Supporting Information

Palladium-catalyzed site-selective C−H polyfluoroarylation of arenes via aryl thianthrenium salts

Chen Chen,*[a,d] Jin-Ping Liu,[a] Xin-Yu Hu,[a] Zi-Yi Wang,[a] Xiao-Xu Zhang,[a] Jia-Hui Song,[a] Yan-Ping Zhu,*[b] Chunjie Ni,*[c] and Bolin Zhu*[a]

[a] Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China. Email: hxxycc@tjnu.edu.cn; hxxyzbl@tjnu.edu.cn.

[b] Key Laboratory of Molecular Pharmacology and Drug Evaluation, Ministry of Education, School of Pharmacy, Yantai University, Shandong, Yantai, 264005, P. R. China. Email: chemzyp@ytu.edu.cn.

[c] School of Pharmacy, Yancheng Teachers University, Yancheng 224007, P. R. China. E-mail: nicj@yctu.edu.cn.

[d] Dean-Cavalry (Tianjin) Ltd., Tianjin 300304, P. R. China.

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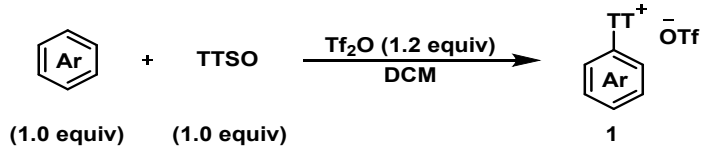
General Information:

The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{31}P NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{31}P NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS analysis of compounds was performed with an orbitrap (Thermo fisher Q-Exactive, APCI source).

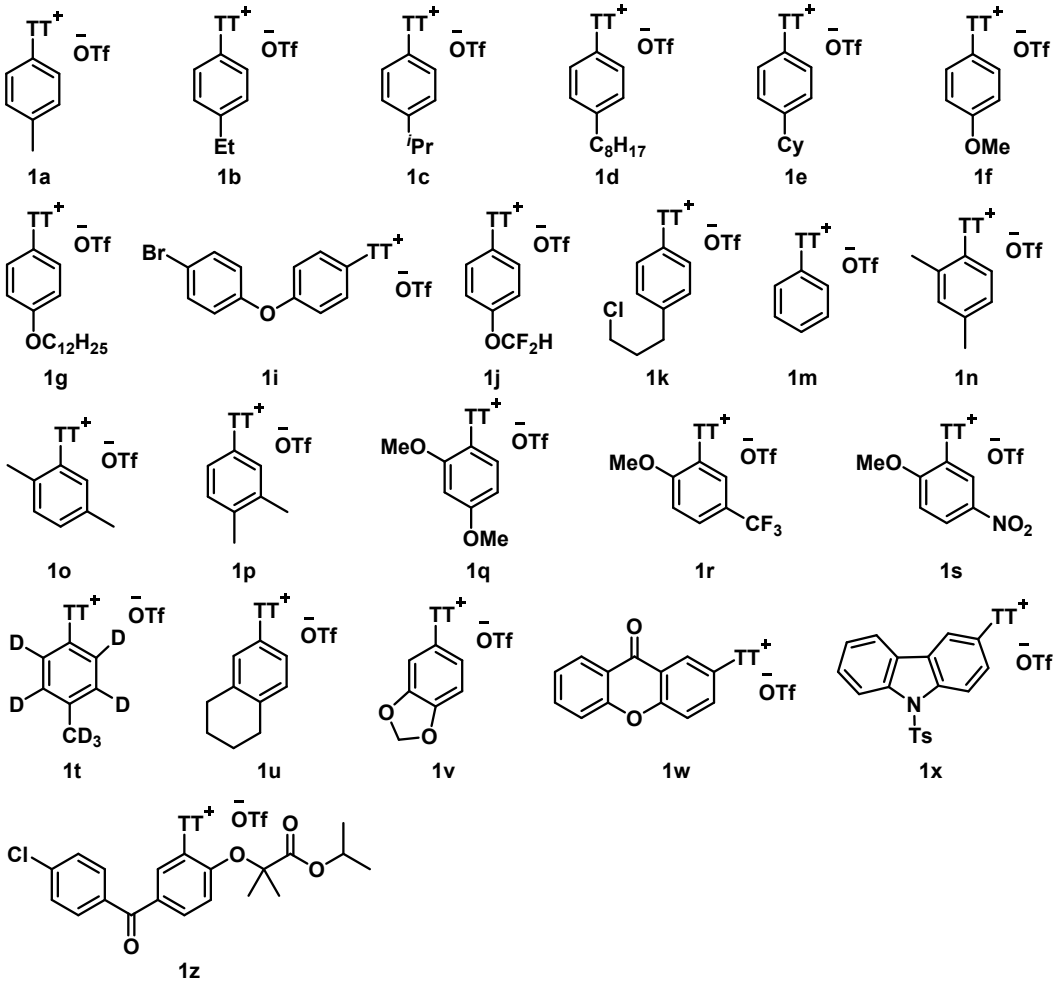
General Procedures for the Synthesis of Substrates:

1. General procedures for the synthesis of aryl thianthrenium salts 1

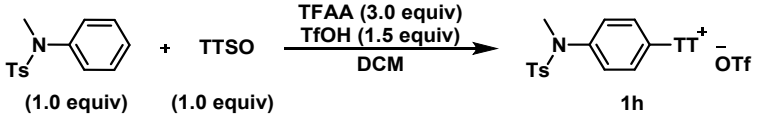
(1)



A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and arenes (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, and then Tf_2O (6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated $NaHCO_3$ solution, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.

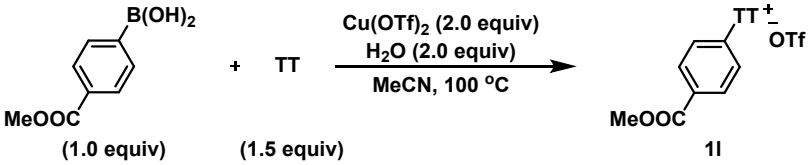


(2)



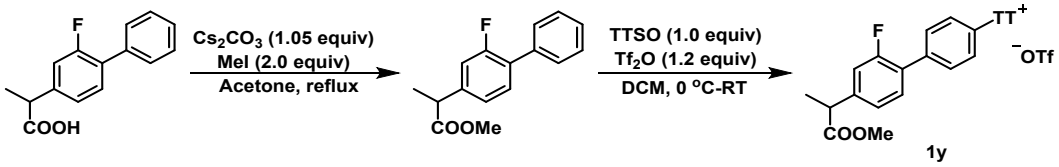
A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and 4-dimethylbenzenesulfonamide (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, trifluoroacetic anhydride (TFAA, 15.0 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 7.5 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM. Drying of organic phase with anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product **1h** was purified by crystallization from DCM/MTBE system as a white solid.

(3)



In a 38 mL sealed tube, the mixture of (4-(methoxycarbonyl)phenyl)boronic acid (3.0 mmol, 1.0 equiv), thianthrene (TT, 4.5 mmol, 1.5 equiv), $Cu(OTf)_2$ (6.0 mmol, 2.0 equiv), H_2O (6.0 mmol, 2.0 equiv) were added in 3.0 mL MeCN. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was stirred in a 100 °C heating mantle for 3 h. After cooling to room temperature, the reaction mixture was added into ammonia solution (50.0 mL, 25-28% solution in water), and the water phase was extracted with DCM (3 x 30.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product **1l** was purified by crystallization from DCM/Et_2O system as a white solid.

(4)

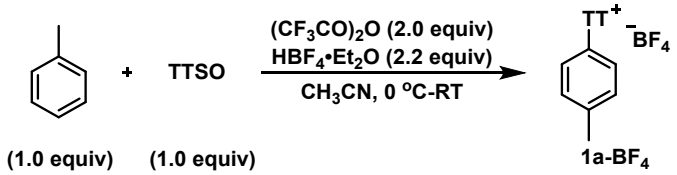


To an oven-dried 100 mL round-bottom flask was charged with flurbiprofen (10.0 mmol, 1.0 equiv), Cs_2CO_3 (10.5 mmol, 1.05 equiv) and acetone (20.0 mL). To the flask was added iodomethane (MeI, 20.0 mmol, 2.0 equiv) and the heterogeneous solution was stirred at reflux for overnight. After the reaction, the crude mixture was diluted with Et_2O (20.0 mL), washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was used without any further purification. The residue was purified by chromatography on silica gel eluting with petroleum ether/ethyl acetate to afford flurbiprofen methyl ester.

A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and flurbiprofen methyl ester (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at

this temperature, and then Tf_2O (6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated $NaHCO_3$ solution, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product **1y** was purified by crystallization from DCM/MTBE system as a brown solid.

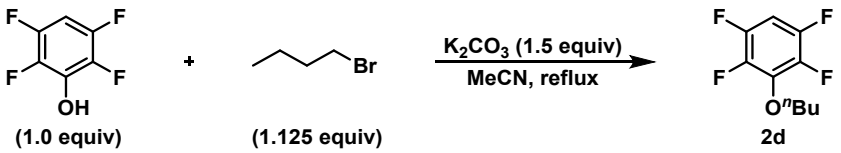
(5)



A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), CH_3CN (10.0 mL) and toluene (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to 0 °C and stirred at this temperature. $(CF_3CO)_2O$ (10.0 mmol, 2.0 equiv) and $HBF_4 \cdot Et_2O$ (11.0 mmol, 2.2 equiv) were added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated $NaHCO_3$ solution, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product **1a-BF_4** was purified by crystallization from DCM/Et_2O system as a white solid.

2. General procedures for the synthesis of polyfluorobenzenes 2

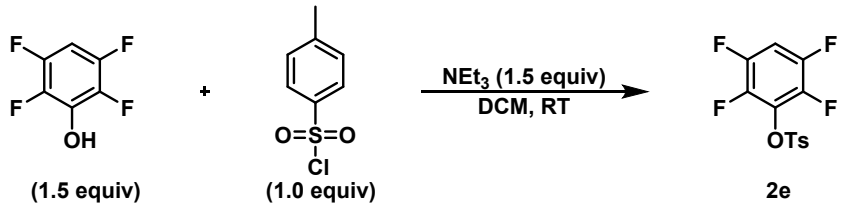
(1)



1-bromobutane (3.4 mmol, 1.125 equiv) was added to a stirred suspension of 2,3,5,6-tetrafluorophenol (3.0 mmol, 1.0 equiv) and K_2CO_3 (4.5 mmol, 1.5 equiv) in MeCN (6.0 mL) under argon atmosphere. The reaction mixture was then stirred for 7 hours under reflux conditions. Upon completion, the reaction mixture was allowed to

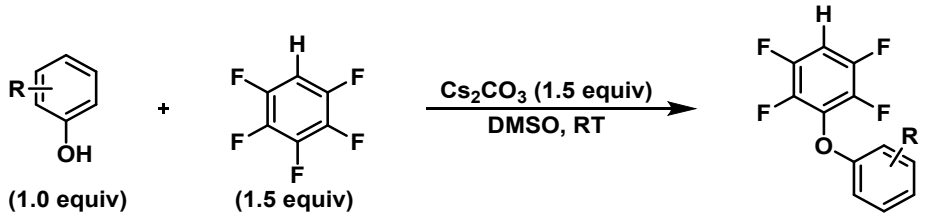
cool to ambient temperature, and H_2O (20.0 mL) and pentane (30.0 mL) were added. After phase separation, the organic layer was washed with 1 M NaOH (20.0 mL) and brine, dried over Na_2SO_4, and evaporated to dryness, affording a pale-yellow oil. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **2d**.

(2)



To a magnetically stirred solution of 2,3,5,6-tetrafluorophenol (4.5 mmol, 1.5 equiv) dissolved in dichloromethane (3.0 mL) and NEt_3 (4.5 mmol, 1.5 equiv) was added *p*-toluenesulfonyl chloride (3.0 mmol, 1.0 equiv) in dichloromethane (1.0 mL). A colourless precipitate immediately formed and stirring was continued for 16 h. The mixture was then treated with water (5.0 mL) and extracted with dichloromethane (3 x 5.0 mL). The combined organic extracts were washed with saturated sodium chloride (5.0 mL), dried ($NaSO_4$) and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **2e**.

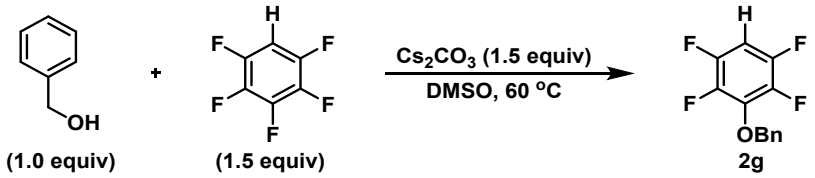
(3)



To an oven-dried 50 mL round-bottom flask was charged with phenols (1.0 equiv), pentafluorobenzene (1.5 equiv), Cs_2CO_3 (1.5 equiv) in DMSO (5.0 mL). The reaction mixture was stirred at room temperature for 12 h, neutralized by a saturated NaCl solution, and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude

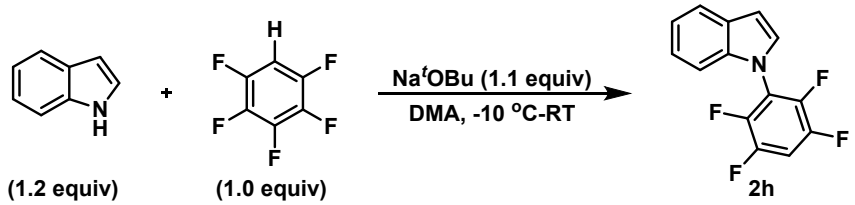
mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the products **2f, 2p, 2q**.

(5)



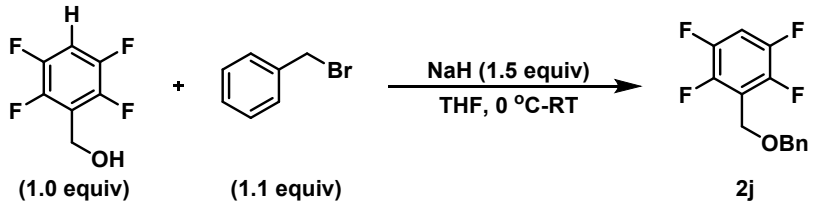
To an oven-dried 50 mL round-bottom flask was charged with phenols (3.0 mmol, 1.0 equiv), pentafluorobenzene (4.5 mmol, 1.5 equiv), Cs_2CO_3 (4.5 mmol, 1.5 equiv) in DMSO (5.0 mL). The reaction mixture was stirred at in a 60 °C heating mantle for 12 h, neutralized by a saturated NaCl solution, and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **2g.**

(6)



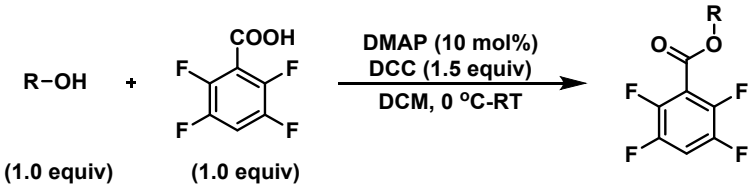
Sodium tert-butoxide (4.3 mmol, 1.1 equiv) was added to a glass vial containing indole (4.7 mmol, 1.2 equiv) in DMA (10.0 mL). The mixture was stirred at room temperature for 10 min, then the mixture was cooled in -10 °C and added to a cooled solution of pentafluorobenzene (3.9 mmol, 1.0 equiv) in DMA (10.0 mL) under stirring. After 15 min the cooling bath was removed to room temperature for 1h. The reaction was mixed with sat. NH_4Cl (aq) (5.0 mL) and water (5.0 mL) then extracted with diethyl ether (4 x 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **2h.**

(7)



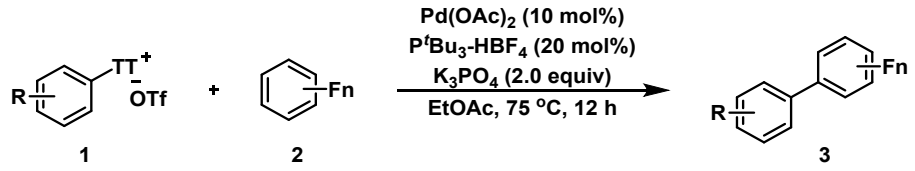
Benzyl alcohol (2.8 mmol, 1.0 equiv) was weighed directly into a Schlenk tube and dried under vacuum for 15 min. Then THF was added and stirred, and NaH (4.2 mmol, 1.5 equiv) was slowly added at 0 °C. After stirring for 30 min, benzyl bromide (3.1 mmol, 1.1 equiv) was added. The mixture was then warmed up to room temperature and the resulting reaction mixture was monitored by TLC. The reaction was quenched by H_2O and extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **2j.**

(8)



In an oven-dried 50 mL round-bottomed flask, DCC (4.5 mmol, 1.5 equiv) and DMAP (10 mol%) were added sequentially to an ice-cold solution of the corresponding alcohol (3.0 mmol, 1.0 equiv) and 2,3,5,6-tetrafluorobenzoic acid (3.0 mmol, 1.0 equiv) in DCM (15.0 mL). After 30 min, the ice-water cooling bath was removed, and the resulting suspension was stirred vigorously at room temperature overnight. Then, the reaction mixture was concentrated to dryness under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the products **2o, 2r, 2s, 2t, 2u, 2v, 2w, 2x.**

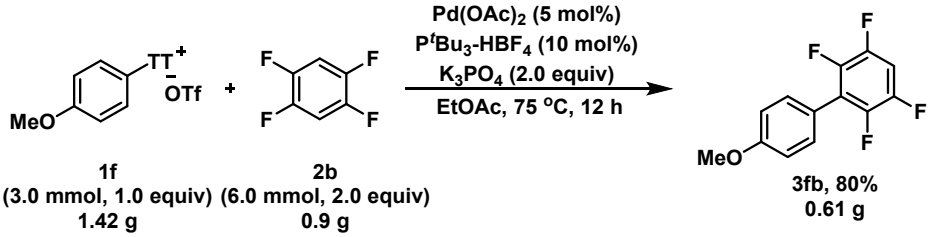
Experimental Procedures:



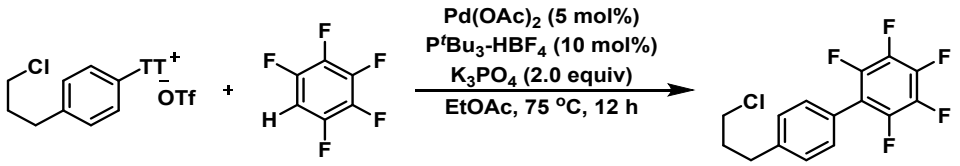
General procedure: In a 38 mL sealed tube, the mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv) or **1** (0.4 mmol, 2.0 equiv), **2** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mol%), P^tBu_3-HBF_4 (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv) were added in 2.0 mL EtOAc. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the products **3aa-3za**, **3ab-3ax**.

Further Explorations:

Gram scale reaction:

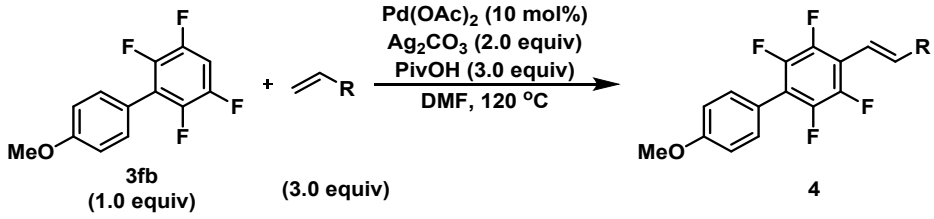


A 100 mL two-necked flask, the mixture of **1f** (3.0 mmol, 1.42 g, 1.0 equiv), **2b** (6.0 mmol, 0.9 g, 2.0 equiv), $Pd(OAc)_2$ (5 mol%), P^tBu_3-HBF_4 (10 mol%), K_3PO_4 (6.0 mmol, 1.27g, 2.0 equiv) were added in 30.0 mL EtOAc. Then, the tube was purged with N_2 for three times. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **3fb** (0.61 g) in 80% yield.

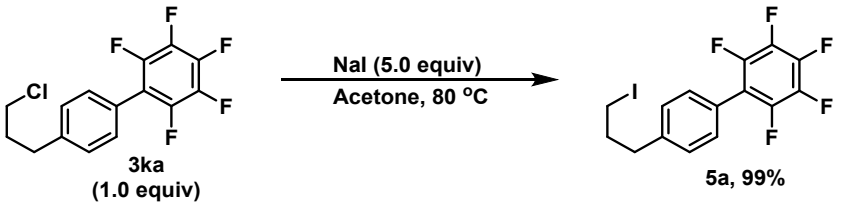


A 100 mL two-necked flask, the mixture of **1k** (3.0 mmol, 1.56 g, 1.0 equiv), **2a** (6.0 mmol, 1.0 g, 2.0 equiv), $Pd(OAc)_2$ (5 mol%), P^tBu_3-HBF_4 (10 mol%), K_3PO_4 (6.0 mmol, 1.27 g, 2.0 equiv) were added in 30.0 mL EtOAc. Then, the tube was purged with N_2 for three times. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **3ka** (0.78 g) in 81% yield.

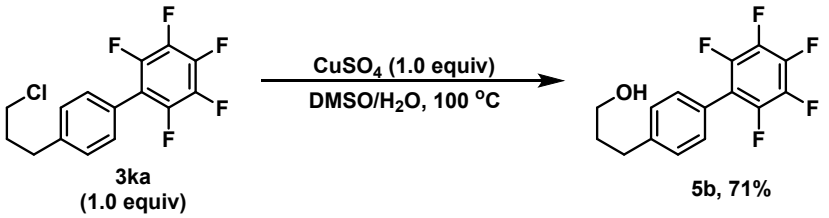
Derivatization:



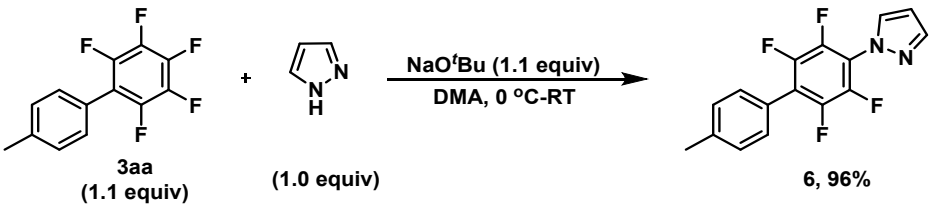
In a 38 mL sealed tube, the mixture of **3fb** (0.2 mmol, 1.0 equiv), **alkene** (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.4 mmol, 2.0 equiv), PivOH (0.6 mmol, 3.0 equiv) were added in 2.0 mL DMF. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was in a 120 °C heating mantle for 12 h. Then, the reaction was cooled to room temperature, and EtOAc (80.0 mL) and water (40.0 mL) were added. The organic layer was separated, and the aqueous phase was extracted with EtOAc (40.0 mL x 2). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the products **4a, 4b, 4c.**



In a 38 mL sealed tube, the mixture of **3ka** (0.2 mmol, 1.0 equiv), NaI (1.0 mmol, 5.0 equiv) were added in acetone (2.0 mL). Then, the tube sealed with PTEF cap. The reaction mixture was in a 80 °C heating mantle for 10 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **5a** in 99% yield.



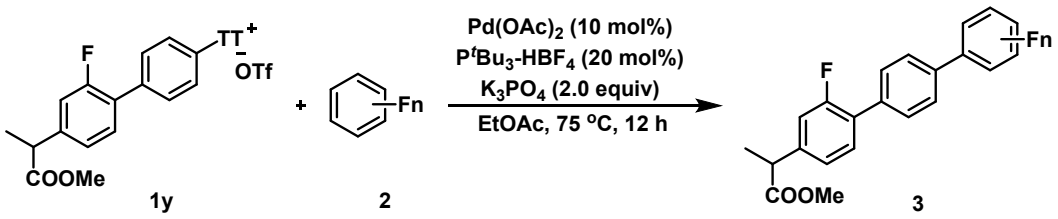
In a 38 mL sealed tube, the mixture of **3ka** (0.3 mmol, 1.0 equiv), $CuSO_4$ (0.3 mmol, 1.0 equiv) were added in H_2O (0.35 mL) and DMSO (0.8 mL). Then, the tube sealed with PTEF cap. The reaction mixture was in a 100 °C heating mantle for 72 h. When the reaction was finished, the mixture was cooled to room temperature and extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, then the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **5b** in 71% yield.



In a 38 mL sealed tube, the mixture of **3aa** (0.2 mmol, 1.1 equiv), pyrazole (0.2 mmol, 1.0 equiv), NaO^{t}Bu (0.22 mmol, 1.1 equiv) were added in DMA (0.2 mL) in 0 °C. Then, the tube sealed with PTEF cap. The reaction mixture was heated to room temperature for 12 h. When the reaction was finished, the mixture was cooled to room

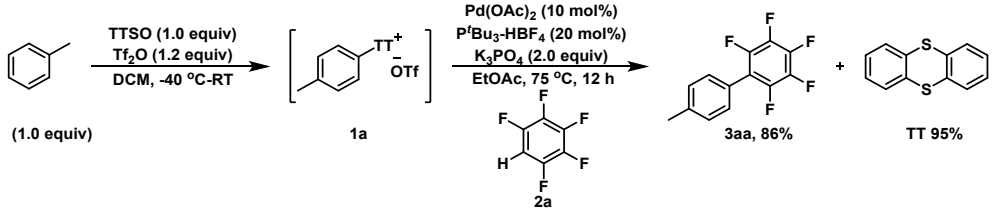
temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **6** in 96% yield.

Late-stage modification of drugs:



In a 38 mL sealed tube, the mixture of **1y** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P^tBu_3-HBF_4 (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv) were added in 2.0 mL EtOAc. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the products **3ys, 3yr, 3yw**.

One-pot C-H thianthrenation/sulfonylation and TT recovery:

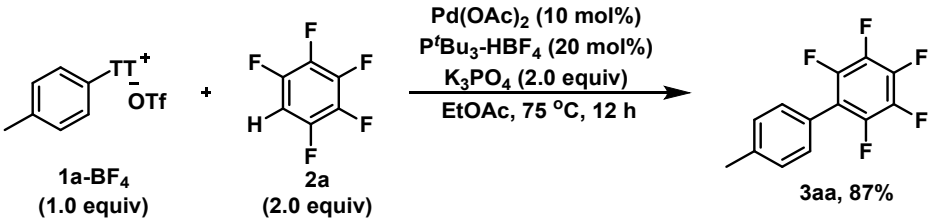


A 10 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 0.2 mmol, 1.0 equiv), DCM (1.0 mL) and toluene (0.2 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, Tf_2O (0.24 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 0.5 h, and then allowed to stir at room temperature for 12 h. The mixture was concentrated to dryness under reduced pressure to give the crude product of **1a**.

In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P^tBu_3-HBF_4 (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv)

were added in 2.0 mL EtOAc. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **3aa** in 86% yield and TT recovery in 95% yield.

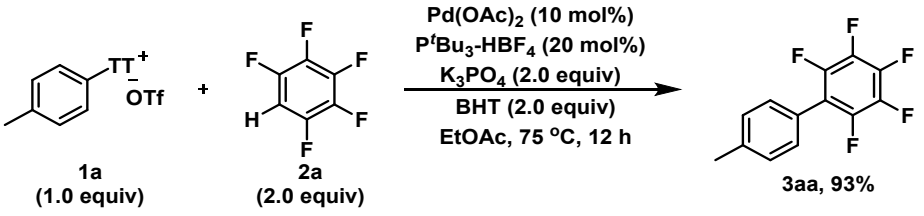
Applicability of ArTT tetrafluoroborate:



In a 38 mL sealed tube, the mixture of **1a-BF_4** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P^tBu_3-HBF_4 (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv) were added in 2.0 mL EtOAc. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **3aa** in 87% yield.

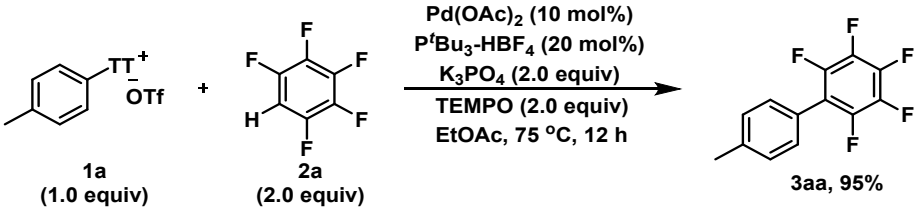
Mechanistic Investigations:

Free radical inhibition test:



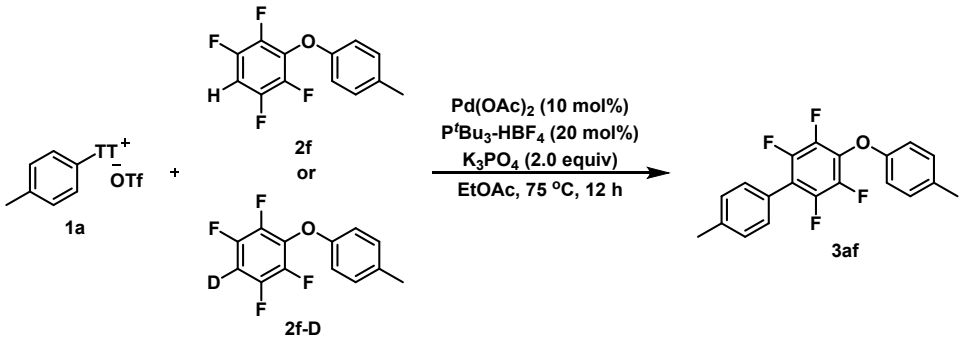
In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P^tBu_3-HBF_4 (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv), BHT (0.4 mmol, 2.0 equiv) were added in 2.0 mL EtOAc. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture in a 75 °C

heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **3aa** in 93% yield.



In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P^tBu_3-HBF_4 (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv), TEMPO (0.4 mmol, 2.0 equiv) were added in 2.0 mL EtOAc. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was in a 75 °C heating mantle for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the product **3aa** in 95% yield.

Kinetic isotope effect (KIE) experiments:



The reaction of **2f** or its deuterated form **2f-D** was carried out with **1a** in two tubes for the given time under the optimized conditions, respectively. The reaction mixtures were concentrated and then examined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Table S1. Yield determined while varying the reaction time (with **2f**)

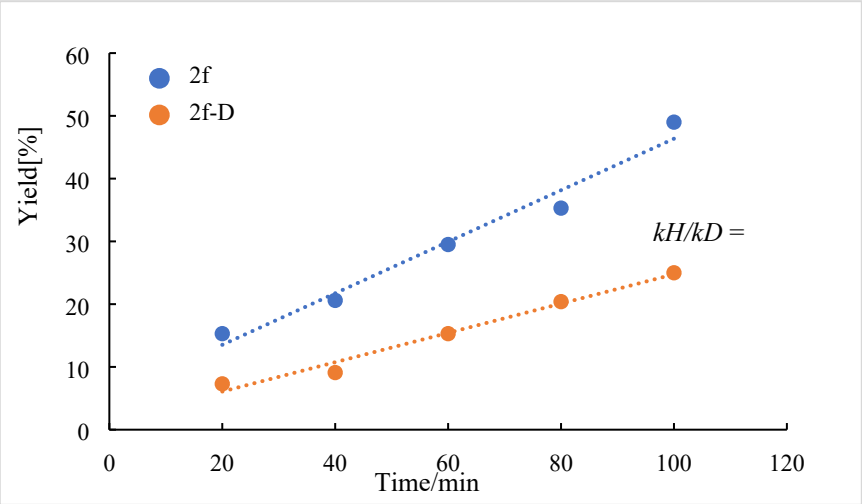
Entry	1	2	3	4	5
Reaction time (min)	20	40	60	80	100

Yield (%)	15.3	20.6	29.5	35.3	49.0

Table S2. Yield determined while varying the reaction time (with **2f-D**)

Entry	1	2	3	4	5
Reaction time (min)	20	40	60	80	100
Yield (%)	7.3	9.1	15.3	20.4	25.0

Figure S1. KIE measured from the parallel reactions of polyfluoroarenes (**2f** and **2f-D**) with **1a**.



Kinetic data: order in catalyst:

The order in catalyst's kinetic data was determined using the generally amounts of **1a** (45.7 mg, 0.1 mmol), **2a** (33.6 mg, 0.2 mmol), K_3PO_4 (42.5 mg, 0.2 mmol), a stock solution was prepared of $Pd(OAc)_2$ (0.002 mmol to 0.015 mmol), P^tBu_3-HBF_4 (0.004 mmol to 0.0300 mmol) in EtOAc (4.0 mL). Subsequently, 1.0 mL of the solution was added to corresponding test tubes respectively. The reactions were worked up by following the general procedure and the yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Table S3. Amounts of catalyst and results used to determine the order in catalyst

Entry	Concentration of catalyst	Reaction time (min)	Average yield (%)	**3aa** (mM)

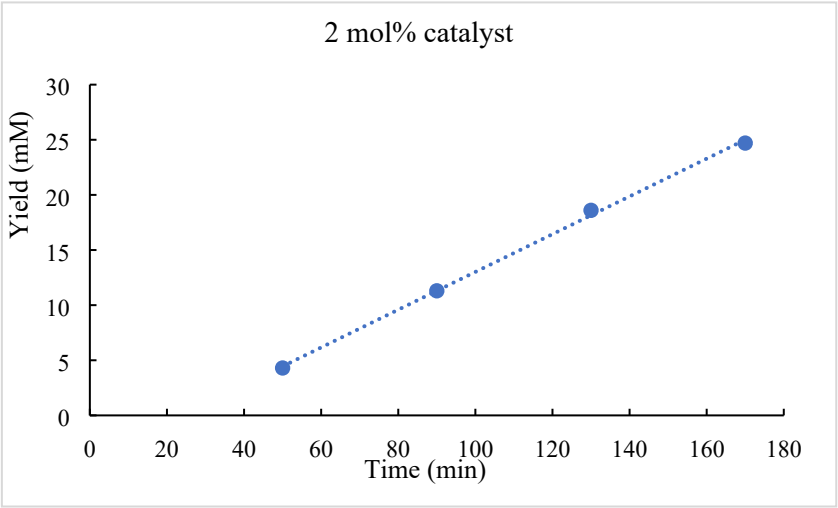
1	2.0 mol % Cat.	50	4.3	4.3
2	2.0 mol % Cat.	90	11.3	11.3
3	2.0 mol % Cat.	130	18.6	18.6
4	2.0 mol % Cat.	170	24.7	24.7

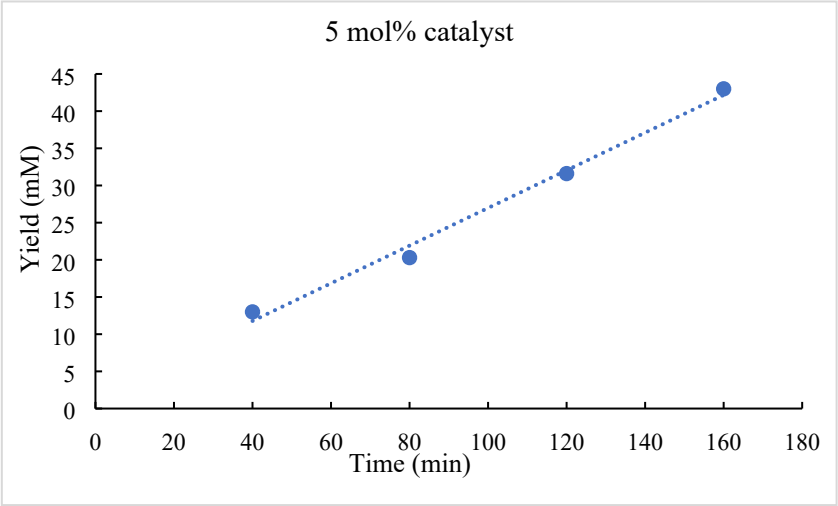
Entry	Concentration of catalyst	Reaction time (min)	Average yield (%)	**3aa** (mM)
1	5.0 mol % Cat.	40	13.0	13.0
2	5.0 mol % Cat.	80	20.3	20.3
3	5.0 mol % Cat.	120	31.6	31.6
4	5.0 mol % Cat.	160	43.0	43.0

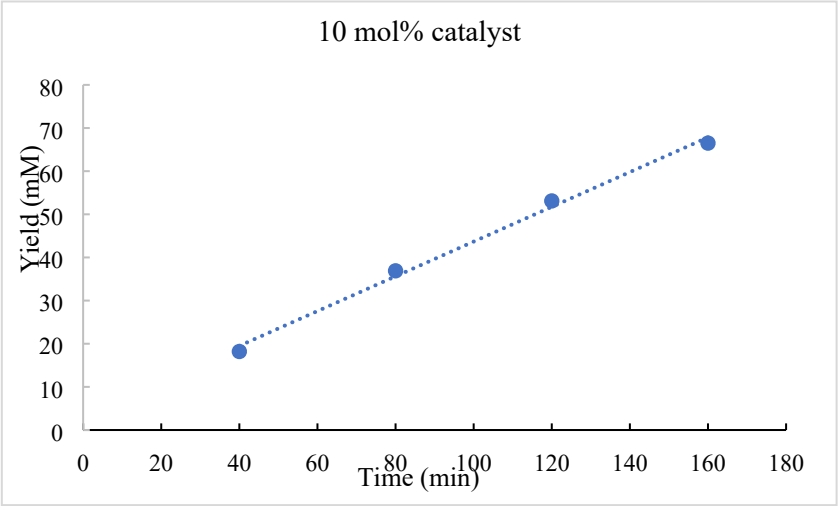
Entry	Concentration of catalyst	Reaction time (min)	Average yield (%)	**3aa** (mM)
1	10.0 mol % Cat.	40	18.2	18.2
2	10.0 mol % Cat.	80	36.9	36.9
3	10.0 mol % Cat.	120	53.1	53.1
4	10.0 mol % Cat.	160	66.5	66.5

Entry	Concentration of catalyst	Reaction time (min)	Average yield (%)	**3aa** (mM)
1	15.0 mol % Cat.	40	27.3	27.3
2	15.0 mol % Cat.	80	41.6	41.6
3	15.0 mol % Cat.	120	63.9	63.9
4	15.0 mol % Cat.	160	75.0	75.0

Figure S1. Plot of **3aa** (mM) verse time (min) using different concentrations of catalyst


2 mol% catalyst
Yield (mM)
30
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
Time (min)


5 mol% catalyst
Yield (mM)
45
40
35
30
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
Time (min)


10 mol% catalyst
Yield (mM)
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
Time (min)

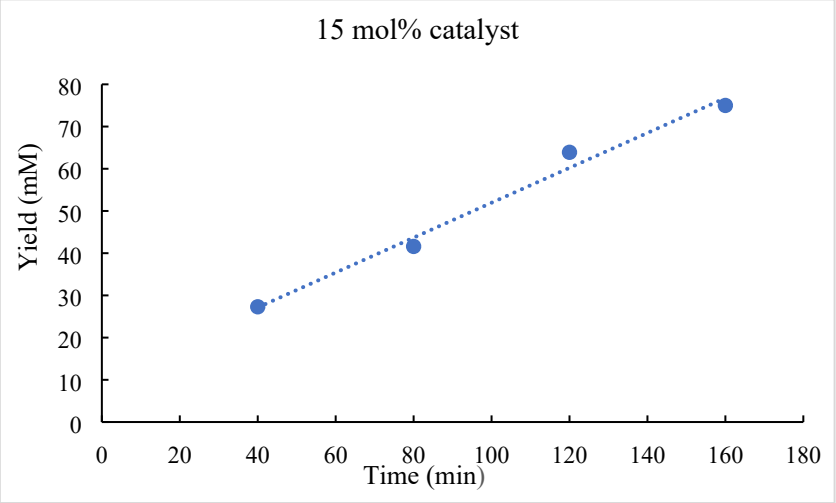
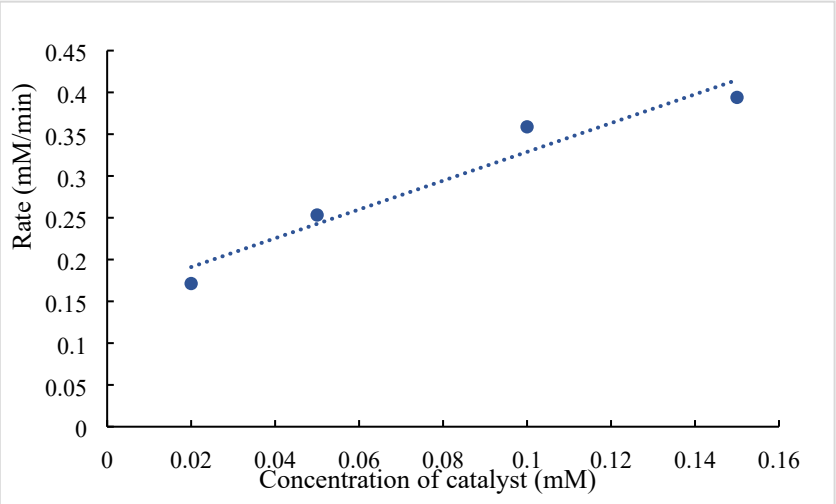


Table S4. Rates determined while varying the concentrations of catalyst

Entry	Concentration of catalyst	Rate (mM/min)
1	0.0200	0.1713
2	0.0500	0.2533
3	0.1000	0.3588
4	0.1500	0.3940

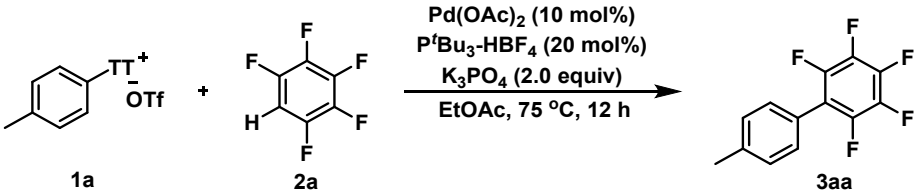
Figure S2. Rates determined while varying the concentrations of catalyst



Time-course of yield:

Seven reactions of **1a** and **2a** were carried out by following the general procedure of the coupling reaction. Each of the reactions was stopped at the times indicated in the following table. The reactions were worked up by following the general procedure

and the yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

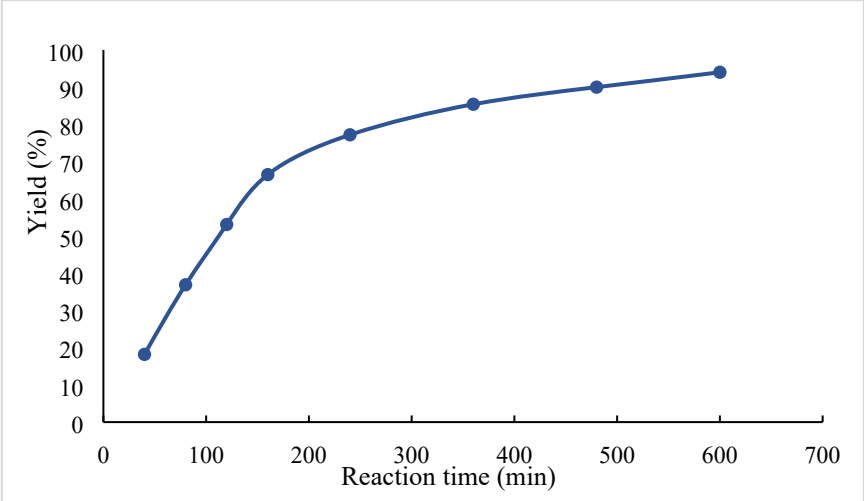


1a 2a 3aa

Table S5. Yield determined while varying the reaction time

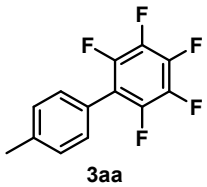
Entry	1	2	3	3	4	5	6	7
Reaction time (min)	40	80	120	160	240	360	480	600
Yield (%)	18.2	36.9	53.1	66.5	77.2	85.4	90.0	94.0

Figure S3. Yield determined while varying the reaction time



Characterization of Products:

2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl (3aa)[1]



3aa

Purification via silica gel column chromatography (petroleum ether) afforded **3aa**.

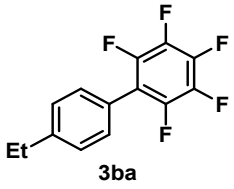
Yield: 96%, 49.6 mg; appearance: white solid; M.P.: 102-104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 4H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 145.3 (m), 143.0 – 142.9 (m), 141.6 – 141.3 (m), 139.4, 139.1 – 138.9 (m), 136.6 – 136.4 (m), 130.0, 129.4, 123.3, 116.1 – 115.8 (m), 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.39 (dd, *J* = 22.6, 7.5 Hz, 2F), -156.17 (t, *J* = 22.6 Hz, 1F), -161.65 to -163.30 (m, 2F).

4'-ethyl-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ba)



3ba

Purification via silica gel column chromatography (petroleum ether) afforded **3ba**.

Yield: 90%, 49.0 mg; appearance: white solid; M.P.: 78-80 °C.

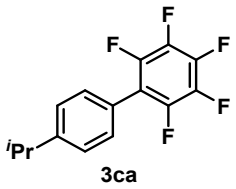
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 145.5 – 145.1 (m), 143.1 – 142.8 (m), 141.6 – 141.1 (m), 139.3 – 138.8 (m), 136.8 – 136.3 (m), 130.0, 128.2, 123.6, 116.2 – 115.7 (m), 28.7, 15.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.39 (dd, *J* = 23.3, 8.6 Hz, 2F), -156.21 (t, *J* = 21.1 Hz, 1F), -162.37 to -162.65 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ calcd for $C_{14}H_9F_5$ 272.0624, found 272.0618.

2,3,4,5,6-pentafluoro-4'-isopropyl-1,1'-biphenyl (3ca)[5]



3ca

Purification via silica gel column chromatography (petroleum ether) afforded **3ca**.

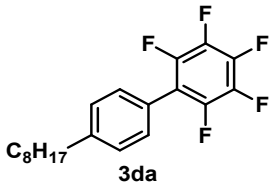
Yield: 92%, 52.7 mg; appearance: white solid; M.P.: 67-68 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 4H), 3.04 – 2.94 (m, 1H), 1.31 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 145.5 – 145.2 (m), 143.1 – 142.8 (m), 141.6 – 141.3 (m), 139.2 – 138.8 (m), 136.8 – 136.4 (m), 130.1, 126.8, 123.7, 116.2 – 115.7 (m), 34.0, 23.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.38 (dd, *J* = 23.3, 8.6 Hz, 2F), -156.22 (t, *J* = 21.1 Hz, 1F), -162.33 to -162.63 (m, 2F).

2,3,4,5,6-pentafluoro-4'-octyl-1,1'-biphenyl (3da)



3da

Purification via silica gel column chromatography (petroleum ether) afforded **3da**.

Yield: 95%, 67.7 mg; appearance: white solid; M.P.: 54-56 °C.

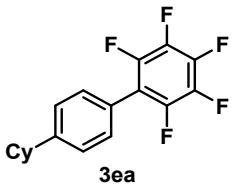
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.44 – 1.28 (m, 10H), 0.94 – 0.89 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6 (m), 144.4, 143.1 – 142.8 (m), 141.6 – 141.3 (m), 139.3 – 138.7 (m), 136.8 – 136.4 (m), 130.0, 128.7, 123.5, 116.2 – 115.7 (m), 35.8, 31.9, 31.3, 29.5, 29.4, 29.3, 22.7, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.38 (dd, *J* = 22.6, 7.5 Hz, 2F), -156.25 (t, *J* = 18.8 Hz, 1F), -162.40 to -162.63 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{20}H_{21}F_5$ 356.1563, found 356.1557.

4'-cyclohexyl-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ea)



3ea

Purification via silica gel column chromatography (petroleum ether) afforded **3ea**.

Yield: 99%, 64.6 mg; appearance: white solid; M.P.: 93-95 °C.

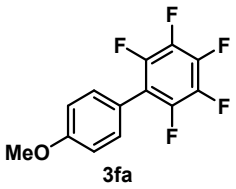
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 2.64 – 2.53 (m, 1H), 1.92 (dd, *J* = 21.2, 9.2 Hz, 4H), 1.80 (d, *J* = 12.8 Hz, 1H), 1.52 – 1.38 (m, 4H), 1.35 – 1.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 145.5 – 145.3 (m), 143.1 – 142.7 (m), 141.4 – 141.2 (m), 139.1 – 138.7 (m), 136.9 – 136.2 (m), 130.0, 127.2, 123.7, 116.0 – 115.8 (m), 44.4, 34.3, 26.8, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.37 (dd, *J* = 22.6, 7.5 Hz, 2F), -156.23 (t, *J* = 18.8 Hz, 1F), -162.40 to -162.60 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}F_5$ 327.1167, found 327.1170.

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



3fa

Purification via silica gel column chromatography (petroleum ether) afforded **3fa**.

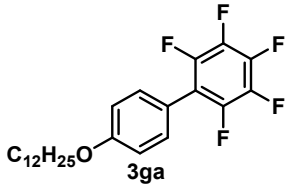
Yield: 95%, 52.1 mg; appearance: white solid; M.P.: 114-116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 145.5 – 145.2 (m), 143.0 – 142.8 (m), 141.3 – 141.1 (m), 139.1 – 138.8 (m), 136.7 – 136.4 (m), 131.4, 118.4, 115.7 – 115.5 (m), 114.2, 55.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.67 (dd, *J* = 22.6, 7.5 Hz, 2F), -156.50 (t, *J* = 18.8 Hz, 1F), -162.49 to -163.27 (m, 2F).

4'-(dodecyloxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ga)



3ga

Purification via silica gel column chromatography (petroleum ether) afforded **3ga**.

Yield: 87%, 74.6 mg; appearance: white solid; M.P.: 78-79 °C.

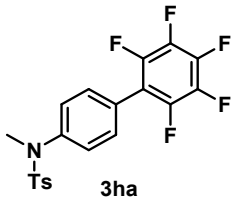
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.51 – 1.43 (m, 2H), 1.33 – 1.23 (m, 16H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 131.4, 114.7, 68.1, 31.9, 29.7, 29.6, 29.4, 29.2, 26.0, 22.7, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.64 (dd, *J* = 23.7, 8.6 Hz, 2F), -156.64 (t, *J* = 21.1 Hz, 1F), -162.49 to -162.70 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{24}H_{29}F_5O$ 428.2139, found 428.2133.

***N*,4-dimethyl-*N*-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)benzenesulfonamide (3ha)**



3ha

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **3ha**.

Yield: 81%, 69.2 mg; appearance: white solid; M.P.: 111-113 °C.

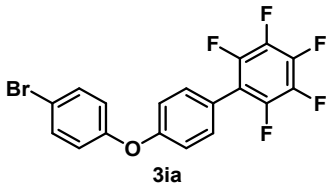
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.26 (m, 4H), 3.24 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7 – 144.8 (m), 143.9, 143.0 – 142.6 (m), 142.5, 141.8 – 141.3 (m), 139.3 – 139.0 (m), 138.9 – 138.7 (m), 136.6 – 136.3 (m), 133.1, 130.6, 129.4, 127.7, 126.3, 124.9, 37.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.10 (dd, *J* = 23.7, 9.0 Hz, 2F), -155.10 (t, *J* = 21.1 Hz, 1F), -161.90 to -162.15 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_5NO_2S$ 428.0738, found 428.0739.

4'-(4-bromophenoxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ia)[8]



3ia

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ia**.

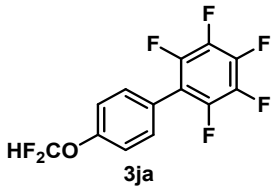
Yield: 54%, 44.8 mg; appearance: white solid; M.P.: 113-115 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 4H), 7.19 (d, *J* = 7.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 145.7 – 145.2 (m), 143.2 – 142.7 (m), 142.0 – 141.4 (m), 139.5 – 138.8 (m), 137.0 – 136.2 (m), 131.9, 121.6, 119.2, 115.5 – 115.0 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.33 (dd, *J* = 23.7, 8.6 Hz, 2F), -155.48 (t, *J* = 21.1 Hz, 1F), -161.91 to -162.21 (m, 2F).

4'-(difluoromethoxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ja)



3ja

Purification via silica gel column chromatography (petroleum ether) afforded **3ja**.

Yield: 70%, 43.4 mg; appearance: colourless oil.

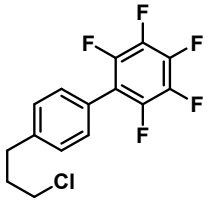
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.58 (t, *J* = 73.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8 – 151.7 (m), 145.5 – 145.2 (m), 143.1 – 142.7 (m), 141.9 – 141.7 (m), 139.4 – 139.0 (m), 131.8, 123.4, 119.7, 118.2, 115.6, 115.0 – 114.6 (m), 113.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.28 (d, *J* = 4.1 Hz, 2F), -143.31 (dd, *J* = 23.3, 8.6 Hz, 2F), -155.02 (t, *J* = 21.1 Hz, 1F), -161.80 to -162.10 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{13}H_5F_7O$ 310.0229, found 310.0223.

4'-(3-chloropropyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ka)



3ka

Purification via silica gel column chromatography (petroleum ether) afforded **3ka**.

Yield: 85%, 54.5 mg; appearance: white solid; M.P.: 68-70 °C.

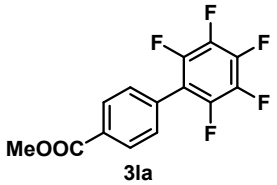
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 56.4 Hz, 4H), 3.54 (d, *J* = 53.6 Hz, 2H), 2.82 (d, *J* = 54.4 Hz, 2H), 2.10 (d, *J* = 52.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 145.2 (m), 143.0 – 142.7 (m), 142.1, 139.3 – 138.8 (m), 136.6 – 136.3 (m), 130.2, 128.9, 124.2, 115.8 – 115.7 (m), 44.1, 33.7, 32.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.36 (dd, *J* = 26.3, 11.3 Hz, 2F), -155.88 (t, *J* = 18.8 Hz, 1F), -162.23 to -162.47 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{15}H_{10}ClF_5$ 320.0391, found 320.0385.

methyl 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-carboxylate (3la)[2]



3la

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3la**.

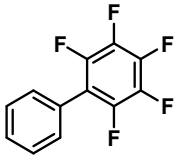
Yield: 91%, 55.0 mg; appearance: white solid; M.P.: 107-109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 145.5 – 145.0 (m), 143.1 – 142.4 (m), 139.6 – 138.8 (m), 130.9, 130.2, 129.8, 115.2 – 114.7 (m), 52.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.78 to -142.00 (m, 2F), -154.13 (t, *J* = 21.1 Hz, 1F), -160.58 to -162.65 (m, 2F).

2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ma)[6]



3ma

Purification via silica gel column chromatography (petroleum ether) afforded **3ma**.

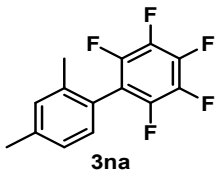
Yield: 93%, 45.4 mg; appearance: white solid; M.P.: 96-98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 145.2 (m), 143.3 – 142.7 (m), 141.8 – 141.4 (m), 139.3 – 140.0 (m), 137.0 – 136.2 (m), 130.1, 129.3, 128.7, 126.4, 116.2 – 115.1 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.29 (dd, J = 22.6, 11.3 Hz, 2F), -155.67 (t, J = 18.8 Hz, 1F), -162.15 to -162.40 (m, 2F).

2,3,4,5,6-pentafluoro-2',4'-dimethyl-1,1'-biphenyl (3na)[6]



3na

Purification via silica gel column chromatography (petroleum ether) afforded **3na**.

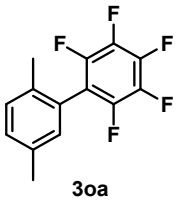
Yield: 68%, 37.0 mg; appearance: colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.15 – 7.06 (m, 2H), 2.40 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 145.1 (m), 143.0 – 142.7 (m), 141.9 – 141.5 (m), 139.6, 139.5 – 138.6 (m), 137.1, 136.7 – 136.1 (m), 131.3, 130.4, 126.8, 122.8, 115.8 – 115.2 (m), 21.2, 19.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -140.59 (dd, J = 22.6, 7.5 Hz, 2F), -155.74 (t, J = 18.8 Hz, 1F), -162.30 to -162.50 (m, 2F).

2,3,4,5,6-pentafluoro-2',5'-dimethyl-1,1'-biphenyl (3oa)[4]



3oa

Purification via silica gel column chromatography (petroleum ether) afforded **3oa**.

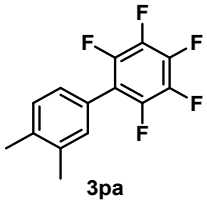
Yield: 78%, 42.5 mg; appearance: white solid; M.P.: 58-60 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 2.41 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4 – 145.1 (m), 143.0 – 142.6 (m), 142.0 – 141.5 (m), 139.3 – 138.6 (m), 136.6 – 136.1 (m), 135.6, 134.2, 131.0, 130.4, 130.4, 125.6, 115.8 – 115.4 (m), 20.8, 19.1

^{19}F NMR (376 MHz, $CDCl_3$) δ -140.62 (dd, *J* = 24.1, 9.0 Hz, 2F), -155.70 (t, *J* = 21.1 Hz, 1F), -162.31 to -162.52 (m, 2F).

2,3,4,5,6-pentafluoro-3',4'-dimethyl-1,1'-biphenyl (3pa)[4]



3pa

Purification via silica gel column chromatography (petroleum ether) afforded **3pa**.

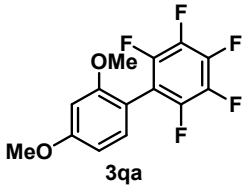
Yield: 83%, 45.2 mg; appearance: white solid; M.P.: 60-62 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.17 (m, 2H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 145.1 (m), 143.2 – 142.7 (m), 139.0 – 138.9 (m), 138.1, 137.1, 131.1, 130.0, 127.5, 123.7, 19.8, 19.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.25 (dd, *J* = 22.6, 7.5 Hz, 2F), -156.38 (t, *J* = 22.6 Hz, 1F), -162.40 to -162.80 (m, 2F).

2,3,4,5,6-pentafluoro-2',4'-dimethoxy-1,1'-biphenyl (3qa)[6]



3qa

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3qa**.

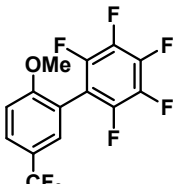
Yield: 84%, 51.1 mg; appearance: white solid; M.P.: 84-85 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 1H), 6.63 – 6.58 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 158.2, 145.9 – 145.6 (m), 143.5 – 143.1 (m), 139.1 – 138.5 (m), 136.5 – 136.0 (m), 132.2, 112.7 – 112.6 (m), 107.5, 104.8, 98.9, 55.6, 55.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -140.40 (dd, *J* = 24.8, 9.4 Hz, 2F), -156.69 to -156.89 (m, 1F), -162.35 to -163.65 (m, 2F).

2,3,4,5,6-pentafluoro-2'-methoxy-5'-(trifluoromethyl)-1,1'-biphenyl (3ra)



3ra

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ra**.

Yield: 81%, 55.4 mg; appearance: white solid; M.P.: 102-104 °C.

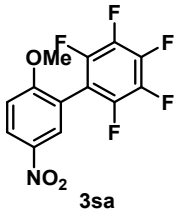
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 145.8 – 145.4 (m), 143.4 – 143.0 (m), 140.0 – 139.5 (m), 139.1 – 138.7 (m), 136.6 – 136.1 (m), 129.0 (q, *J* = 3.0 Hz), 128.6 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 270.0 Hz), 123.2, 122.9, 115.9, 111.2, 56.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.71 (s, 3F), -139.95 to -140.00 (m, 2F), -154.71 to -154.85 (m, 1F), -162.51 to -163.69 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{14}H_6F_8O$ 342.0291, found 342.0285.

2,3,4,5,6-pentafluoro-5'-methoxy-2'-nitro-1,1'-biphenyl (3sa)



3sa

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3sa**.

Yield: 65%, 41.5 mg; appearance: white solid; M.P.: 97-99 °C.

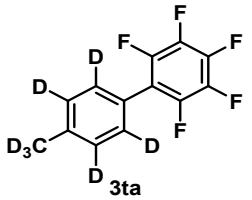
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 9.2, 2.8 Hz, 1H), 8.18 (d, *J* = 2.8 Hz, 1H), 7.12 (d, *J* = 9.2 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 145.7 – 145.4 (m), 143.3 – 143.0 (m), 142.7 – 142.3 (m), 141.2, 140.2 – 139.7 (m), 139.1 – 138.7 (m), 136.6 – 136.1 (m), 127.7, 127.3, 116.1, 111.0, 56.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.50 to -139.95 (m, 2F), -153.66 (t, *J* = 21.1 Hz, 1F), -161.82 to -162.18 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{13}H_6F_5NO_3$ 319.0268, found 319.0262.

2,3,4,5,6-pentafluoro-4'-(methyl-*d_3*)-1,1'-biphenyl-2',3',5',6'-*d_4* (3ta)



3ta

Purification via silica gel column chromatography (petroleum ether) afforded **3ta**.

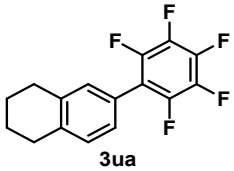
Yield: 93%, 49.3 mg; appearance: white solid; M.P.: 110-112 °C.

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6 – 145.2 (m), 143.1 – 142.8 (m), 141.5 – 141.4 (m), 139.3 – 138.8 (m), 136.8 – 136.4 (m), 129.9 – 129.8 (m), 129.7 – 129.5 (m), 129.4 – 129.2 (m), 129.1 – 129.0 (m), 128.9 – 128.7 (m), 123.2 – 123.1 (m), 20.6 – 20.1 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.46 (dd, *J* = 23.3, 8.6 Hz, 2F), -156.25 (t, *J* = 21.1 Hz, 1F), -162.40 to -162.64 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{13}D_7F_5$ 265.0907, found 265.0902.

6-(perfluorophenyl)-1,2,3,4-tetrahydronaphthalene (3ua)[4]



3ua

Purification via silica gel column chromatography (petroleum ether) afforded **3ua**.

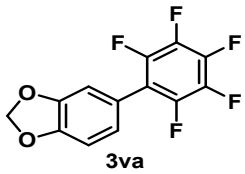
Yield: 97%, 57.9 mg; appearance: white solid; M.P.: 84-86 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 2.89 – 2.81 (m, 4H), 1.89 – 1.83 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 – 145.2 (m), 143.2 – 142.7 (m), 141.5 – 141.1 (m), 139.4 – 138.8 (m), 138.7, 137.7, 136.8 – 136.2 (m), 130.7, 129.5, 127.0, 123.3, 116.6 – 115.8 (m), 29.34, 29.26, 23.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.10 to -143.40 (m, 2F), -156.39 (t, *J* = 21.4 Hz, 1F), -162.45 to -162.70 (m, 2F).

5-(perfluorophenyl)benzo[*d*][1,3]dioxole (3va)[1]



3va

Purification via silica gel column chromatography (petroleum ether) afforded **3va**.

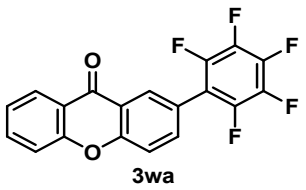
Yield: 95%, 54.8 mg; appearance: white solid; M.P.: 81-82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.87 (m, 3H), 6.04 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 148.0, 145.5 – 145.4 (m), 143.1 – 142.7 (m), 141.6 – 140.6 (m), 139.2 – 138.6 (m), 136.9 – 136.3 (m), 124.2, 119.4, 115.7 – 115.5 (m), 110.3, 108.6, 101.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -141.25 to -144.15 (m, 2F), -155.90 to -156.20 (m, 1F), -162.20 to -162.55 (m, 2F).

2-(perfluorophenyl)-9*H*-xanthen-9-one (3wa)[8]



3wa

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3wa**.

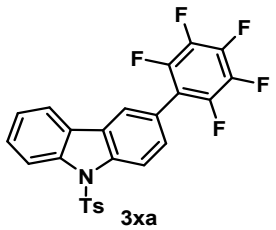
Yield: 82%, 59.4 mg; appearance: white solid; M.P.: 204-206 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.35 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.81 – 7.73 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 156.3, 156.1, 145.6 – 145.3 (m), 143.1 – 142.7 (m), 142.2 – 141.6 (m), 139.5 – 139.0 (m), 136.9 – 136.4 (m), 136.1, 135.2, 128.9, 126.8, 124.4, 122.2, 122.0, 121.8, 118.8, 118.1, 114.7 – 114.2 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.03 (dd, *J* = 23.7, 9.0 Hz, 2F), 154.33 (t, *J* = 21.8 Hz, 1F), -161.40 to -161.76 (m, 2F).

3-(perfluorophenyl)-9-tosyl-9*H*-carbazole (3xa)



3xa

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3xa**.

Yield: 72%, 70.2 mg; appearance: white solid; M.P.: 238-240 °C.

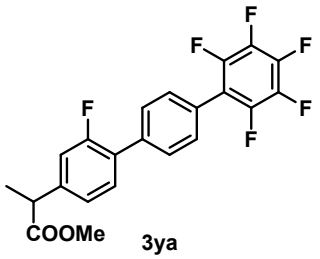
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.00 – 7.89 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4 – 145.1 (m), 139.2 – 138.4 (m), 135.1 – 134.9 (m), 129.8, 129.1, 128.0, 126.6, 124.1, 121.9, 121.8, 120.2, 115.2, 115.1, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.85 to -143.35 (m, 2F), -155.16 to -155.44 (m, 1F), -161.75 to -162.20 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{15}F_5NO_2S$ 488.0738, found 488.0738.

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



3ya

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ya**.

Yield: 89%, 75.5 mg; appearance: white solid; M.P.: 128-129 °C.

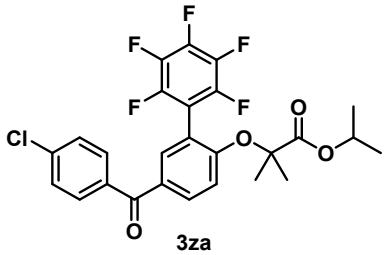
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.18 (t, *J* = 10.0 Hz, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 1.56 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 160.9, 158.5, 145.9 – 144.9 (m), 143.2 – 142.7 (m), 142.5 (d, *J* = 7.0 Hz), 141.7 –141.4 (m), 139.2 – 138.7 (m), 137.0 – 136.1 (m), 130.7 (d, *J* = 3.0 Hz), 130.2, 129.1 (d, *J* = 1.0 Hz), 126.7 (d, *J* = 13.0 Hz), 125.6, 123.7 (d, *J* = 3.0 Hz), 115.5, 115.2, 52.2, 44.9, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.28 (s, 1F), -143.10 (dd, *J* = 23.7, 9.0 Hz, 2F), -155.34 to -155.48 (m, 1F), -162.05 to -162.21 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{15}F_6O_2$ 425.0971, found 425.0973.

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



3za

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3za**.

Yield: 74%, 78.0 mg; appearance: colourless oil.

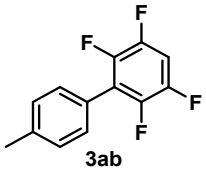
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 3H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.11 – 5.01 (m, 1H), 1.59 (s, 6H), 1.19 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 172.6, 157.2, 138.7, 135.9, 134.6, 132.7 131.9, 131.2, 129.8, 128.7, 117.2, 114.9, 80.2, 69.6, 25.0, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.42 (dd, *J* = 23.7, 8.6 Hz, 2F), -154.94 (t, *J* = 21.4 Hz, 1F), -162.56 to -162.86 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}ClF_5O_4$ 527.1043, found 527.1043.

2,3,5,6-tetrafluoro-4'-methyl-1,1'-biphenyl (3ab)[3]



3ab

Purification via silica gel column chromatography (petroleum ether) afforded **3ab**.

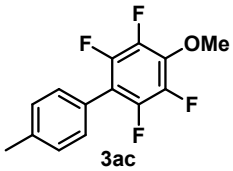
Yield: 85%, 40.8 mg; appearance: white solid; M.P.: 81-83 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.11 – 6.98 (m, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 – 147.3 (m), 145.1 – 144.8 (m), 142.6 – 142.4 (m), 139.3, 129.9, 129.3, 124.4, 121.7 – 121.5 (m), 104.7 – 104.3 (m), 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.37 (dd, *J* = 22.6, 11.3 Hz, 2F), -144.02 (dd, *J* = 22.6, 15.0 Hz, 2F).

2,3,5,6-tetrafluoro-4-methoxy-4'-methyl-1,1'-biphenyl (3ac)[2]



3ac

Purification via silica gel column chromatography (petroleum ether) afforded **3ac**.

Yield: 90%, 48.6 mg; appearance: white solid; M.P.: 37-39 °C.

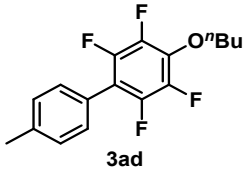
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 4.12 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 – 145.3 (m), 143.3 – 142.8 (m), 142.5 – 142.1

(m), 140.1 – 139.8 (m), 138.9, 137.4 – 137.0 (m), 130.0, 129.3, 124.2, 114.3 (t, *J* = 17.0 Hz), 62.2, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -145.28 (dd, *J* = 22.2, 9.0 Hz, 2F), -158.37 (dd, *J* = 22.6, 9.4 Hz, 2F).

4-butoxy-2,3,5,6-tetrafluoro-4'-methyl-1,1'-biphenyl (3ad)[7]



3ad

Purification via silica gel column chromatography (petroleum ether) afforded **3ad**.

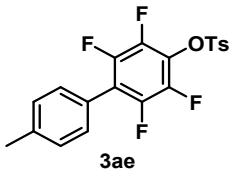
Yield: 92%, 48.6 mg; appearance: white solid; M.P.: 44-46 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.87 – 1.75 (m, 2H), 1.61 – 1.48 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7 – 145.2 (m), 143.2 – 142.8 (m), 140.4 – 140.2 (m), 138.8, 136.7 – 136.6 (m), 130.0, 129.3, 124.3, 114.4 – 114.2 (m), 75.1 (t, *J* = 3.0 Hz), 31.9, 21.3, 18.8, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -145.49 (dd, *J* = 22.6, 11.3 Hz, 2F), -157.70 (dd, *J* = 22.6, 11.3 Hz, 2F).

2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-yl 4-methylbenzenesulfonate (3ae)



3ae

Purification via silica gel column chromatography (petroleum ether) afforded **3ae**.

Yield: 57%, 46.8 mg; appearance: white solid; M.P.: 111-113 °C.

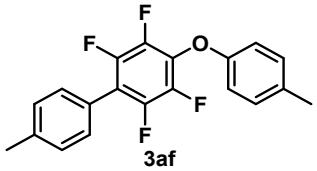
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 4H), 2.51 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 130.1, 129.9, 129.4, 128.6, 21.9, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.88 to -143.13 (m, 2F), -151.60 to -151.92 (m, 2F).

HRMS(APCI) m/z: $[M–H]^+$ Calcd for $C_{20}H_{13}F_4O_3S$ 409.0527, found 409.0527.

2,3,5,6-tetrafluoro-4'-methyl-4-(p-tolyloxy)-1,1'-biphenyl (3af)



3af

Purification via silica gel column chromatography (petroleum ether) afforded **3af**.

Yield: 95%, 65.8 mg; appearance: white solid; M.P.: 119-121 °C.

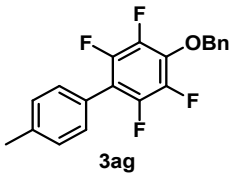
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 145.8 – 145.3 (m), 143.2 – 142.9 (m), 140.8 – 140.4 (m), 139.2, 133.2, 130.2, 130.0, 129.4, 124.0, 115.5, 21.3, 20.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -144.10 (dd, *J* = 15.0, 11.3 Hz, 2F), -154.80 to -155.00 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{20}H_{14}F_4O$ 346.0981, found 346.0975.

4-(benzyloxy)-2,3,5,6-tetrafluoro-4'-methyl-1,1'-bipheny (3ag)[7]



3ag

Purification via silica gel column chromatography (petroleum ether) afforded **3ag**.

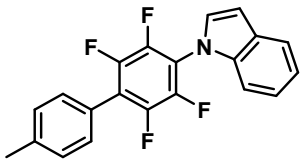
Yield: 87%, 60.3 mg; appearance: white solid; M.P.: 116-118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.31 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6 – 145.2 (m), 143.1 – 142.6 (m), 140.5 – 140.2 (m), 138.9, 135.7, 130.0, 129.3, 128.8, 128.6, 128.3, 124.2, 114.7 (t, *J* = 17.0 Hz), 76.4 (t, *J* = 4.0 Hz), 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -145.08 to -145.29 (m, 2F), -156.46 to -156.76 (m, 2F).

1-(2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-yl)-1*H*-indole (3ah)[7]



3ah

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ah**.

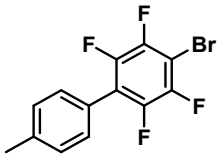
Yield: 85%, 60.3 mg; appearance: white solid; M.P.: 131-133 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.45 – 7.30 (m, 6H), 6.90 – 6.85 (m, 1H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 – 145.4 (m), 144.4 – 144.1 (m), 143.3 – 142.9 (m), 141.9 – 141.6 (m), 139.6, 136.3, 130.0, 129.5, 128.7, 128.3, 123.8, 123.1, 121.2, 120.1 – 119.7 (m), 117.5 – 117.1 (m), 110.5, 105.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.75 to -143.05 (m, 2F), -146.50 to -146.76 (m, 2F).

4-bromo-2,3,5,6-tetrafluoro-4'-methyl-1,1'-biphenyl (3ai)



3ai

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ai**.

Yield: 45%, 28.7 mg; appearance: white solid; M.P.: 103-105 °C.

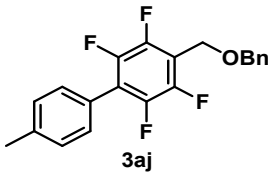
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 – 145.1 (m), 143.9 – 143.6 (m), 143.0 – 142.6 (m), 139.5, 129.8, 129.4, 123.9, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.78 (td, *J* = 13.2, 4.9 Hz, 2F), -142.18 (td, *J* = 13.2, 4.5 Hz, 2F).

HRMS(APCI) m/z: $[M+H]^+$ $C_{13}H_8BrF_4$ 318.9740, found 318.9740.

4-((benzyloxy)methyl)-2,3,5,6-tetrafluoro-4'-methyl-1,1'-biphenyl (3aj)



3aj

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3aj**.

Yield: 93%, 67.0 mg; appearance: white solid; M.P.: 75-77 °C.

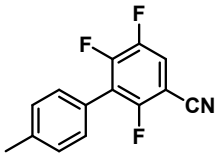
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 9H), 4.71 (s, 2H), 4.63 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.5, 129.9, 129.3, 128.5, 127.9, 127.8, 124.3, 121.0, 124.4 – 124.2 (m), 120.1 – 120.9 (m), 115.0 – 114.6 (m), 72.9, 59.3, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.89 to -144.05 (m, 2F), -144.20 to -144.37 (m, 2F).

HRMS(APCI) m/z: $[M–H]^+$ Calcd for $C_{21}H_{15}F_4O$ 359.1064, found 359.1058.

2,5,6-trifluoro-4'-methyl-[1,1'-biphenyl]-3-carbonitrile (3ak)[2]



3ak

Purification via silica gel column chromatography (petroleum ether) afforded **3ak**.

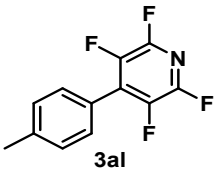
Yield: 87%, 43.0 mg; appearance: white solid; M.P.: 80-82 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 – 8.24 (m, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 139.5, 129.8, 129.4, 123.0, 121.3 – 120.7 (m), 120.2, 120.0, 112.8, 20.9.

^{19}F NMR (376 MHz, DMSO-d_6) δ -112.61 (dd, J = 11.3, 7.5 Hz, 1F), -127.18 (dd, J = 22.6, 7.5 Hz, 1F), -139.01 (dd, J = 22.6, 15.0 Hz, 1F).

2,3,5,6-tetrafluoro-4-(*p*-tolyl)pyridine (3al)[1]



3al

Purification via silica gel column chromatography (petroleum ether) afforded **3al**.

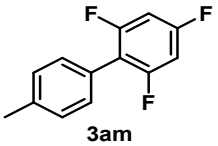
Yield: 98%, 47.3 mg; appearance: white solid; M.P.: 98-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 144.9 (m), 143.0 – 142.6 (m), 141.0, 138.2 – 137.7 (m),133.6 – 133.5 (m), 129.6, 122.9, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.06 (td, *J* = 30.5, 14.7 Hz, 2F), -145.34 (td, *J* = 30.1, 14.3 Hz, 2F).

2,4,6-trifluoro-4'-methyl-1,1'-biphenyl (3am)[3]



3am

Purification via silica gel column chromatography (petroleum ether) afforded **3am**.

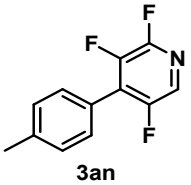
Yield: 54%, 24.0 mg; appearance: white solid; M.P.: 70-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.82 – 6.73 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 – 162.7 (m), 161.6 – 161.4 (m), 159.2 – 158.9 (m), 138.3, 130.1, 129.1, 125.3, 115.2 – 114.9 (m), 100.8 – 100.0 (m), 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.56 to -109.61 (m, 1F), -111.39 to -111.43 (m, 2F).

2,3,5-trifluoro-4-(*p*-tolyl)pyridine (3an)[2]



3an

Purification via silica gel column chromatography (petroleum ether) afforded **3an**.

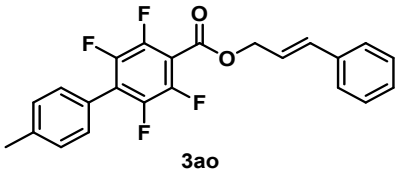
Yield: 42%, 18.7 mg; appearance: white solid; M.P.: 55-57 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4 – 155.2 (m), 152.8 – 152.6 (m), 150.2 – 150.0 (m), 147.9 – 147.5 (m), 140.4, 129.7, 129.5, 128.8 – 128.2 (m), 123.3 – 123.2 (m), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.31 to -89.40 (m, 1F), -132.70 to -132.86 (m, 1F), -141.00 to -141.20 (m, 1F).

cinnamyl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-carboxylate (3ao)



3ao

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ao**.

