Supplementary Information

Regioselective Polyfluoroarylation of Alkenyl C–H Bonds *via* Aryl to Vinyl 1,4-Palladium Migration

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Experimental procedures and analytical data

Contents:

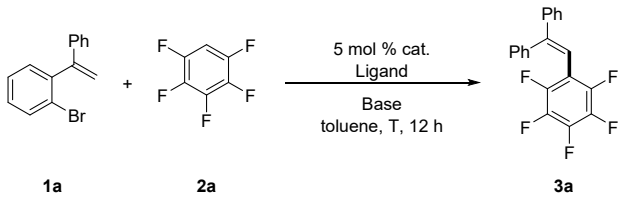
1. General considerations

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 or $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm and $\delta(^{13}C)$, 77.16 ppm). $^{19}F\{^{1}H\}$ NMR spectra are not calibrated by an internal reference. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. The *gem*-disubstituted ethylenes **1**[1], polyfluoroarenes[2] and phosphines[3] were prepared by the reported methods.

2. Optimization of the reaction conditions

A mixture of substrates **1a**, **2a**, the catalyst, ligand, and base in toluene was vigorously stirred for 12 h under an argon atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant mixture was used to measure the yield by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

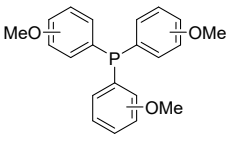
Table S1. Optimization of the reaction conditions[a]



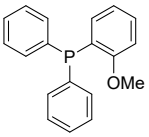
1a **2a** **3a**

Entry	**1a**:**2a** (molar ratio)	Catalyst (5 mol %)	Ligand (mol %)	Base (equiv)	T (°C)	Yield of **3a**[b] (%)
1	1:3	$Pd(OAc)_2$	PPh_3 (10)	CsOAc (2)	100	trace
2	1:3	$Pd(OAc)_2$	Xphos (10)	CsOAc (2)	100	19
3	1:3	$Pd(OAc)_2$	$P(4\text{-}FC_6H_4)_3$ (10)	CsOAc (2)	100	trace
4	1:3	$Pd(OAc)_2$	dppf (10)	CsOAc (2)	100	36
5	1:3	$Pd(OAc)_2$	dppp (10)	CsOAc (2)	100	13
6	1:3	$Pd(OAc)_2$	DPEphos (10)	CsOAc (2)	100	53
7	1:3	$Pd(OAc)_2$	Xantphos (10)	CsOAc (2)	100	trace
8	1:3	$Pd(OAc)_2$	**L1** (10)	CsOAc (2)	100	51
9	1:3	$Pd(OAc)_2$	**L2-L6** (10)	CsOAc (2)	100	0-50

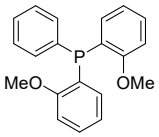
10	1:3	$Pd(OAc)_2$	**L7** (10)	CsOAc (2)	100	79
11	1:3	$Pd(OAc)_2$	**L8** (10)	CsOAc (2)	100	30
12	1:3	$Pd(OAc)_2$	**L7** (10)	CsOPiv (2)	100	30
13	1:3	$Pd(OAc)_2$	**L7** (10)	Cs_2CO_3 (2)	100	15
14	1:3	$Pd(OAc)_2$	**L7** (10)	K_2CO_3 (2)	100	trace
15	1:3	$Pd(OAc)_2$	**L7** (10)	KOAc (2)	100	trace
16	1:3	$Pd(OAc)_2$	**L7** (10)	LiO^{t}Bu (2)	100	trace
17	1:3	$Pd(OAc)_2$	**L7** (10)	CsOAc (3)	100	96
18	1:3	$Pd(OAc)_2$	**L7** (10)	CsOAc (4)	100	95
19	1:2.5	$Pd(OAc)_2$	**L7** (10)	CsOAc (3)	100	96
20	1:2	$Pd(OAc)_2$	**L7** (10)	CsOAc (3)	100	84
21	1:1.5	$Pd(OAc)_2$	**L7** (10)	CsOAc (3)	100	75
22	1:1	$Pd(OAc)_2$	**L7** (10)	CsOAc (3)	100	42
23	1:2.5	$Pd(OAc)_2$	**L7** (6)	CsOAc (3)	100	96
24	1:2.5	$Pd(OAc)_2$	**L7** (5)	CsOAc (3)	100	88
25	**1:2.5**	**$Pd(OAc)_2$**	**L7 (6)**	**CsOAc (3)**	**90**	**96**
26	1:2.5	$Pd(OAc)_2$	**L7** (6)	CsOAc (3)	80	82
27	1:2.5	$Pd(TFA)_2$	**L7** (6)	CsOAc (3)	90	61
28	1:2.5	$PdCl_2$	**L7** (6)	CsOAc (3)	90	16
29	1:2.5	$Pd(PPh_3)_4$	**L7** (6)	CsOAc (3)	90	12
30[c]	**1:2.5**	**$Pd(OAc)_2$**	**L7 (6)**	**CsOAc (3)**	**90**	**97 (96)**[d]



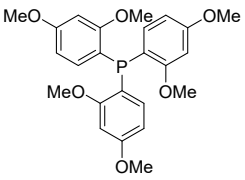
L1, 2-OMe, 51%
L2, 3-OMe, trace
L3, 4-OMe, 0%



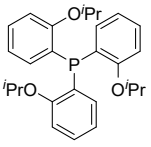
L4, trace



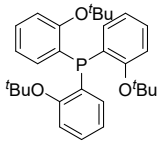
L5, 27%



L6, 50%



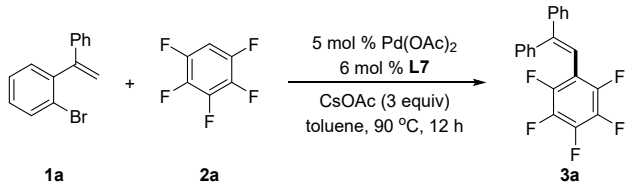
L7, 79%



L8, 30%

[a] Conditions: **1a** (0.2 mmol), **2a**, catalyst (5 mol %), ligand, base, toluene (2 mL), T °C, argon, 12 h. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] **2a** (0.3 mmol), toluene (3 mL). [d] Isolated yield given in parenthesis.

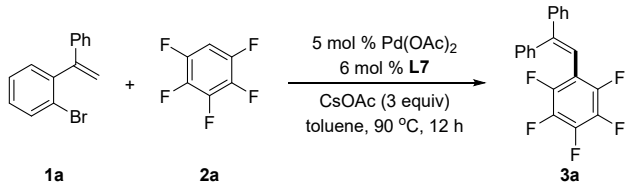
3. General procedure for the C–H polyfluoroarylation



1a **2a** **3a**

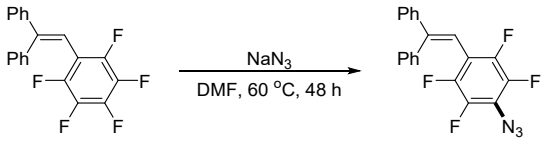
A typical procedure for the C–H polyfluoroarylation of alkenes 1 – *synthesis of 3a*: Under an argon atmosphere a mixture of alkene **1a** (78 mg, 0.3 mmol), 1,2,3,4,5-pentafluorobenzene **2a** (126 mg, 0.75 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), **L7** (7.8 mg, 0.018 mmol), and CsOAc (173 mg, 0.9 mmol) in 3 mL of toluene was stirred at 90 °C for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C) to afford **3a** as a white solid (100 mg, 96%).

4. Gram-scale preparation and synthetic applications



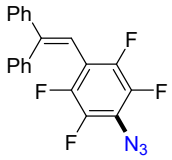
1a **2a** **3a**

Gram-scale preparation of compound 3a: Under an argon atmosphere a mixture of alkene **1a** (1037 mg, 4 mmol), 1,2,3,4,5-pentafluorobenzene **2a** (1681 mg, 10 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), **L7** (105 mg, 0.24 mmol), and CsOAc (2303 mg, 12 mmol) in 40 mL of toluene was stirred at 90 °C for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL), filtered through a short pad of celite, and rinsed with 30 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) to afford **3a** as a white solid (1.3466 g, 97%).

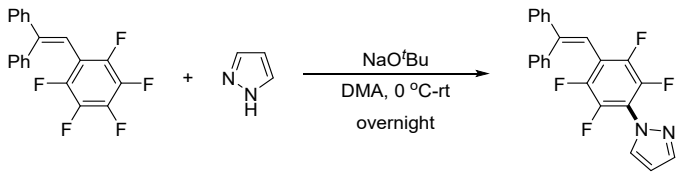


3a **5**, 88%

Coupling of 3a with sodium azide: A mixture of **3a** (104 mg, 0.3 mmol) and NaN_3 (42 mg, 0.6 mmol) in DMF (2 mL) was stirred at 60 °C for 48 h. Water was added and the mixture was extracted with ethyl acetate. The organic phase was washed with water, treated with brine, dried over $MgSO_4$, and evaporated. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 20:1, v/v) to afford **5** as a white solid (97 mg, 88%).



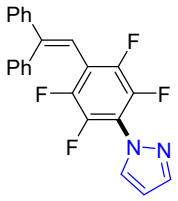
(2-(4-Azido-2,3,5,6-tetrafluorophenyl)ethene-1,1-diyl)dibenzene (5): Compound **5** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 20:1, v/v). 97 mg, 88% yield; white solid, m.p.: 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.26 (m, 8 H), 7.19–7.06 (m, 2 H), 6.61 (s, 1 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.1, 144.3 (dm, J = 246.8 Hz), 142.0–141.6 (m), 139.6, 139.5–139.2 (m), 129.6, 128.8, 128.5, 128.4, 128.4, 118.6–118.1 (m), 113.9 (t, J = 18.0 Hz), and 111.6 (t, J = 2.2 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -138.98 (dd, J = 21.5, 9.7 Hz, 2 F), -152.81 (dd, J = 21.1, 9.9 Hz, 2 F). HRMS Calcd for $C_{20}H_{12}F_4N_3$ $[M+H]^+$: 370.0962, found: 370.0971.



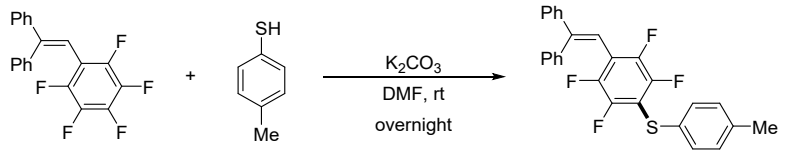
3a **6**, 87%

Coupling of 3a with pyrazole: NaO^{t}Bu (32 mg, 0.33 mmol) in DMA (1 mL) was added to pyrazole (21 mg, 0.3 mmol) in DMA (1 mL) and the mixture was cooled down to 0 °C. A solution of **3a** (0.33) in DMA (1 mL) was added dropwise to the reaction. After 15 min stirring at 0 °C, the reaction was warmed up to rt. Water was

added and the mixture was extracted with ethyl acetate. The organic phase was washed with water, treated with brine, dried over $MgSO_4$, and evaporated. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 1:2, v/v) to afford **6** as a white solid (103 mg, 87%).

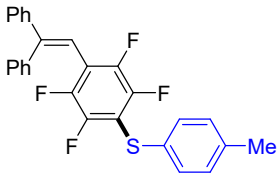


1-(4-(2,2-Diphenylvinyl)-2,3,5,6-tetrafluorophenyl)-1*H*-pyrazole (6): Compound **6** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 1:2, v/v). 103 mg, 87% yield; white solid, m.p.: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.6 Hz, 1 H), 7.56 (s, 1 H), 7.31–7.10 (m, 8 H), 7.09–6.96 (m, 2 H), 6.54 (s, 1 H), 6.39 (t, *J* = 2.1 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.8, 145.8–145.4 (m), 143.3–142.8 (m), 142.3, 141.7, 140.7–140.3 (m), 139.4, 132.2, 129.5, 128.9, 128.5, 128.5, 128.4, 118.9–118.5 (m), 117.8 (t, *J* = 17.7 Hz), 111.4, and 107.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -138.10 (td, *J* = 12.6, 3.7 Hz, 2 F), -149.48 (td, *J* = 12.6, 3.7 Hz, 2 F). HRMS Calcd for $C_{23}H_{15}F_4N_2$ $[M+H]^+$: 395.1166, found: 395.1170.

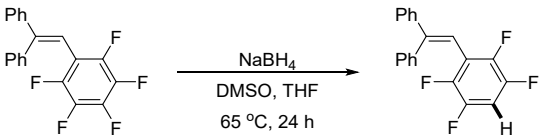


3a **7**, 64%

Coupling of 3a with thiol: A mixture of **3a** (104 mg, 0.3 mmol), 4-methylbenzenethiol (41 mg, 0.33 mmol) and K_2CO_3 (83 mg, 0.6 mmol) in DMF (6 mL) was stirred overnight at rt. Water was added and the mixture was extracted with ethyl acetate. The organic phase was washed with water, treated with brine, dried over $MgSO_4$, and evaporated. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 20:1, v/v) to afford **5** as a white solid (87 mg, 64%).

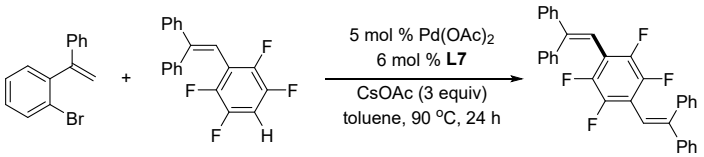


(4-(2,2-Diphenylvinyl)-2,3,5,6-tetrafluorophenyl)(*p*-tolyl)sulfane (7): Compound **7** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 20:1, v/v). 87 mg, 64% yield; white solid, m.p.: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.26 (m, 10 H), 7.15 (t, J = 7.7 Hz, 4 H), 6.68 (s, 1 H), 2.36 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.4, 146.9 (dm, J = 244.8 Hz), 144.1 (dm, J = 248.8 Hz), 141.8, 139.5, 138.0, 130.9, 130.2, 129.9, 129.6, 128.9, 128.5, 128.5, 128.4, 128.3, 119.2 (t, J = 17.8 Hz), 112.6 (t, J = 20.4 Hz), 112.1 (t, J = 2.2 Hz), and 21.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -134.30 (dd, J = 24.3, 11.8 Hz, 2 F), -138.21 (dd, J = 24.0, 11.7 Hz, 2 F). HRMS Calcd for $C_{27}H_{19}F_4S$ $[M+H]^+$: 451.1138, found: 451.1138.



3a **4m**, 86%

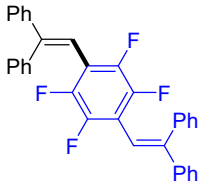
Hydrodefluorination of 3a with NaBH$_4$: $NaBH_4$ (23 mg, 0.6mmol) dissolved in DMSO (3 mL) was slowly added to **3a** (104 mg, 0.3 mmol) in THF (3 mL) and the mixture was stirred at 65 °C for 24 h. Water was added and the mixture was extracted with ethyl acetate. The organic phase was washed with water, treated with brine, dried over $MgSO_4$, and evaporated. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) to afford **4m** as a white solid (85 mg, 86%).



1a **4m** **4m'**, 86%

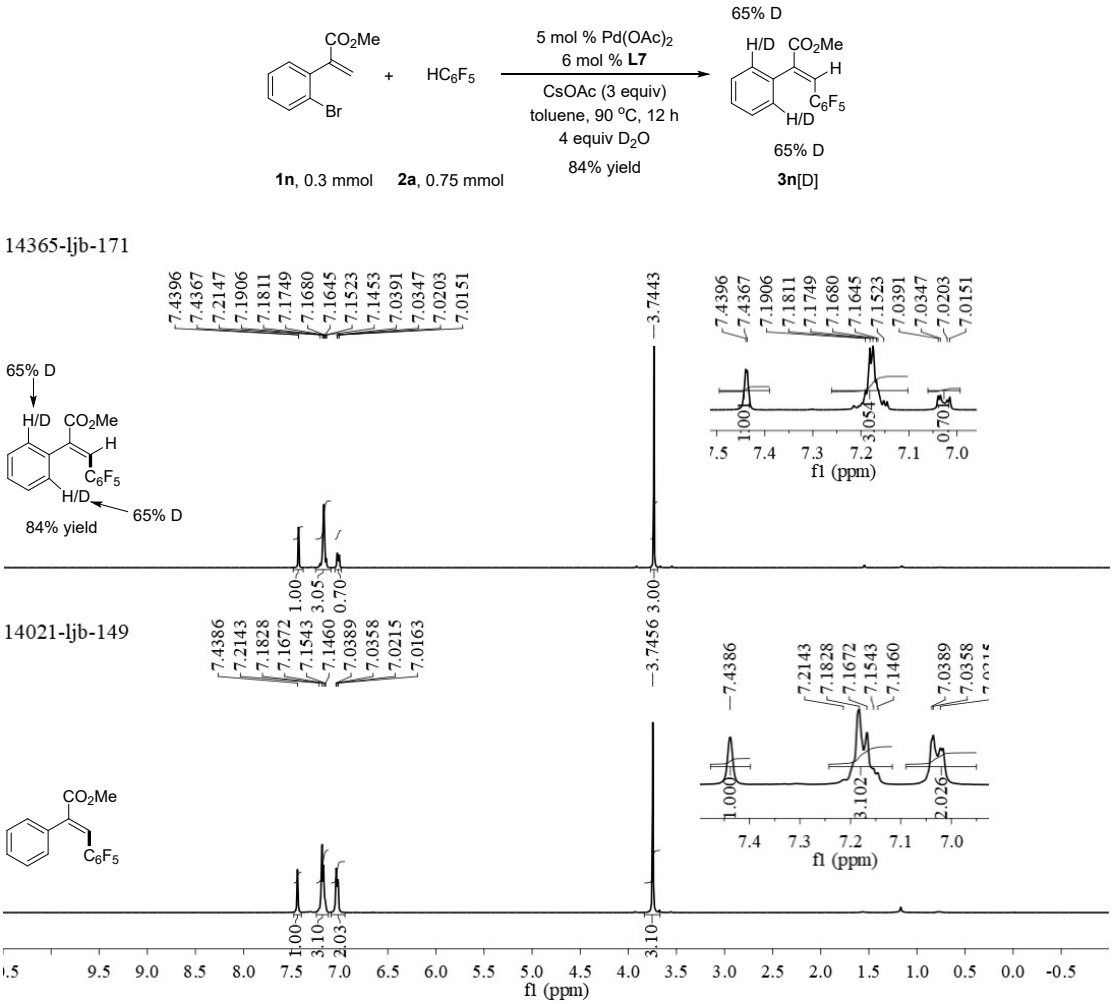
***Synthesis of 4m'*:** Under an argon atmosphere a mixture of alkene **1a** (78 mg, 0.3 mmol), **4m** (246 mg, 0.75 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), **L7** (7.8 mg, 0.018 mmol), and CsOAc (173 mg, 0.9 mmol) in 3 mL of toluene was stirred at 90 °C for 24

h. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 15:1, v/v) to afford **4m'** as a white solid (131 mg, 86%).

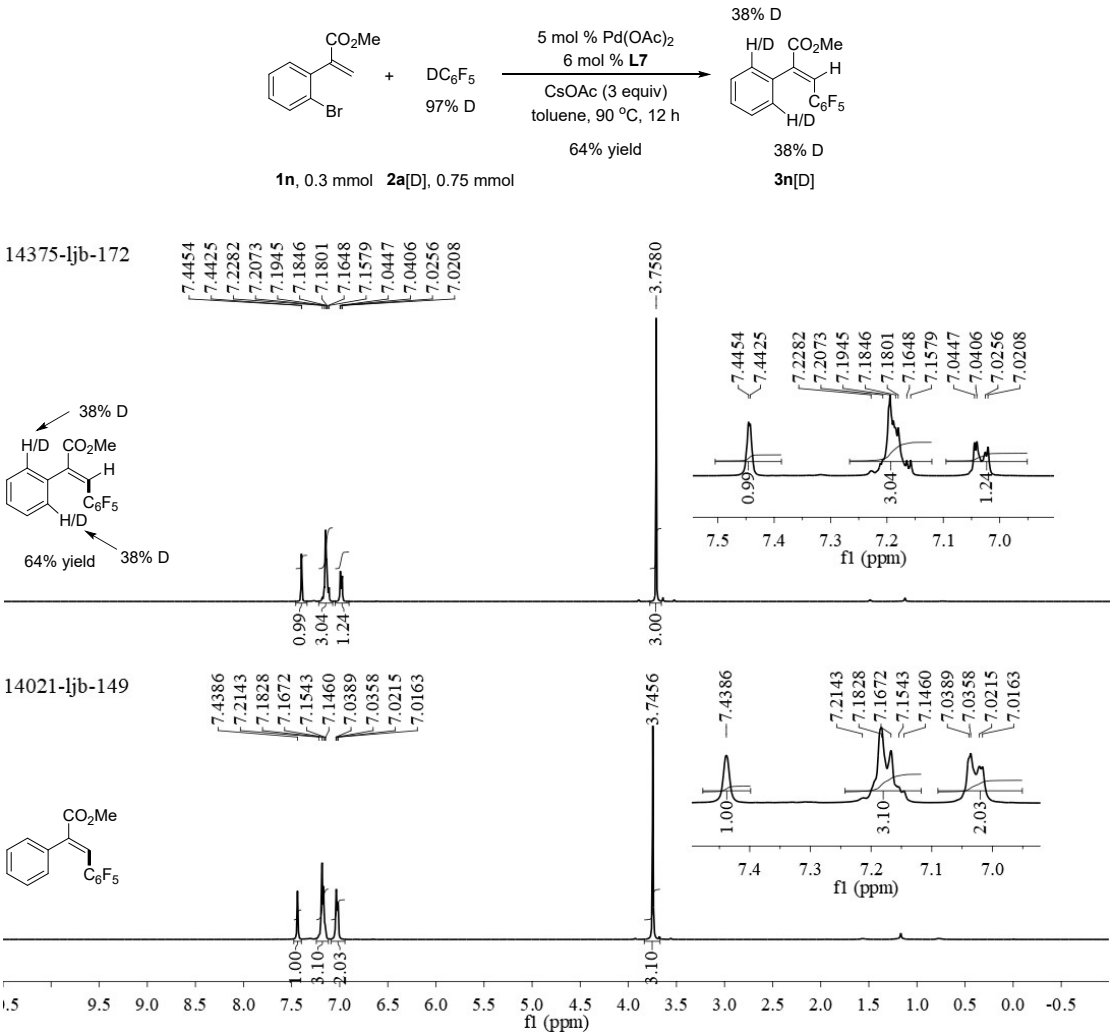


((Perfluoro-1,4-phenylene)bis(ethene-2,1,1-triyl))tetrabenzene (4m'): Compound **4m'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 15:1, v/v). 131 mg, 86% yield; white solid, m.p.: 195-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 10 H), 7.19–7.10 (m, 6 H), 7.02–6.93 (m, 4 H), 6.49 (s, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.6, 145.3–144.9 (m), 142.9–142.4 (m), 142.0, 139.7, 129.6, 128.7, 128.5, 128.4, 128.2, 116.8–116.3 (m), and 112.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -140.47 (s, 4 F). HRMS Calcd for $C_{34}H_{23}F_4$ $[M+H]^+$: 507.1730, found: 507.1737.

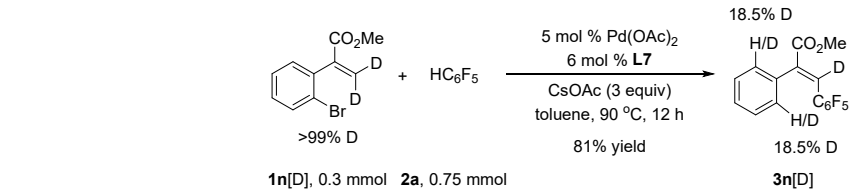
5. Deuterium-labelling experiments

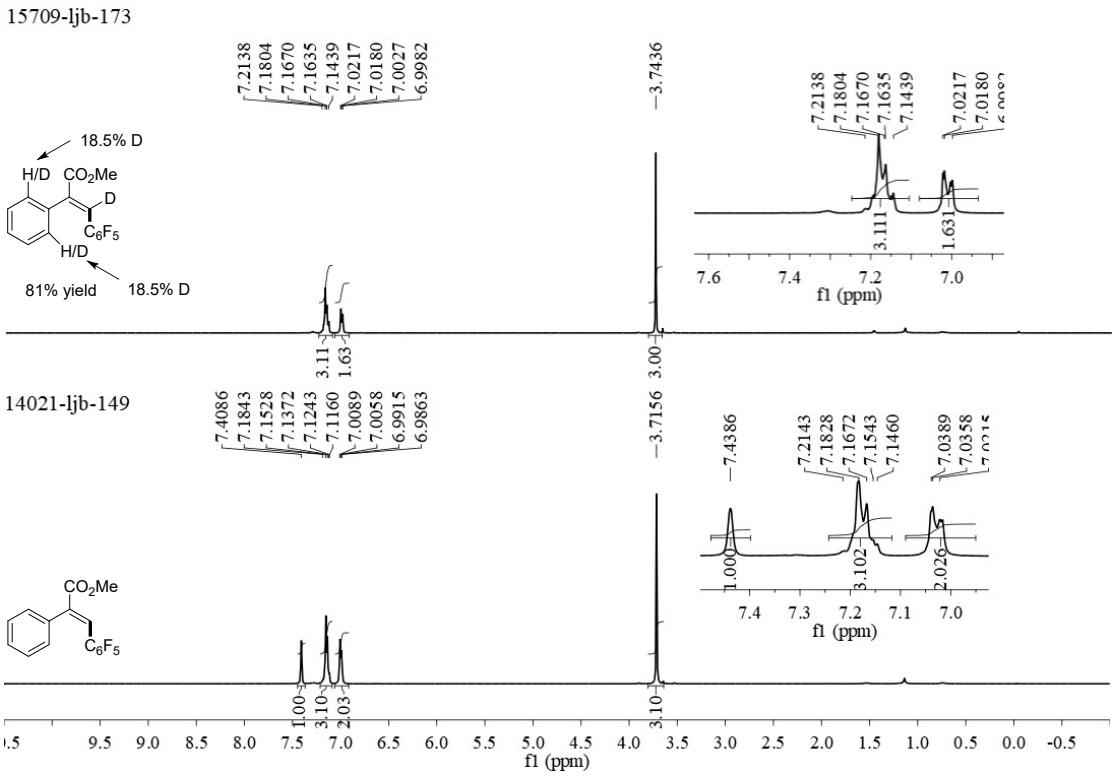


Under an argon atmosphere a mixture of alkene **1n** (72 mg, 0.3 mmol), 1,2,3,4,5-pentafluorobenzene **2a** (126 mg, 0.75 mmol), D_2O (24 mg, 1.2 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), **L7** (7.8 mg, 0.018 mmol), and CsOAc (173 mg, 0.9 mmol) in 3 mL of toluene was stirred at 90 °C for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 3:1, v/v) to afford a white solid (83 mg, 84%). m.p.: 44-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.2 Hz, 1 H), 7.26–7.10 (m, 3 H), 7.07–6.69 (m, 0.70 H), 3.74 (s, 3 H).



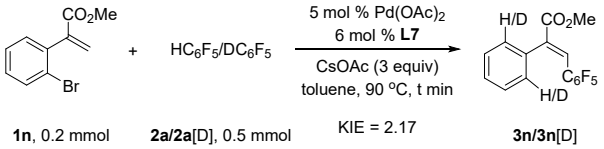
Under an argon atmosphere a mixture of alkene **1n** (72 mg, 0.3 mmol), 1,2,3,4,5-pentafluorobenzene **2a**[D][4] (127 mg, 0.75 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), **L7** (7.8 mg, 0.018 mmol), and CsOAc (173 mg, 0.9 mmol) in 3 mL of toluene was stirred at 90 °C for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 3:1, v/v) to afford a white solid (64 mg, 64%). m.p.: 68-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 1.2 Hz, 1 H), 7.27–7.12 (m, 3 H), 7.10–6.95 (m, 1.24 H), 3.76 (s, 3 H).



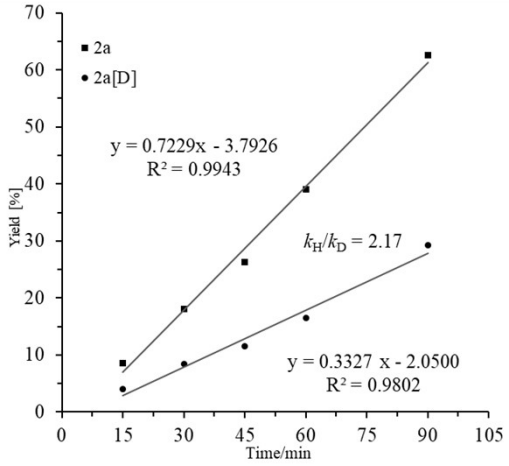


Under an argon atmosphere a mixture of alkene **1n**[D] (73 mg, 0.3 mmol), 1,2,3,4,5-pentafluorobenzene **2a** (126 mg, 0.75 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), **L7** (7.8 mg, 0.018 mmol), and CsOAc (173 mg, 0.9 mmol) in 3 mL of toluene was stirred at 90 °C for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a short pad of celite, and rinsed with 5 mL of CH_2Cl_2. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 2:1, v/v) to afford a white solid (80 mg, 81%). m.p.: 54-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.10 (m, 3 H), 7.10–6.95 (m, 1.63 H), 3.74 (s, 3 H).

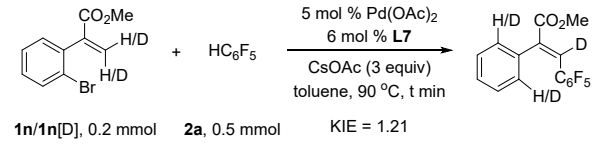
6. Kinetic isotope effect (KIE) experiments



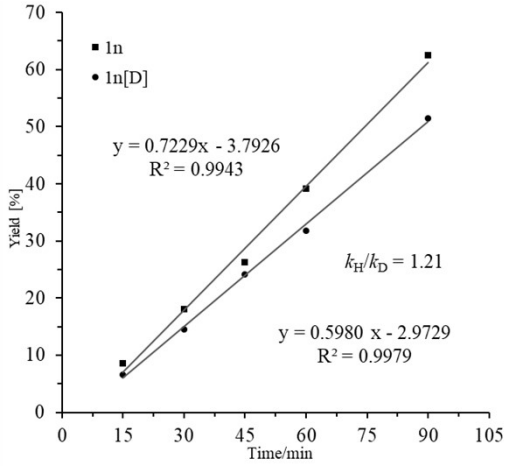
1n, 0.2 mmol **2a/2a**[D], 0.5 mmol KIE = 2.17 **3n/3n**[D]



The reaction of **2a** or its deuterated form **2a**[D] was carried out with **1n** in two tubes for the given time under the optimized conditions, respectively. The reaction mixtures were concentrated and purified by flash column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 1:1, v/v), and then examined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.



1n/**1n**[D], 0.2 mmol **2a**, 0.5 mmol KIE = 1.21

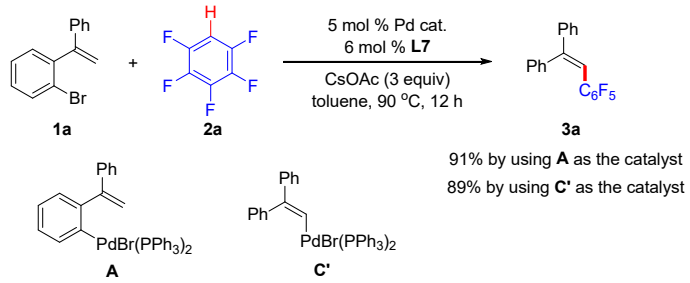


The reaction of **1n** or its deuterated form **1n**[D] was carried out with **2a** in two

tubes for the given time under the optimized conditions, respectively. The reaction mixtures were concentrated and purified by flash column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/CH_2Cl_2 = 1:1, v/v), and then examined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

7. Intermediate verification experiments

Under an argon atmosphere a mixture of alkene **1a** (52 mg, 0.2 mmol), 1,2,3,4,5-pentafluorobenzene (**2a**, 84 mg, 0.5 mmol), intermediate complex **A** or **C'** (8.9 mg, 0.01 mmol), **L7** (5.3 mg, 0.012 mmol) and CsOAc (115 mg, 0.6 mmol) in 2 mL of toluene was stirred at 90 °C for 12 h. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The yields of **3a** (91% by using **A** as the catalyst and 89% by using **C'** as the catalyst) were determined by ^1H NMR spectroscopy by means of 1,3,5-trimethoxybenzene as the internal standard.



8. X-Ray crystallographic study

Single crystal X-ray diffraction study for compound **3j** was 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 structure was solved by direct methods and refined by full-matrix least squares on 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 number CCDC 2222843 for

3j. 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).

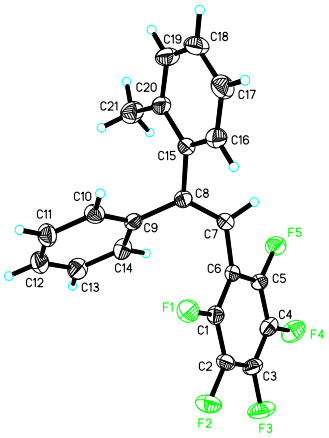


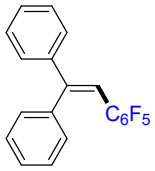
Figure S1. Molecular structure of **3j**.

Table S2. Crystal Data and Structure Refinement for 3j

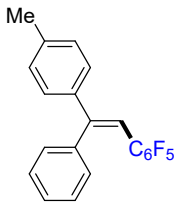
Identification code	lj-797	
Empirical formula	$C_{21}H_{13}F_5$	
Formula weight	360.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.338(3) Å	α = 90°
	b = 5.6821(11) Å	β = 113.49(3)°
	c = 12.867(3) Å	γ = 90°
Volume	827.3(3) Å^3	
Z	2	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	0.123 mm^{-1}	
F(000)	368	
Crystal size	0.190 x 0.150 x 0.110 mm^3	
Theta range for data collection	3.601 to 24.998°.	
Index ranges	-11<=h<=14, -6<=k<=5, -14<=l<=13	
Reflections collected	2276	
Independent reflections	1741 [R(int) = 0.0139]	
Completeness to theta = 25.242°	89.4 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5487
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1741 / 1 / 237
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0297, wR_2 = 0.0765
R indices (all data)	R_1 = 0.0352, wR_2 = 0.0796
Absolute structure parameter	-0.3(5)
Extinction coefficient	0.086(8)
Largest diff. peak and hole	0.143 and -0.106 e.Å^{-3}

9. Analytical data

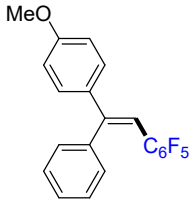


(2-(Perfluorophenyl)ethene-1,1-diyl)dibenzene (3a)[6]: Following the general procedure, compound **3a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 100 mg, 96% yield; white solid, m.p.: 43-44 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 5 H), 7.21–7.12 (m, 3 H), 7.03–6.94 (m, 2 H), 6.46 (d, *J* = 1.0 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.4, 145.6 (dm, *J* = 11.2 Hz), 141.8–141.4 (m), 139.5, 139.3–138.6 (m), 136.6–136.1 (m), 129.5, 128.9, 128.5, 128.4, 128.4, 113.2 (td, *J* = 18.1, 4.0 Hz), and 111.1 (d, *J* = 1.8 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -138.77 (dd, *J* = 23.0, 8.0 Hz, 2 F), -156.30 (t, *J* = 20.9 Hz, 1 F), -162.89 (td, *J* = 22.4, 7.8 Hz, 2 F).

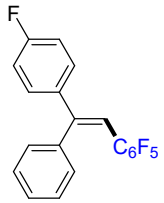


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(*p*-tolyl)vinyl)benzene (3b): Following the general procedure, compound **3b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 102 mg, 94%; white solid, m.p.: 81-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.06 (m, 5 H), 7.02

(d, J = 8.1 Hz, 2 H), 6.99–6.91 (m, 2 H), 6.41 (s, 1 H), 2.24 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 144.3 (dm, J = 248.4 Hz), 141.9–141.3 (m), 139.7, 139.3–138.6 (m), 136.6–136.1 (m), 129.6, 129.2, 128.3, 113.4 (td, J = 18.1, 3.8 Hz), 110.2 (d, J = 1.7 Hz), and 21.3. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -138.85 (dd, J = 23.0, 7.9 Hz, 2 F), -156.56 (t, J = 20.9 Hz, 1 F), -163.01 (td, J = 22.4, 7.8 Hz, 2 F). HRMS Calcd for $C_{21}H_{14}F_5$ $[M+H]^+$: 361.1010, found: 361.1014.

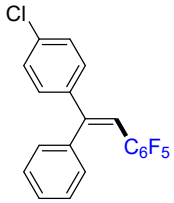


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-(4-methoxyphenyl)-2-phenylvinyl)benzene (3c): Following the general procedure, compound **3c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 10:1, v/v). 97 mg, 86% yield; white solid, m.p.: 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.20 (m, 5 H), 7.14–7.03 (m, 2 H), 6.93–6.81 (m, 2 H), 6.48 (d, J = 0.8 Hz, 1 H), 3.81 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 150.8, 144.3 (dm, J = 246.3 Hz), 141.7–141.2 (m), 139.7, 139.1–138.6 (m), 136.5–136.1 (m), 134.3, 129.7, 129.6, 128.3, 114.0–112.9 (m), 109.2 (d, J = 1.7 Hz), and 55.4. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -138.99 (dd, J = 22.9, 7.8 Hz, 2 F), -156.77 (t, J = 21.0 Hz, 1 F), -163.11 (td, J = 22.3, 7.7 Hz, 2 F). HRMS Calcd for $C_{21}H_{14}F_5O$ $[M+H]^+$: 377.0959, found: 377.0958.

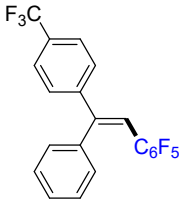


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-(4-fluorophenyl)-2-phenylvinyl)benzene (3d): Following the general procedure, compound **3d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 101 mg, 92% yield; white solid, m.p.: 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 5 H), 7.14–7.01 (m, 4 H), 6.53 (d, J = 0.7 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 249.0 Hz), 150.4, 144.3 (dm, J = 246.8 Hz), 141.9–141.4 (m), 139.3,

139.3–138.6 (m), 137.9 (d, J = 3.4 Hz), 136.6–136.1 (m), 130.2 (d, J = 8.2 Hz), 129.5, 128.6, 128.5, 115.4 (d, J = 21.7 Hz), 113.1 (td, J = 18.0, 3.9 Hz), and 110.9. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -112.85 (s, 1 F), -138.92 (dd, J = 22.8, 7.8 Hz, 2 F), -156.18 (t, J = 20.8 Hz, 1 F), -162.69– -163.15 (m, 1 F). HRMS Calcd for $C_{20}H_{11}F_6$ $[M+H]^+$: 365.0759, found: 365.0756.

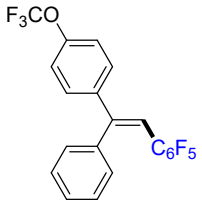


(*E*)-1-(2-(4-Chlorophenyl)-2-phenylvinyl)-2,3,4,5,6-pentafluorobenzene (3e): Following the general procedure, compound **3e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 107 mg, 94%; white solid, m.p.: 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 7 H), 7.01–6.91 (m, 2 H), 6.45 (d, J = 1.0 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.2, 144.3 (dm, J = 247.0 Hz), 142.0–141.5 (m), 140.2, 139.5–138.6 (m), 136.7–136.1 (m), 134.9, 129.7, 129.5, 128.7, 128.5, 112.9 (td, J = 18.0, 3.9 Hz), and 111.5 (d, J = 1.9 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -138.76 (dd, J = 22.4, 7.8 Hz, 2 F), -155.87 (t, J = 20.9 Hz, 1 F), -162.71 (td, J = 22.2, 8.0 Hz, 2 F). HRMS Calcd for $C_{20}H_{11}ClF_5$ $[M+H]^+$: 381.0464, found: 381.0463.

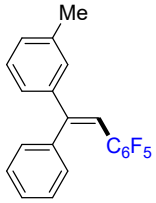


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(4-(trifluoromethyl)phenyl)vinyl)benzene (3f): Following the general procedure, compound **3f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 94 mg, 76% yield; white solid, m.p.: 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 1 H), 7.37 (d, J = 8.1 Hz, 1 H), 7.28–7.12 (m, 3 H), 6.98 (d, J = 6.6 Hz, 2 H), 6.53 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.1, 145.2, 144.3 (dm, J = 247.6 Hz), 140.7 (dm, J = 252.6 Hz), 139.2–138.6 (m), 136.7–136.2 (m), 130.8 (q, J = 32.6 Hz), 129.4, 128.8, 128.8, 128.7, 125.5 (q, J = 3.7

Hz), 124.2 (q, J = 270.0 Hz), 113.1, and 112.7 (td, J = 18.0, 4.0 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.65 (s, 3 F), -138.63 (dd, J = 22.3, 7.6 Hz, 2 F), -155.38 (t, J = 20.9 Hz, 1 F), -162.51 (td, J = 22.5, 7.6 Hz, 2 F). HRMS Calcd for $C_{21}H_{11}F_8$ $[M+H]^+$: 415.0728, found: 415.0727.

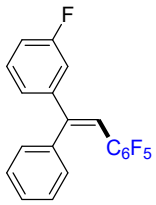


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(4-(trifluoromethoxy)phenyl)vinyl)benzene (3g): Following the general procedure, compound **3g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 108 mg, 84% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.38 (m, 2 H), 7.38–7.27 (m, 3 H), 7.23 (d, J = 8.1 Hz, 2 H), 7.16–7.06 (m, 2 H), 6.61 (d, J = 0.7 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.1, 149.7 (d, J = 1.4 Hz), 144.4 (dm, J = 247.1 Hz), 142.1–141.6 (m), 140.4, 139.6–138.7 (m), 136.7–136.2 (m), 129.9, 129.5, 128.7, 128.6, 120.9, 120.7 (q, J = 255.8 Hz), 112.9 (td, J = 18.1, 3.9 Hz), and 111.9 (d, J = 1.5 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -57.92 (s, 3 F), -138.87 (dd, J = 23.3, 8.8 Hz, 2 F), -155.93 (t, J = 21.3 Hz, 1 F), -162.82 (dt, J = 23.5, 8.7 Hz, 2 F). HRMS Calcd for HRMS Calcd for $C_{21}H_{11}F_8O$ $[M+H]^+$: 431.0677, found: 431.0679.

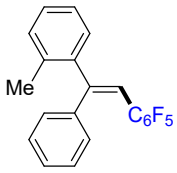


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(*m*-tolyl)vinyl)benzene (3h): Following the general procedure, compound **3h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 105 mg, 97% yield; white solid, m.p.: 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–6.93 (m, 9 H), 6.45 (d, J = 0.9 Hz, 1 H), 2.24 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.5, 144.3 (dm, J = 246.9 Hz), 141.9–141.3 (m), 139.6, 139.4–138.6 (m), 138.1, 136.8–136.1 (m), 129.6, 129.5, 129.1, 128.4, 125.7, 113.3 (td, J = 18.2, 4.0 Hz), 111.0 (d, J

= 1.7 Hz), and 21.5. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -138.86 (dd, *J* = 23.0, 8.0 Hz, 2 F), -156.43 (t, *J* = 20.8 Hz, 1 F), -162.87– -163.09 (m, 2 F). HRMS Calcd for $C_{23}H_{21}$ $[M+H]^+$: 297.1638, found: 297.1636. HRMS Calcd for $C_{21}H_{14}F_5$ $[M+H]^+$: 361.1010, found: 361.1013.

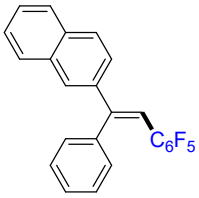


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-(3-fluorophenyl)-2-phenylvinyl)benzene (3i): Following the general procedure, compound **3i** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 107 mg, 98% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 4 H), 7.23–7.00 (m, 5 H), 6.63 (d, *J* = 1.0 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.3 Hz), 150.3, 144.3 (dm, *J* = 247.1 Hz), 144.0 (d, *J* = 7.4 Hz), 140.6 (dm, *J* = 252.2 Hz), 139.1–138.7 (m), 136.7–1336.1 (m), 129.9 (d, *J* = 8.2 Hz), 129.5, 128.7, 128.5, 124.1 (d, *J* = 2.8 Hz), 115.7 (d, *J* = 21.2 Hz), 115.4 (d, *J* = 22.3 Hz), 112.9 (td, *J* = 18.0, 3.9 Hz), and 112.1 (d, *J* = 1.8 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -113.02 (s, 1 F), -138.73 (dd, *J* = 22.4, 7.9 Hz, 2 F), -155.85 (t, *J* = 20.8 Hz, 1 F), -162.65– -163.80 (m, 2 F). HRMS Calcd for $C_{20}H_{11}F_6$ $[M+H]^+$: 365.0759, found: 365.0759.

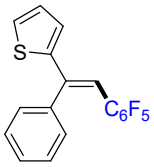


(*E*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(*o*-tolyl)vinyl)benzene (3j): Following the general procedure, compound **3j** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 98 mg, 91% yield; white solid, m.p.: 105-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.04 (m, 7 H), 6.97–6.86 (m, 2 H), 6.16 (d, *J* = 1.0 Hz, 1 H), 2.01 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 144.4 (dm, *J* = 246.8 Hz), 142.3, 142.0–141.4 (m), 139.7, 139.5–138.7 (m), 136.7–136.2 (m), 130.7, 130.2, 128.5, 128.4, 128.4, 128.3, 125.9, 113.2–

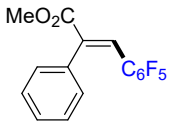
112.7 (m), and 20.5. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -139.11 (dd, J = 22.6, 8.0 Hz, 2 F), -156.24 (t, J = 20.9 Hz, 1 F), -162.55– -162.83 (m, 2 F). HRMS Calcd for $C_{21}H_{14}F_5$ $[M+H]^+$: 361.1010, found: 361.1012.



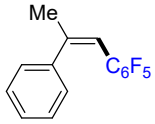
(*E*)-2-(2-(Perfluorophenyl)-1-phenylvinyl)naphthalene (3k): Following the general procedure, compound **3k** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 107 mg, 90% yield; white solid, m.p.: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.59 (m, 4 H), 7.42–7.28 (m, 3 H), 7.23–7.08 (m, 3 H), 7.08–6.94 (m, 2 H), 6.55 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.3, 144.3 (dm, J = 247.1 Hz), 141.9–141.4 (m), 139.5, 139.3–138.6 (m), 136.6–136.1 (m), 133.5, 133.2, 129.6, 128.5, 128.5, 128.5, 128.1, 128.1, 127.7, 126.7, 126.6, 126.0, 113.5–112.9 (m), and 111.6 (d, J = 1.3 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -138.67 (dd, J = 22.9, 7.8 Hz, 2 F), -156.12 (t, J = 21.0 Hz, 1 F), -162.74 (td, J = 22.4, 7.7 Hz, 2 F). HRMS Calcd for $C_{24}H_{14}F_5$ $[M+H]^+$: 397.1010, found: 397.1005.



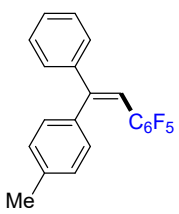
(*E*)-2-(2-(Perfluorophenyl)-1-phenylvinyl)thiophene (3l): Following the general procedure, compound **3l** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 72 mg, 68% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 4 H), 7.25–7.18 (m, 2 H), 7.06–6.98 (m, 1 H), 6.96–6.88 (m, 1 H), 6.69 (d, J = 0.7 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.7–145.2 (m), 144.5, 143.2–142.9 (m), 141.8–141.3 (m), 139.3–138.3 (m), 136.5–136.0 (m), 129.3, 128.8, 128.4, 128.1, 127.7, 126.7, 112.6 (td, J = 18.0, 4.0 Hz), and 109.3 (d, J = 1.7 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -138.39 (dd, J = 23.0, 7.9 Hz, 2 F), -156.00 (t, J = 20.9 Hz, 1 F), -162.84 (td, J = 23.0, 8.0 Hz, 2 F). HRMS Calcd for $C_{18}H_{10}F_5S$ $[M+H]^+$: 353.0418, found: 353.0415.



Methyl (*E*)-3-(perfluorophenyl)-2-phenylacrylate (3m): Following the general procedure, compound **3m** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 2:1, v/v). 84 mg, 85% yield; white solid, m.p.: 69-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1 H), 7.24–7.12 (m, 3 H), 7.08–6.94 (m, 2 H), 3.75 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 145.4–145.0 (m), 143.0–142.2 (m), 141.2, 140.2–139.7 (m), 137.6 (dm, J = 251.5 Hz), 134.5, 129.1, 128.7, 128.2, 124.5 (d, J = 1.7 Hz), 110.8 (td, J = 17.7, 4.0 Hz), and 52.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -137.27– -137.38 (m, 2 F), -153.45 (t, J = 20.8 Hz, 1 F), -161.80– -162.17 (m, 2 F). HRMS Calcd for $C_{16}H_{10}F_5O_2$ $[M+H]^+$: 329.0595, found: 329.0600.

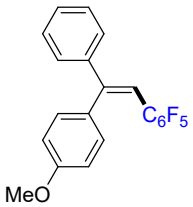


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-phenylprop-1-en-1-yl)benzene (3n): Following the general procedure, compound **3n** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 23 mg, 26% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.14 (m, 3 H), 7.08–6.99 (m, 2 H), 6.07 (t, J = 1.2 Hz, 1 H), 2.25 (d, J = 1.4 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 144.2 (dm, J = 245.7 Hz), 141.6–141.1 (m), 140.8, 139.1–138.5 (m), 136.5–136.0 (m), 128.4, 128.0, 127.1, 113.5–112.9 (m), 110.1 (d, J = 1.6 Hz), and 25.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -139.79 (dd, J = 23.9, 8.9 Hz, 2 F), -157.06 (t, J = 21.2 Hz, 1 F), -162.70– -163.83 (m, 2 F). HRMS Calcd for $C_{15}H_{10}F_5$ $[M+H]^+$: 285.0697, found: 285.0685.

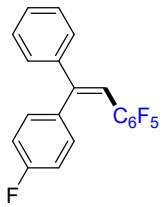


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(*p*-tolyl)vinyl)benzene (3o):

Following the general procedure, compound **3o** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 101 mg, 93% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 5 H), 6.90 (dd, *J* = 34.1, 8.0 Hz, 4 H), 6.40 (s, 1 H), 2.21 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.4, 144.3 (dm, *J* = 246.8 Hz), 142.0, 141.9–141.3 (m), 139.3–138.6 (m), 138.3, 136.7–136.1 (m), 129.5, 129.1, 128.8, 128.5, 128.4, 113.4 (td, *J* = 18.1, 3.9 Hz), 110.7 (d, *J* = 1.4 Hz), and 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -138.80 (dd, *J* = 22.9, 7.9 Hz, 2 F), -156.57 (t, *J* = 20.9 Hz, 1 F), -162.91 (td, *J* = 22.2, 7.8 Hz, 2 F). HRMS Calcd for $C_{21}H_{14}F_5$ [M+H]$^{+}$: 361.1010, found: 361.1012.

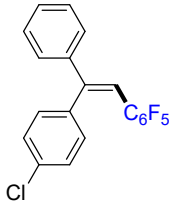


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-(4-methoxyphenyl)-2-phenylvinyl)benzene (3p): Following the general procedure, compound **3p** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 10:1, v/v). 108 mg, 95% yield; white solid, m.p.: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5 H), 7.11–7.00 (m, 2 H), 6.90–6.77 (m, 2 H), 6.53 (d, *J* = 0.6 Hz, 1 H), 3.83 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 151.0, 144.3 (dm, *J* = 246.8 Hz), 142.1, 141.8–141.2 (m), 139.3–138.6 (m), 136.7–136.1 (m), 131.8, 130.9, 128.8, 128.5, 128.4, 114.2–113.2 (m), 110.3 (d, *J* = 1.7 Hz), and 55.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -138.89 (dd, *J* = 23.1, 8.0 Hz, 2 F), -156.70 (t, *J* = 20.9 Hz, 1 F), -162.93 (td, *J* = 23.0, 8.1 Hz, 2 F). HRMS Calcd for $C_{21}H_{14}F_5O$ [M+H]$^{+}$: 377.0959, found: 377.0961.

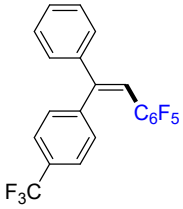


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-(4-fluorophenyl)-2-phenylvinyl)benzene (3q): Following the general procedure, compound **3q** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 90 mg, 82% yield;

white solid, m.p.: 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.33 (m, 5 H), 7.18–7.07 (m, 2 H), 7.06–6.95 (m, 2 H), 6.62 (d, *J* = 0.7 Hz, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 246.5 Hz), 150.3, 144.3 (dm, *J* = 247.0 Hz), 142.0–141.4 (m), 139.5–138.6 (m), 136.7–136.2 (m), 135.5 (d, *J* = 3.4 Hz), 131.4 (d, *J* = 8.1 Hz), 129.0, 128.6, 128.4, 115.5 (d, *J* = 21.5 Hz), 113.0 (td, *J* = 18.0, 3.9 Hz), and 111.4 (d, *J* = 1.1 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -112.88 (s, 1 F), -138.83 (dd, *J* = 23.6, 8.8 Hz, 2 F), -155.95 (t, *J* = 21.2 Hz, 1 F), -159.18– -166.49 (m, 2 F). HRMS Calcd for $C_{20}H_{11}F_6$ $[M+H]^+$: 365.0759, found: 365.0758.

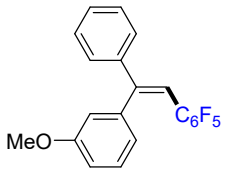


(*Z*)-1-(2-(4-Chlorophenyl)-2-phenylvinyl)-2,3,4,5,6-pentafluorobenzene (3r): Following the general procedure, compound **3r** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 97 mg, 85% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.19 (m, 5 H), 7.18–7.11 (m, 2 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 6.47 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.2, 144.3 (dm, *J* = 247.3 Hz), 142.0–141.5 (m), 141.3, 139.4–138.6 (m), 138.0, 136.6–136.2 (m), 134.4, 130.9, 129.1, 128.8, 128.6, 128.4, 112.8 (td, *J* = 17.9, 3.9 Hz), and 111.6 (d, *J* = 1.9 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -138.72 (dd, *J* = 22.5, 7.8 Hz, 2 F), -155.61 (t, *J* = 20.9 Hz, 1 F), -162.32– -162.54 (m, 2 F). HRMS Calcd for $C_{20}H_{11}ClF_5$ $[M+H]^+$: 381.0464, found: 381.0460.

