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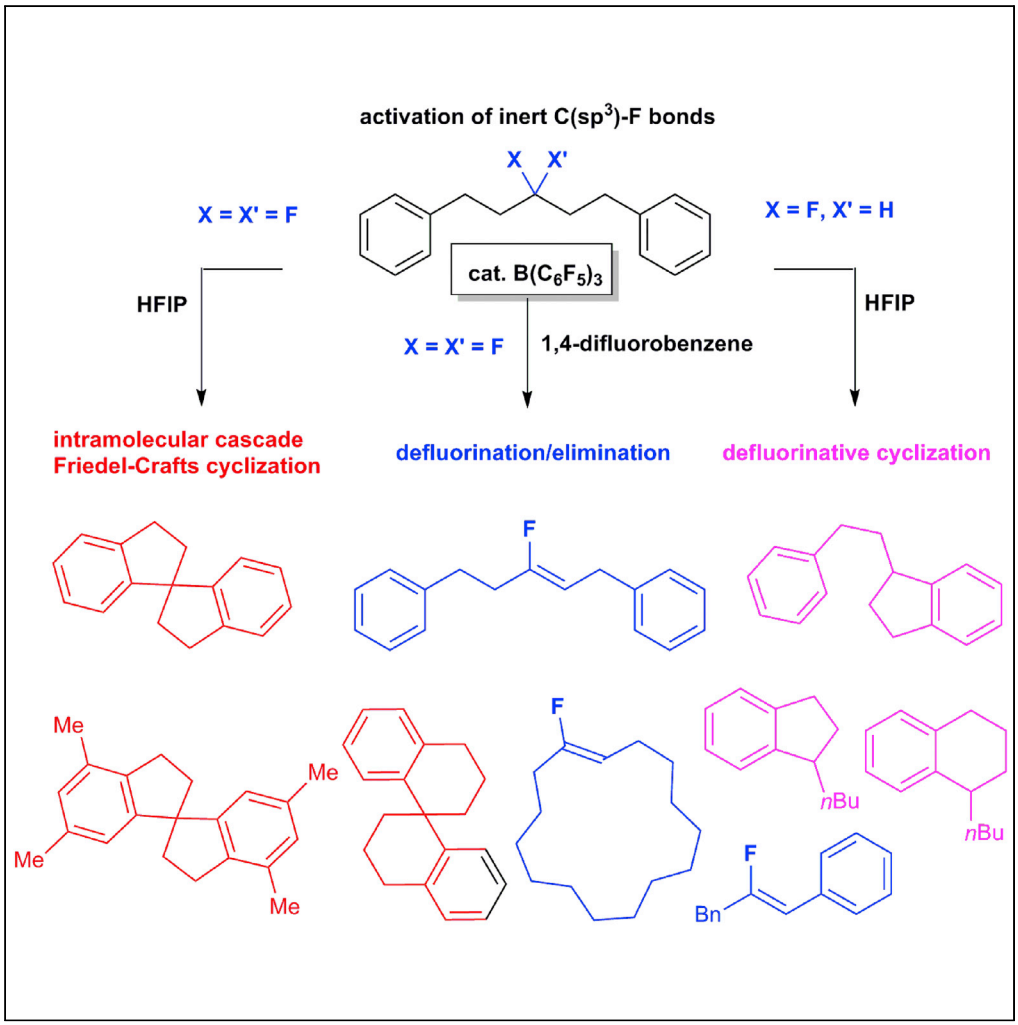

Jiandong Wang,
Yuta Ogawa,
Norio Shibata

nozshiba@nitech.ac.jp

HIGHLIGHTS

C(sp^3)-F bond activation in general unactivated fluorocarbons

The activation of C(sp^3)-F bonds in aliphatic *gem*-difluoroalkanes

The selective activation of inert C(sp^3)-F bonds catalyzed by $B(C_6F_5)_3$

An intramolecular cascade defluorinative Friedel-Crafts cyclization

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Activation of Saturated Fluorocarbons to Synthesize Spirobiindanes, Monofluoroalkenes, and Indane Derivatives

Jiandong Wang,[1] Yuta Ogawa,[1] and Norio Shibata[1,2,3,*]

SUMMARY

Fluorinated organic compounds are produced in abundance by the pharmaceutical and agrochemical industry, making such compounds attractive as building blocks for further functionalization. Unfortunately, activation of C(sp^3)-F bond in saturated fluorocarbons, especially for aliphatic *gem*-difluoroalkanes, remains challenging. Here we describe the selective activation of inert C(sp^3)-F bonds catalyzed by $B(C_6F_5)_3$. In hexafluoro-2-propanol (HFIP), chemically robust aliphatic *gem*-difluorides are converted in high yields to the corresponding substituted 2,2′,3,3′-tetrahydro-1,1′-spirobiindenes via a $B(C_6F_5)_3$-catalyzed intramolecular cascade Friedel-Crafts cyclization, not requiring a silicon-based trapping reagent. However, in the absence of a hydrogen-bonding donor solvent such as HFIP, the aliphatic *gem*-difluorides preferentially engage in a defluorination/elimination process that provides monofluorinated alkenes in good yields. Furthermore, a series of substituted 1-alkyl-2,3-dihydro-1*H*-indenes was obtained in high yield from the $B(C_6F_5)_3$-catalyzed defluorinative cyclization of aliphatic secondary monofluorides in HFIP. The protocol could inspire development of a new class of main-group Lewis acid-catalyzed C(sp^3)-F bond activation in general unactivated fluorocarbons.

INTRODUCTION

The demand for the selective activation of C-F bonds is growing as a result of the increased availability of fluorinated compounds in the pharmaceutical and agrochemical industries (Amii and Uneyama, 2009; Ahrens et al., 2015; Kuehnel et al., 2013; Hamel and Paquin, 2018; Klare, 2017). Recently, remarkable progress has been made in the transition-metal-mediated heterolysis of C(sp^2)-F bonds in aromatic and vinylic fluorocarbons (Ahrens et al., 2015; Kuehnel et al., 2013; Pike et al., 2017; Guo et al., 2015; Luo et al., 2018). However, the defluorinative functionalization of C(sp^3)-F bonds in unactivated aliphatic fluorides is less frequently reported and still a challenging issue in synthetic organic chemistry (Stahl et al., 2013; Shen et al., 2015). Indeed, the notorious chemical robustness of C-F bonds not only stems from their thermodynamic stability—the C-F bond is among the strongest covalent single bonds that carbon can form—but also from kinetic factors because the fluoride moiety is neither a good leaving group nor a good Lewis base (O'Hagan, 2008; Nolte et al., 2012).

The direct abstraction of the fluoride moiety in inert C(sp^3)-F bonds by *p*-block-based Lewis acids that exhibit high fluoride affinity has emerged as a promising strategy for the degradation of saturated fluorocarbons (Stahl et al., 2013; Shen et al., 2015), because of that the formation of covalent bonds between fluorine and main-group elements (e.g., B, Al, Si, and P), which are more stable than C-F bonds, may offer a thermodynamic driving force for the scission of the C-F bonds (Stahl et al., 2013). In addition, the stronger Lewis acidity of fluorophilic electrophiles is essential for the direct heterolytic cleavage of C(sp^3)-F bonds, given the high activation barrier. The substitution of the fluoride in C(sp^3)-F bonds to form C-H, C-C, and C-heteroatom bonds has been initiated by neutral, strong aluminum- and boron-based Lewis acids (Stahl et al., 2013; Greb, 2018; Morgan et al., 2013; Koerte et al., 2017; Ahrens et al., 2013; Jaiswal et al., 2017) or cationic species such as $[CPh_3]^+$, $[SiEt_3]^+$, $[iBu_2Al]^+$, $[(C_6F_5)_3FP]^+$, and even P(III) dications such as $[(bipy)PPh]^{2+}$ bearing weakly coordinating counter anions such as $[B(C_6F_5)_4]^-$ (Stahl et al., 2013; Klahn et al., 2007; Gu et al., 2009; Forster et al., 2017; Douvris and Ozerov, 2008; Scott et al., 2005; Großekappenberg et al., 2015; Zhu et al., 2016; Chitnis et al., 2018).

In their seminal reports, Olah and co-workers described the cleavage of unactivated C(sp^3)-F bonds initiated by boron-based Lewis acids, specifically the preferential abstraction of fluorides from aliphatic

[1]Department of Nanopharmaceutical Sciences and Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-5888, Japan

[2]Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, 688 Yingbin Avenue, 321004 Jinhua, China

[3]Lead Contact

*Correspondence: nozshiba@nitech.ac.jp

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fluorohaloalkanes by boron trifluoride to generate the stable BF_4^- anion and Friedel-Crafts-type alkylation products with excess arenes (Olah et al., 1957; Olah and Kuhn, 1964). Consistent with the greater stability of tertiary carbocations derived from tertiary aliphatic fluorides, Oshima and co-workers have reported that $BF_3{\cdot}OEt_2$ catalyzes C-C bond couplings between silicon enolates and tertiary fluorides (Hirano et al., 2004). Subsequently, Stephan et al. have reported the splitting of unactivated C(sp^3)-F bonds using stoichiometric amounts of $B(C_6F_5)_3$ and a phosphine as frustrated Lewis pairs (FLPs) to produce $[R_3PR'][FB(C_6F_5)_3]$ salts (Caputo and Stephan, 2012). Alternatively, using catalytic amounts of $B(C_6F_5)_3$ with an excess of Et_3SiH, a C-H bond is formed at the expense of the corresponding C(sp^3)-F bond (Caputo and Stephan, 2012). Furthermore, $HB(C_6F_5)_2$ has been used to induce the direct C(sp^3)-F borylation of secondary and primary aliphatic fluoroalkanes via an initial dehydrofluorination and a subsequent borylation of the resulting olefin intermediates (Bamford et al., 2018). Recently, Moran and co-workers have reported the Friedel-Crafts reactions of tertiary fluoroalkanes with an excess of arenes (3.0–5.0 equiv.) catalyzed by $B(C_6F_5)_3$ in $MeNO_2$ under ambient atmosphere; interestingly, in this case the Lewis acid $B(C_6F_5)_3$ absorbs water to generate $[(C_6F_5)_3B(OH_2)_n]$, which then acts as a Brønsted acid (Dryzhakov and Moran, 2016; Dryzhakov et al., 2017; Beringhelli et al., 2001). Despite the general progress in this area, the development of alternative catalytic methods based on boron-based Lewis acids as fluorophilic electrophiles for the activation of inert C(sp^3)-F bonds in saturated fluorocarbons remains highly desirable.

The modification of C(sp^3)-F bonds in aliphatic *gem*-difluoroalkanes is much more difficult than in the corresponding saturated monofluorocarbons because the strength of C-F bonds increases with the number of geminal fluorine atoms (Hamel and Paquin, 2018; O'Hagan, 2008). Indeed, in most cases, the fluorine moiety in *gem*-difluorides is found at activated benzylic, allylic, or propargylic positions (Figure 1A), as well as at the α-position of a carbonyl group or in *gem*-difluorocyclopropanes (Hamel and Paquin, 2018; Song et al., 2017). In a representative example of unactivated aliphatic *gem*-difluoroalkanes from Ozerov and coworkers, the ethylation of 1,1-difluorocyclopentane was observed together with the reduction side product cyclopentane (67:33) by gas chromatography-mass spectrometry analysis as one special case (Figure 1B) by using catalytic amounts of $[Et_2Al][HCB_{11}H_5Br_6]$ in the presence of an excess amount of $AlEt_3$ (Gu et al., 2009). In 2018, the group of Young reported two examples for the monodefluorination of an acyclic aliphatic *gem*-difluoromethyl group in 1,1-difluoroethane and 1,1-difluorodecane: using FLPs obtained from $Al(C_6F_5)_3$ and P(*o*-Tol)$_3$, the α-fluoroalkylphosphonium salts were generated in moderate yield (Figure 1C) (Mandal et al., 2018). Building upon our long-standing interest in the activation of inert C(sp^3)-F bonds (Haufe et al., 2012; Tanaka et al., 2016; Cui et al., 2018), we discovered in this study that a catalytic amount of the Lewis acid $B(C_6F_5)_3$ activated the C(sp^3)-F bond in aliphatic *gem*-difluoroalkanes of type **1** to selectively generate substituted 2,2′,3,3′-tetrahydro-1,1′-spirobiindenes (**2**) and monofluorinated alkenes (**3**) in good yield (Figure 1D). Moreover, this method was also used for the functionalization of the C(sp^3)-F bond in secondary monofluoroalkanes to C(sp^3)-C(sp^3) bonds in good yield. The use of hydrogen-bonding hexafluoro-2-propanol (HFIP) as the solvent was essential to induce the catalyst turnover for the defluorinative Friedel-Crafts alkylation.

RESULTS AND DISCUSSION

Optimization Study

Initially, based on the pioneering work of Olah and Stephan on the activation of C(sp^3)-F bonds in saturated monofluoroalkanes initiated by boron-based Lewis acids (Olah et al., 1957; Olah and Kuhn, 1964; Caputo and Stephan, 2012), we attempted to use stoichiometric amounts of $BF_3{\cdot}OEt_2$ and $B(C_6F_5)_3$ (2.2 equiv.) to induce cleavage of the C(sp^3)-F bond in unactivated *gem*-difluoroalkane **1a** (Table 1, entries 1 and 2). Although no reaction was detected upon using $BF_3{\cdot}OEt_2$, the use of a stoichiometric amount of $B(C_6F_5)_3$ afforded 2,2′,3,3′-tetrahydro-1,1′-spirobi[indene] **2a** in 85% yield. This result was very encouraging, considering that examples of the activation of C(sp^3)-F bonds in inert aliphatic *gem*-difluoroalkanes are extremely rare (Figure 1) (Gu et al., 2009; Mandal et al., 2018). Subsequently, we turned our attention to the development of a catalytic $B(C_6F_5)_3$-induced cascade intramolecular Friedel-Crafts cyclization (Lan et al., 2006; Birman et al., 1999; Li et al., 2016; Zheng et al., 2018).

Recently, HFIP has attracted considerable attention as a solvent to promote Friedel-Crafts acylations and alkylations (Motiwala et al., 2015; Vekariya and Aube, 2016; Tang et al., 2018) owing to its unique properties, which include reduced nucleophilicity, a strong propensity to engage as a hydrogen-bonding donor, and the ability to stabilize cationic intermediates (Colomer et al., 2017). Indeed, intermolecular Friedel-Crafts alkylations by hydrogen-bonding interactions between activated benzylic C-F bonds and HFIP in the

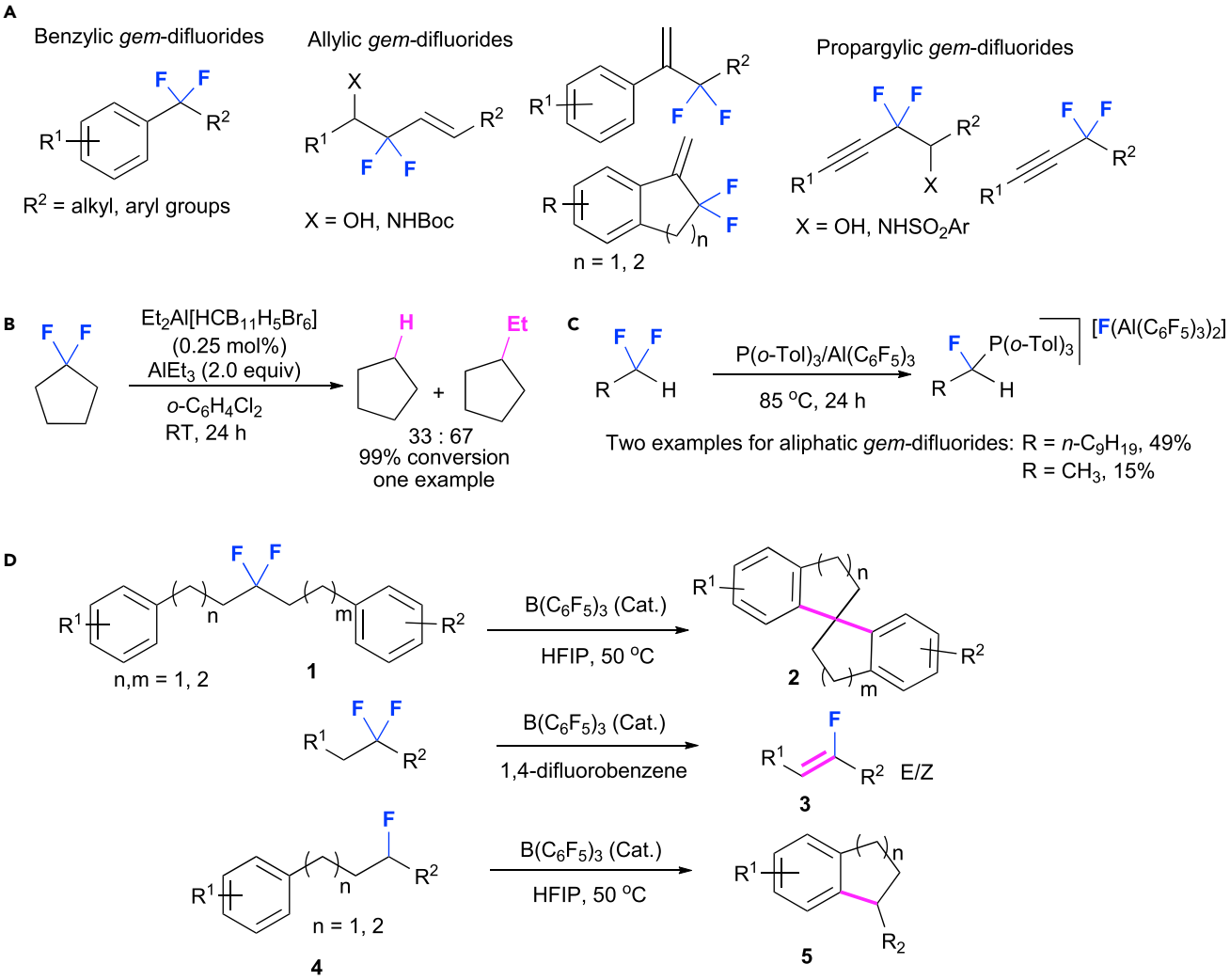


Figure 1. Activation of C(sp^3)-F Bonds in *gem*-Difluoroalkanes

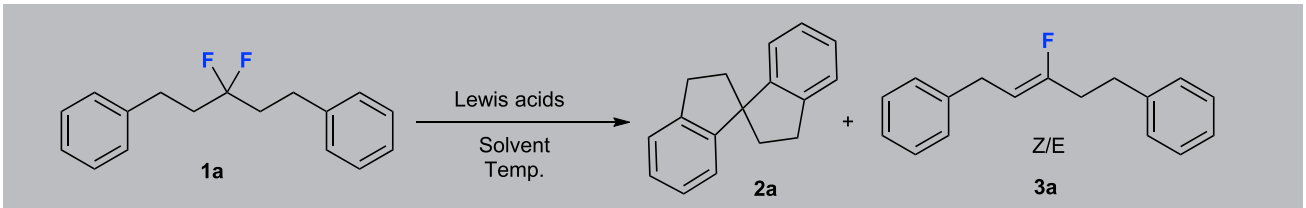
(A) Activated benzylic, allylic, and propargylic *gem*-difluoroalkanes.

(B) $[Et_2Al][HCB_{11}H_5Br_6]$-induced C($sp^3$)-F functionalization of 1,1-difluorocyclopentane.

(C) Monodefluorination of a *gem*-difluoromethyl group initiated by the FLP $Al(C_6F_5)_3/P(o\text{-}Tol)_3$.

(D) Synthesis of spirobiindanes, monofluoroalkenes, and 1-alkyl-2,3-dihydro-1H-indenes via a $B(C_6F_5)_3$-catalyzed activation of C(sp^3)-F bonds (this work).

absence of any Lewis or Brønsted acids has been reported by Paquin and co-workers (Champagne et al., 2014, 2015). Using a combination of the hydrogen-bonding-donor solvent HFIP and $B(C_6F_5)_3$ (20 mol %) in the absence of any silicon-based trapping reagent, afforded the defluorinative Friedel-Crafts-type product **2a** in 75% yield (Table 1, entry 5). It is worth noting here that moisture was strictly excluded in our method, owing to the hydrolysis of **1a** under acidic conditions. When using "wet" HFIP, i.e., HFIP that was used as purchased under an atmosphere of argon without any precaution to exclude moisture, the corresponding hydrolysis product (1,5-diphenylpentan-3-one) was observed as the major product and **2a** was obtained in only 27% yield (Table 1, entry 7). Upon adding H_2O (2.2 equiv.), the intramolecular Friedel-Crafts transformation was completely suppressed, and the quantitative hydrolysis into a ketone was confirmed instead when prolonging the reaction time (Table 1, entry 9). Other reaction parameters, such as solvents, concentration, and temperature, were also investigated (for more details, see also Table S1). Finally, we were able to identify the optimal reaction conditions for the synthesis of spirobiindanes **2**: $B(C_6F_5)_3$ (20 mol%) in HFIP (0.05 M) at 50°C for 2 h (Table 1, entry 8). In the absence of $B(C_6F_5)_3$, or when using other hydrogen-bonding solvents such as iPrOH, CF_3CH_2OH, or $(CF_3)_2PhOH$, the reaction did not proceed (Table 1, entries 10–13). Unexpected results were obtained using 1,2-dichlorobenzene as the solvent. Indeed, the formation of



Entry	Lewis Acids (Equiv.)	Solvent (0.1M)	T (°C)	t (h)	Yields (%)	
					2a	3a[a]
1	$BF_3{\cdot}OEt_2$ (2.2)	CH_2Cl_2	RT	30	NR	NR
2	$B(C_6F_5)_3$ (2.2)	CH_2Cl_2	RT	30	85	0
3	$B(C_6F_5)_3$ (0.2)	CH_2Cl_2	RT	30	Trace	0
4	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$	RT	17	28	0
5	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$	50	2	75	0
6	$B(C_6F_5)_3$ (0.1)	$(CF_3)_2CHOH$	50	20	16	0
7	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[b]	50	2	27	0
8	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[c]	50	2	84	0
9	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[c] H_2O (2.2 equiv.)	50	2	0[d]	0[d]
10	$B(C_6F_5)_3$ (0.2)	iPrOH[c]	50	2	NR	NR
11	$B(C_6F_5)_3$ (0.2)	CF_3CH_2OH[c]	50	2	NR	NR
12	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2PhOH$[c]	50	2	NR	NR
13	–	$(CF_3)_2CHOH$[c]	50	2	NR	NR
14	$B(C_6F_5)_3$ (0.2)	*o*-$C_6H_4Cl_2$	160	3	0	64
15	$B(C_6F_5)_3$ (0.1)	*o*-$C_6H_4Cl_2$	160	3	0	30
16	–	*o*-$C_6H_4Cl_2$	160	3	NR	NR
17	$B(C_6F_5)_3$ (0.2)	*o*-$C_6H_4Cl_2$	220	3	0	81[e]
18	$B(C_6F_5)_3$ (0.2)	*p*-$C_6H_4F_2$	reflux	3	0	75
19	$B(C_6F_5)_3$ (0.2)	*p*-$C_6H_4F_2$	reflux	24	0	87[f]

Table 1. Optimization of the Selective Cleavage of C(sp^3)-F Bonds in Aliphatic *gem*-Difluoroalkanes

RT, room temperature; NR, no reaction.

[a]Determined by ^{19}F NMR analysis using $PhCF_3$ as the internal standard.

[b]$(CF_3)_2CHOH$ was used as purchased without any precaution to exclude moisture. The hydrolysis product 1,5-diphenylpentan-3-one was observed as the major product.

[c]Concentration: 0.05 M.

[d]The hydrolysis product 1,5-diphenylpentan-3-one was obtained in quantitative yield after 12 h at 50°C.

[e]*Z*/*E* = 7.3:1.

[f]*Z*/*E* = 7.1:1.

monofluoroalkene **3a**, derived from the defluorination/elimination sequence of aliphatic *gem*-difluoroalkane **1a** (Yanai et al., 2011; Yang et al., 2013; Surmont et al., 2009; Li et al., 2018; Drouin et al., 2018), was observed in good yield when conducting the reaction at very high temperatures (Table 1, entries 14, 17). Specifically, when the temperature was increased from 160°C to 220°C in a sealed tube, the yield of the elimination product **3a** increased from 64% to 81% with good stereoselectivity (*Z*/*E* = 7.3:1), whereas no reaction was detected in the absence of $B(C_6F_5)_3$ (entry 16). These results indicate that the increased reaction temperature is beneficial for the defluorination/elimination. Furthermore, after screening the reaction

conditions to find an acceptable reaction temperature (for further details, see also Table S2) in the presence of $B(C_6F_5)_3$ (20 mol%), we discovered that stirring the reaction mixture in refluxing 1,4-difluorobenzene (boiling point 88–89°C) instead of using harsher reaction conditions (220°C) afforded **3a** in 87% yield with good stereoselectivity (*Z*/*E* = 7.1:1).

Substrate Scope

With the optimized reaction conditions in hand, we explored the substrate scope (Figure 2). First, we examined intramolecular Friedel-Crafts reactions as shown in Figure 2A. For aliphatic *gem*-difluoroalkanes substituted with alkyl groups (**1a**-**h**), good to high yields were observed; in particular, *gem*-difluoroalkane **1f**, bearing a methyl group at the C2 position of the benzene ring, generated the desired product (**2f**) in high yield (up to 90%). However, for methoxy-substituted *gem*-difluorides **1c** and **1g**, substantially lower yields were observed due to the presence of the electron-rich heteroatom acting as a Lewis base that is able to provide lone electron pairs to interact with the Lewis acid catalyst. This unexpected donor-acceptor interaction between the oxygen atom and the electron-deficient boron moiety hampered the fluoride abstraction via the $C(sp^3)$-F→$B(C_6F_5)_3$ interaction, leading to decreased yields. In contrast, *gem*-difluoroalkanes (**1i**-**m**) with a halogen (F, Cl, Br) group at the C2 or C4 position afforded acceptable yields (57–79%), whereas dialkyl-substituted substrates **1n** and **1o** furnished good to excellent product yields (up to 95%). Naphthyl-type 2,2′,3,3′-tetrahydro-1,1′-spirobi[cyclopenta[b]naphthalene] **2p** was also prepared in good yield (84%). Moreover, 4,6-dimethyl-2,2′,3,3′-tetrahydro-1,1′-spirobi[indene] **2q** and 4-bromo-4′-methyl-2,2′,3,3′-tetrahydro-1,1′-spirobi[indene] **2r** were generated in moderate yields (42% and 59%, respectively). Six-membered spiro-compound **2s** and five- or six-membered spiro-compound **2t** were also prepared in high yields (up to 90%). As shown in Figure 2B, the substrate scope for the defluorination/elimination process was explored. When using symmetric substrates, the desired acyclic monofluoroalkenes (**3a**, **3e**-**g**, **3j**-**k**, **3n**-**o**, **3u**, and **3aa**) were prepared in moderate to good yields (up to 84%) with good *Z*/*E* stereocontrol. Specifically, substrates with electron-donating substituents such as methyl, methoxy, or dialkyl groups on the benzene ring gave the desired products (**3e**-**g** and **3n**-**o**) in moderate to good yields (51%–70%) in refluxing 1,4-difluorobenzene. Halogen groups were well tolerated in the elimination transformation, although an unexpected decrease in yield (38%) was observed for the preparation of bromo-substituted **3j**, albeit that the stereocontrol was high (*Z*/*E* = 25:1). In addition, benzylic *gem*-difluoroalkanes afforded **3bb** and **3cc** in merely low to moderate yields (41% and 25%, respectively), and only the *Z*-isomer is formed, even though the fluorinated moiety is located at the activated position and was thus expected to be removed more easily. For cyclic *gem*-difluoroalkanes (Strobach and Boswell, 1971), the formation of six-membered substrates was favored, i.e., **3dd** and **3ee** were prepared in 80% and 64% yield, respectively. Furthermore, the defluorination of large-ring-type *gem*-difluoroalkanes proceeded smoothly to afford the corresponding cyclic monofluoroalkenes **3gg** and **3hh** in good yields, albeit that the *Z*/*E* selectivity was low.

$B(C_6F_5)_3$ Catalyzed Friedel-Crafts Reactions of Secondary Aliphatic Fluorides

Although the cleavage of the $C(sp^3)$-F bond in unactivated aliphatic monofluorides was expected to be easier than in the corresponding saturated *gem*-difluoroalkanes, the Friedel-Crafts alkylation of secondary monofluorinated alkanes was less successful (Hamel and Paquin, 2018; Stahl et al., 2013). Under the previously established optimal reaction conditions for the synthesis of spirobiindanes **2**, using 20 mol % $B(C_6F_5)_3$ in HFIP, an intramolecular defluorinative cyclization of secondary fluorocarbon **4a** was observed in good yield (90%; Figure 3A, entry 1). Subsequently, upon decreasing the catalyst loading to 2 mol %, the desired 1-phenethyl-2,3-dihydro-1H-indene (**5a**) was smoothly prepared (91%; Figure 3A, entry 5). However, in the absence of a Lewis-acidic catalyst, a reaction was not observed (Figure 3A, entry 6), which demonstrates the crucial importance of $B(C_6F_5)_3$ for abstraction of fluoride. Subsequently, we explored the substrate scope (Figure 3B) of this reaction. With long-chain symmetric substrates with electron-donating groups (**4a**-**f**), good to high yields were observed (70%–93%). Conversely, yields for the intramolecular Friedel-Crafts transformation of halogen-substituted monofluoroalkanes **5g**-**j** were a bit lower (68%–80%). Similarly, 2,3-dimethyl- and 2,4-dimethyl-substituted **4k** and **4l** were converted into the cyclic products **5k** and **5l** in 50% and 67% yield, respectively, whereas the naphthyl-type product **5m** was obtained in 79% yield. Miscellaneous monofluorides **4n**-**p** furnished the desired alkyl-substituted indanes in moderate to good yields (44%–91%). Six-membered ring products **5r** and **5s** were also prepared in 82%–85% yield. However, benzylic secondary monofluoride **4q** furnished 1-phenyl-2,3-dihydro-1H-indene (**5q**) in merely 29% yield. It should be noted that an increased yield (46%) for the synthesis of

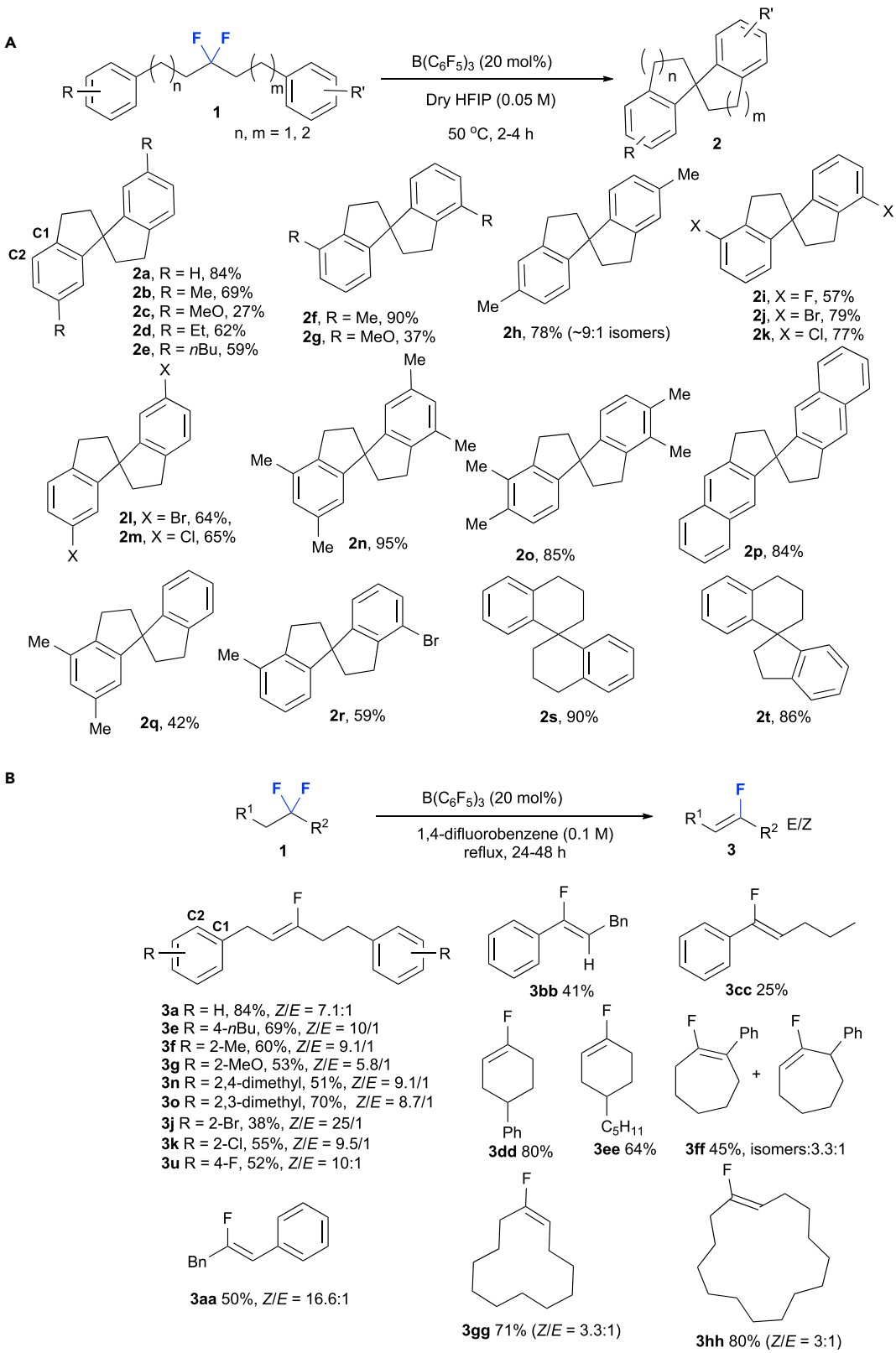
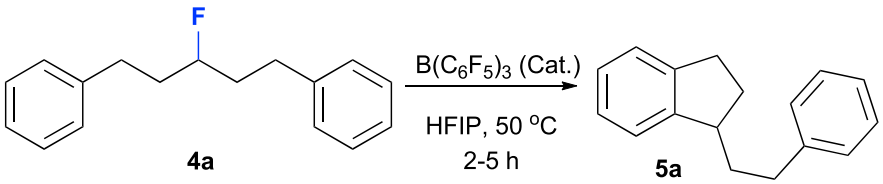


Figure 2. Substrate Scope of the Defluorination of Aliphatic *gem*-Difluoroalkanes to Afford Spirobiindanes 2 and Monofluoroalkenes 3

(A) Intramolecular Friedel-Crafts reactions.

(B) Defluorination/elimination reactions.

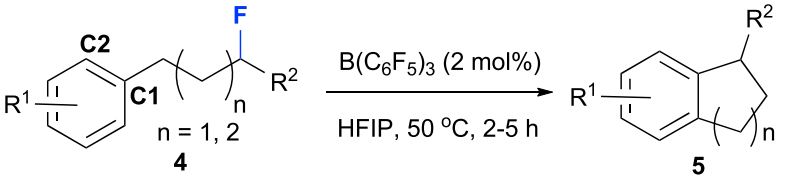
A

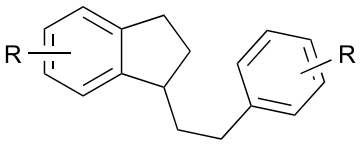


Entry	$B(C_6F_5)_3$ (mol%)	HFIP (M)	Time (h)	Yields* (%)
1	20	0.05	2	90
2	10	0.05	2	93
3	10	0.1	3	78
4	5	0.05	5	92
5	2	0.05	5	91
6	0	0.05	12	0

* Isolated yields

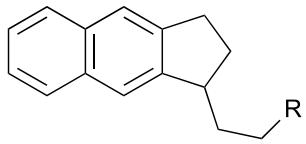
B



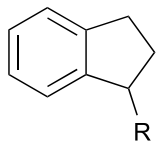


5a R =H, 91%
5b R = 2-Me, 85%
5c R = 4-Me, 90%
5d R = 4-Et, 93%
5e R = 4-*n*Bu, 86%
5f R = 4-MeO,70%

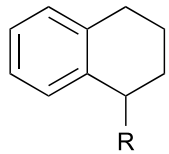
5g R = 2-Br, 80%
5h R = 2-Cl, 75%
5i R = 4-F, 68%
5j R = 2-F, 68%
5k R = 2,4-dimethyl, 50%
5l R = 2,3-dimethyl, 67%



5m R = 2-naphthyl, 79%



5n R = Bn, 91%
5o R = *n*Bu, 62%
5p R = isopentyl, 44%
5q R = Ph, 29% (46%)*



5r R = Et, 82%
5s R = *n*Bu, 85%

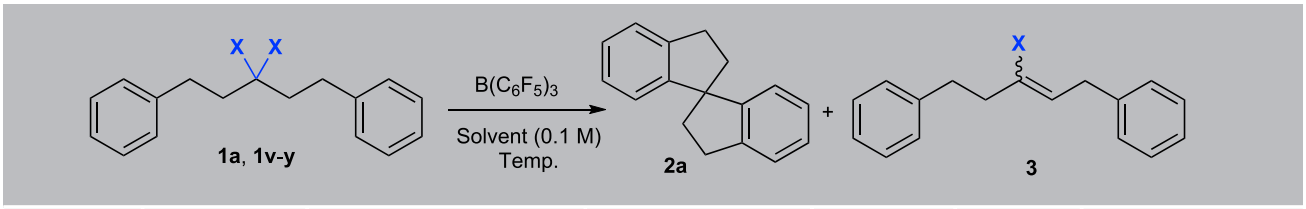
* **5q** was prepared in 46% yield only in HFIP without $B(C_6F_5)_3$

Figure 3. Intramolecular Friedel-Crafts Cyclization of Secondary Monofluoroalkanes 4

(A) Optimization of reaction conditions.

(B) Substrate Scope.

5q was observed in the absence of a Lewis acid catalyst. Although intermolecular Friedel-Crafts alkylations of primary benzylic monofluoride using excess amounts of electrophiles in HFIP in the absence of acids have already been reported (Champagne et al., 2014), we have observed the first example of the functionalization of a secondary benzylic monofluoride such as **4q** in the absence of any catalyst or additive (Figure 3B).



Entry	X[a]	Lewis Acids (Equiv.)	Solvent (0.1M)	T (°C)	t (h)	Yields (%)	
						2a	3a[b]
1	F	$B(C_6F_5)_3$ (2.2)	CH_2Cl_2	RT	30	85	0
2	**1v** (C=O)	$B(C_6F_5)_3$ (2.2)	CH_2Cl_2	RT	30	NR	NR
3	MeO	$B(C_6F_5)_3$ (2.2)	CH_2Cl_2	RT	30	ND[c]	ND[c]
4	Cl	$B(C_6F_5)_3$ (2.2)	CH_2Cl_2	RT	30	NR	NR
5	Br	$B(C_6F_5)_3$ (2.2)	CH_2Cl_2	RT	30	0	29
6	F	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[d]	50	2	84	0
7	**1v** (C=O)	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[d]	50	2	NR	NR
8	MeO	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[d]	50	2	NR	NR
9	Cl	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[d]	50	2	0	63
10	Cl	–	$(CF_3)_2CHOH$[d]	50	2	0	61
11	Br	$B(C_6F_5)_3$ (0.2)	$(CF_3)_2CHOH$[d]	50	2	0	81
12	Br	–	$(CF_3)_2CHOH$[d]	50	2	0	86
13	F	$B(C_6F_5)_3$ (0.2)	*p*-$C_6H_4F_2$	reflux	24	0	87
14	MeO	$B(C_6F_5)_3$ (0.2)	*p*-$C_6H_4F_2$	reflux	24	0	0
15	Cl	$B(C_6F_5)_3$ (0.2)	*p*-$C_6H_4F_2$	reflux	24	0	Trace
16	Br	$B(C_6F_5)_3$ (0.2)	*p*-$C_6H_4F_2$	reflux	24	0	9

Table 2. Control Experiments to Probe Reaction Mechanism

NR, no reaction; RT, room temperature; ND, not detected.

[a]Substrates: 1,5-diphenylpentan-3-one (**1v**), (3,3-dimethoxypentane-1,5-diyl)dibenzene (**1w**), (3,3-dichloropentane-1,5-diyl)dibenzene (**1x**), and (3,3-dibromopentane-1,5-diyl)dibenzene (**1y**).

[b]NMR yields.

[c]Complex mixture.

[d]Concentration (0.05 M).

Mechanistic Investigations

We found that the donor-acceptor interactions between the fluorine moiety of $C(sp^3)$-F bonds in unactivated aliphatic *gem*-difluoroalkanes, a weak Lewis base, and the strong Lewis acid $B(C_6F_5)_3$, is of vital importance; this is emphasized by the overwhelming chemoselectivity for the Friedel-Crafts cyclization of $C(sp^3)$-F bonds rather than the cleavage of weaker C-halogen bonds or the removal of other good leaving groups (Table 2). Specifically, when using a stoichiometric amount of $B(C_6F_5)_3$ (2.2 equiv.) in CH_2Cl_2 at room temperature for 30 h, *gem*-difluoroalkane **1a** afforded only the desired 2,2′,3,3′-tetrahydro-1,1′-spirobi[indene] **2a** in 85% yield, whereas the formation of elimination product **3a** was not observed. In contrast, the intramolecular Friedel-Crafts cyclization was not observed when using 1,5-diphenylpentan-3-one (**1v**), (3,3-dimethoxypentane-1,5-diyl)dibenzene (**1w**), (3,3-dichloropentane-1,5-diyl)dibenzene (**1x**), and (3,3-dibromopentane-1,5-diyl)dibenzene (**1y**) (Table 2, entries 1–5). Although the cleavage of C-OMe bonds of substrate **1w** by $B(C_6F_5)_3$ (2.2 equiv.) was observed, as the electron-rich heteroatom is a good Lewis base, only a complex mixture was found, and the formation of **2a** was not observed (Table 2, entry 3). For the *gem*-dibromoalkane **1y**, the formation of an unexpected elimination product in 29% yield was detected, which was ascribed to the ability of the bromine to act as a good leaving group (Table 2, entry 5). In

addition, under optimized conditions of HFIP, the formation of C(sp^3)-C(sp^3) bonds was only detected for *gem*-difluoroalkane **1a**, but not for the relatively weaker C(sp^3)-OMe, C(sp^3)-Cl, and C(sp^3)-Br bonds (Table 2, entries 6–12). However, the unexpected elimination products (monochloroalkene **3x** and monobromoalkene **3y**) were formed in of 63% and 81% yield, respectively (Table 2, entry 9 and 11). Interestingly, in the absence of $B(C_6F_5)_3$ but still using HFIP as solvent, the yields of elimination products **3x** and **3y** remained essentially unchanged (61% and 86%, respectively). In other words, it is the hydrogen-bonding interaction between HFIP and either the C(sp^3)-Cl or C(sp^3)-Br bonds rather than the interaction with Lewis acids $B(C_6F_5)_3$ that governs the elimination process. Similarly, under the standard reaction conditions for the defluorinative elimination of **1a**, i.e., treatment with $B(C_6F_5)_3$ (20 mol %) in refluxing 1,4-difluorobenzene for 24 h, *gem*-difluoride **1a** afforded the desired monofluorinated olefin **3a** in 87% yield, whereas a reaction was not observed for the corresponding aliphatic halides and ketals, with the exception of (3,3-dibromopentane-1,5-diyl)dibenzene, which afforded the monobromoalkene elimination product in 9% yield (Table 2, entries 13–16). Therefore the synthesis of spirobiindanes and monofluoroalkenes from aliphatic *gem*-difluoroalkanes **1** catalyzed by $B(C_6F_5)_3$ proceeds from a C-F bond activation process.

