

Supporting Information

Fluoroarylation of gem-Difluorostyrenes through Pd-Catalyzed Aryl C–H Bond Activation Cascade

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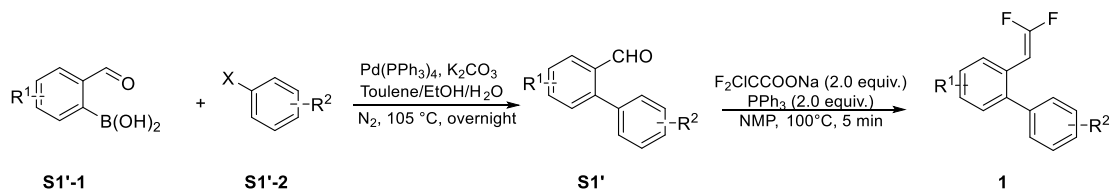
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I. General

Unless otherwise stated, all experiments were carried out under nitrogen atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^1H NMR and ^{13}C NMR spectra were obtained on Bruker AVANCE III 400 instrument in CDCl_3 using TMS as an internal standard, operating at 400 MHz and 101 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For CDCl_3 , the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; CHCl_3 δ H (7.28 ppm) and CDCl_3 δ C (77.03 ppm). ^{19}F NMR were recorded on a Bruker AVANCE III 400. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartlet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra [HRMS (ESI-TOF)] were obtained on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source.

II. Preparation of the starting materials

1. General procedure for the synthesis of 1

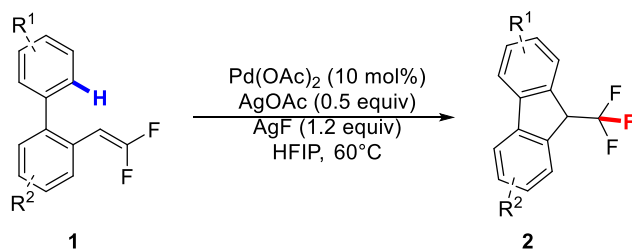


X = Br or I

To a solution of **S1'-1** (5.0 mmol, 1 equiv.) and **S1'-2** (5.5 mmol, 1.1 equiv.) in toluene (8 mL), ethanol (2 mL) and water (2 mL), $\text{Pd(PPh}_3)_4$ (3 mol%) and K_2CO_3 (12.5 mmol, 2.5 equiv.) were added. The resulting mixture was reflux overnight under a nitrogen atmosphere. After completion of the reaction, the mixture was extracted three times with diethyl ether. The combined organic phases were dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to deliver **S1'**.¹

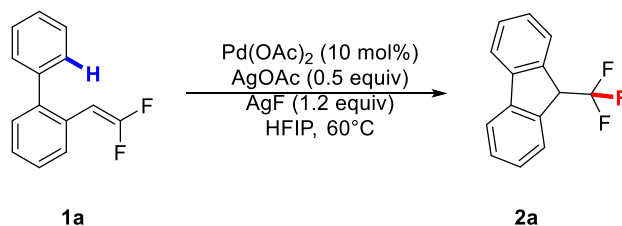
In a 50 mL oven-dried round-bottom flask with a stir bar, the **S1'** (1.0 equiv.), triphenyl phosphine (8 mmol, 2.0 equiv.) were dissolved in NMP (25 mL), then the mixture was heated to 100 °C. To the reaction mixture at 100 °C was added sodium 2-chloro-2,2-difluoroacetate (8 mmol, 2.0 equiv.) slowly (**Caution:** gas evolution observed). After the reaction finished according to the TLC, the reaction mixture was cooled to room temperature, quenched with water and extracted with EtOAc. The combined organic layers were washed with H_2O_2 (30 wt% in water, 10 mL), brine (50 mL \times 4) and dried over Na_2SO_4 . After solvent was removed under reduced pressure, the crude residue was purified by column chromatography on silica gel to afford the **1**.²

III. General procedure for the palladium-catalyzed fluoroarylation



In an oven-dried 10 mL Schlenk tube equipped with a stir bar, Pd(OAc)₂ (10 mol%), AgOAc (0.5 equiv.), AgF (1.2 equiv.), **1** (0.2 mmol) and anhydrous HFIP (1.0 mL) were added under N₂ atmosphere and then the reaction tube was capped. After stirring at 60 °C for 4 h, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by column chromatography on silica gel to afford the desired product **2**.

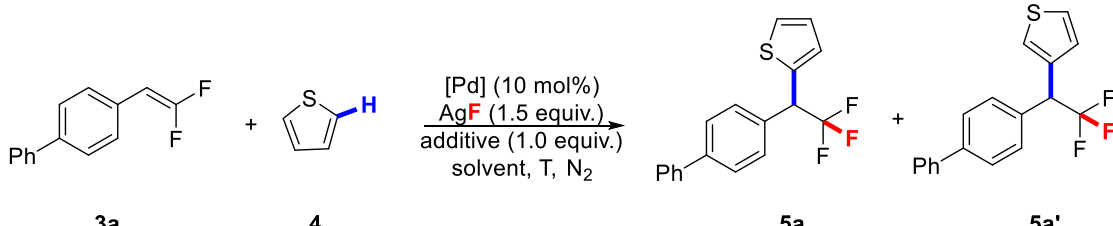
IV. Gram scale-up experiment of 1a



In an oven-dried 50 mL Schlenk tube equipped with a stir bar, Pd(OAc)₂ (0.11 g, 10 mol%), AgOAc (0.42 g, 0.5 equiv.), AgF (0.76 g, 1.2 equiv.), **1a** (1.08 g, 5.0 mmol) and anhydrous HFIP (10.0 mL) were added under N₂ atmosphere and then the reaction tube was capped. After stirring at 60 °C for 12 h, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by column chromatography on silica gel (petroleum ether-EtOAc = 100:1) to afford the desired product **2a** (0.85 g, 3.65 mmol, 73%).

V. Conditions screening for fluoroheteroarylation of gem-difluoroalkenes

Table S1. Reaction condition optimization

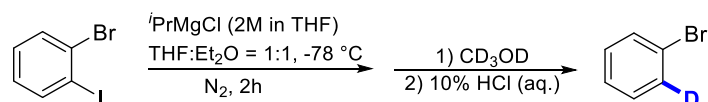


Entry	[Cat.]	Additive	T.	Ligand	Solvent	Yield ^a	5a:5a' ^b
1	[allylPdCl] ₂	/	80	XPhos	cyclohexane	N.R.	/
2	[allylPdCl] ₂	/	100	XPhos	cyclohexane	N.R.	/
3	[allylPdCl] ₂	/	100	XPhos	1,4-dioxane	N.R.	/
4	[allylPdCl] ₂	AgOAc	60	/	HFIP	72	77:23
5	Pd(OAc) ₂	AgOAc	60	/	HFIP	72	80:20
6	Pd(Ph ₃ P) ₂ Cl ₂	AgOAc	60	/	HFIP	63	80:20
7	Pd(TFA) ₂	AgOAc	60	/	HFIP	65	78:22
8	Pd(CH ₃ CN) ₂ Cl ₂	AgOAc	60	/	HFIP	67	75:25
9	Pd(OAc) ₂	AgOAc	40	/	HFIP	30	85:15
10	Pd(OAc) ₂	AgOAc	25	/	HFIP	17	84:16
11	Pd(OAc) ₂	AgOAc	80	/	HFIP	75	75:25
12	Pd(OAc) ₂	Ag ₂ CO ₃	60	/	HFIP	34	76:24
13	Pd(OAc) ₂	AgOAc	60	Ph ₃ P	HFIP	65	78:22
14	Pd(OAc) ₂	AgOAc	60	XPhos	HFIP	70	80:20
15	Pd(OAc) ₂	AgOAc	60	Xantphos	HFIP	68	75:25
16	Pd(OAc) ₂	AgOAc	60	/	TFE	trace	/
17	Pd(OAc) ₂	AgOAc	60	/	IPA	N.R.	/

^aReaction conditions: **3a** (0.2 mmol), **4** (0.3 mmol), [Pd] (10 mol%), AgF (1.5 equiv.), additive (1.0 equiv.), Solvent (1 mL), under N₂, 12h, GC-MS yield. ^bRegioselectivity was determined by GC-MS.

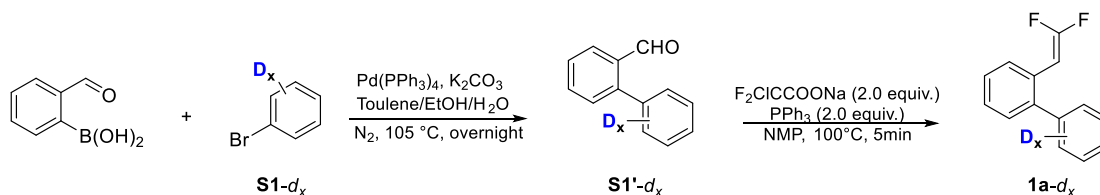
VI. Deuterium-labeling experiments

1. Synthesis of 1-bromobenzene-2-*d*



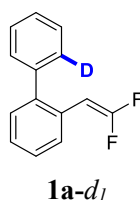
1-Bromo-2-iodobenzene (10 mmol, 1 equiv.) was dissolved in a mixture of THF and Et₂O (50 mL, 1:1) under argon atmosphere and cooled to -78 °C. 5.1 mL (10.2 mmol, 1.02 equiv.) isopropyl magnesium chloride (2 M in THF) were added dropwise under vigorous stirring over 15 minutes. The reaction mixture was stirred for 2 h at -78 °C before adding 1.2 mL methanol-*d*₄ and slowly warming it up to room temperature. After the addition of 50 mL 10% aq. HCl and stirring the mixture for 30 minutes, the organic layer was removed and the aqueous layer was extracted 3 times with 10

mL Et₂O and the combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was used directly for the next step without further purification.¹

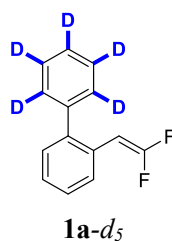


To a solution of boronic acid (5.0 mmol, 1 equiv.) and **S1-*d*₁** or **S1-*d*₅** (5.5 mmol, 1.1 equiv.) in toluene (8 mL), ethanol (2 mL) and water (2 mL), Pd(PPh₃)₄ (3 mol%) and K₂CO₃ (12.5 mmol, 2.5 equiv.) were added. The resulting mixture was reflux overnight under a nitrogen atmosphere. After completion of the reaction, the mixture was extracted three times with diethyl ether. The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to deliver **S1'-*d*₁** or **S1'-*d*₅**.¹

In a 50 mL oven-dried round-bottom flask with a stir bar, the **S1'-*d*₁** or **S1'-*d*₅** (1.0 equiv.), triphenyl phosphine (8 mmol, 2.0 equiv.) were dissolved in NMP (25 mL), then the mixture was heated to 100 °C. To the reaction mixture at 100 °C was added sodium 2-chloro-2,2-difluoroacetate (8 mmol, 2.0 equiv.) slowly (**Caution:** gas evolution observed). After the reaction finished according to the TLC, the reaction mixture was cooled to room temperature, quenched with water and extracted with EtOAc. The combined organic layers were washed with H₂O₂ (30 wt% in water, 10 mL), brine (50 mL × 4) and dried over Na₂SO₄. After solvent was removed under reduced pressure, the crude residue was purified by column chromatography on silica gel to afford the **1a-*d*₁** or **1a-*d*₅**.



2-(2,2-difluorovinyl)-1,1'-biphenyl-2'-*d*₁ (1a-*d*₁): ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.55-7.31 (m, 7H), 5.26 (dd, *J* = 26.1, 4.2 Hz, 1H).



2-(2,2-difluorovinyl)-1,1'-biphenyl-2',3',4',5',6'-*d*₅ (1a-*d*₅): ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.44-7.29 (m, 3H), 5.27 (dd, *J* = 26.1, 4.2 Hz, 1H).

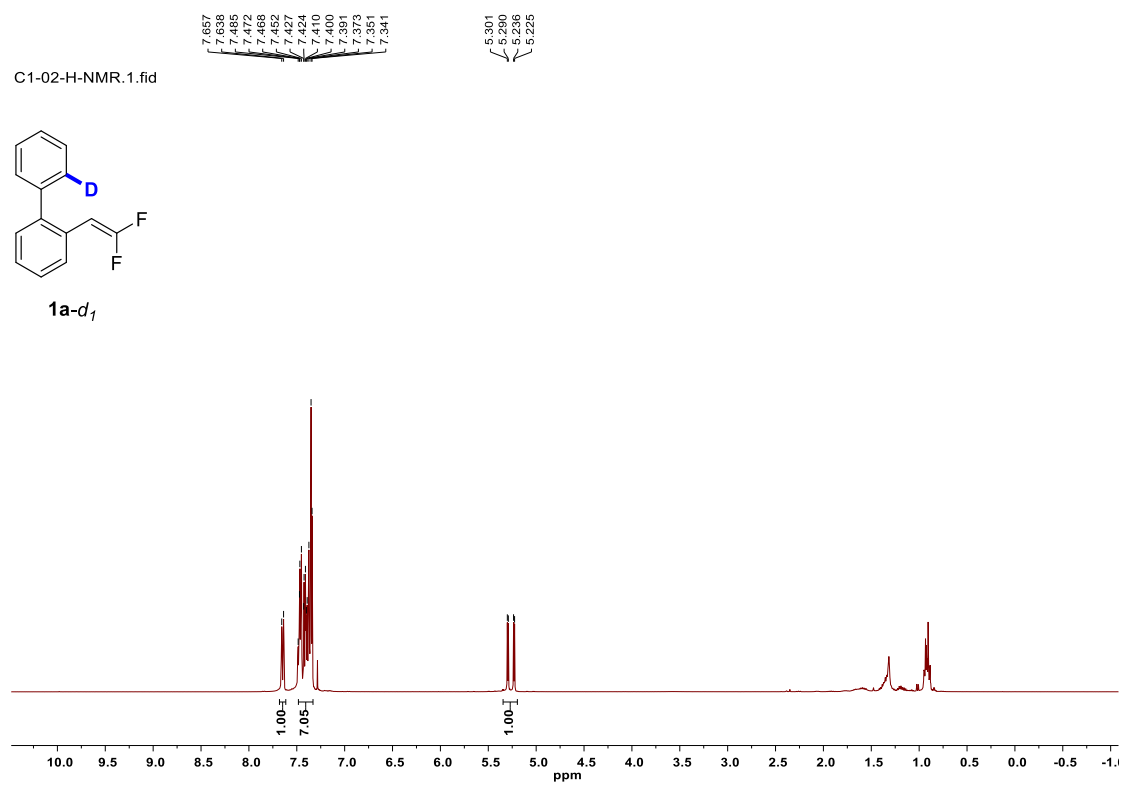


Figure S1. ¹H NMR spectrum of **1a-d₁**

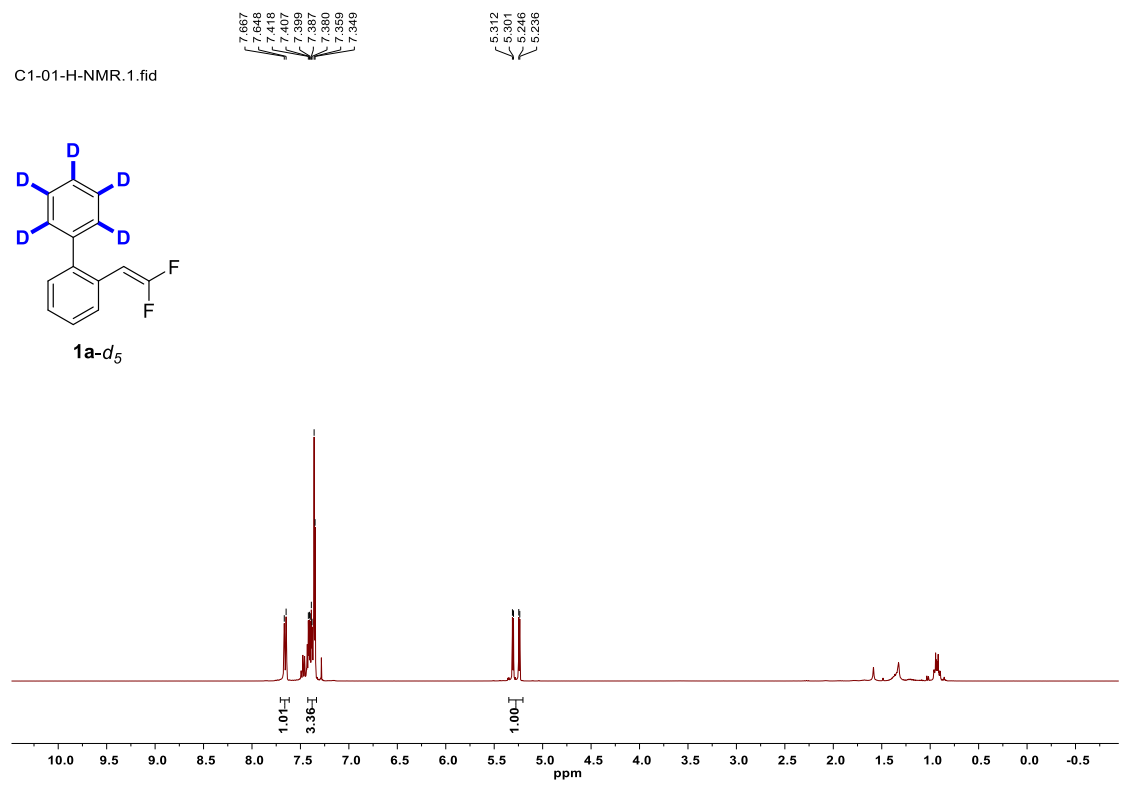
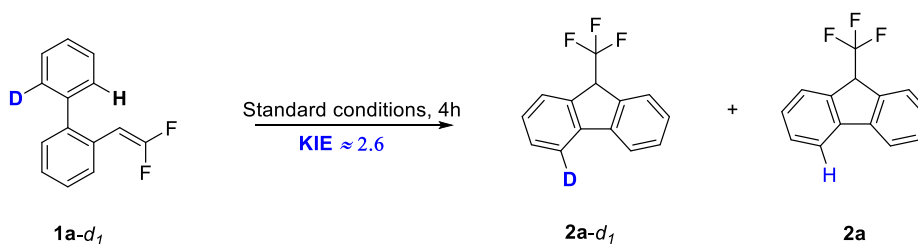


Figure S2. ¹H NMR spectrum of **1a-d₅**

2. Intramolecular KIE experiments



In an oven-dried 10 mL Schlenk tube equipped with a stir bar, Pd(OAc)₂ (10 mol%), AgOAc (0.5 equiv.), AgF (1.2 equiv.), **1a-d₁** (0.2 mmol) and anhydrous HFIP (1.0 mL) were added under N₂ atmosphere and then the reaction tube was capped. After stirring at 60 °C for 4 h, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by column chromatography on silica gel (PE:EtOAc = 100:1) to afford the desired product **2a-d₁** and **2a** (white solid, 0.036 g, 78% yield). The 2.6:1 ratio of **2a-d₁** to **2a** indicated that the current palladium-catalyzed fluoroarylation reaction may involve the aromatic C–H activation pathway.

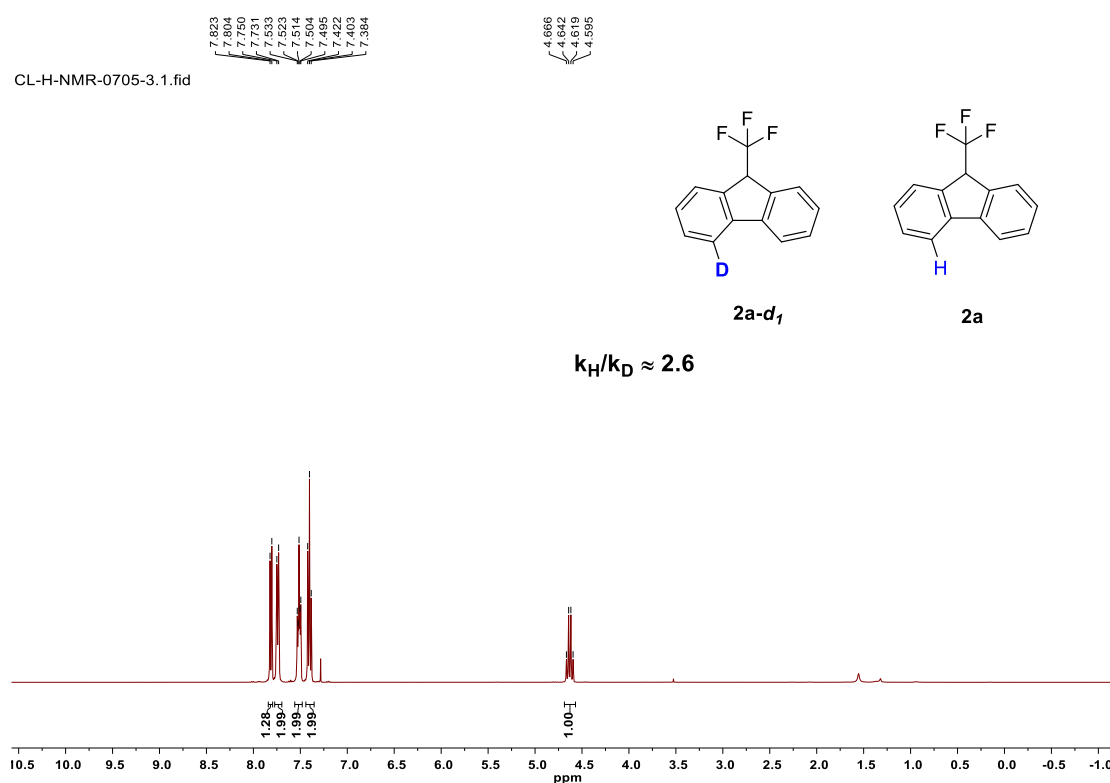
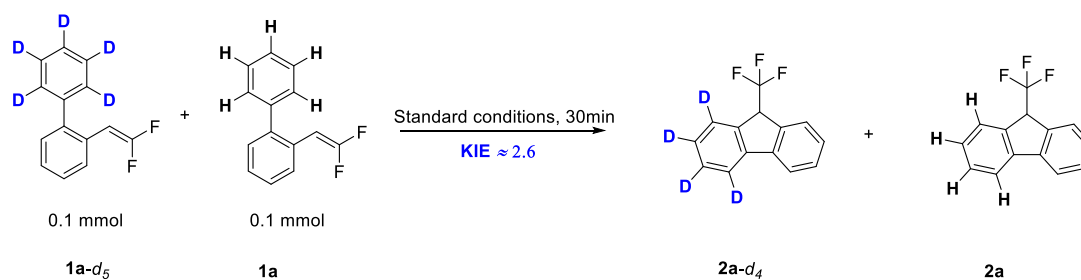


Fig S3. ¹H NMR spectrum of mixture **2a/2a-d₁**

3. Intermolecular competing KIE experiments



In an oven-dried 10 mL Schlenk tube equipped with a stir bar, Pd(OAc)₂ (10 mol%), AgOAc (0.5 equiv.), AgF (1.2 equiv.), **1a-d₅** (0.1 mmol), **1a** (0.1 mmol) and anhydrous HFIP (1.0 mL) were added under N₂ atmosphere and then the reaction tube was capped. After stirring at 60 °C for 30 min, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by column chromatography on silica gel (PE:EtOAc = 100:1) to afford the desired product **2a-d₄** and **2a** (white solid, 0.023 g, 50% yield). The 2.6:1 ratio of **2a** to **2a-d₄** demonstrated that the cleavage of the aromatic C–H bond in **1a** is involved in the rate-determining step.

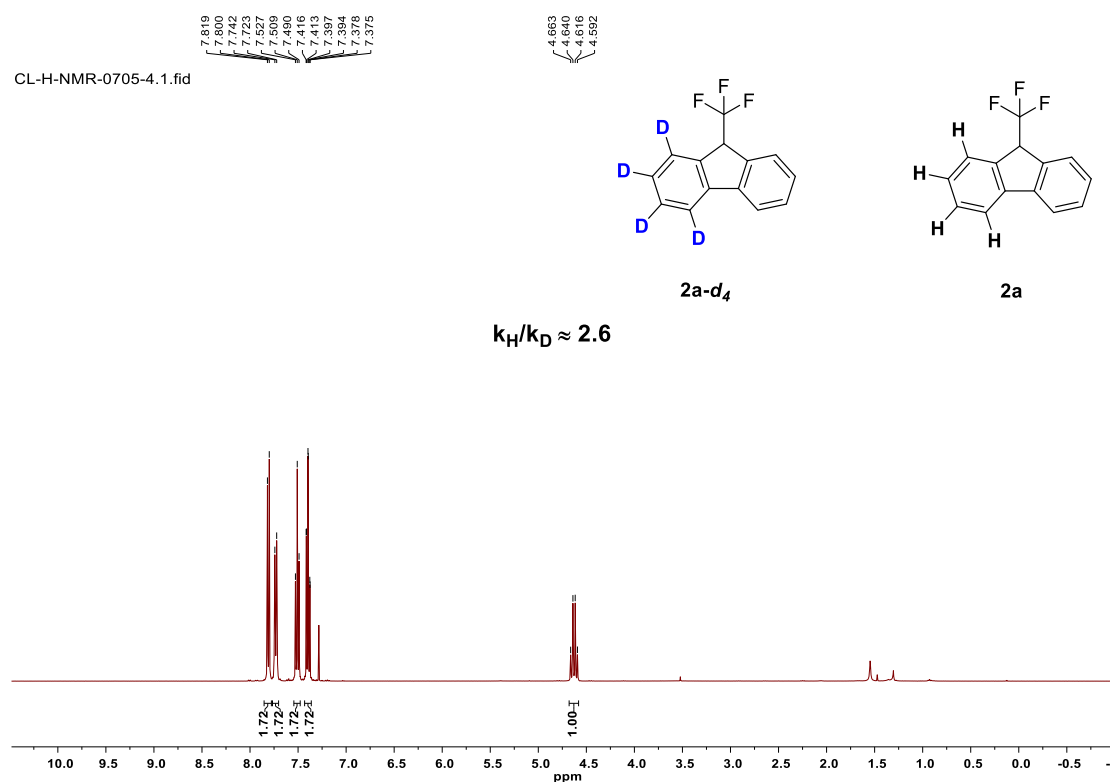
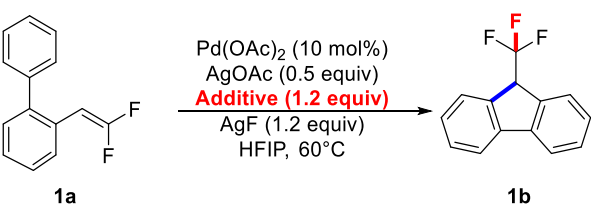


Fig S4. ¹H NMR spectrum of mixture **2a/2a-d₄**

4. Radical trapping experiments

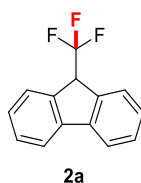
Table S2. Radical trapping experiments with radical scavengers



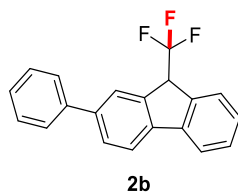
Entry	additive	yield
1	TEMPO	62%
2	ethene-1,1-diyl dibenzene	67%

In an oven-dried 10 mL Schlenk tube equipped with a stir bar, Pd(OAc)₂ (10 mol%), AgOAc (0.5 equiv.), AgF (1.2 equiv.), additive (1.2 equiv.), **1a** (0.1 mmol) and anhydrous HFIP (1.0 mL) were added under N₂ atmosphere and then the reaction tube was capped. After stirring at 60 °C for 4 h. The yields were determined by GC-MS. Radical trapping experiments demonstrated that the reaction mechanism does not involve radical process.

VII. Characterization of all products

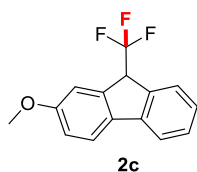


9-(trifluoromethyl)-9H-fluorene (2a): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2a** (38.3mg, 82% yield) as white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.40 (tt, *J* = 7.5, 1.1 Hz, 2H), 4.63 (q, *J* = 9.4 Hz, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 142.2, 137.3 (q, *J* = 2.2 Hz), 129.1, 127.7 (q, *J* = 278.5 Hz), 127.6, 125.9 (d, *J* = 1.5 Hz), 120.2, 51.3 (q, *J* = 29.3 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -67.75 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd. for C₁₄H₈F₃: 233.0584; found: 233.0588.

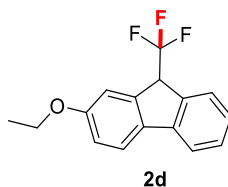


2-phenyl-9-(trifluoromethyl)-9H-fluorene (2b): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2b** (39.6 mg, 64% yield) as white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.91-7.83 (m, 2H), 7.81-7.75 (m, 2H), 7.74 (d, *J* = 1.3 Hz, 1H), 7.72 (s, 1H), 7.59-7.52 (m, 3H), 7.49-7.41 (m, 2H), 4.69 (q, *J* = 9.4 Hz, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.9, 141.3, 141.0, 140.9, 138.1 (q, *J* = 2.1 Hz), 137.6 (q, *J* = 2.1 Hz), 129.2, 128.9, 128.3, 127.7, 127.6, 127.3,

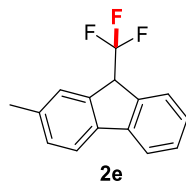
126.4 (q, $J = 278.8$ Hz), 126.0, 125.0, 120.5, 120.3, 51.4 (q, $J = 29.2$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -67.50 (d, $J = 3.6$ Hz, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{20}\text{H}_{12}\text{F}_3$: 309.0897; found: 309.0897.



2-methoxy-9-(trifluoromethyl)-9H-fluorene (2c): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2c** (40.6 mg, 77% yield) as white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.64 (m, 3H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.28 (s, 1H), 7.05 (dd, $J = 8.4, 2.4$ Hz, 1H), 4.57 (q, $J = 9.5$ Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 159.8, 142.2, 139.0 (q, $J = 2.0$ Hz), 136.8 (q, $J = 2.3$ Hz), 135.0, 129.0, 126.5, 126.3 (q, $J = 278.7$ Hz), 125.8 (d, $J = 1.6$ Hz), 120.9, 119.4, 115.0, 111.8 (d, $J = 1.5$ Hz), 55.6, 51.3 (q, $J = 29.2$ Hz) ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.84 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{O}$: 263.0689; found: 263.0683.

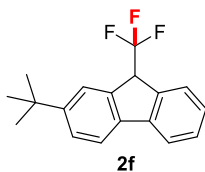


2-ethoxy-9-(trifluoromethyl)-9H-fluorene (2d): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2d** (46.1 mg, 83% yield) as white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.73-7.65 (m, 3H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.04 (dd, $J = 8.4, 2.3$ Hz, 1H), 4.57 (q, $J = 9.5$ Hz, 1H), 4.21-4.07 (m, 2H), 1.49 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 142.2, 139.0 (q, $J = 2.1$ Hz), 136.8 (q, $J = 2.0$ Hz), 134.9, 129.0, 126.4, 126.3 (q, $J = 278.7$ Hz), 125.8, 120.9, 119.4, 115.5, 112.3, 63.9, 51.2 (q, $J = 29.2$ Hz), 14.8 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -67.83 (s, 3F) ppm; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{O}$: 277.0846; found: 277.0848.

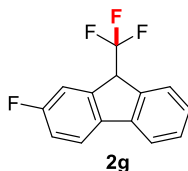


2-methyl-9-(trifluoromethyl)-9H-fluorene (2e): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2e** (43.1 mg, 87% yield) as white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.70 (t, $J = 8.0$ Hz, 2H), 7.54 (s, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.41-7.34 (m, 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 4.58 (q, $J = 9.5$ Hz, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 142.2, 139.5, 137.6, 137.5 (q, $J = 2.3$ Hz), 137.1 (d, $J = 2.4$ Hz), 129.8, 128.9, 127.1, 126.5, 126.4 (q, $J = 278.7$ Hz), 125.9, 119.9, 119.9, 51.1 (q, $J = 29.2$ Hz), 21.6 ppm; ^{19}F NMR (376 MHz,

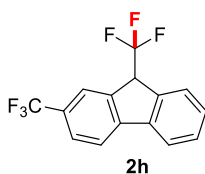
CDCl₃) δ -67.73 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for C₁₅H₁₀F₃: 247.0740; found: 247.0747.



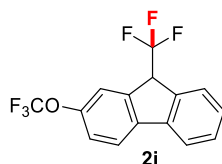
2-(tert-butyl)-9-(trifluoromethyl)-9H-fluorene (2f): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2f** (46.4 mg, 80% yield) as white solid; **¹H NMR** (400 MHz, CDCl₃) δ 7.85-7.66 (m, 4H), 7.54 (dd, J = 8.1, 1.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 4.59 (q, J = 9.5 Hz, 1H), 1.42 (s, 9H) ppm; **¹³C NMR** (101 MHz, CDCl₃) δ 151.1, 142.2, 139.5, 137.4 (d, J = 2.4 Hz), 137.3 (d, J = 2.3 Hz), 129.0, 127.1, 126.4 (q, J = 278.7 Hz), 126.2, 125.8, 122.8 (d, J = 1.2 Hz), 119.9, 119.7, 51.3 (q, J = 29.1 Hz), 35.0, 31.5 ppm; **¹⁹F NMR** (376 MHz, CDCl₃) δ -67.72 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for C₁₈H₁₆F₃: 289.1210; found: 289.1215.



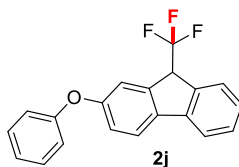
2-fluoro-9-(trifluoromethyl)-9H-fluorene (2g): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2g** (34.7 mg, 69% yield) as white solid; **¹H NMR** (400 MHz, CDCl₃) δ 7.79-7.66 (m, 3H), 7.50 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.24-7.17 (m, 1H), 4.60 (q, J = 9.3 Hz, 1H) ppm; **¹³C NMR** (101 MHz, CDCl₃) δ 163.8, 161.3, 141.3, 138.2 (d, J = 2.6 Hz), 137.1 (t, J = 2.0 Hz), 129.2, 126.0 (q, J = 278.8 Hz), 127.3, 125.9, 121.2 (d, J = 8.8 Hz), 119.9, 116.3 (d, J = 22.9 Hz), 113.6 (d, J = 23.0 Hz), 51.3 (q, J = 29.5 Hz) ppm; **¹⁹F NMR** (376 MHz, CDCl₃) δ -67.88 (s, 3F), -113.67 (s, 1F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for C₁₄H₆F₄: 251.0489; found: 251.0492.



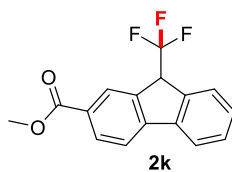
2,9-bis(trifluoromethyl)-9H-fluorene (2h): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2h** (37.4 mg, 62% yield) as white solid; **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.87 (dd, J = 13.6, 7.8 Hz, 2H), 7.81-7.74 (m, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.51-7.44 (m, 1H), 4.68 (q, J = 9.2 Hz, 1H) ppm; **¹³C NMR** (101 MHz, CDCl₃) δ 145.6, 140.7, 137.9 (q, J = 2.2 Hz), 137.7 (q, J = 2.4 Hz), 129.9, 129.4, 128.9, 126.5 (q, J = 3.8 Hz), 126.1, 125.9 (d, J = 278.9 Hz), 125.5, 122.9 (q, J = 5.1 Hz), 121.0, 120.4, 51.3 (q, J = 29.8 Hz) ppm; **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.03 (s, 3F), -67.67 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for C₁₅H₆F₆: 301.0457; found: 301.0455.



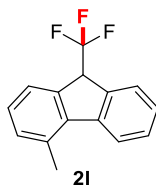
2-(trifluoromethoxy)-9-(trifluoromethyl)-9H-fluorene (2i): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2i** (39.4 mg, 62% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83-7.76 (m, 2H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.58 (d, $J = 2.2$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.43 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.41-7.35 (m, 1H), 4.63 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.7 (d, $J = 1.5$ Hz), 140.9, 140.8, 138.9 (d, $J = 2.2$ Hz), 137.4 (q, $J = 1.9$ Hz), 129.3, 128.0, 126.0 (d, $J = 1.6$ Hz), 125.9 (q, $J = 278.8$ Hz), 122.1, 121.0, 120.6 (q, $J = 257.4$ Hz), 120.4, 119.2, 51.3 (q, $J = 29.8$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -58.0 (s, 3F), -67.8 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H] $^-$ Calcd. for $\text{C}_{15}\text{H}_6\text{F}_6\text{O}$: 317.0407; found: 317.0408.



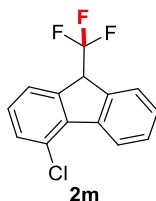
2-phenoxy-9-(trifluoromethyl)-9H-fluorene (2j): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2j** (48.9 mg, 75% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 1.9$ Hz, 1H), 7.75-7.69 (m, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.44-7.34 (m, 4H), 7.24-7.07 (m, 4H), 4.60 (q, $J = 9.4$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.2, 157.2, 141.7, 139.1 (q, $J = 2.2$ Hz), 137.4, 137.2 (q, $J = 2.0$ Hz), 129.9, 129.2, 127.0, 126.2 (q, $J = 278.8$ Hz), 125.9 (d, $J = 1.5$ Hz), 123.5, 121.1, 119.8, 119.8, 118.9, 116.9 (d, $J = 1.4$ Hz), 51.3 (q, $J = 29.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.81 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H] $^-$ Calcd. for $\text{C}_{20}\text{H}_{12}\text{F}_3\text{O}$: 325.0846; found: 325.0843.



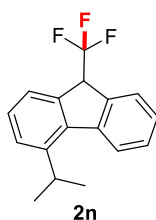
methyl 9-(trifluoromethyl)-9H-fluorene-2-carboxylate (2k): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2k** (37.3 mg, 64% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.38 (s, 1H), 8.26-8.17 (m, 1H), 7.91-7.81 (m, 2H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.49-7.41 (m, 1H), 4.66 (q, $J = 9.3$ Hz, 1H), 3.98 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.8, 146.6, 141.0, 138.3 (d, $J = 2.1$ Hz), 137.3 (d, $J = 2.2$ Hz), 131.0, 129.4, 129.3, 128.8, 127.1 (d, $J = 1.6$ Hz), 126.1, 126.0 (q, $J = 278.9$ Hz), 121.1, 120.0, 52.2, 51.2 (q, $J = 29.6$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.61 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H] $^-$ Calcd. for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{O}_2$: 291.0638; found: 291.0633.



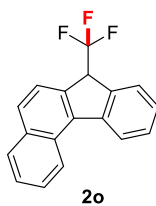
4-methyl-9-(trifluoromethyl)-9H-fluorene (2l): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2l** (36.2 mg, 73% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 6.1$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.32-7.27 (m, 2H), 4.61 (q, $J = 9.4$ Hz, 1H), 2.76 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.2, 140.2, 137.6 (q, $J = 2.2$ Hz), 133.4, 131.5, 129.0, 127.2, 126.9, 126.4 (q, $J = 278.8$ Hz), 125.9, 123.4, 123.4 (d, $J = 1.8$ Hz), 51.1 (q, $J = 28.9$ Hz), 21.0 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.76 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{10}\text{F}_3$: 247.0740; found: 247.0744.



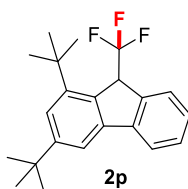
4-chloro-9-(trifluoromethyl)-9H-fluorene (2m): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2m** (18.7 mg, 35% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.49 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.66-7.62 (m, 1H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.50-7.42 (m, 2H), 7.37-7.27 (m, 1H), 4.64 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.9, 139.5 (q, $J = 2.1$ Hz), 138.9, 137.3 (q, $J = 2.1$ Hz), 130.8, 129.2, 129.1, 128.1, 128.1, 126.0 (q, $J = 279.0$ Hz), 125.6, 124.2, 51.3 (q, $J = 29.3$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.73 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{14}\text{H}_7\text{F}_3\text{Cl}$: 267.0914; found: 267.0919.



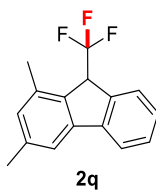
4-isopropyl-9-(trifluoromethyl)-9H-fluorene (2n): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2n** (38.6 mg, 70% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.9$ Hz, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.42-7.35 (m, 2H), 4.60 (q, $J = 9.4$ Hz, 1H), 3.94-3.76 (m, 1H), 1.45 (dd, $J = 14.0, 6.8$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.7, 142.6, 139.0, 137.8 (p, $J = 2.0$ Hz), 129.0, 127.6, 126.8, 126.4 (q, $J = 279.0$ Hz), 125.9 (d, $J = 1.7$ Hz), 125.6, 123.9, 123.3 (d, $J = 1.8$ Hz), 51.0 (q, $J = 28.8$ Hz), 29.5, 22.9, 22.6 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.70 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_3$: 275.1053; found: 275.1051.



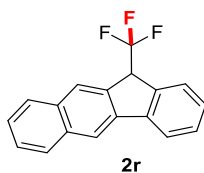
7-(trifluoromethyl)-7H-benzo[c]fluorene (2o): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2o** (42.6 mg, 75% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.78 (d, $J = 8.5$ Hz, 1H), 8.42 (d, $J = 7.9$ Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.88-7.82 (m, 2H), 7.74-7.68 (m, 1H), 7.62 (t, $J = 7.5$ Hz, 2H), 7.49-7.42 (m, 1H), 4.67 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.3, 138.2, 137.6, 136.1, 134.5, 129.3, 129.3, 129.2, 128.7, 127.1, 126.8, 126.5 (q, $J = 279.2$ Hz), 126.1, 125.8, 123.9, 123.3, 123.0, 51.5 (q, $J = 28.9$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.03 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{18}\text{H}_{10}\text{F}_3$: 283.0740; found: 283.0745.



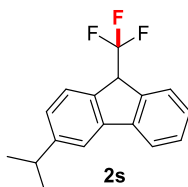
1,3-di-tert-butyl-9-(trifluoromethyl)-9H-fluorene (2p): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2p** (58.1 mg, 84% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 1.8$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 1.9$ Hz, 1H), 7.47 (t, $J = 7.3$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 5.21 (q, $J = 7.5$ Hz, 1H), 1.57 (s, 9H), 1.46 (s, 9H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.8, 148.9, 143.3, 142.3, 138.8 (d, $J = 1.9$ Hz), 131.4 (q, $J = 2.1$ Hz), 128.7, 126.9, 126.2 (q, $J = 280.6$ Hz), 125.9, 125.4 (d, $J = 1.6$ Hz), 119.6, 114.8, 52.2 (q, $J = 27.2$ Hz), 37.7, 34.9, 32.4 (d, $J = 1.9$ Hz), 31.4 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -65.43 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_3$: 345.1836; found: 345.1835.



