Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Regioselective and late-stage polyfluoroarylation of arenes with divers fluoroaryl nucleophiles via Pd-catalysis

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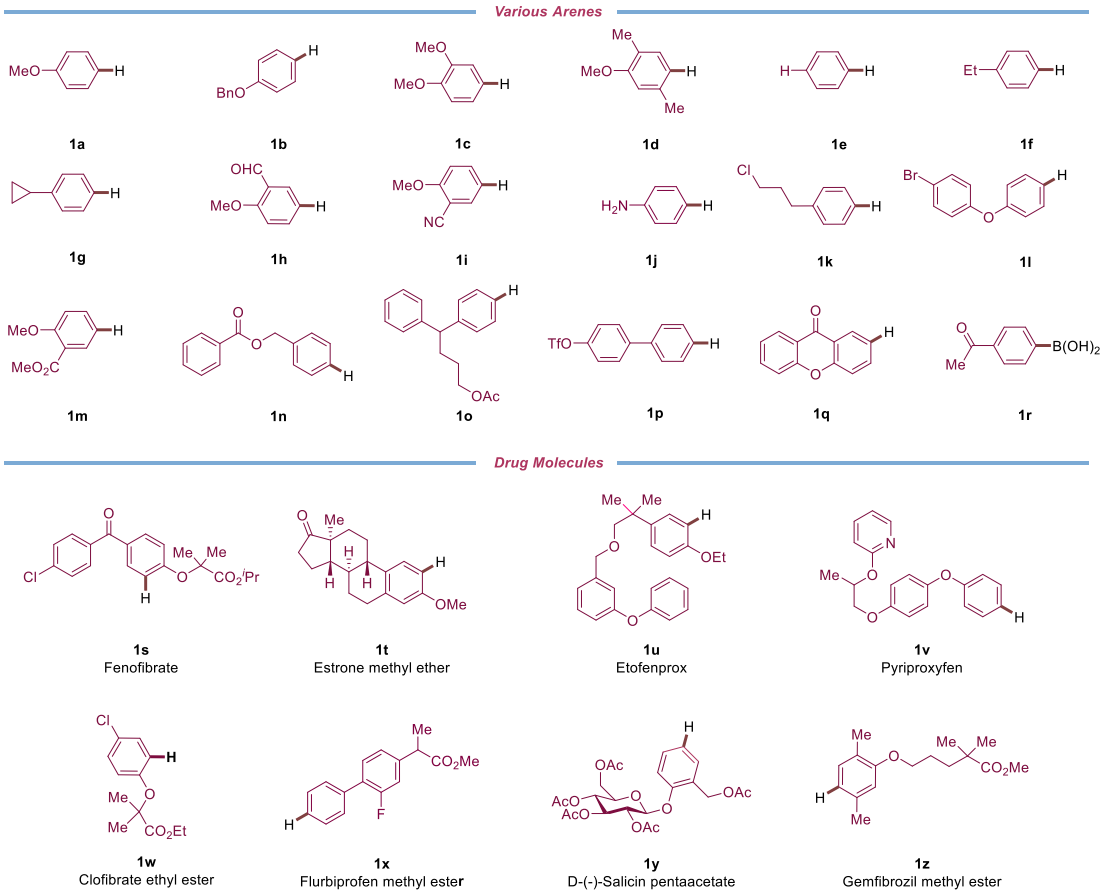
1. General information

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quaternary, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). All regents and solvents were purchased from commercial sources and purified commonly before used.

2. Various of arenes

Figure S1: Arenes and Drug molecules

All arenes and drug molecules are commercially available.



3. Various of fluoroaryl nucleophiles

All fluoroaryl nucleophiles are commercially available, and reagent information is shown in the following Figure S2–S4.

Figure S2: Various of fluorobenzoic acids

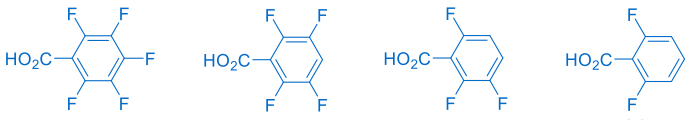


Figure S3: Various of fluorophenylboric acids

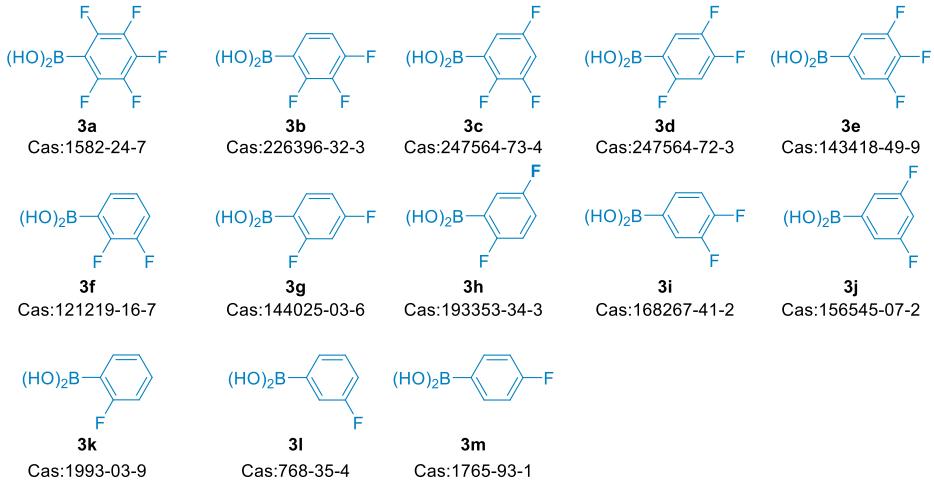


Figure S4: Various of fluorobenzenes

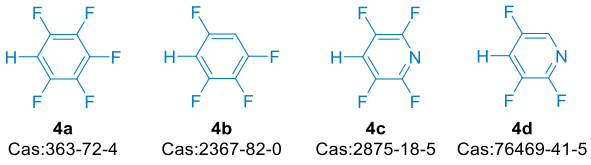


Figure S5: Structure of 19 Ar^F

Varying the F-content (1F-5F) and F-substitution patterns on phenyl groups will lead to 19 Ar^F.

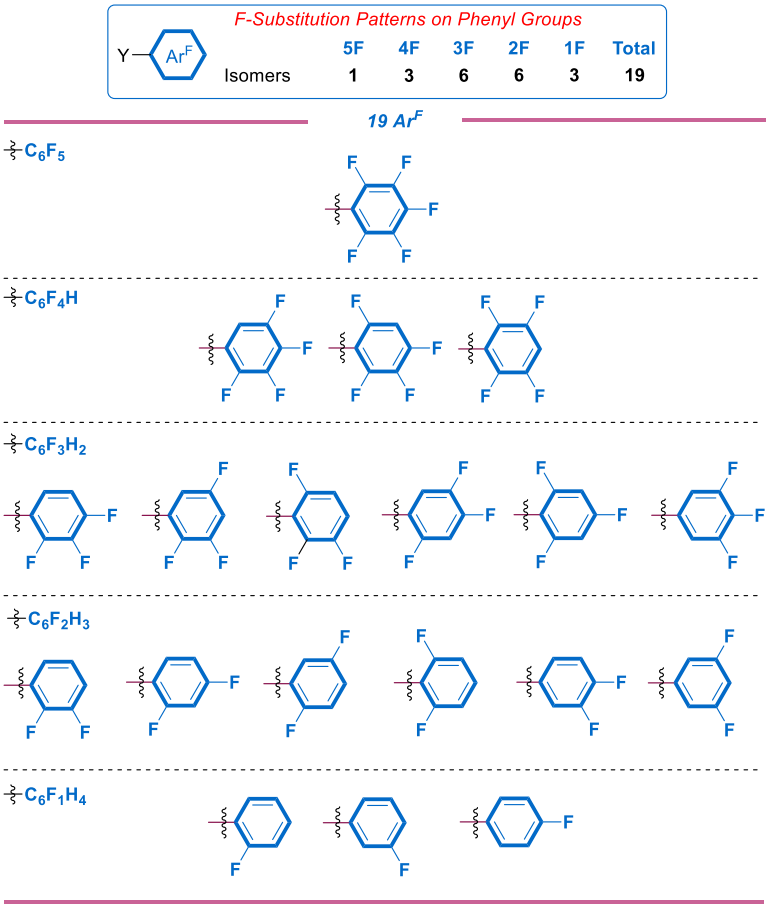


Table S1: Introduce Ar^F (Varying the F-content (1F–5F) and F-substitution patterns on phenyl groups) into aromatic ring by employing Ar^F–CO_2H as polyfluoroaryl nucleophiles.

(Representative examples)

Entry	References	Ar^F–CO_2H	Ar^F
1	*Chem. Commun.*, 2021, **57**, 3696–3699	Ar^F–CO_2K	5
2	*Org. Lett.*, 2019, **21**, 4734–4738	Ar^F–CO_2Na	4
3	*Chem. Commun.*, 2019, **55**, 6445–6448	Ar^F–CO_2H	1
4	*Adv. Syn. Cat.*, 2018, **360**, 3239–3244	Ar^F–CO_2K	4
5	*RSC Adv.*, 2017, **7**, 34722–34729	Ar^F–CO_2K	4
6	*Org. Lett.*, 2015, **17**, 1256–1259	Ar^F–CO_2K	3
7	*Tetrahedron Lett.*, 2013, **54**, 283–286	Ar^F–CO_2H	1
8	*Org. Lett.*, 2010, **12**, 1000–1003	Ar^F–CO_2K	7
9	Angew. Chem., Int. Ed., 2009, **48**, 9350 –9354	Ar^F–CO_2K	6
10	*Org. Lett.*, 2008, **10**, 3161–3164	Ar^F–CO_2H	1

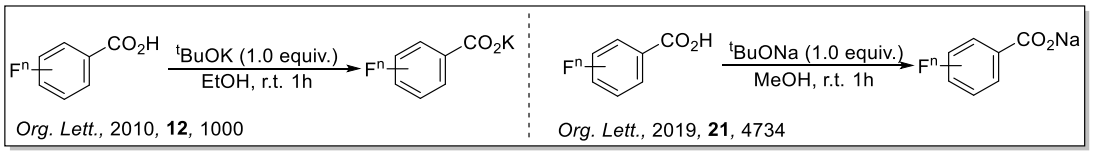


Table S2: Introduce Ar^F (Varying the F-content (1F–5F) and F-substitution patterns on phenyl groups) into aromatic ring by employing Ar^F–[B] as polyfluoroaryl nucleophiles.

(Representative examples)

Entry	References	Ar^F–[B]	Ar^F
1	*ACS Catal.*, 2021, **11**, 14803–14810	Ar^F–$B(OH)_2$ Ar^F–Bpin	4
2	*ACS Catal.*, 2020, **10**, 352–357	Ar^F–B(dan)	3
3	*ChemCatChem.*, 2019, **11**, 5387–5396	Ar^F–Bpin	8
5	*ACS Catal.*, 2018, **8**, 2989–2994	Ar^F–$B(OH)_2$ Ar^F–Bpin	7
6	*J. Am. Chem. Soc.*, 2017, **139**, 12418–12421	Ar^F–$B(OH)_2$	6
7	*J. Org. Chem.*, 2017, **82**, 13188–13203	Ar^F–$B(OH)_2$	7
8	*Angew. Chem., Int. Ed.*, 2017, **56**, 1021–1025	Ar^F–Bpin	5
9	*Tetrahedron.*, 2011, **67**, 5432–5436	Ar^F–$B(OH)_2$	1
10	*J. Am. Chem. Soc.*, 2010, **132**, 14073–14075	Ar^F–$B(OH)_2$	2
11	*Org. Lett.*, 2005, **7**, 4915–4917	Ar^F–$B(OH)_2$	1

Table S3: Introduce Ar^F (Varying the F-content (1F–5F) and F-substitution patterns on phenyl groups) into aromatic ring by employing Ar^F–H as polyfluoroaryl nucleophiles.

(Representative examples)

Entry	References	Ar^F–H	Ar^F
1	*ACS Catal.*, 2017, **7**, 7421−7430	Ar^F−H	6
2	*J Catal.*, 2015, **321**, 62–69	Ar^F−H	4
3	*Tetrahedron Lett.*, 2015, **56**, 123−126	Ar^F−H	3
4	*Chem. Commun.*, 2014, **50**, 8927−8929	Ar^F−H	4
5	*Eur. J. Org. Chem.*, 2014, **2014**, 3323–3327	Ar^F−H	3
6	*J. Fluorine. Chem*., 2014, **165** ,76–80	Ar^F−H	2
7	*Appl. Organometal. Chem.*, 2014, **28**, 180–185	Ar^F−H	3
8	*Adv. Synth. Catal.*, 2014, **356**, 429–436	Ar^F−H	3
9	*Eur. J. Org. Chem.*, 2014, **201**4, 1327–1332	Ar^F−H	4
10	*Angew. Chem., Int. Ed.*, 2013, **52**, 1781–1784	Ar^F−H	3
11	*Tetrahedron Lett.*, 2013, **54**, 1285–1289	Ar^F−H	6
12	*J. Fluorine Chem.*, 2013, **151**, 50–57	Ar^F−H	3
13	*Org. Biomol. Chem.*, 2012, **10**, 2289–2299	Ar^F−H	3
14	*Org. Lett.*, 2011, **13**, 276–279	Ar^F−H	7
15	*J. Am. Chem. Soc.*, 2011, **133**, 13577–13586	Ar^F−H	4
16	*Tetrahedron Lett.*, 2011, **52**, 5525−5529	Ar^F−H	2
17	*J. Am. Chem. Soc.*, 2010, **132**, 16377–16379	Ar^F−H	3
18	*Org. Lett.*, 2009, **11**, 3346–3349	Ar^F−H	7
19	*Org. Lett.*, 2006, **8**, 5097–5100	Ar^F−H	2

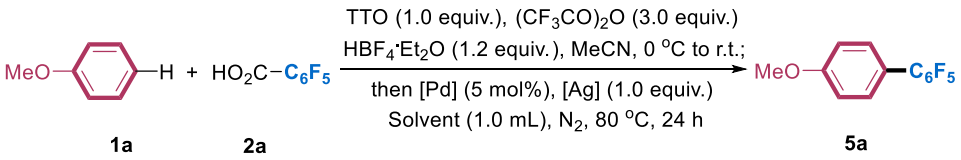
Table S4: Introduce Ar^F (Varying the F-content (1F-5F) and F-substitution patterns on phenyl groups) into aromatic ring by employing Ar^F–X as polyfluoroaryl nucleophiles.

(Representative examples)

Entry	References	Ar^F–X	Ar^F
1	*Chem.–Eur. J.*, 2021, **27**, 11061–11064	Ar^F–F	1
2	*Chem. Commun.,* 2019*,* **55***,** 6*503–6506	Ar^F–$SnBu_3$	5
3	*Angew. Chem., Int. Ed.*, 2019, **58**, 17788–17795	Ar^F–$GeEt_3$	4
4	*Org. Lett.*, 2018, **20**, 2543–2546	Ar^F–F	2
5	*ACS Catal.*, 2016, **6**, 369–375	Ar^F–Br	2
6	*Chem.–Eur. J.*, 2015, **21**, 3895–3900	Ar^F–I	2
7	*Chem.–Eur. J.*, 2014, **20**, 2040–2048	Ar^F–F	3
8	*Organometallics*, 2014, **33**, 3669−3672	Ar^F–F Ar^F–$Si(OMe)_3$	2
9	*Tetrahedron*, 2014, **70**, 3720−3725	Ar^F–BF_3	1
10	Organometallics, 2012, **31**, 1329–1334	Ar^F–Br Ar^F–$B(OH)_2$	3
11	*Org. Lett.*, 2012, **14**, 3316–3319	Ar^F–F	8
12	*Adv. Synth. Catal.*, 2003*,* **345***,* 979–985	Ar^F–Br, Ar^F–I	2

4. Condition optimization

Table S5: Decarboxylative polyfluoroarylation[a]

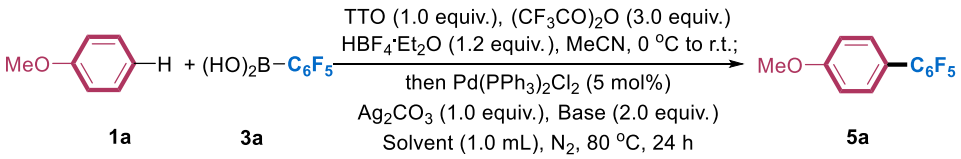


1a 2a 5a

Entry	5% [Pd]	1.0 equiv. [Ag]	Solvent	Yield[b] (%)
1	$PdCl_2$	Ag_2CO_3	DCE	51
2	$PdCl_2$	Ag_2CO_3	DMA	41
3	$PdCl_2$	Ag_2CO_3	DMF	47
4	$PdCl_2$	Ag_2CO_3	DMSO	58
5	$PdCl_2$	Ag_2CO_3	EA	50
6	$PdCl_2$	Ag_2CO_3	THF	39
7	$Pd(OAc)_2$	Ag_2CO_3	DMSO	71
8	$Pd(PPh_3)_4$	Ag_2CO_3	DMSO	18
9	$Pd_2(dba)_3$	Ag_2CO_3	DMSO	39
10	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	DMSO	77
11	$Pd(PPh_3)_2Cl_2$	Ag_2O	DMSO	25
12	$Pd(PPh_3)_2Cl_2$	$AgNO_3$	DMSO	n.d.
13	$Pd(PPh_3)_2Cl_2$	AgOTf	DMSO	23
14	—	Ag_2CO_3	DMSO	n.d.
15	$Pd(PPh_3)_2Cl_2$	—	DMSO	n.d.
16	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	DCE	71
17	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	DMA	73
18	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	DMF	68
19	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	EA	36
20	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	THF	35

[a]For decarboxylative coupling. **1a** (33 μL, 0.3 mmol), TTO (69.7 mg, 0.3 mmol, 1.0 equiv.), trifluoroacetic anhydride (126 μL, 0.9 mmol, 3.0 equiv.), $HBF_4{\cdot}Et_2O$ (49 μL, 0.36 mmol, 1.20 equiv.) in MeCN (1.0 mL) at 0 °C for 1 h, r.t. for another 2 h; then **Reaction condition A: 2a** (95.4 mg, 0.45 mmol, 1.5 equiv.), [Pd] (5 mol%), [Ag] (0.3 mmol, 1.0 equiv.) in Solvent (1.0 mL) at 80 °C for 24 h. [b]The yield was determined by ^1H NMR analysis using CH_2Br_2 as the internal standard. n.d. = not detected.

Table S6: Suzuki-Miyaura coupling[a]

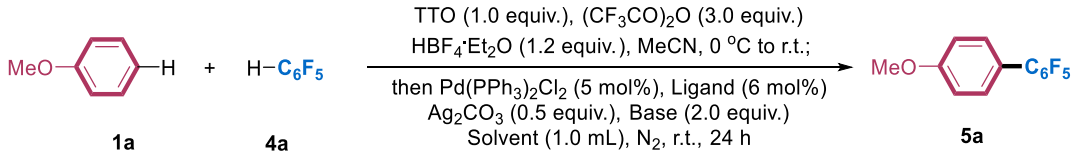


1a 3a 5a

Entry	5% [Pd]	1.0 equiv. [Ag]	Base	Solvent	Yield[b] (%)
1	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	—	DMSO	67
2	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	—	DCE	trace
3	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	—	DMA	38
4	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	—	THF	n.d.
5	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	K_2CO_3	DMSO	72
7	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	^{t}BuONa	DMSO	74
8	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	Cs_2CO_3	DMSO	76
9	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	CsF	DMSO	78

[a]For Suzuki–Miyaura coupling. **1a** (33 μL, 0.3 mmol), TTO (69.7 mg, 0.3 mmol, 1.0 equiv.), trifluoroacetic anhydride (126 μL, 0.9 mmol, 3.0 equiv.), $HBF_4{\cdot}Et_2O$ (49 μL, 0.36 mmol, 1.20 equiv.) in MeCN (1.0 mL) at 0 °C for 1 h, r.t. for another 2 h; then **Reaction condition B: 3a** (95.3mg, 0.45 mmol), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), Ag_2CO_3 (82.7 mg, 0.3 mmol, 1.0 equiv.) and Base (0.6 mmol, 2.0 equiv.) in Solvent (1.0 mL) at 80 °C for 24 h. [b]The yield was determined by ^{1}H NMR analysis using CH_2Br_2 as the internal standard.

Table S7: C–H/C–H coupling[a]

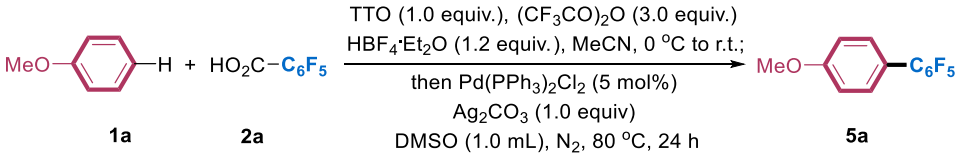


1a 4a 5a

Entry	5% [Pd]	[Ag]	Base	Ligand	Solvent	Yield[b] (%)
1	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	K_2CO_3	–	DMSO	12
2	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	K_2CO_3	–	DMA	55
3	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	K_2CO_3	–	DCE	26
4	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	K_2CO_3	–	THF	53
5	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	K_2CO_3	–	EA	39
6	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	–	DMA	61
7	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	^{t}BuONa	–	DMA	56
8	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	Cs_2CO_3	–	DMA	45
9	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	–	–	DMA	33
10	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	PPh_3	DMA	56
11	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	DavePhos	DMA	65
12	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	JohnPhos	DMA	74
13	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	RuPhos	DMA	69
14	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	X-Phos	DMA	58
15	$Pd(PPh_3)_2Cl$	1.0 eq Ag_2CO_3	CsF	CyJohnPhos	DMA	67
16	$Pd(PPh_3)_2Cl$	0.5 eq Ag_2CO_3	CsF	JohnPhos	DMA	73

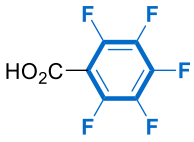
[a]For C–H/C–H coupling. **1a** (33 μL, 0.3 mmol), TTO (69.7 mg, 0.3 mmol, 1.0 equiv.), trifluoroacetic anhydride (126 μL, 0.9 mmol, 3.0 equiv.), $HBF_4{\cdot}Et_2O$ (49 μL, 0.36 mmol, 1.20 equiv.) in MeCN (1.0 mL) at 0 °C for 1 h, r.t. for another 2 h; then **Reaction condition C: 4a** (134 μL, 1.2 mmol, 1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), Ag_2CO_3 (41.4 mg, 0.15 mmol, 0.5 equiv.), Base (0.6 mmol, 2.0 equiv.), Ligand (6 mol%) in Solvent (1.0 mL) at 25 °C for 24 h. [b]The yield was determined by ^{1}H NMR analysis using CH_2Br_2 as the internal standard.

Table S8. Full Optimiazation[a, b]

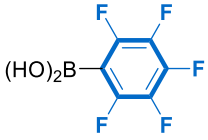


1a 2a 5a

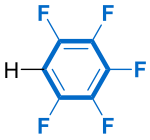
Entry	Variation from the "standard" conditions	Yield[c] (%)
1	none	77
2	$PdCl_2$ instead of $Pd(PPh_3)_2Cl_2$	58
3	$Pd_2(dba)_3$ instead of $Pd(PPh_3)_2Cl_2$	39
4	DCE instead of DMSO	71
5	DMA instead of DMSO	73
6	AgOTf instead of Ag_2CO_3	23
7	Ag_2O instead Ag_2CO_3	25
8	no $Pd(PPh_3)_2Cl_2$	n.d.[d]
9	no Ag_2CO_3	n.d.[d]
10	**3a** instead of **2a**	67
11	**3a** instead of **2a**, CsF was added	78
12	**4a** instead of **2a**, DMA instead of DMSO CsF was added	61
13[b]	**4a** instead of **2a**, DMA instead of DMSO CsF and JohnPhos were added	73



2a
Perfluorobenzoic acid



3a
Perfluorophenylboric acid



4a
Pentafluorobenzene

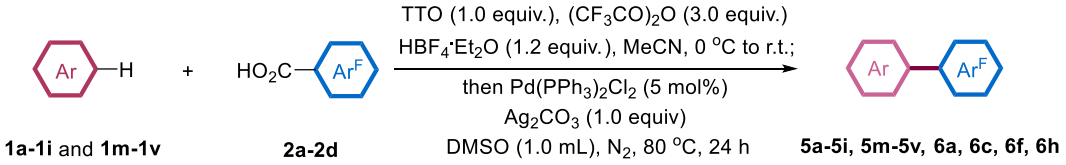
[a]Reaction conditions for decarboxylation coupling: **1a** (33 μL, 0.3 mmol), TTO (69.7 mg, 0.3 mmol, 1.0 equiv.), trifluoroacetic anhydride (126 μL, 0.9 mmol, 3.0 equiv.), $HBF_4{\cdot}Et_2O$ (49 μL, 0.36 mmol, 1.20 equiv.) in MeCN (1.0 mL) at 0 °C for 1 h, r.t. 2 h; then **2a** (95.4 mg, 0.45 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), Ag_2CO_3 (82.7 mg, 0.3 mmol, 1 equiv.) in DMSO (1.0 mL) at 80 °C for 24 h. [b]Reaction conditions for Suzuki–Miyaura and C–H/C–H couplings: See Table S2 and S3 for details. [c]The yield was determined by ^1H NMR analysis using CH_2Br_2 as the internal standard. [d]n.d. = not detected. TTO: Thianthrene S-oxide.

5. General procedure for the coupling reaction

◆ Decarboxylative coupling is selected as the preferred method, and Suzuki-Miyaura and C−H/C−H couplings are used as the supplementary methods.

◆ Cheap and accessible raw materials were preferentially selected as coupling reagent.

1) Procedure A: Reaction conditions for decarboxylative polyfluoroarylation.



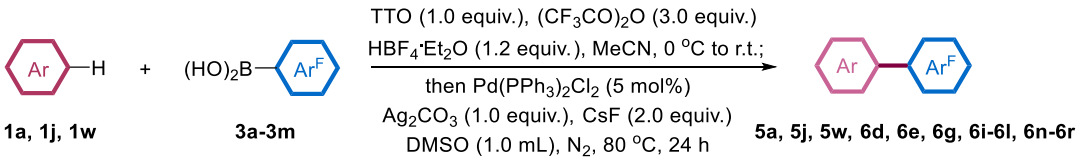
In situ activation step: Under ambient atmosphere arene **1a**–**1i** and **1m**–**1v** (0.3 mmol), thianthrene–S–oxide (69.7 mg, 0.3 mmol 1.0 equiv.), and MeCN (1.0 mL) were added in an oven-dried 10 mL test tube. After cooling to 0 °C, $HBF_4{\cdot}Et_2O$ (49 µL, 0.36 mmol, 1.20 equiv.) was added, followed by trifluoroacetic anhydride (126 µL, 0.9 mmol, 3.0 equiv.) leading to a dark purple solution which quickly lost its color. The vial was sealed with a screw-cap, and the mixture was stirred at **x** °C for 1 h, followed by stirring at 25 °C for **y** h. Further, the resulting beige reaction mixture was concentrated under reduced pressure, and diluted with 5 mL CH_2Cl_2. The CH_2Cl_2 solution was poured into a saturated aqueous $NaHCO_3$ solution (ca. 5 mL). The mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × ca. 5 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (2 × ca. 5 mL, 5 % w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Then, **Condition A:** The residue, Ar^F–CO_2H **2a**–**2d** (0.45 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), Ag_2CO_3 (82.7 mg, 0.3 mmol, 1 equiv.) were added in an oven-dried 10 mL test tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then DMSO (1.0 mL) was added in the test tube via syringe. The mixture was stirred at 80 °C for 24 h. The crude product residue was purified by column chromatography on silica gel or thin layer chromatography (pure PE to PE/EA : 5/1) to afford the purified product (**5a**–**5i**, **5m**–**5v**, **6a**, **6c**, **6f**, **6h**).

NOTE: 2.2 equivalent of HBF_4 Et_2O was used for **1o**, **1t** and **1v**. The extraction operation is necessary after the in situ activation step.

The temperature and reaction time in situ activation step are as follows:

Temperature:	Time:
	y = 2 h: **1a**–**1c**, **1f**, **1h**, **1l**, **1m**, **1q**–**1w**, **1y**, **1z**
x = 0 °C: **1a**, **1b**, **1d**–**1f**, **1h**–**1t**, **1v**–**1z.**	**y** = 12 h: **1d**, **1e**, **1g**, **1i**–**1k**, **1n**, **1x**
x = -40 °C: **1c**, **1g**, **1u**	**y** = 24 h: **1o**, **1p**,

2) Procedure B: Reaction conditions for Suzuki–Miyaura coupling.



1a, 1j, 1w **3a-3m** **5a, 5j, 5w, 6d, 6e, 6g, 6i-6l, 6n-6r**

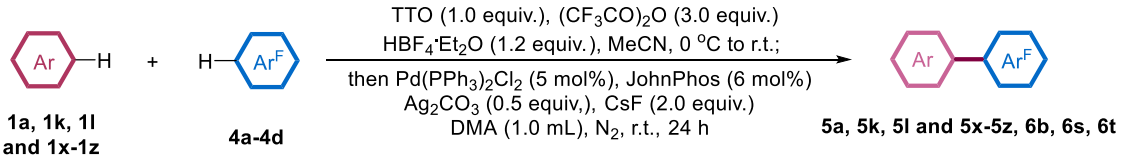
In situ activation step: Under ambient atmosphere arene **1a**, **1j, 1w** (0.3 mmol), thianthrene–S–oxide (69.7 mg, 0.3 mmol 1.0 equiv.), and MeCN (1.0 mL) were added in an oven-dried 10 mL test tube. After cooling to 0 °C, $HBF_4{\cdot}Et_2O$ (49 µL, 0.36 mmol, 1.20 equiv.) was added, followed by trifluoroacetic anhydride (126 µL, 0.9 mmol, 3.0 equiv.) leading to a dark purple solution which quickly lost its color. The vial was sealed with a screw-cap, and the mixture was stirred at **x** °C for 1 h, followed by stirring at 25 °C for **y** h. Further, the resulting beige reaction mixture was concentrated under reduced pressure, and diluted with 5 mL CH_2Cl_2. The CH_2Cl_2 solution was poured into a saturated aqueous $NaHCO_3$ solution (ca. 5 mL). The mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × ca. 5 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (2 × ca. 5 mL, 5 % w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Then, **Condition B**: The residue, Ar^F–$B(OH)_2$ **3a**–**3m** (0.45 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), Ag_2CO_3 (82.7 mg, 0.3 mmol, 1.0 equiv.) and CsF (91.1 mg, 0.6 mmol, 2.0 equiv.) were added in an oven-dried 10 mL test tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then DMSO (1.0 mL) was added in the test tube via syringe. The mixture was stirred at 80 °C for 24 h. The crude product residue was purified by column chromatography on silica gel or thin layer chromatography (pure PE to PE/EA : 5/1) to afford the purified product (**5a**, **5j**, **5w**, **6d**, **6e**, **6g**, **6i**–**6l**, **6n**–**6r**).

NOTE: The extraction operation is necessary after the in situ activation step.

The temperature and reaction time <u>in situ activation step</u> are as follows:

Temperature:	Time:
	y = 2 h: **1a**–**1c**, **1f**, **1h**, **1l**, **1m**, **1q**–**1w**, **1y**, **1z**
x = 0 °C: **1a**, **1b**, **1d**–**1f**, **1h**–**1t**, **1v**–**1z.**	**y** = 12 h: **1d**, **1e**, **1g**, **1i**–**1k**, **1n**, **1x**
x = -40 °C: **1c**, **1g**, **1u**	**y** = 24 h: **1o**, **1p**,

3) Procedure C: Reaction conditions for C–H/C–H coupling.



1a, 1k, 1l and 1x-1z | **4a-4d** | **5a, 5k, 5l and 5x-5z, 6b, 6s, 6t**

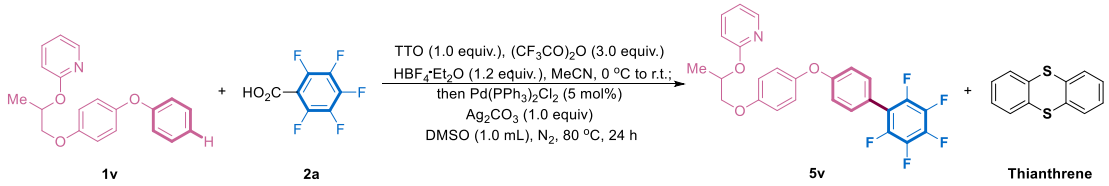
In situ activation step: Under ambient atmosphere arene **1a**, **1k**, **1l** and **1x**–**1z** (0.3 mmol), thianthrene–S–oxide (69.7 mg, 0.3 mmol 1.0 equiv.), and MeCN (1.0 mL) were added in an oven-dried 10 mL test tube. After cooling to 0 °C, $HBF_4{\cdot}Et_2O$ (49 µL, 0.36 mmol, 1.20 equiv.) was added, followed by trifluoroacetic anhydride (126 µL, 0.9 mmol, 3.0 equiv.) leading to a dark purple solution which quickly lost its color. The vial was sealed with a screw-cap, and the mixture was stirred at **x** °C for 1 h, followed by stirring at 25 °C for **y** h. Further, the resulting beige reaction mixture was concentrated under reduced pressure, and diluted with 5 mL CH_2Cl_2. The CH_2Cl_2 solution was poured into a saturated aqueous $NaHCO_3$ solution (ca. 5 mL). The mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × ca. 5 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (2 × ca. 5 mL, 5 % w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Then, **Condition C**: The residue, Ar^F–H **4a**–**4d** (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), JohnPhos (5.4 mg, 6 mol%), Ag_2CO_3 (41.4 mg, 0.15 mmol, 0.5 equiv.) and CsF (91.1 mg, 0.6 mmol, 2.0 equiv.) were added in an oven-dried 10 mL test tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then DMA (1.0 mL) was added in the test tube via syringe. The mixture was stirred at r.t. for 24 h. The crude product residue was purified by column chromatography on silica gel or thin layer chromatography (pure PE to DCM/MeOH: 30/1) to afford the purified product (**5a**, **5k**, **5l**, **5x**–**5z**, **6b**, **6s**, **6t**).

NOTE: The extraction operation is necessary after the in situ activation step.

The temperature and reaction time <u>in situ activation step</u> are as follows:

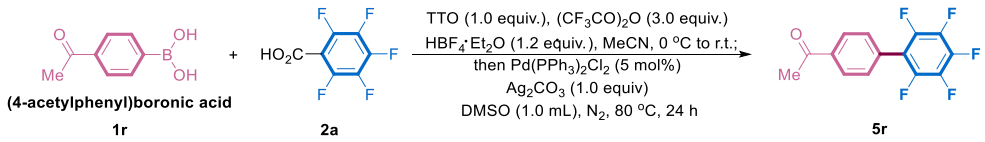
Temperature:	Time:
	y = 2 h: **1a**–**1c**, **1f**, **1h**, **1l**, **1m**, **1q**–**1w**, **1y**, **1z**
x = 0 °C: **1a**, **1b**, **1d**–**1f**, **1h**–**1t**, **1v**–**1z.**	**y** = 12 h: **1d**, **1e**, **1g**, **1i**–**1k**, **1n**, **1x**
x = -40 °C: **1c**, **1g**, **1u**	**y** = 24 h: **1o**, **1p**,

4) Gram-scale experiment and recovery of TT



In situ activation step: Under ambient atmosphere pyriproxyfen **1v** (1.0 g, 3.11 mmol), thianthrene–S–oxide (720.2 mg, 3.11 mmol, 1.0 equiv.), and MeCN (10 mL) were added in an oven-dried 10 mL test tube. After cooling to 0 °C, $HBF_4{\cdot}Et_2O$ (0.51 mL, 3.72 mmol, 1.20 equiv.) was added, followed by trifluoroacetic anhydride (1.30 mL, 9.3 mmol, 3.0 equiv.) leading to a dark purple solution which quickly lost its color. The vial was sealed with a screw-cap, and the mixture was stirred at 0 °C for 1 h, followed by stirring at 25 °C for 2 h. Further, the resulting beige reaction mixture was concentrated under reduced pressure, and diluted with 50 mL CH_2Cl_2. The CH_2Cl_2 solution was poured into a saturated aqueous $NaHCO_3$ solution (ca. 50 mL). The mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × ca. 50 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (2 × ca. 50 mL, 5 % w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Then, **Condition A:** The residue, pentafluorobenzoic acid **2a** (0.99 g, 4.67 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (109.5 mg, 5 mol%), Ag_2CO_3 (854.6 mg, 3.1 mmol, 1 equiv.) were added in an oven-dried 50 mL test tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then DMSO (10.3 mL) was added in the test tube via syringe. The mixture was stirred at 80 °C for 24 h. The crude product residue was purified by column chromatography on silica gel or thin layer chromatography (pure PE to PE/EA : 50/1) to afford the purified product **5v** (1.15 g, 74% yield) and thianthrene (0.51 g, 75% yield).

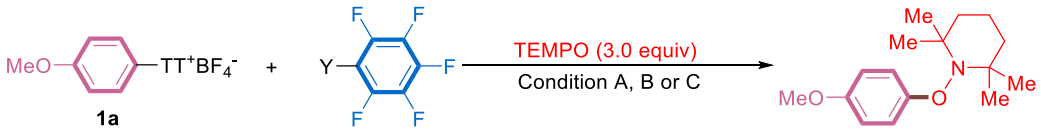
5) The synthesis of 1-(2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (5r)



(4-acetylphenyl)boronic acid (1r) + 2a → 5r

In situ activation step: Under ambient atmosphere 4-Acetylphenylboronic acid **1r** (49.2 mg, 0.3 mmol), thianthrene–S–oxide (69.7 mg, 0.3 mmol 1.0 equiv.), and MeCN (1.0 mL) were added in an oven-dried 10 mL test tube. After cooling to 0 °C, $HBF_4{\cdot}Et_2O$ (49 µL, 0.36 mmol, 1.20 equiv.) was added, followed by trifluoroacetic anhydride (126 µL, 0.9 mmol, 3.0 equiv.) leading to a dark purple solution which quickly lost its color. The vial was sealed with a screw-cap, and the mixture was stirred at 0 °C for 1 h, followed by stirring at 25 °C for 2 h. Further, the resulting beige reaction mixture was concentrated under reduced pressure, and diluted with 5 mL CH_2Cl_2. The CH_2Cl_2 solution was poured into a saturated aqueous $NaHCO_3$ solution (ca. 5 mL). The mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × ca. 5 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (2 × ca. 5 mL, 5 % w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Then, **Condition A:** The residue, pentafluorobenzoic acid **2a** (95.4 mg, 0.45 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (10.6 mg, 5 mol%), Ag_2CO_3 (82.7 mg, 0.3 mmol, 1 equiv.) were added in an oven-dried 10 mL test tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then DMSO (1.0 mL) was added in the test tube via syringe. The mixture was stirred at 80 °C for 24 h. The crude product residue was purified by column chromatography on silica gel or thin layer chromatography (pure PE to PE/EA : 40/1) to afford the purified product **5r** (43.8 mg, 51% yield).

6. Radical trapping experiment



Y = CO_2H (**n.d.**); Y= $B(OH)_2$ (**n.d.**); Y = H (**n.d.**)

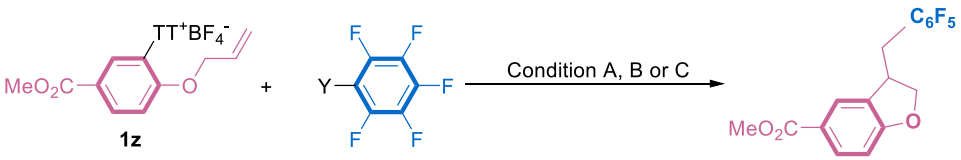
Y = CO_2H: A reaction under the optimized reaction conditions was conducted in the presence of 3.0 equivalents of TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) as a radical scavenger. Under such conditions, the corresponding TEMPO-adduct was not detected by HRMS (ESI).

Y = $B(OH)_2$: A reaction under the optimized reaction conditions was conducted in the presence of 3.0 equivalents of TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) as a radical scavenger. Under such conditions, the corresponding TEMPO-adduct was not detected by HRMS (ESI).

Y = H: A reaction under the optimized reaction conditions was conducted in the presence of 3.0 equivalents of TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) as a radical scavenger. Under such conditions, the corresponding TEMPO-adduct was not detected by HRMS (ESI).

Reaction procedures are consistent with those described in Page S13-S15.

7. Radical clock cyclization experiment



Y = CO_2H (**n.d.**); Y= $B(OH)_2$ (**n.d.**); Y = H (**n.d.**)

Y = CO_2H: Under the optimized reaction **Condition A**, the corresponding cyclization product was not detected by HRMS (ESI).

Y = $B(OH)_2$: Under the optimized reaction **Condition B**, the corresponding cyclization product was not detected by HRMS (ESI).

Y = H: Under the optimized reaction **Condition C**, the corresponding cyclization product was not detected by HRMS (ESI).

Reaction procedures are consistent with those described in Page S13-S15.

8. Control experiments for SMC and C–H/C–H coupling

Figure S5: SMC

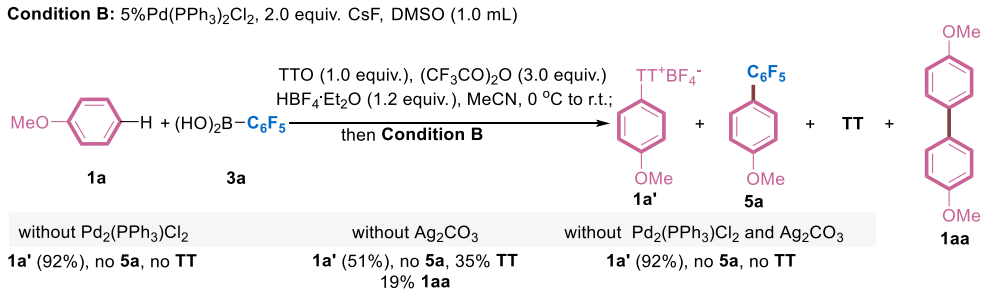
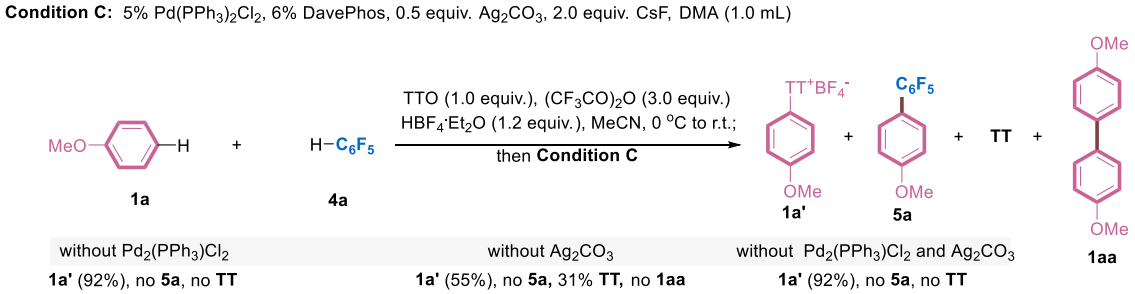


Figure S6: C–H/C–H coupling



9. Possible pathways for Suzuki–Miyaura coupling

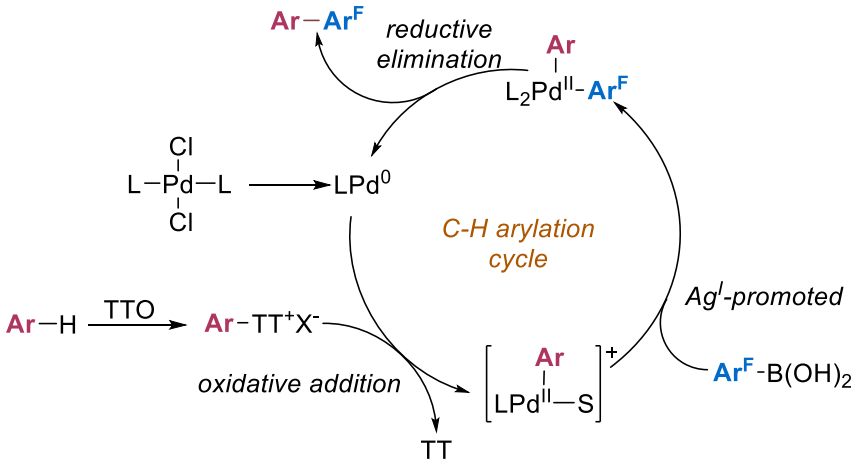


Figure S7: Possible pathways for SMC

According to previous reports[1-5] and our experimental results, we propose a possible catalytic cycle for SMC.

10. Possible pathways for C–H/C–H coupling

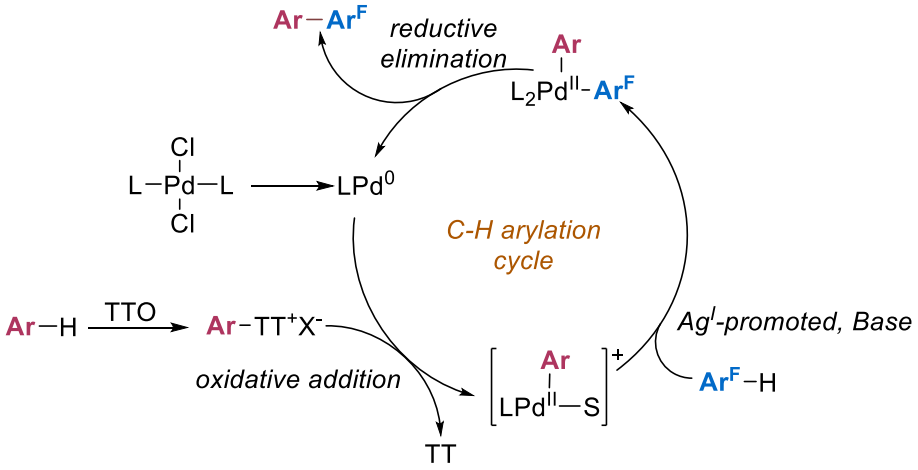


Figure S8: Possible pathways for C–H/C–H coupling

According to previous reports[1, 6-9] and our experimental results, we propose a possible catalytic cycle for C–H/C–H coupling.

11. References

[1] B. Lansbergen, P. Granatino and T. Ritter, Site-Selective C–H alkylation of Complex Arenes by a Two-Step Aryl Thianthrenation-Reductive Alkylation Sequence, *J. Am. Chem. Soc.*, 2021, **143**, 7909–7914.

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[5] K. Hirabayashi, A. Mori, J. Kawashima, M. Suguro, Y. Nishihara and T. Hiyama, Palladium-Catalyzed Cross-Coupling of Silanols, Silanediols, and Silanetriols Promoted by Silver(I) Oxide, *J. Org. Chem.*, 2000, **65**, 5342–5349.

[6] N. Lebrasseur and L. Larrosa, Room Temperature and Phosphine Free Palladium Catalyzed Direct C-2 Arylation of Indoles, *J. Am. Chem. Soc.*, 2008, **130**, 2926–2927.

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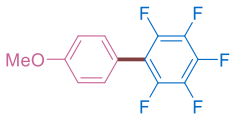
12. Characterization of compounds

2,3,4,5,6-Pentafluoro-4'-phenoxy-1,1'-biphenyl (5a)



5a

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 73% yield, 73.6 mg.

R_f = 0.40 (PE / EA = 50 / 1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.03 – 7.01 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 144.3 (d of m, *J* = 241.6 Hz), 140.2 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 241.6 Hz), 131.6, 118.52, 115.9 (td, *J* = 18.1, 4.5 Hz), 114.4, 77.2, 55.5.

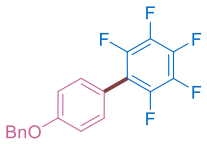
^{19}F NMR (565 MHz, $CDCl_3$) δ -143.68 (dd, *J* = 22.6, 5.7 Hz), -156.59 (t, *J* = 19.78 Hz), -162.62 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_8F_5O^+$ $[M+H]^+$ 275.0490. found m/z 275.0486.

These data are in agreement with those reported previously in the literature.[A]

[A] R. Takahashi, T. Seo, K. Kubota and H. Ito, Palladium-Catalyzed Solid-State Polyfluoroarylation of Aryl Halides Using Mechanochemistry, *ACS Catal*., 2021, **11**, 14803−14810.

4'-(Benzyloxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5b)



5b

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 52% yield, 54.6 mg.

R_f = 0.45 (PE / EA = 50 / 1)

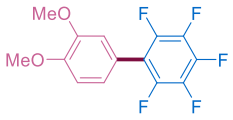
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.11 – 7.08 (m, 2H), 5.13 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 144.3 (d of m, *J* = 241.6 Hz), 140.2 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 256.7 Hz), 136.7, 131.6, 128.8, 128.3, 127.6, 118.8, 115.2 (td, *J* = 16.6, 4.5 Hz), 77.2, 70.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.58 (dd, *J* = 22.6, 11.3 Hz), -156.43 (t, *J* = 22.6 Hz), -162.50 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{19}H_{12}F_5O^+$ $[M+H]^+$ 351.0803. found m/z 351.0809.

2,3,4,5,6-Pentafluoro-3',4'-dimethoxy-1,1'-biphenyl (5c)



5c

The crude product was purified by PE / EA (pure PE to 30 : 1) as an eluent.

Light yellow solid 58% yield, 52.9 mg.

R_f = 0.40 (PE / EA = 30 / 1)

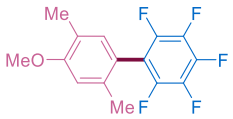
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.96 (m, 2H), 6.92 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 149.1, 144.4 (d of m, *J* = 256.7 Hz), 140.3 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 241.6 Hz), 123.2, 118.6, 115.9 (td, *J* = 18.1, 4.5 Hz), 113.3, 111.3, 77.2, 56.1, 56.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.22 (dd, *J* = 28.3, 5.7 Hz), -156.34 (t, *J* = 19.8 Hz), -162.5 (td, *J* = 19.8 Hz, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{14}H_{10}F_5O_2^+$ $[M+H]^+$ 305.0595. found m/z 305.0605.

(R)-2,3,4,5,6-pentafluoro-4'-methoxy-2',5'-dimethyl-1,1'-biphenyl (5d)



5d

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow oil 66% yield, 59.8 mg.

R_f = 0.35 (PE / EA = 50 / 1)

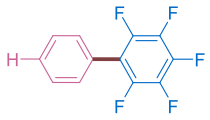
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.80 (s, 1H), 3.88 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 144.4 (d of m, *J* = 241.6 Hz), 140.5 (d of m, *J* = 241.6 Hz), 137.8 (d of m, *J* = 256.7 Hz), 136.2, 132.6, 124.6, 117.2, 115.7 (td, *J* = 19.6, 4.5 Hz), 112.0, 77.2, 55.4, 19.9, 15.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -140.61 (dd, *J* = 25.4, 8.5 Hz), -156.18 (t, *J* = 19.78 Hz), -162.68 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{15}H_{11}F_5NaO^+$ $[M+Na]^+$ 325.0622. found m/z 325.0627.

2,3,4,5,6-Pentafluoro-1,1'-biphenyl (5e)



5e

The crude product was purified by pure PE as an eluent.

White solid 74% yield, 54.2 mg.

R_f = 0.5 (pure PE)

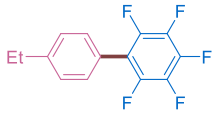
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (m), 142.5 (d of m, *J* = 196.3 Hz), 138.0 (d of m, *J* = 362.4 Hz), 130.3, 129.5, 128.9, 126.6, 116.1 (td, *J* = 27.2, 6.0 Hz), 77.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.28 (dd, *J* = 22.6, 11.3 Hz), -155.68 (t, *J* = 19.78 Hz), -162.31 (td, *J* = 21.2, 7.5 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{12}H_6F_5^+$ $[M+H]^+$ 245.0384. found m/z 245.0381.

4'-Ethyl-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5f)



5f

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 75% yield, 61.2 mg.

R_f = 0.40 (PE / EA = 50 / 1)

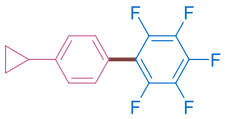
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 4H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 144.4 (d of m, *J* = 256.7 Hz), 140.4 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 241.6 Hz), 130.2, 128.4, 123.7, 116.1 (td, *J* = 16.6, 4.5 Hz), 77.2, 28.8, 15.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.39 (dd, *J* =17.0, 11.3 Hz), -156.22 (t, *J* = 19.8 Hz), -162.5 (td, *J* =25.4, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{14}H_{10}F_5^+$ $[M+H]^+$ 273.0697. found m/z 273.0686.

4'-Cyclopropyl-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5g)



5g

The crude product was purified by pure PE as an eluent.

Colorless solid 70% yield, 59.7 mg.

R_f = 0.50 (pure PE)

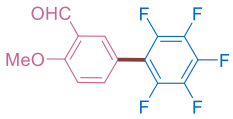
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 1.99 – 1.95 (m, 1H), 1.09 – 1.01 (m, 2H), 0.82 – 0.75 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 144.3 (d of m, *J* = 241.6 Hz), 140.3 (d of m, *J* = 241.6 Hz), 138.0 (d of m, *J* = 241.6 Hz), 130.2, 126.0, 123.4, 116.1 (td, *J* = 16.6, 4.5 Hz), 77.2, 29.9, 15.5, 9.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.41 (dd, *J* = 22.6, 11.3 Hz), -156.27 (t, *J* = 22.60 Hz), -162.53 (td, *J* = 22.6, 11.3 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{15}H_{10}F_5^+$ $[M+H]^+$ 285.0697. found m/z 285.0710.

2',3',4',5',6'-Pentafluoro-4-methoxy-[1,1'-biphenyl]-3-carbaldehyde (5h)



5h

The crude product was purified by PE / EA (pure PE to 40 : 1) as an eluent.

Light yellow solid 73% yield, 66.1 mg.

R_f = 0.35 (PE / EA = 50 / 1)

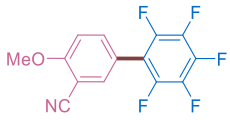
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.89 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 189.0, 162.3, 144.3 (d of m, *J* = 241.6 Hz), 140.6 (d of m, *J* = 256.76 Hz), 138.0 (d of m, *J* = 241.6 Hz), 130.5, 125.1, 119.0, 114.7 (td, *J* = 16.6, 3.0 Hz), 112.4, 77.2, 56.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.41 (dd, *J* = 22.6, 11.3 Hz), -155.26 (t, *J* = 22.6 Hz), -162.04 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{14}H_8F_5O_2^+$ $[M+H]^+$ 303.0439. found m/z 303.0433.

2',3',4',5',6'-Pentafluoro-4-methoxy-[1,1'-biphenyl]-3-carbonitrile (5i)



5i

The crude product was purified by PE / EA (pure PE to 10 : 1) as an eluent.

Light yellow solid 71% yield, 63.7 mg.

R_f = 0.40 (PE / EA = 5 / 1)

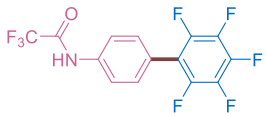
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 10.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8, 144.3 (d of m, *J* = 241.6 Hz), 140.9 (d of m, *J* = 256.7 Hz), 138.1 (d of m, *J* = 256.7 Hz), 136.3, 135.4, 119.1, 115.7, 113.7 (td, *J* = 16.6, 3.0 Hz), 112.0, 102.8, 77.2, 56.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.39 (dd, *J* = 28.3, 5.7 Hz), -154.25 (t, *J* = 19.8 Hz), -161.45 (td, *J* = 25.4, 11.3 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{14}H_7F_5NO^+$ $[M+H]^+$ 300.0442. found m/z 300.0451.

2,2,2-Trifluoro-N-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)acetamide (5j)



5j

The crude product was purified by PE / EA (pure PE to 20 : 1) as an eluent.

White solid 65% yield, 69.2 mg.

R_f = 0.40 (PE / EA = 10 / 1)

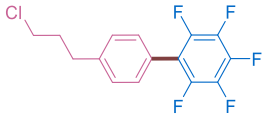
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (151 MHz, DMSO) δ 155.1, 154.9, 154.6, 154.4, 143.7 (d of m, *J* = 241.6 Hz), 139.8 (d of m, *J* = 241.6 Hz), 137.5, 137.3 (d of m, *J* = 241.6 Hz), 130.8, 122.7, 121.1, 116.7, 115.0 (td, *J* = 18.1, 3.0 Hz), 114.8, 39.5 (m).

^{19}F NMR (565 MHz, DMSO) δ -74.1, -143.71 (dd, *J* = 22.6, 5.7 Hz), -156.29 (t, *J* = 22.6 Hz), -162.85 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{14}H_6F_8NO^+$ $[M+H]^+$ 356.0316. found m/z 356.0309.

4'-(3-Chloropropyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5k)



5k

The crude product was purified by PE / EA (pure PE to 20 : 1) as an eluent.

Light yellow solid 52% yield, 49.9 mg.

R_f = 0.35 (PE / EA = 10 / 1)

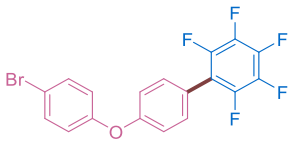
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.18 – 2.13 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3 (d of m, *J* = 241.6 Hz), 142.3, 140.4 (d of m, *J* = 241.6 Hz), 138.0 (d of m, *J* = 241.6 Hz), 130.4, 129.1, 124.3, 115.9 (td, *J* = 16.6, 3.0 Hz), 77.2, 44.2, 33.9, 32.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.39 (dd, *J* = 25.4, 8.5 Hz), -155.98 (t, *J* = 22.6 Hz), -162.43 (td, *J* = 22.6, 11.3 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{15}H_{10}ClF_5Na^+$ $[M+Na]^+$ 343.0283. found m/z 343.0294.

4'-(4-Bromophenoxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (5l)



5l

The crude product was purified by pure PE as an eluent.

Light yellow solid 75% yield, 93.1 mg.

R_f = 0.5 (pure PE)

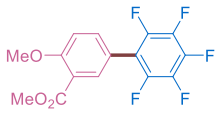
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 155.6, 144.3 (d of m, *J* = 241.6 Hz), 140.5 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 241.6 Hz), 133.1, 131.9, 121.4, 121.3, 118.6, 116.8, 115.4 (td, *J* = 16.6, 3.0 Hz), 77.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.33 (dd, *J* = 22.6, 11.3 Hz), -155.64 (t, *J* = 22.60 Hz), -162.15 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{18}H_8BrF_5NaO^+$ $[M+Na]^+$ 436.9571. found m/z 436.9592.

Methyl 2',3',4',5',6'-pentafluoro-4-methoxy-[1,1'-biphenyl]-3-carboxylate (5m)



5m

The crude product was purified by PE / EA (pure PE to 20 : 1) as an eluent.

White solid 67% yield, 66.7 mg.

R_f = 0.40 (PE / EA = 10 / 1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 159.8, 144.3 (d of m, *J* = 241.6 Hz), 140.5 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 256.7 Hz), 135.2, 133.7, 120.5, 118.2, 114.8 (td, *J* = 18.1, 4.5 Hz), 112.5, 77.2, 56.3, 52.3.

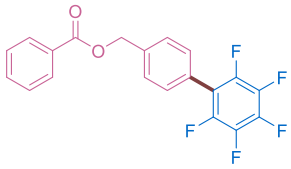
^{19}F NMR (565 MHz, $CDCl_3$) δ -143.44 (dd, *J* = 22.6, 11.3 Hz), -155.59 (t, *J* = 19.78 Hz), -162.20 (td, *J* = 22.6, 7.5 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{15}H_{10}F_5O_3^+$ $[M+H]^+$ 333.0545. found m/z 333.0539.