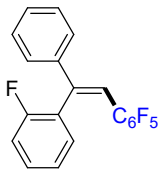


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-phenyl-2-(4-(trifluoromethyl)phenyl)vinyl)benzene (3s): Following the general procedure, compound **3s** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 100 mg, 81% yield; white solid, m.p.: 62-63 °C. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2 H), 7.48–7.32 (m, 5 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 6.70 (d, *J* = 0.8 Hz, 1 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.0, 144.2 (dm, *J* = 247.0 Hz), 143.3, 142.2–141.6 (m), 141.0, 139.7–138.6 (m), 136.7–136.2 (m), 130.4 (*J* = 32.4 Hz), 129.9, 129.2, 128.7, 128.4, 125.5 (q, *J* = 3.7 Hz), 124.1 (*J* = 270.4 Hz), and 112.78–112.1 (m). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -62.68 (s, 3 F), -138.73 (dd, *J* = 23.8, 9.2 Hz, 2 F), -155.12 (t, *J* = 21.3 Hz, 1 F), -161.12– -162.47 (m, 2 F). HRMS Calcd for $C_{21}H_{11}F_8$ $[M+H]^+$: 415.0728, found: 415.0729.

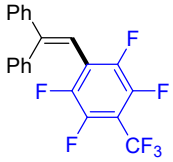


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-(3-methoxyphenyl)-2-phenylvinyl)benzene (3t): Following the general procedure, compound **3t** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 10:1, v/v)). 108 mg, 96% yield; colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.32 (m, 5 H), 7.22 (t, *J* = 7.9 Hz, 1 H), 6.88 (dd, *J* = 8.0, 2.2 Hz, 1 H), 6.78–6.64 (m, 2 H), 6.61 (s, 1 H), 3.74 (s, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.5, 151.2, 144.4 (dm, *J* = 246.9 Hz), 142.0–141.4 (m), 140.8, 139.4–138.5 (m), 136.6–136.0 (m), 129.4, 128.8, 128.44, 128.39, 122.0, 115.2, 113.8, 113.2 (td, *J* = 18.2, 3.9 Hz), 111.1 (d, *J* = 1.7 Hz), and 55.2. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -138.75 (dd, *J* = 23.0, 8.0 Hz, 2 F), -156.29 (t, *J* = 20.9 Hz, 1 F), -162.83– -165.17 (m, 2 F). HRMS Calcd for $C_{21}H_{14}F_5O$ $[M+H]^+$: 377.0959, found: 377.0963.

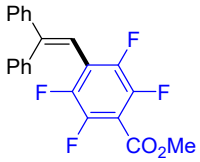


(*Z*)-1,2,3,4,5-Pentafluoro-6-(2-(2-fluorophenyl)-2-phenylvinyl)benzene (3u): Following the general procedure, compound **3u** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 100 mg, 92% yield; white solid, m.p.: 115-116 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.15 (m, 6

H), 7.02–6.86 (m, 3 H), 6.65 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0 (d, *J* = 247.7 Hz), 145.7–145.2 (m), 143.0–142.8 (m), 142.0–141.5 (m), 140.5, 139.5–138.4 (m), 136.6–135.9 (m), 131.6 (d, *J* = 3.1 Hz), 130.5 (d, *J* = 8.1 Hz), 129.0, 128.6, 127.5, 126.8 (d, *J* = 15.2 Hz), 124.2 (d, *J* = 3.6 Hz), 116.1 (d, *J* = 21.8 Hz), 113.8 (d, *J* = 1.4 Hz), and 112.8 (td, *J* = 18.0, 4.0 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -112.75 (s, 1 F), -139.12 (dd, *J* = 22.2, 7.7 Hz, 2 F), -155.72 (t, *J* = 20.9 Hz, 1 F), -162.72– -163.02 (m, 2 F). HRMS Calcd for $C_{20}H_{11}F_6$ $[M+H]^+$: 365.0759, found: 365.0760.

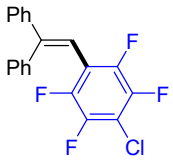


(2-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)ethene-1,1-diyl)dibenzene (4a): Following the general procedure, compound **4a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 114 mg, 96% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.38 (m, 5 H), 7.38–7.29 (m, 3 H), 7.15 (dd, *J* = 7.9, 1.4 Hz, 2 H), 6.66 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.9, 145.8–145.1 (m), 143.3–142.5 (m), 141.5, 139.2, 129.5, 129.2, 128.9, 128.7, 128.6, 128.5, 122.5 (t, *J* = 17.4 Hz), 110.9, and 108.6–107.2 (m). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -56.14 (t, *J* = 21.6 Hz, 3 F), -137.00 (td, *J* = 15.8, 6.2 Hz, 2 F), -141.52– -141.83 (m, 2 F). HRMS Calcd for $C_{21}H_{12}F_7$ $[M+H]^+$: 397.0822, found: 397.0824.

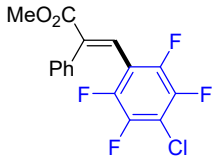


Methyl 4-(2,2-diphenylvinyl)-2,3,5,6-tetrafluorobenzoate (4b): Following the general procedure, compound **4b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 3:1, v/v). 109 mg, 94% yield; pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.35 (m, 5 H), 7.35–7.26 (m, 3 H), 7.19–7.09 (m, 2 H), 6.68 (s, 1 H), 3.97 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.4, 152.3, 144.7 (dm, *J* = 254.5 Hz), 144.0 (dm, *J* = 248.0 Hz), 141.6, 139.3, 129.5,

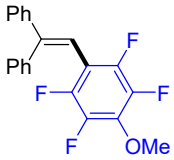
129.0, 128.6, 128.5, 128.4, 121.4 (t, J = 17.5 Hz), 111.5, 110.6 (t, J = 15.7 Hz), and 53.1. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -137.98 (td, J = 15.2, 4.5 Hz, 2 F), -140.27 (td, J = 15.1, 4.5 Hz, 2 F). HRMS Calcd for $C_{22}H_{15}F_4O_2$ $[M+H]^+$: 387.1003, found: 387.1005.



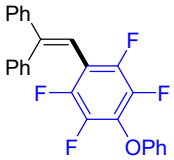
(2-(4-Chloro-2,3,5,6-tetrafluorophenyl)ethene-1,1-diyl)dibenzene (4c): Following the general procedure, compound **4c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 96 mg, 97% yield; white solid, m.p.: 81-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.28 (m, 8 H), 7.21–7.11 (m, 2 H), 6.66 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 145.7–145.1 (m), 143.2–142.6 (m), 141.7, 139.5, 129.6, 128.9, 128.5, 128.5, 128.4, 117.0 (t, J = 17.8 Hz), 111.5 (t, J = 2.2 Hz), and 110.7 (tt, J = 19.4, 2.8 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -137.87– -138.17 (m, 2 F), -141.93– -142.27 (m, 2 F). HRMS Calcd for $C_{20}H_{12}ClF_4$ $[M+H]^+$: 363.0558, found: 363.0554.



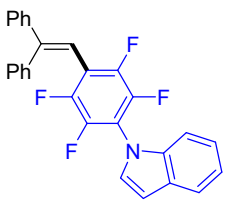
Methyl (*E*)-3-(4-chloro-2,3,5,6-tetrafluorophenyl)-2-phenylacrylate (4d): Following the general procedure, compound **4d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 2:1, v/v). 87 mg, 84% yield; white solid, m.p.: 67-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1 H), 7.25–7.13 (m, 3 H), 7.09–6.99 (m, 2 H), 3.76 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 145.7–144.8 (m), 143.0–142.4 (m), 141.3, 134.5, 129.1, 128.8, 128.3, 124.8 (t, J = 2.0 Hz), 114.5 (t, J = 17.6 Hz), 112.5 (tt, J = 18.9, 2.7 Hz), and 52.9. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -136.55– -136.93 (m, 2 F), -140.86– -141.21 (m, 2 F). HRMS Calcd for $C_{16}H_{10}ClF_4O_2$ $[M+H]^+$: 345.0300, found: 345.0303.



(2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)ethene-1,1-diyl)dibenzene (4e): Following the general procedure, compound **4e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 99 mg, 92% yield; white solid, m.p.: 45–46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 5 H), 7.18–7.11 (m, 3 H), 7.06–6.96 (m, 2 H), 6.48 (s, 1 H), 3.91 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.3, 144.5 (dm, J = 245.4 Hz), 142.3–141.9 (m), 140.0–139.4 (m), 137.6–137.2 (m), 129.6, 128.6, 128.4, 128.4, 128.3, 128.2, 112.1 (t, J = 2.0 Hz), 111.5 (t, J = 18.1 Hz), and 62.1 (t, J = 3.6 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -140.37– -140.48 (m, 2 F), -158.76– -158.94 (m, 2 F). HRMS Calcd for $C_{21}H_{15}F_4O$ $[M+H]^+$: 359.1054, found: 359.1052.

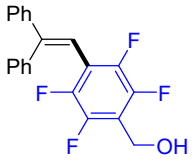


(2-(2,3,5,6-Tetrafluoro-4-phenoxyphenyl)ethene-1,1-diyl)dibenzene (4f): Following the general procedure, compound **4f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 122 mg, 97% yield; white solid, m.p.: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.32 (m, 10 H), 7.31–7.23 (m, 2 H), 7.20 (t, J = 7.4 Hz, 1 H), 7.05 (d, J = 8.2 Hz, 2 H), 6.76 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4, 151.1, 144.7 (dm, J = 246.7 Hz), 141.8, 141.6 (dm, J = 248.8 Hz), 139.7, 132.6–132.2 (m), 129.9, 129.6, 128.8, 128.5, 128.4, 128.4, 128.3, 123.7, 115.5, 114.4 (t, J = 18.0 Hz), and 111.7. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -139.15 (dd, J = 22.2, 9.5 Hz, 2 F), -155.14 (dd, J = 22.3, 9.4 Hz, 2 F). HRMS Calcd for $C_{26}H_{17}F_4O$ $[M+H]^+$: 421.1210, found: 421.1213.

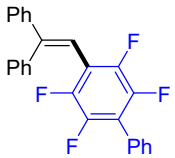


1-(4-(2,2-Diphenylvinyl)-2,3,5,6-tetrafluorophenyl)-1*H*-indole (4g):

Following the general procedure, compound **4g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 15:1, v/v). 128 mg, 96% yield; pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 1 H), 7.63–7.34 (m, 12 H), 7.33–7.26 (m, 2 H), 6.92 (dd, *J* = 3.3, 0.5 Hz, 1 H), 6.89 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.7, 144.4 (dm, *J* = 247.6 Hz), 142.9 (dm, *J* = 250.3 Hz), 141.8, 139.6, 136.4, 129.6, 128.9, 128.8, 128.6, 128.5, 128.5, 128.4, 128.4, 123.2, 121.3, 117.6–117.1 (m), 111.6, 110.5, and 105.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -137.86– -138.04 (m, 2 F), -146.85– -147.17 (m, 2 F). HRMS Calcd for $C_{28}H_{18}F_4N$ [M+H]$^+$: 444.1370, found: 444.1366.

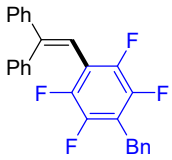


(4-(2,2-Diphenylvinyl)-2,3,5,6-tetrafluorophenyl)methanol (4h): Following the general procedure, compound **4h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 1:1, v/v). 61 mg, 57% yield; white solid, m.p.: 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 5 H), 7.35–7.24 (m, 3 H), 7.22–7.08 (m, 2 H), 6.68 (s, 1 H), 4.78 (d, *J* = 3.6 Hz, 2 H), 2.38 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.1, 144.9 (dm, *J* = 245.5 Hz), 143.9 (dm, *J* = 247.1 Hz), 141.9, 139.6, 129.6, 128.8, 128.5, 128.4, 128.3, 118.10 (t, *J* = 17.5 Hz), 117.0 (t, *J* = 17.9 Hz), 112.2, and 52.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -139.36 (dd, *J* = 22.5, 12.8 Hz, 2 F), -146.06 (dd, *J* = 22.5, 12.8 Hz, 2 F). HRMS Calcd for $C_{21}H_{15}F_4O$ [M+H]$^+$: 359.1054, found: 359.1060.

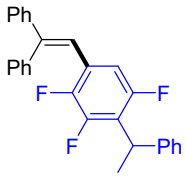


4-(2,2-Diphenylvinyl)-2,3,5,6-tetrafluoro-1,1'-biphenyl (4i): Following the general procedure, compound **4i** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 20:1, v/v). 47 mg, 39% yield; white solid, m.p.: 172-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 5 H), 7.44–7.37 (m, 5 H), 7.36–7.28 (m, 3 H), 7.25–7.14 (m, 2 H), 6.72 (s, 1 H). ^{13}C{^{1}H} NMR (100

MHz, $CDCl_3$) δ 150.9, 144.4 (dm, *J* = 246.4 Hz), 143.8 (dm, *J* = 244.8 Hz), 142.1, 139.8, 130.3 (t, *J* = 1.9 Hz), 129.7, 129.1, 128.8, 128.6, 128.6, 128.4, 128.4, 128.3, 127.7, 119.2 (t, *J* = 16.8 Hz), 117.0 (t, *J* = 17.7 Hz), and 112.5 (t, *J* = 2.3 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -139.57 (dd, *J* = 22.6, 12.4 Hz, 2 F), -145.14 (dd, *J* = 22.6, 12.4 Hz, 2 F). HRMS Calcd for $C_{26}H_{17}F_4$ $[M+H]^+$: 405.1261, found: 405.1255.

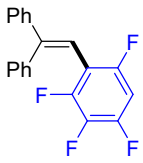


(2-(4-Benzyl-2,3,5,6-tetrafluorophenyl)ethene-1,1-diyl)dibenzene (4j): Following the general procedure, compound **4j** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 10:1, v/v). 50 mg, 40% yield; white solid, m.p.: 95–96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.27 (m, 13 H), 7.26–7.17 (m, 2 H), 6.73 (s, 1 H), 4.09 (s, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 144.9 (dm, *J* = 243.2 Hz), 143.9 (dm, *J* = 246.3 Hz), 142.0, 139.8, 138.0, 129.7, 128.8, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 126.8, 118.1 (t, *J* = 18.7 Hz), 116.3 (t, *J* = 17.6 Hz), 112.5 (t, *J* = 2.1 Hz), and 28.7. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -139.71 (dd, *J* = 22.7, 12.2 Hz, 2 F), -144.70 (dd, *J* = 22.5, 12.6 Hz, 2 F). HRMS Calcd for $C_{27}H_{19}F_4$ $[M+H]^+$: 419.1417, found: 419.1419.

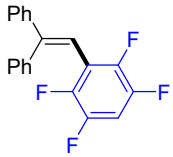


(2-(2,3,5,6-Tetrafluoro-4-(1-phenylethyl)phenyl)ethene-1,1-diyl)dibenzene (4k): Following the general procedure, compound **4k** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 10:1, v/v). 45 mg, 35% yield; white solid, m.p.: 88–89 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.27 (m, 13 H), 7.25–7.19 (m, 2 H), 6.72 (s, 1 H), 4.67 (q, *J* = 7.4 Hz, 1 H), 1.84 (d, *J* = 7.4 Hz, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 145.0 (dm, *J* = 243.7 Hz), 144.0 (dm, *J* = 246.3 Hz), 142.7, 142.1, 139.8, 129.7, 128.6, 128.6, 128.5, 128.4, 128.2, 127.3, 126.8, 122.9 (t, *J* = 16.2 Hz), 116.1 (t, *J* = 17.7 Hz), 112.5 (t, *J* = 1.9 Hz), 35.0, and 18.5 (t, *J* = 2.6 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -139.67 (dd, *J* =

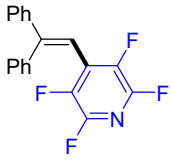
22.2, 12.1 Hz, 2 F), -143.80 (dd, J = 22.2, 12.1 Hz, 2 F). HRMS Calcd for $C_{28}H_{22}F_3$ $[M+H]^+$: 415.1668, found: 415.1656.



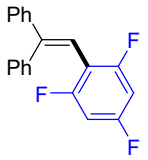
(2-(2,3,4,6-Tetrafluorophenyl)ethene-1,1-diyl)dibenzene (4l): Following the general procedure, compound **4l** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 76 mg, 77% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 5 H), 7.19–7.10 (m, 3 H), 7.02–6.97 (m, 2 H), 6.55–6.45 (m, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.6 (dm, J = 245.9 Hz), 150.5–150.1 (m), 149.8 (dm, J = 249.1 Hz), 148.0–147.6 (m), 142.1, 139.8, 137.3 (dm, J = 246.2 Hz), 129.6, 128.6, 128.4, 128.4, 128.3, 128.1, 113.5–113.0 (m), 112.4, and 100.6 (ddd, J = 28.5, 21.3, 3.7 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -113.62 (d, J = 10.7 Hz, 1 F), -131.19 (dd, J = 21.7, 5.6 Hz, 1 F), -133.98 (dd, J = 22.9, 5.5 Hz, 1 F), -165.48 (td, J = 21.8, 11.0 Hz, 1 F). HRMS Calcd for $C_{20}H_{13}F_4$ $[M+H]^+$: 329.0948, found: 329.0944.



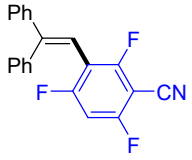
(2-(2,3,5,6-Tetrafluorophenyl)ethene-1,1-diyl)dibenzene (4m): Following the general procedure, compound **4m** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 107 mg, 65% yield; white solid, m.p.: 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5 H), 7.35–7.26 (m, 3 H), 7.19–7.08 (m, 2 H), 6.97–6.85 (m, 1 H), 6.67 (s, 1 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.0, 145.9 (dm, J = 243.5 Hz), 145.4–144.9 (m), 142.9–142.6 (m), 141.9, 139.6, 129.6, 128.8, 128.5, 128.4, 128.3, 128.3, 118.8 (t, J = 17.6 Hz), 112.4 (t, J = 2.3 Hz), and 104.5 (t, J = 23.6 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -139.45 (dd, J = 22.2, 12.5 Hz, 2 F), -139.90 (dd, J = 23.0, 12.6 Hz, 2 F). HRMS Calcd for $C_{20}H_{13}F_4$ $[M+H]^+$: 329.0948, found: 329.0950.



4-(2,2-Diphenylvinyl)-2,3,5,6-tetrafluoropyridine (4n): Following the general procedure, compound **4n** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2/Et_3N = 95:5:1, v/v). 88 mg, 89% yield; pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.27 (m, 8 H), 7.15–7.07 (m, 2 H), 6.66 (s, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.0, 143.6 (dm, *J* = 242.8 Hz), 140.91, 139,4 (dm, *J* = 257.6 Hz), 138.9, 131.3 (tt, *J* = 15.9, 3.0 Hz), 129.5, 129.5, 129.1, 128.7, 128.6, 128.6, and 110.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -91.90 (td, *J* = 29.2, 13.8 Hz, 2 F), -140.44 (td, *J* = 29.3, 13.8 Hz, 2 F). HRMS Calcd for $C_{19}H_{14}F_4N$ [M+H]$^+$: 330.0900, found: 330.0904.

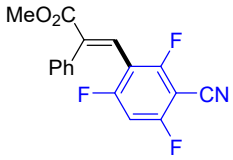


(2-(2,4,6-Trifluorophenyl)ethene-1,1-diyl)dibenzene (4o): Following the general procedure, compound **4o** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)). 16 mg, 17% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.18 (m, 5 H), 7.17–7.10 (m, 3 H), 7.05–6.95 (m, 2 H), 6.51 (s, 1 H), 6.46–6.35 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.8 (dm, *J* = 247.5 Hz), 160.6 (dm, *J* = 248.9 Hz), 149.0, 142.4, 140.2, 129.7, 128.4, 128.3, 128.1, 127.8, 112.1 (td, *J* = 20.0, 4.8 Hz), and 100.5–99.7 (m). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -106.99 (d, *J* = 6.8 Hz, 2 F), -109.57 (t, *J* = 6.2 Hz, 1 F). HRMS Calcd for $C_{20}H_{14}F_3$ [M+H]$^+$: 311.1042, found: 311.1044.



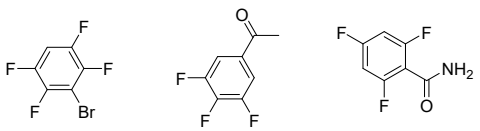
3-(2,2-Diphenylvinyl)-2,4,6-trifluorobenzonitrile (4p): Following the general procedure, compound **4p** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 1:1, v/v). 76 mg, 80% yield; white solid, m.p.: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5 H), 7.36–7.27 (m, 3 H),

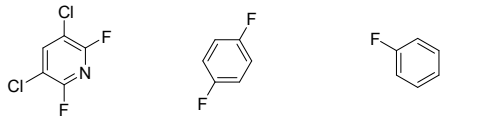
7.17–7.06 (m, 2 H), 6.70 (td, J = 8.9, 1.7 Hz, 1 H), 6.58 (s, 1 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3 (dm, J = 260.4 Hz), 162.2 (dm, J = 261.5 Hz), 161.3 (dm, J = 262.1 Hz), 151.3, 141.4, 139.3, 129.4, 128.8, 128.4, 128.4, 128.3, 114.2–113.5 (m), 110.7, 108.7 (d, J = 1.4 Hz), 101.8–100.9 (m), and 89.1 (td, J = 20.2, 4.4 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -94.61 (t, J = 9.8 Hz, 1 F), -99.87 (d, J = 9.7 Hz, 1 F), -103.41 (d, J = 9.9 Hz, 1 F). HRMS Calcd for $C_{21}H_{13}F_3N$ $[M+H]^+$: 336.0995, found: 336.0991.



Methyl (*E*)-3-(3-cyano-2,4,6-trifluorophenyl)-2-phenylacrylate (4q): Following the general procedure, compound **4q** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/CH_2Cl_2 = 1:1, v/v). 76 mg, 80% yield; white solid, m.p.: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 0.9 Hz, 1 H), 7.37–7.25 (m, 3 H), 7.17–7.06 (m, 2 H), 6.73 (td, J = 8.9, 1.9 Hz, 1 H), 3.87 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 163.1 (dm, J = 262.1 Hz), 161.0 (dm, J = 262.9 Hz), 141.3, 134.4, 129.0, 128.8, 128.3, 124.2, 111.9–111.2 (m), 108.3 (d, J = 1.5 Hz), 102.2–101.4 (m), 89.6 (td, J = 19.9, 4.4 Hz), and 52.9. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -93.49 (dd, J = 10.8, 8.3 Hz, 1 F), -98.59 (d, J = 7.6 Hz, 1 F), -100.65 (d, J = 11.0 Hz, 1 F). HRMS Calcd for $C_{17}H_{11}F_3NO_2$ $[M+H]^+$: 318.0736, found: 318.0733.

Unsuccessful substrates





10. References

1 (*a*) Q. N. Wang, R. J. Chen, J. Lou, D. H. Zhang, Y.-G. Zhou and Z. K. Yu, Highly Regioselective C–H Alkylation of Alkenes Through an Aryl to Vinyl 1,4-Palladium Migration/C–C Cleavage Cascade, *ACS Catal.*, 2019, **9**, 11669–11675; (*b*) G. H. Chen, J. Y. Gui, L. C. Li and J. Liao, Chiral Sulfoxide-Olefin Ligands: Completely Switchable Stereoselectivity in Rhodium-Catalyzed Asymmetric Conjugate Additions, *Angew. Chem. Int. Ed.*, 2011, **50**, 7681–7685.

2 (*a*) C. B. Liu, H. Wang, X. Xing, Y. Xu and J.-A. Ma, B. Zhang, Selective C4–F Bond Cleavage of Pentafluorobenzene: Synthesis of *N*-Tetrafluoroarylated Heterocyclic Compounds, *Tetrahedron Lett.*, 2013, **54**, 4649–4652; (*b*) C. B. Liu, L. M. Cao, X. G. Yin, H. L. Xu and B. Zhang, Selective C4–F Bond Cleavage/C–O Bond Formation of Polyfluoroarenes with Phenols and Benzyl Alcohols, *J. Fluorine Chem.*, 2013, **156**, 51–60; (*c*) S. Xu, G. J. Wu, F. Ye, X. Wang, H. Li, X. Zhao, Y. Zhang and J. B. Wang, Copper(I)-Catalyzed Alkylation of Polyfluoroarenes Through Direct C–H Bond Functionalization, *Angew. Chem. Int. Ed.*, 2015, **54**, 4669–4672; (*d*) W. L. Xie, J. Heo, D. Kim and S. Chang, Copper-Catalyzed Direct C–H Alkylation of Polyfluoroarenes by Using Hydrocarbons as an Alkylating Source, *J. Am. Chem. Soc.*, 2020, **142**, 7487–7496; (*e*) T. D. Schoch, M. Mondal, J. D. Weaver, Catalyst-Free Hydrodefluorination of Perfluoroarenes with $NaBH_4$, *Org. Lett.*, 2021, **23**, 1588–1593.

3 (*a*) N. Takeda, T. Tagawa and M. Unno, Synthesis, Reactivities, and Coordination Chemistry of Tris(2-isopropoxyphenyl)phosphine, *Heteroat. Chem.*, 2014, **25**, 628–635; (*b*) T. Bura, S. Beaupré, M.-A. Légaré, J. Quinn, E. Rochette, J. T. Blaskovits, F.-G. Fontaine, A. Pron, Y. N. Li and M. Leclerc, Direct Heteroarylation Polymerization: Guidelines for Defect-Free Conjugated Polymers, *Chem. Sci.*, 2017, **8**, 3913–3925; (*c*) Z. Y. Yang, C. R. Shen and K. W. Dong, Hydroxyl Group-Enabled Highly Efficient Ligand for Pd-Catalyzed Telomerization of 1,3-Butadiene with CO_2, *Chin. J. Chem.*, 2022, **40**, 2734–2740.

4 S. A. Johnson, E. T. Taylor and S. J. Cruise, A Combined Experimental and Computational Study of Unexpected C–F Bond Activation Intermediates and Selectivity in the Reaction of Pentafluorobenzene with a $(PEt_3)_2Ni$ Synthon, *Organometallics*, 2009, **28**, 3842–3855.

5 (*a*) 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; (*b*) G. Zhang, Y.-K. Song, F. Zhang, Z.-J. Xue, M.-Y. Li, G.-S. Zhang, B.-B. Zhu, J. Wei, C. S. Li, C.-G. Feng and G.-Q. Lin, Palladium-Catalyzed Allene Synthesis Enabled by β-Hydrogen Elimination from sp^2-Carbon, *Nat. Commun.*, 2021, **12**, 728–727.

6 Z. H. He, S. Kirchberg, R. Frçhlich and A. Studer, Oxidative Heck Arylation for the Stereoselective Synthesis of Tetrasubstituted Olefins Using Nitroxides as Oxidants, *Angew. Chem. Int. Ed.*, 2012, **51**, 3699–3702.

11. Copies of NMR spectra

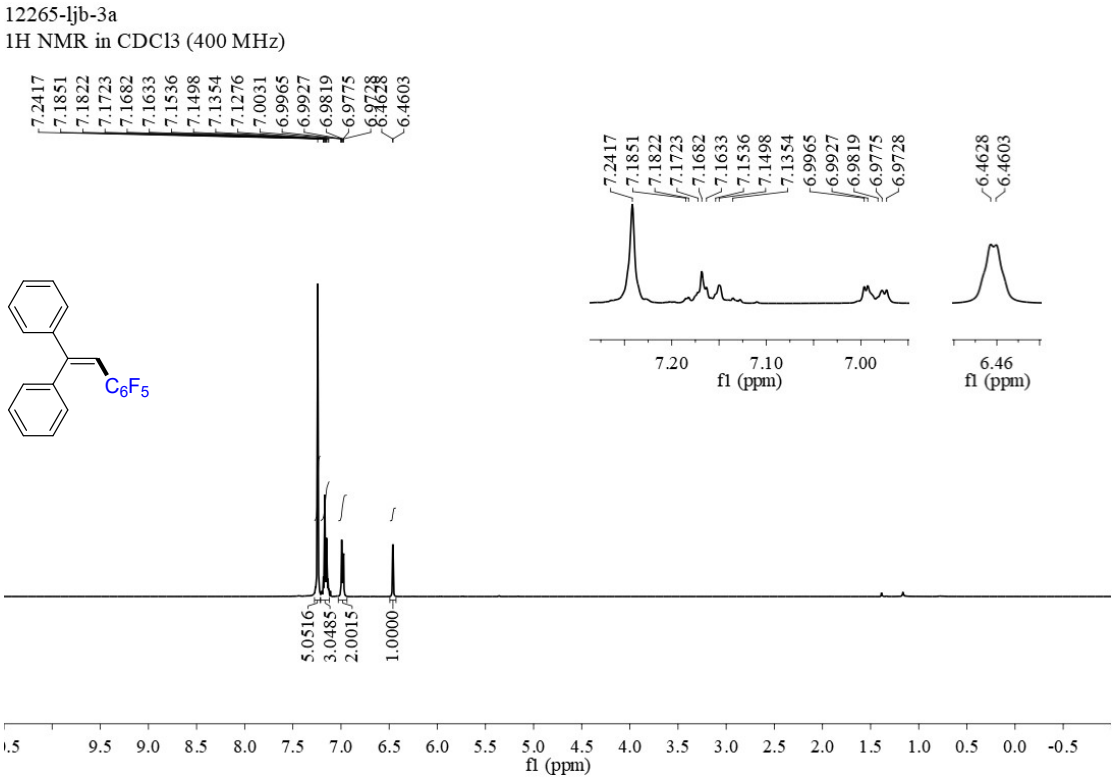


Figure S2. ^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 25 °C, 400 MHz).

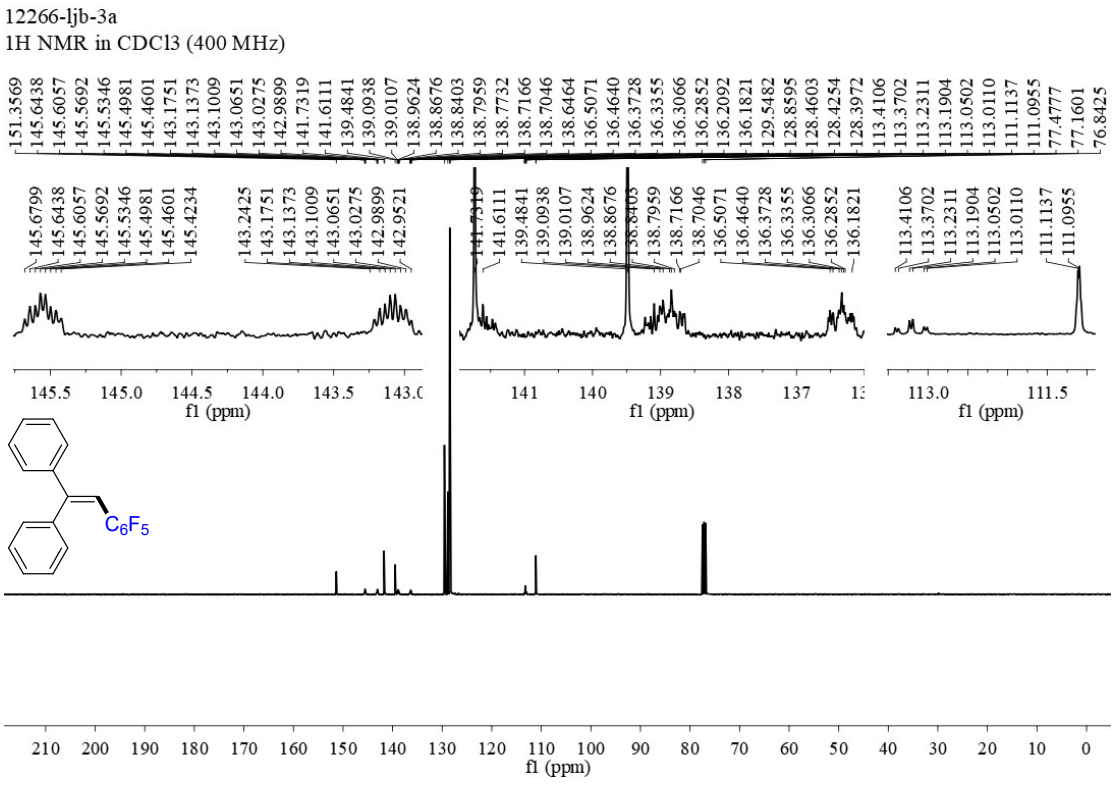


Figure S3. ^{13}C{^{1}H} NMR spectrum of compound **3a** ($CDCl_3$, 25 °C, 100 MHz).

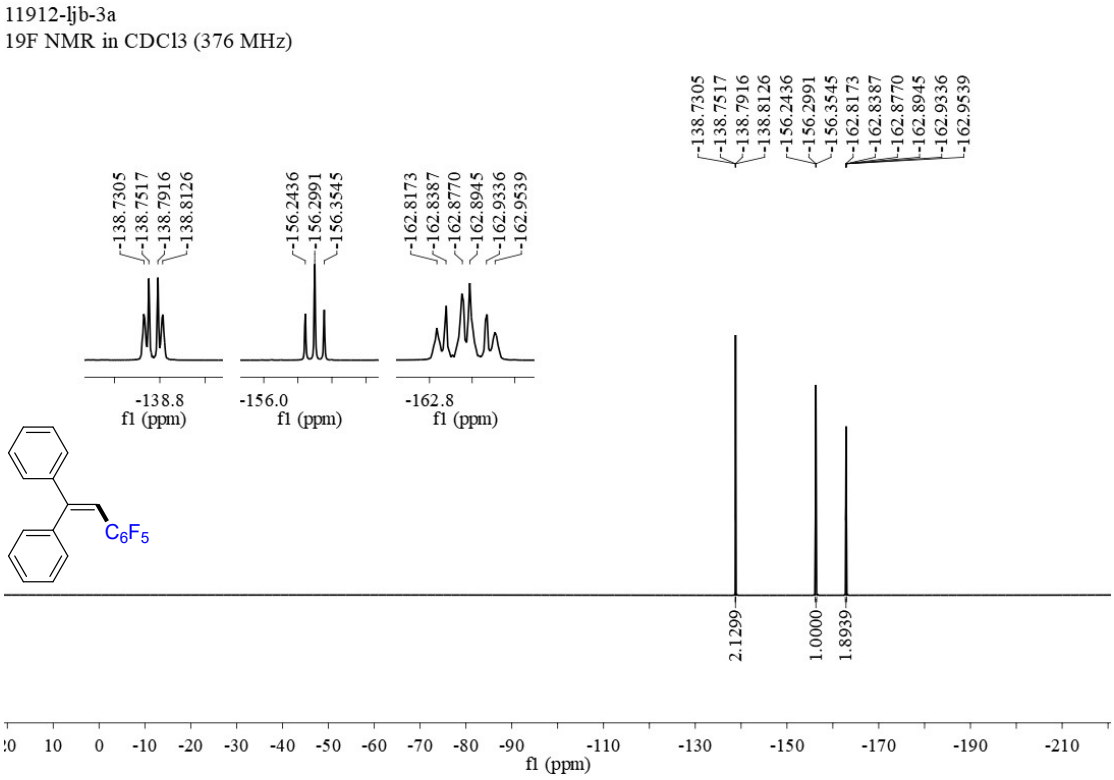


Figure S4. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3a** ($CDCl_3$, 25 °C, 376 MHz).

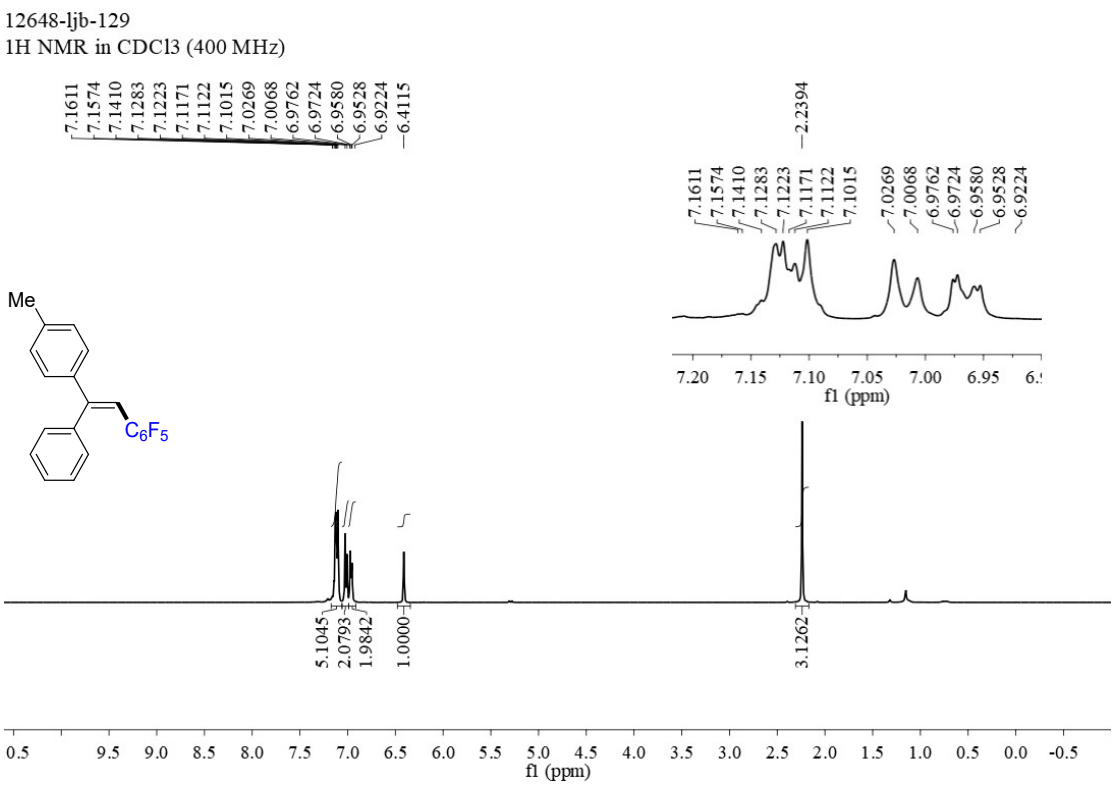


Figure S5. ^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 25 °C, 400 MHz).

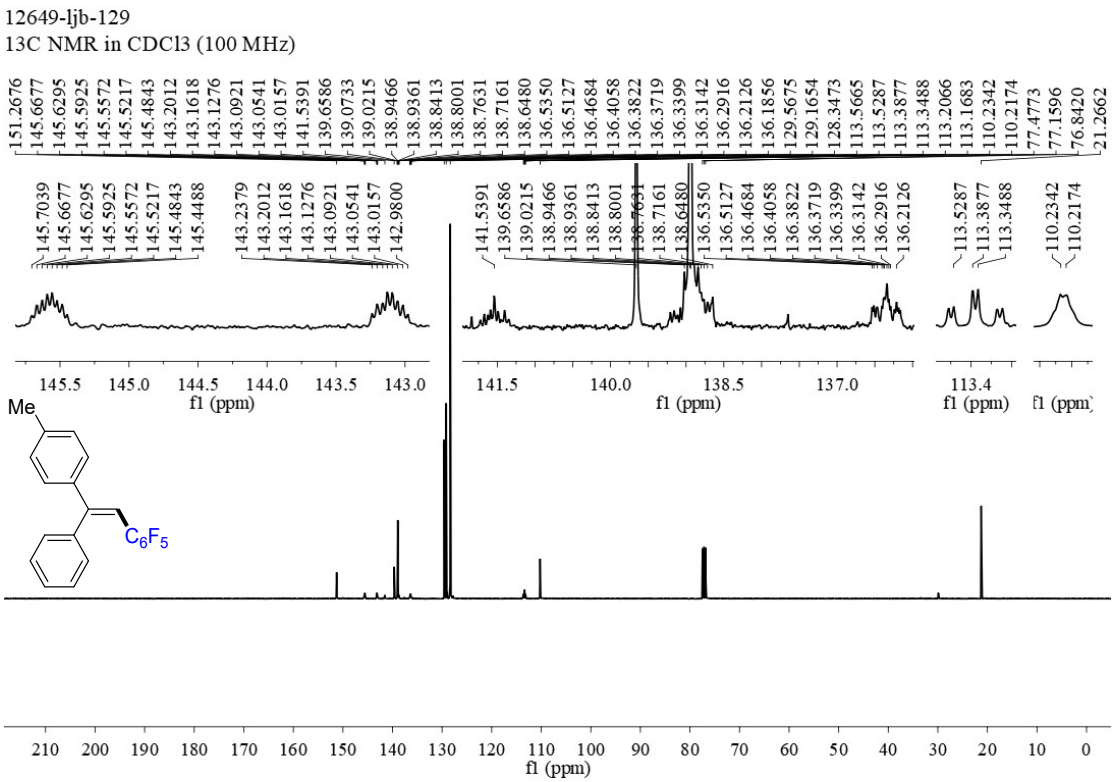


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b** ($CDCl_3$, 25 °C, 100 MHz).

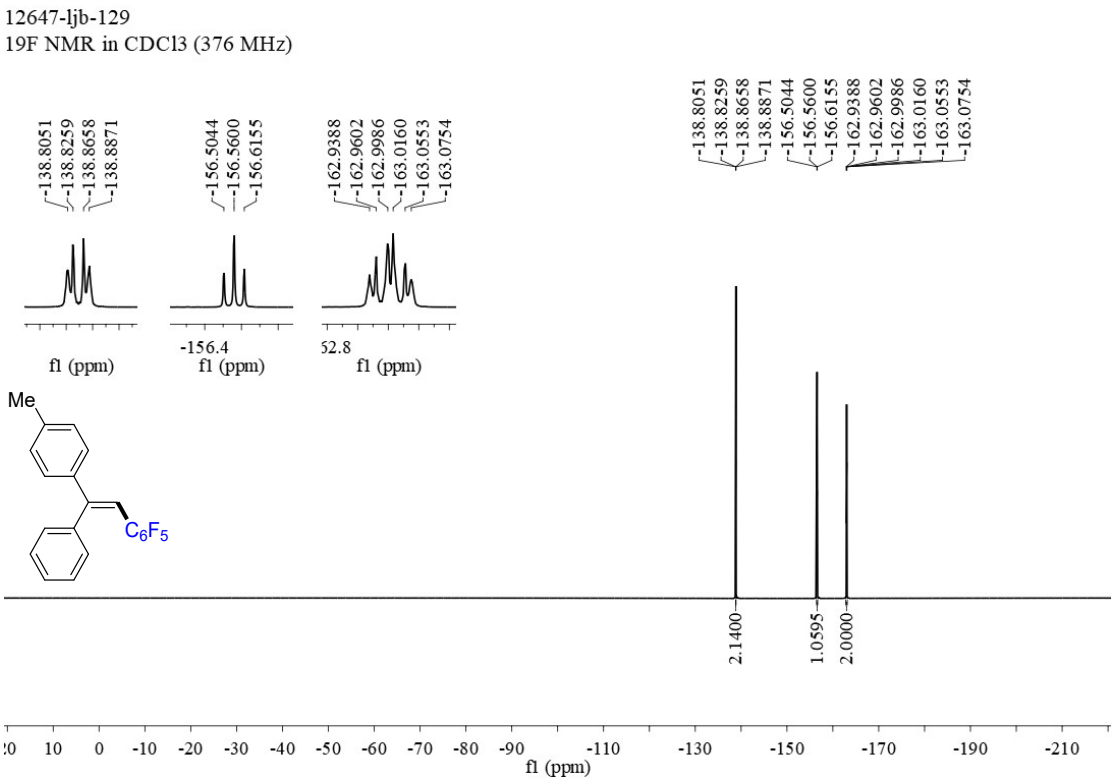


Figure S7. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3b** ($CDCl_3$, 25 °C, 376 MHz).

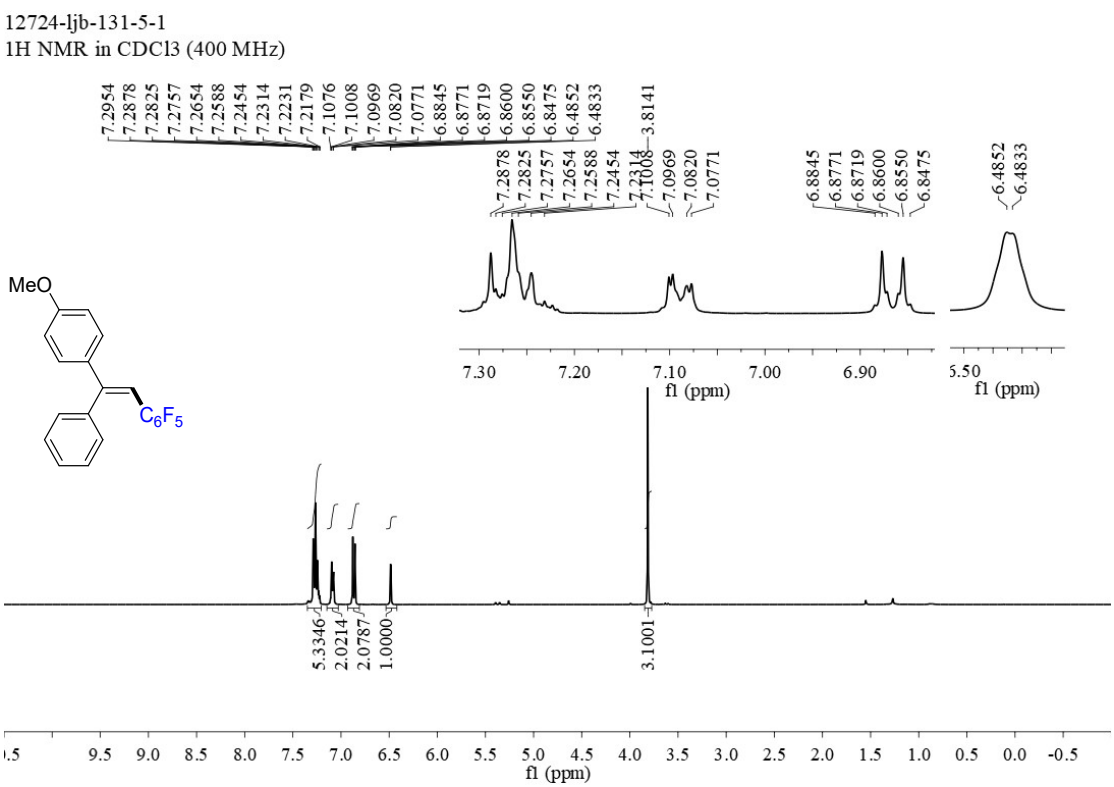


Figure S8. ^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 25 °C, 400 MHz).

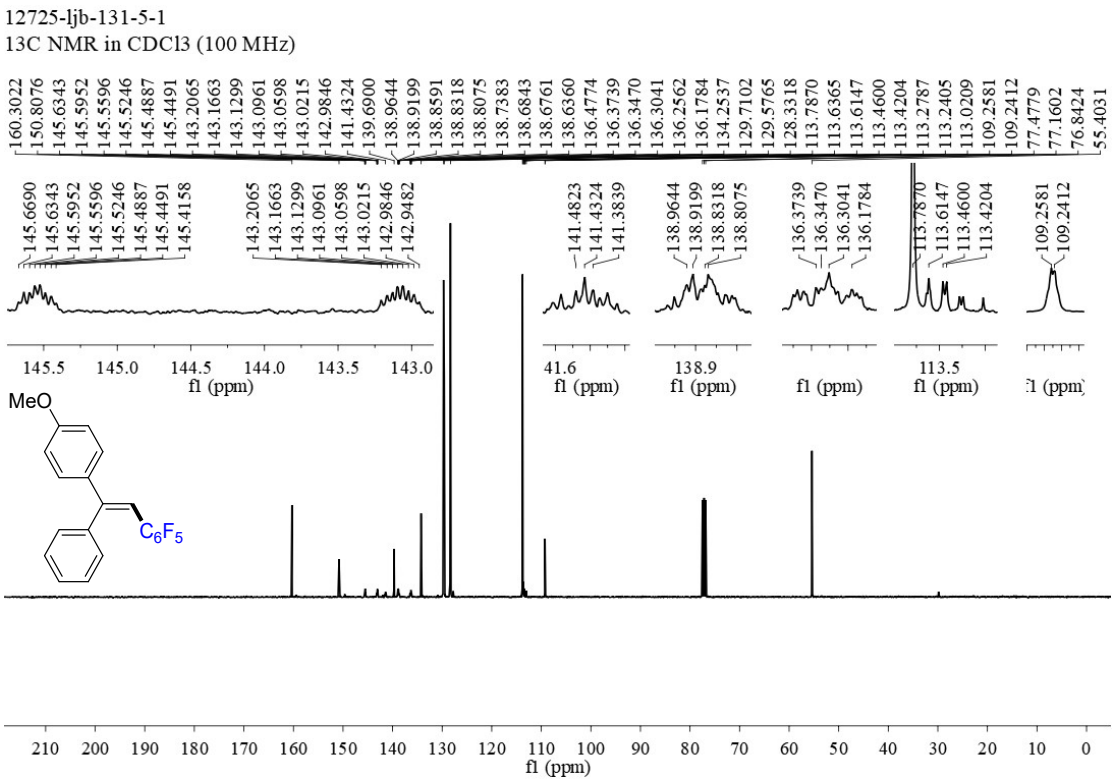


Figure S9. ^{13}C{^{1}H} NMR spectrum of compound **3c** ($CDCl_3$, 25 °C, 100 MHz).

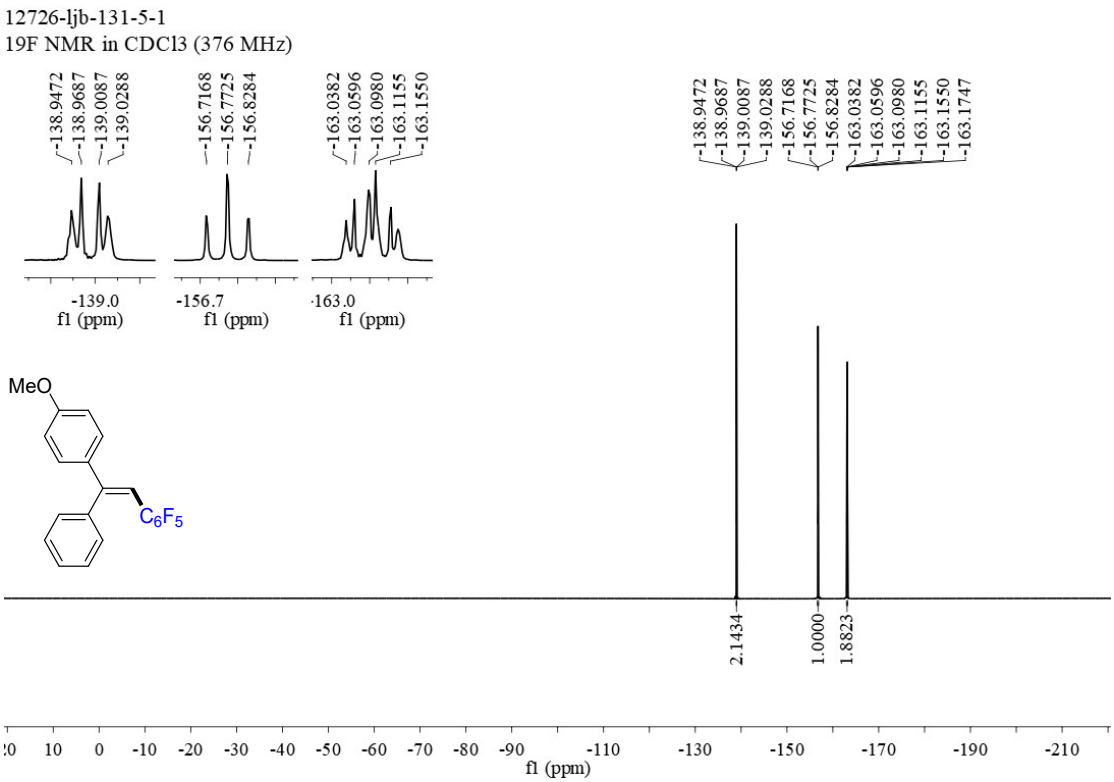


Figure S10. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3c** ($CDCl_3$, 25 °C, 376 MHz).

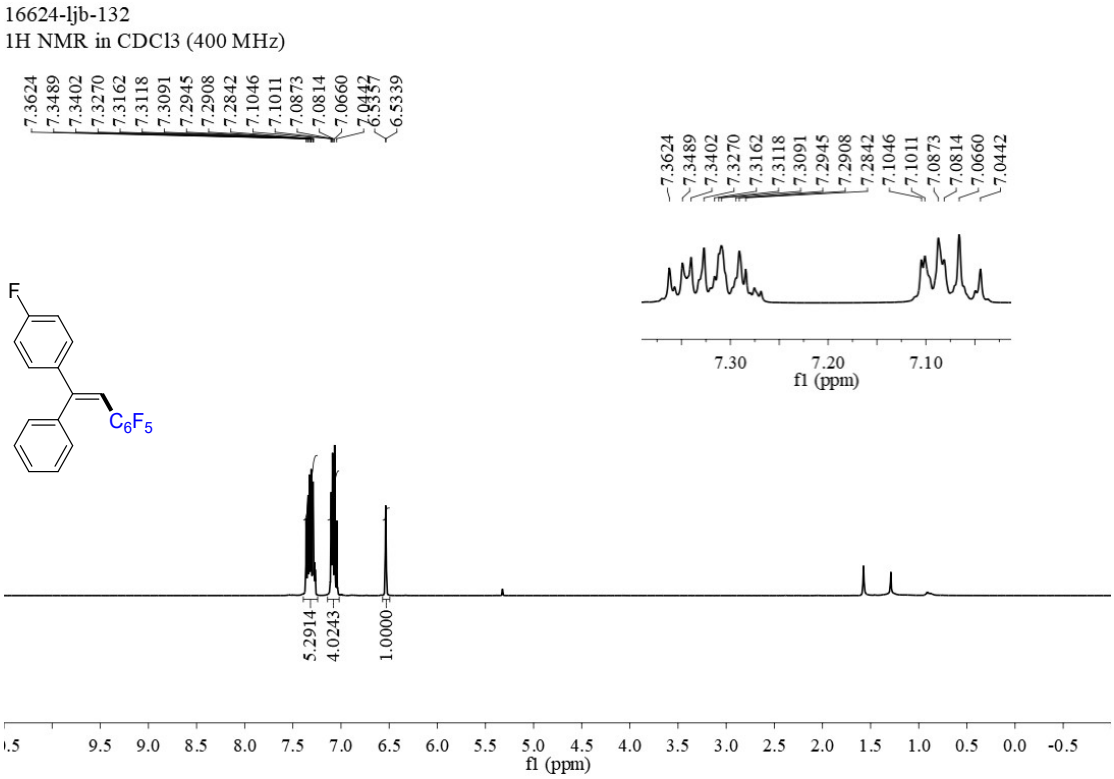


Figure S11. ^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 25 °C, 400 MHz).