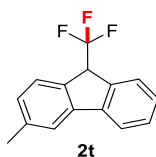
1,3-dimethyl-9-(trifluoromethyl)-9H-fluorene (2q): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2q** (42.4 mg, 81% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.65-7.44 (m, 2H), 7.45-7.32 (m, 1H), 7.05 (s, 1H), 4.61 (q, $J = 8.2$ Hz, 1H), 2.51 (s, 3H), 2.48 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.0, 142.4, 139.1, 138.3 (d, $J = 2.1$ Hz), 136.0, 133.2, 130.9, 129.0, 127.2, 126.8 (q, $J = 280.0$ Hz), 126.2, 120.0, 118.5, 50.7 (q, $J = 29.0$ Hz), 21.4, 20.0 (q, $J = 4.0$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.50 (d, $J = 3.6$ Hz, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3$: 261.0897; found: 261.0893.



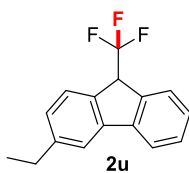
11-(trifluoromethyl)-11H-benzo[b]fluorene (2r): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2r** (48.8 mg, 86% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.5$ Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.97-7.88 (m, 2H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.67-7.58 (m, 1H), 7.57-7.49 (m, 2H), 7.46-7.37 (m, 1H), 5.04 (q, $J = 8.1$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.8, 141.2, 138.5, 133.7, 133.4 (q, $J = 1.7$ Hz), 130.9, 130.7, 129.1, 129.1, 127.2, 127.0, 126.3 (q, $J = 281.5$ Hz), 126.1 (d, $J = 1.9$ Hz), 125.6, 125.1 (q, $J = 4.2$ Hz), 120.0, 118.4, 51.2 (q, $J = 29.2$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -65.66 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for $\text{C}_{18}\text{H}_{10}\text{F}_3$: 283.0740; found: 283.0747.



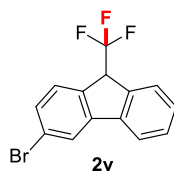
3-isopropyl-9-(trifluoromethyl)-9H-fluorene (2s): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2s** (45.2 mg, 82% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.70-7.63 (m, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 8.1$ Hz, 1H), 7.29 (dd, $J = 7.9, 1.6$ Hz, 1H), 4.59 (q, $J = 9.5$ Hz, 1H), 3.31-2.94 (m, 1H), 1.39 (d, $J = 6.9$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.2, 142.4, 142.3, 137.7 (q, $J = 2.2$ Hz), 134.9 (q, $J = 2.2$ Hz), 129.0, 127.4, 126.5 (q, $J = 278.7$ Hz), 126.1, 125.9, 125.7, 120.1, 118.1, 51.0 (q, $J = 29.2$ Hz), 34.3, 24.1 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.81 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_3$: 275.1053; found: 275.1058.



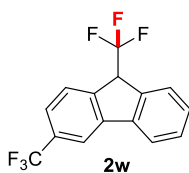
3-methyl-9-(trifluoromethyl)-9H-fluorene (2t): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2t** (43.1 mg, 87% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 9.6$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.21 (d, $J = 7.7$ Hz, 1H), 4.58 (q, $J = 9.4$ Hz, 1H), 2.50 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.3 (d, $J = 3.9$ Hz), 139.0, 137.7 (q, $J = 2.3$ Hz), 134.5 (q, $J = 2.3$ Hz), 129.0, 128.5, 127.5, 126.4 (q, $J = 278.7$ Hz), 125.9 (d, $J = 1.5$ Hz), 125.6, 120.8, 120.1, 117.8, 51.0 (q, $J = 29.3$ Hz), 21.6 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.94 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H]⁻ Calcd. for $\text{C}_{15}\text{H}_{10}\text{F}_3$: 247.0740; found: 247.0746.



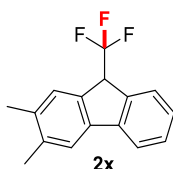
3-ethyl-9-(trifluoromethyl)-9H-fluorene (2u): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2u** (46.1 mg, 88% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 4.59 (q, $J = 9.5$ Hz, 1H), 2.81 (q, $J = 7.6$ Hz, 2H), 1.37 (t, $J = 7.6$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.5, 142.3, 137.7 (q, $J = 2.1$ Hz), 134.7 (q, $J = 2.1$ Hz), 129.0, 127.5 (d, $J = 2.5$ Hz), 126.4 (q, $J = 278.7$ Hz), 125.9 (d, $J = 0.9$ Hz), 125.68 (d, $J = 0.9$ Hz), 120.1, 119.6, 51.0 (q, $J = 29.2$ Hz), 29.0, 15.7 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.86 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H] $^-$ Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3$: 261.0897; found: 261.0899.



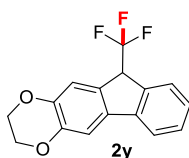
3-bromo-9-(trifluoromethyl)-9H-fluorene (2v): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2v** (21.7 mg, 35% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 1.6$ Hz, 1H), 7.74 (dd, $J = 17.5, 7.6$ Hz, 2H), 7.64-7.48 (m, 3H), 7.42 (t, $J = 7.5$ Hz, 1H), 4.57 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.3, 140.9, 137.6 (d, $J = 2.0$ Hz), 136.0, 130.8, 129.3, 128.4, 127.3, 127.1 (q, $J = 275.7$ Hz), 126.0, 123.6, 123.5, 120.5, 51.0 (q, $J = 29.6$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.83 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H] $^-$ Calcd. for $\text{C}_{14}\text{H}_7\text{F}_3\text{Br}$: 310.9689; found: 310.9694.



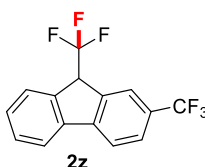
3,9-bis(trifluoromethyl)-9H-fluorene (2w): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2w** (40.4 mg, 67% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 1.7$ Hz, 1H), 7.84 (t, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 7.9$ Hz, 1H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 4.68 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.0, 140.8, 137.4 (q, $J = 2.1$ Hz), 131.7 (q, $J = 32.4$ Hz), 130.1, 129.4, 128.6, 127.3, 126.3, 126.0, 124.4 (q, $J = 3.7$ Hz), 122.8 (q, $J = 272.4$ Hz), 120.7, 117.1 (q, $J = 3.8$ Hz), 51.4 (q, $J = 29.7$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.45 (s, 3F), -67.60 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : [M - H] $^-$ Calcd. for $\text{C}_{15}\text{H}_7\text{F}_6$: 301.0457; found: 301.0451.



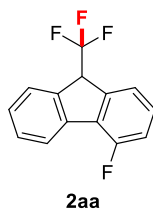
2,3-dimethyl-9-(trifluoromethyl)-9H-fluorene (2x): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2x** (42.9 mg, 82% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.58 (s, 1H), 7.53-7.45 (m, 2H), 7.36 (t, $J = 7.5$ Hz, 1H), 4.56 (q, $J = 9.5$ Hz, 1H), 2.40 (d, $J = 5.6$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.5, 140.0, 137.6, 137.4 (q, $J = 2.2$ Hz), 136.4, 135.0 (q, $J = 2.3$ Hz), 128.9, 127.0, 126.9, 126.5 (q, $J = 278.6$ Hz), 125.8 (d, $J = 1.5$ Hz), 121.3, 119.8, 51.0 (q, $J = 29.2$ Hz), 20.2, 20.1 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.87 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3$: 261.0897; found: 261.0899.



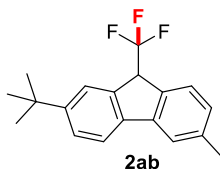
10-(trifluoromethyl)-2,3-dihydro-10H-fluoreno[2,3-b][1,4]dioxine (2y): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2y** (39.7 mg, 68% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78-7.58 (m, 2H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.39-7.28 (m, 1H), 7.27 (s, 1H), 7.22 (s, 1H), 4.51 (q, $J = 9.4$ Hz, 1H), 4.33 (s, 4H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.6, 143.5, 142.1, 137.4 (q, $J = 2.3$ Hz), 135.7, 130.3 (q, $J = 2.2$ Hz), 129.0, 126.7, 126.3 (q, $J = 278.7$ Hz), 125.7, 119.5, 115.0, 108.9, 64.4, 64.4, 50.8 (q, $J = 29.3$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -68.23 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{O}_2$: 291.0638; found: 291.0633.



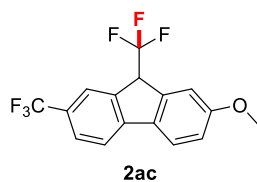
2,9-bis(trifluoromethyl)-9H-fluorene (2z): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2z** (38.6 mg, 64% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (s, 1H), 7.87 (dd, $J = 12.1, 7.8$ Hz, 3H), 7.77 (dd, $J = 8.0, 3.1$ Hz, 3H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.50 - 7.45 (m, 2H), 4.67 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.6, 140.7, 137.8 (d, $J = 2.1$ Hz), 137.7 (q, $J = 2.2$ Hz), 129.7 (q, $J = 32.4$ Hz), 129.4, 128.9, 126.5 (q, $J = 3.9$ Hz), 126.1 (d, $J = 1.5$ Hz), 125.9 (d, $J = 278.9$ Hz), 125.5, 122.9 (q, $J = 5.1$ Hz), 121.0, 120.4, 51.3 (q, $J = 29.7$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -61.98 (s, 3F), -67.67 (d, $J = 9.4$ Hz, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_7\text{F}_6$: 301.0457; found: 301.0452.



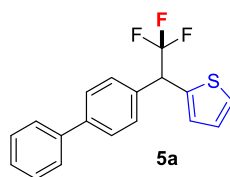
4-fluoro-9-(trifluoromethyl)-9H-fluorene (2aa): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2aa** (39.3 mg, 78% yield) as white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.57-7.48 (m, 2H), 7.42 (td, $J = 7.6, 1.2$ Hz, 1H), 7.35 (td, $J = 7.9, 5.1$ Hz, 1H), 7.24-7.16 (m, 1H), 4.67 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.5, 157.0, 139.8 (dd, $J = 6.1, 2.2$ Hz), 139.3 (d, $J = 3.1$ Hz), 136.6 (q, $J = 2.3$ Hz), 129.4, 128.9 (d, $J = 7.2$ Hz), 127.8, 126.0 (q, $J = 278.8$ Hz), 125.7, 123.8 (d, $J = 6.1$ Hz), 121.7 (dd, $J = 3.3, 1.4$ Hz), 116.3 (d, $J = 19.7$ Hz), 51.7 (q, $J = 29.5, 28.8$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.81 (d, $J = 9.3$ Hz, 1F), -119.53 (dd, $J = 9.8, 5.0$ Hz, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{14}\text{H}_7\text{F}_4$: 251.0489; found: 251.0482.



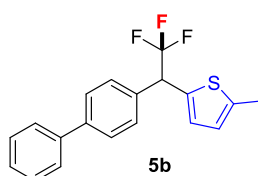
2-(tert-butyl)-6-methyl-9-(trifluoromethyl)-9H-fluorene (2ab): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 100:1) gave **2ab** (49.8 mg, 82% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 (d, $J = 2.0$ Hz, 1H), 7.69-7.63 (m, 2H), 7.56-7.50 (m, 2H), 7.29 (d, $J = 7.4$ Hz, 1H), 4.55 (q, $J = 9.6$ Hz, 1H), 2.47 (s, 3H), 1.42 (s, 9H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.6, 139.6, 139.5, 137.6 (d, $J = 2.5$ Hz), 137.2 (d, $J = 2.2$ Hz), 137.1, 129.8, 126.5, 126.5 (q, $J = 278.6$ Hz), 126.1, 122.8 (d, $J = 1.5$ Hz), 119.7, 119.3, 51.1 (q, $J = 29.0$ Hz), 35.0, 31.5, 21.6 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.69 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{19}\text{H}_{18}\text{F}_3$: 303.1366; found: 303.1369.



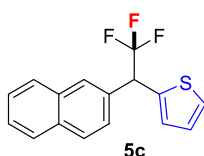
2-methoxy-7,9-bis(trifluoromethyl)-9H-fluorene (2ac): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **2ac** (35.2 mg, 53% yield) as white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (s, 1H), 7.87 (dd, $J = 12.1, 7.8$ Hz, 2H), 7.77 (dd, $J = 8.0, 3.1$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.50-7.45 (m, 1H), 4.67 (q, $J = 9.3$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.6, 145.6, 139.7 (q, $J = 2.0$ Hz), 137.1 (q, $J = 2.1$ Hz), 133.5, 128.6 (q, $J = 141.5$ Hz), 126.6 (q, $J = 278.7$ Hz), 126.5 (q, $J = 3.8$ Hz), 122.8, 121.9, 119.5, 115.5, 111.7, 55.7, 51.2 (q, $J = 29.7$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -61.85 (s, 3F), -67.75 (d, $J = 9.3$ Hz, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_9\text{F}_6\text{O}$: 331.0563; found: 331.0561.



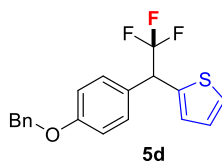
2-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)thiophene (5a): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **5a** (47.0 mg, 74% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (t, $J = 7.2$ Hz, 4H), 7.59-7.45 (m, 4H), 7.43-7.31 (m, 2H), 7.23- 7.01 (m, 2H), 5.00 (q, $J = 9.3$ Hz, 0.8H, Major isomer), 4.86 (q, $J = 9.5$ Hz, 0.2H, Minor isomer) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.4, 140.4, 137.1, 133.8, 129.5, 128.9, 127.6, 127.6, 127.5, 127.2, 127.0, 125.9, 123.9, 51.0 (q, $J = 29.2$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.51 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{18}\text{H}_{12}\text{F}_3\text{S}$: 317.0617; found: 317.0612.



2-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)-5-methylthiophene (5b): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **5b** (47.0 mg, 74% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76-7.33 (m, 9H), 6.93 (s, 1H), 6.69 (s, 1H), 4.89 (q, $J = 9.5$ Hz, 0.88H, Major isomer), 4.80 (d, $J = 9.8$ Hz, 0.12H, Minor isomer), 2.49 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.3, 140.6, 140.4, 134.5, 134.0, 129.4, 128.9, 127.6, 127.5, 127.5, 127.2, 125.1, 123.1 (d, $J = 224.8$ Hz), 51.1 (q, $J = 29.0$ Hz), 15.2 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.88 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{S}$: 331.0774; found: 331.0778.

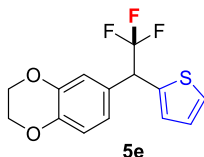


2-(2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl)thiophene (5c): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **5c** (32.1 mg, 55% yield) as white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05-7.80 (m, 4H), 7.69-7.45 (m, 3H), 7.40-7.02 (m, 3H), 5.12 (q, $J = 9.3$ Hz, 0.8H, Major isomer), 4.98 (q, $J = 9.6$ Hz, 0.2H, Minor isomer) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.2, 133.3, 133.1, 132.3, 128.7, 128.5, 128.2, 127.7, 127.6, 127.0, 126.7, 126.6, 126.4, 126.0, 51.4 (q, $J = 29.2$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.51 (s, 3F) ppm; **HRMS** (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{S}$: 291.0461; found: 291.0465.

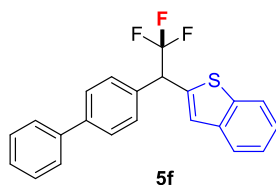


2-(1-(4-(benzyloxy)phenyl)-2,2,2-trifluoroethyl)thiophene (5d): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 30:1) gave **5d** (54.2 mg, 78% yield) as white solid; $^1\text{H NMR}$ (400

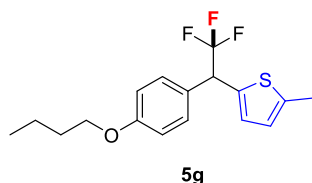
MHz, CDCl₃) δ 7.62-6.93 (m, 11H), 5.10 (s, 2H), 4.89 (q, *J* = 9.3 Hz, 0.87H, Major isomer), 4.75 (q, *J* = 9.6 Hz, 0.13H, Minor isomer) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 158.9, 137.6, 136.8, 130.3, 128.7, 128.1, 127.6, 127.3, 126.9, 125.7, 124.3, 122.6 (d, *J* = 213.8 Hz), 115.1, 70.1, 50.5 (q, *J* = 29.1 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -67.55 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd. for C₁₉H₁₄F₃SO: 347.0723; found: 347.0727.



6-(2,2,2-trifluoro-1-(thiophen-2-yl)ethyl)-2,3-dihydrobenzo[b][1,4]dioxine (5e): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 30:1) gave **5e** (31.2 mg, 52% yield) as white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.22 (m, 1H), 7.15-6.82 (m, 5H), 4.82 (q, *J* = 9.3 Hz, 0.85H, Major isomer), 4.68 (q, *J* = 9.7 Hz, 0.15H, Minor isomer), 4.28 (s, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 143.8, 143.6, 137.4, 127.9, 127.3, 126.9, 125.7, 123.6 (d), 122.2 (d, *J* = 16.3 Hz), 118.0, 117.5, 64.4, 64.3, 50.5 (q, *J* = 29.2 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -67.86 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd. for C₁₄H₁₀F₃SO₂: 299.0359; found: 299.0364.



2-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)benzo[b]thiophene (5f): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 50:1) gave **5f** (49.3 mg, 60% yield) as white solid; ¹H NMR (400 MHz, CDCl₃) δ 8.14-7.34 (m, 14H), 5.15 (q, *J* = 9.3 Hz, 0.7H, Major isomer), 5.05 (q, *J* = 9.3 Hz, 0.2H, Minor isomer) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.4, 140.4, 140.0, 138.1, 132.8, 129.8, 129.6, 128.8, 127.6, 127.5, 127.1, 124.7, 124.4, 123.8, 122.9, 121.7, 49.6 (q, *J* = 28.6 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -66.60 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd. for C₂₂H₁₄F₃S: 367.0774; found: 367.0778.



2-(1-(4-butoxyphenyl)-2,2,2-trifluoroethyl)-5-methylthiophene (5g): Flash column chromatography on a silica gel (petroleum ether-EtOAc = 30:1) gave **5g** (37.6 mg, 60% yield) as white solid ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.11-6.79 (m, 3H), 6.67 (d, *J* = 3.6 Hz, 1H), 4.79 (q, *J* = 9.7 Hz, 1H), 4.00 (t, *J* = 6.3 Hz, 2H), 2.47 (s, 3H), 1.93-1.70 (m, 2H), 1.54 (q, *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 140.3, 135.2, 130.1, 127.1, 126.9, 125.0, 124.4, 114.7, 67.7, 50.6 (q, *J* = 29.1 Hz), 31.3, 19.3, 15.2, 13.9 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -67.93 (s, 3F) ppm; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd. for C₁₇H₁₈F₃SO: 327.1036; found: 327.1038.

VIII.X-Ray data for 2q and 2x

X-ray for 2q

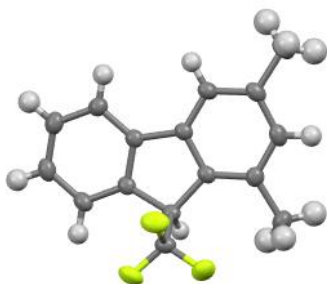


Fig S5. X-ray structure of 2q

Identification code	A
Empirical formula	C ₁₆ H ₁₃ F ₃
Formula weight	262.26
Temperature/K	193.00
Crystal system	monoclinic
Space group	P21/c
a/Å	12.8122(6)
b/Å	4.8770(2)
c/Å	20.0701(9)
α/°	90
β/°	98.304(2)
γ/°	90
Volume/Å ³	1240.93(10)
Z	4
ρ _{calc} /cm ³	1.404
μ/mm ⁻¹	0.604
F(000)	544.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	6.066 to 120.762
Index ranges	-16 ≤ h ≤ 14, -6 ≤ k ≤ 6, -23 ≤ l ≤ 25
Reflections collected	7925
Independent reflections	2603 [R _{int} = 0.0400, R _{sigma} = 0.0394]
Data/restraints/parameters	2603/0/174
Goodness-of-fit on F ²	1.100
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0578, wR ₂ = 0.1846
Final R indexes [all data]	R ₁ = 0.0647, wR ₂ = 0.1934

Largest diff. peak/hole / e Å⁻³ 0.35/-0.34

X-ray for **2x**

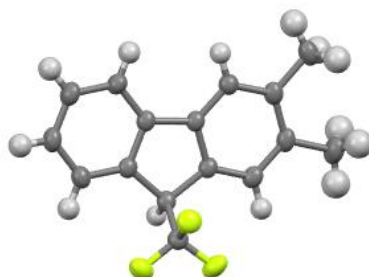


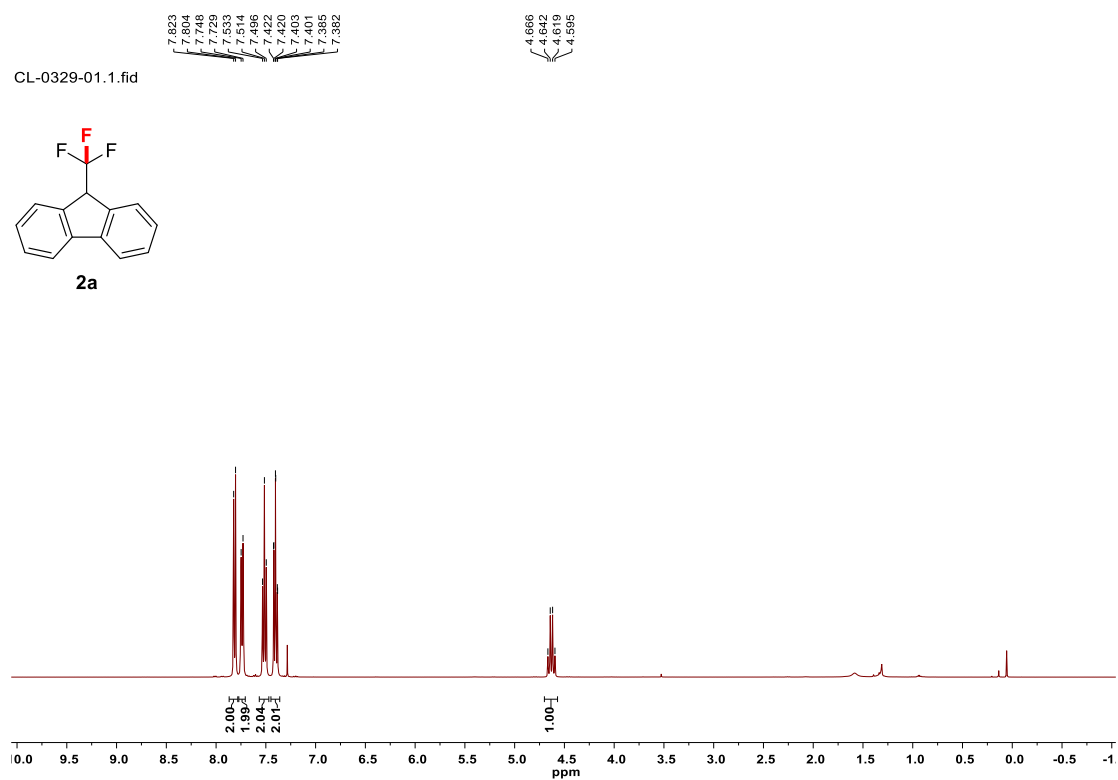
Fig S6. X-ray structure of **2x**

Identification code	A
Empirical formula	C ₁₆ H ₁₃ F ₃
Formula weight	262.26
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	4.8272(4)
b/Å	9.3359(8)
c/Å	14.3768(13)
α/°	87.031(4)
β/°	80.964(4)
γ/°	77.047(3)
Volume/Å ³	623.49(9)
Z	2
ρ _{calc} /cm ³	1.397
μ/mm ⁻¹	0.601
F(000)	272.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	9.968 to 120.3
Index ranges	-6 ≤ h ≤ 6, -11 ≤ k ≤ 12, -18 ≤ l ≤ 18
Reflections collected	6808
Independent reflections	2690 [R _{int} = 0.0497, R _{sigma} = 0.0551]
Data/restraints/parameters	2690/0/175
Goodness-of-fit on F ²	1.088
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0715, wR ₂ = 0.2043
Final R indexes [all data]	R ₁ = 0.0776, wR ₂ = 0.2135
Largest diff. peak/hole / e Å ⁻³	0.41/-0.46

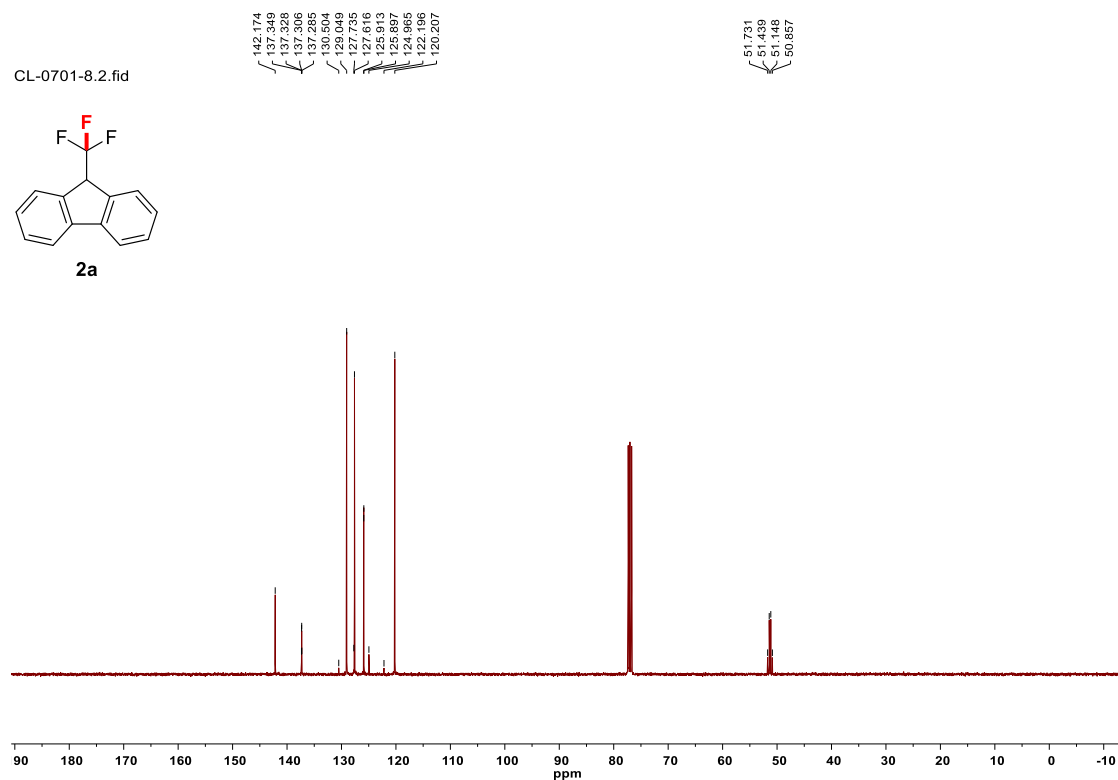
IX. References

1. H. Guo, S. Zhang, X.-J. Feng, X. Yu, Y. Yamamoto, and M. Bao, *Org. Lett.* 2022, **24**, 2596.
2. H.-J. Tang, L.-Z. Lin, C. Feng, and T.-P. Loh, *Angew. Chem. Int. Ed.* 2017, **56**, 9872.

X. NMR spectra

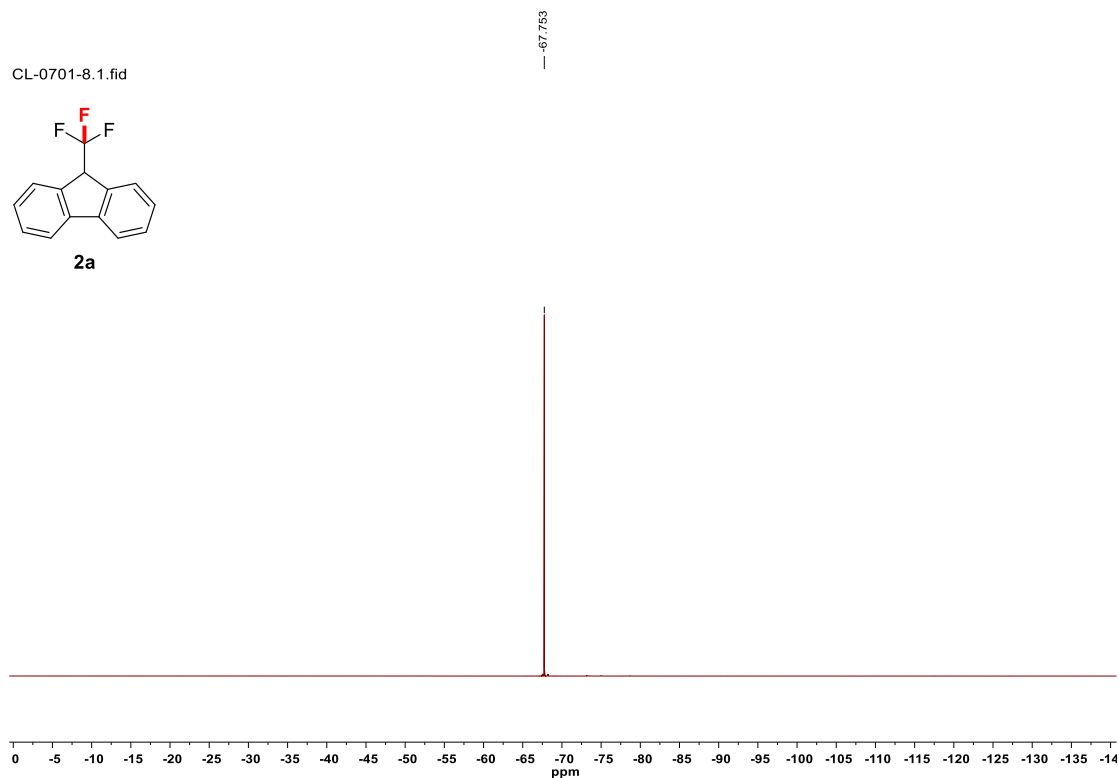
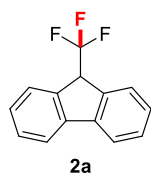


¹H NMR spectrum of **2a** (400 MHz, CDCl₃)



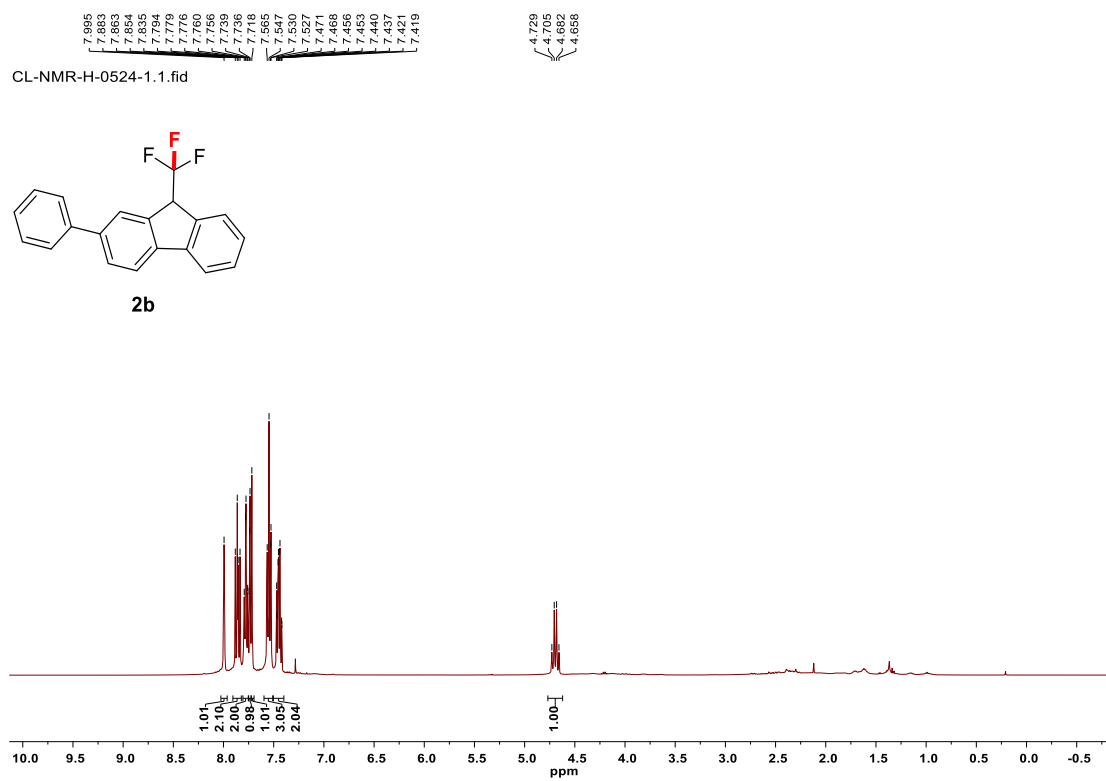
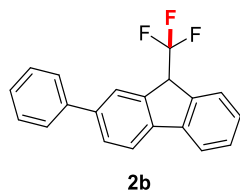
¹³C NMR spectrum of **2a** (101 MHz, CDCl₃)

CL-0701-8-1.fid



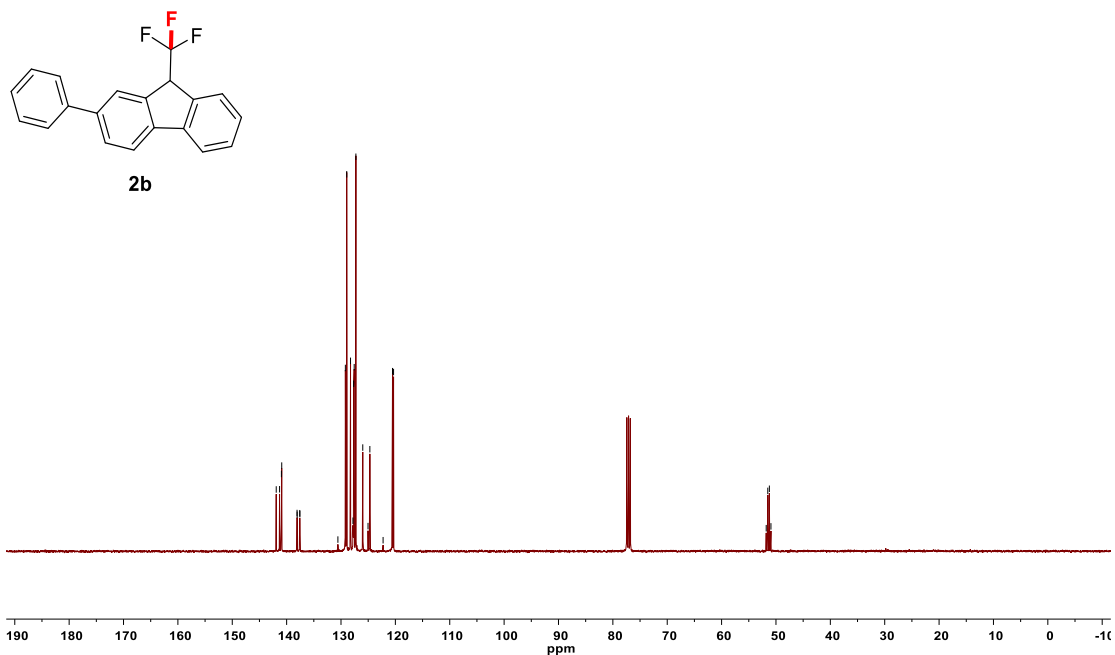
^{19}F NMR spectrum of **2a** (376 MHz, CDCl_3)

CL-NMR-H-0524-1-1.fid



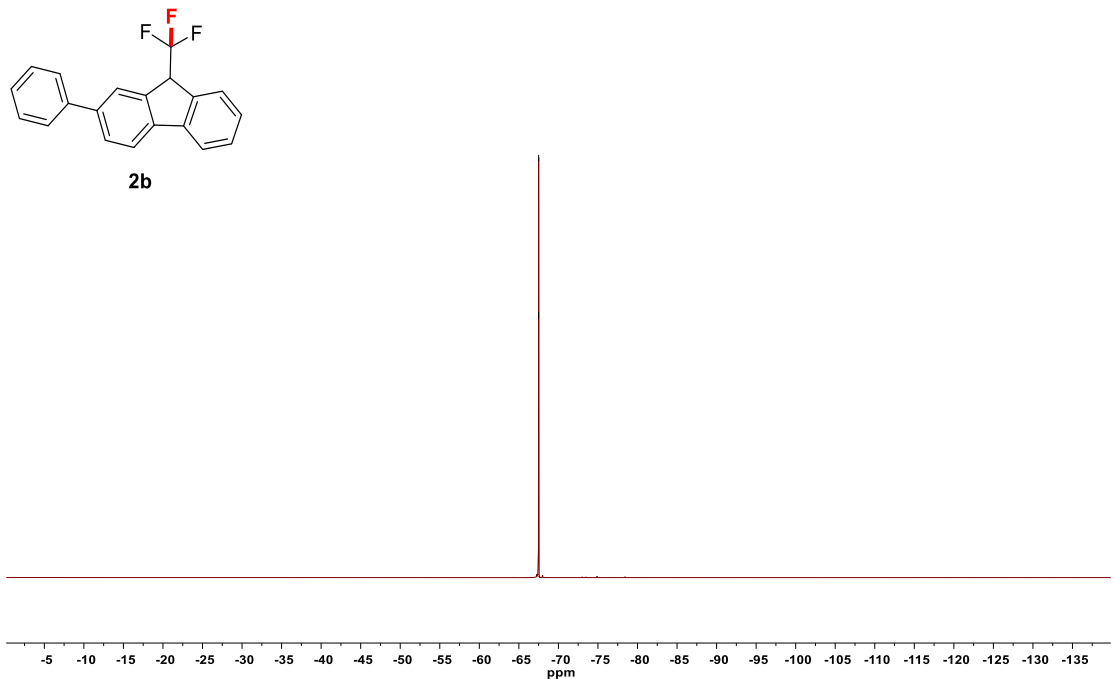
^1H NMR spectrum of **2b** (400 MHz, CDCl_3)

CL-C-NMR-0526-1.2.fid



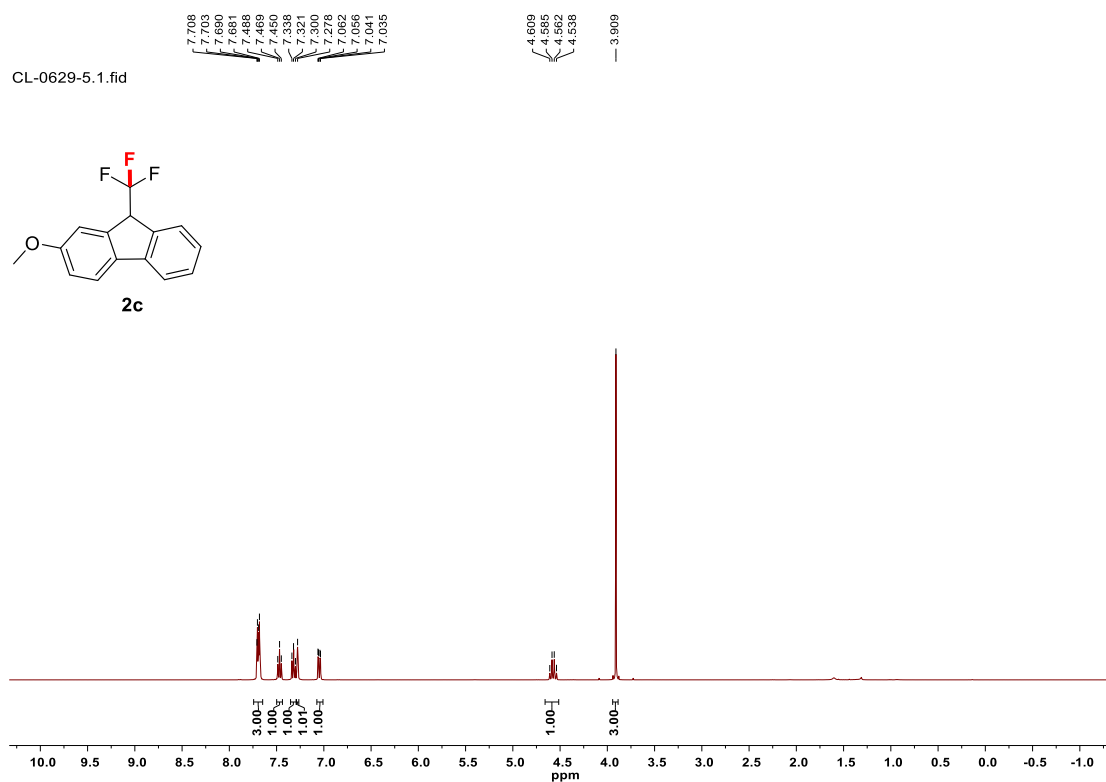
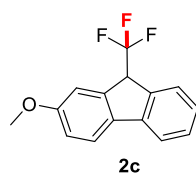
^{13}C NMR spectrum of **2b** (101 MHz, CDCl_3)

CL-C-NMR-0526-1.1.fid



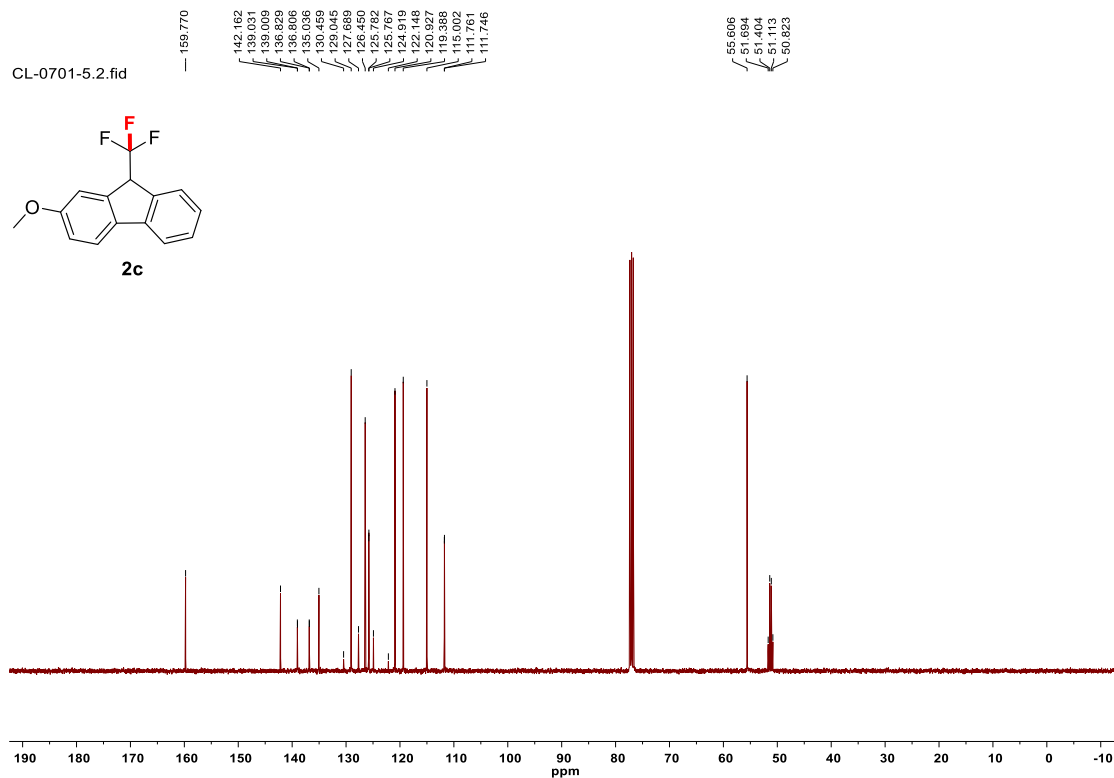
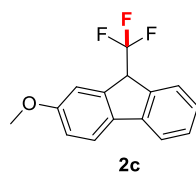
^{19}F NMR spectrum of **2b** (376 MHz, CDCl_3)