Yield: 90%, 72.1 mg; appearance: white solid; M.P.: 93-95 °C.

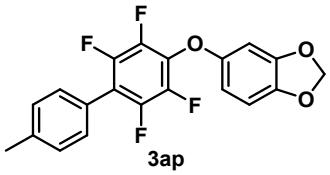
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.39 – 7.34 (m, 4H), 7.32 – 7.25 (m, 3H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.42 – 6.34 (m, 1H), 5.06 (dd, *J* = 6.4, 1.2 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 146.5 – 146.1 (m), 145.3 – 144.9 (m), 143.9 – 143.6 (m), 142.8 – 142.4 (m), 139.9, 135.9, 135.2, 129.8, 129.4, 128.6, 128.3, 126.7, 124.1 – 123.7 (m), 121.8, 111.2 – 110.8 (m), 67.0, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.46 to -139.74 (m, 2F), -142.48 to -142.84 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{23}H_{16}F_4O_2$ 400.1086, found 400.1081.

5-((2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-yl)oxy)benzo[*d*][1,3]dioxole (3ap)



3ap

Purification via silica gel column chromatography (petroleum ether) afforded **3ap**.

Yield: 87%, 65.5 mg; appearance: white solid; M.P.: 140-142 °C.

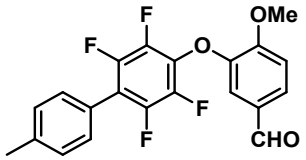
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.50 – 6.46 (m, 1H), 5.98 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 148.4, 145.7 – 145.2 (m), 143.9, 143.3 – 142.8 (m), 140.8 – 140.3 (m), 139.2, 130.0, 129.4, 108.0, 107.8, 101.7, 99.1, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.96 (dd, *J* = 22.6, 11.3 Hz, 2F), -155.11 (dd, *J* = 22.6, 11.3 Hz, 2F).

HRMS(APCI) m/z: $[M+H]^+$ $C_{20}H_{13}F_4O_3$ 377.0795, found 377.0800.

4-methoxy-3-((2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-yl)oxy)benzaldehyde (3aq)



3aq

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) afforded **3aq**.

Yield: 93%, 72.6 mg; appearance: white solid; M.P.: 184-186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.67 – 7.62 (m, 1H), 7.42 – 7.36 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 4.03 (s, 3H), 2.43 (s, 3H).

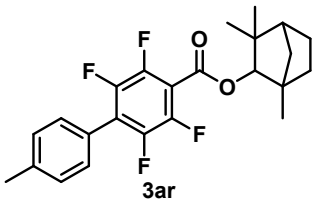
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 154.6, 146.9, 139.3, 130.0, 129.8, 129.4, 129.2, 123.7, 117.2, 114.1, 112.0, 56.4, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.46 to -143.71 (m, 2F), -155.22 to -155.40 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}F_4O_3$ 391.0952, found 391.0952.

1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-

biphenyl]-4-carboxylate (3ar)



3ar

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ar**.

Yield: 95%, 79.9 mg; appearance: white solid; M.P.: 79-81 °C.

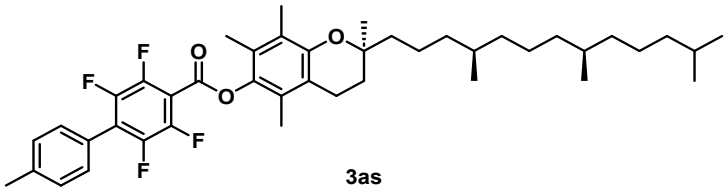
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.68 (d, *J* = 1.2 Hz, 1H), 2.44 (s, 3H), 1.88 – 1.79 (m, 2H), 1.79 – 1.71 (m, 1H), 1.68 (d, *J* = 10.4 Hz, 1H), 1.56 – 1.45 (m, 1H), 1.28 (d, *J* = 10.0 Hz, 1H), 1.23 (s, 3H), 1.21 – 1.14 (m, 4H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 146.4 – 146.0 (m), 145.3 – 145.0 (m), 143.8 – 143.5 (m), 142.8 – 142.4 (m), 139.8, 129.9, 129.4, 123.7 – 123.3 (m), 111.5, 89.4, 48.4, 48.3, 41.3, 39.6, 29.6, 26.6, 25.7, 21.4, 20.1, 19.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.63 to -139.81 (m, 2F), -142.76 to -142.97 (m, 2F).

HRMS(APCI) m/z: $[M–H]^+$ Calcd for $C_{24}H_{23}F_4O_2$ 419.1639, found 419.1640.

(*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-carboxylate (3as)



3as

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3as**.

Yield: 99%, 138.0 mg; appearance: white solid; M.P.: 180-182 °C.

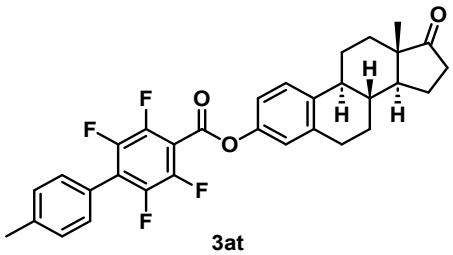
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.16 (s, 6H), 2.12 (s, 3H), 1.90 – 1.75 (m, 2H), 1.64 – 1.48 (m, 4H), 1.46 – 1.34 (m, 4H), 1.29 – 1.25 (m, 7H), 1.20 – 1.02 (m, 7H), 0.92 – 0.82 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 150.0, 146.4 – 146.1 (m), 145.3 – 145.0 (m), 143.8 – 143.4 (m), 142.9 – 142.5 (m), 140.3, 140.0, 129.9, 129.5, 126.5, 124.8, 124.3 – 123.8 (m), 123.6, 123.4, 117.7, 111.4 – 110.9 (m), 75.2, 39.4, 37.7 – 37.2 (m), 32.8, 32.7, 31.0, 28.0, 24.8, 24.4, 22.7, 22.6, 21.4, 21.0, 20.7, 19.74, 19.68, 13.0, 12.1, 11.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -138.95 to 139.20 (m, 2F), -142.25 to 142.49 (m, 2F).

HRMS(APCI) m/z: $[H]^+$ Calcd for $C_{43}H_{56}F_4O_3$ 696.4166, found 696.4160.

(8*S*,9*S*,13*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-carboxylate (3at)



3at

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **3at**.

Yield: 82%, 88.0 mg; appearance: white solid; M.P.: 192-194 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 5H), 7.07 – 6.99 (m, 2H), 2.97 (dd, *J* = 8.8, 4.0 Hz, 2H), 2.57 – 2.48 (m, 1H), 2.44 (s, 3H), 2.37 – 2.29 (m, 1H), 2.22 – 2.04 (m, 3H), 2.01 – 1.96 (m, 1H), 1.71 – 1.56 (m, 4H), 1.54 – 1.42 (m, 3H), 0.93 (s, 3H).

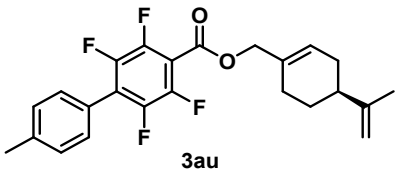
^{13}C NMR (100 MHz, $CDCl_3$) δ 220.7, 148.1, 140.1, 138.4, 138.3, 129.9, 129.5, 126.6, 123.6 – 123.5 (m), 121.3, 118.5, 50.4, 47.9, 44.2, 38.0, 35.8, 31.5, 29.4, 26.3, 25.8, 21.6, 21.4, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -138.90 to -139.15 (m, 2F), -142.25 to -142.50 (m, 2F).

HRMS(APCI) m/z: $[H]^+$ Calcd for $C_{32}H_{28}F_4O_3$ 536.1975, found 536.1970.

(*S*)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 2,3,5,6-tetrafluoro-4'-methyl-

[1,1'-biphenyl]-4-carboxylate (3au)



3au

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3au**.

Yield: 96%, 80.3 mg; appearance: white solid; M.P.: 70-72 °C.

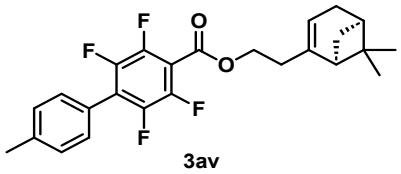
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.90 (s, 1H), 4.83 – 4.78 (m, 2H), 4.76 – 4.71 (m, 2H), 2.43 (s, 3H), 2.23 – 2.14 (m, 4H), 2.07 – 1.98 (m, 1H), 1.92 – 1.85 (m, 1H), 1.75 (s, 3H), 1.57 – 1.50 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 149.4, 146.4 – 146.1 (m), 145.2 – 145.0 (m), 143.8 – 143.5 (m), 142.8 – 142.5 (m), 139.9, 131.7, 129.8, 129.4, 127.4, 127.3, 123.7 – 123.5 (m), 111.4 – 111.2 (m), 108.9, 70.6, 40.7, 30.5, 27.2, 26.3, 21.4, 21.3, 20.74, 20.69.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.62 to -139.94 (m, 2F), -142.60 to -142.95 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}F_4O_2$ 419.1629, found 419.1629.

2-((1*S*,5*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-carboxylate (3av)



3av

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3av**.

Yield: 97%, 83.9 mg; appearance: white solid; M.P.: 72-74 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 1H), 4.48 – 4.37 (m, 2H), 2.47 – 2.39 (m, 6H), 2.30 – 2.20 (m, 2H), 2.11 (d, *J* = 5.6 Hz, 2H), 1.30 (s, 3H), 1.19 (d, *J* = 8.4 Hz, 1H), 0.85 (s, 3H).

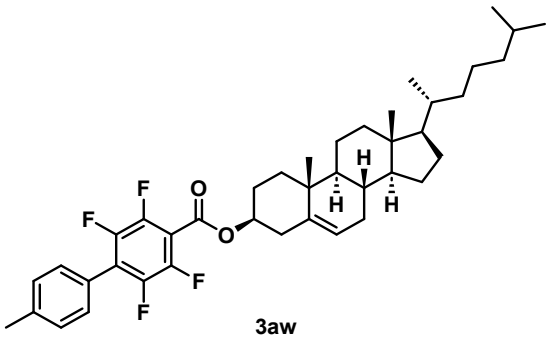
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 146.3 – 146.0 (m), 145.2 – 144.9 (m), 143.7 –

143.5 (m), 143.3, 142.7 – 142.4 (m), 139.8, 129.8, 129.4, 123.6, 119.4, 111.5 – 111.2 (m), 64.8, 45.6, 40.6, 38.0, 35.7, 31.6, 31.3, 26.2, 21.4, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -136.65 to -140.62 (m, 2F), -142.65 to -43.00 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{25}F_4O_2$ 433.1785, found 433.1785.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-carboxylate (3aw)



3aw

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3aw**.

Yield: 91%, 118.8 mg; appearance: white solid; M.P.: 199-121 °C.

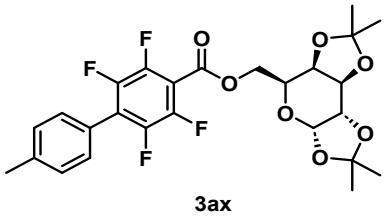
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.46 (d, *J* = 3.6 Hz, 1H), 5.02 – 4.90 (m, 1H), 2.54 – 2.47 (m, 2H), 2.43 (s, 3H), 2.08 – 1.70 (m, 6H), 1.63 – 1.45 (m, 5H), 1.40 – 1.09 (m, 12H), 1.06 (s, 3H), 1.04 – 0.97 (m, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 6H), 0.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 146.1 – 145.9 (m), 145.1 – 144.9 (m), 143.6 – 143.4 (m), 142.7 – 142.5 (m), 139.8, 139.1, 129.9, 129.4, 123.7, 123.2, 112.0 – 111.6 (m), 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.9, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.7, 24.3, 23.8, 22.8, 22.6, 21.4, 21.0, 19.3, 18.7, 11.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -140.18 to -140.42 (m, 2F), -142.77 to -142.98 (m, 2F).

HRMS(APCI) m/z: $[M–H]^+$ Calcd for $C_{41}H_{51}F_4O_2$ 651.3830, found 651.3831.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-carboxylate (3ax)



3ax

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **3ax**.

Yield: 95%, 100.0 mg; appearance: colourless oil.

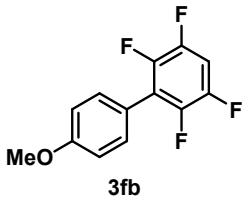
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.56 (d, *J* = 4.8 Hz, 1H), 4.68 – 4.59 (m, 2H), 4.54 – 4.48 (m, 1H), 4.38 – 4.31 (m, 2H), 4.21 – 4.15 (m, 1H), 2.43 (s, 3H), 1.54 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 146.5 – 145.9 (m), 145.3 – 145.0 (m), 144.0 – 143.5 (m), 142.7 – 142.4 (m), 139.9, 129.9, 129.4, 123.8 – 123.3 (m), 110.9 – 110.7 (m), 109.8, 108.9, 96.2, 70.9, 70.7, 70.4, 65.9, 65.2, 25.9, 24.9, 24.4, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.35 to -139.65 (m, 2F), -142.61 to -142.86 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}F_4O_7$ 527.1687, found 527.1687.

2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (3fb)[1]



3fb

Purification via silica gel column chromatography (petroleum ether) afforded **3fb**.

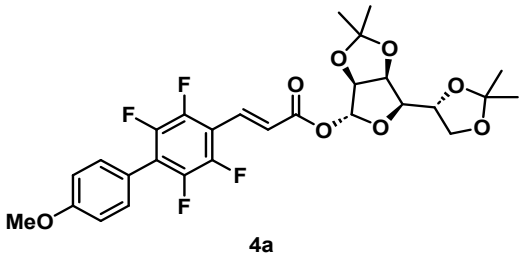
Yield: 80%, 41.0 mg; appearance: white solid; M.P.: 104-106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.06 – 7.00 (m, 3H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 147.6 – 147.2 (m), 145.1 – 144.8 (m), 142.7 – 142.4 (m), 131.4, 121.2 (t, *J* = 17.0 Hz), 119.5, 114.1, 104.2 (t, *J* = 23.0 Hz), 55.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.10 to -139.70 (m, 2F), -144.05 to -144.50 (m, 2F).

(3a*S*,4*R*,6*R*,6a*S*)-6-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl (*E*)-3-(2,3,5,6-tetrafluoro-4'-methoxy-[1,1'-biphenyl]-4-yl)acrylate (4a)



4a

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **4a**.

Yield: 95%, 108.0 mg; appearance: white solid; M.P.: 155-157 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 16.4 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 16.4 Hz, 1H), 6.29 (s, 1H), 4.95 – 4.91 (m, 1H), 4.82 (d, *J* = 5.6 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.15 – 4.05 (m, 3H), 3.87 (s, 3H), 1.52 (s, 3H), 1.48 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H).

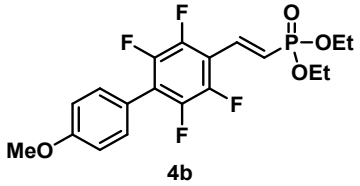
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 160.5, 147.1 – 146.7 (m), 145.2 – 145.0 (m), 144.6 – 144.0 (m), 142.8 – 142.3 (m), 131.5, 130.8, 124.7 (t, *J* = 8.0 Hz), 118.9, 114.2, 113.3, 112.2 (t, *J* = 14.0 Hz), 109.4, 101.3, 85.1, 82.4, 79.3, 72.9, 66.8, 55.3, 27.0, 25.9, 25.1, 24.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -140.50 (dd, *J* = 23.7, 13.9 Hz, 2F), -144.26 (dd, *J* = 23.7, 13.9 Hz, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{28}H_{28}F_4O_8$ 568.1720, found 568.1716.

diethyl (*E*)-(2-(2,3,5,6-tetrafluoro-4'-methoxy-[1,1'-biphenyl]-4-

yl)vinyl)phosphonate (4b)



4b

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **4b**.

Yield: 88%, 73.6 mg; appearance: white solid; M.P.: 72-74 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 24.4, 18.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.68 (t, *J* = 18.0 Hz, 1H), 4.20 – 4.10 (m, 4H), 3.84 (s, 3H), 1.36 (t, *J* = 6.8 Hz, 6H).

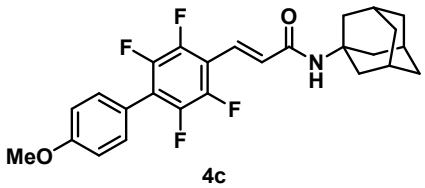
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 146.7 – 146.5 (m), 145.2 – 144.8 (m), 144.4 – 143.9 (m), 142.8 – 142.4 (m), 133.0 – 132.8 (m), 131.4, 124.5 (t, *J* = 8.0 Hz), 122.6 (t, *J* = 9.0 Hz), 121.7 – 121.3 (m), 118.9, 114.1, 113.2 – 112.6 (m), 62.1 (d, *J* = 5.0 Hz), 55.2, 16.3 (d, *J* = 6.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.09 to -142.20 (m, 2F), -144.49 to -144.62 (m, 2F).

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.10.

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}F_4O_4P$ 419.1030, found 419.1030.

(*E*)-*N*-((3s,5s,7s)-adamantan-1-yl)-3-(2,3,5,6-tetrafluoro-4'-methoxy-[1,1'-biphenyl]-4-yl)acrylamide (4c)



4c

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **4c**.

Yield: 85%, 78.1 mg; appearance: white solid; M.P.: 231-232 °C.

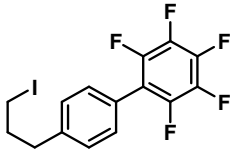
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 5.44 (s, 1H), 3.87 (s, 3H), 2.10 (s, 9H), 1.72 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 160.3, 146.8 – 146.5 (m), 145.1 – 144.9 (m), 144.4 – 144.1 (m), 142.8 – 142.6 (m), 131.4, 129.4, 125.2, 120.8 – 120.4 (m), 119.2, 114.1, 113.2 – 112.9 (m), 55.3, 52.5, 41.5, 36.3, 29.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -141.20 to -141.70 (m, 2F), -144.72 to -145.12 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}F_4NO_2$ 460.1894, found 460.1894.

2,3,4,5,6-pentafluoro-4'-(3-iodopropyl)-1,1'-biphenyl (5a)



5a

Purification via silica gel column chromatography (petroleum ether) afforded **5a**.

Yield: 99%, 81.6 mg; appearance: white solid; M.P.: 82-84 °C.

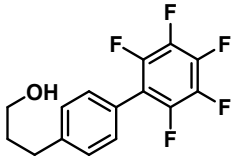
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 3.22 (t, *J* = 6.8 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.25 – 2.13 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4 – 145.1 (m), 143.0 – 142.6 (m), 141.8, 141.7 – 141.4 (m), 139.2 – 138.7 (m), 136.7 – 136.3 (m), 130.2, 128.9, 124.2, 115.8 – 115.2 (m), 36.0, 34.5, 6.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.31 (dd, *J* = 23.7, 8.6 Hz, 2F), -155.81 (t, *J* = 21.1 Hz, 1F), -162.17 to -162.42 (m, 2F).

HRMS(APCI) m/z: $[M]^+$ Calcd for $C_{15}H_{10}F_5I$ 411.9747, found 411.9742.

3-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)propan-1-ol (5b)



5b

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) afforded **5b**.

Yield: 71%, 42.9 mg; appearance: white solid; M.P.: 90-92 °C.

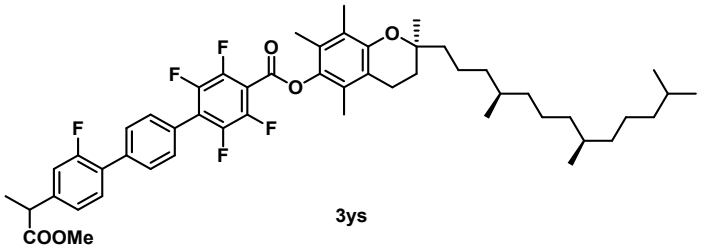
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.00 – 1.90 (m, 2H), 1.51 – 1.39 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 – 145.1 (m), 143.2, 143.0 – 142.9 (m), 141.7 – 141.4 (m), 139.2 – 138.8 (m), 136.8 – 136.3 (m), 130.1, 128.8, 123.8, 116.0 – 115.6 (m), 62.1, 33.9, 31.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.35 (dd, *J* = 24.8, 8.6 Hz, 2F), 155.96 (t, *J* = 21.4 Hz, 1F), -161.18 to -163.50 (m, 2F).

HRMS(APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}F_5O$ 303.0803, found 303.0803.

(*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 2,2'',3,5,6-pentafluoro-4''-(3-oxobutan-2-yl)-[1,1':4',1''-terphenyl]-4-carboxylate (3ys)



3ys

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **3ys**.

Yield: 93%, 160.5 mg; appearance: white solid; M.P.: 102-104 °C.

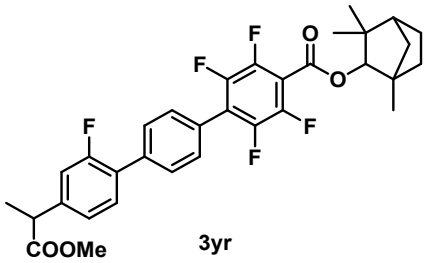
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.14 (m, 2H), 3.80 (q, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.17 (d, *J* = 4.4 Hz, 6H), 2.13 (s, 3H), 1.92 – 1.74 (m, 2H), 1.62 – 1.51 (m, 6H), 1.47 – 1.36 (m, 4H), 1.34 – 1.23 (m, 10H), 1.20 – 1.05 (m, 6H), 0.93 – 0.83 (m, 13H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 161.1, 158.5, 150.0, 146.6 – 145.9 (m), 145.5 –145.0 (m), 143.9 – 143.2 (m), 142.9 – 142.5 (m), 140.4 – 139.8 (m), 140.3, 140.1 – 139.9 (m), 137.0, 130.7 (d, *J* = 3.0 Hz), 130.2, 129.2, 126.8, 126.5, 125.8, 124.8, 123.7 (d, *J* = 2.0 Hz), 123.4, 117.7, 115.5, 115.3, 111.7 – 111.2 (m), 75.2, 52.2, 44.9, 39.3, 37.6 – 37.2 (m), 32.8 – 32.6 (m), 28.0, 24.8, 24.4, 22.7, 22.6, 21.0, 20.6, 19.72, 19.65, 18.5, 13.0, 12.1, 11.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.13 (s, 1F), -138.55 to - 138.90 (m, 2F), -141.92 to -142.22 (m, 2F).

HRMS(APCI) m/z: $[H]^+$ Calcd for $C_{52}H_{63}F_5O_5$ 862.4596, found 862.4590.

1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2,2'',3,5,6-pentafluoro-4''-(1-methoxy-1-oxopropan-2-yl)-[1,1':4',1''-terphenyl]-4-carboxylate (3yr)



3yr

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **3yr**.

Yield: 94%, 110.3 mg; appearance: white solid; M.P.: 96-98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 4.69 (d, *J* = 1.6 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 1.86 – 1.65 (m, 4H), 1.55 (d, *J* = 7.2 Hz, 3H), 1.53 – 1.46 (m, 1H), 1.30 – 1.19 (m, 5H), 1.16 (s, 3H), 0.92 (s, 3H).

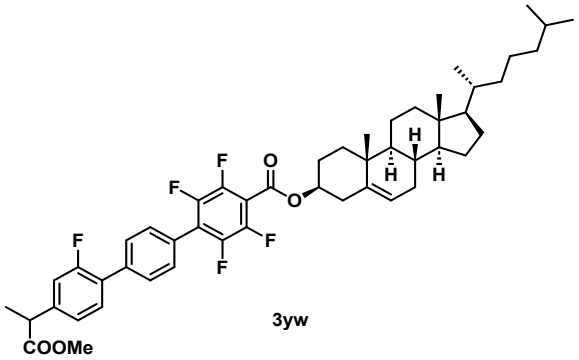
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 160.9, 160.1, 158.4, 146.4 – 146.1 (m), 145.3 –145.0 (m), 143.9 – 143.5 (m), 142.9 – 142.6 (m), 142.5 (d, *J* = 7.0 Hz), 136.8, 130.6 (d, *J* = 3.0 Hz), 130.1, 129.1 (d, *J* = 3.0 Hz), 126.7 (d, *J* = 13.0 Hz), 125.9, 123.7 (d, *J* = 3.0 Hz), 122.9 (t, *J* = 16.0 Hz), 115.4 (d, *J* = 24.0 Hz), 111.9 (t, *J* = 16.0 Hz), 89.5, 52.2, 48.4, 48.3, 44.9, 41.3, 39.6, 29.6, 26.6, 25.7, 20.1, 19.2, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.17 (s, 1F), -139.25 to -139.55 (m, 2F), -142.42 to -142.66 (m, 2F).

HRMS(APCI) m/z: $[H]^+$ Calcd for $C_{33}H_{31}F_5O_4$ 586.2143, found 586.2137.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2,2'',3,5,6-pentafluoro-4''-(1-methoxy-1-

oxopropan-2-yl)-[1,1':4',1''-terphenyl]-4-carboxylate (3yw)



3yw

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) afforded **3yw**.

Yield: 65%, 106.5 mg; appearance: white solid; M.P.: 198-200 °C.

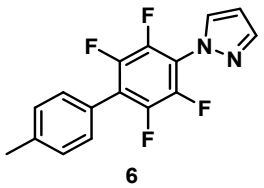
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.57 – 7.52 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.21 – 7.13 (m, 2H), 5.46 (d, *J* = 3.6 Hz, 1H), 5.03 – 4.88 (m, 1H), 3.78 (q, *J* = 6.8 Hz, 1H), 3.71 (s, 3H), 2.55 – 2.46 (m, 2H), 2.10 – 1.70 (m, 6H), 1.60 – 1.49 (m, 8H), 1.40 – 1.10 (m, 12H), 1.07 (s, 3H), 1.05 – 0.98 (m, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 1.6 Hz, 3H), 0.86 (d, *J* = 1.6 Hz, 3H), 0.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 160.9, 159.0, 158.5, 146.2 – 145.7 (m), 145.2 – 144.9 (m), 143.7 – 143.3 (m), 142.8 – 142.3 (m), 139.1, 136.8, 130.7 (d, *J* = 4.0 Hz), 130.1, 129.2 (d, *J* = 2.0 Hz), 126.7 (d, *J* = 13.0 Hz), 125.9, 123.7 (d, *J* = 2.0 Hz), 123.3, 123.0 – 122.6 (m), 115.4 (d, *J* = 23.0 Hz), 112.5 – 112.1 (m), 56.6, 56.1, 52.2, 50.0, 44.9, 42.3, 39.7, 39.5, 37.9, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.7, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 18.4, 11.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.17 (s, 1F), -139.84 to -140.08 (m, 2F), -142.48 to -142.69 (m, 2F).

HRMS(APCI) m/z: $[H]^+$ Calcd for $C_{50}H_{59}F_5O_4$ 818.4334, found 818.4328.

1-(2,3,5,6-tetrafluoro-4'-methyl-[1,1'-biphenyl]-4-yl)-1*H*-pyrazole (6)[7]



6

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded **6**.

Yield: 96%, 58.8 mg; appearance: white solid; M.P.: 158-160 °C.

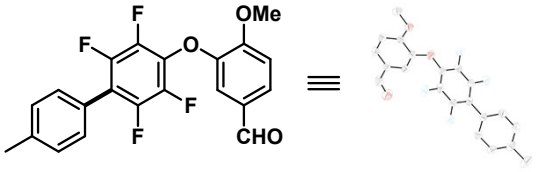
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.6 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.52 – 6.50 (m, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6 – 145.3 (m), 143.5 – 143.2 (m), 143.1 – 142.8 (m), 142.3, 141.0 – 140.7 (m), 139.7, 132.1, 129.9, 129.5, 123.5, 120.7 – 120.2 (m), 118.9 – 118.7 (m), 107.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.60 to -143.20 (m, 2F), -148.75 to -149.20 (m, 2F).

X-ray Data:

Figure S4. X-ray structure and crystallographic data of **3aq**



(CCDC 2413238)

Crystal data and structure refinement for 3aq

CCDC number	2413238
Empirical formula	$C_{21}H_{14}F_4O_3$
Formula weight	390.32
Temperature [K]	293(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	7.4827(4)
b [Å]	8.6179(4)
c [Å]	14.3333(7)
α [°]	85.385(4)
β [°]	75.972(5)
γ [°]	81.865(4)
Volume [Å^3]	886.68(8)
Z	2
ρ_{calc} [gcm^{-3}]	1.462
μ [mm^{-1}]	1.083
F(000)	400
Crystal size [mm^3]	0.13×0.14×0.15
Crystal colour	colourless
Crystal shape	block
Radiation	Cu K_α (λ=1.54184 Å)
2θ range [°]	6.36 to 134.15 (0.84 Å)
Index ranges	−8 ≤ h ≤ 8 −10 ≤ k ≤ 10 −17 ≤ l ≤ 17
Reflections collected	11827
Independent reflections	3155 R_{int} = 0.0718 R_{sigma} = 0.0475
Completeness to θ = 67.077°	99.8 %

Data / Restraints / Parameters	3155 / 0 / 256
Absorption correction T_{min}/T_{max} (method)	0.0587 / 1.0000 (multi-scan)
Goodness-of-fit on F^2	1.048
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0568 wR_2 = 0.1621
Final *R* indexes [all data]	R_1 = 0.0713 wR_2 = 0.1827
Largest peak/hole [eÅ^{-3}]	0.20/−0.22
Extinction coefficient	0.0038(11)

References:

[1] Chen, F.; Min, Q.-Q.; Zhang, X. Pd-catalyzed direct arylation of polyfluoroarenes on water under mild conditions using PPh_3 ligand. *J. Org. Chem.* **2012**, *77*, 2992−2998.

[2] Rene, O.; Fagnou, K. Room-temperature direct arylation of polyfluorinated arenes under biphasic conditions. *Org. Lett.* **2010**, *12*, 2116–2119.

[3] Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. Catalytic intermolecular direct arylation of perfluorobenzenes. *J. Am. Chem. Soc.* **2006**, *128*, 8754–8756.

[4] Li, H.; Liu, J.; Sun, C.-L.; Li, B.-J.; Shi, Z.-J. Palladium-catalyzed cross-coupling of polyfluoroarenes with simple arenes. *Org. Lett.* **2011**, *13*, 276–279.

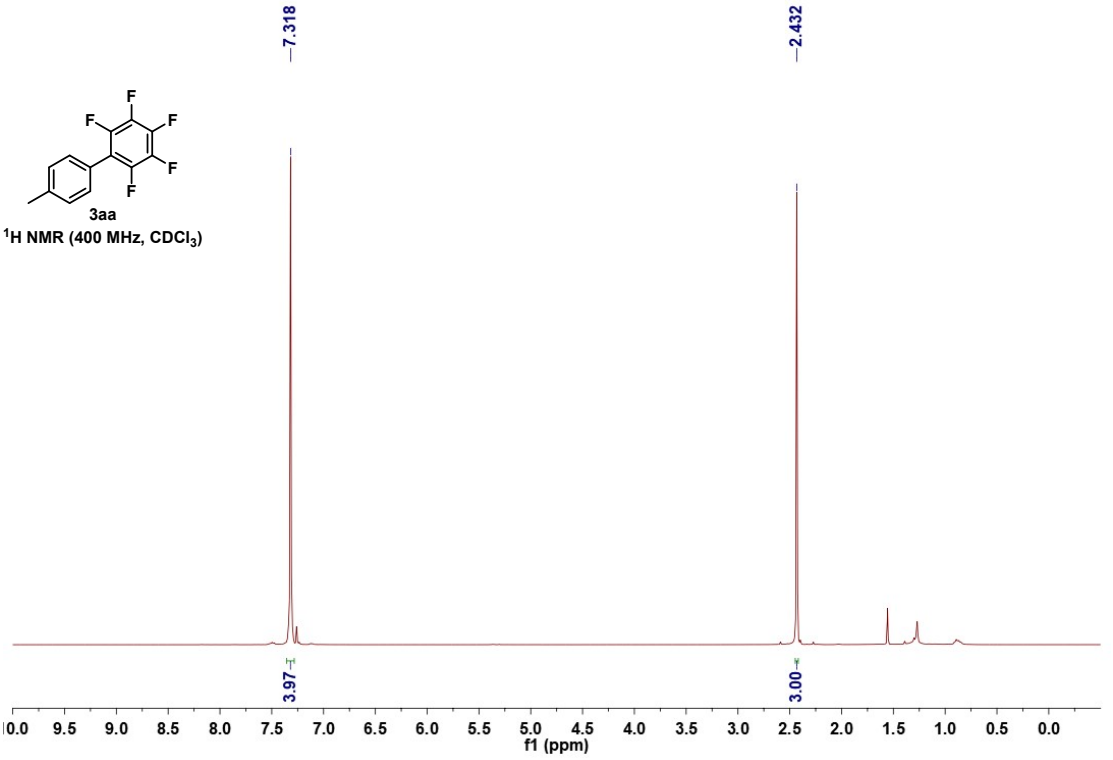
[5] Lin, X.; You, Y.; Weng, Z. Direct palladium-catalyzed desulfitative C–C coupling of polyfluoroarenes with arylsulfinate salts: water-accelerated reactions. *J. Fluor. Chem.* **2014**, *165*, 76–80.

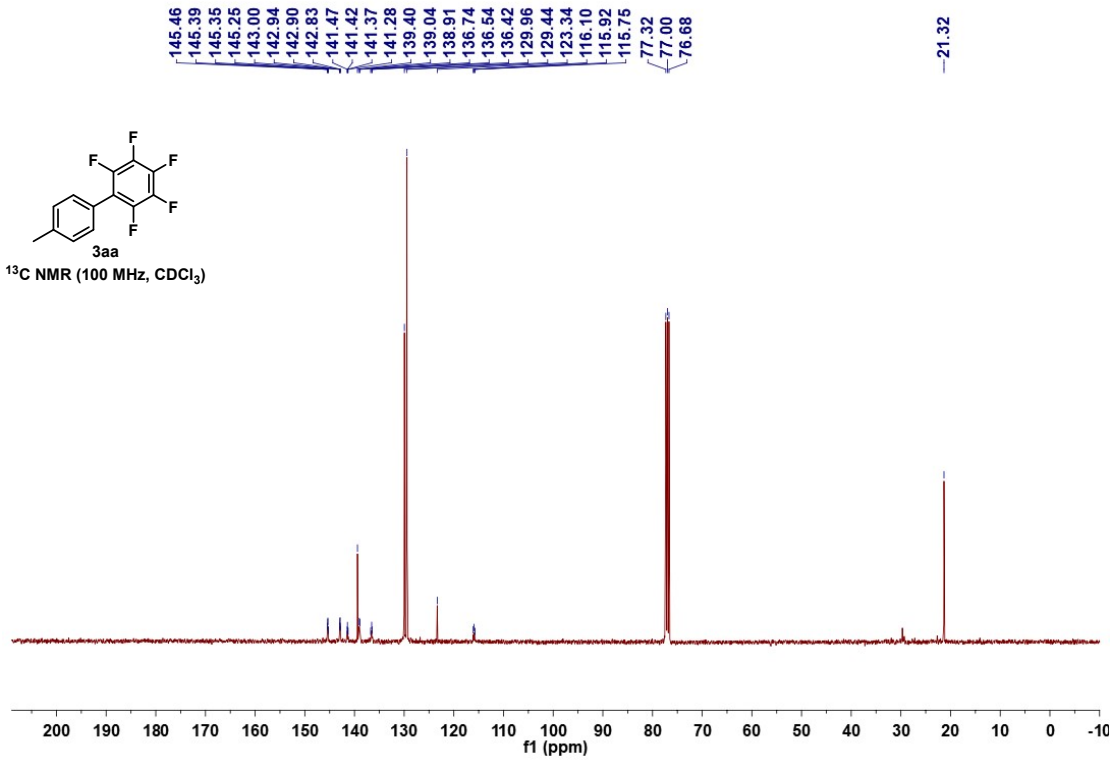
[6] Hofer, M.; Genoux, A.; Kumar, R.; Nevado, C. Gold-catalyzed direct oxidative arylation with boron coupling partners. *Angew. Chem. Int. Ed.* **2017**, *56*, 1021–1025.

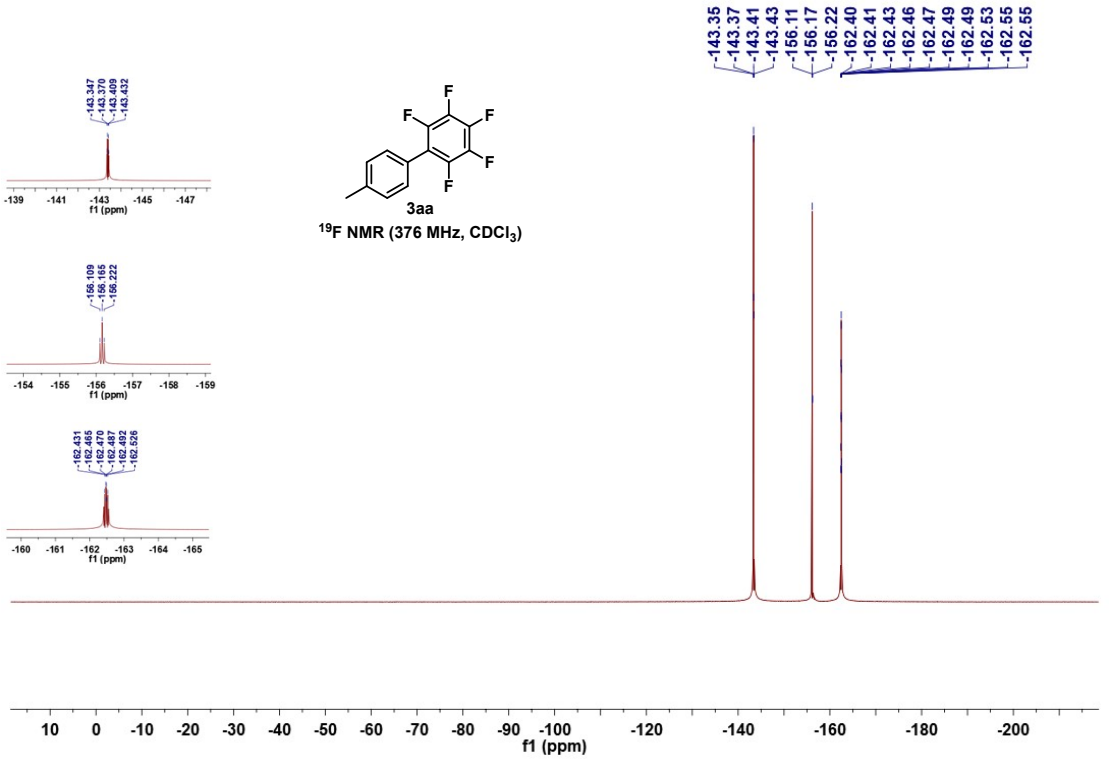
[7] Bardin, V. V.; Shabalin, A. Yu.; Adonin, N. Yu. Weakly nucleophilic potassium aryltrifluoroborates in palladium-catalyzed Suzuki–Miyaura reactions: relative reactivity of K[4-$RC_6F_4BF_3$] and the role of silver-assistance in acceleration of transmetallation. *Beilstein J. Org. Chem.* **2015**, *11*, 608–616.

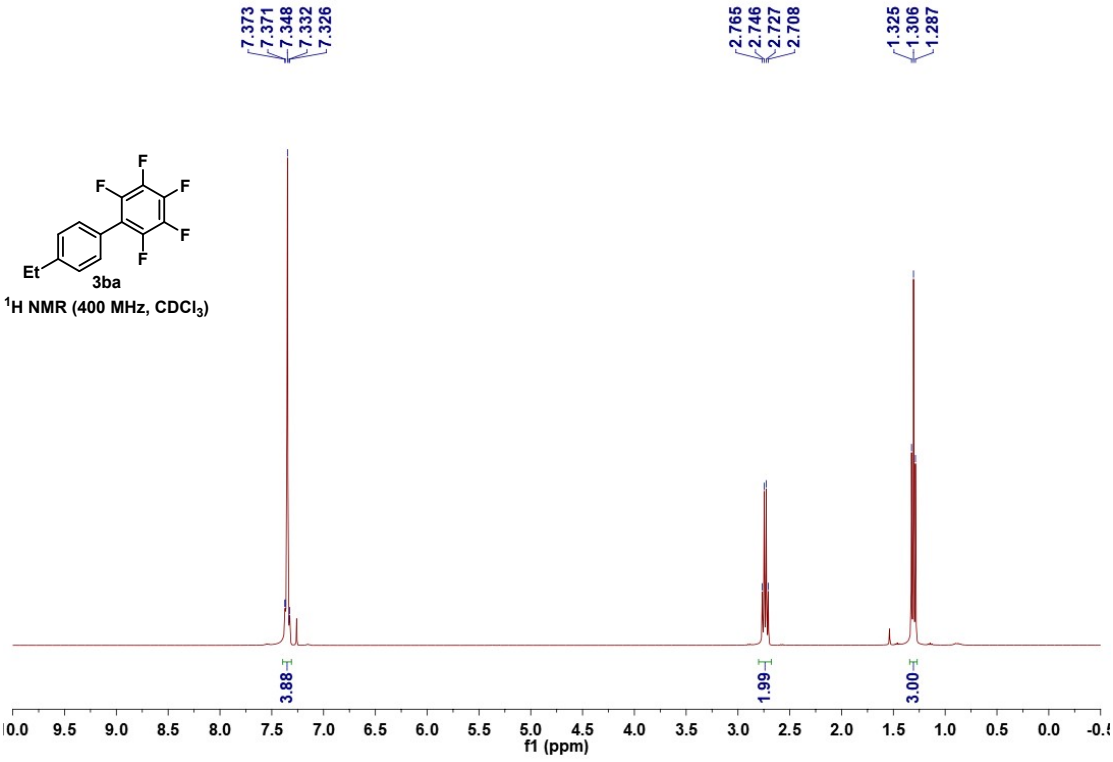
[8] CN114956924B, Henan Institute of Science and Techenology, Method for synthesizing polyfluorinated aromatic hydrocarbon through series/coupling reaction, 2024-01-30.

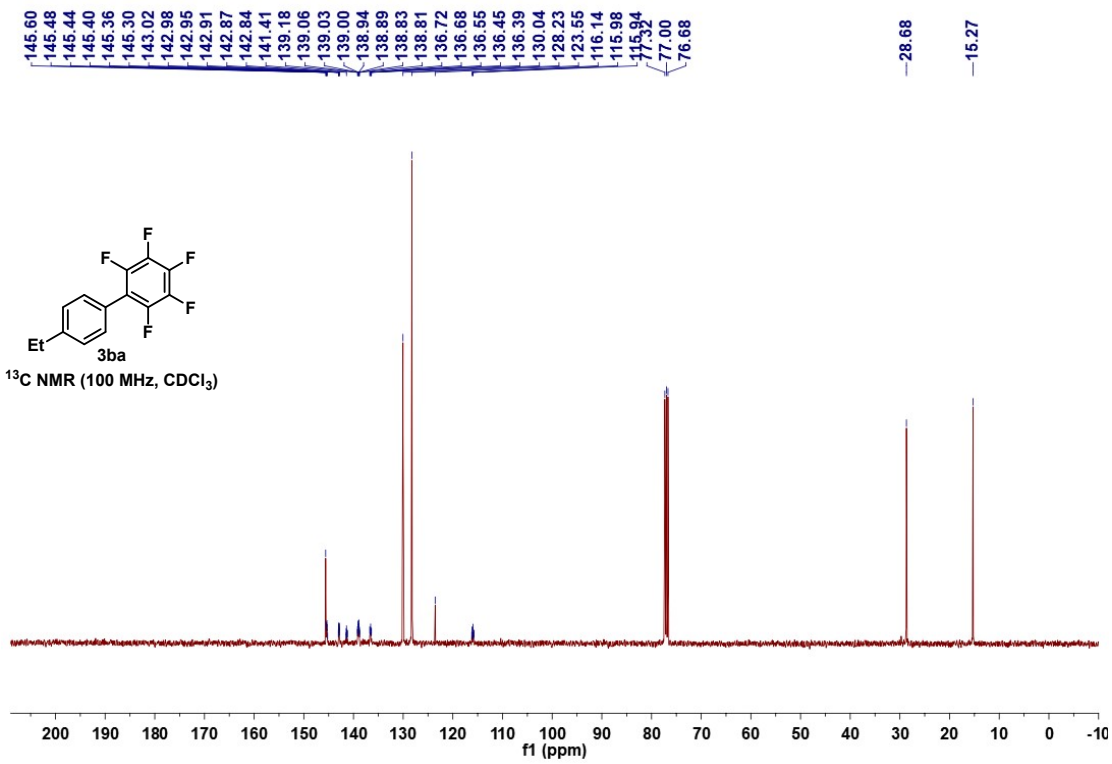
NMR Spectra:


7.318
2.432
3aa
1H NMR (400 MHz, CDCl3)
3.97
3.00
f1 (ppm)


145.46
145.39
145.35
145.25
143.00
142.94
142.90
142.83
141.47
141.42
141.37
141.28
139.40
139.04
138.91
136.74
136.54
136.42
129.96
129.44
123.34
116.10
115.92
115.75
77.32
77.00
76.68
21.32
3aa
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-143.347
-143.370
-143.409
-143.432
-139
-141
-143
-145
-147
f1 (ppm)
-156.109
-156.165
-156.222
-154
-155
-156
-157
-158
-159
f1 (ppm)
-162.431
-162.465
-162.470
-162.487
-162.492
-162.526
-160
-161
-162
-163
-164
-165
f1 (ppm)
F
F
F
F
F
3aa
19F NMR (376 MHz, CDCl3)
-143.35
-143.37
-143.41
-143.43
-156.11
-156.17
-156.22
-162.40
-162.41
-162.43
-162.46
-162.47
-162.49
-162.49
-162.53
-162.55
-162.55
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.373
7.371
7.348
7.332
7.326
2.765
2.746
2.727
2.708
1.325
1.306
1.287
F
F
F
F
F
Et
3ba
1H NMR (400 MHz, CDCl3)
3.88
1.99
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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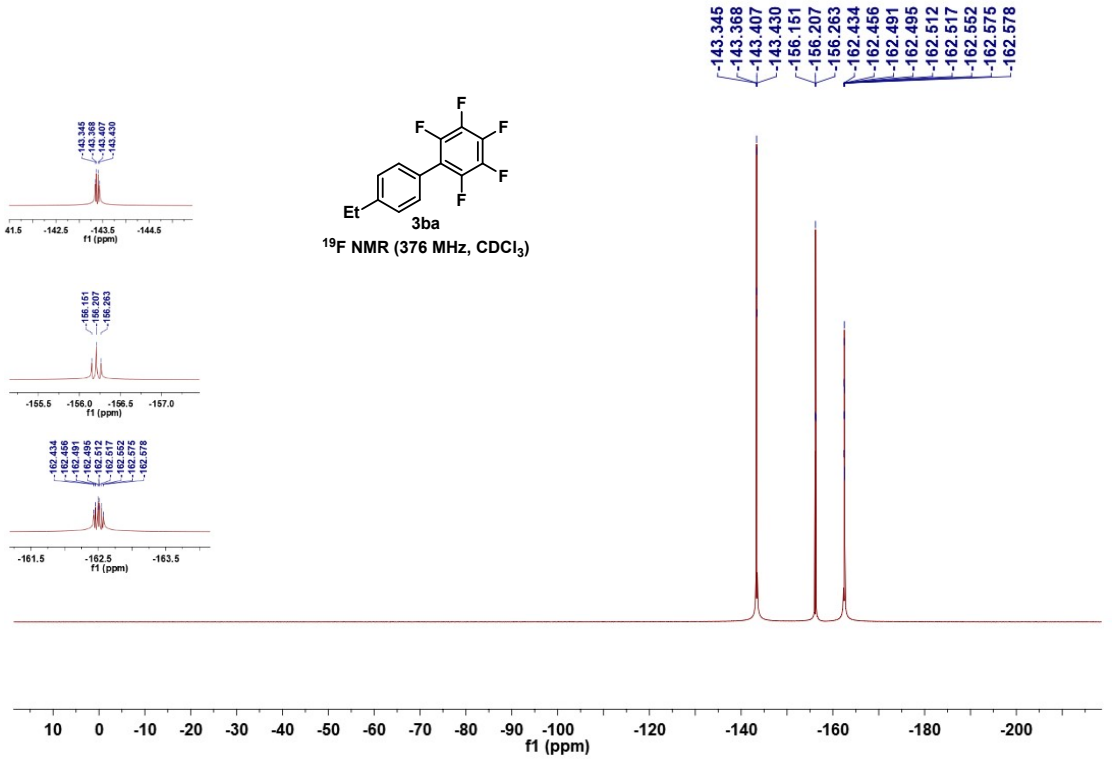
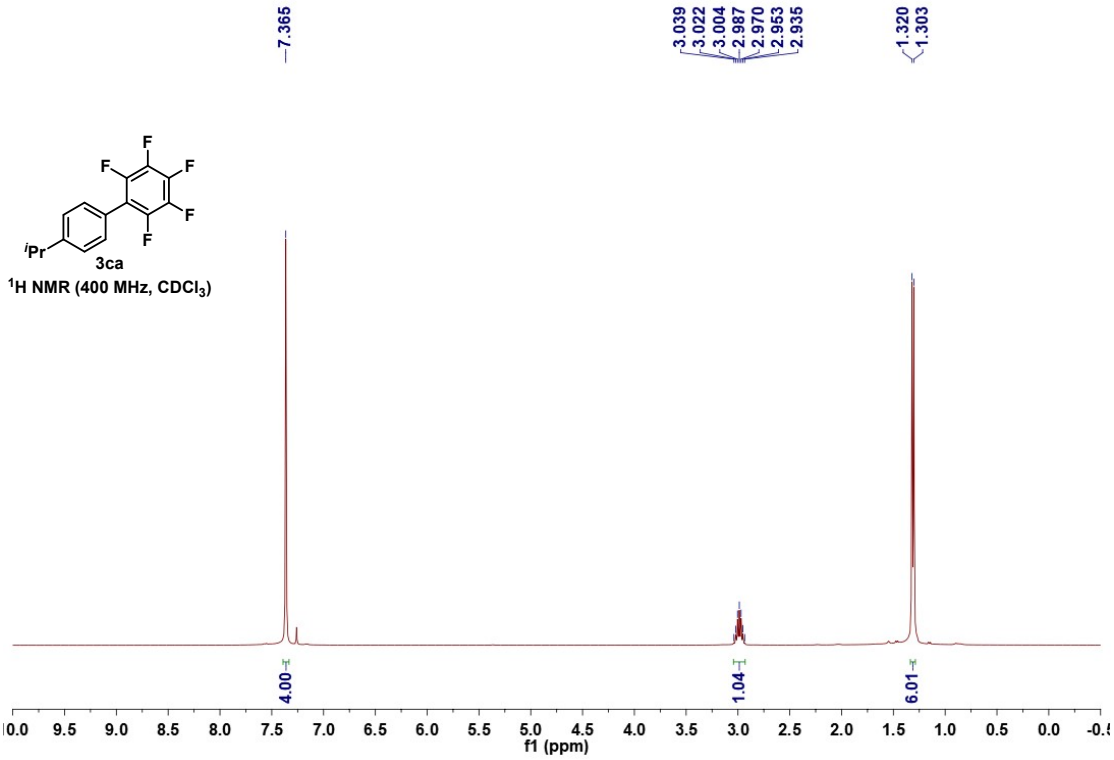
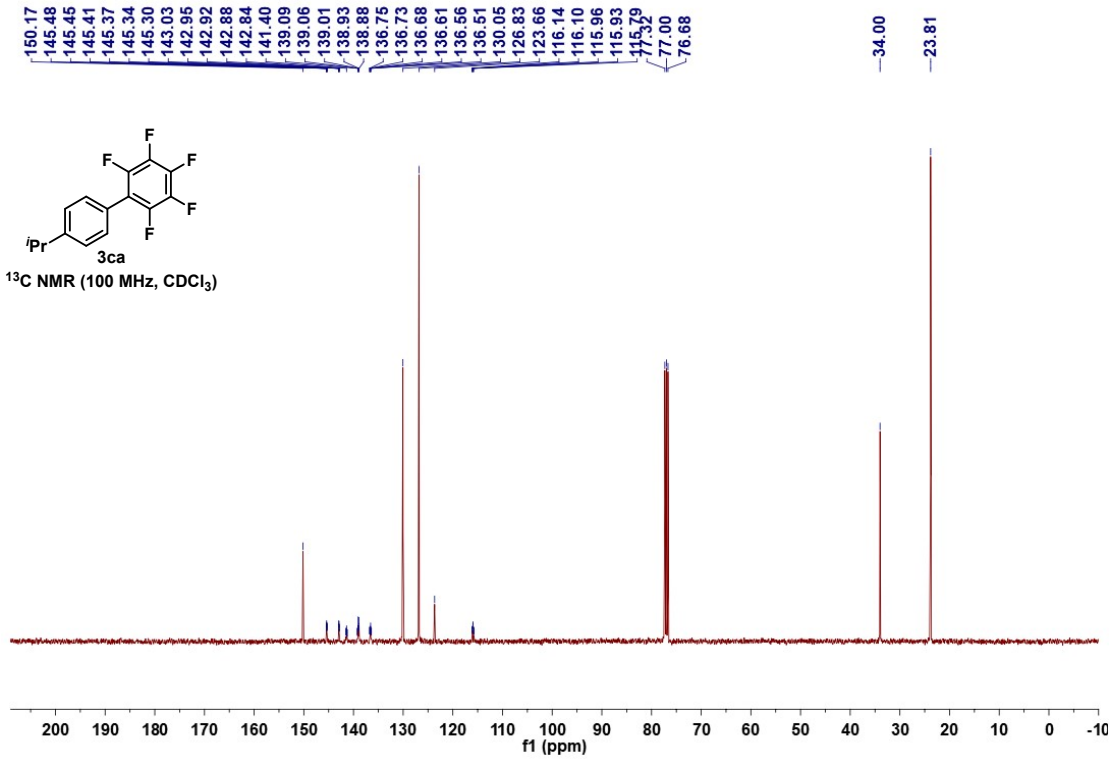
145.48
145.44
145.40
145.36
145.30
143.02
142.98
142.95
142.91
142.87
142.84
141.41
139.18
139.06
139.03
139.00
138.94
138.89
138.83
138.81
136.72
136.68
136.55
136.45
136.39
130.04
128.23
123.55
116.14
115.98
115.94
77.32
77.00
76.68
28.68
15.27
F
F
F
F
F
Et
3ba
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-143.345
-143.368
-143.407
-143.430
-156.151
-156.207
-156.263
-162.434
-162.456
-162.491
-162.495
-162.512
-162.517
-162.552
-162.575
-162.578
F
F
F
F
F
Et
3ba
^{19}F NMR (376 MHz, CDCl$_3$)
41.5 -142.5 -143.5 -144.5
f1 (ppm)
-155.5 -156.0 -156.5 -157.0
f1 (ppm)
-161.5 -162.5 -163.5
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.365
3.039
3.022
3.004
2.987
2.970
2.953
2.935
1.320
1.303
F
F
F
F
F
iPr
3ca
1H NMR (400 MHz, CDCl3)
4.00
1.04
6.01
f1 (ppm)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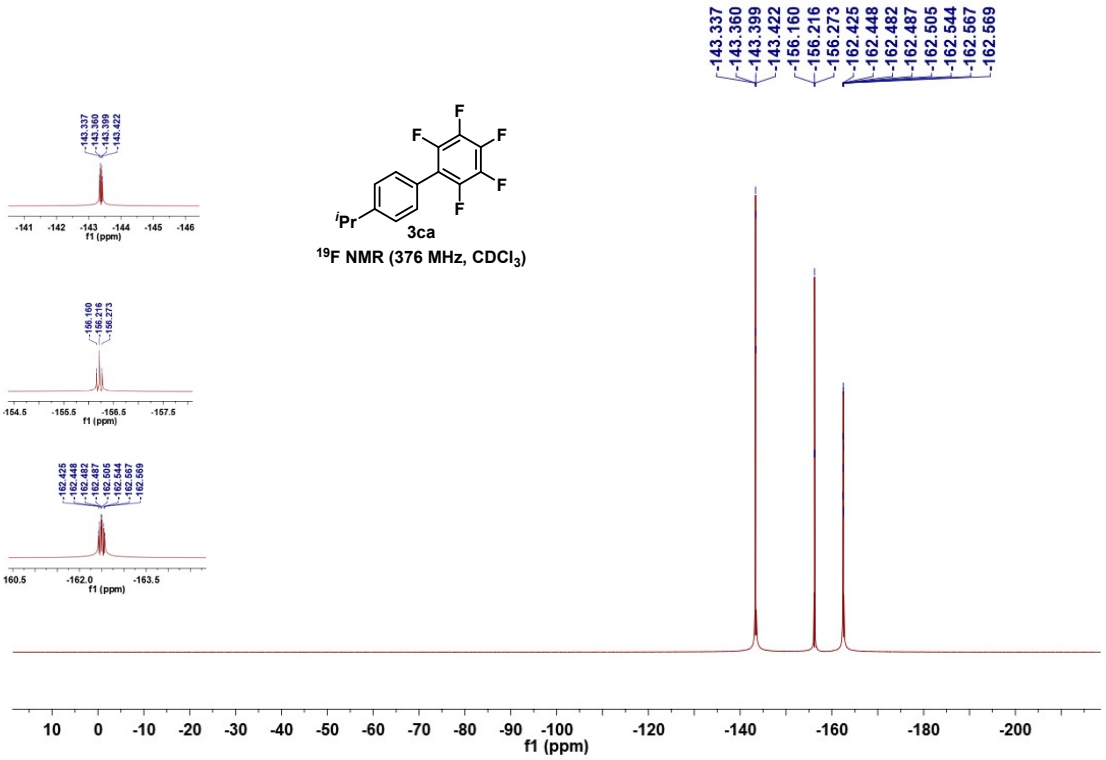
145.48
145.45
145.41
145.37
145.34
145.30
143.03
142.95
142.92
142.88
142.84
141.40
139.09
139.06
139.01
138.93
138.88
136.75
136.73
136.68
136.61
136.56
136.51
130.05
126.83
123.66
116.14
116.10
115.96
115.93
115.79
77.32
77.00
76.68
34.00
23.81
F
F
F
F
F
iPr
3ca
13C NMR (100 MHz, CDCl3)
f1 (ppm)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-156.273
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-162.448
-162.482
-162.487
-162.505
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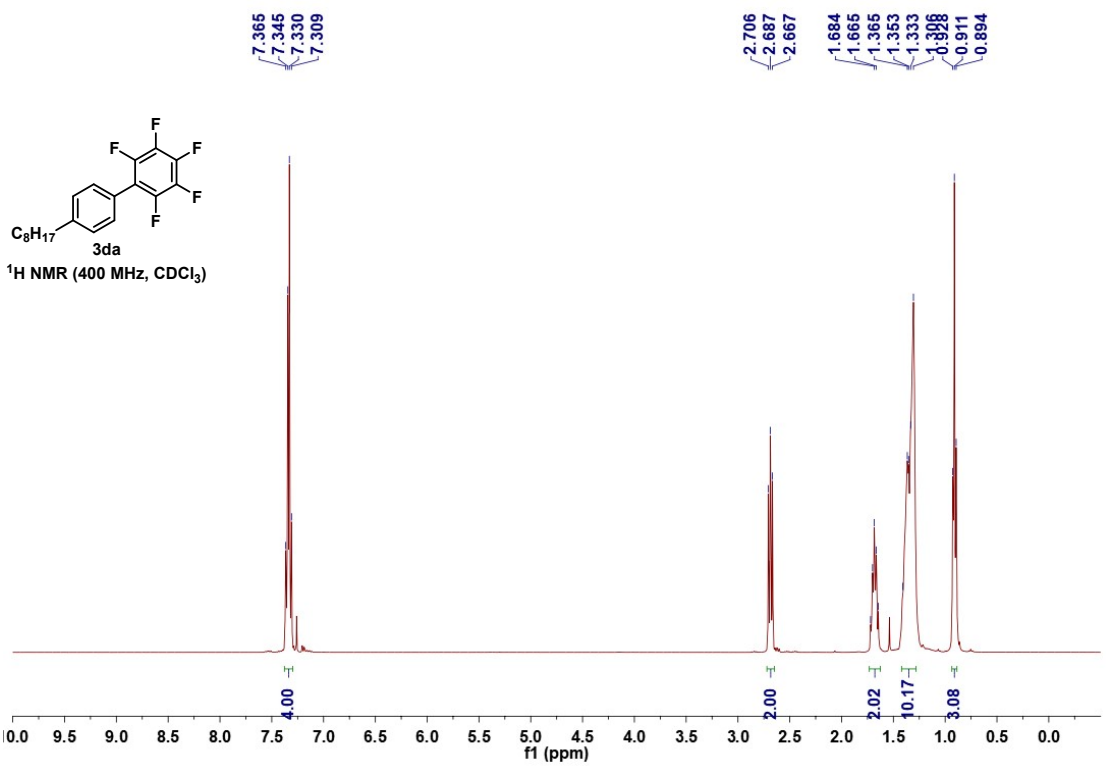
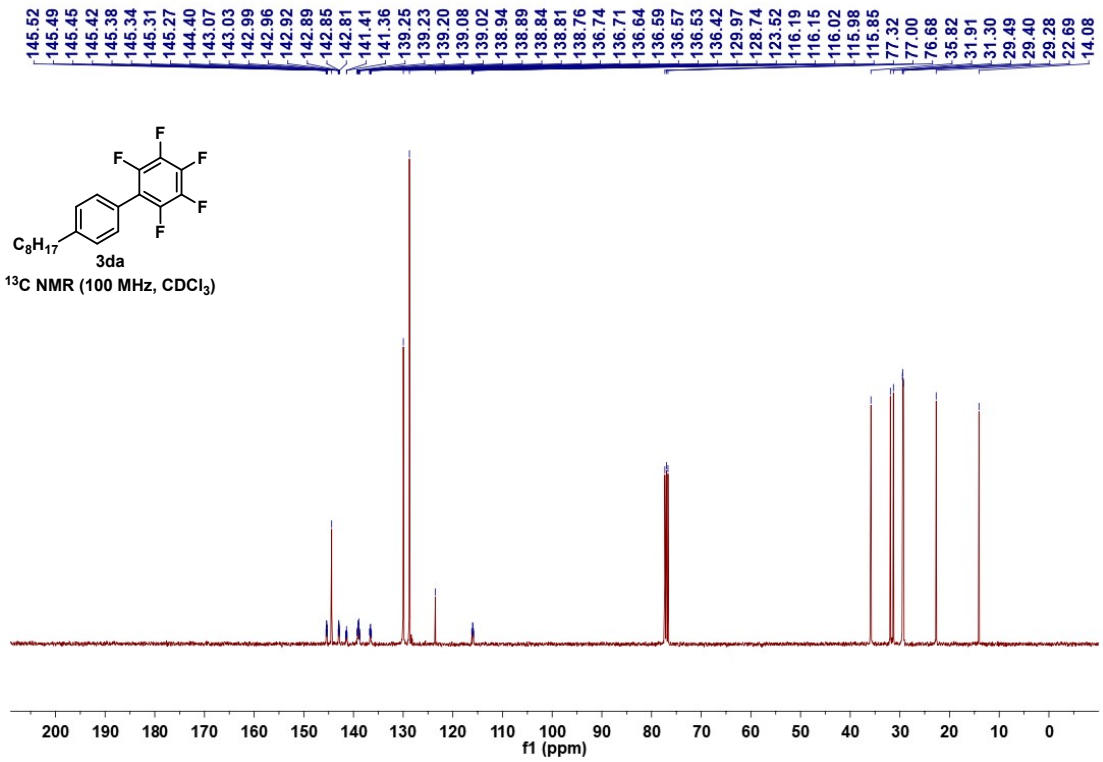
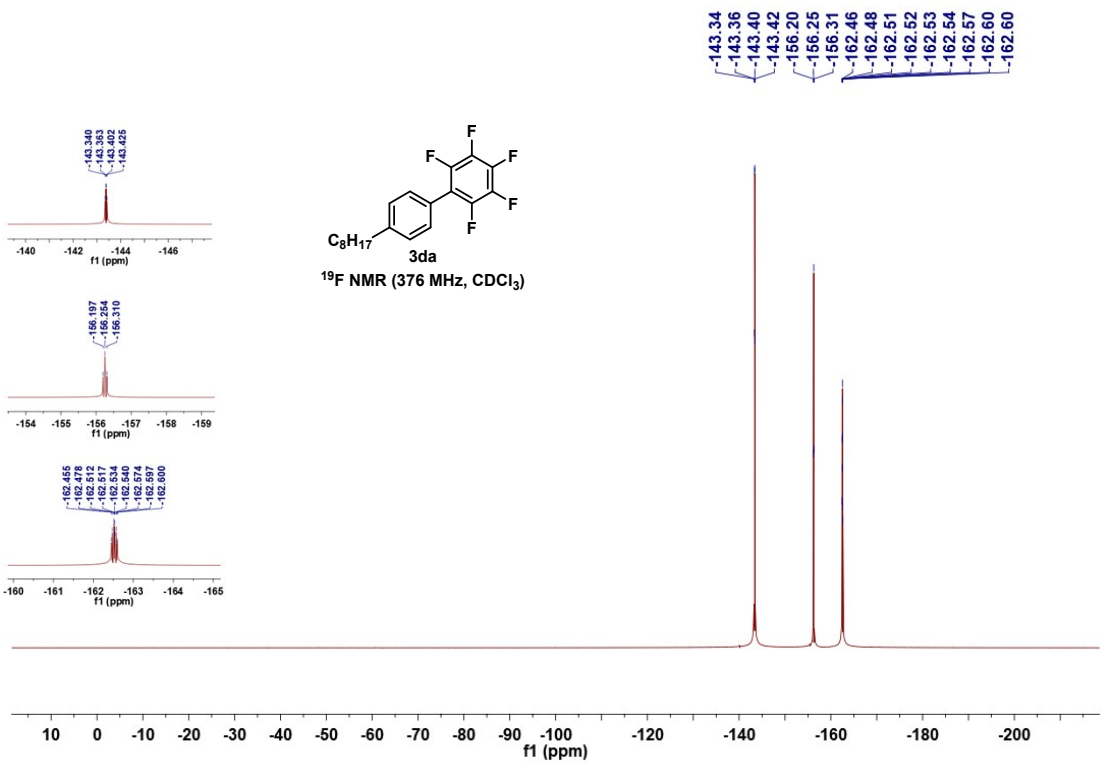
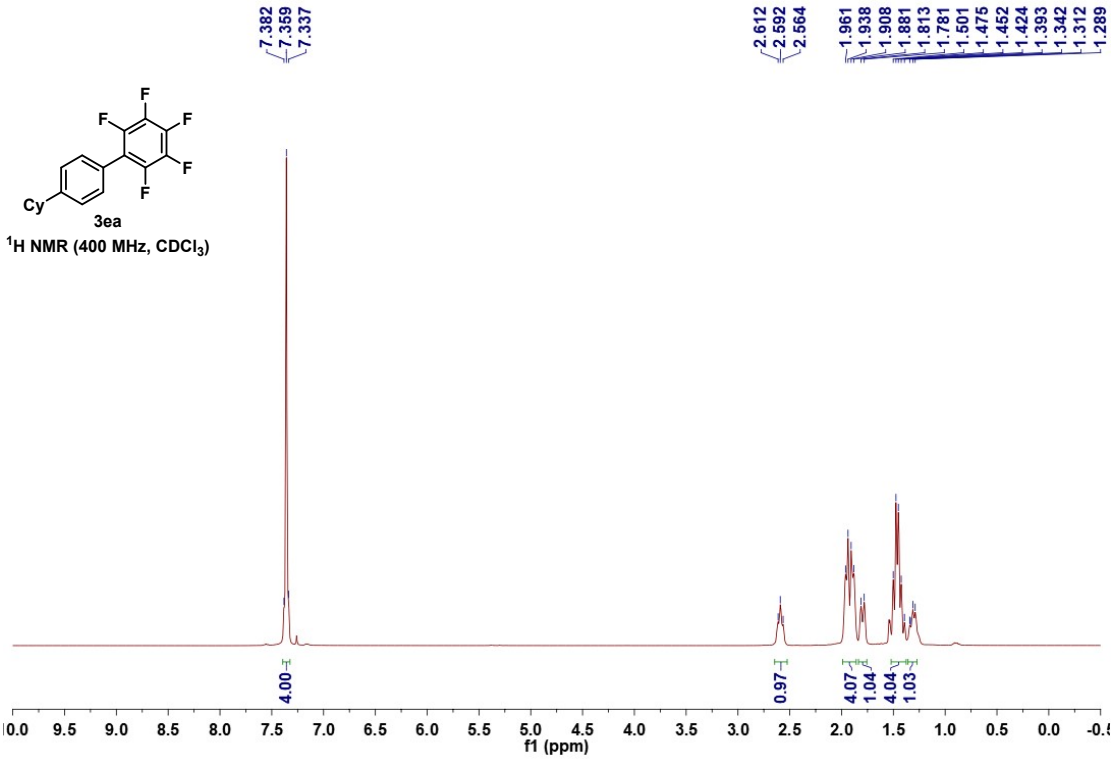
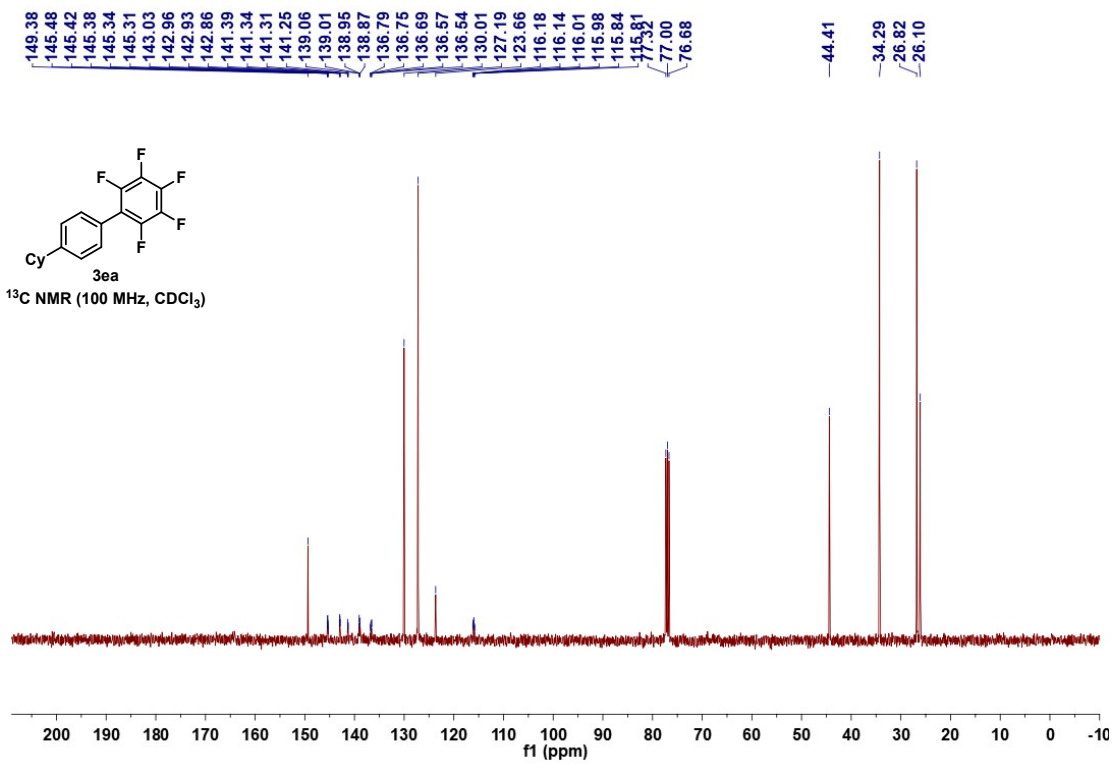
F
F
F
F
iPr
3ca
19F NMR (376 MHz, CDCl3)
f1 (ppm)

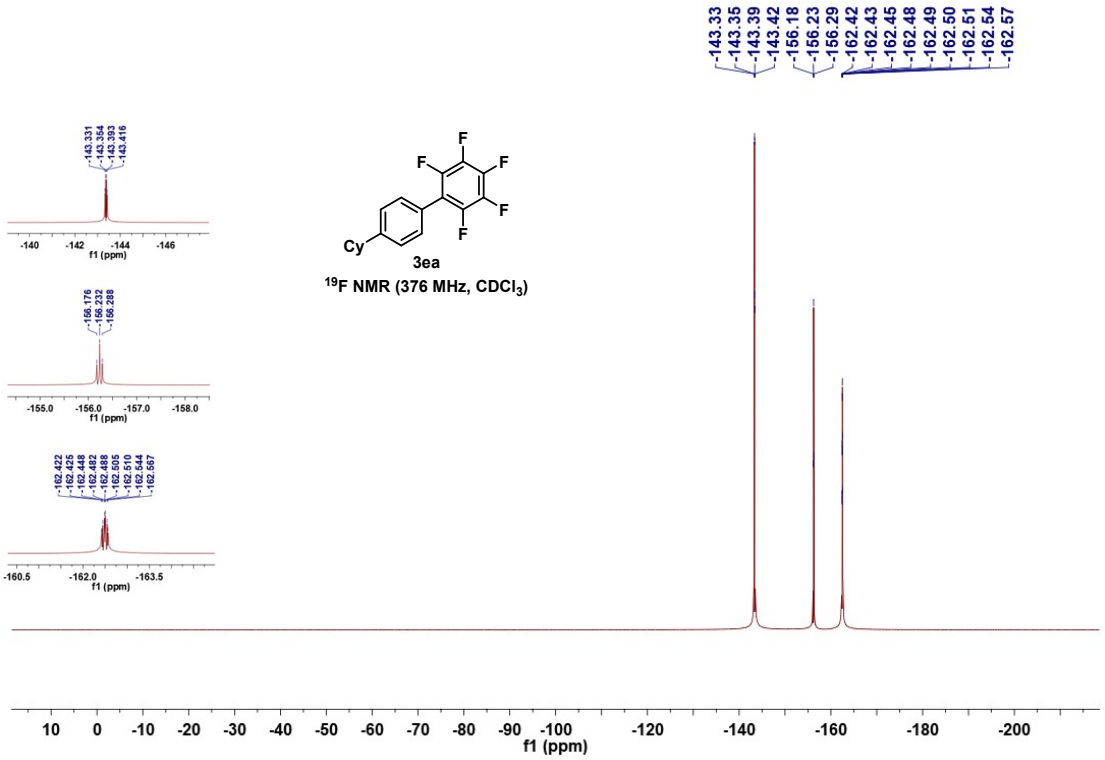

7.365
7.345
7.330
7.309
2.706
2.687
2.667
1.684
1.665
1.365
1.353
1.333
0.911
0.894
F
F
F
F
F
C8H17
3da
1H NMR (400 MHz, CDCl3)
4.00
2.00
2.02
10.17
3.08
f1 (ppm)

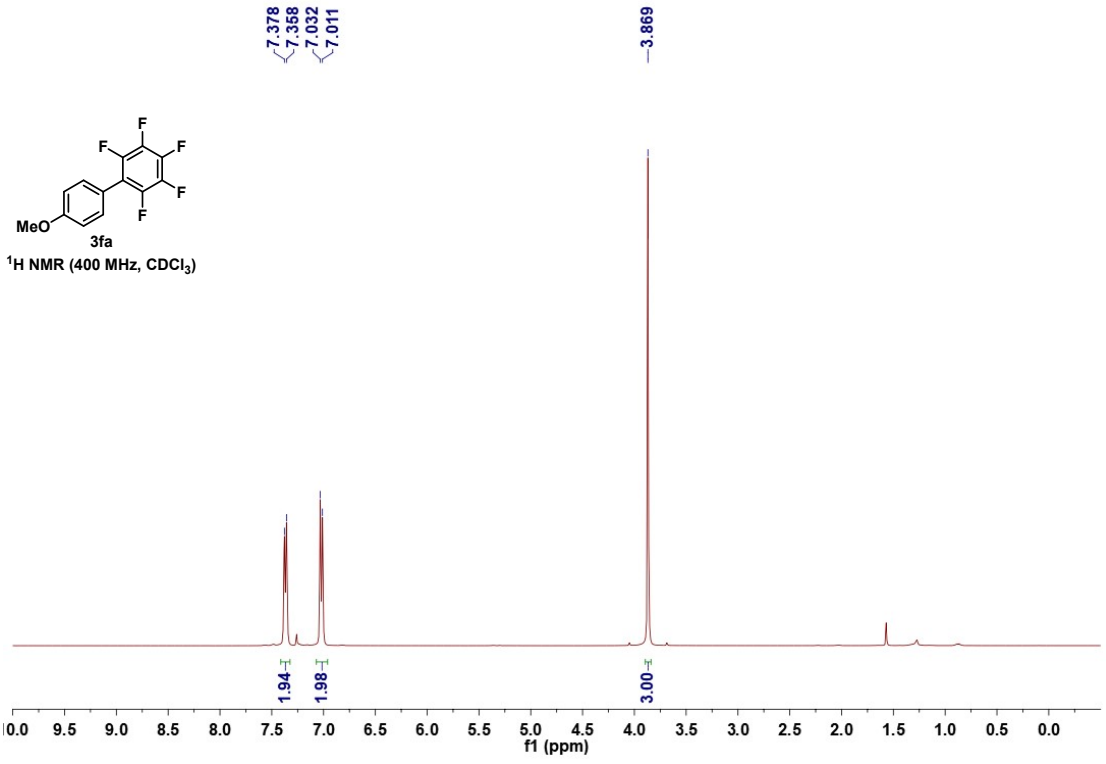

145.52
145.49
145.45
145.42
145.38
145.34
145.31
145.27
144.40
143.07
143.03
142.99
142.96
142.92
142.89
142.85
142.81
141.41
141.36
139.25
139.23
139.20
139.08
139.02
138.94
138.89
138.84
138.81
138.76
136.74
136.71
136.64
136.59
136.57
136.53
136.42
129.97
128.74
123.52
116.19
116.15
116.02
115.98
115.85
77.32
77.00
76.68
35.82
31.91
31.30
29.49
29.40
29.28
22.69
14.08
F
F
F
F
F
C8H17
3da
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

