Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2023

Supplementary Information

Site-selective olefinic C−H cyanation *via* alkenyl sulfonium salts

Juan Ma,[a,b] Jie Lin,[a,b] Zilong Huang,[a,b] Ping Wu,[a] Yong-Gui Zhou,*[a] and Zhengkun Yu*[a,c]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, P. R. China

[b] University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[c] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China

E-mail: zkyu@dicp.ac.cn; ygzhou@dicp.ac.cn

Experimental procedures and analytical data

Contents:

1. General considerations

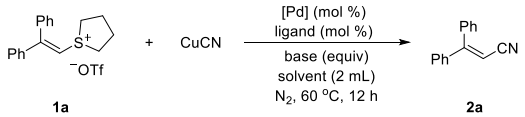
The solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm and $\delta(^{13}C)$, 77.16 ppm), or DMSO-d_6 ($\delta(^{1}H)$, 2.50 ppm and $\delta(^{13}C)$, 39.50 ppm). X-Ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. Known compounds **1a-1b**,[1] **1a'**,[2a] **1e**,[1] **1h**,[1] **1j**,[1] **1n**,[1] **1p**,[1] **1t-1u**,[3] **3a**,[1] **3m**,[1] **3r**,[1] **3t-3v**[4] and **Int-Pd'**[2b] were prepared by the literature procedures and their spectroscopic features are in good agreement with those reported in the literature.

2. Experimental procedures

2.1 Optimization of the reaction conditions

A mixture of substrate **1a**, CuCN, catalyst, ligand, and base in the reaction solvent was vigorously stirred for 12 h under nitrogen atmosphere. After cooling to ambient temperature, the reaction mixture was filtered through a short pad of celite, and rinsed with 10 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant mixture was used to measure the yield by ^{1}H NMR spectroscopy using $MeNO_2$ as the internal standard.

Table S1. Optimization of the reaction conditions[a]

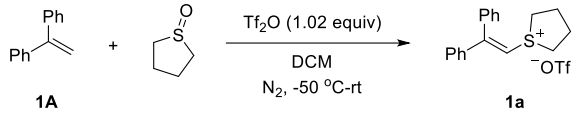


Entry	[Pd]	Ligand (mol %)	CuCN (equiv)	Base (equiv)	Solvent	Yield of **2a**[b] (%)
1	$Pd(PPh_3)_4$	Xphos (6)	1.2	Na_2CO_3 (1.5)	EtOAc	39
2	$Pd(PPh_3)_4$	dppe (6)	1.2	Na_2CO_3 (1.5)	EtOAc	54
3	**$Pd(PPh_3)_4$**	**dppp (6)**	**1.2**	**Na_2CO_3 (1.5)**	**EtOAc**	**99(98)[c]**
4	$PdCl_2$	dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	6
5	$Pd(OAc)_2$	dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	trace
6	$Pd(PPh_3)_4$	dppp (6)	1.2	K_2CO_3 (1.5)	EtOAc	53
7	$Pd(PPh_3)_4$	dppp (6)	1.2	Na_2CO_3 (1.5)	toluene	19
8	$Pd(PPh_3)_4$	dppp (6)	1.2	Na_2CO_3 (1.5)	DCE	99
9[d]	$Pd(PPh_3)_4$	dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	58
10[e]	$Pd(PPh_3)_4$	dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	0
11[f]	$Pd(PPh_3)_4$	dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	53
12	$Pd(PPh_3)_4$	dppp (5)	1.2	Na_2CO_3 (1.5)	EtOAc	63
13	$Pd(PPh_3)_4$	dppp (6)	1.0	Na_2CO_3 (1.5)	EtOAc	92
14		dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	0
15	$Pd(PPh_3)_4$		1.2	Na_2CO_3 (1.5)	EtOAc	22

16	$Pd(PPh_3)_4$	dppp (6)	1.2		EtOAc	23
17[g]	$Pd(PPh_3)_4$	dppp (6)	1.2	Na_2CO_3 (1.5)	EtOAc	0
18[h]	**$Pd(PPh_3)_4$**	**dppp (6)**	**1.2**	**Na_2CO_3 (1.5)**	**EtOAc**	**99(96)[c]**

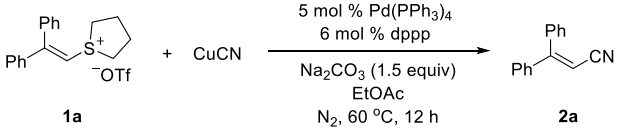
[a] Conditions: **1a** (0.2 mmol), CuCN (0.2-0.24 mmol), [Pd] (0-5 mol %), ligand (0-6 mol %), base (0-1.5 equiv), solvent (2 mL), 60 °C, N_2, 12 h. [b] Determined by ^1H NMR analysis of the crude product using $MeNO_2$ as the internal standard. [c] Isolated yields given in parentheses. [d] Using TMSCN. [e] Using $K_4[Fe(CN)_6]\cdot 3H_2O$. [f] 3 mol % $Pd(PPh_3)_4$. [g] Air atmosphere. [h] **1a** (0.3 mmol), CuCN (0.36 mmol), Na_2CO_3 (0.45 mmol). Xphos = 2-dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-bipheny; dppe = 1,2-bis(diphenylphosphino)ethane.

2.2 Synthesis of sulfonium salts



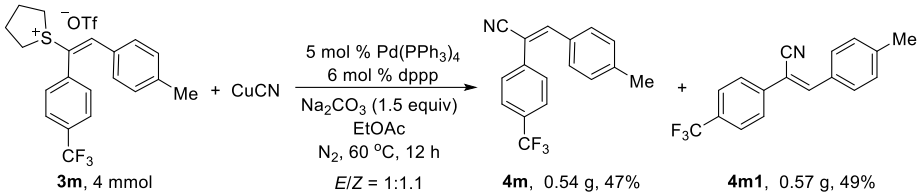
A typical procedure for the synthesis of sulfonium salts 1, 3 and 5 — *Synthesis of 1a:* A mixture of tetrahydrothiophene 1-oxide (1.10 g, 10.2 mmol) in CH_2Cl_2 (50 mL) was cooled to -50 °C under N_2 atmosphere and Tf_2O (1.02 equiv) was added dropwise. After the reaction mixture was stirred for 15 min, 1,1-diphenylethylene (1.80 g, 10.0 mmol) was added. The mixture was allowed to warm up to ambient temperature, and stirred for 6 h. After 1,1-diphenylethylene was completely consumed by TLC monitoring on silica gel, the resultant mixture was evaporated all the volatiles under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/methanol = 20:1, v/v), affording **1a** (3.40 g, 82%) as a white solid.

2.3 Synthesis of alkenyl nitriles (2)

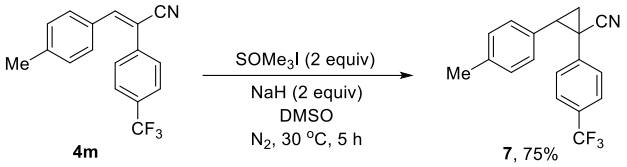


A typical procedure for the synthesis of compounds (2) — *Synthesis of 2a*: A mixture of 1-(2,2-diphenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethane-sulfonate (**1a**) (125 mg, 0.3 mmol), CuCN (32 mg, 0.36 mmol), $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) and Na_2CO_3 (48 mg, 0.45 mmol) in EtOAc (2 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. After **1a** was completely consumed by TLC monitoring on silica gel, the reaction mixture was filtered through a short pad of celite, and rinsed with 15 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/EtOAc = 35:1, v/v), affording **2a** (59 mg, 96%) as pale yellow liquid.

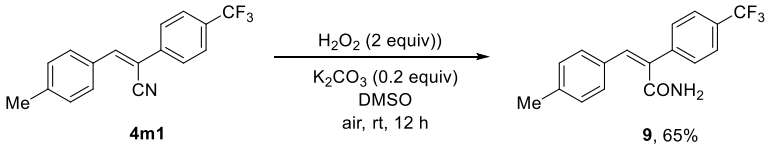
2.4 Gram-scale preparation and derivatization of alkenyl nitriles



Gram-scale preparation of compounds 4m and 4m1: A mixture of **3m** (1.99 g, 4 mmol), CuCN (430 mg, 4.8 mmol), $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) and Na_2CO_3 (636 mg, 6 mmol) in EtOAc (27 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. After cooled to ambient temperature, the resultant mixture was filtered through a short pad of celite, followed by rinsing with 25 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 4:1, v/v), affording **4m** (0.54 g, 47%) and **4m1** (0.57 g, 49%) as white solids.



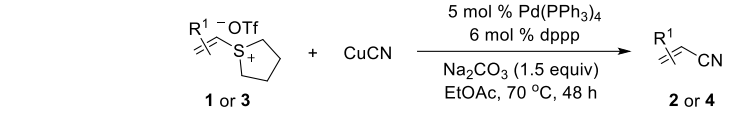
Synthesis of 7: Under nitrogen atmosphere, a mixture of $SOMe_3I$ (132 mg, 0.6 mmol) and NaH (24 mg, 0.6 mmol) in DMSO (1.0 mL) was stirred until gas evolution ceased. (*E*)-3-(*p*-Tolyl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile (**4m**) (86 mg, 0.3 mmol) in DMSO (1.0 mL) was then added and the resulting mixture was stirred at 30 °C for 5 h. After **4m** was completely consumed by TLC monitoring on silica gel, the reaction was quenched with water (10 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 4:1, v/v), affording **7** (68 mg, 75%) as a white solid.



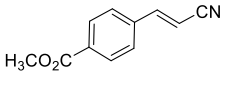
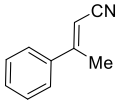
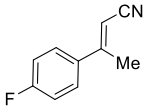
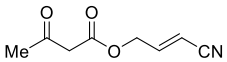
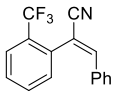
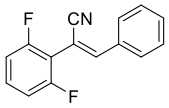
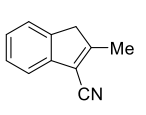
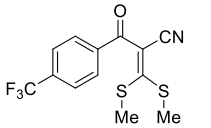
Synthesis of 9: A mixture of (*Z*)-3-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)-acrylonitrile (**4m1**) (86 mg, 0.3 mmol) and K_2CO_3 (9 mg, 0.06 mmol) in DMSO (1 mL) was stirred until the mixture was homogeneous. At this point H_2O_2 (84 μL, 0.6 mmol) was added and the resulting mixture was stirred at ambient temperature for 12 h. After **4m1** was completely consumed by TLC monitoring on silica gel, the reaction was quenched with water (10 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant residue was purified by column

chromatography on silica gel (eluent: petroleum ether (60-90 °C)/EtOAc = 2:1, v/v), affording **9** (59.5 mg, 65%) as a white solid.

Table S2. Unsuccessful cyanation of alkenyl sulfonium salts[a]



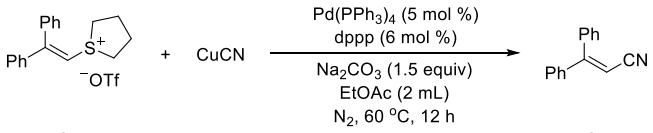
1 or **3** → **2** or **4**

			
2aa, N.D.	**2ab**, 16%[b]	**2ac**, N.D.	**2ad**, N.D.
			
4aa, N.D.	**4ab**, N.D.	**4ac**, N.D.	**4ad**, N.D.

[a] Conditions: alkenyl sulfonium salts (0.3 mmol), CuCN (0.36 mmol), $Pd(PPh_3)_4$ (5 mol %), dppp (6 mol %), Na_2CO_3 (0.45 mmol), EtOAc (2 mL), 70 °C, N_2, 48 h. [b] Isolated yield.

2.5 Radical trapping study

***1,1-Diphenylethylene and BHT-trapping radical experiments*:** A mixture of **1a** (125 mg, 0.3 mmol), CuCN (32 mg, 0.36 mmol), $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol), Na_2CO_3 (48 mg, 0.45 mmol) and 1,1-diphenylethylene (1.5 equiv) or BHT (1.5 equiv) in EtOAc (2 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. After cooled to ambient temperature, the reaction mixture was filtered through a short pad of celite, and rinsed with 15 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant mixture was determined by ^1H NMR analysis of the crude product using $MeNO_2$ as the internal standard.



1a — 1.2 equiv — **2a**

radical scanvenger: 1,1-diphenylethyle		99%
(1.5 equiv)	BHT	99%
	TEMPO	27%

3. X-Ray crystallographic studies

Single crystal X-ray diffraction studies for compounds **3m**, **5b**, **4m**, **4m1**, **6b** and **6c** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on $\boldsymbol{F^2}$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions.

Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 2208095 for **3m**, 2164693 for **5b**, 2208092 for **4m**, 2208089 for **4m1**, 2164690 for **6b** and 2164692 for **6c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

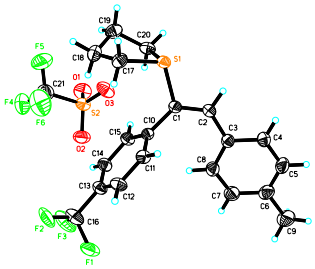


Figure S1. Molecular structure of compound **3m**.

Table S3. Crystal data and structure refinement for compound **3m**

Identification code	mj-255_compound3m	
Empirical formula	$C_{21}H_{20}F_6O_3S_2$	
Formula weight	498.49	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.5403(4) Å	α = 86.284(4)°
	b = 10.9206(5) Å	β = 87.563(4)°
	c = 11.0143(5) Å	γ = 78.588(4)°
Volume	1121.96(9) $Å^3$	
Z	2	
Density (calculated)	1.476 Mg/m^3	
Absorption coefficient	2.806 mm^{-1}	
F(000)	512	
Crystal size	0.170 x 0.140 x 0.120 mm^3	
Theta range for data collection	4.024 to 67.176°	
Index ranges	-9<=h<=11, -13<=k<=12, -13<=l<=13	
Reflections collected	11883	
Independent reflections	3975 [R(int) = 0.0284]	
Completeness to theta = 67.684°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5867	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3975 / 36 / 318	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1197	

R indices (all data)	R1 = 0.0498, wR2 = 0.1265
Extinction coefficient	0.0073(6)
Largest diff. peak and hole	0.487 and -0.338 e.Å^{-3}

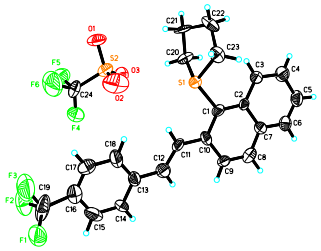


Figure S2. Molecular structure of compound **5b**.

Table S4. Crystal data and structure refinement for compound **5b**

Identification code	mj-242_compound5b	
Empirical formula	$C_{24}H_{20}F_6O_3S_2$	
Formula weight	534.52	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 20.002(4) Å	α= 90°
	b = 9.008(3) Å	β = 90°
	c = 26.434(9) Å	γ = 90°
Volume	4763(2) Å^3	
Z	8	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	0.295 mm^{-1}	
F(000)	2192	
Crystal size	0.200 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.920 to 24.997°	
Index ranges	-23<=h<=18, -6<=k<=10, -21<=l<=29	
Reflections collected	7677	
Independent reflections	5566 [R(int) = 0.1057]	
Completeness to theta = 25.242°	90.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7768	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5566 / 6 / 631	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0839, wR2 = 0.1640	
R indices (all data)	R1 = 0.2208, wR2 = 0.2565	
Absolute structure parameter	0.0(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.307 and -0.309 e.Å^{-3}	

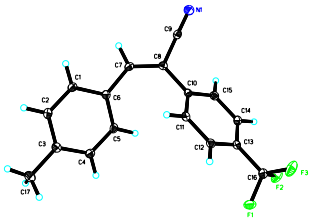


Figure S3. Molecular structure of compound **4m**.

Table S5. Crystal data and structure refinement for compound **4m**

Identification code	MJ-2_compound4m	
Empirical formula	$C_{17}H_{12}F_3N$	
Formula weight	287.28	
Temperature	100(2) K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0544(4) Å	α = 108.761(2)°
	b = 8.6353(5) Å	β = 92.933(2)°
	c = 12.0033(6) Å	γ = 115.474(2)°
Volume	695.89(6) $Å^3$	
Z	2	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.587 mm^{-1}	
F(000)	296	
Crystal size	0.170 x 0.130 x 0.110 mm^3	
Theta range for data collection	3.469 to 56.997°	
Index ranges	-10<=h<=9, -10<=k<=10, -14<=l<=14	
Reflections collected	6838	
Independent reflections	2713 [R(int) = 0.0434]	
Completeness to theta = 53.594°	95.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7513 and 0.5391	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2713 / 0 / 191	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1345	
R indices (all data)	R1 = 0.0564, wR2 = 0.1386	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.289 and -0.329 e.$Å^{-3}$	

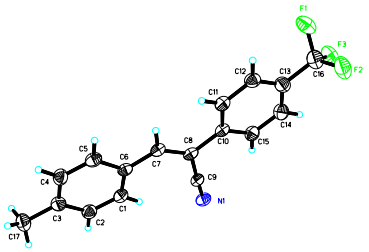


Figure S4. Molecular structure of compound **4m1**.

Table. S6 Crystal data and structure refinement for compound **4m1**

Identification code	20220422dL_0m_compound4m1	
Empirical formula	$C_{17}H_{12}F_3N$	
Formula weight	287.28	
Temperature	293(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 31.110(4) Å	α = 90°
	b = 7.1135(11) Å	β = 91.471(8)°
	c = 12.8170(17) Å	γ = 90°
Volume	2835.5(7) $Å^3$	
Z	8	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.576 mm^{-1}	
F(000)	1184	
Crystal size	0.180 x 0.130 x 0.110 mm^3	
Theta range for data collection	4.949 to 53.936°	
Index ranges	-33<=h<=37, -5<=k<=8, -13<=l<=15	
Reflections collected	8816	
Independent reflections	2533 [R(int) = 0.0669]	
Completeness to theta = 53.594°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7507 and 0.5141	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2533 / 39 / 218	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.2153	
R indices (all data)	R1 = 0.1060, wR2 = 0.2472	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.298 and -0.434 e.$Å^{-3}$	

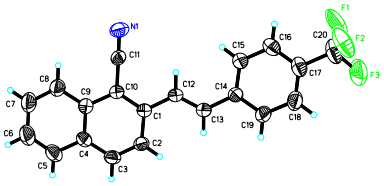


Figure S5. Molecular structure of compound **6b**.

Table S7. Crystal data and structure refinement for compound **6b**

Identification code	MJ-244_compound6b	
Empirical formula	$C_{20}H_{12}F_3N$	
Formula weight	323.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.961(3) Å	α = 90°
	b = 7.6248(15) Å	β = 93.304(19)°
	c = 13.249(2) Å	γ = 90°
Volume	1609.7(5) $Å^3$	
Z	4	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	664	
Crystal size	0.190 x 0.160 x 0.130 mm^3	
Theta range for data collection	3.084 to 24.994°	
Index ranges	-13<=h<=18, -7<=k<=9, -10<=l<=15	
Reflections collected	4214	
Independent reflections	2608 [R(int) = 0.0245]	
Completeness to theta = 25.242°	89.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9213	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2608 / 36 / 245	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1210	
R indices (all data)	R1 = 0.0973, wR2 = 0.1652	
Extinction coefficient	0.030(3)	
Largest diff. peak and hole	0.127 and -0.120 $e.Å^{-3}$	

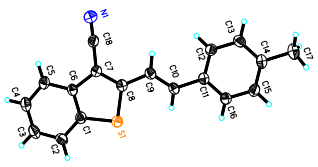
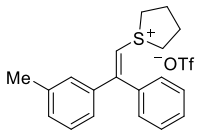


Figure S6. Molecular structure of compound **6c**.

Table S8. Crystal data and structure refinement for compound **6c**

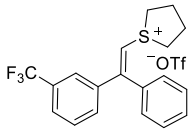
Identification code	mj-235_compound6c	
Empirical formula	$C_{18}H_{13}NS$	
Formula weight	275.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 8.055(2) Å	α = 90°
	b = 11.224(2) Å	β = 90°
	c = 15.398(2) Å	γ = 90°
Volume	1392.1(5) $Å^3$	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.220 mm^{-1}	
F(000)	576	
Crystal size	0.190 x 0.150 x 0.110 mm^3	
Theta range for data collection	3.383 to 25.498°	
Index ranges	-7<=h<=9, -13<=k<=11, -18<=l<=15	
Reflections collected	4012	
Independent reflections	2228 [R(int) = 0.0377]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.2410	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2228 / 1 / 183	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0939	
R indices (all data)	R1 = 0.0649, wR2 = 0.1046	
Absolute structure parameter	0.02(7)	
Extinction coefficient	0.106(6)	
Largest diff. peak and hole	0.164 and -0.214 e.$Å^{-3}$	

4. Analytical data

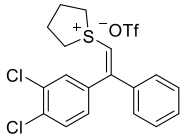


(*E*)-1-(2-Phenyl-2-(*m*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1c** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 35:1, v/v). 1.40 g, 71%; white solid, m.p.: 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–6.99 (m, 8 H), 6.97–6.81 (m, 2 H), 3.73–3.57 (m, 2 H), 3.57–3.40 (m, 2 H), 2.61–2.40 (m, 2 H), 2.28 (d, *J* = 28.0 Hz, 3 H), 2.24–2.06 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 162.3,

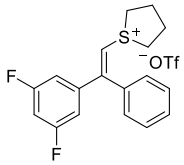
139.4, 137.2, 135.8, 131.3 (d, *J* = 5.4 Hz), 129.9, 129.2, 129.0, 128.9, 126.6, 120.8 (q, *J* = 320.5 Hz), 111.3, 48.8, 29.2, and 21.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.4. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{21}S$ 281.1358; Found 281.1357.



(*E*)-1-(2-Phenyl-2-(3-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1d** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 0.50 g, 68%; white solid, m.p.: 133–134 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.15–7.95 (m, 2 H), 7.95–7.73 (m, 3 H), 7.46–7.20 (m, 3 H), 7.05 (d, *J* = 7.4 Hz, 2 H), 3.94–3.73 (m, 2 H), 3.73–3.49 (m, 2 H), 2.16–1.88 (m, 2 H), 1.75–1.55 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d6) δ 144.9, 134.8, 132.6, 132.1, 131.3, 130.7 (q, *J* = 32.3 Hz), 130.6, 130.0, 128.8, 127.3 (dd, *J* = 10.2, 3.7 Hz), 124.3, 123.6 (q, *J* = 271.4 Hz), 115.9, 45.1, and 28.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{18}F_3S$ 335.1076; Found 335.1077.

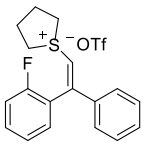


(*Z*)-1-(2-(3,4-Dichlorophenyl)-2-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1f** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 30:1, v/v). 1.70 g, 90%; white solid, m.p.: 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 1 H), 7.51–7.35 (m, 5 H), 7.33 (d, *J* = 2.0 Hz, 1 H), 7.21 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.03 (s, 1 H), 3.80–3.61 (m, 4 H), 2.68–2.52 (m, 2 H), 2.34–2.18 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 159.9, 136.5, 135.7, 135.2, 133.9, 131.9, 131.6, 131.2, 129.3, 129.2, 129.1, 112.6, 48.9, and 29.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{18}H_{17}Cl_2S$ 335.0423; Found 335.0426.

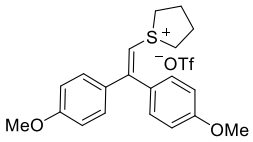


(*E*)-1-(2-(3,5-Difluorophenyl)-2-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1g** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 35:1, v/v). 0.90 g, 64%; white solid, m.p.: 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.18 (m, 5 H), 7.04 (d, *J* = 15.4 Hz, 1 H), 6.99–6.76 (m, 3 H), 3.86–3.68 (m, 2 H), 3.68–3.53 (m, 2 H), 2.65–2.47 (m, 2 H), 2.37–2.14 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 164.6 (d, *J* = 12.9 Hz), 162.1 (d, *J* = 12.8 Hz), 159.2, 138.8 (t, *J* = 9.5 Hz), 136.1, 134.8, 131.7, 130.8, 129.5 (d, *J* = 16.8 Hz), 129.0 (d, *J* = 29.0 Hz), 120.7 (q, *J* = 320.2 Hz), 114.8, 113.3–112.5 (m), 112.2 (d, *J* = 26.8 Hz), 105.8 (t, *J* = 25.0

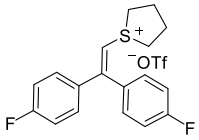
Hz), 48.8, and 29.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.4, -106.5, -108.1. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{18}H_{17}F_2S$ 303.1014; Found 303.1037.



(*Z*)-1-(2-(2-Fluorophenyl)-2-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1i** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 50:1, v/v). 1.90 g, 72%; white solid, m.p.: 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.40 (m, 1 H), 7.37–7.13 (m, 7 H), 7.08 (td, *J* = 7.5, 1.6 Hz, 1 H), 7.05 (s, 1 H), 3.72–3.60 (m, 2 H), 3.55–3.43 (m, 2 H), 2.57–2.41 (m, 2 H), 2.27–2.12 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 160.3, 157.8, 155.0, 136.2, 132.6 (d, *J* = 8.4 Hz), 131.3 (d, *J* = 7.5 Hz), 128.9, 128.5, 125.2 (d, *J* = 3.4 Hz), 122.9 (d, *J* = 14.9 Hz), 120.6 (q, *J* = 318.4 Hz), 116.4 (d, *J* = 21.6 Hz), 113.6, 48.0, and 29.0. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.3, -113.4. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{18}H_{18}FS$ 285.1108; Found 285.1107.

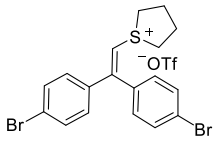


1-(2,2-Bis(4-methoxyphenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1k** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 25:1, v/v). 1.90 g, 80%; white solid, m.p.: 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 2 H), 7.12 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 6.83 (d, *J* = 8.9 Hz, 2 H), 6.66 (s, 1 H), 3.83 (s, 3 H), 3.77 (s, 3 H), 3.74–3.63 (m, 2 H), 3.58–3.45 (m, 2 H), 2.63–2.46 (m, 2 H), 2.31–2.17 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 162.2, 161.9, 161.3, 131.4, 131.1, 129.9, 128.0, 120.8 (q, *J* = 318.6 Hz), 114.6, 114.2, 107.4, 55.5, 55.5, 48.9, and 29.1. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{23}O_2S$ 327.1413; Found 327.1415.

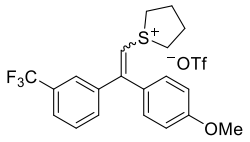


1-(2,2-Bis(4-fluorophenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1l** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 1.60 g, 78%; white solid, m.p.: 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.8, 5.2 Hz, 1 H), 7.31–7.19 (m, 4 H), 7.06 (t, *J* = 8.6 Hz, 1 H), 6.96 (s, 1 H), 3.88–3.71 (m, 2 H), 3.71–3.56 (m, 2 H), 2.75–2.49 (m, 2 H), 2.40–2.19 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6 (d, *J* = 81.1 Hz), 163.1 (d, *J* = 79.5 Hz), 160.1, 133.4 (d, *J* = 3.1 Hz), 131.9 (d, *J* = 8.6 Hz), 131.7 (d, *J* = 3.4 Hz), 131.5 (d, *J* = 8.8 Hz), 120.8 (q, *J* = 320.2 Hz), 116.7 (d, *J* = 22.0 Hz), 116.2 (d, *J* = 21.9 Hz), 111.5, 48.9, and 29.4.

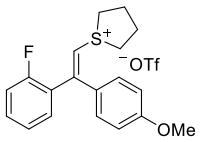
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.4, -107.7, -108.9. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{18}H_{17}F_2S$ 303.1014; Found 303.1015.



1-(2,2-Bis(4-bromophenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1m** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 0.80 g, 71%; white solid, m.p.: 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.27 (d, *J* = 8.7 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 6.99 (s, 1 H), 3.80–3.67 (m, 2 H), 3.67–3.44 (m, 2 H), 2.68–2.44 (m, 2 H), 2.23–2.20 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 135.8, 134.1, 132.7, 132.1, 131.2, 130.6, 126.2, 125.1, 120.7, 112.5 (q, *J* = 318.4 Hz), 48.8, and 29.3. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{18}H_{17}Br_2S$ 422.9412; Found 422.9424.

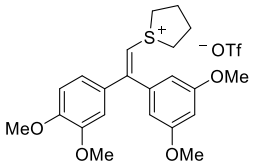


(*E*)-1-(2-(4-Methoxyphenyl)-2-(3-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1q** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 1.00 g, 32% (*E*/*Z* = 1.2:1); white solid, m.p.: 114–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.75–7.51 (m, 2 H), 7.48–7.33 (m, 2 H), 7.24 (s, 1 H), 7.09 (d, *J* = 8.6 Hz, 1 H), 6.93 (d, *J* = 8.6 Hz, 1 H), 6.90–6.70 (m, 2 H), 3.74 (s, 2 H), 3.72–3.42 (m, 5 H), 2.55–2.40 (m, 2 H), 2.18–2.10 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 161.2, 159.8, 159.5, 138.4, 136.5, 132.9, 132.3, 131.1, 130.5, 129.8, 129.3, 128.7, 127.2, 126.9, 126.6, 125.7, 125.4, 123.4 (q, *J* = 271.0 Hz), 120.4 (q, *J* = 318.6 Hz), 114.5, 114.0, 112.3, 109.6, 77.4, 55.1, 48.5 (d, *J* = 6.2 Hz), and 28.8 (d, *J* = 10.7 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.6, -62.7, -78.4. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{20}F_3OS$ 365.1181; Found 365.1184.

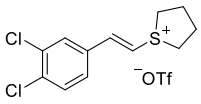


(*E*)-1-(2-(2-Fluorophenyl)-2-(4-methoxyphenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1r** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 1.70 g, 77%; white solid, m.p.: 127–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.42 (m, 1 H), 7.35 (d, *J* = 8.9 Hz, 2 H), 7.29–7.23 (m, 1 H), 7.20 (t, *J* = 9.1 Hz, 1 H), 7.12 (td, *J* = 7.5, 1.7 Hz, 1 H), 7.00 (s, 1 H), 6.82 (d, *J* = 9.0 Hz, 2 H), 3.74 (s, 3 H), 3.68 (dt, *J* = 13.6, 6.9 Hz, 2 H), 3.59–3.41 (m, 2 H), 2.65–2.46 (m, 2 H), 2.34–2.16 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 159.0 (d, *J* = 246.9

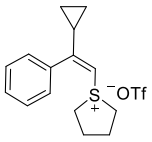
Hz), 154.6, 132.5 (d, *J* = 8.3 Hz), 131.3 (d, *J* = 1.9 Hz), 130.3, 128.5, 125.1 (d, *J* = 3.5 Hz), 123.1 (d, *J* = 15.1 Hz), 120.7 (d, *J* = 318.6 Hz), 116.3 (d, *J* = 21.8 Hz), 114.3, 110.4, 55.4, 48.0, and 28.9. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.3, -113.7. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{20}FOS$ 315.1213; Found 315.1229.



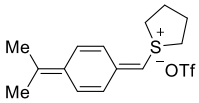
(*Z*)-1-(2-(3,4-Dimethoxyphenyl)-2-(3,5-dimethoxyphenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1s** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 25:1, v/v). 2.70 g, 42%; white solid, m.p.: 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1 H), 6.89 (s, 1 H), 6.78 (d, *J* = 8.5 Hz, 1 H), 6.72 (d, *J* = 8.5 Hz, 1 H), 6.51 (s, 1 H), 6.28 (d, *J* = 1.9 Hz, 2 H), 3.85 (s, 3 H), 3.81 (s, 3 H), 3.75 (s, 6 H), 3.66–3.47 (m, 4 H), 2.67–2.46 (m, 2 H), 2.30–2.11 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 161.3 (d, *J* = 1.6 Hz), 151.9, 149.2, 137.9, 128.9, 123.6, 120.6 (q, *J* = 320.5 Hz), 110.5 (d, *J* = 3.5 Hz), 108.8, 107.4, 101.3, 56.3, 55.9, 55.5, 48.5, and 29.1. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.4. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{22}H_{27}O_4S$ 387.1625; Found 387.1630.



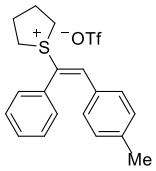
(*E*)-1-(3,4-Dichlorostyryl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1v** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 30:1, v/v). 3.60 g, 74%; white solid, m.p.: 94–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.9 Hz, 1 H), 7.50–7.33 (m, 3 H), 7.10 (d, *J* = 15.3 Hz, 1 H), 3.91–3.67 (m, 2 H), 3.61–2.46 (m, 2 H), 2.64–2.40 (m, 2 H), 2.37–2.20 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 147.1, 135.7, 133.3, 132.4, 131.2, 130.4, 127.9, 120.7 (q, *J* = 318.3 Hz), 114.7, 47.9, and 29.0. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{12}H_{13}Cl_2S$ 259.0110; Found 259.0113.



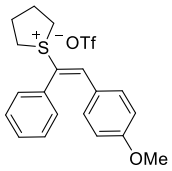
(*Z*)-1-(2-Cyclopropyl-2-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1w** was obtained by column chromatography on silica gel (CH_2Cl_2/methanol = 20:1, v/v). 1.00 g, 12%; white solid, m.p.: 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.37 (m, 3 H), 7.18–7.02 (m, 2 H), 6.51 (s, 1 H), 3.65–3.53 (m, 2 H), 3.53–3.40 (m, 2 H), 2.67–2.45 (m, 2 H), 2.34–2.14 (m, 2 H), 2.07–1.92 (m, 1 H), 1.09–0.89 (m, 2 H), 0.77–0.59 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 134.1, 129.9, 129.2, 128.1, 109.3, 48.2, 29.1, 20.0, and 8.6. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{15}H_{19}S$ 231.1202; Found 231.1204.



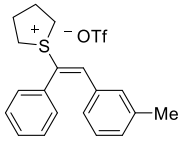
1-((4-(Propan-2-ylidene)cyclohexa-2,5-dien-1-ylidene)methyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **1x** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 2.20 g, 39%; white solid, m.p.: 148–149 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 6.46 (s, 1 H), 3.95–3.80 (m, 2 H), 3.50–3.37 (m, 2 H), 2.58–2.44 (m, 5 H), 2.40–2.26 (m, 5 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 141.7, 134.8, 129.8, 126.7, 109.6, 48.4, 29.1, 21.5, and 19.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{14}H_{19}S$ 219.1202; Found 219.1215.



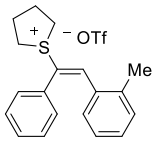
(*E*)-1-(1-Phenyl-2-(*p*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3b** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 3.30 g, 63%; white solid, m.p.: 150–152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.48 (m, 4 H), 7.39–7.27 (m, 2 H), 6.95 (d, *J* = 7.7 Hz, 2 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 4.06–3.82 (m, 2 H), 3.53–3.34 (m, 2 H), 2.23 (s, 3 H), 2.16–1.97 (m, 2 H), 1.72–1.51 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.0, 142.0, 131.1, 130.8, 130.7, 130.4, 130.0, 129.5, 122.4, 119.2, 45.0, 28.8, and 21.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.1. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{21}S$ 281.1358; Found 281.1357.



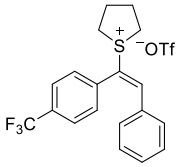
(*E*)-1-(2-(4-Methoxyphenyl)-1-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3c** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 3.00 g, 68%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.41 (m, 4 H), 7.34–7.20 (m, 2 H), 6.85 (d, *J* = 8.9 Hz, 2 H), 6.55 (d, *J* = 8.9 Hz, 2 H), 3.88–3.67 (m, 2 H), 3.59 (s, 3 H), 3.44–3.29 (m, 2 H), 2.04–1.85 (m, 2 H), 1.64–1.43 (m, 2 H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 147.1, 132.4, 130.7, 130.4, 130.2, 129.7, 124.7, 120.5 (q, *J* = 320.9 Hz), 119.9, 113.9, 55.1, 44.6, and 28.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{21}OS$ 297.1308; Found 297.1309.



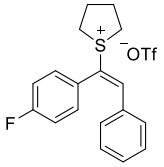
(*E*)-1-(1-Phenyl-2-(*m*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3d** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 2.60 g, 52%; white solid, m.p.: 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.44 (m, 5 H), 7.44–7.22 (m, 4 H), 7.14 (d, *J* = 15.8 Hz, 1 H), 4.36–3.85 (m, 2 H), 3.73–3.30 (m, 2 H), 2.71–2.27 (m, 7 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 140.4, 136.0, 135.6, 131.4, 129.1, 128.8, 128.3, 128.2, 127.3, 120.8 (q, *J* = 318.8 Hz), 121.4, 120.1, 48.0, 29.0, and 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.1. HRMS (ESI-TOF) m/z: [M-OTf]$^+$ Calcd for $C_{19}H_{21}S$ 281.1358; Found 281.1359.



(*E*)-1-(1-Phenyl-2-(*o*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3e** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 2.30 g, 45%; white solid, m.p.: 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1 H), 7.55–7.42 (m, 3 H), 7.30 (d, *J* = 3.5 Hz, 2 H), 7.11 (d, *J* = 3.7 Hz, 2 H), 6.89–6.64 (m, 2 H), 4.04–3.87 (m, 2 H), 3.64–3.38 (m, 2 H), 2.40 (s, 3 H), 2.19–2.07 (m, 2 H), 1.83–1.60 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.9, 138.4, 131.3, 130.7, 130.5, 130.4, 130.2, 130.0, 129.5, 129.0, 125.6, 125.4, 120.6 (q, *J* = 306.4 Hz), 44.9, 28.5, and 19.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.4. HRMS (ESI-TOF) m/z: [M-OTf]$^+$ Calcd for $C_{19}H_{21}S$ 281.1358; Found 281.1357.

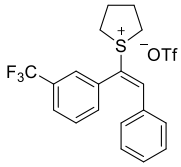


(*E*)-1-(2-Phenyl-1-(4-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3f** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 2.20 g, 64%; white solid, m.p.: 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2 H), 7.75 (s, 1 H), 7.61 (d, *J* = 7.9 Hz, 2 H), 7.29 (t, *J* = 7.3 Hz, 1 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.01 (d, *J* =7.7 Hz, 2 H), 4.11–3.81 (m, 2 H), 3.65–3.40 (m, 2 H), 2.22–1.99 (m, 2 H), 1.83–1.59 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.4, 134.0, 132.9 (q, *J* = 33.3 Hz), 132.0, 131.4, 131.3, 130.6, 128.9, 127.4 (q, *J* = 3.6 Hz), 124.8, 122.4, 120.7 (q, *J* = 318.5 Hz), 45.2, and 28.8. HRMS (ESI-TOF) m/z: [M-OTf]$^+$ Calcd for $C_{19}H_{18}F_3S$ 335.1076; Found 335.1077.

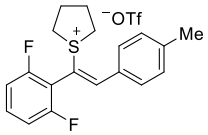


(*E*)-1-(1-(4-Fluorophenyl)-2-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3g** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1,

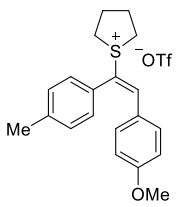
v/v). 2.50 g, 68%; white solid, m.p.: 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 5.1 Hz, 1 H), 7.61–7.56 (m, 1 H), 7.45–7.40 (m, 1 H), 7.39–7.32 (m, 1 H), 7.32–7.22 (m, 2 H), 7.17 (t, *J* = 7.7 Hz, 1 H), 7.05–6.99 (m, 2 H), 6.83 (t, *J* = 8.6 Hz, 1 H), 3.98–3.87 (m, 2 H), 3.56–3.44 (m, 2 H), 2.17–2.02 (m, 2 H), 1.77–1.59 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.0, 162.5, 148.1, 146.3, 132.9 (d, *J* = 8.9 Hz), 132.5 (d, *J* = 53.8 Hz), 130.9 (d, *J* = 63.5 Hz), 129.1 (d, *J* = 82.6 Hz), 128.7 (d, *J* = 3.2 Hz), 125.8 (d, *J* = 3.7 Hz), 123.4 (d, *J* = 2.2 Hz), 120.7 (q, *J* = 320.6 Hz), 117.9 (d, *J* = 21.9 Hz), 115.9 (d, *J* = 21.8 Hz), 44.9, and 28.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.1, -107.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{18}H_{18}FS$ 285.1108; Found 285.1116.



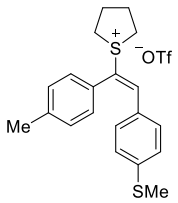
(*E*)-1-(2-Phenyl-1-(3-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3h** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 0.80 g, 52%; white solid, m.p.: 149–150 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15–7.95 (m, 2 H), 7.95–7.73 (m, 3 H), 7.46–7.20 (m, 3 H), 7.05 (d, *J* = 7.4 Hz, 2 H), 3.94-3.73 (m, 2 H), 3.73–3.49 (m, 2 H), 2.16–1.88 (m, 2 H), 1.75–1.55 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 144.9, 134.8, 132.6, 132.1, 131.3, 130.7 (q, *J* = 32.3 Hz), 130.6, 130.0, 128.8, 127.3 (dd, *J* = 10.2, 3.7 Hz), 124.3, 123.6 (q, *J* = 271.4 Hz), 115.9, 45.1, and 28.3. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ -61.2, -77.9. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{18}F_3S$ 335.1076; Found 335.1075.



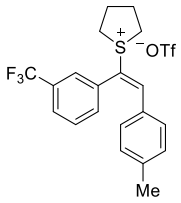
(*Z*)-1-(1-(2,6-Difluorophenyl)-2-(*p*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3j** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 30:1, v/v). 4.40 g, 72%; white solid, m.p.: 92–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1 H), 7.72–7.60 (m, 1 H), 7.16 (t, *J* = 8.1 Hz, 2 H), 7.01 (d, *J* = 8.1 Hz, 2 H), 6.90 (d, *J* = 8.2 Hz, 2 H), 4.06–3.88 (m, 2 H), 3.52–3.33 (m, 2 H), 2.34–2.12 (m, 5 H), 1.94–1.73 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 5.3 Hz), 158.1 (d, *J* = 5.6 Hz), 153.0, 143.0, 134.8 (t, *J* = 10.2 Hz), 129.9 (d, *J* = 5.8 Hz), 129.1, 120.7 (q, *J* = 320.5 Hz), 113.3 (dd, *J* = 22.0, 2.9 Hz), 110.8, 107.7 (t, *J* = 20.6 Hz), 45.4 (d, *J* = 4.2 Hz), 29.0, and 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.2, -108.4. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{19}F_2S$ 317.1170; Found 317.1169.



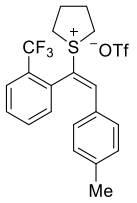
(*E*)-1-(2-(4-Methoxyphenyl)-1-(*p*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3k** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 2.80 g, 61%; white solid, m.p.: 157–159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1 H), 7.38 (d, *J* = 7.8 Hz, 2 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 3.92 (dt, *J* = 12.8, 6.4 Hz, 2 H), 3.73 (s, 3 H), 3.38 (dt, *J* = 12.8, 6.4 Hz, 2 H), 2.44 (s, 3 H), 2.17–2.02 (m, 2 H), 1.78–1.54 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 147.8, 141.6, 132.8, 131.5, 130.4, 127.0, 125.1, 120.4, 114.3, 55.5, 45.0, 28.9, and 21.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{23}OS$ 311.1464; Found 311.1463.



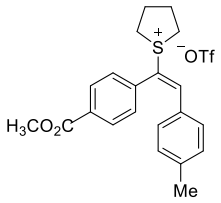
(*E*)-1-(2-(4-(Methylthio)phenyl)-1-(*p*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3l** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 30:1, v/v). 1.40 g, 23%; white solid, m.p.: 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1 H), 7.38 (d, *J* = 7.8 Hz, 2 H), 7.21 (d, *J* = 7.9 Hz, 2 H), 6.98 (d, *J* = 8.6 Hz, 2 H), 6.92 (d, *J* = 8.6 Hz, 2 H), 3.92 (dt, *J* = 12.9, 6.5 Hz, 2 H), 3.43 (dt, *J* = 12.9, 6.4 Hz, 2 H), 2.54–2.43 (m, 3 H), 2.40 (s, 3 H), 2.22–2.02 (m, 2 H), 1.80–1.54 (m, 2 H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 143.7, 141.6, 131.4, 131.0, 130.2, 128.6, 126.9, 125.3, 122.5, 119.2, 45.0, 28.8, 21.6, and 14.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{23}S_2$ 327.1236; Found 327.1237.



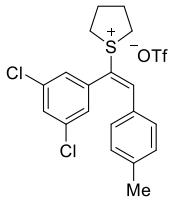
(*E*)-1-(2-(*p*-Tolyl)-1-(3-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3n** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 30:1, v/v). 4.20 g, 83%; white solid, m.p.: 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1 H), 7.75 (t, *J* = 7.7 Hz, 1 H), 7.68 (d, *J* = 10.6 Hz, 2 H), 7.57 (s, 1 H), 6.94 (d, *J* = 8.1 Hz, 2 H), 6.83 (d, *J* = 8.2 Hz, 2 H), 3.93 (dt, *J* = 13.2, 6.5 Hz, 2 H), 3.46 (dt, *J* = 12.9, 6.3 Hz, 2 H), 2.21 (s, 3 H), 2.15–1.95 (m, 2 H), 1.77–1.57 (m, 2 H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.5, 142.2, 134.5, 132.6 (d, *J* = 32.9 Hz), 131.6, 131.4, 130.7, 129.6, 129.2, 127.7 (q, *J* = 3.5 Hz), 127.0 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 271.2 Hz), 120.7 (q, *J* = 318.5 Hz), 120.7, 45.2, 28.7, and 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.7, -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{20}F_3S$ 349.1232; Found 349.1237.



(*E*)-1-(2-(*p*-Tolyl)-1-(2-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3o** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 3.20 g, 82%; white solid, m.p.: 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 7.6 Hz, 2 H), 7.77 (t, *J* = 7.7 Hz, 1 H), 7.72 (s, 1 H), 7.65 (d, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 8.1 Hz, 2 H), 6.80 (d, *J* = 8.1 Hz, 2 H), 4.21 (dt, *J* = 14.1, 7.2 Hz, 1 H), 3.98–3.82 (m, 1 H), 3.75 (dt, *J* = 13.1, 6.5 Hz, 1 H), 2.99 (dt, *J* = 13.5, 6.9 Hz, 1 H), 2.35–2.06 (m, 6 H), 1.97 (dt, *J* = 12.8, 6.7 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9, 142.3, 134.6, 132.7, 131.9, 130.6, 129.8 (q, *J* = 30.1 Hz), 129.6, 129.5, 128.5, 128.3 (q, *J* = 4.8 Hz), 123.2 (q, *J* = 272.6 Hz), 120.8 (q, *J* = 318.5 Hz), 119.6, 49.4, 43.5, 28.9, 28.7, and 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -59.2, -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{20}F_3S$ 349.1232; Found 349.1233.

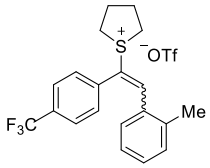


(*E*)-1-(1-(4-(Methoxycarbonyl)phenyl)-2-(*p*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3p** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 30:1, v/v). 3.50 g, 69%; white solid, m.p.: 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 2 H), 7.66 (s, 1 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 6.93 (d, *J* = 8.2 Hz, 2 H), 6.85 (d, *J* = 8.2 Hz, 2 H), 4.04–3.85 (m, 5 H), 3.48 (dt, *J* = 12.9, 6.4 Hz, 2 H), 2.21 (s, 3 H), 2.09 (td, *J* = 13.4, 7.5 Hz, 2 H), 1.73–1.58 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 148.0, 141.9, 134.7, 132.2, 131.3, 130.8, 130.6, 129.4, 129.3, 122.3 (q, *J* = 318.7 Hz), 121.2, 52.5, 45.0, 28.6, and 21.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{21}H_{23}O_2S$ 339.1413; Found 339.1416.

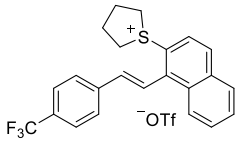


(*E*)-1-(1-(3,5-Dichlorophenyl)-2-(*p*-tolyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3q** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 3.00 g, 53%; white solid, m.p.: 143–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1 H), 7.55 (t, *J* = 1.7 Hz, 1 H), 7.30 (d, *J* = 1.8 Hz, 2 H), 7.02 (d, *J* = 8.1 Hz, 2 H), 6.92 (d, *J* = 8.1 Hz, 2 H), 4.06–3.92 (m, 2 H), 3.56–3.36 (m, 2 H), 2.27 (s, 3 H), 2.25–2.12 (m, 2 H), 1.91–1.72 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8,

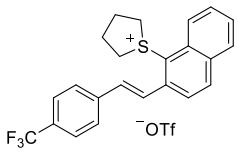
142.4, 137.3, 133.6, 131.3, 130.8, 129.8, 129.2, 128.8, 120.8 (J = 318.4 Hz), 119.4, 45.4, 28.8, and 21.6. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -78.5. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{19}Cl_2S$ 349.0579; Found 349.0578.



1-(2-(*o*-Tolyl)-1-(4-(trifluoromethyl)phenyl)vinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **3s** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 2.40 g, 64% (*E*/*Z* = 2.2:1); white solid, m.p.: 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 0.3 H), 7.74 (d, J = 8.1 Hz, 2 H), 7.65–7.55 (m, 2 H), 7.55–7.44 (m, 2 H), 7.32 (d, J = 16.6 Hz, 1 H), 7.12 (s, 0.3 H), 6.78 (d, J = 16.7 Hz, 0.7 H), 6.69 (d, J = 7.8 Hz, 0.3 H), 4.12–3.87 (m, 2 H), 3.67 (dt, J = 12.8, 6.3 Hz, 1.37 H), 3.57 (dt, J = 13.0, 6.3 Hz, 0.63 H), 2.60–2.47 (m, 1.4 H), 2.47–2.30 (m, 4.3 H), 2.23–2.07 (m, 0.9 H), 1.85–1.70 (m, 0.6 H).$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 146.4, 140.4, 140.1, 138.9, 138.5, 138.4, 135.5, 133.9, 131.4, 131.2, 130.8, 130.7, 130.5, 130.4, 129.2, 127.5, 127.0 (q, J = 3.6 Hz), 126.0, 125.9 (q, J = 3.9 Hz), 125.4, 125.3 (d, J = 1.9 Hz), 124.2, 122.6 (q, J = 37.6 Hz), 48.3, 45.3, 29.2, 28.8, 20.7, and 20.0. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.6, -63.0, -78.3. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{20}H_{20}F_3S$ 349.1232; Found 349.1233.

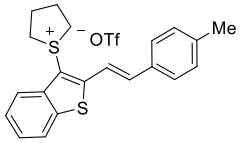


(*E*)-1-(1-(4-(Trifluoromethyl)styryl)naphthalen-2-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **5a** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 1.40 g, 51%; white solid, m.p.: 167–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.5 Hz, 1 H), 8.40 (d, J = 8.2 Hz, 1 H), 8.21 (d, J = 16.1 Hz, 1 H), 8.10 (q, J = 8.1 Hz, 2 H), 7.98 (d, J = 8.1 Hz, 2H), 7.90–7.78 (m, 2 H), 7.72 (t, J = 10.2 Hz, 2 H), 7.47 (d, J = 16.1 Hz, 1 H), 4.21–4.04 (m, 4 H), 2.50–2.31 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d6) δ 140.8, 139.9, 133.5, 131.6, 131.3, 129.4, 129.0 (q, J = 31.6 Hz), 128.5, 128.3, 128.1, 126.6, 125.9 (q, J = 3.6 Hz), 125.7, 124.6 (q, J = 231.0 Hz), 124.0, 122.7, 121.0 (q, J = 319.4 Hz), 47.7, and 29.1. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ -56.3, -73.1. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{23}H_{20}F_3S$ 385.1232; Found 385.1252.

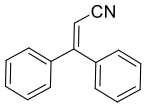


(*E*)-1-(2-(4-(Trifluoromethyl)styryl)naphthalen-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **5b** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1,

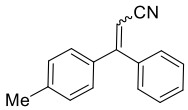
v/v). 3.10 g, 68%; white solid, m.p.: 203–205 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.45 (d, *J* = 8.7 Hz, 1 H), 8.24 (d, *J* = 8.0 Hz, 1 H), 8.19 (d, *J* = 4.7 Hz, 1 H), 8.16 (d, *J* = 12.1 Hz, 1 H), 8.09 (d, *J* = 8.6 Hz, 1 H), 8.00 (d, *J* = 8.1 Hz, 2 H), 7.95–7.89 (m, 1 H), 7.86 (d, *J* = 8.2 Hz, 2 H), 7.79 (t, *J* = 7.5 Hz, 1 H), 7.70 (d, *J* = 16.0 Hz, 1 H), 4.30–4.18 (m, 2 H), 4.18–4.00 (m, 2 H), 2.87–2.72 (m, 2 H), 2.49–2.30 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6) δ 143.4, 140.2, 135.6, 135.2, 133.8, 130.5, 130.2, 129.9, 128.1, 127.7, 127.3, 125.8 (q, *J* = 3.5 Hz), 125.4, 123.0, 115.7, 43.8, and 28.5. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ -62.6, -78.2. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ Calcd for $C_{23}H_{20}F_3S$ 385.1232; Found 385.1234.



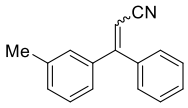
(*E*)-1-(2-(4-Methylstyryl)benzo[*b*]thiophen-3-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate: Following the general procedure, compound **5c** was obtained by column chromatography on silica gel (eluent: CH_2Cl_2/methanol = 20:1, v/v). 3.30 g, 78%; yellow solid, m.p.: 230–232 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.22 (d, *J* = 7.0 Hz, 1 H), 7.89 (s, 1 H), 7.86 (d, *J* = 9.9 Hz, 1 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.64–7.55 (m, 2 H), 7.49 (d, *J* = 15.9 Hz, 1 H), 7.31 (d, *J* = 7.9 Hz, 2 H), 4.15–4.02 (m, 2 H), 4.02–3.90 (m, 2 H), 2.80–7.67 (d, *J* = 9.4 Hz, 2 H), 2.47–2.38 (m, 2 H), 2.36 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.7, 139.8, 137.2, 136.8, 134.1, 132.5, 129.7, 127.7, 126.7, 124.2, 121.5, 119.1, 117.6, 108.6, 43.9, 29.0, and 21.0. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ -77.8. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ Calcd for $C_{21}H_{21}S_2$ 337.1079; Found 337.1089.



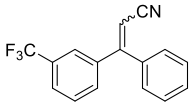
3,3-Diphenylacrylonitrile:[5] Following the general procedure, compound **2a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 59 mg, 96%; pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.42 (m, 6 H), 7.42–7.35 (m, 2 H), 7.35–7.28 (m, 2 H), 5.75 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 138.7, 137.0, 130.4, 129.9, 129.4, 128.6, 128.5, 128.4, 117.8, and 94.8.



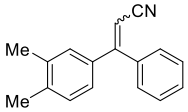
3-Phenyl-3-(*p*-tolyl)acrylonitrile:[5] Following the general procedure, compound **2b** was obtained by thin layer chromatography (eluent: petroleum ether (60−90 °C)/EtOAc = 10:1, v/v). 65 mg, 98%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 3 H), 7.40–7.25 (m, 4 H), 7.22–7.17 (m, 2 H), 5.72 (s, 0.58 H), 5.68 (s, 0.42 H), 2.42 (s, 1.44 H), 2.40 (s, 1.56 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3, 163.2, 141.0, 140.4, 139.3, 137.3, 136.1, 134.3, 130.4, 130.0, 129.7, 129.5, 129.3, 128.7, 128.7, 128.6, 128.5, 118.3, 118.2, 94.3, 94.0, 21.5, and 21.4.



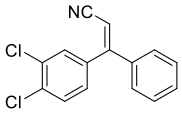
3-Phenyl-3-(*m*-tolyl)acrylonitrile:[5] Following the general procedure, compound **2c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 30:1, v/v). 59 mg, 90%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.09 (m, 7.7 H), 7.01–6.91 (m, 1.3 H), 5.59 (s, 1 H), 5.58 (s, 1 H), 2.25 (s, 1 H), 2.21 (s, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2, 138.9, 138.9, 138.4, 138.2, 137.1, 137.0, 131.2, 130.8, 130.4, 130.0, 129.9, 129.5, 129.0, 128.6, 128.5, 128.5, 128.4, 128.4, 126.7, 125.7, 118.0, 94.7, 21.4, and 21.3.



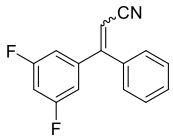
3-Phenyl-3-(3-(trifluoromethyl)phenyl)acrylonitrile:[5] Following the general procedure, compound **2d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 76 mg, 93%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.65–7.55 (m, 2 H), 7.51–7.35 (m, 3 H), 7.33–7.21 (m, 2 H), 5.84 (s, 1 H), 5.77 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.6, 138.1, 137.9, 133.0, 131.2 (q, *J* = 32.6 Hz), 131.0, 129.6, 129.4, 129.1, 128.9, 128.4, 126.8 (q, *J* = 3.7 Hz), 126.4 (q, *J* = 3.8 Hz), 125.2, 125.2 (q, *J* = 270.8 Hz), 117.4, 96.6, and 96.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.6, -62.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}F_3N$ 274.0838; Found 274.0839.



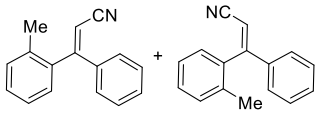
3-(3,4-Dimethylphenyl)-3-phenylacrylonitrile:[6] Following the general procedure, compound **2e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 65 mg, 93%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.27 (m, 5 H), 7.22–7.17 (m, 1 H), 7.15–6.96 (m, 2 H), 5.70 (s, 0.64 H), 5.65 (s, 0.36 H), 2.31 (s, 1.38 H), 2.29 (s, 1.71 H), 2.28 (s, 1.10 H), 2.24 (s, 1.95 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.4, 163.3, 139.7, 139.3, 139.0, 137.4, 137.1, 136.9, 136.5, 134.7, 130.6, 130.3, 130.0, 129.9, 129.8, 129.6, 129.5, 128.6, 128.6, 128.5, 127.2, 126.1, 118.2, 94.1, 93.8, 19.8, 19.8, and 19.8.



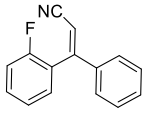
(*Z*)-3-(3,4-Dichlorophenyl)-3-phenylacrylonitrile:[7] Following the general procedure, compound **2f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 30:1, v/v). 72 mg, 96%; white solid, m.p.: 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.55 (d, *J* = 8.3 Hz, 1 H), 7.50–7.45 (m, 2 H), 7.43–7.38 (t, *J* = 7.6 Hz, 2 H), 7.34 (dd, *J* = 8.3, 1.7 Hz, 1 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 5.79 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7, 137.9, 137.0, 134.5, 133.2, 131.4, 131.0, 130.8, 129.1, 128.9, 128.4, 117.3, and 96.2.



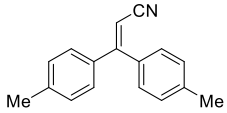
3-(3,5-Difluorophenyl)-3-phenylacrylonitrile: Following the general procedure, compound **2g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 30:1, v/v). 62 mg, 86%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.26 (m, 4 H), 7.19 (d, *J* = 7.5 Hz, 1 H), 6.93–6.69 (m, 3 H), 5.72 (s, 1 H), 5.66 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2 (dd, *J* = 12.9, 1.6 Hz), 161.7 (dd, *J* = 12.6, 2.2 Hz), 160.6 (dt, *J* = 9.4, 2.3 Hz), 142.1 (t, *J* = 9.2 Hz), 140.1 (t, *J* = 9.6 Hz), 137.6, 135.9, 131.0, 130.6, 129.5, 129.0, 128.9, 128.3, 117.1 (d, *J* = 11.9 Hz), 112.9–112.7 (m), 111.8–111.5 (m), 106.0, 105.8, 105.5, 105.3, 97.0, and 96.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}F_2N$ 242.0776; Found 242.0777.



(*E*)-3-Phenyl-3-(*o*-tolyl)acrylonitrile and (*Z*)-3-phenyl-3-(*o*-tolyl)acrylonitrile:[5] Following the general procedure, compound **2h** and **2h'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 2:1, v/v). 16 mg, 24%; white solid, m.p.: 104–106 ºC, and 21.8 mg, 33%; colorless liquid. **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.38 (m, 2 H), 7.36–7.29 (m, 3 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.12 (t, *J* = 7.4 Hz, 2 H), 5.41 (s, 1 H), 1.91 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.7, 139.7, 137.2, 136.2, 131.0, 130.4, 129.6, 129.5, 128.8, 126.1, 117.8, 96.9, and 20.4. **2h'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 4 H), 7.33–7.22 (m, 5 H), 5.98 (s, 1 H), 2.09 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2, 137.5, 136.8, 136.0, 130.9, 130.7, 129.5, 129.3, 129.0, 127.2, 126.3, 117.5, 96.4, and 19.8.

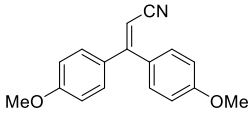


(*Z*)-3-(2-Fluorophenyl)-3-phenylacrylonitrile:[7] Following the general procedure, compound **2i** was obtained by thin layer chromatography (eluent: petroleum ether (60−90 °C)/EtOAc = 10:1, v/v). 44 mg, 66%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.42 (m, 2 H), 7.42–7.35 (m, 3 H), 7.35–7.30 (m, 2 H), 7.30–7.24 (m, 1 H), 7.23–7.15 (m, 1 H), 5.97 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6 (d, *J* = 249.0 Hz), 157.4, 137.5, 131.9 (d, *J* = 8.3 Hz), 131.3 (d, *J* = 2.6 Hz), 130.8, 128.9, 127.3, 124.8 (d, *J* = 14.6 Hz), 124.5 (d, *J* = 3.6 Hz), 117.1, 116.4 (d, *J* = 21.2 Hz), and 97.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -111.6.

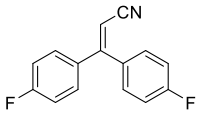


3,3-Di-*p*-tolylacrylonitrile:[6] Following the general procedure, compound **2j** was obtained by column chromatography on silica gel (eluent: petroleum ether

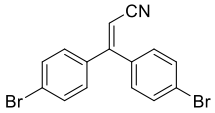
(60−90 °C)/EtOAc = 10:1, v/v). 66 mg, 94%; white solid, m.p.: 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 2 H), 7.33–7.26 (m, 2 H), 7.26–7.17 (m, 4 H), 5.69 (s, 1 H), 2.45 (s, 3 H), 2.42 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2, 140.8, 140.3, 136.4, 134.4, 129.6, 129.4, 129.3, 128.6, 118.4, 93.4, 21.5, and 21.4.



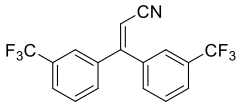
3,3-Bis(4-methoxyphenyl)acrylonitrile:[8] Following the general procedure, compound **2k** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 68 mg, 86%; white solid, m.p.: 94–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 5.44 (s, 1 H), 3.75 (s, 3 H), 3.73 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.3, 161.5, 161.0, 131.6, 131.3, 130.2, 129.5, 118.8, 114.0, 113.8, 91.5, 55.4, and 55.4.



3,3-Bis(4-fluorophenyl)acrylonitrile:[6] Following the general procedure, compound **2l** was obtained by thin layer chromatography (eluent: petroleum ether (60−90 °C)/EtOAc = 50:1, v/v). 72 mg, 99%; white solid, m.p.: 74−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.7, 5.3 Hz, 2 H), 7.22 (dd, *J* = 8.7, 5.3 Hz, 2 H), 7.08 (t, *J* = 8.6 Hz, 2 H), 7.01 (t, *J* = 8.6 Hz, 2 H), 5.61 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2 (d, *J* = 252.1 Hz), 163.7 (d, *J* = 251.1 Hz), 160.9, 134.9 (d, *J* = 3.1 Hz), 132.9 (d, *J* = 3.3 Hz), 131.7 (d, *J* = 8.6 Hz), 130.5 (d, *J* = 8.5 Hz), 117.7, 115.9 (d, *J* = 21.9 Hz), 115.9 (d, *J* = 21.9 Hz), and 94.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.32, -109.67.

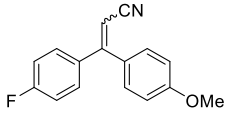


3,3-Bis(4-bromophenyl)acrylonitrile:[6] Following the general procedure, compound **2m** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 10:1, v/v). 64 mg, 59%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.55 (m, 2 H), 7.55–7.46 (m, 2 H), 7.36–7.27 (m, 2 H), 7.21–7.10 (m, 2 H), 5.74 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.8, 137.3, 135.4, 132.2, 132.1, 131.2, 130.0, 125.4, 124.9, 117.4, and 95.8.

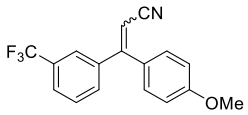


3,3-Bis(3-(trifluoromethyl)phenyl)acrylonitrile:[9] Following the general procedure, compound **2n** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 96 mg, 94%; white solid, m.p.: 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.61 (m, 5 H), 7.60–7.52 (m, 2 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 5.90 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 139.0, 137.2, 132.9, 131.8, 132.2–130.9 (m), 129.7 (d, *J* = 4.2 Hz), 127.7 (d, *J* = 6.5

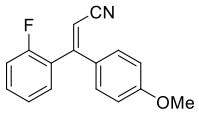
Hz), 127.5 (q, *J* = 3.6 Hz), 127.2 (q, *J* = 3.6 Hz), 126.3 (q, *J* = 3.8 Hz), 125.3–124.8 (m), 122.3 (d, *J* = 6.6 Hz), 119.6 (d, *J* = 6.5 Hz), 116.8, and 98.1. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.8, -62.9.



3-(4-Fluorophenyl)-3-(4-methoxyphenyl)acrylonitrile:[10] Following the general procedure, compound **2p** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 2:1, v/v). 47 mg, 62% (*E*/*Z* = 1.2:1); white solid, m.p.: 54–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.36 (m, 2 H), 7.33–7.27 (m, 1 H), 7.25–7.20 (m, 1 H), 7.13 (t, *J* = 8.6 Hz, 1 H), 7.06 (t, *J* = 8.6 Hz, 1 H), 6.96 (d, *J* = 8.8 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 1 H), 5.65 (s, 0.52 H), 5.56 (s, 0.47 H), 3.86 (s, 1.43 H), 3.84 (s, 1.57 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.06 (d, *J* = 249.9 Hz), 163.63 (d, *J* = 248.9 Hz), 161.7, 161.7, 161.6, 161.3, 135.6 (d, *J* = 3.4 Hz), 133.4 (d, *J* = 3.2 Hz), 131.7 (d, *J* = 8.5 Hz), 131.3, 131.0, 130.7 (d, *J* = 8.6 Hz), 130.1, 129.1, 118.4, 118.3, 115.8 (d, *J* = 21.7 Hz), 115.7 (d, *J* = 21.7 Hz), 114.2, 114.0, 93.3, 92.9, 55.5, and 55.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ ^{19}F NMR (376 MHz, CDCl3) δ -110.0, -110.4.

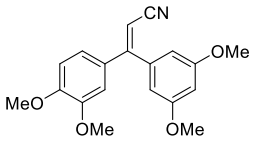


3-(4-Methoxyphenyl)-3-(3-(trifluoromethyl)phenyl)acrylonitrile: Following the general procedure, compound **2q** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 86 mg, 95%; white solid, m.p.: 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.36 (m, 6 H), 7.31 (d, *J* = 8.8 Hz, 0.72 H), 7.12 (d, *J* = 8.8 Hz, 1.28 H), 6.87 (d, *J* = 8.8 Hz, 0.72 H), 6.80 (d, *J* = 8.8 Hz, 1.28 H), 5.65 (s, 0.65 H), 5.53 (s, 0.35 H), 3.75 (s, 2 H), 3.72 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9, 161.4, 161.2, 161.0, 140.4, 138.2, 132.9, 132.0, 131.2 (q, *J* = 32.5 Hz), 131.0 (q, *J* = 32.5 Hz), 130.2, 129.9, 129.3, 128.5, 126.9 (q, *J* = 3.6 Hz), 126.6 (q, *J* = 3.6 Hz), 126.3 (q, *J* = 3.8 Hz), 125.3 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.9 Hz), 123.7 (q, *J* = 270.9 Hz), 117.9, 117.8, 114.4, 114.2, 94.9, 94.0, 55.5, and 55.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.6, 62.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3NO$ 304.0944; Found 304.0945.

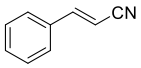


3-(2-Fluorophenyl)-3-(4-methoxyphenyl)acrylonitrile: Following the general procedure, compound **2r** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 45 mg, 58%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 1 H), 7.23 (td, *J* = 7.4, 1.7 Hz, 1 H), 7.18–7.09 (m, 3 H), 7.05 (t, *J* = 9.1 Hz, 1 H), 6.76 (d, *J* = 8.9 Hz, 2 H), 5.75 (s, 1 H), 3.68 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 160.7, 158.2, 156.5, 131.6 (d, *J* = 8.4 Hz), 131.2 (d, *J* = 2.7 Hz), 129.6, 128.9, 125.0 (d, *J* = 14.8 Hz), 124.4 (d, *J* = 3.7 Hz), 117.6, 116.4, 116.2, 114.2, 95.2, and 55.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

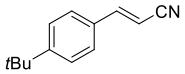
δ 112.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}FNO$ 254.0976; Found 254.0979.



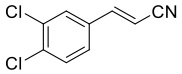
(*Z*)-3-(3,4-Dimethoxyphenyl)-3-(3,5-dimethoxyphenyl)acrylonitrile:[11] Following the general procedure, compound **2s** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 4:1, v/v). 94.3 mg, 97%; white solid, m.p.: 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.2 Hz, 1 H), 6.81 (d, *J* = 7.6 Hz, 2 H), 6.53 (s, 3 H), 5.65 (s, 1 H), 3.88 (s, 3 H), 3.81 (s, 3 H), 3.76 (s, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5, 160.6, 151.1, 148.8, 139.0, 131.0, 122.2, 118.1, 110.9, 110.7, 107.7, 102.1, 93.2, 56.0, and 55.5.



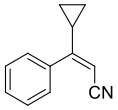
Cinnamonitrile:[12] Following the general procedure, compound **2t** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 25:1, v/v). 31 mg, 79%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.36 (m, 6 H), 5.88 (d, *J* = 16.7 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.6, 133.6, 131.3, 129.2, 127.4, 118.2, and 96.4.



(*E*)-3-(4-(*tert*-Butyl)phenyl)acrylonitrile:[13] Following the general procedure, compound **2u** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 30 mg, 53%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.45−7.35 (m, 5 H), 5.84 (d, *J* = 16.6 Hz, 1 H), 1.33 (s, 9 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.0, 150.4, 130.8, 127.3, 126.1, 118.5, 95.3, 35.0, and 31.1.

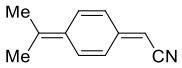


(*E*)-3-(3,4-Dichlorophenyl)acrylonitrile:[11] Following the general procedure, compound **2v** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 2:1, v/v). 40.1 mg, 67%; white solid, m.p.: 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.0 Hz, 1 H), 7.46 (d, *J* = 8.4 Hz, 1 H), 7.32–7.28 (m, 1 H), 7.26 (s, 1 H), 5.89 (d, *J* = 16.7 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 135.2, 133.5, 133.4, 131.1, 129.0, 126.4, 117.5, and 98.5.

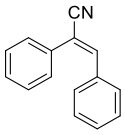


(*Z*)-3-Cyclopropyl-3-phenylacrylonitrile:[14] Following the general procedure, compound **2w** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 2:1, v/v). 42 mg, 83%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.36 (m, 5 H), 5.20 (s, 1 H), 1.85–1.69 (m, 1 H),

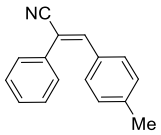
1.08–0.92 (m, 2 H), 0.80–0.62 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 167.9, 137.1, 129.4, 128.4, 127.6, 117.7, 92.1, 18.5, and 8.7.



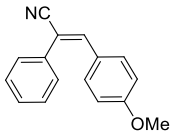
2-(4-(Propan-2-ylidene)cyclohexa-2,5-dien-1-ylidene)acetonitrile: Following the general procedure, compounds **2x** were obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 13 mg, 28%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 5.59 (d, *J* = 1.0 Hz, 1 H), 2.45 (d, *J* = 1.0 Hz, 3 H), 2.38 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 140.7, 135.3, 129.6, 125.8, 118.0, 94.5, 21.3, and 20.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}N$ 157.0891; Found 157.0889.



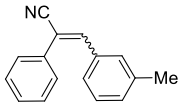
(*E*)-2,3-Diphenylacrylonitrile:[12] Following the general procedure, compound **4a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 54 mg, 88%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.21 (m, 6 H), 7.21–7.16 (m, 1 H), 7.13 (t, *J* = 7.4 Hz, 2 H), 7.06 (d, *J* = 7.3 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.2, 133.6, 132.7, 129.9, 129.8, 129.4, 129.1, 128.9, 128.6, 120.2, and 114.4.



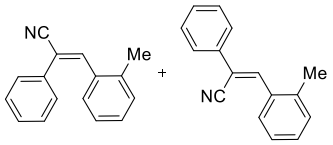
(*E*)-2-Phenyl-3-(*p*-tolyl)acrylonitrile: Following the general procedure, compound **4b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 40 mg, 97%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.19 (m, 5 H), 7.17 (s, 1 H), 6.90 (q, *J* = 8.4 Hz, 4 H), 2.17 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 140.4, 132.9, 130.7, 129.9, 129.3, 129.2, 129.1, 128.9, 120.4, 113.2, and 21.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}N$ 220.1121; Found 220.1123.



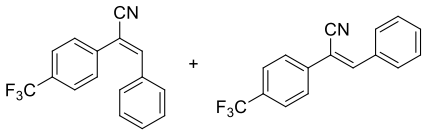
(*E*)-3-(4-Methoxyphenyl)-2-phenylacrylonitrile: Following the general procedure, compound **4c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 72 mg, 96%; white solid, m.p.: 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 5 H), 7.17 (s, 1 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 3.67 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 143.9, 133.2, 131.7, 129.2, 129.1, 128.9, 126.1, 120.7, 114.0, 111.5, and 55.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}NO$ 236.1070; Found 236.1071.



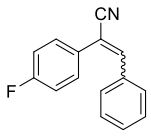
(*E*)-2-Phenyl-3-(*m*-tolyl)acrylonitrile: Following the general procedure, compound **4d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 3:1, v/v). 27.2 mg, 41%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.30 (m, 4.1 H), 7.30–7.12 (m, 3.4 H), 7.10 (d, *J* = 4.9 Hz, 1.2 H), 6.88–7.02 (m, 1.3 H), 2.32 (s, 1.1 H), 2.23 (s, 1.9 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.5, 144.1, 139.1, 138.4, 133.7, 133.6, 132.9, 132.6, 130.8, 130.7, 130.1, 129.9, 129.9, 129.4, 129.3, 129.1, 129.0, 129.0, 128.6, 128.5, 126.9, 126.0, 120.4, 114.6, 114.2, 21.4, and 21.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}N$ 220.1121; Found 220.1123.



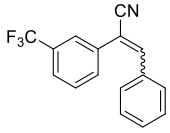
(*E*)-2-Phenyl-3-(*o*-tolyl)acrylonitrile and (*Z*)-2-phenyl-3-(*o*-tolyl)acrylonitrile:[15] Following the general procedure, compound **4e** and **4e'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/Et_2O = 50:1, v/v). 18.0 mg, 27%; colorless liquid, and 6.9 mg, 10%; colorless liquid. **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1 H), 7.26–7.15 (m, 5 H), 7.15–7.06 (m, 2 H), 6.95–6.82 (m, 2 H), 2.24 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.3, 137.1, 133.2, 132.4, 130.7, 129.6, 129.2, 129.0, 128.9, 128.8, 125.9, 120.1, 115.6, and 20.0. **4e'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1 H), 7.26–7.03 (m, 7 H), 6.91 (d, *J* = 7.6 Hz, 2 H), 2.20 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.4, 136.4, 133.7, 132.4, 131.1, 130.2, 129.9, 129.6, 129.2, 128.7, 127.0, 119.8, 113.1, and 19.5.



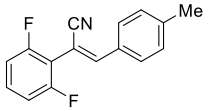
(*E*)-3-Phenyl-2-(4-(trifluoromethyl)phenyl)acrylonitrile and (*Z*)-3-Phenyl-2-(4-(trifluoromethyl)phenyl)acrylonitrile:[15] Following the general procedure, compound **4f** and **4f'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 46 mg, 56%; white solid, m.p.: 81–83 ^{o}C, and 35 mg, 43%; white solid, m.p.: 133–134 ^{o}C. **4f:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 7.36 (s, 1 H), 7.25–7.19 (m, 1 H), 7.19–7.12 (m, 3 H), 7.04 (d, *J* = 7.4 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.8, 136.4, 133.0, 131.3 (q, *J* = 32.8 Hz), 130.4, 129.8, 129.5, 128.9, 126.1 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.4 Hz), 119.6, and 113.0. **4f':** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.86 (m, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 2 H), 7.62 (s, 1 H), 7.58–7.40 (m, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 138.0, 133.3, 131.3, 131.1 (q, *J* = 32.9 Hz), 129.6, 129.2, 126.4, 126.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 270.6 Hz), 117.6, and 110.3.



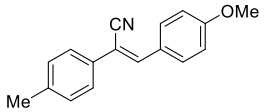
2-(4-Fluorophenyl)-3-phenylacrylonitrile:[15] Following the general procedure, compound **4g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 30:1, v/v). 66 mg, 98%; white solid, m.p.: 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.23 (m, 6 H), 7.22–7.11 (m, 2 H), 7.07 (t, *J* = 8.5 Hz, 0.49 H), 6.94 (t, *J* = 8.6 Hz, 1.51 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 162.0, 161.8, 144.4, 142.9, 133.4, 132.5, 131.9 (d, *J* = 8.3 Hz), 130.9 (d, *J* = 8.4 Hz), 130.0, 129.7 (d, *J* = 3.0 Hz), 129.5, 129.3, 128.8, 128.7, 120.0 (d, *J* = 8.2 Hz), 116.4, 116.2, 115.9, 115.7, 114.2, and 113.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.1, -110.8.



3-Phenyl-2-(3-(trifluoromethyl)phenyl)acrylonitrile:[16] Following the general procedure, compound **4h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 58 mg, 71%; white solid, m.p.: 46–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2 H), 7.60 (d, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.49 (s, 1 H), 7.35 (t, *J* = 7.3 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 2 H), 7.16 (d, *J* = 7.5 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.8, 133.6, 133.0, 132.4, 131.7 (q, *J* = 32.8 Hz), 130.5, 129.8 (d, *J* = 2.2 Hz), 128.9, 126.2 (q, *J* = 3.7 Hz), 126.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.9 Hz), 119.6, and 112.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.7, -62.9.

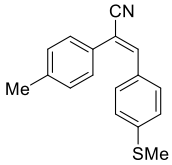


(*Z*)-2-(2,6-Difluorophenyl)-3-(*p*-tolyl)acrylonitrile: Following the general procedure, compound **4j** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 33 mg, 43%; yellow solid, m.p.: 86–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1 H), 7.41 (ddd, *J* = 14.7, 8.3, 6.5 Hz, 1 H), 7.15–6.91 (m, 6 H), 2.32 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 6.4 Hz), 159.0 (d, *J* = 6.3 Hz), 149.7, 141.6, 131.7 (t, *J* = 10.0 Hz), 130.9, 129.7, 129.3, 129.0, 118.8, 112.3 (dd, *J* = 19.6, 5.2 Hz), 110.6 (t, *J* = 19.6 Hz), 99.6, and 21.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{12}F_2N$ 256.0932; Found 256.0930.

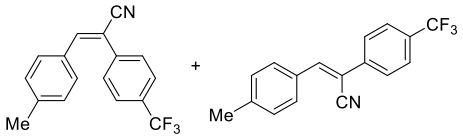


(*Z*)-3-(4-Methoxyphenyl)-2-(*p*-tolyl)acrylonitrile:[17] Following the general procedure, compound **4k** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 67 mg, 92%; colorless liquid.

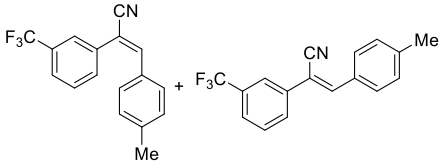
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2 H), 7.24 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 6.76 (d, *J* = 8.9 Hz, 2 H), 3.79 (s, 3 H), 2.39 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.8, 143.4, 139.2, 131.7, 130.2, 129.8, 128.7, 126.3, 120.8, 114.0, 111.6, 55.3, and 21.4.



(*Z*)-3-(4-(Methylthio)phenyl)-2-(*p*-tolyl)acrylonitrile: Following the general procedure, compound **4l** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 63 mg, 80%; yellow solid, m.p.: 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.1 Hz, 2 H), 7.11 (s, 1 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 6.96 (q, *J* = 8.6 Hz, 4 H), 2.32 (s, 3 H), 2.26 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.9, 141.6, 139.3, 130.1, 129.9, 129.9, 129.8, 128.6, 125.3, 120.5, 113.1, 21.4, and 14.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}NS$ 266.0998; Found 266.1002.

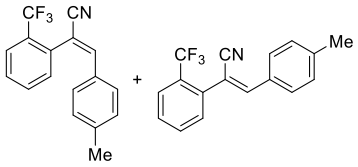


(*E*)-3-(*p*-Tolyl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile and (*Z*)-3-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile: Following the general procedure, compound **4m** and **4m1** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 42 mg, 49%; white solid, m.p.: 76–77 °C, and 41 mg, 48%; white solid, m.p.: 146–148 °C. **4m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2 H), 7.42 (d, *J* = 8.2 Hz, 2 H), 7.32 (s, 1 H), 6.96 (q, *J* = 8.4 Hz, 4 H), 2.23 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.9, 141.1, 136.7, 131.1 (q, *J* = 32.7 Hz), 130.2, 129.9, 129.6, 126.1 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 270.7 Hz), 119.8, 111.8, and 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.8. **4m1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2 H), 7.67 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.47 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 142.1, 138.2, 130.9 (q, *J* = 32.8 Hz), 130.6, 129.9, 129.7, 126.3, 126.1 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.2 Hz), 117.8, 109.0, and 21.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3N$ 288.0995; Found 288.0996.

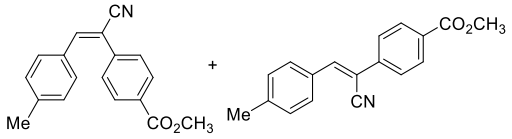


(*E*)-3-(*p*-Tolyl)-2-(3-(trifluoromethyl)phenyl)acrylonitrile and (*Z*)-3-(*p*-tolyl)-2-(3-(trifluoromethyl)phenyl)acrylonitrile: Following the general procedure, compound **4n** and **4n'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 58 mg, 67%; white solid, m.p.: 64–65 °C, and 27 mg, 31%; white solid, m.p.: 88–89 °C. **4n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1 H),

7.72 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 7.57 (t, *J* = 7.8 Hz, 1 H), 7.49 (s, 1 H), 7.13 (q, *J* = 8.4 Hz, 4 H), 2.40 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.8, 141.2, 133.9, 132.4, 131.7 (q, *J* = 32.8 Hz), 130.1, 129.9, 129.8, 129.6, 126.0 (dq, *J* = 7.8, 3.7 Hz), 125.0, 123.9 (q, *J* = 270.9 Hz), 119.9, 111.6, and 21.5. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.9. **4n'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1 H), 7.93 (t, *J* = 8.7 Hz, 3 H), 7.73 (d, *J* = 7.6 Hz, 1 H), 7.70–7.58 (m, 2 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 2.51 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 142.0, 135.7, 131.7 (q, *J* = 32.7 Hz), 130.6, 129.9, 129.8, 129.7, 129.4, 125.7 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.9 Hz), 122.7 (q, *J* = 3.8 Hz), 117.9, 109.0, and 21.7. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3N$ 288.0995; Found 288.0996.

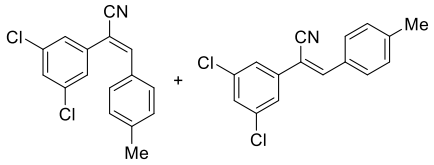


(E)-3-(*p*-Tolyl)-2-(2-(trifluoromethyl)phenyl)acrylonitrile: Following the general procedure, compound **4o** and **4o'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 32 mg, 38%; yellow liquid, and 21 mg, 25%; yelllow solid, m.p.: 72–74 °C. **4o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.62 (m, 4 H), 7.58 (d, *J* = 7.7 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 7.7 Hz, 1 H), 7.27 (s, 1 H), 7.17 (d, *J* = 16.6 Hz, 1 H), 2.45 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.0, 139.7, 137.8, 135.3, 134.8, 131.8, 130.3 (q, *J* = 32.5 Hz), 127.8, 127.2, 126.1, 125.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.2 Hz), 122.9, 119.1, 111.2, and 20.7. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.6. **4o'**: 8.06 (d, *J* = 7.8 Hz, 1 H), 7.89 (d, *J* = 2.0 Hz, 1 H), 7.77 (d, *J* = 7.8 Hz, 1 H), 7.68 (t, *J* = 7.7 Hz, 1 H), 7.62 (d, *J* = 8.3 Hz, 2 H), 7.54 (t, *J* = 7.7 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 2.42 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 137.1 (d, *J* = 1.2 Hz), 132.7 (d, *J* = 1.7 Hz), 132.3, 130.6, 130.0, 129.9, 129.6, 128.7 (q, *J* = 30.0 Hz), 126.2 (q, *J* = 5.4 Hz), 126.2, 124.0 (q, *J* = 272.2 Hz), 117.2, 116.6, and 21.3. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -59.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3N$ 288.0995; Found 288.0997.

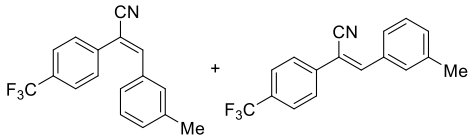


Methyl (*E*)-4-(1-cyano-2-(*p*-tolyl)vinyl)benzoate and methyl (*Z*)-4-(1-cyano-2-(*p*-tolyl)vinyl)benzoate: Following the general procedure, compound **4p** and **4p'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 58 mg, 70%; white solid, m.p.: 96–99 °C. 13 mg, 10%; white solid, m.p.: 112–114 °C. **4p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 7.31 (s, 1 H), 6.95 (s, 4 H), 3.85 (s, 3 H), 2.23 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.4, 145.7, 141.0, 137.6, 130.8, 130.4, 130.3, 129.9, 129.5, 129.1, 119.9, 112.3, 52.4, and 21.5. **4p'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2 H), 7.83 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.5 Hz, 2 H), 7.60 (s,

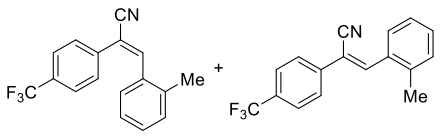
1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 3.94 (s, 3 H), 2.42 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 144.1, 142.0, 139.0, 130.8, 130.5, 130.4, 129.9, 129.7, 125.9, 117.9, 109.6, 52.4, and 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2$ 278.1176; Found 278.1175.



(*E*)-2-(3,5-Dichlorophenyl)-3-(*p*-tolyl)acrylonitrile and (*Z*)-2-(3,5-dichlorophenyl)-3-(*p*-tolyl)acrylonitrile: Following the general procedure, compound **4q** and **4q'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 77 mg, 89%; white solid, m.p.: 89–90 °C. and 8 mg, 9%; white solid, m.p.: 134–135 °C. **4q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2 H), 7.45 (d, *J* = 1.6 Hz, 2 H), 7.41 (s, 1 H), 7.27 (s, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 2.34 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 142.3, 137.7, 135.9, 130.3, 130.0, 129.8, 128.9, 124.4, 117.5, 107.8, and 21.8. **4q'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2 H), 7.20 (d, *J* = 1.8 Hz, 2 H), 6.99 (q, *J* = 8.3 Hz, 4 H), 2.26 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 146.3, 141.5, 135.9, 135.9, 130.0, 129.8, 129.7, 129.5, 127.4, 119.5, 110.3, and 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{12}Cl_2N$ 288.0341; Found 288.0343.

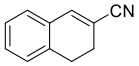


(*E*)-3-(*m*-Tolyl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile and (*Z*)-3-(*m*-tolyl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile: Following the general procedure, compound **4r** and **4r'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 35 mg, 41%; white solid, m.p.: 63–64 °C, and 31 mg, 36%; white solid, m.p.: 87–88 °C. **4r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.2 Hz, 2 H), 7.35 (s, 1 H), 7.05 (d, *J* = 5.2 Hz, 2 H), 6.89 (s, 1 H), 6.83 (d, *J* = 3.9 Hz, 1 H), 2.17 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 146.2, 138.7, 136.6, 133.0, 131.5, 131.3, 130.7, 129.6, 128.8, 126.8, 126.1 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.5 Hz), 119.7, 112.8, and 21.3. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.9. **4r'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.55 (m, 6 H), 7.50 (s, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.24–7.14 (m, 1 H), 2.34 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.5, 139.0, 138.1, 133.3, 132.2, 131.1 (q, *J* = 32.7 Hz), 130.3, 129.1, 126.7, 126.4, 126.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 270.6 Hz), 117.7, 110.0, and 21.5. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3N$ 288.0995; Found 288.0991.

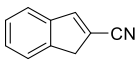


(*E*)-3-(*o*-Tolyl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile and (*Z*)-3-(*o*-tolyl)-2-(4-

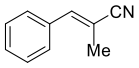
(trifluoromethyl)phenyl)acrylonitrile: Following the general procedure, compound **4s** and **4s'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 17 mg, 20%; white solid, m.p.: 66–67 °C, and 14 mg, 16%; white solid, m.p.: 103–105 °C. **4s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1 H), 7.45 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.17 (d, *J* = 3.8 Hz, 2 H), 6.97–6.89 (m, 1 H), 6.83 (d, *J* = 7.7 Hz, 1H), 2.27 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.3, 137.2, 136.0, 132.5, 131.1 (q, *J* = 32.6 Hz), 130.9, 130.1, 129.4, 128.9, 126.2, 125.8 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.5 Hz), 119.4, 114.3, and 20.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.5. **4s'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 1 H), 7.90 (s, 1 H), 7.83 (d, *J* = 8.2 Hz, 2 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.47–7.25 (m, 3 H), 2.45 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.1, 137.9, 137.8, 132.6, 131.0 (q, *J* = 32.6 Hz), 130.8, 130.7, 128.1, 126.5, 126.4, 126.1 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 270.4 Hz), 117.3, 112.4, and 19.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3N$ 288.0995; Found 288.0998.



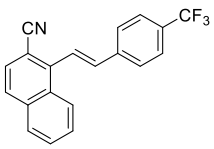
3,4-Dihydronaphthalene-2-carbonitrile:[18] Following the general procedure, compound **4t** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 4:1, v/v). 46 mg, 99%; yellow solid, m.p.: 55–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.11 (m, 2 H), 7.11–6.95 (m, 3 H), 2.80 (t, *J* = 8.3 Hz, 2 H), 2.43 (td, *J* = 8.3, 1.4 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.7, 135.4, 131.2, 130.3, 128.0, 127.2, 119.7, 109.6, 26.7, and 24.7.



1*H*-indene-2-carbonitrile:[19] Following the general procedure, compound **4u** was obtained by thin layer chromatography (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 23.6 mg, 56%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 7.54–7.50 (m, 2 H), 7.43–7.35 (m, 2 H), 3.69 (d, *J* = 1.5 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.3, 143.2, 141.5, 128.5, 127.6, 124.2, 123.4, 117.2, 114.3, and 41.0.

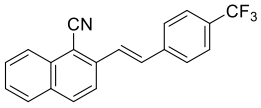


(*E*)-2-Methyl-3-phenylacrylonitrile:[13] Following the general procedure, compound **4v** was obtained by thin layer chromatography (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 26.8 mg, 62%; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.35 (m, 3 H), 7.35–7.29 (d, *J* = 8.4 Hz, 2 H), 7.20 (s, 1 H), 2.14 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.4, 134.0, 129.3, 129.3, 128.7, 121.3, 109.6, and 16.8.

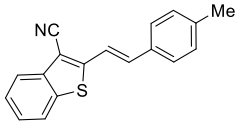


(*E*)-1-(4-(Trifluoromethyl)styryl)-2-naphthonitrile: Following the general

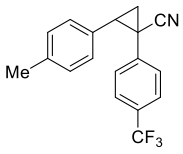
procedure, compound **6a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 50.7 mg, 52%; yellow solid, m.p.: 129–130 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (t, *J* = 7.0 Hz, 2 H), 7.93 (d, *J* = 11.6 Hz, 1 H), 7.90 (d, *J* = 3.0 Hz, 1 H), 7.76 (d, *J* = 7.6 Hz, 1 H), 7.74–7.62 (m, 6 H), 7.24 (d, *J* = 16.0 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 139.8, 133.3, 132.8, 132.4, 131.0, 130.4 (q, *J* = 32.6 Hz), 128.7, 127.9, 127.3, 126.8, 126.1, 126.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.4 Hz), 124.5, 122.9, 118.1, and 110.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{13}F_3N$ 324.0995; Found 324.0990.



(*E*)-2-(4-(Trifluoromethyl)styryl)-1-naphthonitrile: Following the general procedure, compound **6b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 96 mg, 99%; white solid, m.p.: 154–156 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1 H), 7.97 (d, *J* = 8.8 Hz, 1 H), 7.79–7.89 (m, 2 H), 7.73–7.59 (m, 6 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.34 (d, *J* = 16.2 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.7, 139.5, 133.0, 132.9, 132.5, 132.3, 130.5 (q, *J* = 32.4 Hz), 129.1, 128.5, 127.7, 127.4, 127.1, 125.9 (q, *J* = 3.7 Hz), 125.6, 124.1 (q, *J* = 270.2 Hz), 121.8, 116.7, and 108.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{13}F_3N$ 324.0995; Found 324.0990.

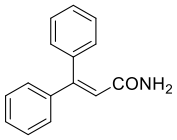


(*E*)-2-(4-Methylstyryl)benzo[*b*]thiophene-3-carbonitrile: Following the general procedure, compound **6c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 62 mg, 75%; yellow solid, m.p.: 150–151 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.49–7.31 (m, 5 H), 7.23–7.09 (m, 3 H), 2.36 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.0, 139.9, 138.1, 136.5, 136.1, 132.5, 129.7, 127.4, 126.4, 126.0, 122.4, 122.2, 117.9, 114.5, 103.9, and 21.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}NS$ 276.0841; Found 276.0849.

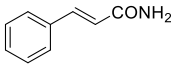


2-(*p*-Tolyl)-1-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbonitrile: Following the general procedure, compound **7** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 35:1, v/v). 68 mg, 75%; white solid, m.p.: 108–109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2 H), 7.47 (d, *J* = 8.3 Hz, 2 H), 7.21 (s, 4 H), 2.80 (t, *J* = 8.5 Hz, 1 H), 2.36 (s, 3 H), 2.26 (dd, *J* = 7.7, 6.7 Hz, 1 H), 2.03 (dd, *J* = 9.0, 6.4 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

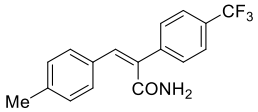
140.5, 138.1, 131.3, 129.9 (q, J = 32.8 Hz), 129.6, 128.0, 126.1 (q, J = 3.7 Hz), 125.7, 124.0 (q, J = 270.5 Hz), 119.4, 36.4, 23.8, 22.6, and 21.2. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}F_3N$ 302.1151; Found 302.1154.



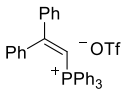
3,3-Diphenylacrylamide:[20] Following the general procedure, compound **8a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 1:1, v/v). 48 mg, 72%; white solid, m.p.: 146–147 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (m, 3 H), 7.28–7.06 (m, 7 H), 6.28 (s, 1 H), 5.97 (s, 1 H), 5.11 (s, 1 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.8, 151.1, 140.7, 138.2, 129.3, 129.1, 128.9, 128.8, 128.5, 128.01, and 121.8.



Cinnamamide:[20] Following the general procedure, compound **8b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 1:1, v/v). 35 mg, 78%; white solid, m.p.: 143–144 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 15.7 Hz, 1 H), 7.51 (dd, J = 6.6, 2.9 Hz, 2 H), 7.44–7.29 (m, 3 H), 6.47 (d, J = 15.7 Hz, 1 H), 5.87 (d, J = 67.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.1, 142.6, 134.6, 130.1, 129.0, 128.1, and 119.7.



(*Z*)-3-(*p*-Tolyl)-2-(4-(trifluoromethyl)phenyl)acrylamide: Following the general procedure, compound **9** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 4:1, v/v). 59 mg, 65%; white solid, m.p.: 180–181 °C. ^1H NMR (400 MHz, DMSO-d6) δ 7.91 (s, 1 H), 7.89 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.3 Hz, 2 H), 7.56 (s, 1 H), 7.38 (d, J = 7.9 Hz, 2 H), 7.19 (d, J = 7.8 Hz, 2 H), 4.33 (s, 1 H), 2.32 (s, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO) δ 167.0, 140.9, 137.7, 131.1, 129.2 (q, J = 31.7 Hz), 128.7, 127.7, 126.4, 125.3 (q, J = 3.6 Hz), 124.2 (q, J = 270.4 Hz), 66.5, 66.0, and 20.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}F_3NO$ 306.1100; Found 306.1104.