CL-0629-5.1.fid



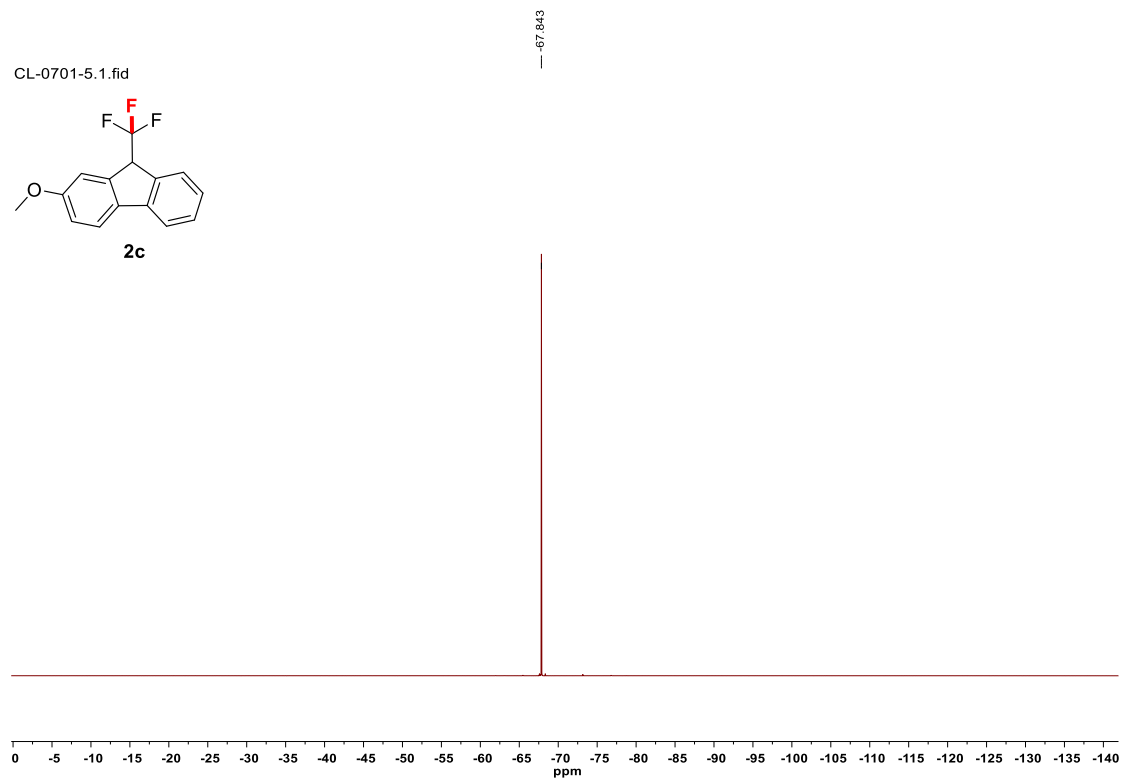
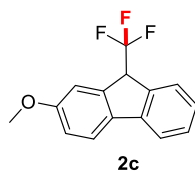
¹H NMR spectrum of **2c** (400 MHz, CDCl₃)

CL-0701-5.2.fid



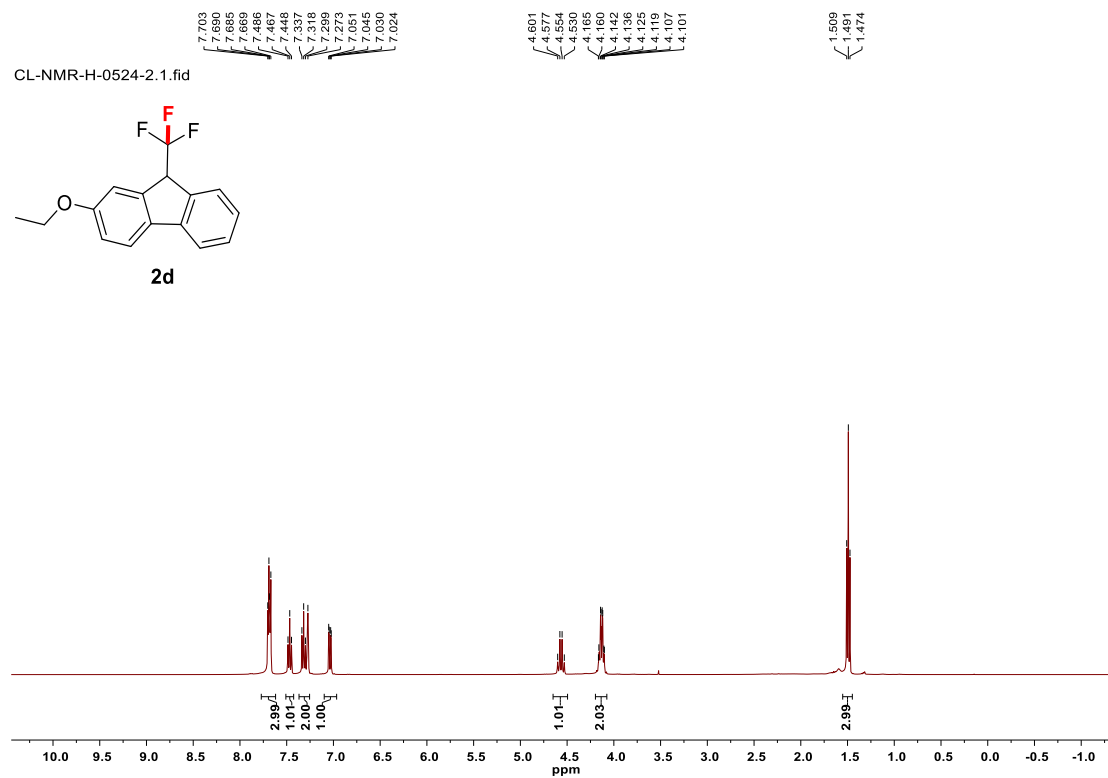
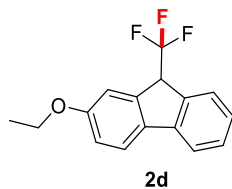
¹³C NMR spectrum of **2c** (101 MHz, CDCl₃)

CL-0701-5.1.fid

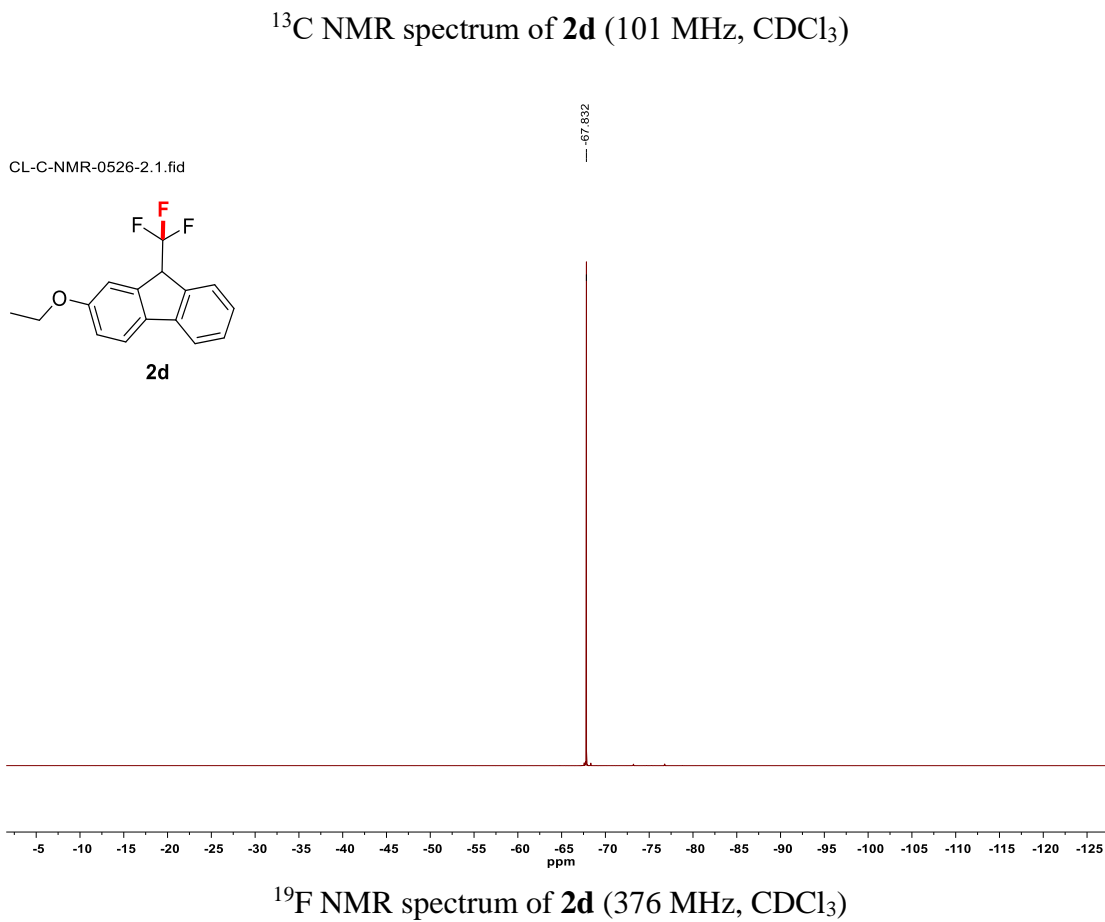
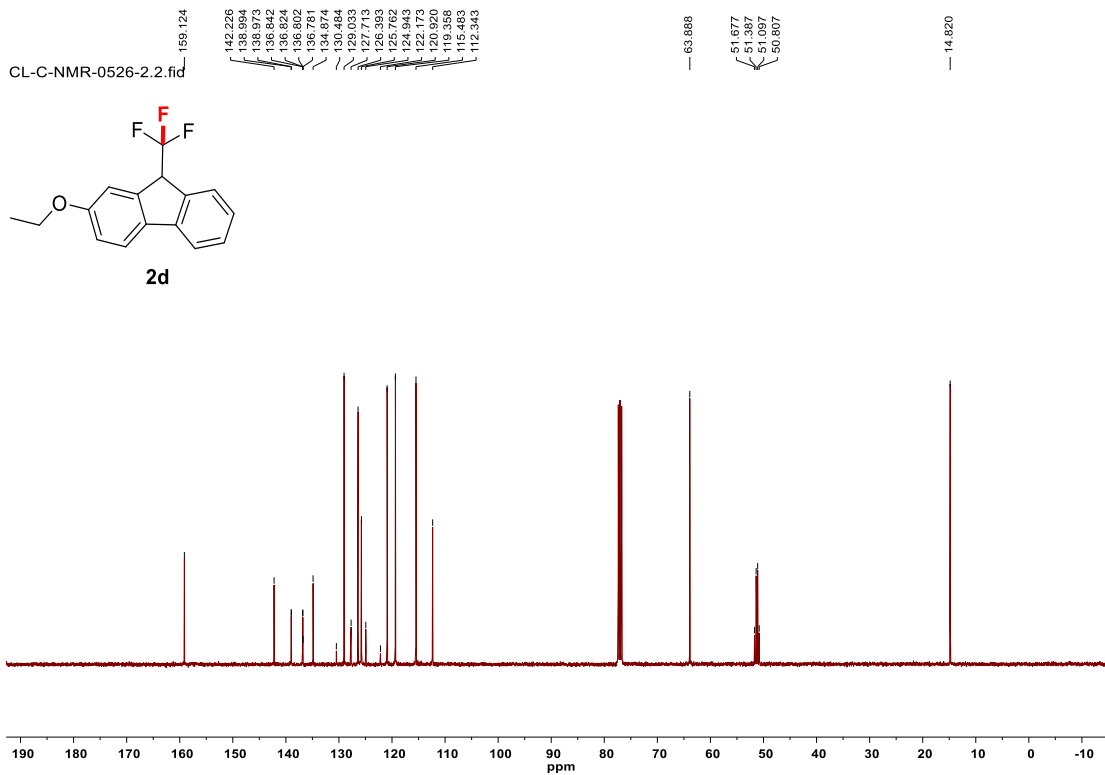


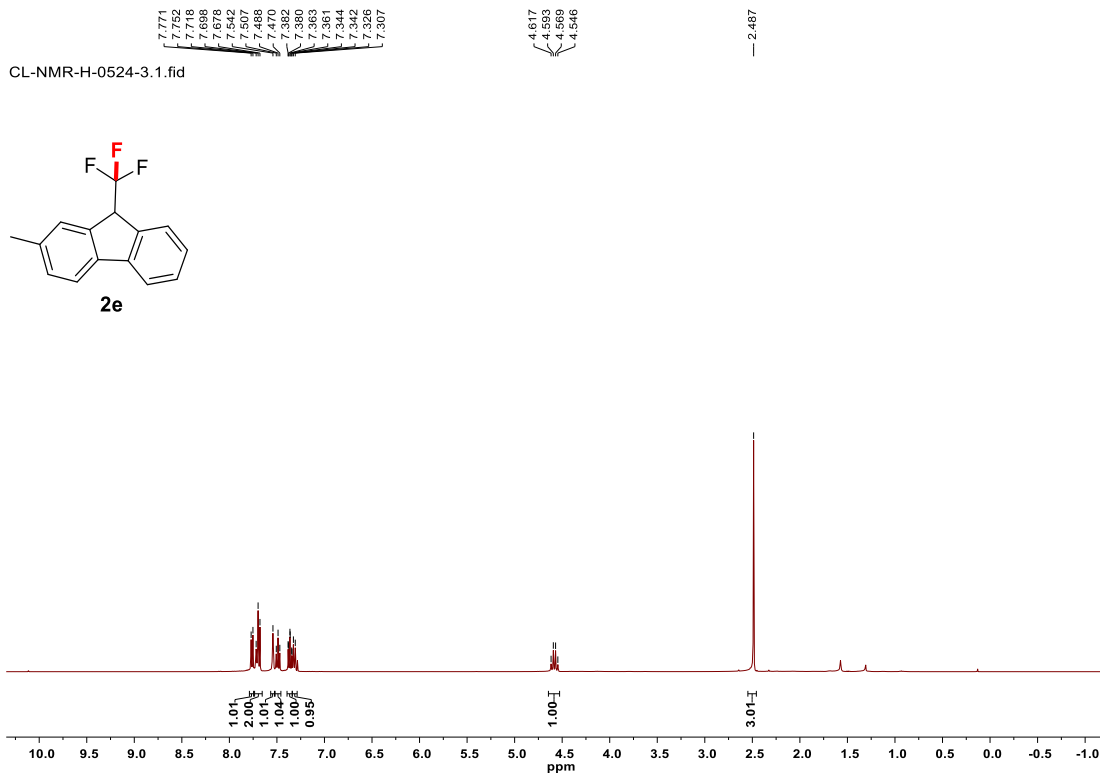
¹⁹F NMR spectrum of **2c** (376 MHz, CDCl₃)

CL-NMR-H-0524-2.1.fid

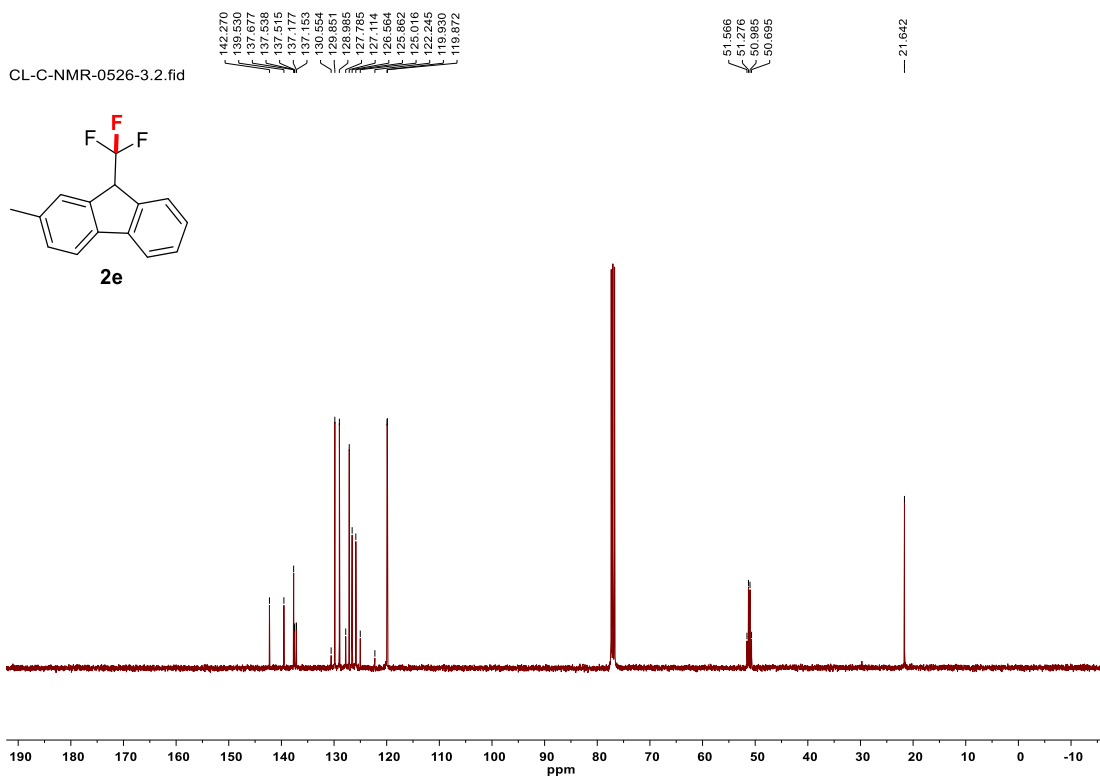


¹H NMR spectrum of **2d** (400 MHz, CDCl₃)



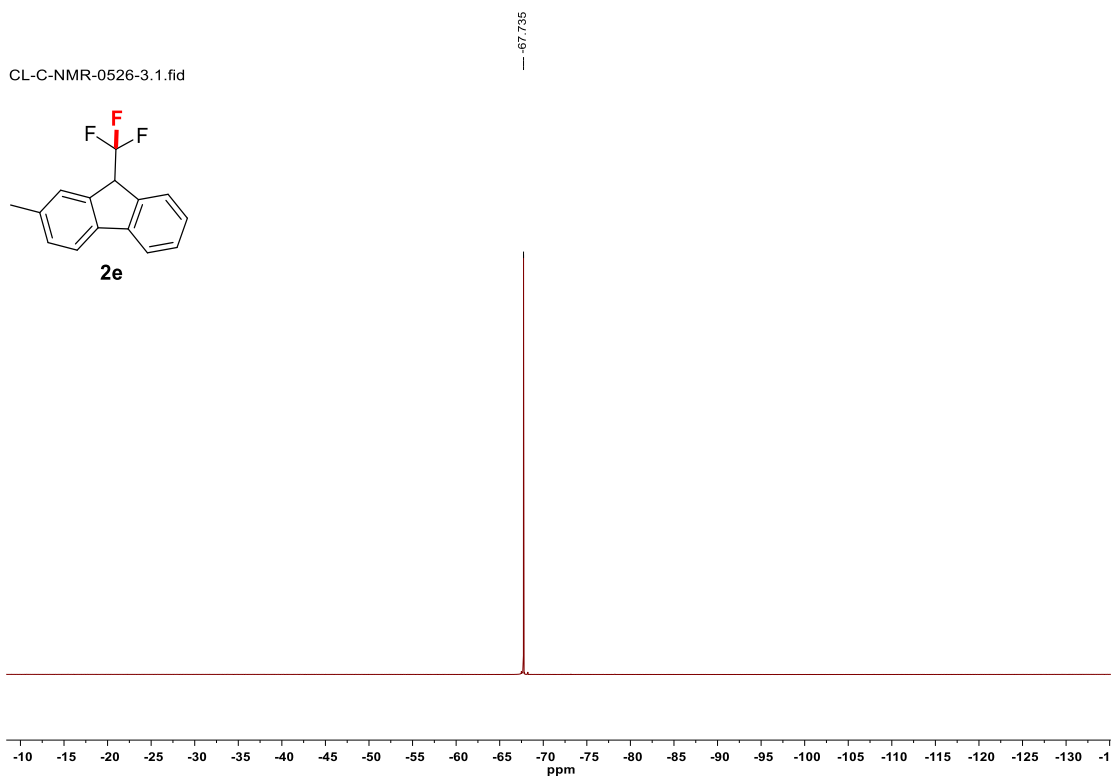
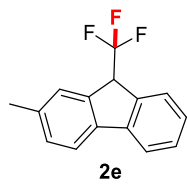


¹H NMR spectrum of **2e** (400 MHz, CDCl₃)



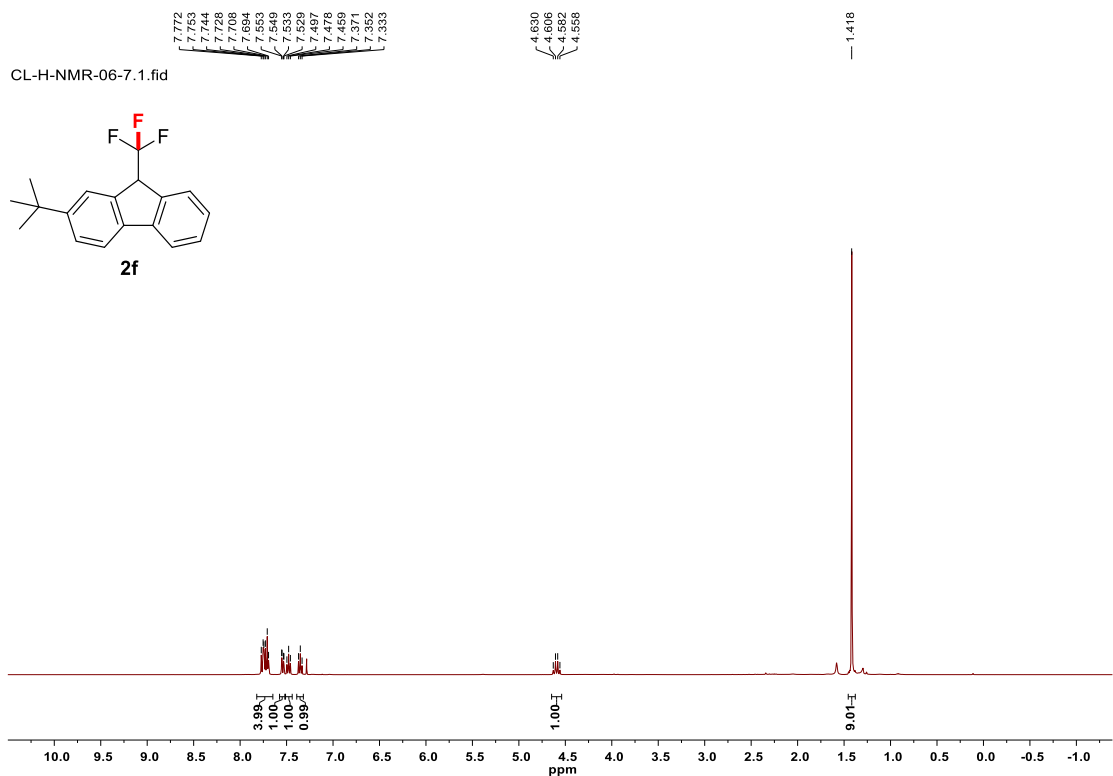
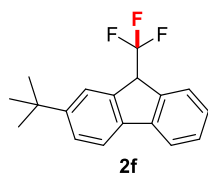
¹³C NMR spectrum of **2e** (101 MHz, CDCl₃)

CL-C-NMR-0526-3.1.fid



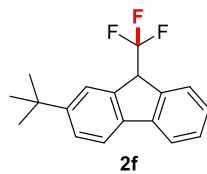
^{19}F NMR spectrum of **2e** (376 MHz, CDCl_3)

CL-H-NMR-06-7.1.fid



^1H NMR spectrum of **2f** (400 MHz, CDCl_3)

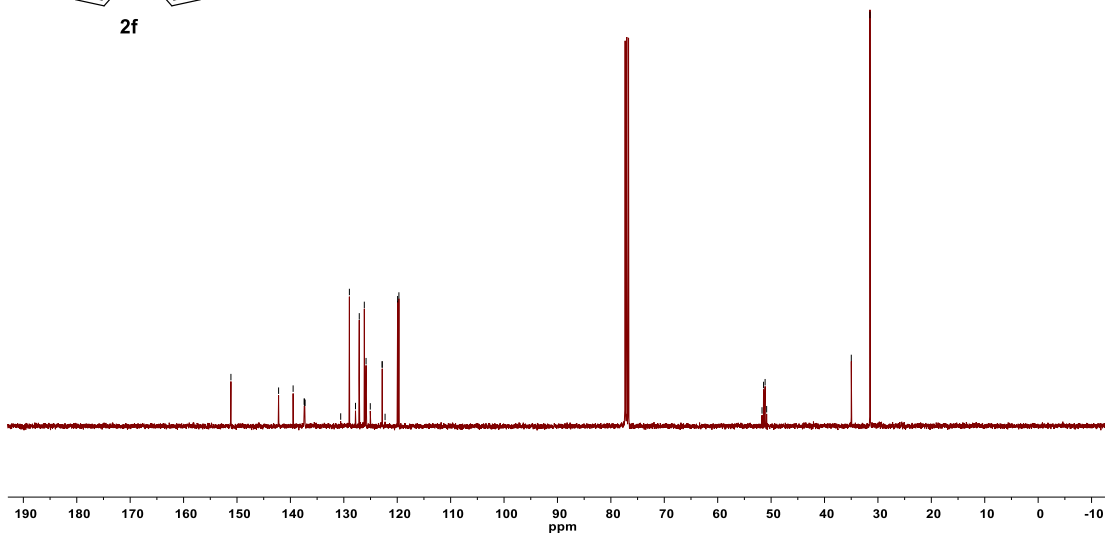
CL-C-NMR-0607-7.1.fid



151.138
142.211
139.491
137.990
137.303
137.280
130.694
128.957
127.914
126.183
125.836
125.044
122.820
122.808
122.574
119.687

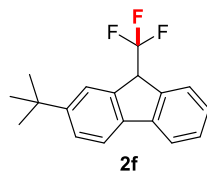
51.702
51.413
51.124
50.834

34.987
31.488

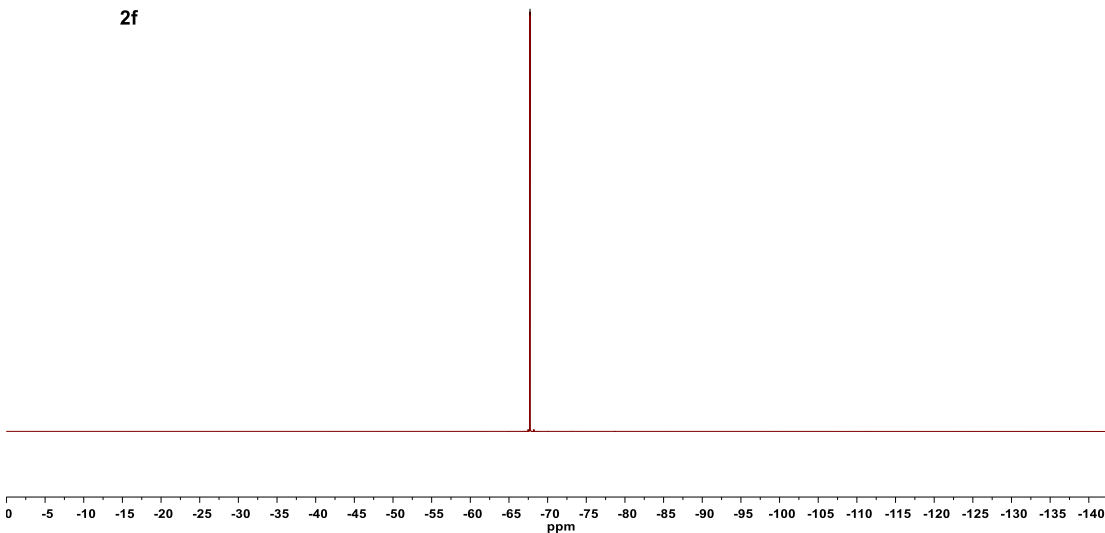


¹³C NMR spectrum of **2f** (101 MHz, CDCl₃)

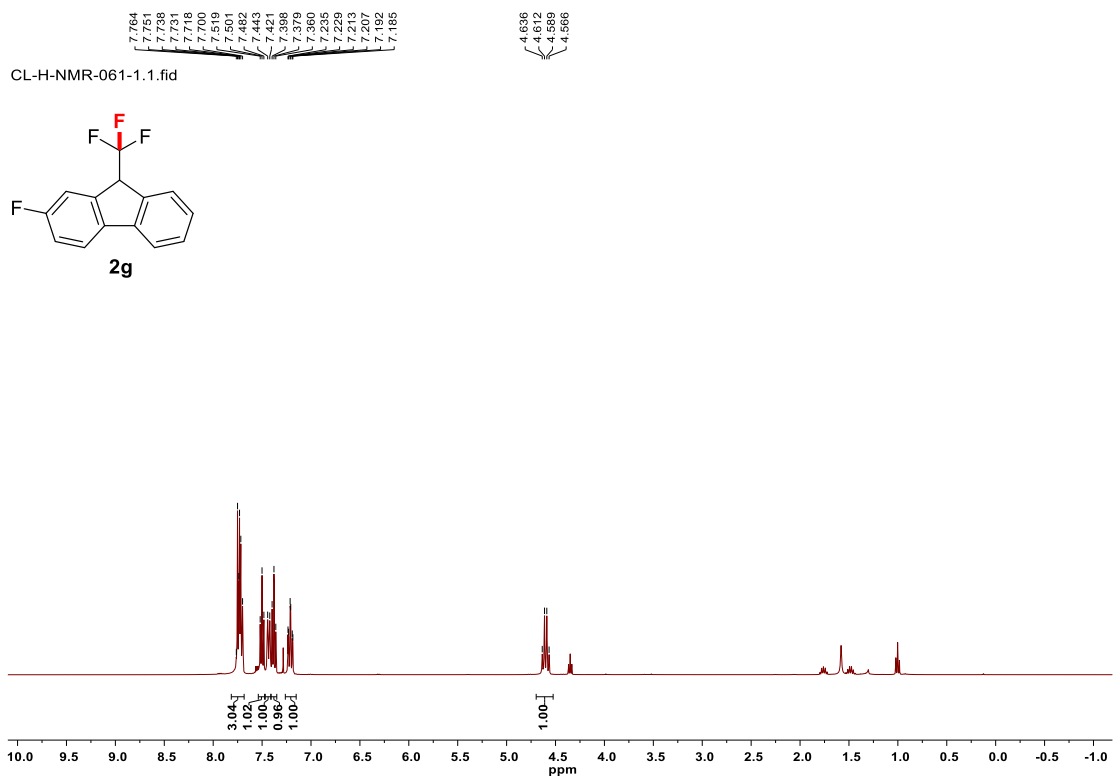
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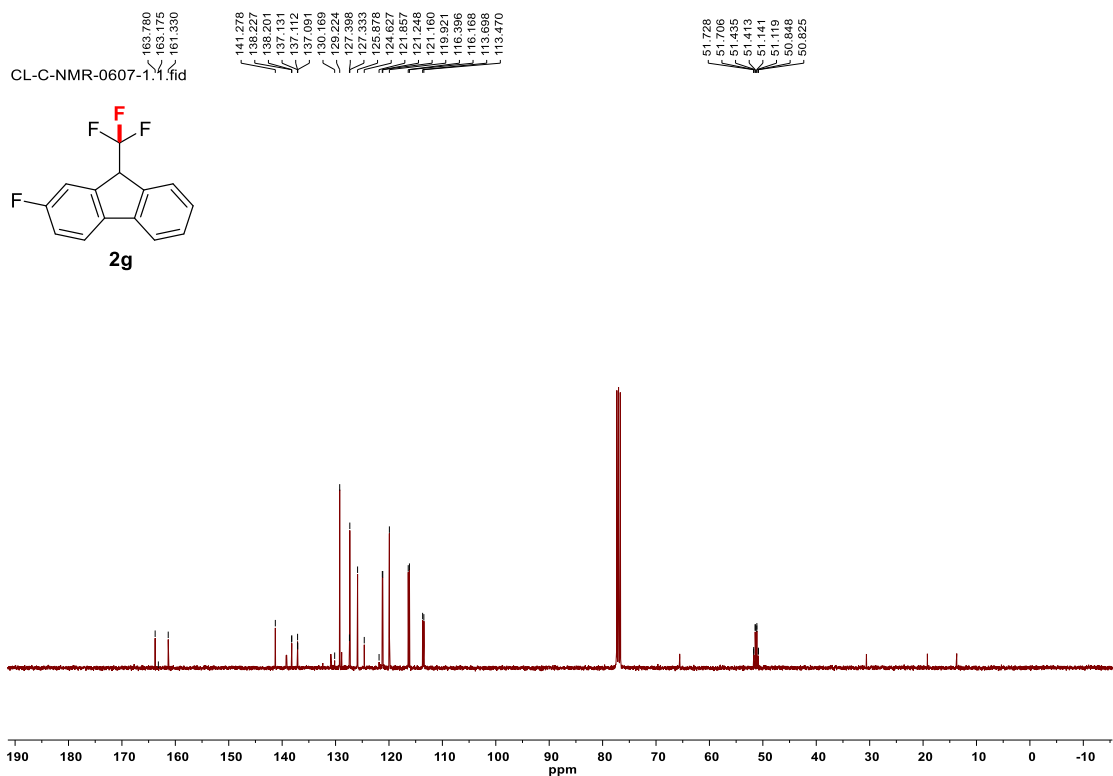
-67.722



¹⁹F NMR spectrum of **2f** (376 MHz, CDCl₃)

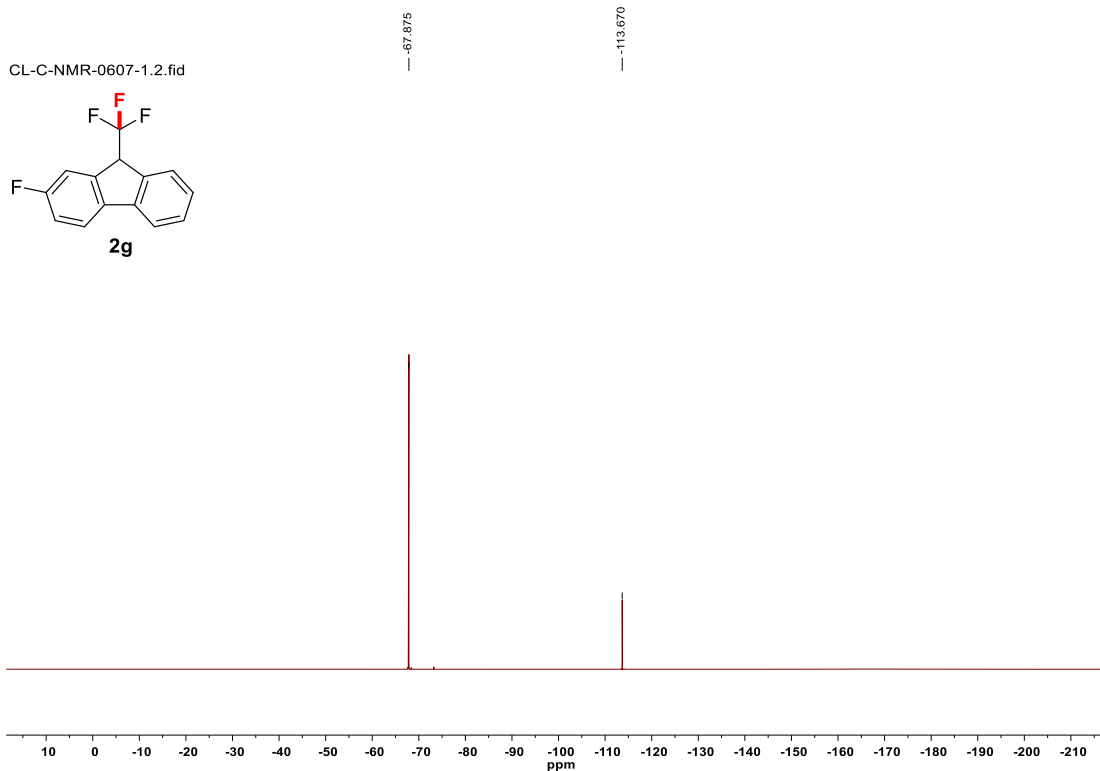
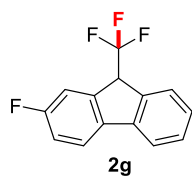


^1H NMR spectrum of **2g** (400 MHz, CDCl_3)



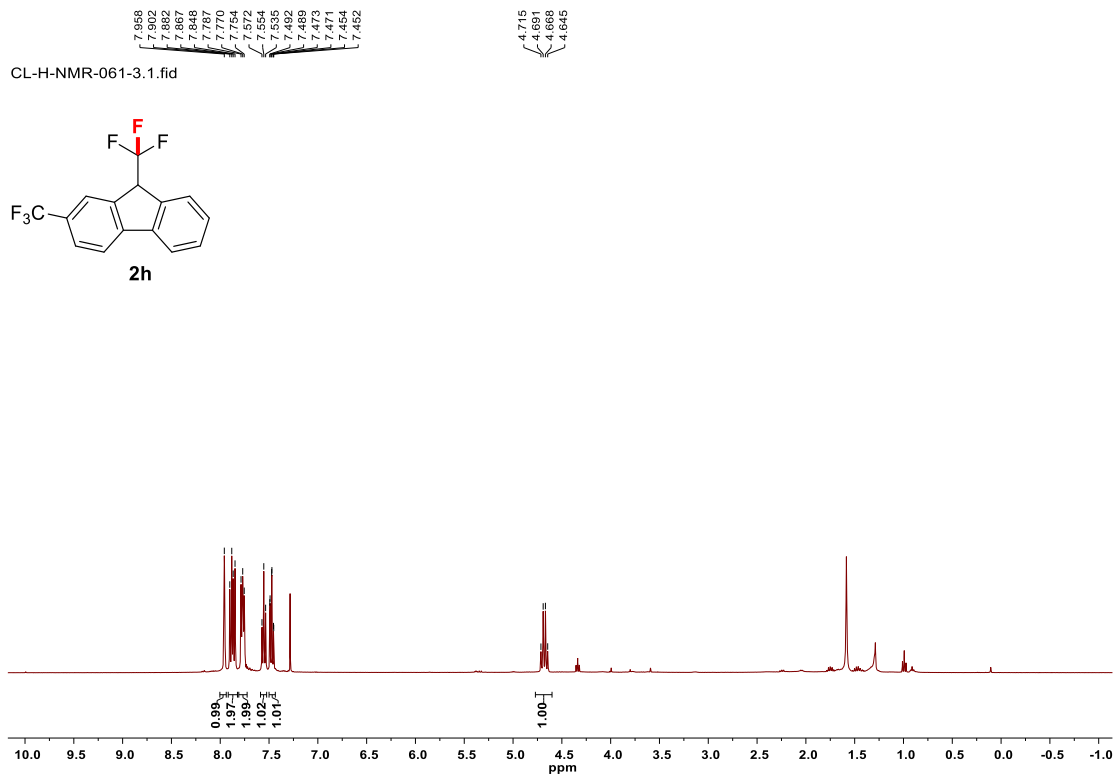
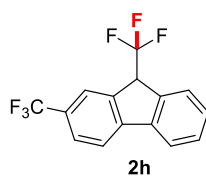
^{13}C NMR spectrum of **2g** (101 MHz, CDCl_3)

CL-C-NMR-0607-1.2.fid

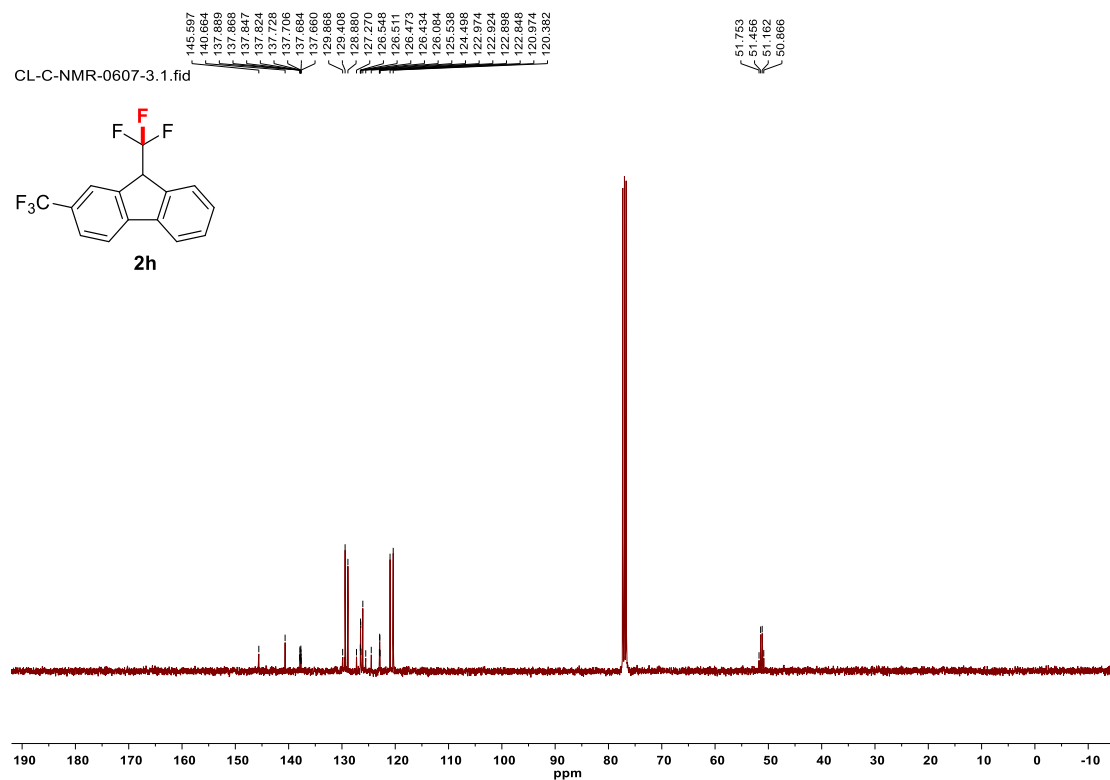


¹⁹F NMR spectrum of **2g** (376 MHz, CDCl₃)