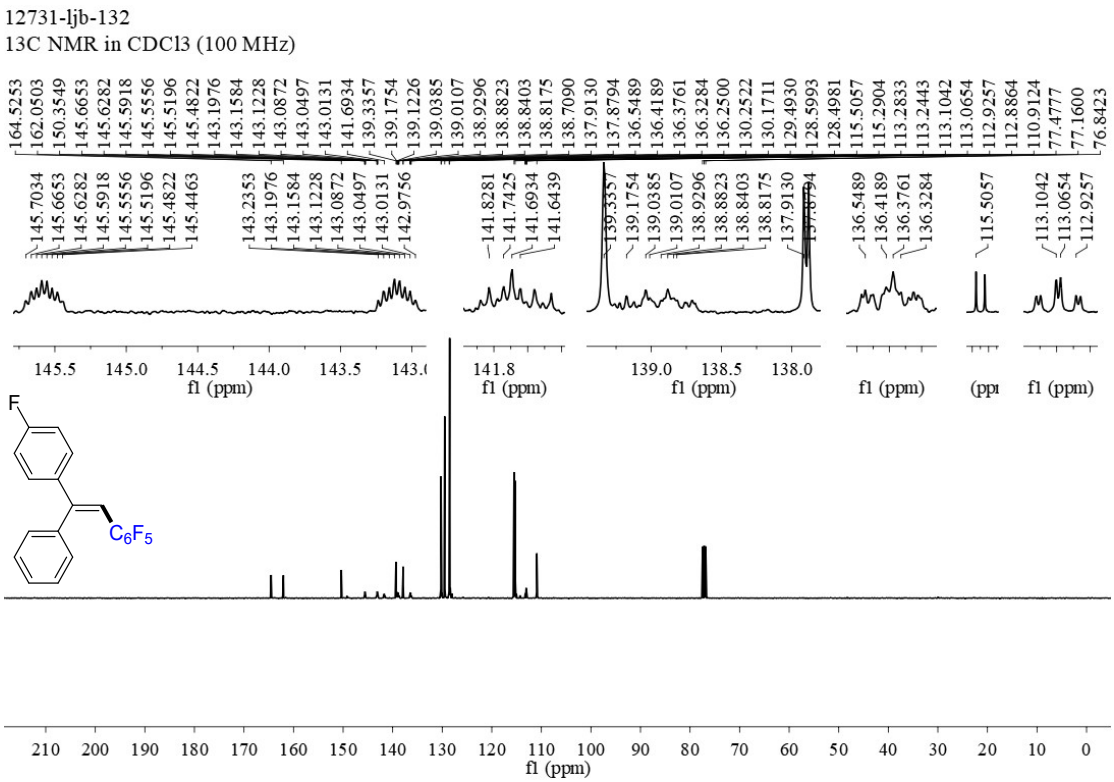


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3d** ($CDCl_3$, 25 °C, 100 MHz).

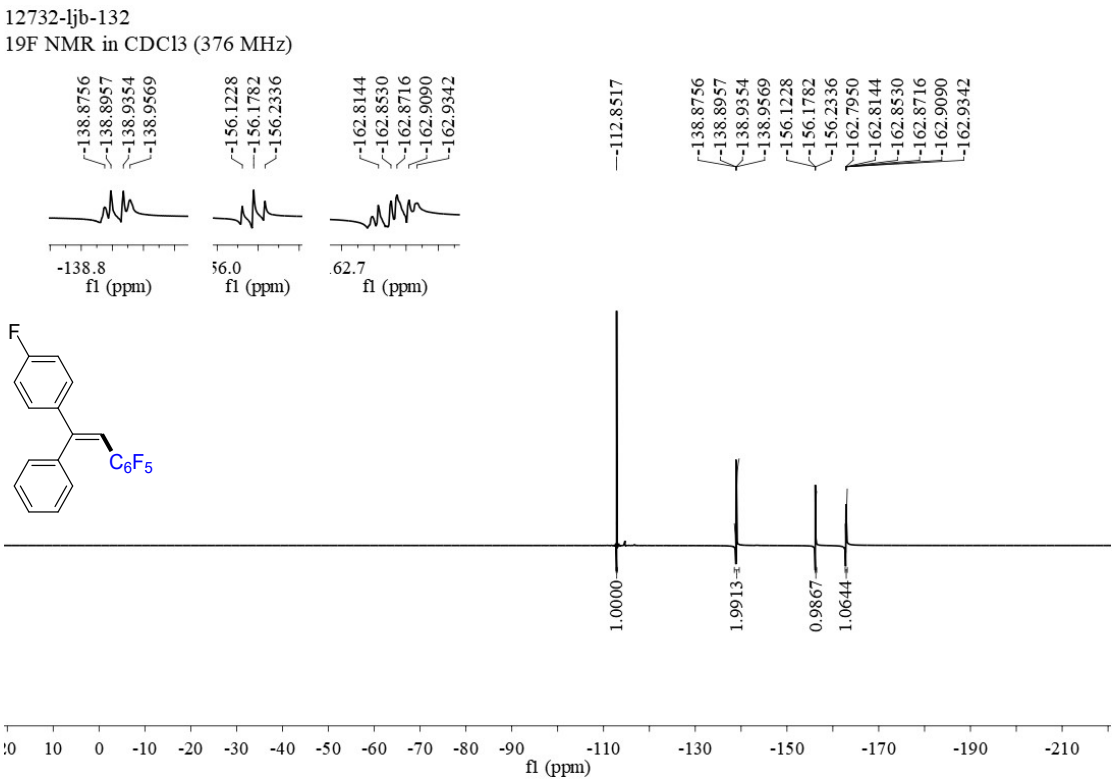


Figure S13. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3d** ($CDCl_3$, 25 °C, 376 MHz).

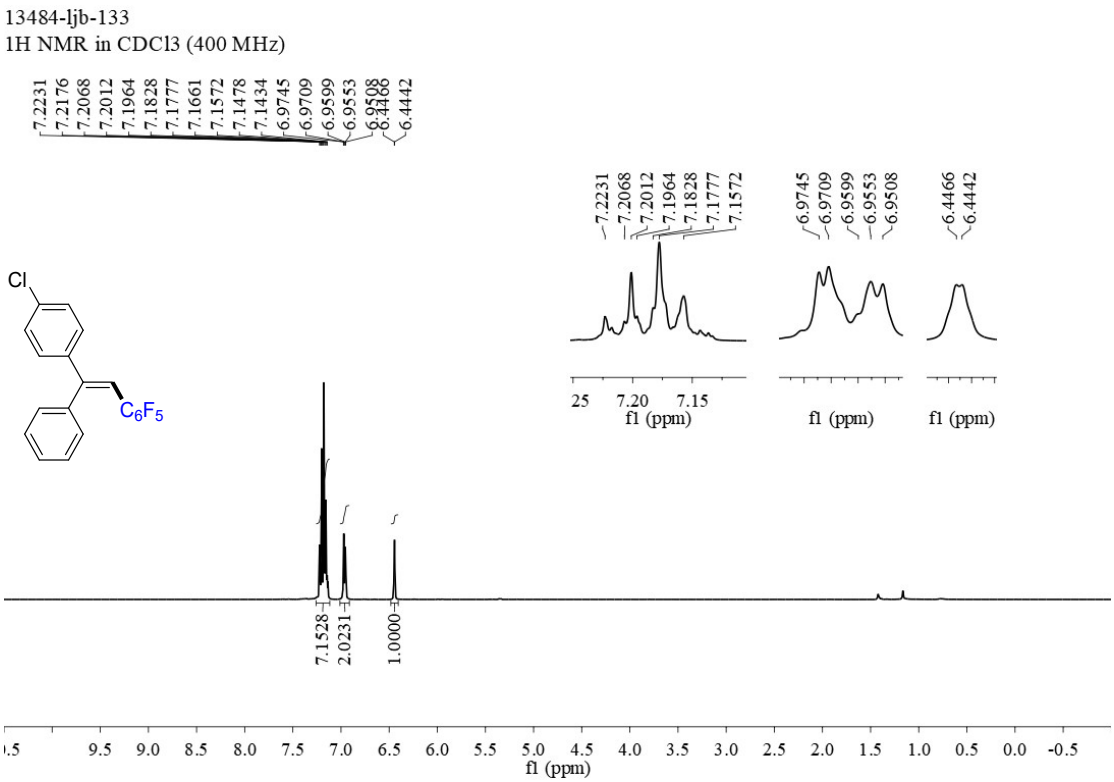


Figure S14. ^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 25 °C, 400 MHz).

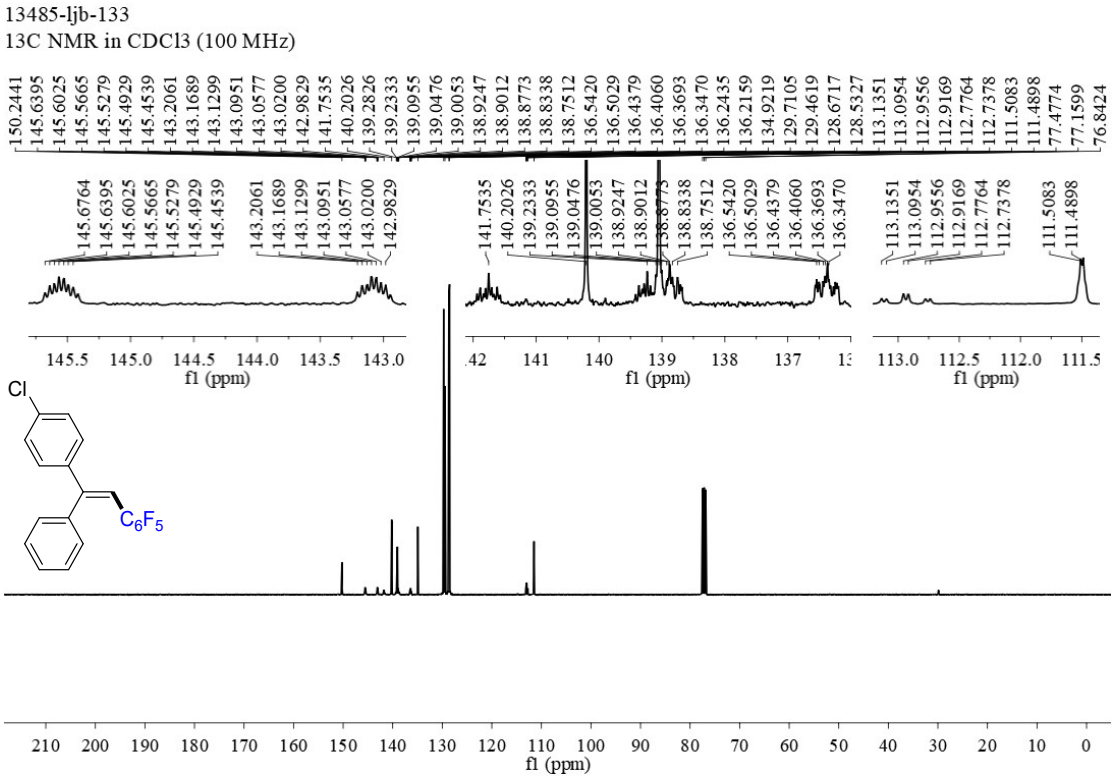


Figure S15. ^{13}C{^{1}H} NMR spectrum of compound **3e** ($CDCl_3$, 25 °C, 100 MHz).

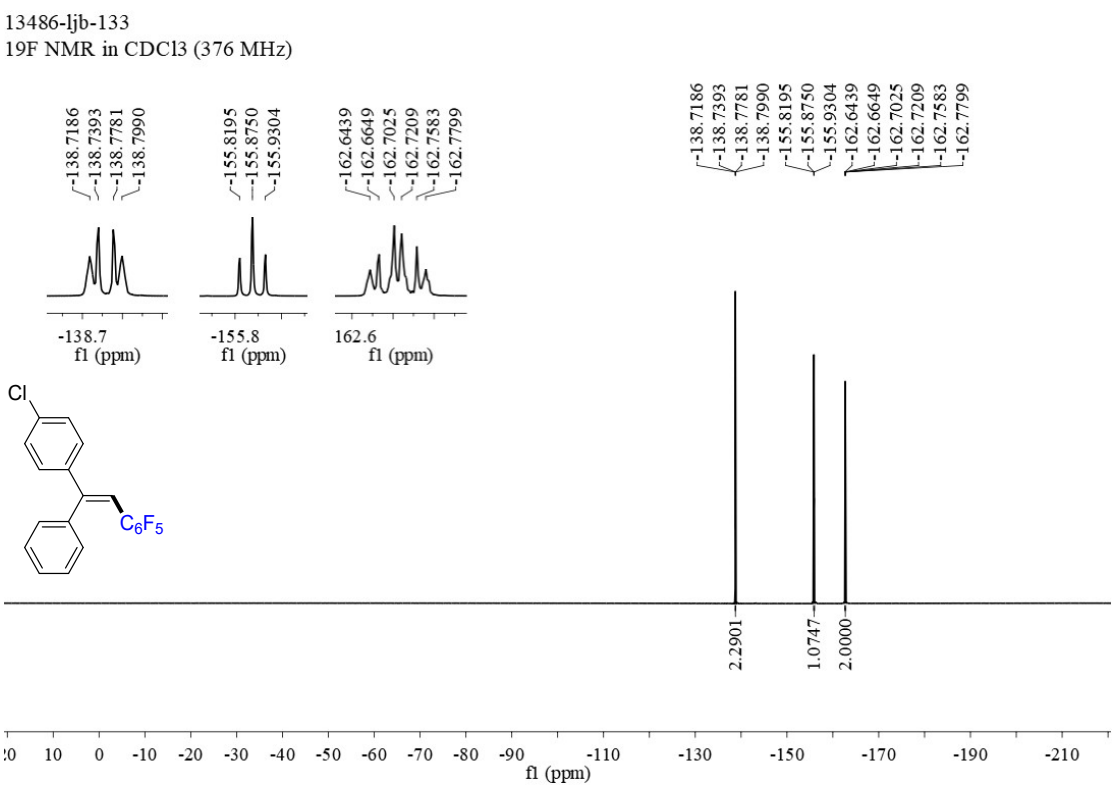


Figure S16. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3e** ($CDCl_3$, 25 °C, 376 MHz).

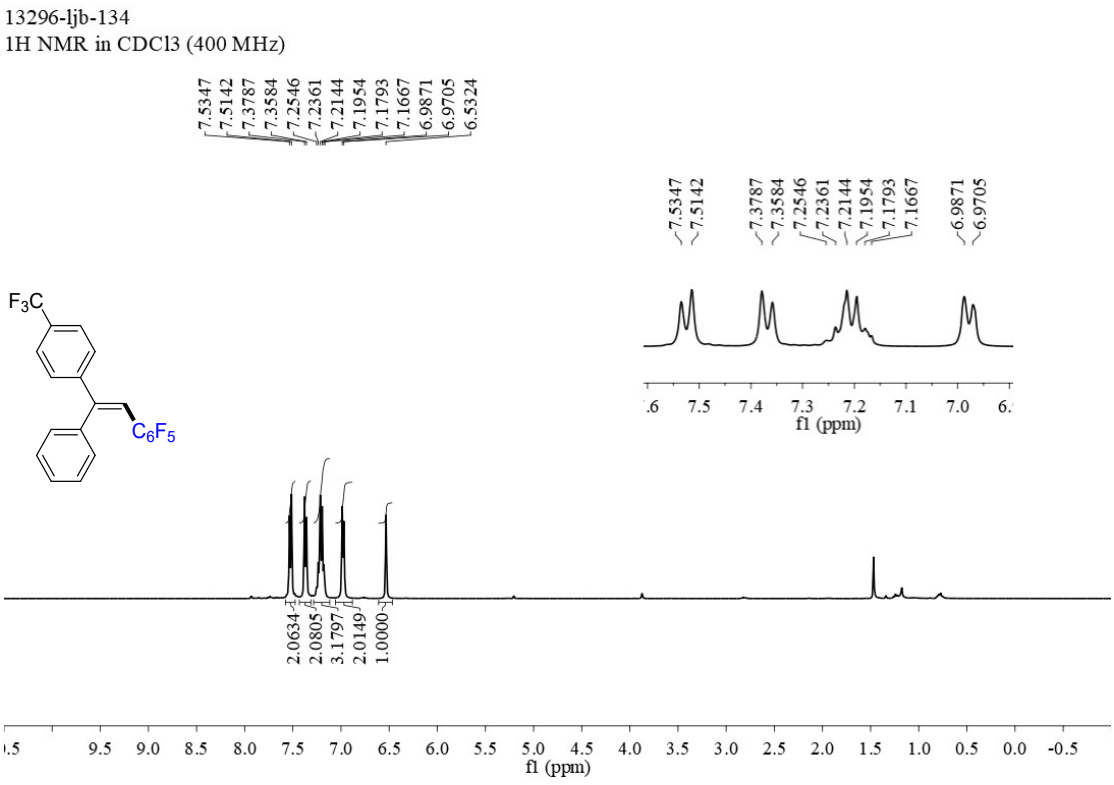


Figure S17. ^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 25 °C, 400 MHz).

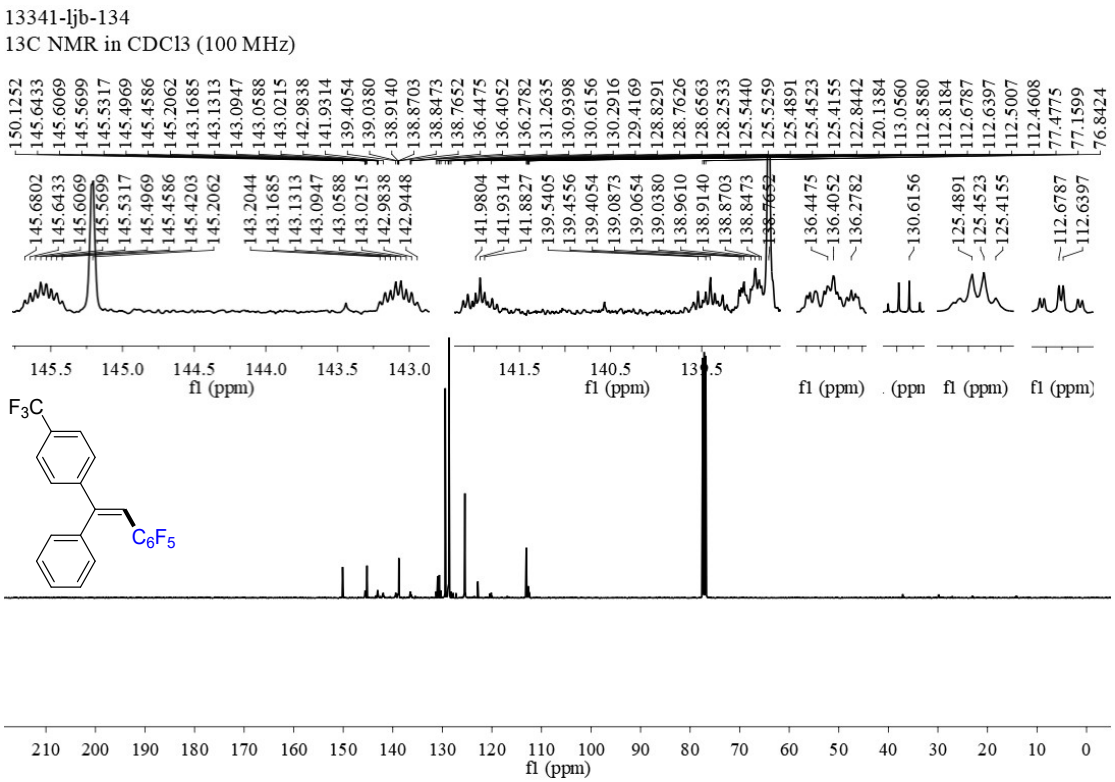


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3f** ($CDCl_3$, 25 °C, 100 MHz).

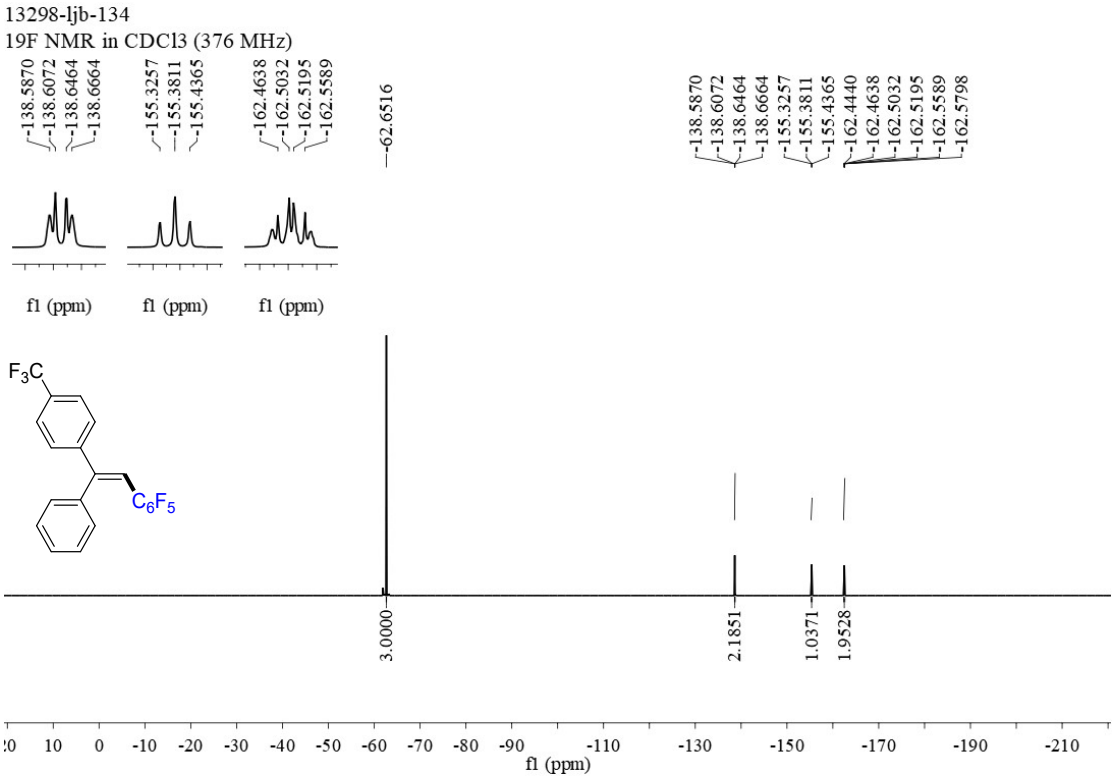


Figure S19. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3f** ($CDCl_3$, 25 °C, 376 MHz).

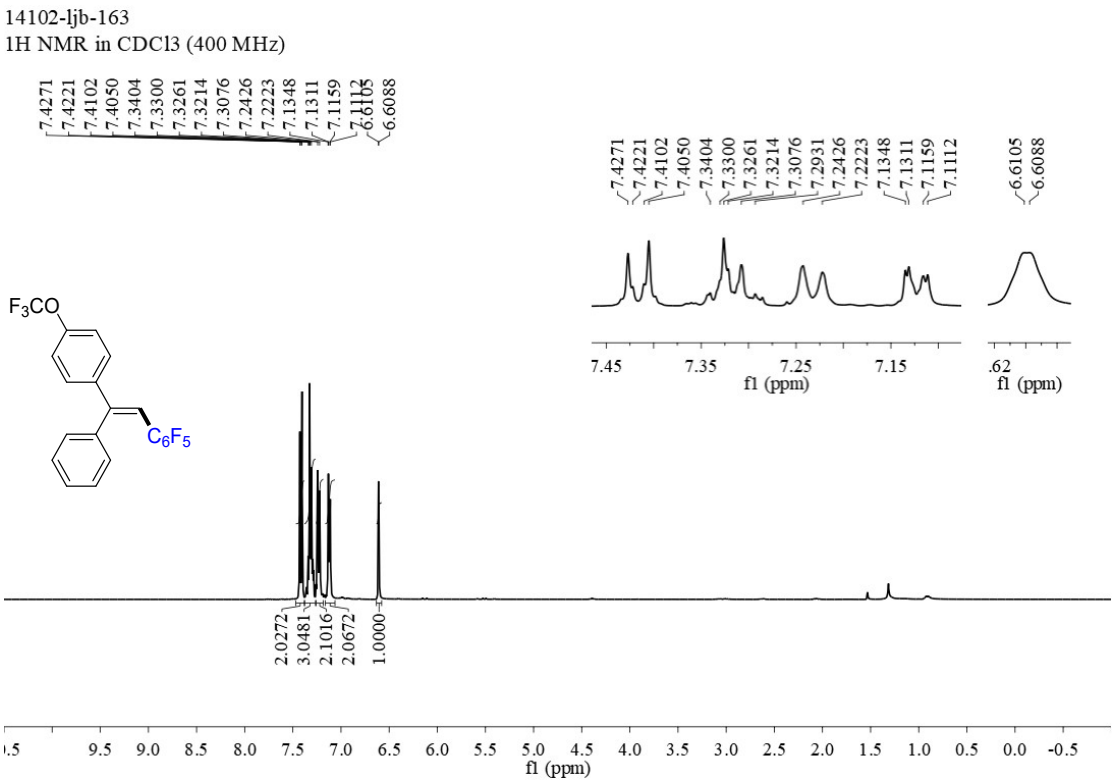


Figure S20. ^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 25 °C, 400 MHz).

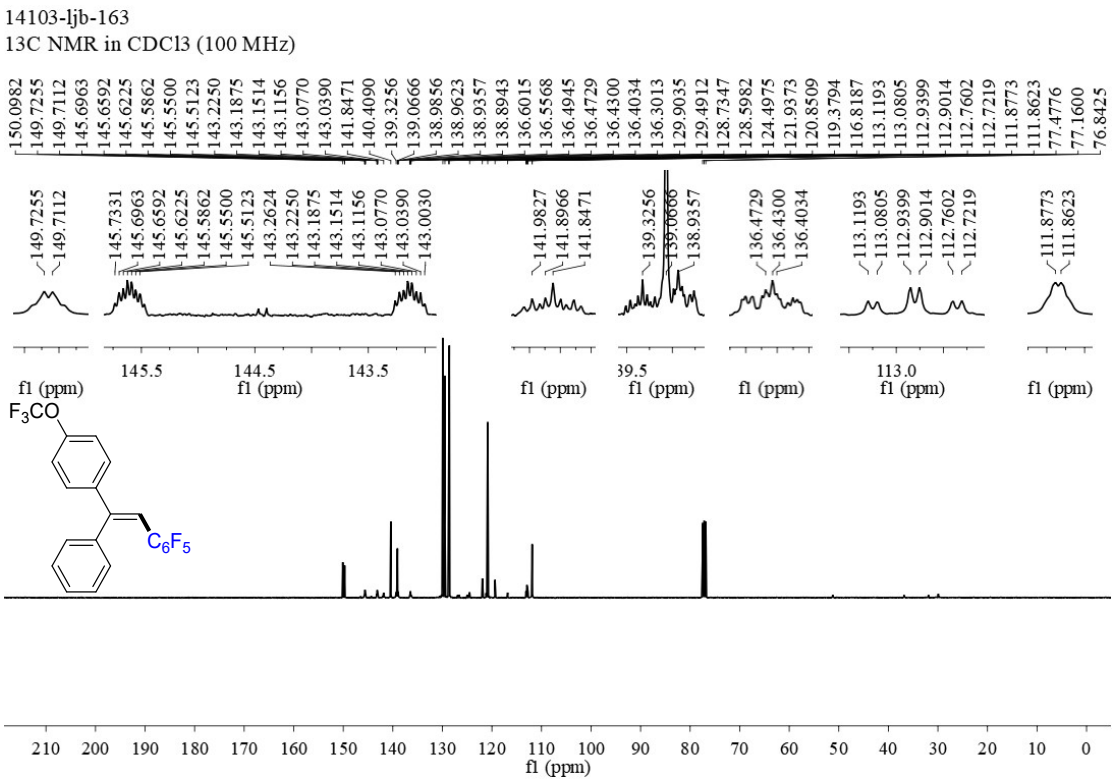


Figure S21. ^{13}C{^{1}H} NMR spectrum of compound **3g** ($CDCl_3$, 25 °C, 100 MHz).

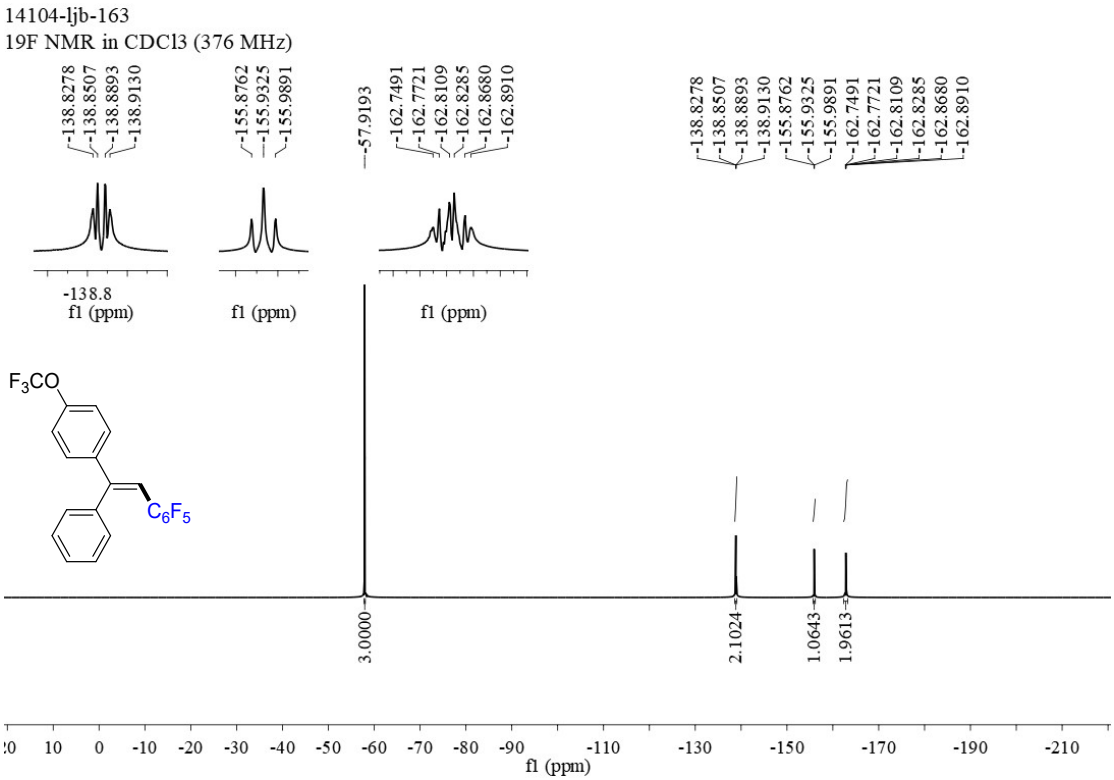


Figure S22. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3g** ($CDCl_3$, 25 °C, 376 MHz).

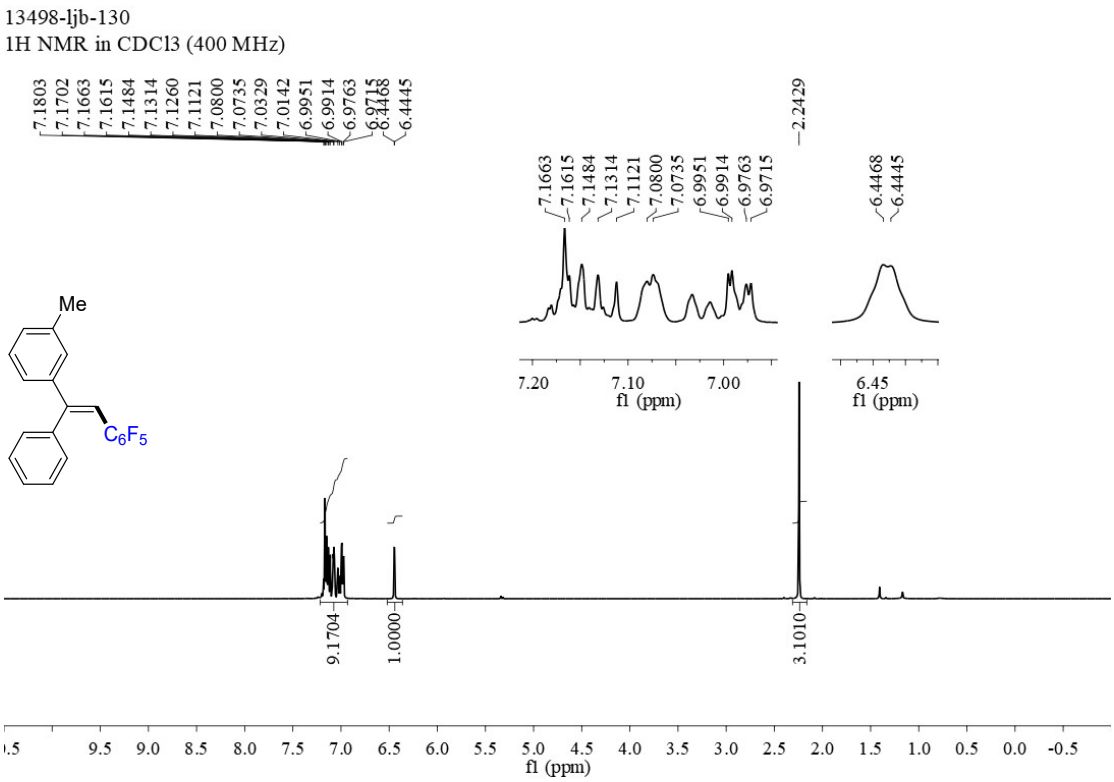


Figure S23. ^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 25 °C, 400 MHz).

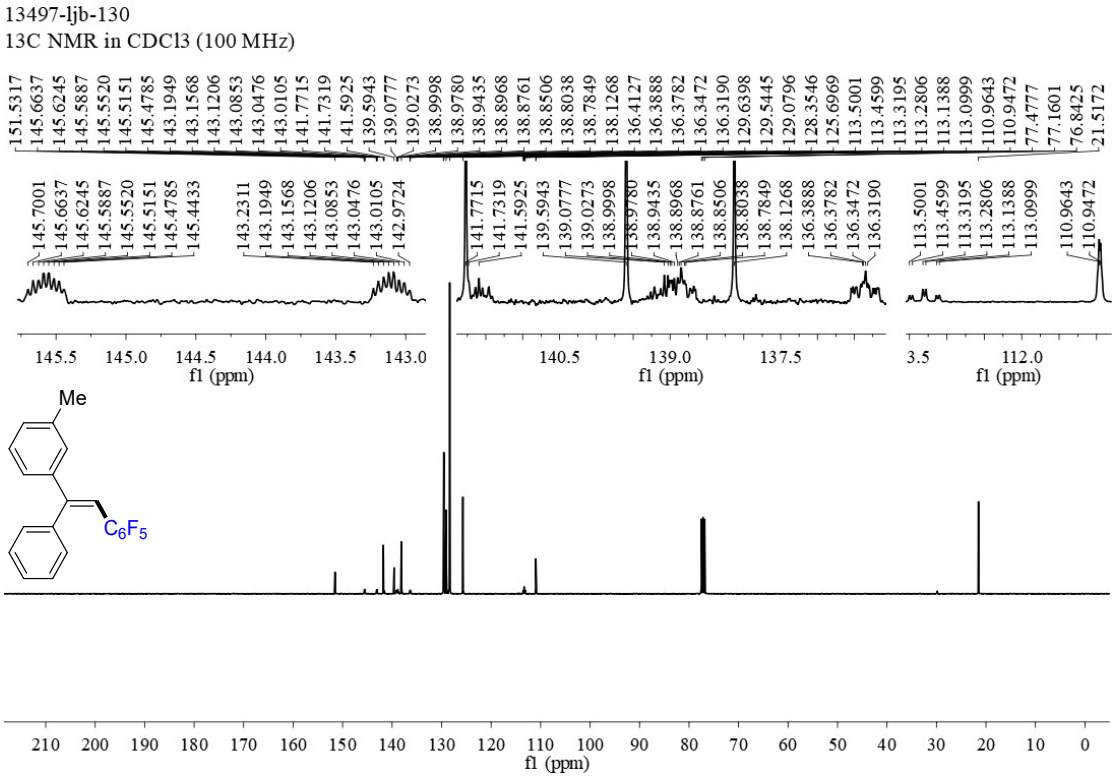


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3h** ($CDCl_3$, 25 °C, 100 MHz).

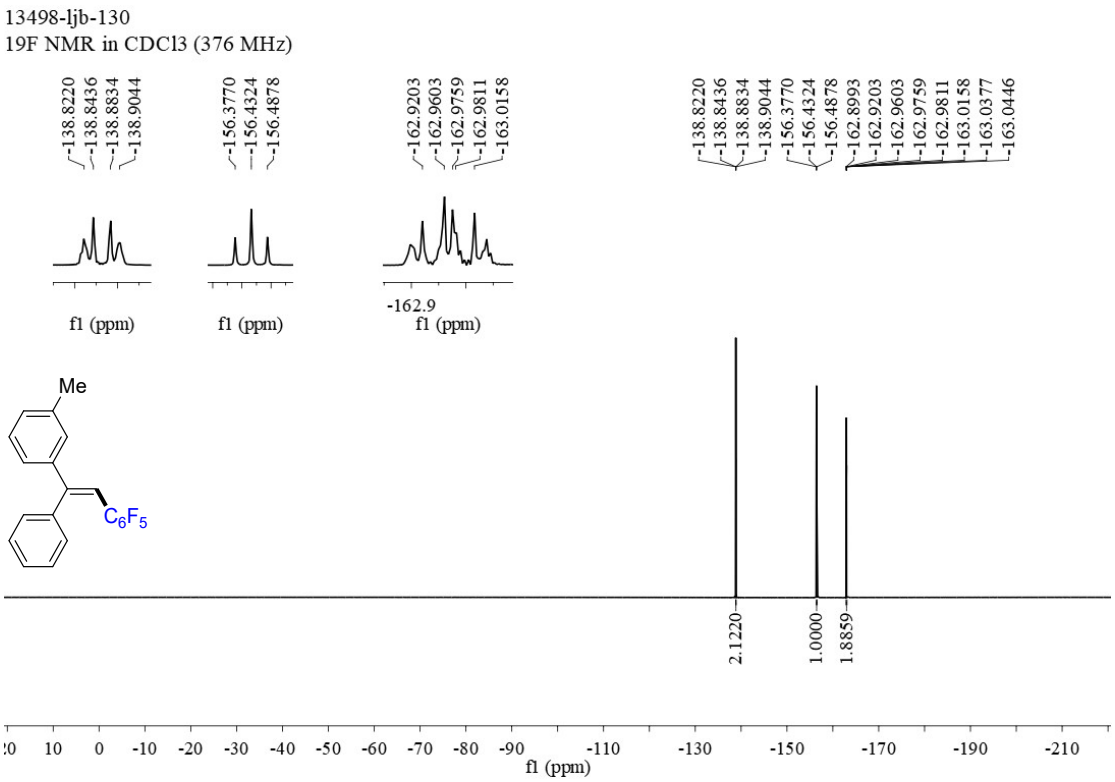


Figure S25. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3h** ($CDCl_3$, 25 °C, 376 MHz).

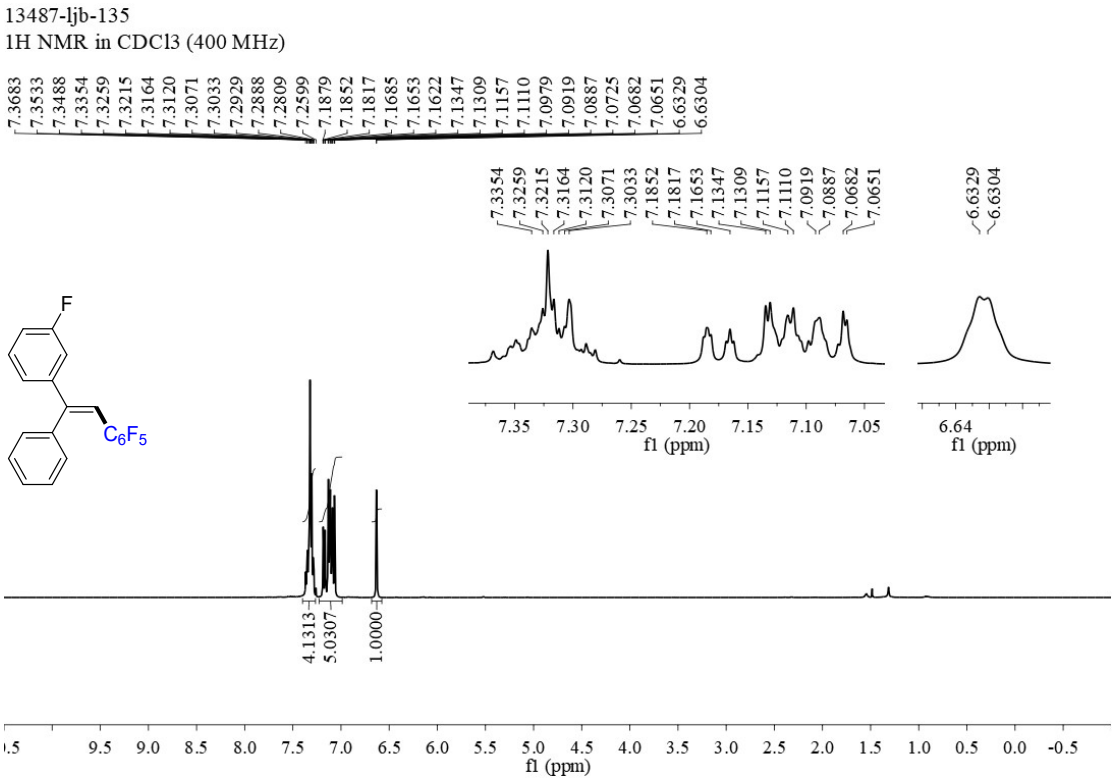


Figure S26. ^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 25 °C, 400 MHz).

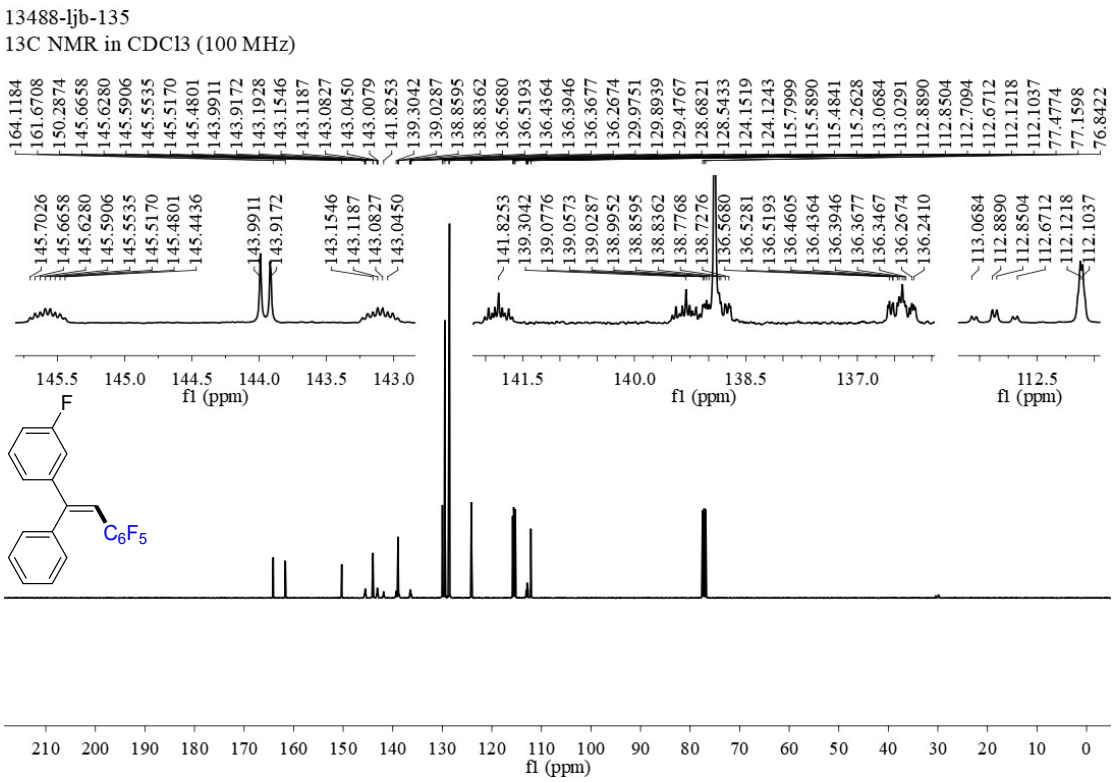


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3i** ($CDCl_3$, 25 °C, 100 MHz).

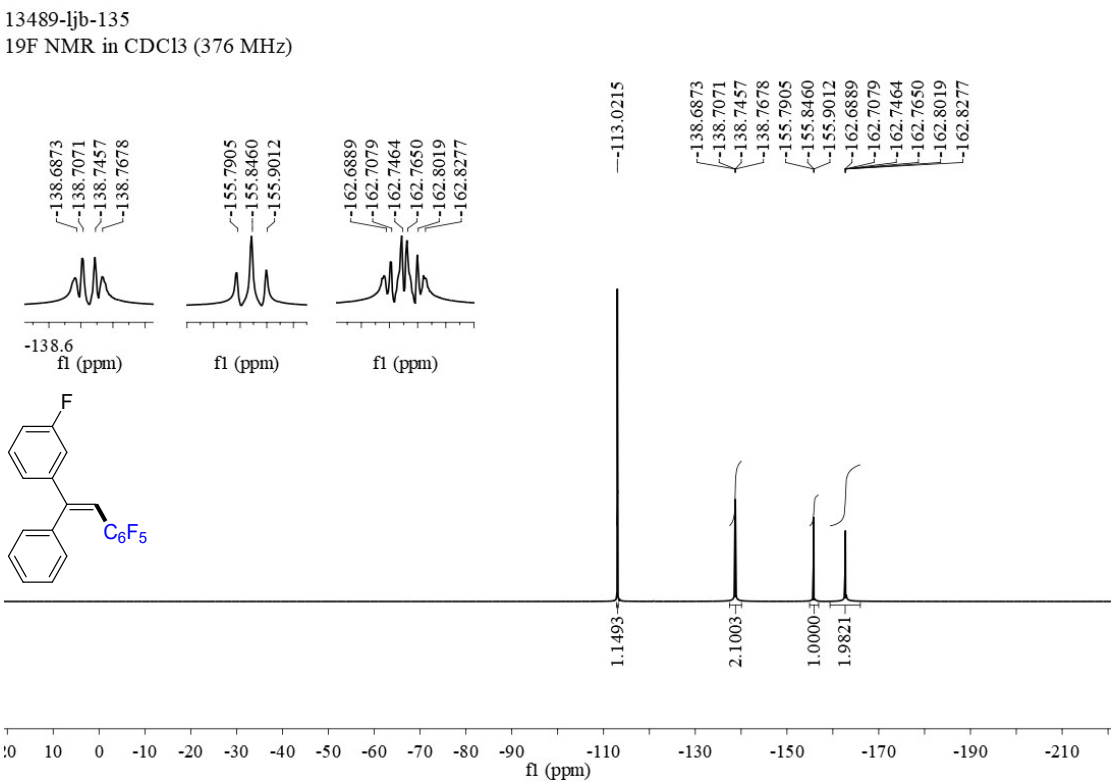


Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3i** ($CDCl_3$, 25 °C, 376 MHz).

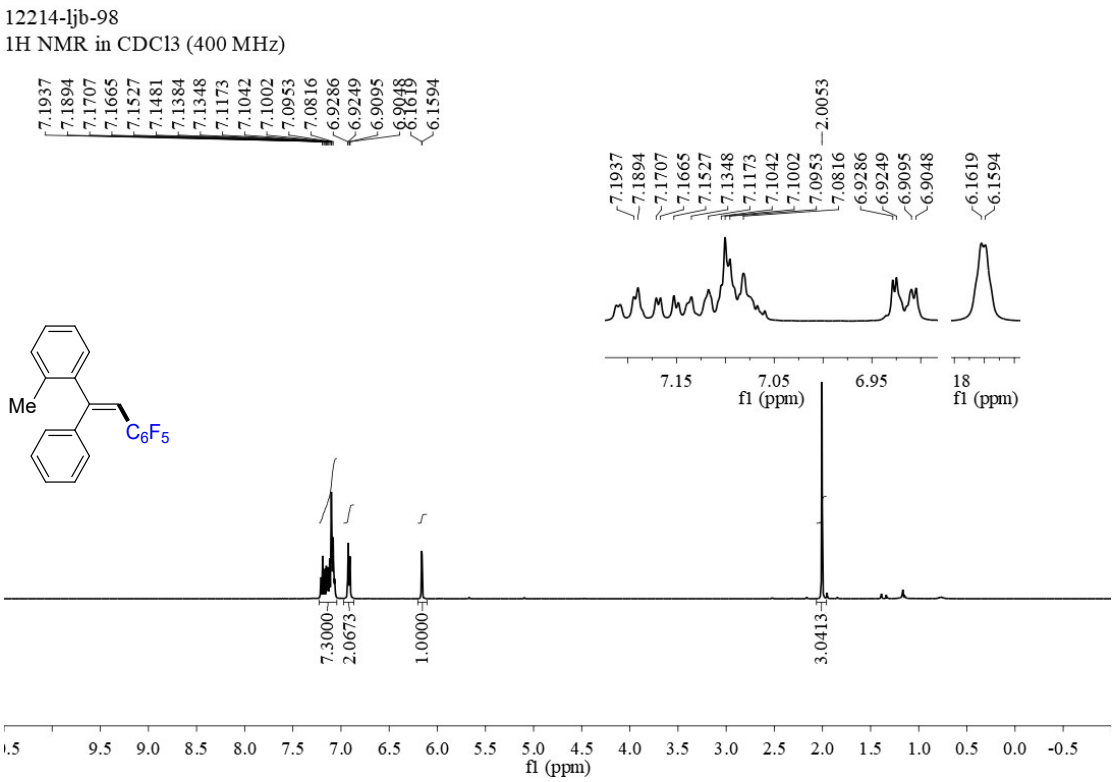


Figure S29. ^{1}H NMR spectrum of compound **3j** ($CDCl_3$, 25 °C, 400 MHz).

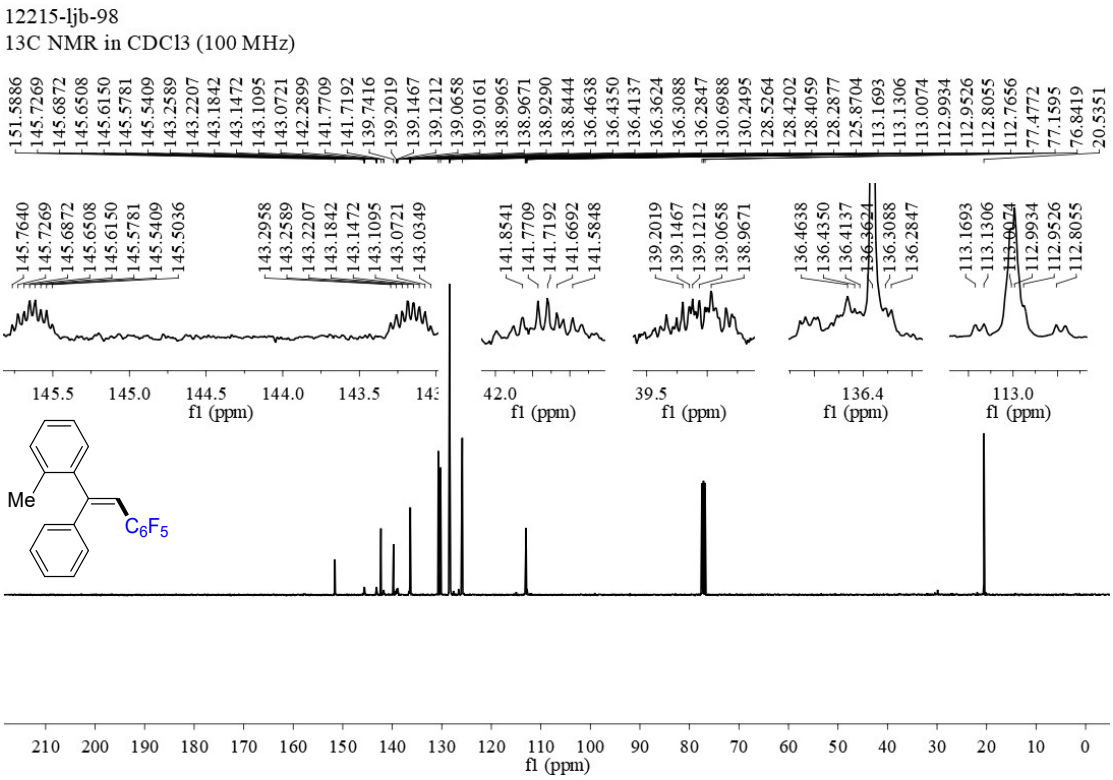


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3j** ($CDCl_3$, 25 °C, 100 MHz).