(2,2-Diphenylvinyl)triphenylphosphonium trifluoromethanesulfonate: Following the general procedure, compound **Int-P** was obtained by column chromatography on silica gel (CH_2Cl_2/methanol = 20:1, v/v). 128 mg, 72%; white solid, m.p.: 144–145 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76–7.67 (m, 3 H), 7.67–7.52 (m, 12 H), 7.50–7.38 (m, 5 H), 7.14 (t, J = 7.5 Hz, 1 H), 7.03 (d, J = 18.0 Hz, 1 H), 6.94 (t, J = 7.7 Hz, 2 H), 6.77 (d, J = 7.4 Hz, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7 (d, J = 2.3 Hz), 139.6 (d, J = 17.0 Hz), 135.8 (d, J = 6.7 Hz), 134.7 (d, J = 2.9 Hz), 133.3 (d, J = 10.5

Hz), 131.9, 131.9 (t, J = 9.8 Hz), 130.4, 130.3, 129.9, 128.9, 128.9, 128.8, 128.5, 128.4, 128.4, 120.9 (q, J = 321.1 Hz), 119.4 (d, J = 90.3 Hz), and 102.5 (d, J = 93.0 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -78.0. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 13.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{32}H_{26}P$ 441.1767; Found 441.1770.

5. References

1 Y. He, Z. L. Huang, J. Ma, J. Lin, Y.-G. Zhou and Z. K. Yu, Transition-Metal-Free Olefinic C–H Azidoalkylthiolation *via* C(sp^3)–S Bond Cleavage of Vinylsulfonium Salts, *Adv. Synth. Catal.*, 2022, **364**, 3023–3034.

2 (a) A. Desaintjean, S. Belrhomari, L. Rousseau, G. Lefevre and P. Knochel, Iron-Catalyzed Cross-Coupling of Functionalized Benzylmanganese Halides with Alkenyl Iodides, Bromides, and Triflates, *Org. Lett.*, 2019, **21**, 8684–8688; (b) J. Lin, Z. L. Huang, J. Ma, B.-H. Xu, Y.-G. Zhou, and Z. K. Yu, Tunable Construction of Multisubstituted 1,3-Dienes and Allenes *via* a 1,4-Palladium Migration/Carbene Insertion Cascade, *J. Org. Chem.*, 2022, **87**, 12019–12035.

3 Y.-L. Zhang, L. Yang, J. Wu, C. Y. Zhu and P. Wang, Vinyl Sulfonium Salts as the Radical Acceptor for Metal-Free Decarboxylative Alkenylation, *Org. Lett.*, 2020, **22**, 7768–7772.

4 L.-H. Zou, B. Liu, C. Wang, Z. Y. Shao, J. Q. Zhou, A. D. Shao and J. Wen, Selective Synthesis of Alkyl Amines and *N*-Vinylazoles from Vinyl Sulfonium Salts with *N*-Nucleophiles, *Org. Chem. Front.*, 2022, **9**, 3231–3236.

5 X. S. Lu and Y. H. Huang, Stereospecific Cyanation of the Olefinic C–H Bond Enabled by 1,4-Rhodium Migration. *Org. Chem. Front.*, 2021, **8**, 3008–3013.

6 L. Hao, F. Wu, Z.-C. Ding, S.-X. Xu, Y.-L. Ma, L. Chen and Z.-P. Zhan, Synthesis of Acrylonitriles Through an $FeCl_3$-Catalyzed Domino Propargylic Substitution/ Aza-Meyer-Schuster Rearrangement Sequence, *Chem. Eur. J.*, 2012, **18**, 6453–6456.

7 Q. Z. Yan, D. Y. Kong, M. N. Li, G. H. Hou and G. F. Zi, Highly Efficient Rh-Catalyzed Asymmetric Hydrogenation of *α,β*-Unsaturated Nitriles, *J. Am. Chem. Soc.*, 2015, 137, 10177–10181.

8 S. Lucks and H. Brunner, *In Situ* Generated Palladium on Aluminum Phosphate as Catalytic System for the Preparation of *β,β*-Diarylated Olefins by Matsuda-Heck Reaction, *Org. Process Res. Dev.*, 2017, **21**, 1835–1842.

9 P. W. Groundwater and J. T. Sharp, Electrocyclic Aromatic Substitution by Nitrile Ylides to give 3*H*-2-Benzazepines: Substituent Effects and Mechanism, *Tetrahedron*, 1992, **48**, 7951–7964.

10 S. J. Taylor and M. R. Netherton, Synthesis of the Benzhydryl Motif *via* a Suzuki-Miyaura Coupling of Arylboronic Acids and 3-Chloroacrylonitriles, *J. Org. Chem.*, 2006, **71**, 397–400.

11 Y. C. Mu, T. T. Nguyen, M. J. Koh, R. R. Schrock and A. H. Hoveyda, *E*- and *Z*-, Di- and Tri-Substituted Alkenyl Nitriles Through Catalytic Cross-Metathesis, *Nat. Chem.*, 2019, **11**, 478–487.

12 W. Zhou, J. J. Xu, L. R. Zhang and N. Jiao, An Efficient Transformation from Benzyl or Allyl Halides to Aryl and Alkenyl Nitriles, *Org. Lett.*, 2010, **12**, 2888–2891.

13 P. K. Hota, G. Vijaykumar, A. Pariyar, S. C. Sau, T. K. Sen and S. K. Mandal, An Abnormal *N*-Heterocyclic Carbene-Based Palladium Dimer: Aqueous Oxidative Heck Coupling Under

Ambient Temperature, *Adv. Synth. Catal.*, 2015, **357**, 3162–3170.

14 J. B. Metternich, D. G. Artiukhin, M. C. Holland, M. Bremen-Kühne, J. Neugebauer and R. Gilmour, Photocatalytic *E*→*Z* Isomerization of Polarized Alkenes Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity, *J. Org. Chem.*, 2017, **82**, 9955−9977.

15 K. Paudel, S. Xu and K. Y. Ding, Switchable Cobalt-Catalyzed *α*-Olefination and *α*-Alkylation of Nitriles with Primary Alcohols, *Org. Lett.*, 2021, **23**, 5028–5032.

16 B. Zupancic and M. Kokalj, Aromatic *α,β*-Unsaturated Nitriles *via* Polyethylene Glycol-Catalyzed Two-Phase Aldol-Type Condensation, *Synthesis*, 1981, **11**, 913–915.

17 S. Raouafi, F. Aloui, A. Raouafi and B. B. Hassine, Synthesis and Characterization of Phenanthrene Derivatives for Optoelectronic Applications, *C. R. Chimie*, 2017, **20**, 697–703.

18 Y. Gan, G. N. Wang, X. Xie and Y. H. Liu, Nickel-Catalyzed Cyanation of Phenol Derivatives with $Zn(CN)_2$ Involving C–O Bond Cleavage, *J. Org. Chem.*, 2018, **83**, 14036–14048.

19 X. Wang and A. Studer, Metal-Free Direct C–H Cyanation of Alkenes, *Angew. Chem. Int. Ed.*, 2018, **57**, 11792–11796.

20 S. Ghosh and C. K. Jana, Aminofluorene-Mediated Biomimetic Domino Amination-Oxygenation of Aldehydes to Amides, *Org. Lett.*, 2016, **18**, 5788–5791.

6. Copies of NMR spectra

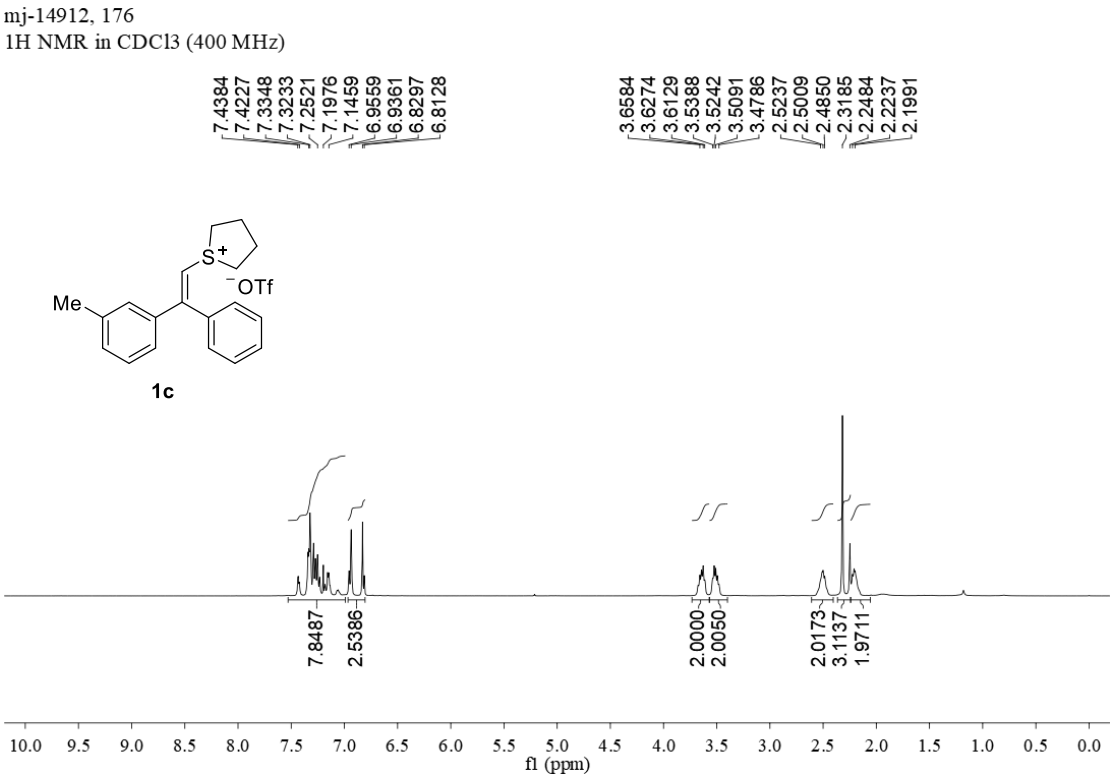


Figure S7. ^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 25 °C, 400 MHz).

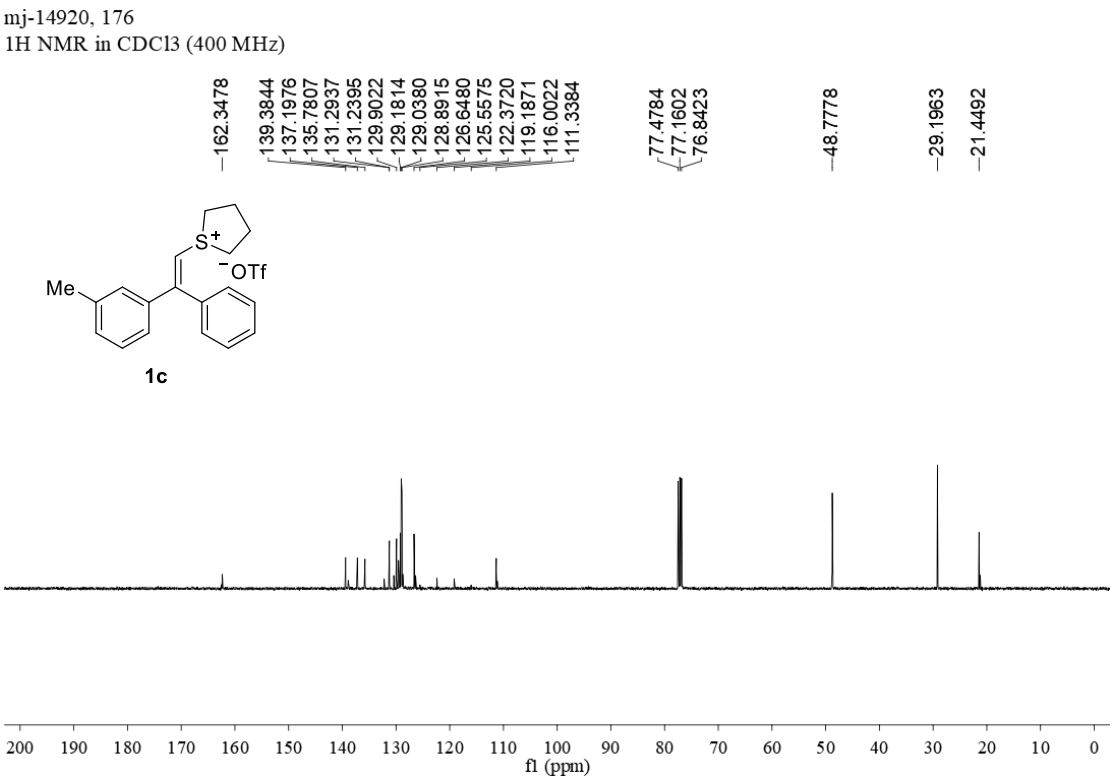


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1c** ($CDCl_3$, 25 °C, 100 MHz).

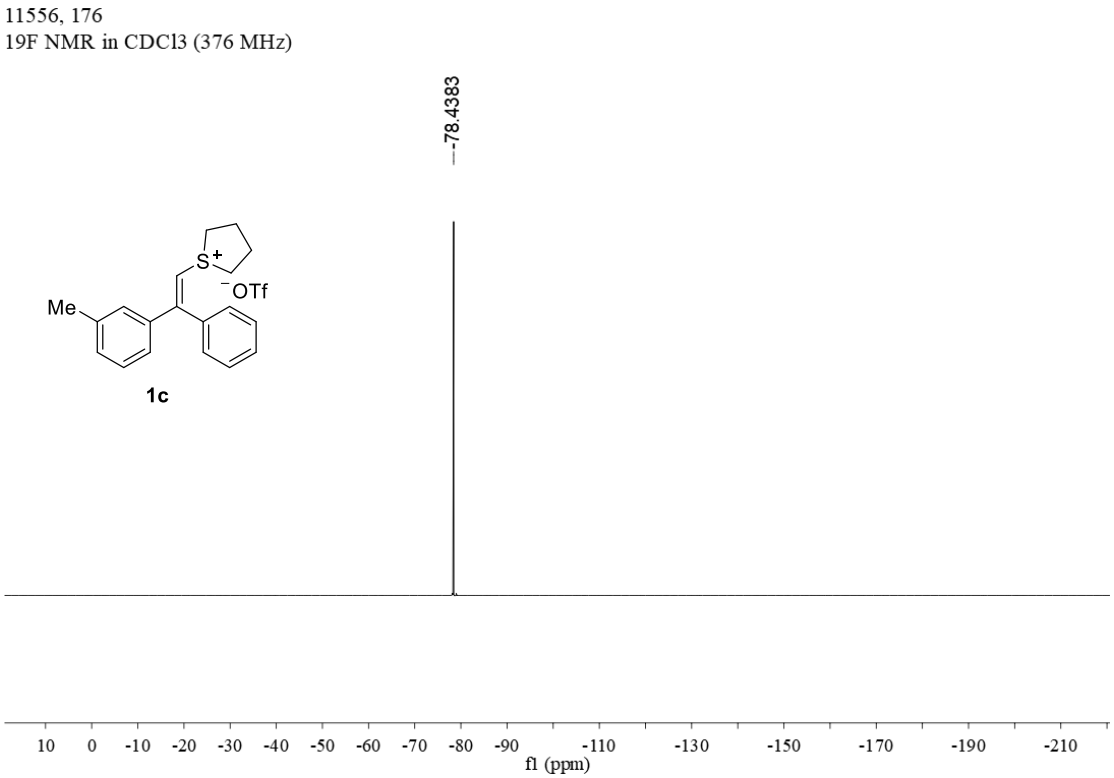


Figure S9. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1c** ($CDCl_3$, 25 °C, 376 MHz).

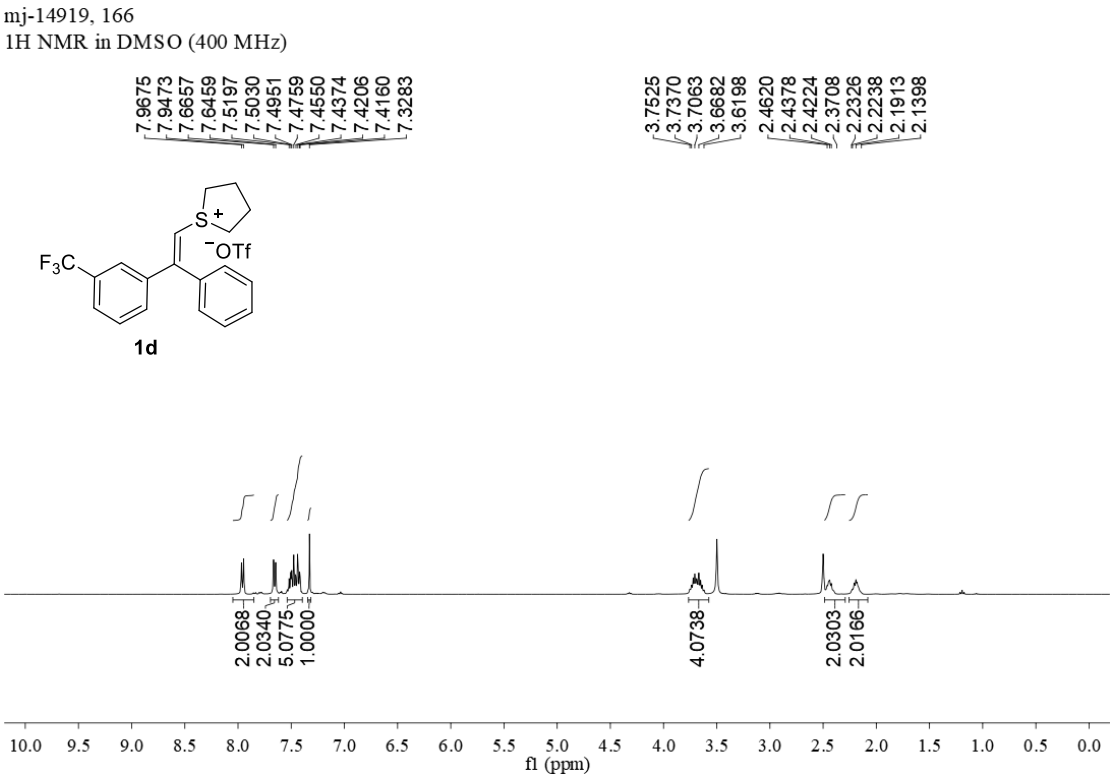


Figure S10. ^{1}H NMR spectrum of compound **1d** (DMSO-d_6, 25 °C, 400 MHz).

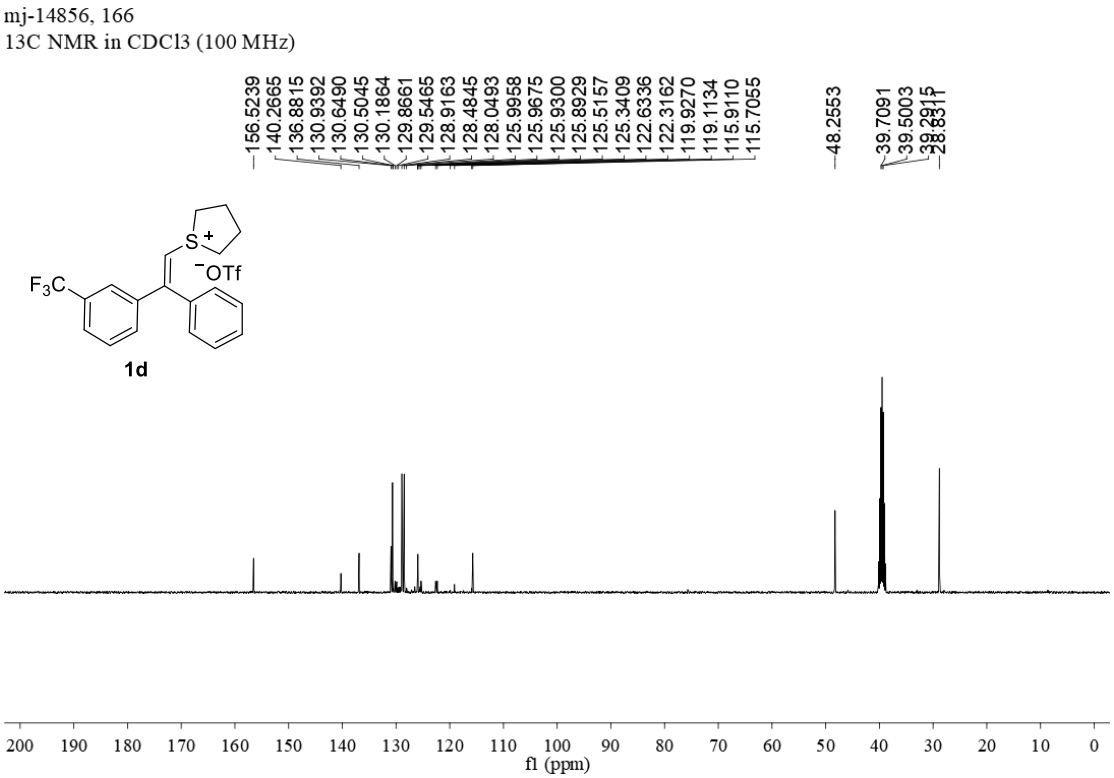


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1d** (DMSO-d_6, 25 °C, 100 MHz).

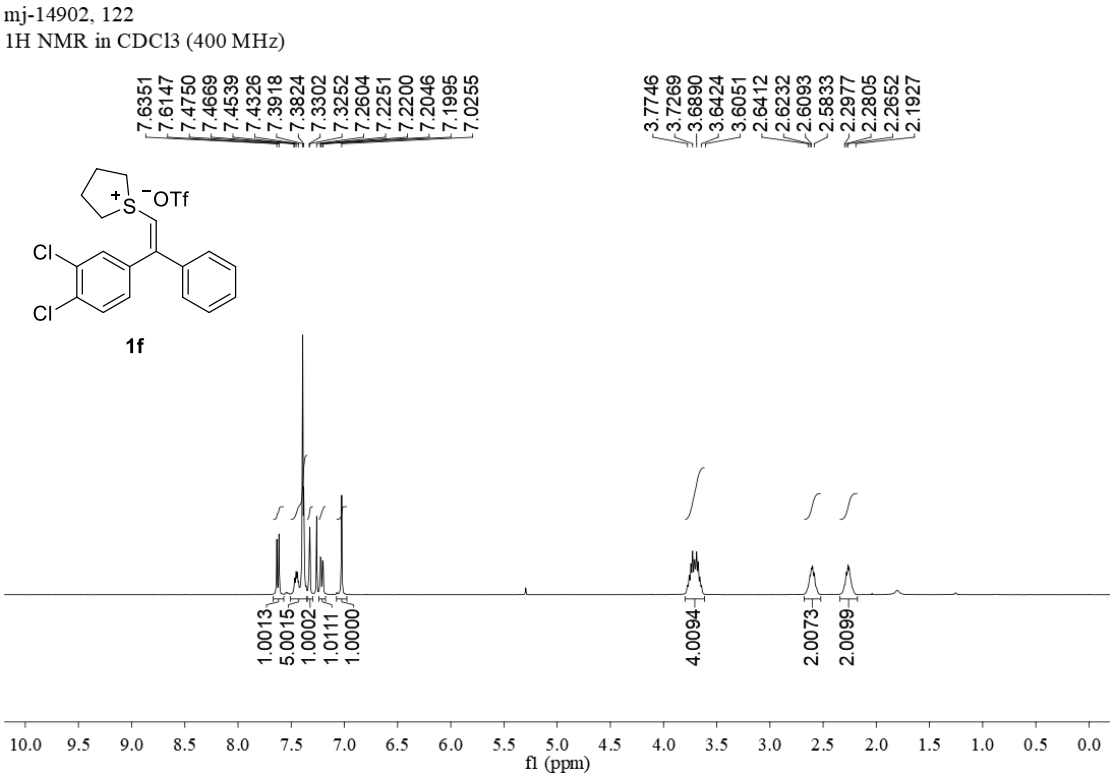


Figure S12. ^{1}H NMR spectrum of compound **1f** ($CDCl_3$, 25 °C, 400 MHz).

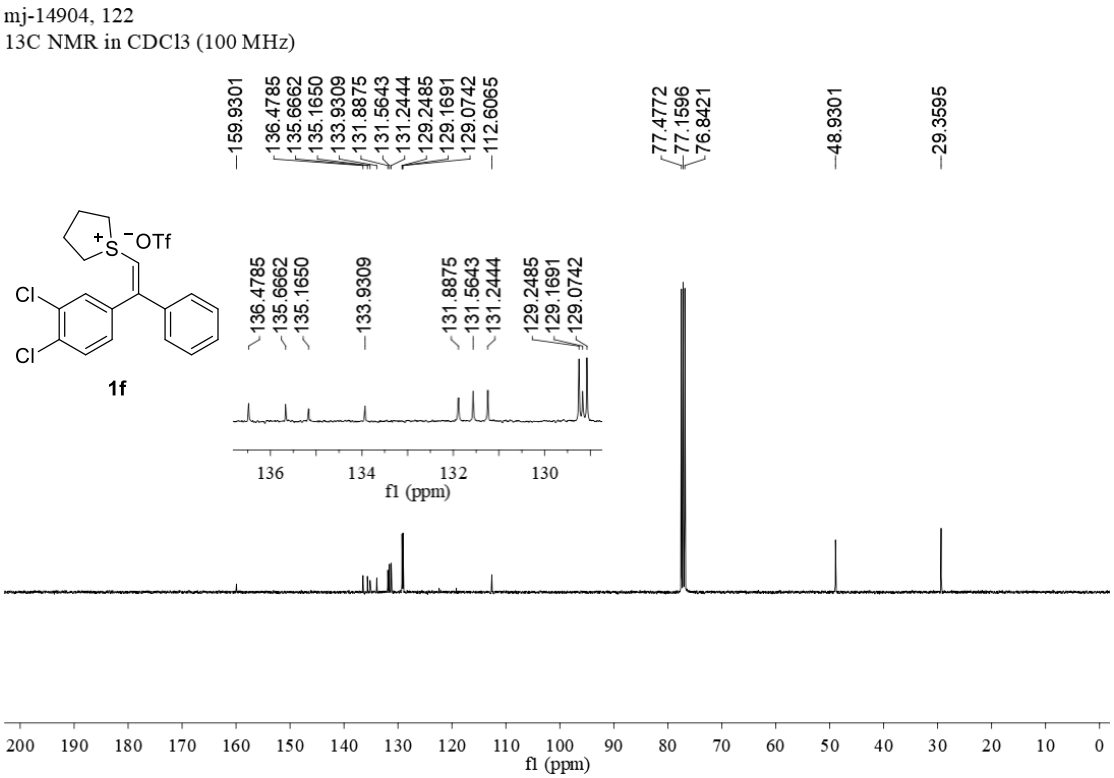


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** ($CDCl_3$, 25 °C, 100 MHz).

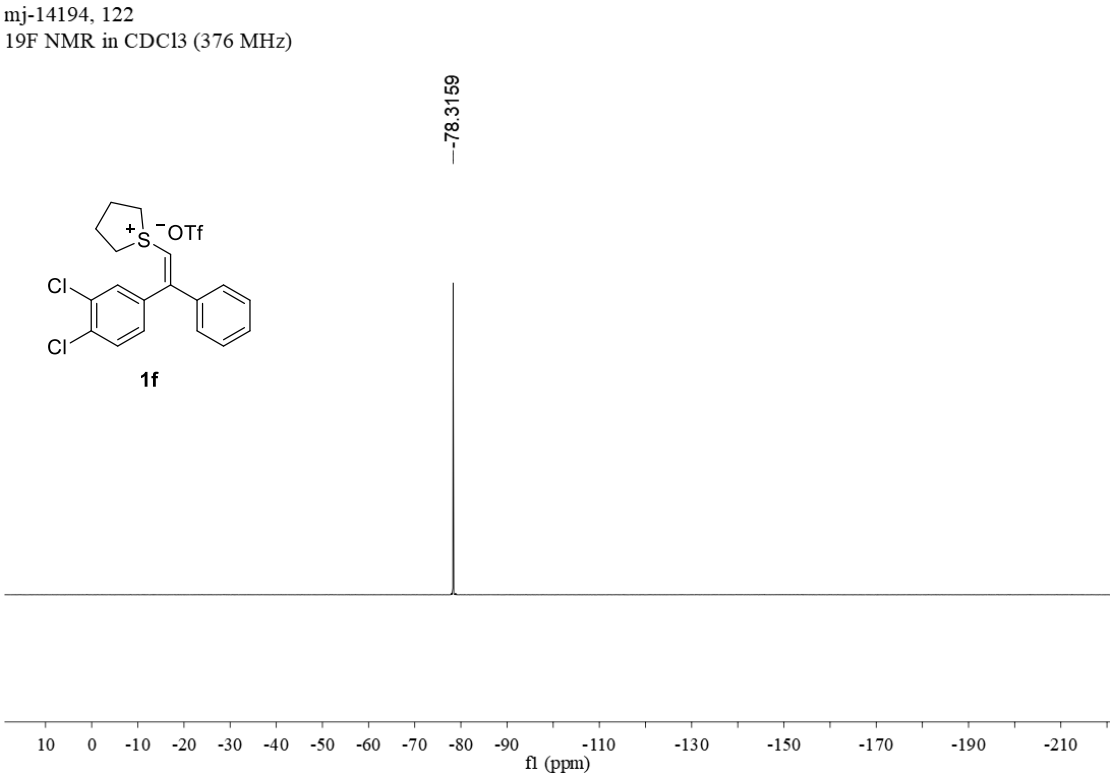


Figure S14. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1f** ($CDCl_3$, 25 °C, 376 MHz).

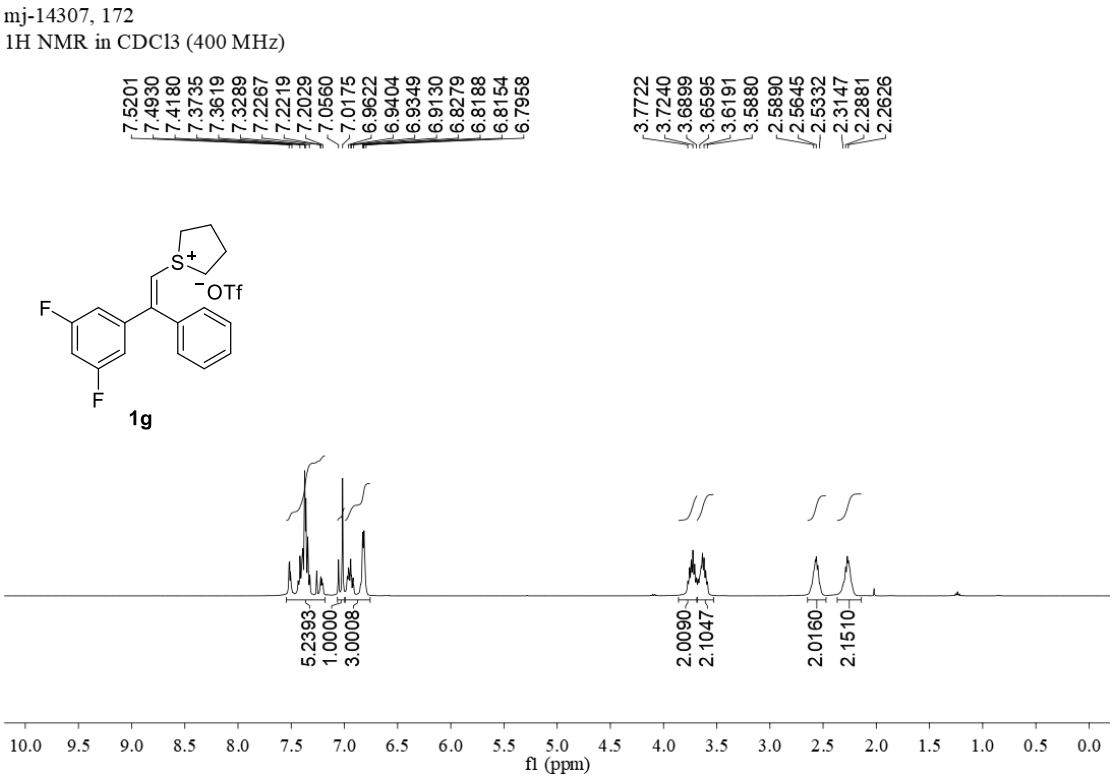


Figure S15. ^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 25 °C, 400 MHz).

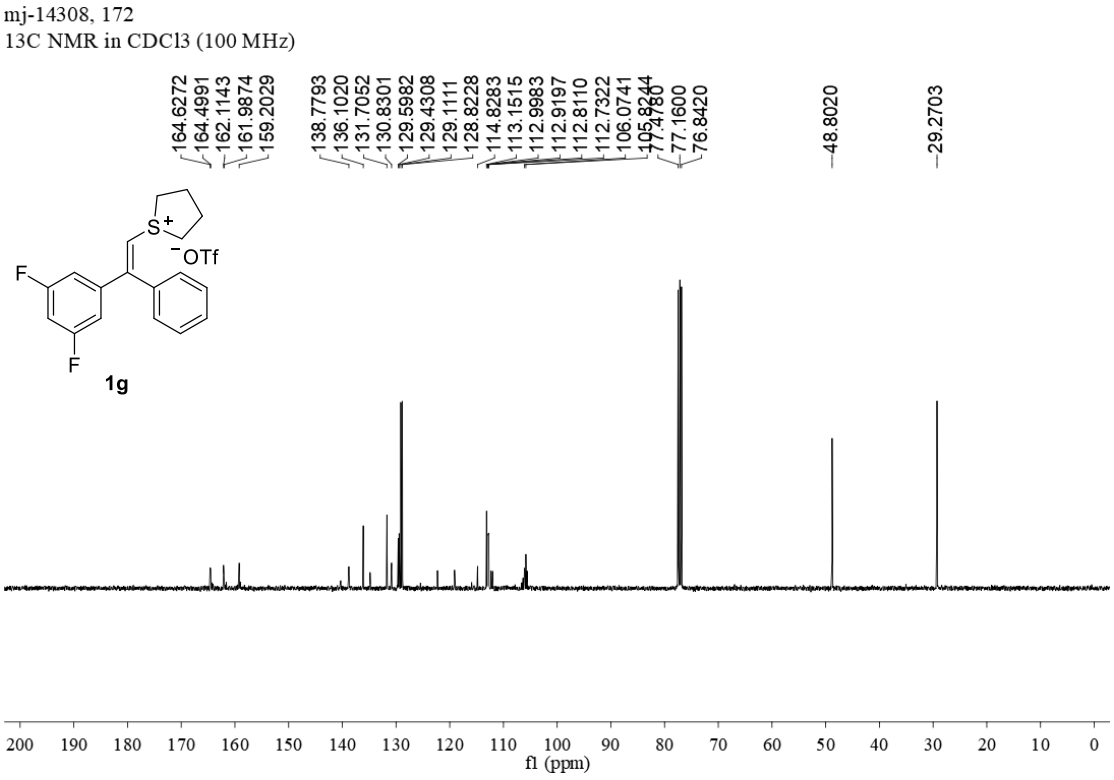


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1g** ($CDCl_3$, 25 °C, 100 MHz).

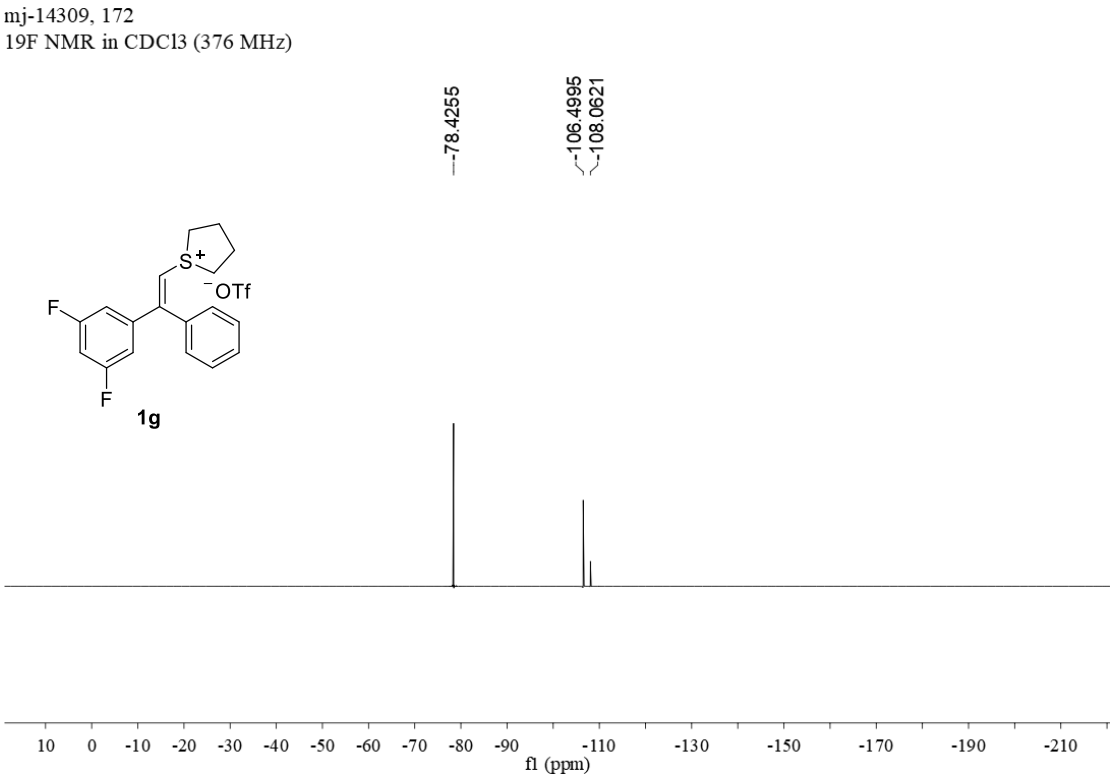


Figure S17. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1g** ($CDCl_3$, 25 °C, 376 MHz).

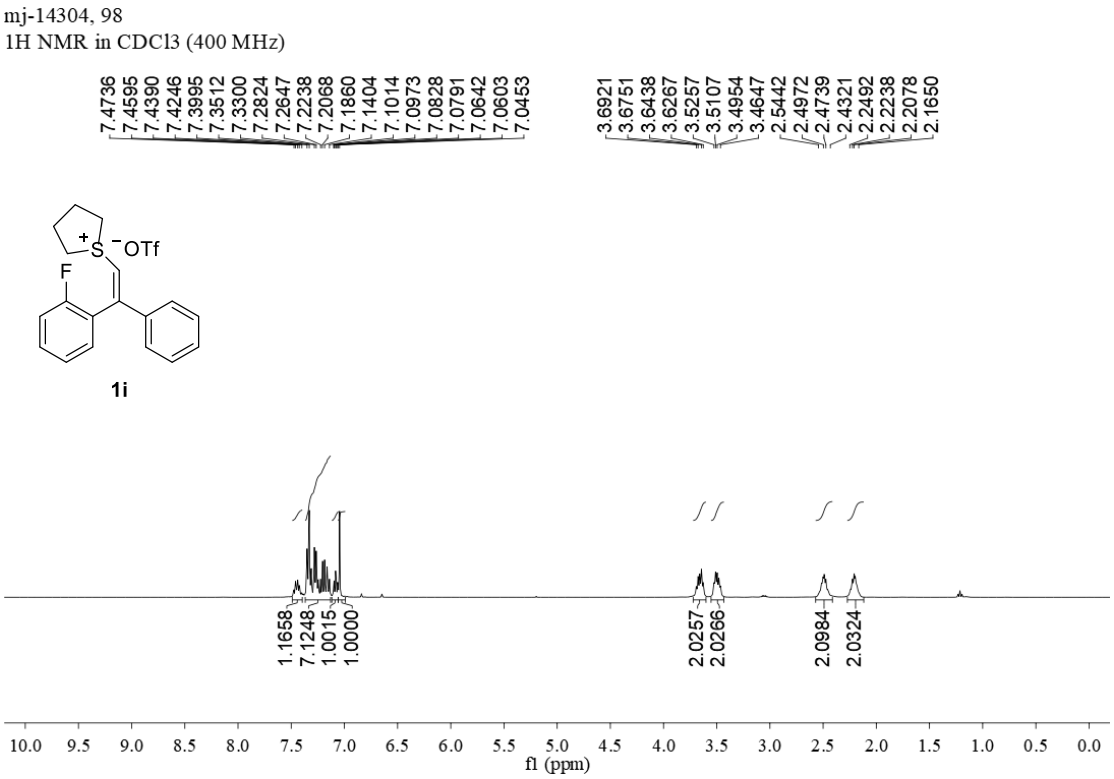


Figure S18. ^{1}H NMR spectrum of compound **1i** ($CDCl_3$, 25 °C, 400 MHz).

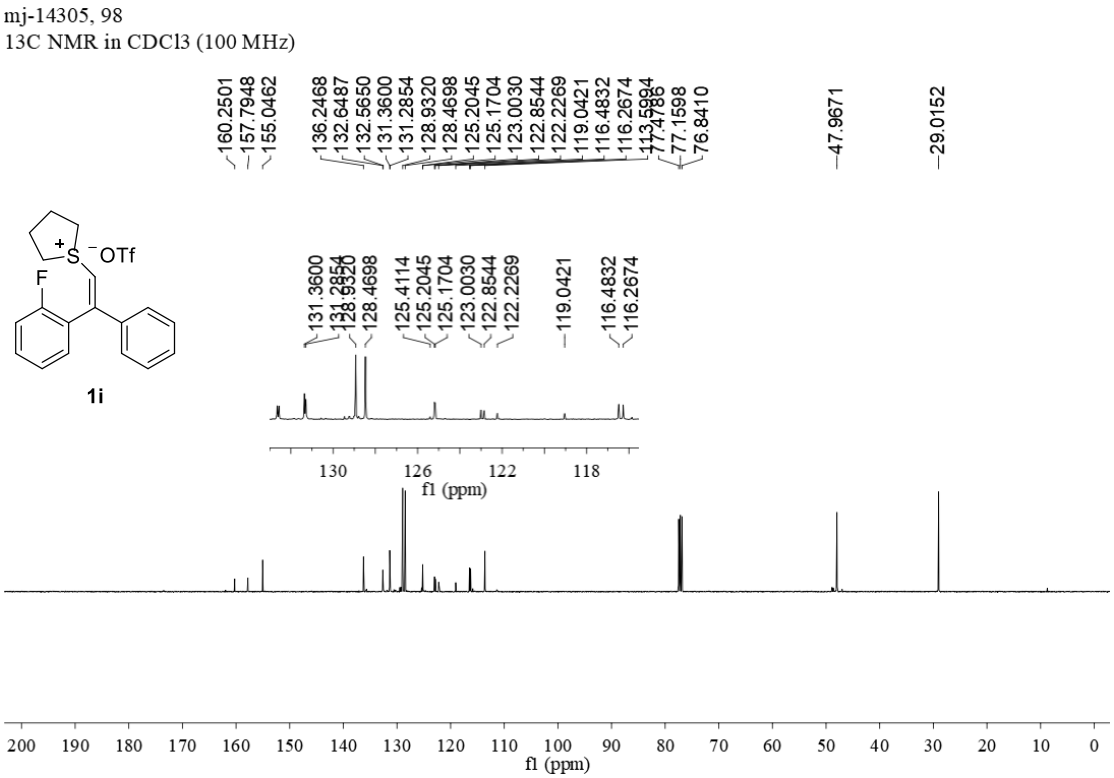


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1i** ($CDCl_3$, 25 °C, 100 MHz).

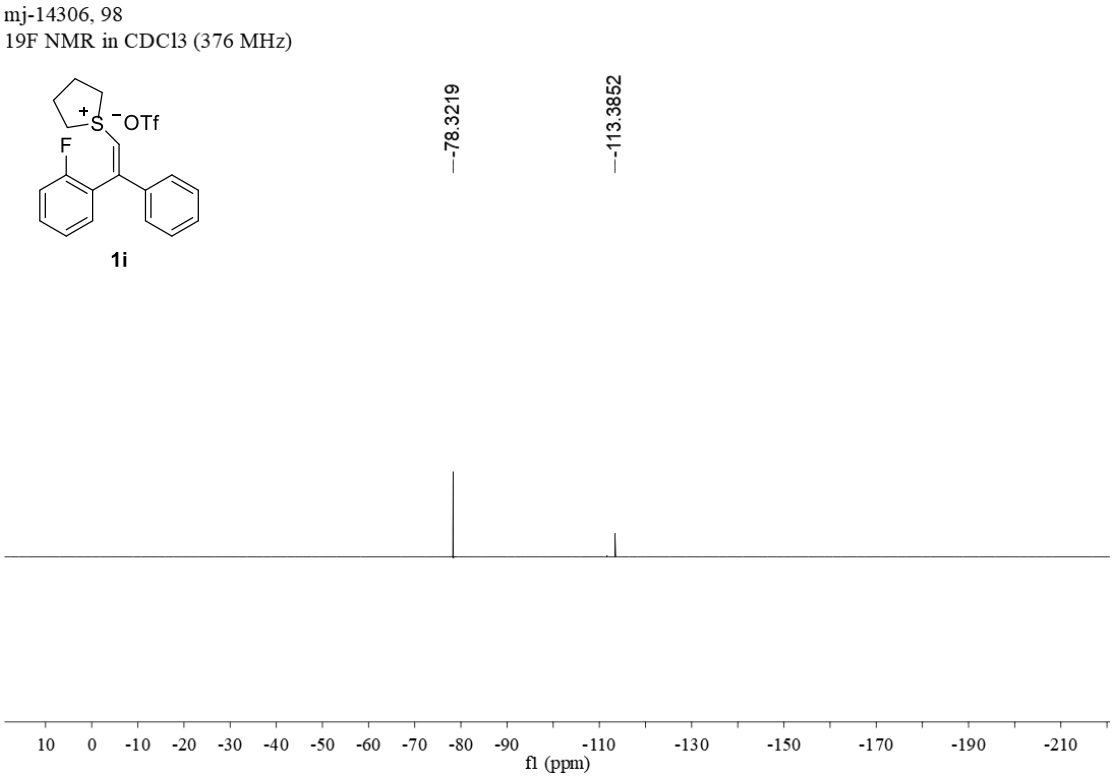


Figure S20. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1i** ($CDCl_3$, 25 °C, 376 MHz).

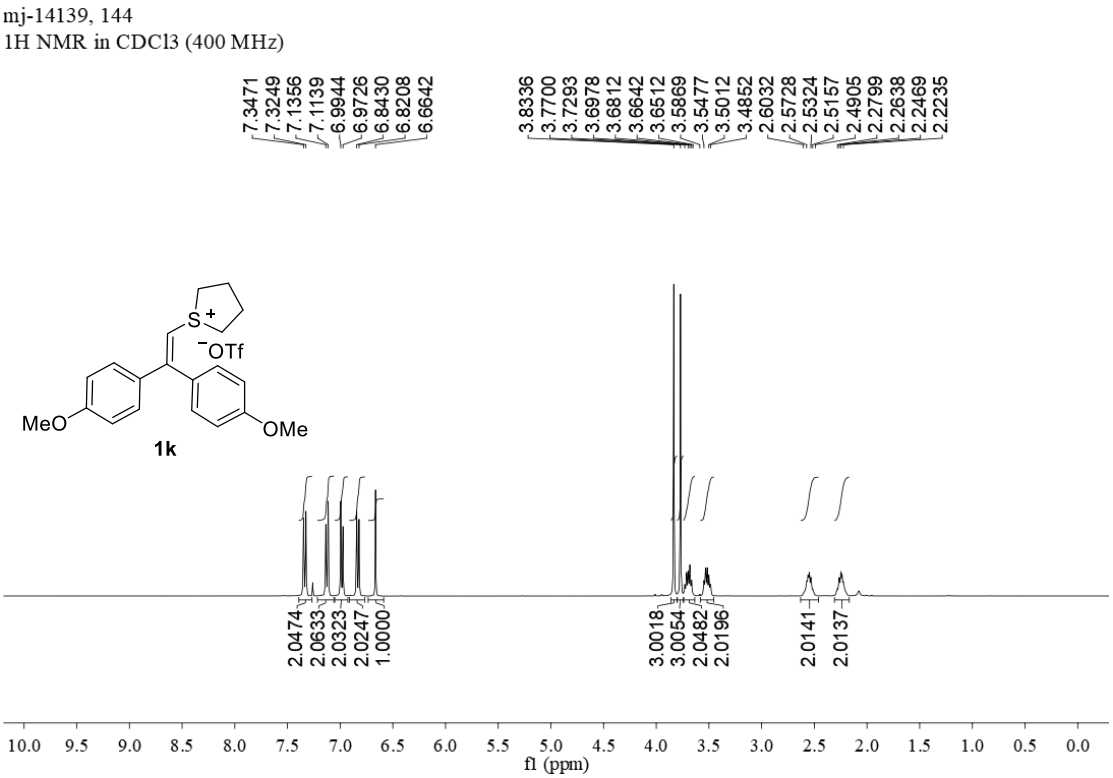


Figure S21. ^{1}H NMR spectrum of compound **1k** ($CDCl_3$, 25 °C, 400 MHz).

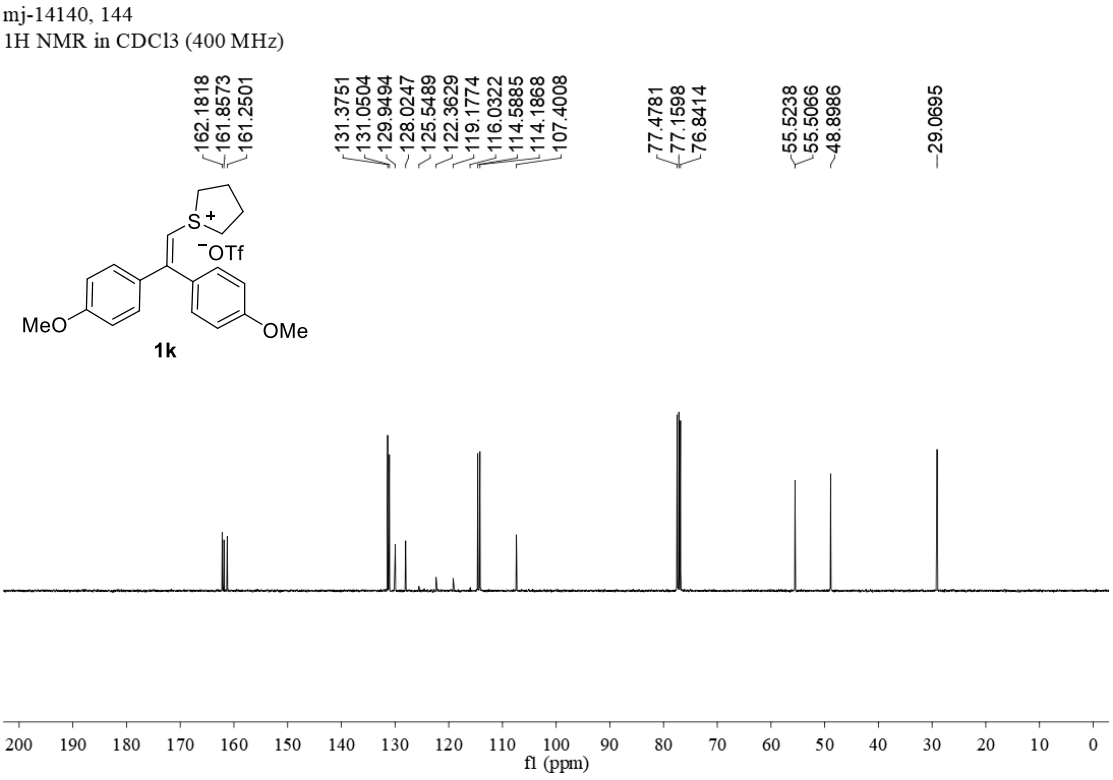


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1k** ($CDCl_3$, 25 °C, 100 MHz).

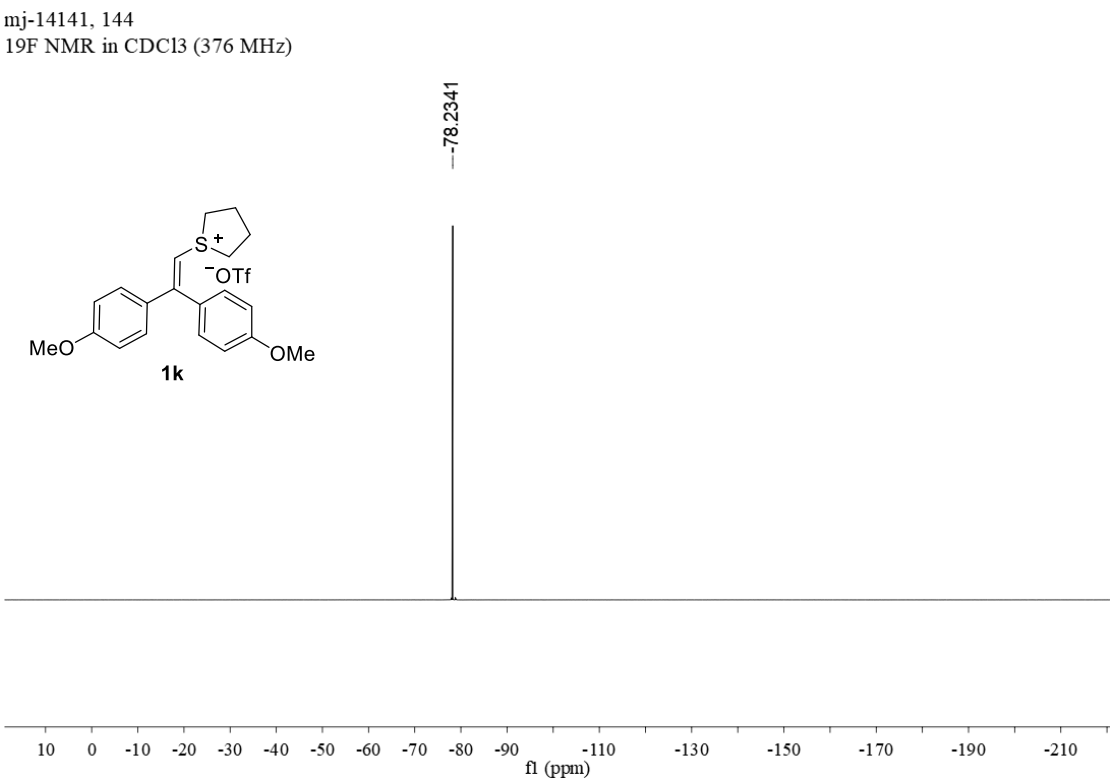


Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1k** ($CDCl_3$, 25 °C, 376 MHz).

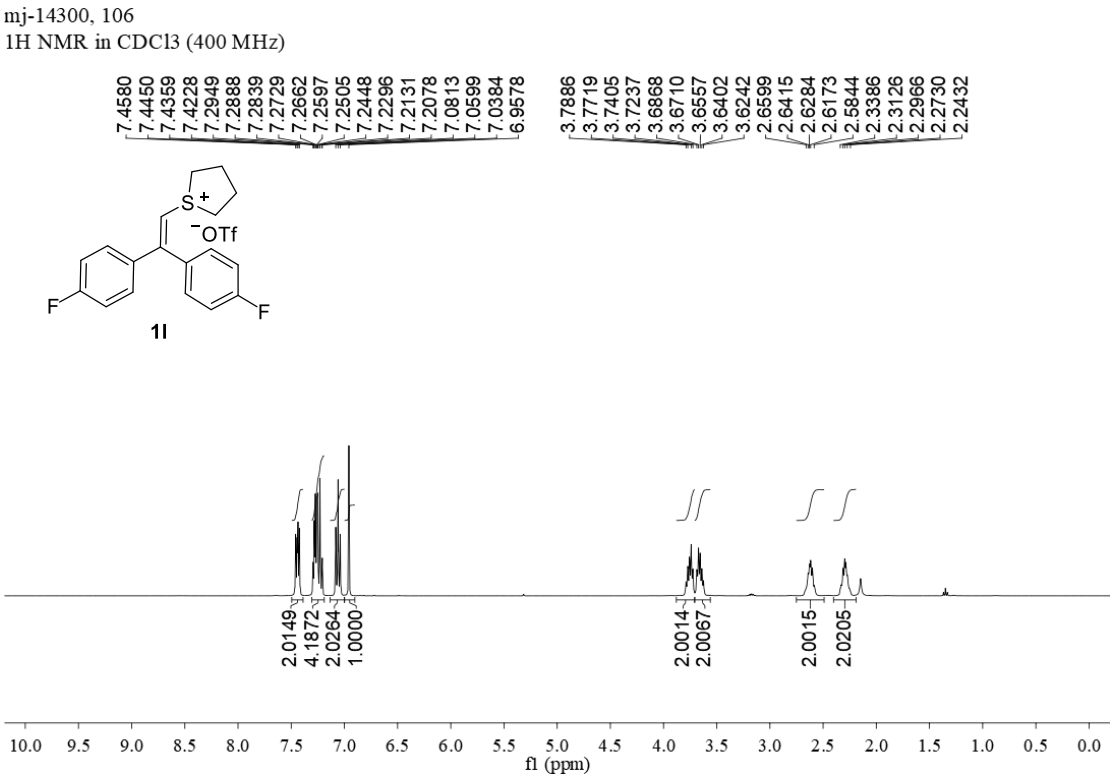


Figure S24. ^{1}H NMR spectrum of compound **1l** ($CDCl_3$, 25 °C, 400 MHz).

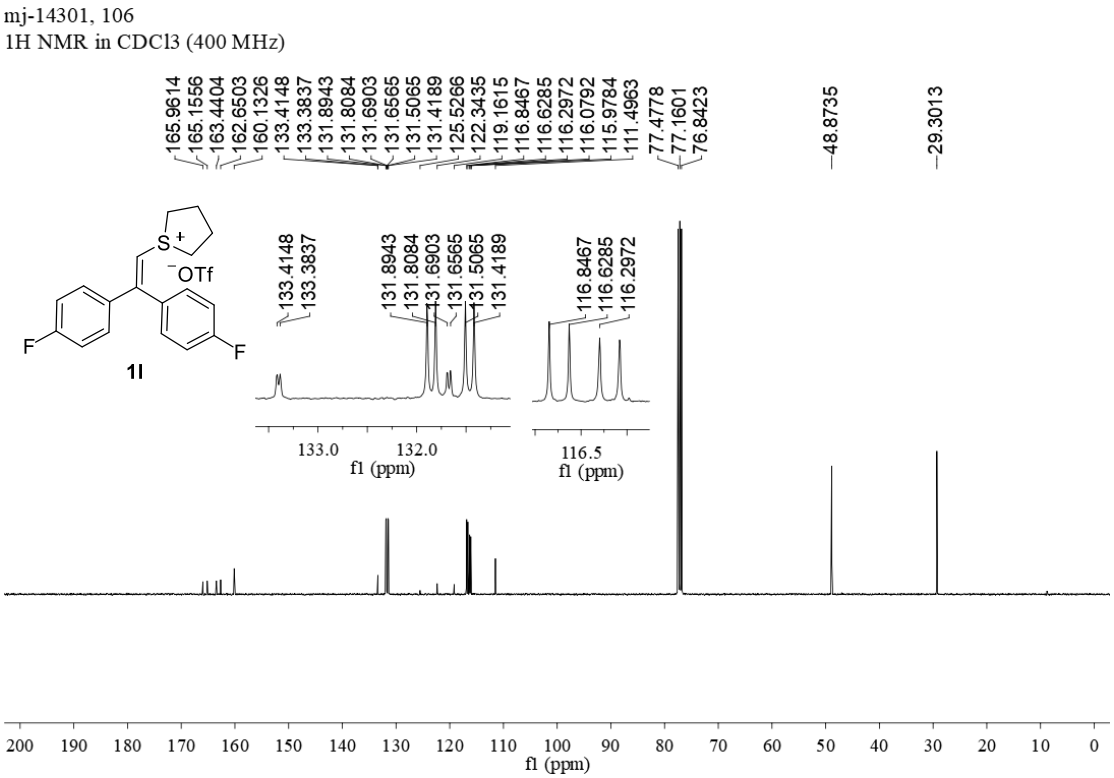


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1l** ($CDCl_3$, 25 °C, 100 MHz).

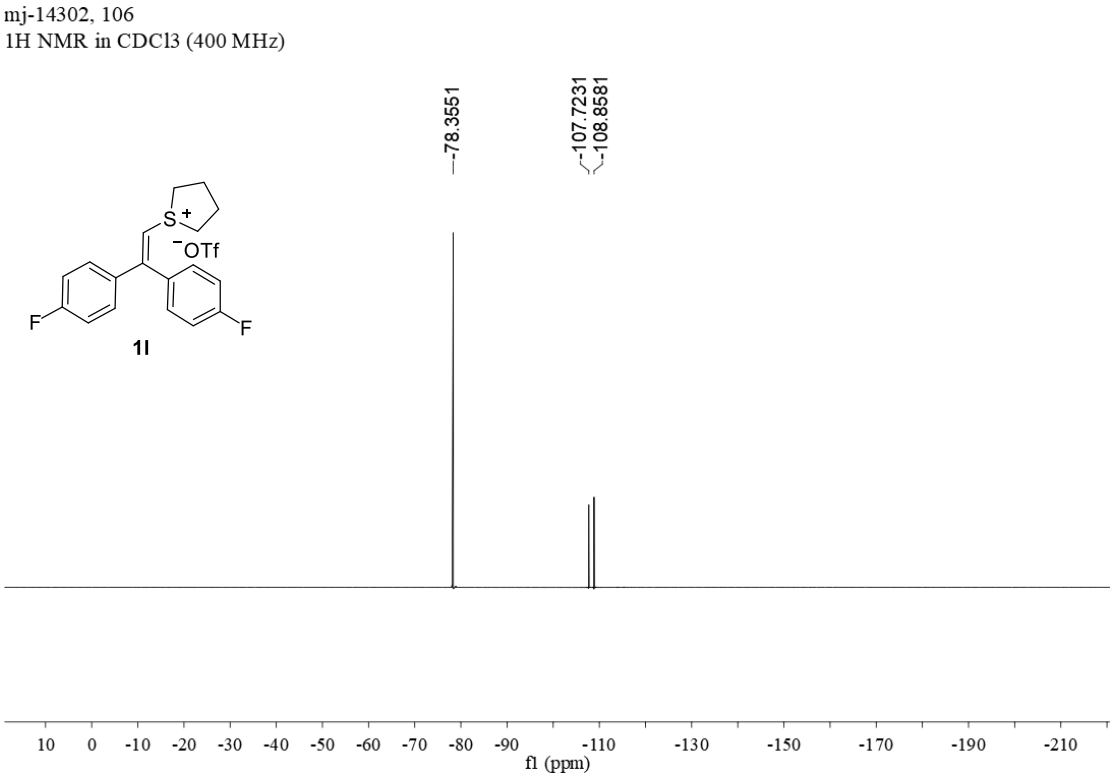


Figure S26. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1l** ($CDCl_3$, 25 °C, 376 MHz).

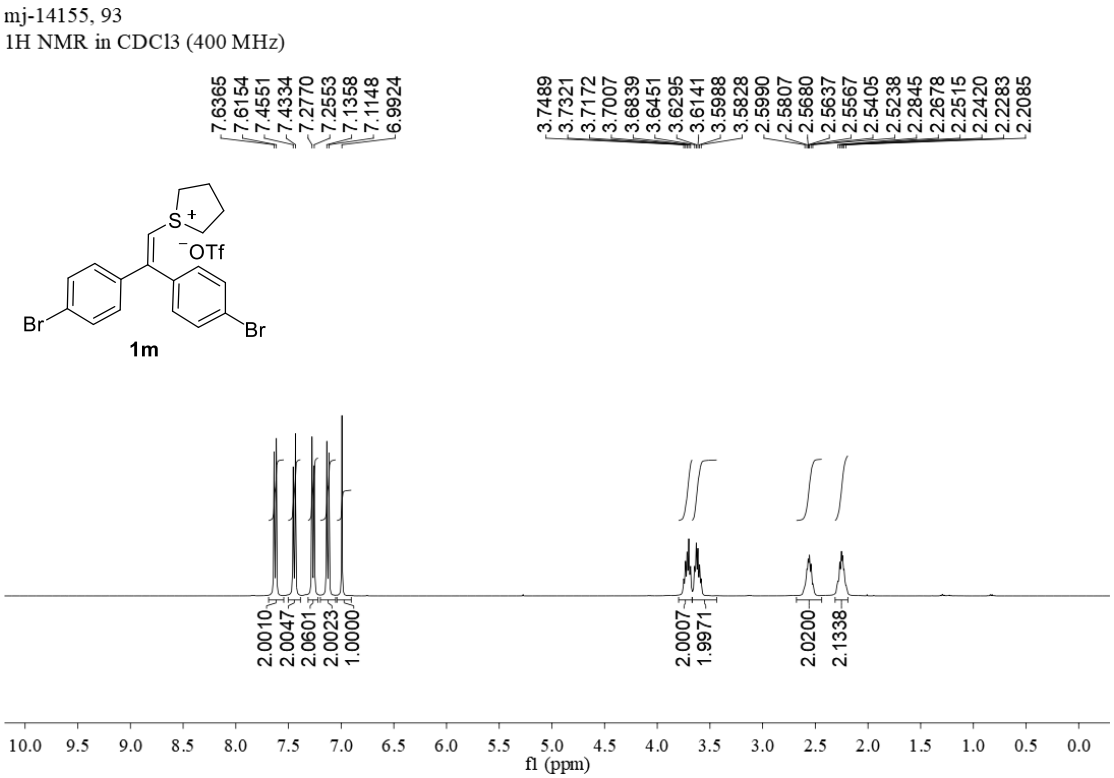


Figure S27. ^{1}H NMR spectrum of compound **1m** ($CDCl_3$, 25 °C, 400 MHz).

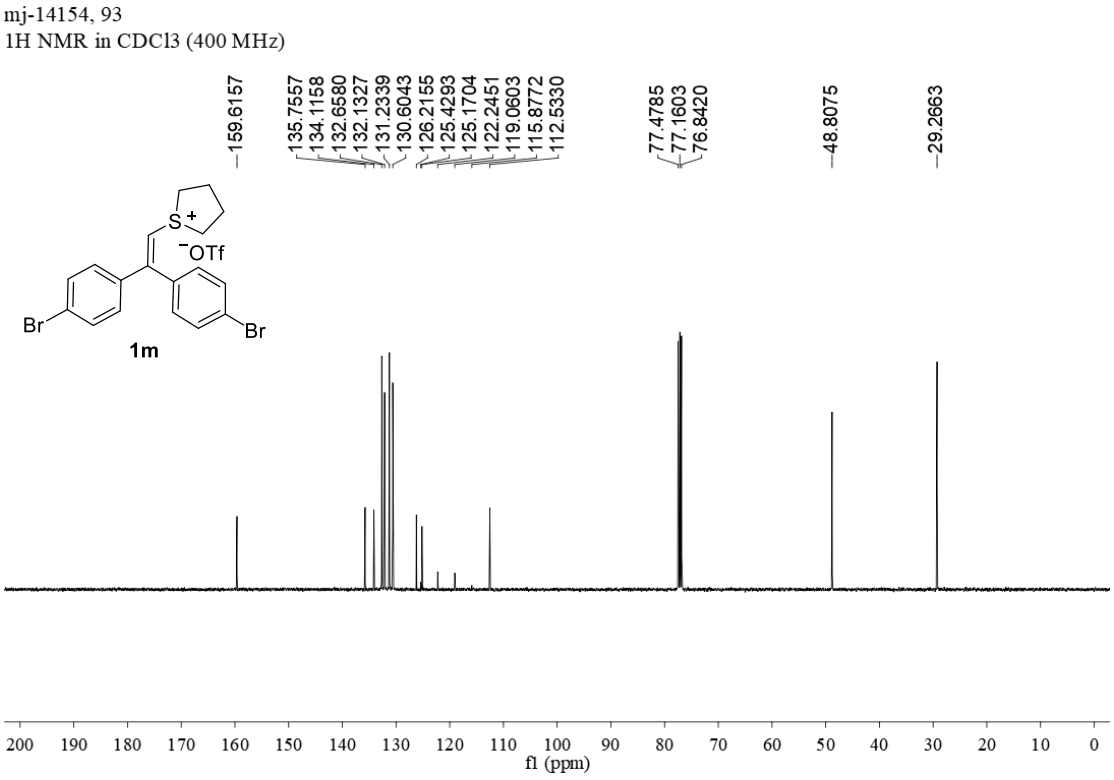


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1m** ($CDCl_3$, 25 °C, 100 MHz).

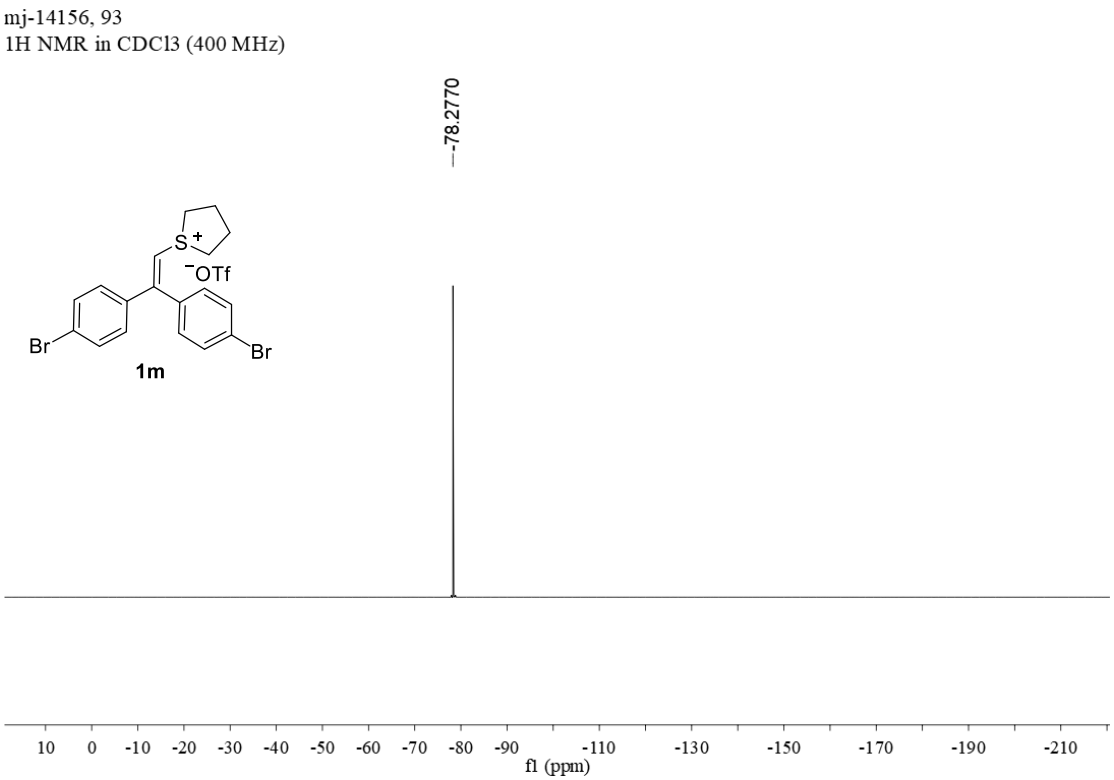


Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1m** ($CDCl_3$, 25 °C, 376 MHz).

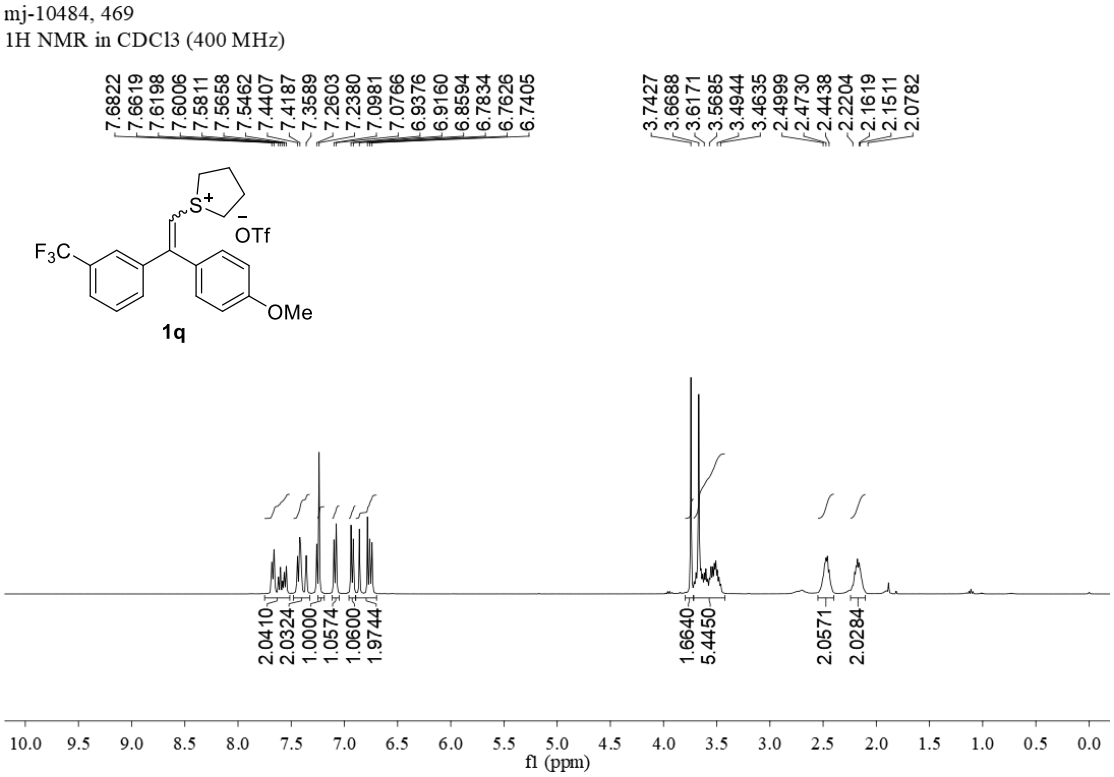


Figure S30. ^{1}H NMR spectrum of compound **1q** ($CDCl_3$, 25 °C, 400 MHz).

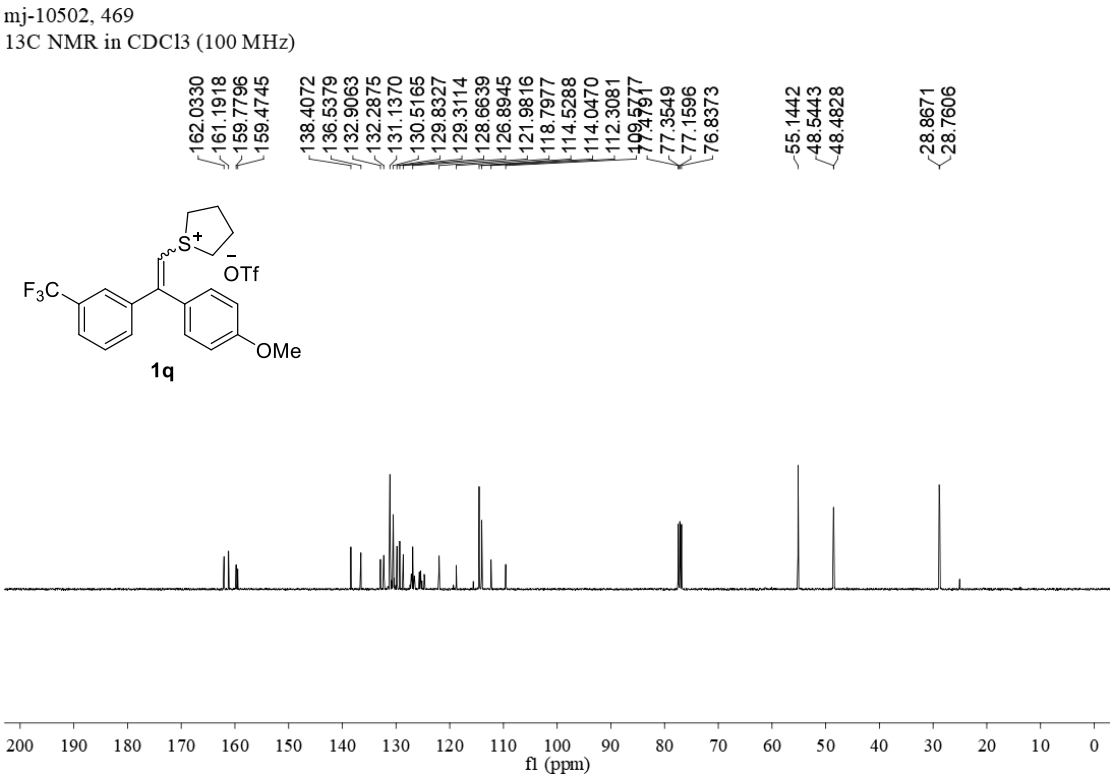


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1q** ($CDCl_3$, 25 °C, 100 MHz).

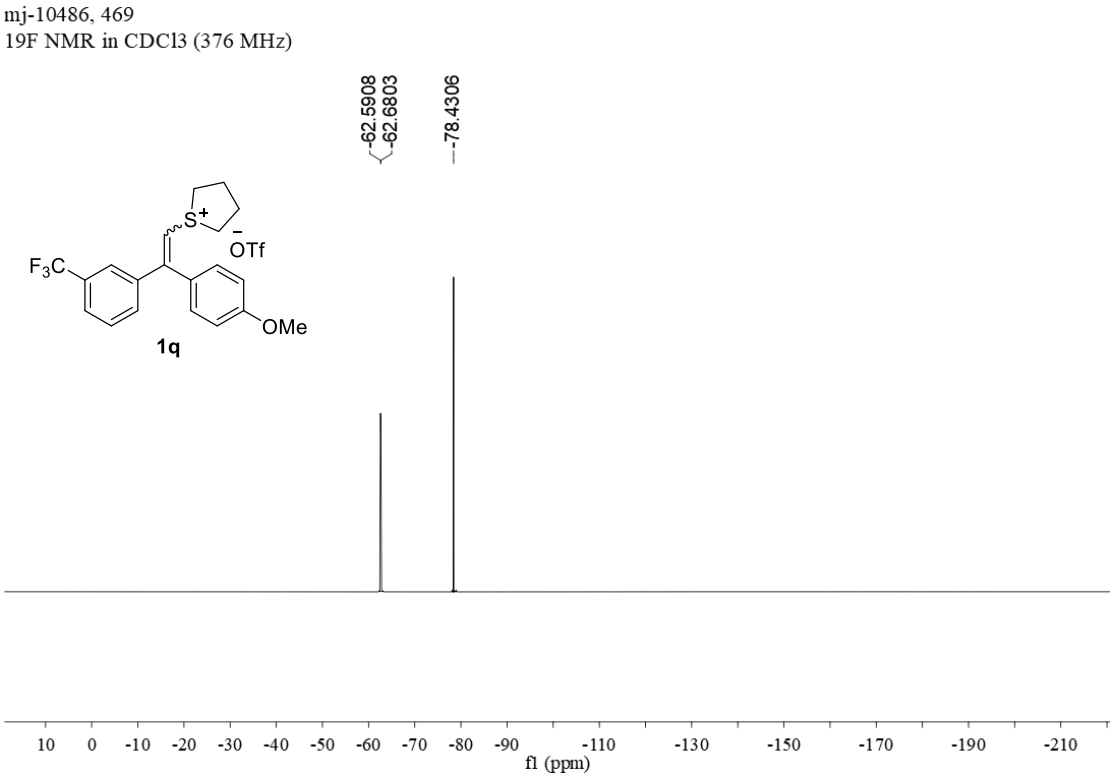


Figure S32. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1q** ($CDCl_3$, 25 °C, 376 MHz).

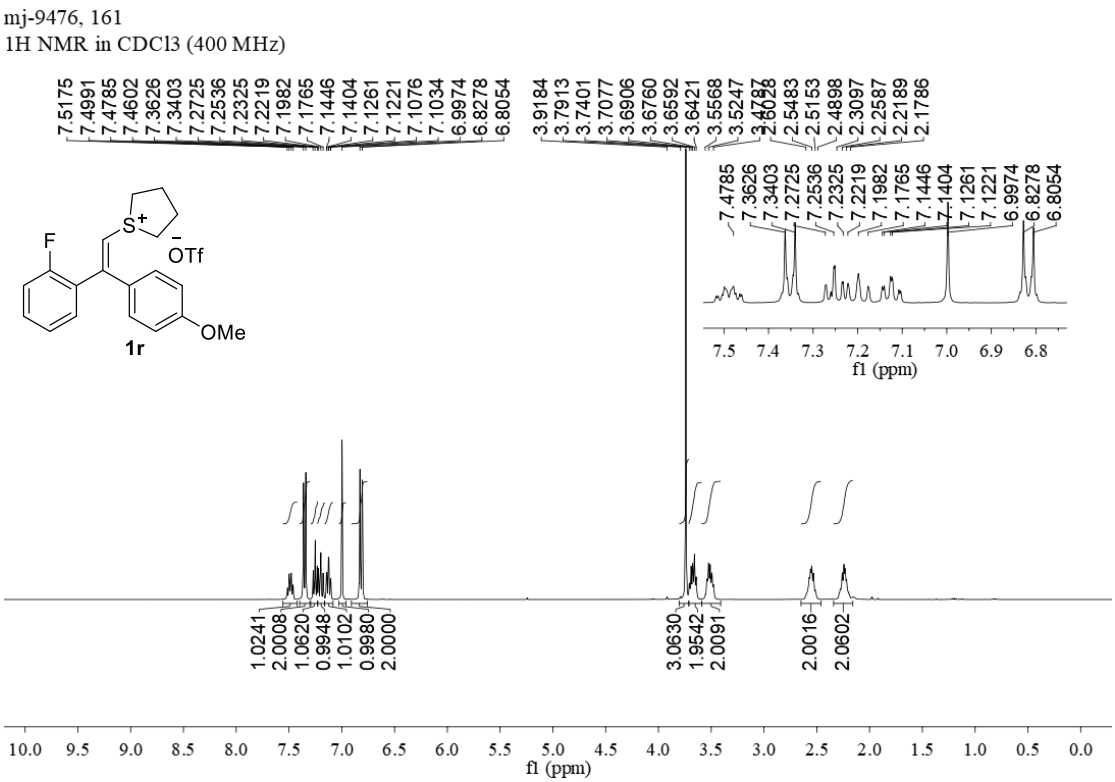


Figure S33. ^{1}H NMR spectrum of compound **1r** ($CDCl_3$, 25 °C, 400 MHz).

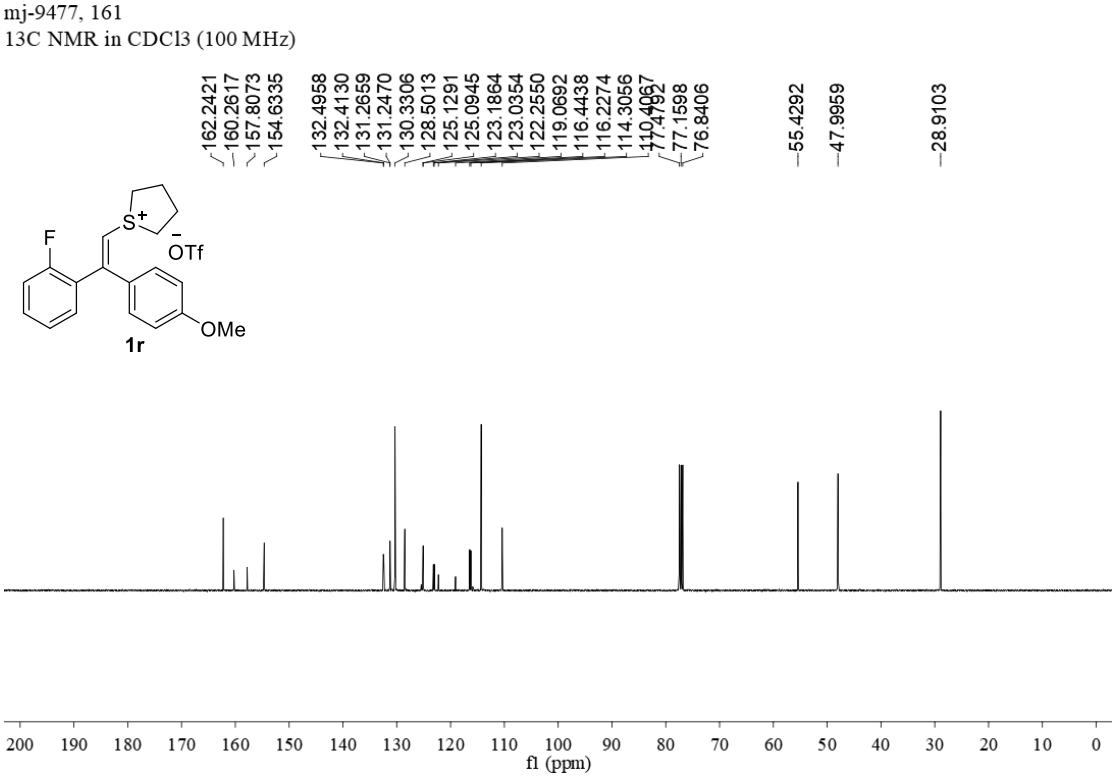


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1r** ($CDCl_3$, 25 °C, 100 MHz).

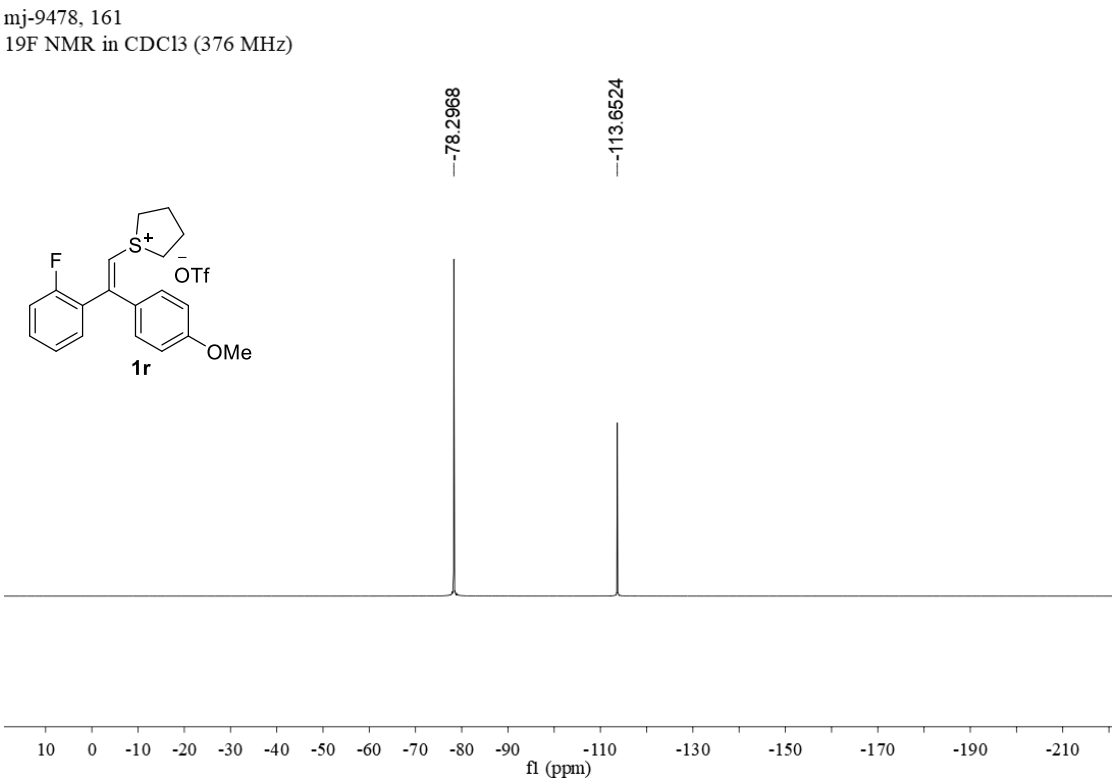


Figure S35. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1r** ($CDCl_3$, 25 °C, 376 MHz).

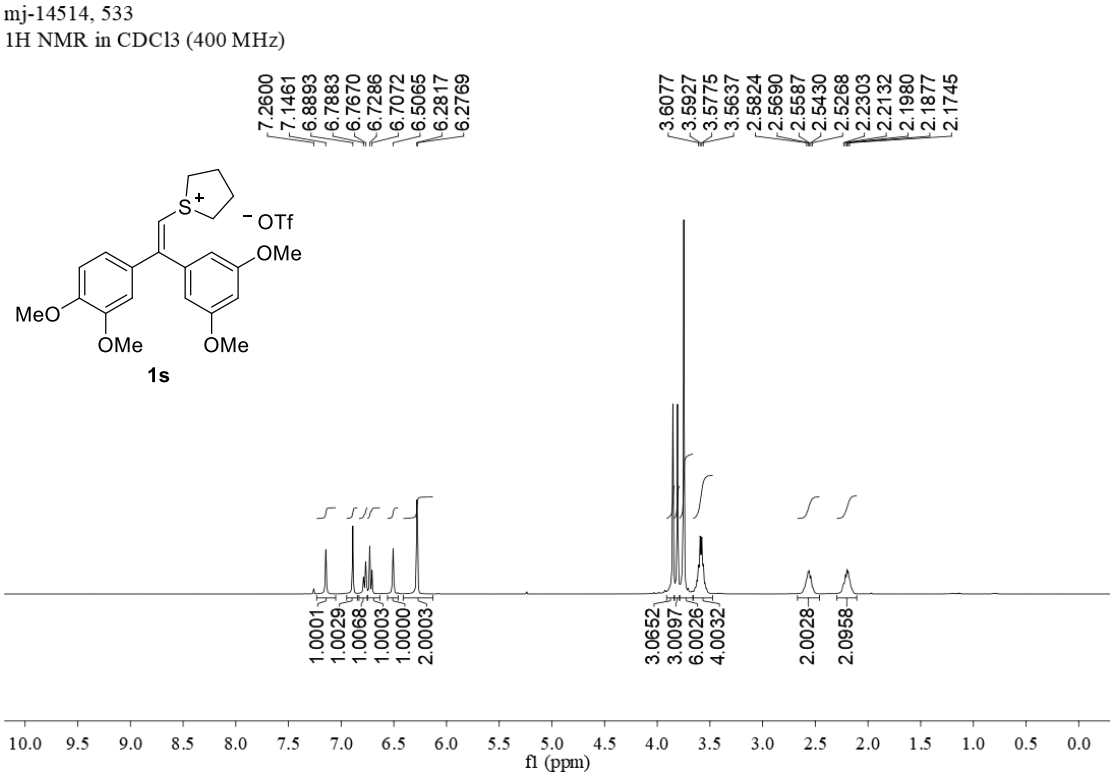


Figure S36. ^{1}H NMR spectrum of compound **1s** ($CDCl_3$, 25 °C, 400 MHz).

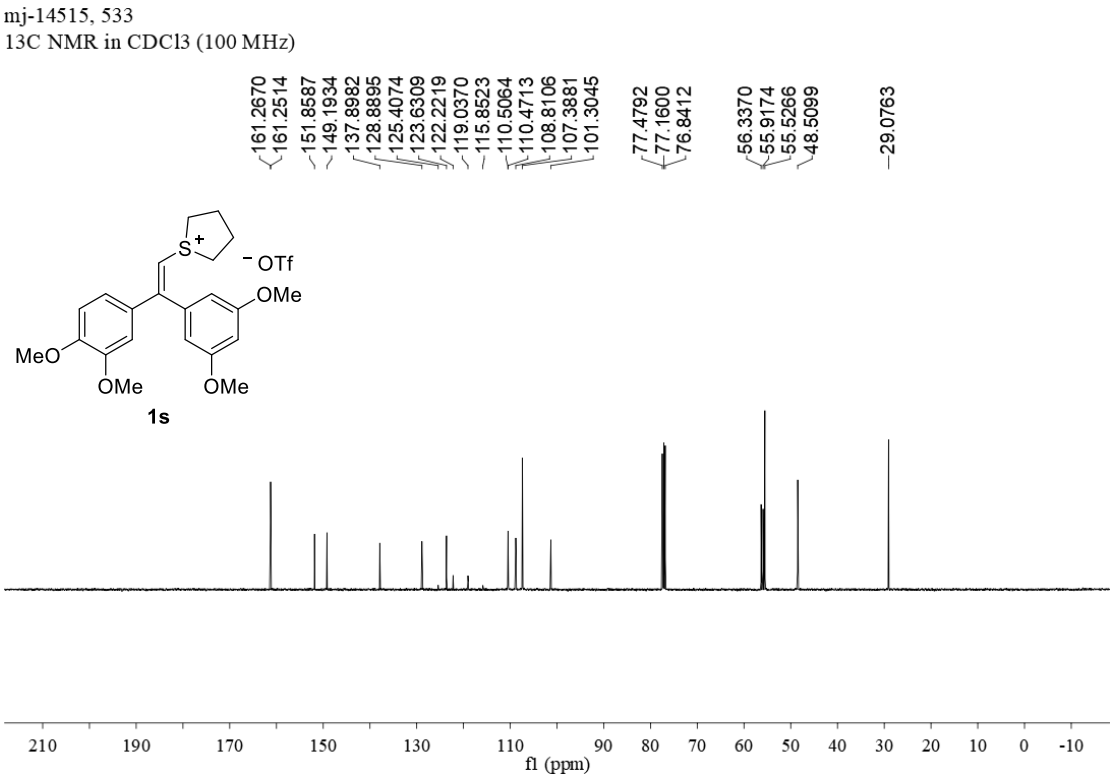


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1s** ($CDCl_3$, 25 °C, 100 MHz).

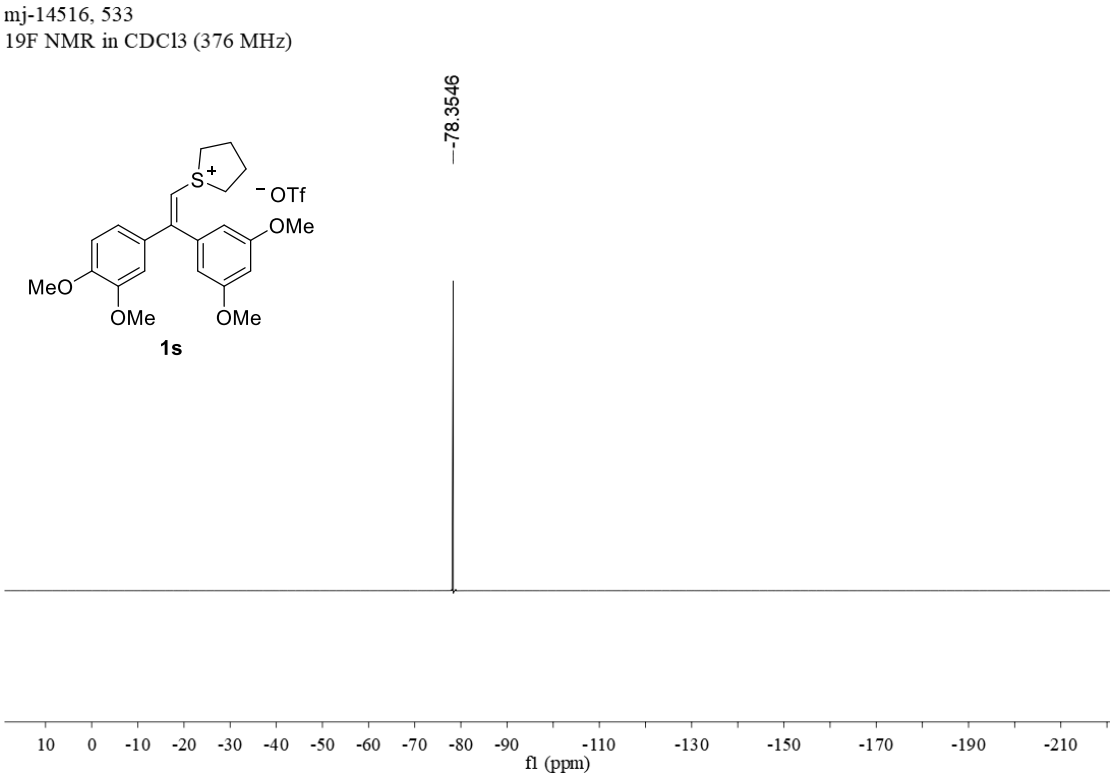


Figure S38. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1s** ($CDCl_3$, 25 °C, 376 MHz).

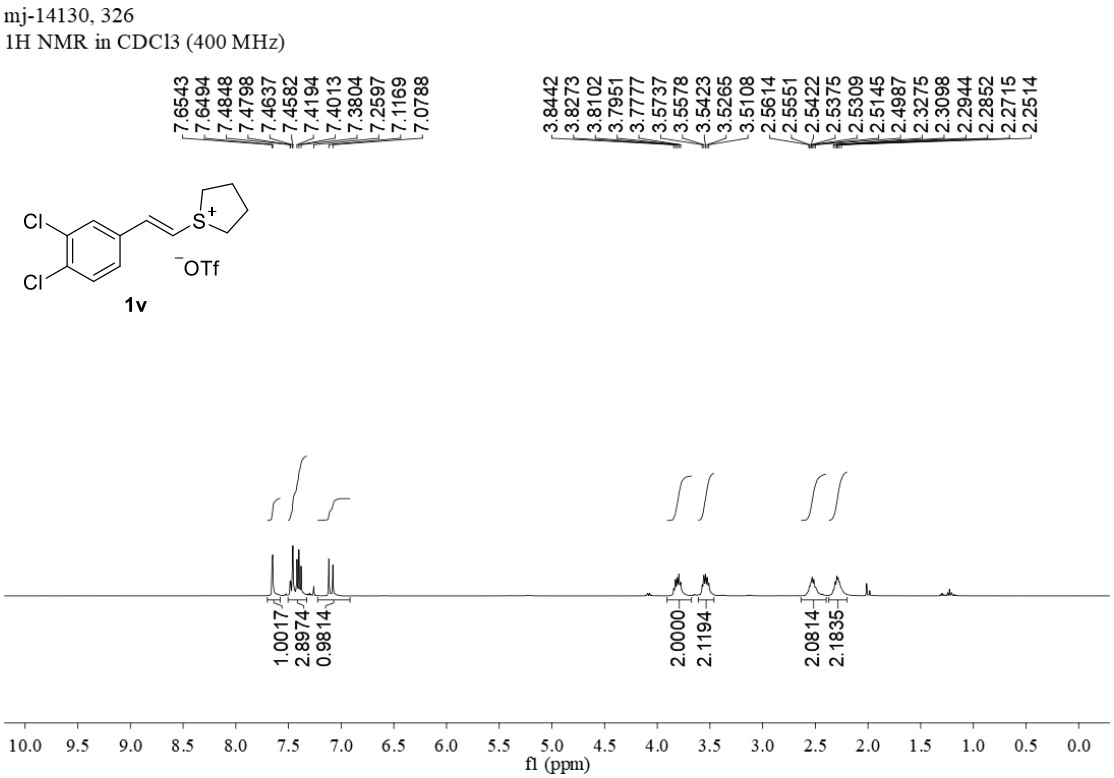


Figure S39. ^{1}H NMR spectrum of compound **1v** ($CDCl_3$, 25 °C, 400 MHz).