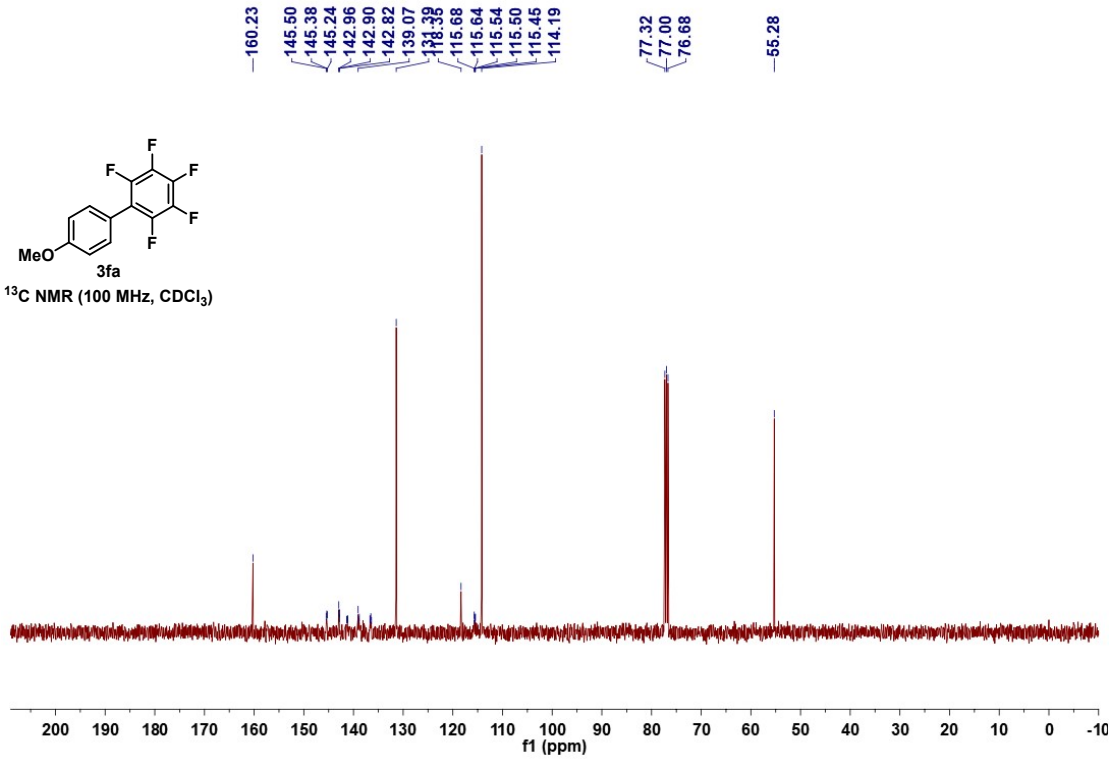

-143.34
-143.36
-143.40
-143.42
-156.20
-156.25
-156.31
-162.46
-162.48
-162.51
-162.52
-162.53
-162.54
-162.57
-162.60
-162.60
-143.340
-143.383
-143.402
-143.425
-140 -142 -144 -146
f1 (ppm)
-156.197
-156.254
-156.310
-154 -155 -156 -157 -158 -159
f1 (ppm)
-162.455
-162.478
-162.512
-162.517
-162.534
-162.540
-162.574
-162.597
-162.600
-160 -161 -162 -163 -164 -165
f1 (ppm)
F
F
F
F
F
C8H17
3da
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

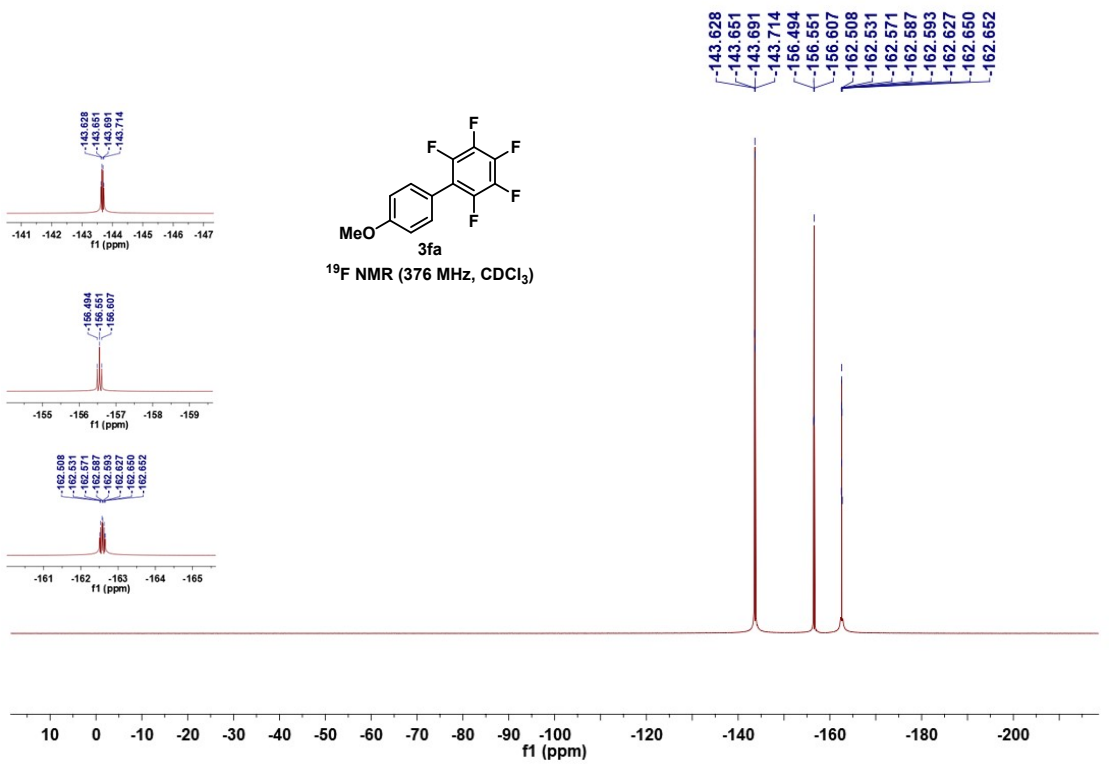

7.382
7.359
7.337
2.612
2.592
2.564
1.961
1.938
1.908
1.881
1.813
1.781
1.501
1.475
1.452
1.424
1.393
1.342
1.312
1.289
F
F
F
F
F
Cy
3ea
^{1}H NMR (400 MHz, CDCl$_3$)
4.00
0.97
4.07
1.04
4.04
1.03
f1 (ppm)

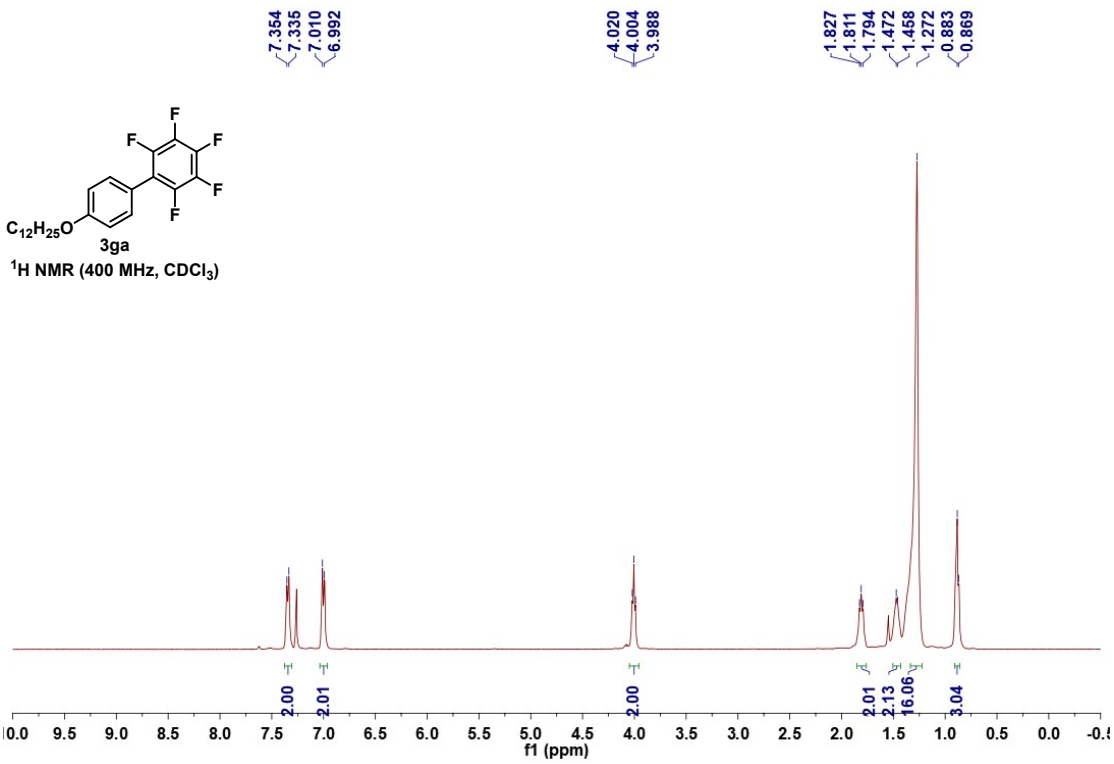

149.38
145.48
145.42
145.38
145.34
145.31
143.03
142.96
142.93
142.86
141.39
141.34
141.31
141.25
139.06
139.01
138.95
138.87
136.79
136.75
136.69
136.57
136.54
130.01
127.19
123.66
116.18
116.14
116.01
115.98
115.84
115.81
77.32
77.00
76.68
44.41
34.29
26.82
26.10
F
F
F
F
F
Cy
3ea
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

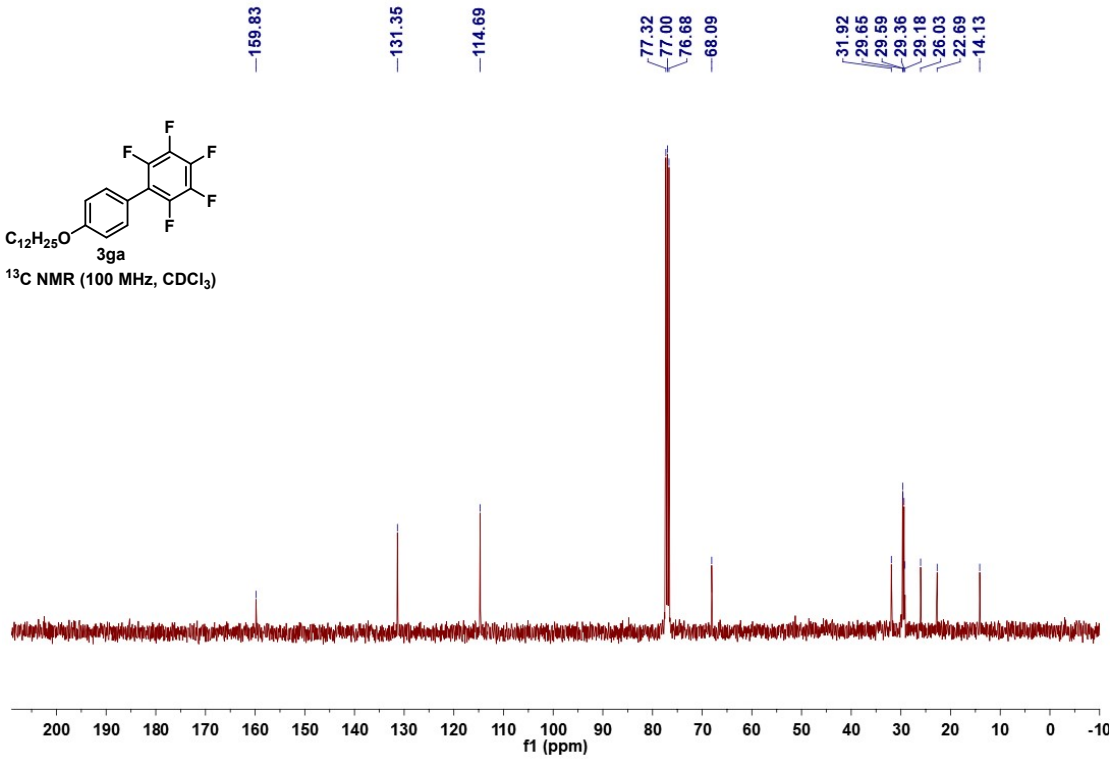

-143.33
-143.35
-143.39
-143.42
-156.18
-156.23
-156.29
-162.42
-162.43
-162.45
-162.48
-162.49
-162.50
-162.51
-162.54
-162.57
F
F
F
F
F
Cy
3ea
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)

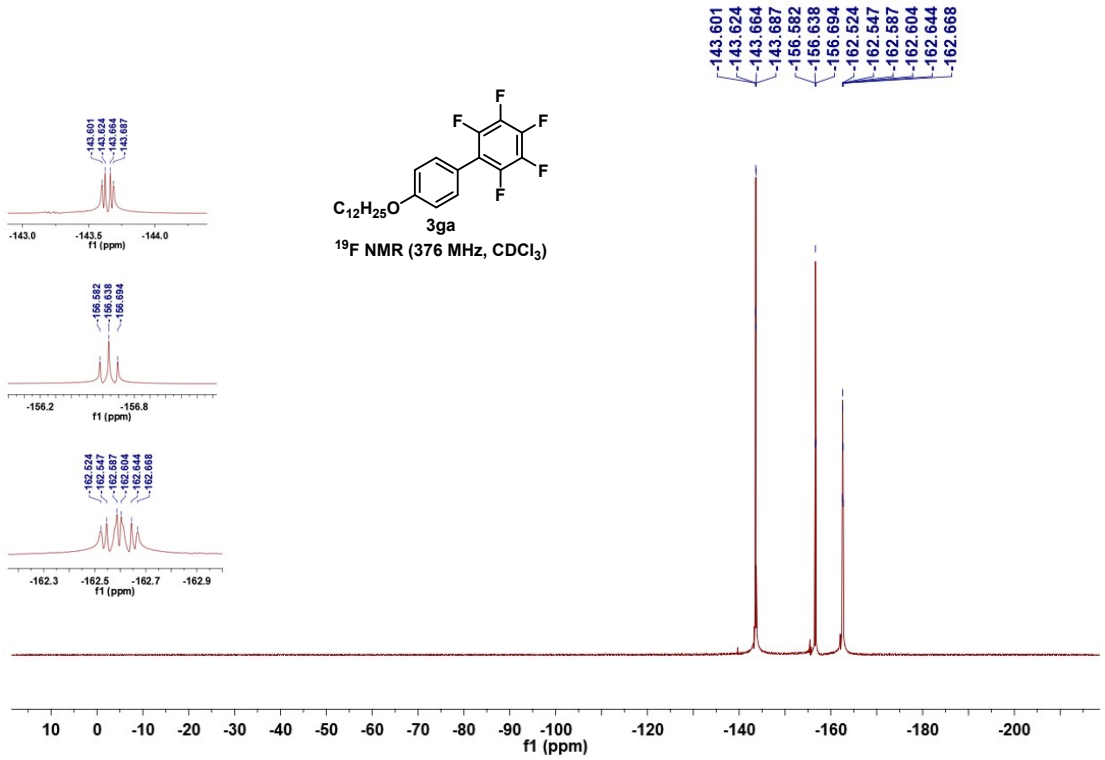

7.378
7.358
7.032
7.011
3.869
F
F
F
F
F
MeO
3fa
^{1}H NMR (400 MHz, CDCl$_3$)
1.94
1.98
3.00
f1 (ppm)

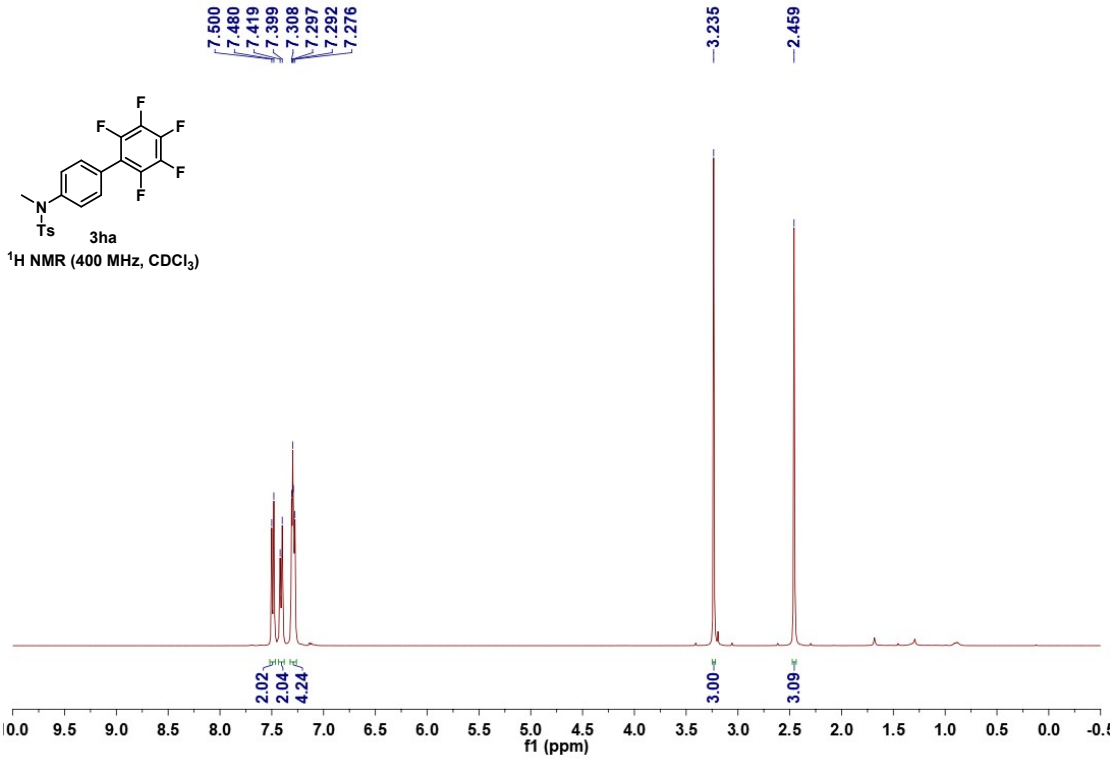

160.23
145.50
145.38
145.24
142.96
142.90
142.82
139.07
131.39
118.35
115.68
115.64
115.54
115.50
115.45
114.19
77.32
77.00
76.68
55.28
F
F
F
F
F
MeO
3fa
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

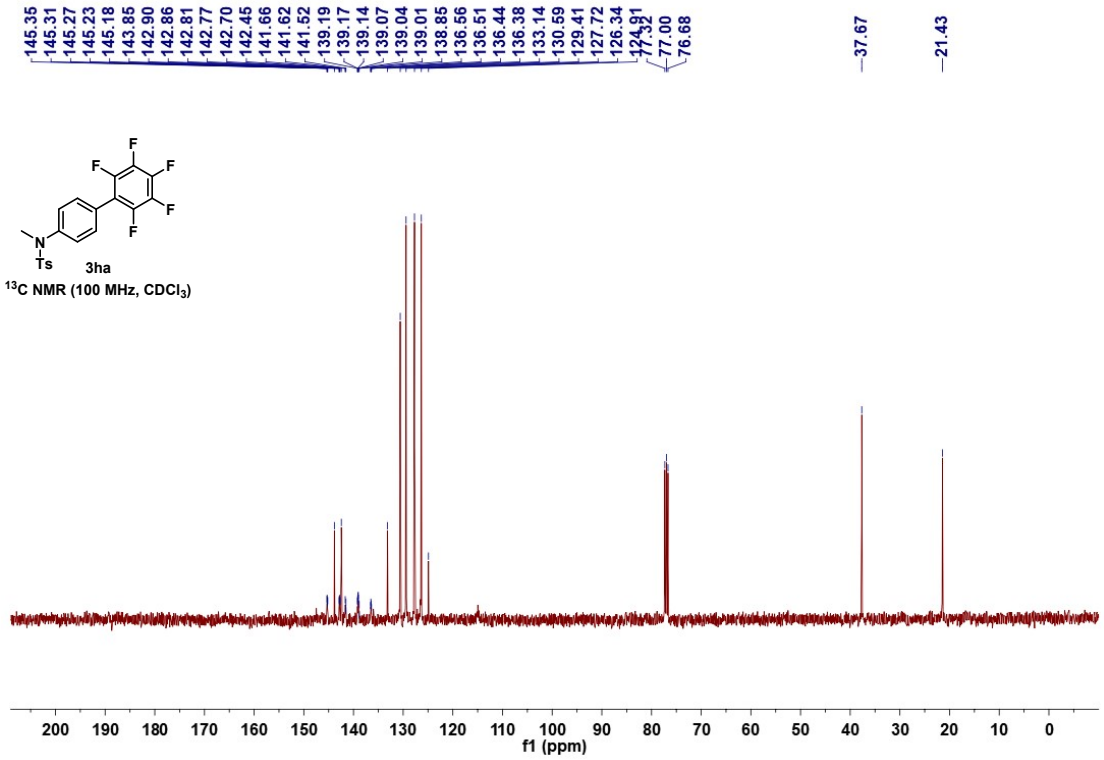

-143.628
-143.651
-143.691
-143.714
-156.494
-156.551
-156.607
-162.508
-162.531
-162.571
-162.587
-162.593
-162.627
-162.650
-162.652
F
F
F
F
F
MeO
3fa
^{19}F NMR (376 MHz, CDCl$_3$)
-141 -142 -143 -144 -145 -146 -147
-155 -156 -157 -158 -159
-161 -162 -163 -164 -165
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

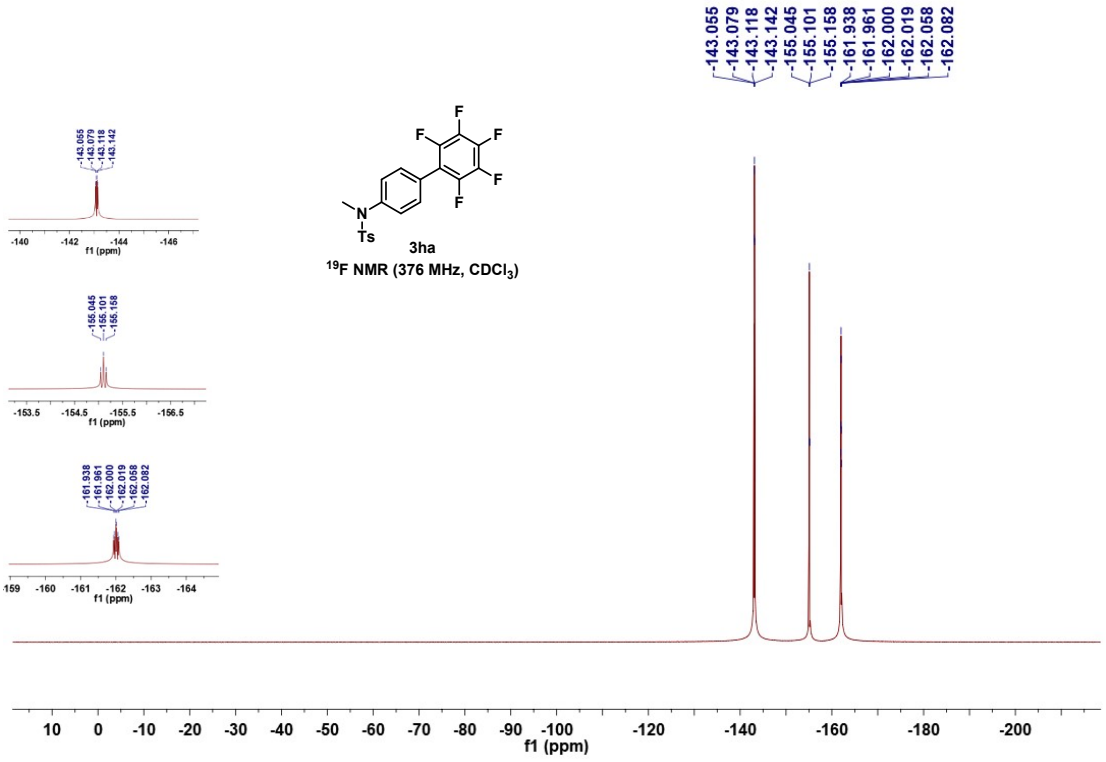

7.354
7.335
7.010
6.992
4.020
4.004
3.988
1.827
1.811
1.794
1.472
1.458
1.272
0.883
0.869
F
F
F
F
F
C12H25O
3ga
1H NMR (400 MHz, CDCl3)
2.00
2.01
2.00
2.01
2.13
16.06
3.04
f1 (ppm)

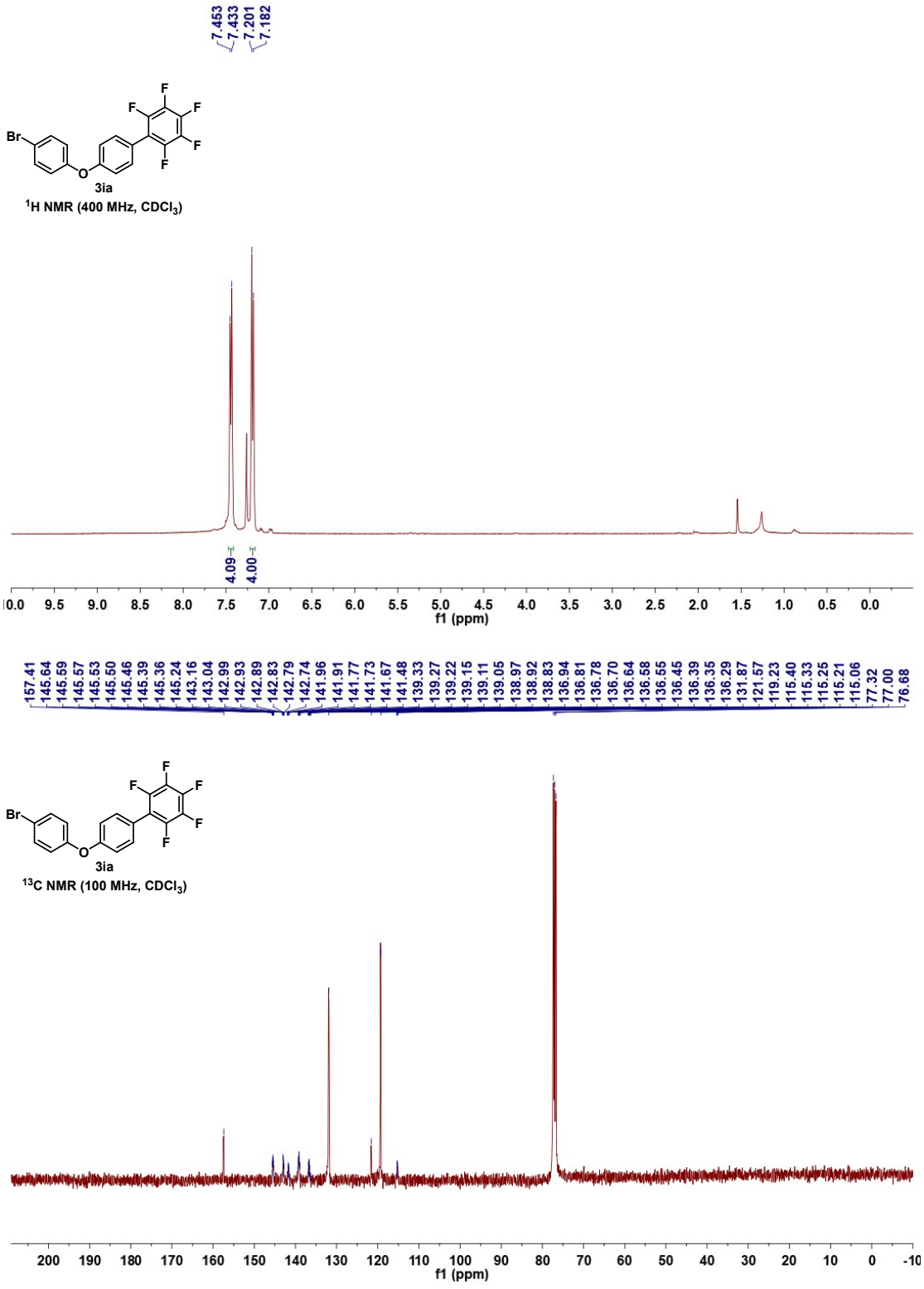

159.83
131.35
114.69
77.32
77.00
76.68
68.09
31.92
29.65
29.59
29.36
29.18
26.03
22.69
14.13
F
F
F
F
F
C12H25O
3ga
13C NMR (100 MHz, CDCl3)
f1 (ppm)

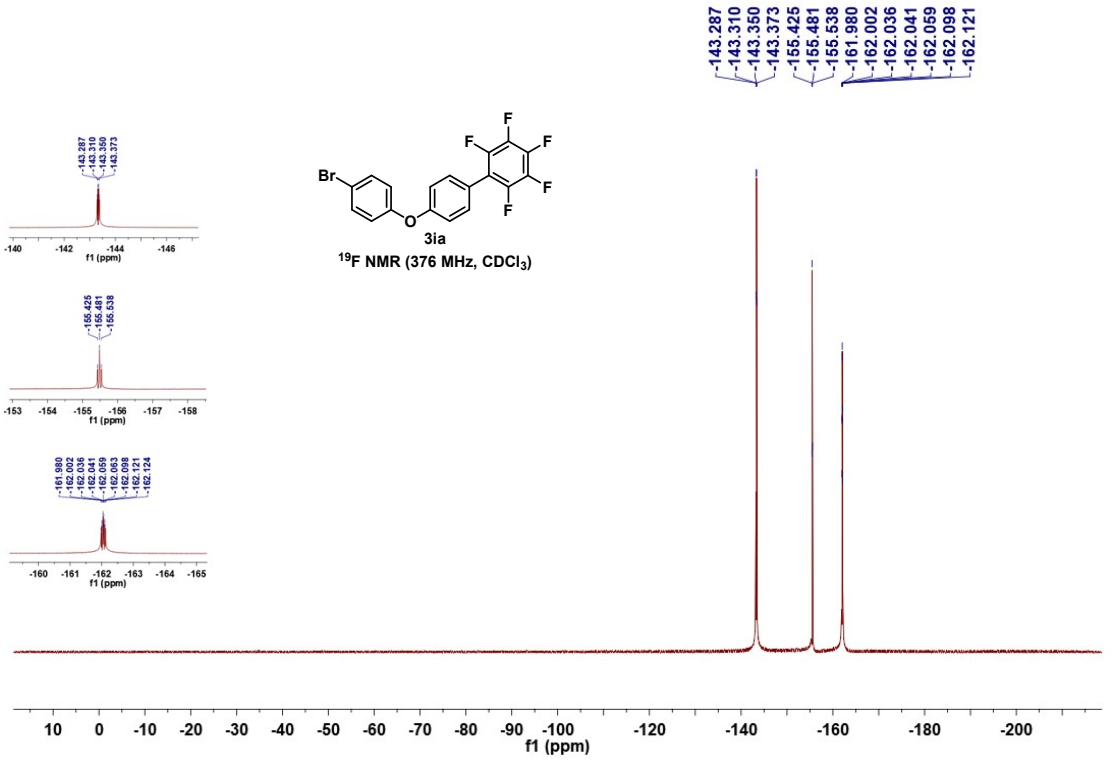

-143.601
-143.624
-143.664
-143.687
-156.582
-156.638
-156.694
-162.524
-162.547
-162.587
-162.604
-162.644
-162.668
F
F
F
F
F
$C_{12}H_{25}O$
3ga
^{19}F NMR (376 MHz, $CDCl_3$)
f1 (ppm)

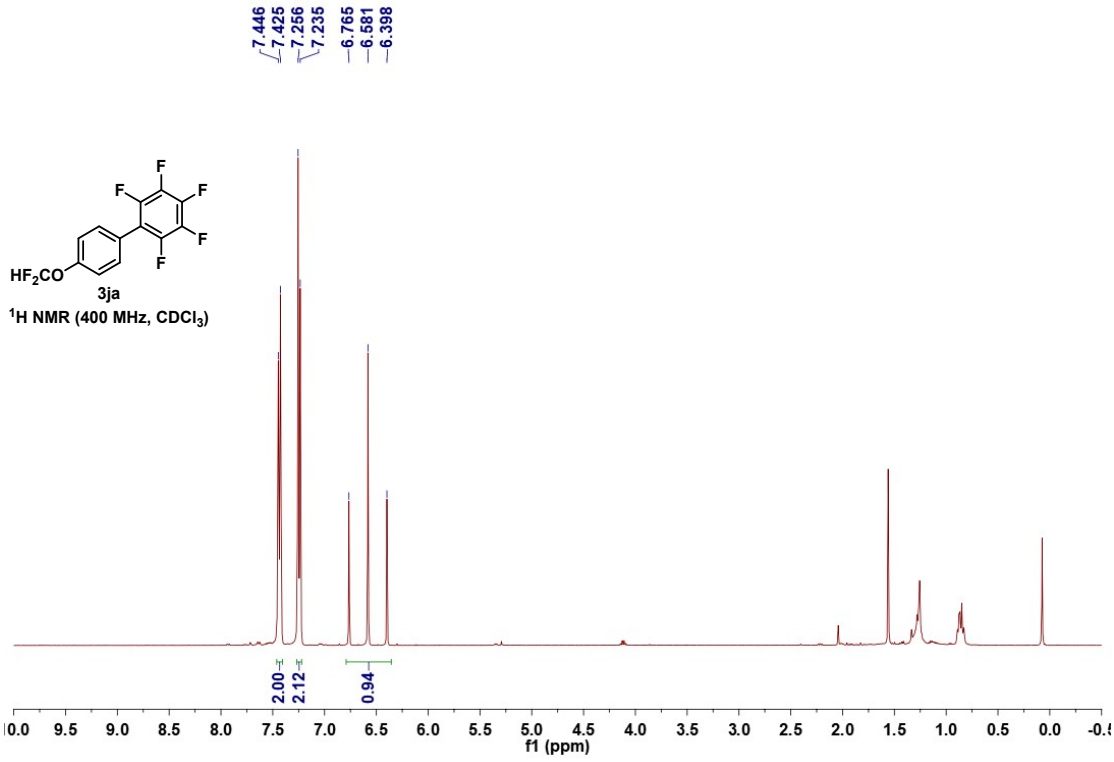

7.500
7.480
7.419
7.399
7.308
7.297
7.292
7.276
3.235
2.459
F
F
F
F
F
N
Ts
3ha
^{1}H NMR (400 MHz, $CDCl_3$)
2.02
2.04
4.24
3.00
3.09
f1 (ppm)

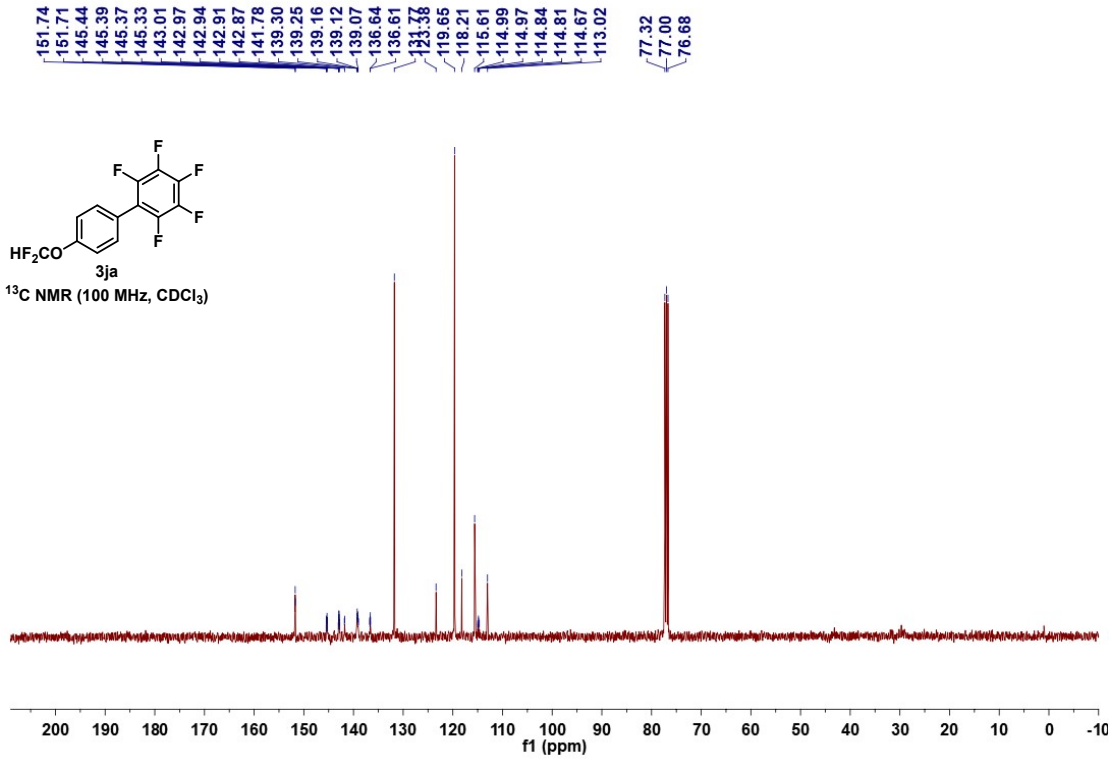

145.35
145.31
145.27
145.23
145.18
143.85
142.90
142.86
142.81
142.77
142.70
142.45
141.66
141.62
141.52
139.19
139.17
139.14
139.07
139.04
139.01
138.85
136.56
136.51
136.44
136.38
133.14
130.59
129.41
127.72
126.34
77.32
77.00
76.68
37.67
21.43
F
F
F
F
F
N
Ts
3ha
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

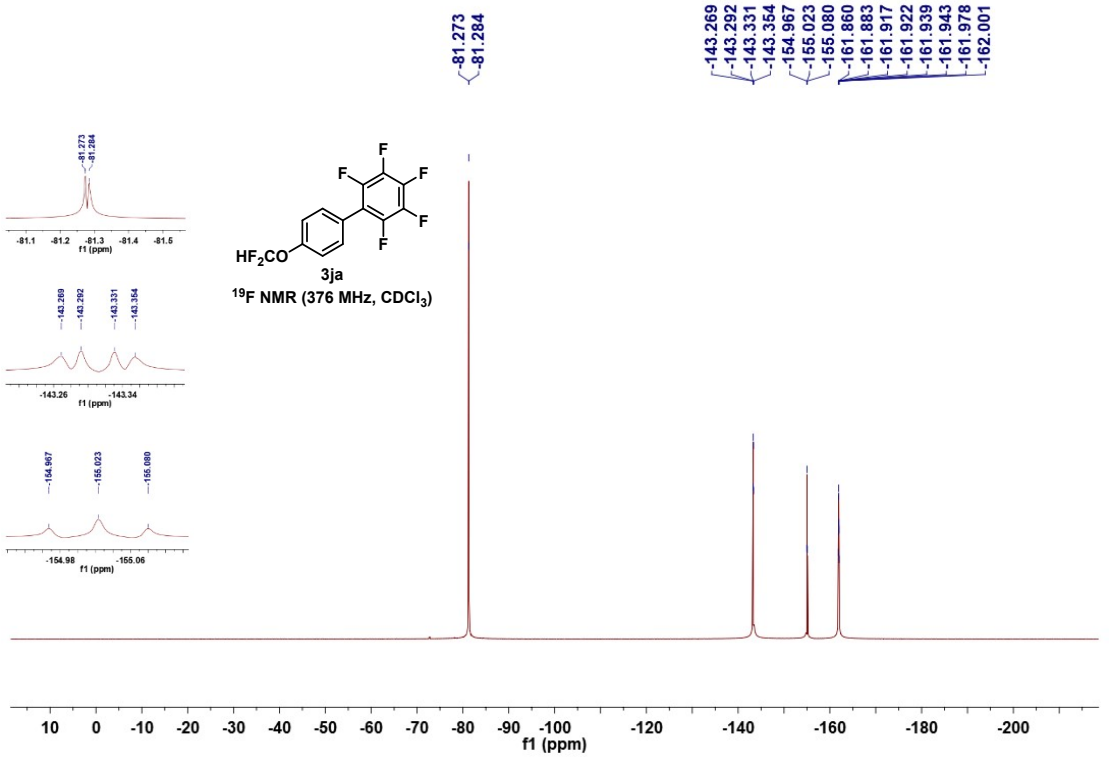

-143.055
-143.079
-143.118
-143.142
-155.045
-155.101
-155.158
-161.938
-161.961
-162.000
-162.019
-162.058
-162.082
F
F
F
F
F
N
Ts
3ha
^{19}F NMR (376 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

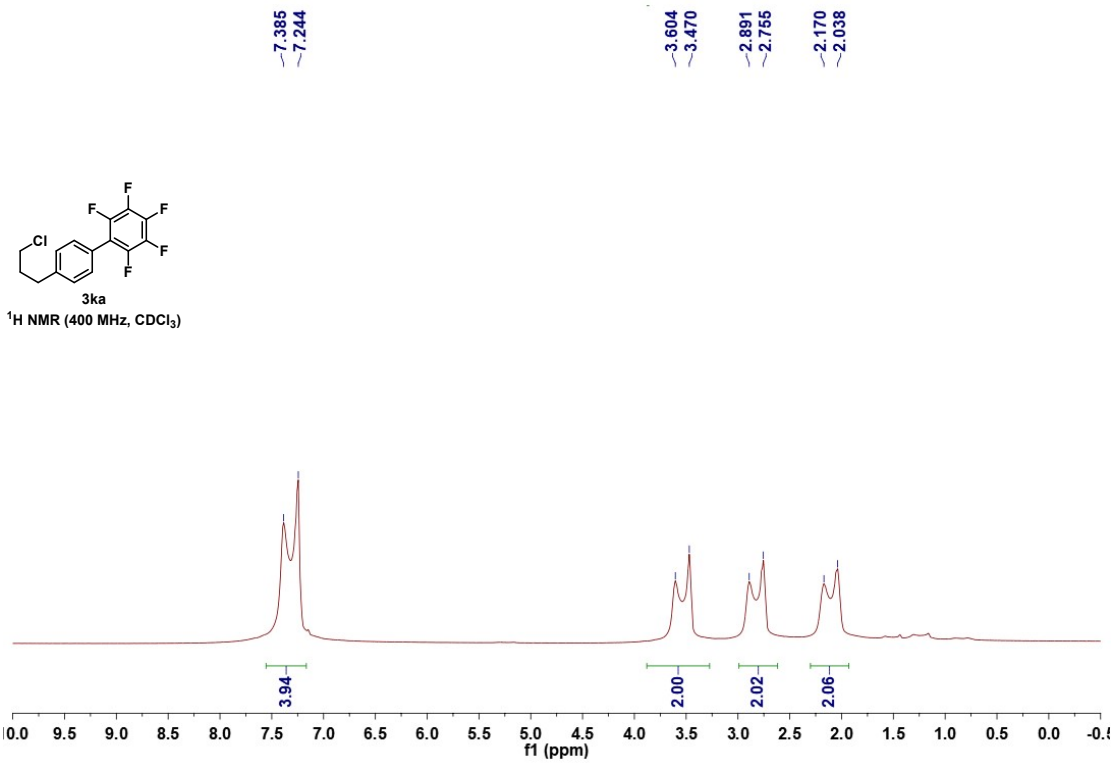

7.453
7.433
7.201
7.182
Br
O
F
F
F
F
F
3ia
^{1}H NMR (400 MHz, CDCl$_3$)
4.09
4.00
f1 (ppm)
157.41
145.64
145.59
145.57
145.53
145.50
145.46
145.39
145.36
145.24
143.16
143.04
142.99
142.93
142.89
142.83
142.79
142.74
141.96
141.91
141.77
141.73
141.67
141.48
139.33
139.27
139.22
139.15
139.11
139.05
138.97
138.92
138.83
136.94
136.81
136.78
136.70
136.64
136.58
136.55
136.45
136.39
136.35
136.29
131.87
121.57
119.23
115.40
115.33
115.25
115.21
115.06
77.32
77.00
76.68
Br
O
F
F
F
F
F
3ia
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

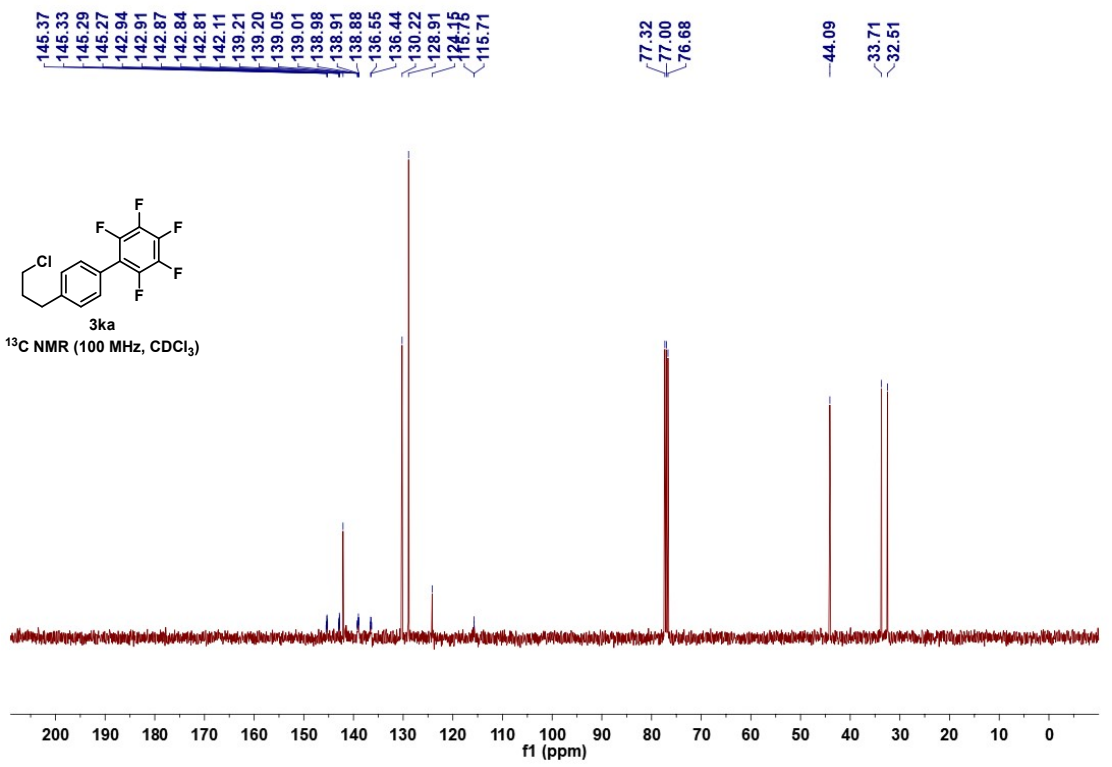

-143.287
-143.310
-143.350
-143.373
-155.425
-155.481
-155.538
-161.980
-162.002
-162.036
-162.041
-162.059
-162.098
-162.121
F
F
F
F
F
Br
O
3ia
19F NMR (376 MHz, CDCl3)
f1 (ppm)

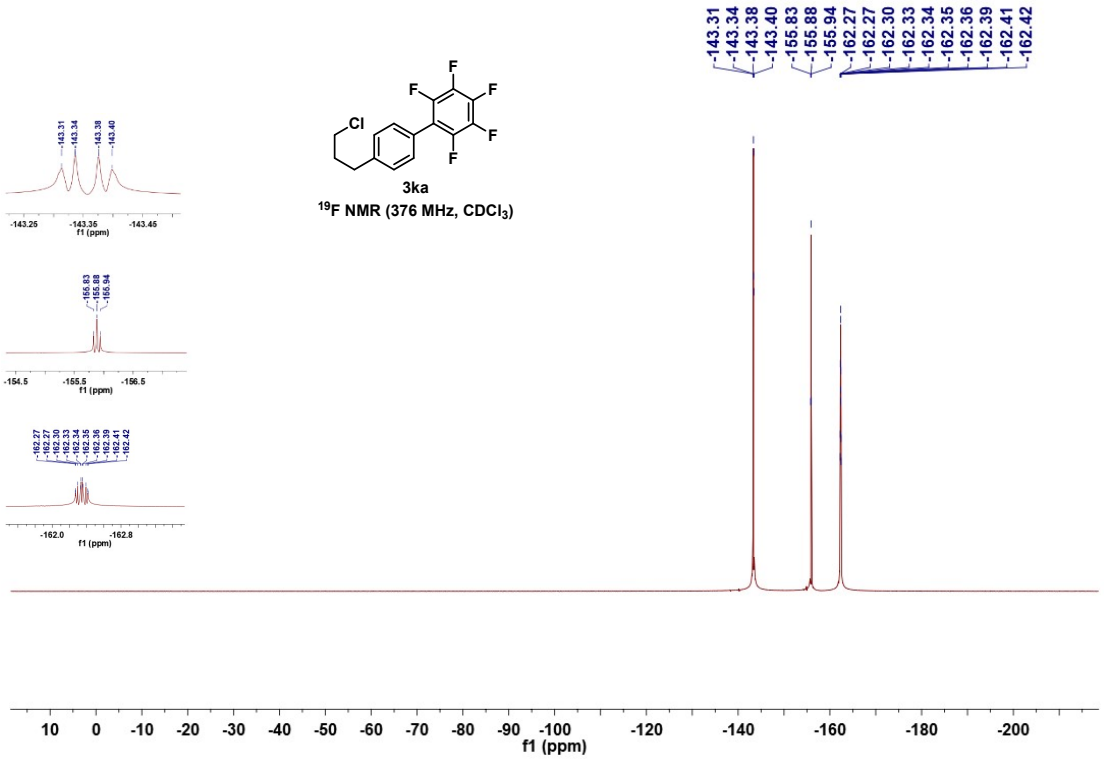

7.446
7.425
7.256
7.235
6.765
6.581
6.398
F
F
F
F
F
HF2CO
3ja
1H NMR (400 MHz, CDCl3)
2.00
2.12
0.94
f1 (ppm)

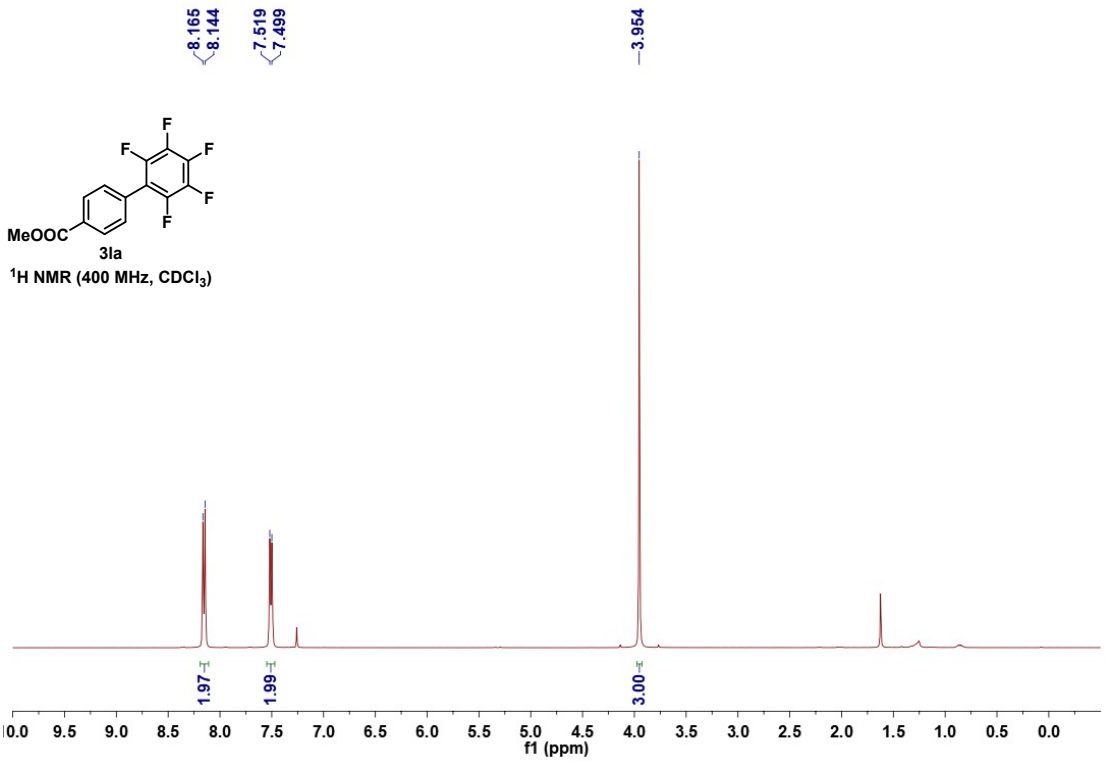

151.74
151.71
145.44
145.39
145.37
145.33
143.01
142.97
142.94
142.91
142.87
141.78
139.30
139.25
139.16
139.12
139.07
136.64
136.61
119.65
118.21
115.61
114.99
114.97
114.84
114.81
114.67
113.02
77.32
77.00
76.68
F
F
F
F
F
HF2CO
3ja
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

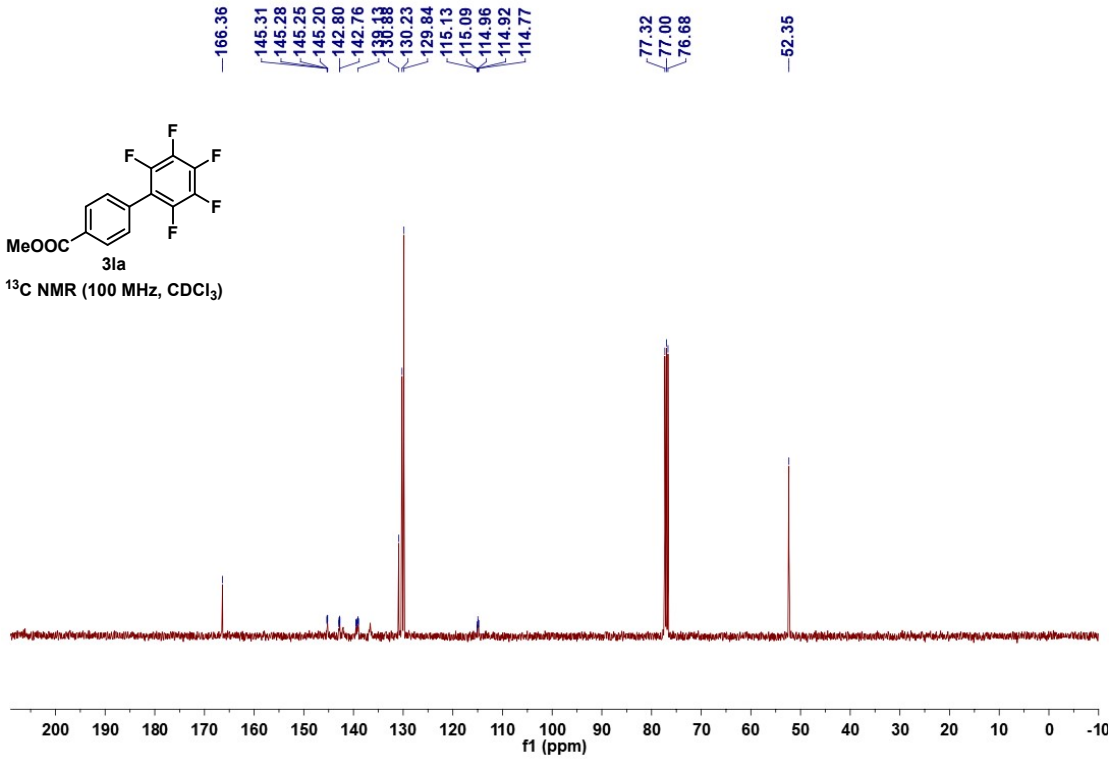

-81.273
-81.284
-143.269
-143.292
-143.331
-143.354
-154.967
-155.023
-155.080
-161.860
-161.883
-161.917
-161.922
-161.939
-161.943
-161.978
-162.001
F
F
F
F
F
HF2CO
3ja
19F NMR (376 MHz, CDCl3)
-81.1 -81.2 -81.3 -81.4 -81.5
f1 (ppm)
-143.26
-143.34
-154.98
-155.06
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

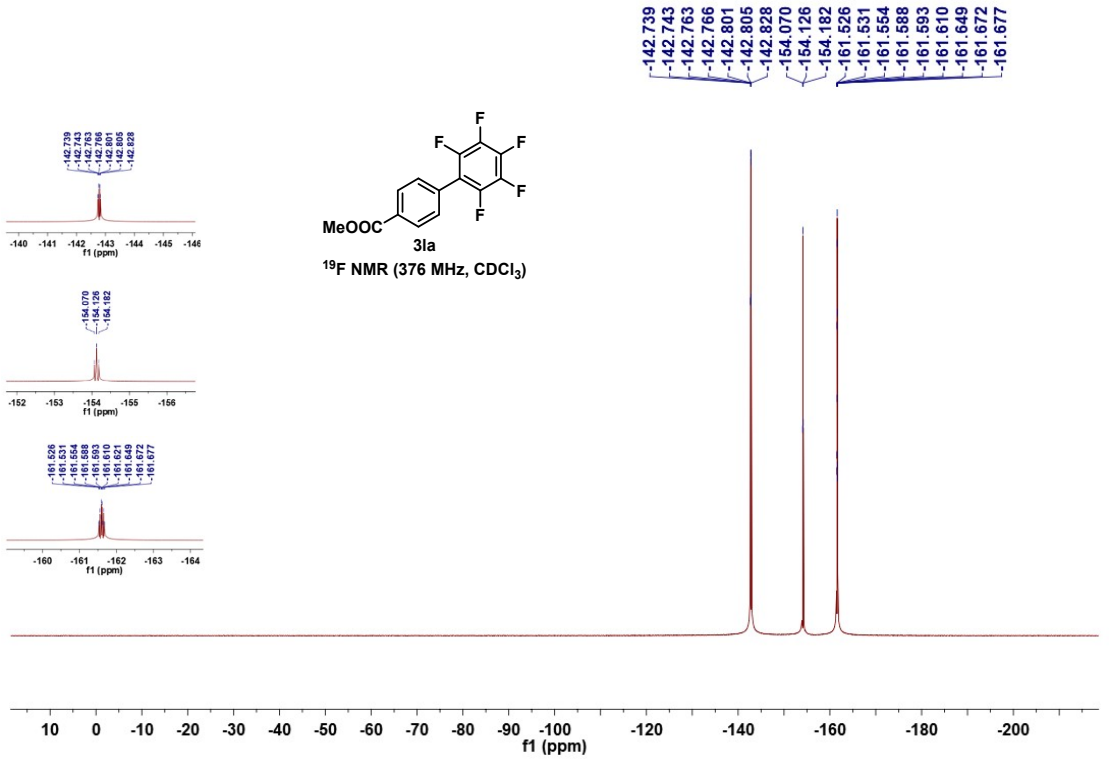

7.385
7.244
3.604
3.470
2.891
2.755
2.170
2.038
F
F
F
F
F
Cl
3ka
^{1}H NMR (400 MHz, CDCl$_3$)
3.94
2.00
2.02
2.06
f1 (ppm)

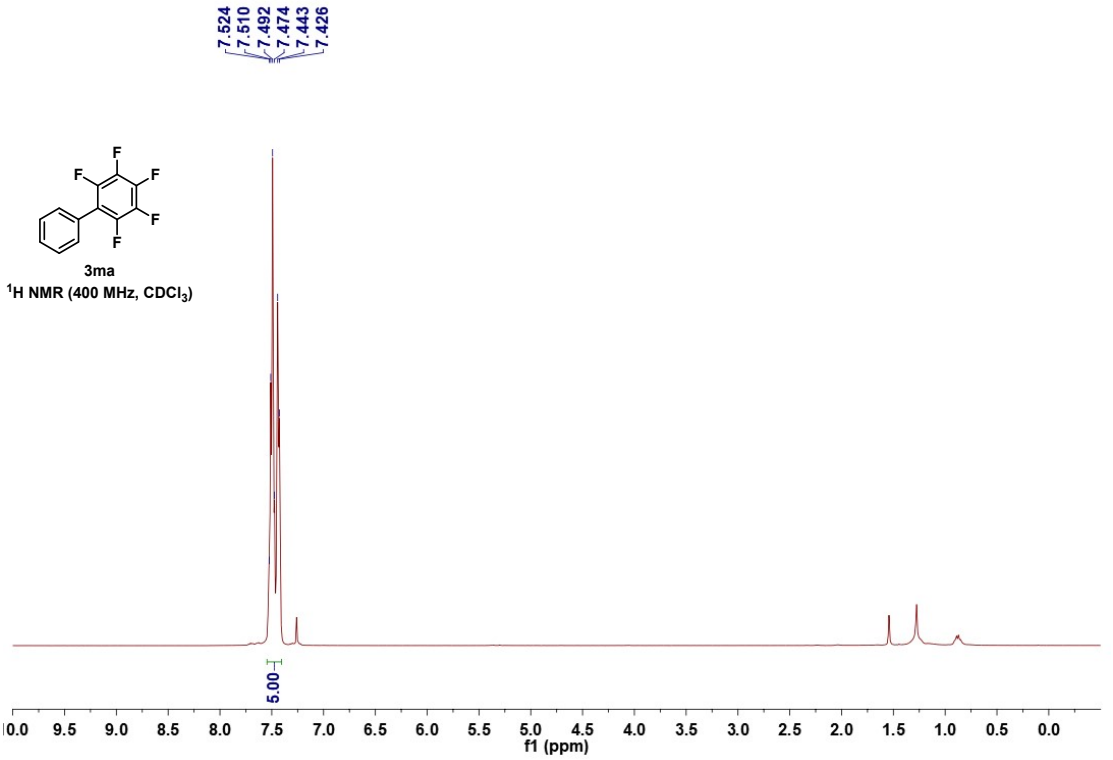

145.37
145.33
145.29
145.27
142.94
142.91
142.87
142.84
142.81
142.11
139.21
139.20
139.05
139.01
138.98
138.91
138.88
136.55
136.44
130.22
128.91
115.71
77.32
77.00
76.68
44.09
33.71
32.51
F
F
F
F
F
Cl
3ka
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

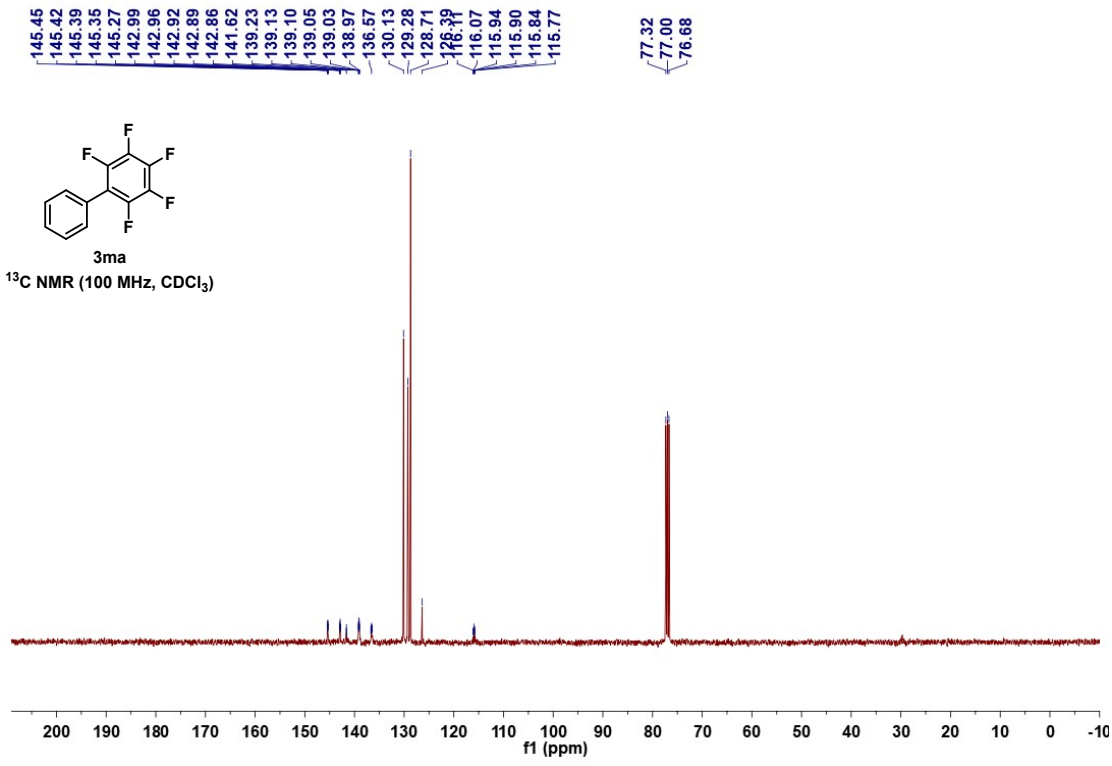

-143.31
-143.34
-143.38
-143.40
-155.83
-155.88
-155.94
-162.27
-162.27
-162.30
-162.33
-162.34
-162.35
-162.36
-162.39
-162.41
-162.42
F
F
F
F
F
Cl
3ka
^{19}F NMR (376 MHz, $CDCl_3$)
f1 (ppm)

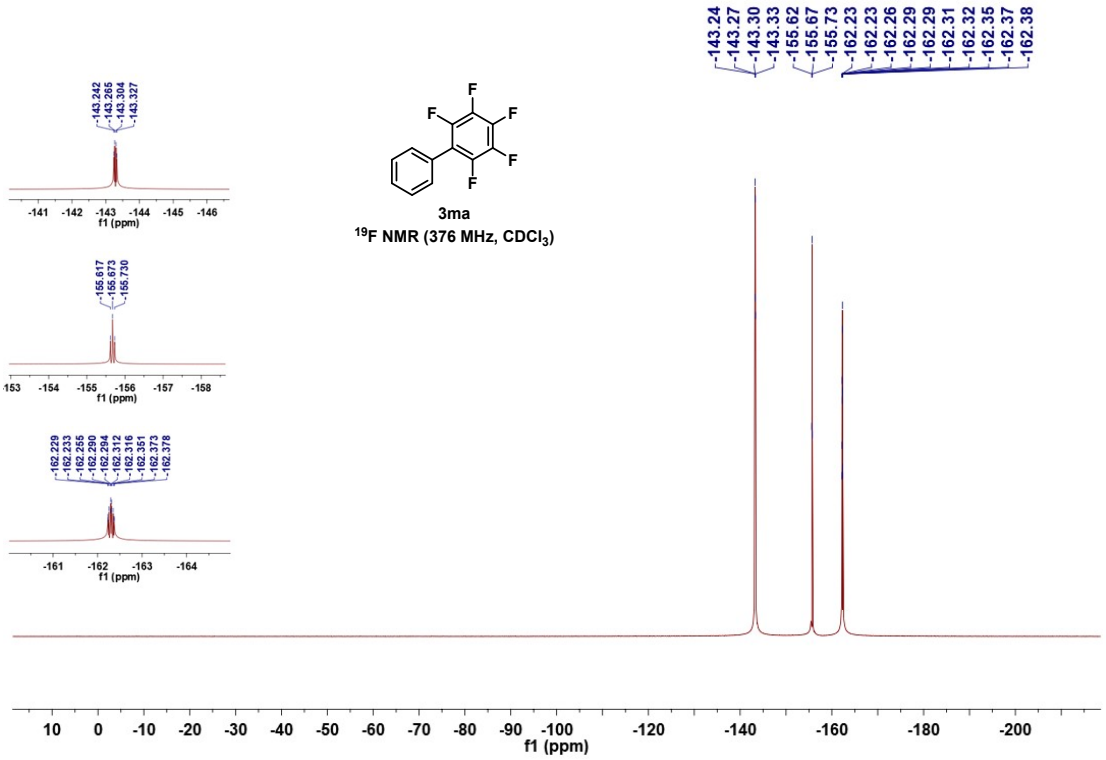

8.165
8.144
7.519
7.499
3.964
F
F
F
F
F
MeOOC
3la
^{1}H NMR (400 MHz, $CDCl_3$)
1.97
1.99
3.00
f1 (ppm)

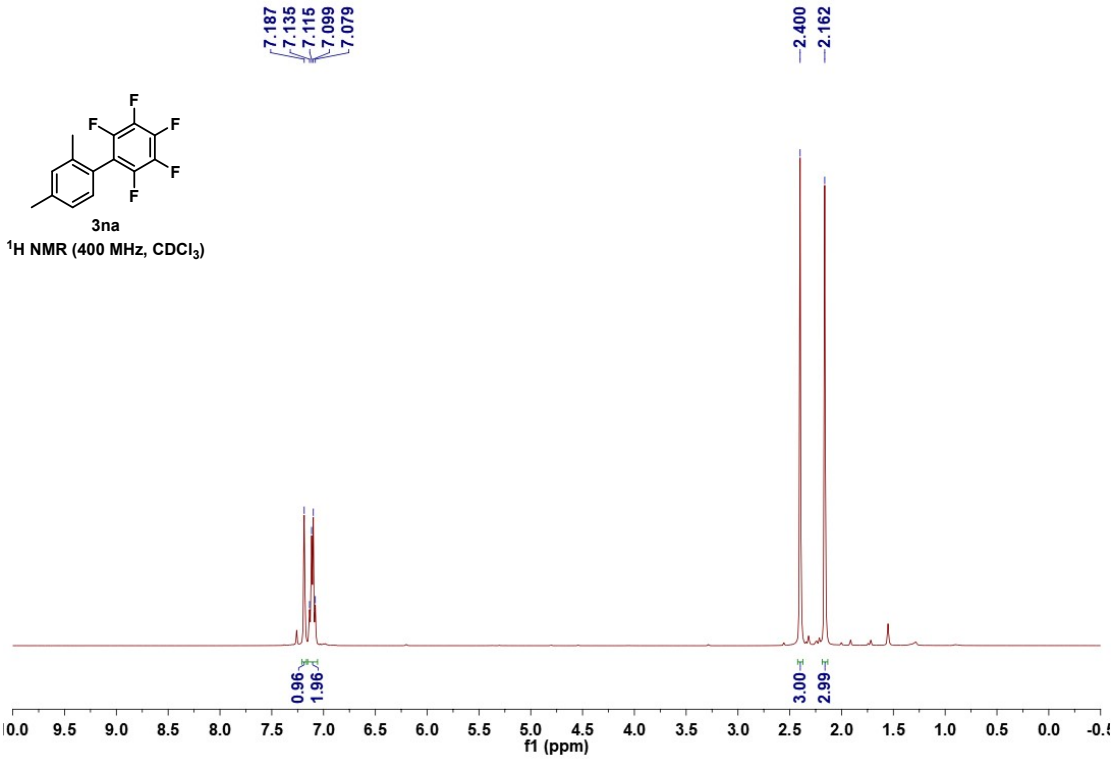

166.36
145.31
145.28
145.25
145.20
142.80
142.76
130.23
129.84
115.13
115.09
114.96
114.92
114.77
77.32
77.00
76.68
52.35
F
F
F
F
F
MeOOC
3la
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

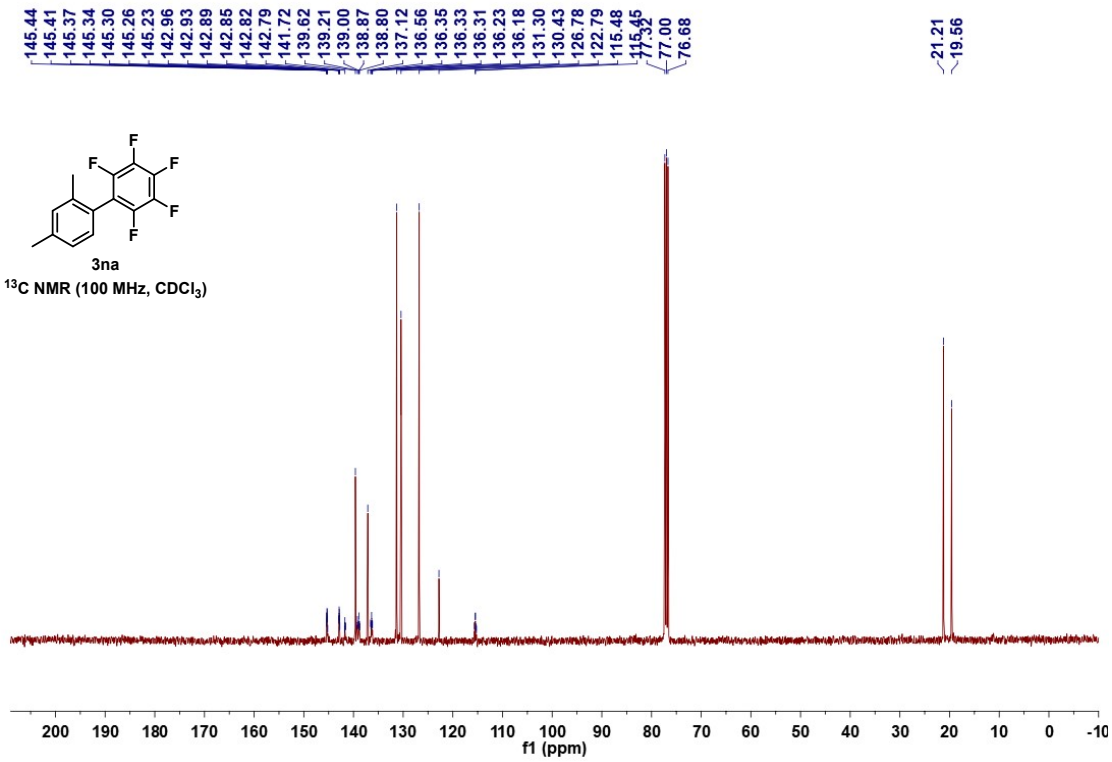

-142.739
-142.743
-142.763
-142.766
-142.801
-142.805
-142.828
-154.070
-154.126
-154.182
-161.526
-161.531
-161.554
-161.588
-161.593
-161.610
-161.649
-161.672
-161.677
F
F
F
F
F
MeOOC
3la
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

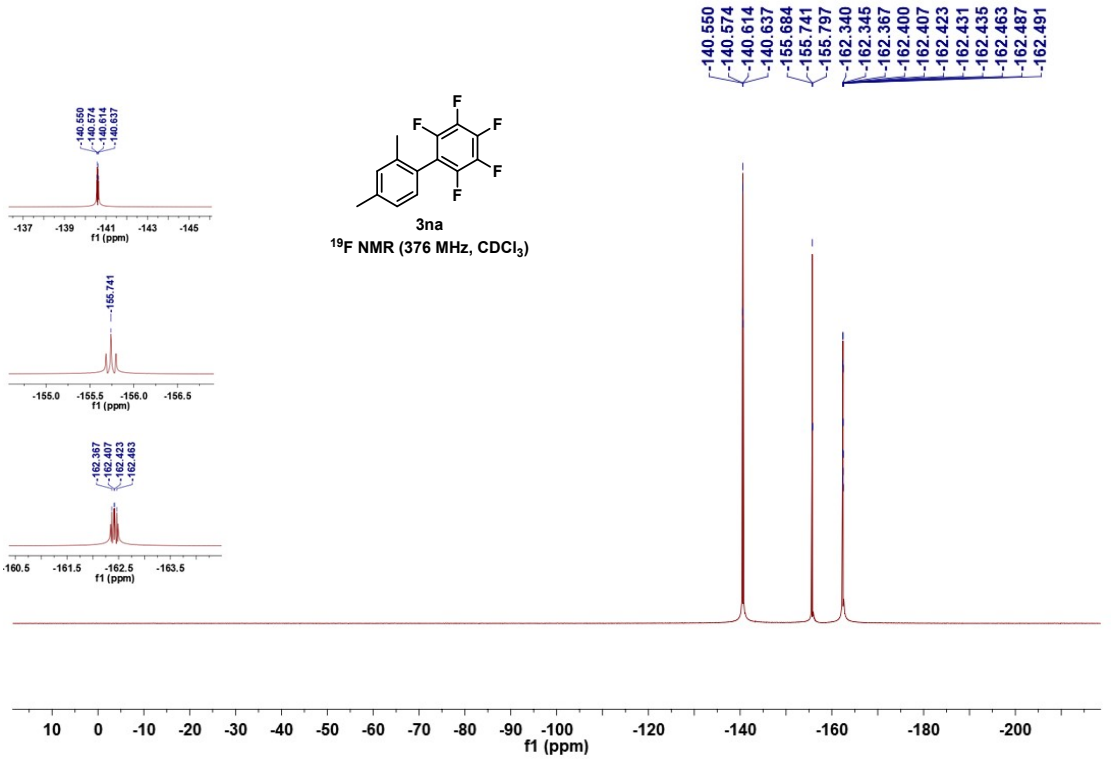

7.524
7.510
7.492
7.474
7.443
7.426
F
F
F
F
F
3ma
1H NMR (400 MHz, CDCl3)
5.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

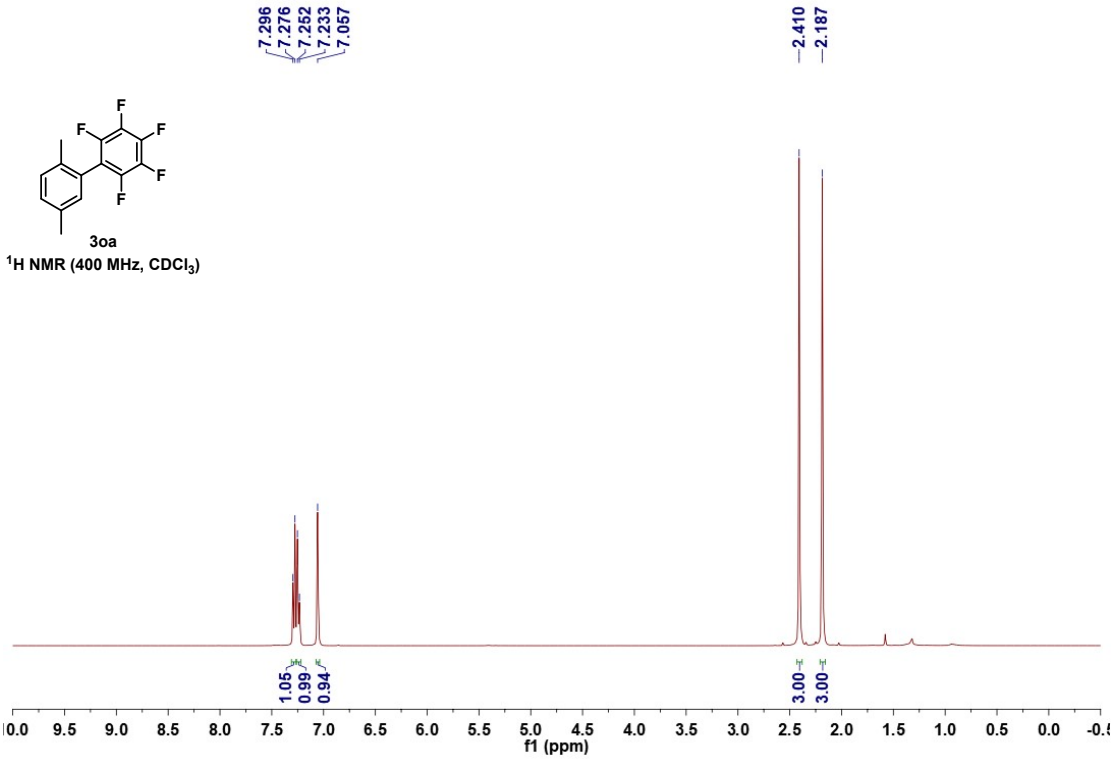

145.45
145.42
145.39
145.35
145.27
142.99
142.96
142.92
142.89
142.86
141.62
139.23
139.13
139.10
139.05
139.03
138.97
136.57
130.13
129.28
128.71
116.07
115.94
115.90
115.84
115.77
77.32
77.00
76.68
F
F
F
F
F
3ma
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