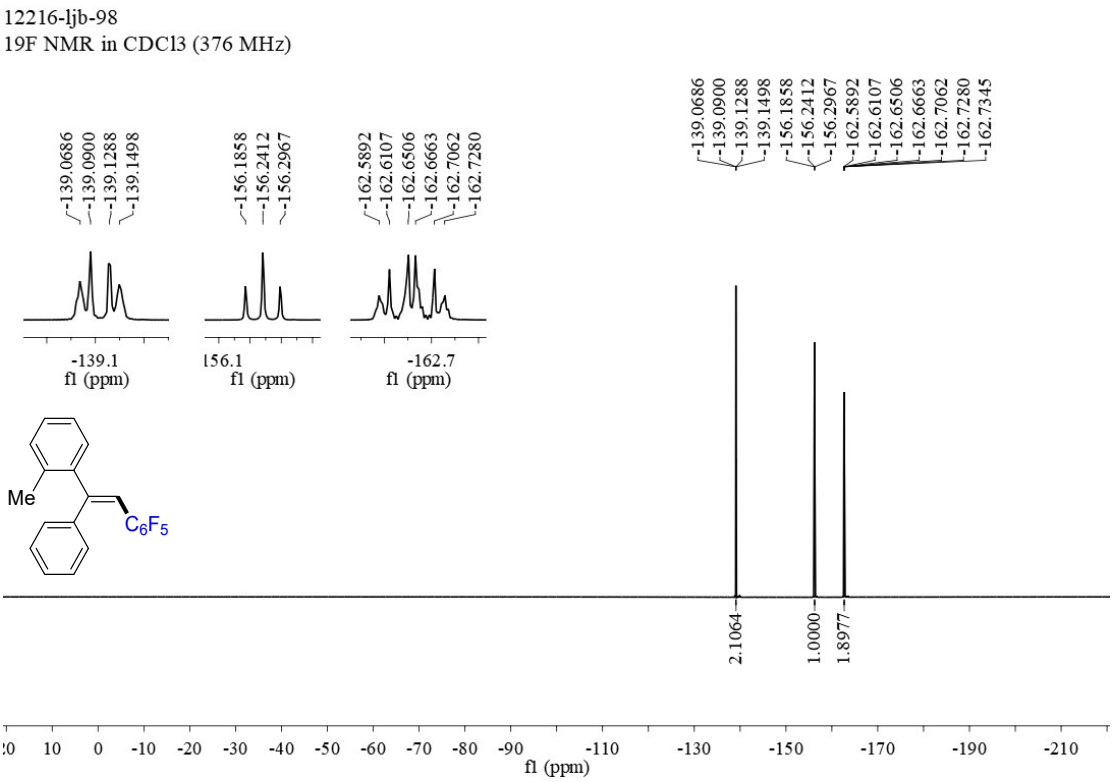


Figure S31. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3j** ($CDCl_3$, 25 °C, 376 MHz).

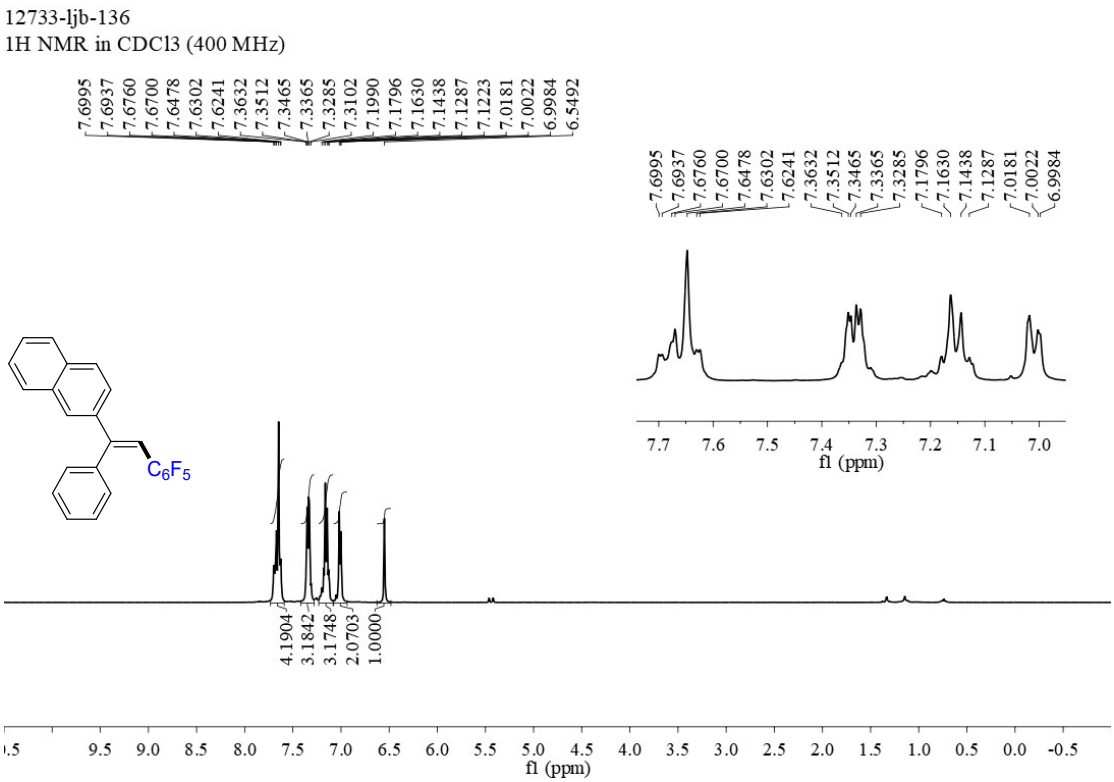


Figure S32. ^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 25 °C, 400 MHz).

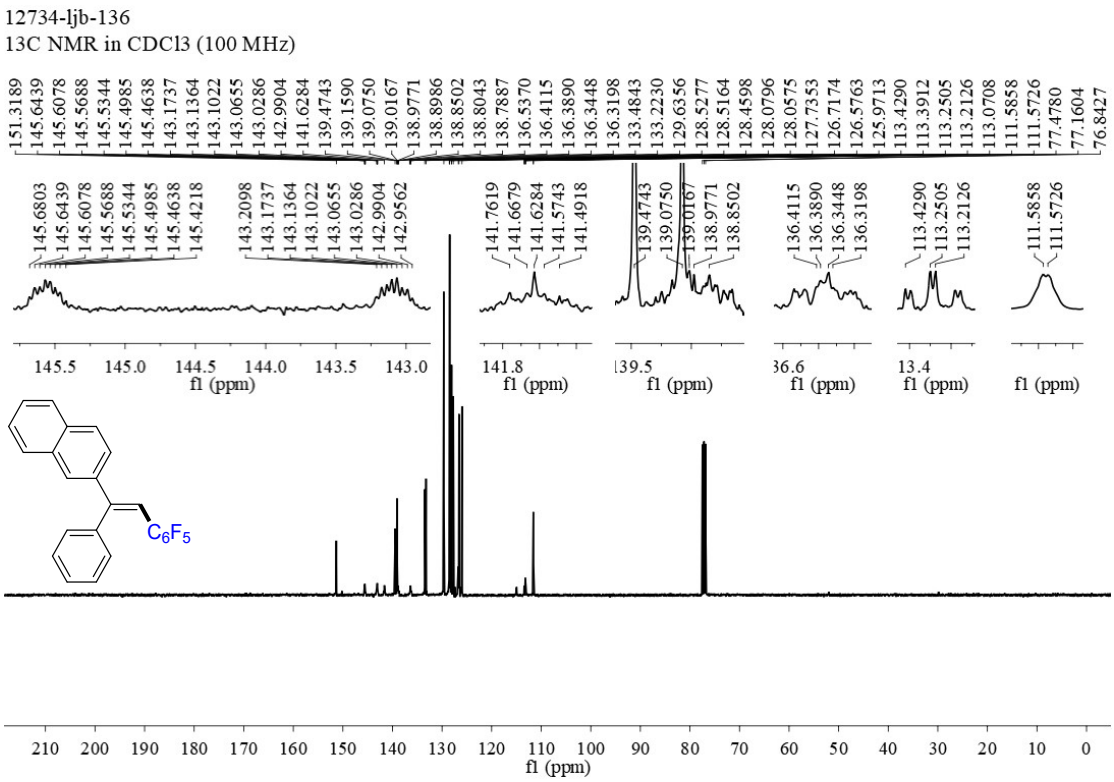


Figure S33. ^{13}C{^{1}H} NMR spectrum of compound **3k** ($CDCl_3$, 25 °C, 100 MHz).

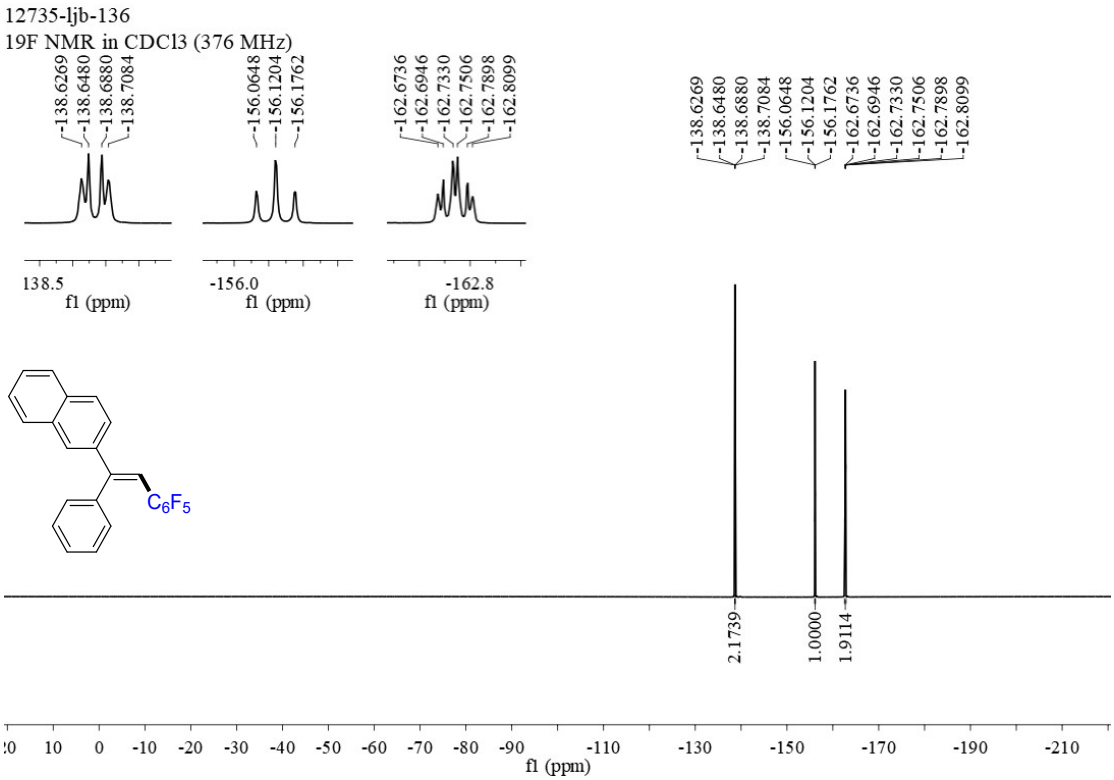


Figure S34. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3k** ($CDCl_3$, 25 °C, 376 MHz).

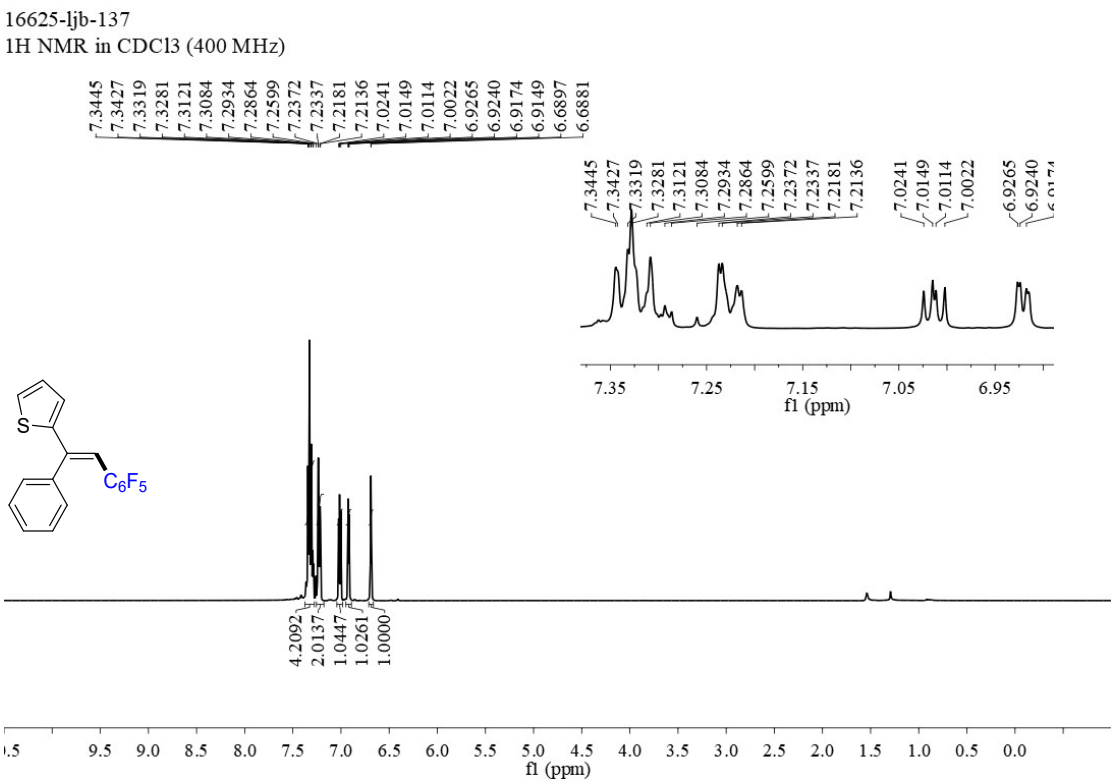


Figure S35. ^{1}H NMR spectrum of compound **3l** ($CDCl_3$, 25 °C, 400 MHz).

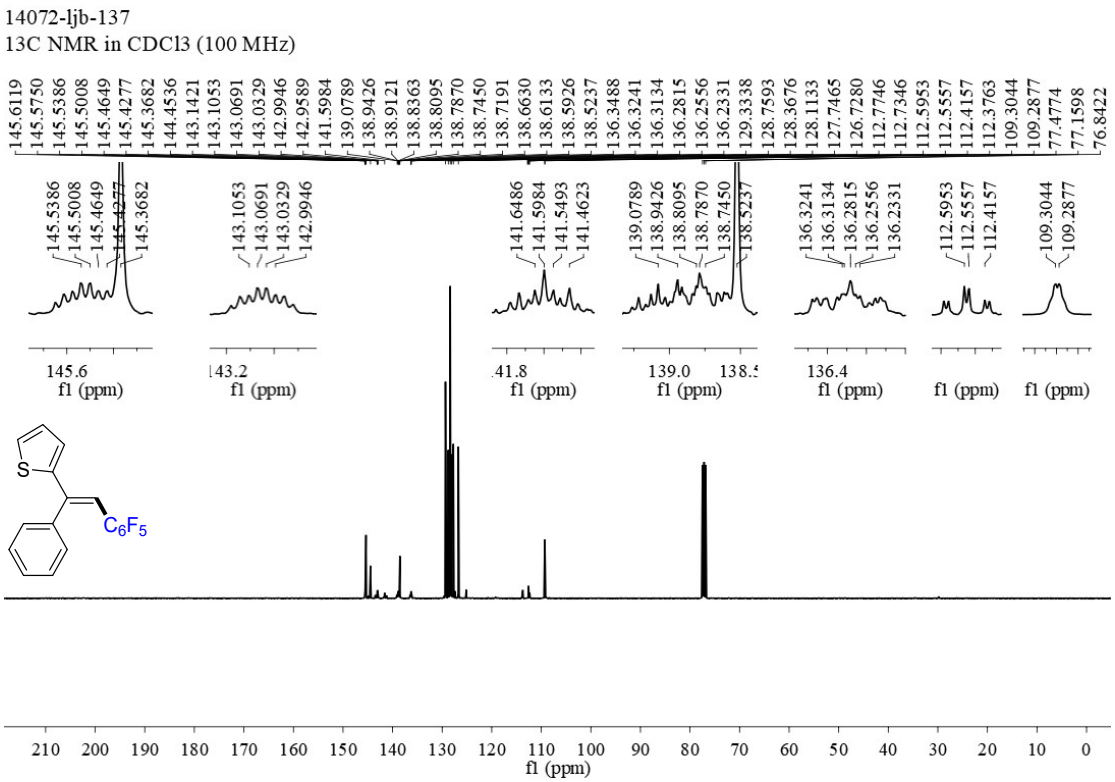


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3l** ($CDCl_3$, 25 °C, 100 MHz).

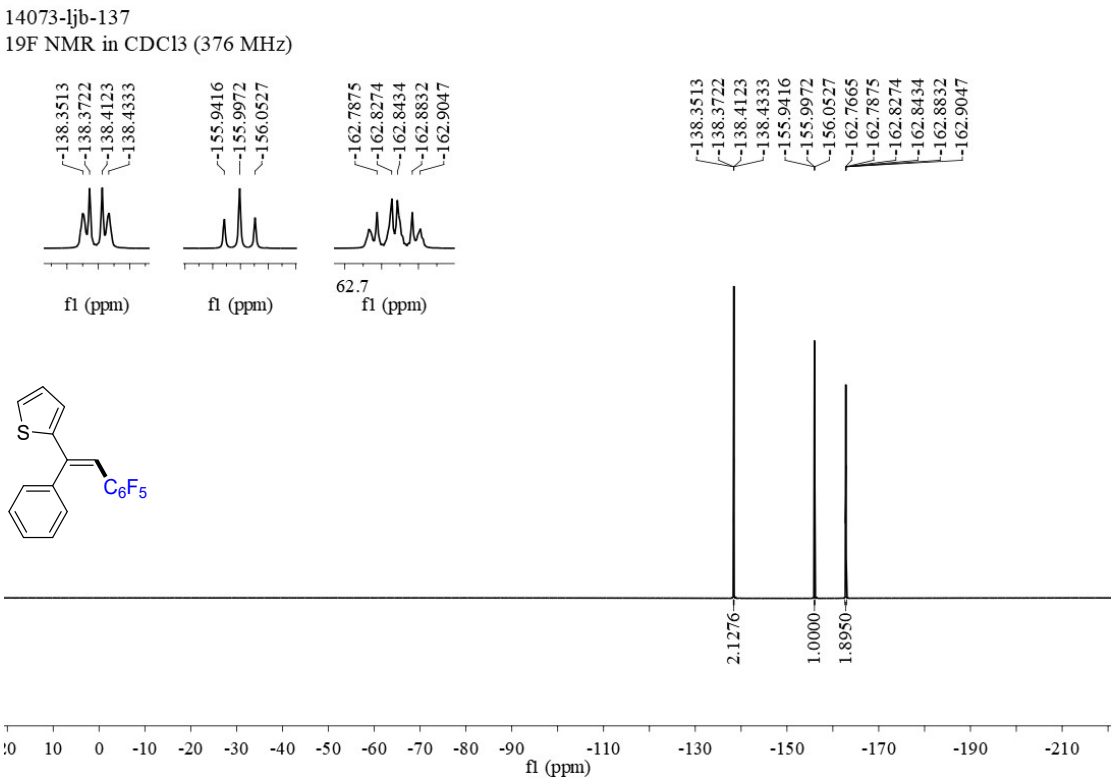


Figure S37. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3l** ($CDCl_3$, 25 °C, 376 MHz).

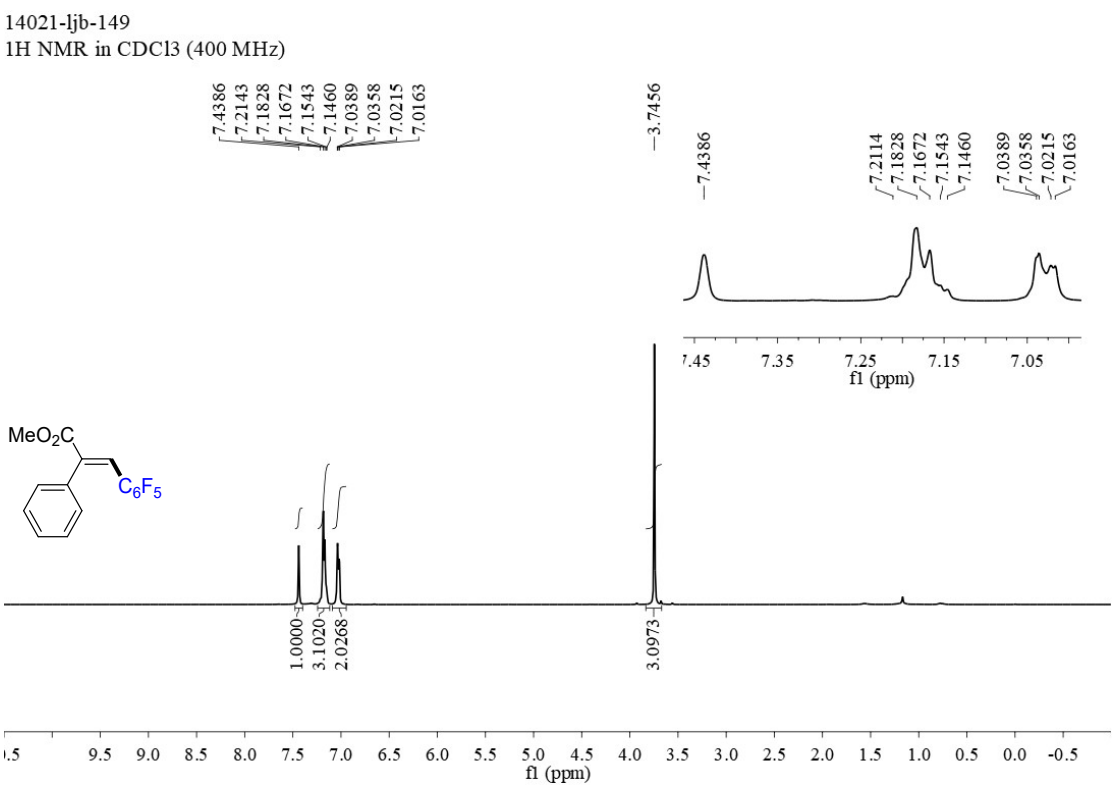


Figure S38. ^{1}H NMR spectrum of compound **3m** ($CDCl_3$, 25 °C, 400 MHz).

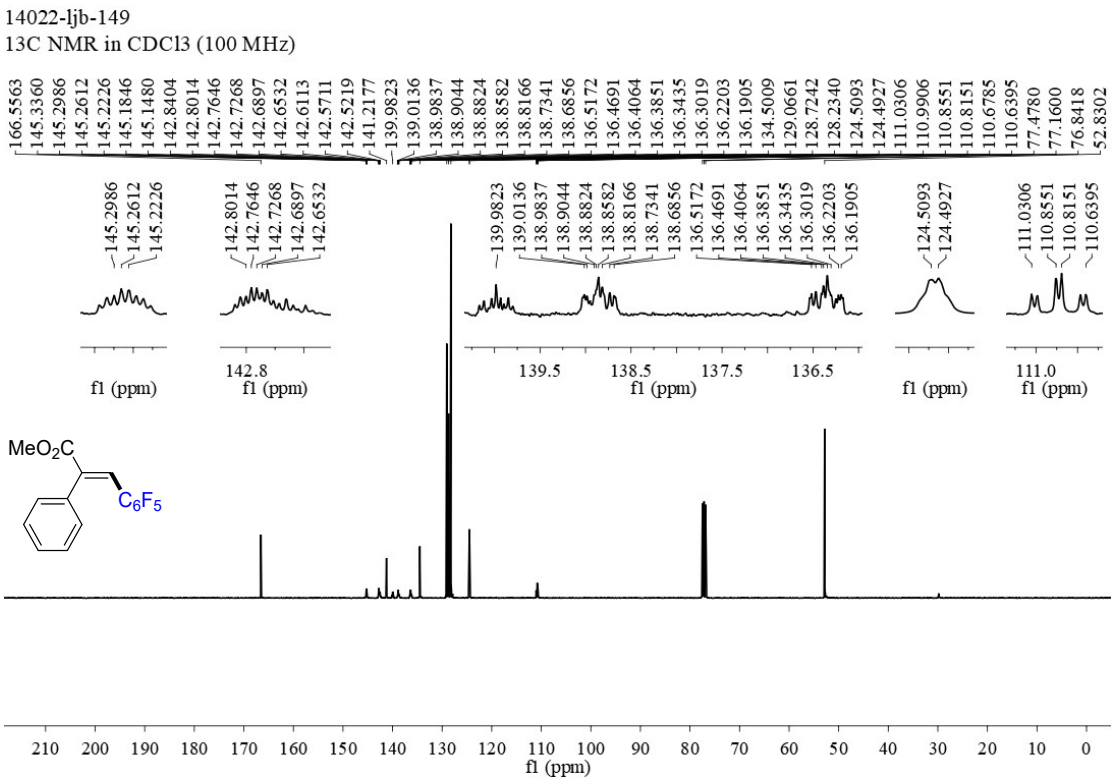


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3m** ($CDCl_3$, 25 °C, 100 MHz).

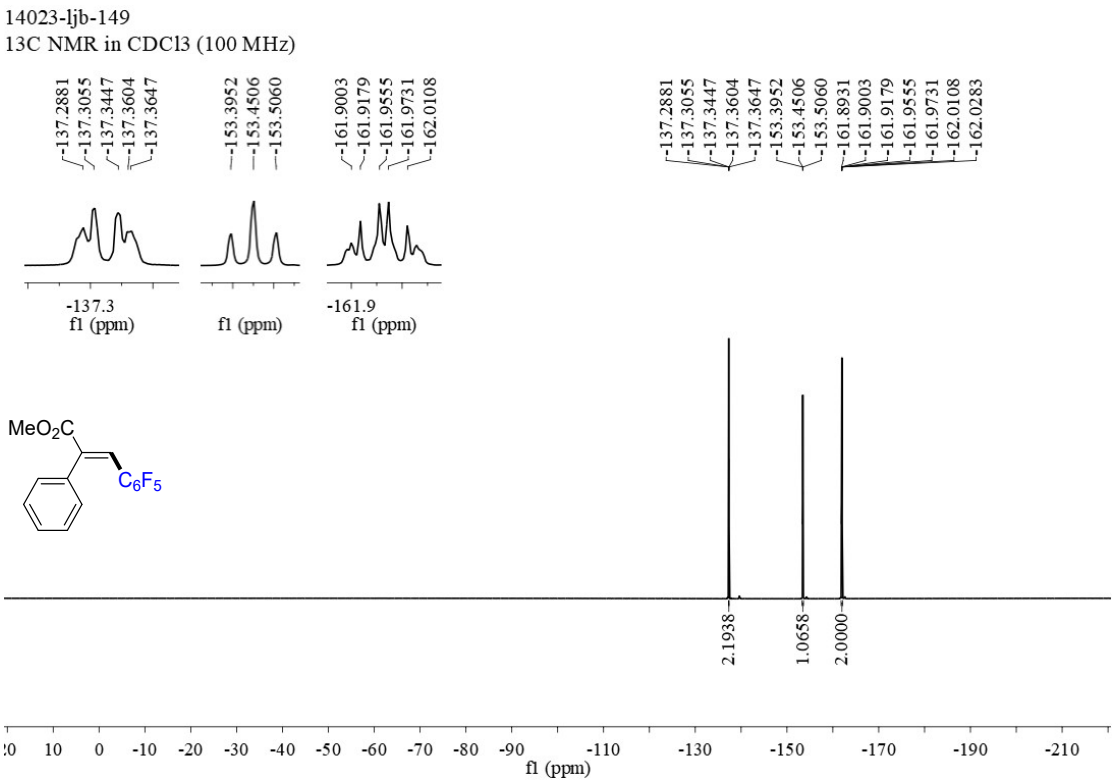


Figure S40. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3m** ($CDCl_3$, 25 °C, 376 MHz).

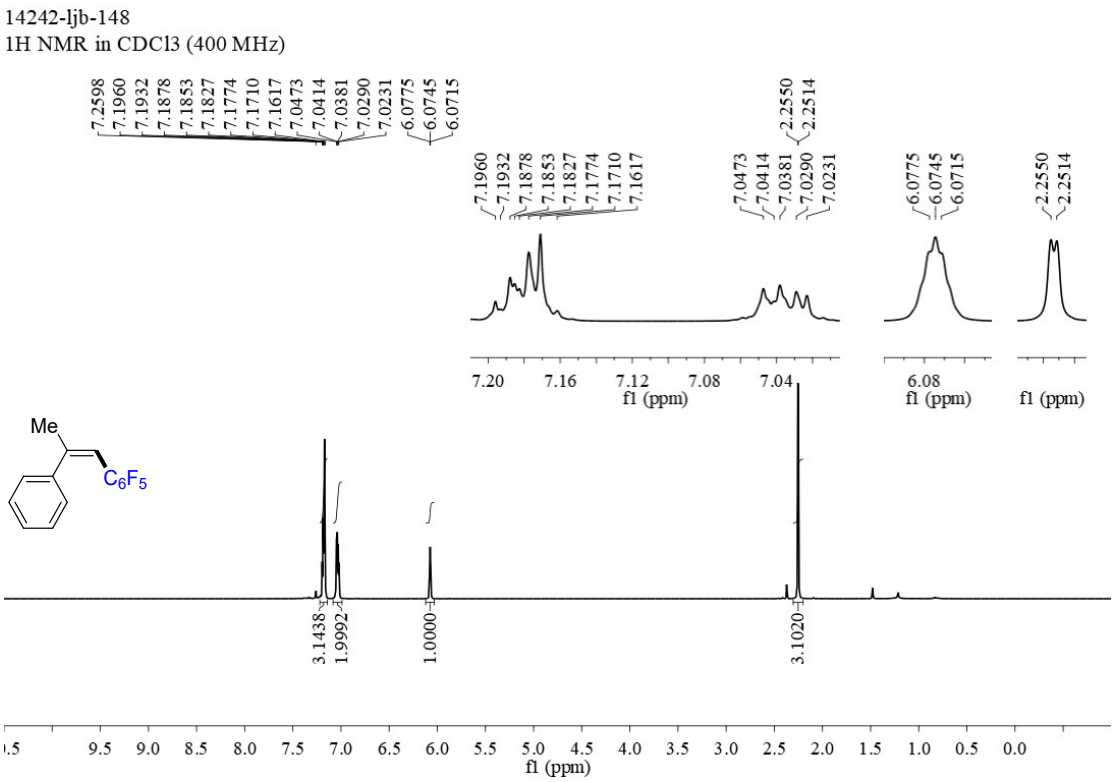


Figure S41. ^{1}H NMR spectrum of compound **3n** ($CDCl_3$, 25 °C, 400 MHz).

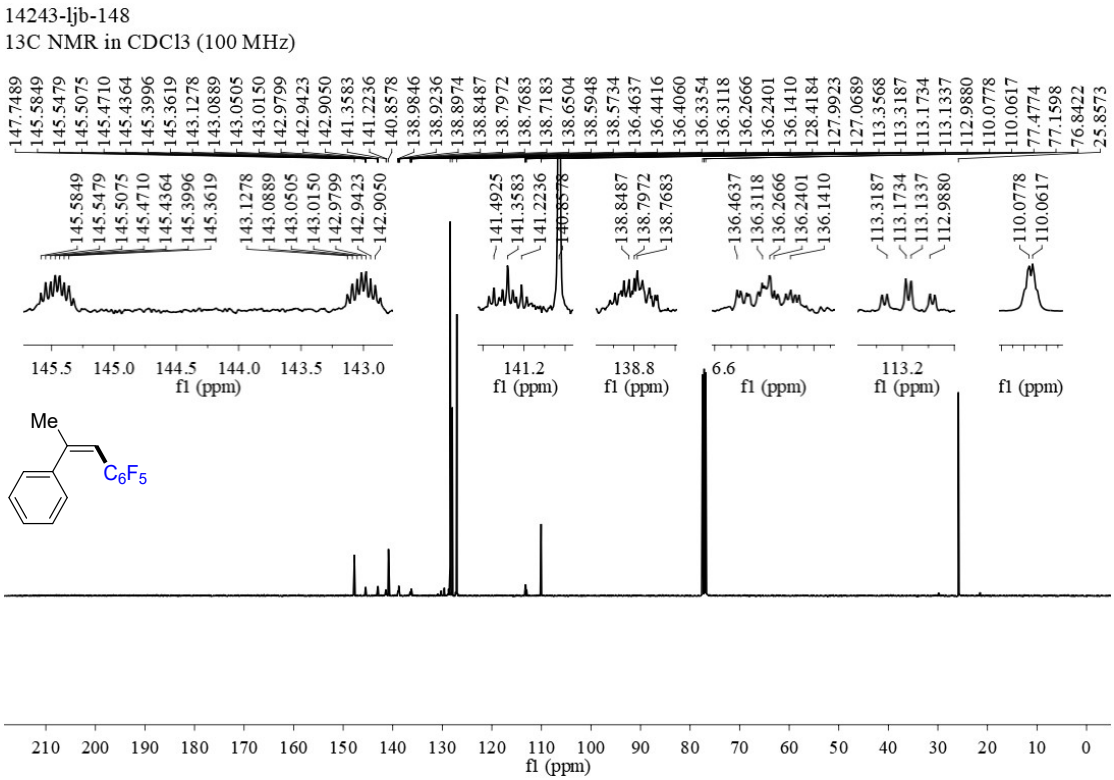


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3n** ($CDCl_3$, 25 °C, 100 MHz).

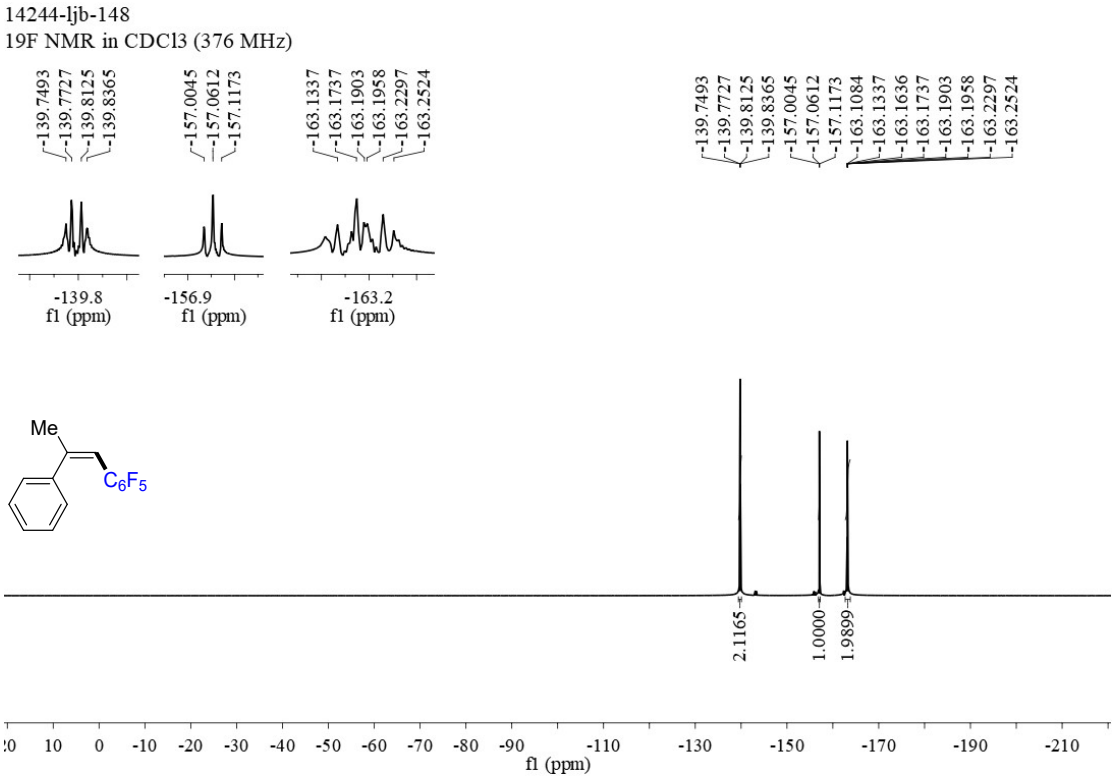


Figure S43. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3n** ($CDCl_3$, 25 °C, 376 MHz).

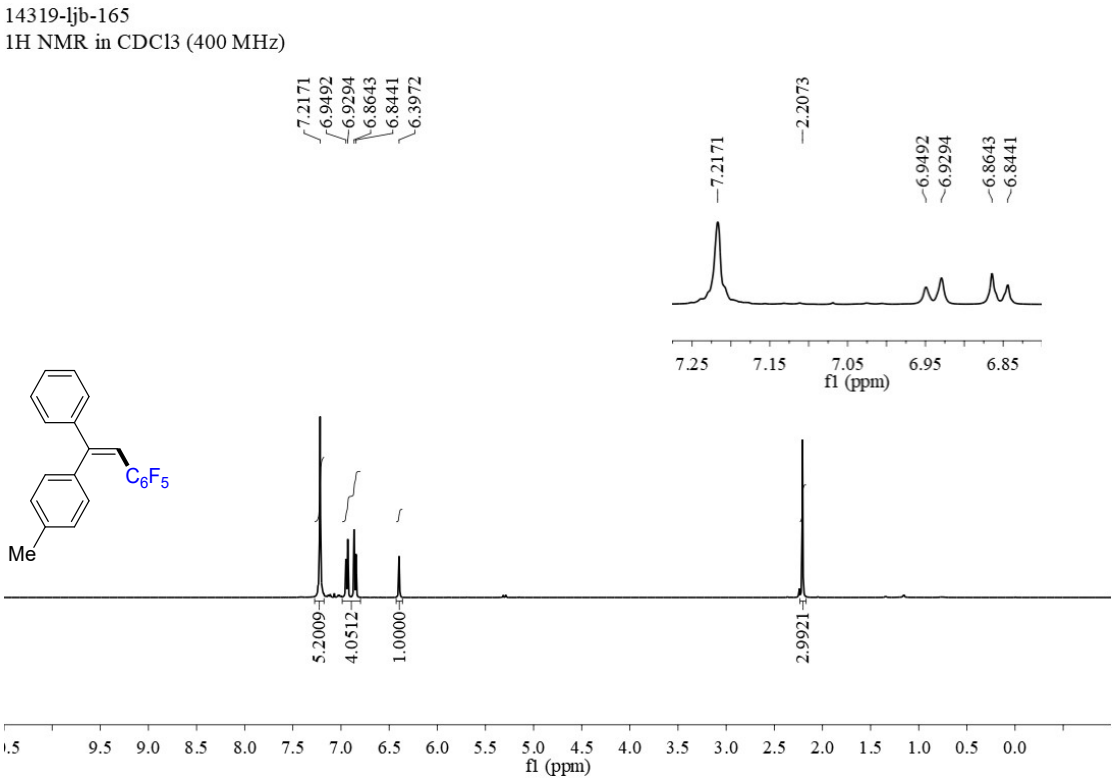


Figure S44. ^{1}H NMR spectrum of compound **3o** ($CDCl_3$, 25 °C, 400 MHz).

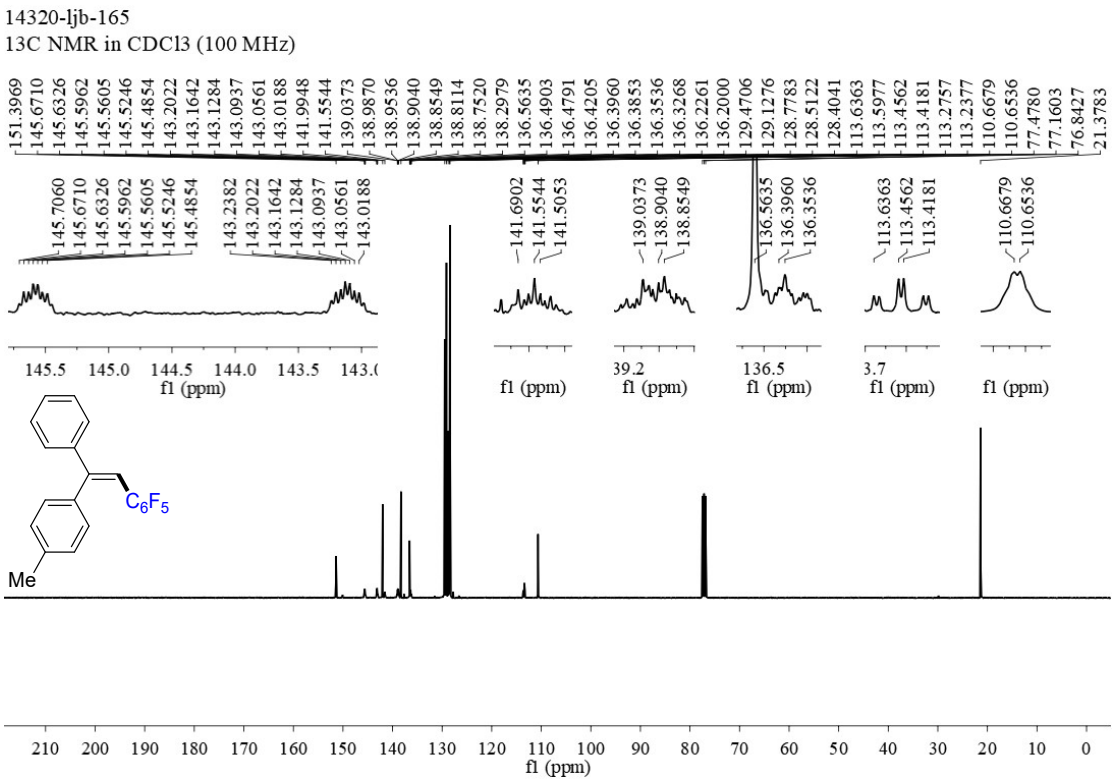


Figure S45. ^{13}C{^{1}H} NMR spectrum of compound **3o** ($CDCl_3$, 25 °C, 100 MHz).

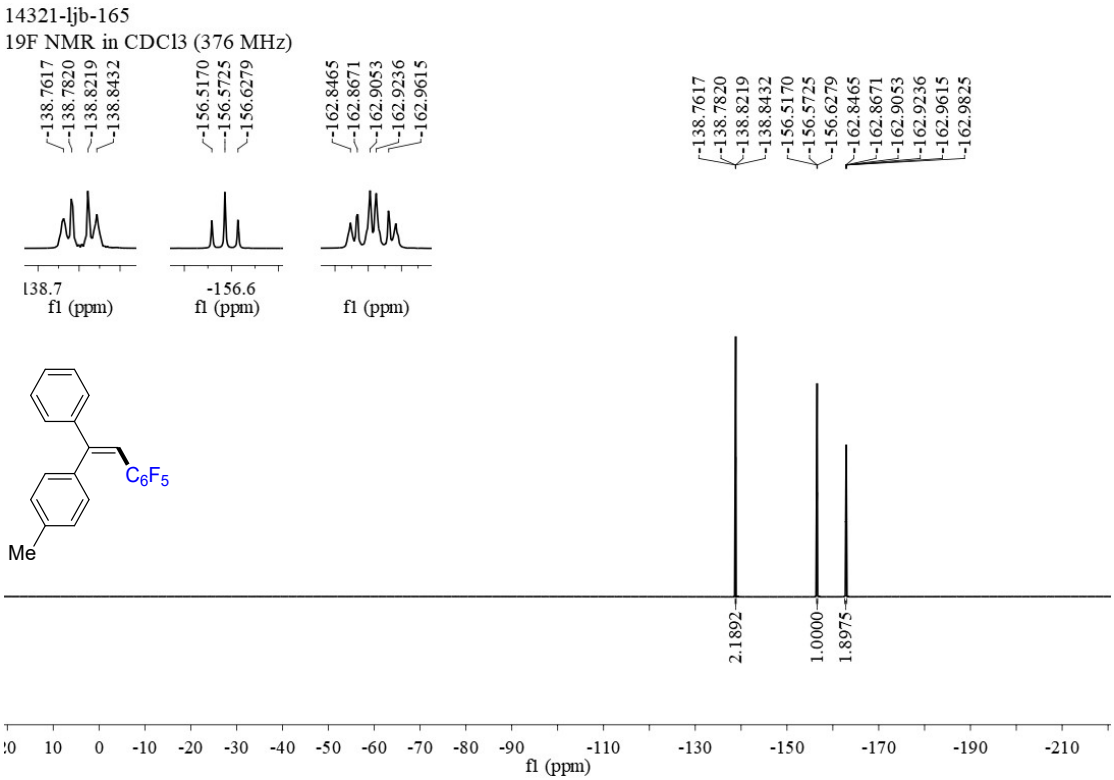


Figure S46. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3o** ($CDCl_3$, 25 °C, 376 MHz).

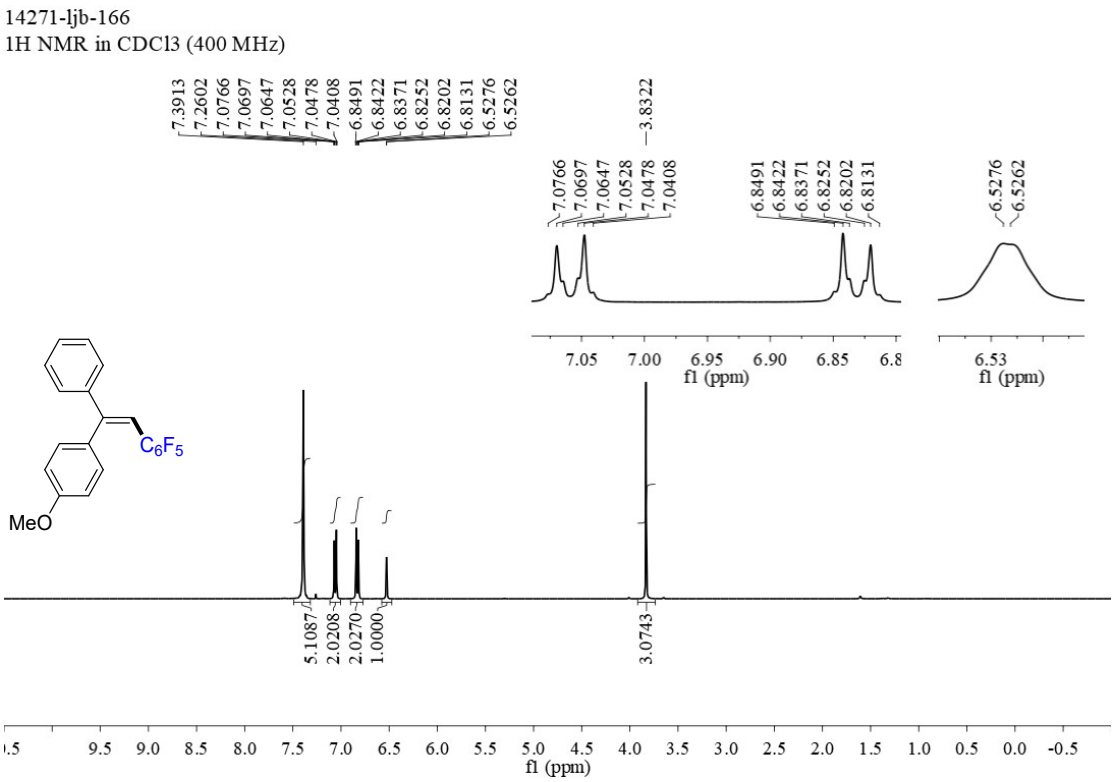


Figure S47. ^{1}H NMR spectrum of compound **3p** ($CDCl_3$, 25 °C, 400 MHz).

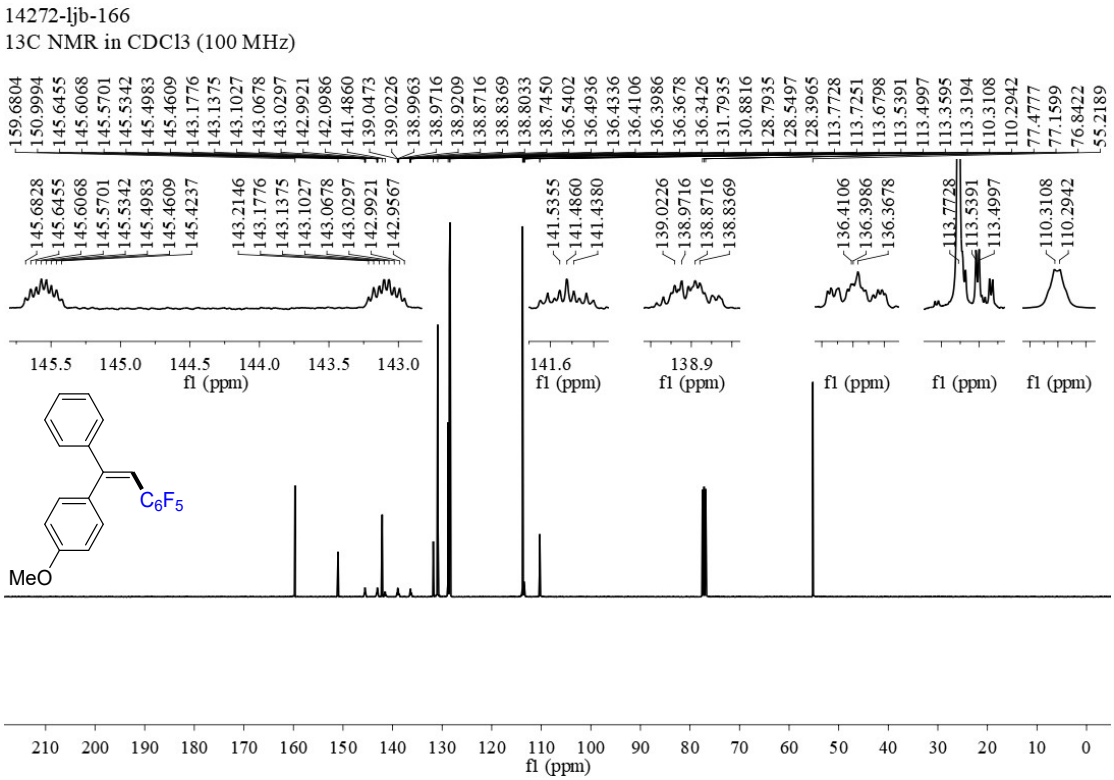


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3p** ($CDCl_3$, 25 °C, 100 MHz).

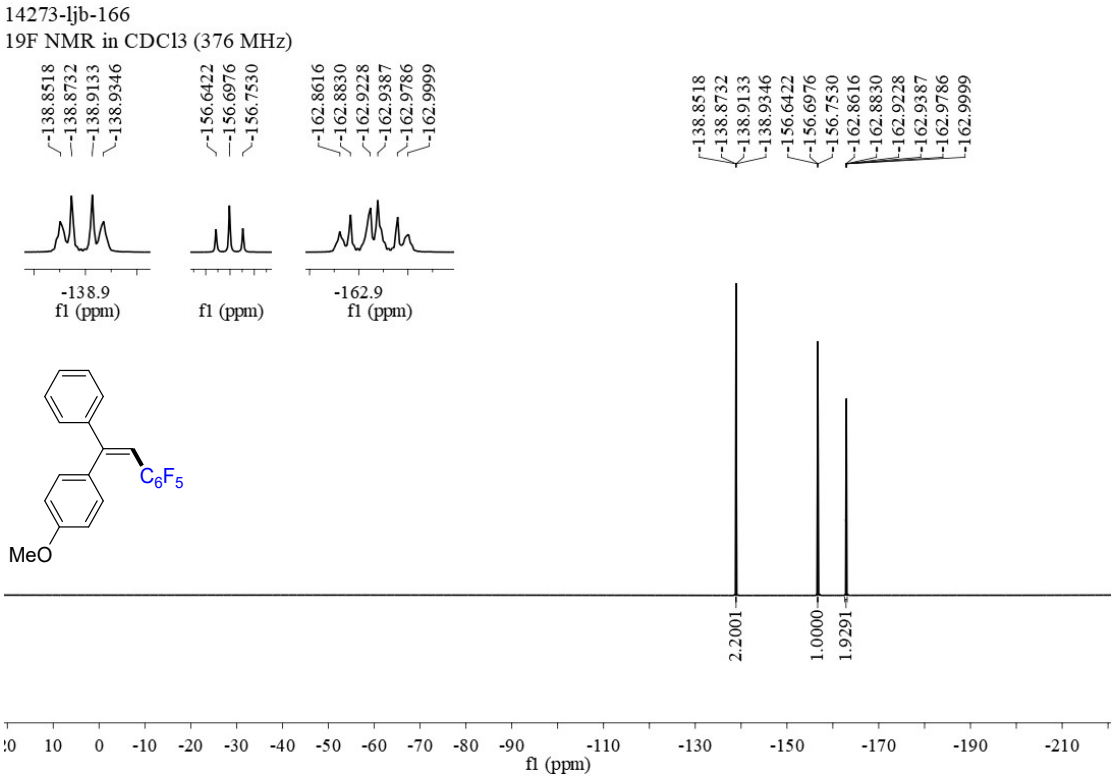


Figure S49. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3p** ($CDCl_3$, 25 °C, 376 MHz).