These data are in agreement with those reported previously in the literature.[B]

[B] M. Hofer, A. Genoux, R. Kumar and C. Nevado, Gold-Catalyzed Direct Oxidative Arylation with Boron Coupling Partners, *Angew. Chem., Int. Ed.*, 2017, **56**, 1021–1025.

(2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)methyl benzoate (5n)



5n

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow solid 65% yield, 73.7 mg.

R_f = 0.35 (PE / EA = 50 / 1)

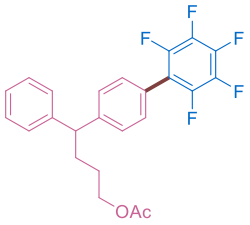
^{1}H NMR (600 MHz, CDC_3) δ 8.12 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 3H), 7.46 (t, *J* = 6.9 Hz, 3H), 5.45 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 144.3 (d of m, *J* = 241.6 Hz), 140.6 (d of m, *J* = 241.6 Hz), 138.0 (d of m, *J* = 256.7 Hz), 137.5, 133.3, 130.5, 130.0, 129.8, 129.2, 128.6, 128.4, 126.4, 115.6 (td, *J* = 16.6, 4.5 Hz), 77.2, 66.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.16 (dd, *J* = 22.6, 11.3 Hz), -155.29 (t, *J* = 19.78 Hz), -162.07 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{20}H_{11}F_5NaO_2^+$ $[M+Na]^+$ 401.0571. found m/z 401.0572.

4-(2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)-4-phenylbutyl acetate (5o)



5o

The crude product was purified by PE / EA (pure PE to 20 : 1) as an eluent.

Light yellow viscous liquid 60% yield, 78.1 mg.

R_f = 0.45 (PE / EA = 10 / 1)

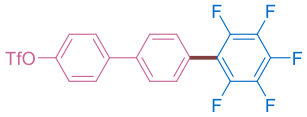
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (q, *J* = 9.0 Hz, 4H), 7.31 – 7.26 (m, 4H), 7.20 – 7.17 (m, 1H), 4.13 (t, *J* = 6.0 Hz, 1H), 4.09 – 4.03 (m, 2H), 2.47 – 2.38 (m, 2H), 1.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 145.6, 145.1(m), 143.4, 140.4 (d of m, *J* = 256.7 Hz), 137.9 (d of m, *J* = 241.6 Hz), 130.4, 128.8, 128.2, 127.9, 126.7, 124.5, 115.7 (td, *J* = 18.8, 4.5 Hz), 77.2, 62.8, 47.7, 34.2, 20.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.23 (dd, *J* = 22.6, 8.5 Hz), -155.90 (t, *J* = 22.6 Hz), -162.36 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{24}H_{19}F_5NaO_2^+$ $[M+Na]^+$ 457.1197. found m/z 457.1188.

2'',3'',4'',5'',6''-Pentafluoro-[1,1':4',1''-terphenyl]-4-yl trifluoromethanesulfonate (5p)



5p

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 50% yield, 70.2 mg.

R_f = 0.35 (PE / EA = 50 / 1)

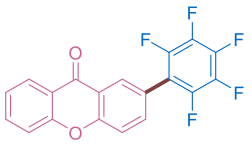
^{1}H NMR (600 MHz, CDC_3) δ 7.71 – 7.68 (m, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.38 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 144.4 (d of m, *J* = 256.7 Hz), 140.8, 140.7 (d of m, *J* = 241.6 Hz), 140.4, 138.1 (d of m, *J* = 241.6 Hz), 130.9, 129.1, 127.6, 126.3, 122.0, 120.0, 117.9, 115.8, 115.4 (td, *J* = 16.6, 4.5 Hz), 77.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -72.83, -143.18 (dd, *J* = 22.6, 5.7 Hz), -155.09 (t, *J* = 22.6 Hz), -161.99 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{19}H_9F_8O_3S^+$ $[M+H]^+$ 469.0139. found m/z 469.0116.

2-(Perfluorophenyl)-9H-xanthen-9-one (5q)



5q

The crude product was purified by PE / EA (pure PE to 40 : 1) as an eluent.

White solid 67% yield, 72.8 mg.

R_f = 0.40 (PE / EA = 30 / 1)

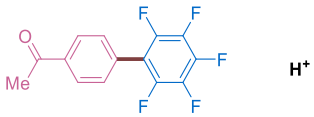
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79 –7.75 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 156.5, 156.2, 144.4 (d of m, *J* = 362.4 Hz), 142.1(m), 138.0 (d of m, *J* = 422.8 Hz), 135.3, 129.1, 127.0, 124.5, 122.3, 122.2, 121.9, 118.9, 118.2, 114.6 (td, *J* = 25.7, 6.0 Hz), 77.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -147.79 (dd, *J* = 22.56, 7.52 Hz), -159.12 (t, *J* = 20.68 Hz), -166.35 (td, *J* = 22.56, 7.52 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{19}H_8F_5O_2^+$ $[M+H]^+$ 363.0439. found m/z 363.0436.

1-(2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (5r)



5r

The crude product was purified by PE / EA (pure PE to 40 : 1) as an eluent.

White solid 51% yield, 43.8 mg.

R_f = 0.40 (PE / EA = 30 / 1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 2.55 (s, 3H).

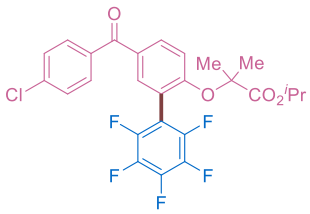
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 144.2 (d of m, *J* = 241.6 Hz), 141.5 (d of m, *J* = 256.7 Hz), 138.1 (d of m, *J* = 256.7 Hz), 137.6, 131.2, 130.6, 128.7, 115.0 (td, *J* = 18.1, 4.5 Hz), 77.2, 26.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -142.82 (dd, *J* = 22.6, 11.3 Hz), -154.08 (t, *J* = 19.78 Hz), -161.60 (td, *J* = 22.6, 7.5 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{14}H_8F_5O^+$ $[M+H]^+$ 287.0490. found m/z 287.0485. These data are in agreement with those reported previously in the literature.[C]

[C] D. S. Lee, P. Y. Choy, C. M. So, J. Wang, C. P. Lau and F. Y. Kwong, Palladium-catalyzed direct arylation of polyfluoroarenes with aryl tosylates and mesylates, *RSC Adv.*, 2012, **2**, 9179–9182.

Isopropyl (s)-2-((5-(4-chlorobenzoyl)-2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)oxy)-2-methylpropanoate (5s)



5s

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow viscous liquid 77% yield, 121.5 mg.

R_f = 0.43 (PE / EA = 50 / 1)

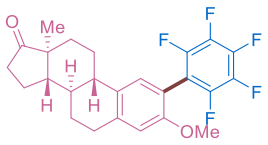
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 1H), 5.07 (m, 1H), 1.60 (s, 6H), 1.20 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 172.7, 157.3, 144.6 (d of m, *J* = 347.3 Hz), 140.8 (d of m, *J* = 256.7 Hz), 138.8, 138.5 (d of m, *J* = 241.6 Hz), 136.1, 134.7, 132.9, 131.3, 130.0, 128.8, 117.2 (td, *J* = 13.6, 3.0 Hz), 115.1, 77.2, 69.7, 25.1, 21.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -139.43 (dd, *J* = 22.6 Hz), -154.96 (t, *J* = 19.78 Hz), -162.71 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{26}H_{21}ClF_5O_4^+$ $[M+H]^+$ 527.1043. found m/z 527.1057.

(2R,8R,9S,13S,14S)-3-methoxy-13-methyl-2-(perfluorophenyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5t)



5t

The crude product was purified by PE / EA (pure PE to 15 : 1) as an eluent.

Light brown solid 58% yield, 78.3 mg.

R_f = 0.30 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.76 (s, 1H), 3.78 (s, 3H), 2.99 (dd, *J* = 9.6, 4.7 Hz, 2H), 2.52 (dd, *J* = 18.7, 8.7 Hz, 1H), 2.40 – 2.27 (m, 2H), 2.21 – 2.04 (m, 3H), 1.95 (dd, *J* = 11.7, 2.8 Hz, 1H), 1.70 – 1.46 (m, 6H), 0.93 (s, 3H).

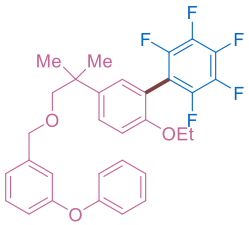
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 144.6 (d of m, *J* = 377.5 Hz), 140.5 (d of m, *J* = 377.5 Hz), 139.9, 137.7 (d of m, *J* = 407.8 Hz), 132.3, 128.9, 113.0 (td, *J* = 16.6, 6.0

Hz), 112.7, 111.7, 77.2, 55.8, 50.5, 48.1, 43.9, 38.3, 36.0, 31.6, 30.0, 26.6, 26.0, 21.7, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -140.11 – -140.36 (m), -156.47 (t, *J* = 19.78 Hz), -163.19 – -163.30 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{25}H_{24}F_5O_2^+$ $[M+H]^+$ 451.1691. found m/z 451.1688.

(R)-2'-ethoxy-2,3,4,5,6-pentafluoro-5'-(2-methyl-1-((3-phenoxybenzyl)oxy)propan-2-yl)-1,1'-biphenyl (5u)



5u

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Colorless viscous liquid 71% yield, 115.5 mg.

R_f = 0.35 (PE / EA = 50 / 1)

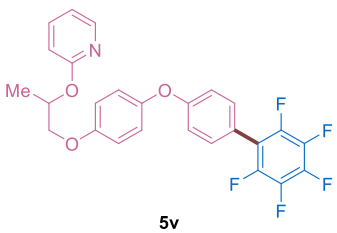
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 – 7.02 (m, 3H), 6.99 (s, 1H), 6.96 – 6.93 (m, 2H), 4.50 (s, 2H), 4.08 (q, *J* = 6.8 Hz, 2H), 3.49 (s, 2H), 1.39 (s, 6H), 1.34 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 157.3, 154.7, 144.6 (d of m, *J* = 241.6 Hz), 141.3 (m), 141.0, 139.7, 137.7 (d of m, *J* = 241.6 Hz), 129.8, 129.7, 128.8, 123.4, 122.1, 119.1, 117.8, 117.7, 115.0, 113.5 (t, *J* = 19.6 Hz), 111.9, 80.2, 77.2, 72.9, 64.2, 38.7, 26.2, 14.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -139.9 (dd, *J* = 25.4, 8.5 Hz), -156.62 (t, *J* = 22.6 Hz), -163.5 (td, *J* = 22.6, 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{31}H_{27}F_5NaO_3^+$ $[M+Na]^+$ 565.1773. found m/z 565.1779.

2-((1-(4-((2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)oxy)phenoxy)propan-2-yl)oxy)pyridine (5v)



5v

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow oil 76% yield, 111.1 mg.

R_f = 0.40 (PE / EA = 30 / 1)

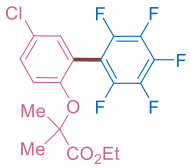
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (m, 1H), 7.57 (m, 1H), 7.36 (m, 2H), 7.04 (d, *J* = 9.0 Hz, 4H), 7.00 – 6.96 (m, 2H), 6.86 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.63 (m, 1H), 4.23 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.11 (dd, *J* = 9.6, 4.8 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3, 159.8, 155.9, 149.3, 146.9, 144.3 (d of m, *J* = 241.6 Hz), 140.3 (d of m, *J* = 256.7 Hz), 138.8, 137.1 (m), 131.7, 121.5, 112.0, 117.3, 116.9, 116.1, 115.6 (td, *J* = 16.6, 3.0 Hz), 111.8, 77.2, 71.2, 69.34, 17.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.45 (dd, *J* = 19.8, 8.5 Hz), -156.12 (t, *J* = 22.60 Hz), -162.35 (td, *J* = 22.6, 11.3 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{26}H_{19}F_5NO_3^+$ $[M+H]^+$ 488.1280. found m/z 488.1276.

Ethyl 2-((5-chloro-2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)oxy)-2-methylpropanoate (5w)



5w

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 65% yield, 79.6 mg.

R_f = 0.40 (PE / EA = 50 / 1)

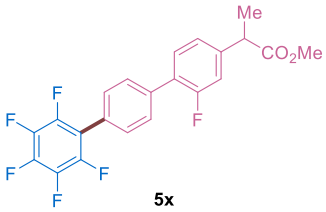
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 6H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 152.2, 144.5 (d of m, *J* = 377.5 Hz), 140.9 (d of m, *J* = 392.6 Hz), 137.7 (d of m, *J* = 377.5 Hz), 131.8, 130.3, 126.5, 119.4, 117.7, 112.1 (td, *J* = 27.2, 6.0 Hz), 80.0, 77.2, 61.8, 24.9, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.40 (dd, *J* = 22.6, 7.5 Hz), -155.16 (t, *J* = 20.7 Hz), -163.0 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{18}H_{15}ClF_5O_3^+$ $[M+H]^+$ 409.0624. For found m/z. 409.0630.

Methyl 2-(2,2'',3'',4'',5'',6''-hexafluoro-[1,1':4',1''-terphenyl]-4-yl)propanoate (5x)



5x

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 82% yield, 104.3 mg.

R_f = 0.35 (PE / EA = 50 / 1)

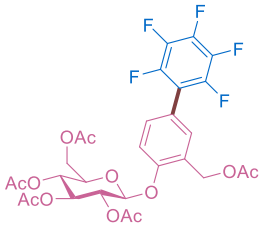
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 12.0 Hz, 1H), 3.80 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 160.7, 159.0, 144.4 (d of m, *J* = 256.7 Hz), 142.7, 142.6, 140.6 (d of m, *J* = 256.7 Hz), 138.0 (d of m, *J* = 241.6 Hz), 136.6, 130.8, 130.7, 130.3, 129.3, 129.2, 126.9, 126.8, 125.8, 123.9, 123.8, 115.6 (td, *J* = 16.6, 3.0 Hz), 115.5, 115.4, 77.2, 52.3, 45.1, 18.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.28 (m), -143.07 (dd, *J* = 25.4, 8.5 Hz), -155.50 (td, *J* = 19.8, 11.3 Hz), -162.13 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{22}H_{14}F_6NaO_2^+$ $[M+Na]^+$ 447.0790. found m/z 447.0796.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3-(acetoxymethyl)-2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5y)



5y

The crude product was purified by DCM / MeOH (50 : 1) as an eluent.

Light brown solid 73% yield, 145.1 mg.

R_f = 0.45 (DCM / MeOH = 30 / 1)

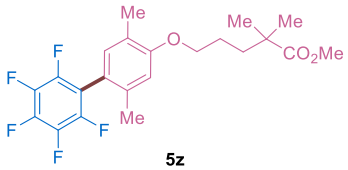
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.32 (d, *J* = 12.0 Hz, 1H), 7.17 (d, *J* = 6.0 Hz, 1H), 5.34 – 5.28 (m, 2H), 5.20 – 5.12 (m, 3H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.27 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.18 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.92 – 3.89 (m, 1H), 2.08 (s, 3H), 2.08 (s, 3H), 2.04 – 2.03 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 170.5, 170.3, 169.5, 169.3, 155.0, 144.2 (d of m, *J* = 241.6 Hz), 140.5 (d of m, *J* = 256.7 Hz), 137.9 (d of m, *J* = 241.6 Hz), 131.2, 126.9, 121.4, 115.6, 115.1 (td, *J* = 16.6, 3.0 Hz), 98.9, 77.2, 72.2, 71.0, 68.3, 61.9, 60.6, 20.9, 20.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -143.34 (dd, *J* = 22.6, 5.7 Hz), -155.48 (td, *J* = 21.2, 9.4 Hz), -162.1(td, *J* = 21.2, 7.5 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{29}H_{28}F_5O_{12}^+$ $[M+H]^+$ 663.1495. found m/z 663.1504.

Methyl 2,2-dimethyl-5-((2',3',4',5',6'-pentafluoro-2,5-dimethyl-[1,1'-biphenyl]-4-yl)oxy)pentanoate (5z)



5z

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Colorless viscous liquid 56% yield, 72.3 mg.

R_f = 0.35 (PE / EA = 30 / 1)

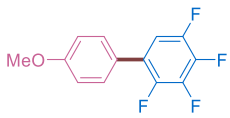
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.75 (s, 1H), 3.99 (t, *J* = 5.4 Hz, 2H), 3.68 (s, 3H), 2.22 (s, 3H), 2.14 (s, 3H), 1.76 (t, *J* = 9.3 Hz, 4H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 158.0, 144.4 (d of m, *J* = 241.6 Hz), 140.5 (d of m, *J* = 256.7 Hz), 137.7 (d of m, *J* = 241.6 Hz), 136.1, 132.5, 124.7, 117.0, 115.7 (td, *J* = 19.6, 3.0 Hz), 112.7, 77.2, 68.1, 51.8, 42.2, 37.2, 25.3, 25.2, 19.8, 15.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -140.65 (dd, *J* = 22.6, 5.7 Hz), -156.31 (t, *J* = 19.78 Hz), -162.77 (td, *J* = 22.6, 11.3 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{22}H_{24}F_5O_3^+$ $[M+H]^+$ 431.1640. found m/z 431.1633.

2,3,4,5-Tetrafluoro-4'-methoxy-1,1'-biphenyl (6a)



6a

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 79% yield, 60.9 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.04 – 6.99 (m, 3H), 3.86 (s,

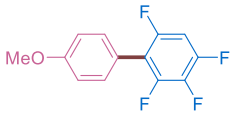
3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 147.2 (d of m, *J* = 256.7 Hz), 144.9 (d of m, *J* = 241.6 Hz), 141.5 (d of m, *J* = 256.7 Hz), 139.5 (d of m, *J* = 256.7 Hz), 130.2, 130.1, 125.3(m), 114.4, 111.1 (dt, *J* = 19.6, 3.0 Hz), 77.2, 55.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -139.94 (m), -144.2 (m), -155.5 (t, *J* = 19.8 Hz), -158.12 (td, *J* = 21.2, 7.5 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_8F_4NaO^+$ $[M+Na]^+$ 279.0403. found m/z 279.0401.

2,3,4,6-Tetrafluoro-4'-methoxy-1,1'-biphenyl (6b)



6b

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 69% yield, 53.1 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.03 – 7.00 (m, 2H), 6.88 – 6.83 (m, 1H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 154.4 (d of m, *J* = 241.6 Hz), 150.2 (d of m, *J* = 75.5 Hz), 148.5 (d of m, *J* = 75.5 Hz), 137.7 (d of m, *J* = 256.7 Hz), 131.5, 119.7, 115.9 (m), 114.2, 101.0 (m), 77.2, 55.4.

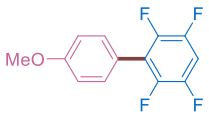
^{19}F NMR (565 MHz, $CDCl_3$) δ -118.42 (dd, *J* = 17.0, 5.7 Hz), -134.27 (m), -135.82 (d, *J* = 22.6 Hz), -165.04 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_8F_4NaO^+$ $[M+Na]^+$ 279.0403. found m/z 279.0405.

These data are in agreement with those reported previously in the literature.[D]

[D] F. Chen, Q.-Q. Min and X. Zhang, Pd-Catalyzed Direct Arylation of Polyfluoroarenes on Water under Mild Conditions Using PPh_3 Ligand, *J. Org. Chem.*, 2012, **77**, 2992−2998.

2,3,5,6-Tetrafluoro-4'-methoxy-1,1'-biphenyl (6c)



6c

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 66% yield, 50.7 mg.

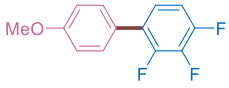
R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 8.8, 1.2 Hz, 2H), 7.06 – 6.99 (m, 3H), 3.87 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 146.4 (d of m, *J* = 241.6 Hz), 143.9 (d of m, *J* = 241.6 Hz), 131.6, 121.47 (t, *J* = 16.6 Hz), 119.7, 114.3, 104.5 (t, *J* = 22.7 Hz), 77.2, 55.5.
^{19}F NMR (565 MHz, $CDCl_3$) δ-139.44 (m), -144.28 (m).
HRMS (ESI-TOF): m/z calcd. For $C_{13}H_8F_4NaO^+$ $[M+Na]^+$ 279.0403. found m/z 279.0407.

These data are in agreement with those reported previously in the literature.[D]

[D] F. Chen, Q.-Q. Min and X. Zhang, Pd-Catalyzed Direct Arylation of Polyfluoroarenes on Water under Mild Conditions Using PPh_3 Ligand, *J. Org. Chem.*, 2012, **77**, 2992−2998.

2,3,4-Trifluoro-4'-methoxy-1,1'-biphenyl (6d)



6d

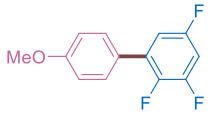
The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 83% yield, 59.3 mg.

R_f = 0.40 (pure PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 9.0, 1.8 Hz, 2H), 7.12 (m, 2.4 Hz, 1H), 7.05 – 6.98 (m, 3H), 3.87 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 151.1 (dd, *J* = 9.8, 2.3 Hz), 149.6 (dd, *J* = 10.6, 3.0 Hz), 149.4 (dd, *J* = 10.6, 1.5 Hz), 148.0 (dd, *J* = 10.6, 3.0 Hz), 141.3 (t, *J* = 15.9 Hz), 139.6 (t, *J* = 15.9 Hz), 130.1, 130.0, 126.6 (dd, *J* = 10.6, 4.5 Hz), 123.7, 114.3, 112.1 (dd, *J* = 17.3, 3.8 Hz), 77.2, 55.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ-136.62 (m), -139.18 (m), -160.33 (td, *J* = 19.8, 7.5 Hz).
HRMS (ESI-TOF): m/z calcd. For $C_{13}H_9F_3NaO^+$ $[M+Na]^+$ 261.0498. found m/z 261.0494.

[E] R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu and L. Liu, Copper-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350–9354.

2,3,5-Trifluoro-4'-methoxy-1,1'-biphenyl (6e)



6e

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 82% yield, 58.6 mg.

R_f = 0.40 (pure PE)

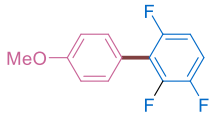
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.92 (m, 1H), 6.90 – 6.84 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 158.5 (dd, *J* = 10.6, 3.0 Hz), 156.9 (dd, *J* = 10.6, 3.0 Hz), 151.1 (d of m, *J* = 256.7 Hz), 145.5 (dd, *J* = 12.1, 3.0 Hz), 143.8 (dd, *J* = 12.1, 4.5 Hz), 131.6 (m), 130.2 (d, *J* = 3.0 Hz), 126.2, 114.3, 111.4 (d, *J* = 24.2 Hz), 103.7 (m), 77.2, 55.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.81(m), -133.37(q, *J* = 11.3 Hz), -148.85(m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_9F_3NaO^+$ $[M+Na]^+$ 261.0498. found m/z 261.0492.

2,3,6-Trifluoro-4'-methoxy-1,1'-biphenyl (6f)



6f

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow oil 69% yield, 49.3 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.06 (m, 1H), 7.02 – 7.00 (m, 2H), 6.92 – 6.88(m, 1H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 155.5 (d of m, *J* = 241.6 Hz), 148.7 (d of m, *J* = 45.3 Hz), 147.1 (d of m, *J* = 45.3 Hz), 131.6, 120.6, 120.1 (m), 115.2 (m), 114.1, 110.9 (m), 77.2, 55.4.

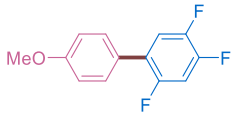
^{19}F NMR (565 MHz, $CDCl_3$) δ -120.04 (m), -138.18 (m), -142.19 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_9F_3NaO^+$ $[M+Na]^+$ 261.0498. found m/z 261.0492.

These data are in agreement with those reported previously in the literature.[E]

[E] R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu and L. Liu, Copper-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350–9354.

2,4,5-Trifluoro-4'-methoxy-1,1'-biphenyl (6g)



6g

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 80% yield, 57.1 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.12 – 7.06 (m, 1H), 6.89 – 6.82 (m, 3H), 3.72 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 154.7 (d of m, *J* = 241.6 Hz), 149.0 (d of m, *J* = 256.7 Hz), 147.0 (d of m, *J* = 241.6 Hz), 130.1, 130.0, 126.4, 125.3 (m), 117.9 (m), 114.2, 106.1 (m), 77.2, 55.4.

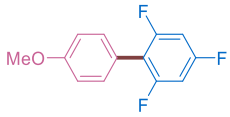
^{19}F NMR (565 MHz, $CDCl_3$) δ -119.63 (m), -136.00 (m), -142.98 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_9F_3NaO^+$ $[M+Na]^+$ 261.0498. found m/z 261.0495.

These data are in agreement with those reported previously in the literature.[F]

[F] Y. Mutoh, K. Yamamoto and S. Saito, Suzuki–Miyaura Cross-Coupling of 1,8-Diaminonaphthalene (dan)-Protected Arylboronic Acids, *ACS Catal.*, 2020, **10**, 352−357.

2,4,6-Trifluoro-4'-methoxy-1,1'-biphenyl (6h)



6h

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 65% yield, 46.4 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.75 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (t, *J* = 16.6 Hz), 161.3 (m), 160.7 (t, *J* = 15.1 Hz), 159.6 (m), 131.6, 120.6, 114.6 (td, *J* = 19.6, 4.5 Hz), 114.0, 100.5 (m), 77.2, 55.4.

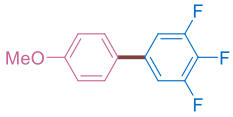
^{19}F NMR (565 MHz, $CDCl_3$) δ -109.86 (m), -111.57 (t, *J* = 8.5 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_9F_3NaO^+$ $[M+Na]^+$ 261.0498. found m/z 261.0493.

These data are in agreement with those reported previously in the literature.[E]

[E] R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu and L. Liu, Copper-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350–9354.

3,4,5-Trifluoro-4'-methoxy-1,1'-biphenyl (6i)



6i

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 79% yield, 56.4 mg.

R_f = 0.40 (pure PE)

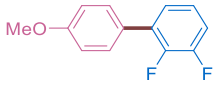
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 7.15 – 7.10 (m, 1H), 7.00 – 6.97 (m, 1H), 3.86 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 152.3 (dd, *J* = 10.6, 4.5 Hz), 150.7 (dd, *J* = 9.1, 4.5 Hz), 139.7 (t, *J* = 15.1 Hz), 138.1 (t, *J* = 16.6 Hz), 137.1 (m), 130.7, 128.0, 114.6, 110.5 (dd, *J* = 18.1, 4.5 Hz), 77.2, 55.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -134.54(m), -163.89(m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_9F_3NaO^+$ $[M+Na]^+$ 261.0498. found m/z 261.0503.

2,3-Difluoro-4'-methoxy-1,1'-biphenyl (6j)



6j

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow oil 84% yield, 55.5 mg.

R_f = 0.40 (pure PE)

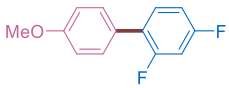
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.15 – 7.10 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 152.1 (d, *J* = 4.6 Hz), 150.5 (d, *J* = 13.6 Hz), 148.8 (d, *J* = 13.6 Hz), 147.2 (d, *J* = 13.6Hz), 131.1 (d, *J* = 10.6 Hz), 130.2 (d, *J* = 3.0 Hz), 127.1 (d, *J* = 1.5 Hz), 125.2 (t, *J* = 2.3 Hz), 124.1 (m), 115.6, 115.5, 114.2, 77.2, 55.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -138.13 (m), -144.08 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}F_2O^+$ $[M+H]^+$ 221.0772. found m/z 221.0768.

2,4-Difluoro-4'-methoxy-1,1'-biphenyl (6k)



6k

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow oil 85% yield, 56.1 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.39 – 7.35 (m, 1H), 7.00 – 6.98 (m, 2H), 6.95 – 6.88 (m, 2H), 3.86 (s, 3H).

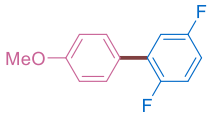
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, *J* =12.1 Hz), 161.2 (d, *J* =10.6 Hz), 160.6 (d, *J* =10.6 Hz), 159.4, 159.0 (d, *J* =10.6 Hz), 131.3, 131.2, 131.1, 131.0, 130.2, 130.1, 127.5, 125.2 (d, *J* = 4.5 Hz) 125.1 (d, *J* = 4.5 Hz), 114.1, 111.6 (m), 104.4 (m), 77.2, 55.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.34(m), -113.8(m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}F_2O^+$ $[M+H]^+$ 221.0772. found m/z 221.0773.

[G] Y. Wei, J. Kan, M. Wang, W. Su and M. Hong, Palladium-Catalyzed Direct Arylation of Electron-Deficient Polyfluoroarenes with Arylboronic Acids, *Org. Lett.*, 2009, **11**, 3346–3349.

2,5-Difluoro-4'-methoxy-1,1'-biphenyl (6l)



6l

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow oil 83% yield, 54.8 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.08 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.94 (m, 1H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 158.1 (d, *J* = 3.0 Hz), 156.6 (d, *J* = 1.5 Hz), 155.0 (d, *J* = 1.5 Hz), 130.2, 130.1, 127.3, 117.2 (dd, *J* = 25.7, 7.6 Hz), 116.6 (dd, *J* = 24.2, 3.0 Hz), 114.6 (dd, *J* = 24.2, 9.1 Hz), 77.2, 55.4.

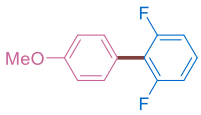
^{19}F NMR (565 MHz, $CDCl_3$) δ -119.19 (m), -124.31 (d, *J* = 5.65 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}F_2O^+$ $[M+H]^+$ 221.0772. found m/z 221.0775.

These data are in agreement with those reported previously in the literature.[H]

[H] W. Wu, E. Cui, Y. Zhang, C. Zhang, F. Zhu, C.-H. Tung and Y. Wang, Involving Single-Atom Silver(0) in Selective Dehalogenation by AgF under Visible-Light Irradiation, *ACS Catal.*, 2019, **9**, 6335−6341.

2,6-Difluoro-4'-methoxy-1,1'-biphenyl (6m)



6m

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow oil 81% yield, 53.5 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 9.0 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.01 – 6.94 (m, 4H), 3.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1 (d, *J* = 7.6 Hz), 159.6, 159.5 (d, *J* = 7.6 Hz), 131.6, 128.5 (t, *J* = 9.8 Hz), 121.4, 118.3 (t, *J* = 18.9 Hz), 111.7 (dd, *J* = 22.7, 6.0 Hz), 77.2, 55.4.

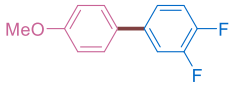
^{19}F NMR (565 MHz, $CDCl_3$) δ -114.76 (t, *J* = 5.7 Hz).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}F_2O^+$ $[M+H]^+$ 221.0772. found m/z 221.0779.

These data are in agreement with those reported previously in the literature.[E]

[E] R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu and L. Liu, Copper-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350–9354.

3,4-Difluoro-4'-methoxy-1,1'-biphenyl (6n)



6n

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow oil 81% yield, 53.4 mg.

R_f = 0.40 (pure PE)

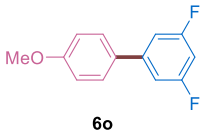
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 2H), 7.21 – 7.17 (m, 1H), 7.11 – 7.09 (m, 1H), 7.06 – 7.02 (m, 1H), 6.85 – 6.82 (m, 2H), 3.71 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 151.4 (d, *J* = 13.6 Hz), 150.4 (d, *J* = 12.1 Hz), 149.8 (d, *J* = 13.6 Hz), 148.8 (d, *J* = 12.1 Hz), 138.1 (m), 131.7, 128.1, 122.6 (m), 117.5 (d, *J* = 16.6 Hz), 115.5 (d, *J* = 18.1 Hz), 114.5, 77.2, 55.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -137.75 (m), -141.31 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}F_2O^+$ $[M+H]^+$ 221.0772. found m/z 221.0763.

3,5-Difluoro-4'-methoxy-1,1'-biphenyl (6o)



6o

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 72% yield, 47.5 mg.

R_f = 0.40 (pure PE)

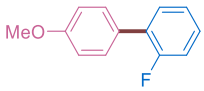
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.09 – 7.05 (m, 2H), 7.00 – 6.97 (m, 2H), 6.76 – 6.73 (m, 1H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3 (d, *J* = 13.6 Hz), 162.6 (d, *J* = 13.6 Hz), 160.12, 144.3 (t, *J* = 9.8 Hz), 131.5 (d, *J* = 1.5 Hz), 128.2, 114.5, 109.5 (dd, *J* = 21.1, 6.0 Hz), 102.1, 101.9, 101.7, 77.2, 55.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.01 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{10}F_2NaO^+$ $[M+Na]^+$ 243.0592. found m/z 243.0589.

2-Fluoro-4'-methoxy-1,1'-biphenyl (6p)



6p

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Yellow oil 86% yield, 52.1 mg.

R_f = 0.40 (pure PE)

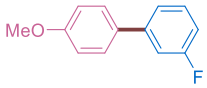
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.45 – 7.42 (m 1H), 7.31 – 7.17 (m, 1H), 7.20 (t, 1H), 7.17 – 7.14 (m, 1H), 7.02 – 7.00 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 159.4, 159.1, 130.6 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 3.0 Hz), 128.9, 128.8, 128.5 (d, *J* = 8.0 Hz), 128.3, 124.4 (d, *J* = 3.5 Hz), 116.3, 116.1, 114.1, 77.2, 55.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -118.20.

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}FNaO^+$ $[M+Na]^+$ 225.0686. found m/z. 225.0695.

3-Fluoro-4'-methoxy-1,1'-biphenyl (6q)



6q

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 87% yield, 52.7 mg.

R_f = 0.40 (pure PE)

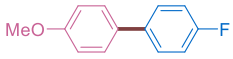
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.26 (d, *J* = 9.6 Hz, 1H), 7.00 (m, 3H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 162.6, 159.7, 143.2 (d, *J* = 7.6 Hz), 132.6 (d, *J* = 1.5 Hz), 130.3 (d, *J* = 9.1 Hz), 128.3, 122.4 (d, *J* = 3.0 Hz), 114.4, 113.6 (m), 77.2, 55.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.25.

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}FNaO^+$ $[M+Na]^+$ 225.0686. found m/z 225.0692.

4-Fluoro-4'-methoxy-1,1'-biphenyl (6r)



6r

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 88% yield, 53.3 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 4H), 7.08 (t, J = 9 Hz, 2H), 6.96 (d, *J* = 6.0 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 161.4, 159.3, 137.1(d, J = 3.0 Hz), 133.0, 128.4, 128.3, 128.2, 115.7, 115.6, 114.4, 77.2, 55.5.

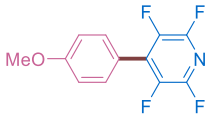
^{19}F NMR (565 MHz, $CDCl_3$) δ -116.70.

HRMS (ESI-TOF): m/z calcd. For $C_{13}H_{11}FNaO^+$ $[M+Na]^+$ 225.0686. found m/z 225.0688.

These data are in agreement with those reported previously in the literature.[F]

[F] Y. Mutoh, K. Yamamoto and S. Saito, Suzuki–Miyaura Cross-Coupling of 1,8-Diaminonaphthalene (dan)-Protected Arylboronic Acids, *ACS Catal.*, 2020, **10**, 352−357.

2,3,5,6-Tetrafluoro-4-(4-methoxyphenyl)pyridine (6s)



6s

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

Light yellow solid 71% yield, 54.8 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.07 – 7.04 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4, 144.2 (d of m, *J* = 241.6 Hz), 139.4 (d of m, *J* = 256.7 Hz), 133.3 (tt, *J* = 13.6, 3.0 Hz), 131.5 (t, *J* = 2.3 Hz), 118.1, 114.6, 77.2, 55.6.

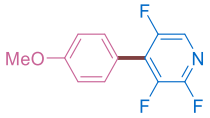
^{19}F NMR (565 MHz, $CDCl_3$) δ -91.28 (m), -145.77 (m).

HRMS (ESI-TOF): m/z calcd. For $C_{12}H_8F_4NO^+$ $[M+H]^+$ 258.0537. found m/z 258.0541.

These data are in agreement with those reported previously in the literature.[I]

[I] A. Dahiya, C. Fricke and F. Schoenebeck, Gold-Catalyzed Chemoselective Couplings of Polyfluoroarenes with Aryl Germanes and Downstream Diversification, *J. Am. Chem. Soc.*, 2020, **142**, 7754−7759.

2,3,5-Trifluoro-4-(4-methoxyphenyl)pyridine (6t)



6t

The crude product was purified by PE / EA (pure PE to 50 : 1) as an eluent.

White solid 55% yield, 39.5 mg.

R_f = 0.40 (pure PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 155.0 (d, *J* = 4.5 Hz), 153.3 (d, *J* = 4.5 Hz), 149.9 (dd, *J* = 16.6, 1.5 Hz), 148.3 (dd, *J* = 16.6, 1.5 Hz), 143.1 (dd, *J* = 31.0, 3.8 Hz), 141.3 (dd, *J* = 31.7, 3.0 Hz), 131.5, 129.6 (m), 128.6 (m), 127.8, 118.4, 114.4, 77.2, 55.5.

^{19}F NMR (565 MHz, $CDCl_3$) -89.55 (t, *J* = 28.25 Hz), -133.06 (d, *J* = 28.25 Hz), -141.54 (d, *J* = 28.25 Hz).

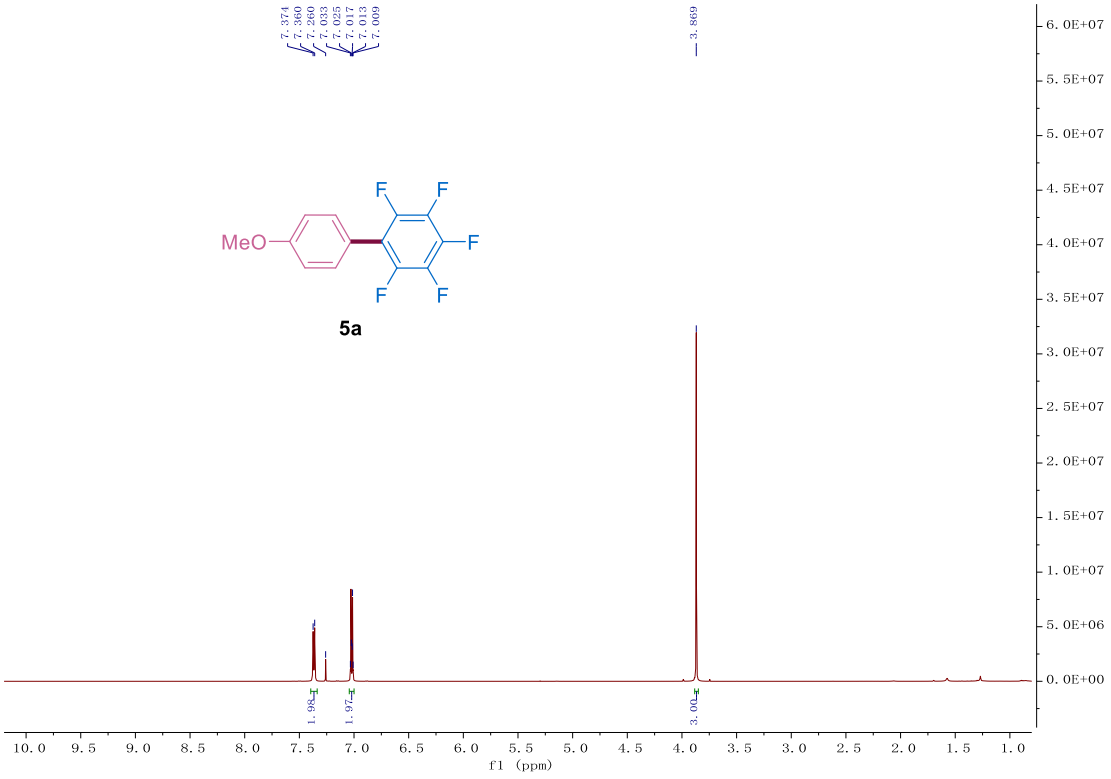
HRMS (ESI-TOF): m/z calcd. For $C_{12}H_9F_3NO^+$ $[M+H]^+$ 240.0631. found m/z 240.0635.

These data are in agreement with those reported previously in the literature.[I]

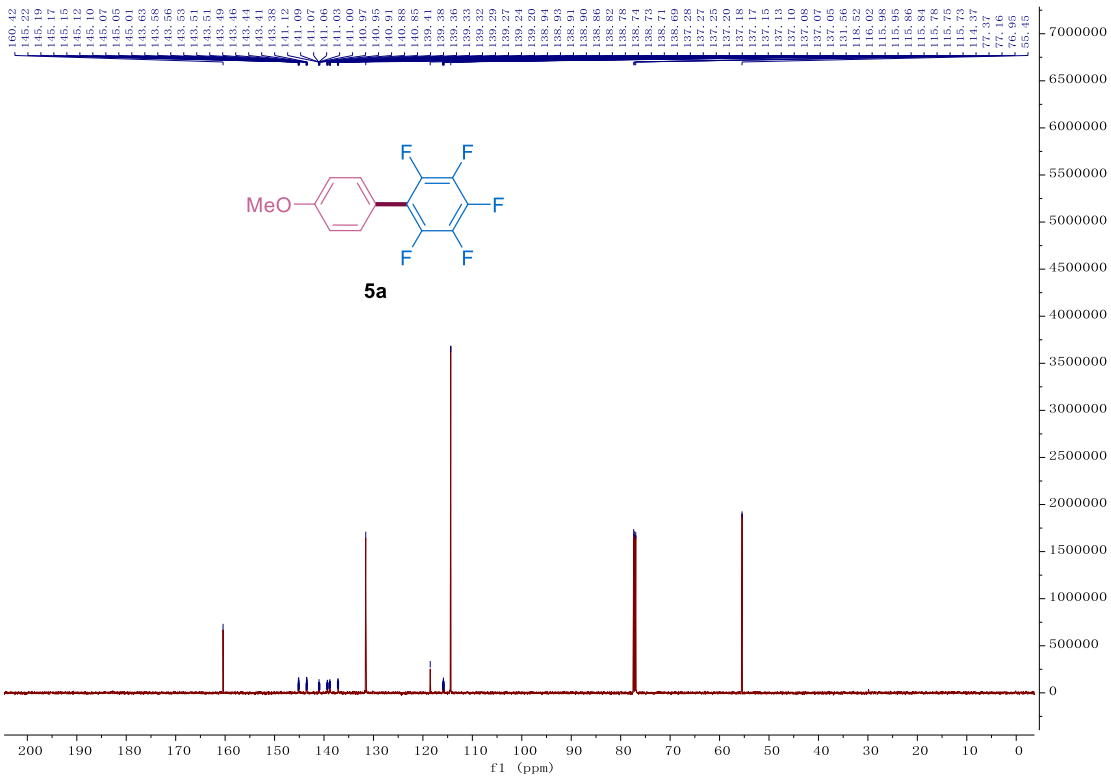
[I] A. Dahiya, C. Fricke and F. Schoenebeck, Gold-Catalyzed Chemoselective Couplings of Polyfluoroarenes with Aryl Germanes and Downstream Diversification, *J. Am. Chem. Soc.*, 2020, **142**, 7754−7759.

13. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

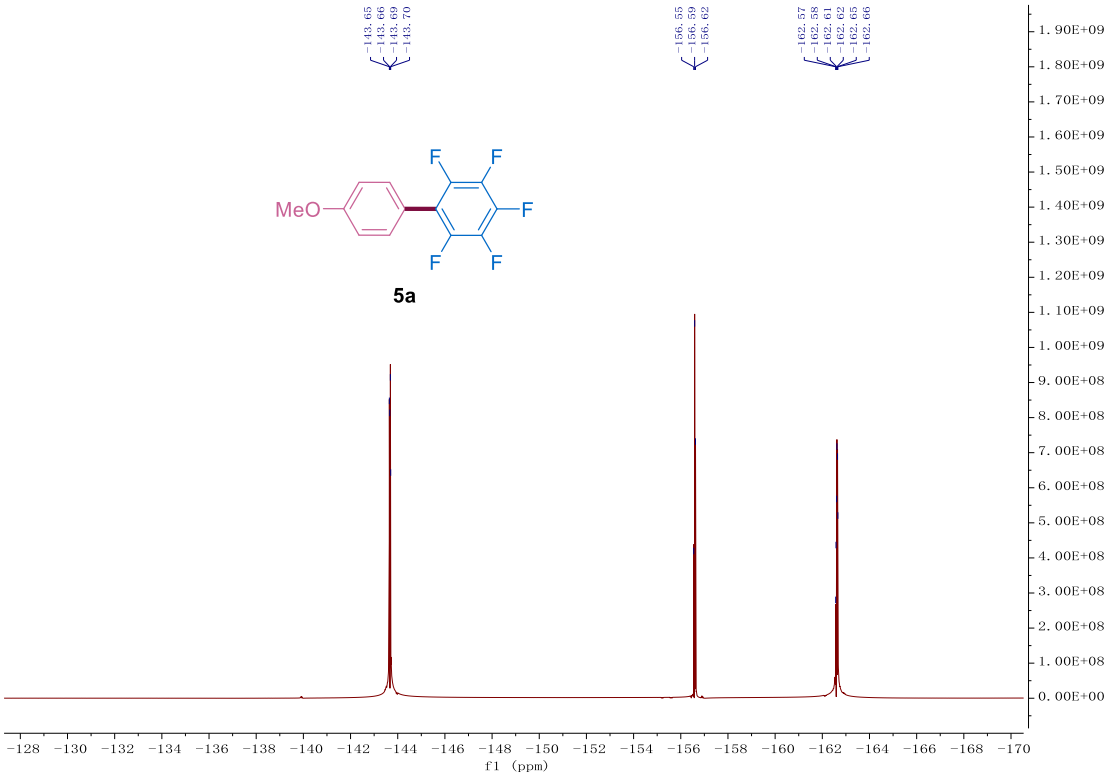
^{1}H NMR of 5a (600 MHz, $CDCl_3$)



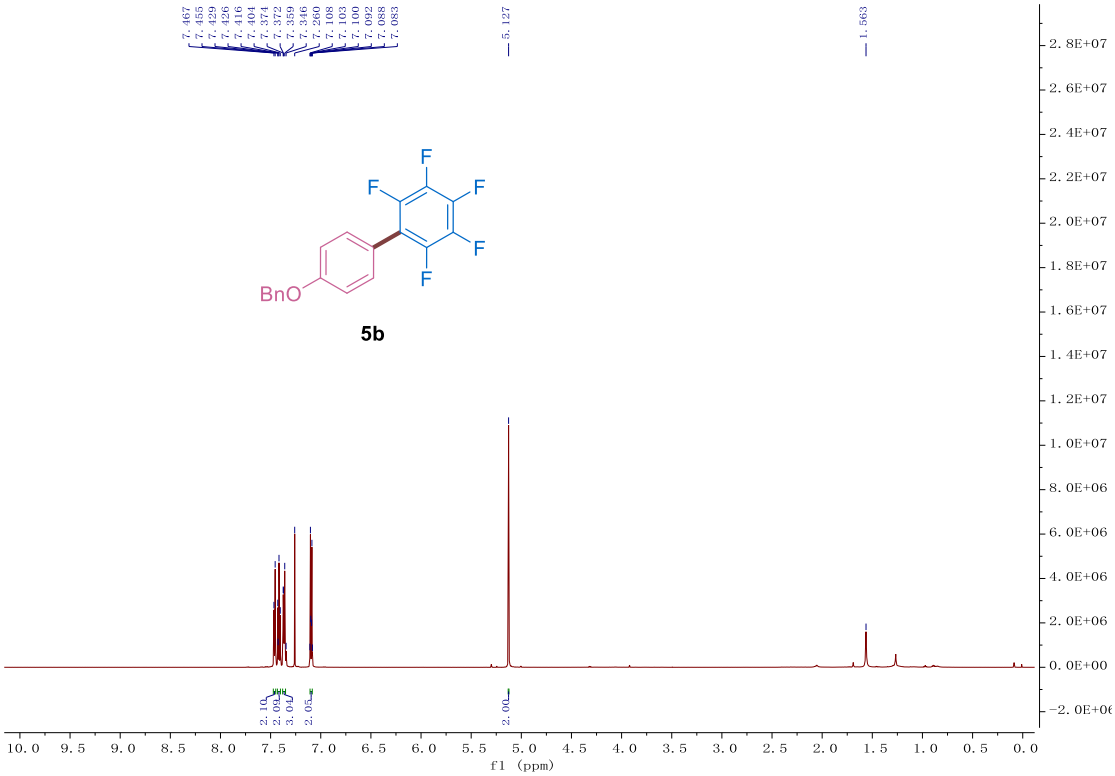
^{13}C NMR of 5a (151 MHz, $CDCl_3$)



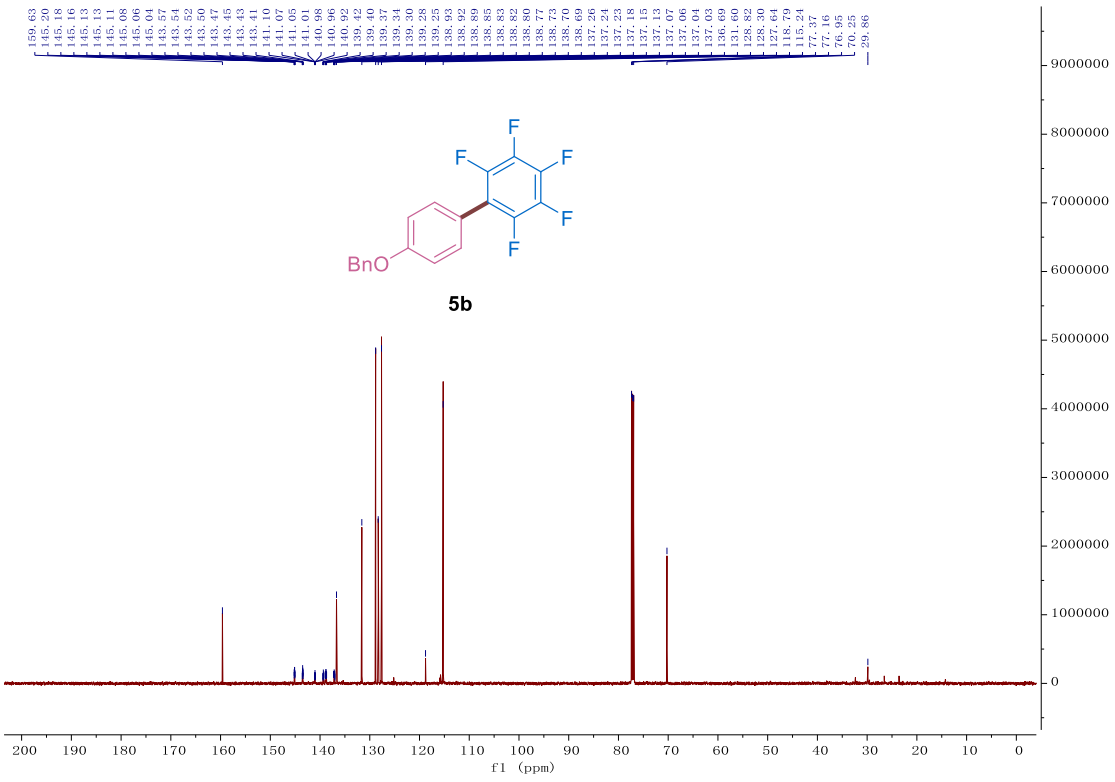
^{19}F NMR of 5a (565 MHz, $CDCl_3$)



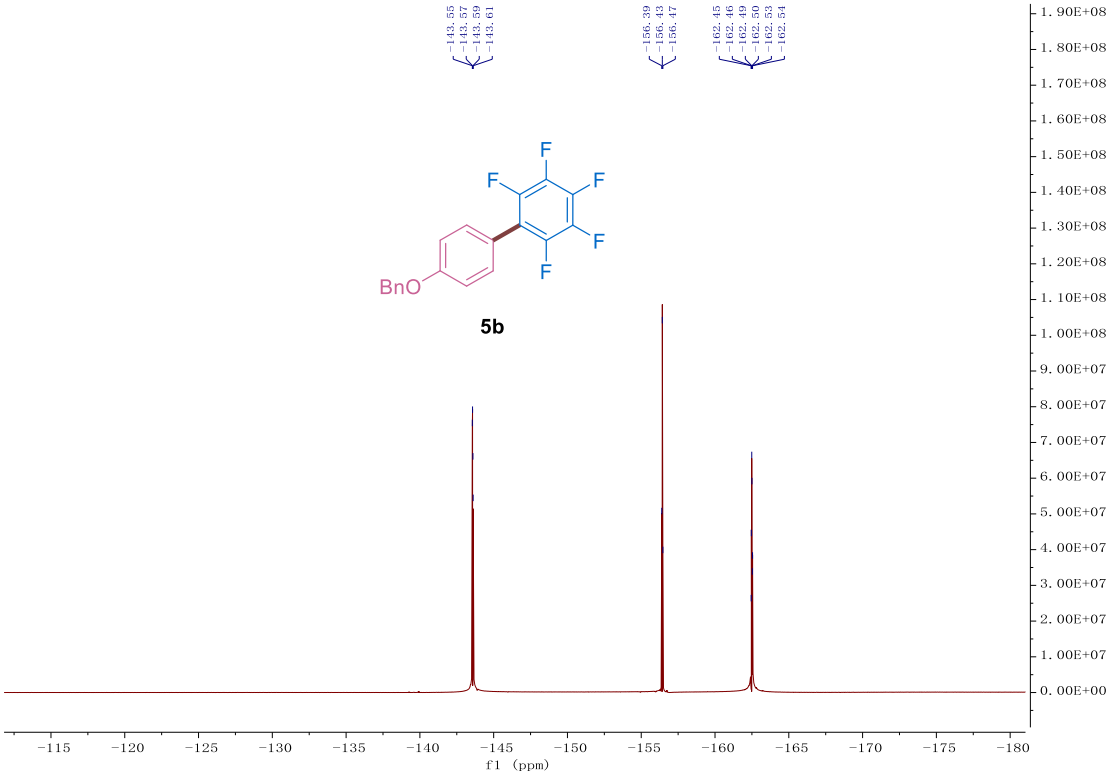
^{1}H NMR of 5b (600 MHz, $CDCl_3$)



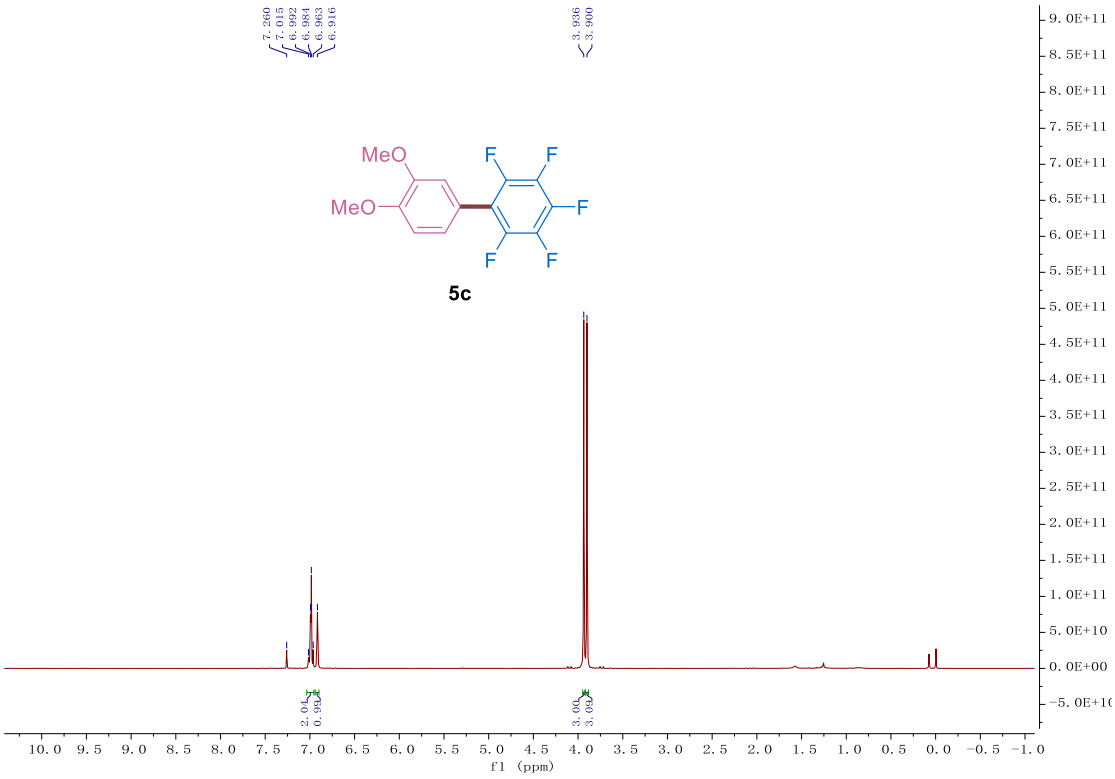
^{13}C NMR of 5b (151 MHz, $CDCl_3$)



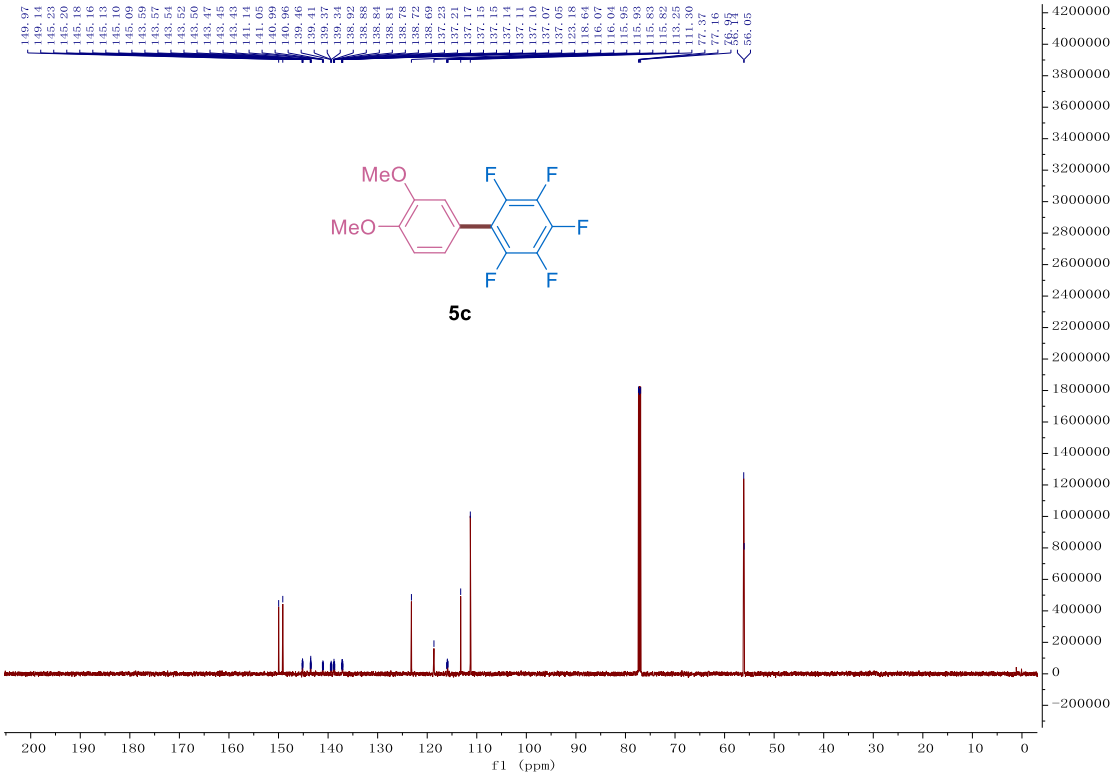
^{19}F NMR of 5b (565 MHz, $CDCl_3$)