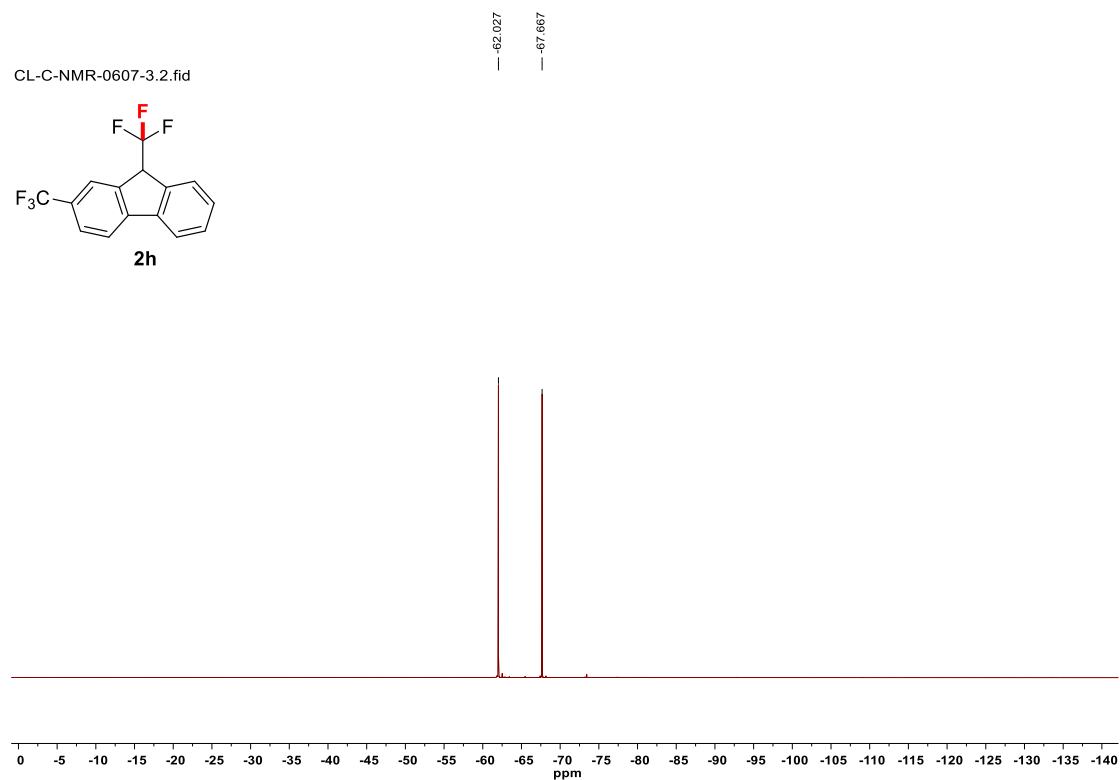
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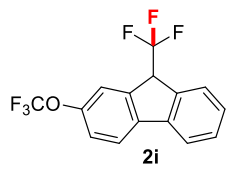
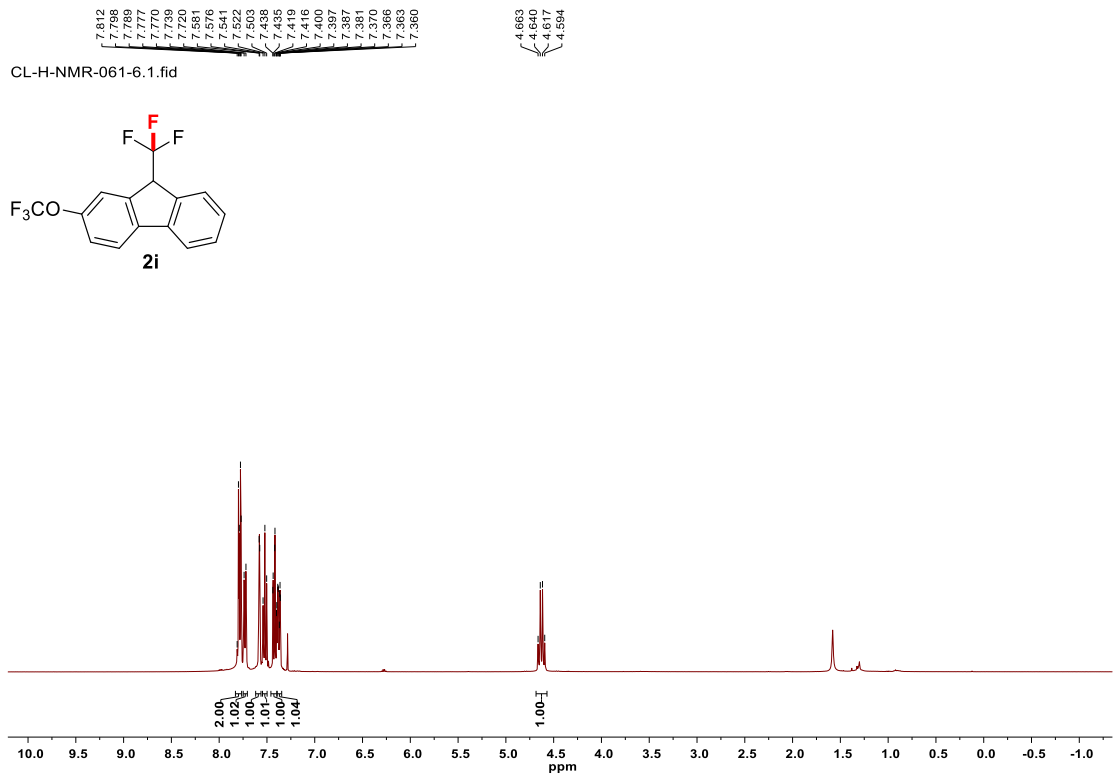
¹H NMR spectrum of **2h** (400 MHz, CDCl₃)



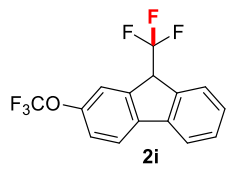
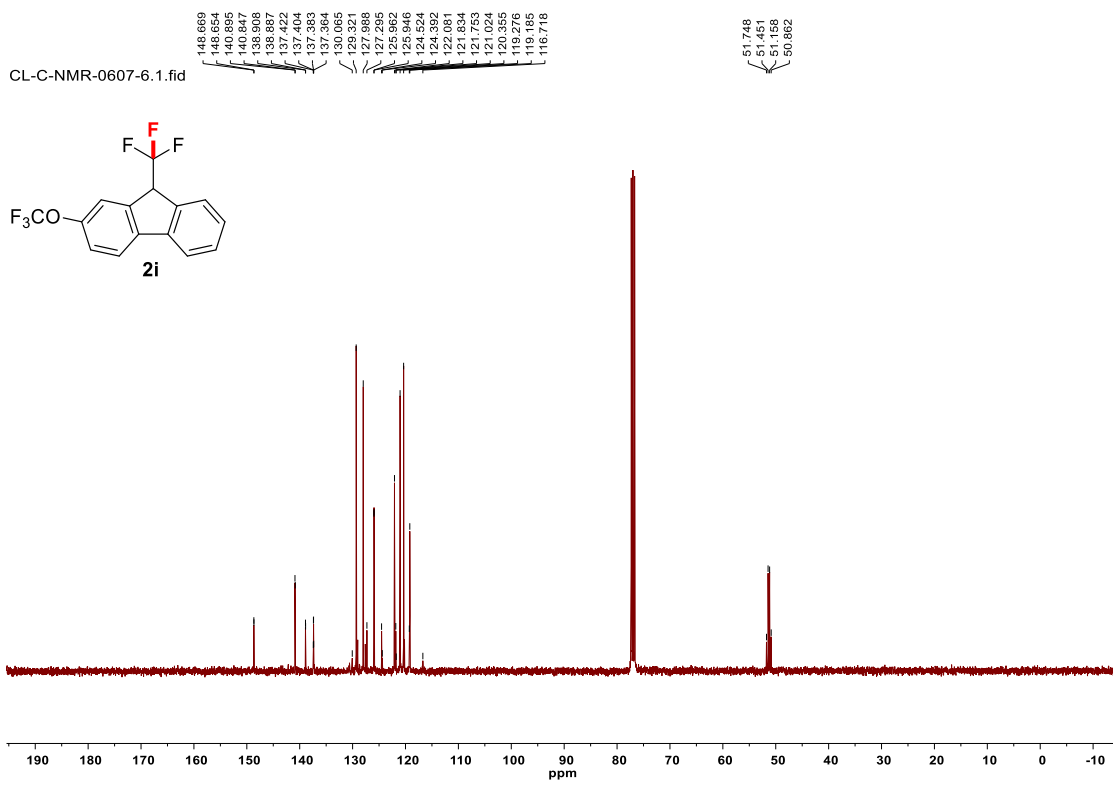
¹³C NMR spectrum of 2h (101 MHz, CDCl₃)



¹⁹F NMR spectrum of 2h (376 MHz, CDCl₃)

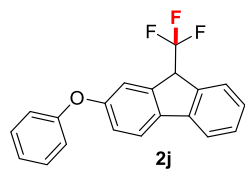


¹H NMR spectrum of **2i** (400 MHz, CDCl₃)



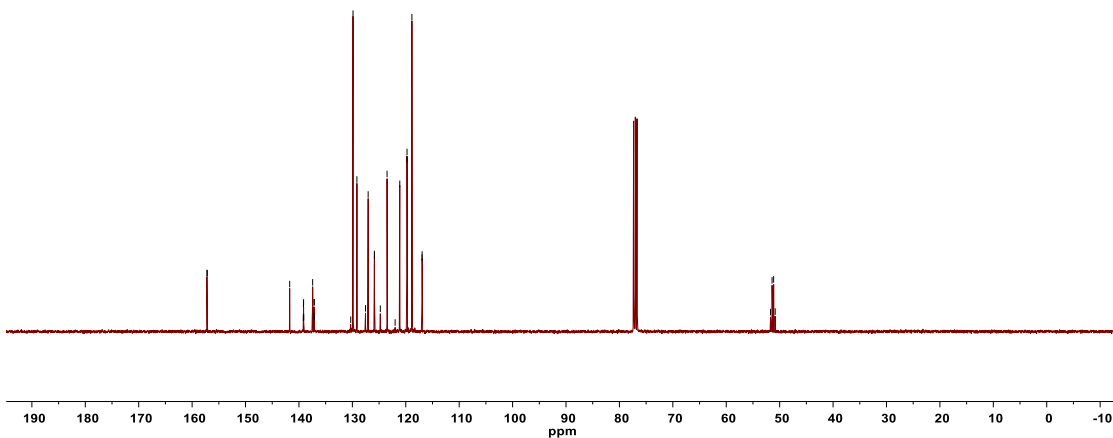
¹³C NMR spectrum of **2i** (101 MHz, CDCl₃)

CL-0701-4.2.fid



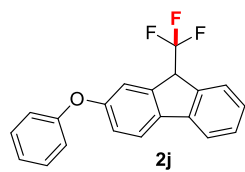
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157.160
141.736
139.174
139.153
139.152
138.109
137.434
137.177
137.159
137.138
137.117
137.077
129.876
129.152
127.536
127.044
125.876
125.881
125.866
123.506
121.994
121.124
119.789
119.767
118.853
118.831
116.837

51.710
51.418
51.127
50.834

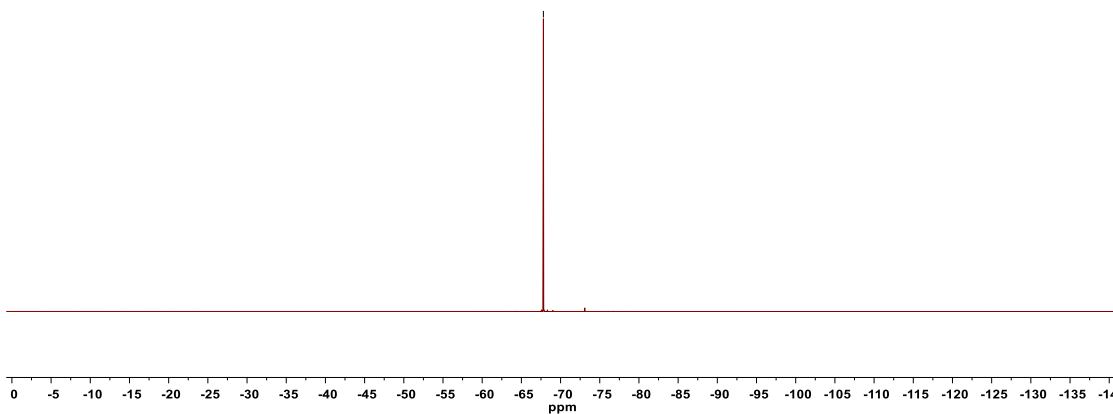


¹³C NMR spectrum of **2j** (101 MHz, CDCl₃)

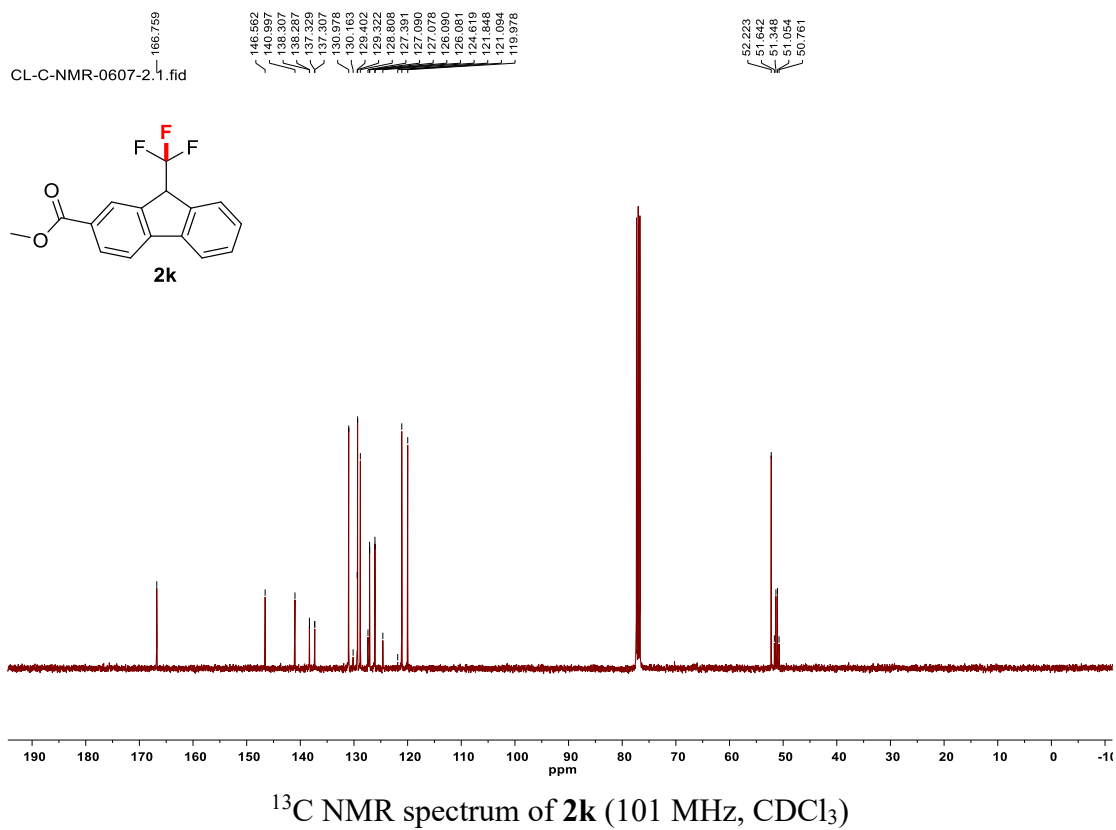
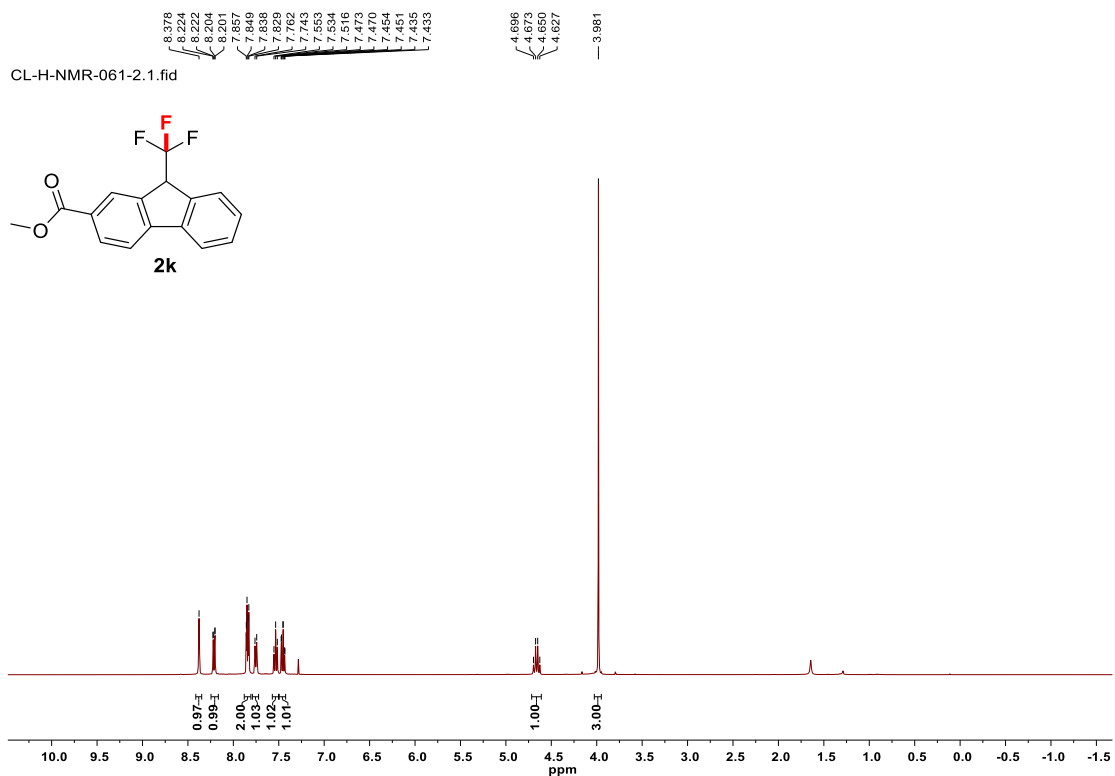
CL-0701-4.1.fid



-67.809

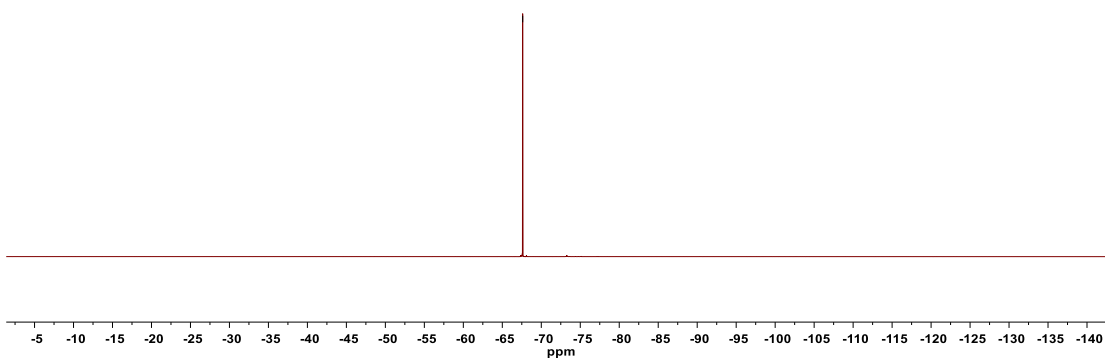
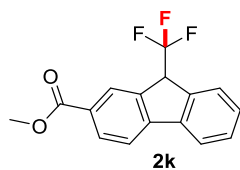


¹⁹F NMR spectrum of **2j** (376 MHz, CDCl₃)

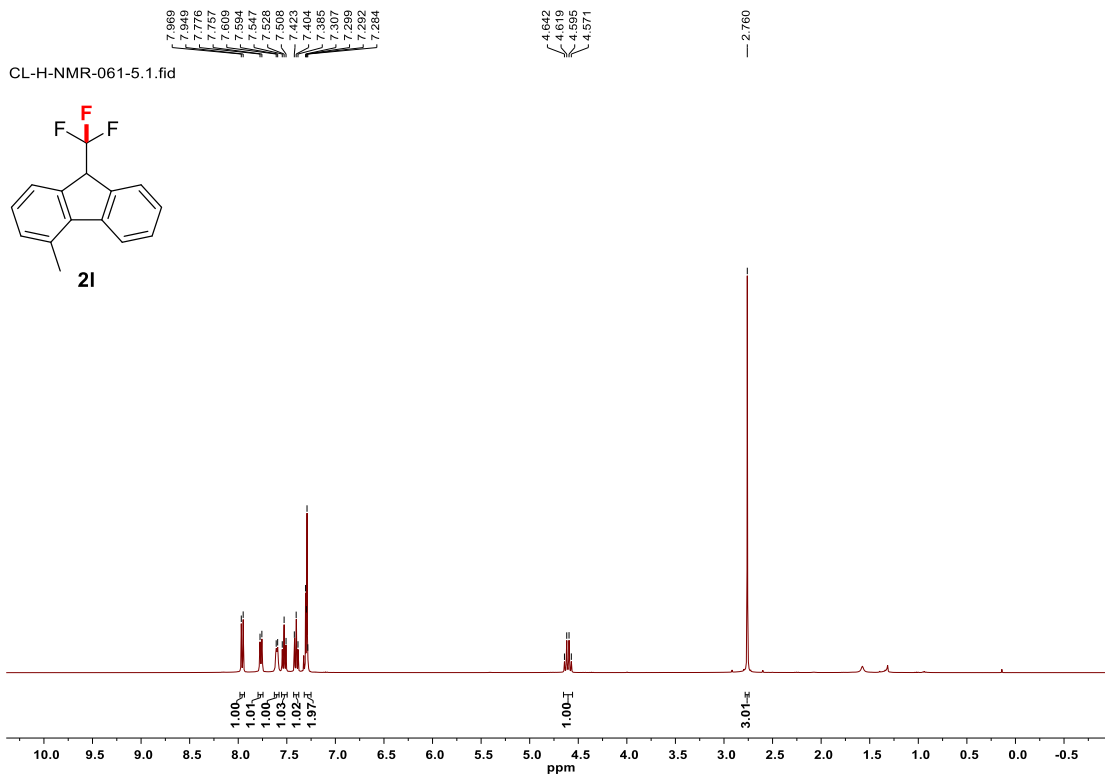


CL-C-NMR-0607-2.2.fid

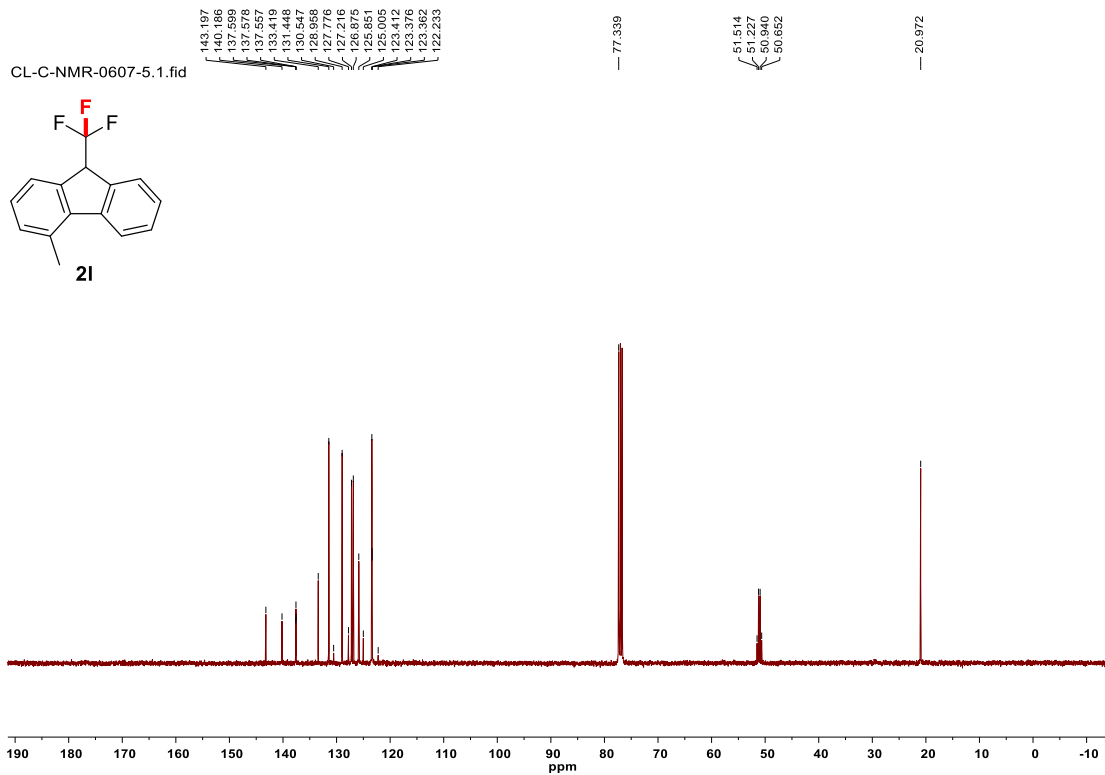
— 67.612



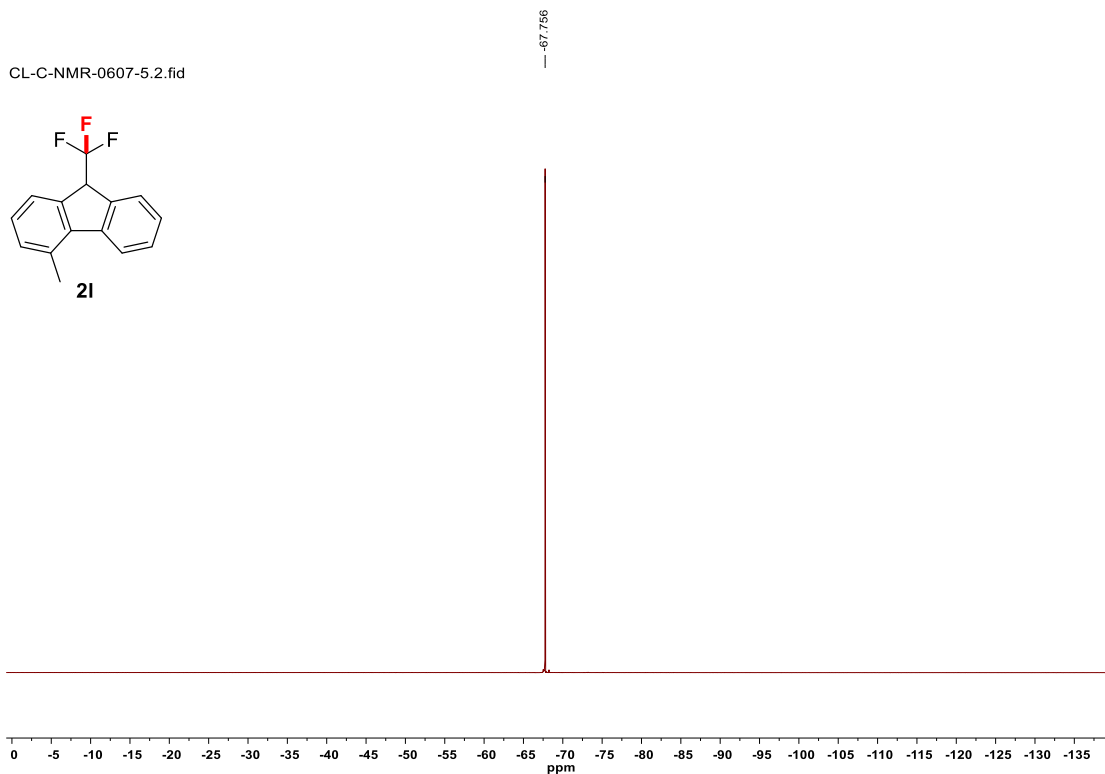
^{19}F NMR spectrum of **2k** (376 MHz, CDCl_3)



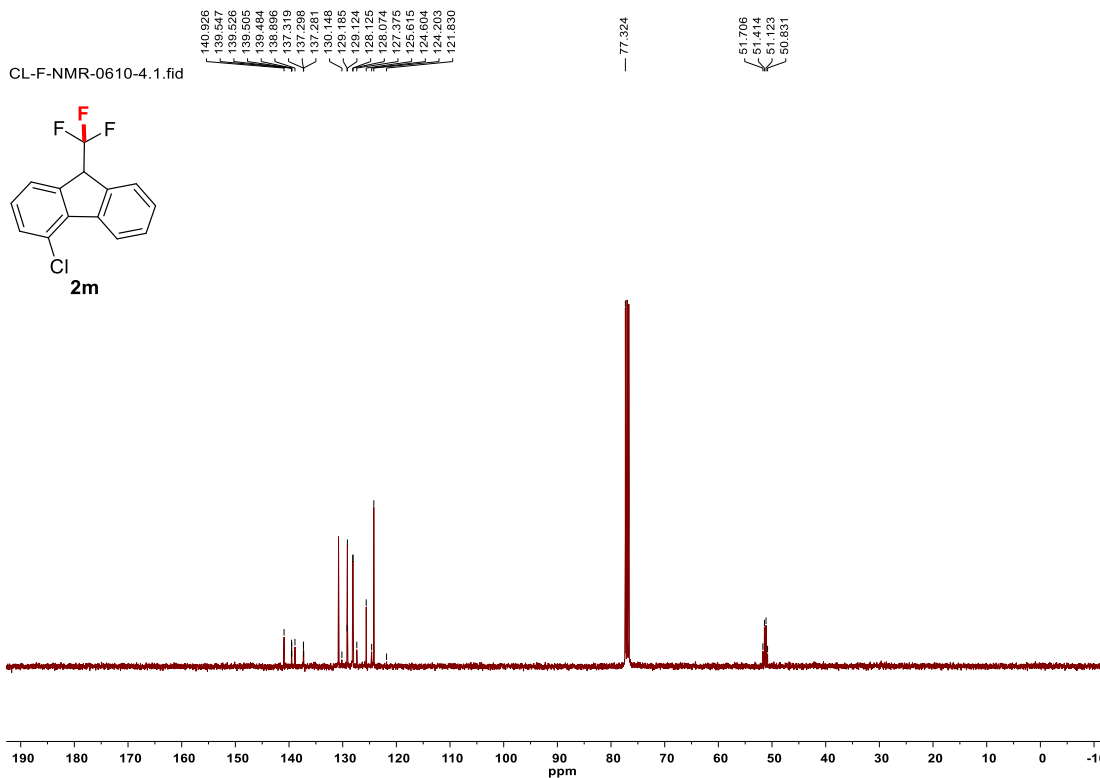
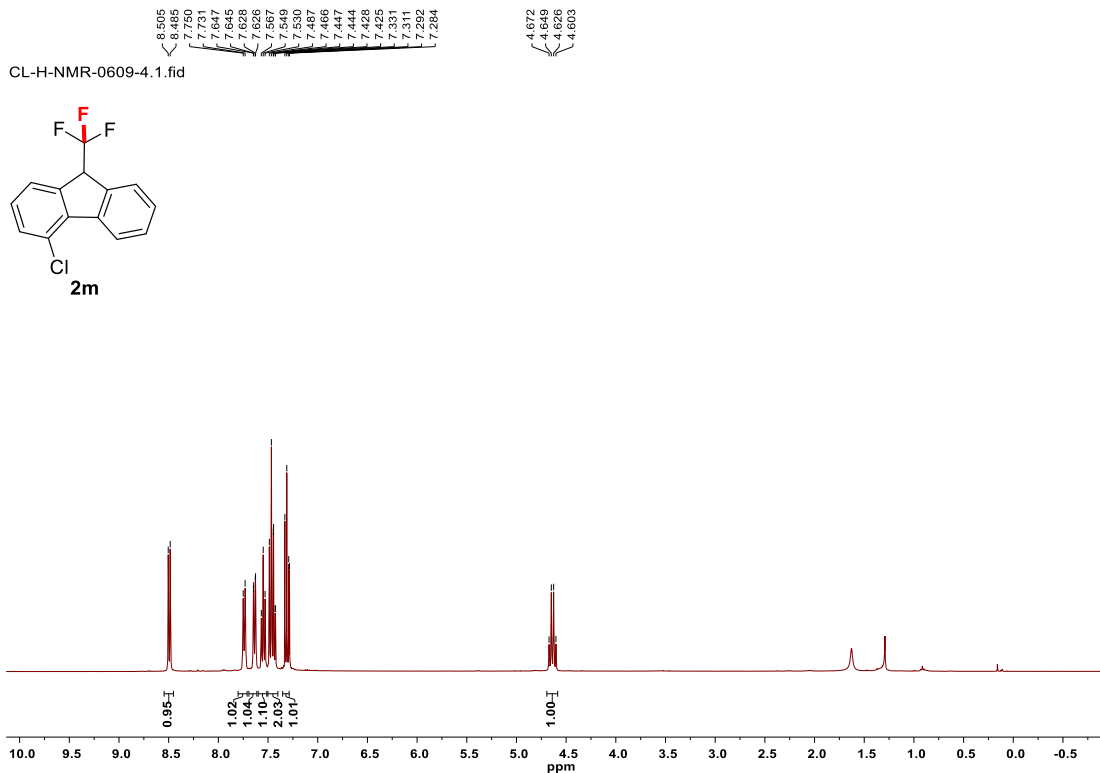
^1H NMR spectrum of **2l** (400 MHz, CDCl_3)



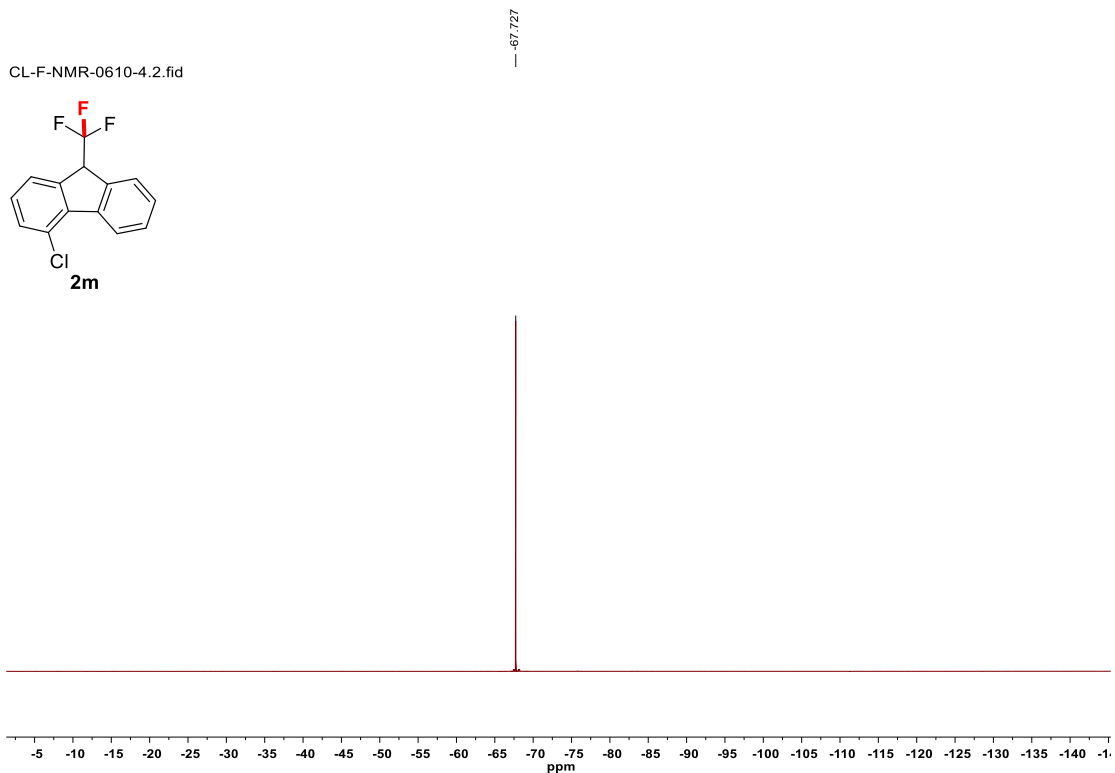
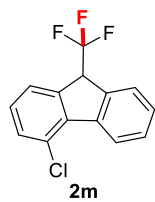
^{13}C NMR spectrum of **2I** (101 MHz, CDCl_3)



^{19}F NMR spectrum of **2I** (376 MHz, CDCl_3)

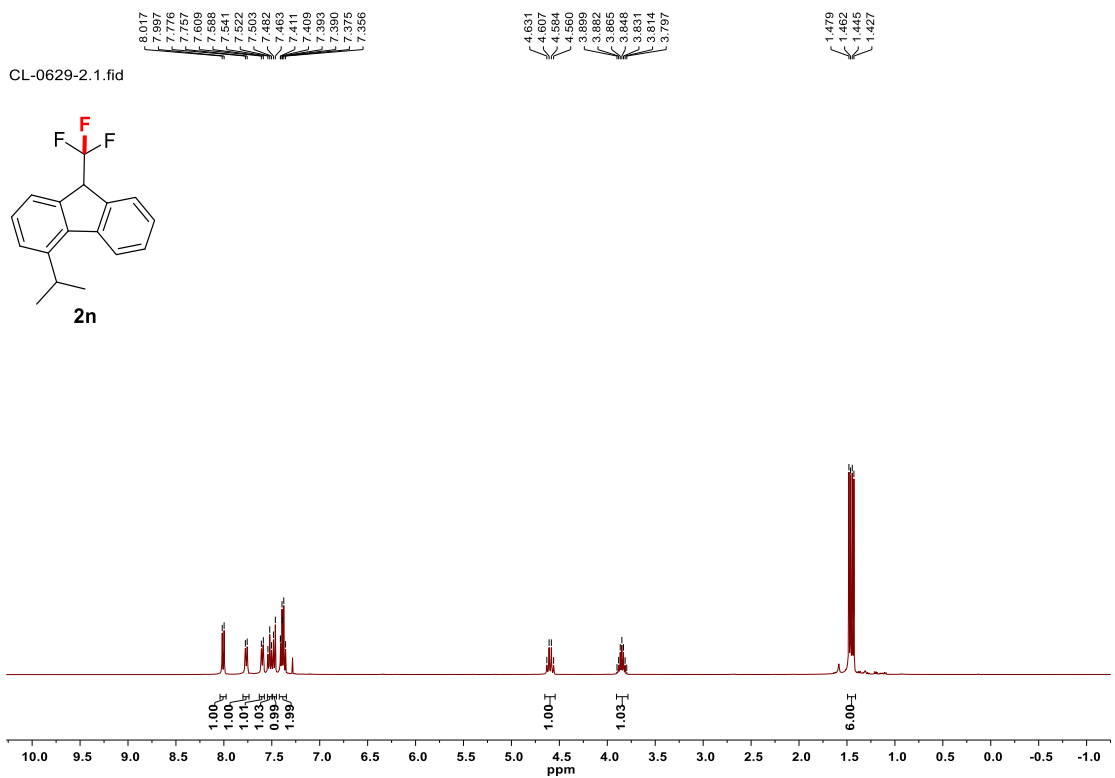
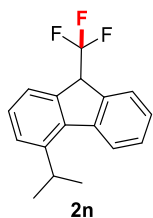


CL-F-NMR-0610-4.2.fid



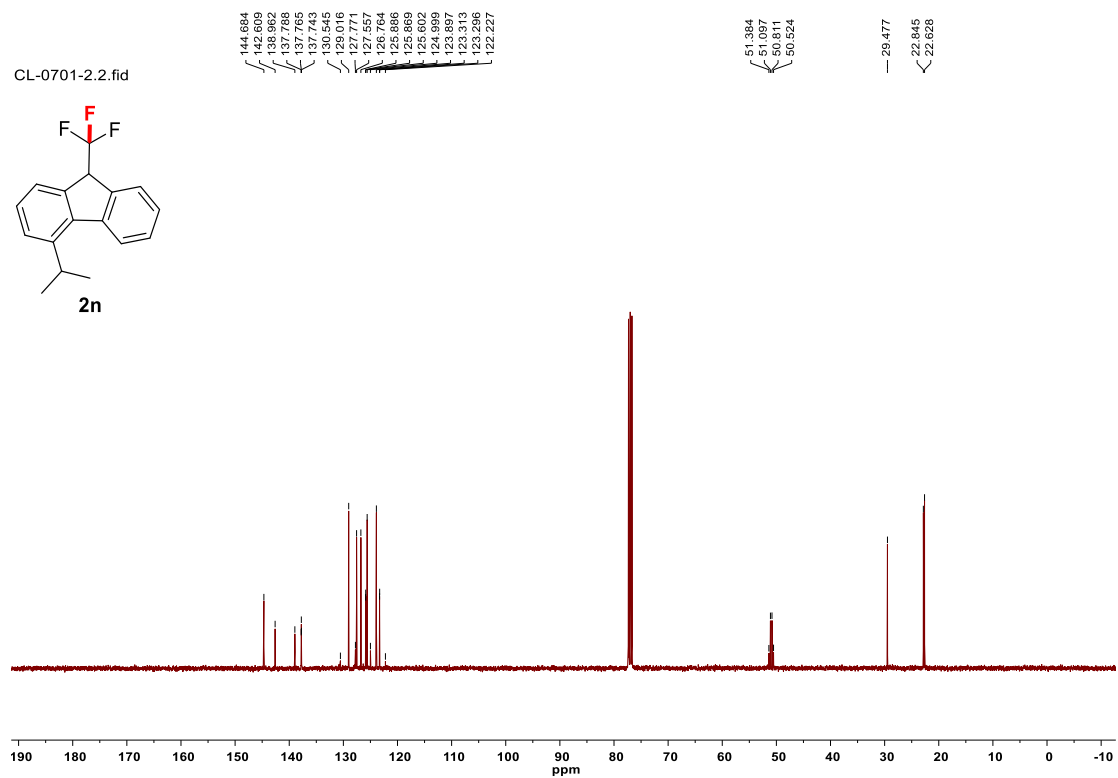
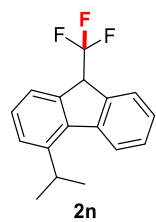
^{19}F NMR spectrum of **2m** (376 MHz, CDCl_3)