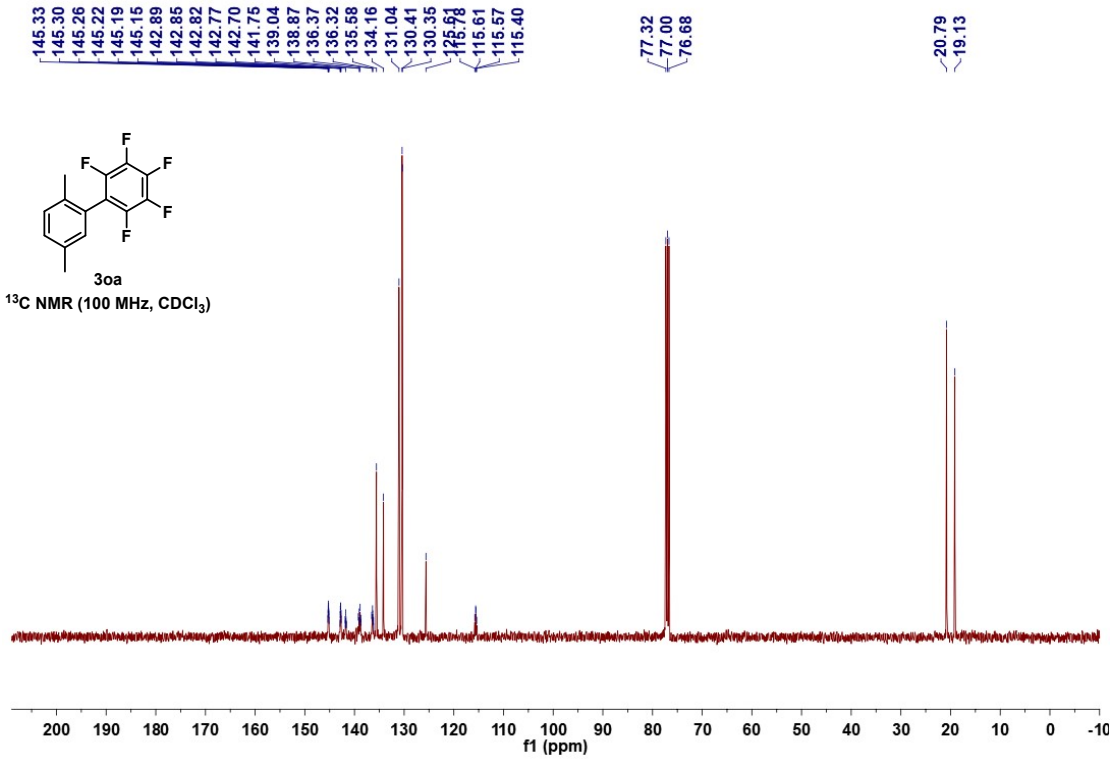

-143.242
-143.265
-143.304
-143.327
-141 -142 -143 -144 -145 -146
f1 (ppm)
-155.617
-155.673
-155.730
153 -154 -155 -156 -157 -158
f1 (ppm)
-162.229
-162.233
-162.255
-162.290
-162.294
-162.312
-162.316
-162.351
-162.373
-162.378
-161 -162 -163 -164
f1 (ppm)
F
F
F
F
F
3ma
19F NMR (376 MHz, CDCl3)
-143.24
-143.27
-143.30
-143.33
-155.62
-155.67
-155.73
-162.23
-162.23
-162.26
-162.29
-162.29
-162.31
-162.32
-162.35
-162.37
-162.38
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

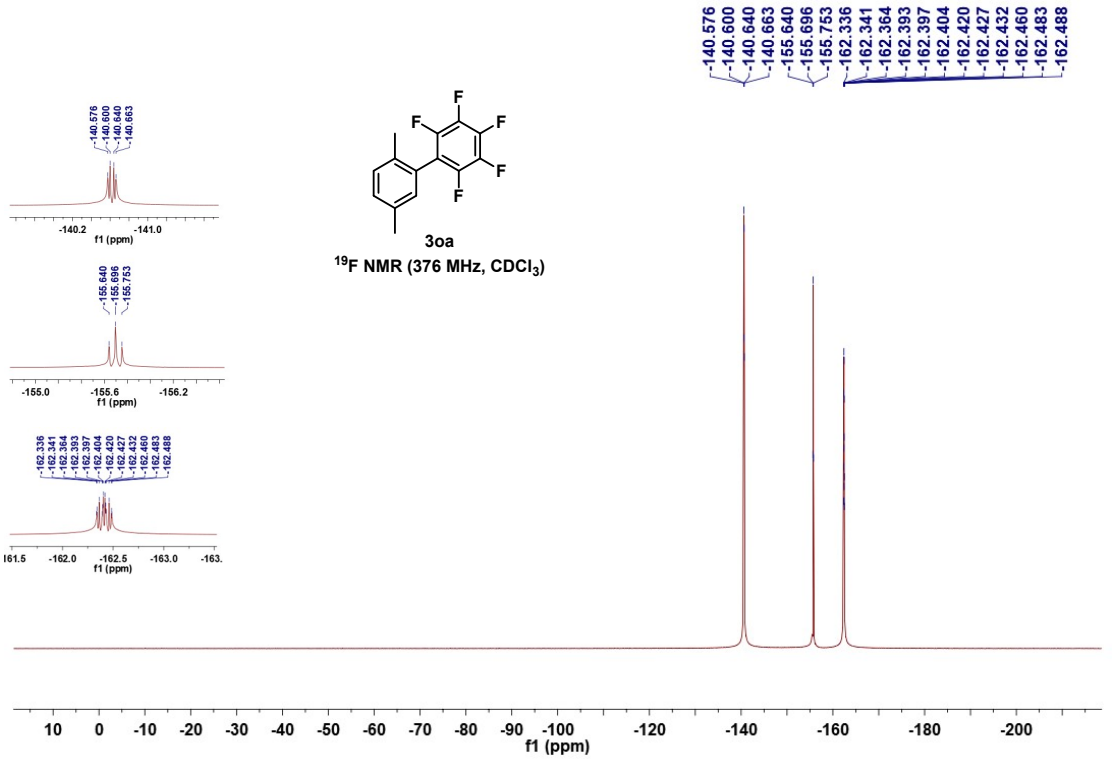

7.187
7.135
7.115
7.099
7.079
2.400
2.162
F
F
F
F
F
3na
1H NMR (400 MHz, CDCl3)
0.96
1.96
3.00
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

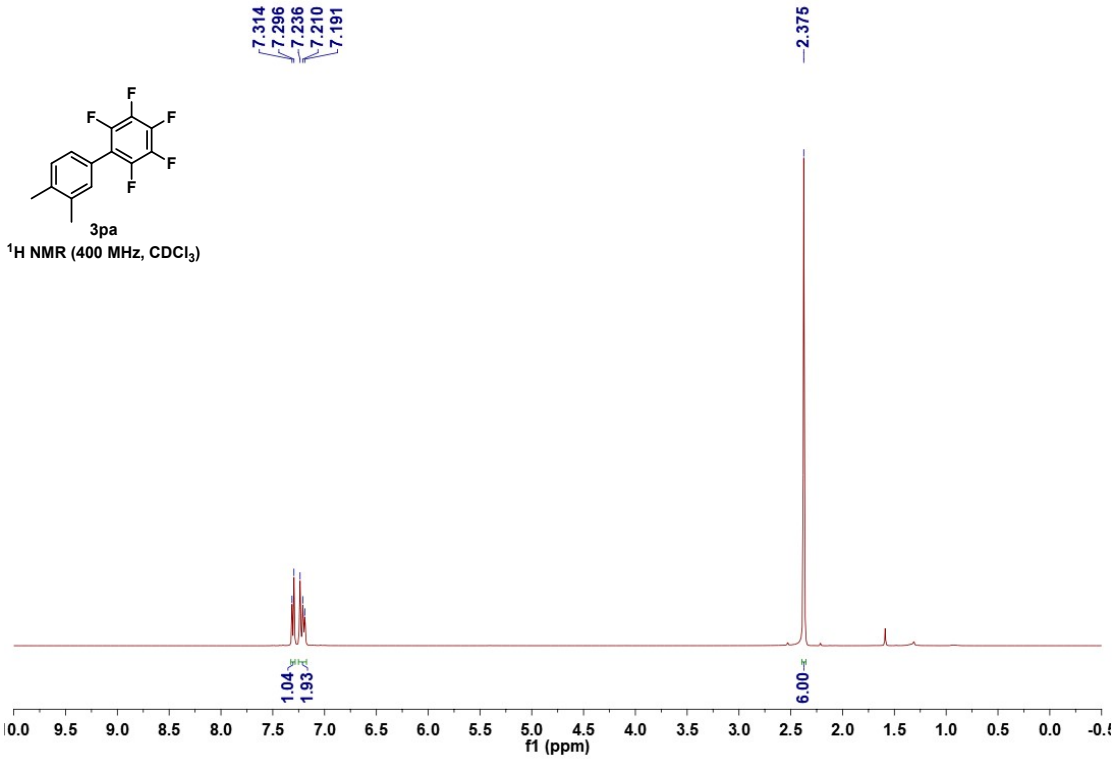

145.44
145.41
145.37
145.34
145.30
145.26
145.23
142.96
142.93
142.89
142.85
142.82
142.79
141.72
139.62
139.21
139.00
138.87
138.80
137.12
136.56
136.35
136.33
136.31
136.23
136.18
131.30
130.43
126.78
122.79
115.48
115.45
77.32
77.00
76.68
21.21
19.56
F
F
F
F
F
3na
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

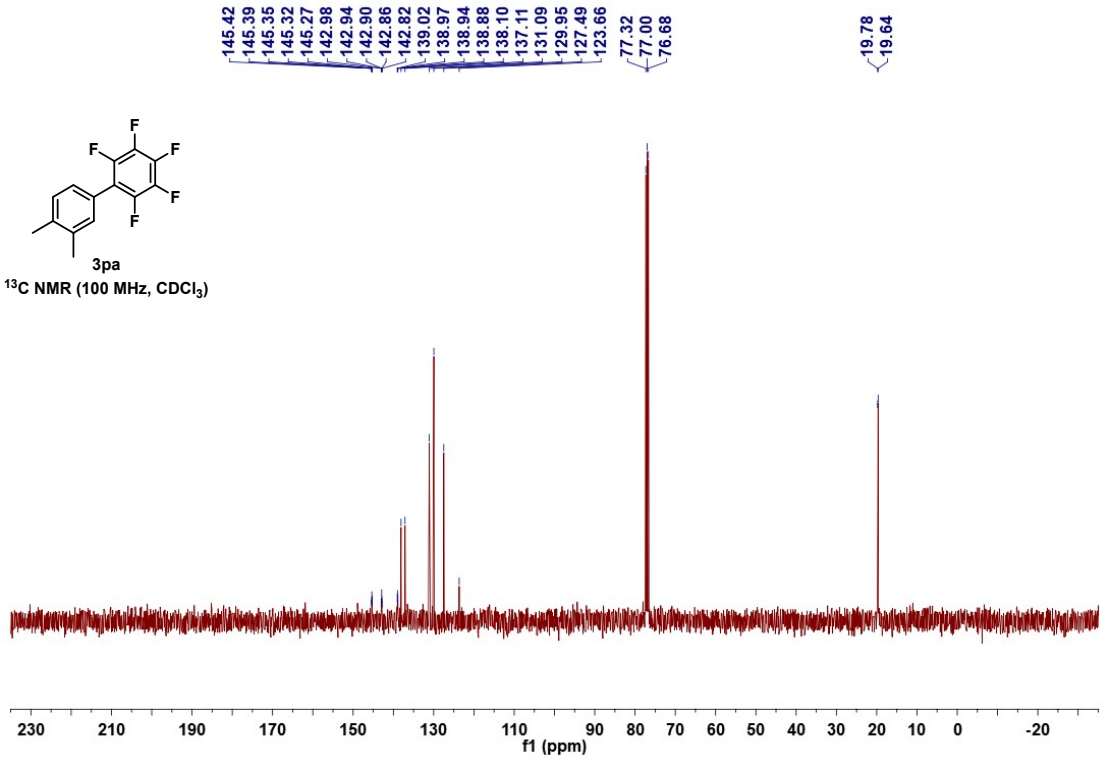

-140.550
-140.574
-140.614
-140.637
-155.684
-155.741
-155.797
-162.340
-162.345
-162.367
-162.400
-162.407
-162.423
-162.431
-162.435
-162.463
-162.487
-162.491
F
F
F
F
F
3na
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

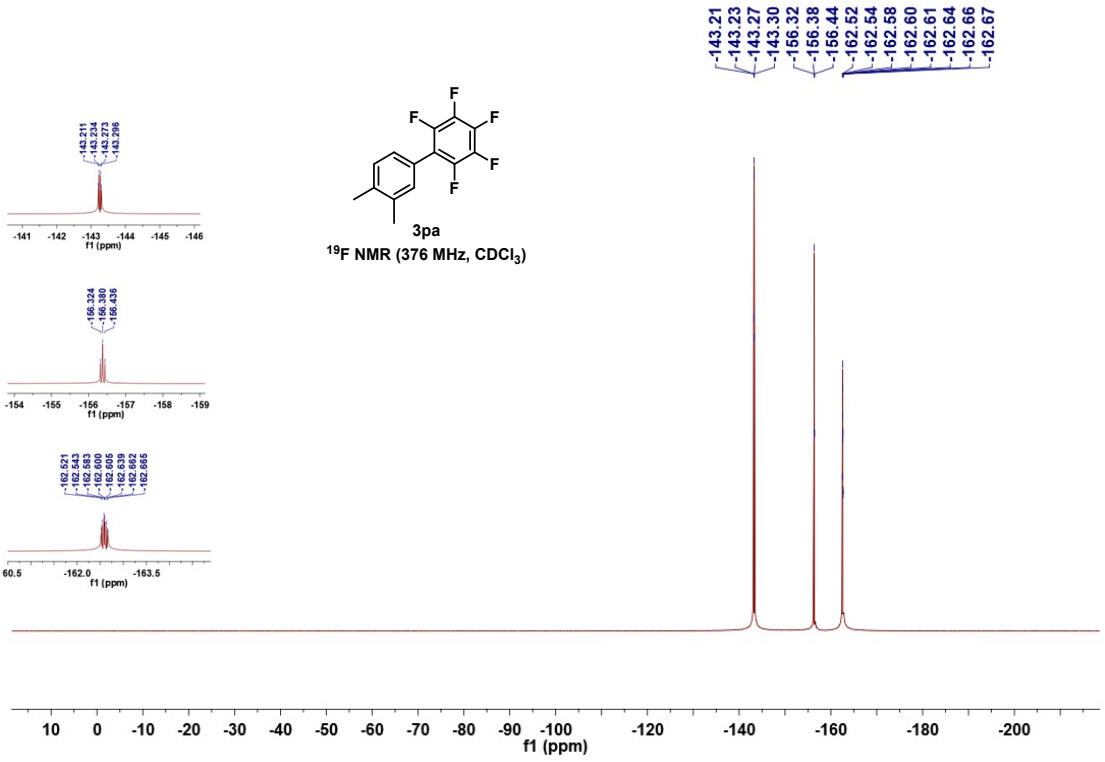

7.296
7.276
7.252
7.233
7.057
2.410
2.187
F
F
F
F
F
3oa
1H NMR (400 MHz, CDCl3)
1.05
0.99
0.94
3.00
3.00
f1 (ppm)

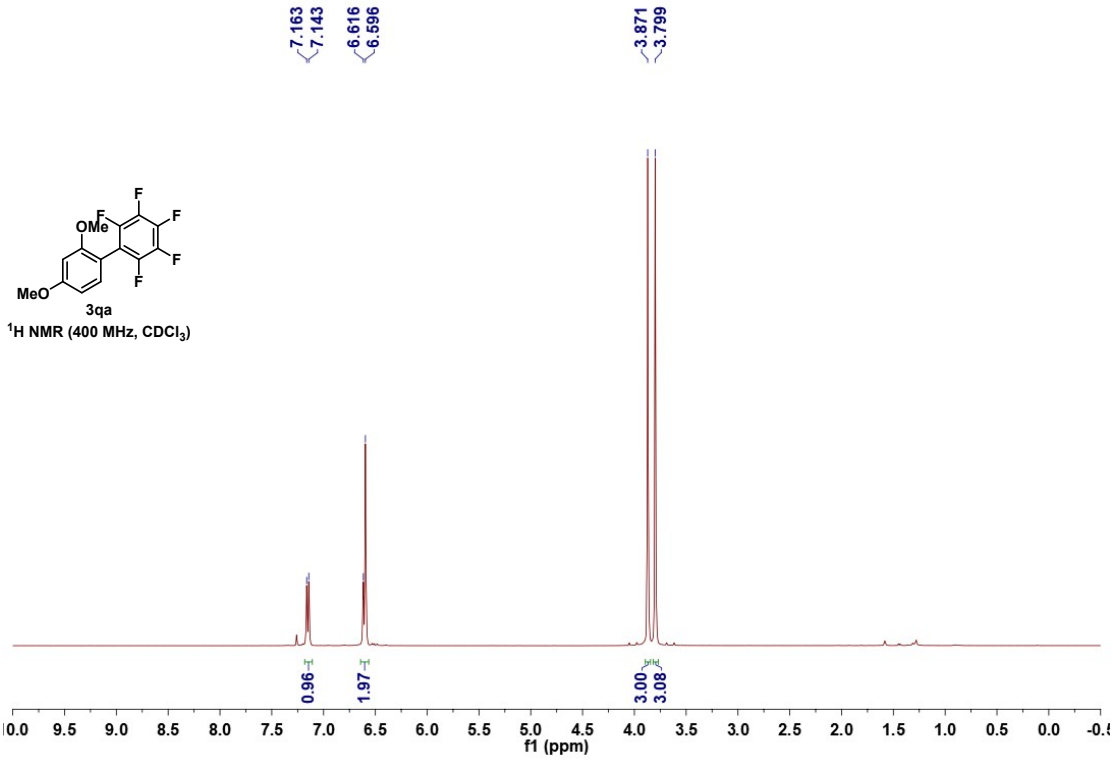

145.33
145.30
145.26
145.22
145.19
145.15
142.89
142.85
142.82
142.77
142.70
141.75
139.04
138.87
136.37
136.32
135.58
134.16
131.04
130.41
130.35
115.61
115.57
115.40
77.32
77.00
76.68
20.79
19.13
F
F
F
F
F
3oa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

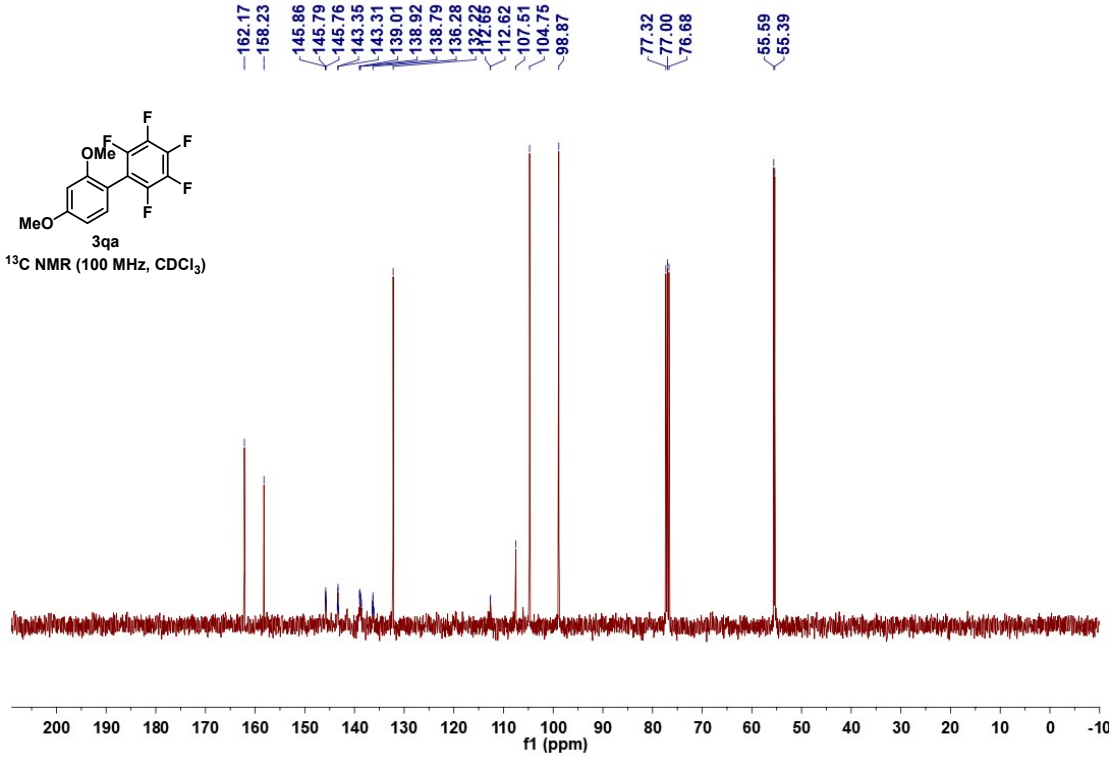

-140.576
-140.600
-140.640
-140.663
-155.640
-155.696
-155.753
-162.336
-162.341
-162.364
-162.393
-162.397
-162.404
-162.420
-162.427
-162.432
-162.460
-162.483
-162.488
F
F
F
F
F
3oa
19F NMR (376 MHz, CDCl3)
f1 (ppm)

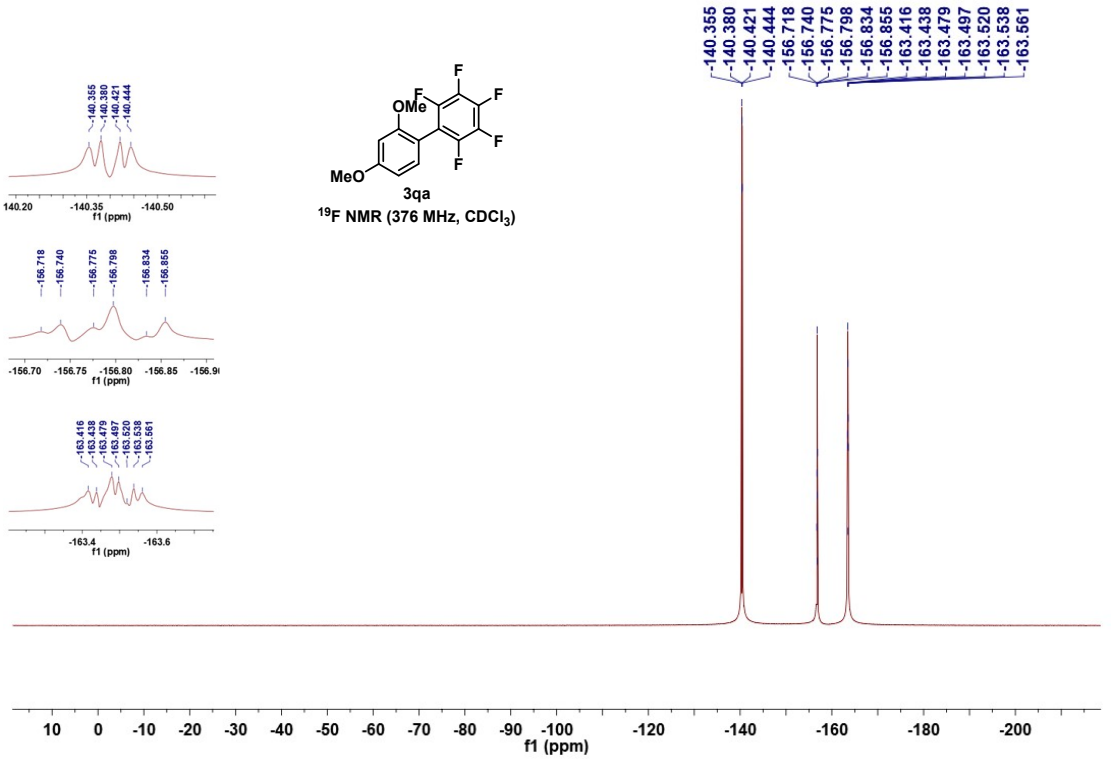

7.314
7.296
7.236
7.210
7.191
2.375
F
F
F
F
F
3pa
1H NMR (400 MHz, CDCl3)
1.04
1.93
6.00
f1 (ppm)


145.42
145.39
145.35
145.32
145.27
142.98
142.94
142.90
142.86
142.82
139.02
138.97
138.94
138.88
138.10
137.11
131.09
129.95
127.49
123.66
77.32
77.00
76.68
19.78
19.64
F
F
F
F
F
3pa
13C NMR (100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
f1 (ppm)


-143.21
-143.23
-143.27
-143.30
-156.32
-156.38
-156.44
-162.52
-162.54
-162.58
-162.60
-162.61
-162.64
-162.66
-162.67
F
F
F
F
F
3pa
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

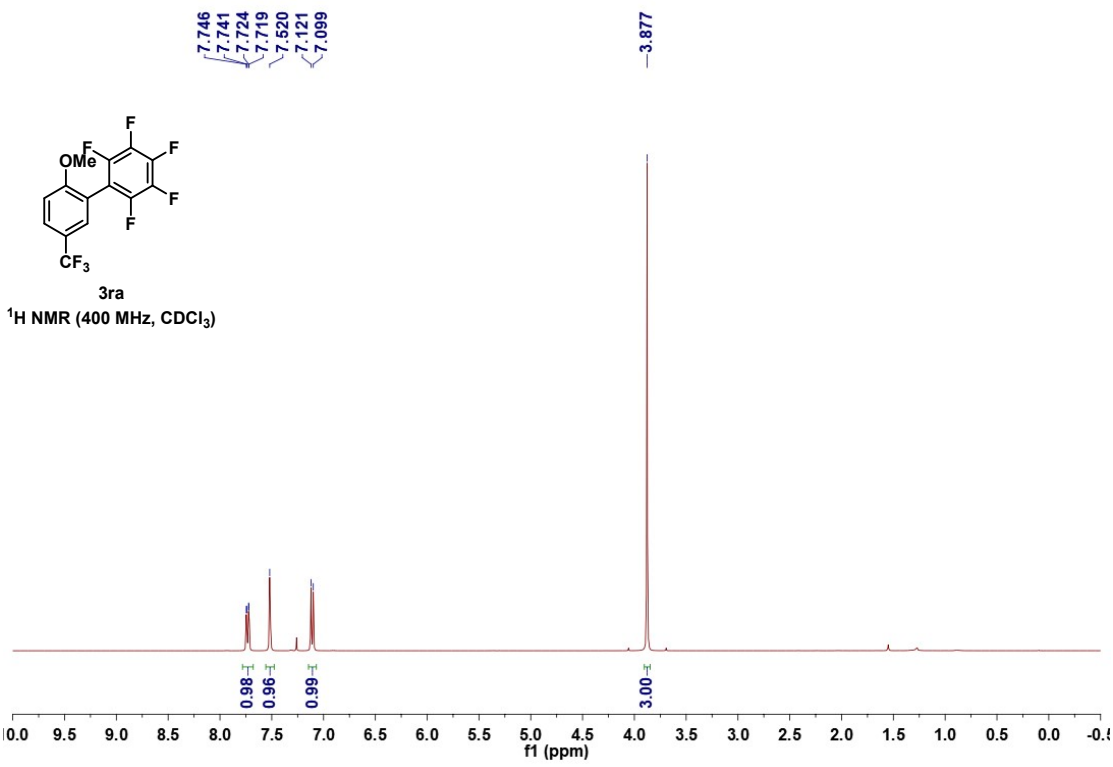

7.163
7.143
6.616
6.596
3.871
3.799
F
F
F
F
F
OMe
MeO
3qa
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
1.97
3.00
3.08
f1 (ppm)


162.17
158.23
145.86
145.79
145.76
143.35
143.31
139.01
138.92
138.79
136.28
112.62
107.51
104.75
98.87
77.32
77.00
76.68
55.59
55.39
F
F
F
F
F
OMe
MeO
3qa
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



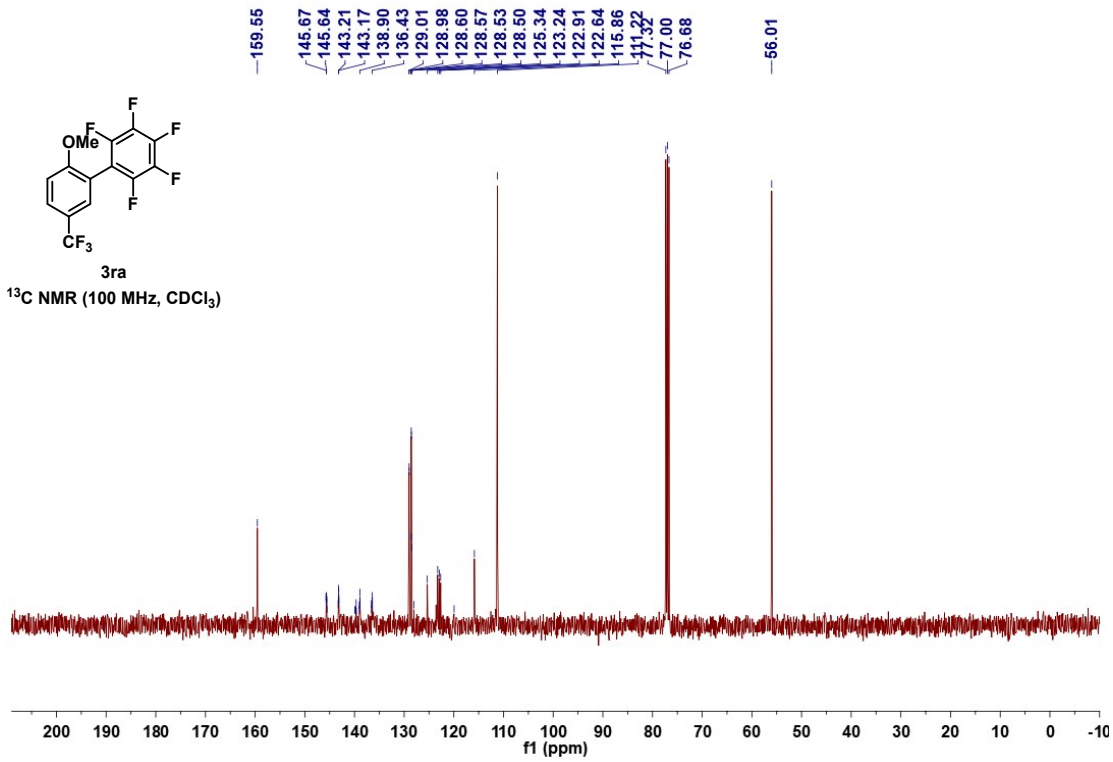
3qa

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



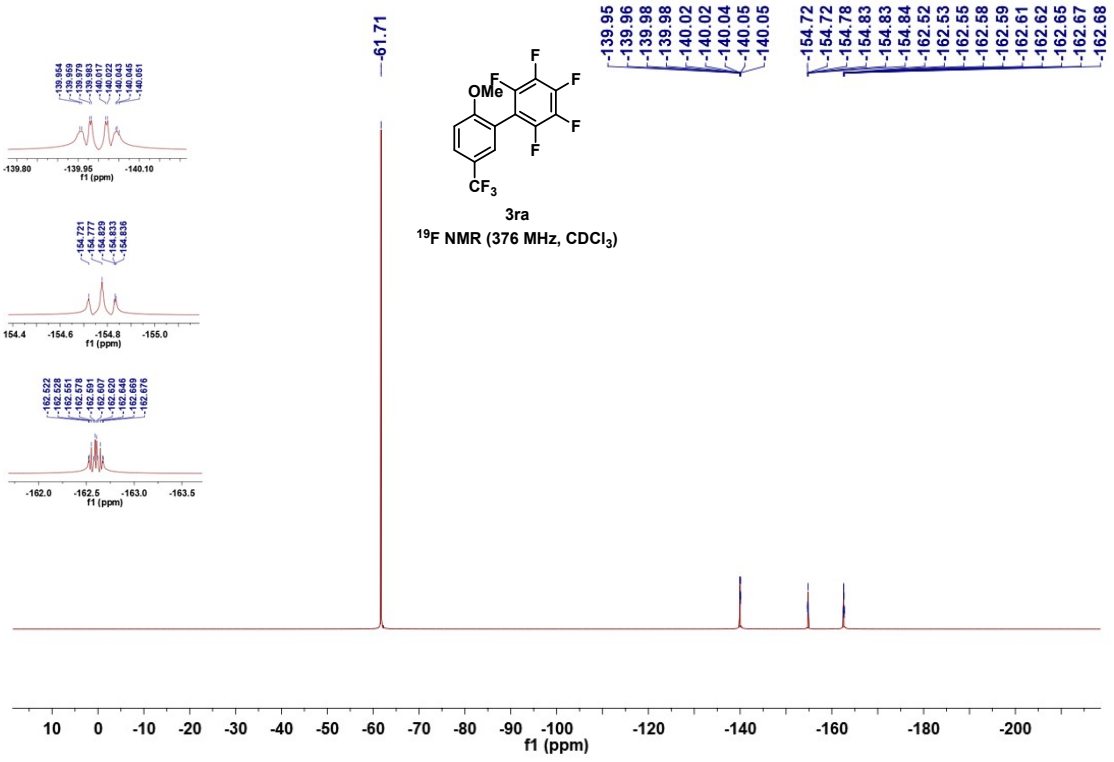
3ra

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



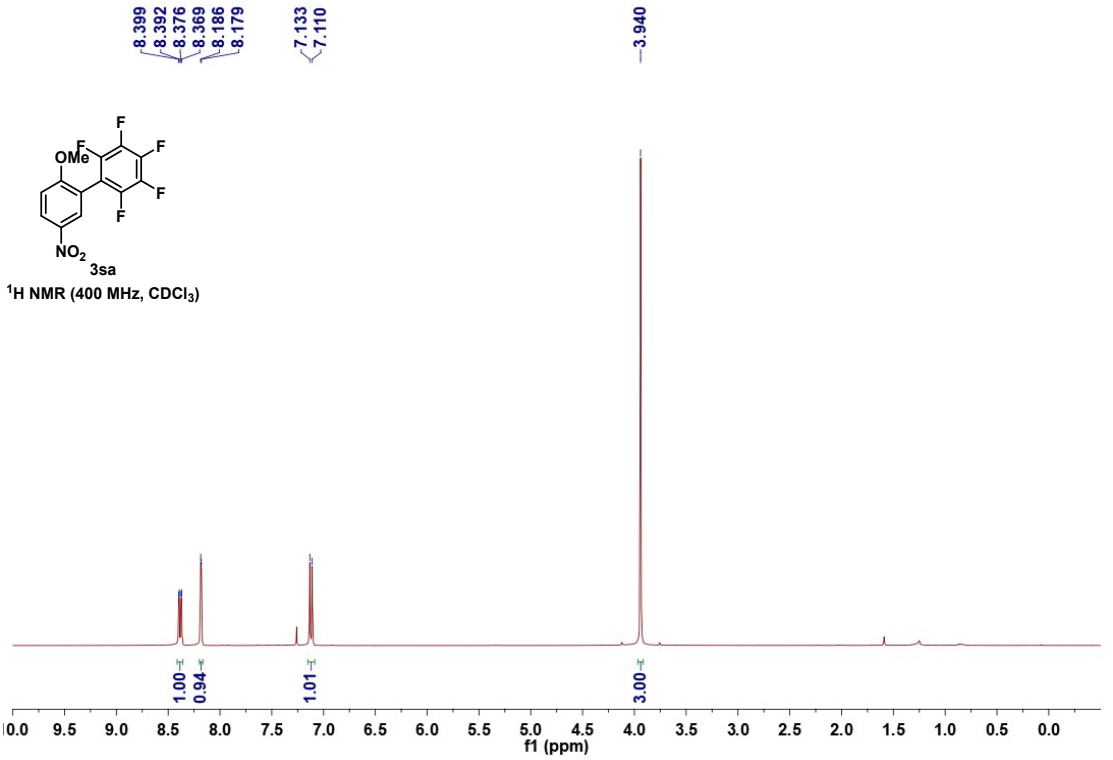
3ra

^{13}C NMR (100 MHz, $CDCl_3$)



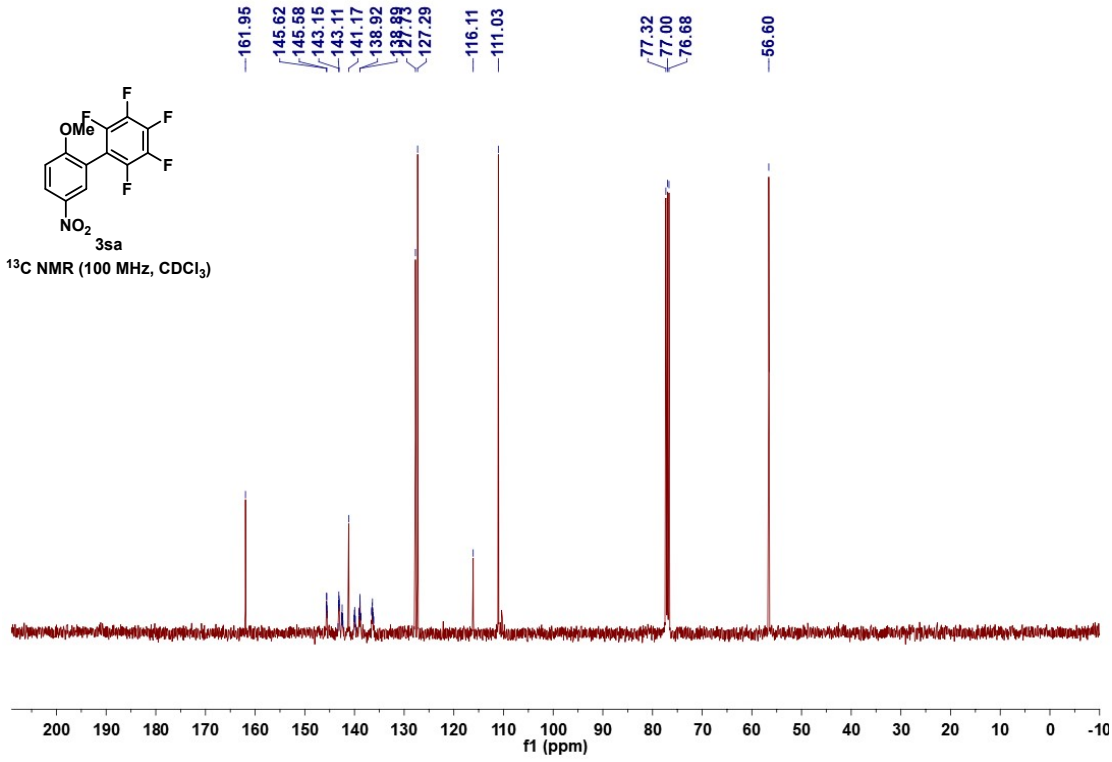
3ra

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



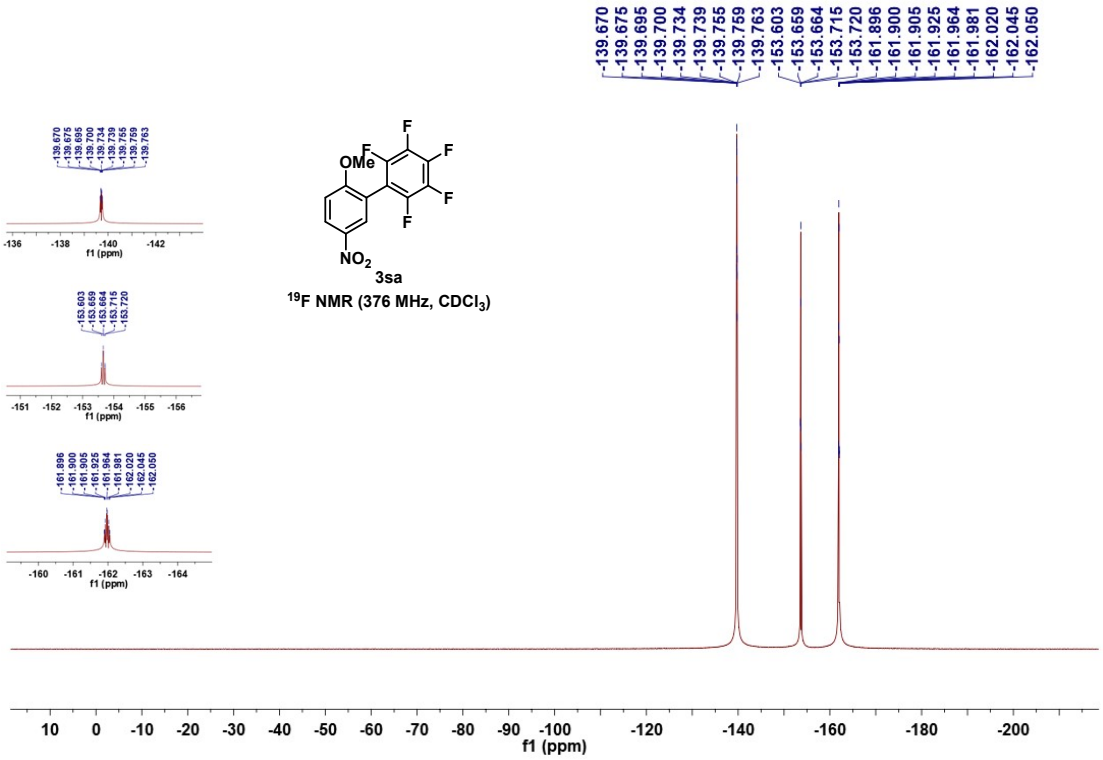
3sa

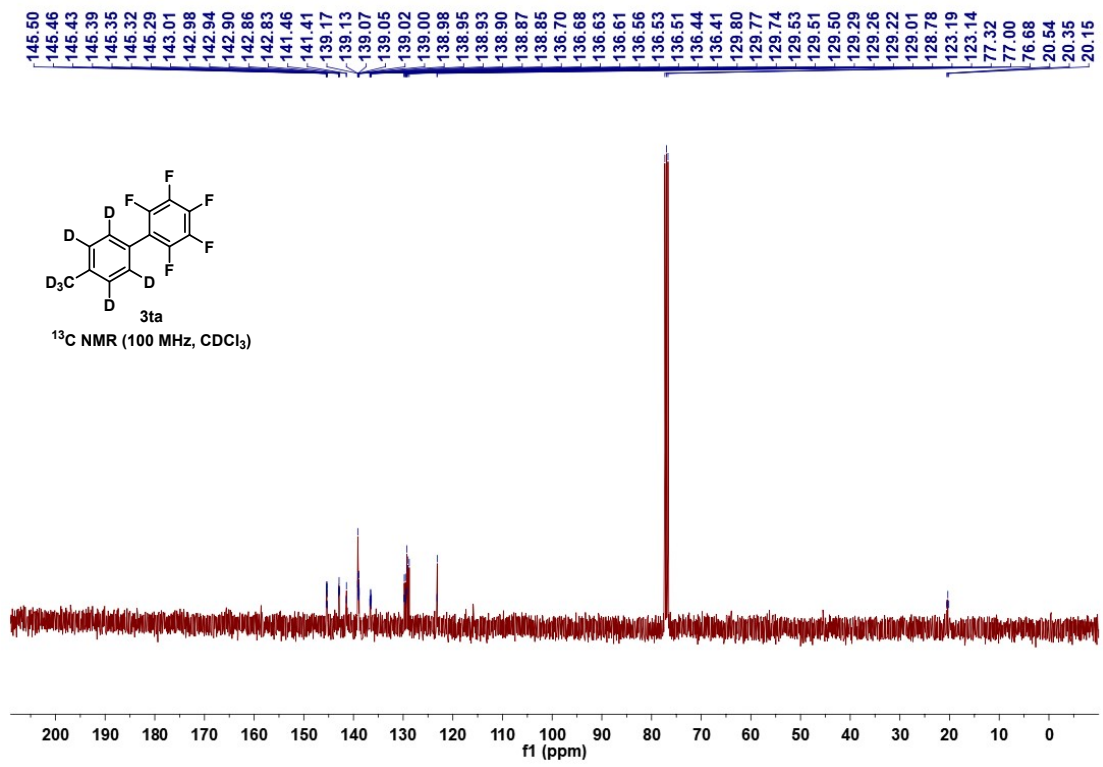
^{1}H NMR (400 MHz, $CDCl_3$)

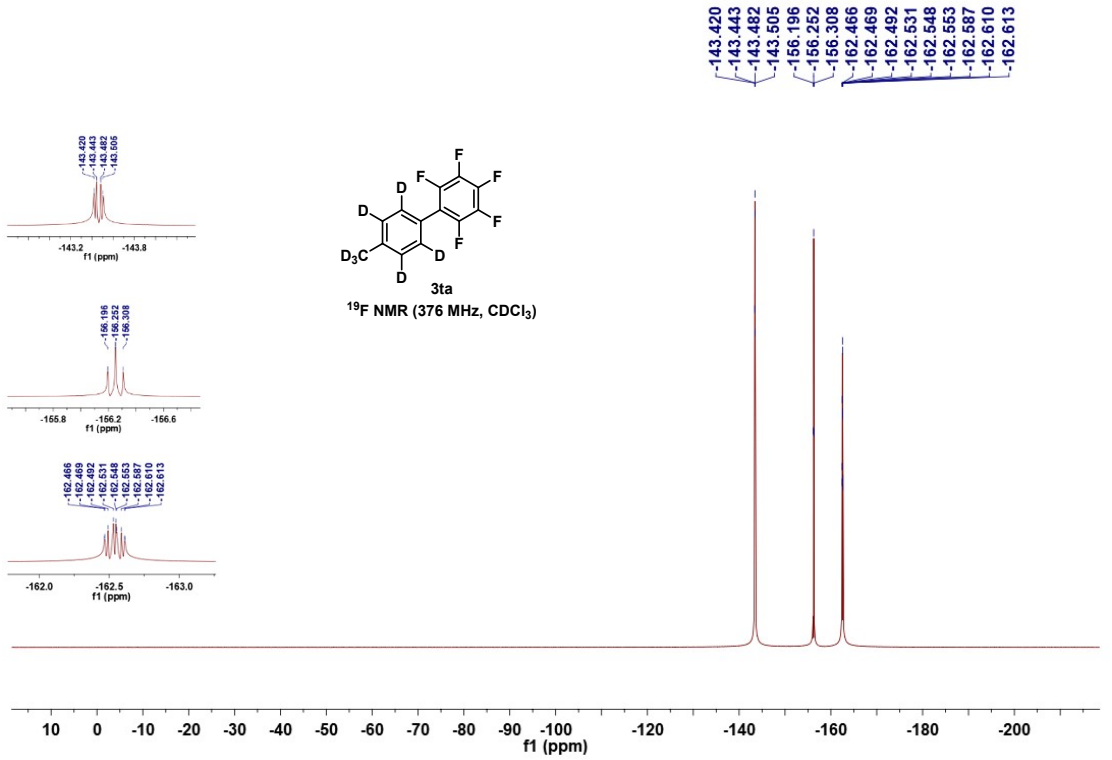


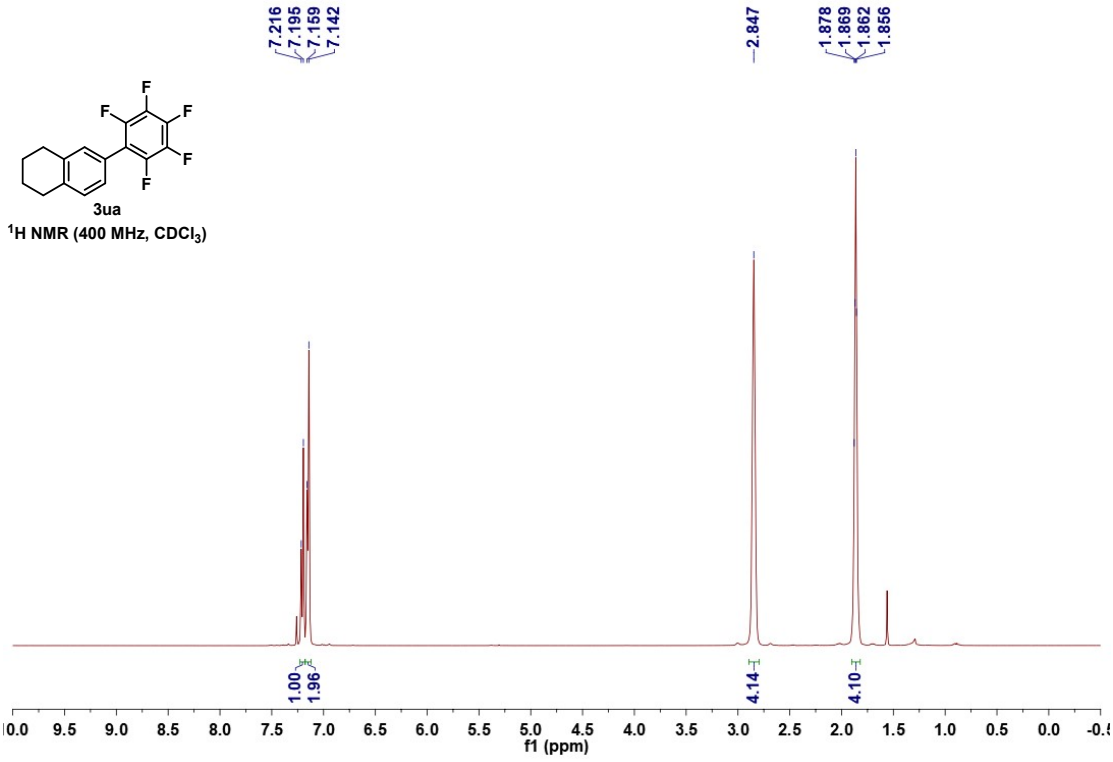
3sa

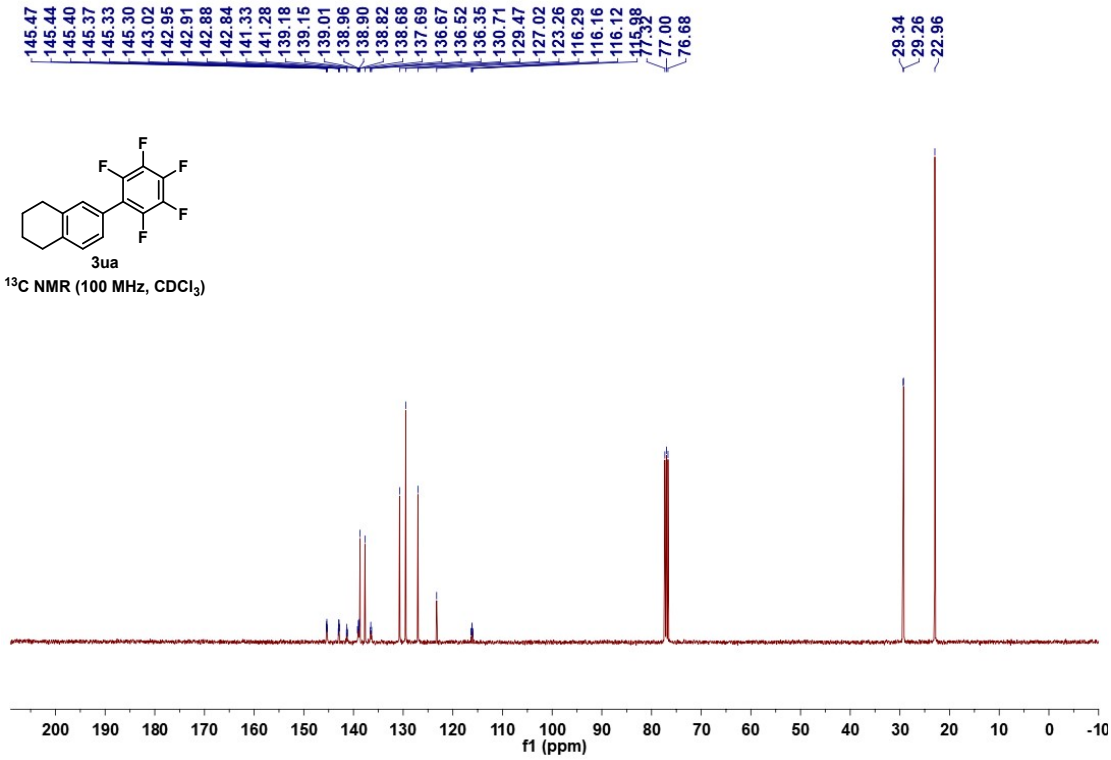
^{13}C NMR (100 MHz, $CDCl_3$)

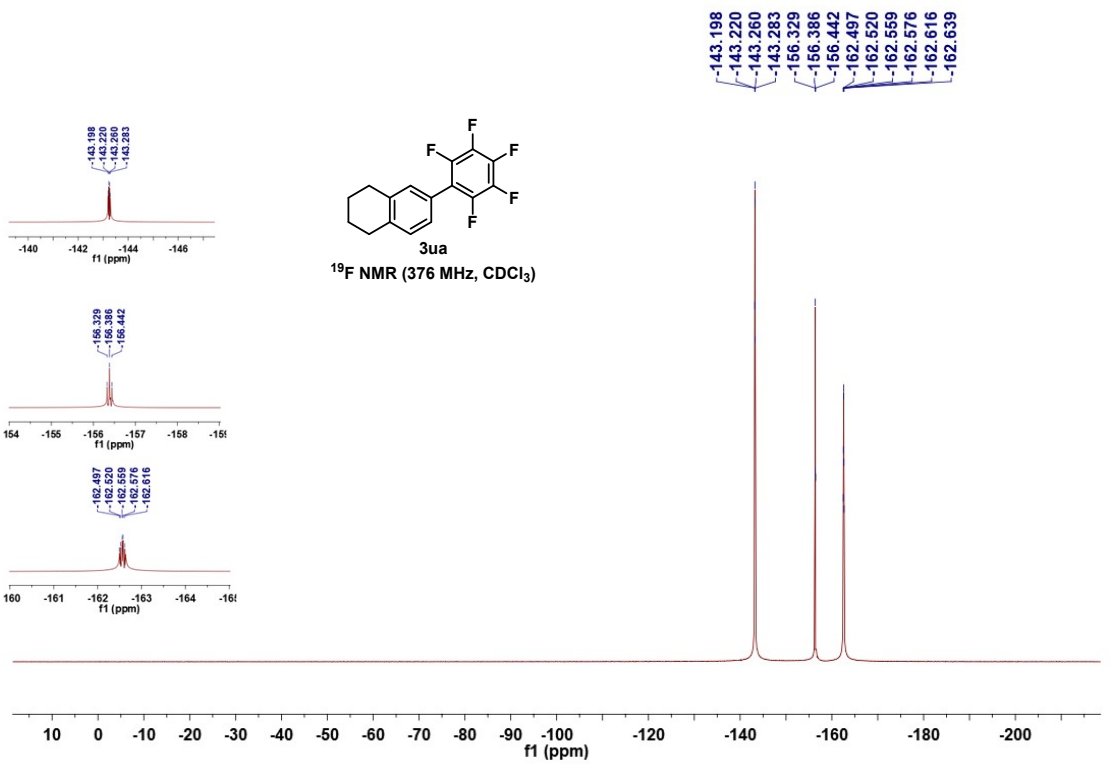

-139.670
-139.675
-139.695
-139.700
-139.734
-139.739
-139.755
-139.759
-139.763
-153.603
-153.659
-153.664
-153.715
-153.720
-161.896
-161.900
-161.905
-161.925
-161.964
-161.981
-162.020
-162.045
-162.050
F
F
F
F
F
OMe
NO2
3sa
19F NMR (376 MHz, CDCl3)
f1 (ppm)

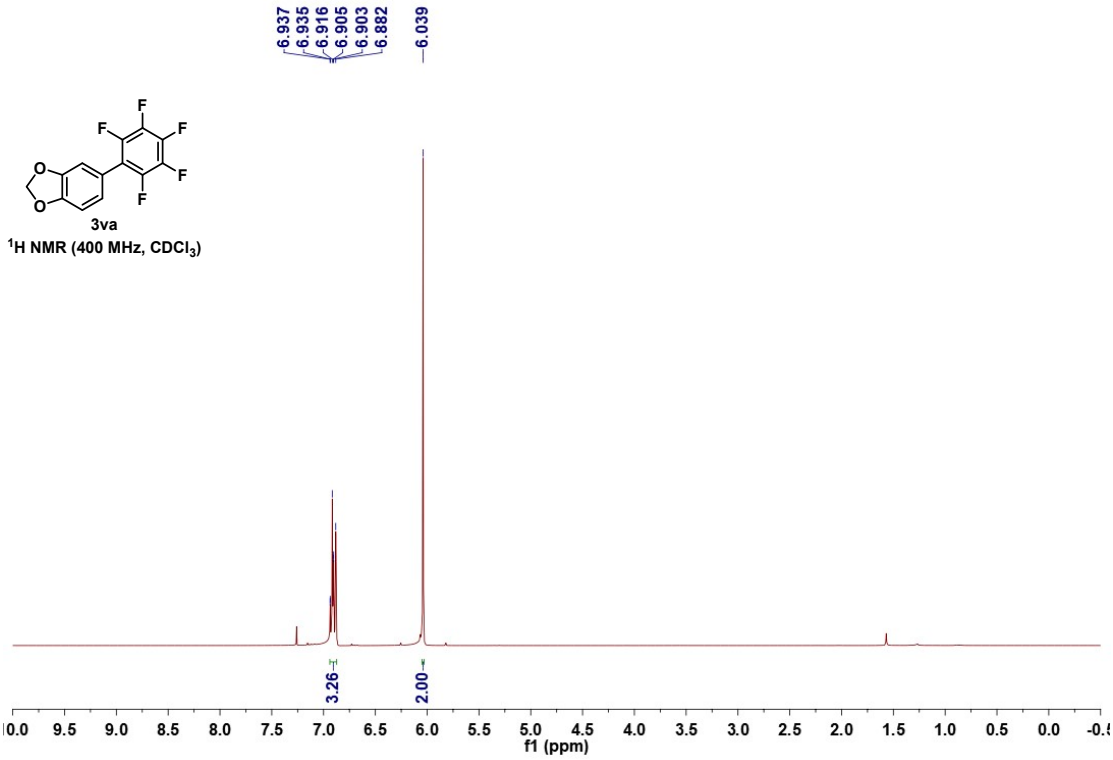

145.50
145.46
145.43
145.39
145.35
145.32
145.29
143.01
142.98
142.94
142.90
142.86
142.83
141.46
141.41
139.17
139.13
139.07
139.05
139.02
139.00
138.98
138.95
138.93
138.90
138.87
138.85
136.70
136.68
136.63
136.61
136.56
136.53
136.51
136.44
136.41
129.80
129.77
129.74
129.53
129.51
129.50
129.29
129.26
129.22
129.01
128.78
123.19
123.14
77.32
77.00
76.68
20.54
20.35
20.15
F
F
F
F
F
D
D
D
D3C
D
D
3ta
13C NMR (100 MHz, CDCl3)
f1 (ppm)

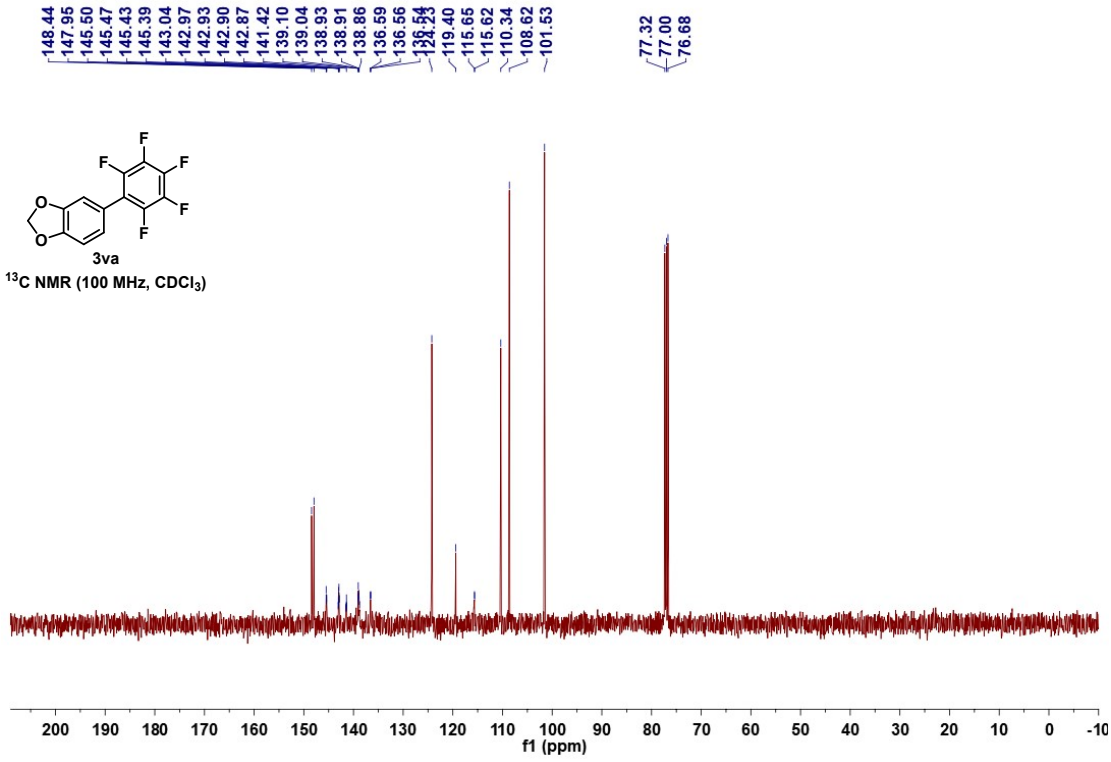

-143.420
-143.443
-143.482
-143.505
-156.196
-156.252
-156.308
-162.466
-162.469
-162.492
-162.531
-162.548
-162.553
-162.587
-162.610
-162.613
3ta
19F NMR (376 MHz, CDCl3)
f1 (ppm)

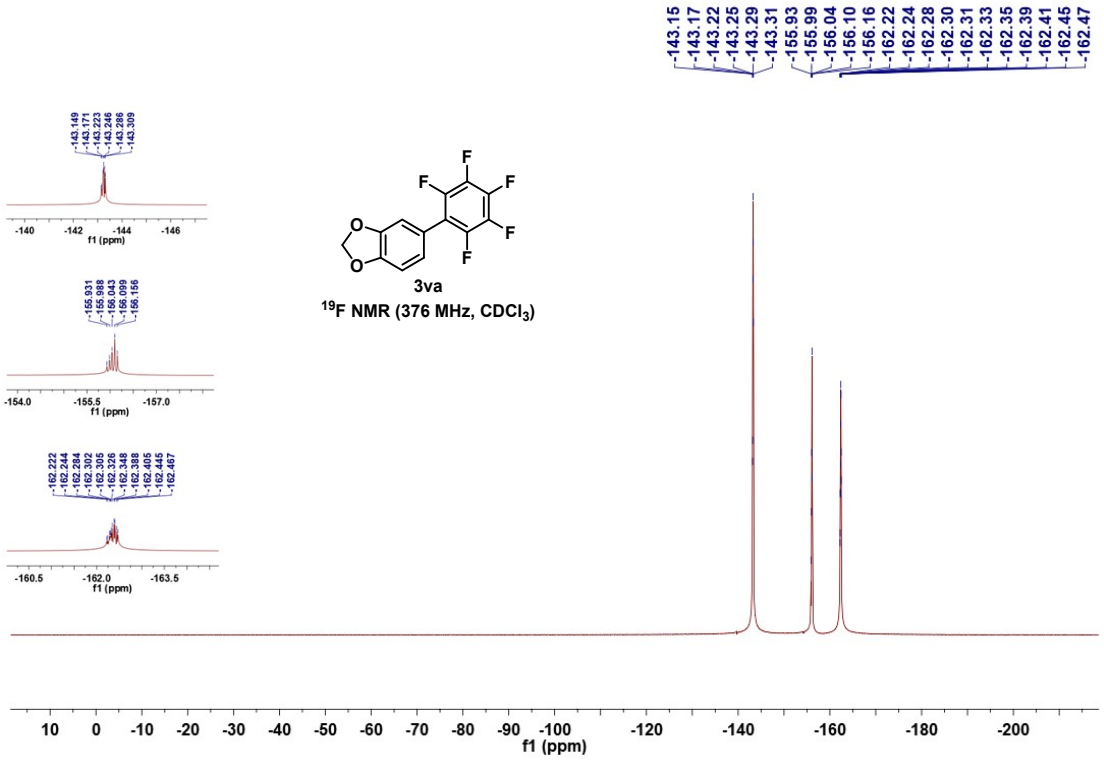

7.216
7.195
7.159
7.142
2.847
1.878
1.869
1.862
1.856
3ua
1H NMR (400 MHz, CDCl3)
1.00
1.96
4.14
4.10
f1 (ppm)

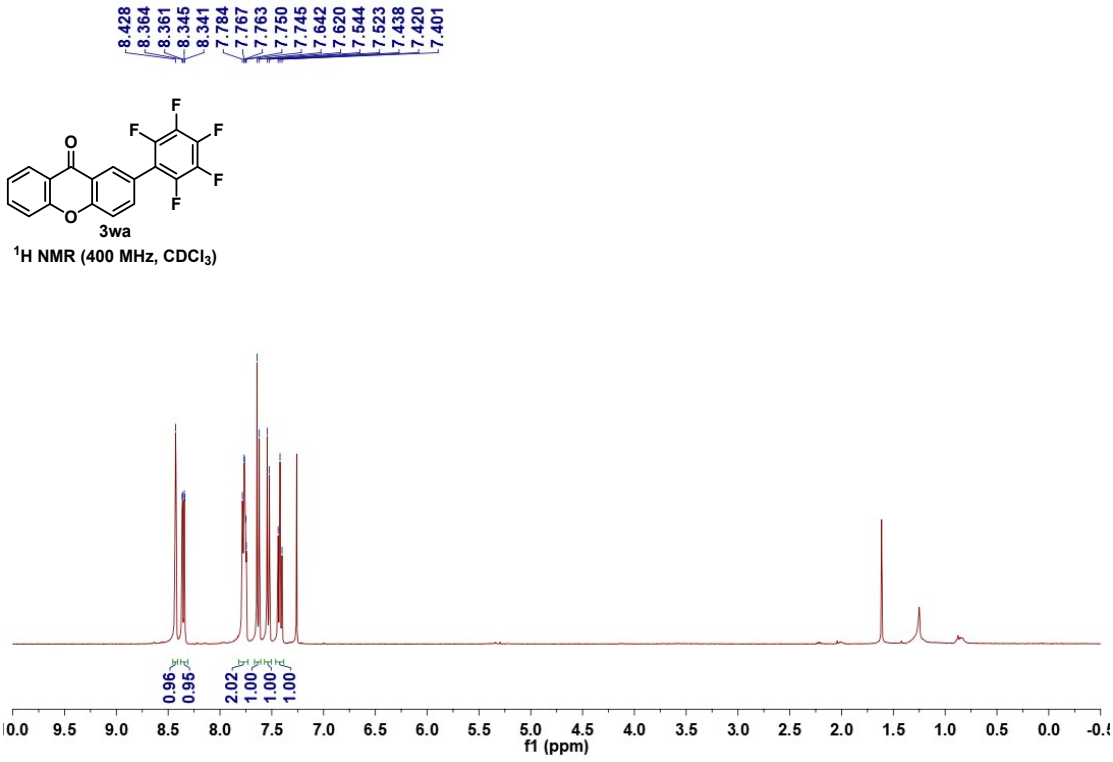

145.47
145.44
145.40
145.37
145.33
145.30
143.02
142.95
142.91
142.88
142.84
141.33
141.28
139.18
139.15
139.01
138.96
138.90
138.82
138.68
137.69
136.67
136.52
136.35
130.71
129.47
127.02
123.26
116.29
116.16
116.12
115.98
77.32
77.00
76.68
29.34
29.26
22.96
F
F
F
F
F
3ua
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

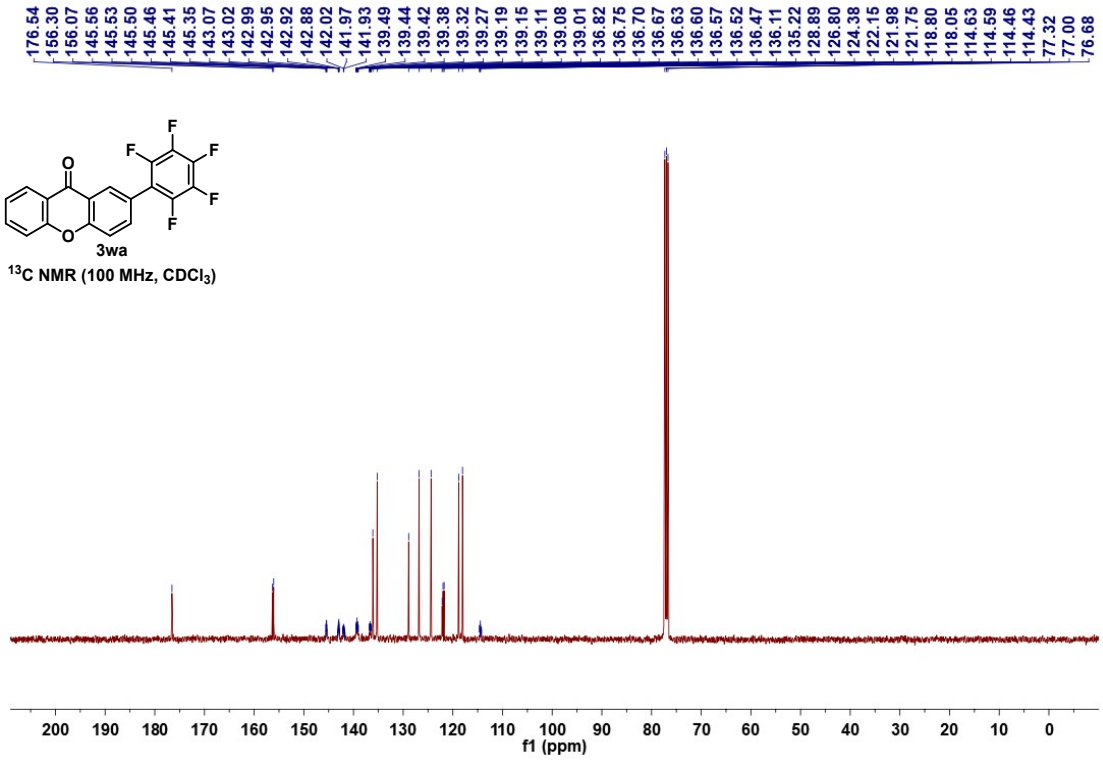

-143.198
-143.220
-143.260
-143.283
-156.329
-156.386
-156.442
-162.497
-162.520
-162.559
-162.576
-162.616
-162.639
F
F
F
F
F
3ua
^{19}F NMR (376 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

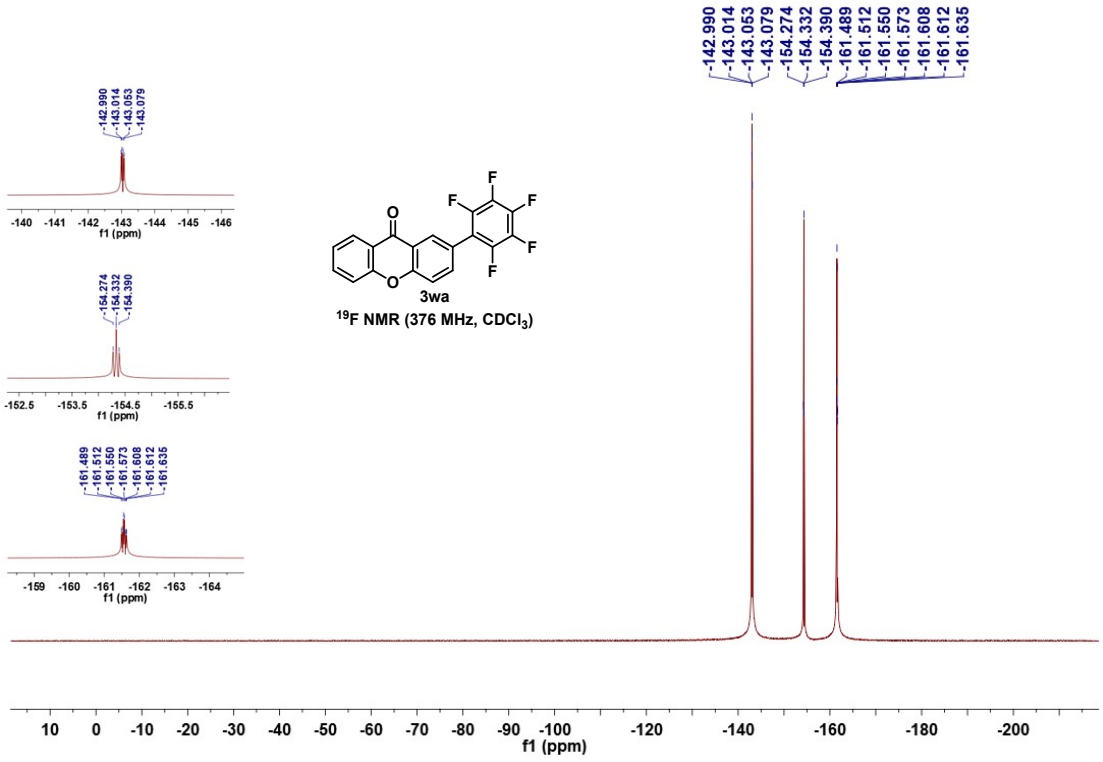

6.937
6.935
6.916
6.905
6.903
6.882
6.039
F
F
F
F
F
O
O
3va
^{1}H NMR (400 MHz, CDCl$_3$)
3.26
2.00
f1 (ppm)

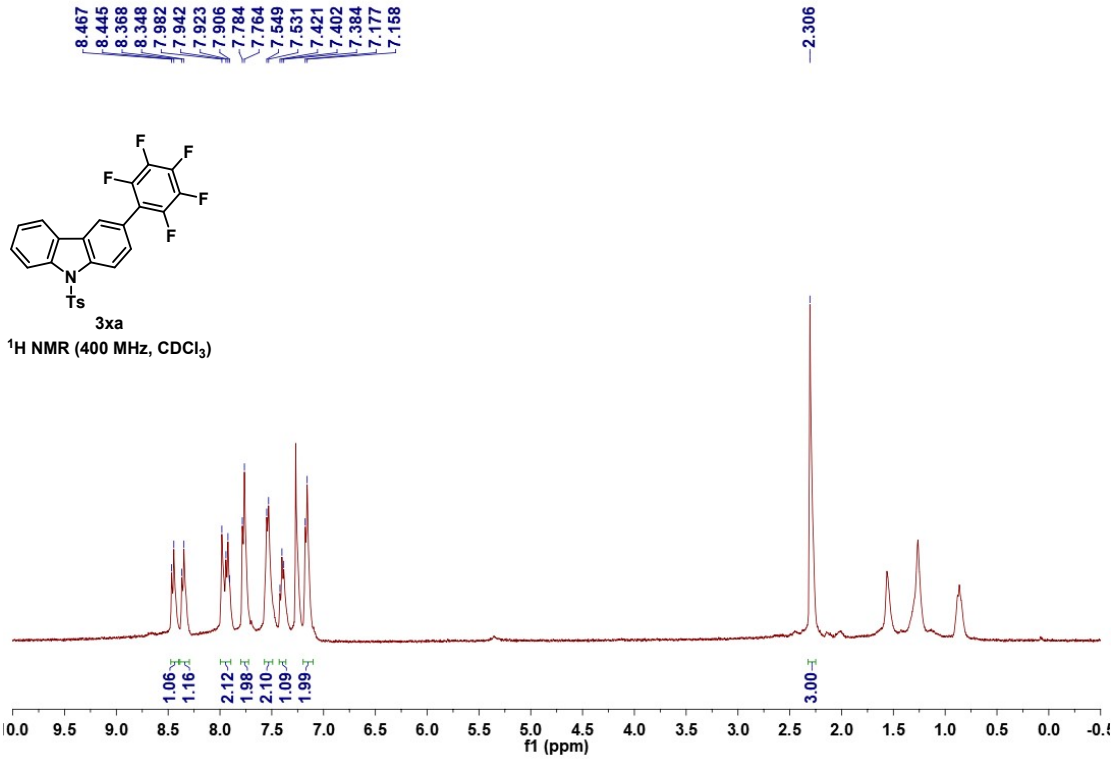

148.44
147.95
145.50
145.47
145.43
145.39
143.04
142.97
142.93
142.90
142.87
141.42
139.10
139.04
138.93
138.91
138.86
136.59
136.56
119.40
115.65
115.62
110.34
108.62
101.53
77.32
77.00
76.68
F
F
F
F
F
O
O
3va
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-143.15
-143.17
-143.22
-143.25
-143.29
-143.31
-155.93
-155.99
-156.04
-156.10
-156.16
-162.22
-162.24
-162.28
-162.30
-162.31
-162.33
-162.35
-162.39
-162.41
-162.45
-162.47
-143.149
-143.171
-143.223
-143.246
-143.286
-143.309
-140
-142
-144
-146
f1 (ppm)
-155.931
-155.988
-156.043
-156.098
-156.156
-154.0
-155.5
-157.0
f1 (ppm)
-162.222
-162.244
-162.284
-162.302
-162.305
-162.326
-162.345
-162.388
-162.405
-162.445
-162.467
-160.5
-162.0
-163.5
f1 (ppm)
F
F
F
F
F
O
O
3va
^{19}F NMR (376 MHz, CDCl$_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