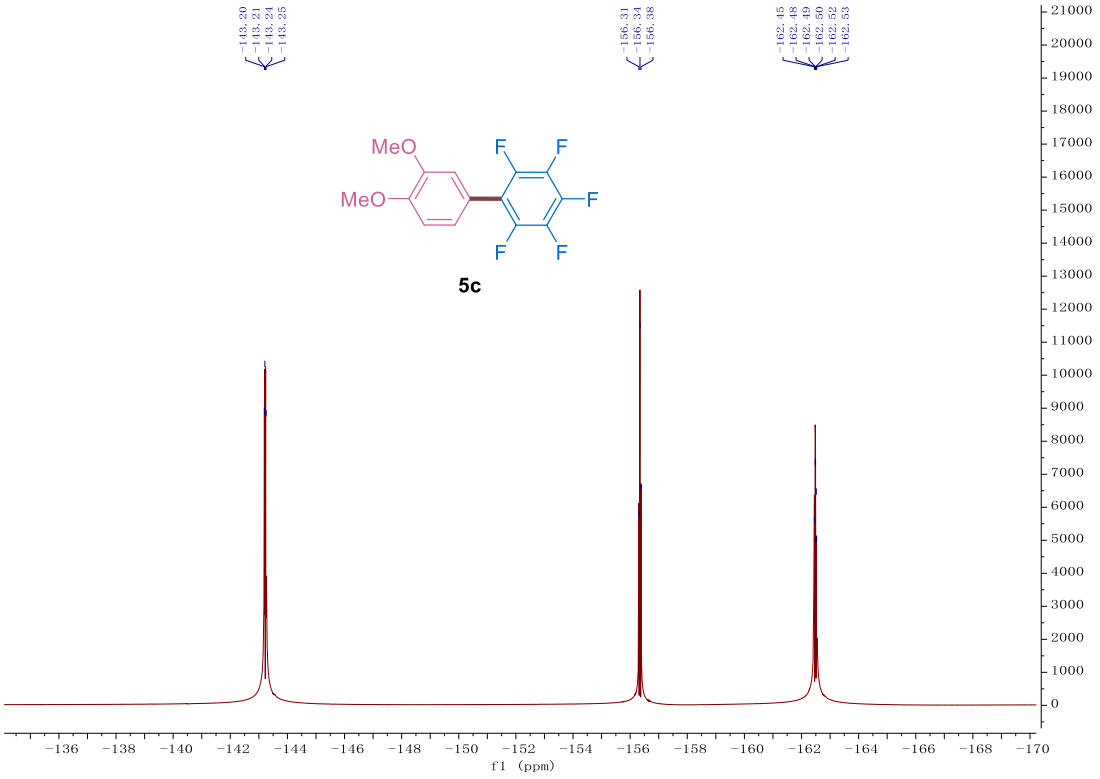
^{1}H NMR of 5c (400 MHz, $CDCl_3$)



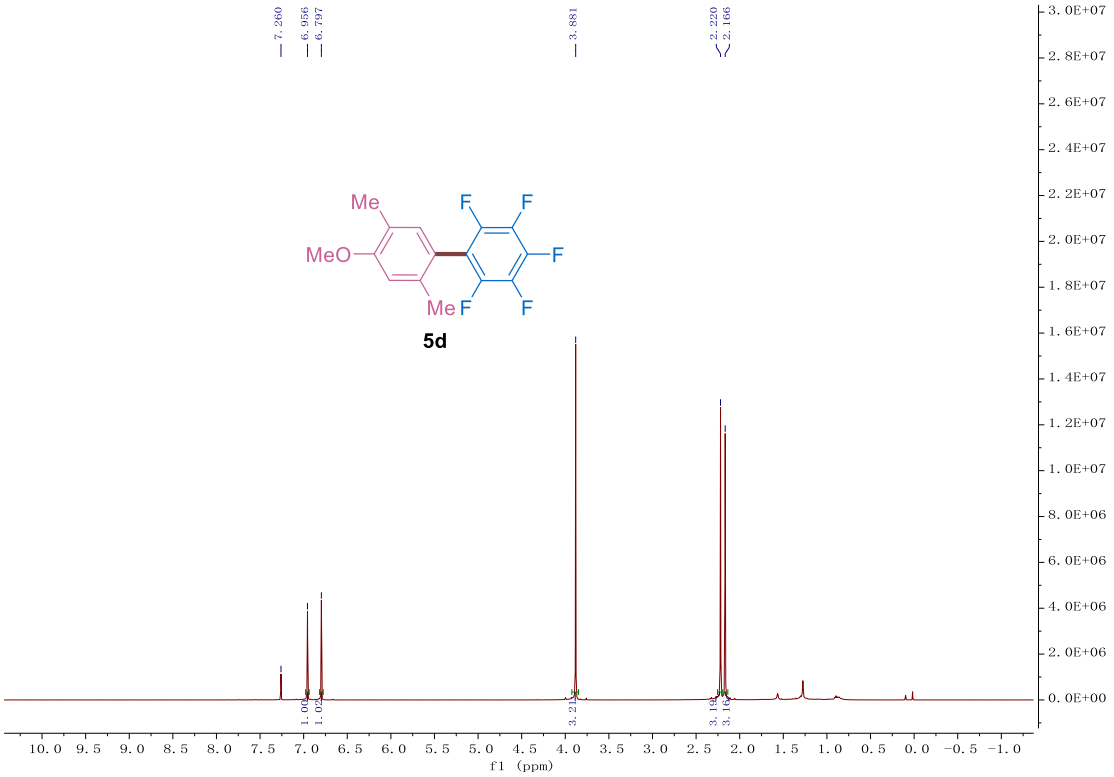
^{13}C NMR of 5c (400 MHz, $CDCl_3$)



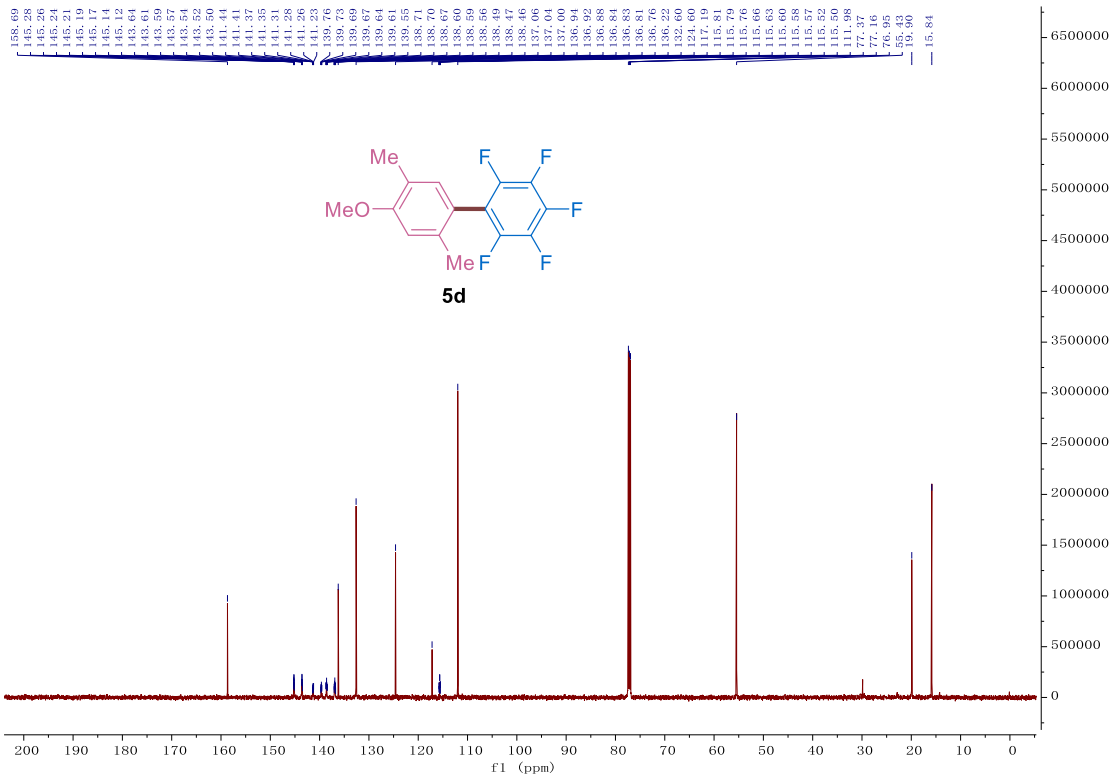
^{19}F NMR of 5c (565 MHz, $CDCl_3$)



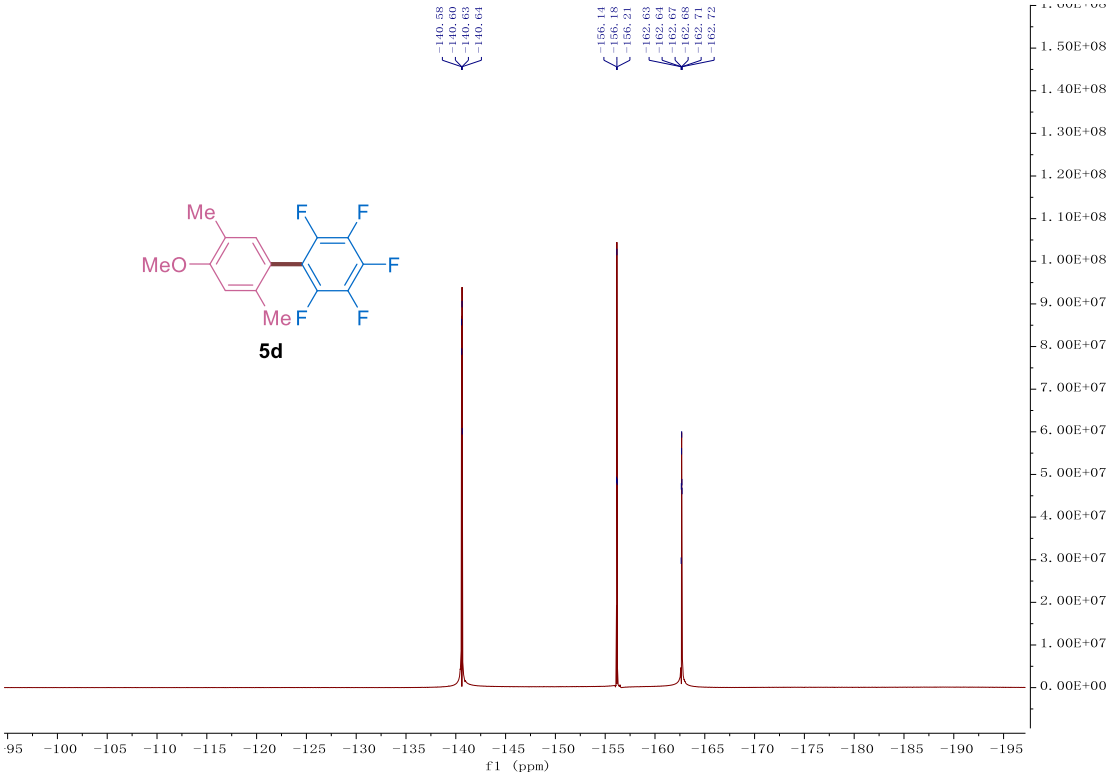
^{1}H NMR of 5d (600 MHz, $CDCl_3$)



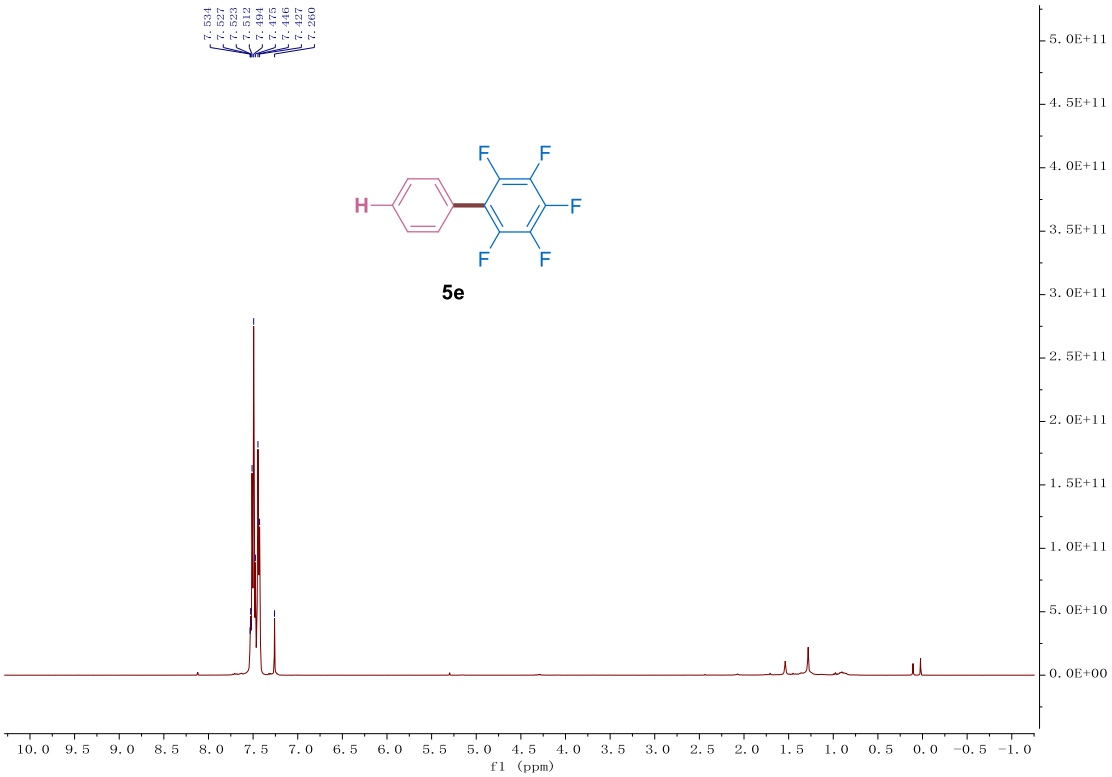
^{13}C NMR of 5d (151 MHz, $CDCl_3$)



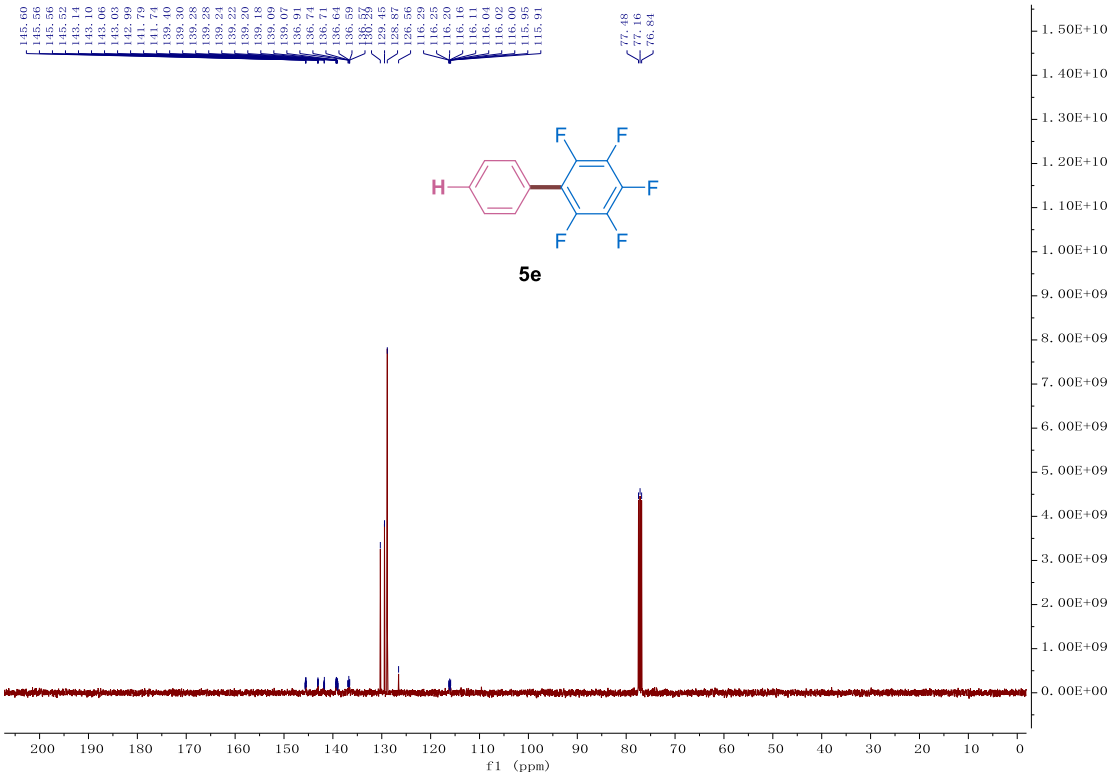
^{13}F NMR of 5d (565 MHz, $CDCl_3$)



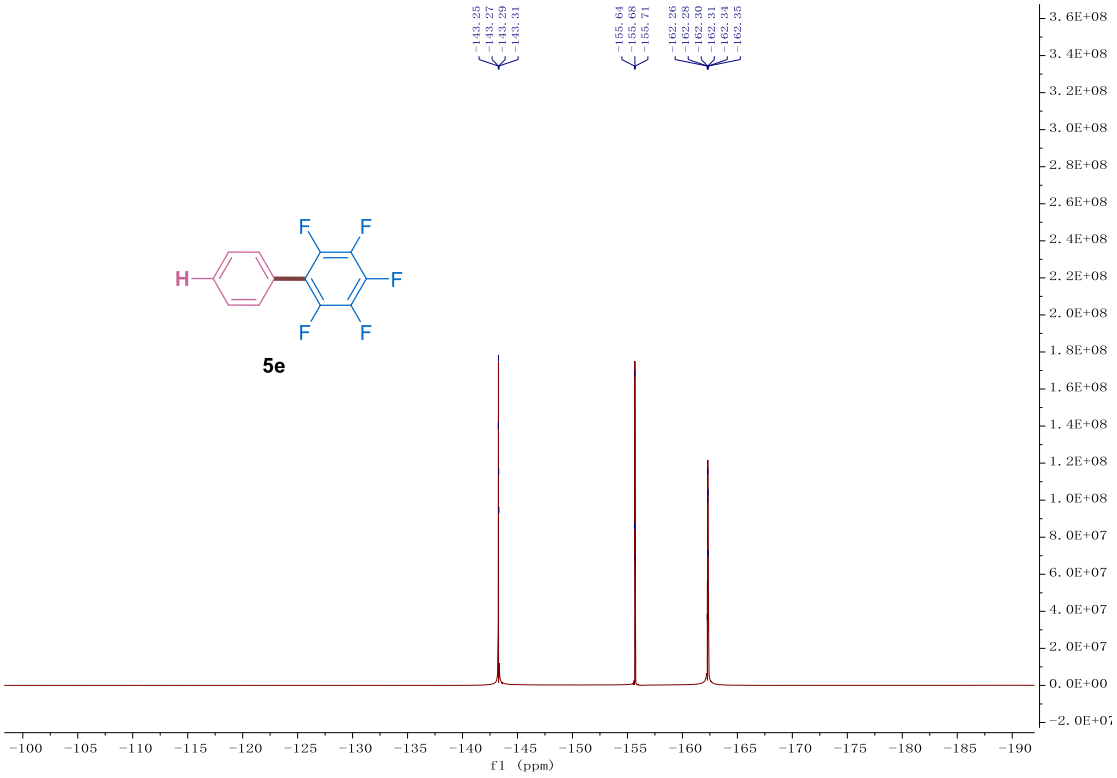
^{1}H NMR of 5e (400 MHz, $CDCl_3$)



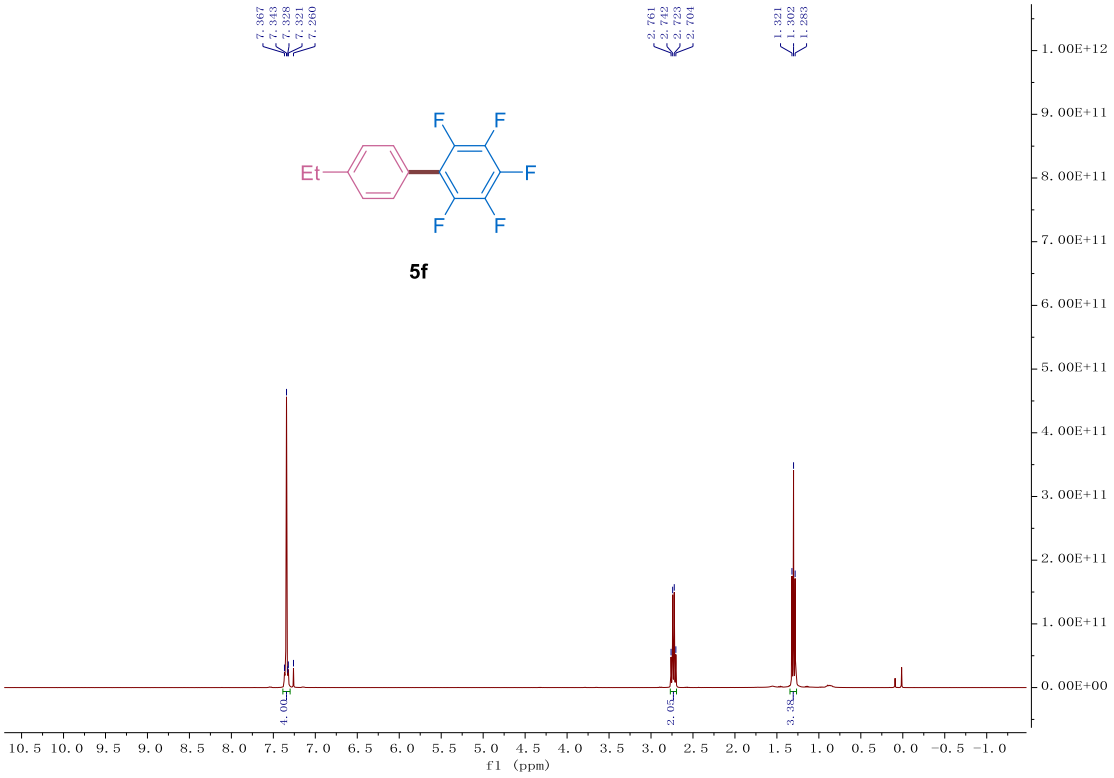
^{13}C NMR of 5e (101 MHz, $CDCl_3$)



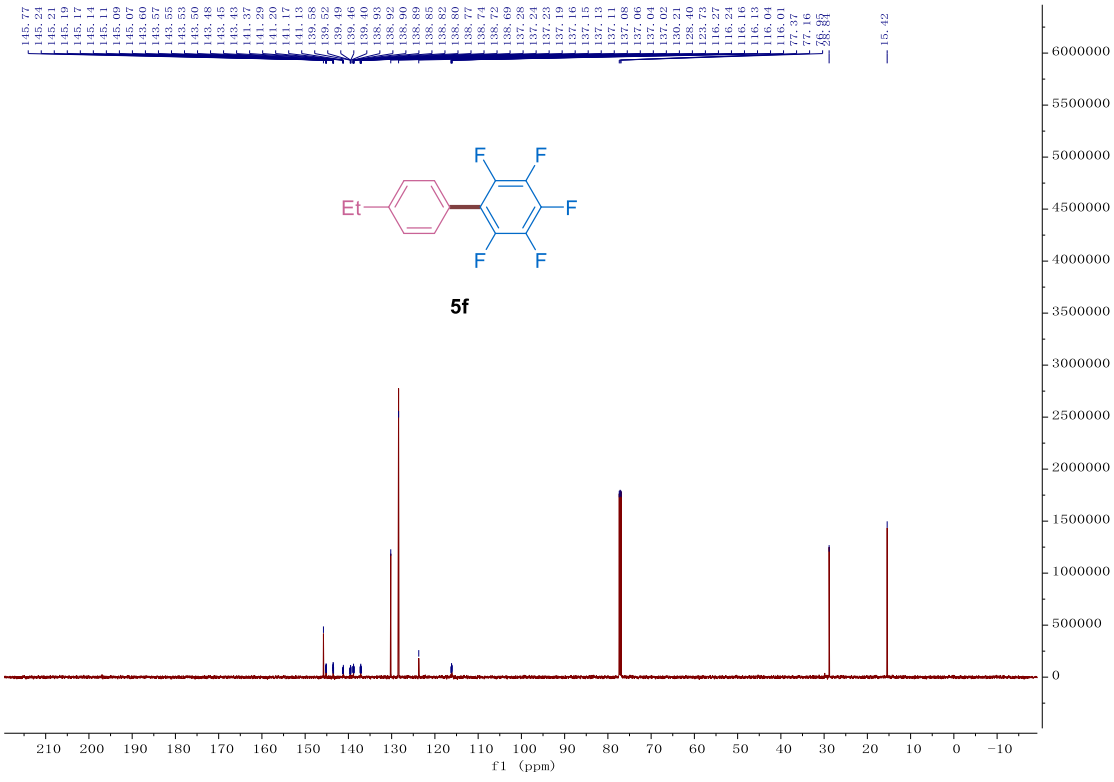
^{19}F NMR of 5e (565 MHz, $CDCl_3$)



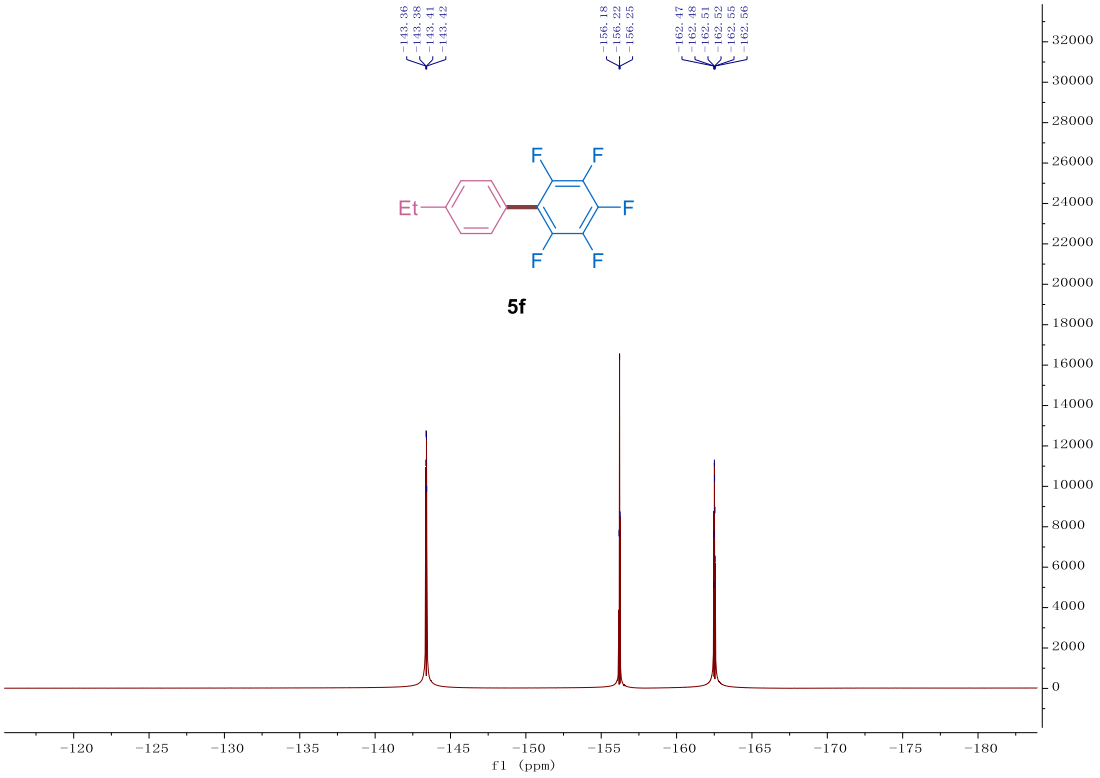
^{1}H NMR of 5f (400 MHz, $CDCl_3$)



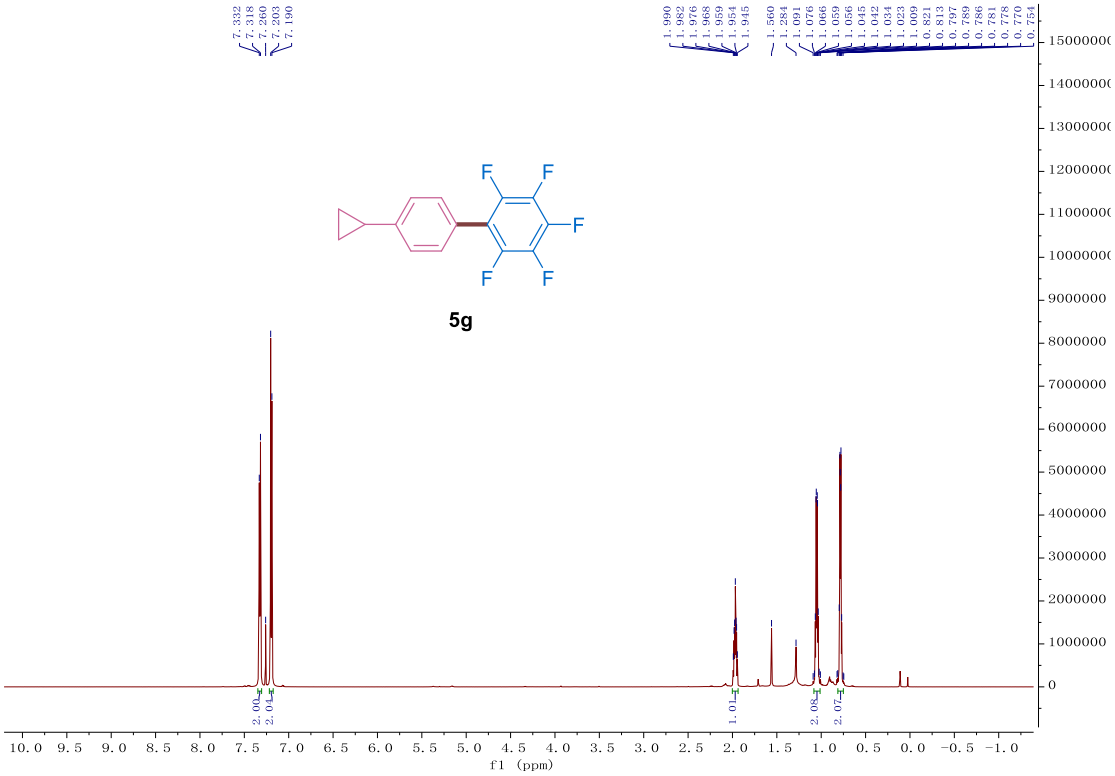
^{13}C NMR of 5f (151 MHz, $CDCl_3$)



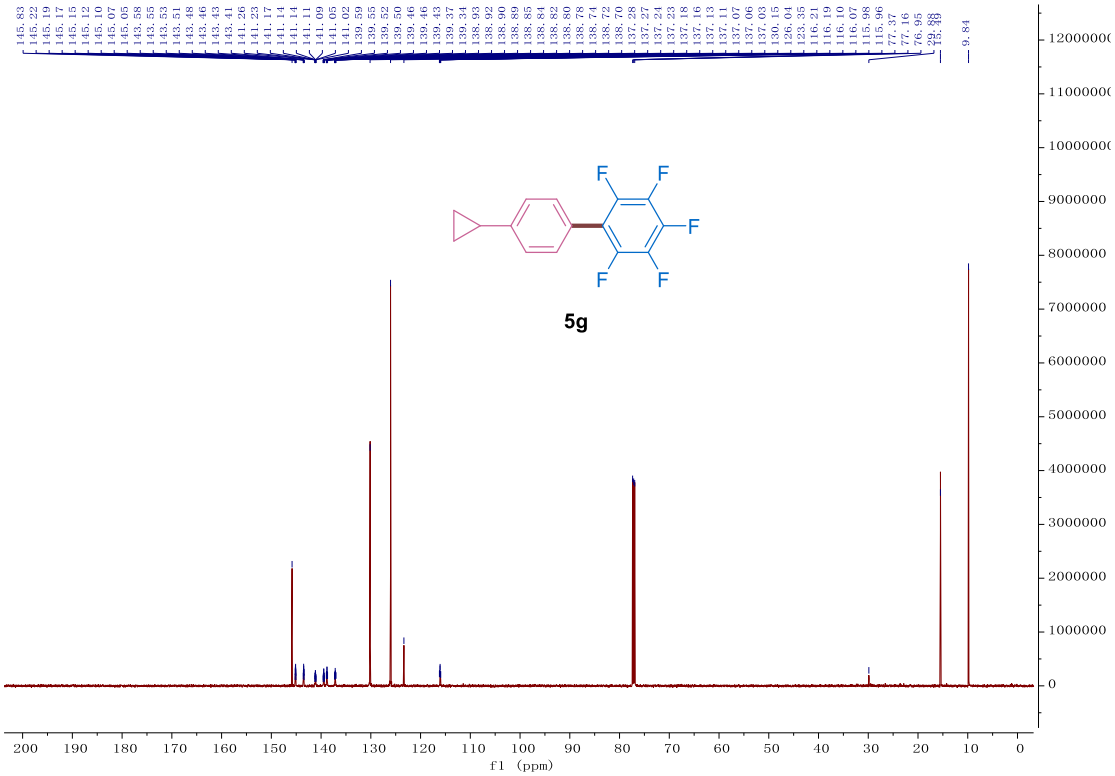
^{19}F NMR of 5f (565 MHz, $CDCl_3$)



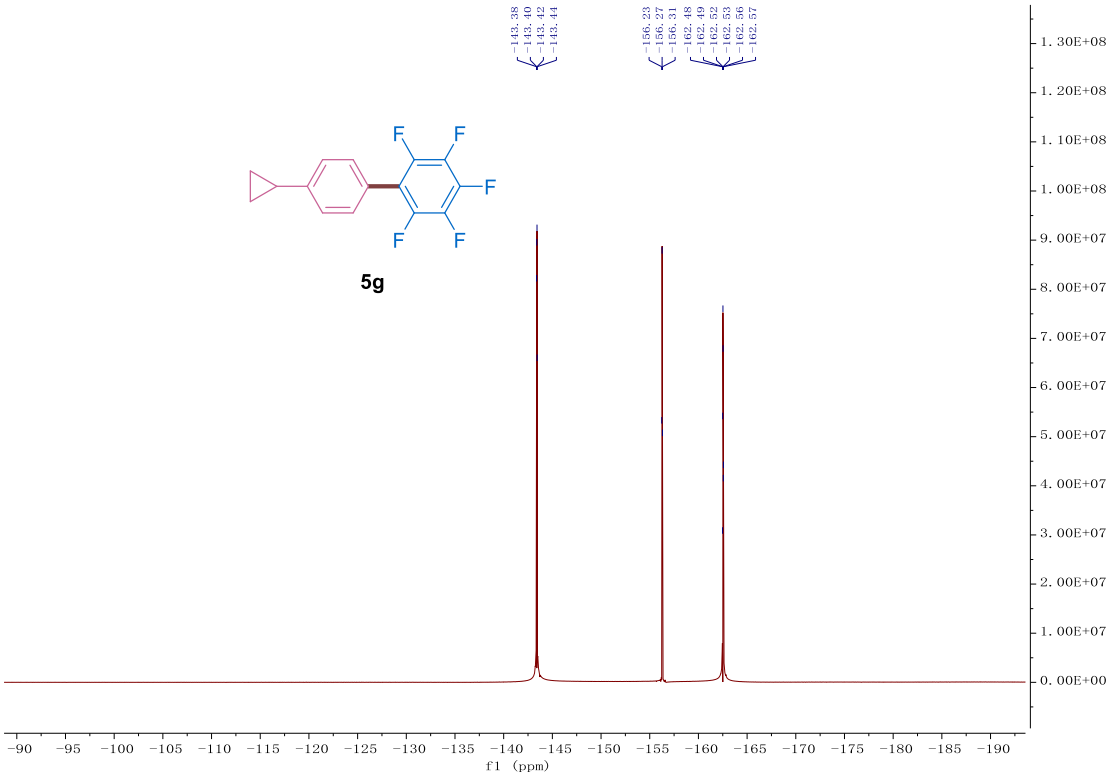
^{1}H NMR of 5g (600 MHz, $CDCl_3$)



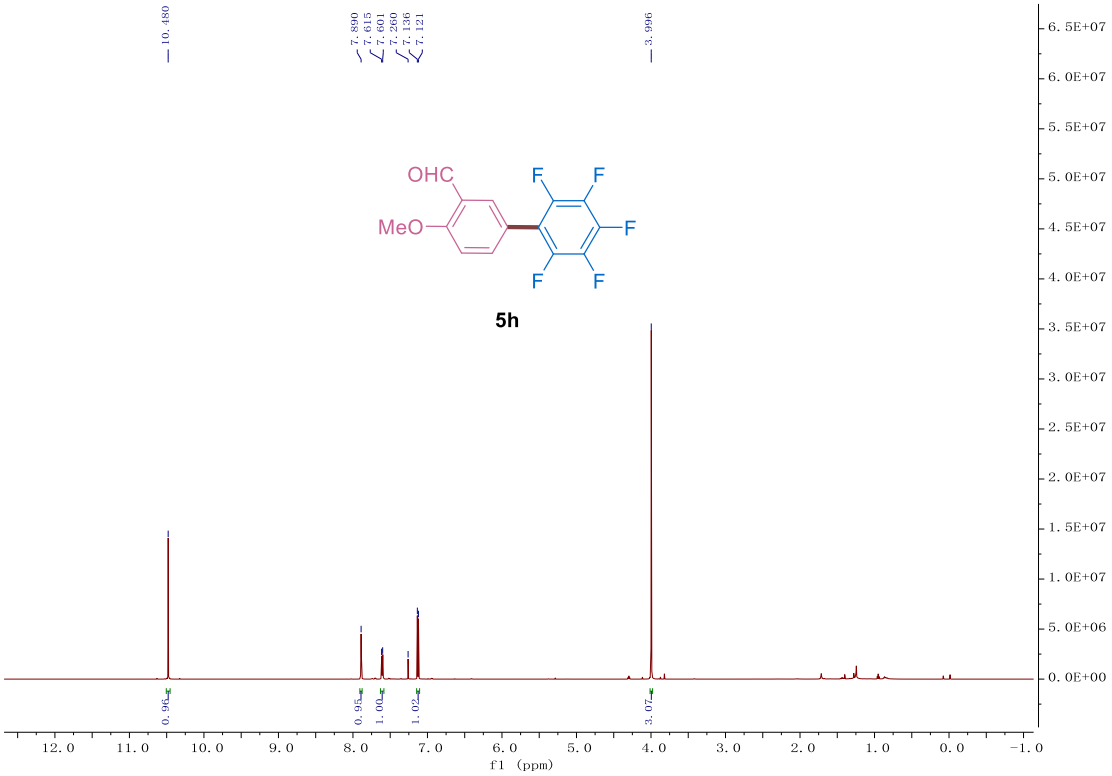
^{13}C NMR of 5g (151 MHz, $CDCl_3$)



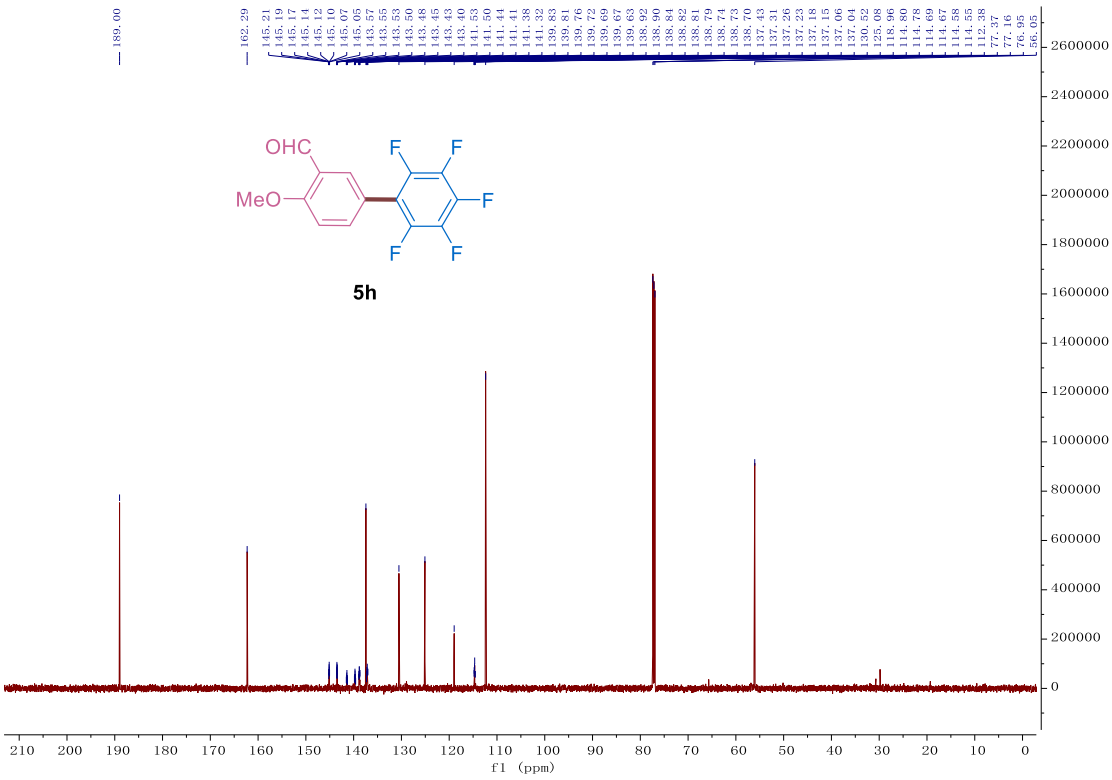
^{19}F NMR of 5g (565 MHz, $CDCl_3$)



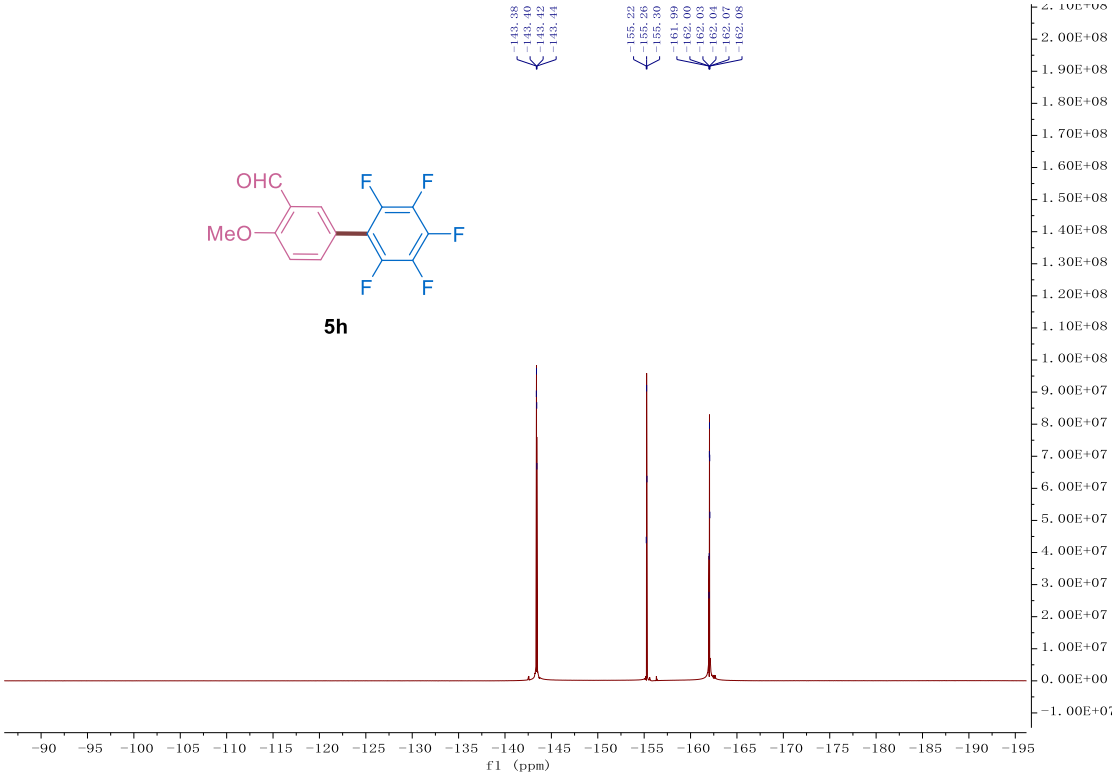
^{1}H NMR of 5h (600 MHz, $CDCl_3$)



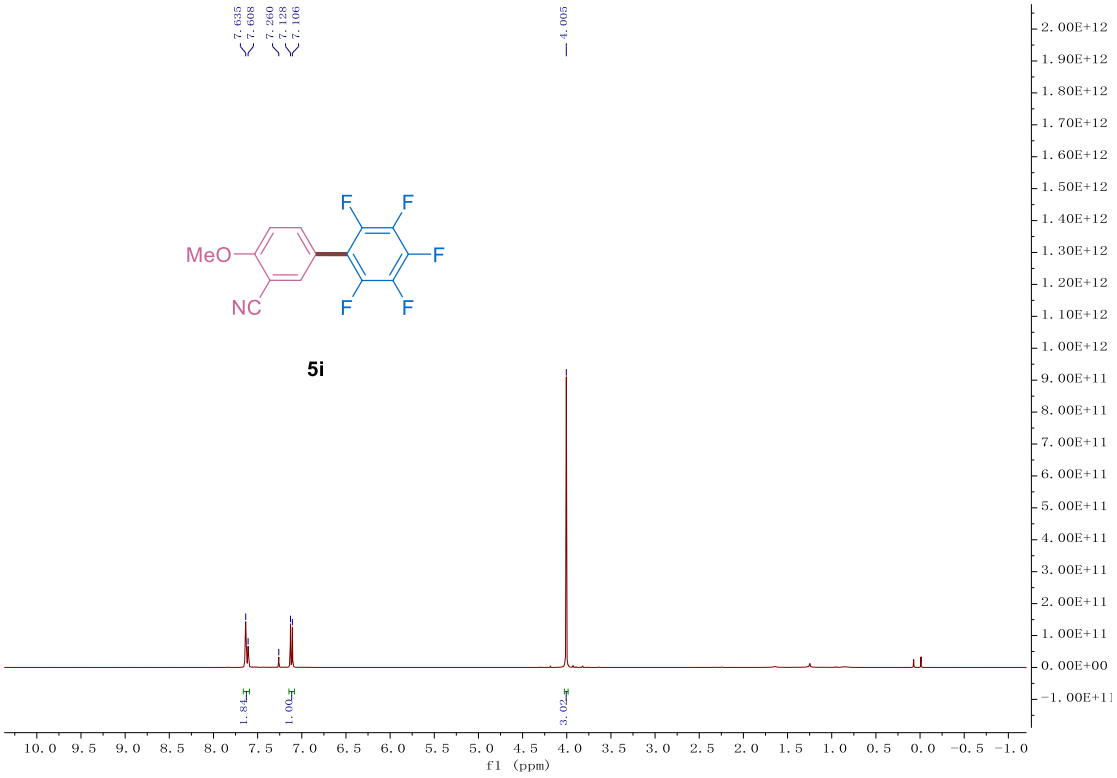
^{13}C NMR of 5h (151 MHz, $CDCl_3$)



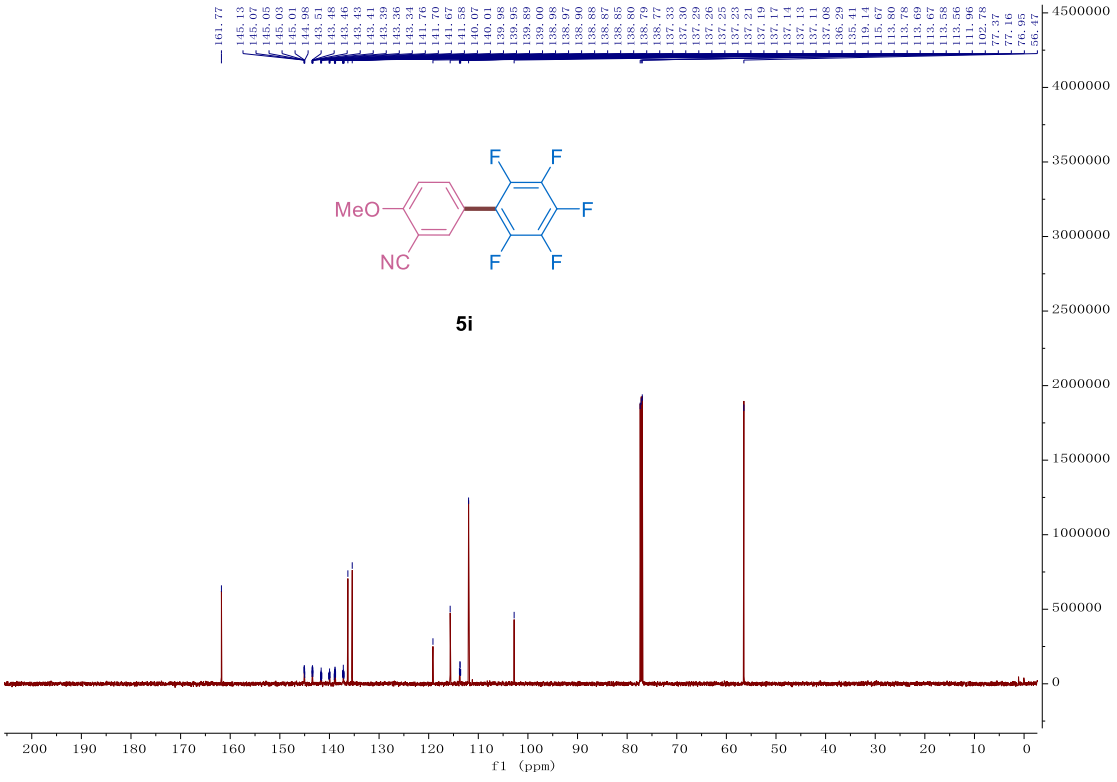
^{19}F NMR of 5h (565 MHz, $CDCl_3$)



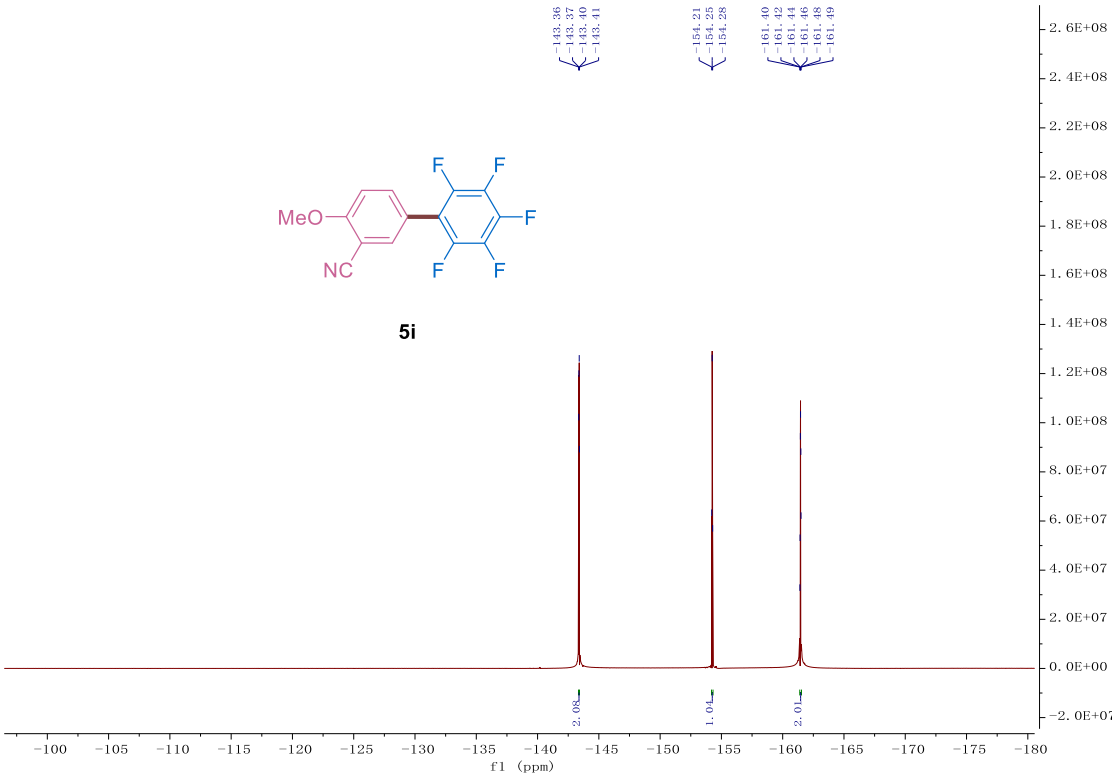
^{1}H NMR of 5i (400 MHz, $CDCl_3$)



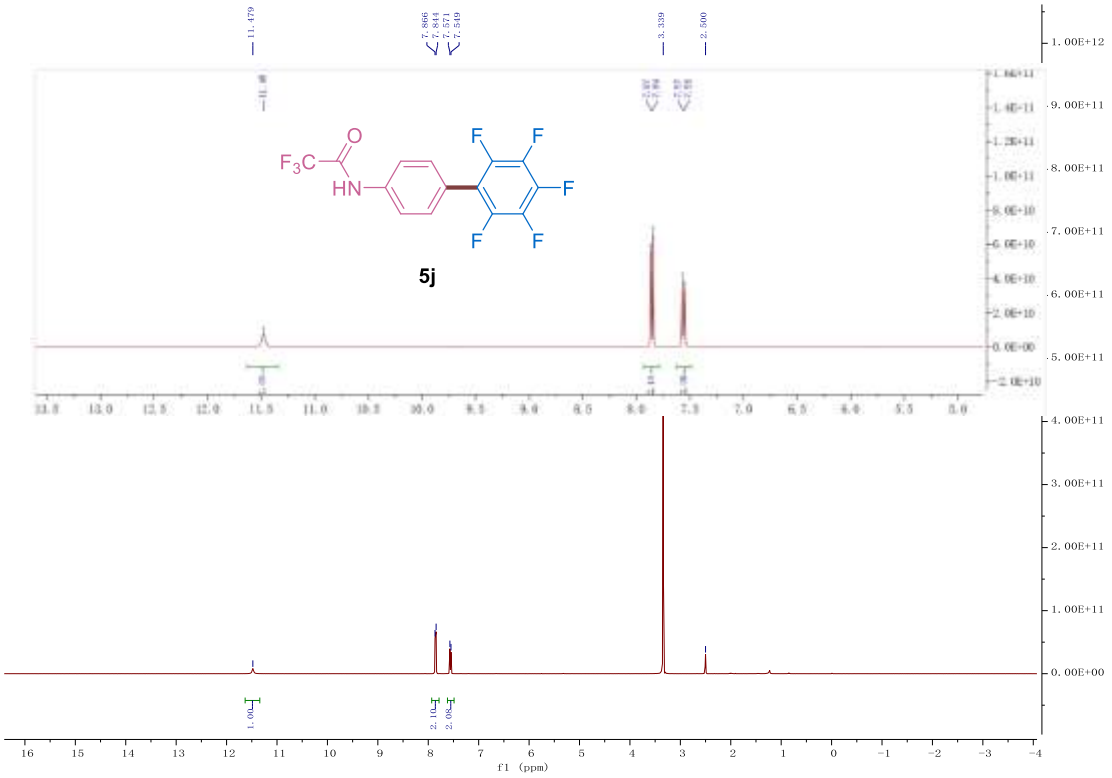
^{13}C NMR of 5i (151 MHz, $CDCl_3$)



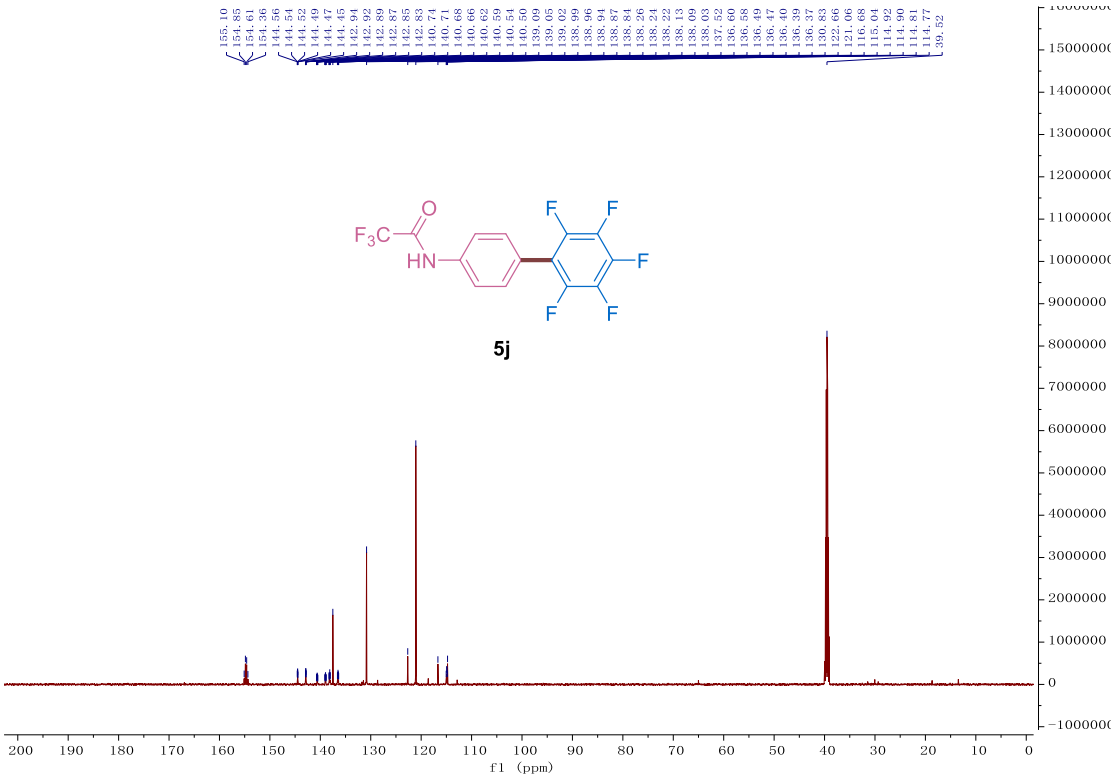
^{19}F NMR of 5i (565 MHz, $CDCl_3$)