CL-0629-2.1.fid



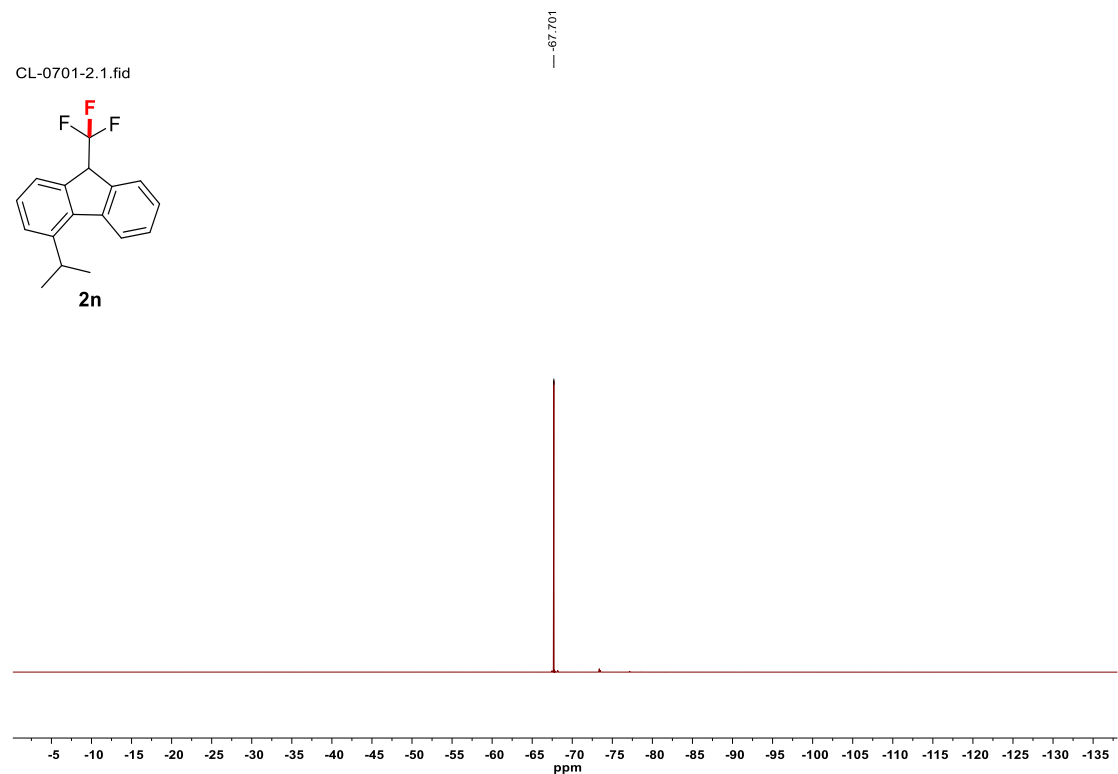
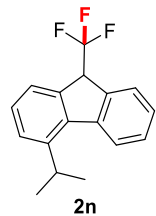
^1H NMR spectrum of **2n** (400 MHz, CDCl_3)

CL-0701-2.2.fid

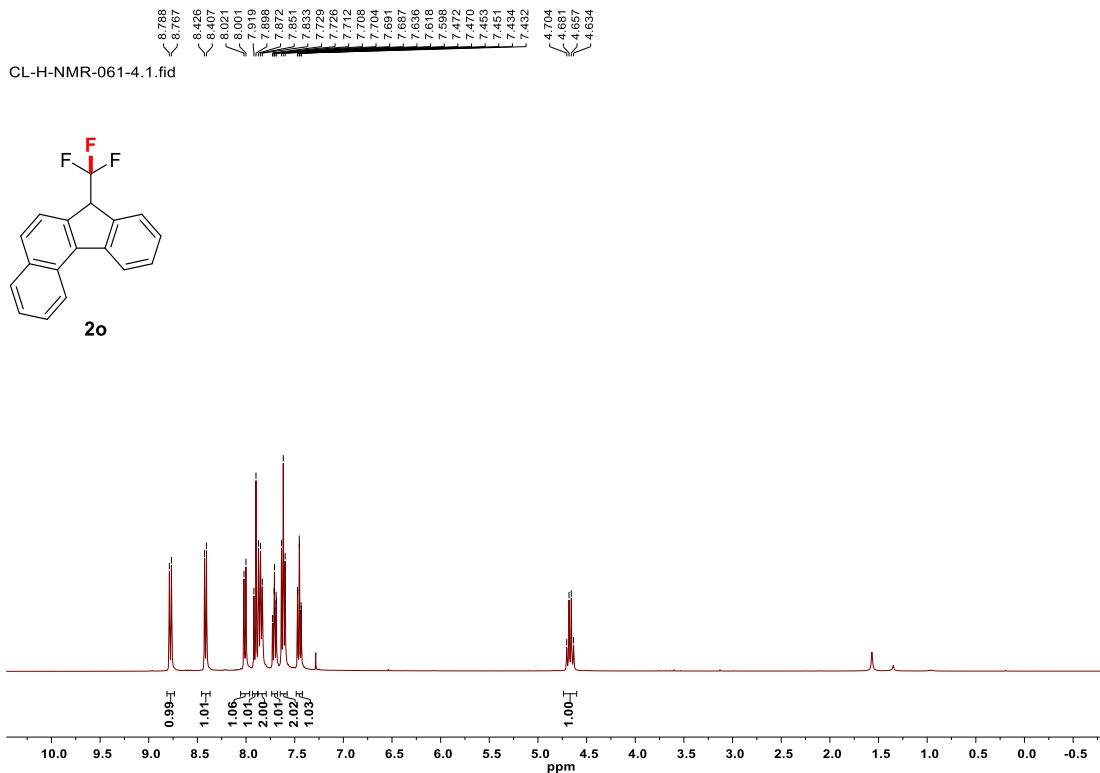


^{13}C NMR spectrum of **2n** (101 MHz, CDCl_3)

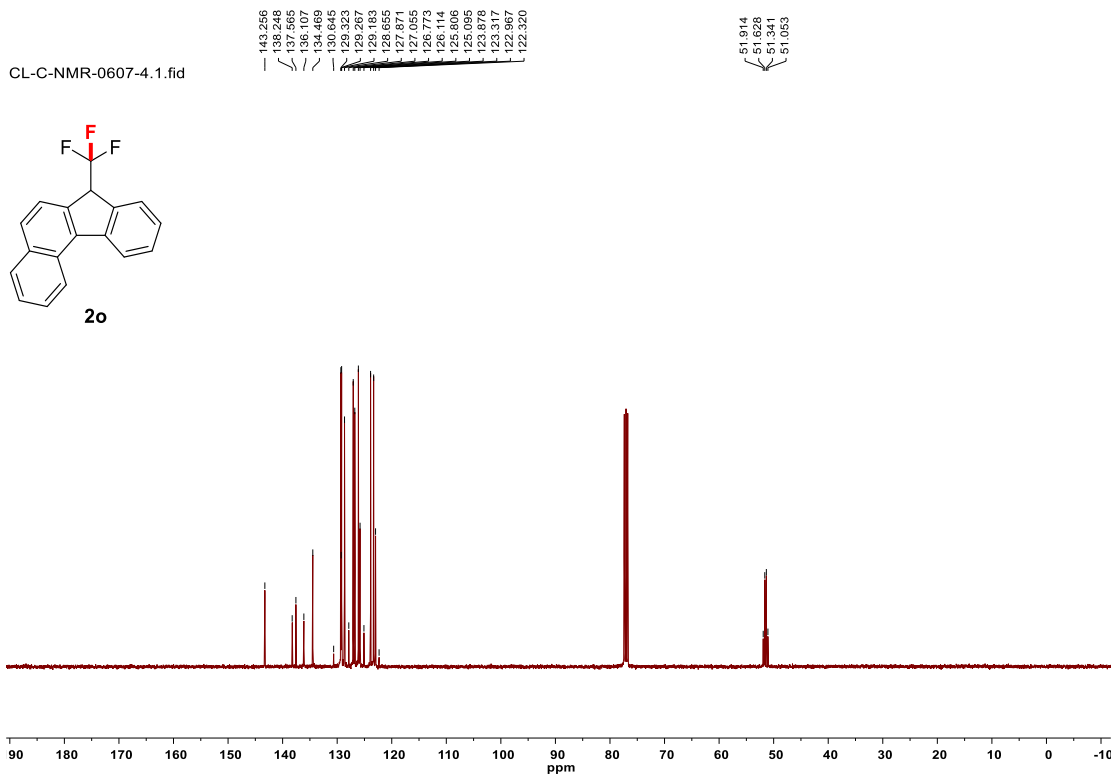
CL-0701-2.1.fid



^{19}F NMR spectrum of **2n** (376 MHz, CDCl_3)



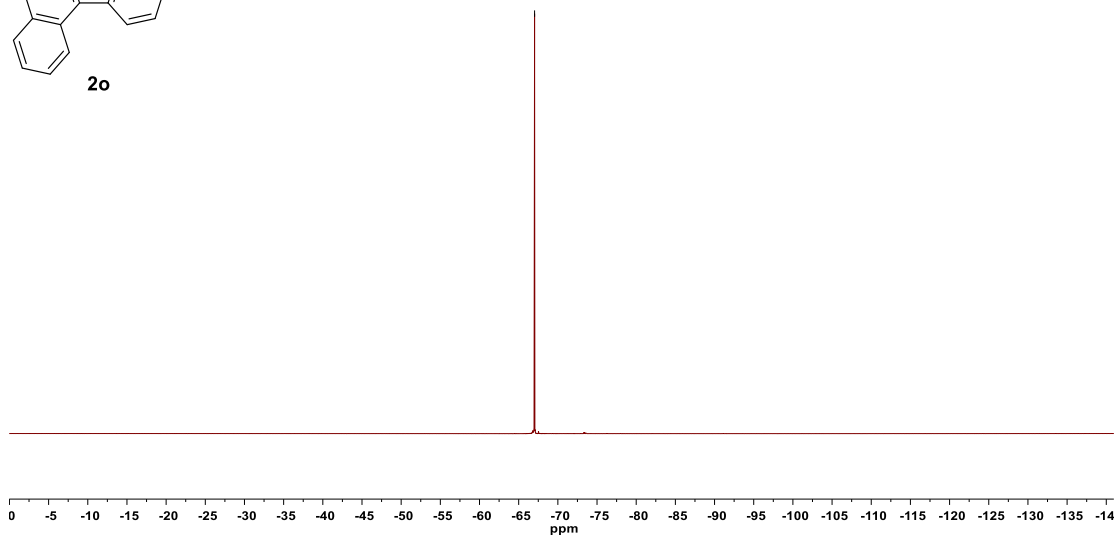
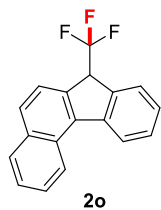
¹H NMR spectrum of **2o** (400 MHz, CDCl₃)



¹³C NMR spectrum of **2o** (101 MHz, CDCl₃)

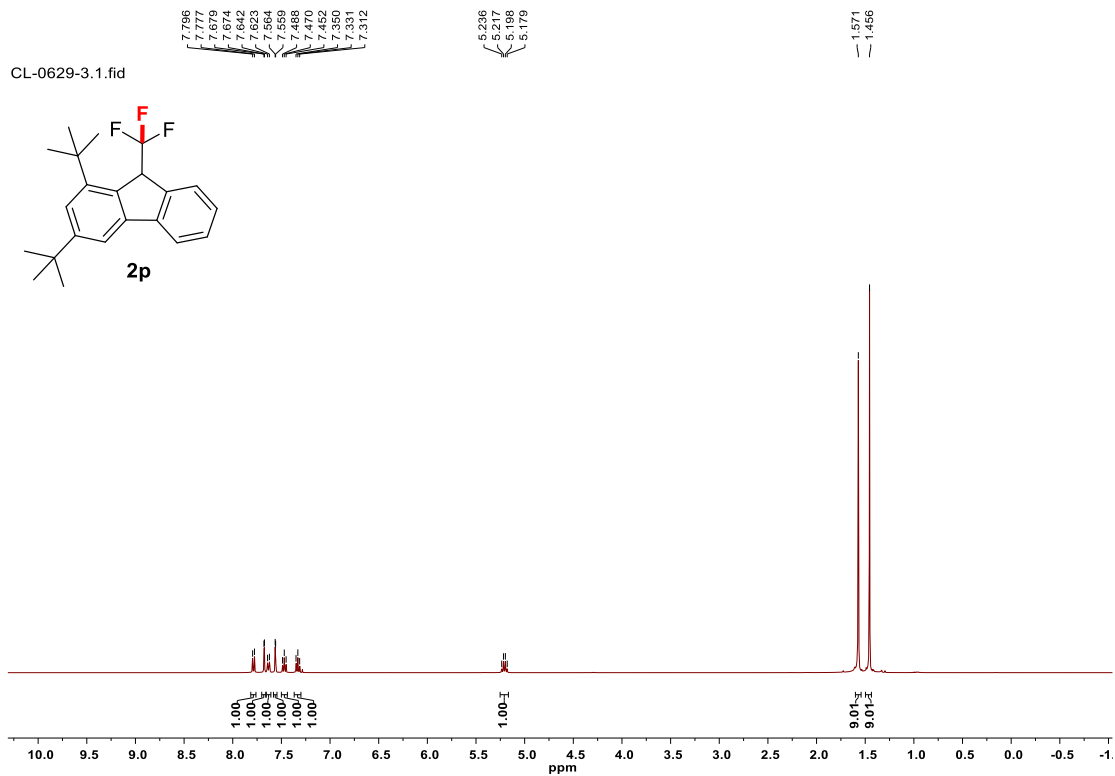
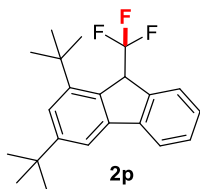
CL-C-NMR-0607-4.2.fid

— 67.029



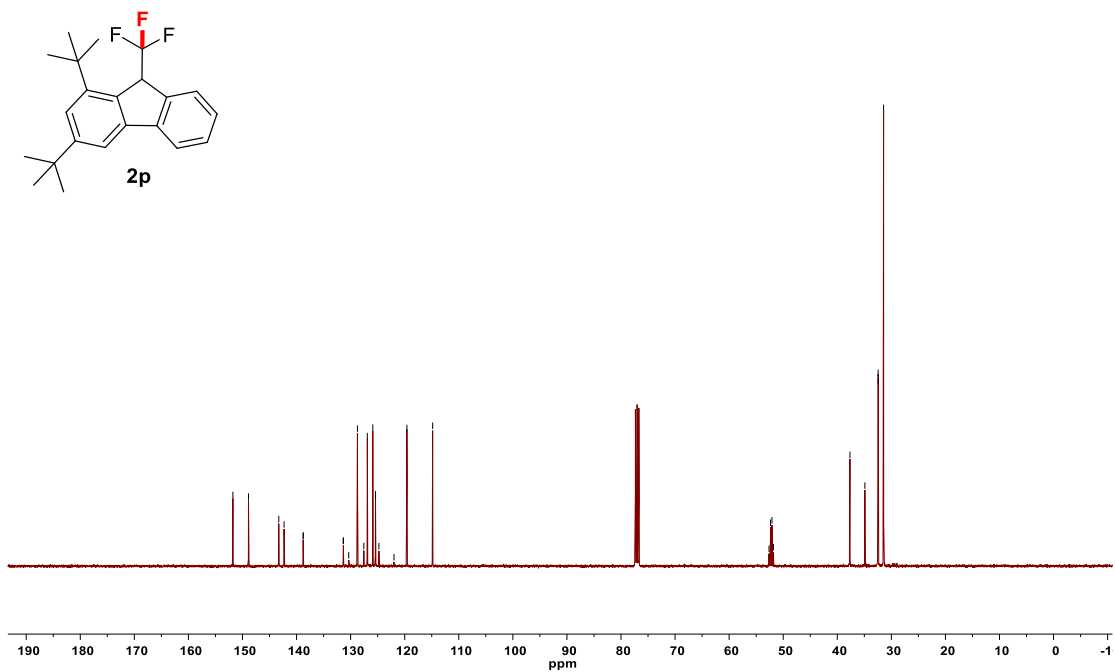
^{19}F NMR spectrum of **2o** (376 MHz, CDCl_3)

CL-0629-3.1.fid



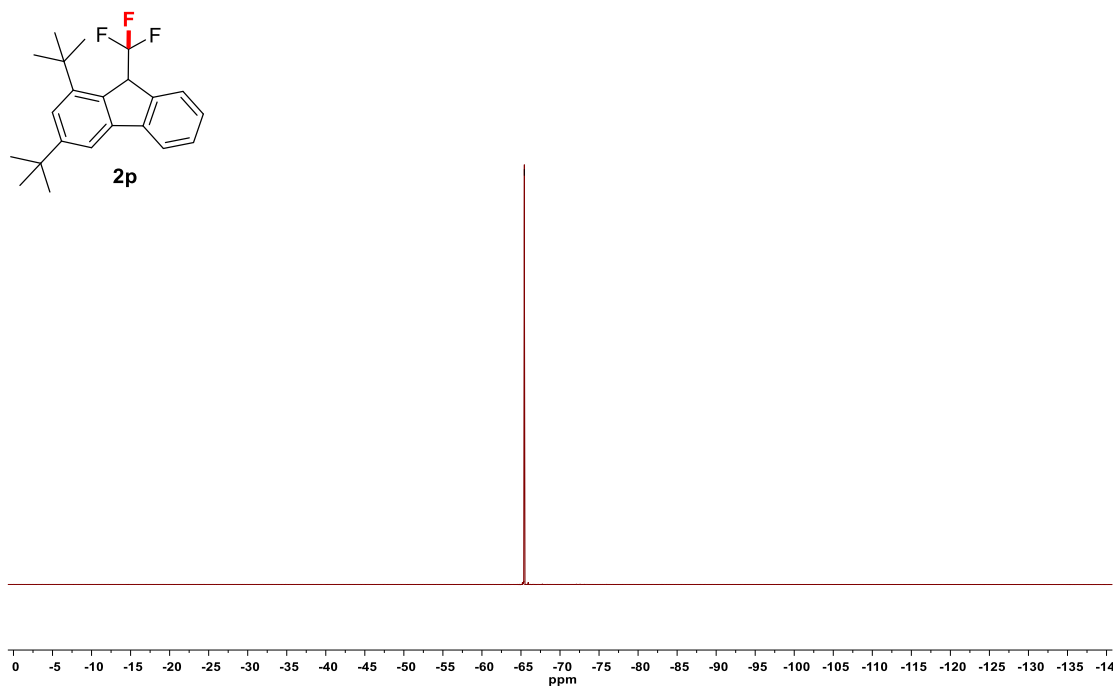
^1H NMR spectrum of **2p** (400 MHz, CDCl_3)

CL-0701-3.2.fid

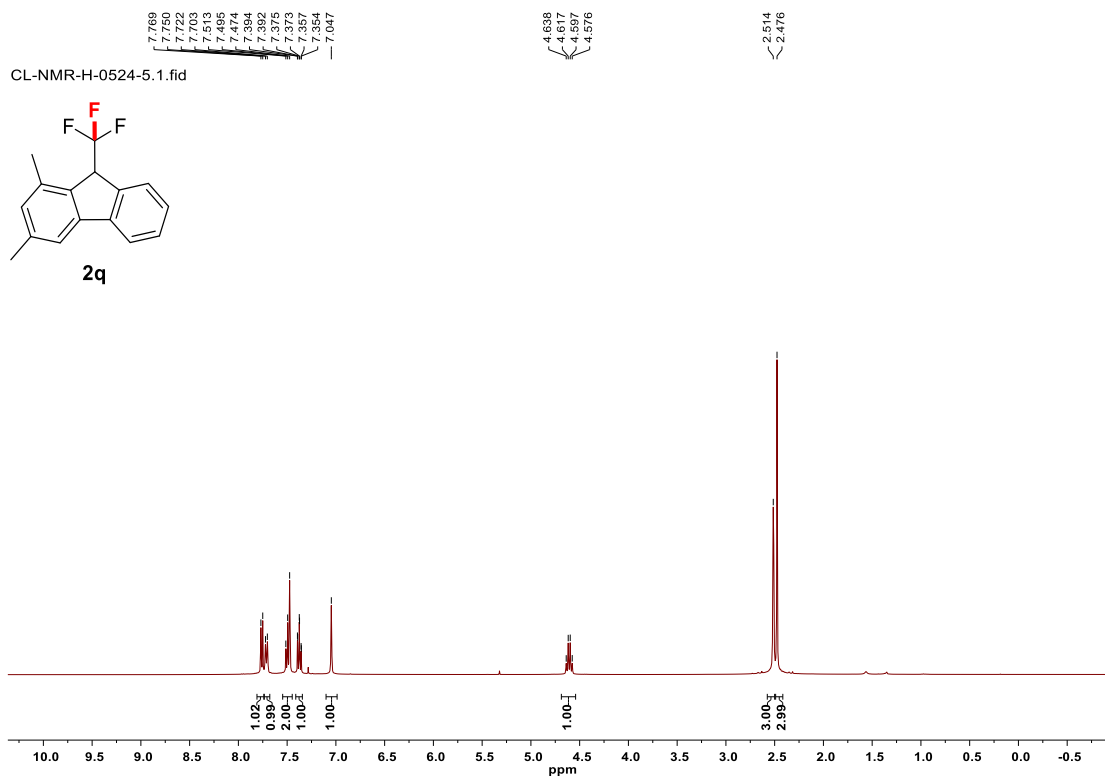


^{13}C NMR spectrum of **2p** (101 MHz, CDCl_3)

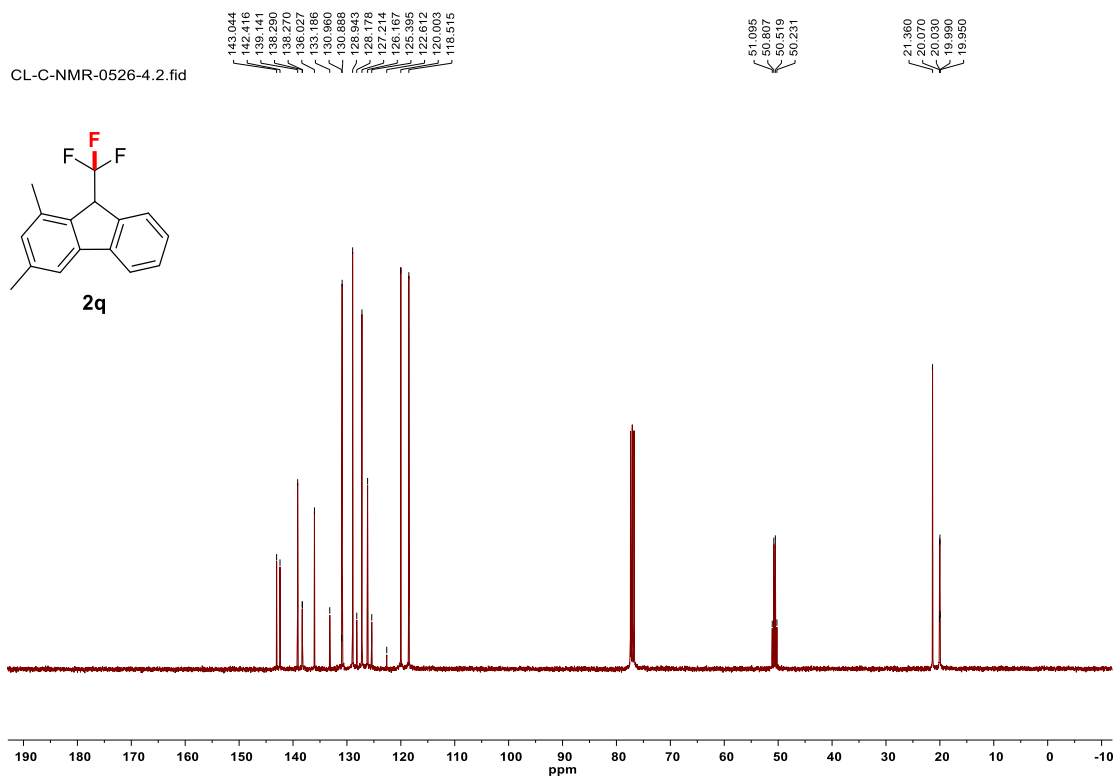
CL-0701-3.1.fid



^{19}F NMR spectrum of **2p** (376 MHz, CDCl_3)

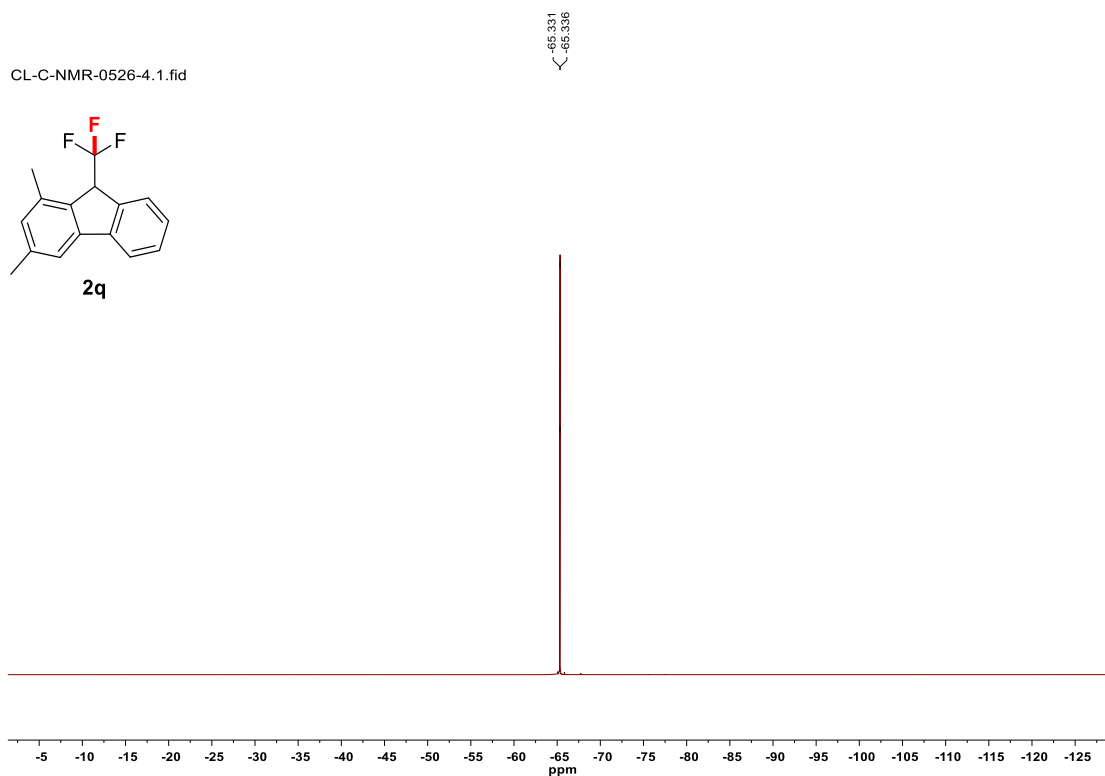
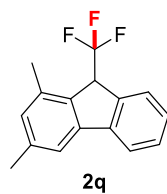


^1H NMR spectrum of **2q** (400 MHz, CDCl_3)



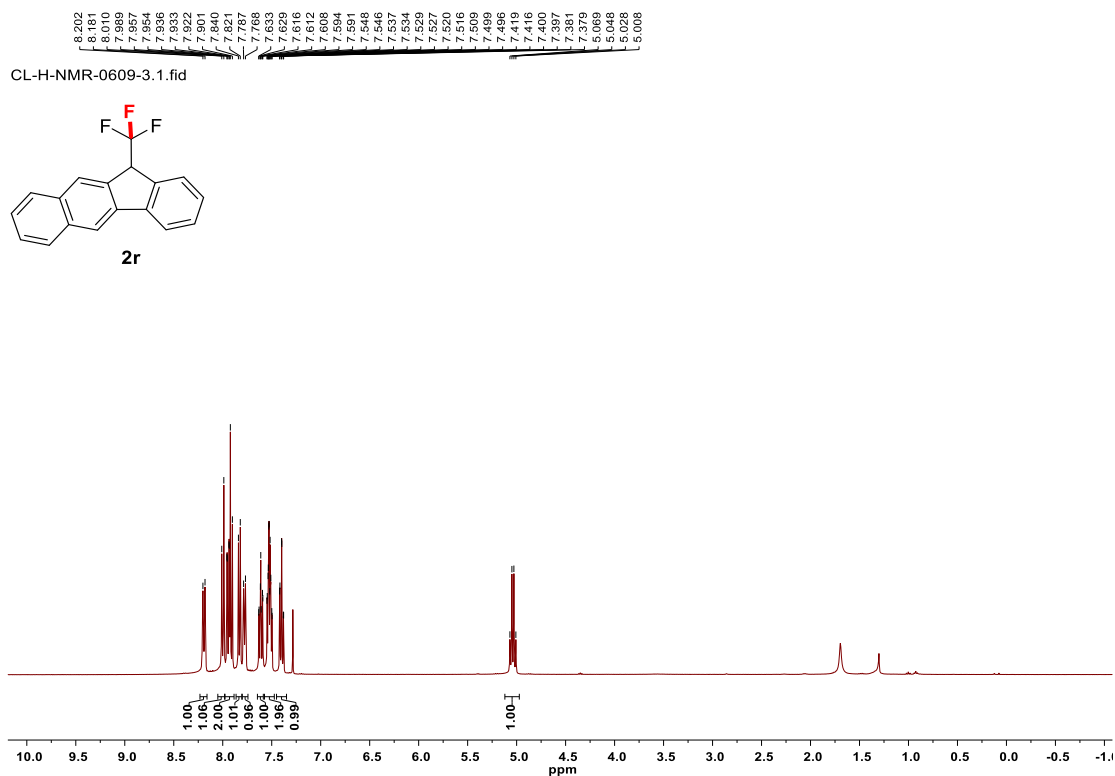
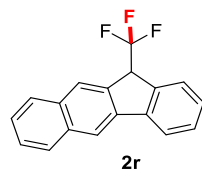
^{13}C NMR spectrum of **2q** (101 MHz, CDCl_3)

CL-C-NMR-0526-4.1.fid

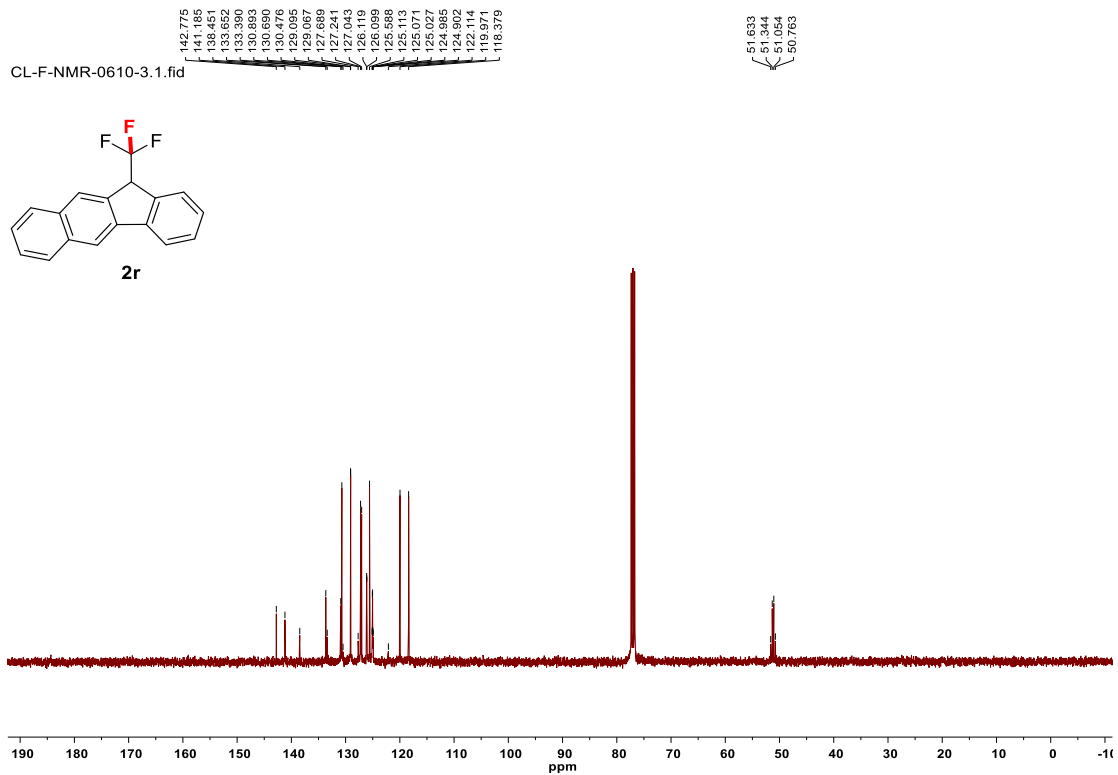


¹⁹F NMR spectrum of **2q** (376 MHz, CDCl₃)

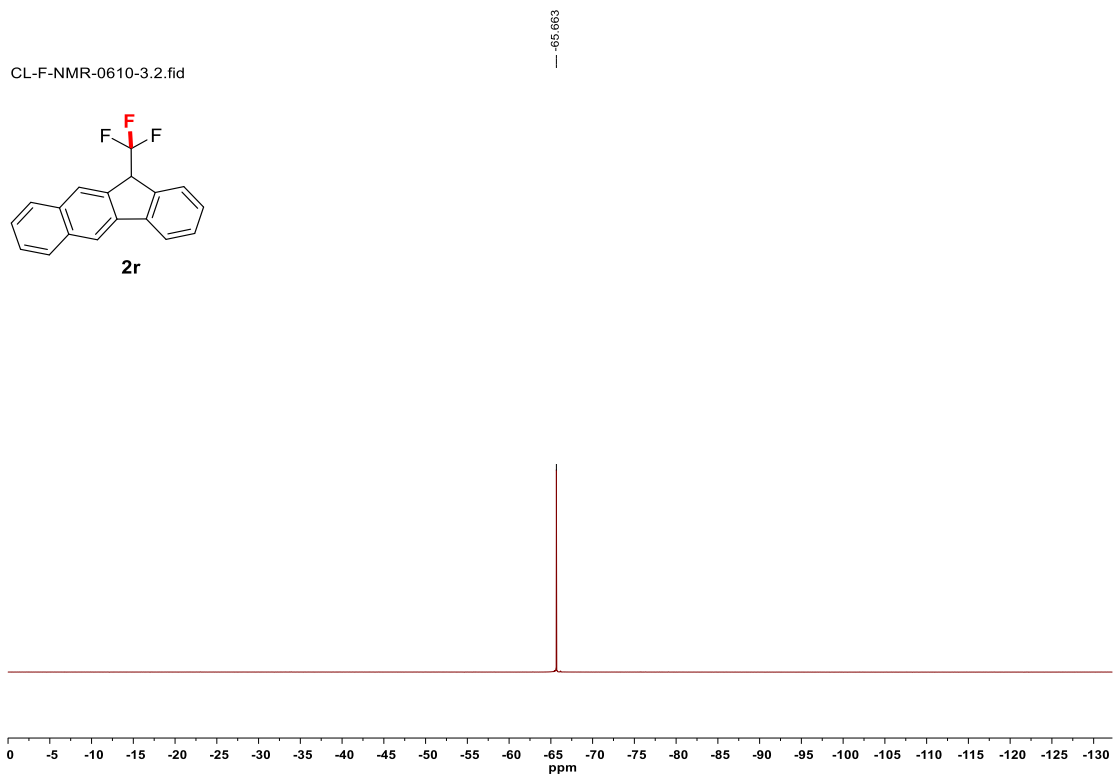
CL-H-NMR-0609-3.1.fid



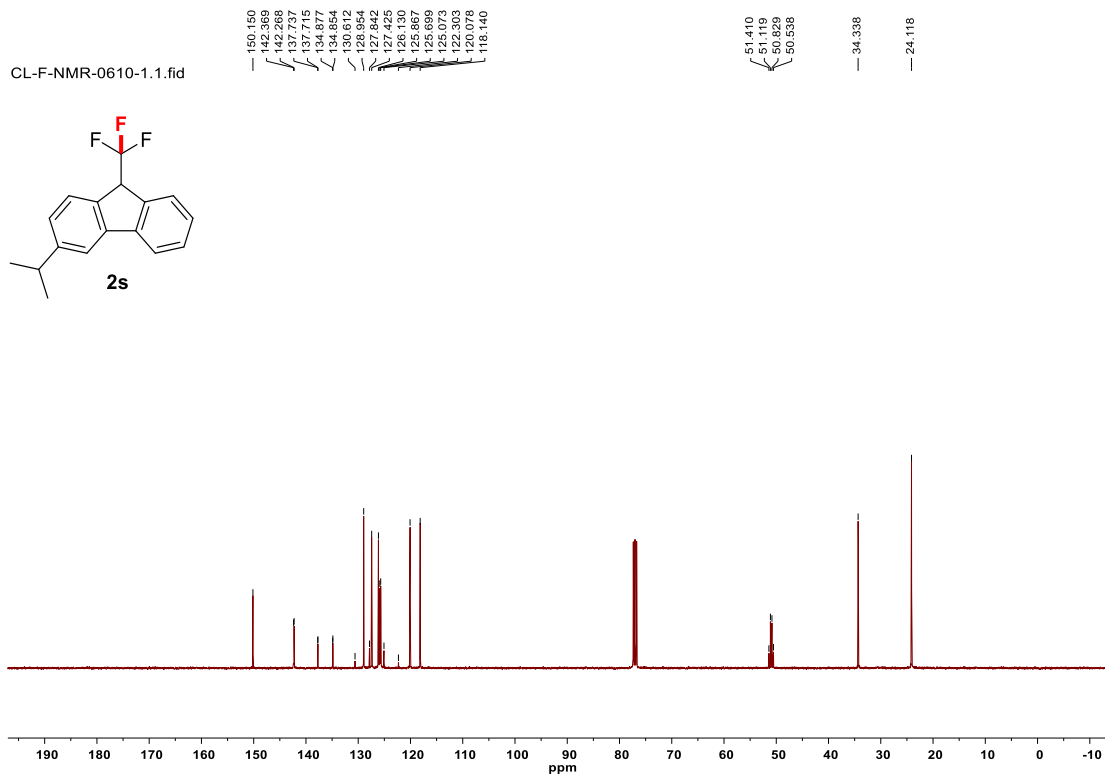
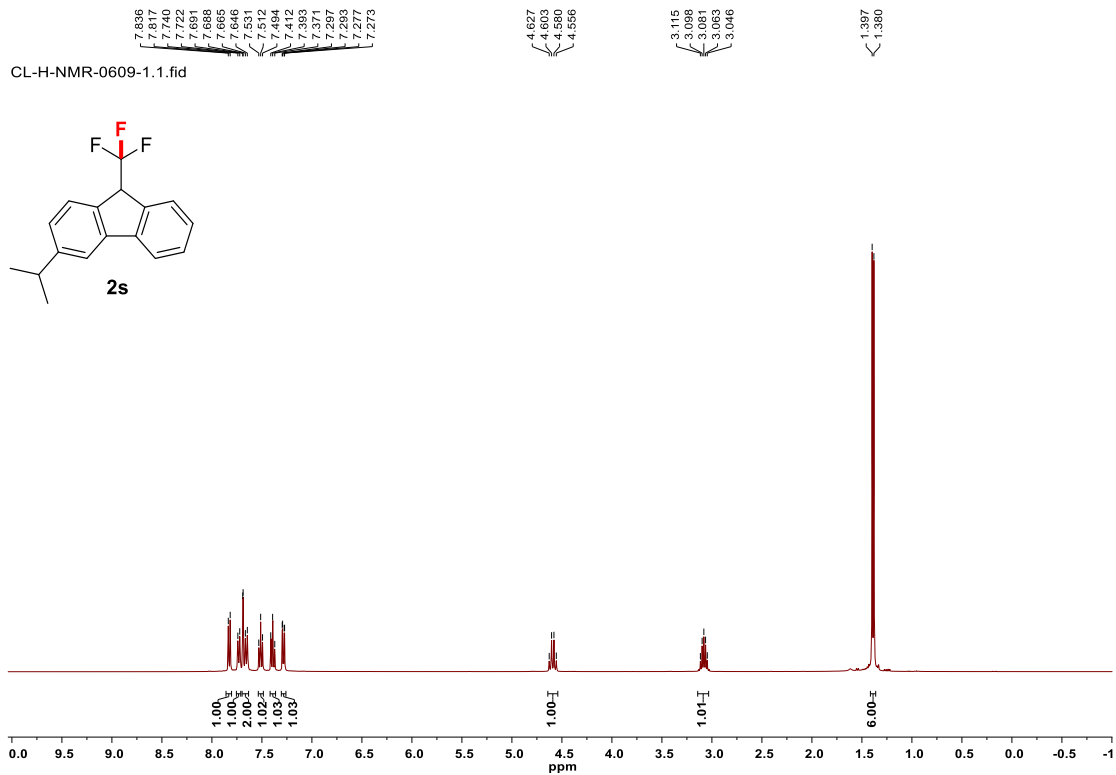
¹H NMR spectrum of **2r** (400 MHz, CDCl₃)



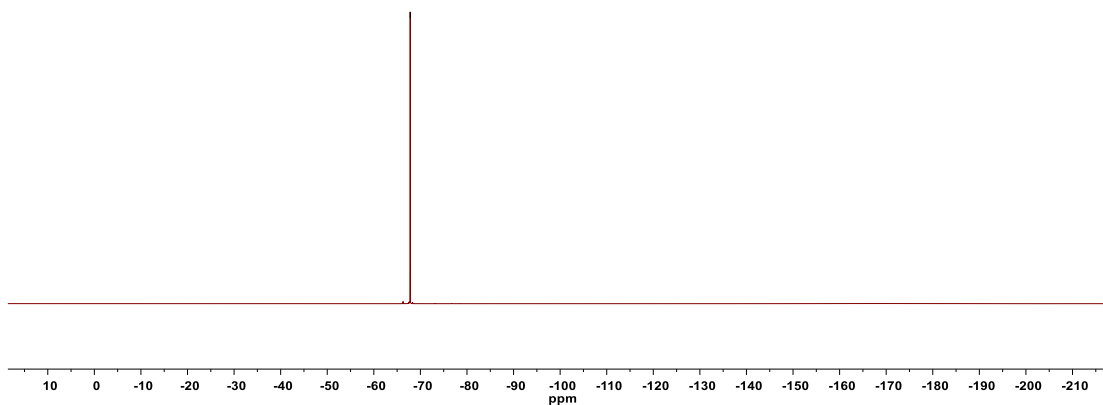
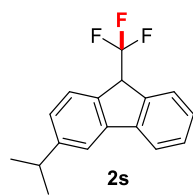
^{13}C NMR spectrum of **2r** (101 MHz, CDCl_3)



^{19}F NMR spectrum of **2r** (376 MHz, CDCl_3)

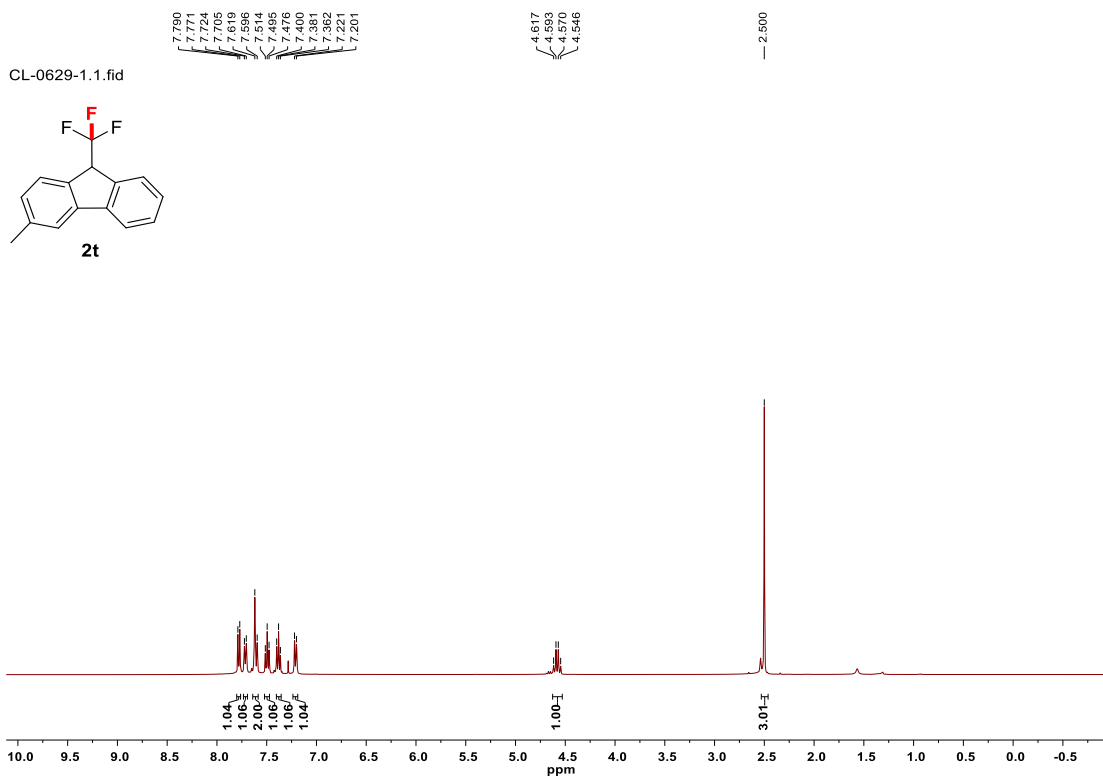
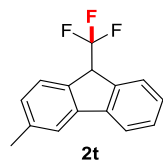