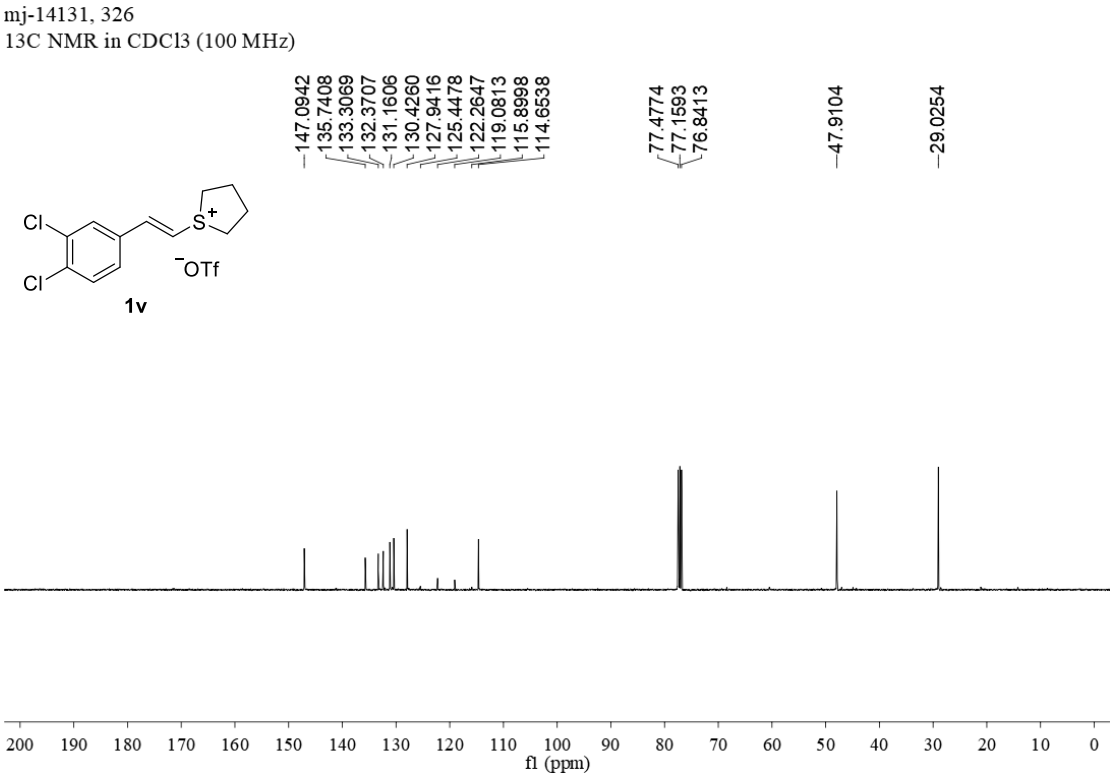


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1v** ($CDCl_3$, 25 °C, 100 MHz).

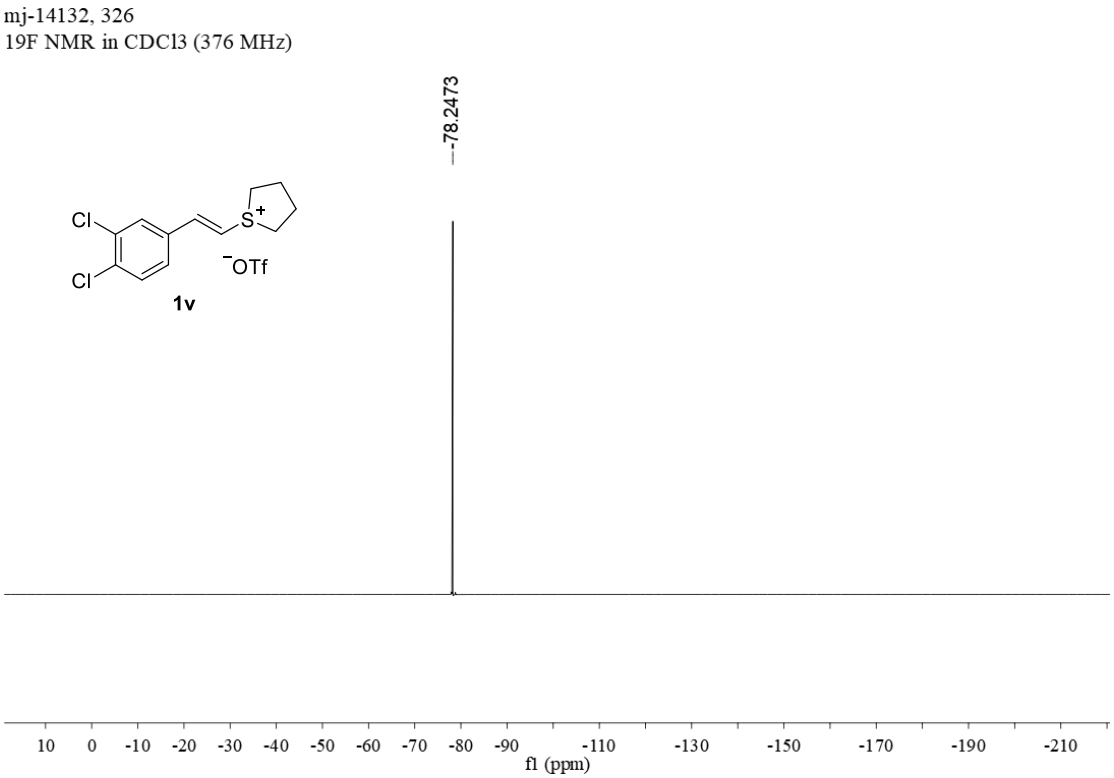


Figure S41. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1v** ($CDCl_3$, 25 °C, 376 MHz).

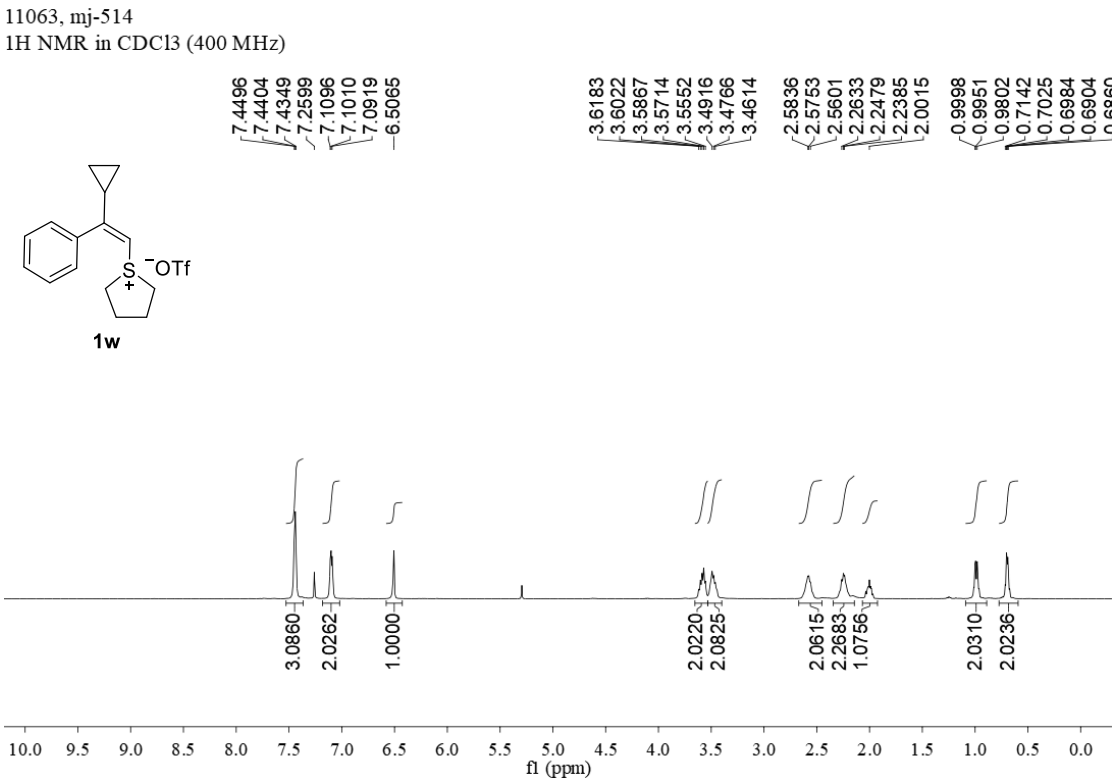


Figure S42. ^{1}H NMR spectrum of compound **1w** ($CDCl_3$, 25 °C, 400 MHz).

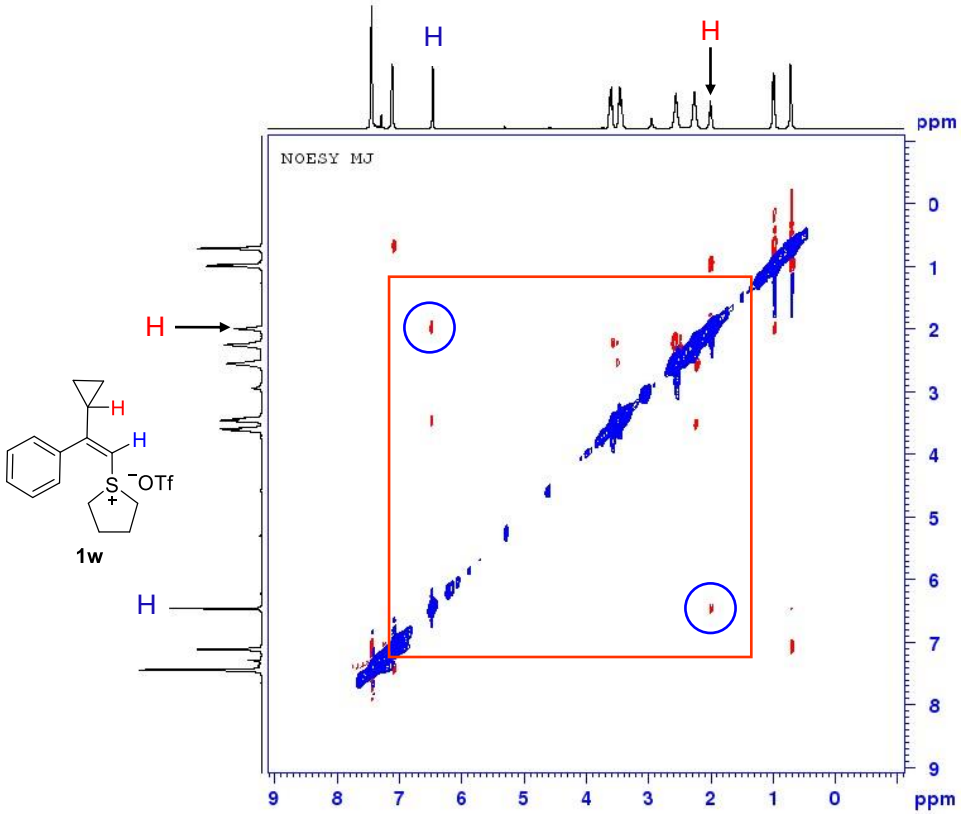


Figure S43. NOE spectrum of compound **1w**.

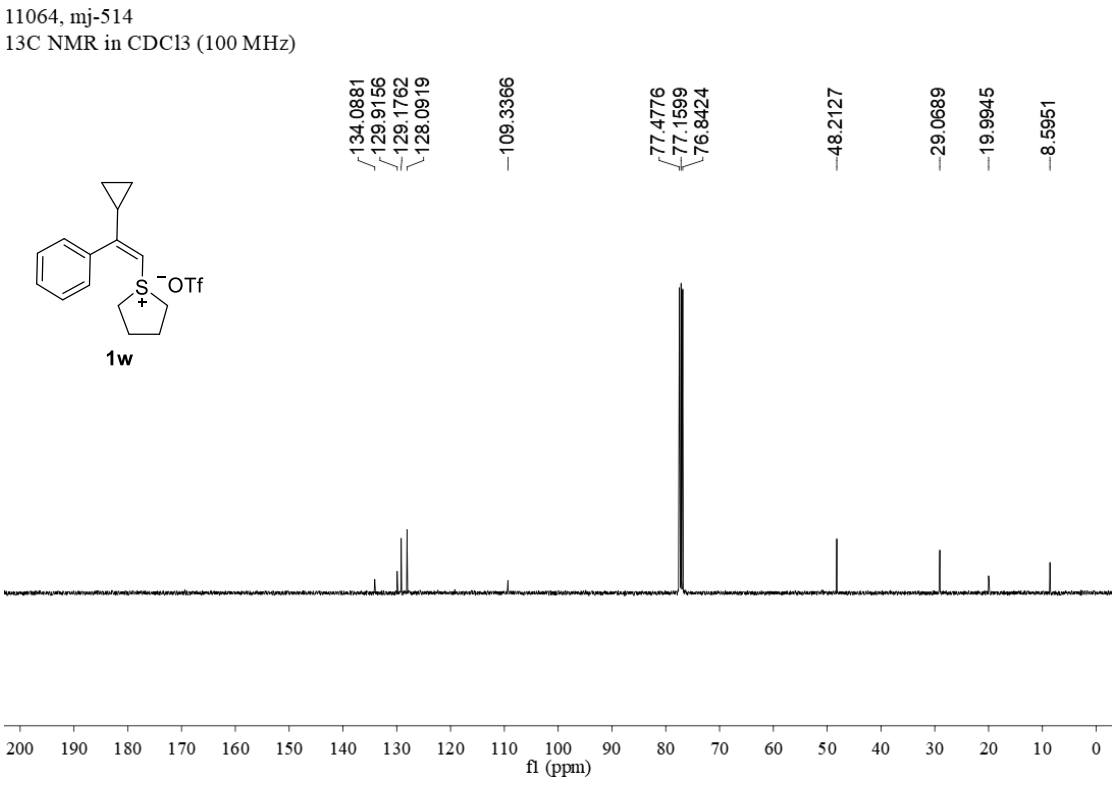


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1w** ($CDCl_3$, 25 °C, 100 MHz).

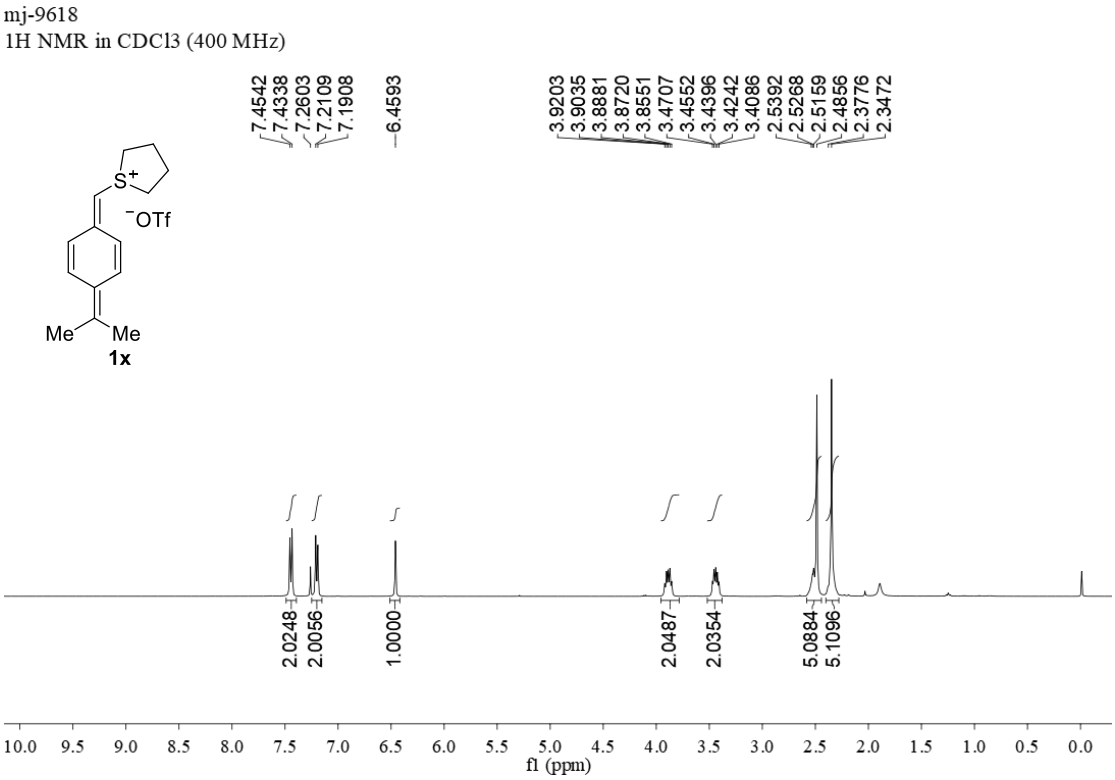


Figure S45. ^{1}H NMR spectrum of compound **1x** ($CDCl_3$, 25 °C, 400 MHz).

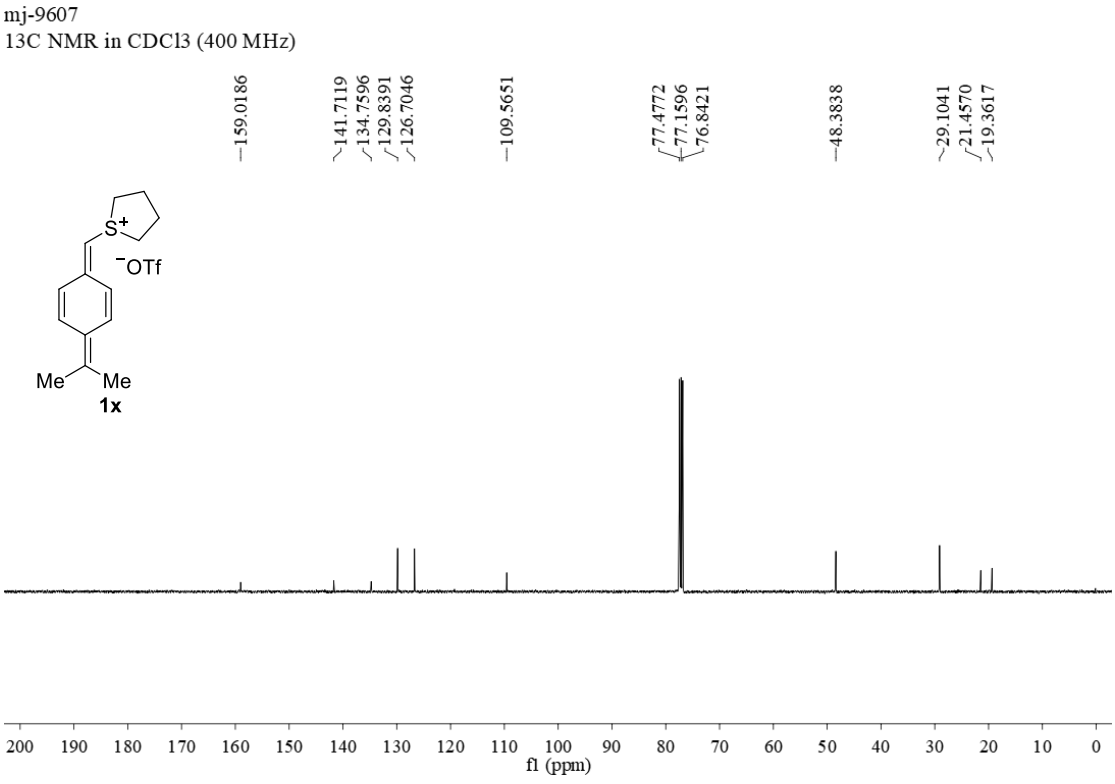


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1x** ($CDCl_3$, 25 °C, 100 MHz).

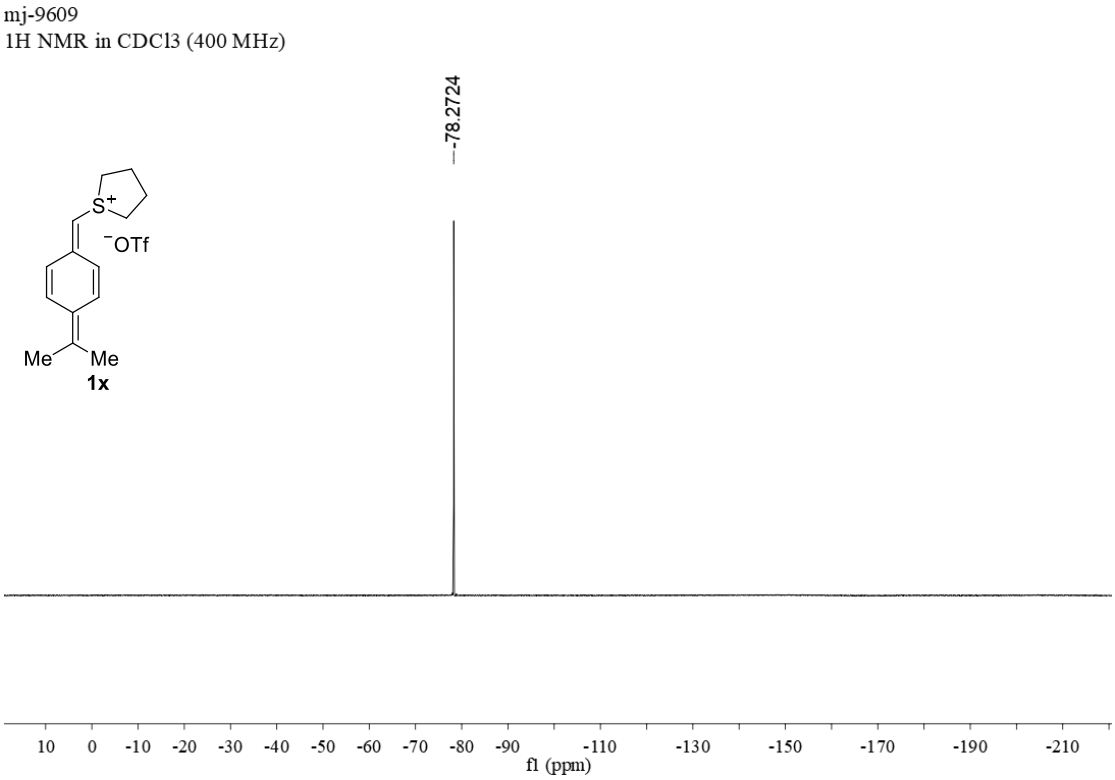


Figure S47. $^{19}F\{^{1}H\}$ NMR spectrum of compound **1x** ($CDCl_3$, 25 °C, 376 MHz).

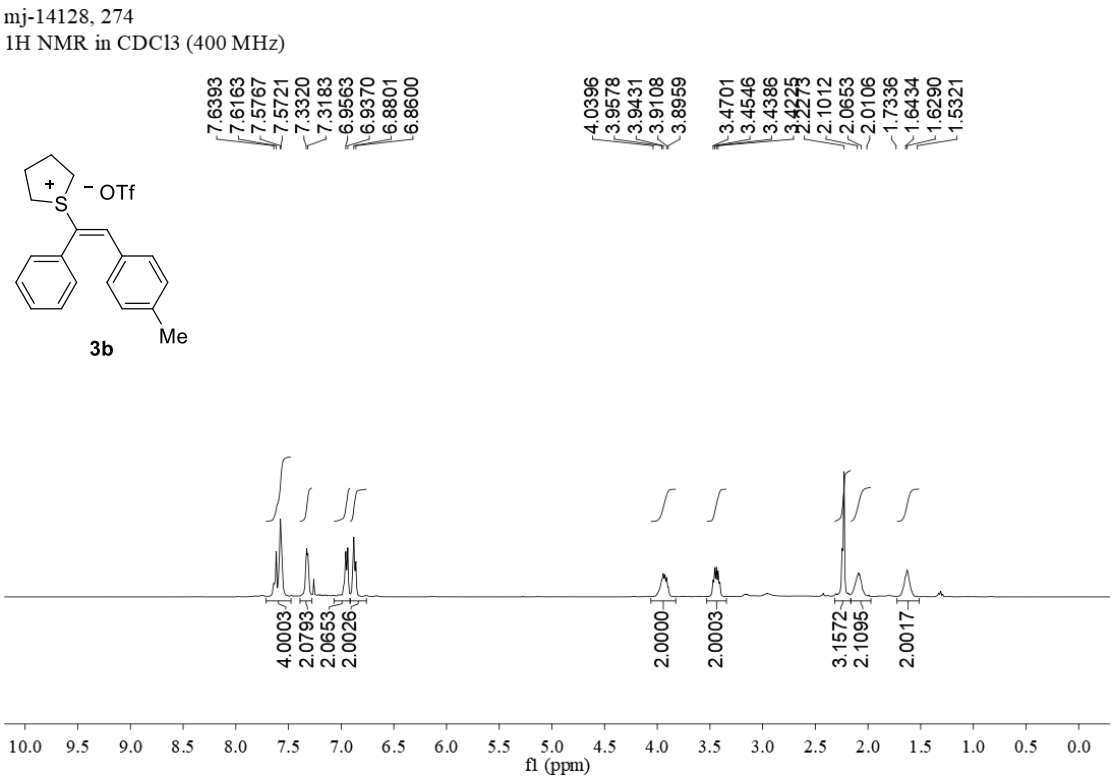


Figure S48. ^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 25 °C, 400 MHz).

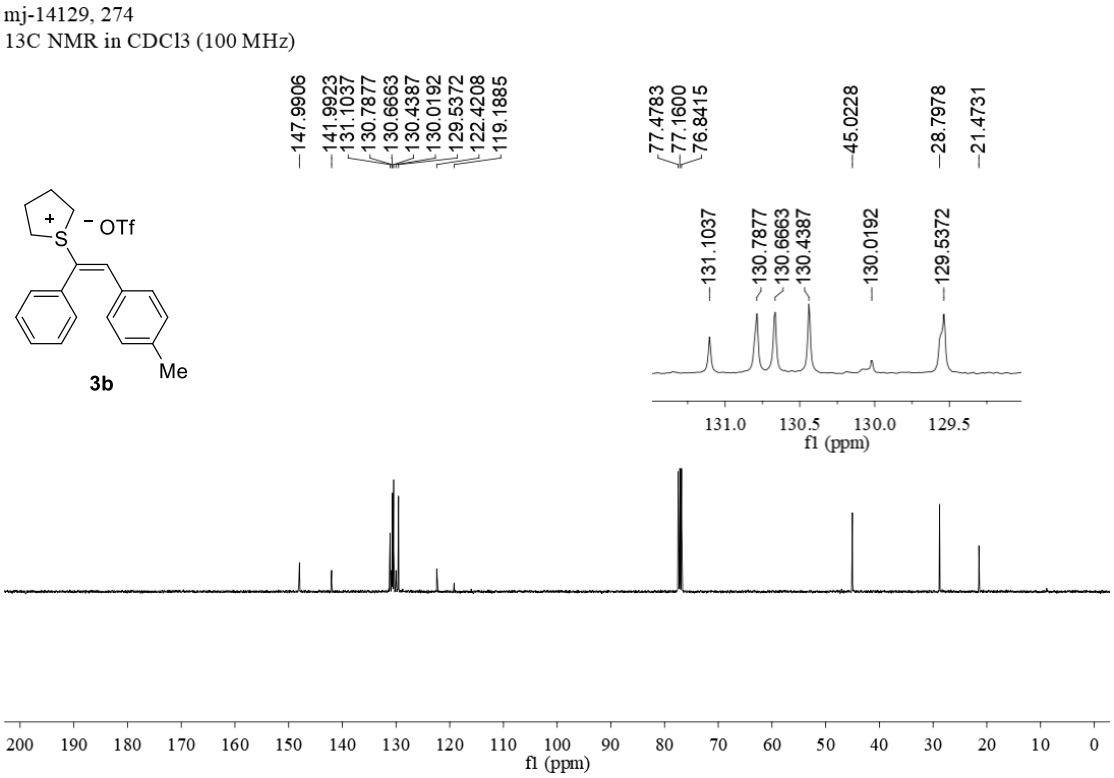


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b** ($CDCl_3$, 25 °C, 100 MHz).

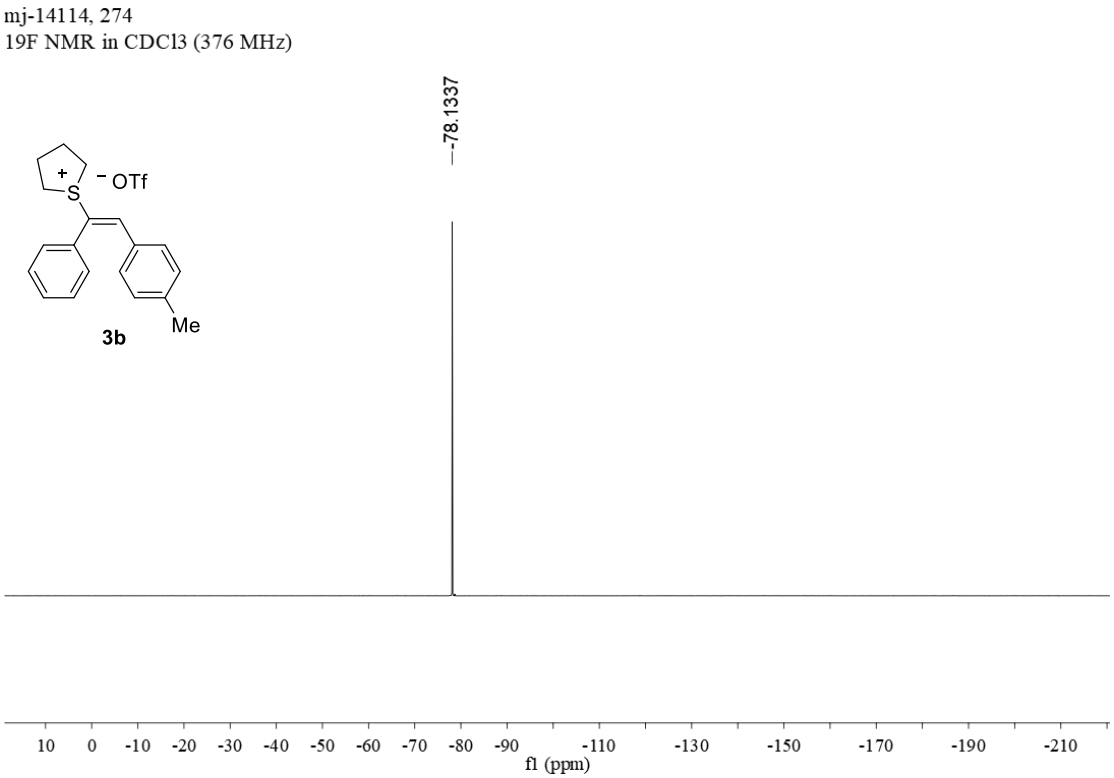


Figure S50. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3b** ($CDCl_3$, 25 °C, 376 MHz).

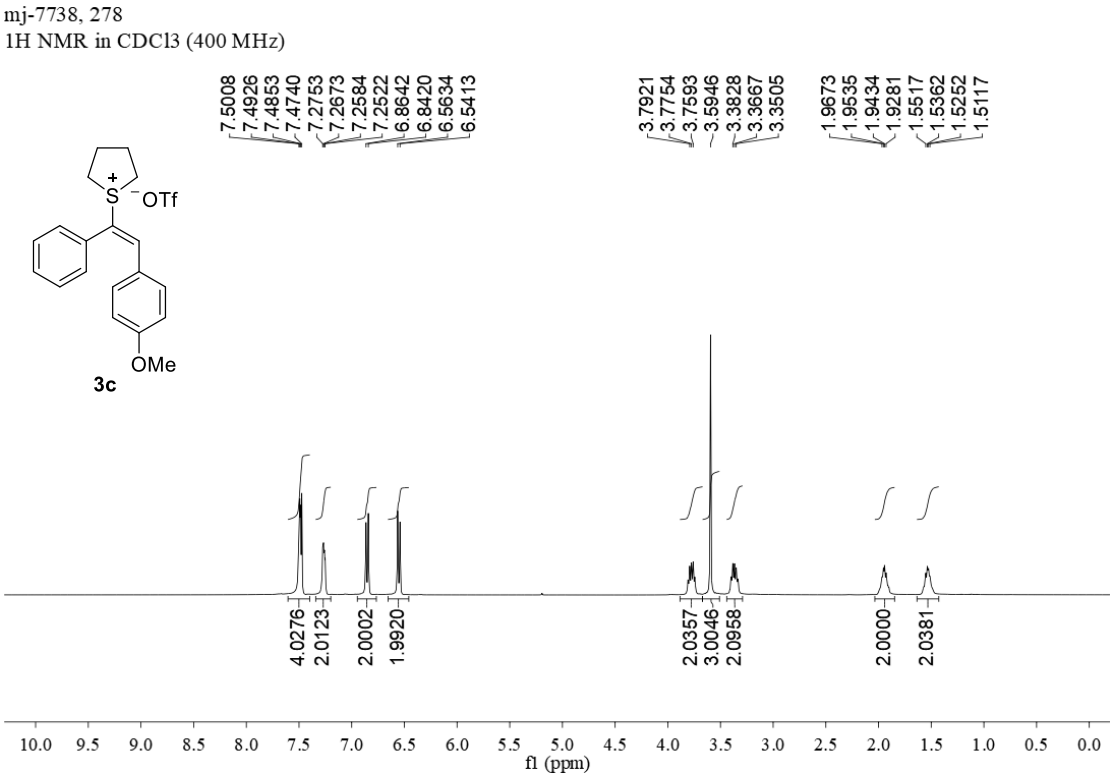


Figure S51. ^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 25 °C, 400 MHz).

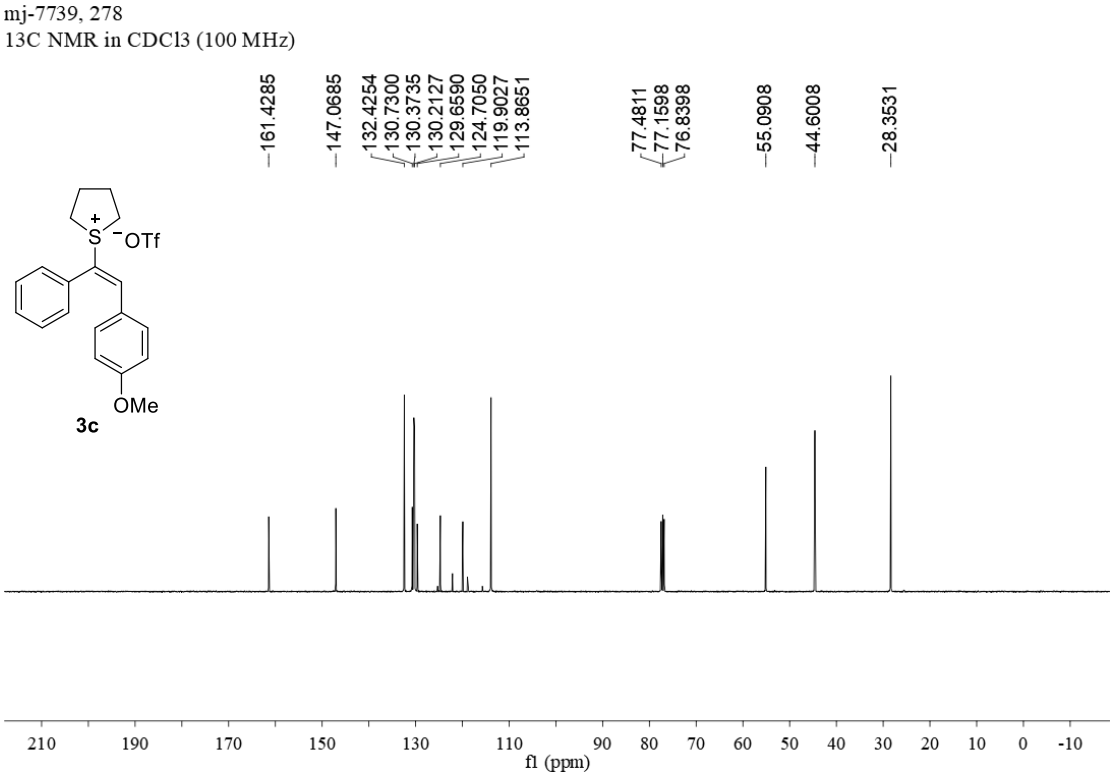


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3c** ($CDCl_3$, 25 °C, 100 MHz).

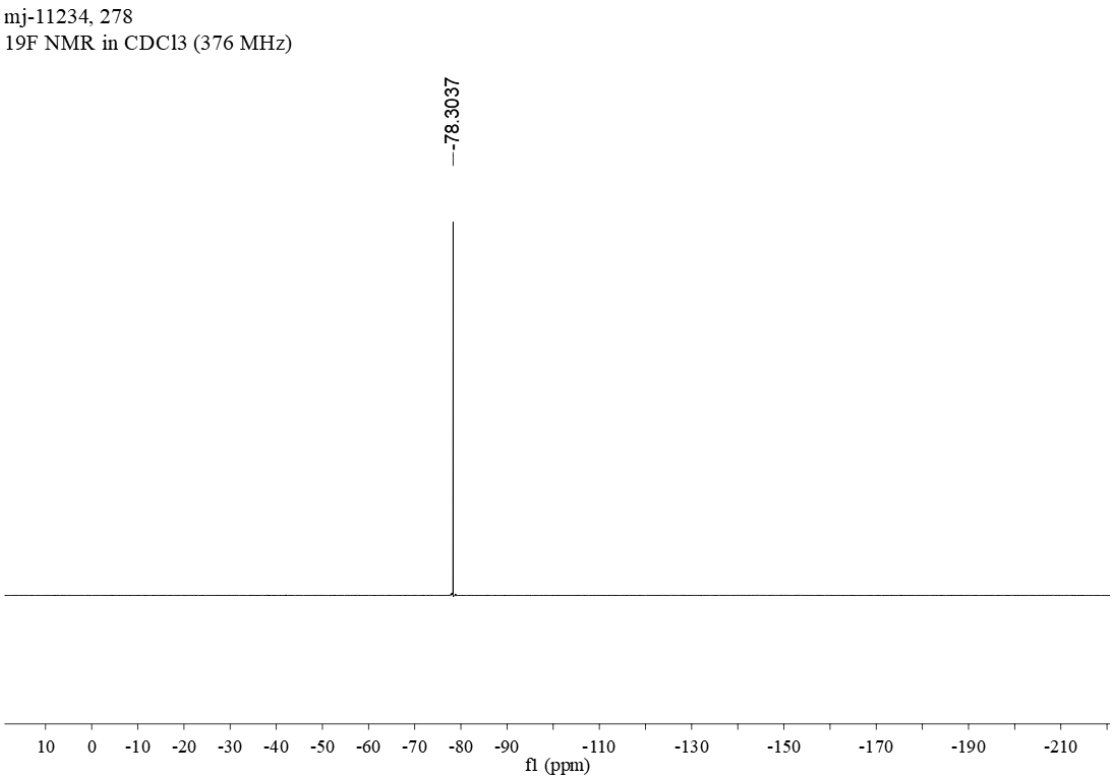


Figure S53. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3c** ($CDCl_3$, 25 °C, 376 MHz).

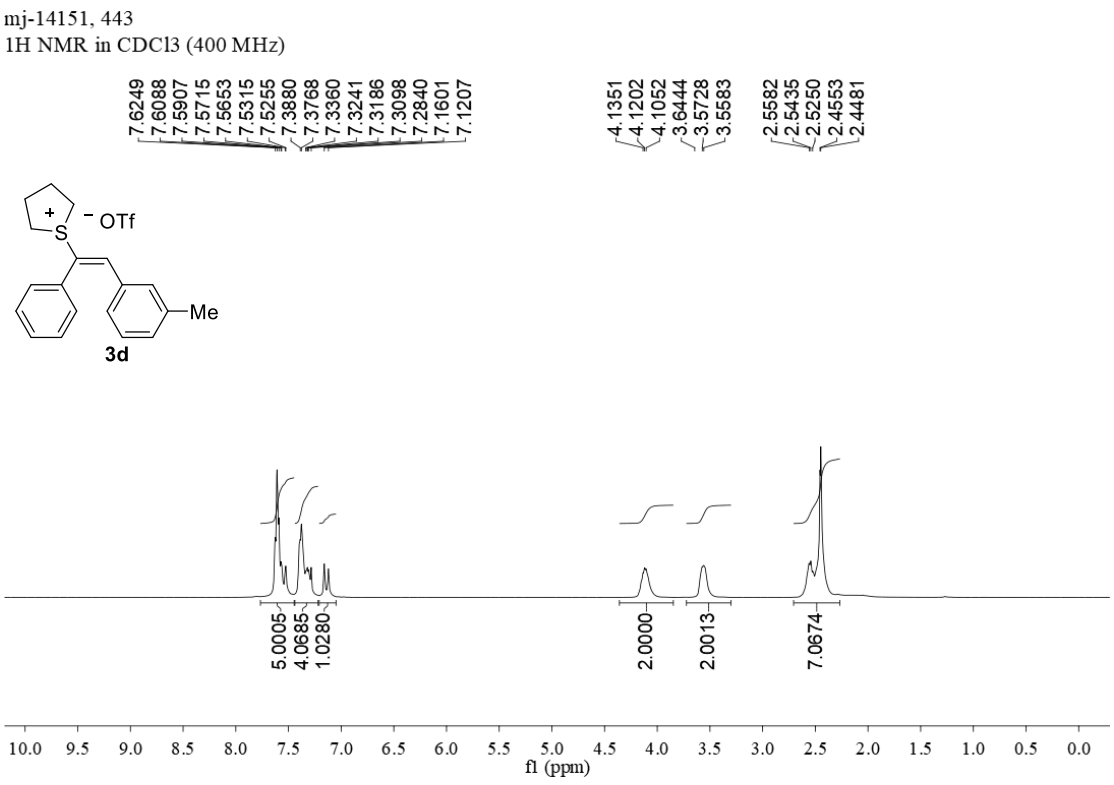


Figure S54. ^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 25 °C, 400 MHz).

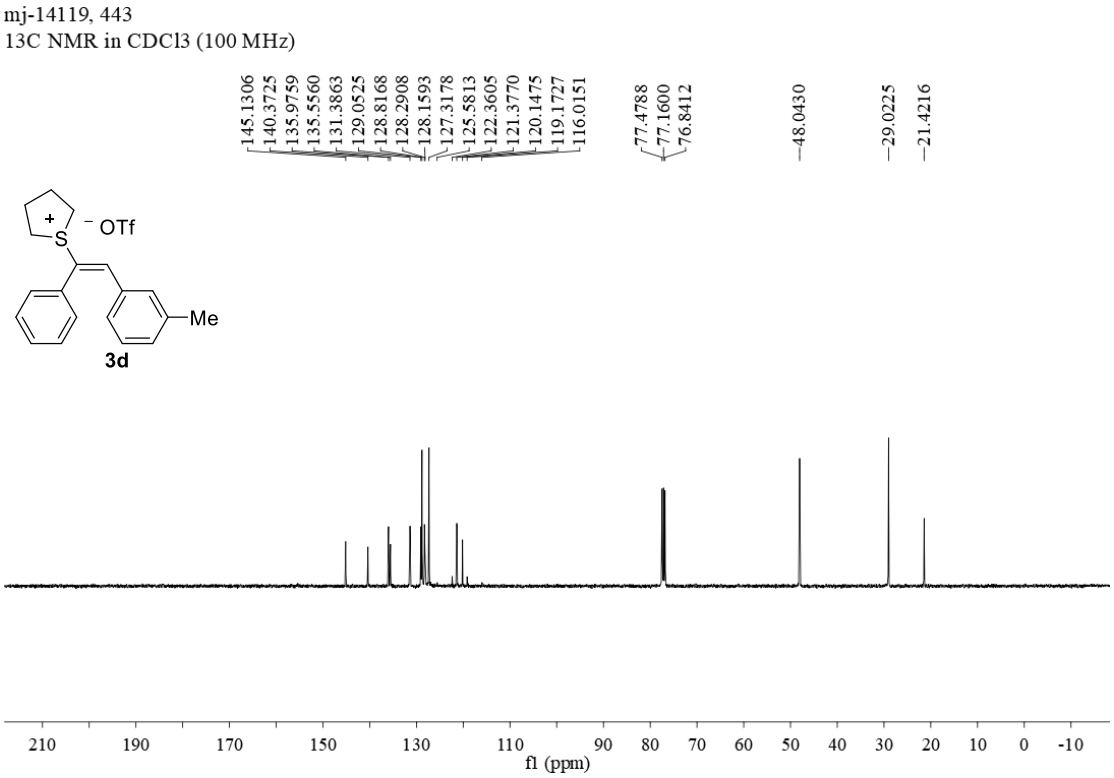


Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3d** ($CDCl_3$, 25 °C, 100 MHz).

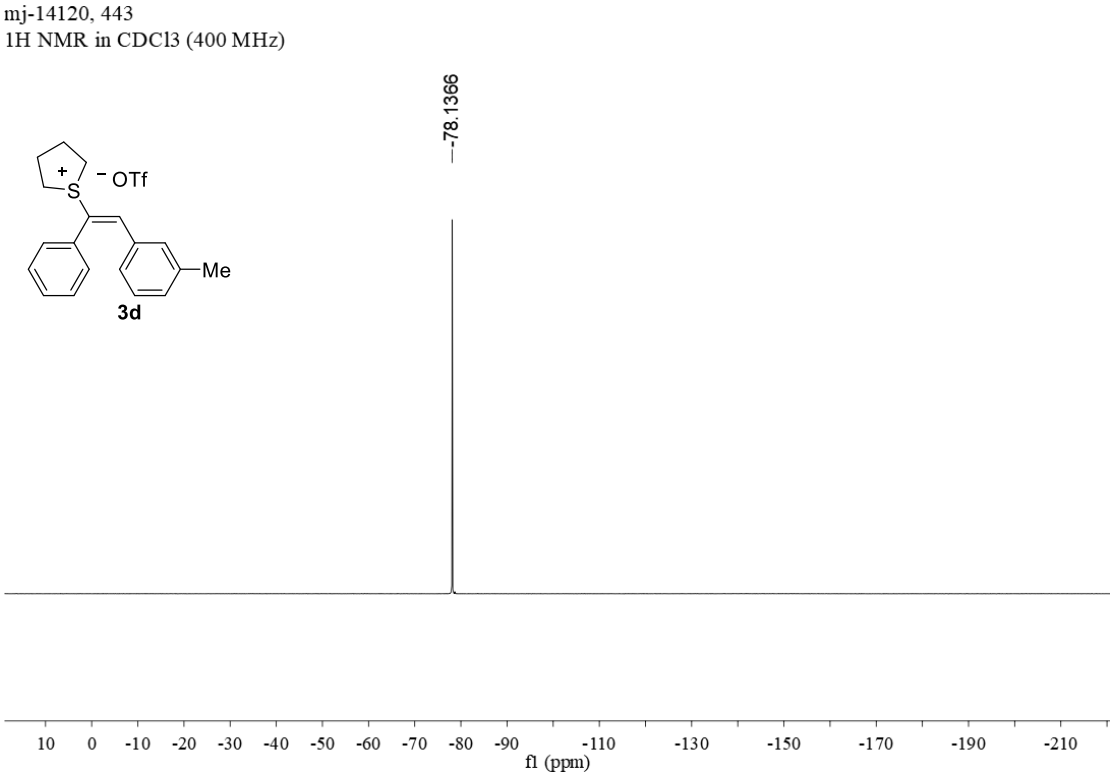


Figure S56. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3d** ($CDCl_3$, 25 °C, 376 MHz).

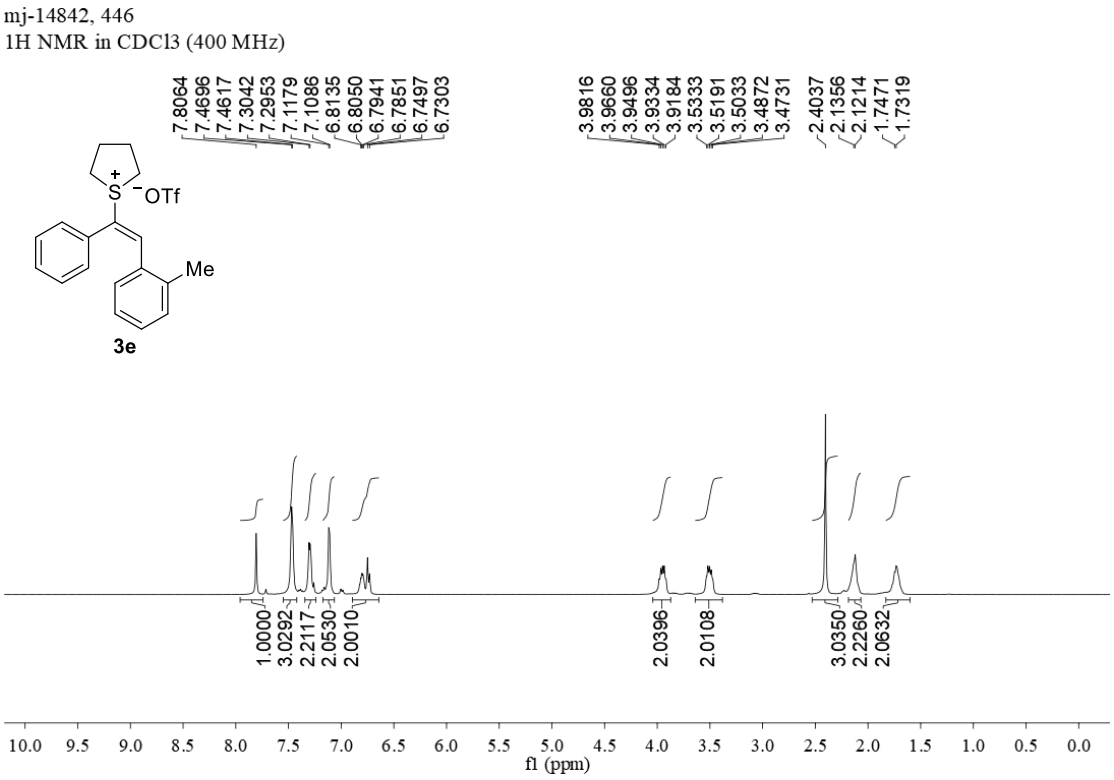


Figure S57. ^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 25 °C, 400 MHz).

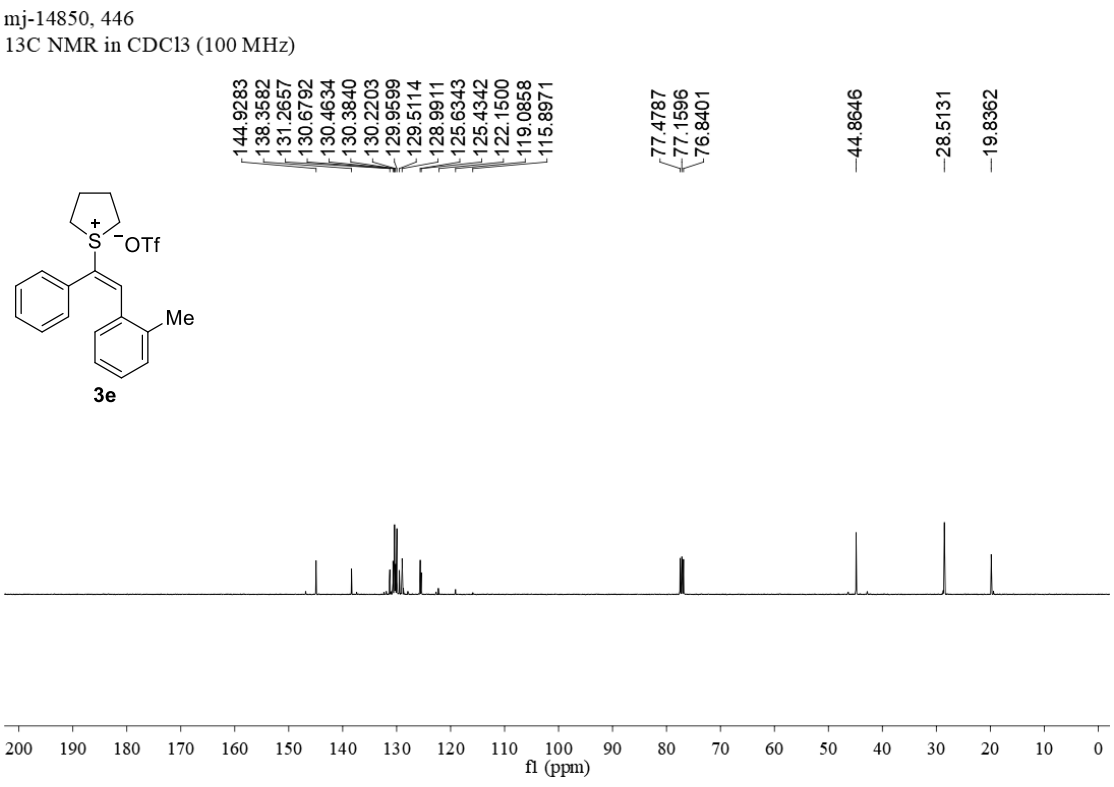


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3e** ($CDCl_3$, 25 °C, 100 MHz).

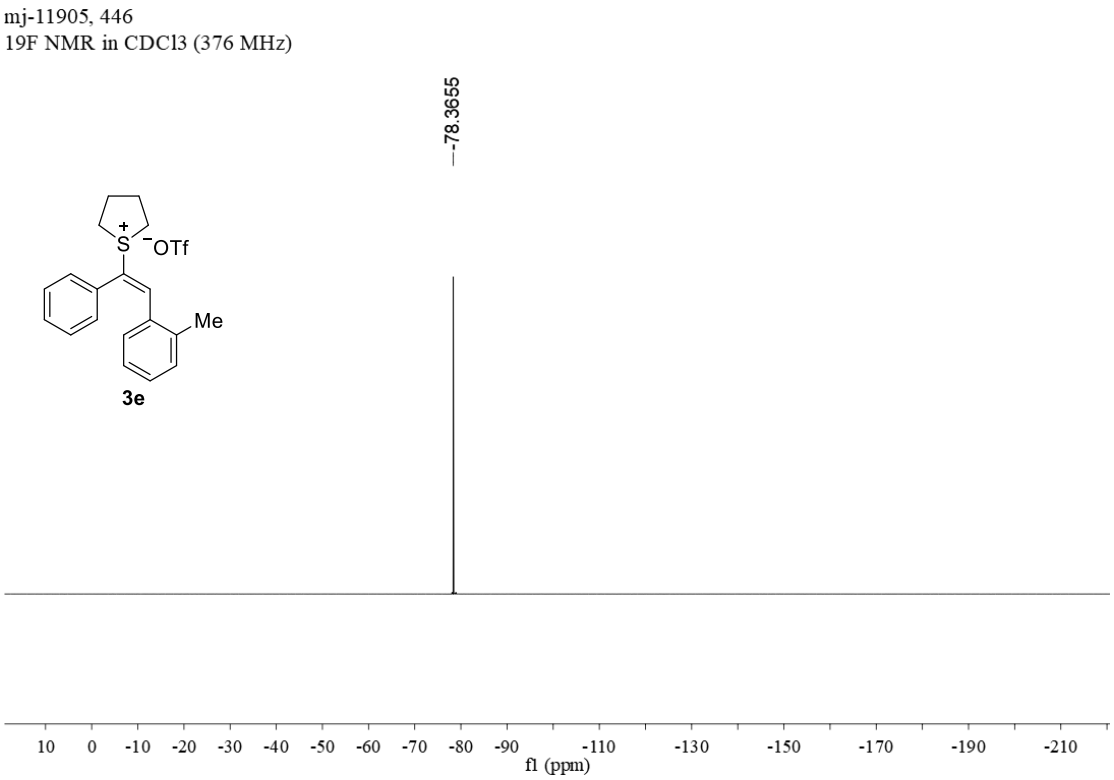


Figure S59. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3e** ($CDCl_3$, 25 °C, 376 MHz).

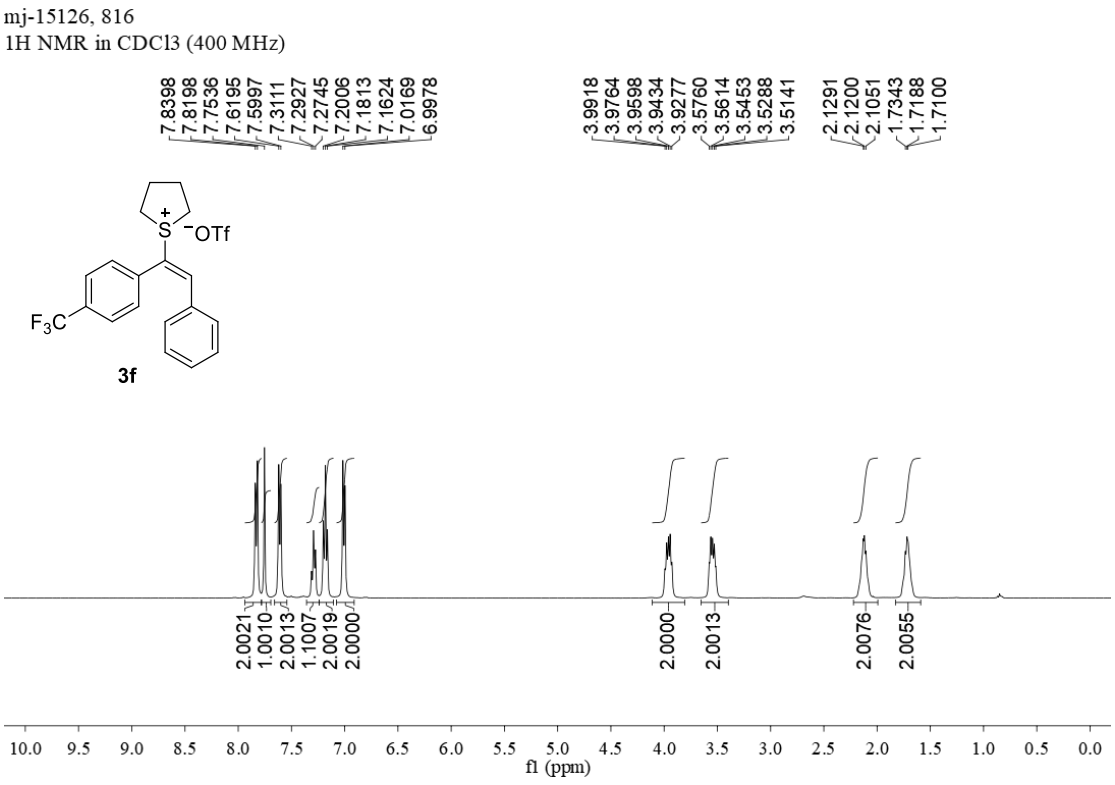


Figure S60. ^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 25 °C, 400 MHz).

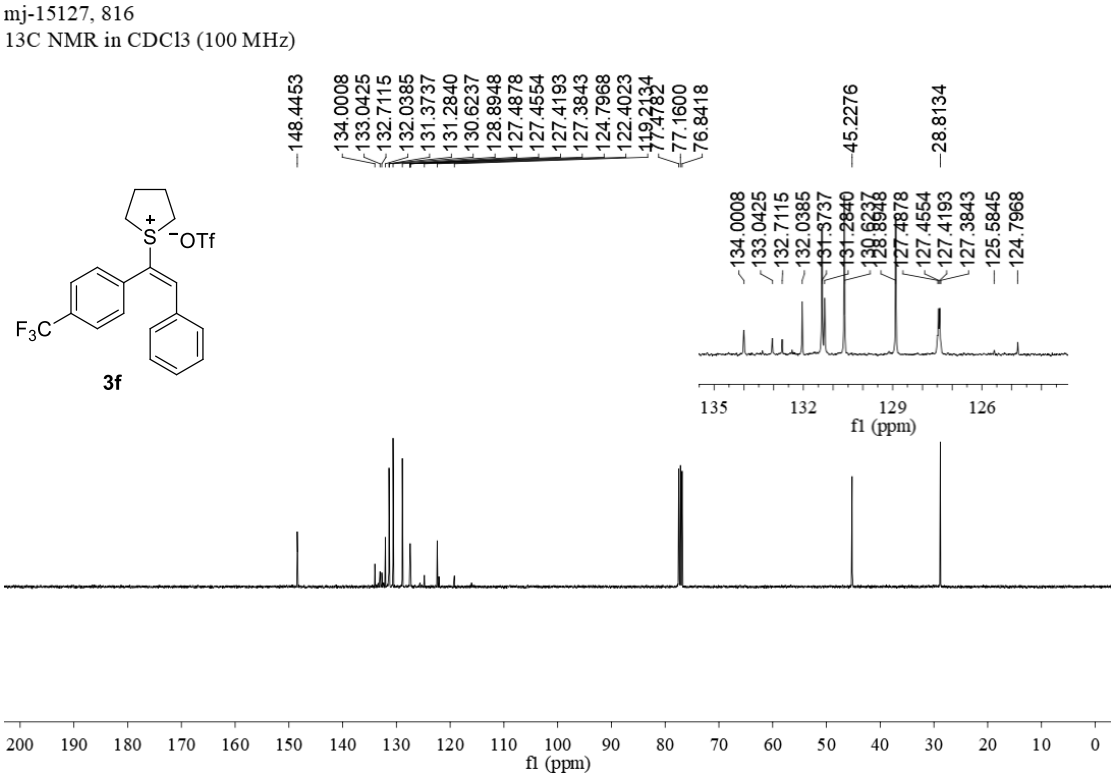


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3f** ($CDCl_3$, 25 °C, 100 MHz).

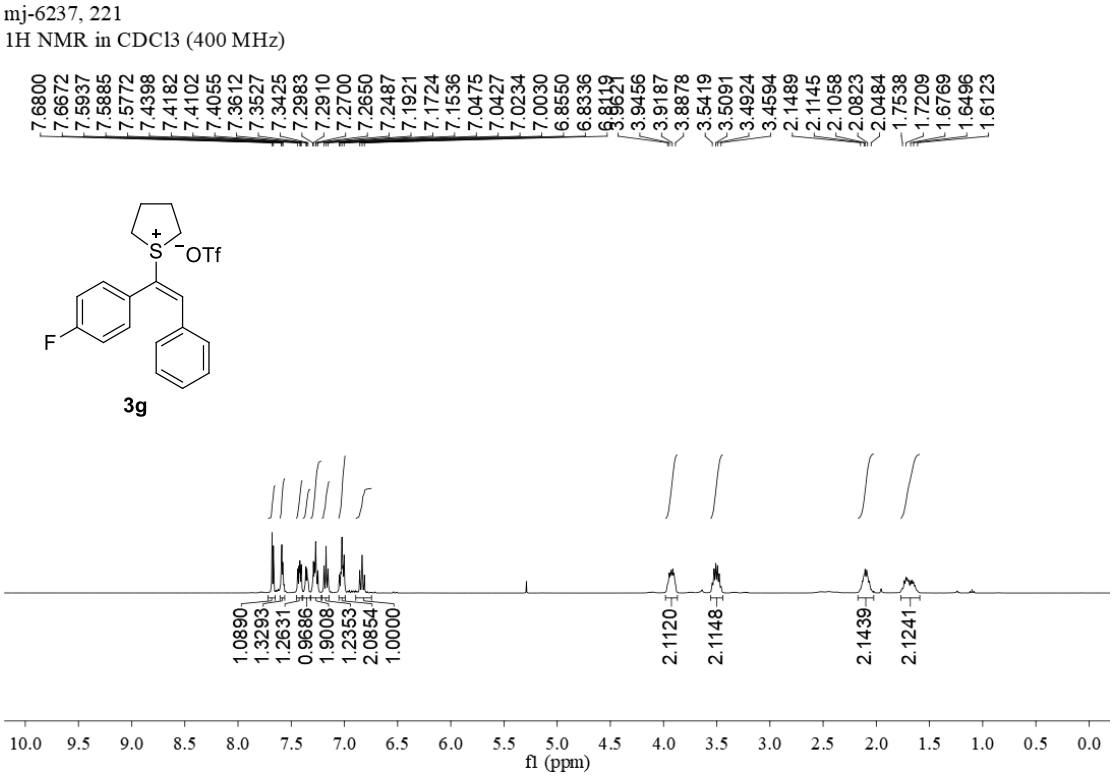


Figure S62. ^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 25 °C, 400 MHz).

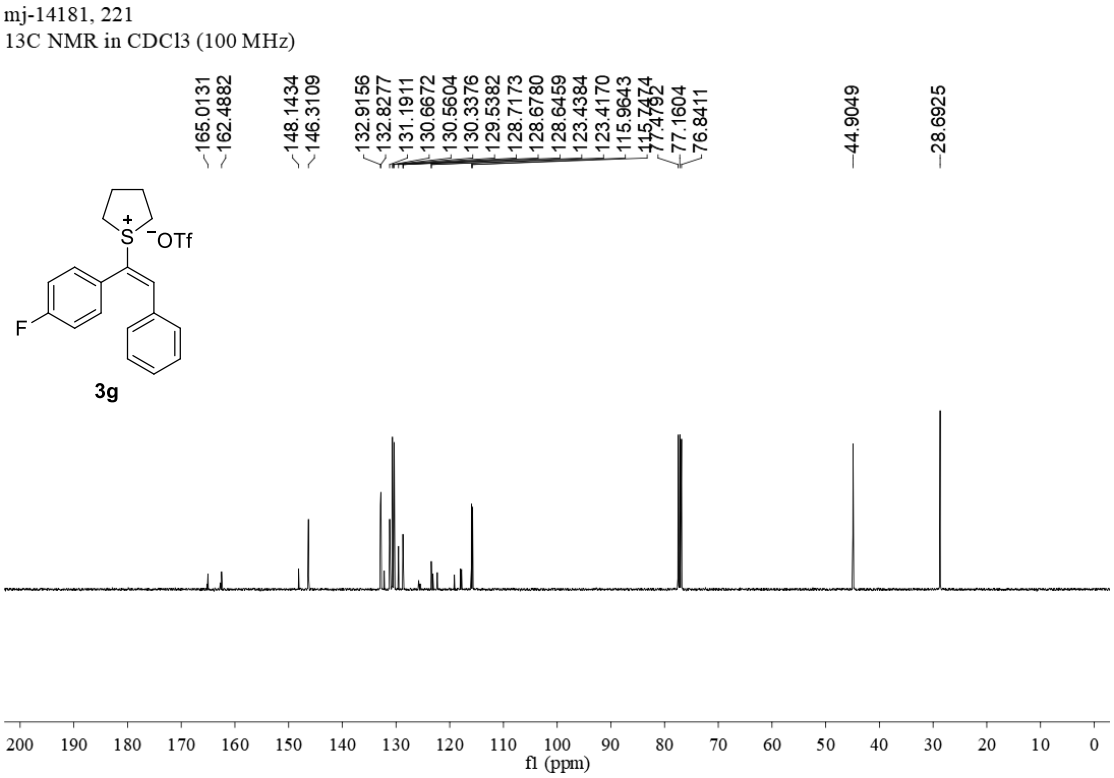


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3g** ($CDCl_3$, 25 °C, 100 MHz).

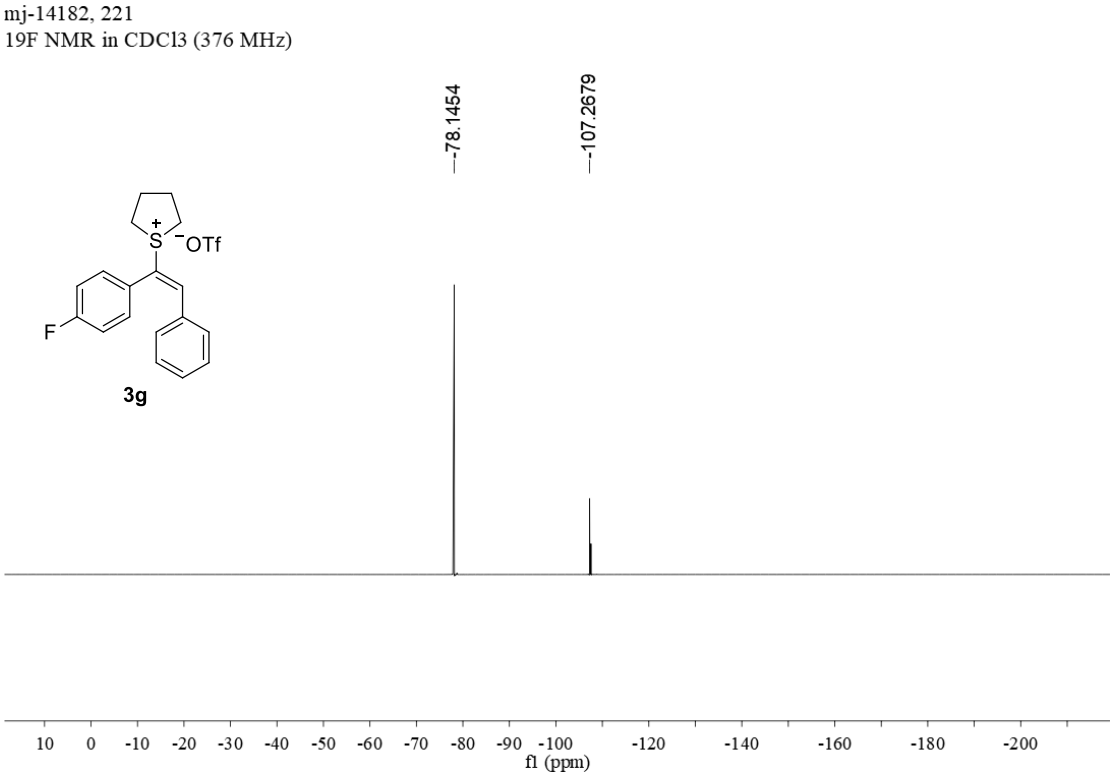


Figure S64. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3g** ($CDCl_3$, 25 °C, 376 MHz).

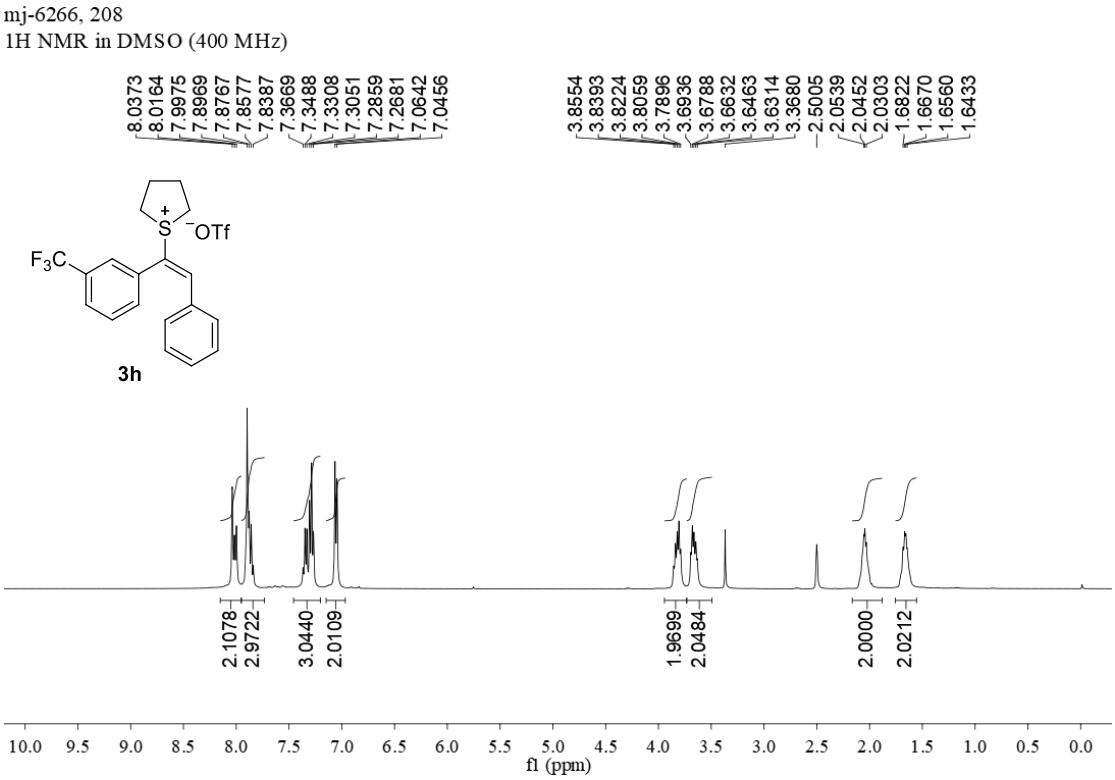


Figure S65. ^{1}H NMR spectrum of compound **3h** (DMSO-d6, 25 °C, 400 MHz).

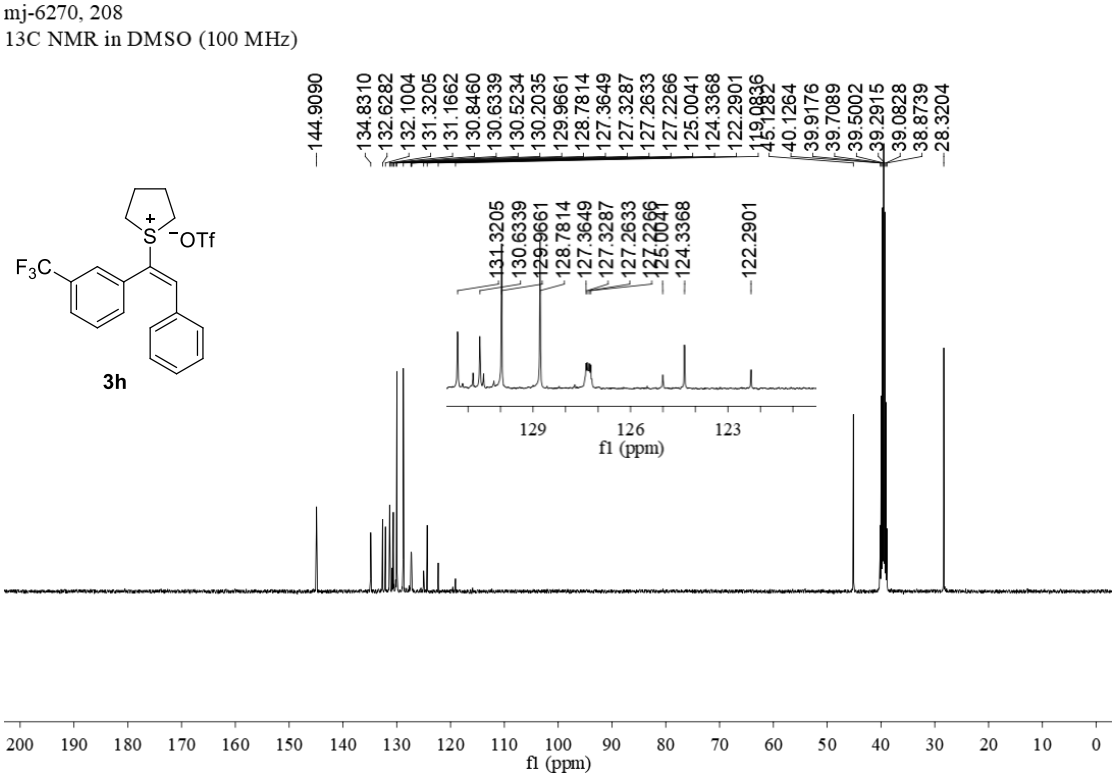


Figure S66. ^{13}C{^{1}H} NMR spectrum of compound **3h** (DMSO-d6, 25 °C, 100 MHz).

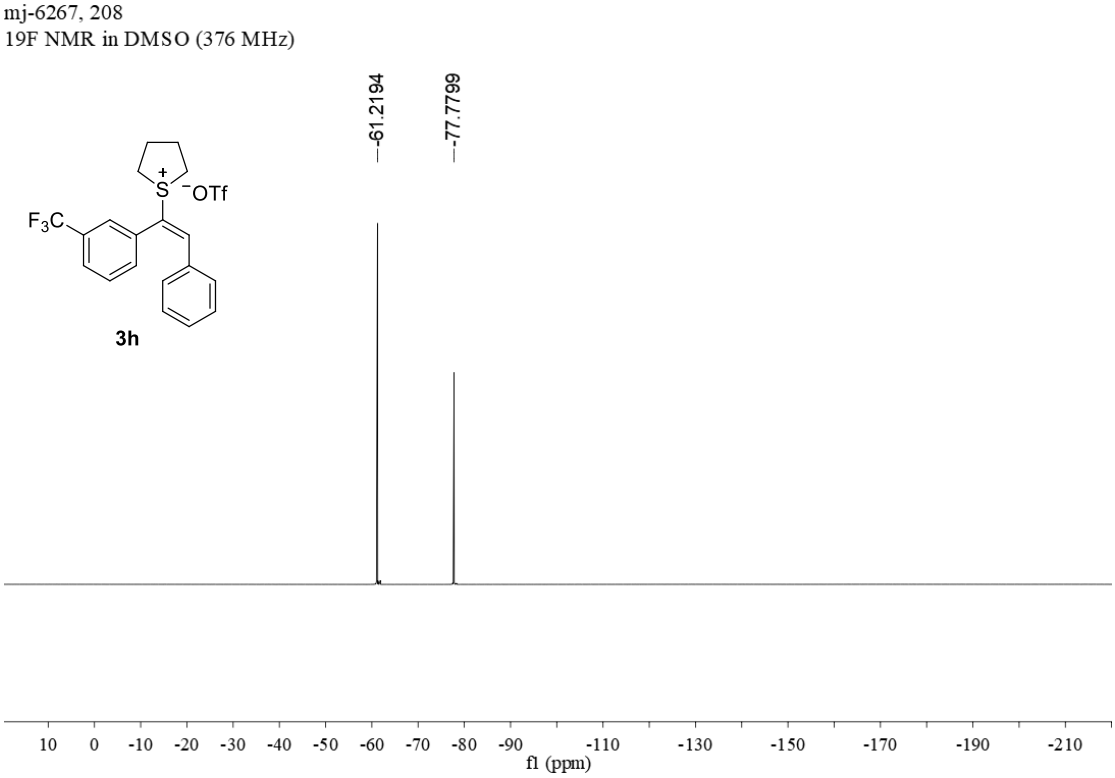


Figure S67. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3h** (DMSO-d6, 25 °C, 376 MHz).

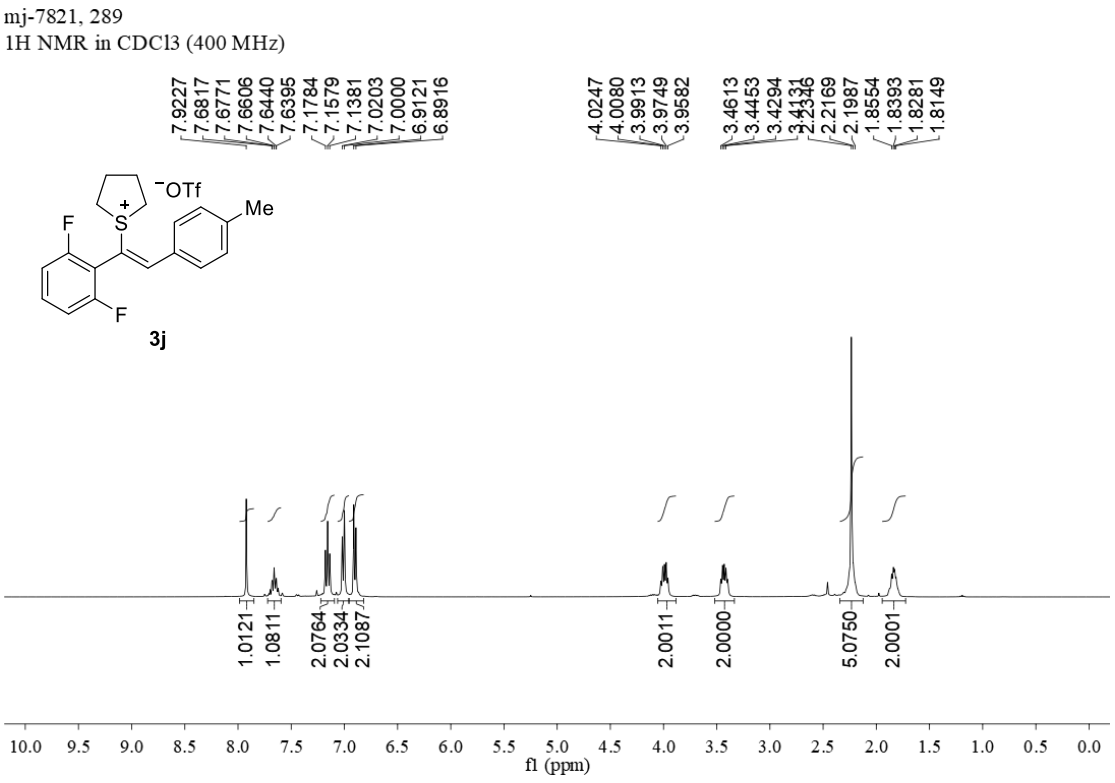


Figure S68. ^{1}H NMR spectrum of compound **3j** ($CDCl_3$, 25 °C, 400 MHz).

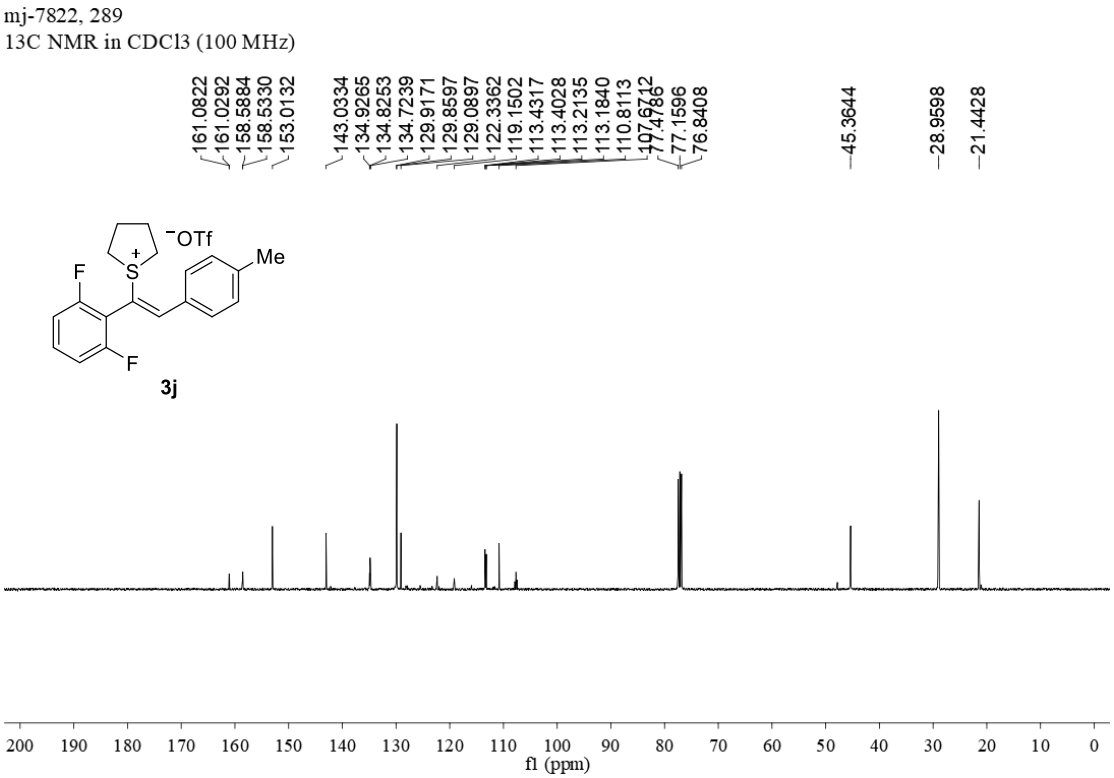


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3j** ($CDCl_3$, 25 °C, 100 MHz).

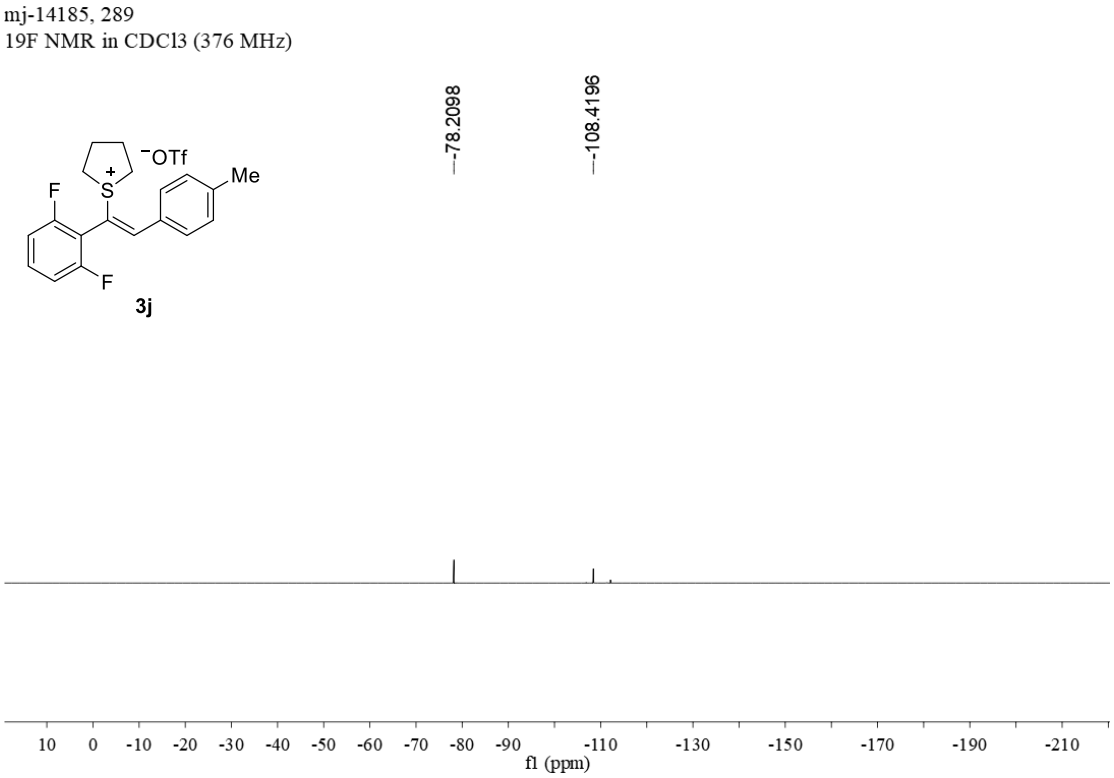


Figure S70. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3j** ($CDCl_3$, 25 °C, 376 MHz).

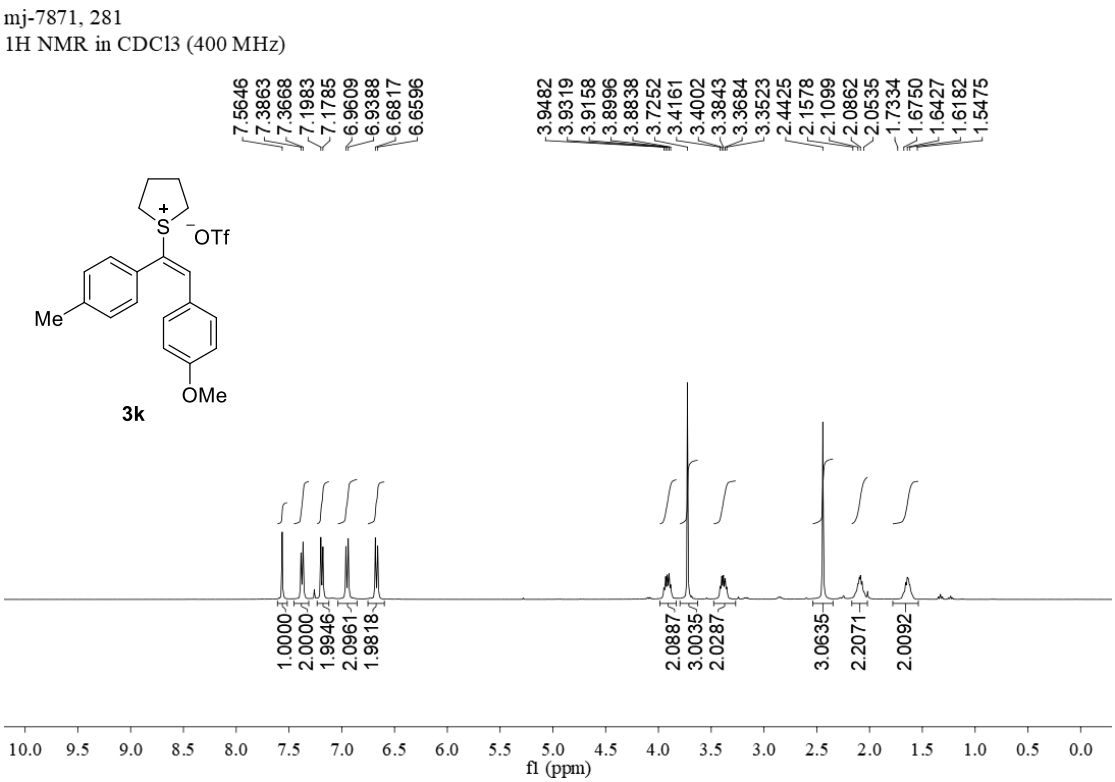


Figure S71. ^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 25 °C, 400 MHz).

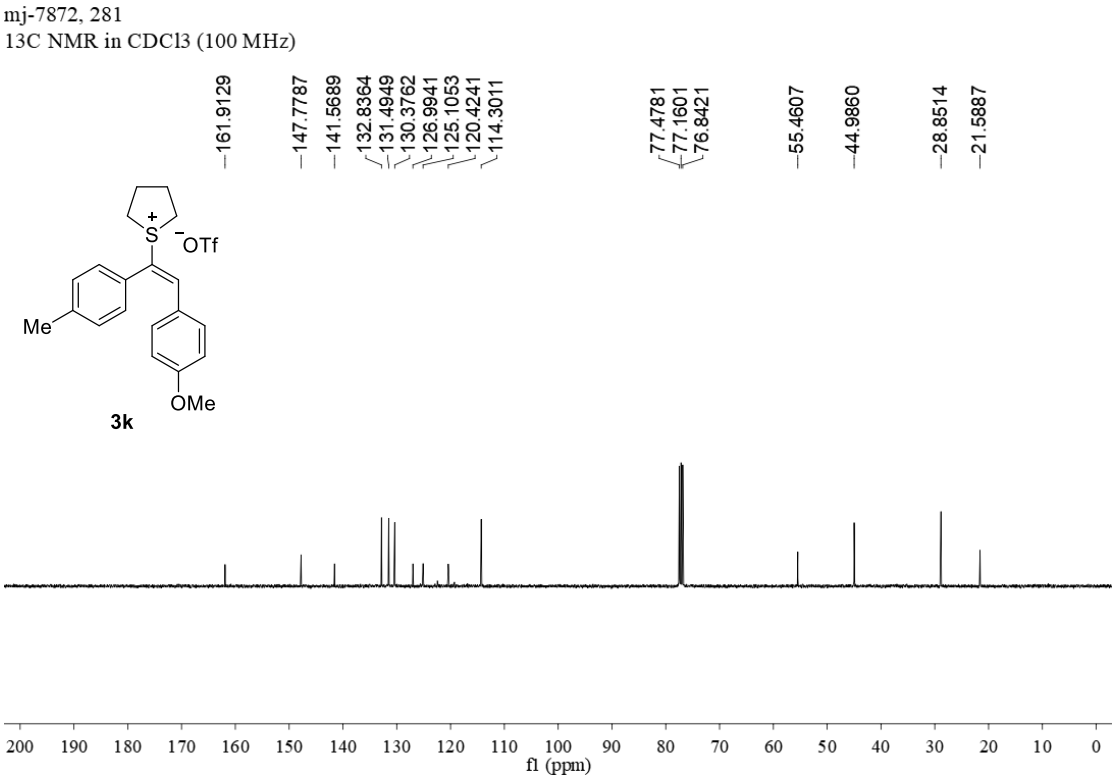


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3k** ($CDCl_3$, 25 °C, 100 MHz).

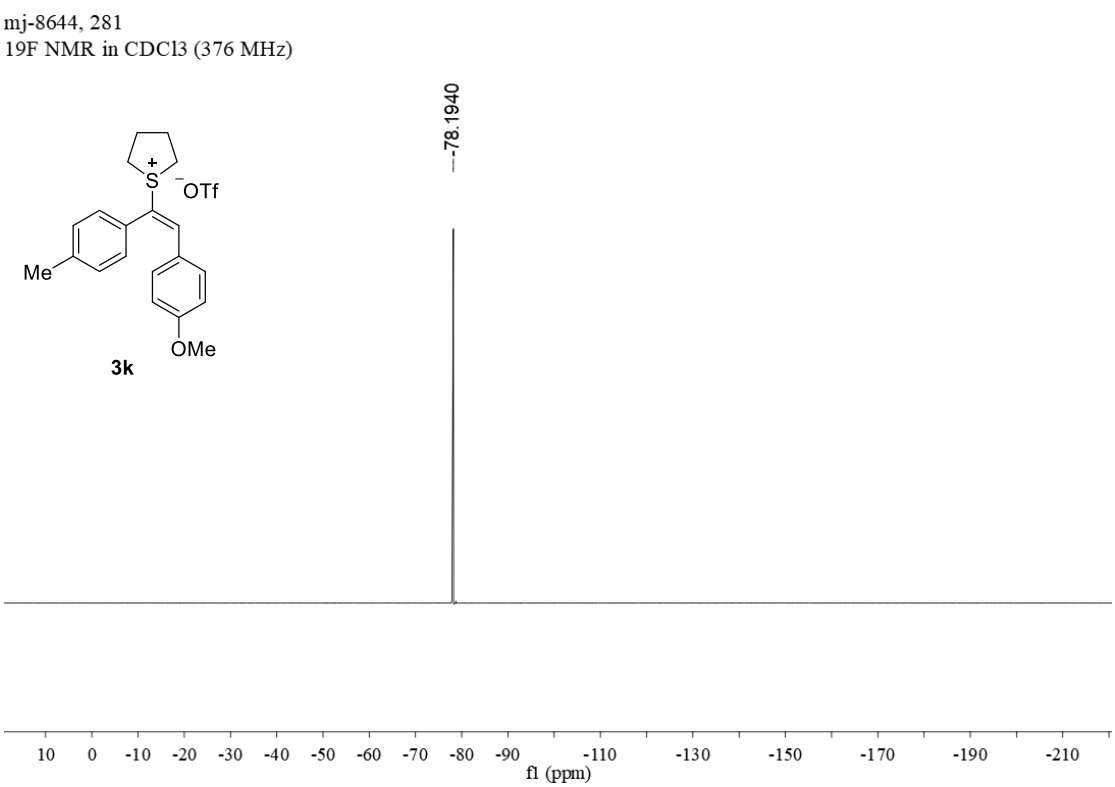


Figure S73. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3k** ($CDCl_3$, 25 °C, 376 MHz).

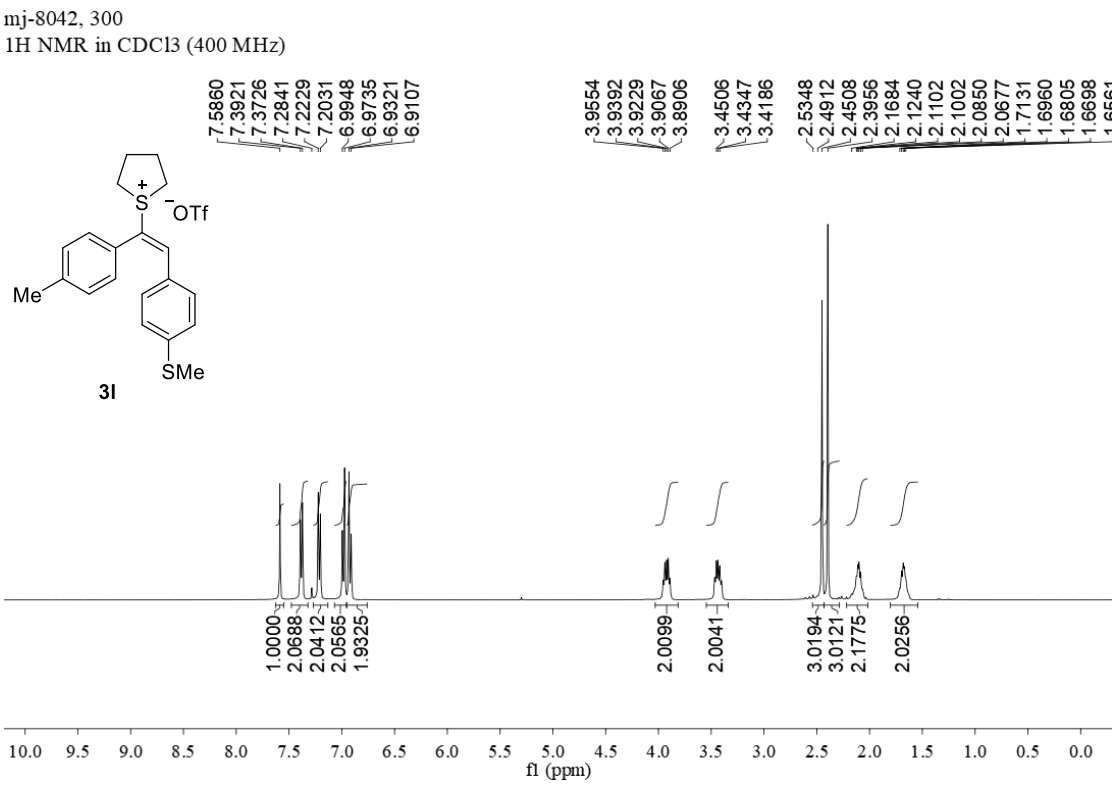


Figure S74. ^{1}H NMR spectrum of compound **3l** ($CDCl_3$, 25 °C, 400 MHz).