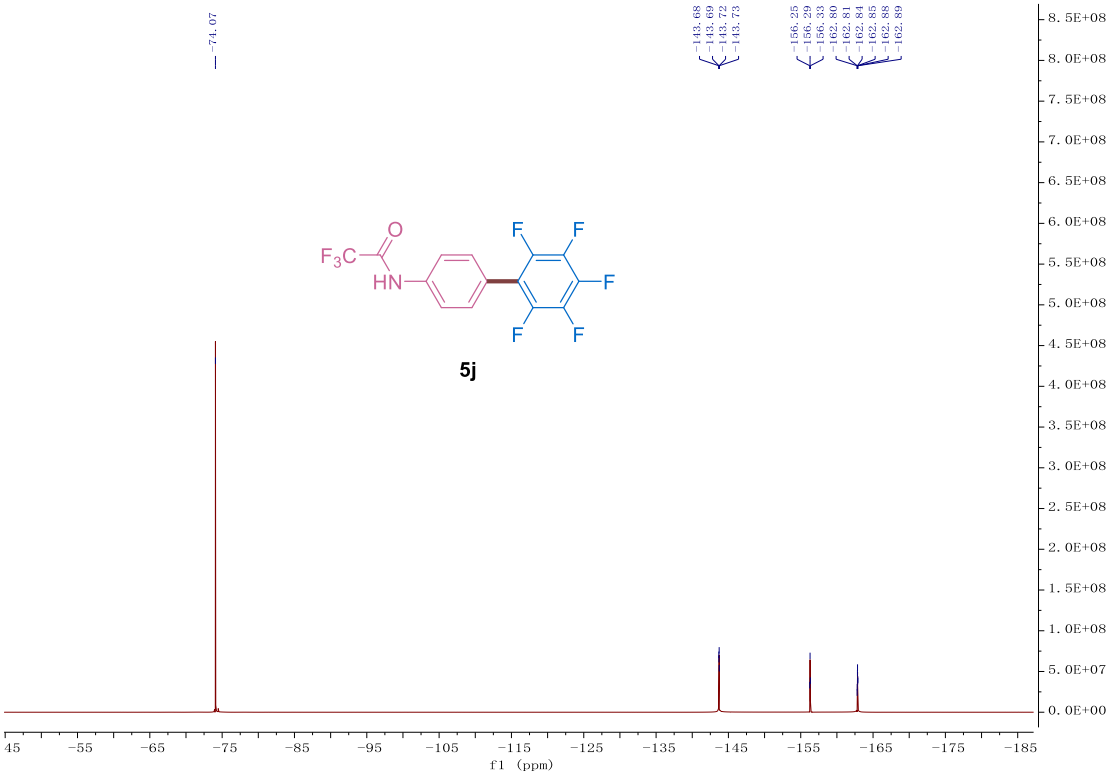
^{1}H NMR of 5j (400 MHz, DMSO-d6)



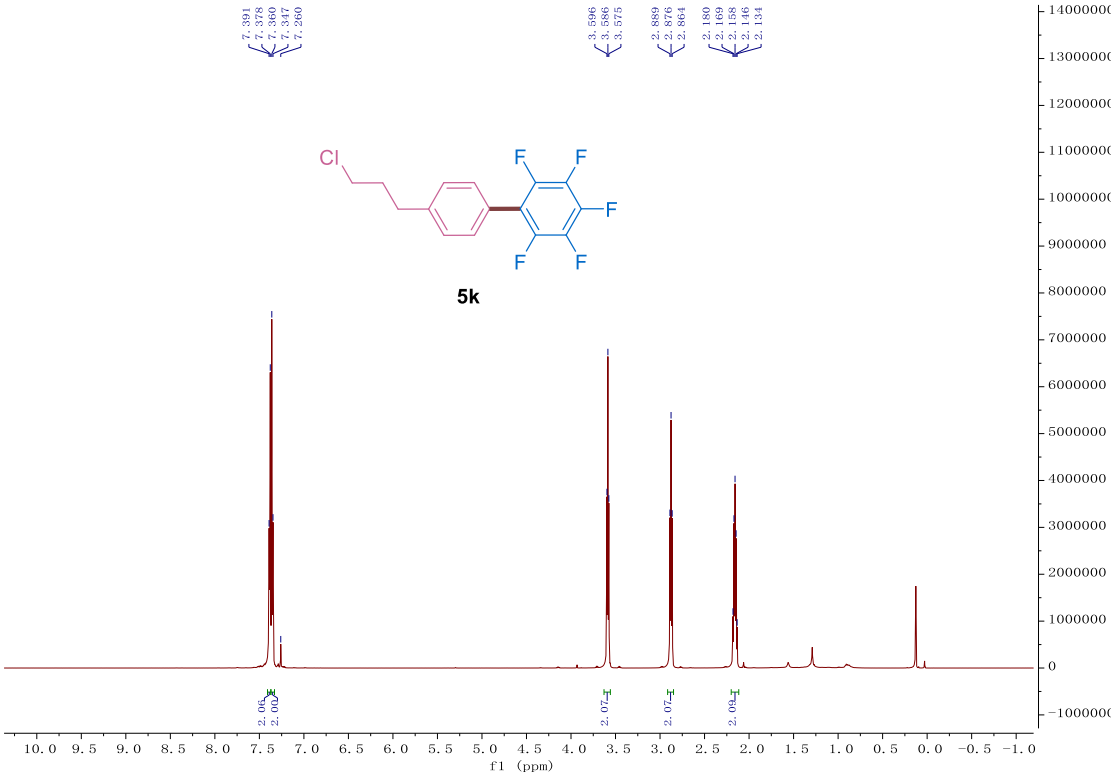
^{13}C NMR of 5j (151 MHz, DMSO-d6)



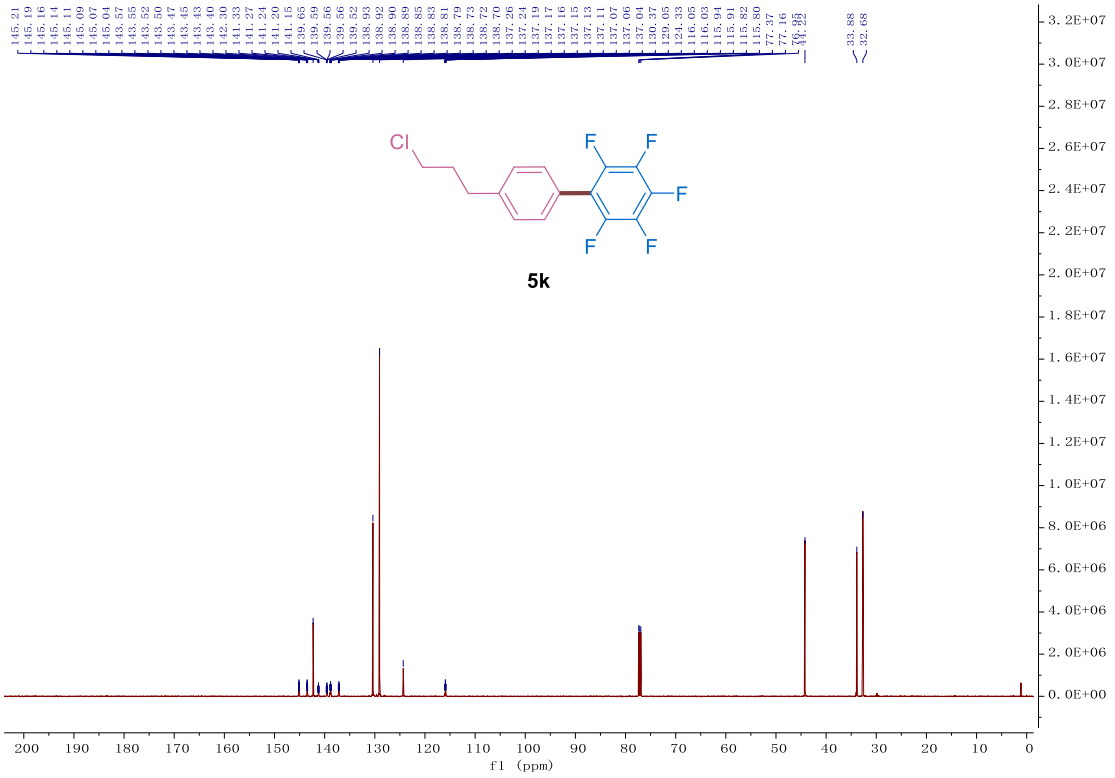
^{19}F NMR of 5j (565 MHz, DMSO-d6)



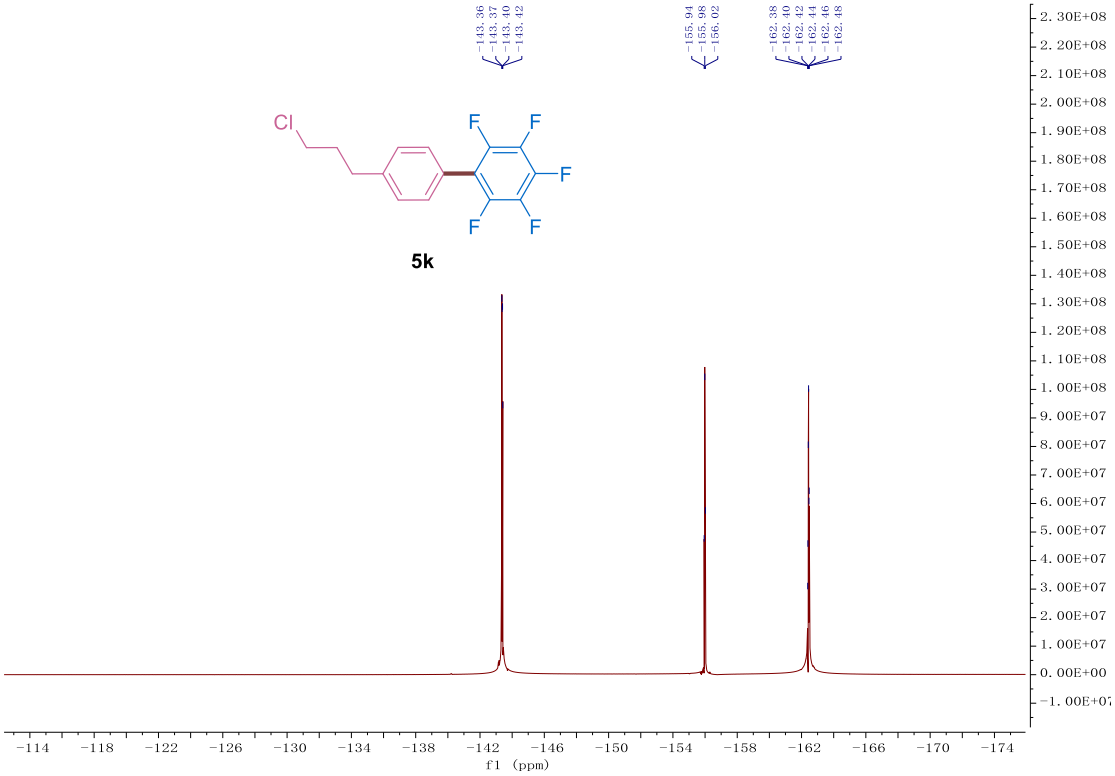
^{1}H NMR of 5k (400 MHz, $CDCl_3$)



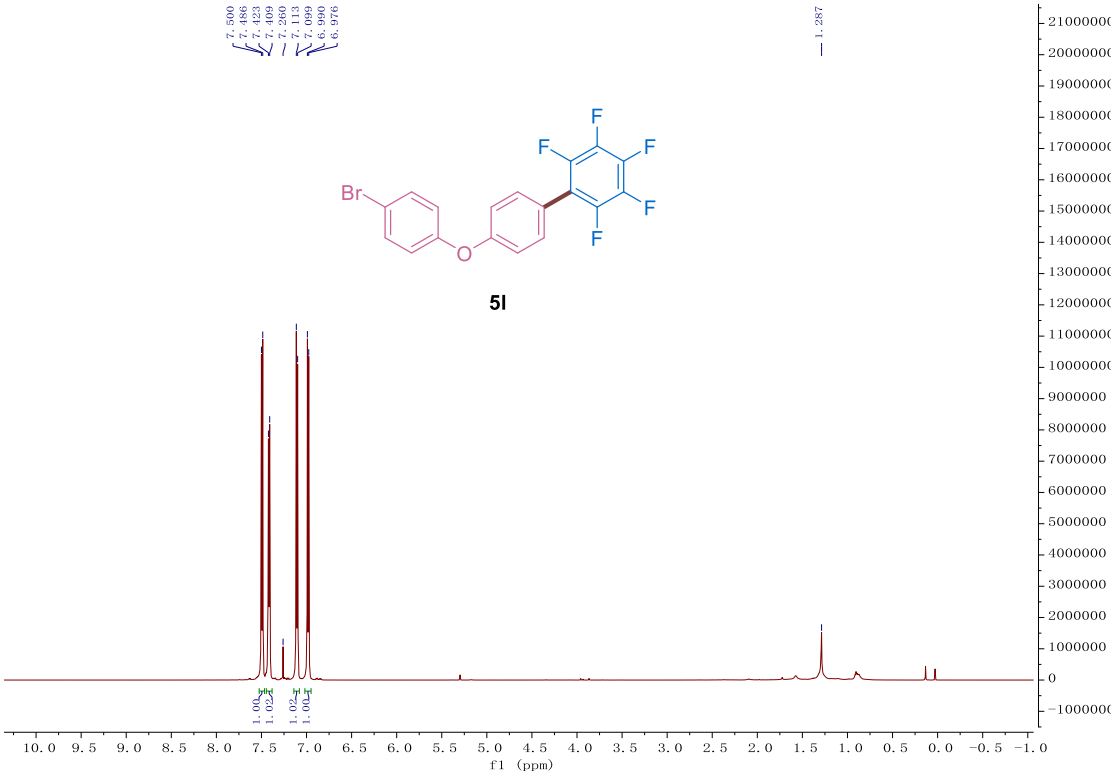
^{13}C NMR of 5k (151 MHz, $CDCl_3$)



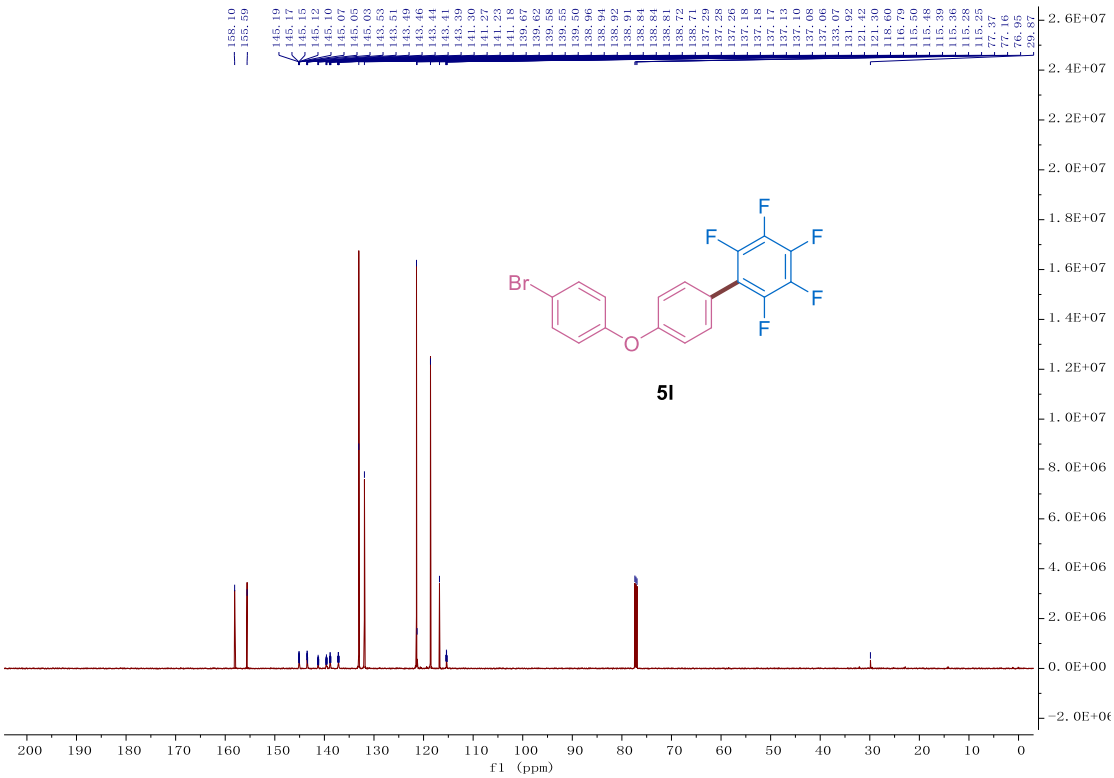
^{19}F NMR of 5k (565 MHz, $CDCl_3$)



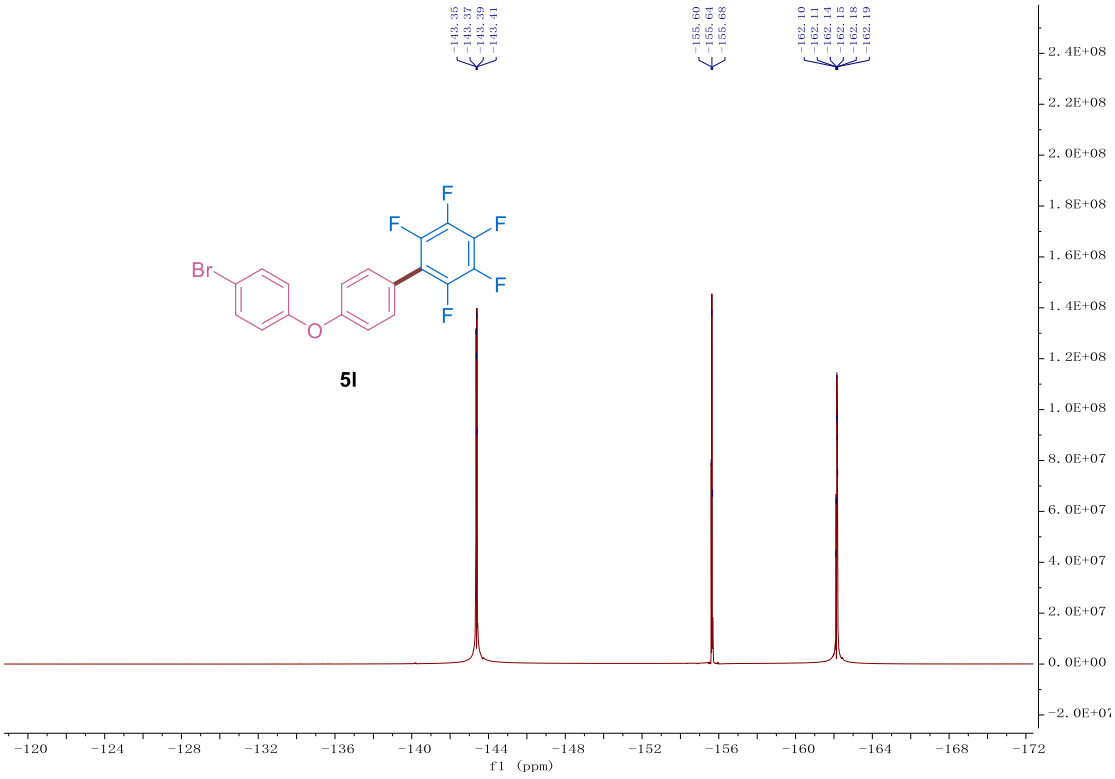
^{1}H NMR of 5l (600 MHz, $CDCl_3$)



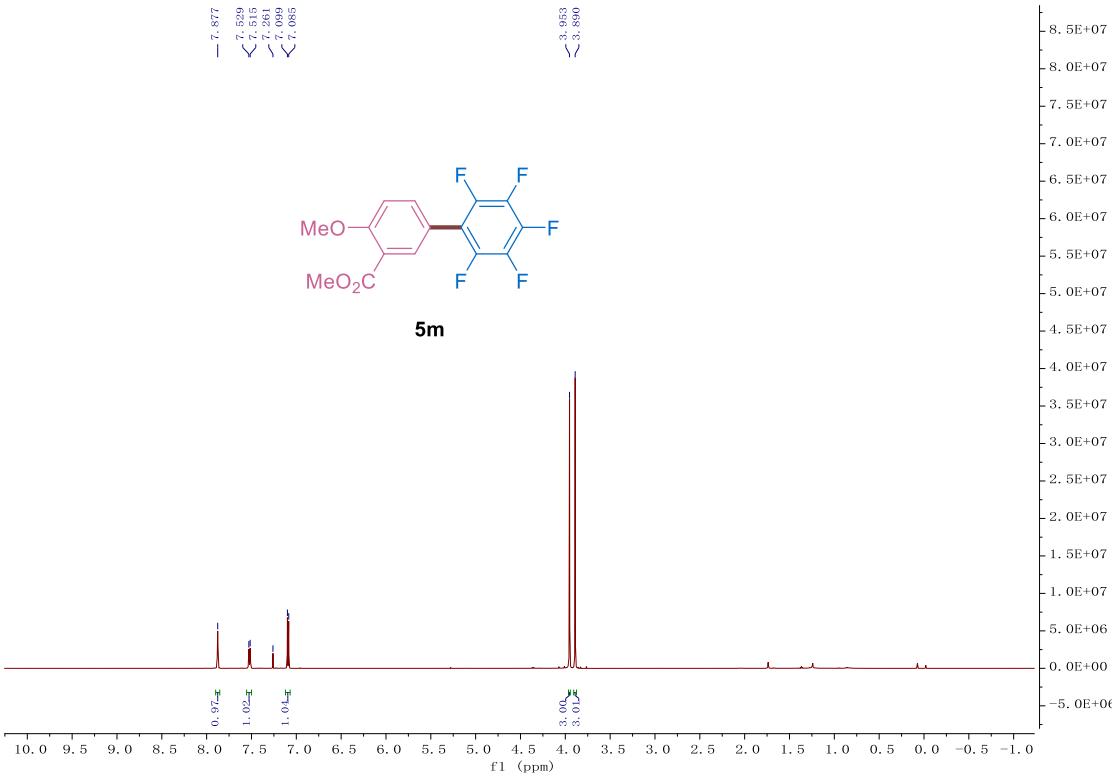
^{13}C NMR of 5l (151 MHz, $CDCl_3$)



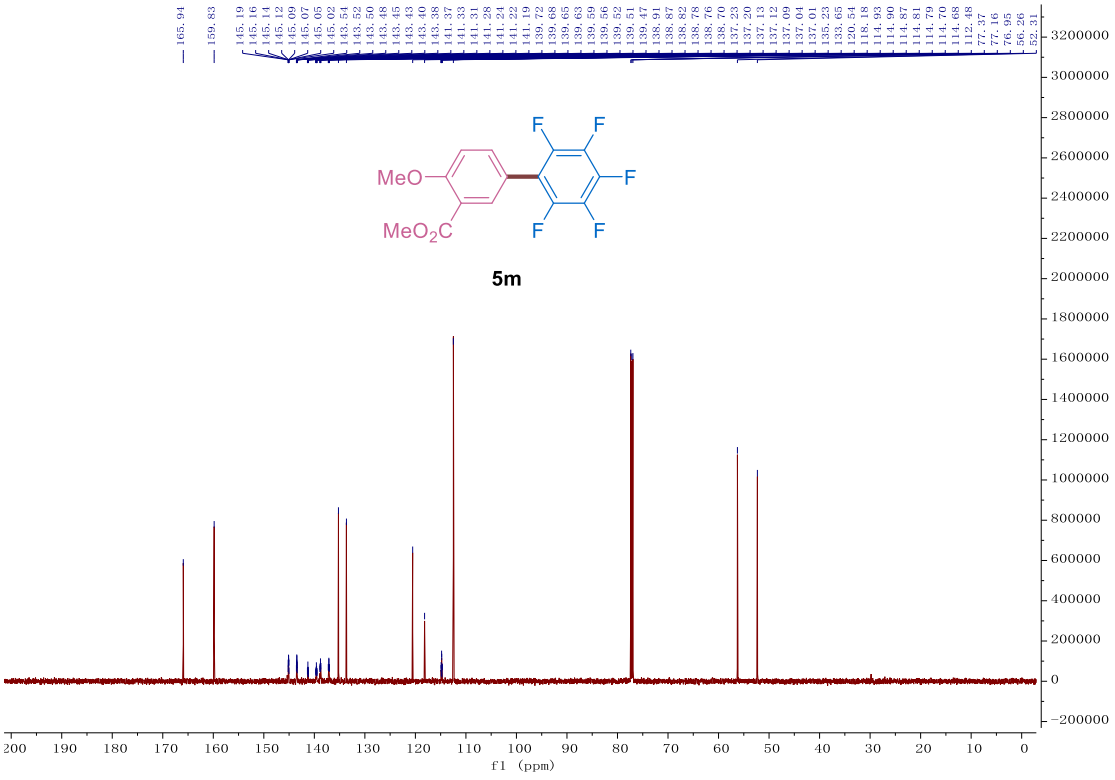
^{19}F NMR of 5l (565 MHz, $CDCl_3$)



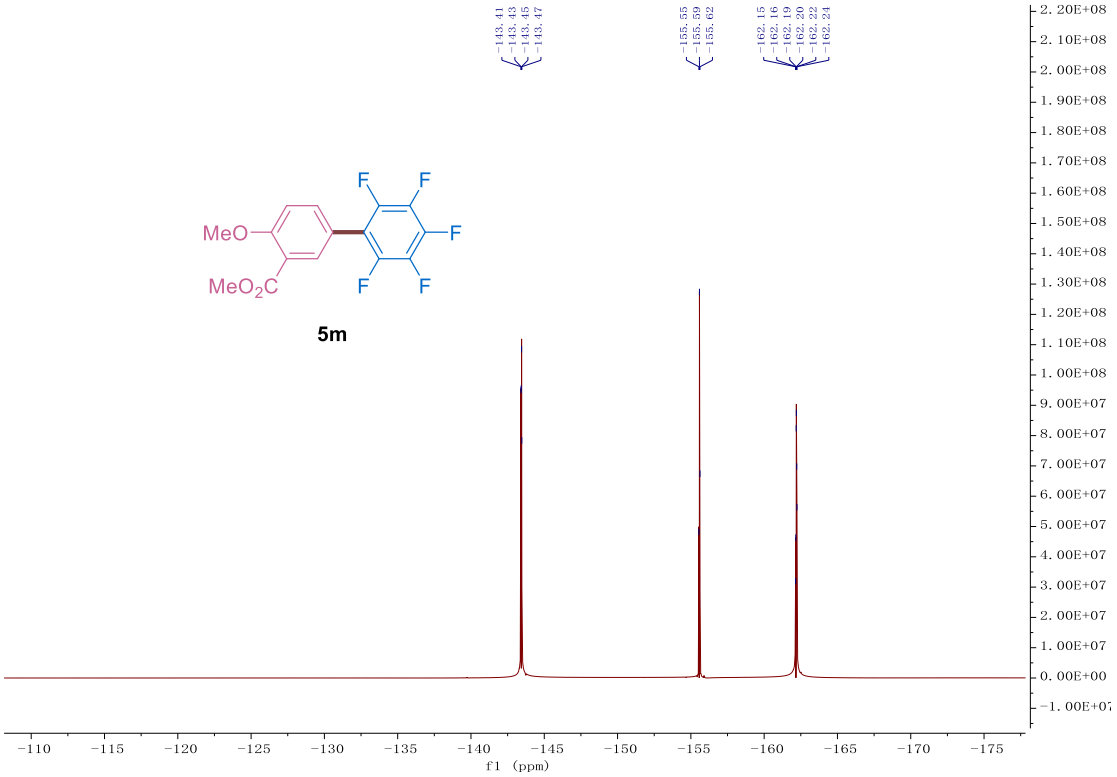
^{1}H NMR of 5m (600 MHz, $CDCl_3$)



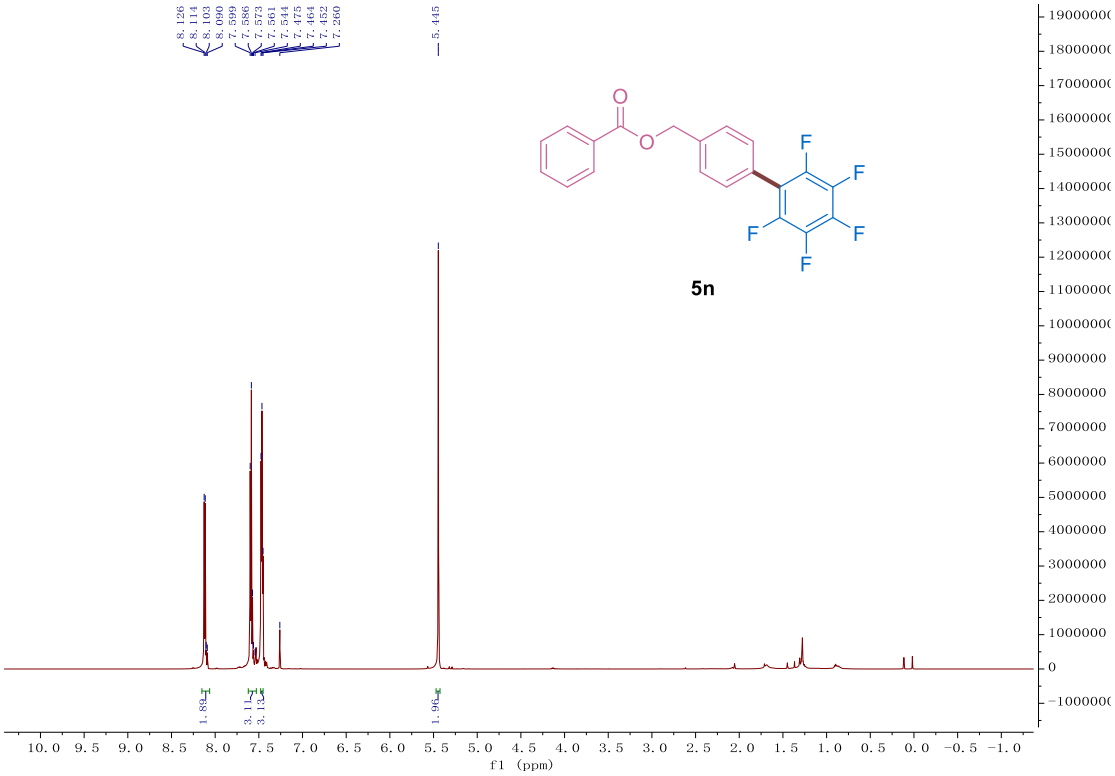
^{13}C NMR of 5m (151 MHz, $CDCl_3$)



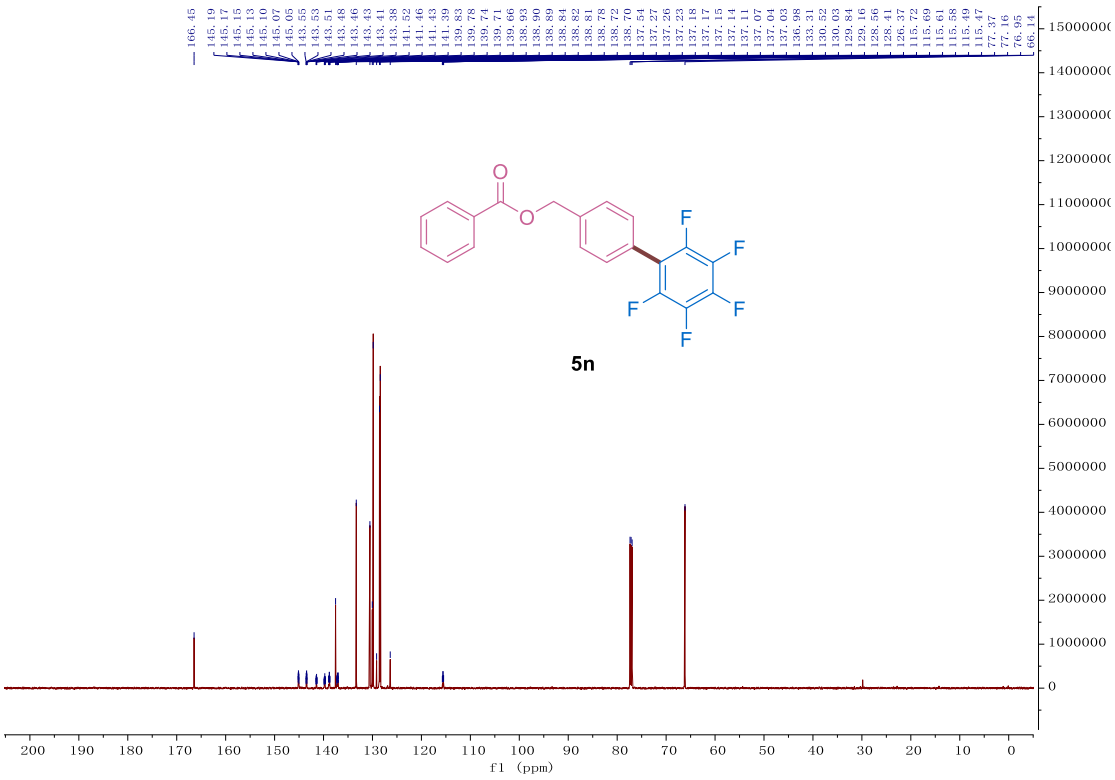
^{19}F NMR of 5m (565 MHz, $CDCl_3$)



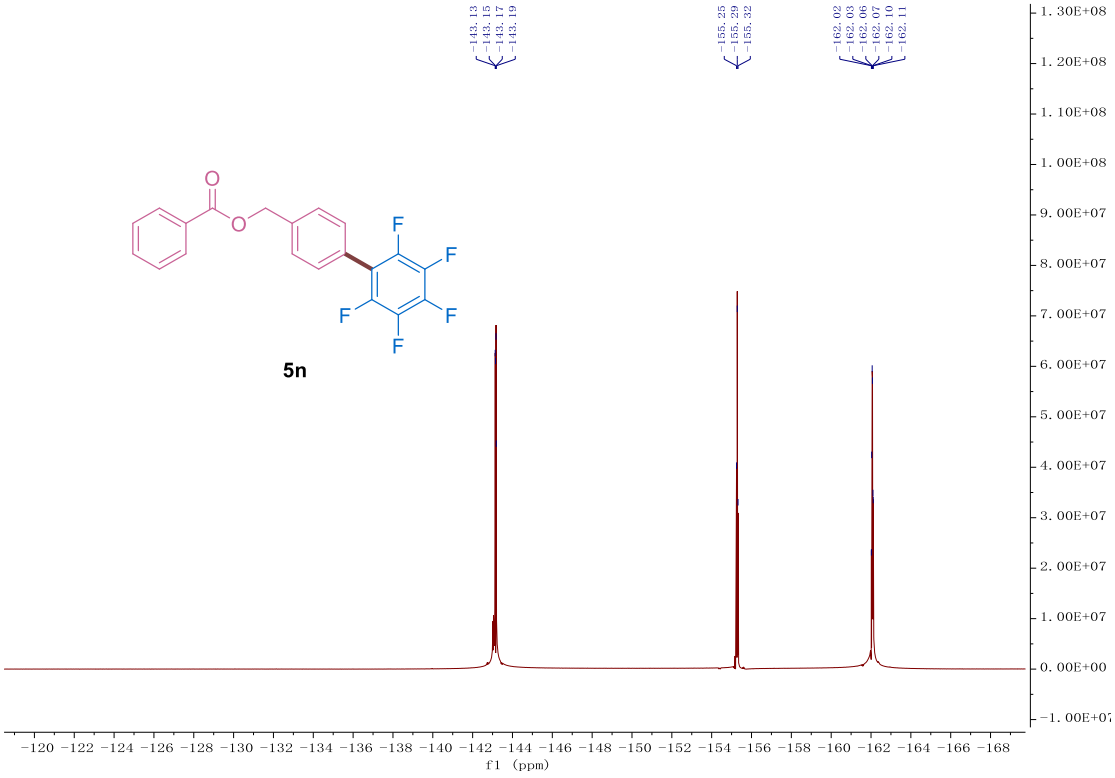
^{1}H NMR of 5n (600 MHz, CDC_3)



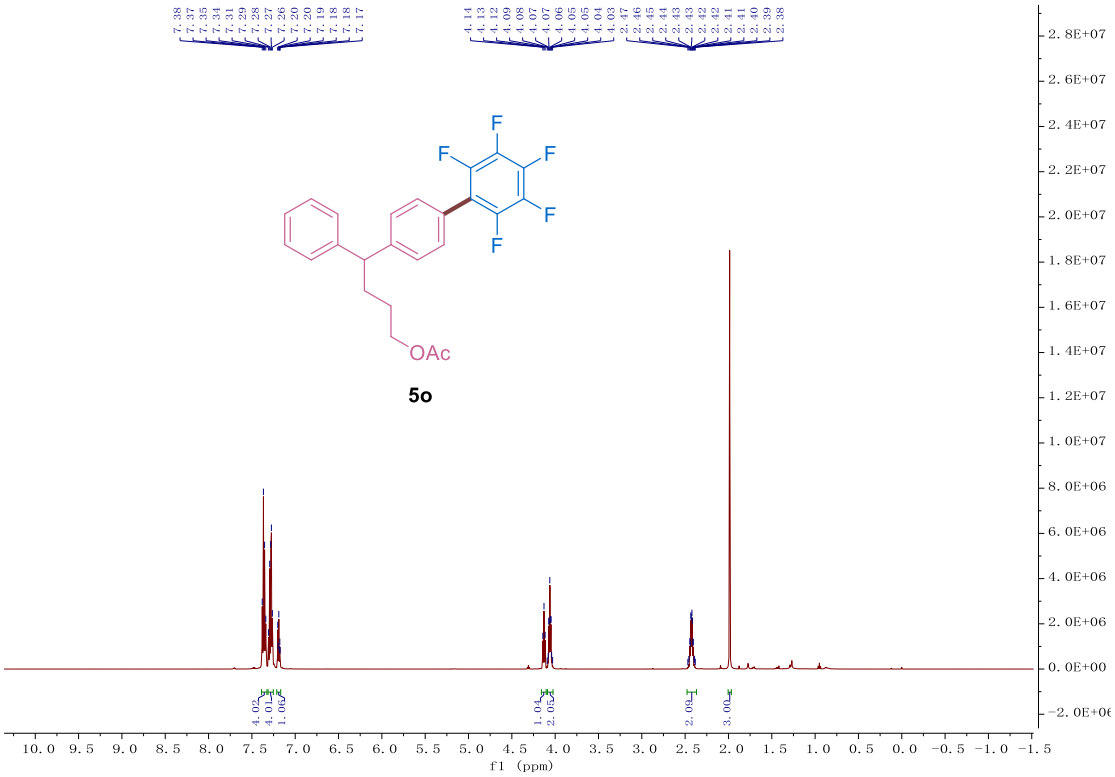
^{13}C NMR of 5n (151 MHz, $CDCl_3$)



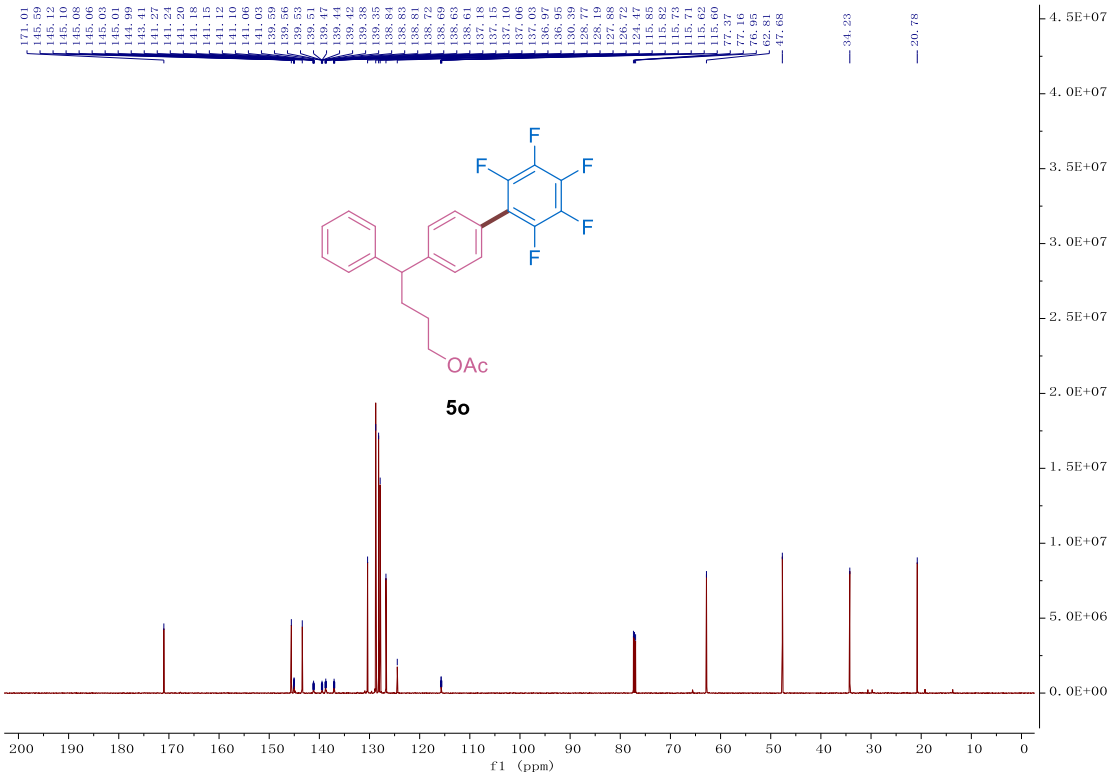
^{19}F NMR of 5n (565 MHz, $CDCl_3$)



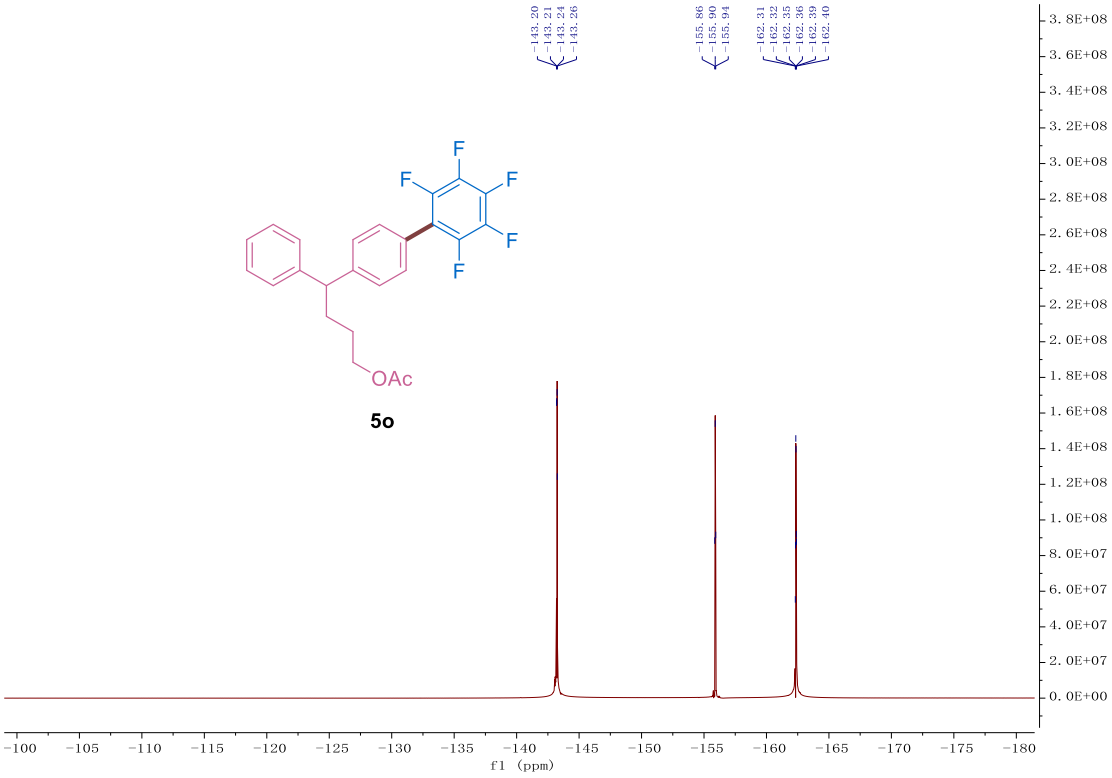
^{1}H NMR of 5o (600 MHz, $CDCl_3$)



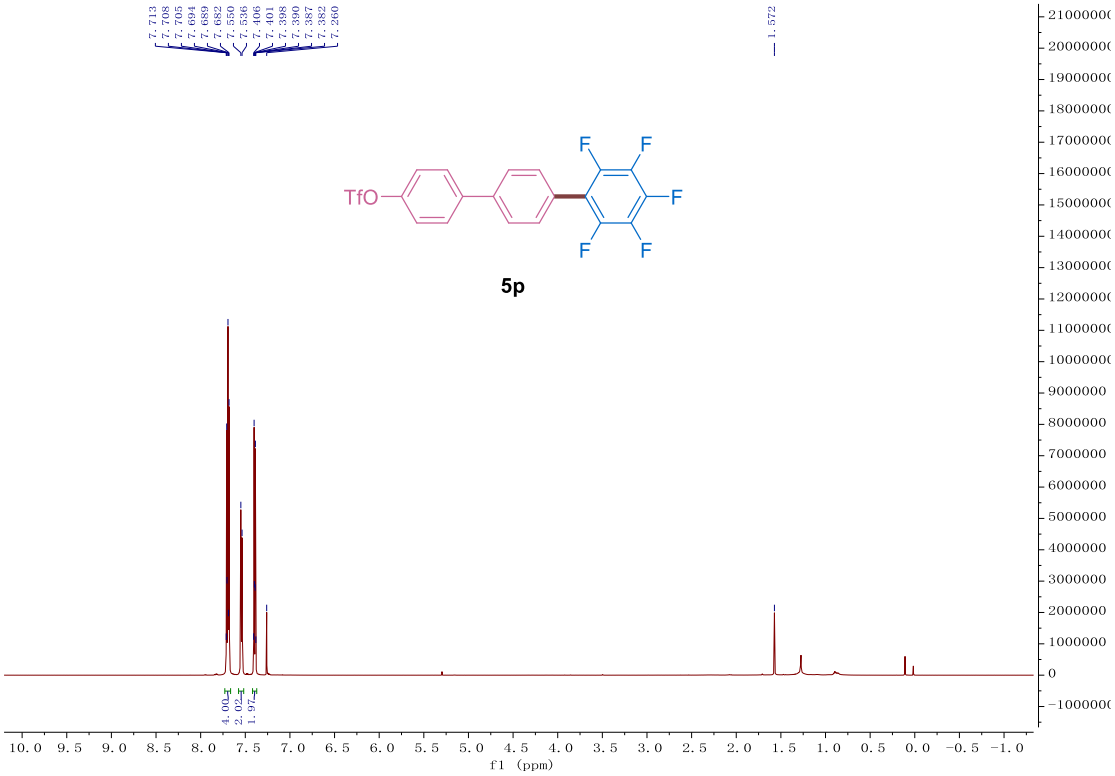
^{13}C NMR of 5o (151 MHz, $CDCl_3$)



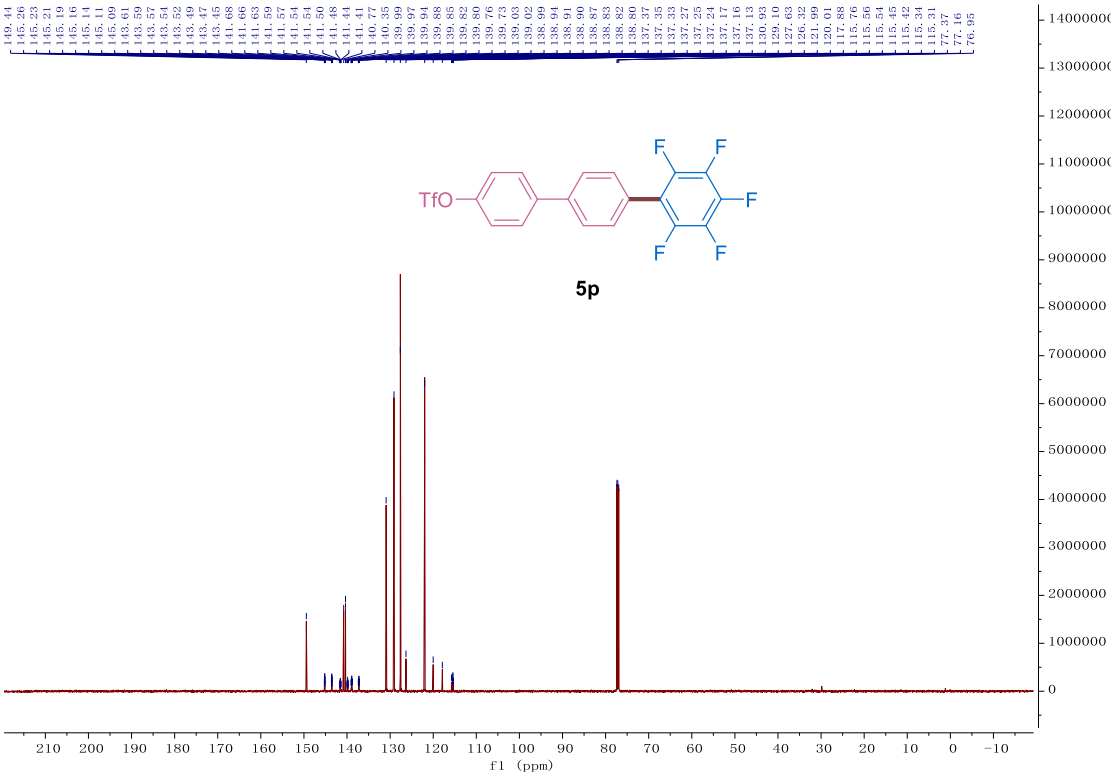
^{19}F NMR of 5o (565 MHz, $CDCl_3$)



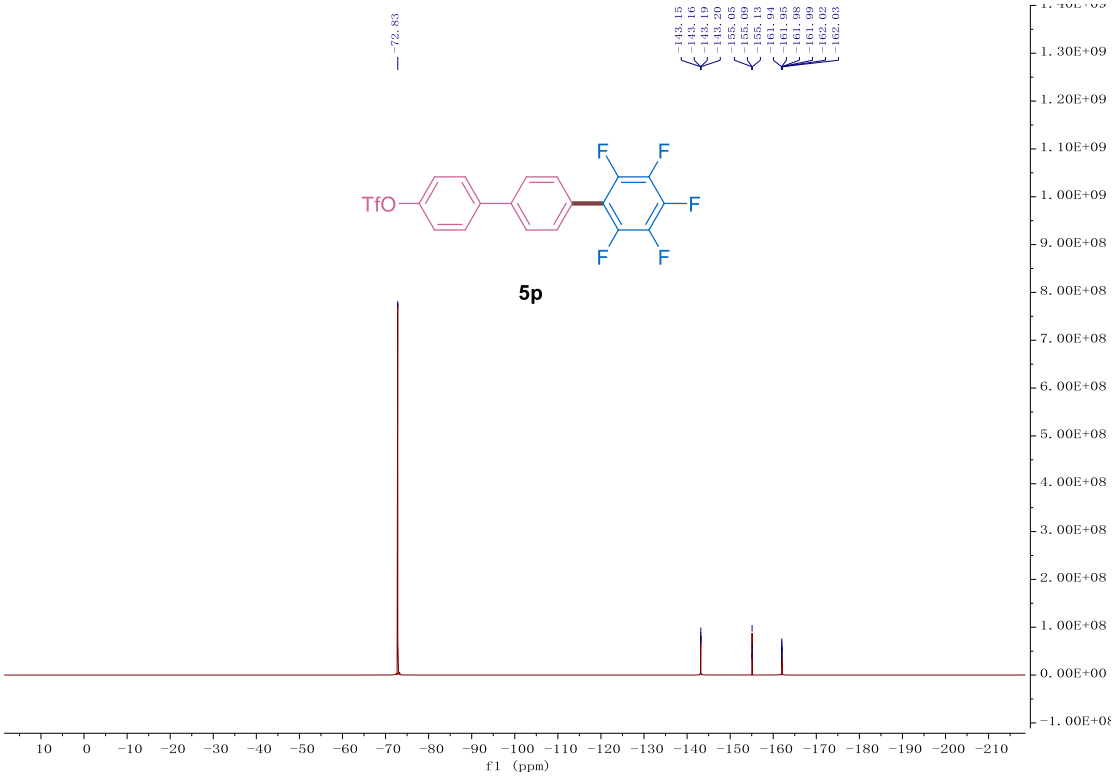
^{1}H NMR of 5p (600 MHz, CDC_3)



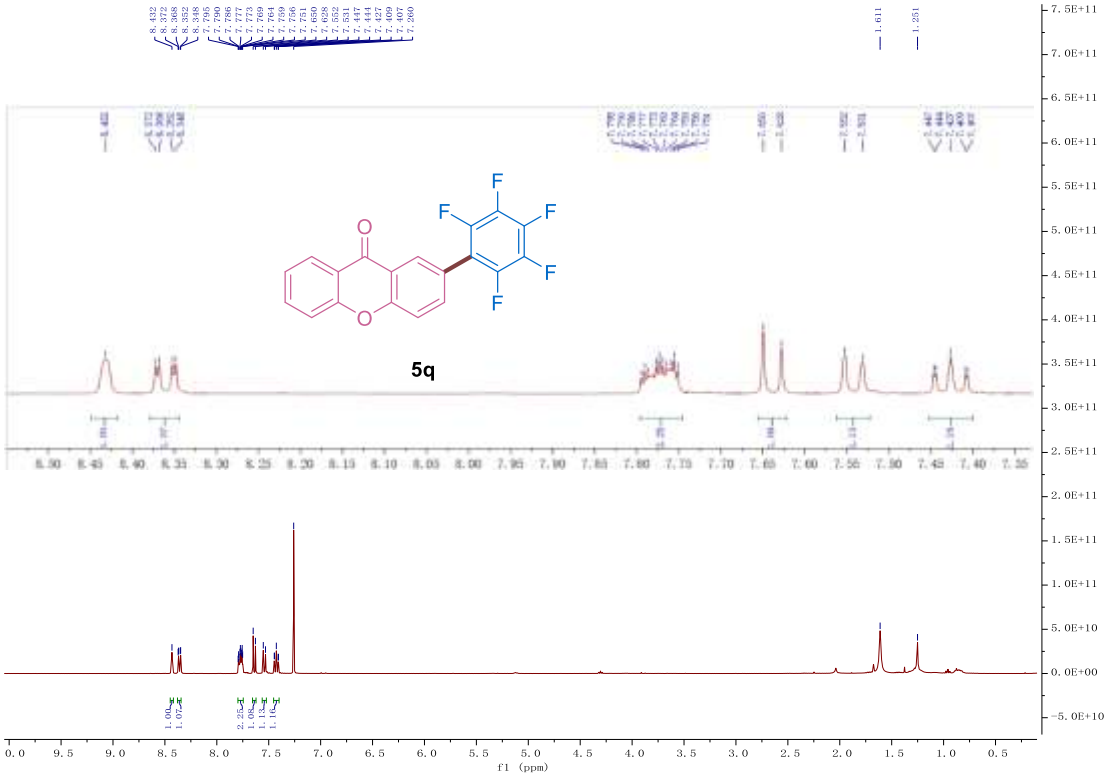
^{13}C NMR of 5p (151 MHz, $CDCl_3$)



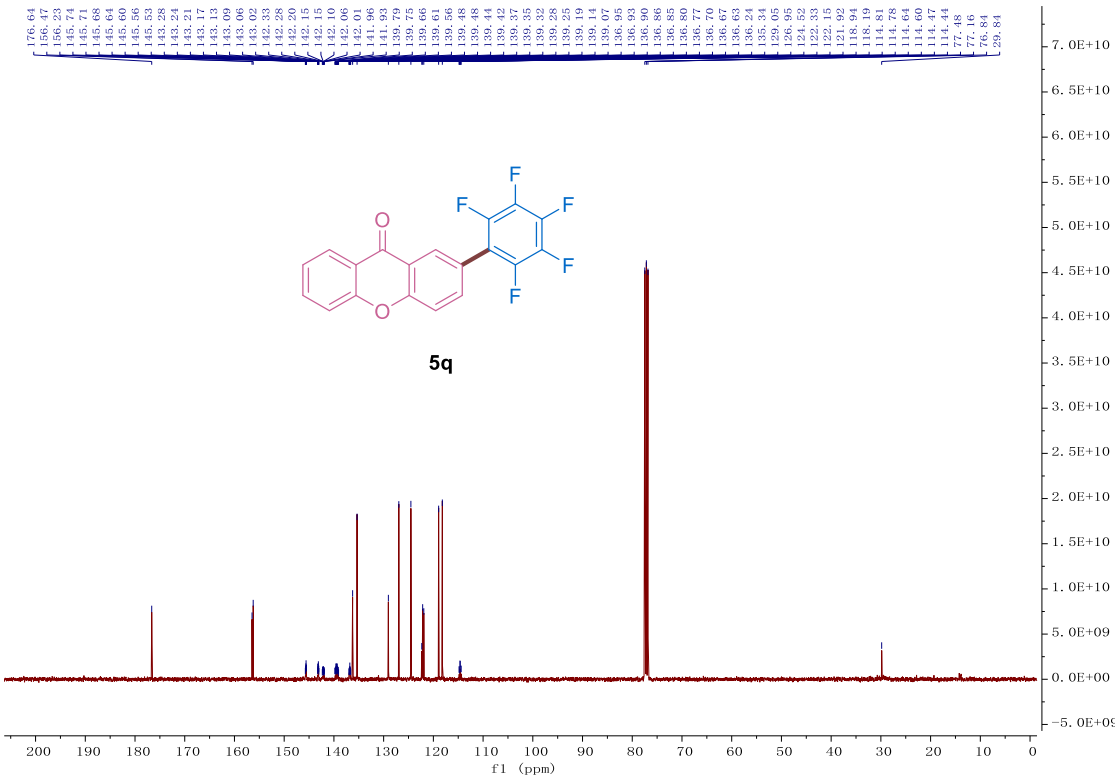
^{19}F NMR of 5p (565 MHz, $CDCl_3$)



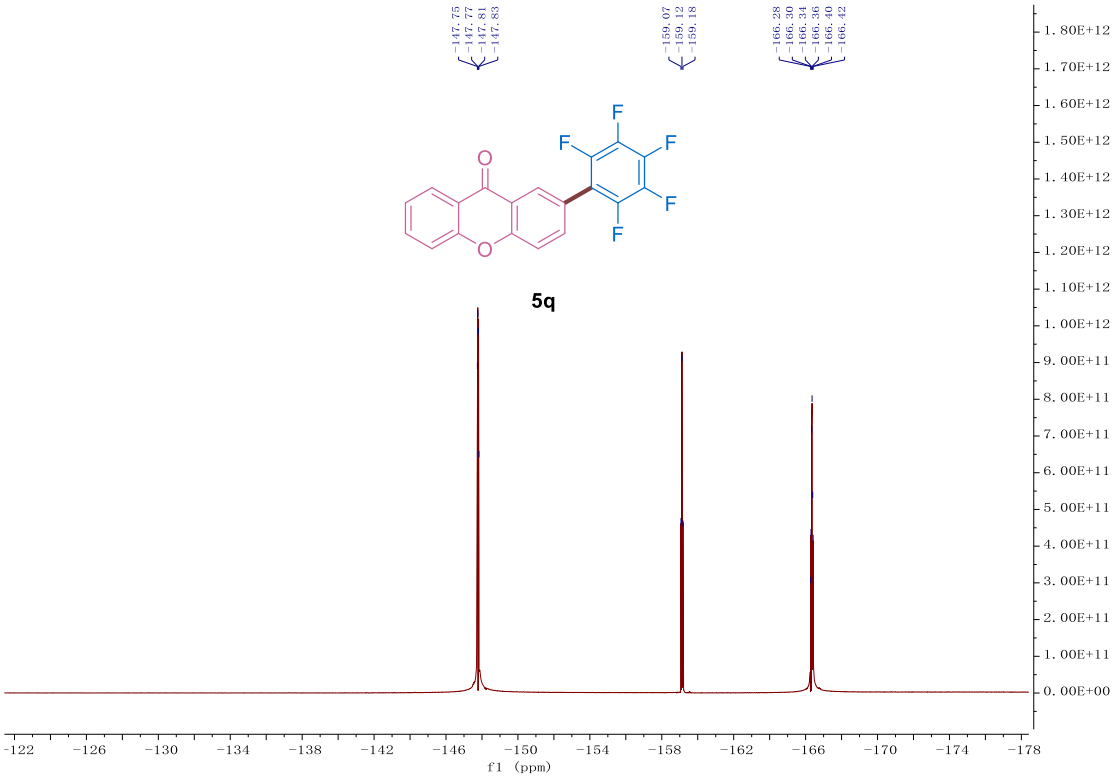
1H NMR of 5q (400 MHz, $CDCl_3$)