Based on the results discussed above, a reaction mechanism of C-F bond cleavage induced by the C(sp^3)-F→$B(C_6F_5)_3$ interaction is proposed in Figure 4A. In our opinion, two effects of HFIP favor the intramolecular Friedel-Crafts process. (1) The strong hydrogen-bonding interaction between the hydrogen-bonding donor solvent HFIP and the fluoride anion in $[FB(C_6F_5)_3]^-$ reduces the Brønsted basicity of the fluoride anion (cf. intermediate **III**) (Lee et al., 2016; Liang et al., 2017), which would result in the suppression of the E1-type elimination. Indeed, it has already been reported that the Lewis basicity of the fluoride anion of CsF or tetrabutylammonium fluoride (TBAF) is decreased in tertiary alcohols or urea (Kim et al., 2006, 2008a, 2008b; Pfeifer et al., 2016). For instance, relative to anhydrous TBAF, the TBAF(*t*-BuOH)$_4$ complex significantly favors nucleophilic substitution over elimination pathways (Kim et al., 2008a, 2008b). (2) HFIP, with its high dielectric constant (ε = 15.7) and low nucleophilicity (Colomer et al., 2017), provides additional stabilization for several carbocation intermediates in the intramolecular Friedel-Crafts alkylation (e.g., Figure 4B, **II**, **IV,** and **VI**). In addition, the alternative and probable reaction pathway via further defluorinative cyclization of monofluoroalkene **3** with a C(sp^2)-F bond was ruled out as shown in Figure 4B. This result also indicates that the selective C-F bond activation by $B(C_6F_5)_3$ is limited to C(sp^3)-F bonds. For benzylic secondary monofluoride (1-fluoropropane-1,3-diyl)dibenzene (**4q**), the hydrogen bonding between the benzylic C(sp^3)-F bond and HFIP could enable the heterolytic cleavage of the C-F bond to generate carbonium ion **VIII** in Figure 4C, followed by the formation of the C(sp^3)-C(sp^3) bond. Accordingly, it is reasonable to extrapolate that in the intramolecular cyclization of aliphatic *gem*-difluoroalkanes **1**, the hydrogen-bond interaction enhances the ability of the fluoride to act as a leaving group, thus promoting the generation of carbonium ion **II** via the removal of a fluoride anion at relative low reaction temperatures. Indeed, without HFIP, higher temperatures were beneficial for the defluorinative elimination to generate monofluoroalkene **3**; the yield of **3a** increases from 64% to 81% when the temperature is increased from 160°C to 220°C in 1,2-dichlorobenznene in a sealed tube (Table 1, entries 14 and 17). Therefore, a combination of the hydrogen-bonding donor solvent HFIP and a catalytic amount of $B(C_6F_5)_3$ promotes the cascade intramolecular Friedel-Crafts reactions of *gem*-difluorides **1**. It also should be pointed out that the HF generated *in situ* from Friedel-Crafts cyclization might enhance the hydrogen-bonding interaction with C(sp^3)-F bonds to improve further the ability of fluoride moiety to act as a leaving group, which would benefit the heterolytic cleavage of C(sp^3)-F bonds induced by $B(C_6F_5)_3$. Indeed, the intermolecular Friedel-Crafts reaction of primary benzylic monofluoride was controlled only by hydrogen-bonding effect initiated by HFIP and HF generated *in situ* (Champagne et al., 2014).

In conclusion, the selective cleavage of C(sp^3)-F bonds in unactivated aliphatic *gem*-difluoroalkanes **1** afforded substituted spirobiindanes **2** and monofluoroalkenes **3** in good yields. In addition, the intramolecular Friedel-Crafts cyclization of aliphatic secondary monofluoroalkanes **4** was also described. The C(sp^3)-F→$B(C_6F_5)_3$ interaction was probed by control experiments by the use of the corresponding ketone, ketal, and other halide-substituted derivatives. Accordingly, the combination of the hydrogen-bonding donor solvent HFIP and a catalytic amount of the Lewis acid $B(C_6F_5)_3$ enables the selective functionalization of inert C(sp^3)-F bonds into C(sp^3)-C(sp^3) bonds.

Limitations of the Study

The substrates with electron-withdrawing groups such as CF_3 and nitro groups are not suitable, which is to support the Friedel-Crafts cyclization mechanism in Figure 4A. We also examined more reactive

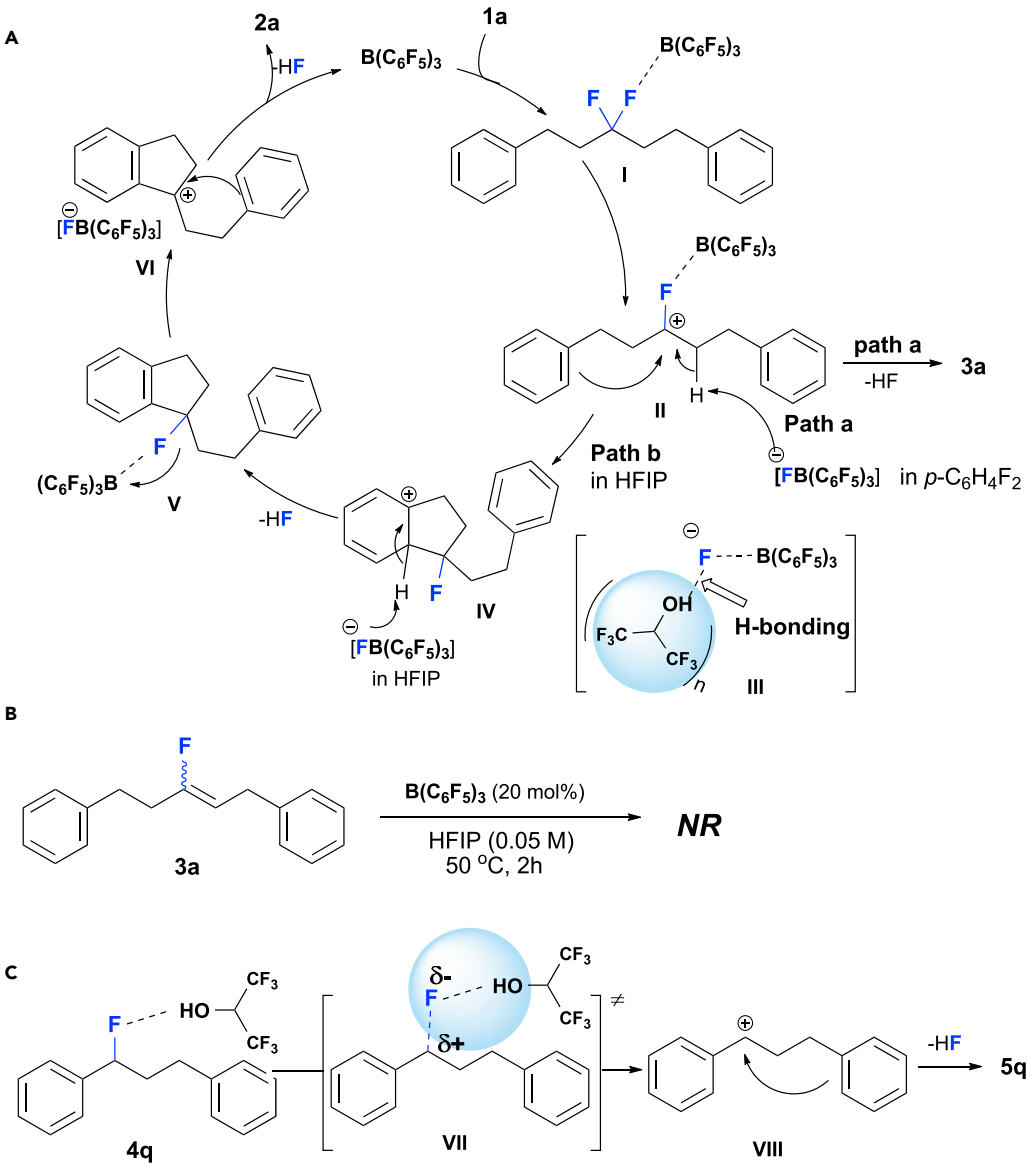


Figure 4. Proposed Reaction Mechanism

(A) Plausible reaction pathway for the defluorinative Friedel-Crafts cyclization and defluorinative elimination of *gem*-difluoroalkanes (**1**).

(B) To rule out the possibility of affording spirobiindanes **2** via the intermediate of monofluoroalkene **3**.

(C) Proposed reaction mechanism for the hydrogen-bonding-induced intramolecular Friedel-Crafts reaction of benzylic monofluoride **4q**.

iodo-substituted substrates, but complex mixtures were obtained. Although the corresponding F-, Cl-, and Br-substituted substrates are acceptable (**2i**, **2j**, **2k**, **2l**, and **2m**, Figure 2A), these results also show some limitation of this method.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.06.018.

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AUTHOR CONTRIBUTIONS

N.S. conceived the concept. J.W. conducted and analyzed the experiments and synthesized compounds. Y.O. prepared the starting materials. N.S. designed and directed the project, and N.S. and J.W. wrote the manuscript. All authors contributed to discussions.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Activation of Saturated Fluorocarbons to Synthesize Spirobiindanes, Monofluoroalkenes, and Indane Derivatives