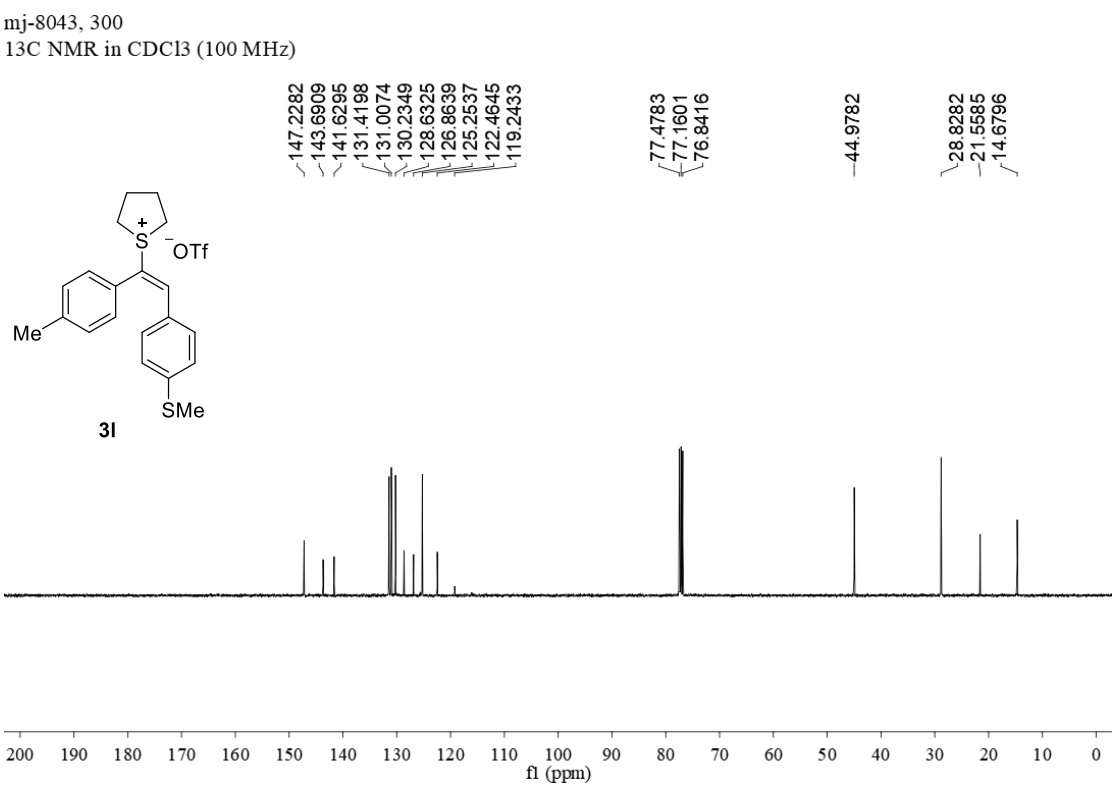


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3l** ($CDCl_3$, 25 °C, 100 MHz).

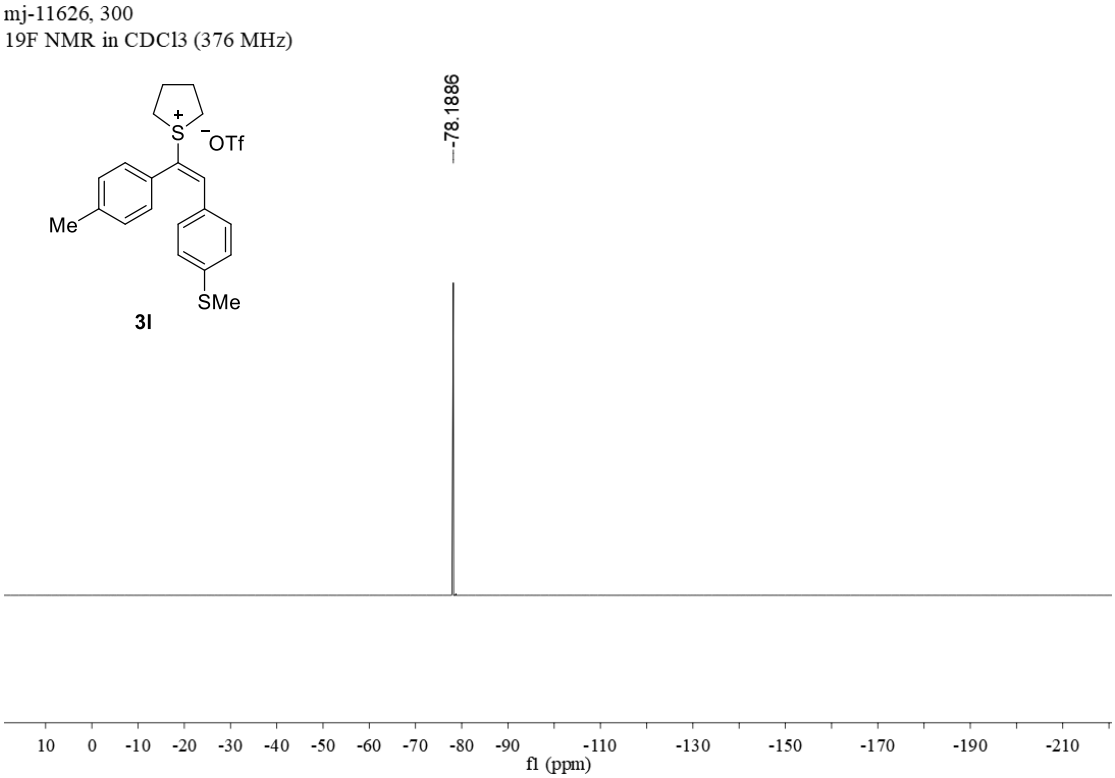


Figure S76. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3l** ($CDCl_3$, 25 °C, 376 MHz).

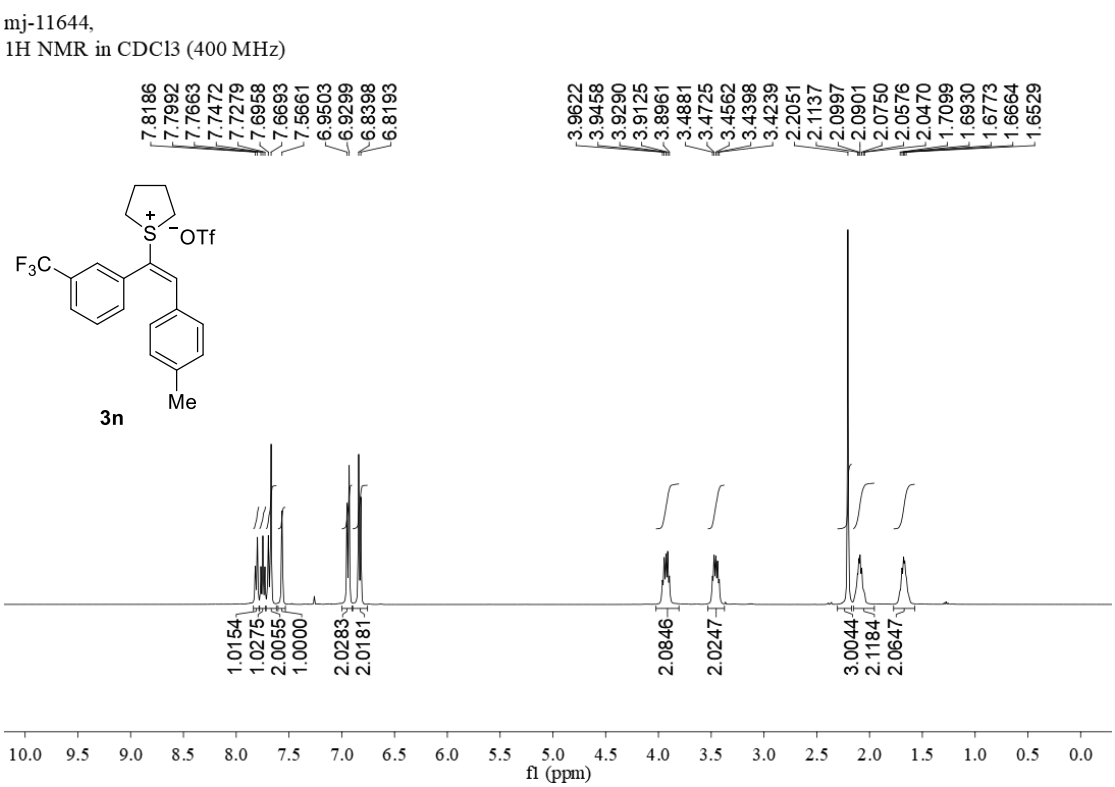


Figure S77. ^{1}H NMR spectrum of compound **3n** ($CDCl_3$, 25 °C, 400 MHz).

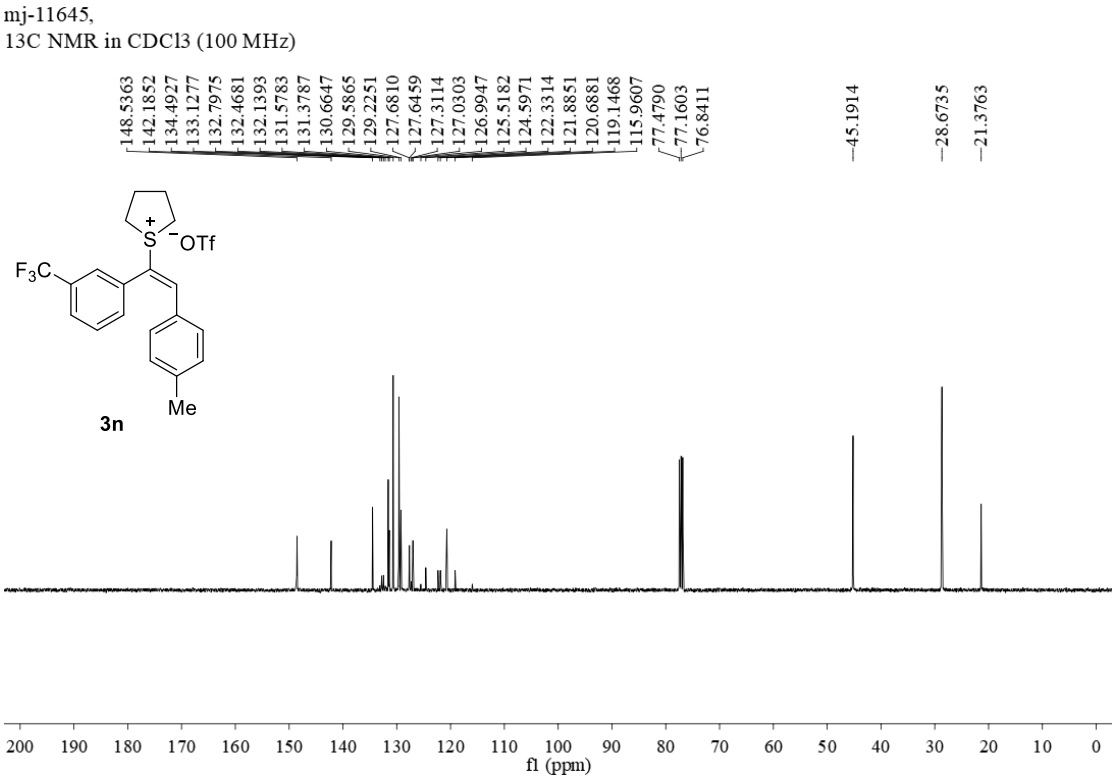


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3n** ($CDCl_3$, 25 °C, 100 MHz).

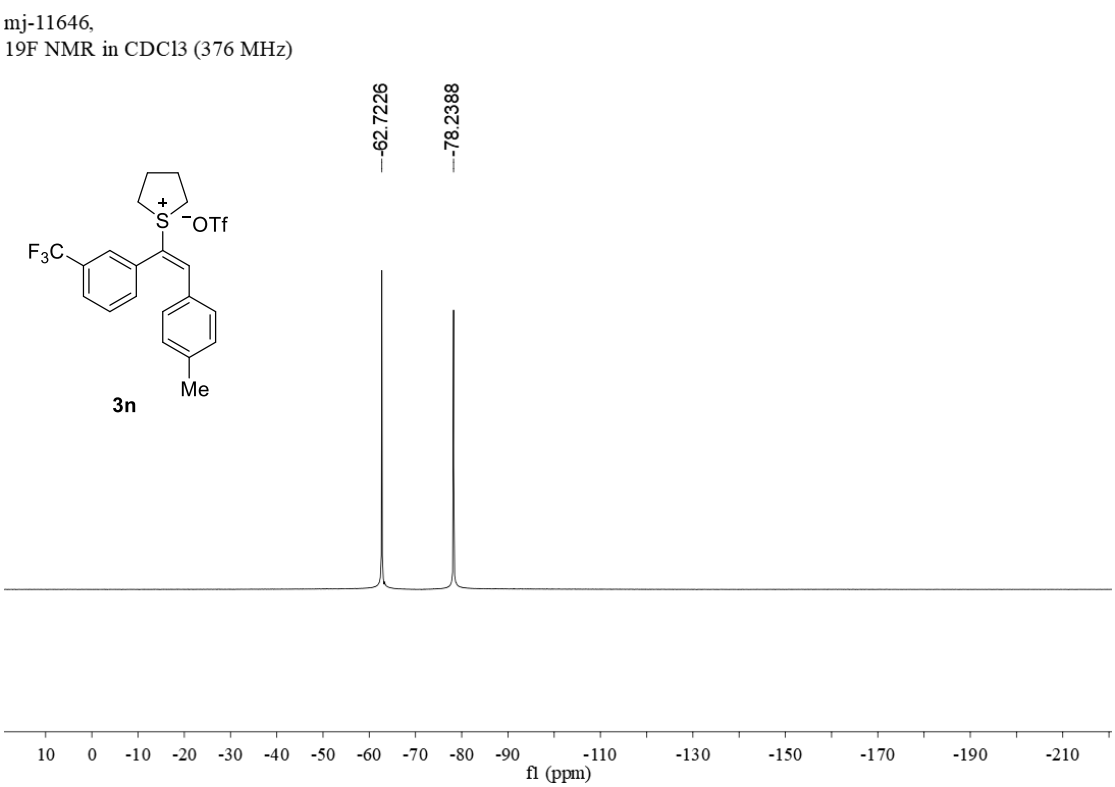


Figure S79. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3n** ($CDCl_3$, 25 °C, 376 MHz).

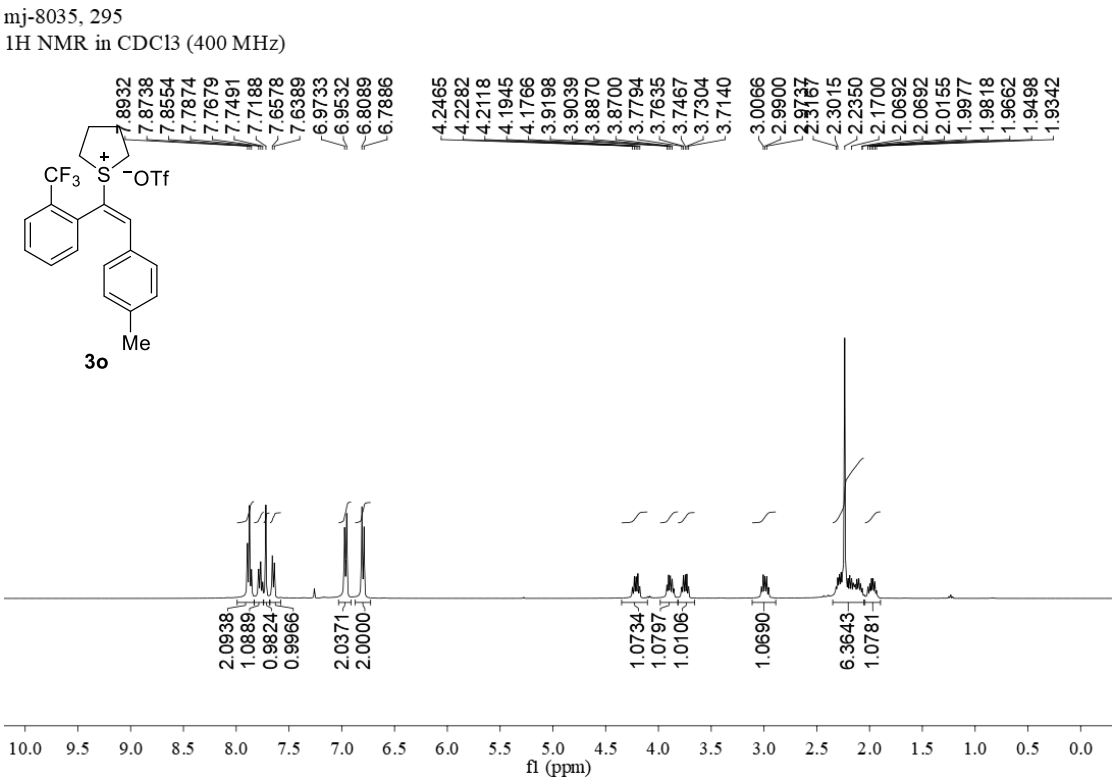


Figure S80. ^{1}H NMR spectrum of compound **3o** ($CDCl_3$, 25 °C, 400 MHz).

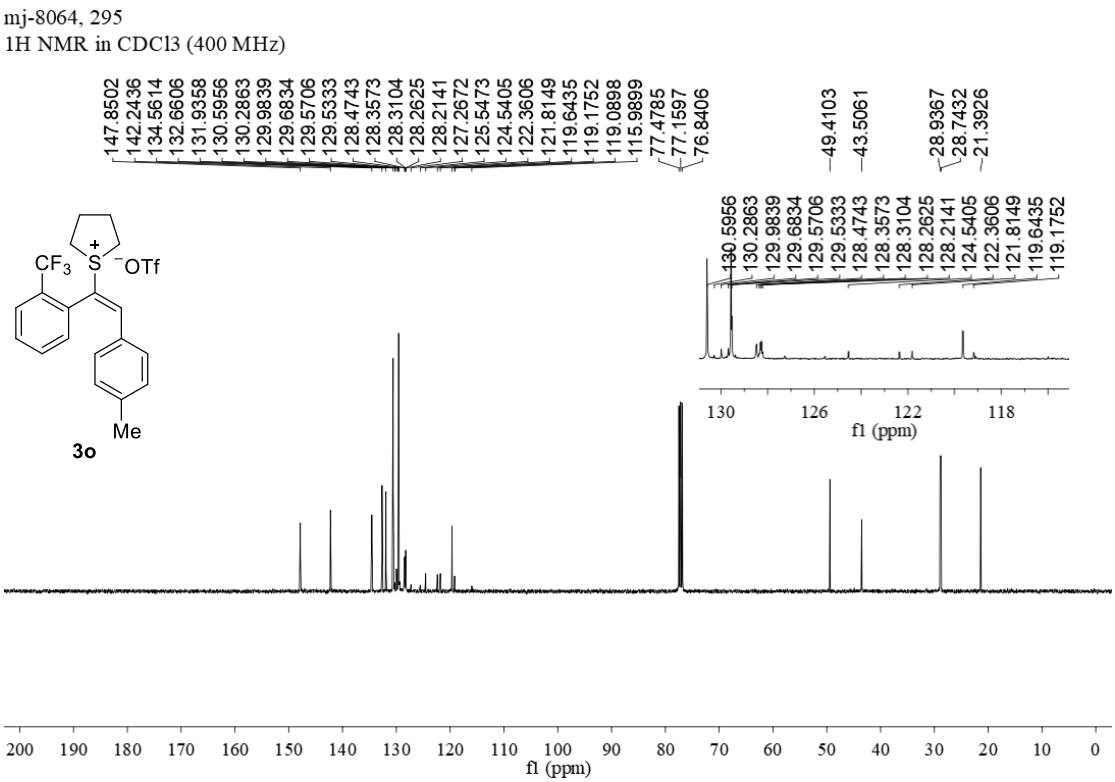


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3o** ($CDCl_3$, 25 °C, 100 MHz).

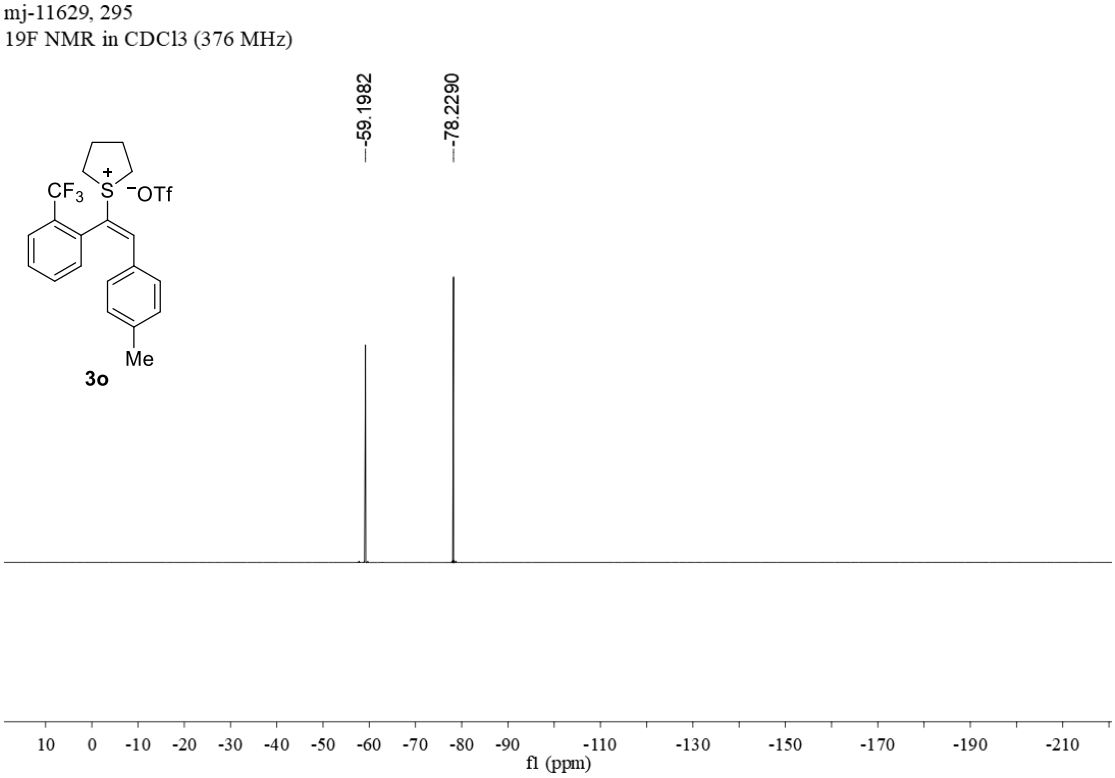


Figure S82. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3o** ($CDCl_3$, 25 °C, 376 MHz).

Figure S83. ^{1}H NMR spectrum of compound **3p** ($CDCl_3$, 25 °C, 400 MHz).

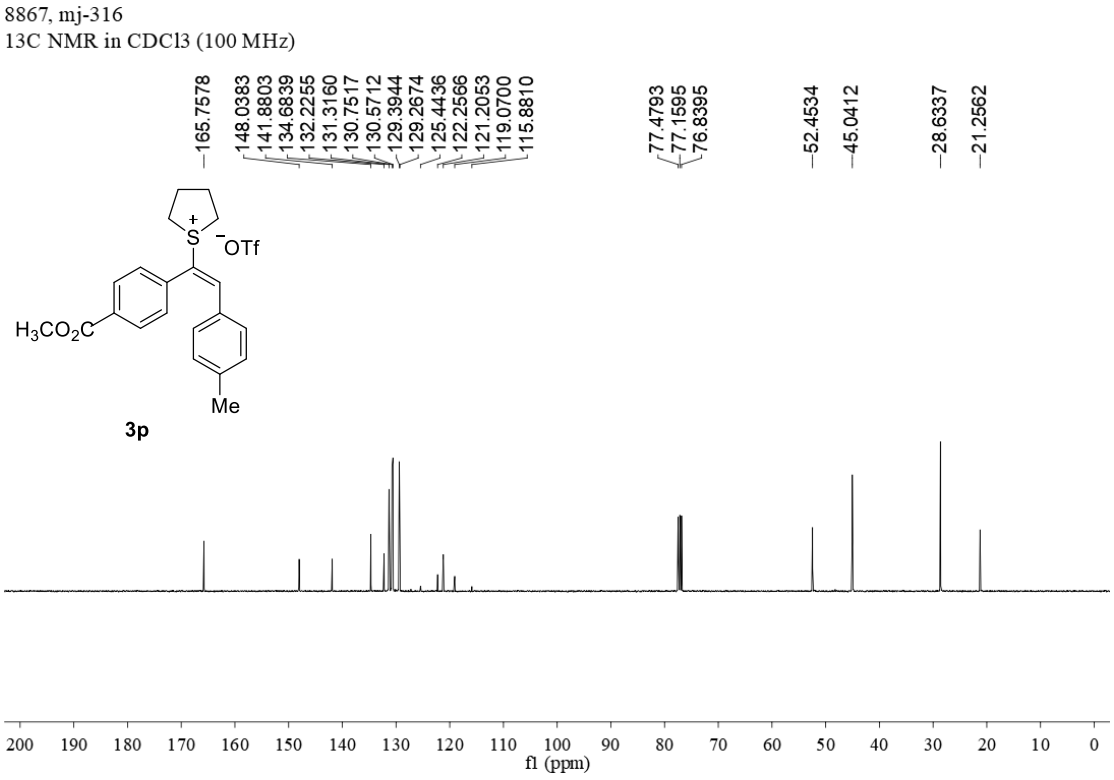


Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3p** ($CDCl_3$, 25 °C, 100 MHz).

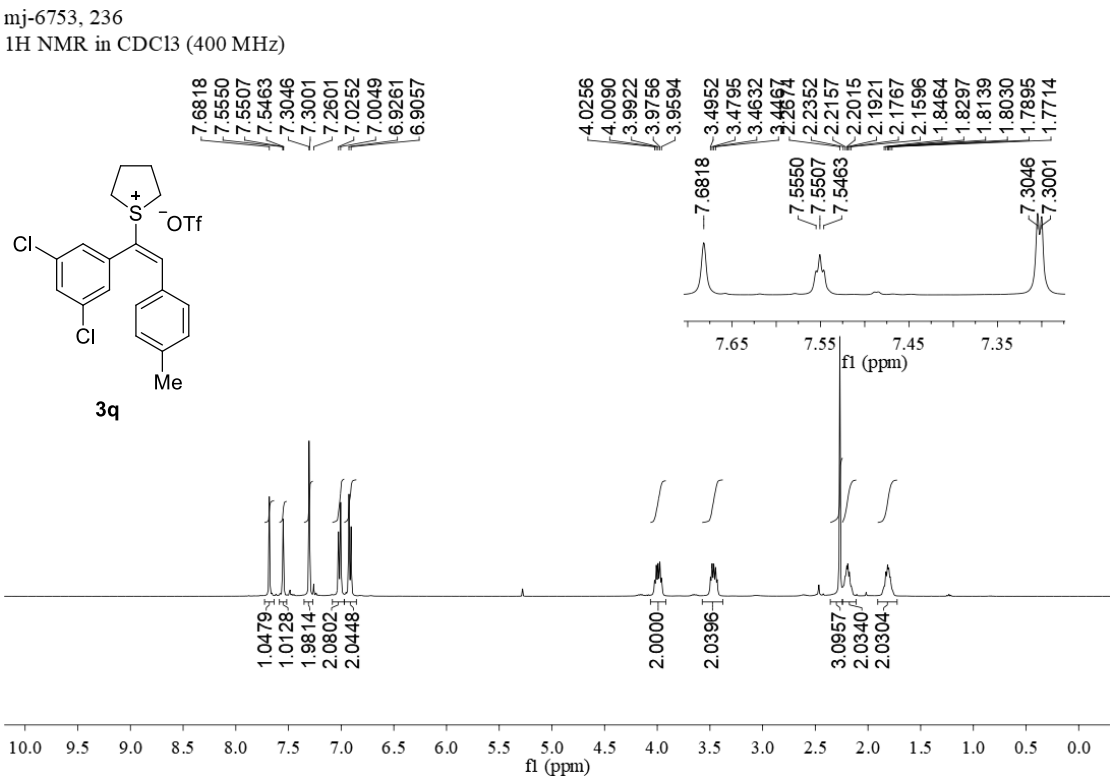


Figure S85. ^{1}H NMR spectrum of compound **3q** ($CDCl_3$, 25 °C, 400 MHz).

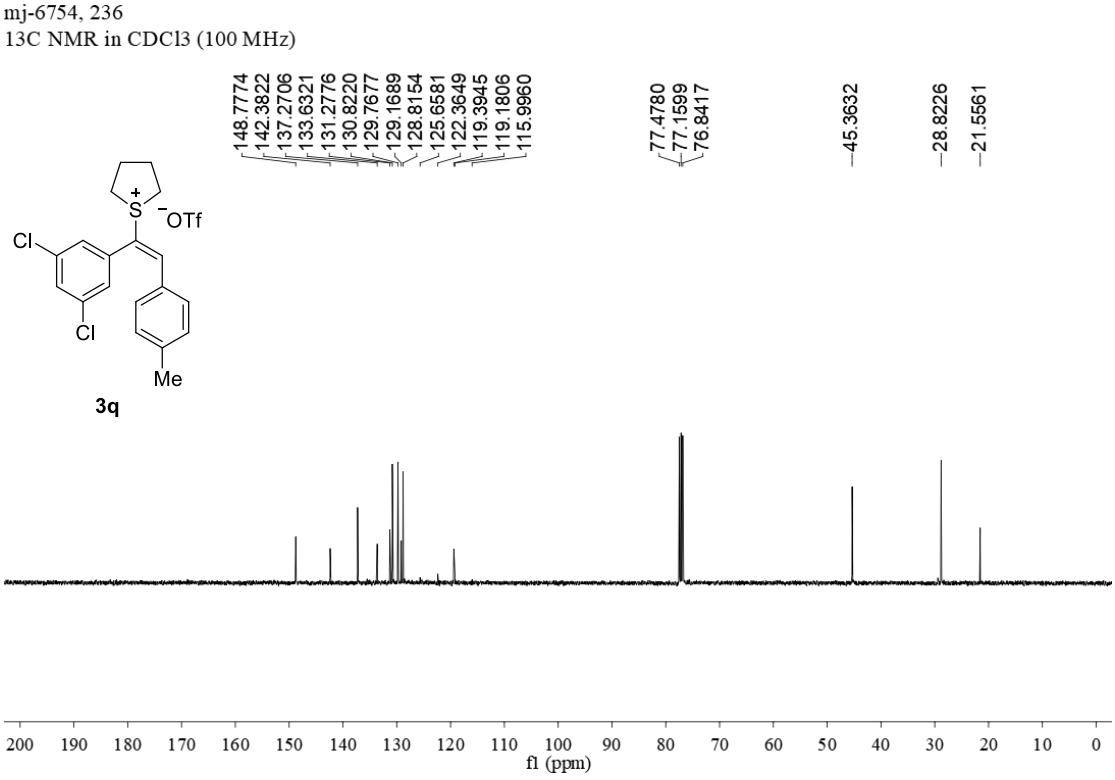


Figure S86. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3q** ($CDCl_3$, 25 °C, 100 MHz).

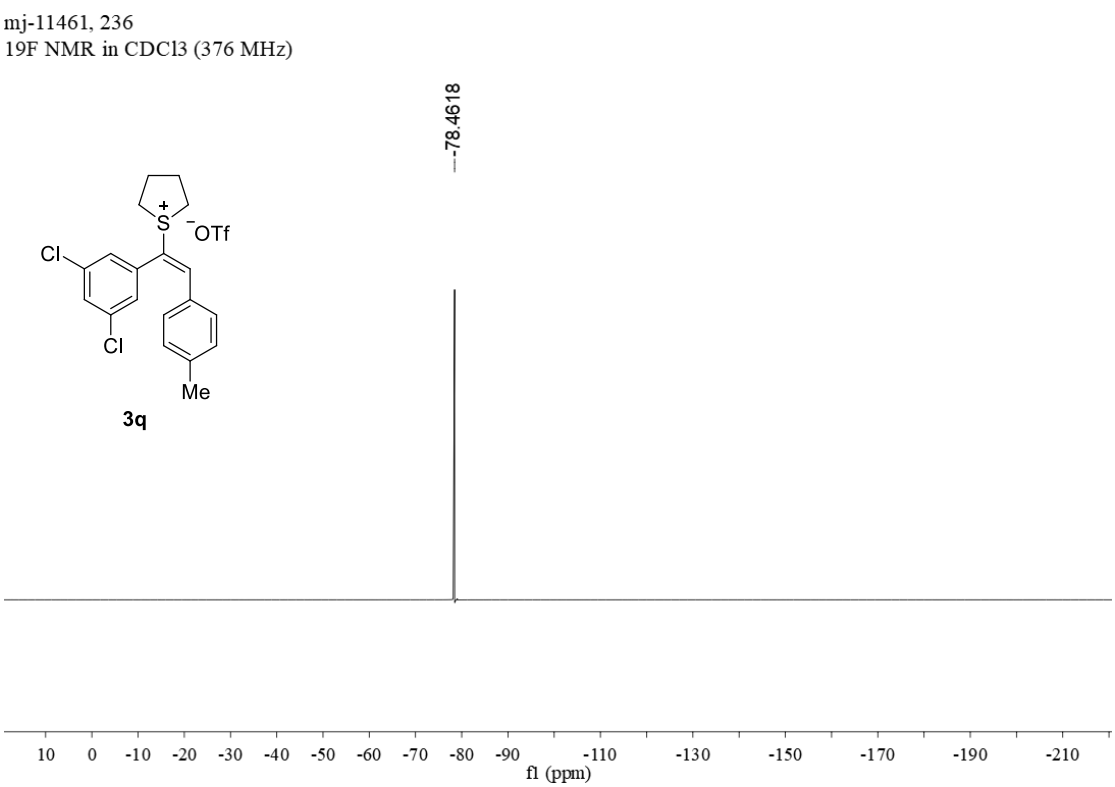


Figure S87. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3q** ($CDCl_3$, 25 °C, 376 MHz).

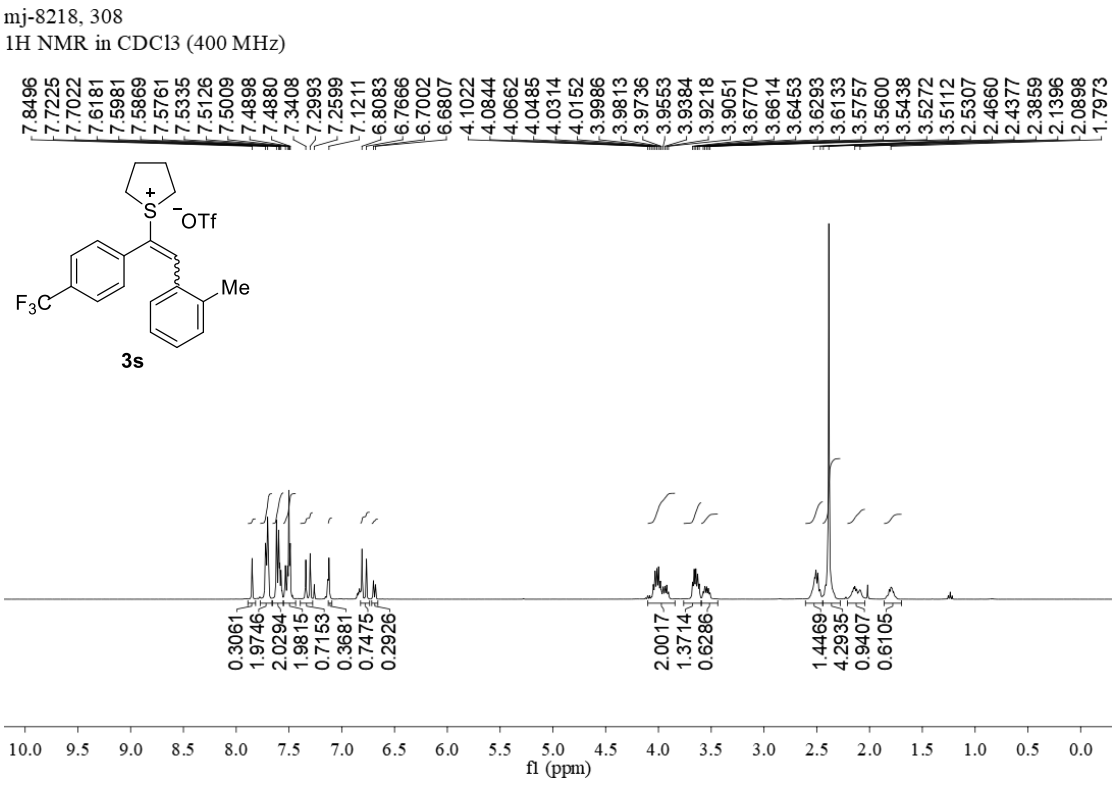


Figure S88. ^{1}H NMR spectrum of compound **3s** ($CDCl_3$, 25 °C, 400 MHz).

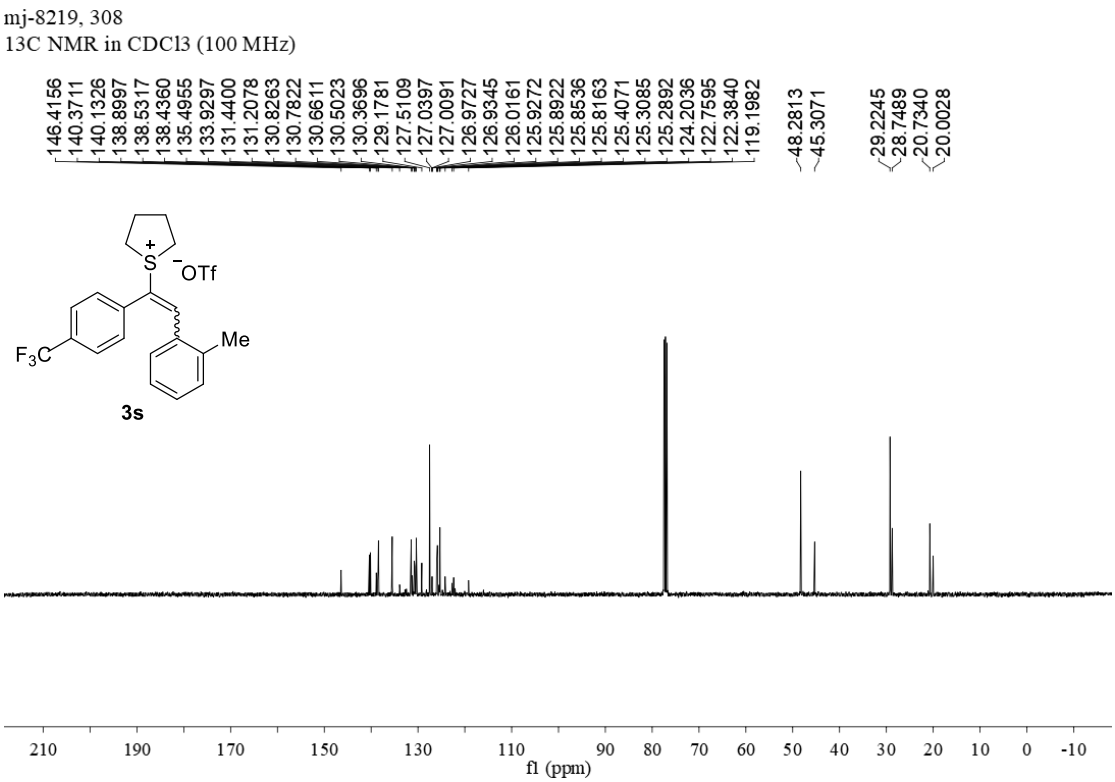


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3s** ($CDCl_3$, 25 °C, 100 MHz).

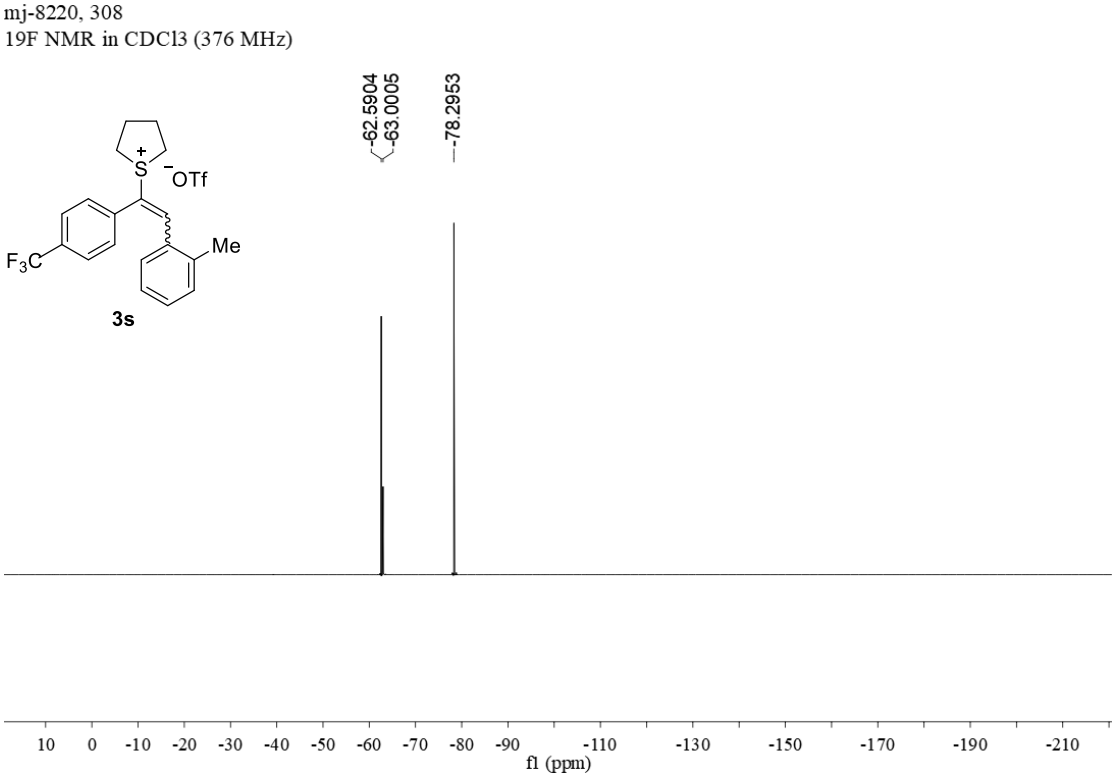


Figure S90. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3s** ($CDCl_3$, 25 °C, 376 MHz).

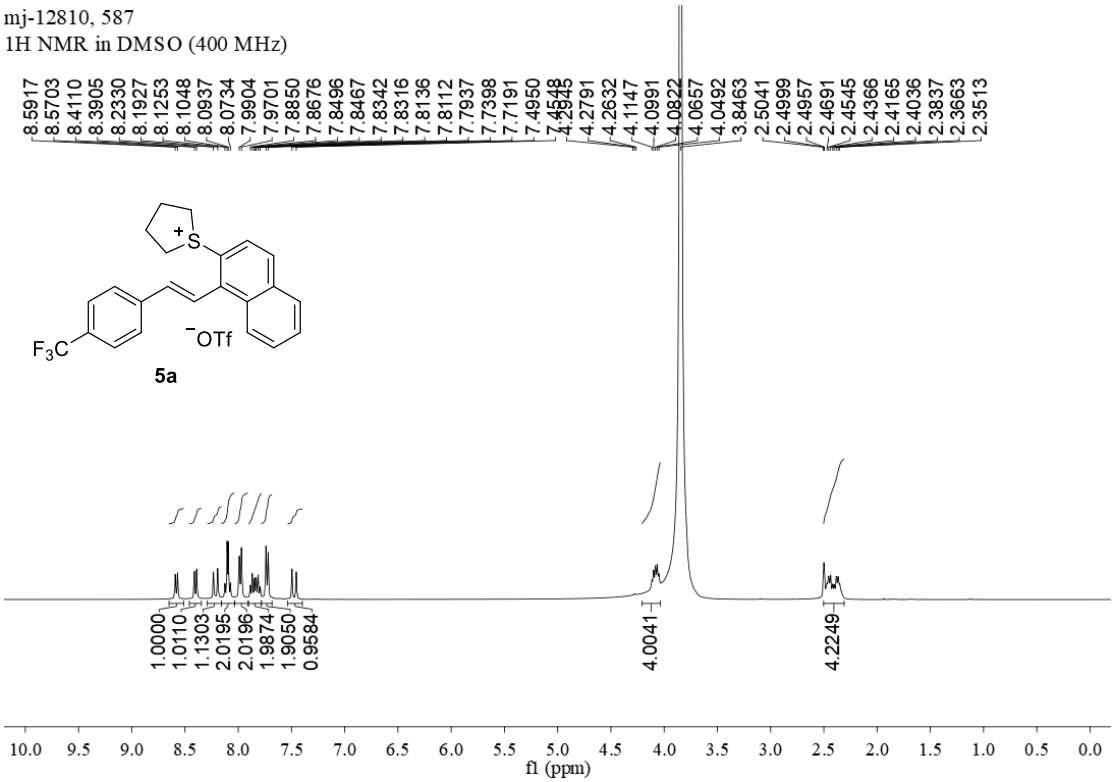


Figure S91. ^{1}H NMR spectrum of compound **5a** (DMSO-d6, 25 °C, 400 MHz).

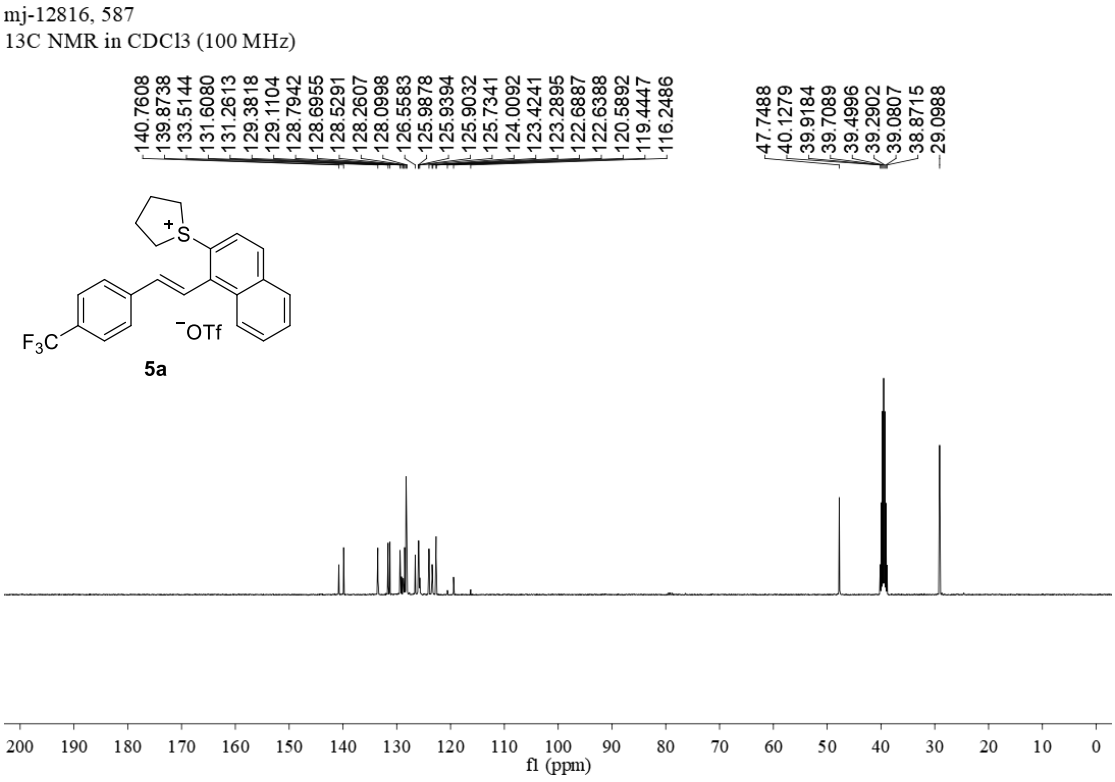


Figure S92. ^{13}C{^{1}H} NMR spectrum of compound **5a** (DMSO-d6, 25 °C, 100 MHz).

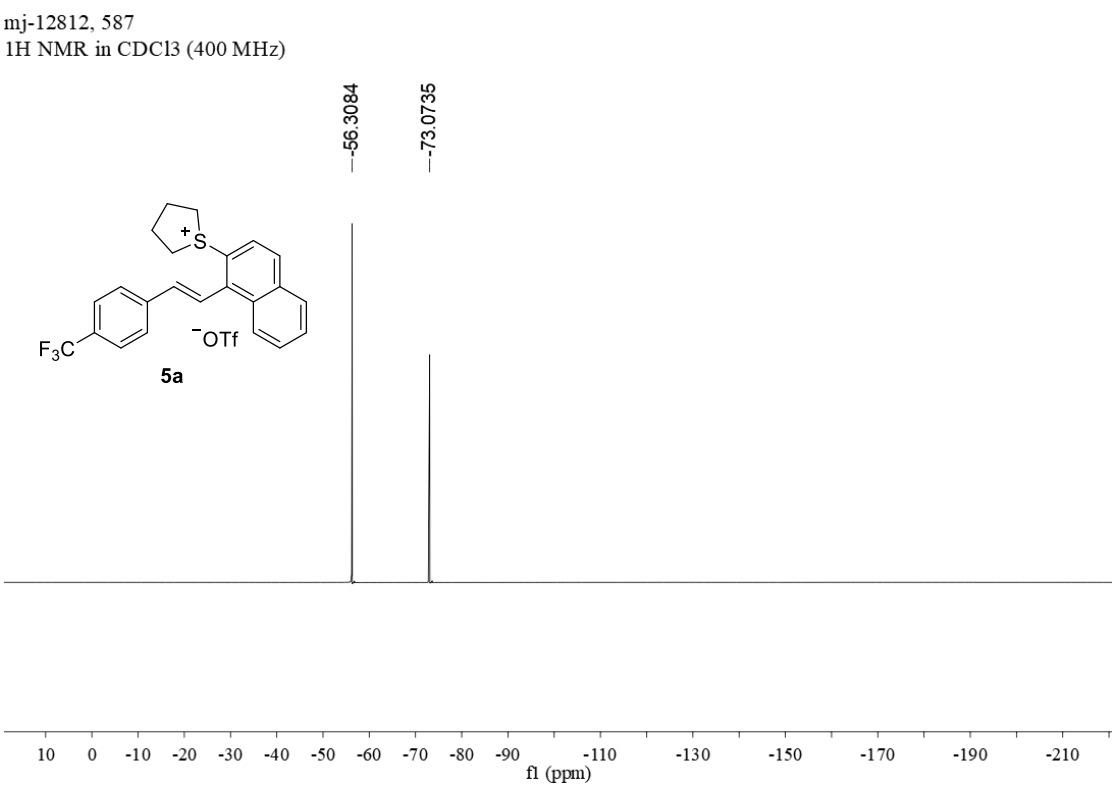


Figure S93. $^{19}F\{^{1}H\}$ NMR spectrum of compound **5a** (DMSO-d6, 25 °C, 376 MHz).

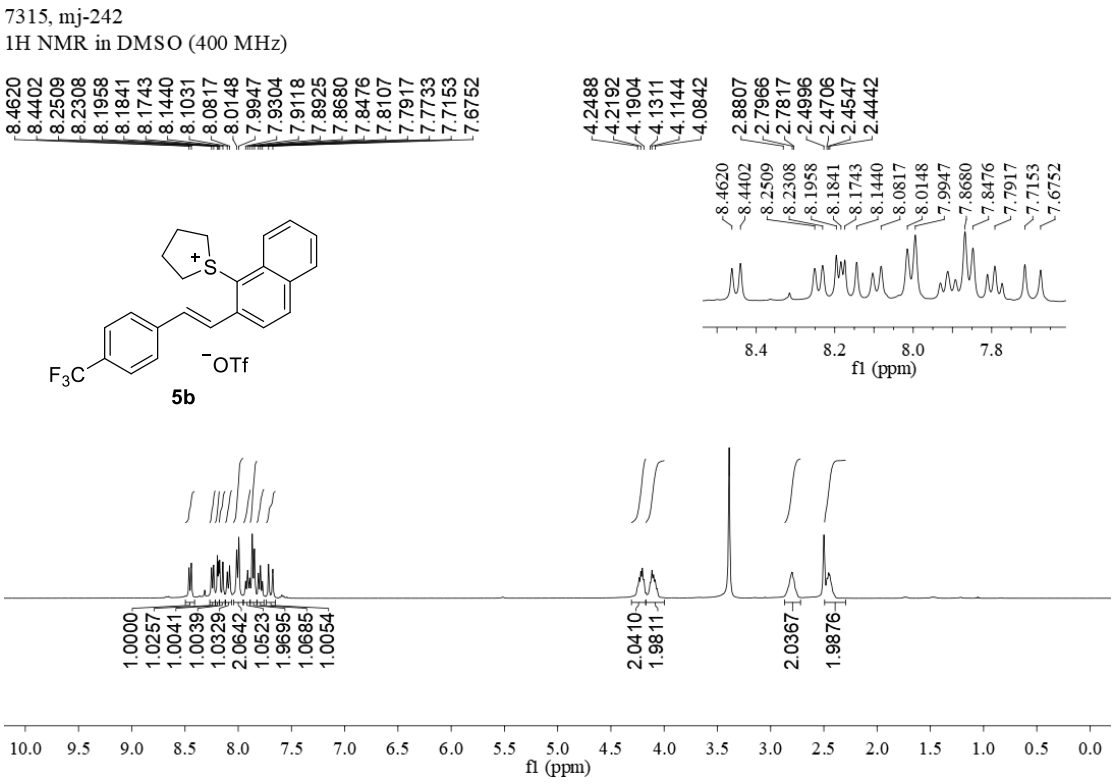


Figure S94. ^{1}H NMR spectrum of compound **5b** (DMSO-d6, 25 °C, 400 MHz).

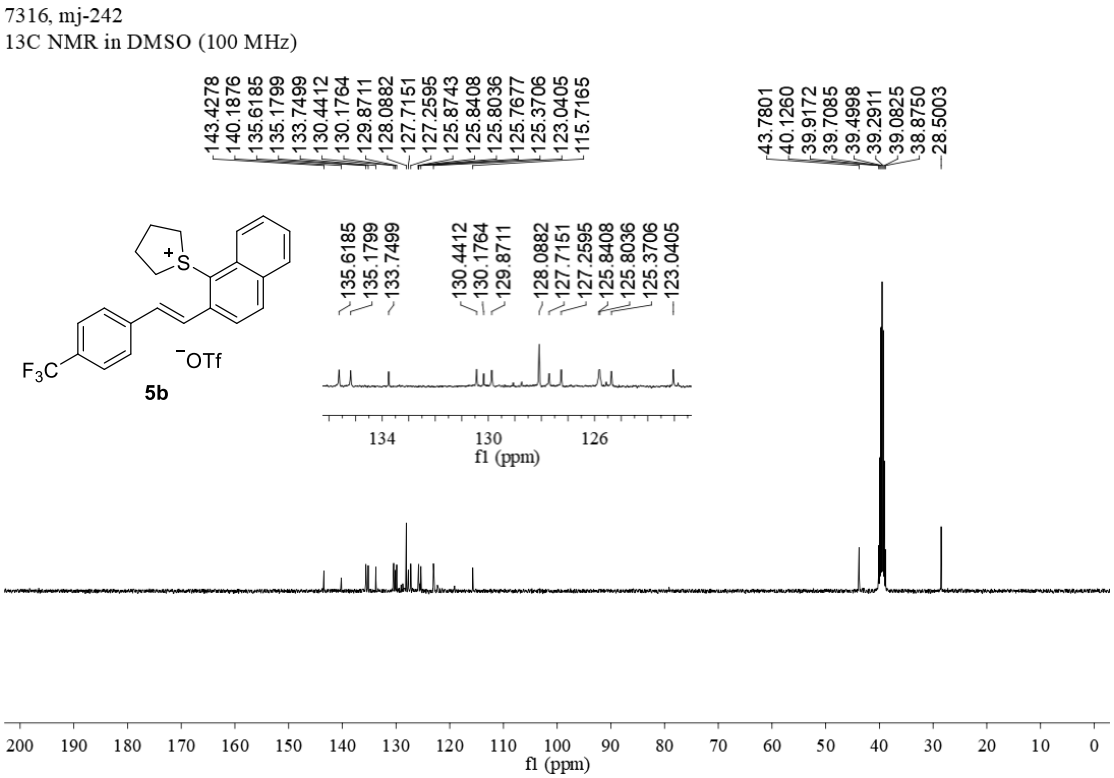


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5b** (DMSO-d6, 25 °C, 100 MHz).

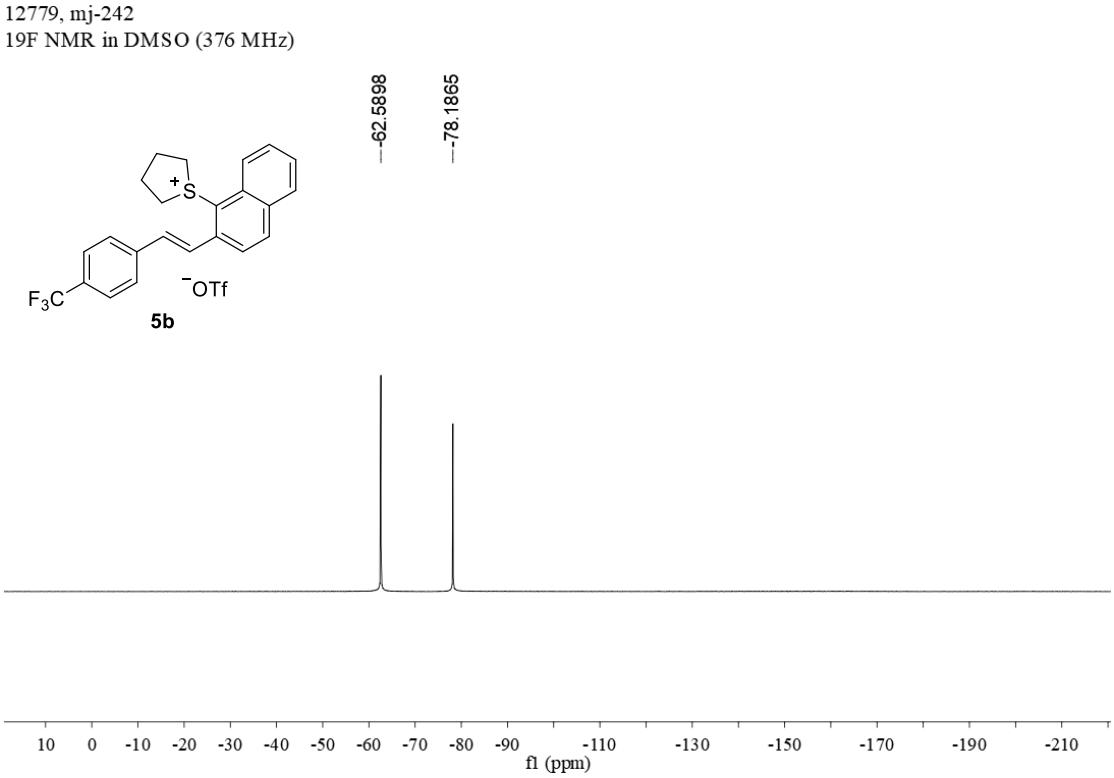


Figure S96. $^{19}F\{^{1}H\}$ NMR spectrum of compound **5b** (DMSO-d6, 25 °C, 376 MHz).

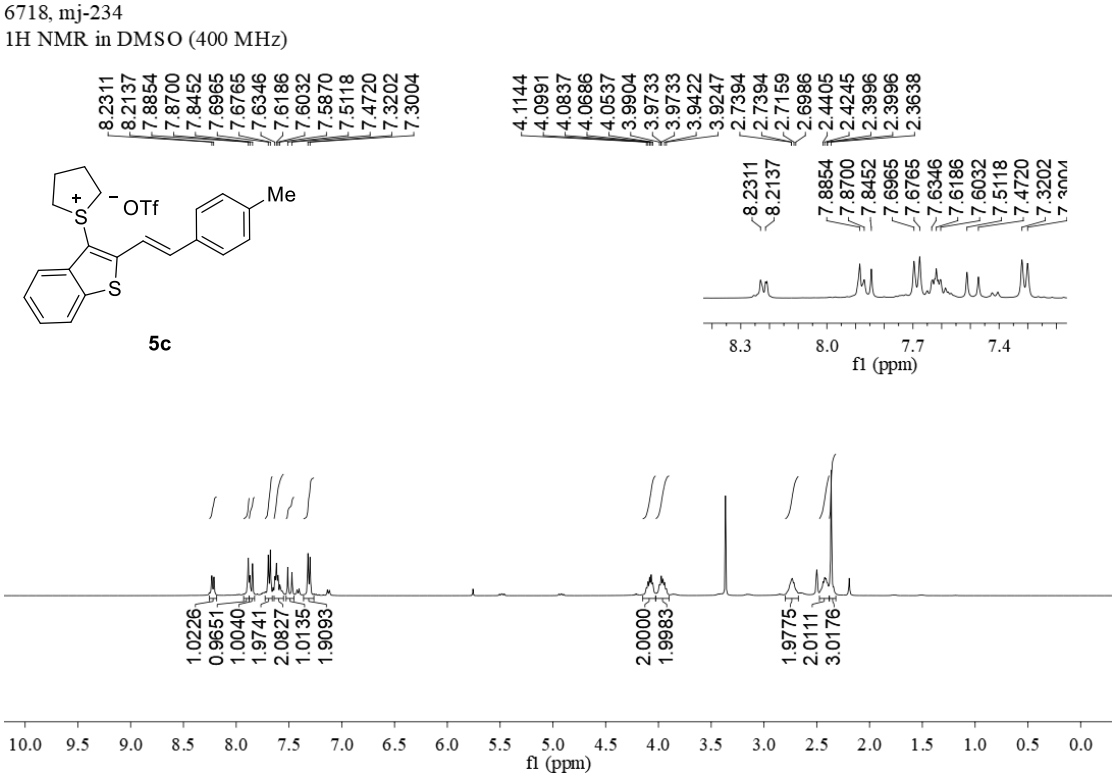


Figure S97. ^{1}H NMR spectrum of compound **5c** (DMSO-d6, 25 °C, 400 MHz).

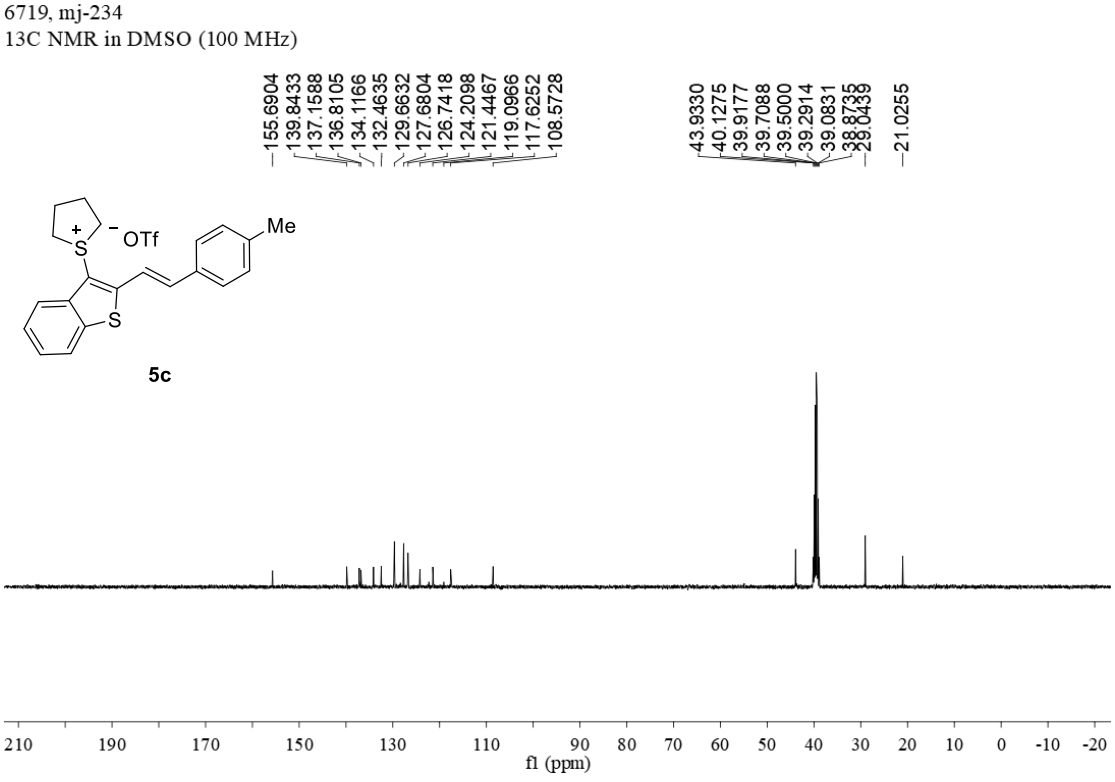


Figure S98. ^{13}C{^{1}H} NMR spectrum of compound **5c** (DMSO-d6, 25 °C, 100 MHz).

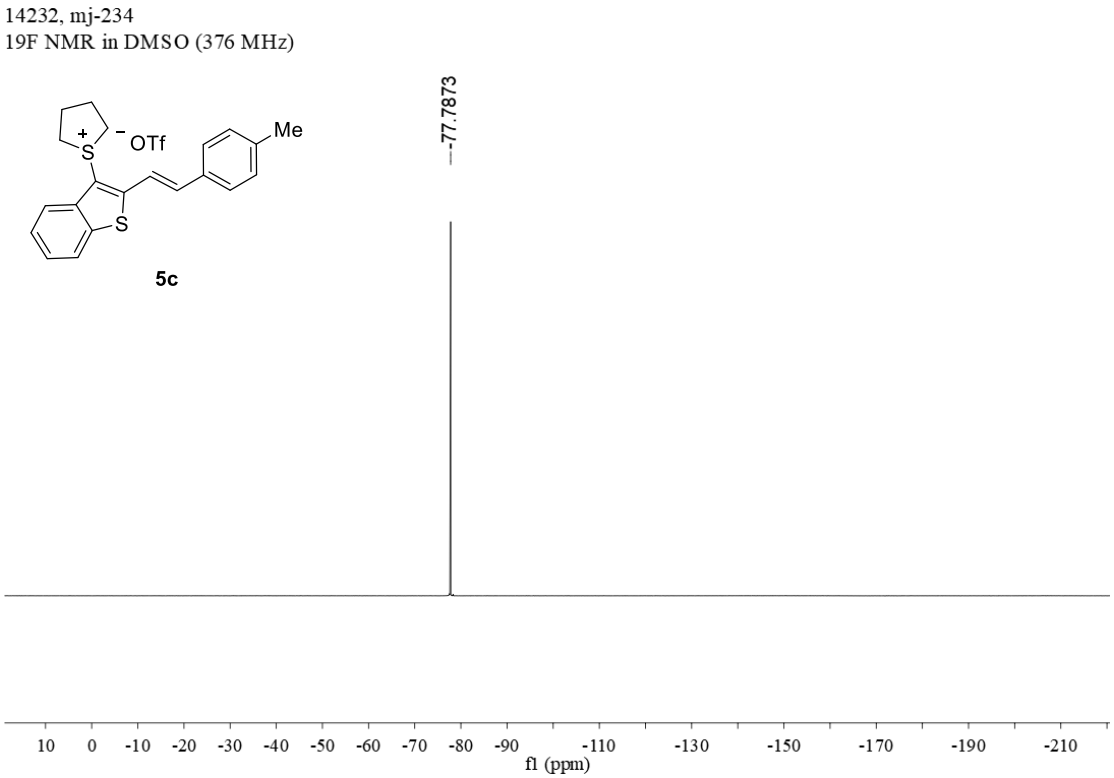


Figure S99. $^{19}F\{^{1}H\}$ NMR spectrum of compound **5c** (DMSO-d6, 25 °C, 376 MHz).

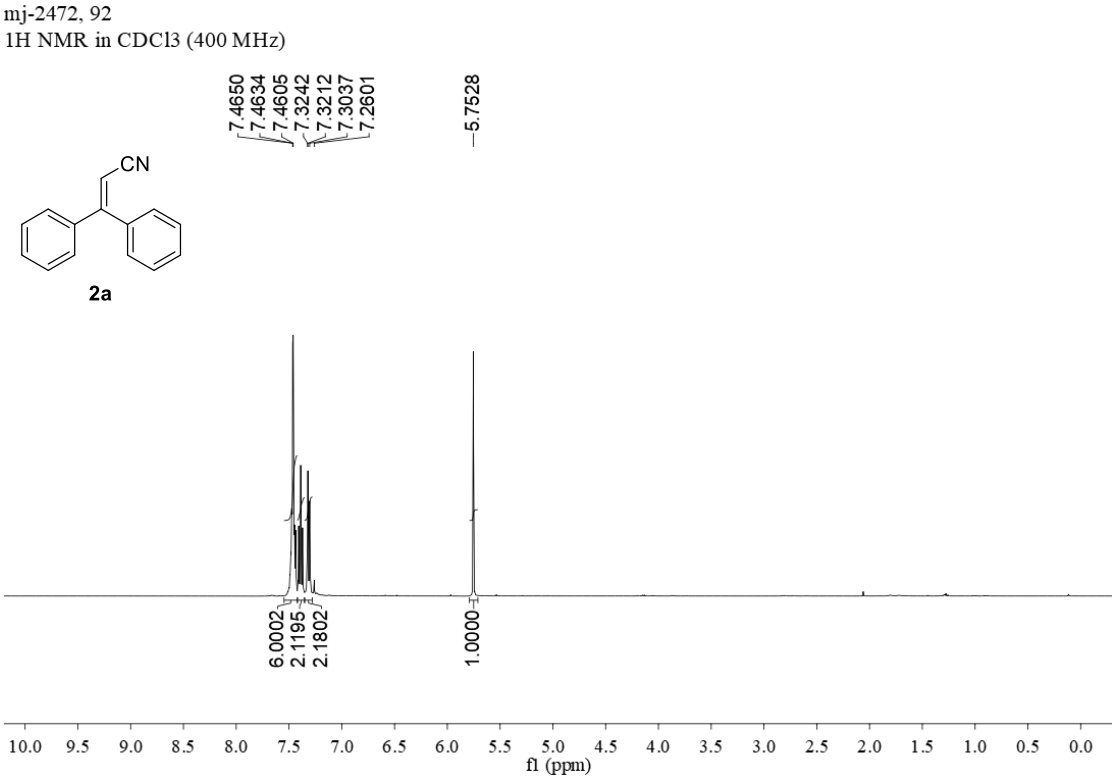


Figure S100. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 25 °C, 400 MHz).

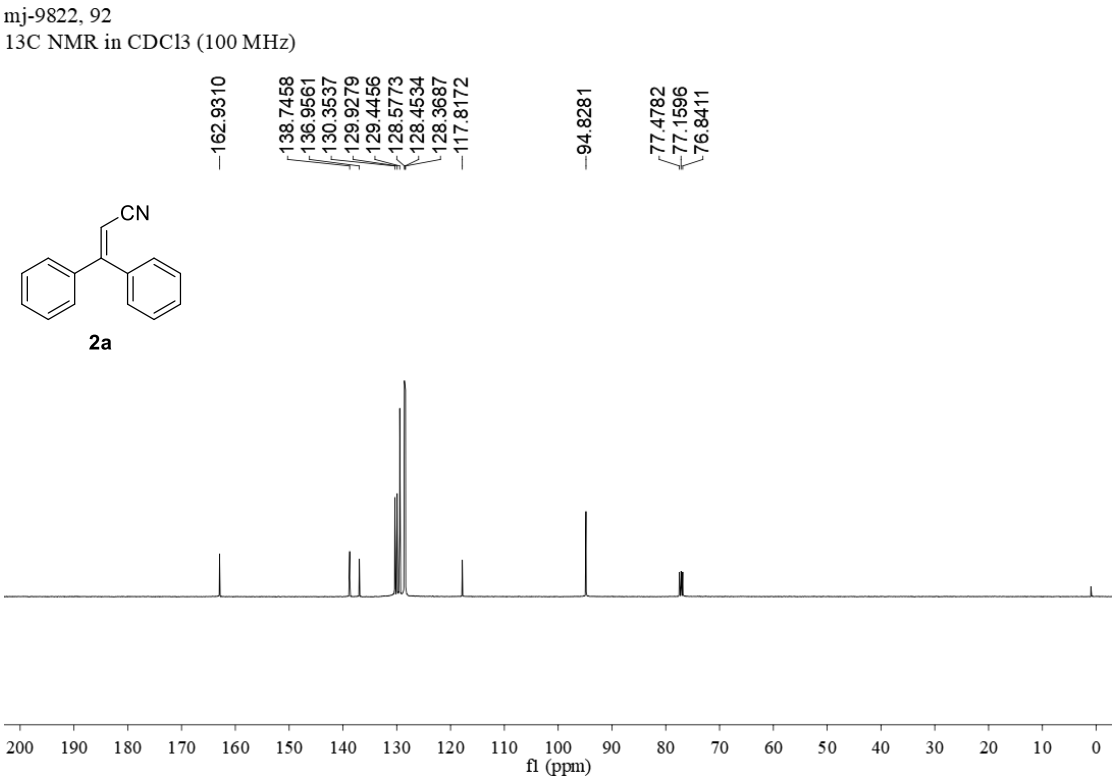


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2a** ($CDCl_3$, 25 °C, 100 MHz).

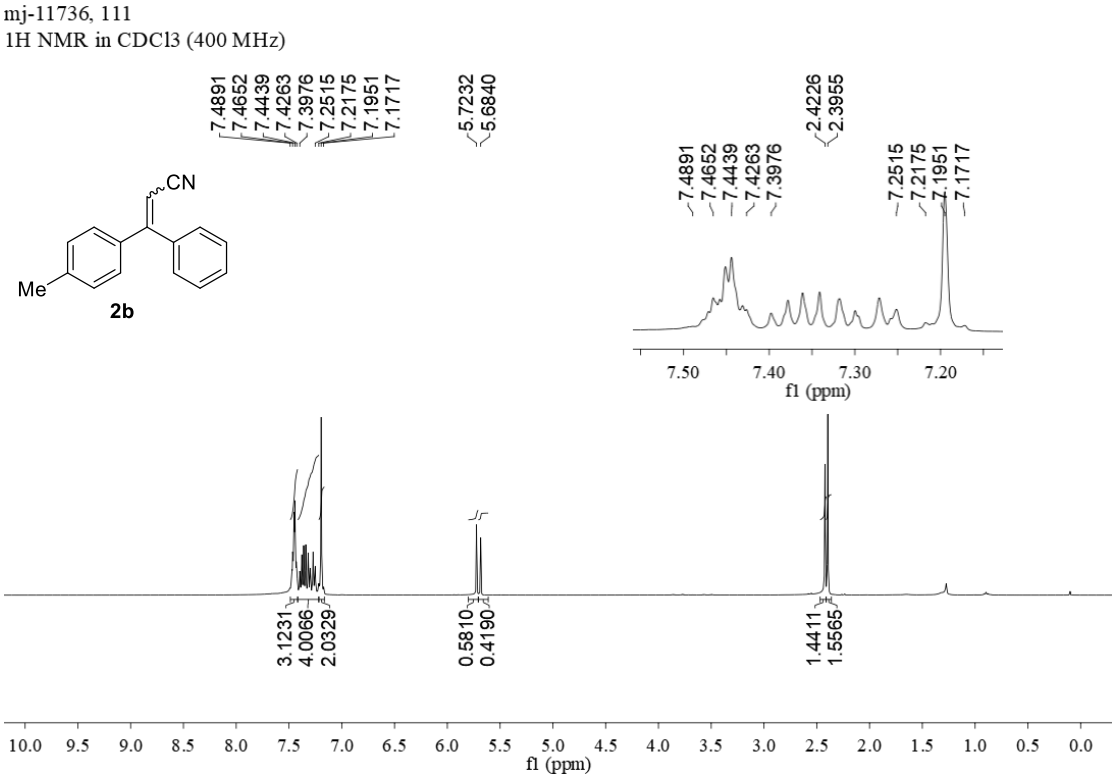


Figure S102. ^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 25 °C, 400 MHz).

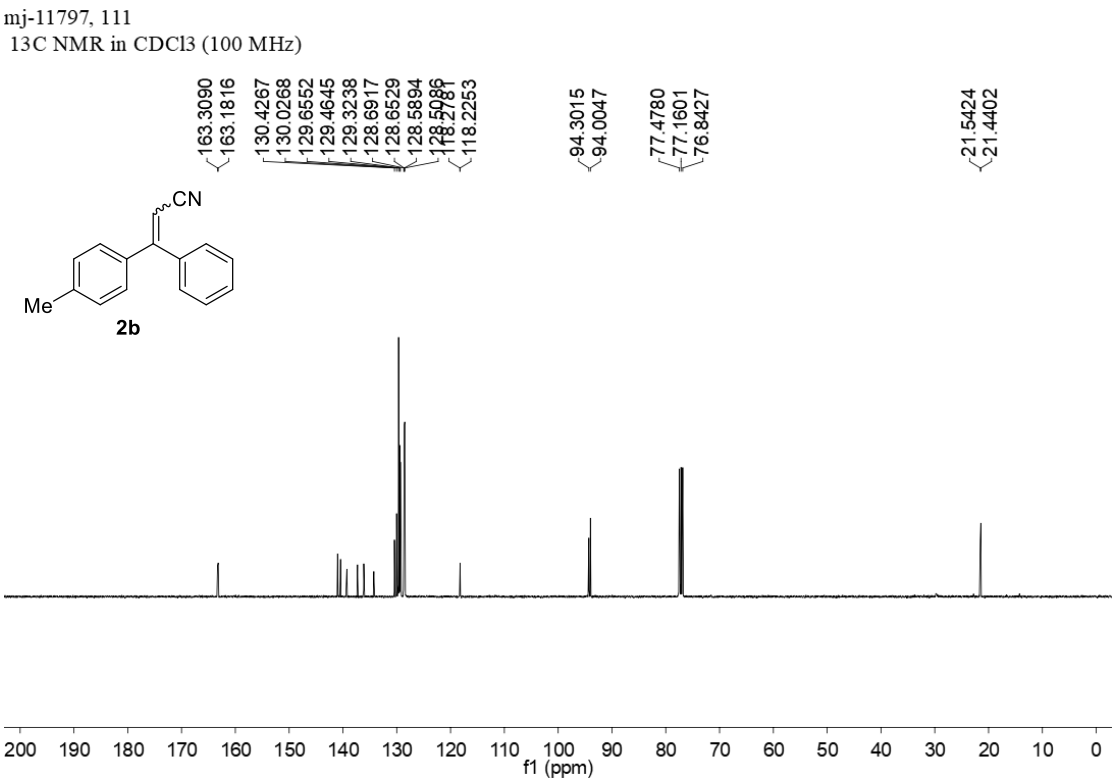


Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2b** ($CDCl_3$, 25 °C, 100 MHz).

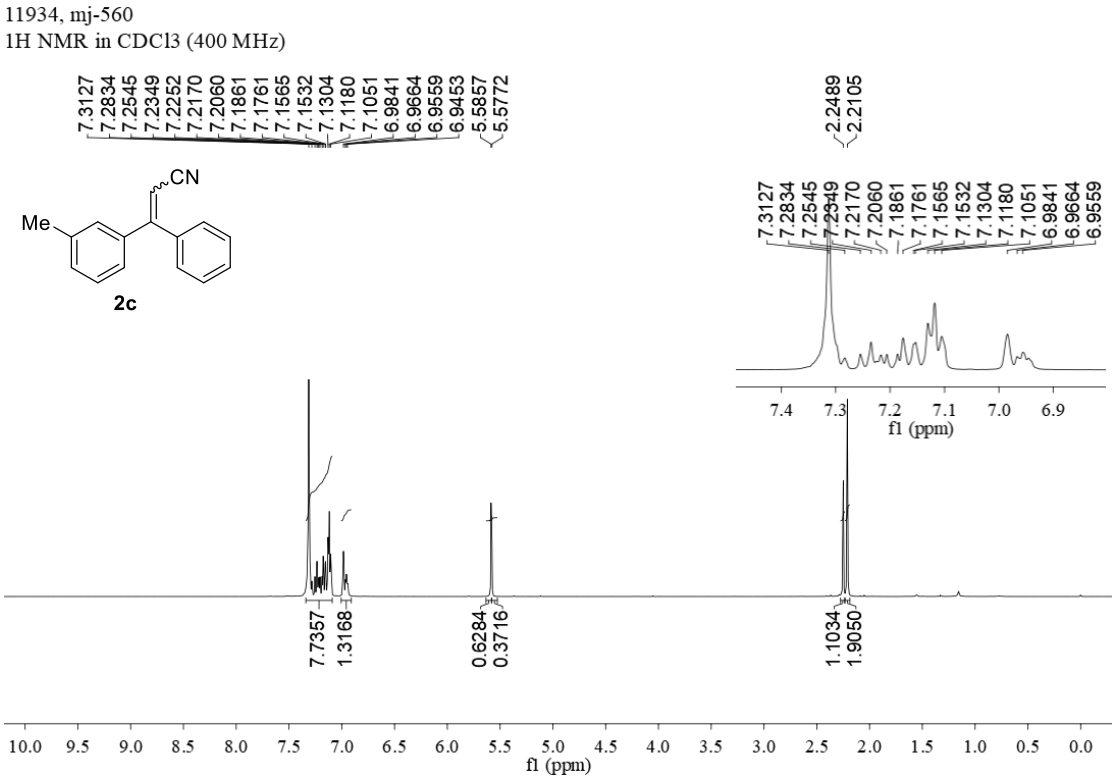


Figure S104. ^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 25 °C, 400 MHz).

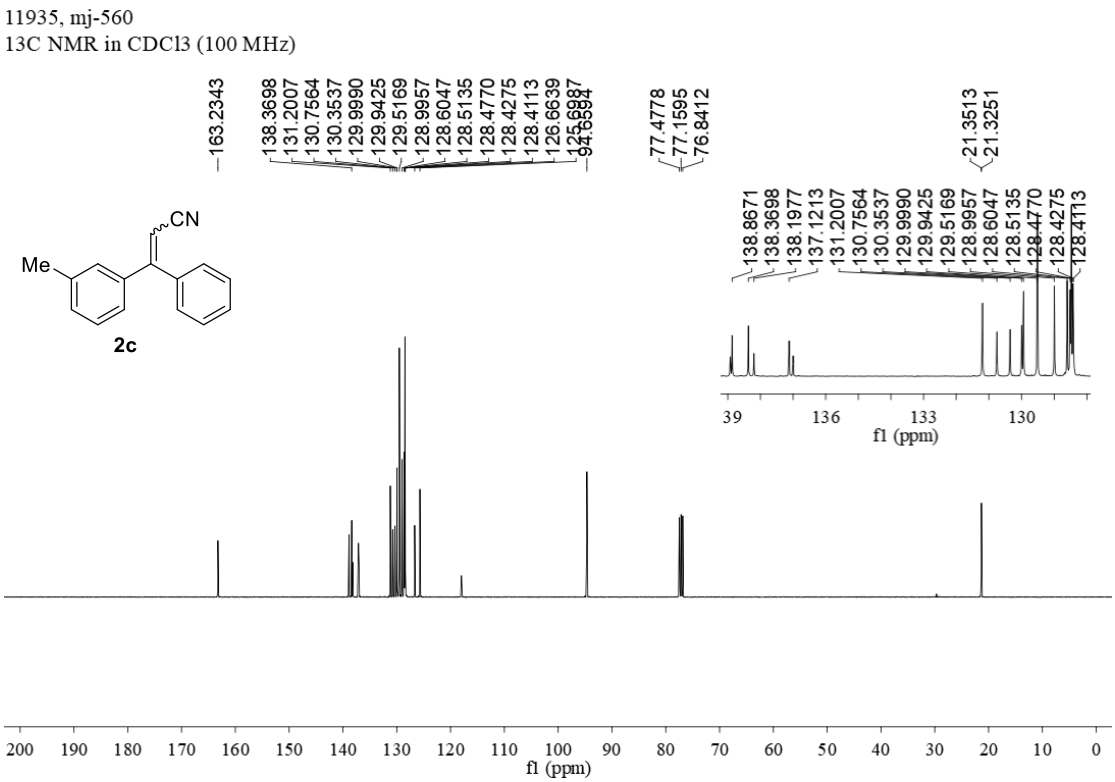


Figure S105. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2c** ($CDCl_3$, 25 °C, 100 MHz).

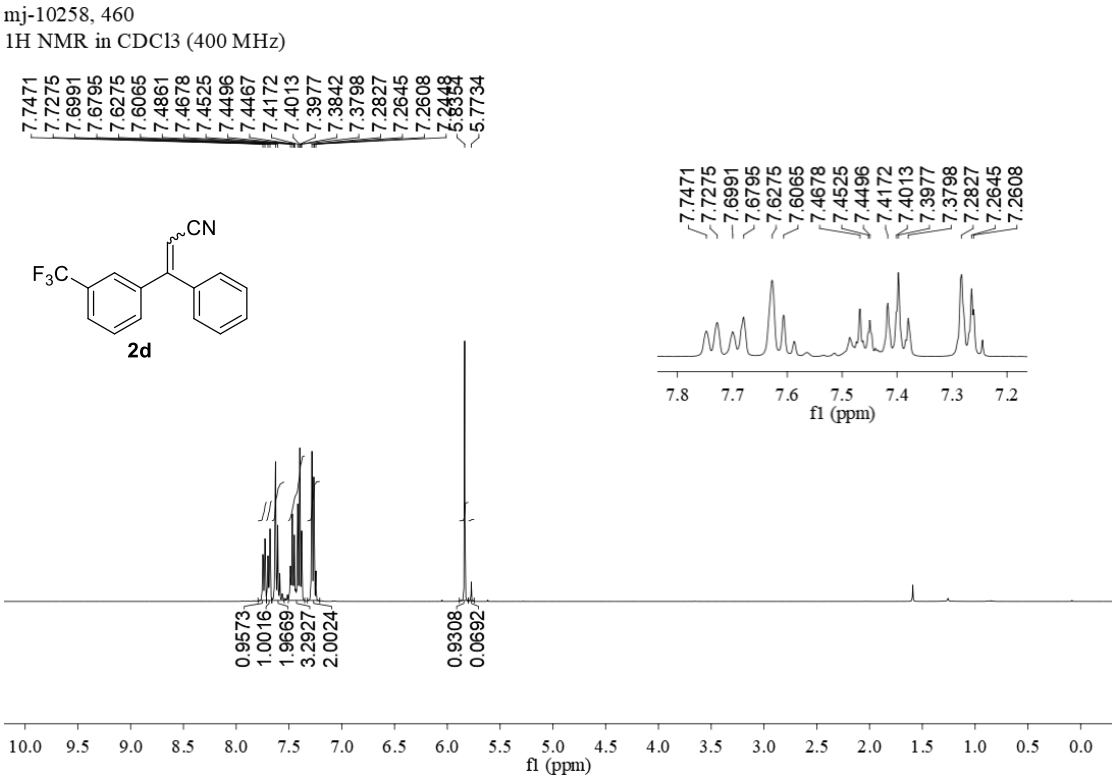


Figure S106. ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 25 °C, 400 MHz).

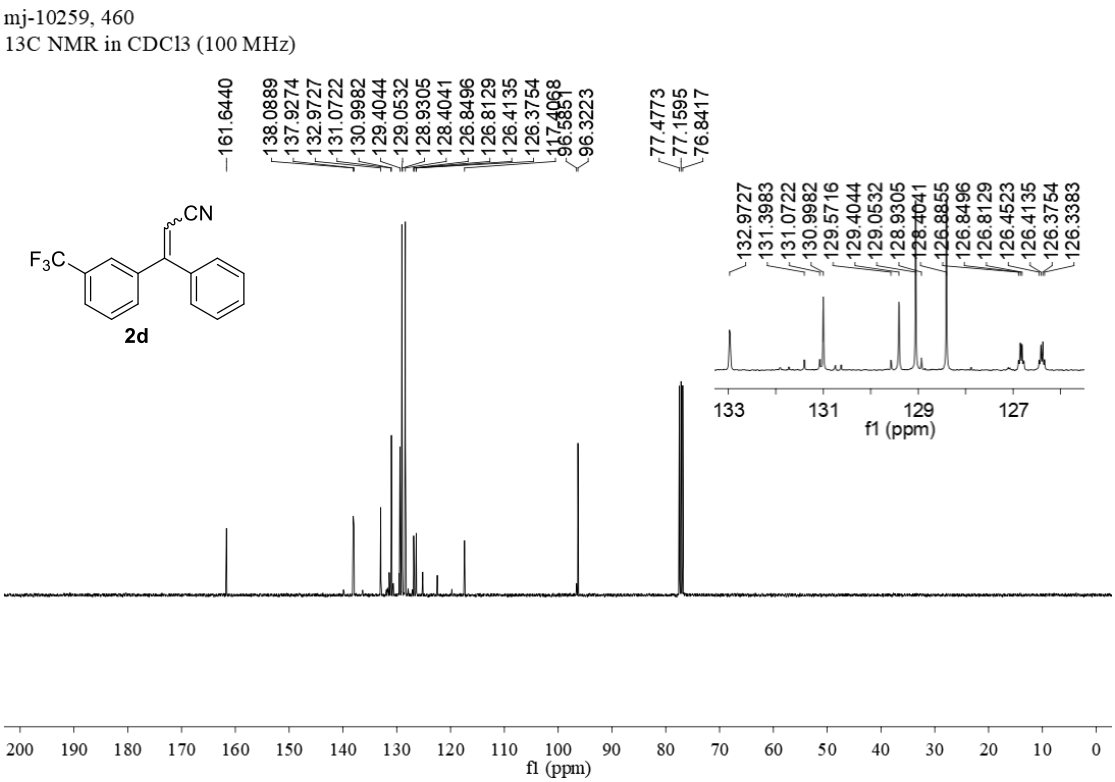


Figure S107. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2d** ($CDCl_3$, 25 °C, 100 MHz).

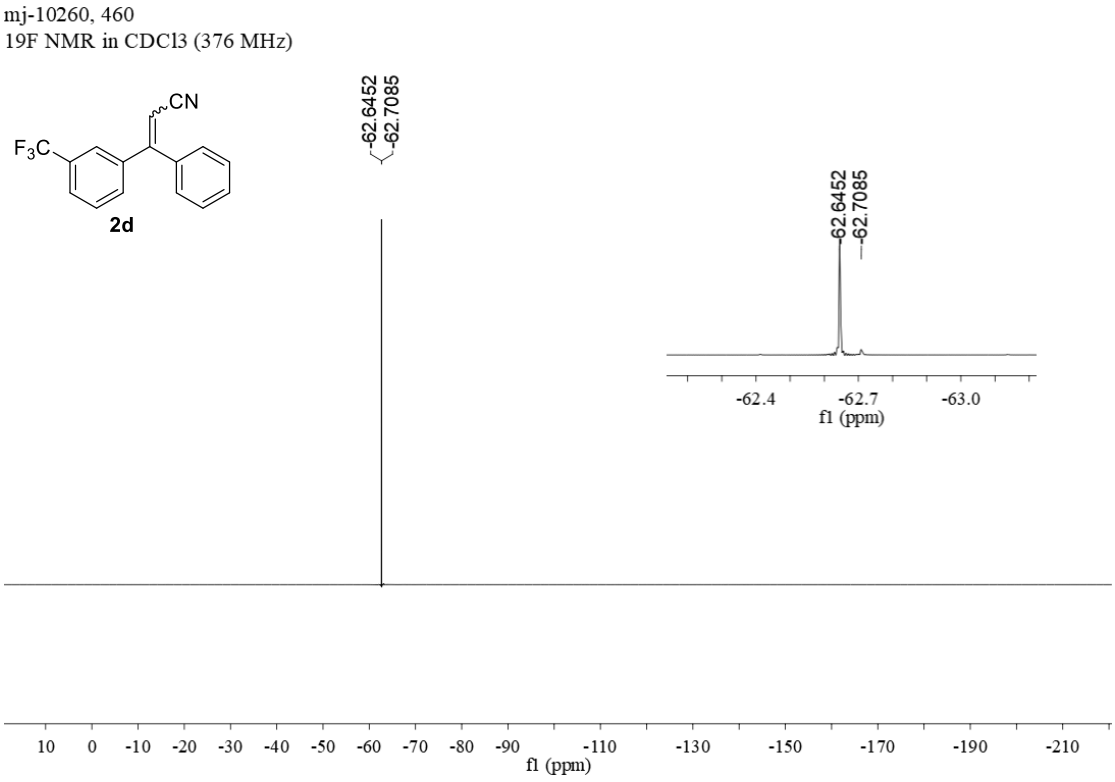


Figure S108. ^{19}F NMR spectrum of compound **2d** ($CDCl_3$, 25 °C, 376 MHz).

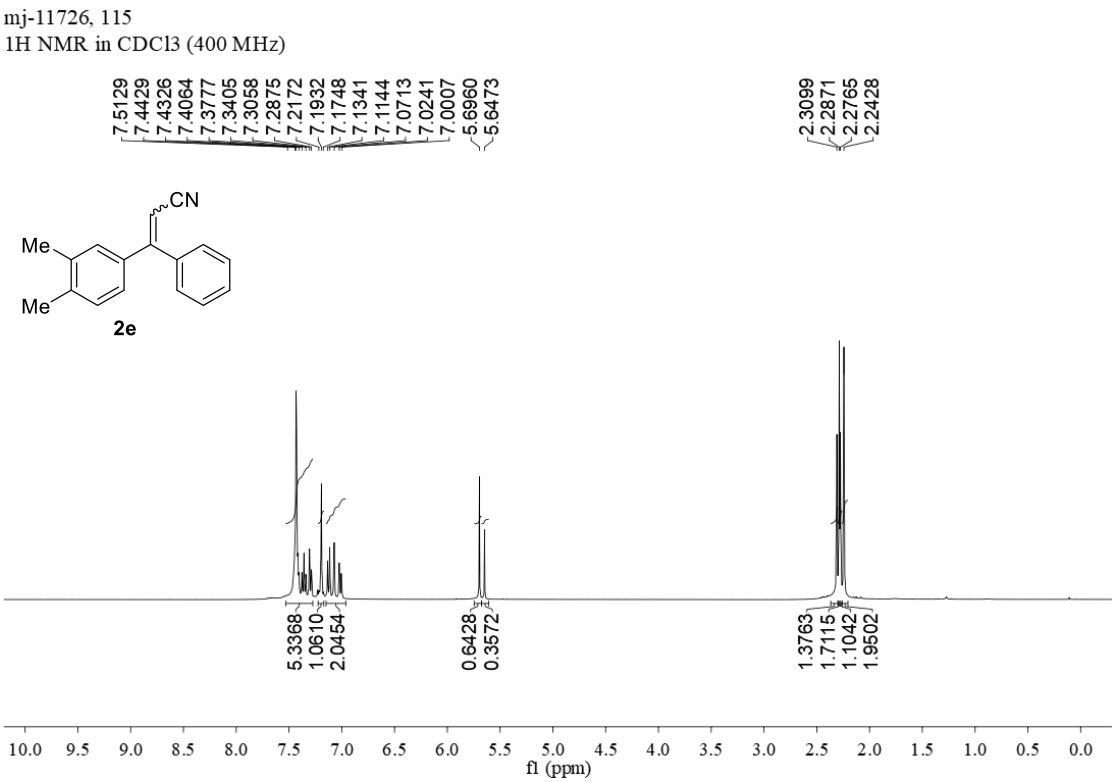


Figure S109. ^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 25 °C, 400 MHz).

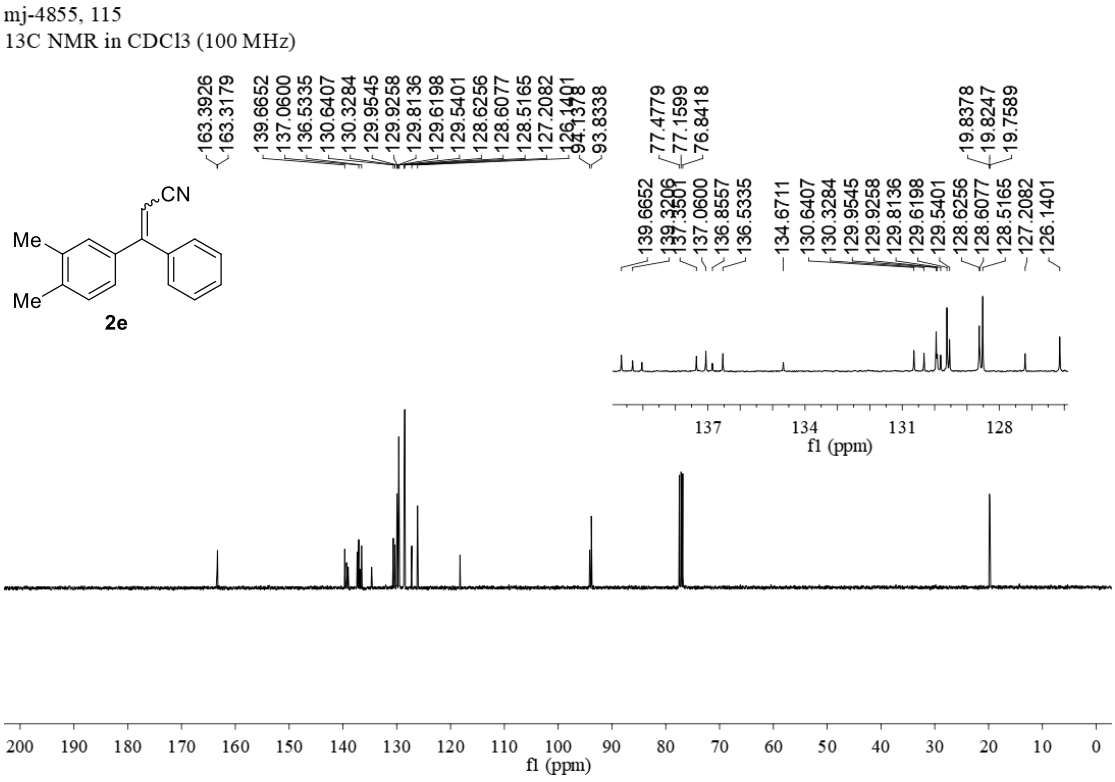


Figure S110. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2e** ($CDCl_3$, 25 °C, 100 MHz).

