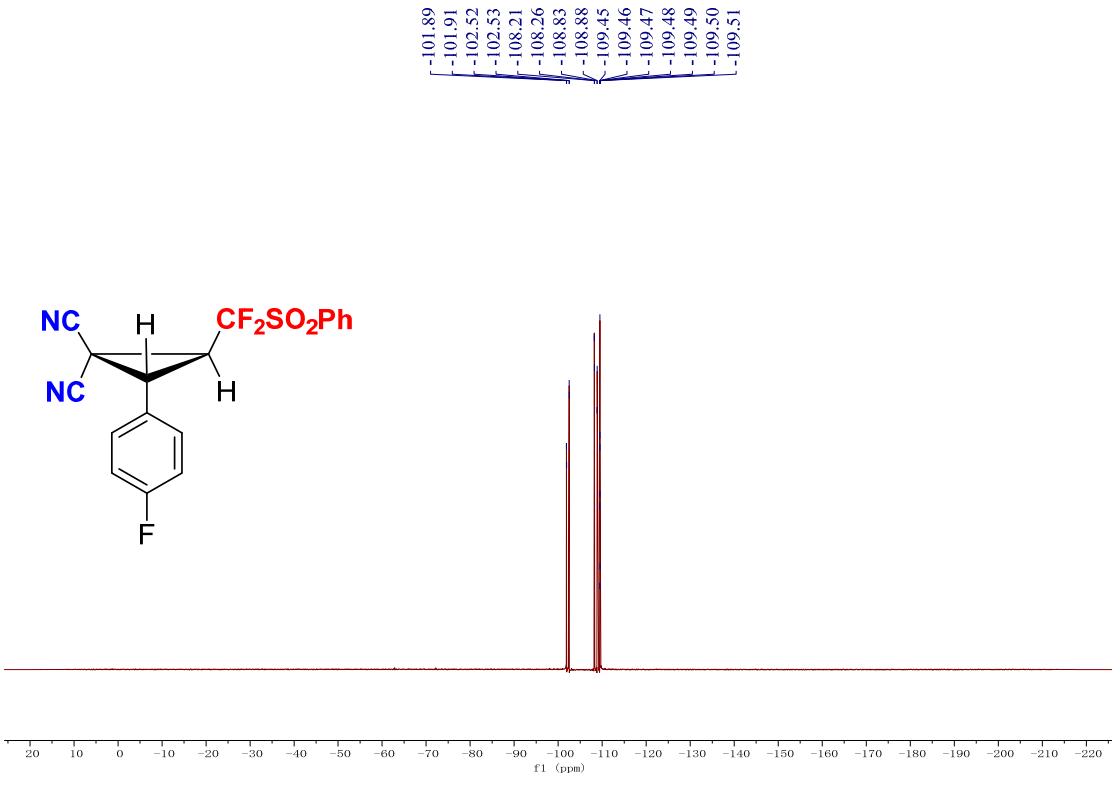
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**



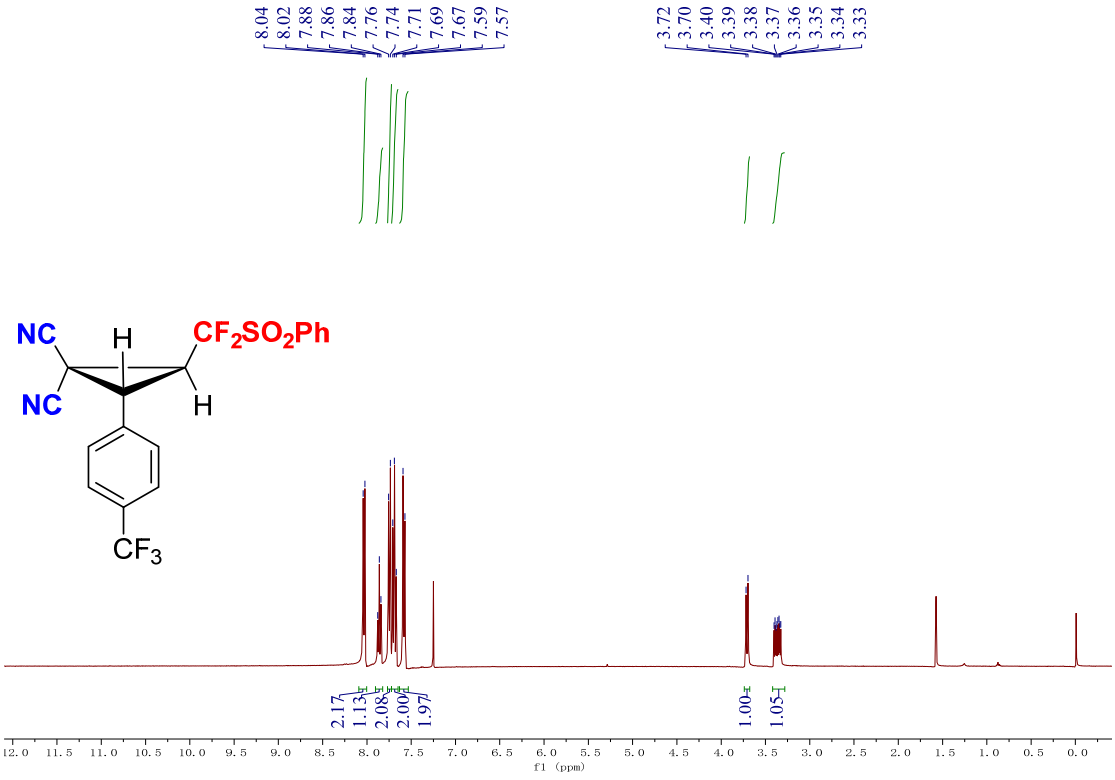
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3h**



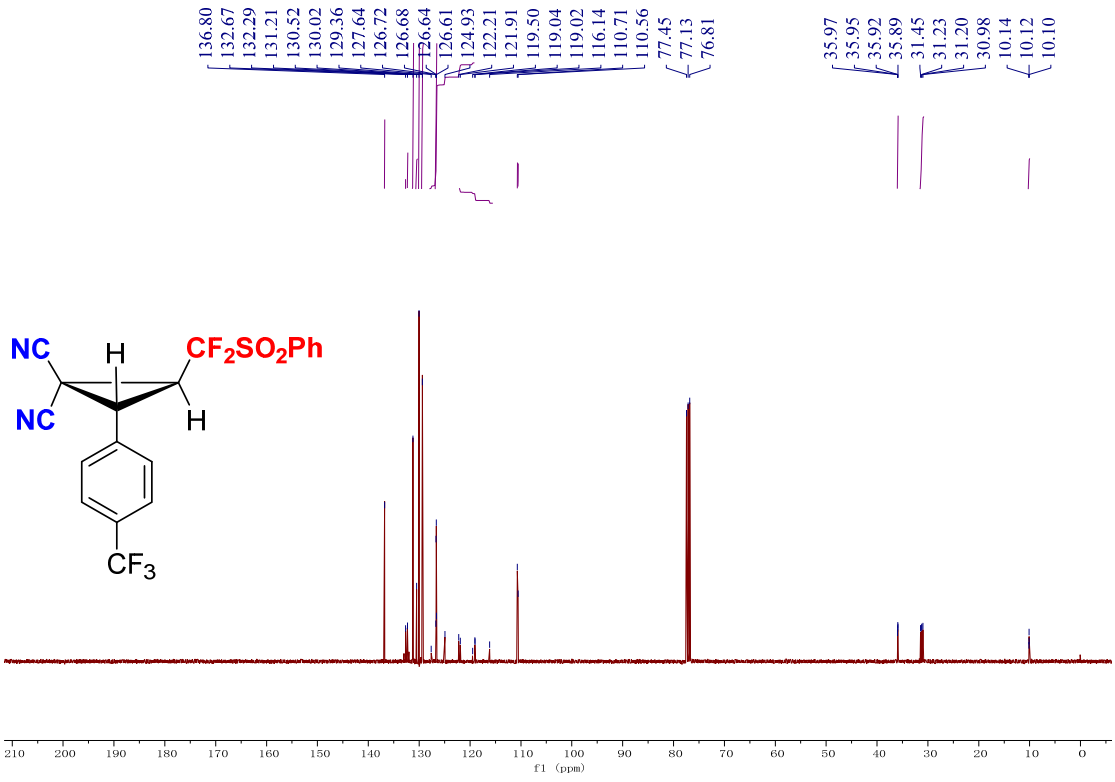
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3h**



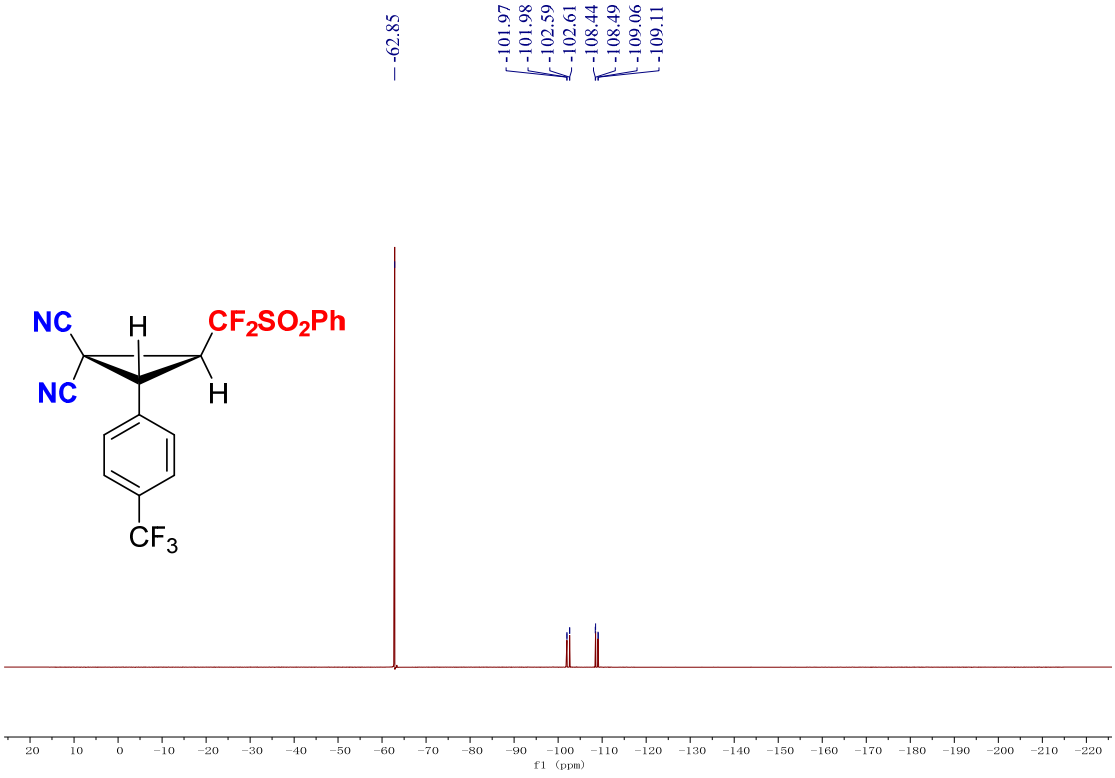
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**



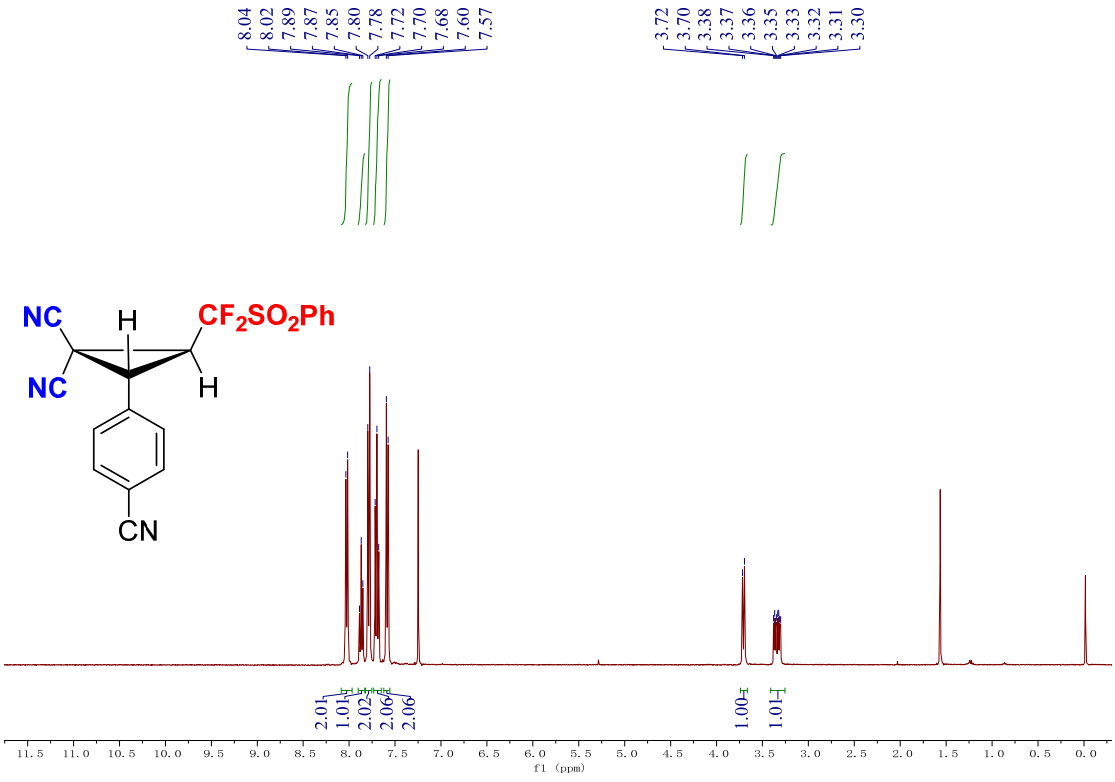
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3i**



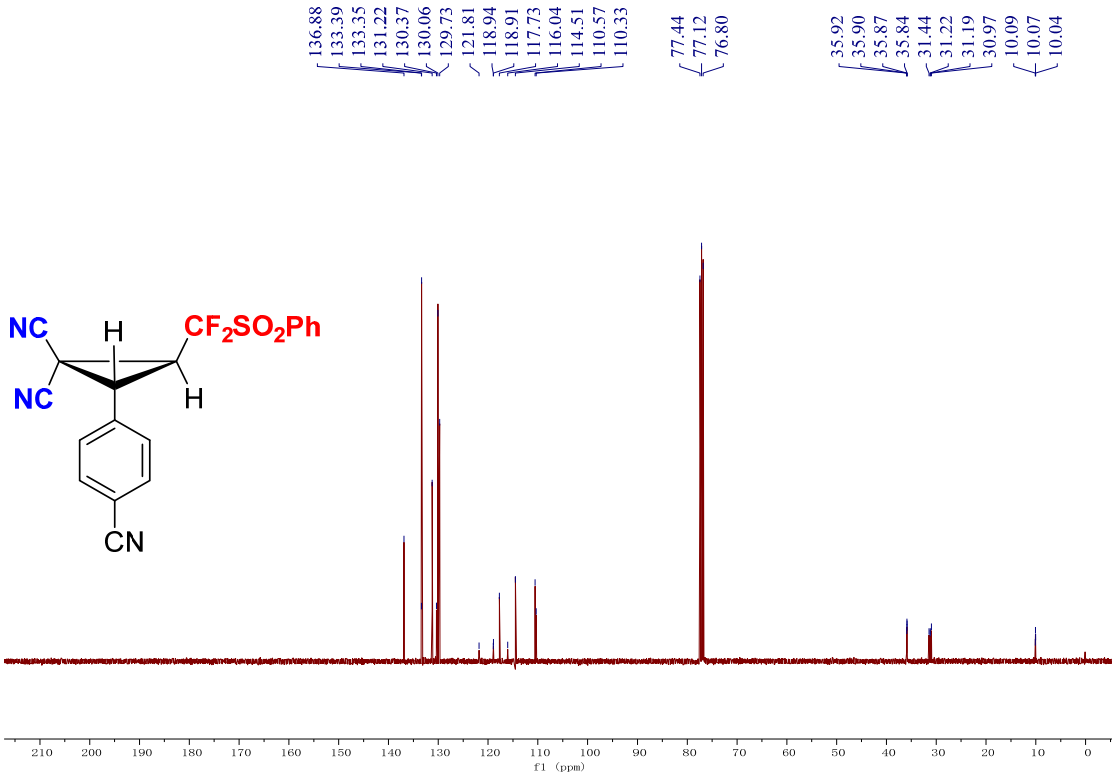
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3i**



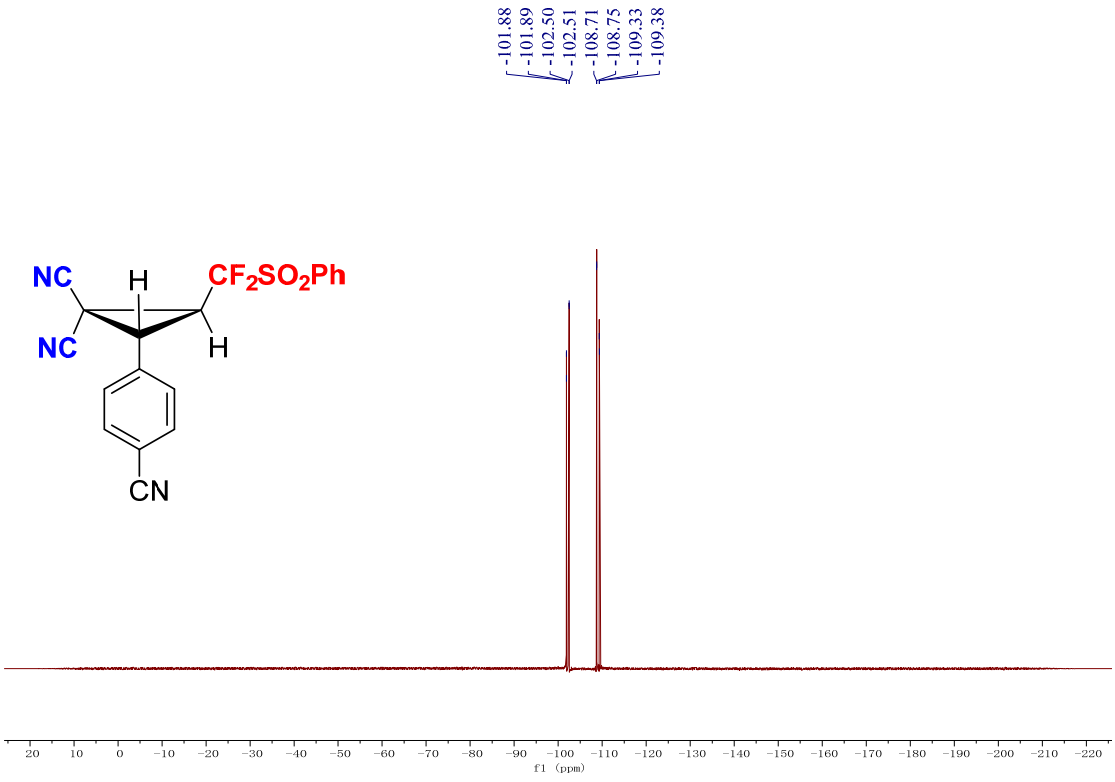
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**



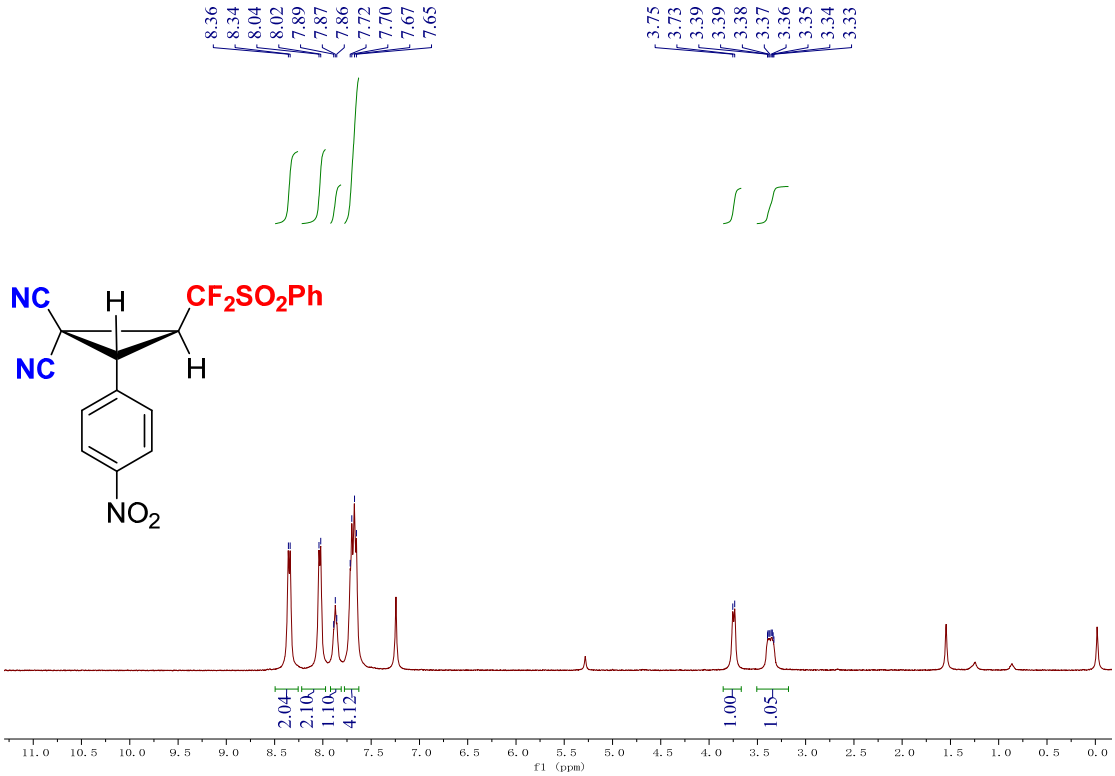
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3j**



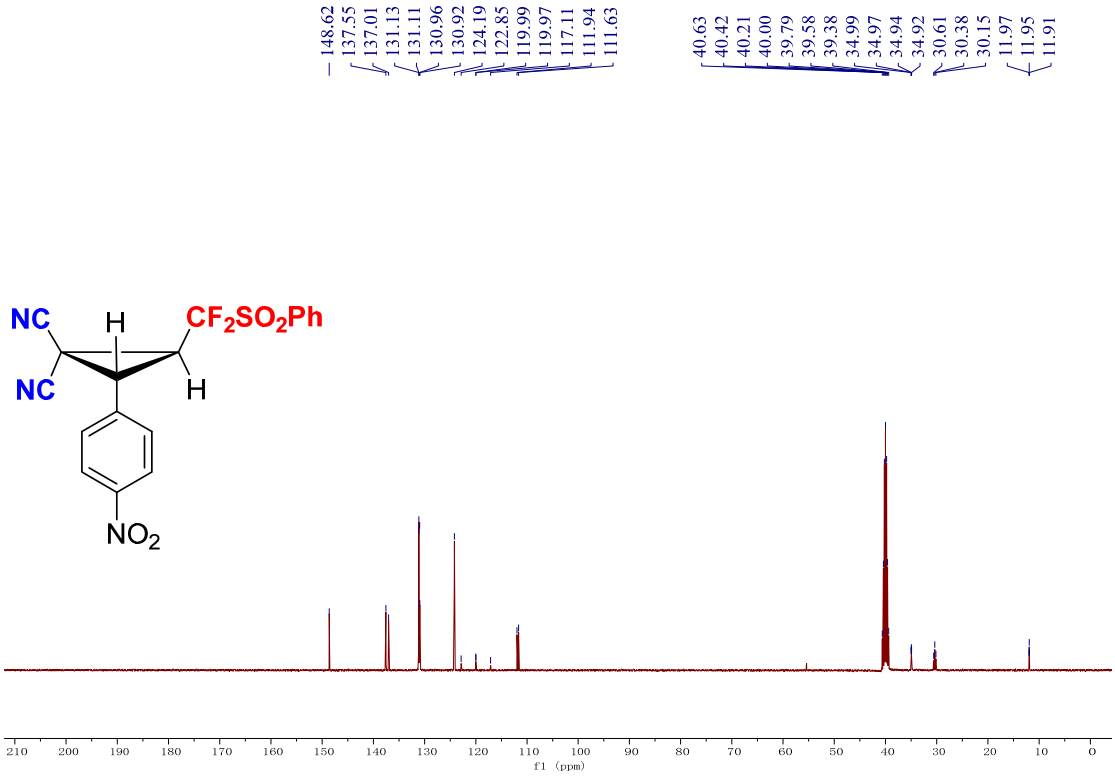
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3j**



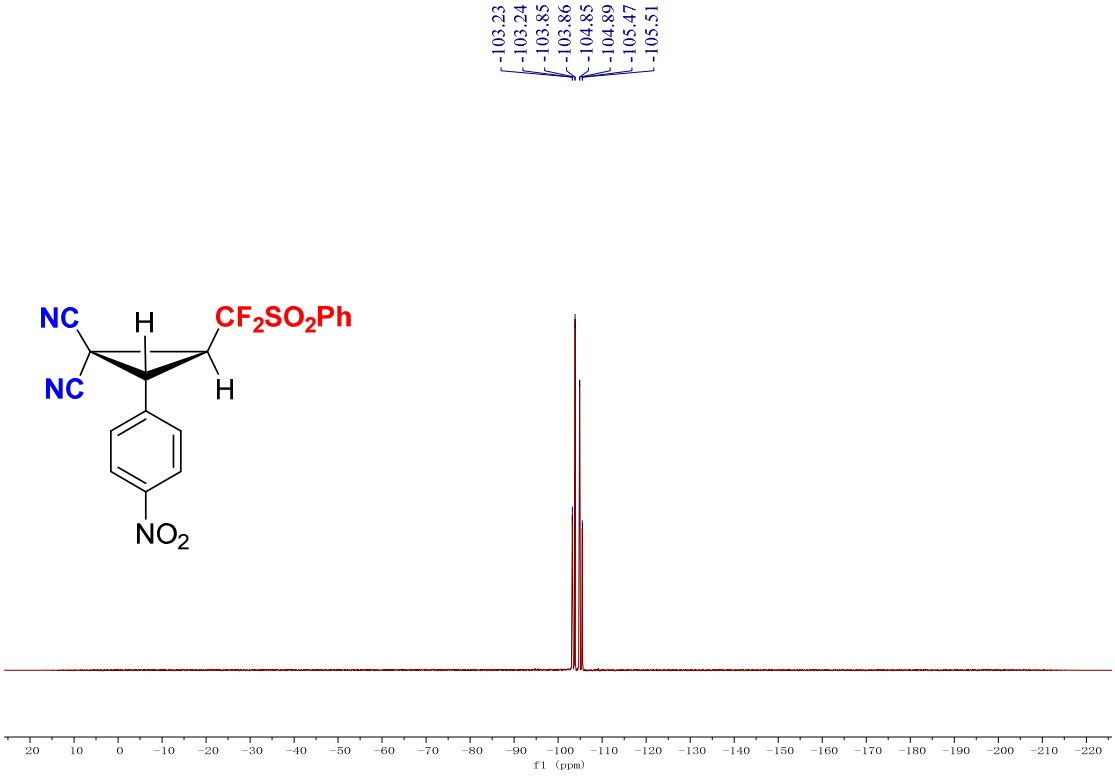
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**



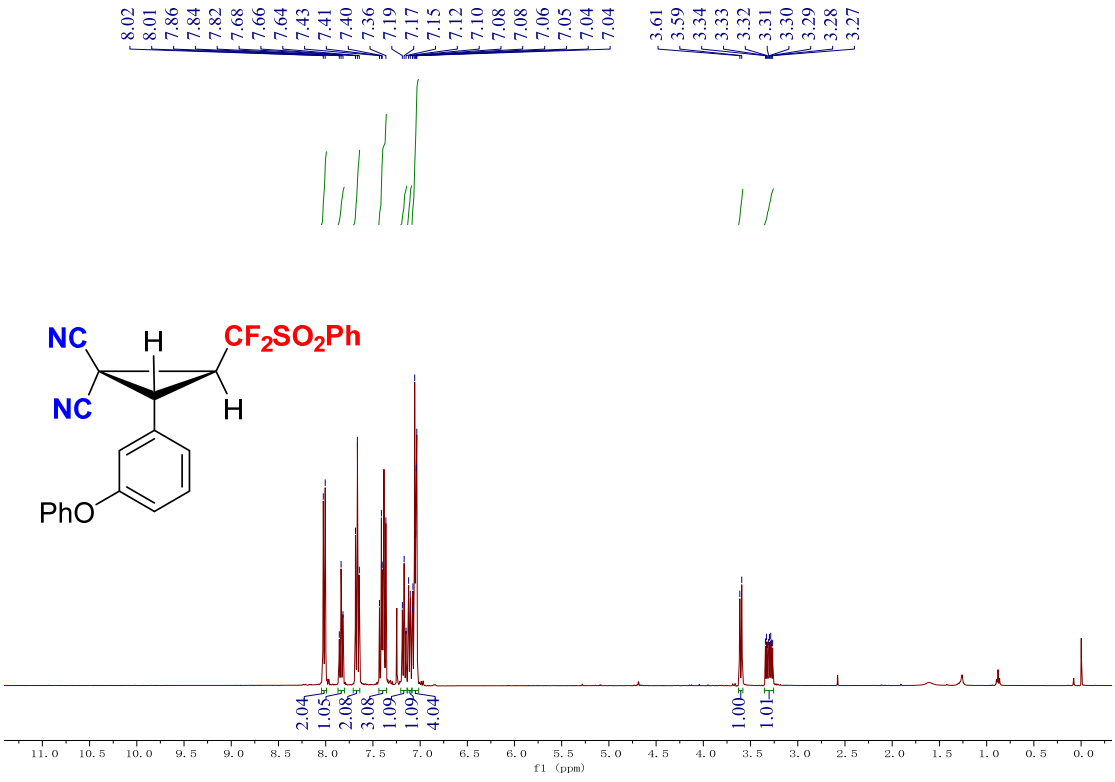
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **3k**



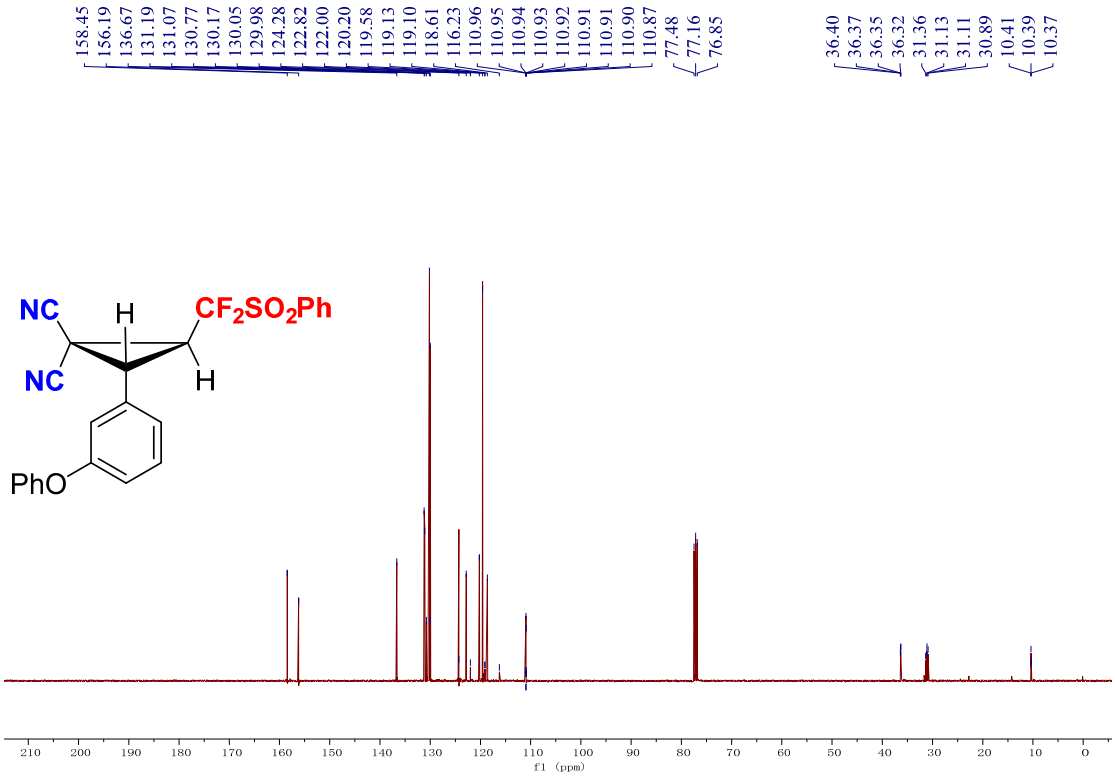
^{19}F NMR (376 MHz, DMSO-d_6) spectrum of **3k**



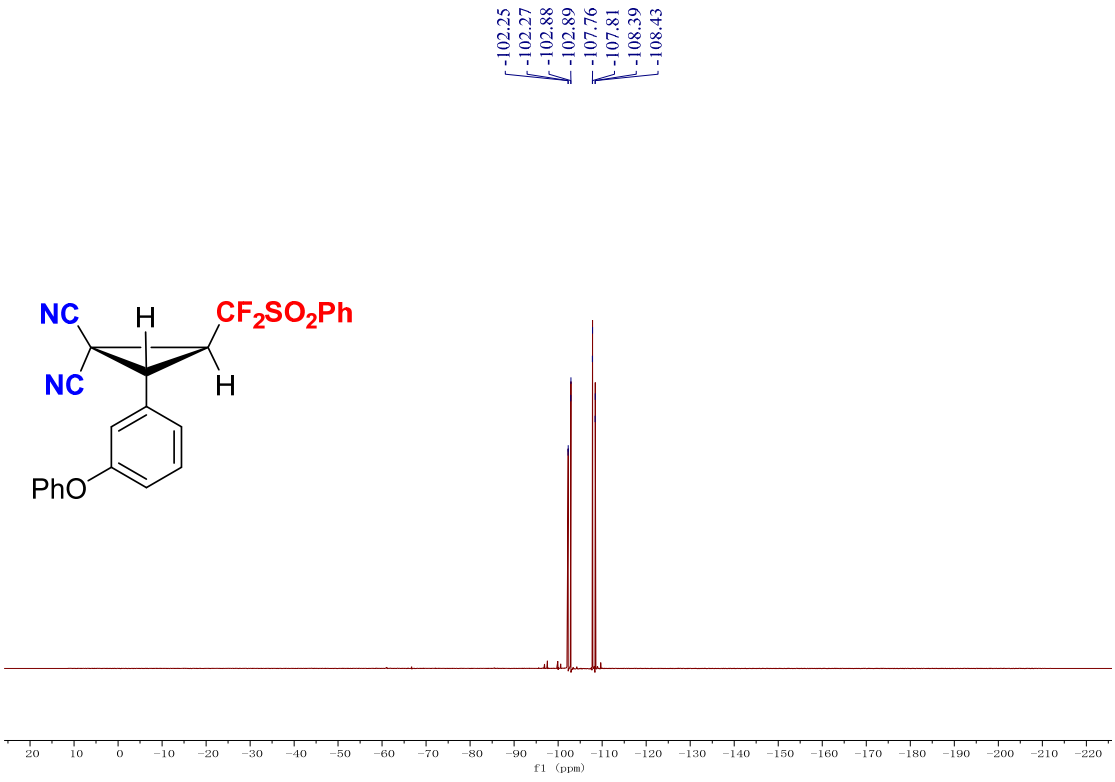
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**



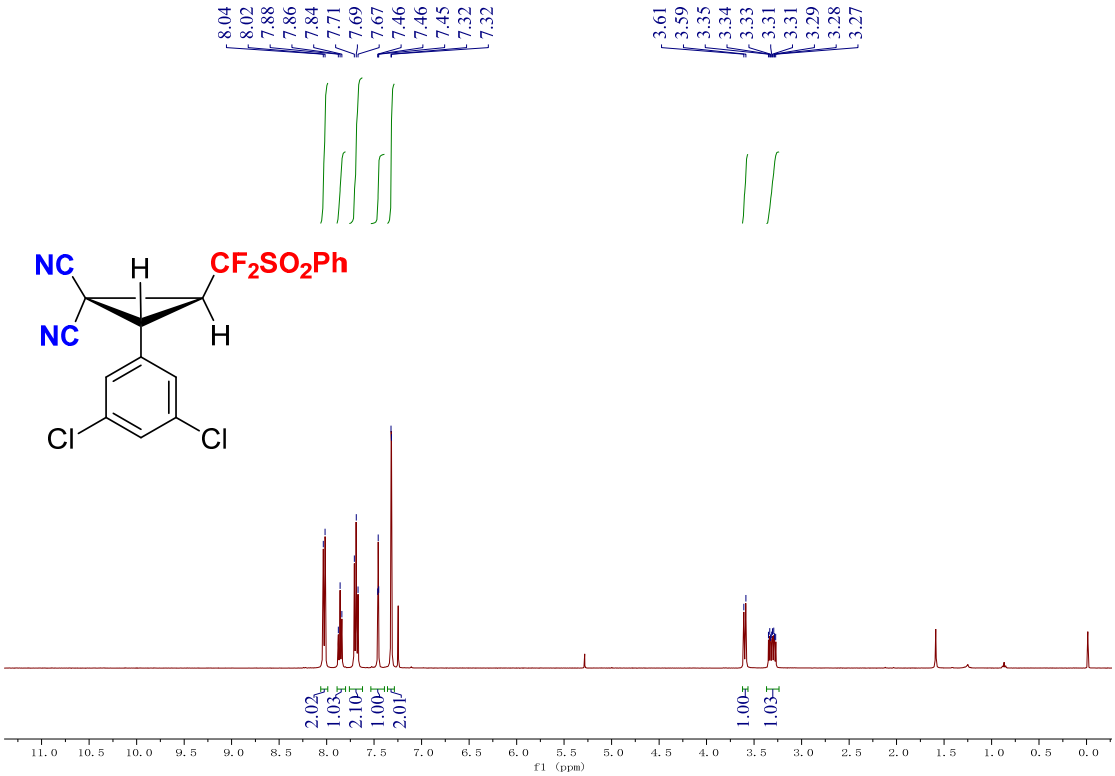
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3l**



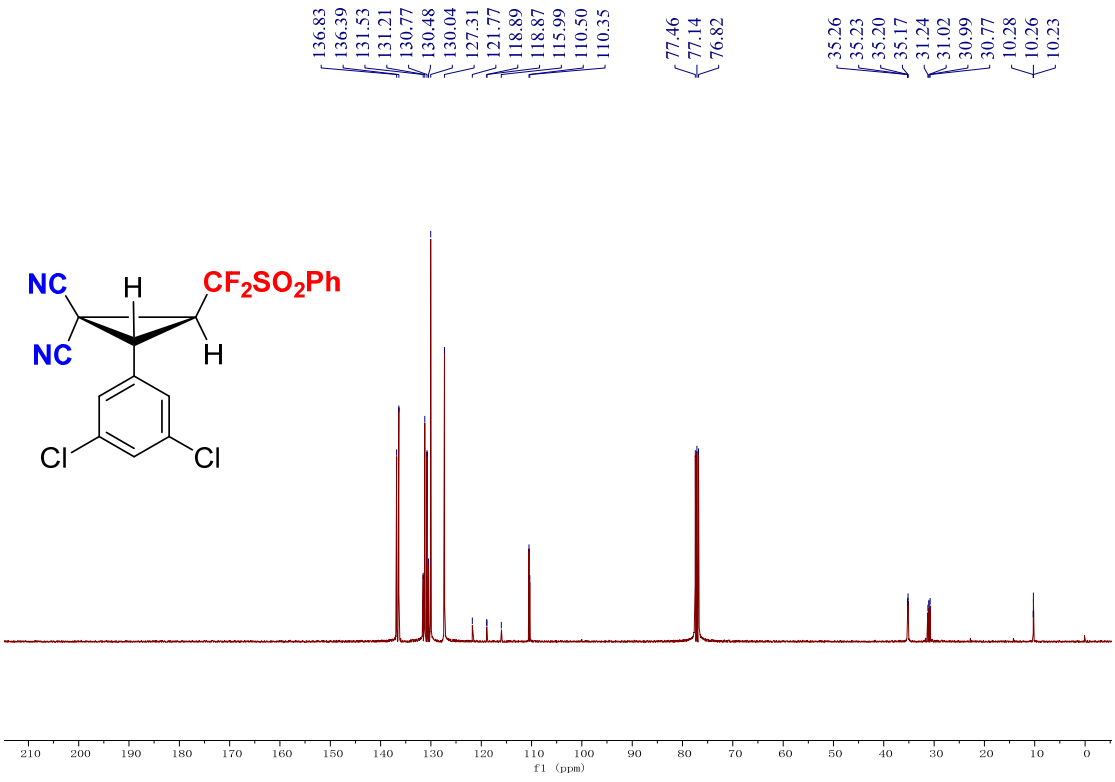
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3l**



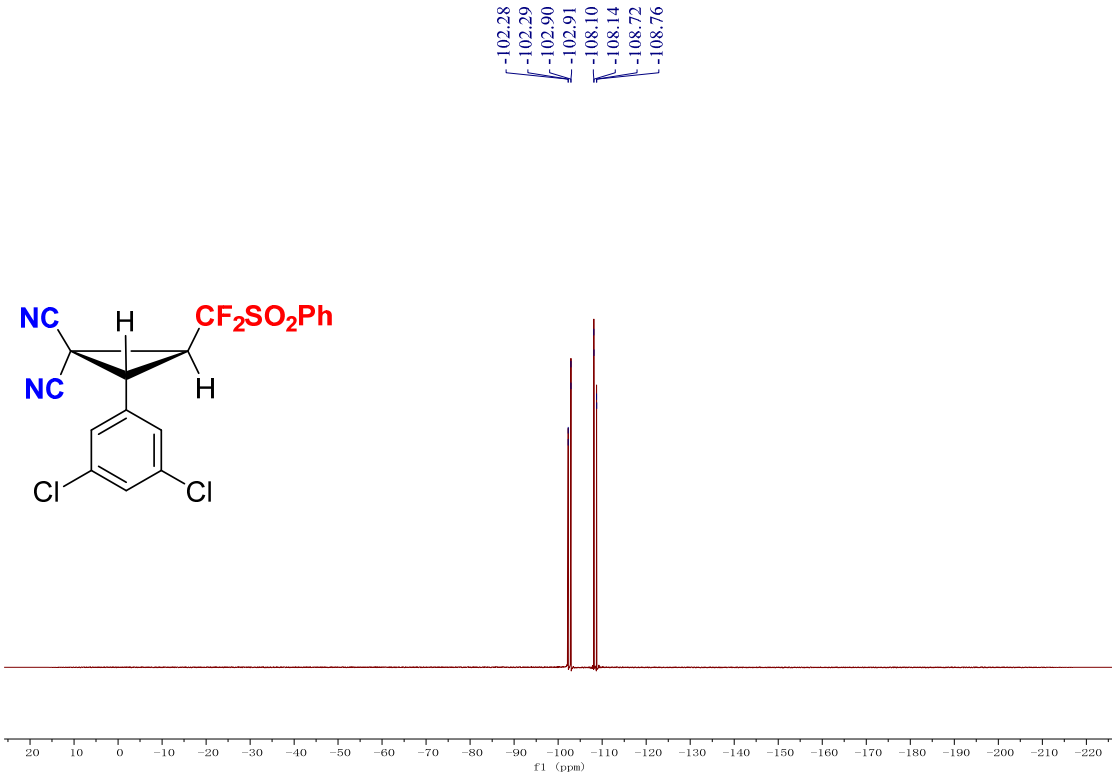
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**



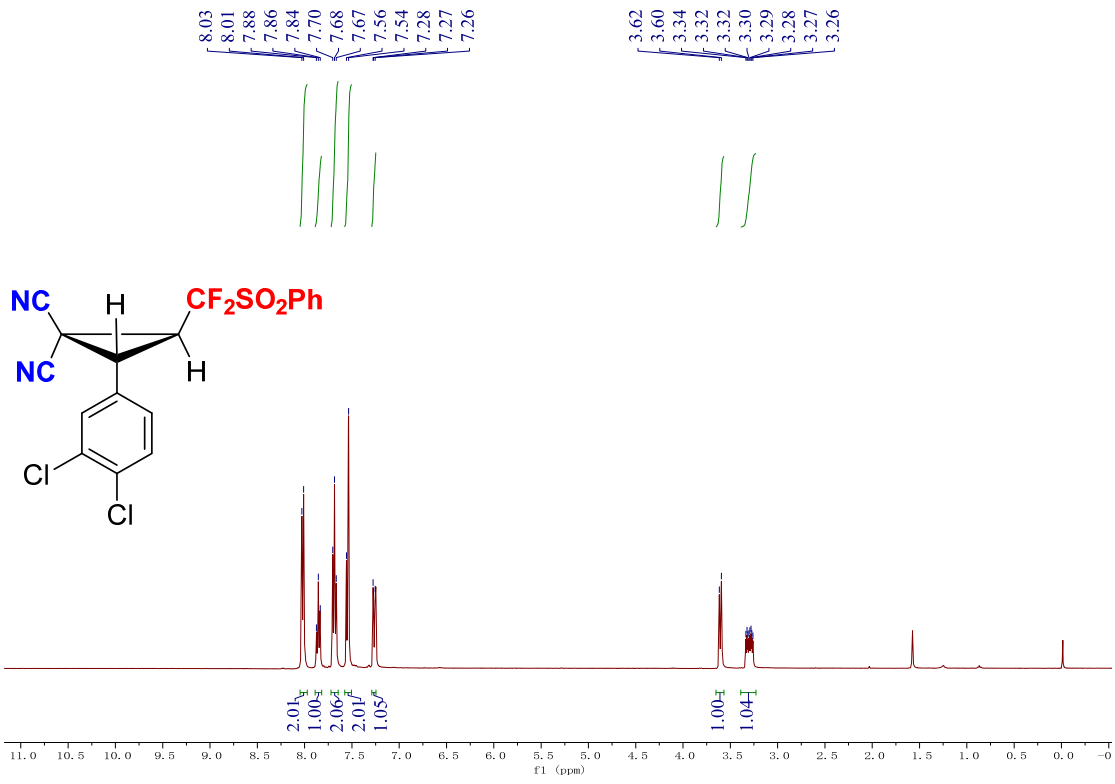
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3m**



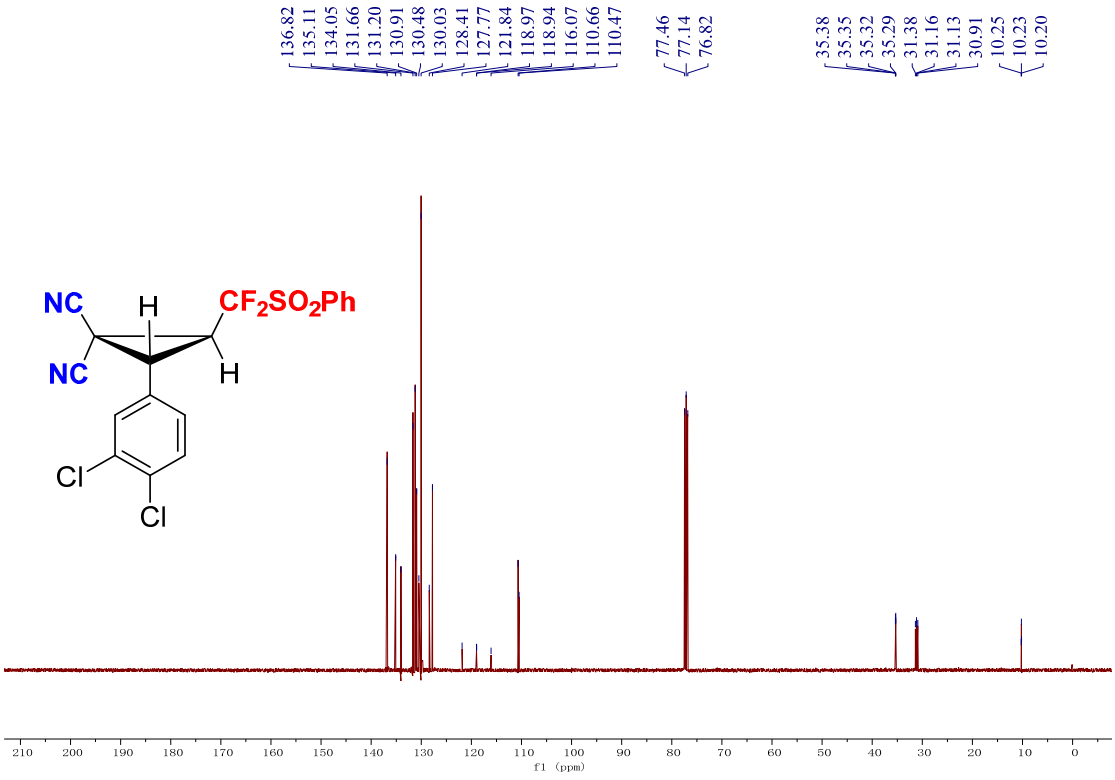
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3m**



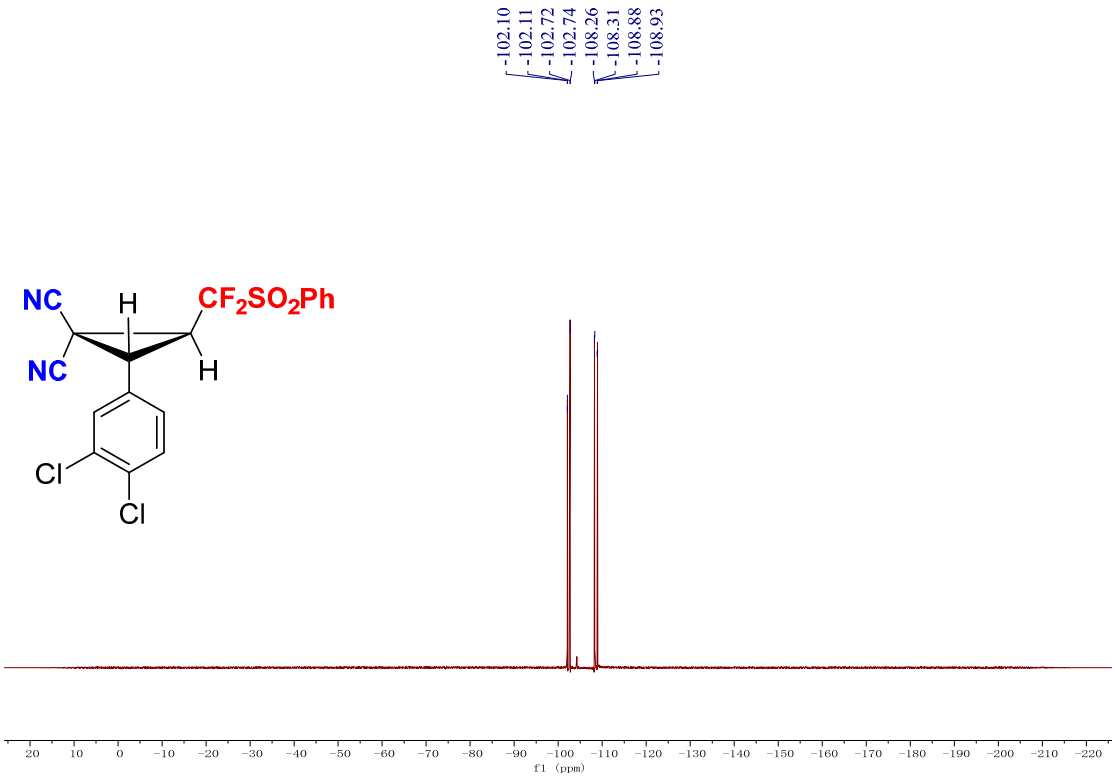
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**