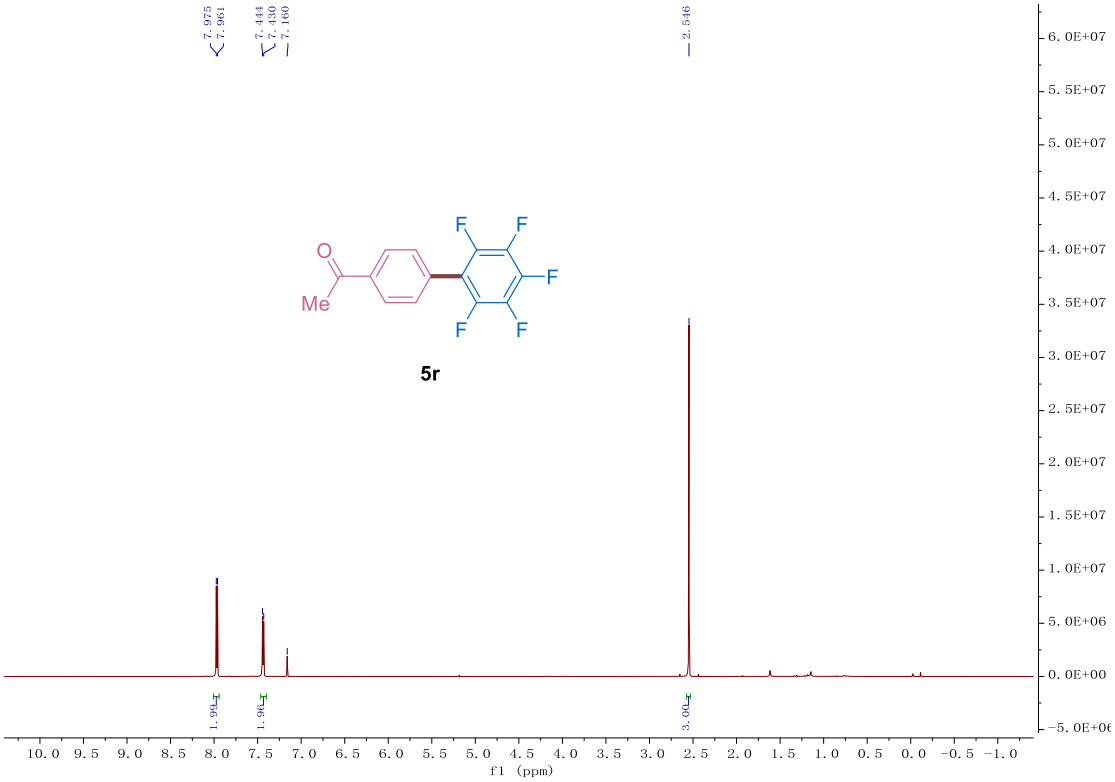
^{13}C NMR of 5q (101 MHz, $CDCl_3$)



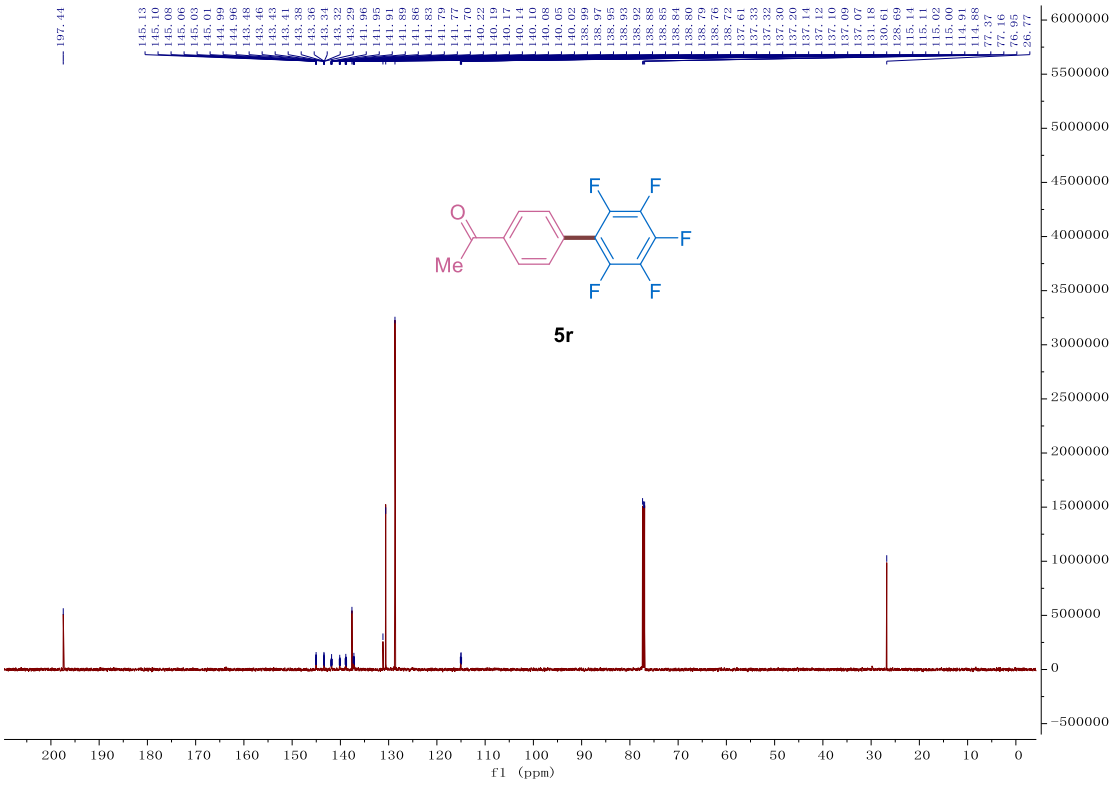
^{19}F NMR of 5q (376 MHz, $CDCl_3$)



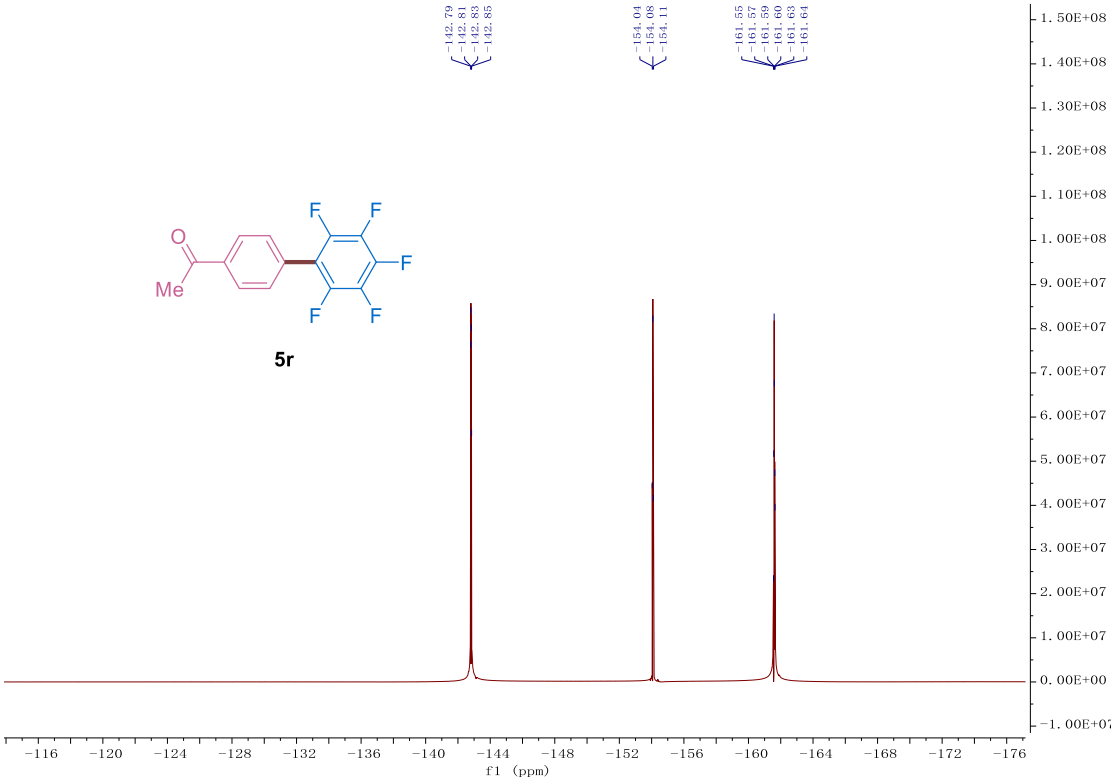
^{1}H NMR of 5r (600 MHz, $CDCl_3$)



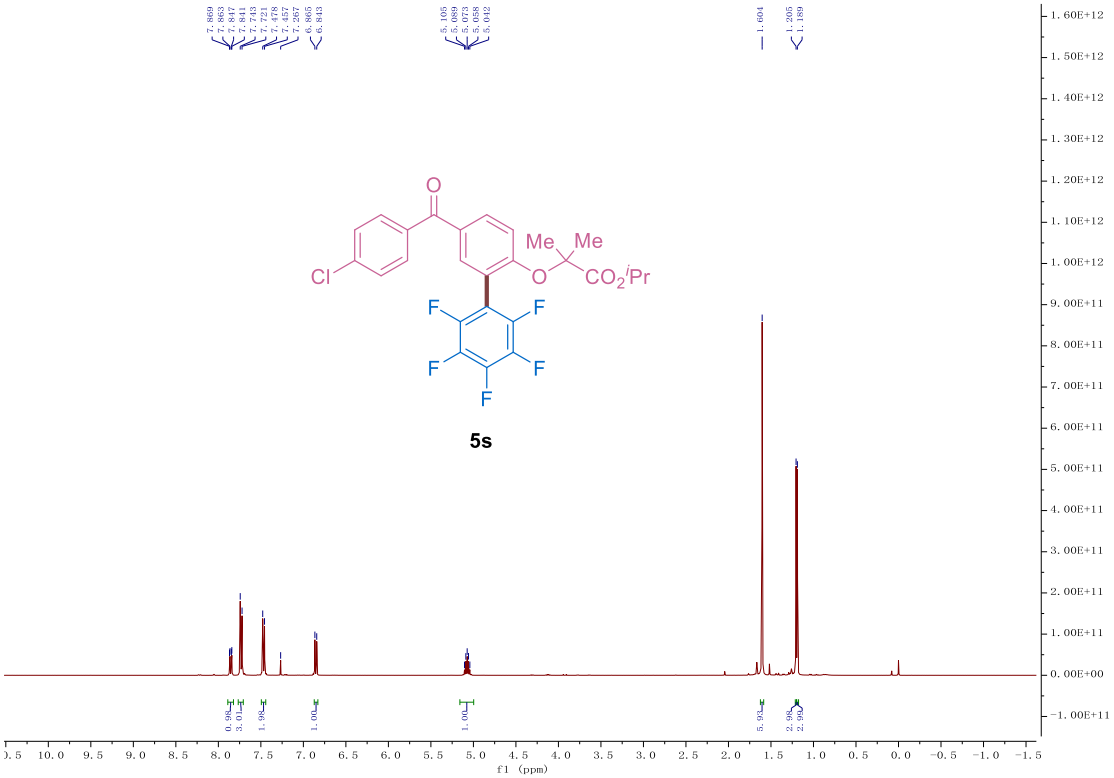
^{13}C NMR of 5r (151 MHz, $CDCl_3$)



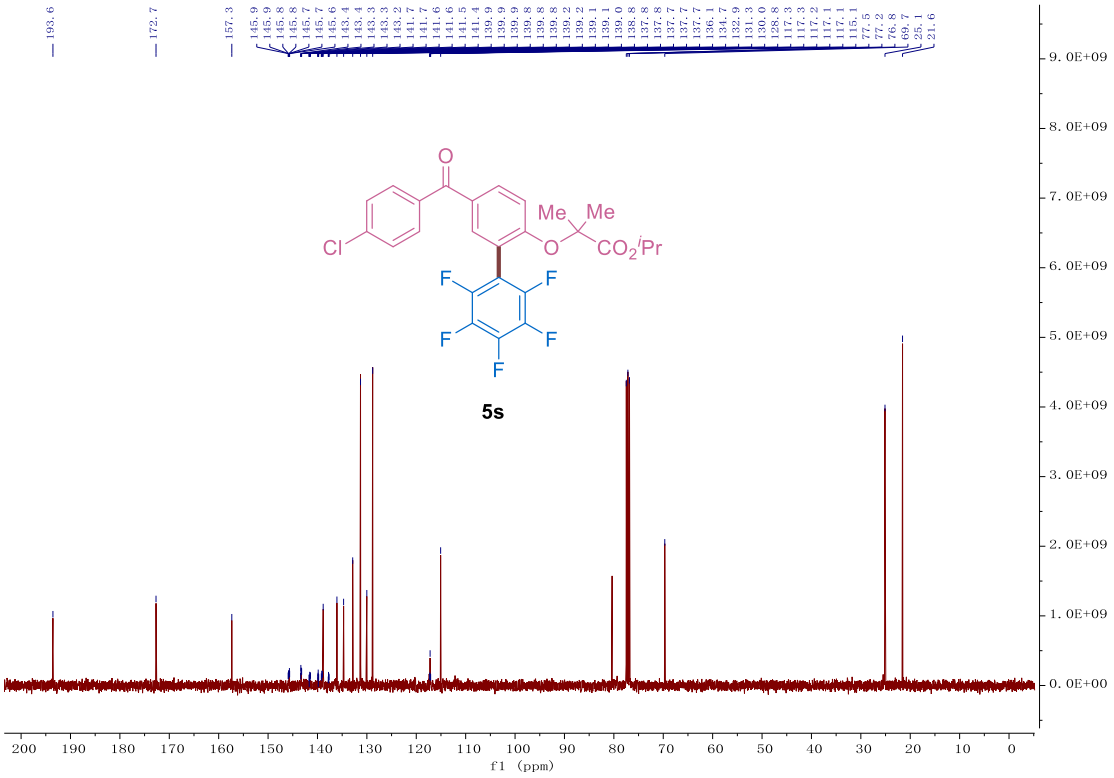
^{19}F NMR of 5r (565 MHz, $CDCl_3$)



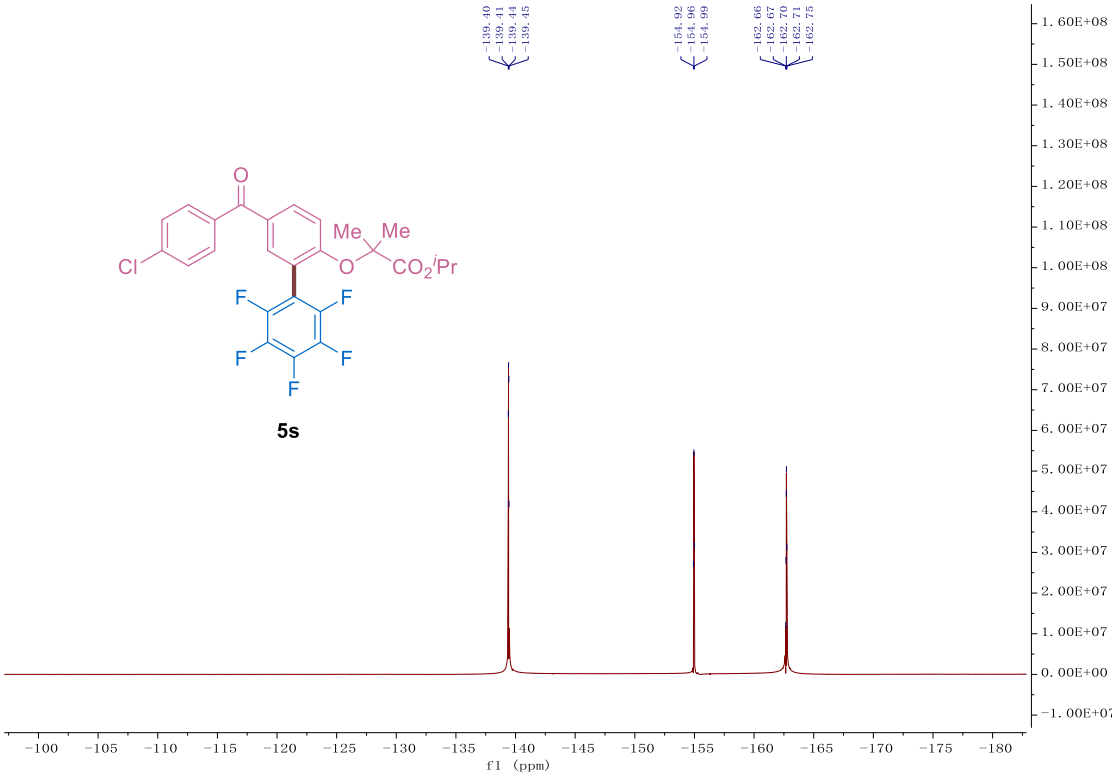
^{1}H NMR of 5s (400 MHz, $CDCl_3$)



^{13}C NMR of 5s (101 MHz, $CDCl_3$)

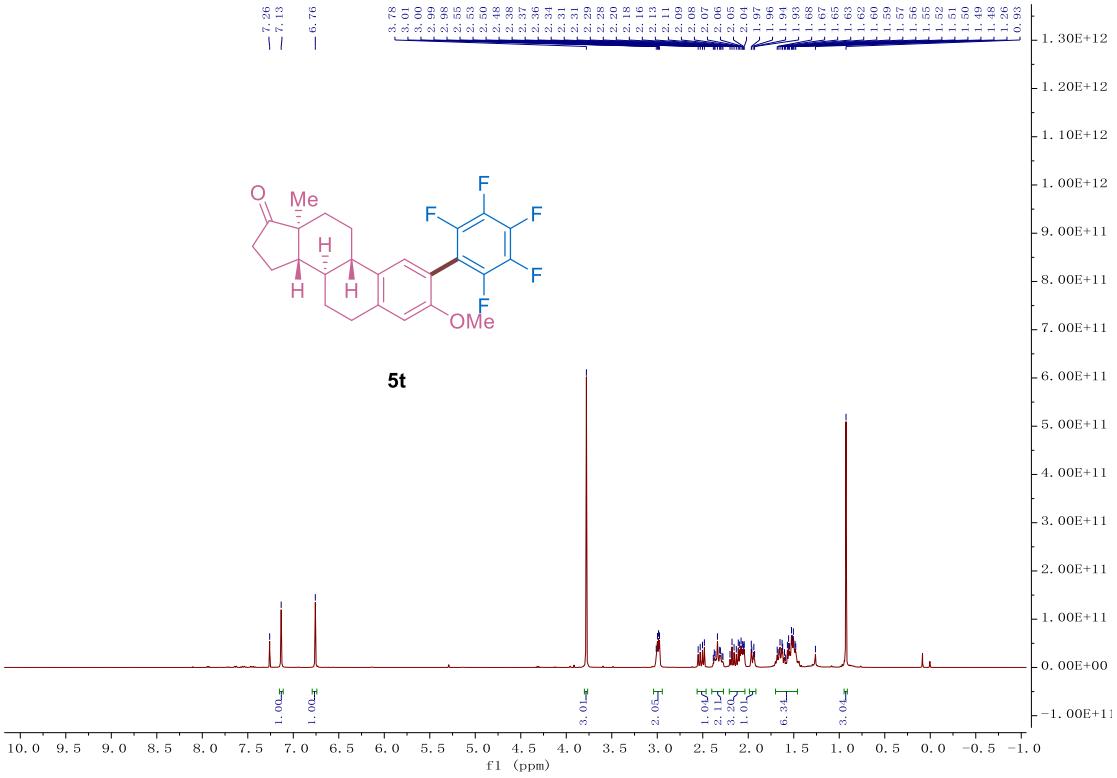


^{19}F NMR of 5s (565 MHz, $CDCl_3$)

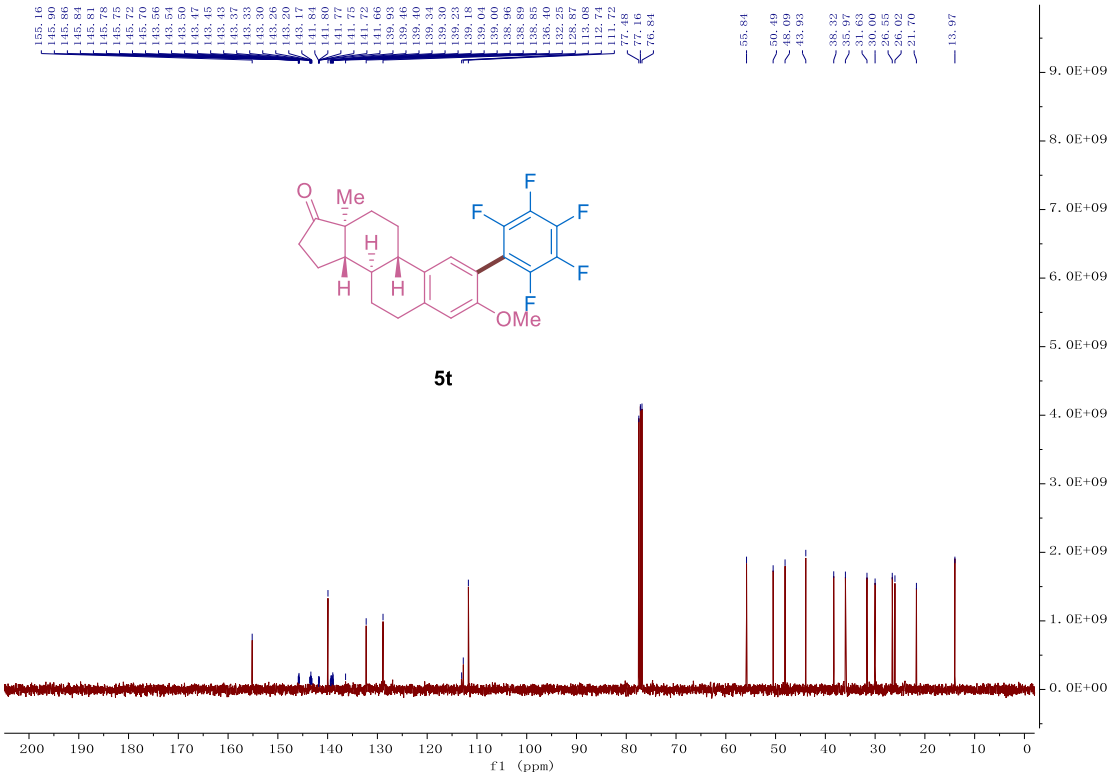


5s

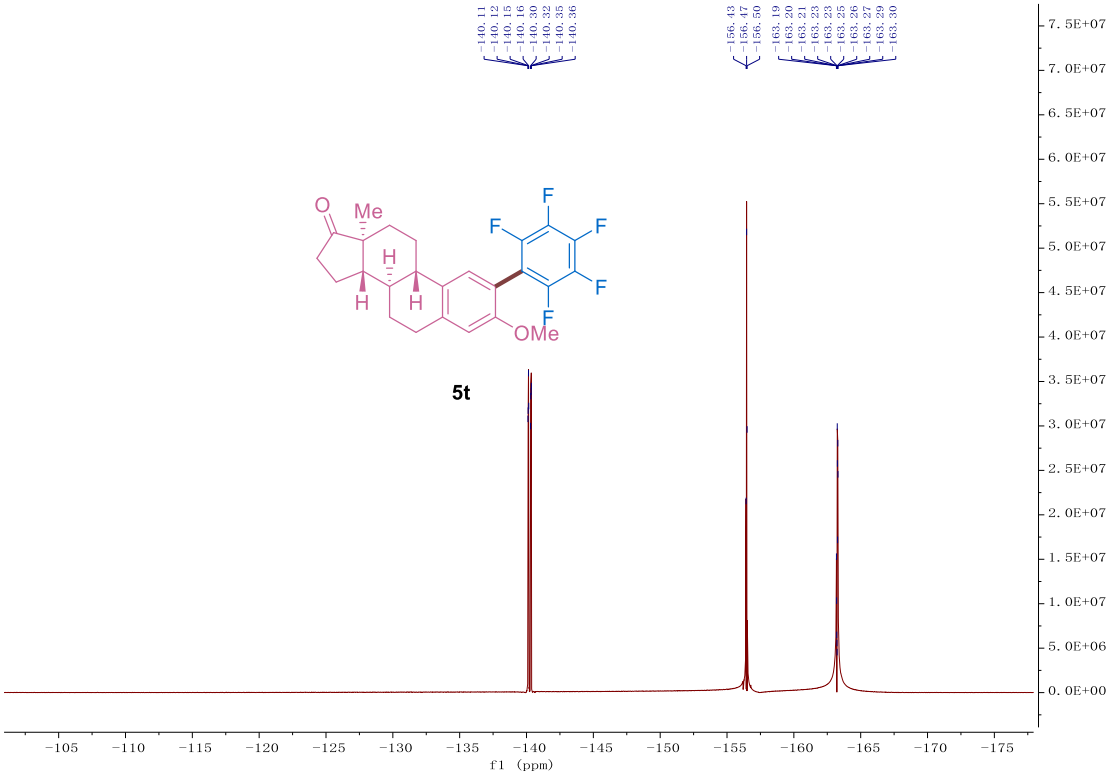
^{1}H NMR of 5t (400 MHz, $CDCl_3$)



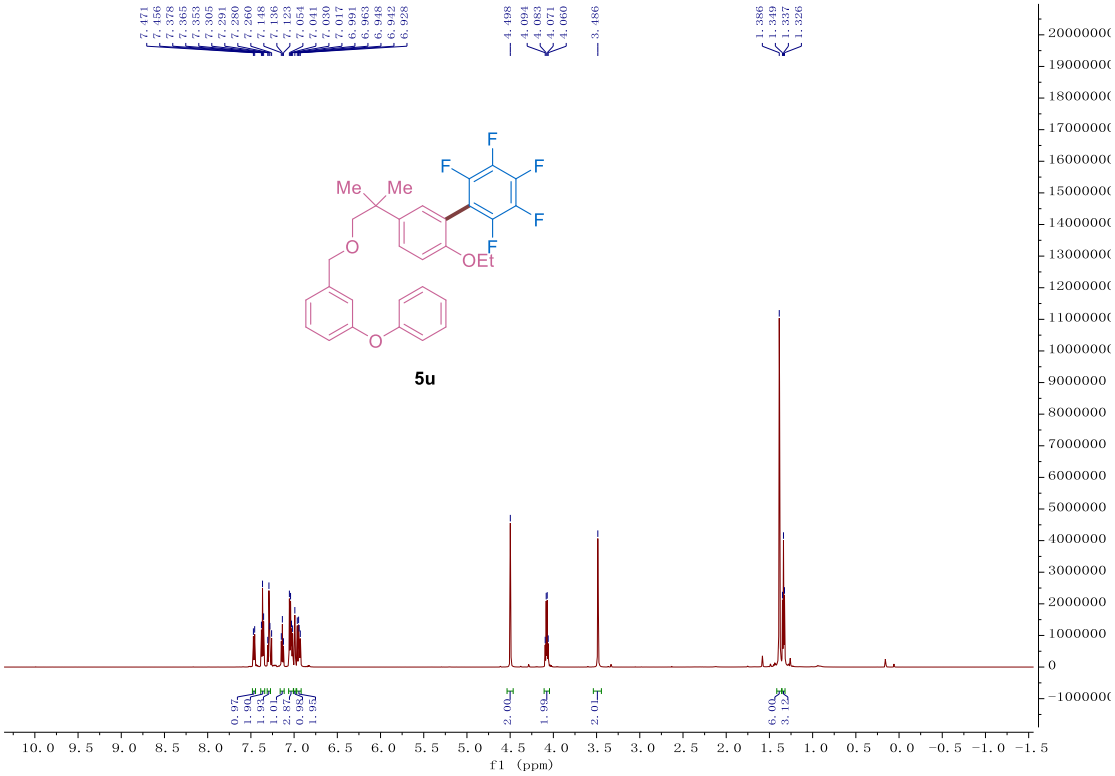
^{13}C NMR of 5t (101 MHz, $CDCl_3$)



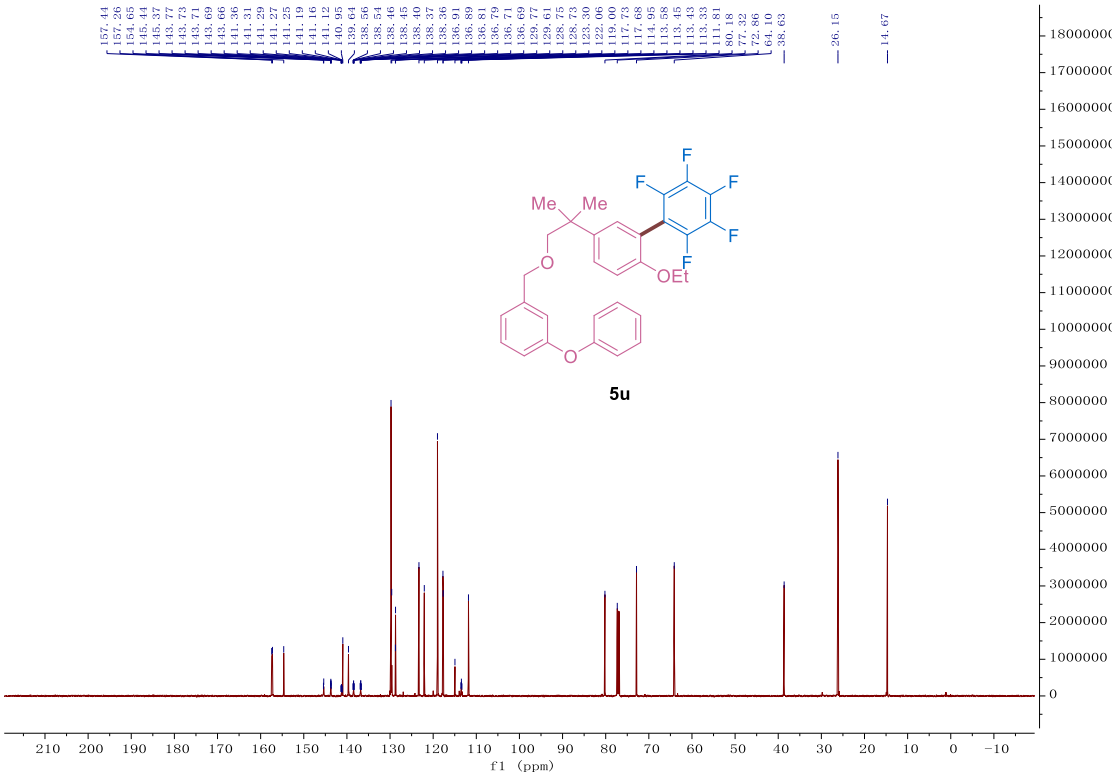
^{19}F NMR of 5t (565 MHz, $CDCl_3$)



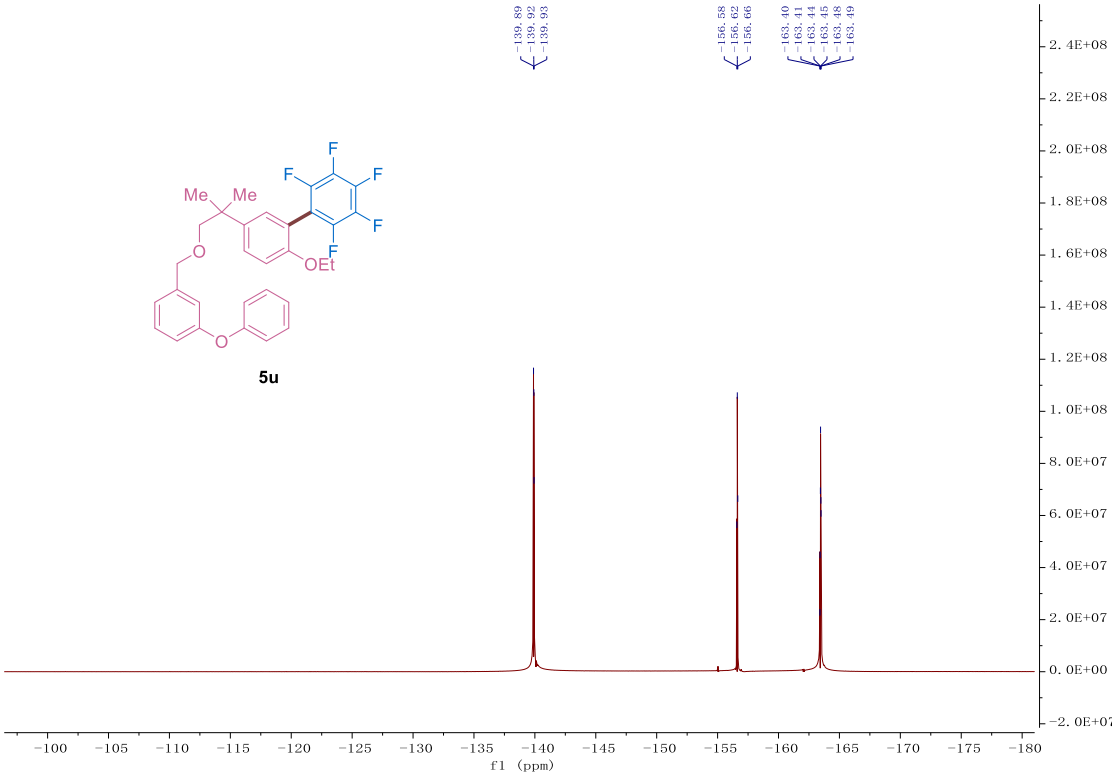
^{1}H NMR of 5u (600 MHz, $CDCl_3$)



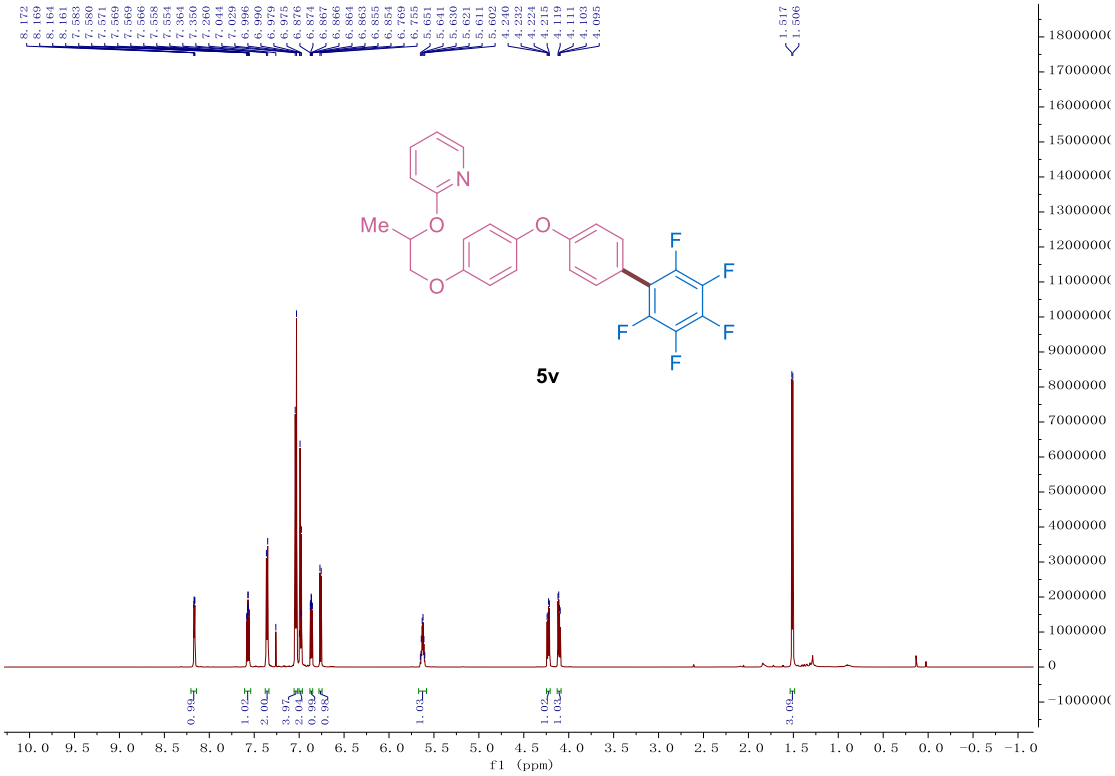
^{13}C NMR of 5u (151 MHz, $CDCl_3$)



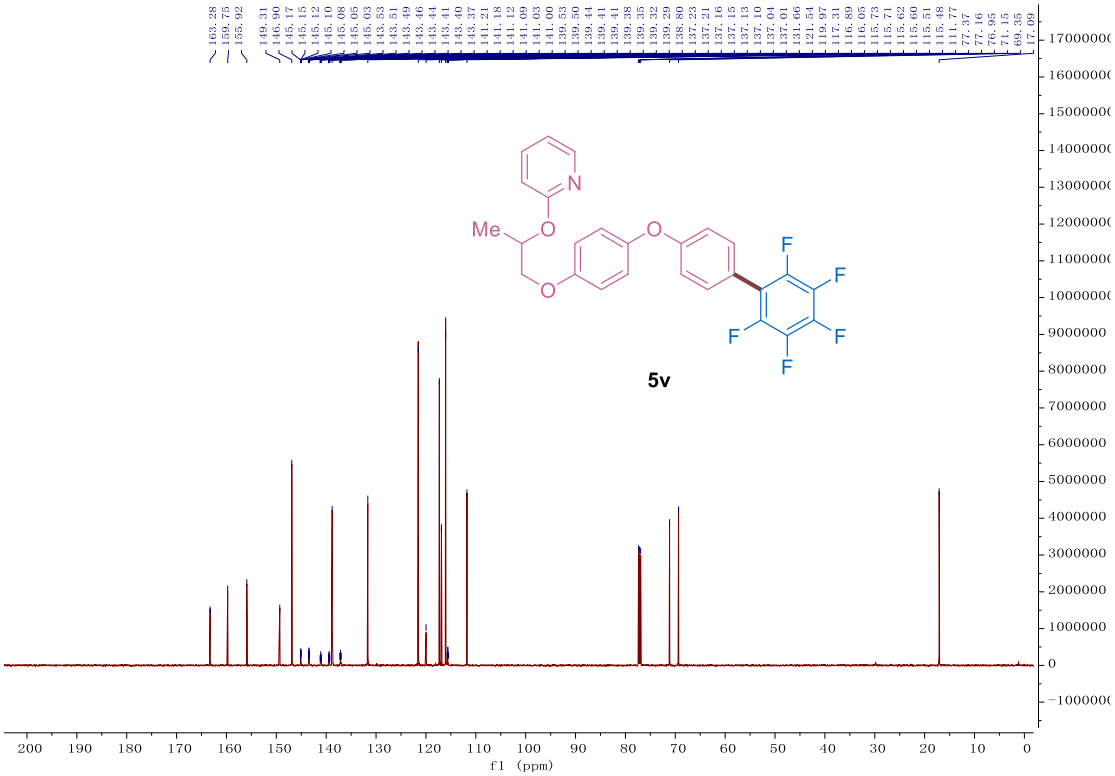
^{19}F NMR of 5u (565 MHz, $CDCl_3$)



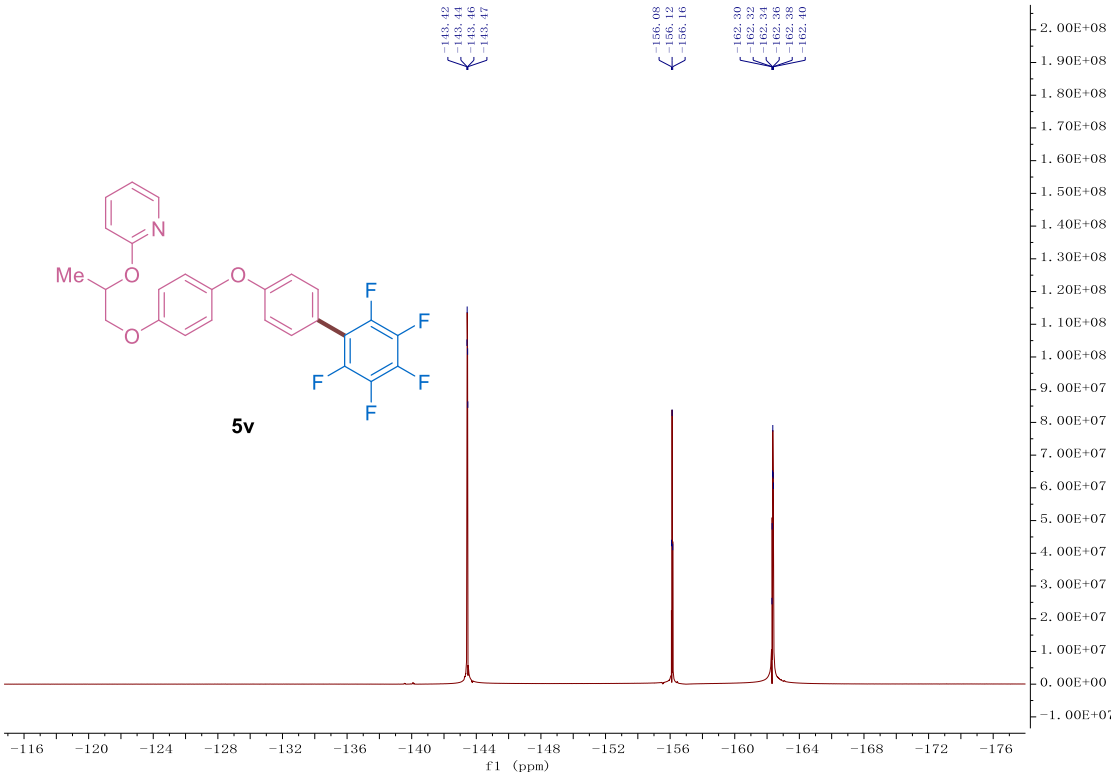
^{1}H NMR of 5v (600 MHz, $CDCl_3$)



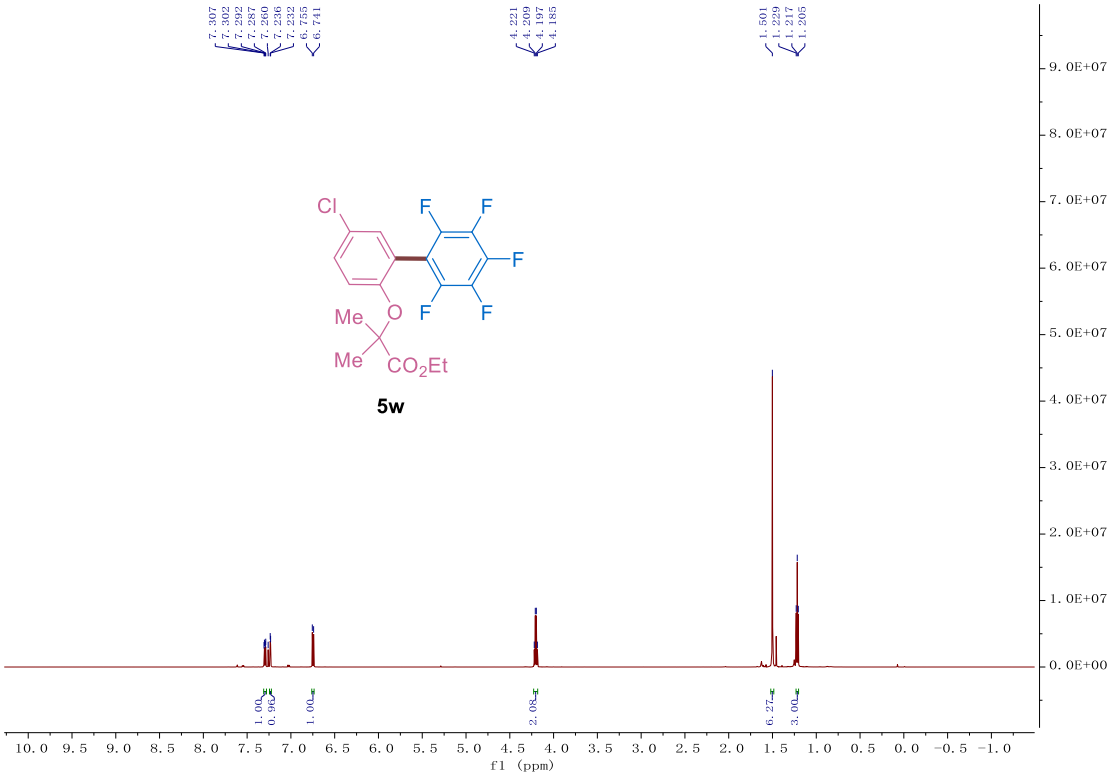
^{13}C NMR of 5v (151 MHz, $CDCl_3$)



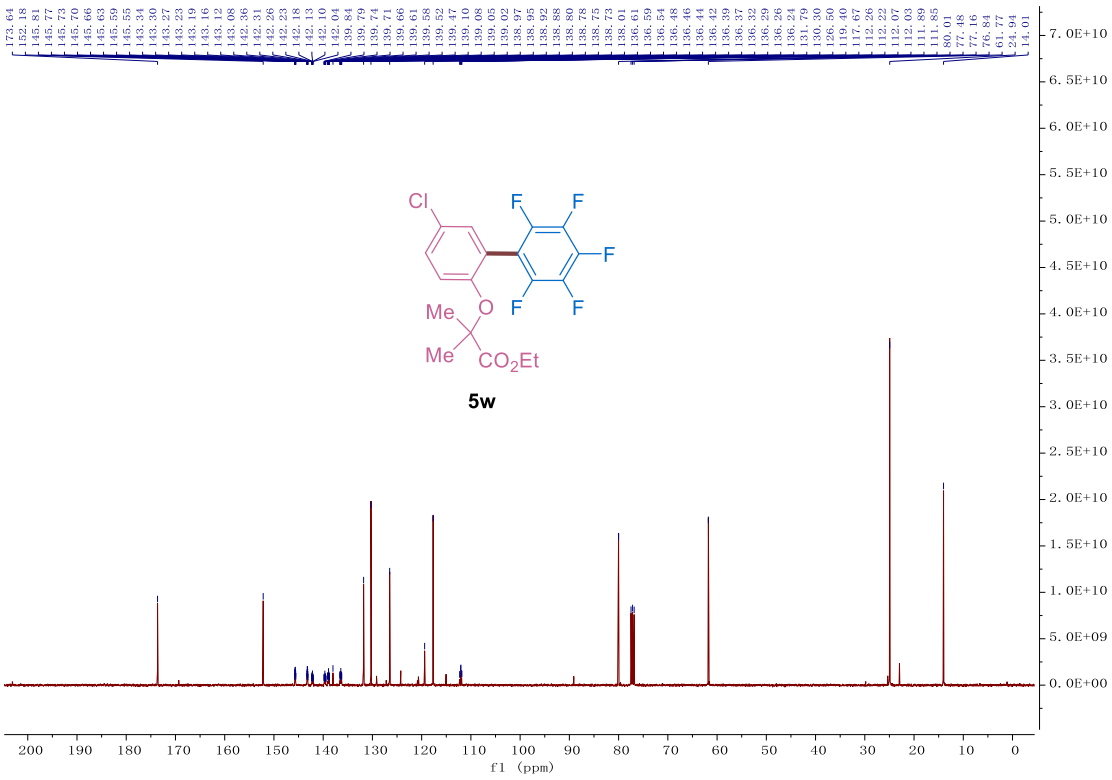
^{19}F NMR of 5v (565 MHz, $CDCl_3$)



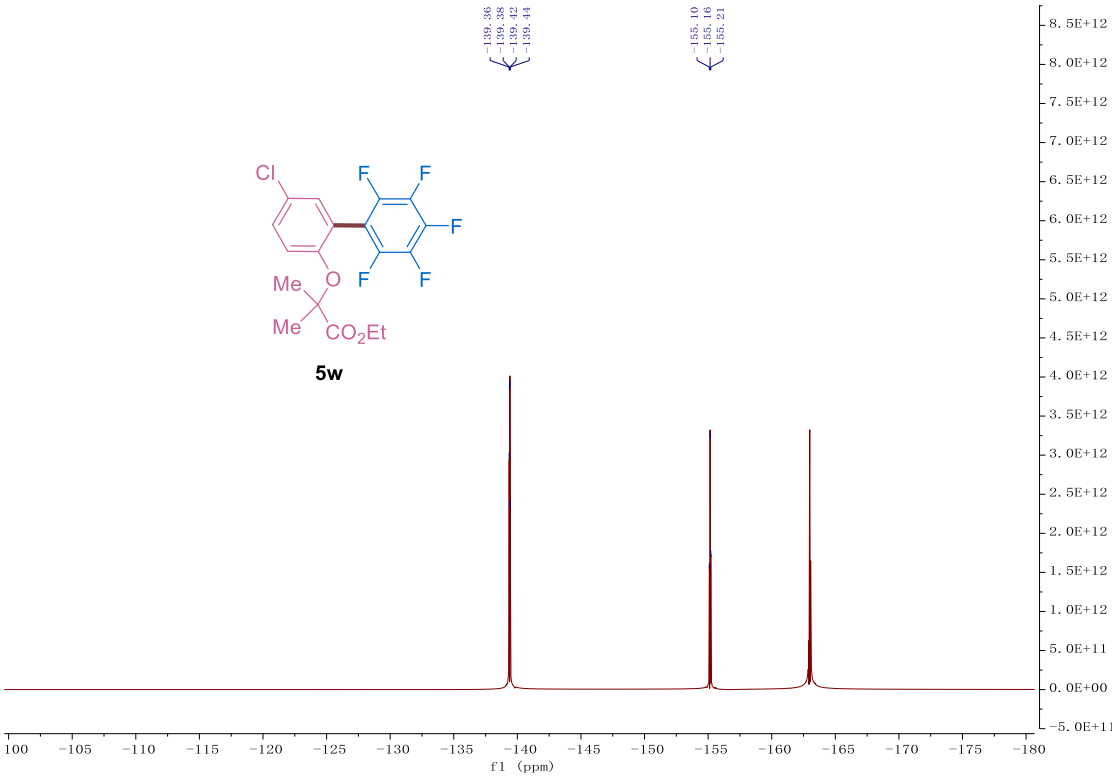
^{1}H NMR of 5w (600 MHz, $CDCl_3$)



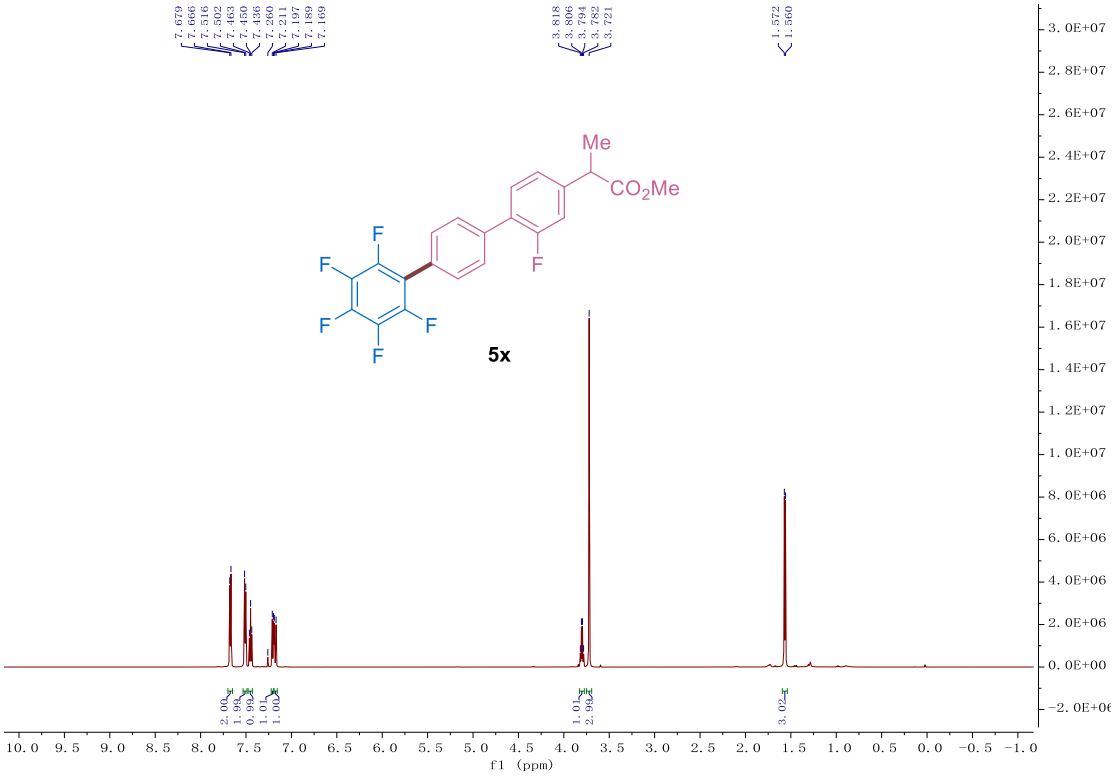
^{13}C NMR of 5w (101 MHz, $CDCl_3$)



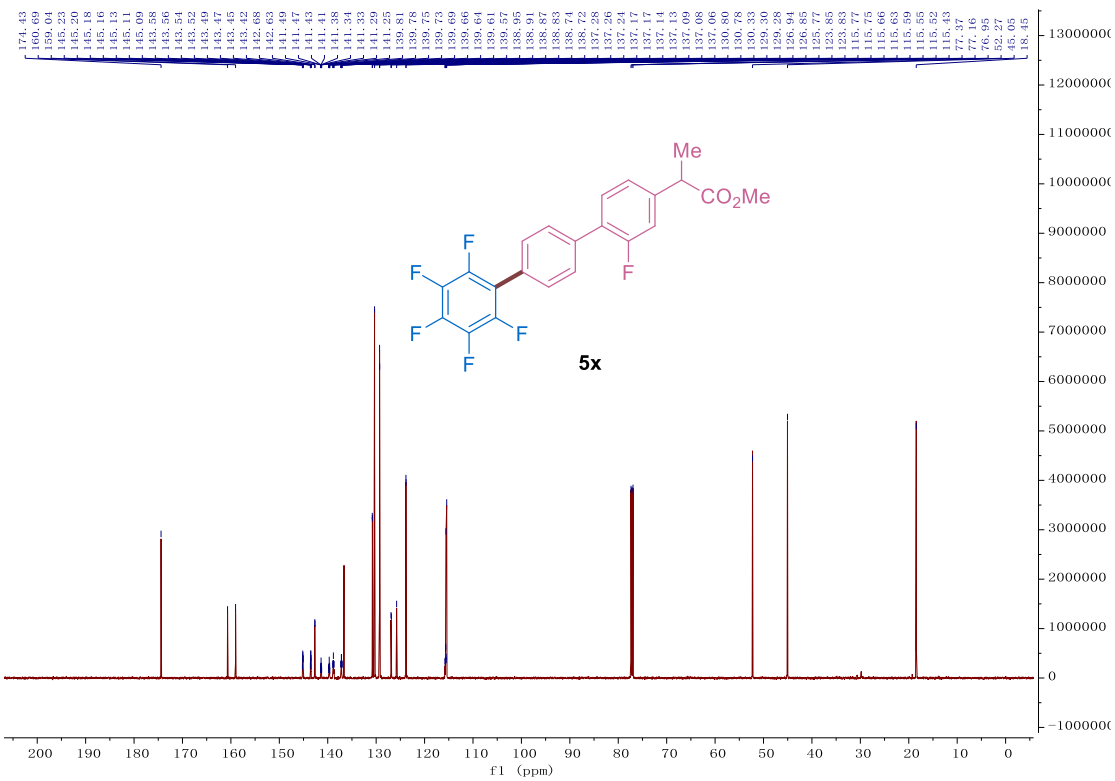
^{19}F NMR of 5w (376 MHz, $CDCl_3$)



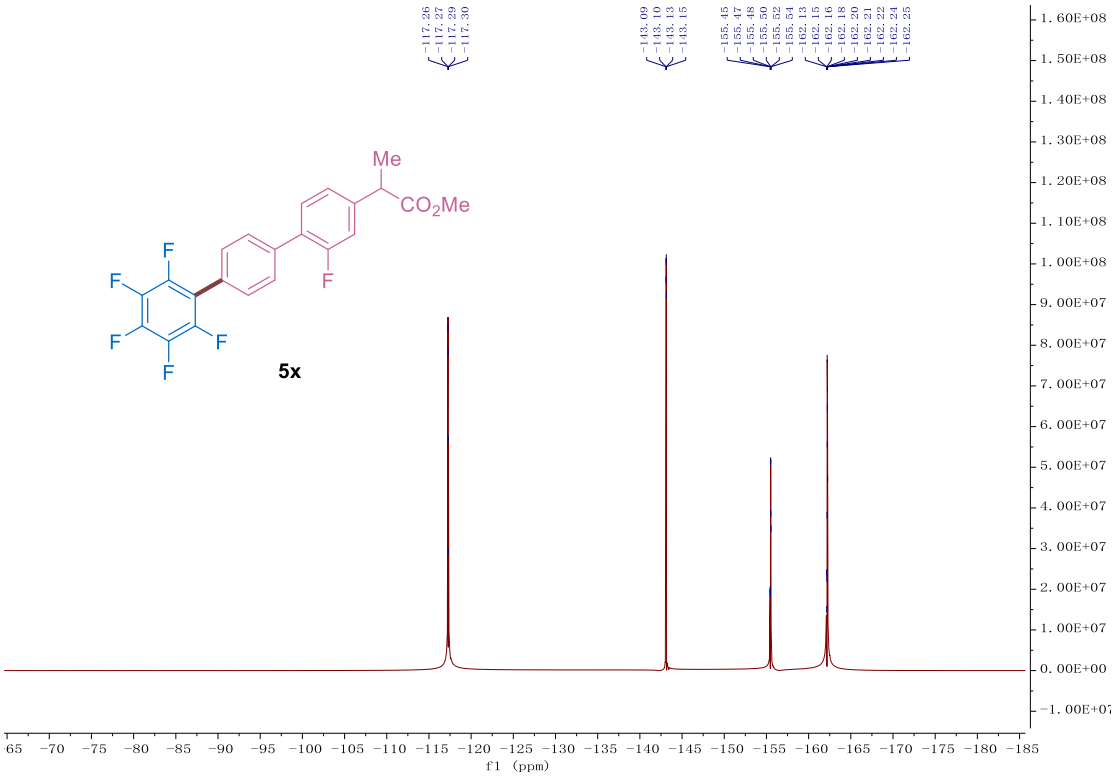
^{1}H NMR of 5x (600 MHz, $CDCl_3$)