8.428
8.364
8.361
8.345
8.341
7.784
7.767
7.763
7.750
7.745
7.642
7.620
7.544
7.523
7.438
7.420
7.401
F
F
F
F
F
O
O
3wa
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
0.95
2.02
1.00
1.00
1.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

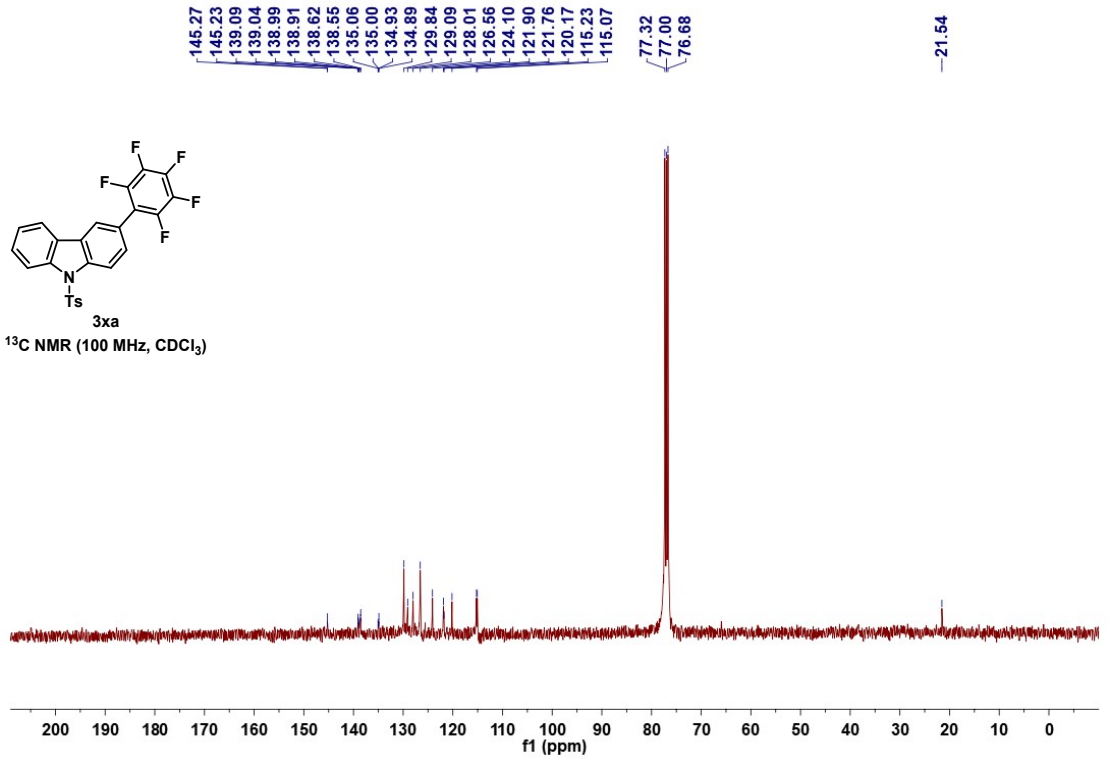

176.54
156.30
156.07
145.56
145.53
145.50
145.46
145.41
145.35
143.07
143.02
142.99
142.95
142.92
142.88
142.02
141.97
141.93
139.49
139.44
139.42
139.38
139.32
139.27
139.19
139.15
139.11
139.08
139.01
136.82
136.75
136.70
136.67
136.63
136.60
136.57
136.52
136.47
136.11
135.22
128.89
126.80
124.38
122.15
121.98
121.75
118.80
118.05
114.63
114.59
114.46
114.43
77.32
77.00
76.68
3wa
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-142.990
-143.014
-143.053
-143.079
-154.274
-154.332
-154.390
-161.489
-161.512
-161.550
-161.573
-161.608
-161.612
-161.635
3wa
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)



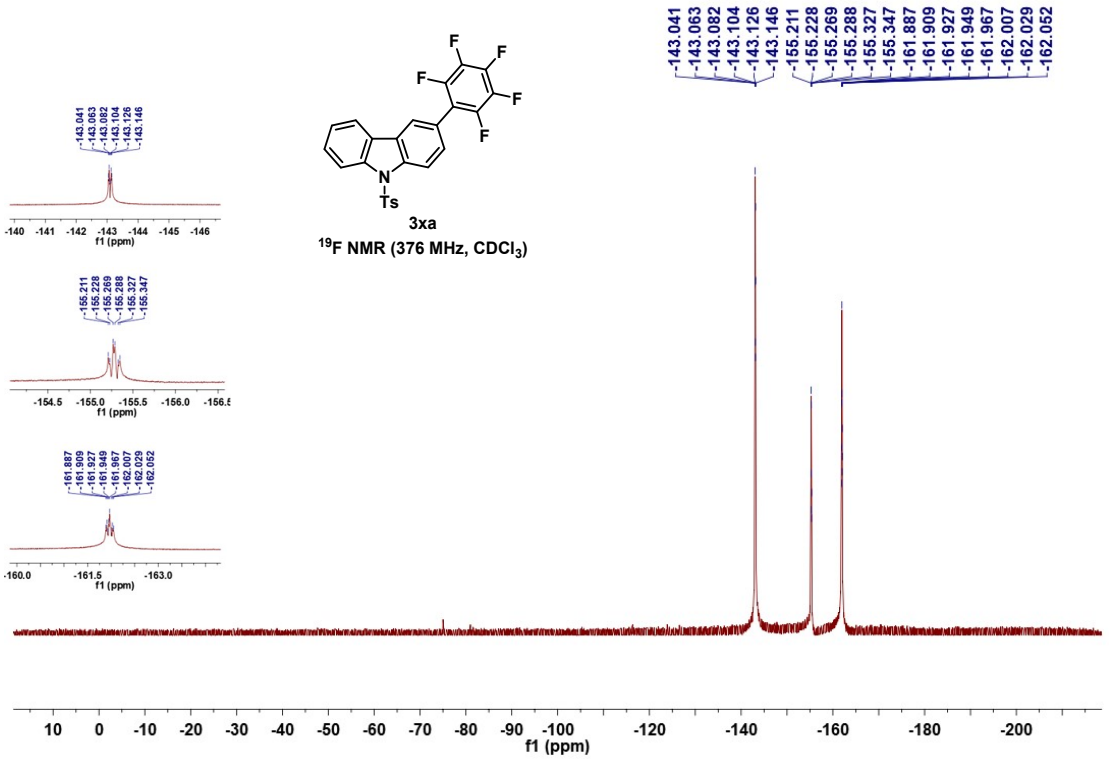
3xa

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



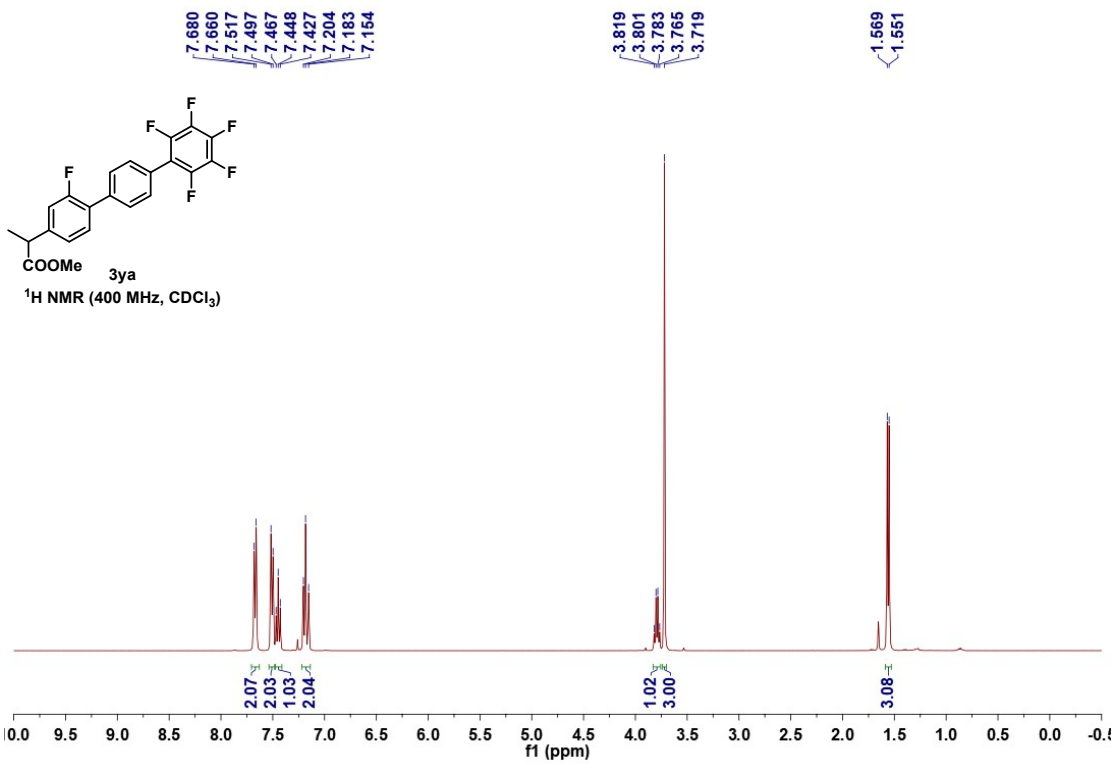
3xa

^{13}C NMR (100 MHz, $CDCl_3$)



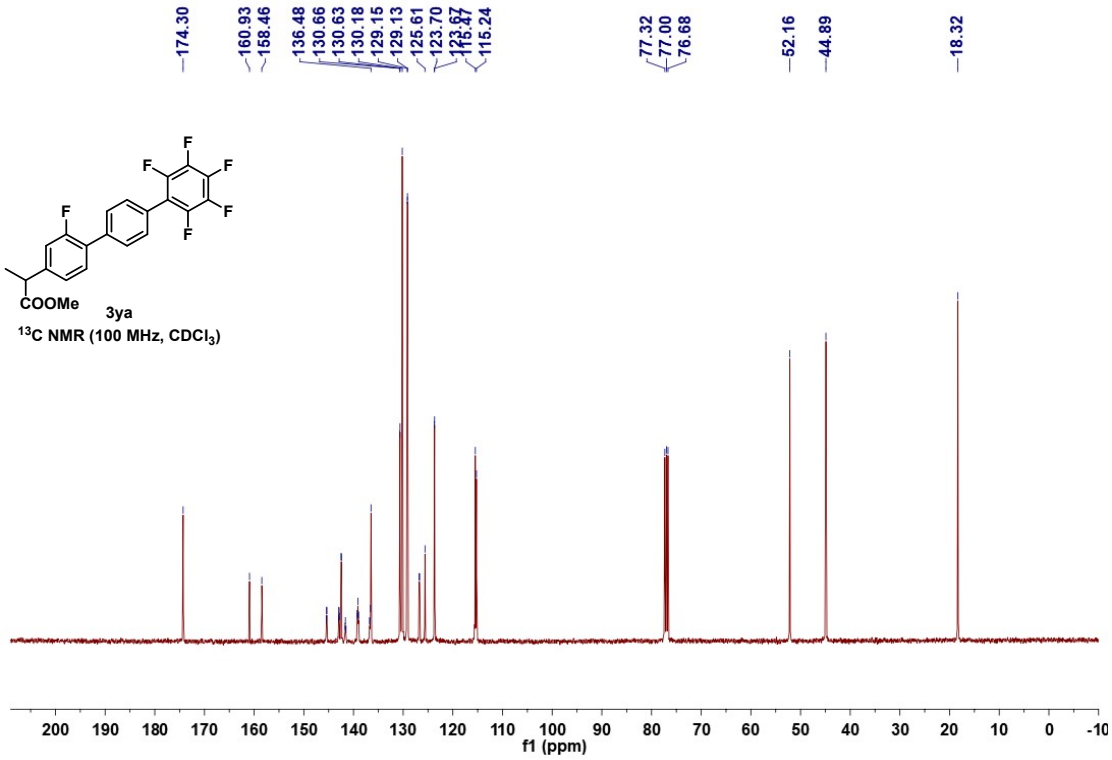
3xa

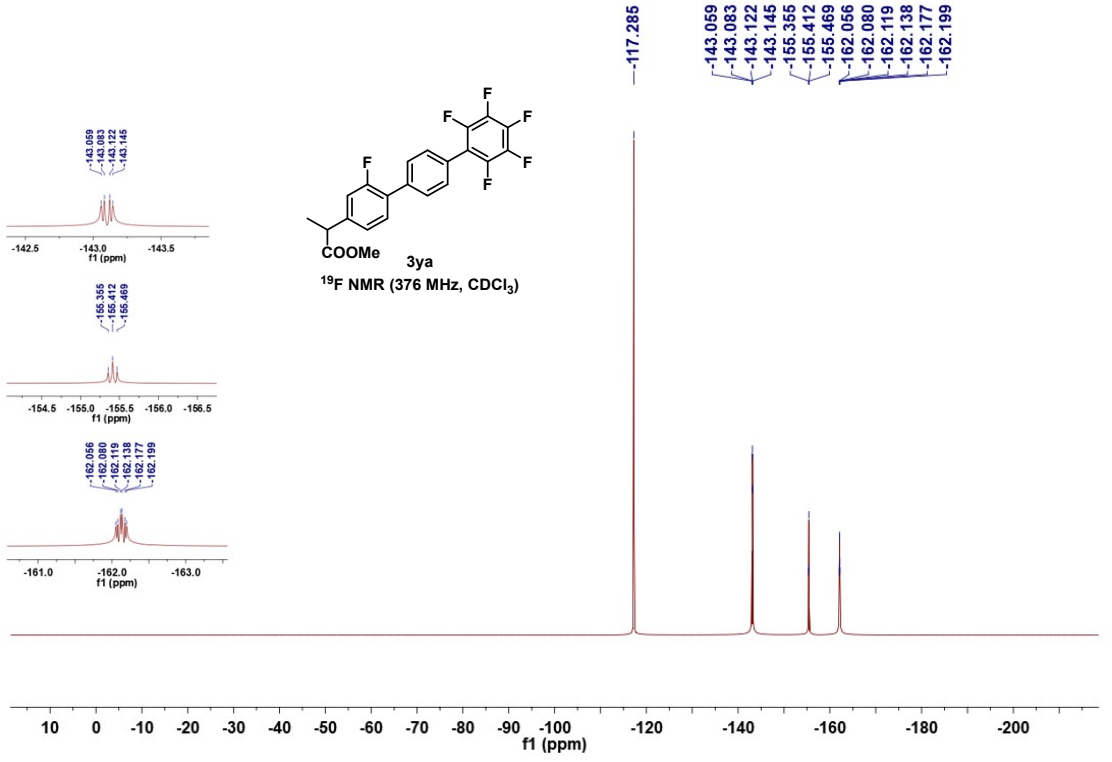
^{19}F NMR (376 MHz, $CDCl_3$)

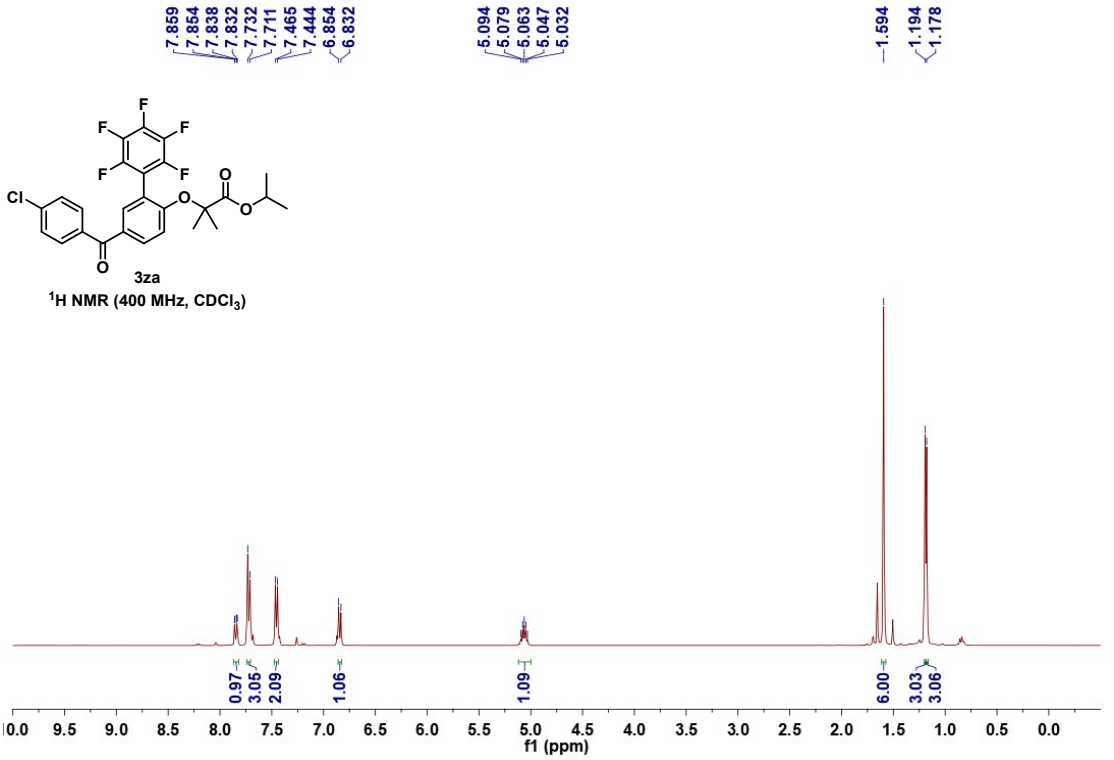


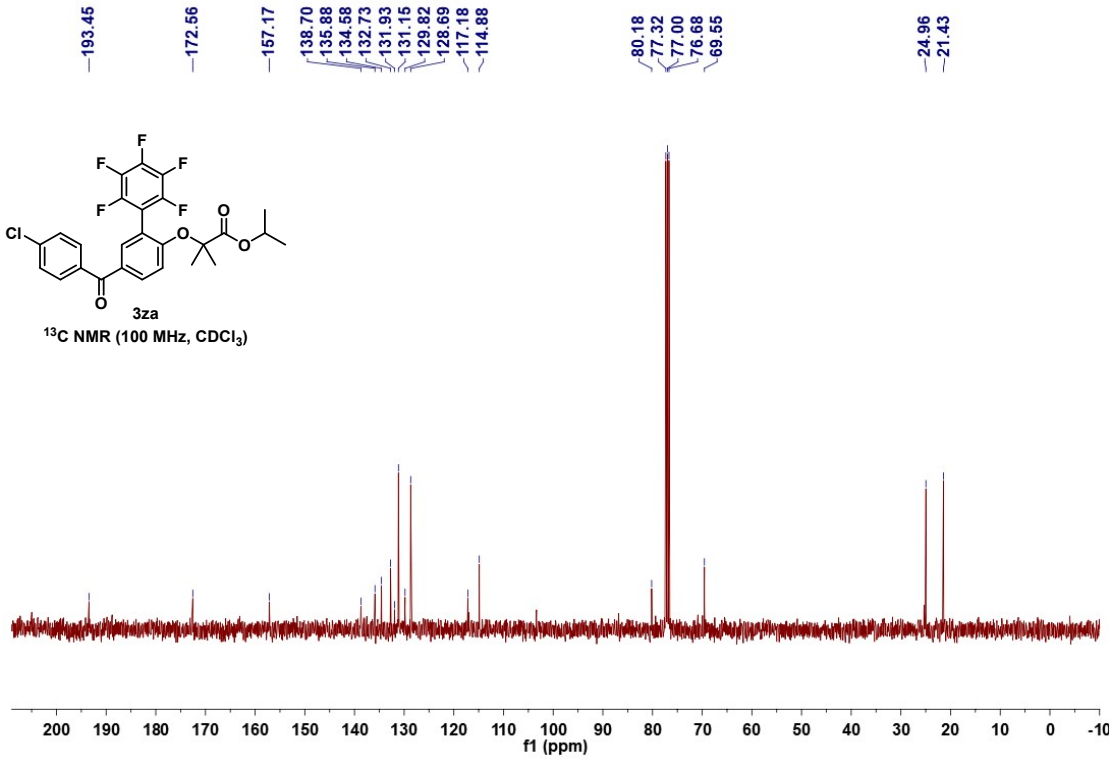
3ya

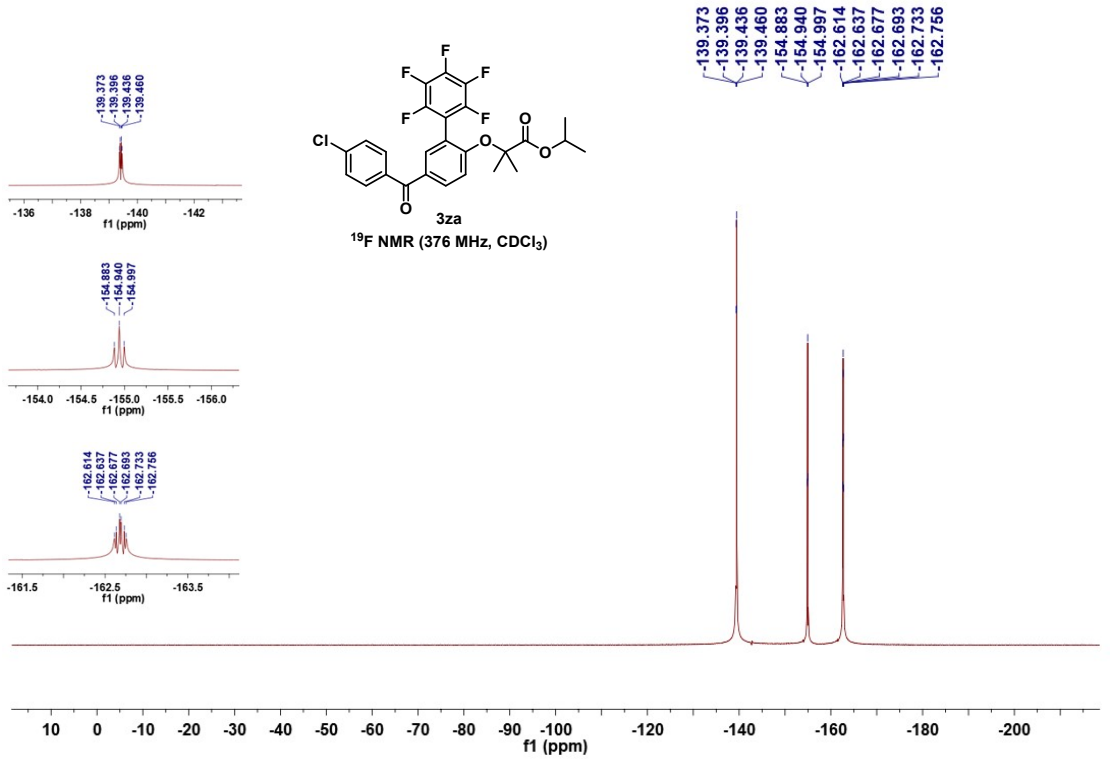
^{1}H NMR (400 MHz, $CDCl_3$)

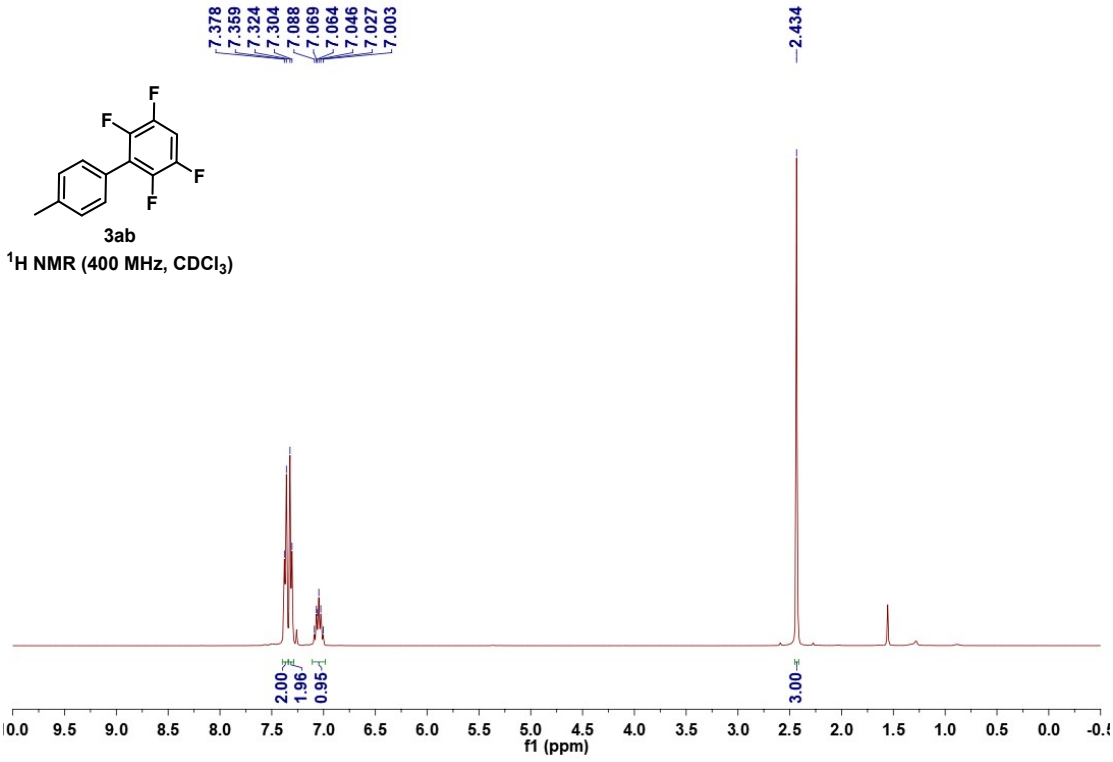

174.30
160.93
158.46
136.48
130.66
130.63
130.18
129.15
129.13
125.61
123.70
115.24
77.32
77.00
76.68
52.16
44.89
18.32
COOMe
3ya
13C NMR (100 MHz, CDCl3)
f1 (ppm)

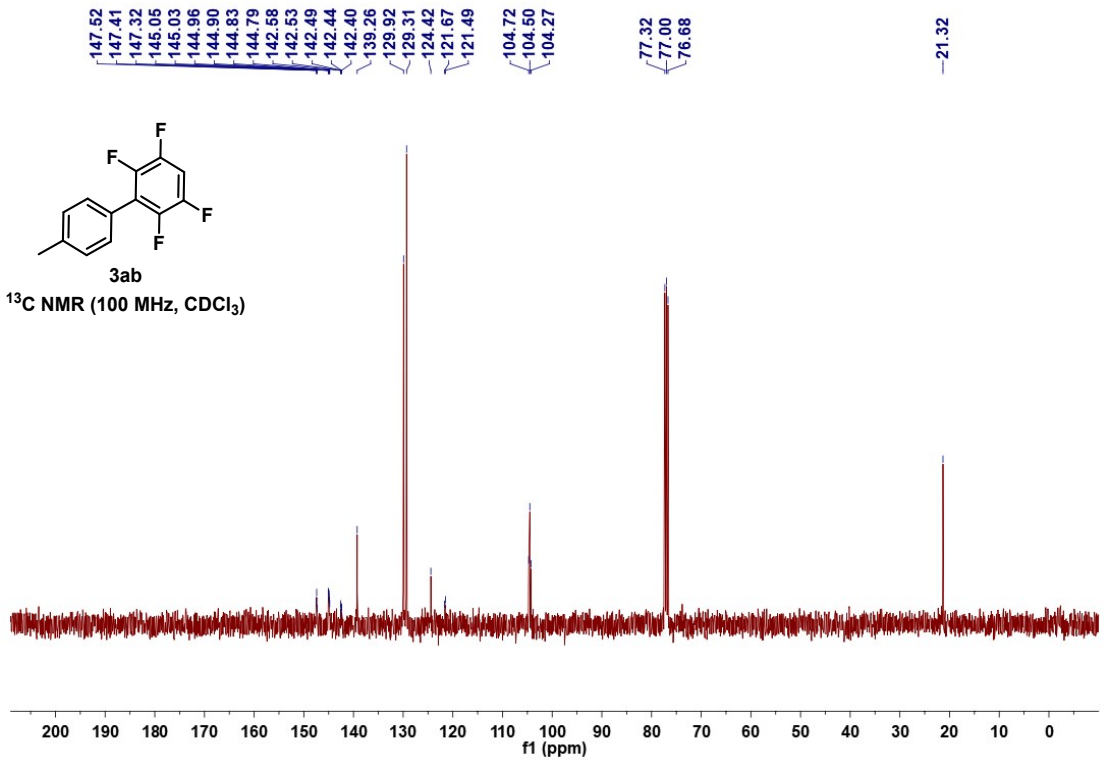

117.285
143.059
143.083
143.122
143.145
155.355
155.412
155.469
162.056
162.080
162.119
162.138
162.177
162.199
COOMe
3ya
19F NMR (376 MHz, CDCl3)
f1 (ppm)

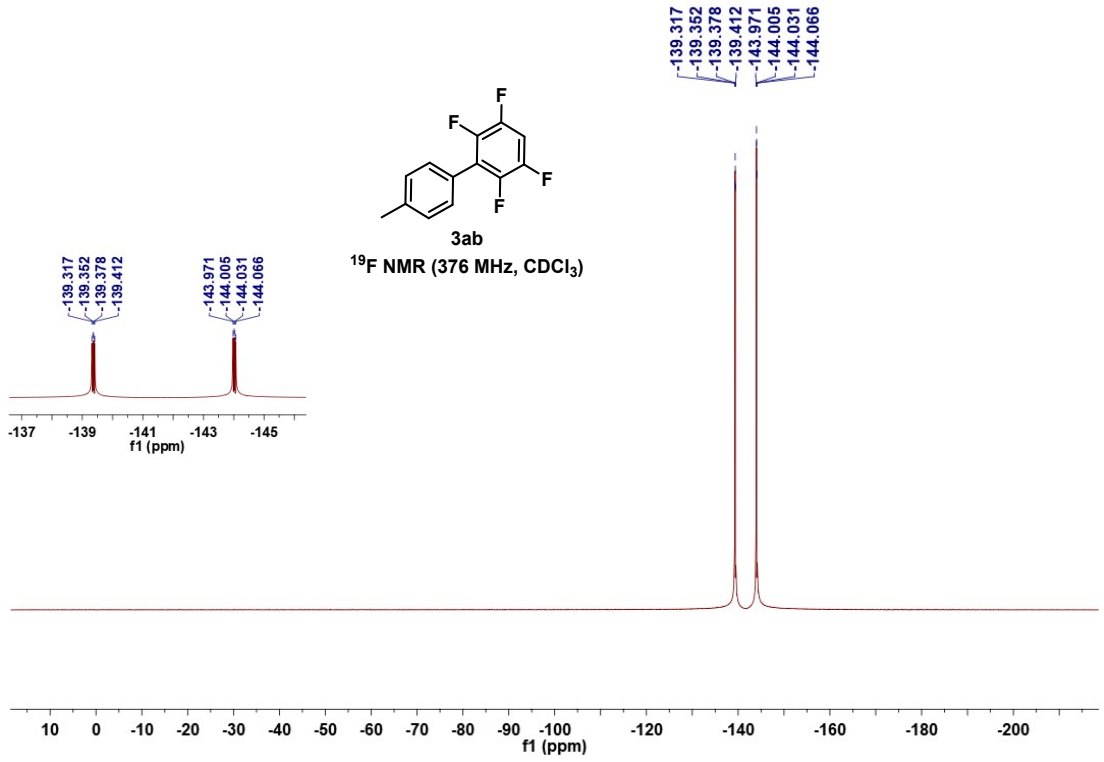

7.859
7.854
7.838
7.832
7.732
7.711
7.465
7.444
6.854
6.832
5.094
5.079
5.063
5.047
5.032
1.594
1.194
1.178
F
F
F
F
F
Cl
O
O
O
O
3za
^{1}H NMR (400 MHz, CDCl$_3$)
0.97
3.05
2.09
1.06
1.09
6.00
3.03
3.06
f1 (ppm)

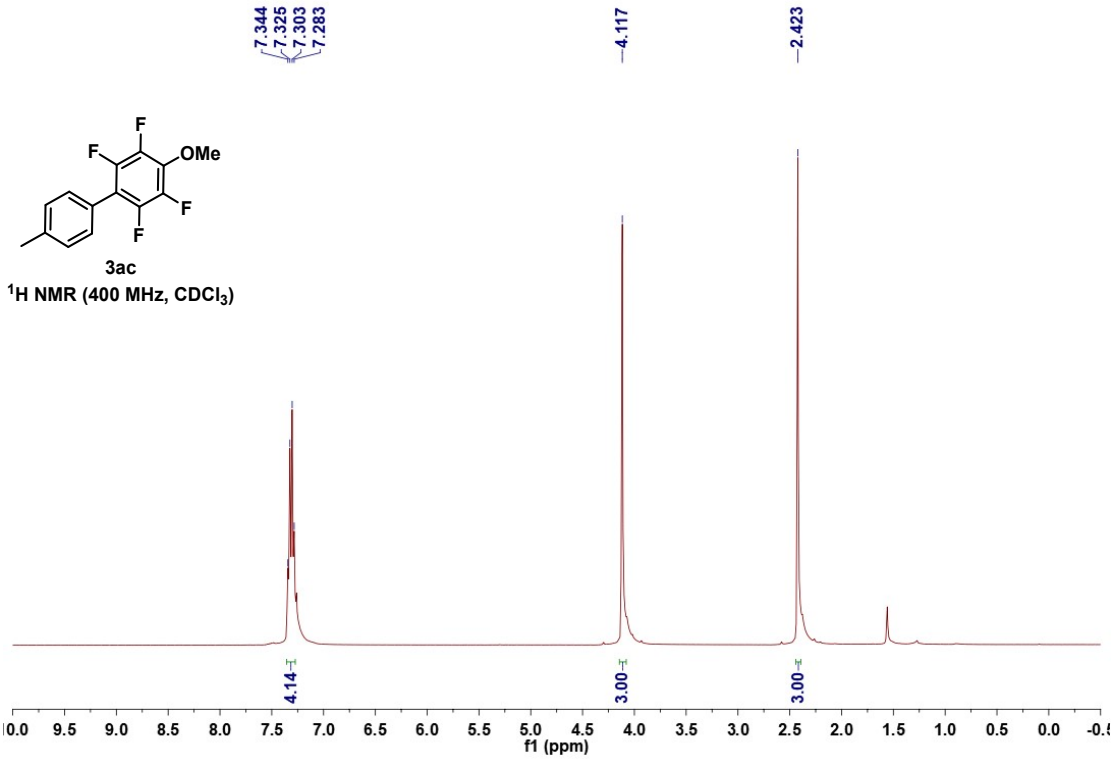

193.45
172.56
157.17
138.70
135.88
134.58
132.73
131.93
131.15
129.82
128.69
117.18
114.88
80.18
77.32
77.00
76.68
69.55
24.96
21.43
F
F
F
F
F
Cl
O
O
O
O
3za
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-139.373
-139.396
-139.436
-139.460
-154.883
-154.940
-154.997
-162.614
-162.637
-162.677
-162.693
-162.733
-162.756
F
F
F
F
F
Cl
O
O
O
O
3za
^{19}F NMR (376 MHz, $CDCl_3$)
f1 (ppm)


7.378
7.359
7.324
7.304
7.088
7.069
7.064
7.046
7.027
7.003
2.434
F
F
F
F
3ab
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
1.96
0.95
3.00
f1 (ppm)

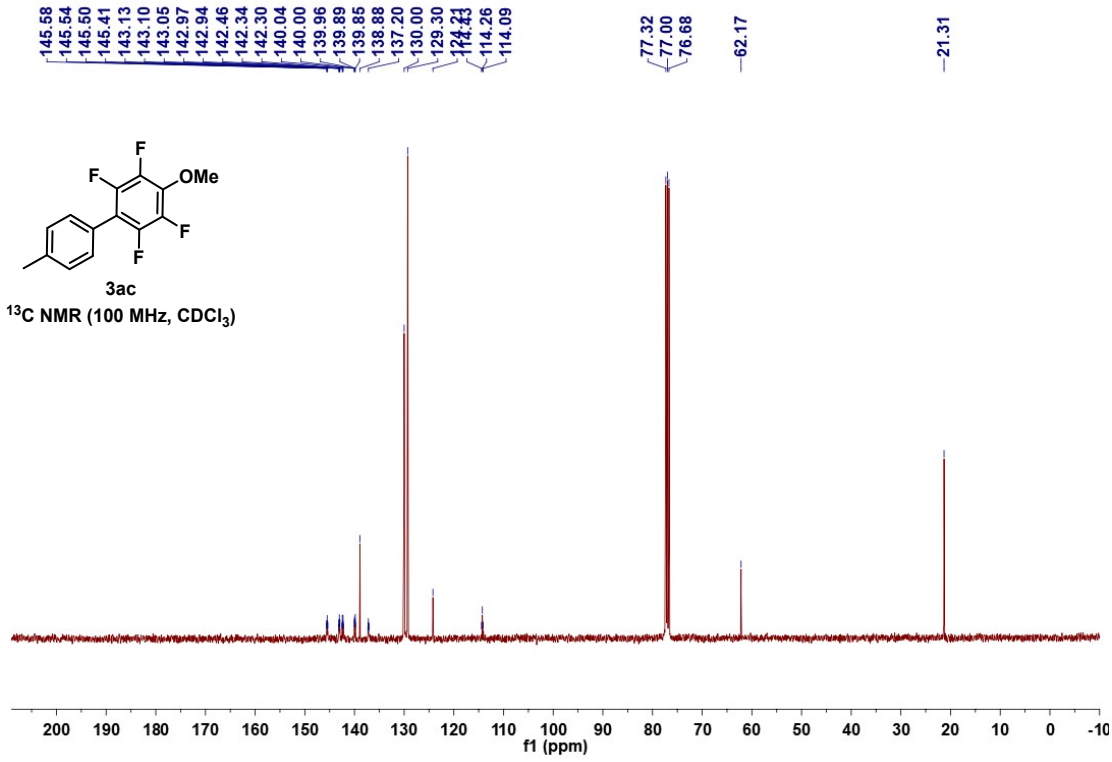

147.52
147.41
147.32
145.05
145.03
144.96
144.90
144.83
144.79
142.58
142.53
142.49
142.44
142.40
139.26
129.92
129.31
124.42
121.67
121.49
104.72
104.50
104.27
77.32
77.00
76.68
21.32
F
F
F
F
3ab
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-139.317
-139.352
-139.378
-139.412
-143.971
-144.005
-144.031
-144.066
F
F
F
F
3ab
19F NMR (376 MHz, CDCl3)
-137 -139 -141 -143 -145
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



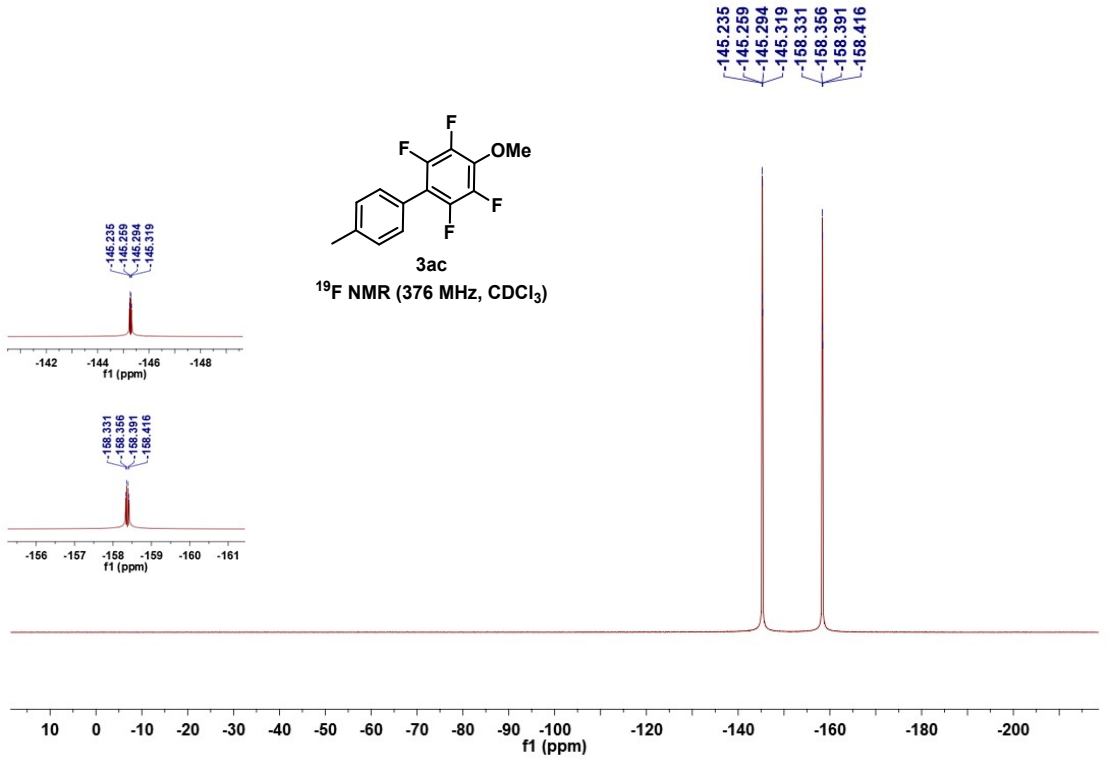
3ac

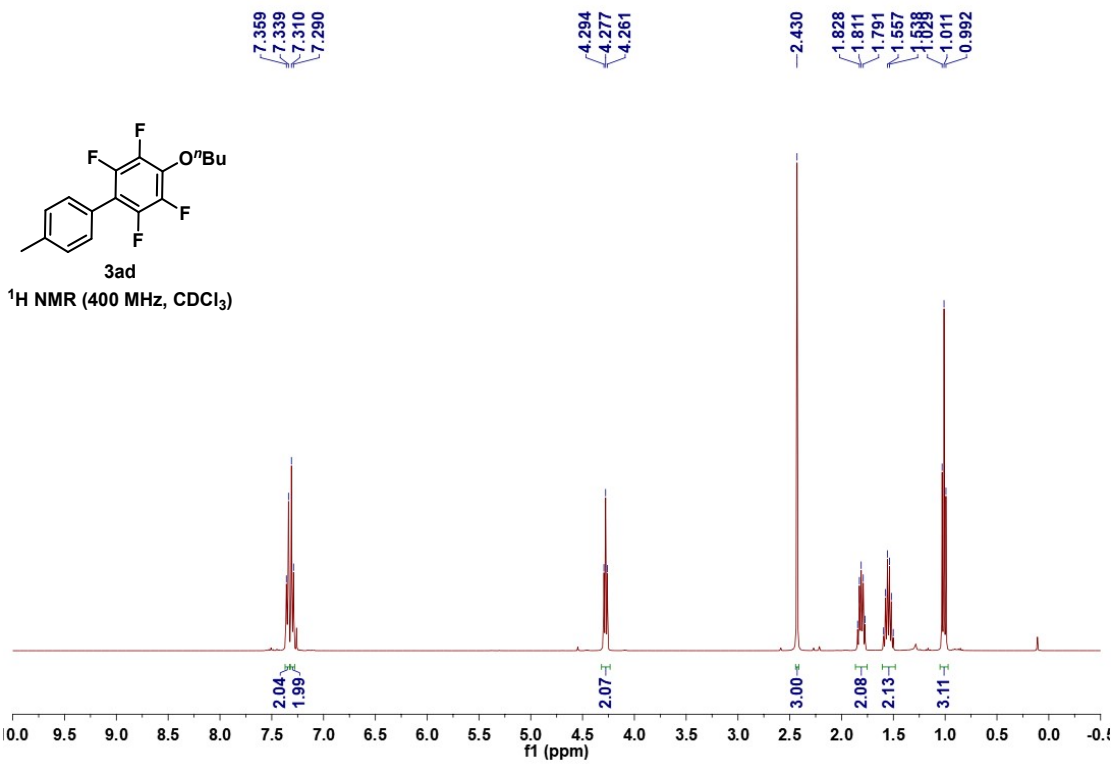
^{1}H NMR (400 MHz, $CDCl_3$)

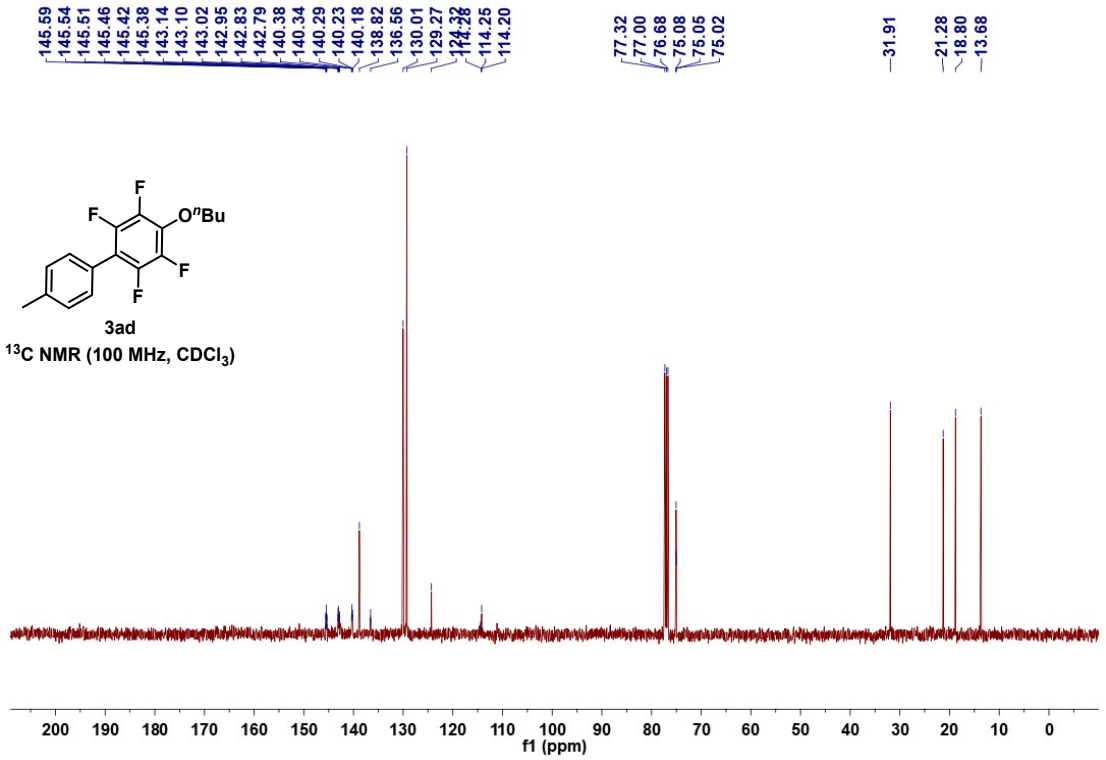


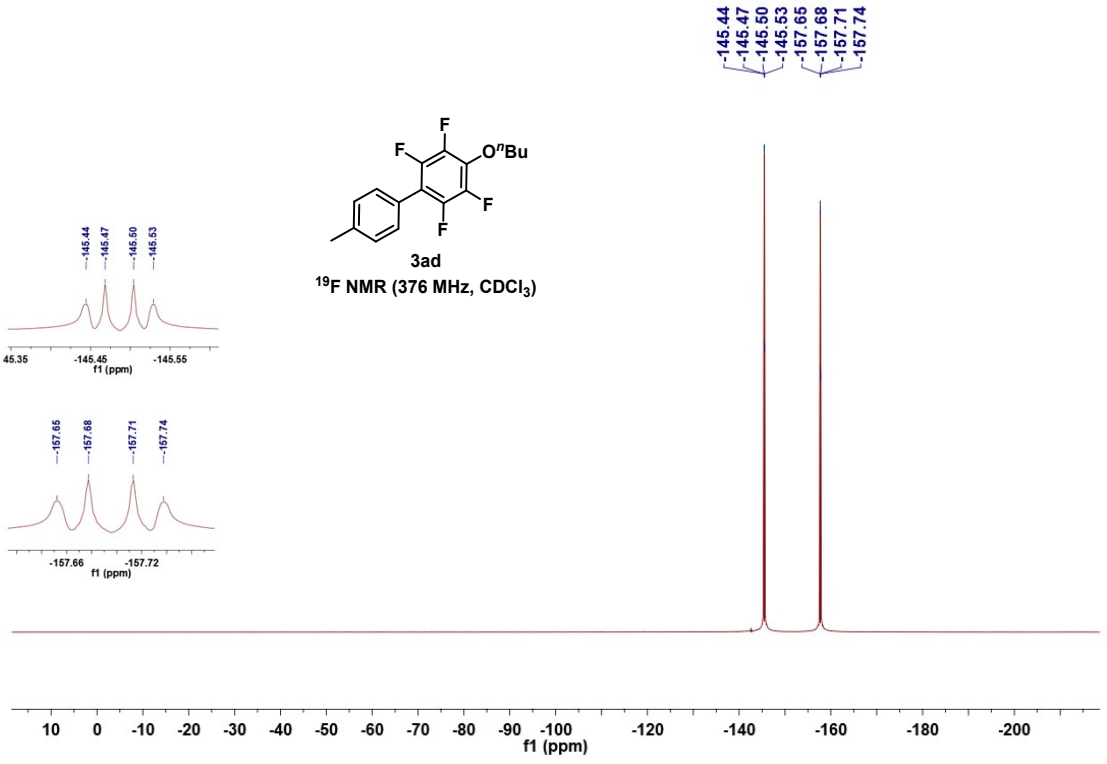
3ac

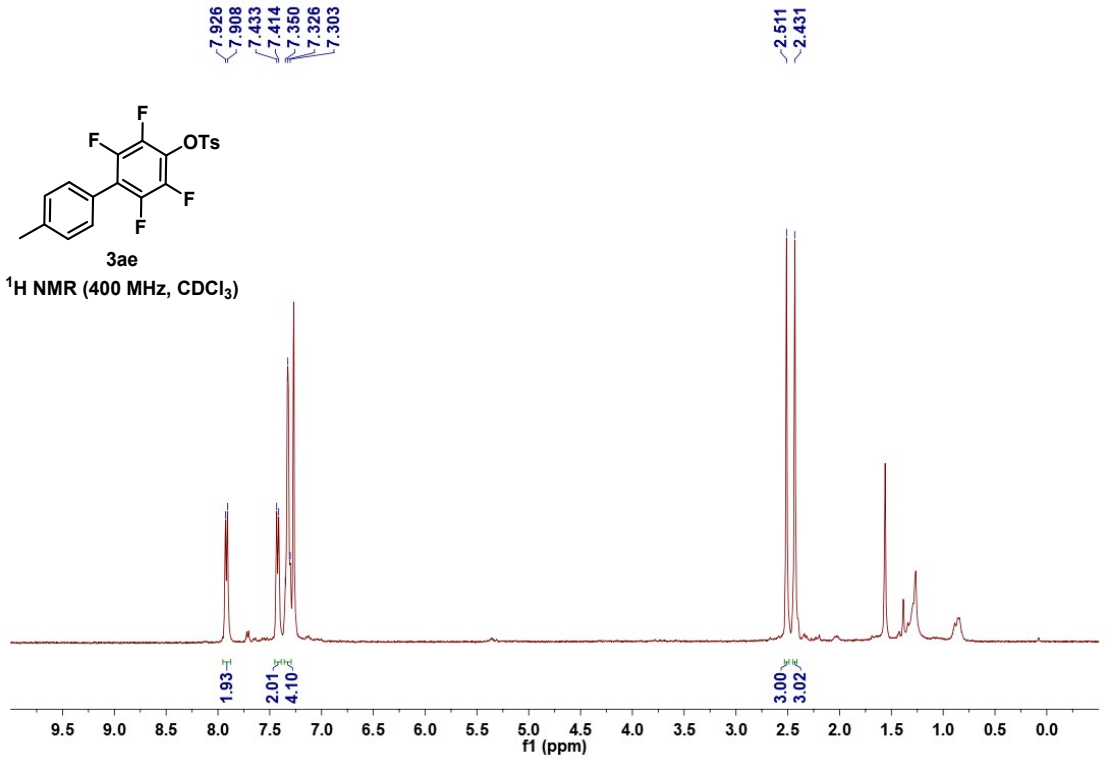
^{13}C NMR (100 MHz, $CDCl_3$)


-145.235
-145.259
-145.294
-145.319
-158.331
-158.356
-158.391
-158.416
F
F
OMe
F
F
3ac
19F NMR (376 MHz, CDCl3)
-145.235
-145.259
-145.294
-145.319
-142
-144
-146
-148
f1 (ppm)
-158.331
-158.356
-158.391
-158.416
-156
-157
-158
-159
-160
-161
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.359
7.339
7.310
7.290
4.294
4.277
4.261
2.430
1.828
1.811
1.791
1.557
1.011
0.992
F
F
OnBu
F
F
3ad
1H NMR (400 MHz, CDCl3)
2.04
1.99
2.07
3.00
2.08
2.13
3.11
f1 (ppm)

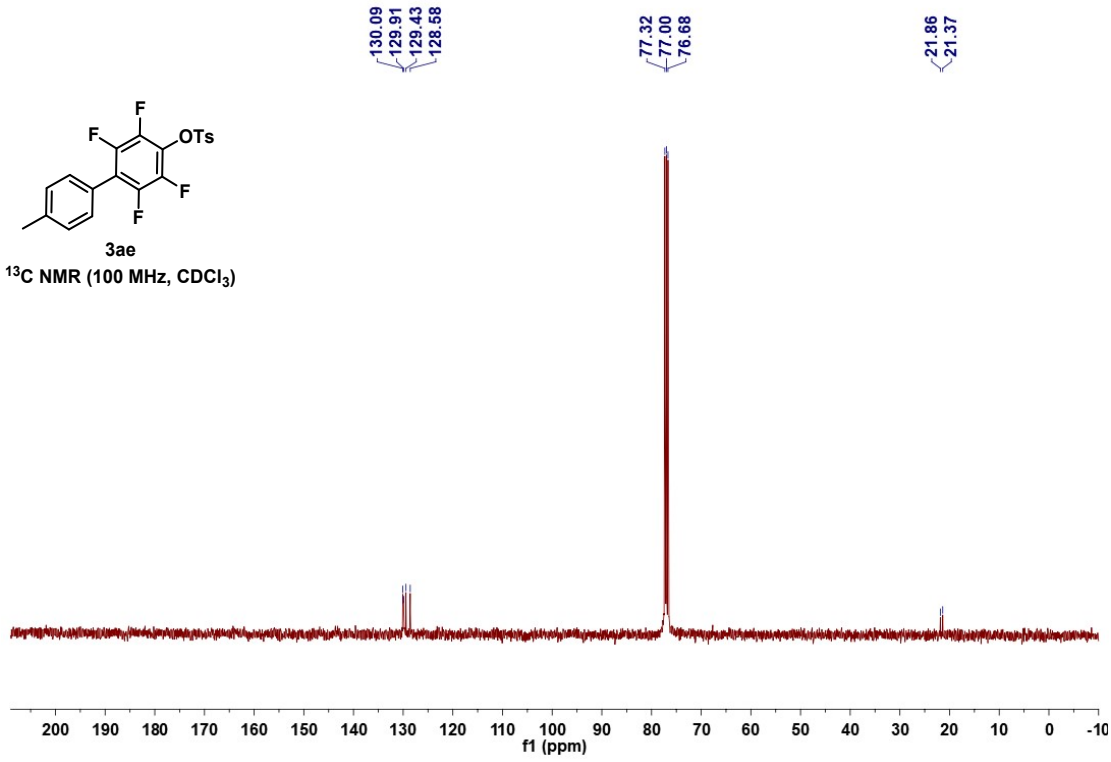

145.59
145.54
145.51
145.46
145.42
145.38
143.14
143.10
143.02
142.95
142.83
142.79
140.38
140.34
140.29
140.23
140.18
138.82
136.56
130.01
129.27
114.25
114.20
77.32
77.00
76.68
75.08
75.05
75.02
31.91
21.28
18.80
13.68
F
F
O^{n}Bu
F
F
3ad
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-145.44
-145.47
-145.50
-145.53
-157.65
-157.68
-157.71
-157.74
F
F
O^{n}Bu
F
F
3ad
^{19}F NMR (376 MHz, CDCl$_3$)
-145.44
-145.47
-145.50
-145.53
45.35
-145.45
-145.55
f1 (ppm)
-157.65
-157.68
-157.71
-157.74
-157.66
-157.72
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



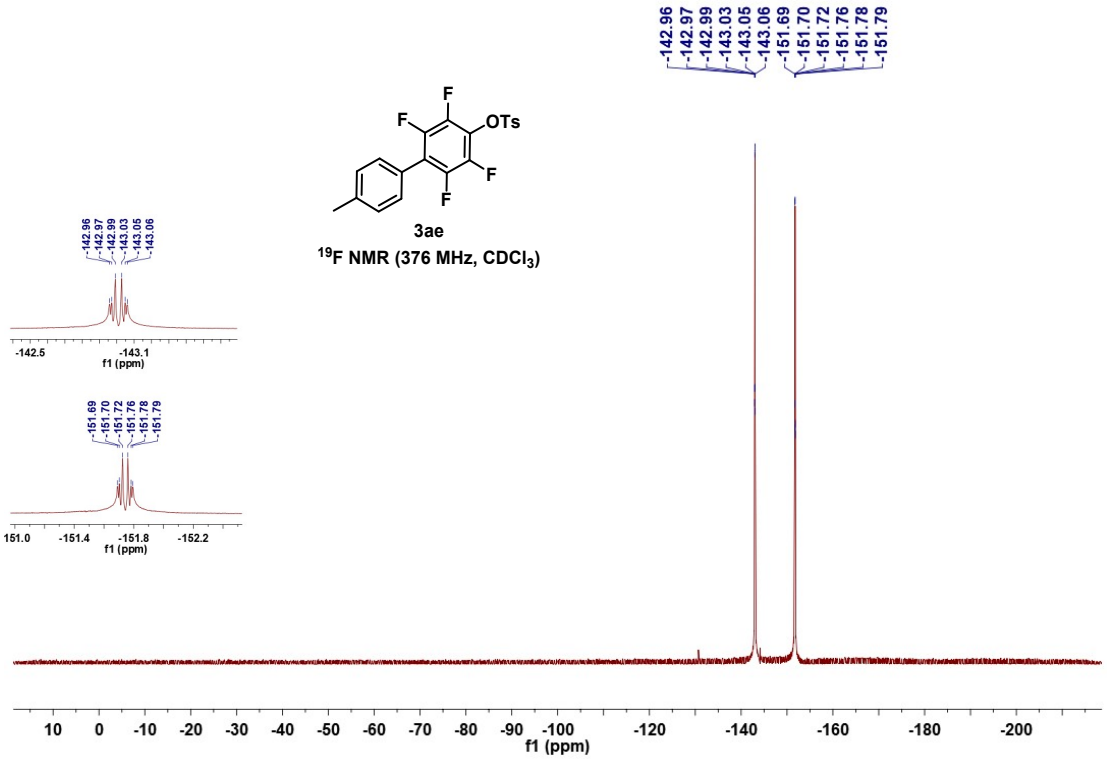
3ae

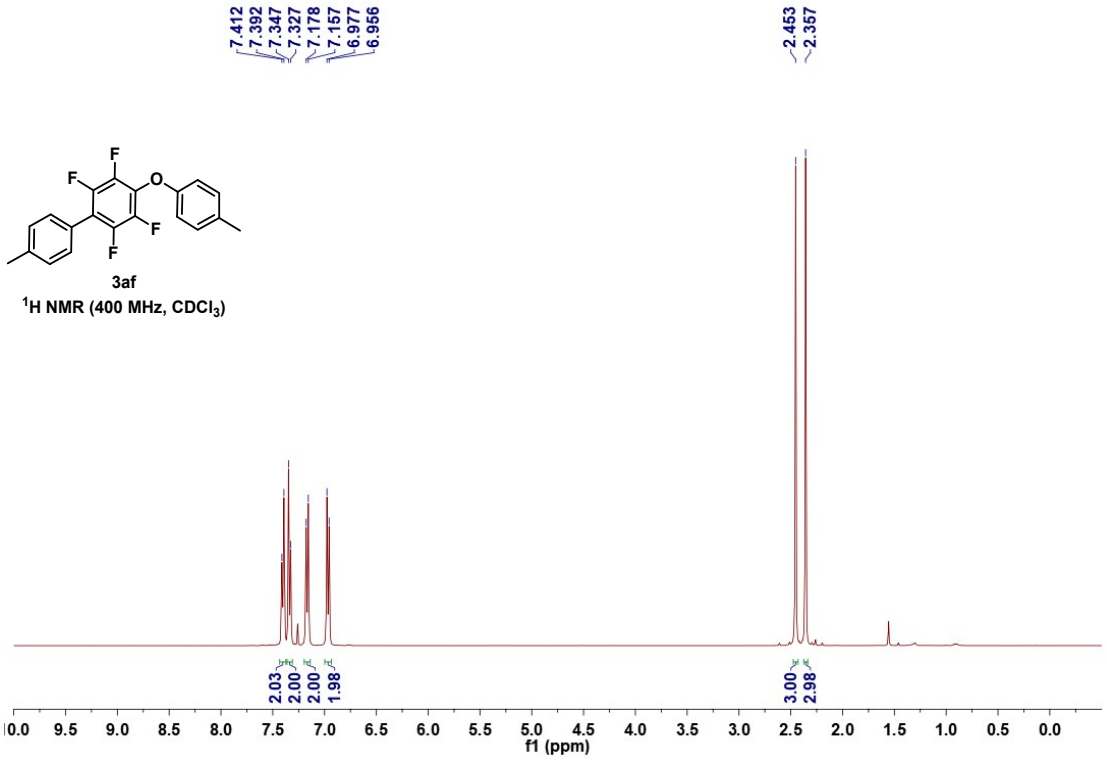
^{1}H NMR (400 MHz, $CDCl_3$)

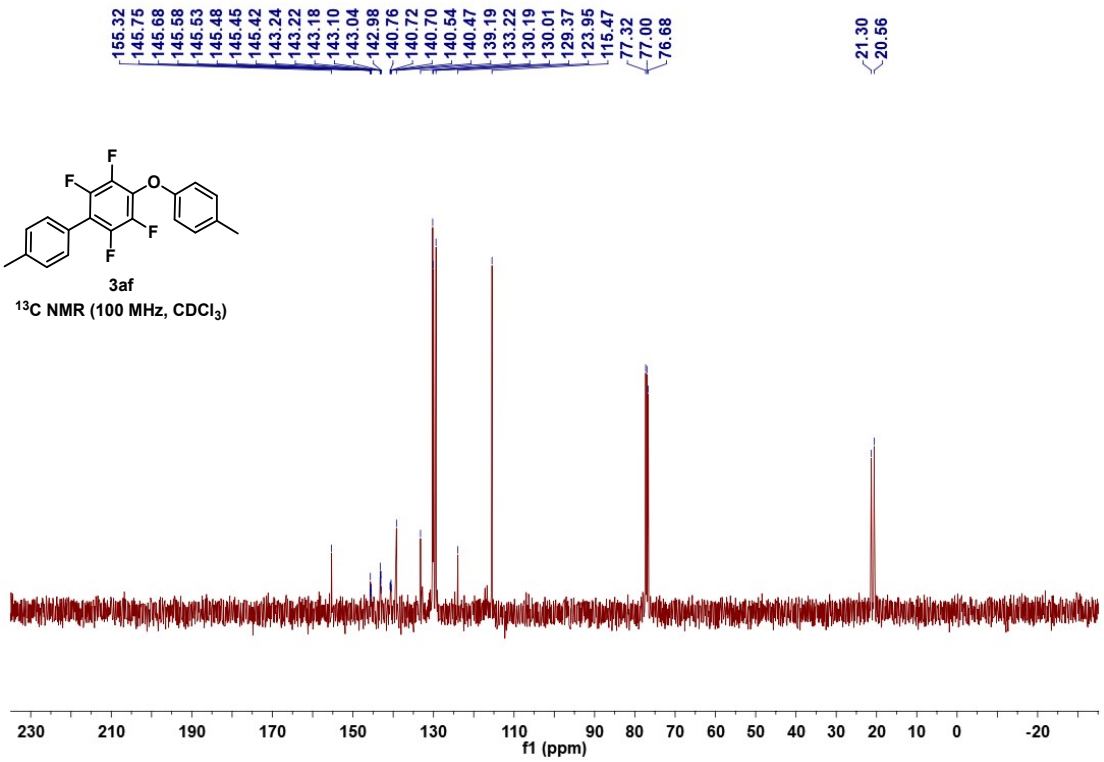


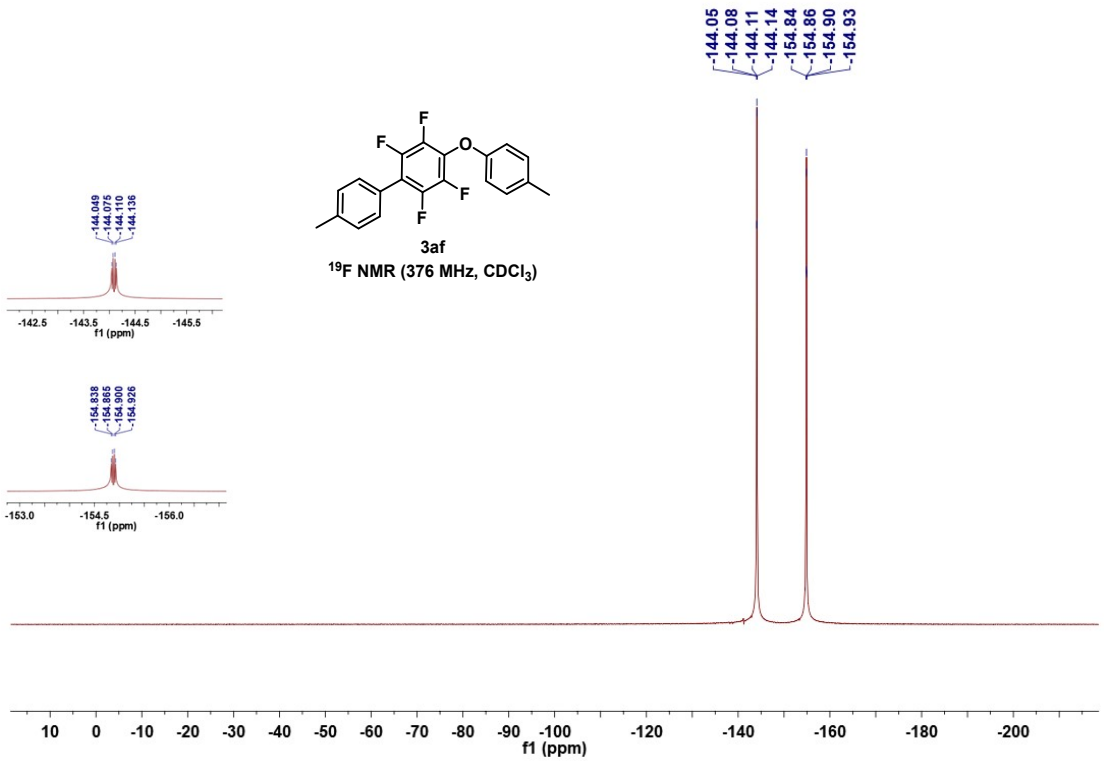
3ae

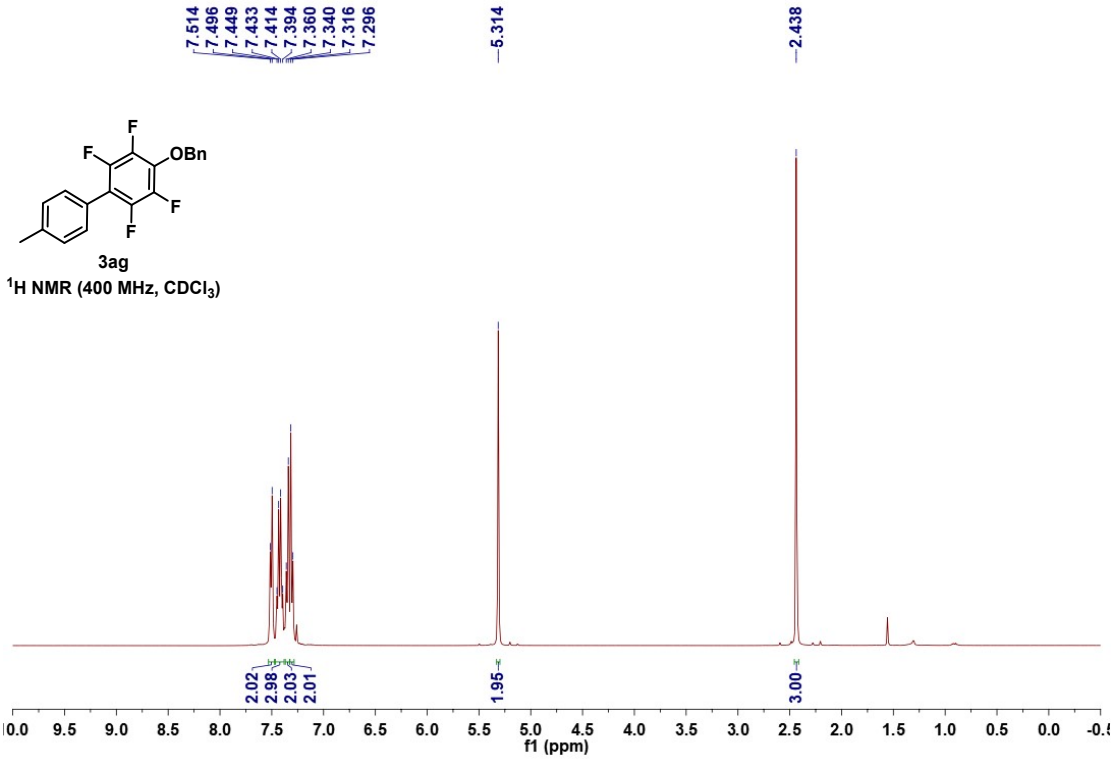
^{13}C NMR (100 MHz, $CDCl_3$)


-142.96
-142.97
-142.99
-143.03
-143.05
-143.06
-151.69
-151.70
-151.72
-151.76
-151.78
-151.79
F
F
OTs
F
F
3ae
19F NMR (376 MHz, CDCl3)
f1 (ppm)


7.412
7.392
7.347
7.327
7.178
7.157
6.977
6.956
2.453
2.357
F
F
O
F
F
3af
1H NMR (400 MHz, CDCl3)
2.03
2.00
2.00
1.98
3.00
2.98
f1 (ppm)

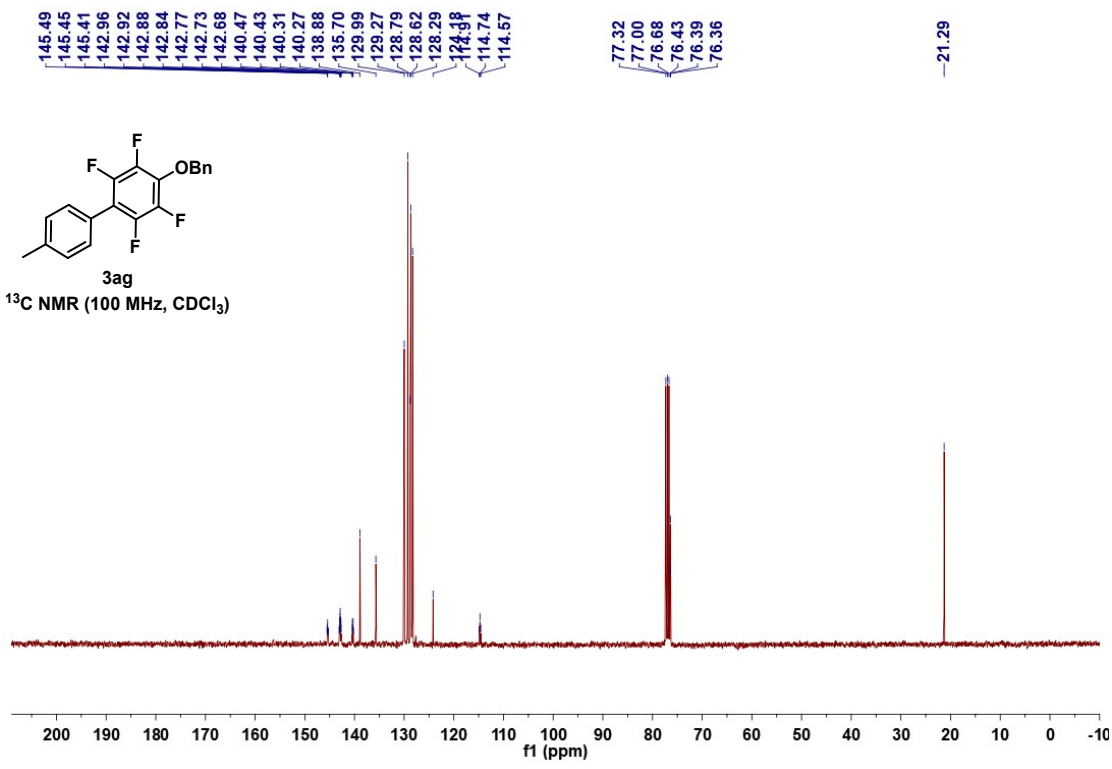

155.32
145.75
145.68
145.58
145.53
145.48
145.45
145.42
143.24
143.22
143.18
143.10
143.04
142.98
140.76
140.72
140.70
140.54
140.47
139.19
133.22
130.19
130.01
129.37
123.95
115.47
77.32
77.00
76.68
21.30
20.56
F
F
O
F
F
3af
13C NMR (100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
f1 (ppm)


-144.05
-144.08
-144.11
-144.14
-154.84
-154.86
-154.90
-154.93
F
F
O
F
F
3af
19F NMR (376 MHz, CDCl3)
-144.049
-144.075
-144.110
-144.136
-142.5
-143.5
-144.5
-145.5
f1 (ppm)
-154.838
-154.865
-154.900
-154.926
-153.0
-154.5
-156.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)



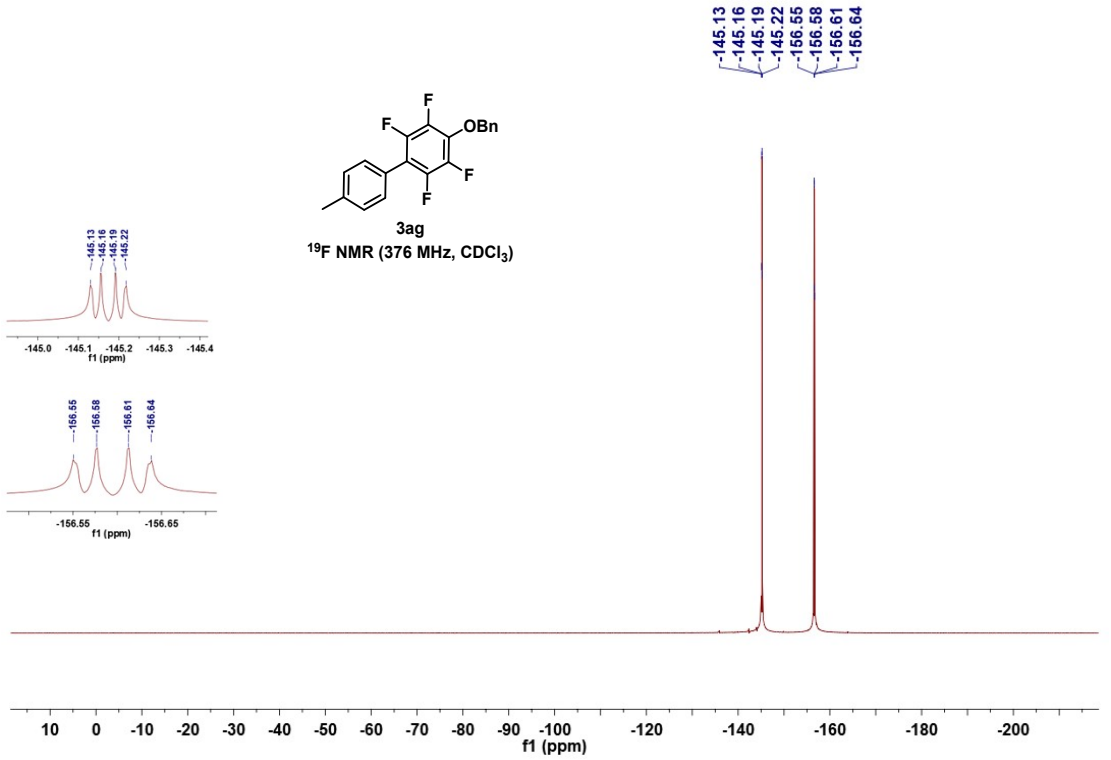
3ag

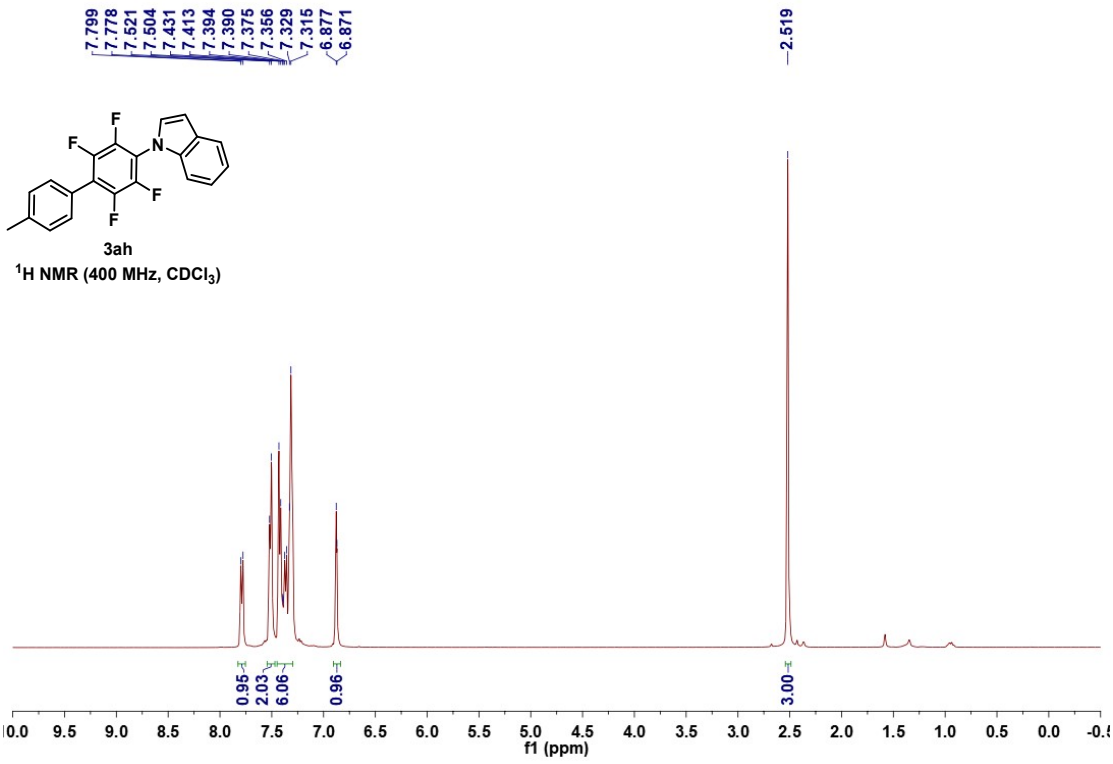
^{1}H NMR (400 MHz, $CDCl_3$)