CL-F-NMR-0610-1.2.fid



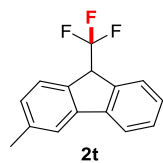
^{19}F NMR spectrum of **2s** (376 MHz, CDCl_3)

CL-0629-1.1.fid



^1H NMR spectrum of **2t** (400 MHz, CDCl_3)

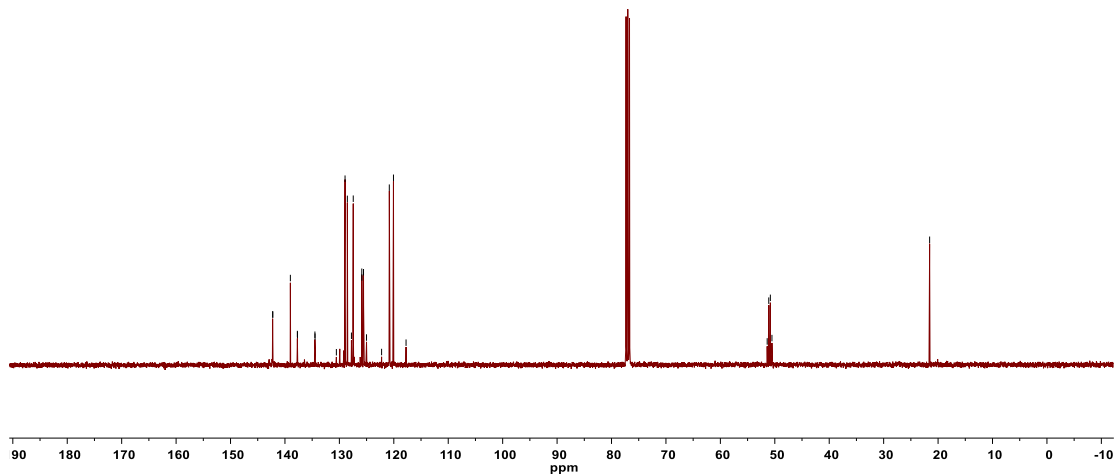
CL-0701-1.2.fid



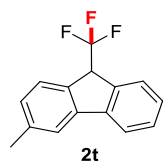
142.265
142.227
139.005
137.720
134.697
134.472
130.553
128.958
128.534
127.783
127.482
126.882
125.988
125.564
125.014
122.243
120.827
120.052
117.750

51.399
51.108
50.817
50.525

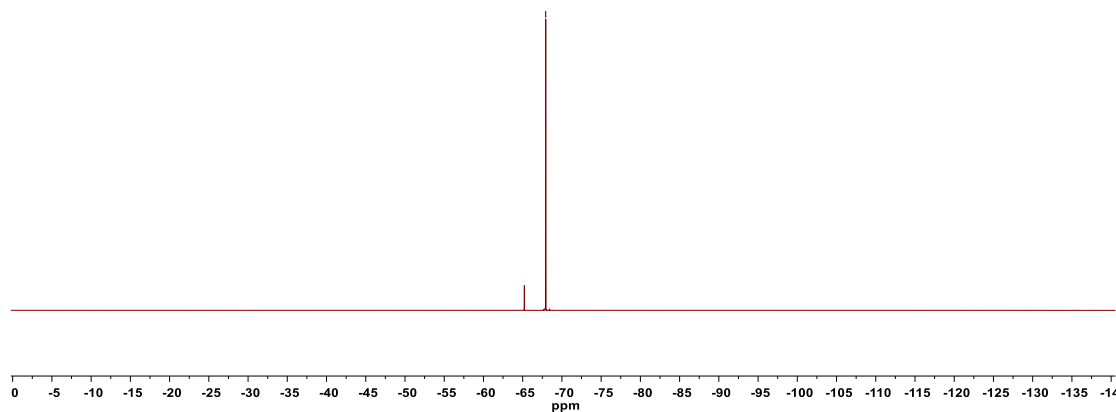
21.553



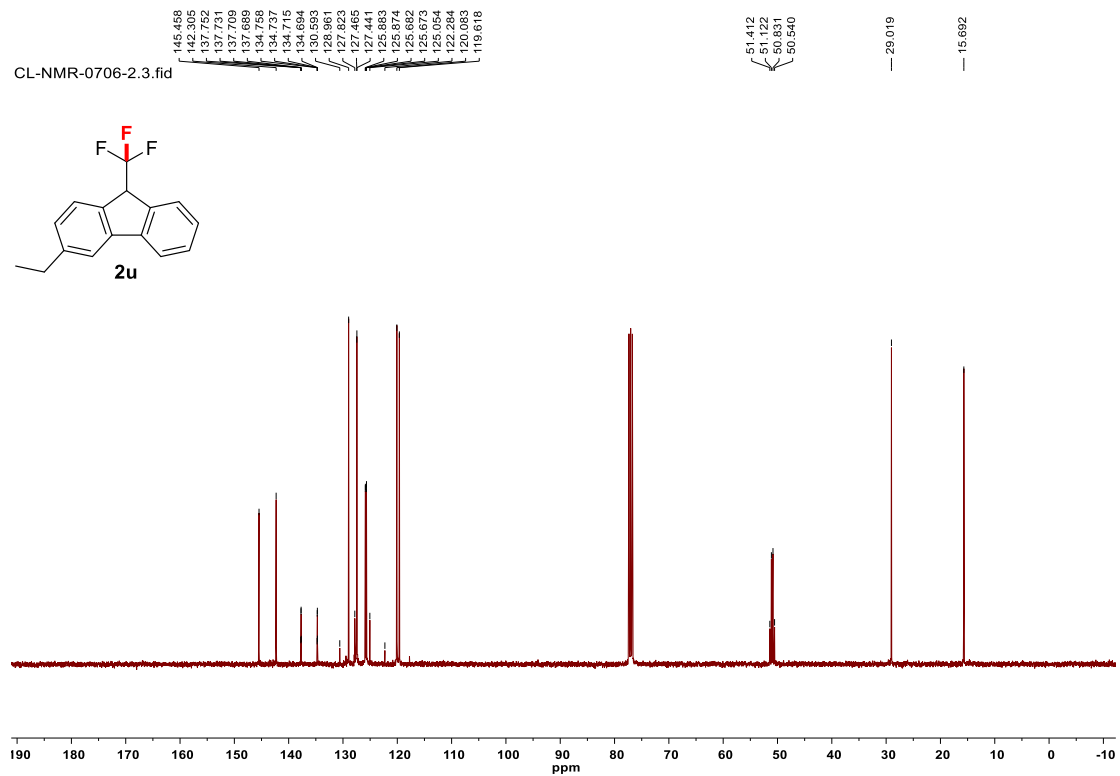
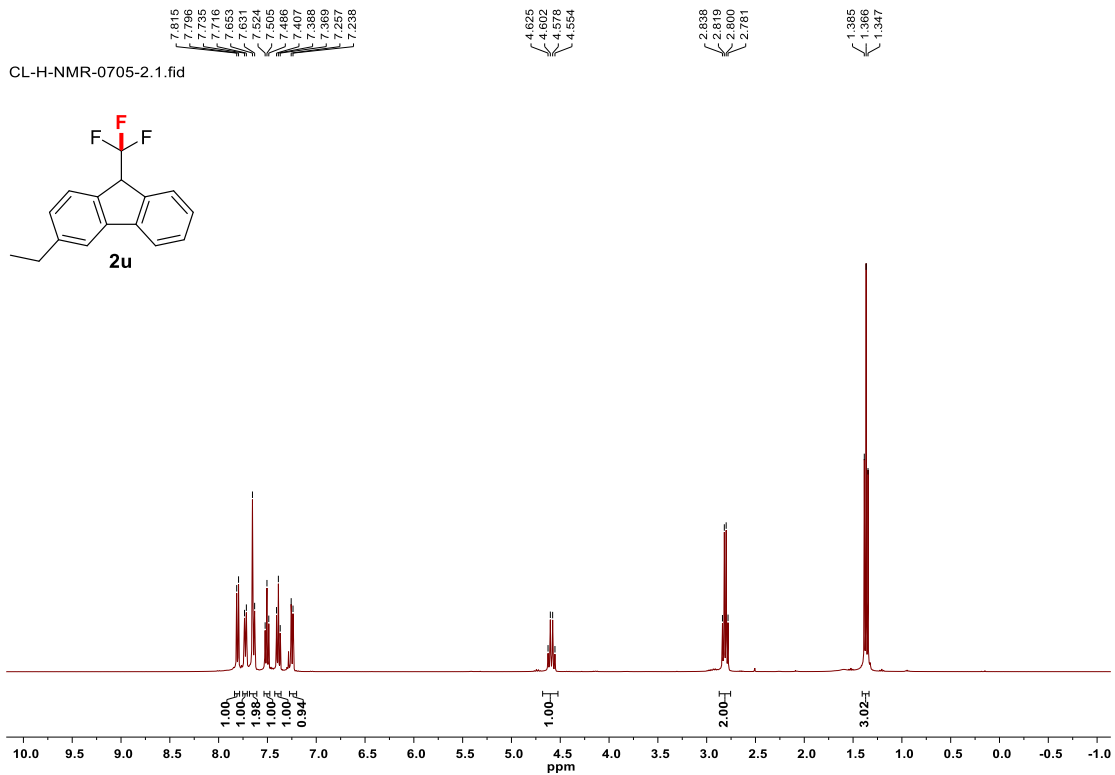
CL-0701-1.1.fid



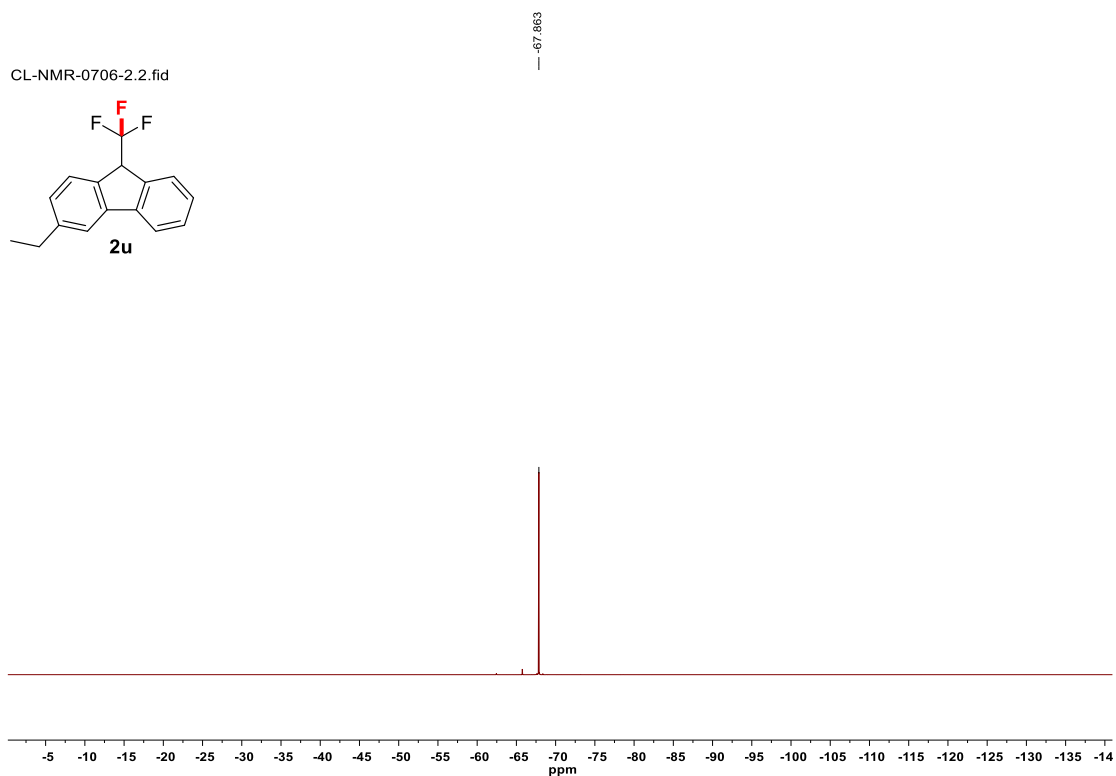
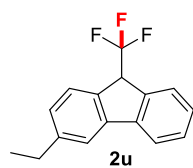
-67.936



^{19}F NMR spectrum of **2t** (376 MHz, CDCl_3)

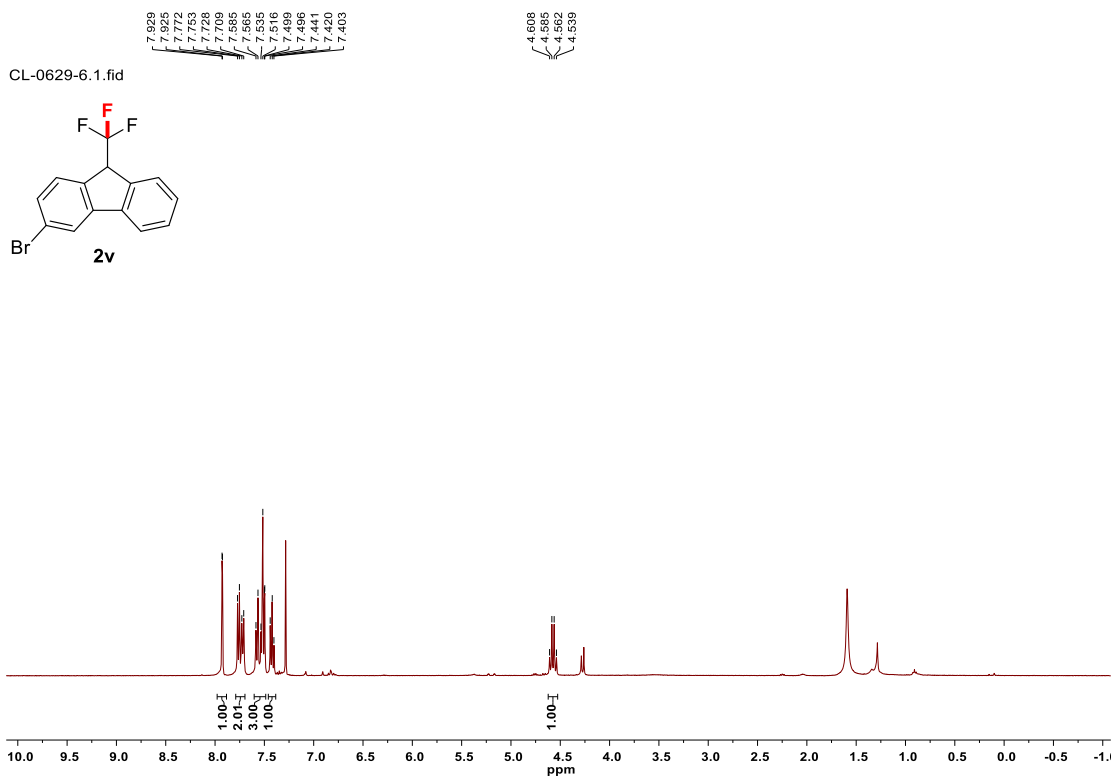
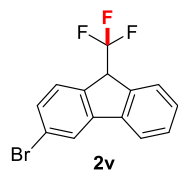


CL-NMR-0706-2.2.fid



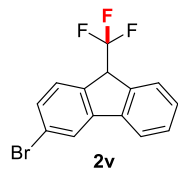
¹⁹F NMR spectrum of **2u** (376 MHz, CDCl₃)

CL-0629-6.1.fid



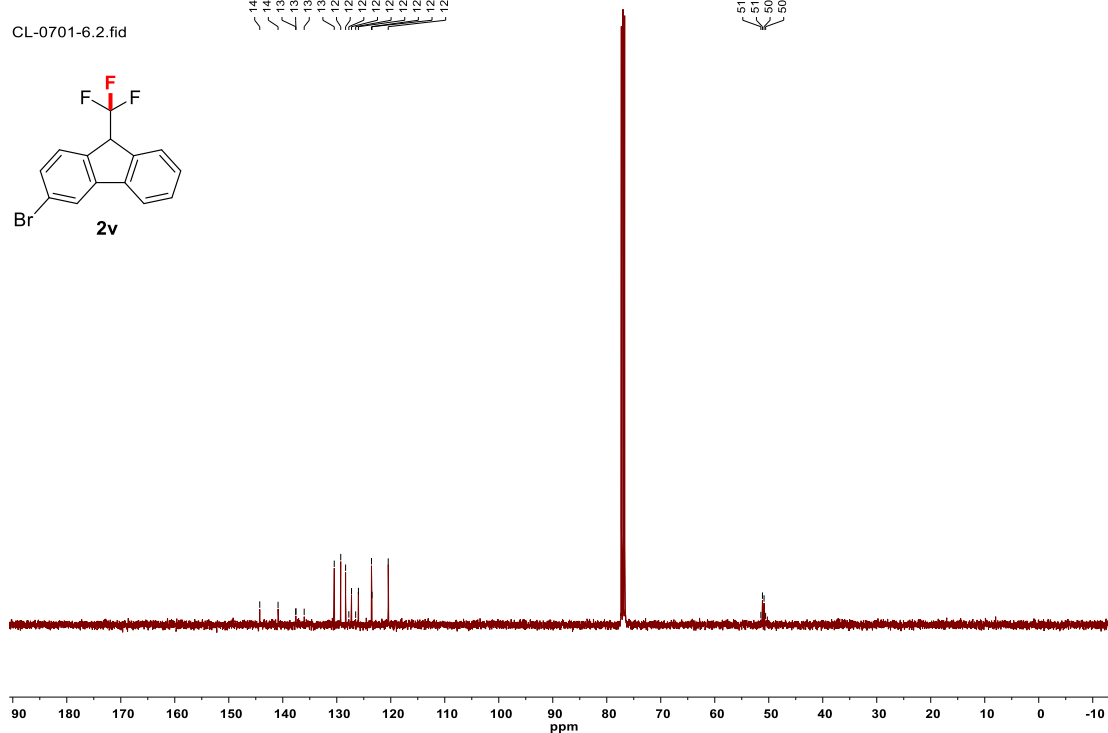
¹H NMR spectrum of **2v** (400 MHz, CDCl₃)

CL-0701-6.2.fid



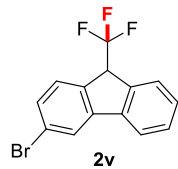
144.263
140.874
137.990
136.700
136.033
130.468
129.266
128.365
127.767
127.267
125.985
125.985
123.571
123.478
120.472

51.461
50.872
50.872
50.577

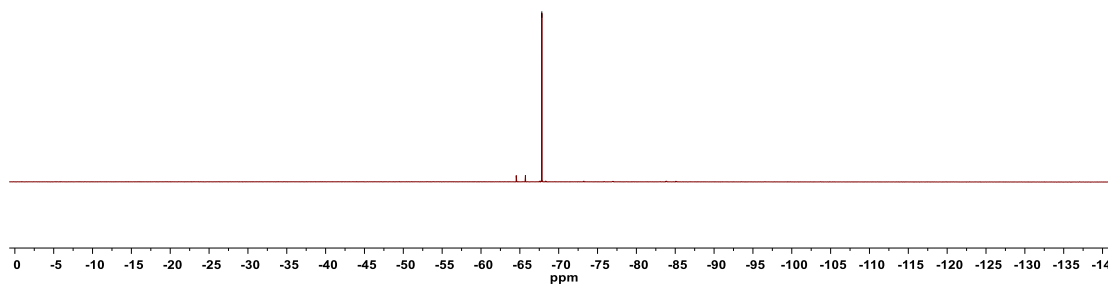


¹³C NMR spectrum of **2v** (101 MHz, CDCl₃)

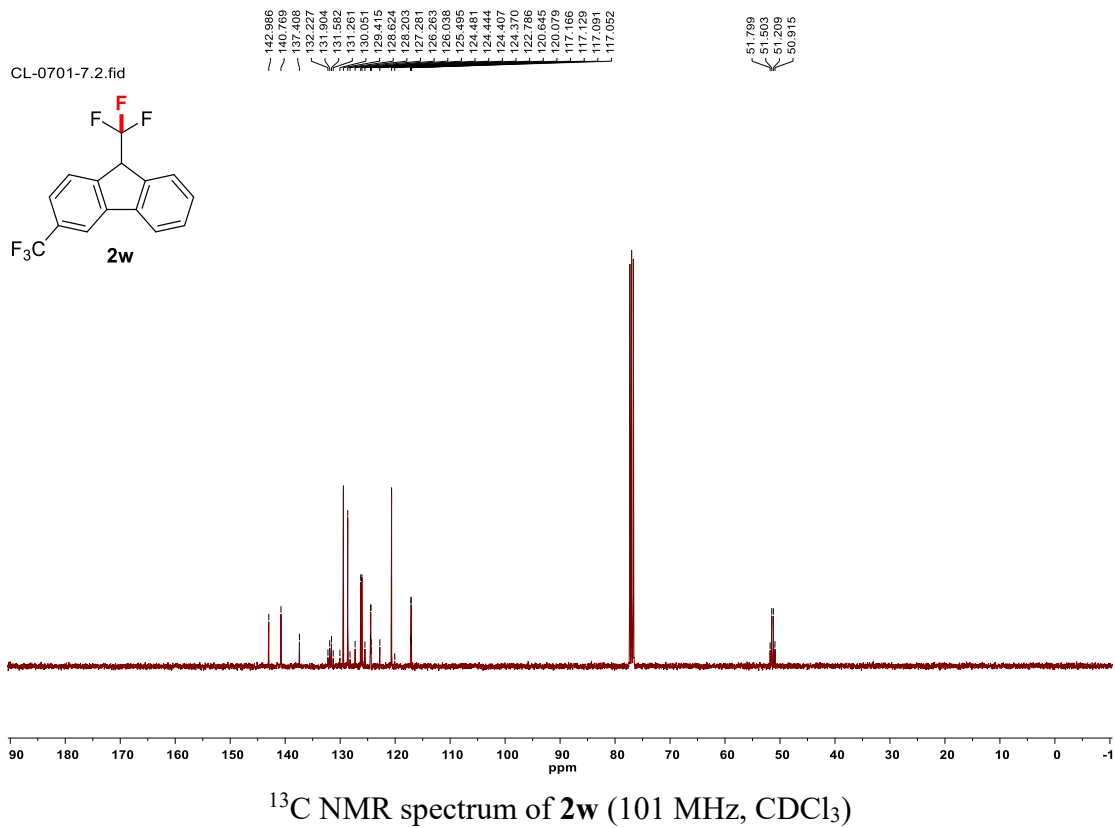
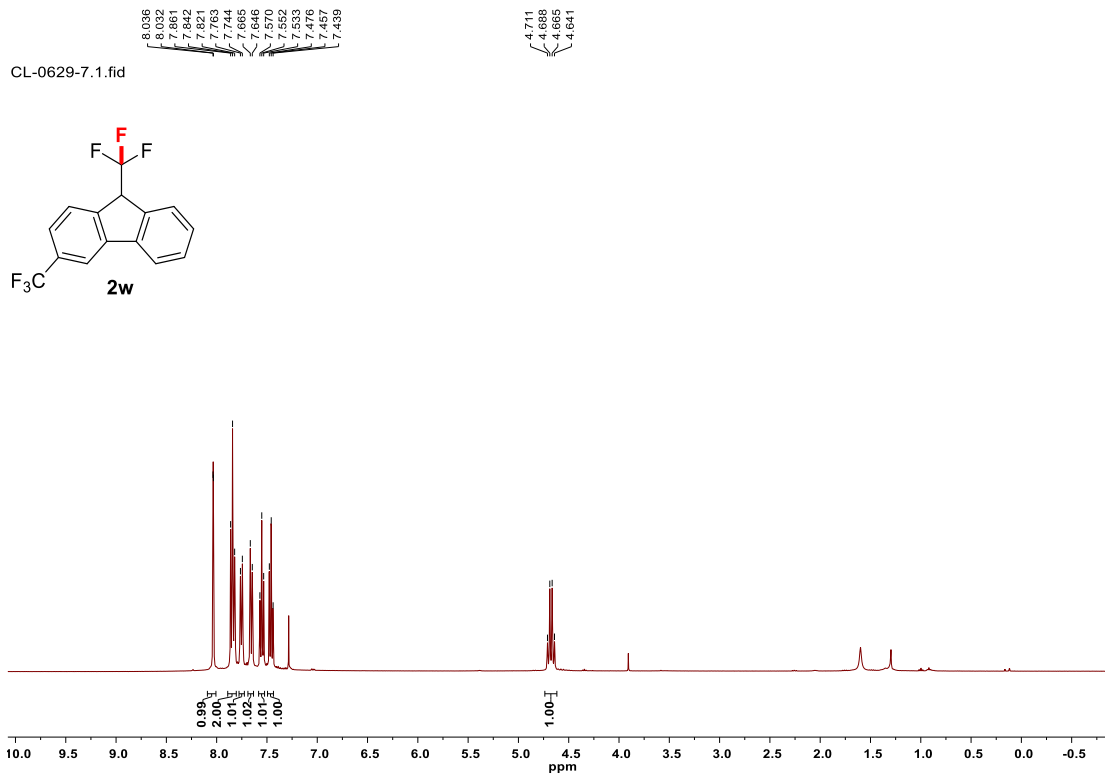
CL-0701-6.1.fid



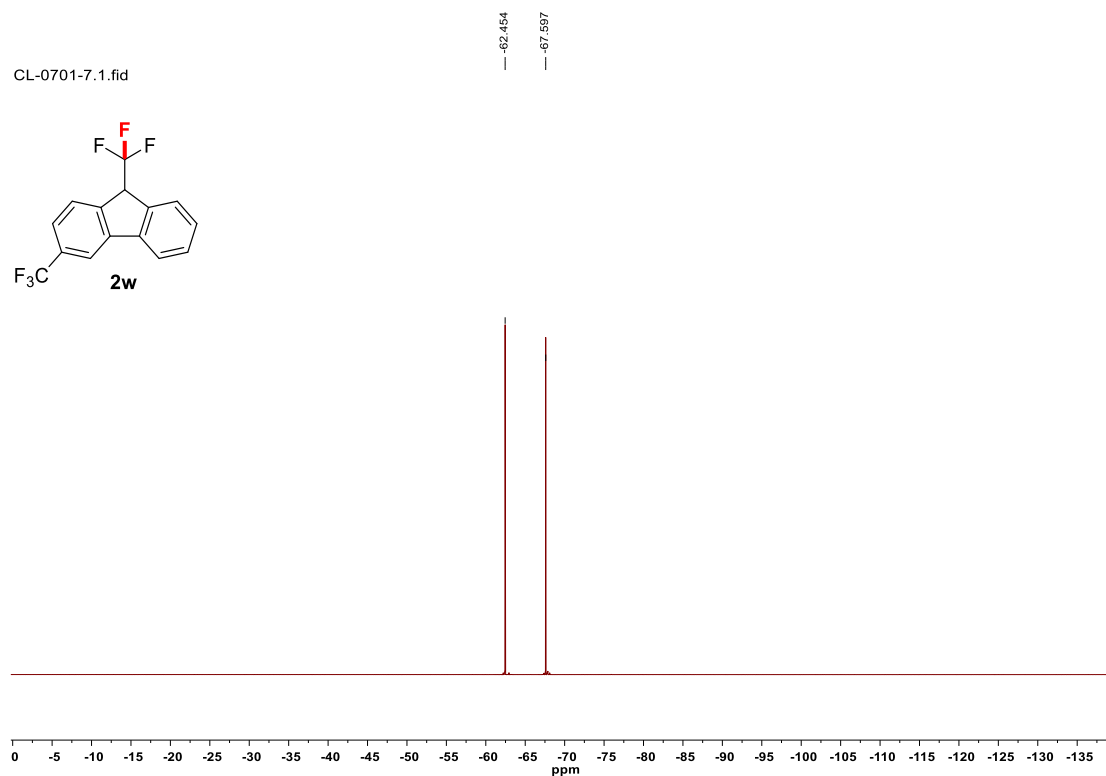
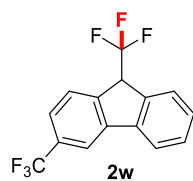
-67.828



¹⁹F NMR spectrum of **2v** (376 MHz, CDCl₃)

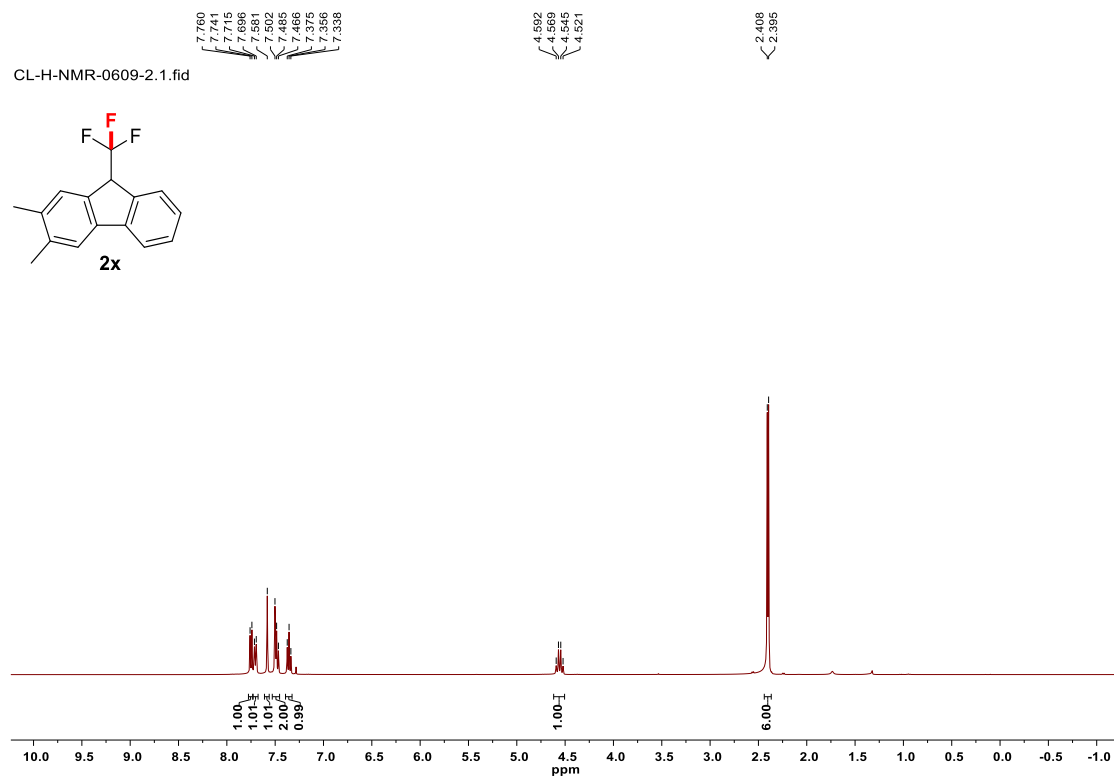
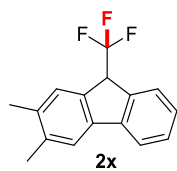


CL-0701-7.1.fid



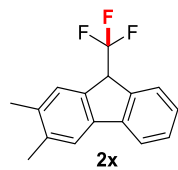
^{19}F NMR spectrum of **2w** (376 MHz, CDCl_3)

CL-H-NMR-0609-2.1.fid



^1H NMR spectrum of **2x** (400 MHz, CDCl_3)

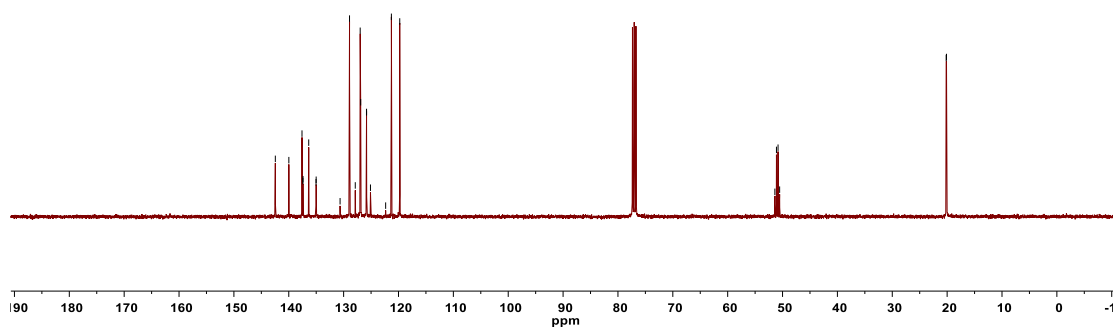
CL-F-NMR-0610-2.1.fid



142.448
139.984
137.597
137.429
136.364
135.028
130.848
128.926
127.878
126.881
126.894
125.835
125.100
122.340
121.293
119.773

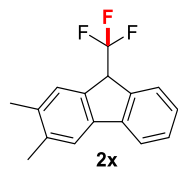
51.368
51.188
50.820
50.530

20.175
20.117

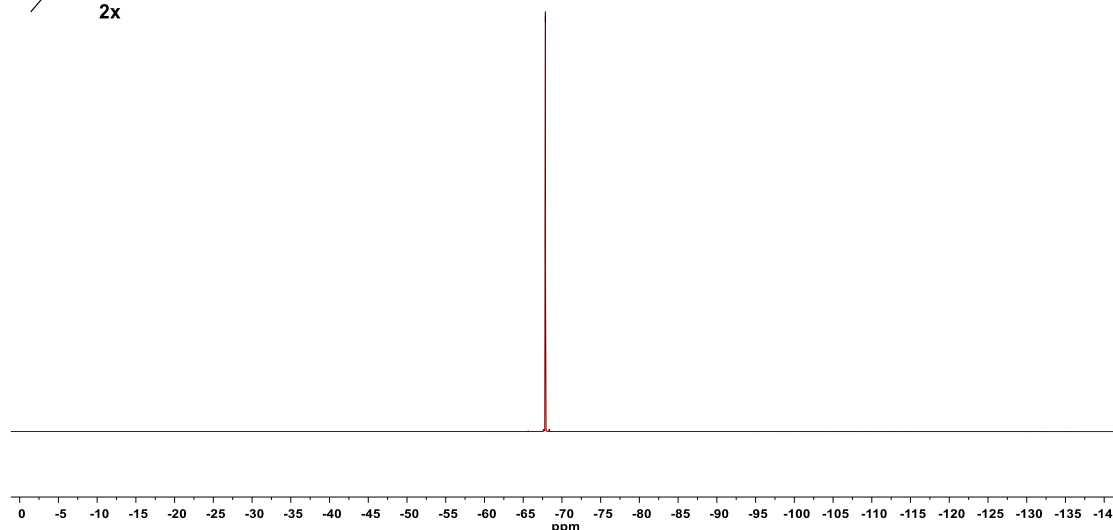


^{13}C NMR spectrum of **2x** (101 MHz, CDCl_3)

CL-F-NMR-0610-2.2.fid

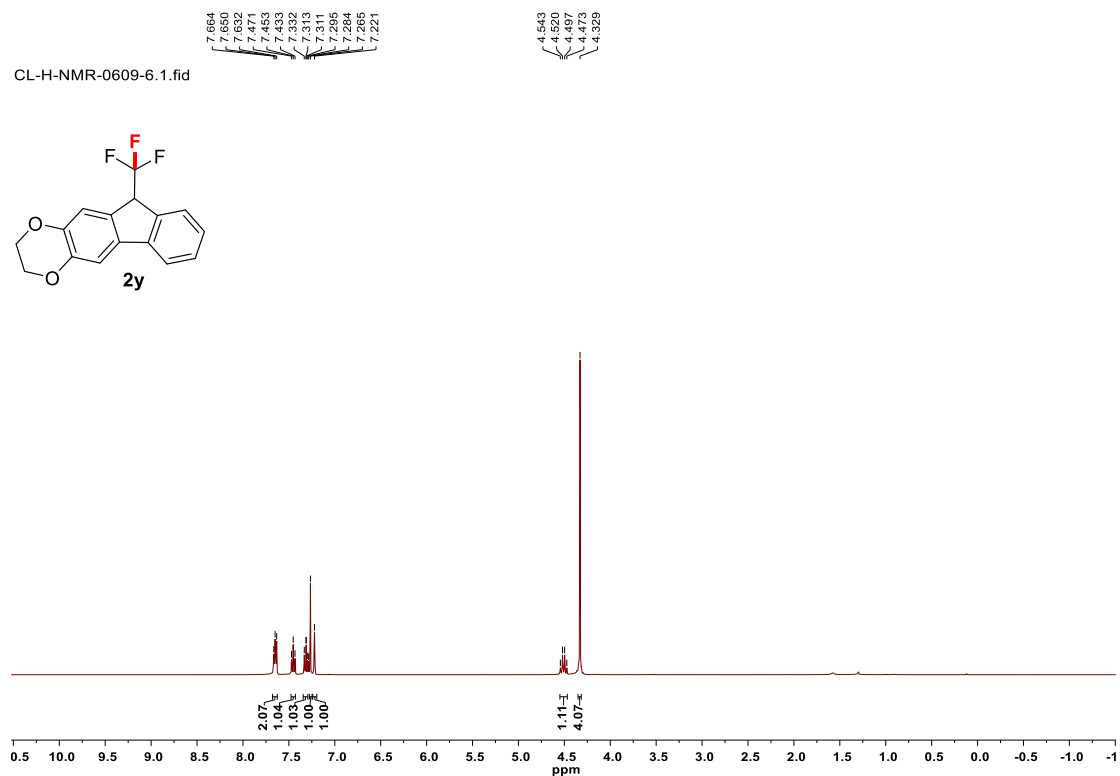
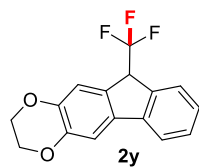


-67.865



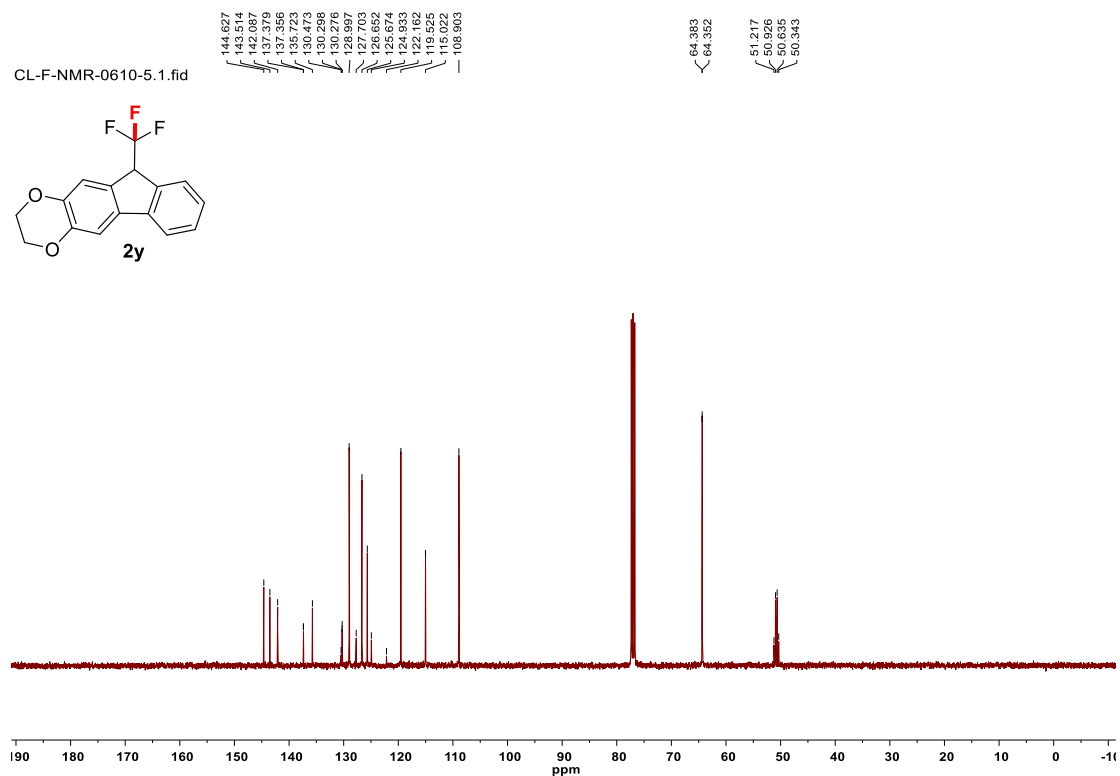
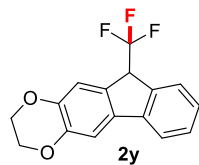
^{19}F NMR spectrum of **2x** (376 MHz, CDCl_3)

CL-H-NMR-0609-6.1.fid



¹H NMR spectrum of **2y** (400 MHz, CDCl₃)

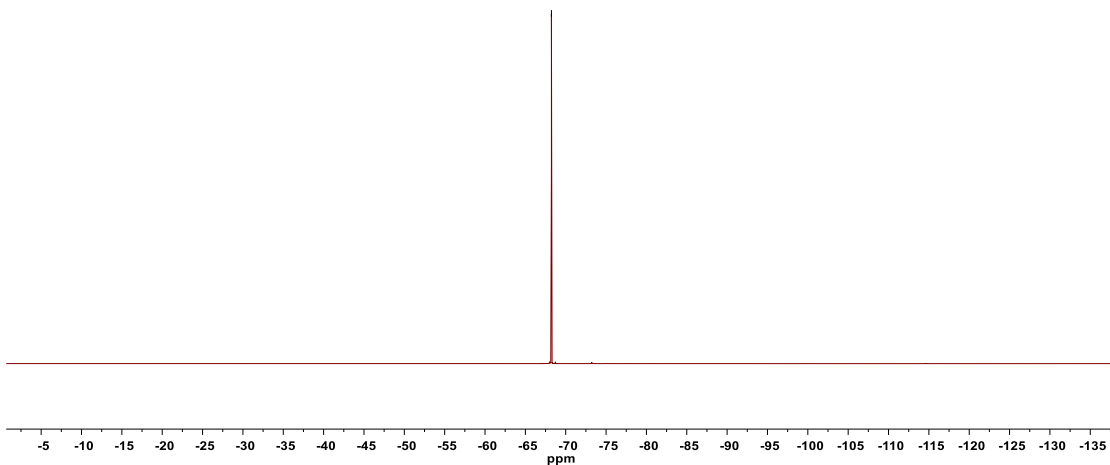
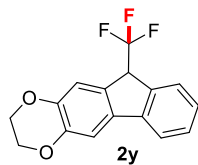
CL-F-NMR-0610-5.1.fid