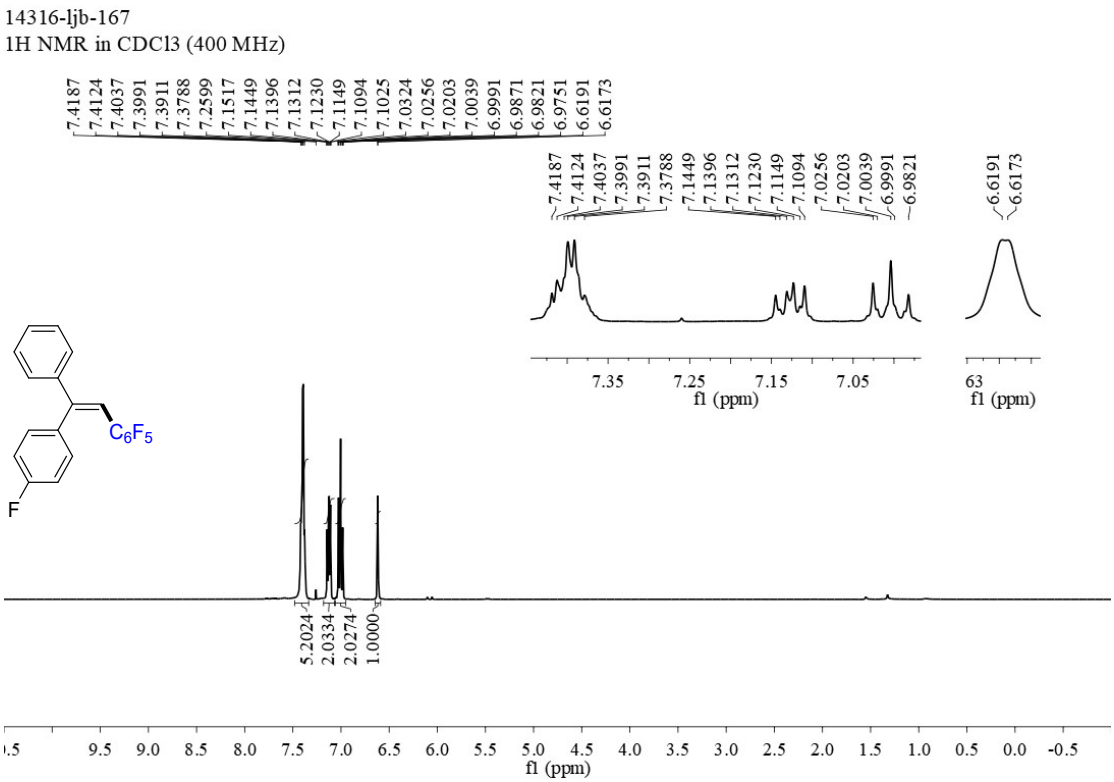


Figure S50. ^{1}H NMR spectrum of compound **3q** ($CDCl_3$, 25 °C, 400 MHz).

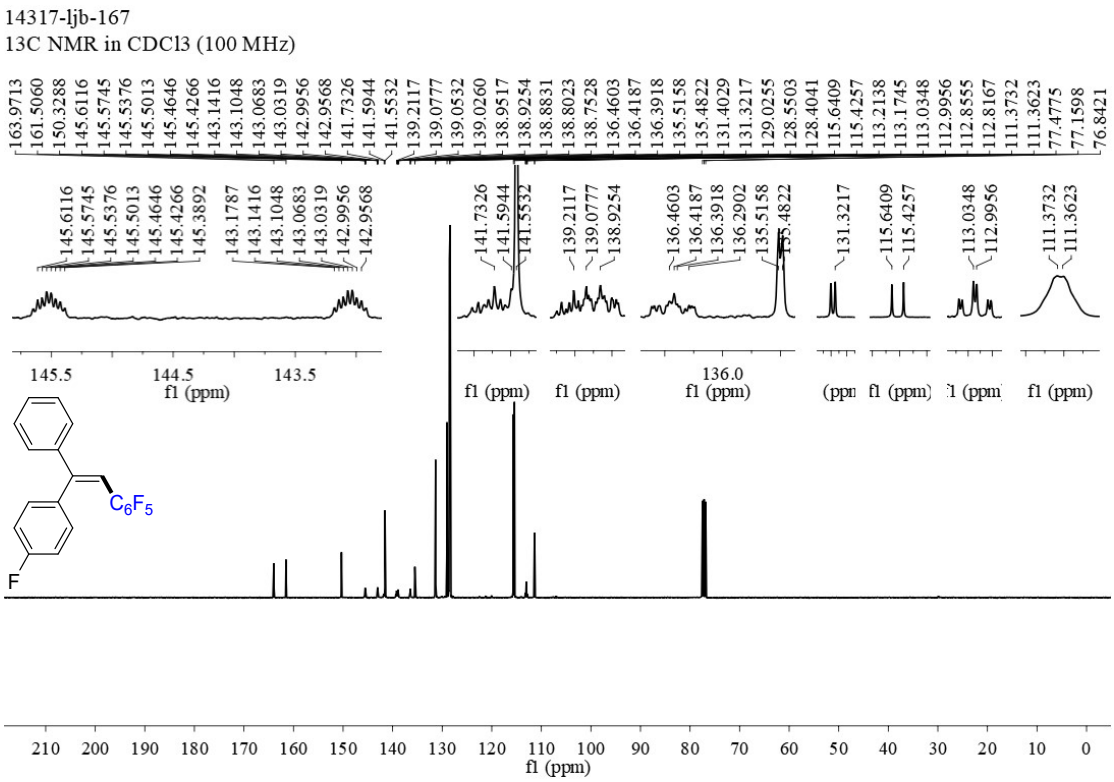


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3q** ($CDCl_3$, 25 °C, 100 MHz).

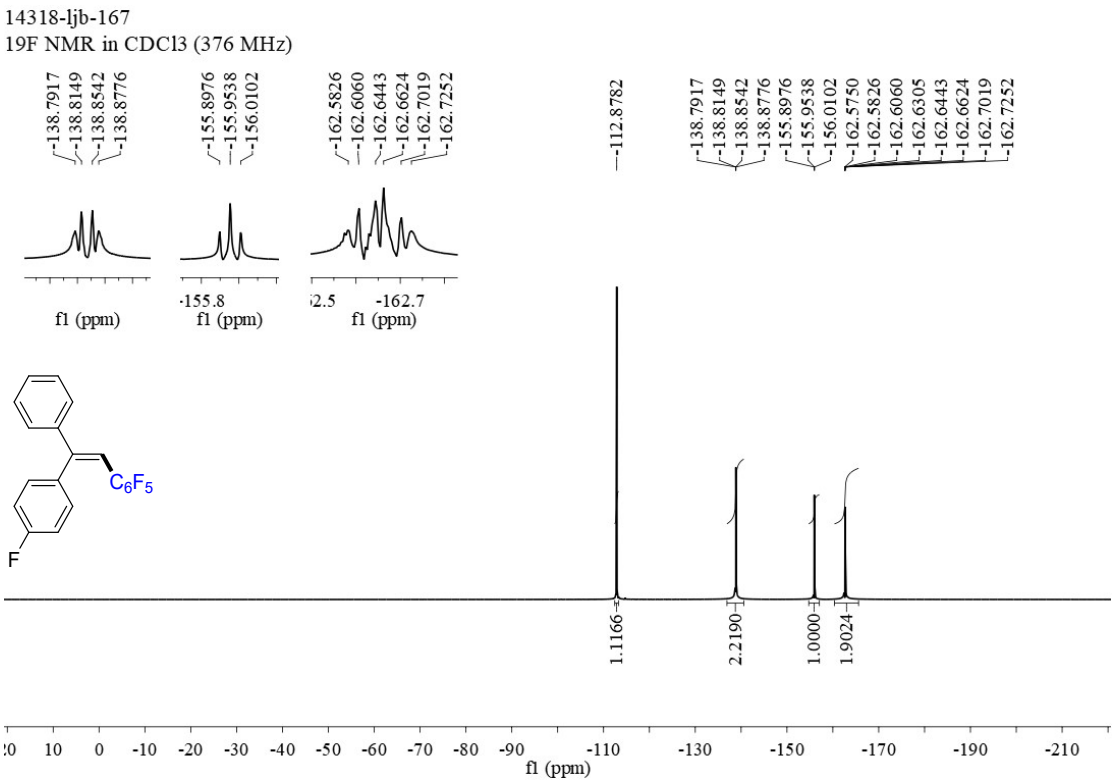


Figure S52. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3q** ($CDCl_3$, 25 °C, 376 MHz).

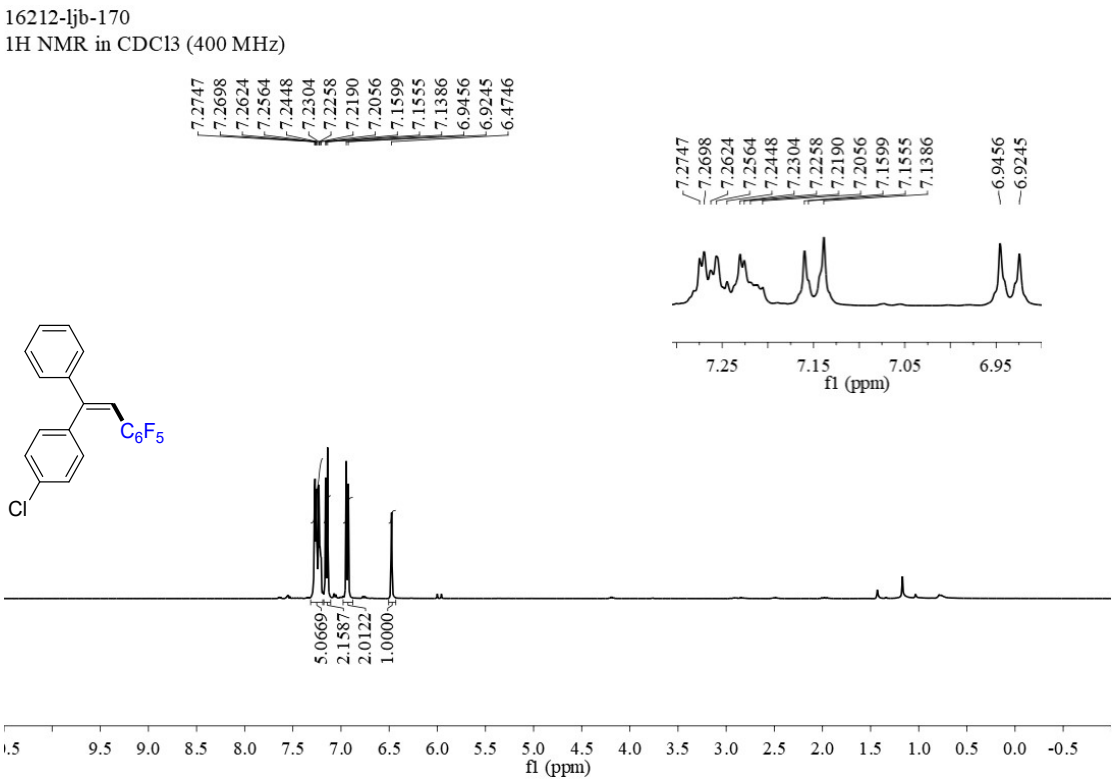


Figure S53. ^{1}H NMR spectrum of compound **3r** ($CDCl_3$, 25 °C, 400 MHz).

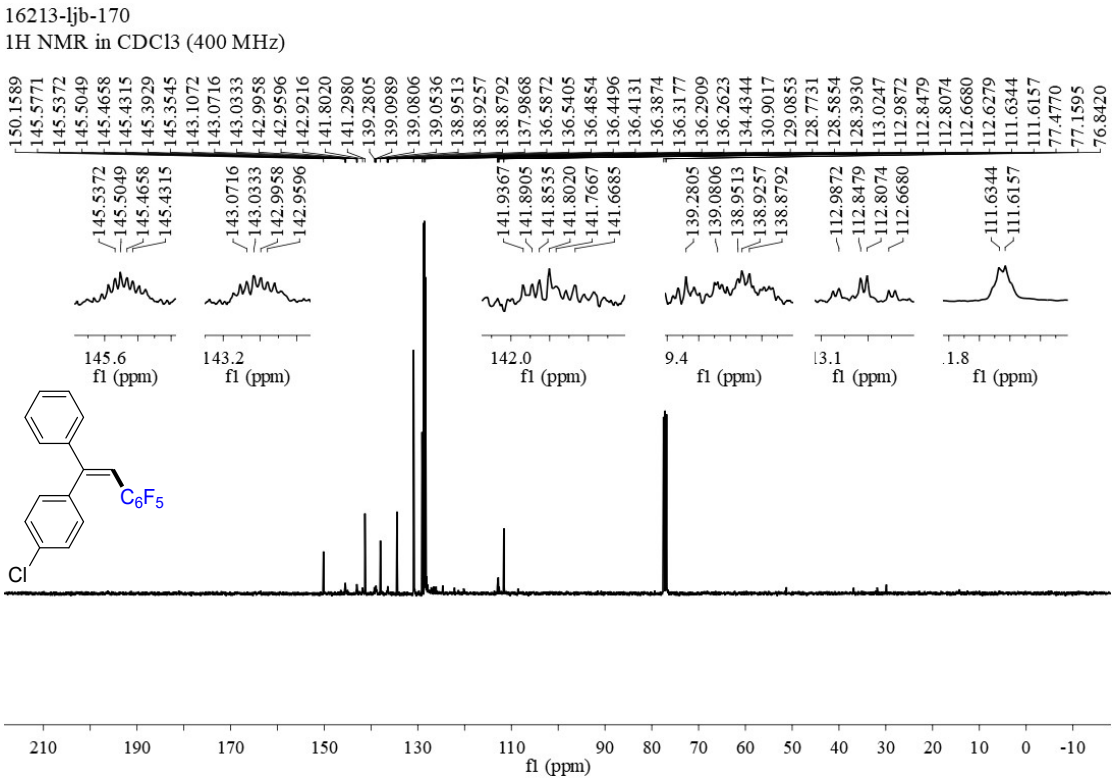


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3r** ($CDCl_3$, 25 °C, 100 MHz).

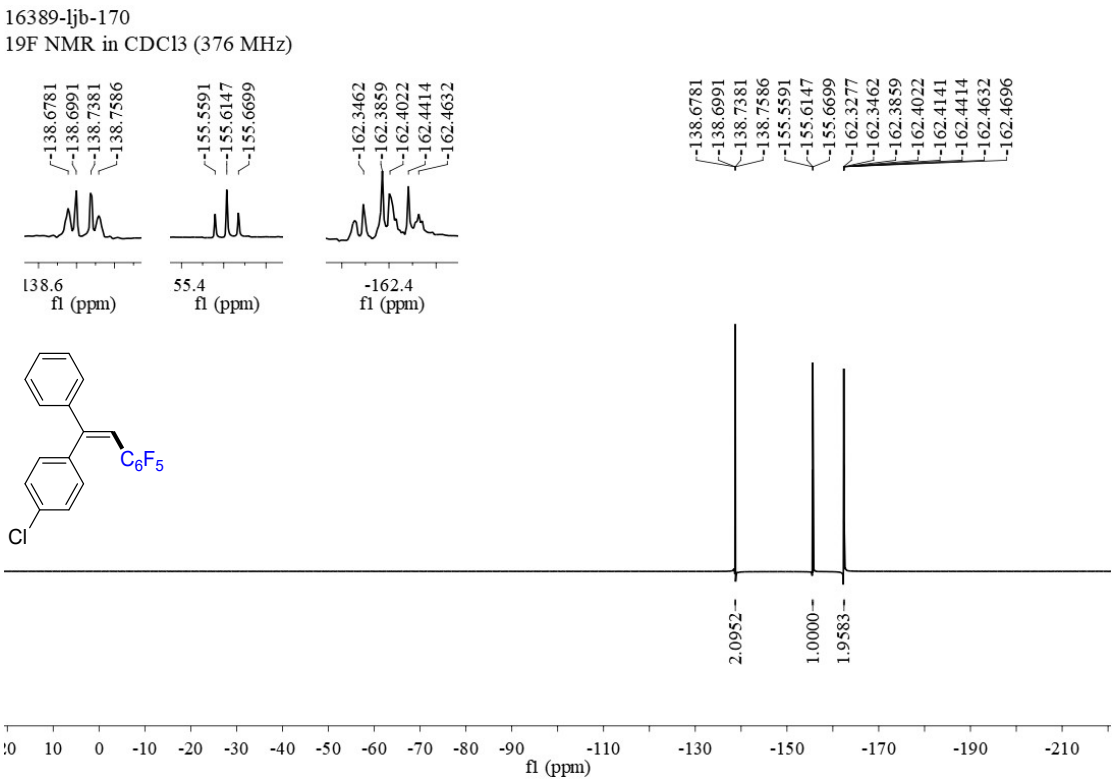


Figure S55. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3r** ($CDCl_3$, 25 °C, 376 MHz).

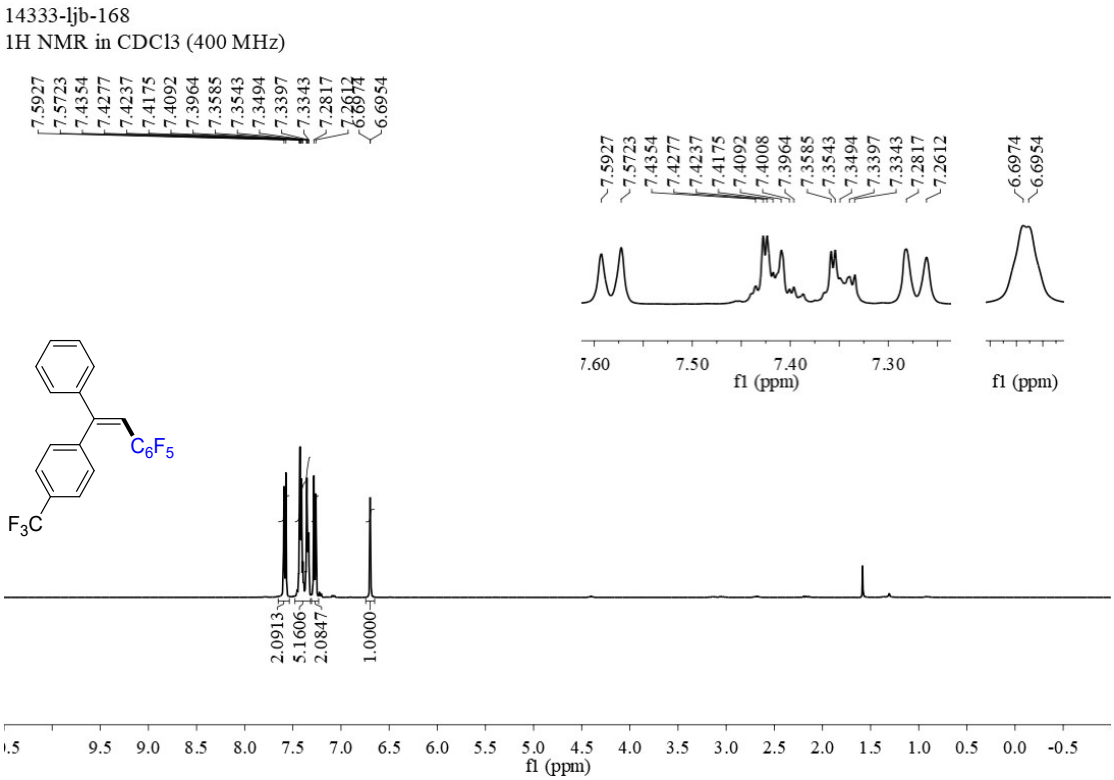


Figure S56. ^{1}H NMR spectrum of compound **3s** ($CDCl_3$, 25 °C, 400 MHz).

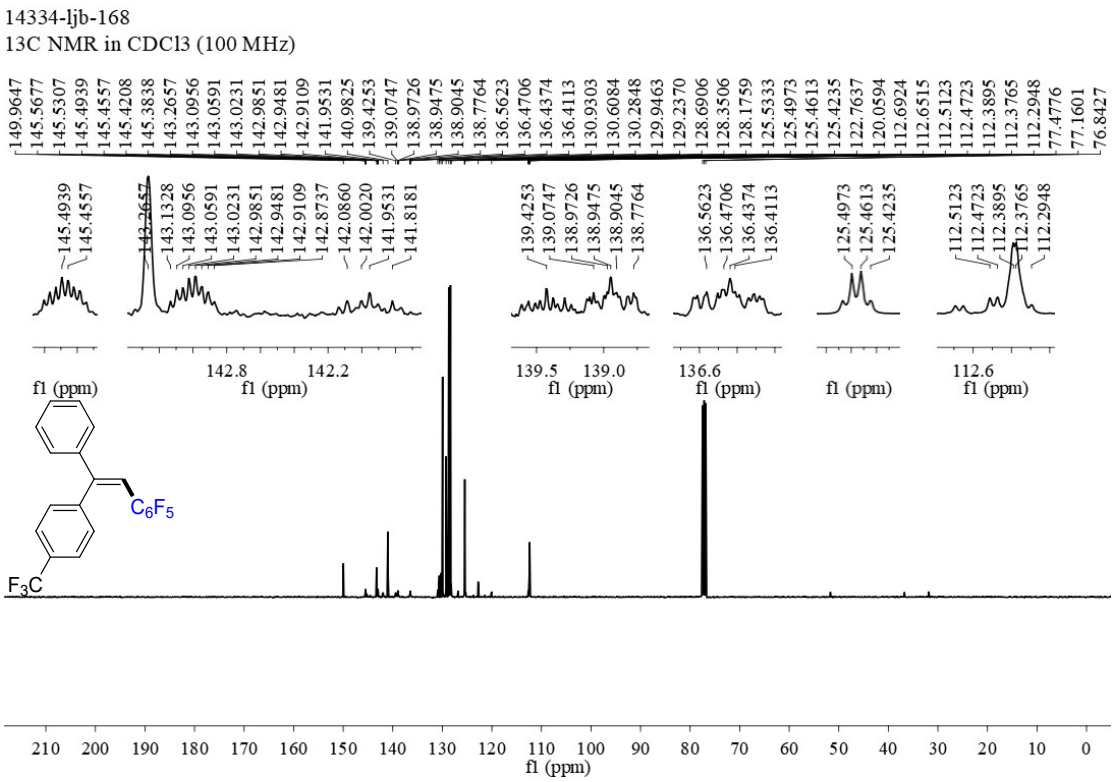


Figure S57. ^{13}C{^{1}H} NMR spectrum of compound **3s** ($CDCl_3$, 25 °C, 100 MHz).

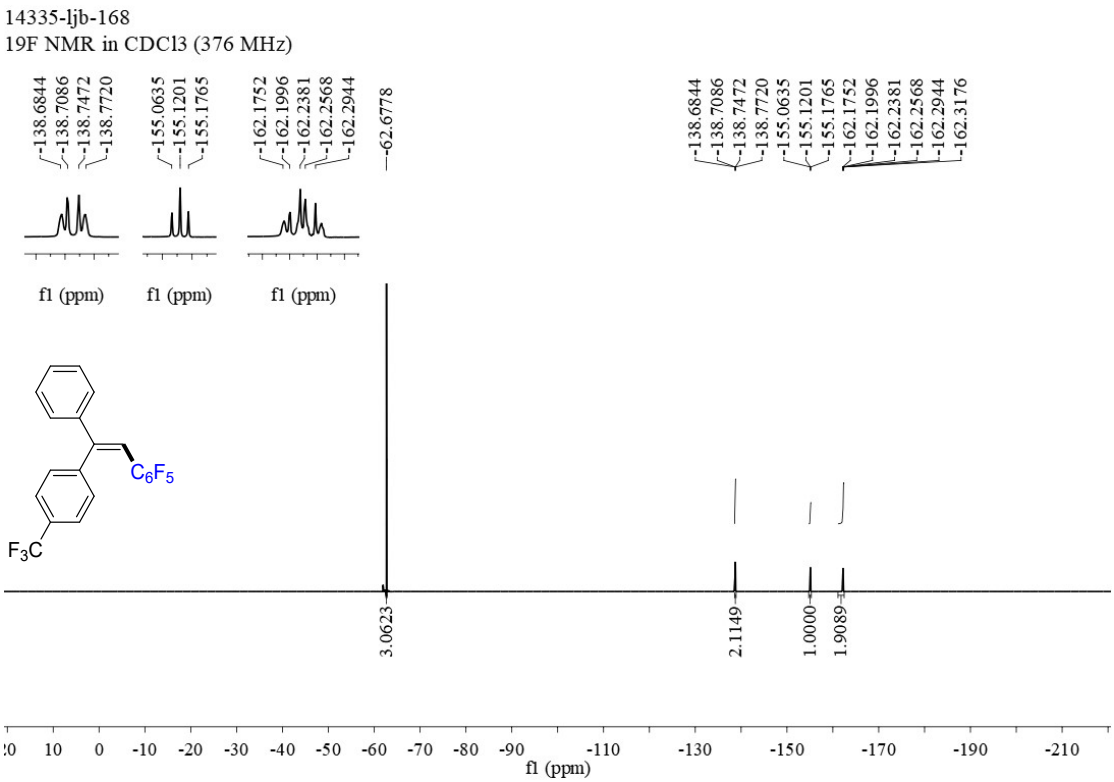


Figure S58. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3s** ($CDCl_3$, 25 °C, 376 MHz).

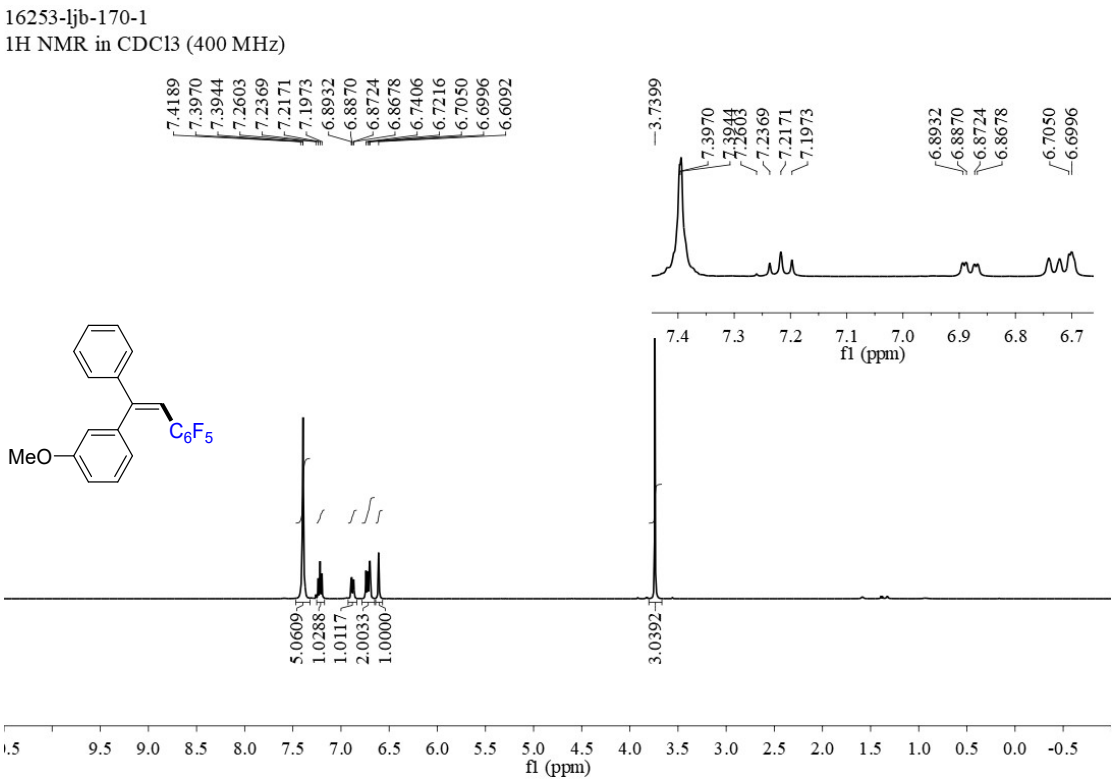


Figure S59. ^{1}H NMR spectrum of compound **3t** ($CDCl_3$, 25 °C, 400 MHz).

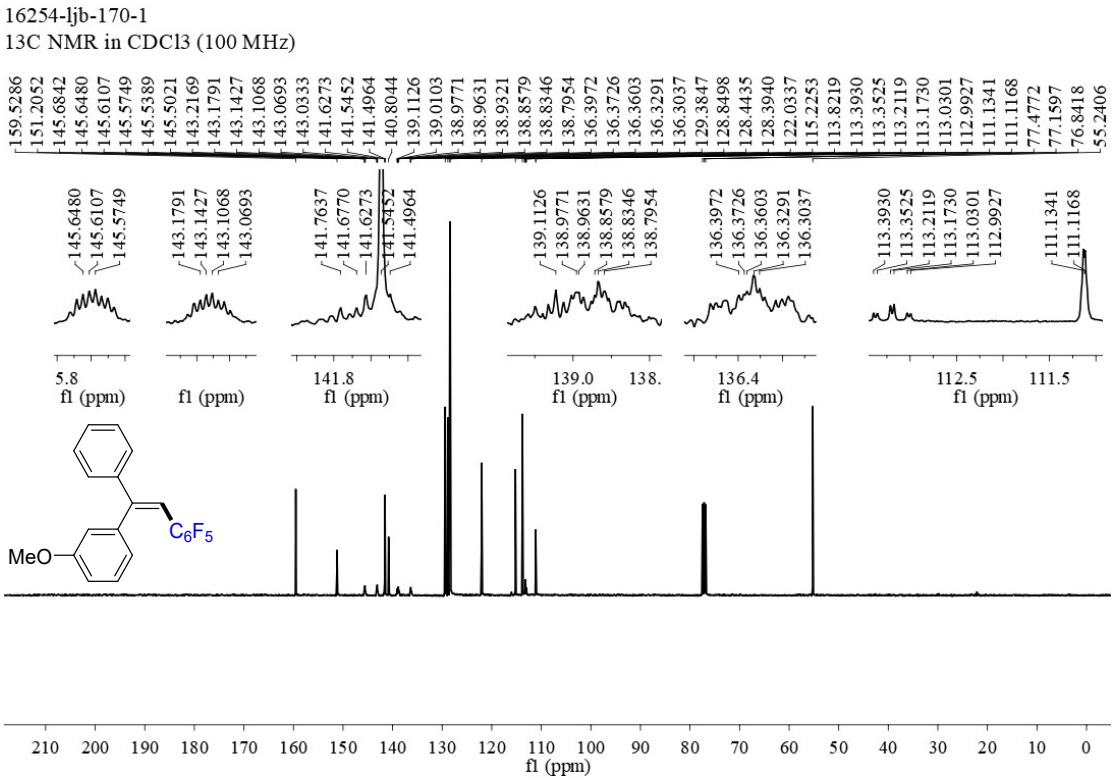


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3t** ($CDCl_3$, 25 °C, 100 MHz).

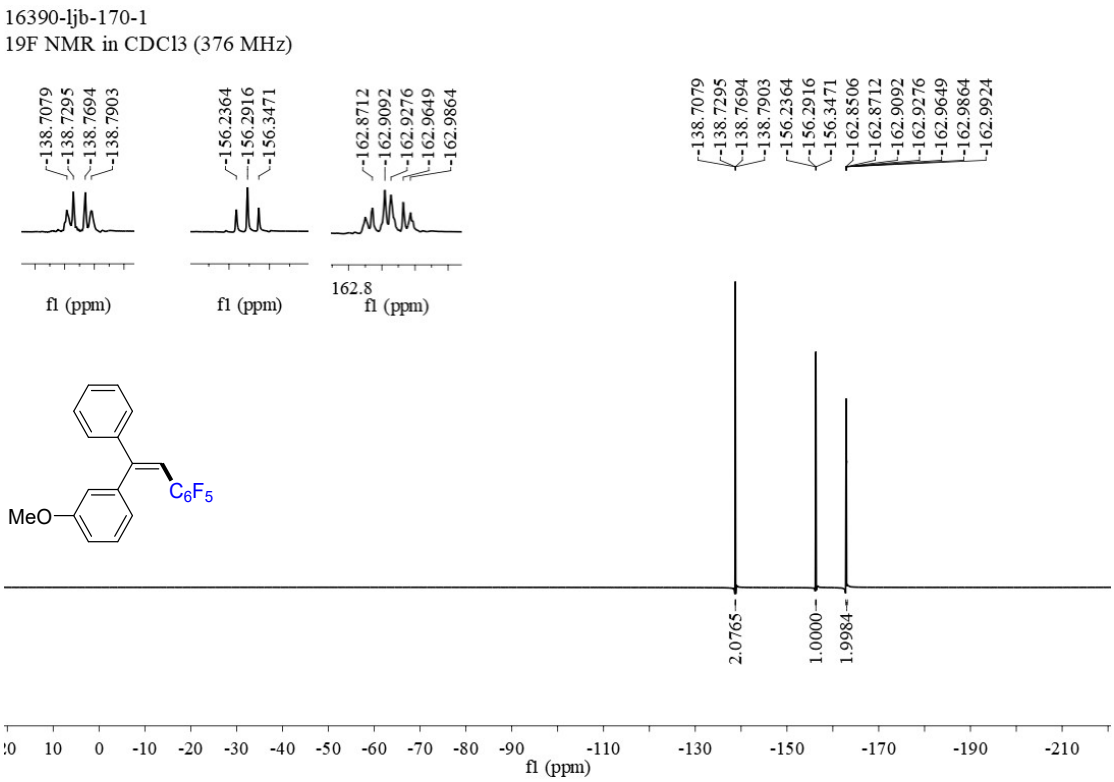


Figure S61. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3t** ($CDCl_3$, 25 °C, 376 MHz).

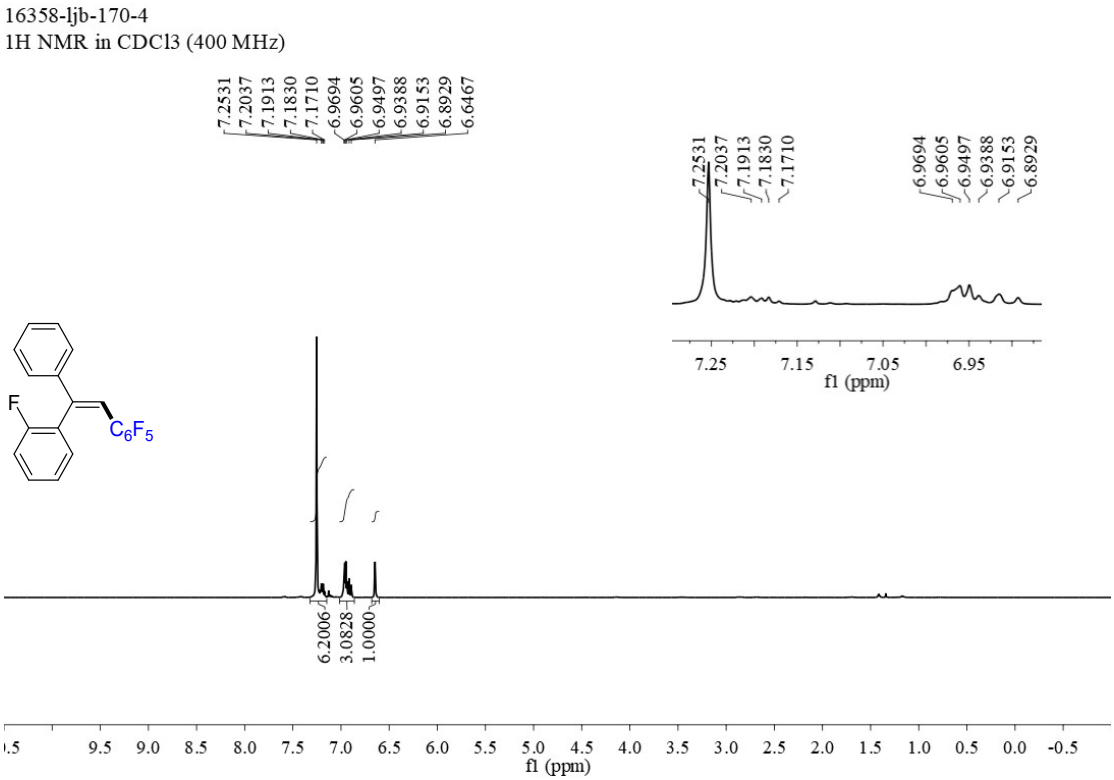


Figure S62. ^{1}H NMR spectrum of compound **3u** ($CDCl_3$, 25 ^{o}C, 400 MHz).

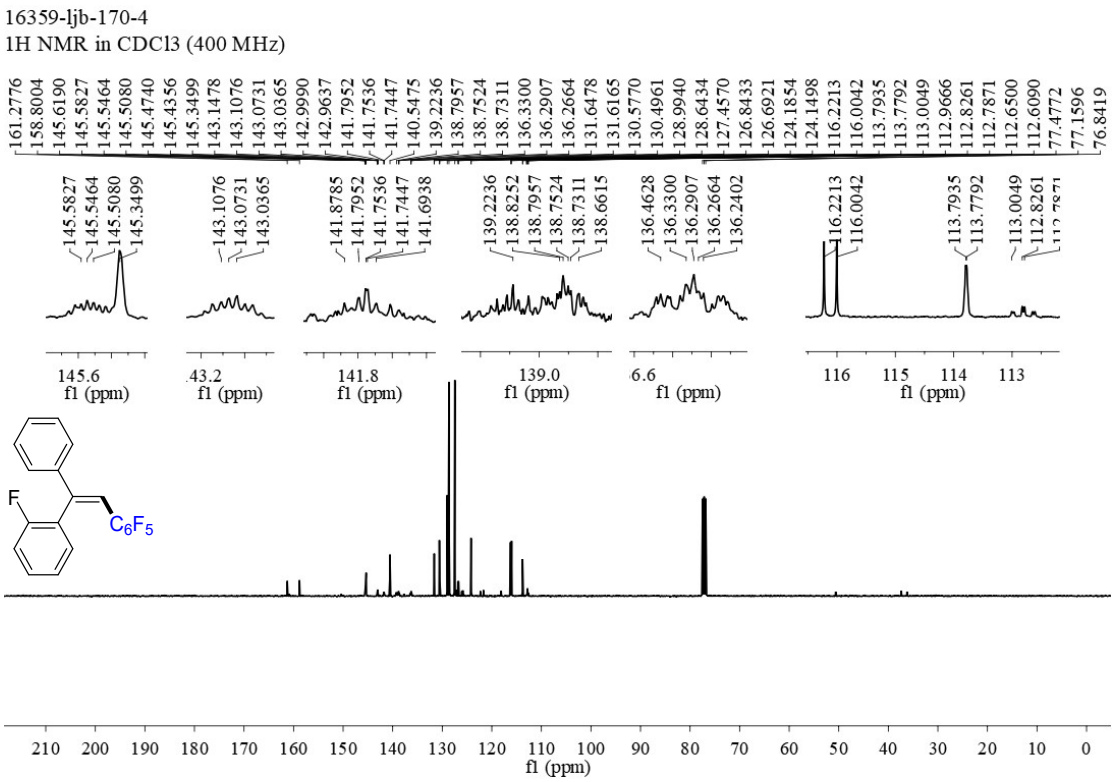


Figure S63. ^{13}C{^{1}H} NMR spectrum of compound **3u** ($CDCl_3$, 25 ^{o}C, 100 MHz).

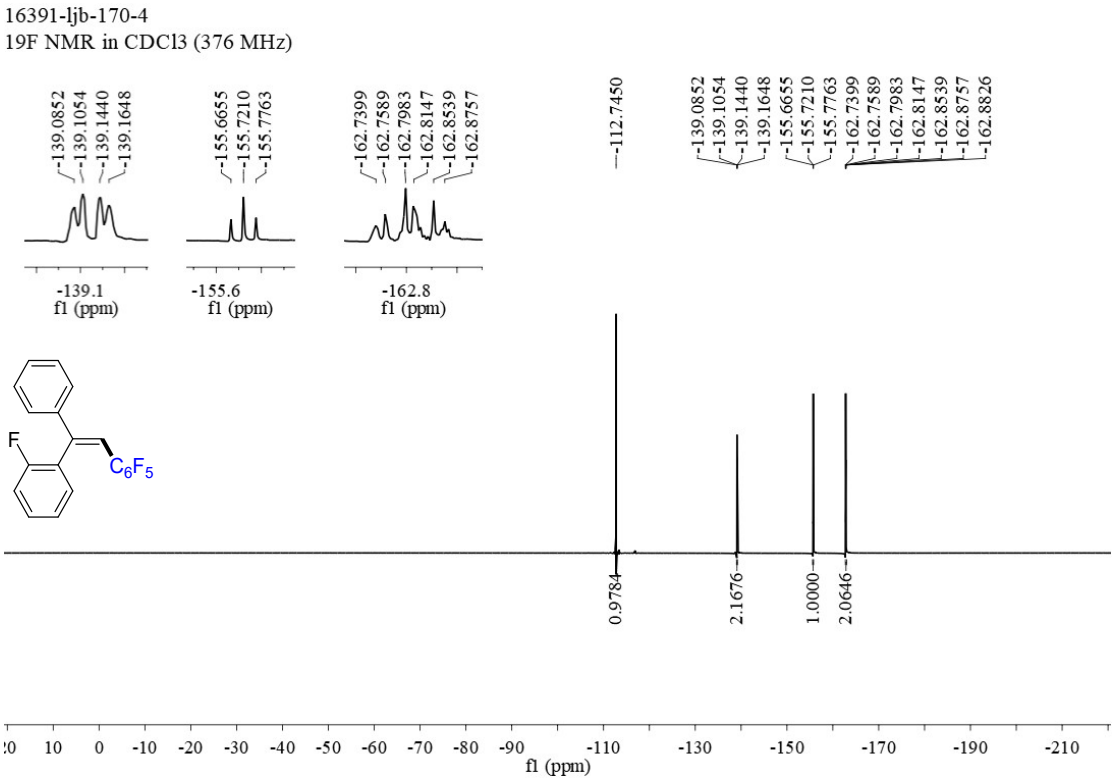


Figure S64. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3u** ($CDCl_3$, 25 °C, 376 MHz).

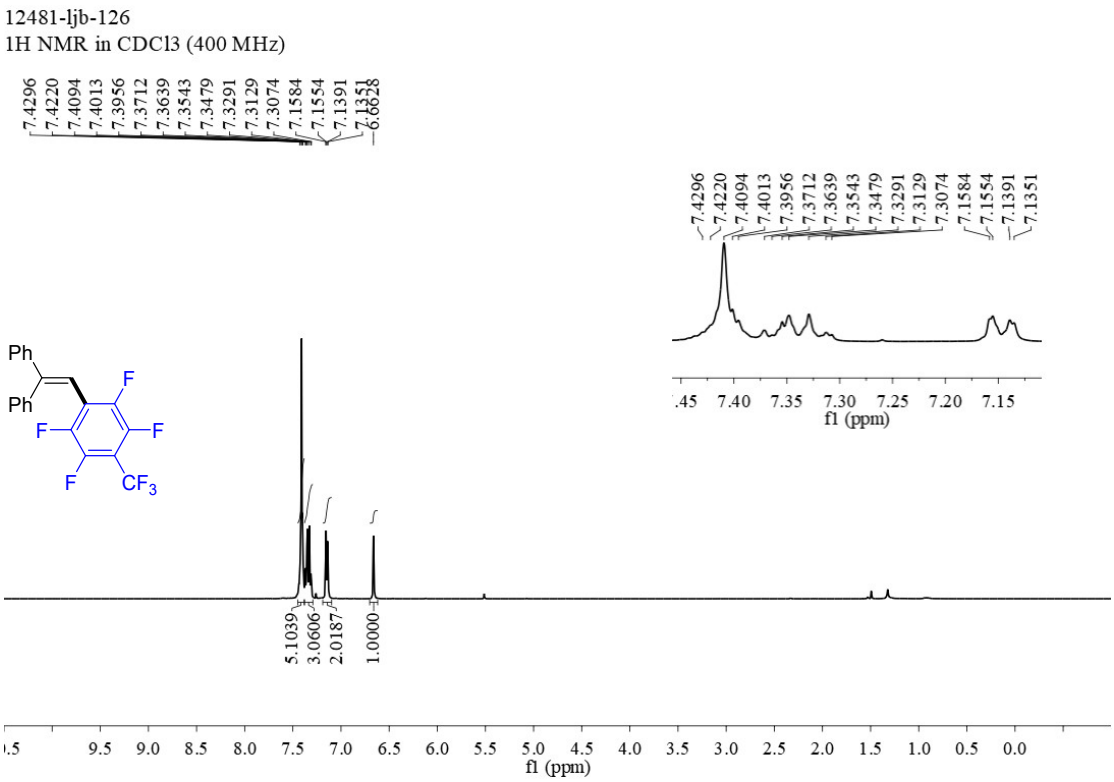


Figure S65. ^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 25 °C, 400 MHz).

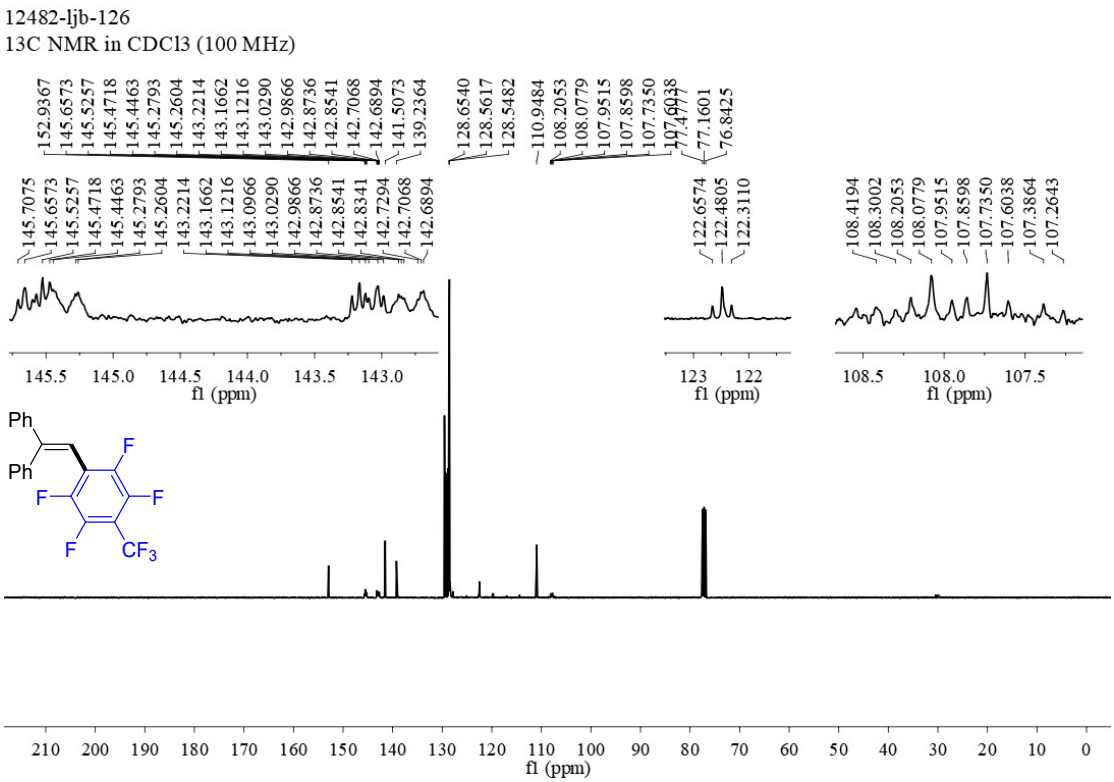


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a** ($CDCl_3$, 25 °C, 100 MHz).

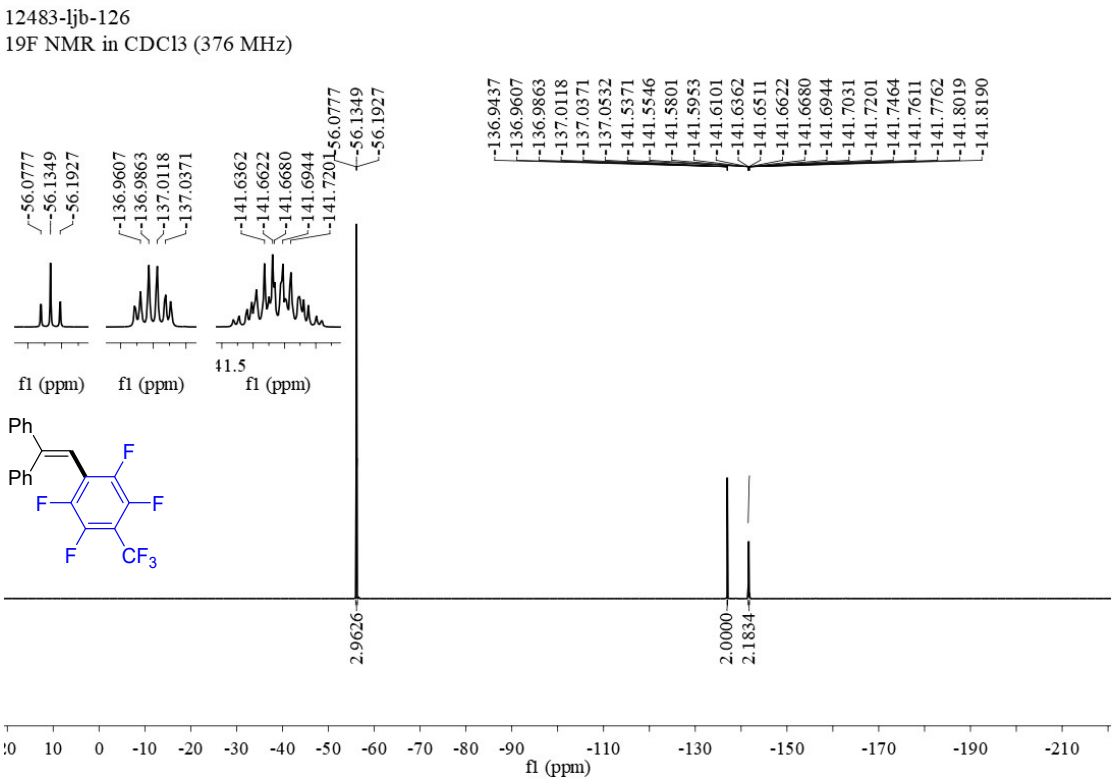


Figure S67. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4a** ($CDCl_3$, 25 °C, 376 MHz).

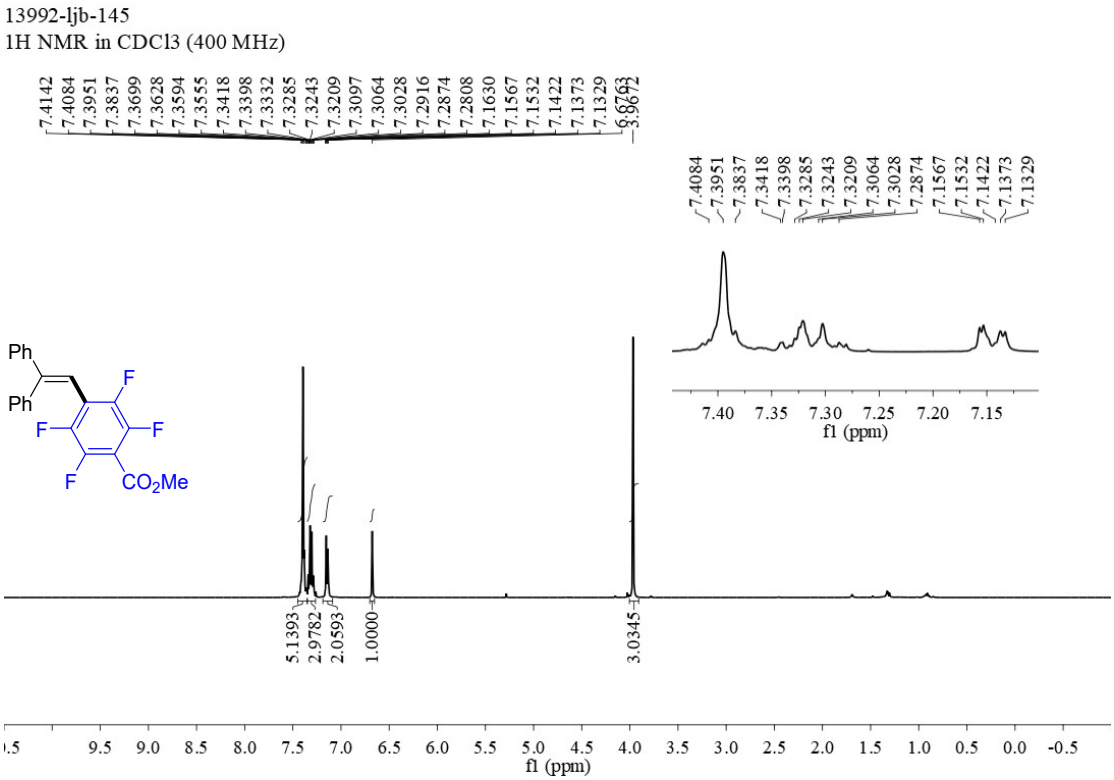


Figure S68. ^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 25 °C, 400 MHz).

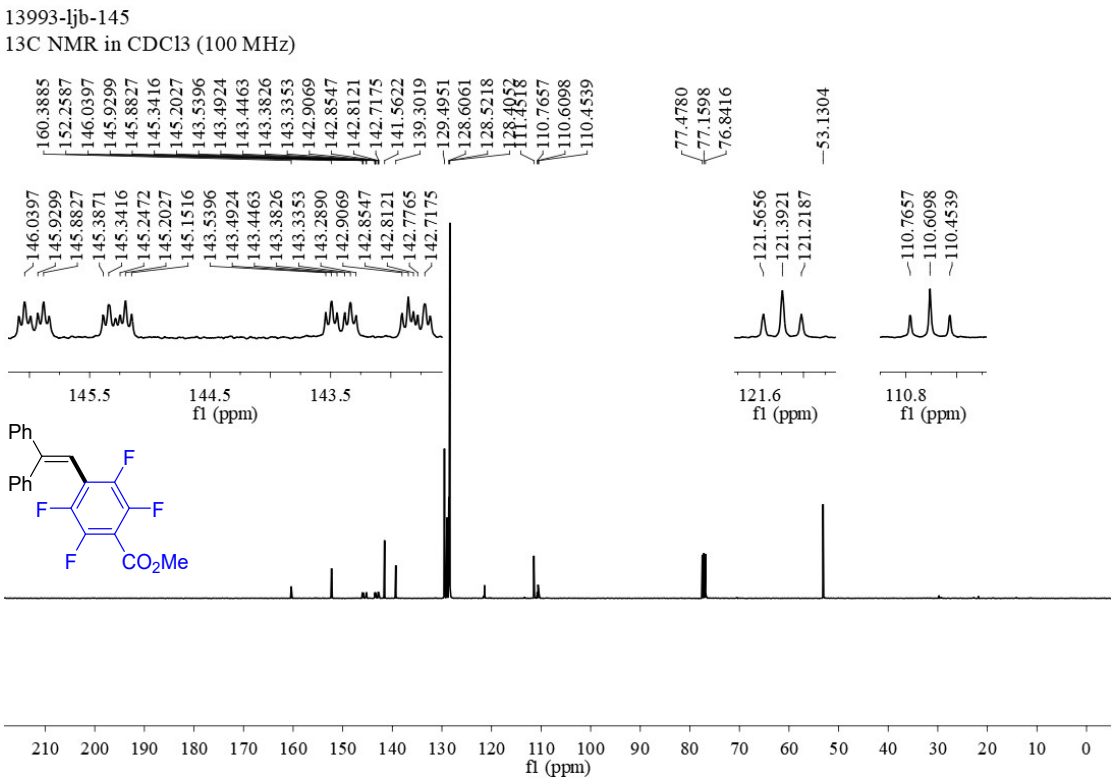


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4b** ($CDCl_3$, 25 °C, 100 MHz).