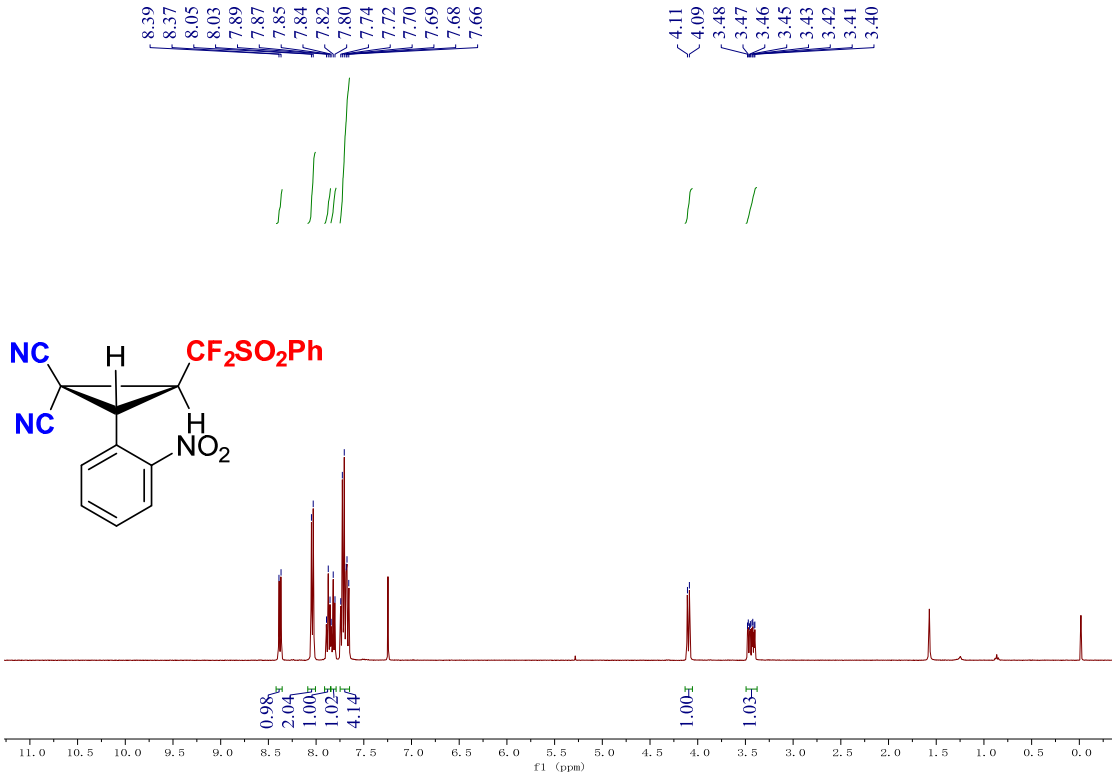
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3n**



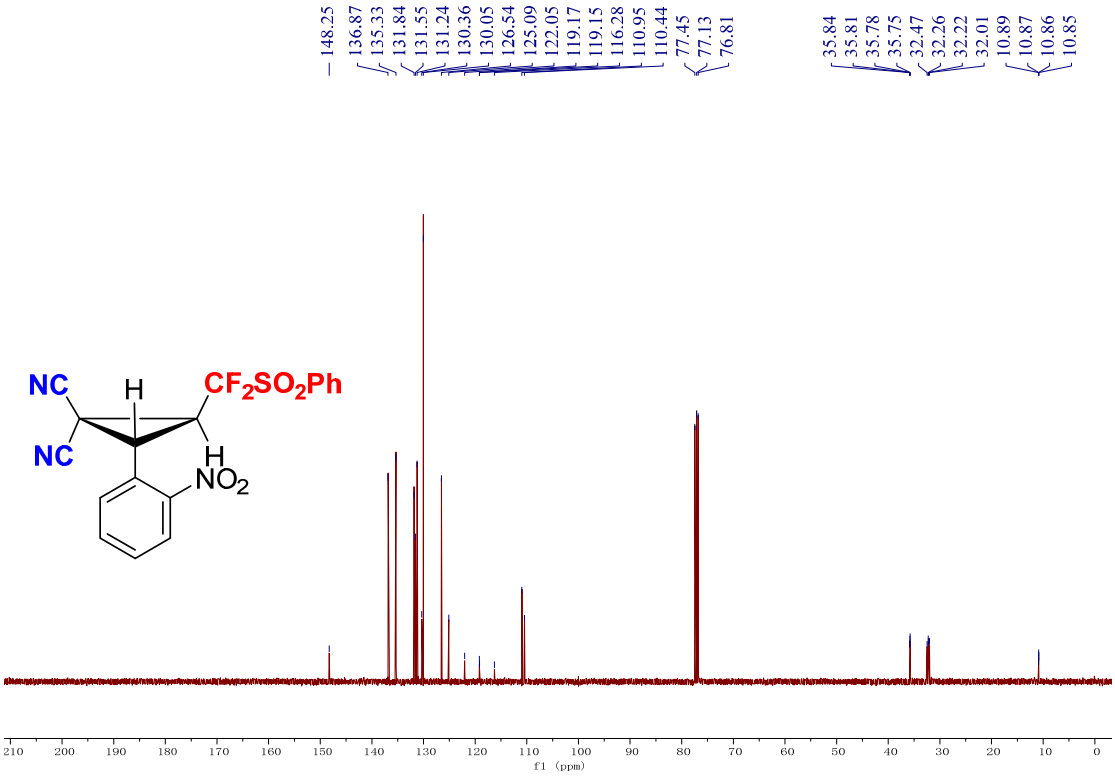
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3n**



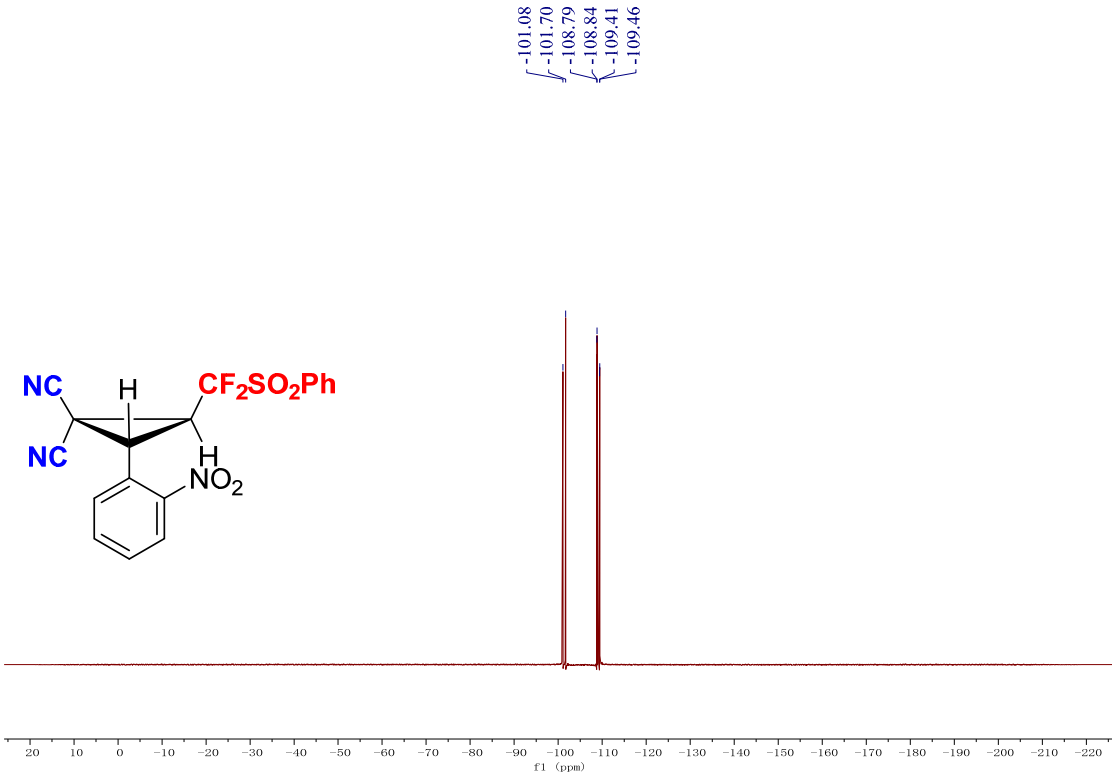
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**



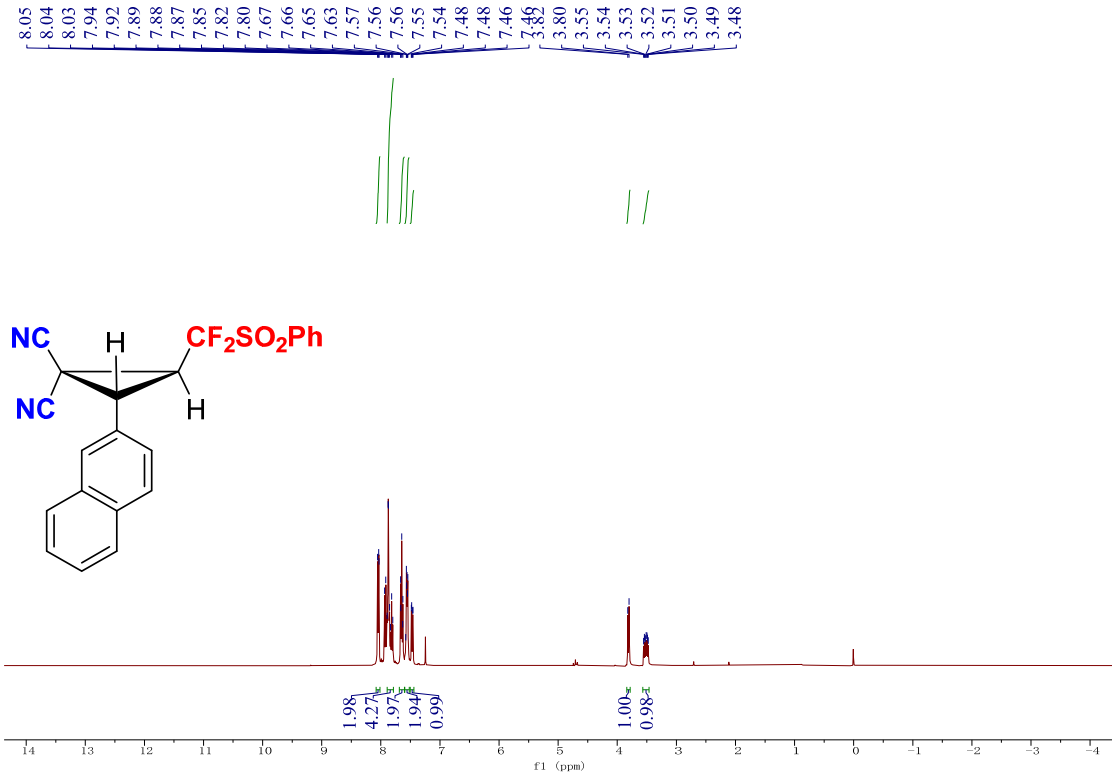
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3o**



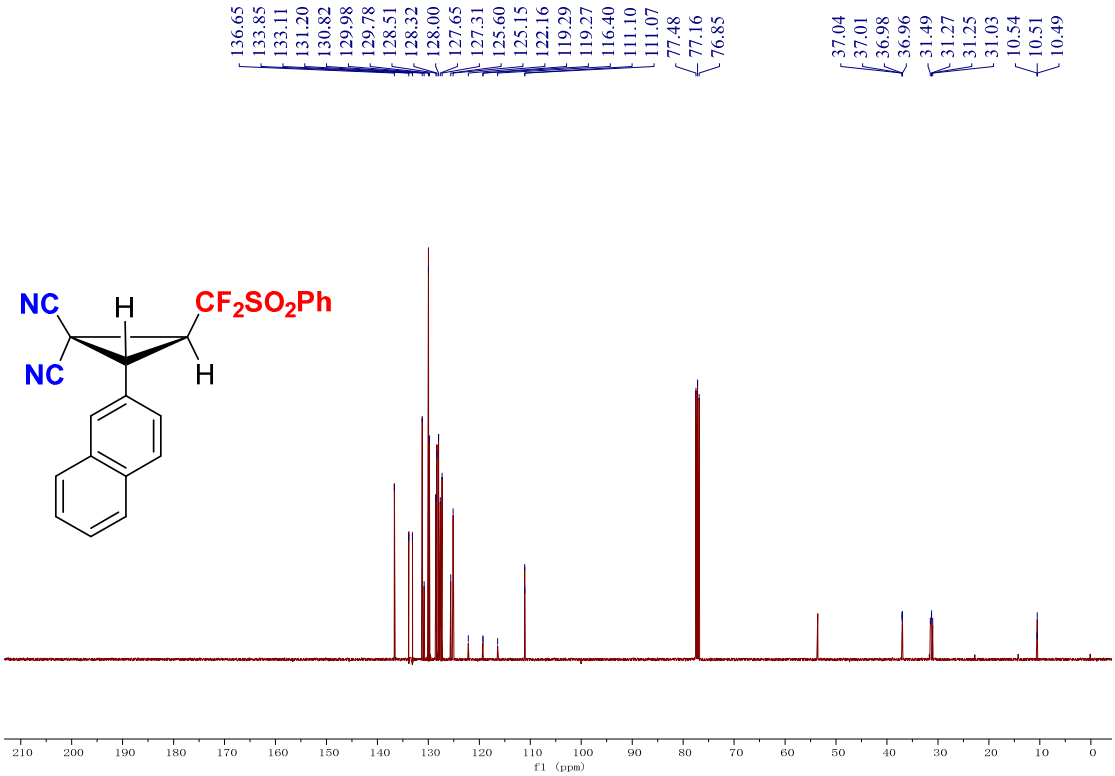
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3o**



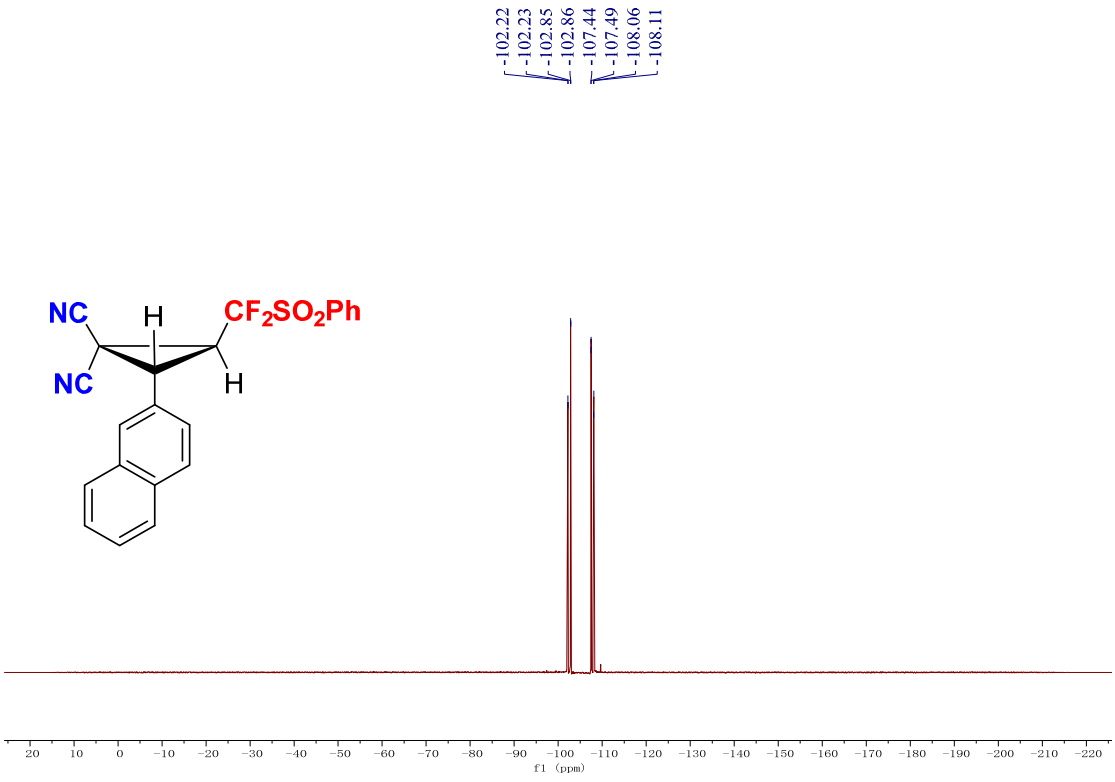
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**



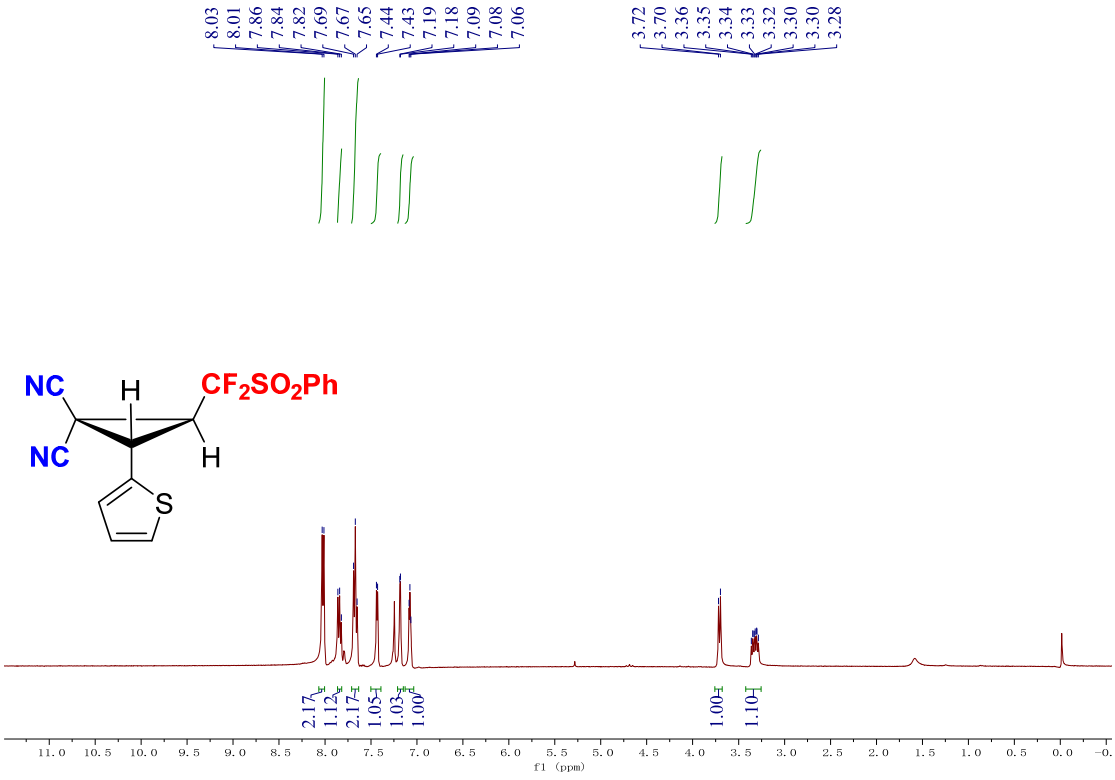
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3p**



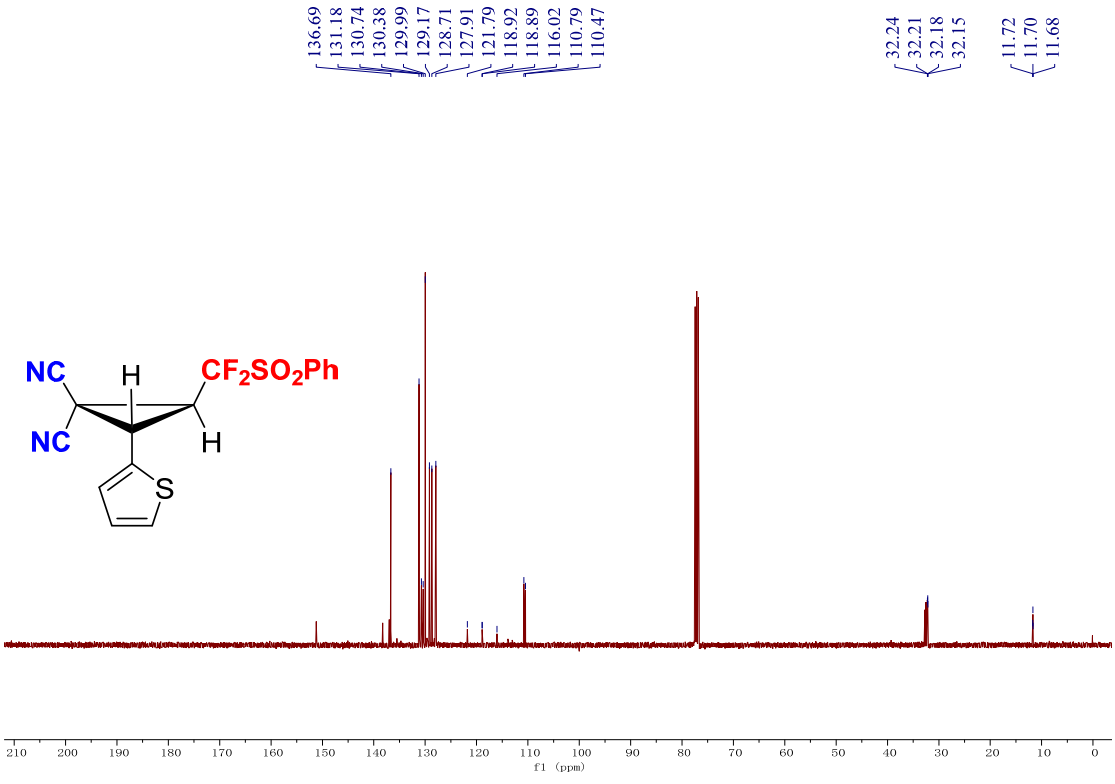
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3p**



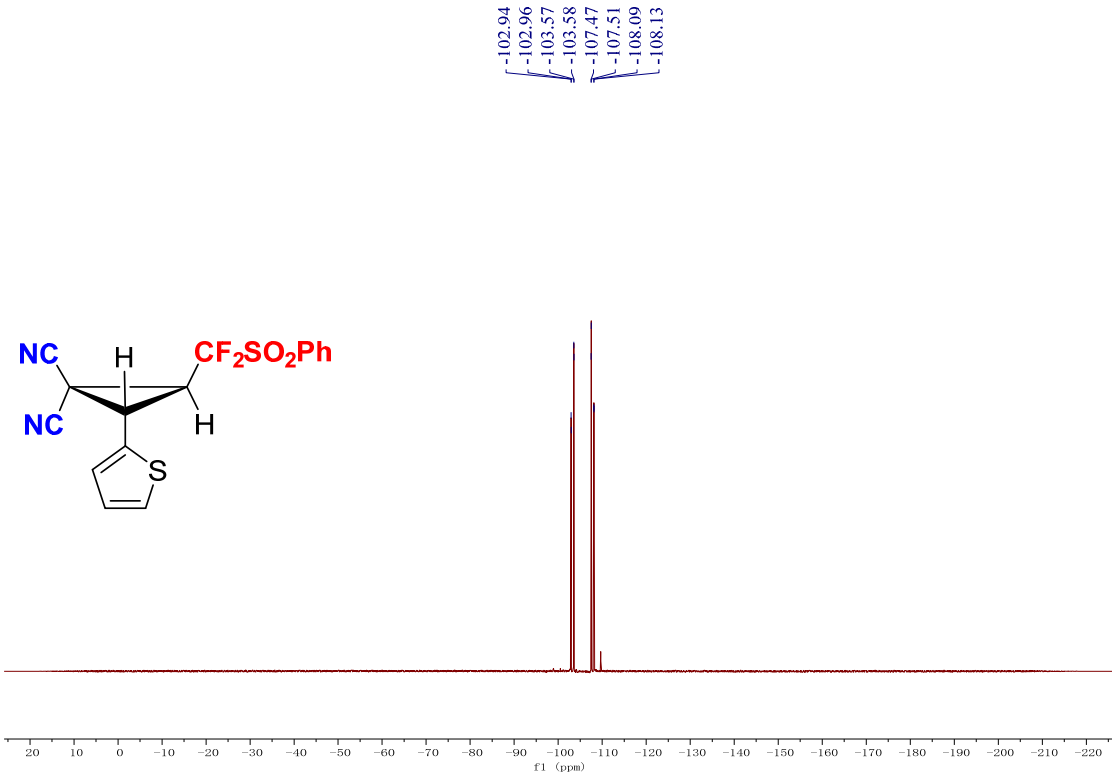
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**



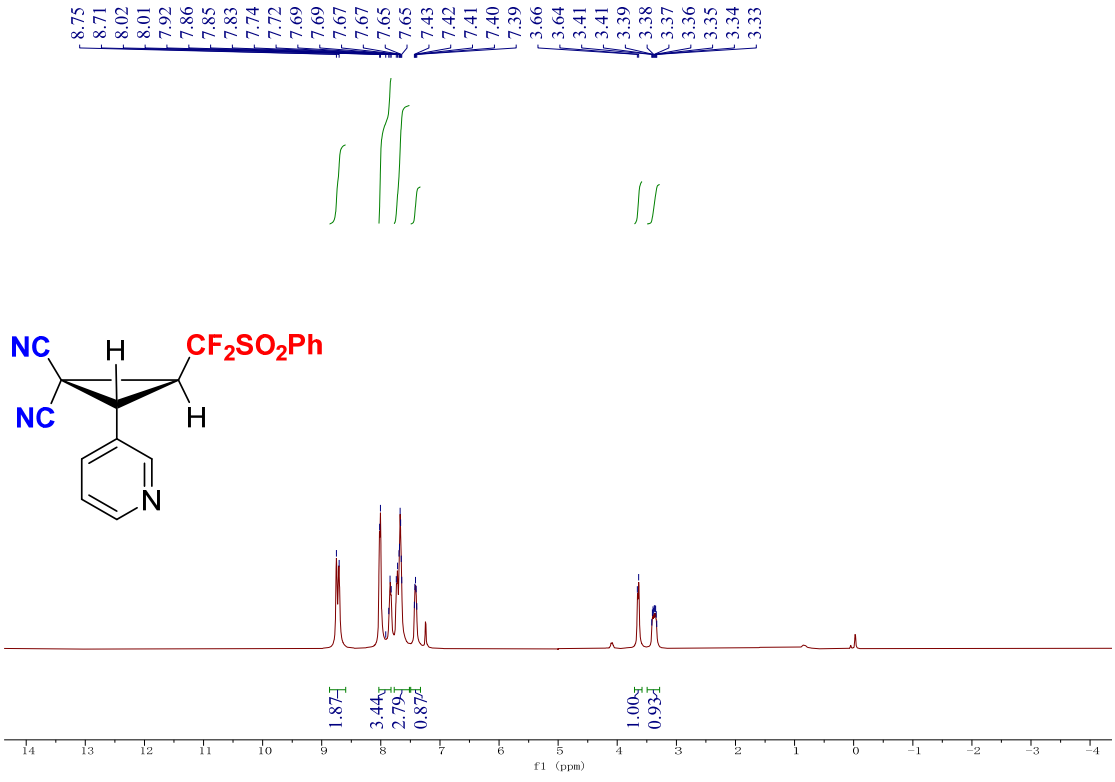
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3q**



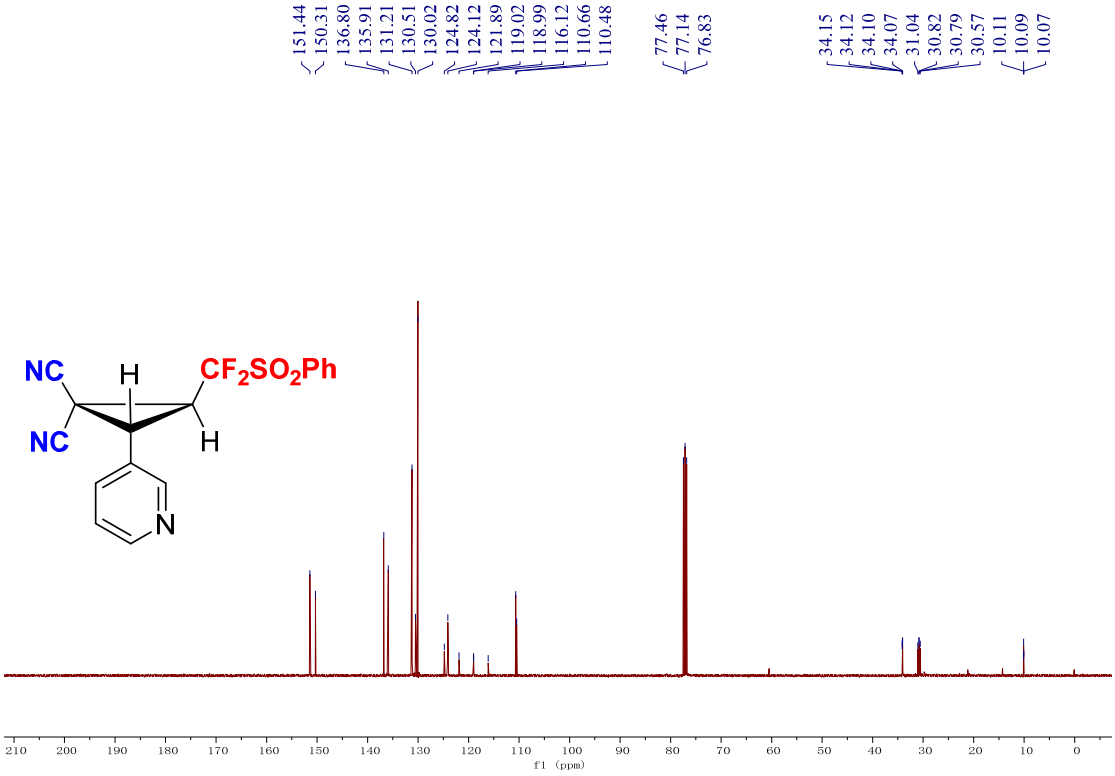
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3q**



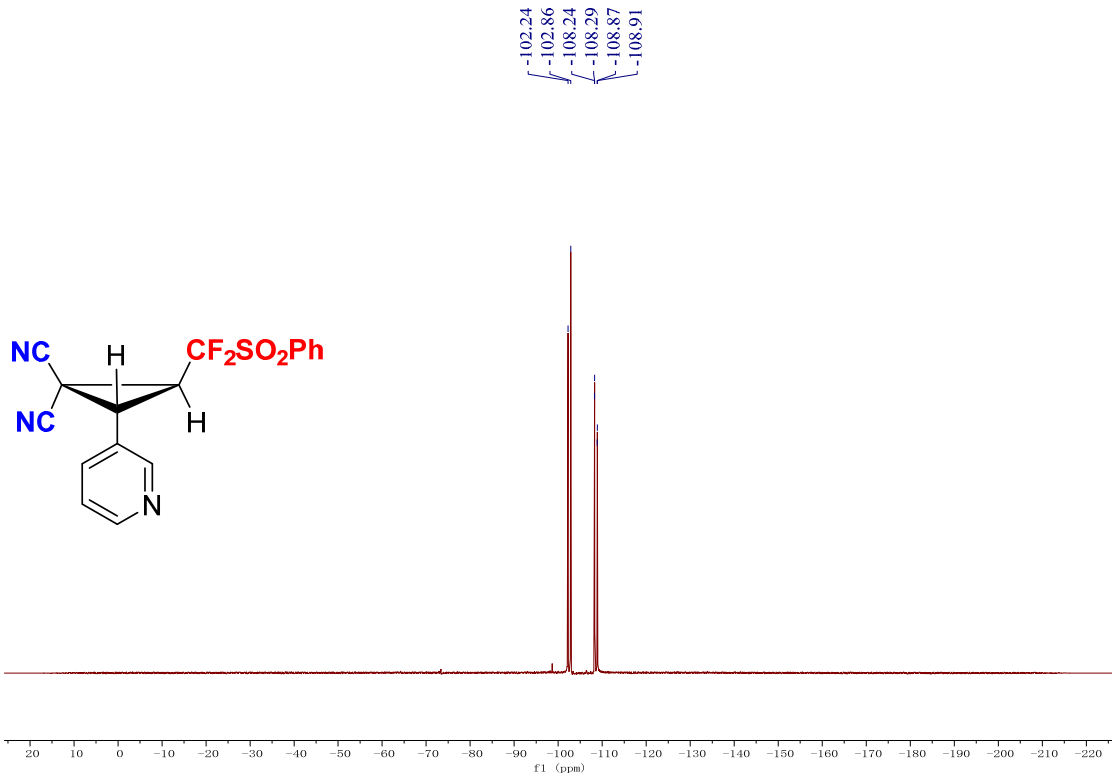
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**



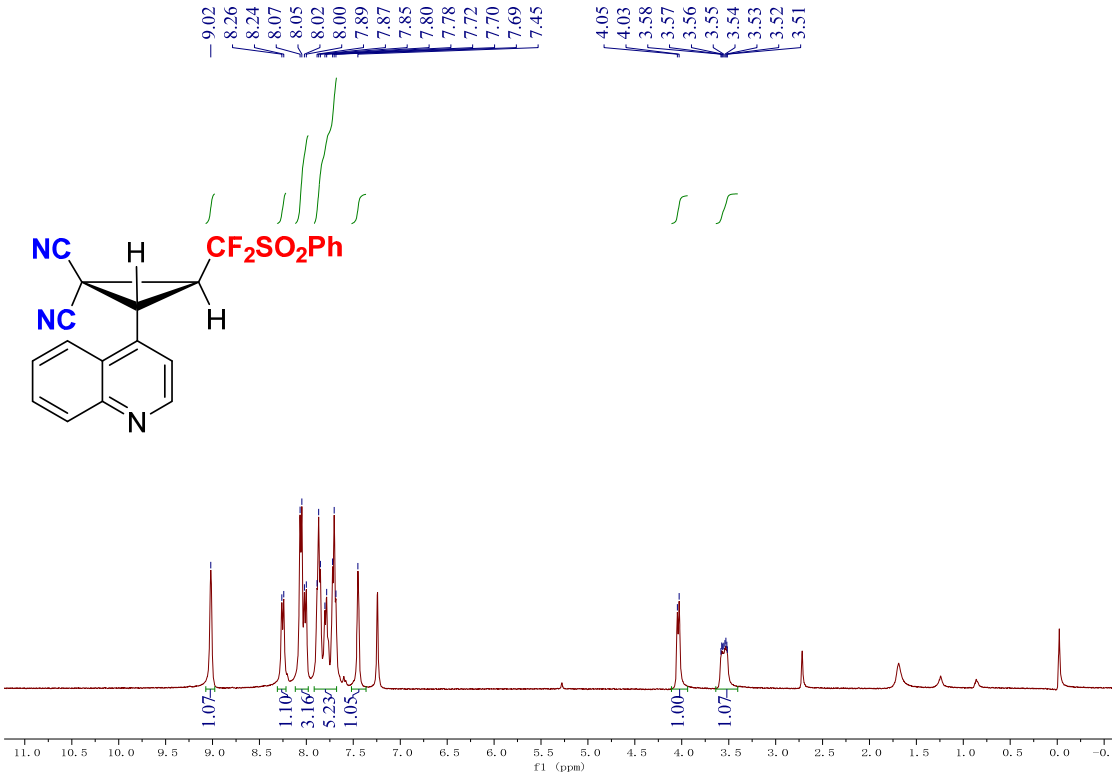
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3r**



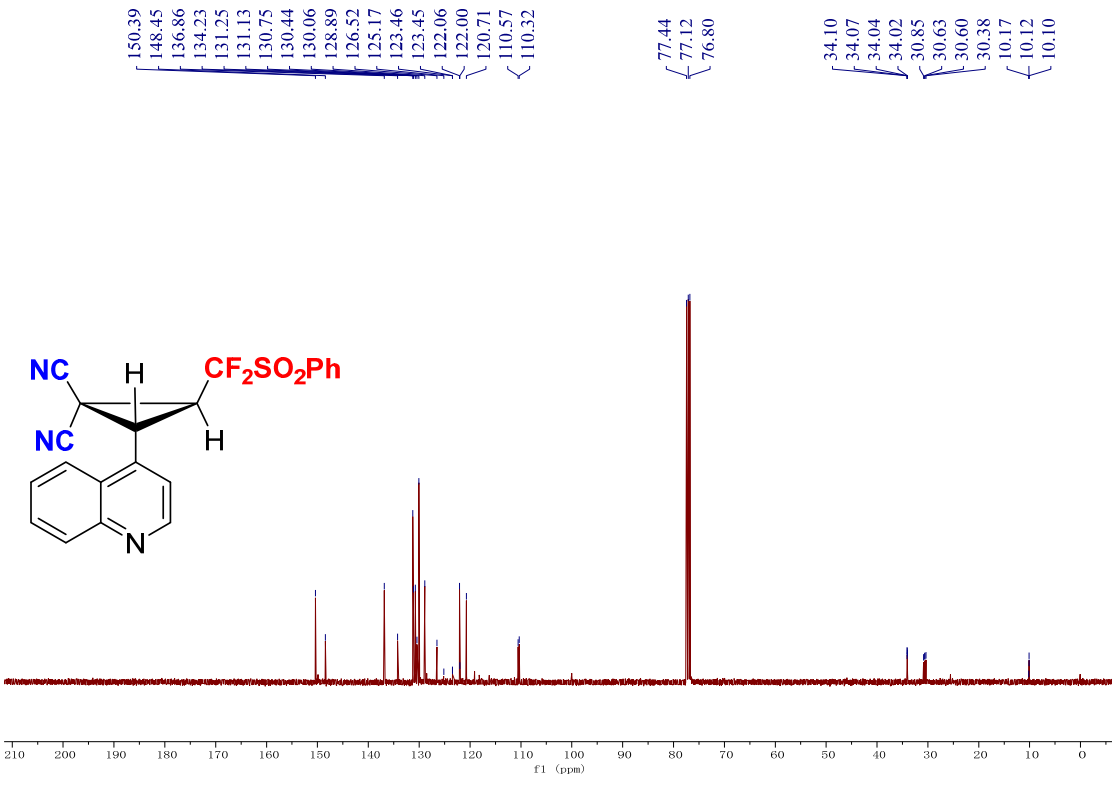
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3r**



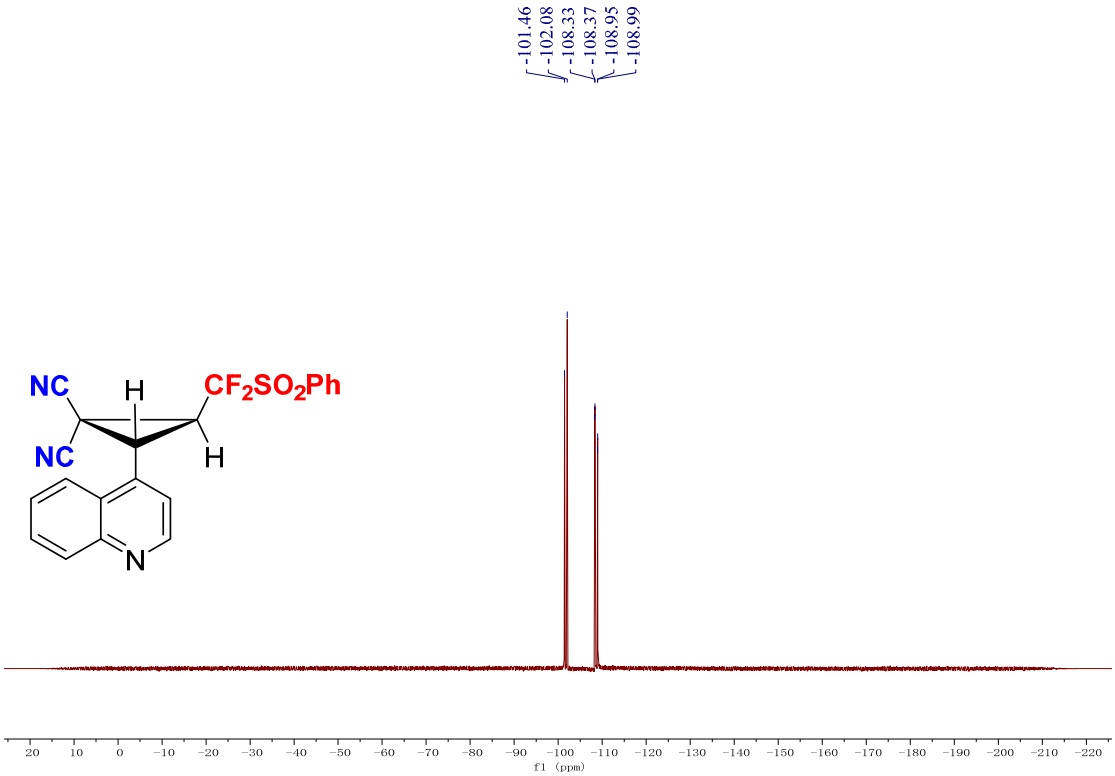
^{1}H NMR (00 MHz, $CDCl_3$) spectrum of **3s**



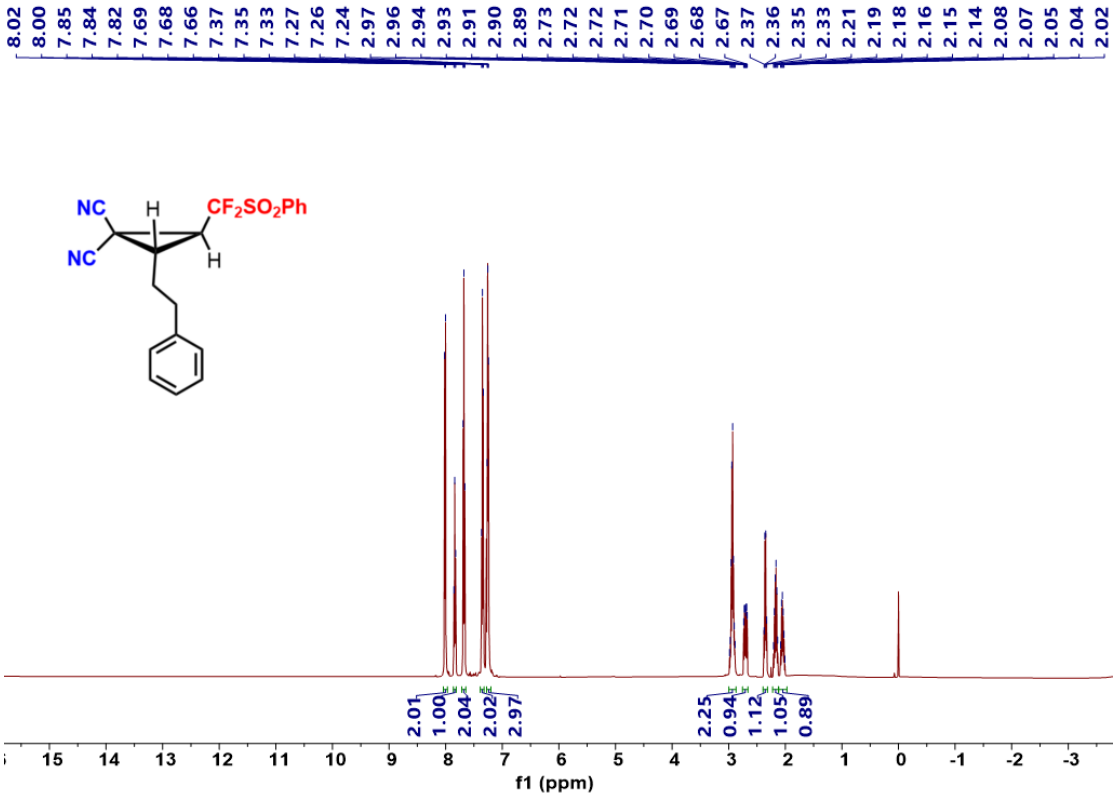
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3s**



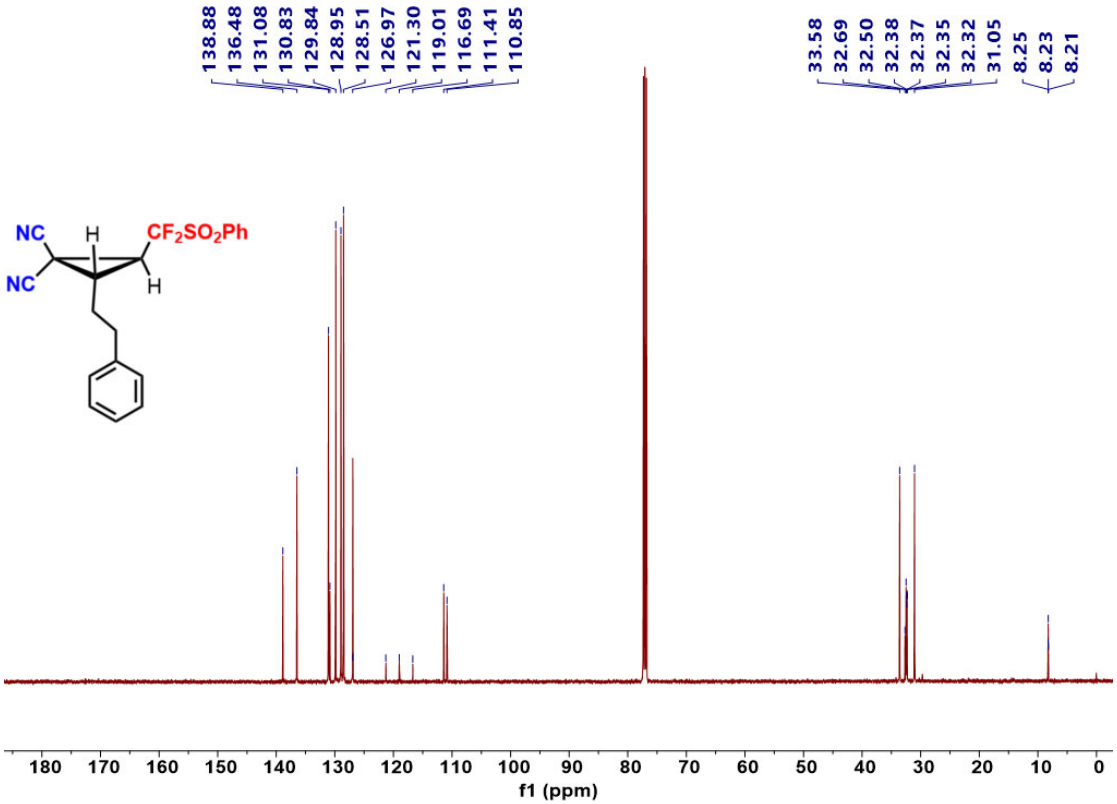
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3s**



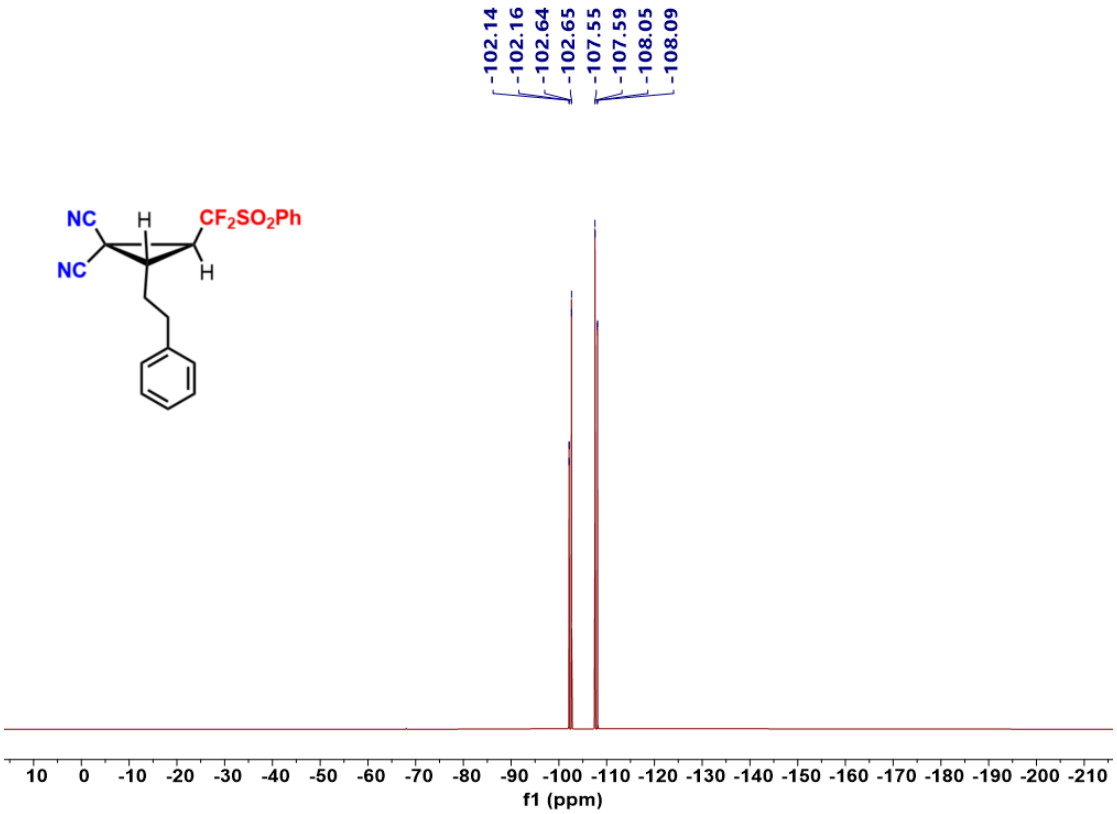
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3t**



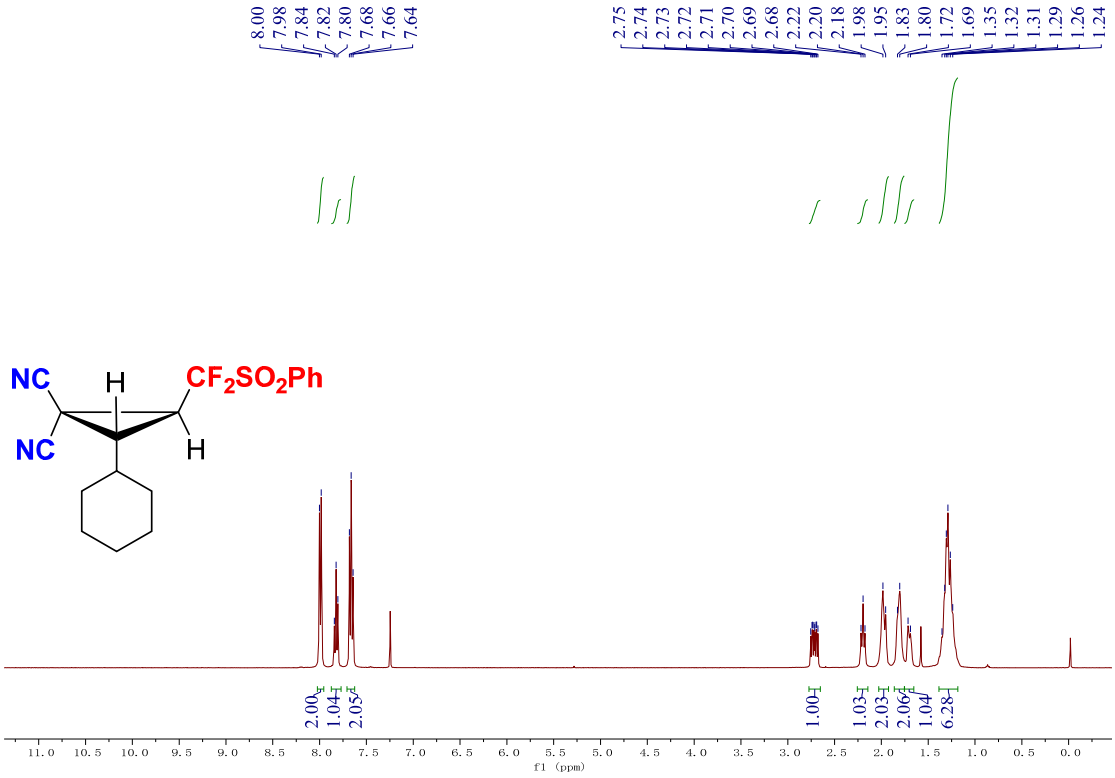
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3t**



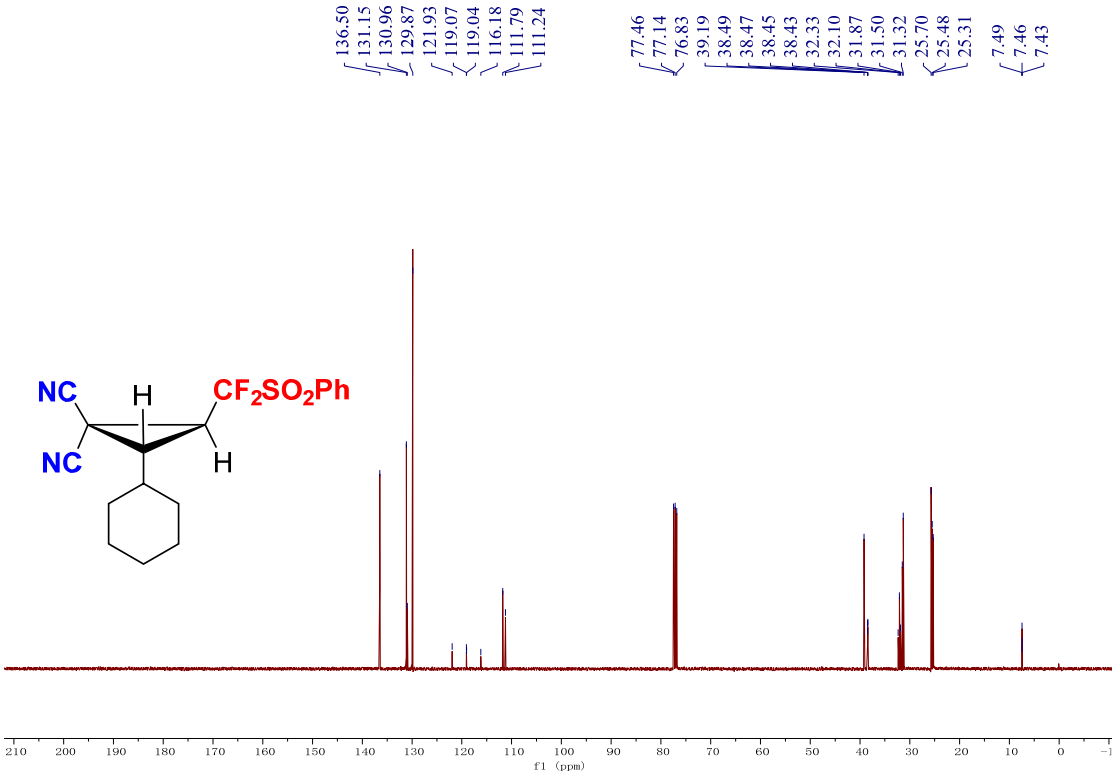
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **3t**