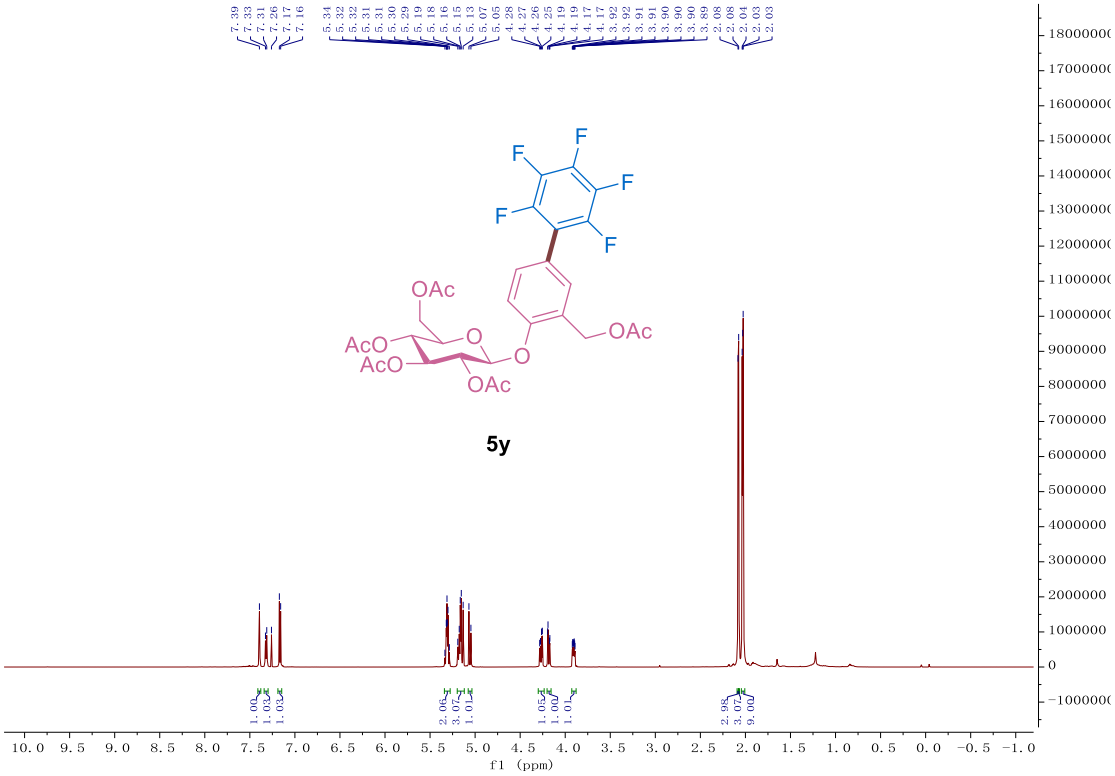
^{13}C NMR of 5x (151 MHz, $CDCl_3$)



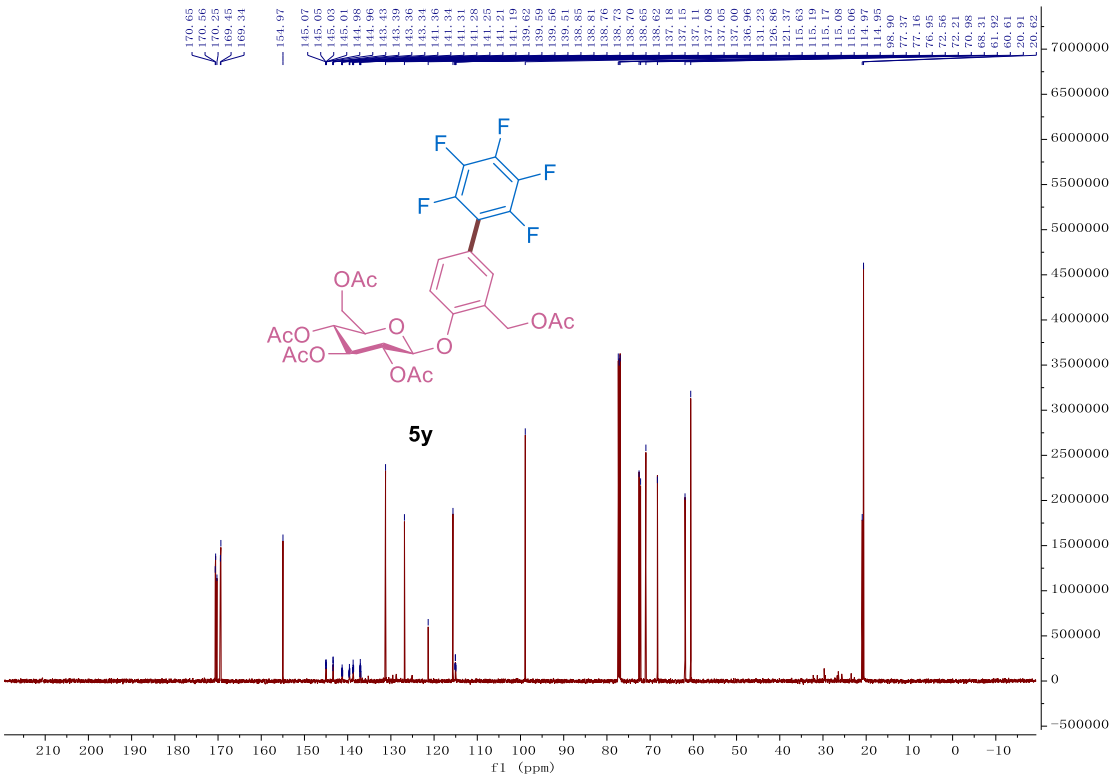
^{19}F NMR of 5x (565 MHz, $CDCl_3$)



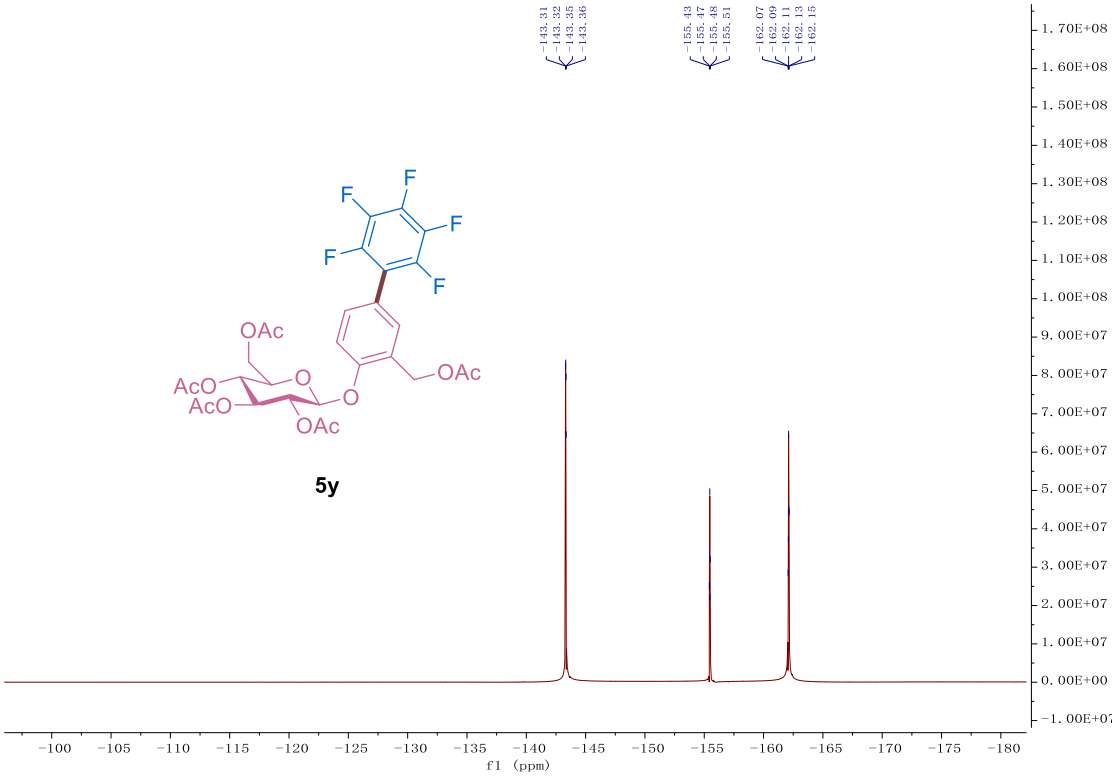
^{1}H NMR of 5y (600 MHz, $CDCl_3$)



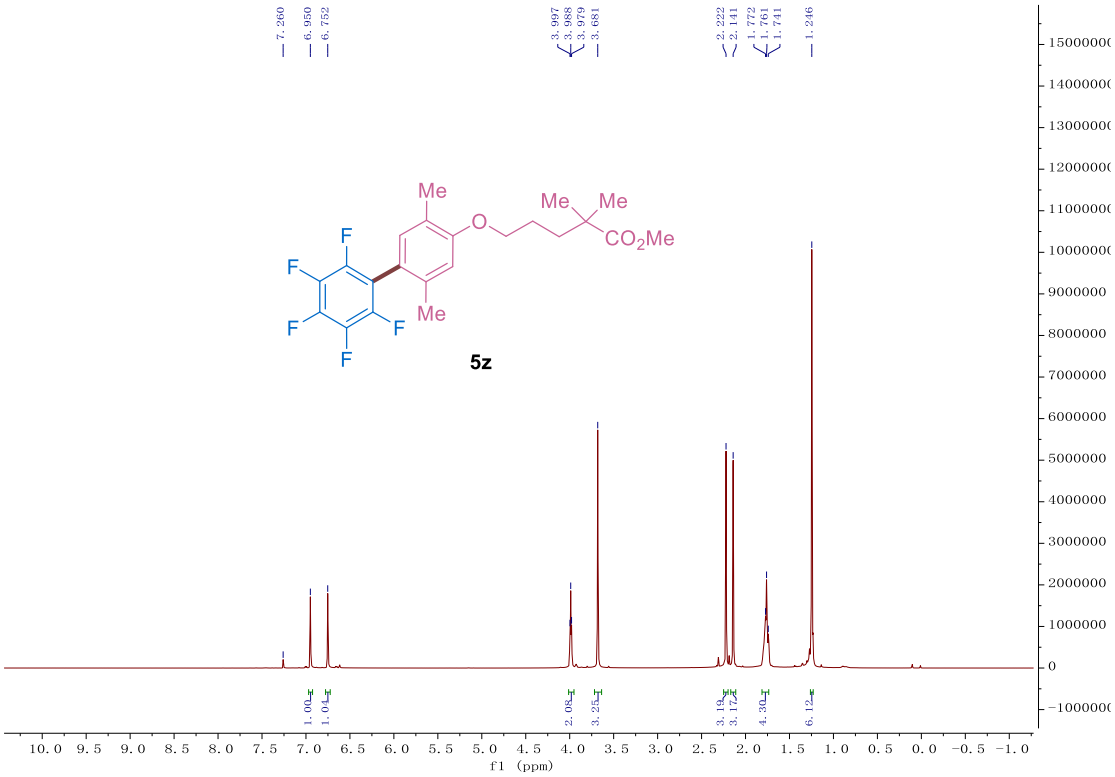
^{13}C NMR of 5y (151 MHz, $CDCl_3$)



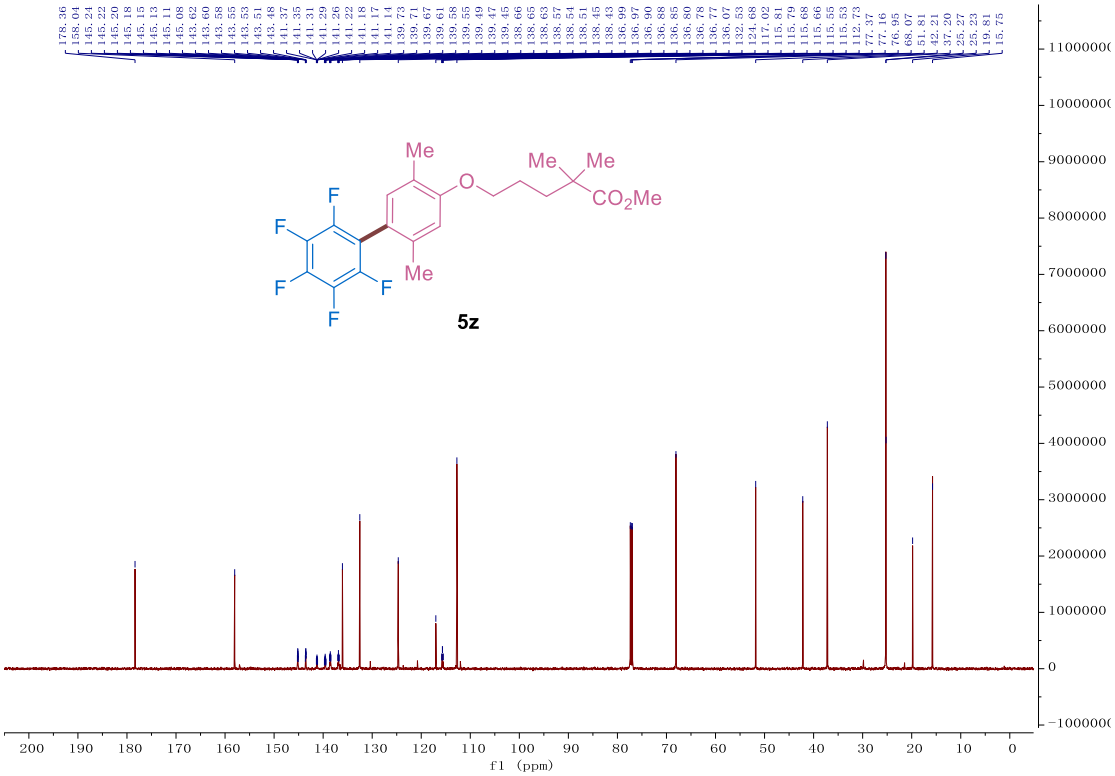
^{19}F NMR of 5y (565 MHz, $CDCl_3$)



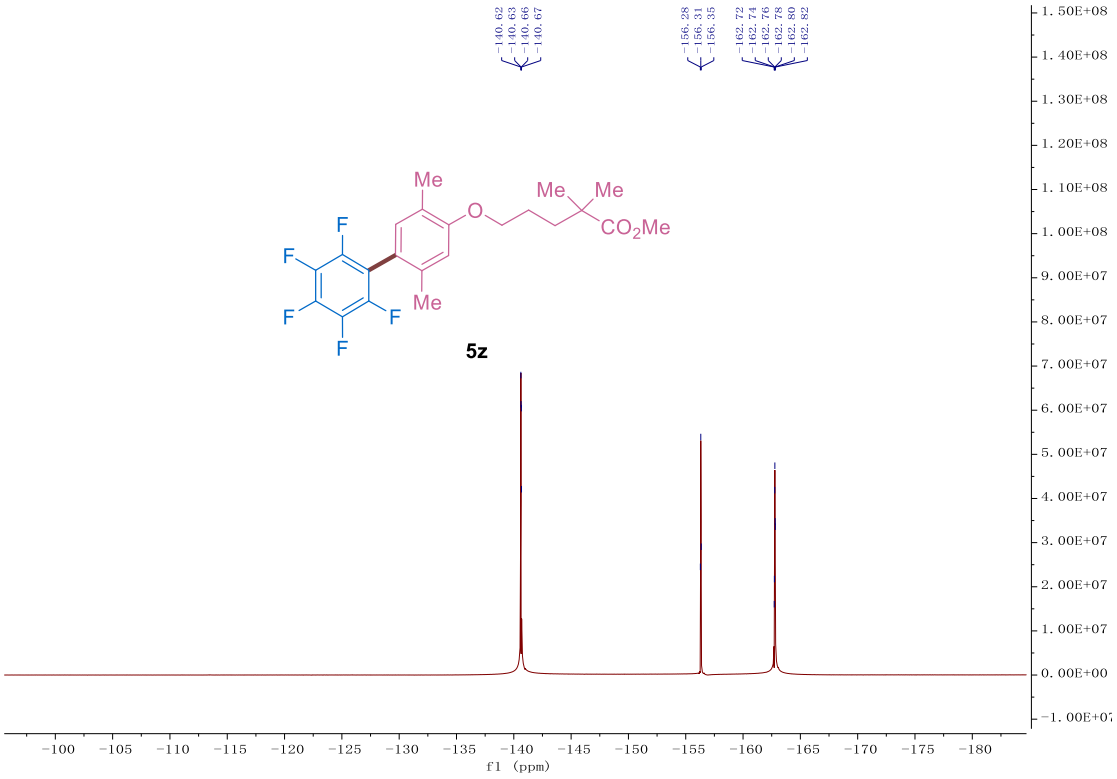
^{1}H NMR of 5z (600 MHz, $CDCl_3$)



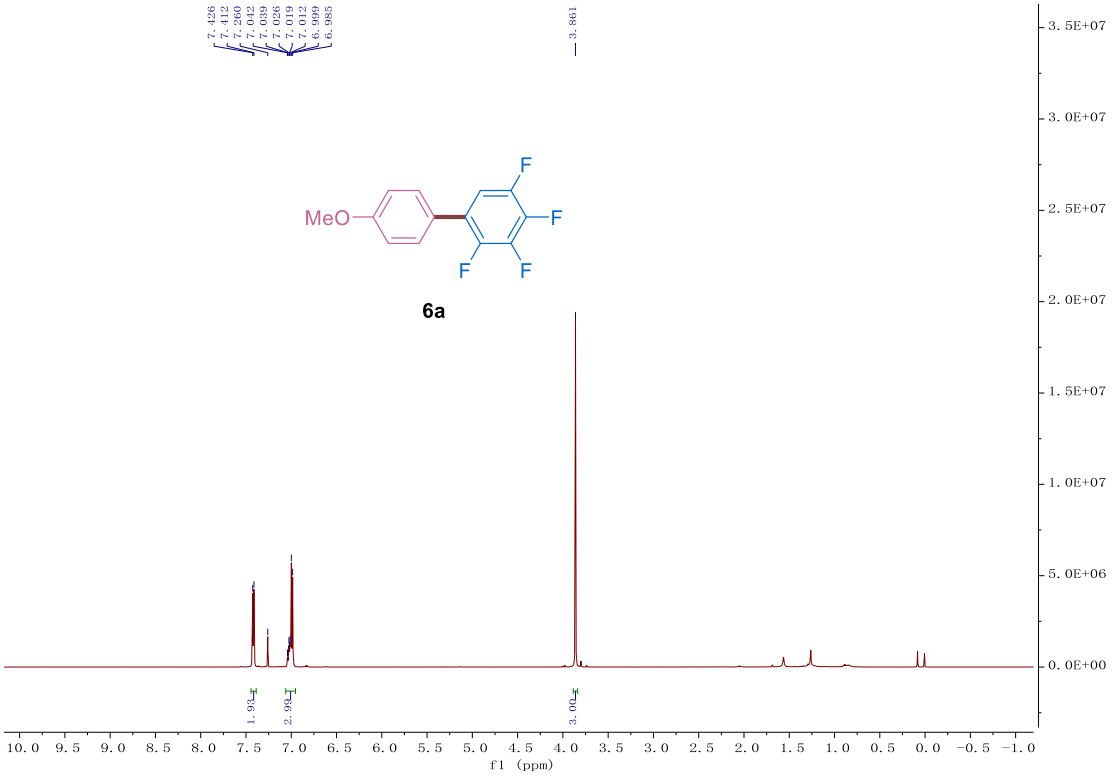
^{13}C NMR of 5z (151 MHz, $CDCl_3$)



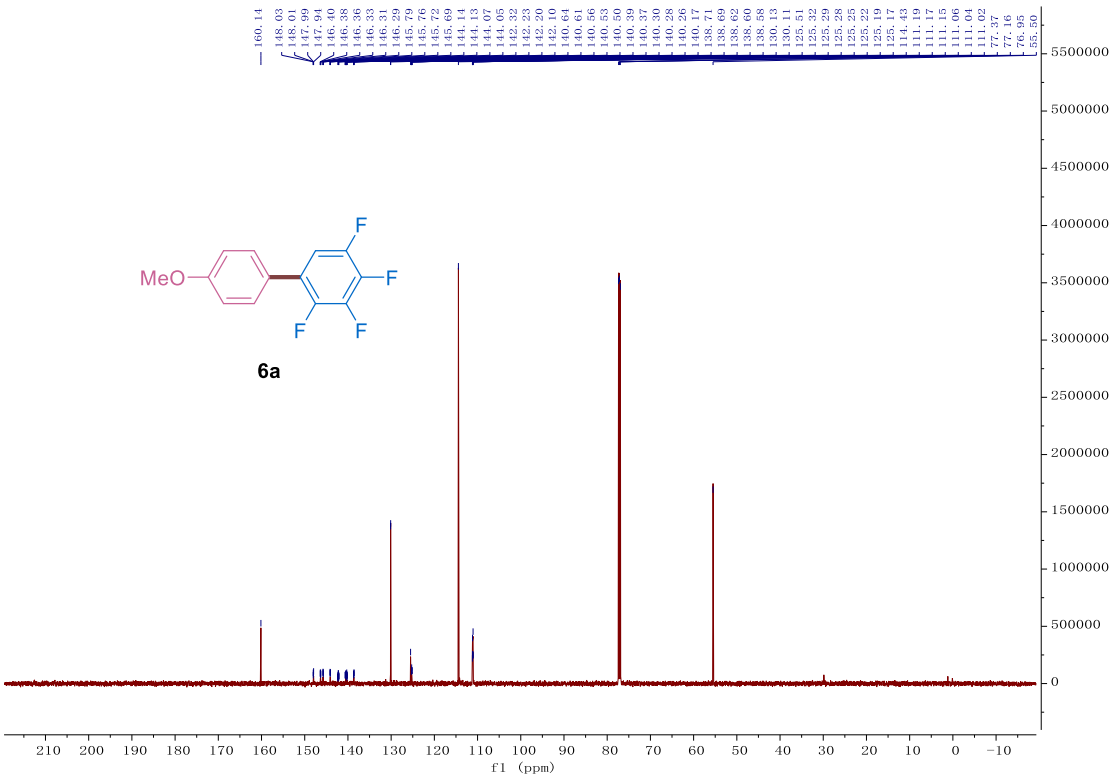
^{19}F NMR of 5z (565 MHz, $CDCl_3$)



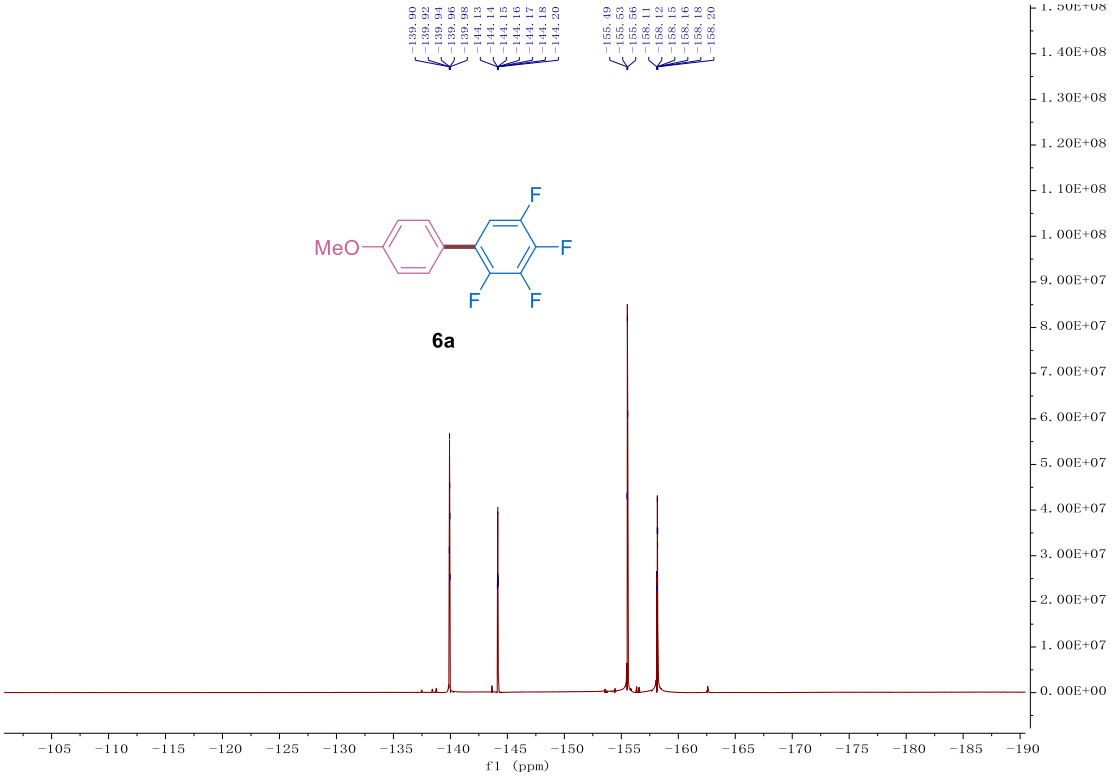
^{1}H NMR of 6a (600 MHz, $CDCl_3$)



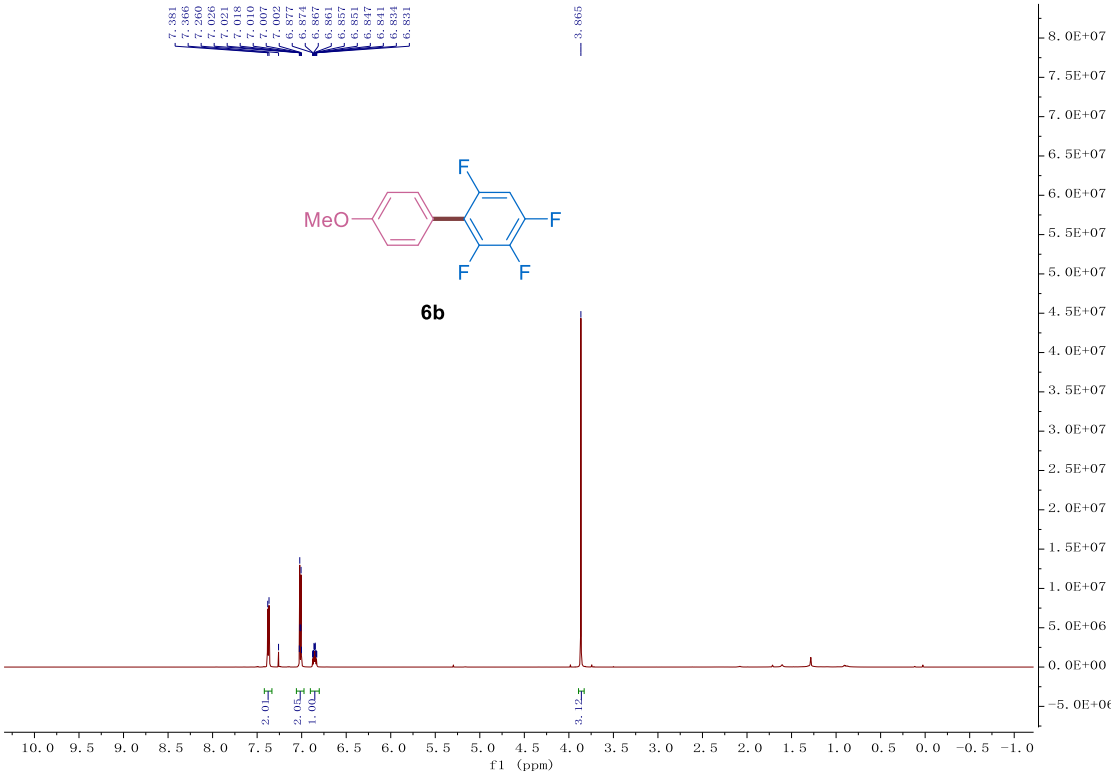
^{13}C NMR of 6a (151 MHz, $CDCl_3$)



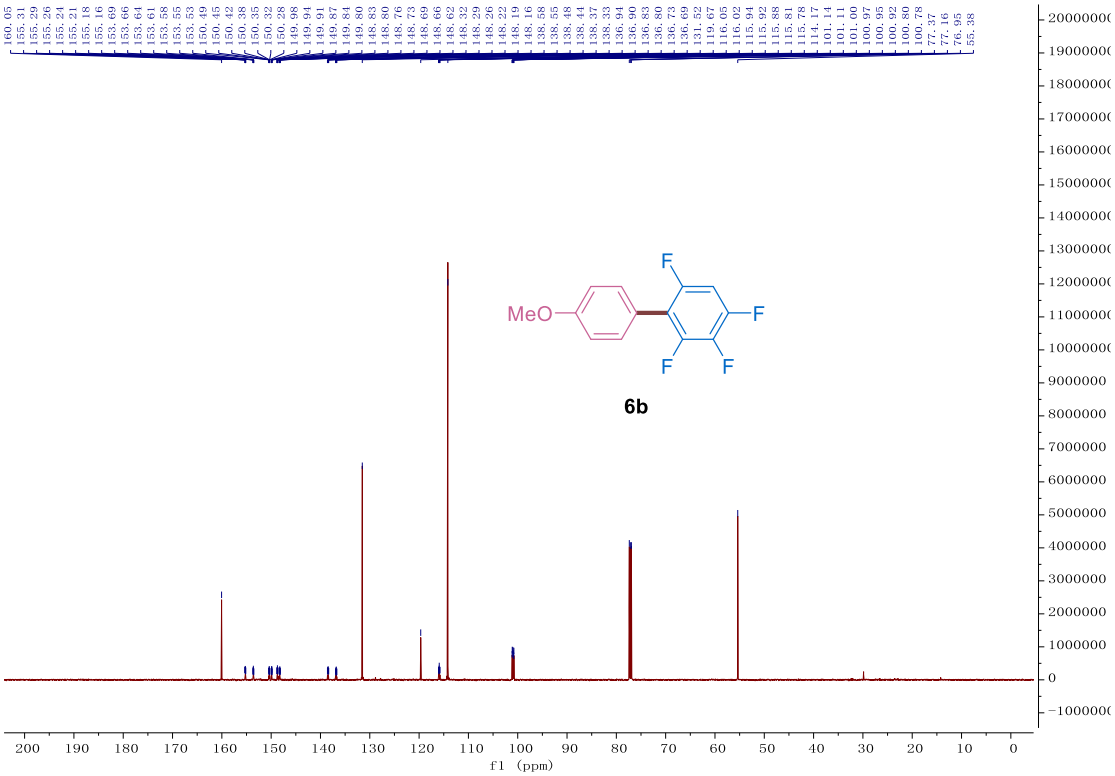
^{19}F NMR of 6a (565 MHz, $CDCl_3$)



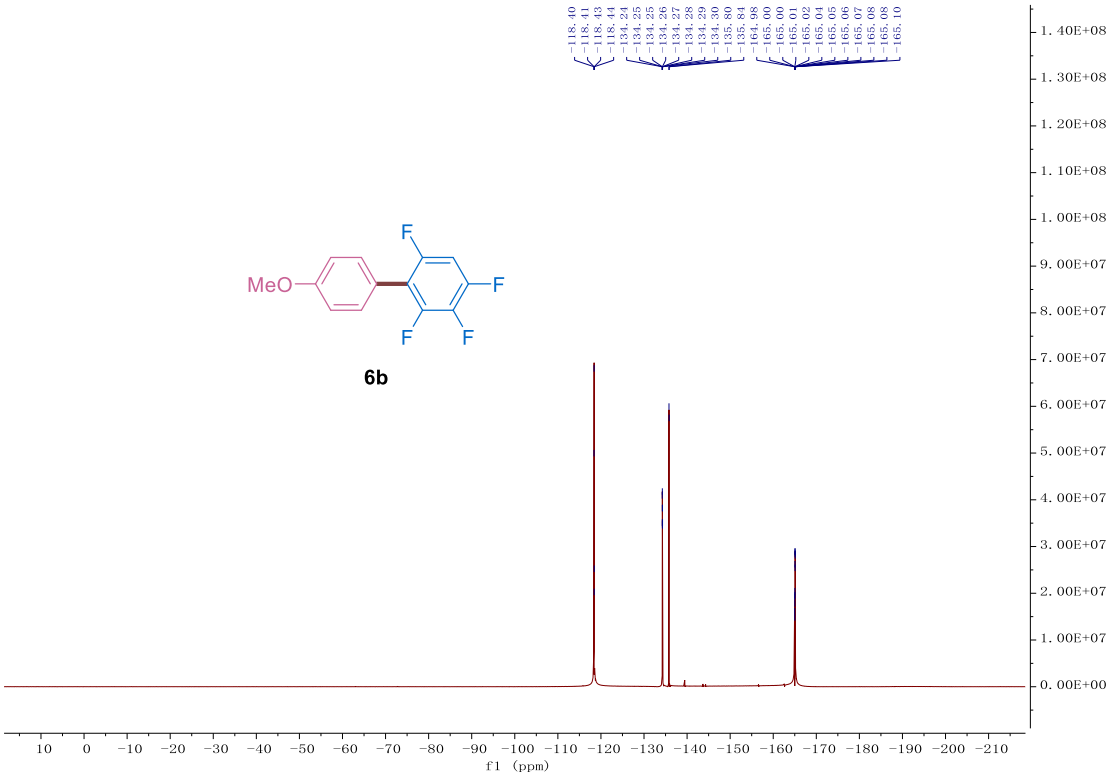
^{1}H NMR of 6b (600 MHz, $CDCl_3$)



^{13}C NMR of 6b (151 MHz, $CDCl_3$)



^{19}F NMR of 6b (565 MHz, $CDCl_3$)



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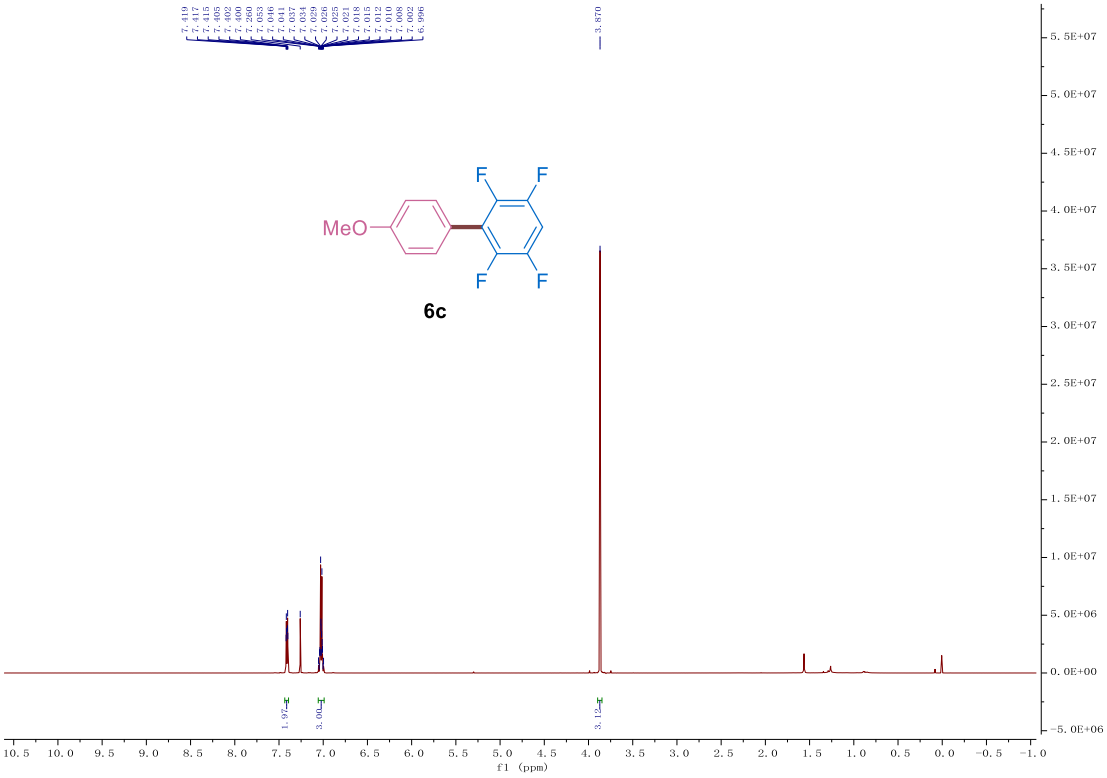
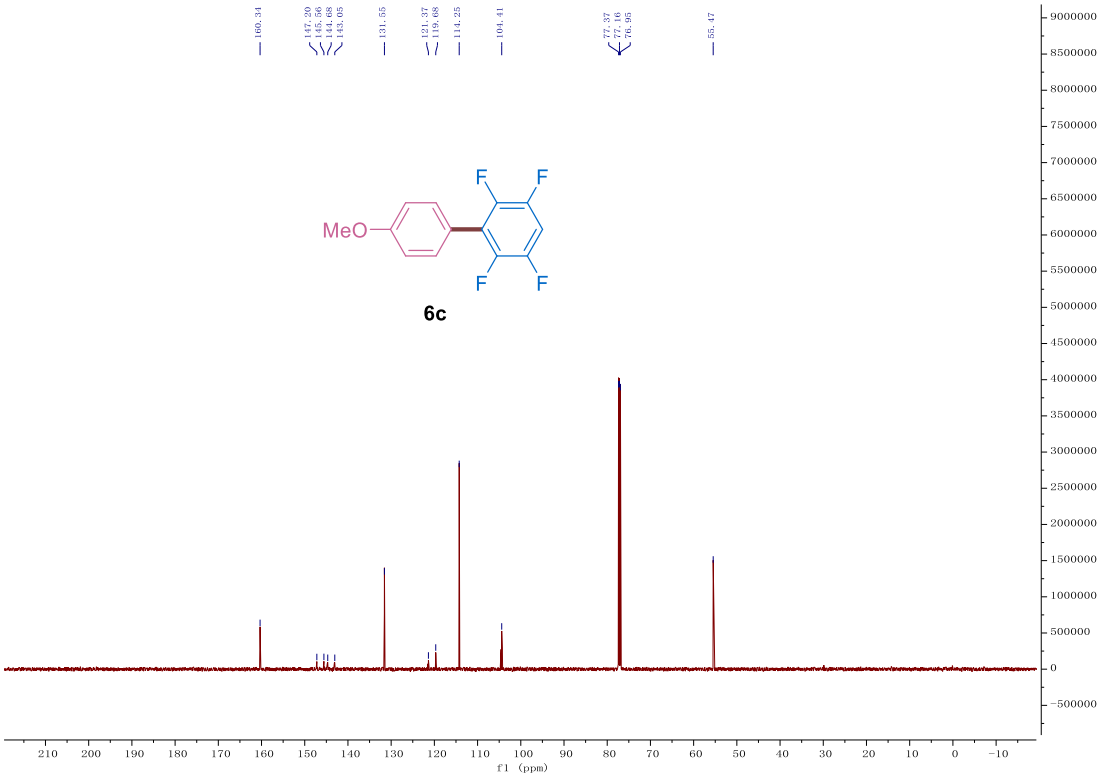
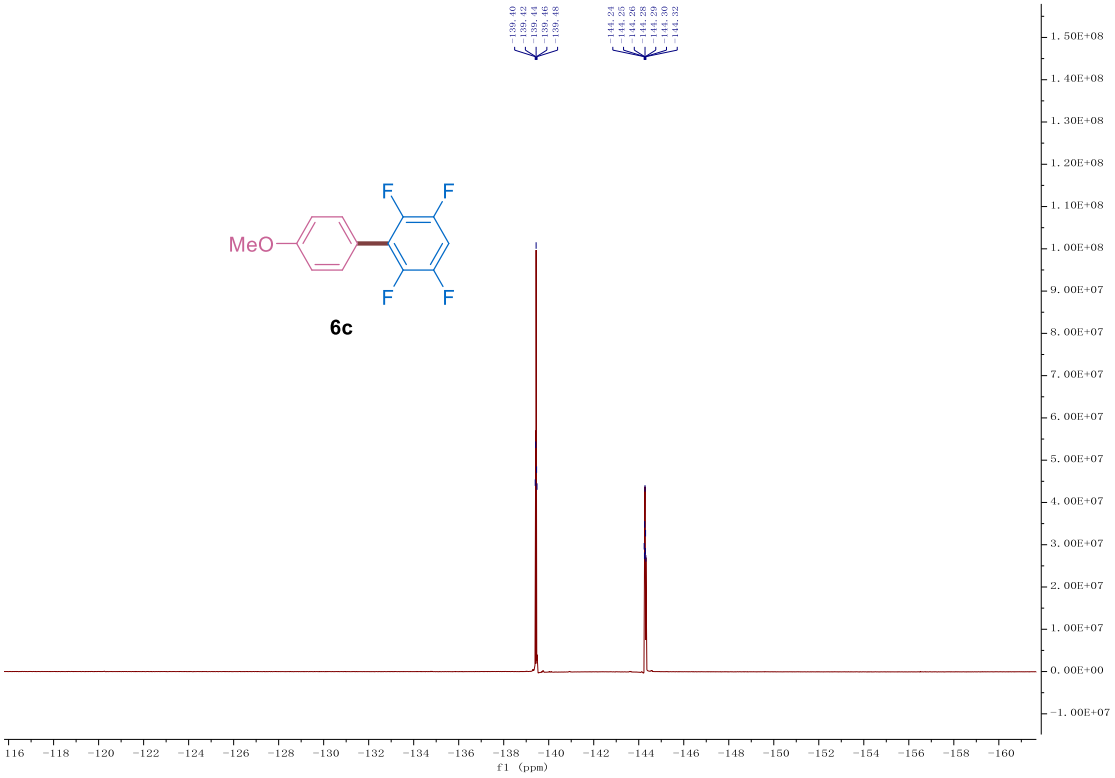


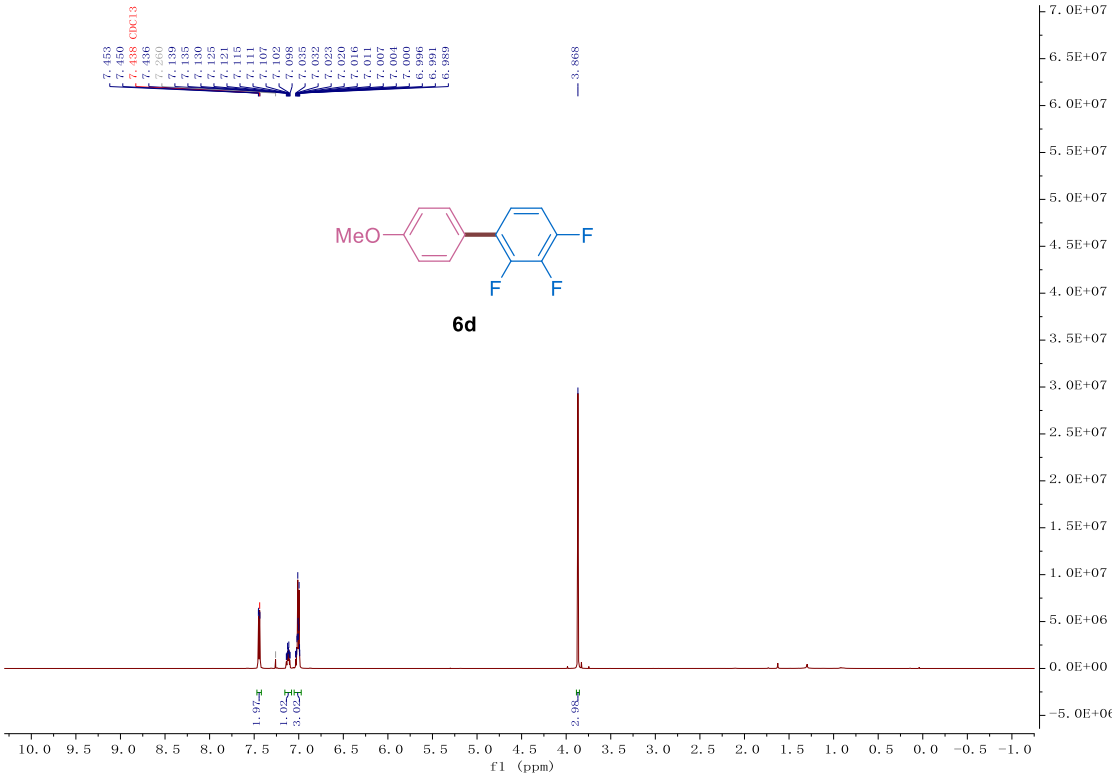
^{13}C NMR of 6c (151 MHz, $CDCl_3$)



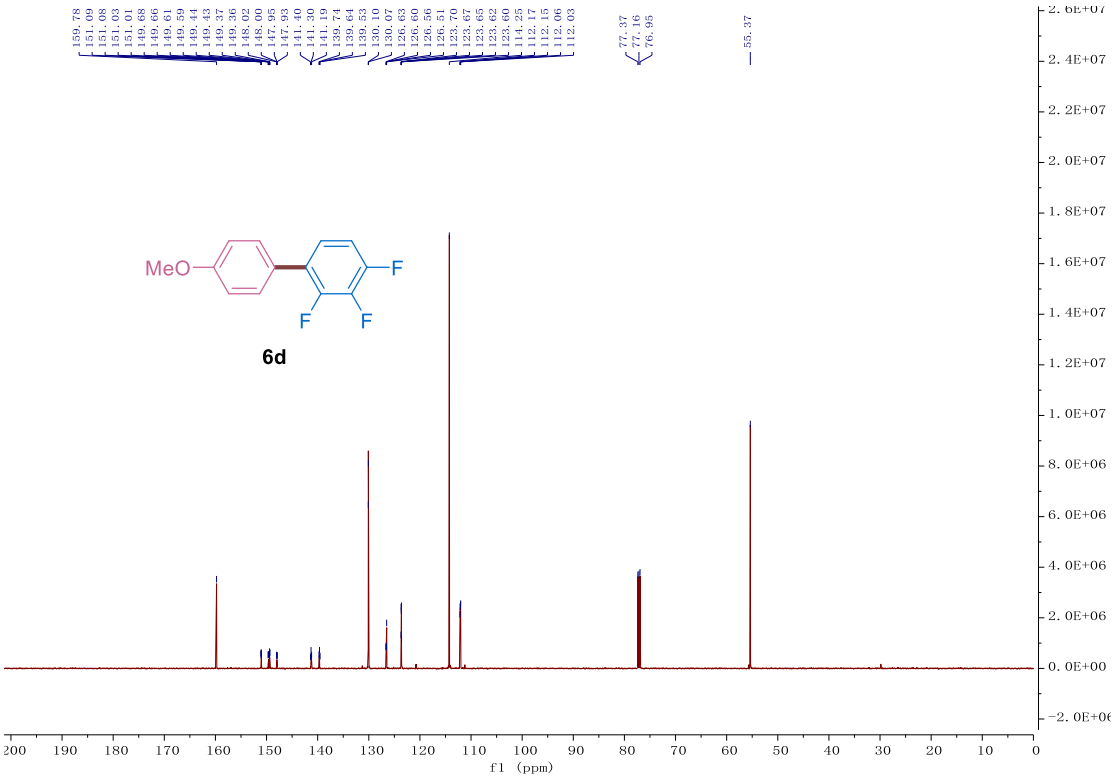
^{19}F NMR of 6c (565 MHz, $CDCl_3$)



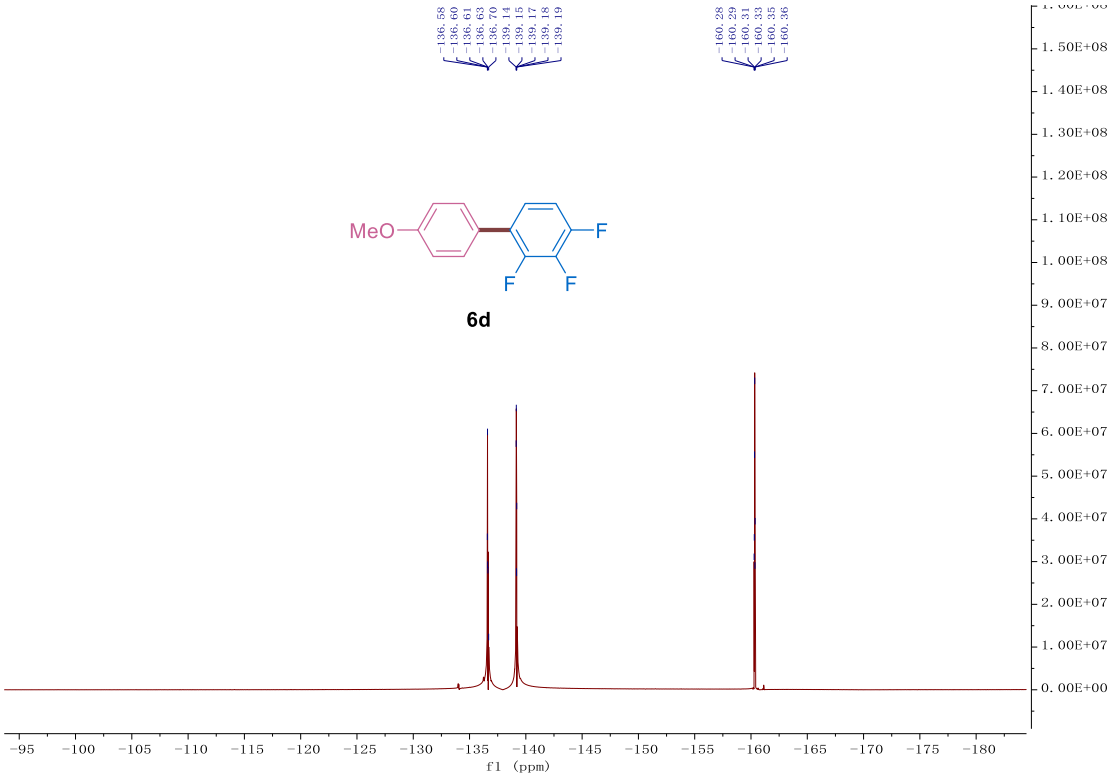
^{1}H NMR of 6d (600 MHz, $CDCl_3$)



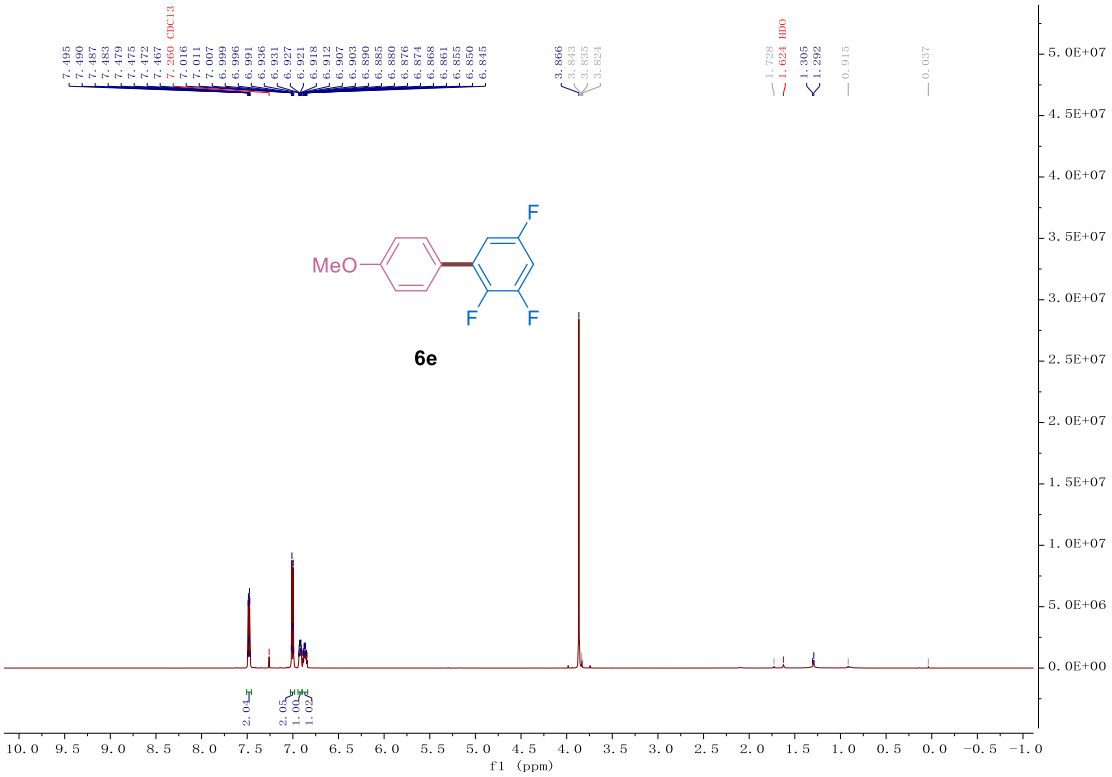
^{13}C NMR of 6d (151 MHz, $CDCl_3$)



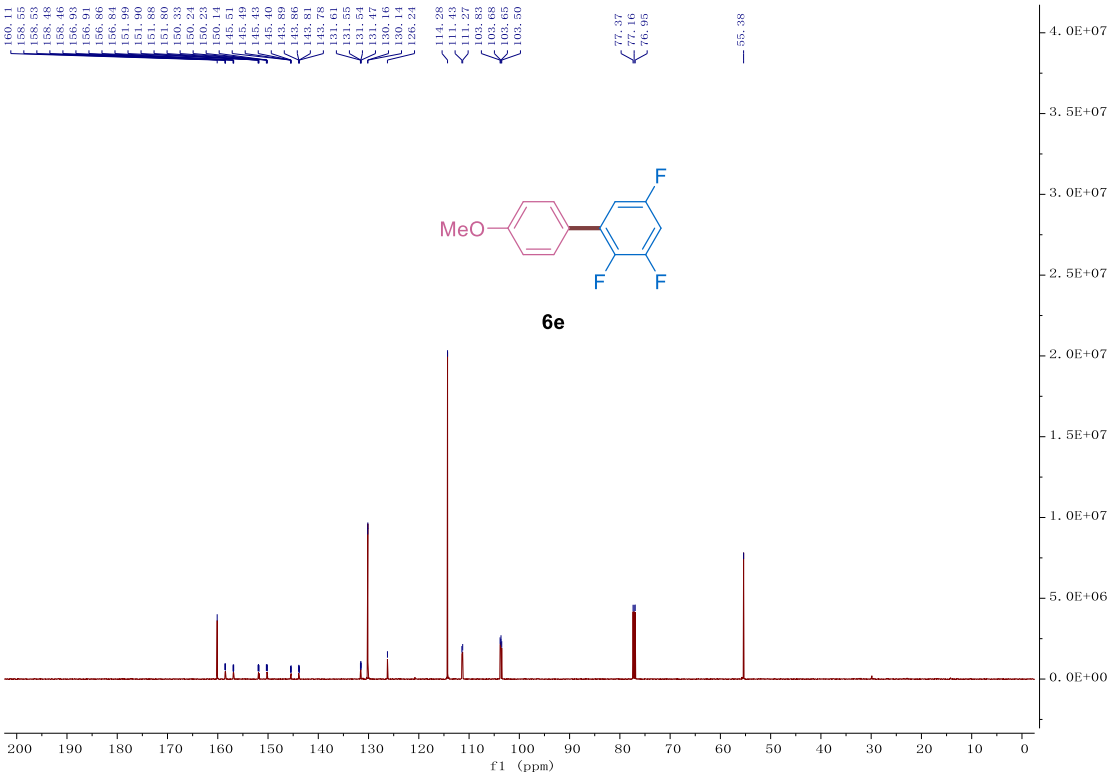
^{19}F NMR of 6d (565 MHz, $CDCl_3$)



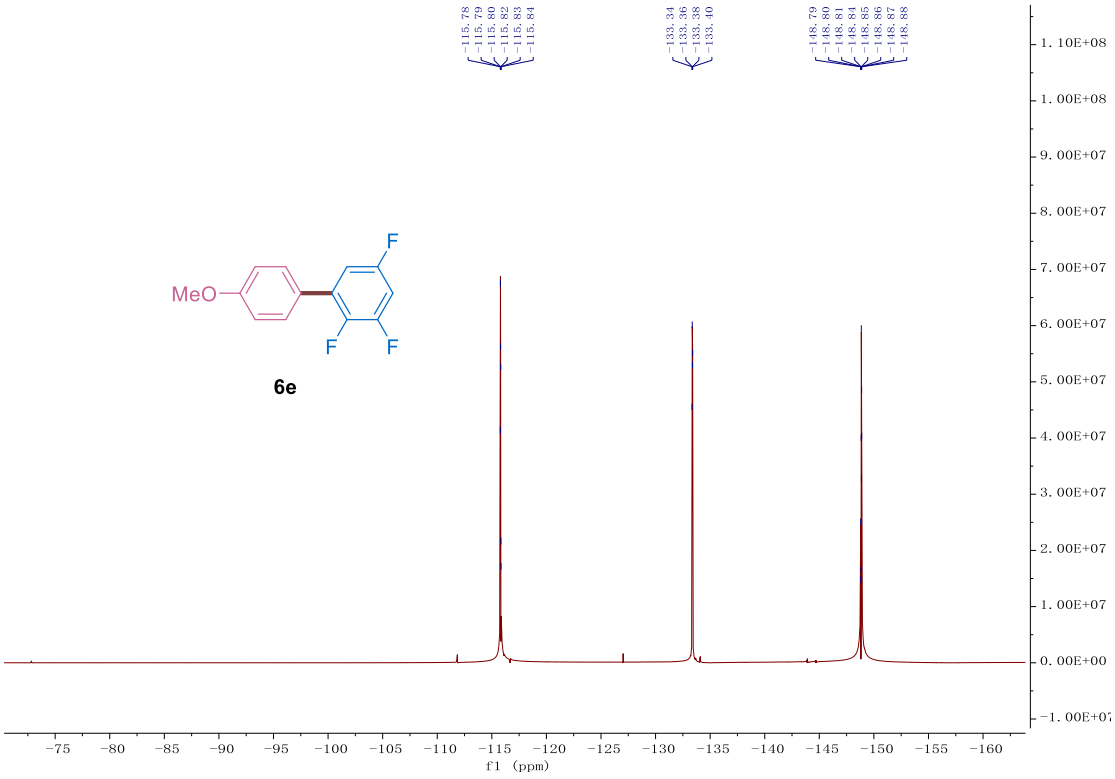
^{1}H NMR of 6e (600 MHz, $CDCl_3$)



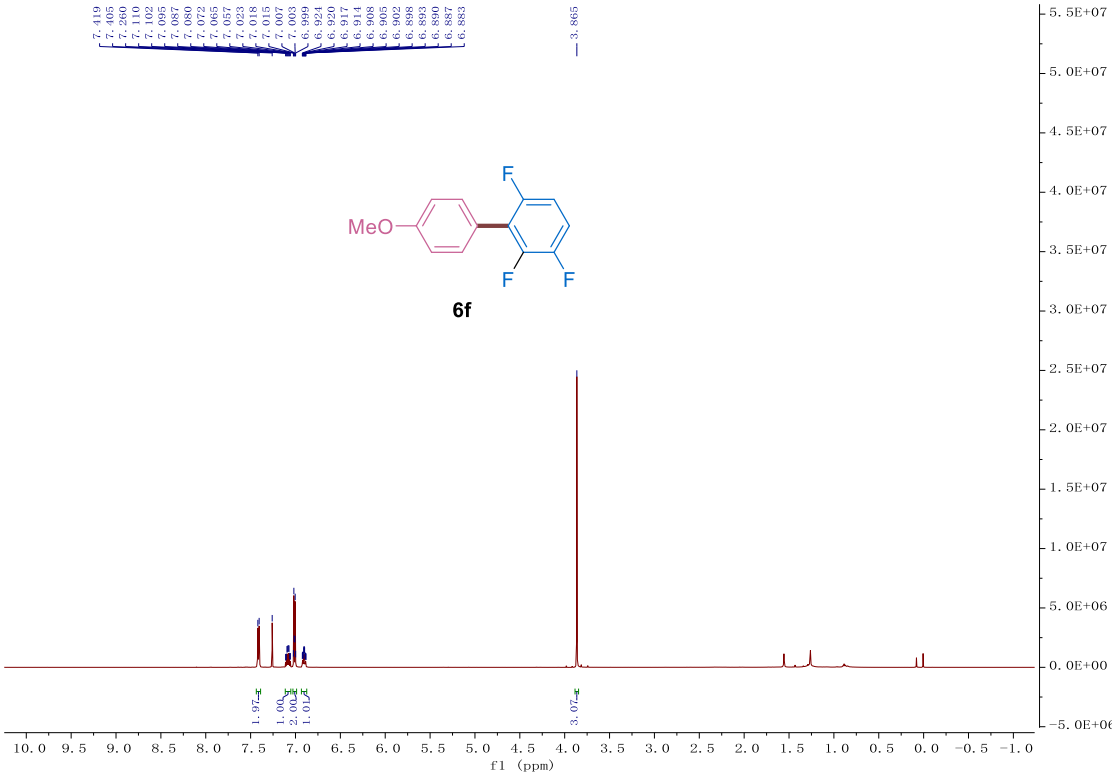
^{13}C NMR of 6e (151 MHz, $CDCl_3$)