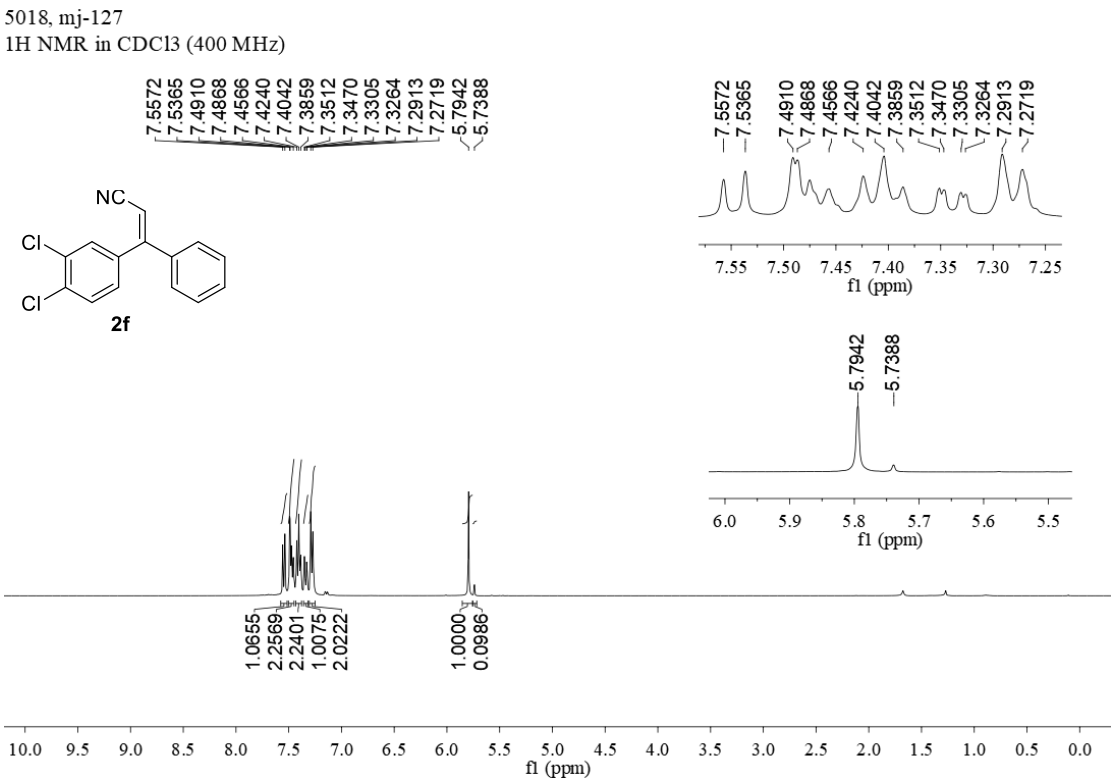


Figure S111. ^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 25 °C, 400 MHz).

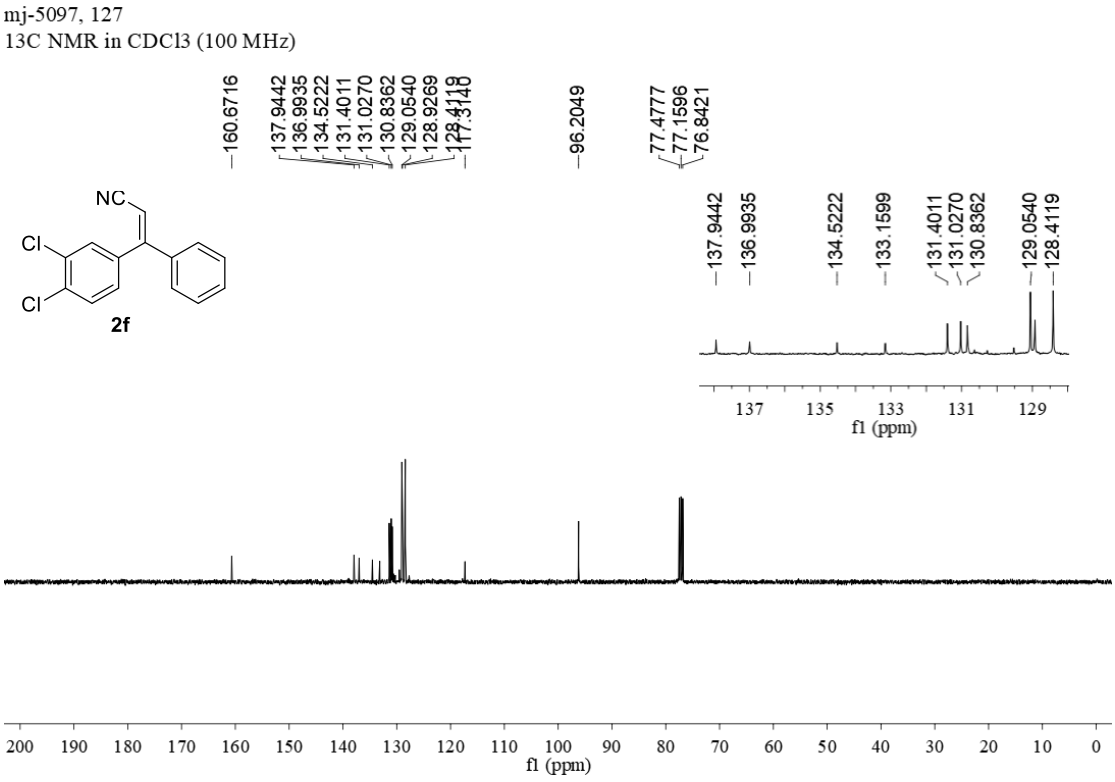


Figure S112. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2f** ($CDCl_3$, 25 °C, 100 MHz).

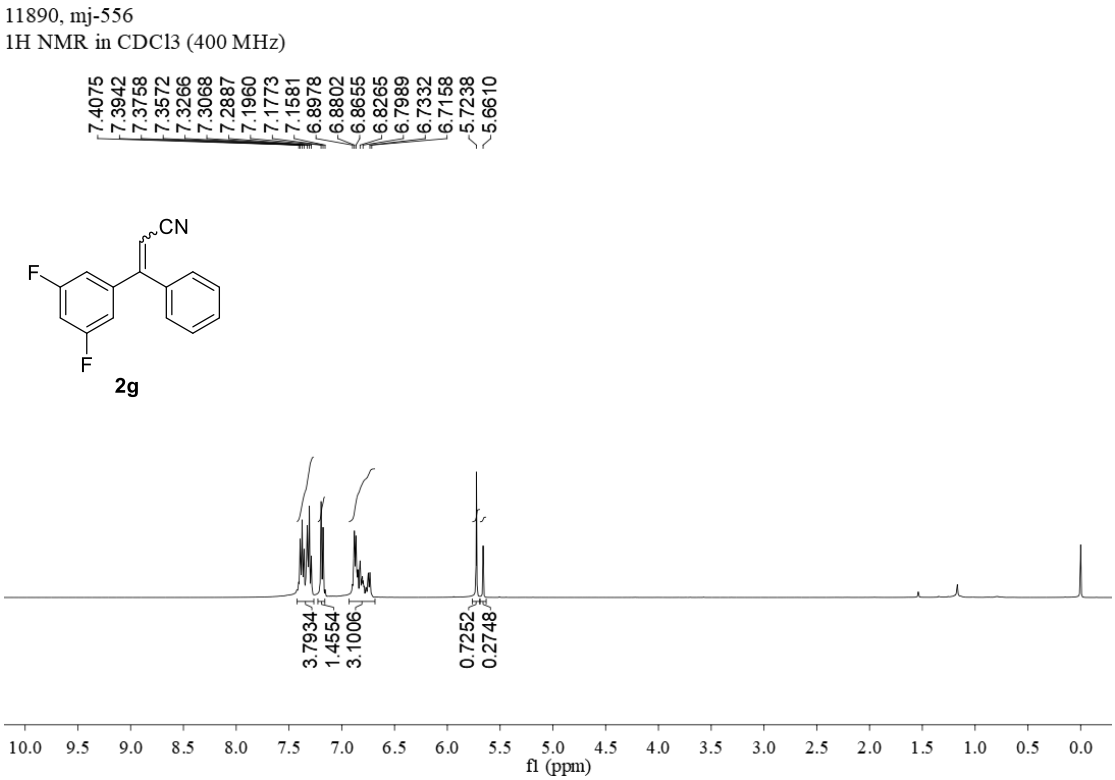


Figure S113. ^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 25 °C, 400 MHz).

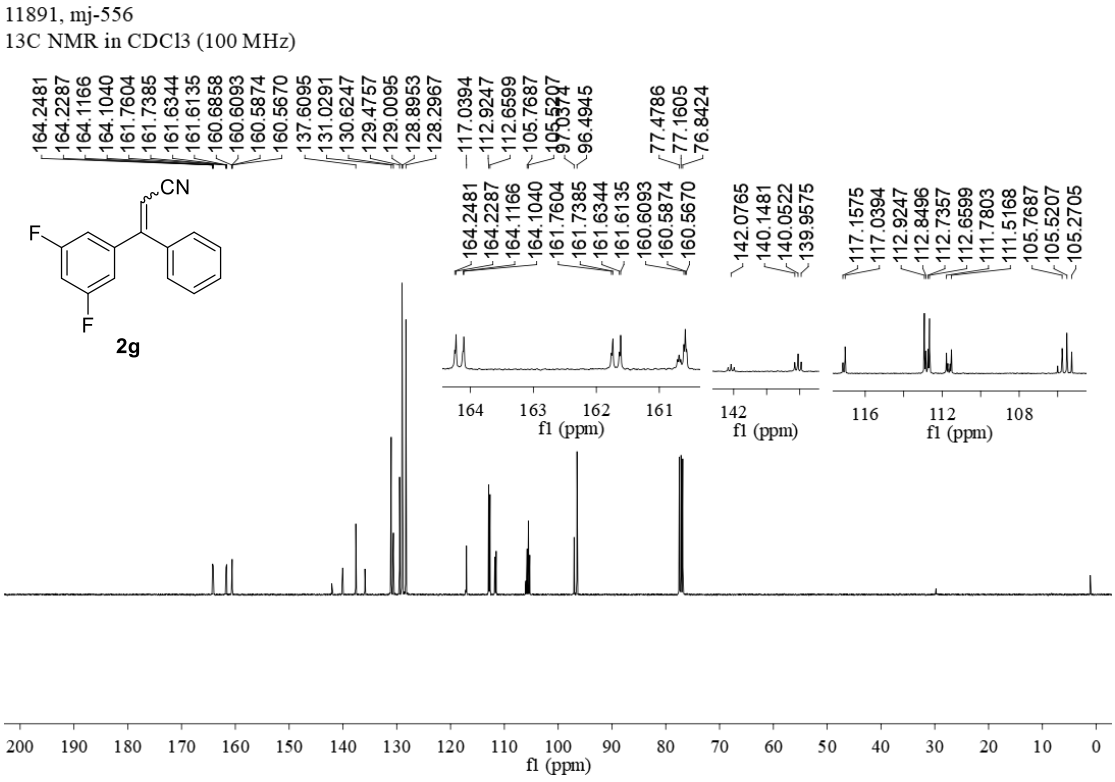


Figure S114. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2g** ($CDCl_3$, 25 °C, 100 MHz).

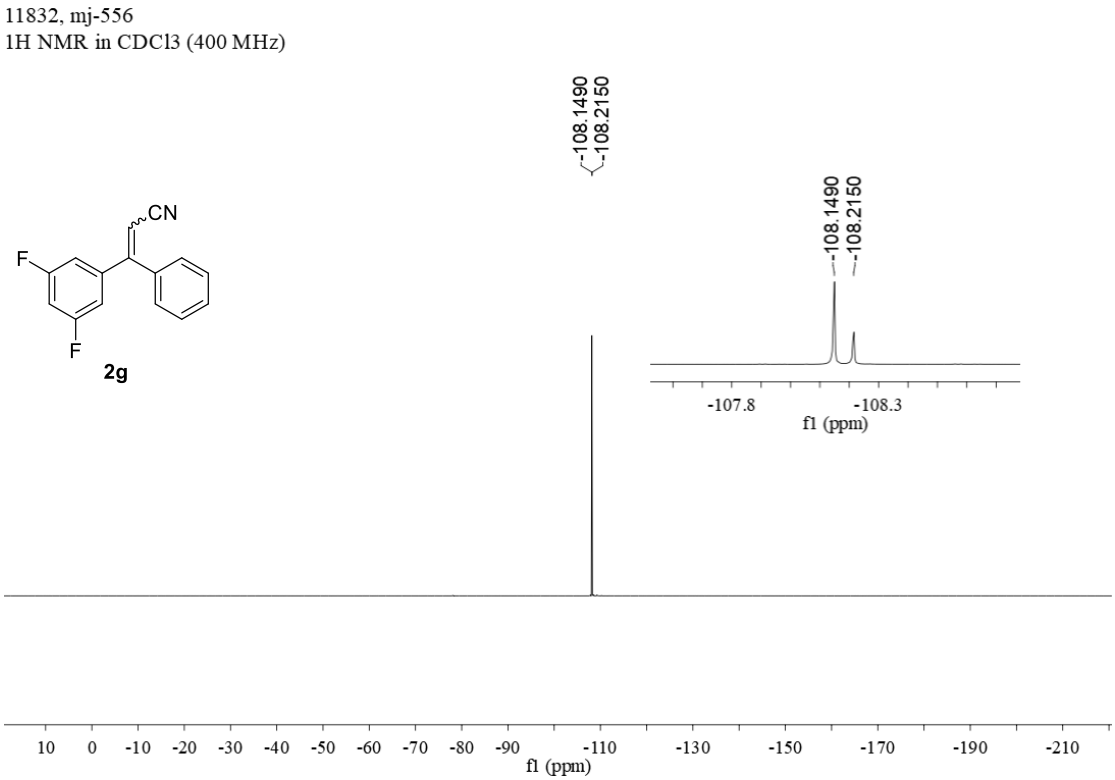


Figure S115. $^{19}F\{^{1}H\}$ NMR spectrum of compound **2g** ($CDCl_3$, 25 °C, 376 MHz).

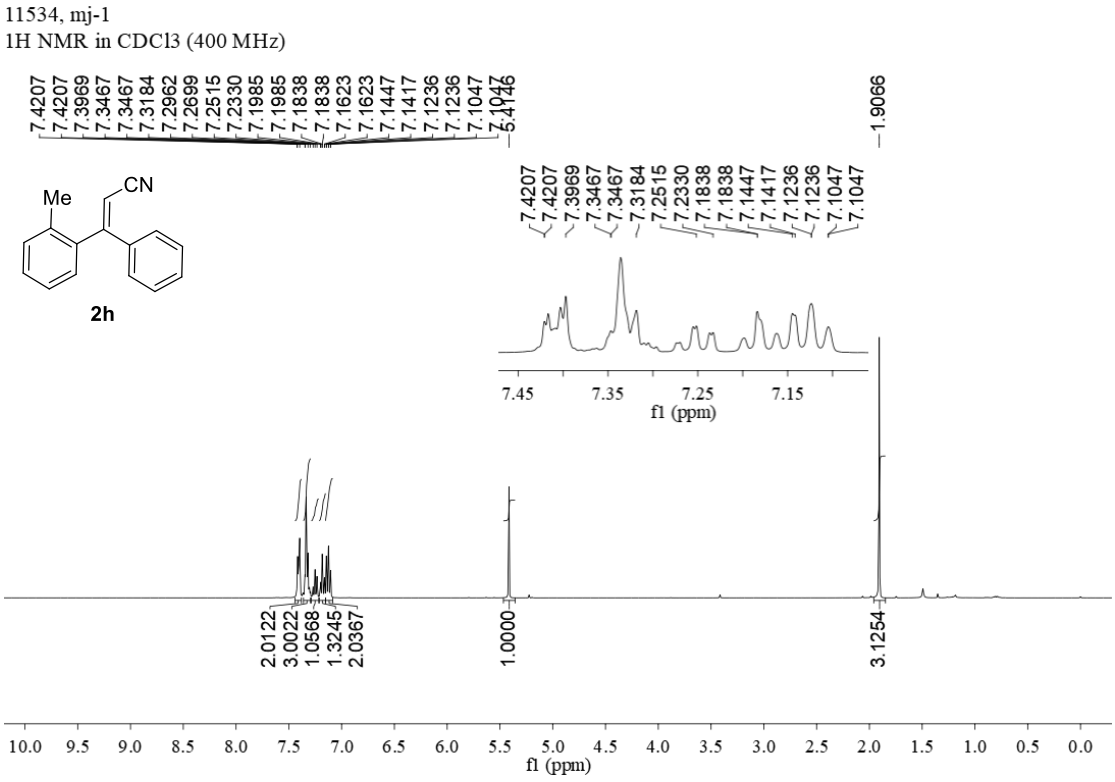


Figure S116. ^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 25 °C, 400 MHz).

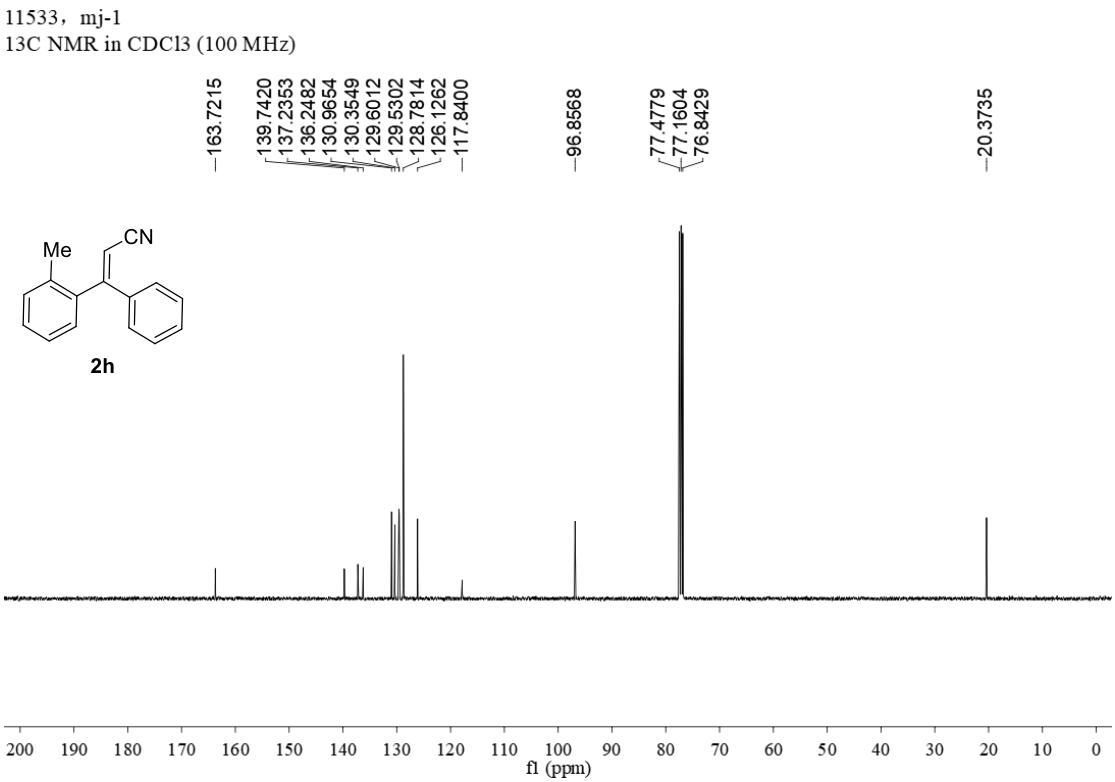


Figure S117. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2h** ($CDCl_3$, 25 °C, 100 MHz).

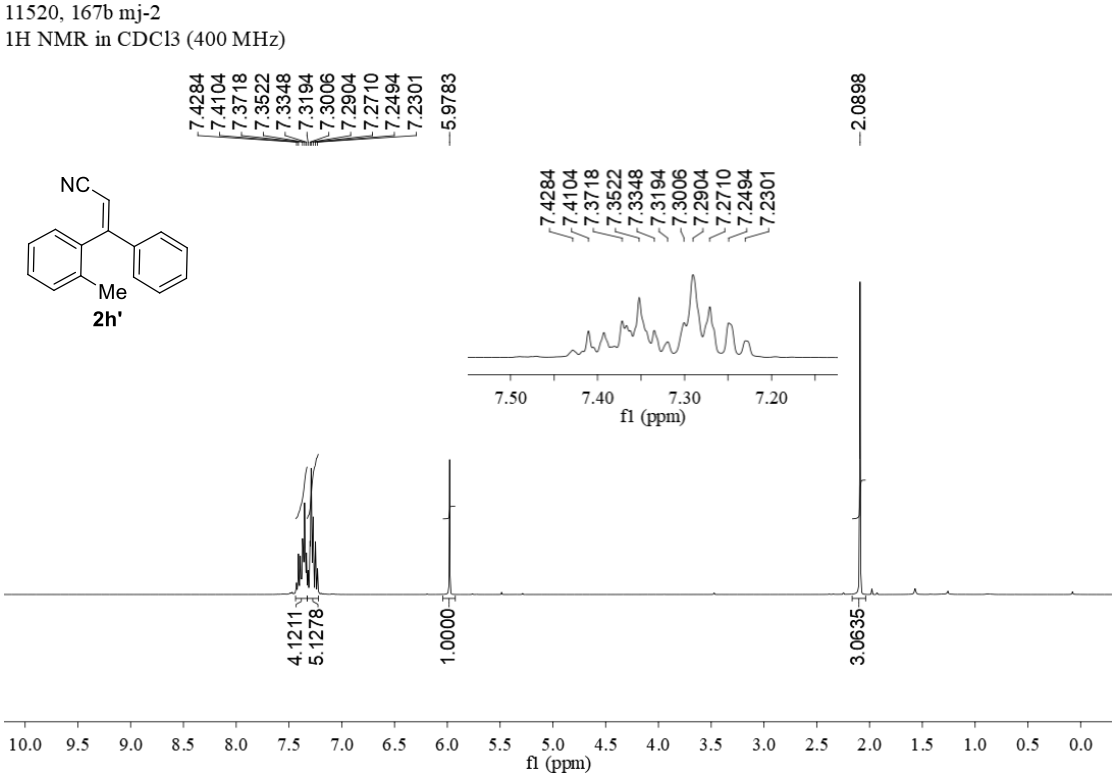


Figure S118. ^{1}H NMR spectrum of compound **2h'** ($CDCl_3$, 25 °C, 400 MHz).

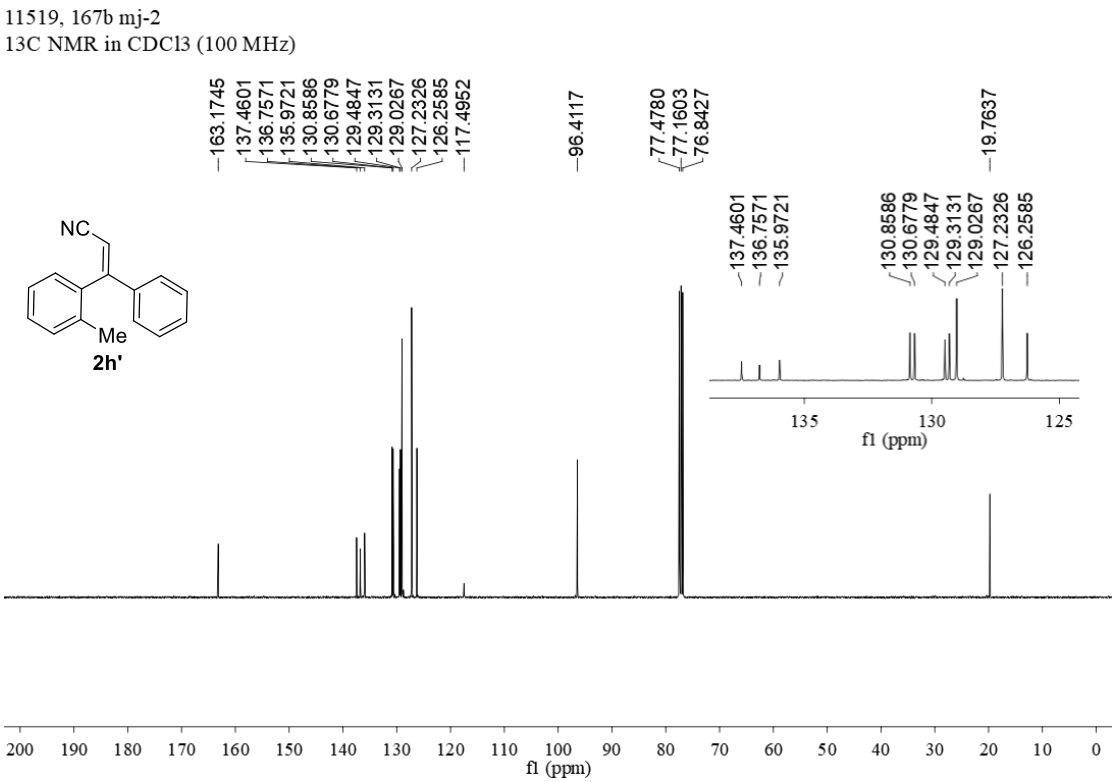


Figure S119. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2h'** ($CDCl_3$, 25 °C, 100 MHz).

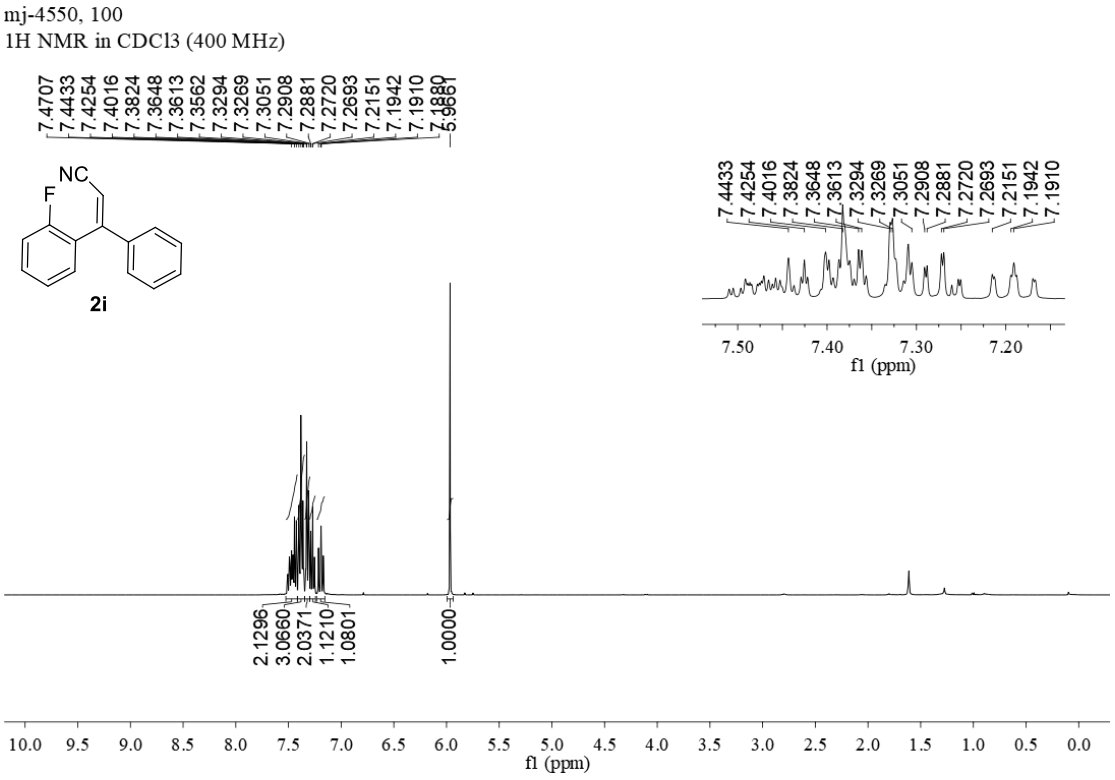


Figure S120. ^{1}H NMR spectrum of compound **2i** ($CDCl_3$, 25 °C, 400 MHz).

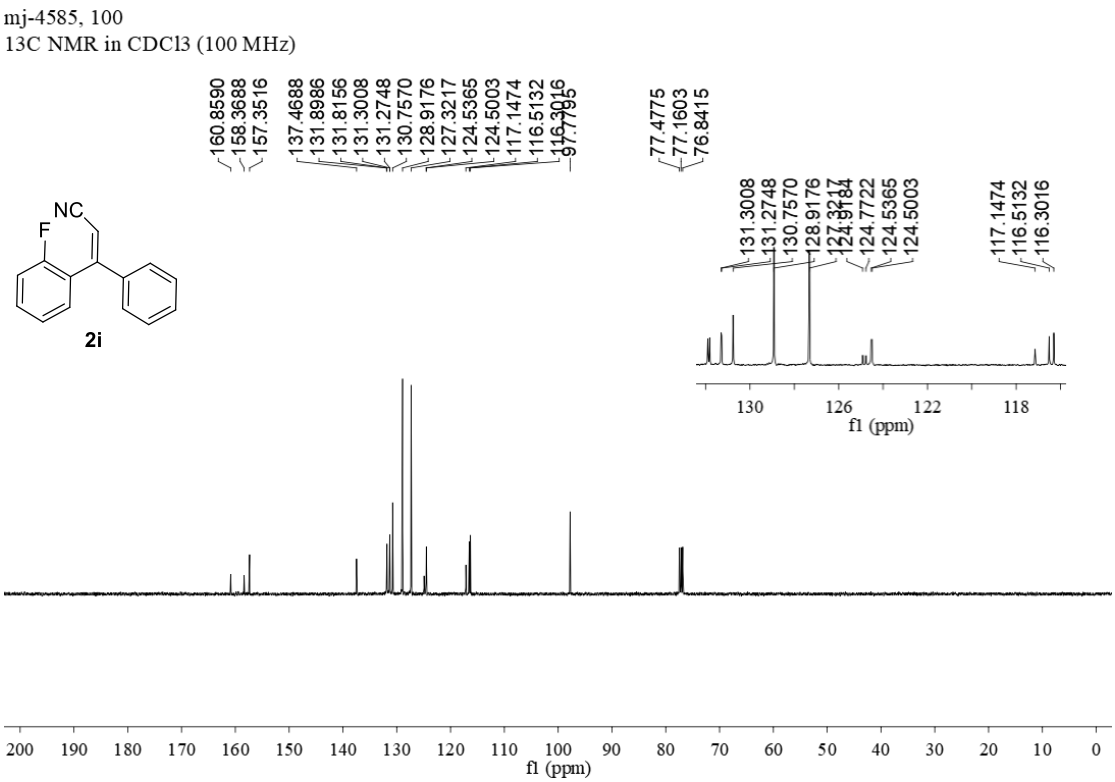


Figure S121. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2i** ($CDCl_3$, 25 °C, 100 MHz).

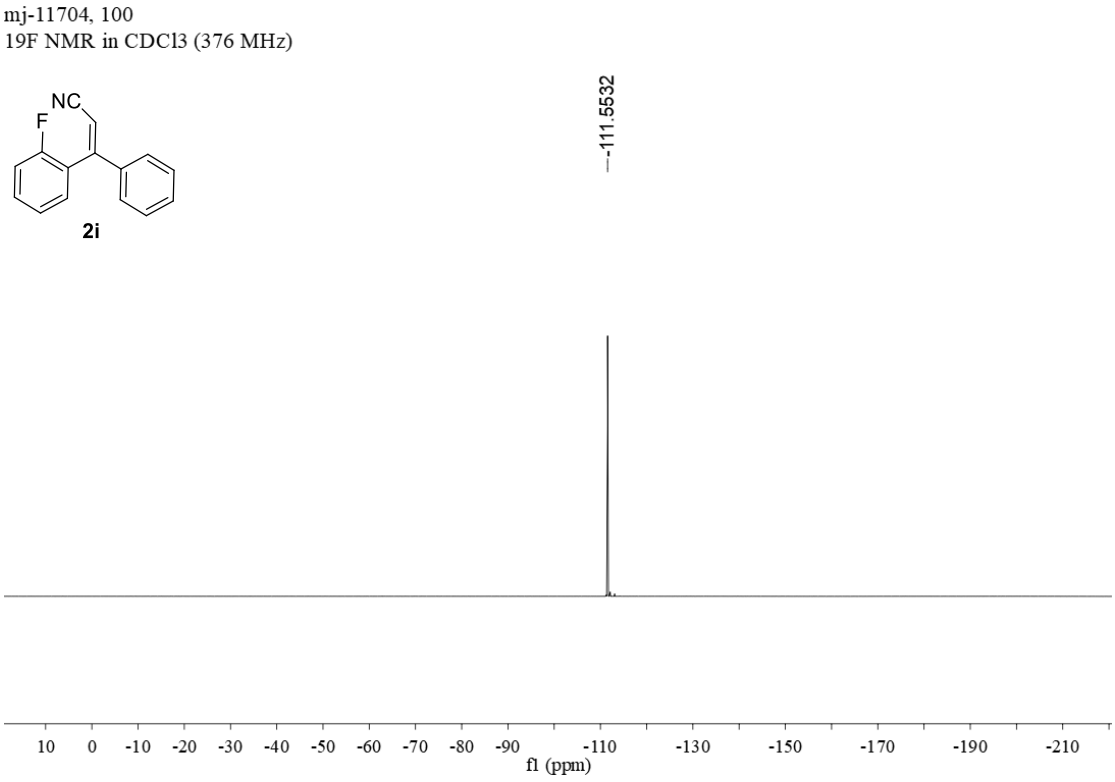


Figure S122. ^{19}F NMR spectrum of compound **2i** ($CDCl_3$, 25 °C, 376 MHz).

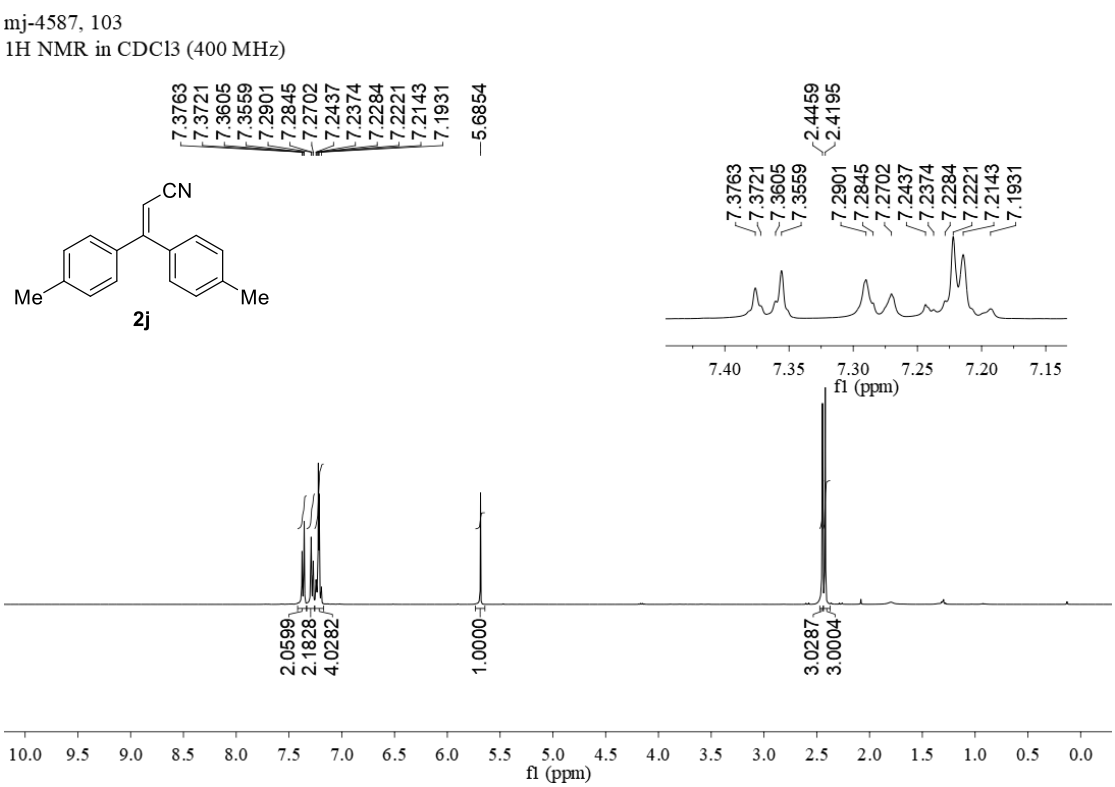


Figure S123. ^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 25 °C, 400 MHz).

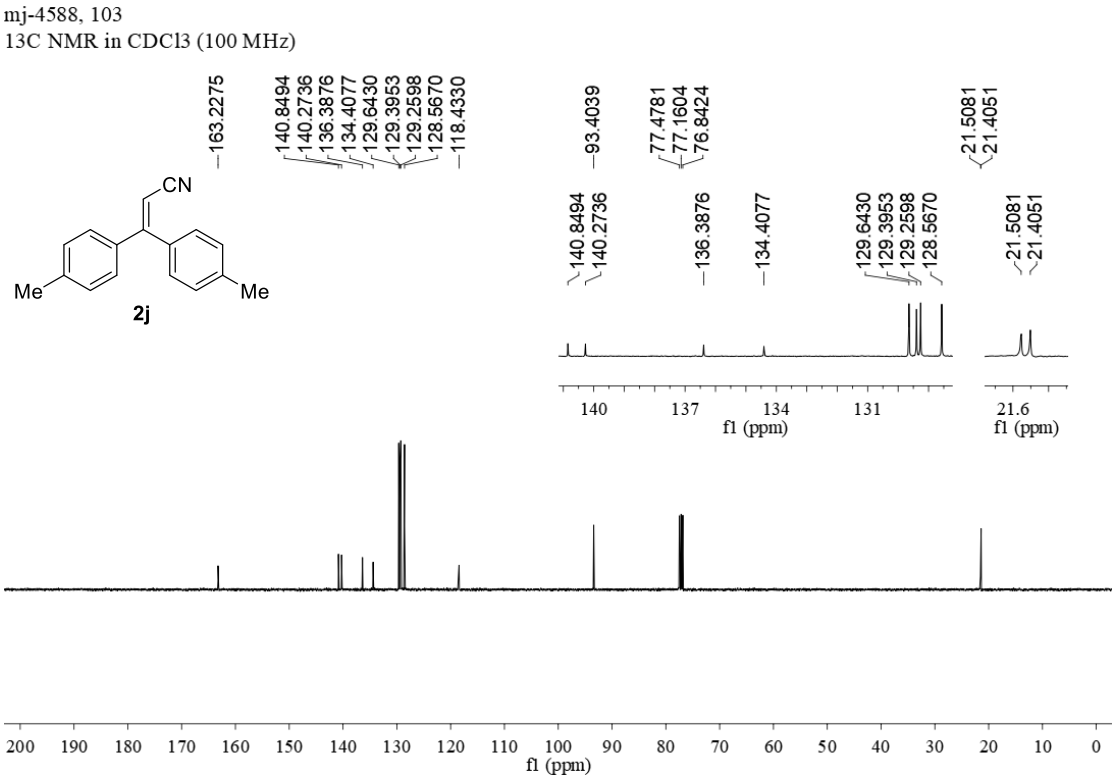


Figure S124. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2j** ($CDCl_3$, 25 °C, 100 MHz).

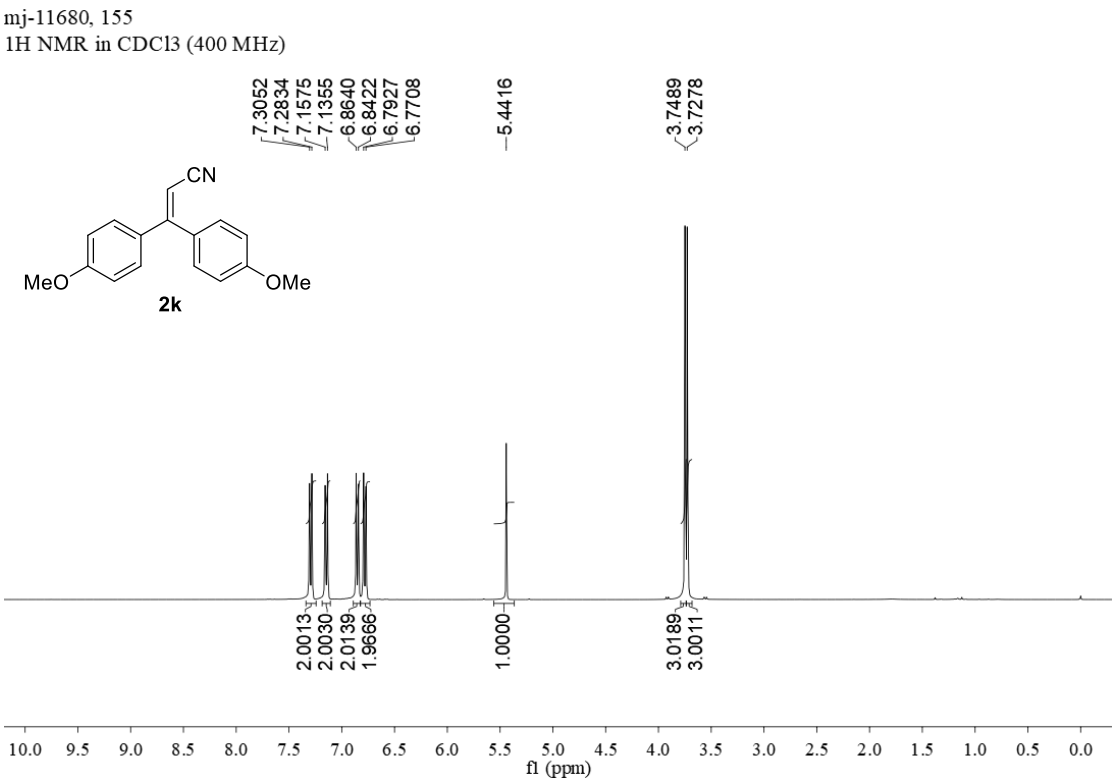


Figure S125. ^{1}H NMR spectrum of compound **2k** ($CDCl_3$, 25 °C, 400 MHz).

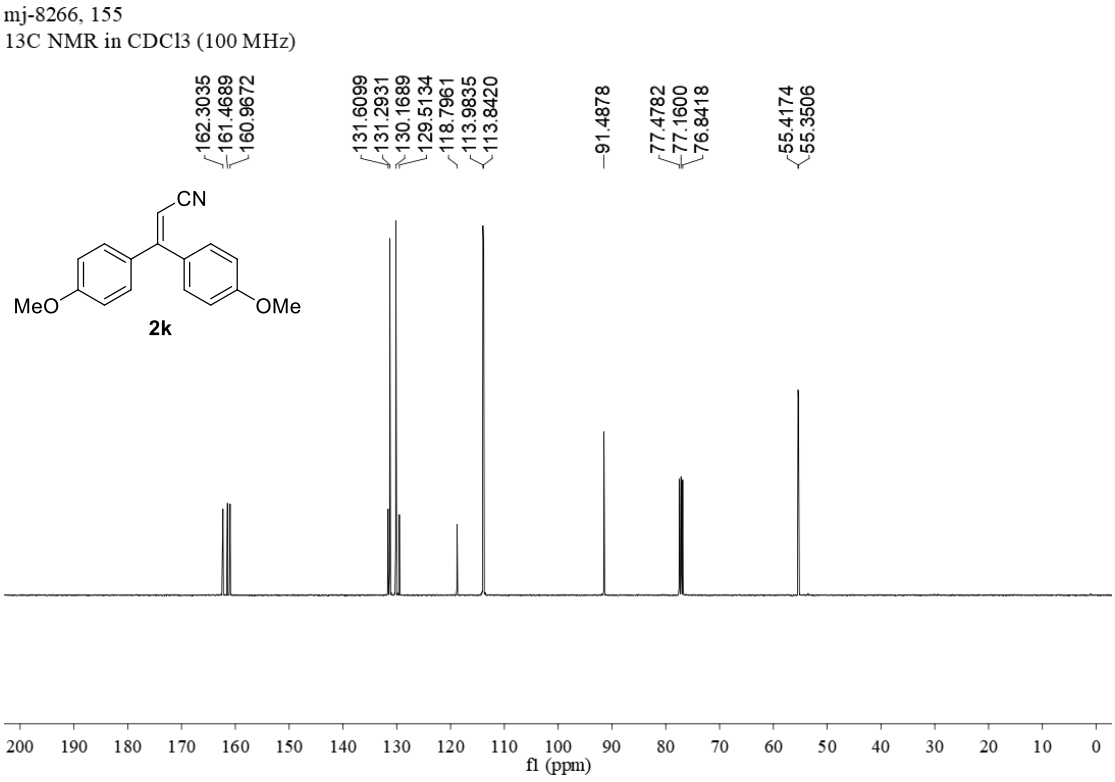


Figure S126. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2k** ($CDCl_3$, 25 °C, 100 MHz).

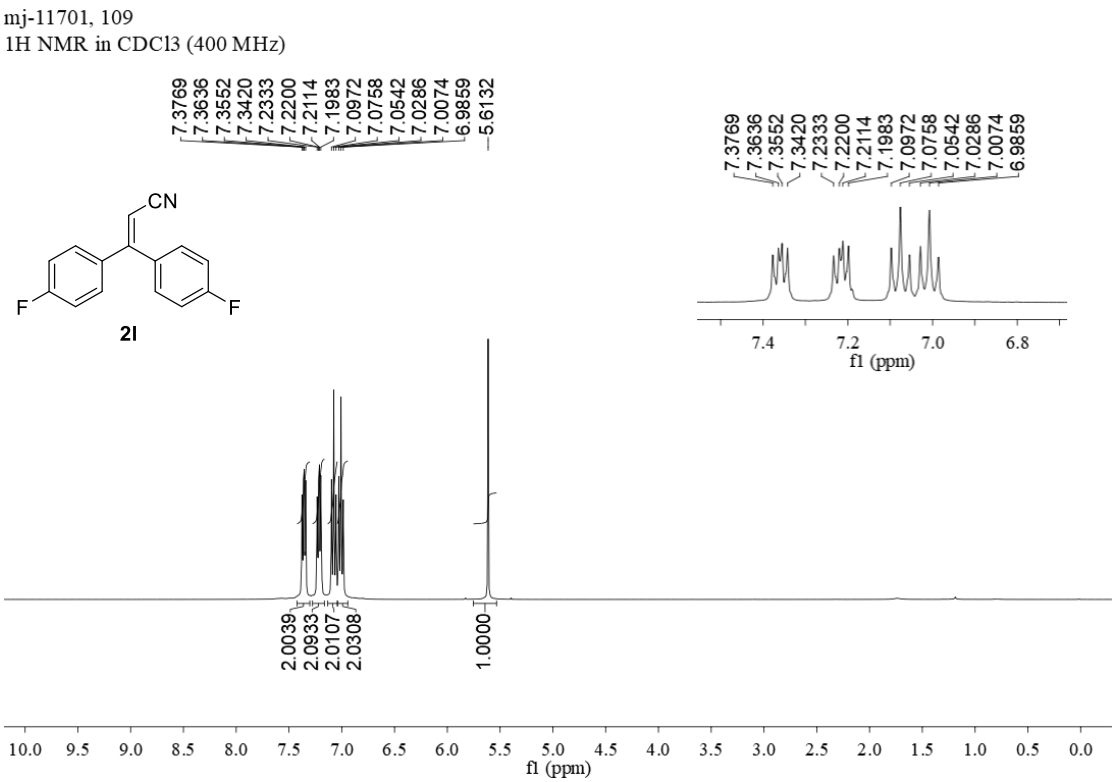


Figure S127. ^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 25 °C, 400 MHz).

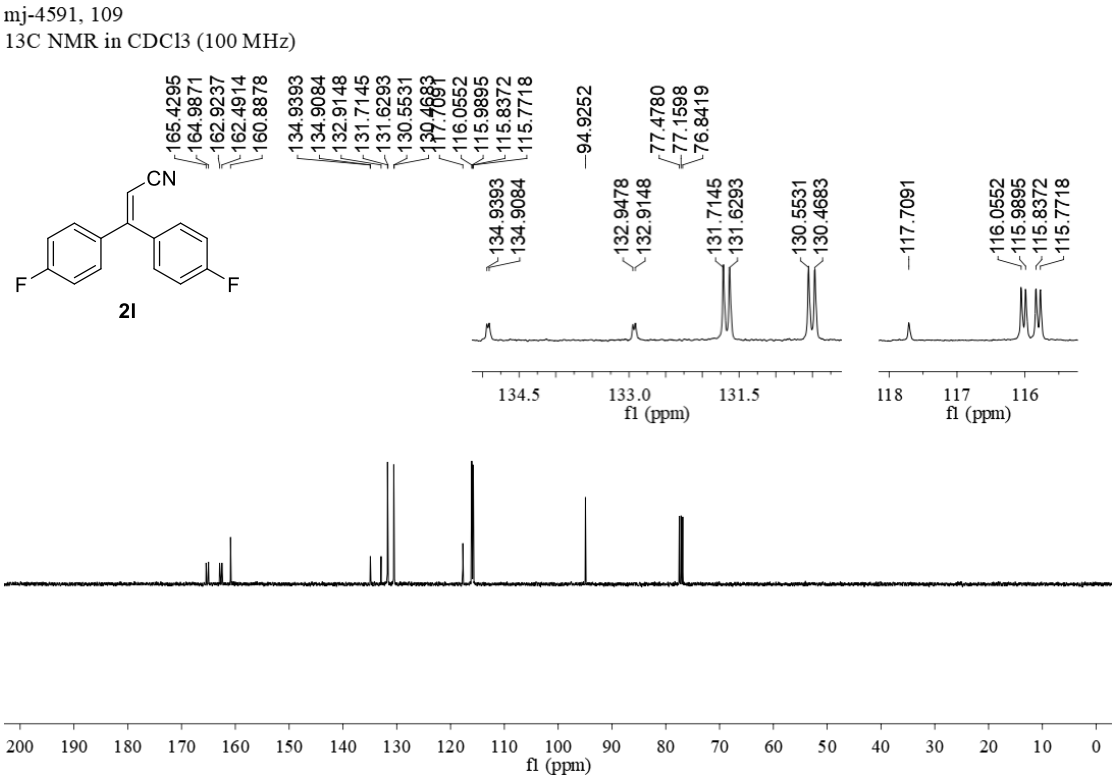


Figure S128. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2l** ($CDCl_3$, 25 °C, 100 MHz).

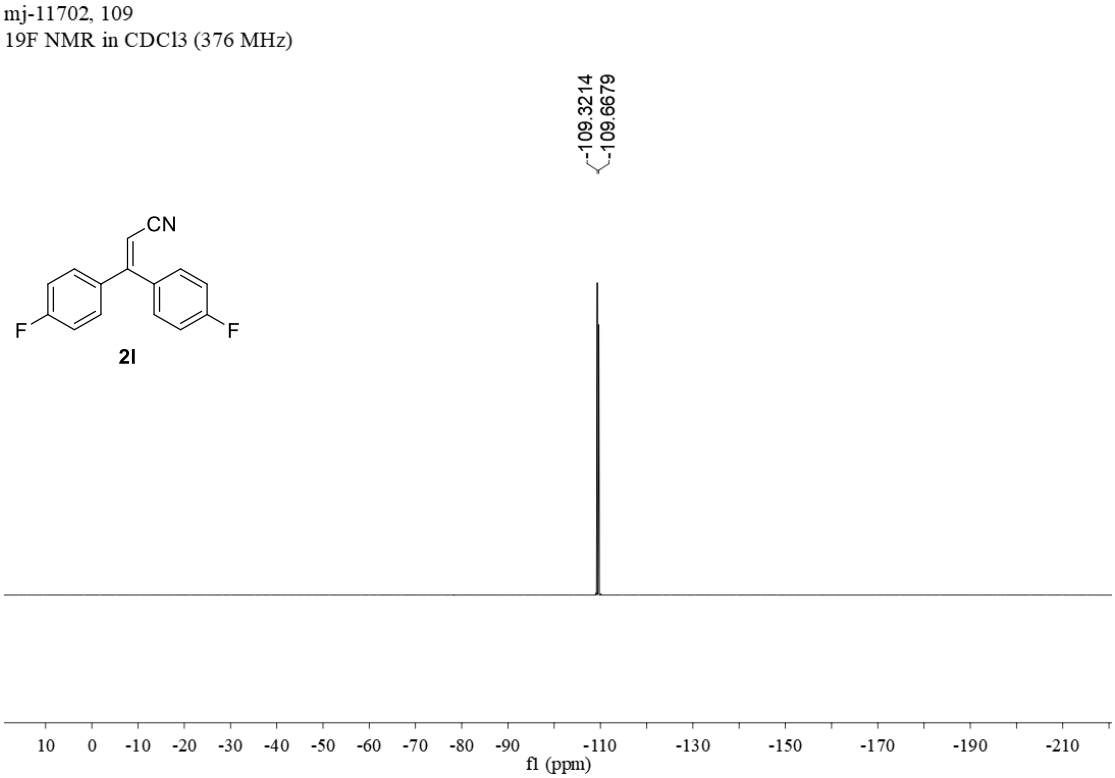


Figure S129. $^{19}F\{^{1}H\}$ NMR spectrum of compound **2l** ($CDCl_3$, 25 °C, 376 MHz).

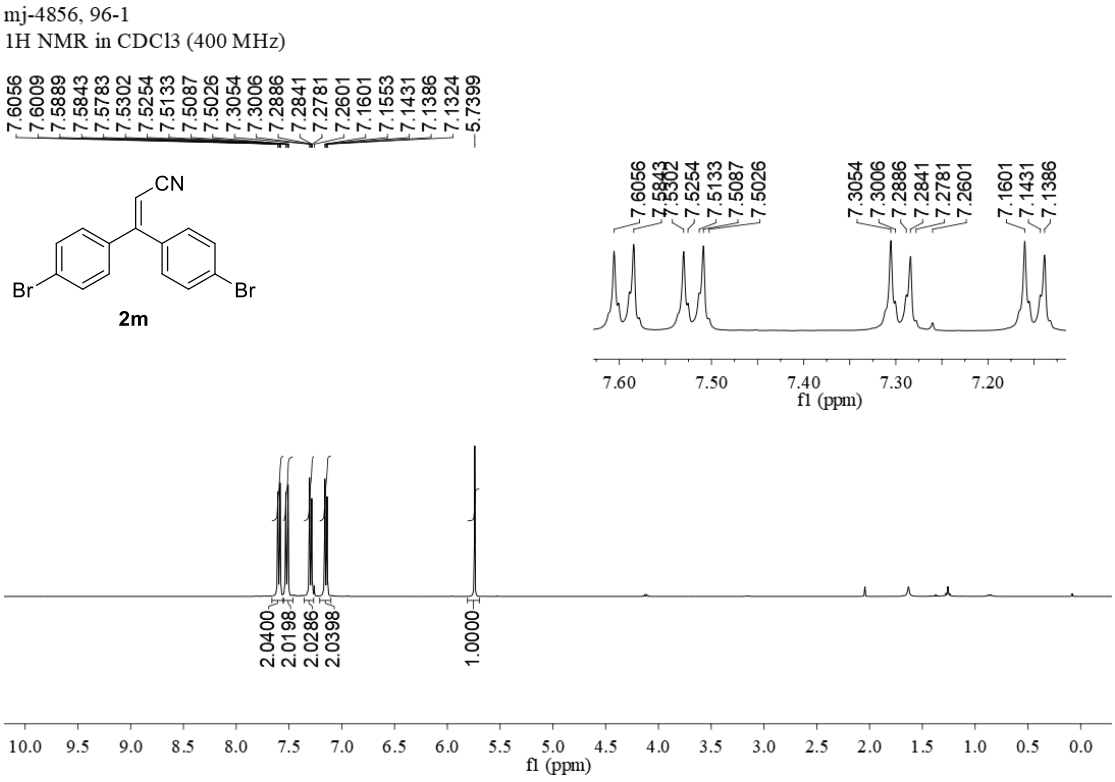


Figure S130. ^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 25 °C, 400 MHz).

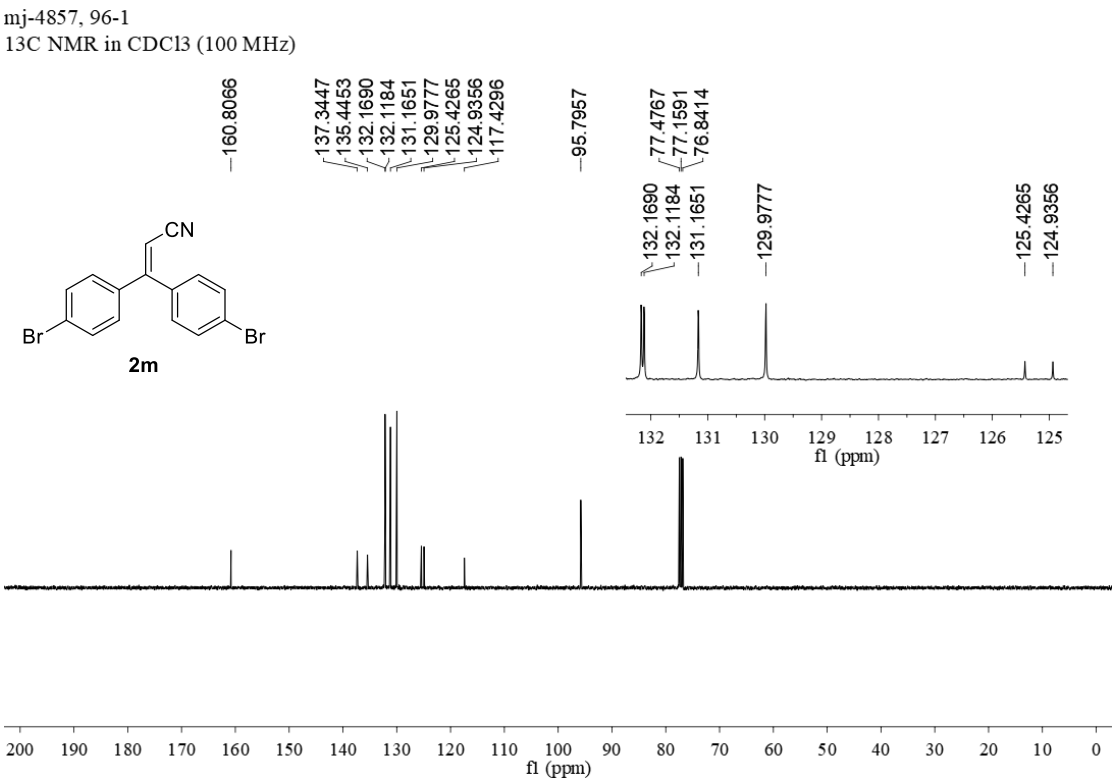


Figure S131. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2m** ($CDCl_3$, 25 °C, 100 MHz).

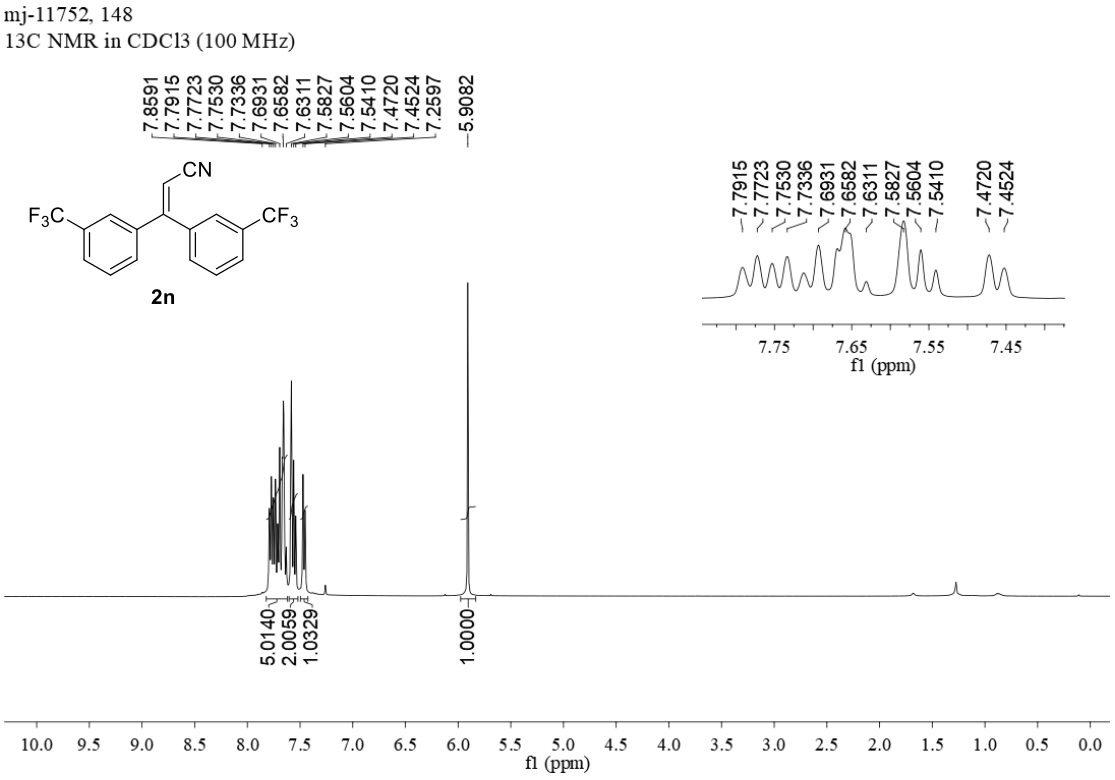


Figure S132. ^{1}H NMR spectrum of compound **2n** ($CDCl_3$, 25 °C, 400 MHz).

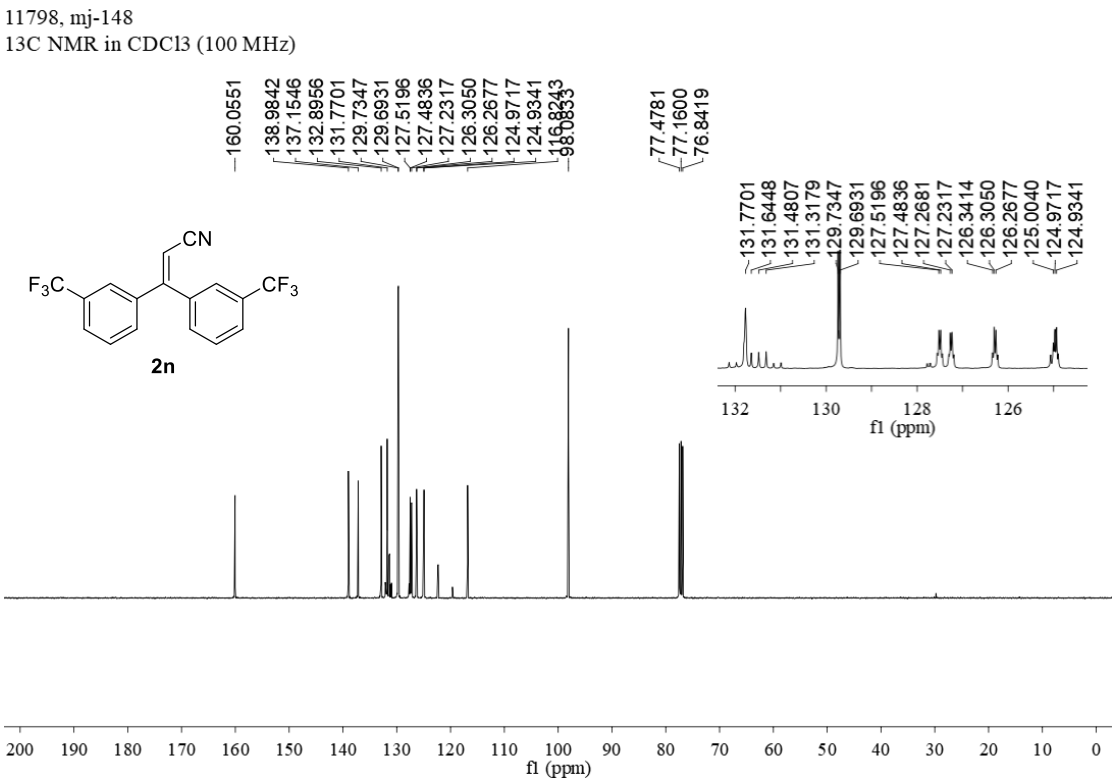


Figure S133. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2n** ($CDCl_3$, 25 °C, 100 MHz).

Figure S134. $^{19}F\{^{1}H\}$ NMR spectrum of compound **2n** ($CDCl_3$, 25 °C, 376 MHz).

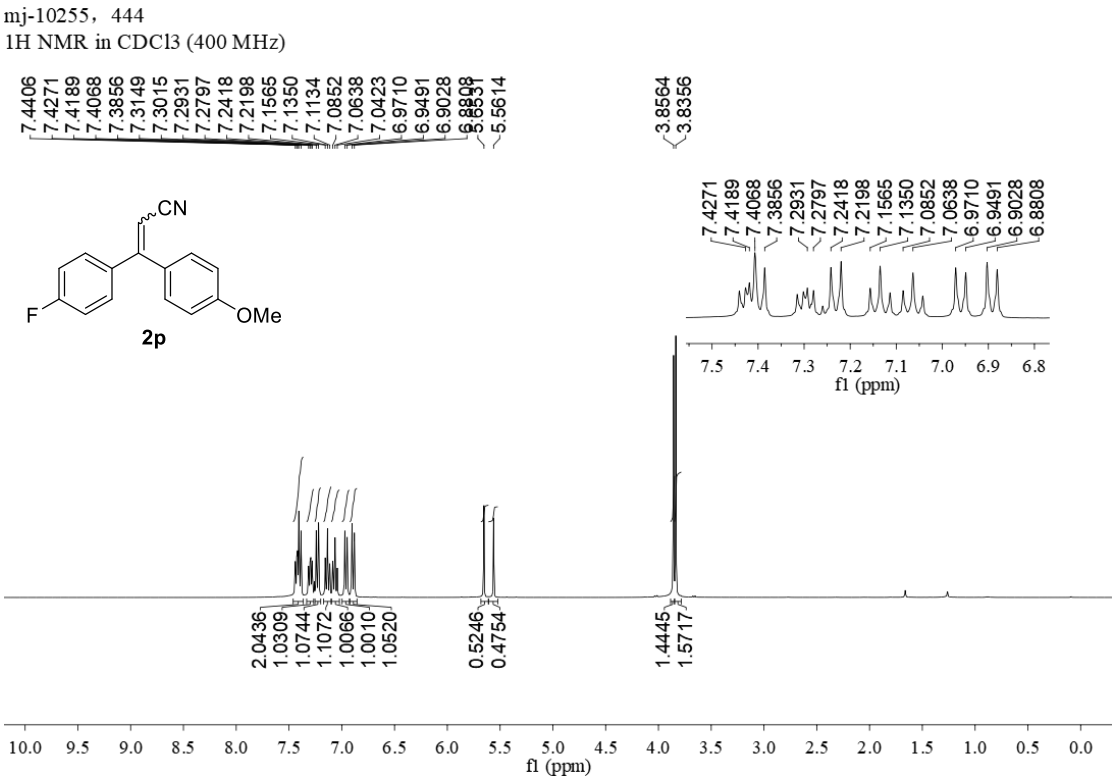


Figure S135. ^{1}H NMR spectrum of compound **2p** ($CDCl_3$, 25 °C, 400 MHz).

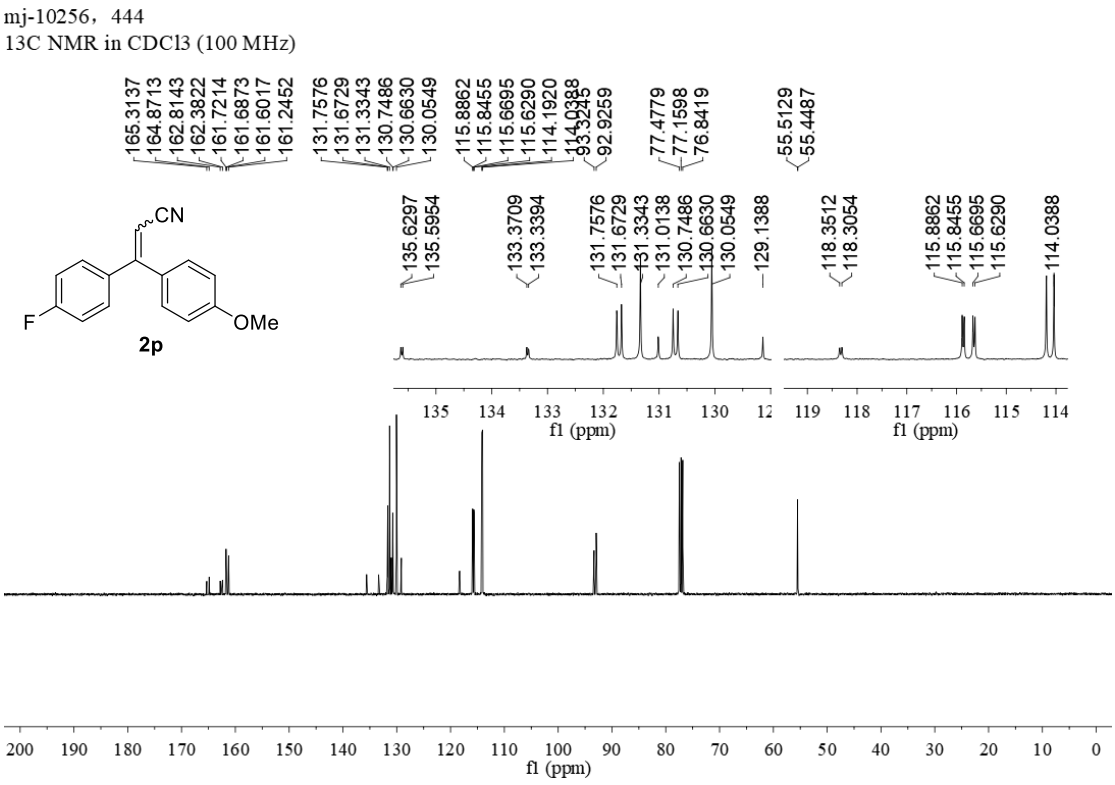


Figure S136. ^{13}C{^{1}H} NMR spectrum of compound **2p** ($CDCl_3$, 25 °C, 100 MHz).

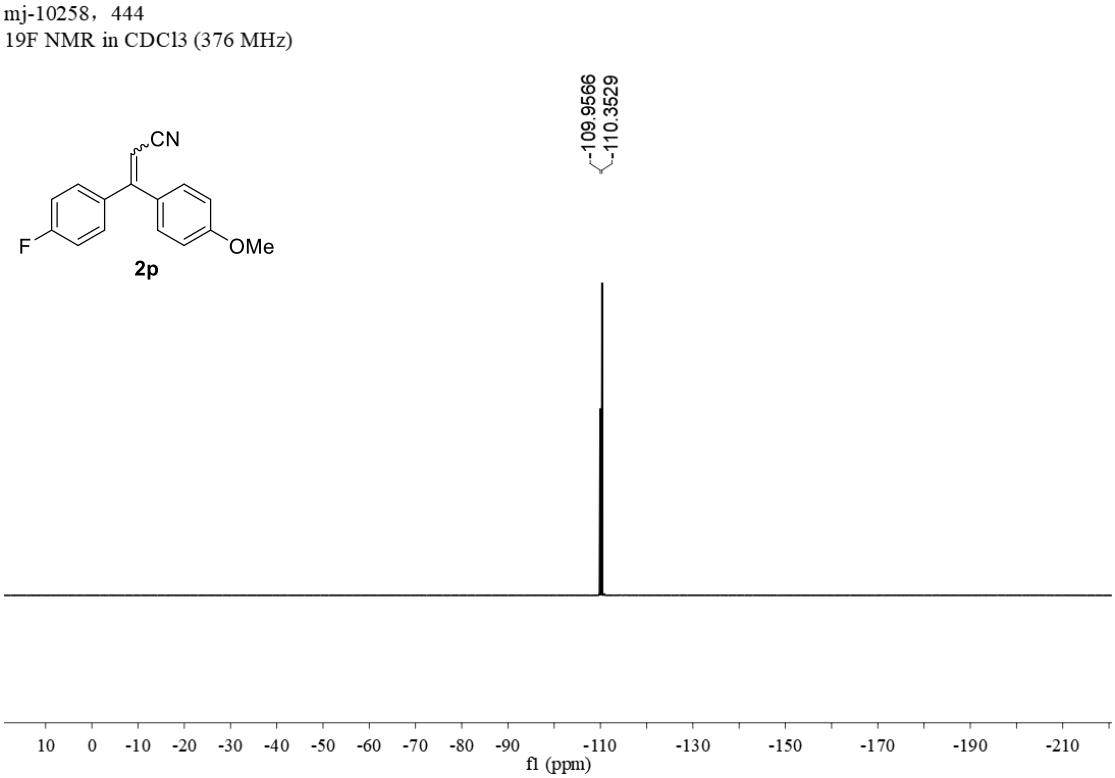


Figure S137. $^{19}F\{^{1}H\}$ NMR spectrum of compound **2p** ($CDCl_3$, 25 °C, 376 MHz).

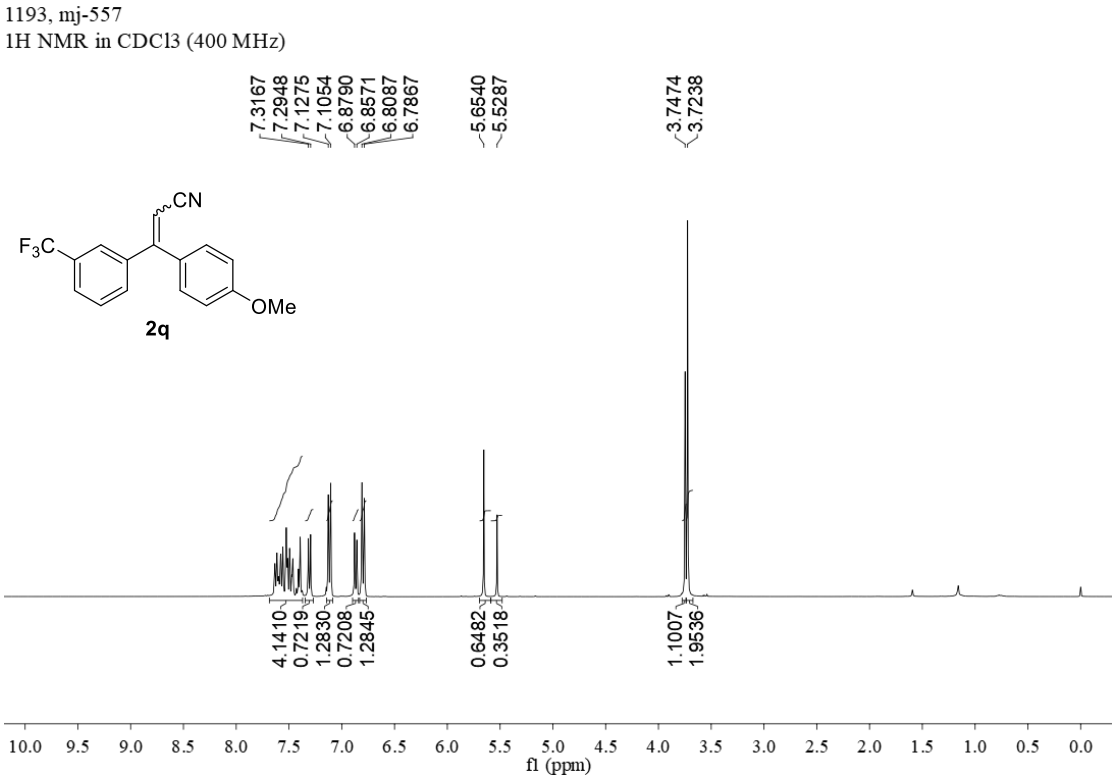


Figure S138. ^{1}H NMR spectrum of compound **2q** ($CDCl_3$, 25 °C, 400 MHz).

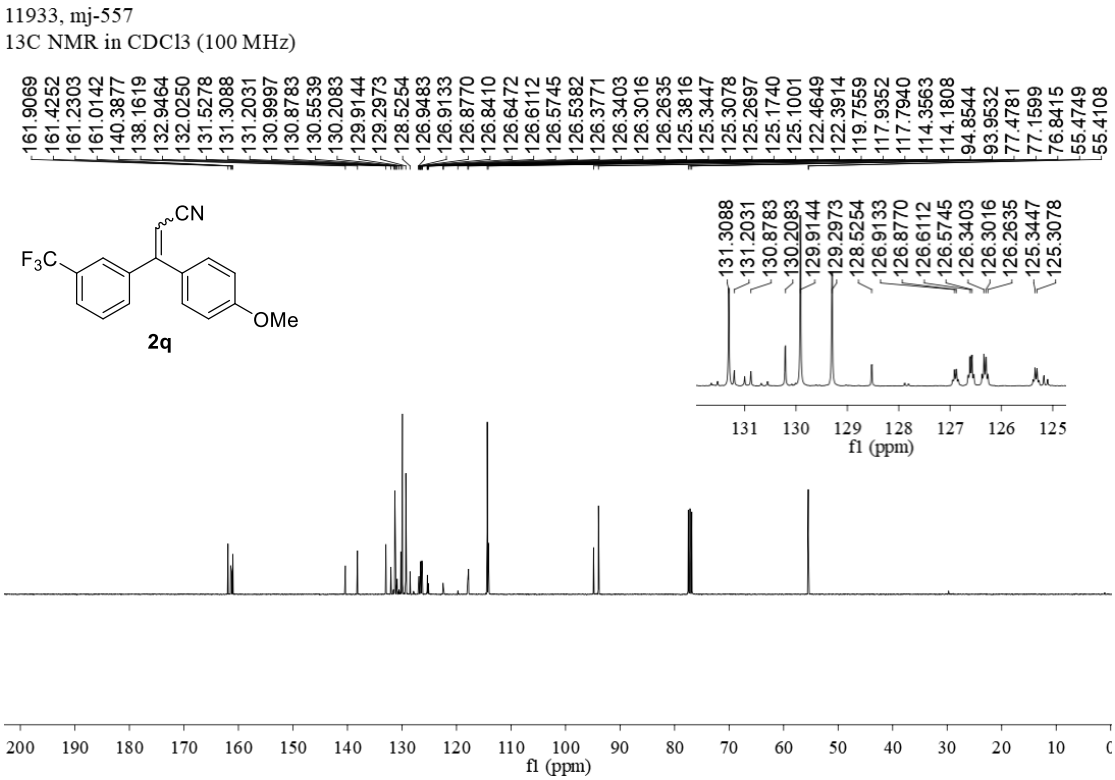


Figure S139. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2q** ($CDCl_3$, 25 °C, 100 MHz).

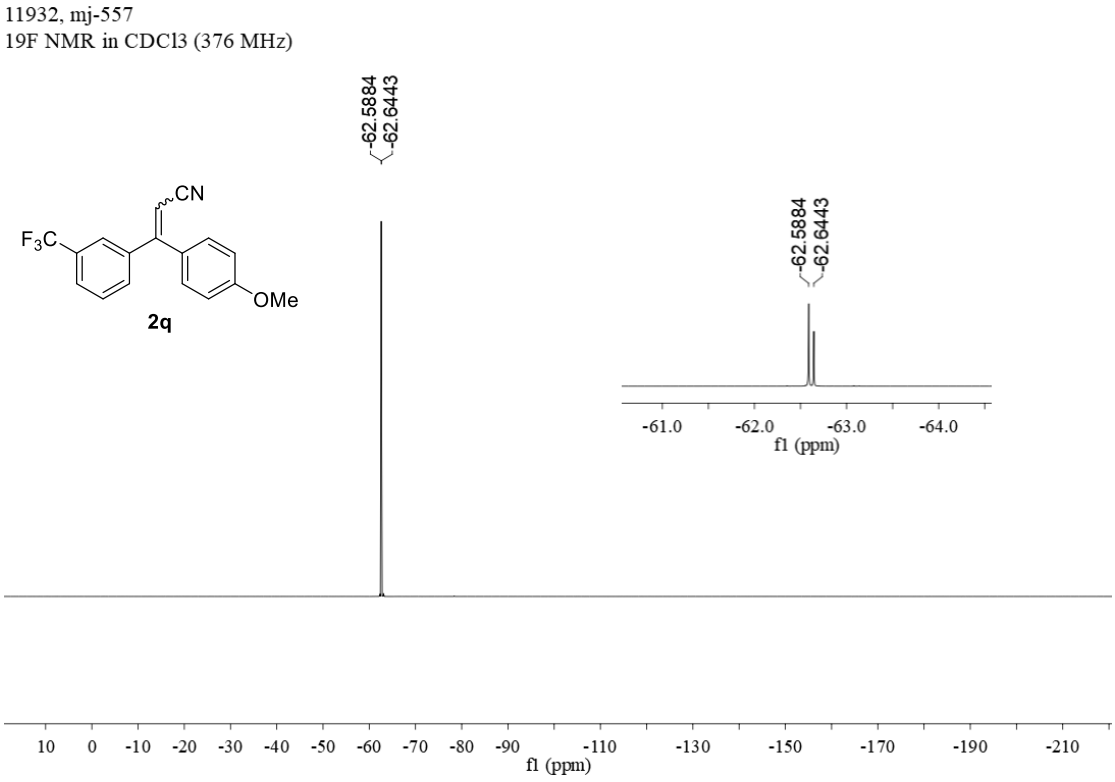


Figure S140. $^{19}F\{^{1}H\}$ NMR spectrum of compound **2q** ($CDCl_3$, 25 °C, 376 MHz).

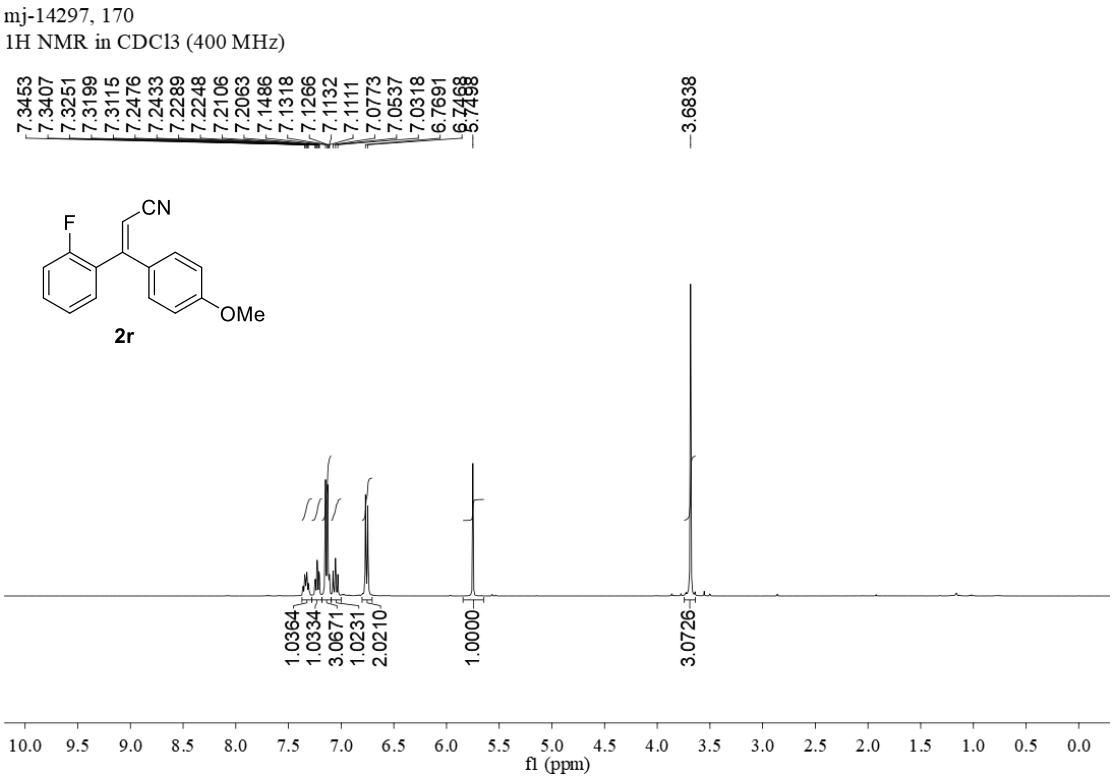


Figure S141. ^{1}H NMR spectrum of compound **2r** ($CDCl_3$, 25 °C, 400 MHz).

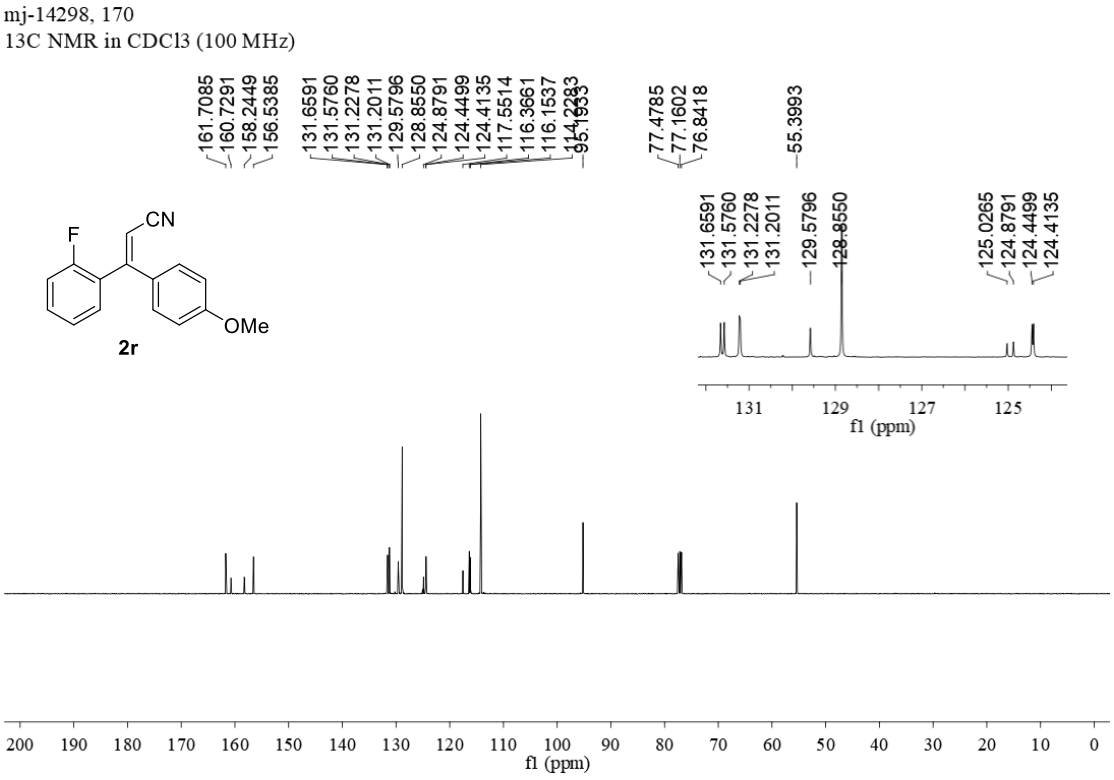


Figure S142. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2r** ($CDCl_3$, 25 °C, 100 MHz).

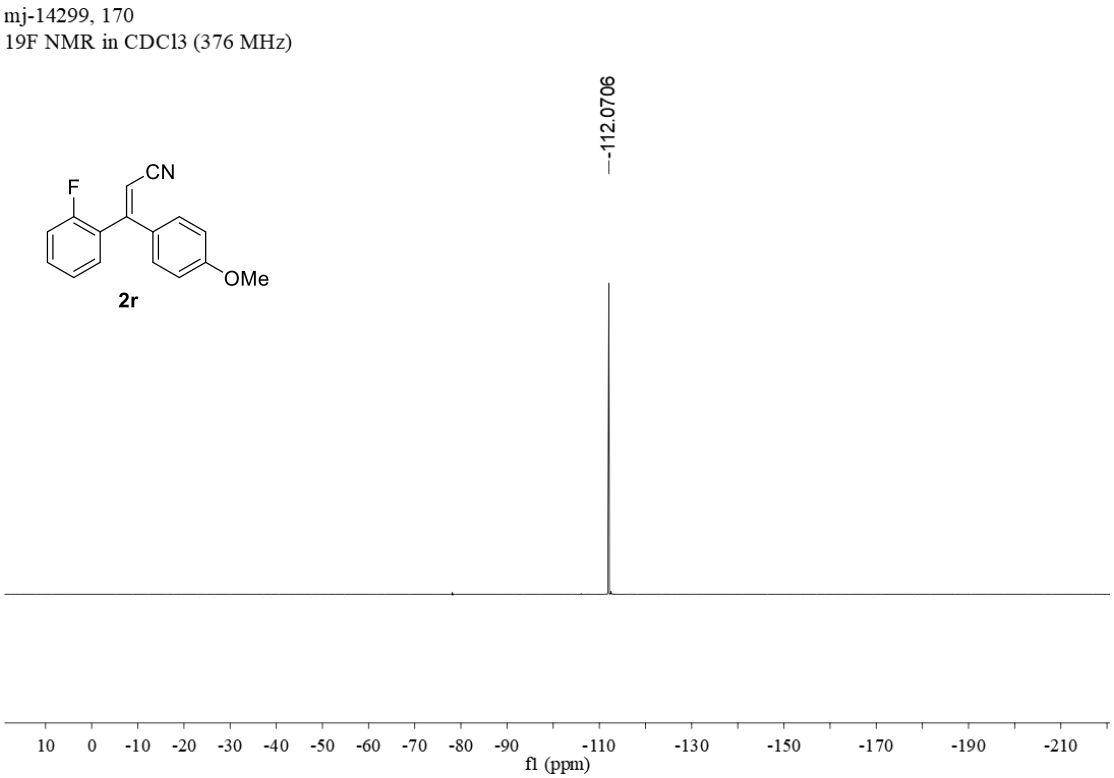


Figure S143. $^{19}F\{^{1}H\}$ NMR spectrum of compound **2r** ($CDCl_3$, 25 °C, 376 MHz).

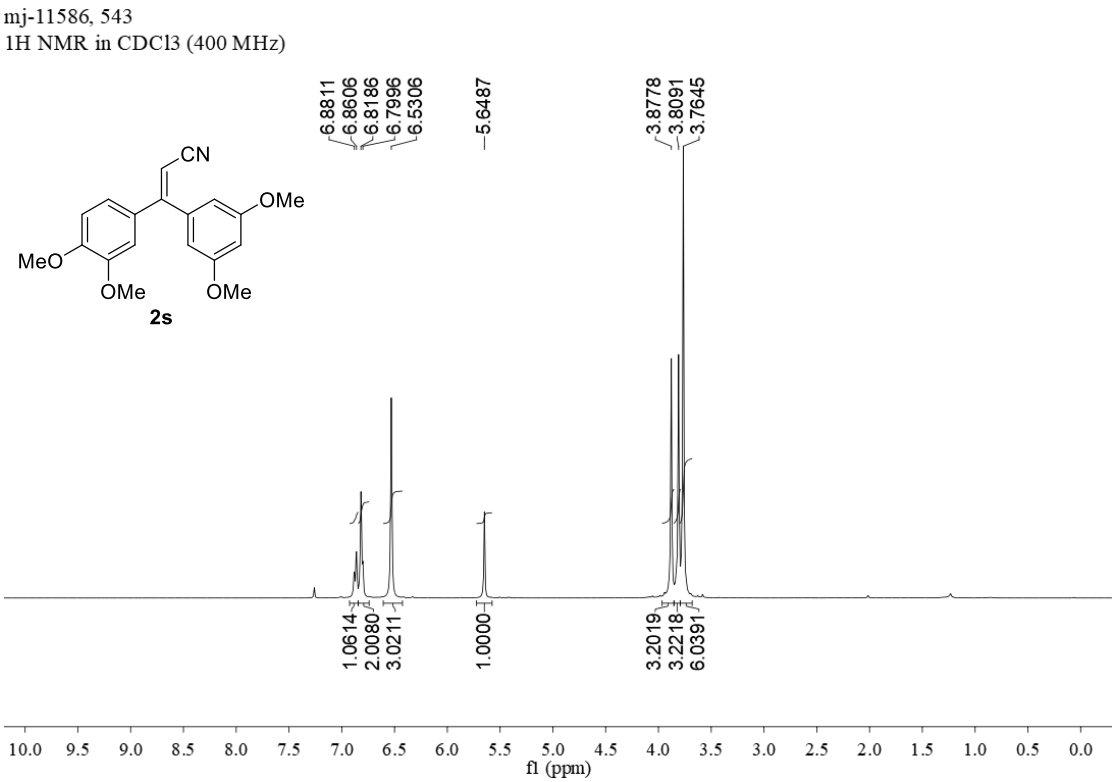


Figure S144. ^{1}H NMR spectrum of compound **2s** ($CDCl_3$, 25 °C, 400 MHz).

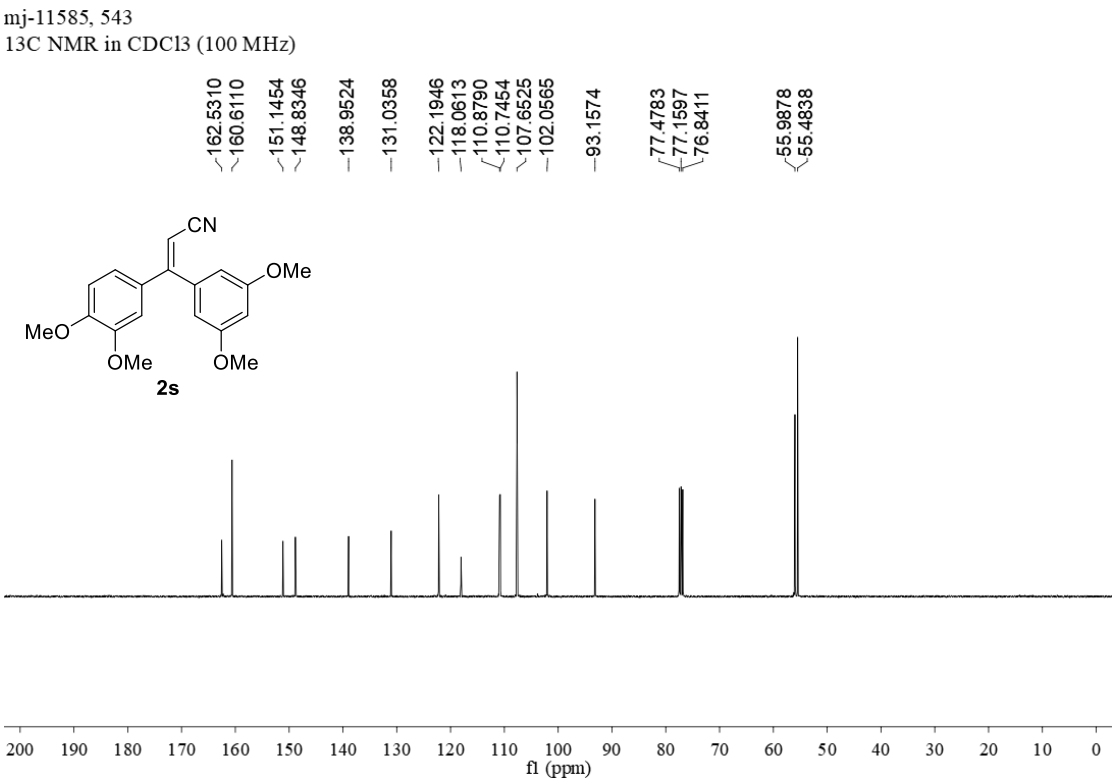


Figure S145. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2s** ($CDCl_3$, 25 °C, 100 MHz).