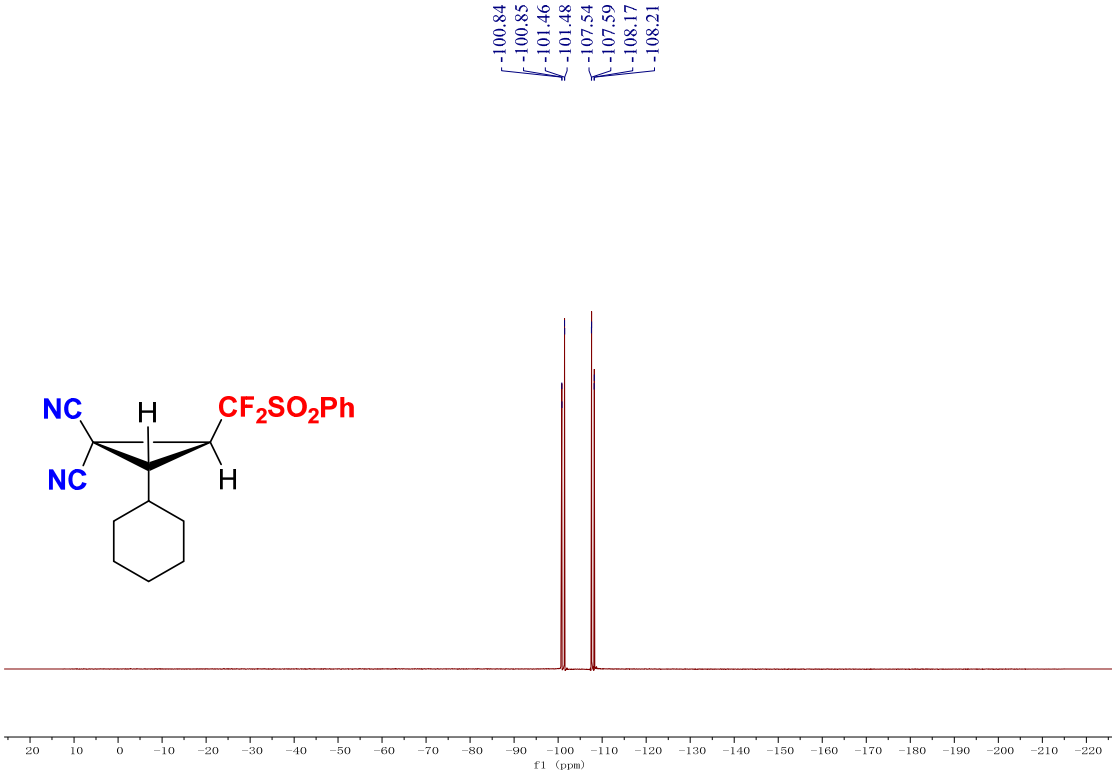
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3u**



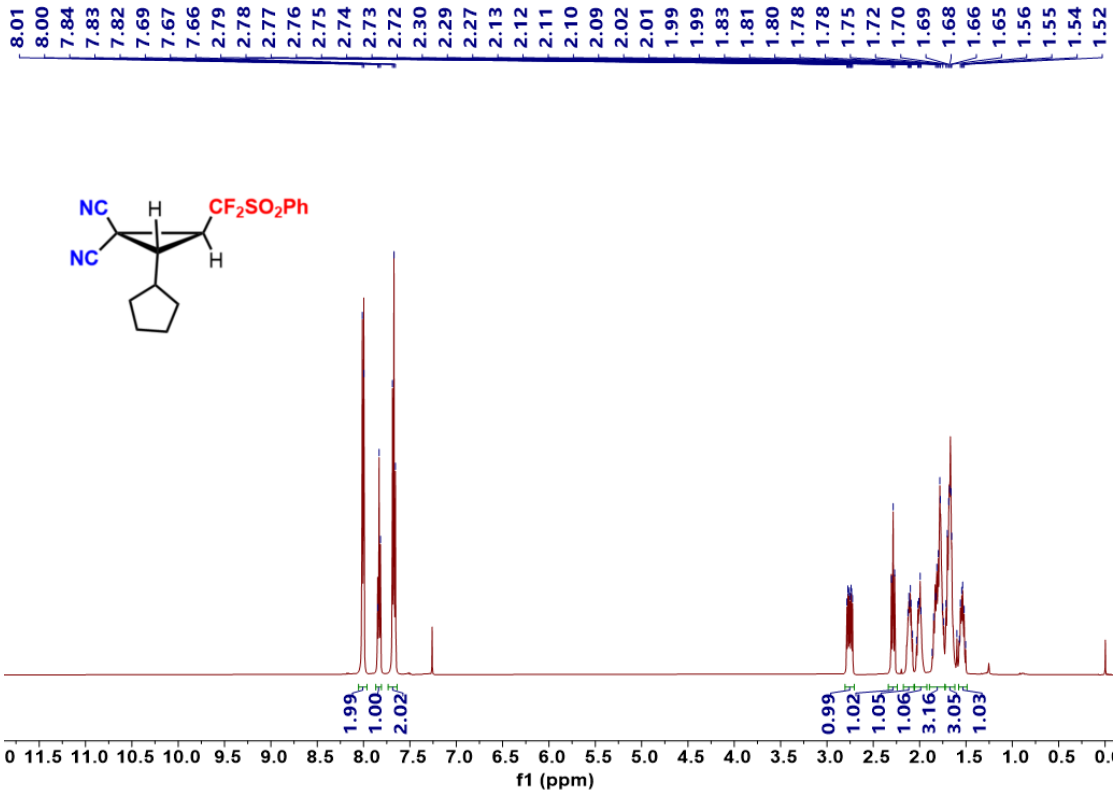
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3u**



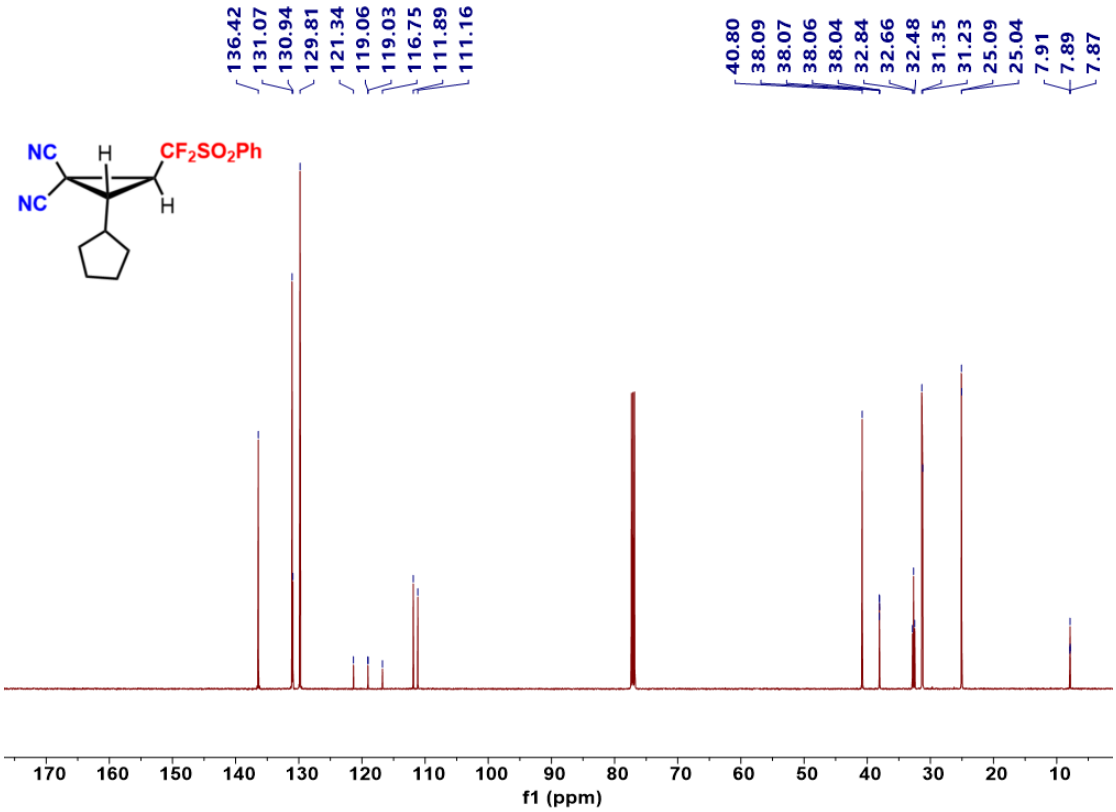
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3u**



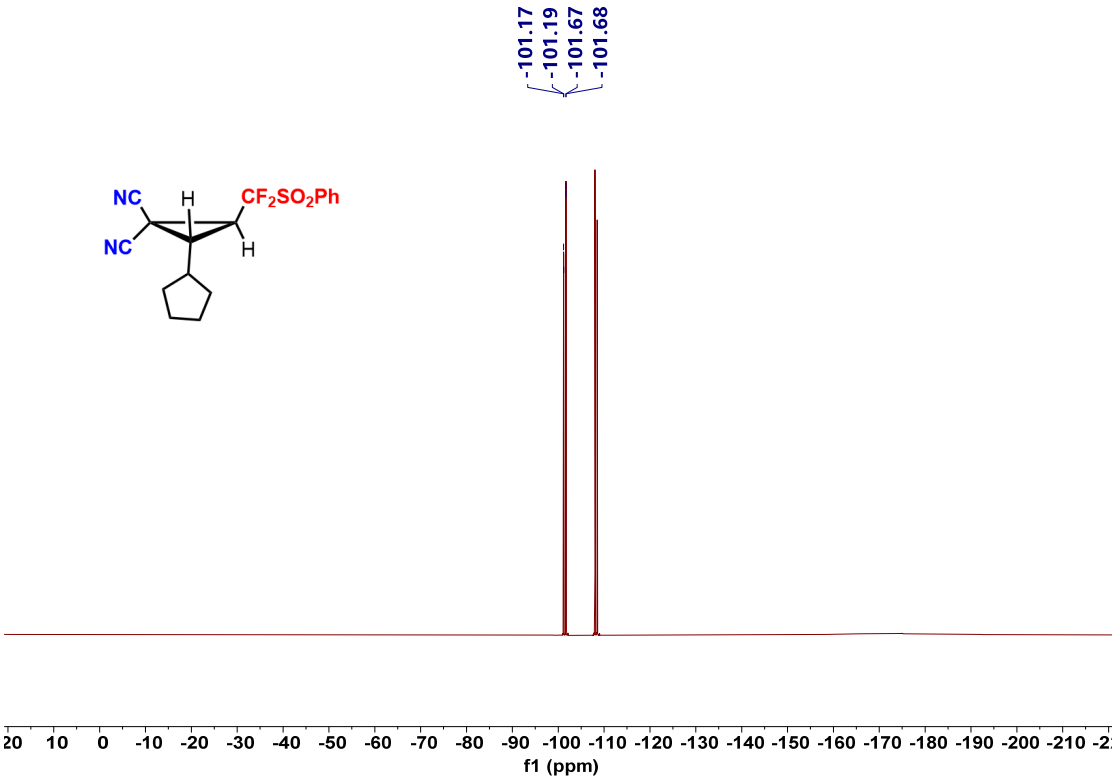
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3v**



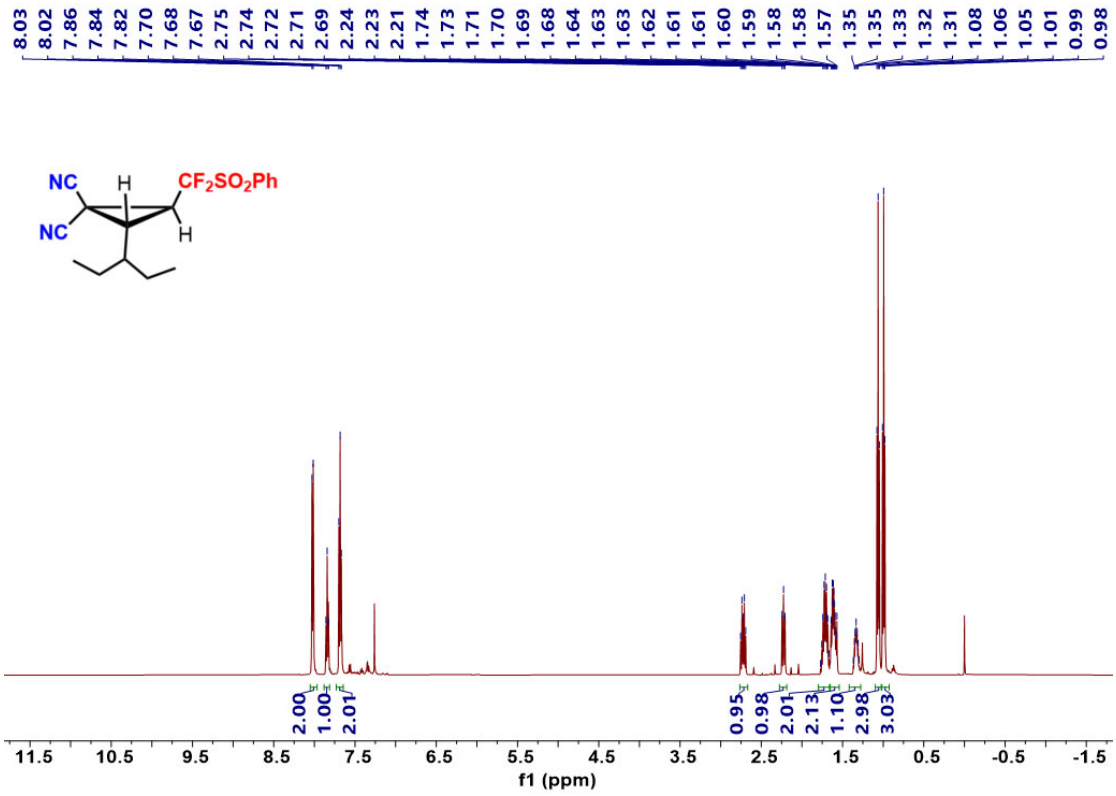
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3v**



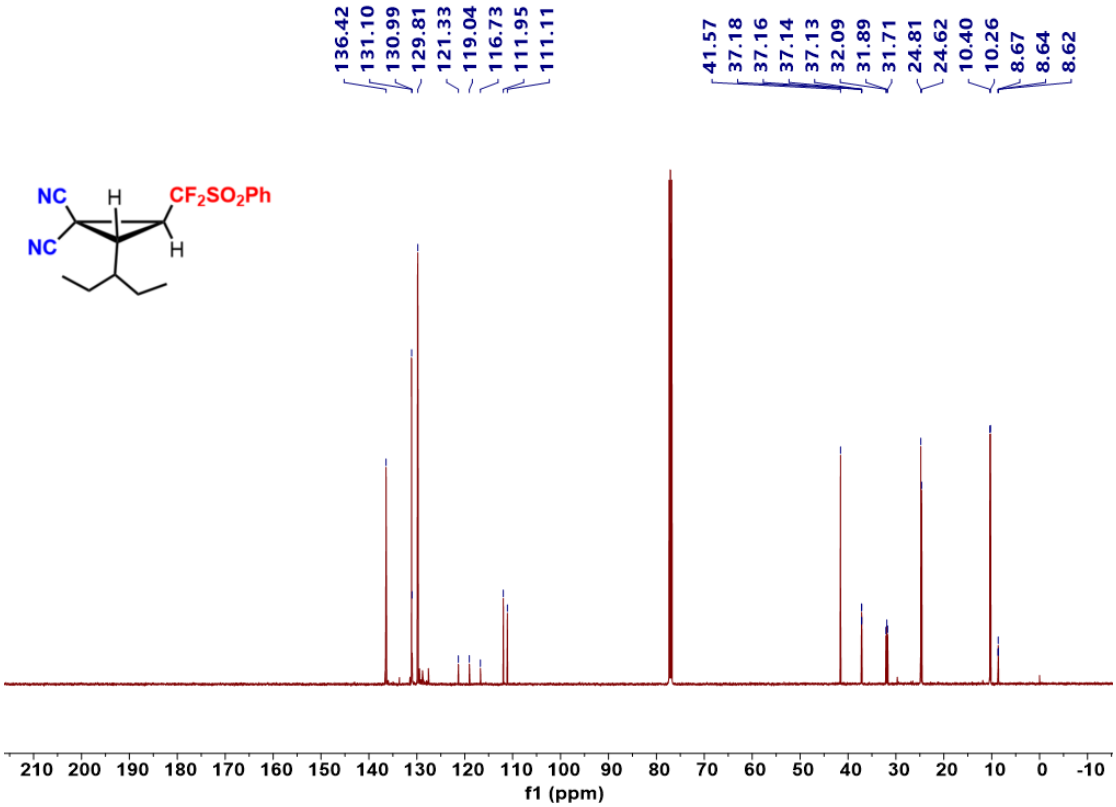
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **3v**



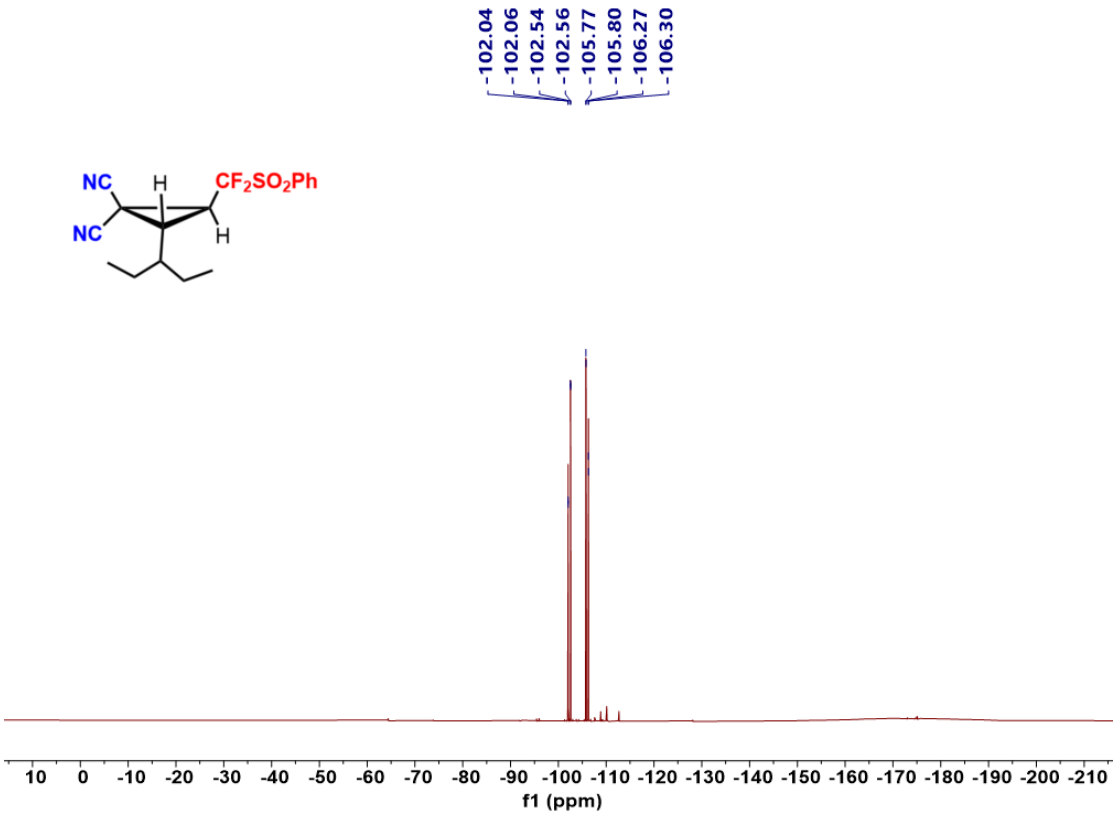
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3w**



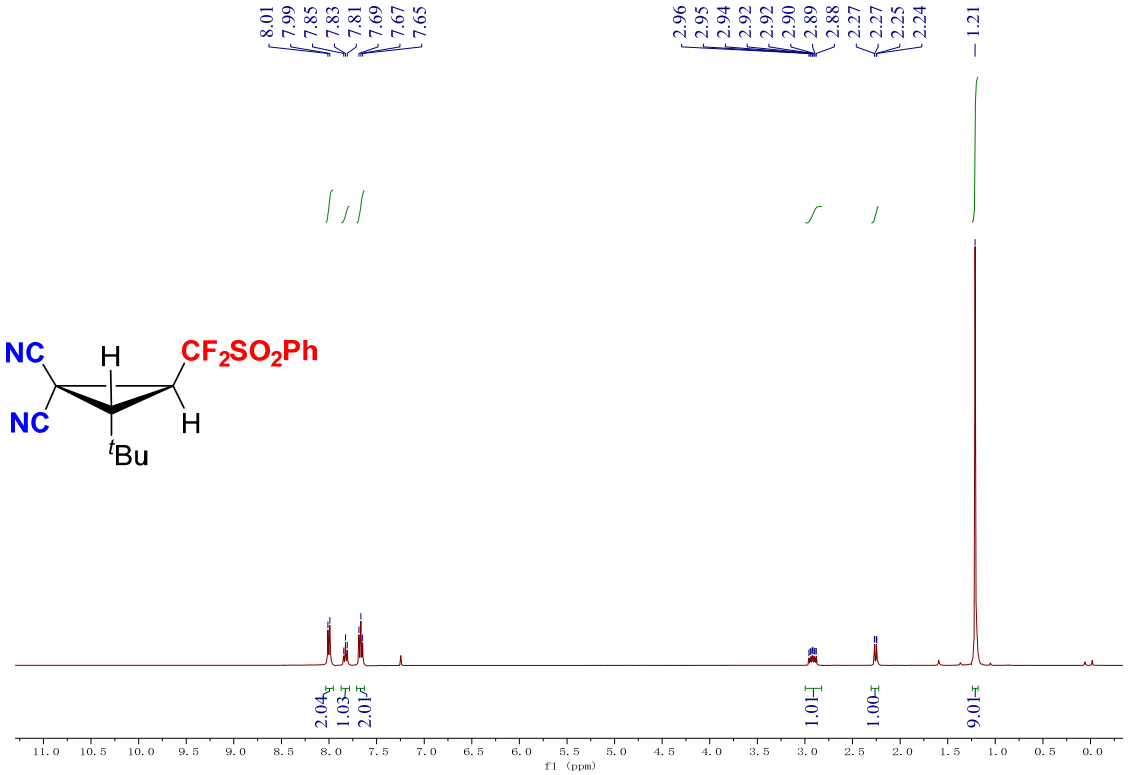
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3w**



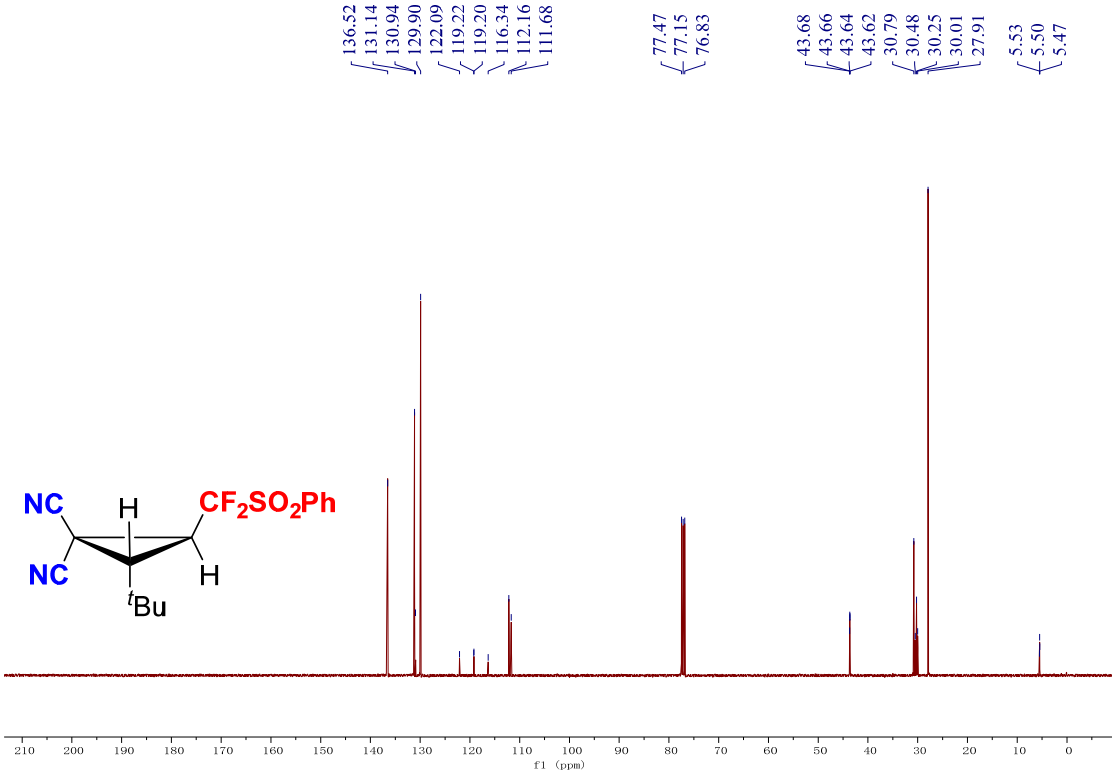
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **3w**



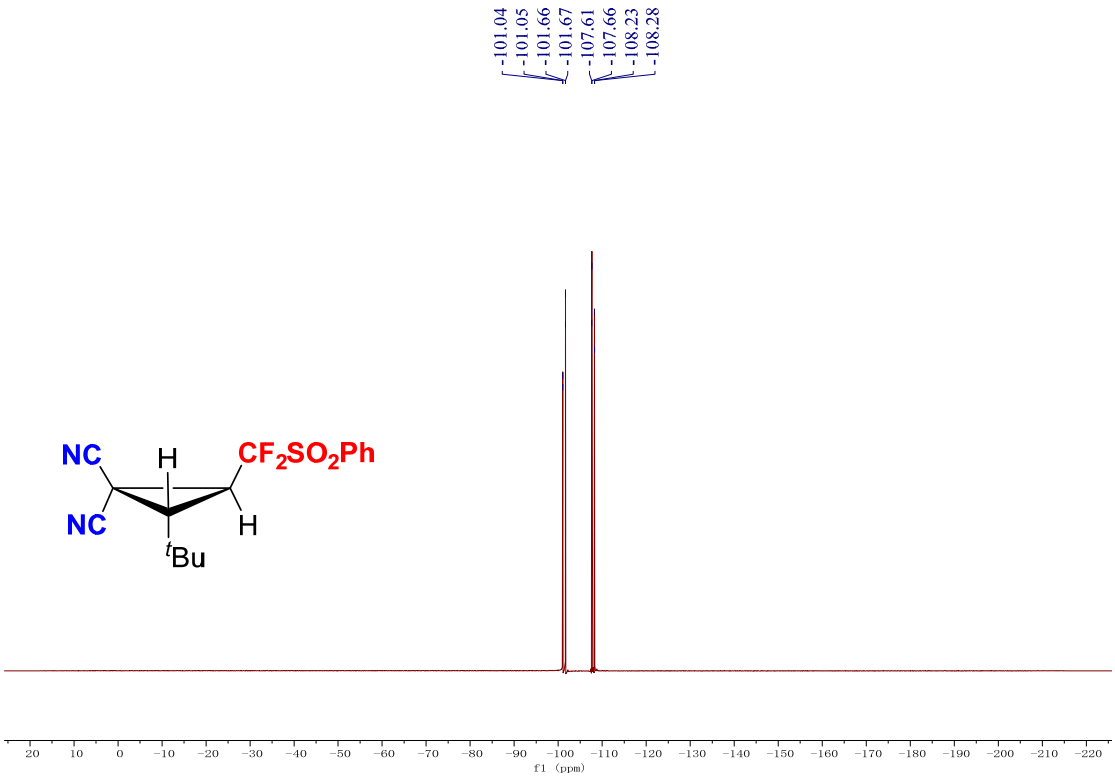
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3x**



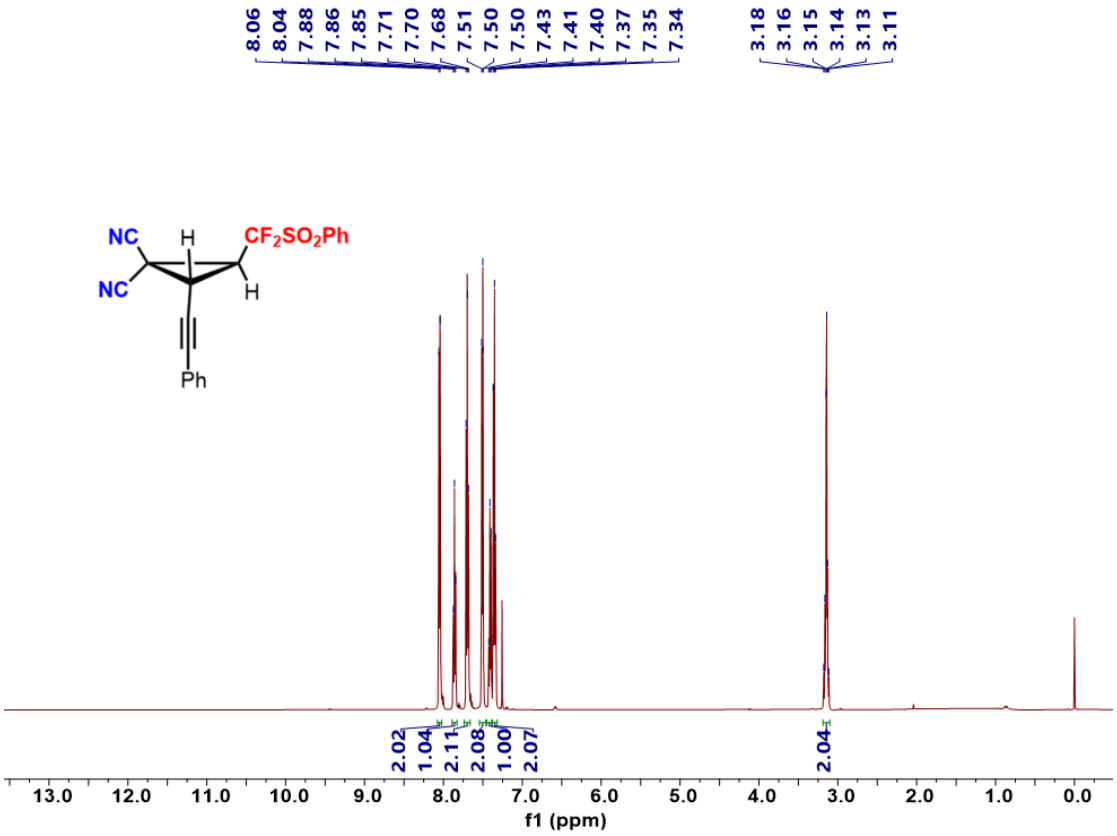
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3x**



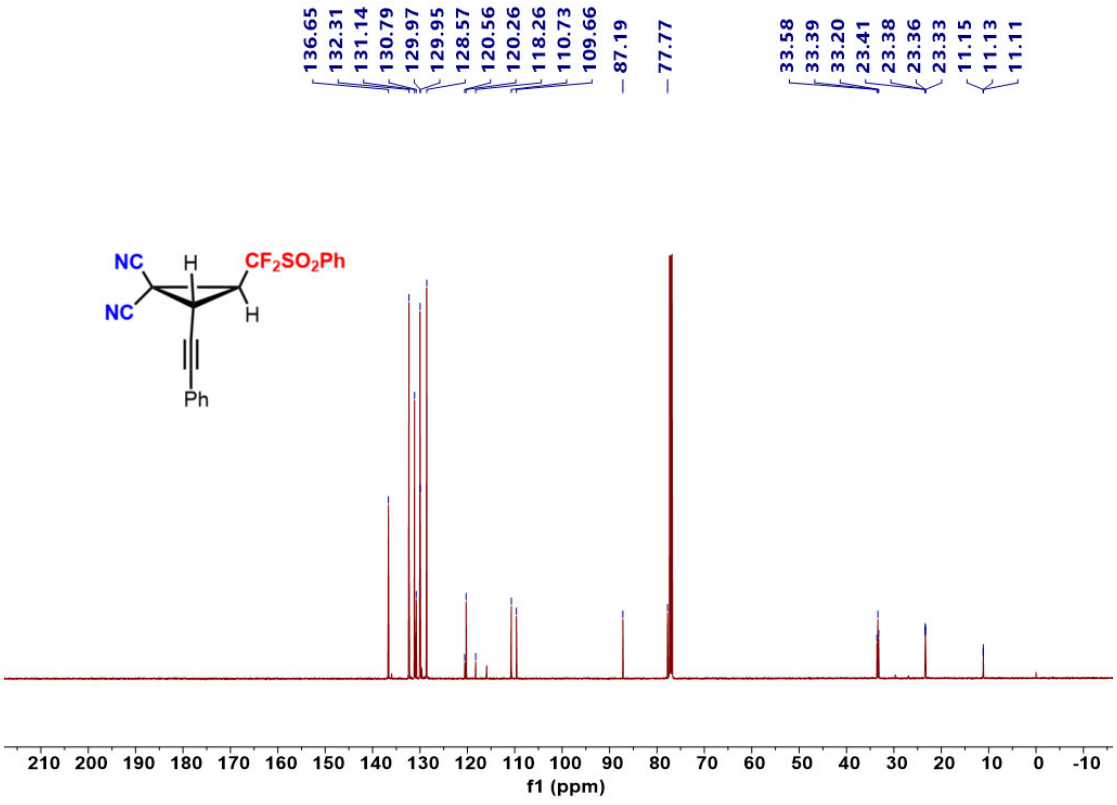
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3x**



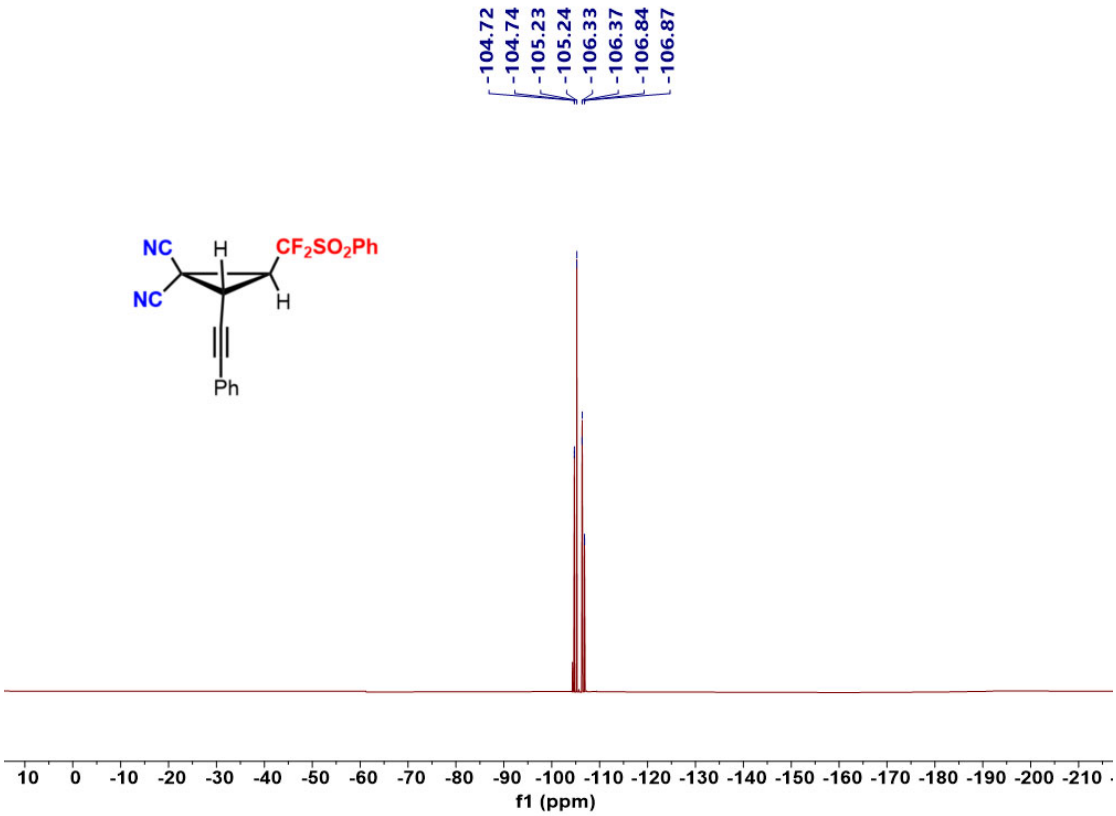
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3y**



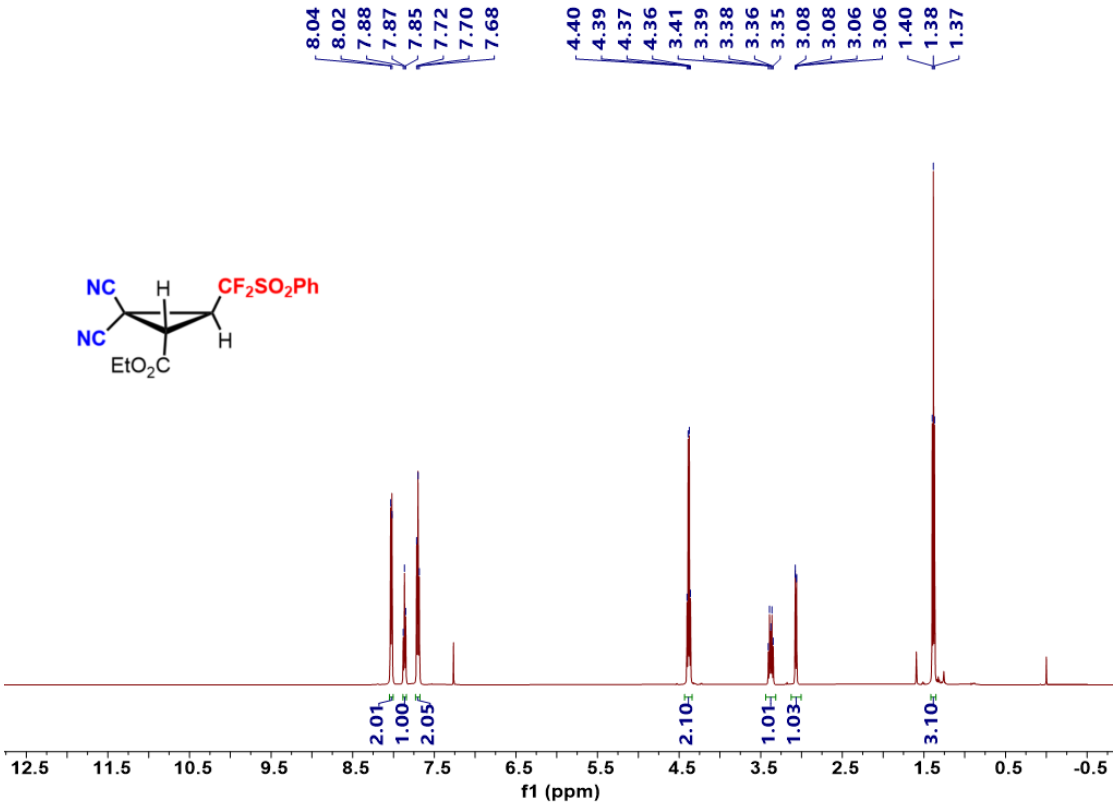
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3y**



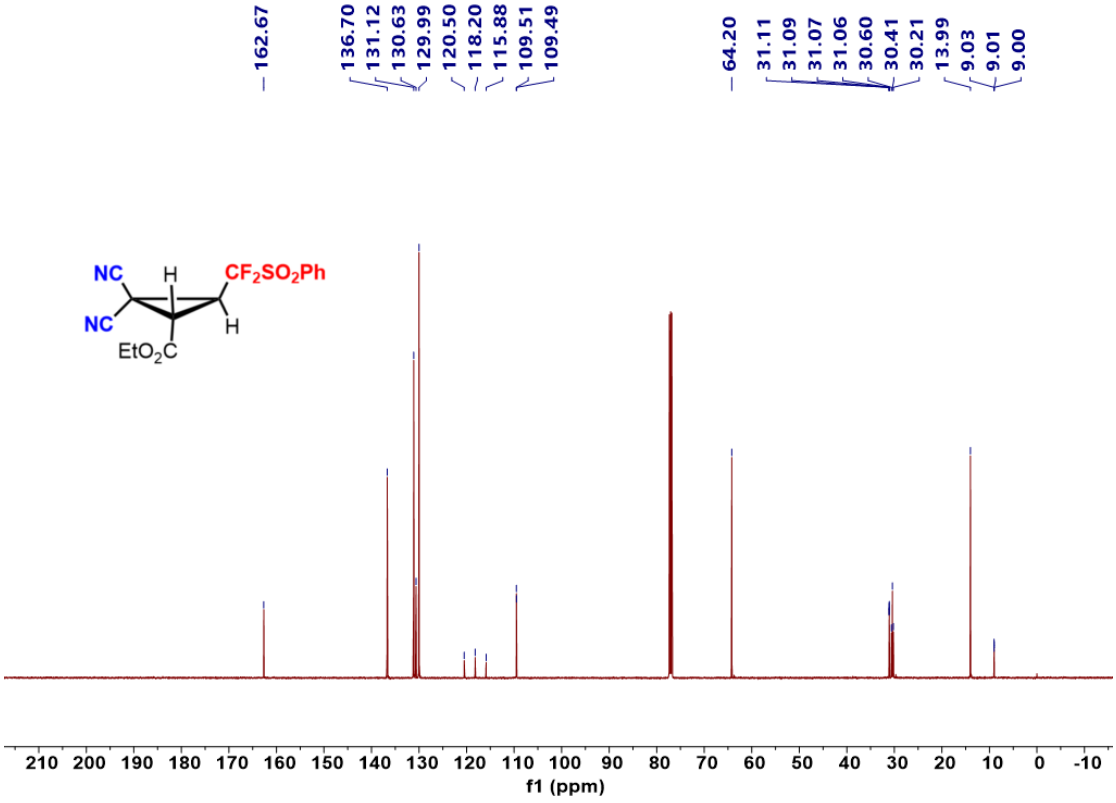
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **3y**



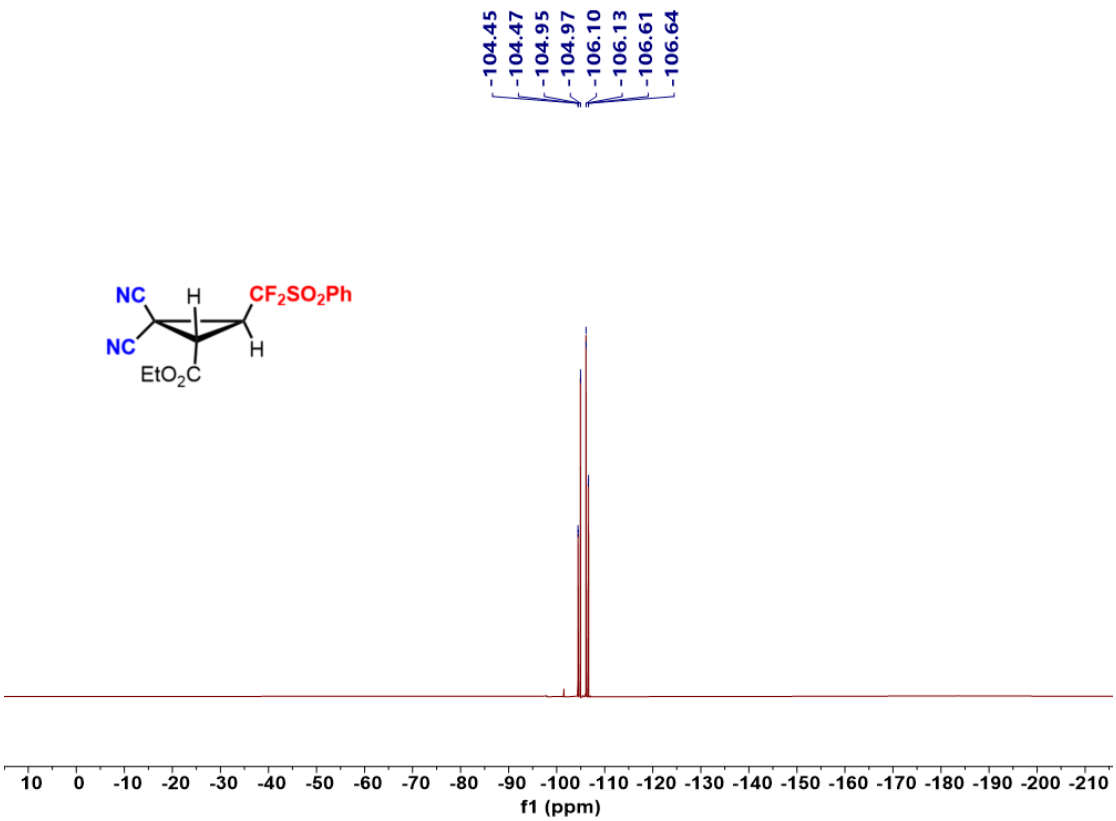
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3z**



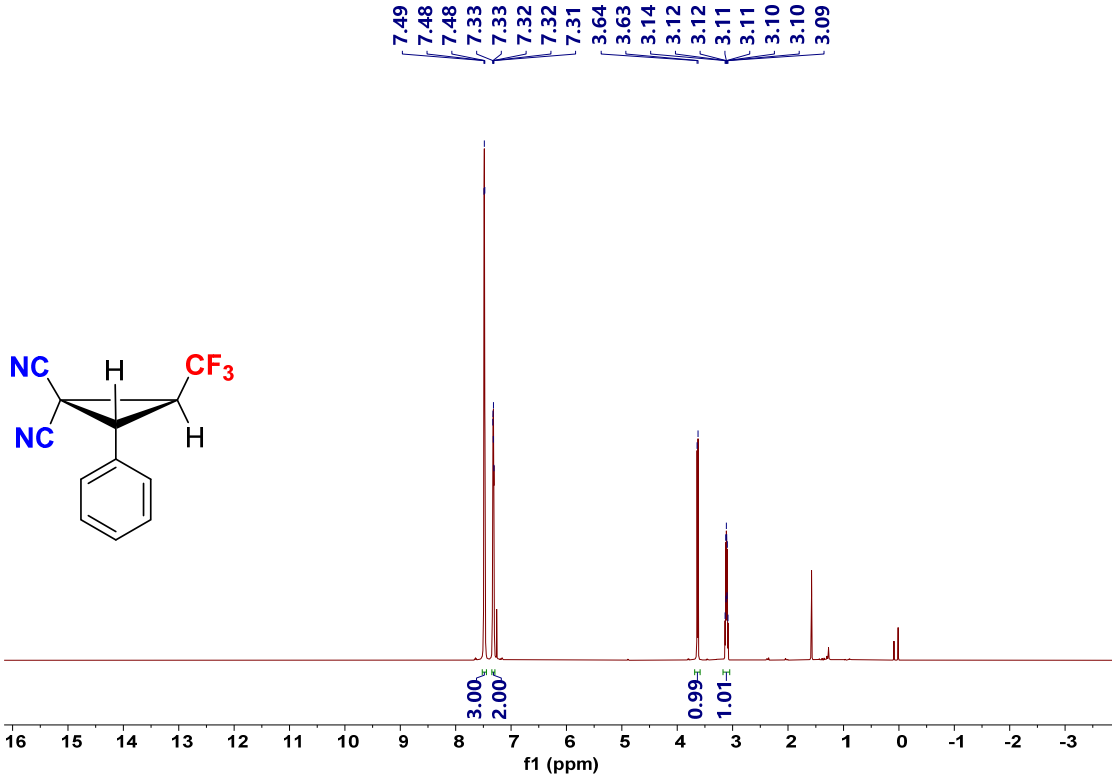
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3z**



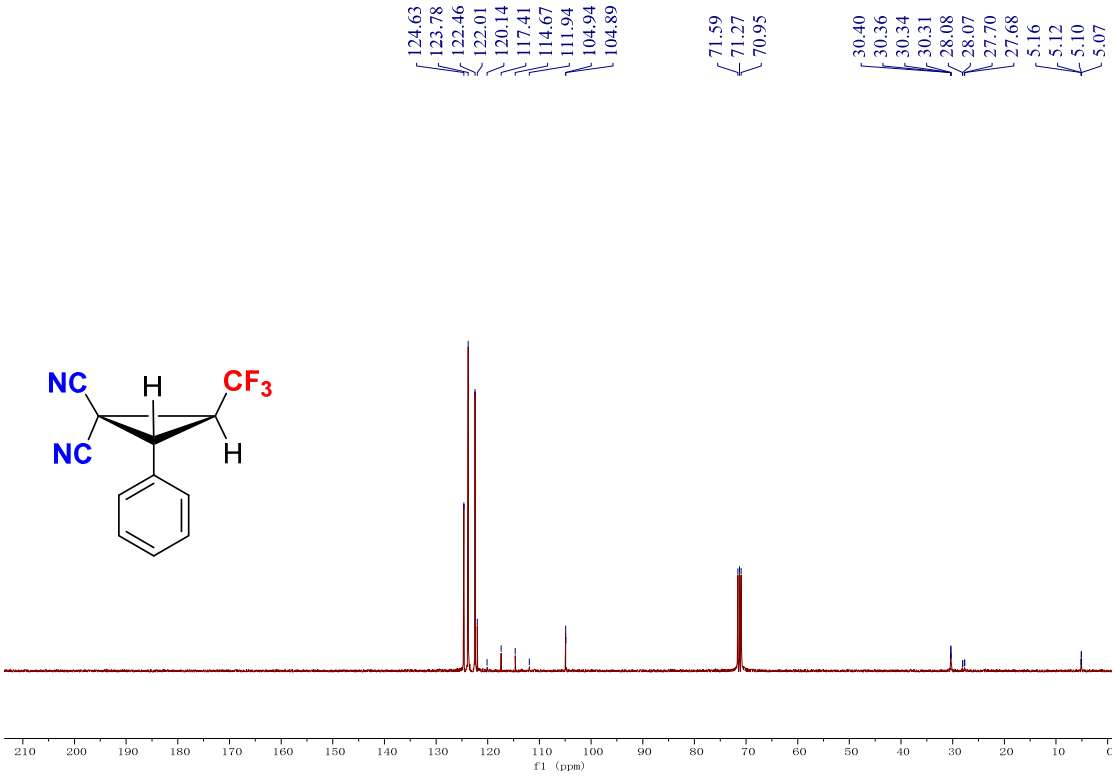
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **3z**