Jiandong Wang, Yuta Ogawa, and Norio Shibata

Supplemental Figures

Figure S1. ^{1}H NMR spectrum of **2a**, related to **Figure 2**

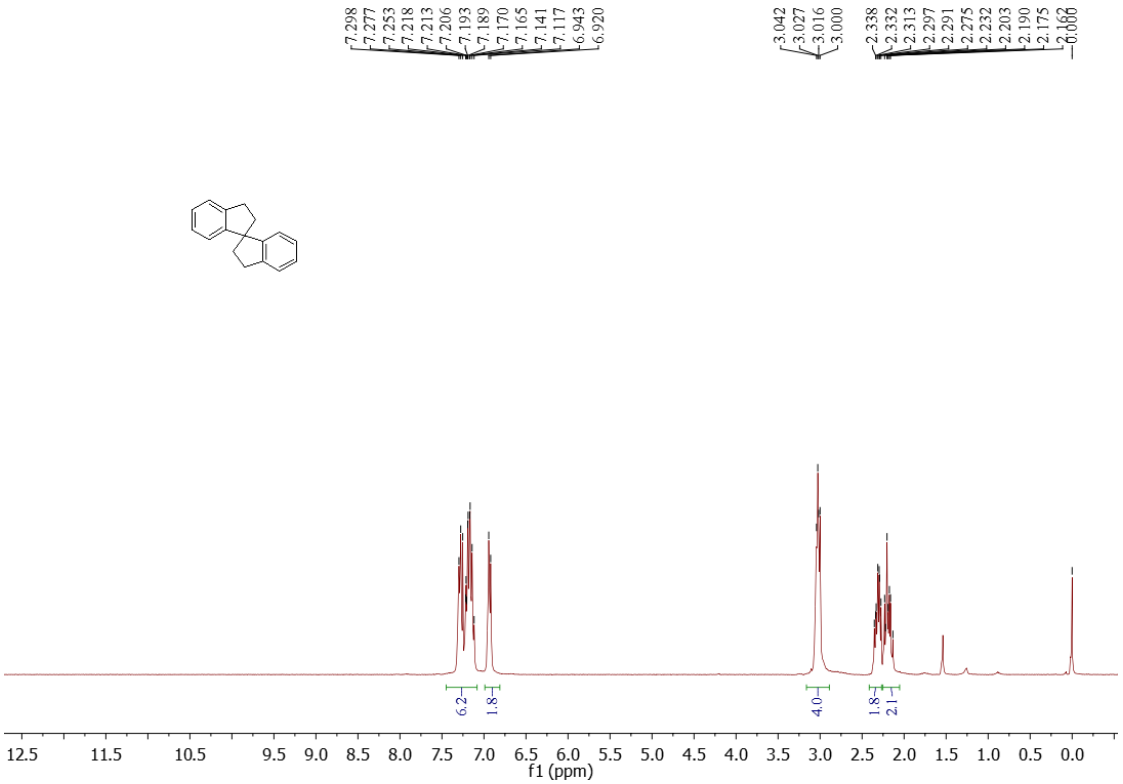


Figure S2. ^{13}C NMR spectrum of **2a**, related to **Figure 2**

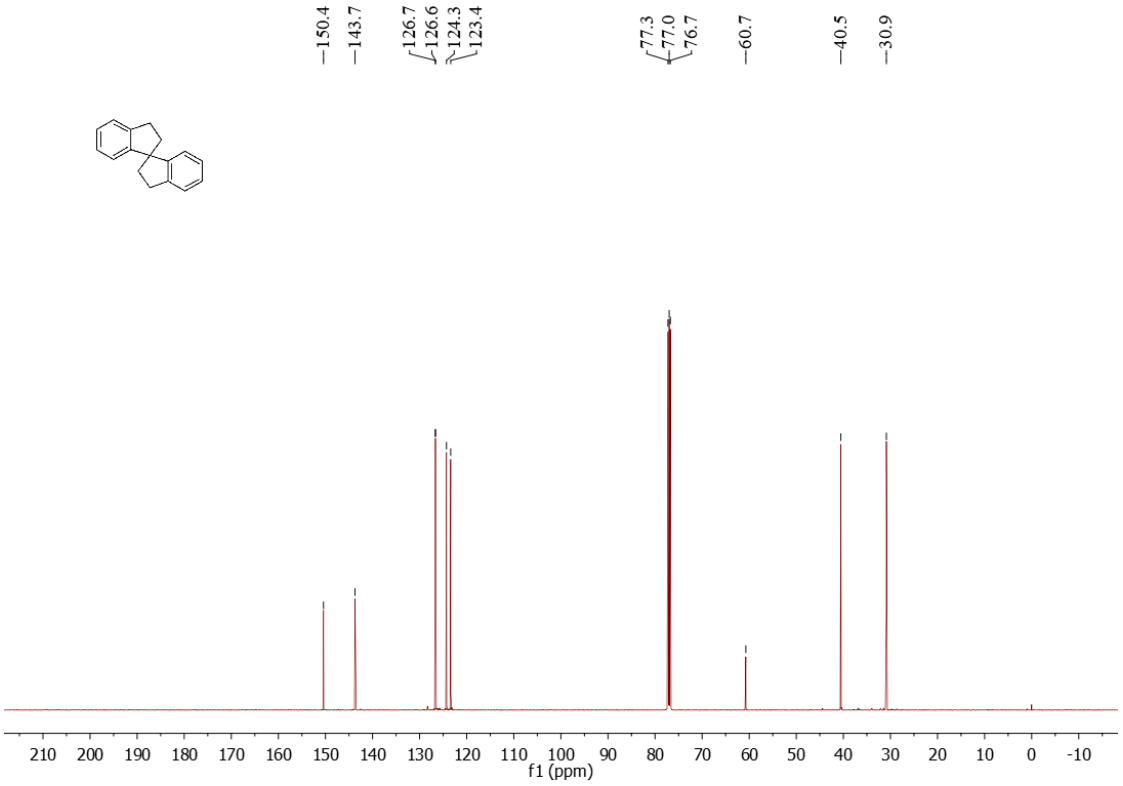


Figure S3. ^{1}H NMR spectrum of **2b**, related to **Figure 2**

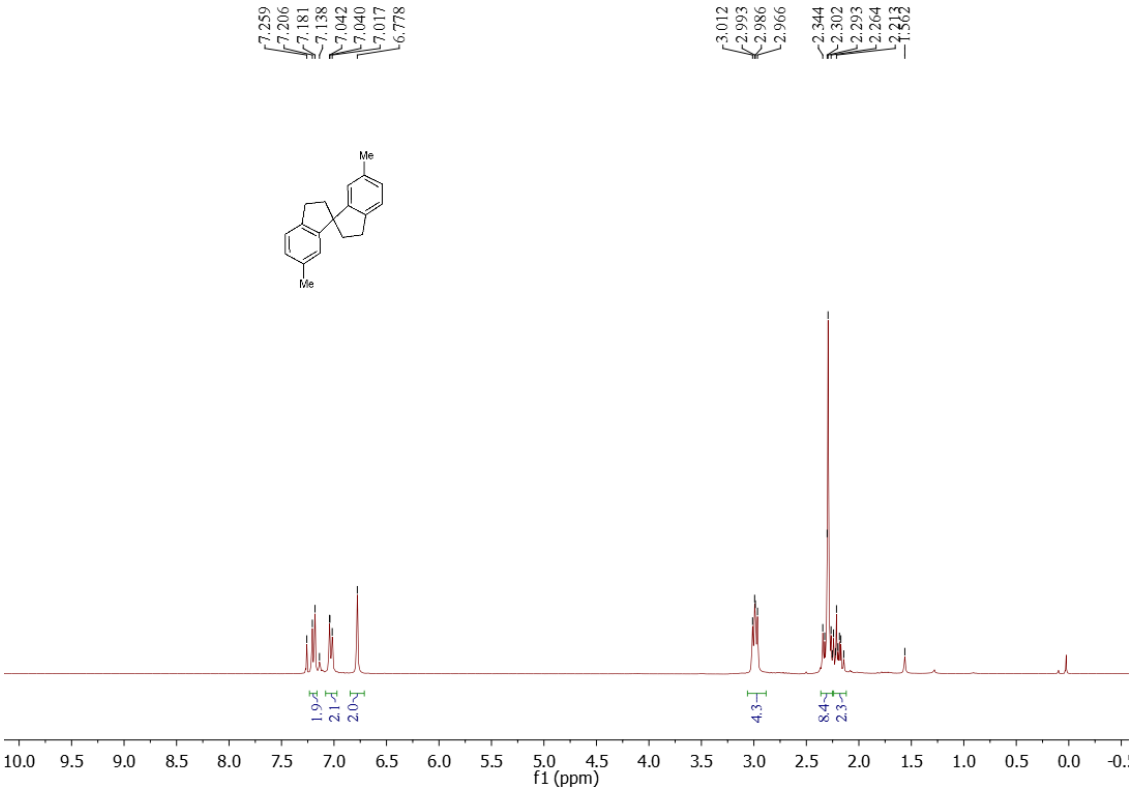


Figure S4. ^{13}C NMR spectrum of **2b**, related to **Figure 2**

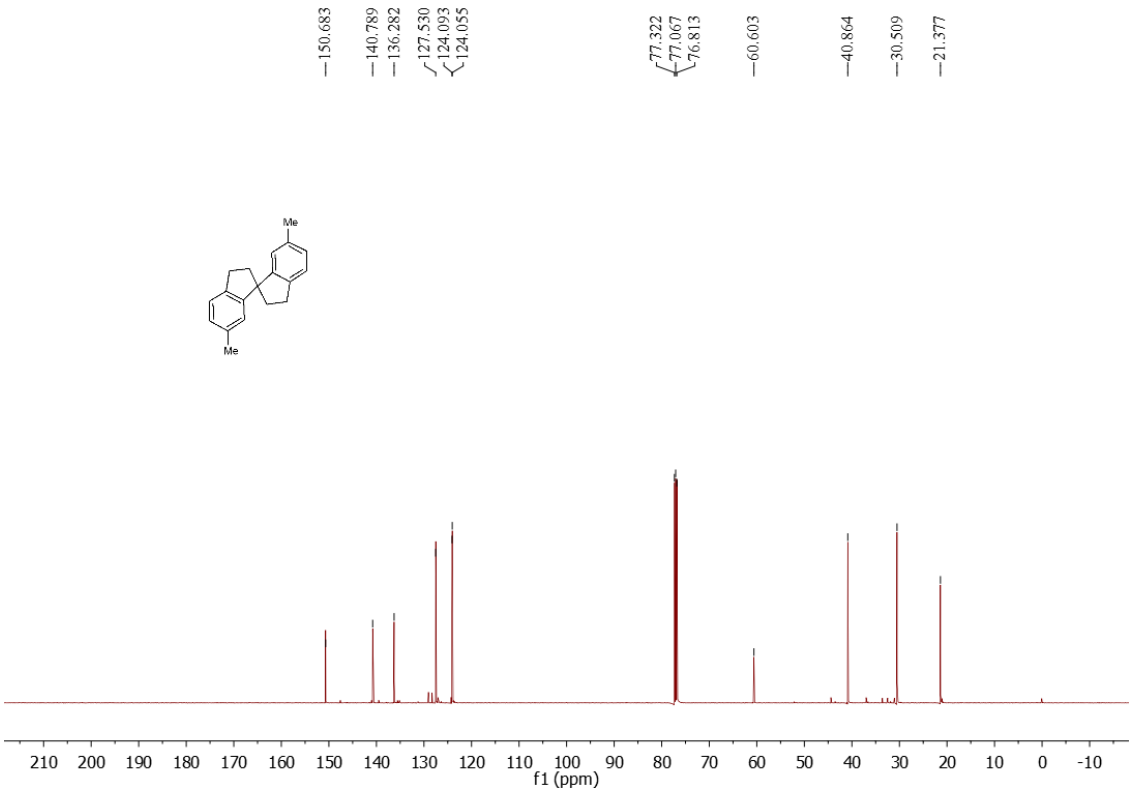


Figure S5. ^{1}H NMR spectrum of **2c**, related to **Figure 2**

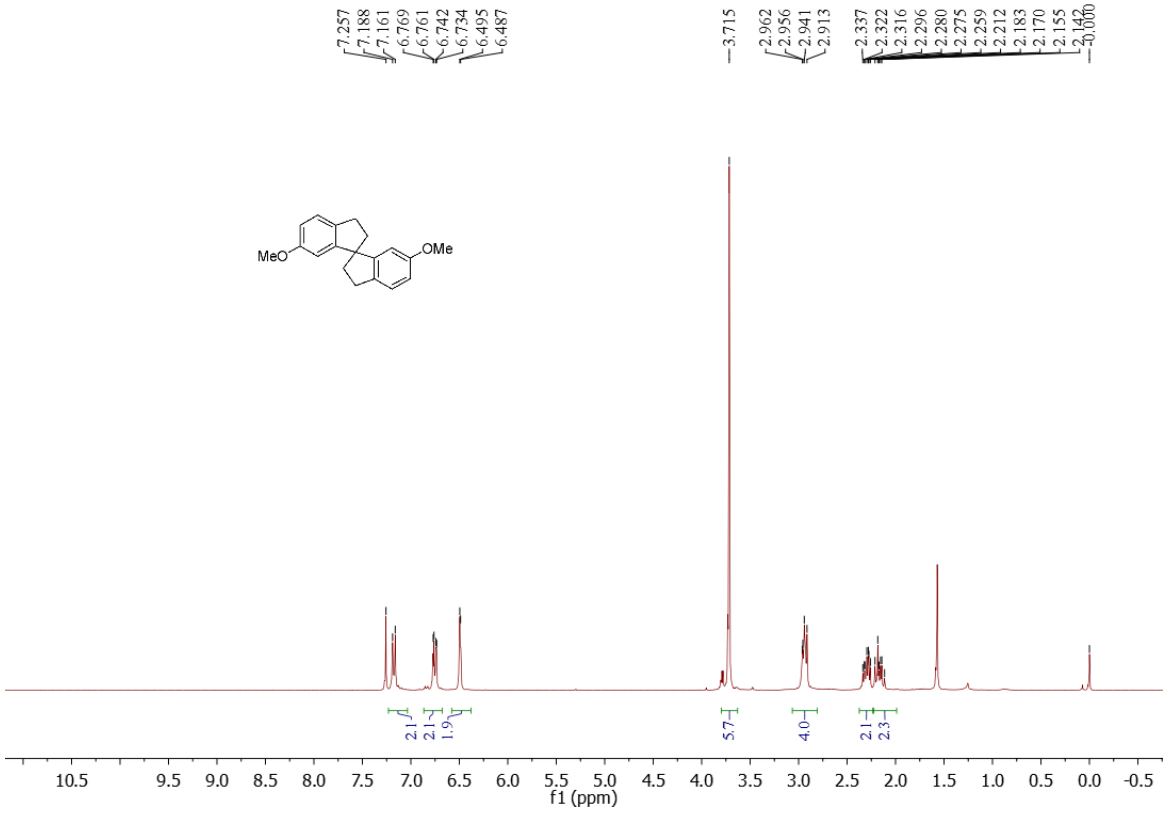


Figure S6. ^{13}C NMR spectrum of **2c**, related to **Figure 2**

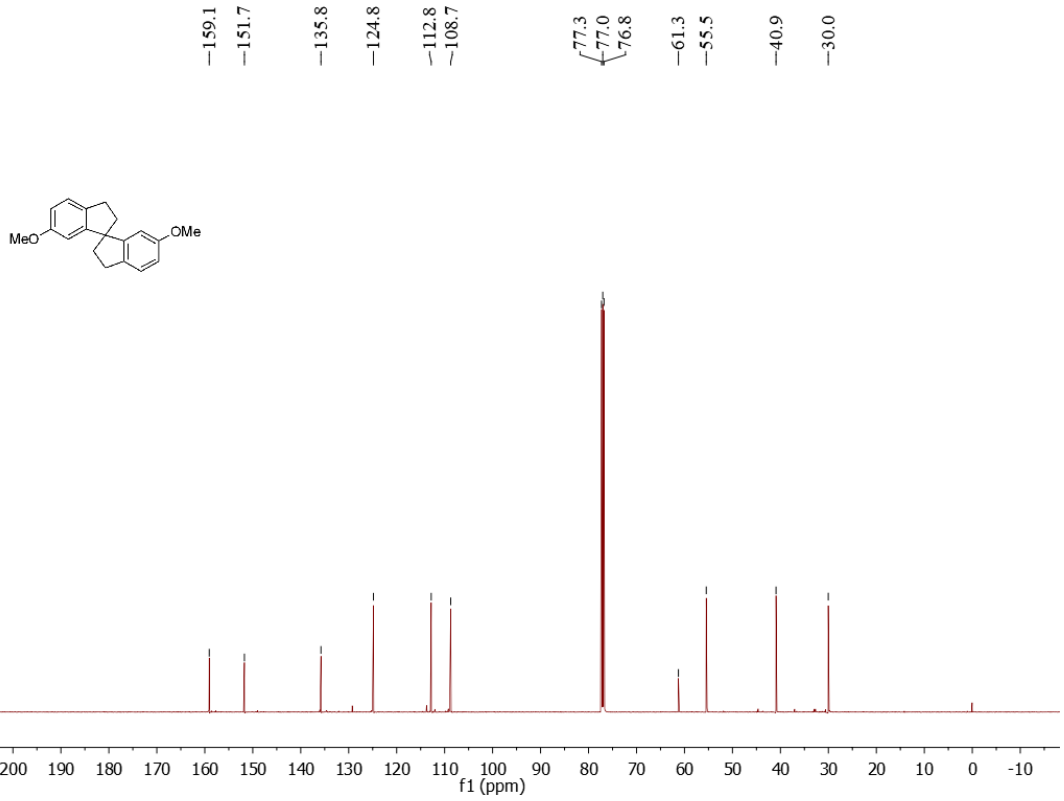


Figure S7. ^{1}H NMR spectrum of **2d**, related to **Figure 2**

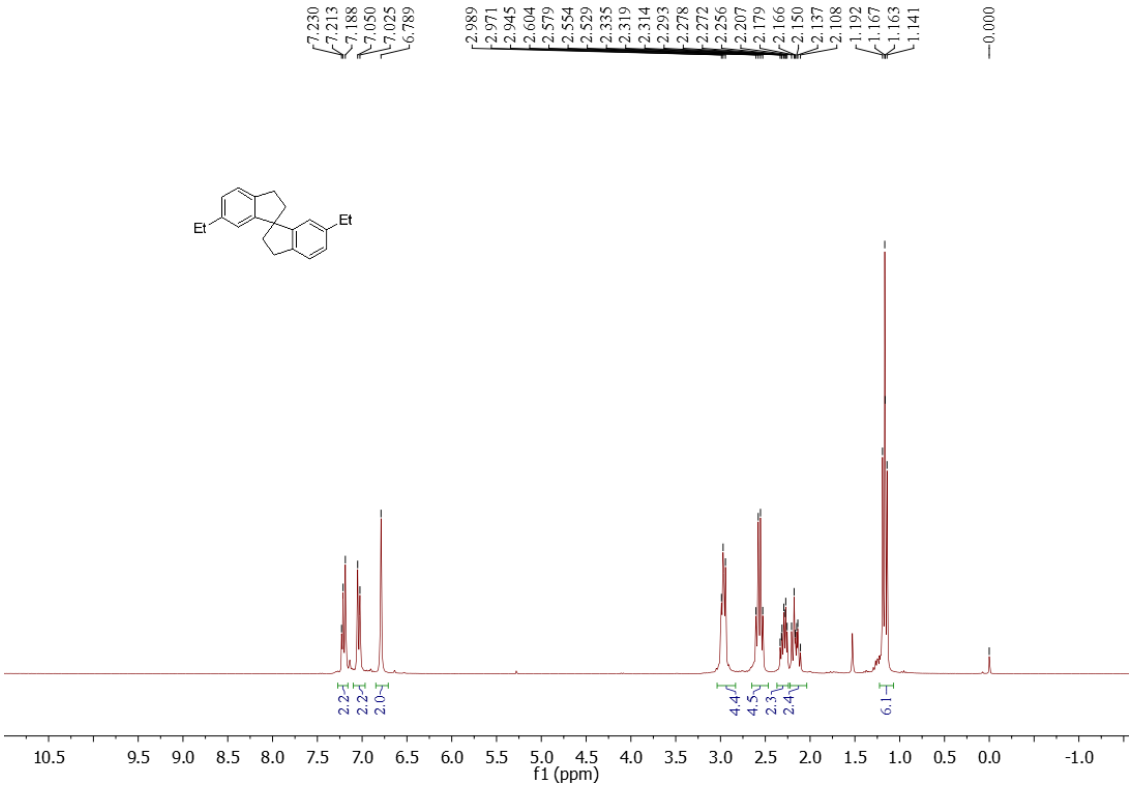


Figure S8. ^{13}C NMR spectrum of **2d**, related to **Figure 2**

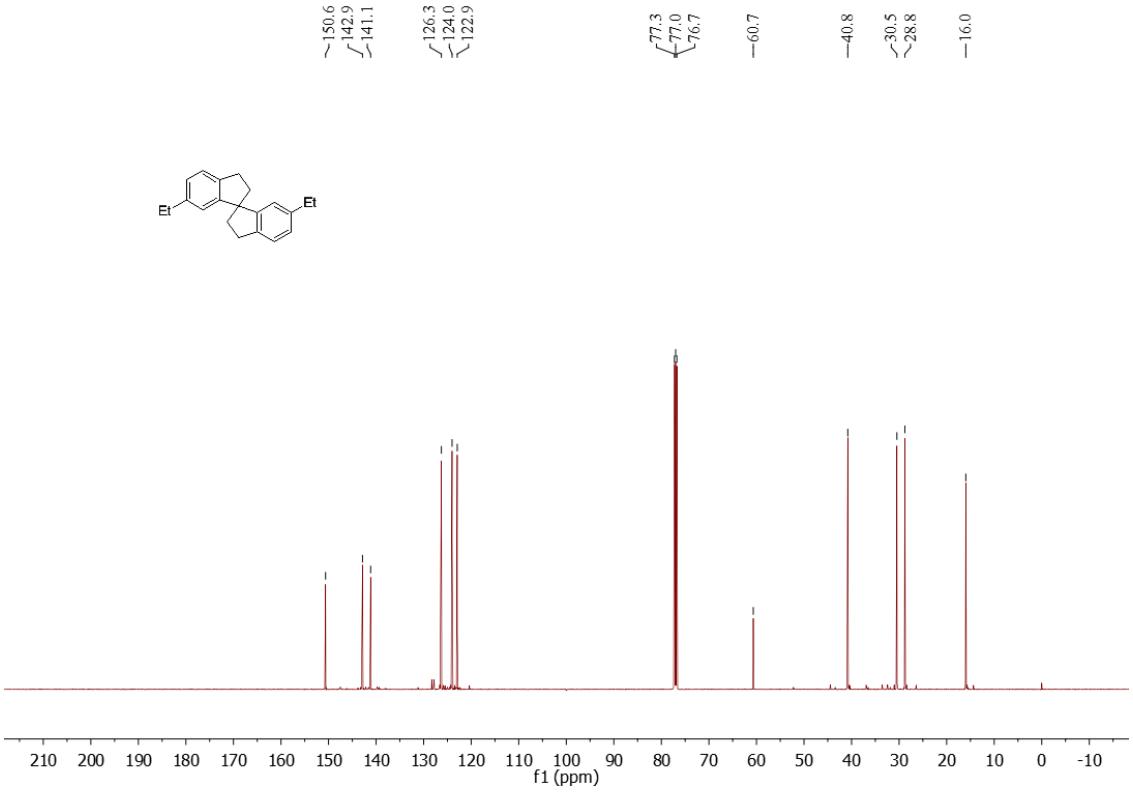


Figure S9. ^{1}H NMR spectrum of **2e**, related to **Figure 2**

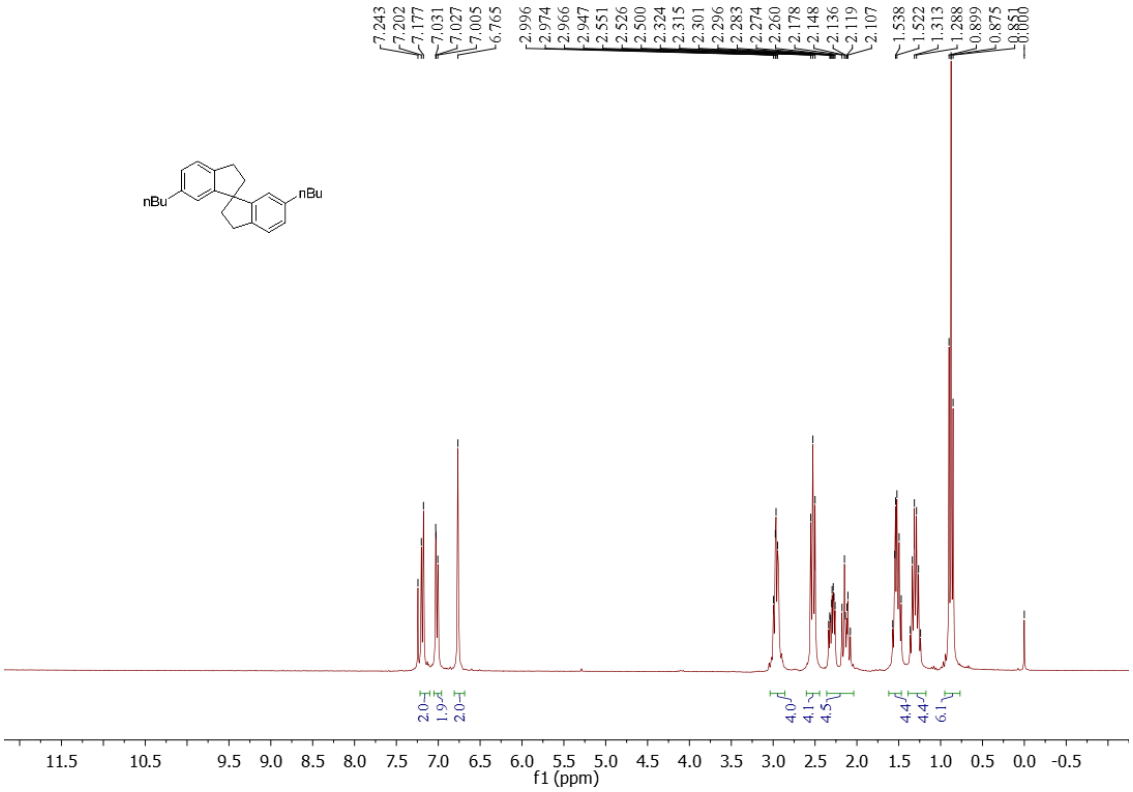


Figure S10. ^{13}C NMR spectrum of **2e**, related to **Figure 2**

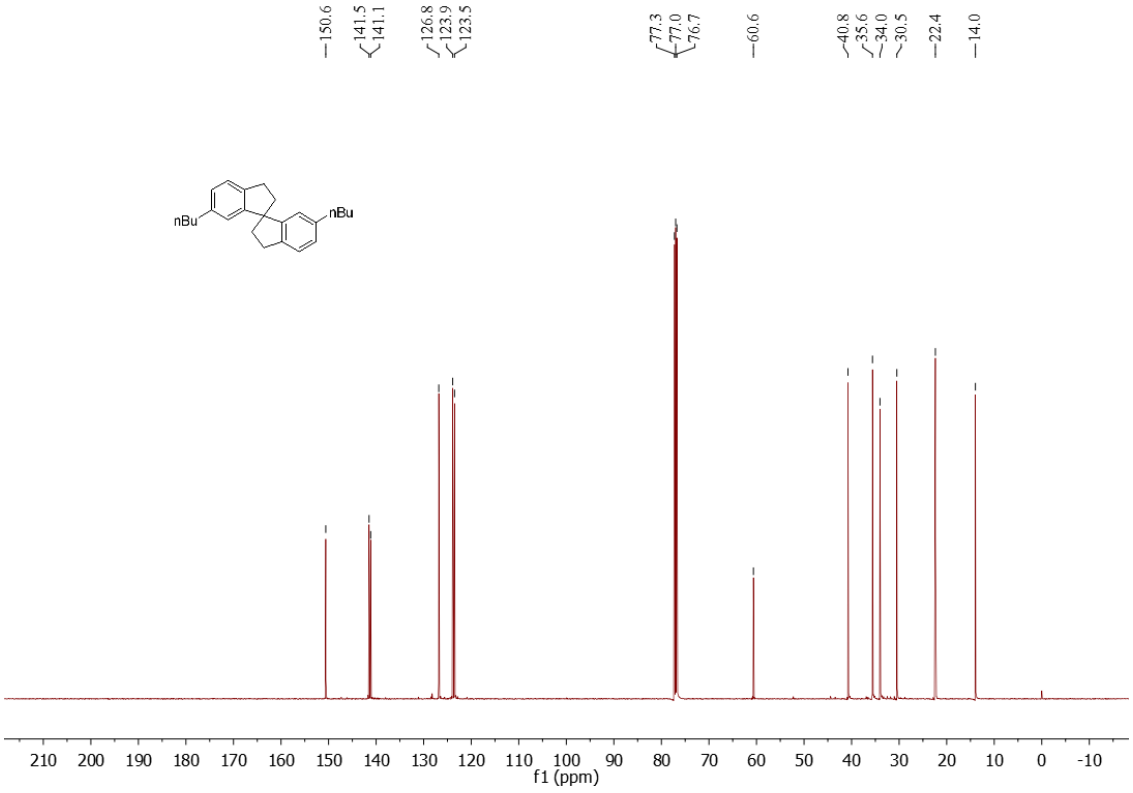


Figure S11. ^{1}H NMR spectrum of **2f**, related to **Figure 2**

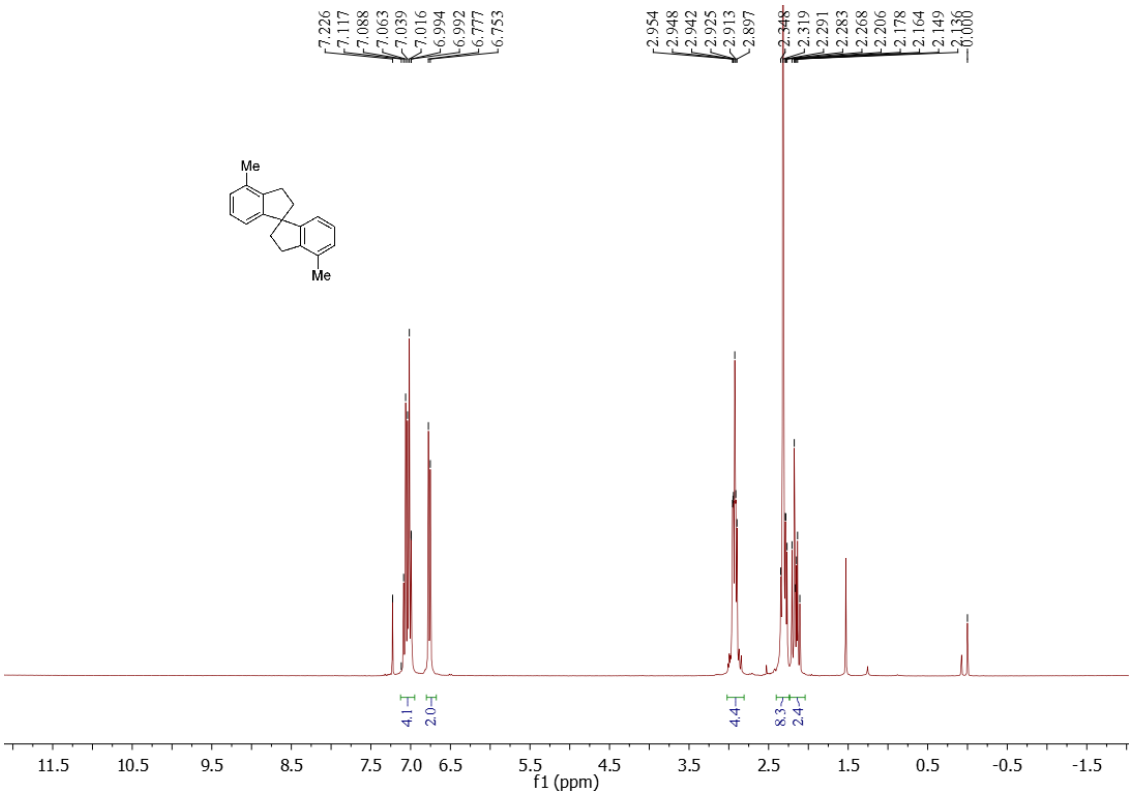


Figure S12. ^{13}C NMR spectrum of **2f**, related to **Figure 2**

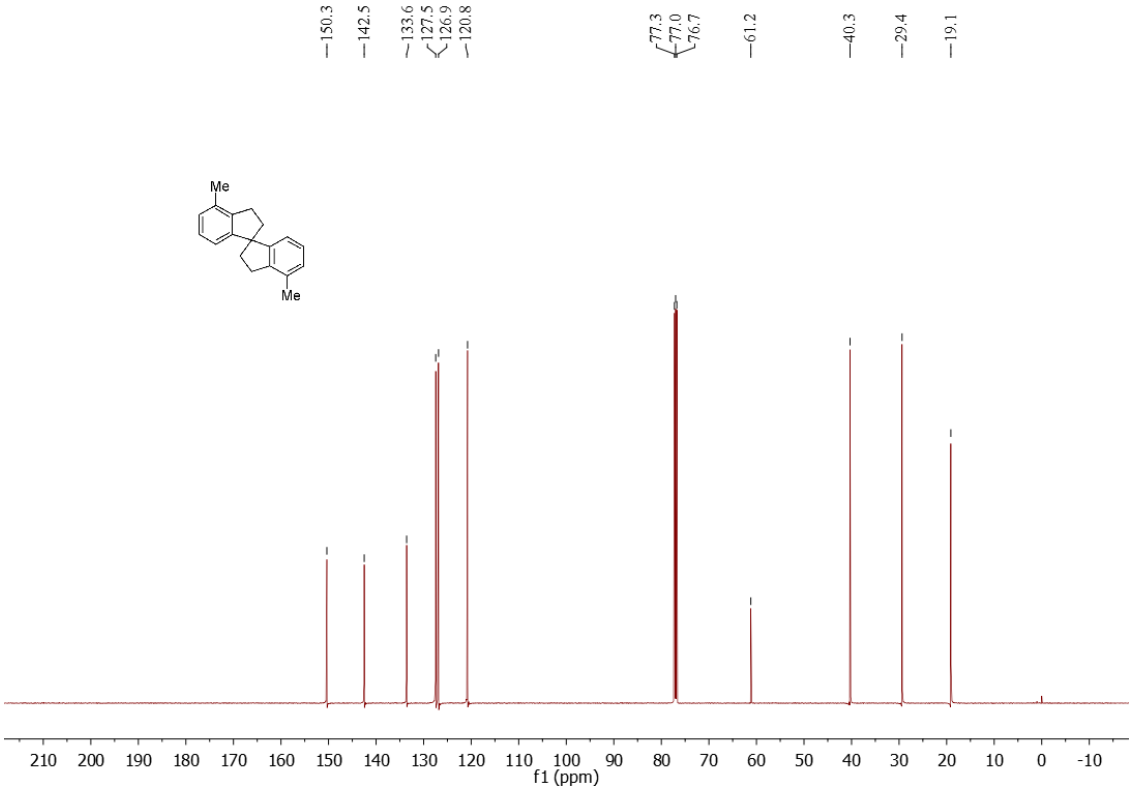


Figure S13. ^{1}H NMR spectrum of **2g**, related to **Figure 2**

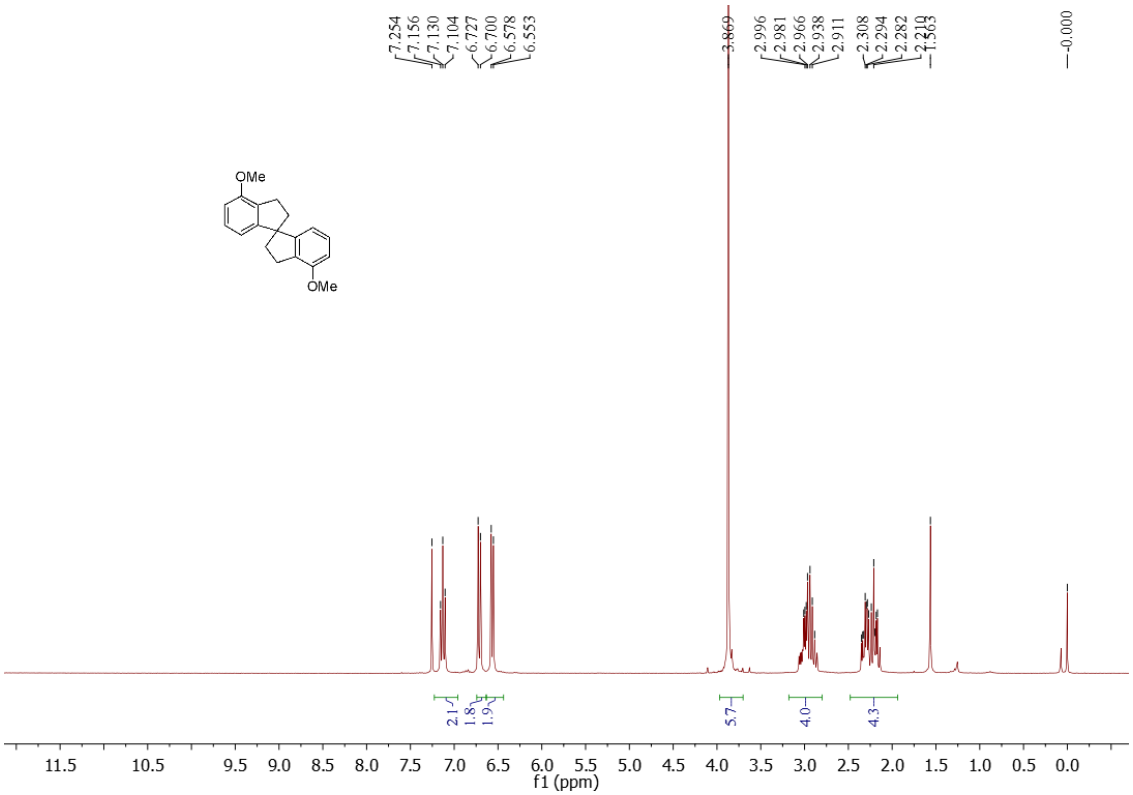


Figure S14. ^{13}C NMR spectrum of **2g**, related to **Figure 2**

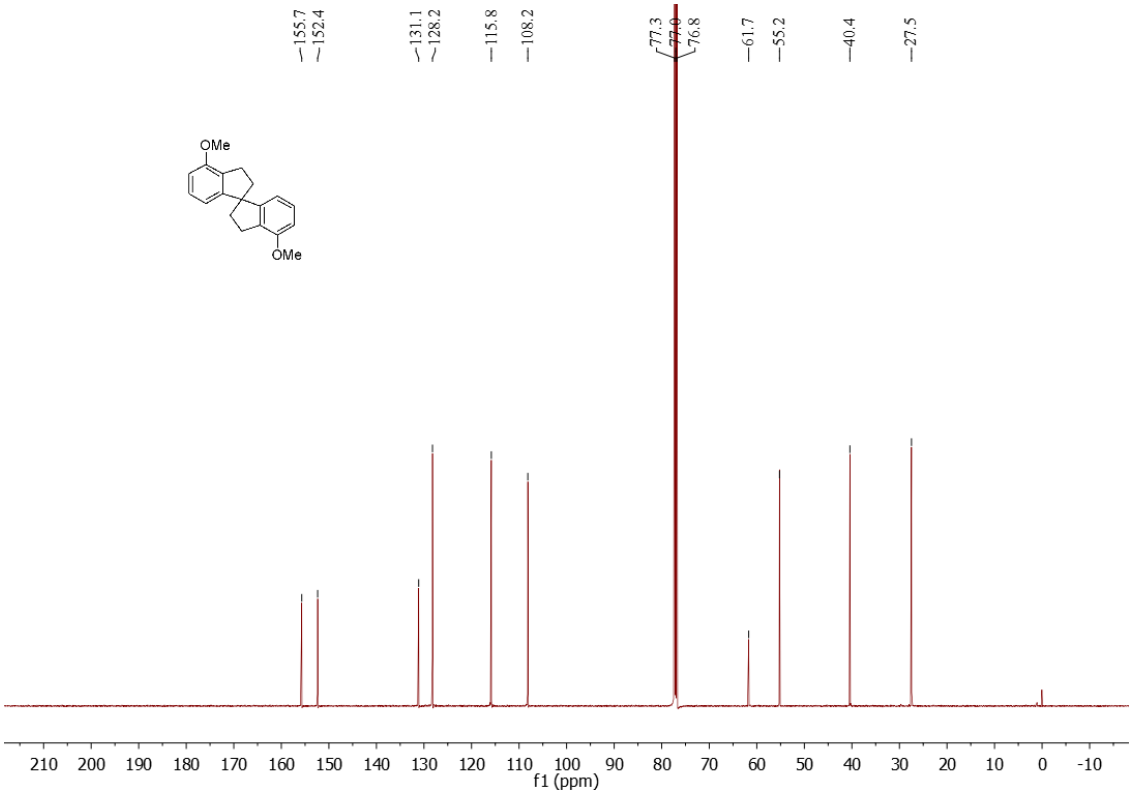


Figure S15. ^{1}H NMR spectrum of **2h**, related to **Figure 2**

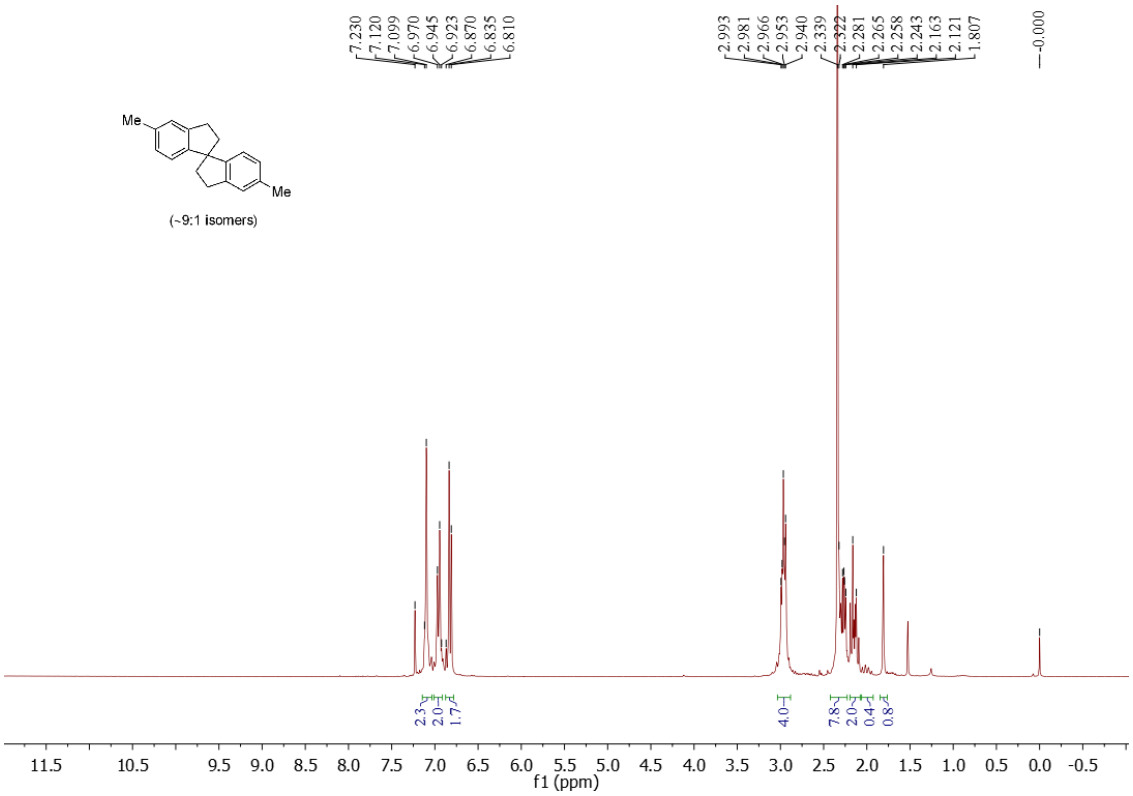


Figure S16. ^{13}C NMR spectrum of **2h**, related to **Figure 2**

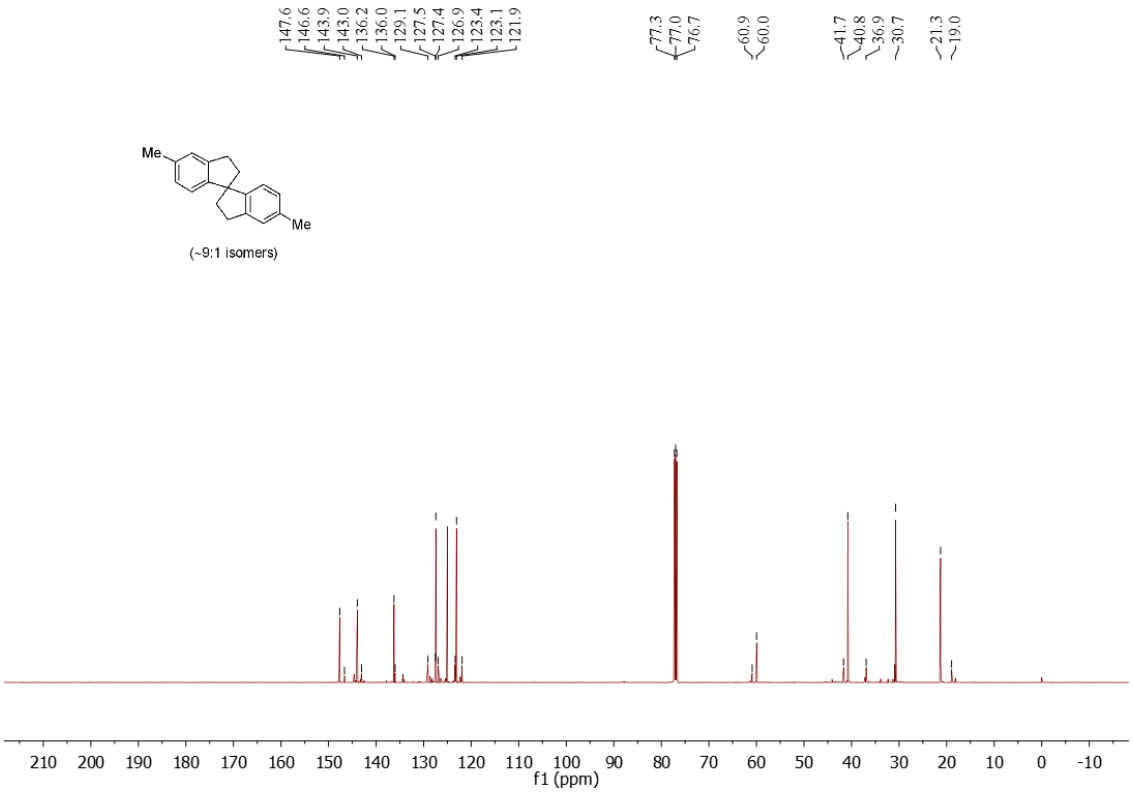


Figure S17. GC-MS analysis of **2h**, related to **Figure 2**

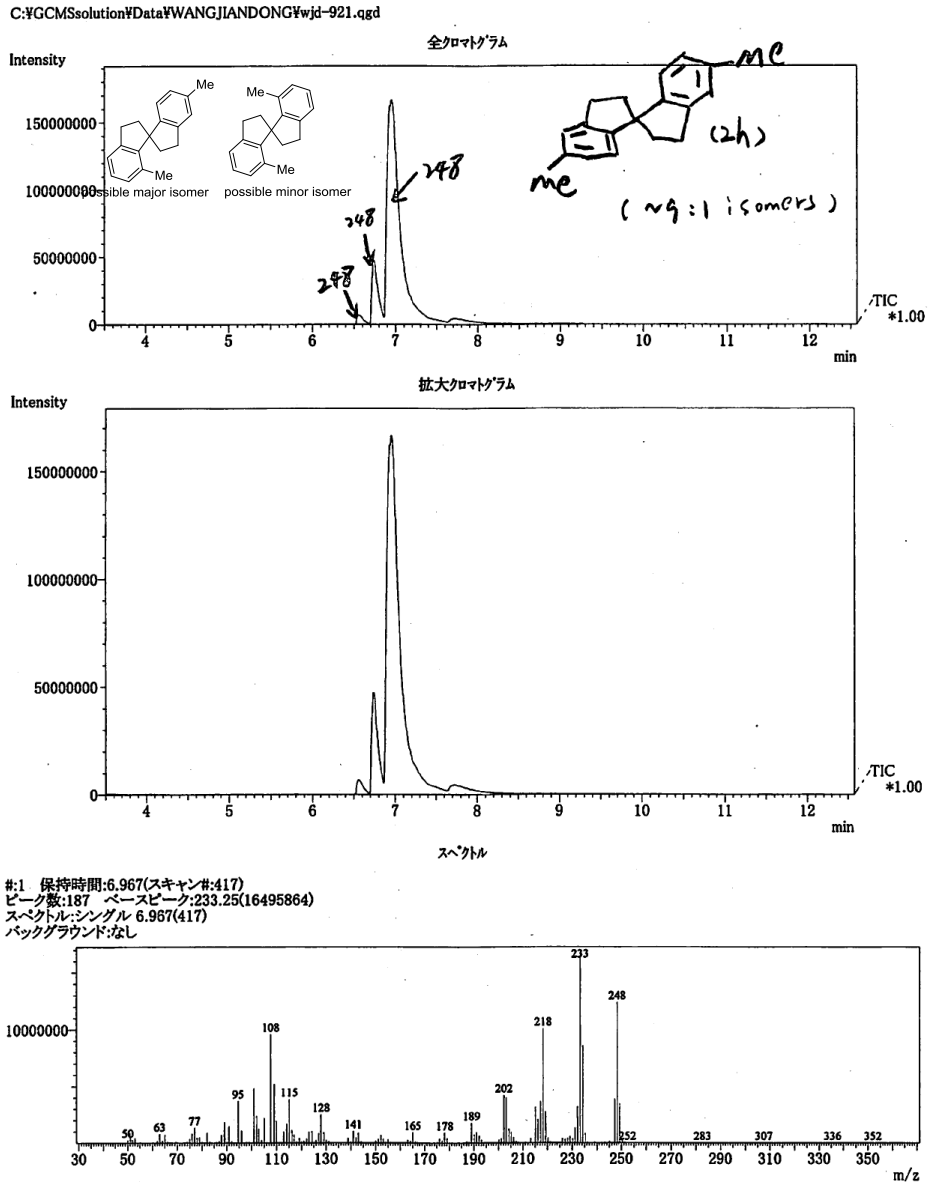