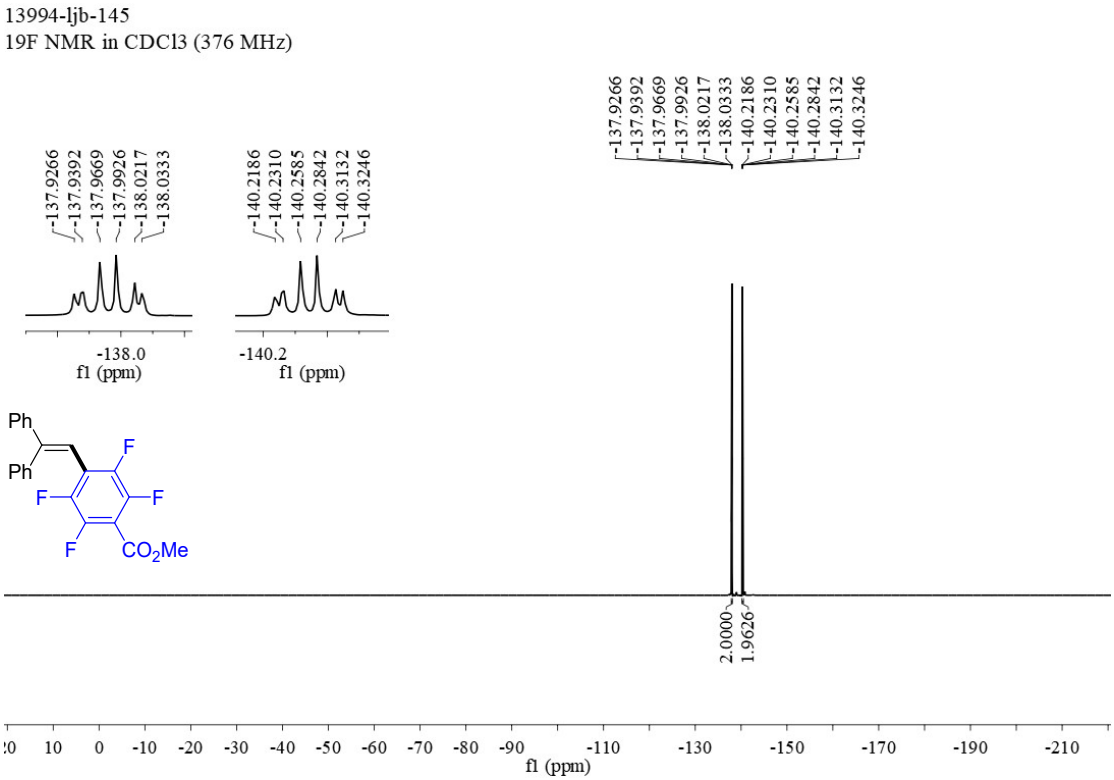


Figure S70. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4b** ($CDCl_3$, 25 °C, 376 MHz).

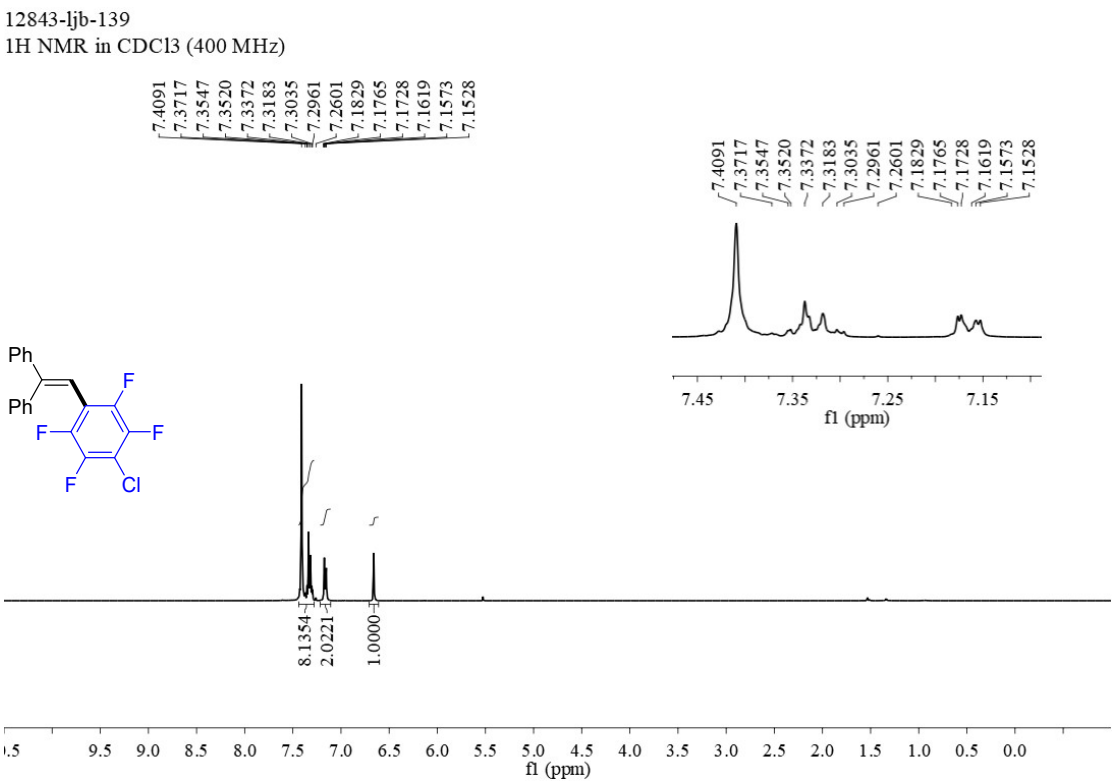


Figure S71. ^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 25 °C, 400 MHz).

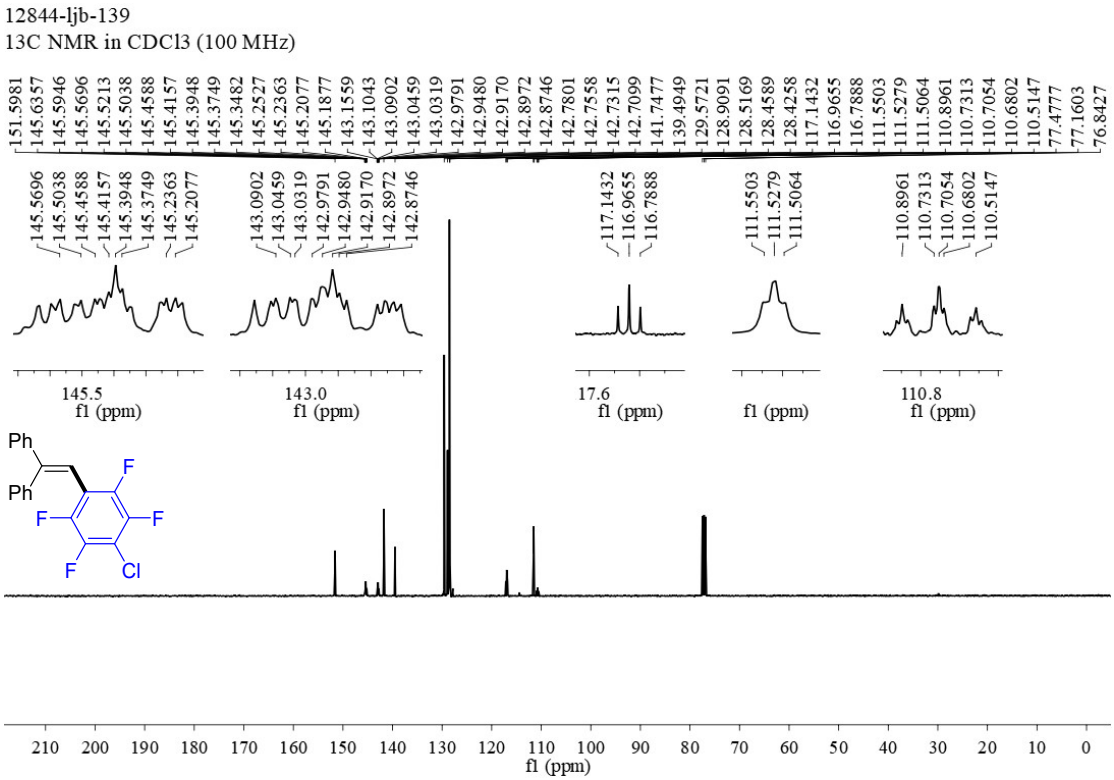


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4c** ($CDCl_3$, 25 °C, 100 MHz).

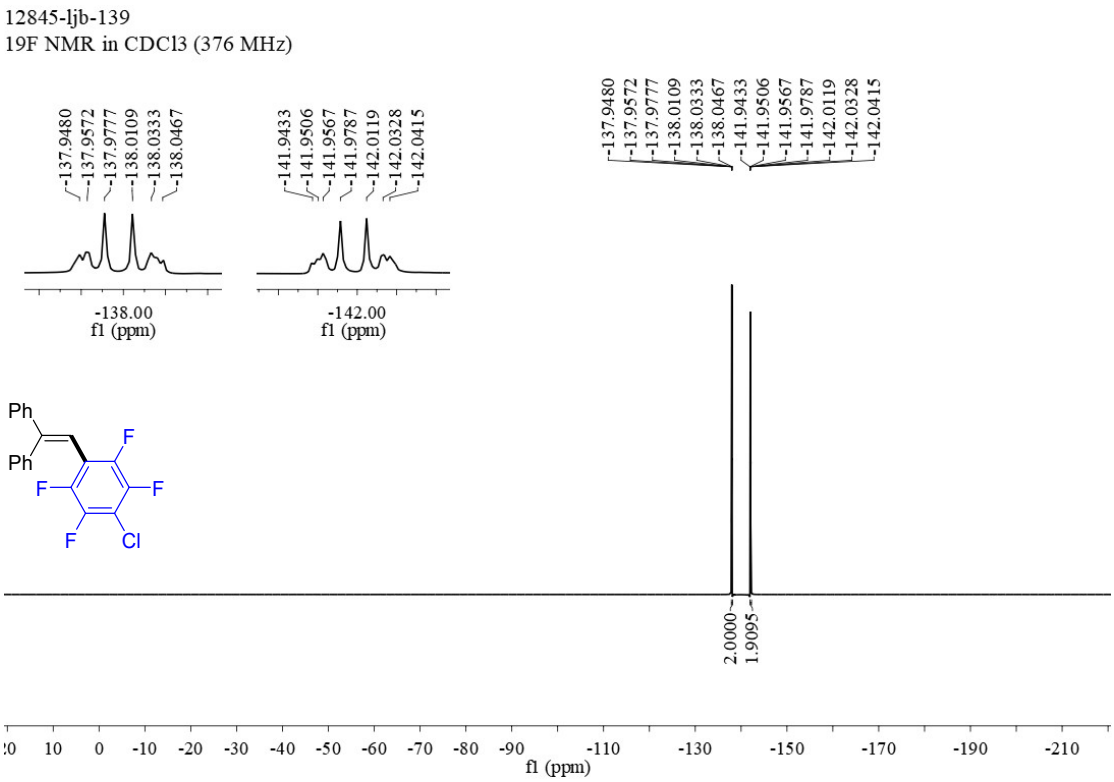


Figure S73. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4c** ($CDCl_3$, 25 °C, 376 MHz).

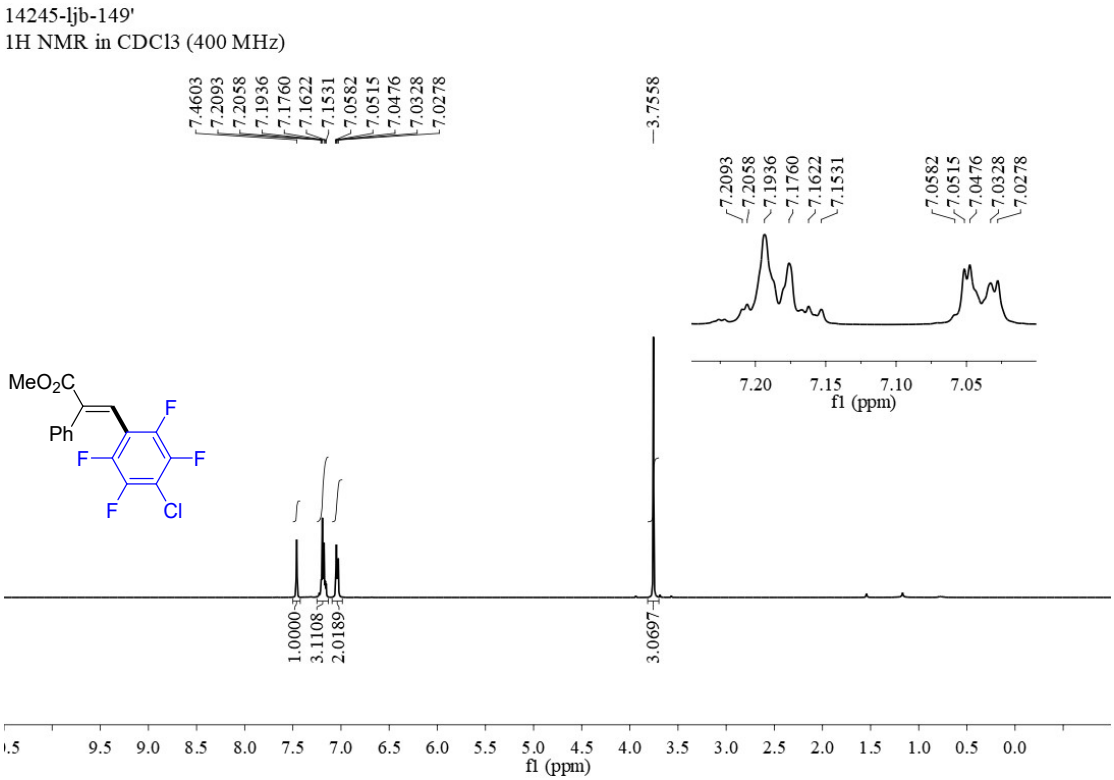


Figure S74. ^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 25 °C, 400 MHz).

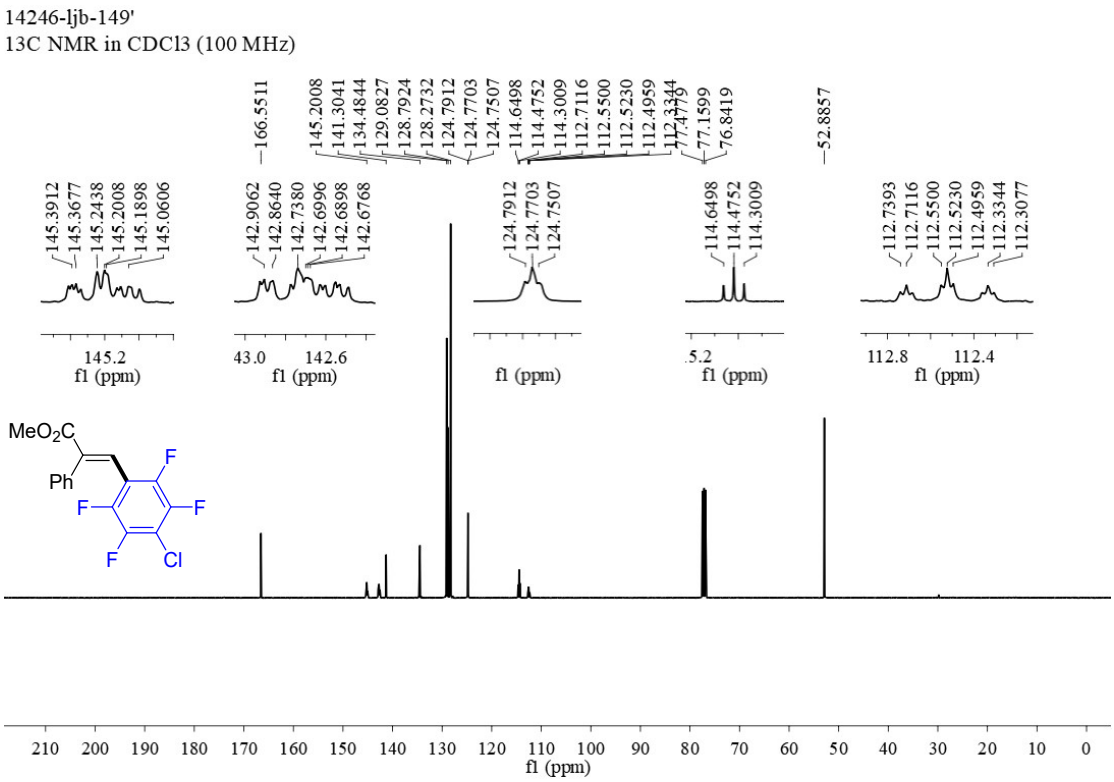


Figure S75. ^{13}C{^{1}H} NMR spectrum of compound **4d** ($CDCl_3$, 25 °C, 100 MHz).

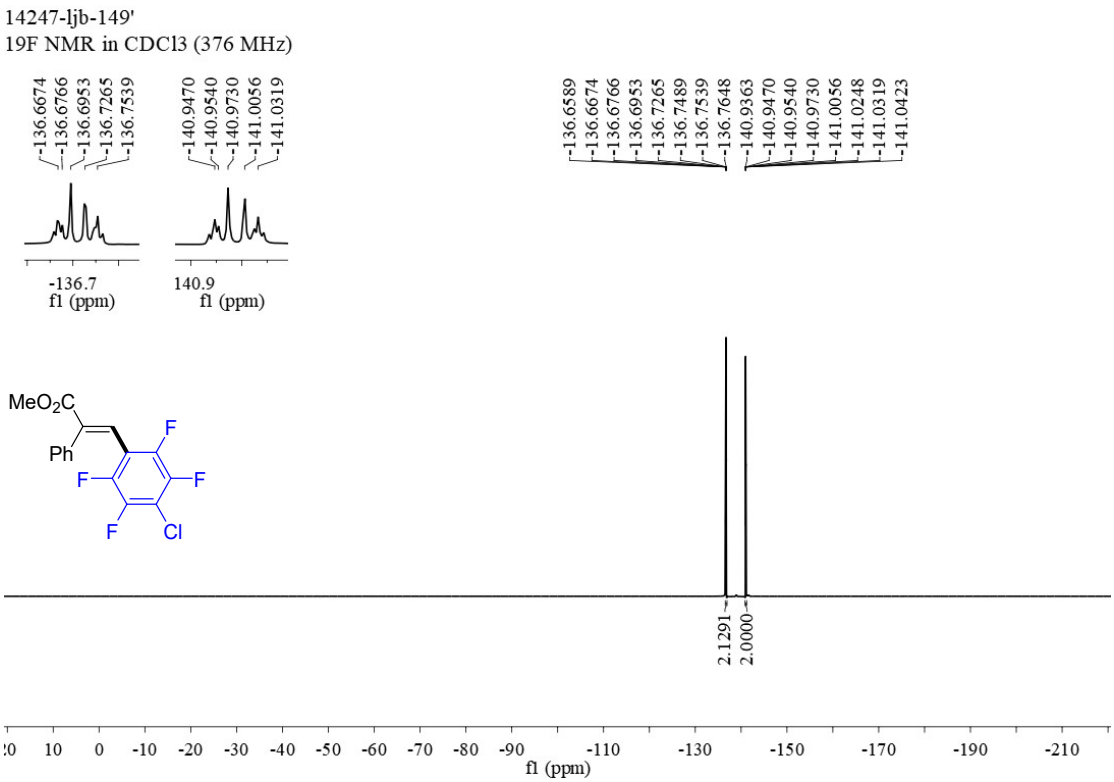


Figure S76. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4d** ($CDCl_3$, 25 °C, 376 MHz).

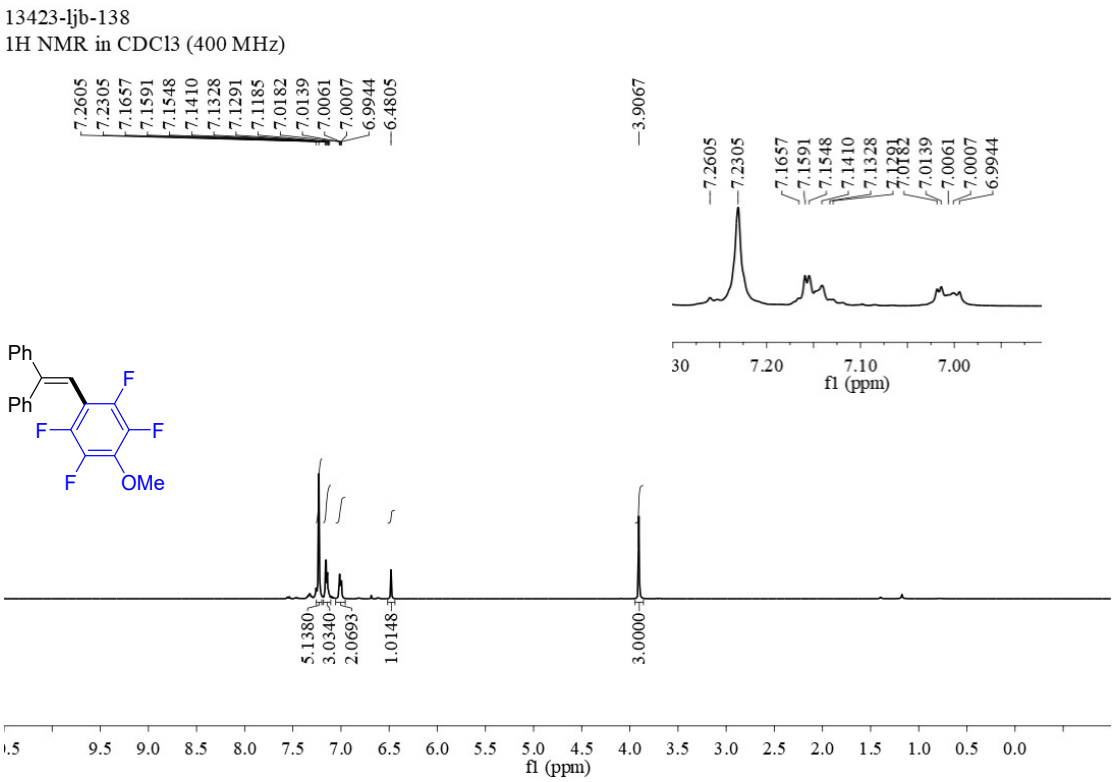


Figure S77. ^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 25 °C, 400 MHz).

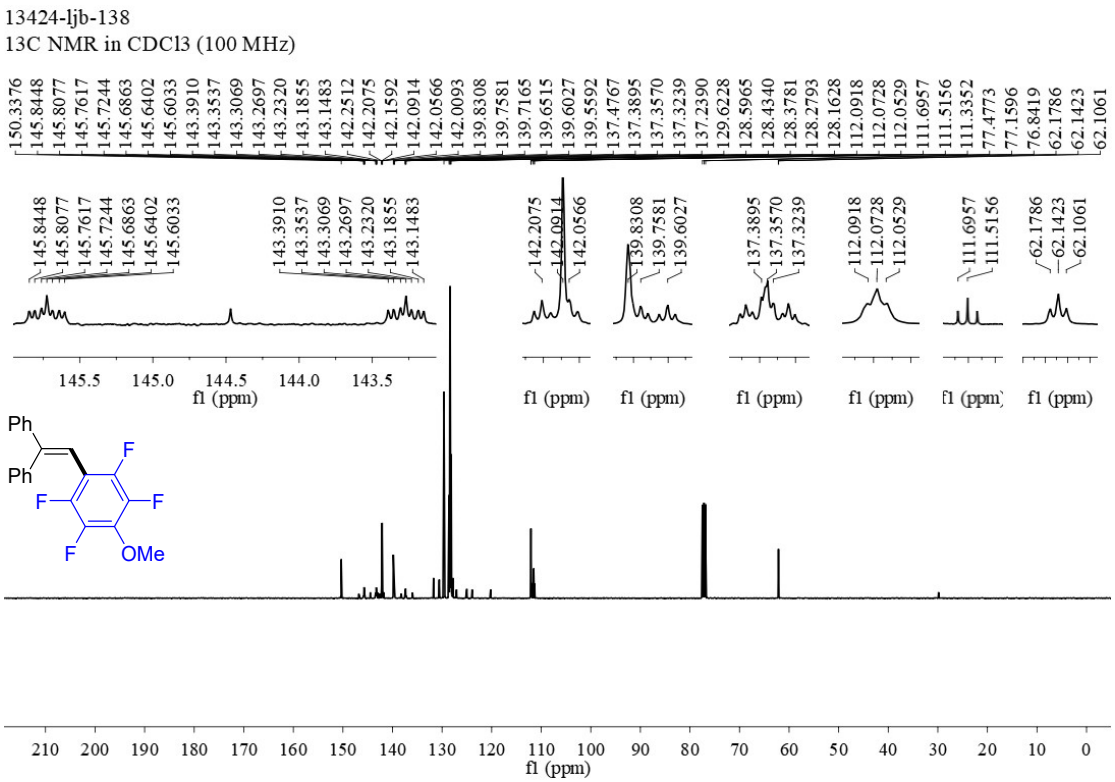


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4e** ($CDCl_3$, 25 °C, 100 MHz).

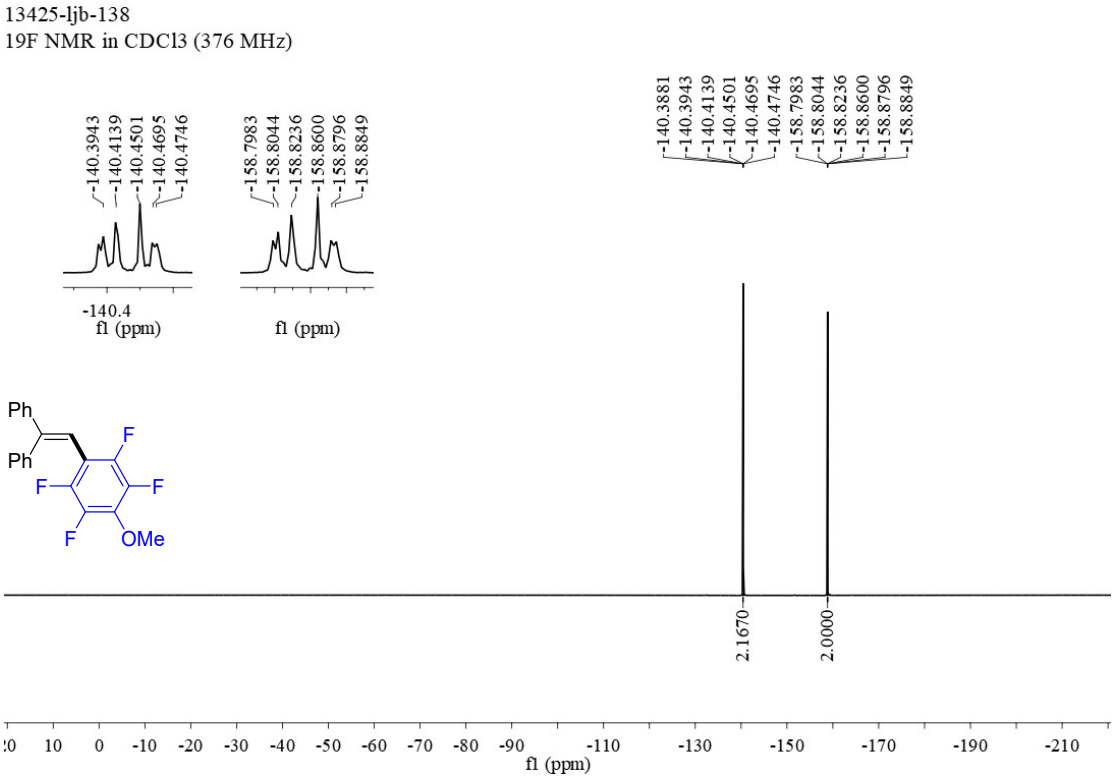


Figure S79 $^{19}F\{^{1}H\}$ NMR spectrum of compound **4e** ($CDCl_3$, 25 °C, 376 MHz).

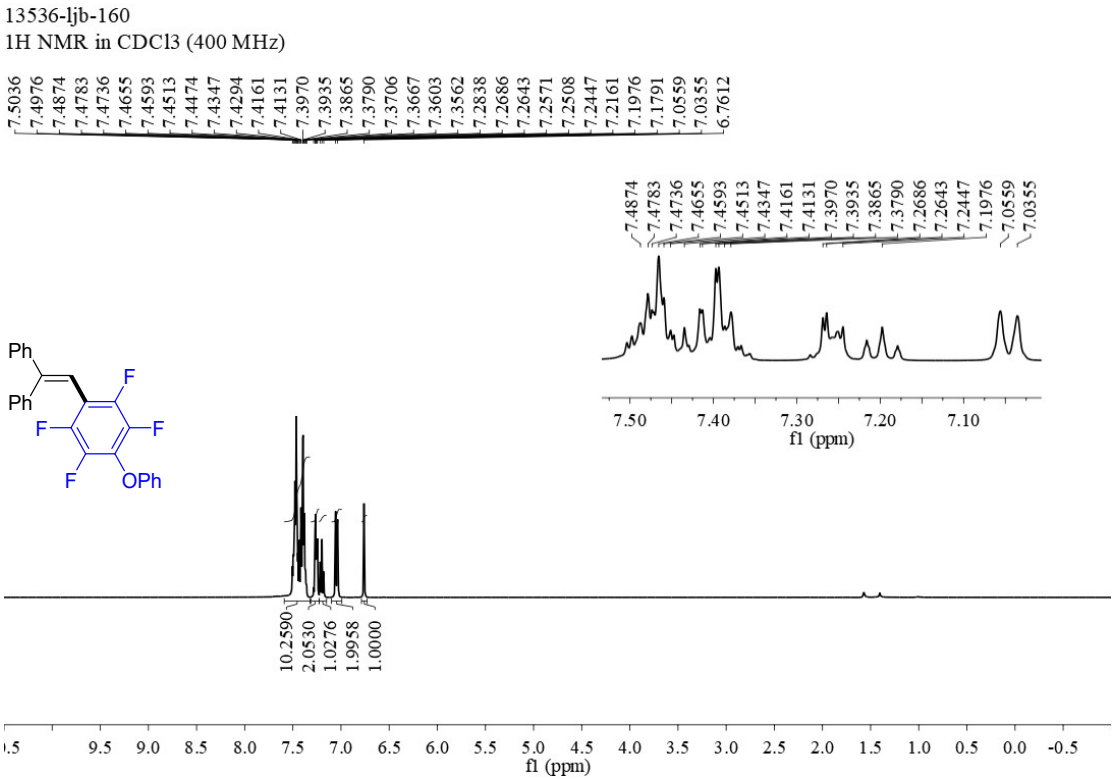


Figure S80. ^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 25 °C, 400 MHz).

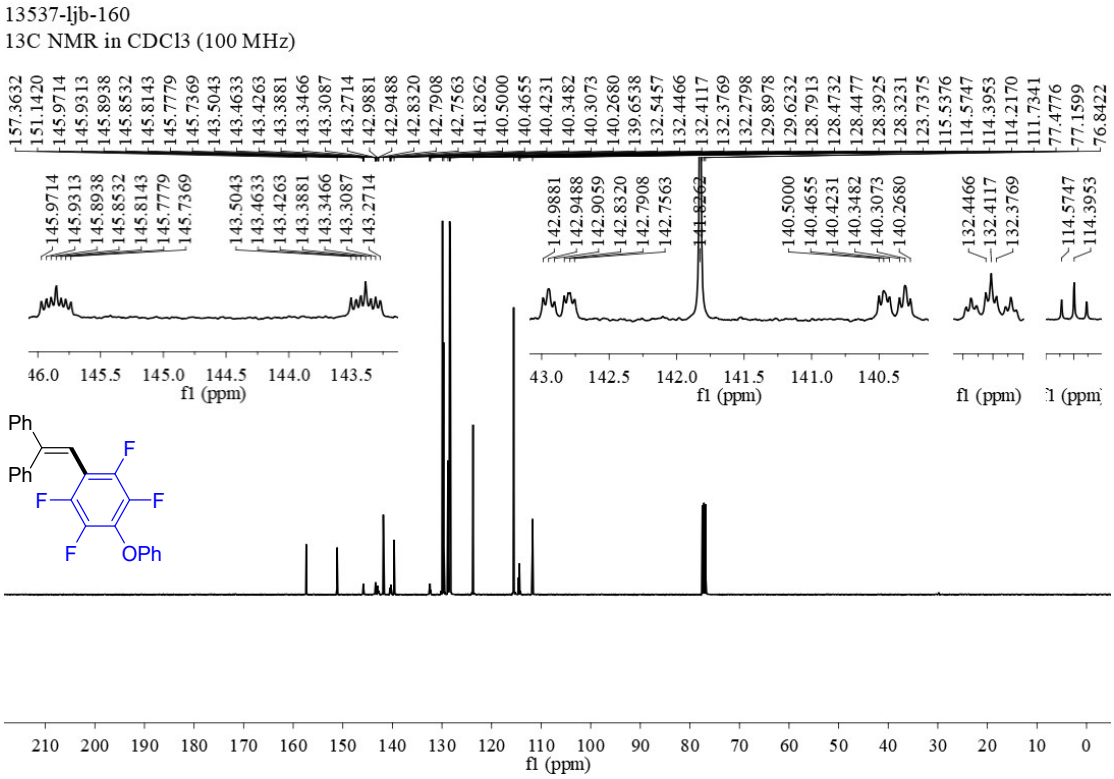


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4f** ($CDCl_3$, 25 °C, 100 MHz).

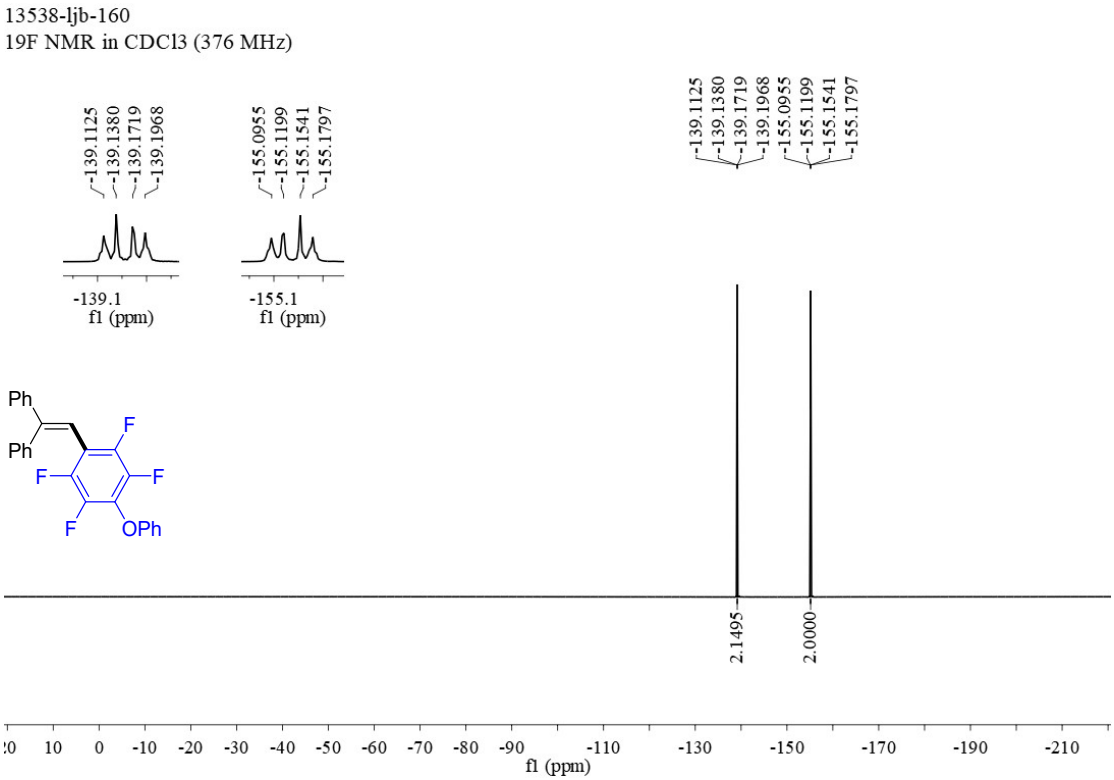


Figure S82. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4f** ($CDCl_3$, 25 °C, 376 MHz).

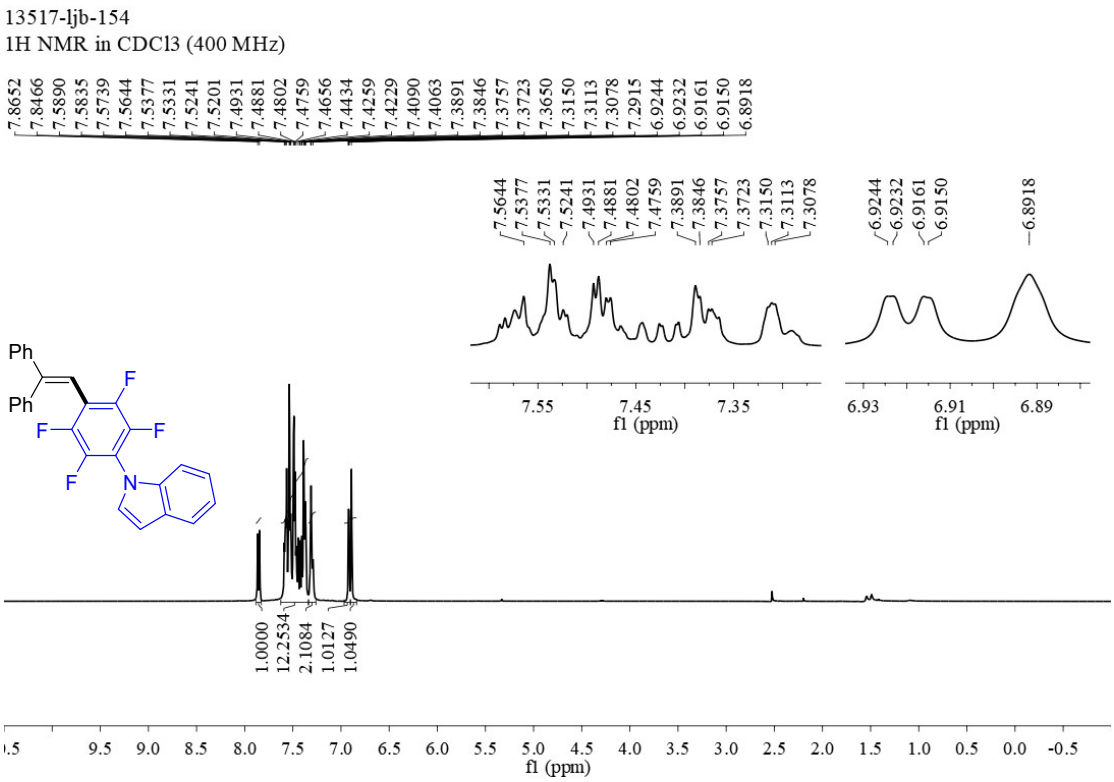


Figure S83. ^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 25 °C, 400 MHz).

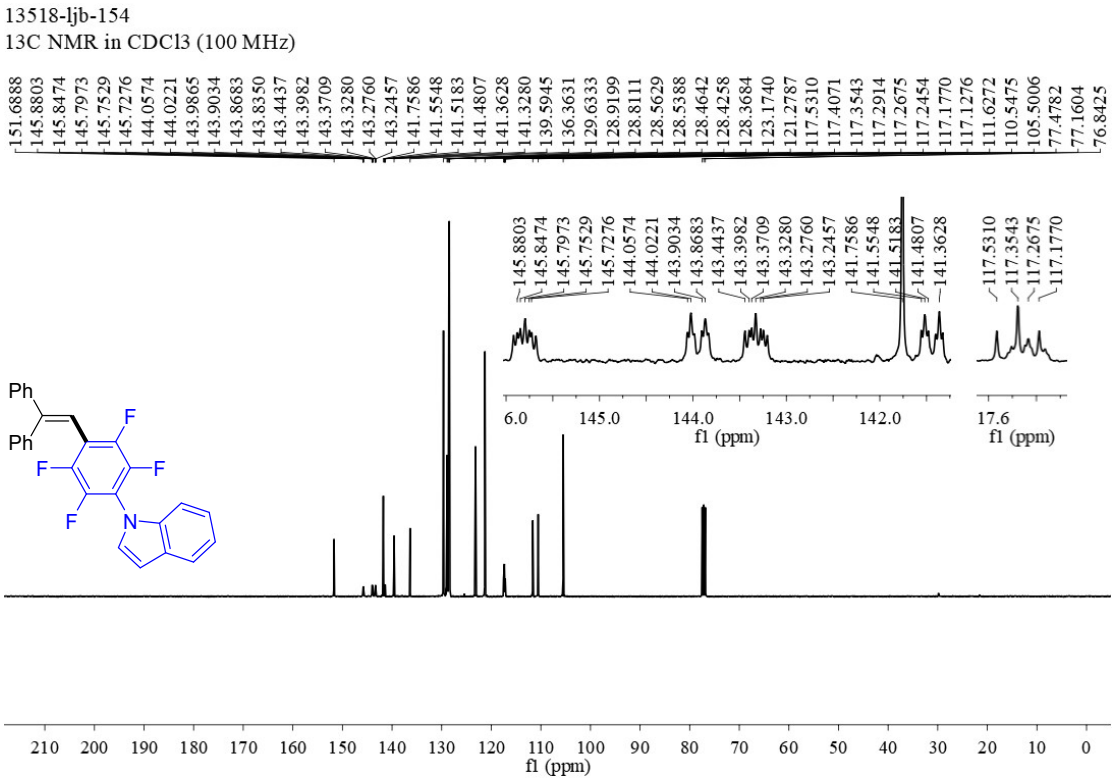


Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4g** ($CDCl_3$, 25 °C, 100 MHz).

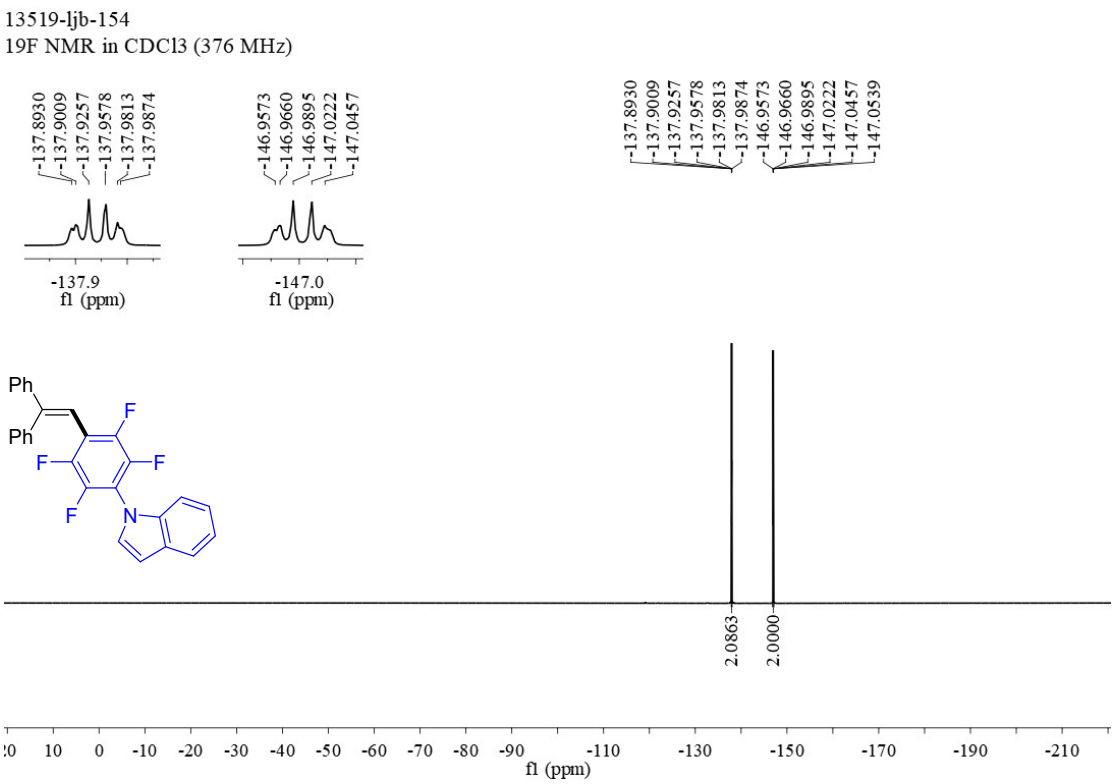


Figure S85. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4g** ($CDCl_3$, 25 °C, 376 MHz).

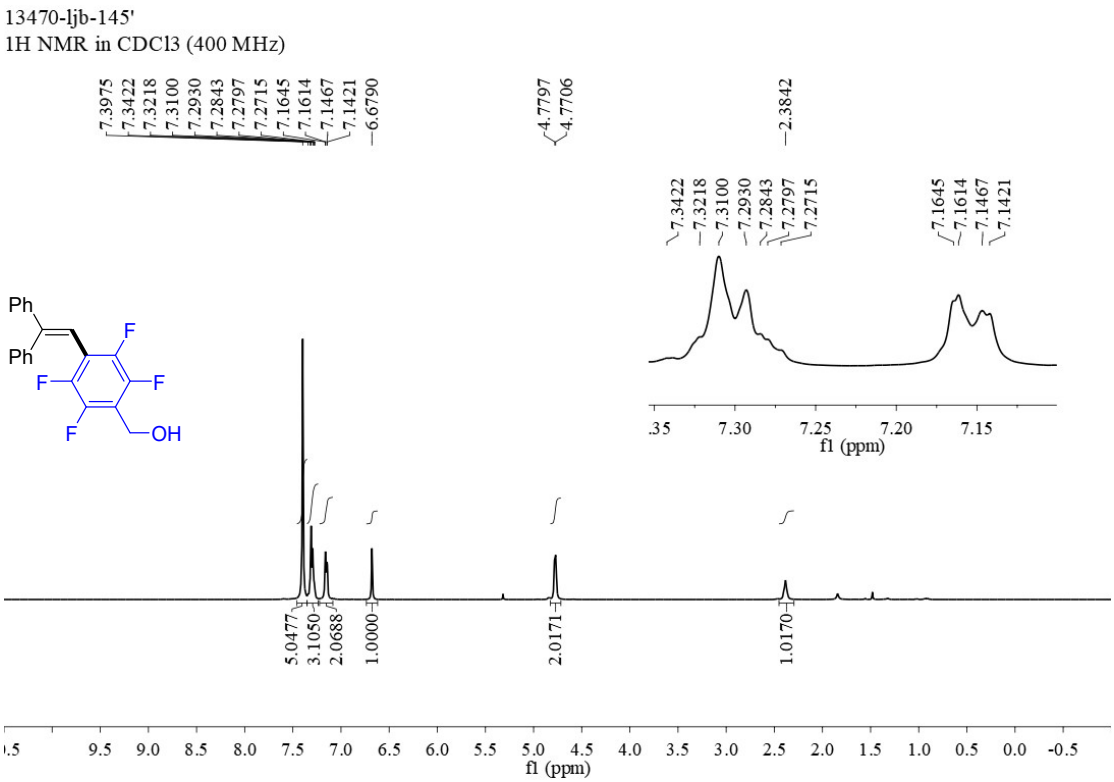


Figure S86. ^{1}H NMR spectrum of compound **4h** ($CDCl_3$, 25 °C, 400 MHz).

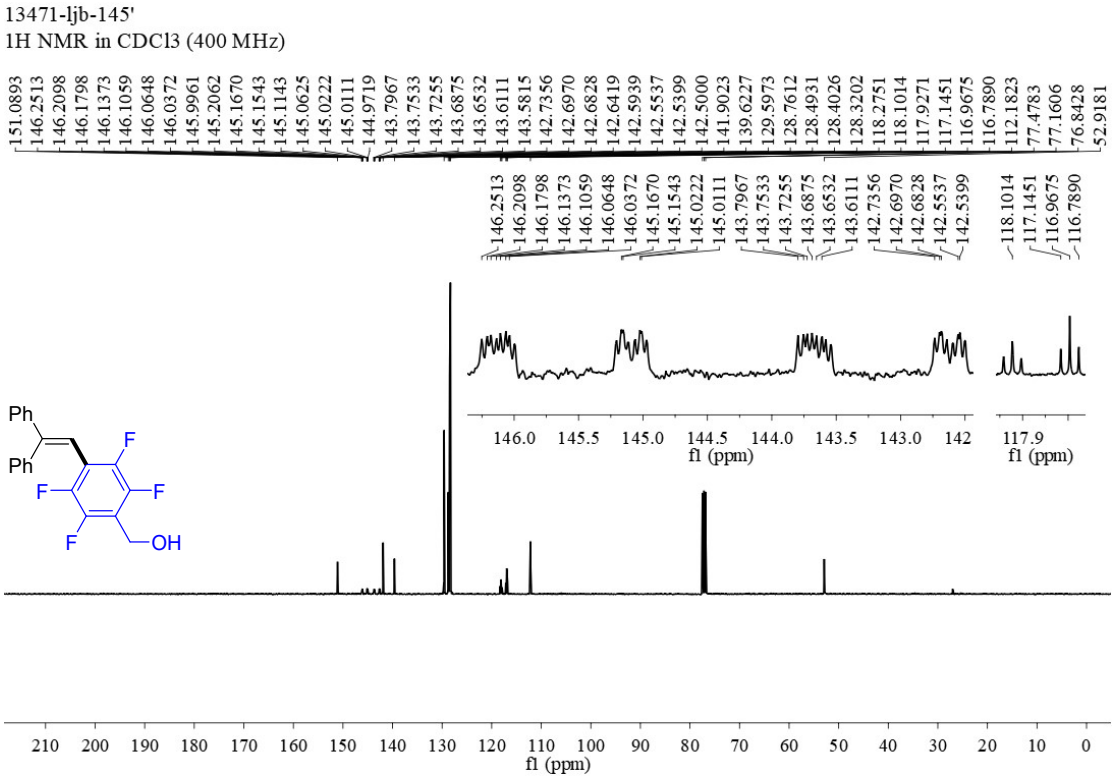


Figure S87. ^{13}C{^{1}H} NMR spectrum of compound **4h** ($CDCl_3$, 25 °C, 100 MHz).

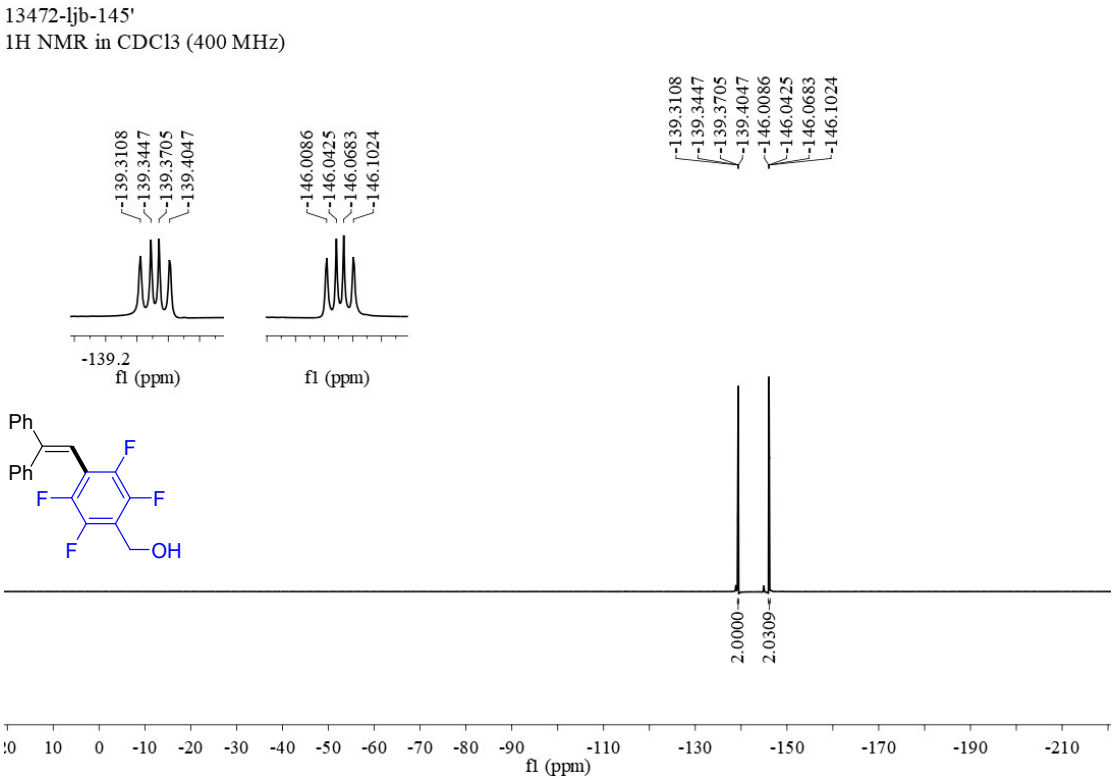


Figure S88. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4h** ($CDCl_3$, 25 °C, 376 MHz).