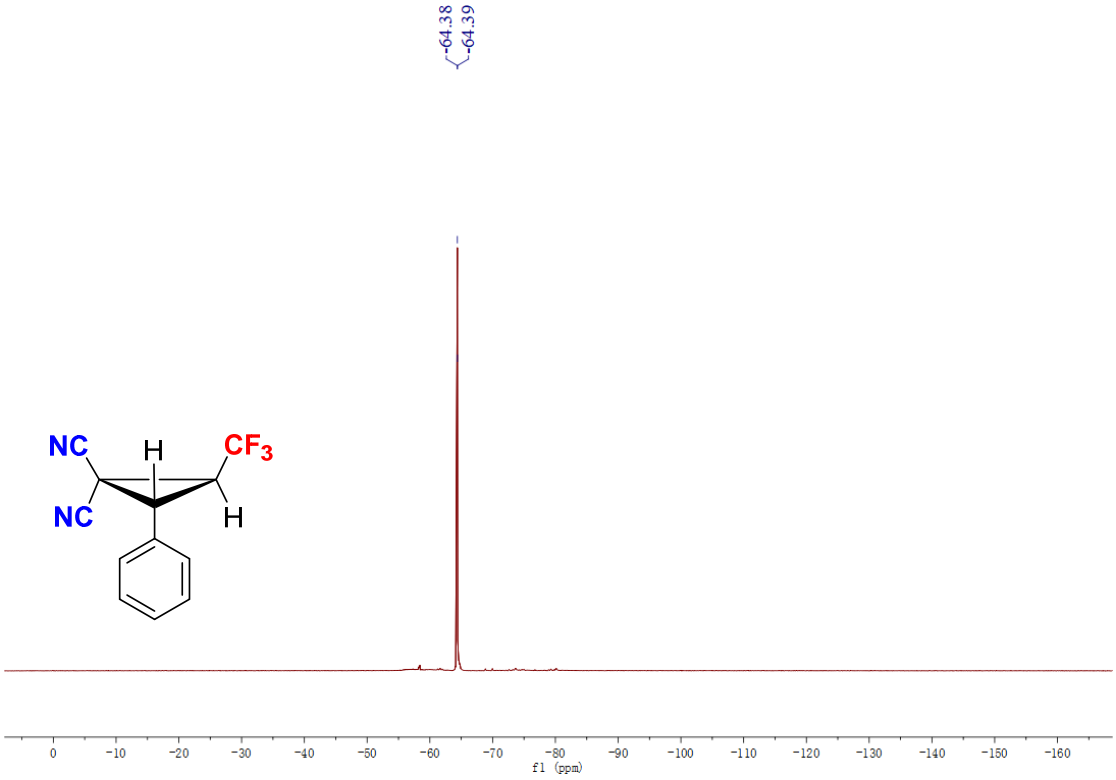
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



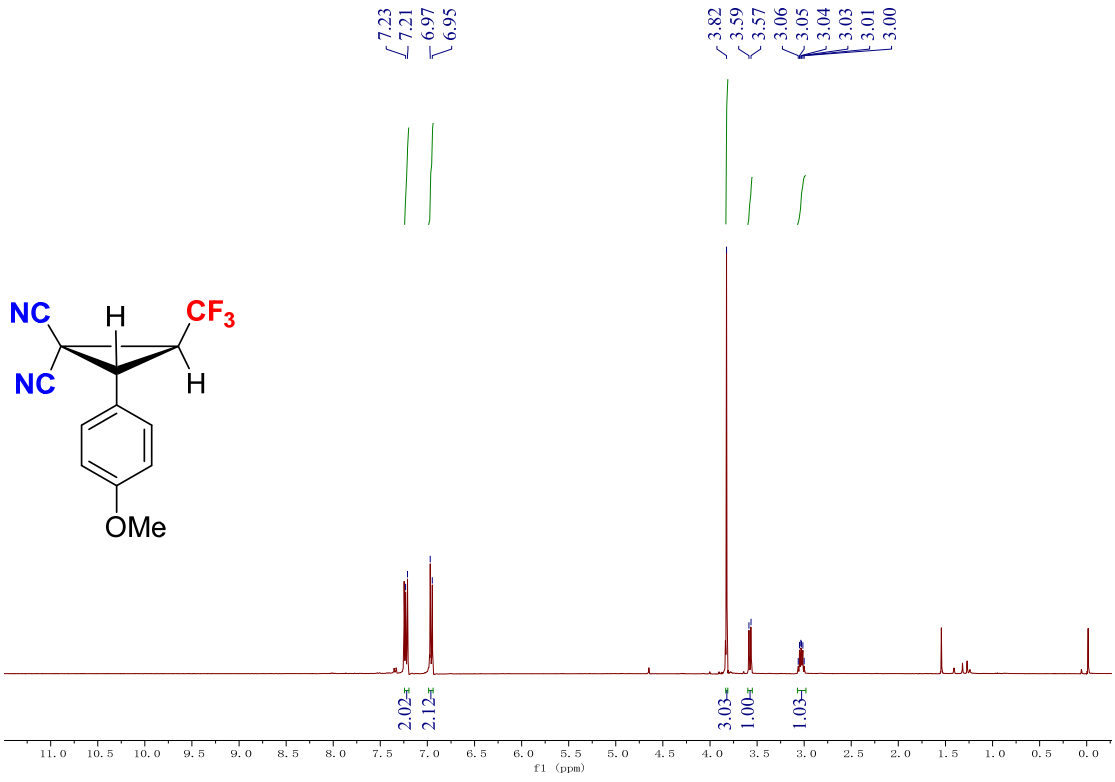
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4a**



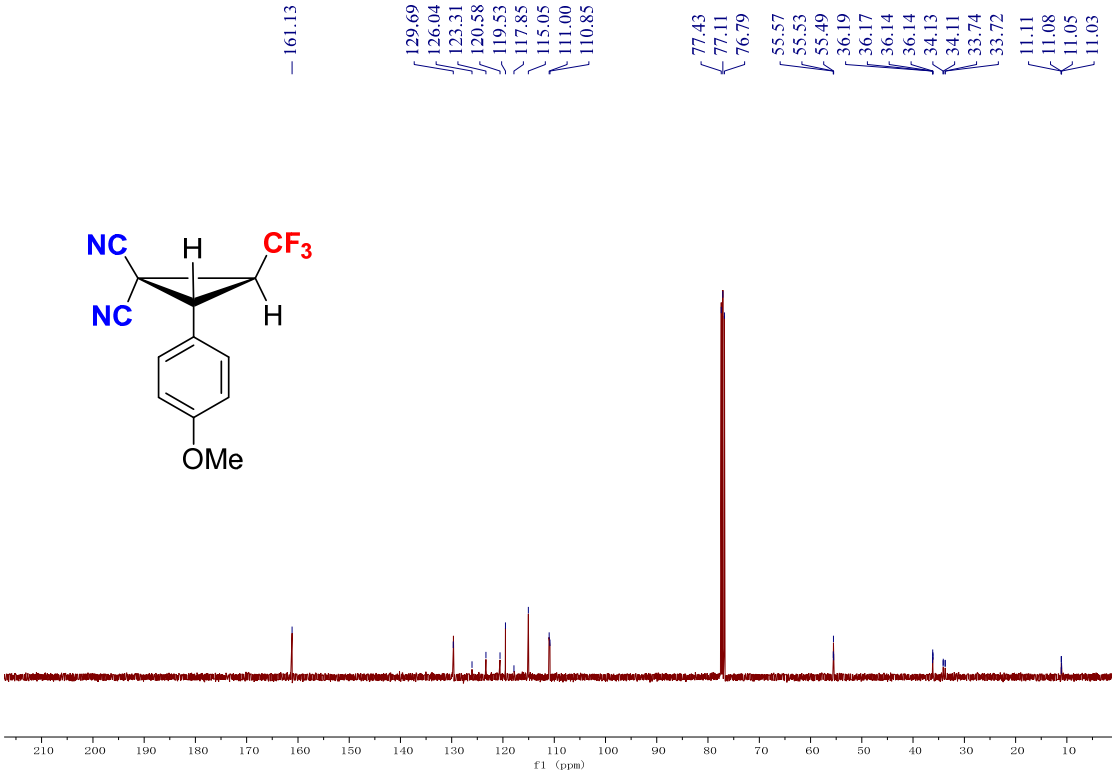
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4a**



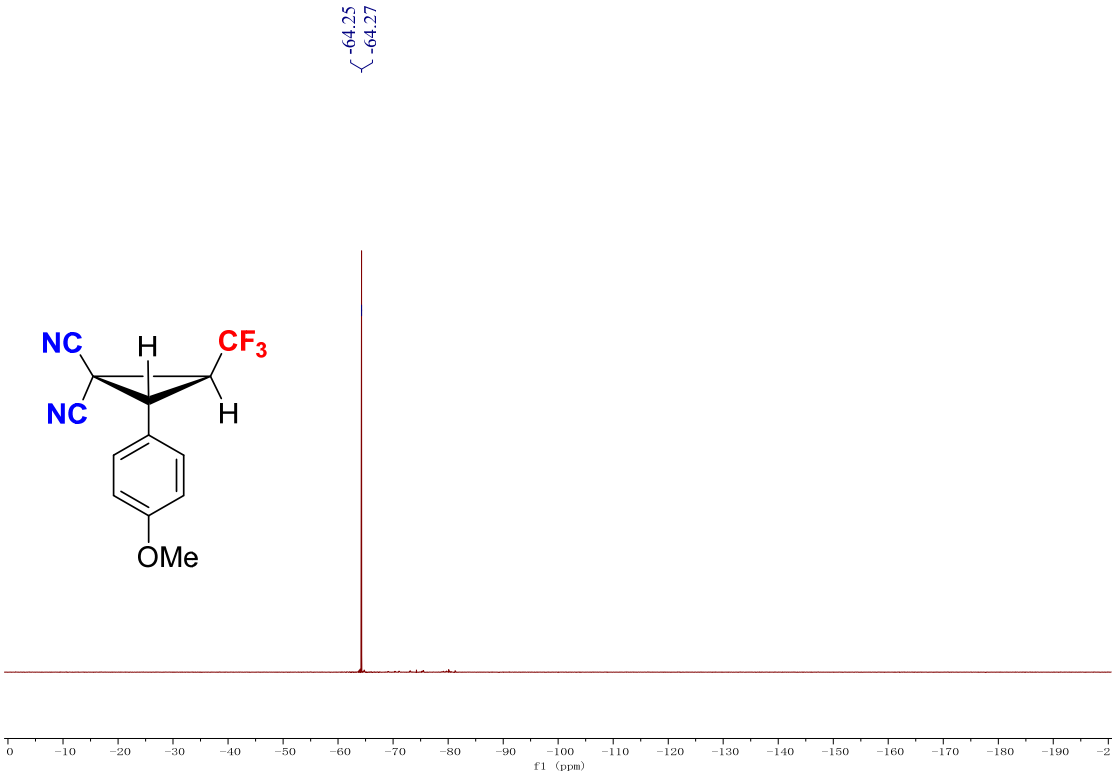
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



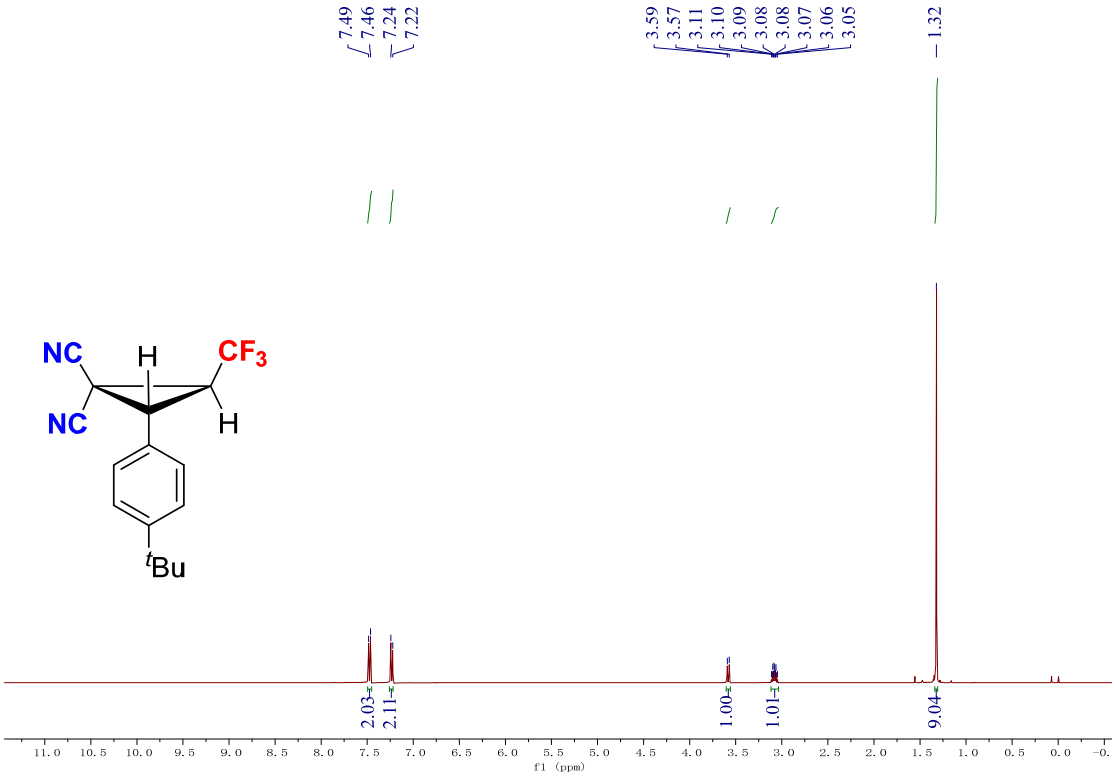
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4b**



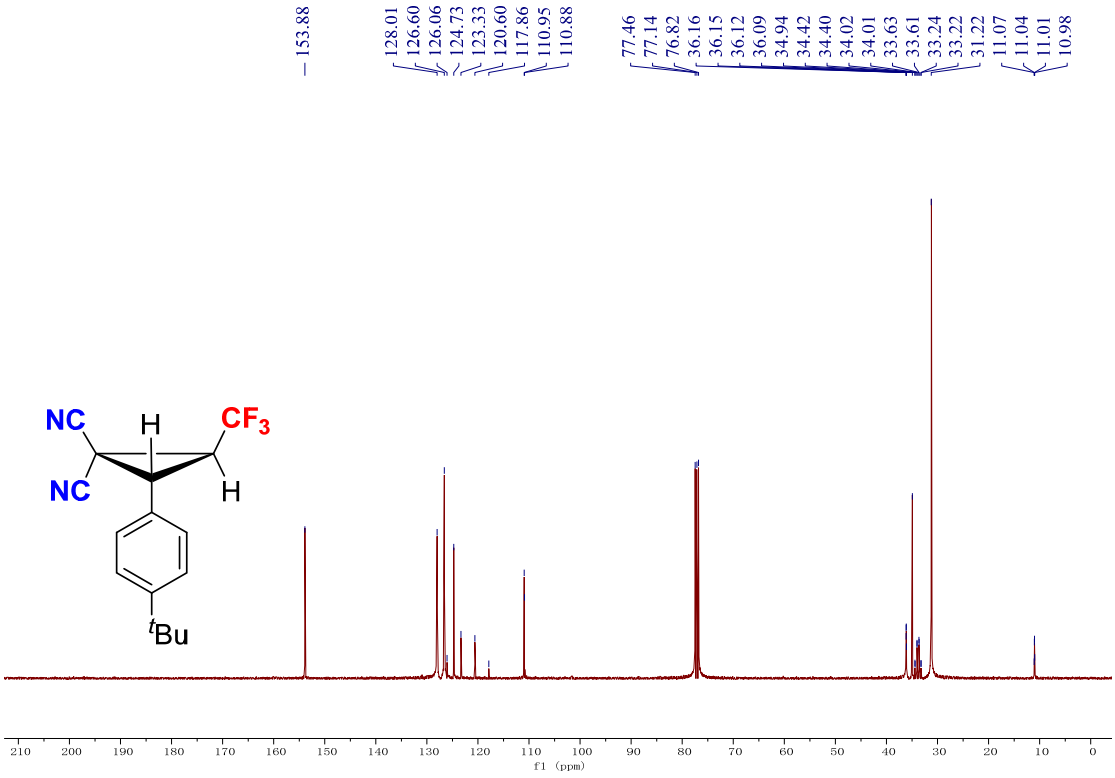
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4b**



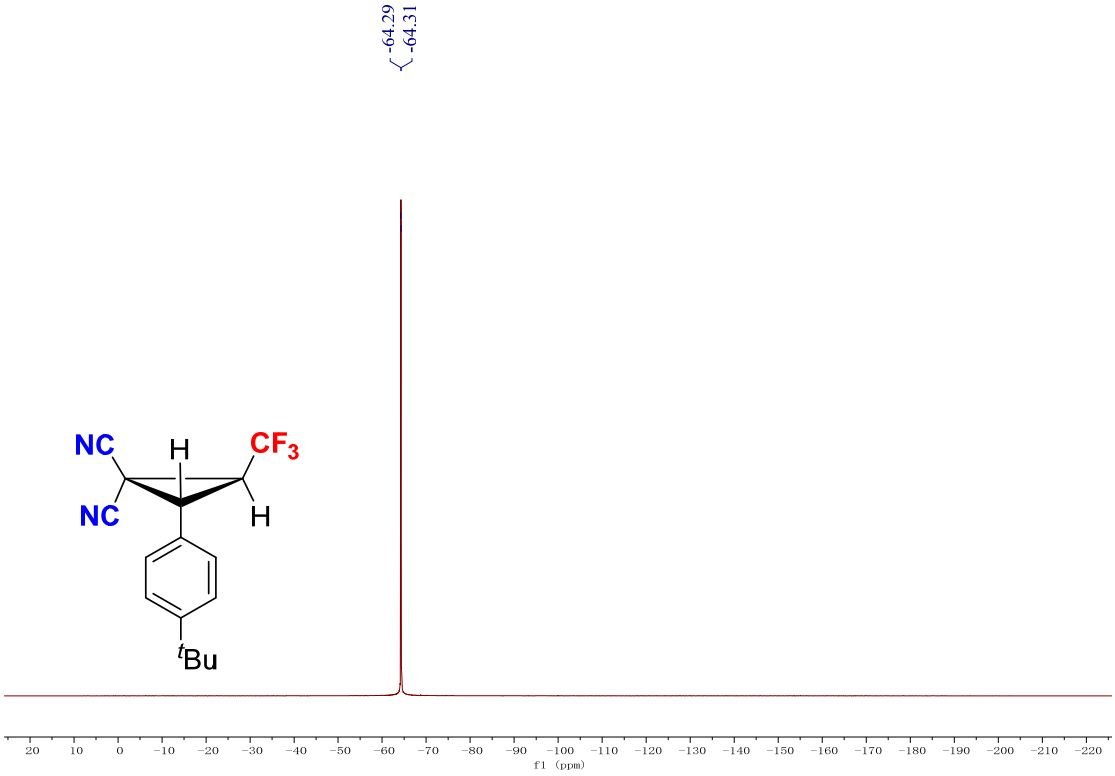
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**



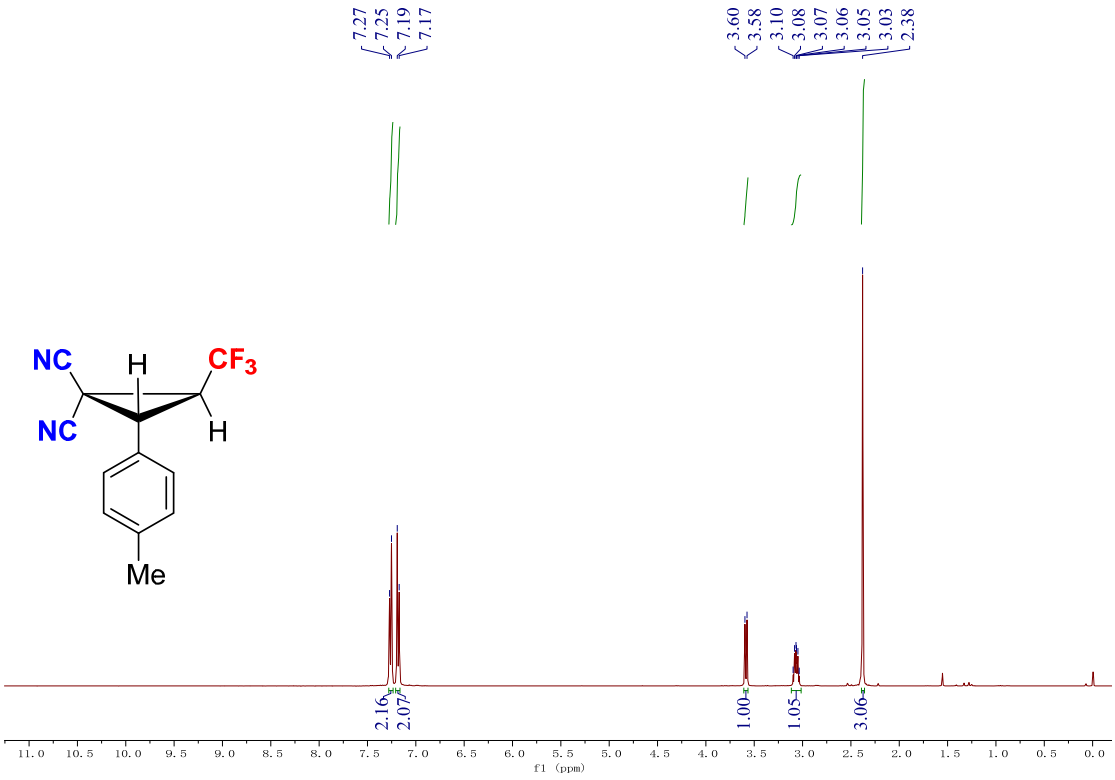
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4c**



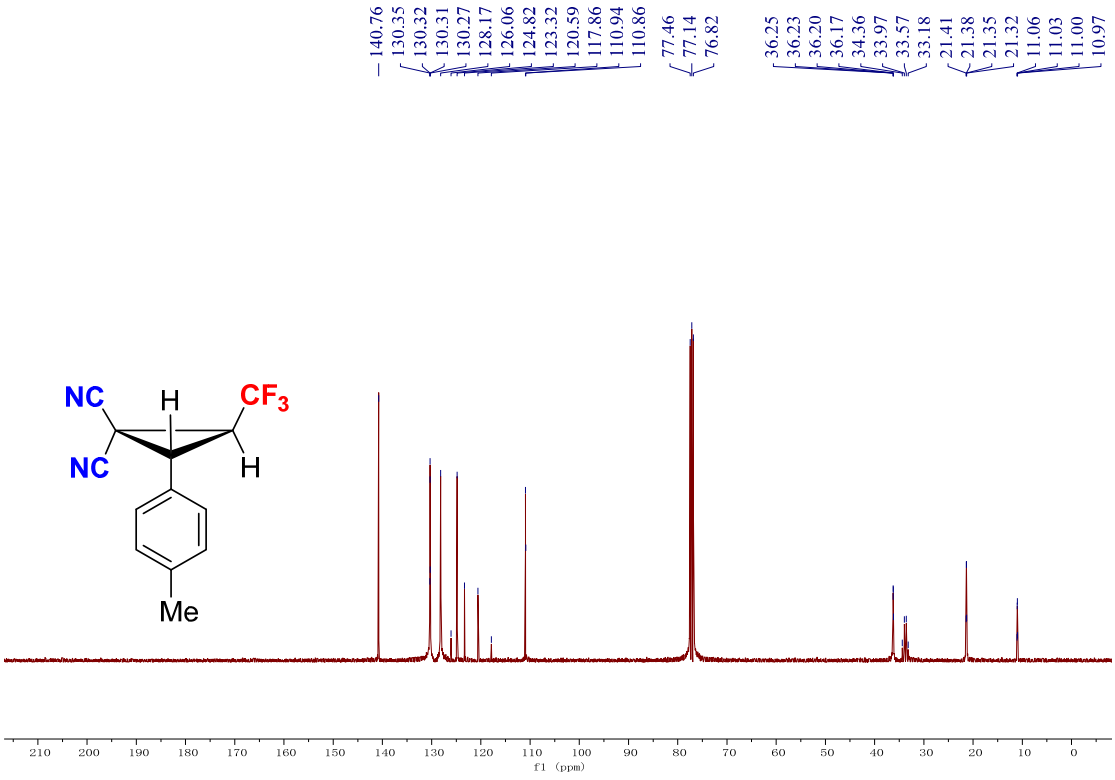
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4c**



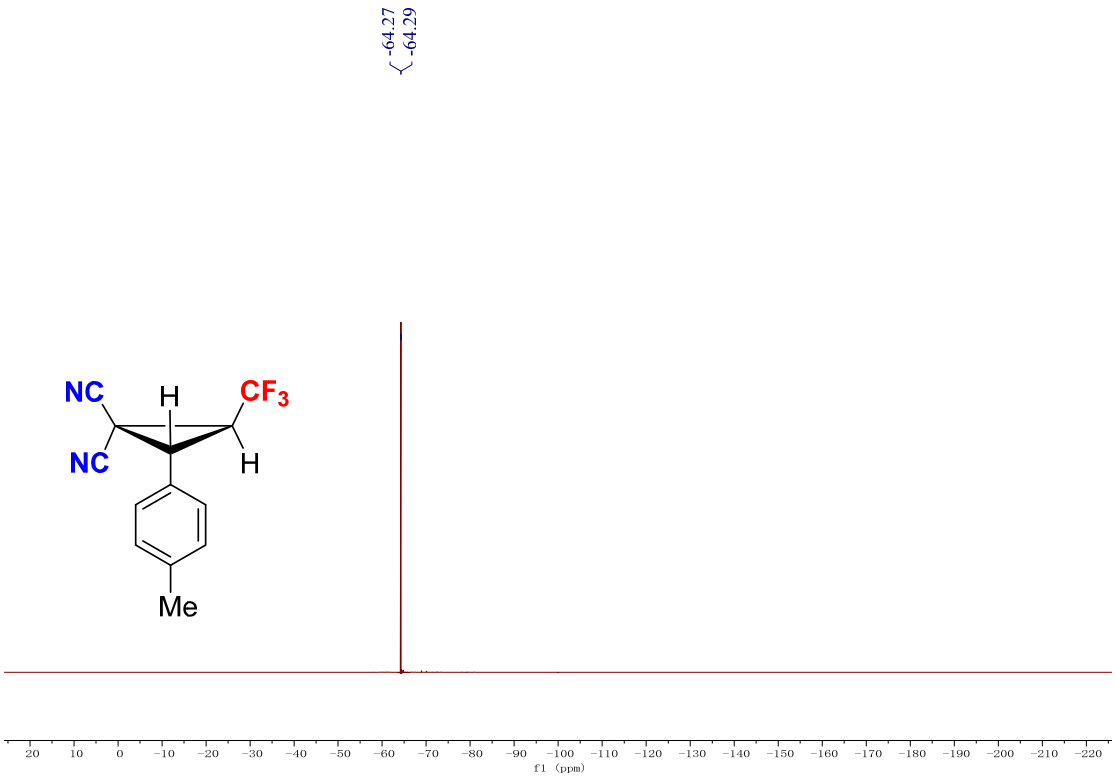
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



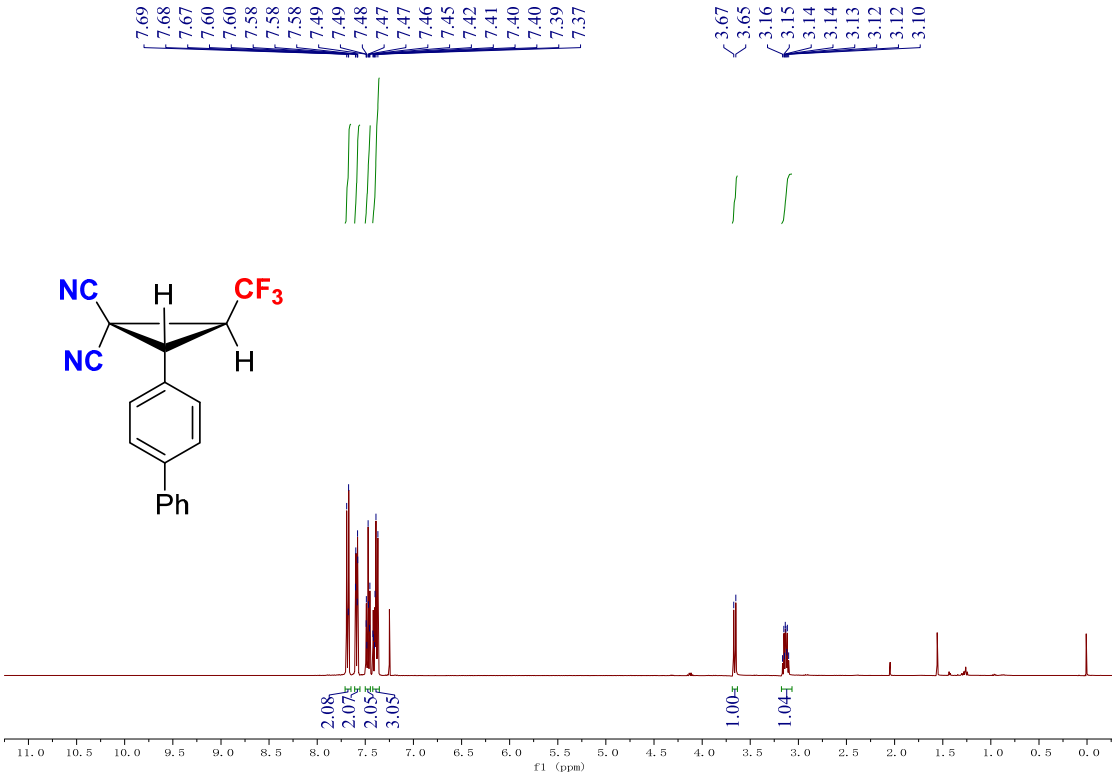
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4d**



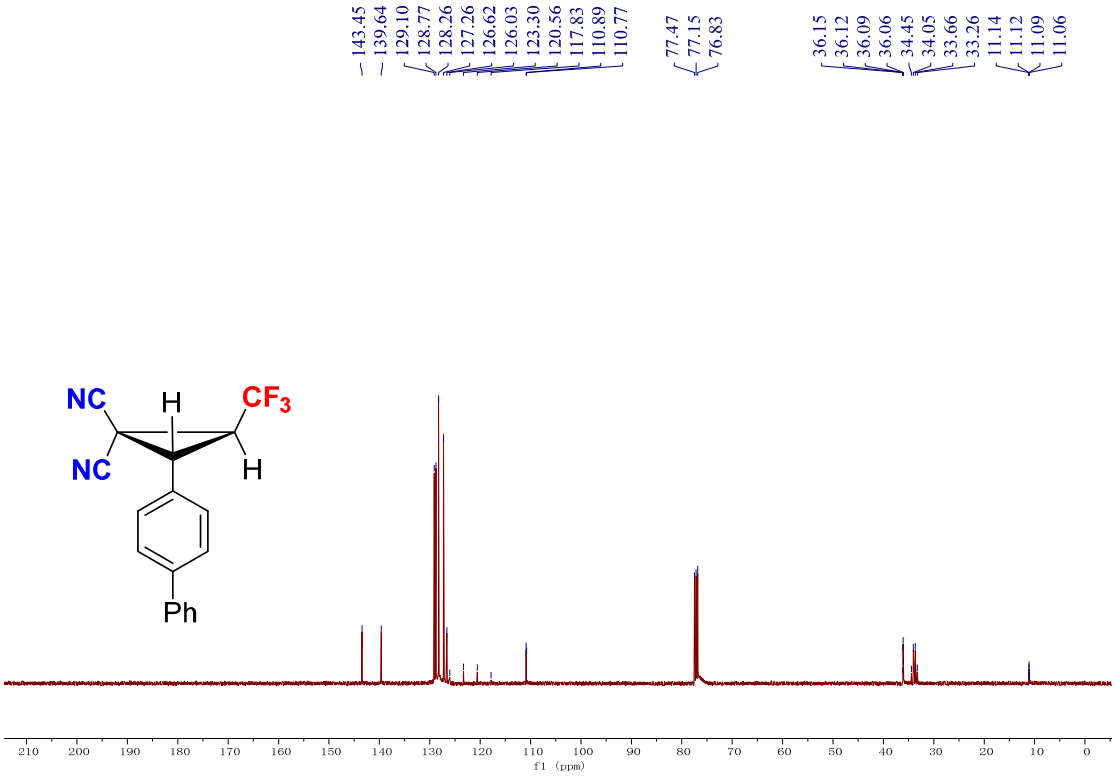
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4d**



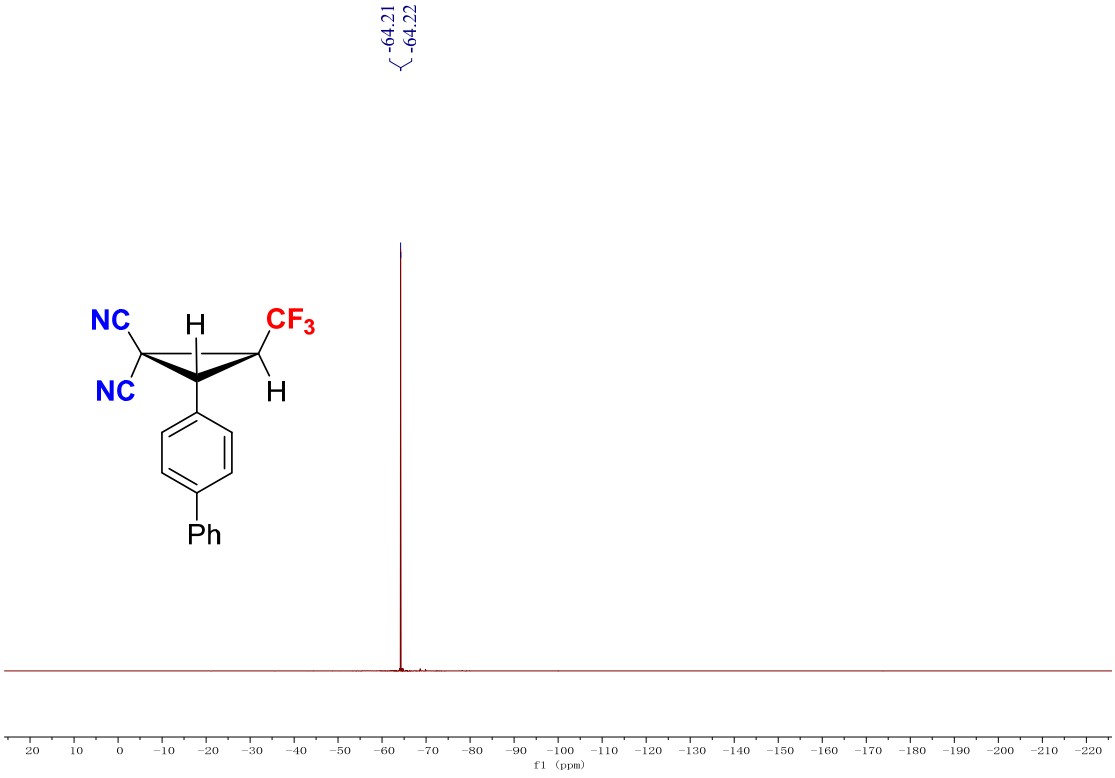
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**



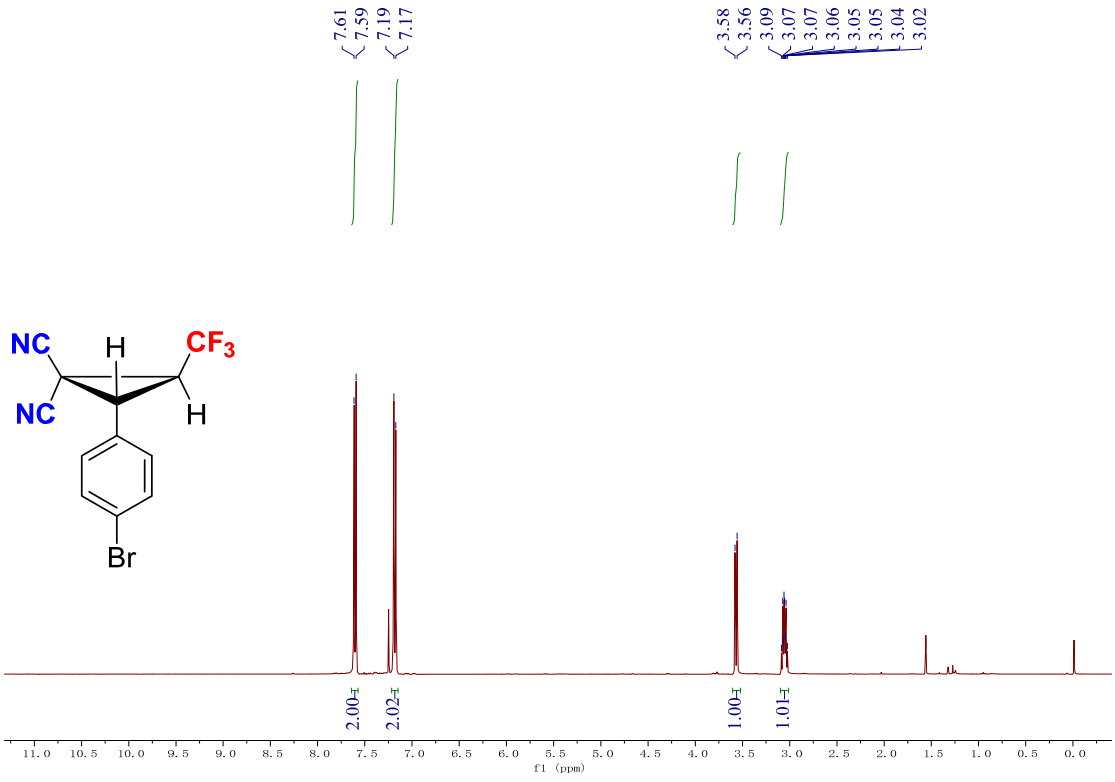
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4e**



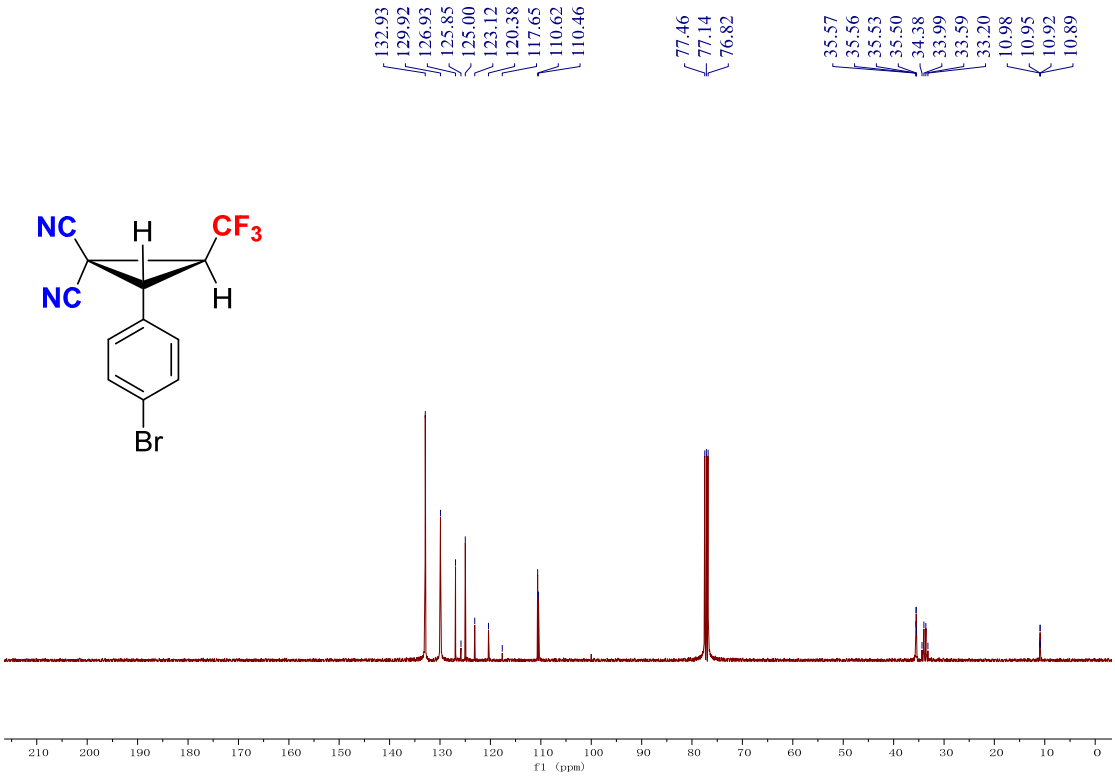
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4e**



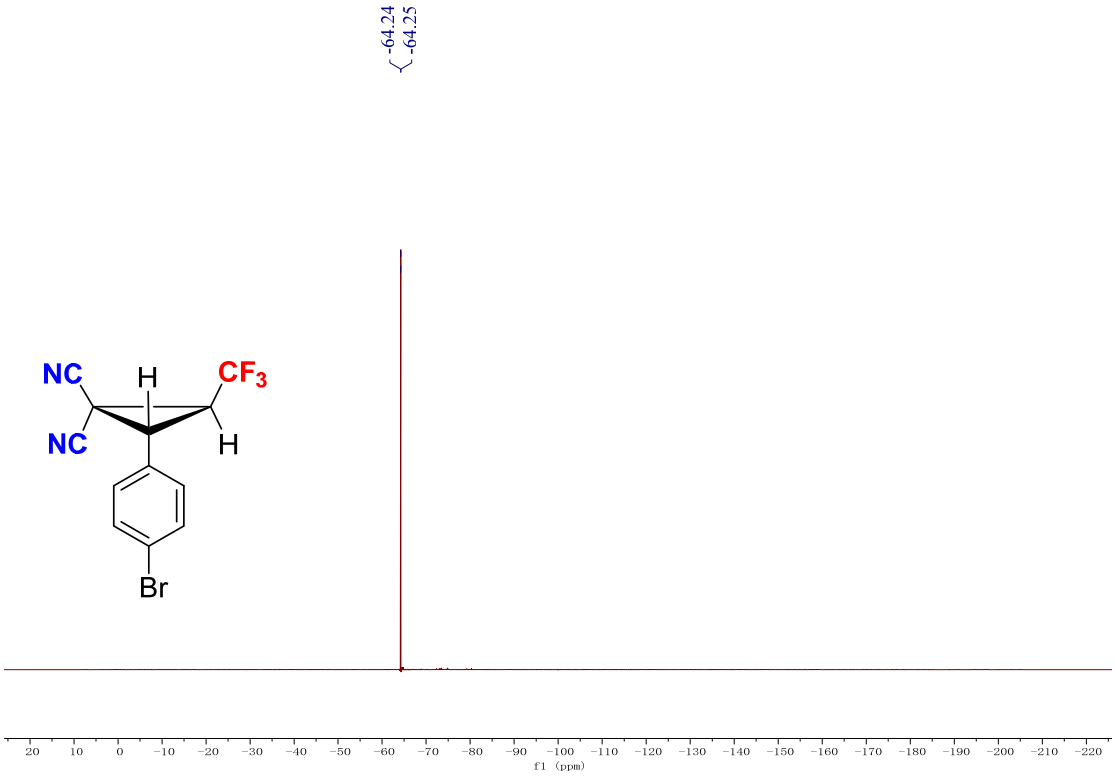
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**



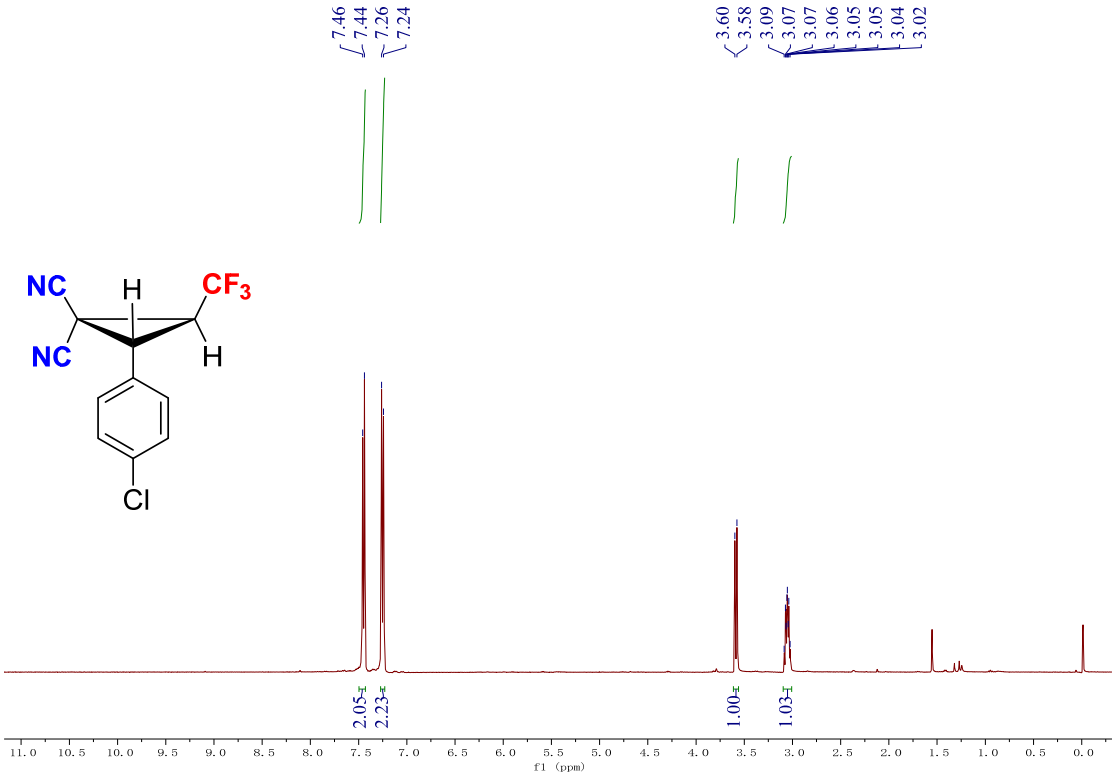
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4f**



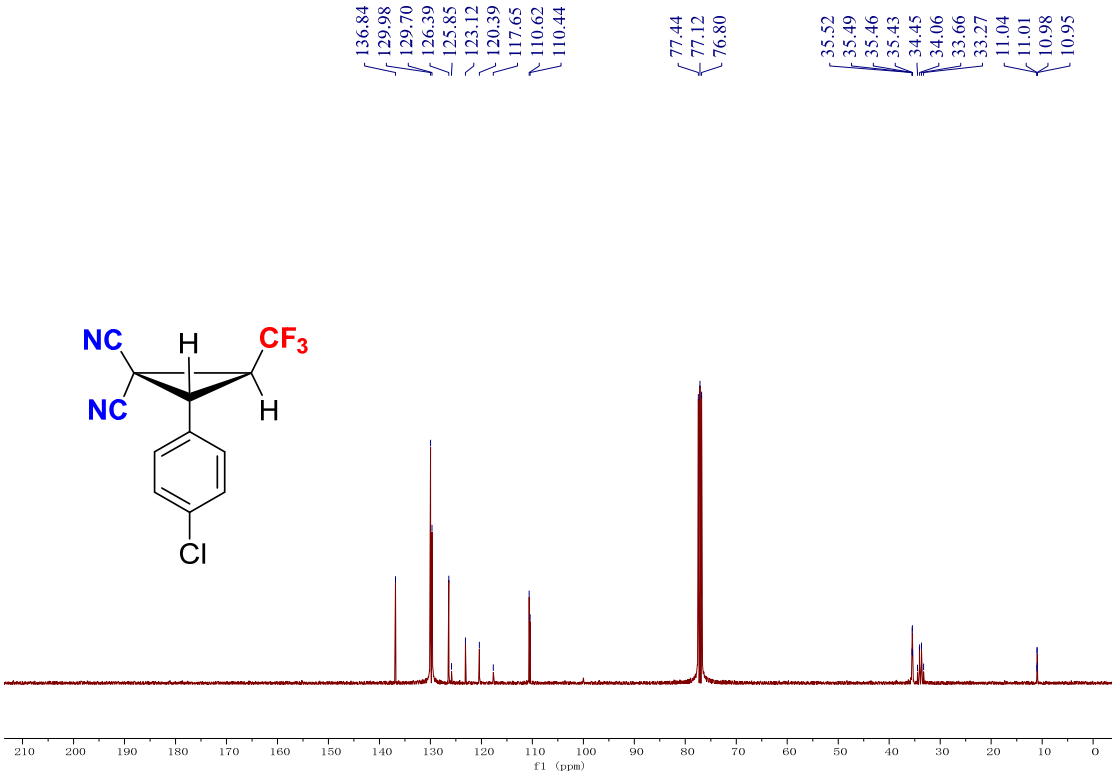
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4f**



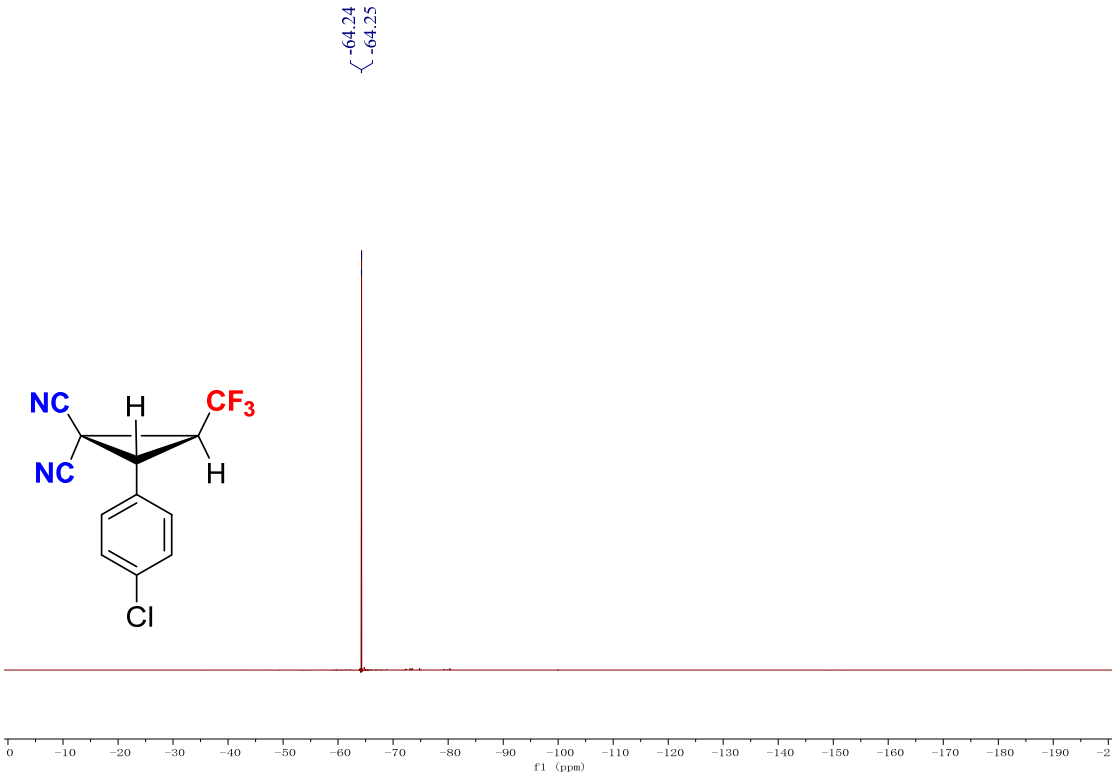
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**



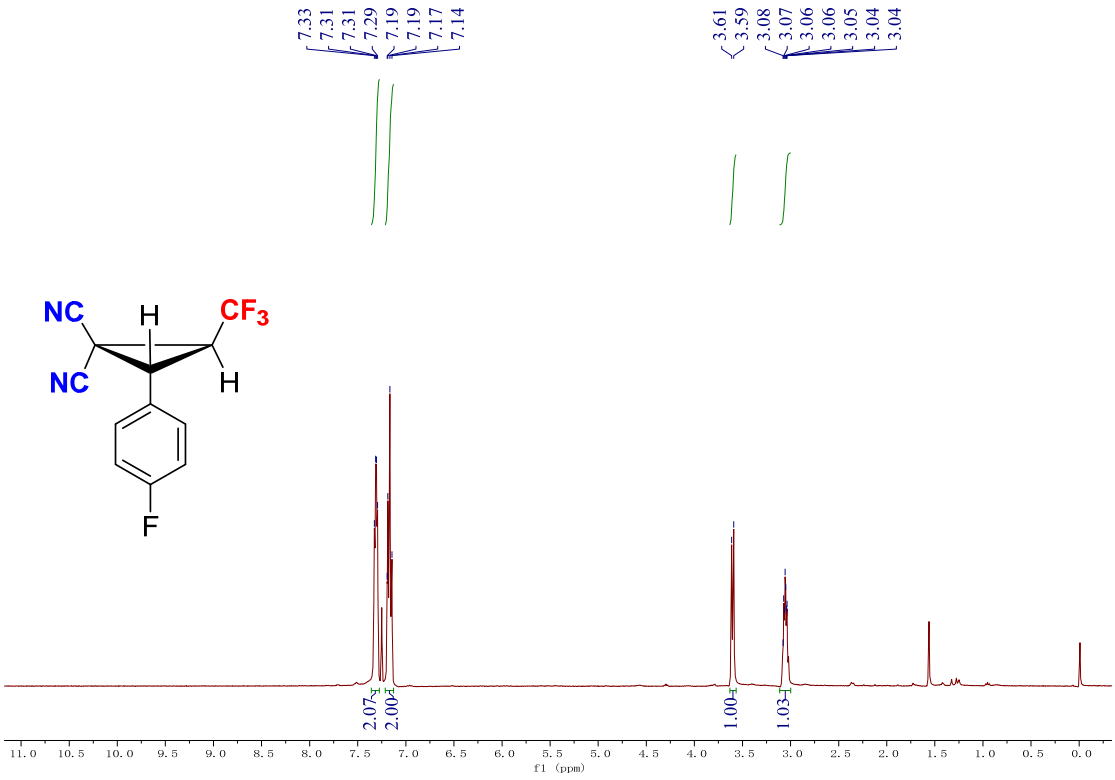
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4g**