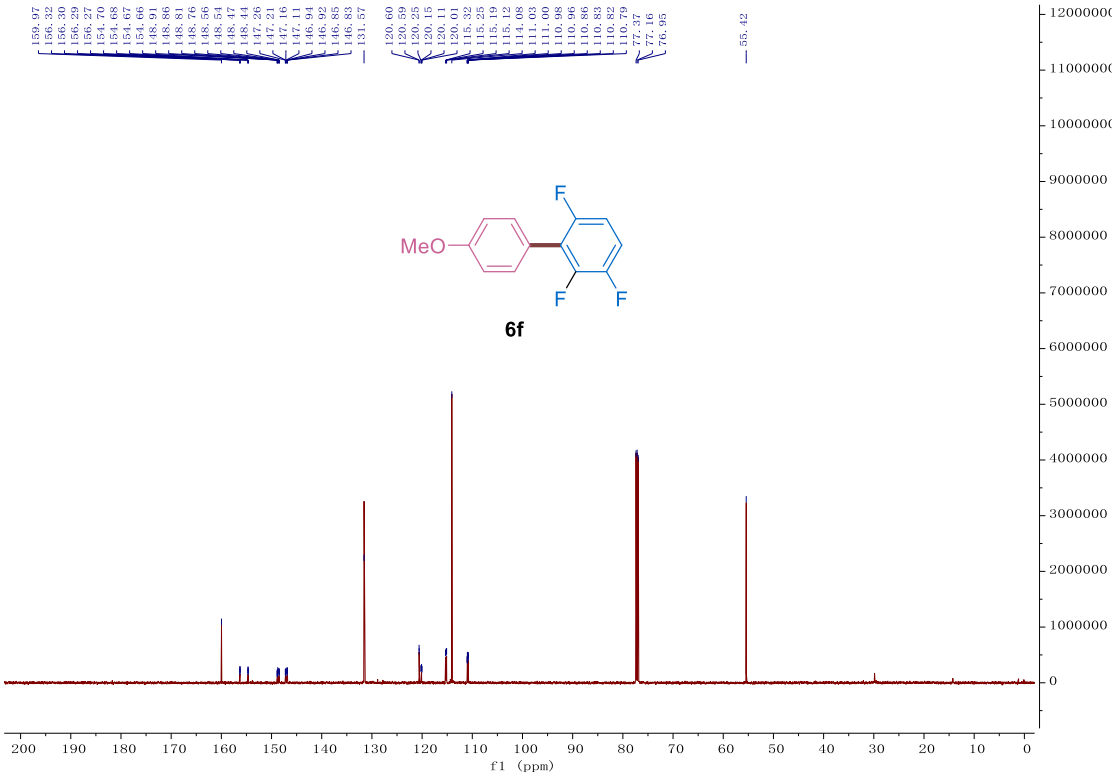
^{19}F NMR of 6e (565 MHz, $CDCl_3$)



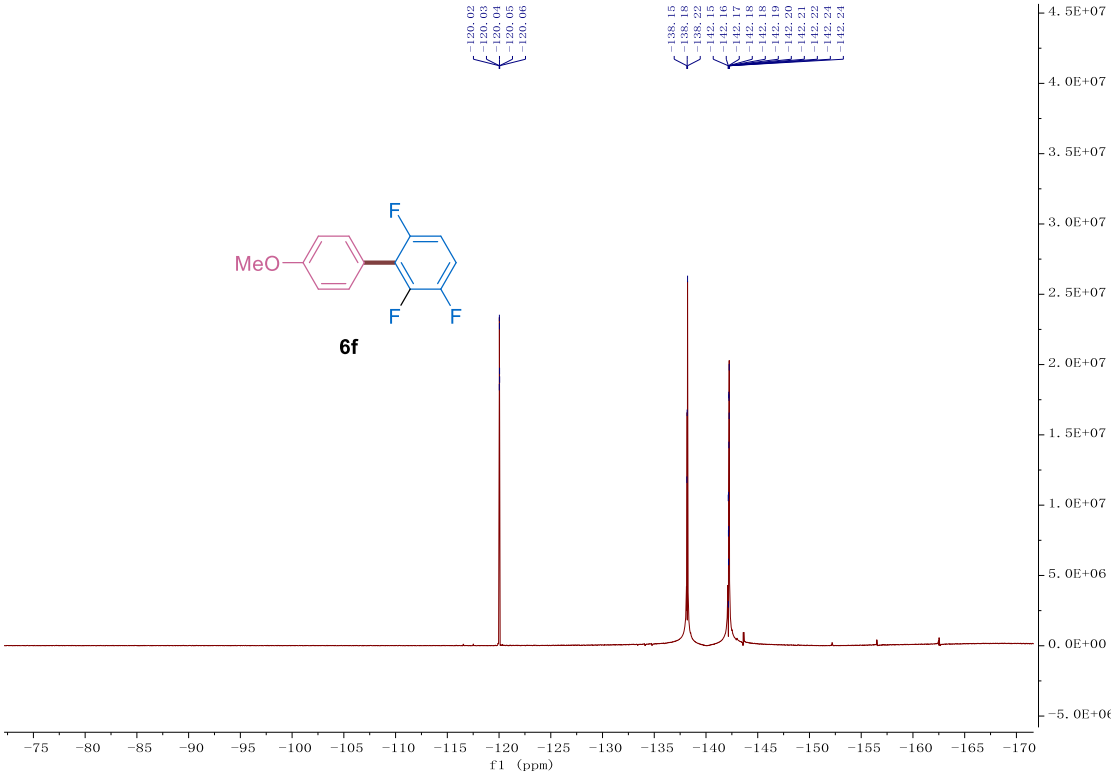
^{1}H NMR of 6f (600 MHz, $CDCl_3$)



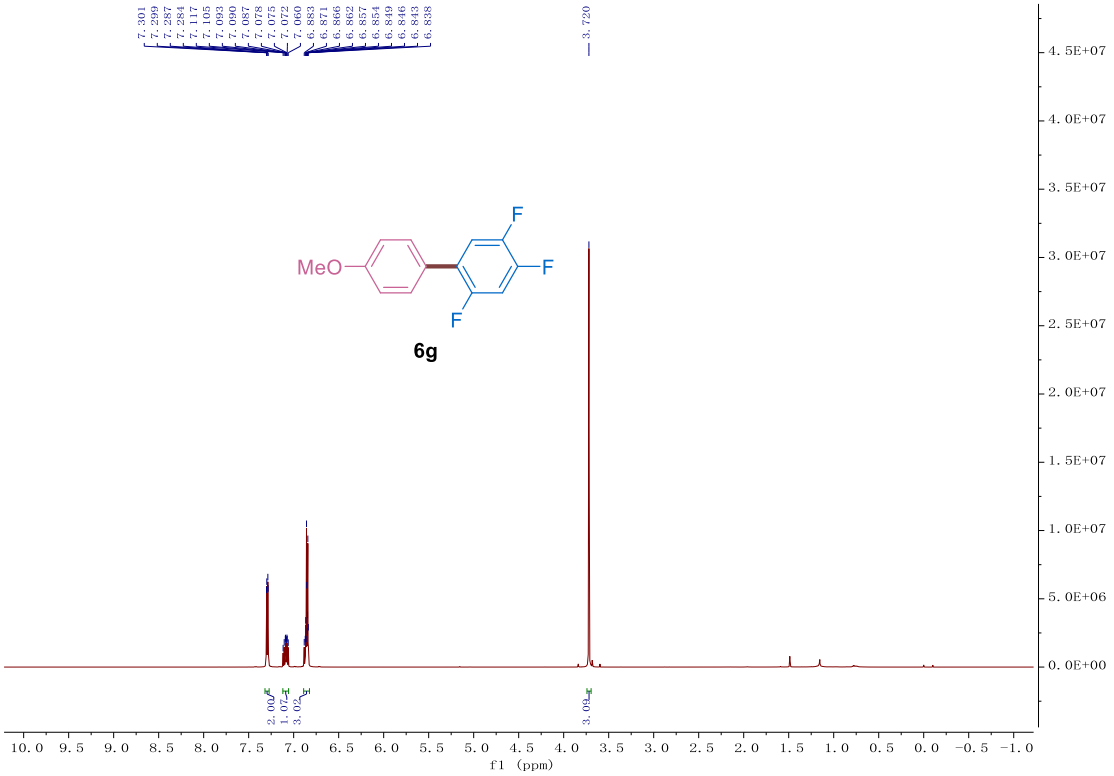
^{13}C NMR of 6f (151 MHz, $CDCl_3$)



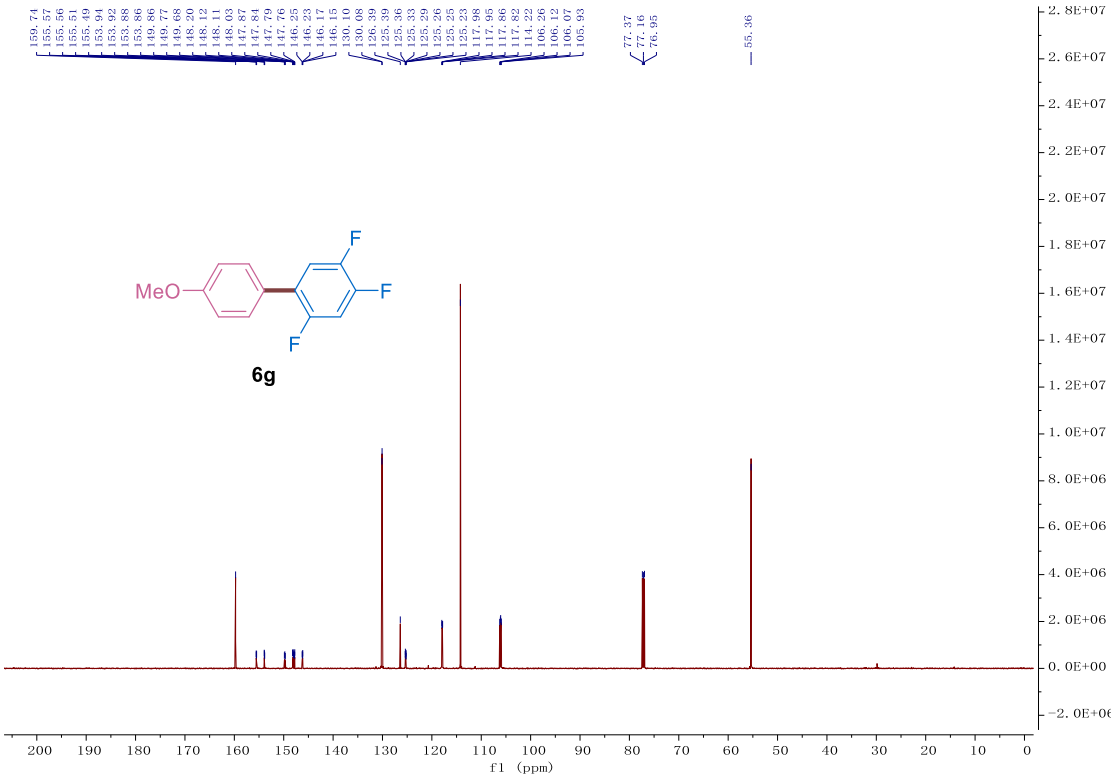
^{19}F NMR of 6f (565 MHz, $CDCl_3$)



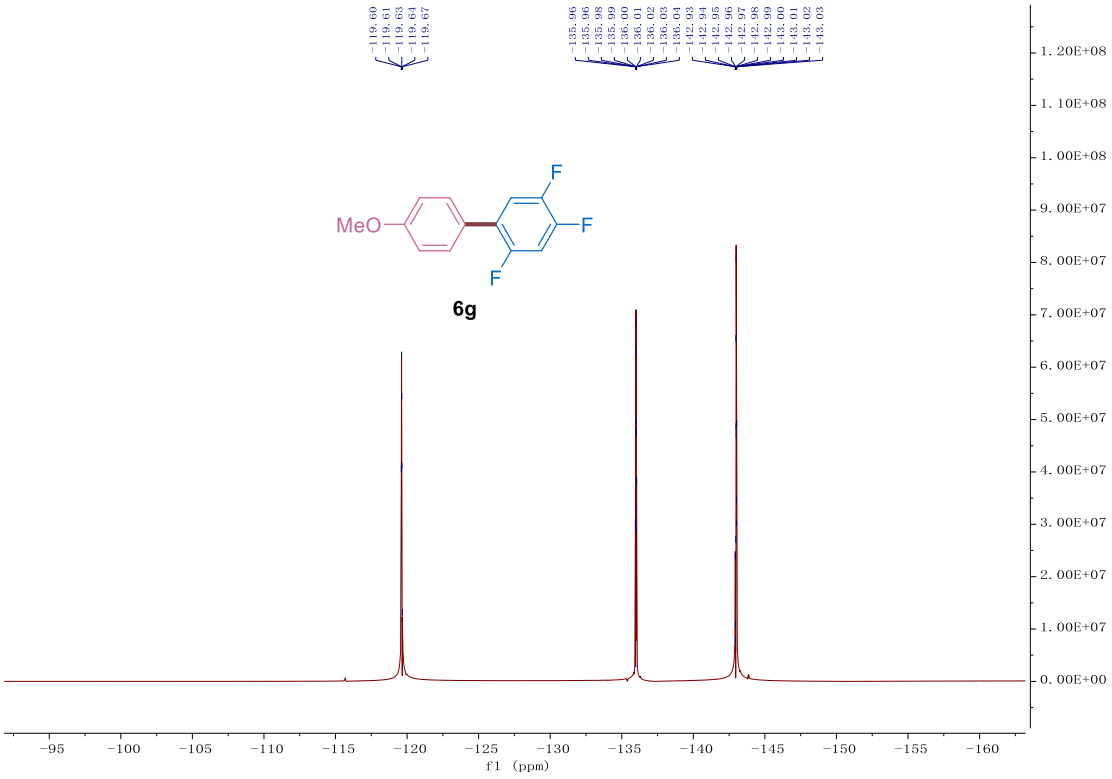
^{1}H NMR of 6g (600 MHz, $CDCl_3$)



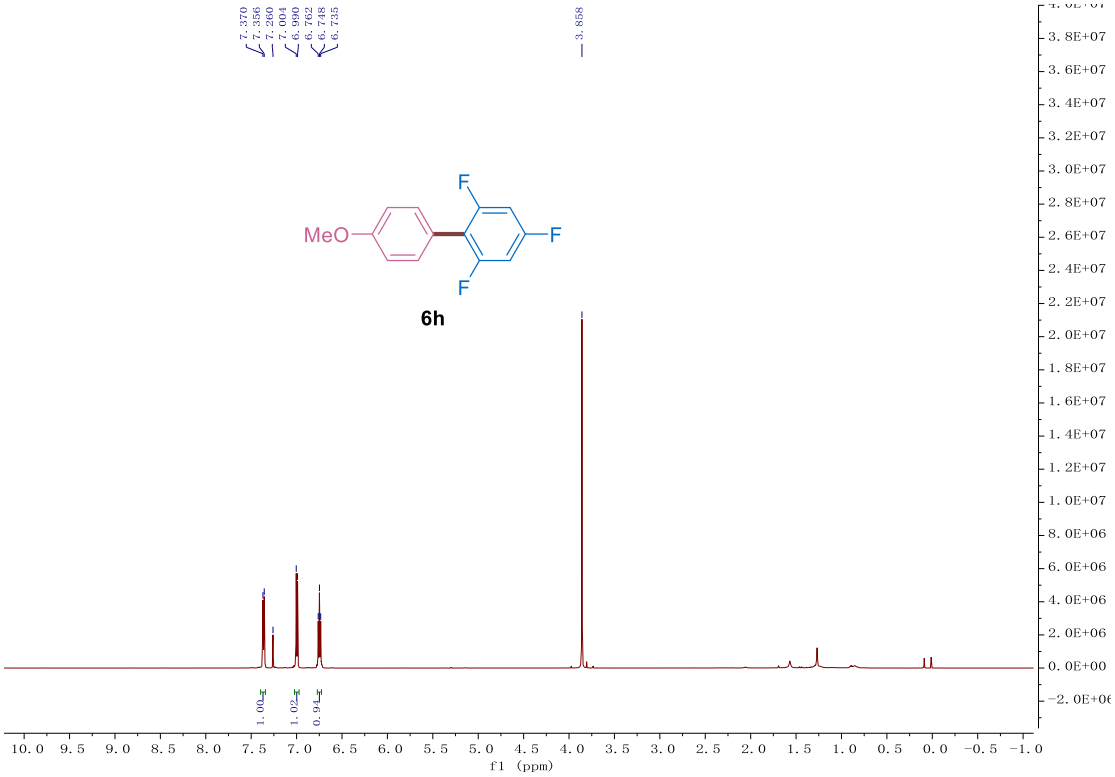
^{13}C NMR of 6g (151 MHz, $CDCl_3$)



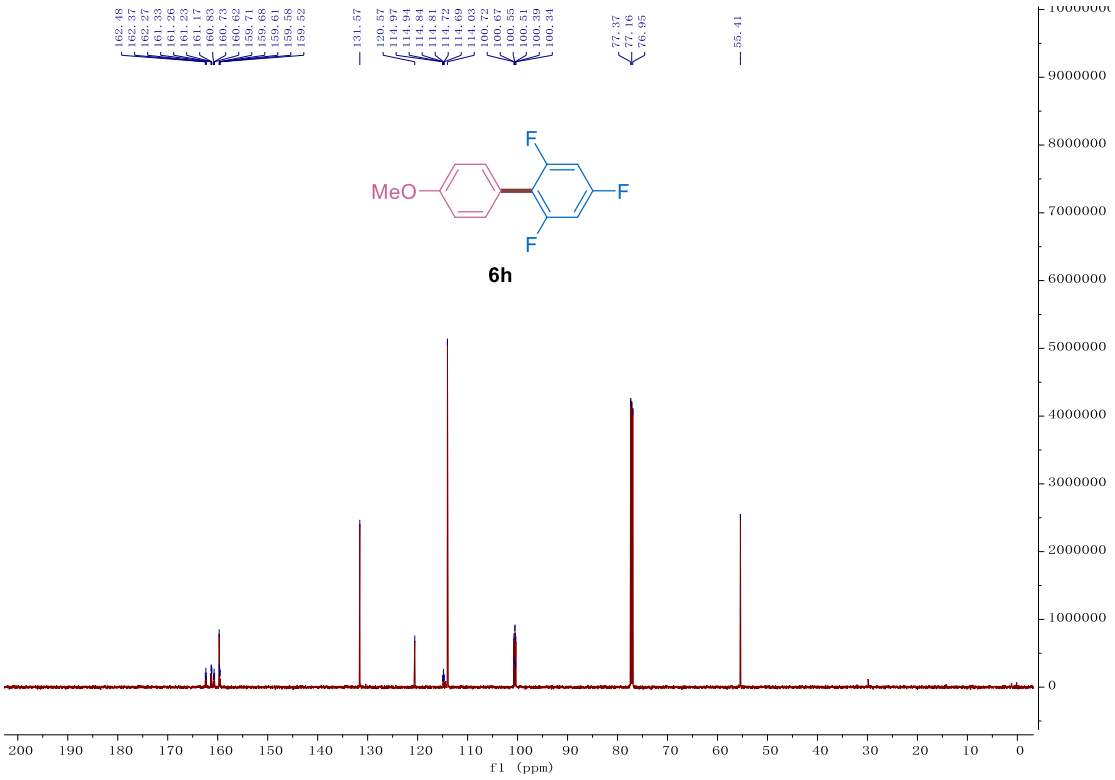
^{19}F NMR of 6g (565 MHz, $CDCl_3$)



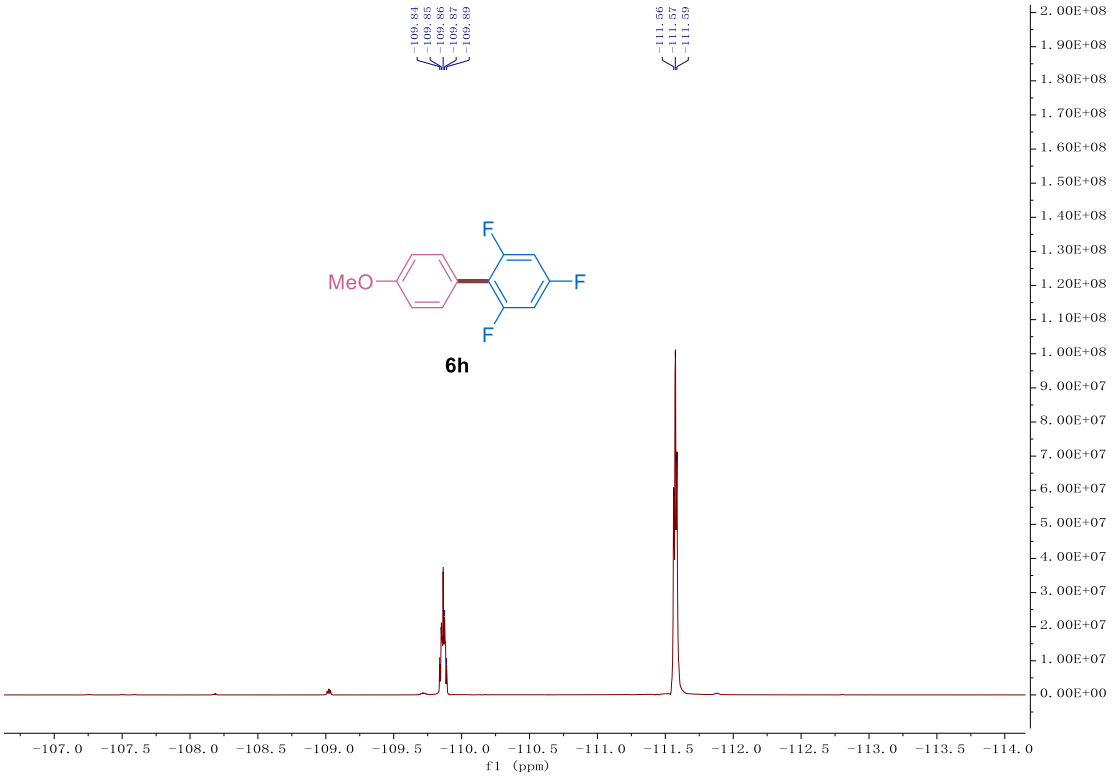
^{1}H NMR of 6h (600 MHz, $CDCl_3$)



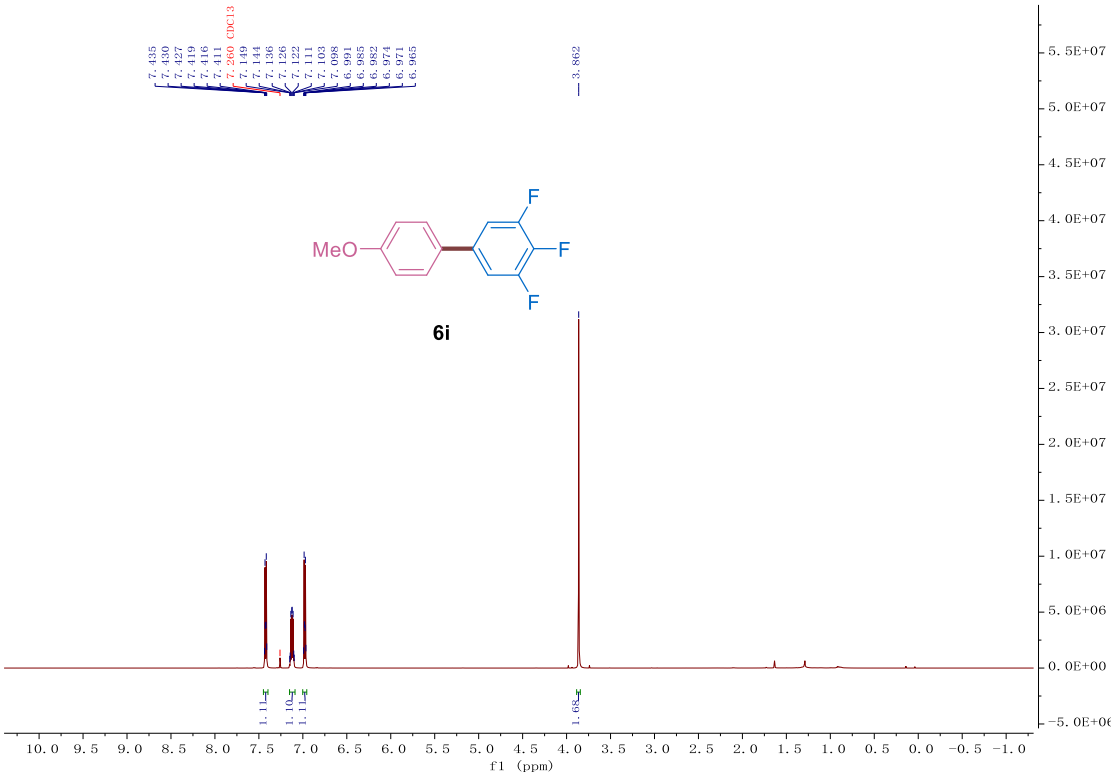
^{13}C NMR of 6h (151 MHz, $CDCl_3$)



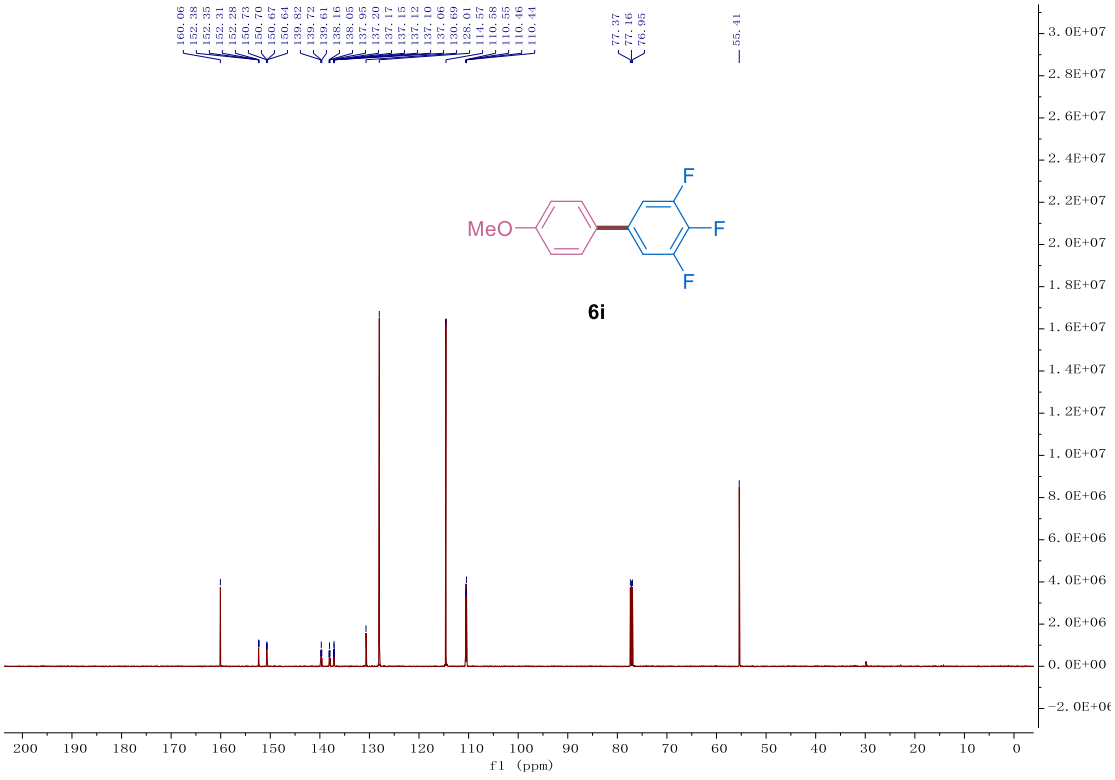
^{19}F NMR of 6h (565 MHz, $CDCl_3$)



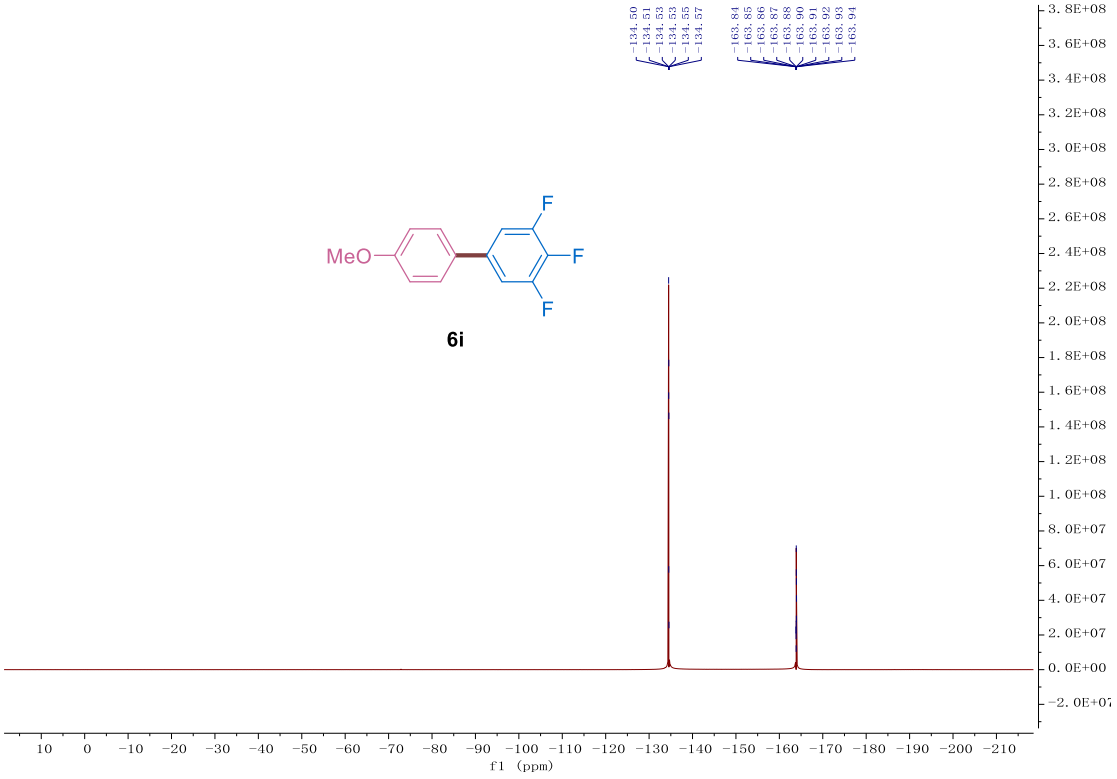
^{1}H NMR of 6i (600 MHz, $CDCl_3$)



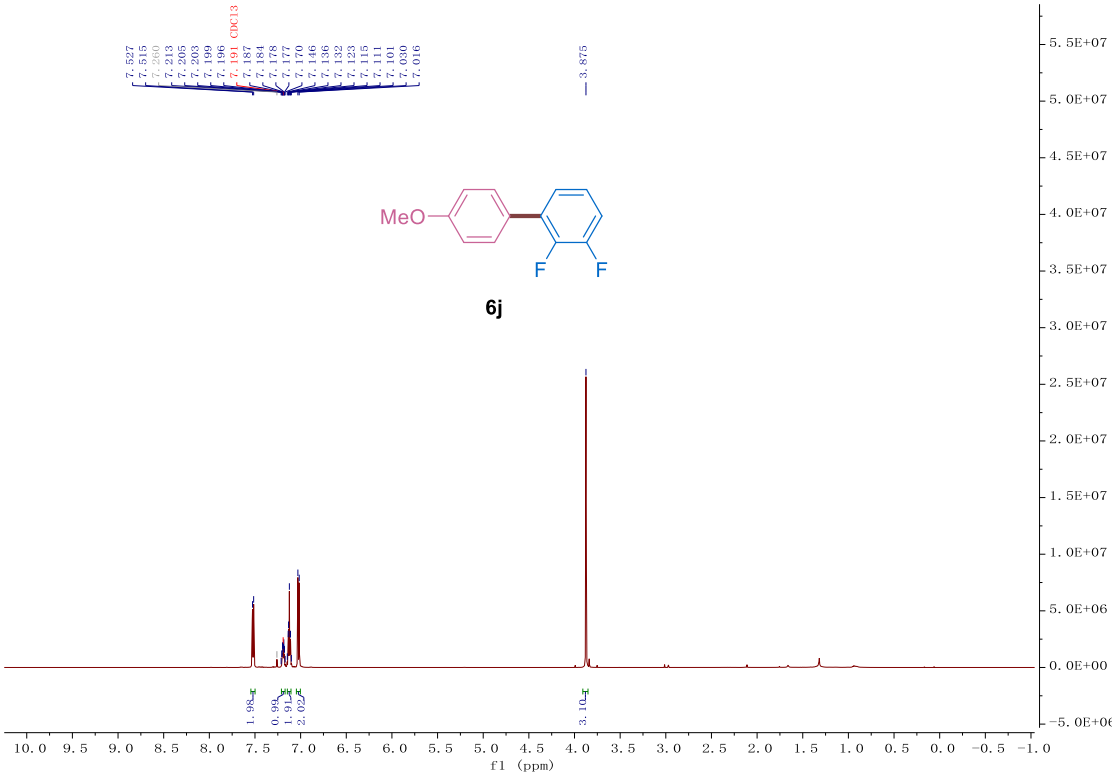
^{13}C NMR of 6i (151 MHz, $CDCl_3$)



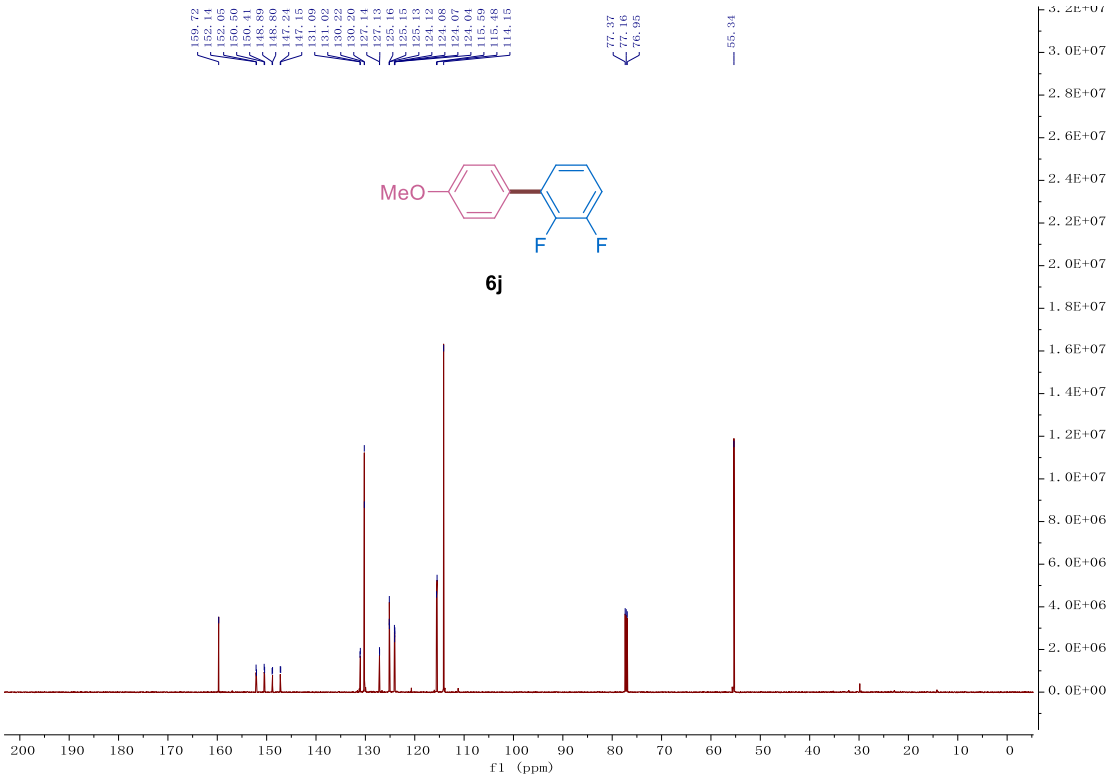
^{19}F NMR of 6i (565 MHz, $CDCl_3$)



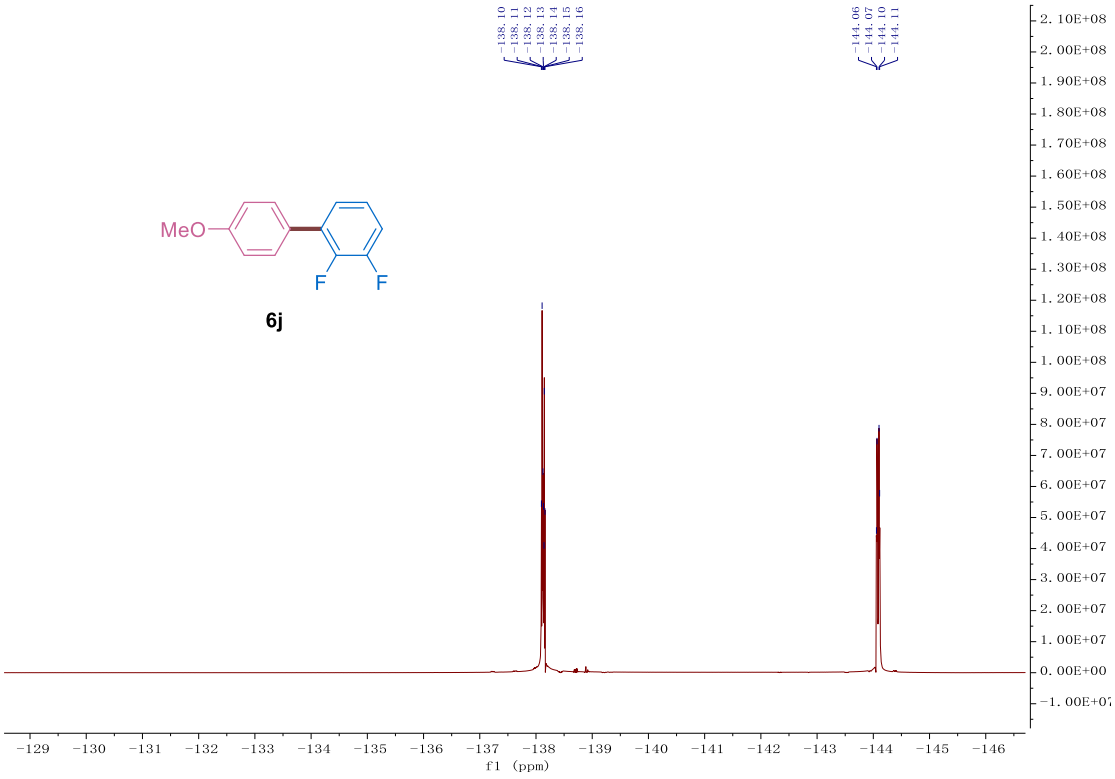
^{1}H NMR of 6j (600 MHz, $CDCl_3$)



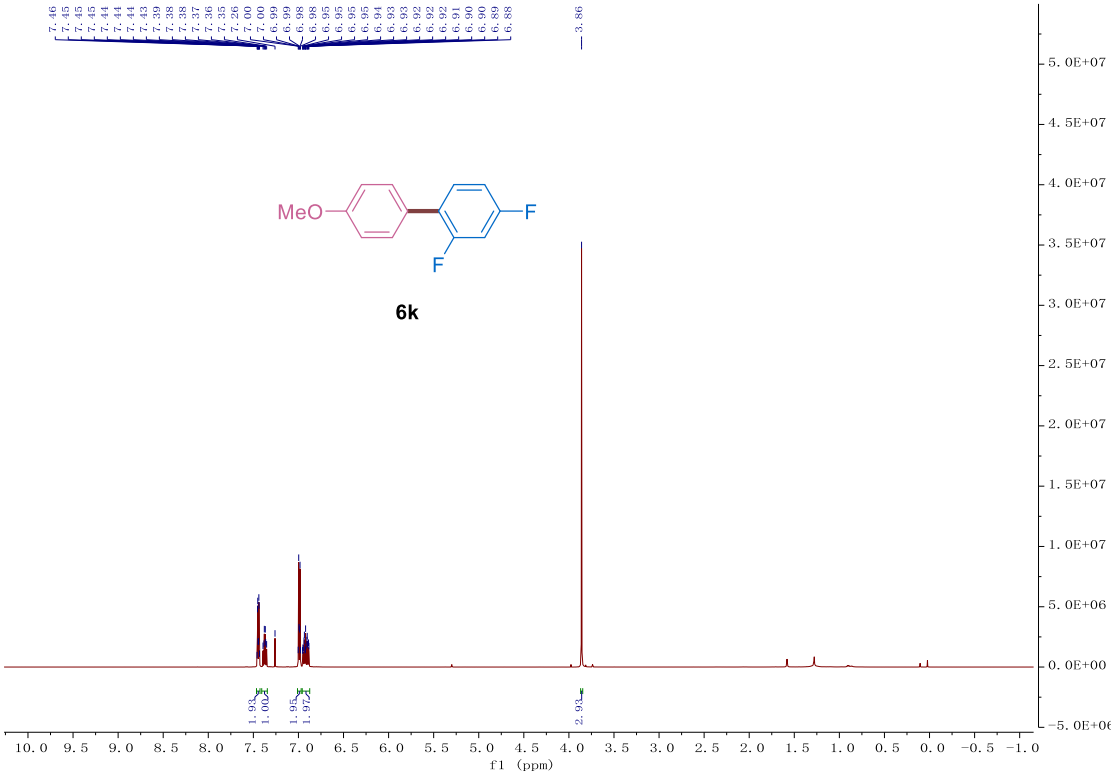
^{13}C NMR of 6j (151 MHz, $CDCl_3$)



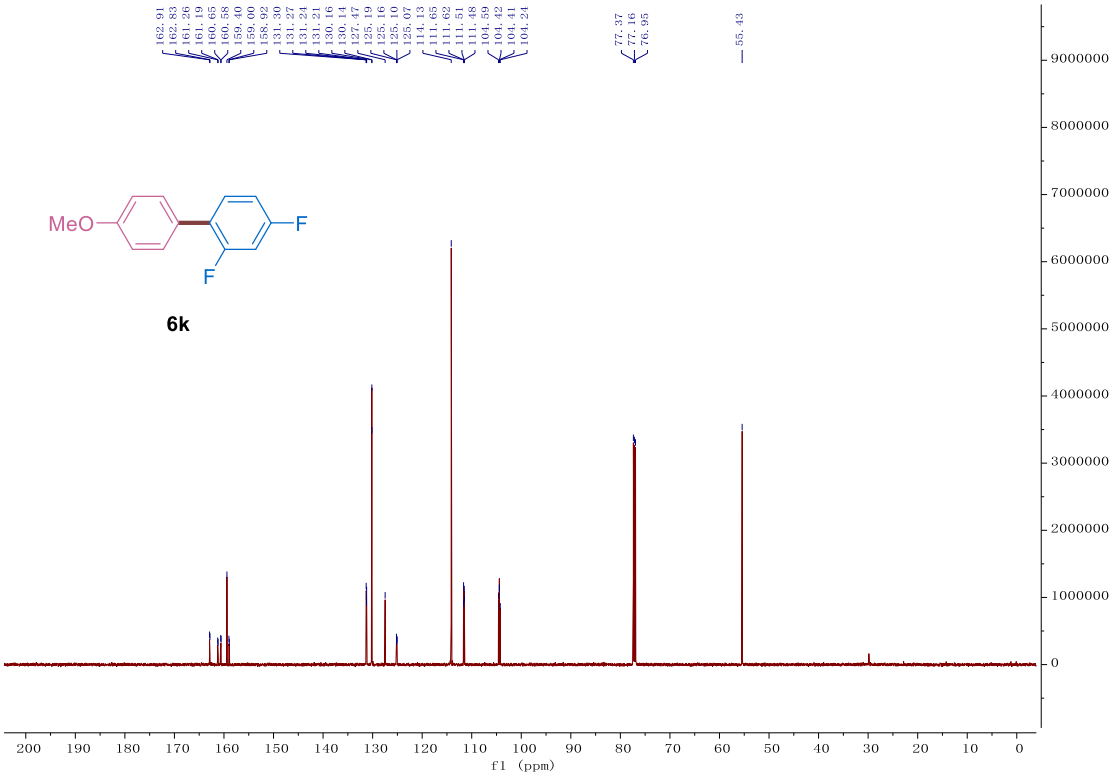
^{19}F NMR of 6j (565 MHz, $CDCl_3$)



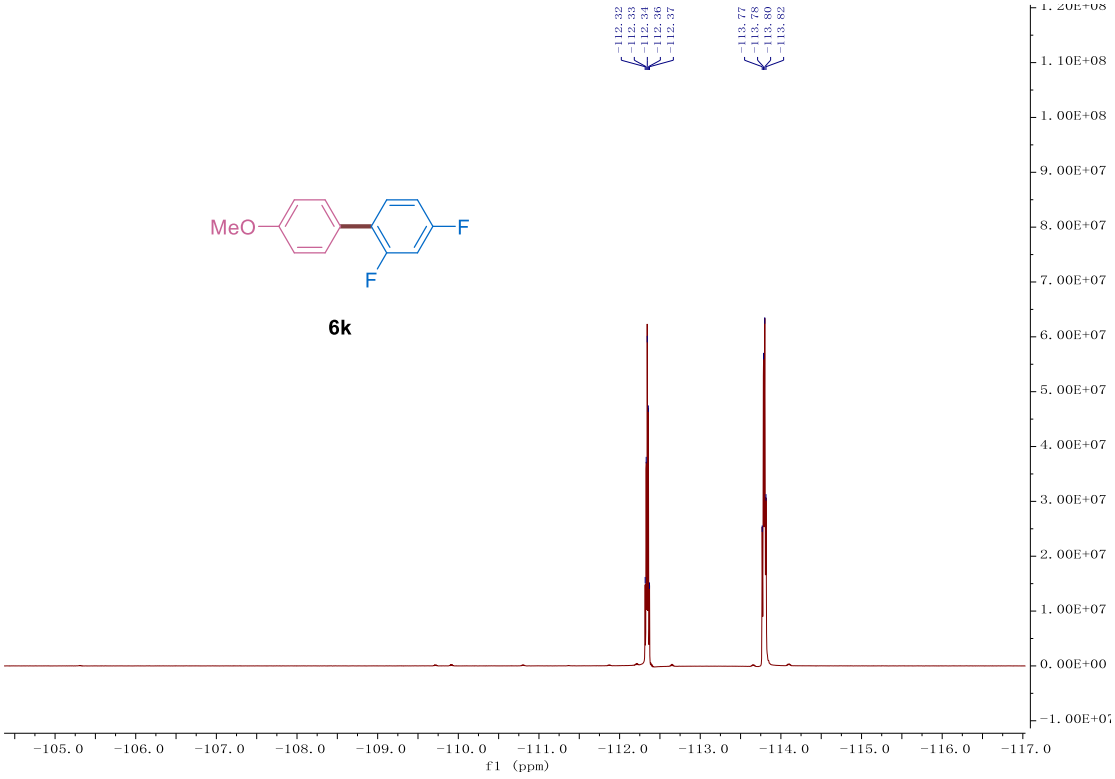
^{1}H NMR of 6k (600 MHz, $CDCl_3$)



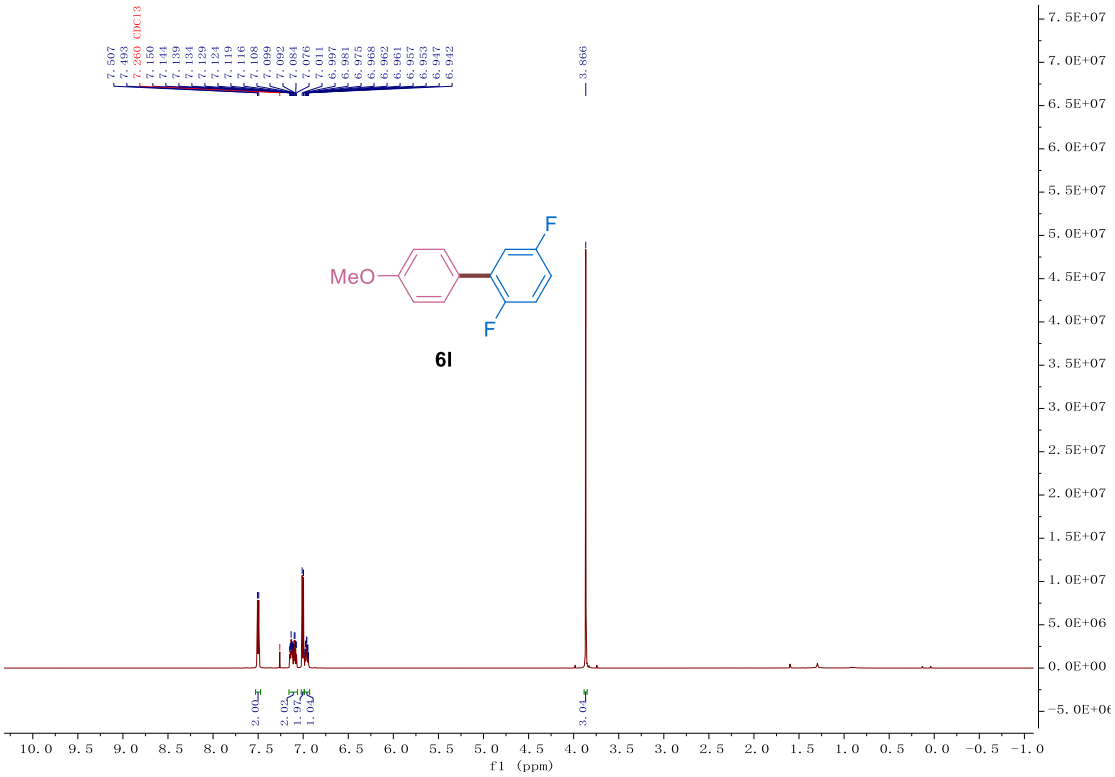
^{13}C NMR of 6k (151 MHz, $CDCl_3$)



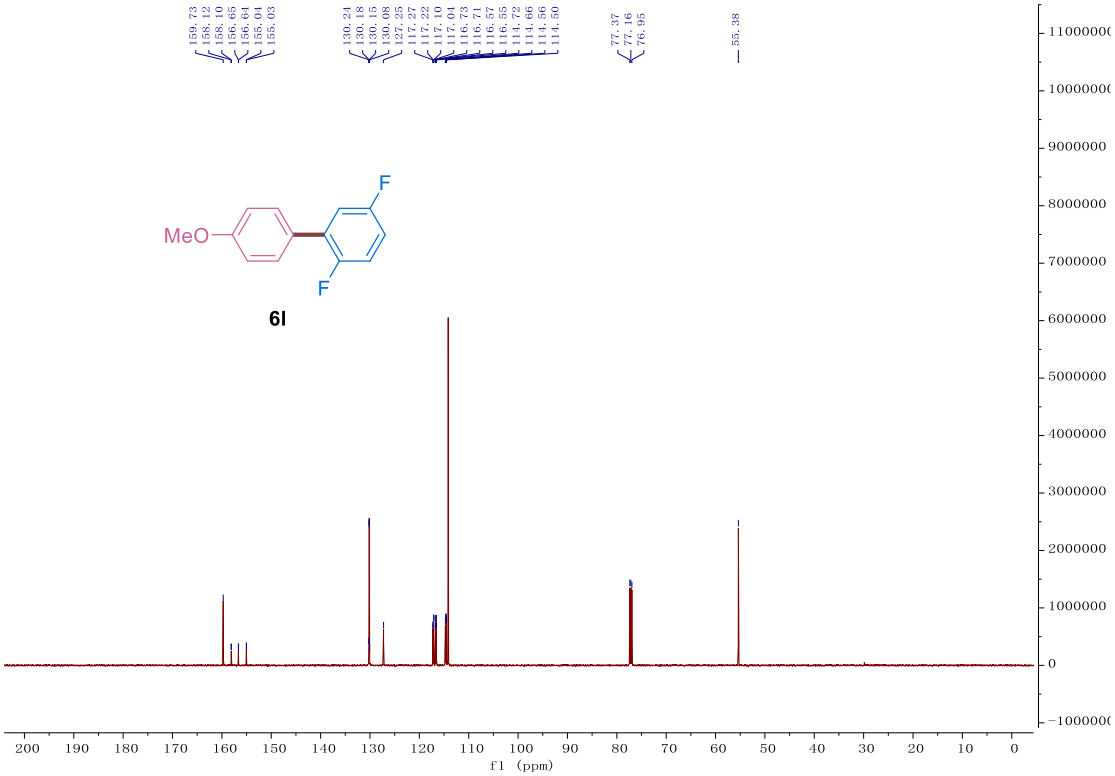
^{19}F NMR of 6k (565 MHz, $CDCl_3$)



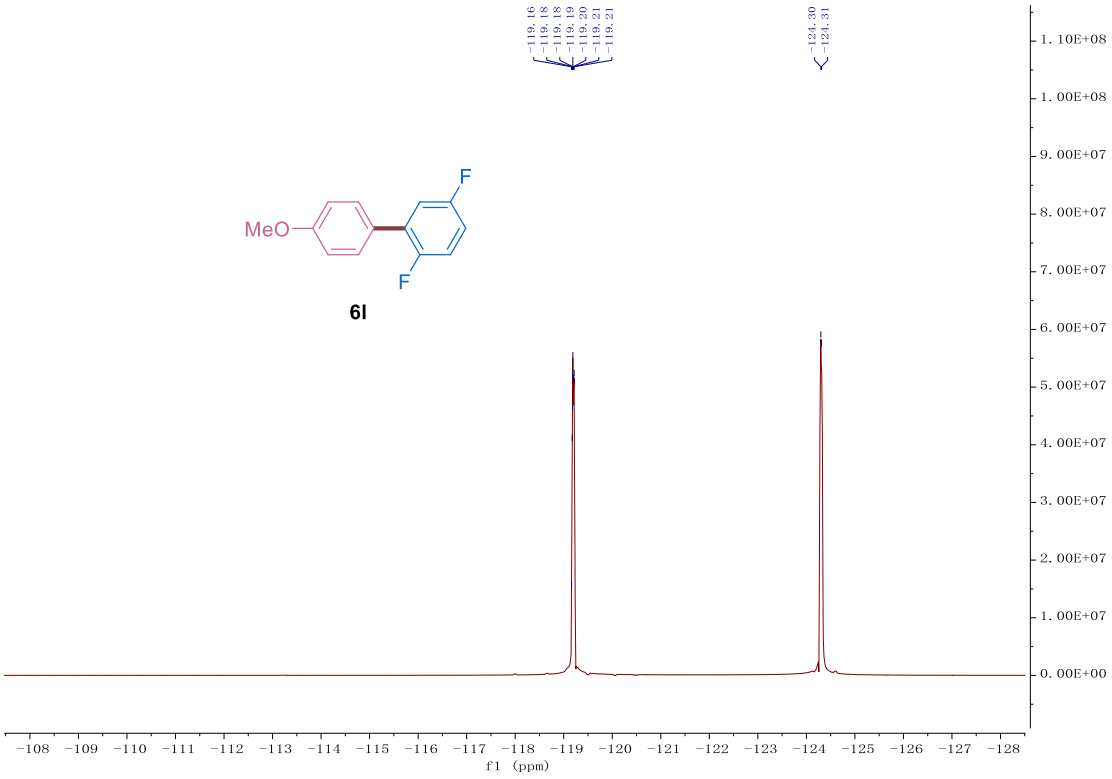
^{1}H NMR of 6l (600 MHz, $CDCl_3$)



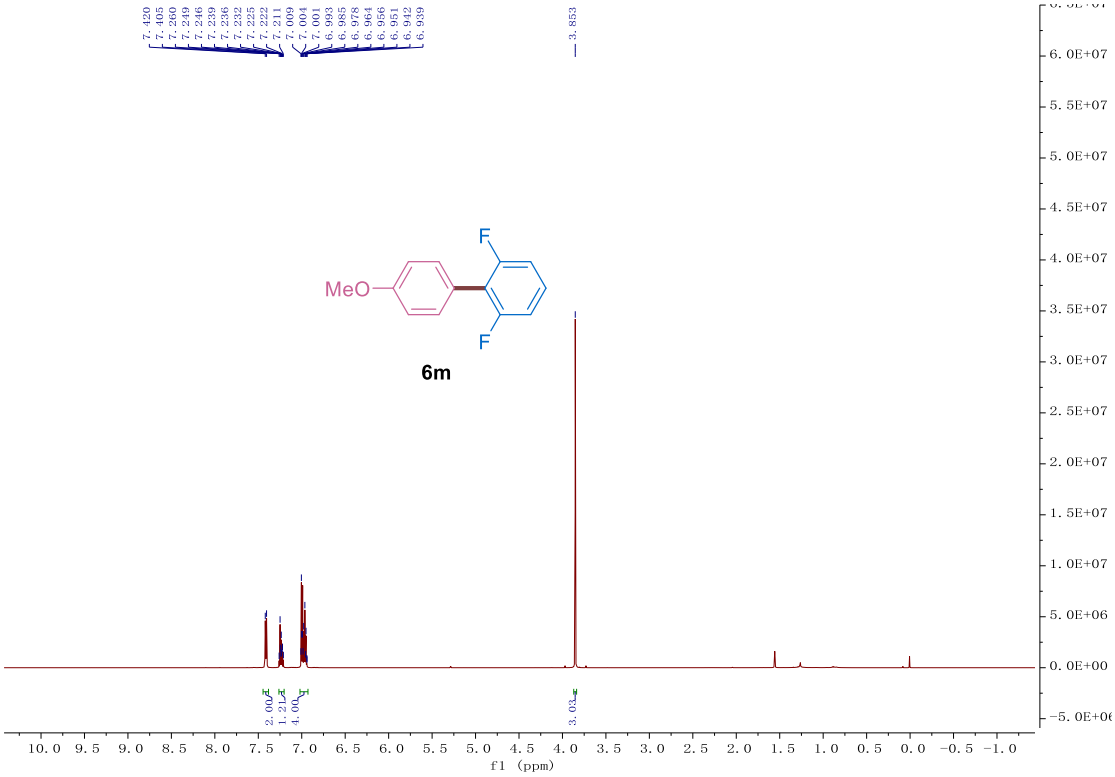
^{13}C NMR of 6l (151 MHz, $CDCl_3$)



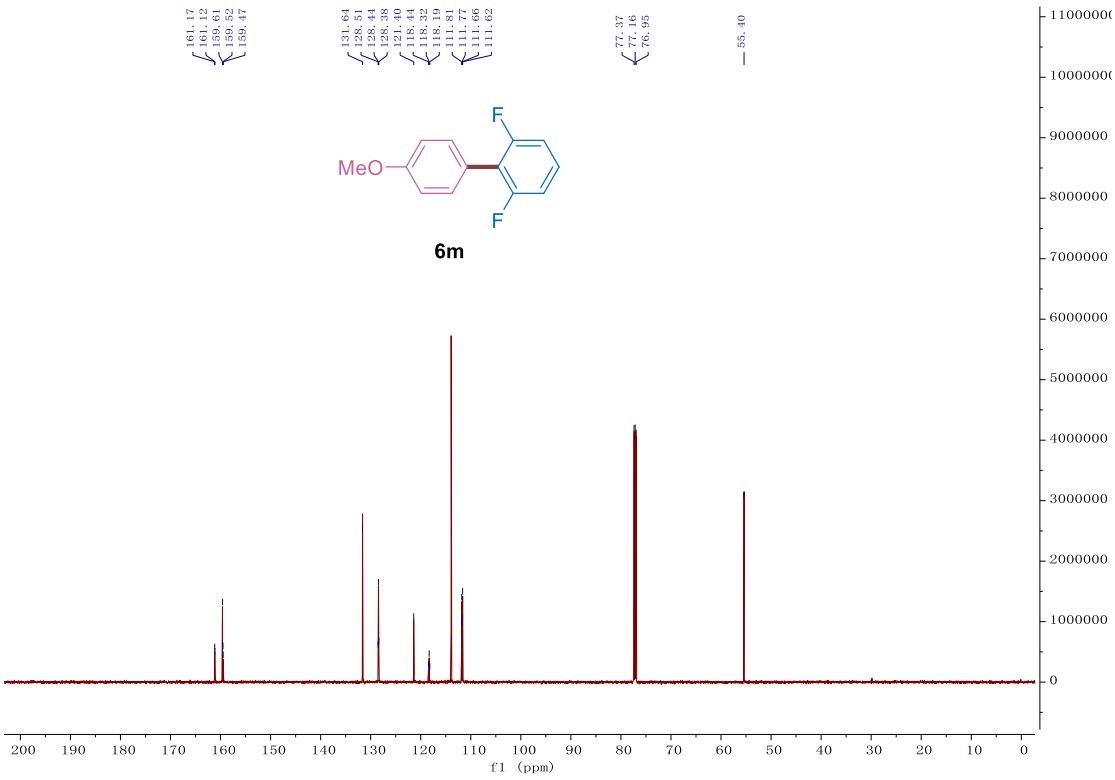
^{19}F NMR of 6l (565 MHz, $CDCl_3$)