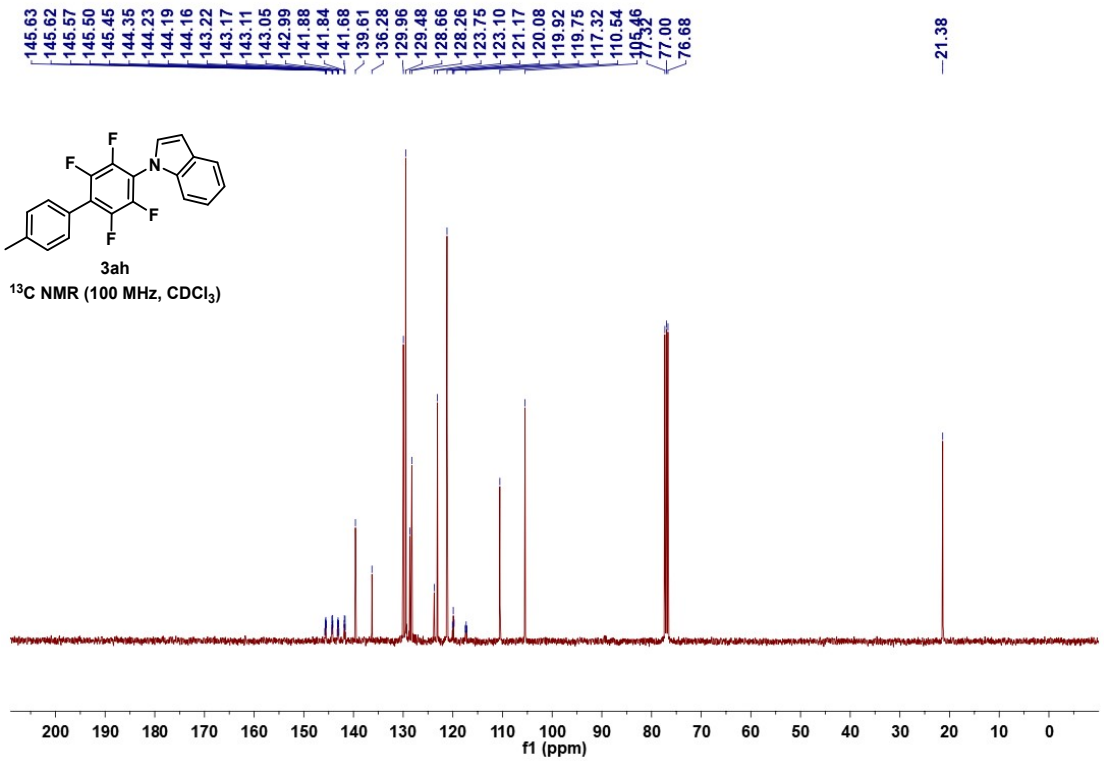


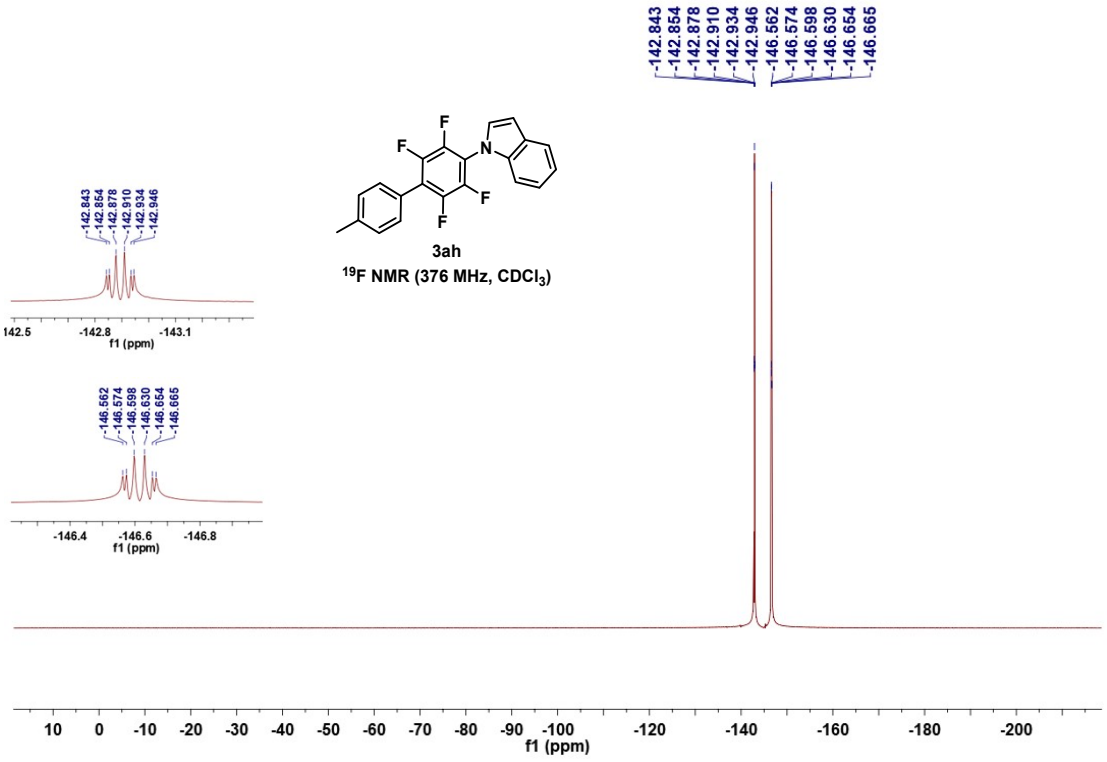
3ag

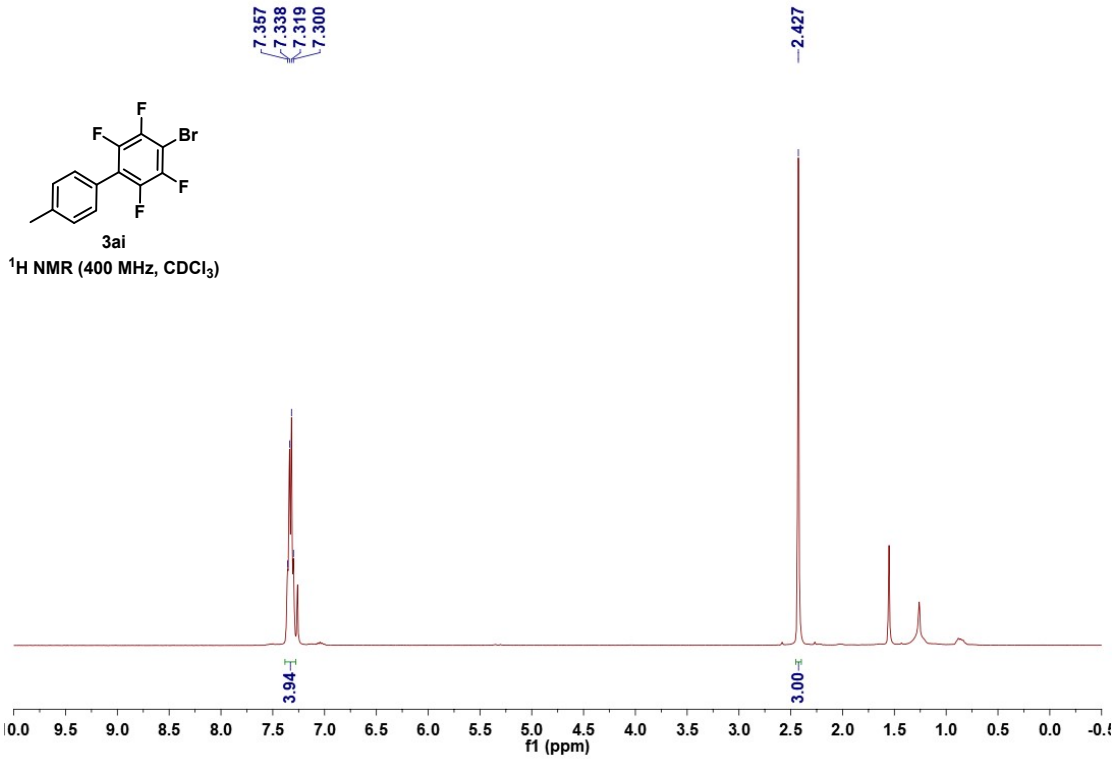
^{13}C NMR (100 MHz, $CDCl_3$)


-145.13
-145.16
-145.19
-145.22
-156.55
-156.58
-156.61
-156.64
F
F
OBn
F
F
3ag
19F NMR (376 MHz, CDCl3)
f1 (ppm)


7.799
7.778
7.521
7.504
7.431
7.413
7.394
7.390
7.375
7.356
7.329
7.315
6.877
6.871
2.519
F
F
N
F
F
3ah
1H NMR (400 MHz, CDCl3)
0.95
2.03
6.06
0.96
3.00
f1 (ppm)

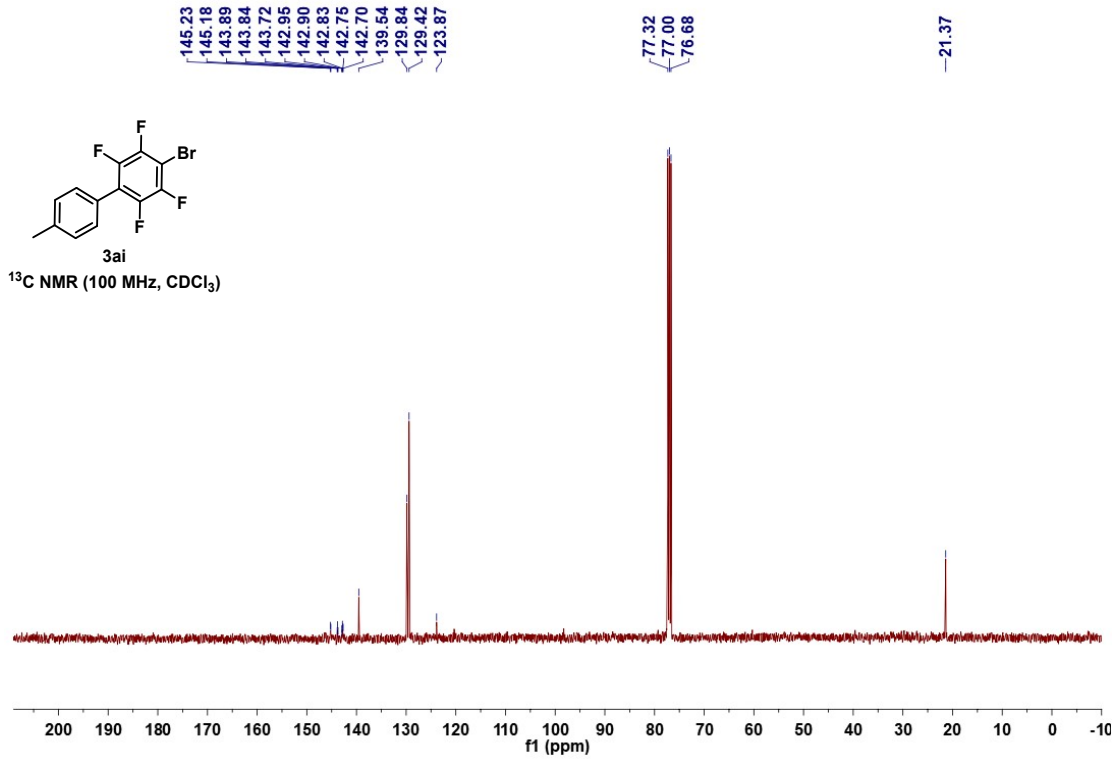

145.63
145.62
145.57
145.50
145.45
144.35
144.23
144.19
144.16
143.22
143.17
143.11
143.05
142.99
141.88
141.84
141.68
139.61
136.28
129.96
129.48
128.66
128.26
123.75
123.10
121.17
120.08
119.92
119.75
117.32
110.54
105.46
77.32
77.00
76.68
21.38
F
F
N
F
F
3ah
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-142.843
-142.854
-142.878
-142.910
-142.934
-142.946
-146.562
-146.574
-146.598
-146.630
-146.654
-146.665
F
F
N
F
F
3ah
19F NMR (376 MHz, CDCl3)
142.5 -142.8 -143.1
f1 (ppm)
-146.4 -146.6 -146.8
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



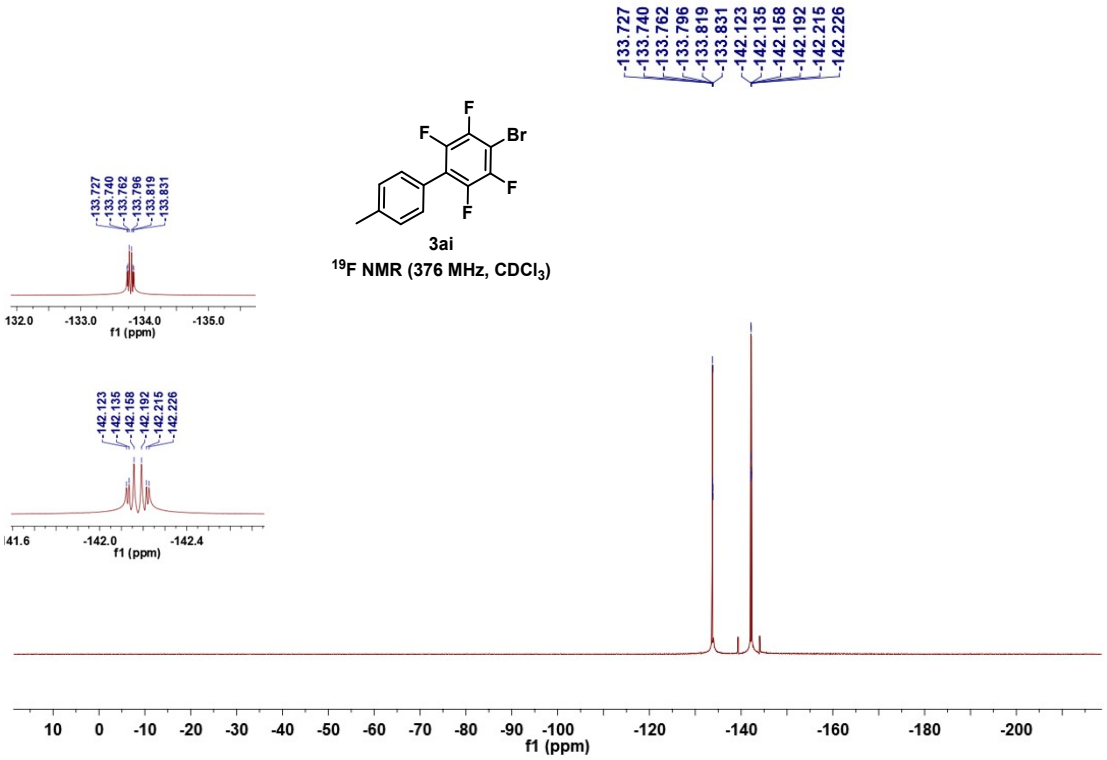
3ai

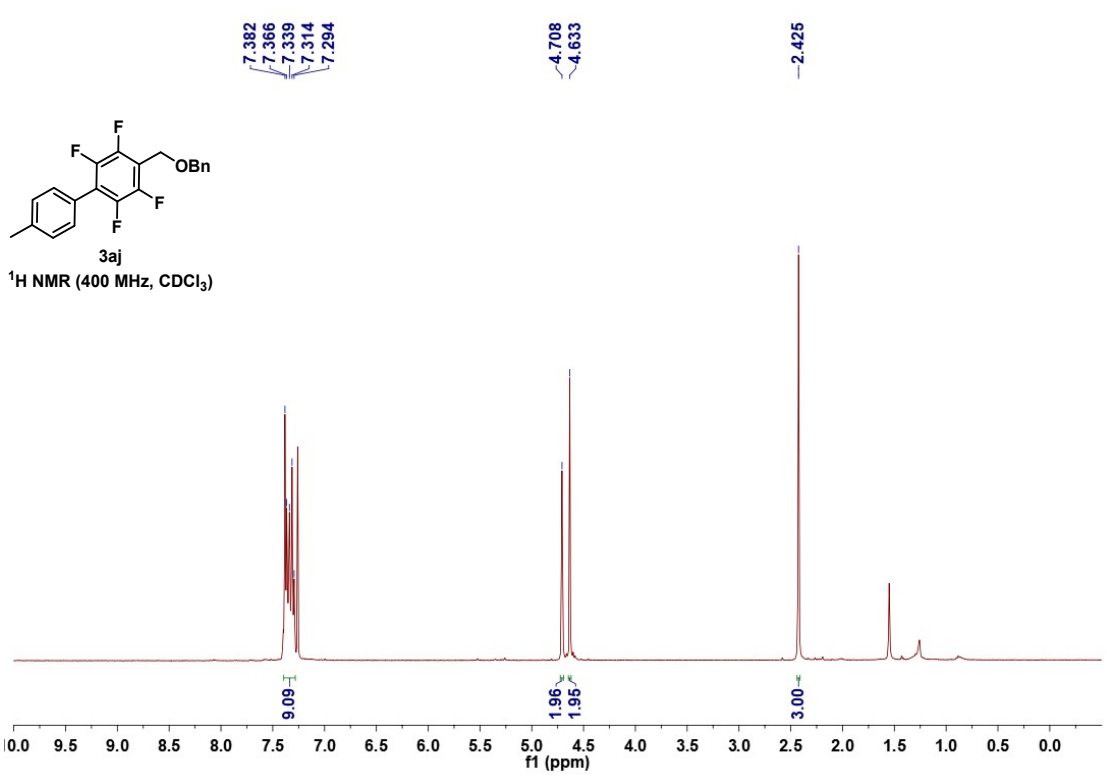
^{1}H NMR (400 MHz, $CDCl_3$)

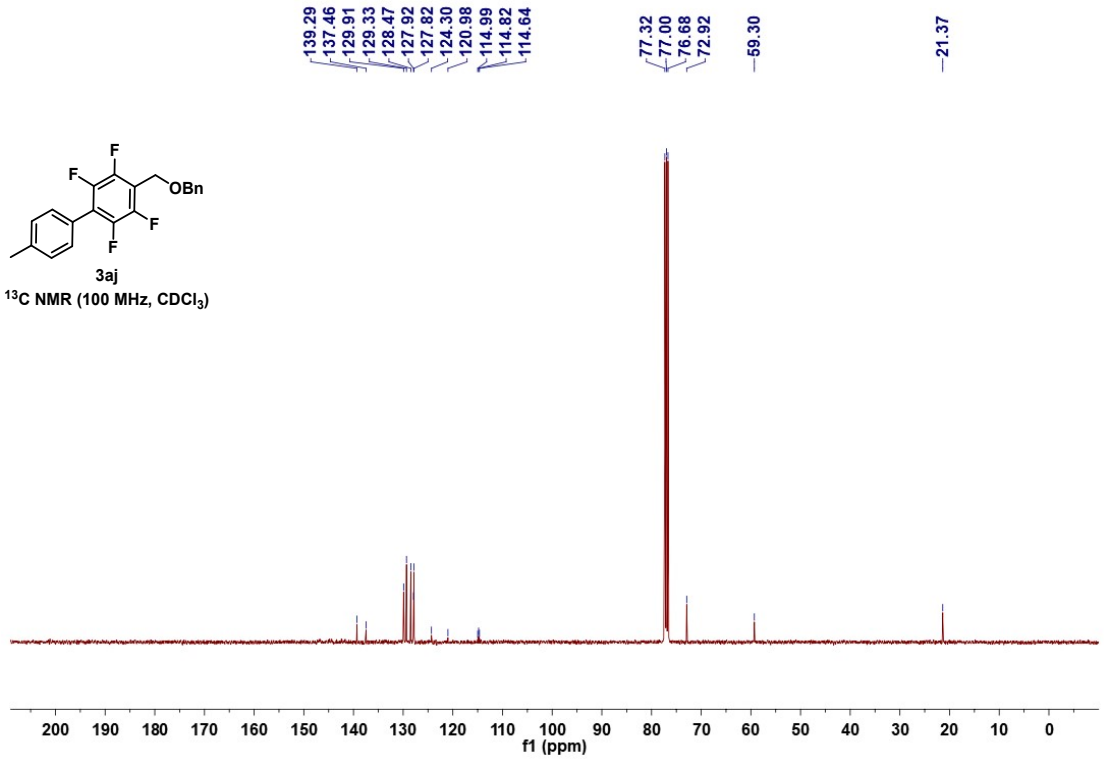


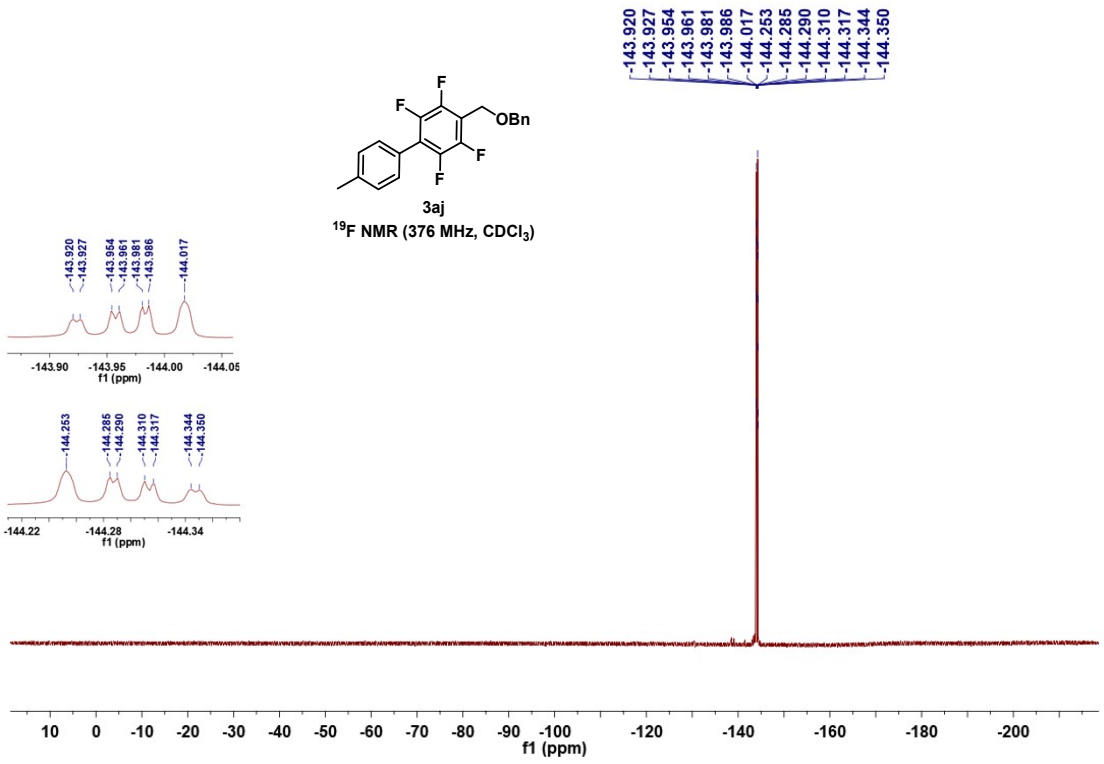
3ai

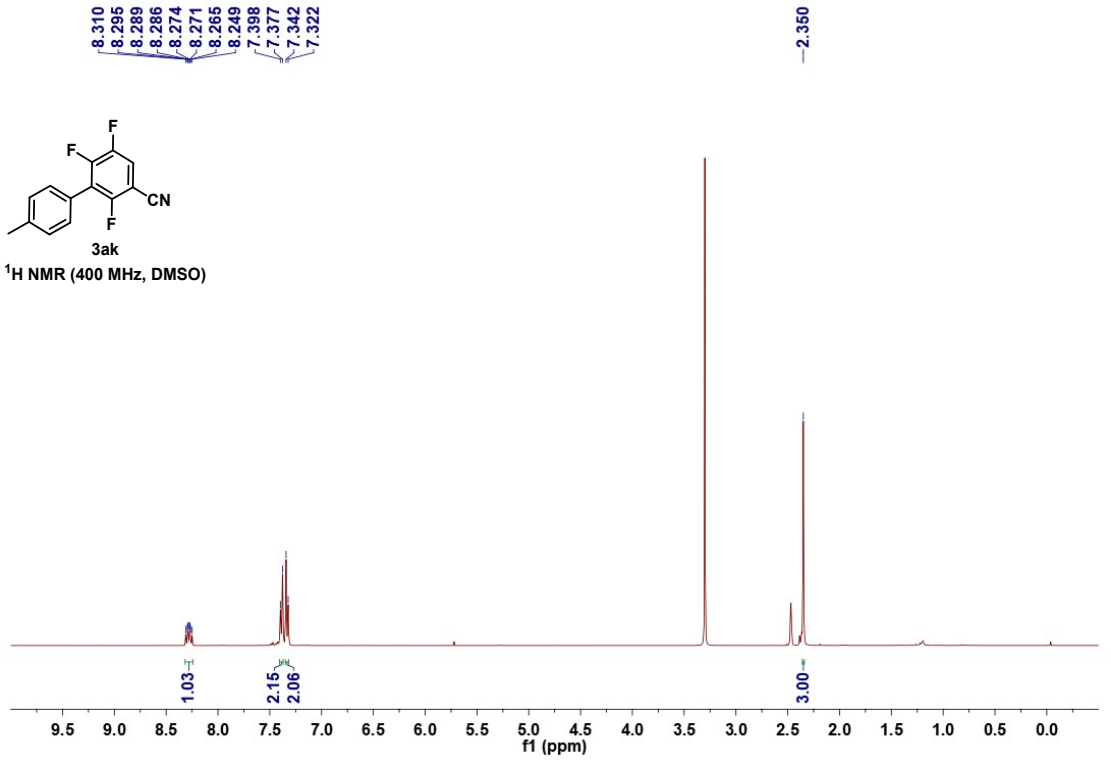
^{13}C NMR (100 MHz, $CDCl_3$)


-133.727
-133.740
-133.762
-133.796
-133.819
-133.831
-142.123
-142.135
-142.158
-142.192
-142.215
-142.226
F
F
Br
F
F
3ai
19F NMR (376 MHz, CDCl3)
f1 (ppm)


7.382
7.366
7.339
7.314
7.294
4.708
4.633
2.425
F
F
OBn
F
F
3aj
1H NMR (400 MHz, CDCl3)
9.09
1.96
1.95
3.00
f1 (ppm)

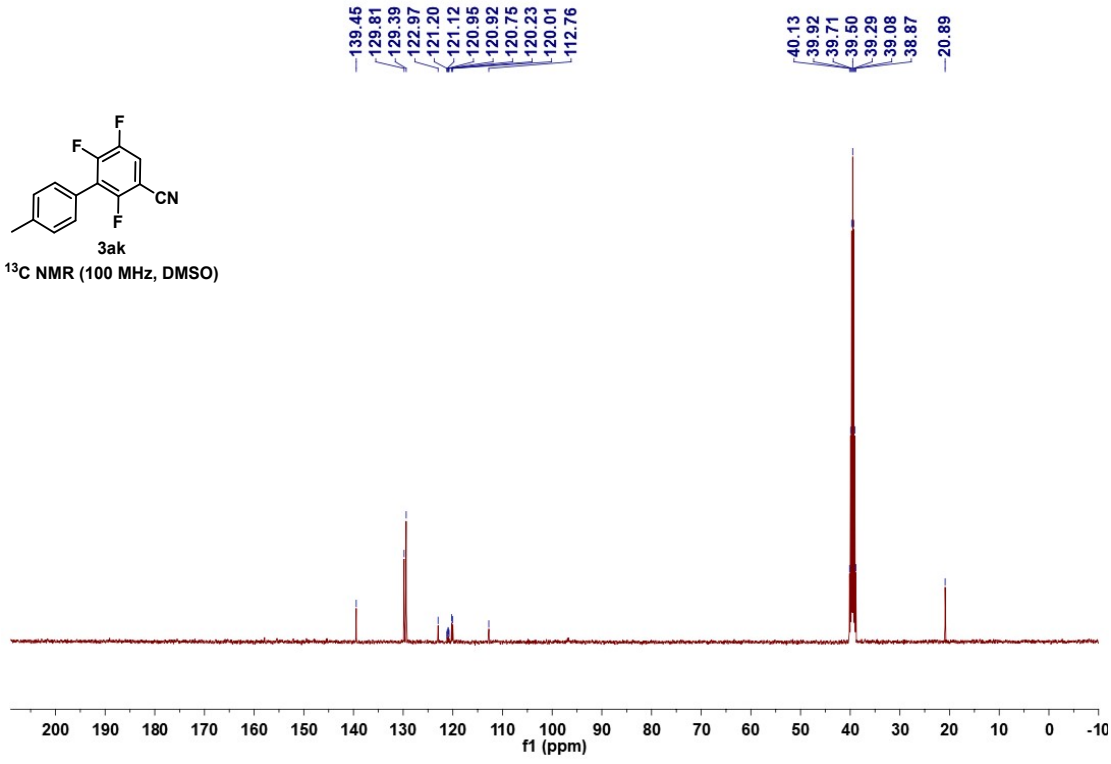

139.29
137.46
129.91
129.33
128.47
127.92
127.82
124.30
120.98
114.99
114.82
114.64
77.32
77.00
76.68
72.92
59.30
21.37
F
F
OBn
F
F
3aj
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-143.920
-143.927
-143.954
-143.961
-143.981
-143.986
-144.017
-144.253
-144.285
-144.290
-144.310
-144.317
-144.344
-144.350
F
F
OBn
F
F
3aj
19F NMR (376 MHz, CDCl3)
-143.920
-143.927
-143.954
-143.961
-143.981
-143.986
-144.017
-143.90
-143.95
-144.00
f1 (ppm)
-144.253
-144.285
-144.290
-144.310
-144.317
-144.344
-144.350
-144.22
-144.28
-144.34
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



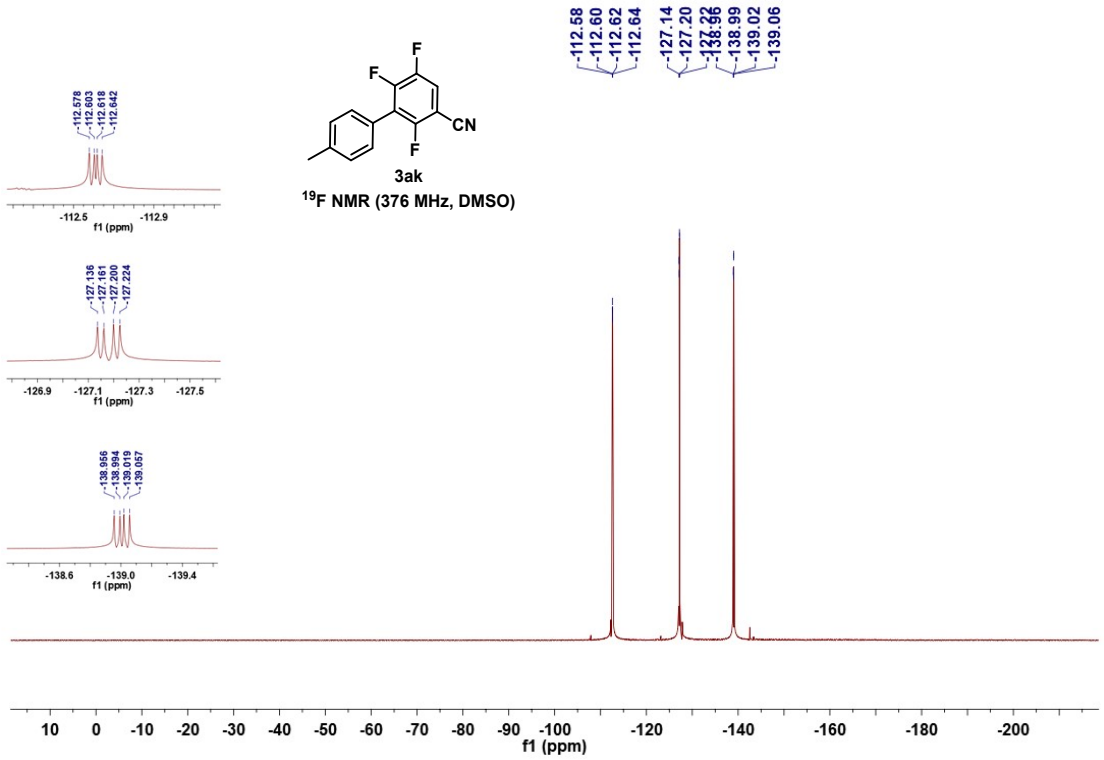
3ak

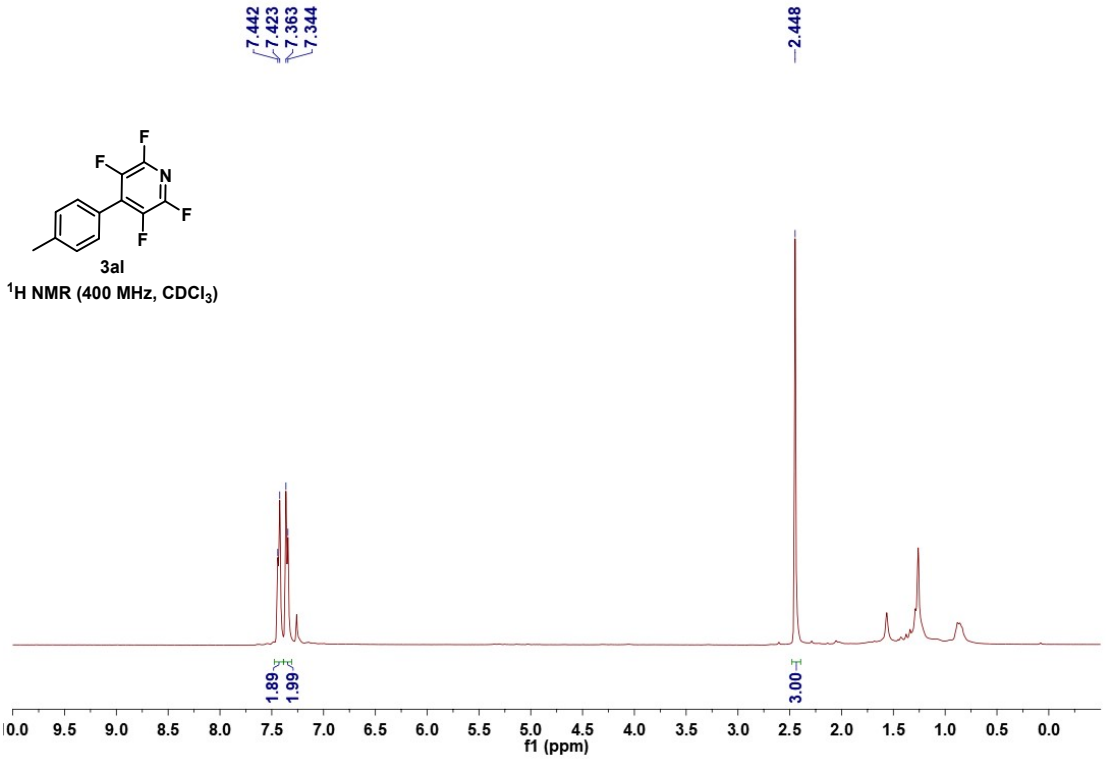
^{1}H NMR (400 MHz, DMSO)

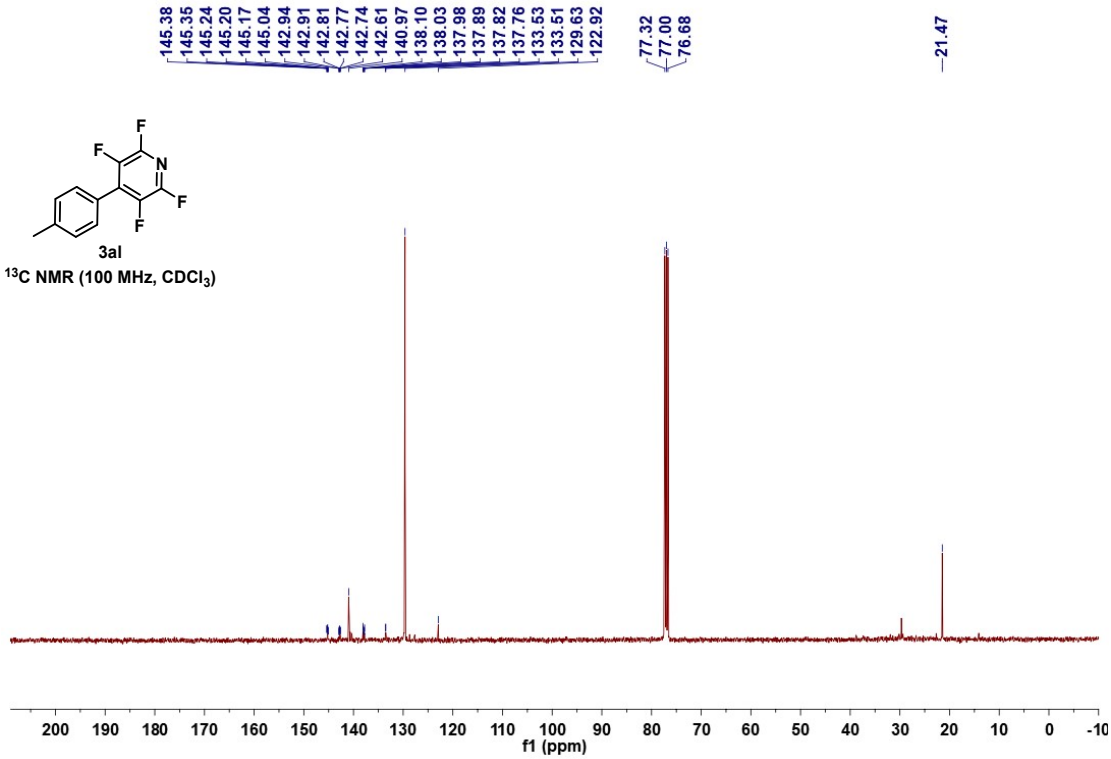


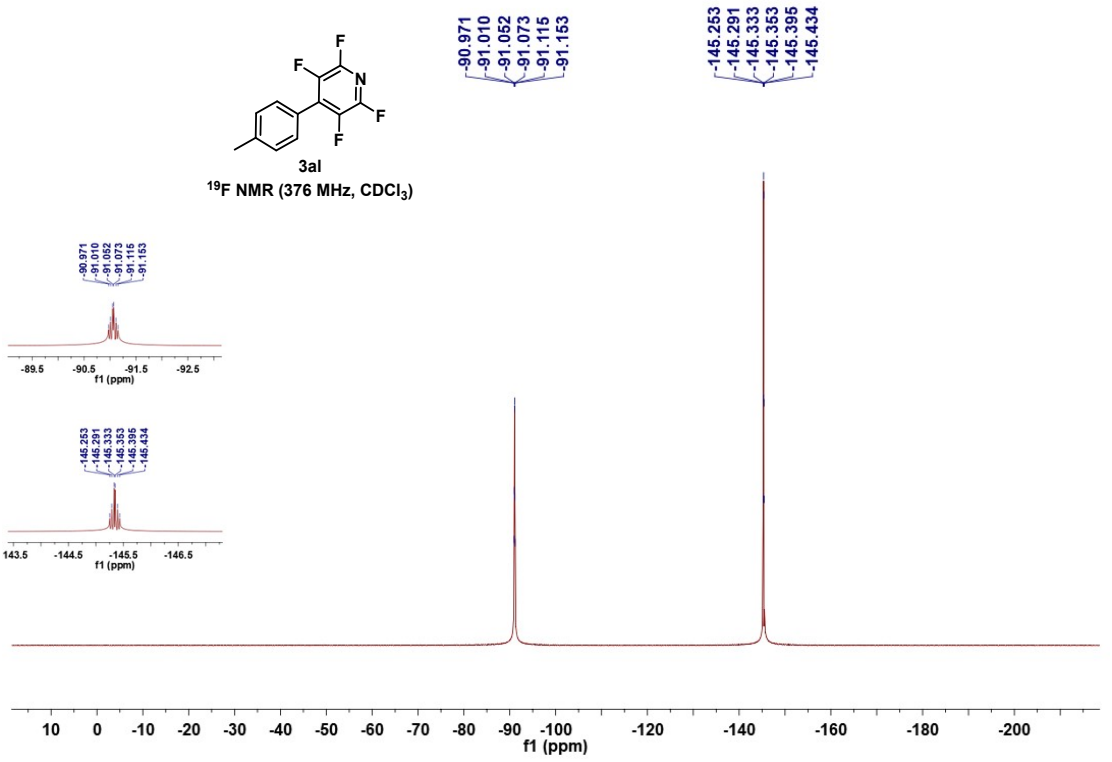
3ak

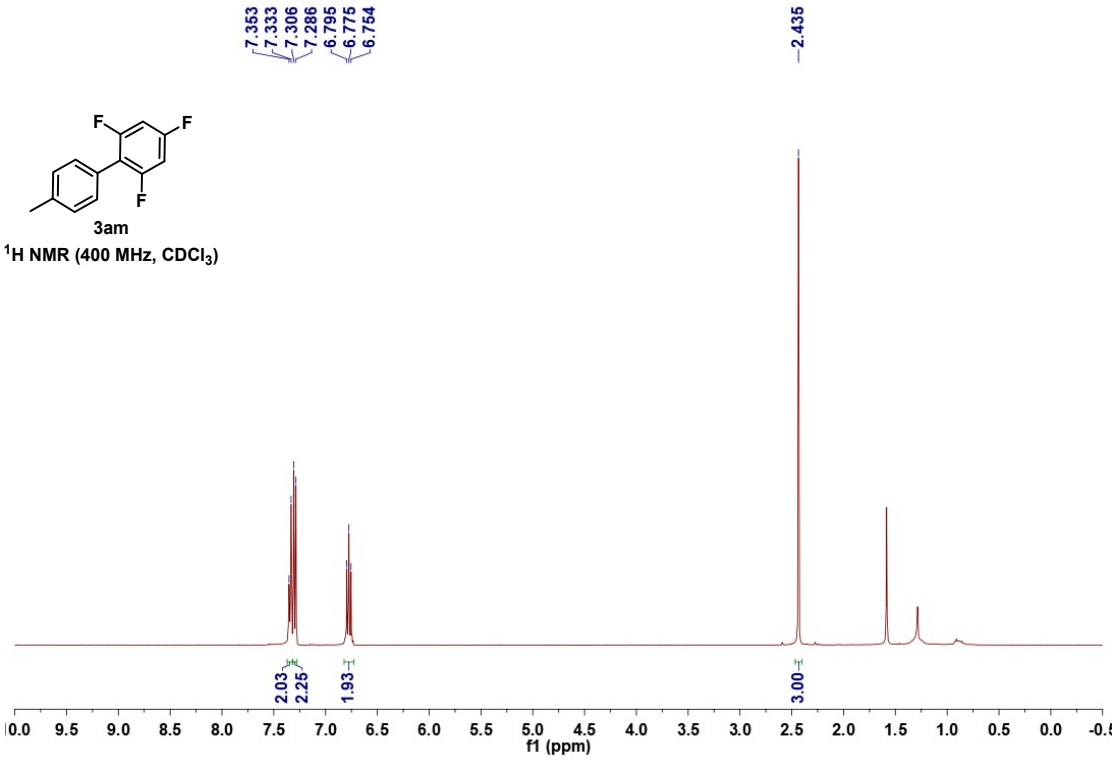
^{13}C NMR (100 MHz, DMSO)


-112.58
-112.60
-112.62
-112.64
-127.14
-127.20
-138.96
-138.99
-139.02
-139.06
F
F
CN
F
3ak
^{19}F NMR (376 MHz, DMSO)
-112.578
-112.603
-112.618
-112.642
-112.5
-112.9
f1 (ppm)
-127.136
-127.161
-127.200
-127.224
-126.9
-127.1
-127.3
-127.5
f1 (ppm)
-138.956
-138.994
-139.019
-139.057
-138.6
-139.0
-139.4
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.442
7.423
7.363
7.344
2.448
F
F
N
F
F
3al
^{1}H NMR (400 MHz, $CDCl_3$)
1.89
1.99
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

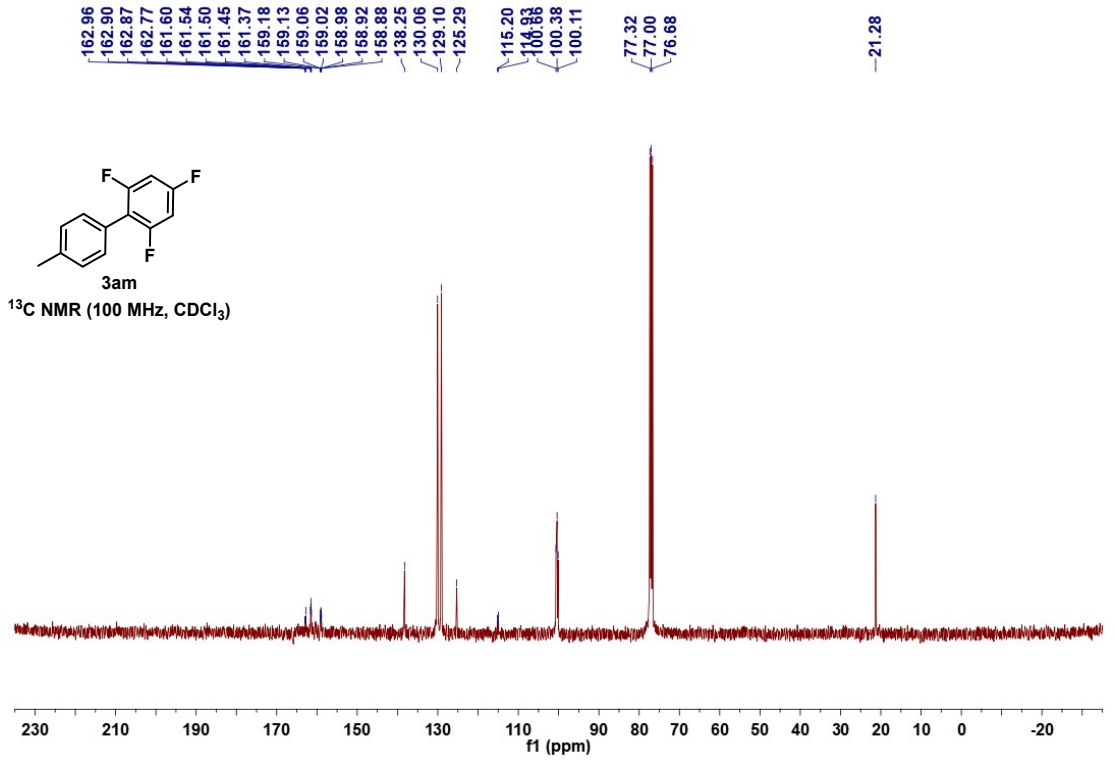

145.38
145.35
145.24
145.20
145.17
145.04
142.94
142.91
142.81
142.77
142.74
142.61
140.97
138.10
138.03
137.98
137.89
137.82
137.76
133.53
133.51
129.63
122.92
77.32
77.00
76.68
21.47
F
F
N
F
F
3al
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-90.971
-91.010
-91.052
-91.073
-91.115
-91.153
-145.253
-145.291
-145.333
-145.353
-145.395
-145.434
F
F
N
F
F
3al
^{19}F NMR (376 MHz, CDCl$_3$)
-89.5 -90.5 -91.5 -92.5
f1 (ppm)
143.5 -144.5 -145.5 -146.5
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



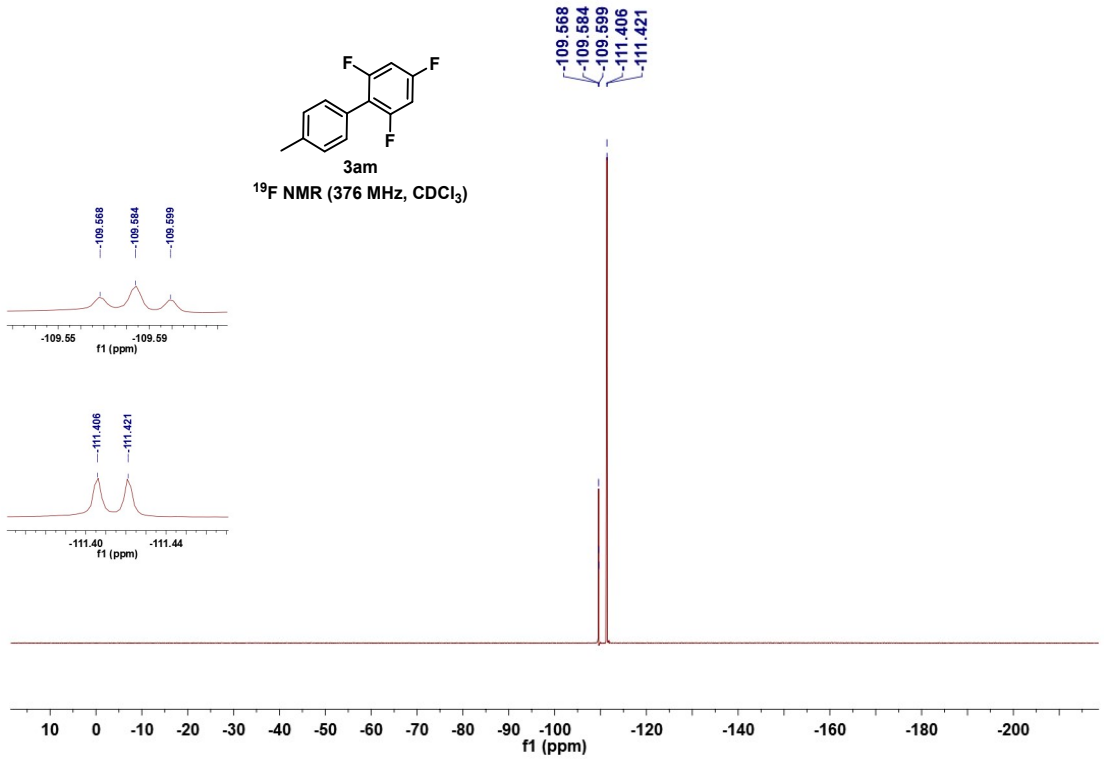
3am

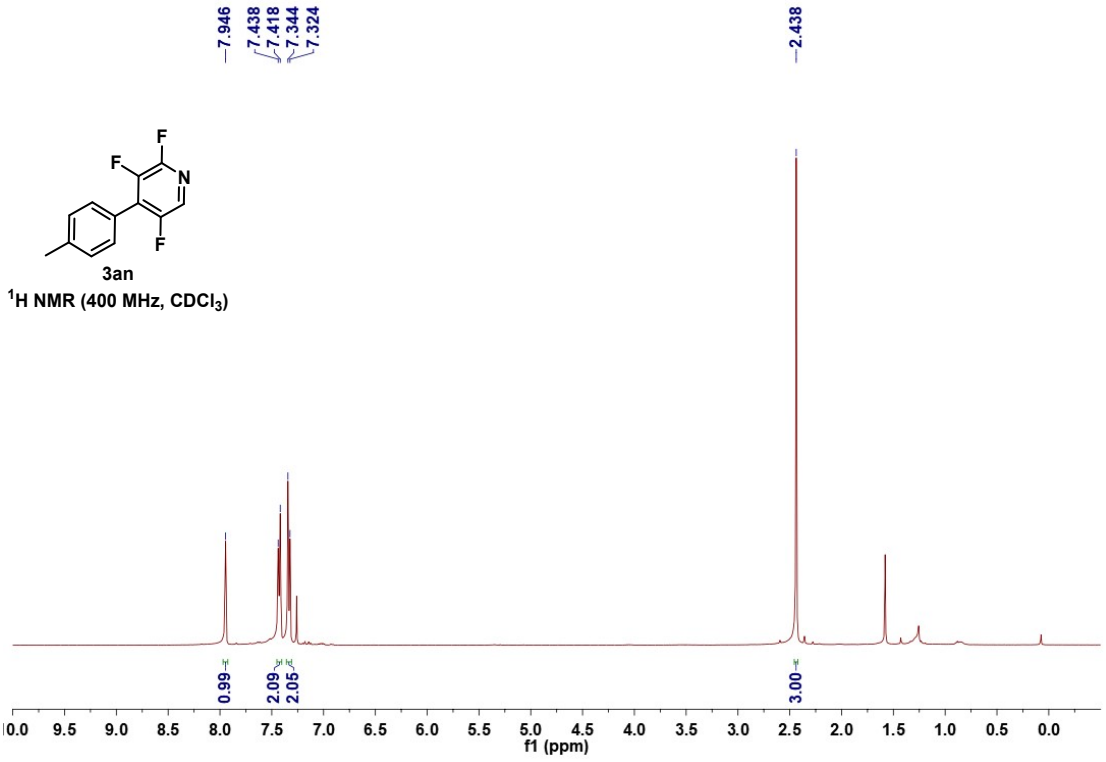
^{1}H NMR (400 MHz, $CDCl_3$)

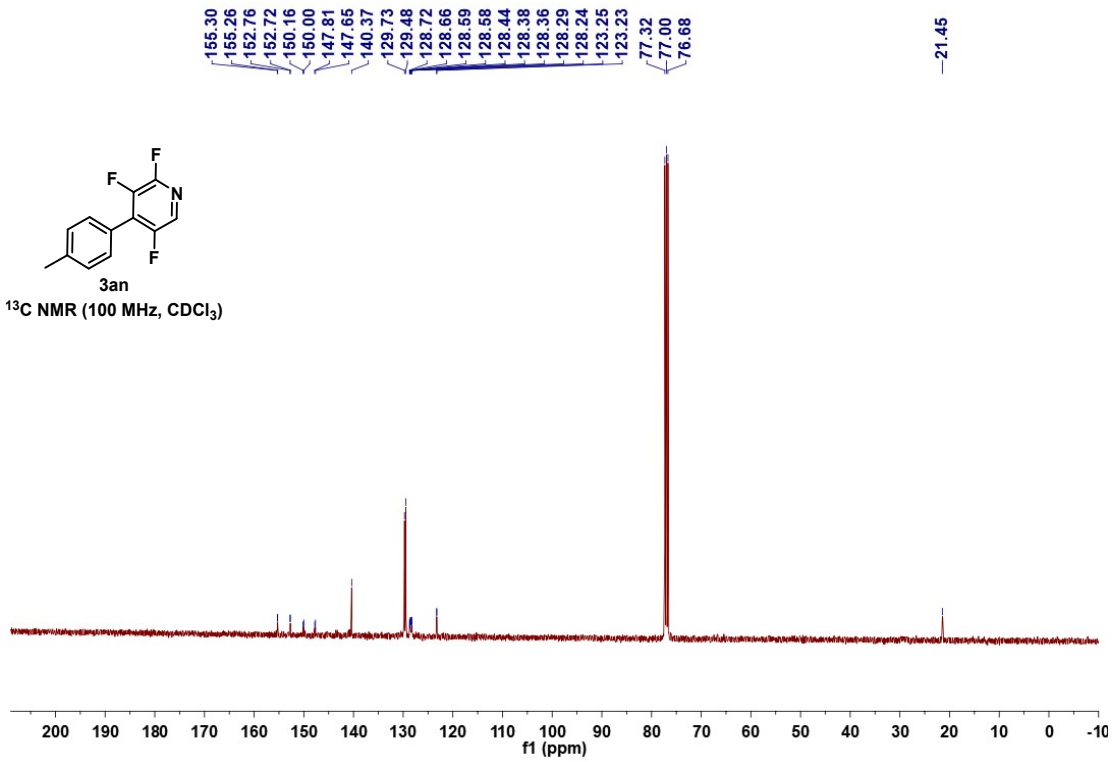


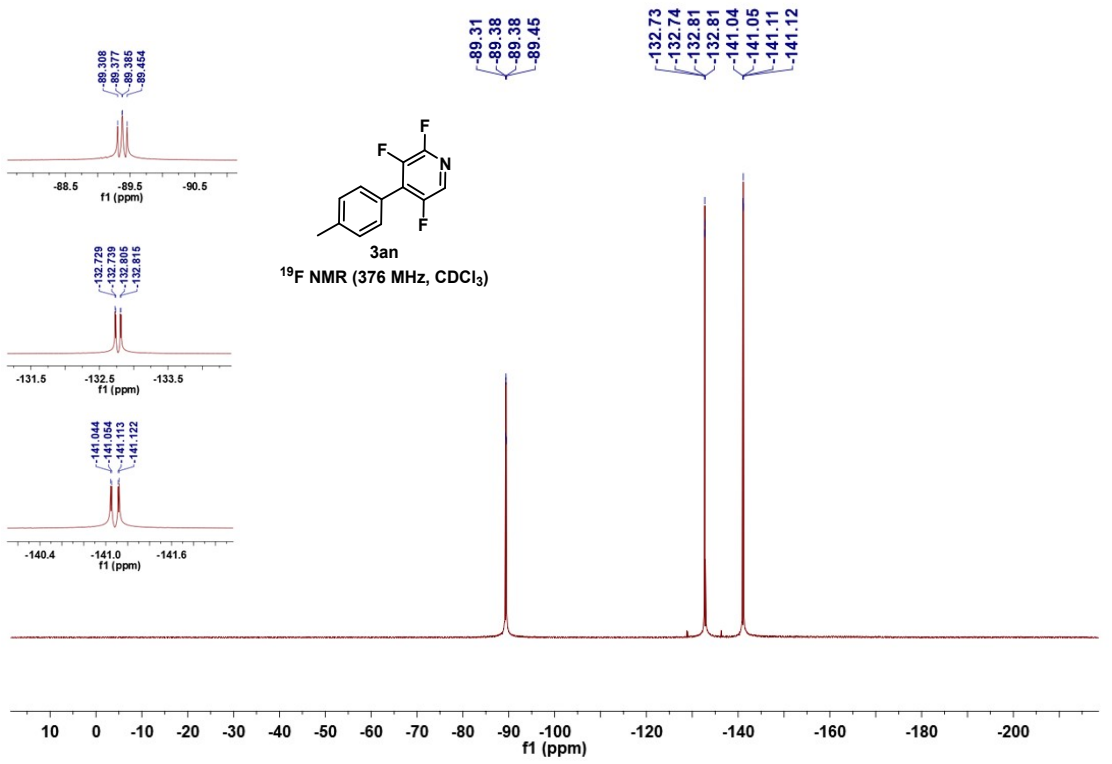
3am

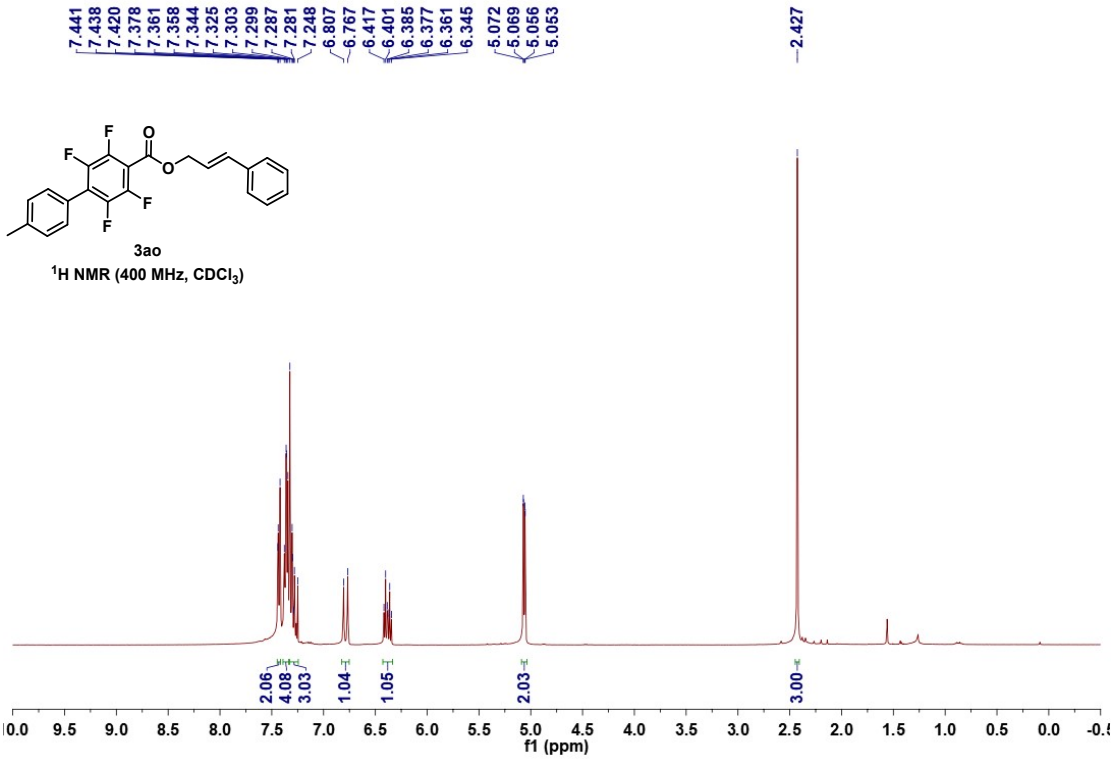
^{13}C NMR (100 MHz, $CDCl_3$)


-109.568
-109.584
-109.599
-111.406
-111.421
F
F
F
3am
^{19}F NMR (376 MHz, $CDCl_3$)
-109.568
-109.584
-109.599
-109.55
-109.59
f1 (ppm)
-111.406
-111.421
-111.40
-111.44
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.946
7.438
7.418
7.344
7.324
2.438
F
F
N
F
3an
^{1}H NMR (400 MHz, $CDCl_3$)
0.99
2.09
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

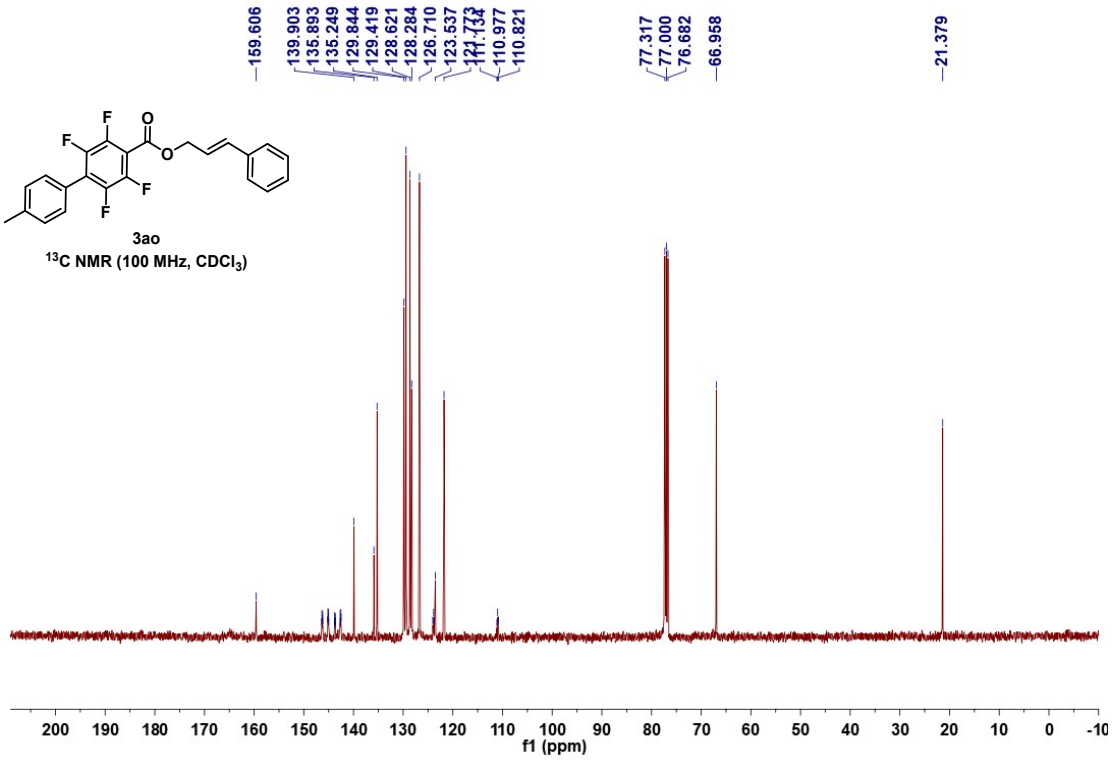

155.30
155.26
152.76
152.72
150.16
150.00
147.81
147.65
140.37
129.73
129.48
128.72
128.66
128.59
128.58
128.44
128.38
128.36
128.29
128.24
123.25
123.23
77.32
77.00
76.68
21.45
F
F
N
F
3an
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


89.308
89.377
89.385
89.454
-88.5
-89.5
-90.5
f1 (ppm)
132.729
132.739
132.805
132.815
-131.5
-132.5
-133.5
f1 (ppm)
141.044
141.054
141.113
141.122
-140.4
-141.0
-141.6
f1 (ppm)
-89.31
-89.38
-89.38
-89.45
-132.73
-132.74
-132.81
-132.81
-141.04
-141.05
-141.11
-141.12
F
F
N
F
3an
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



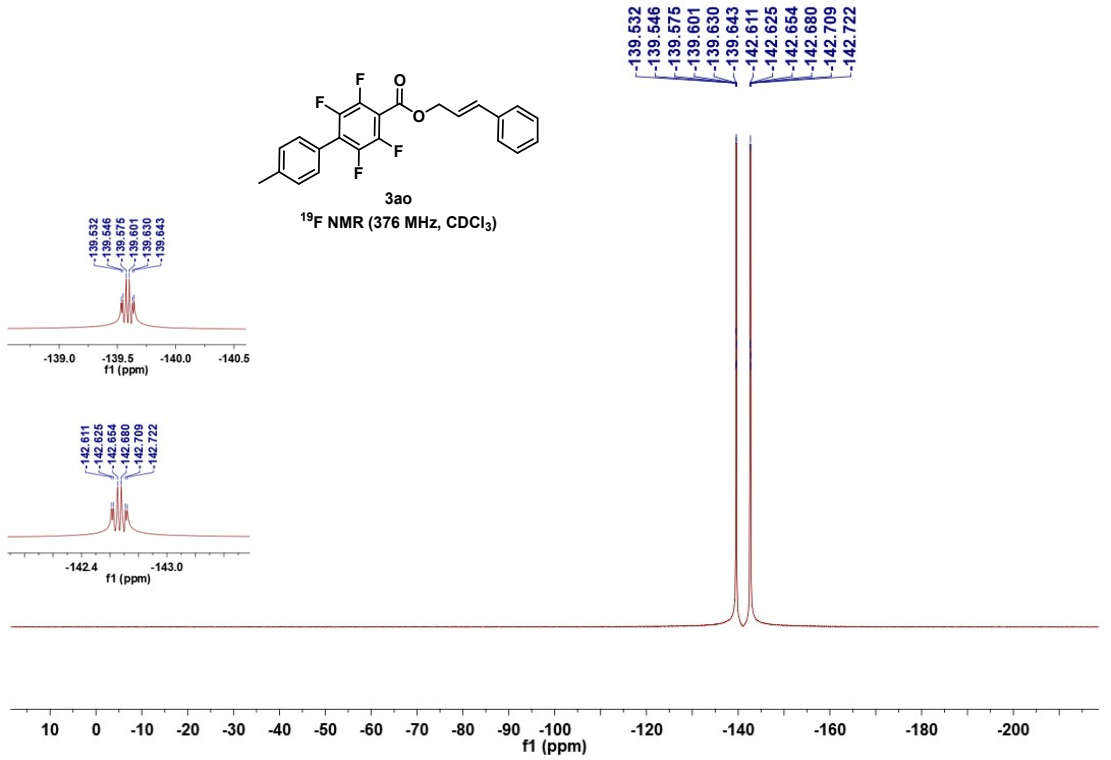
3ao

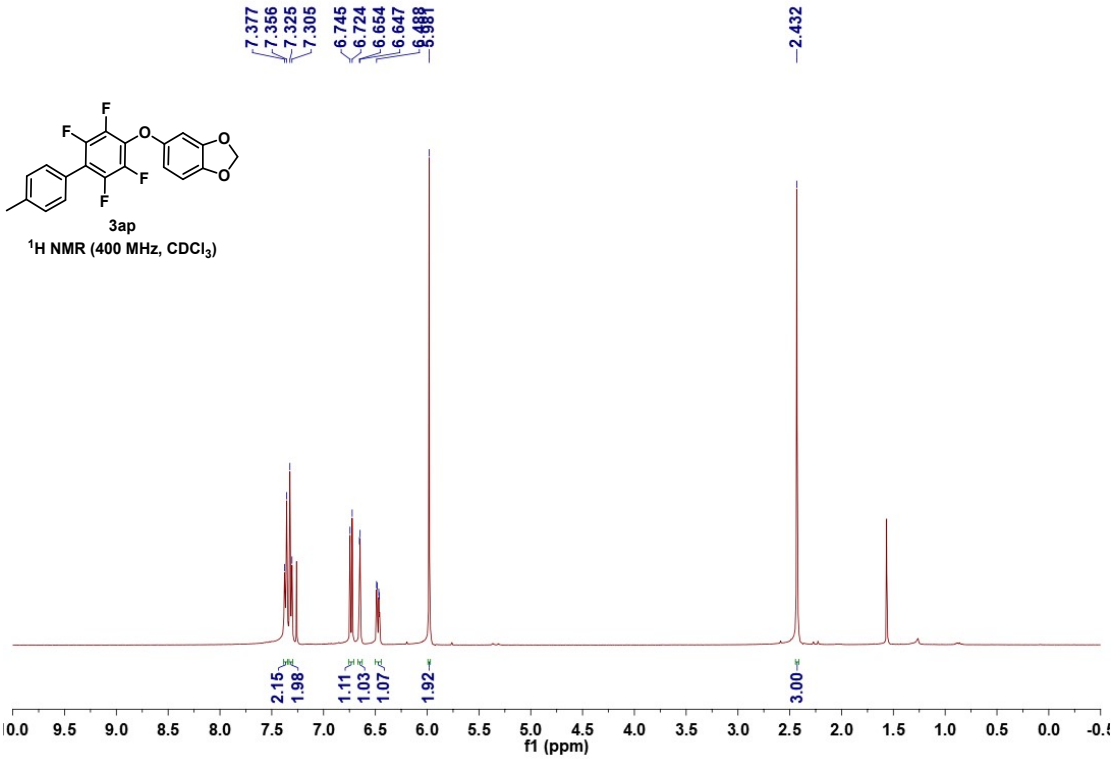
^{1}H NMR (400 MHz, $CDCl_3$)

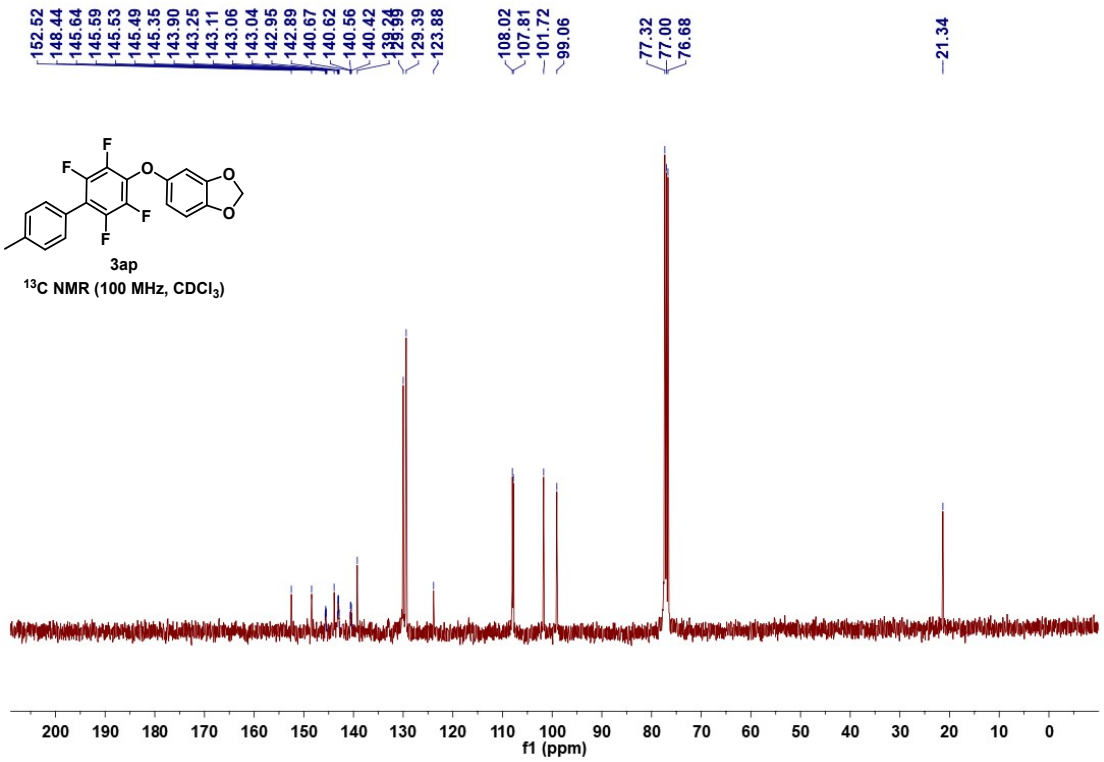


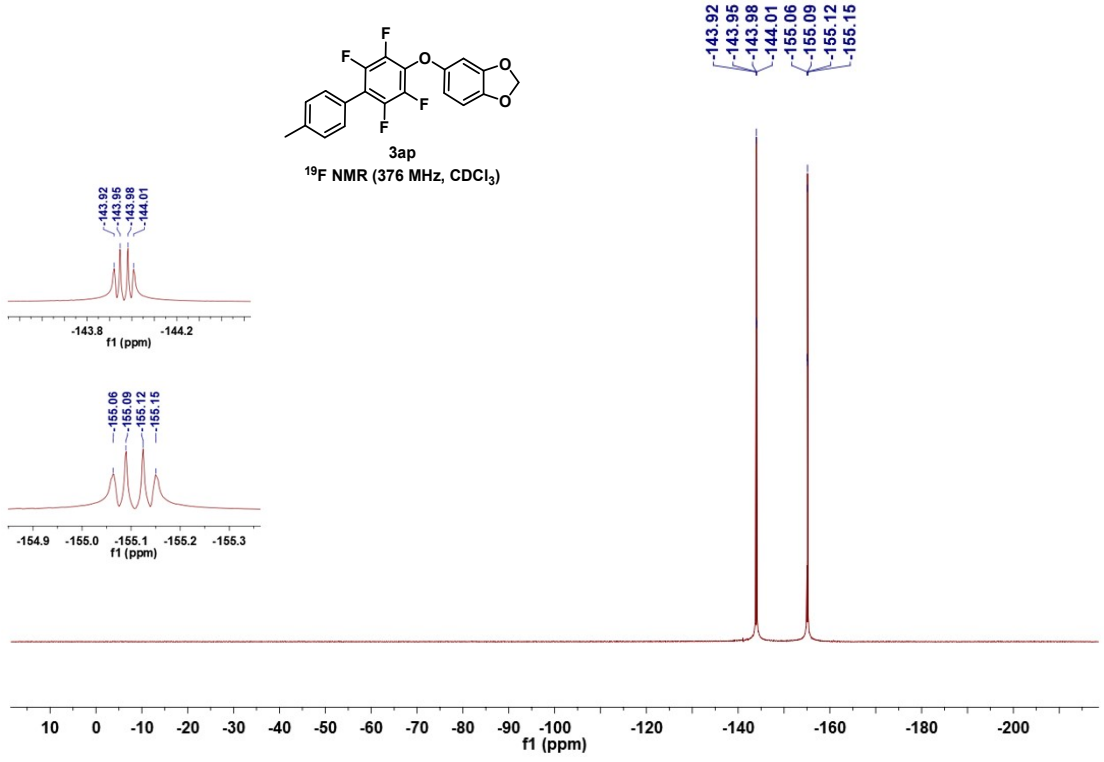
3ao

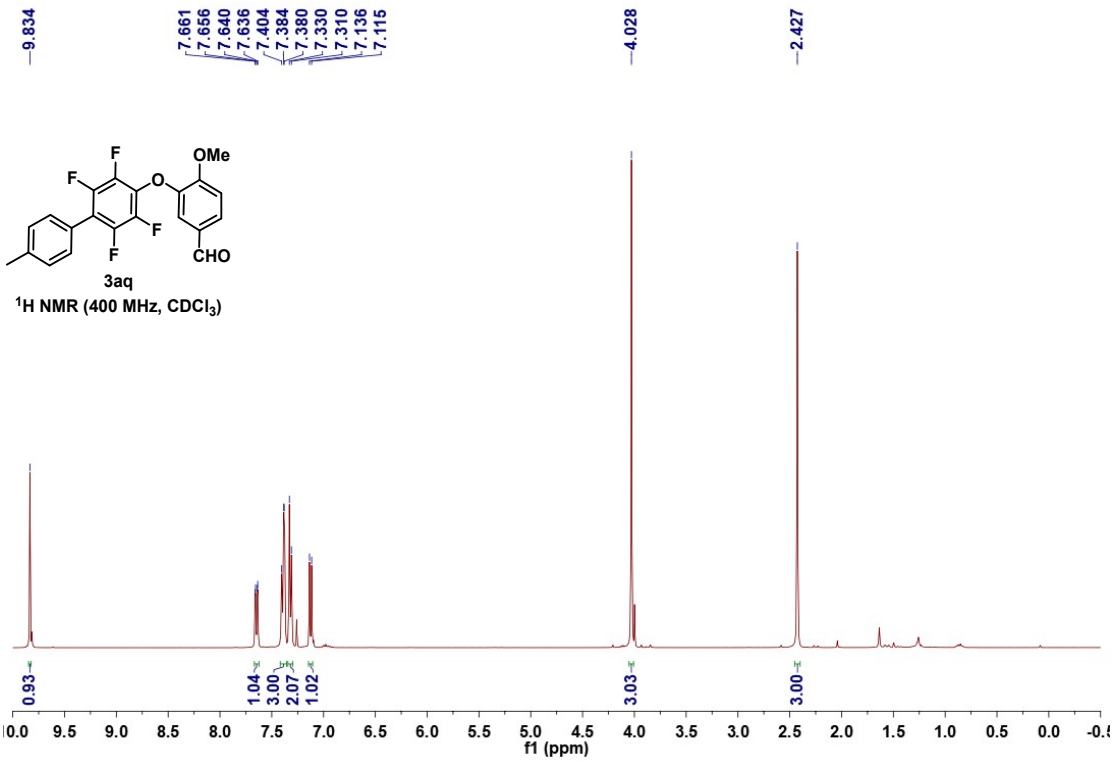
^{13}C NMR (100 MHz, $CDCl_3$)