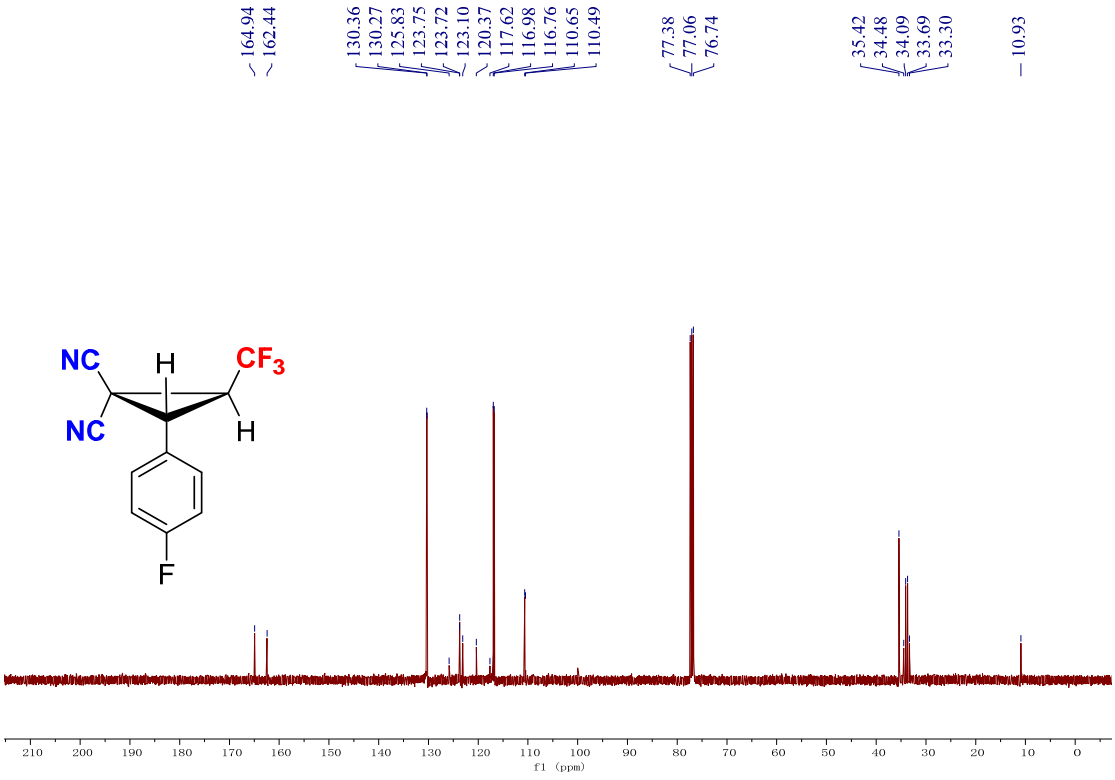
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4g**



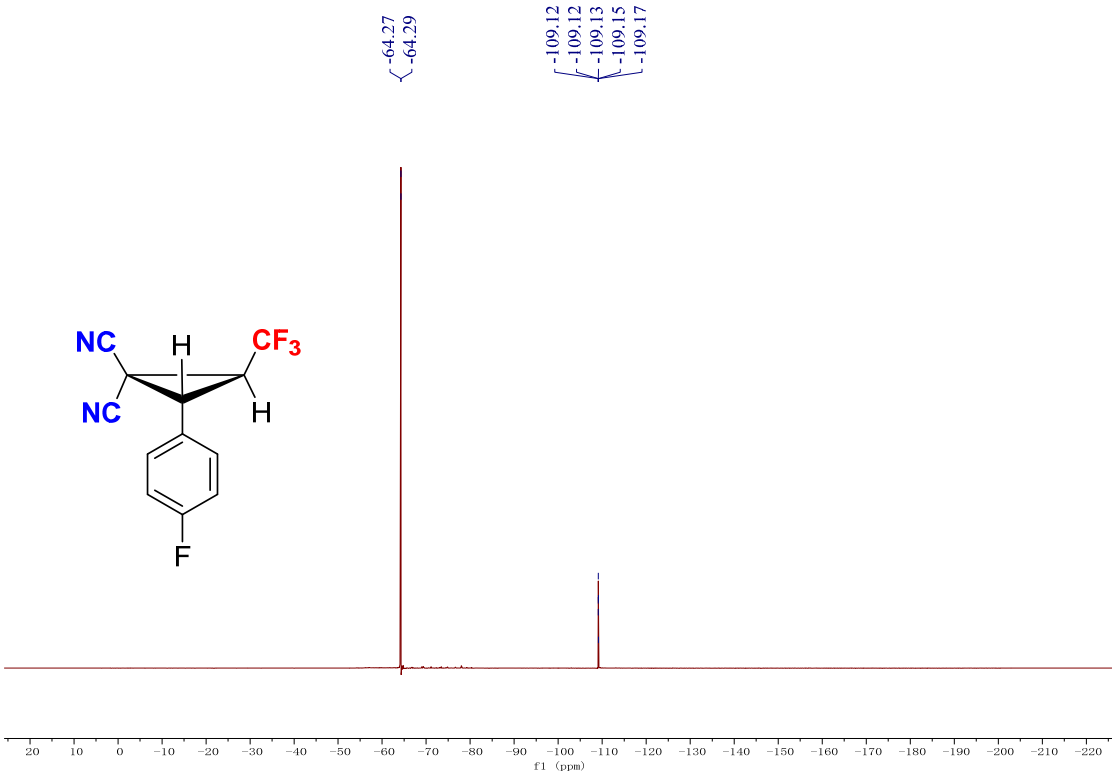
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**



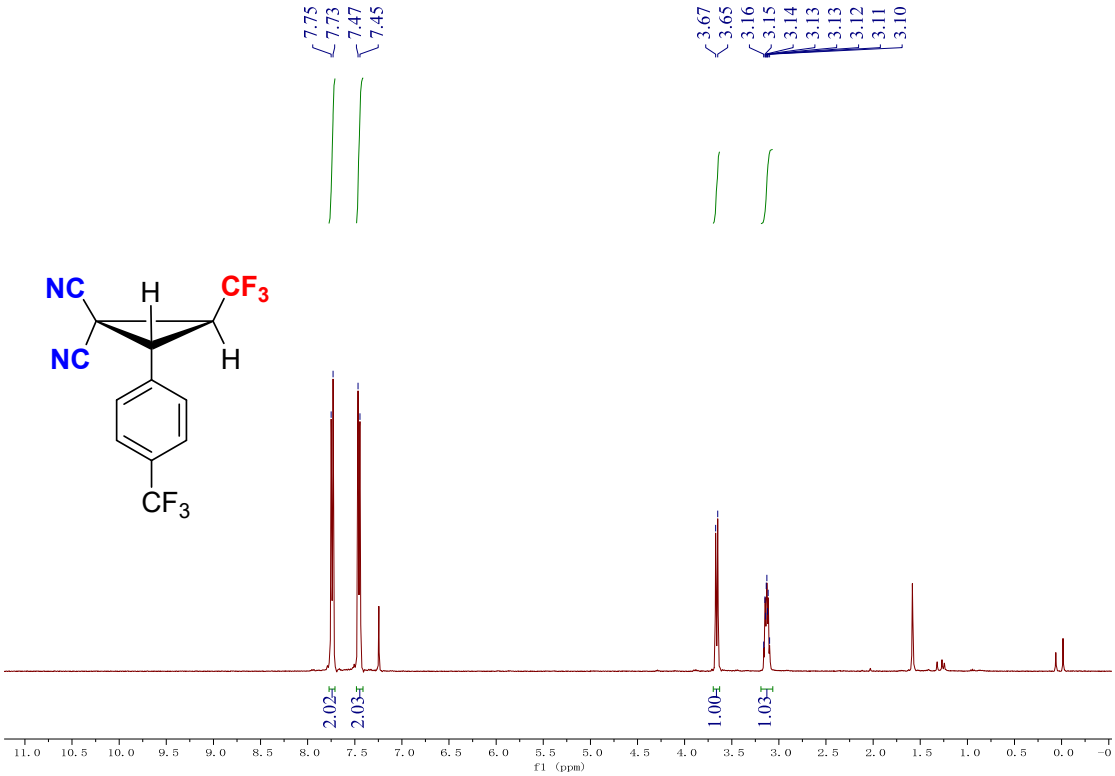
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4h**



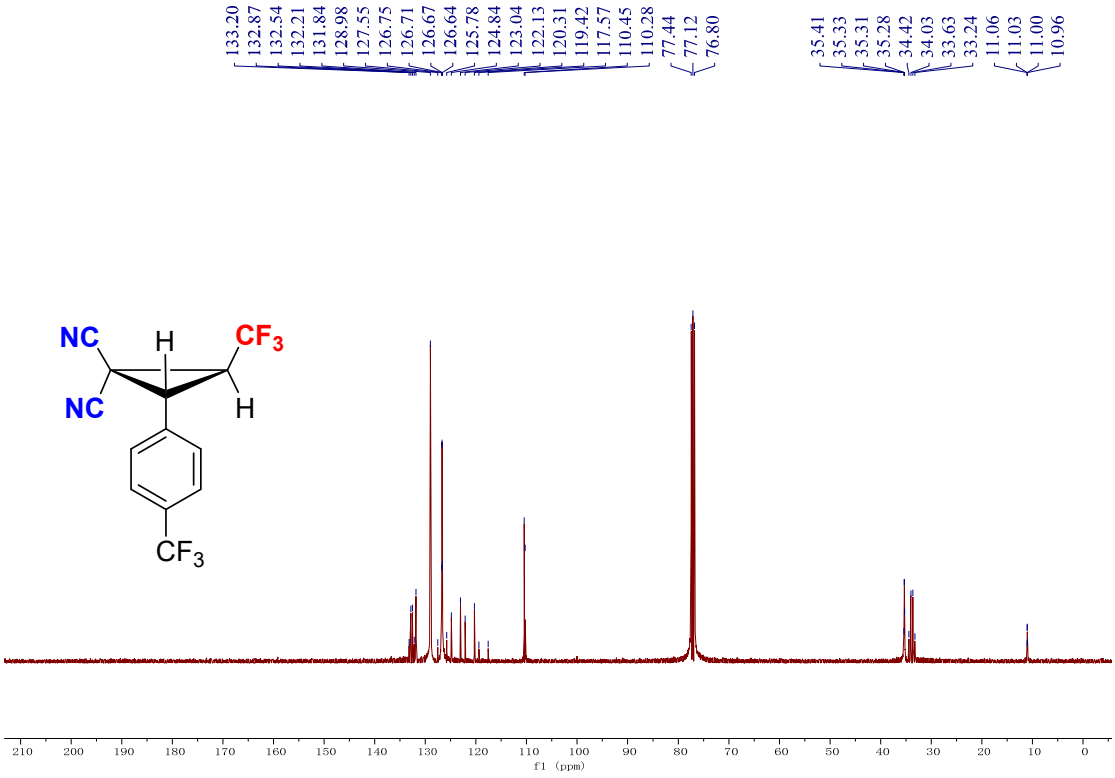
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4h**



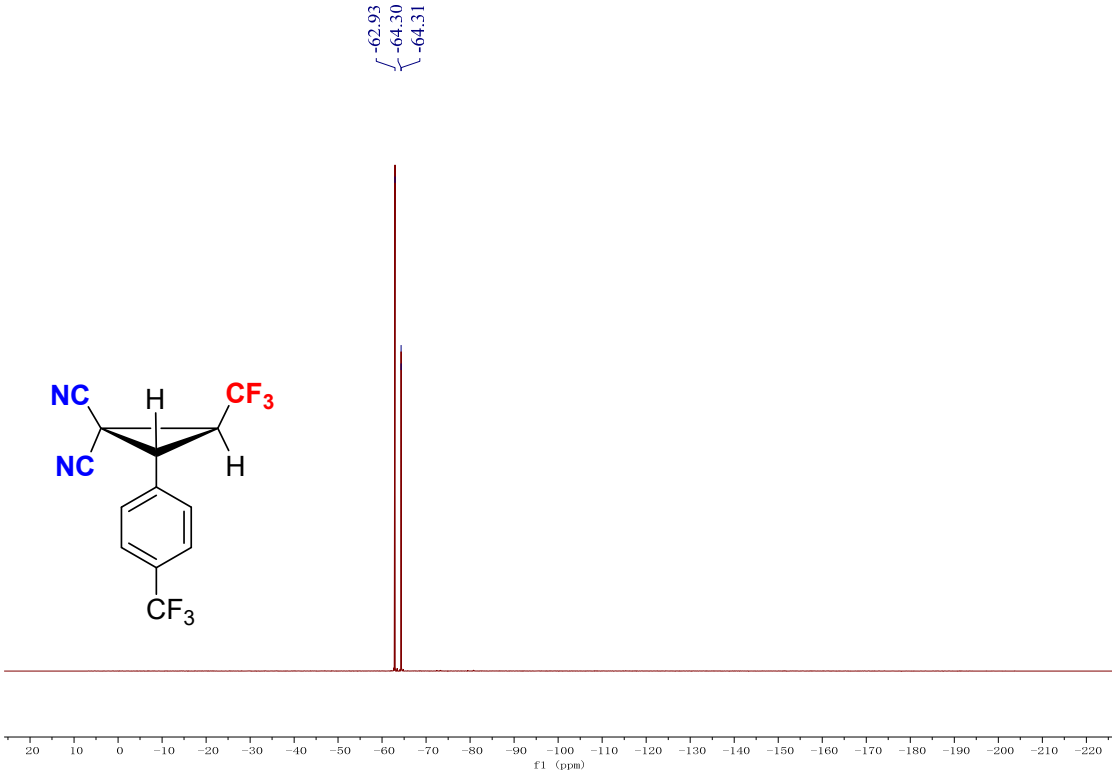
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**



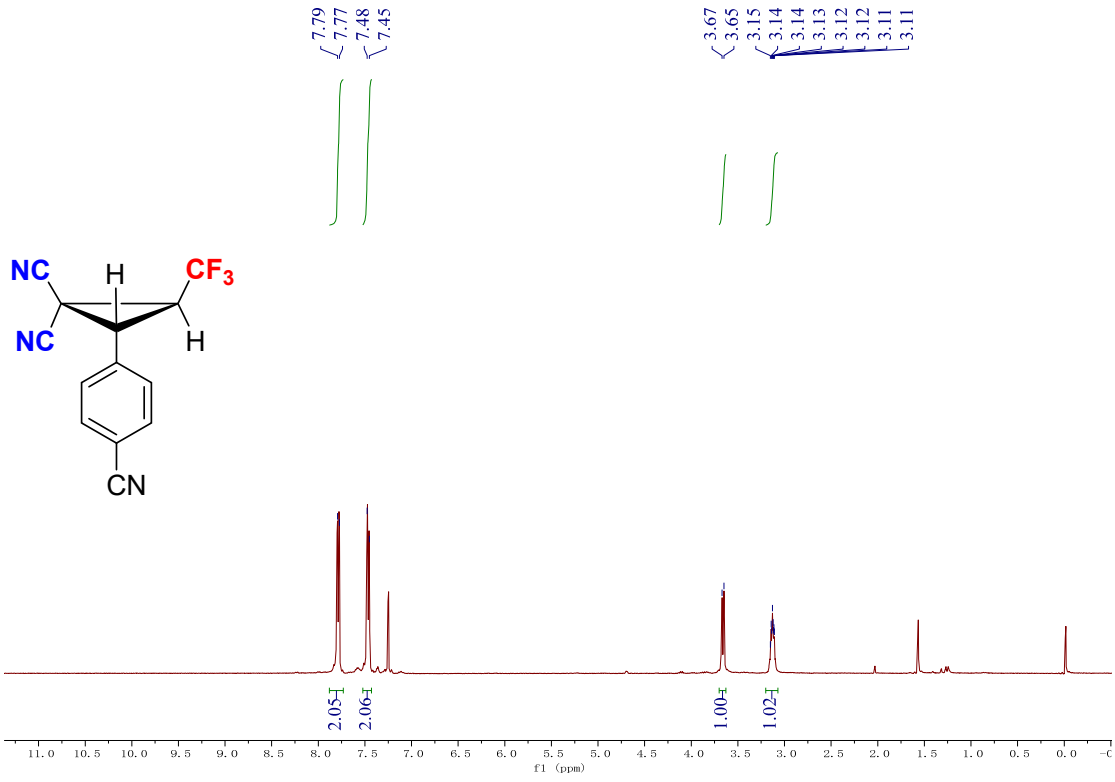
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4i**



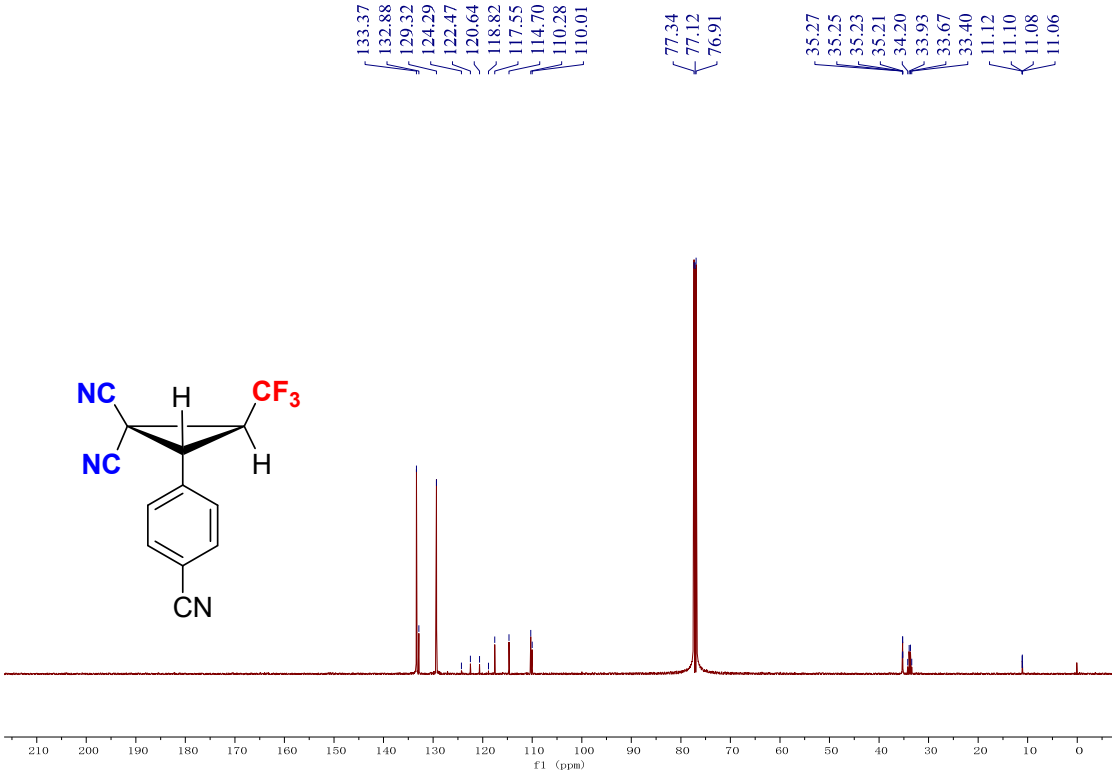
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4i**



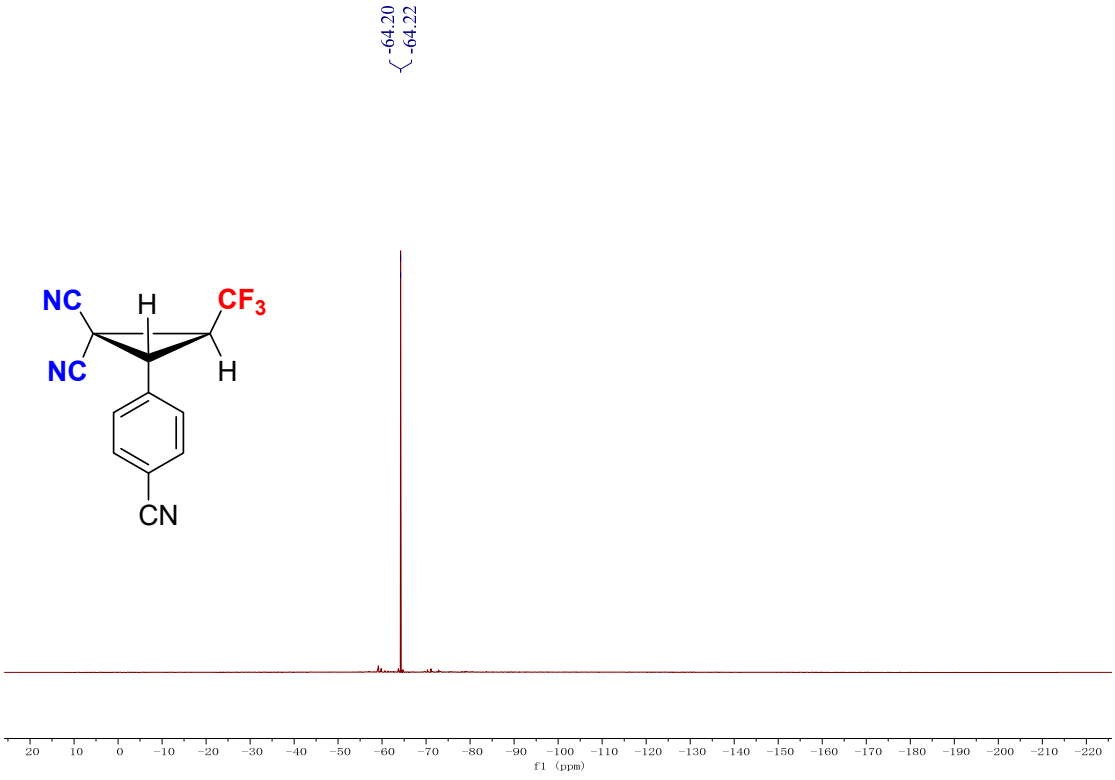
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j**



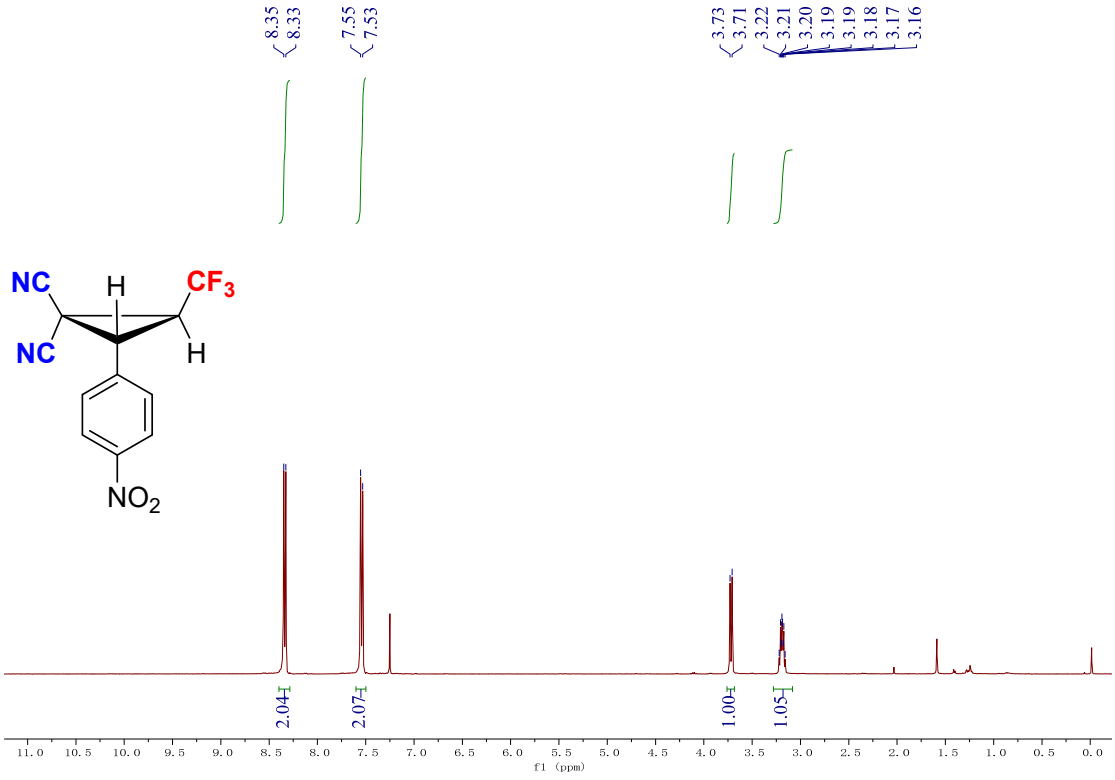
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4j**



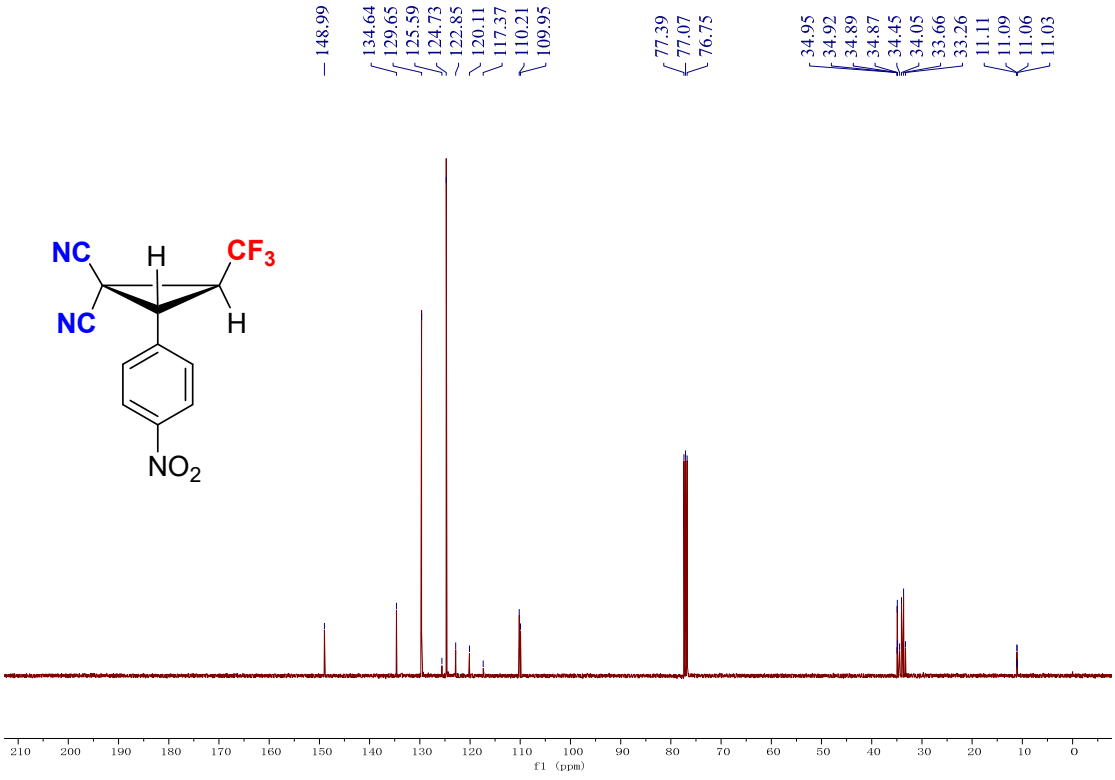
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4j**



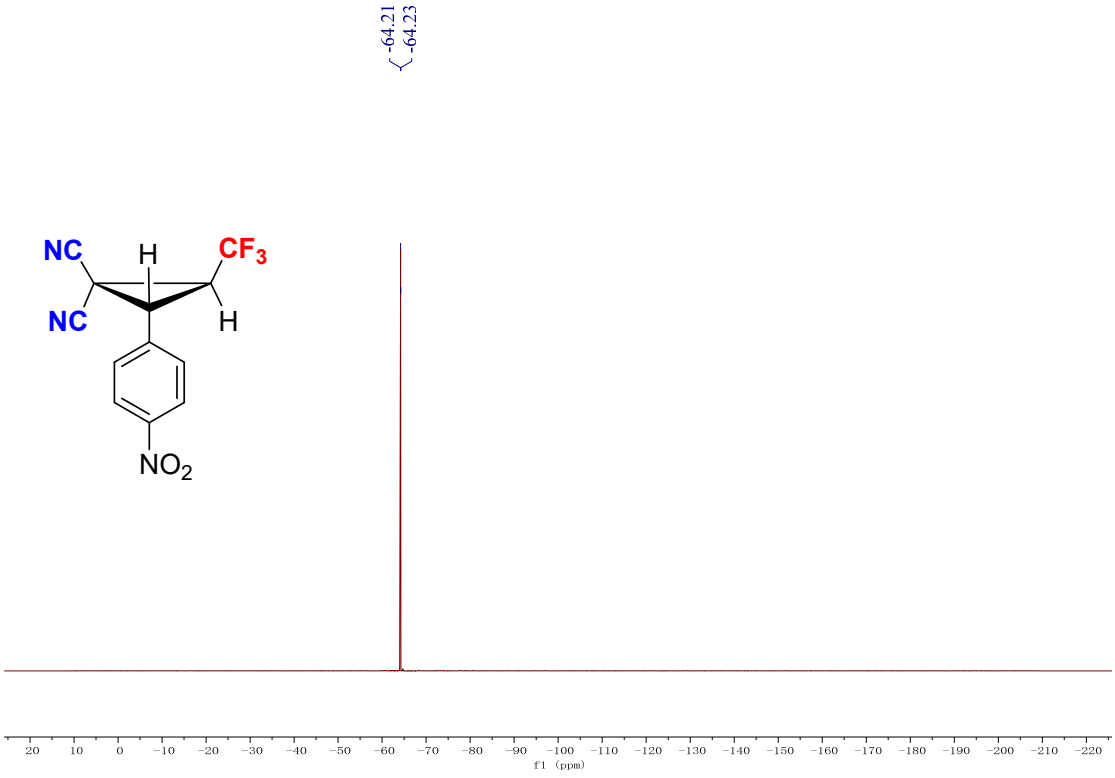
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**



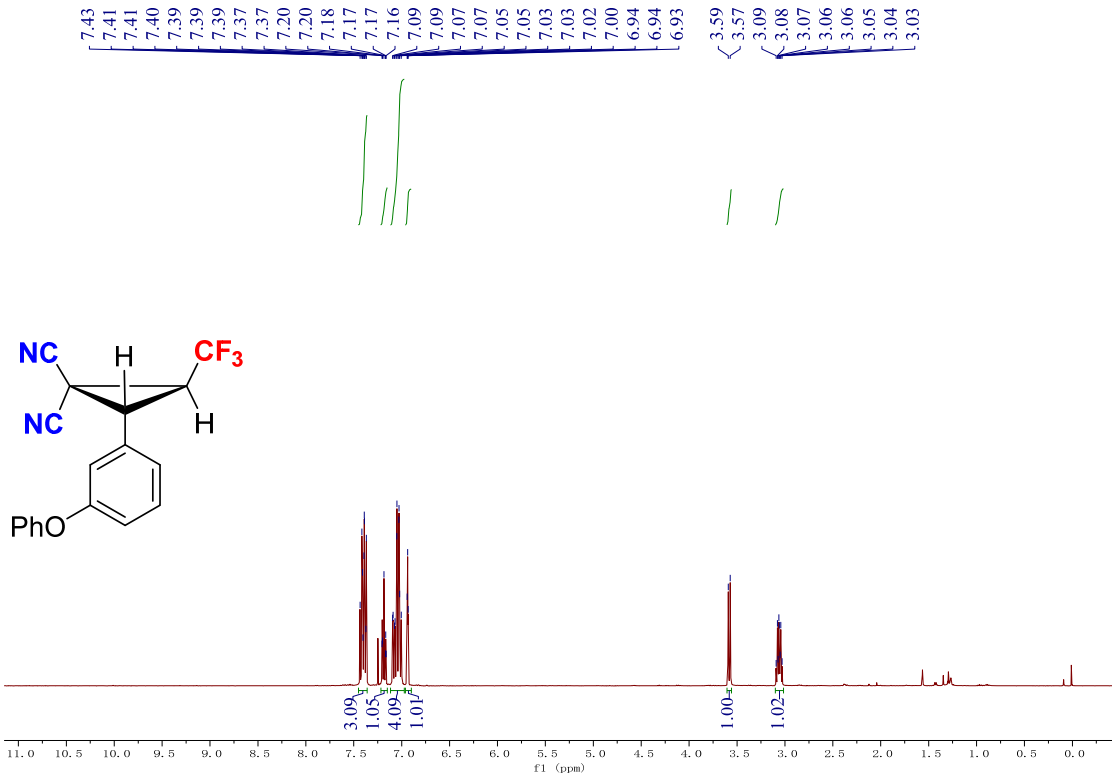
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4k**



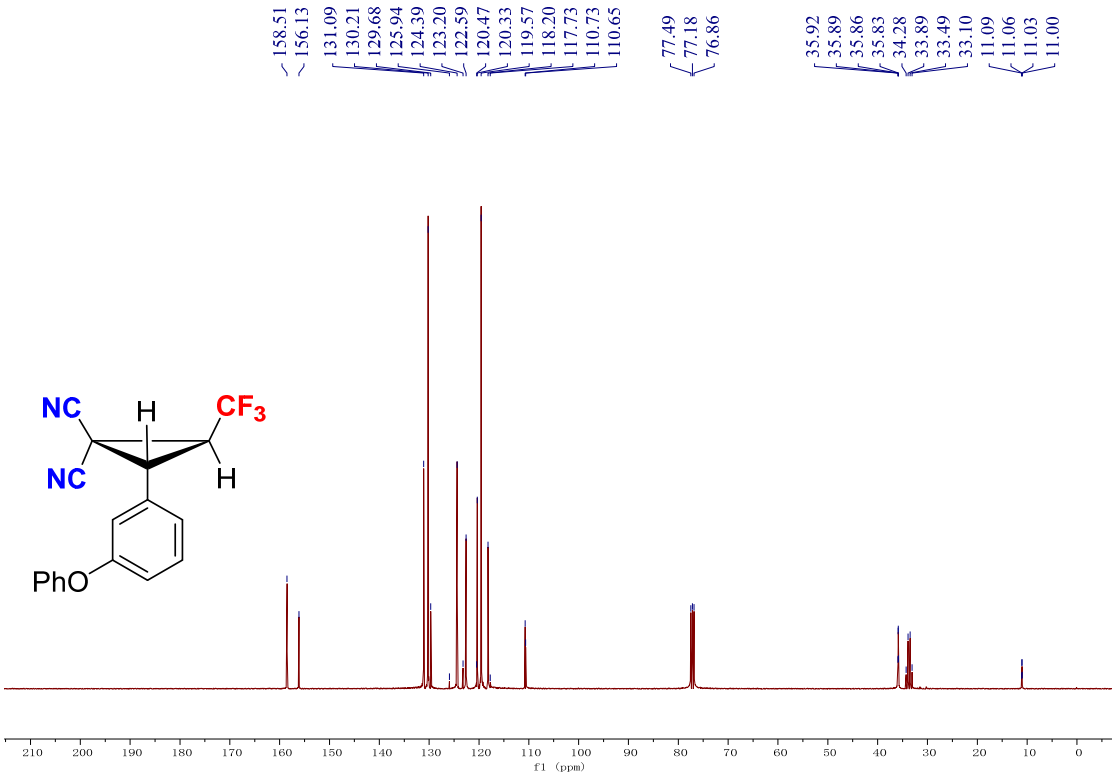
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4k**



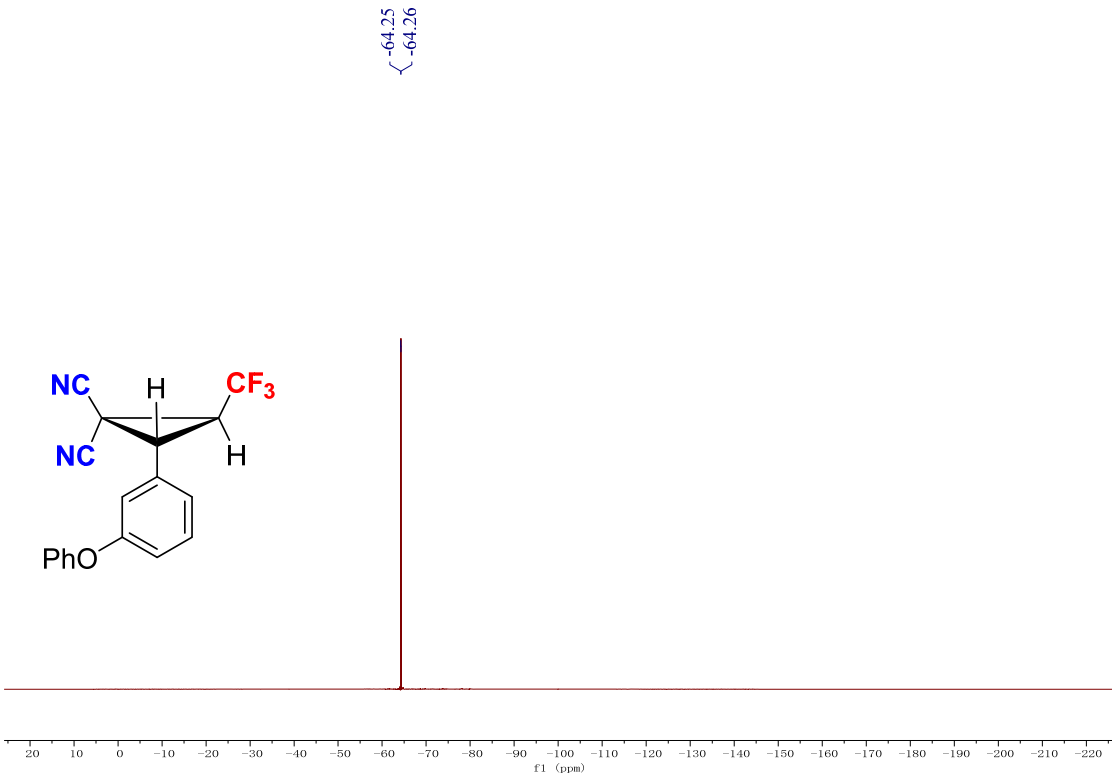
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4l**



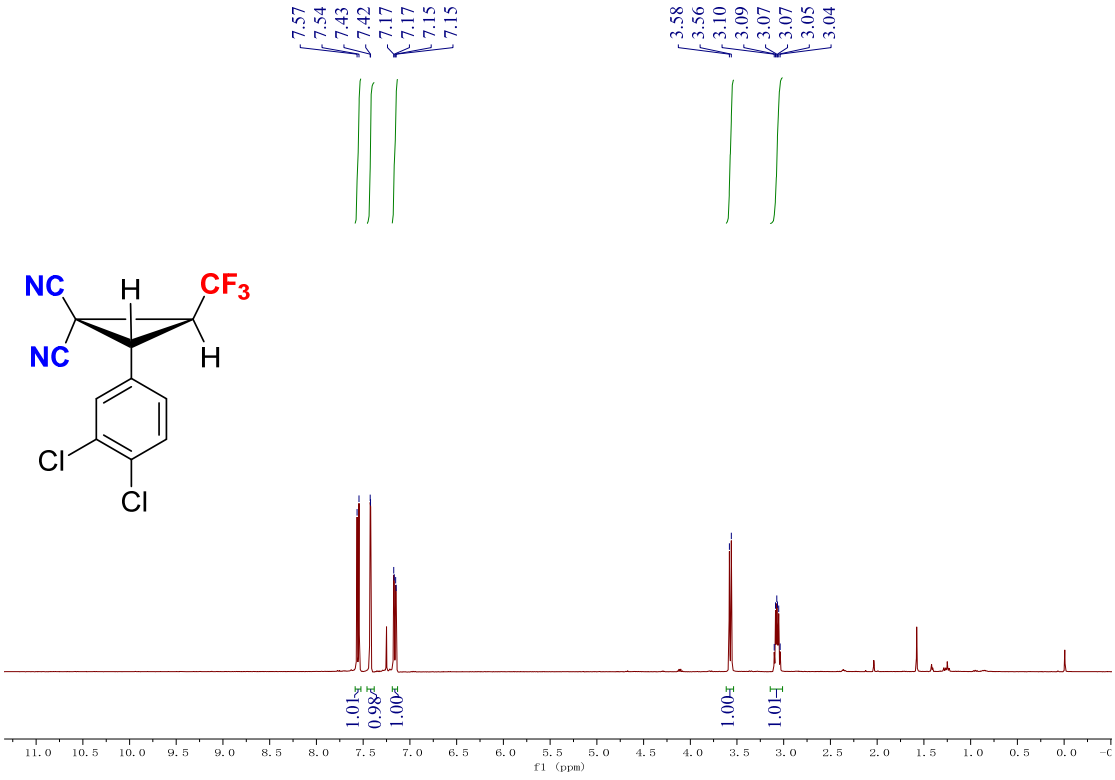
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4l**



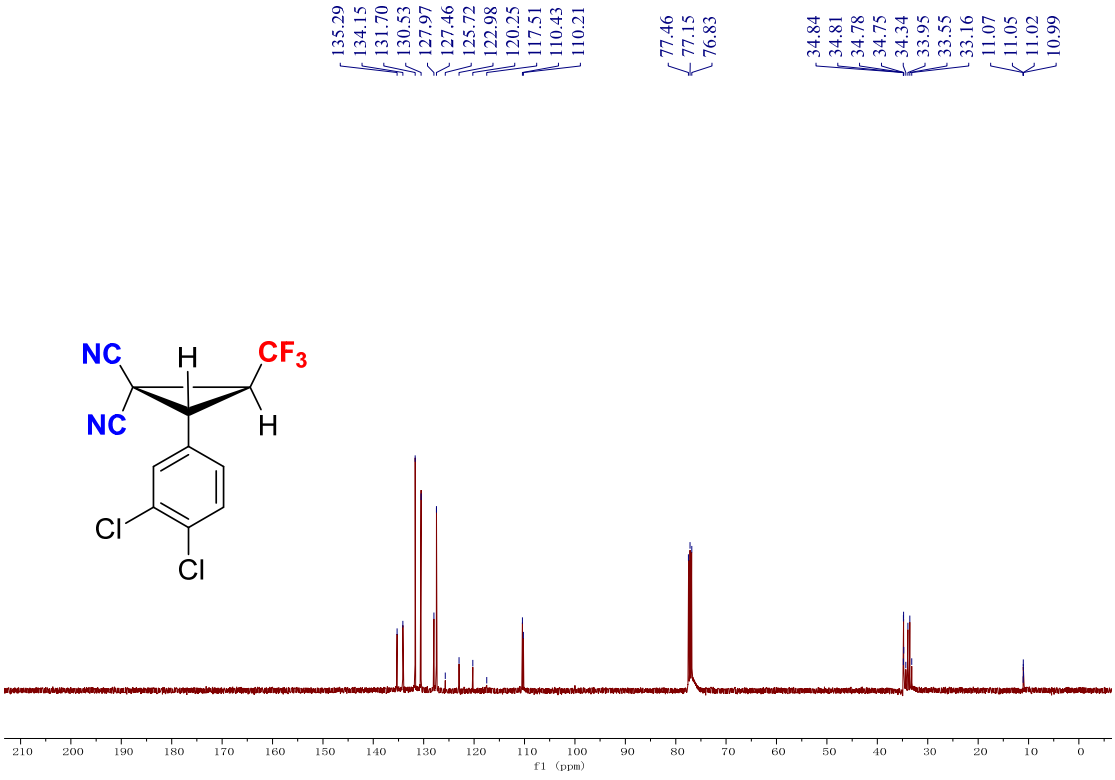
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4l**



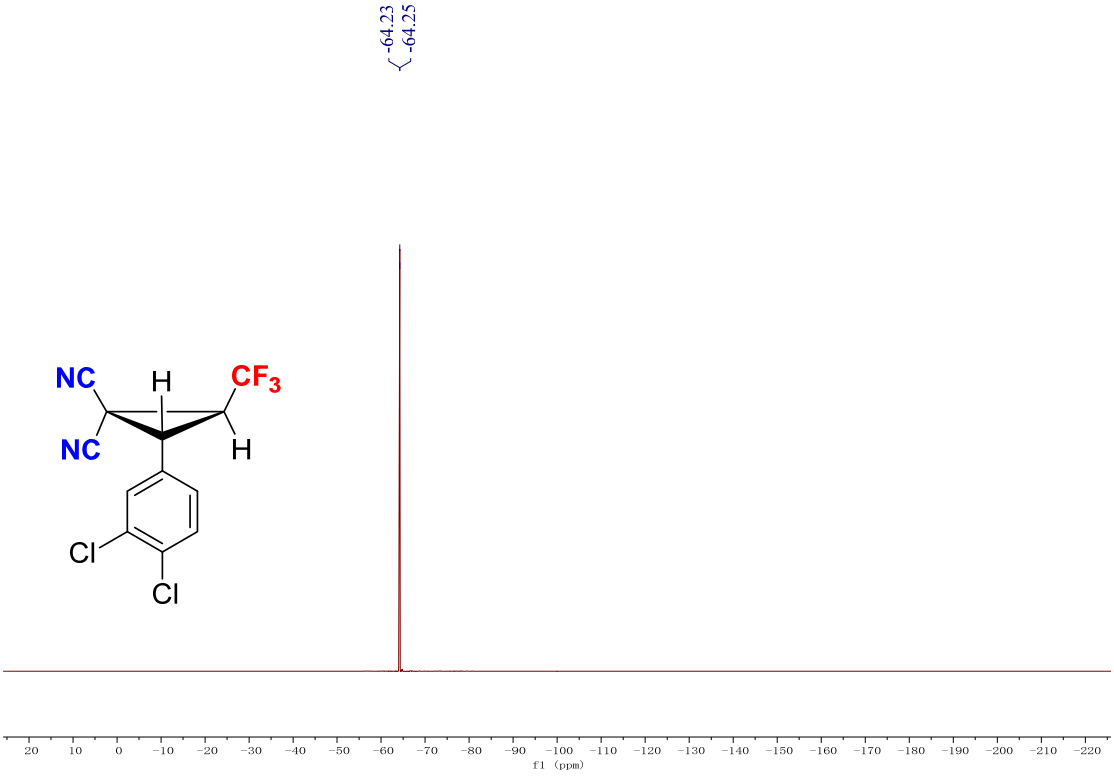
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4m**



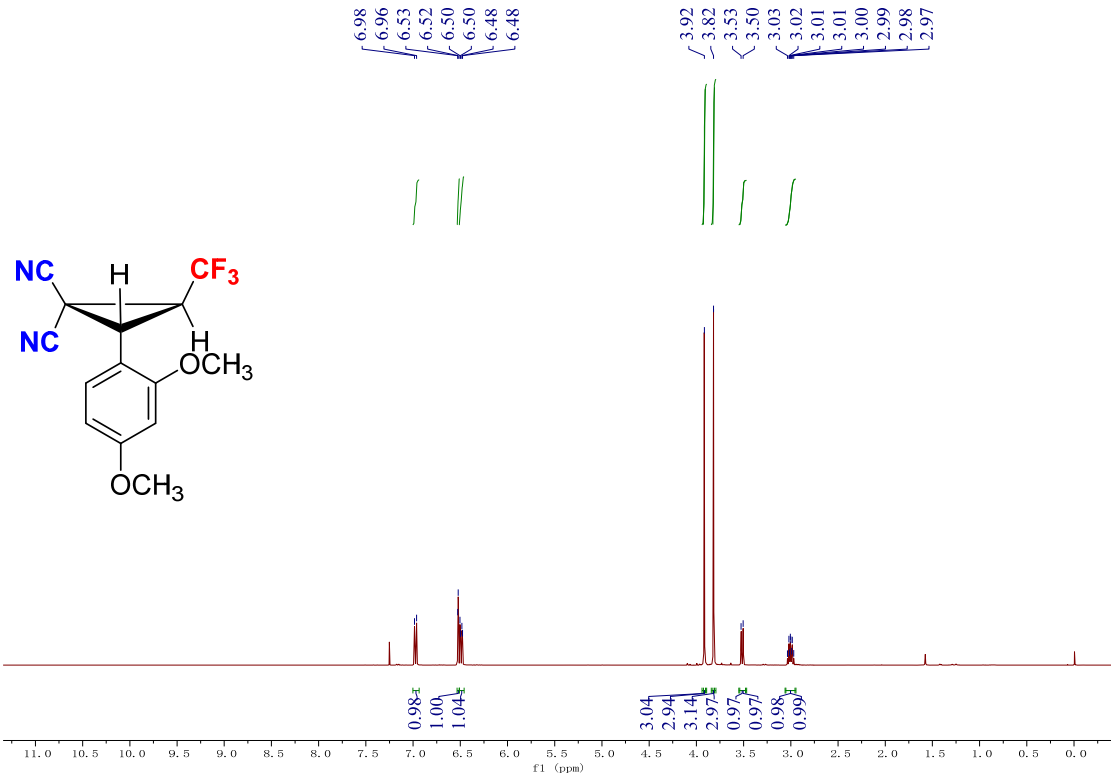
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4m**



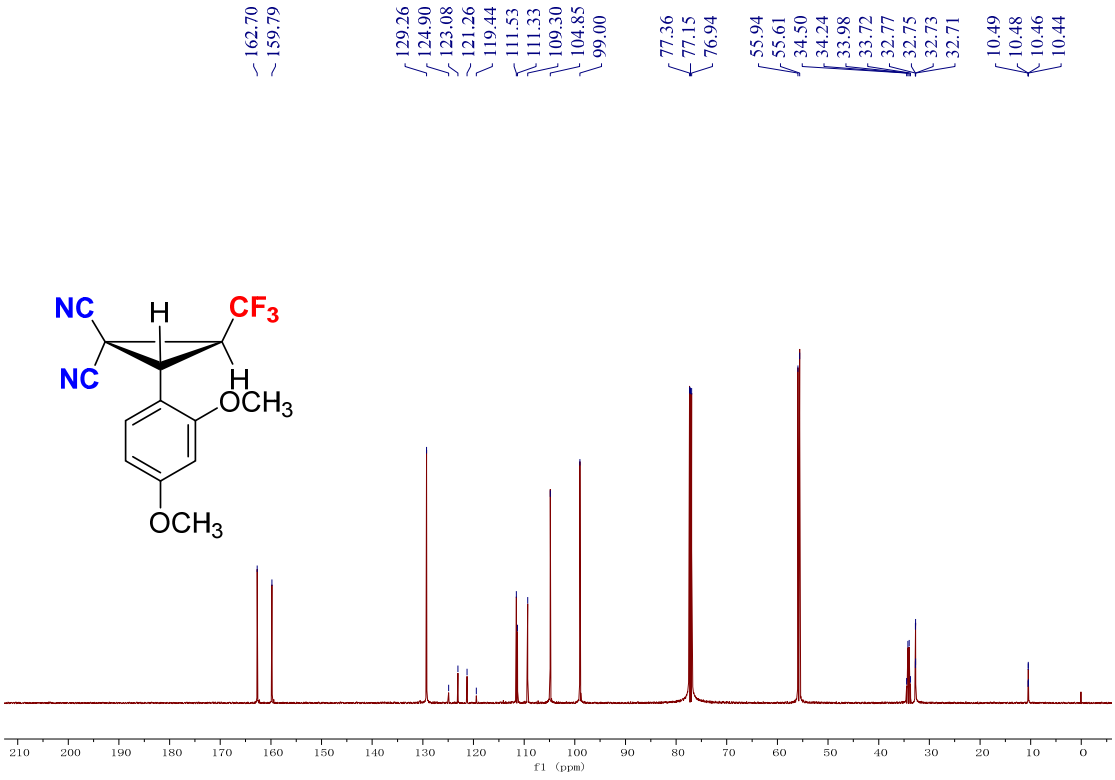
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4m**