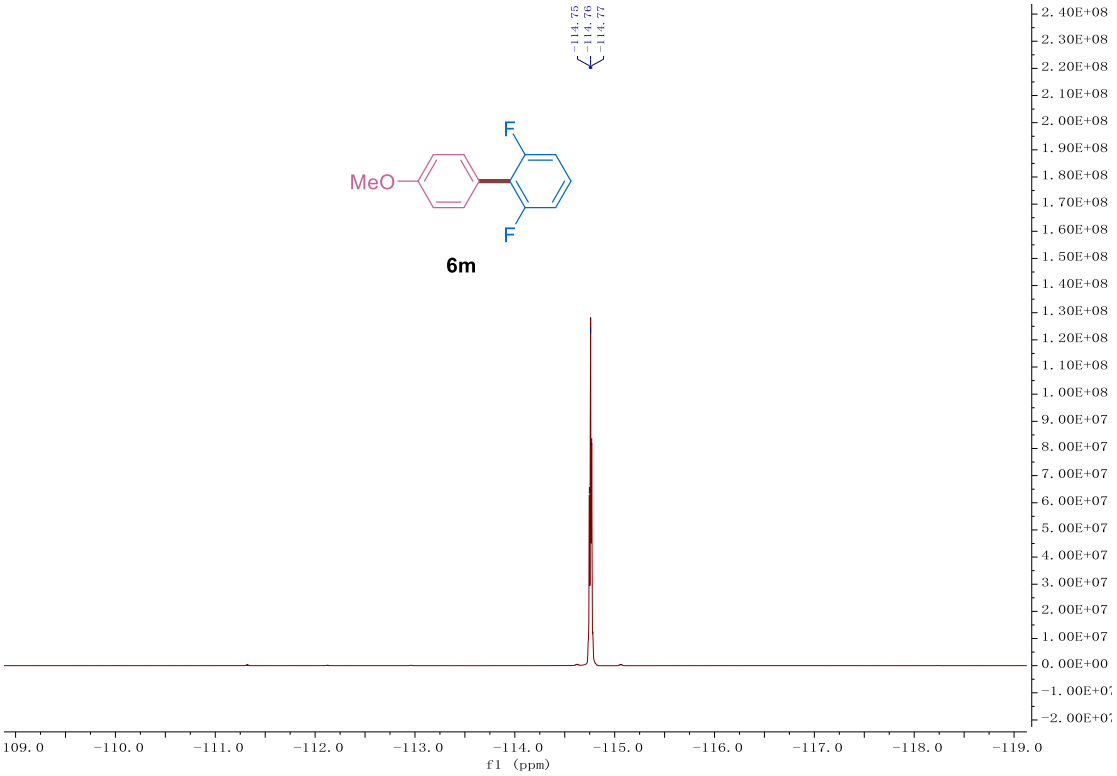
^{1}H NMR of 6m (600 MHz, $CDCl_3$)



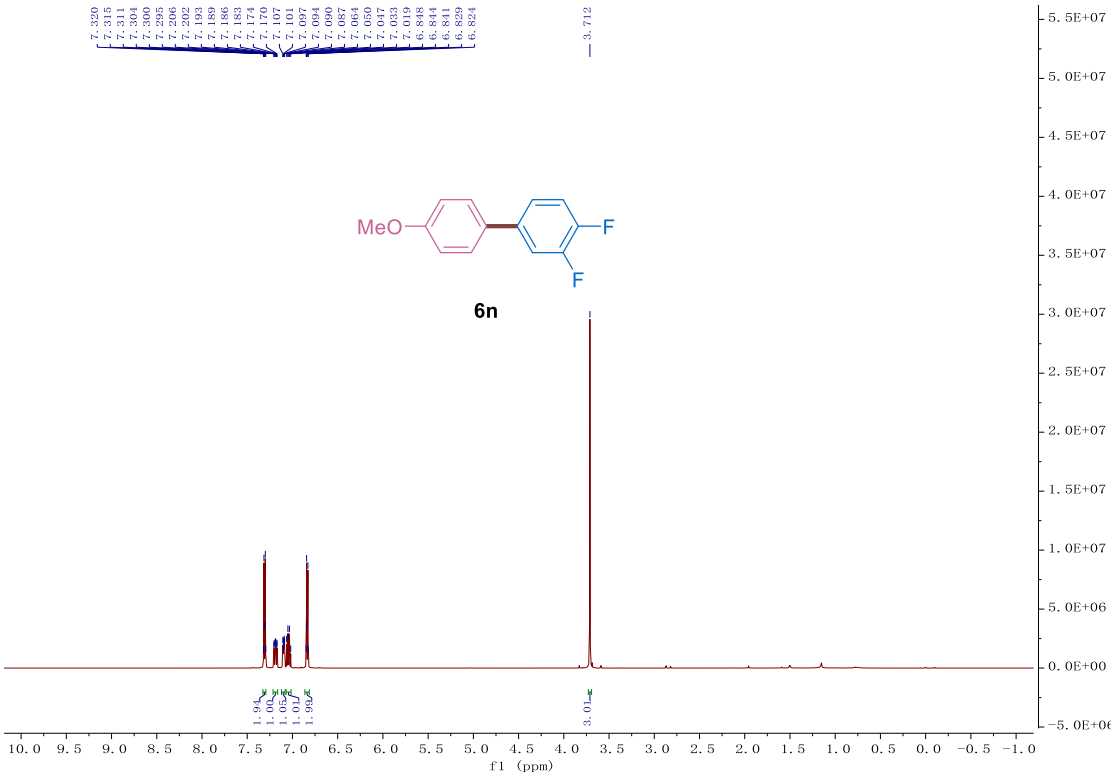
^{13}C NMR of 6m (151 MHz, $CDCl_3$)



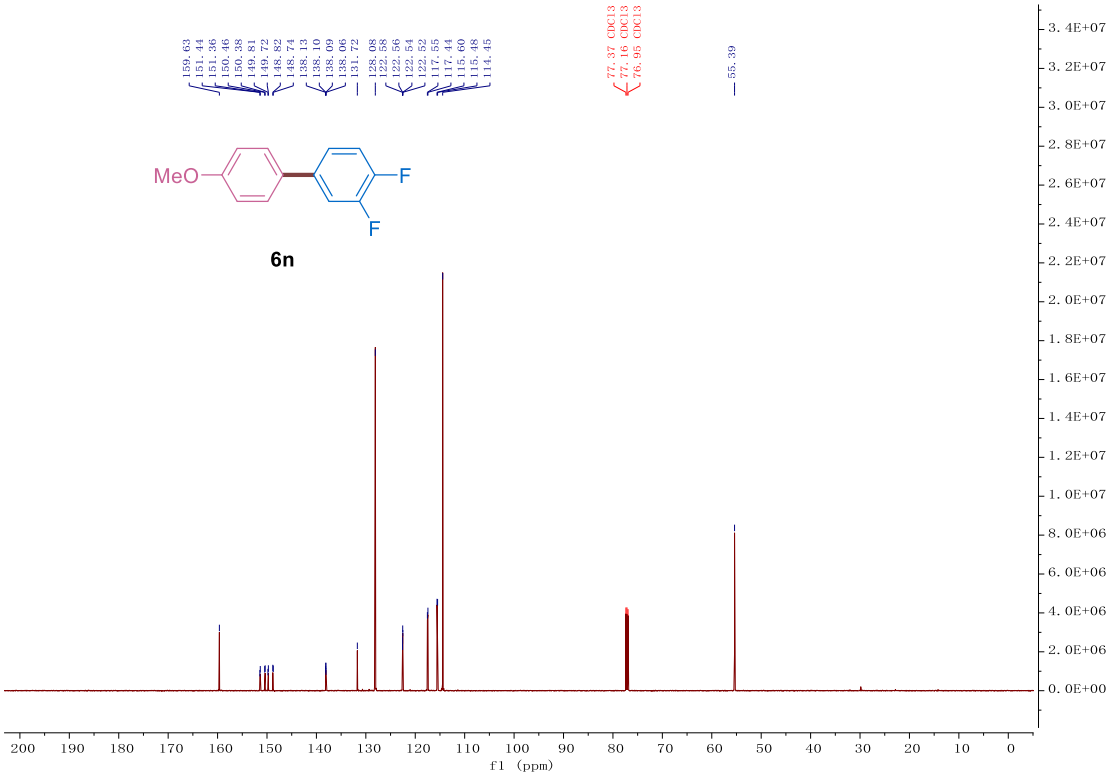
^{19}F NMR of 6m (565 MHz, $CDCl_3$)



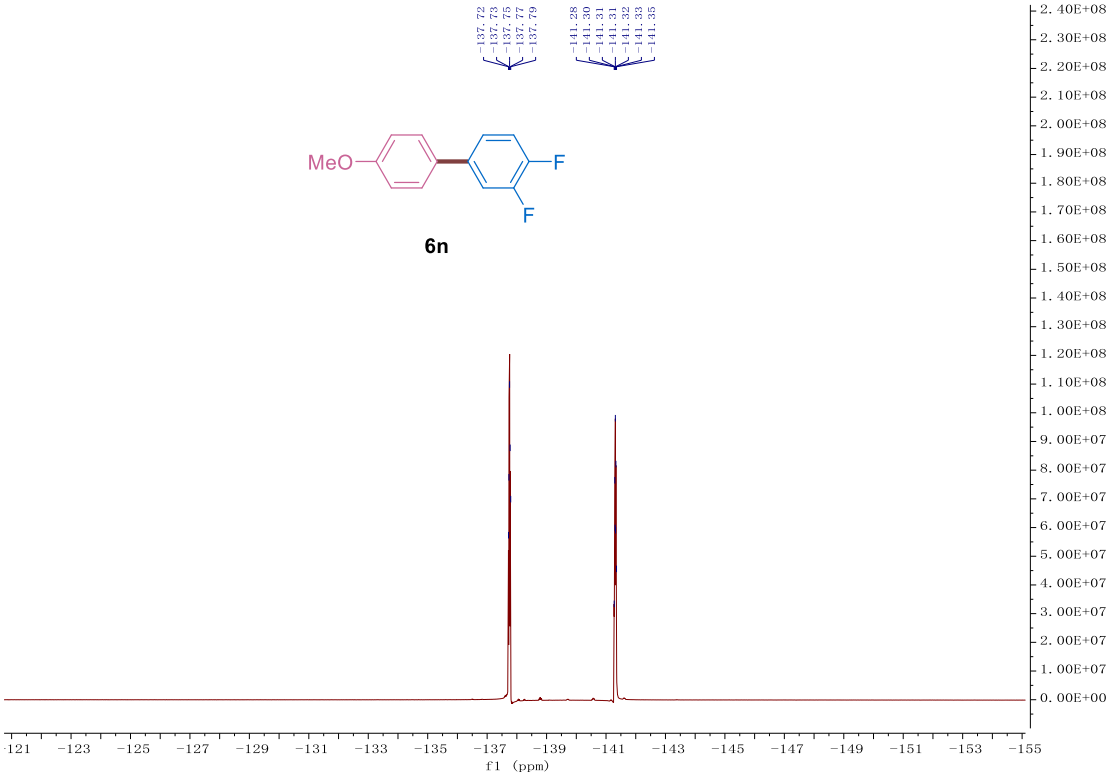
^{1}H NMR of 6n (600 MHz, $CDCl_3$)



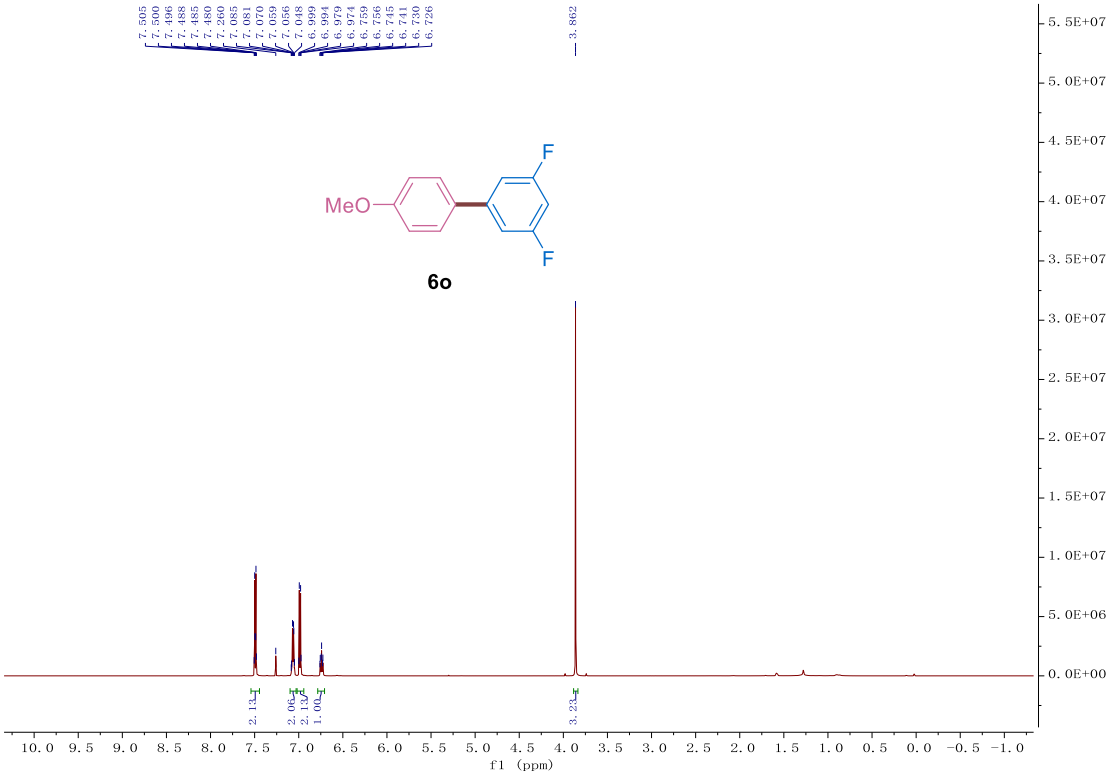
^{13}C NMR of 6n (151 MHz, $CDCl_3$)



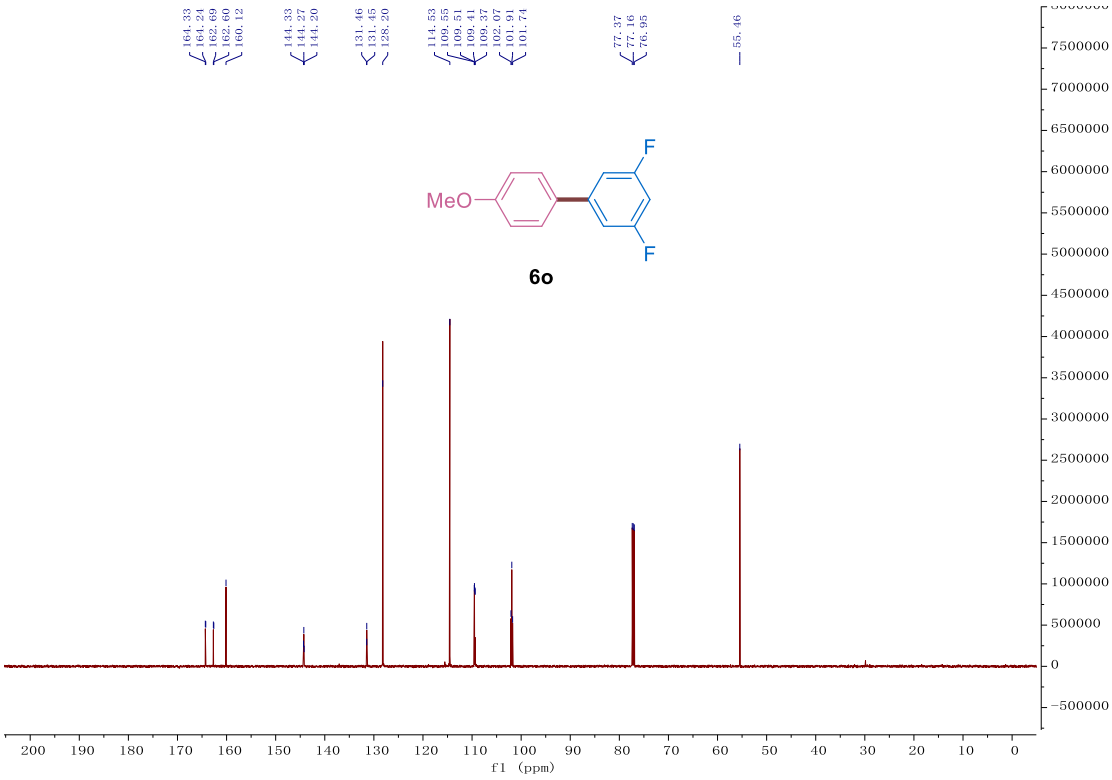
^{19}F NMR of 6n (565 MHz, $CDCl_3$)



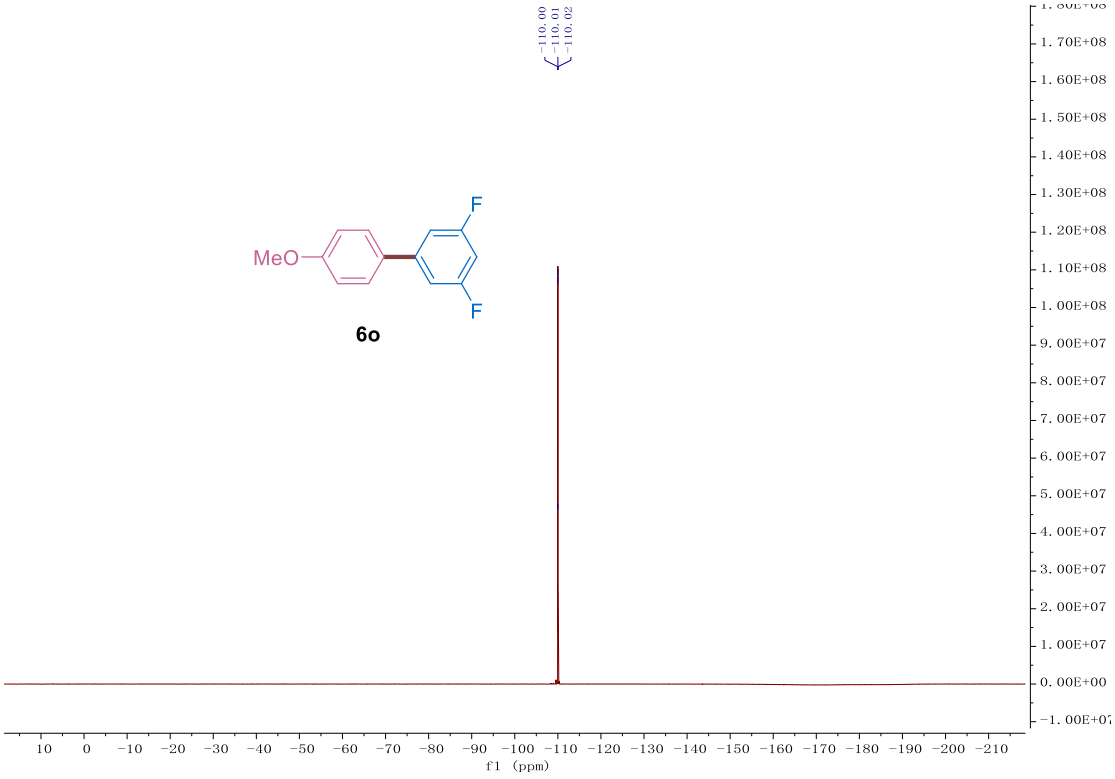
^{1}H NMR of 6o (600 MHz, $CDCl_3$)



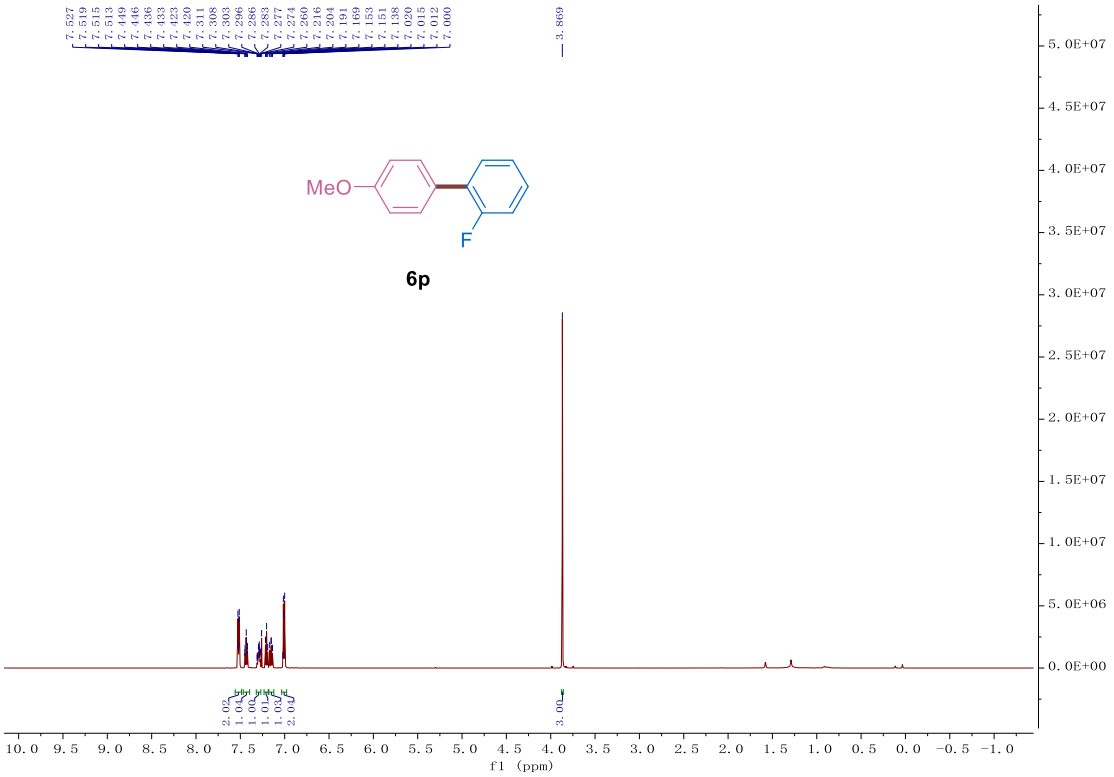
^{13}C NMR of 6o (151 MHz, $CDCl_3$)



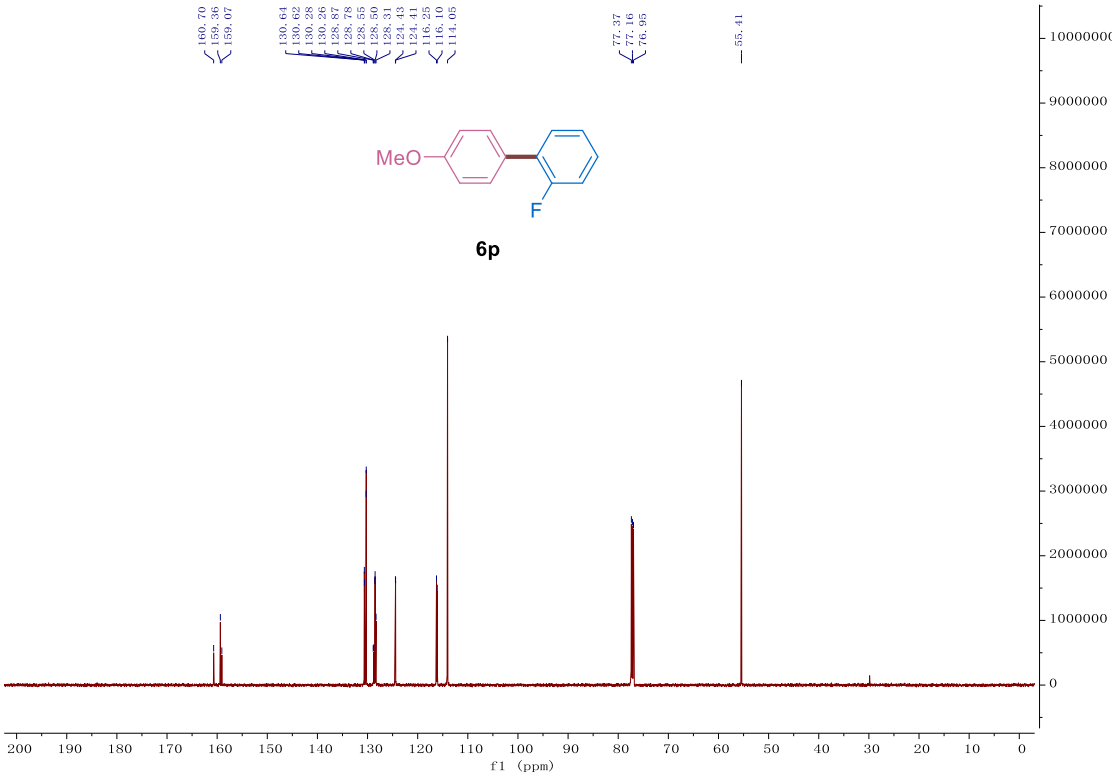
^{19}F NMR of 6o (565 MHz, $CDCl_3$)



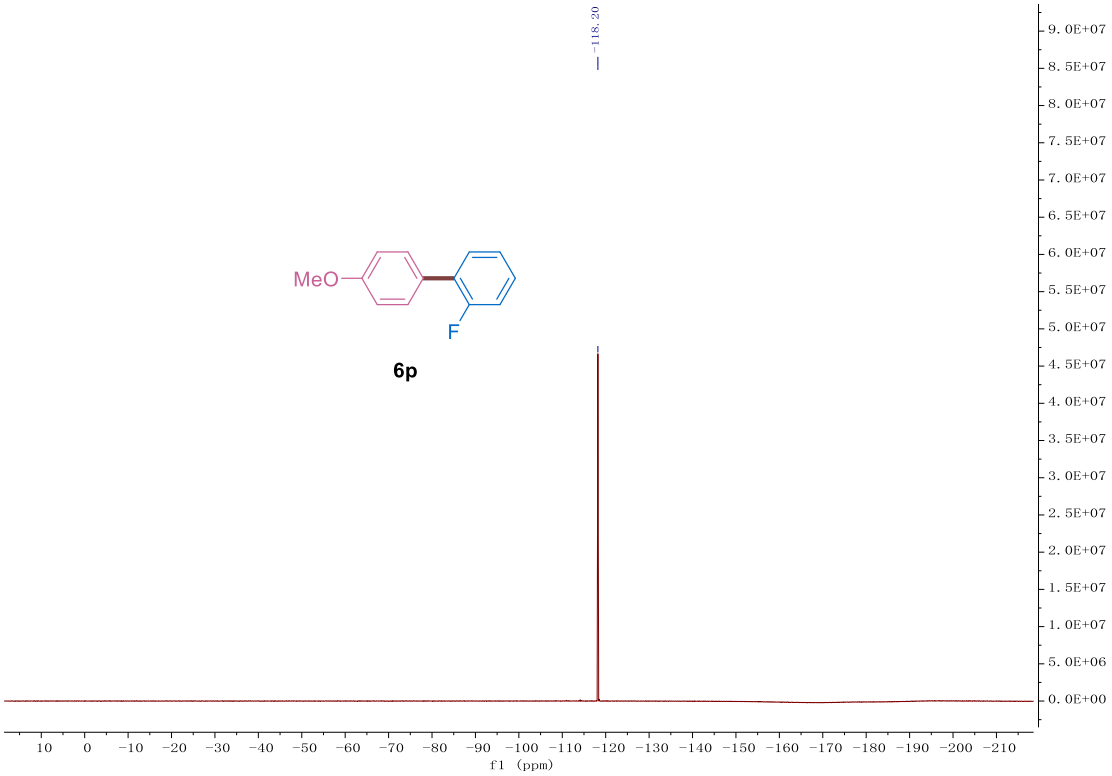
^{1}H NMR of 6p (600 MHz, $CDCl_3$)



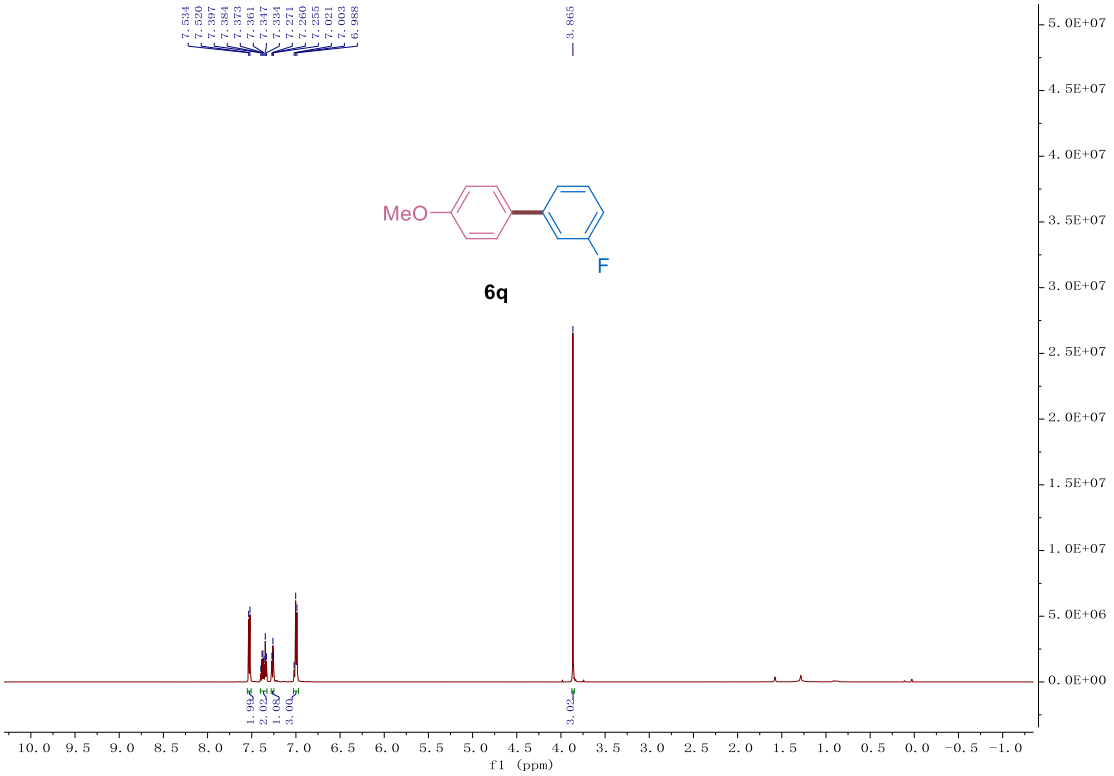
^{13}C NMR of 6p (151 MHz, $CDCl_3$)



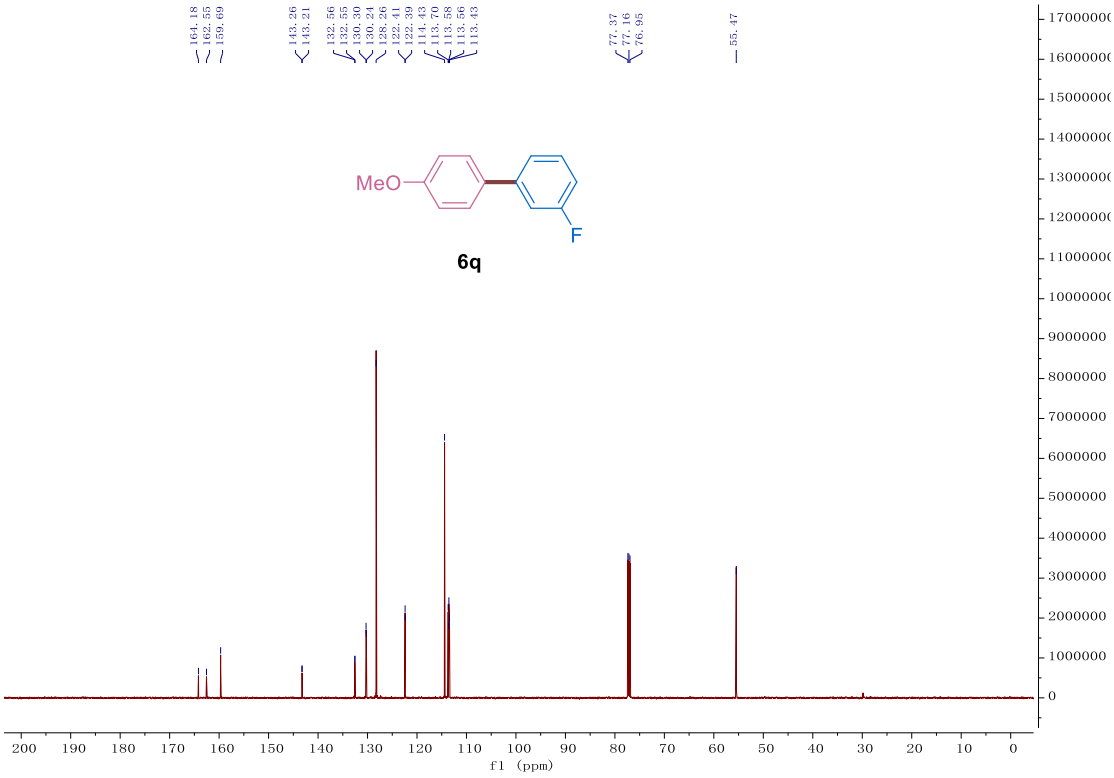
^{19}F NMR of 6p (565 MHz, $CDCl_3$)



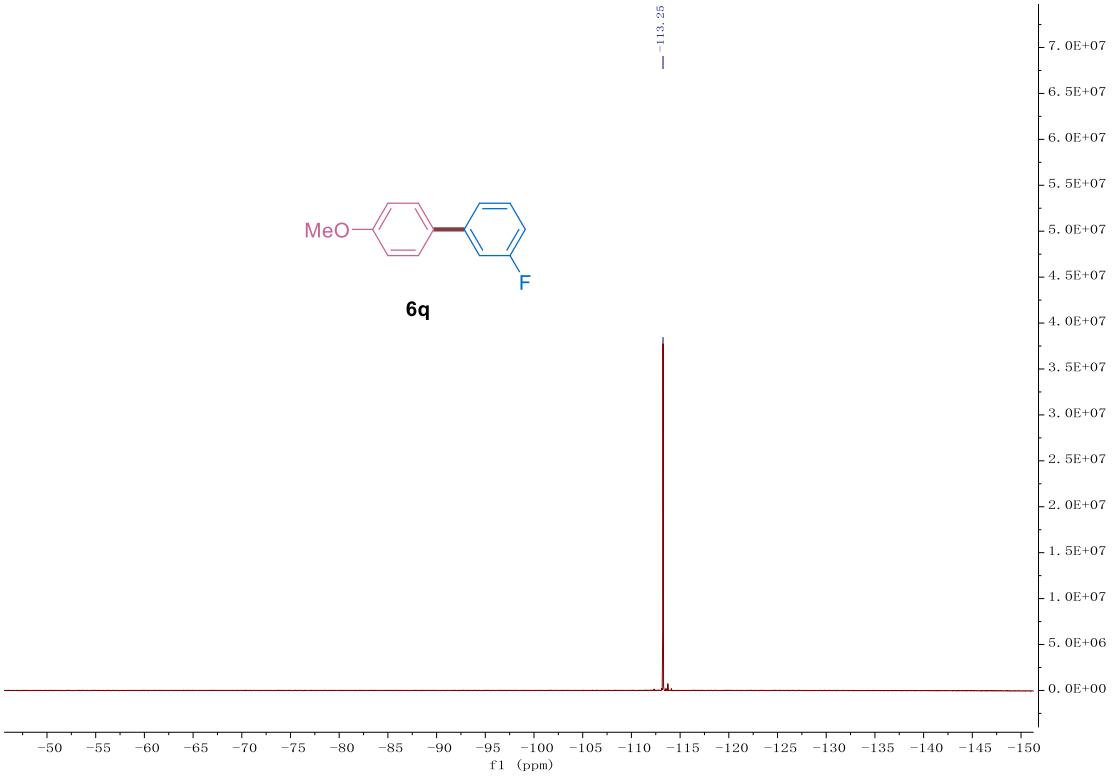
^{1}H NMR of 6q (600 MHz, $CDCl_3$)



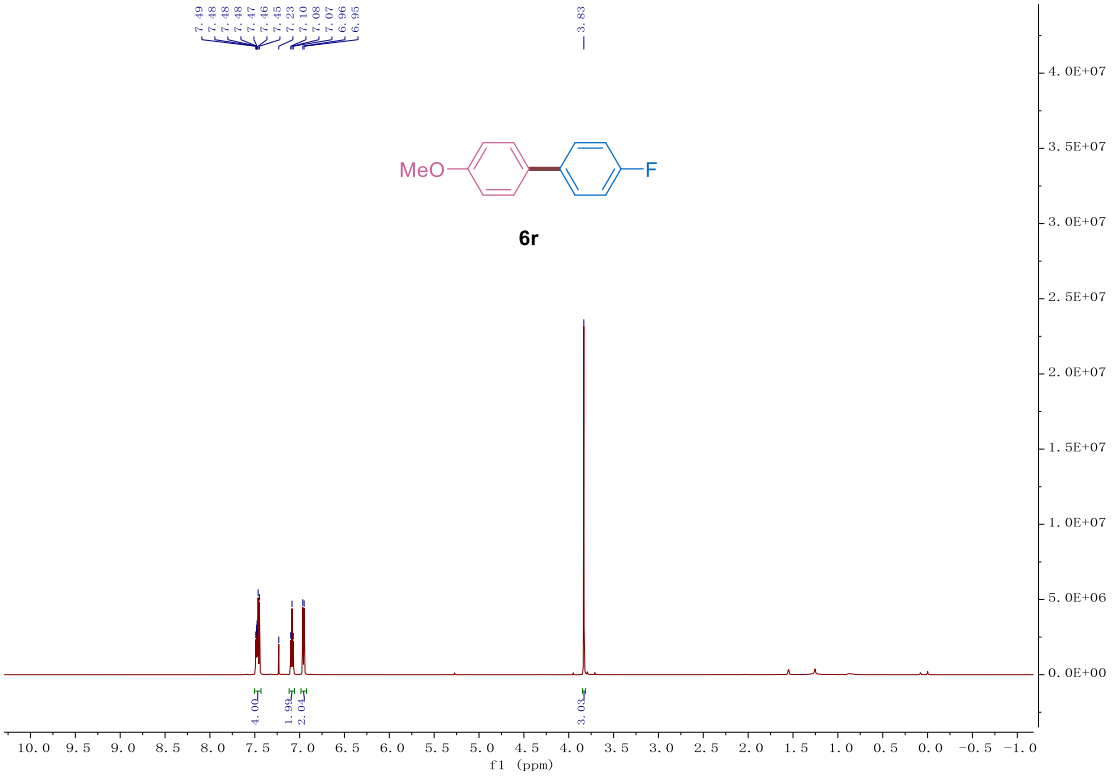
^{13}C NMR of 6q (151 MHz, $CDCl_3$)



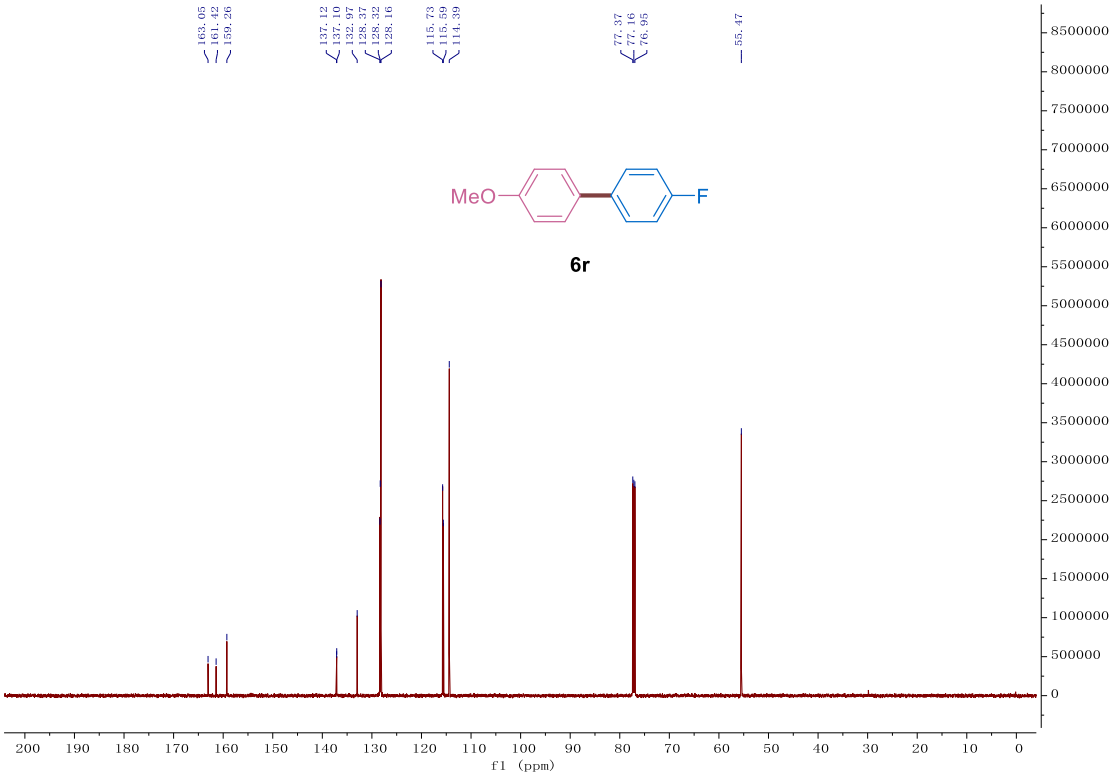
^{19}F NMR of 6q (565 MHz, $CDCl_3$)



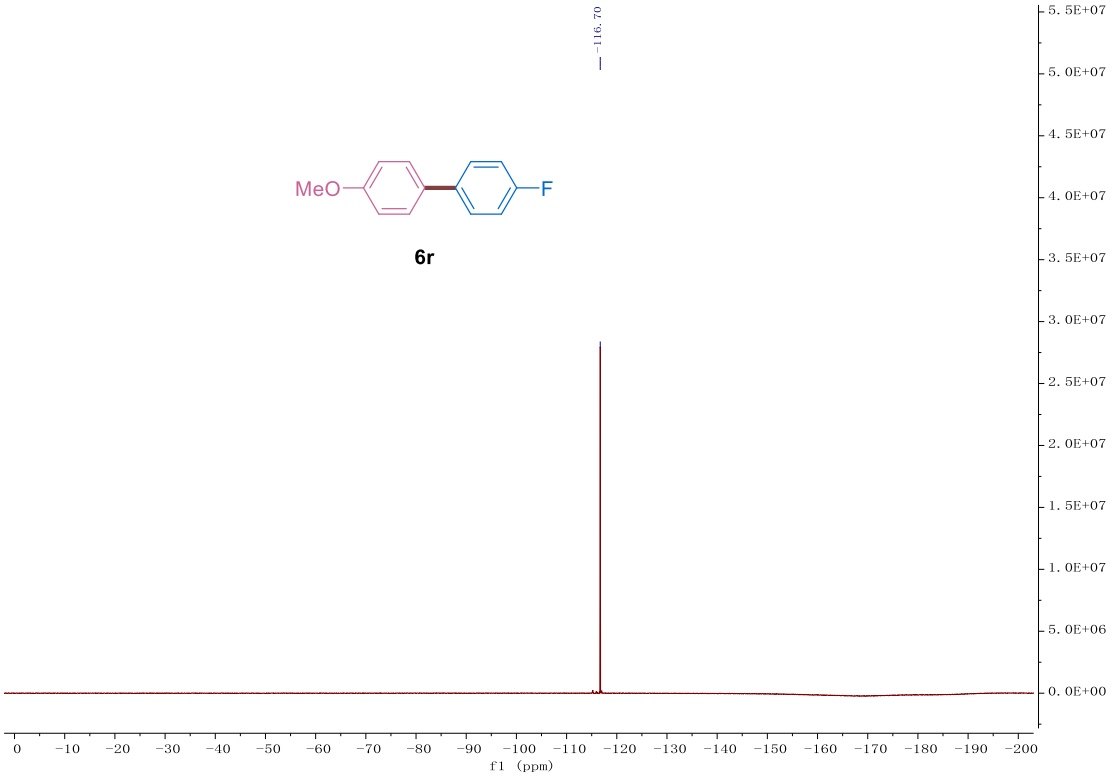
^{1}H NMR of 6r (600 MHz, $CDCl_3$)



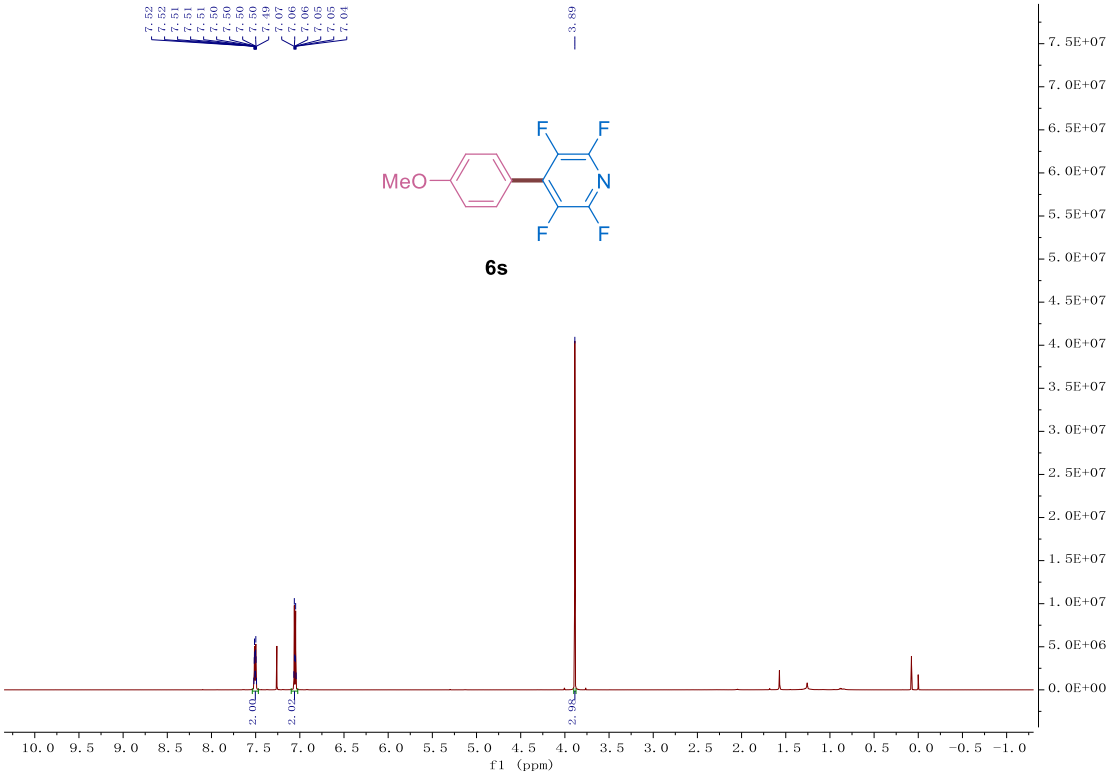
^{13}C NMR of 6r (151 MHz, $CDCl_3$)



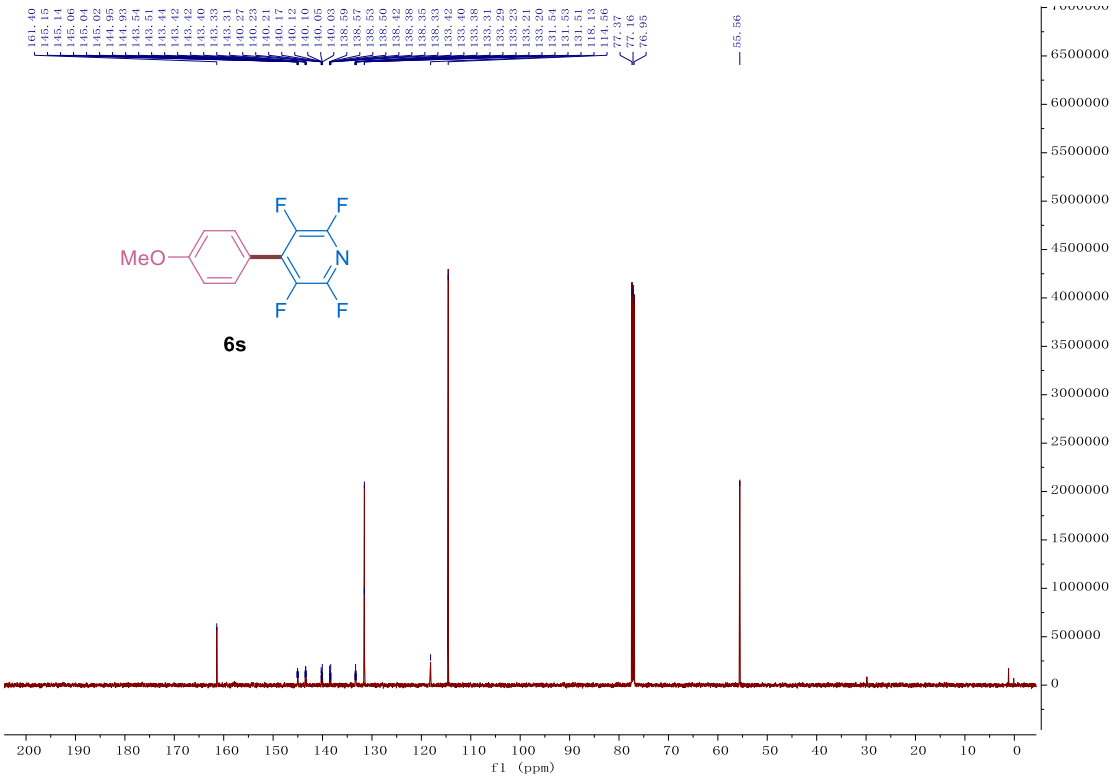
^{19}F NMR of 6r (565 MHz, $CDCl_3$)



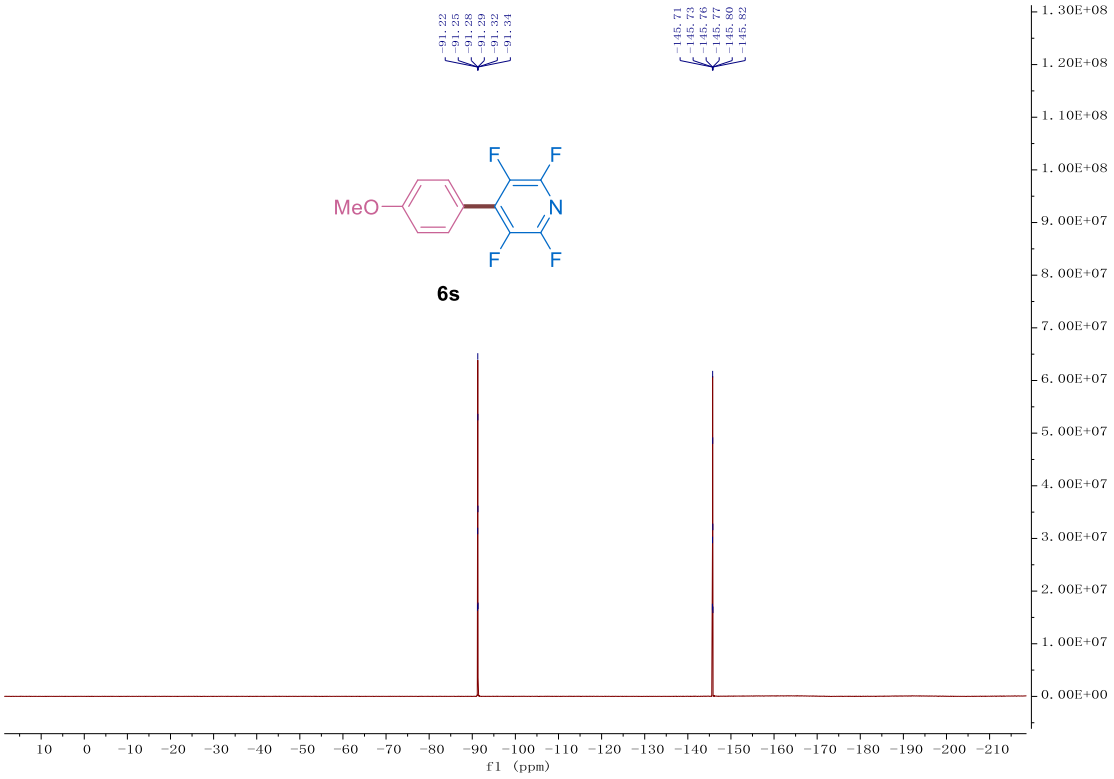
^{1}H NMR of 6s (600 MHz, $CDCl_3$)



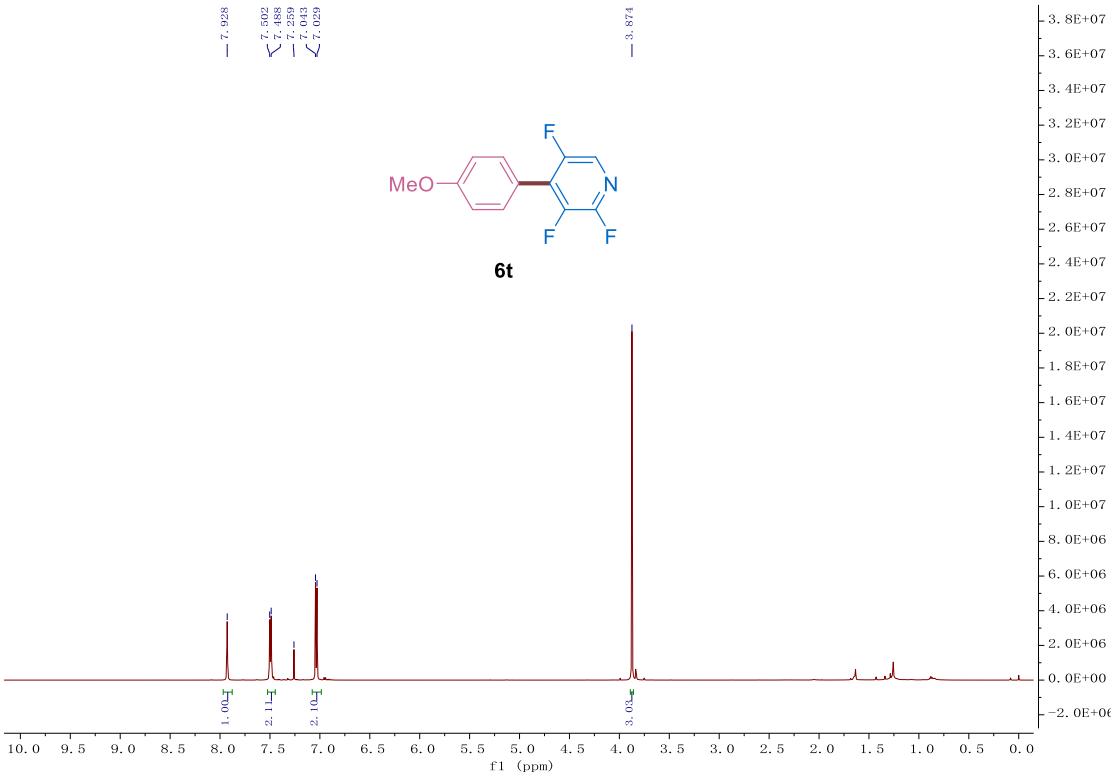
^{13}C NMR of 6s (151 MHz, $CDCl_3$)



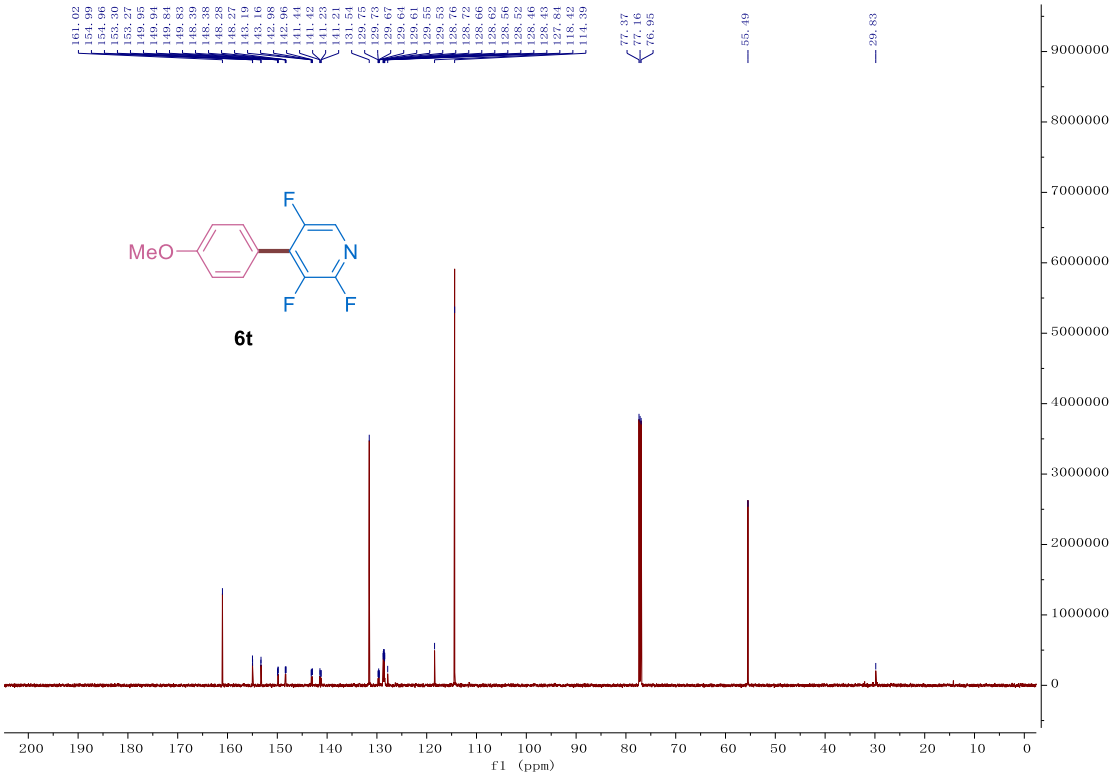
^{19}F NMR of 6s (565 MHz, $CDCl_3$)



^{1}H NMR of 6t (600 MHz, $CDCl_3$)



^{13}C NMR of 6t (151 MHz, $CDCl_3$)



^{19}F NMR of 6t (565 MHz, $CDCl_3$)