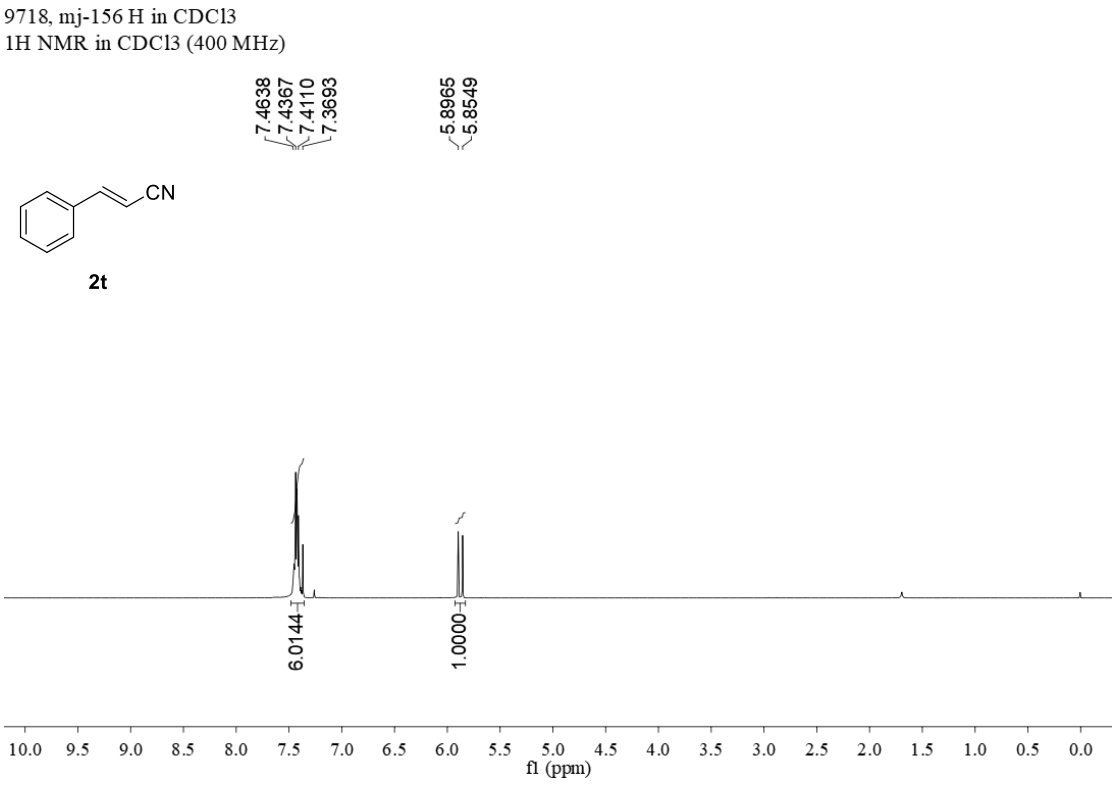


Figure S146. ^{1}H NMR spectrum of compound **2t** ($CDCl_3$, 25 °C, 400 MHz).

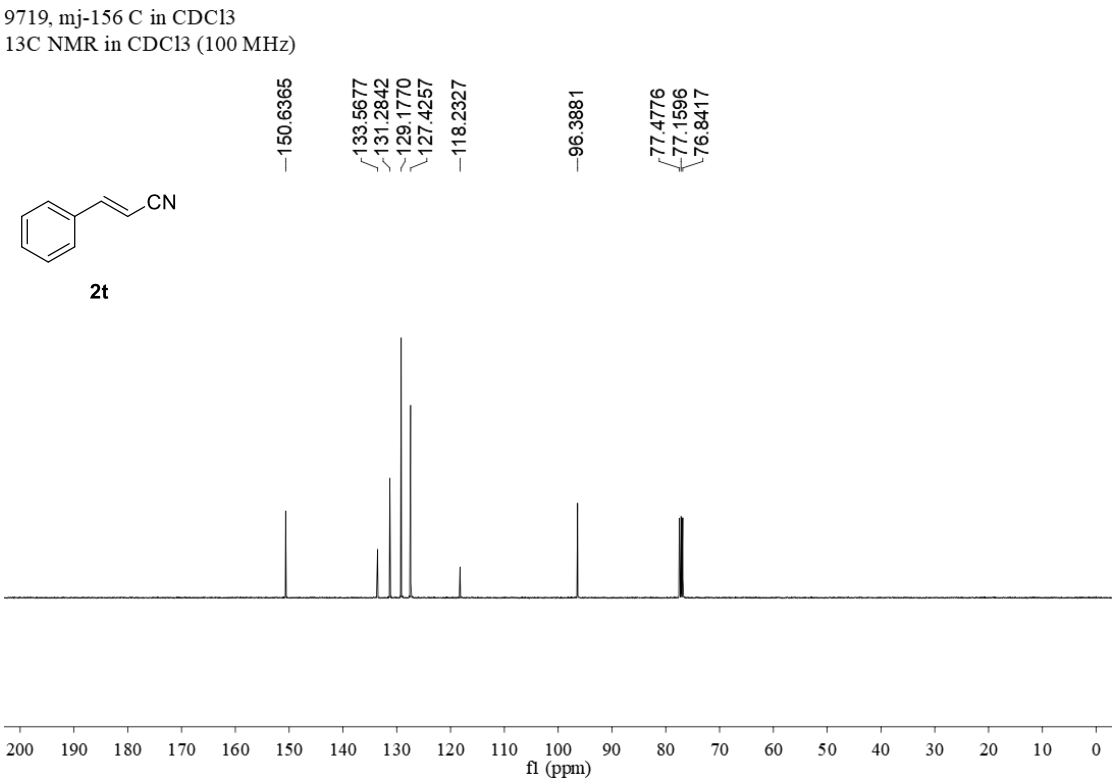


Figure S147. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2t** ($CDCl_3$, 25 °C, 100 MHz).

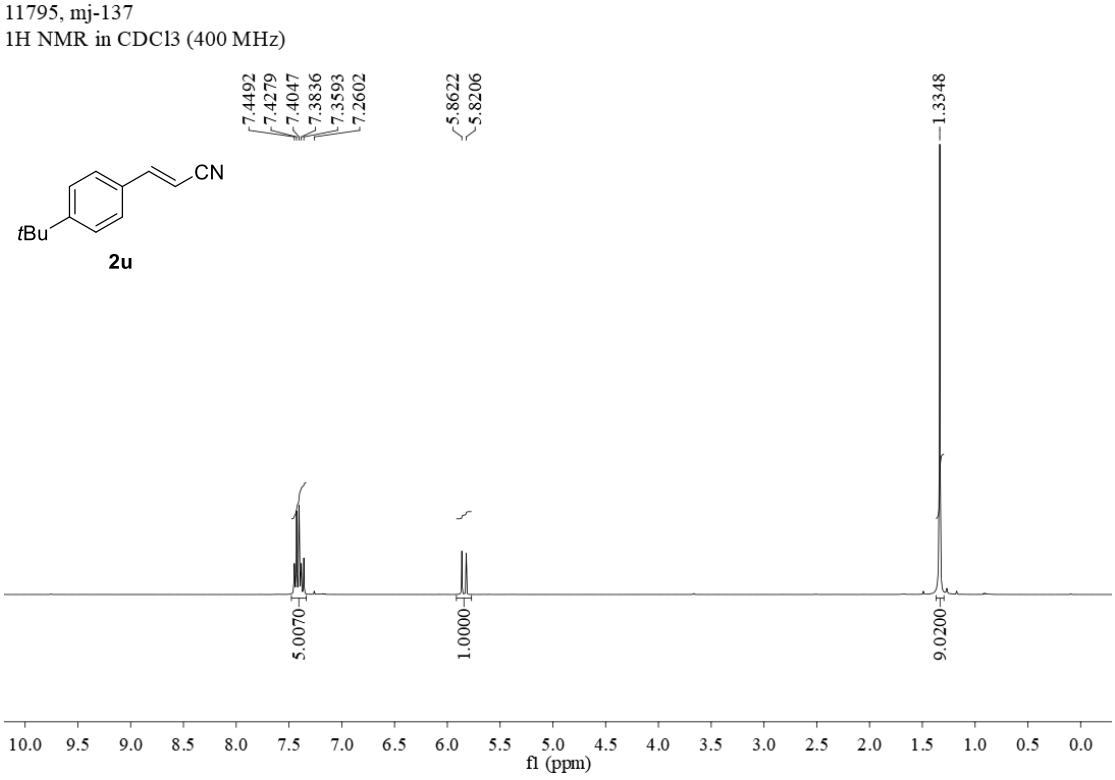


Figure S148. ^{1}H NMR spectrum of compound **2u** ($CDCl_3$, 25 °C, 400 MHz).

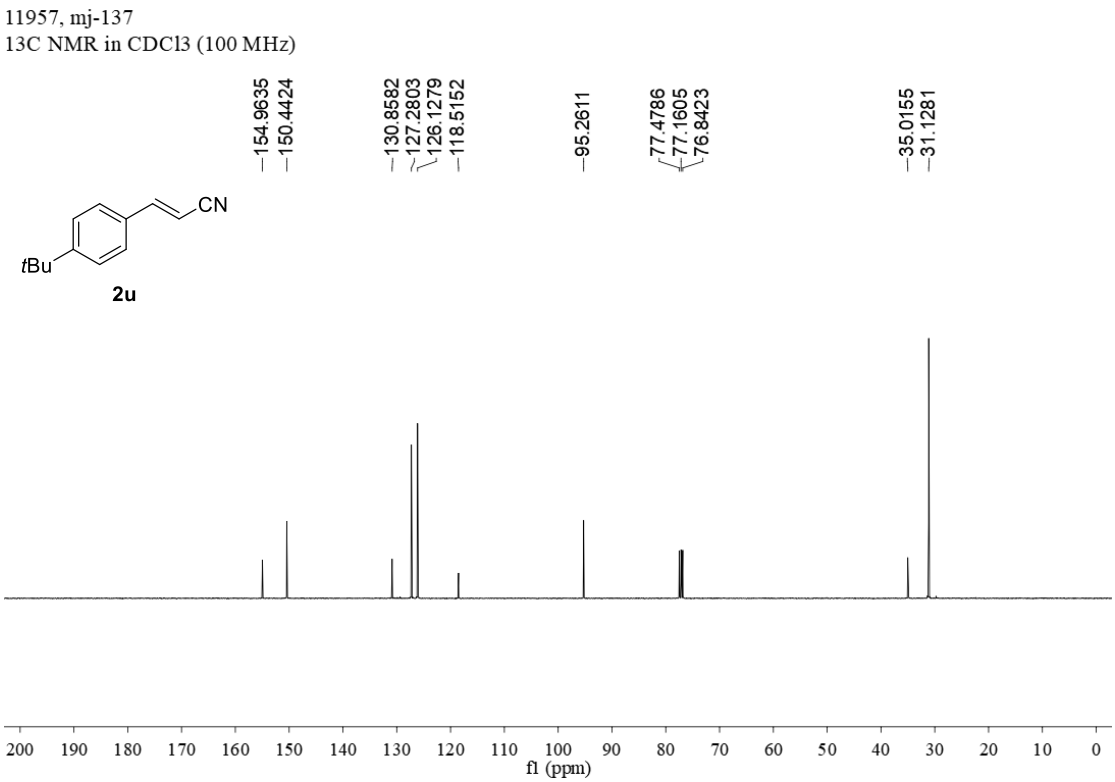


Figure S149. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2u** ($CDCl_3$, 25 °C, 100 MHz).

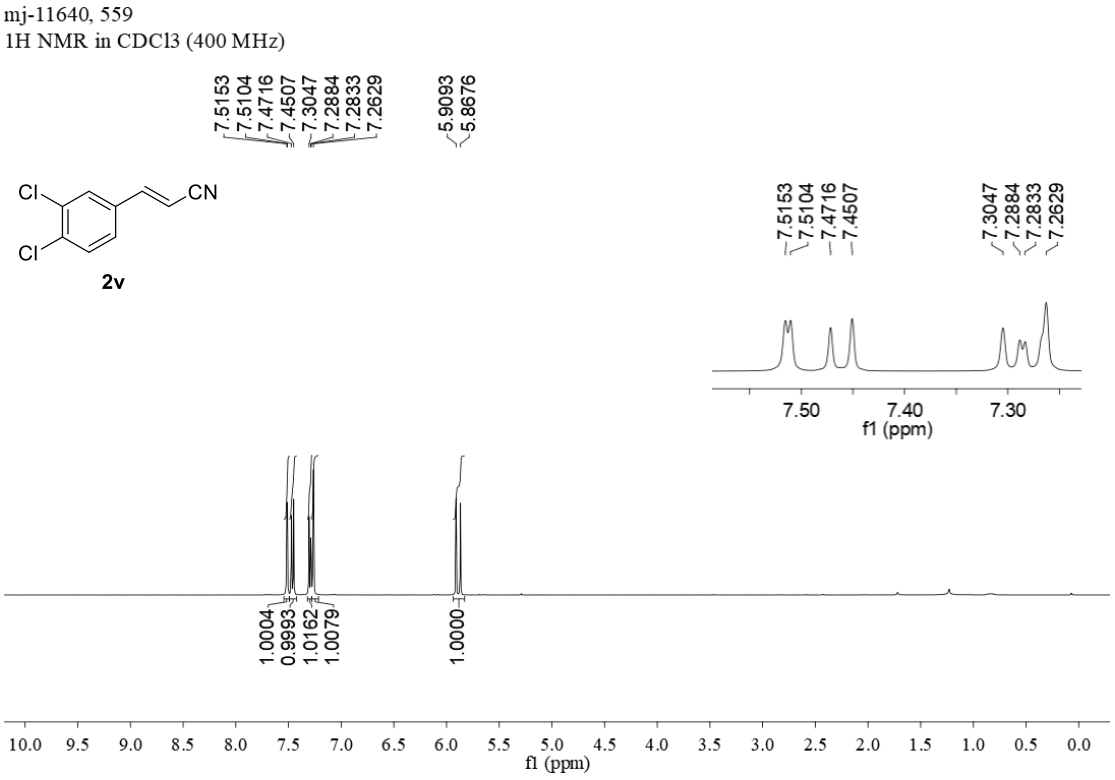


Figure S150. ^{1}H NMR spectrum of compound **2v** ($CDCl_3$, 25 °C, 400 MHz).

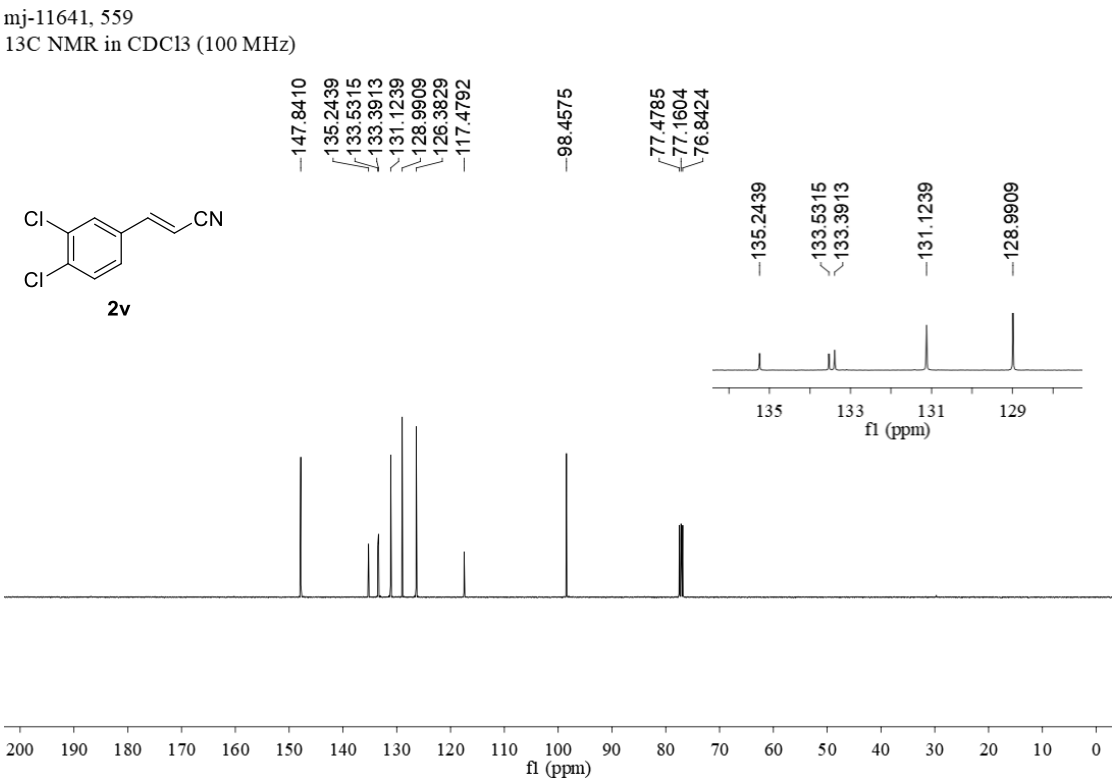


Figure S151. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2v** ($CDCl_3$, 25 °C, 100 MHz).

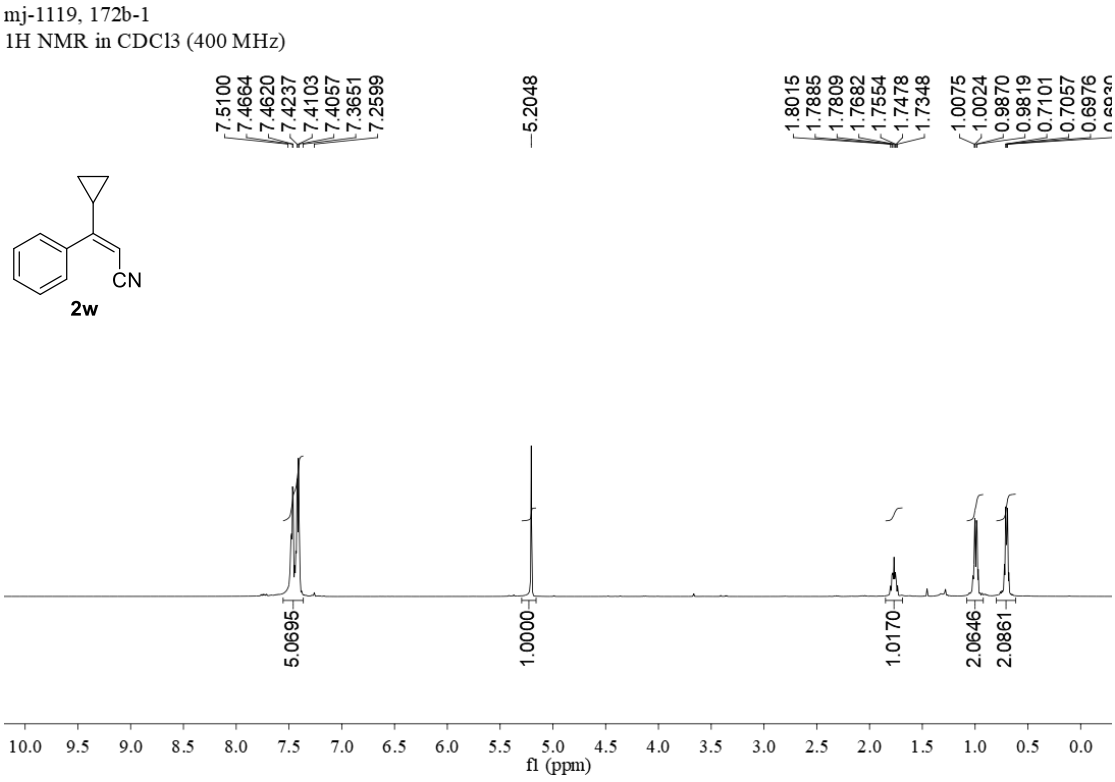


Figure S152. ^{1}H NMR spectrum of compound **2w** ($CDCl_3$, 25 °C, 400 MHz).

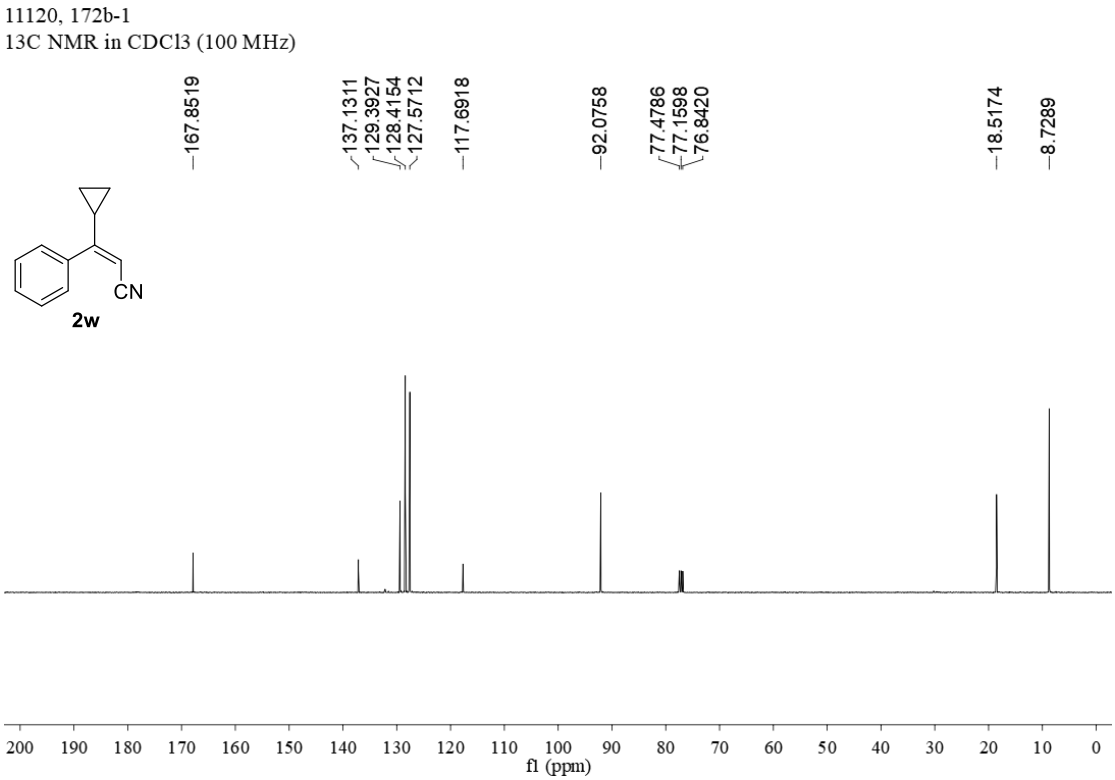


Figure S153. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2w** ($CDCl_3$, 25 °C, 100 MHz).

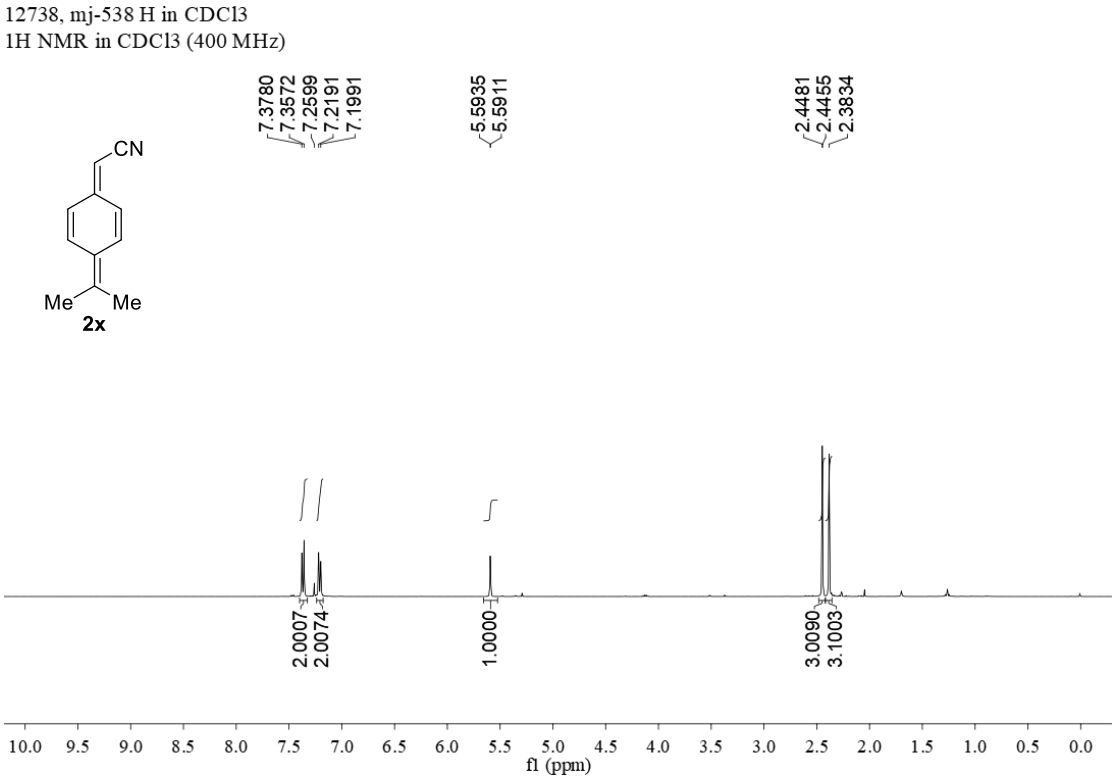


Figure S154. ^{1}H NMR spectrum of compound **2x** ($CDCl_3$, 25 °C, 400 MHz).

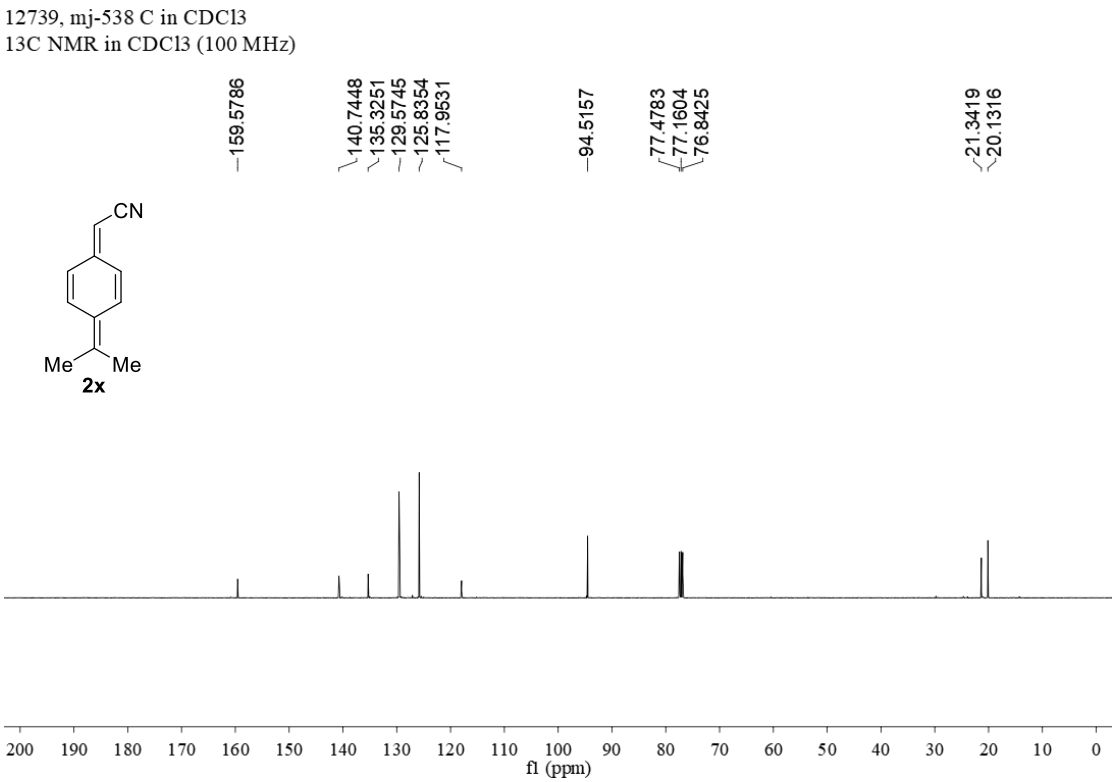


Figure S155. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2x** ($CDCl_3$, 25 °C, 100 MHz).

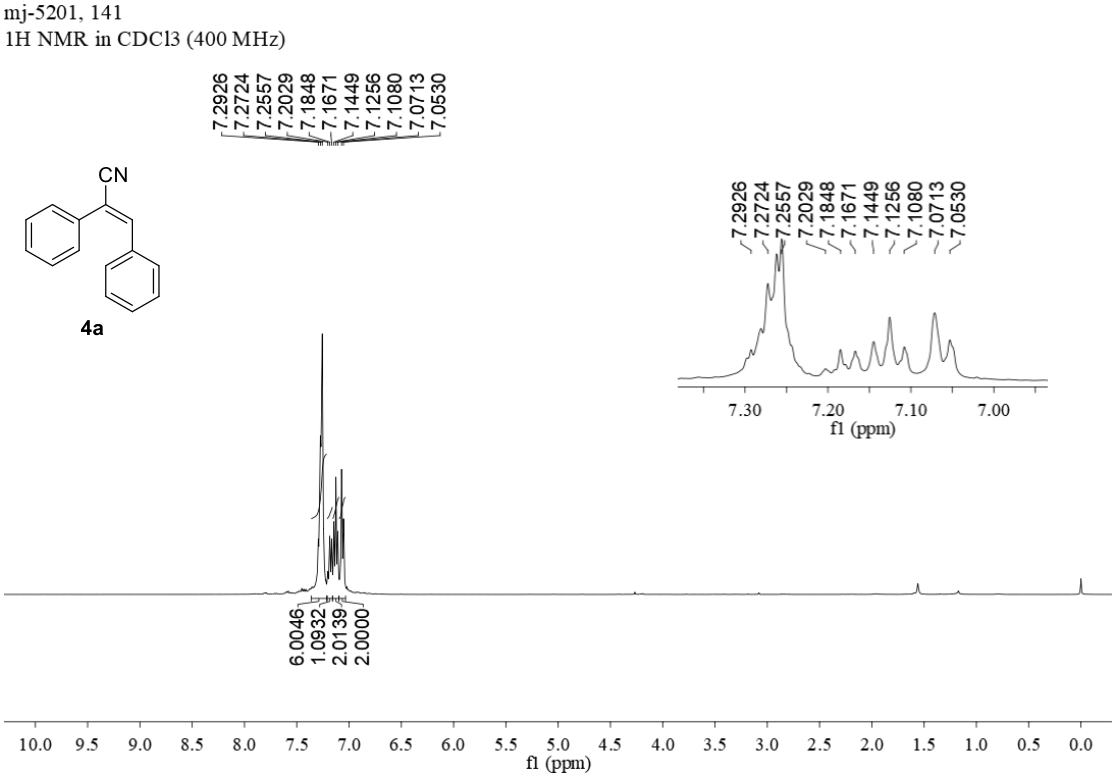


Figure S156. ^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 25 °C, 400 MHz).

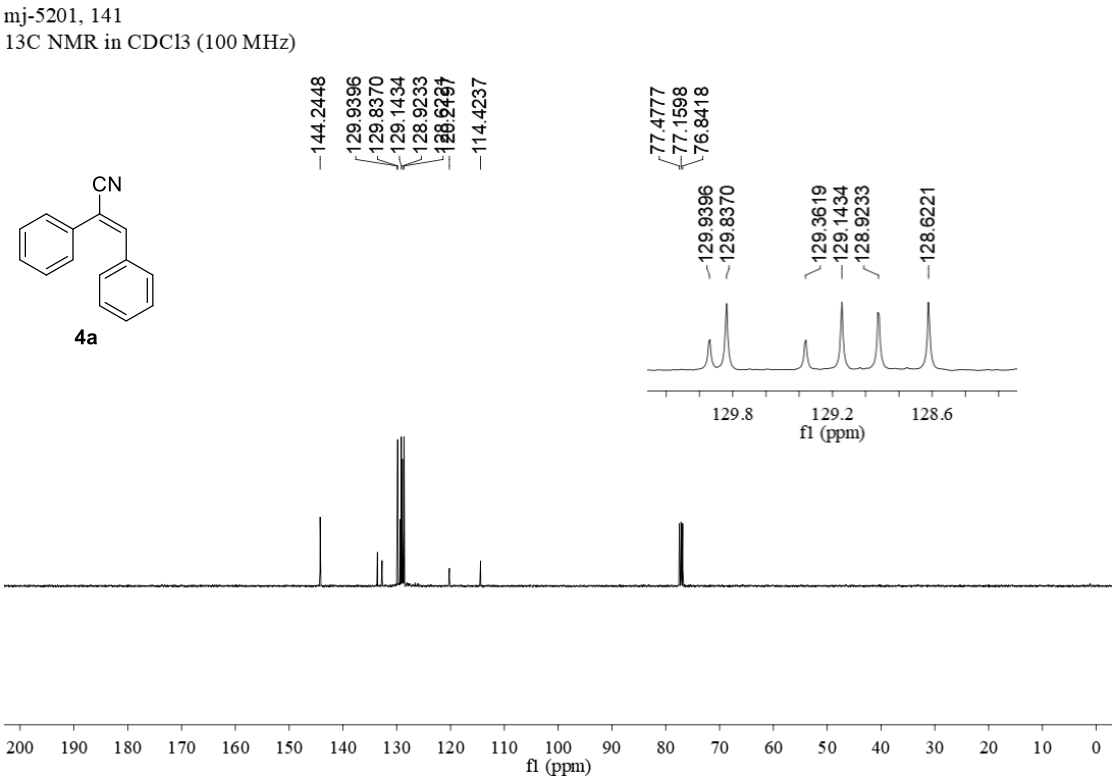


Figure S157. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a** ($CDCl_3$, 25 °C, 100 MHz).

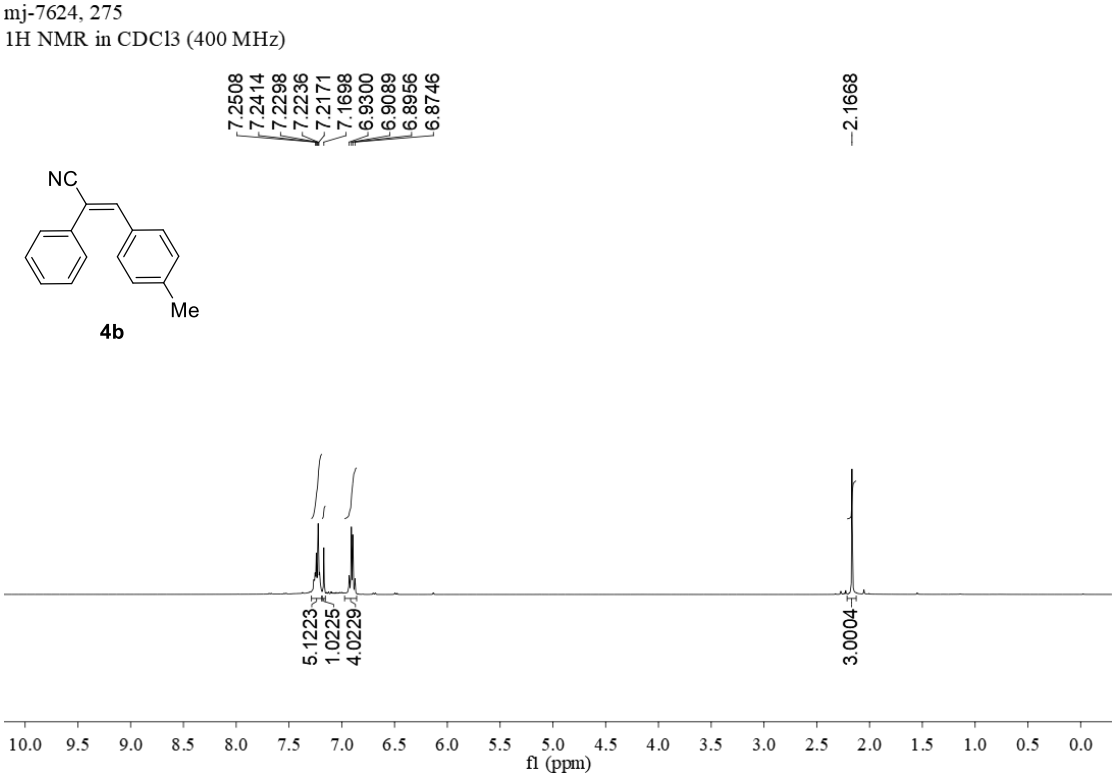


Figure S158. ^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 25 °C, 400 MHz).

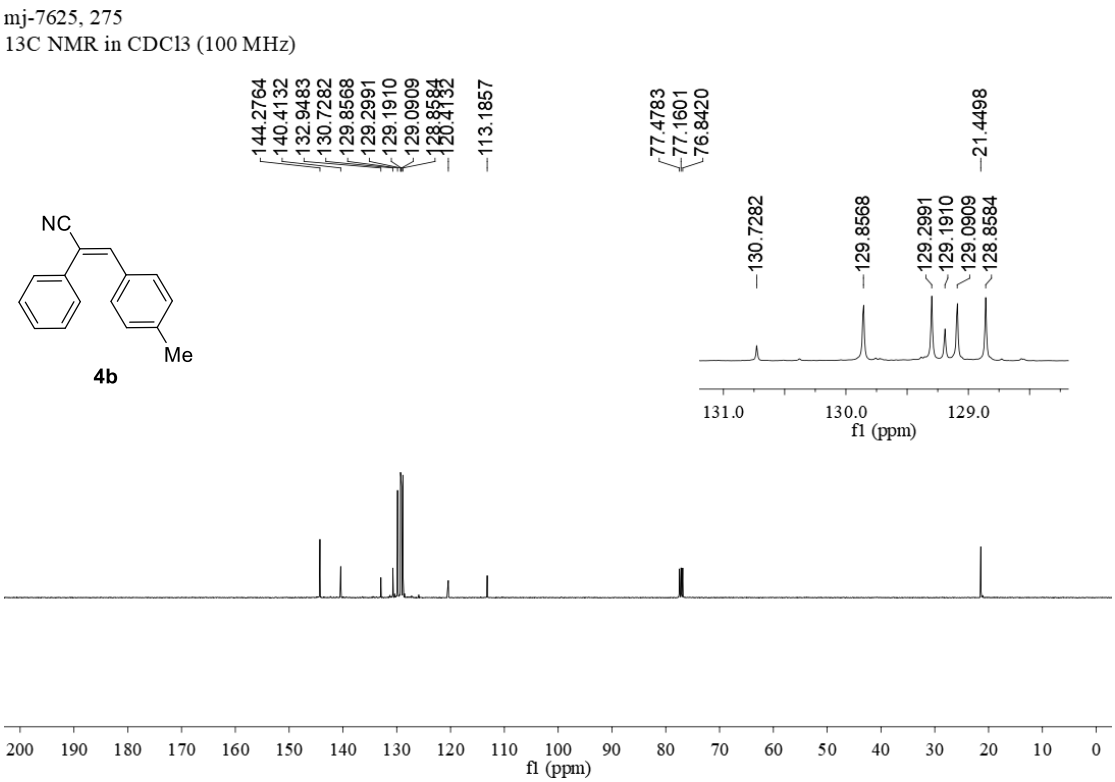


Figure S159. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4b** ($CDCl_3$, 25 °C, 100 MHz).

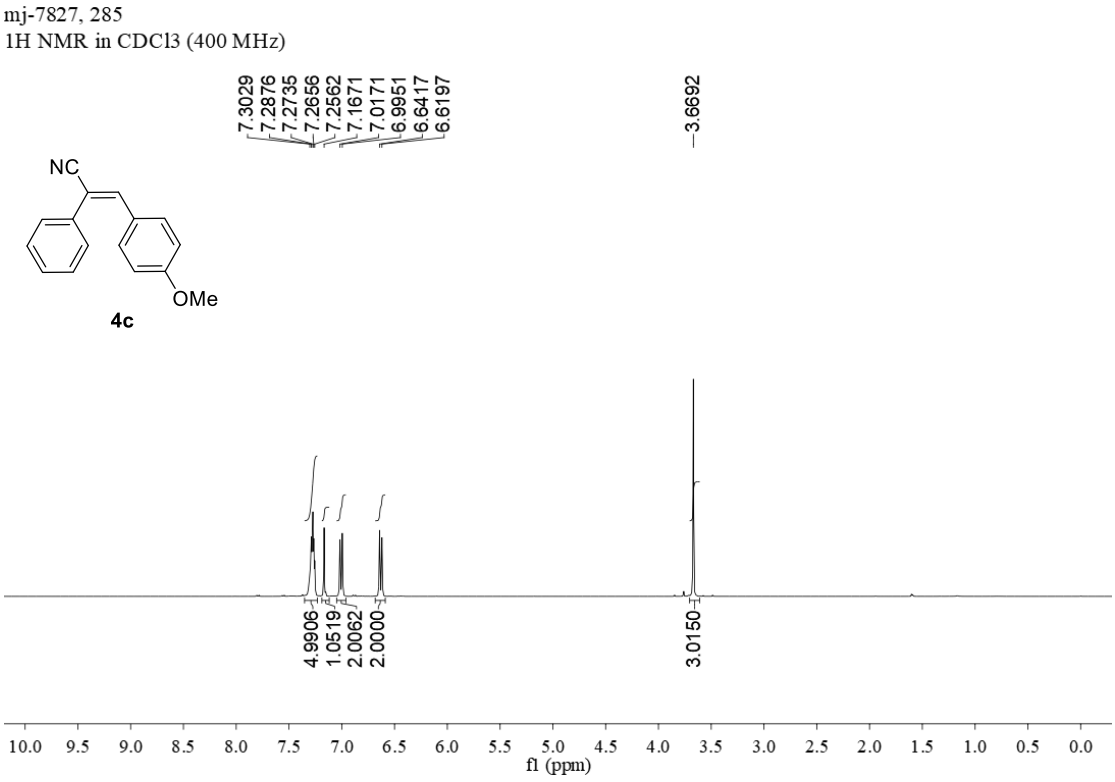


Figure S160. ^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 25 °C, 400 MHz).

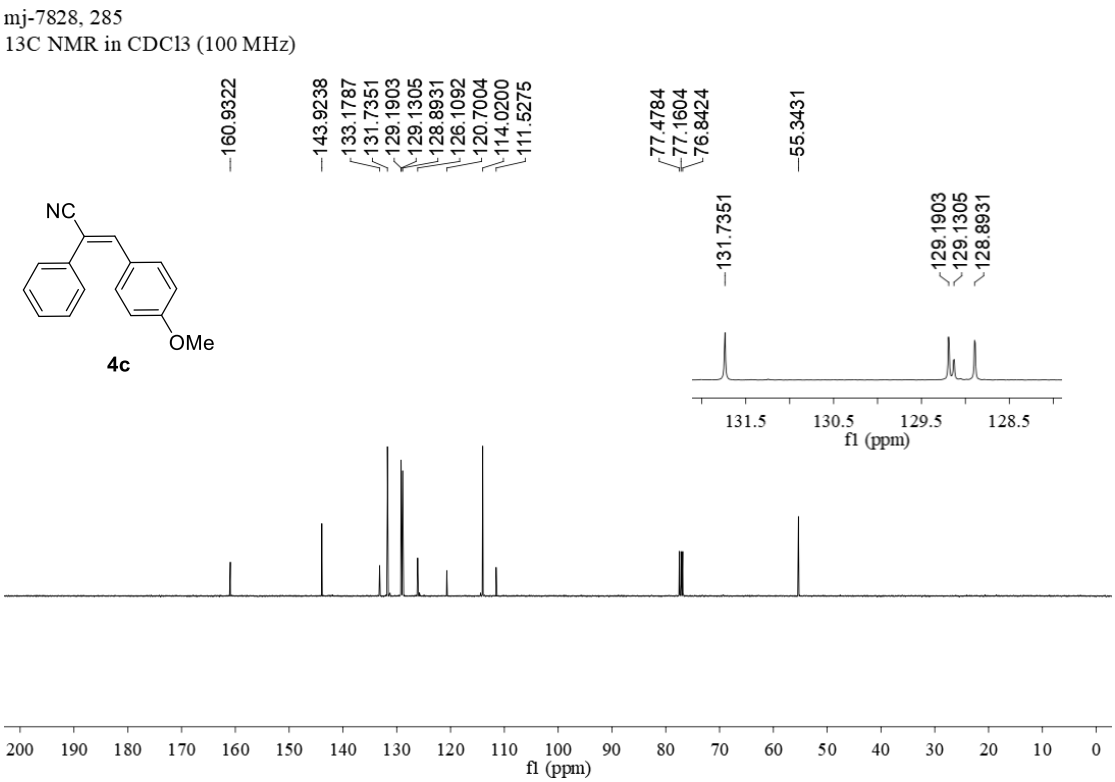


Figure S161. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4c** ($CDCl_3$, 25 °C, 100 MHz).

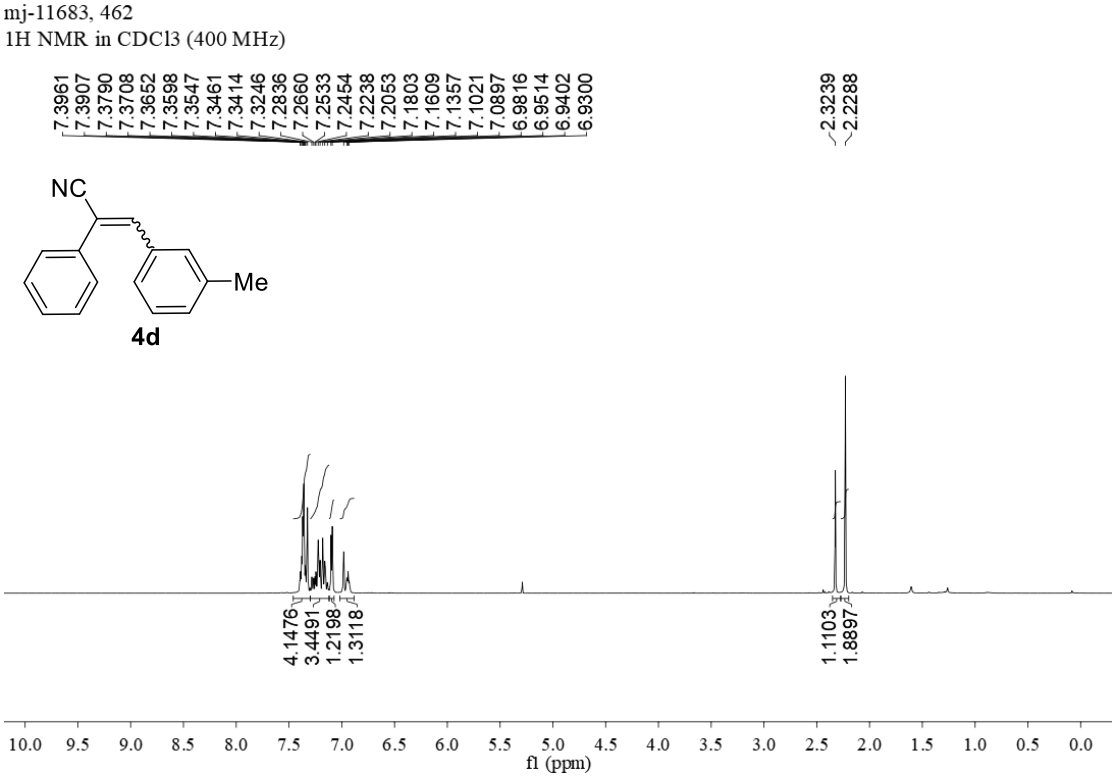


Figure S162. ^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 25 °C, 400 MHz).

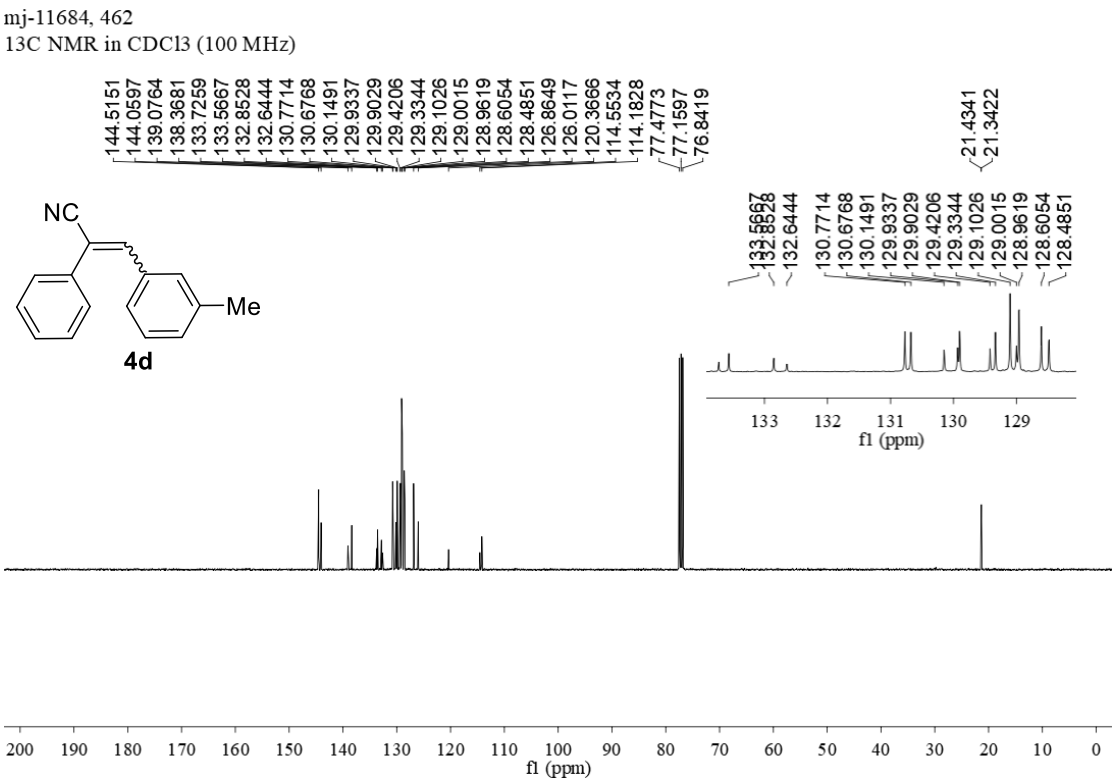


Figure S163. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4d** ($CDCl_3$, 25 °C, 100 MHz).

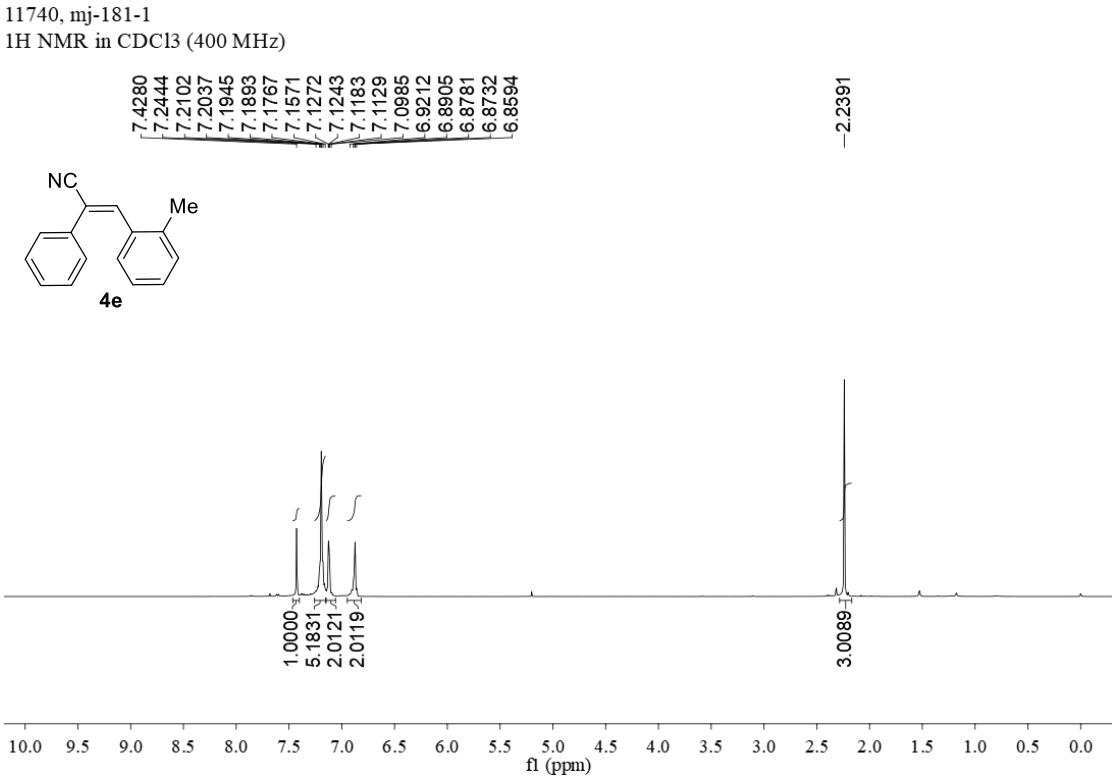


Figure S164. ^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 25 °C, 400 MHz).

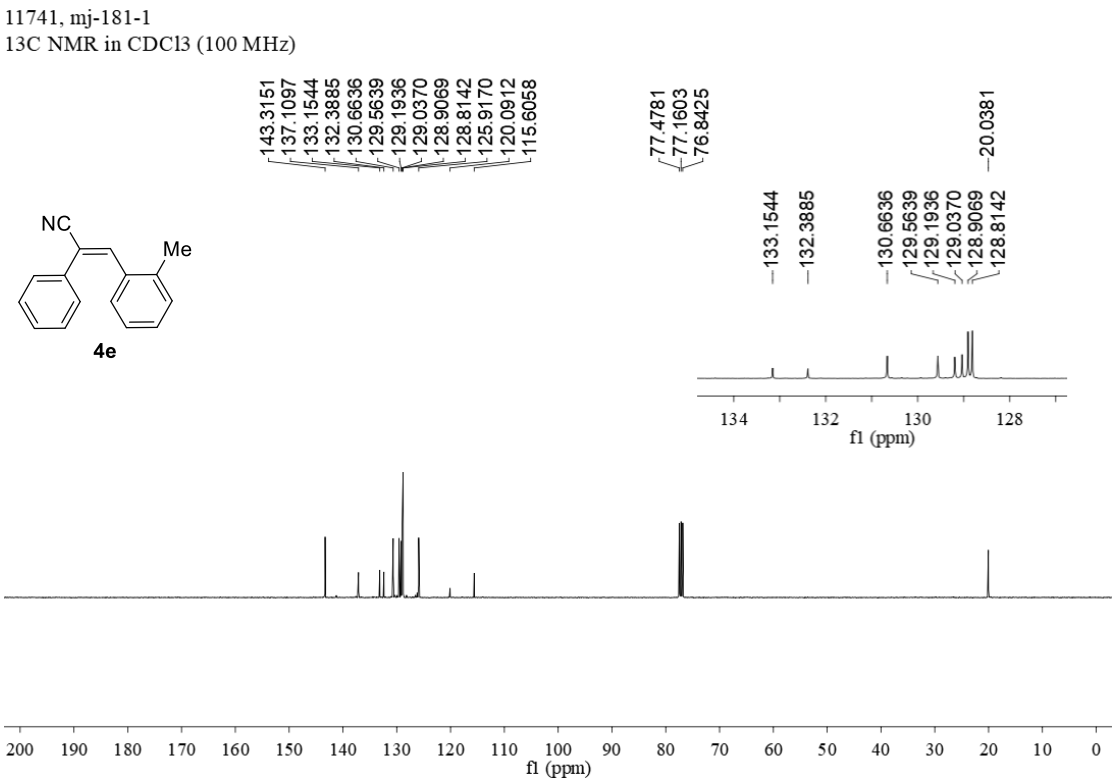


Figure S165. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4e** ($CDCl_3$, 25 °C, 100 MHz).

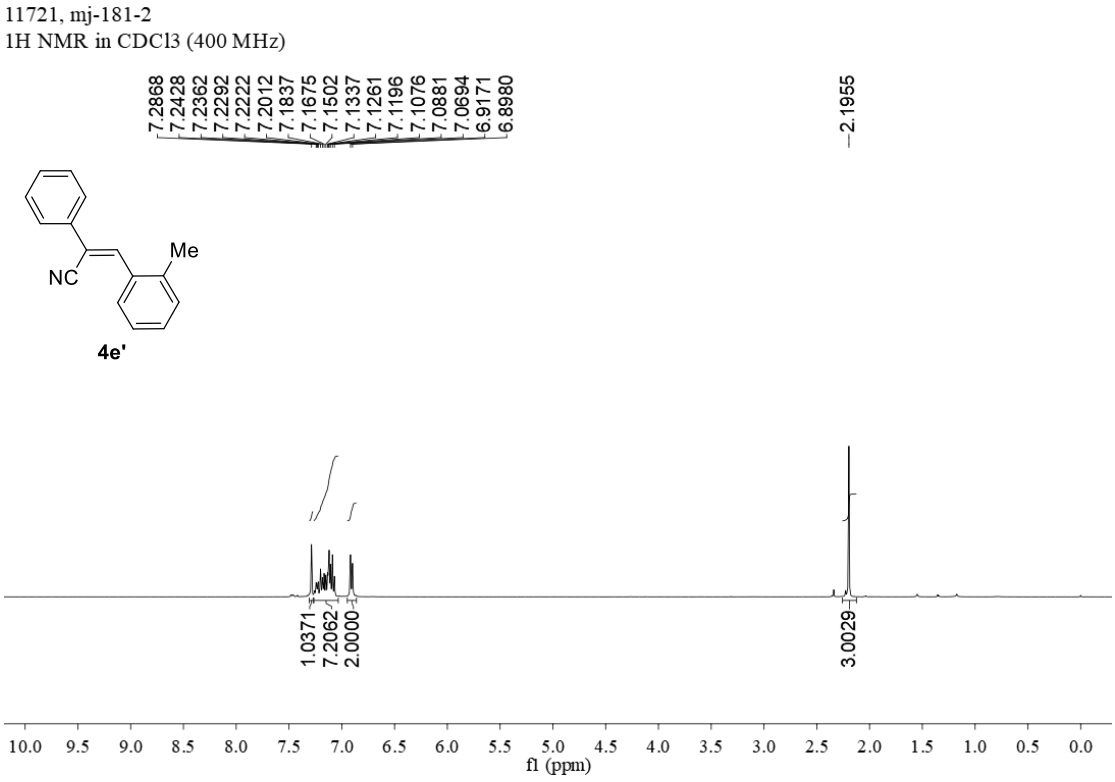


Figure S166. ^{1}H NMR spectrum of compound **4e'** ($CDCl_3$, 25 °C, 400 MHz).

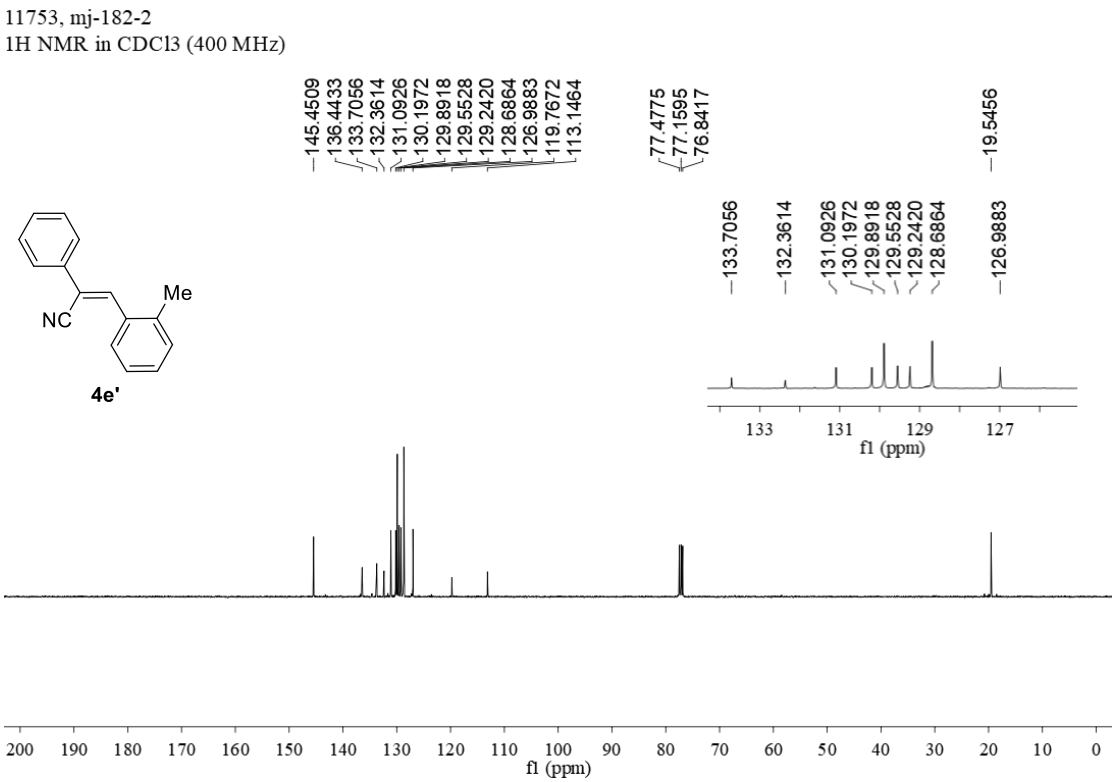


Figure S167. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4e'** ($CDCl_3$, 25 °C, 100 MHz).

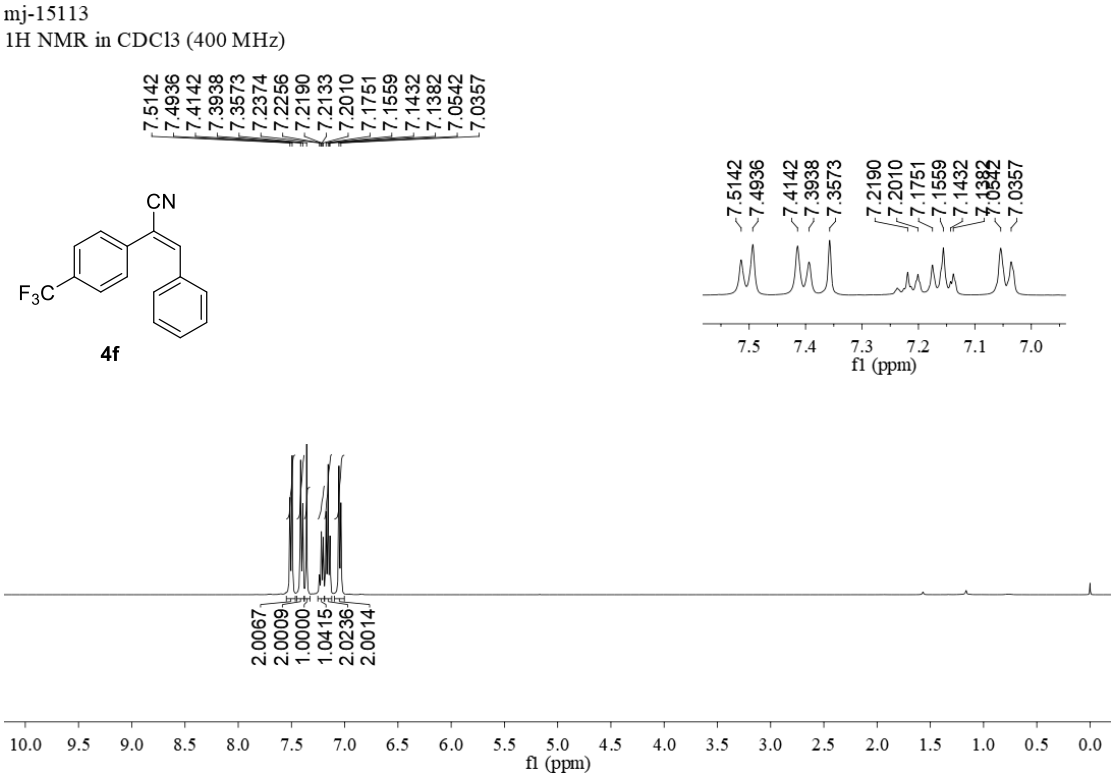


Figure S168. ^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 25 °C, 400 MHz).

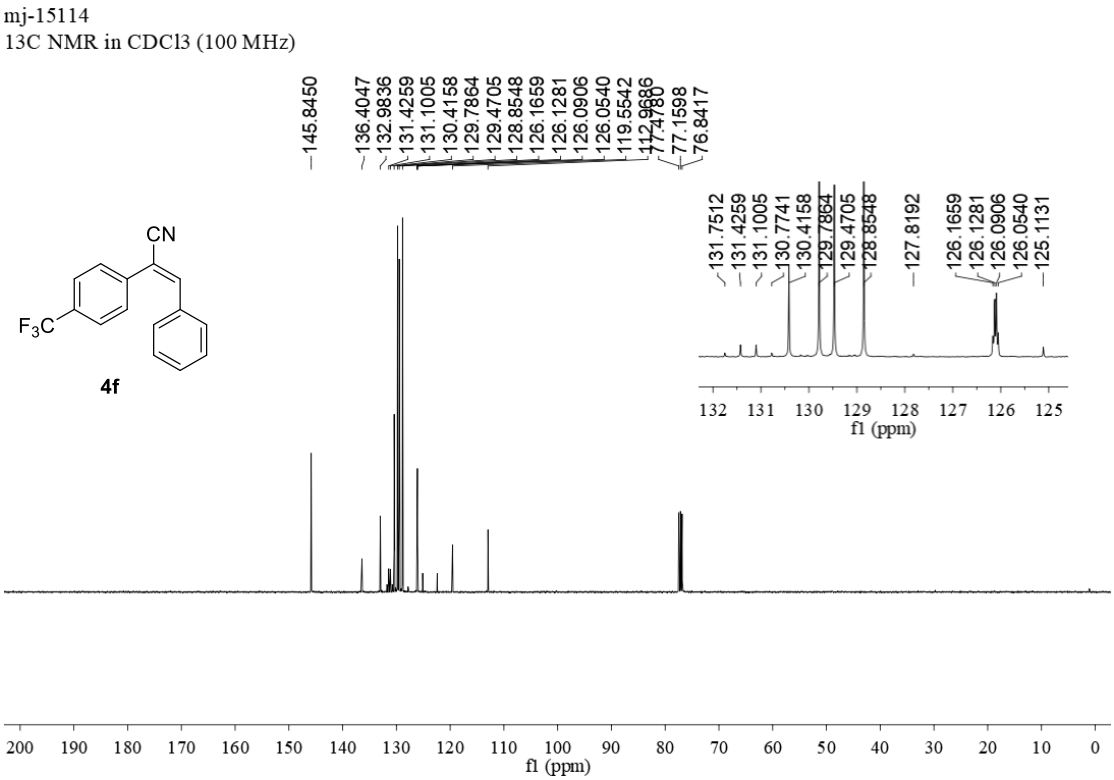


Figure S169. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4f** ($CDCl_3$, 25 °C, 100 MHz).

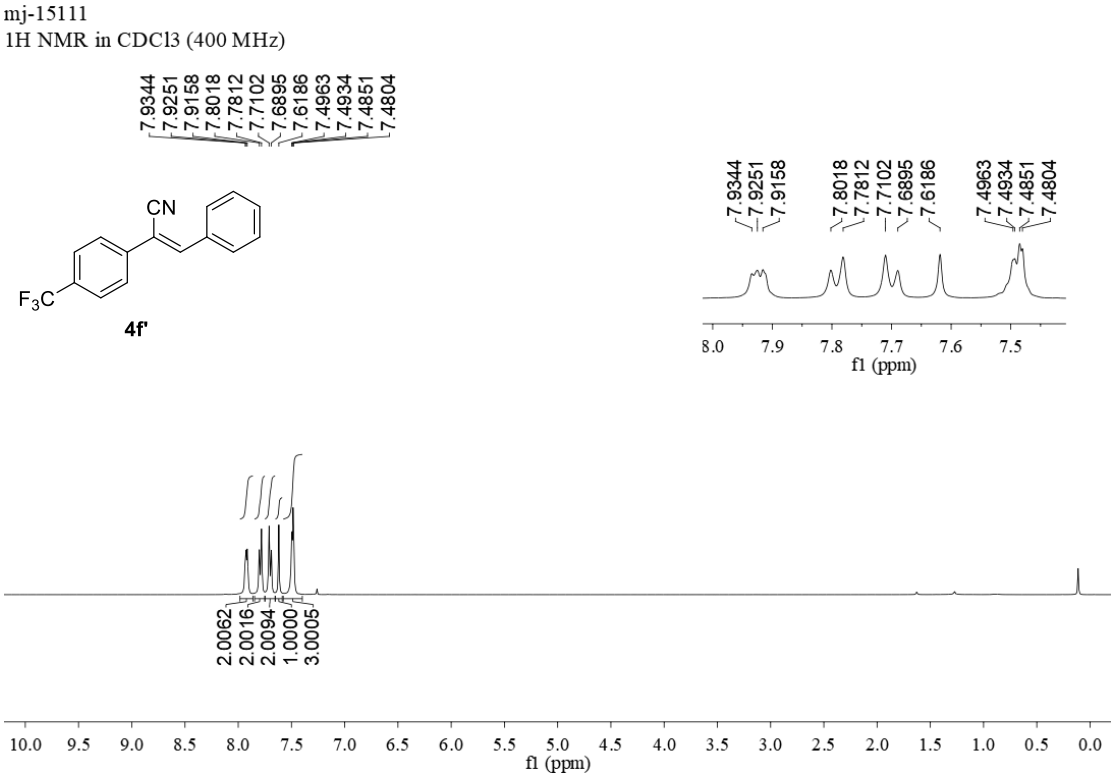


Figure S170. ^{1}H NMR spectrum of compound **4f'** ($CDCl_3$, 25 °C, 400 MHz).

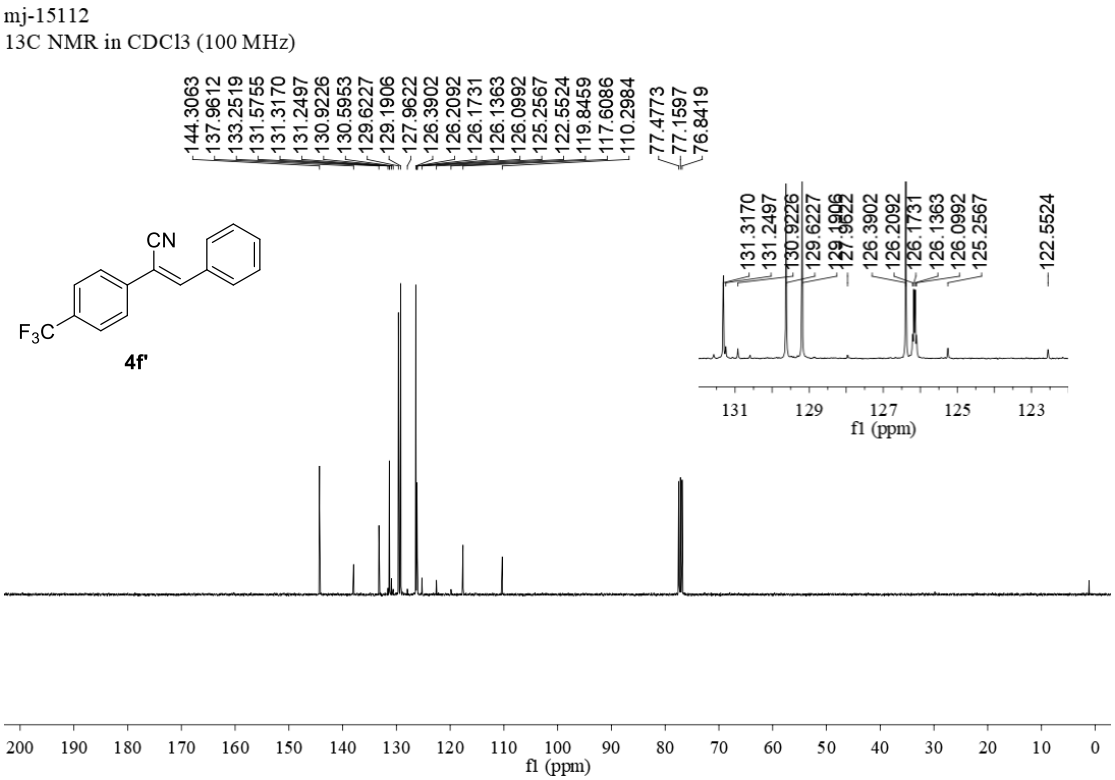


Figure S171. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4f'** ($CDCl_3$, 25 °C, 100 MHz).

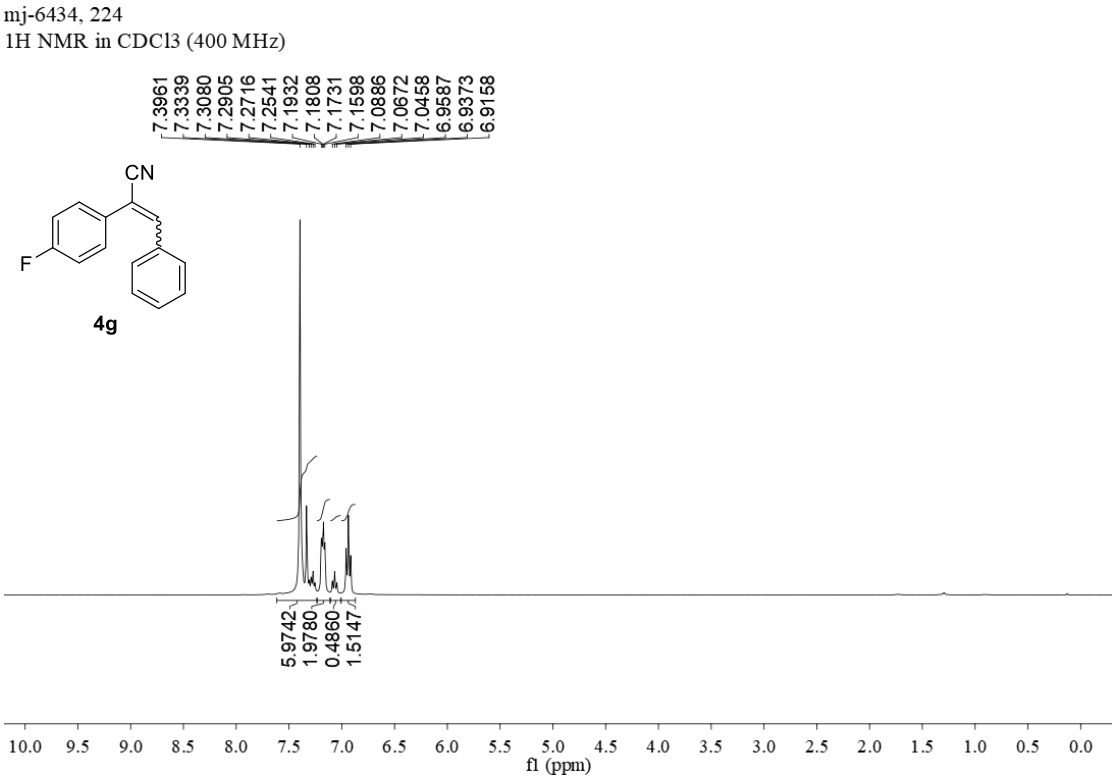


Figure S172. ^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 25 °C, 400 MHz).

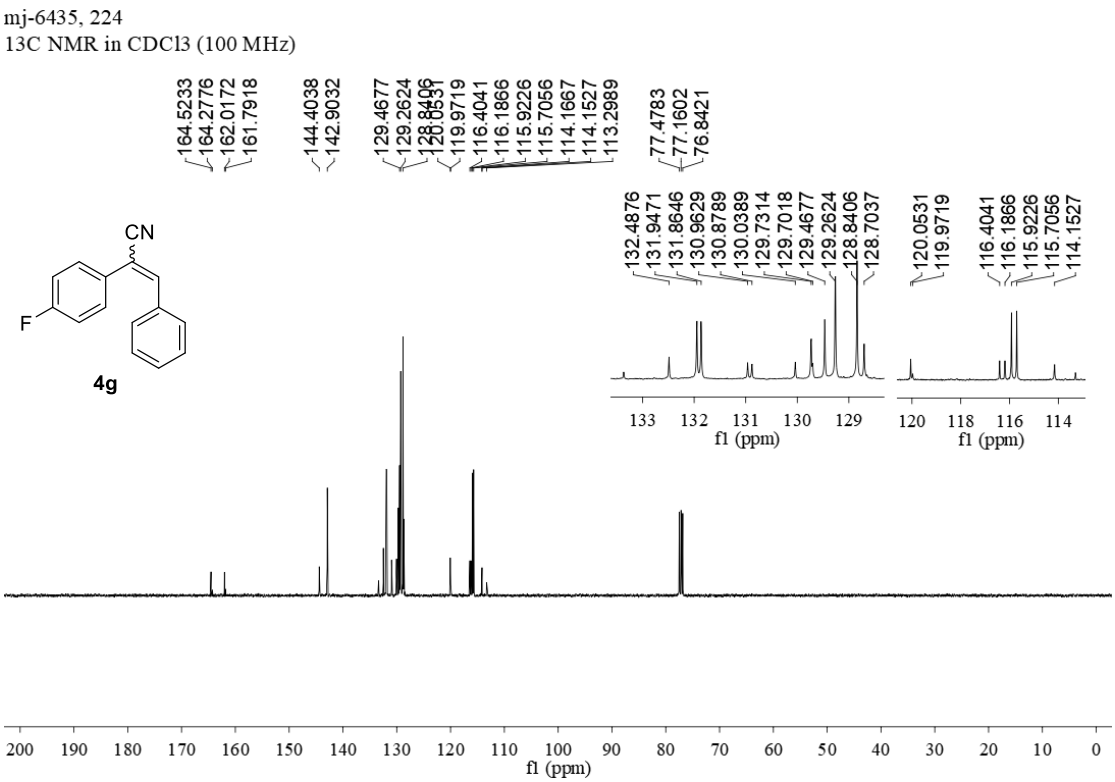


Figure S173. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4g** ($CDCl_3$, 25 °C, 100 MHz).

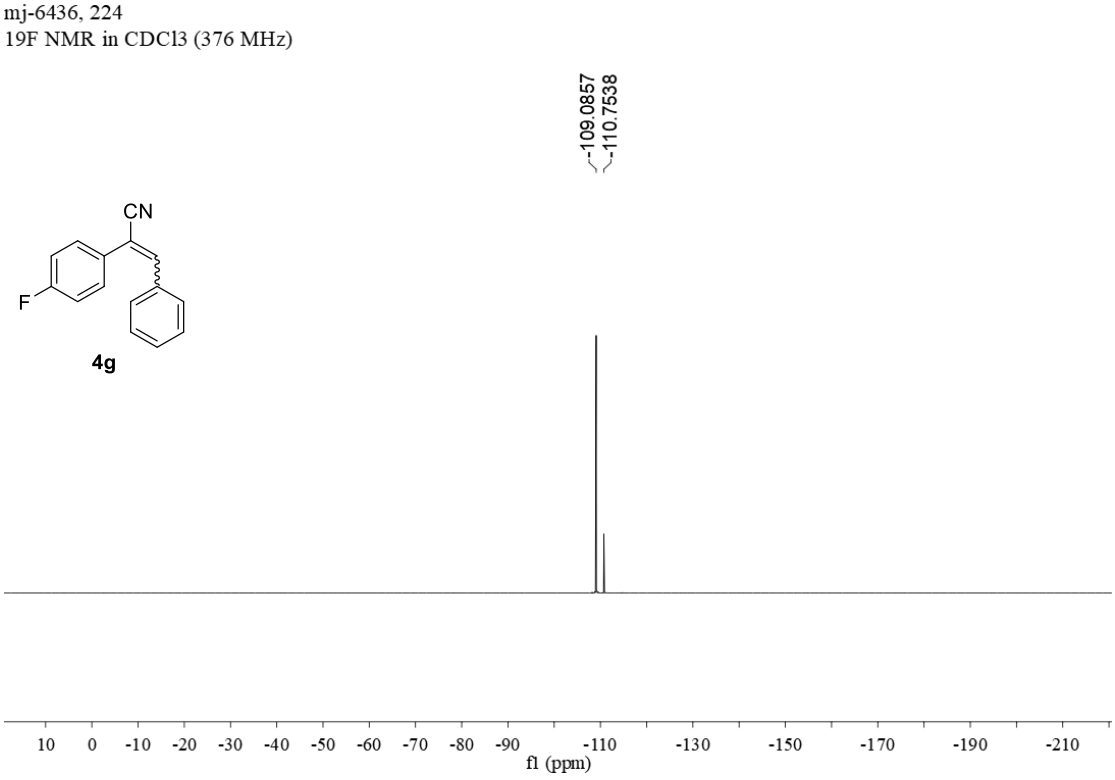


Figure S174. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4g** ($CDCl_3$, 25 °C, 376 MHz).

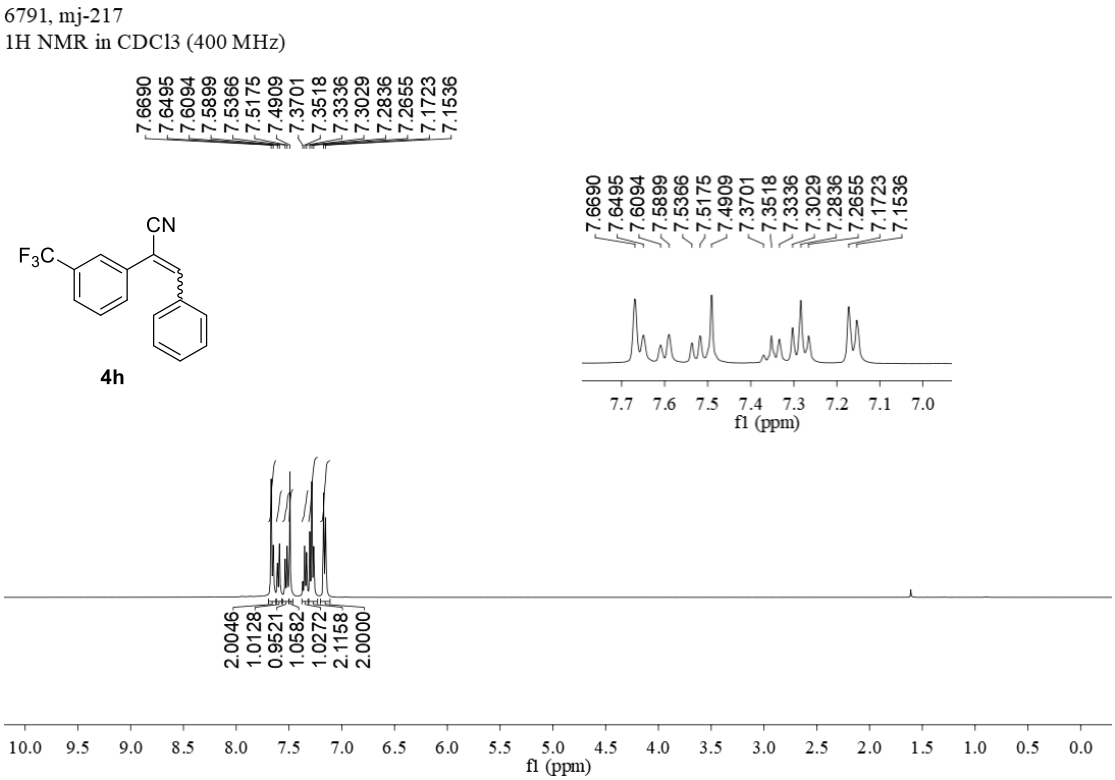


Figure S175. ^{1}H NMR spectrum of compound **4h** ($CDCl_3$, 25 °C, 400 MHz).

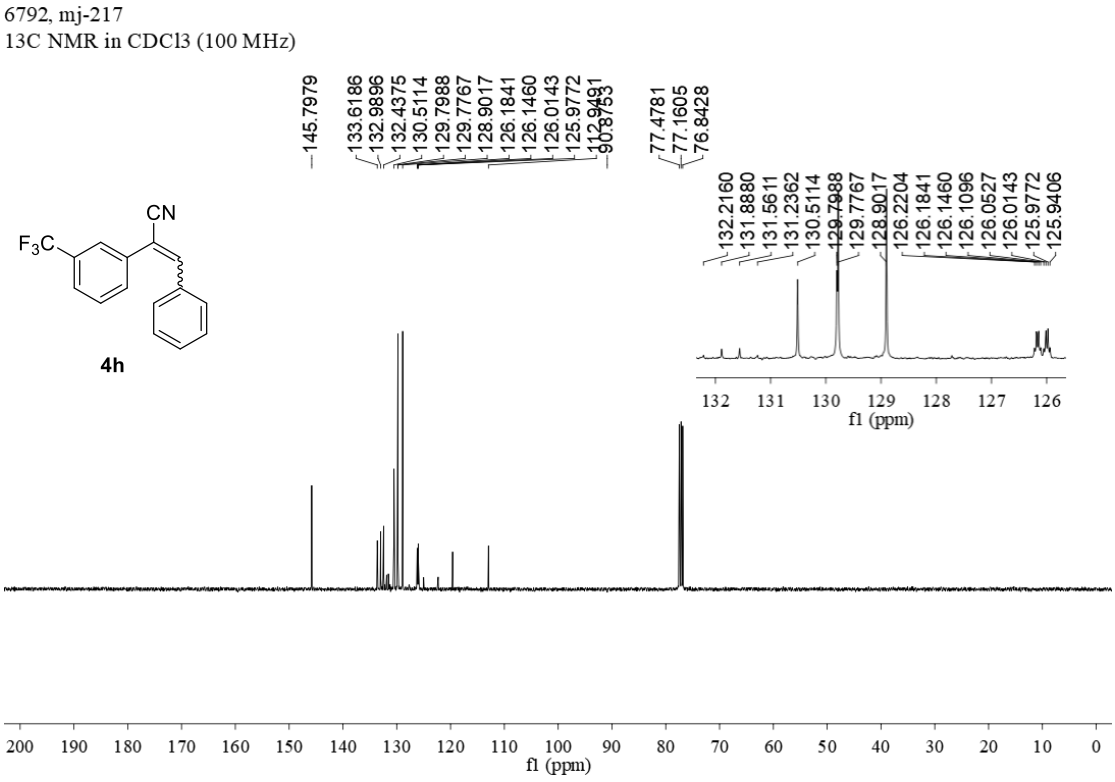


Figure S176. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4h** ($CDCl_3$, 25 °C, 100 MHz).

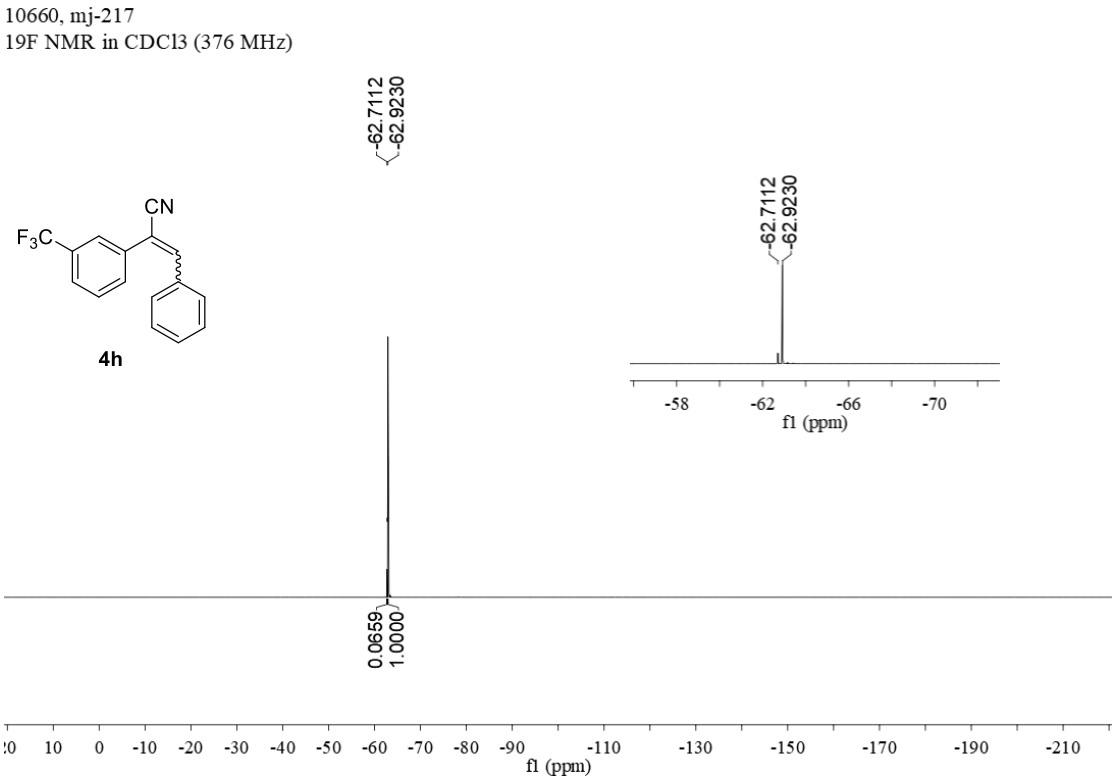


Figure S177. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4h** ($CDCl_3$, 25 °C, 376 MHz).

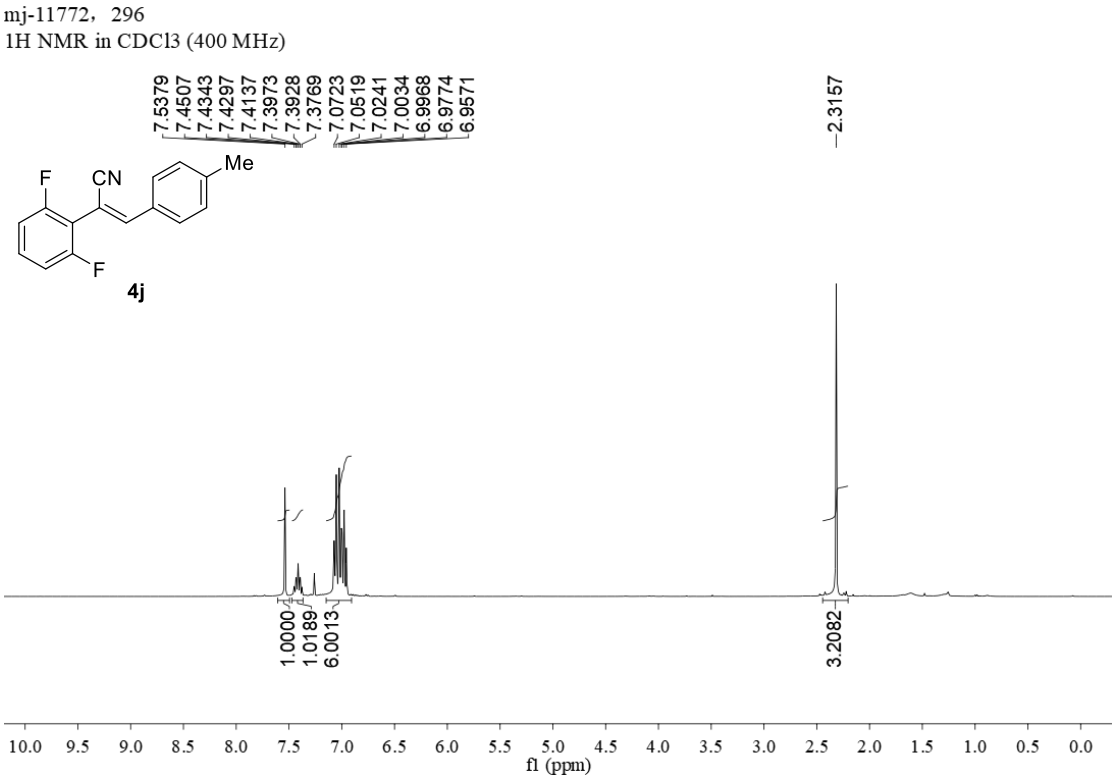


Figure S178. ^{1}H NMR spectrum of compound **4j** ($CDCl_3$, 25 °C, 400 MHz).

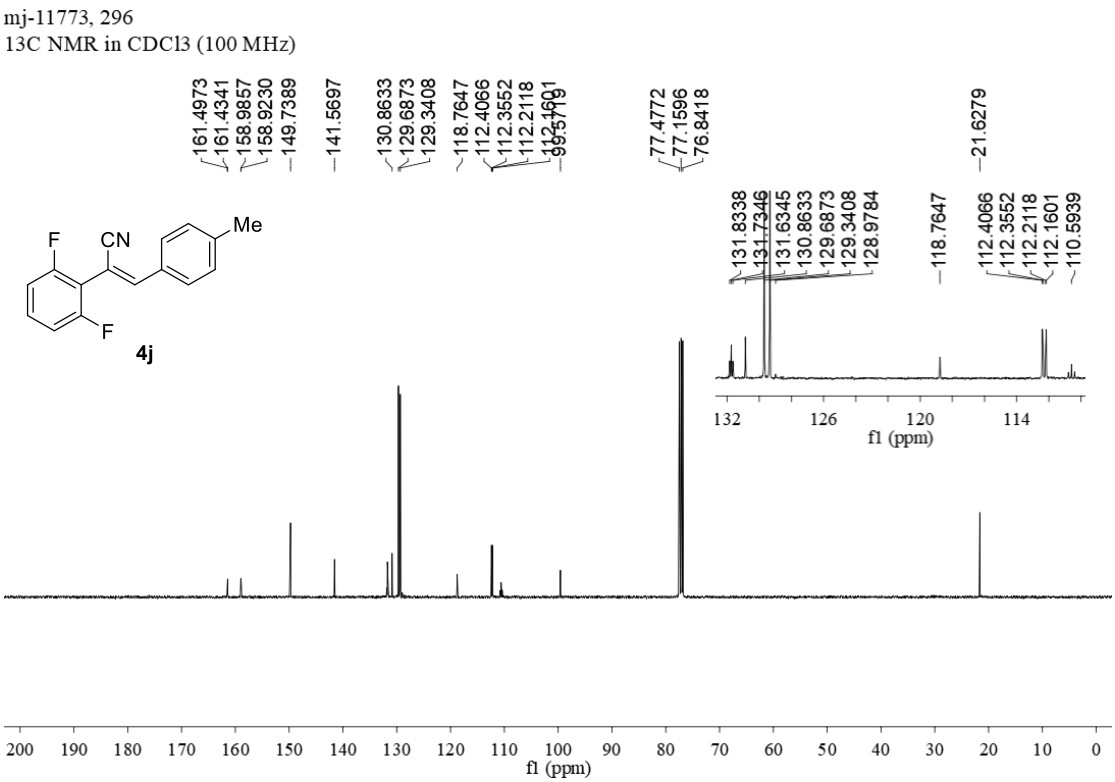


Figure S179. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4j** ($CDCl_3$, 25 °C, 100 MHz).

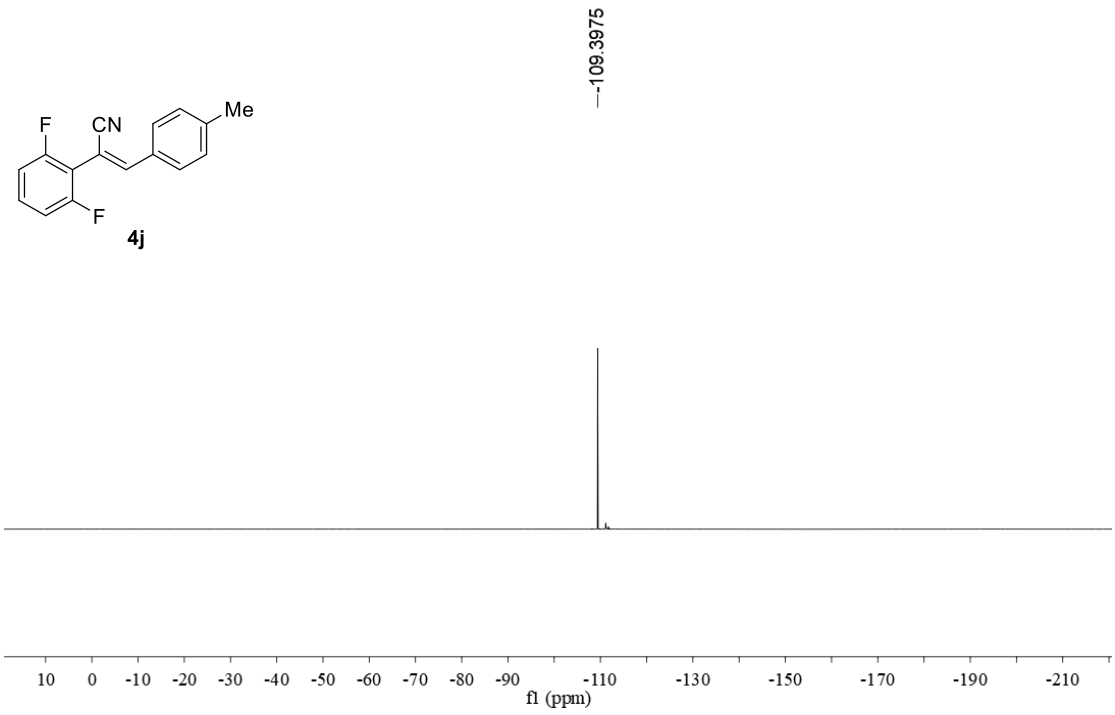


Figure S180. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4j** ($CDCl_3$, 25 °C, 376 MHz).

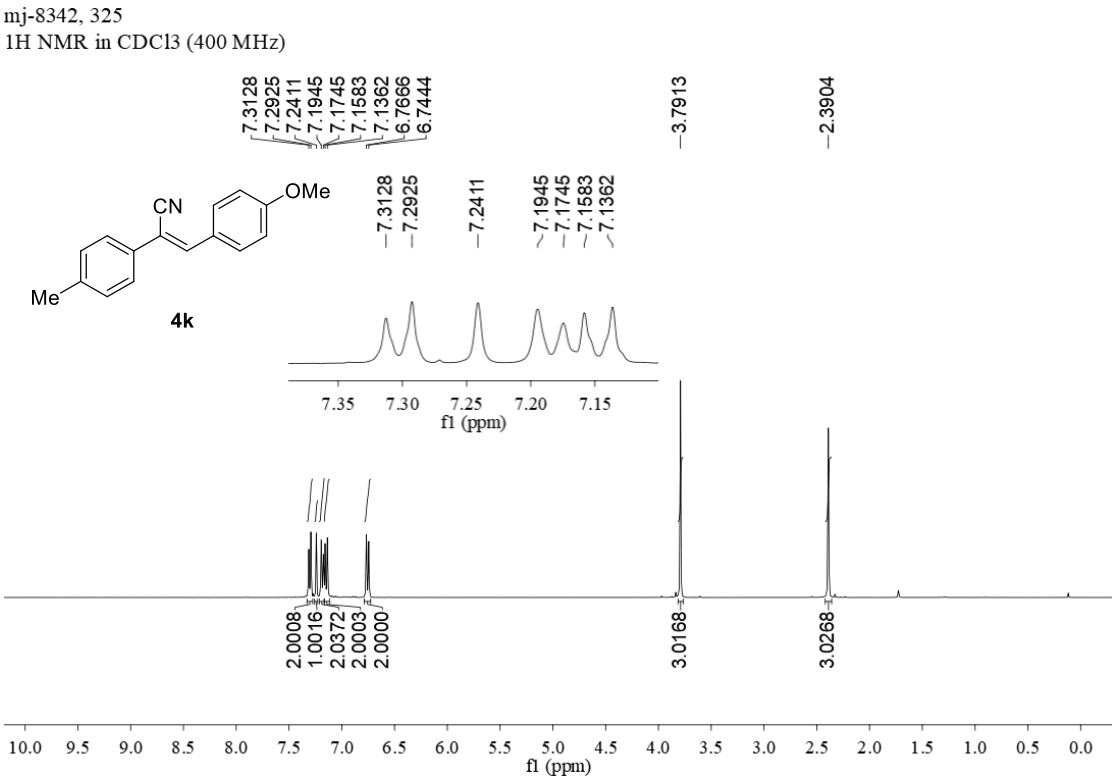


Figure S181. ^{1}H NMR spectrum of compound **4k** ($CDCl_3$, 25 °C, 400 MHz).