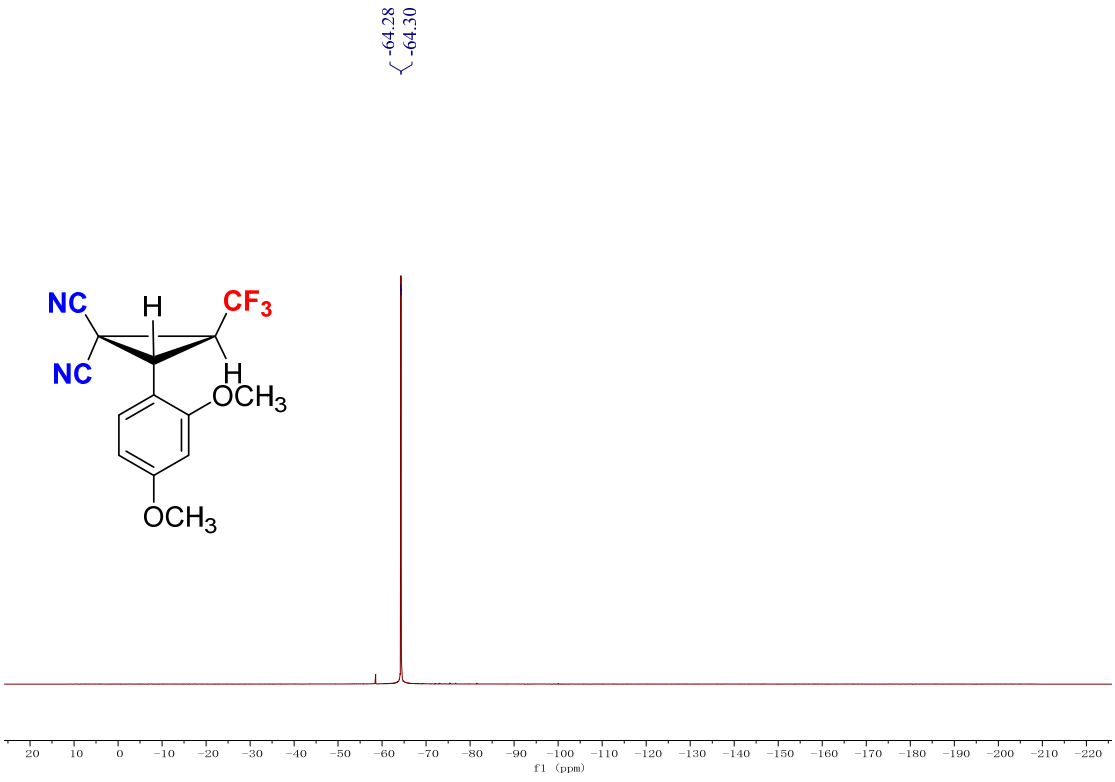
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**



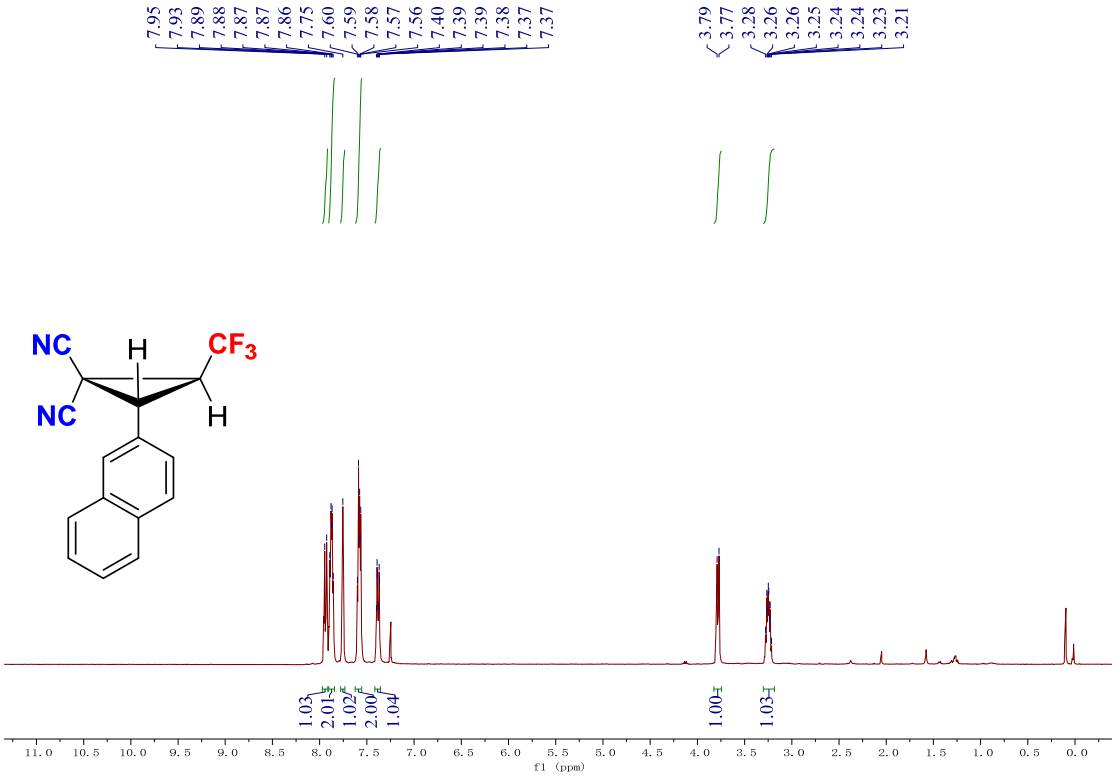
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4n**



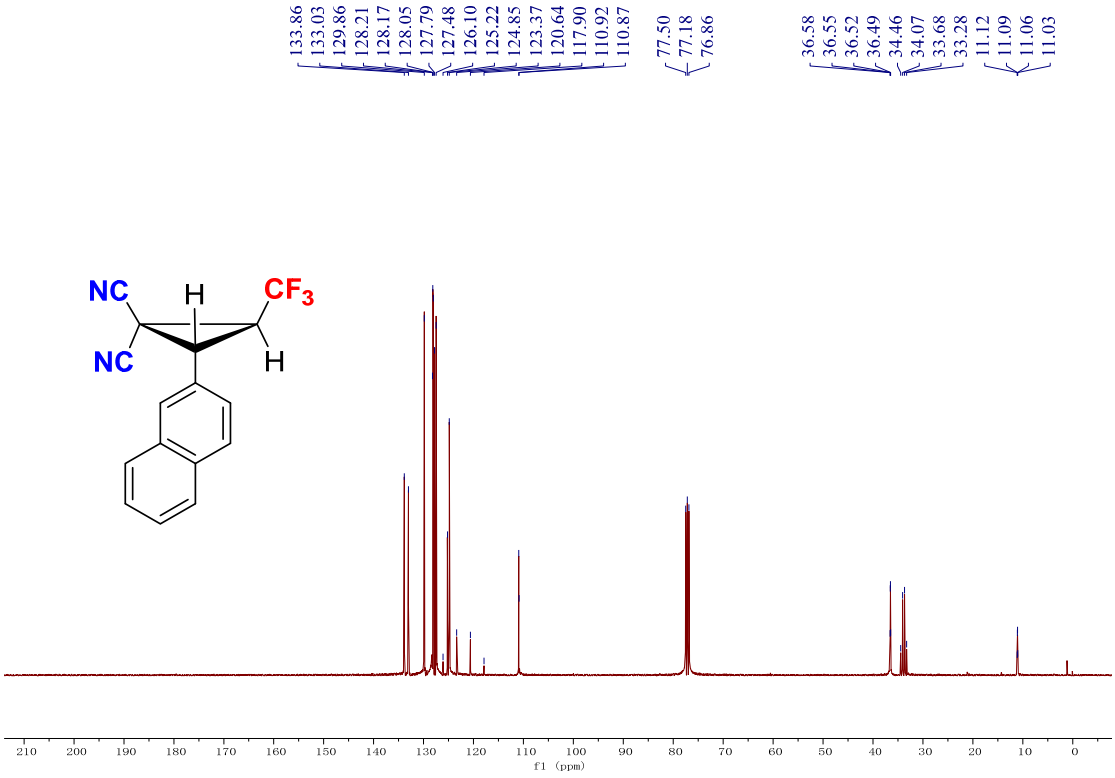
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4n**



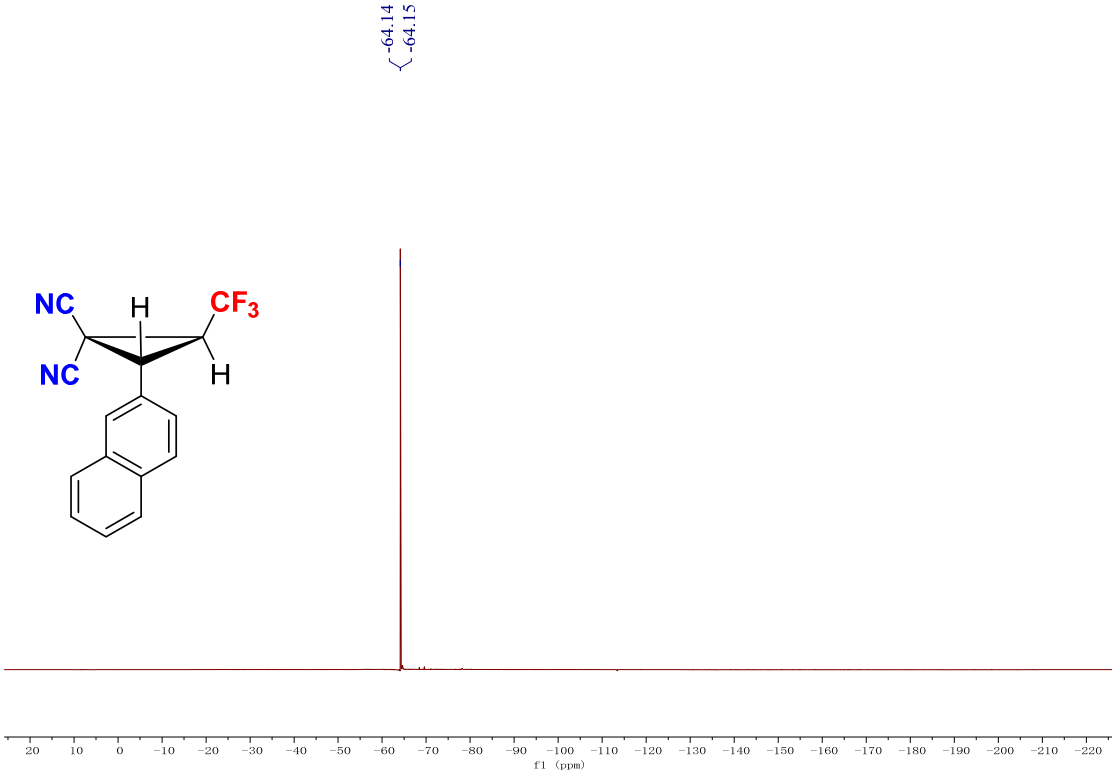
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o**



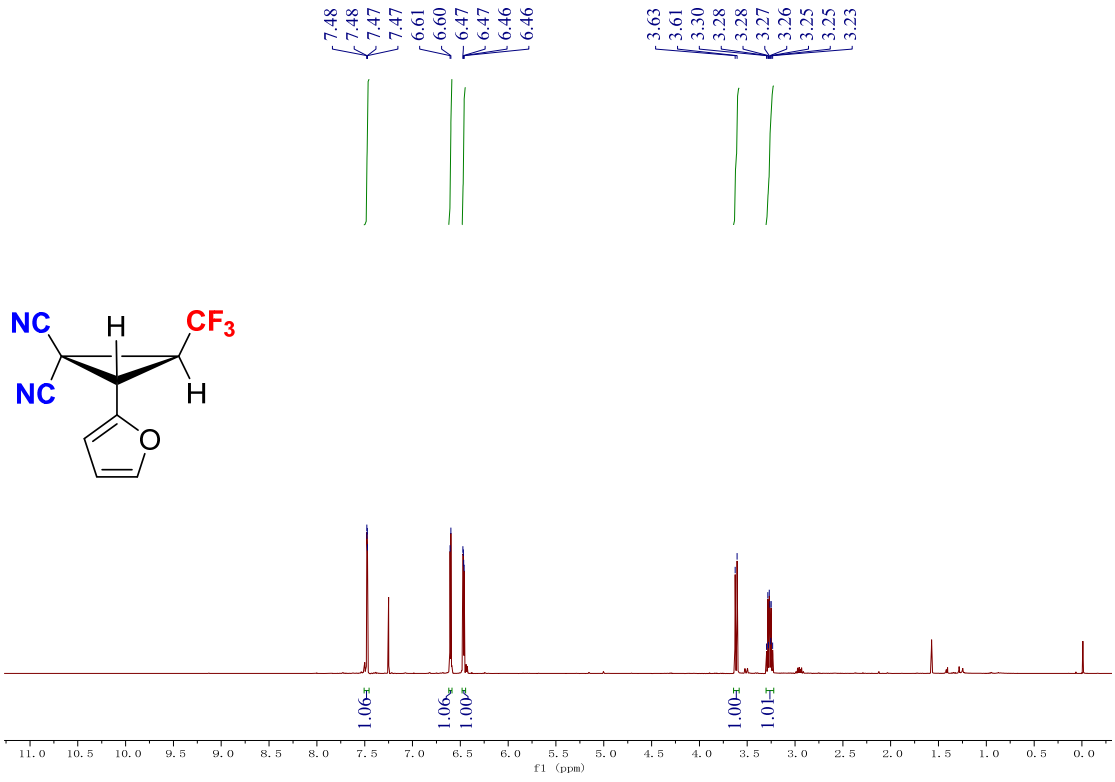
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4o**



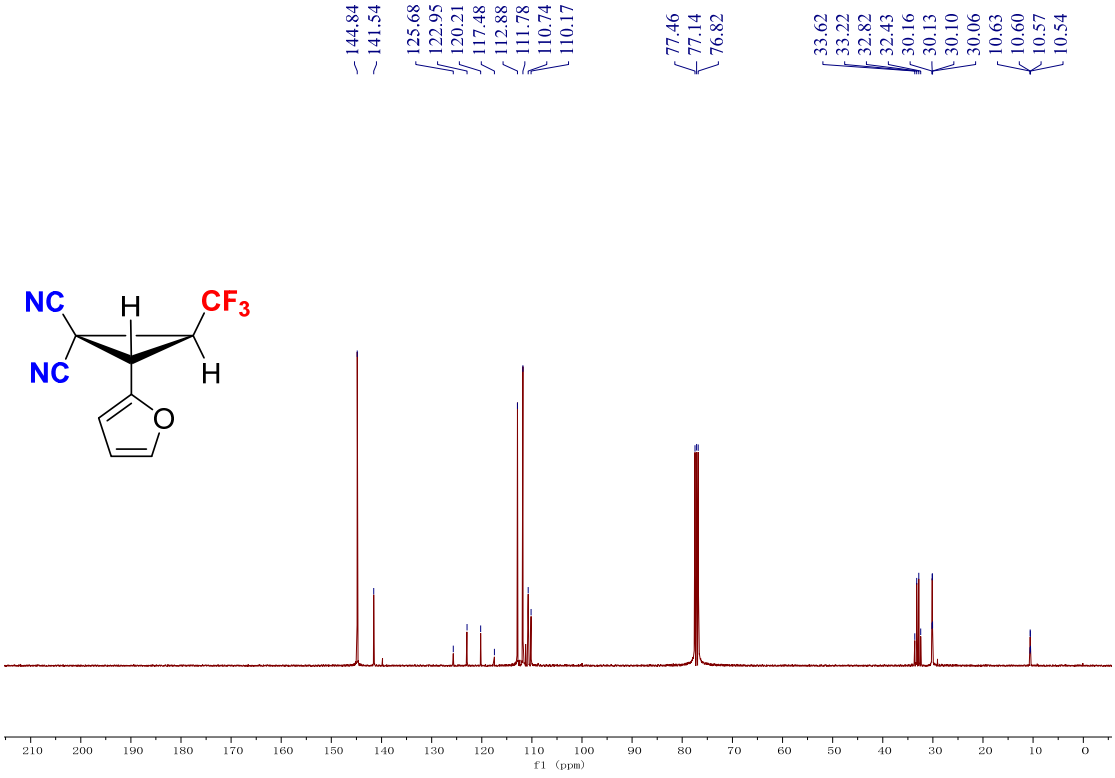
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4o**



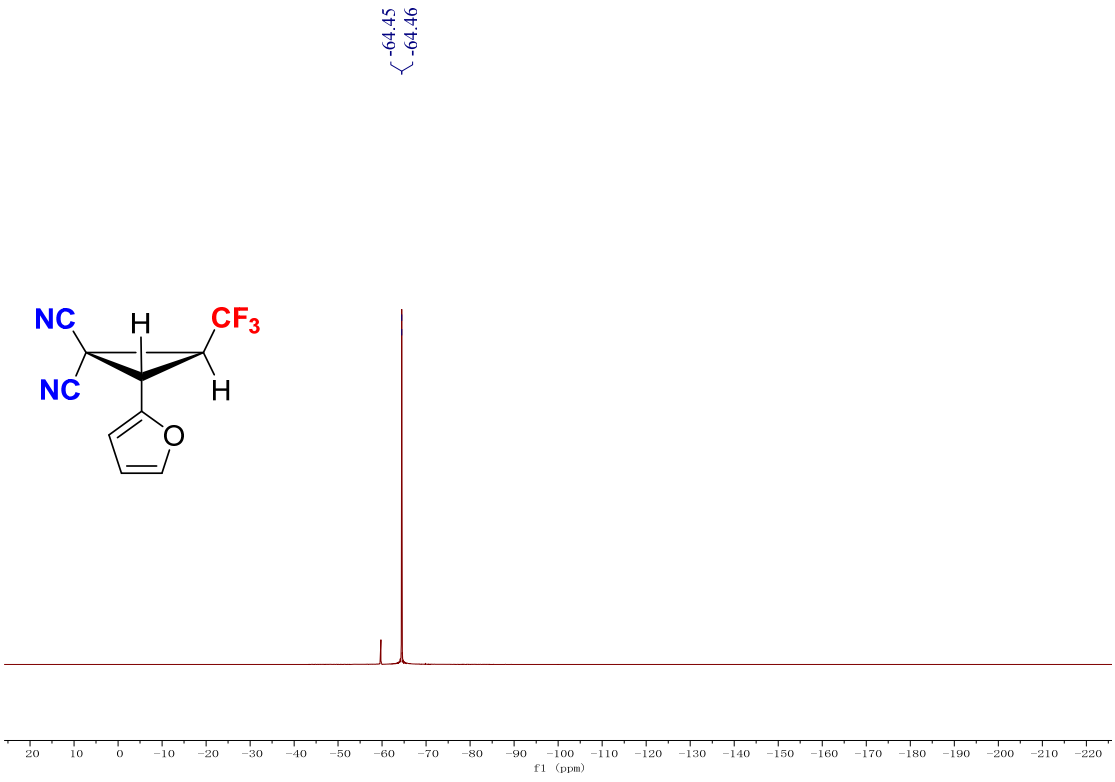
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4p**



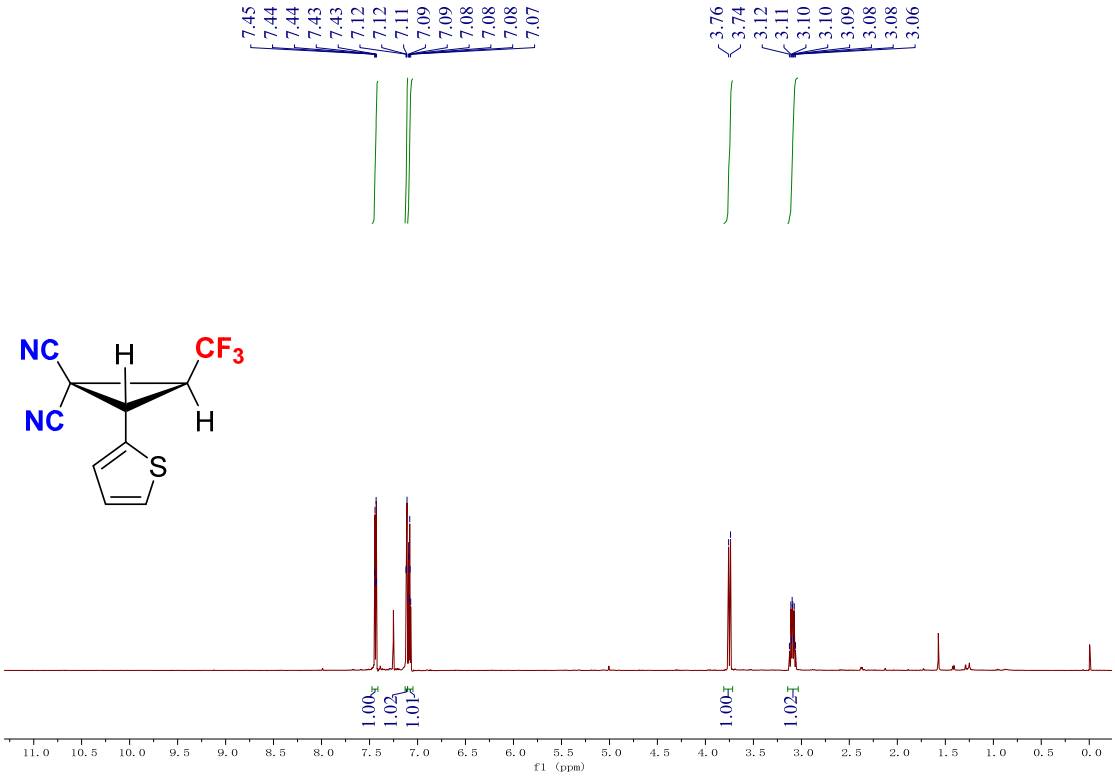
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4p**



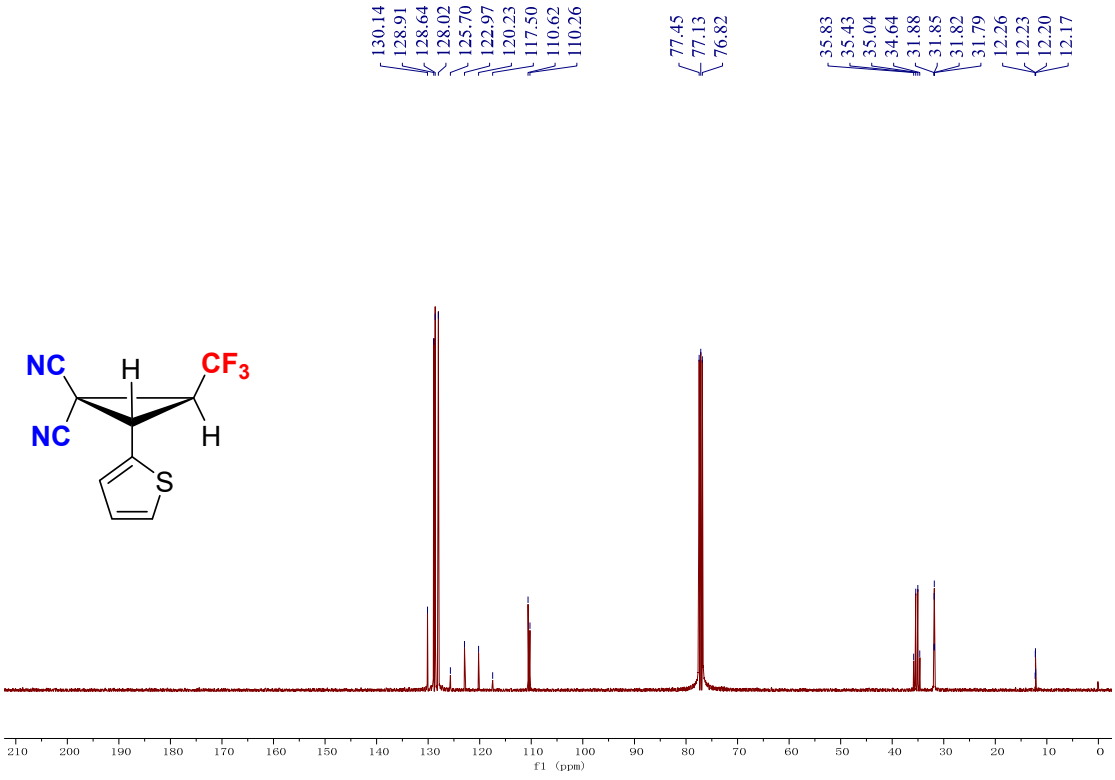
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4p**



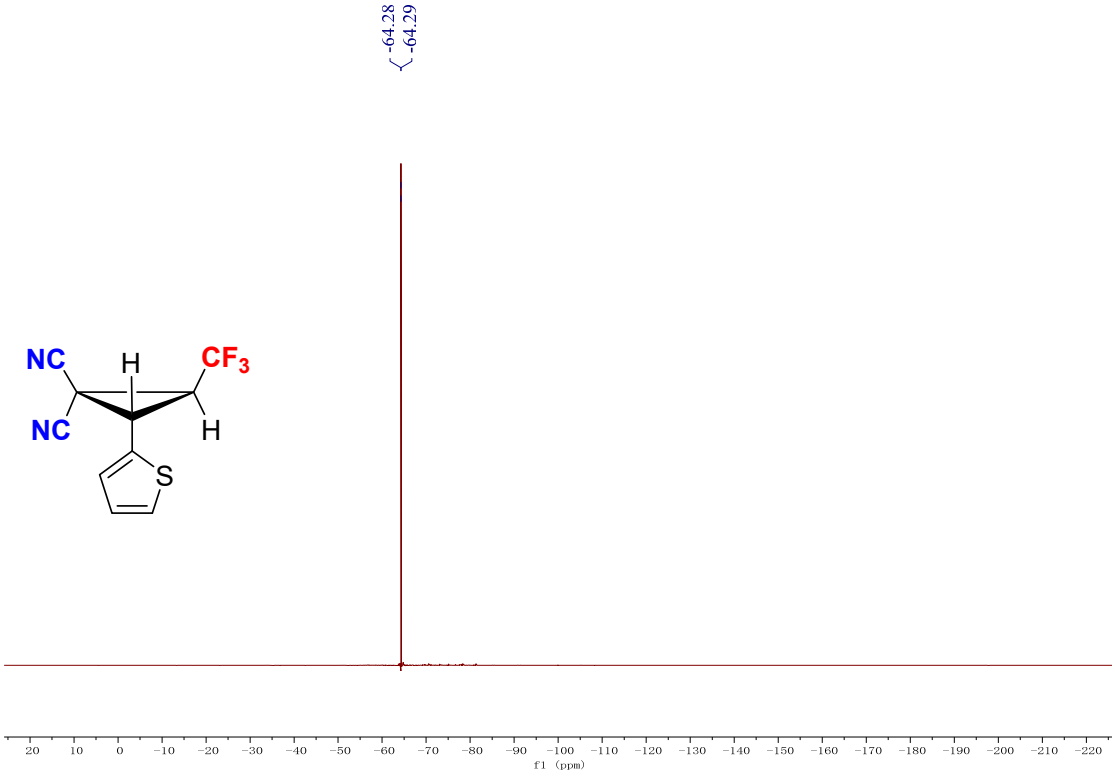
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**



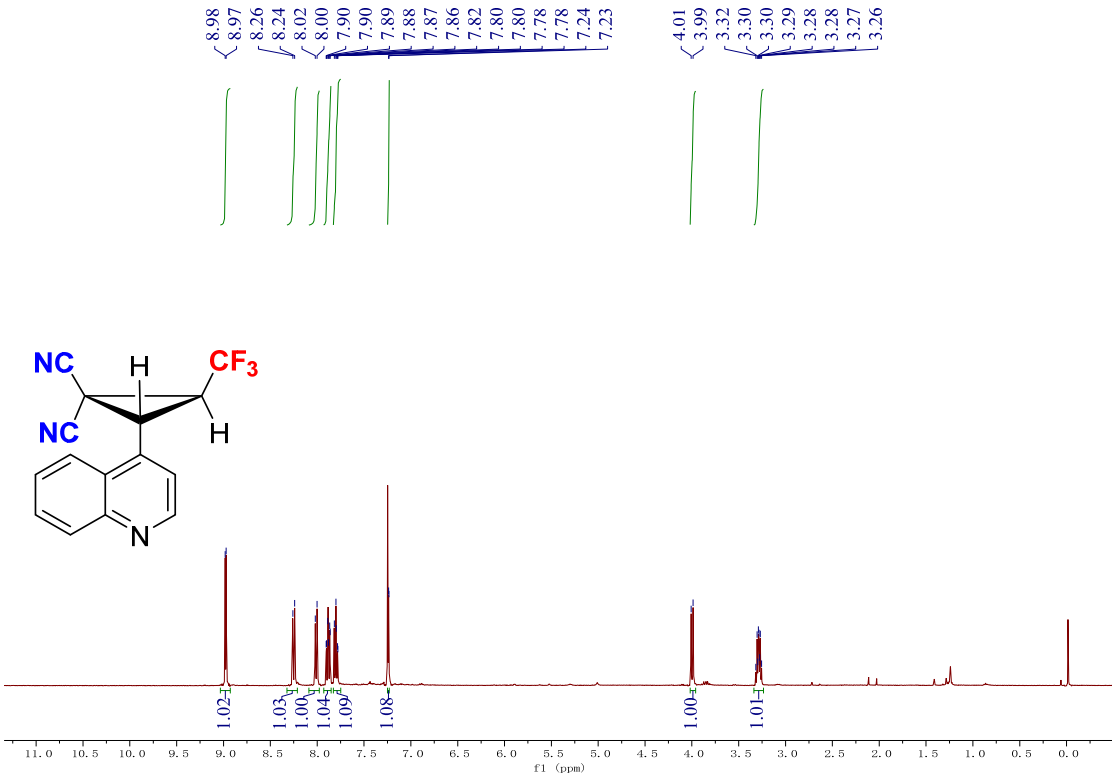
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4q**



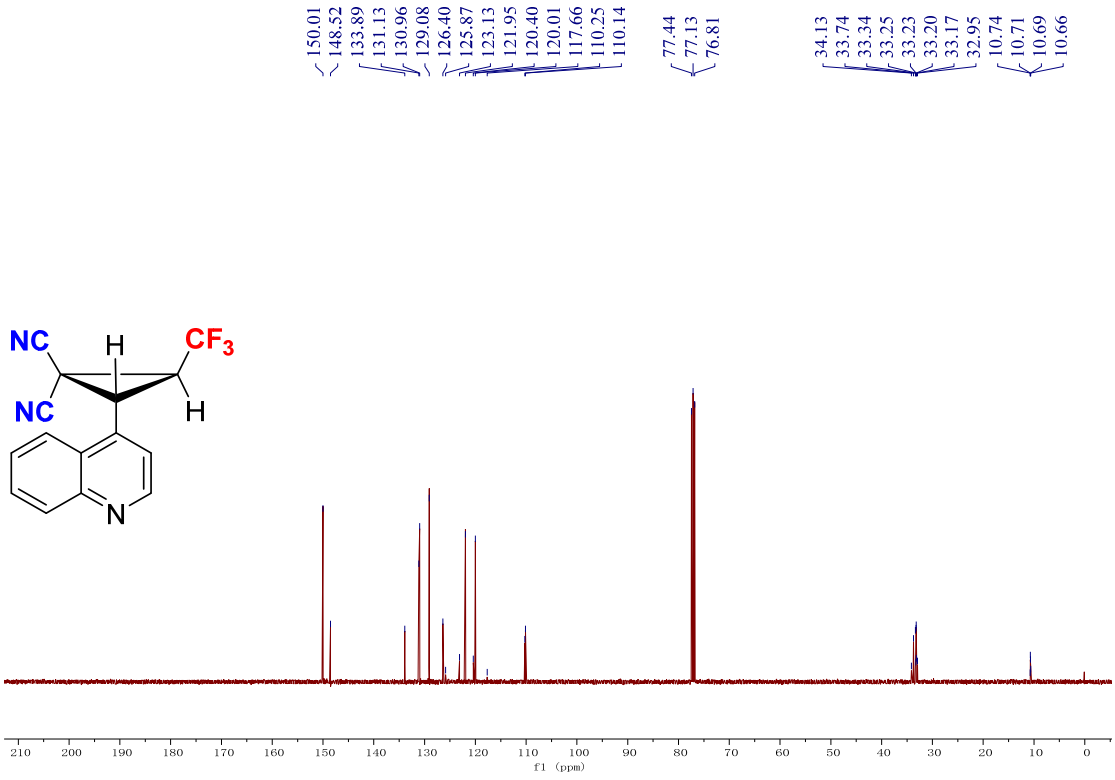
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4q**



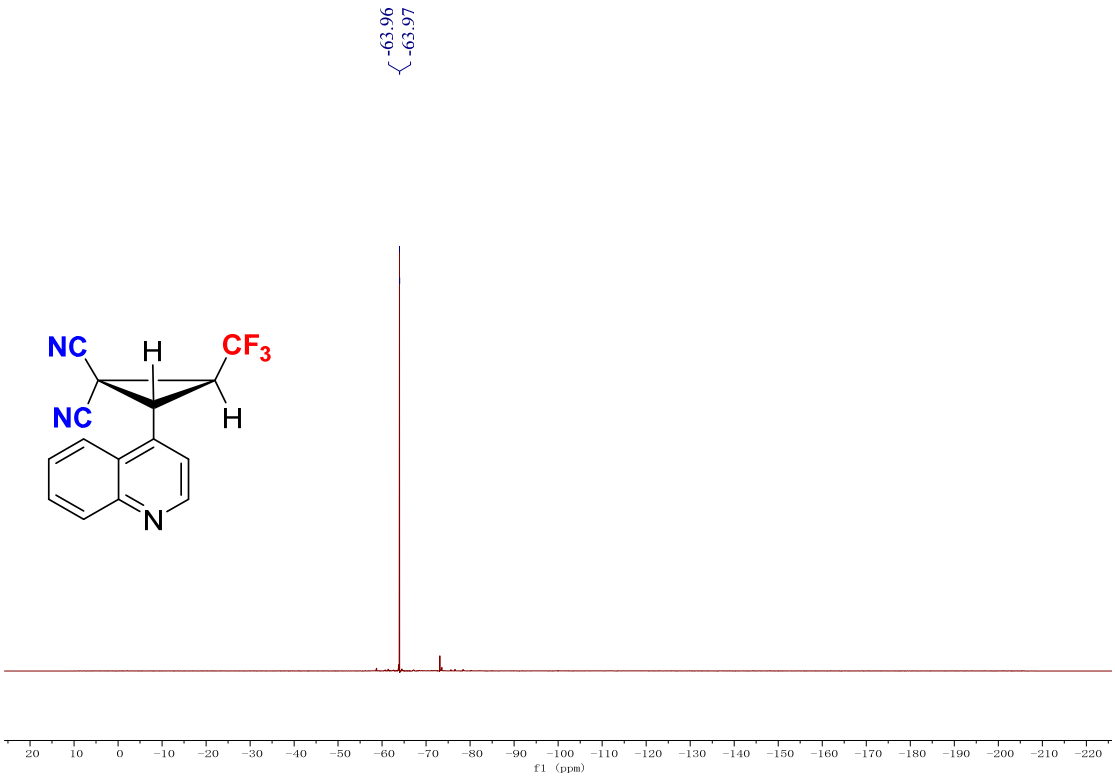
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**



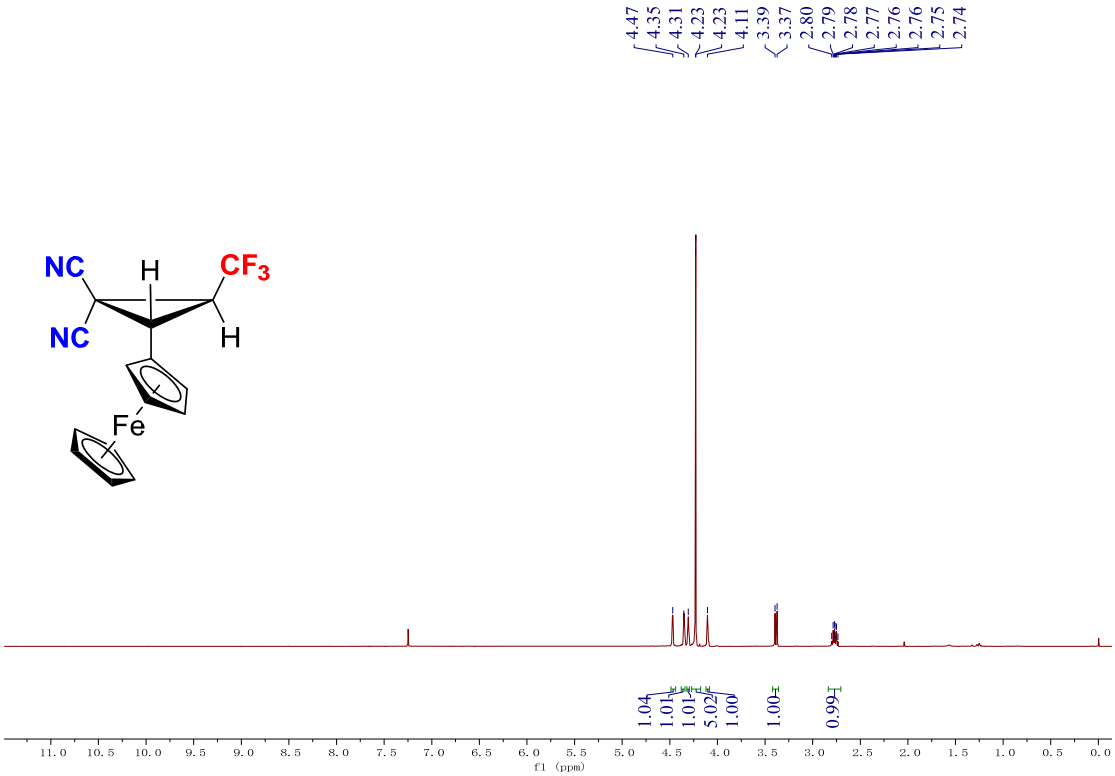
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4r**



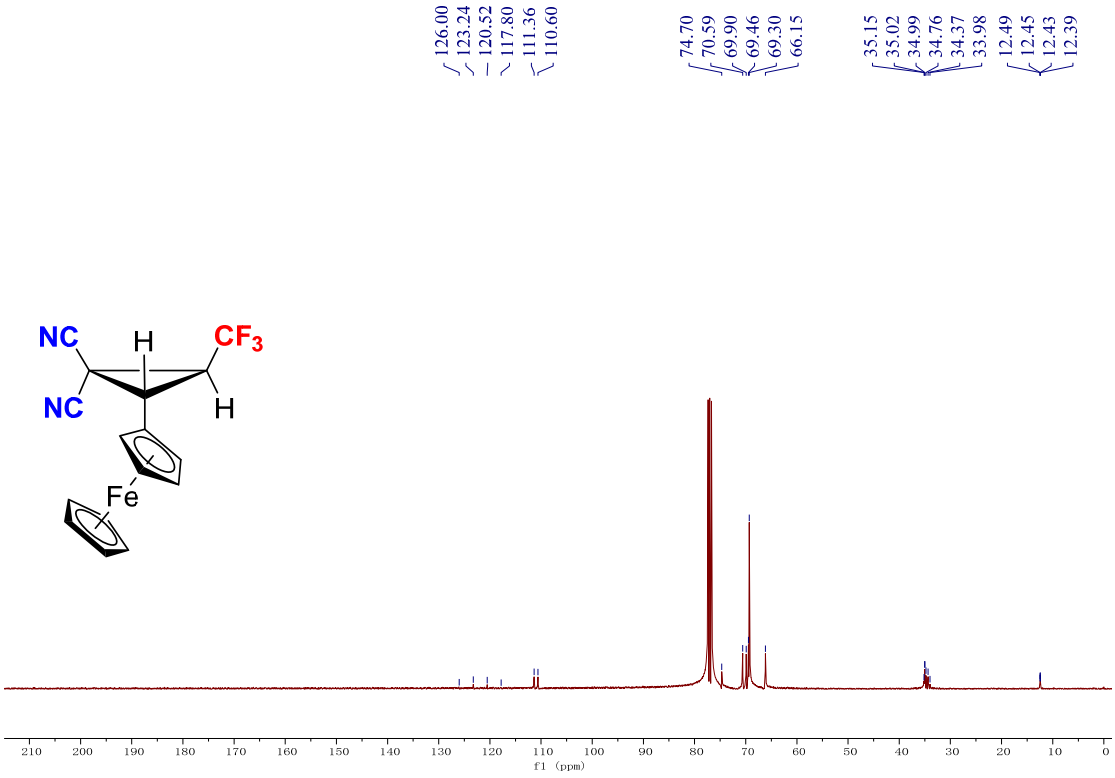
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4r**



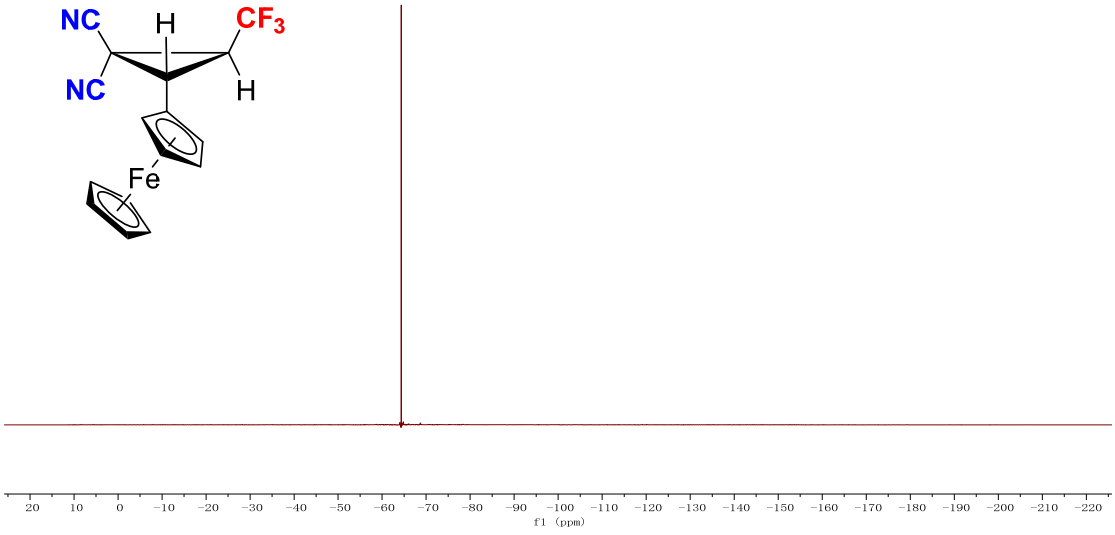
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4s**



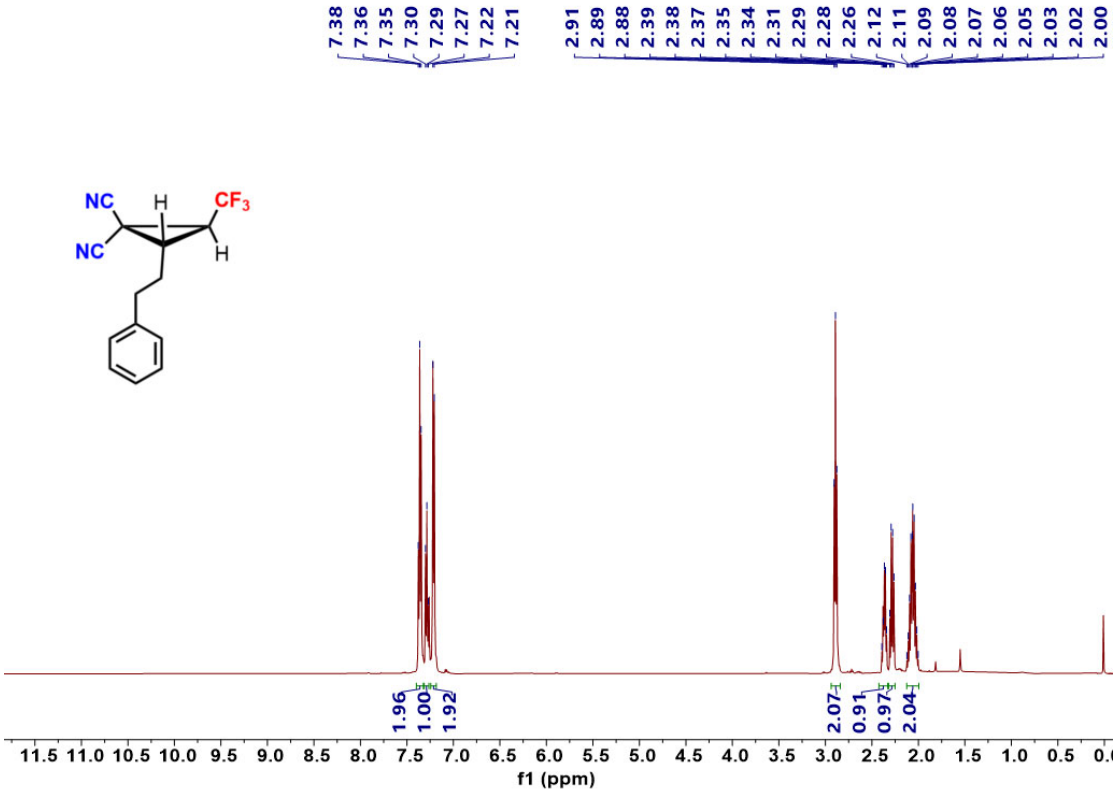
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4s**



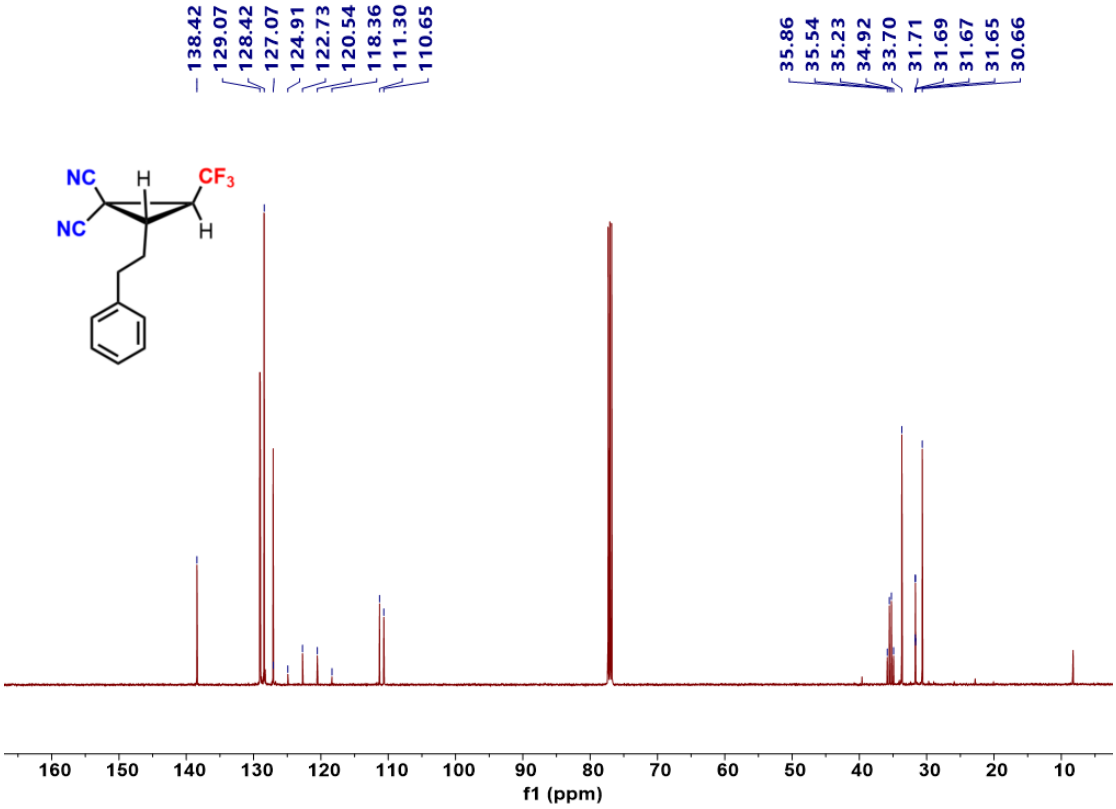
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4s**



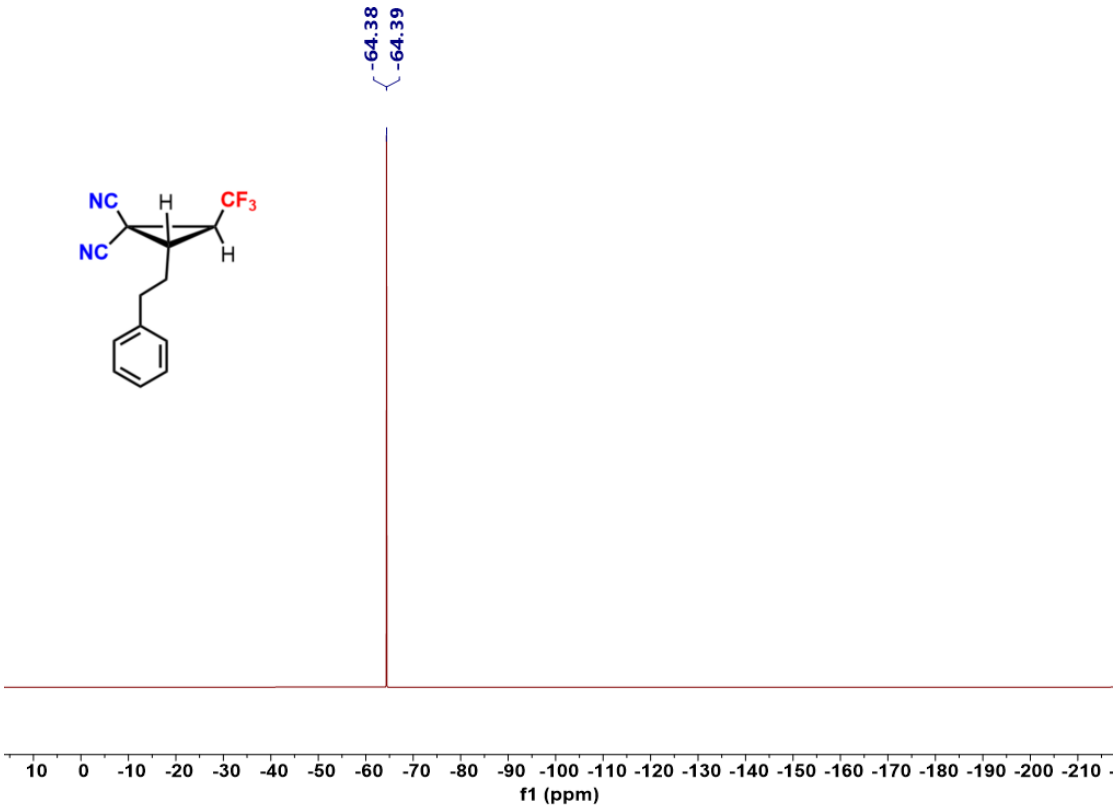
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4t**



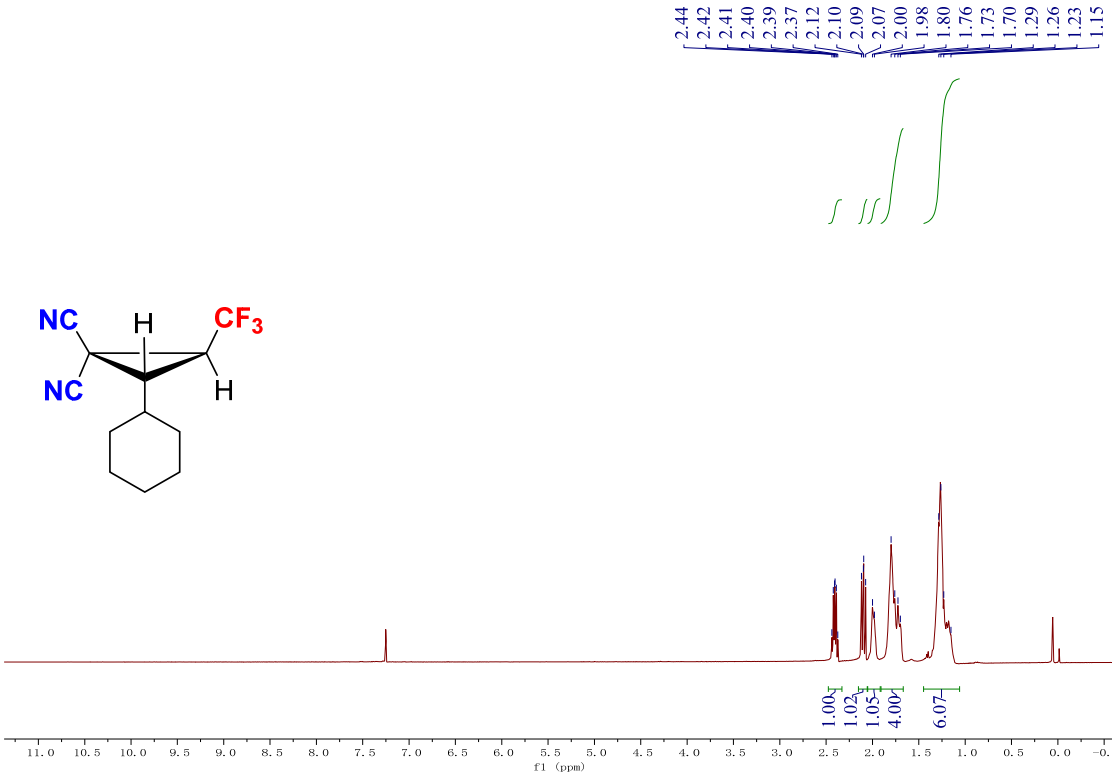
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4t**