¹³C NMR spectrum of **2y** (101 MHz, CDCl₃)

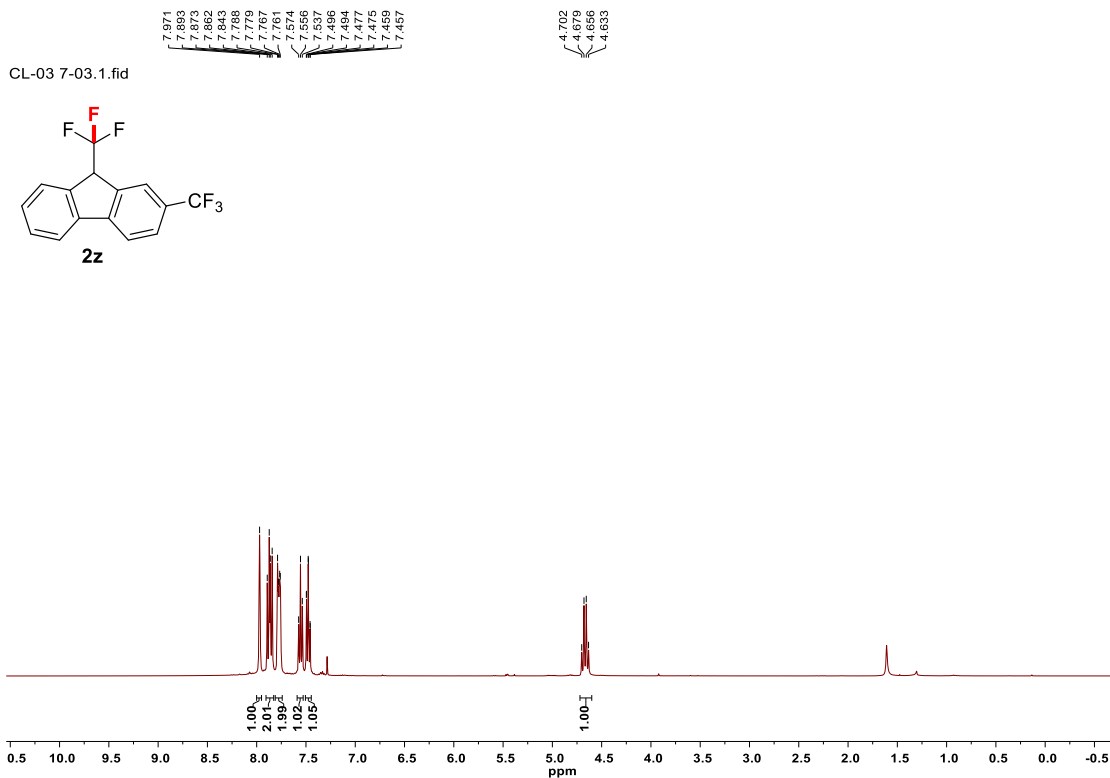
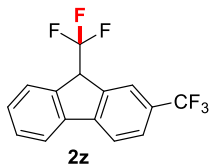
CL-F-NMR-0610-5.2.fid

--68.229



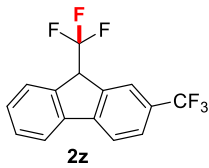
^{19}F NMR spectrum of **2y** (376 MHz, CDCl_3)

CL-03 7-03.1.fid



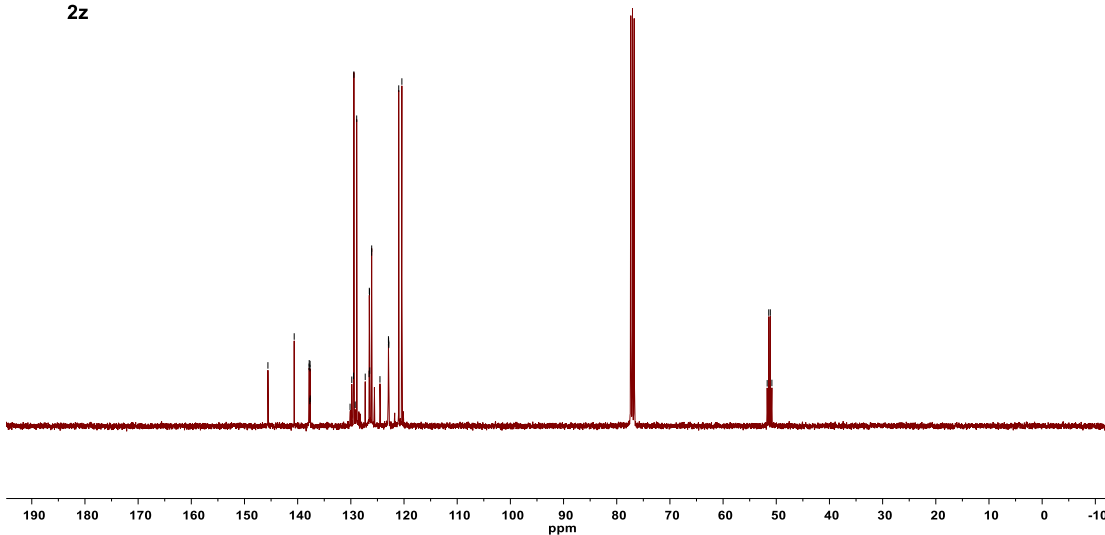
^1H NMR spectrum of **2z** (400 MHz, CDCl_3)

CL-03 7-03.3.fid



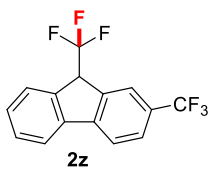
145.593
140.652
137.851
137.831
137.713
137.691
137.668
137.646
130.146
129.924
129.502
129.427
129.180
128.902
128.879
126.564
126.526
126.488
126.449
126.095
126.080
125.524
122.928
122.925
122.903
122.891
122.864
120.994
120.403

51.709
51.414
51.119
50.824

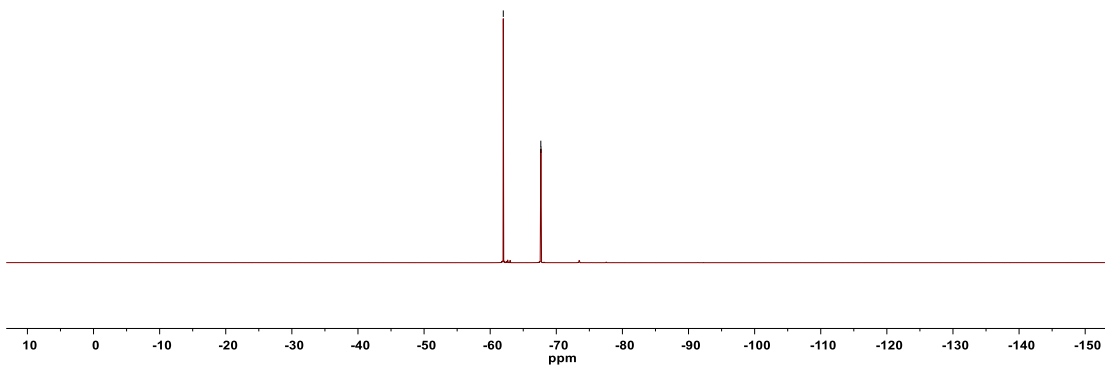


^{13}C NMR spectrum of **2z** (101 MHz, CDCl_3)

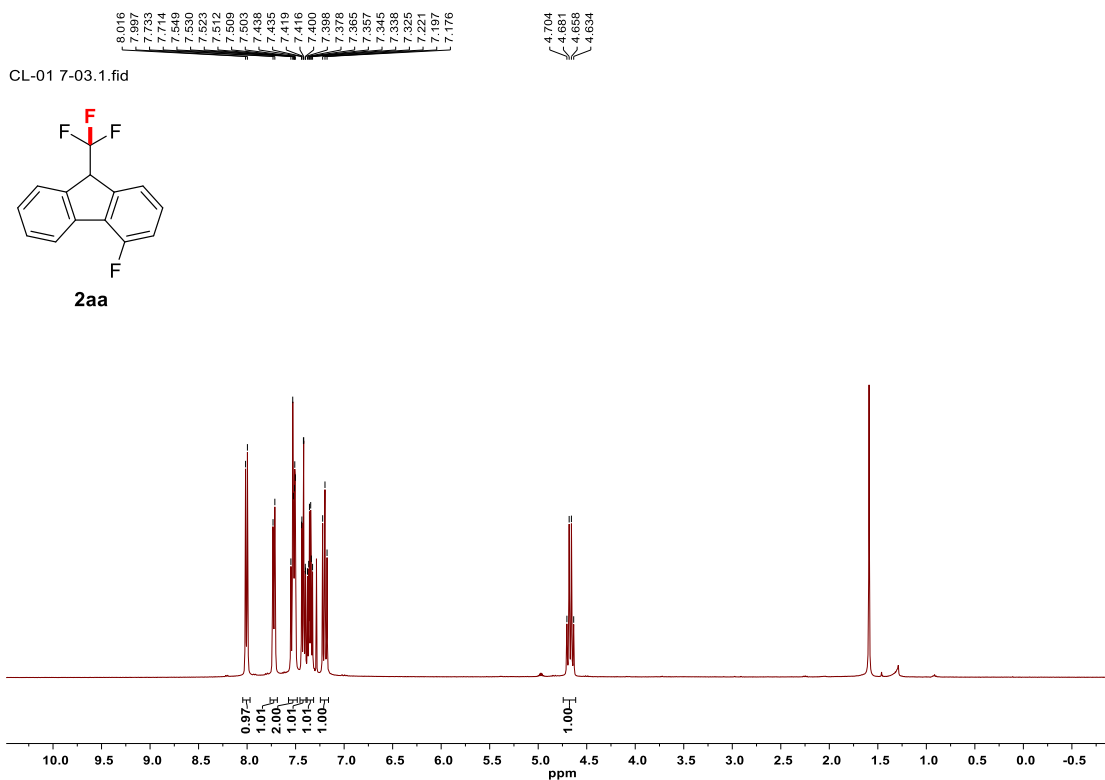
CL-03 7-03.2.fid



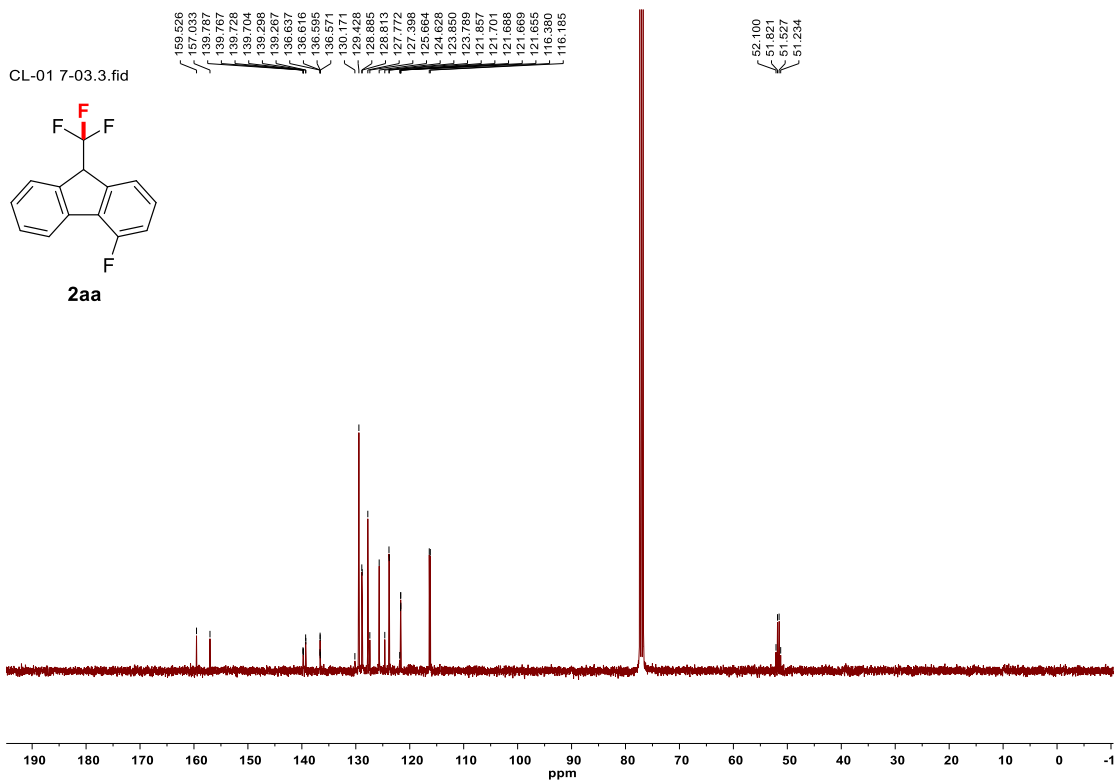
-61.981
-67.657
-67.662



^{19}F NMR spectrum of **2z** (376 MHz, CDCl_3)

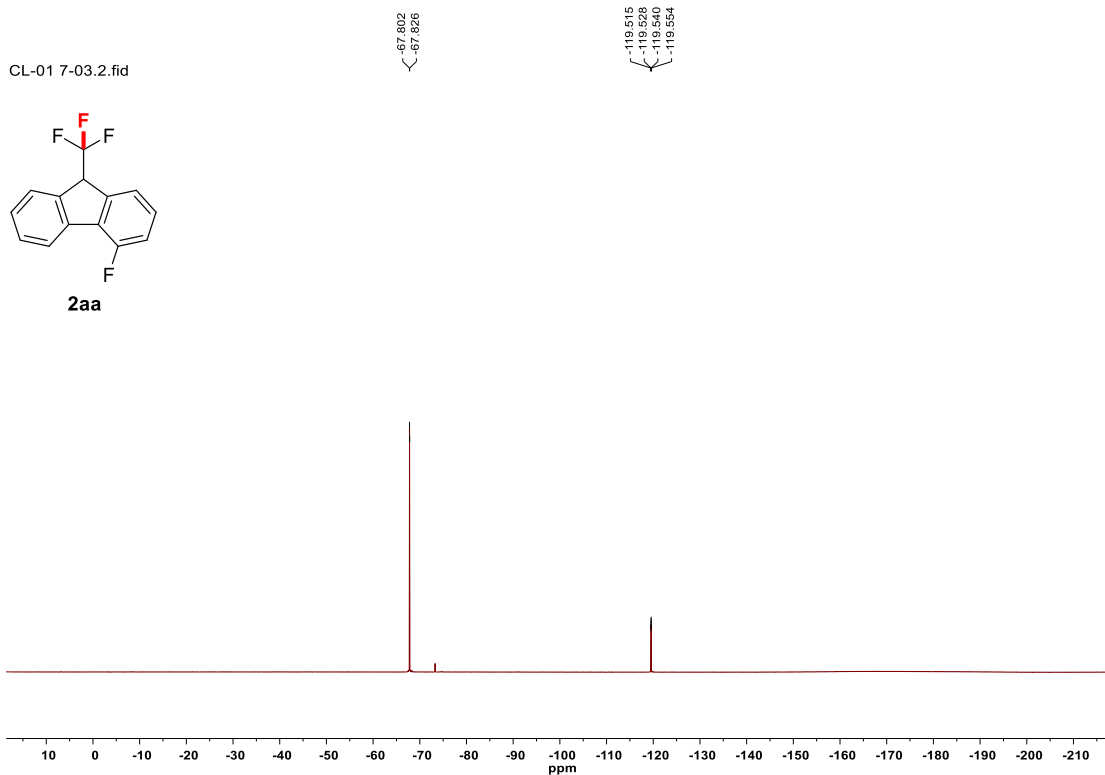
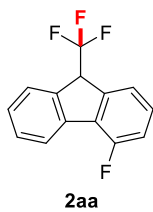


^1H NMR spectrum of **2aa** (400 MHz, CDCl_3)



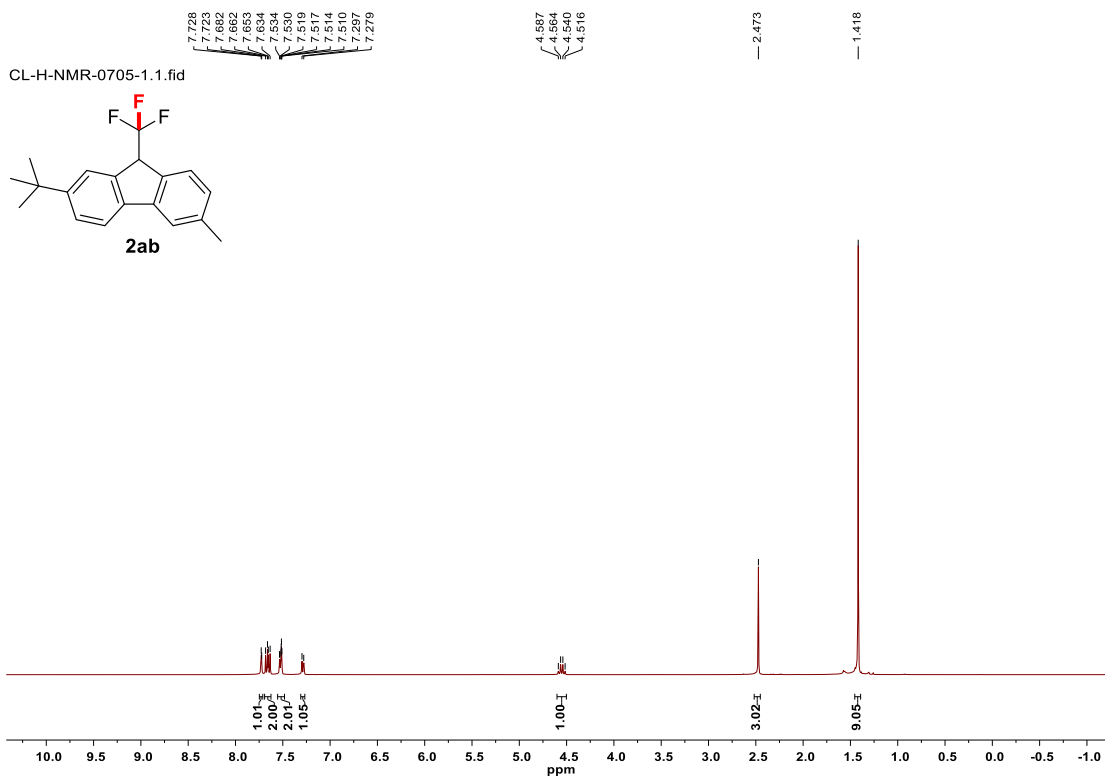
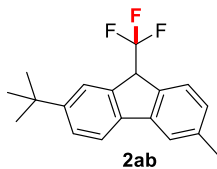
^{13}C NMR spectrum of **2aa** (101 MHz, CDCl_3)

CL-01 7-03.2.fid

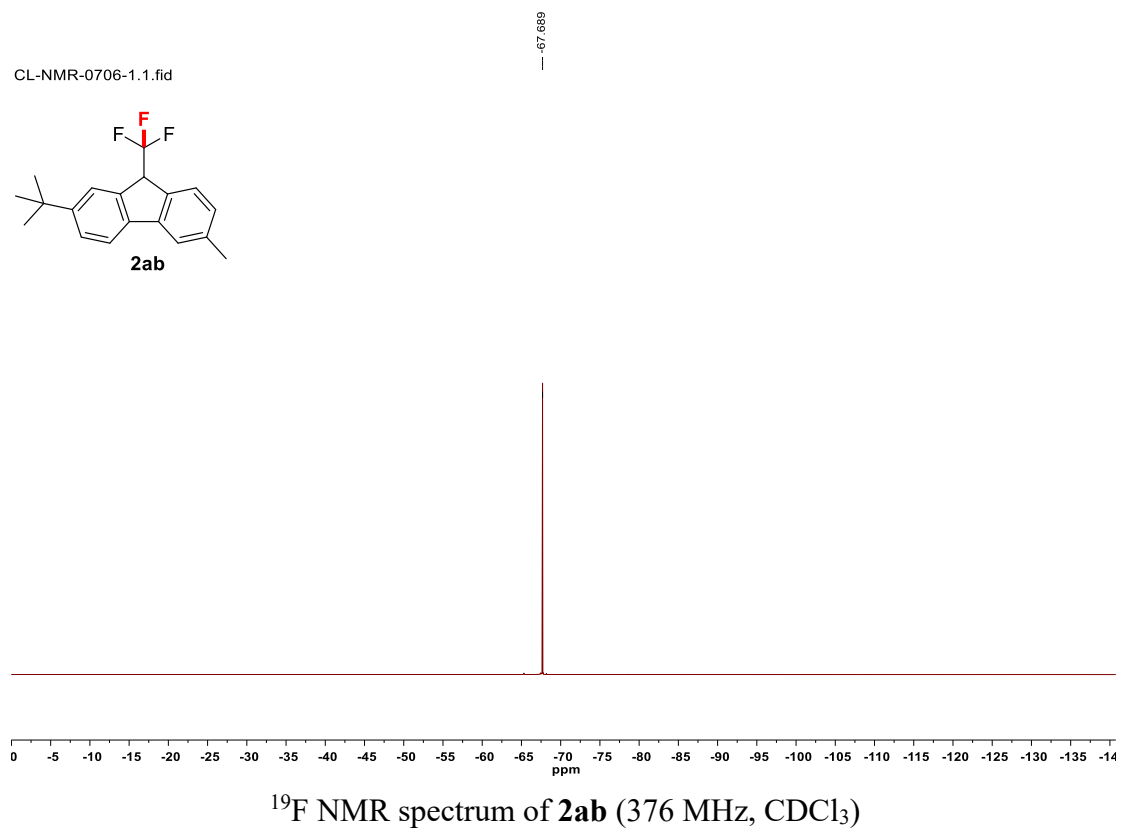
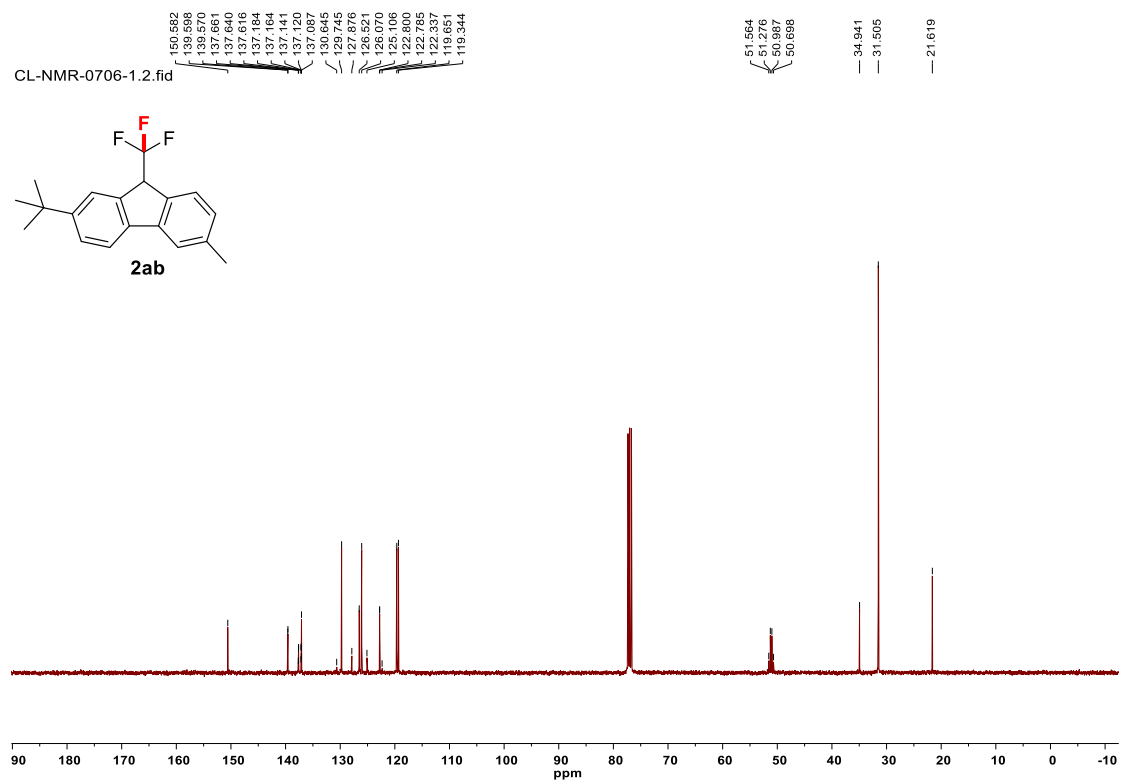


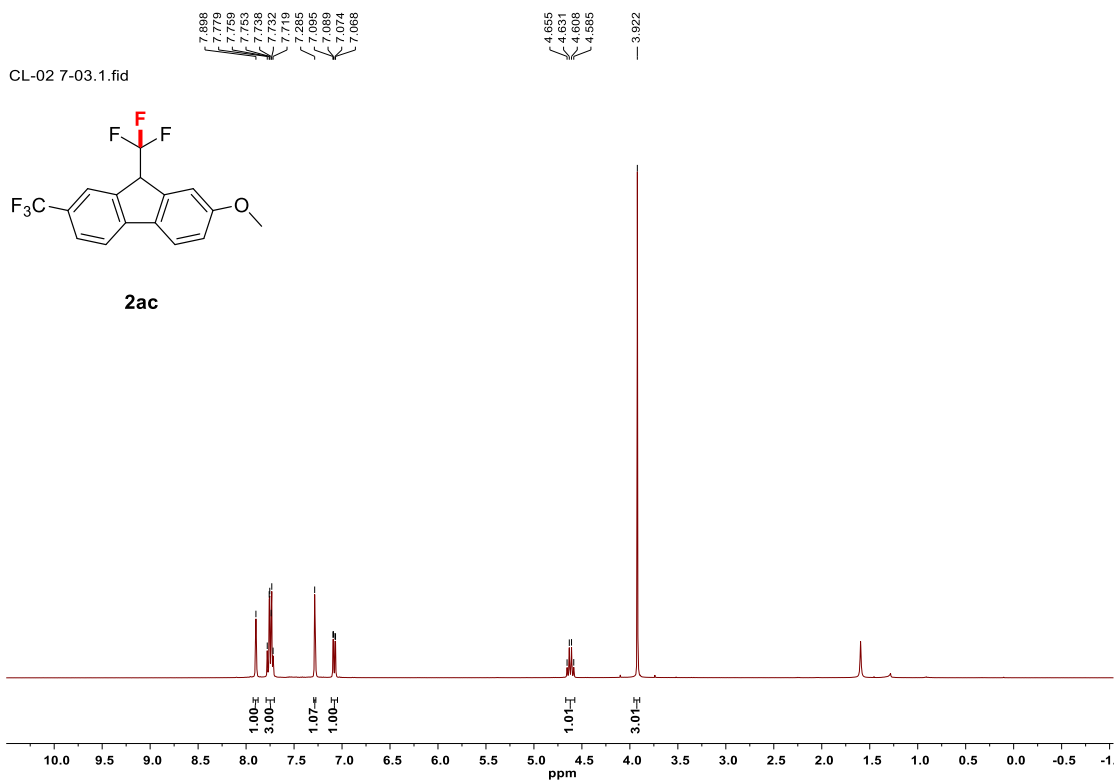
^{19}F NMR spectrum of **2aa** (376 MHz, CDCl_3)

CL-H-NMR-0705-1.1.fid

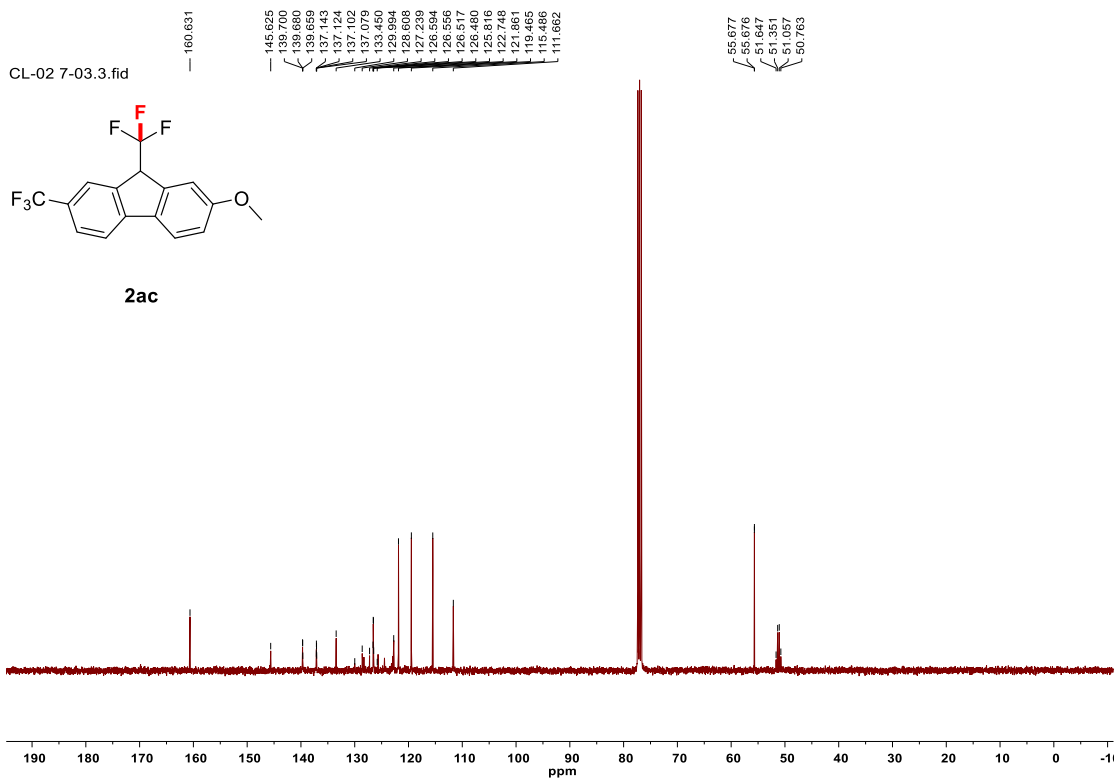


^1H NMR spectrum of **2ab** (400 MHz, CDCl_3)



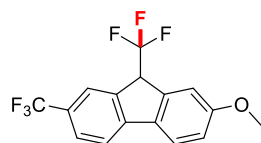


^1H NMR spectrum of **2ac** (400 MHz, CDCl_3)

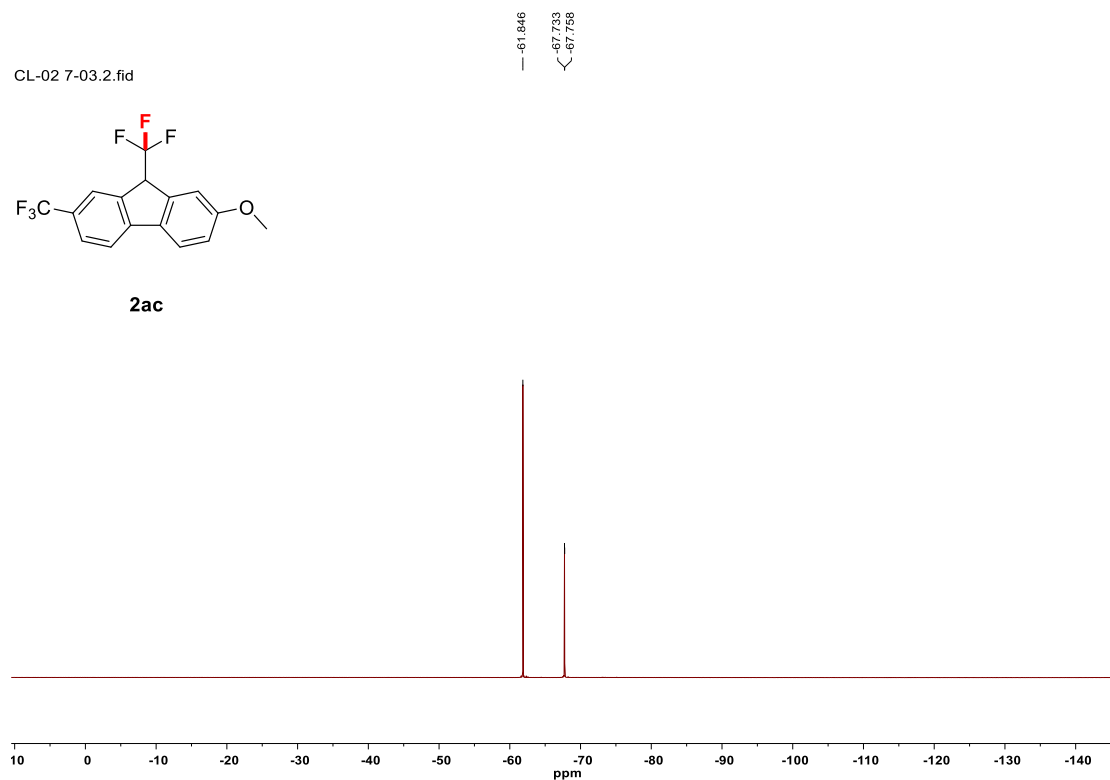


^{13}C NMR spectrum of **2ac** (101 MHz, CDCl_3)

CL-02 7-03.2.fid

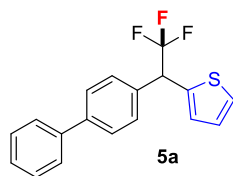


2ac

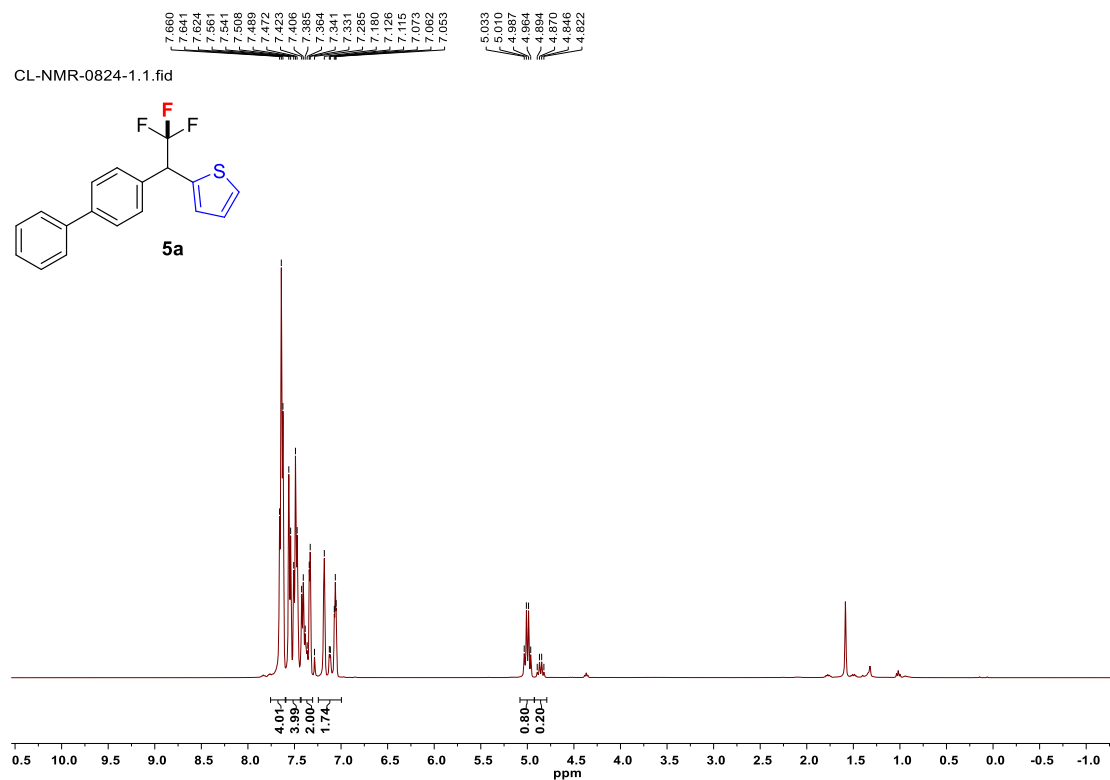


¹⁹F NMR spectrum of **2ac** (376 MHz, CDCl₃)

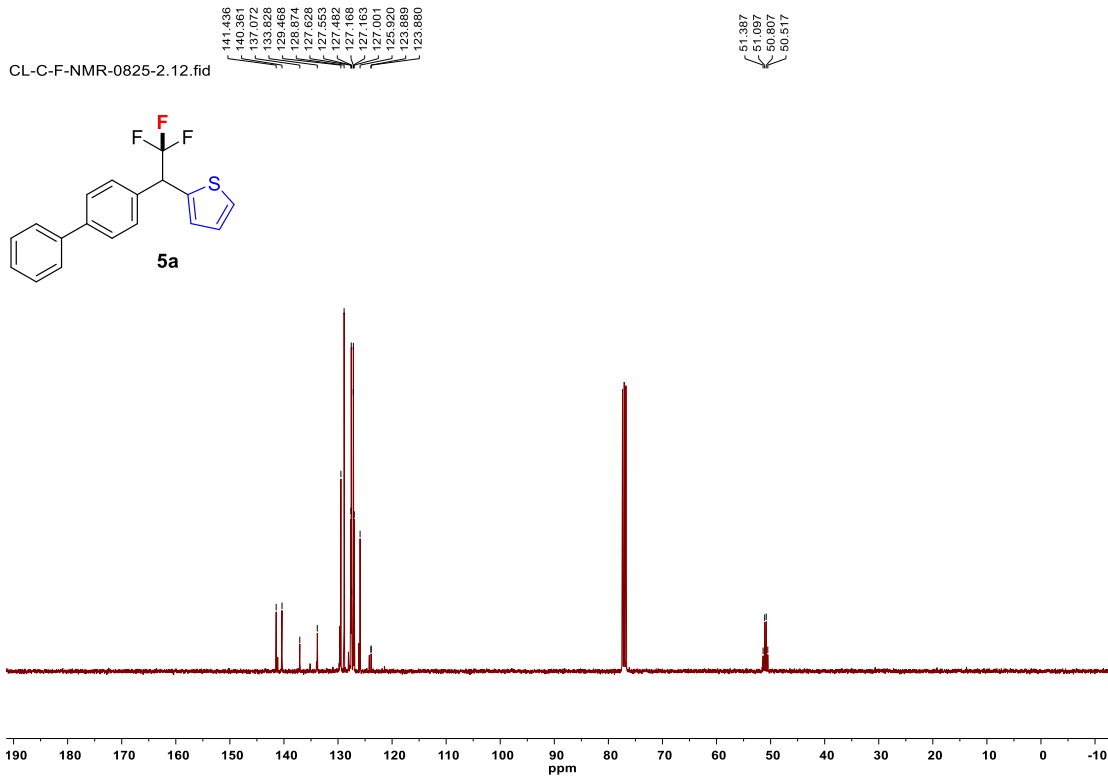
CL-NMR-0824-1.1.fid



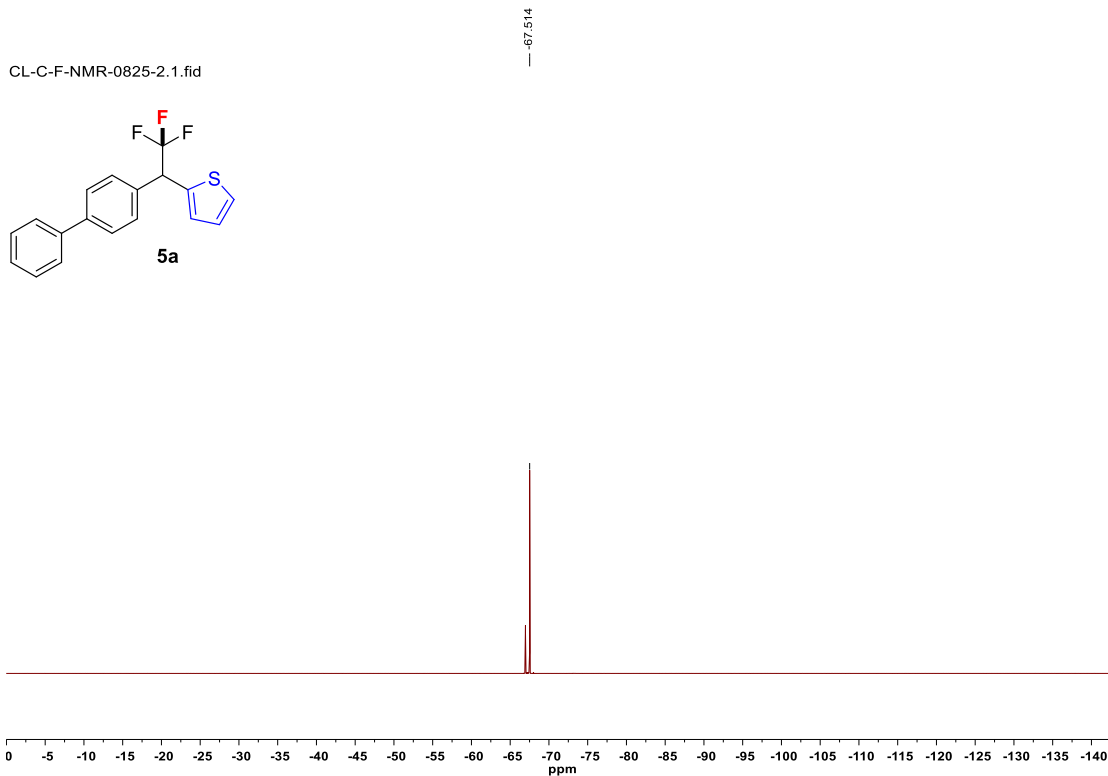
5a



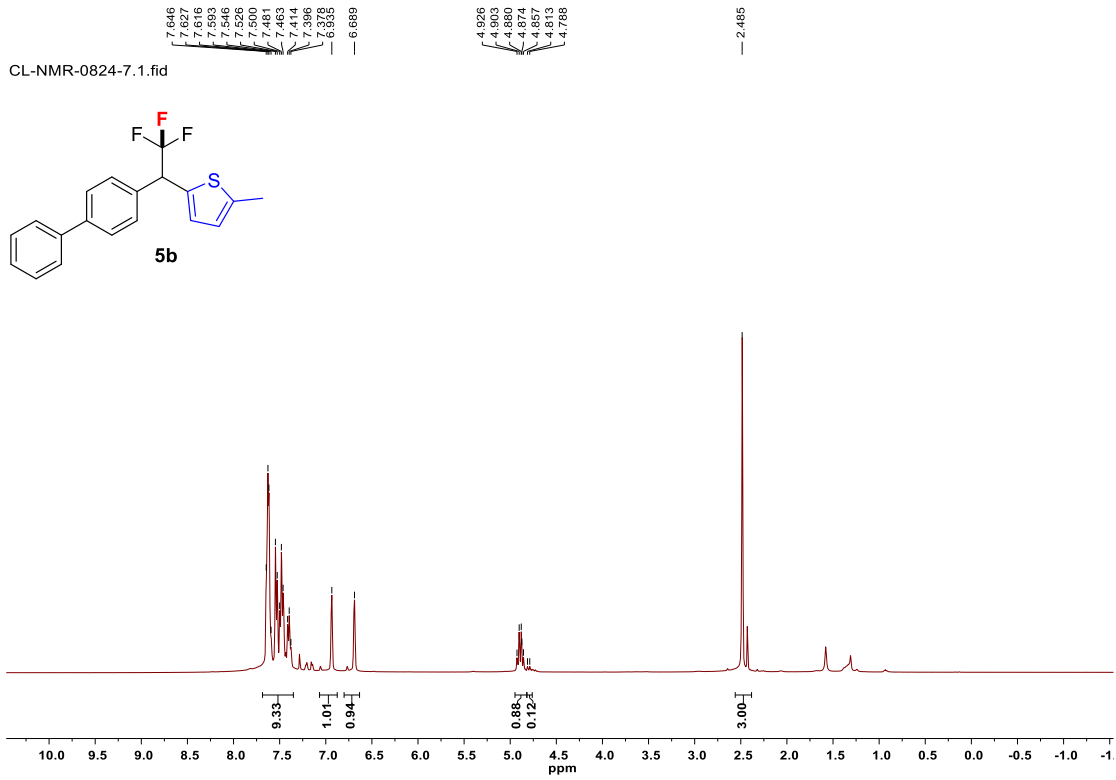
¹H NMR spectrum of **5a** (400 MHz, CDCl₃)