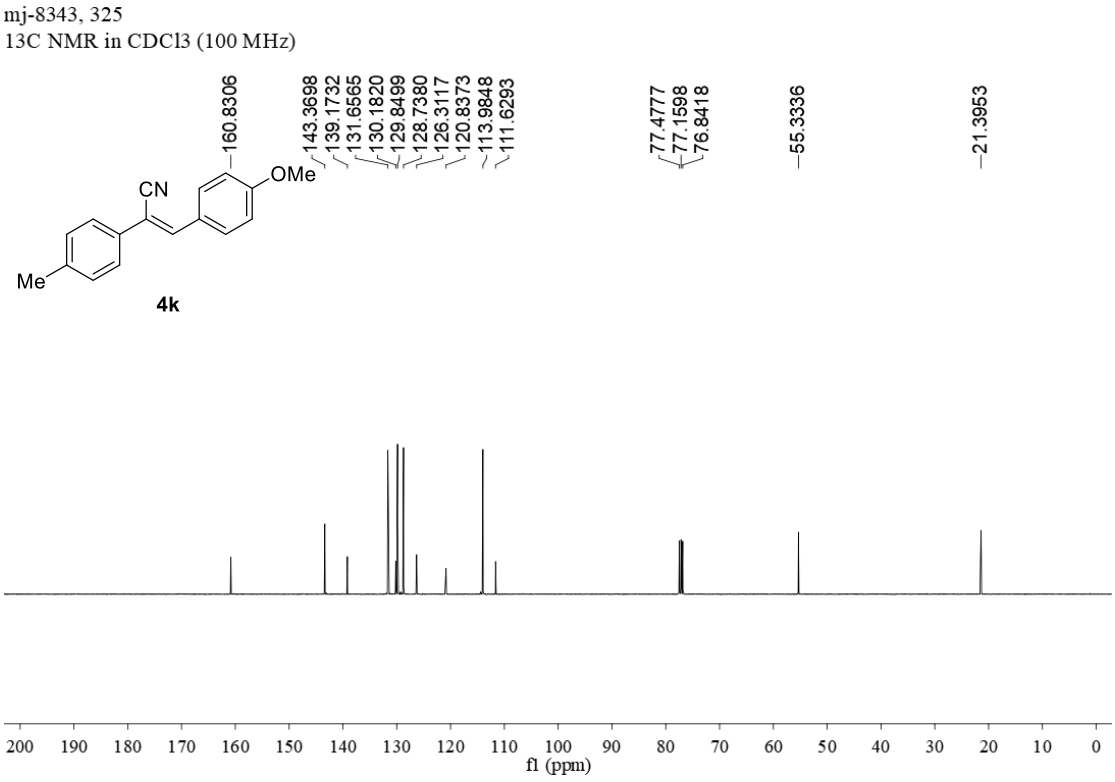


Figure S182. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4k** ($CDCl_3$, 25 °C, 100 MHz).

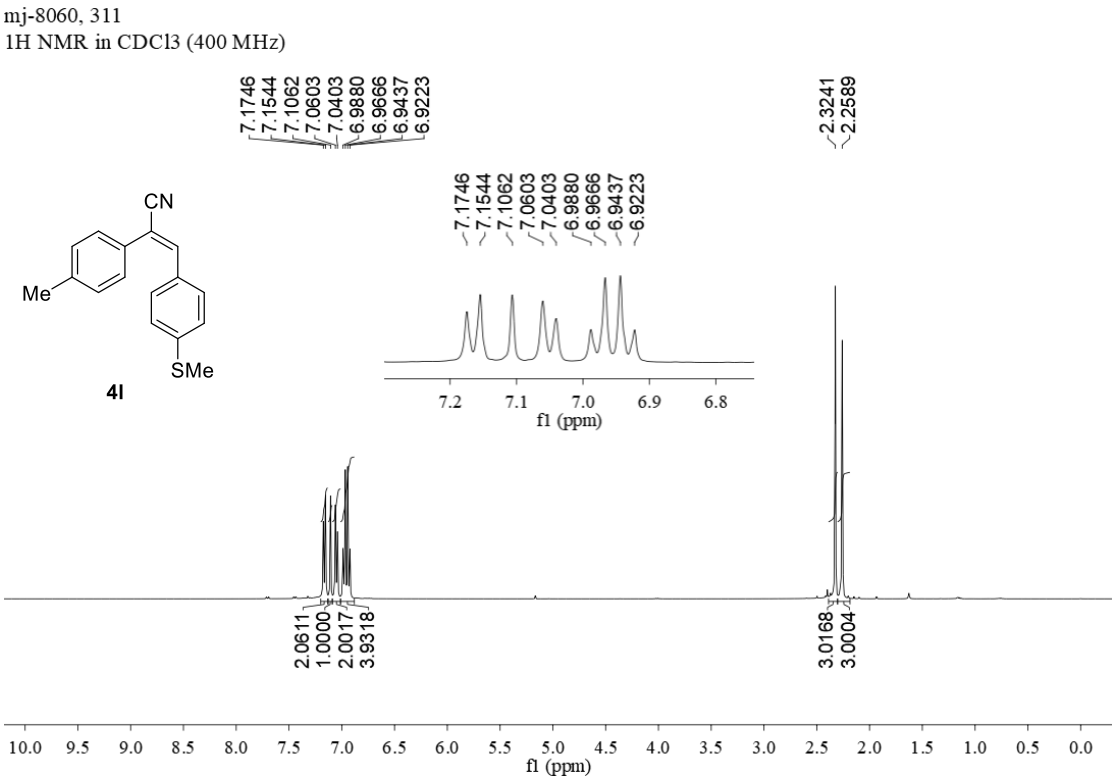


Figure S183. ^{1}H NMR spectrum of compound **4l** ($CDCl_3$, 25 °C, 400 MHz).

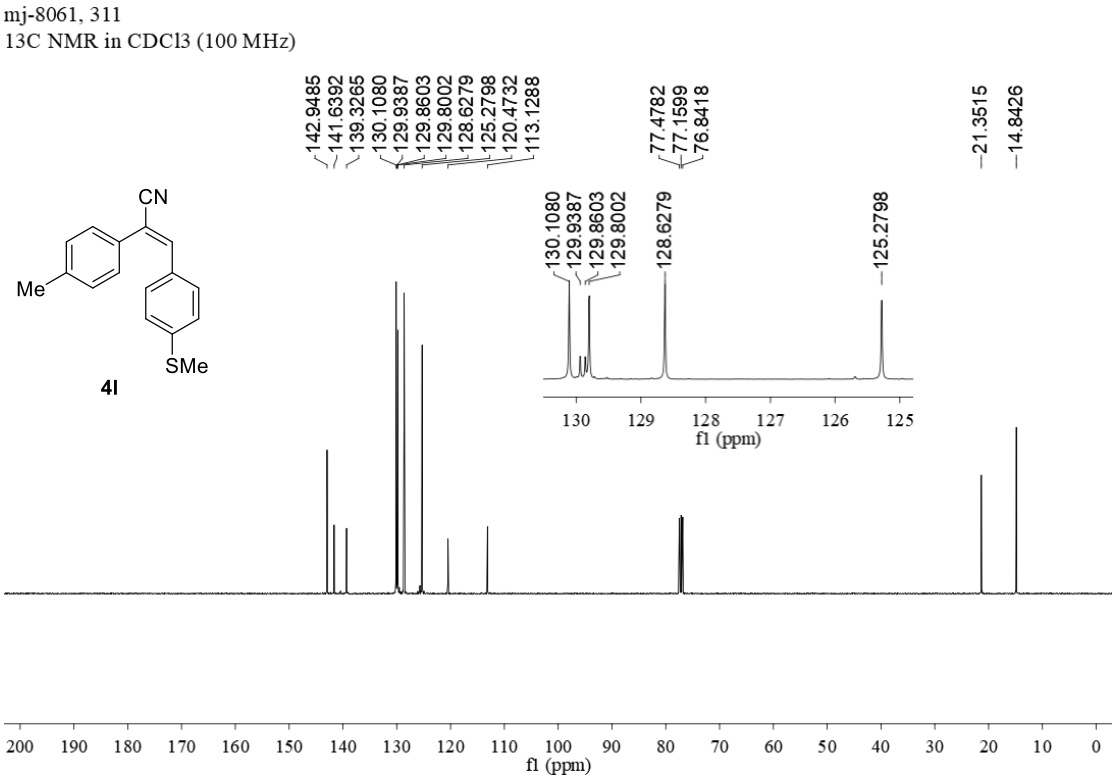


Figure S184. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4l** ($CDCl_3$, 25 °C, 100 MHz).

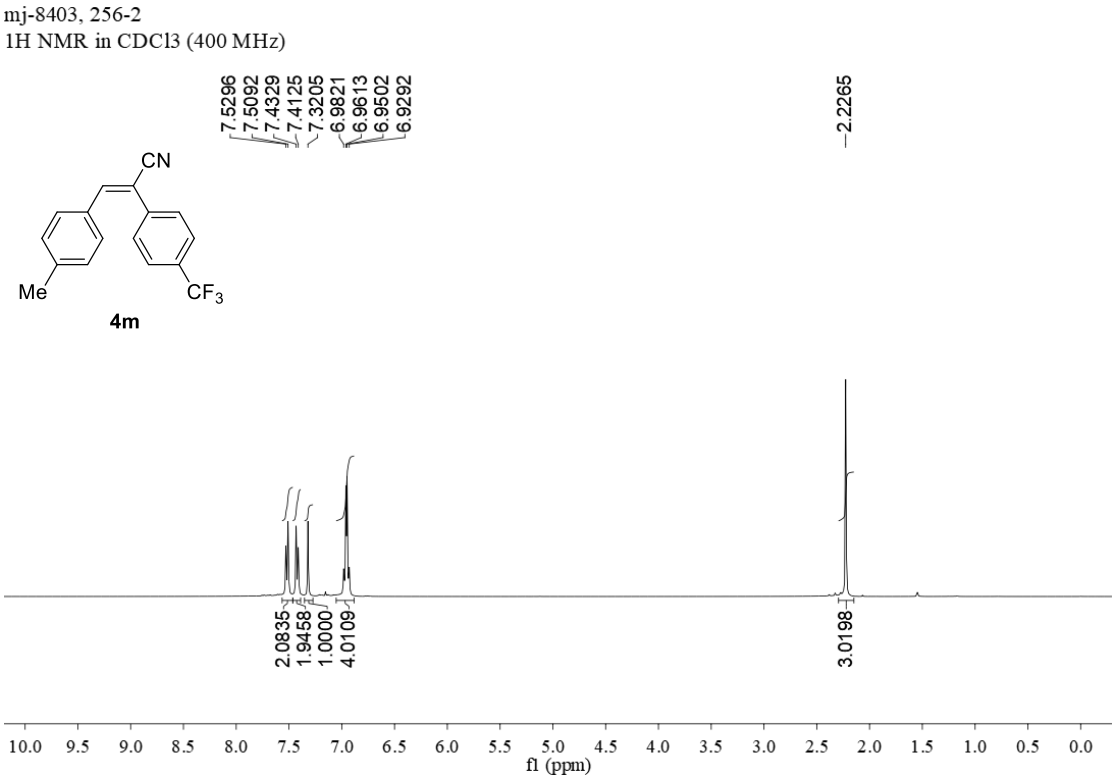


Figure S185. ^{1}H NMR spectrum of compound **4m** ($CDCl_3$, 25 °C, 400 MHz).

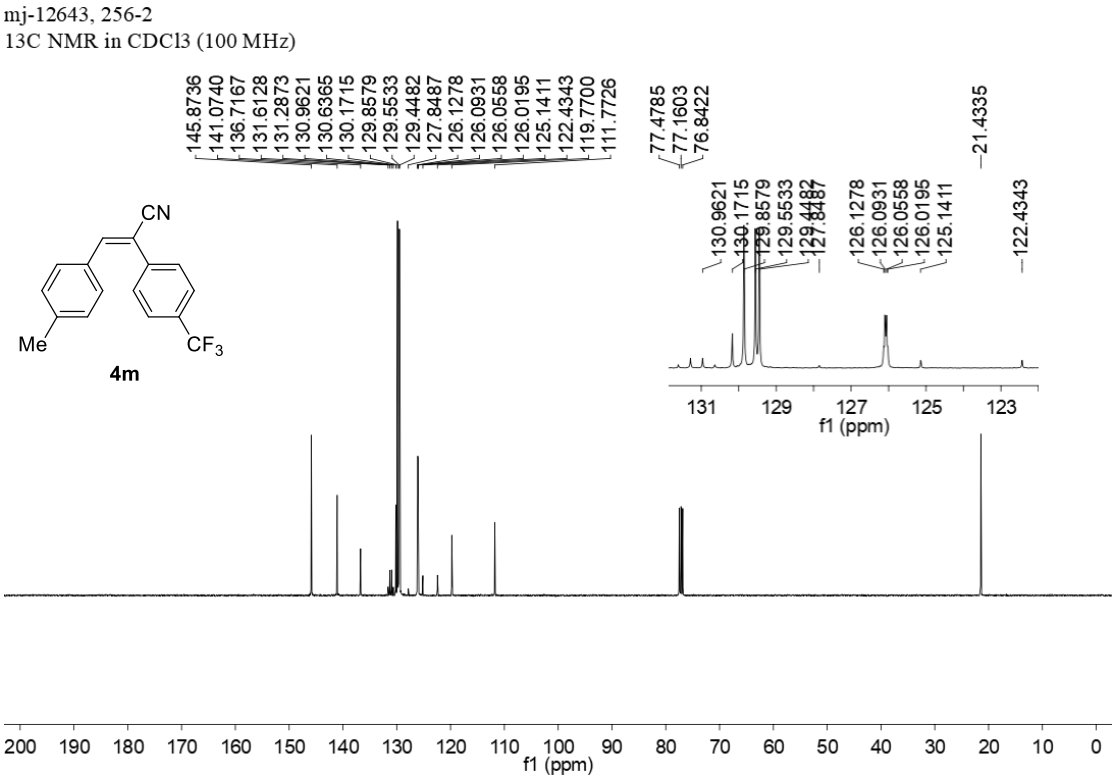


Figure S186. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4m** ($CDCl_3$, 25 °C, 100 MHz).

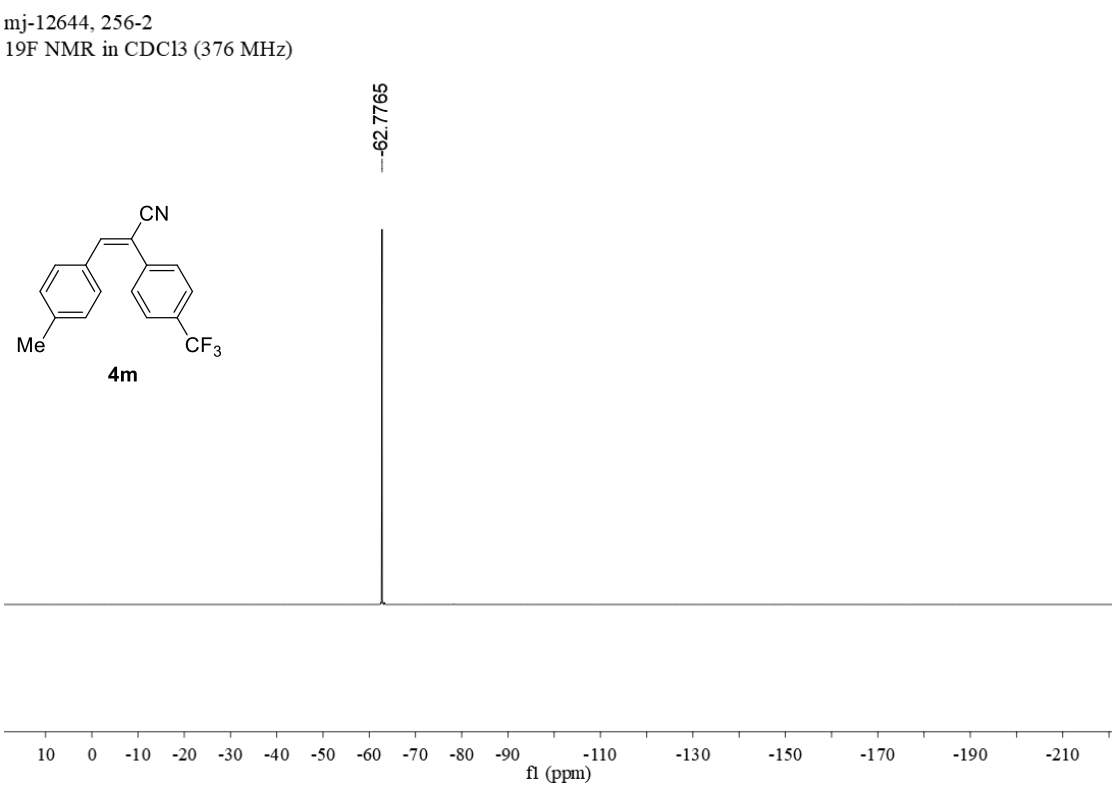


Figure S187. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4m** ($CDCl_3$, 25 °C, 376 MHz).

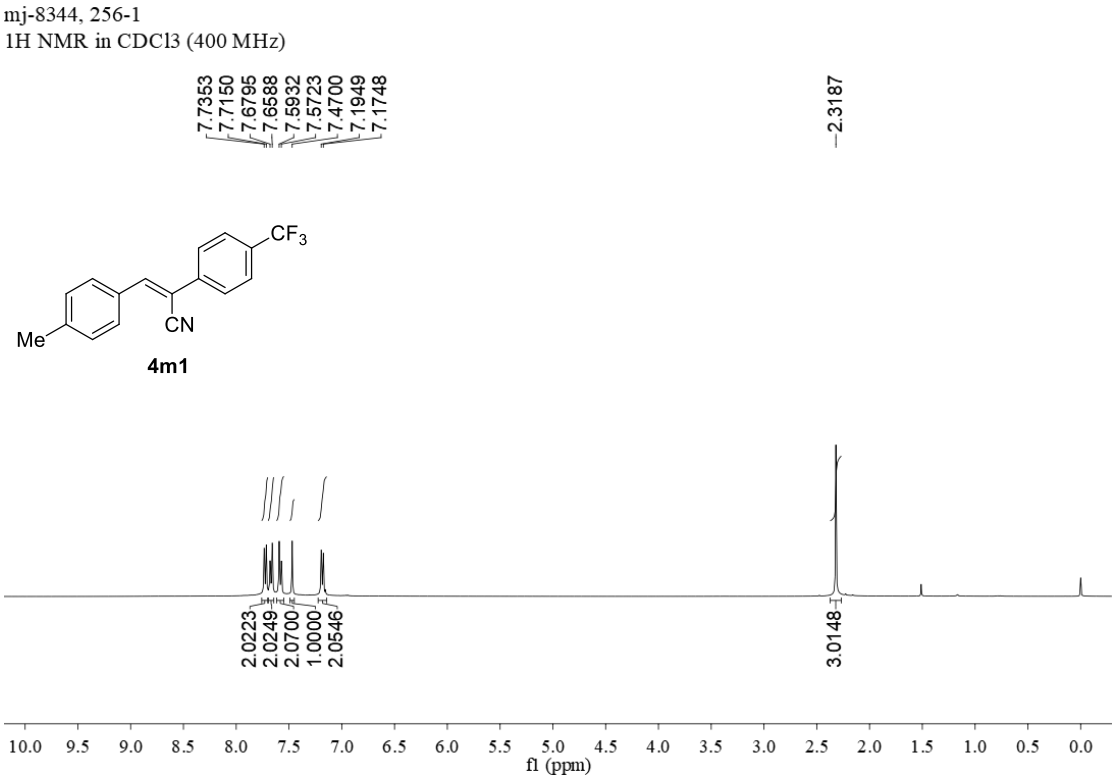


Figure S188. ^{1}H NMR spectrum of compound **4m1** ($CDCl_3$, 25 °C, 400 MHz).

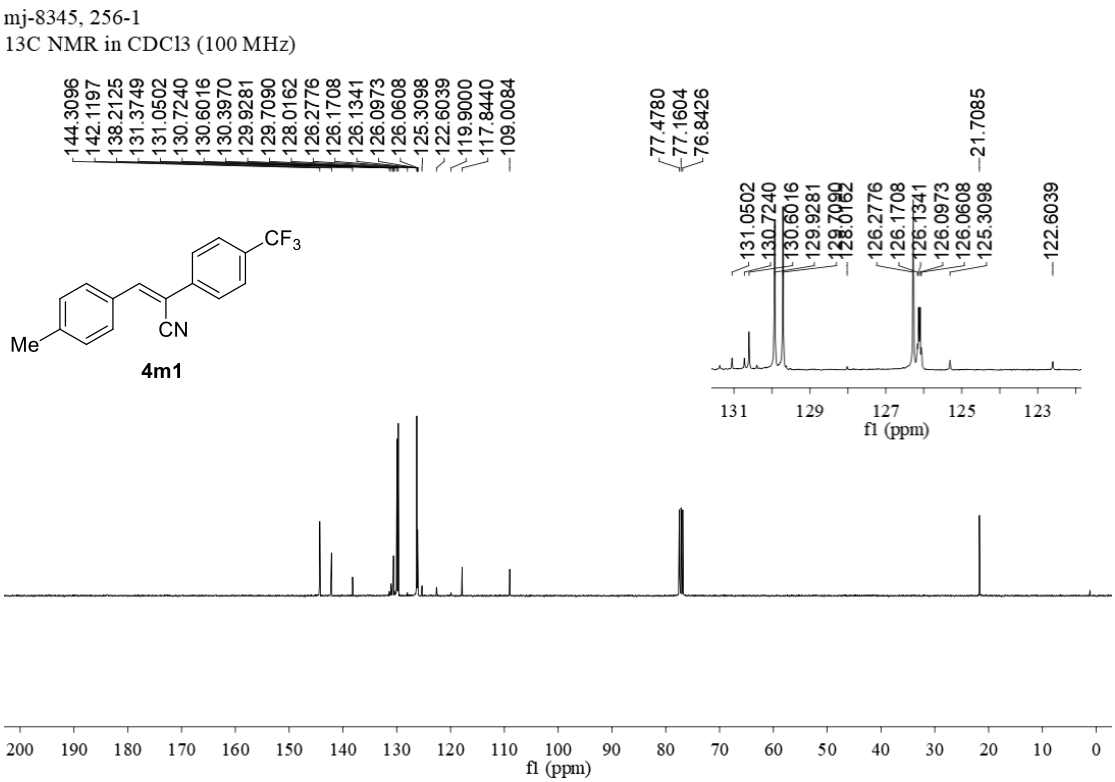


Figure S189. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4m1** ($CDCl_3$, 25 °C, 100 MHz).

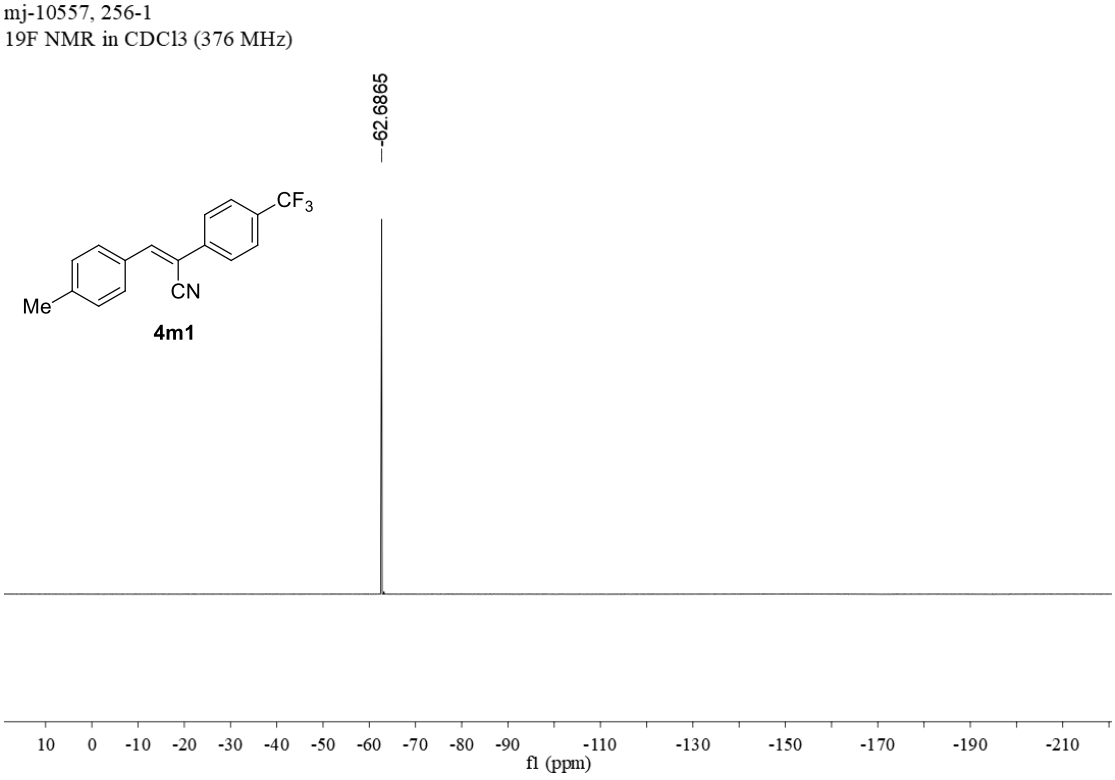


Figure S190. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4m1** ($CDCl_3$, 25 °C, 376 MHz).

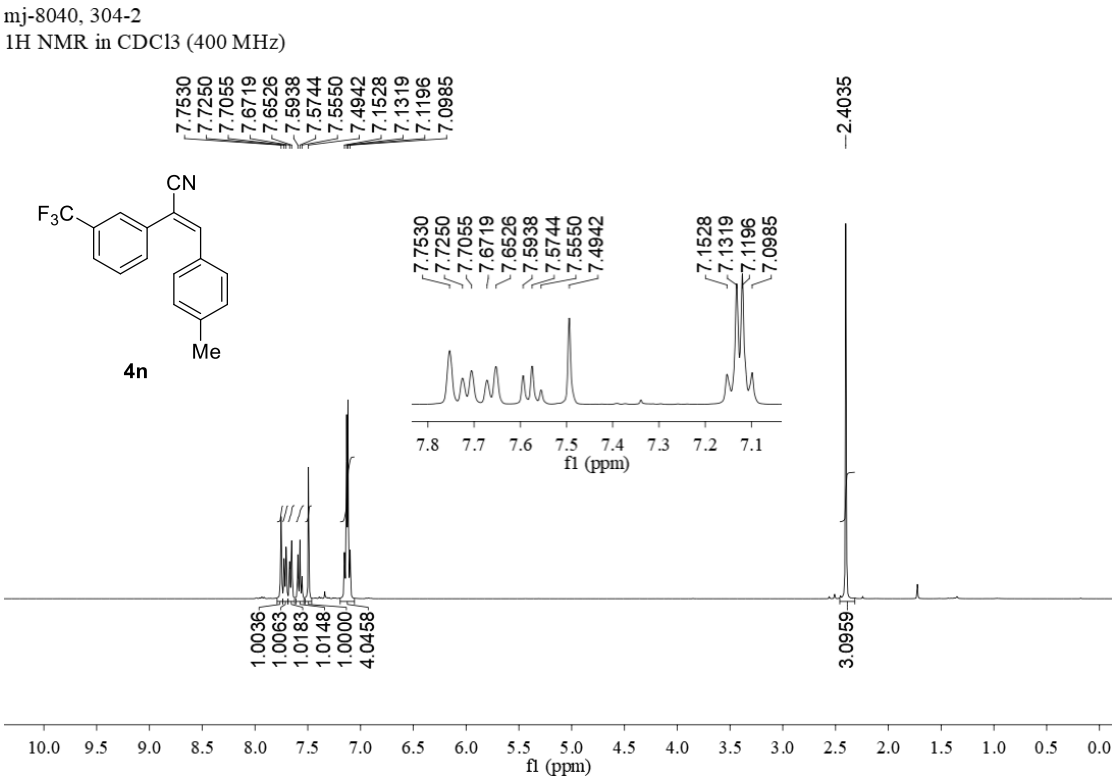


Figure S191. ^{1}H NMR spectrum of compound **4n** ($CDCl_3$, 25 °C, 400 MHz).

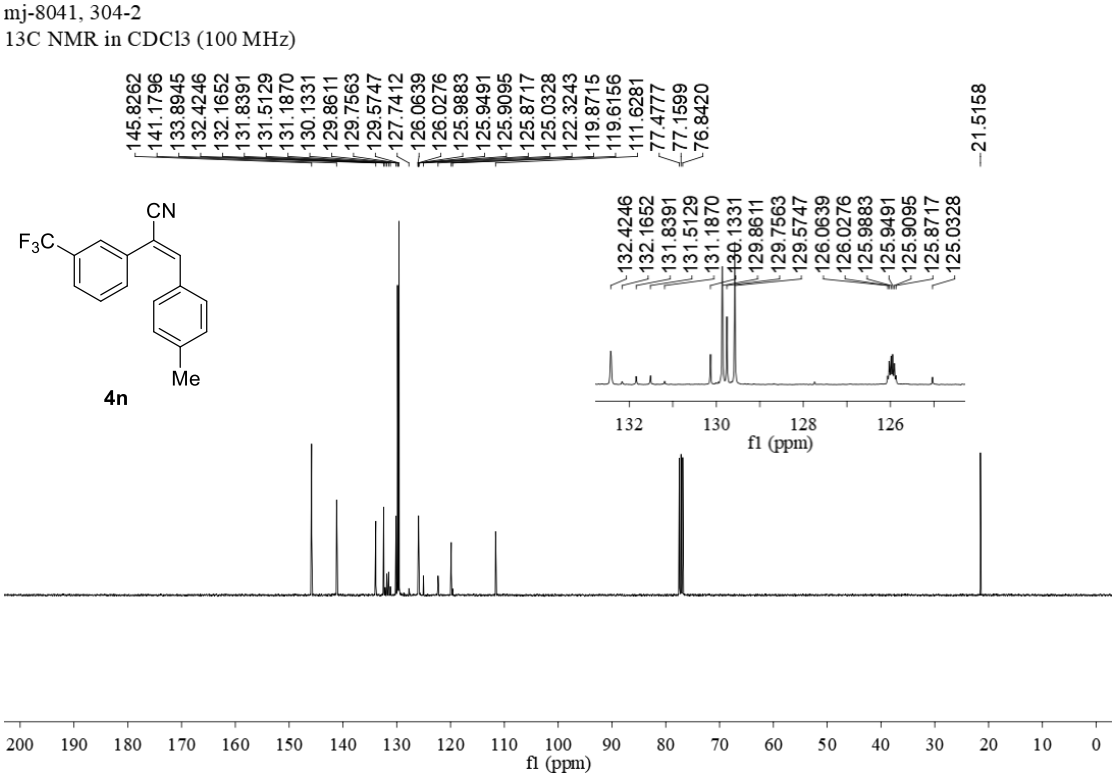


Figure S192. ^{13}C{^{1}H} NMR spectrum of compound **4n** ($CDCl_3$, 25 °C, 100 MHz).

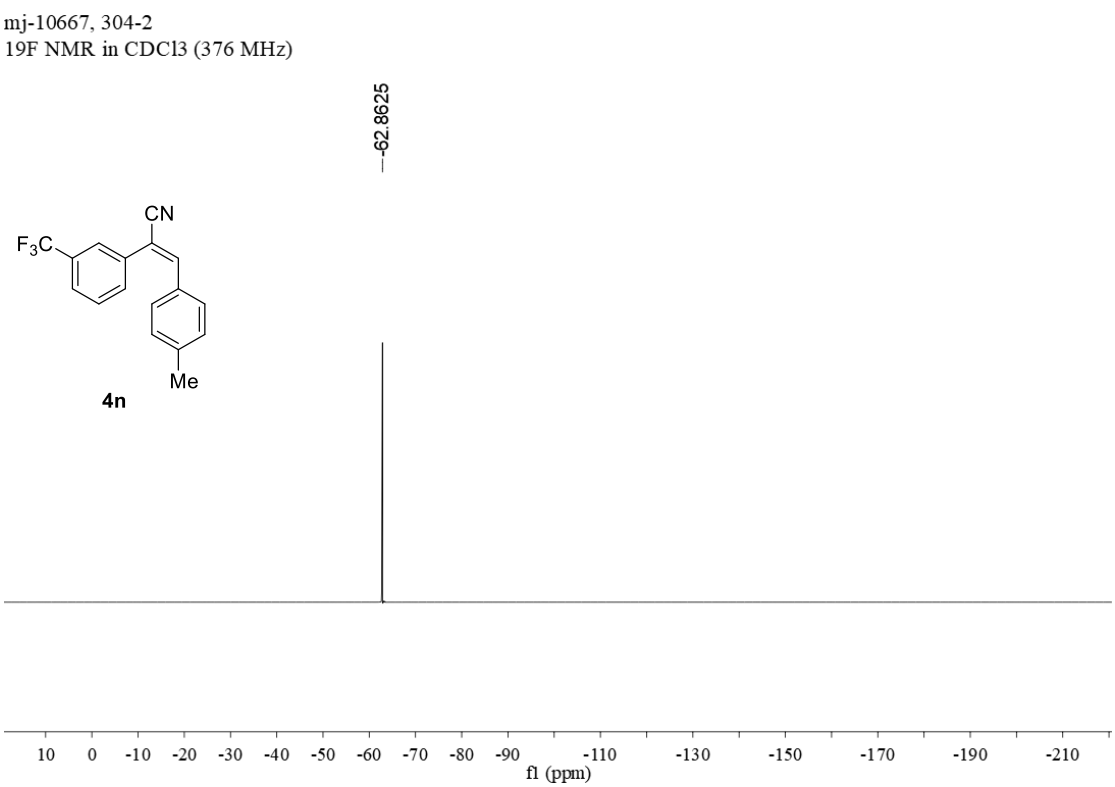


Figure S193. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4n** ($CDCl_3$, 25 °C, 376 MHz).

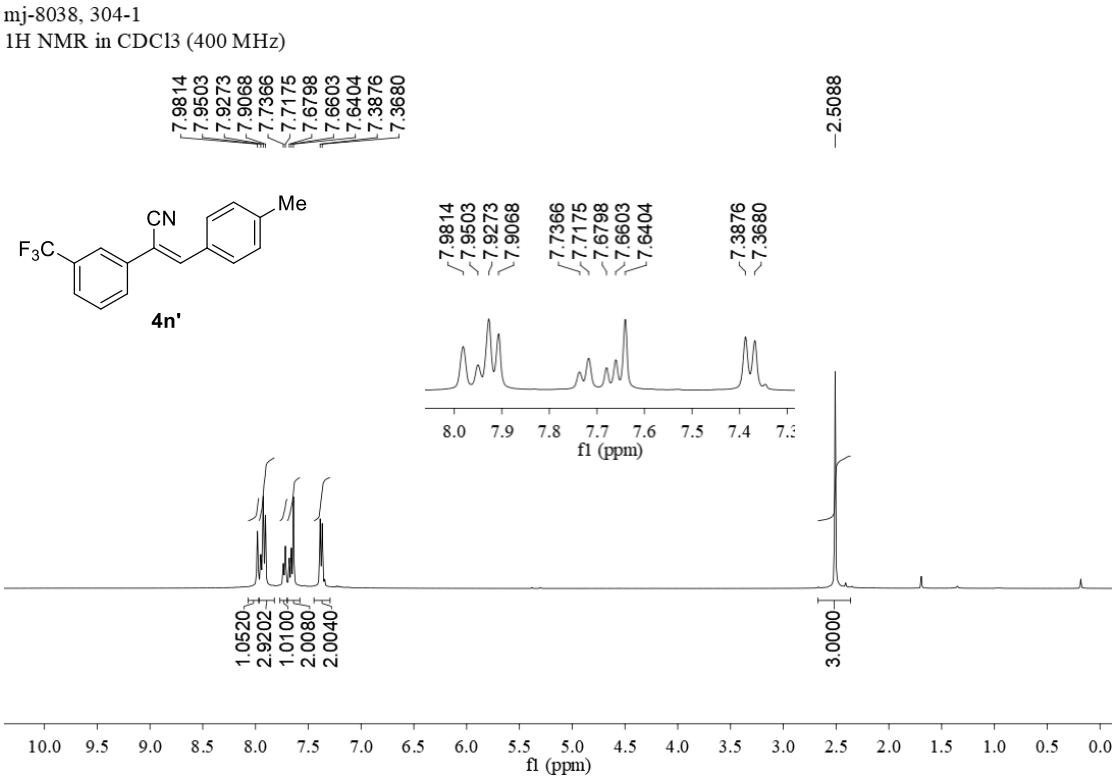


Figure S194. ^{1}H NMR spectrum of compound **4n'** ($CDCl_3$, 25 °C, 400 MHz).

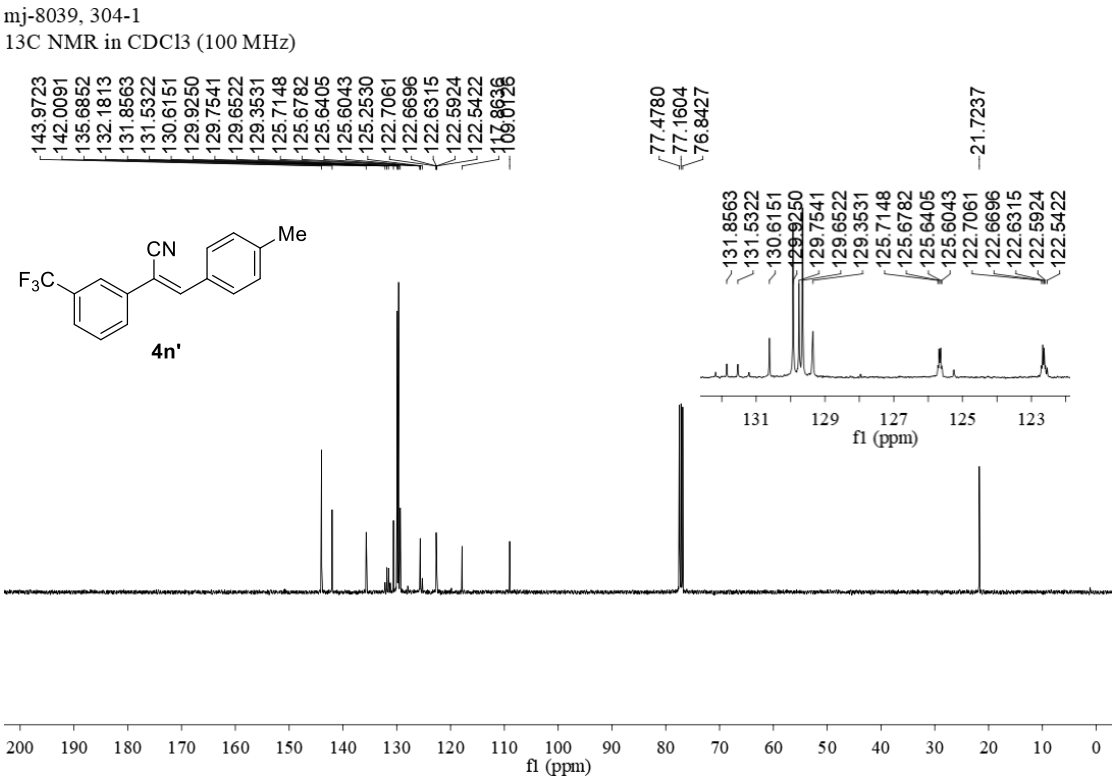


Figure S195. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4n'** ($CDCl_3$, 25 °C, 100 MHz).

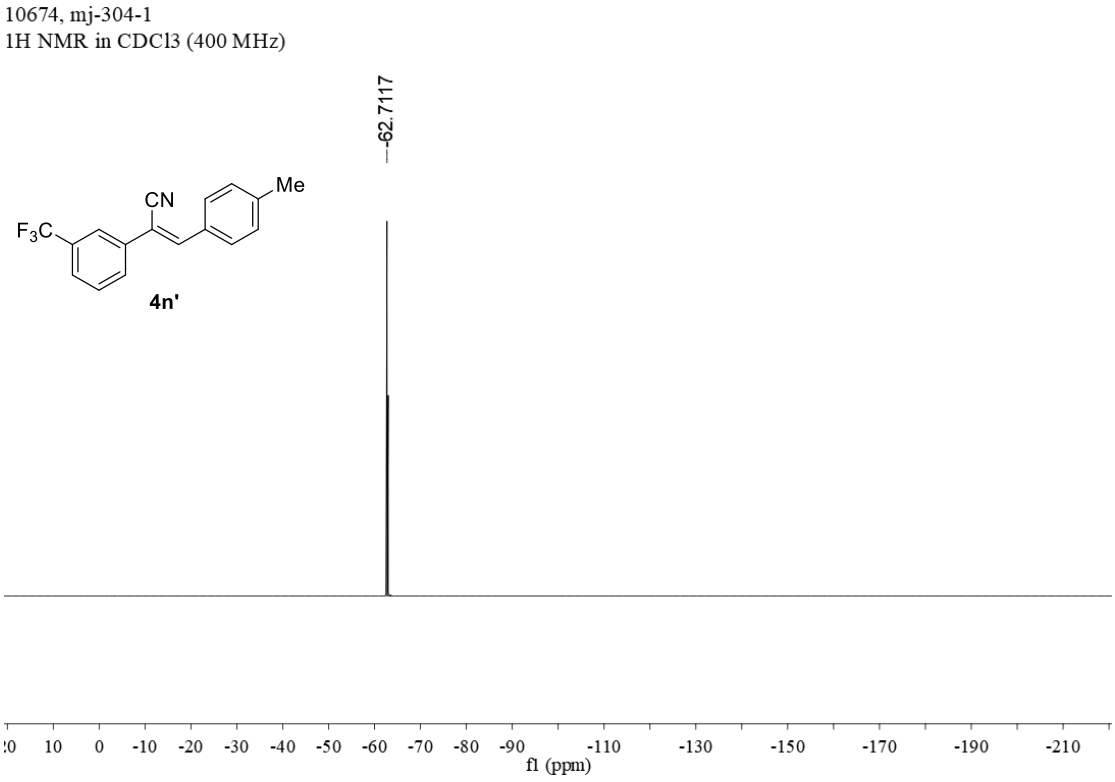


Figure S196. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4n'** ($CDCl_3$, 25 °C, 376 MHz).

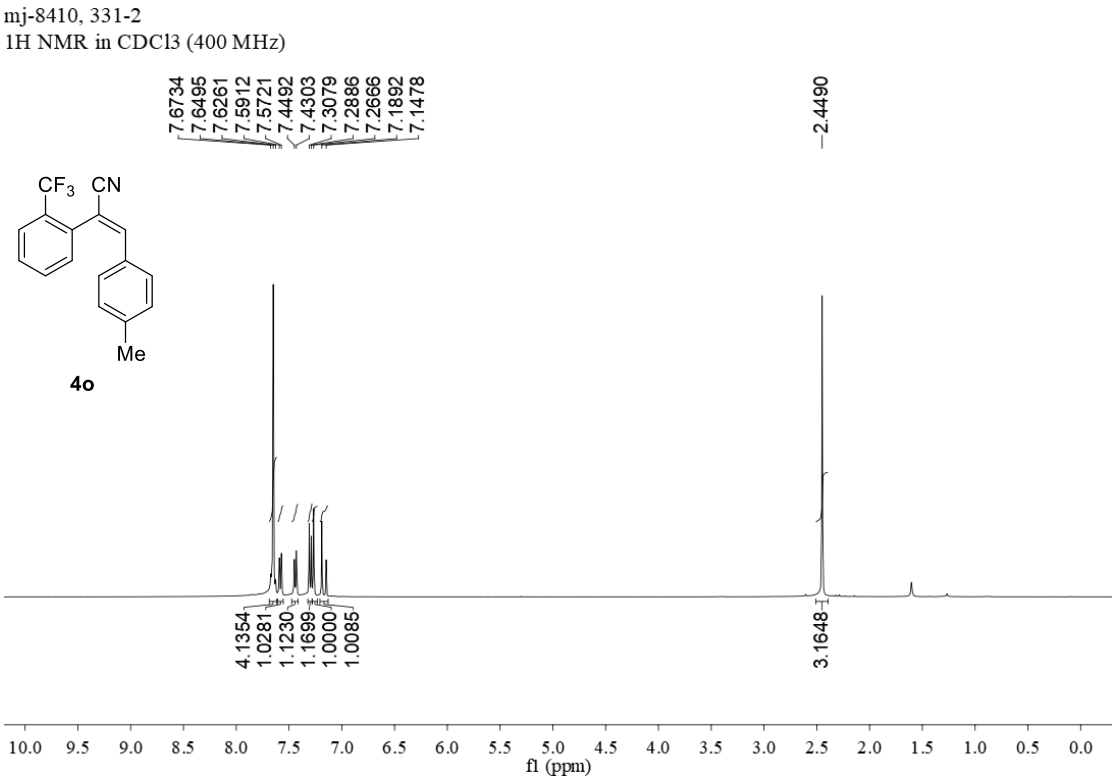


Figure S197. ^{1}H NMR spectrum of compound **4o** ($CDCl_3$, 25 °C, 400 MHz).

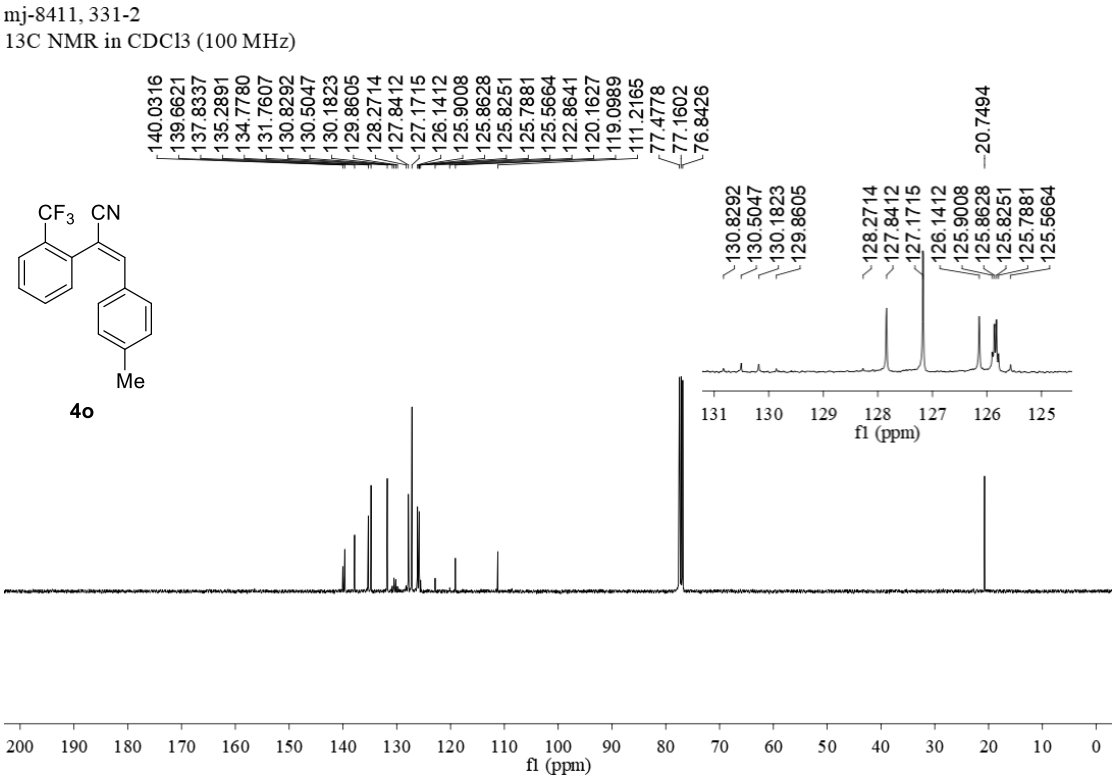


Figure S198. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4o** ($CDCl_3$, 25 °C, 100 MHz).

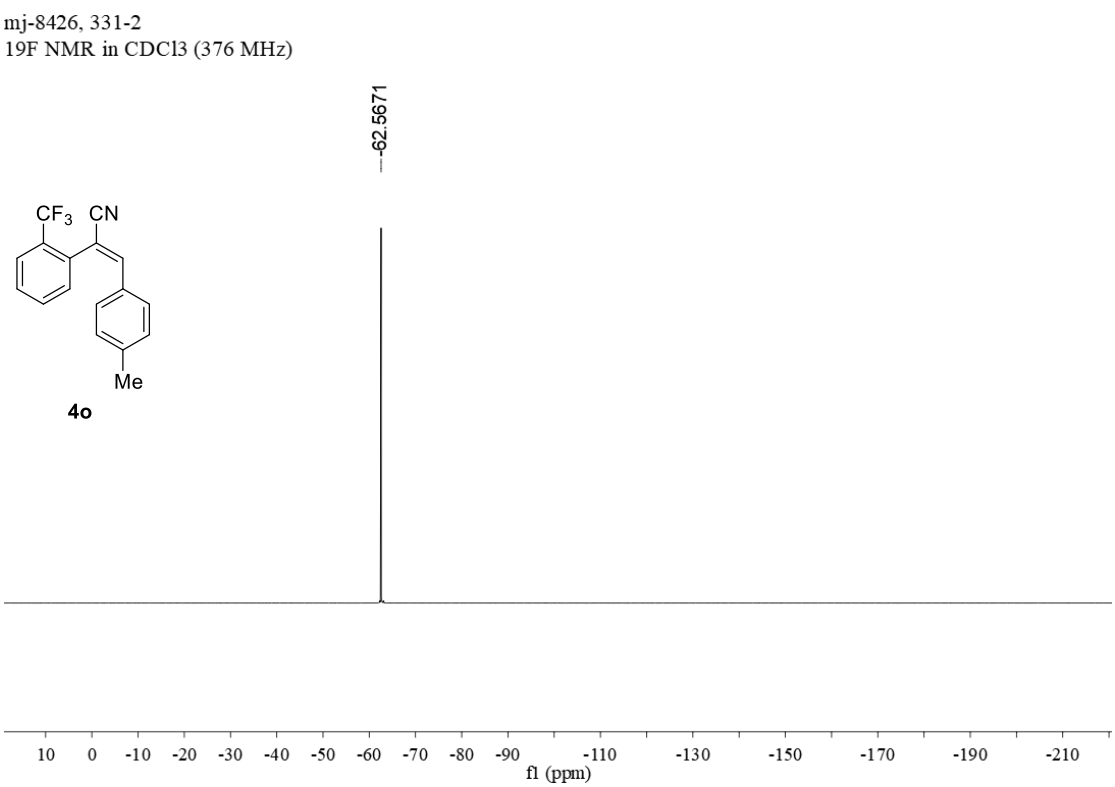


Figure S199. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4o** ($CDCl_3$, 25 °C, 376 MHz).

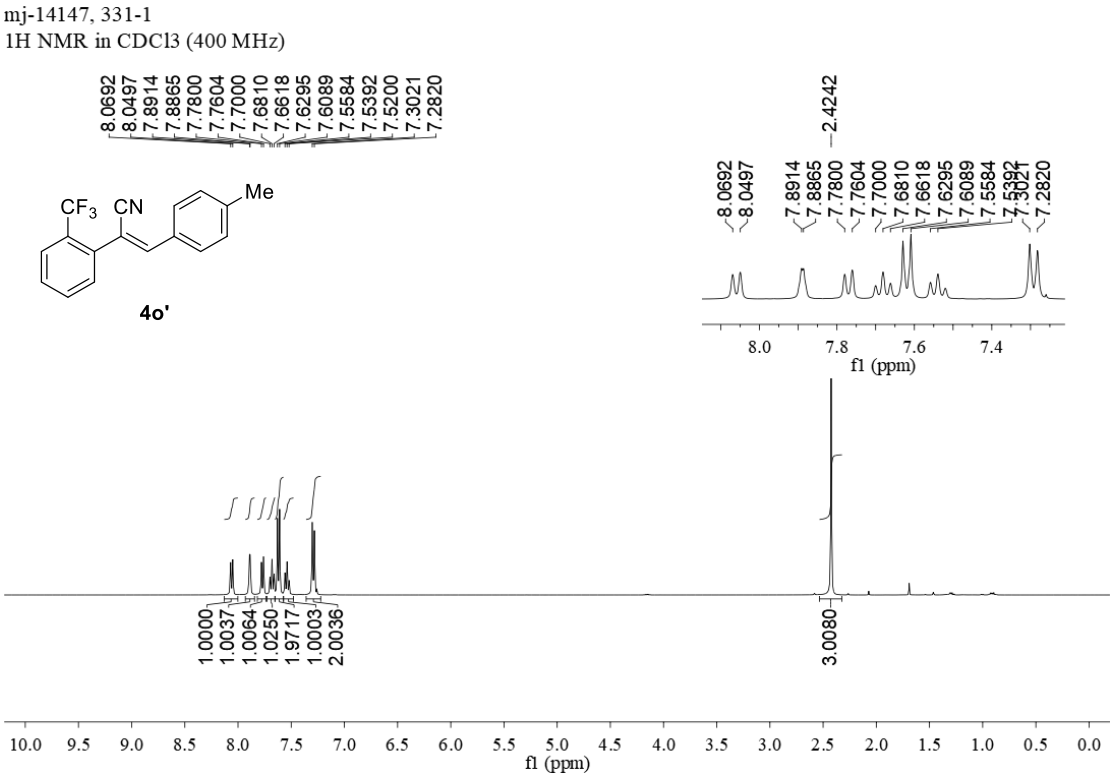


Figure S200. ^{1}H NMR spectrum of compound **4o'** ($CDCl_3$, 25 °C, 400 MHz).

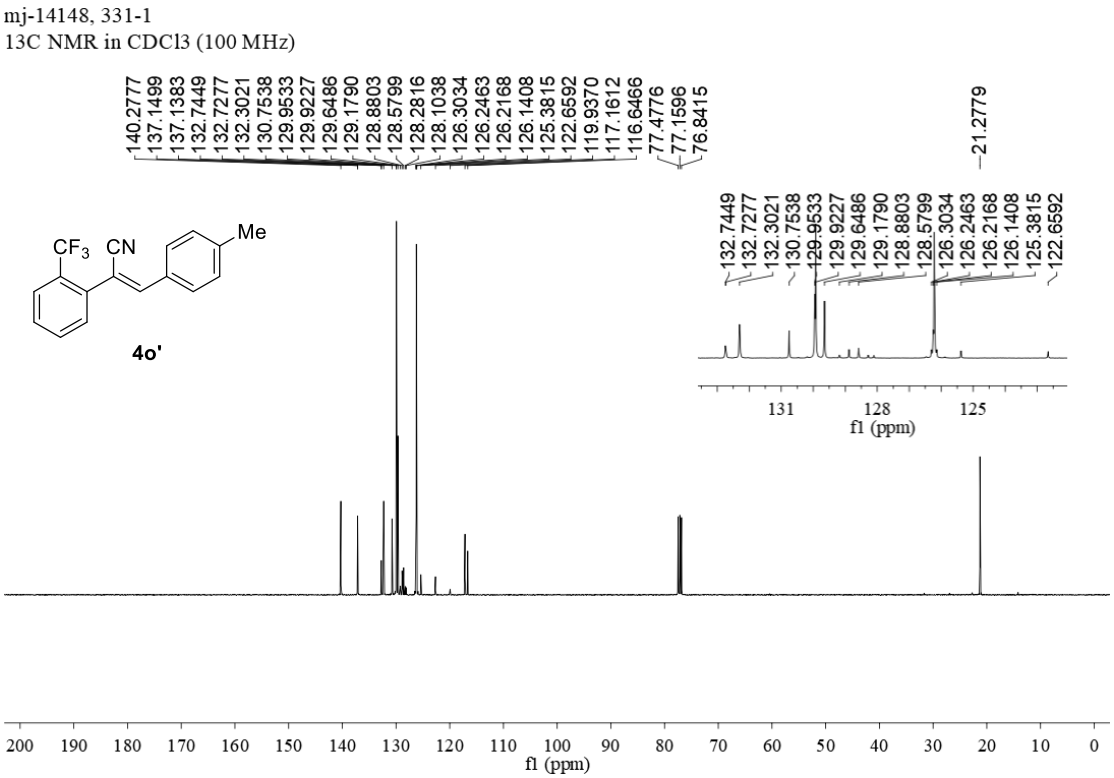


Figure S201. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4o'** ($CDCl_3$, 25 °C, 100 MHz).

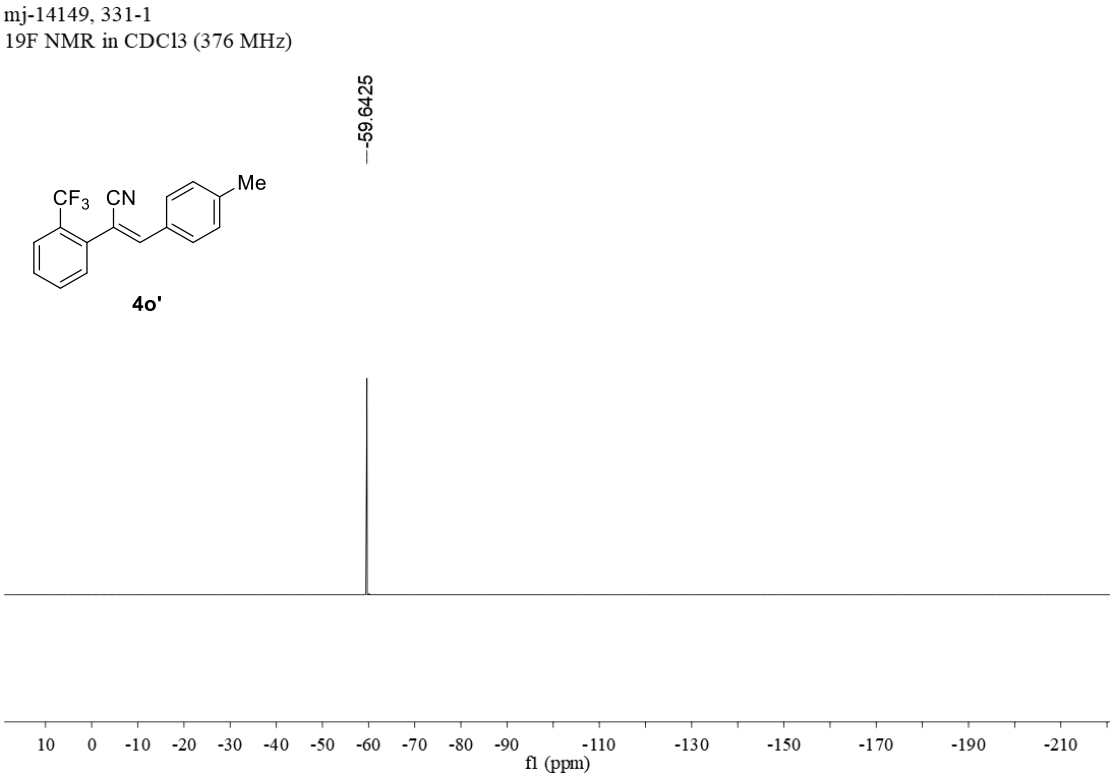


Figure S202. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4o'** ($CDCl_3$, 25 °C, 376 MHz).

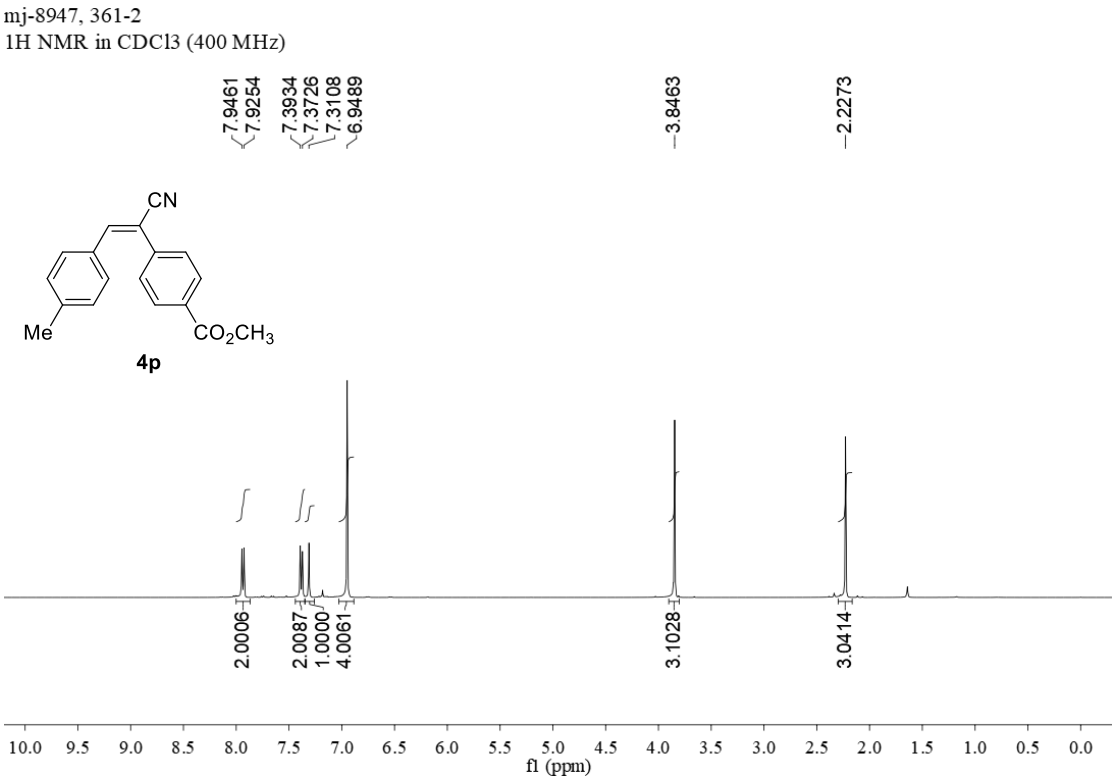


Figure S203. ^{1}H NMR spectrum of compound **4p** ($CDCl_3$, 25 °C, 400 MHz).

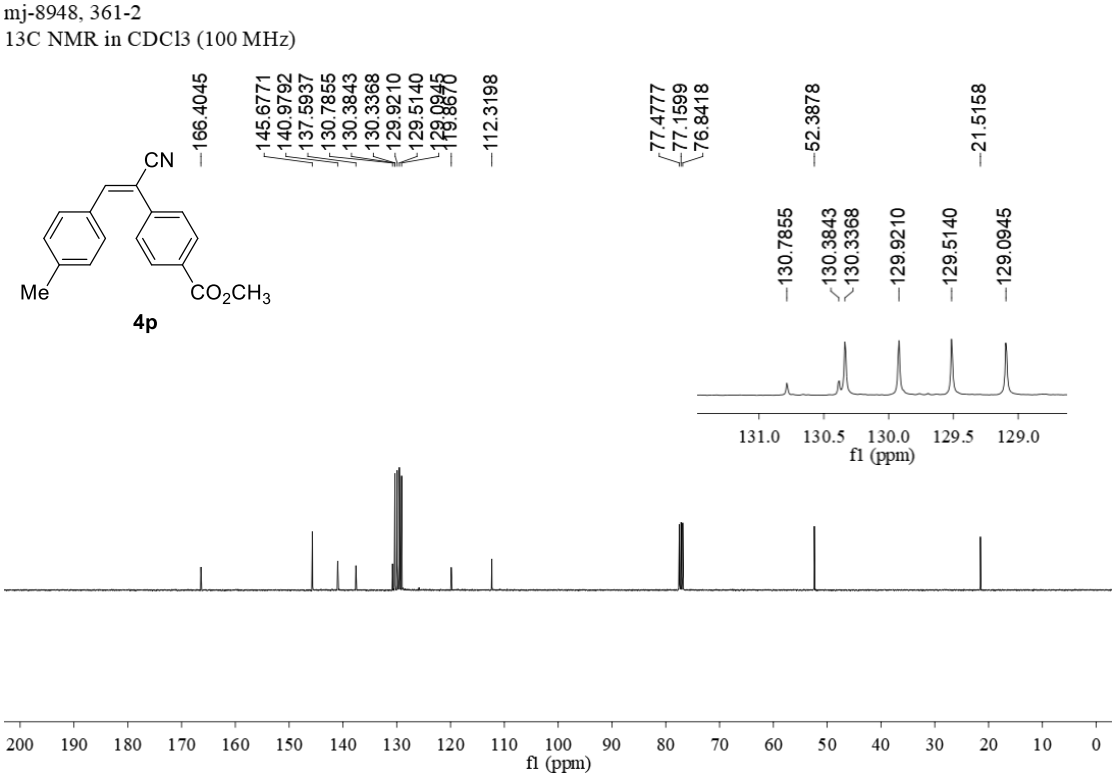


Figure S204. ^{13}C{^{1}H} NMR spectrum of compound **4p** ($CDCl_3$, 25 °C, 100 MHz).

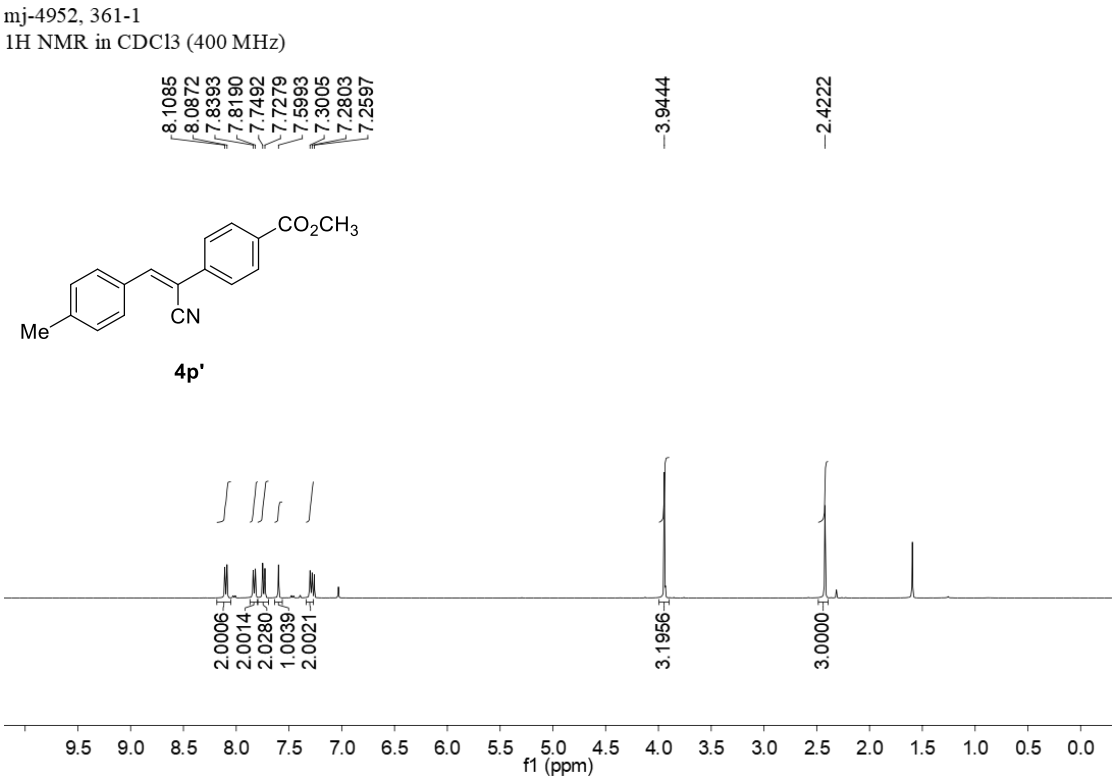


Figure S205. ^{1}H NMR spectrum of compound **4p'** ($CDCl_3$, 25 °C, 400 MHz).

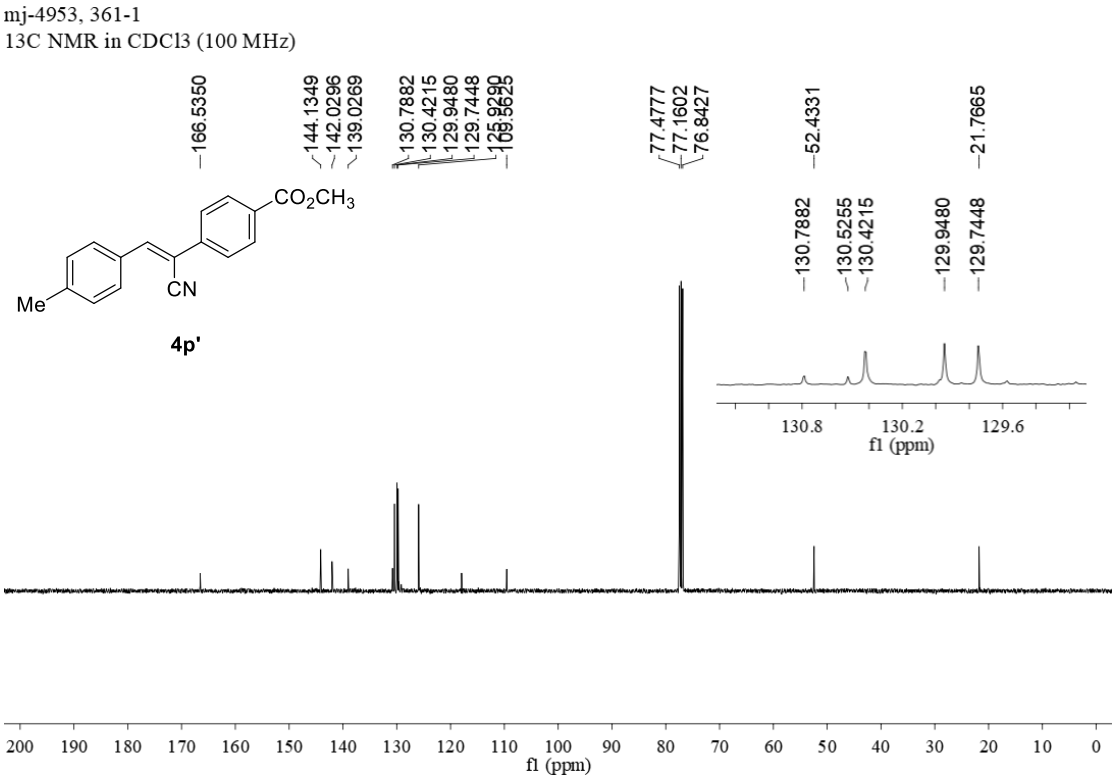


Figure S206. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4p'** ($CDCl_3$, 25 °C, 100 MHz).

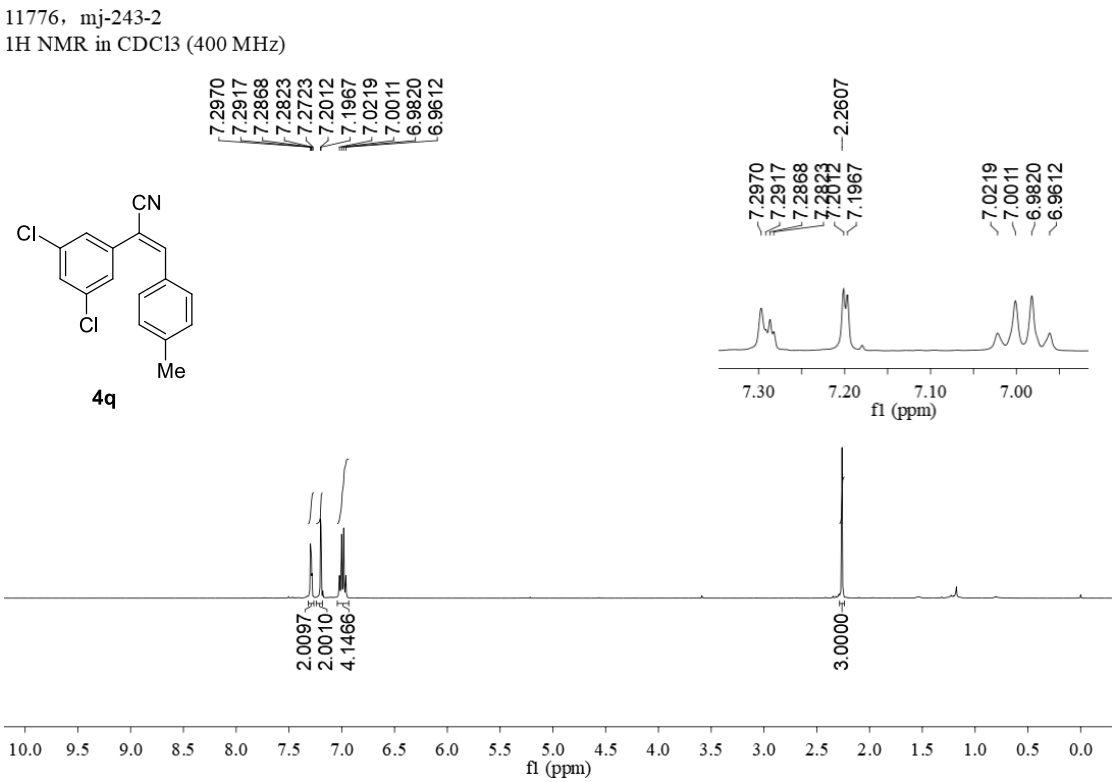


Figure S207. ^{1}H NMR spectrum of compound **4q** ($CDCl_3$, 25 °C, 400 MHz).

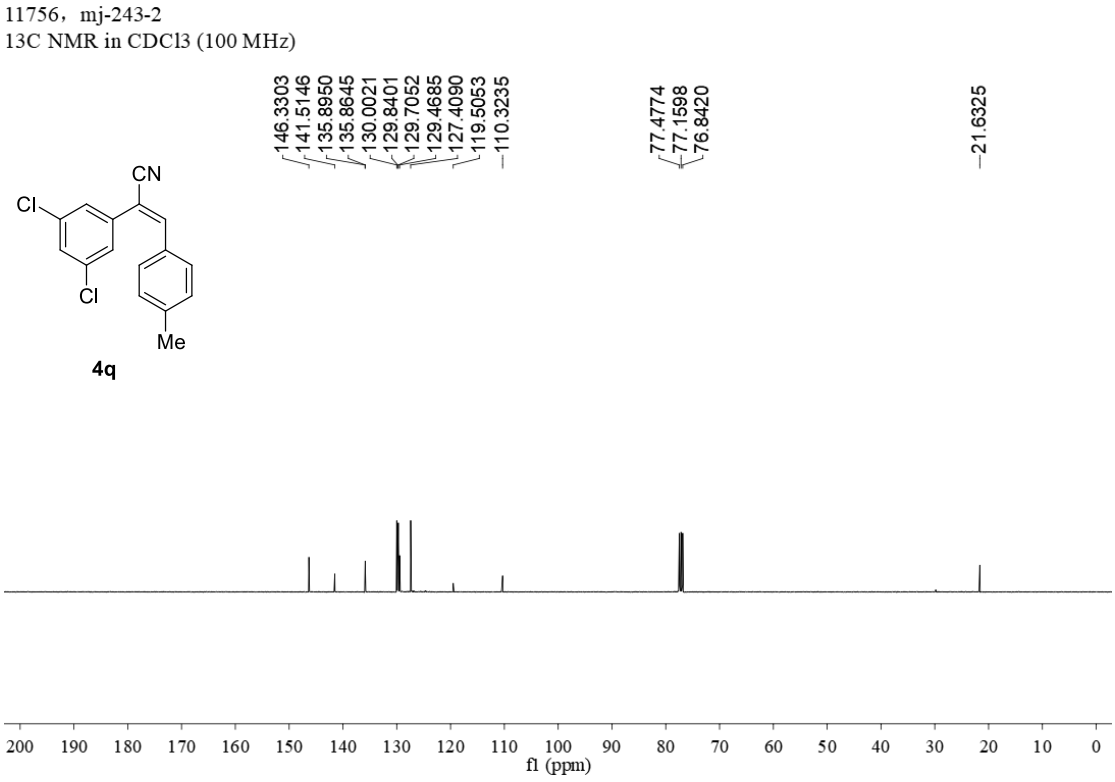


Figure S208. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4q** ($CDCl_3$, 25 °C, 100 MHz).

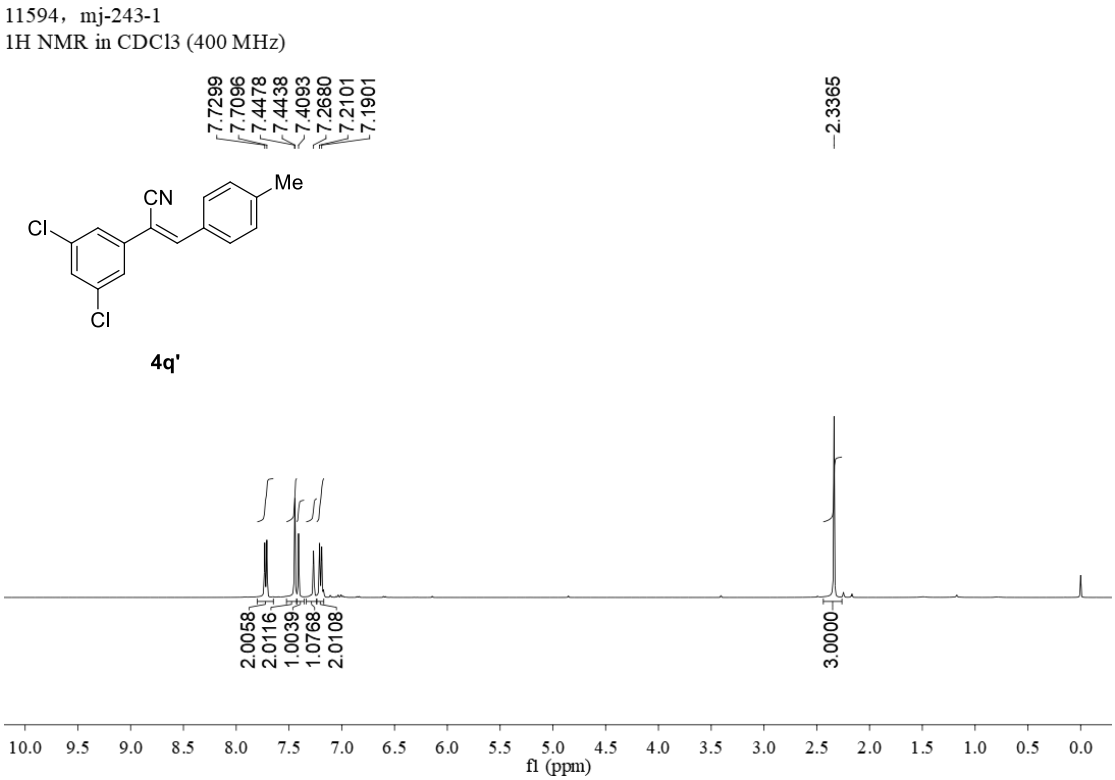


Figure S209. ^{1}H NMR spectrum of compound **4q'** ($CDCl_3$, 25 °C, 400 MHz).

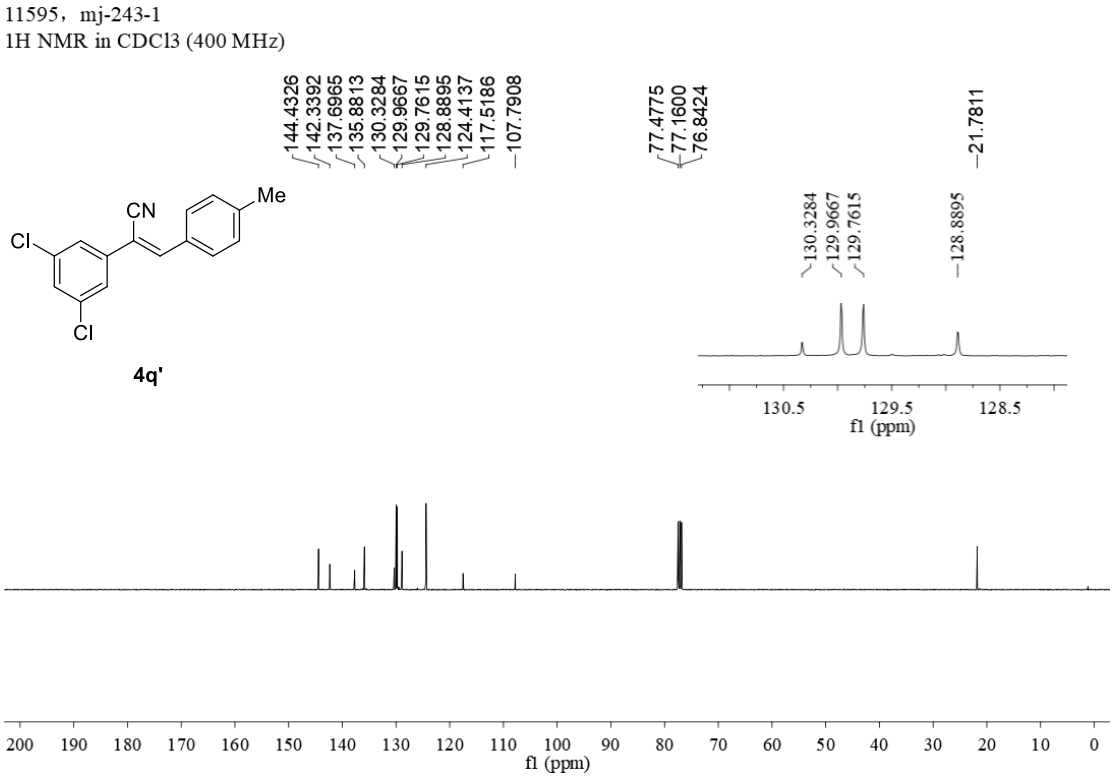


Figure S210. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4q'** ($CDCl_3$, 25 °C, 100 MHz).

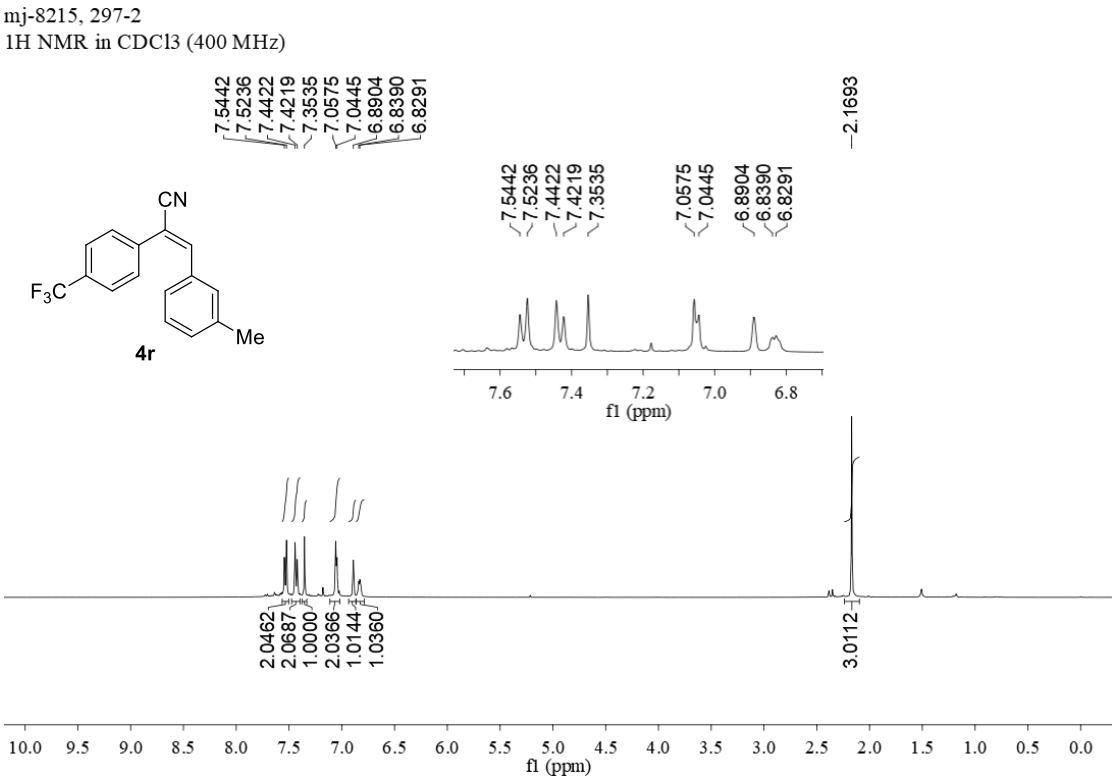


Figure S211. ^{1}H NMR spectrum of compound **4r** ($CDCl_3$, 25 °C, 400 MHz).

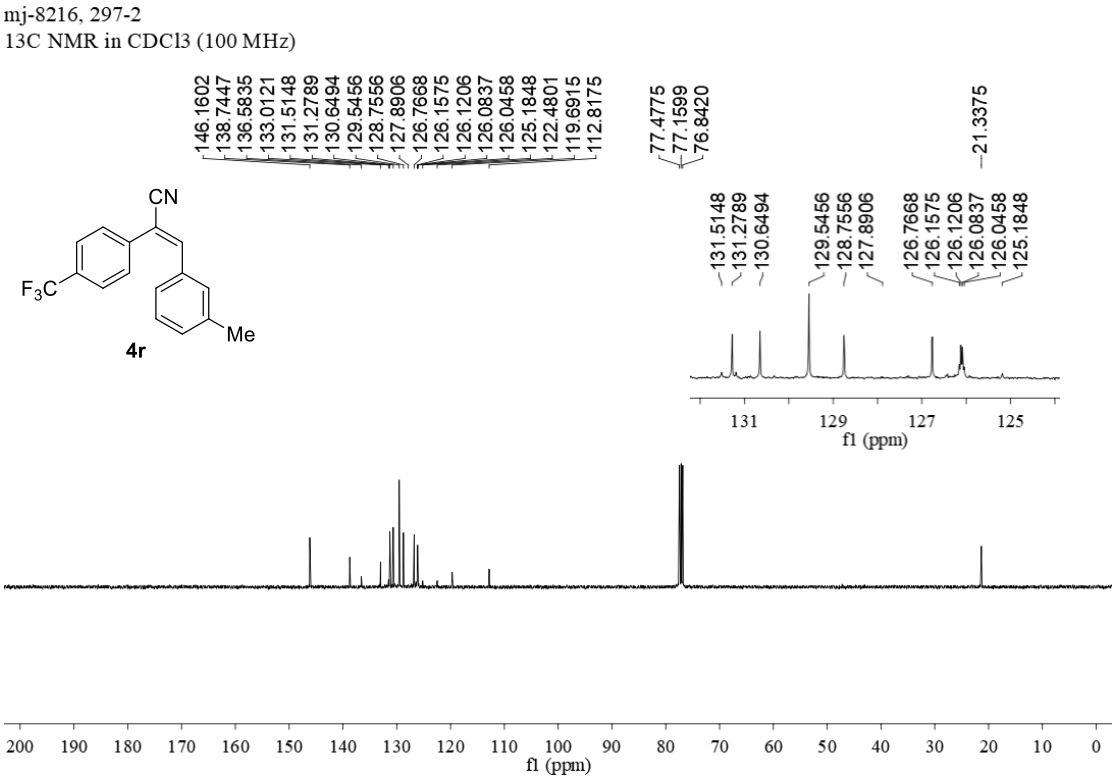


Figure S212. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4r** ($CDCl_3$, 25 °C, 100 MHz).

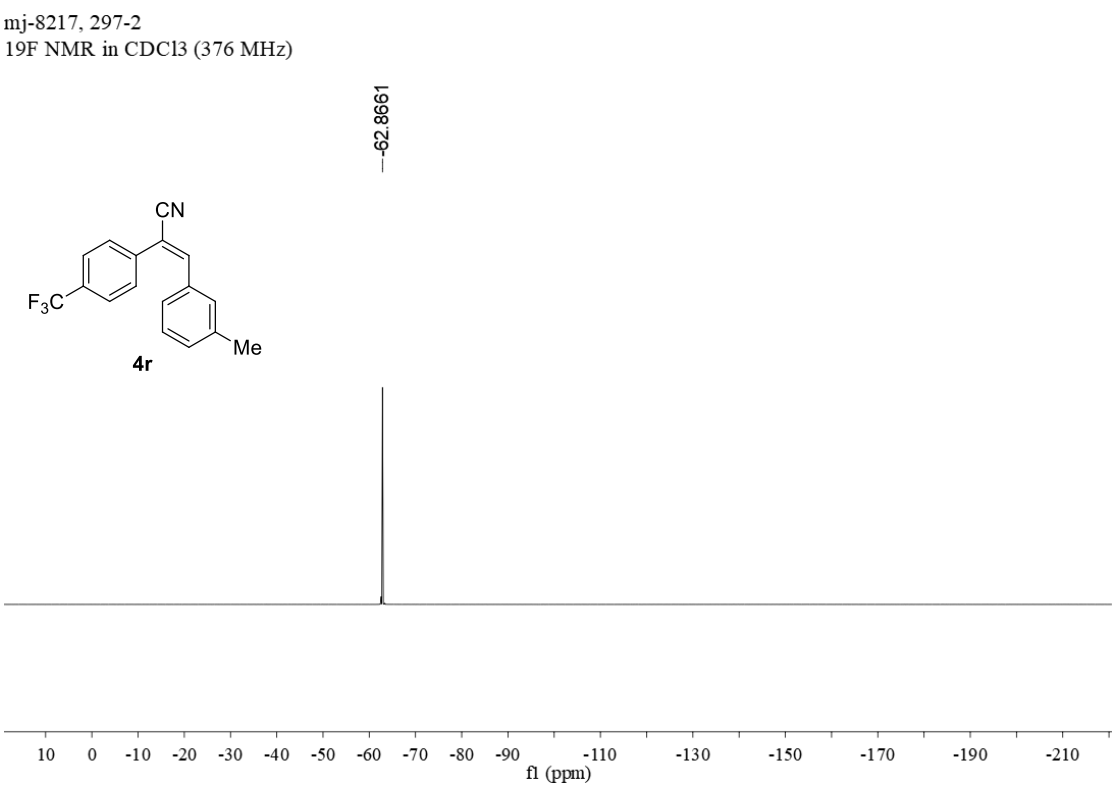


Figure S213. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4r** ($CDCl_3$, 25 °C, 376 MHz).

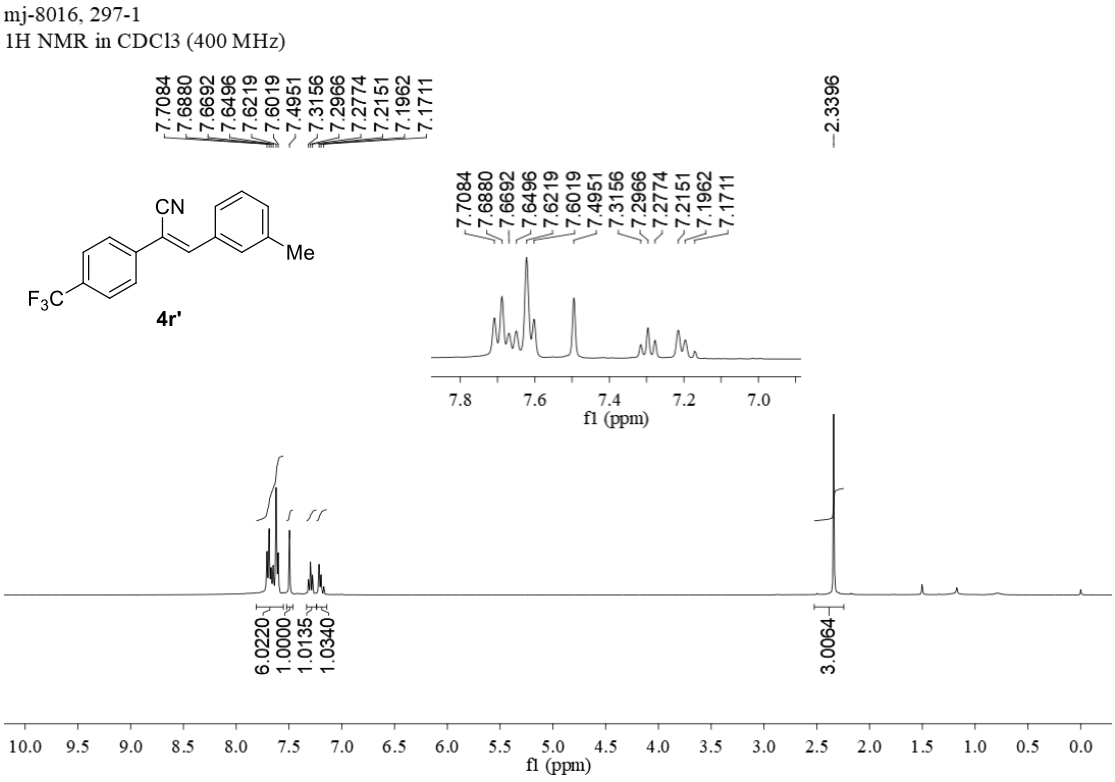


Figure S214. ^{1}H NMR spectrum of compound **4r'** ($CDCl_3$, 25 °C, 400 MHz).

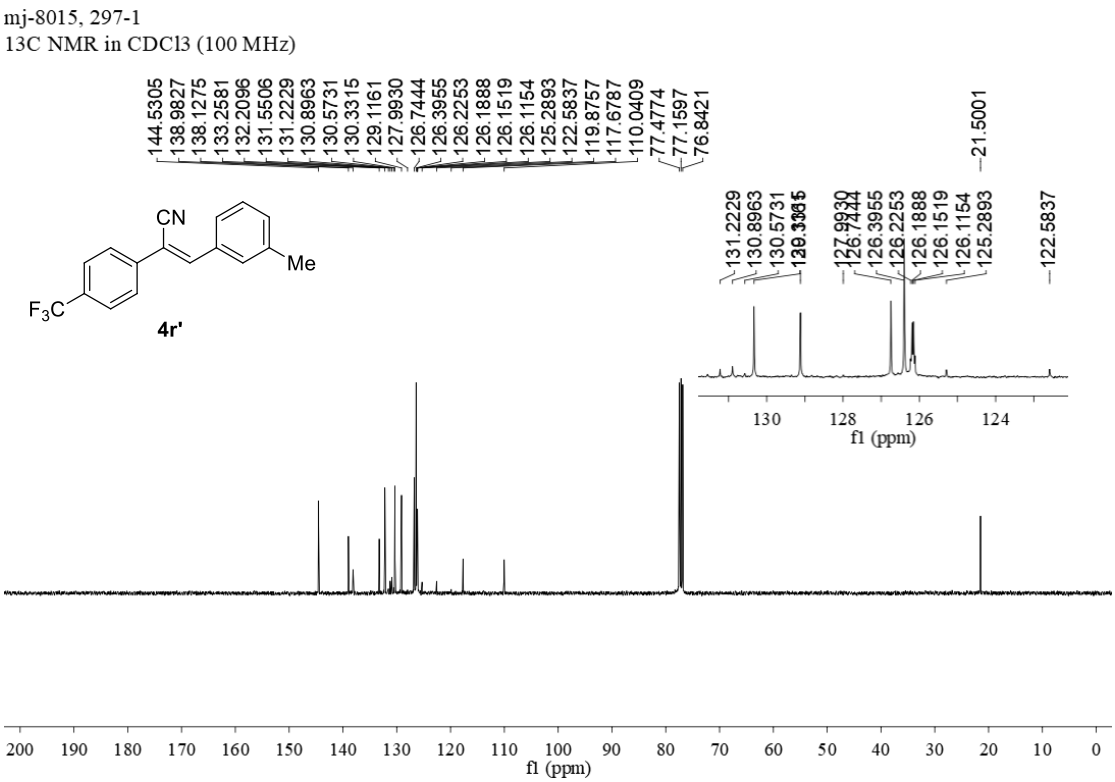


Figure S215. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4r'** ($CDCl_3$, 25 °C, 100 MHz).