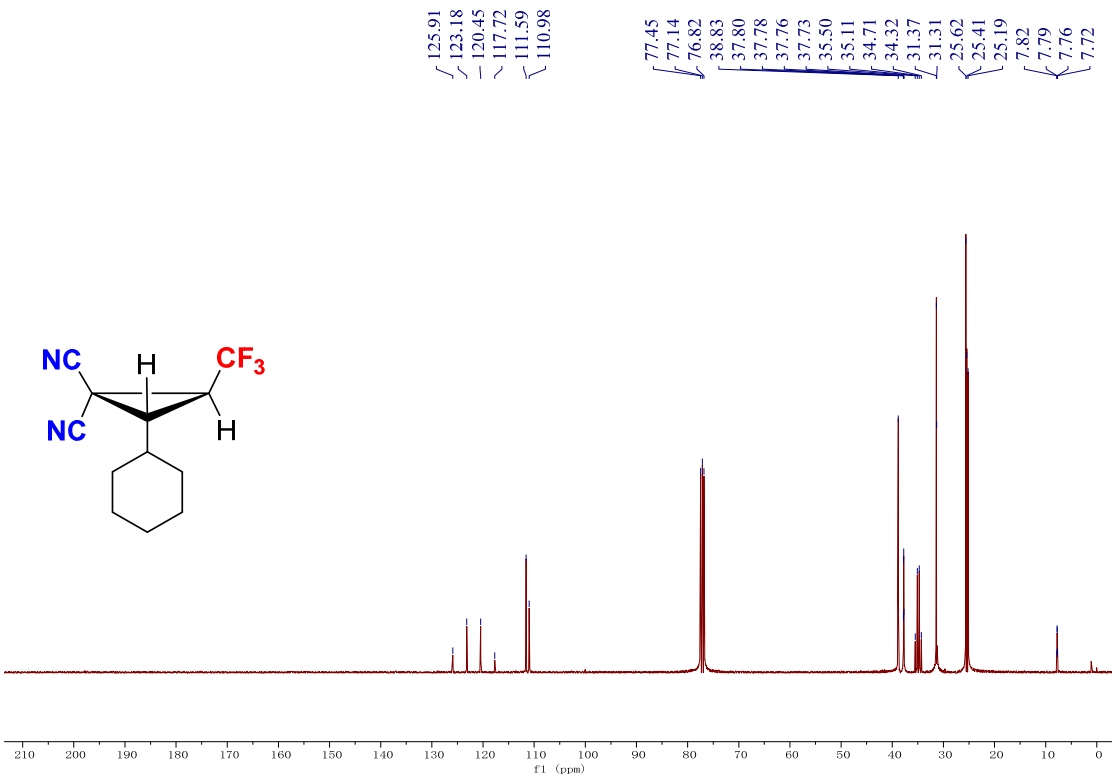
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **4t**



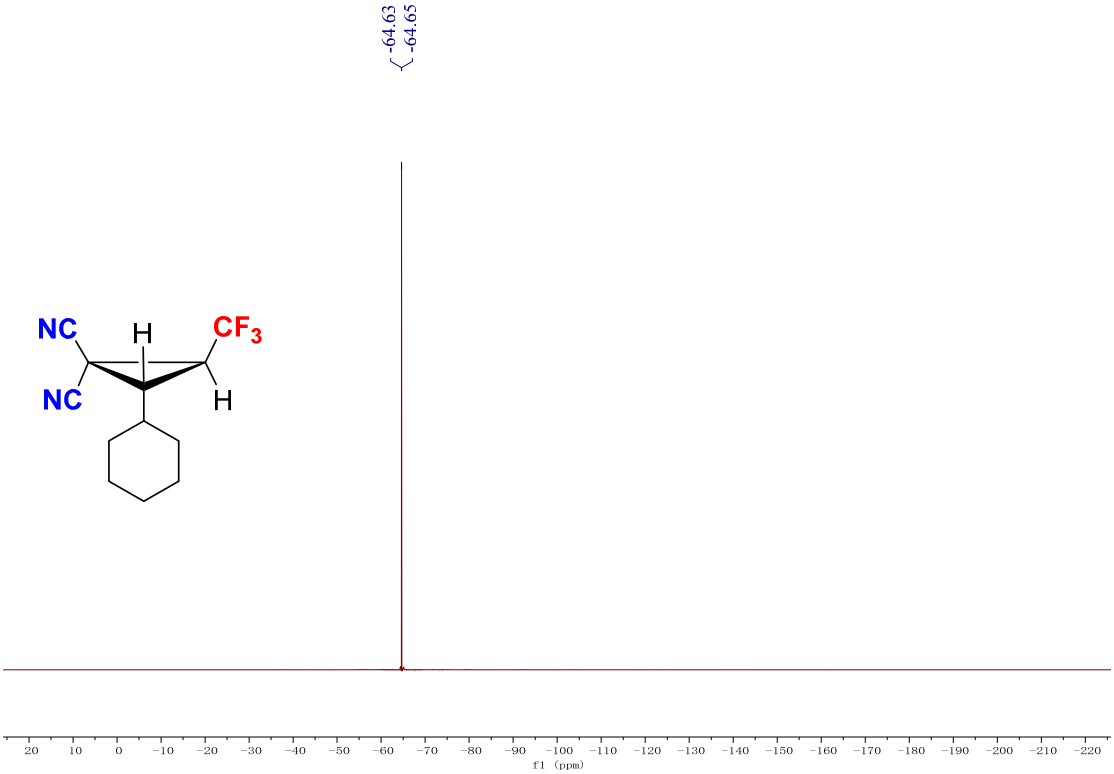
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4u**



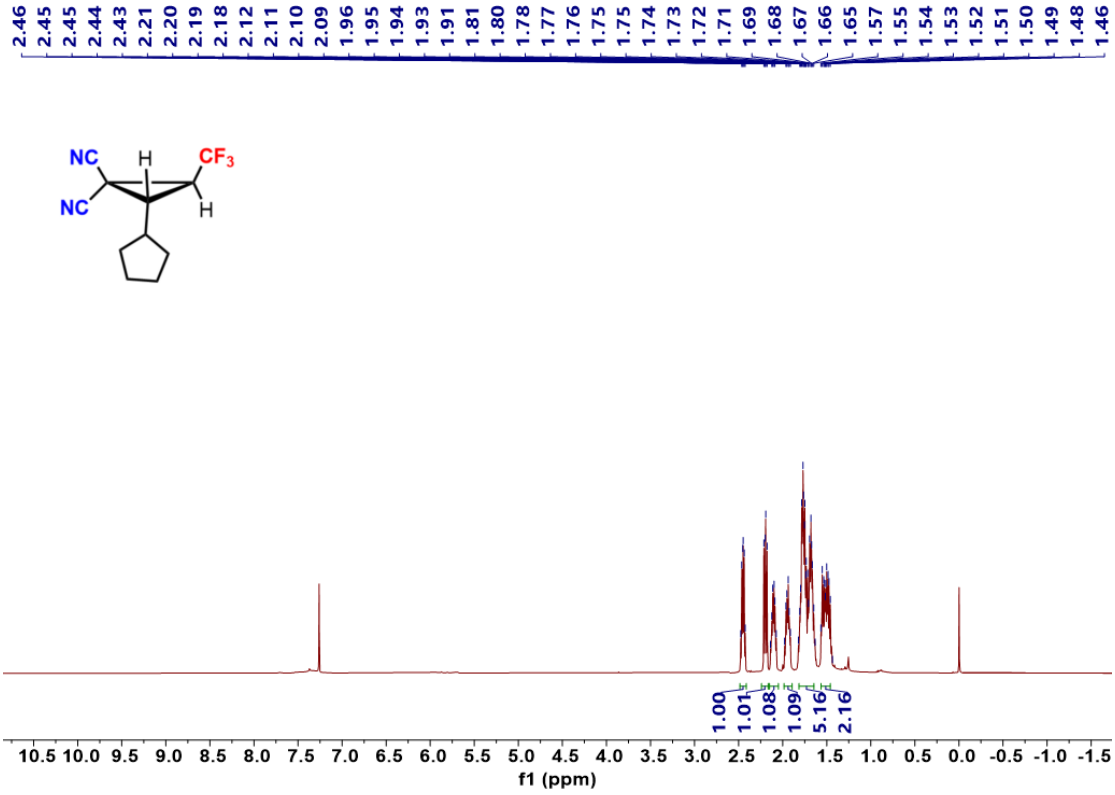
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4u**



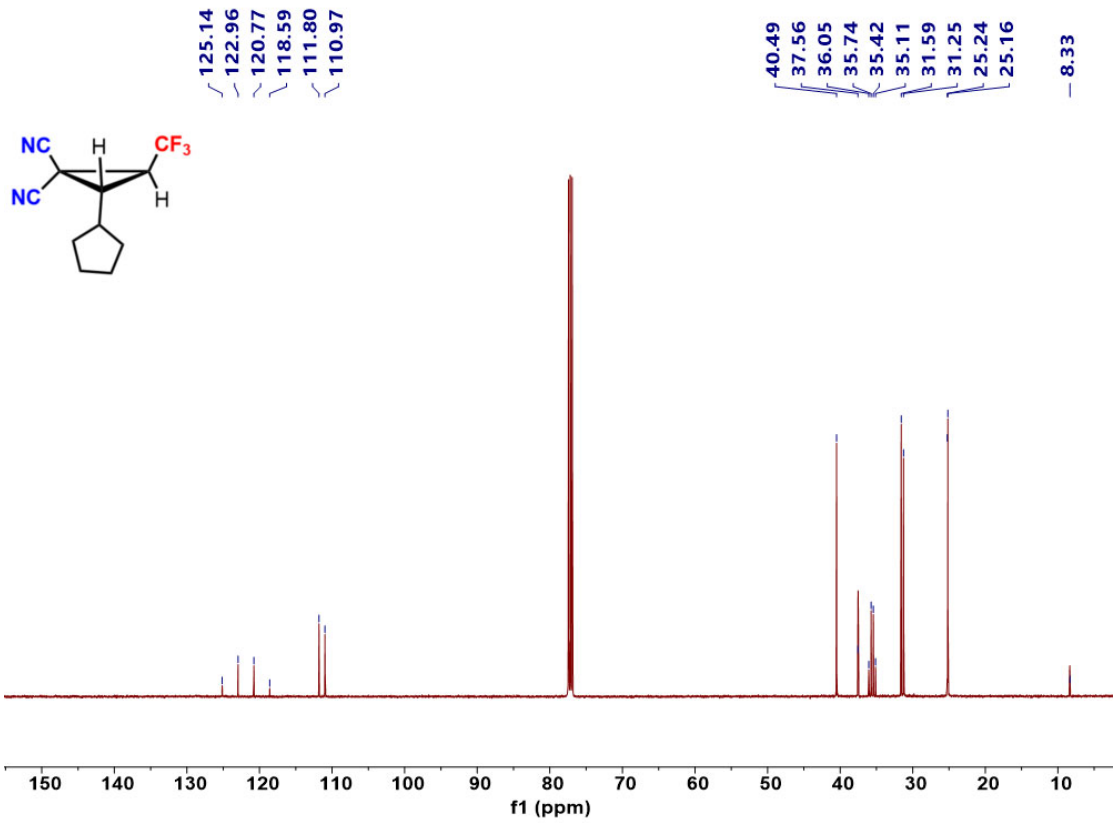
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4u**



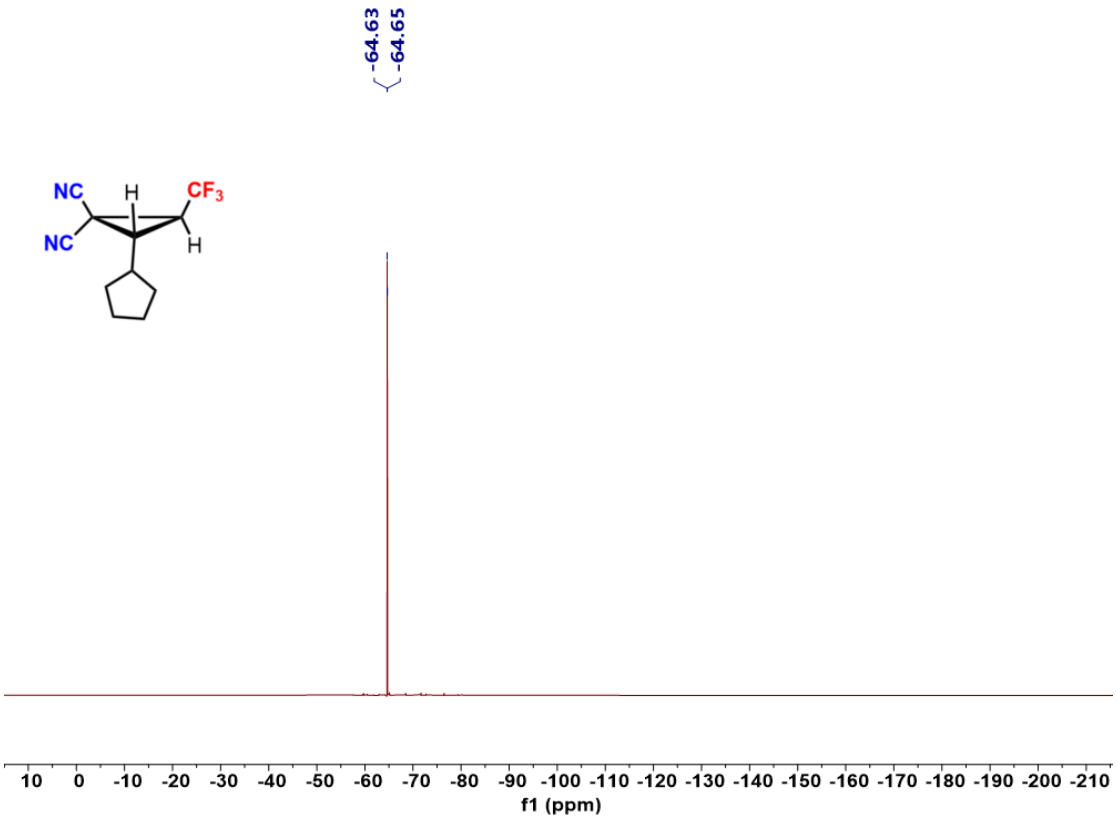
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4v**



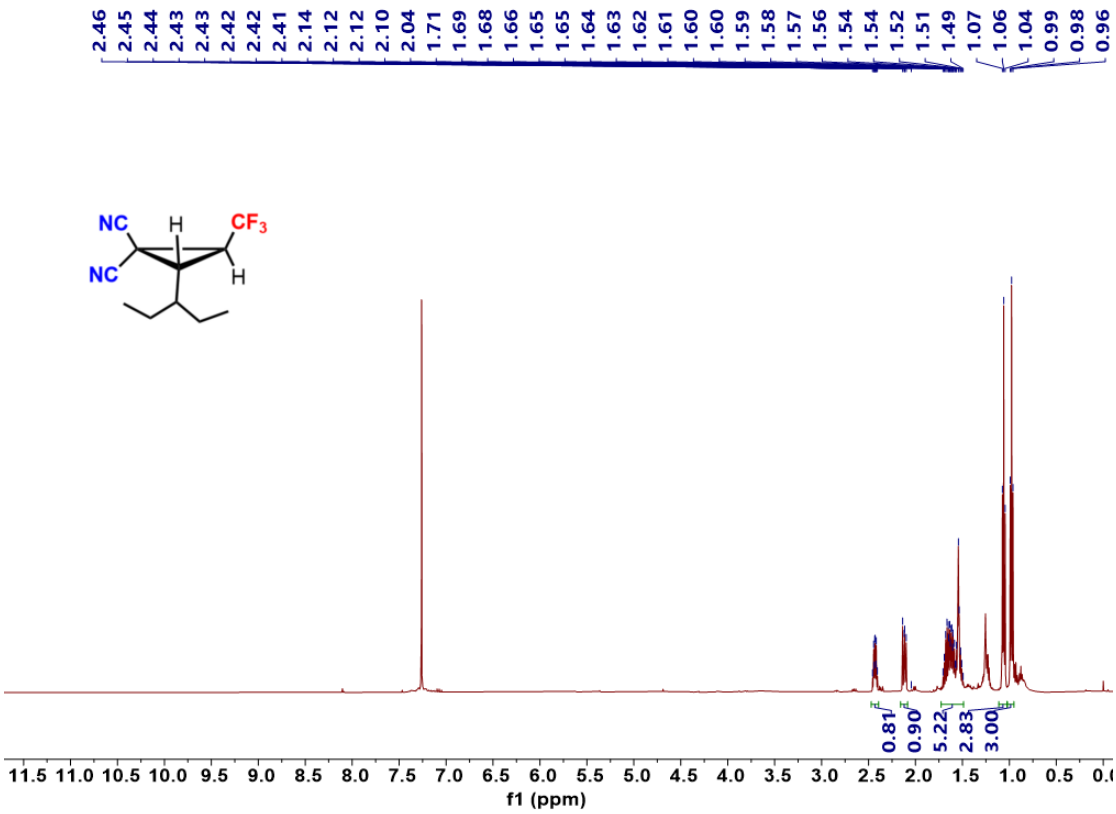
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4v**



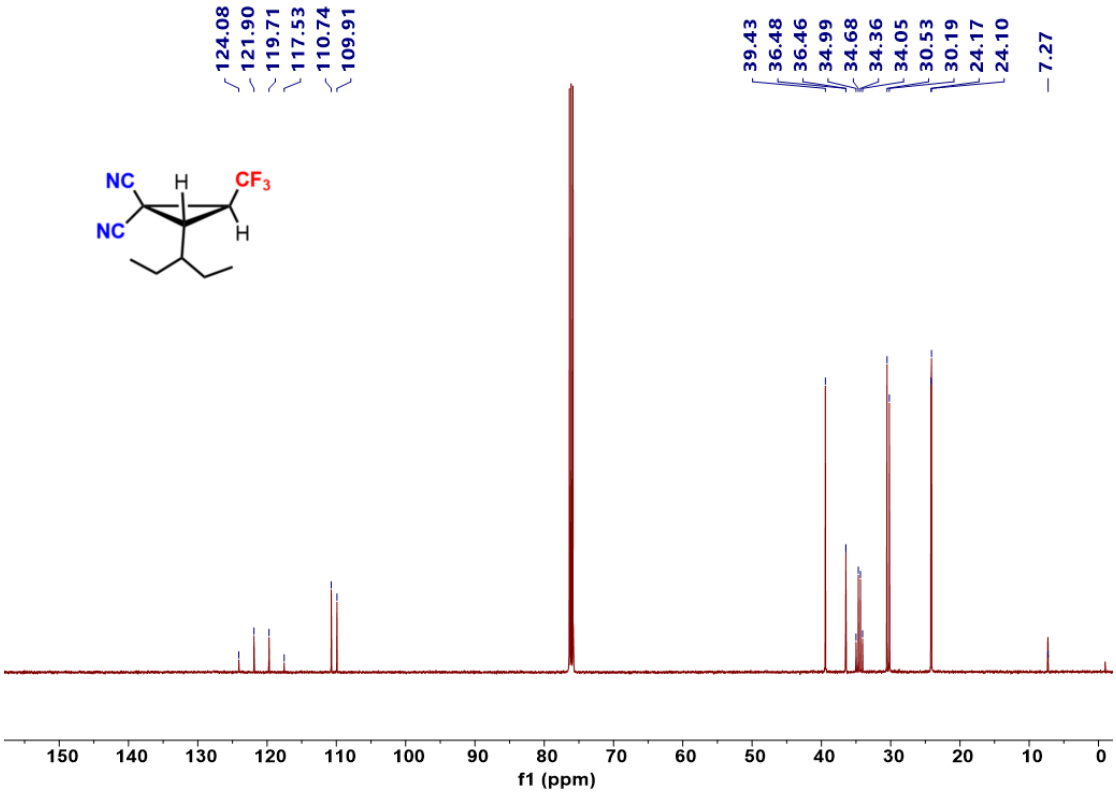
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **4v**



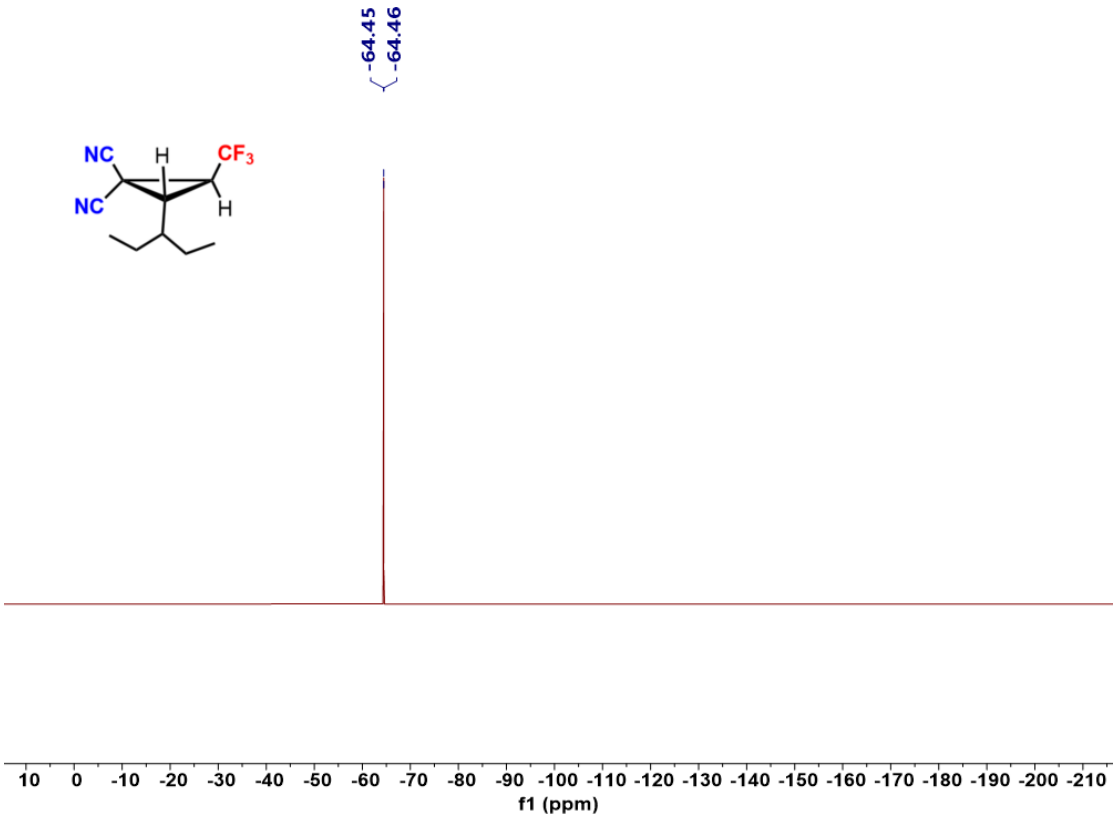
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4w**



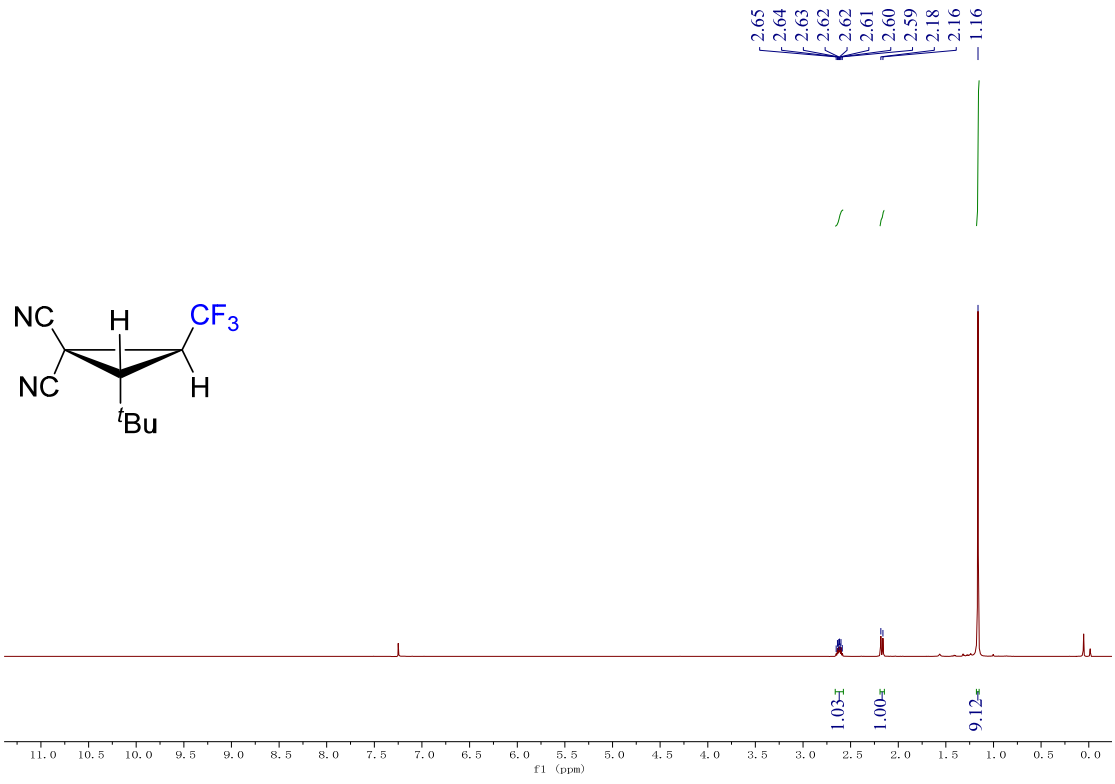
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4w**



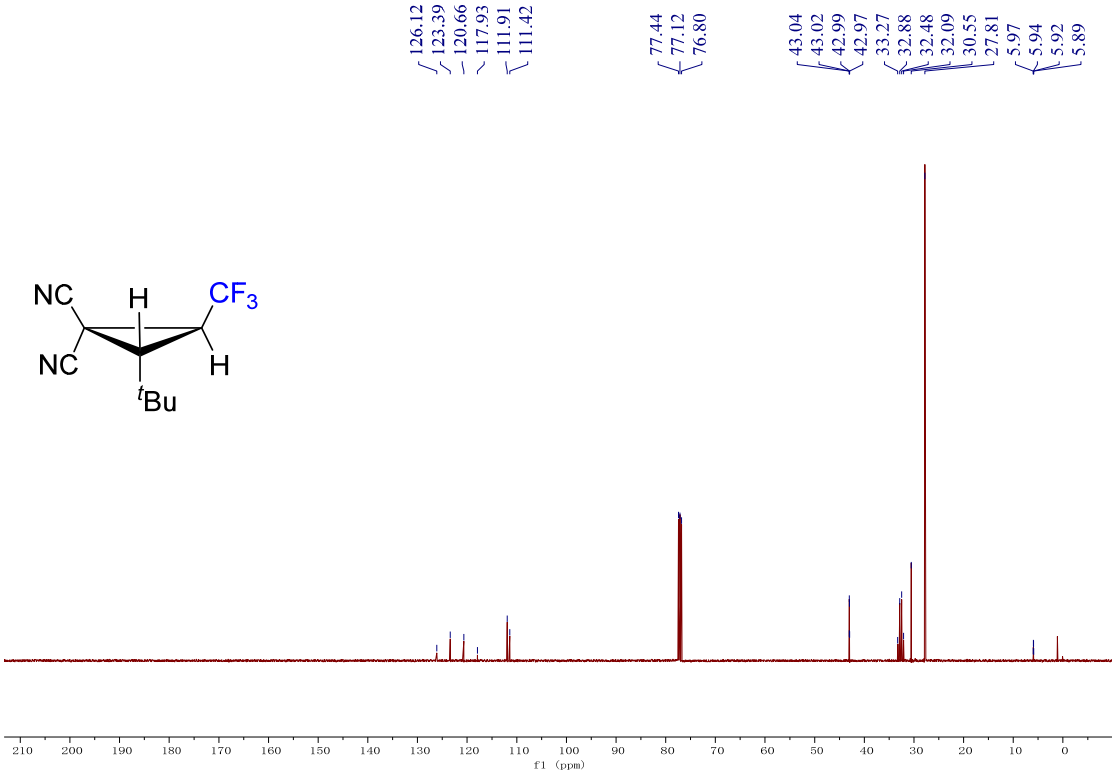
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **4w**



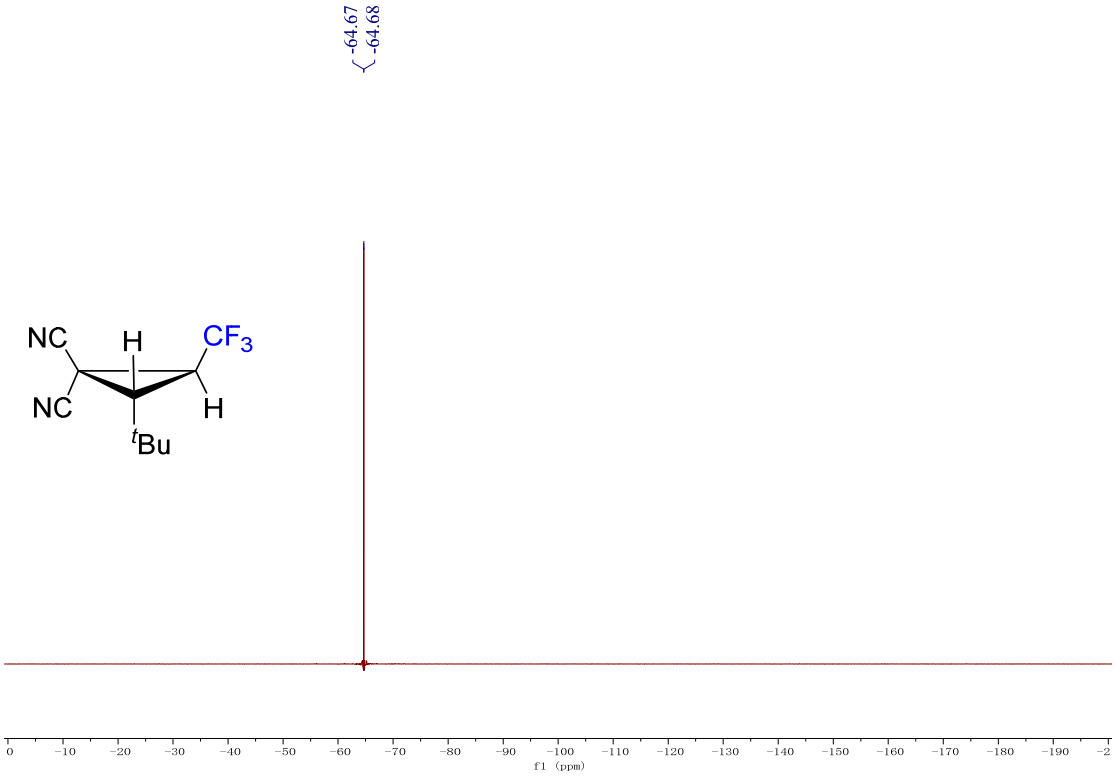
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4x**



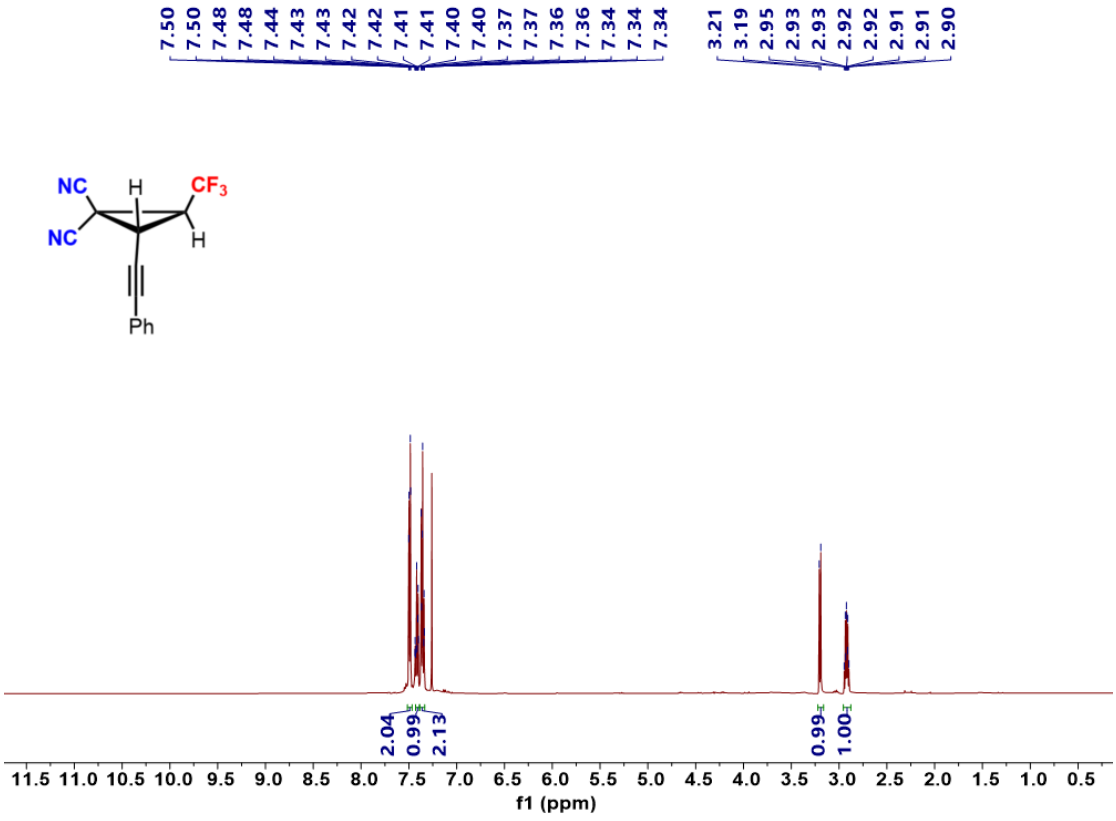
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4x**



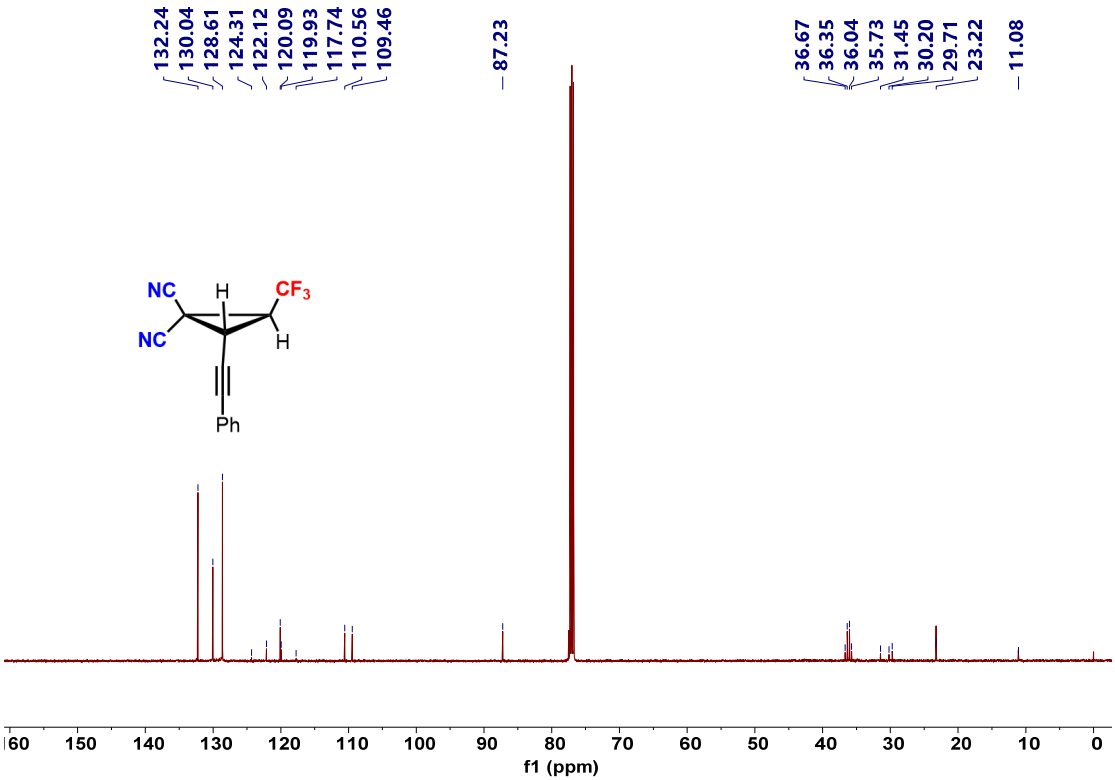
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4x**



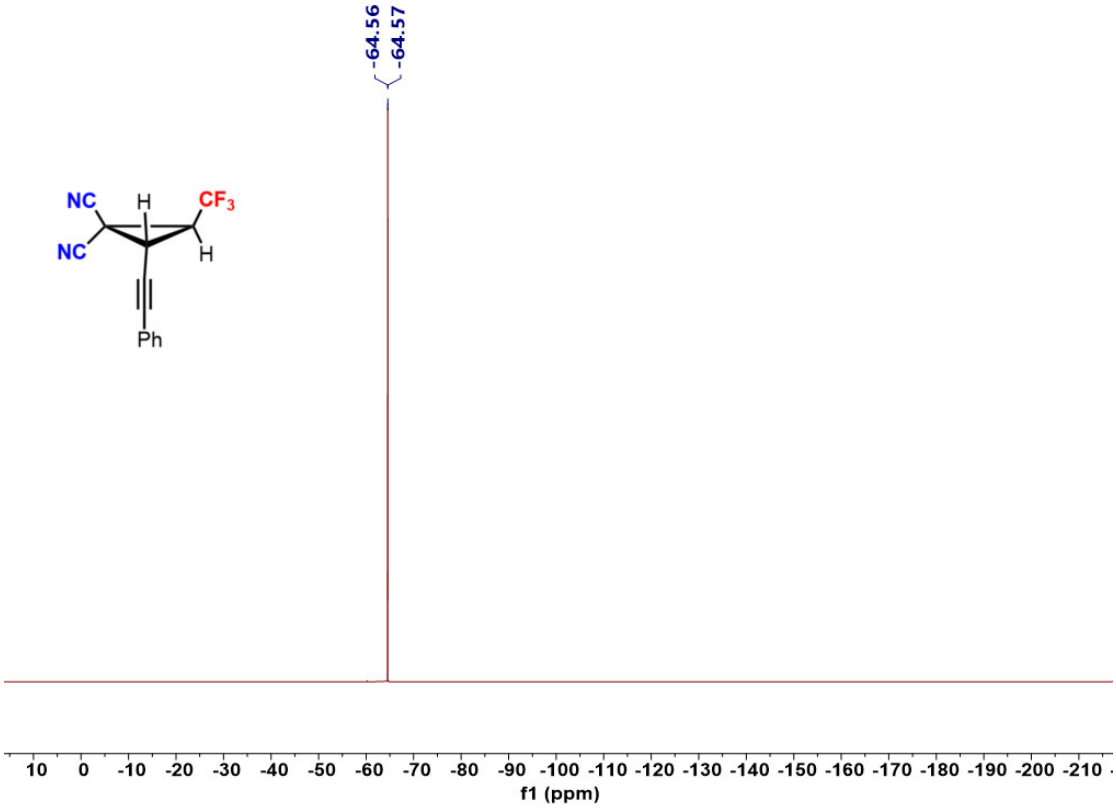
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4y**



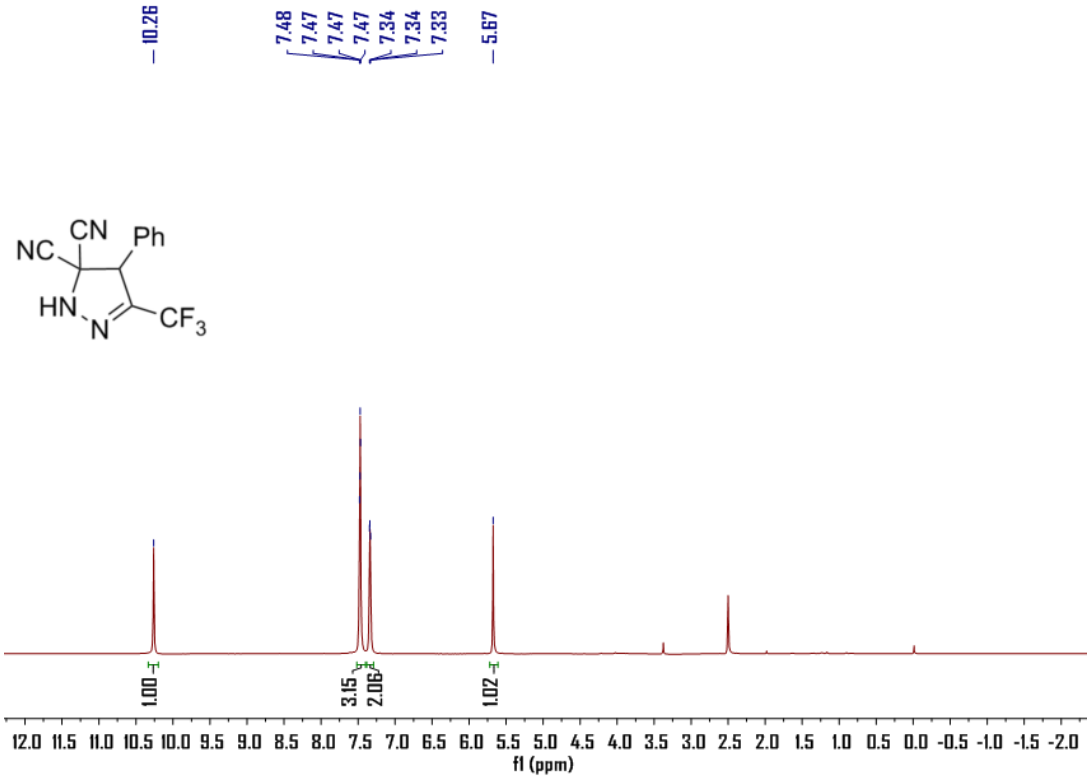
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4y**



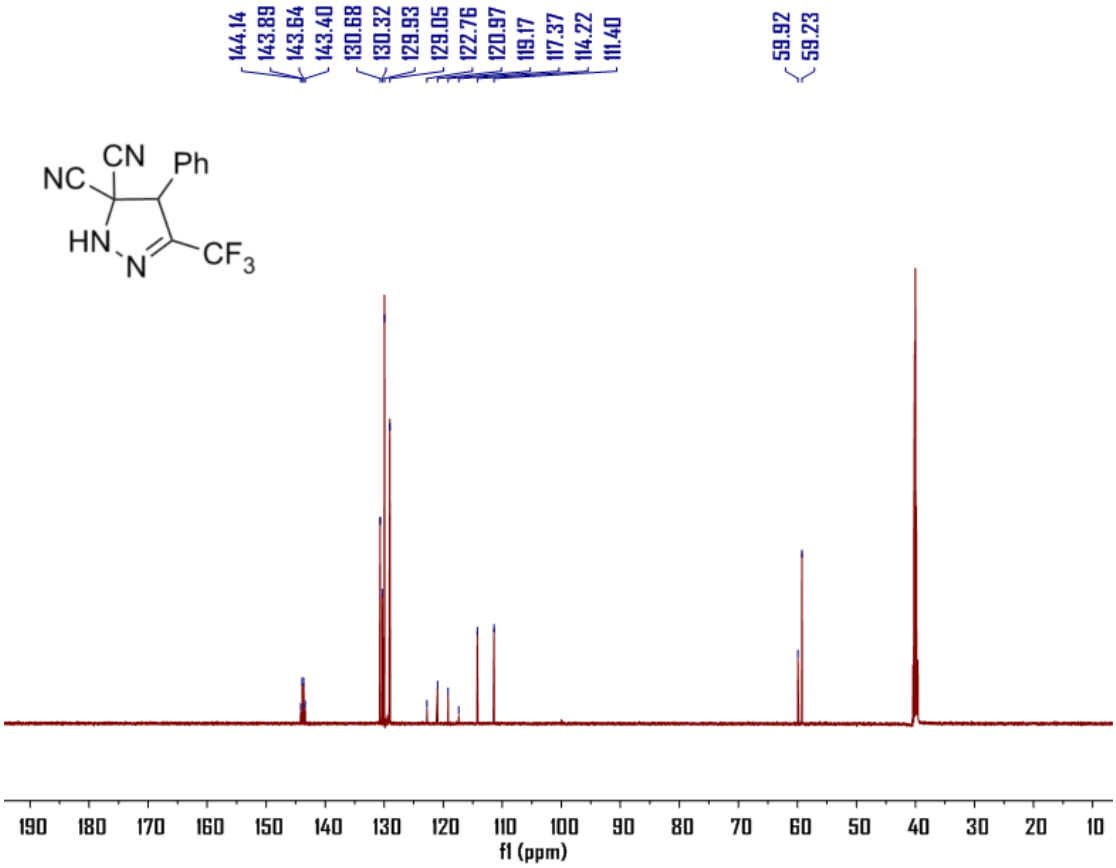
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **4y**



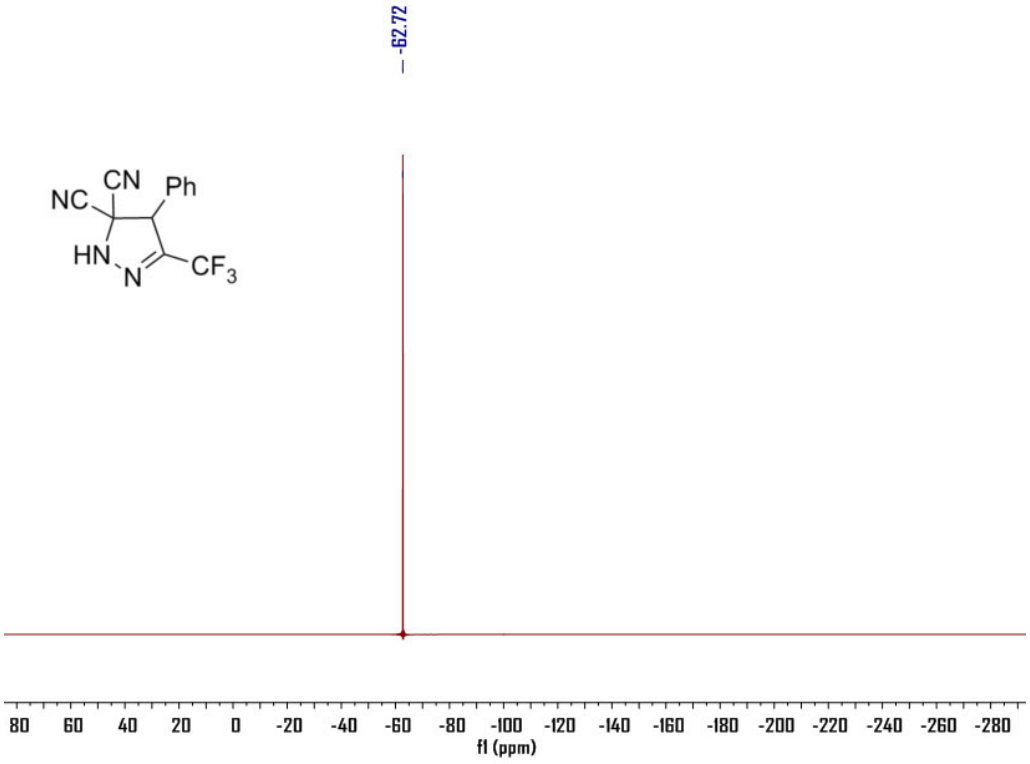
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a'**



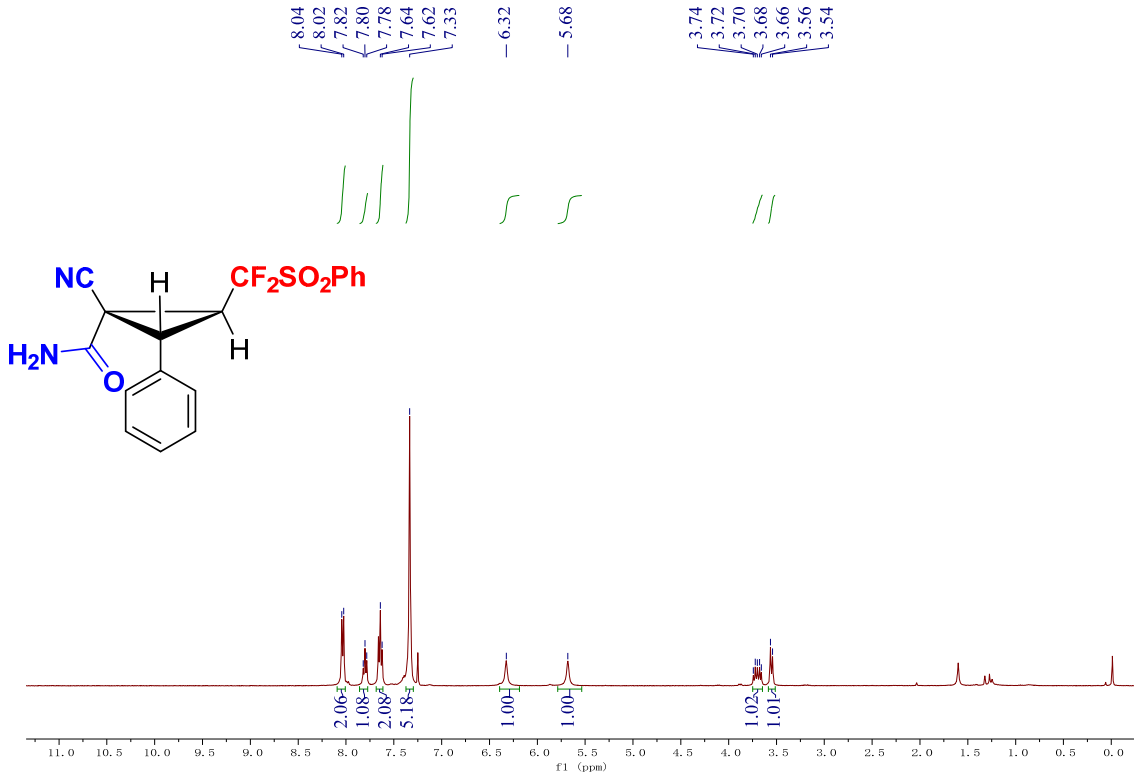
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4a'**



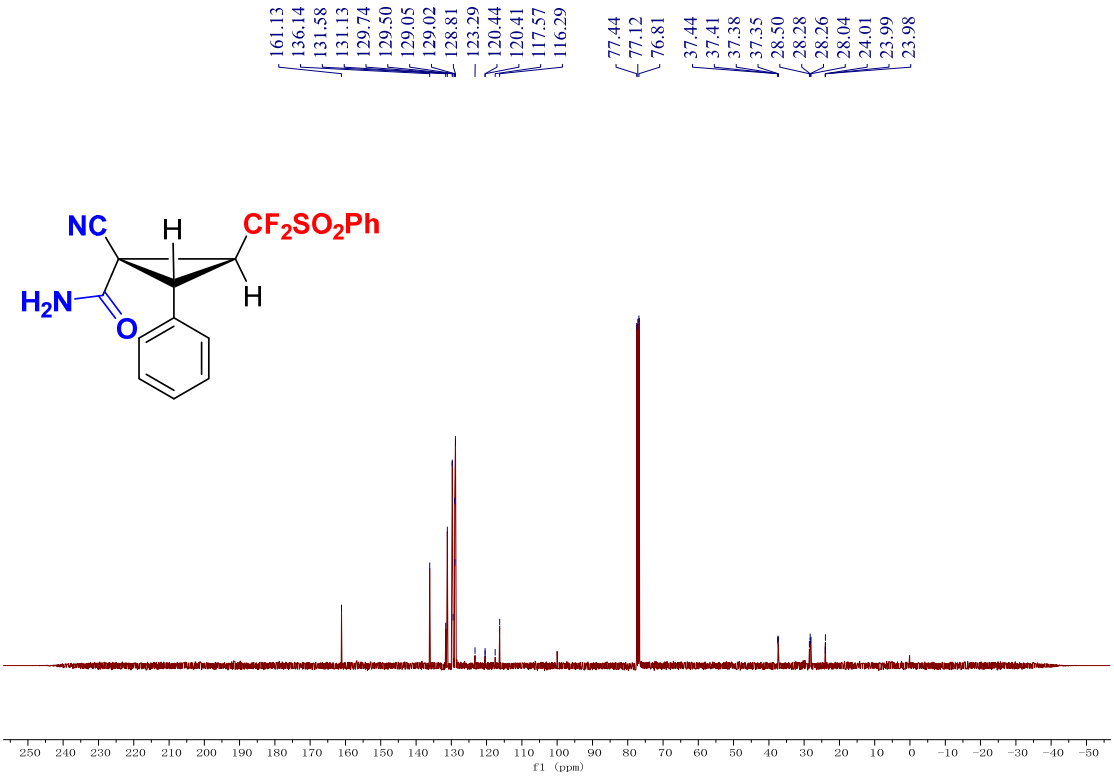
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4a'**