Figure S18. ^{1}H NMR spectrum of **2i**, related to **Figure 2**

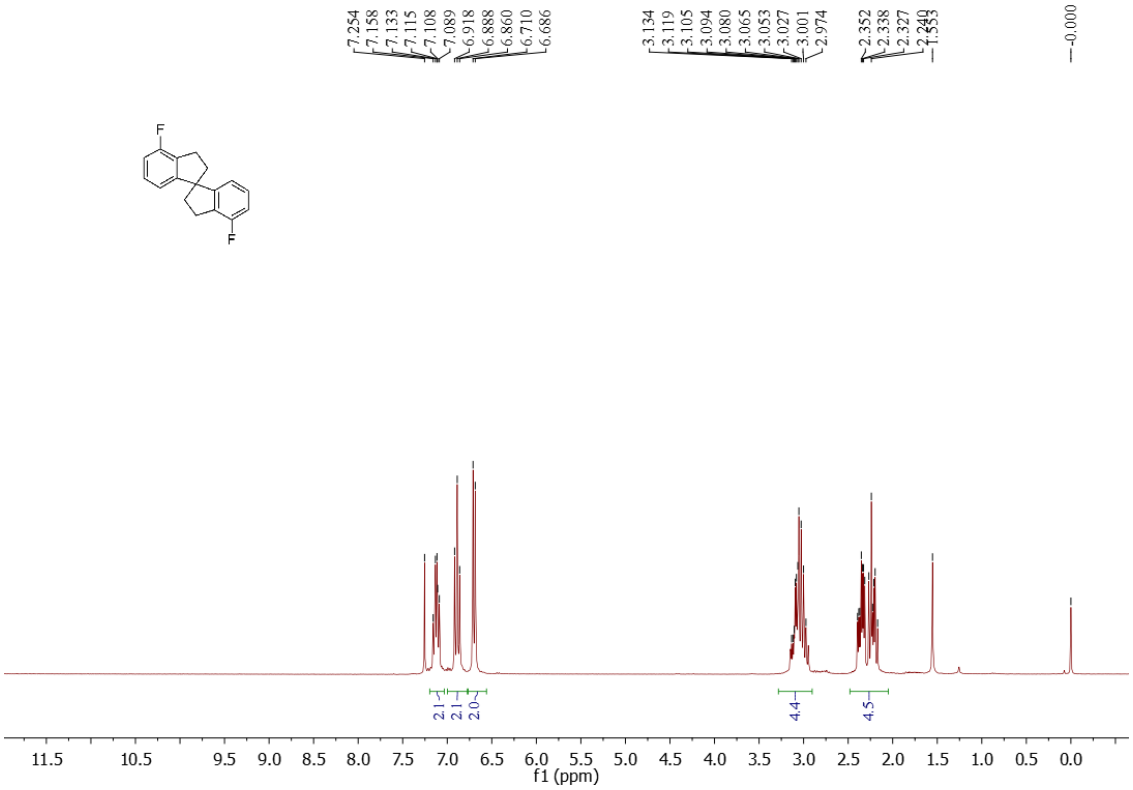


Figure S19. ^{13}C NMR spectrum of **2i**, related to **Figure 2**

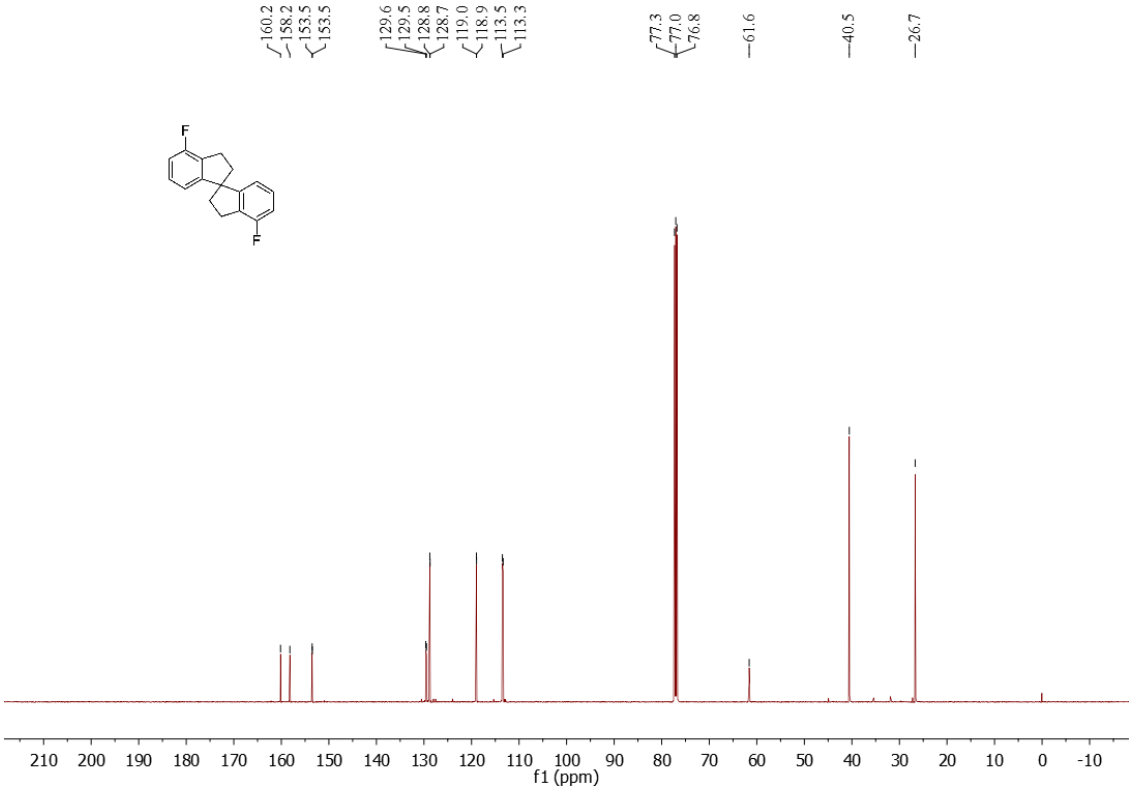


Figure S20. ^{1}H NMR spectrum of **2j**, related to **Figure 2**

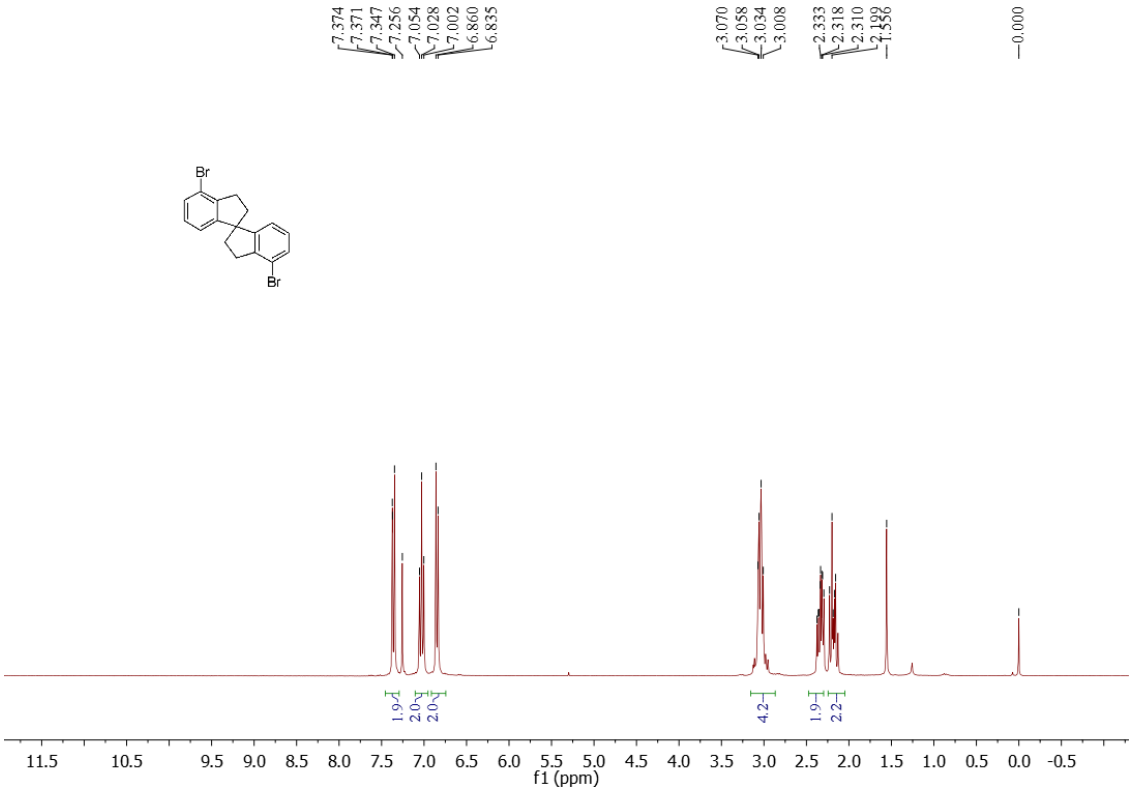


Figure S21. ^{13}C NMR spectrum of **2j**, related to **Figure 2**

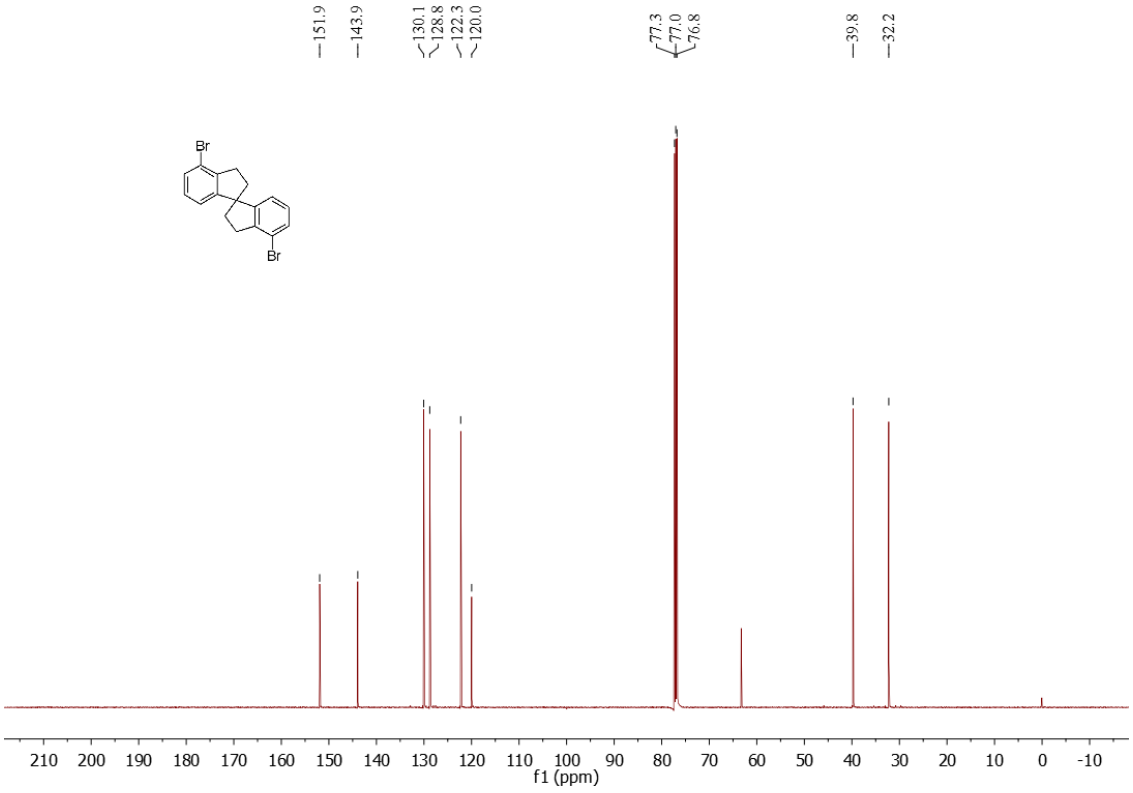


Figure S22. ^{1}H NMR spectrum of **2k**, related to **Figure 2**

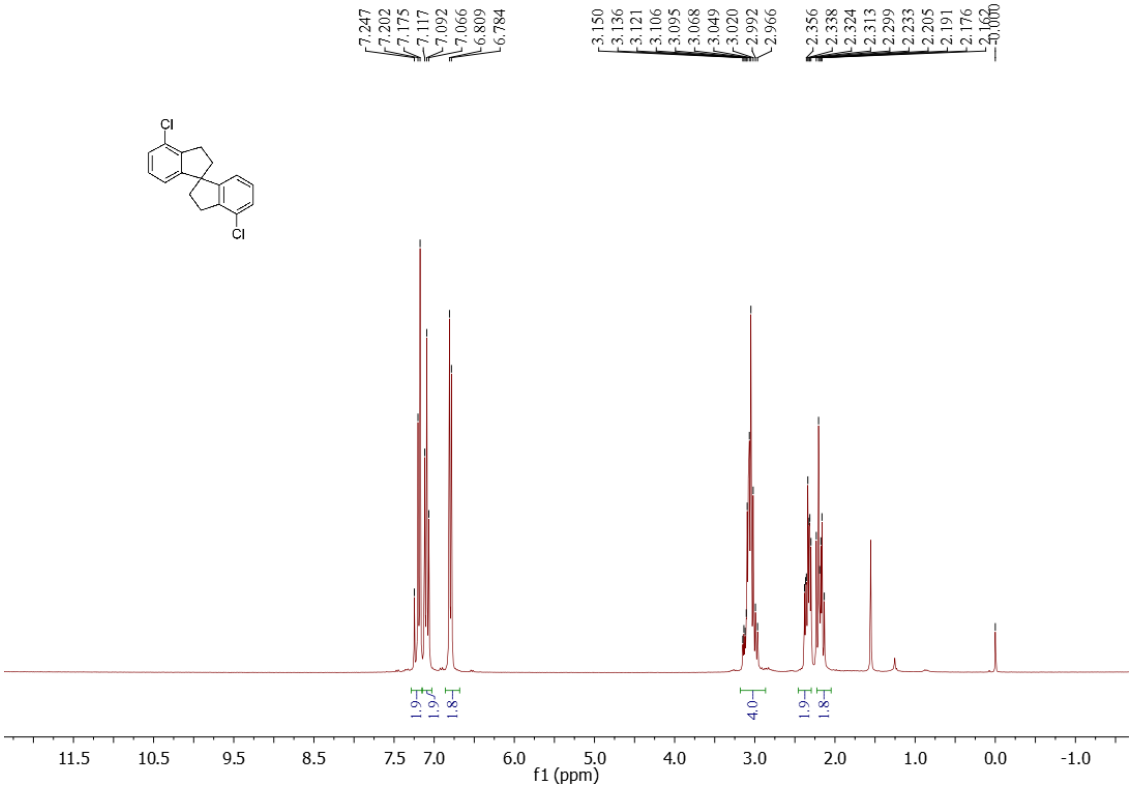


Figure S23. ^{13}C NMR spectrum of **2k**, related to **Figure 2**

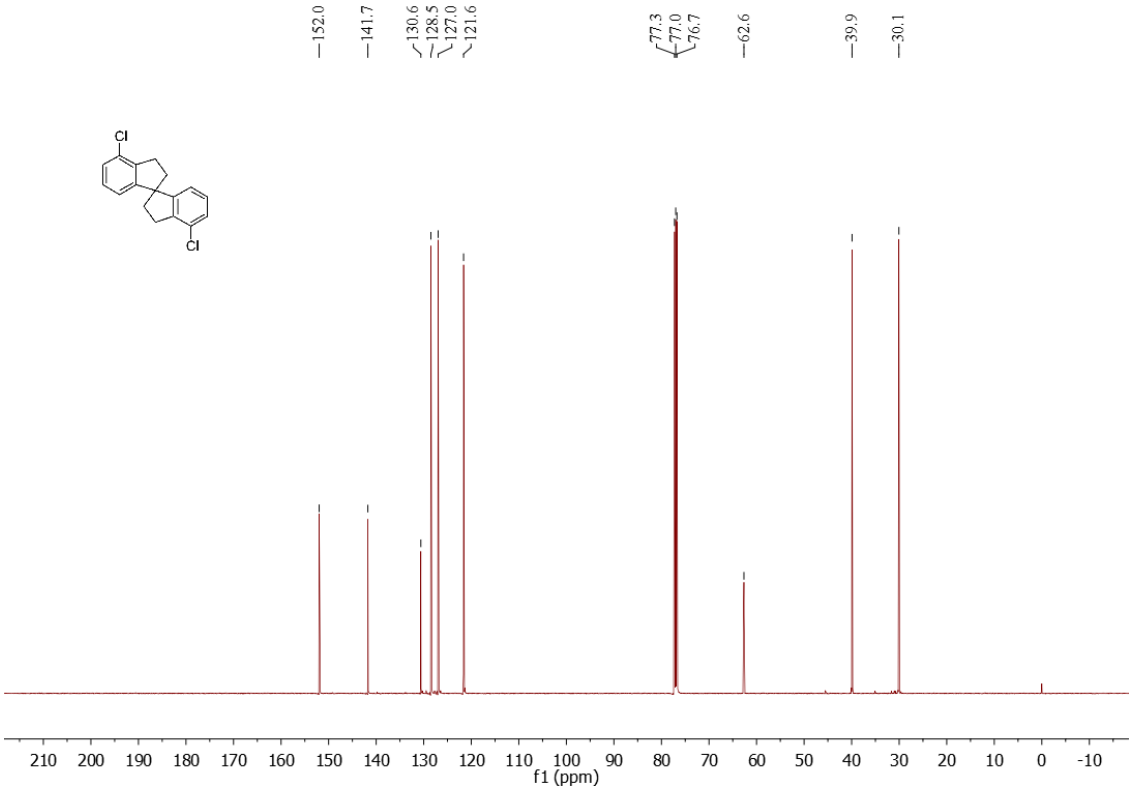


Figure S24. ^{1}H NMR spectrum of **2l**, related to **Figure 2**

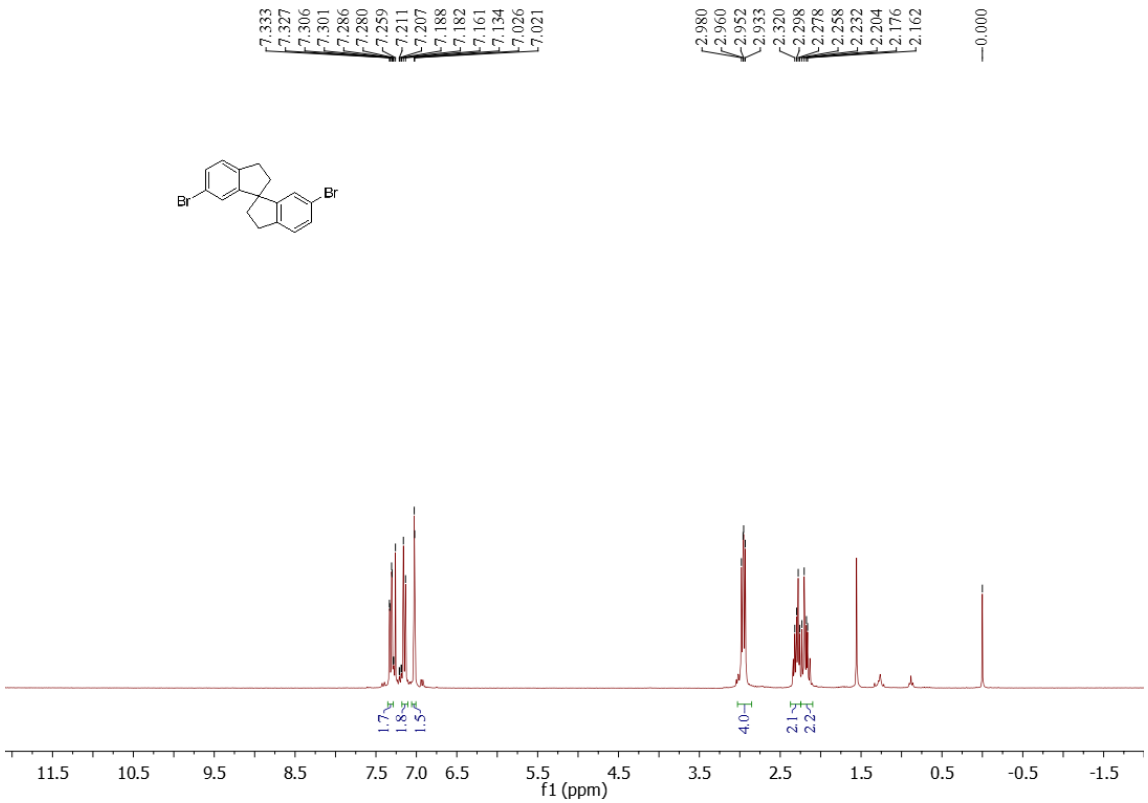


Figure S25. ^{13}C NMR spectrum of **2l**, related to **Figure 2**

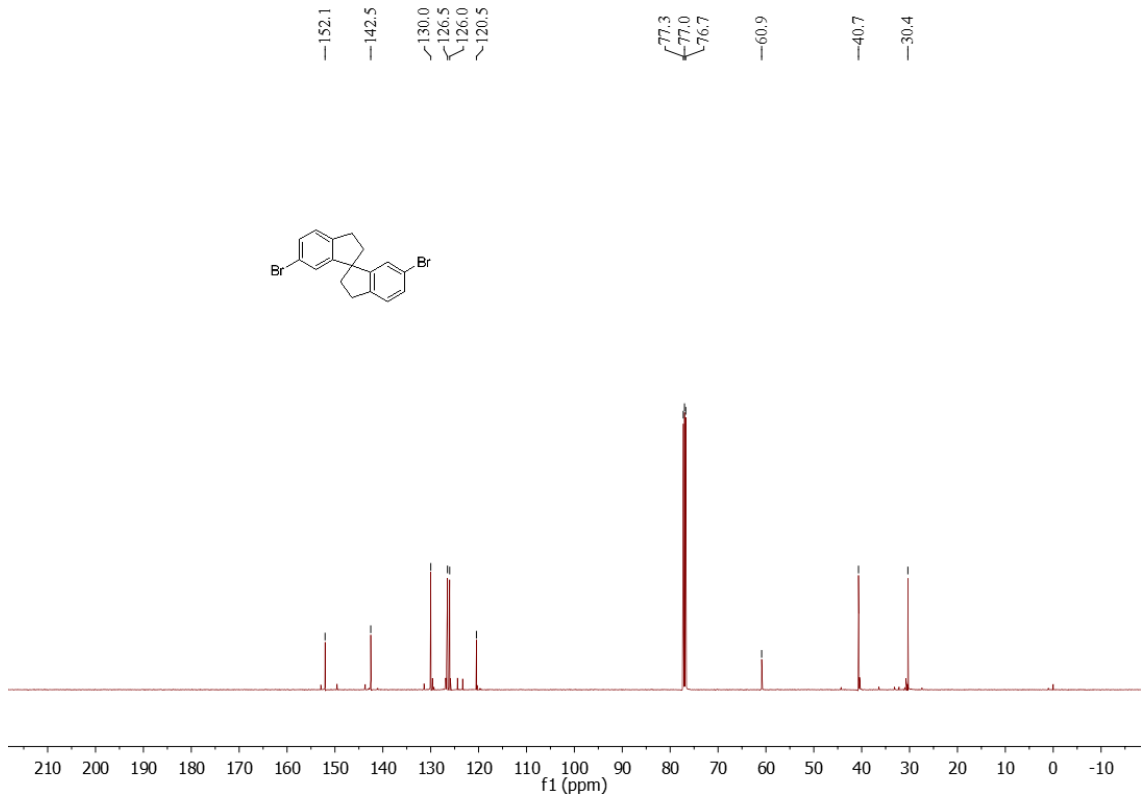


Figure S26. ^{1}H NMR spectrum of **2m**, related to **Figure 2**

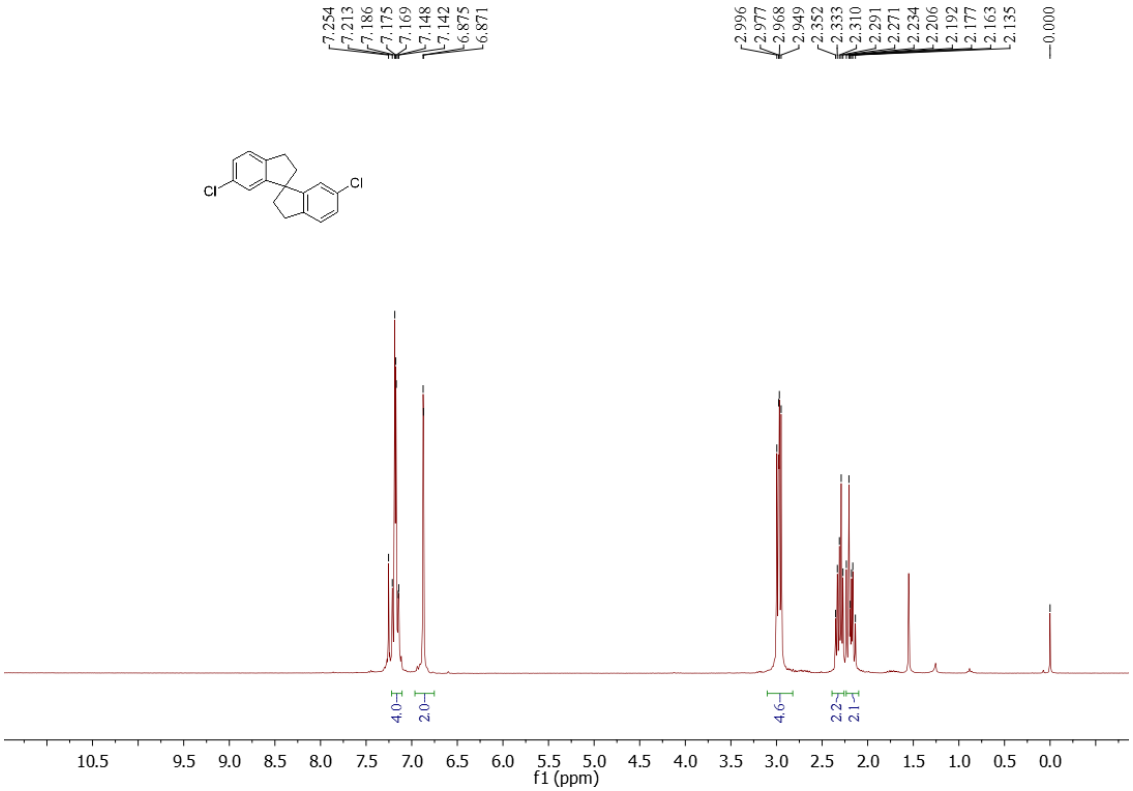


Figure S27. ^{13}C NMR spectrum of **2m**, related to **Figure 2**

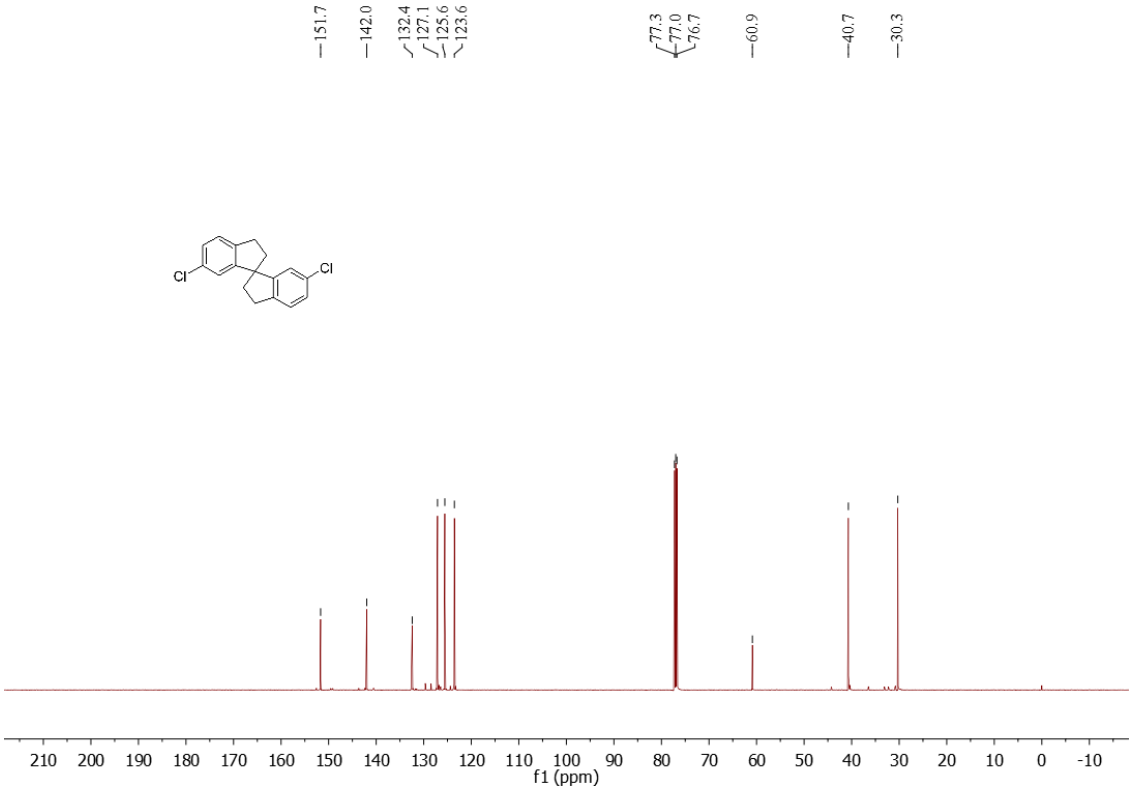


Figure S28. ^{1}H NMR spectrum of **2n**, related to **Figure 2**

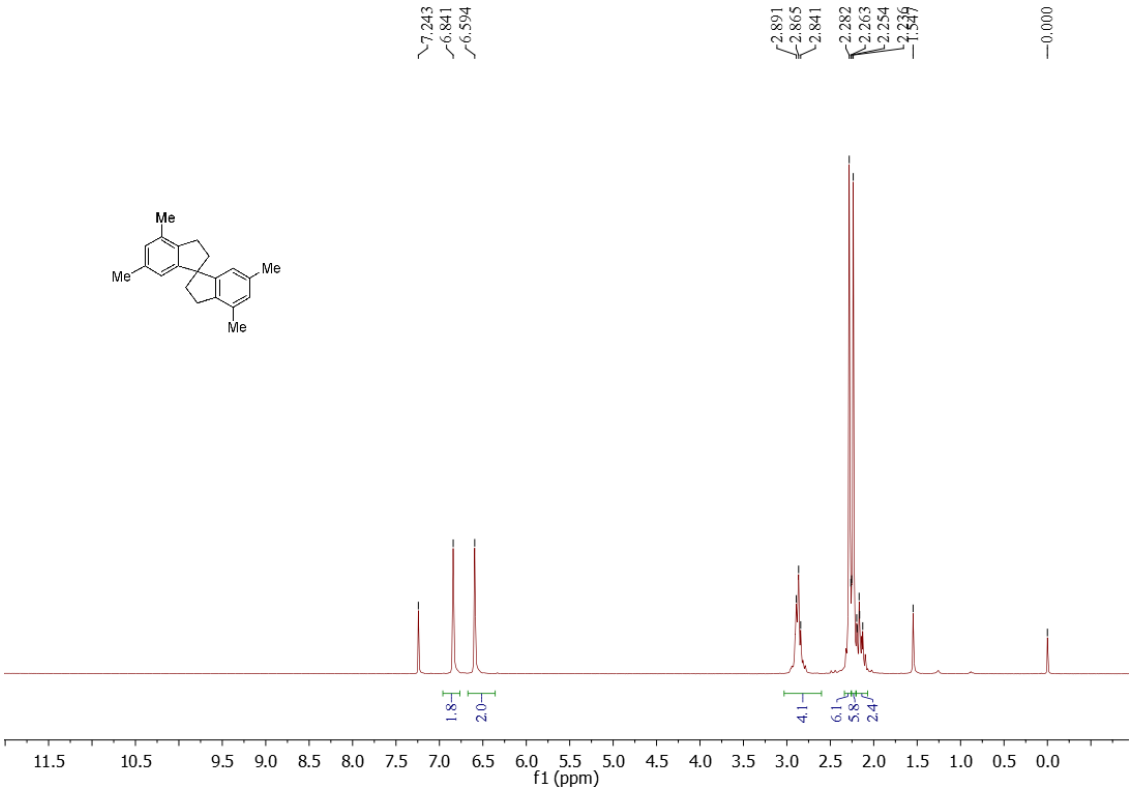


Figure S29. ^{13}C NMR spectrum of **2n**, related to **Figure 2**

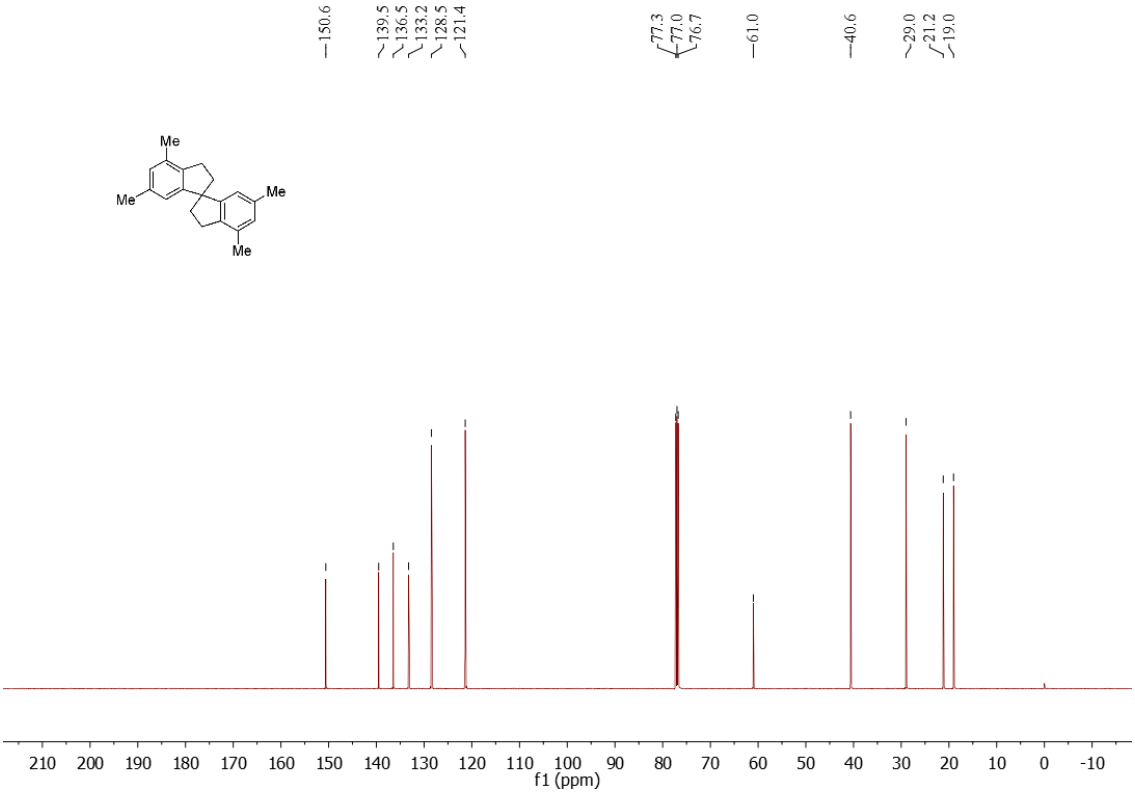


Figure S30. ^{1}H NMR spectrum of **2o**, related to **Figure 2**

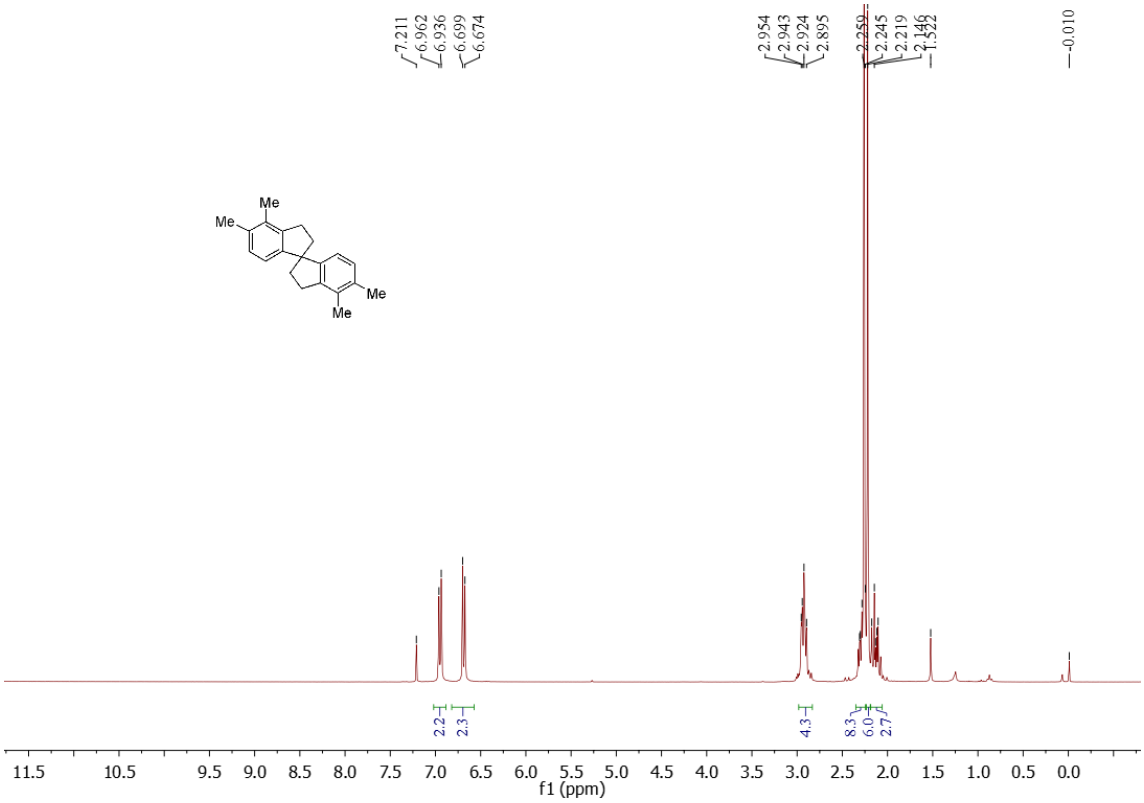


Figure S31. ^{13}C NMR spectrum of **2o**, related to **Figure 2**

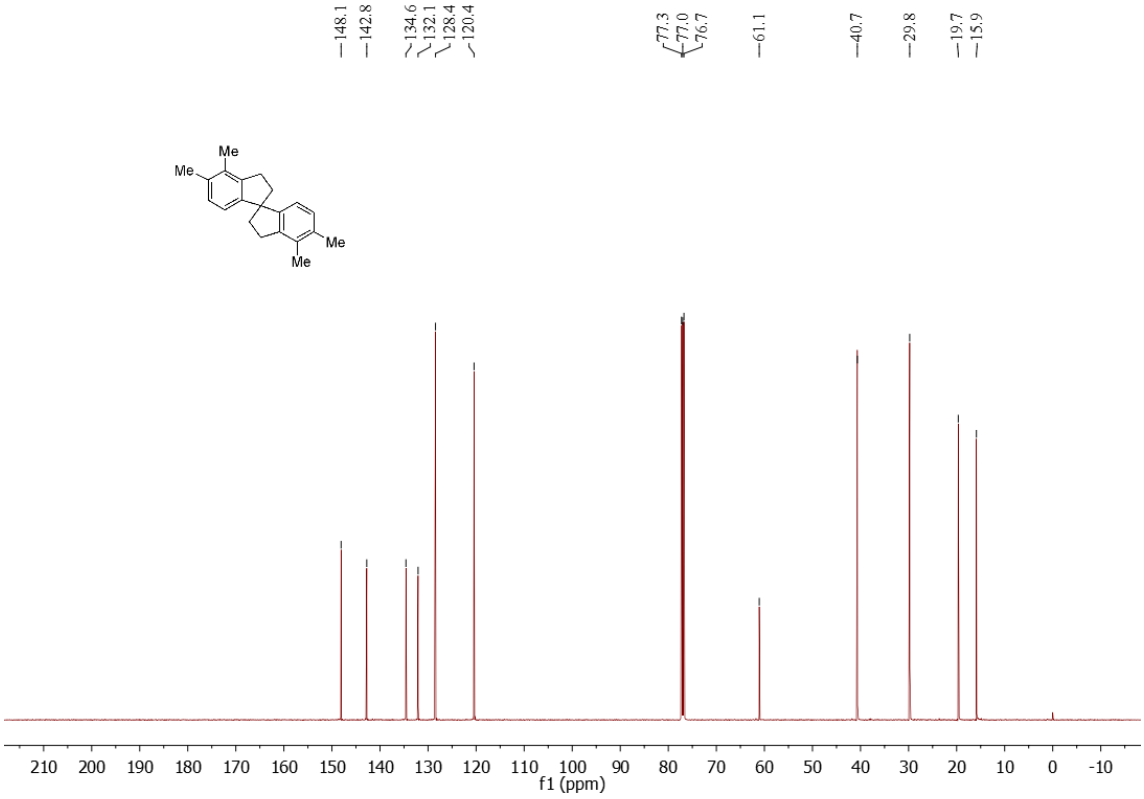


Figure S32. ^{1}H NMR spectrum of **2p**, related to **Figure 2**

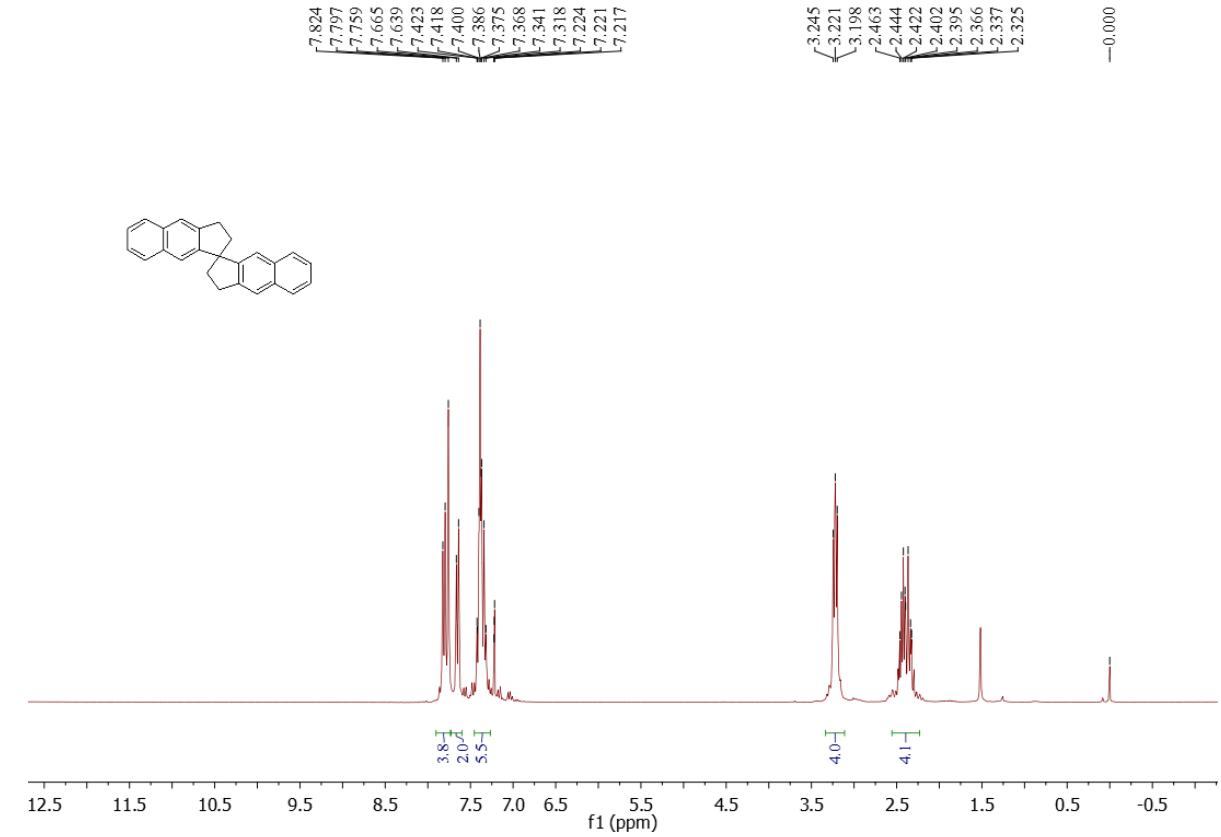


Figure S33. ^{13}C NMR spectrum of **2p**, related to **Figure 2**

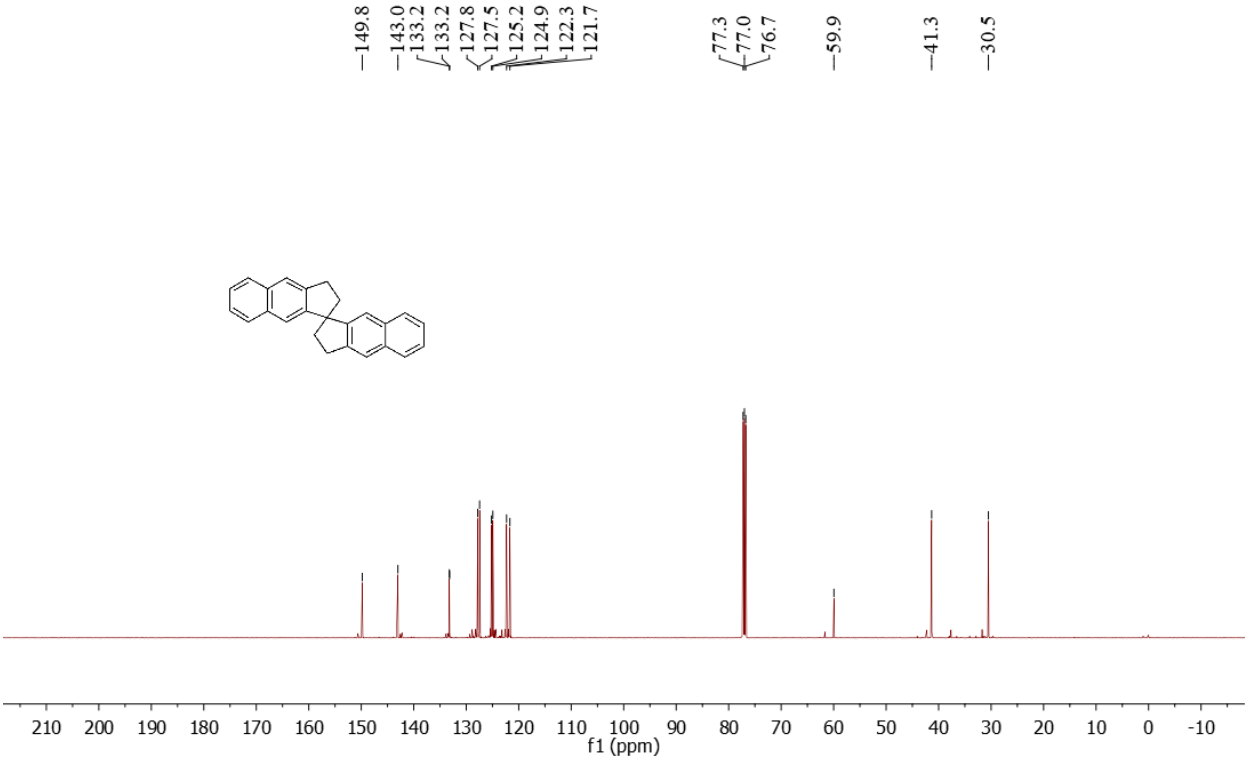


Figure S34. ^{1}H NMR spectrum of **2q**, related to **Figure 2**

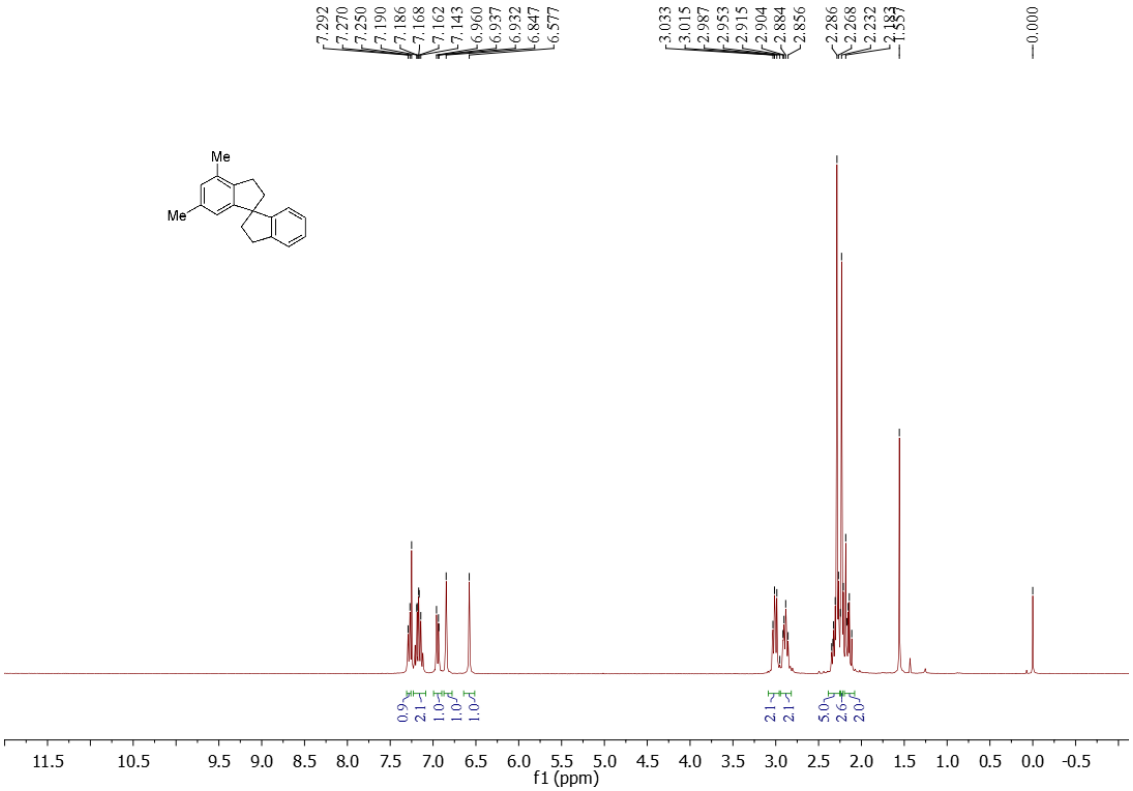


Figure S35. ^{13}C NMR spectrum of **2q**, related to **Figure 2**