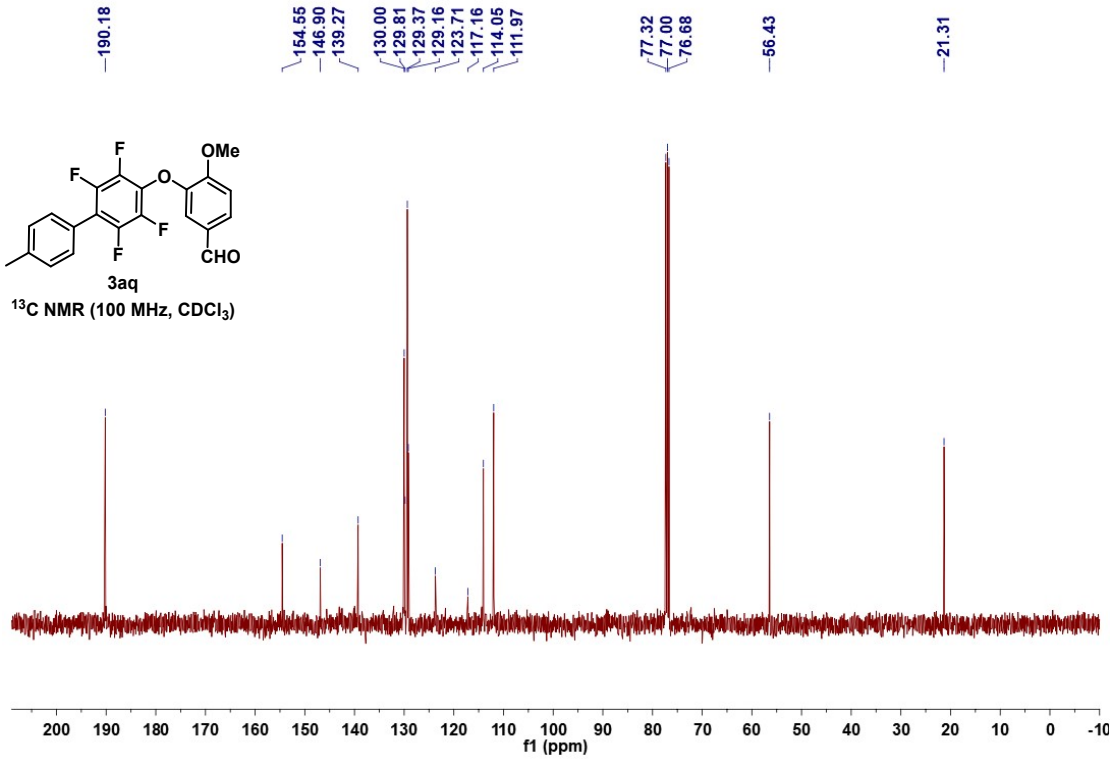

-139.532
-139.546
-139.575
-139.601
-139.630
-139.643
-142.611
-142.625
-142.654
-142.680
-142.709
-142.722
F
O
F
O
F
F
3ao
19F NMR (376 MHz, CDCl3)
f1 (ppm)

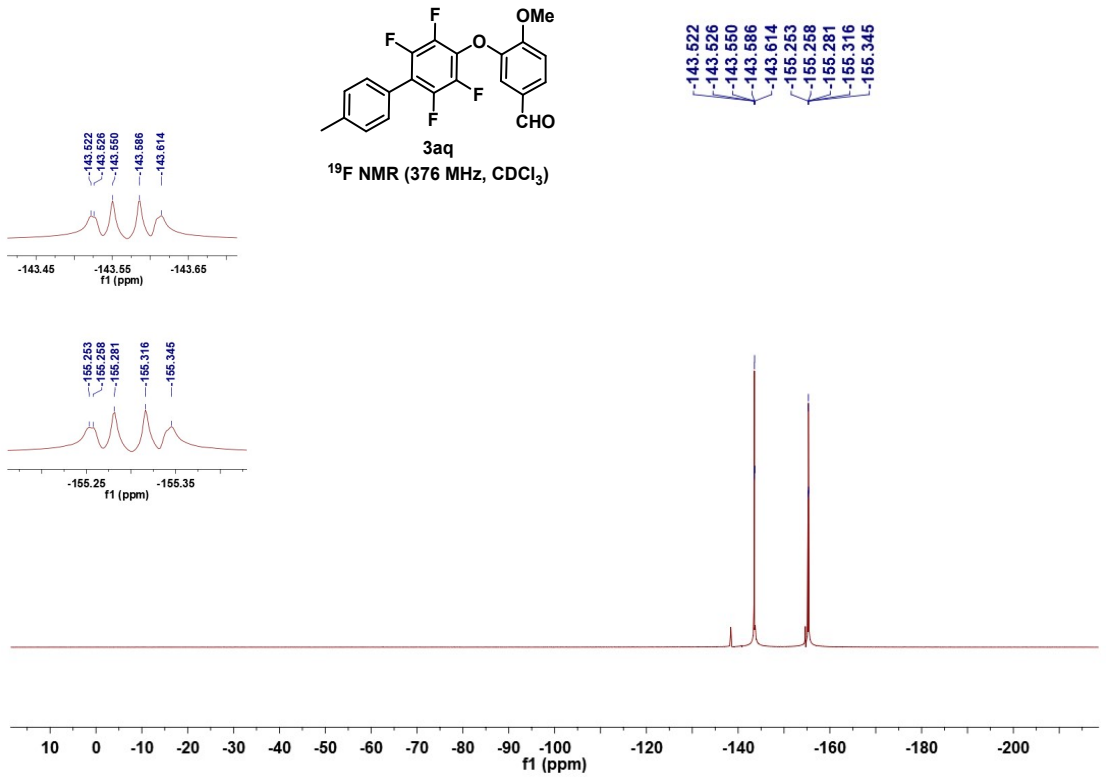

7.377
7.356
7.325
7.305
6.745
6.724
6.654
6.647
2.432
F
F
O
O
O
F
F
3ap
1H NMR (400 MHz, CDCl3)
2.15
1.98
1.11
1.03
1.07
1.92
3.00
f1 (ppm)

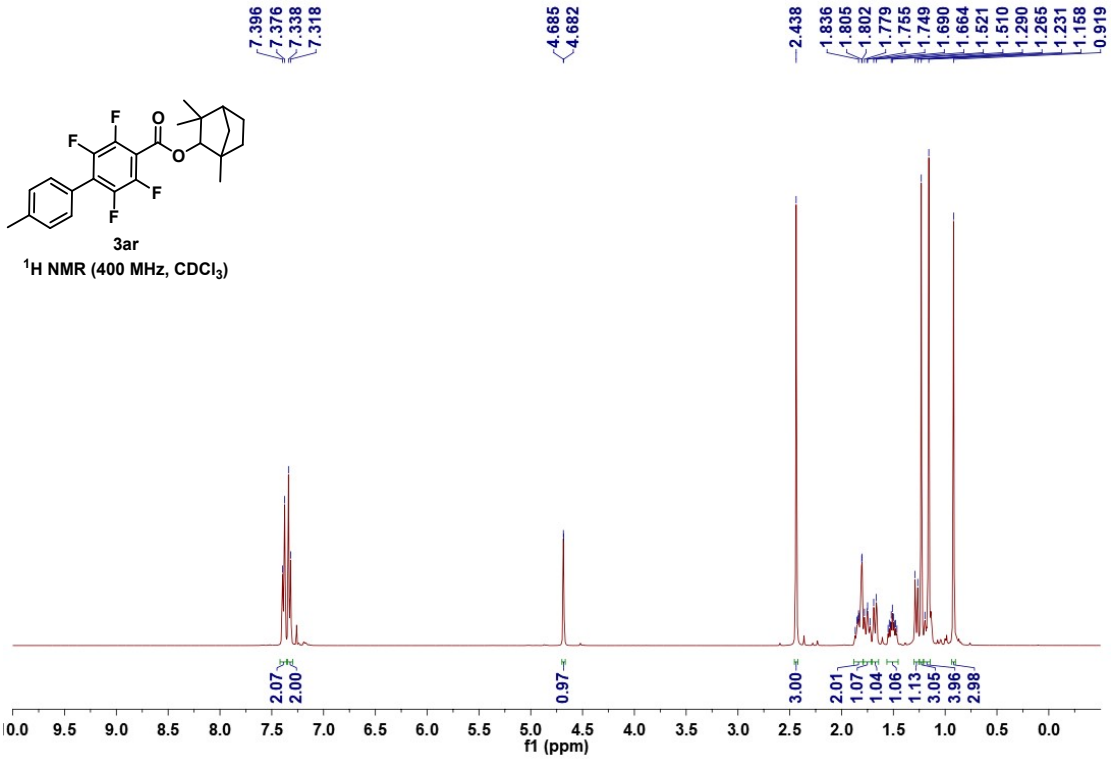

152.52
148.44
145.64
145.59
145.53
145.49
145.35
143.90
143.25
143.11
143.06
143.04
142.95
142.89
140.67
140.62
140.56
140.42
129.39
123.88
108.02
107.81
101.72
99.06
77.32
77.00
76.68
21.34
3ap
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

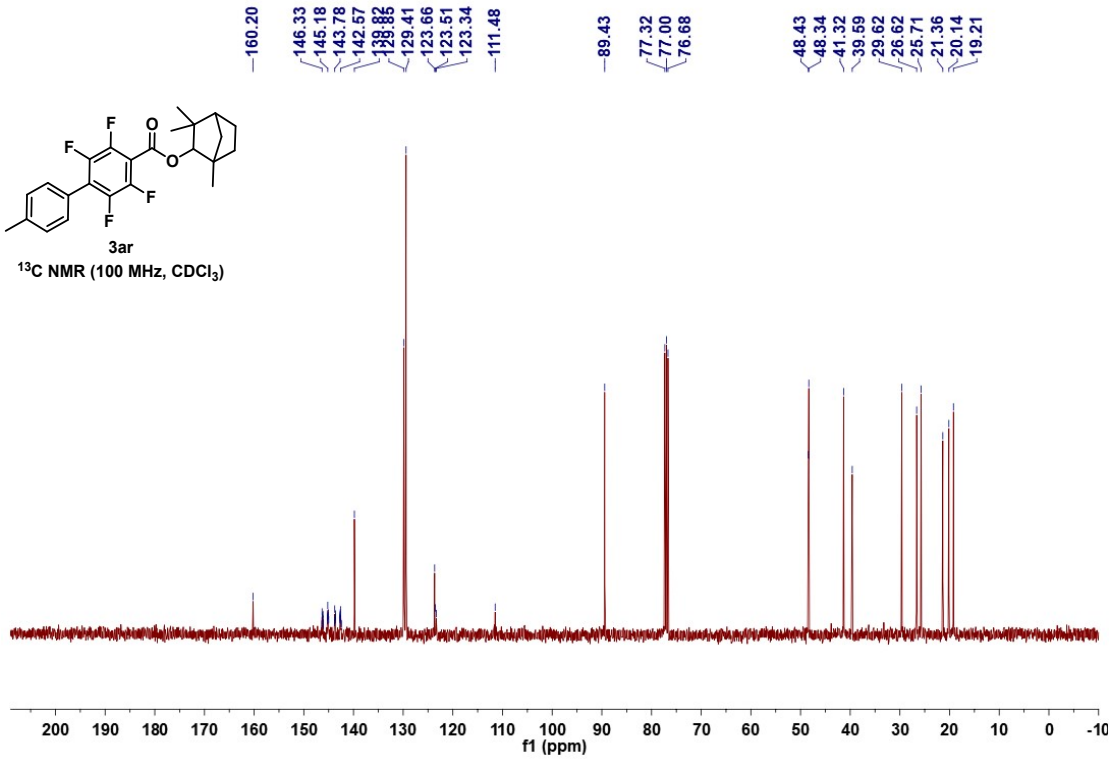

-143.92
-143.95
-143.98
-144.01
-155.06
-155.09
-155.12
-155.15
3ap
19F NMR (376 MHz, CDCl3)
-143.8
-144.2
f1 (ppm)
-154.9
-155.0
-155.1
-155.2
-155.3
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

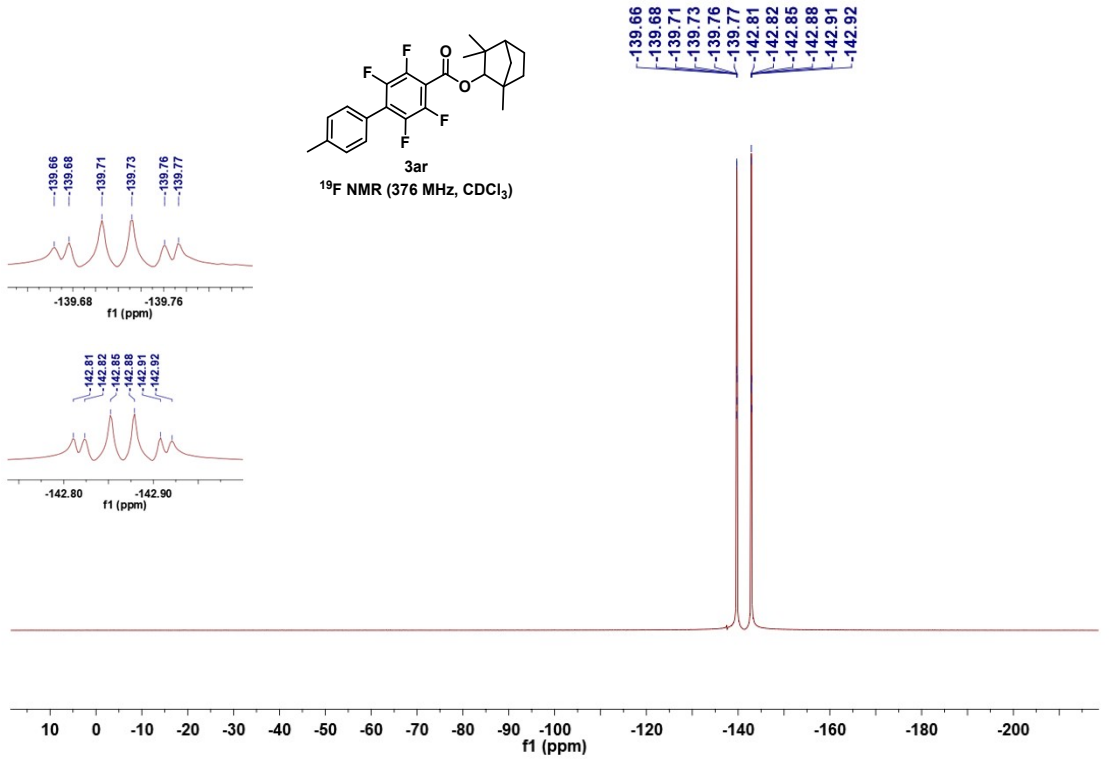

9.834
7.661
7.656
7.640
7.636
7.404
7.384
7.380
7.330
7.310
7.136
7.115
4.028
2.427
F
F
O
OMe
F
F
CHO
3aq
1H NMR (400 MHz, CDCl3)
0.93
1.04
3.00
2.07
1.02
3.03
3.00
f1 (ppm)

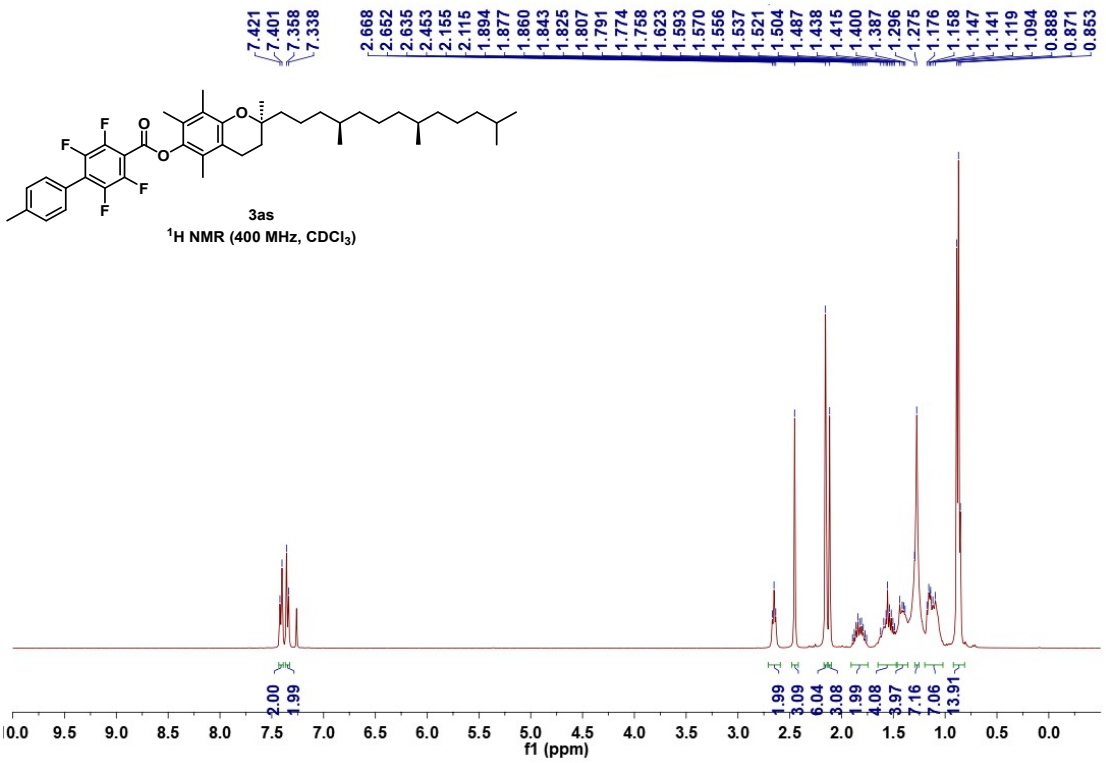

190.18
154.55
146.90
139.27
130.00
129.81
129.37
129.16
123.71
117.16
114.05
111.97
77.32
77.00
76.68
56.43
21.31
F
F
O
OMe
F
F
CHO
3aq
13C NMR (100 MHz, CDCl3)
f1 (ppm)

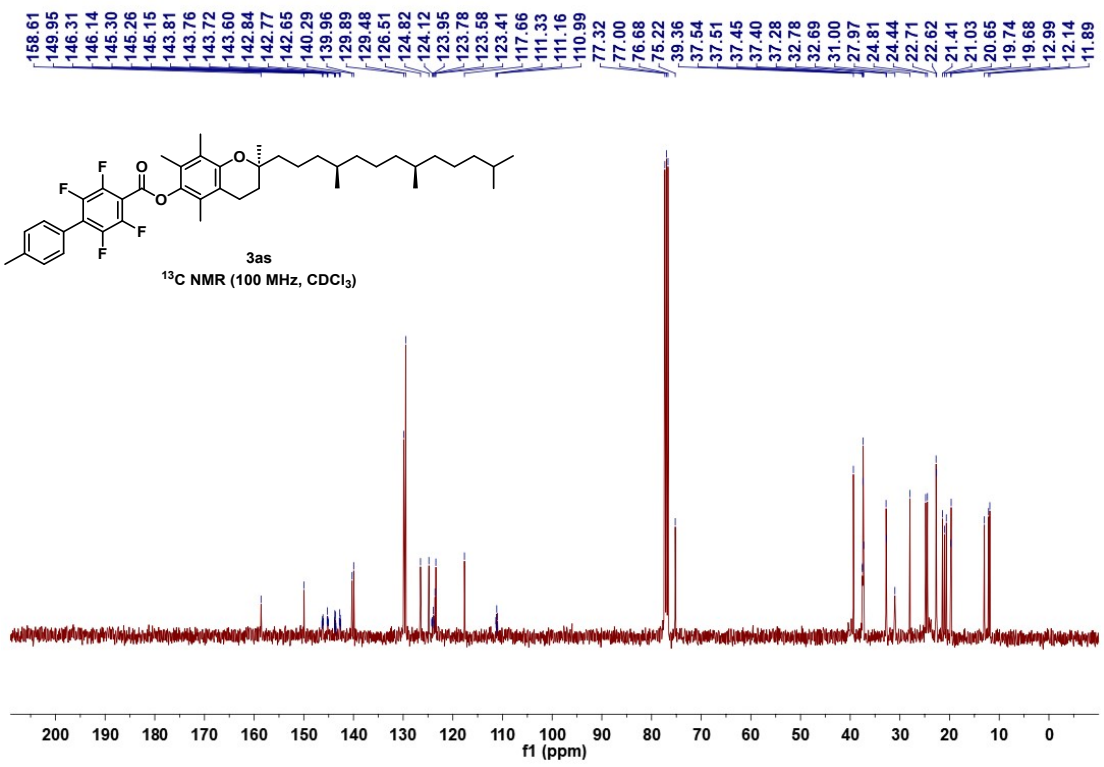

F
OMe
F
O
F
F
CHO
3aq
^{19}F NMR (376 MHz, $CDCl_3$)
-143.522
-143.526
-143.550
-143.586
-143.614
-155.253
-155.258
-155.281
-155.316
-155.345
-143.45
-143.55
-143.65
f1 (ppm)
-155.25
-155.35
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

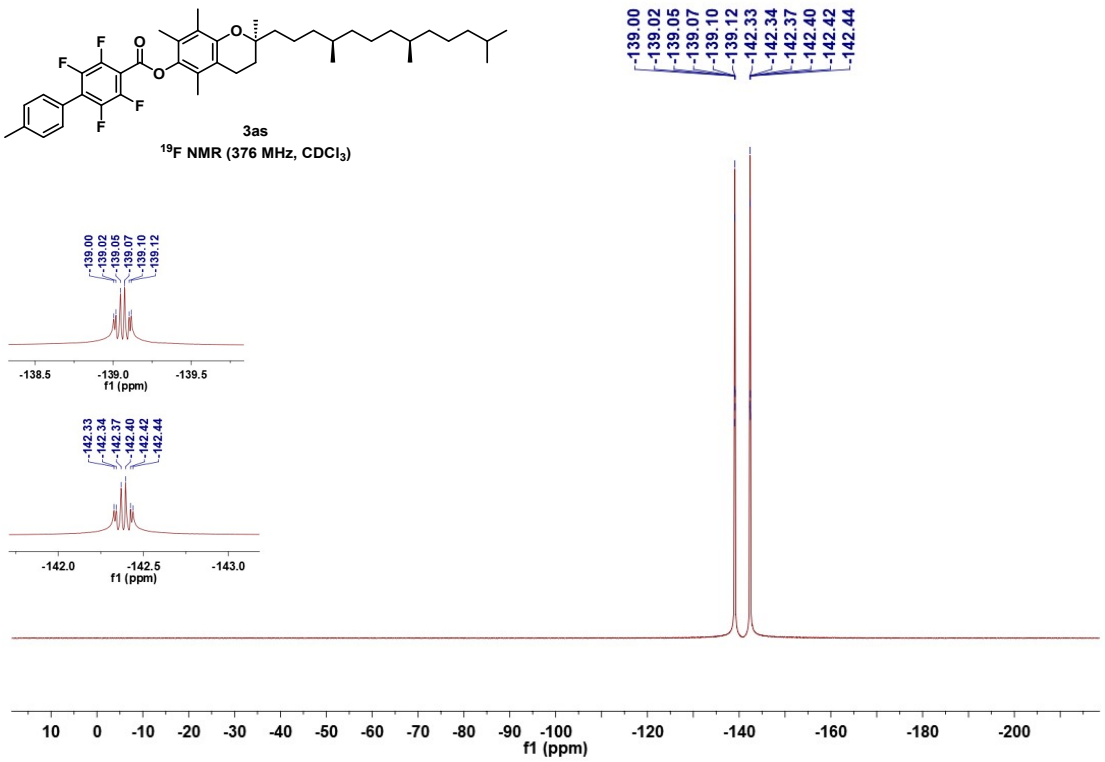

7.396
7.376
7.338
7.318
4.685
4.682
2.438
1.836
1.805
1.802
1.779
1.755
1.749
1.690
1.664
1.521
1.510
1.290
1.265
1.231
1.158
0.919
F
O
F
O
F
F
3ar
^{1}H NMR (400 MHz, $CDCl_3$)
2.07
2.00
0.97
3.00
2.01
1.07
1.04
1.06
1.13
3.05
3.96
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

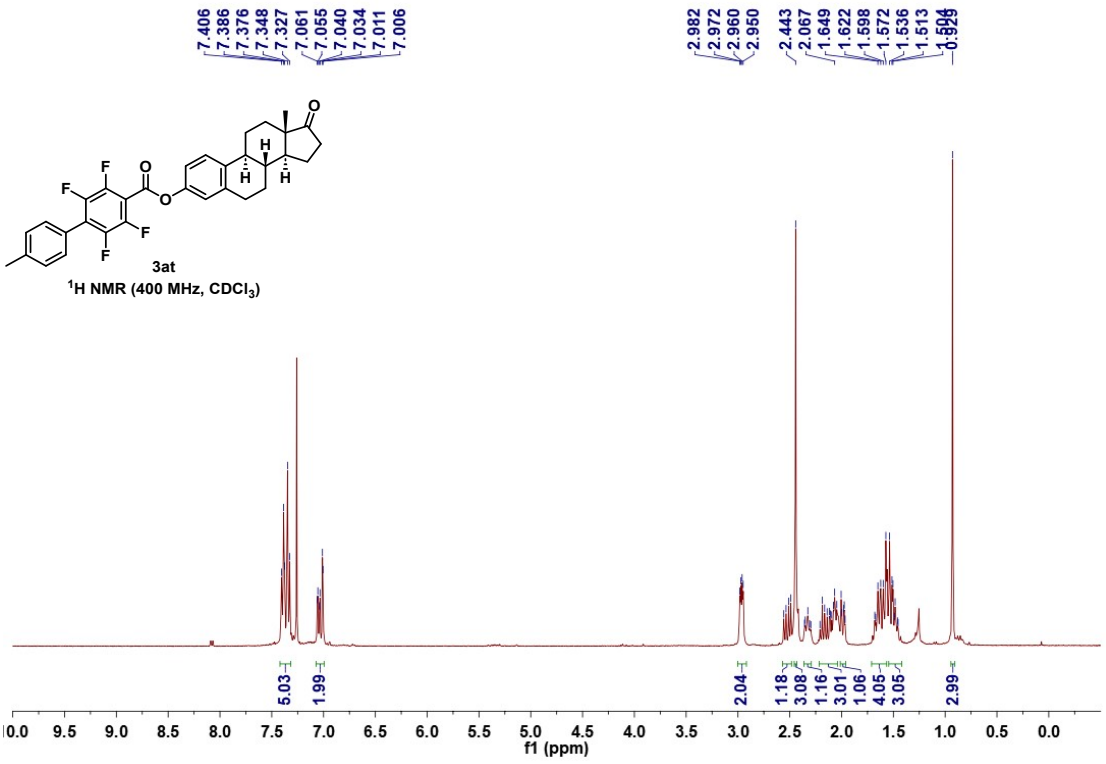

160.20
146.33
145.18
143.78
142.57
129.41
123.66
123.51
123.34
111.48
89.43
77.32
77.00
76.68
48.43
48.34
41.32
39.59
29.62
26.62
25.71
21.36
20.14
19.21
F
O
F
O
F
F
3ar
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

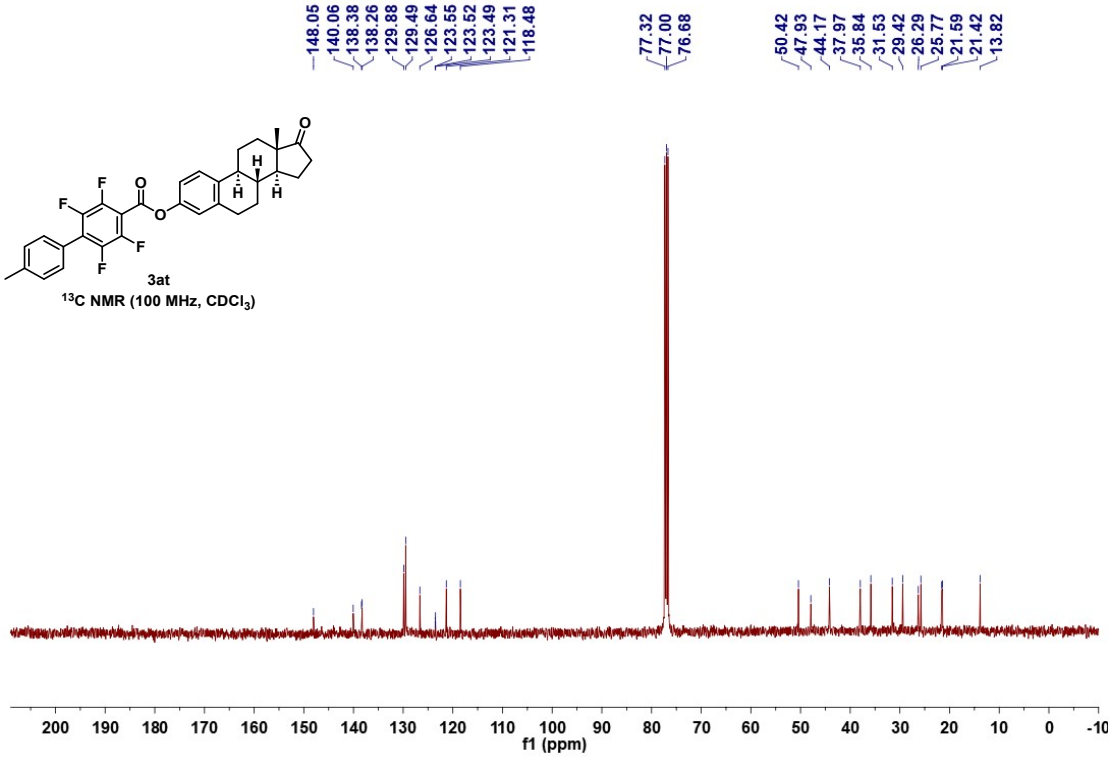

139.66
139.68
139.71
139.73
139.76
139.77
142.81
142.82
142.85
142.88
142.91
142.92
F
O
F
O
F
F
3ar
19F NMR (376 MHz, CDCl3)
-139.68
-139.76
f1 (ppm)
-142.80
-142.90
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

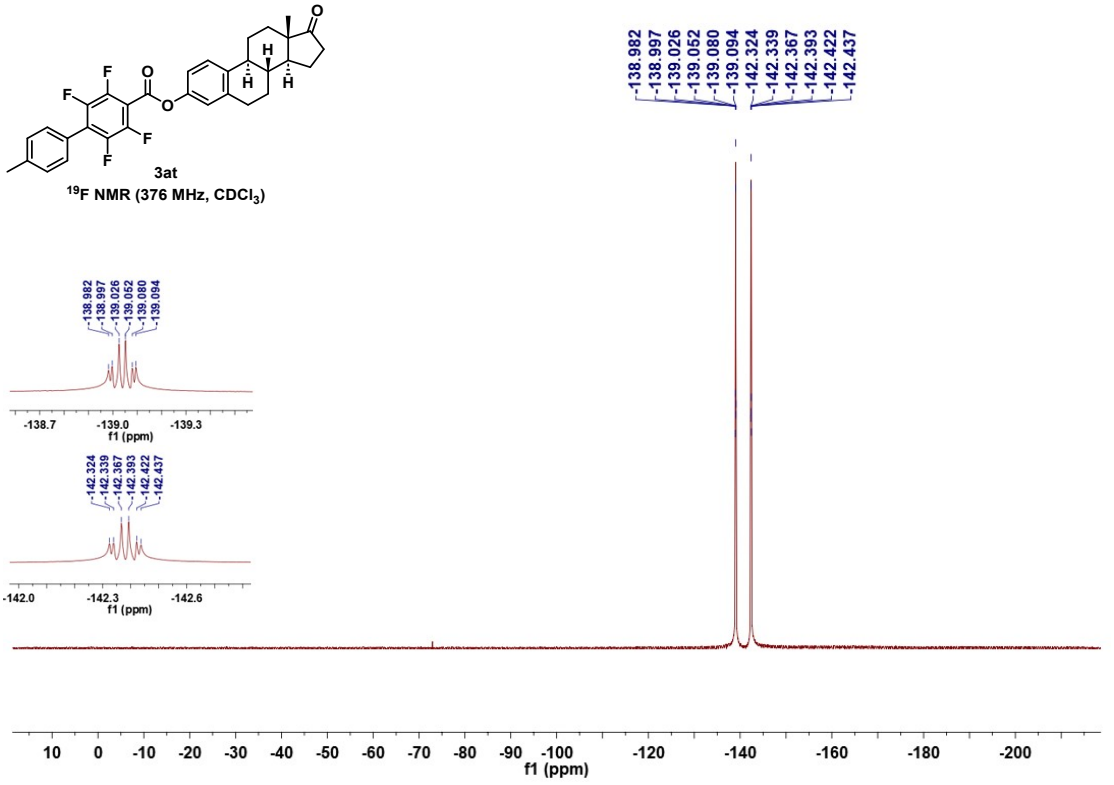

7.421
7.401
7.358
7.338
2.668
2.652
2.635
2.453
2.155
2.115
1.894
1.877
1.860
1.843
1.825
1.807
1.791
1.774
1.758
1.623
1.593
1.570
1.556
1.537
1.521
1.504
1.487
1.438
1.415
1.400
1.387
1.296
1.275
1.176
1.158
1.147
1.141
1.119
1.094
0.888
0.871
0.853
3as
1H NMR (400 MHz, CDCl3)
2.00
1.99
1.99
3.09
6.04
3.08
1.99
4.08
3.97
7.16
7.06
13.91
f1 (ppm)

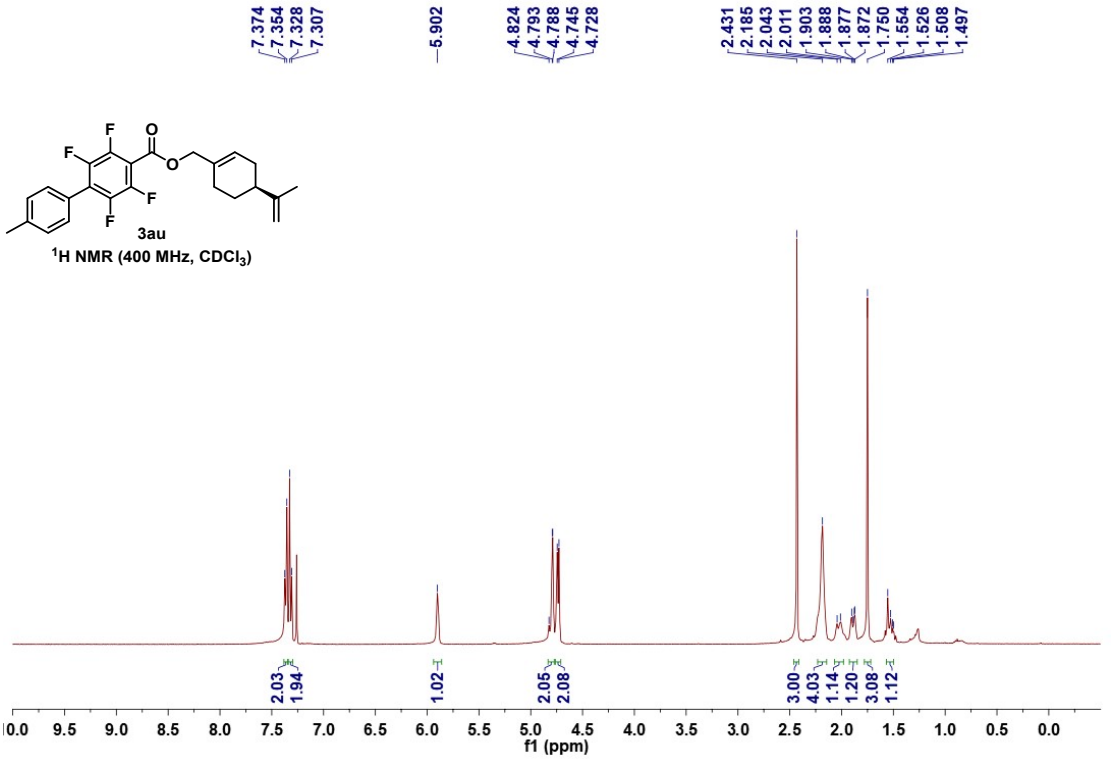

158.61
149.95
146.31
146.14
145.30
145.26
145.15
143.81
143.76
143.72
143.60
142.84
142.77
142.65
140.29
139.96
129.89
129.48
126.51
124.82
124.12
123.95
123.78
123.58
123.41
117.66
111.33
111.16
110.99
77.32
77.00
76.68
75.22
39.36
37.54
37.51
37.45
37.40
37.28
32.78
32.69
31.00
27.97
24.81
24.44
22.71
22.62
21.41
21.03
20.65
19.74
19.68
12.99
12.14
11.89
3as
13C NMR (100 MHz, CDCl3)
f1 (ppm)

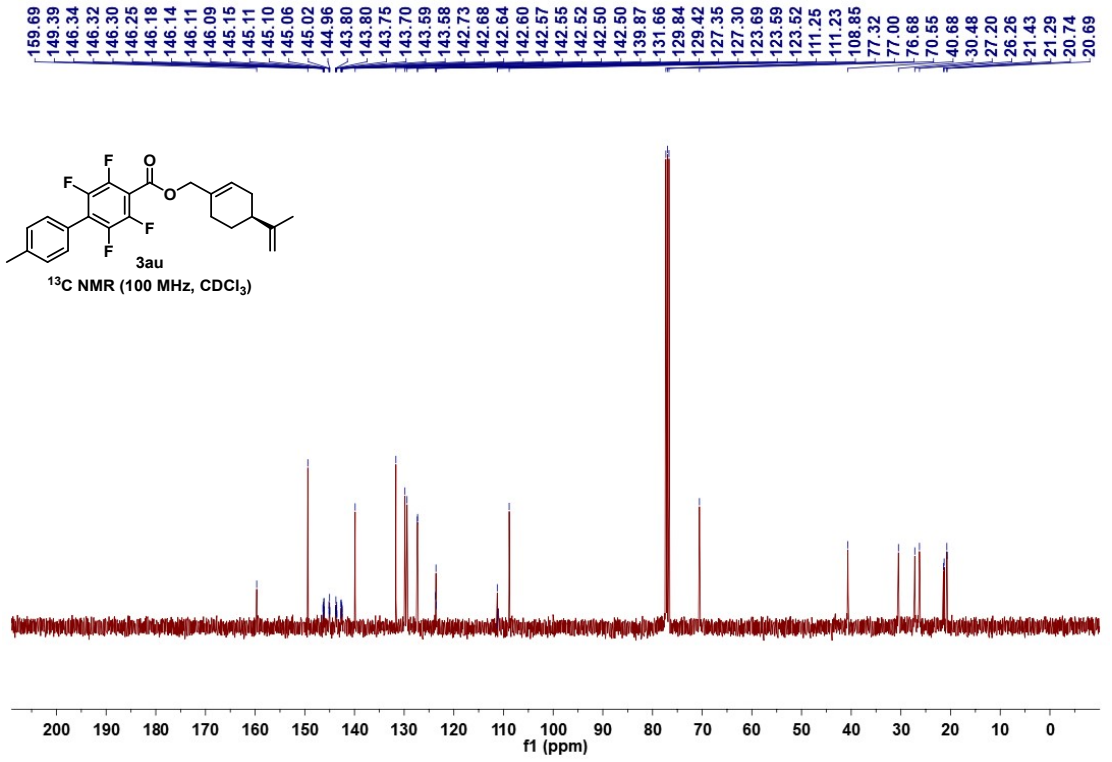

3as
^{19}F NMR (376 MHz, $CDCl_3$)
-139.00
-139.02
-139.05
-139.07
-139.10
-139.12
-142.33
-142.34
-142.37
-142.40
-142.42
-142.44
f1 (ppm)

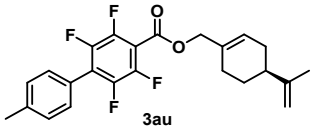

3at
^{1}H NMR (400 MHz, $CDCl_3$)
7.406
7.386
7.376
7.348
7.327
7.061
7.055
7.040
7.034
7.011
7.006
2.982
2.972
2.960
2.950
2.443
2.067
1.649
1.622
1.598
1.572
1.536
1.513
0.925
5.03
1.99
2.04
1.18
3.08
1.16
3.01
1.06
4.05
3.05
2.99
f1 (ppm)


148.05
140.06
138.38
138.26
129.88
129.49
126.64
123.55
123.52
123.49
121.31
118.48
77.32
77.00
76.68
50.42
47.93
44.17
37.97
35.84
31.53
29.42
26.29
25.77
21.59
21.42
13.82
3at
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-138.982
-138.997
-139.026
-139.052
-139.080
-139.094
-142.324
-142.339
-142.367
-142.393
-142.422
-142.437
3at
19F NMR (376 MHz, CDCl3)
f1 (ppm)

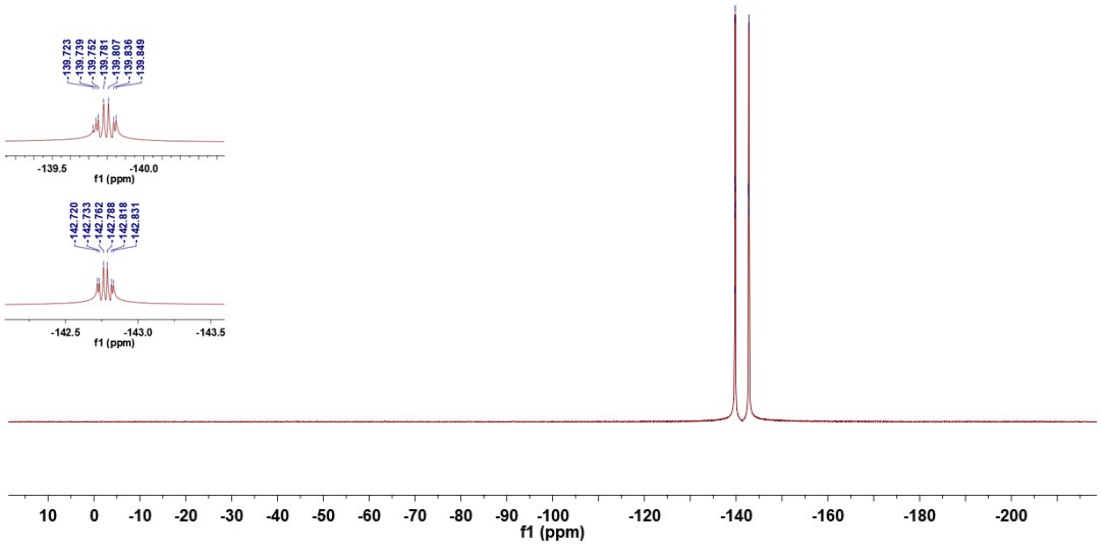

7.374
7.354
7.328
7.307
5.902
4.824
4.793
4.788
4.745
4.728
2.431
2.185
2.043
2.011
1.903
1.888
1.877
1.872
1.750
1.554
1.526
1.508
1.497
F
O
F
O
F
F
3au
^{1}H NMR (400 MHz, CDCl$_3$)
2.03
1.94
1.02
2.05
2.08
3.00
4.03
1.14
1.20
3.08
1.12
f1 (ppm)

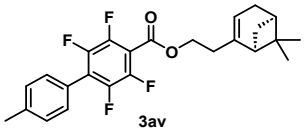

159.69
149.39
146.34
146.32
146.30
146.25
146.18
146.14
146.11
146.09
145.15
145.11
145.10
145.06
145.02
144.96
143.80
143.80
143.75
143.70
143.59
143.58
142.73
142.68
142.64
142.60
142.57
142.55
142.52
142.50
142.50
139.87
131.66
129.84
129.42
127.35
127.30
123.69
123.59
123.52
111.25
111.23
108.85
77.32
77.00
76.68
70.55
40.68
30.48
27.20
26.26
21.43
21.29
20.74
20.69
F
O
F
O
F
F
3au
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



3au

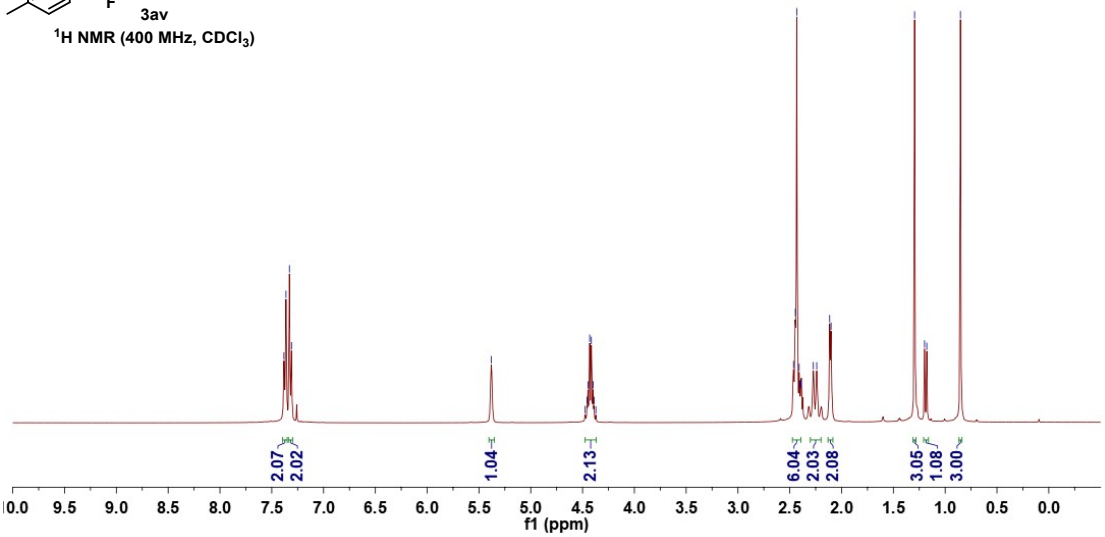
^{19}F NMR (376 MHz, $CDCl_3$)

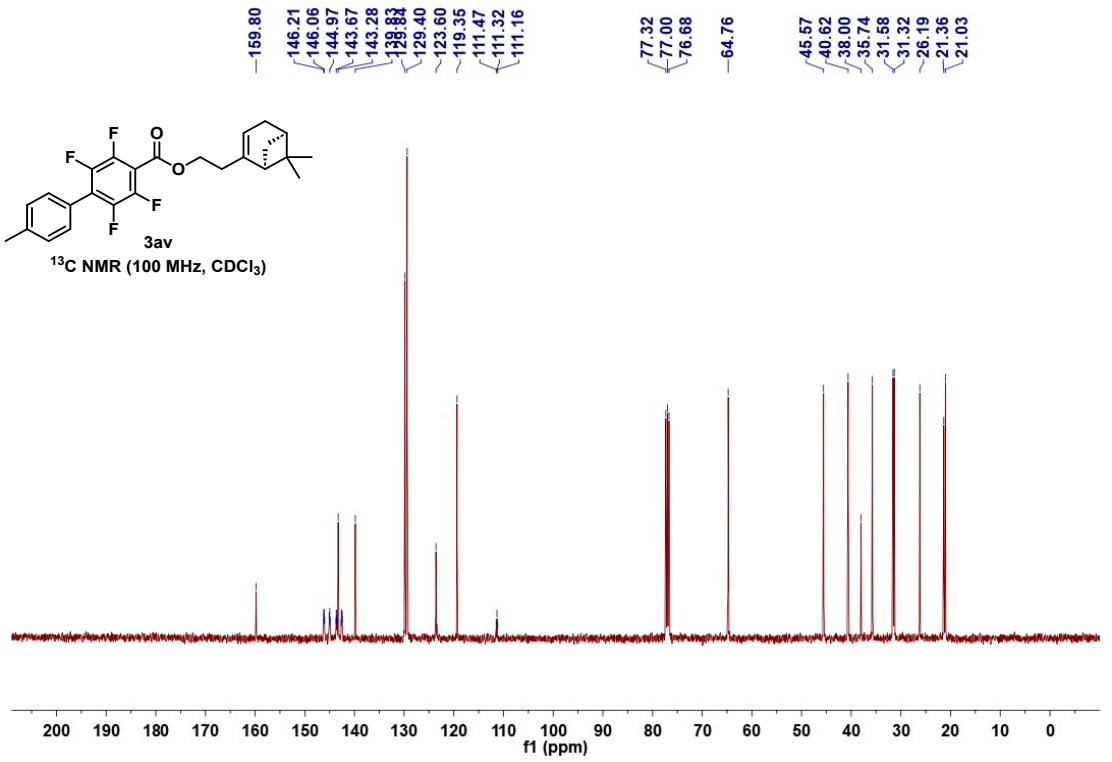


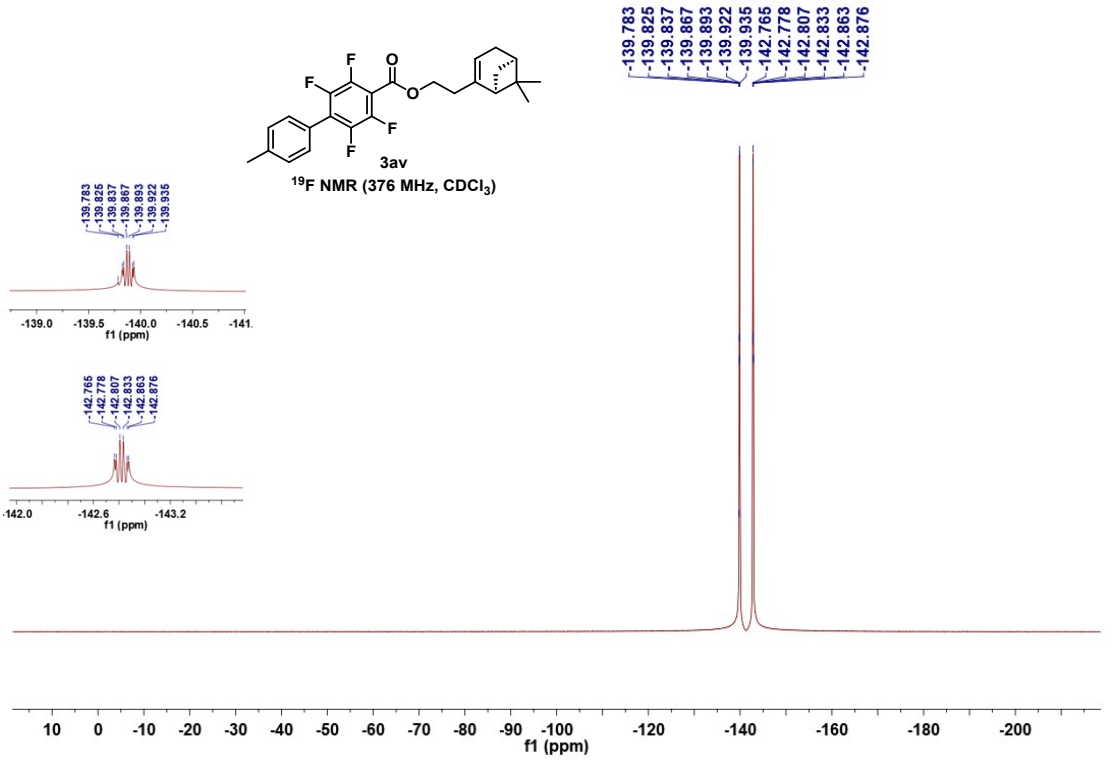


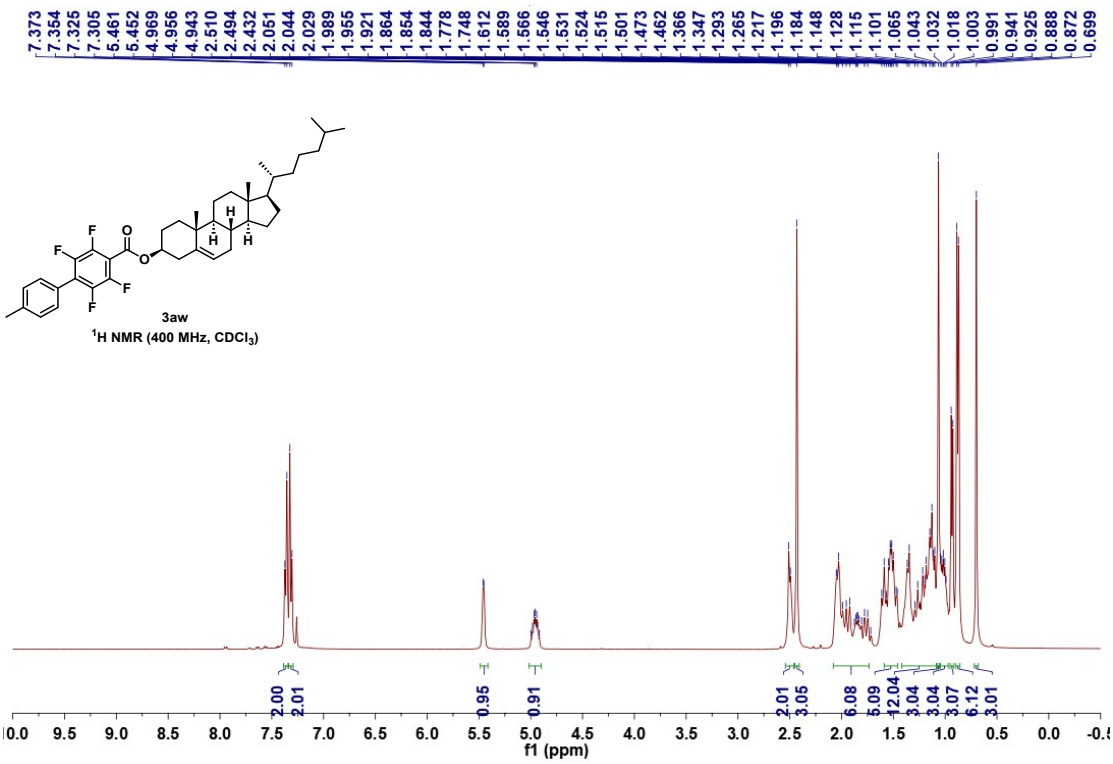
3av

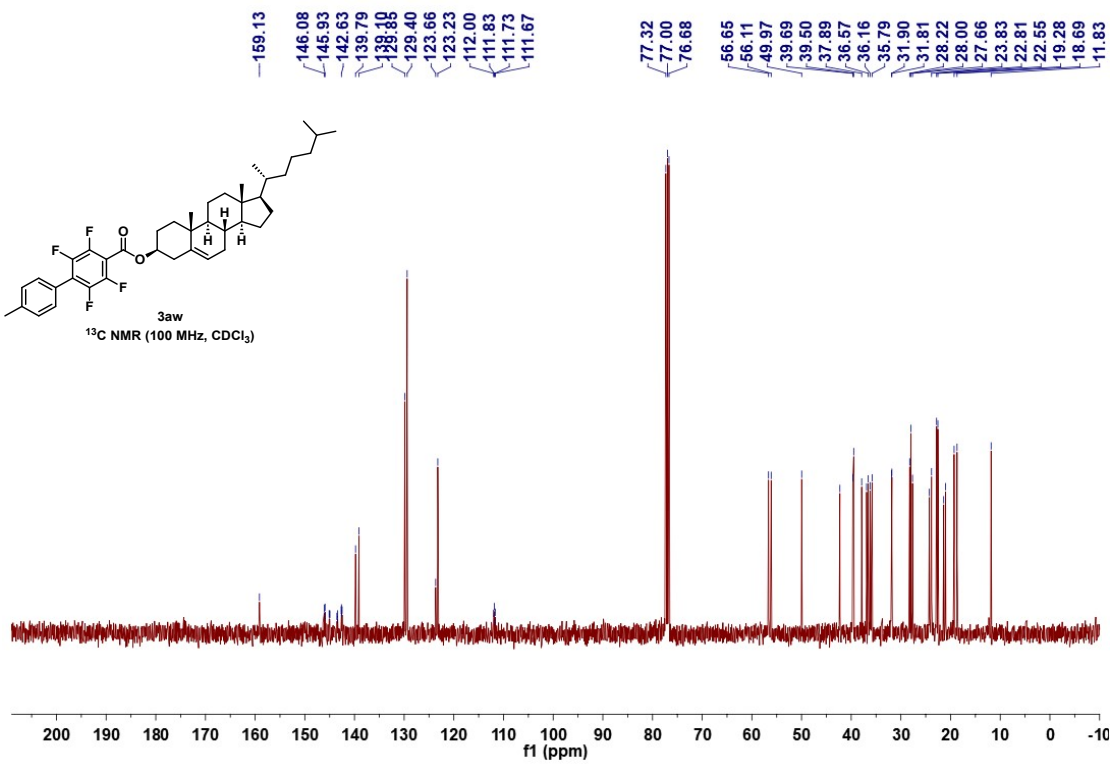
^{1}H NMR (400 MHz, $CDCl_3$)

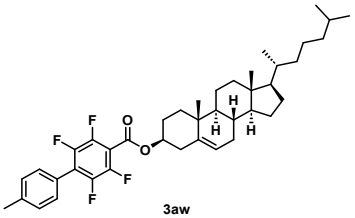



159.80
146.21
146.06
144.97
143.67
143.28
129.40
123.60
119.35
111.47
111.32
111.16
77.32
77.00
76.68
64.76
45.57
40.62
38.00
35.74
31.58
31.32
26.19
21.36
21.03
F
O
F
O
F
F
F
3av
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


139.783
139.825
139.837
139.867
139.893
139.922
139.935
142.765
142.778
142.807
142.833
142.863
142.876
F
O
F
O
F
F
F
3av
19F NMR (376 MHz, CDCl3)
-139.0 -139.5 -140.0 -140.5 -141.
f1 (ppm)
-142.0 -142.6 -143.2
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

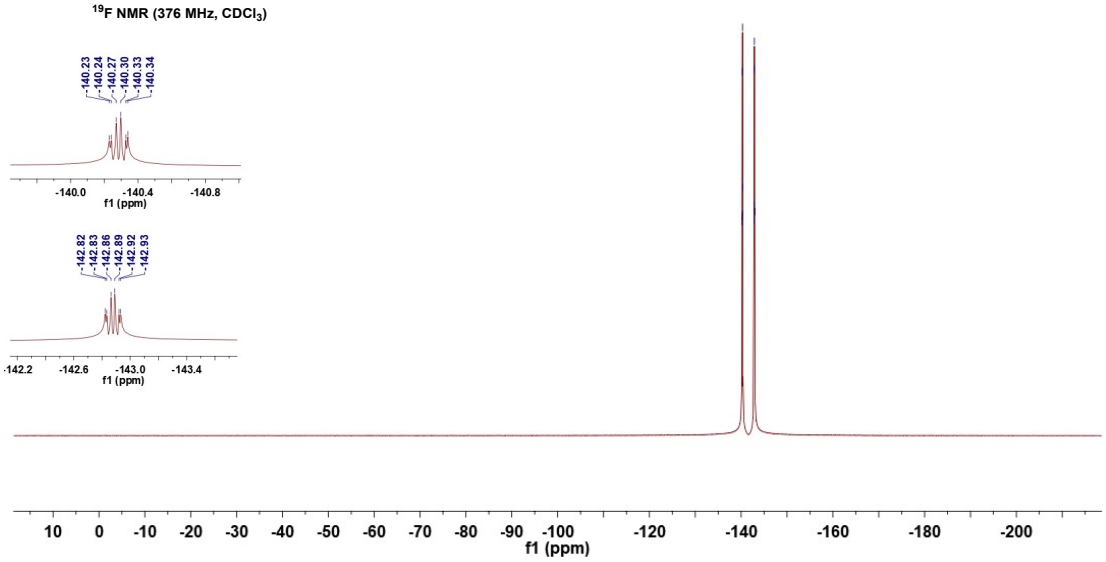

7.373
7.354
7.325
7.305
5.461
5.452
4.969
4.956
4.943
2.510
2.494
2.432
2.051
2.044
2.029
1.989
1.955
1.921
1.864
1.854
1.844
1.778
1.748
1.612
1.589
1.566
1.546
1.531
1.524
1.515
1.501
1.473
1.462
1.366
1.347
1.293
1.265
1.217
1.196
1.184
1.148
1.128
1.115
1.101
1.065
1.043
1.032
1.018
1.003
0.991
0.941
0.925
0.888
0.872
0.699
3aw
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.01
0.95
0.91
2.01
3.05
6.08
5.09
12.04
3.04
3.04
3.07
6.12
3.01
f1 (ppm)

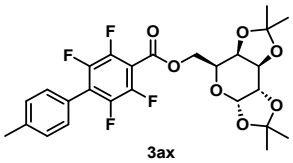

169.13
146.08
145.93
142.63
139.79
129.40
123.66
123.23
112.00
111.83
111.73
111.67
77.32
77.00
76.68
56.65
56.11
49.97
39.69
39.50
37.89
36.57
36.16
35.79
31.90
31.81
28.22
28.00
27.66
23.83
22.81
22.55
19.28
18.69
11.83
3aw
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



3aw

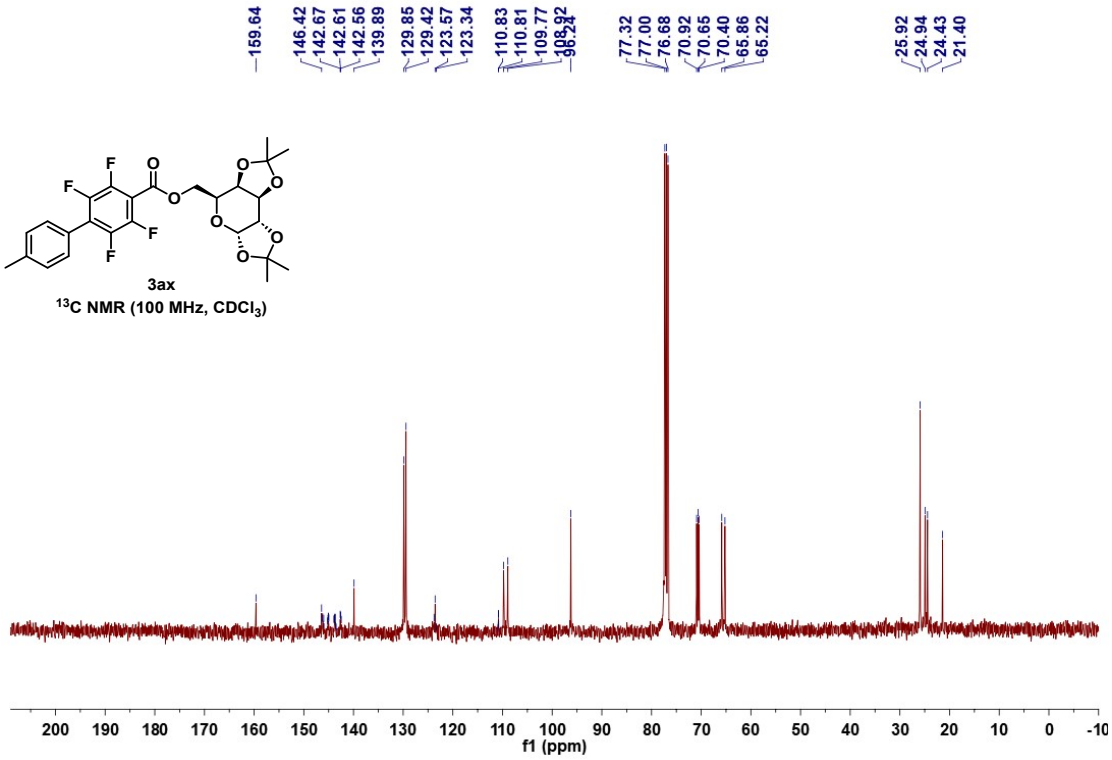
^{19}F NMR (376 MHz, $CDCl_3$)

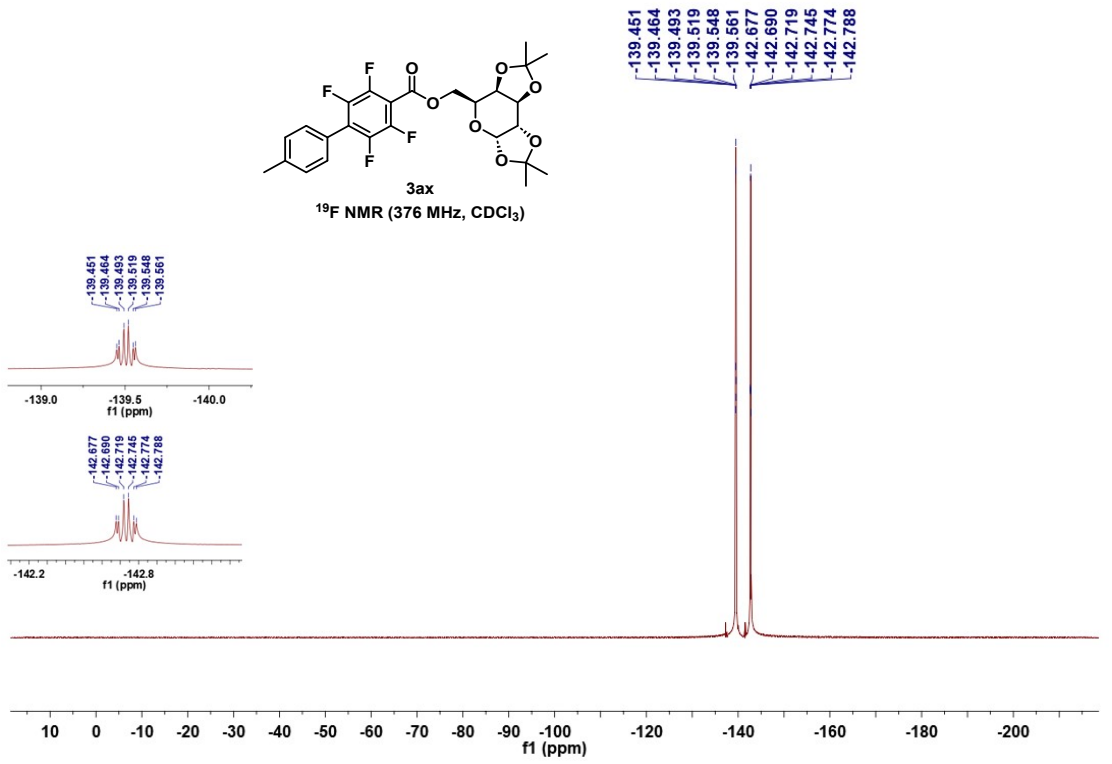


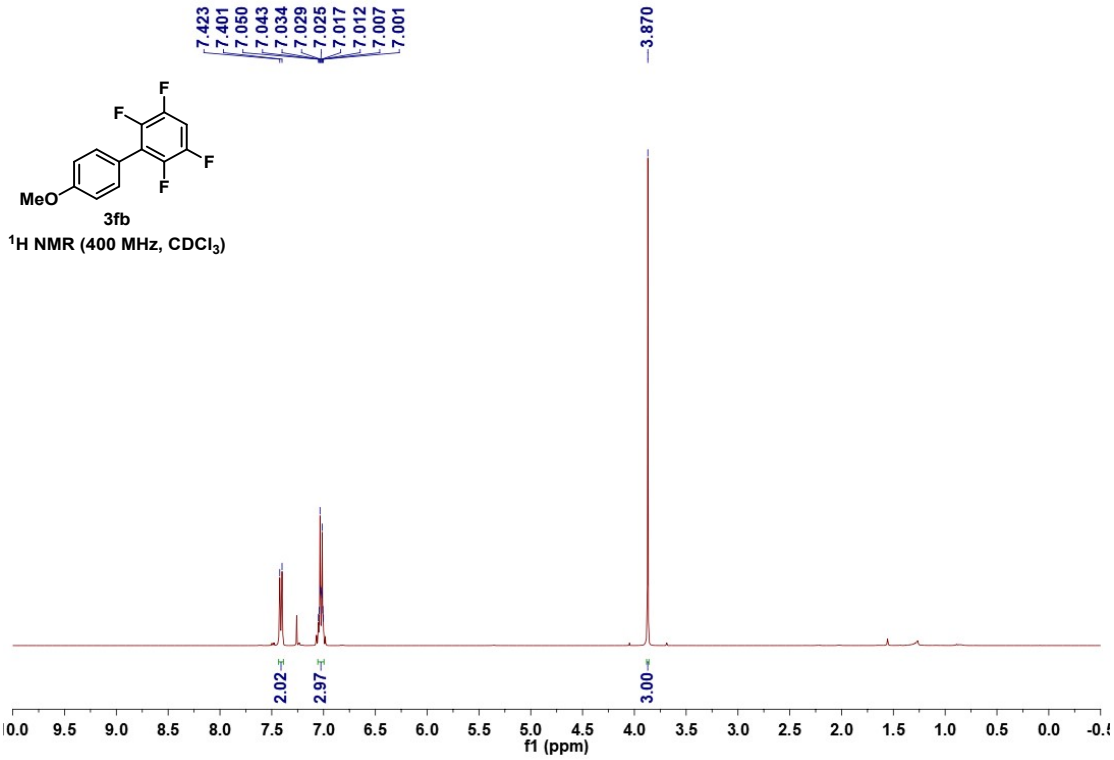


3ax

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

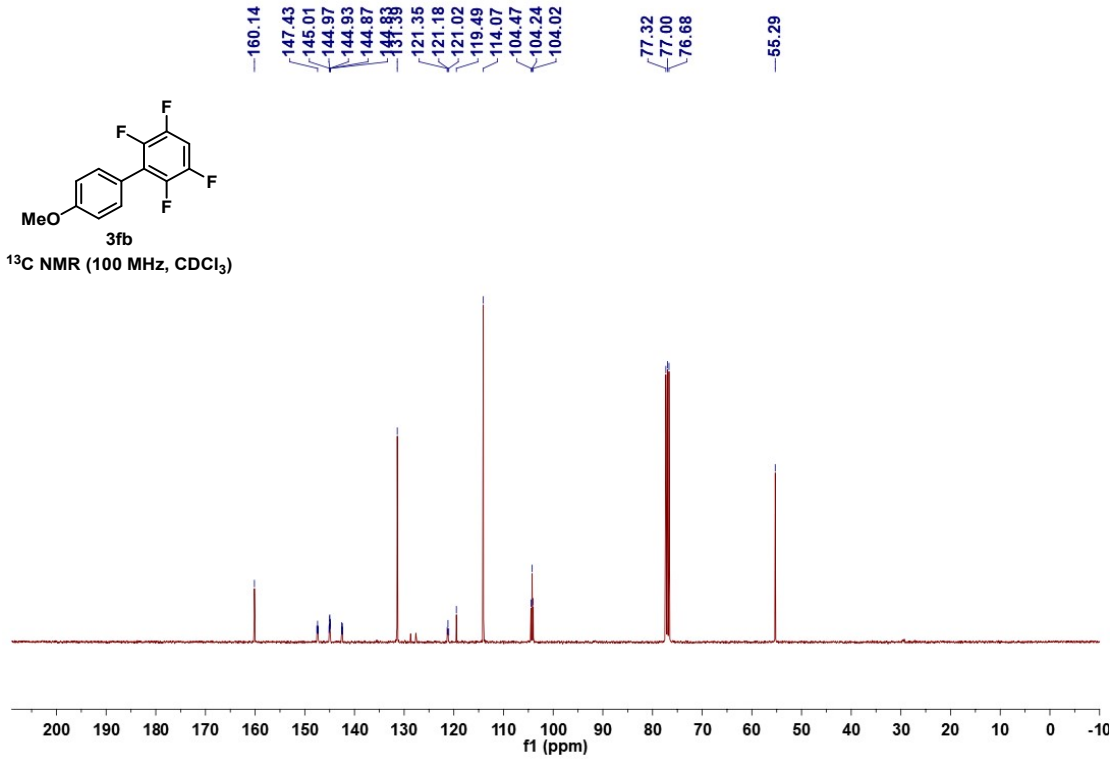

159.64
146.42
142.67
142.61
142.56
139.89
129.85
129.42
123.57
123.34
110.83
110.81
109.77
108.92
96.24
77.32
77.00
76.68
70.92
70.65
70.40
65.86
65.22
25.92
24.94
24.43
21.40
3ax
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-139.451
-139.464
-139.493
-139.519
-139.548
-139.561
-142.677
-142.690
-142.719
-142.745
-142.774
-142.788
3ax
19F NMR (376 MHz, CDCl3)
f1 (ppm)



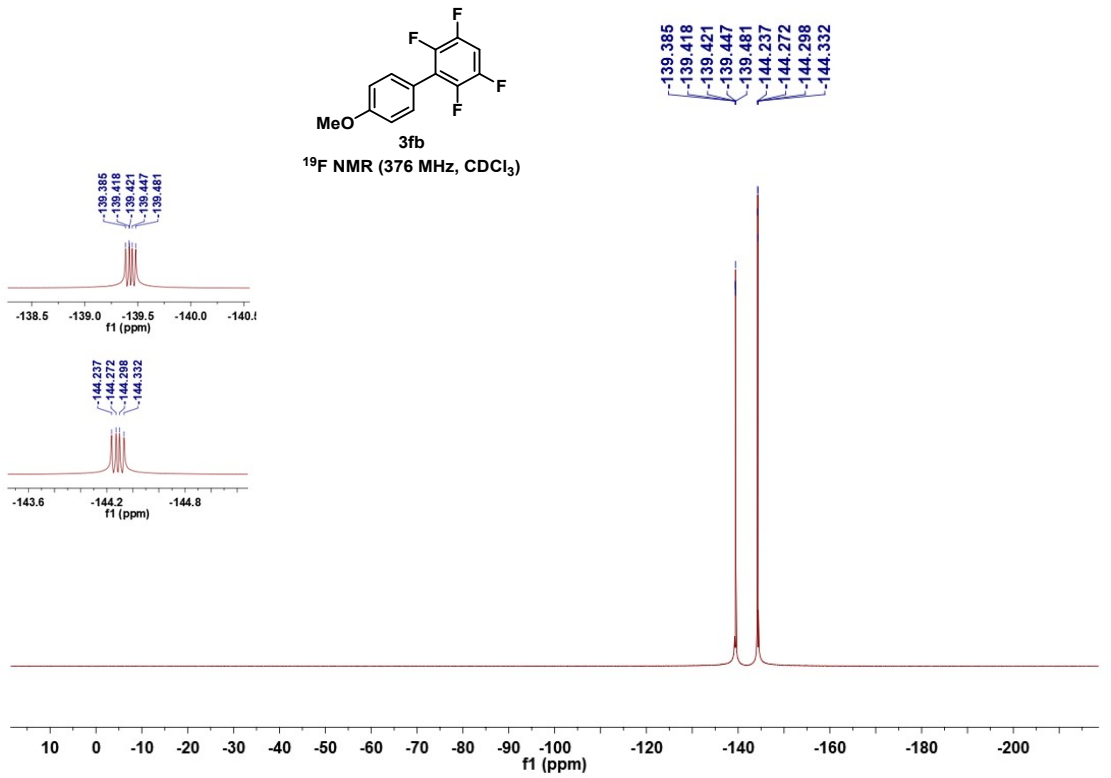
3fb

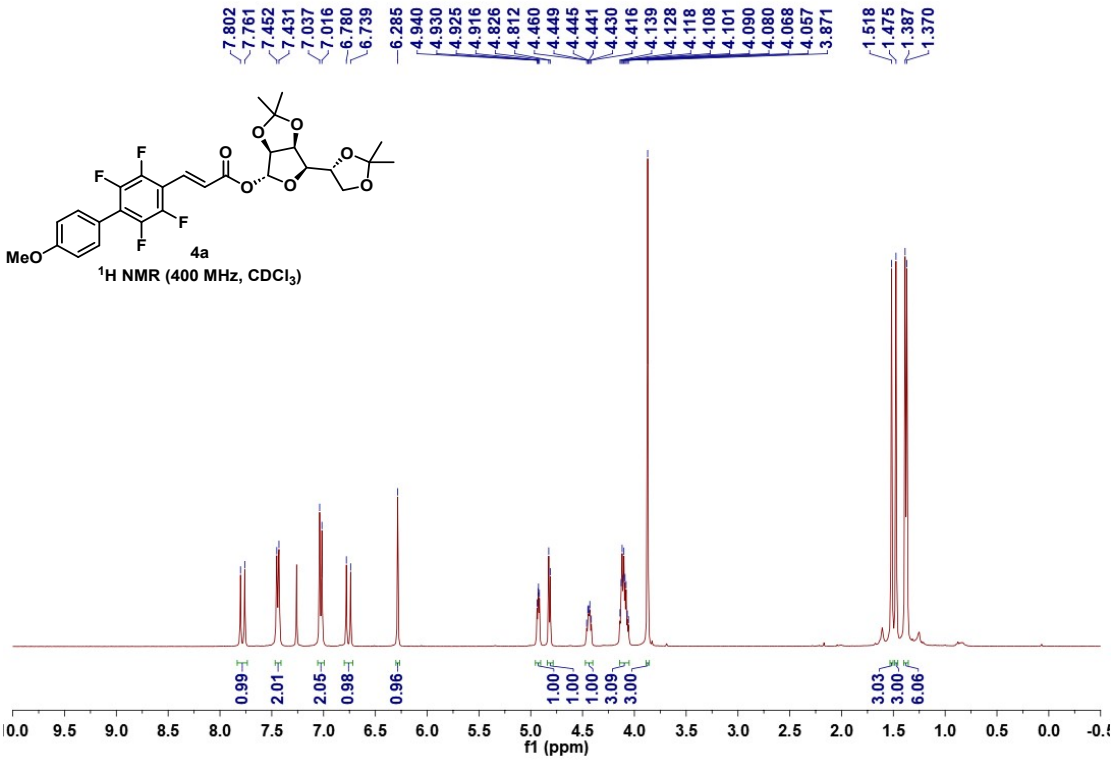
^{1}H NMR (400 MHz, $CDCl_3$)