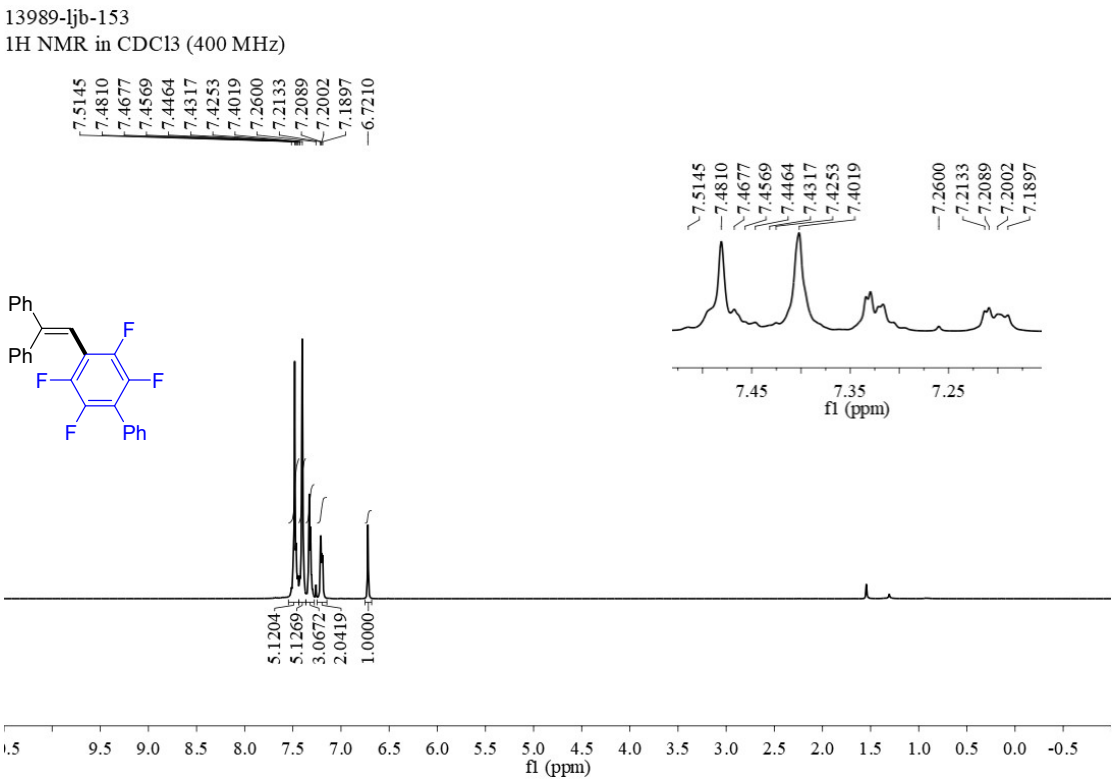


Figure S89. ^{1}H NMR spectrum of compound **4i** ($CDCl_3$, 25 °C, 400 MHz).

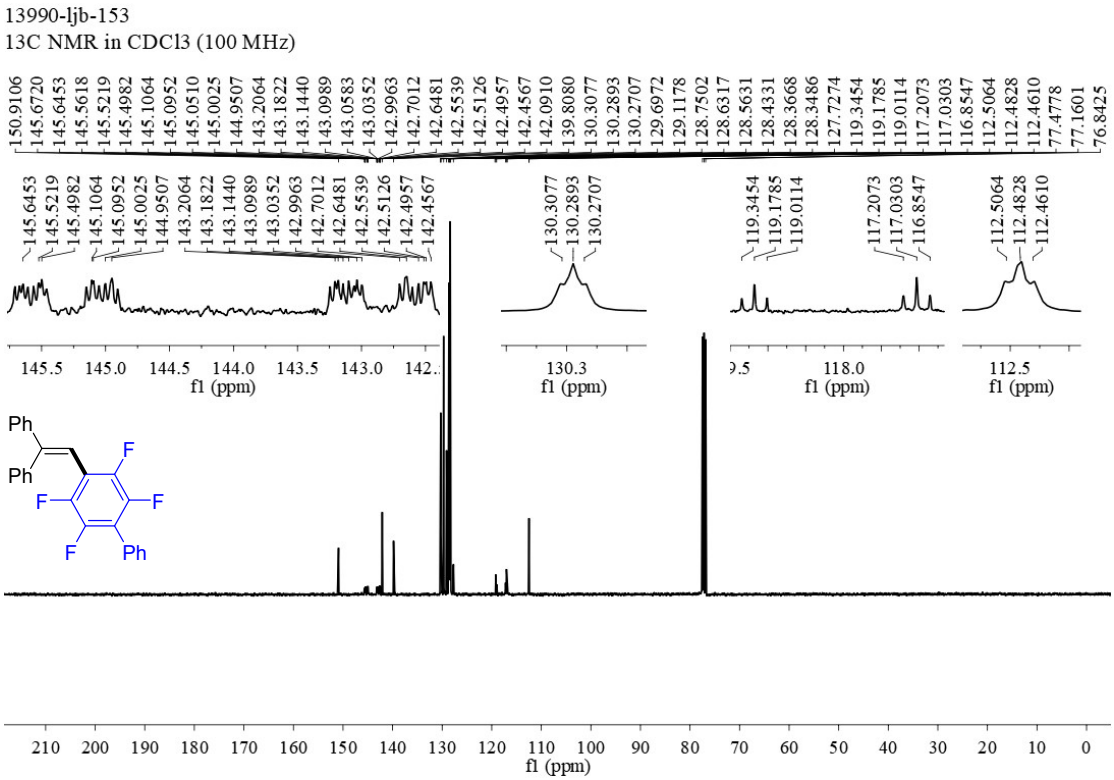


Figure S90. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4i** ($CDCl_3$, 25 °C, 100 MHz).

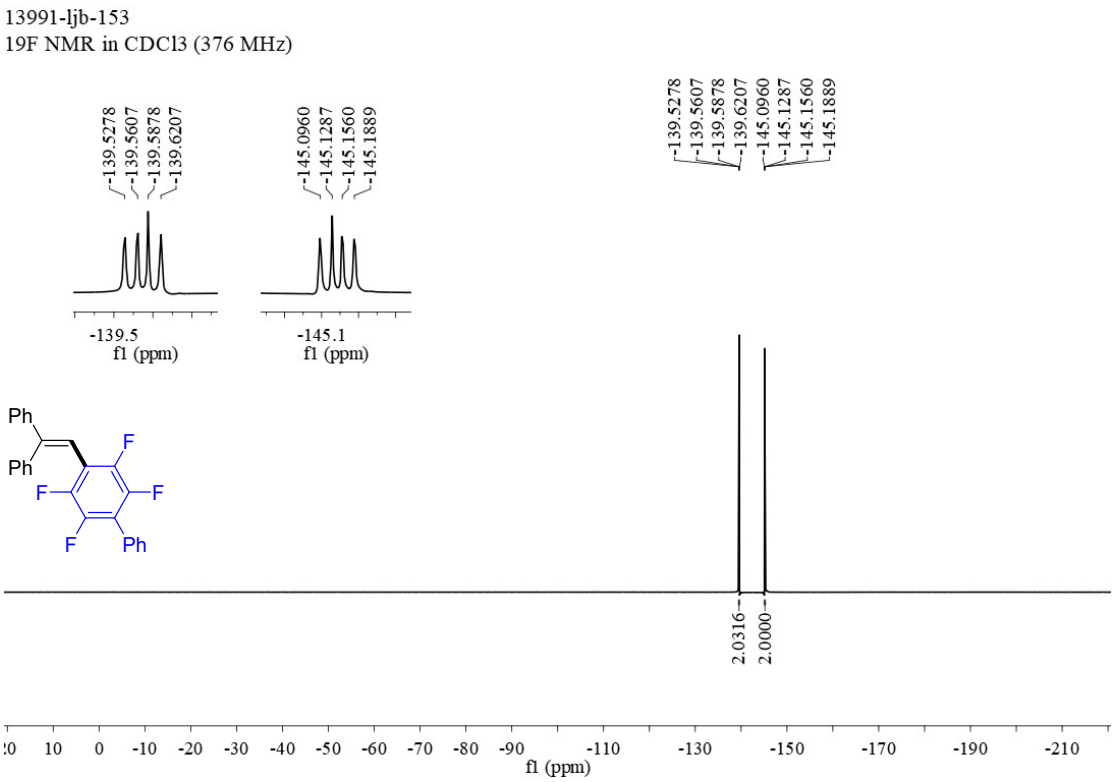


Figure S91. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4i** ($CDCl_3$, 25 °C, 376 MHz).

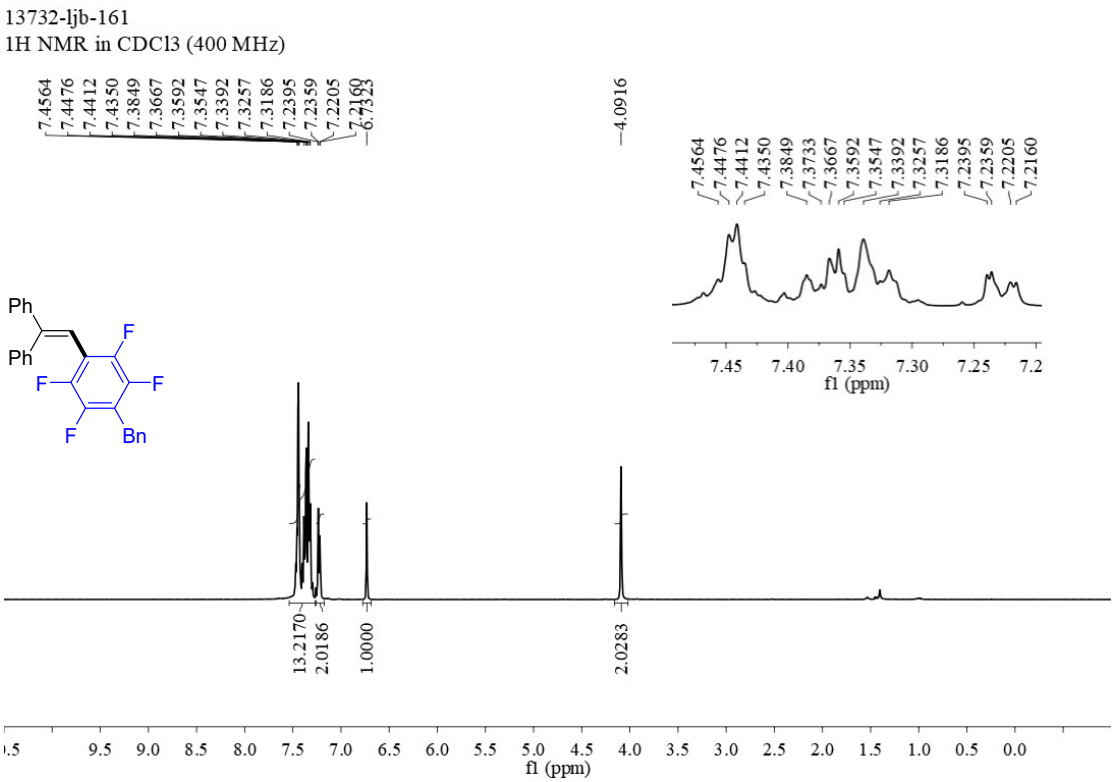


Figure S92. ^{1}H NMR spectrum of compound **4j** ($CDCl_3$, 25 °C, 400 MHz).

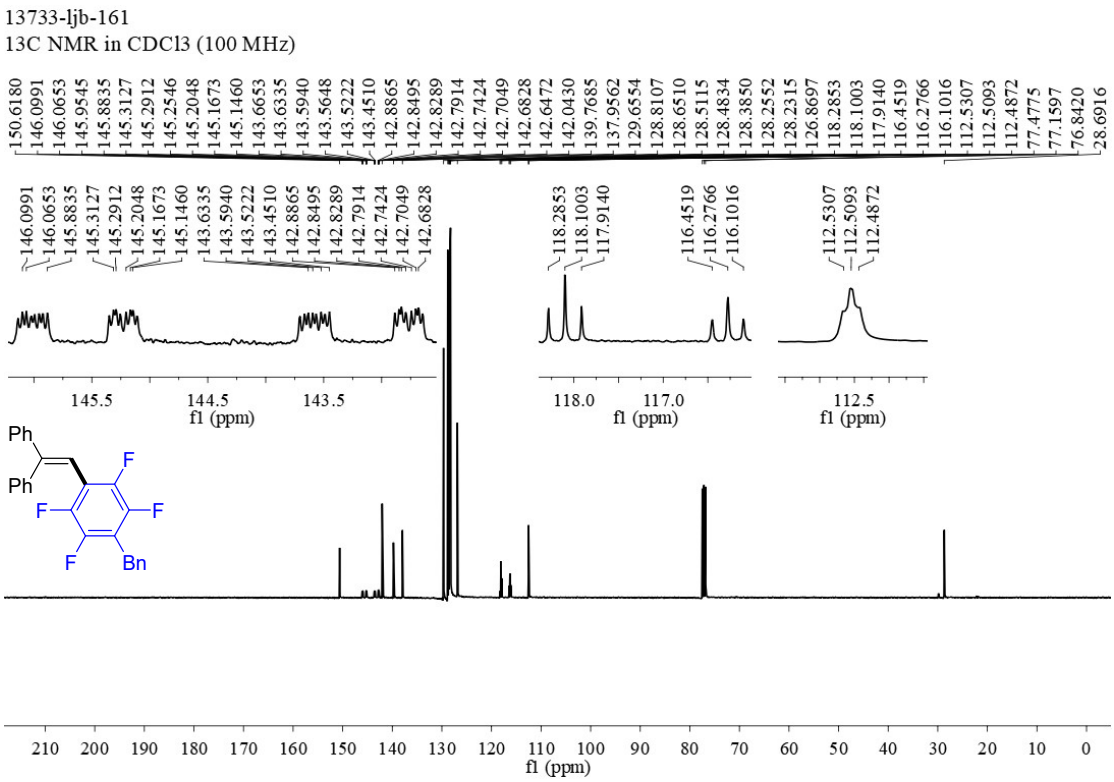


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4j** ($CDCl_3$, 25 °C, 100 MHz).

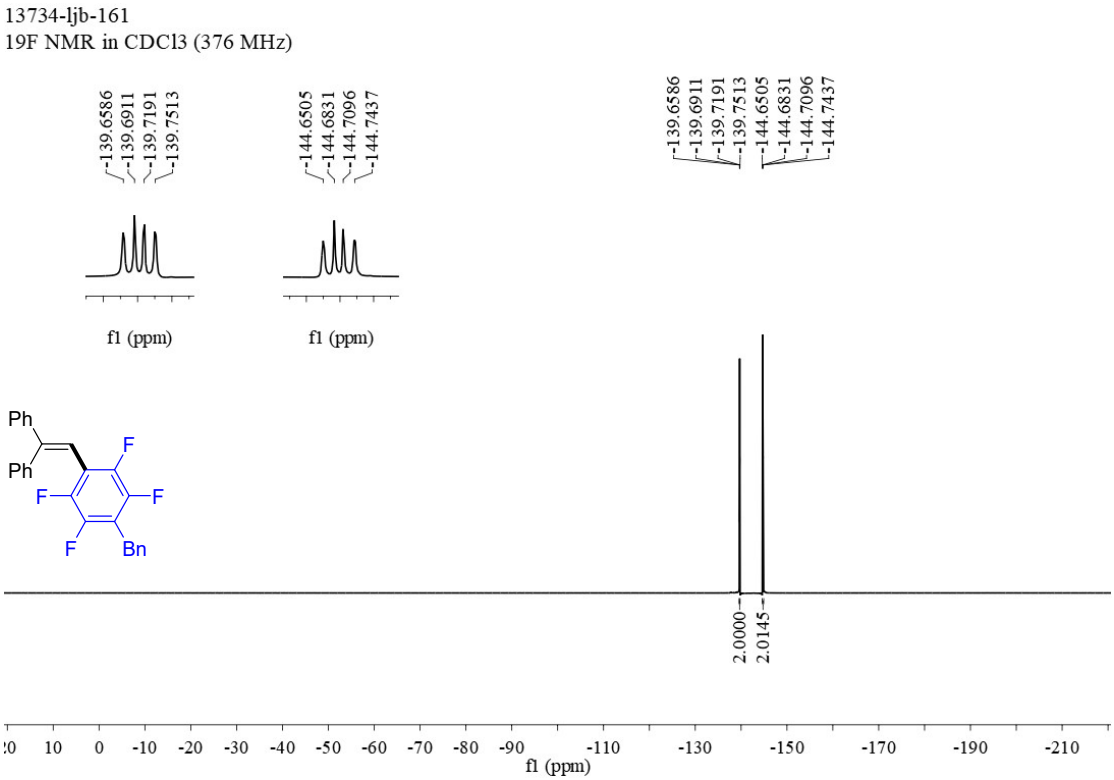


Figure S94. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4j** ($CDCl_3$, 25 °C, 376 MHz).

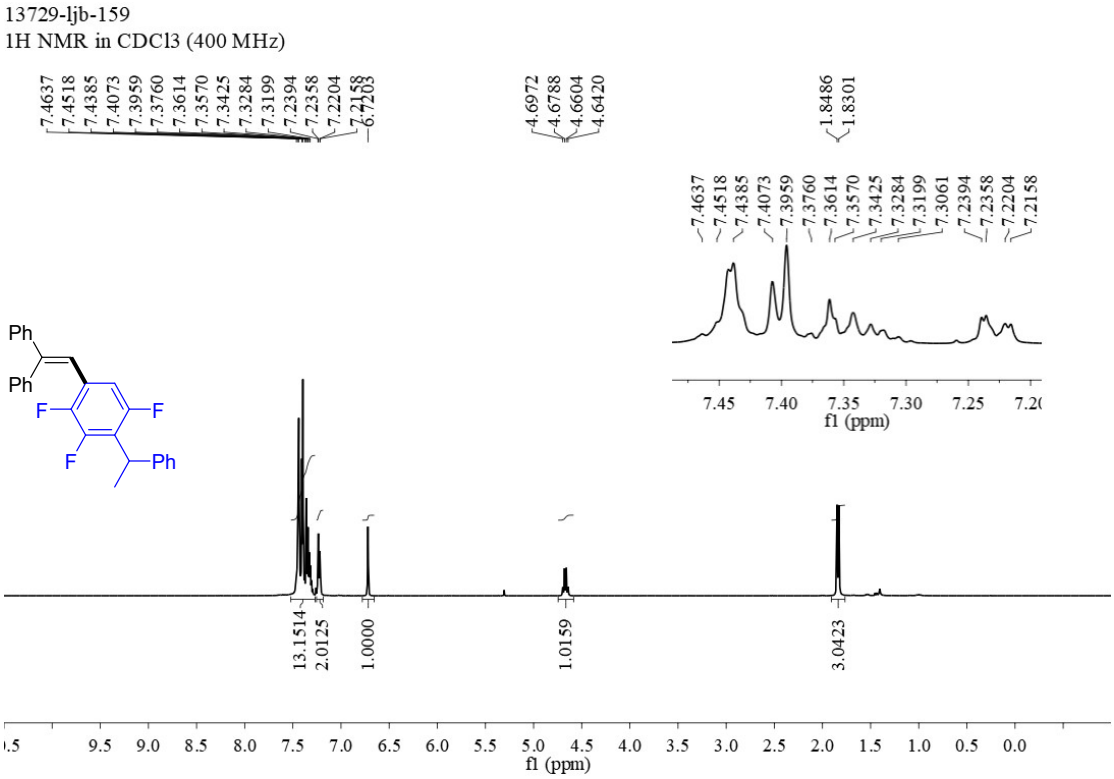


Figure S95. ^{1}H NMR spectrum of compound **4k** ($CDCl_3$, 25 °C, 400 MHz).

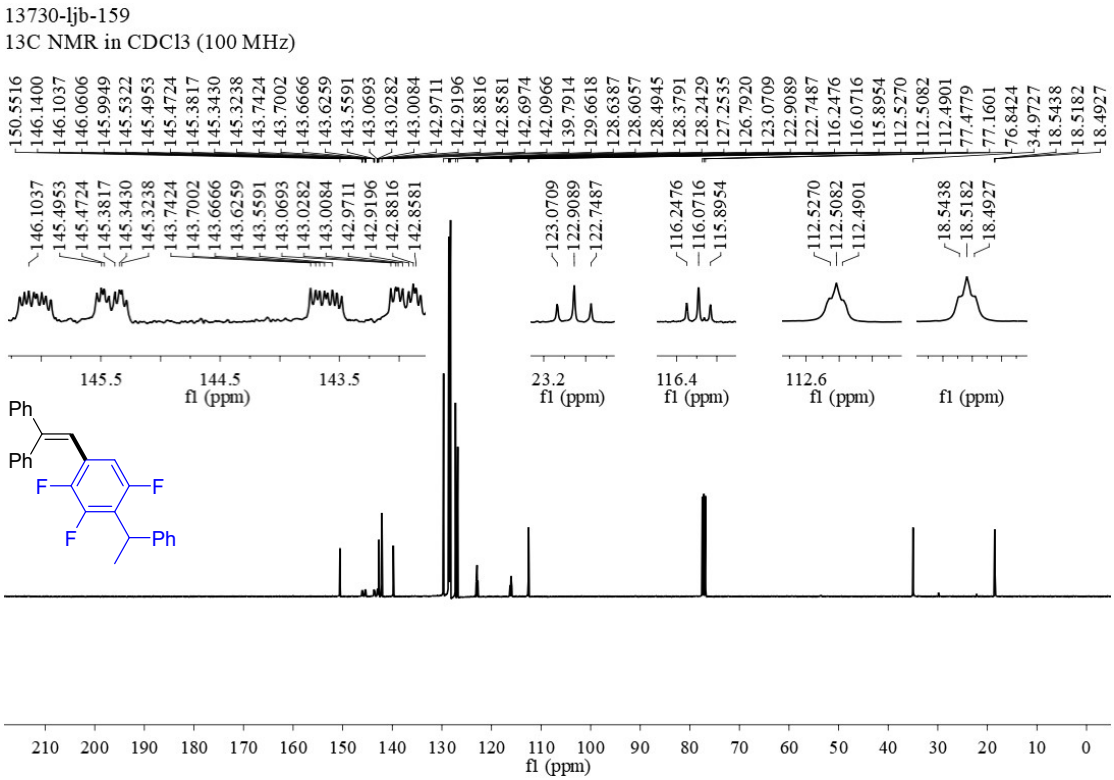


Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4k** ($CDCl_3$, 25 °C, 100 MHz).

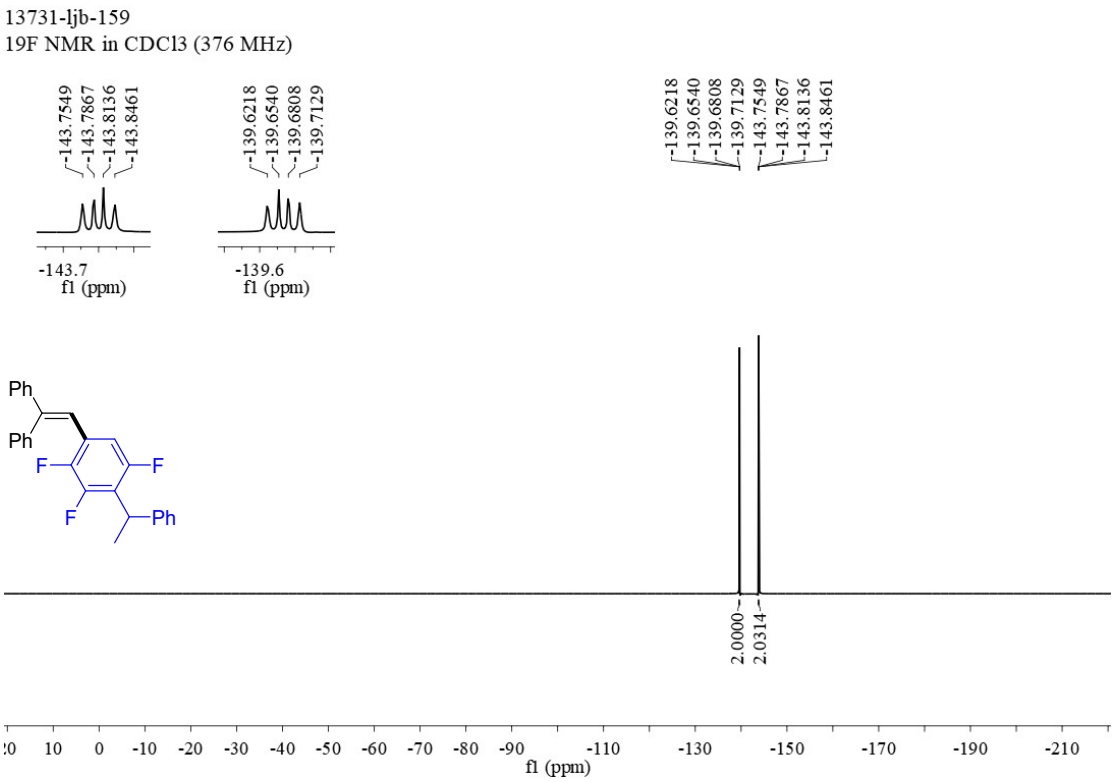


Figure S97. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4k** ($CDCl_3$, 25 °C, 376 MHz).

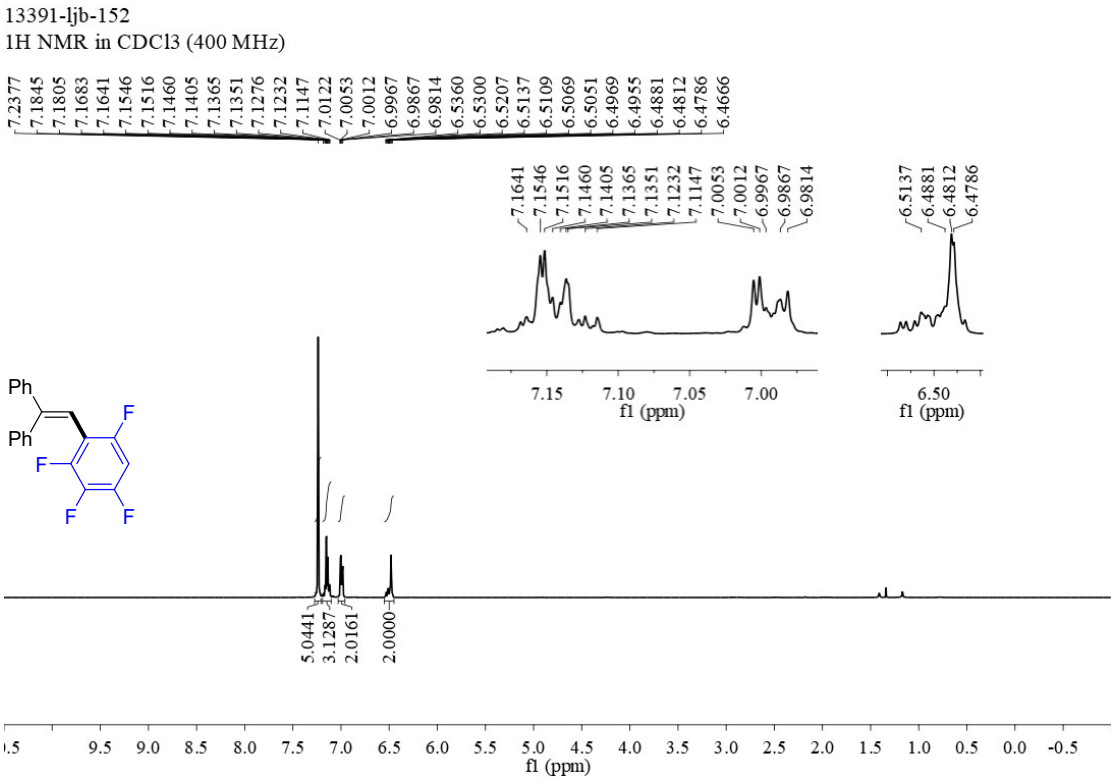


Figure S98. ^{1}H NMR spectrum of compound **4l** ($CDCl_3$, 25 °C, 400 MHz).

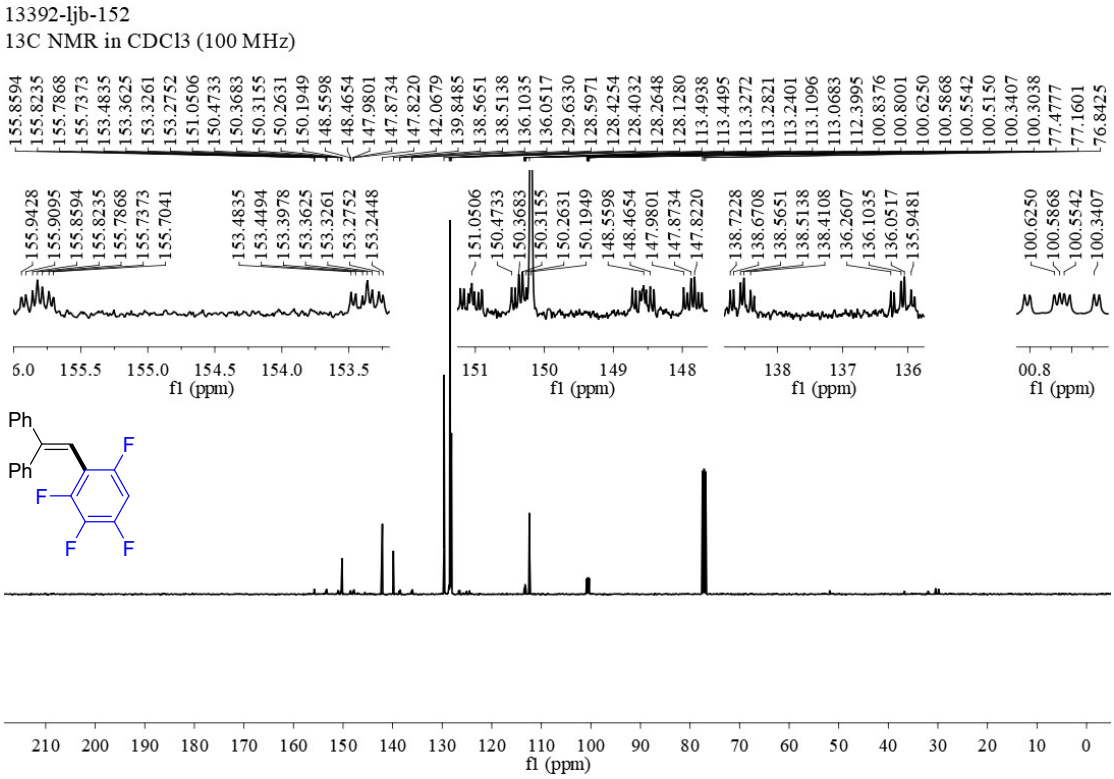


Figure S99. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4l** ($CDCl_3$, 25 °C, 100 MHz).

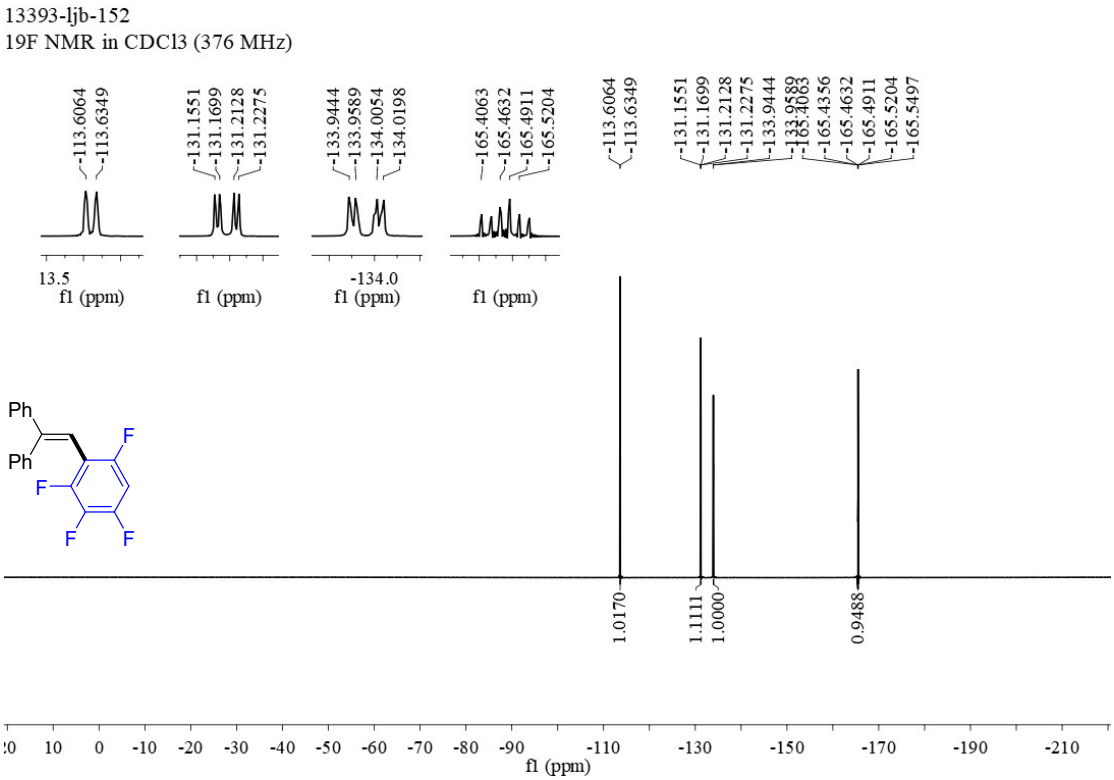


Figure S100. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4l** ($CDCl_3$, 25 °C, 376 MHz).

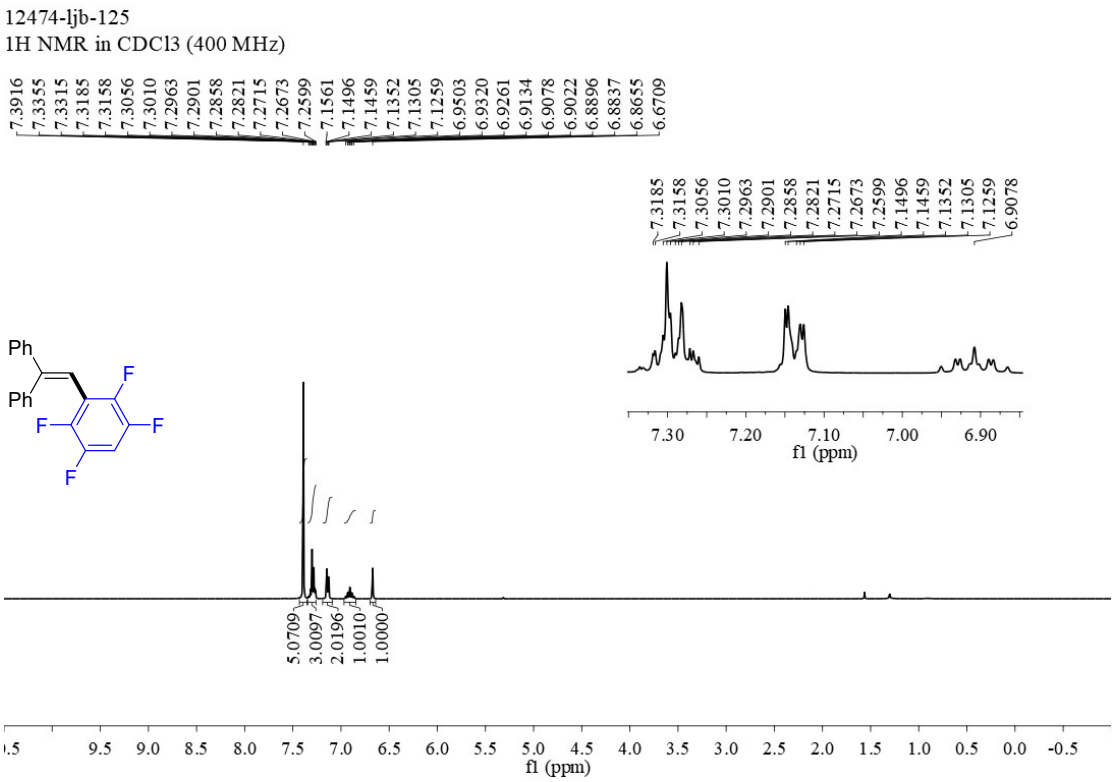


Figure S101. ^{1}H NMR spectrum of compound **4m** ($CDCl_3$, 25 °C, 400 MHz).

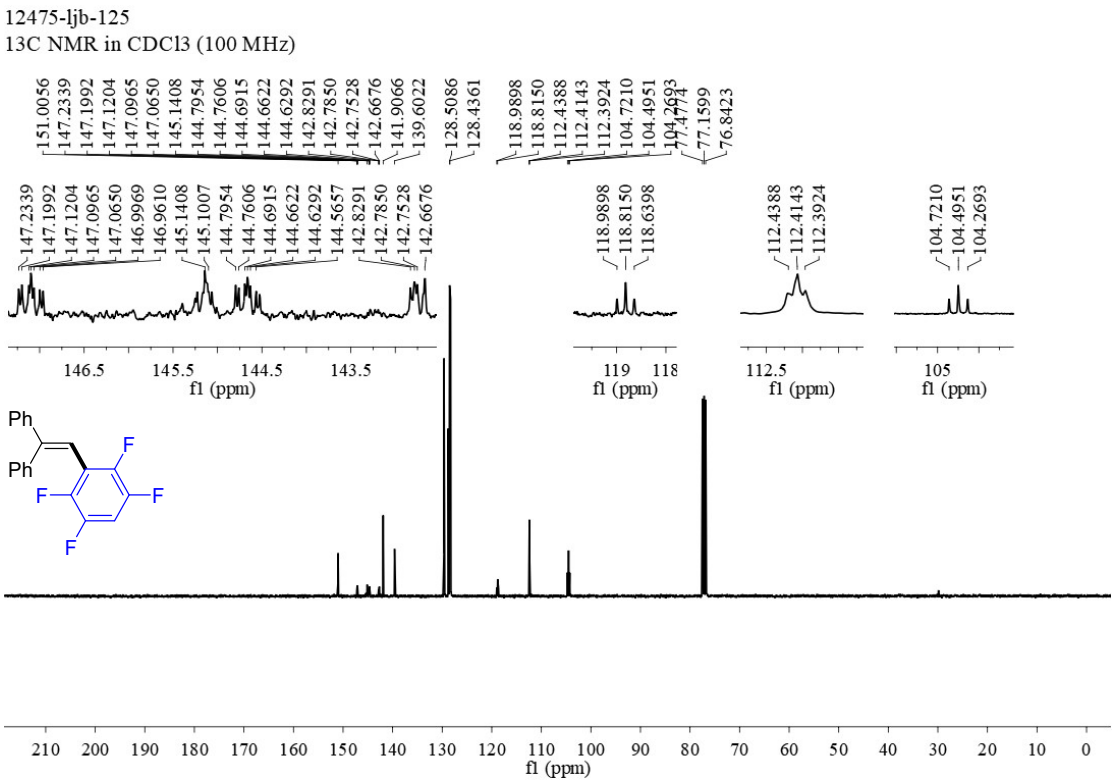


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4m** ($CDCl_3$, 25 °C, 100 MHz).

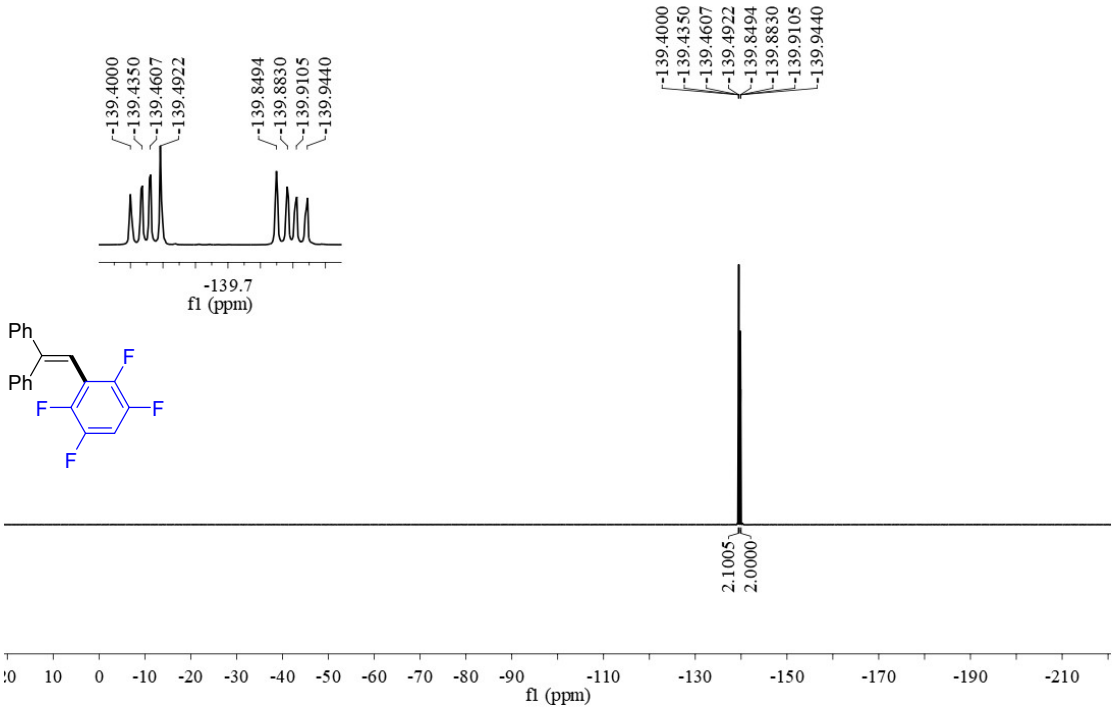


Figure S103. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4m** ($CDCl_3$, 25 °C, 376 MHz).

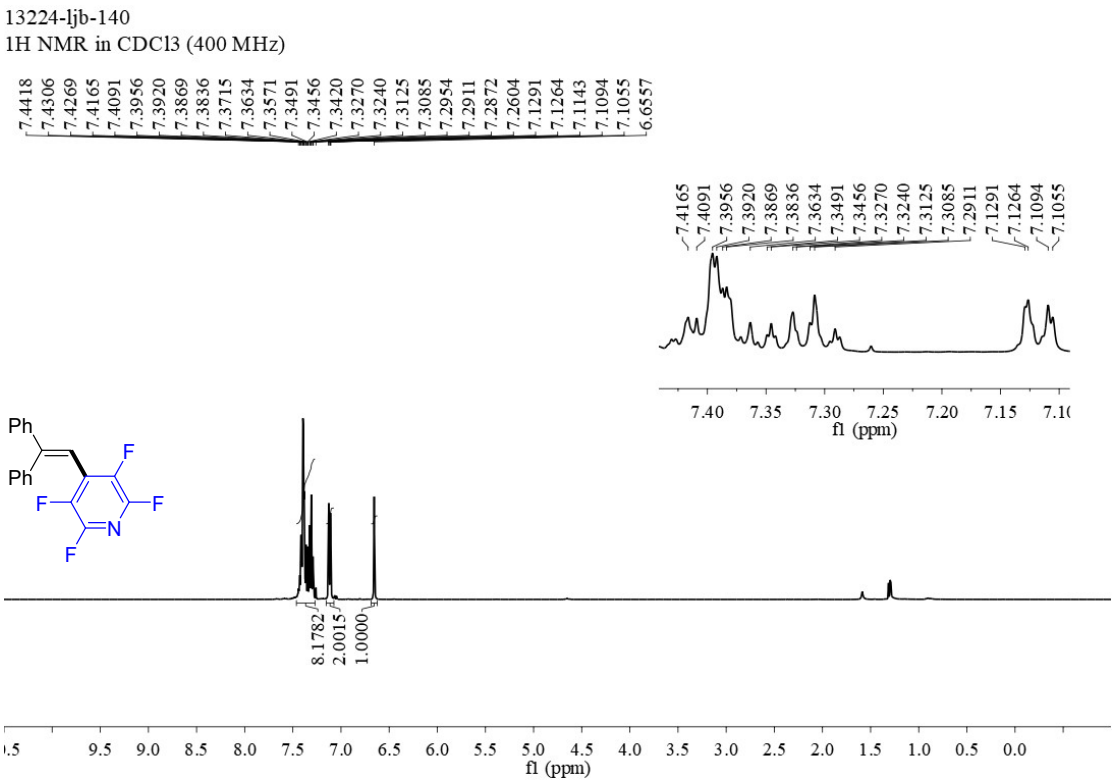


Figure S104. ^{1}H NMR spectrum of compound **4n** ($CDCl_3$, 25 °C, 400 MHz).

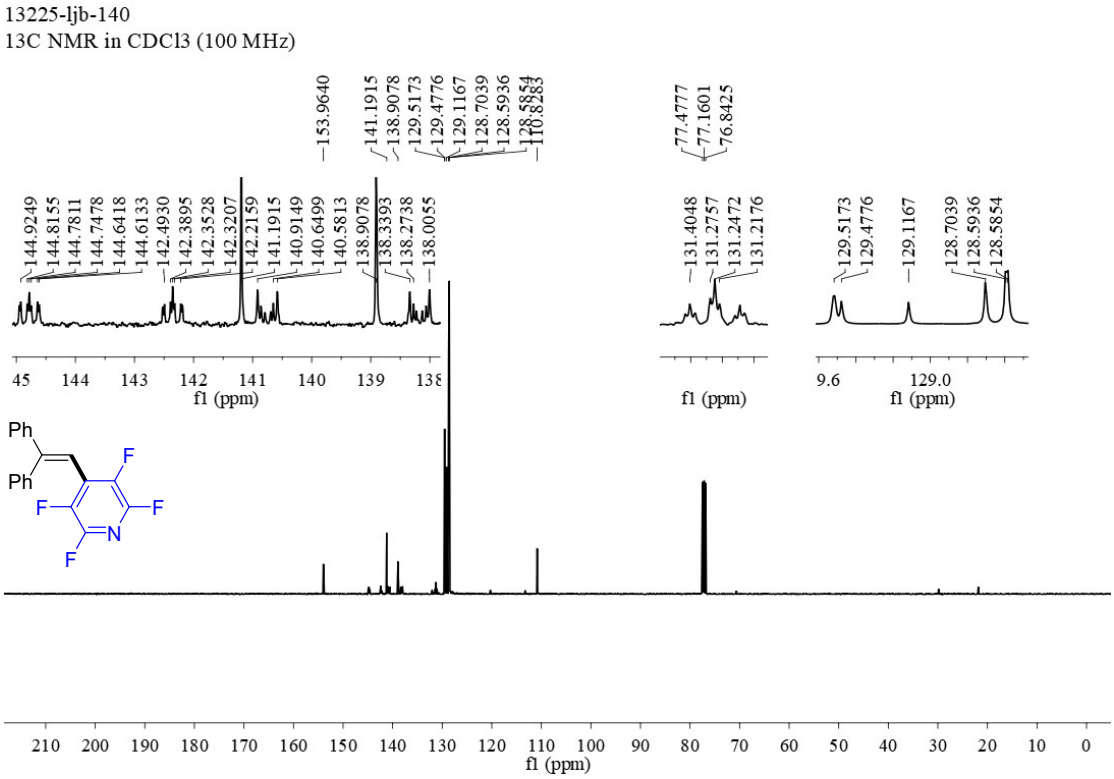


Figure S105. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4n** ($CDCl_3$, 25 °C, 100 MHz).

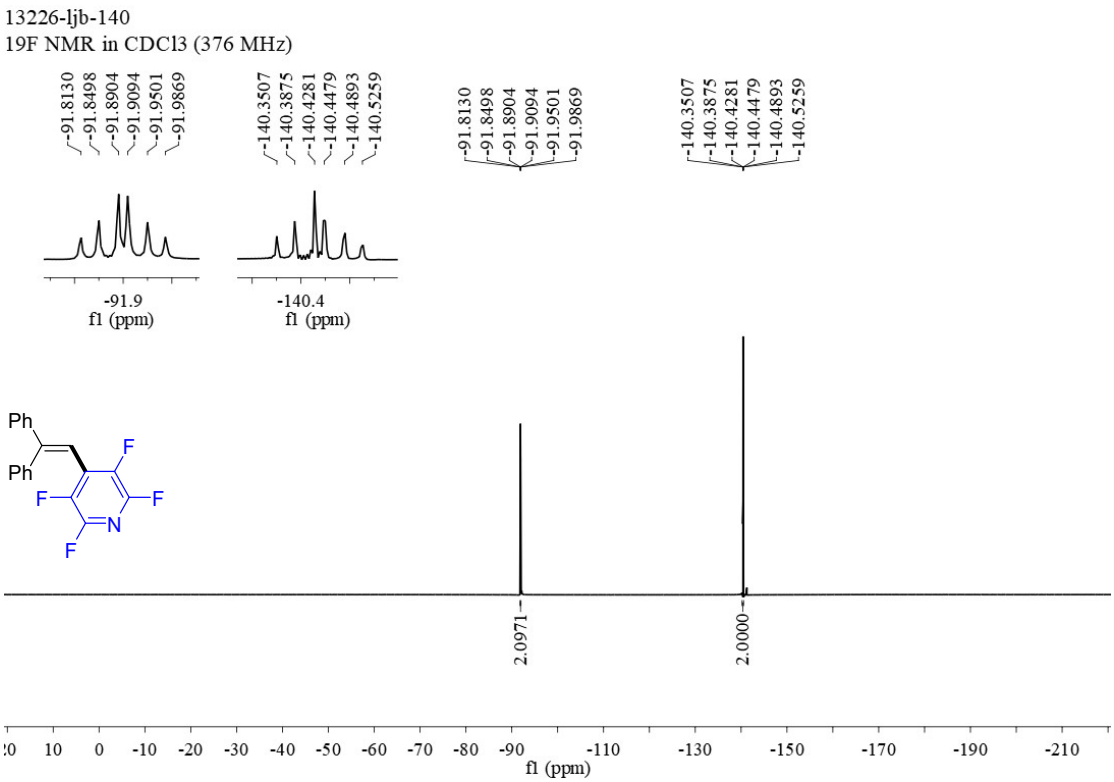


Figure S106. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4n** ($CDCl_3$, 25 °C, 376 MHz).

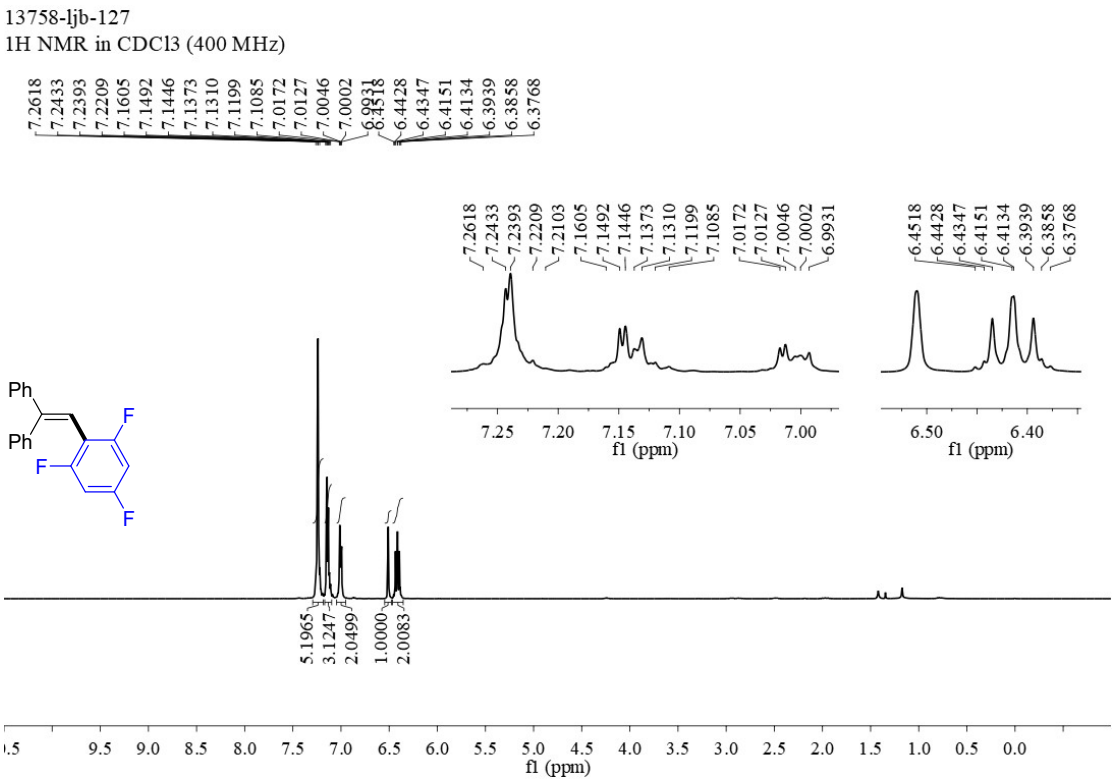


Figure S107. ^{1}H NMR spectrum of compound **4o** ($CDCl_3$, 25 °C, 400 MHz).

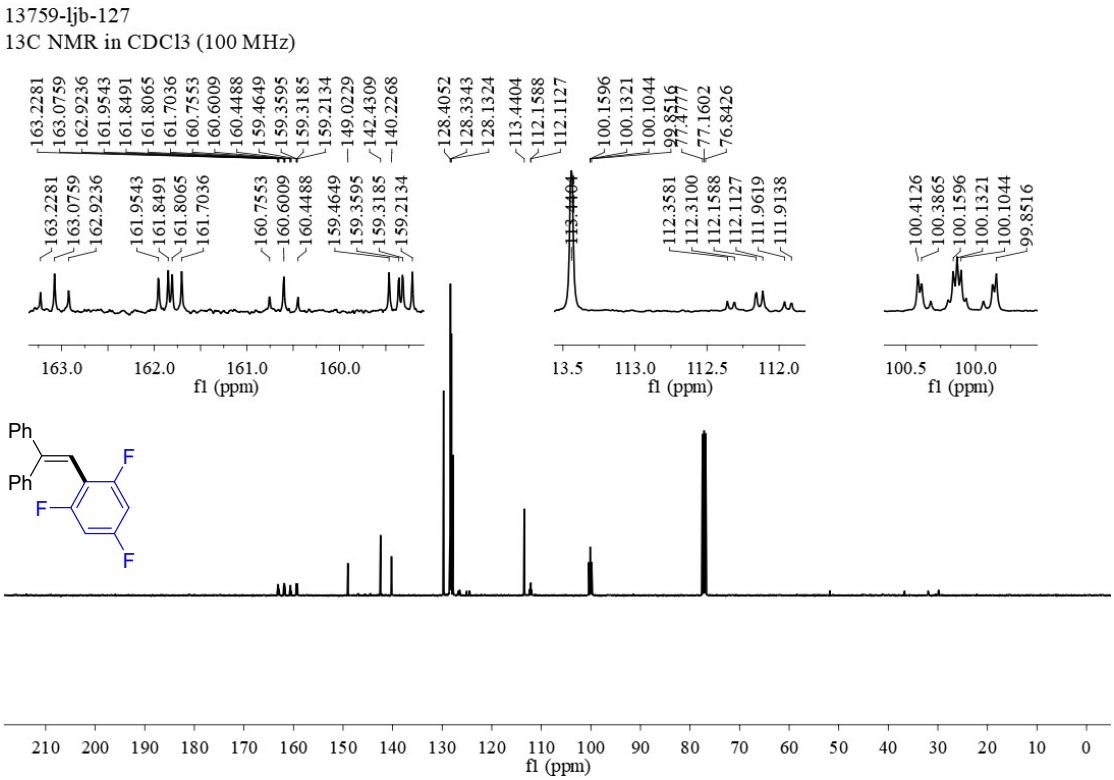


Figure S108. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4o** ($CDCl_3$, 25 °C, 100 MHz).