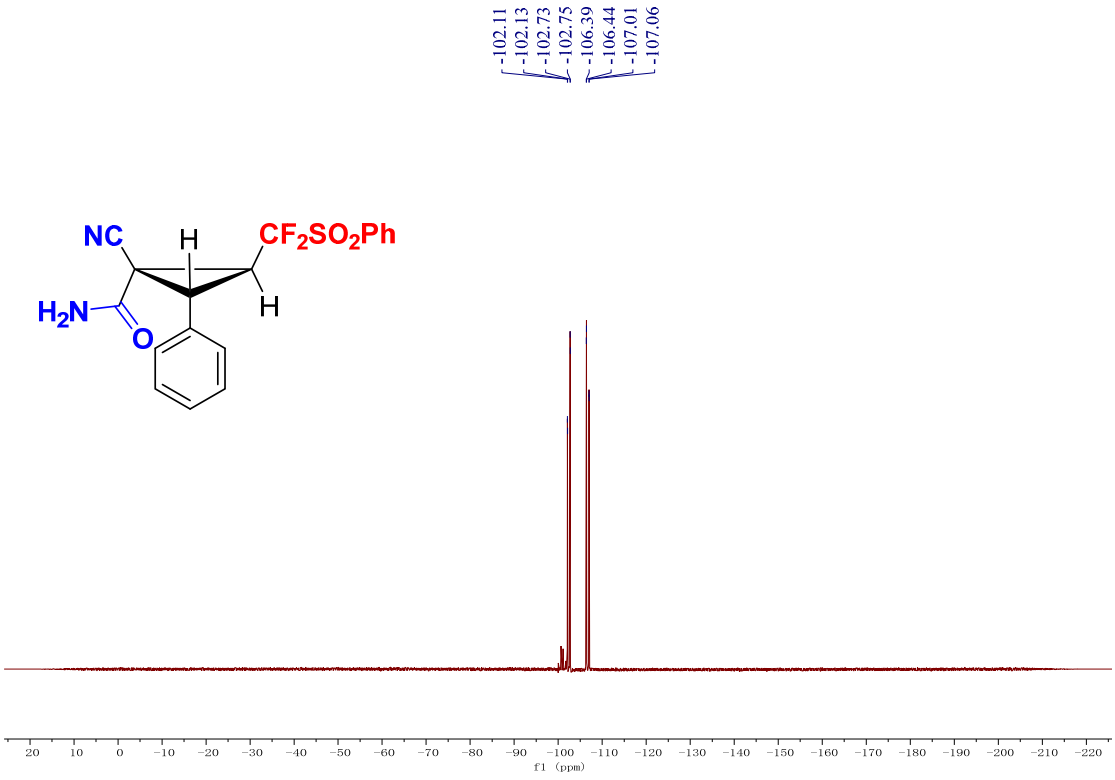
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**



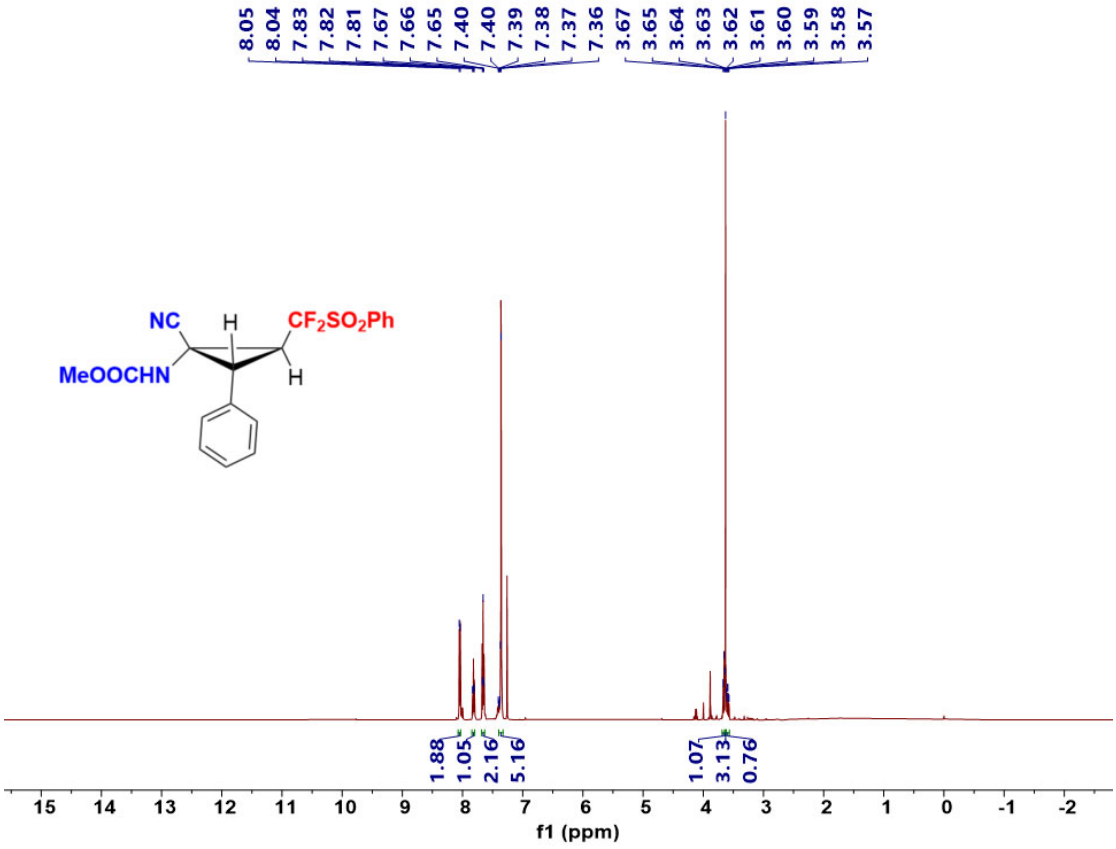
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5a**



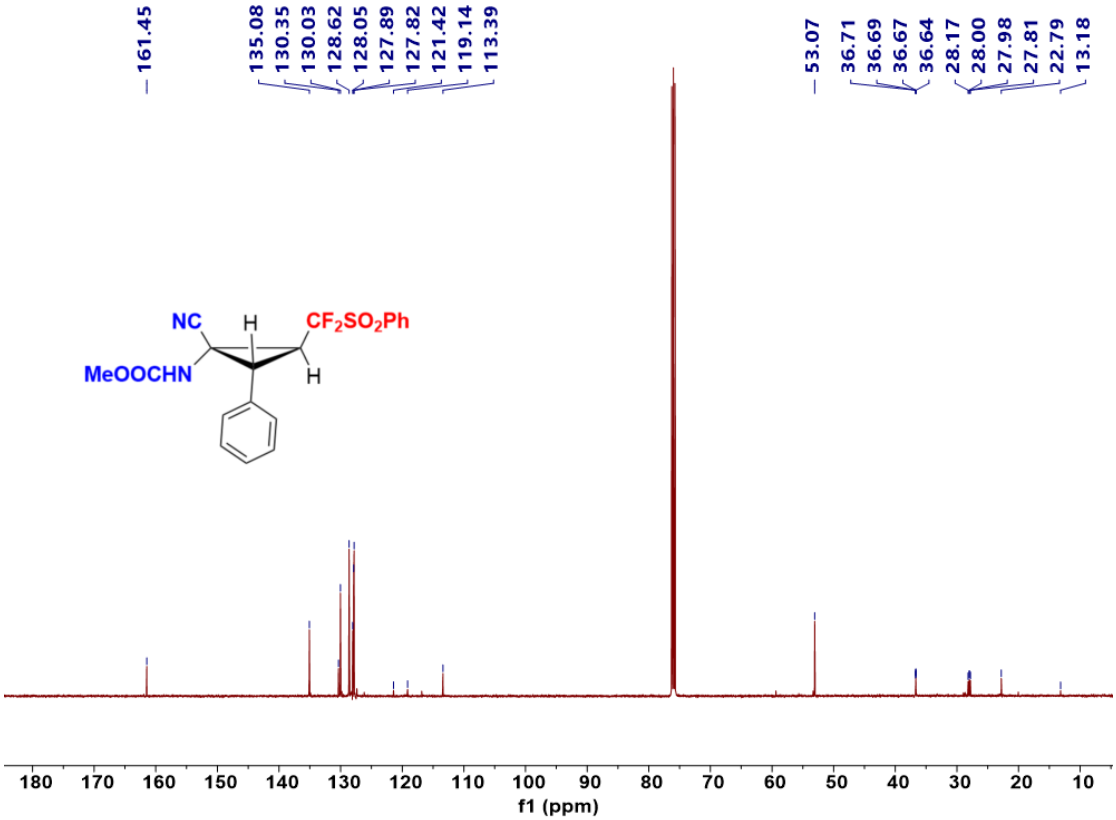
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5a**



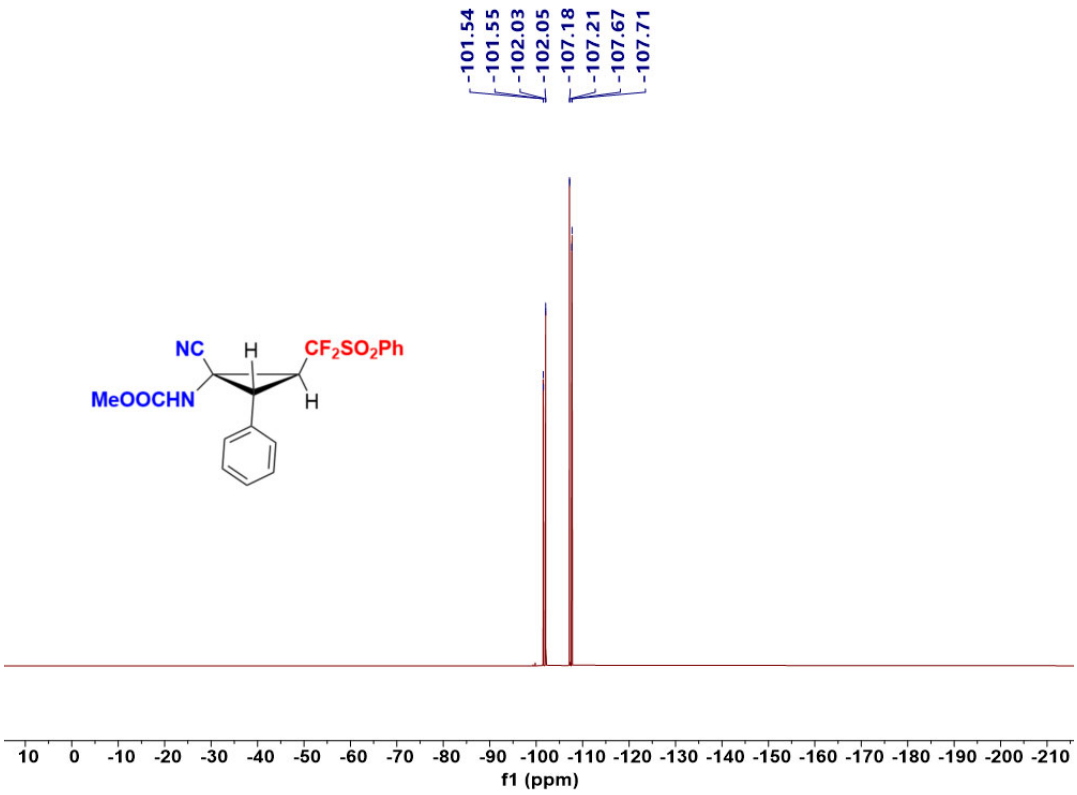
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5b**



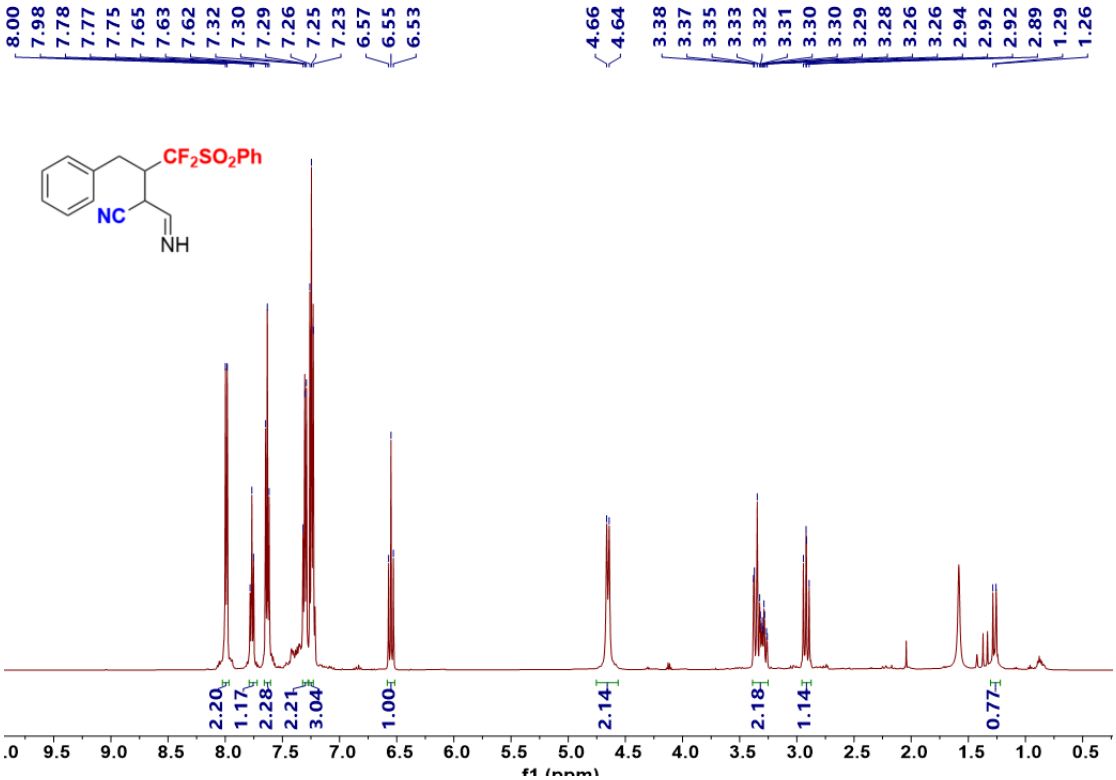
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5b**



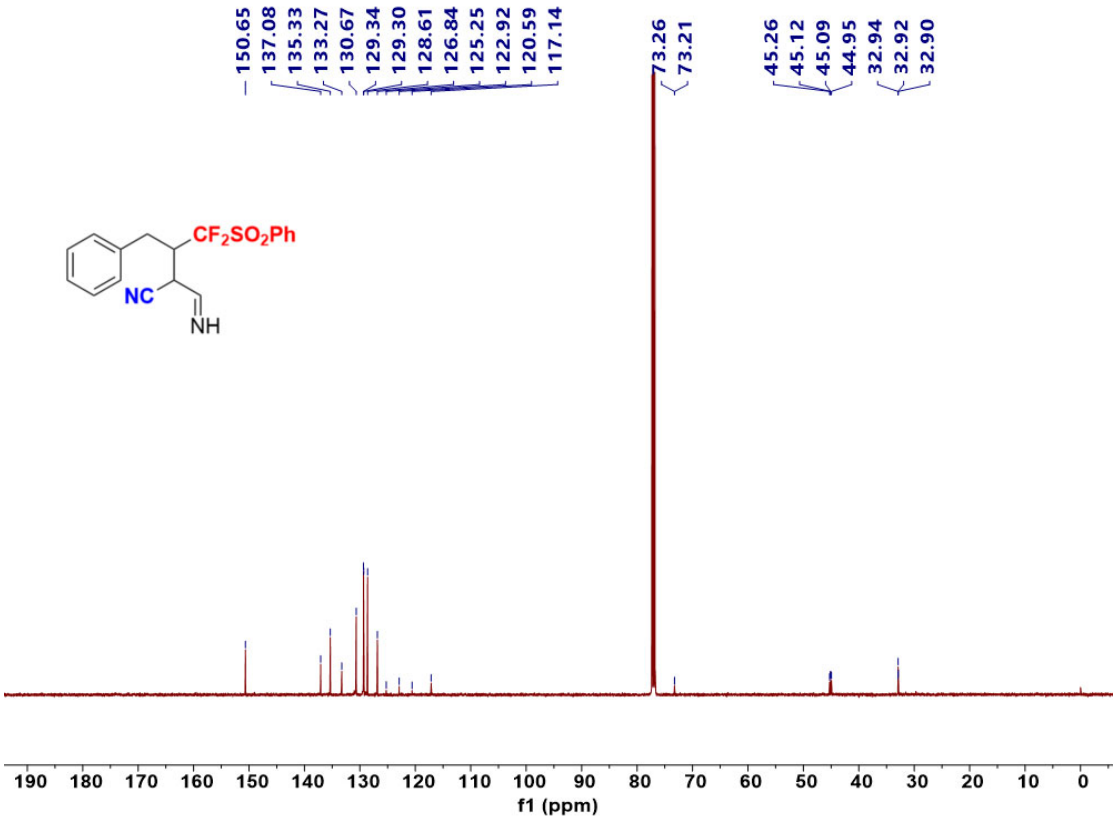
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **5b**



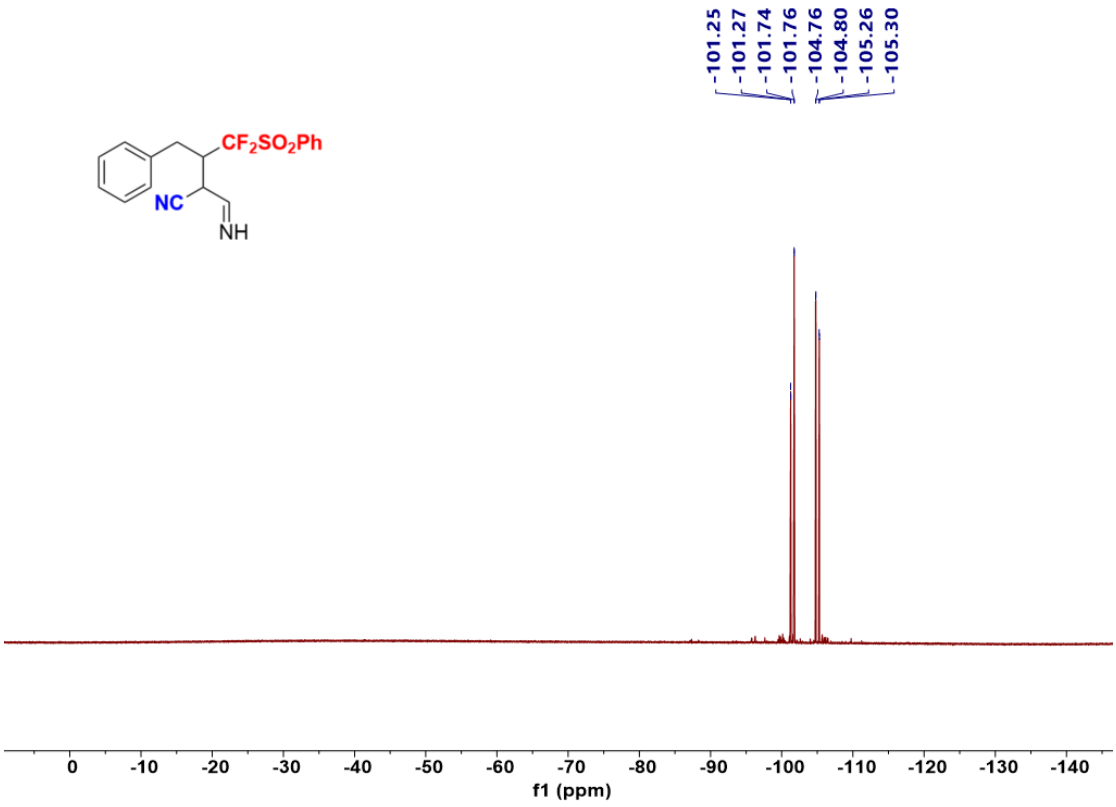
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5c**



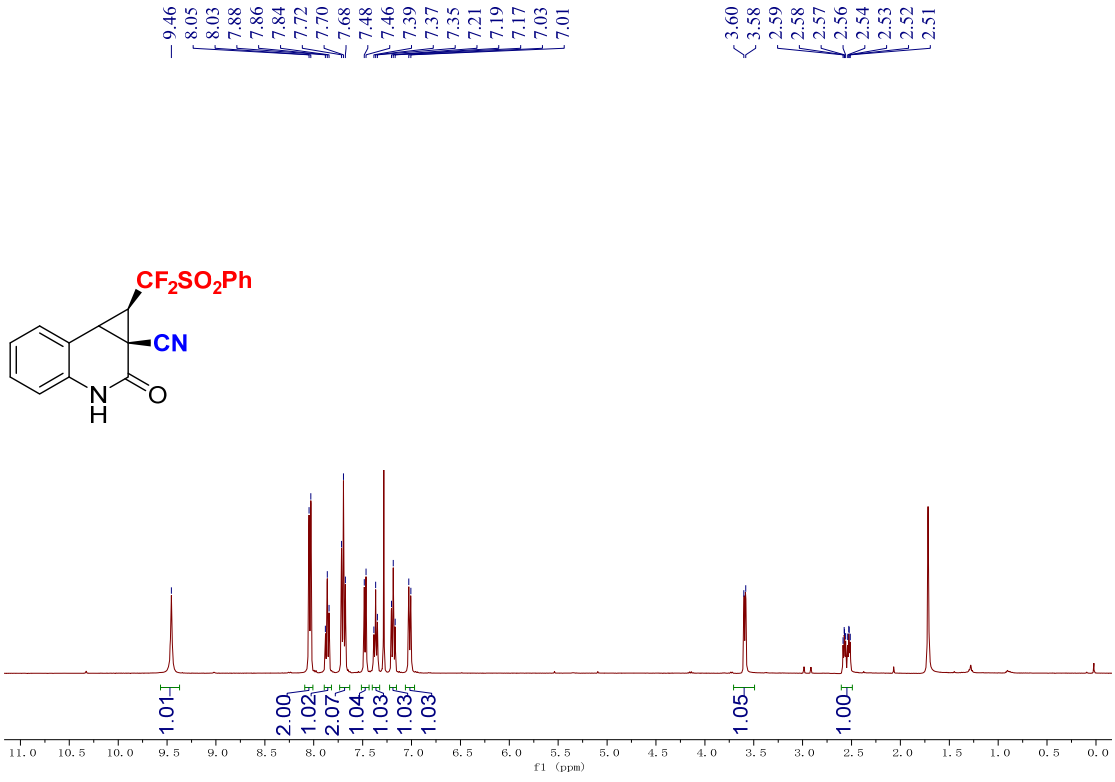
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5c**



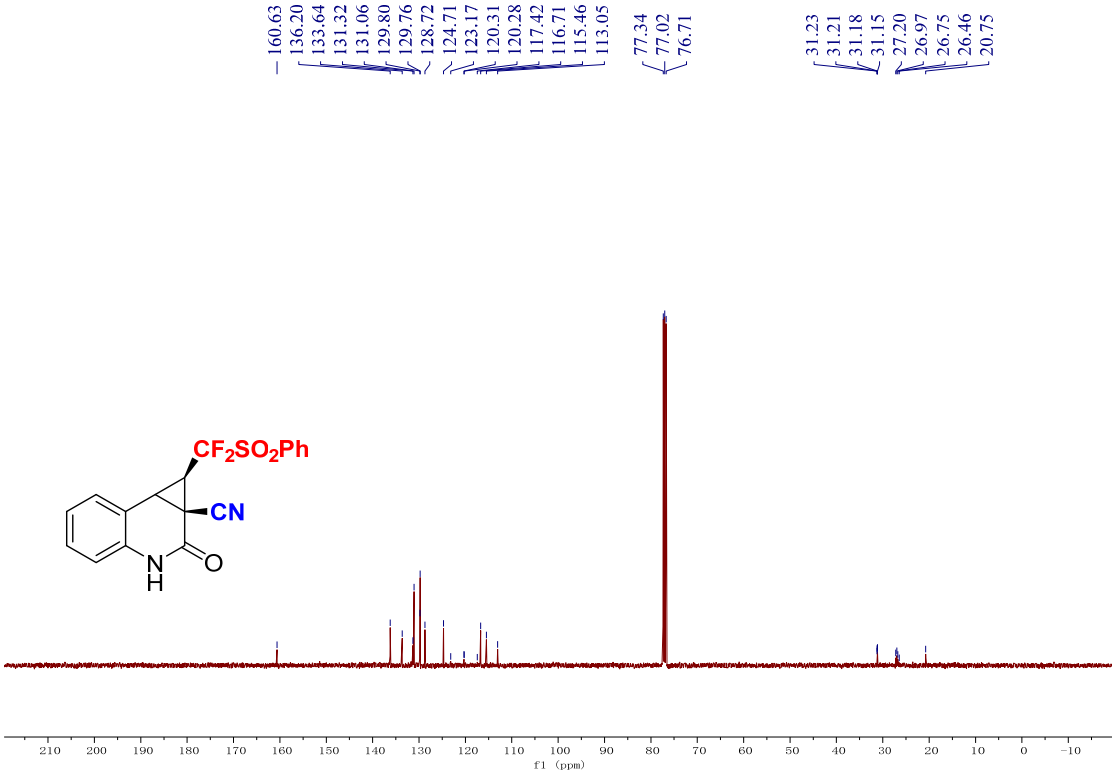
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **5c**



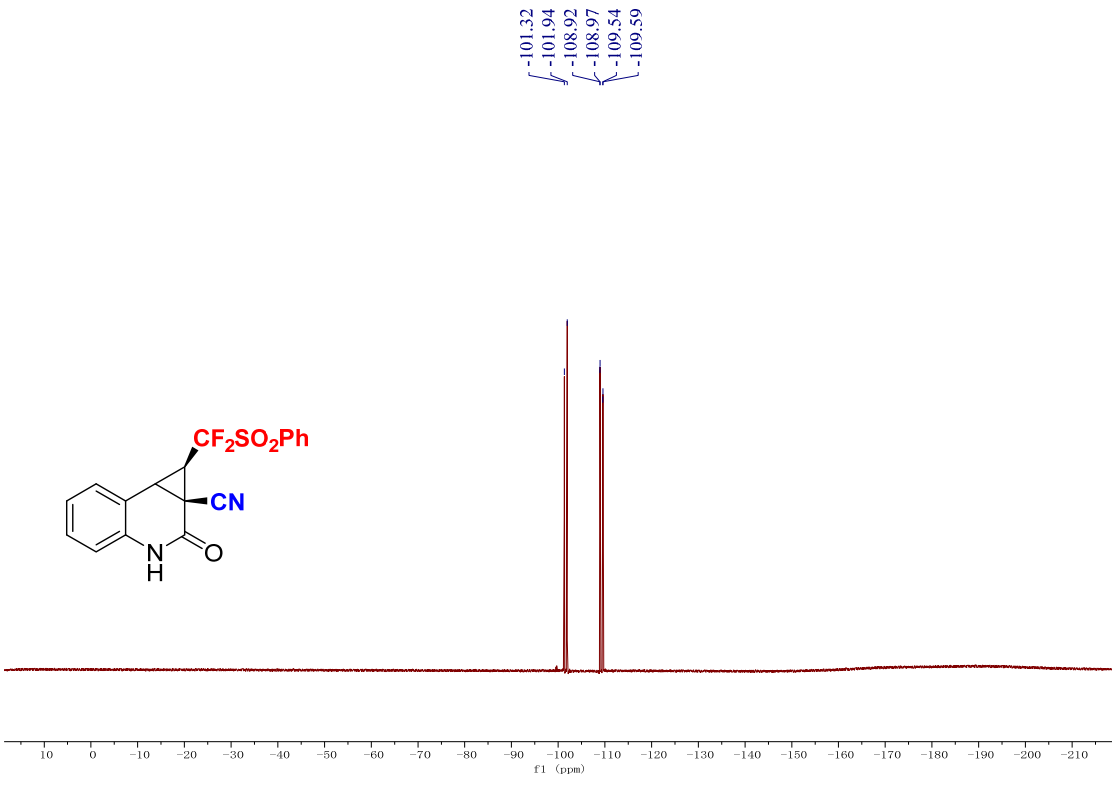
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**



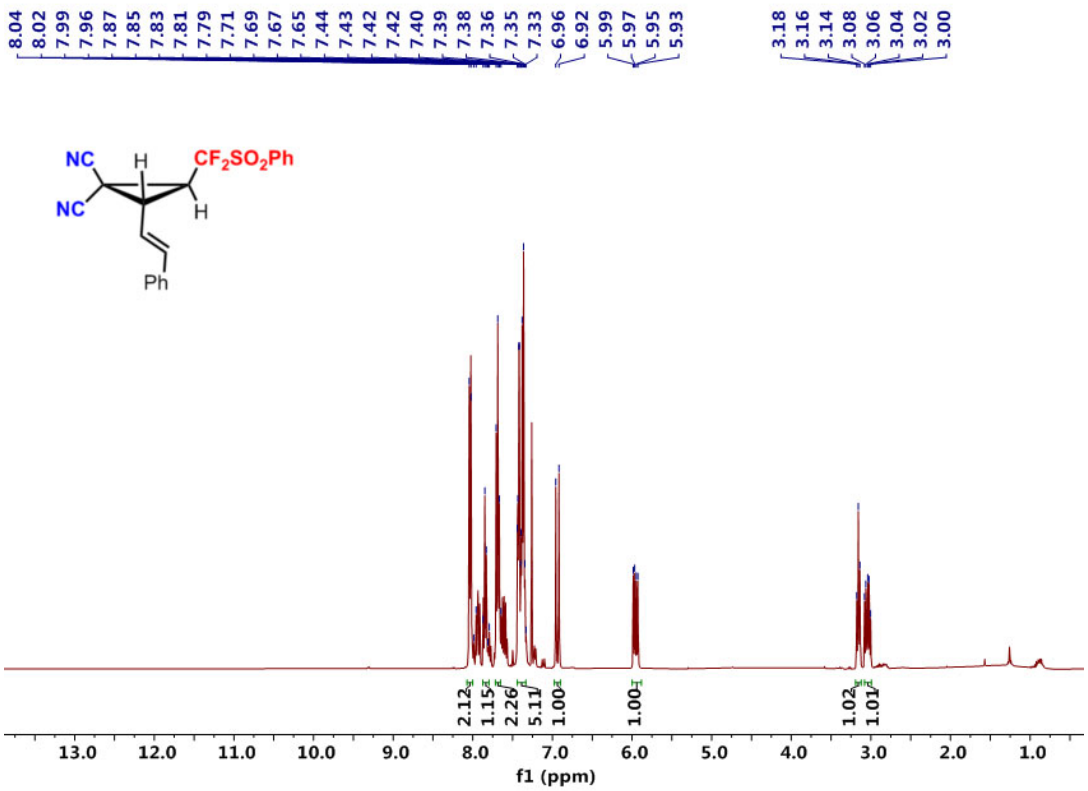
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6**



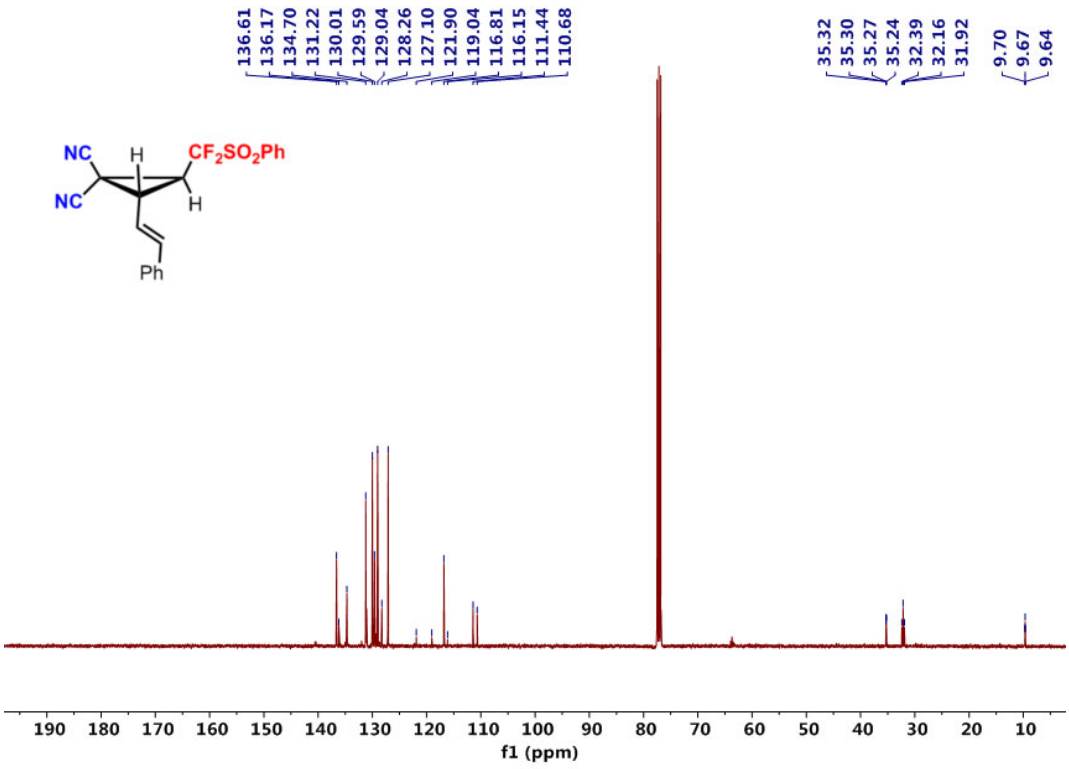
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **6**



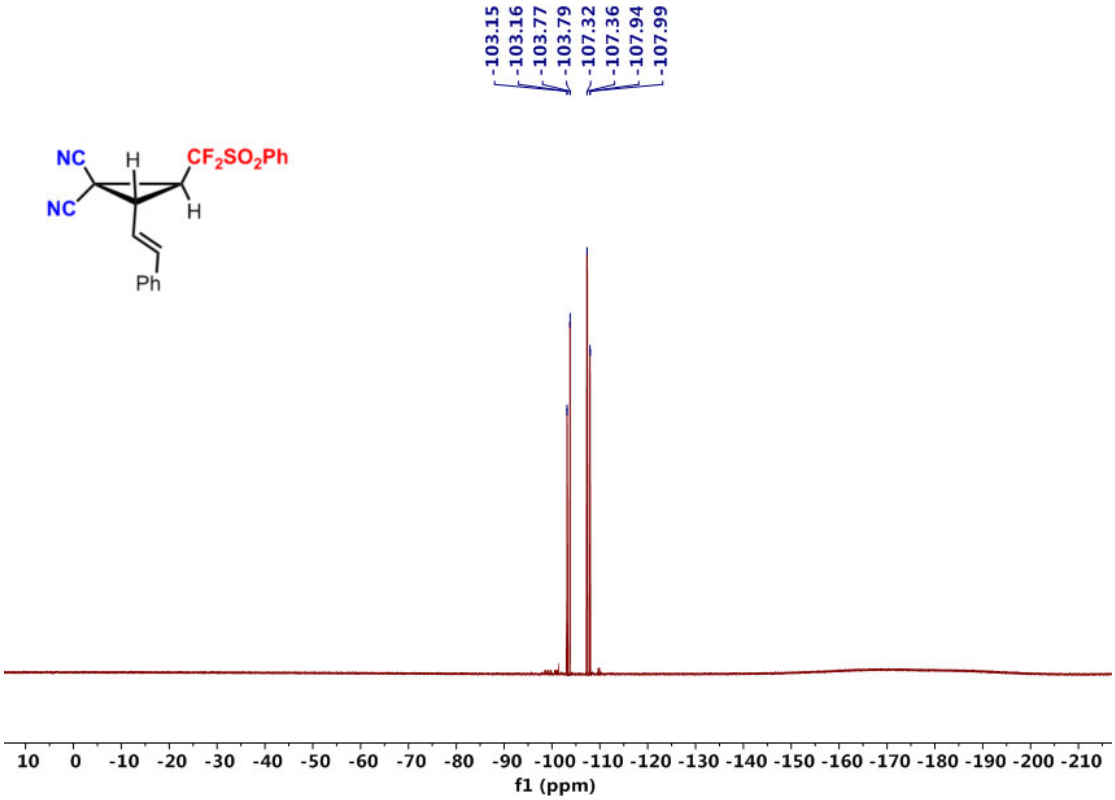
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**



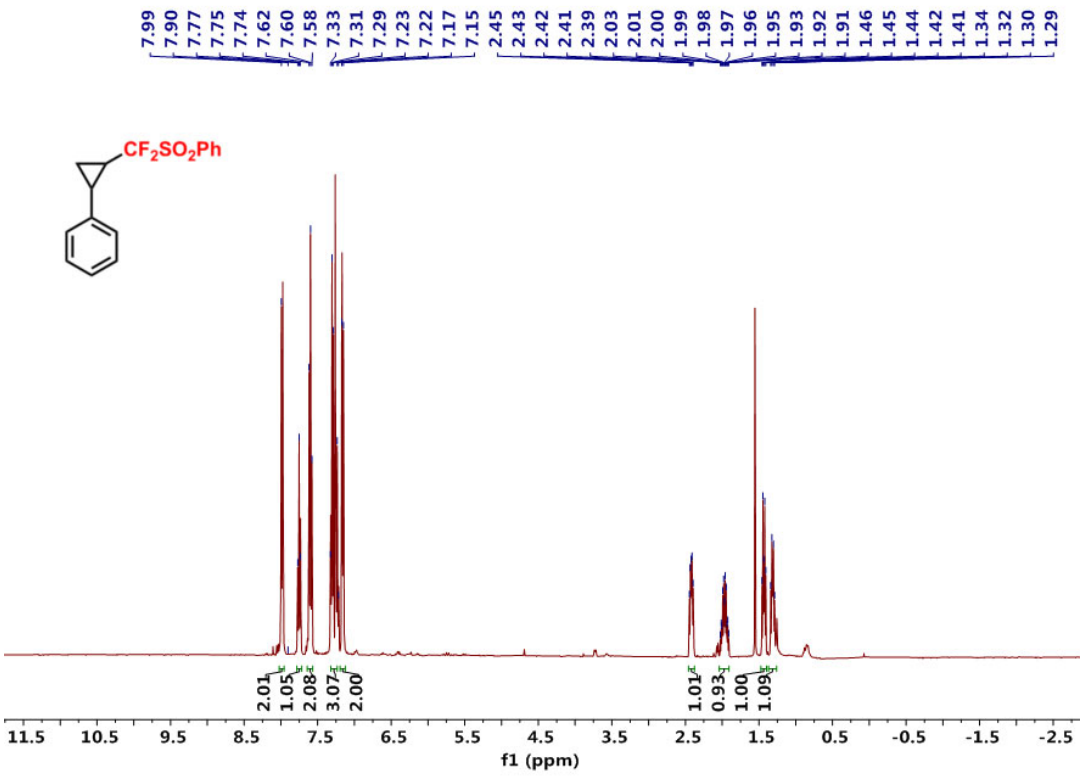
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **7**



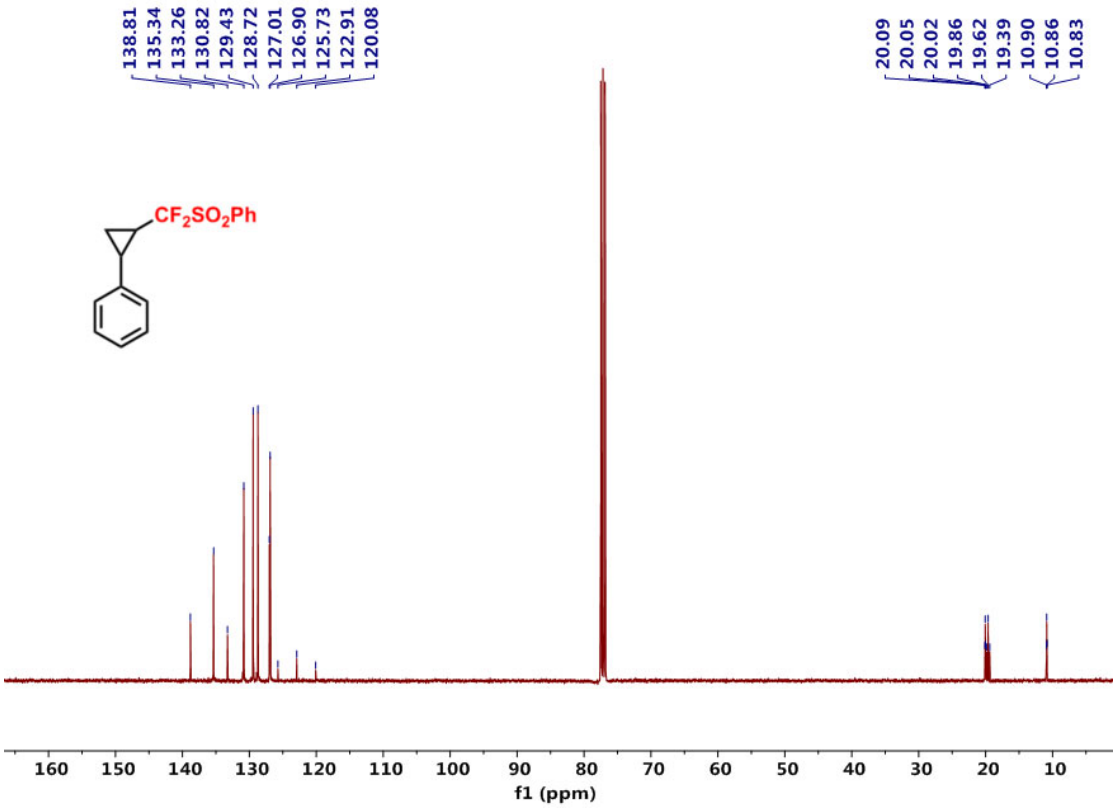
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **7**



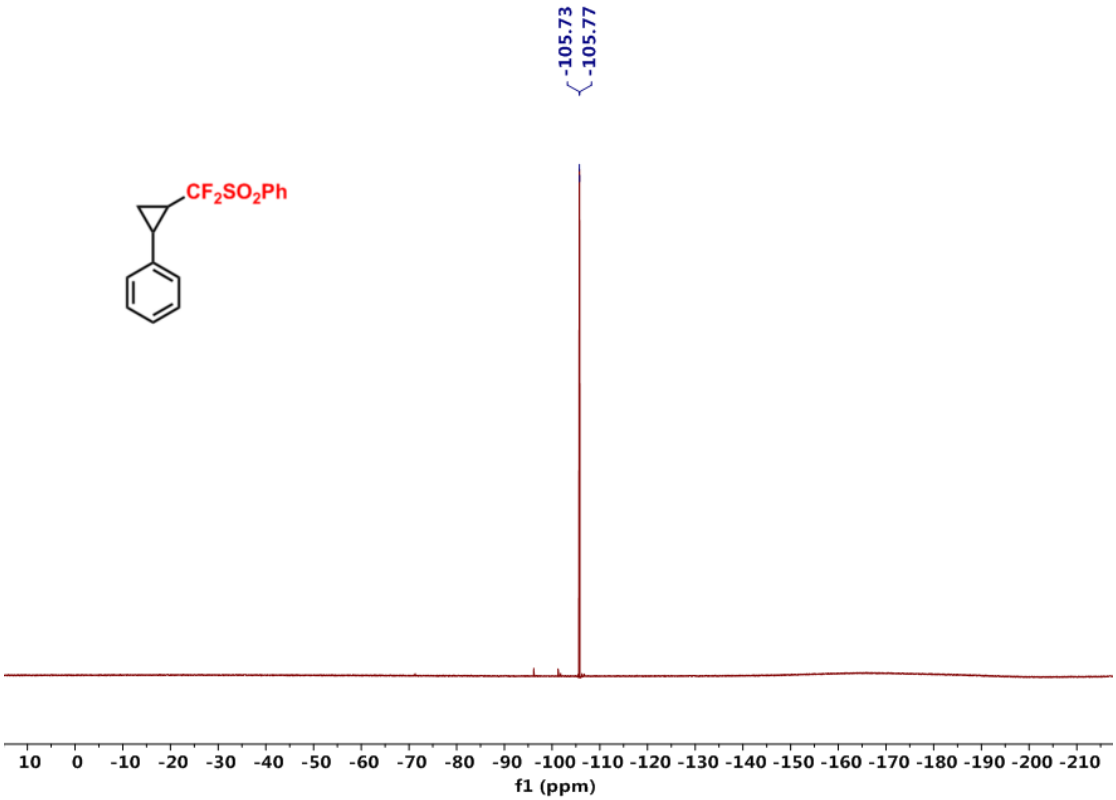
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **9**



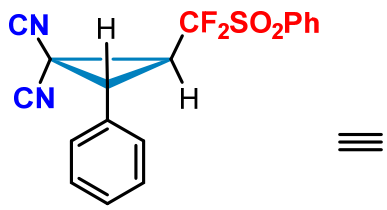
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **9**



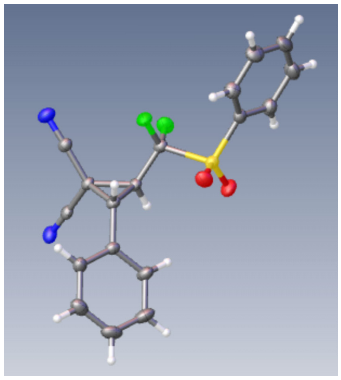
X-Ray Crystallographic Data

For the crystallization process, vacuum-dried pure sample **3a,** or **4i,** and **5** (around 50-80 mg) was transferred into a vial and dissolved in 1 mL of DCM followed by the layering of 5 mL hexane. The vial was kept at room temperature to allow for slow evaporation. Colorless, needle-shaped crystals were formed after 1-2 days. The crystals were subjected to the single crystal X-ray crystallographic analysis.

The X-ray crystallographic structure for **3a**. Crystal data has been deposited to CCDC (number 2163529).



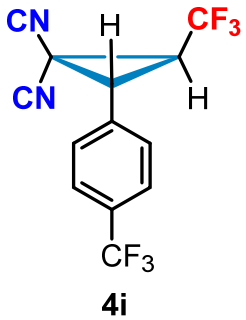
3a



Empirical formula	$C_{18}H_{12}F_2N_2O_2S$
Formula weight	358.36
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	6.3811(4)
b/Å	9.4160(6)
c/Å	14.1943(10)
α/°	94.158(2)
β/°	102.480(2)
γ/°	96.271(2)

Volume/Å^3	823.65(9)
Z	2
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	0.232
F(000)	368.0
Crystal size/mm^3	0.36 × 0.27 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.374 to 59.386
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19
Reflections collected	34354
Independent reflections	4636 [R_{int} = 0.0873, R_{sigma} = 0.0604]
Data/restraints/parameters	4636/0/226
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0540, wR_2 = 0.1466
Final R indexes [all data]	R_1 = 0.0722, wR_2 = 0.1578
Largest diff. peak/hole / e Å^{-3}	0.53/-0.81

The X-ray crystallographic structure for **4i**. Crystal data has been deposited to CCDC (number 2163530).



4i

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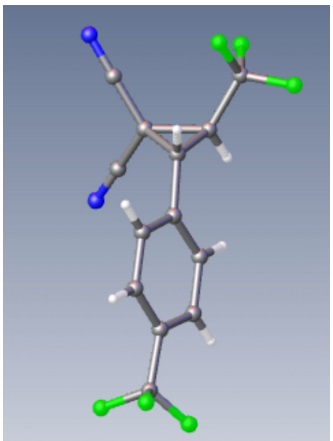
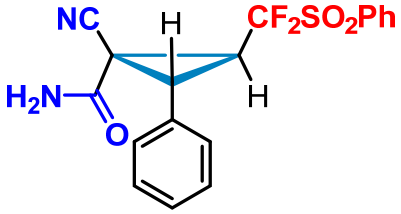


Empirical formula	$C_{13}H_6F_6N_2$
Formula weight	304.20
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.4191(9)
b/Å	12.5633(10)
c/Å	12.8164(12)
α/°	90
β/°	107.388(10)
γ/°	90
Volume/Å^3	1293.7(2)
Z	4
ρ_{calc}g/cm^3	1.562
μ/mm^{-1}	0.155
F(000)	608.0
Crystal size/mm^3	0.32 × 0.27 × 0.19
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.648 to 58.534
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 16$, $-15 \leq l \leq 16$
Reflections collected	10601
Independent reflections	2994 [R_{int} = 0.0258, R_{sigma} = 0.0266]
Data/restraints/parameters	2994/0/190
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0693, wR_2 = 0.2150
Final R indexes [all data]	R_1 = 0.0831, wR_2 = 0.2259
Largest diff. peak/hole / e Å^{-3}	0.74/-0.37

The X-ray crystallographic structure for **5a**. Crystal data has been deposited to CCDC (number 2164517).



5a

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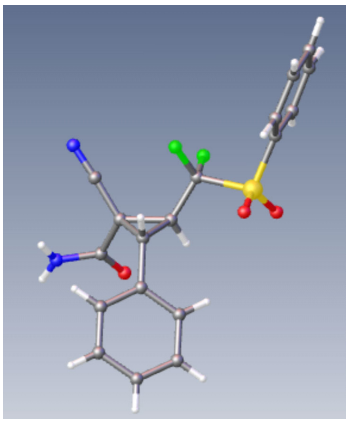
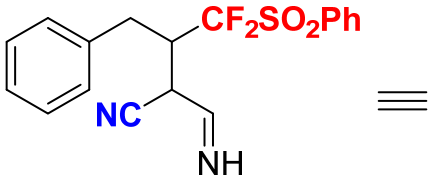


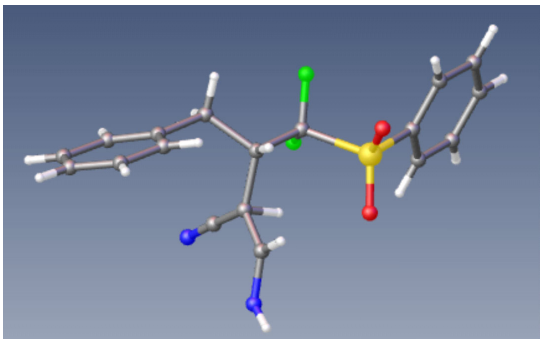
Empirical formula	$C_{18}H_{14}F_2N_2O_3S$
Formula weight	376.37
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.160(2)
b/Å	5.2325(5)
c/Å	20.233(2)
α/°	90
β/°	113.105(4)
γ/°	90
Volume/Å^3	1671.0(3)
Z	4
ρ_{calc}g/cm^3	1.496
μ/mm^{-1}	0.236
F(000)	776.0
Crystal size/mm^3	0.34 × 0.29 × 0.23
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.118 to 59.242
Index ranges	$-23 \leq h \leq 23, -7 \leq k \leq 7, -28 \leq l \leq 28$
Reflections collected	34639
Independent reflections	4685 [R_{int} = 0.1047, R_{sigma} = 0.0850]
Data/restraints/parameters	4685/0/235
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.1090, wR_2 = 0.1098
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.39

The X-ray crystallographic structure for **5c**. Crystal data has been deposited to CCDC (number 2281368).



5c



Empirical formula	$C_{18}H_{16}F_2N_2O_2S$
Formula weight	362.39
Temperature/K	150.00
Crystal system	triclinic
Space group	P-1
a/Å	11.4509(2)
b/Å	11.4766(3)
c/Å	14.0514(3)

α/°	76.0700(10)
β/°	88.9940(10)
γ/°	82.2600(10)
Volume/Å^3	1775.75(7)
Z	4
ρ_{calc}g/cm^3	1.356
μ/mm^{-1}	1.926
F(000)	752.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.482 to 149.842
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	23977
Independent reflections	7255 [R_{int} = 0.0365, R_{sigma} = 0.0432]
Data/restraints/parameters	7255/0/451
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0762, wR_2 = 0.1938
Final R indexes [all data]	R_1 = 0.0806, wR_2 = 0.2037
Largest diff. peak/hole / e Å^{-3}	0.82/-0.57