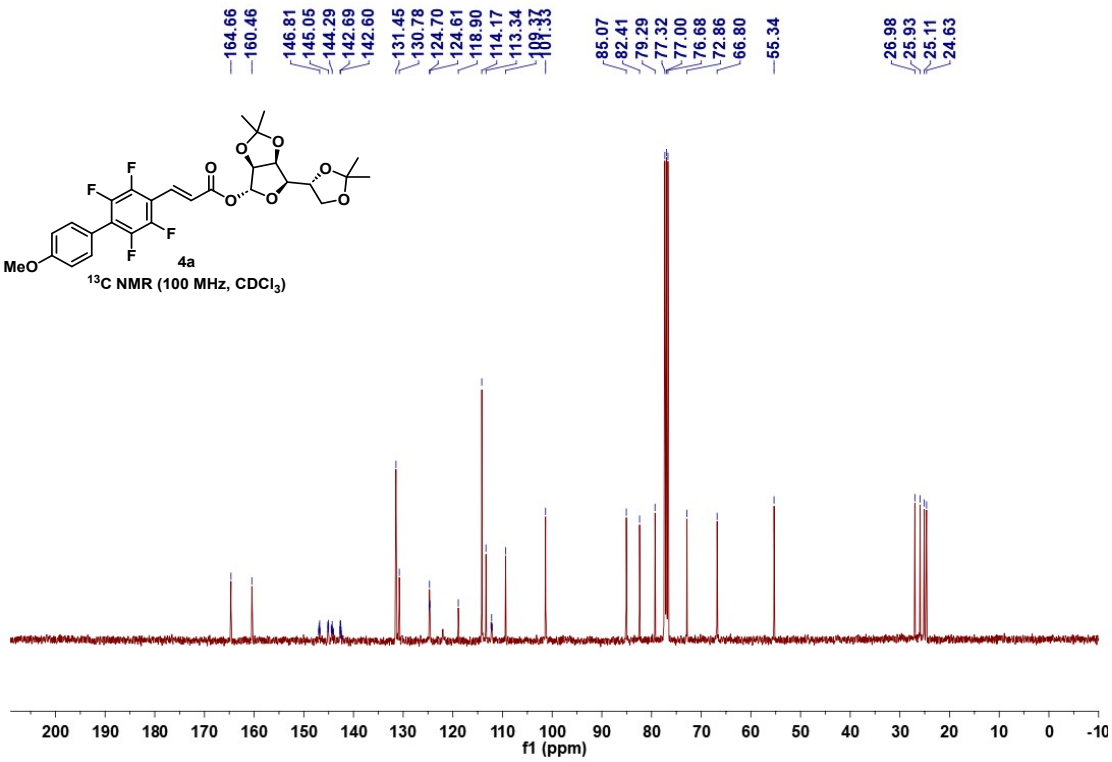


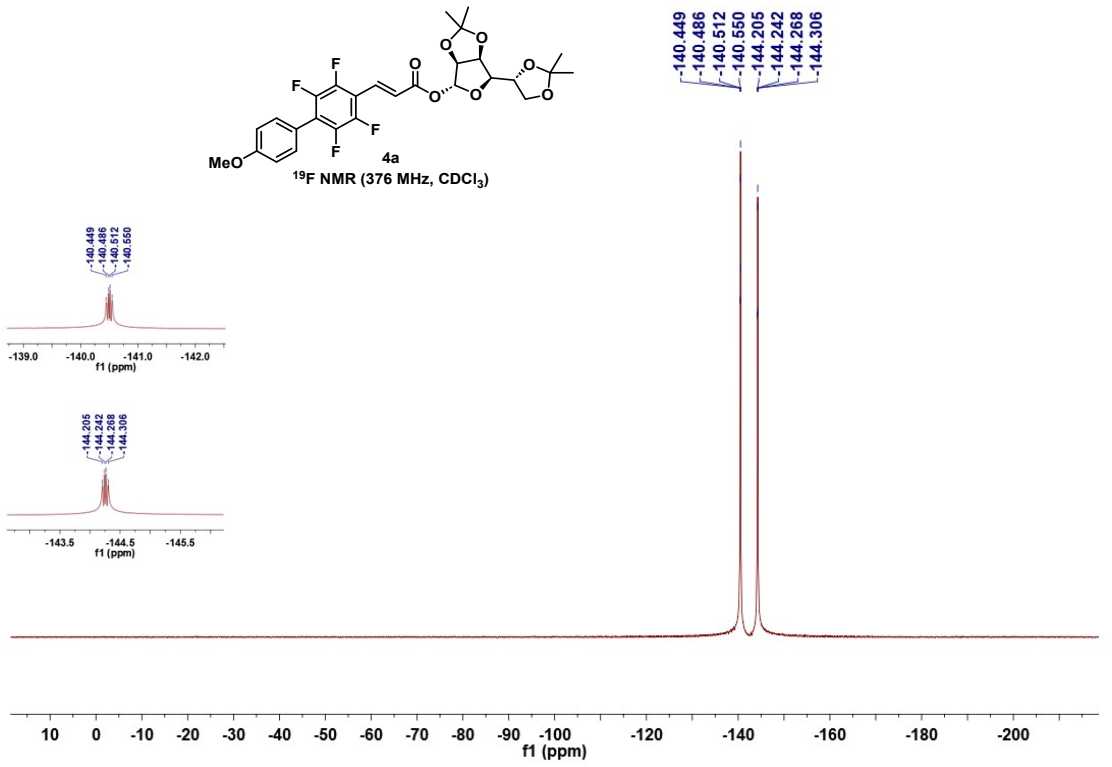
3fb

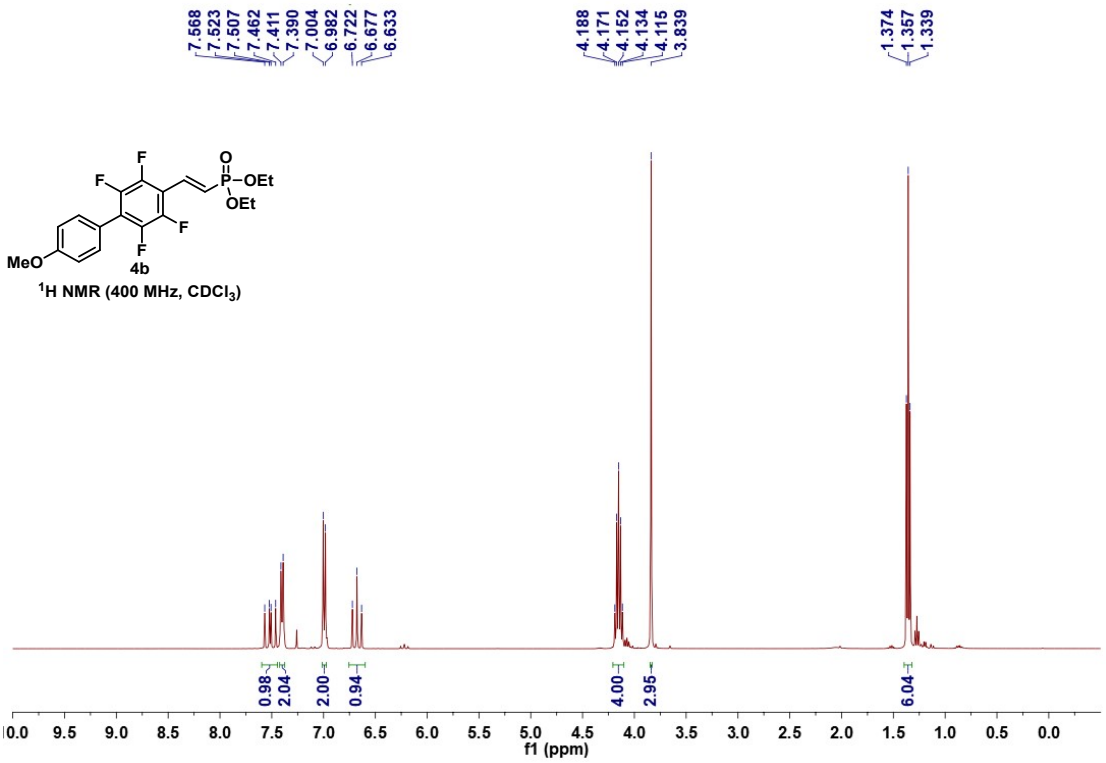
^{13}C NMR (100 MHz, $CDCl_3$)


F
F
F
F
MeO
3fb
^{19}F NMR (376 MHz, CDCl$_3$)
-139.385
-139.418
-139.421
-139.447
-139.481
-144.237
-144.272
-144.298
-144.332
f1 (ppm)

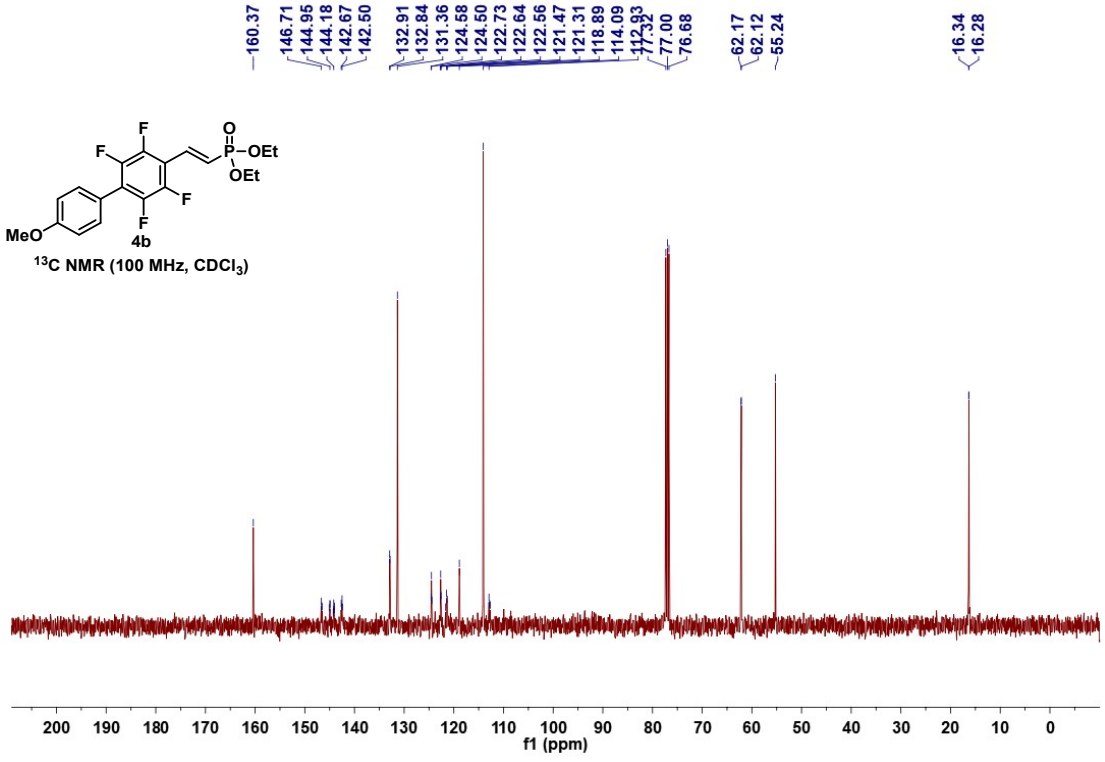

7.802
7.761
7.452
7.431
7.037
7.016
6.780
6.739
6.285
4.940
4.930
4.925
4.916
4.826
4.812
4.460
4.449
4.445
4.441
4.430
4.416
4.139
4.128
4.118
4.108
4.101
4.090
4.080
4.068
4.057
3.871
1.518
1.475
1.387
1.370
F
F
F
F
O
O
O
O
O
O
O
MeO
4a
^{1}H NMR (400 MHz, CDCl$_3$)
0.99
2.01
2.05
0.98
0.96
1.00
1.00
1.00
3.09
3.00
3.03
3.00
6.06
f1 (ppm)


164.66
160.46
146.81
145.05
144.29
142.69
142.60
131.45
130.78
124.70
124.61
118.90
114.17
113.34
85.07
82.41
79.29
77.32
77.00
76.68
72.86
66.80
55.34
26.98
25.93
25.11
24.63
MeO
4a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

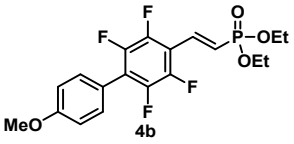

140.449
140.486
140.512
140.550
144.205
144.242
144.268
144.306
MeO
4a
19F NMR (376 MHz, CDCl3)
f1 (ppm)



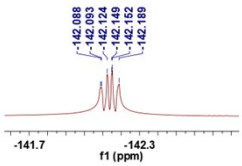
^{1}H NMR (400 MHz, $CDCl_3$)

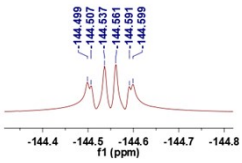


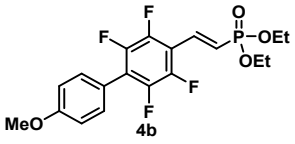
^{13}C NMR (100 MHz, $CDCl_3$)



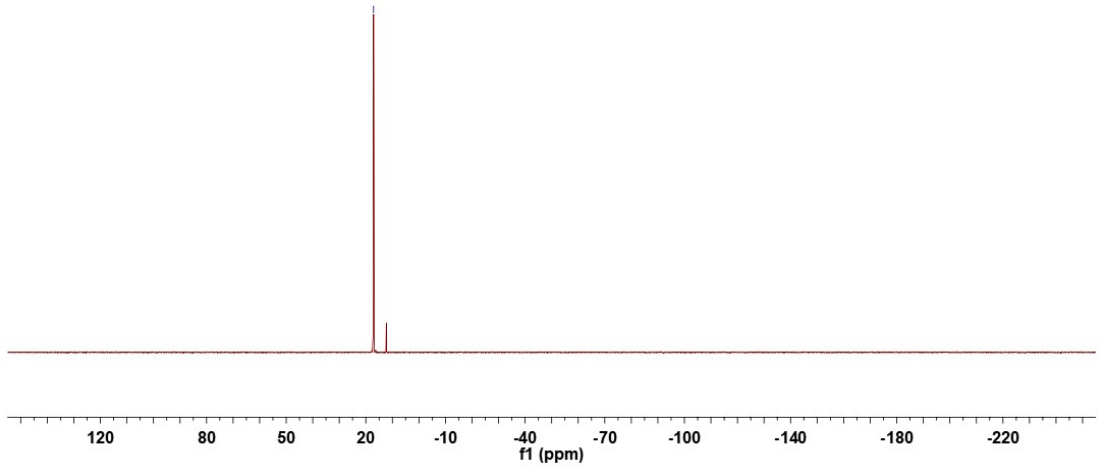
^{19}F NMR (376 MHz, $CDCl_3$)

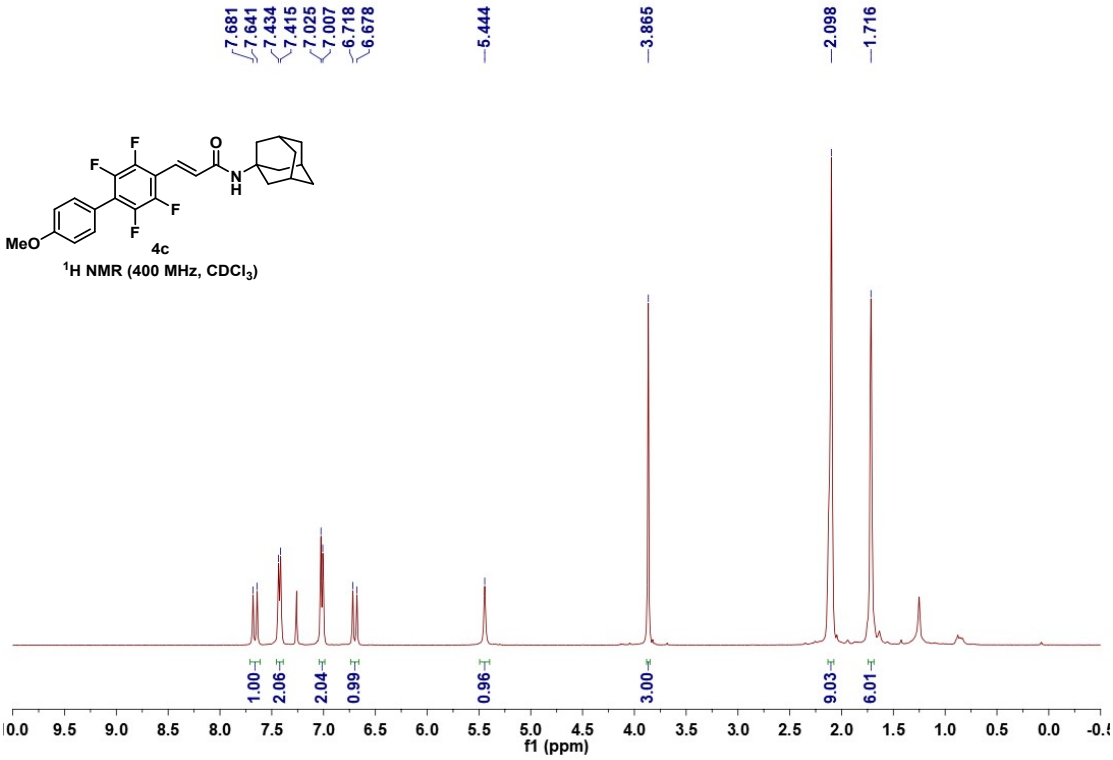


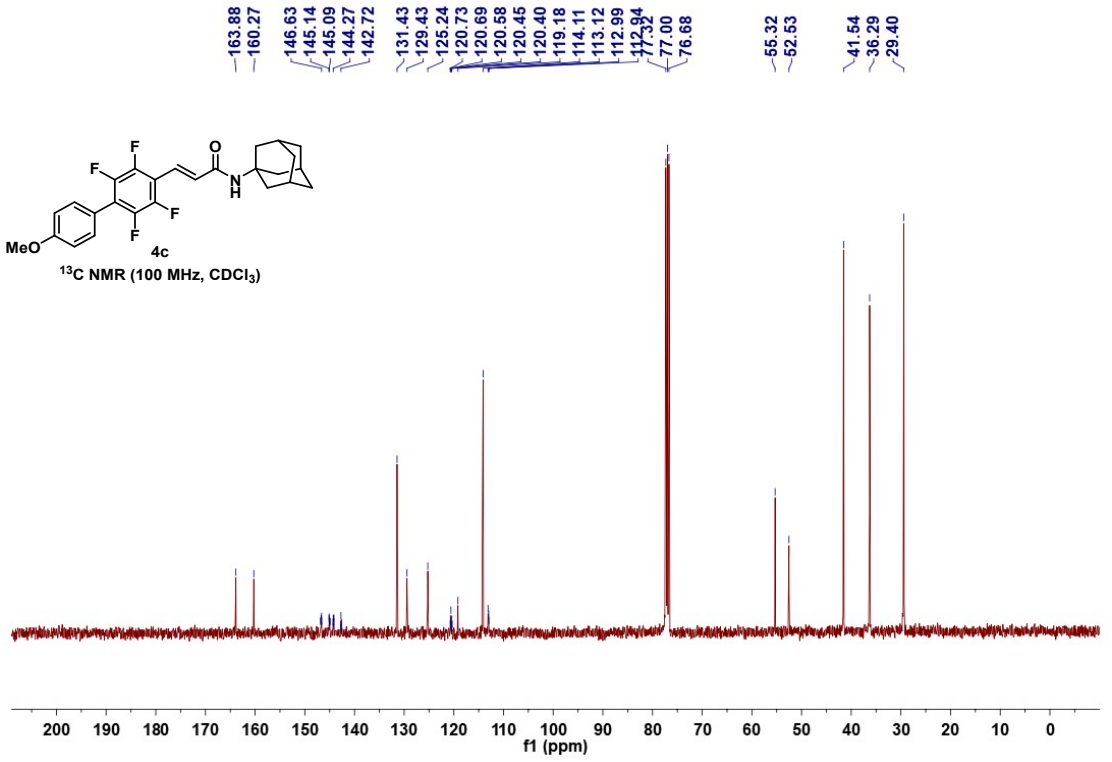


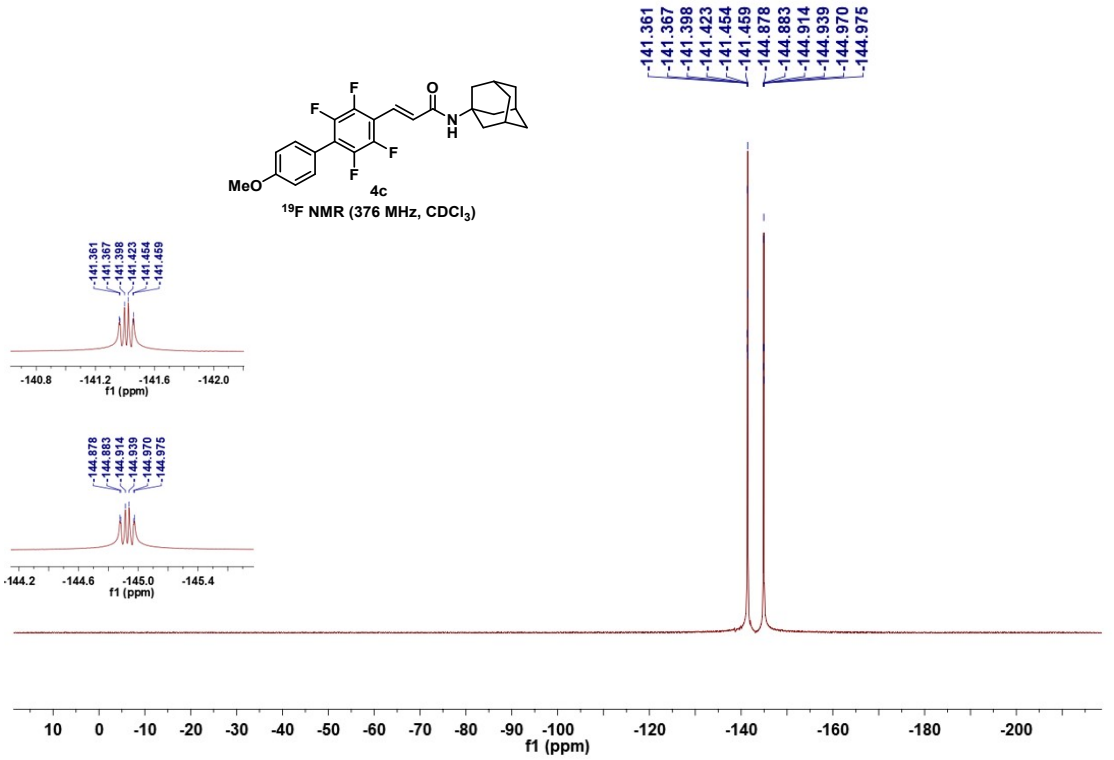


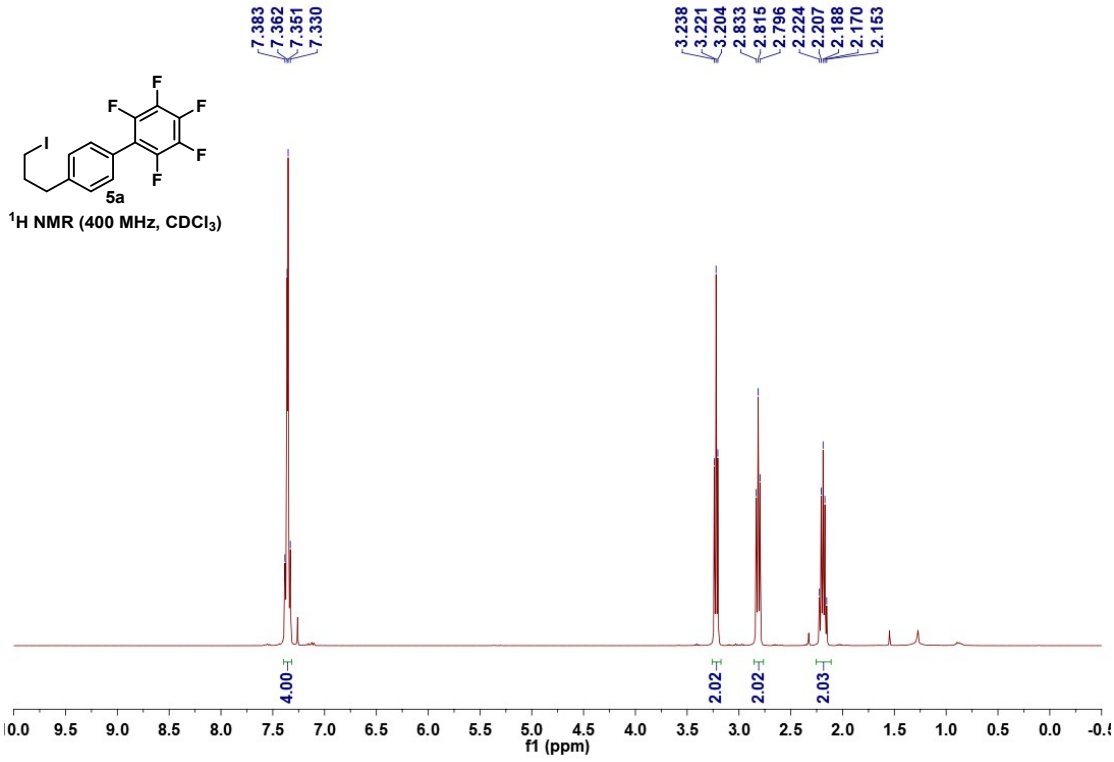
^{31}P NMR (162 MHz, $CDCl_3$)

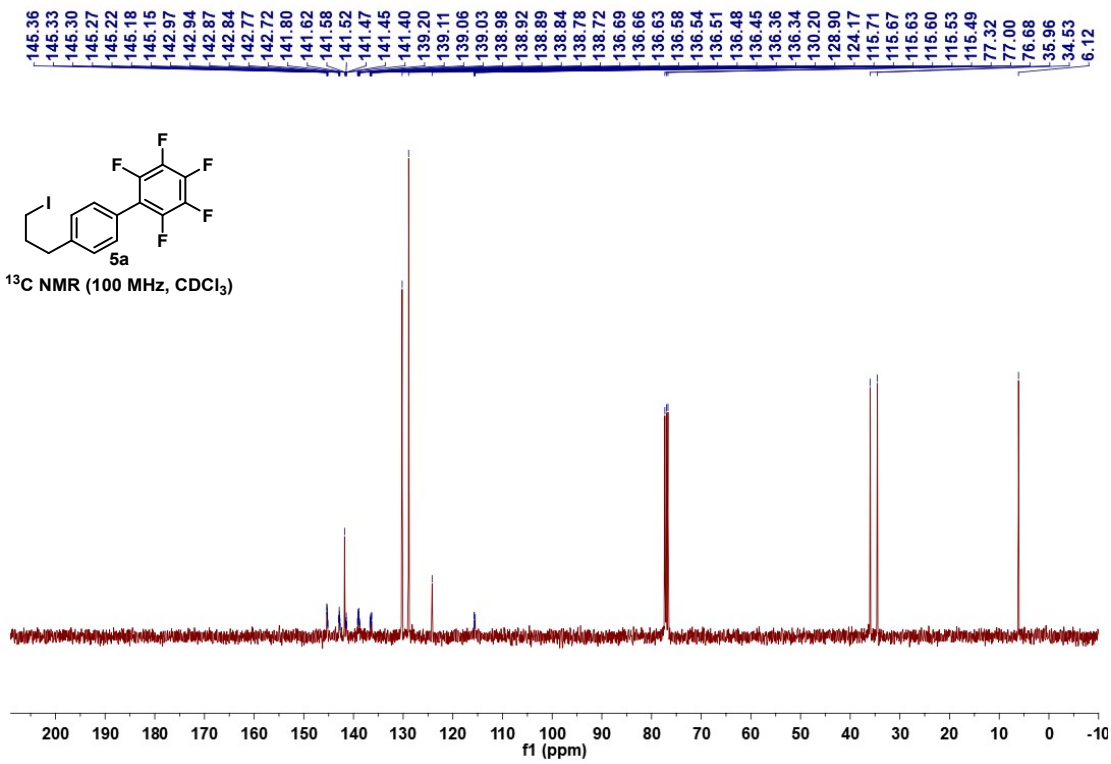


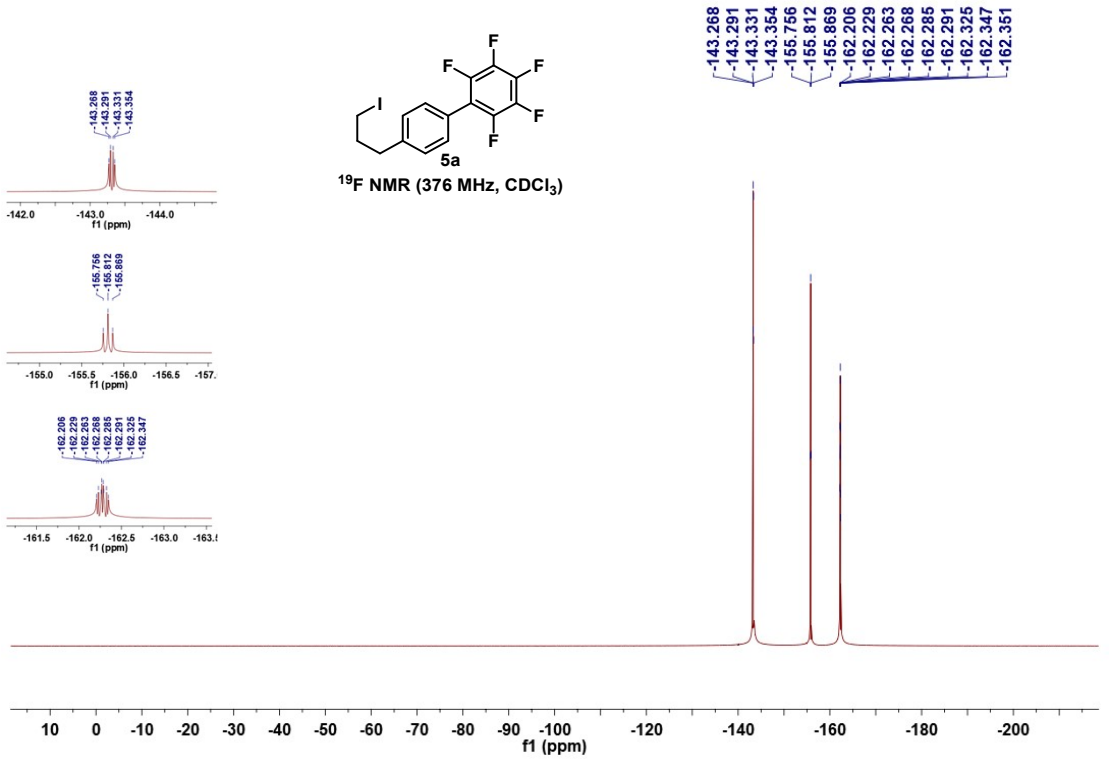

7.681
7.641
7.434
7.415
7.025
7.007
6.718
6.678
5.444
3.865
2.098
1.716
F
F
O
N
H
F
F
MeO
4c
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
2.06
2.04
0.99
0.96
3.00
9.03
6.01
f1 (ppm)

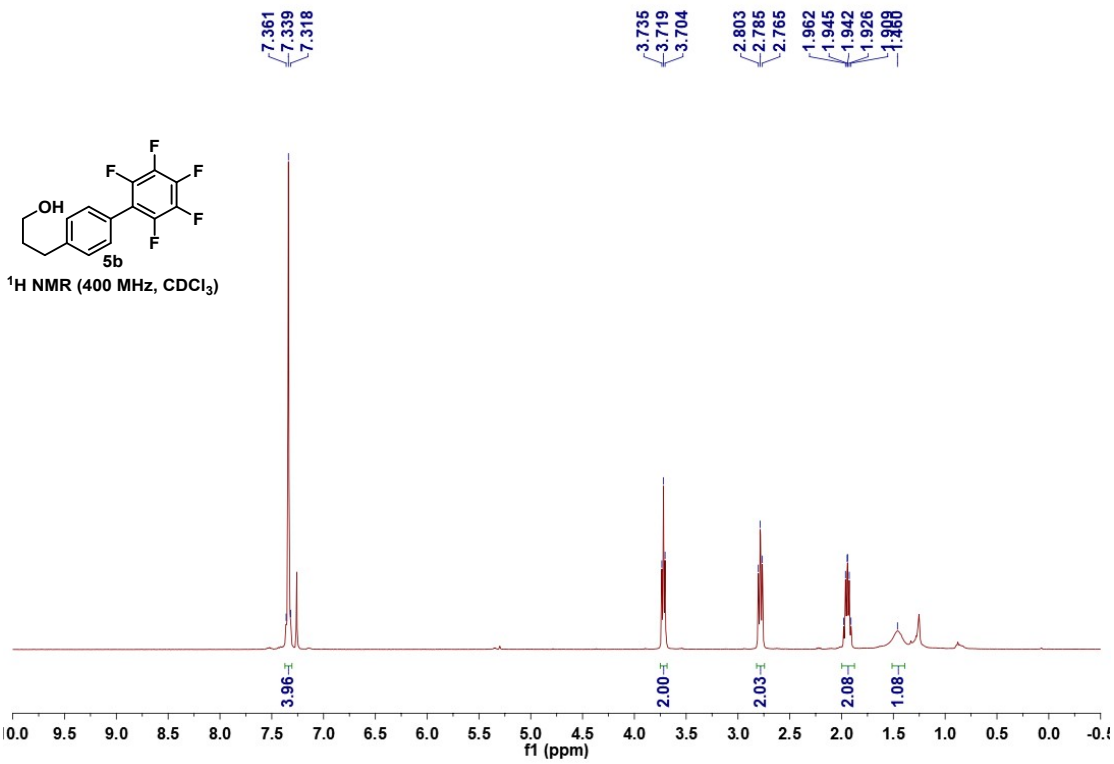

163.88
160.27
146.63
145.14
145.09
144.27
142.72
131.43
129.43
125.24
120.73
120.69
120.58
120.45
120.40
119.18
114.11
113.12
112.99
112.94
77.32
77.00
76.68
55.32
52.53
41.54
36.29
29.40
F
F
O
N
H
F
F
MeO
4c
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

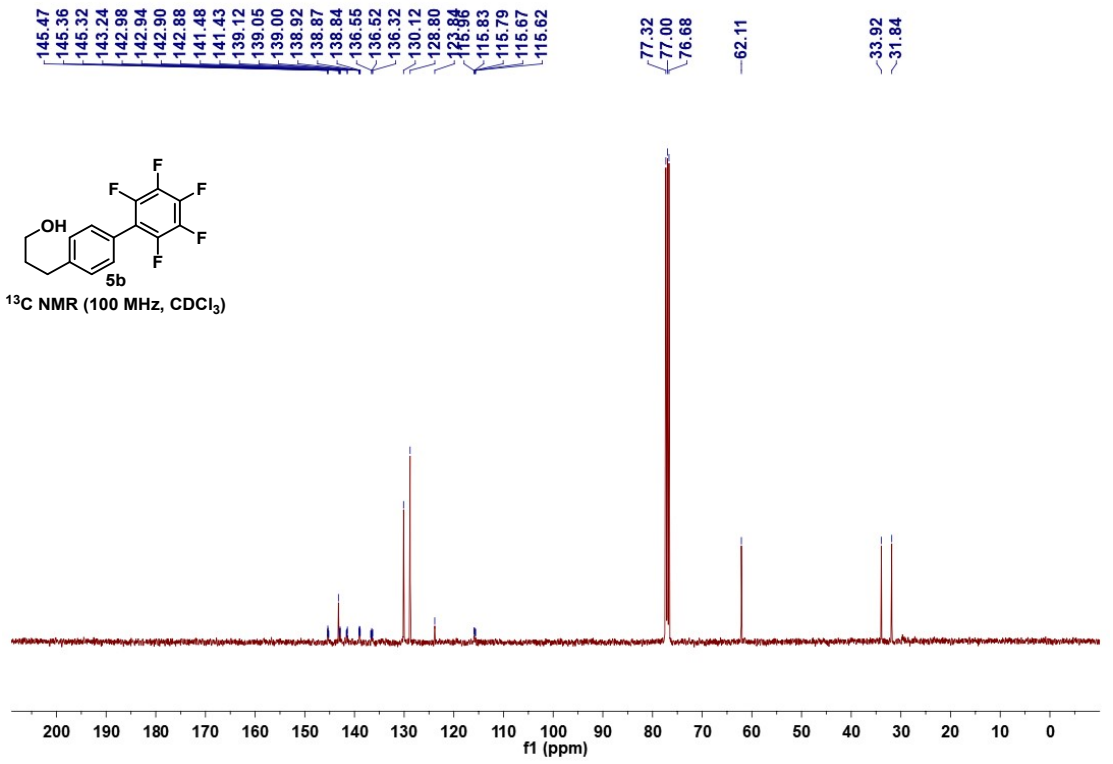

-141.361
-141.367
-141.398
-141.423
-141.454
-141.459
-144.878
-144.883
-144.914
-144.939
-144.970
-144.975
F
F
O
N
H
F
F
MeO
4c
19F NMR (376 MHz, CDCl3)
-140.8
-141.2
-141.6
-142.0
f1 (ppm)
-144.2
-144.6
-145.0
-145.4
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

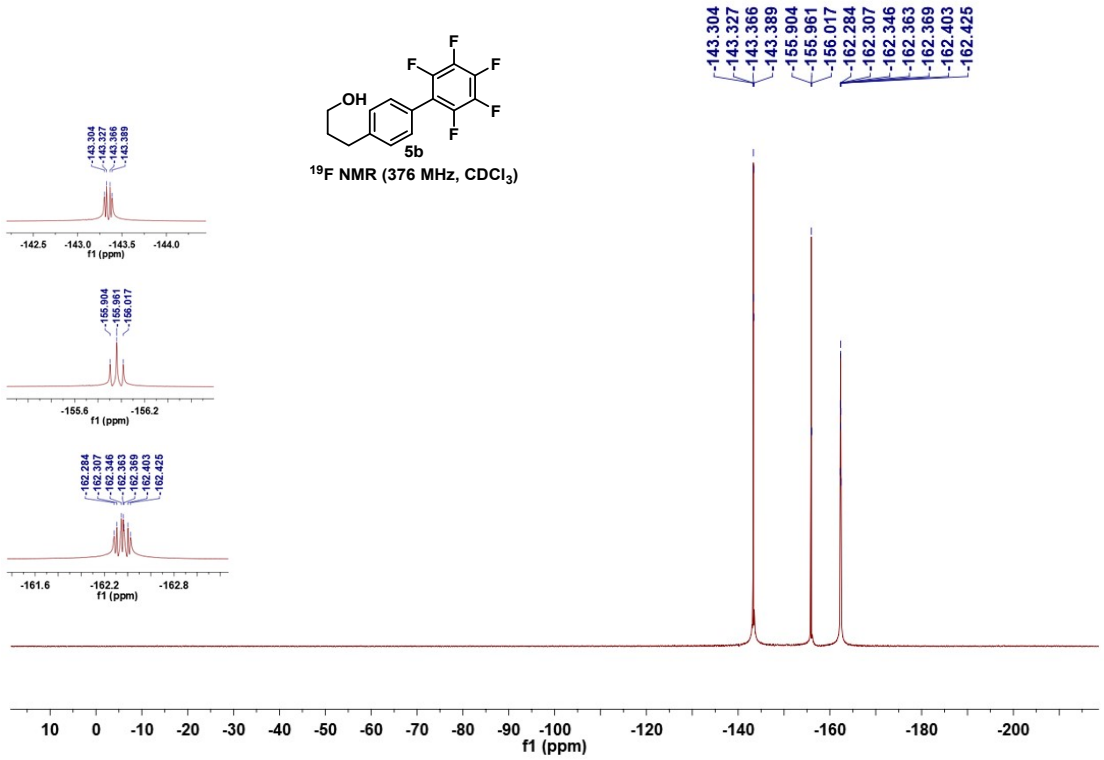

7.383
7.362
7.351
7.330
3.238
3.221
3.204
2.833
2.815
2.796
2.224
2.207
2.188
2.170
2.153
F
F
F
I
F
F
5a
1H NMR (400 MHz, CDCl3)
4.00
2.02
2.02
2.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

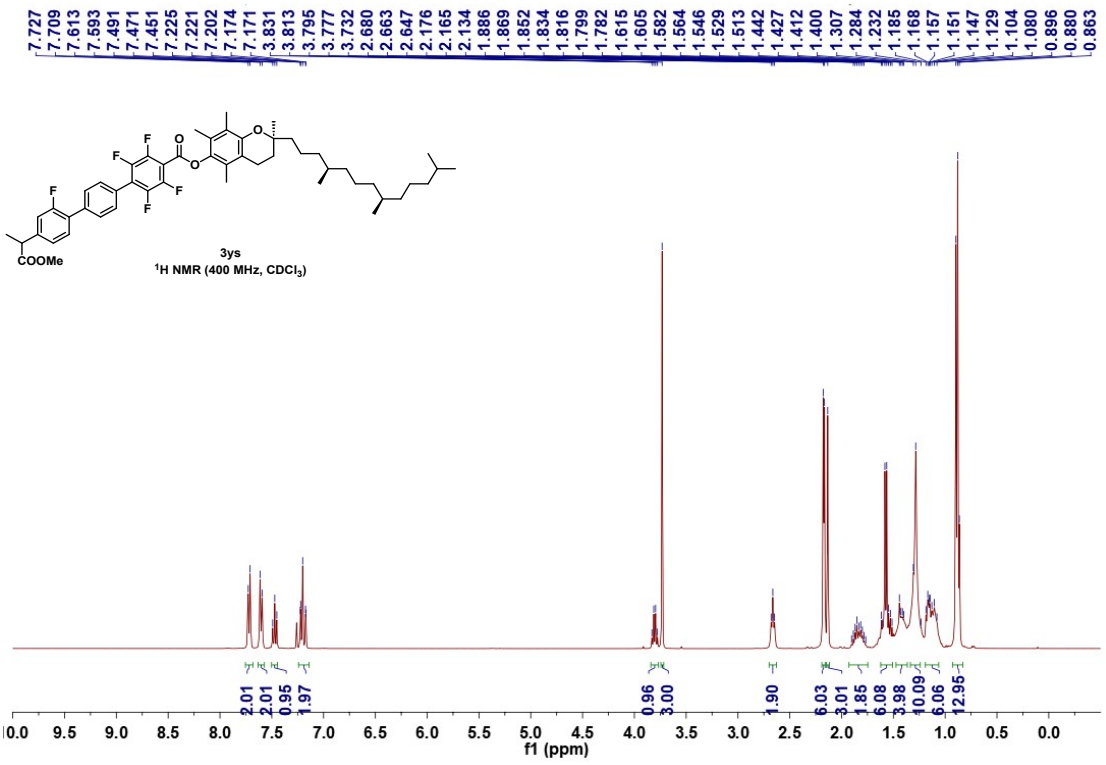

145.36
145.33
145.30
145.27
145.22
145.18
145.15
142.97
142.94
142.87
142.84
142.77
142.72
141.80
141.62
141.58
141.52
141.47
141.45
141.40
139.20
139.11
139.06
139.03
138.98
138.92
138.89
138.84
138.78
138.72
136.69
136.66
136.63
136.58
136.54
136.51
136.48
136.45
136.36
136.34
130.20
128.90
124.17
115.71
115.67
115.63
115.60
115.53
115.49
77.32
77.00
76.68
35.96
34.53
6.12
F
F
F
I
F
F
5a
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

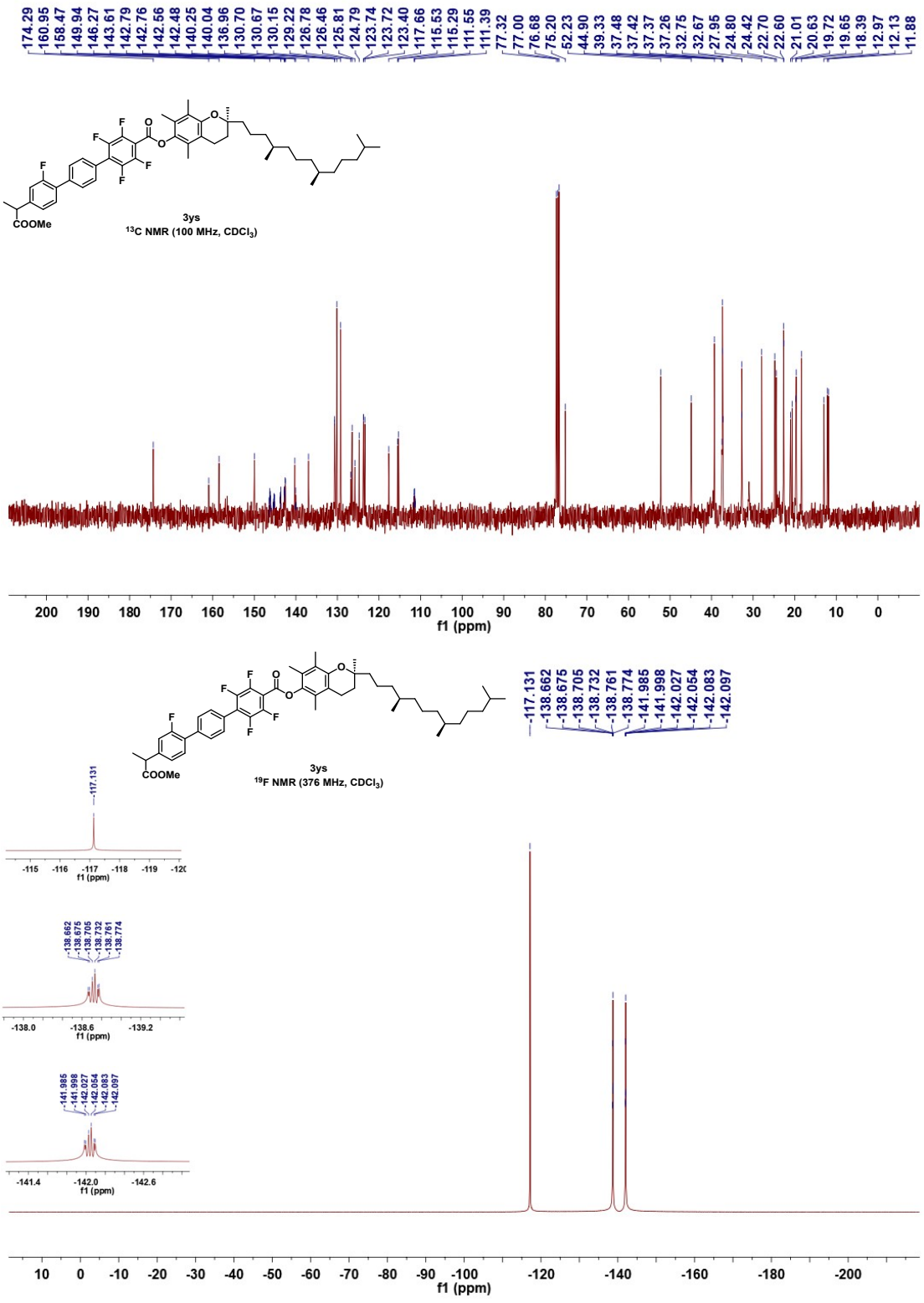

-143.268
-143.291
-143.331
-143.354
-155.756
-155.812
-155.869
-162.206
-162.229
-162.263
-162.268
-162.285
-162.291
-162.325
-162.347
-162.351
F
F
F
I
F
F
5a
^{19}F NMR (376 MHz, CDCl$_3$)
-142.0 -143.0 -144.0
-155.0 -155.5 -156.0 -156.5
-161.5 -162.0 -162.5 -163.0
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

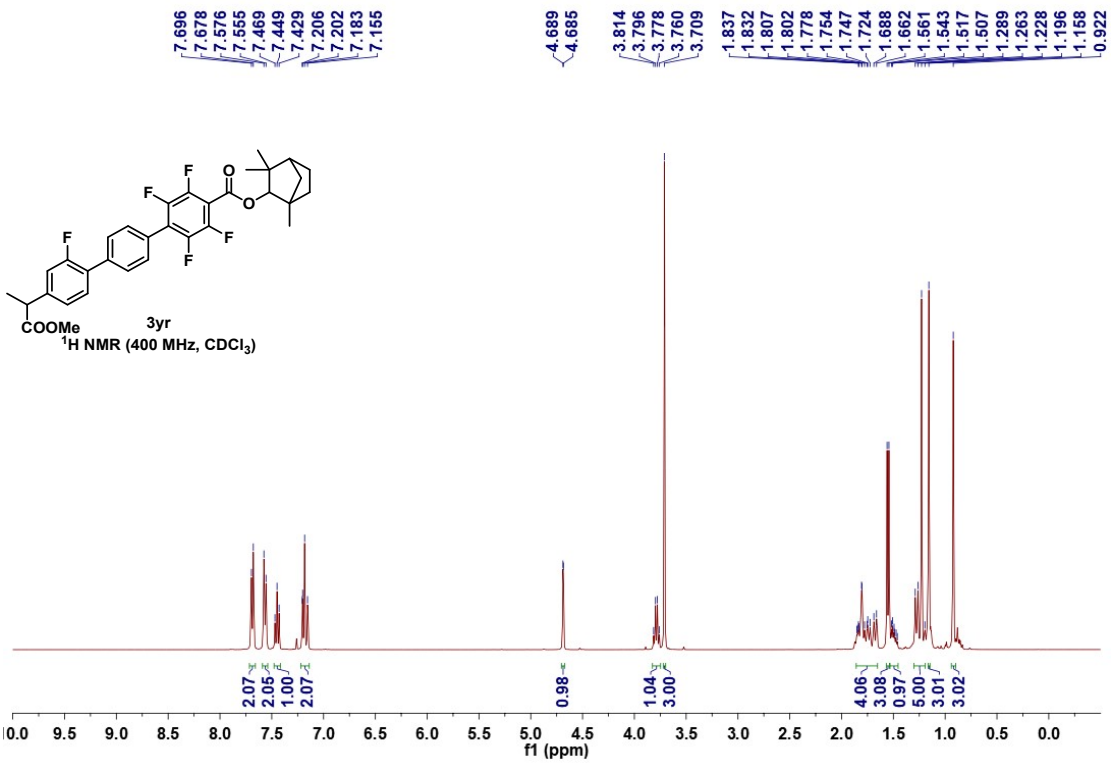

7.361
7.339
7.318
3.735
3.719
3.704
2.803
2.785
2.765
1.962
1.945
1.942
1.926
F
F
F
F
F
OH
5b
^{1}H NMR (400 MHz, CDCl$_3$)
3.96
2.00
2.03
2.08
1.08
f1 (ppm)

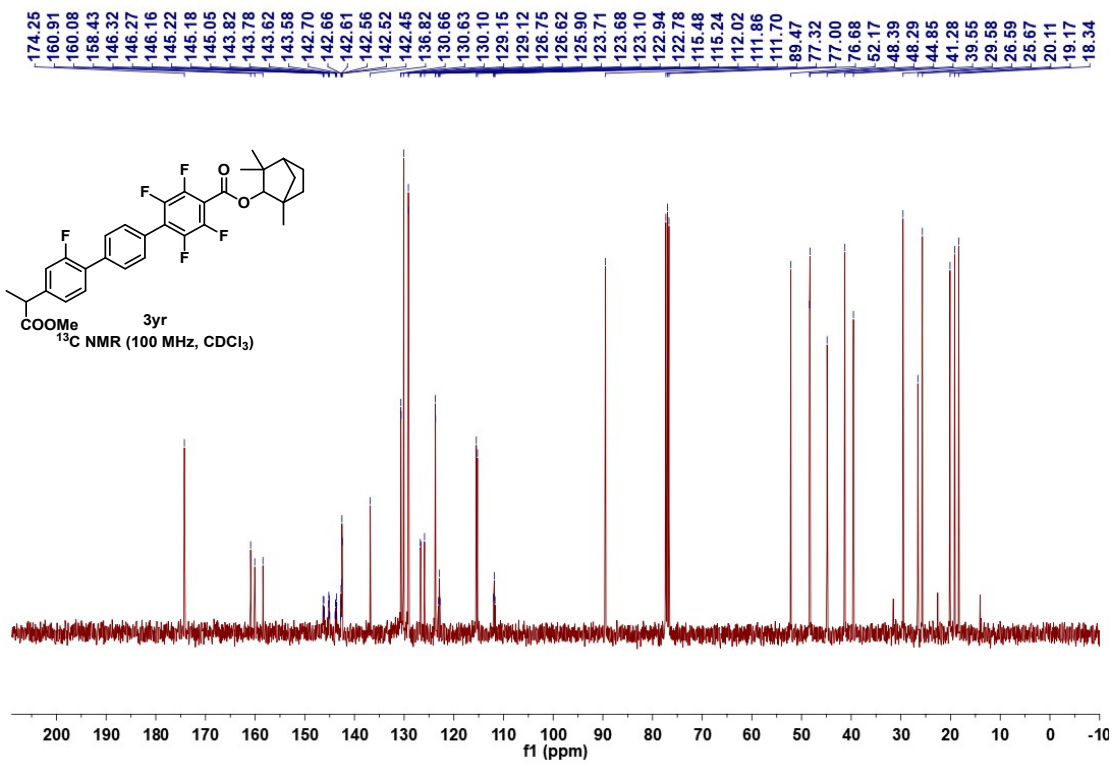

145.47
145.36
145.32
143.24
142.98
142.94
142.90
142.88
141.48
141.43
139.12
139.05
139.00
138.92
138.87
138.84
136.55
136.52
136.32
130.12
128.80
115.83
115.79
115.67
115.62
77.32
77.00
76.68
62.11
33.92
31.84
F
F
F
F
F
OH
5b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

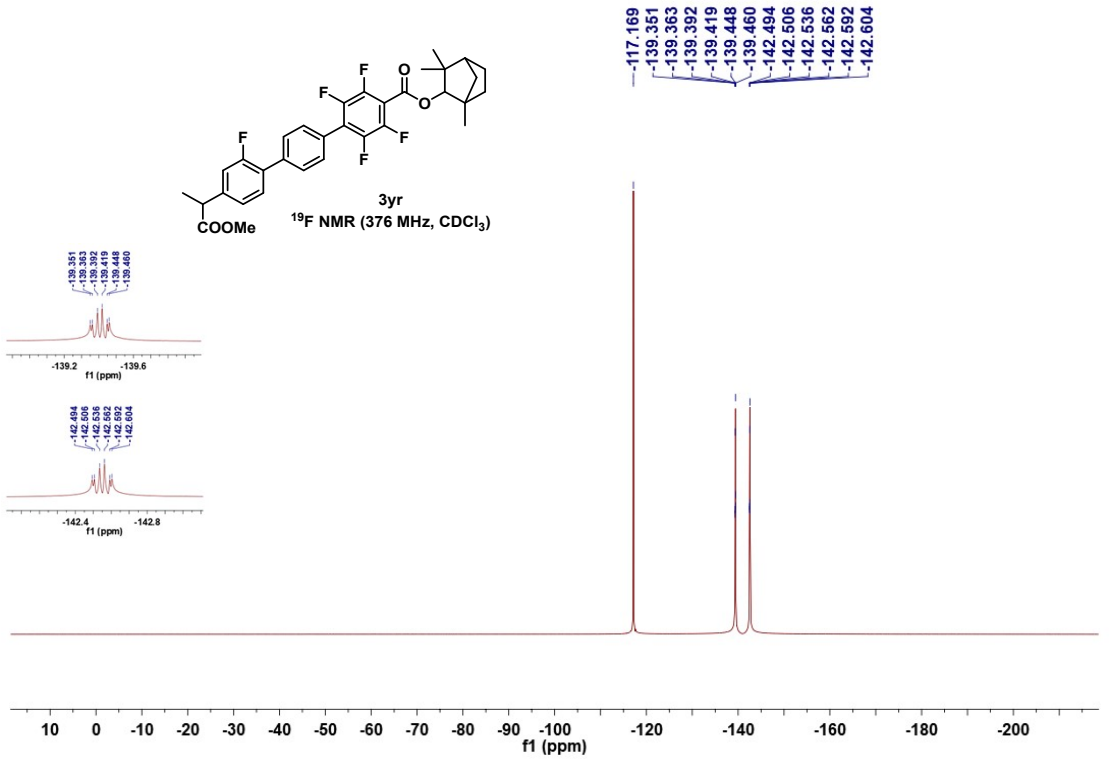

OH
F
F
F
F
F
5b
19F NMR (376 MHz, CDCl3)
-143.304
-143.327
-143.366
-143.389
-155.904
-155.961
-156.017
-162.284
-162.307
-162.346
-162.363
-162.369
-162.403
-162.425
f1 (ppm)

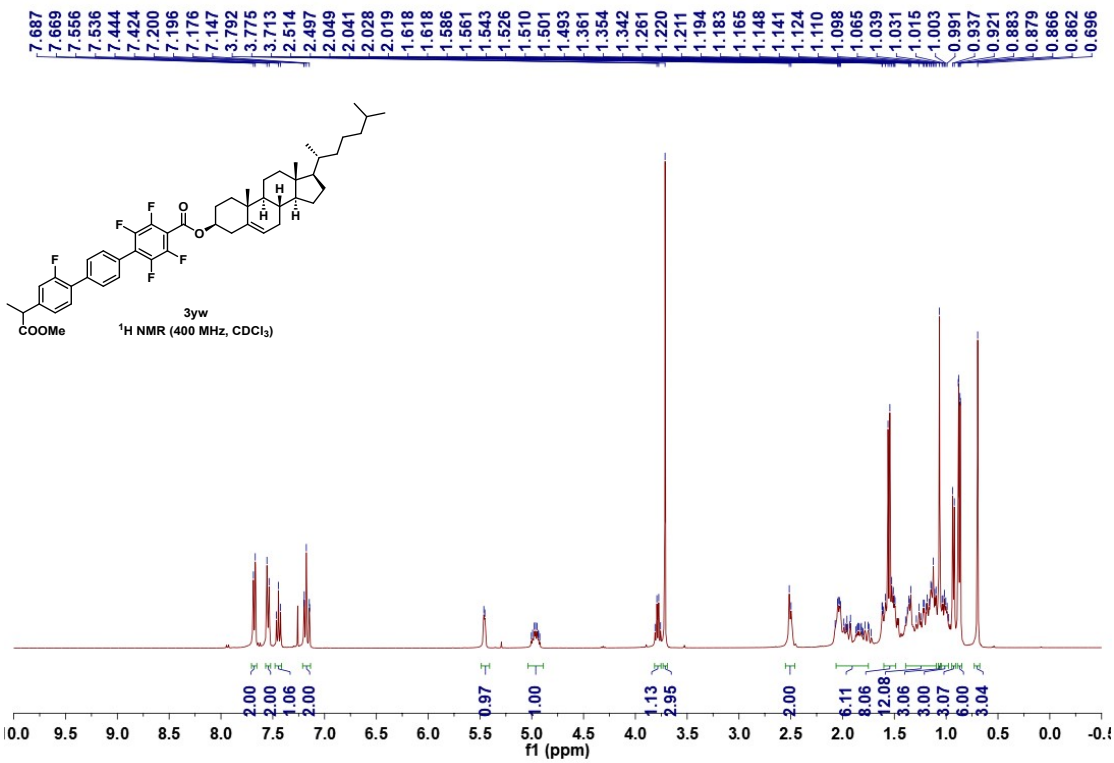

COOMe
3ys
1H NMR (400 MHz, CDCl3)
7.727
7.709
7.613
7.593
7.491
7.471
7.451
7.225
7.221
7.202
7.174
7.171
3.831
3.813
3.795
3.777
3.732
2.680
2.663
2.647
2.176
2.165
2.134
1.886
1.869
1.852
1.834
1.816
1.799
1.782
1.615
1.605
1.582
1.564
1.546
1.529
1.513
1.442
1.427
1.412
1.400
1.307
1.284
1.232
1.185
1.168
1.157
1.151
1.147
1.129
1.104
1.080
0.896
0.880
0.863
2.01
2.01
0.95
1.97
0.96
3.00
1.90
6.03
3.01
1.85
6.08
3.98
10.09
6.06
12.95
f1 (ppm)

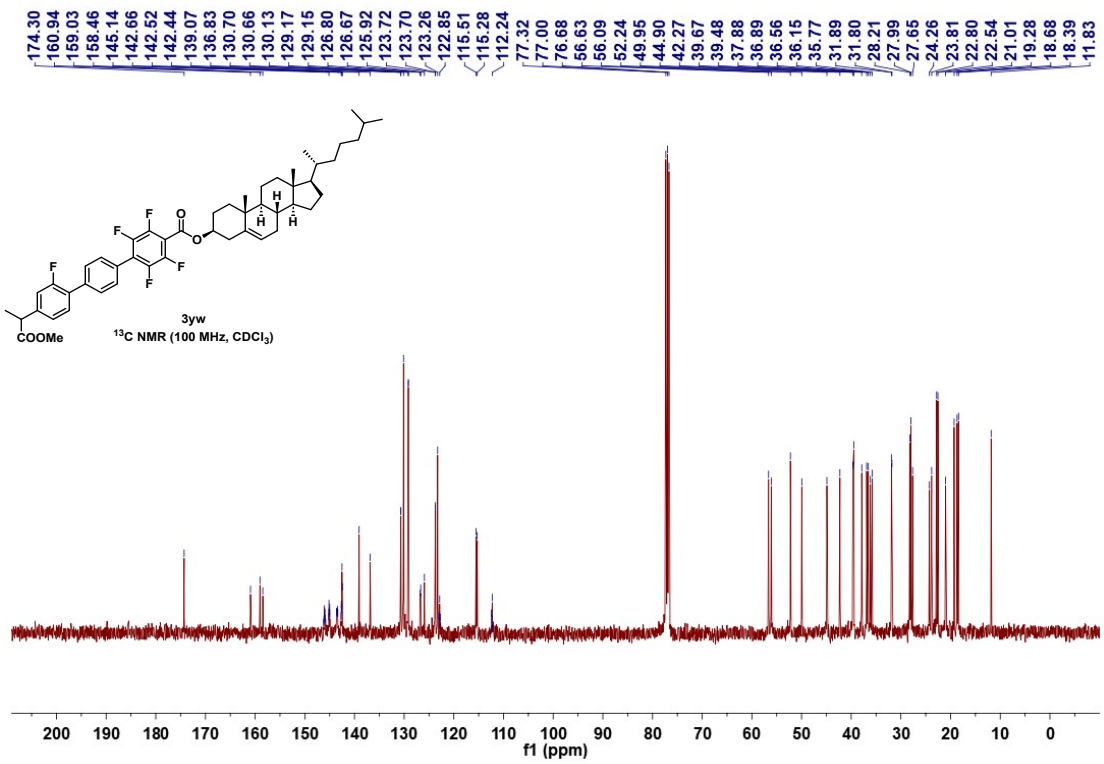

174.29
160.95
158.47
149.94
146.27
143.61
142.79
142.76
142.56
142.48
140.25
140.04
136.96
130.70
130.67
130.15
129.22
126.78
126.46
125.81
124.79
123.74
123.72
123.40
117.66
115.53
115.29
111.55
111.39
77.32
77.00
76.68
75.20
62.23
44.90
39.33
37.48
37.42
37.37
37.26
32.75
32.67
27.95
24.80
24.42
22.70
22.60
21.01
20.63
19.72
19.65
18.39
12.97
12.13
11.88
COOMe
3ys
13C NMR (100 MHz, CDCl3)
f1 (ppm)
-117.131
-138.662
-138.675
-138.705
-138.732
-138.761
-138.774
-141.985
-141.998
-142.027
-142.054
-142.083
-142.097
3ys
19F NMR (376 MHz, CDCl3)
f1 (ppm)

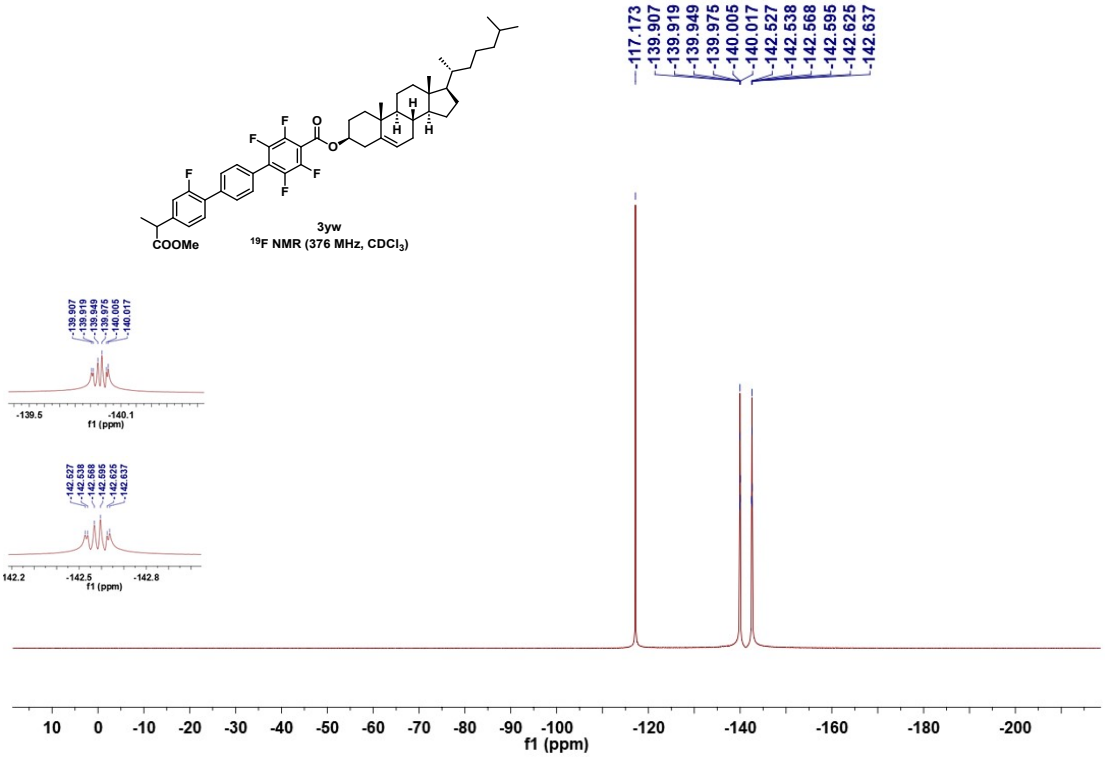

7.696
7.678
7.576
7.555
7.469
7.449
7.429
7.206
7.202
7.183
7.155
4.689
4.685
3.814
3.796
3.778
3.760
3.709
1.837
1.832
1.807
1.802
1.778
1.754
1.747
1.724
1.688
1.662
1.661
1.543
1.517
1.507
1.289
1.263
1.228
1.196
1.158
0.922
F
F
O
O
F
F
F
COOMe
3yr
1H NMR (400 MHz, CDCl3)
2.07
2.05
1.00
2.07
0.98
1.04
3.00
4.06
3.08
0.97
5.00
3.01
3.02
f1 (ppm)

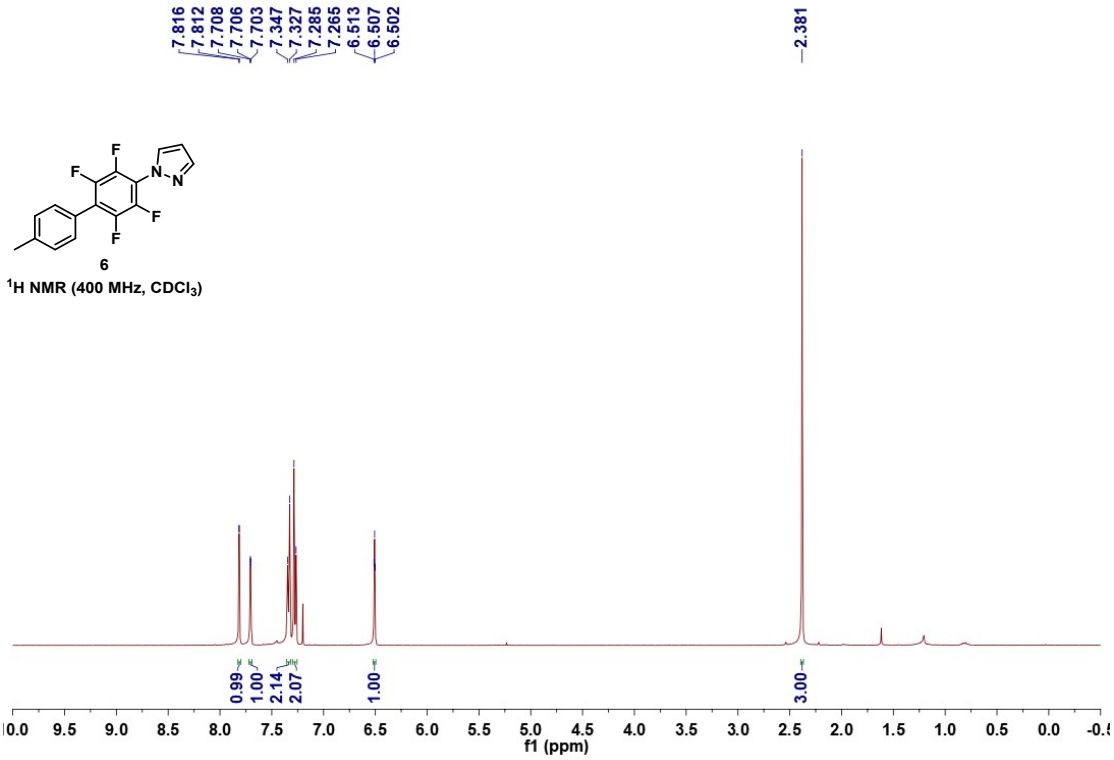

174.25
160.91
160.08
158.43
146.32
146.27
146.16
145.22
145.18
145.05
143.82
143.78
143.62
143.58
142.70
142.66
142.61
142.56
142.52
142.45
136.82
130.66
130.63
130.10
129.15
129.12
126.75
126.62
125.90
123.71
123.68
123.10
122.94
122.78
115.48
115.24
112.02
111.86
111.70
89.47
77.32
77.00
76.68
52.17
48.39
48.29
44.85
41.28
39.55
29.58
26.59
25.67
20.11
19.17
18.34
F
F
O
O
F
F
F
COOMe
3yr
13C NMR (100 MHz, CDCl3)
f1 (ppm)

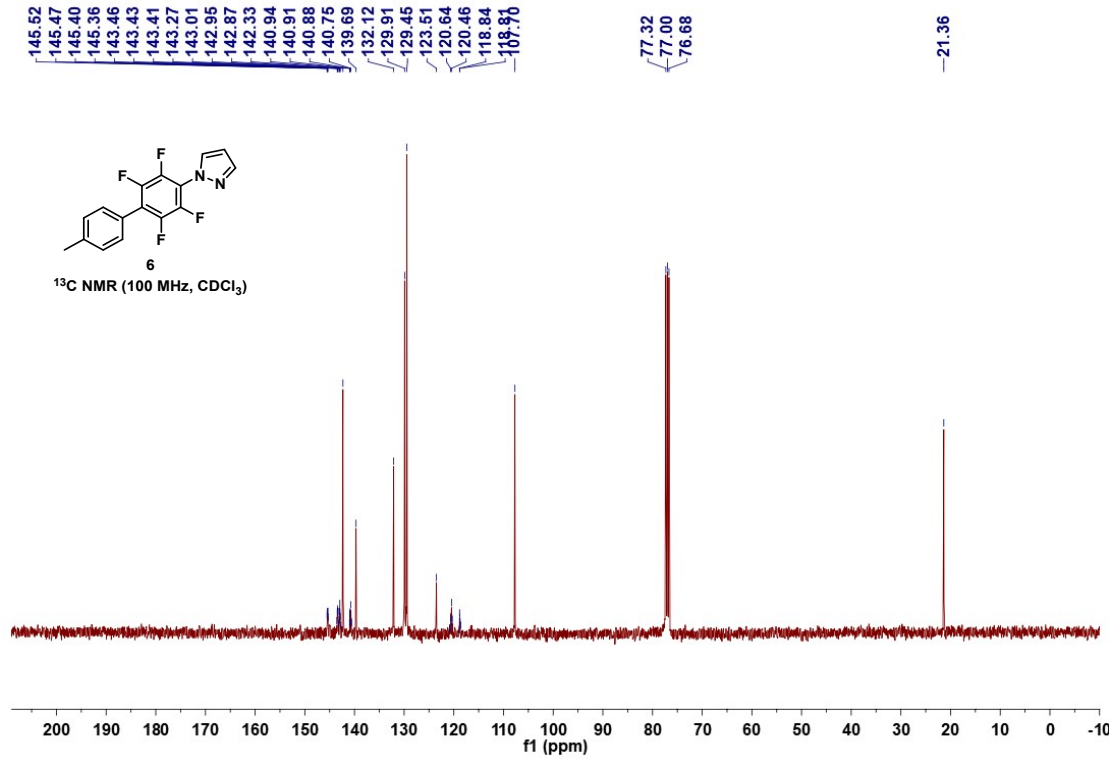

3yr
^{19}F NMR (376 MHz, $CDCl_3$)
COOMe
f1 (ppm)

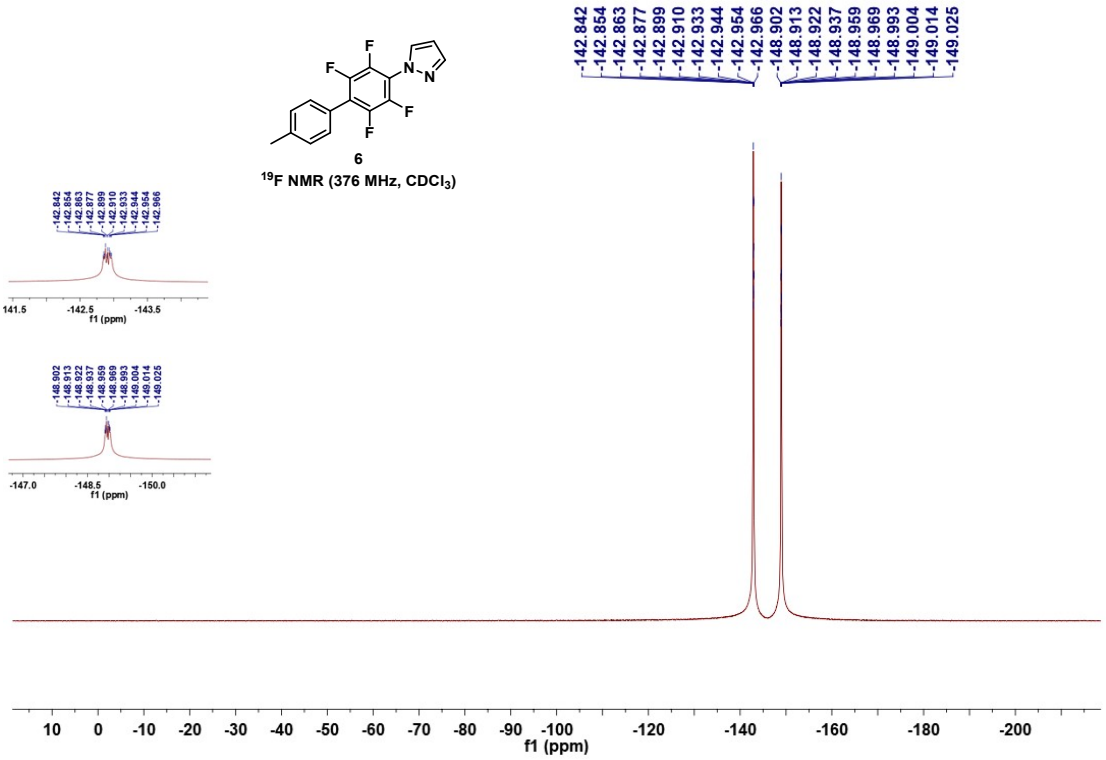

3yw
^{1}H NMR (400 MHz, $CDCl_3$)
COOMe
f1 (ppm)


174.30
160.94
159.03
158.46
145.14
142.66
142.52
142.44
139.07
136.83
130.70
130.66
130.13
129.17
129.15
126.80
126.67
125.92
123.72
123.70
123.26
122.85
115.51
115.28
112.24
77.32
77.00
76.68
56.63
56.09
52.24
49.95
44.90
42.27
39.67
39.48
37.88
36.89
36.56
36.15
35.77
31.89
31.80
28.21
27.99
27.65
24.26
23.81
22.80
22.54
21.01
19.28
18.68
18.39
11.83
3yw
COOMe
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-117.173
-139.907
-139.919
-139.949
-139.975
-140.005
-140.017
-142.527
-142.538
-142.568
-142.595
-142.625
-142.637
3yw
COOMe
19F NMR (376 MHz, CDCl3)
f1 (ppm)


7.816
7.812
7.708
7.706
7.703
7.347
7.327
7.285
7.265
6.513
6.507
6.502
2.381
F
F
N
N
F
F
6
^{1}H NMR (400 MHz, CDCl$_3$)
0.99
1.00
2.14
2.07
1.00
3.00
f1 (ppm)


145.52
145.47
145.40
145.36
143.46
143.43
143.41
143.27
143.01
142.95
142.87
142.33
140.94
140.91
140.88
140.75
139.69
132.12
129.91
129.45
123.51
120.64
120.46
118.84
77.32
77.00
76.68
21.36
F
F
N
N
F
F
6
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-142.842
-142.854
-142.863
-142.877
-142.899
-142.910
-142.933
-142.944
-142.954
-142.966
-148.902
-148.913
-148.922
-148.937
-148.959
-148.969
-148.993
-149.004
-149.014
-149.025
F
F
F
F
N
N
6
19F NMR (376 MHz, CDCl3)
141.5
-142.5
-143.5
f1 (ppm)
-147.0
-148.5
-150.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)