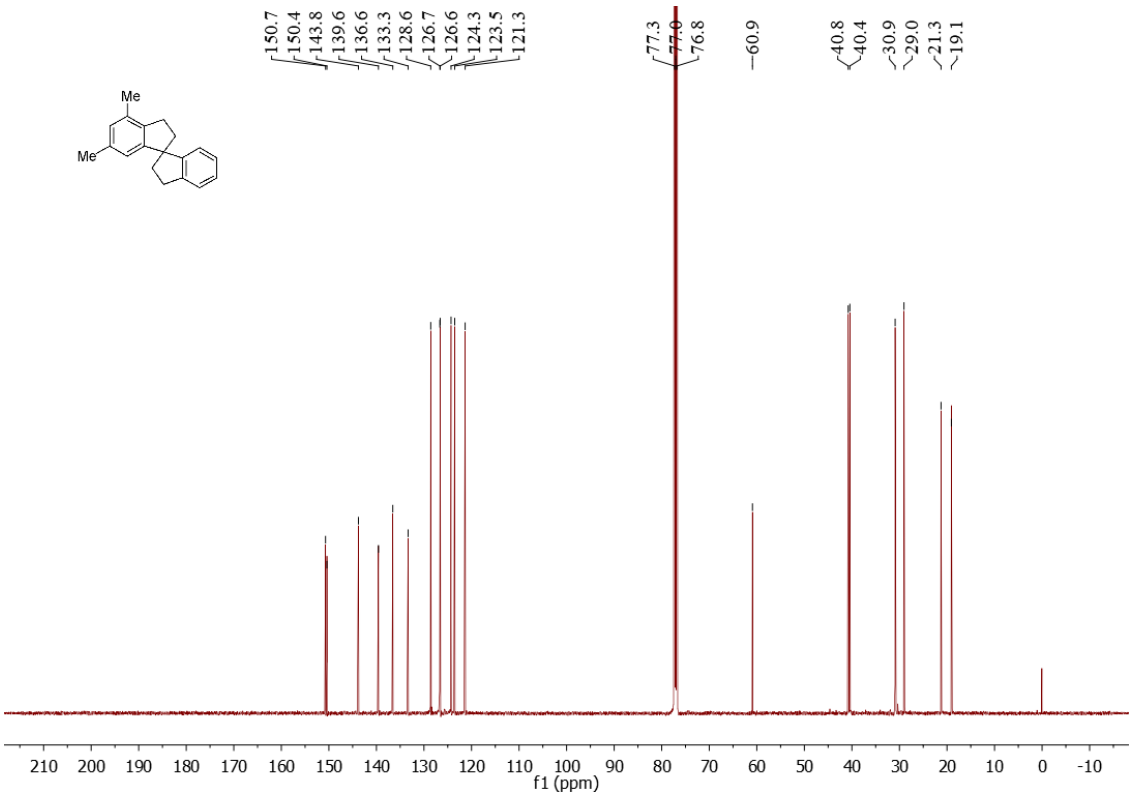


Figure S36. ^{1}H NMR spectrum of **2r**, related to **Figure 2**

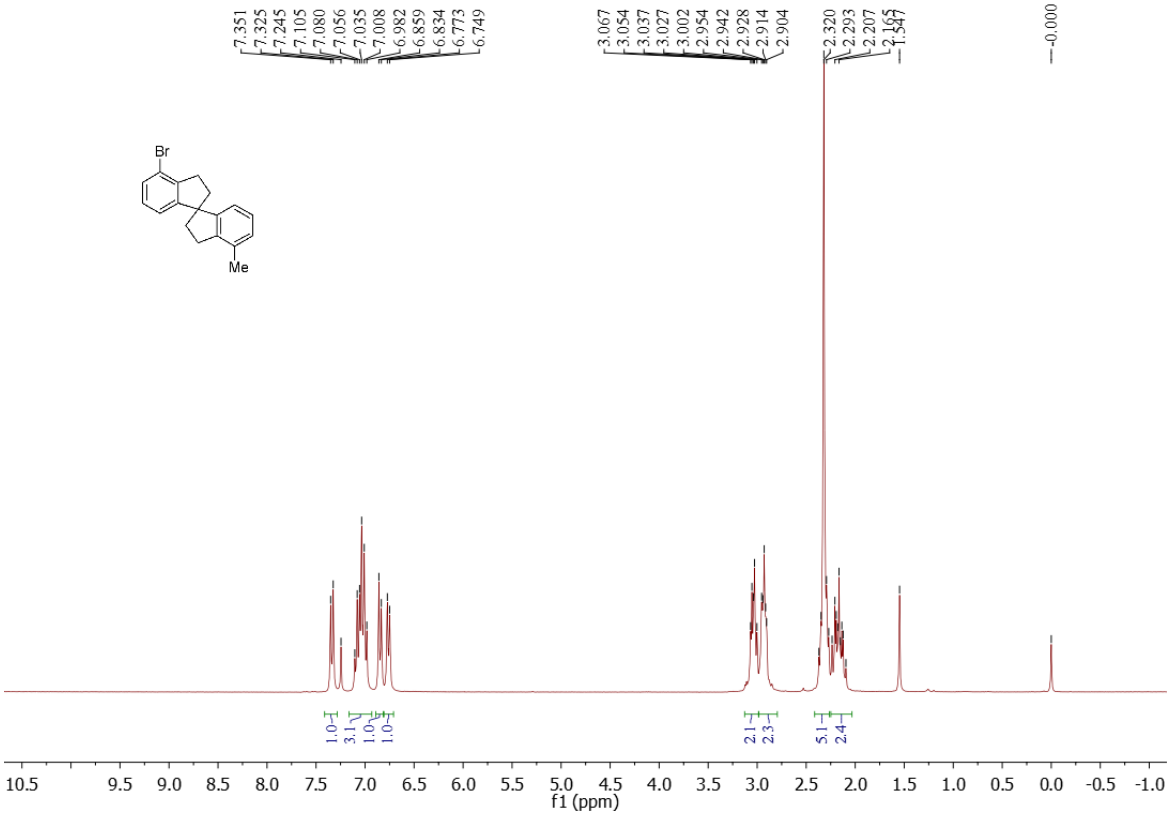


Figure S37. ^{13}C NMR spectrum of **2r**, related to **Figure 2**

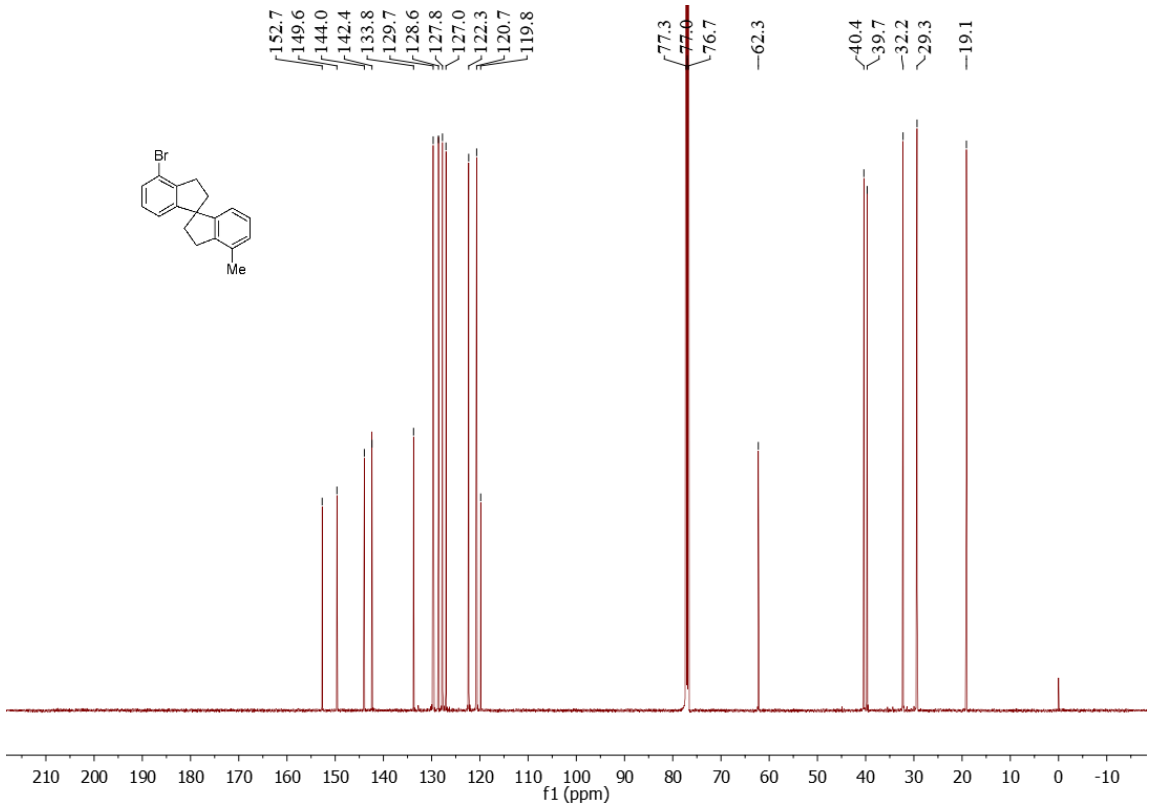


Figure S38. ^{1}H NMR spectrum of **2s**, related to **Figure 2**

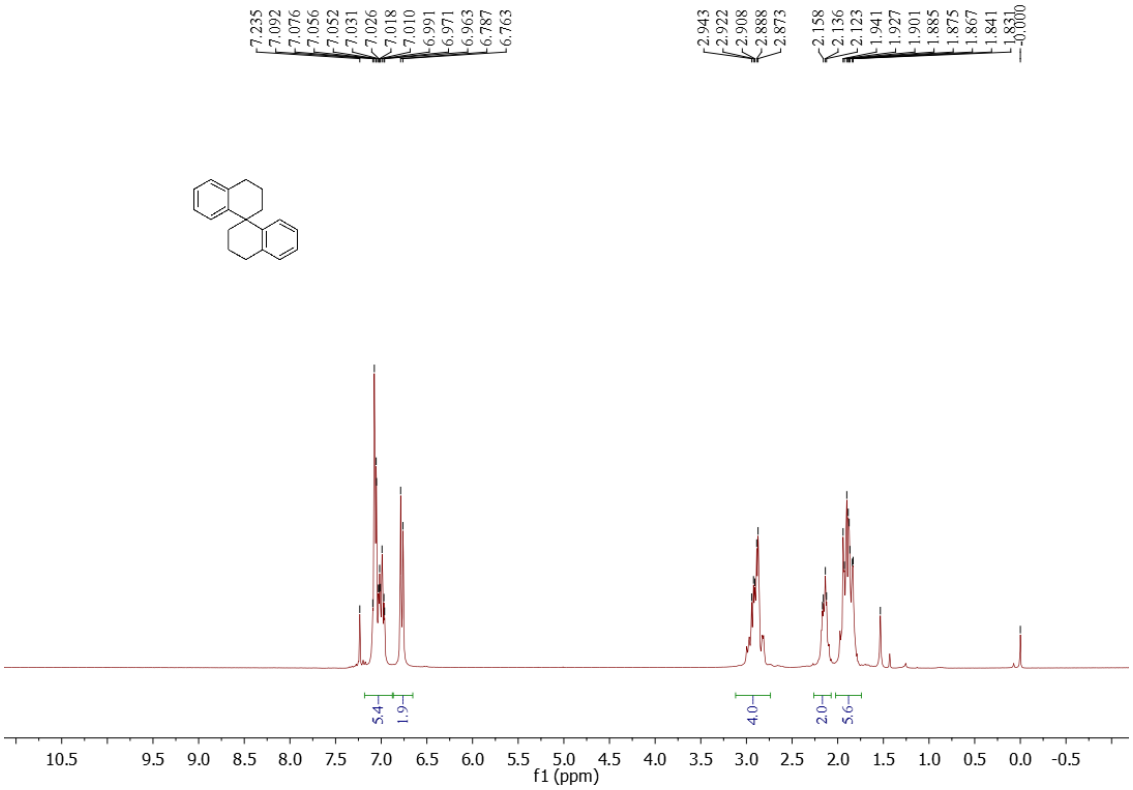


Figure S39. ^{13}C NMR spectrum of **2s**, related to **Figure 2**

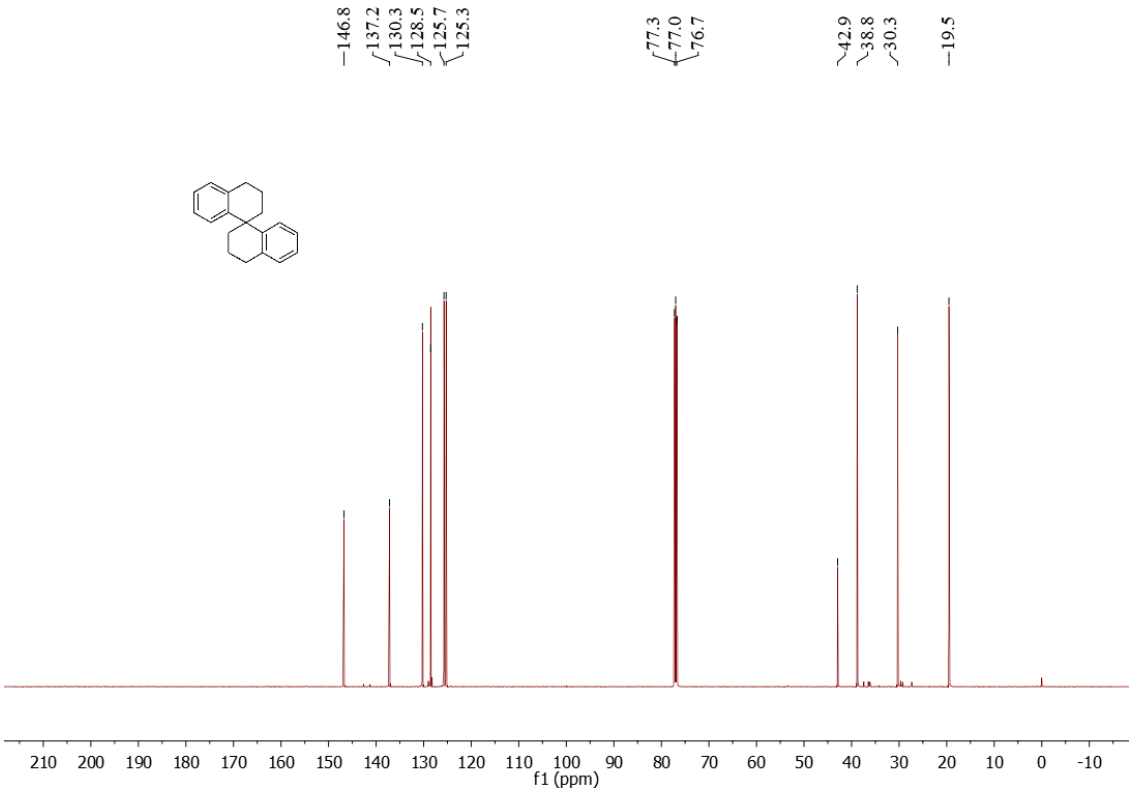


Figure S40. ^{1}H NMR spectrum of **2t**, related to **Figure 2**

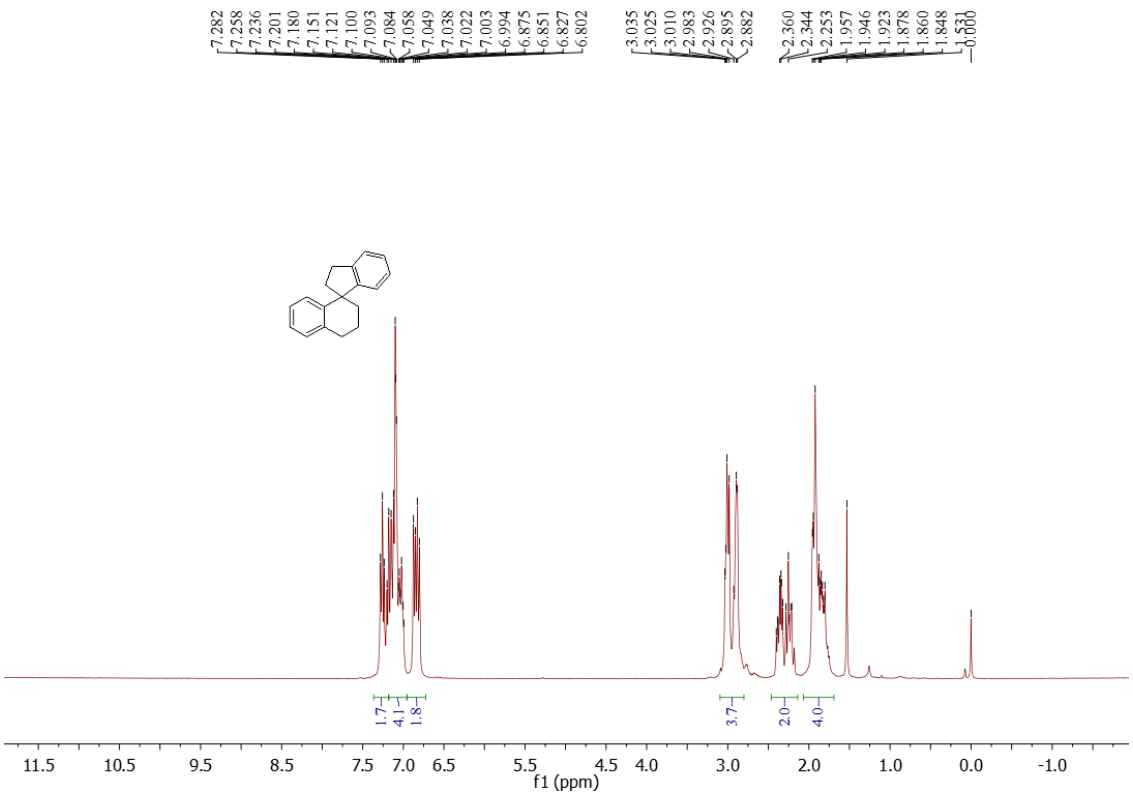


Figure S41. ^{13}C NMR spectrum of **2t**, related to **Figure 2**

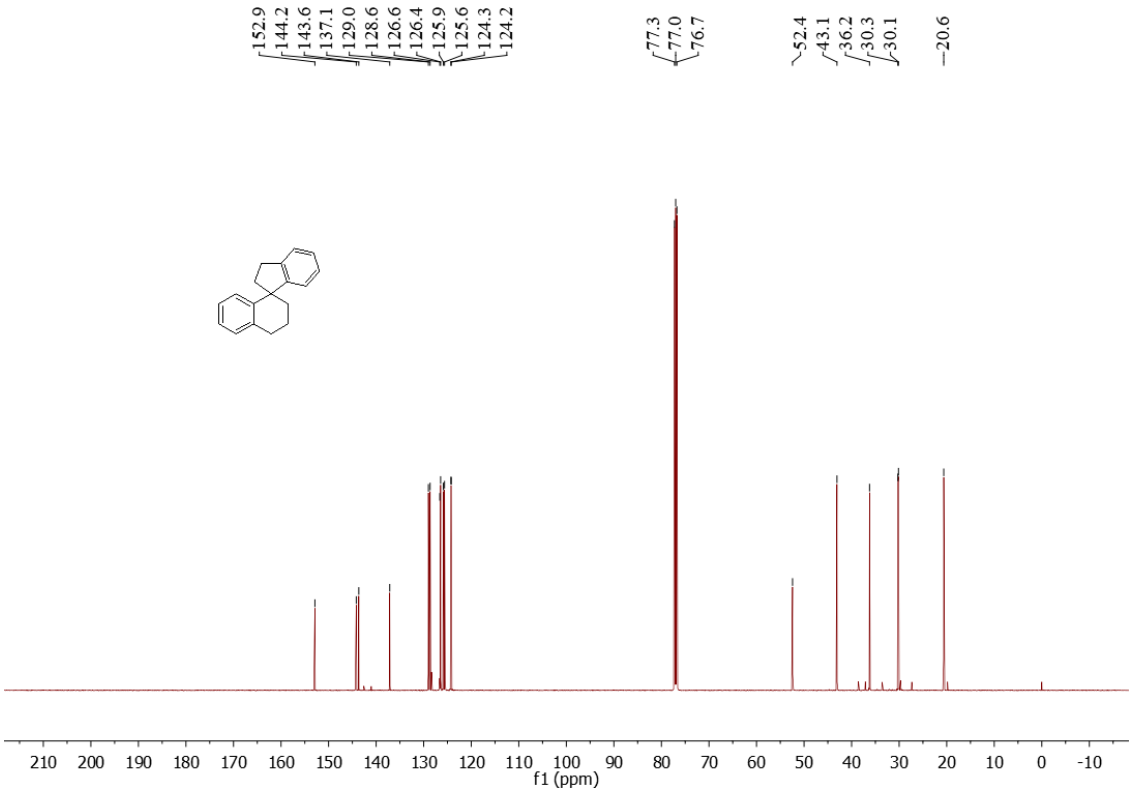


Figure S42. ^{1}H NMR spectrum of **3a**, related to **Figure 2**

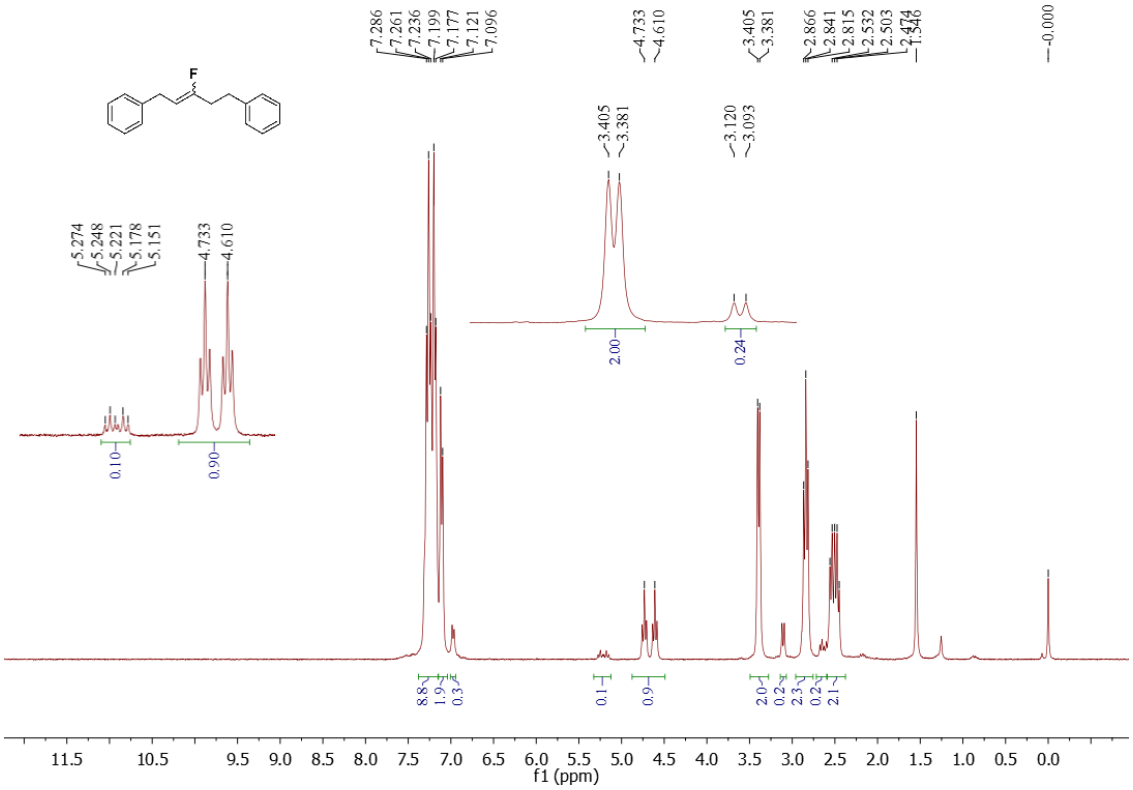


Figure S43. ^{13}C NMR spectrum of **3a**, related to **Figure 2**

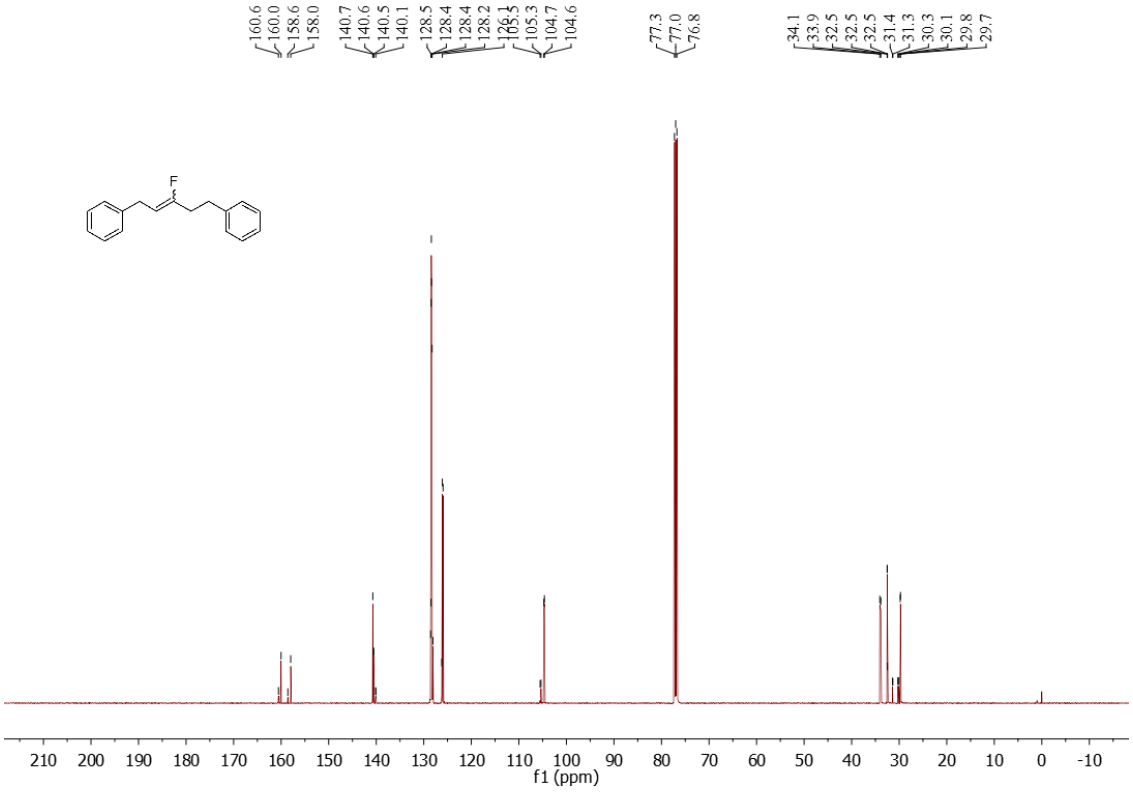


Figure S44. ^{19}F NMR spectrum of **3a**, related to **Figure 2**

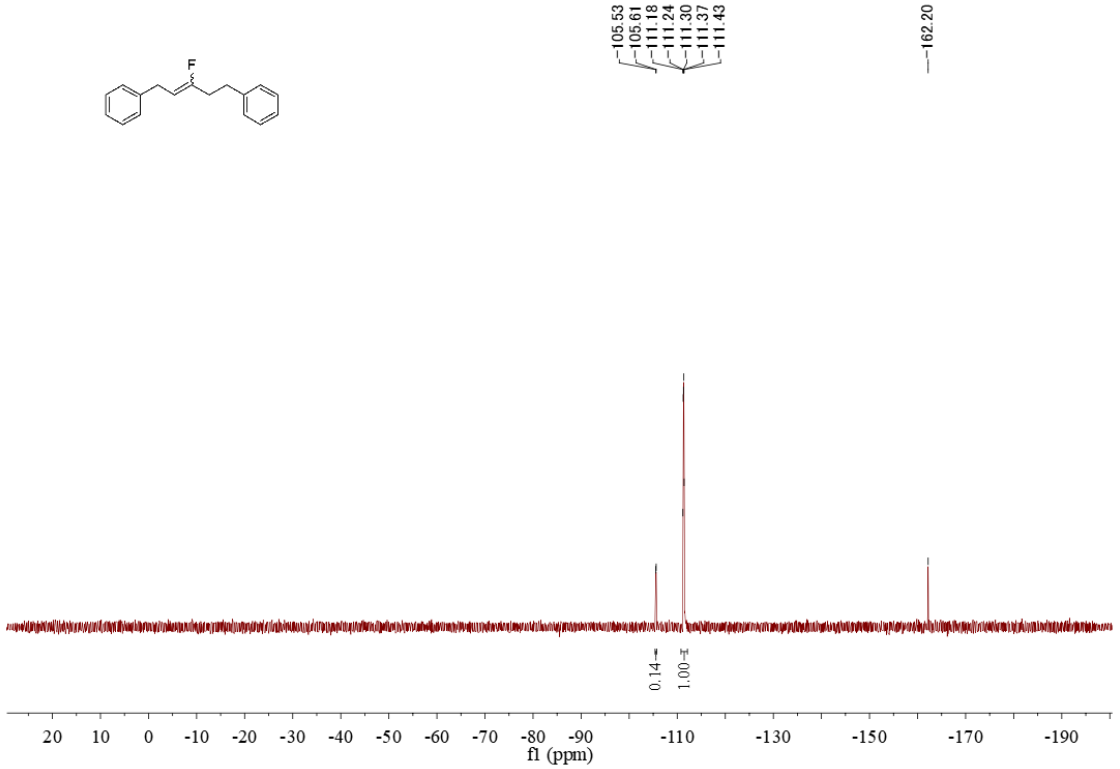


Figure S45. ^{1}H NMR spectrum of **3e**, related to **Figure 2**

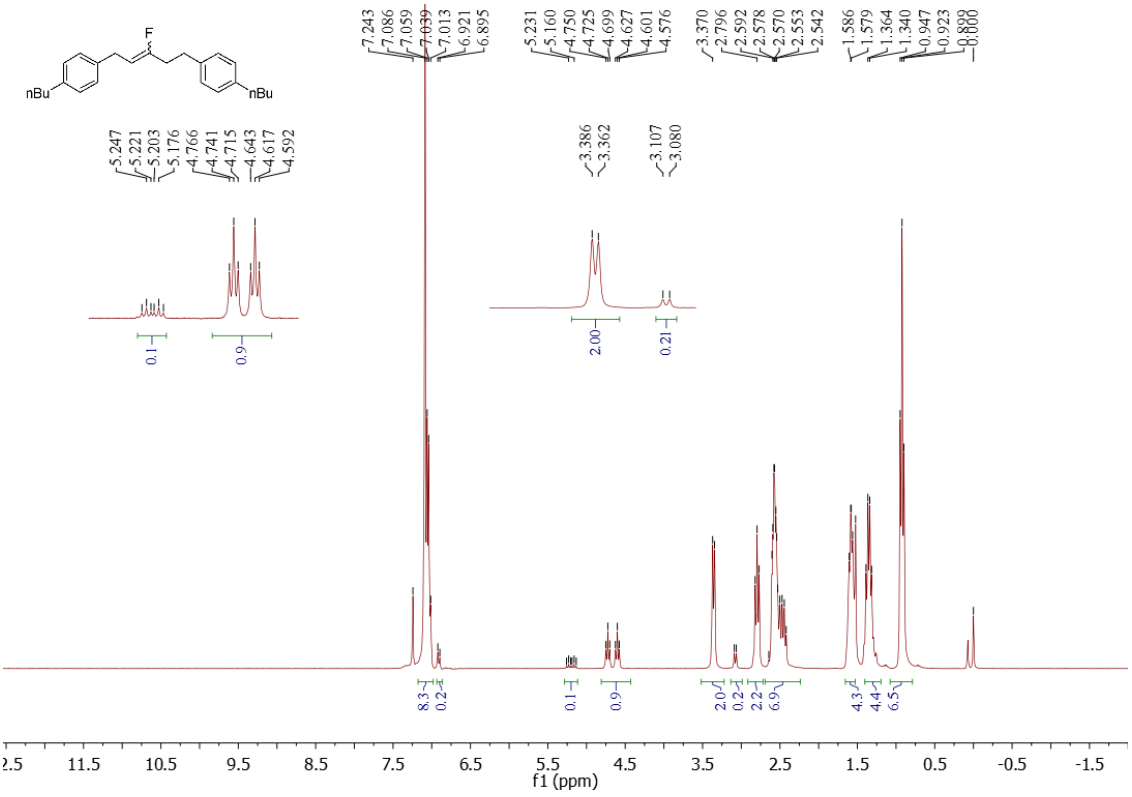


Figure S46. ^{13}C NMR spectrum of **3e**, related to **Figure 2**

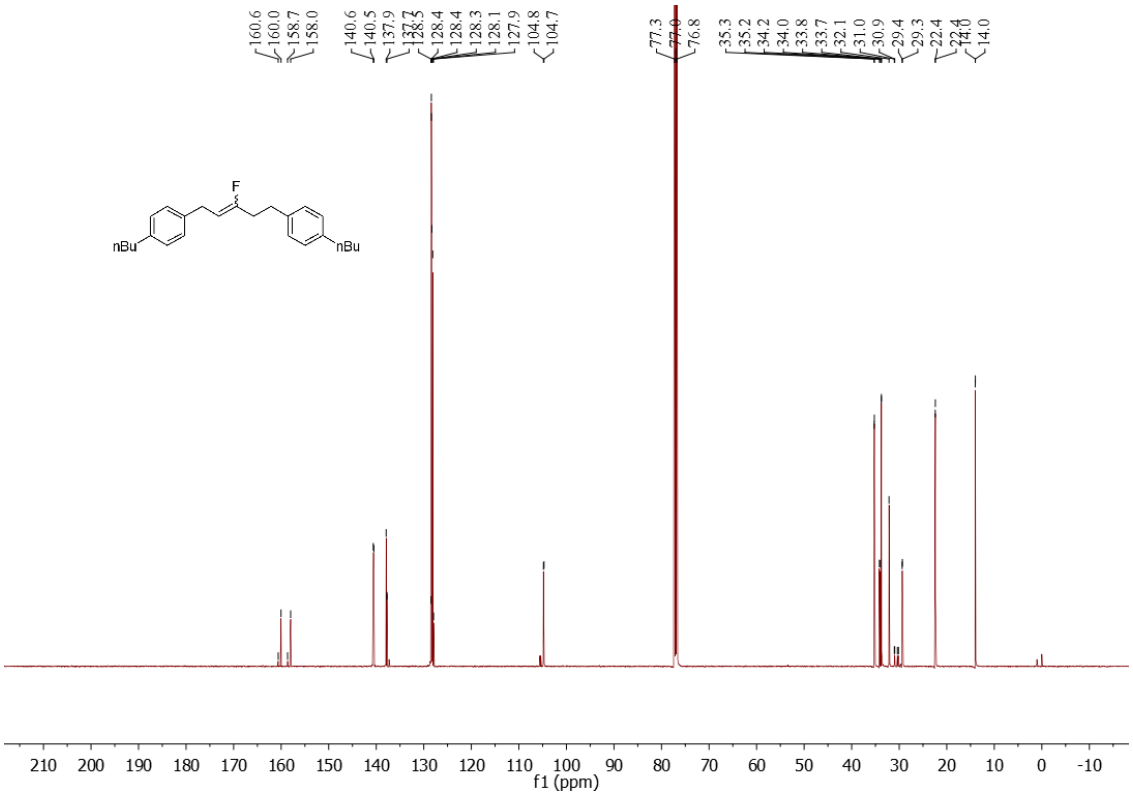


Figure S47. ^{19}F NMR spectrum of **3e**, related to **Figure 2**

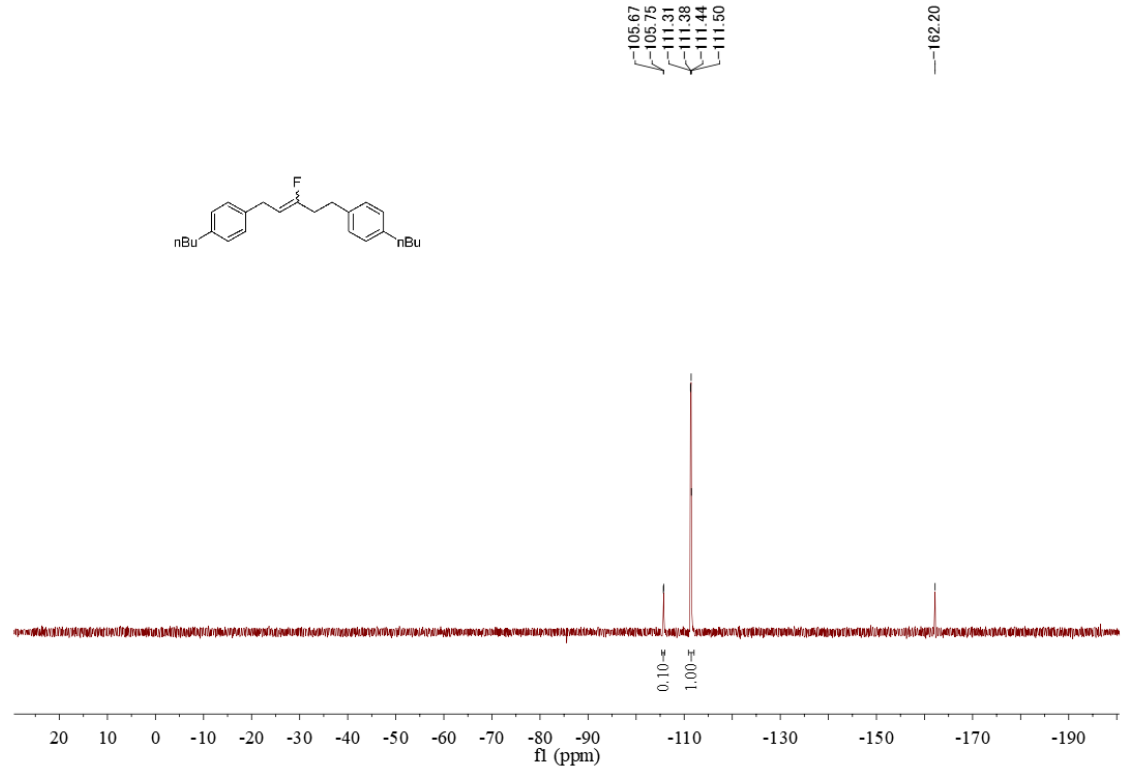


Figure S48. ^{1}H NMR spectrum of **3f**, related to **Figure 2**

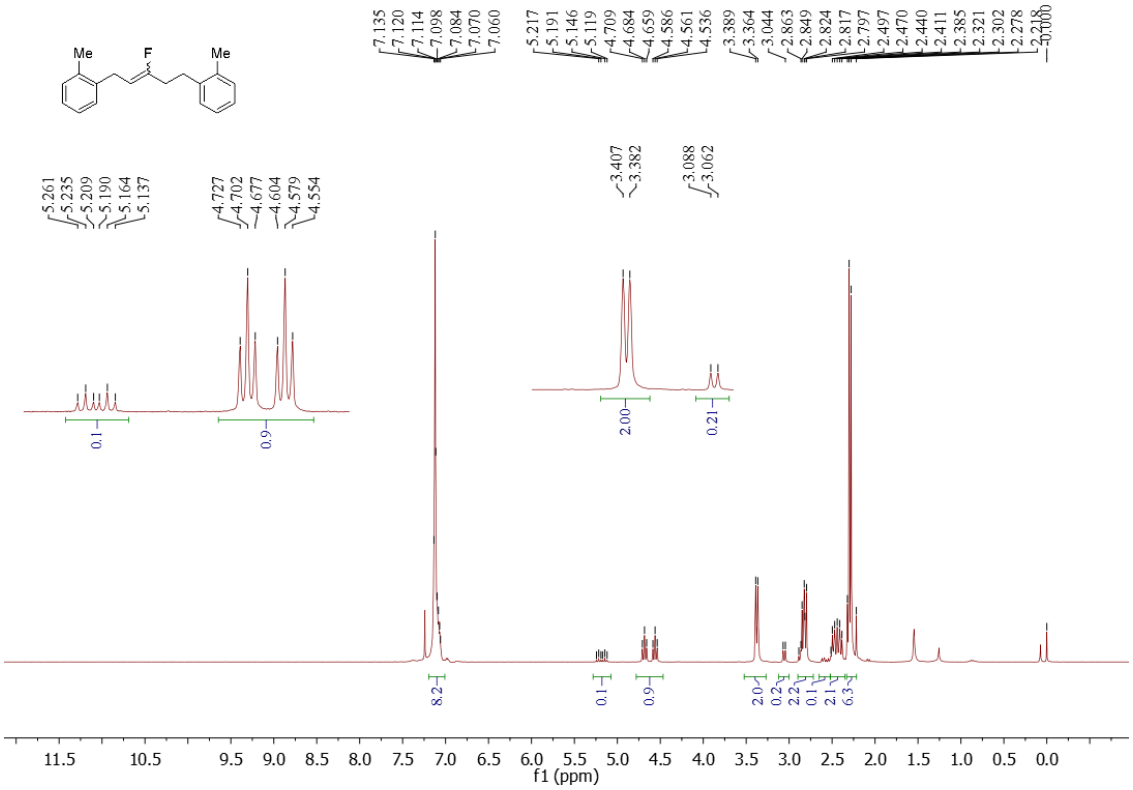


Figure S49. ^{13}C NMR spectrum of **3f**, related to **Figure 2**

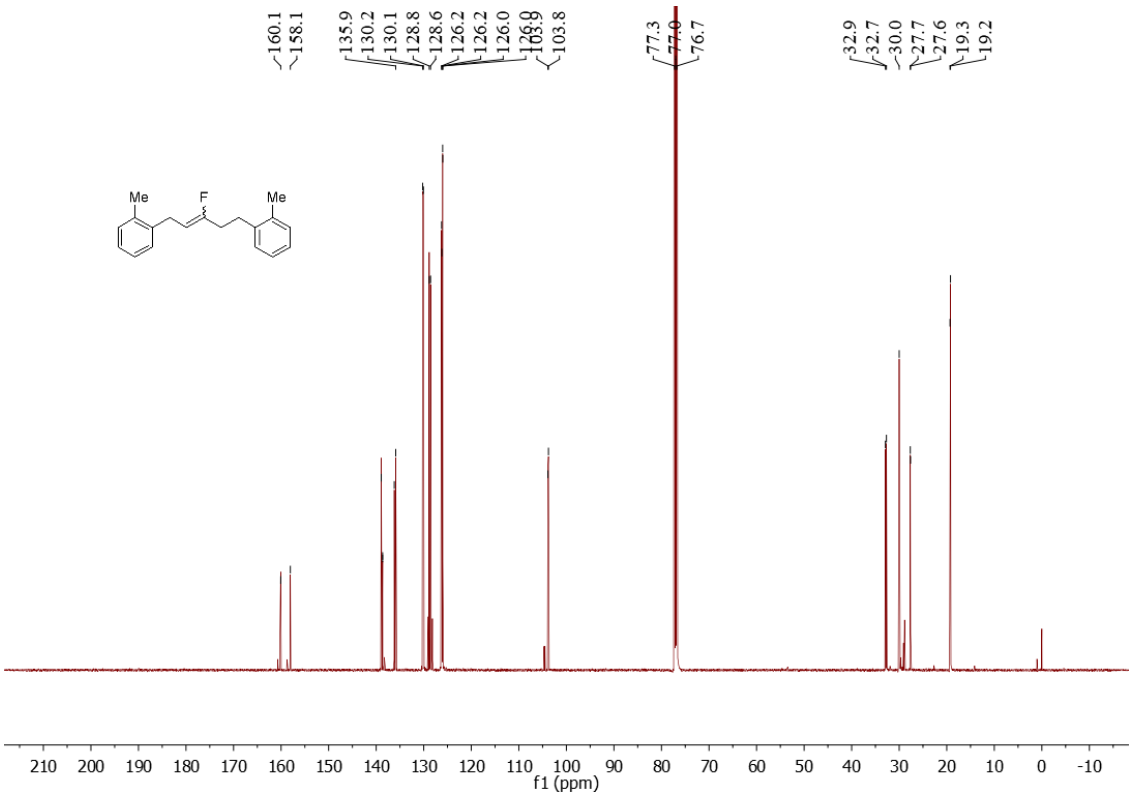


Figure S50. ^{19}F NMR spectrum of **3f**, related to **Figure 2**

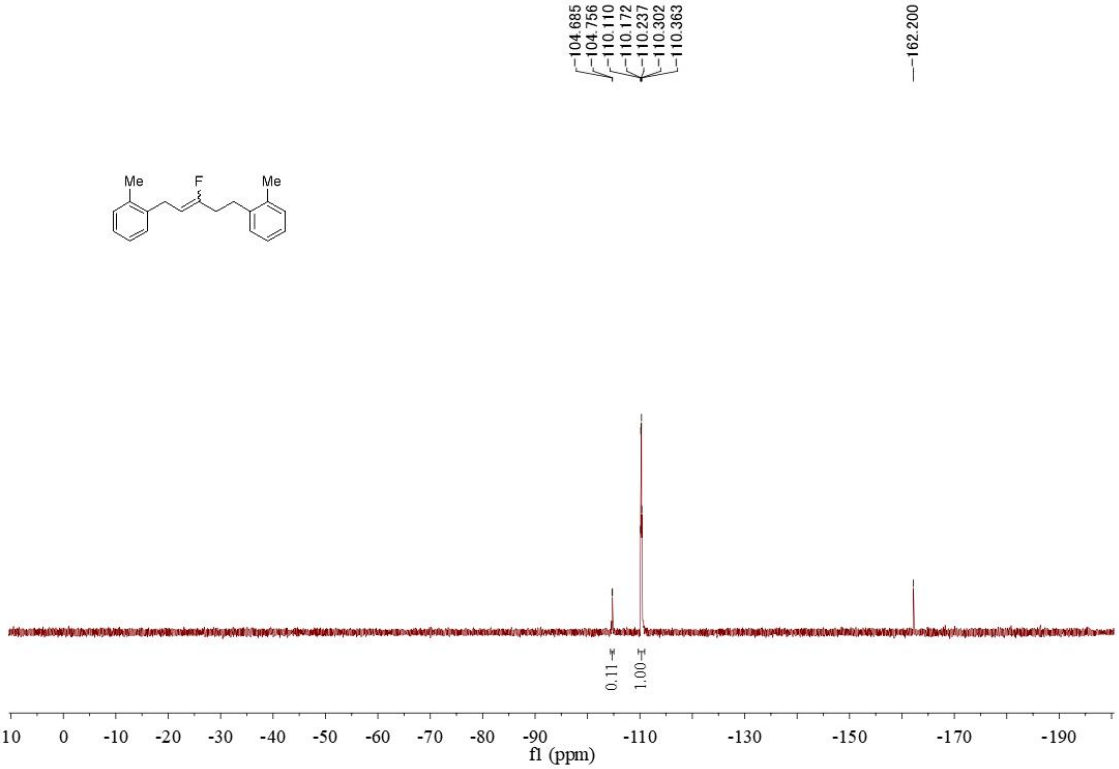


Figure S51. ^{1}H NMR spectrum of **3g**, related to **Figure 2**

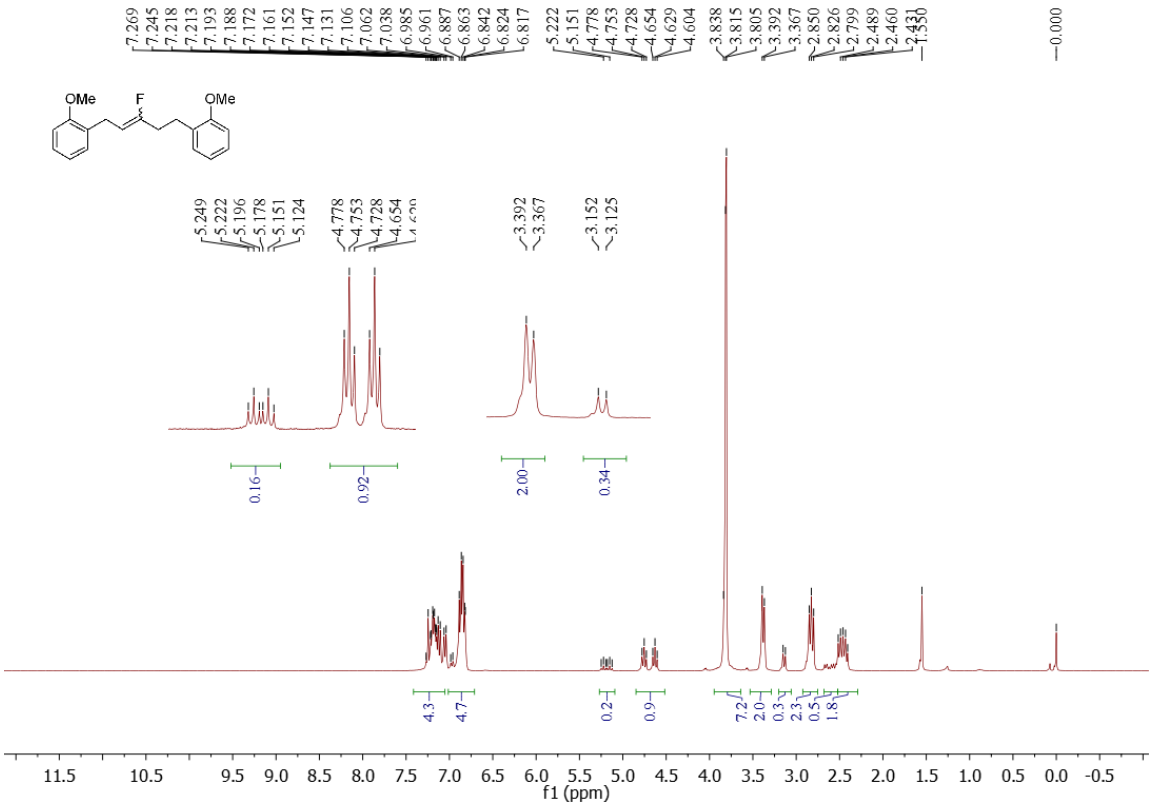


Figure S52. ^{13}C NMR spectrum of **3g**, related to **Figure 2**

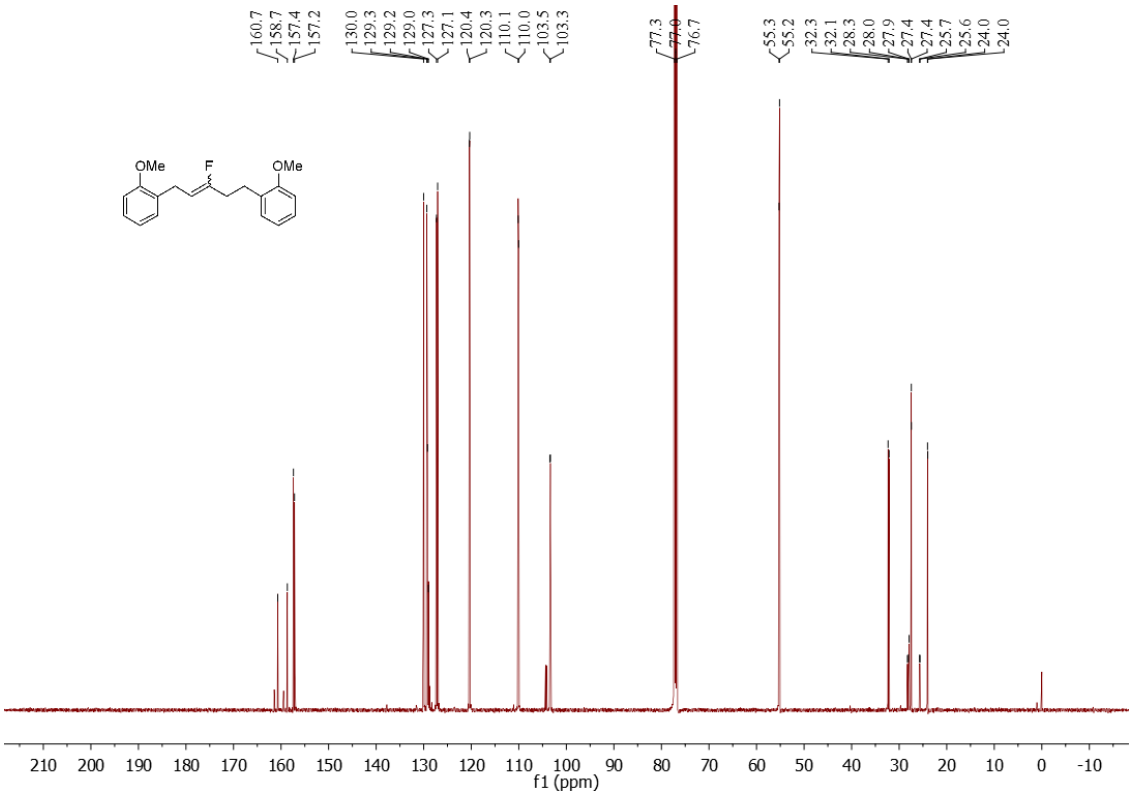