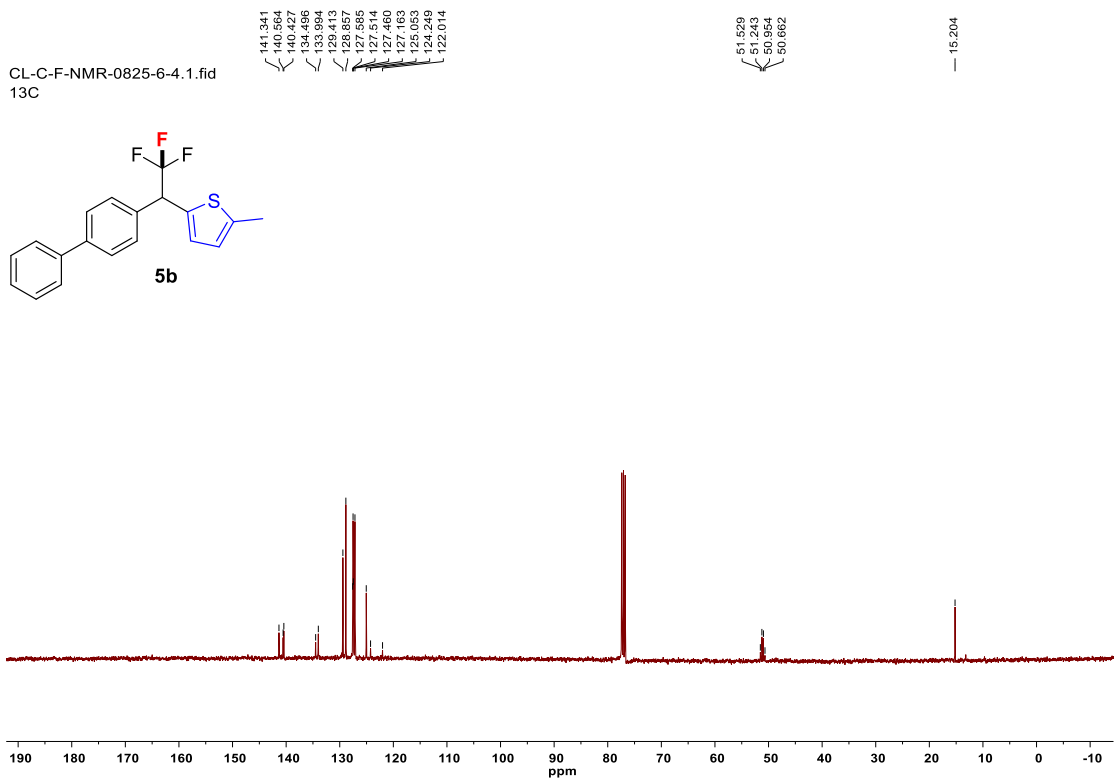
^{13}C NMR spectrum of **5a** (101 MHz, CDCl_3)



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

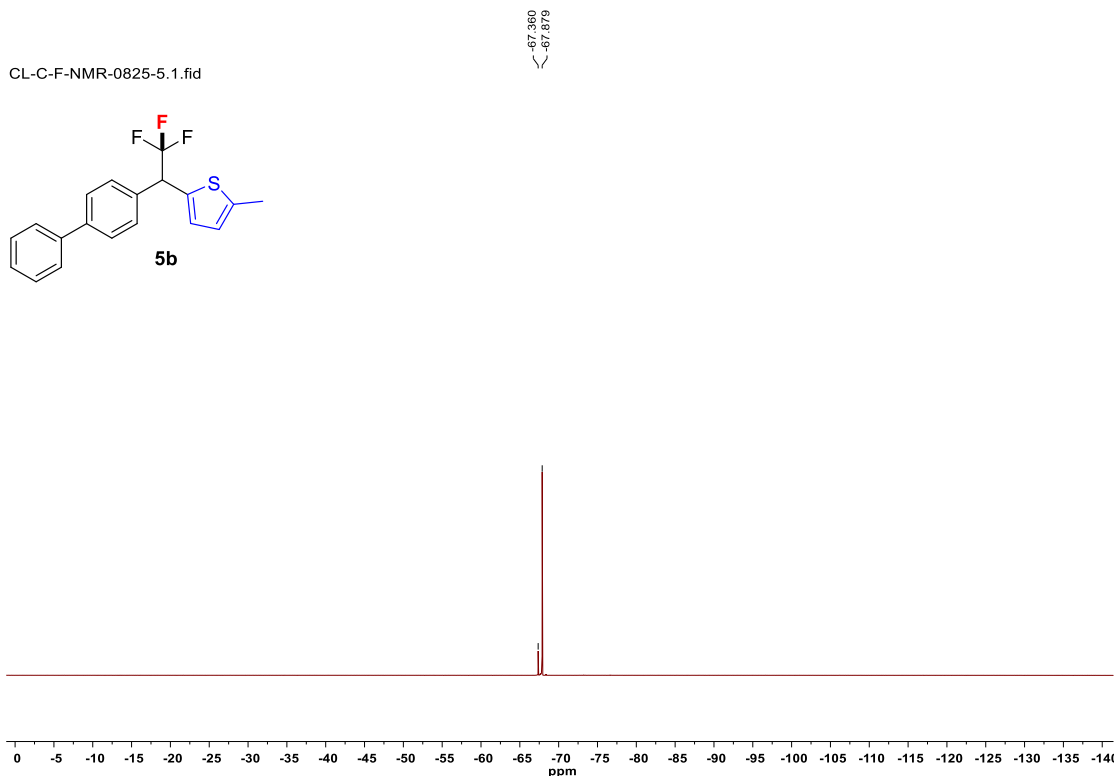
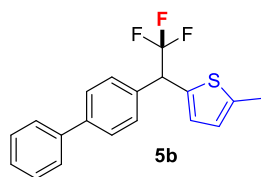


^1H NMR spectrum of **5b** (400 MHz, CDCl_3)



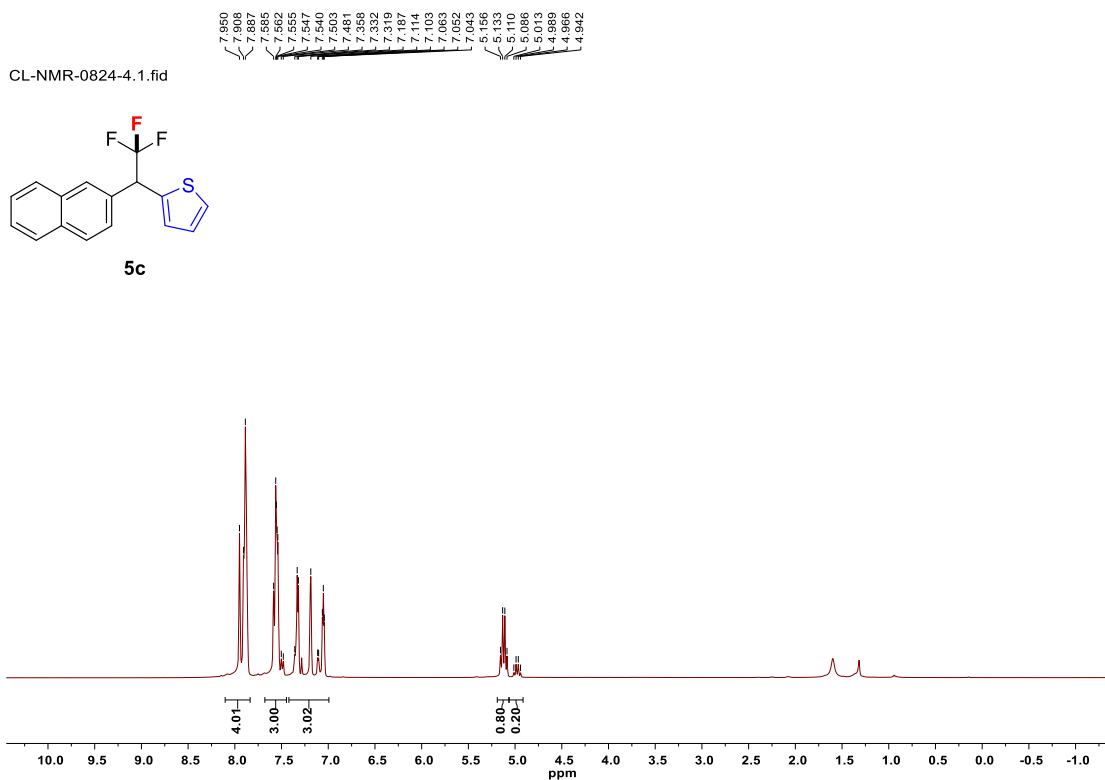
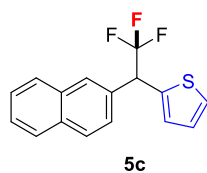
^{13}C NMR spectrum of **5b** (101 MHz, CDCl_3)

CL-C-F-NMR-0825-5.1.fid



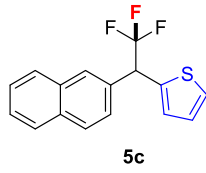
^{19}F NMR spectrum of **5b** (376 MHz, CDCl_3)

CL-NMR-0824-4.1.fid



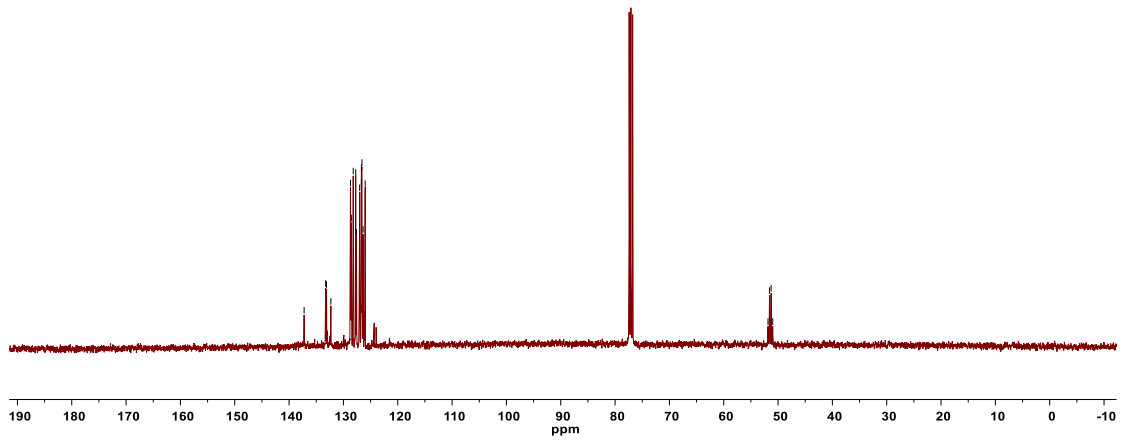
^1H NMR spectrum of **5c** (400 MHz, CDCl_3)

CL-C-F-NMR-0825-3-1.1.fid
13C



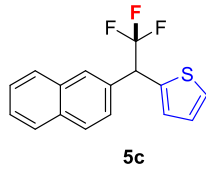
137.235
133.264
133.112
132.716
128.696
128.695
128.192
127.735
127.601
127.006
126.892
126.892
126.378
125.993

51.853
51.563
51.273
50.984

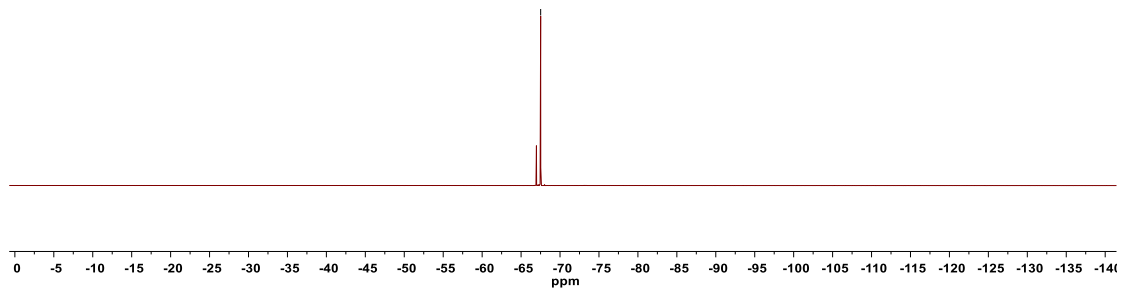


^{13}C NMR spectrum of **5c** (101 MHz, CDCl_3)

CL-C-F-NMR-0825-2.11.fid

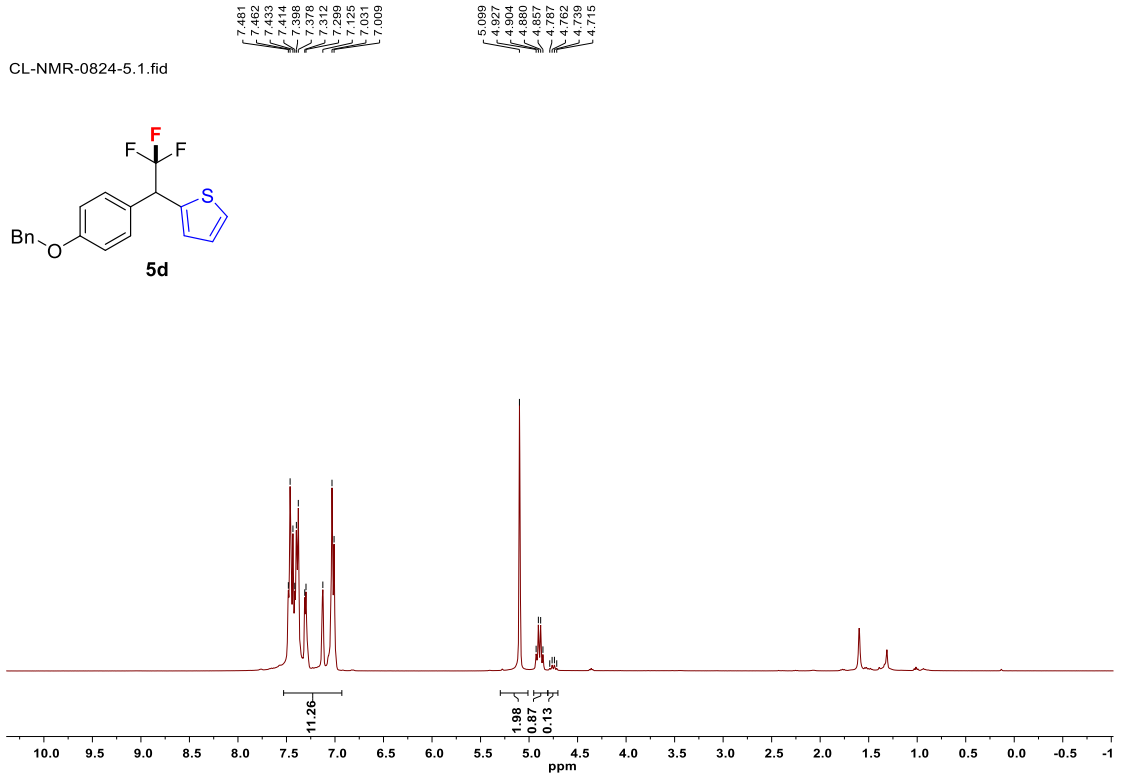
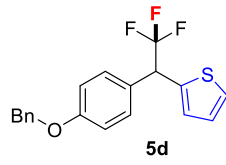


-67.514



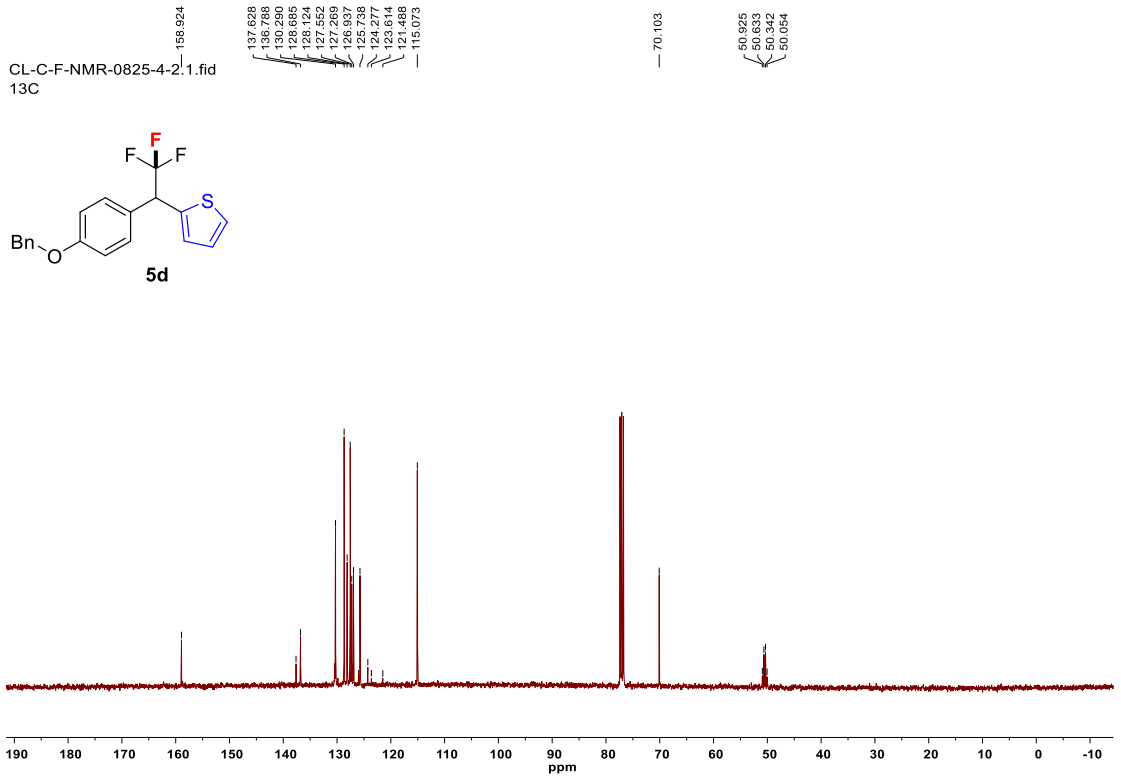
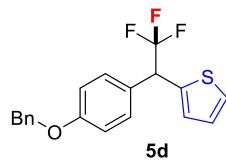
^{19}F NMR spectrum of **5c** (376 MHz, CDCl_3)

CL-NMR-0824-5.1.fid



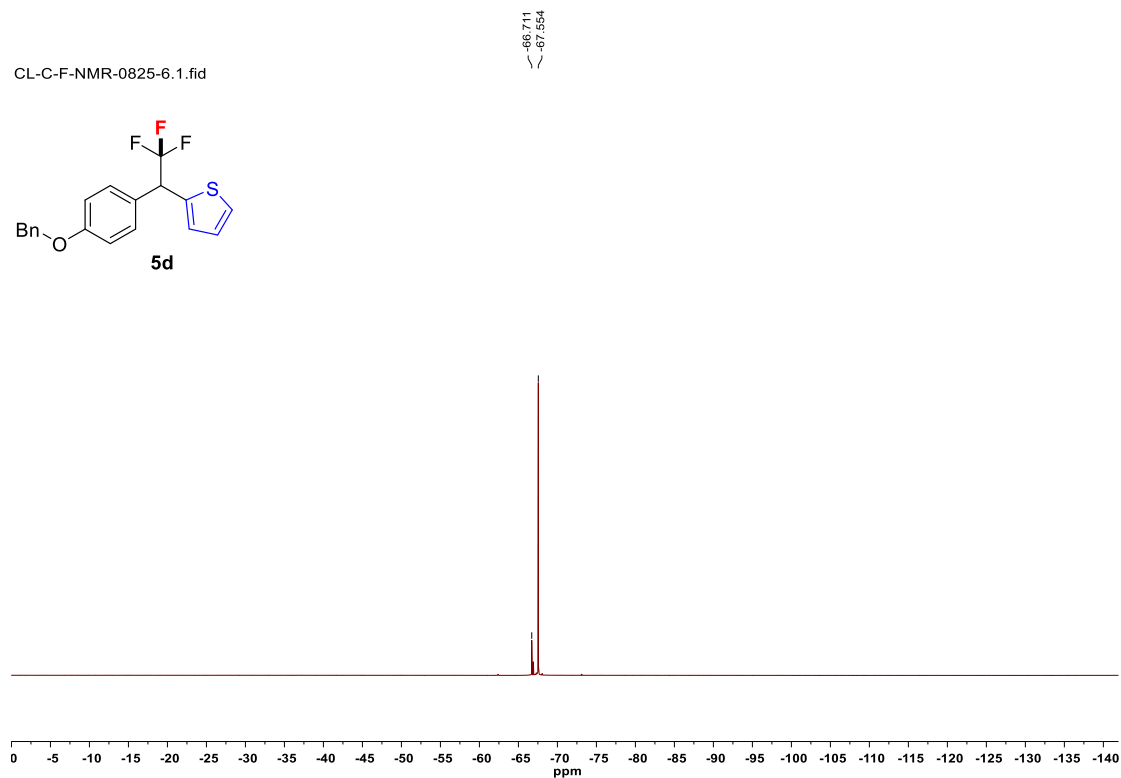
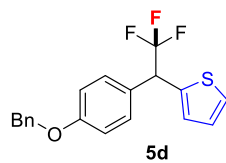
¹H NMR spectrum of **5d** (400 MHz, CDCl₃)

CL-C-F-NMR-0825-4-2.1.fid
13C



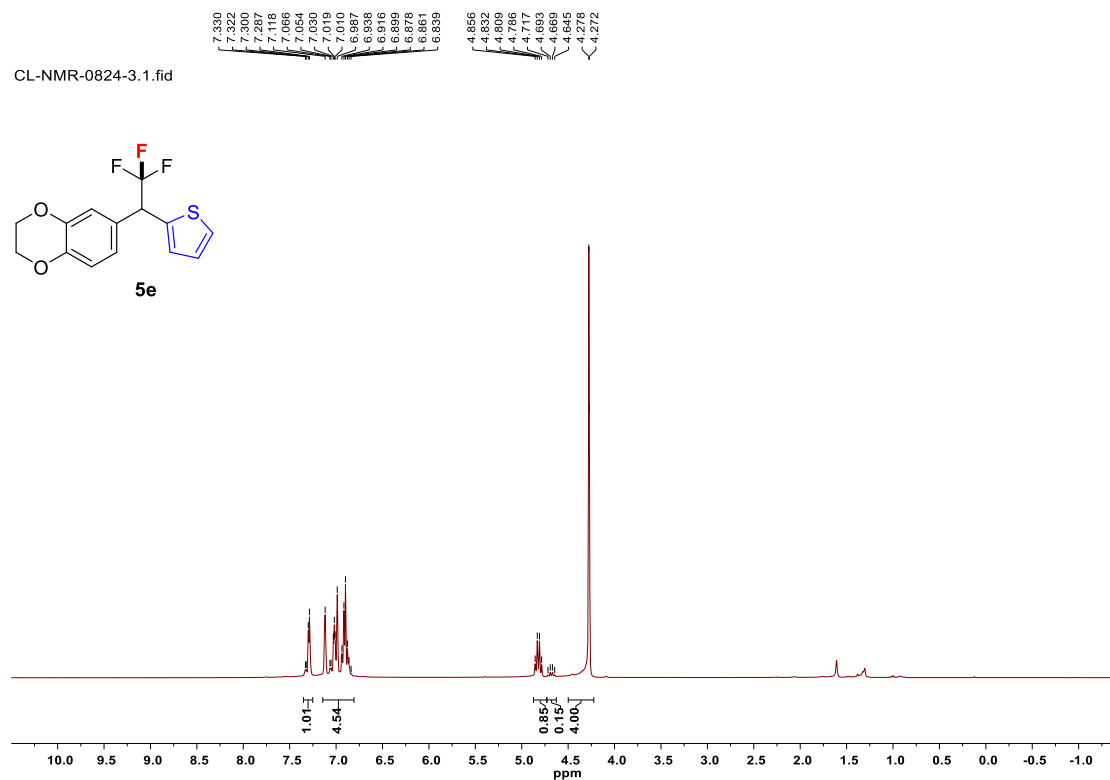
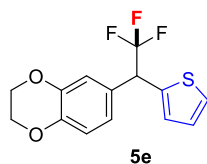
¹³C NMR spectrum of **5d** (101 MHz, CDCl₃)

CL-C-F-NMR-0825-6.1.fid



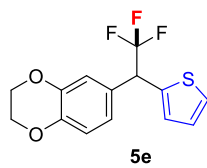
¹⁹F NMR spectrum of **5d** (376 MHz, CDCl₃)

CL-NMR-0824-3.1.fid



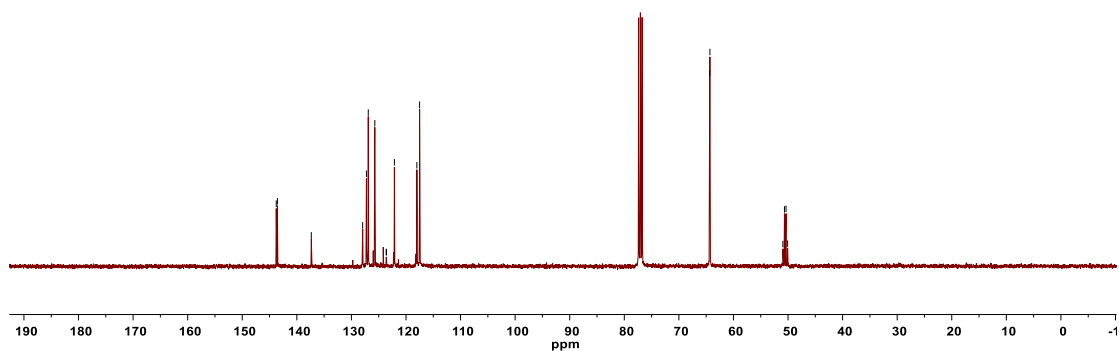
¹H NMR spectrum of **5e** (400 MHz, CDCl₃)

CL-C-F-NMR-0825-1.12.fid

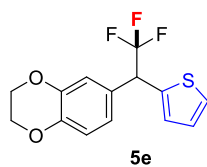


143.773
143.558
137.350
127.940
127.248
126.912
125.711
123.540
123.590
122.125
118.007
117.507

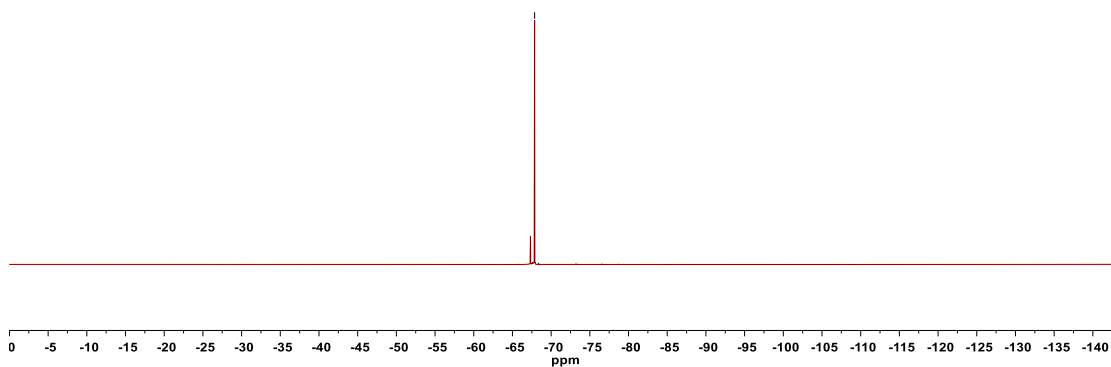
64.349
64.316
50.946
50.655
50.365
50.075

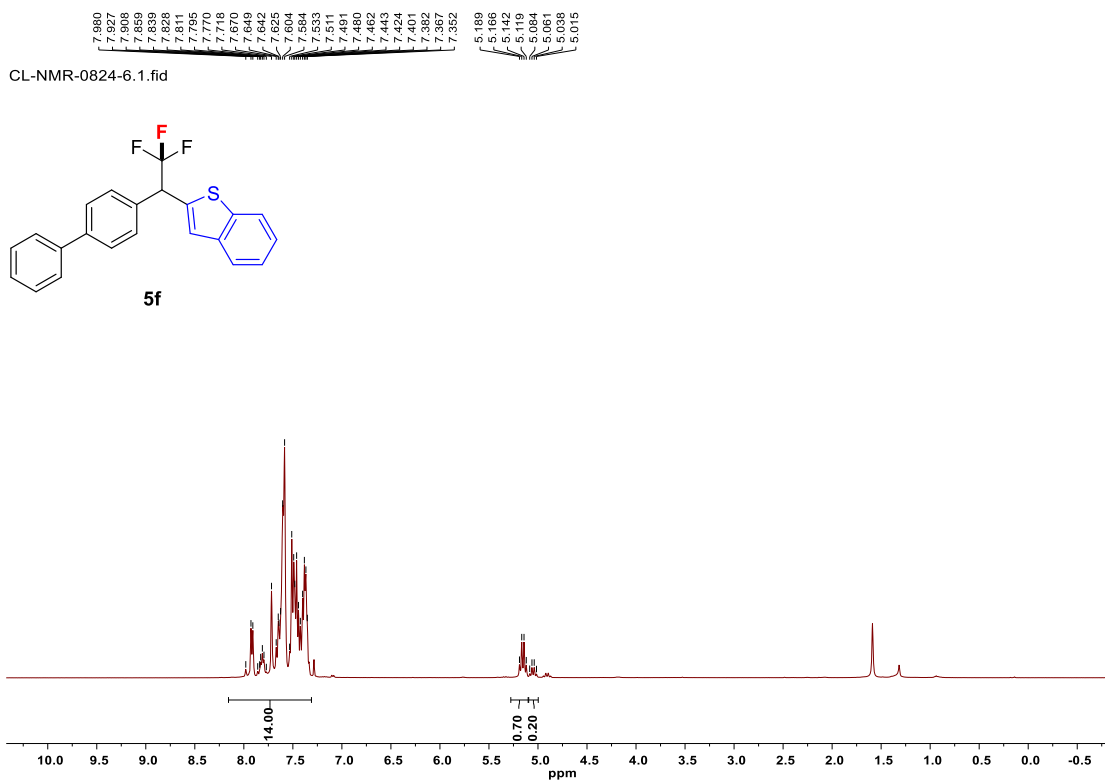


CL-C-F-NMR-0825-1.11.fid

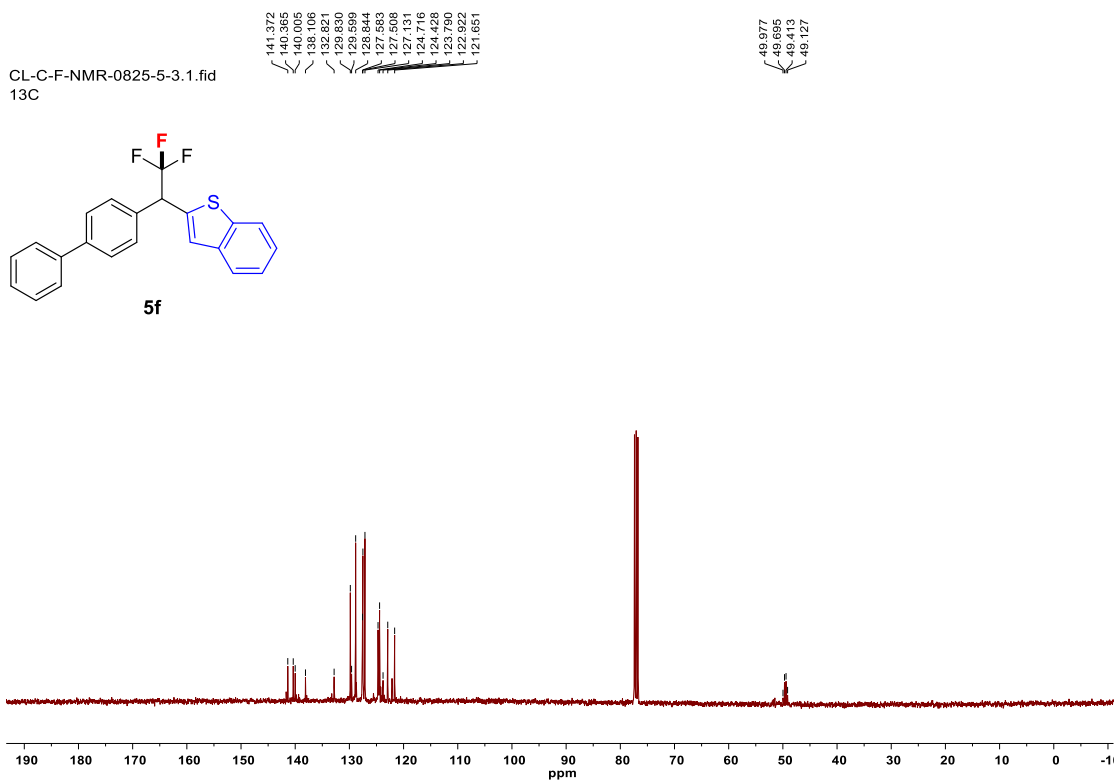


-67.863





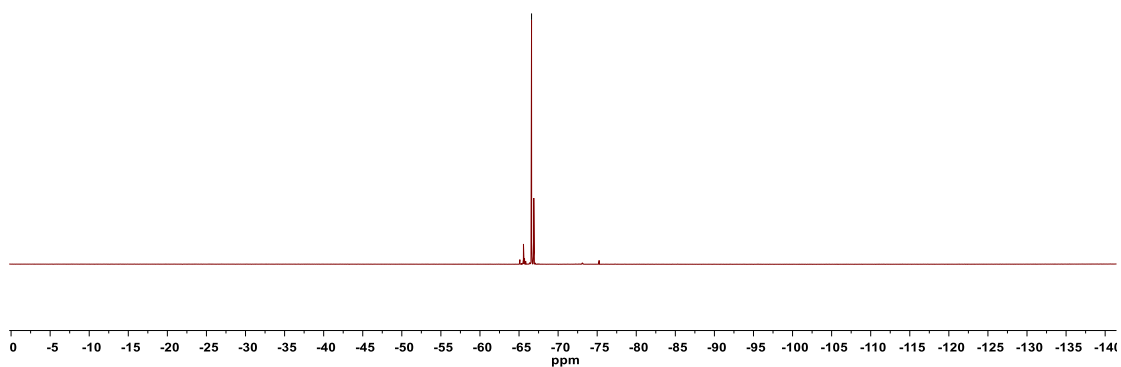
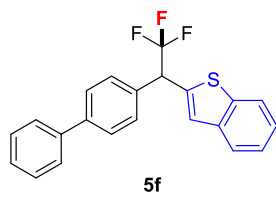
¹H NMR spectrum of **5f** (400 MHz, CDCl₃)



¹³C NMR spectrum of **5f** (101 MHz, CDCl₃)

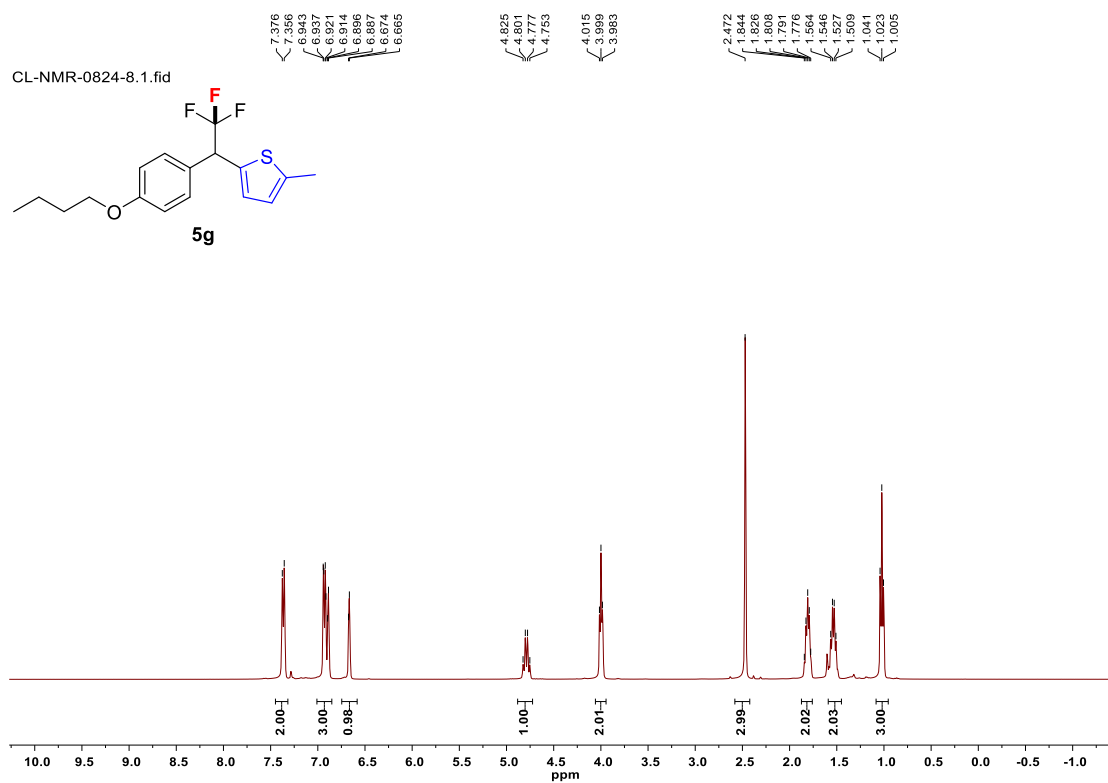
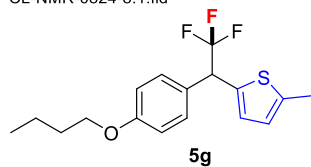
CL-C-F-NMR-0825-4.1.fid

—66.801



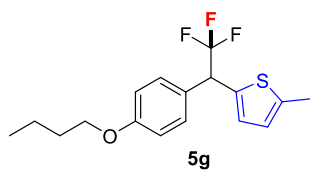
¹⁹F NMR spectrum of **5f** (376 MHz, CDCl₃)

CL-NMR-0824-8.1.fid

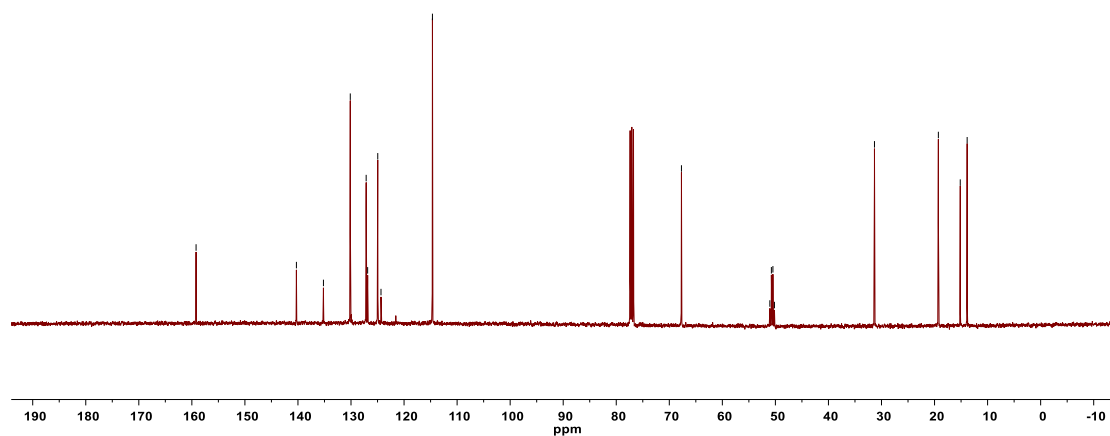


¹H NMR spectrum of **5g** (400 MHz, CDCl₃)

CL-C-F-NMR-0825-7-5.1.fid
13C

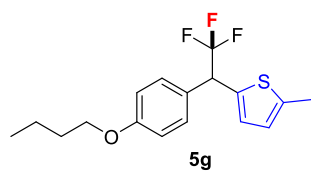


140.291
135.186
130.137
127.142
126.863
124.958
124.346
114.650
-67.710
-51.046
-50.757
-50.469
-50.180
-31.324
-19.280
-15.153
-13.854

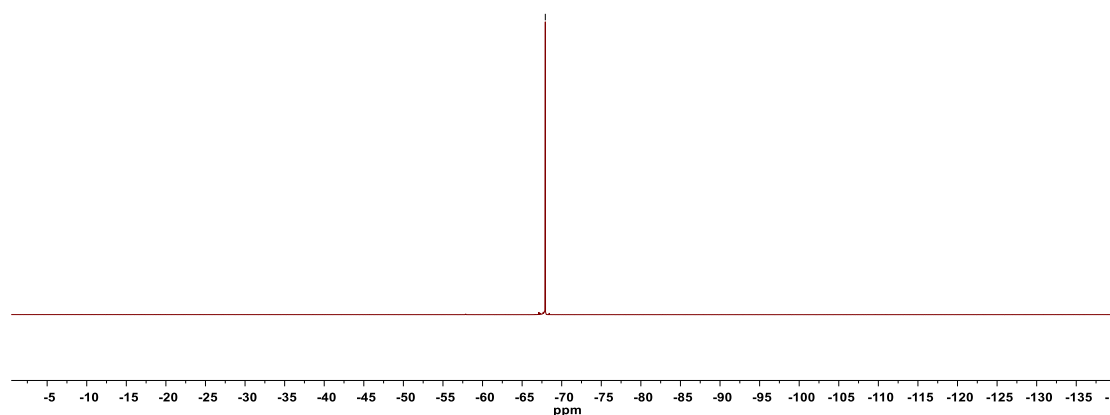


^{13}C NMR spectrum of **5g** (101 MHz, CDCl_3)

CL-C-F-NMR-0825-3.1.fid



-67.929



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