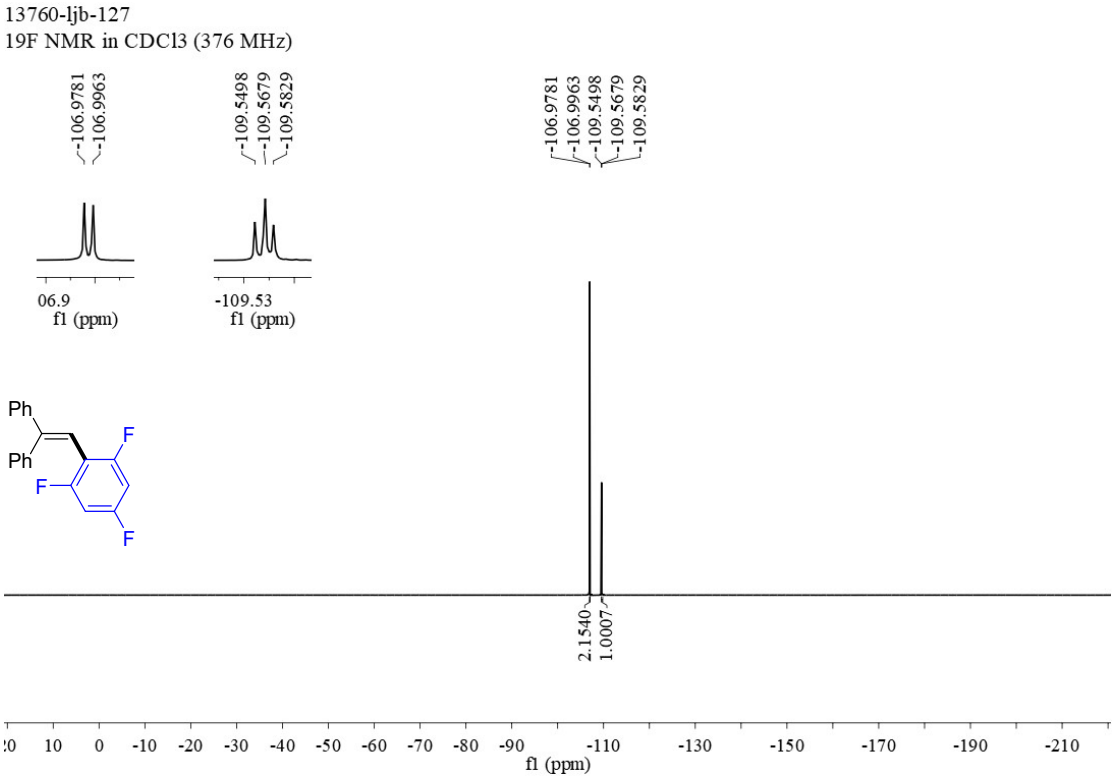


Figure S109. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4o** ($CDCl_3$, 25 °C, 376 MHz).

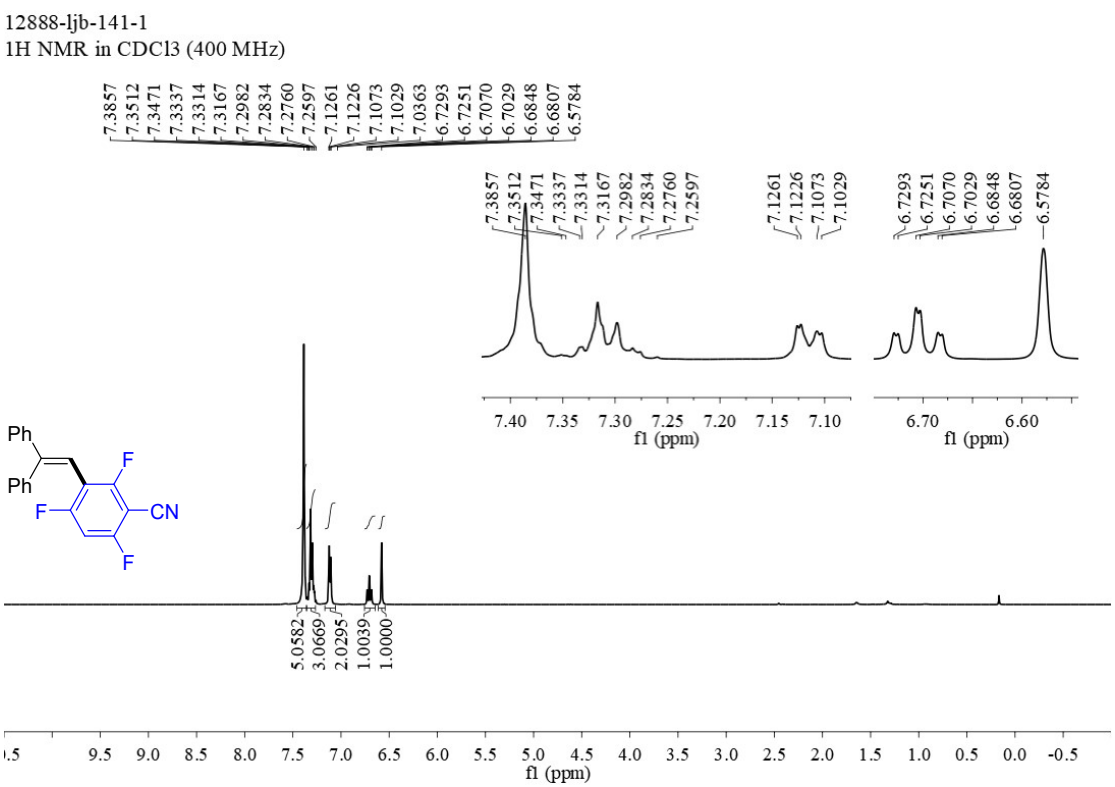


Figure S110. ^{1}H NMR spectrum of compound **4p** ($CDCl_3$, 25 °C, 400 MHz).

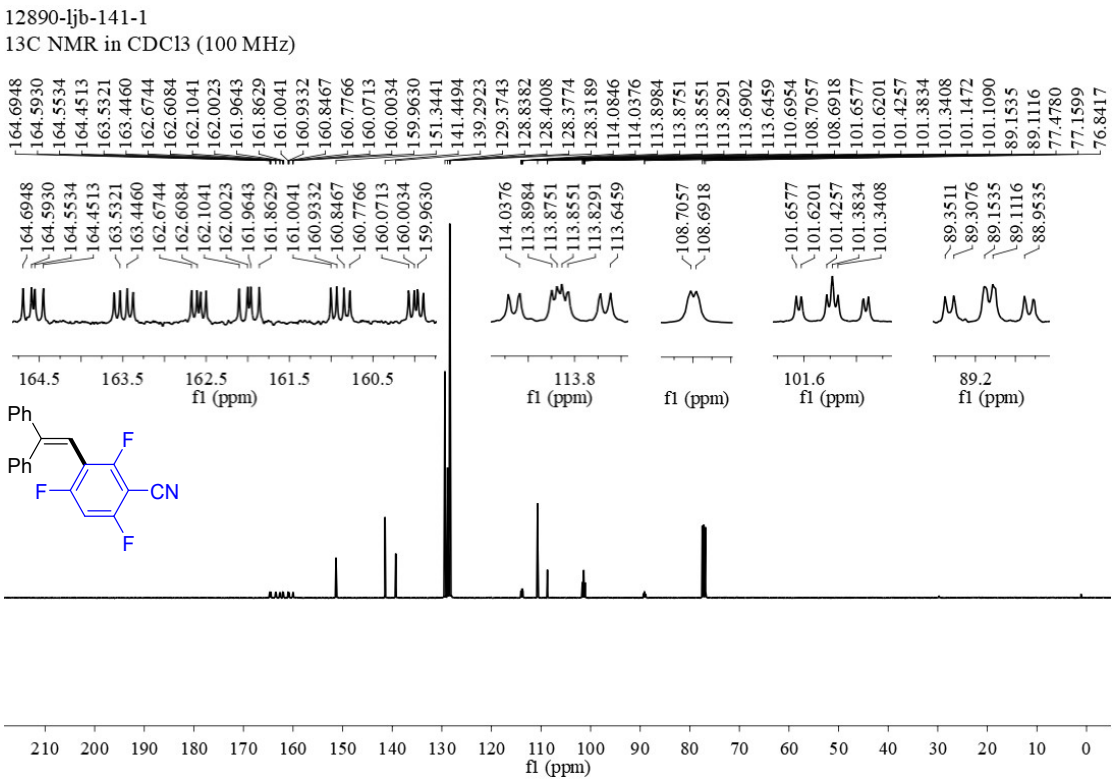


Figure S111. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4p** ($CDCl_3$, 25 °C, 100 MHz).

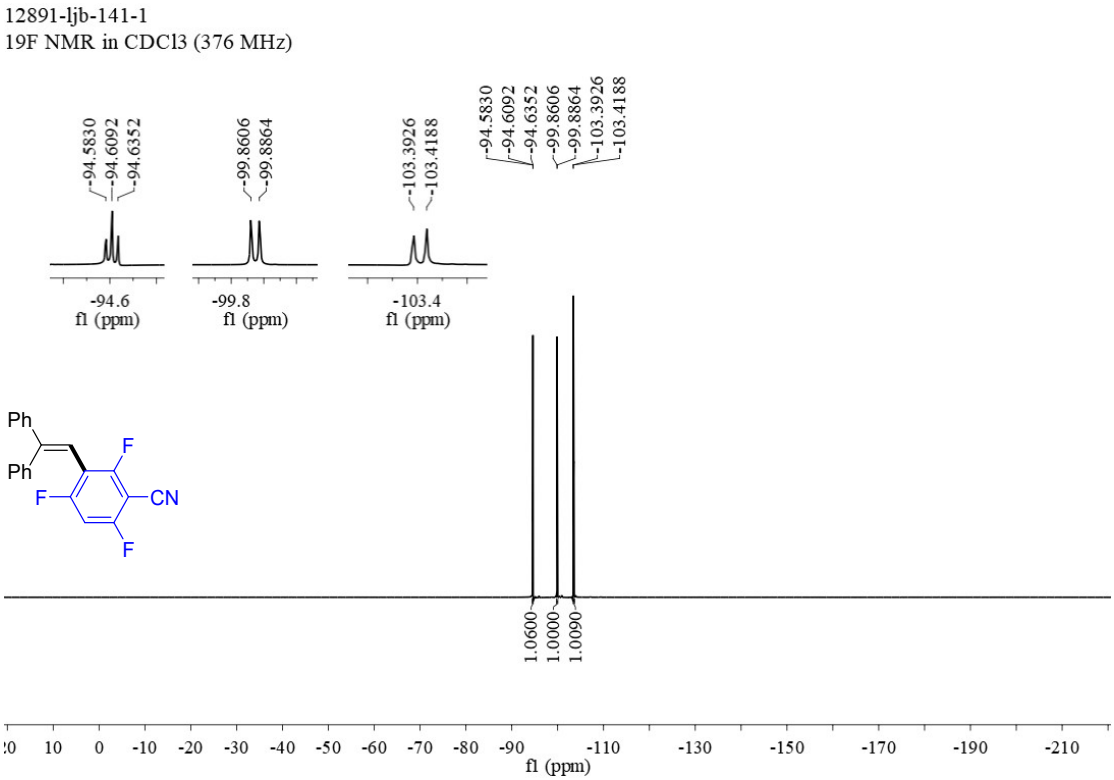


Figure S112. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4p** ($CDCl_3$, 25 °C, 376 MHz).

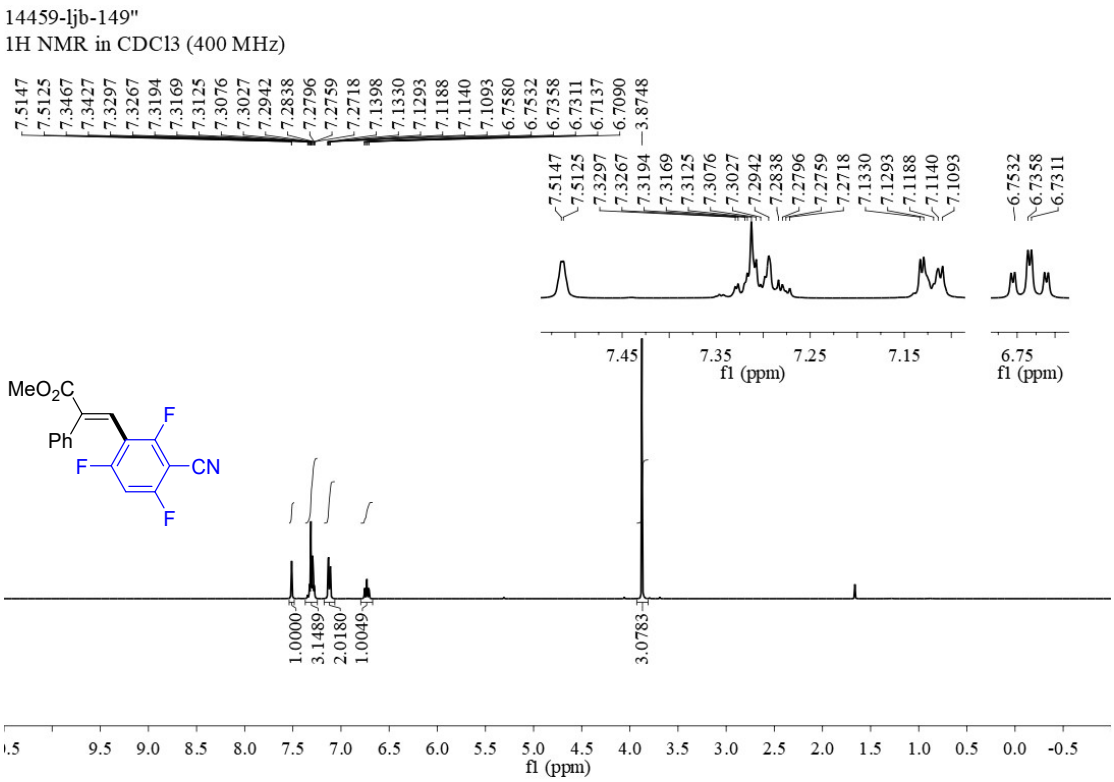


Figure S113. ^{1}H NMR spectrum of compound **4q** ($CDCl_3$, 25 °C, 400 MHz).

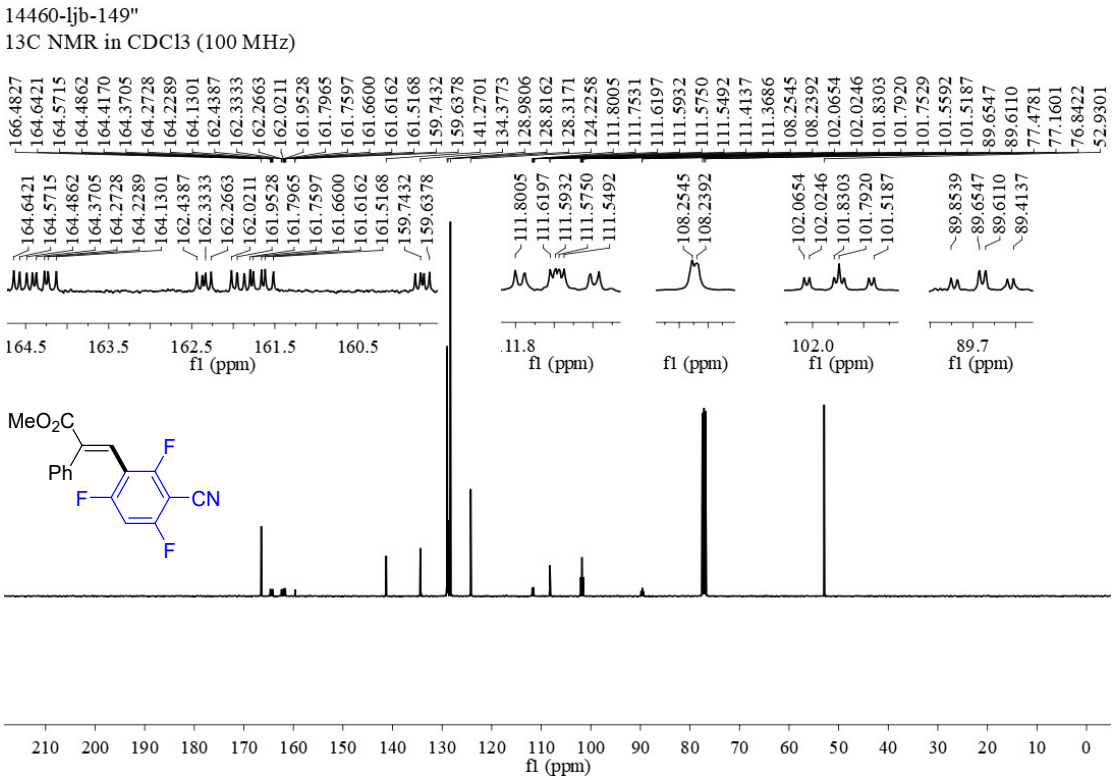


Figure S114. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4q** ($CDCl_3$, 25 °C, 100 MHz).

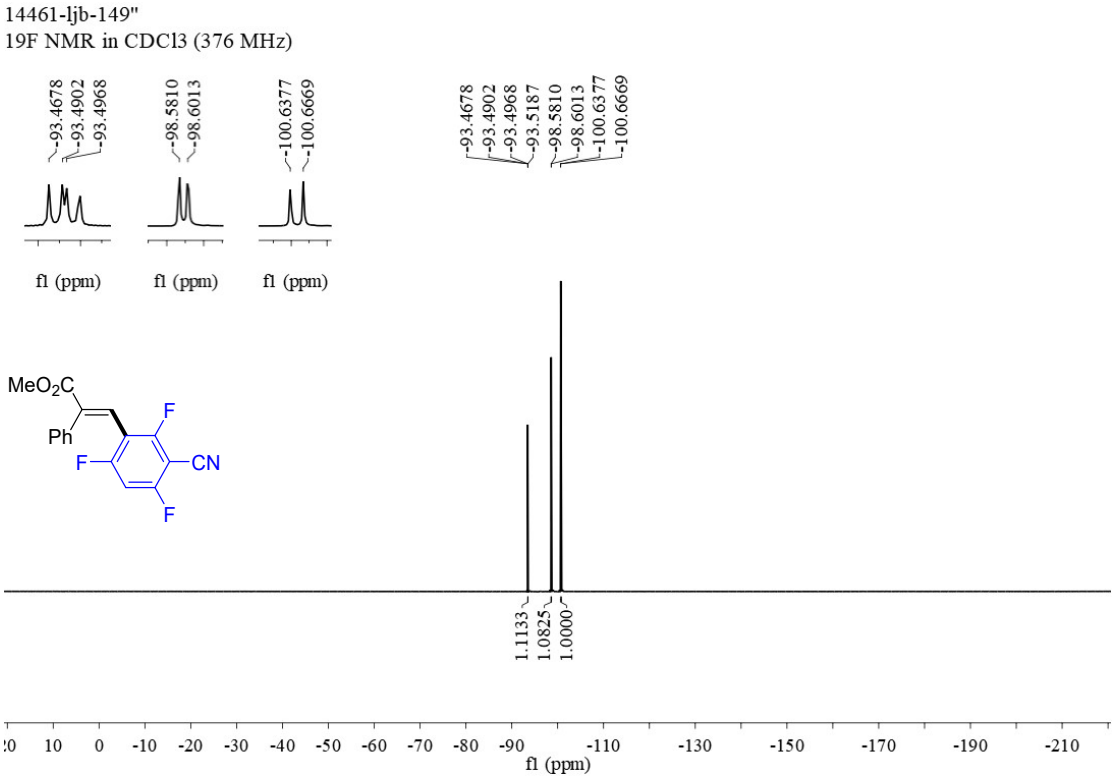


Figure S115. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4q** ($CDCl_3$, 25 °C, 376 MHz).

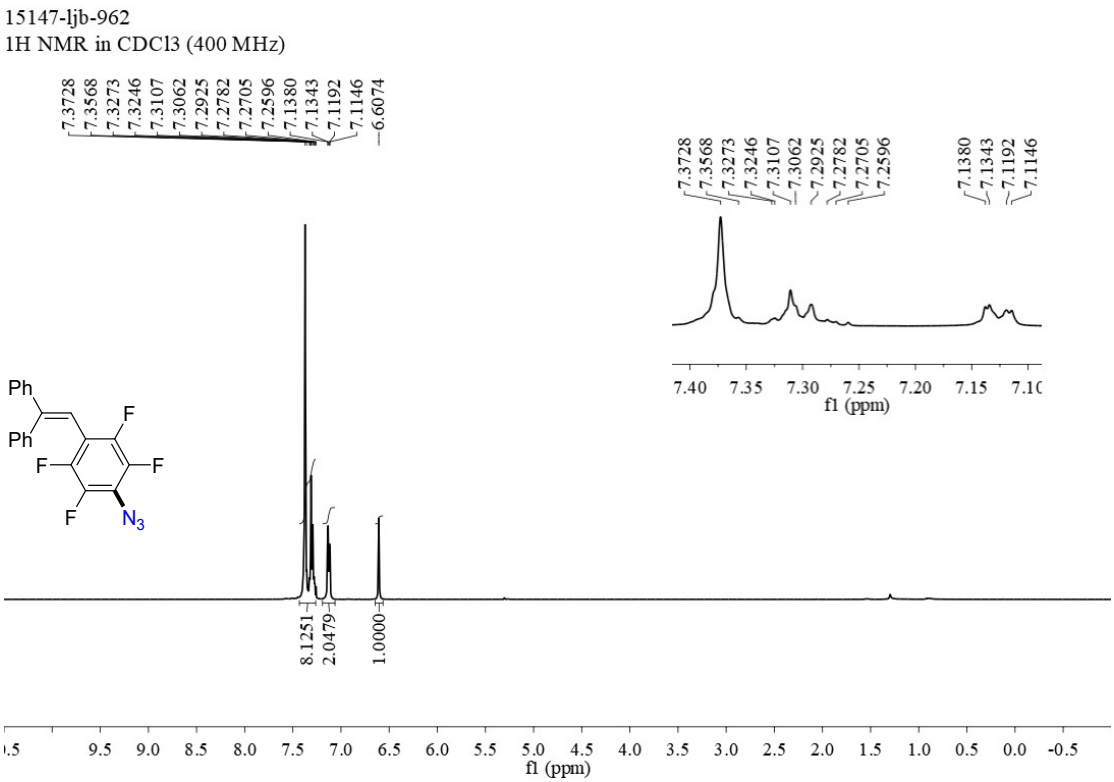


Figure S116. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 25 °C, 400 MHz).

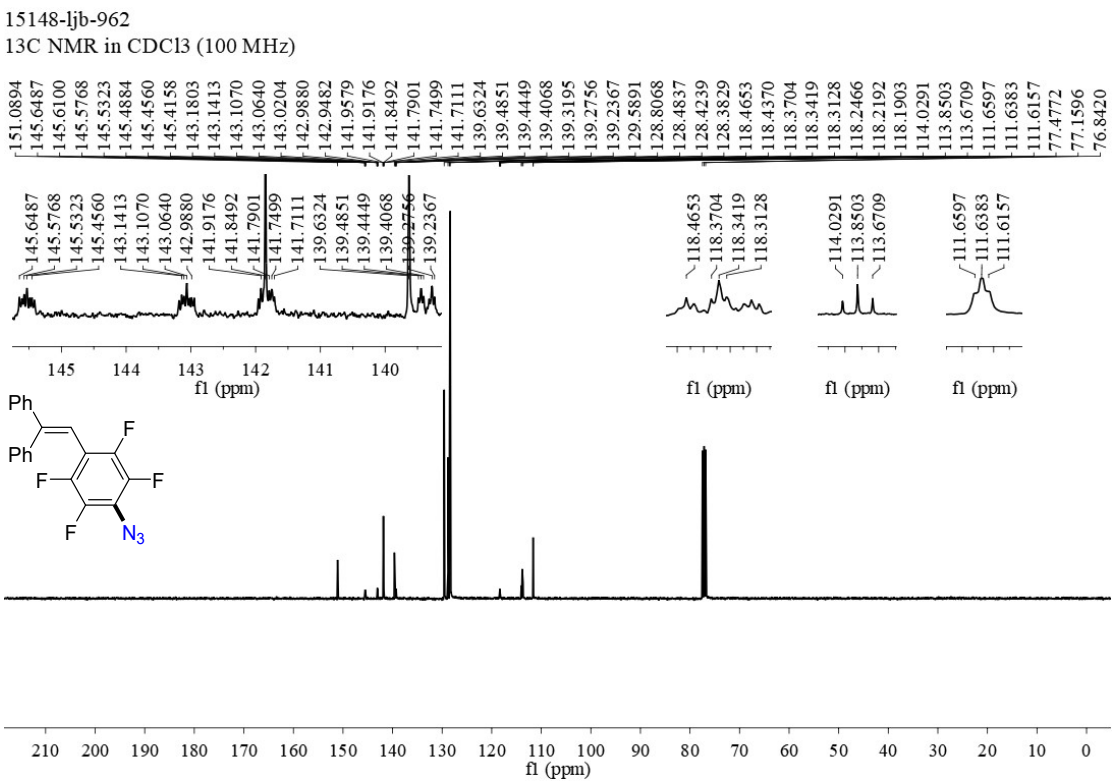


Figure S117. ^{13}C{^{1}H} NMR spectrum of compound **5** ($CDCl_3$, 25 °C, 100 MHz).

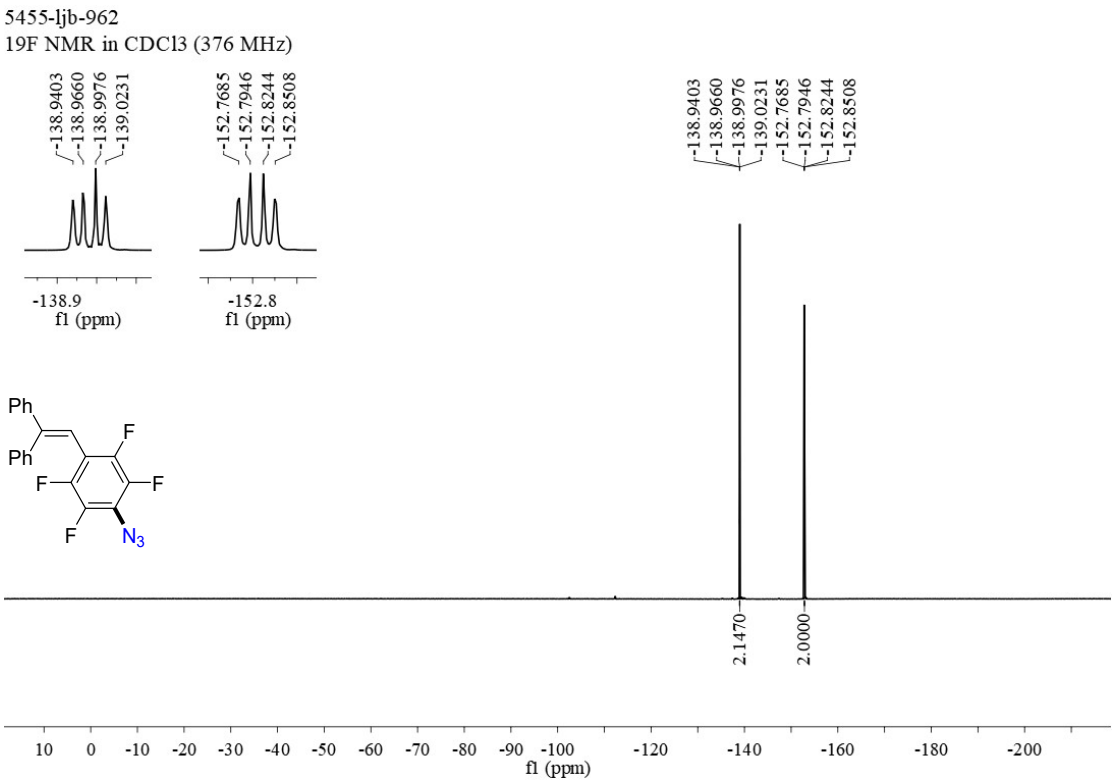


Figure S118. $^{19}F\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$, 25 °C, 376 MHz).

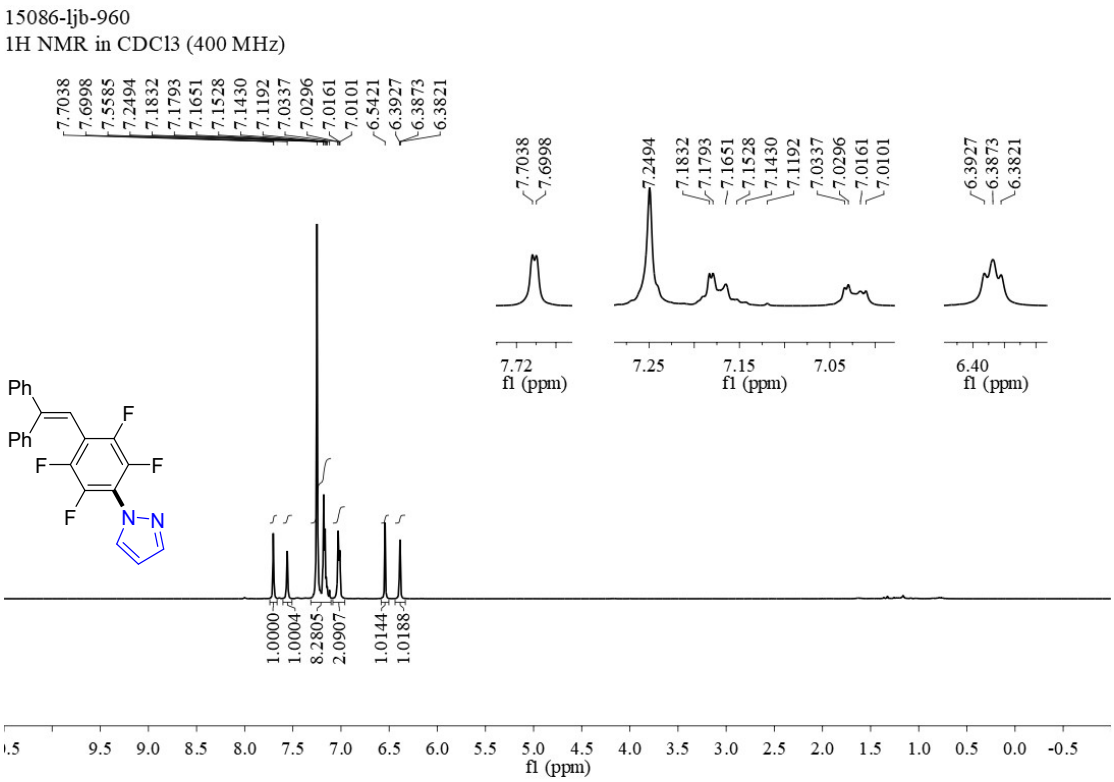


Figure S119. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 25 °C, 400 MHz).

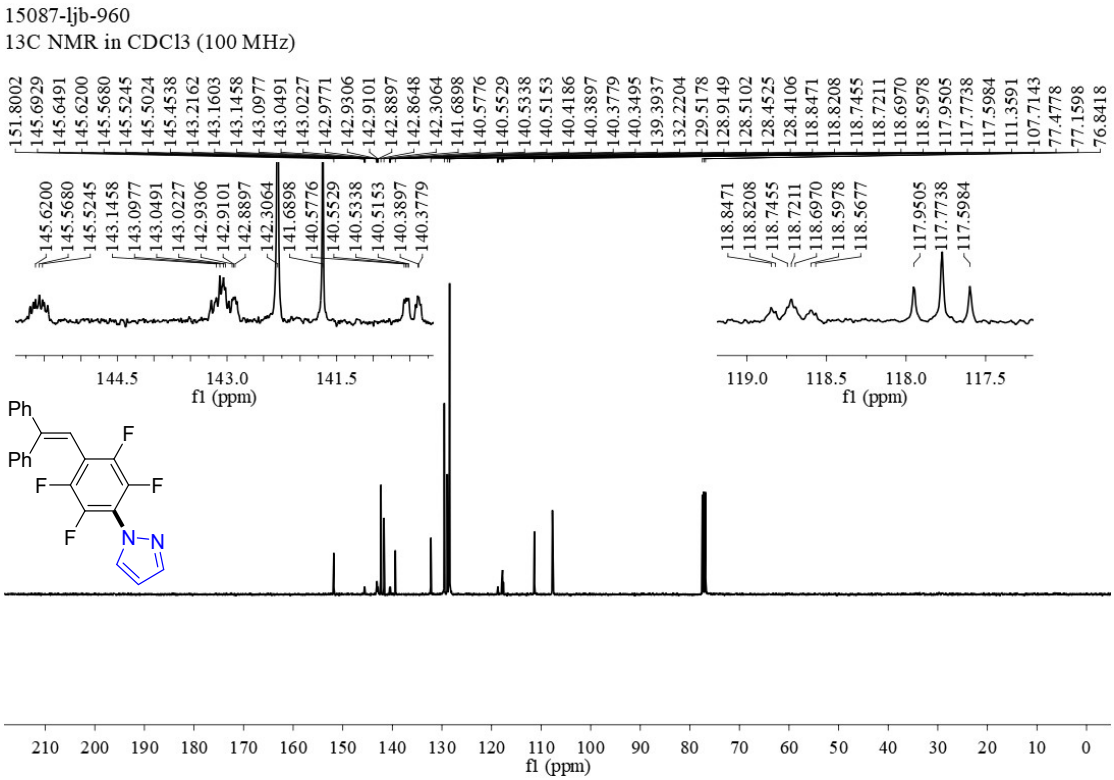


Figure S120. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 25 °C, 100 MHz).

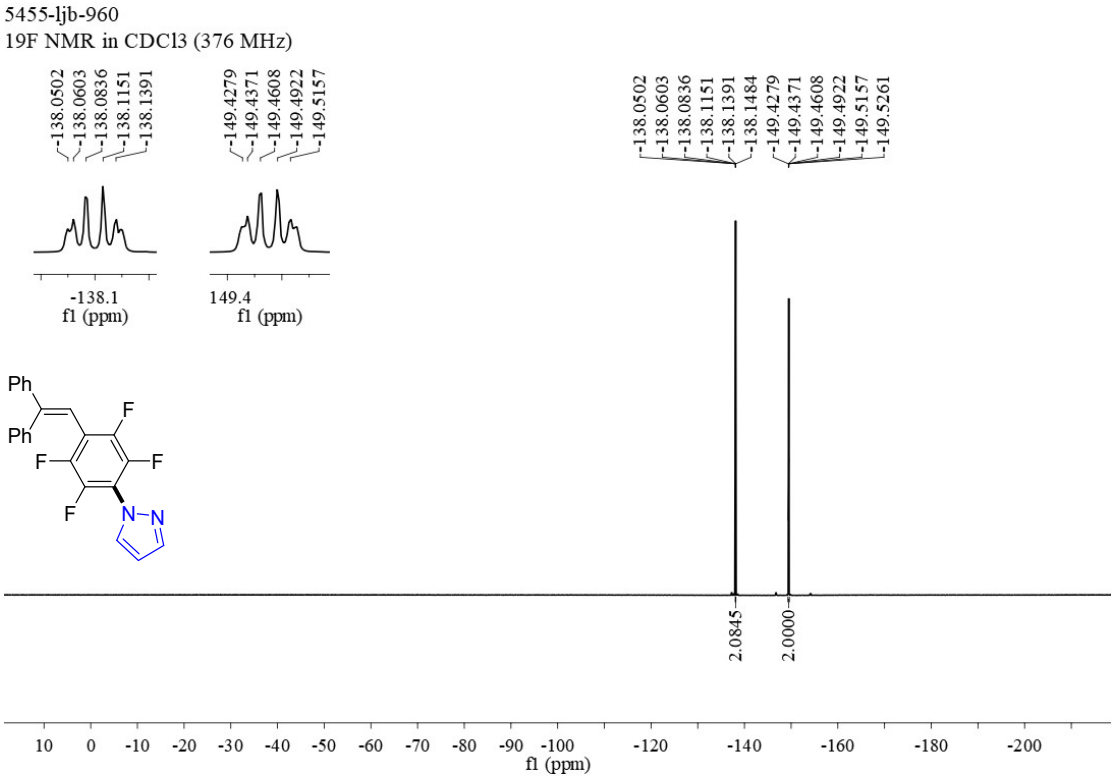


Figure S121. $^{19}F\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 25 °C, 376 MHz).

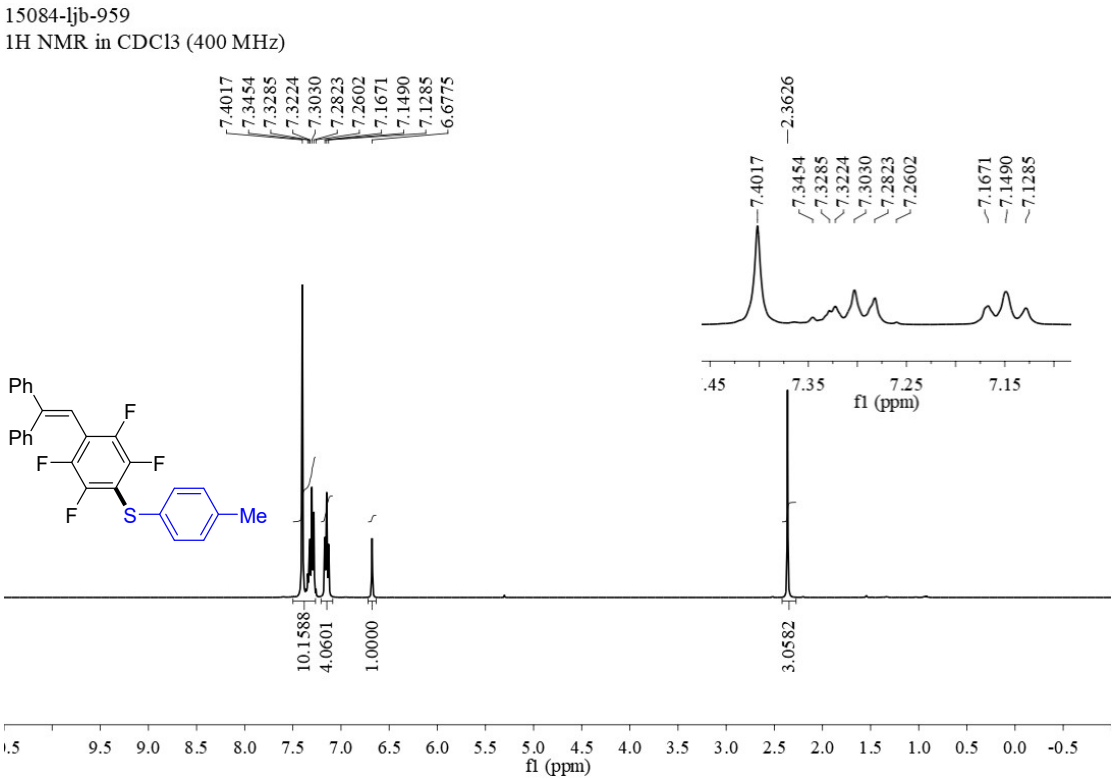


Figure S122. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 25 °C, 400 MHz).

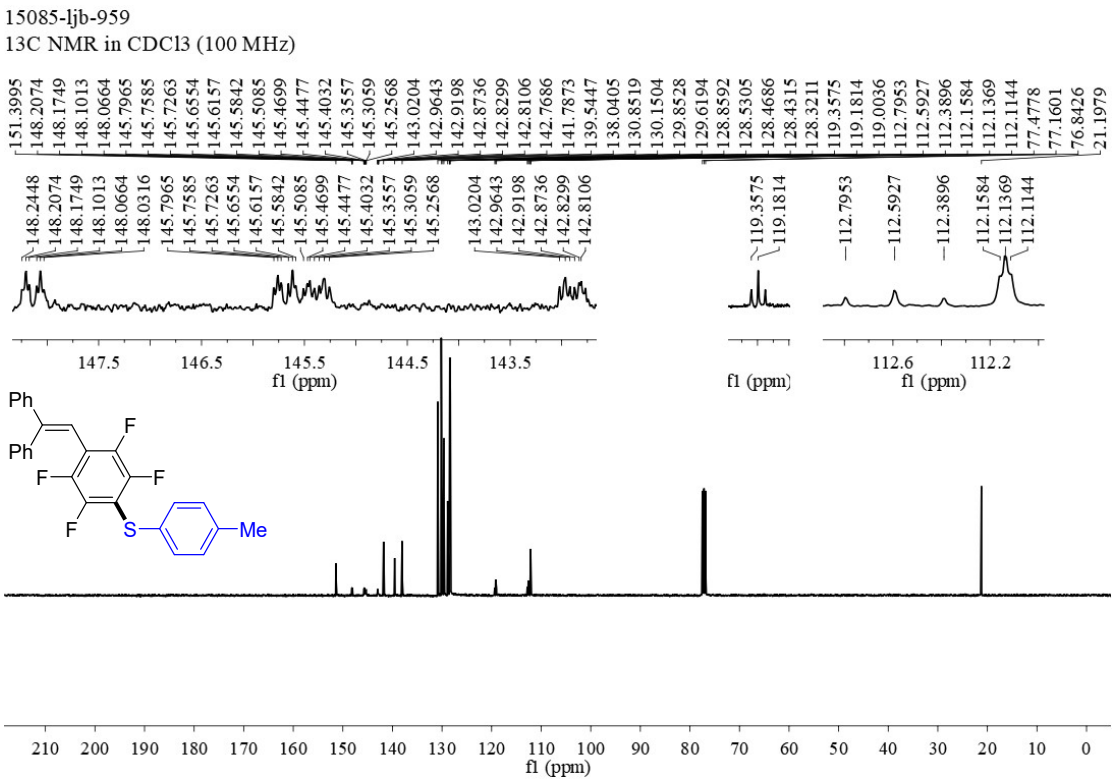


Figure S123. ^{13}C{^{1}H} NMR spectrum of compound **7** ($CDCl_3$, 25 °C, 100 MHz).

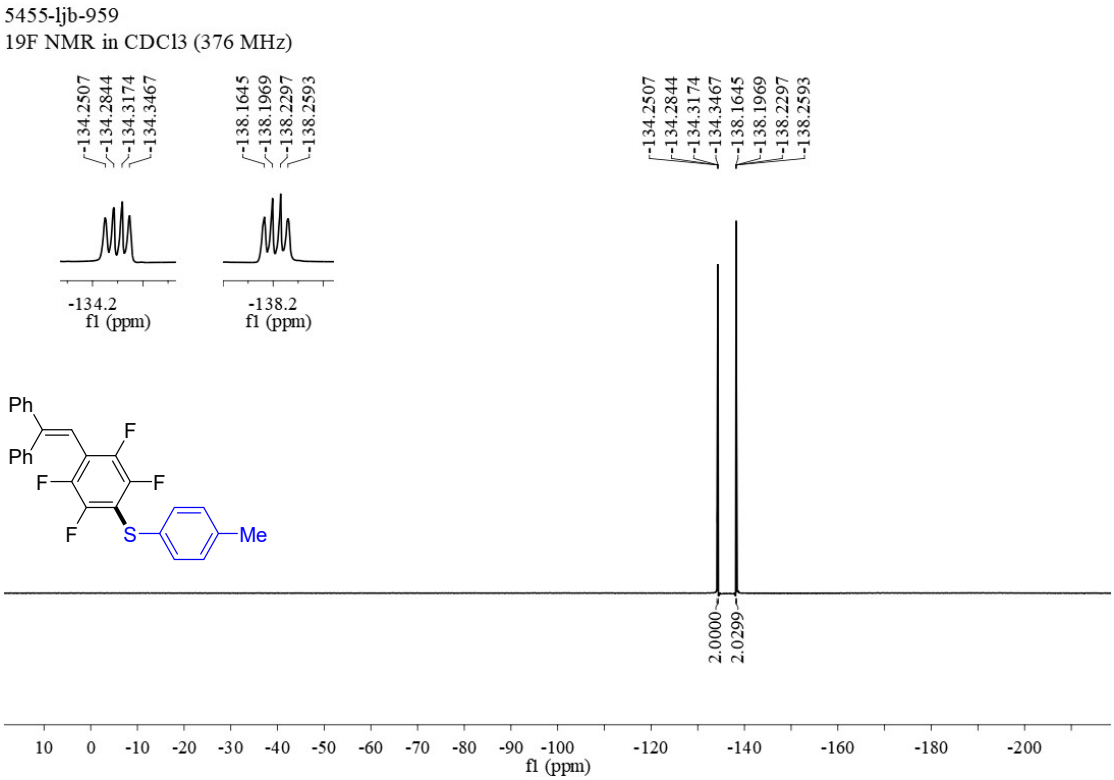


Figure S124. $^{19}F\{^{1}H\}$ NMR spectrum of compound **7** ($CDCl_3$, 25 °C, 376 MHz).

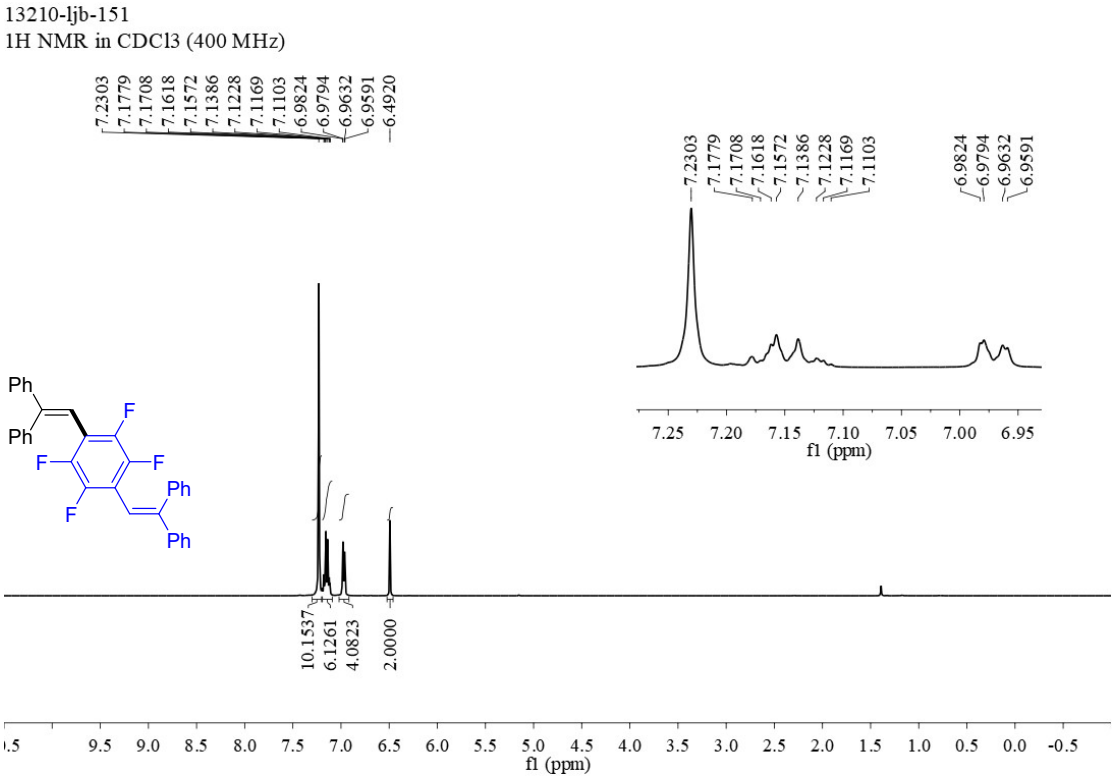


Figure S125. ^{1}H NMR spectrum of compound **4m'** ($CDCl_3$, 25 °C, 400 MHz).

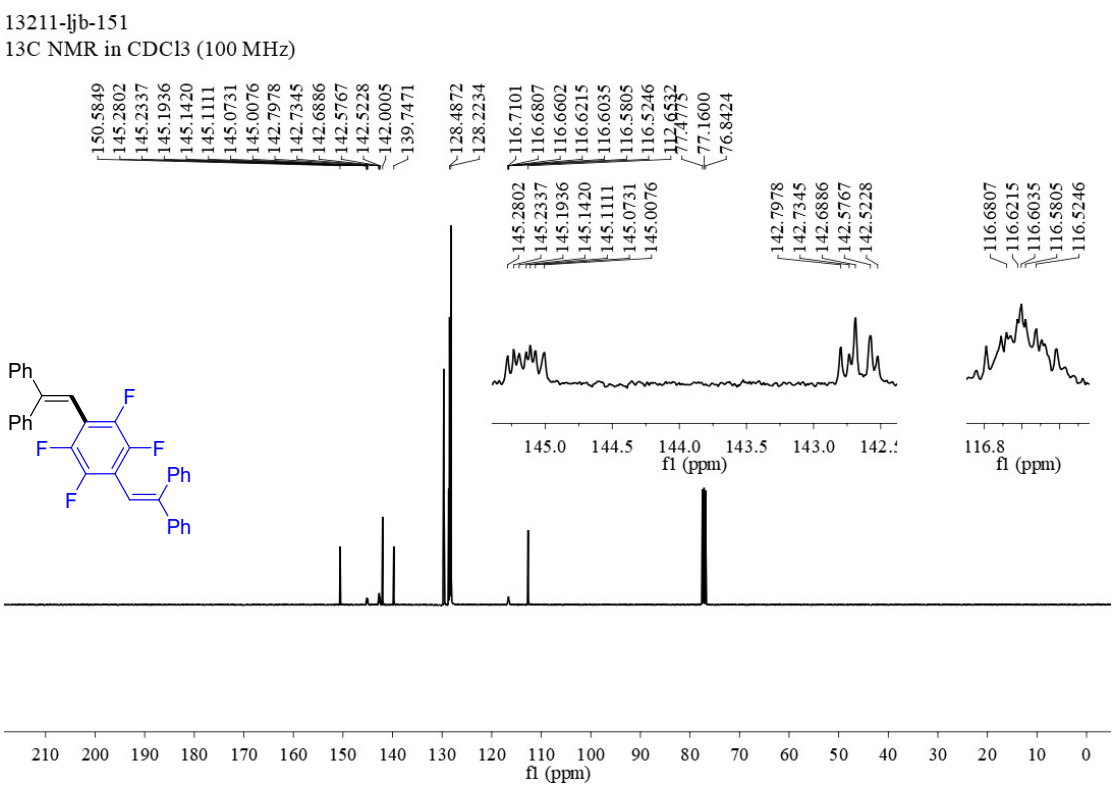


Figure S126. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4m'** ($CDCl_3$, 25 °C, 100 MHz).

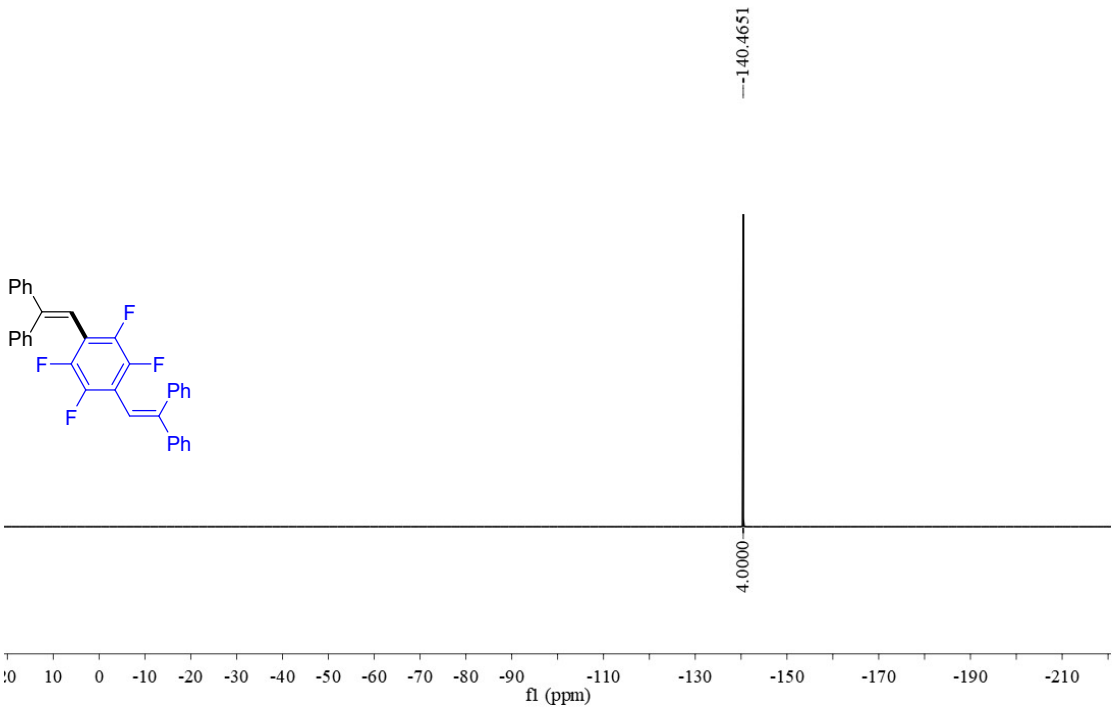


Figure S127. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4m'** ($CDCl_3$, 25 °C, 376 MHz).