Figure S53. ^{19}F NMR spectrum of **3g**, related to **Figure 2**

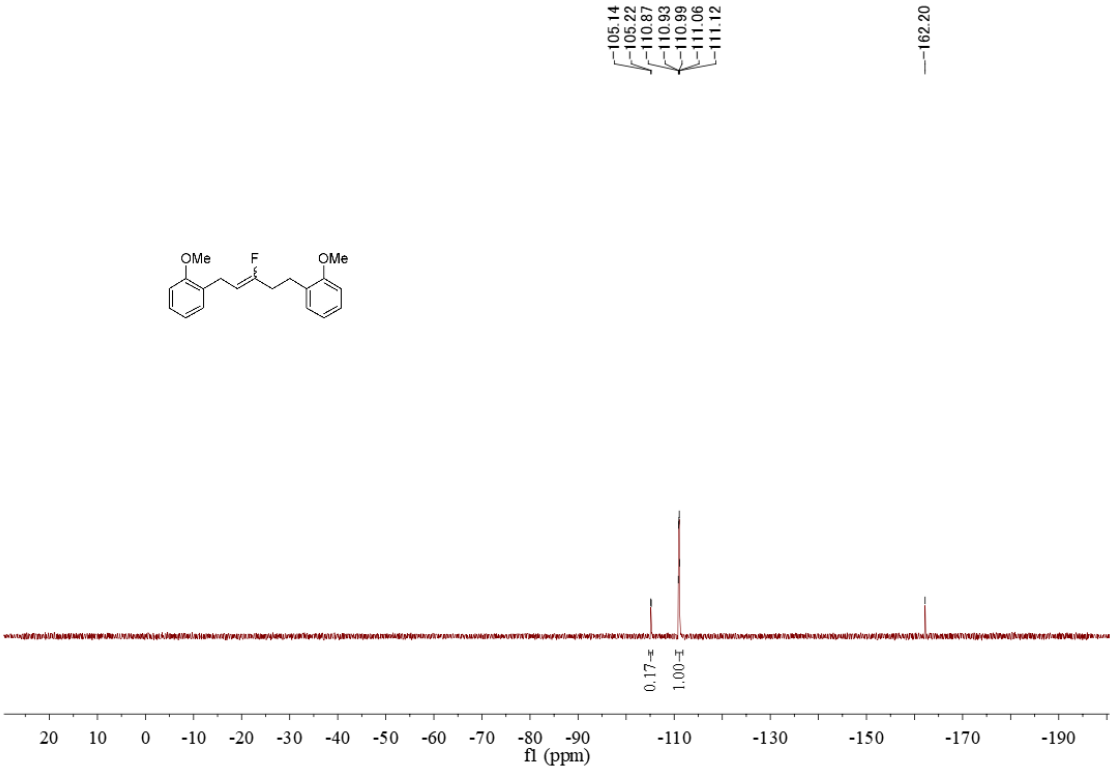


Figure S54. ^{1}H NMR spectrum of **3n**, related to **Figure 2**

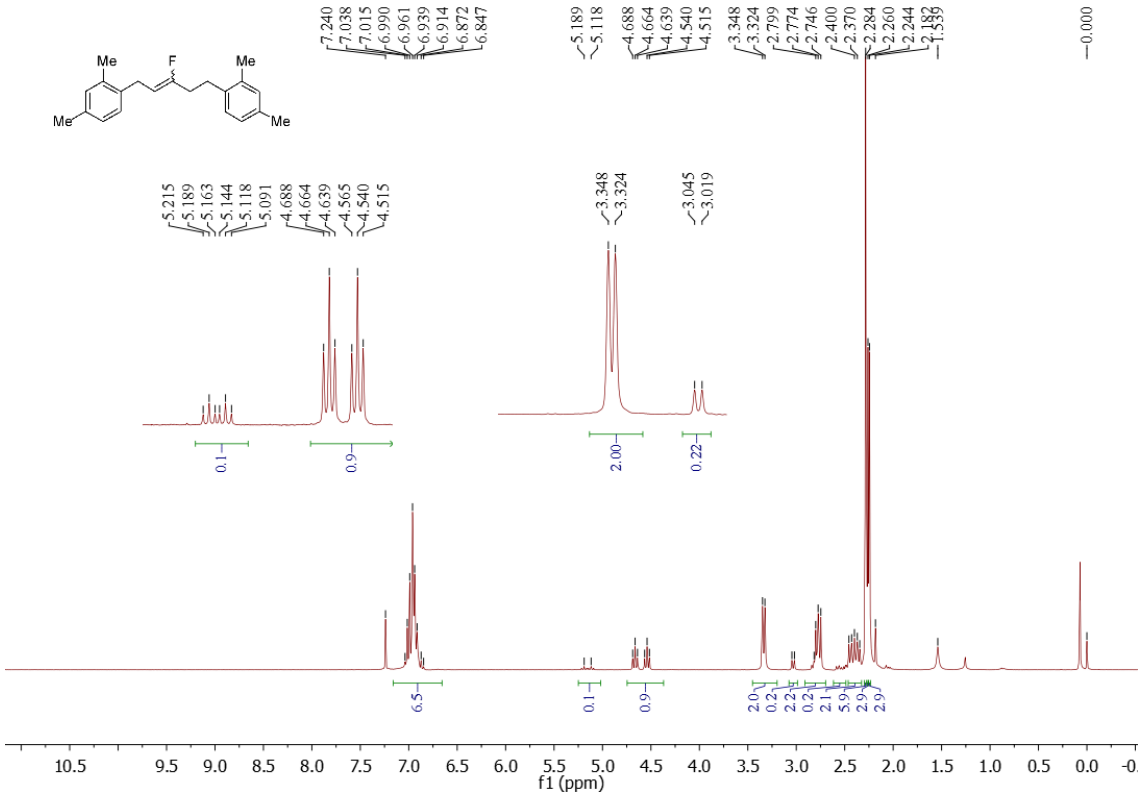


Figure S55. ^{13}C NMR spectrum of **3n**, related to **Figure 2**

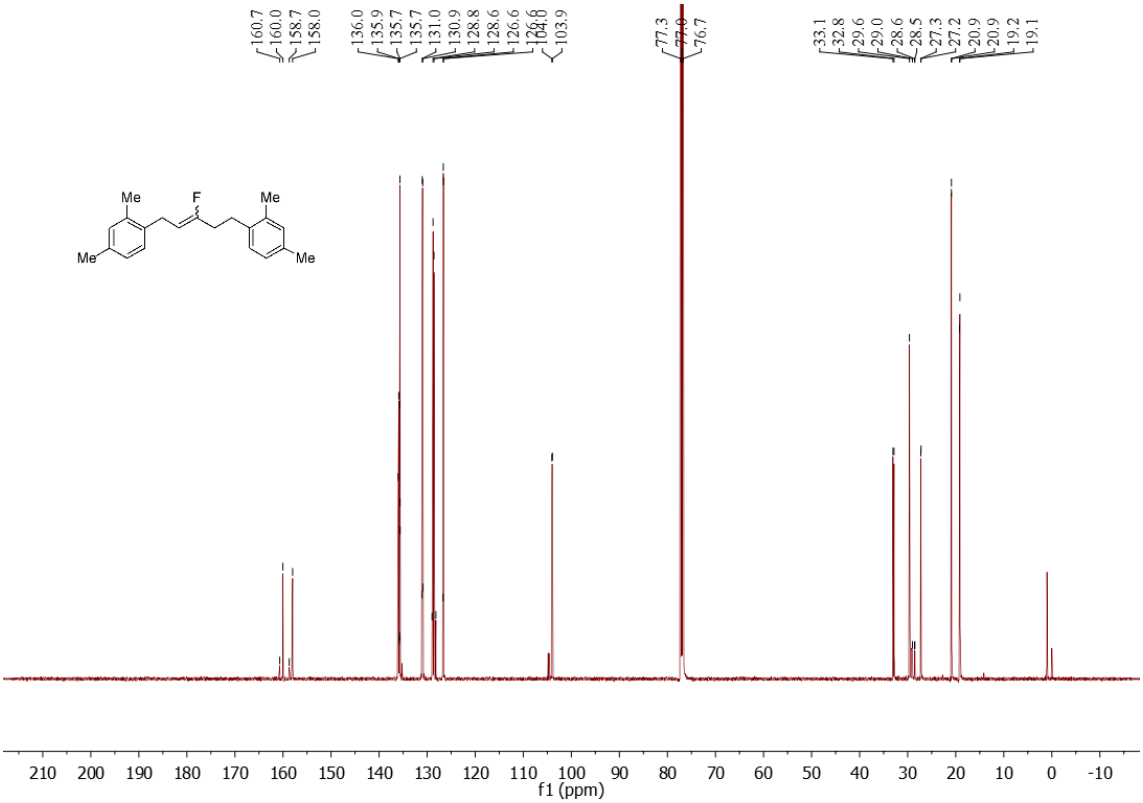


Figure S56. ^{19}F NMR spectrum of **3n**, related to **Figure 2**

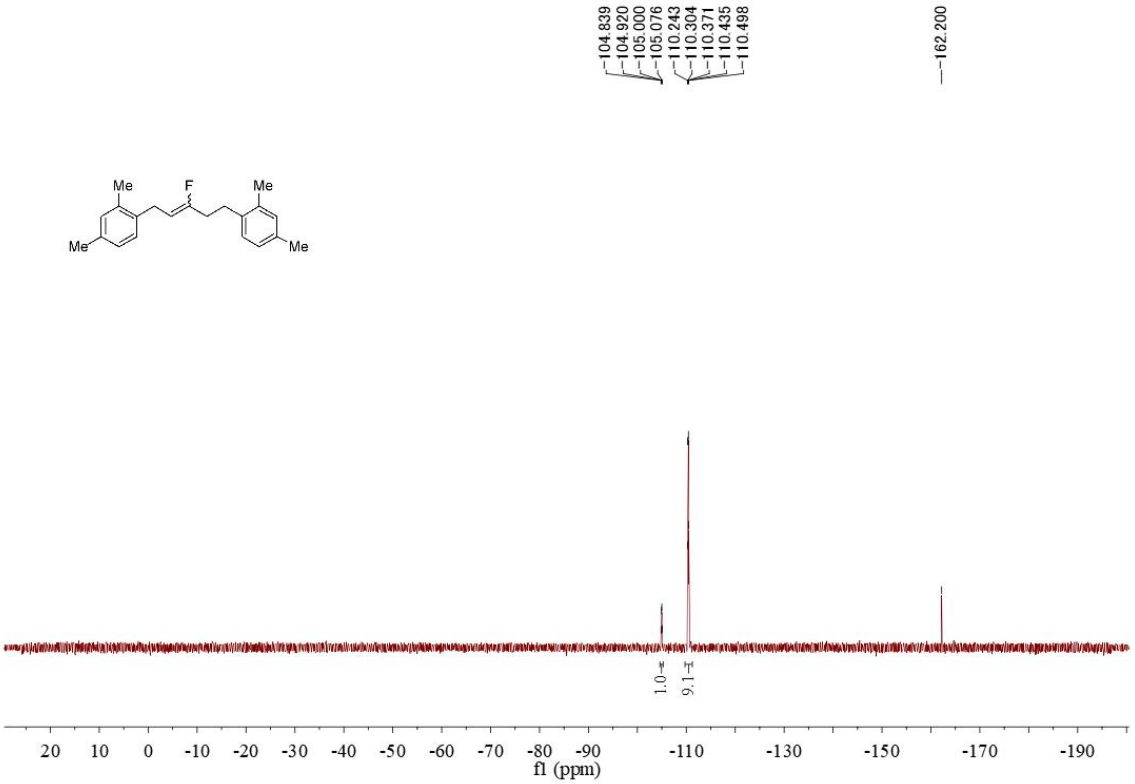


Figure S57. ^{1}H NMR spectrum of **3o**, related to **Figure 2**

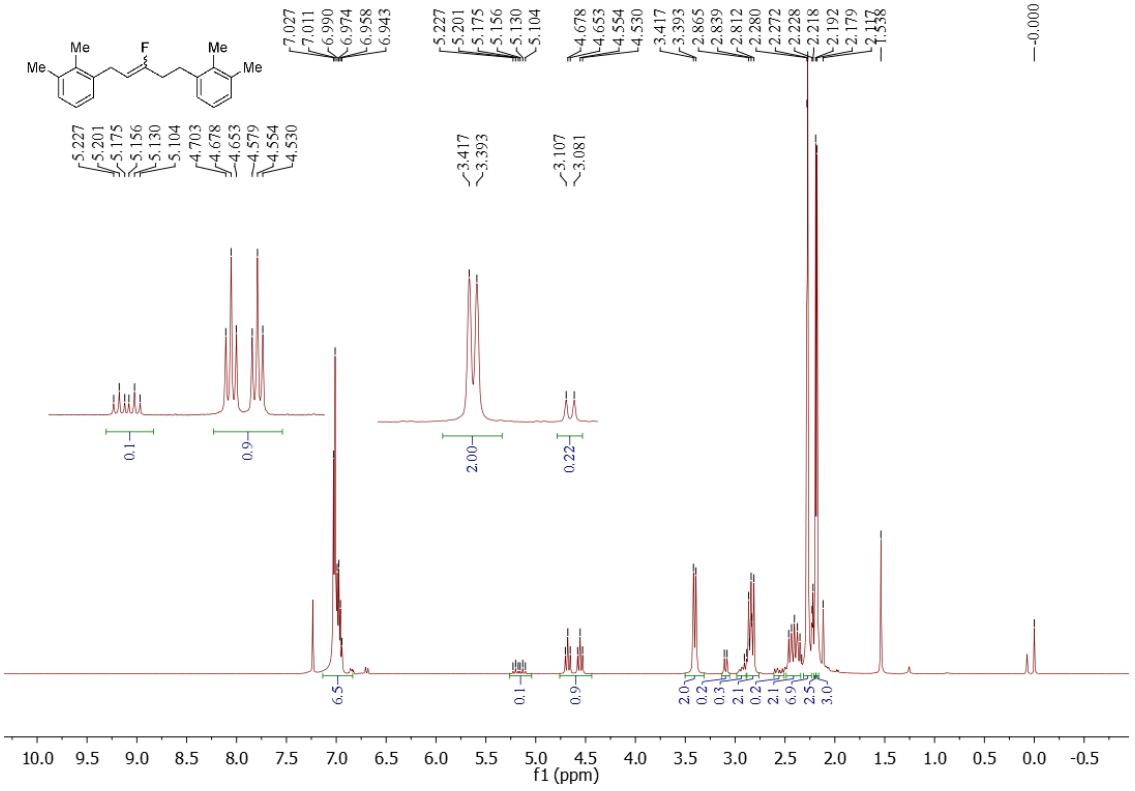


Figure S58. ^{13}C NMR spectrum of **3o**, related to **Figure 2**

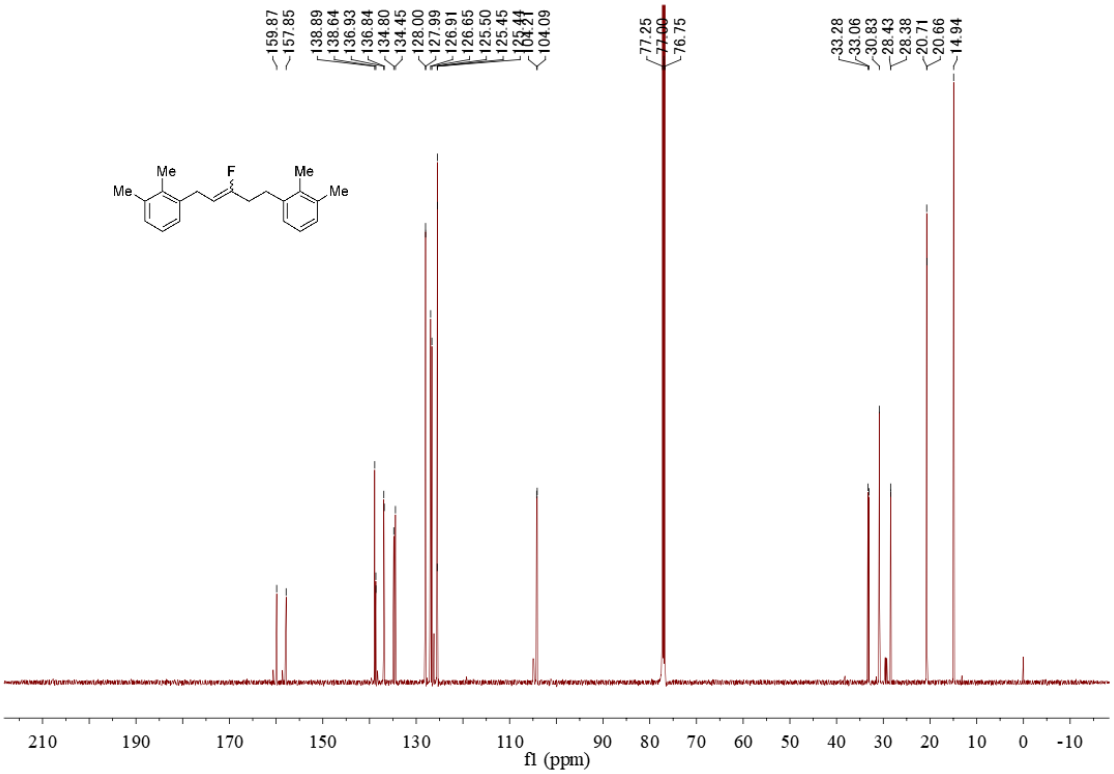


Figure S59. ^{19}F NMR spectrum of **3o**, related to **Figure 2**

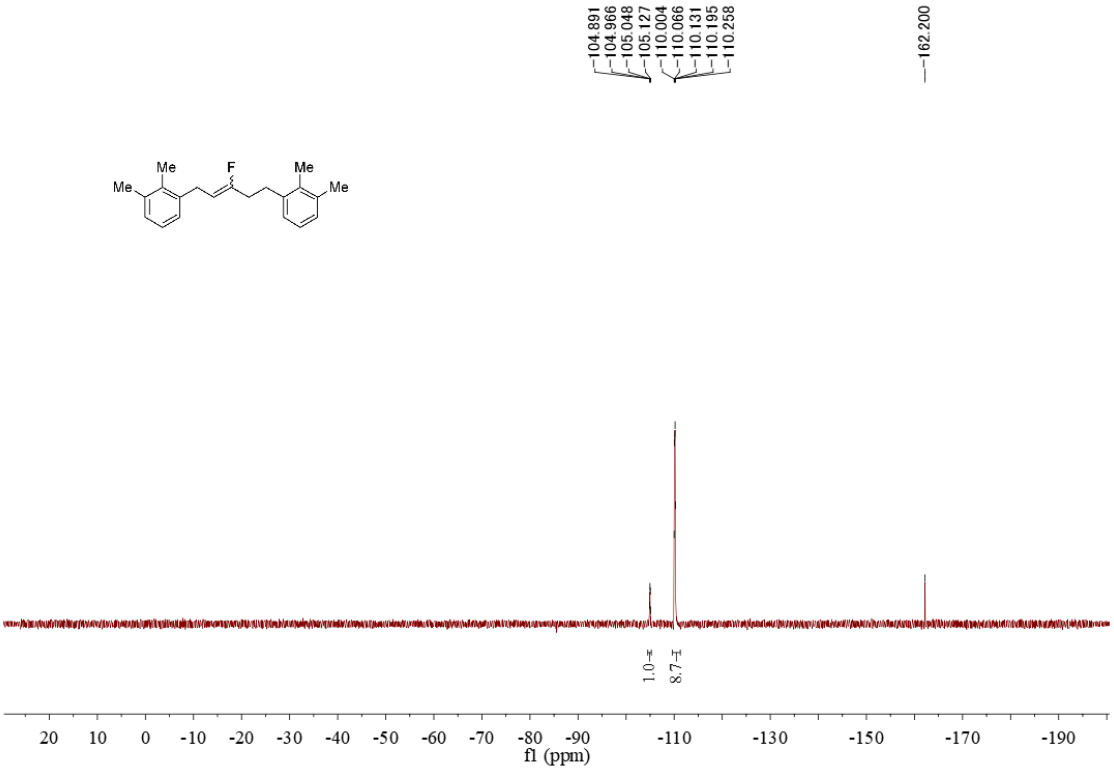


Figure S60. ^{1}H NMR spectrum of **3j**, related to **Figure 2**

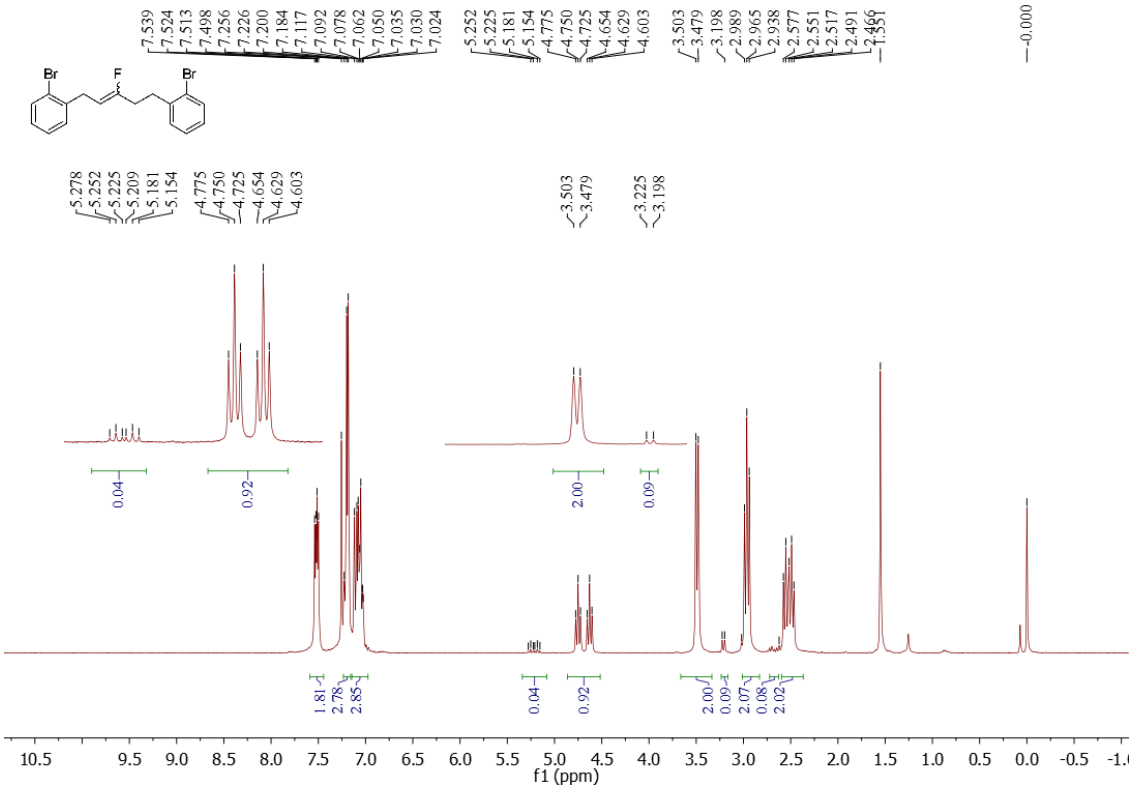


Figure S61. ^{13}C NMR spectrum of **3j**, related to **Figure 2**

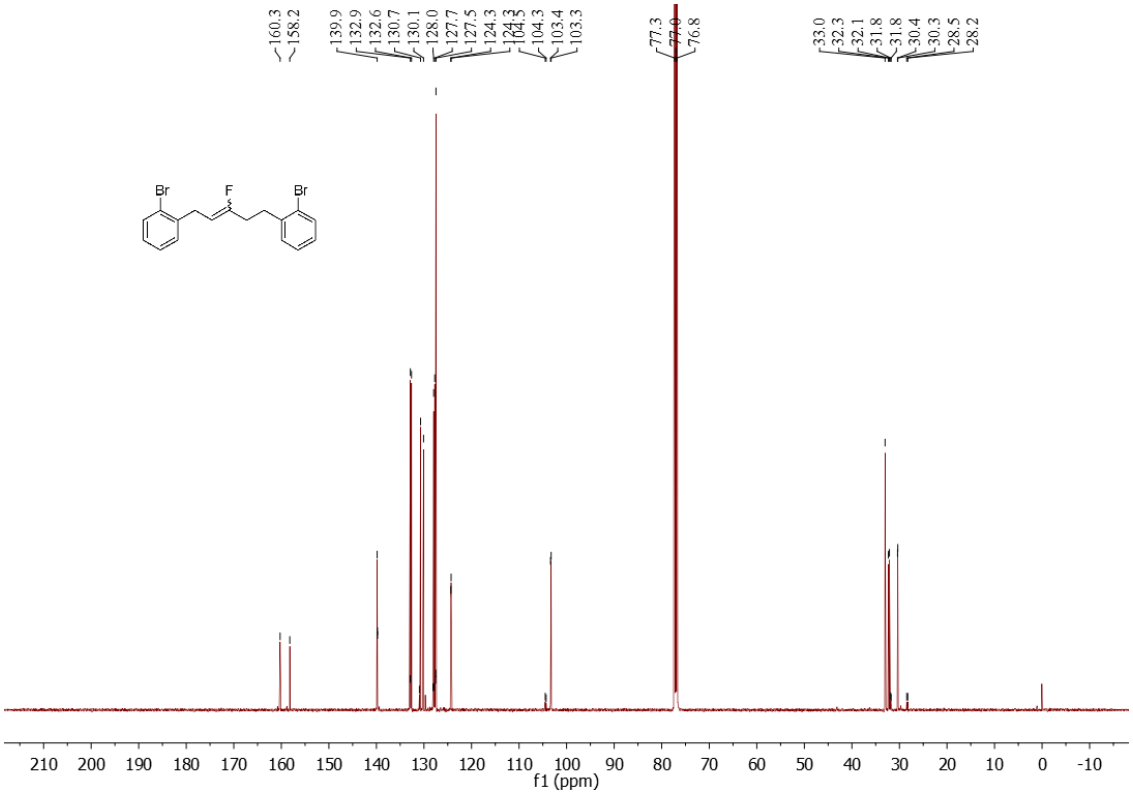


Figure S62. ^{19}F NMR spectrum of **3j**, related to **Figure 2**

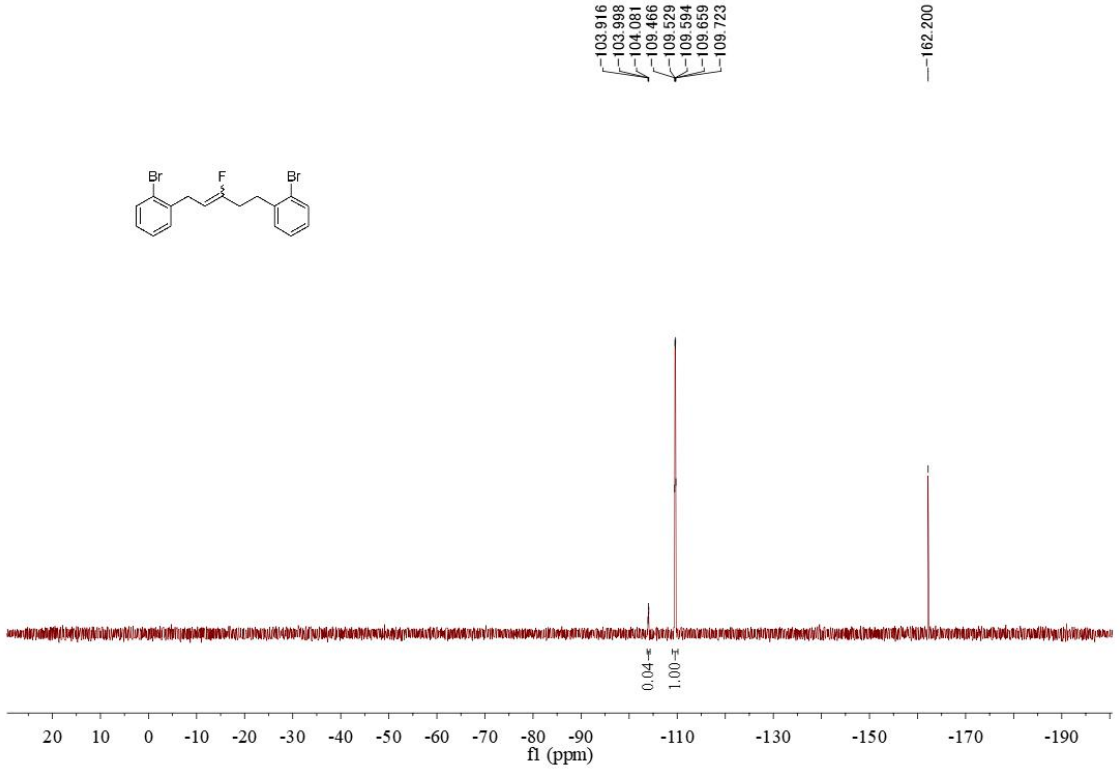


Figure S63. ^{1}H NMR spectrum of **3k**, related to **Figure 2**

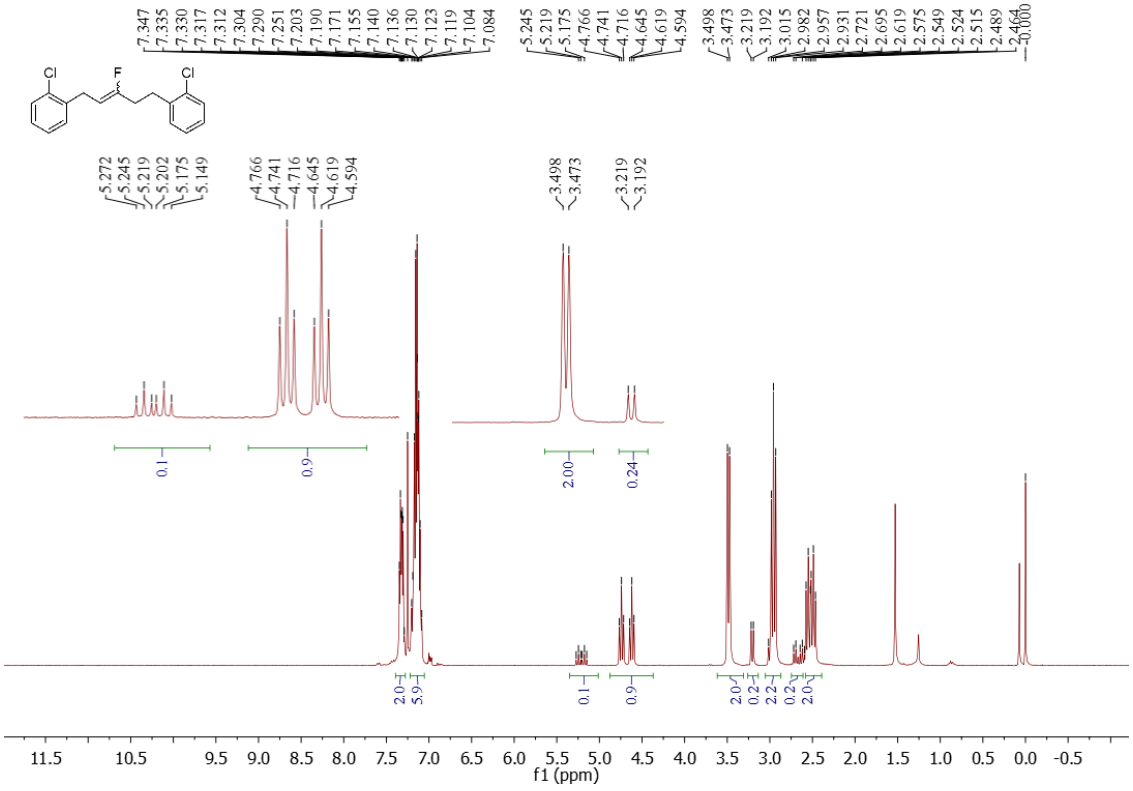


Figure S64. ^{13}C NMR spectrum of **3k**, related to **Figure 2**

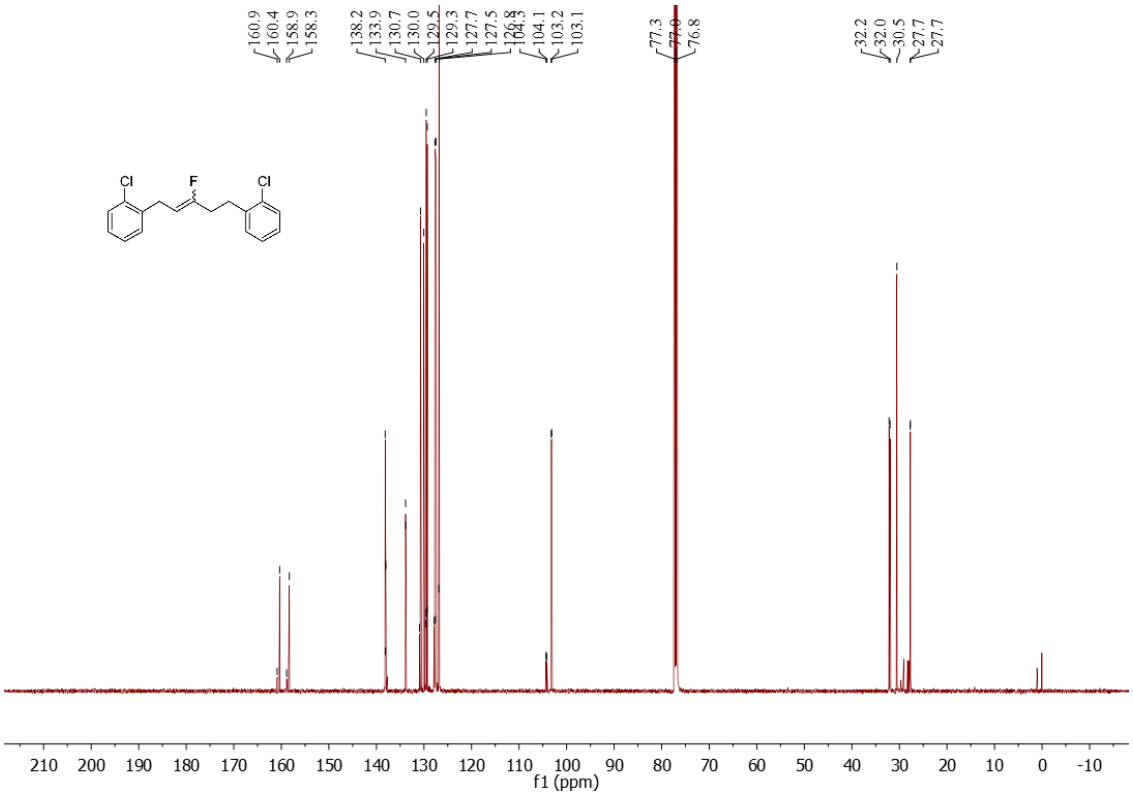


Figure S65. ^{19}F NMR spectrum of **3k**, related to **Figure 2**

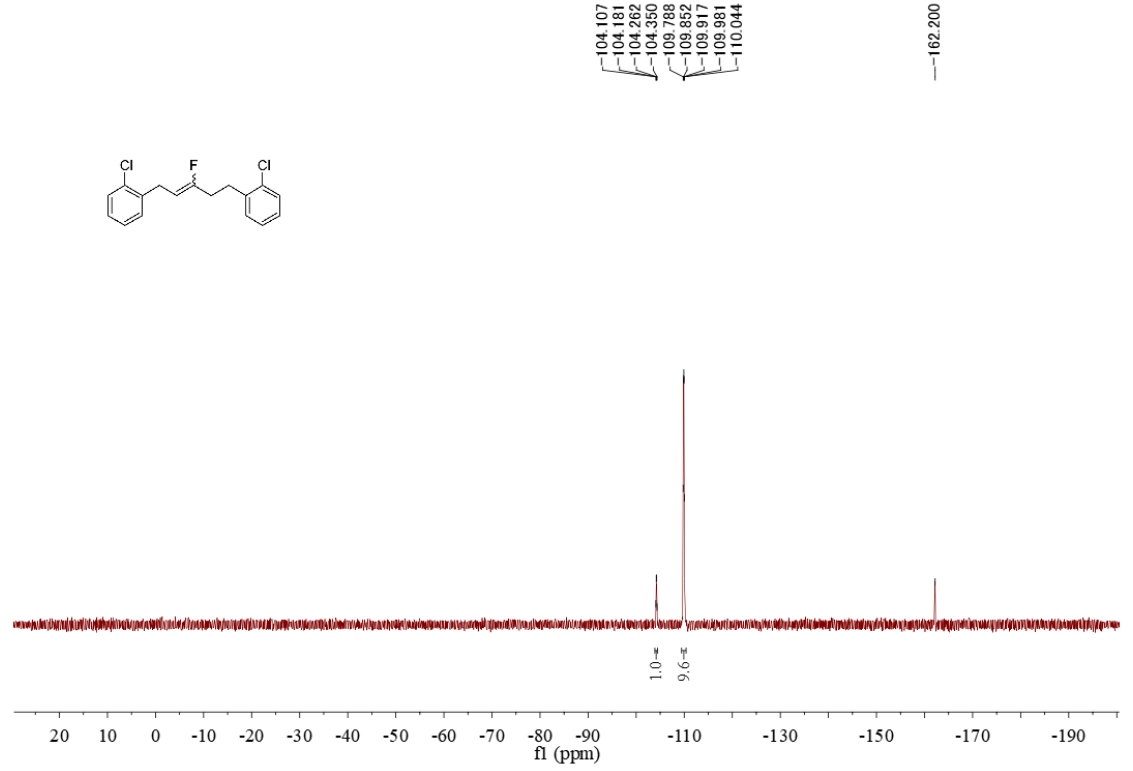


Figure S66. ^{1}H NMR spectrum of **3u**, related to **Figure 2**

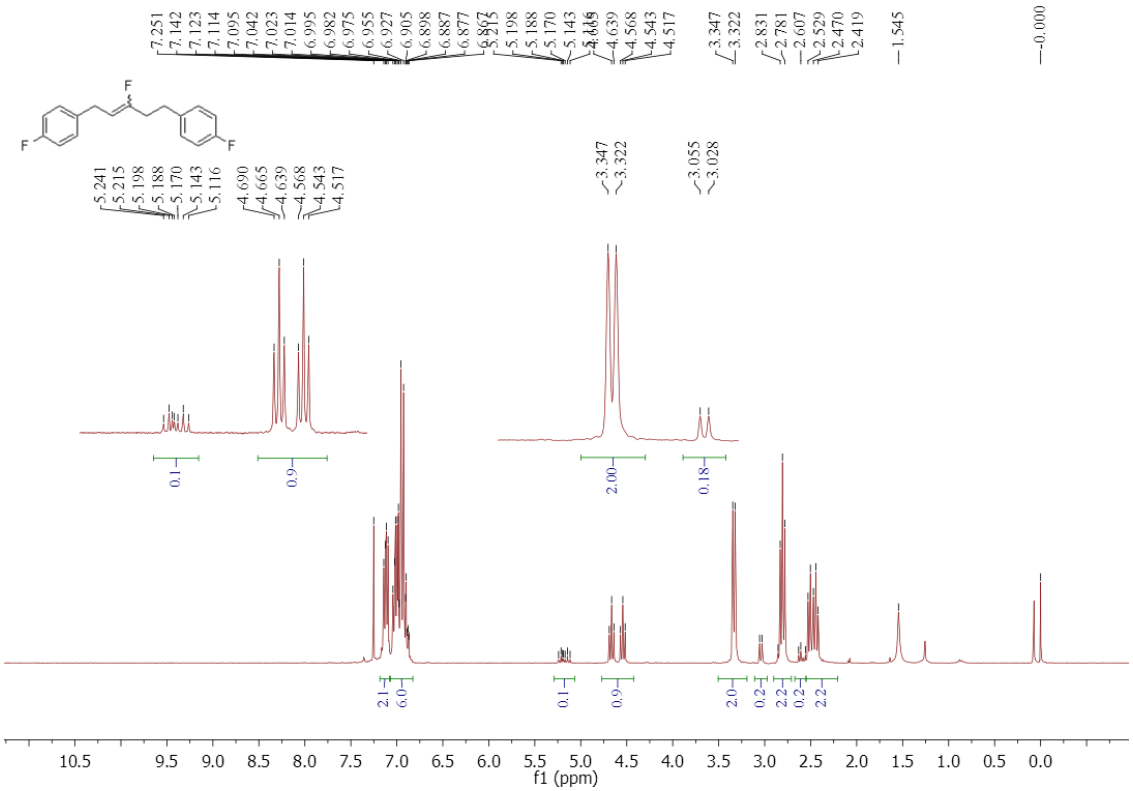


Figure S67. ^{13}C NMR spectrum of **3u**, related to **Figure 2**

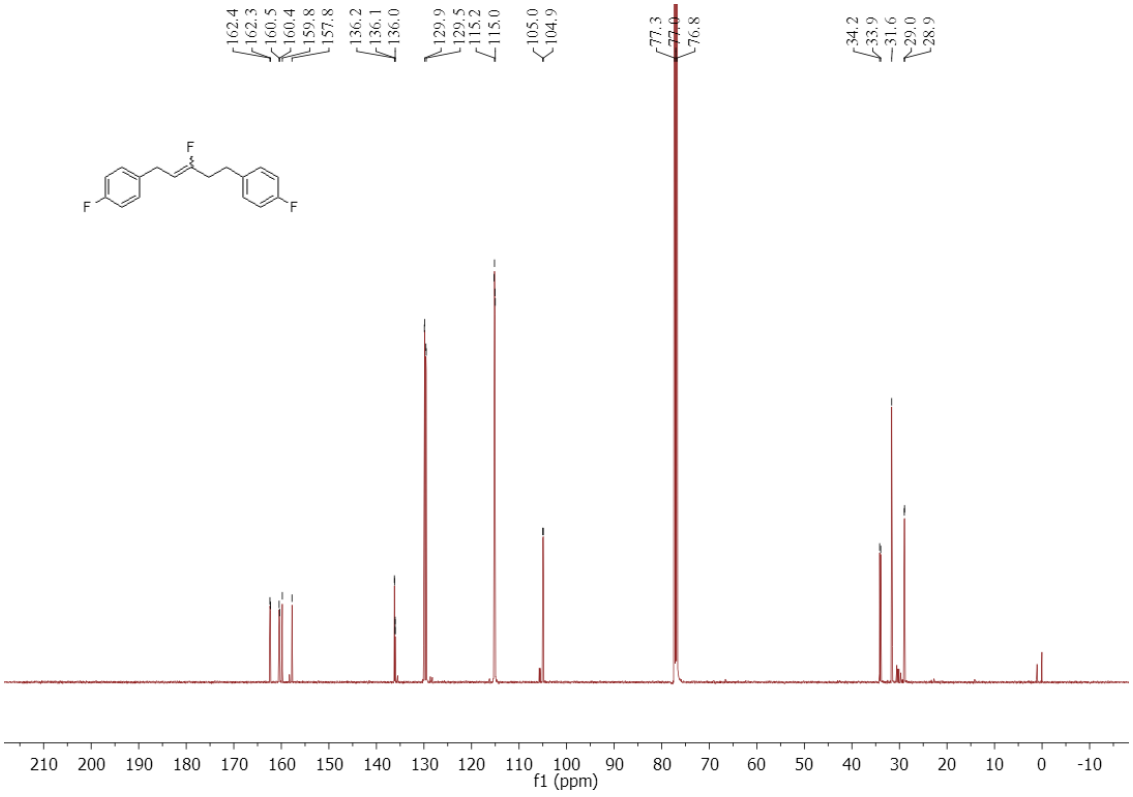


Figure S68. ^{19}F NMR spectrum of **3u**, related to **Figure 2**

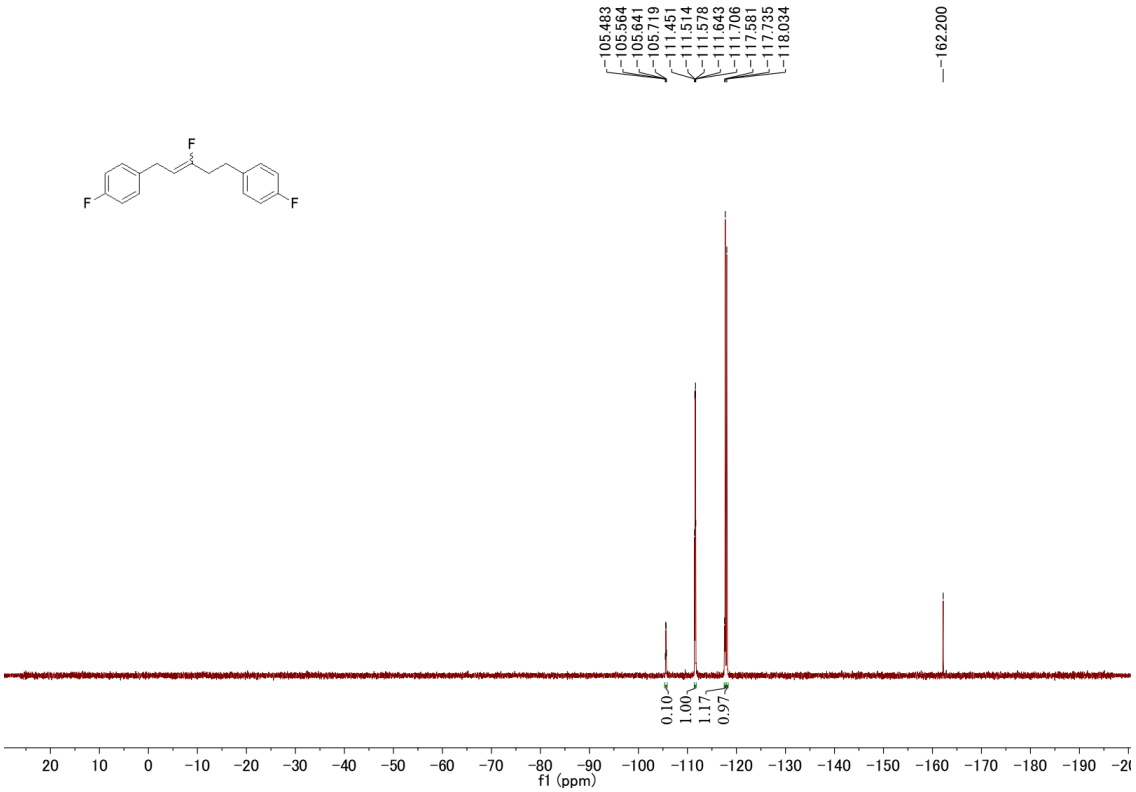


Figure S69. ^{1}H NMR spectrum of **3aa**, related to **Figure 2**

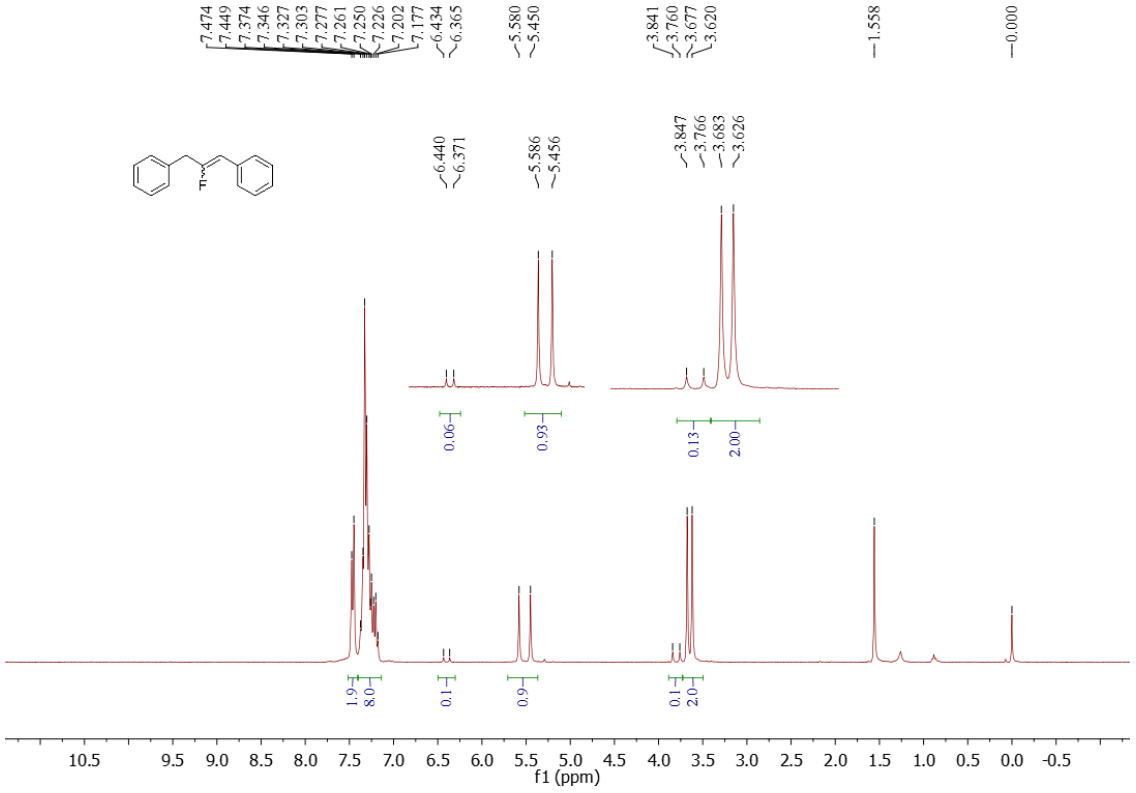


Figure S70. ^{19}F NMR spectrum of **3aa**, related to **Figure 2**

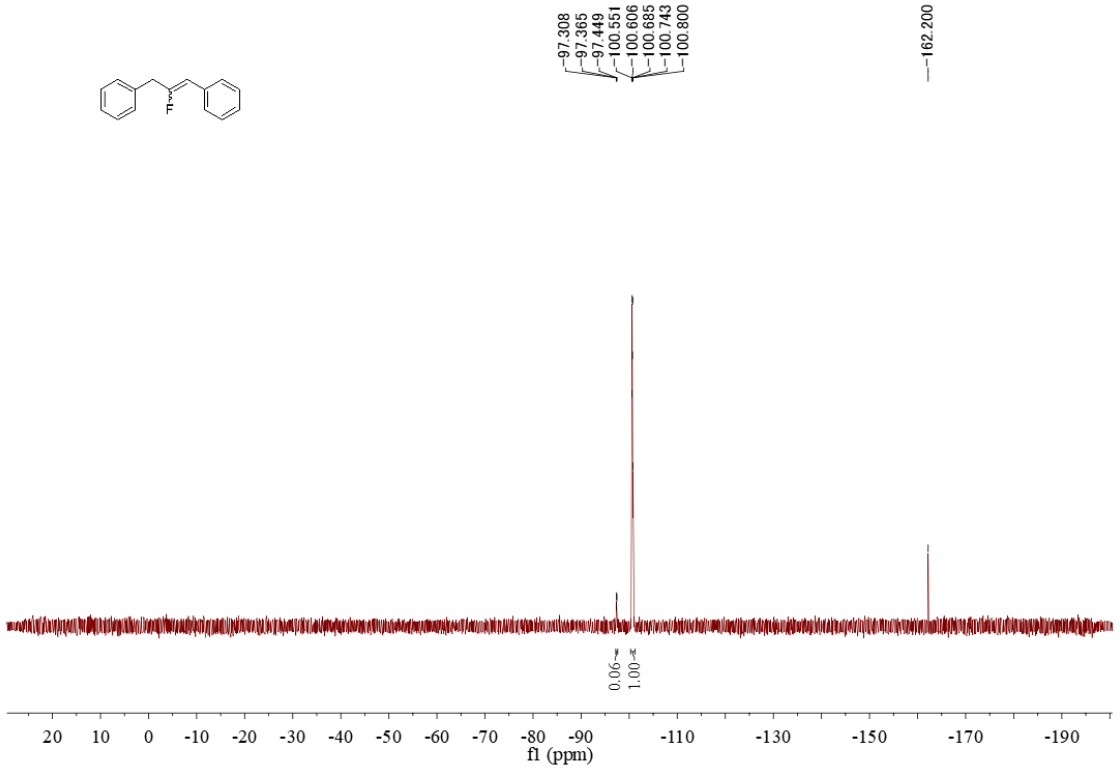