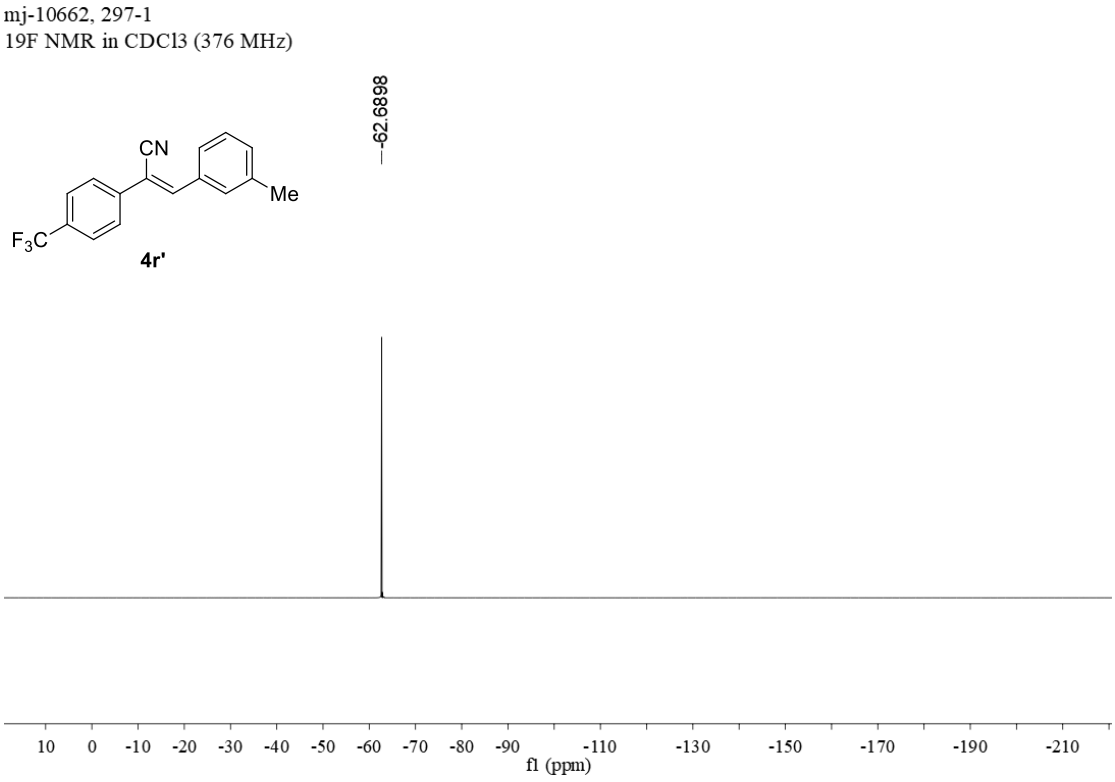


Figure S216. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4r'** ($CDCl_3$, 25 °C, 376 MHz).

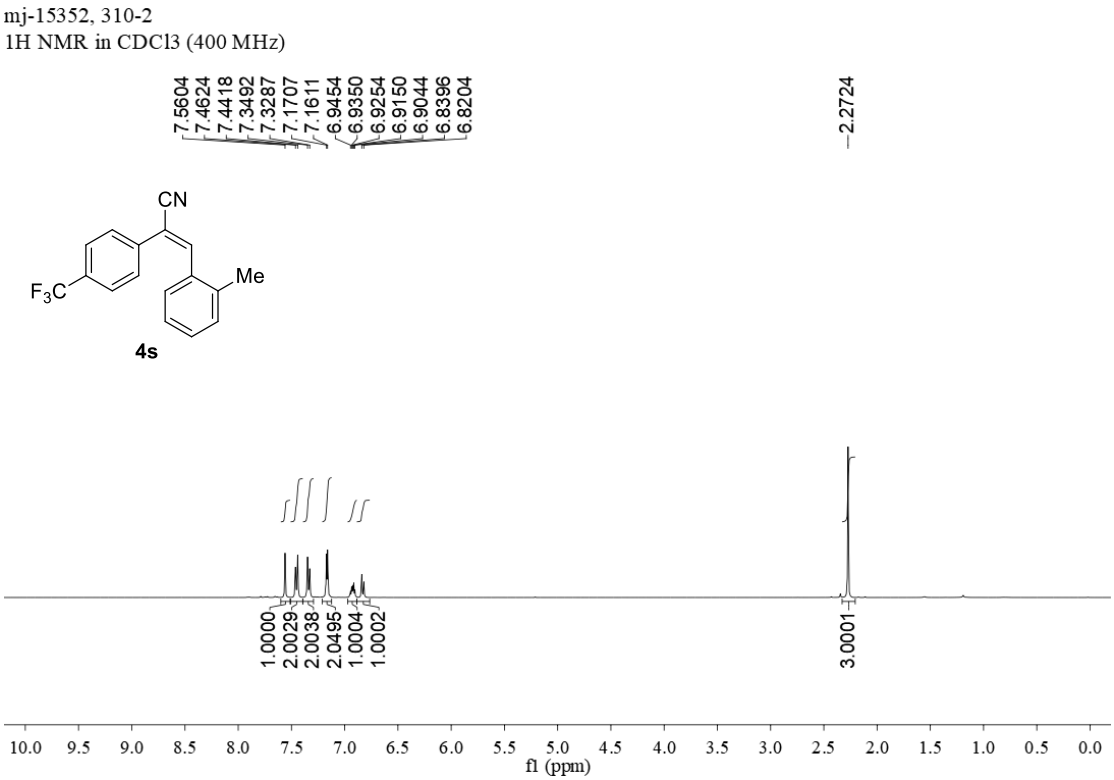


Figure S217. ^{1}H NMR spectrum of compound **4s** ($CDCl_3$, 25 °C, 400 MHz).

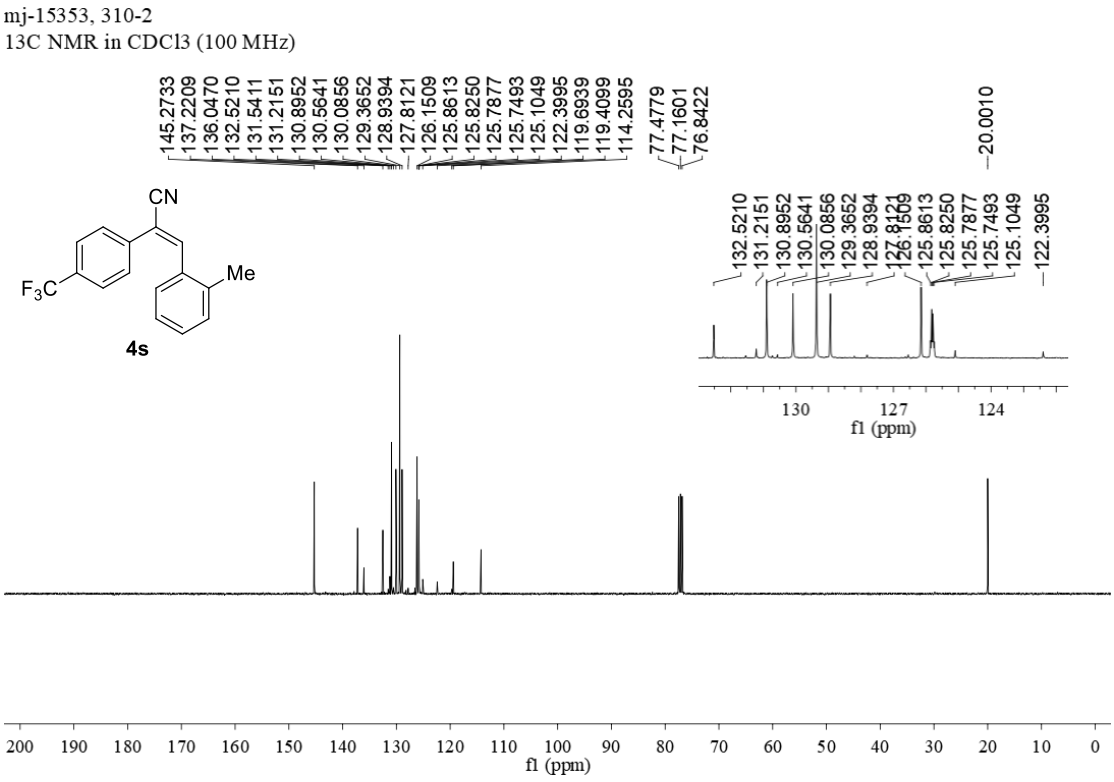


Figure S218. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4s** ($CDCl_3$, 25 °C, 100 MHz).

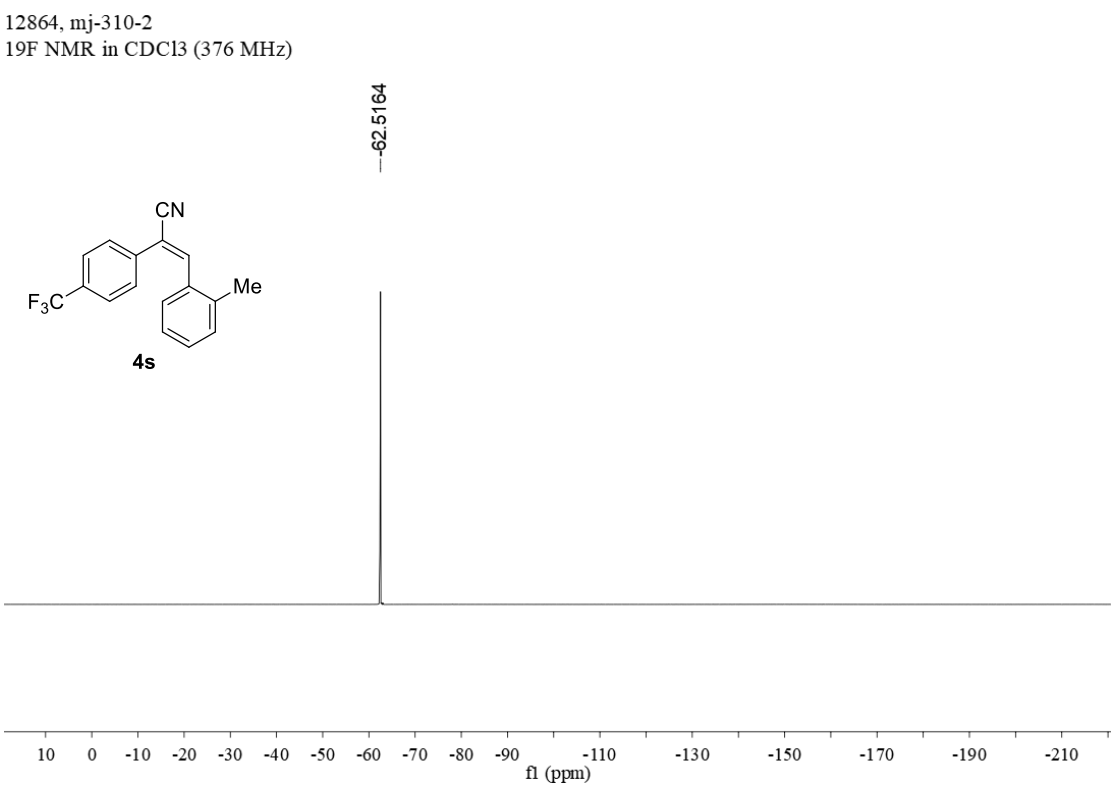


Figure S219. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4s** ($CDCl_3$, 25 °C, 376 MHz).

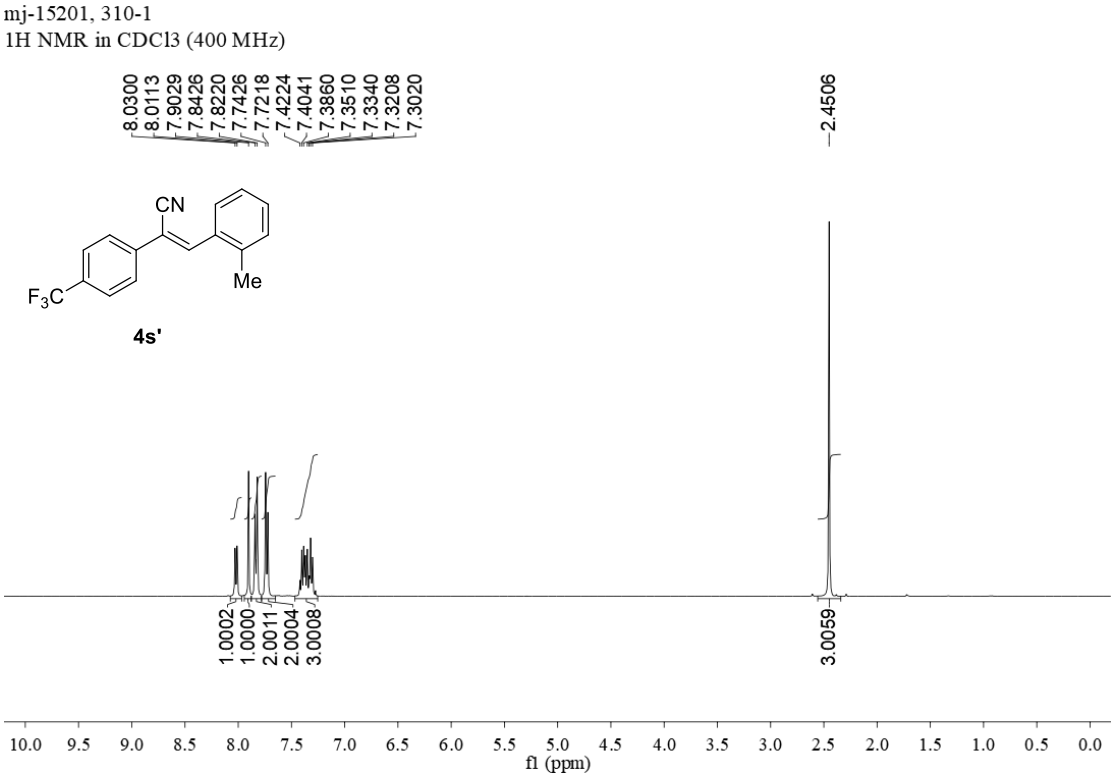


Figure S220. ^{1}H NMR spectrum of compound **4s'** ($CDCl_3$, 25 °C, 400 MHz).

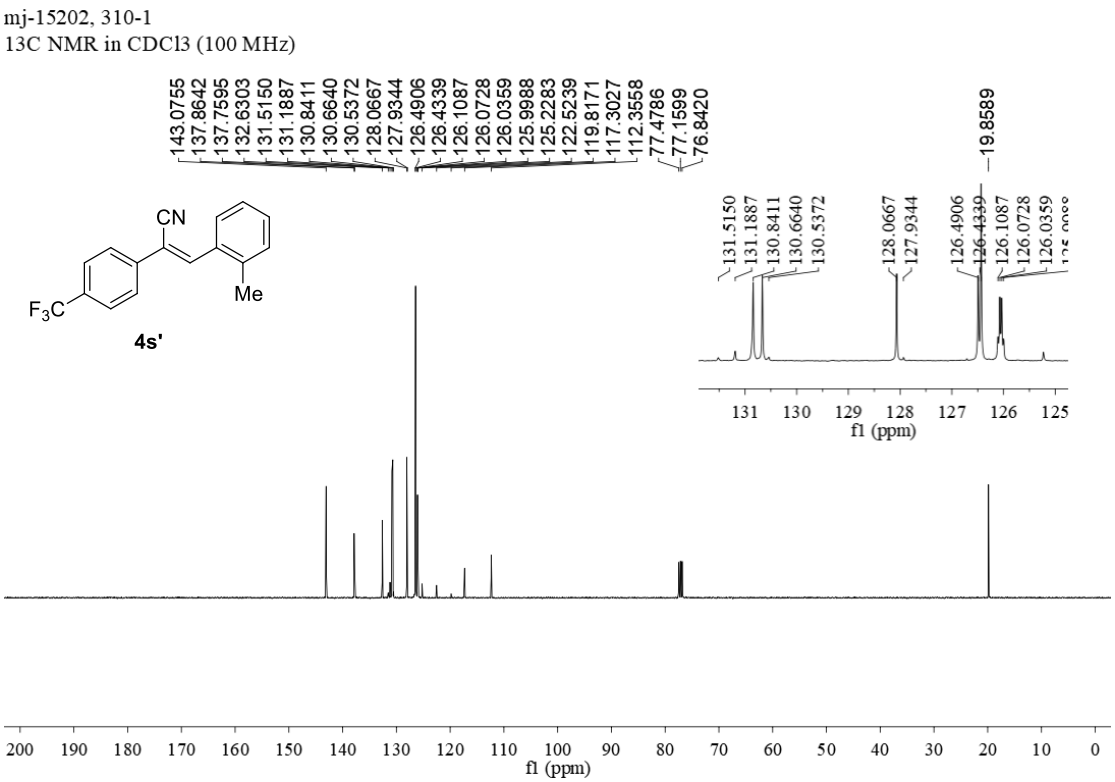


Figure S221. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4s'** ($CDCl_3$, 25 °C, 100 MHz).

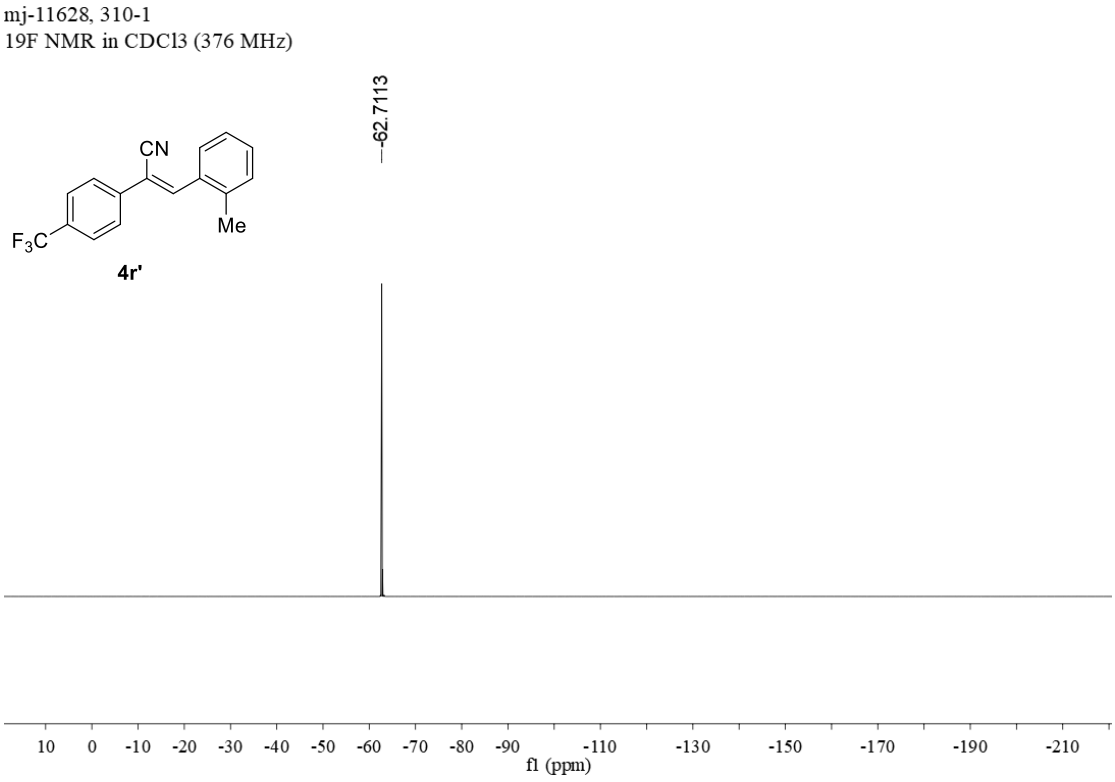


Figure S222. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4r'** ($CDCl_3$, 25 °C, 376 MHz).

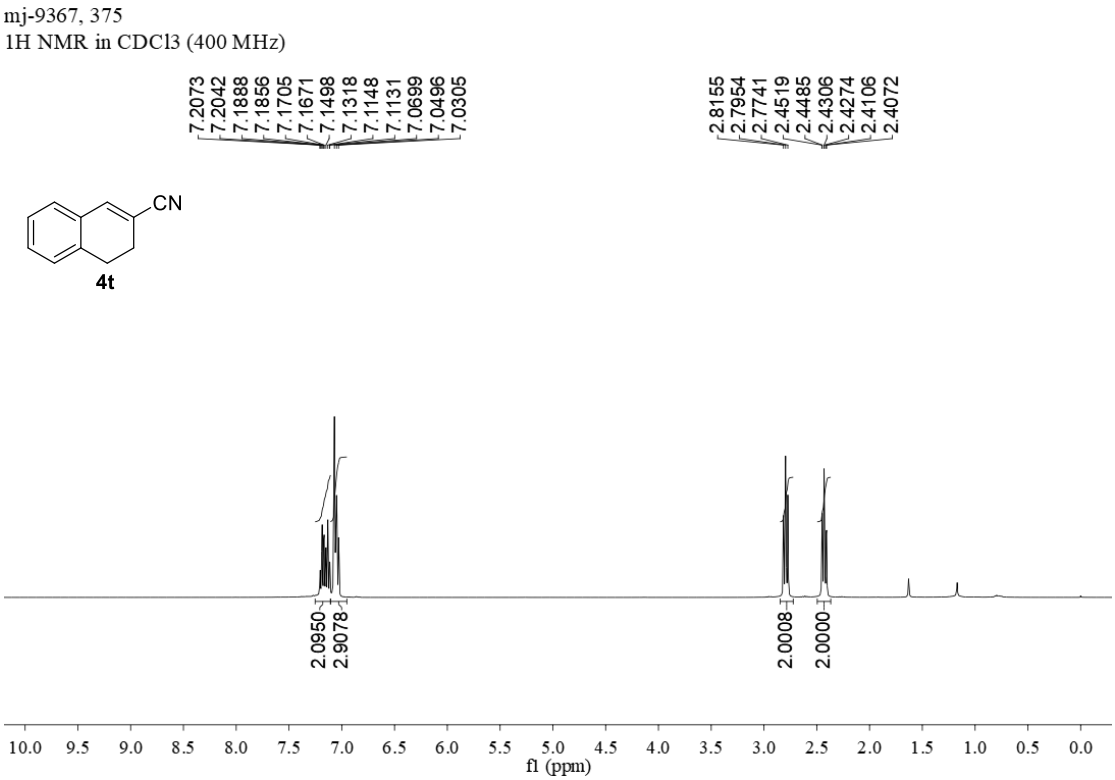


Figure S223. ^{1}H NMR spectrum of compound **4t** ($CDCl_3$, 25 °C, 400 MHz).

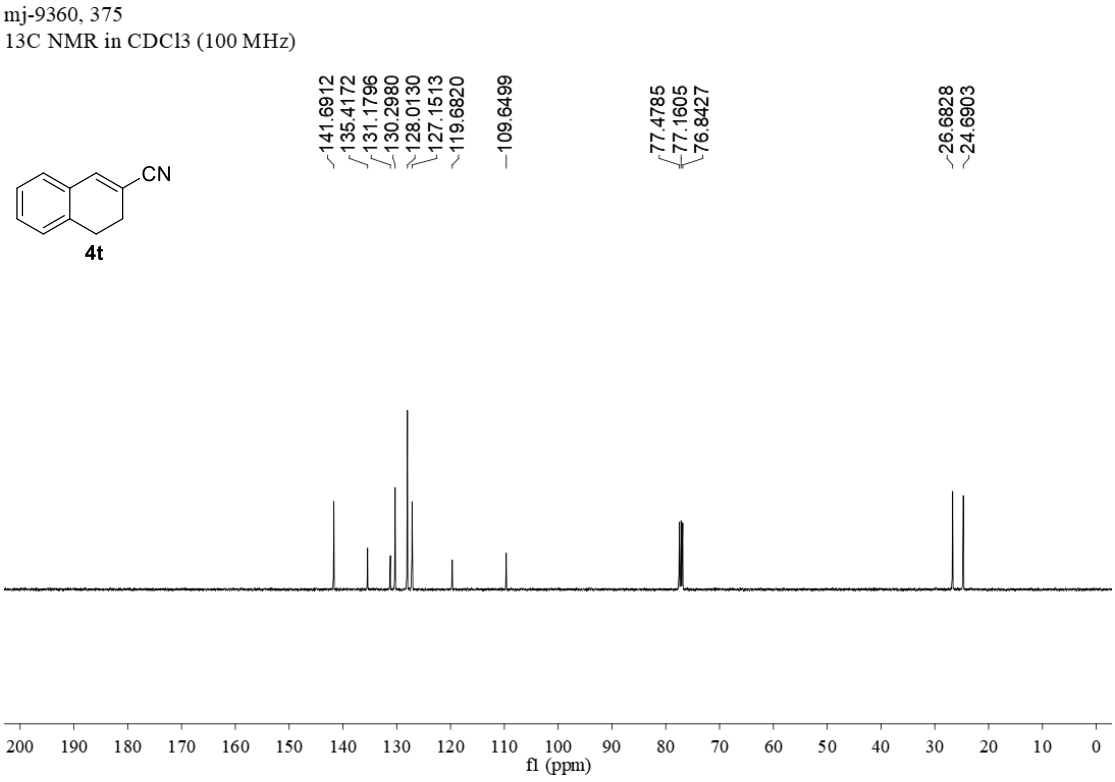


Figure S224. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4t** ($CDCl_3$, 25 °C, 100 MHz).

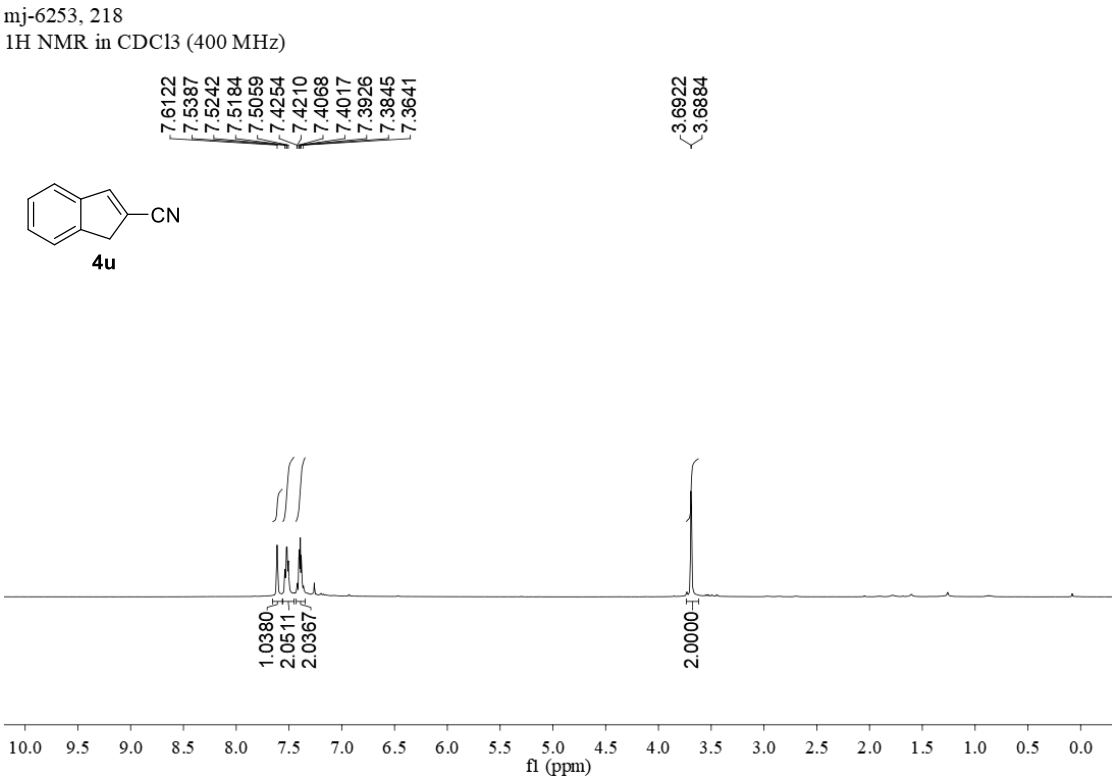


Figure S225. ^{1}H NMR spectrum of compound **4u** ($CDCl_3$, 25 °C, 400 MHz).

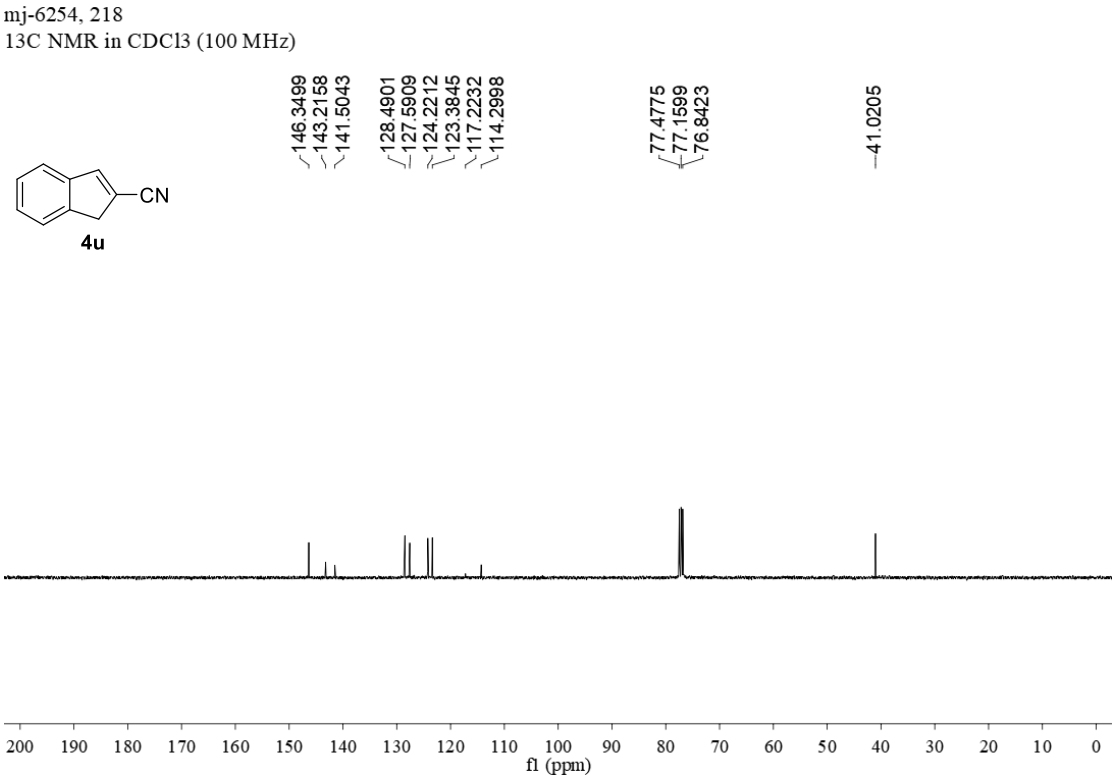


Figure S226. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4u** ($CDCl_3$, 25 °C, 100 MHz).

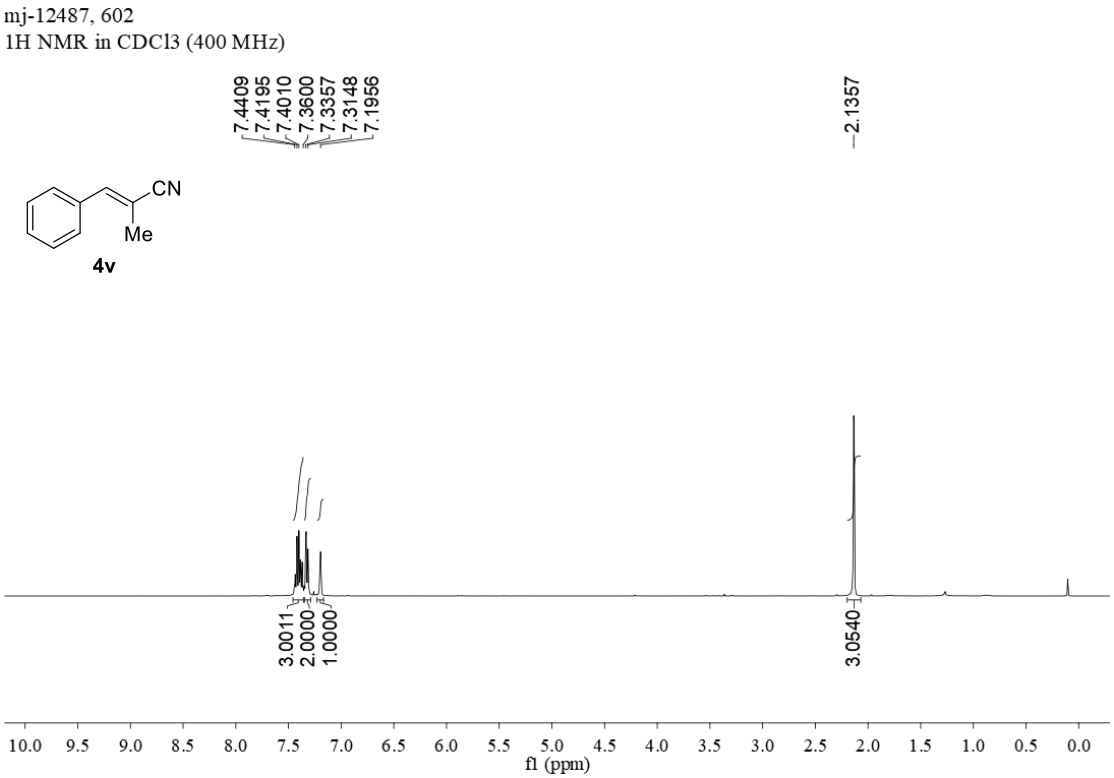


Figure S227. ^{1}H NMR spectrum of compound **4v** ($CDCl_3$, 25 °C, 400 MHz).

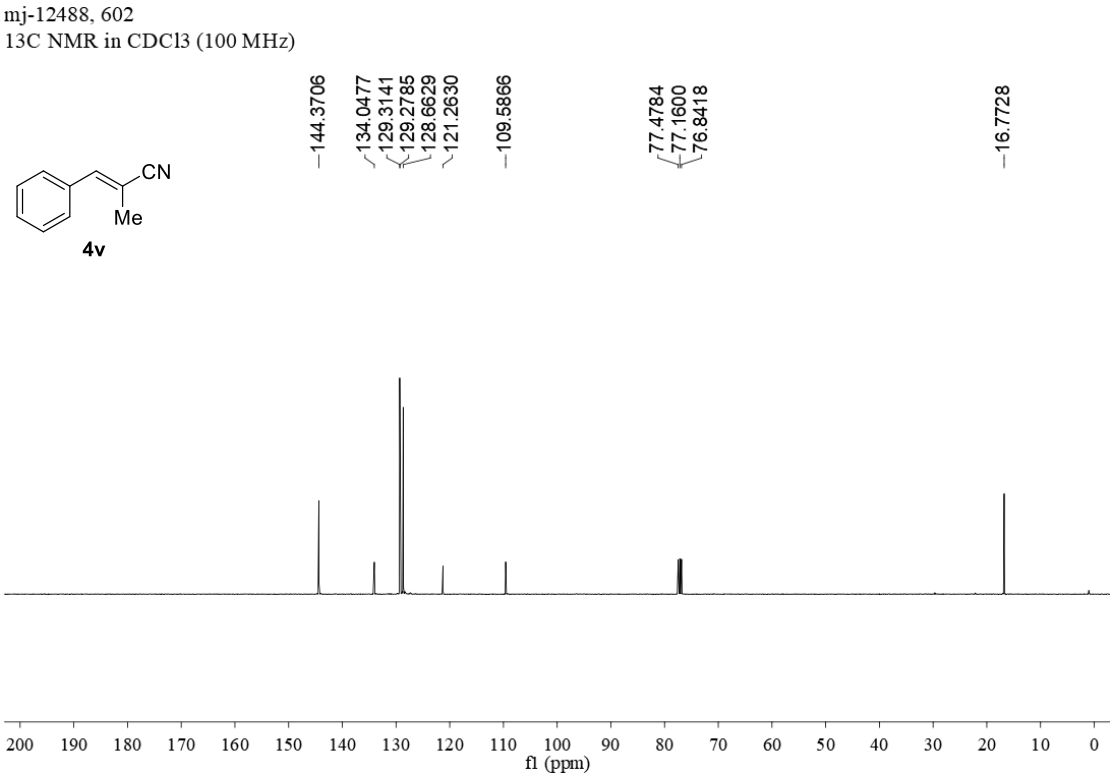


Figure S228. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4v** ($CDCl_3$, 25 °C, 100 MHz).

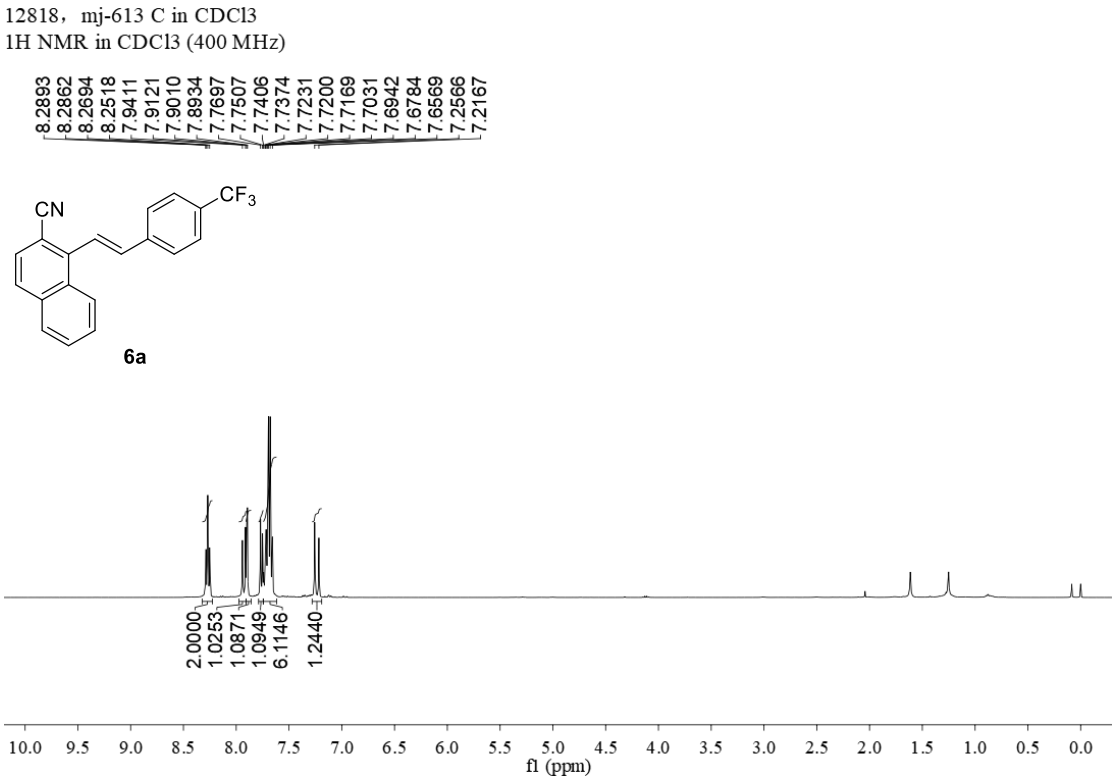


Figure S229. ^{1}H NMR spectrum of compound **6a** ($CDCl_3$, 25 °C, 400 MHz).

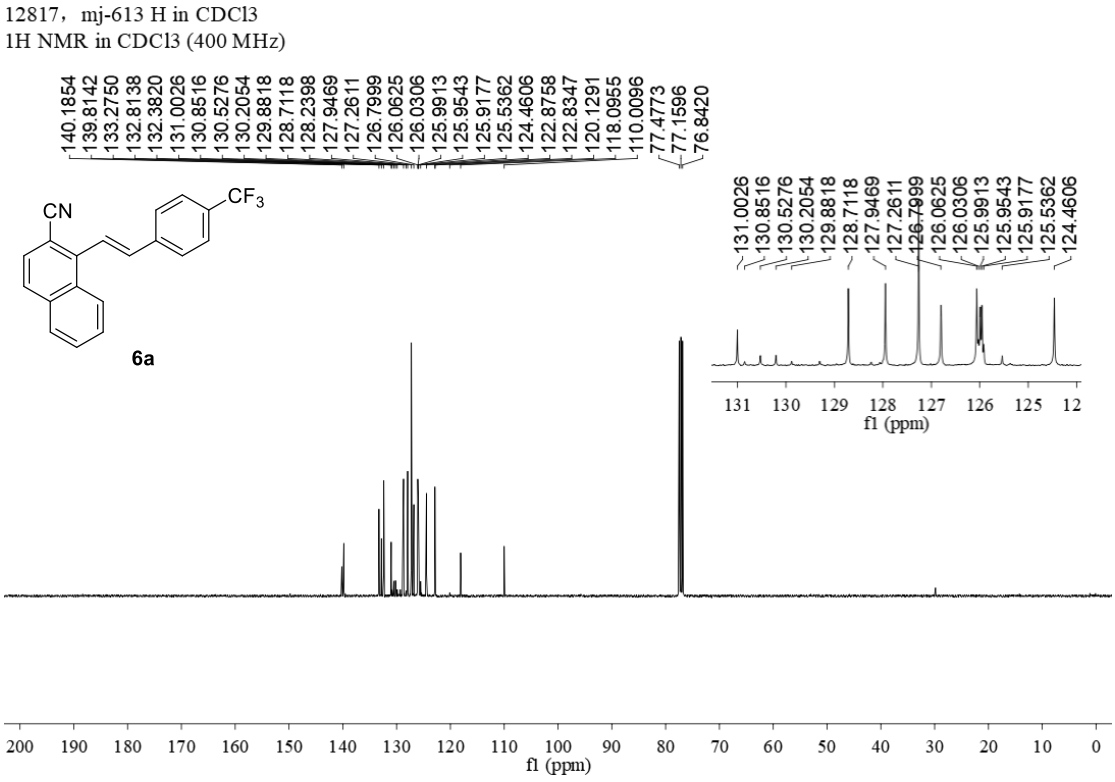


Figure S230. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6a** ($CDCl_3$, 25 °C, 100 MHz).

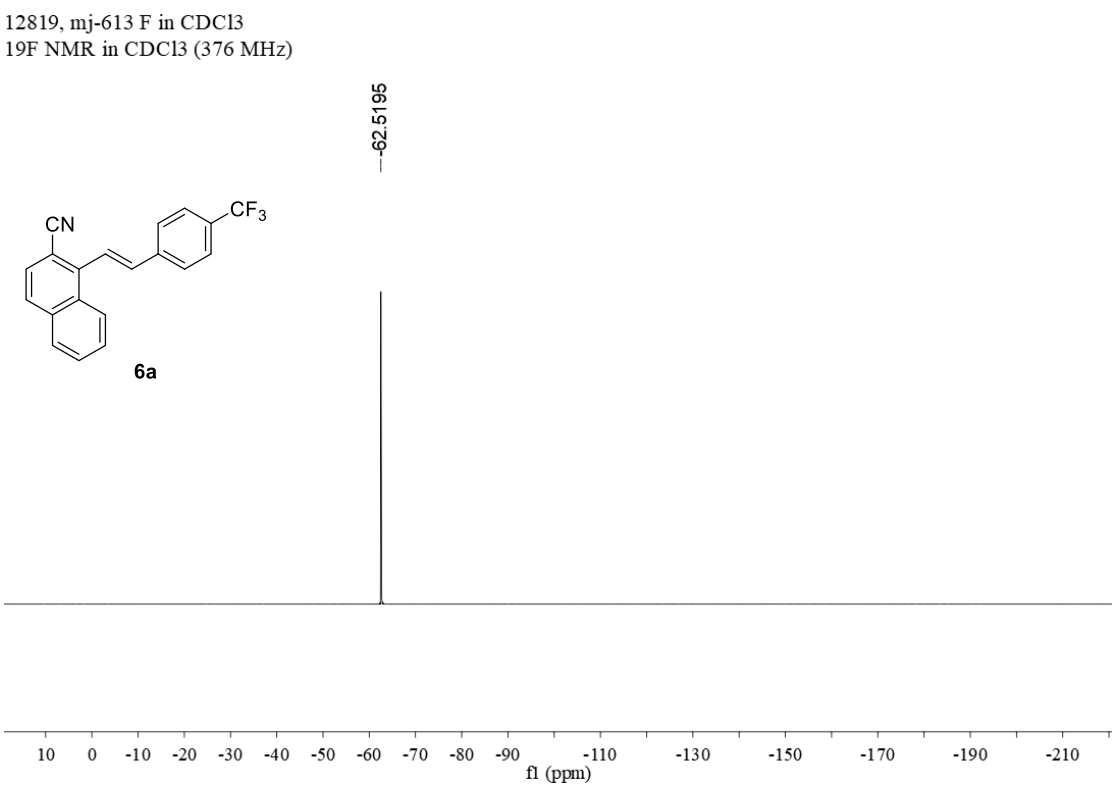


Figure S231. $^{19}F\{^{1}H\}$ NMR spectrum of compound **6a** ($CDCl_3$, 25 °C, 376 MHz).

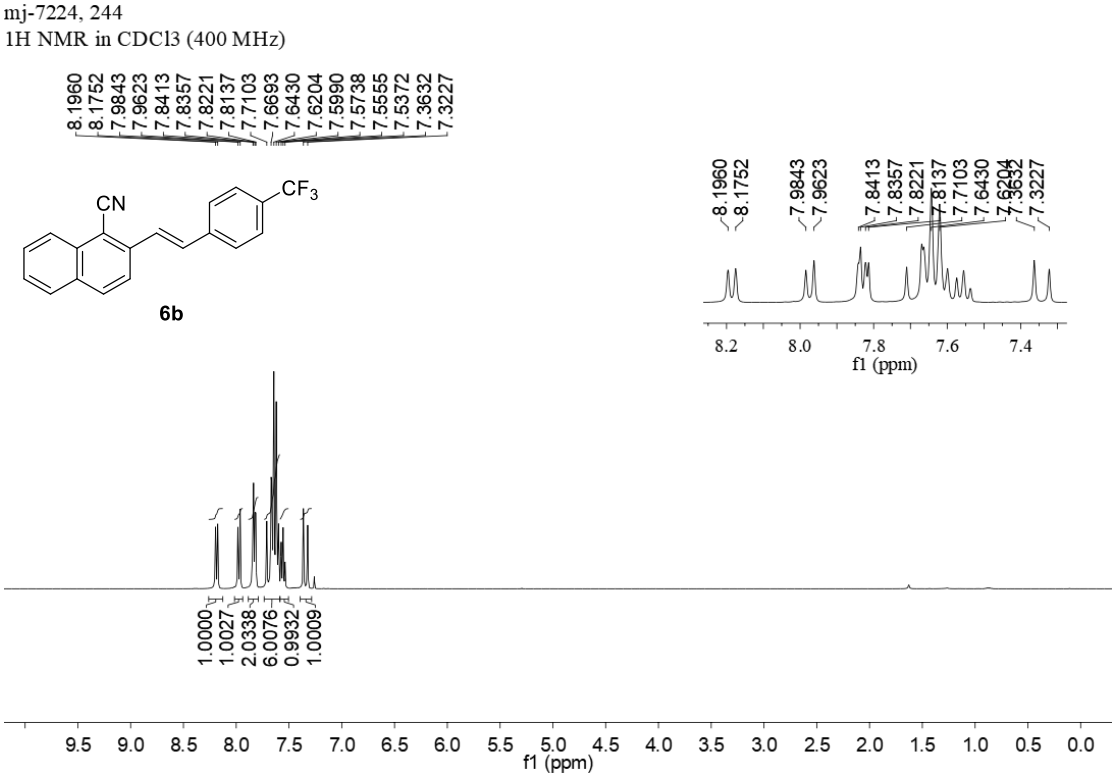


Figure S232. ^{1}H NMR spectrum of compound **6b** ($CDCl_3$, 25 °C, 400 MHz).

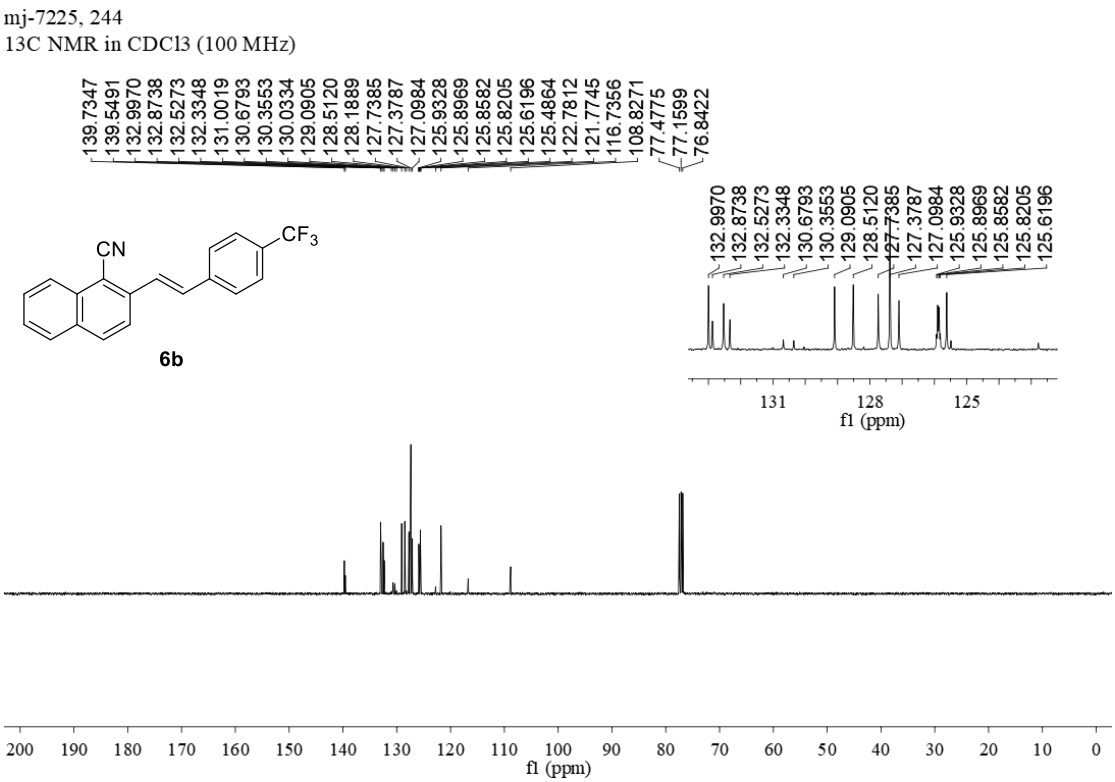


Figure S233. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6b** ($CDCl_3$, 25 °C, 100 MHz).

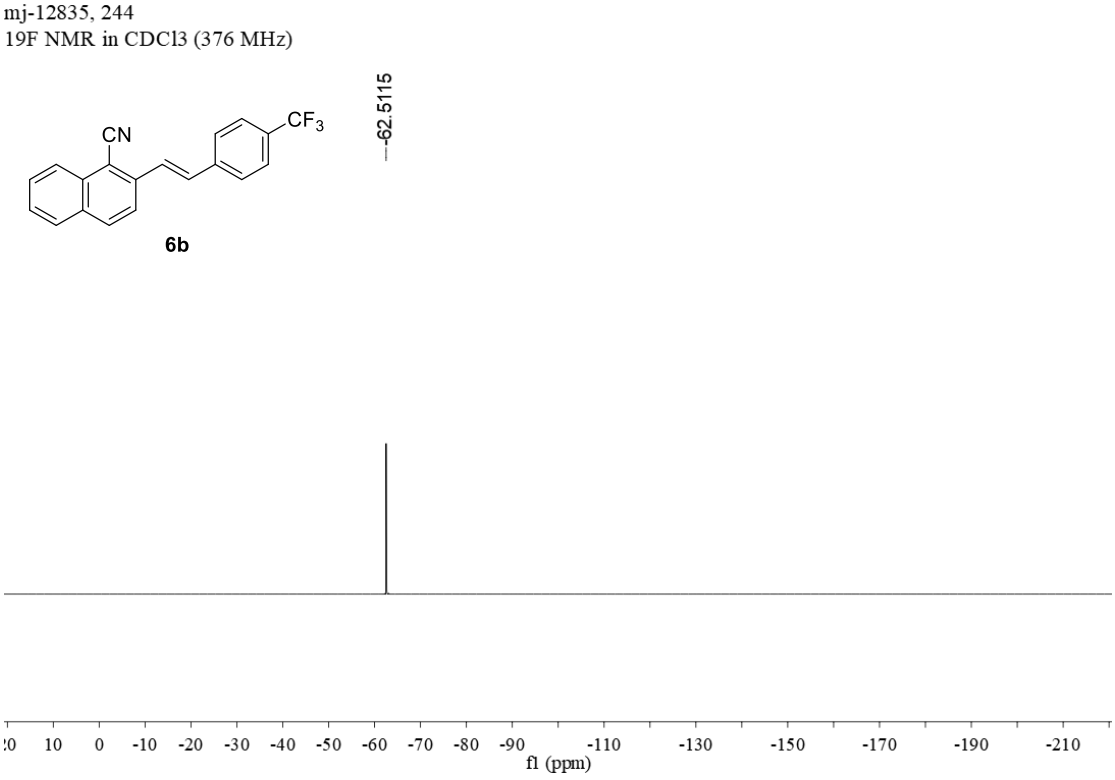


Figure S234. $^{19}F\{^{1}H\}$ NMR spectrum of compound **6b** ($CDCl_3$, 25 °C, 376 MHz).

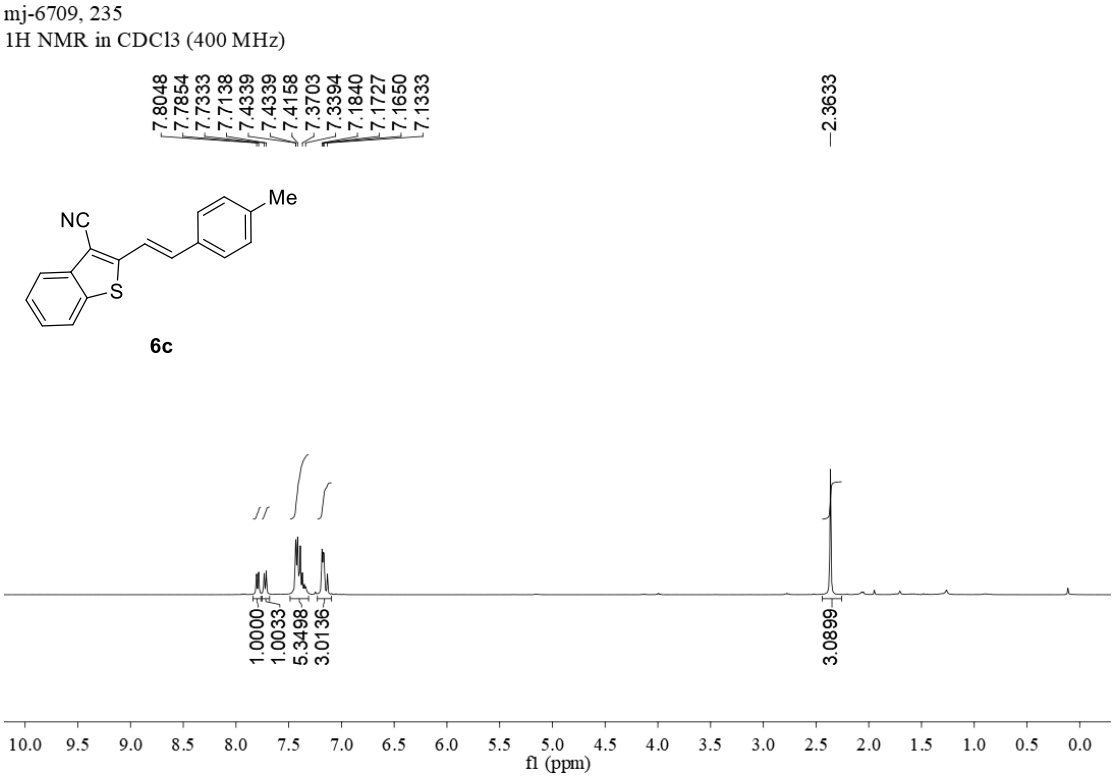


Figure S235. ^{1}H NMR spectrum of compound **6c** ($CDCl_3$, 25 °C, 400 MHz).

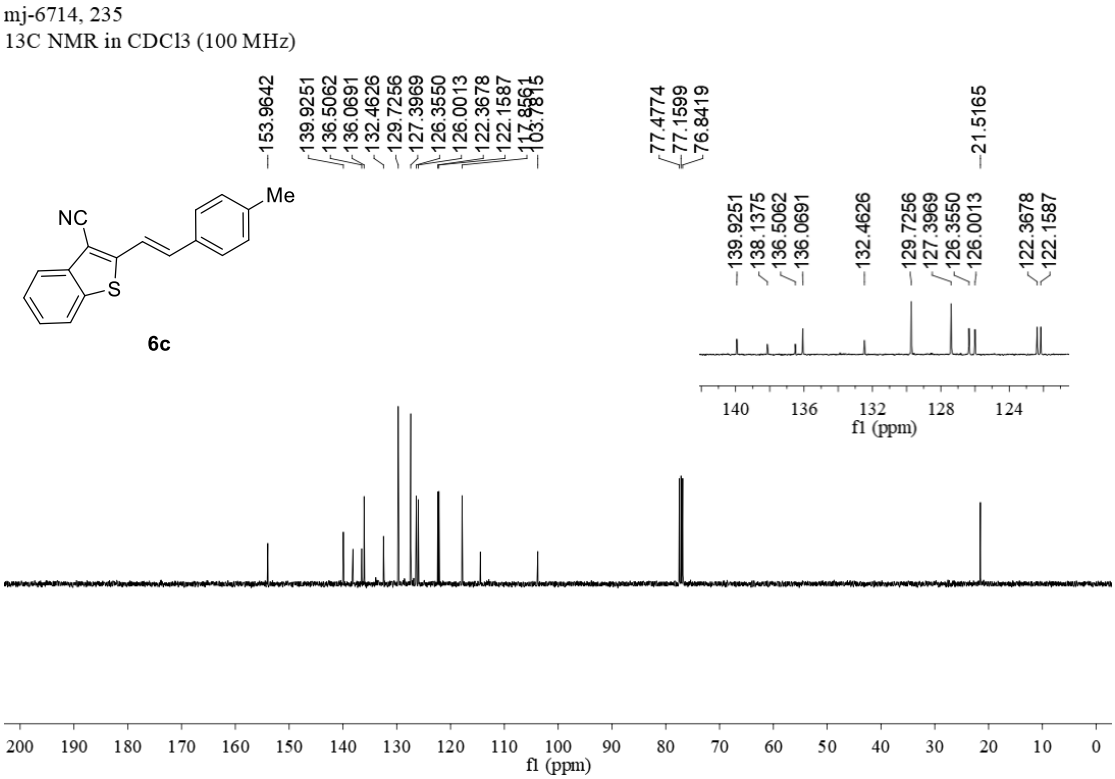


Figure S236. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6c** ($CDCl_3$, 25 °C, 100 MHz).

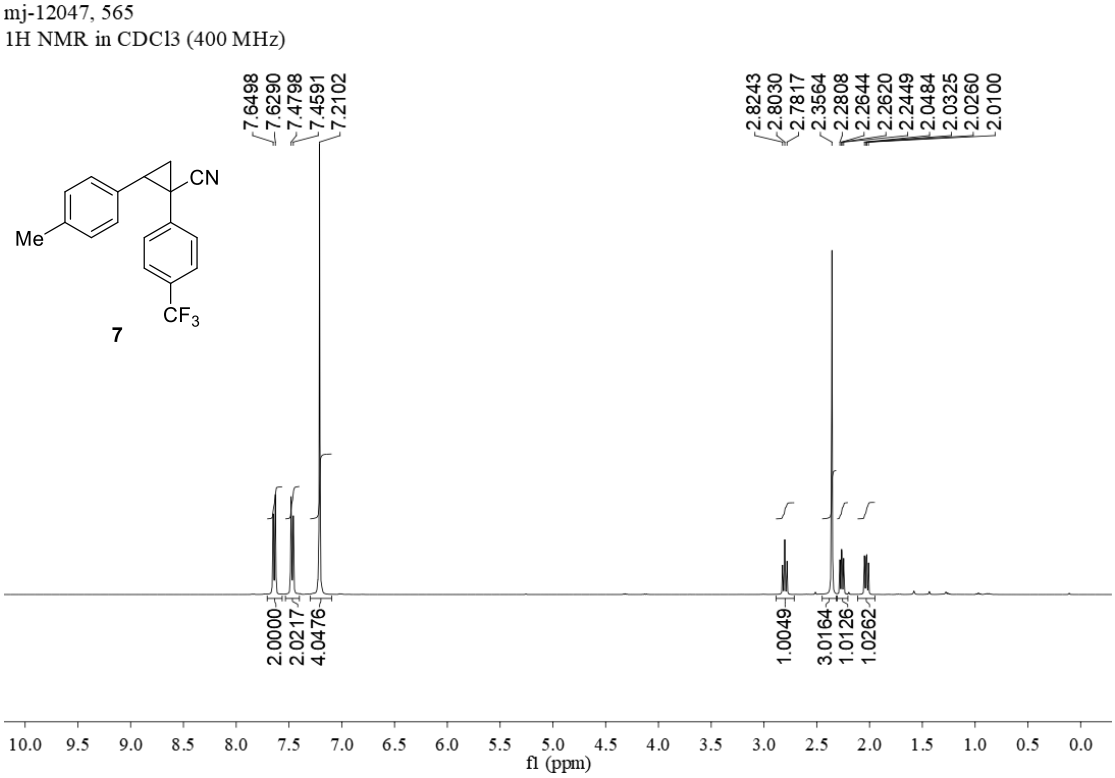


Figure S237. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 25 °C, 400 MHz).

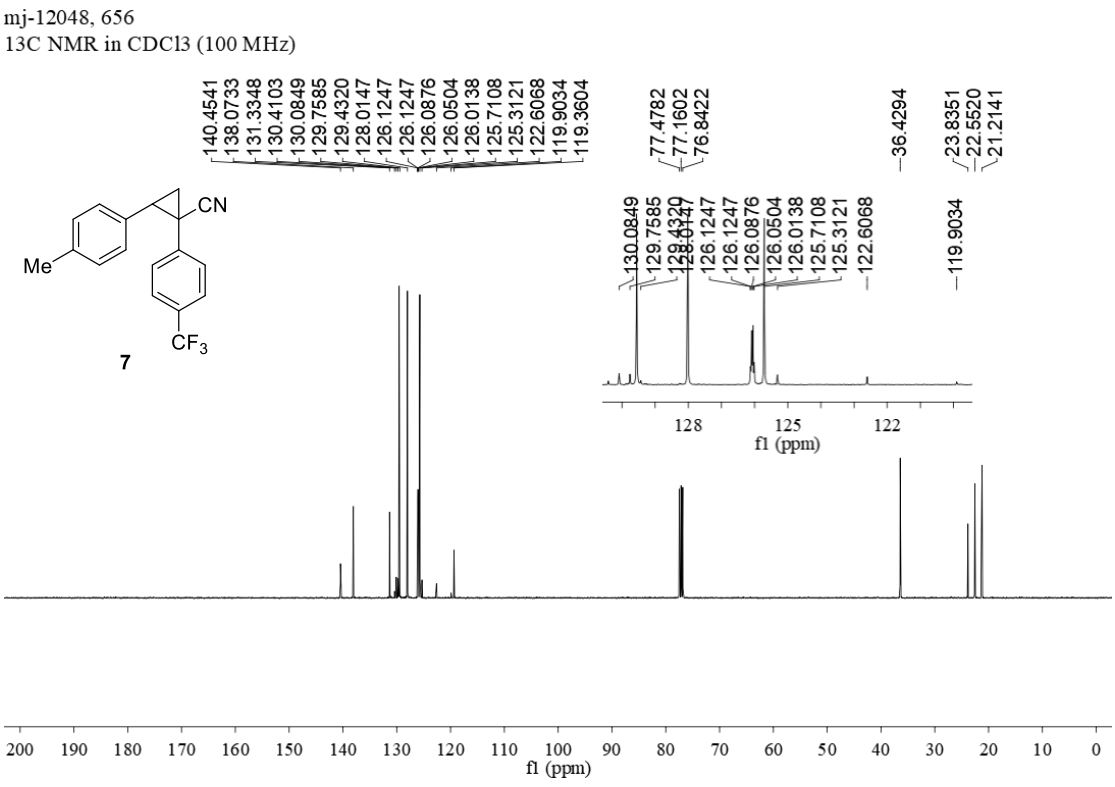


Figure S238. ^{13}C{^{1}H} NMR spectrum of compound **7** ($CDCl_3$, 25 °C, 100 MHz).

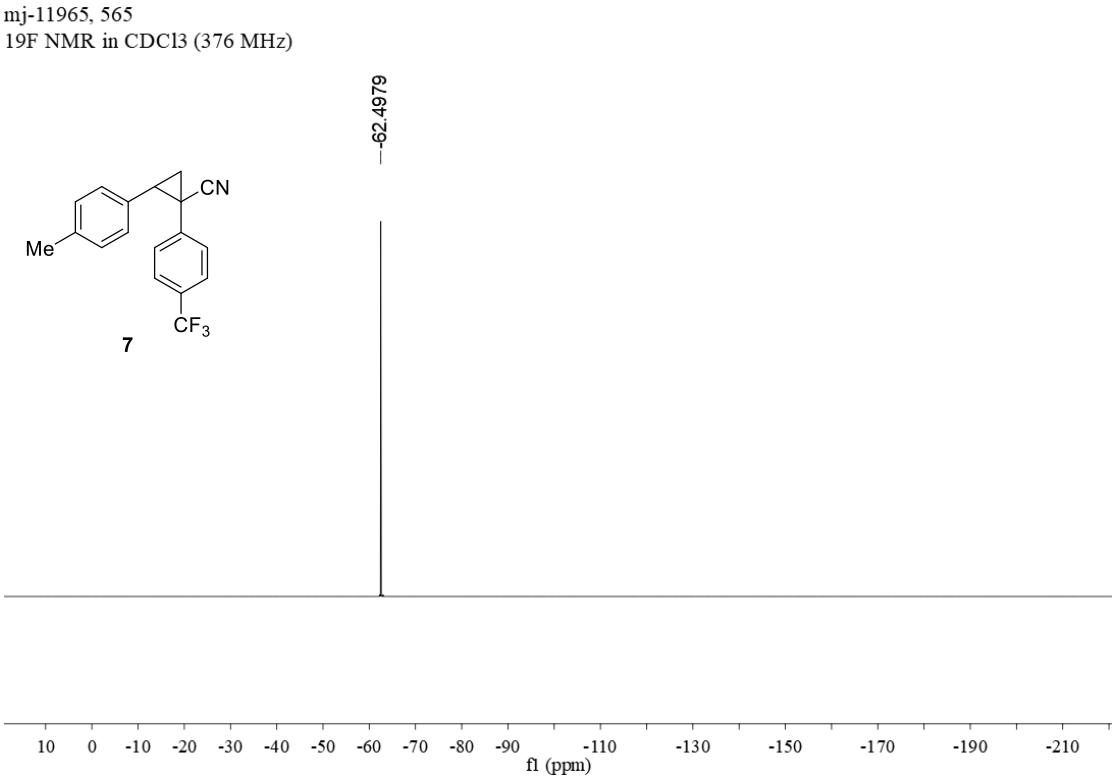


Figure S239. $^{19}F\{^{1}H\}$ NMR spectrum of compound **7** ($CDCl_3$, 25 °C, 376 MHz).

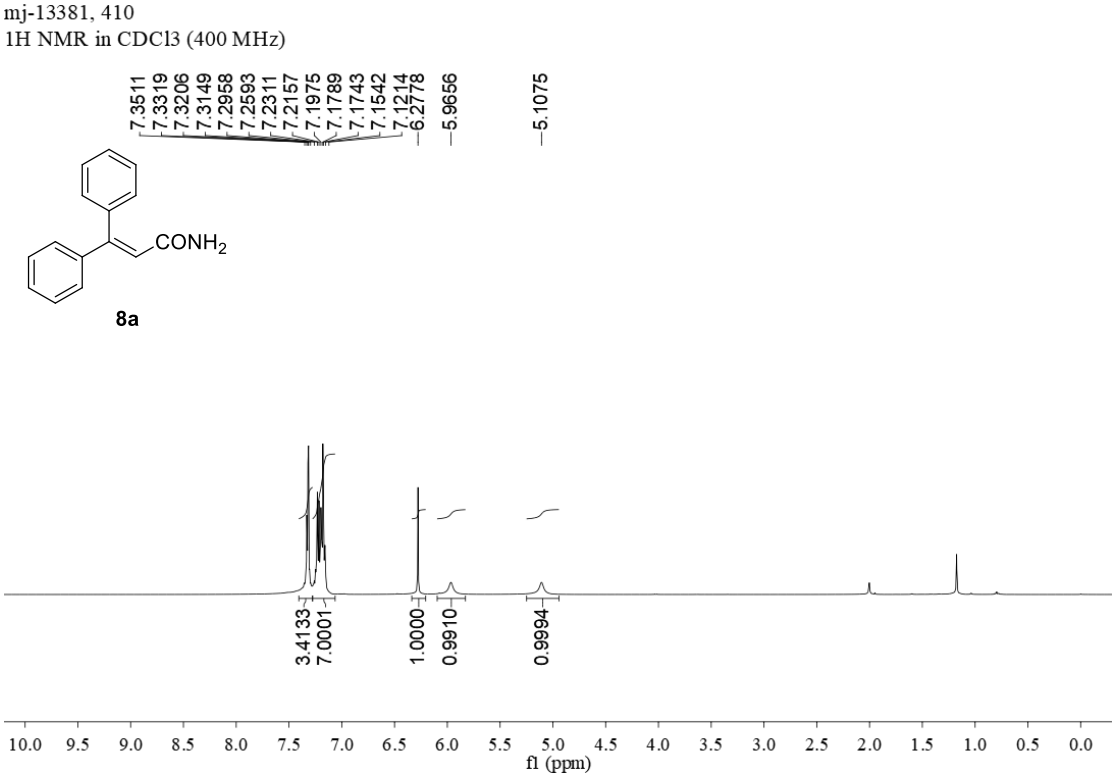


Figure S240. ^{1}H NMR spectrum of compound **8a** ($CDCl_3$, 25 °C, 400 MHz).

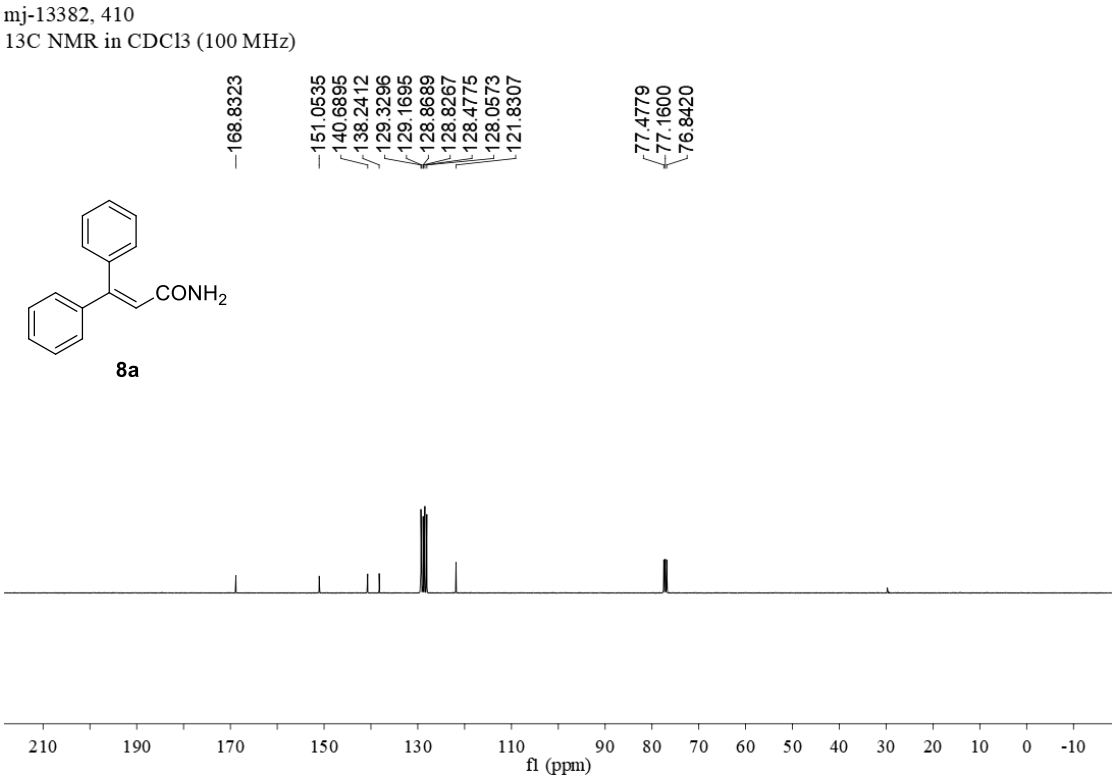


Figure S241. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8a** ($CDCl_3$, 25 °C, 100 MHz).

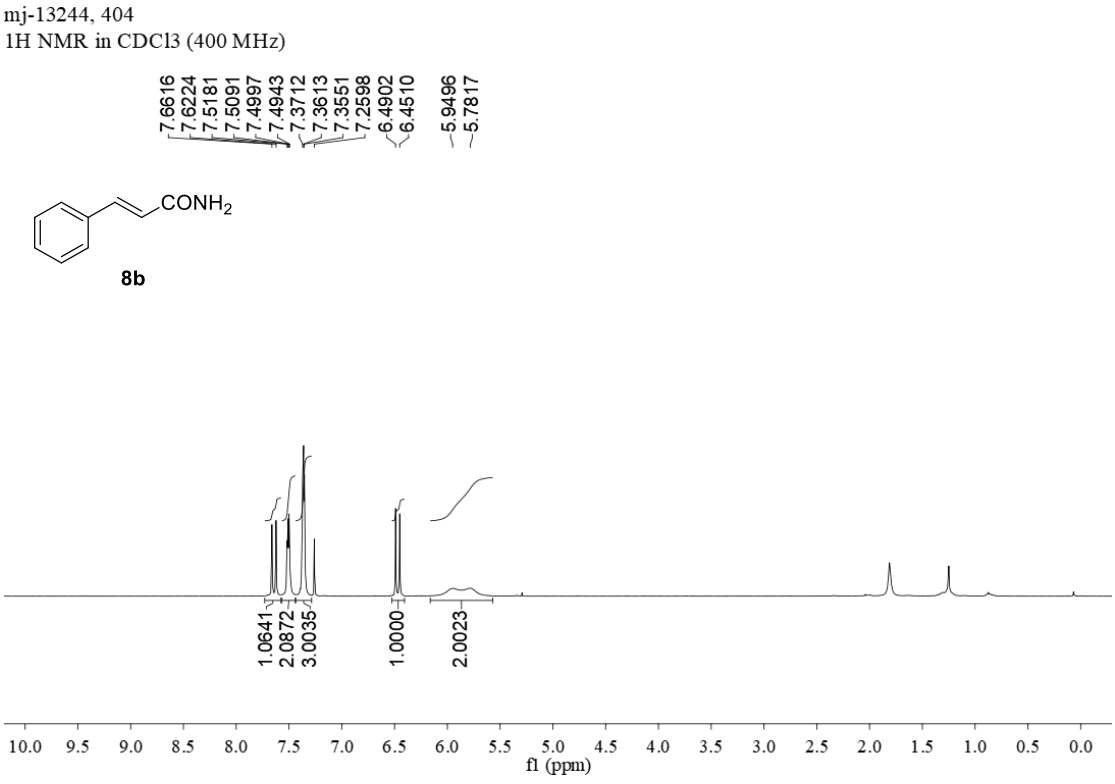


Figure S242. ^{1}H NMR spectrum of compound **8b** ($CDCl_3$, 25 °C, 400 MHz).

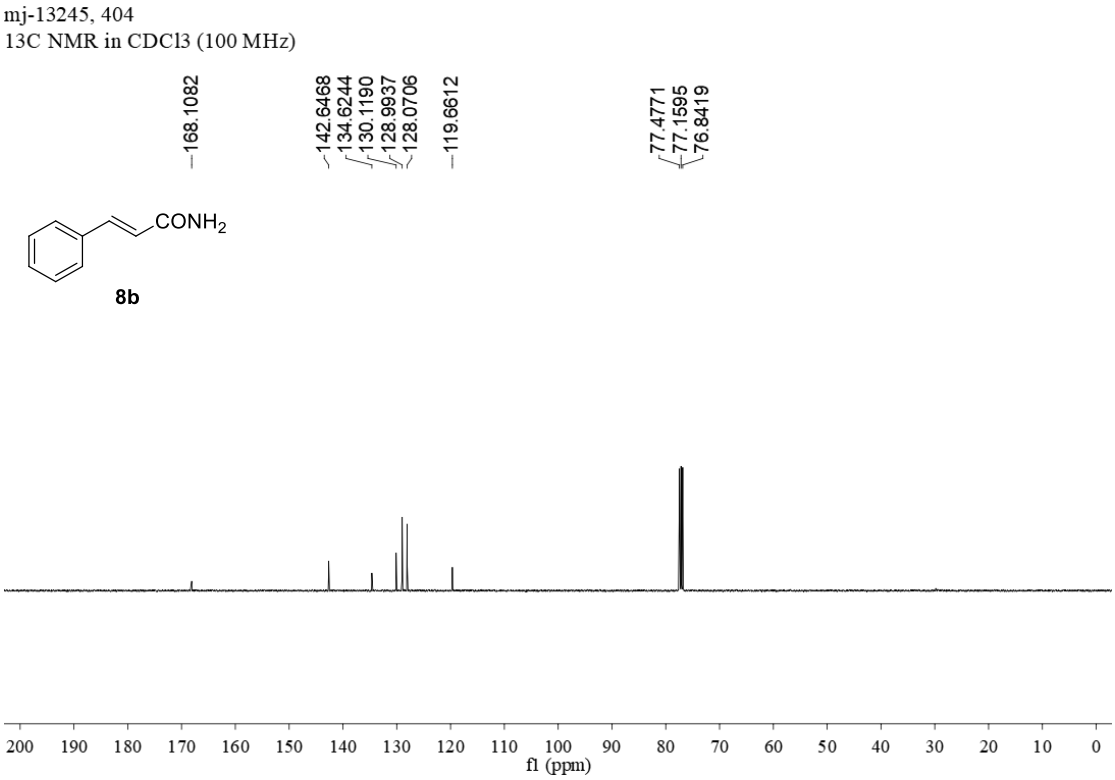


Figure S243. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8b** ($CDCl_3$, 25 °C, 100 MHz).

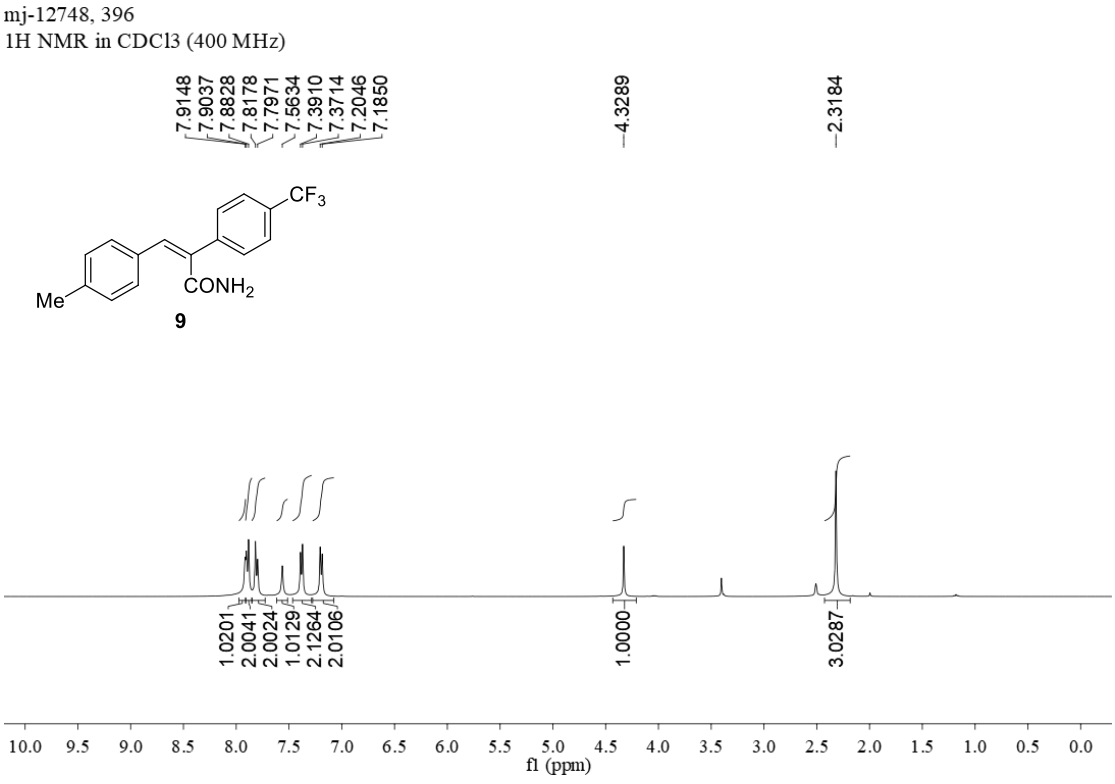


Figure S244. ^{1}H NMR spectrum of compound **9** (DMSO-d6, 25 °C, 400 MHz).

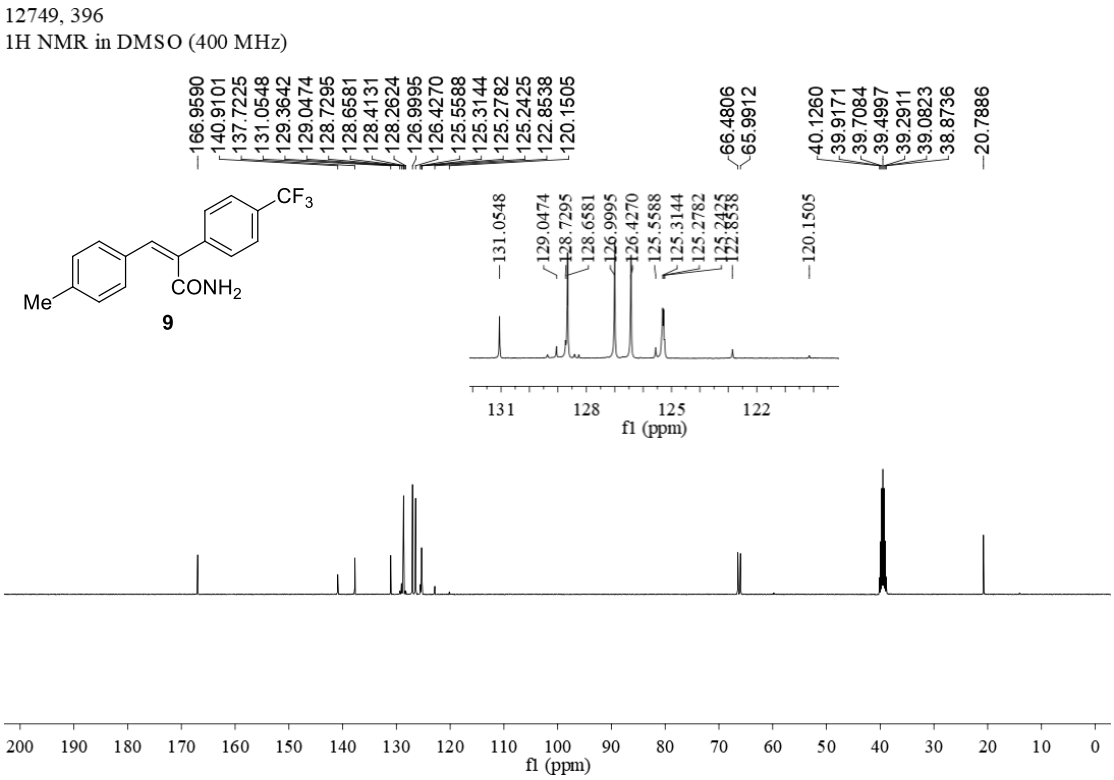


Figure S245. $^{13}C\{^{1}H\}$ NMR spectrum of compound **9** (DMSO-d6, 25 °C, 100 MHz).

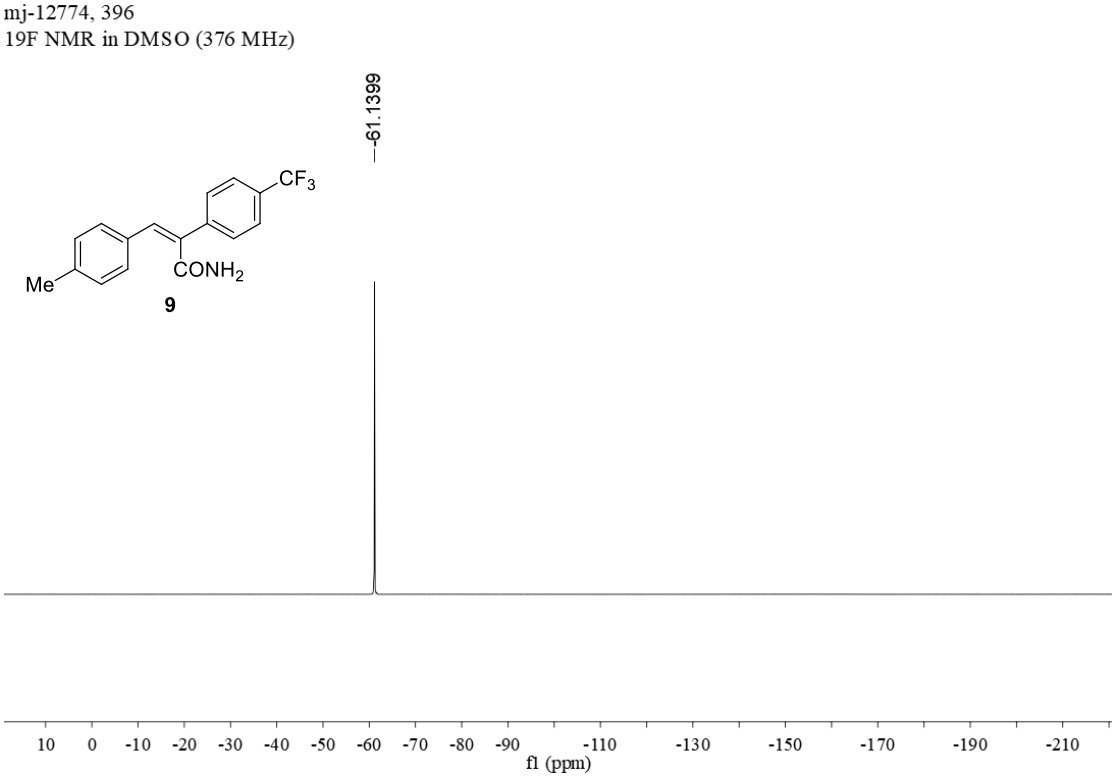


Figure S246. $^{19}F\{^{1}H\}$ NMR spectrum of compound **9** (DMSO-d6, 25 °C, 376 MHz).

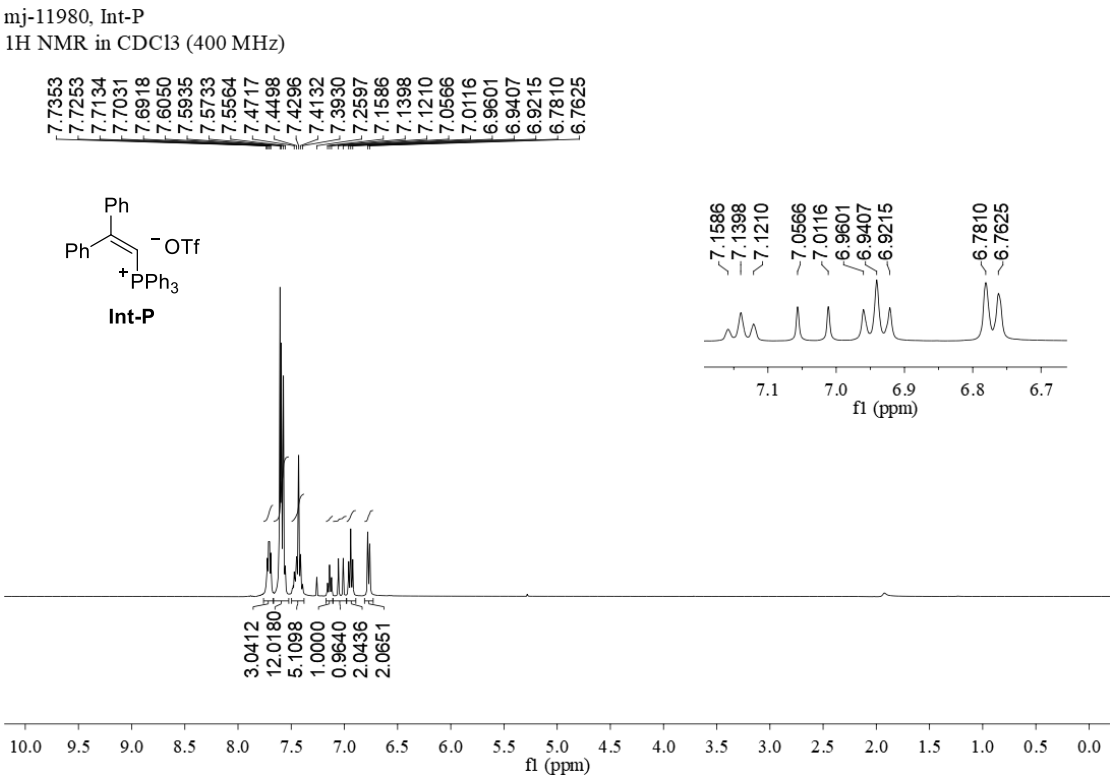


Figure S247. ^{1}H NMR spectrum of compound **Int-P** ($CDCl_3$, 25 °C, 400 MHz).

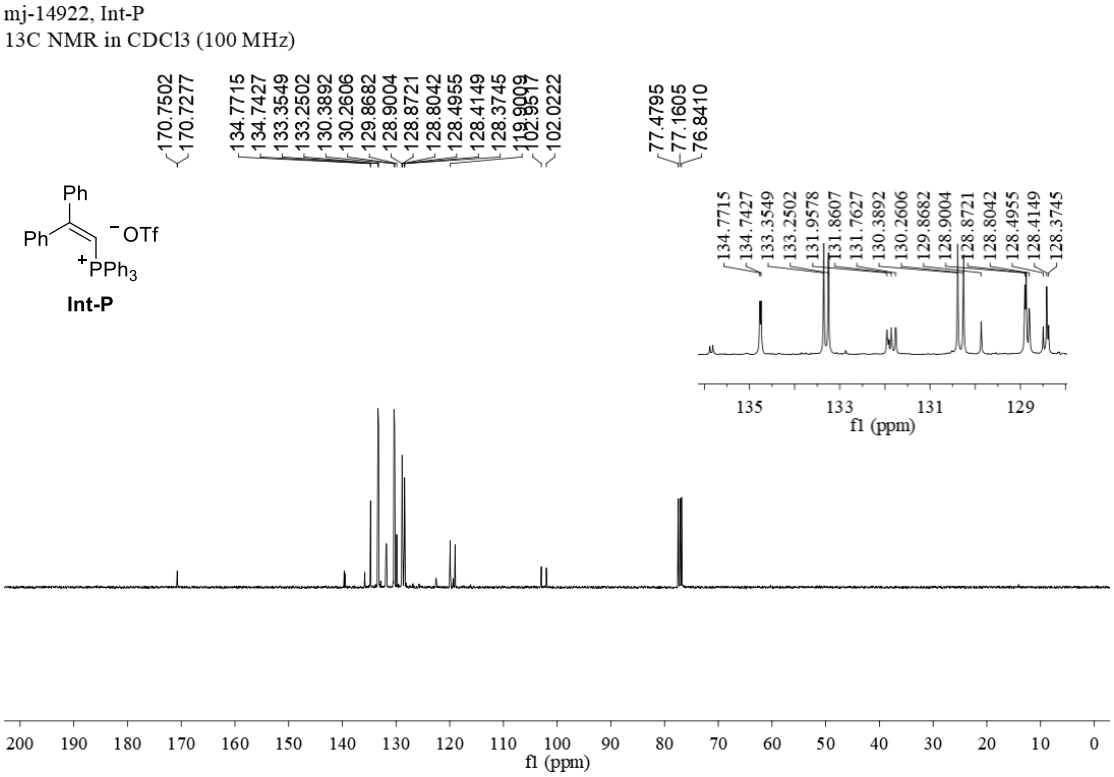


Figure S248. $^{13}C\{^{1}H\}$ NMR spectrum of compound **Int-P** ($CDCl_3$, 25 °C, 100 MHz).

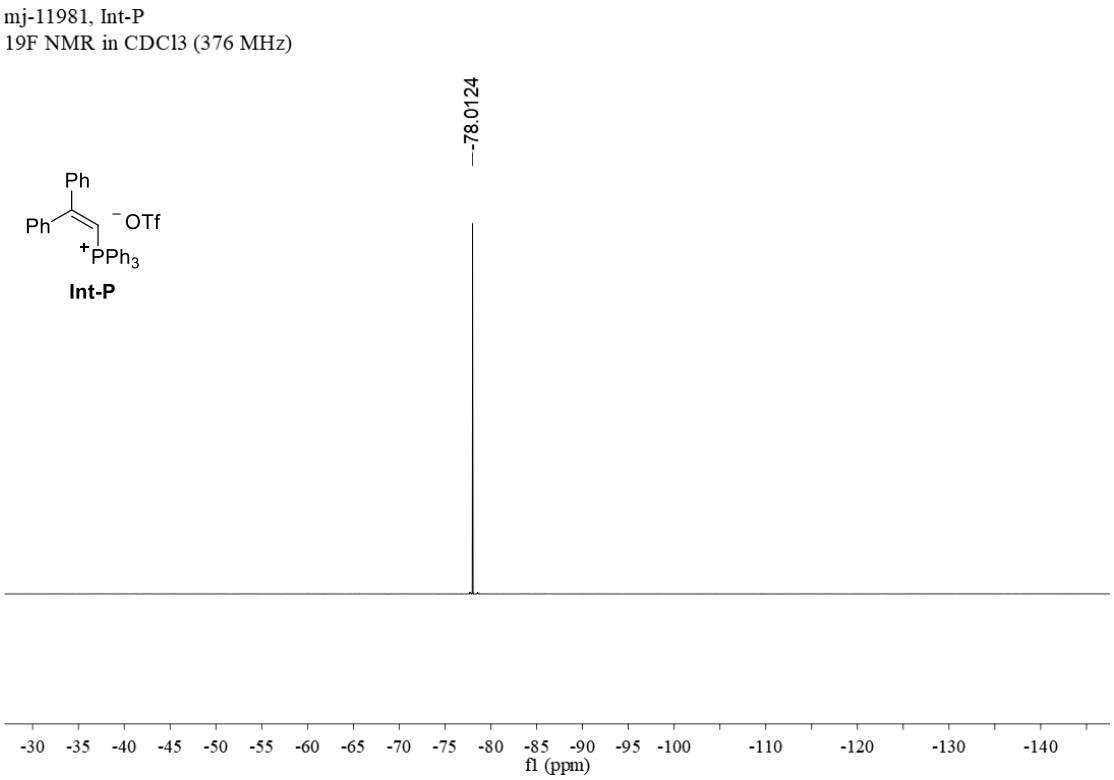


Figure S249. $^{19}F\{^{1}H\}$ NMR spectrum of compound **Int-P** ($CDCl_3$, 25 °C, 376 MHz).

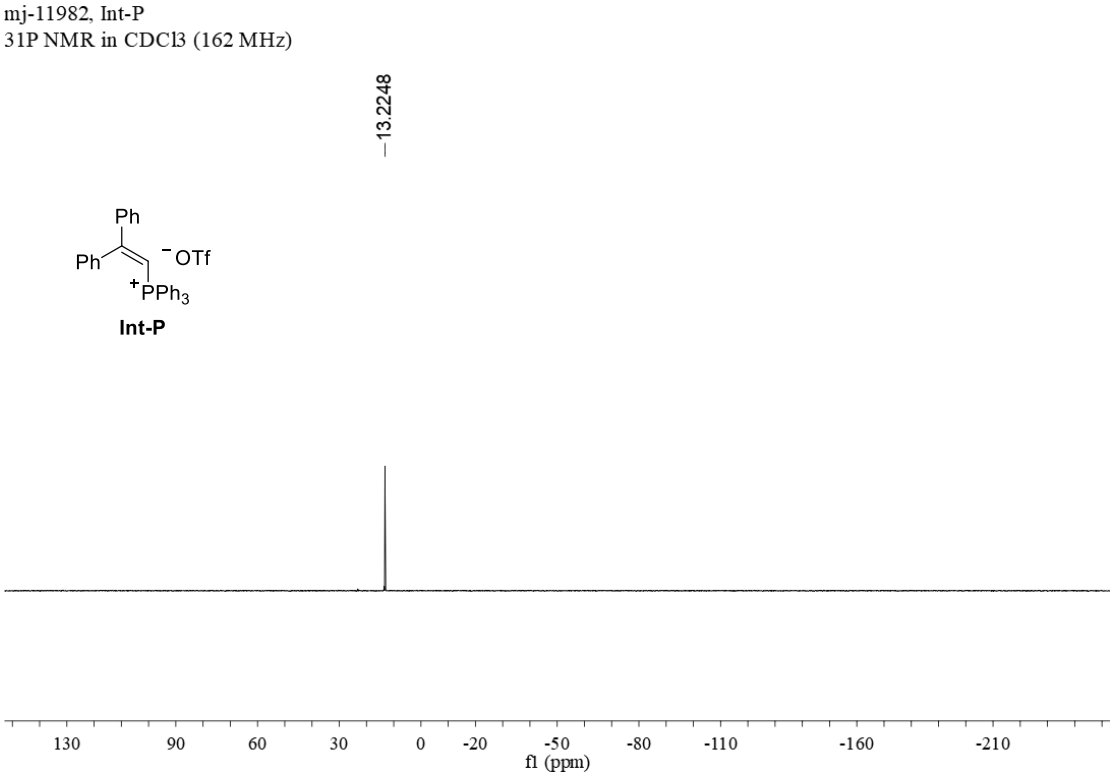


Figure S250. $^{31}P\{^{1}H\}$ NMR spectrum of compound **Int-P** ($CDCl_3$, 25 °C, 162 MHz).