Figure S71. ^{1}H NMR spectrum of **3bb**, related to **Figure 2**

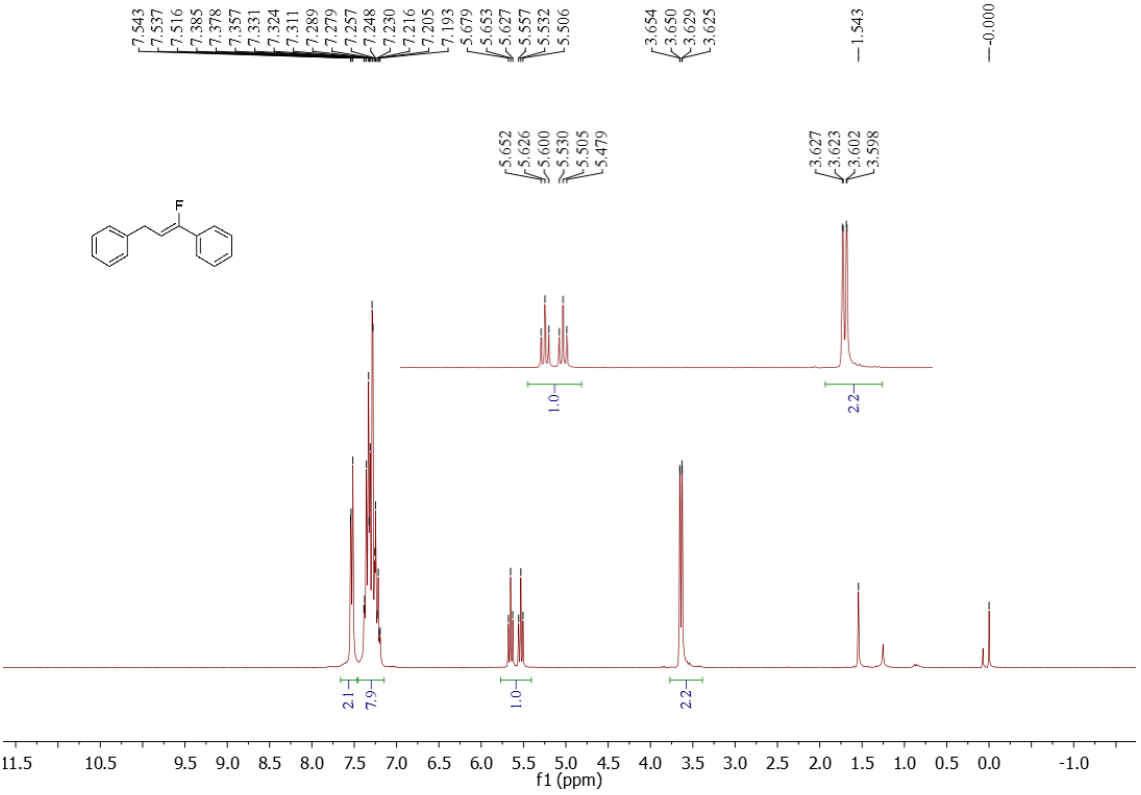


Figure S72. ^{19}F NMR spectrum of **3bb**, related to **Figure 2**

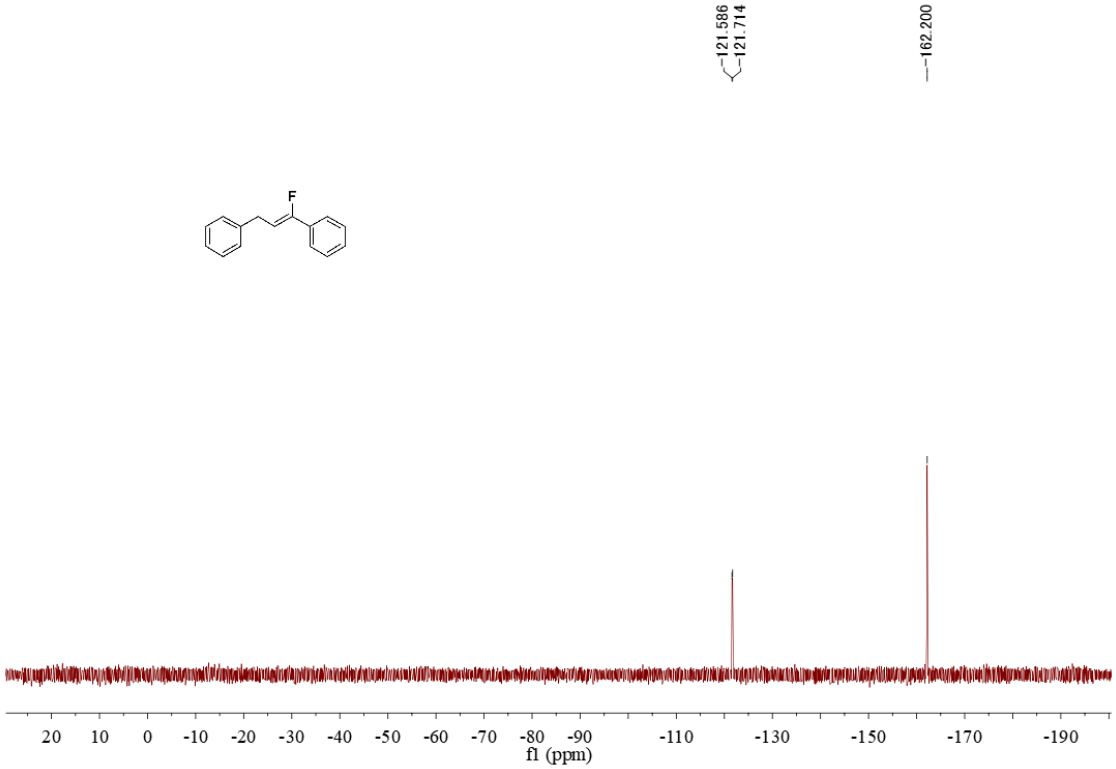


Figure S73. ^{1}H NMR spectrum of **3cc**, related to **Figure 2**

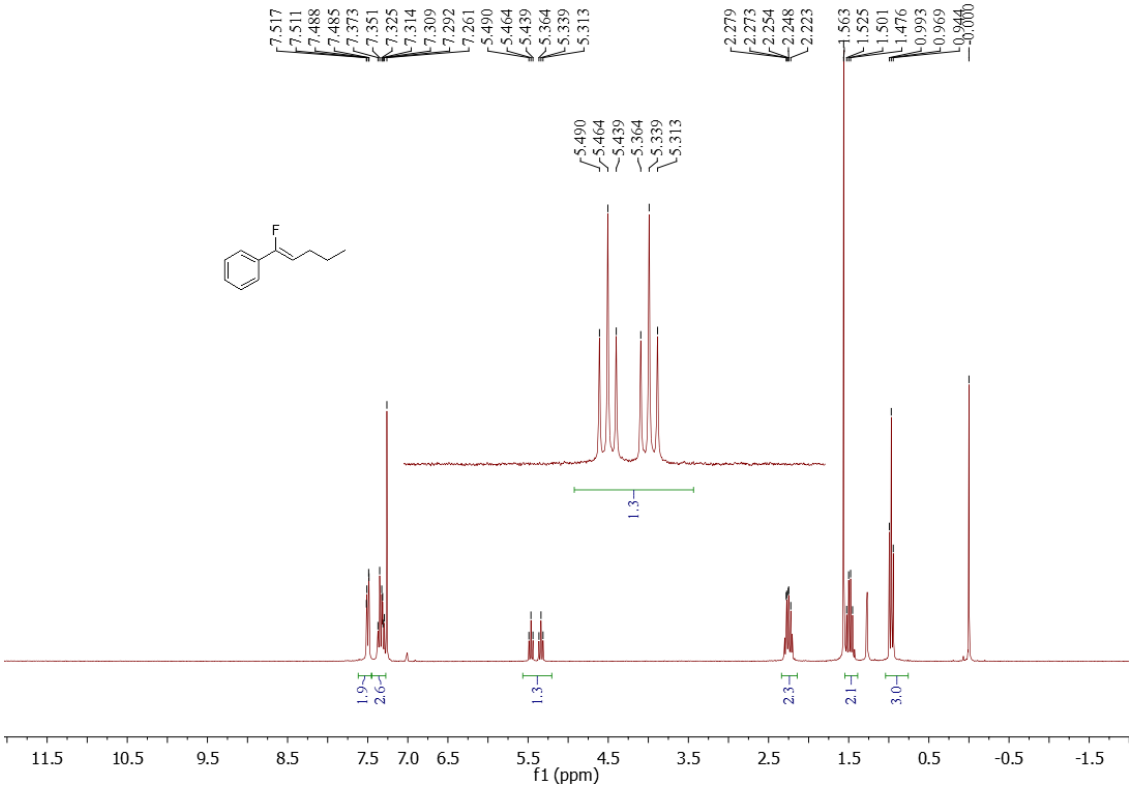


Figure S74. ^{19}F NMR spectrum of **3cc**, related to **Figure 2**

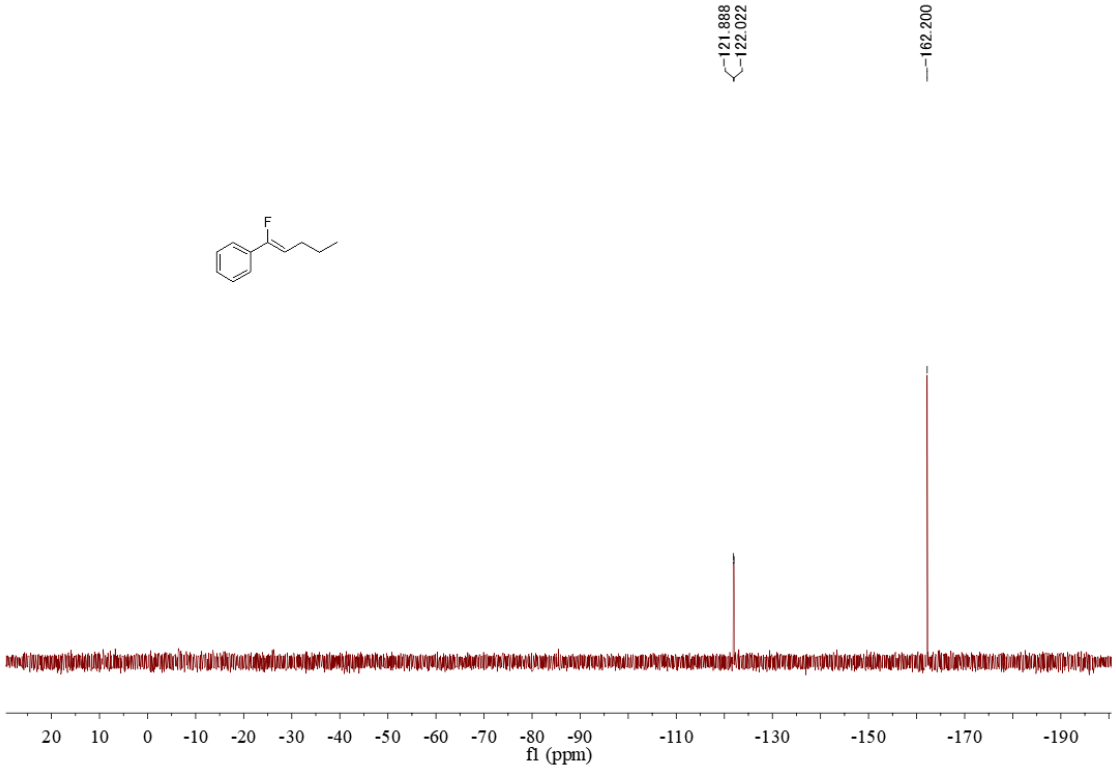


Figure S75. ^{1}H NMR spectrum of **3dd**, related to **Figure 2**

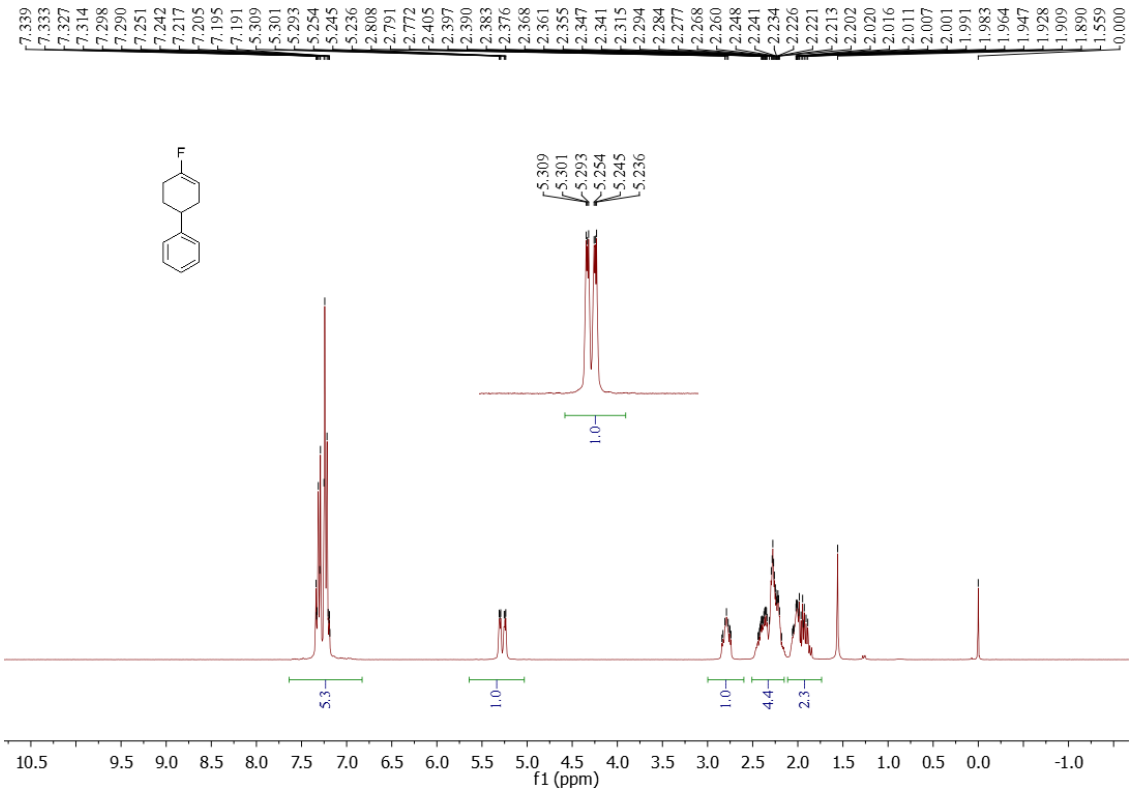


Figure S76. ^{19}F NMR spectrum of **3dd**, related to **Figure 2**

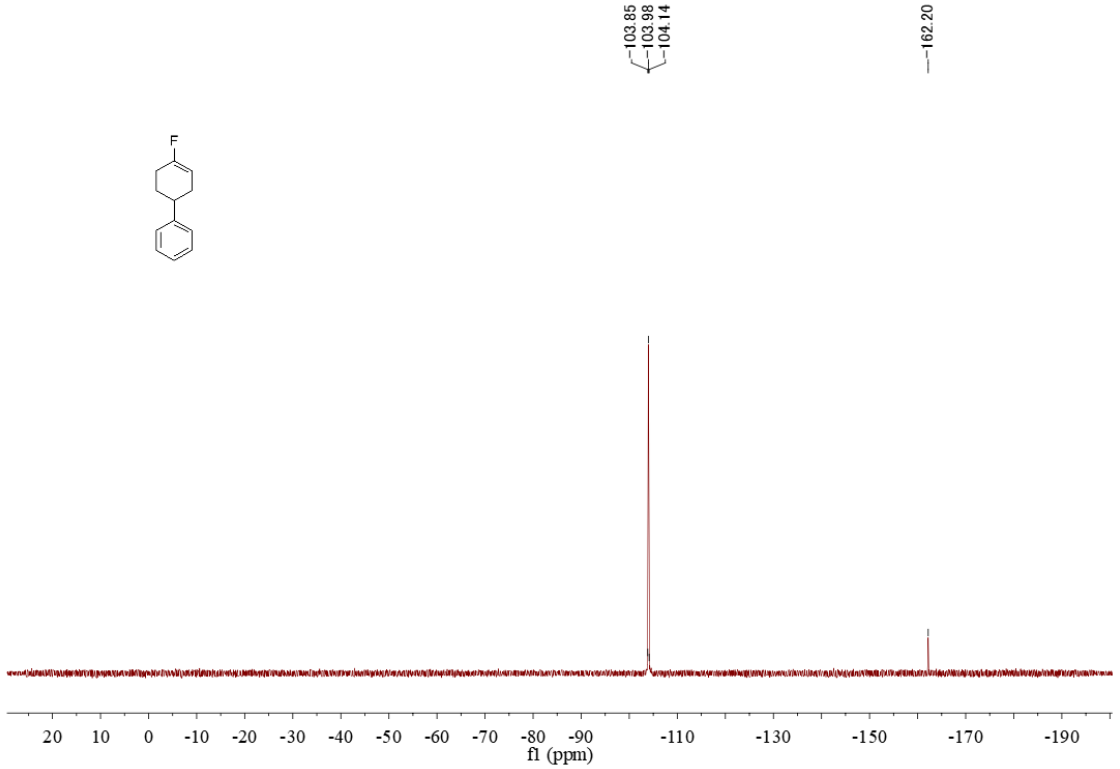


Figure S77. ^{1}H NMR spectrum of **3ee**, related to **Figure 2**

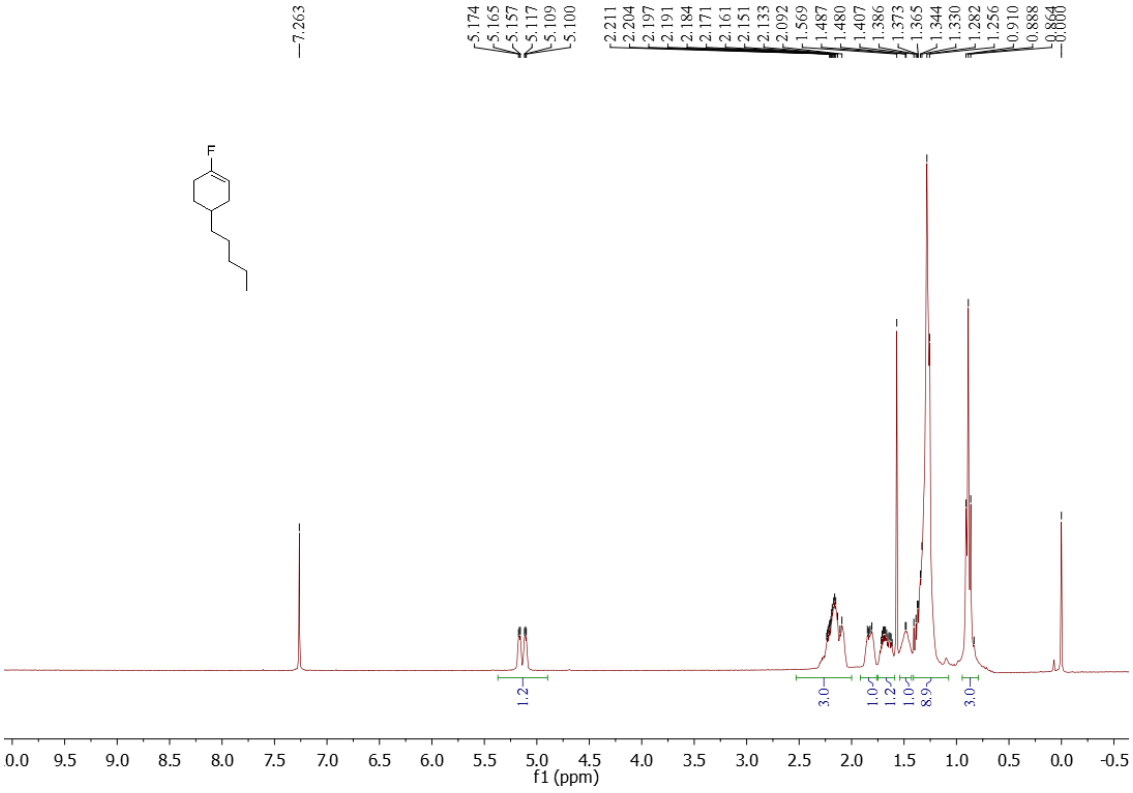


Figure S78. ^{19}F NMR spectrum of **3ee**, related to **Figure 2**

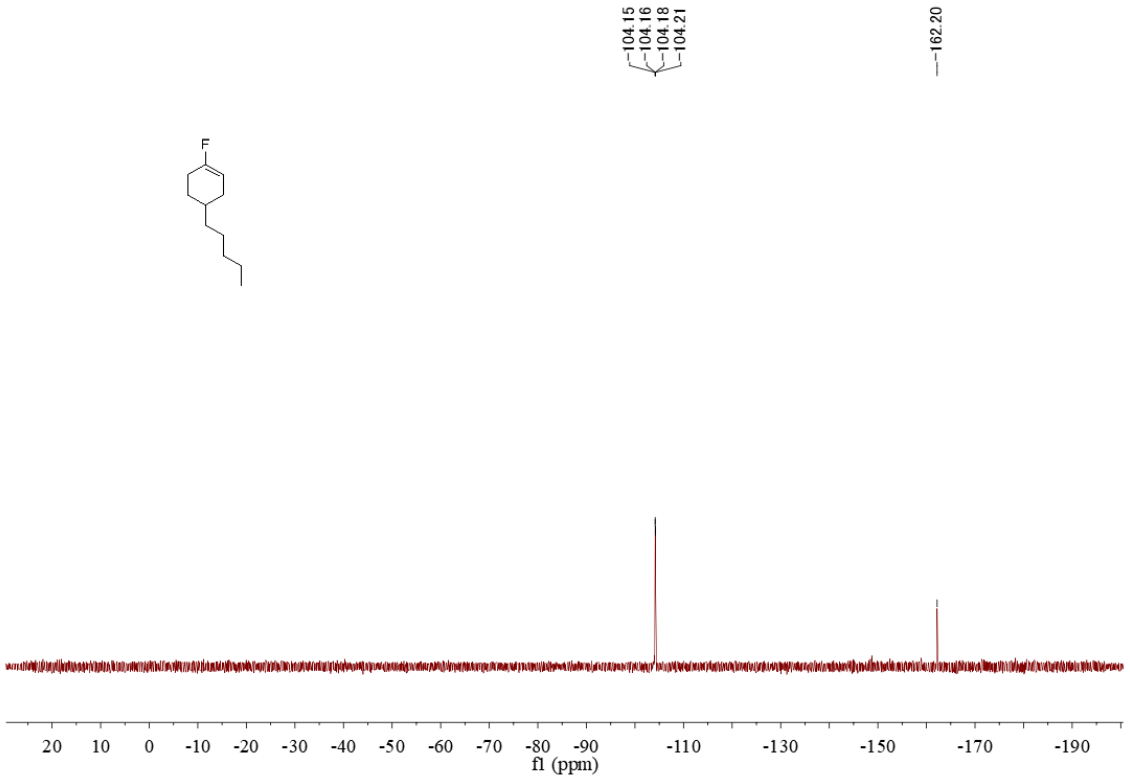


Figure S79. ^{1}H NMR spectrum of **3ff**, related to **Figure 2**

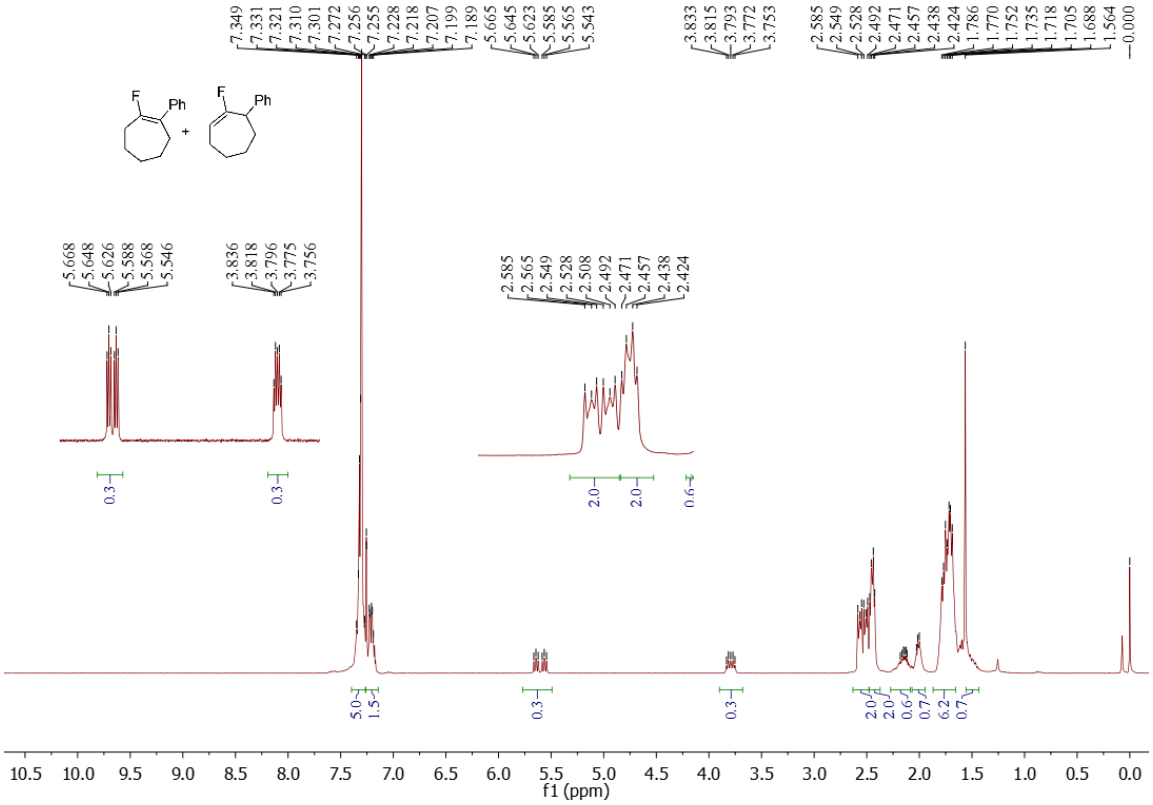


Figure S80. ^{13}C NMR spectrum of **3ff**, related to **Figure 2**

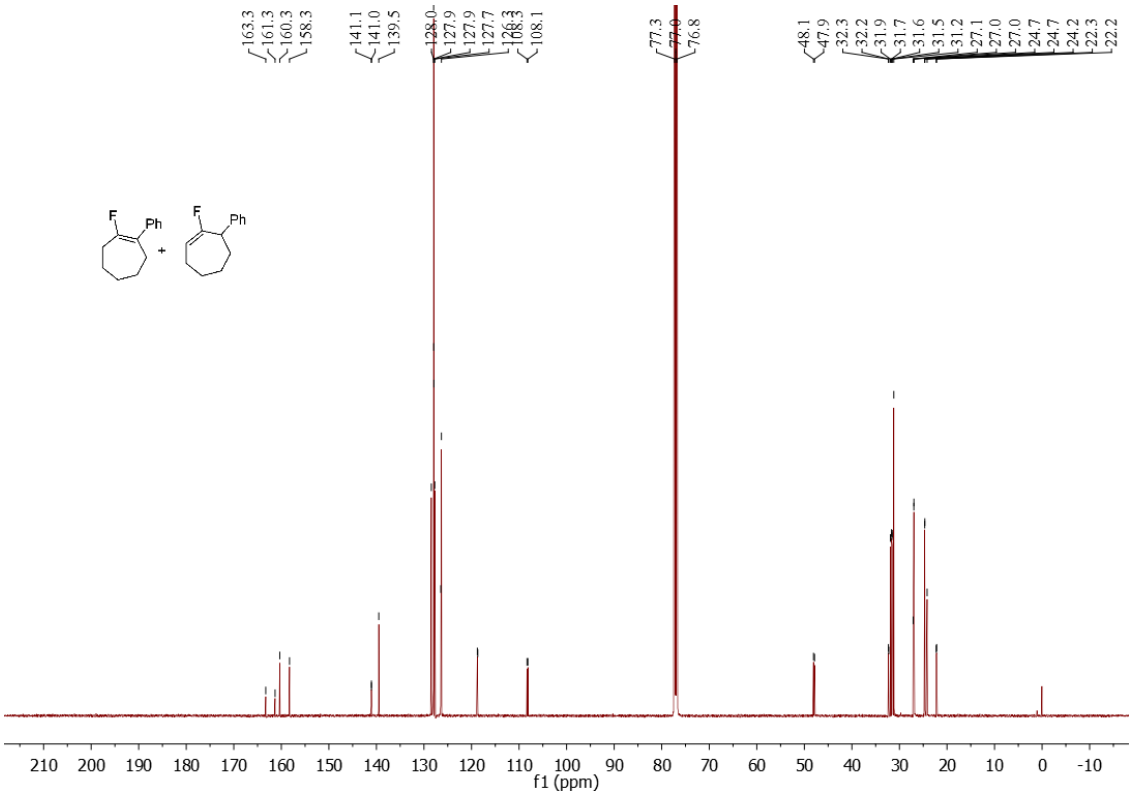


Figure S81. ^{19}F NMR spectrum of **3ff**, related to **Figure 2**

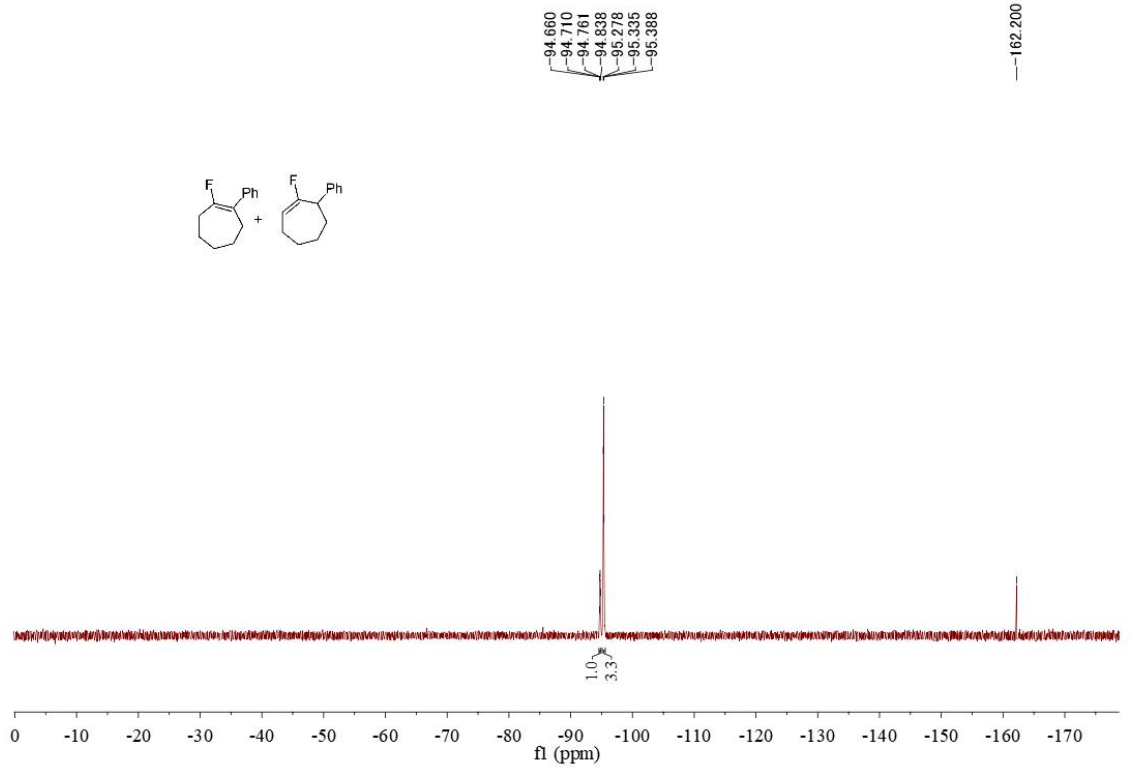


Figure S82. ^{1}H NMR spectrum of **3gg**, related to **Figure 2**

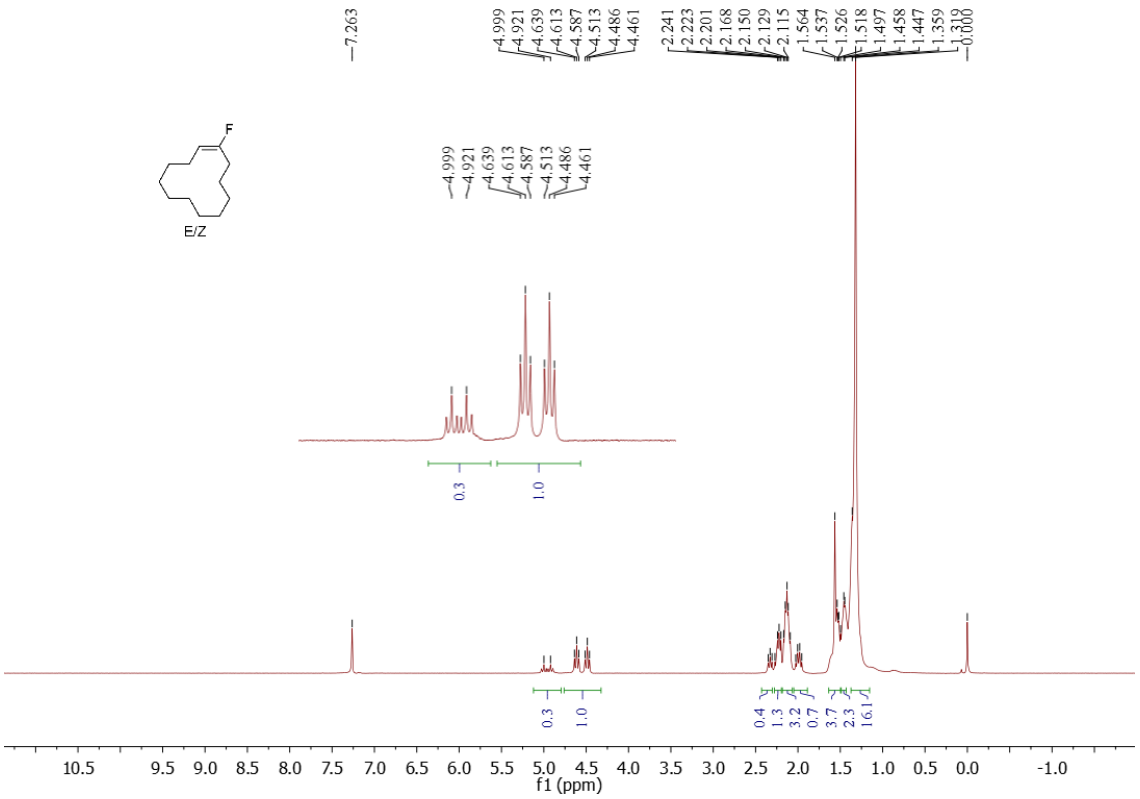


Figure S83. ^{13}C NMR spectrum of **3gg**, related to **Figure 2**

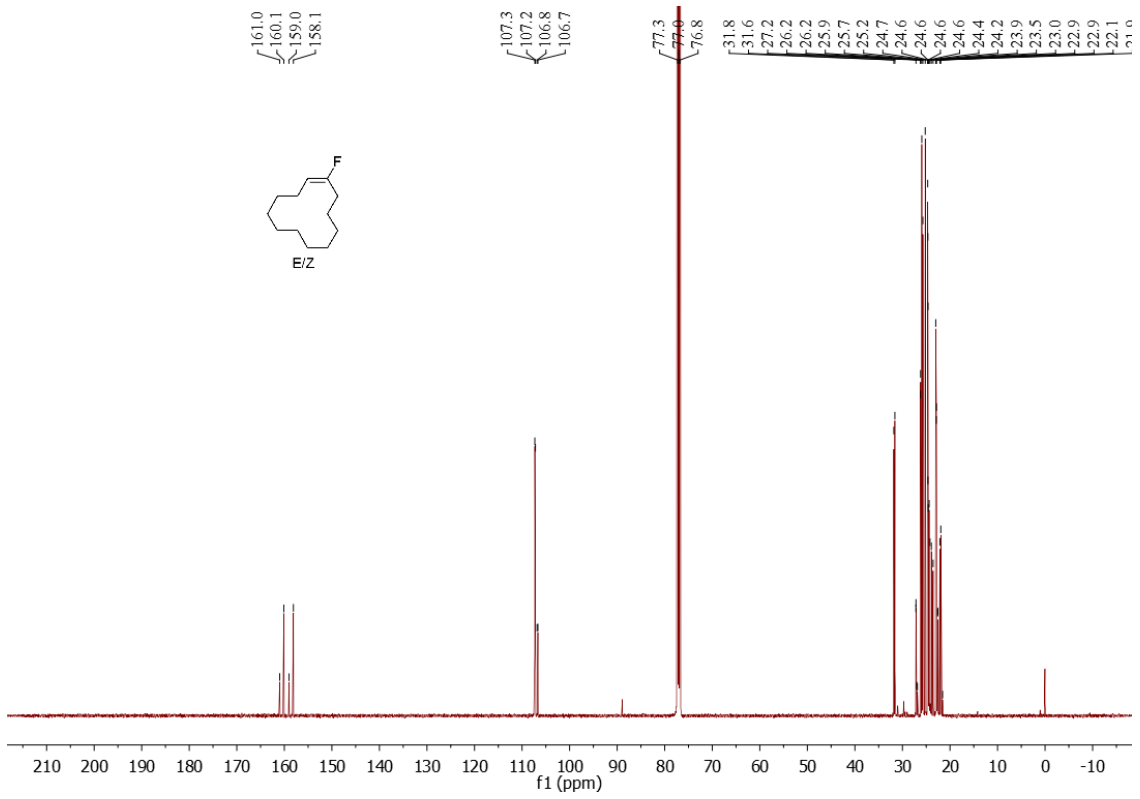


Figure S84. ^{19}F NMR spectrum of **3gg**, related to **Figure 2**

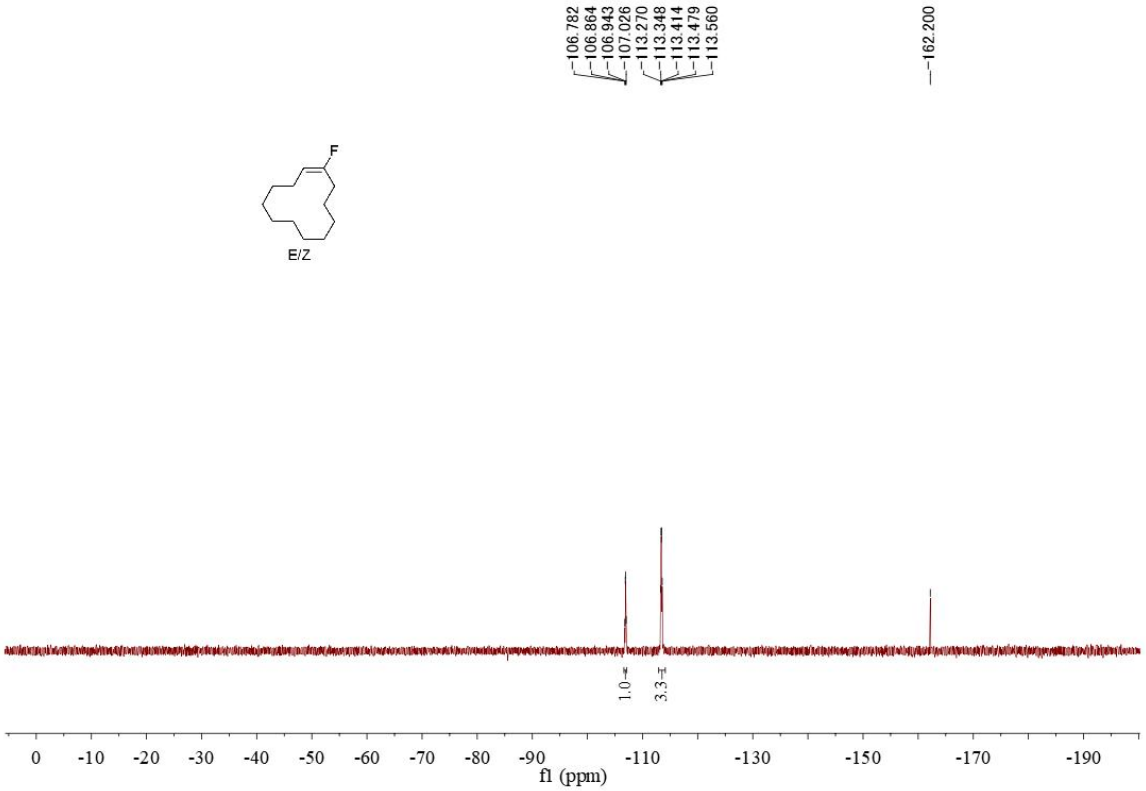


Figure S85. ^{1}H NMR spectrum of (*Z*)-**3hh**, related to **Figure 2**

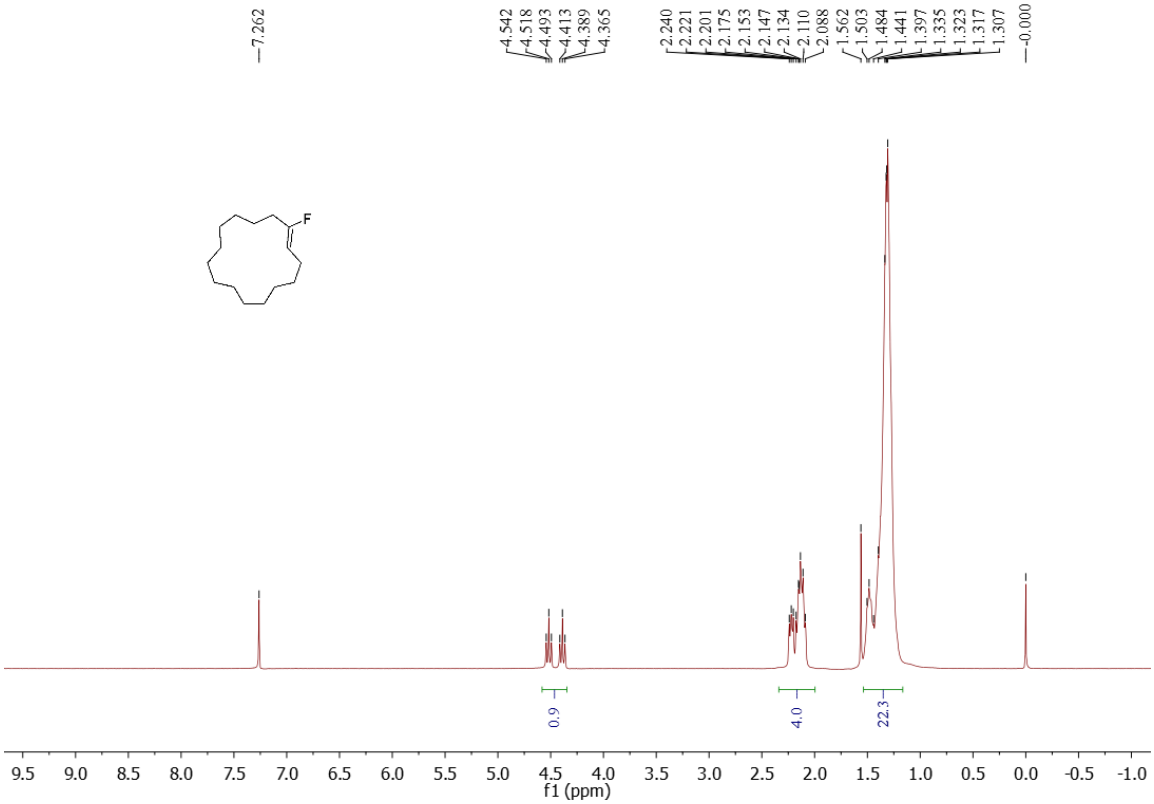


Figure S86. ^{13}C NMR spectrum of (*Z*)-**3hh**, related to **Figure 2**

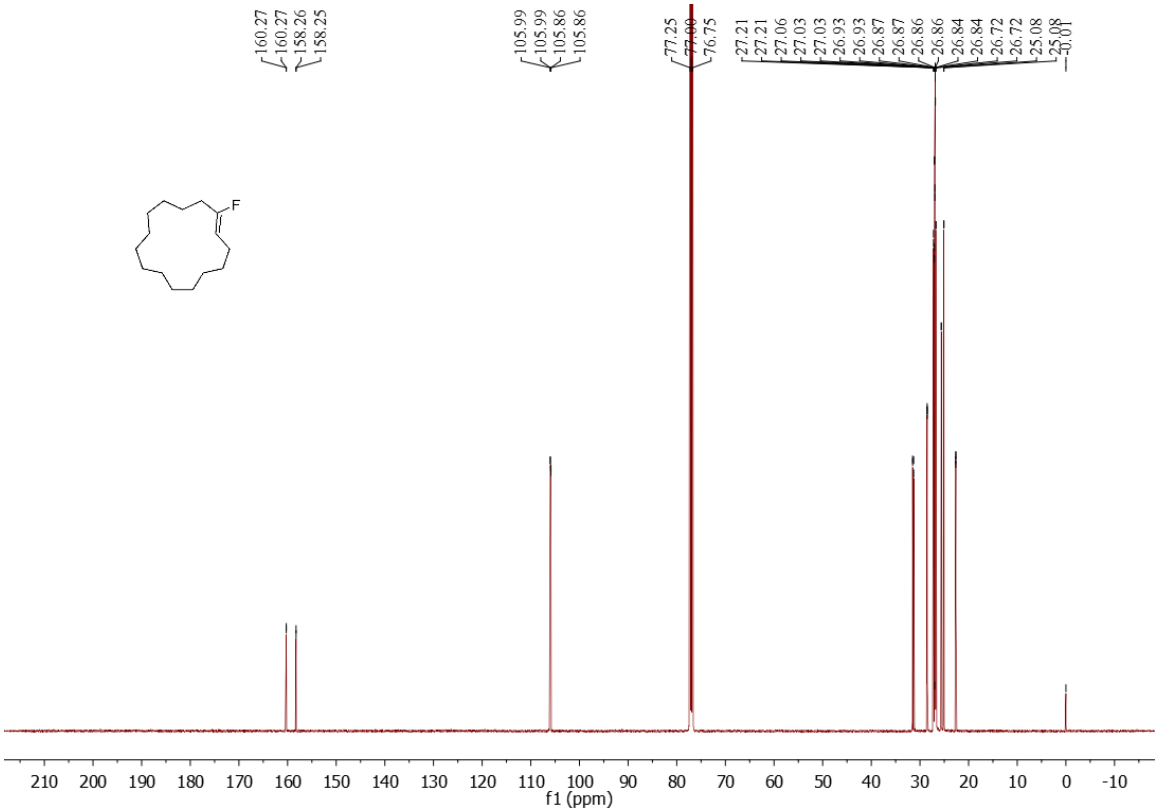


Figure S87. ^{19}F NMR spectrum of (*Z*)-**3hh**, related to **Figure 2**

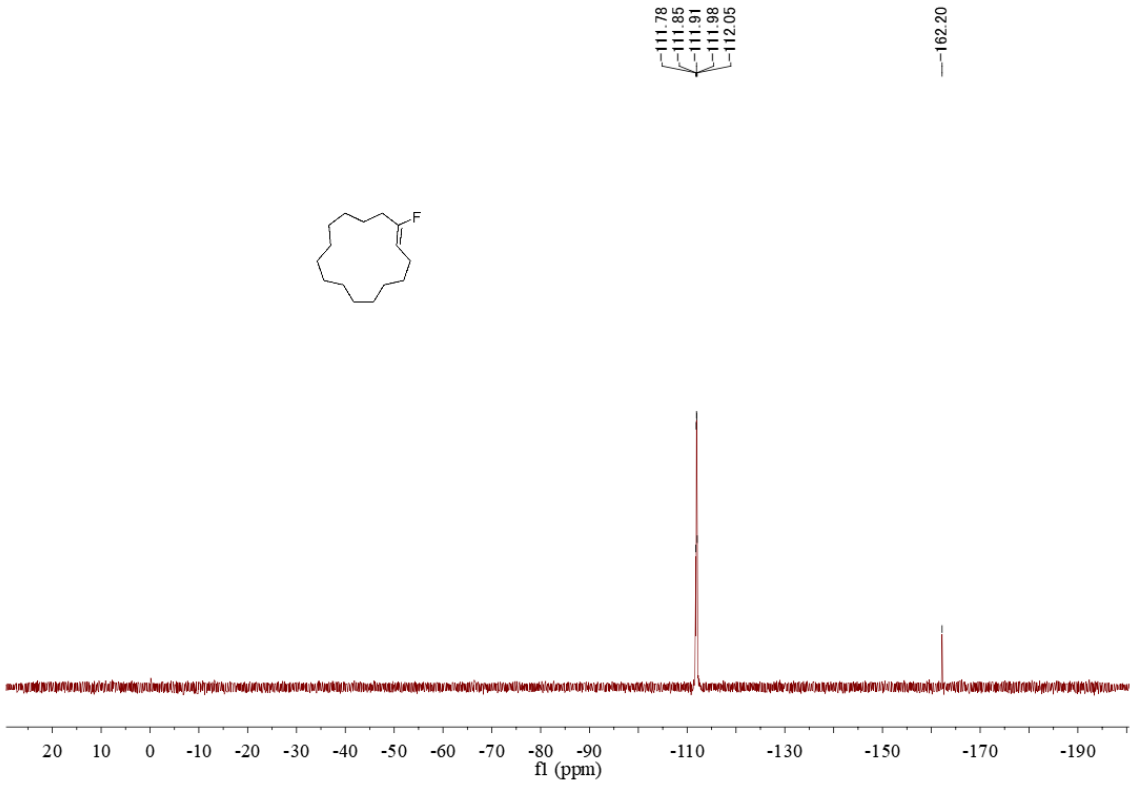


Figure S88. ^{19}F NMR spectrum of **3hh**, related to **Figure 2**

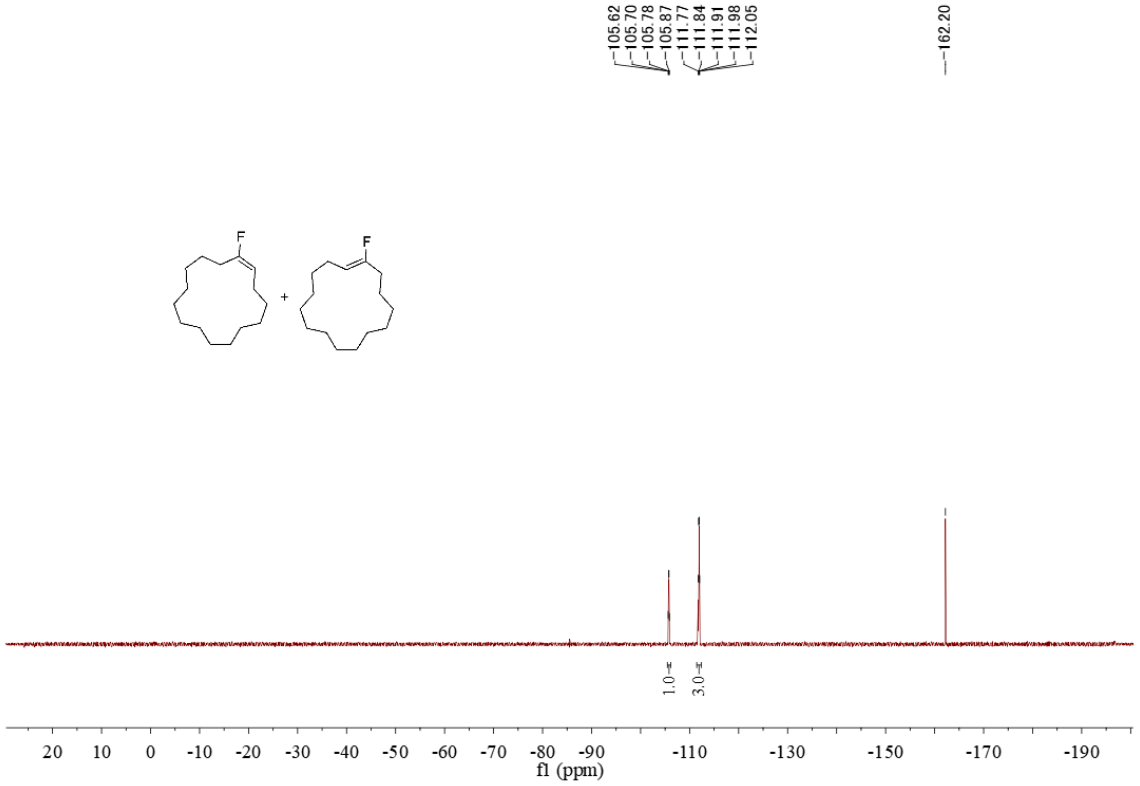


Figure S89. ^{1}H NMR spectrum of **5a**, related to **Figure 3**

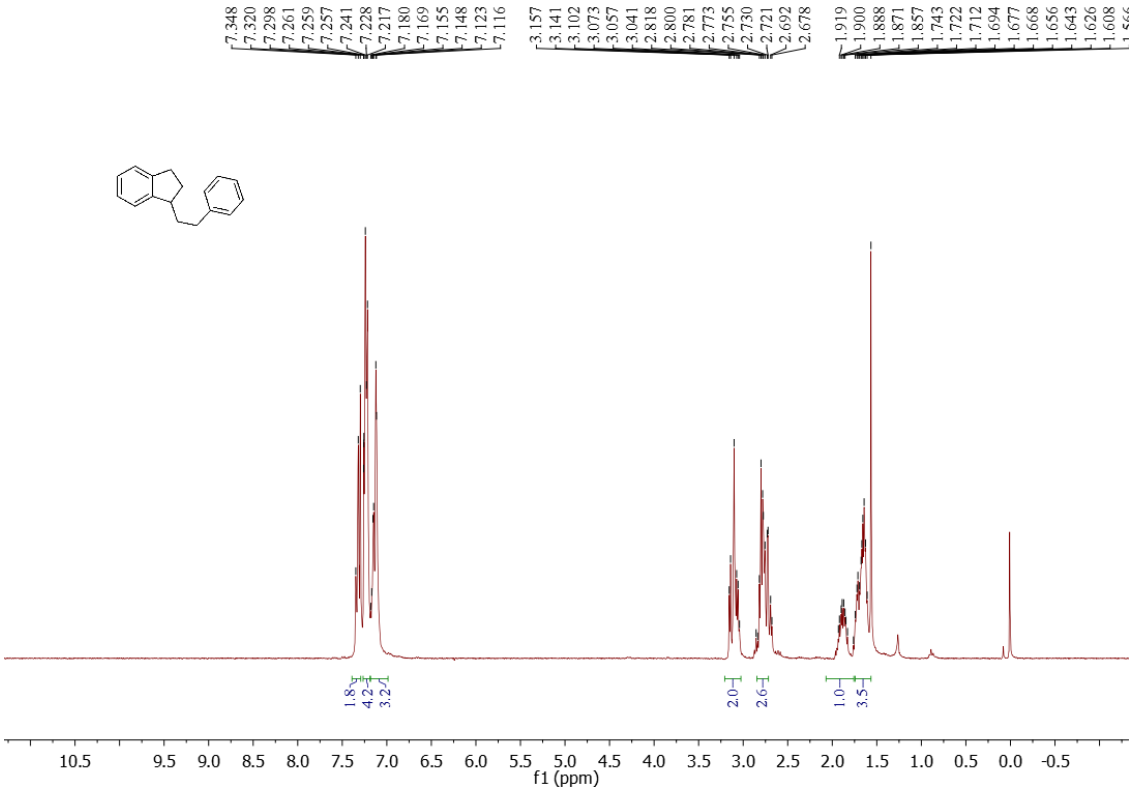


Figure S90. ^{13}C NMR spectrum of **5a**, related to **Figure 3**

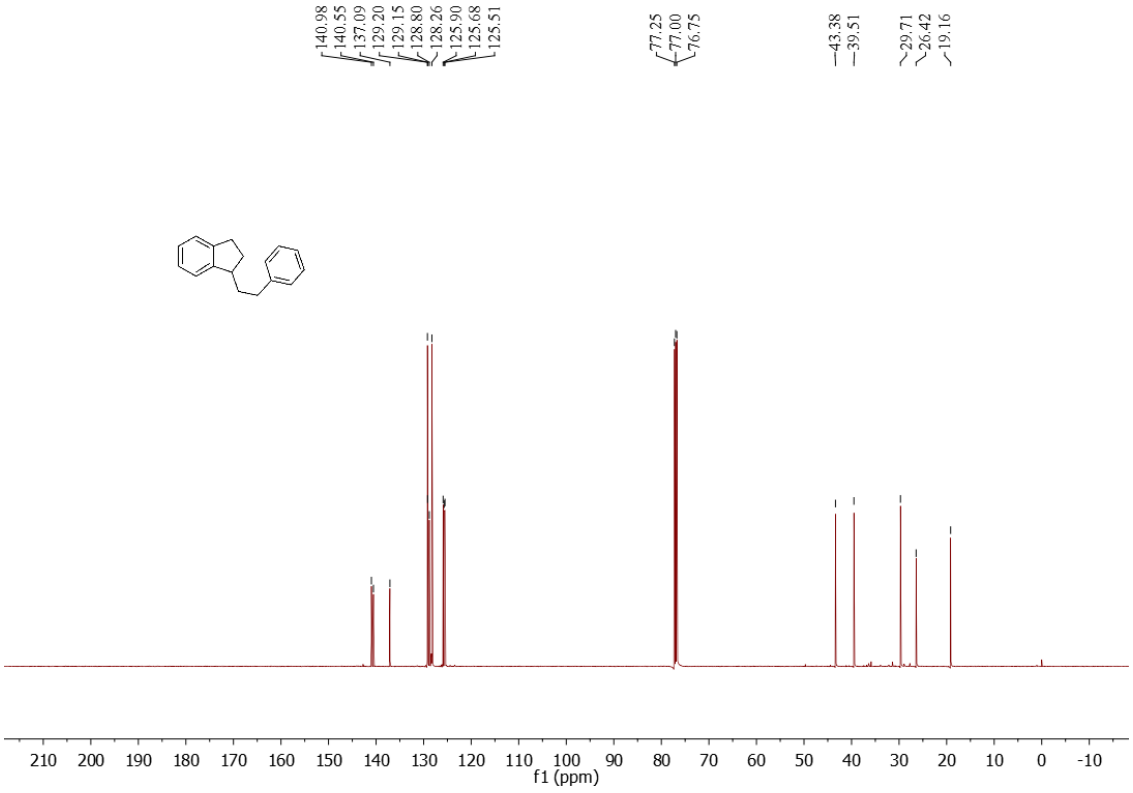


Figure S91. ^{1}H NMR spectrum of **5b**, related to **Figure 3**

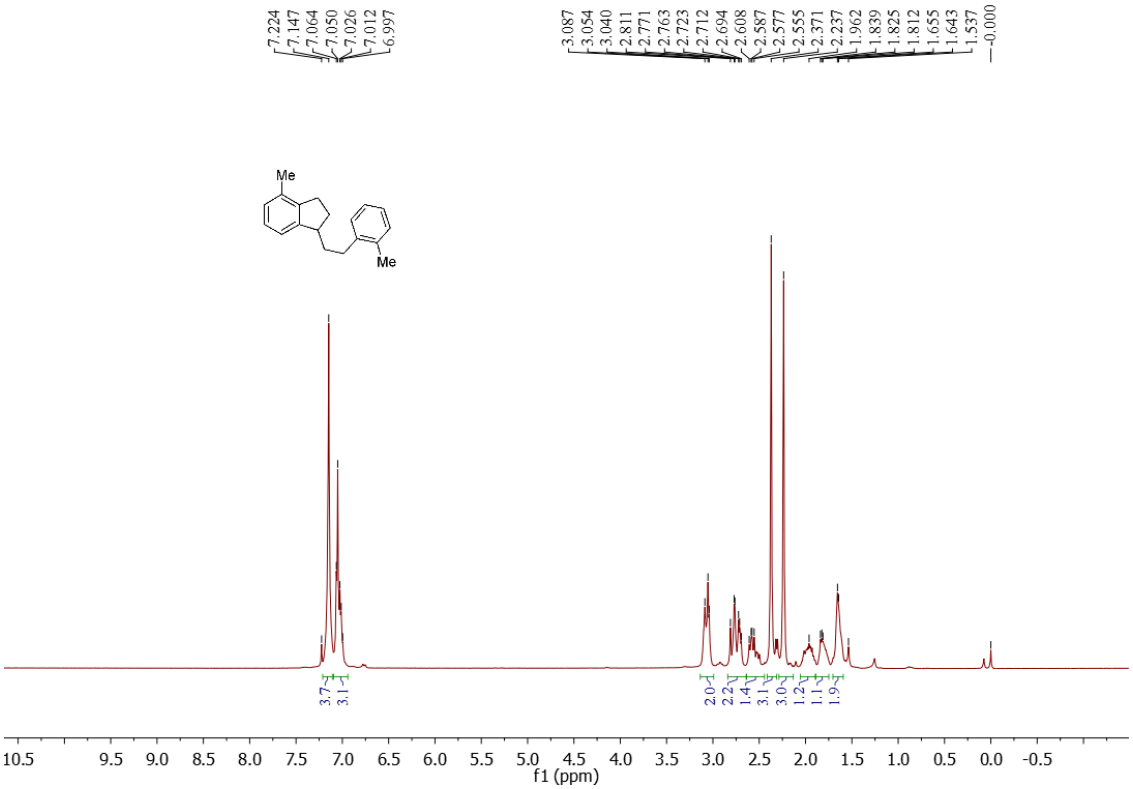


Figure S92. ^{13}C NMR spectrum of **5b**, related to **Figure 3**

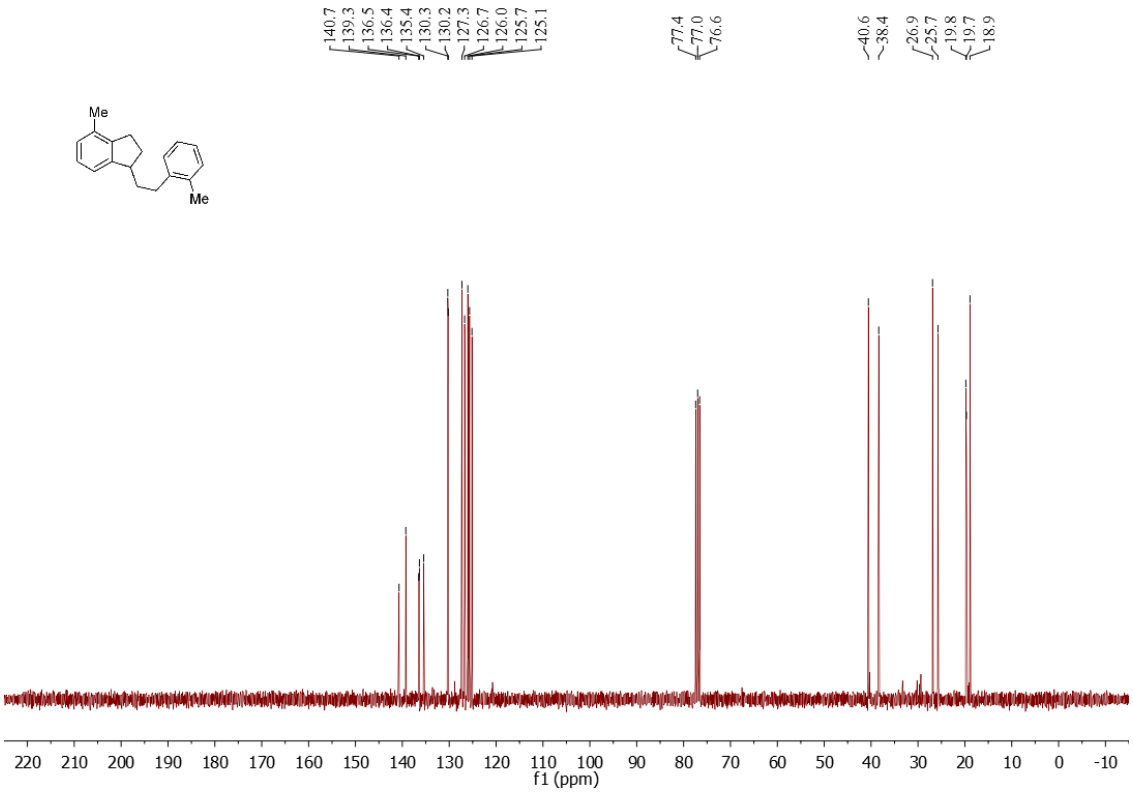


Figure S93. ^{1}H NMR spectrum of **5c**, related to **Figure 3**

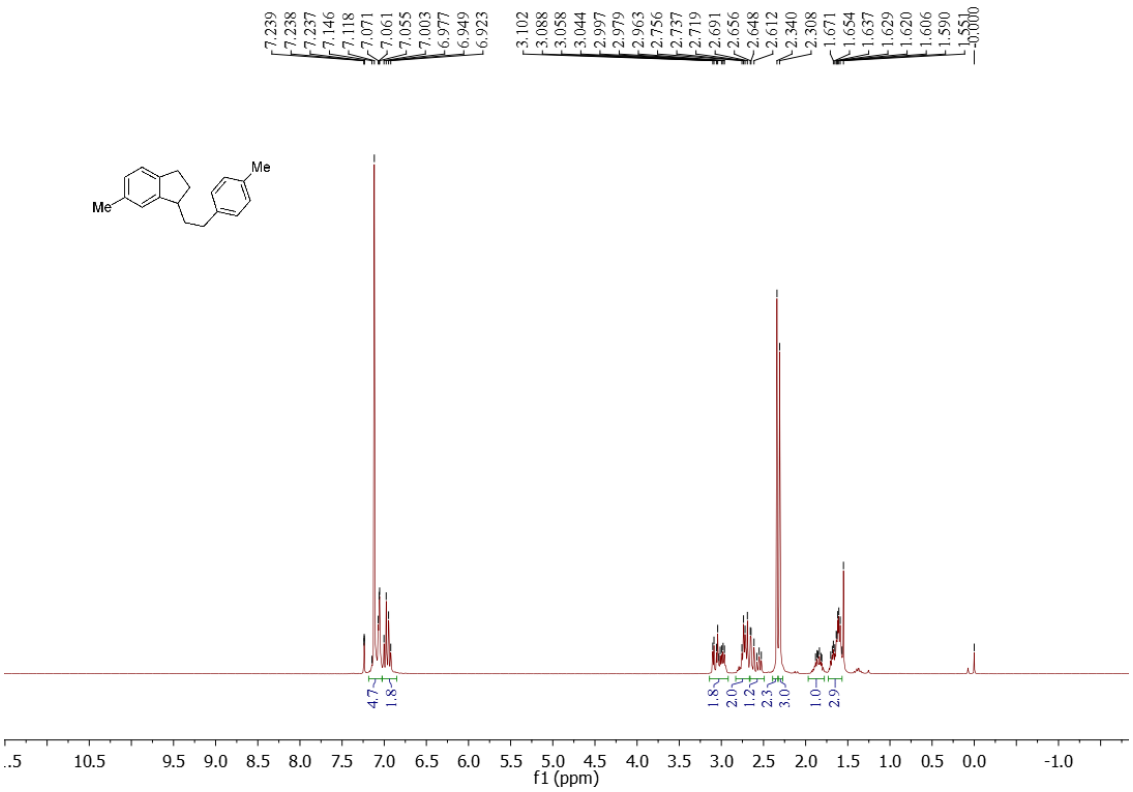


Figure S94. ^{13}C NMR spectrum of **5c**, related to **Figure 3**

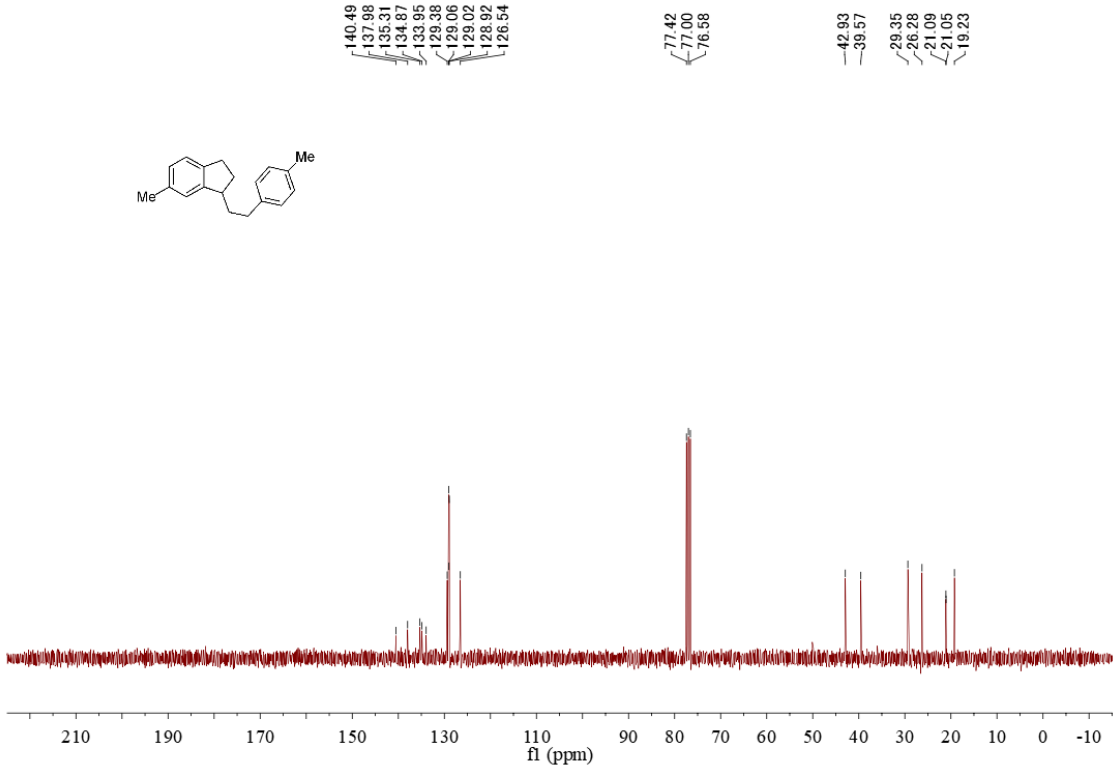


Figure S95. ^{1}H NMR spectrum of **5d**, related to **Figure 3**

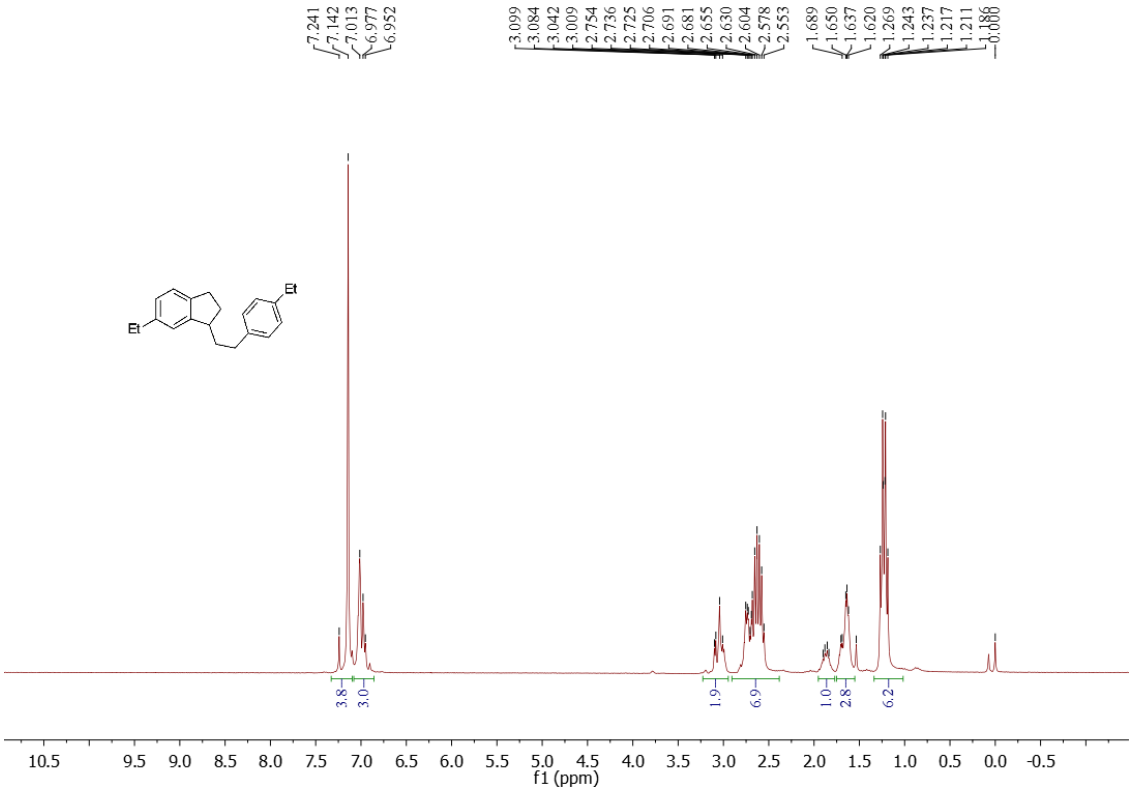


Figure S96. ^{13}C NMR spectrum of **5d**, related to **Figure 3**

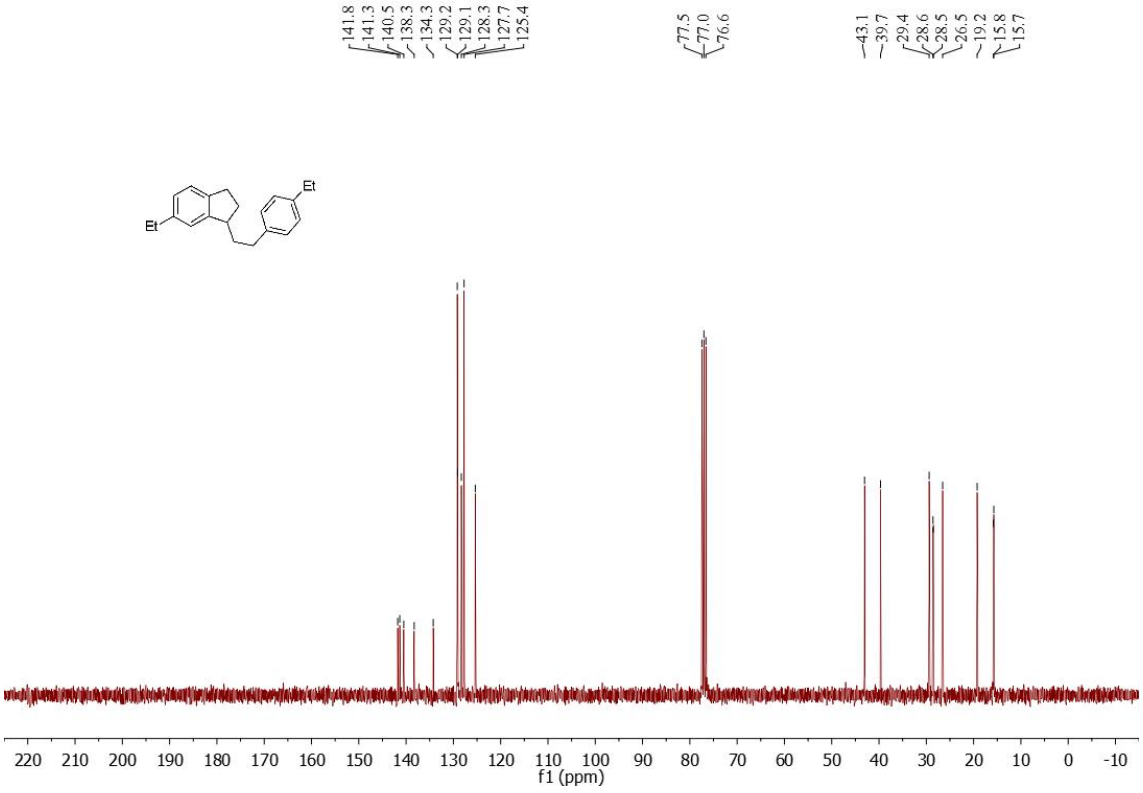


Figure S97. ^{1}H NMR spectrum of **5e**, related to **Figure 3**

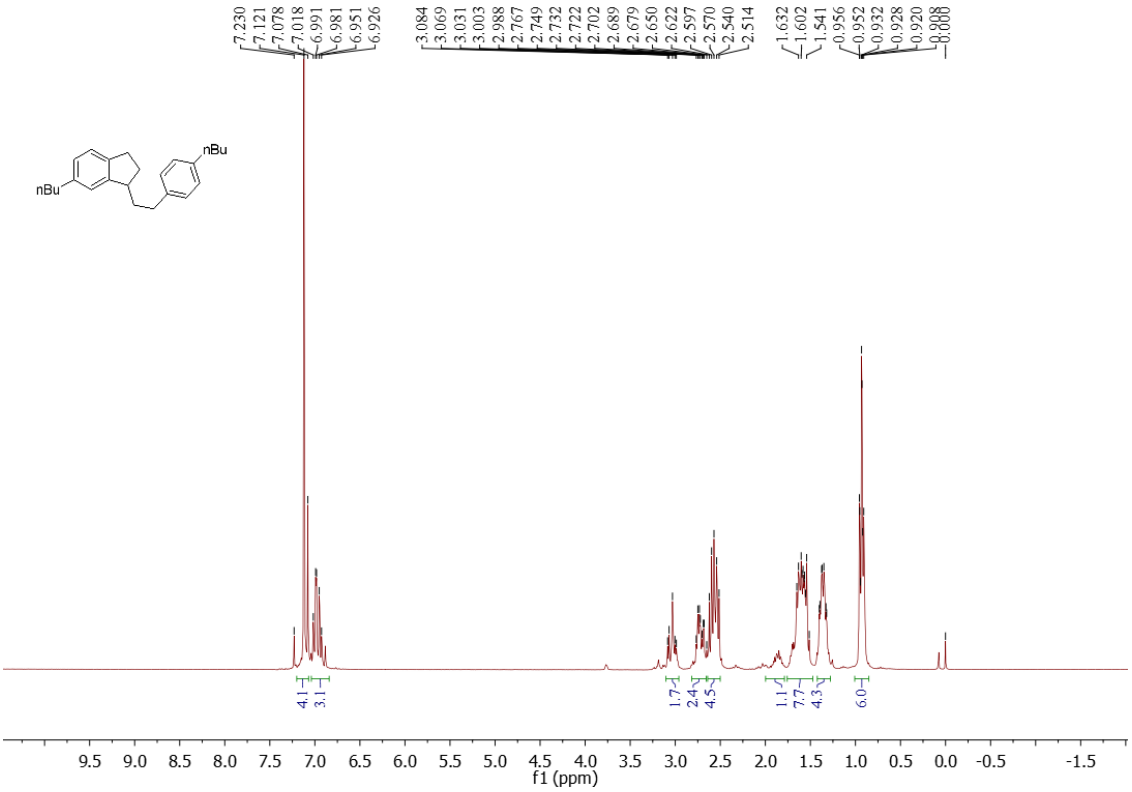


Figure S98. ^{13}C NMR spectrum of **5e**, related to **Figure 3**

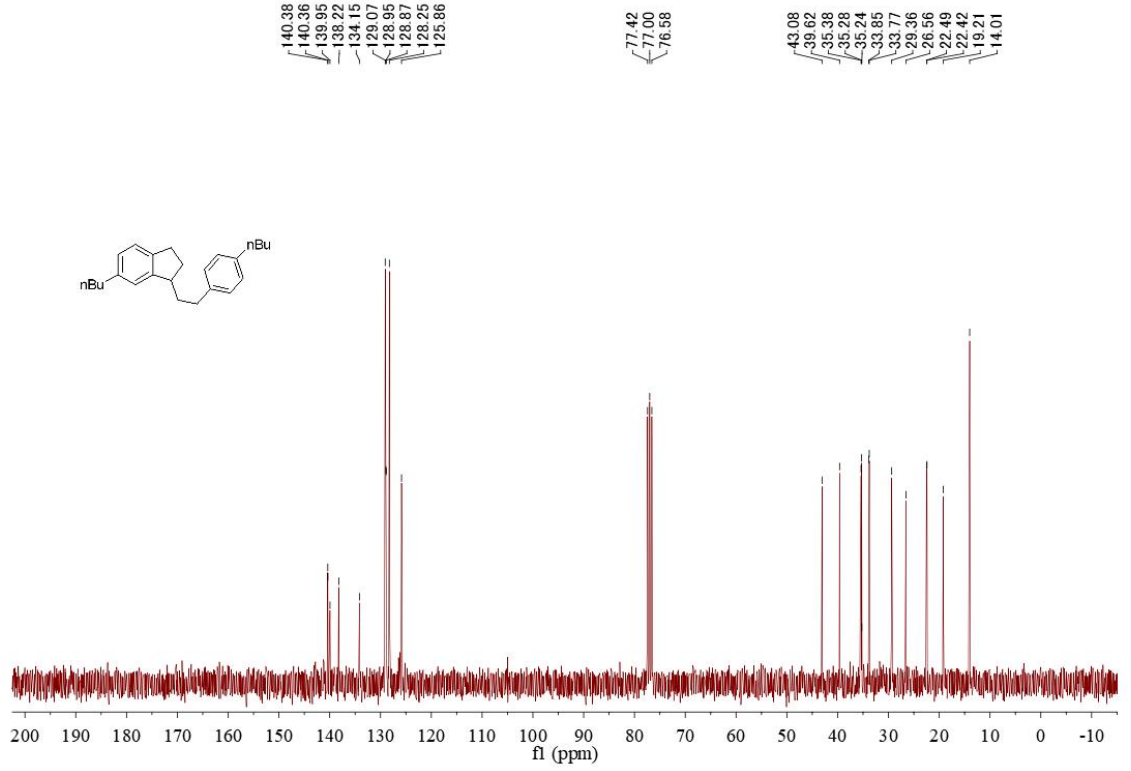


Figure S99. ^{1}H NMR spectrum of **5f**, related to **Figure 3**

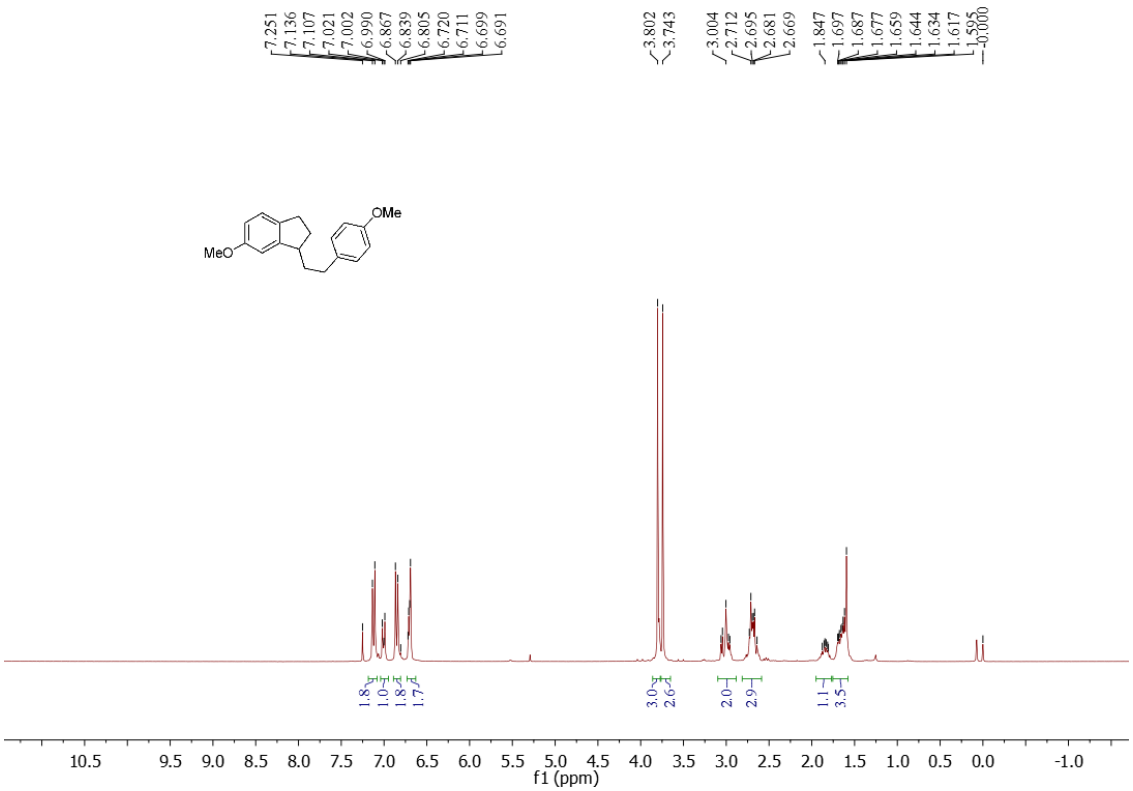


Figure S100. ^{13}C NMR spectrum of **5f**, related to **Figure 3**

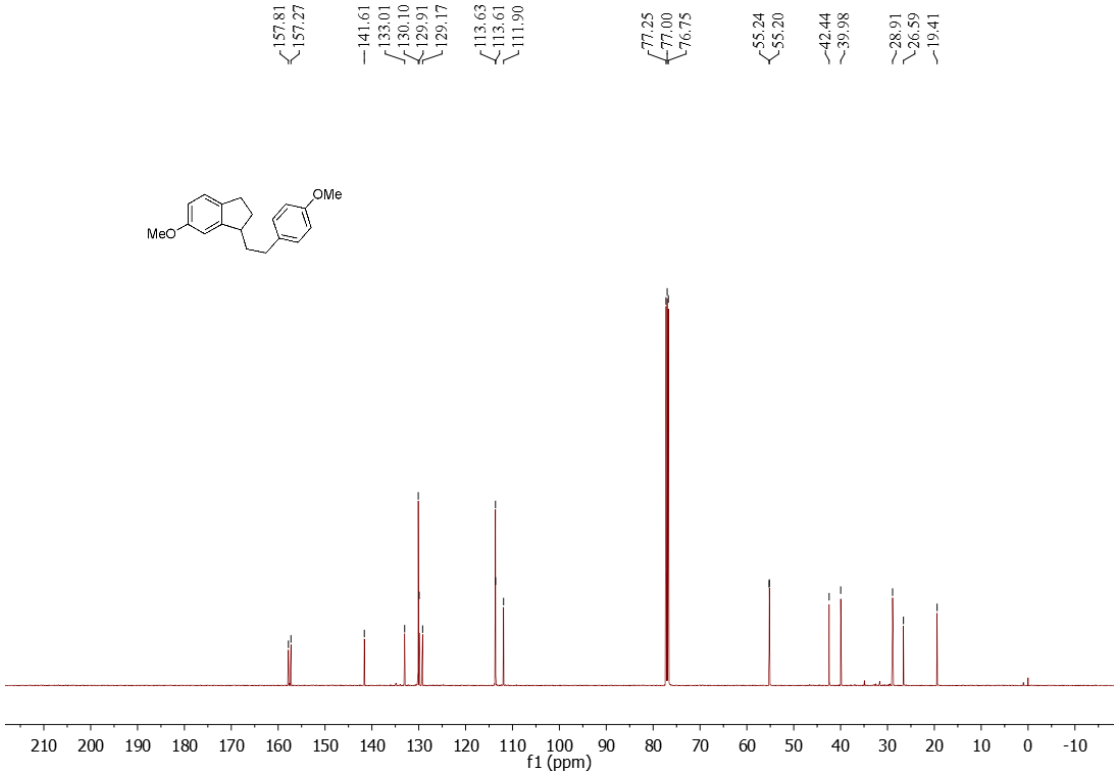


Figure S101. ^{1}H NMR spectrum of **5g**, related to **Figure 3**

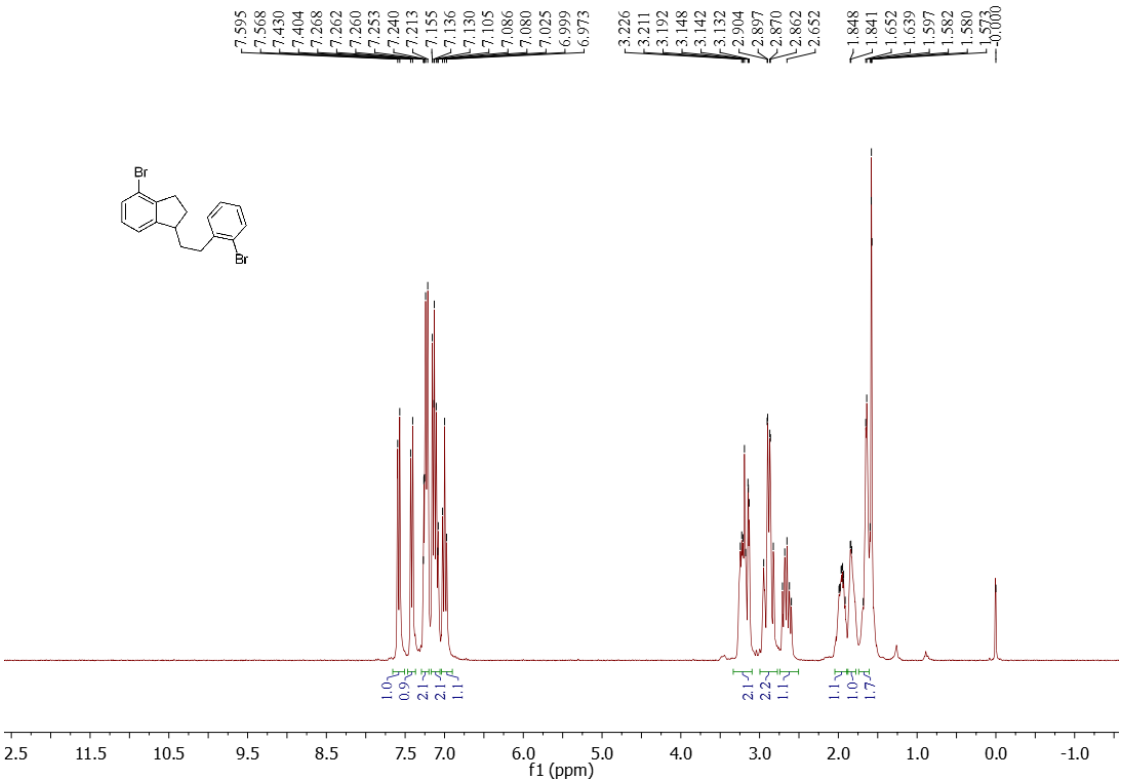


Figure S102. ^{13}C NMR spectrum of **5g**, related to **Figure 3**

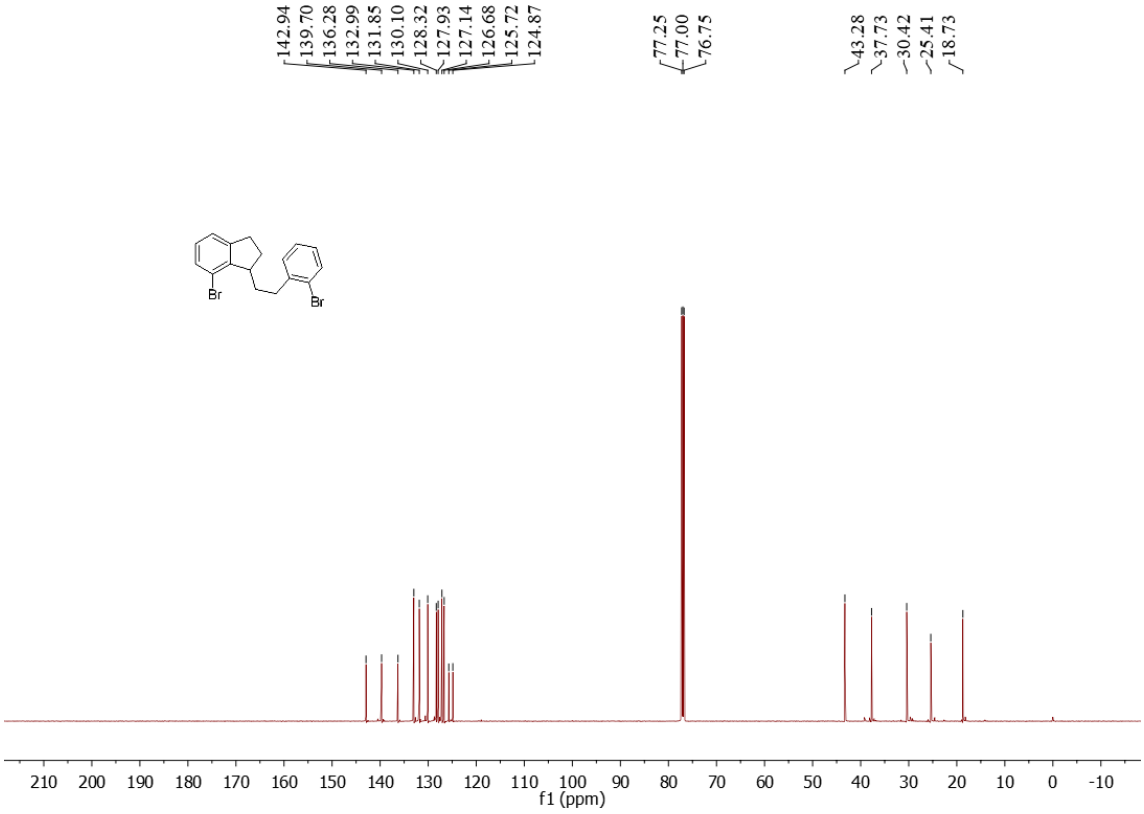


Figure S103. ^{1}H NMR spectrum of **5h**, related to **Figure 3**

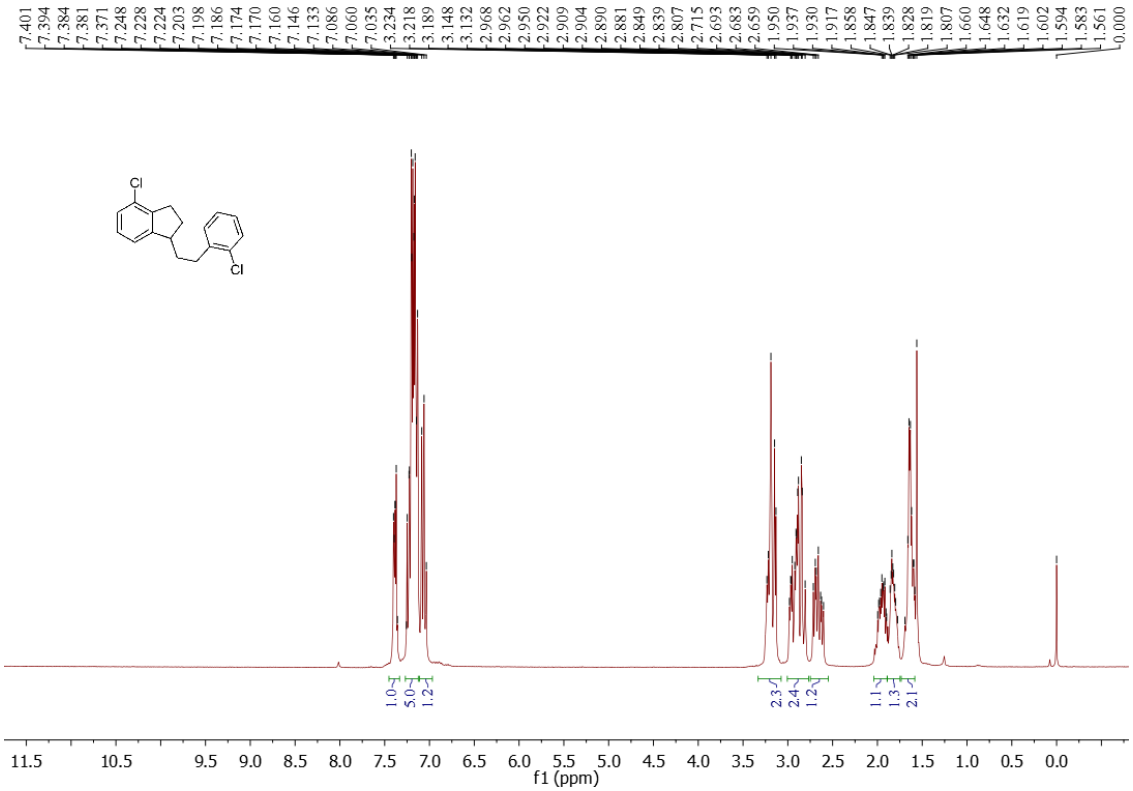


Figure S104. ^{13}C NMR spectrum of **5h**, related to **Figure 3**

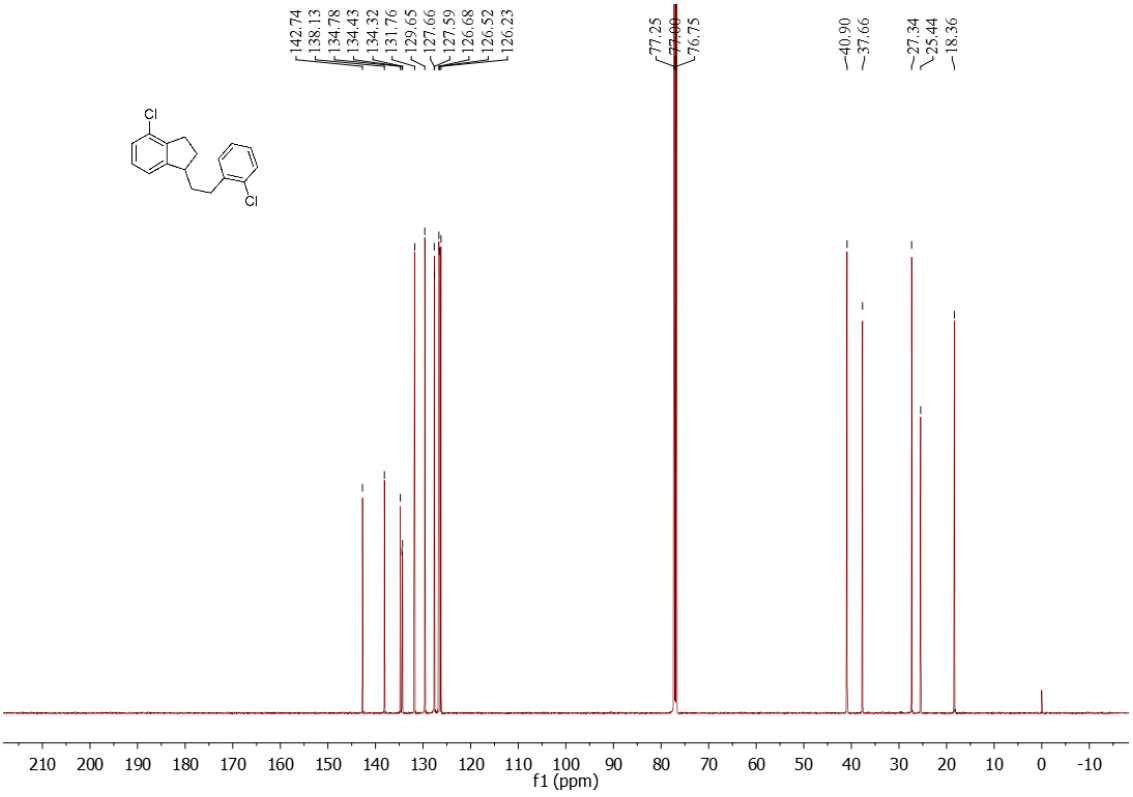


Figure S105. ^{1}H NMR spectrum of **5i**, related to **Figure 3**

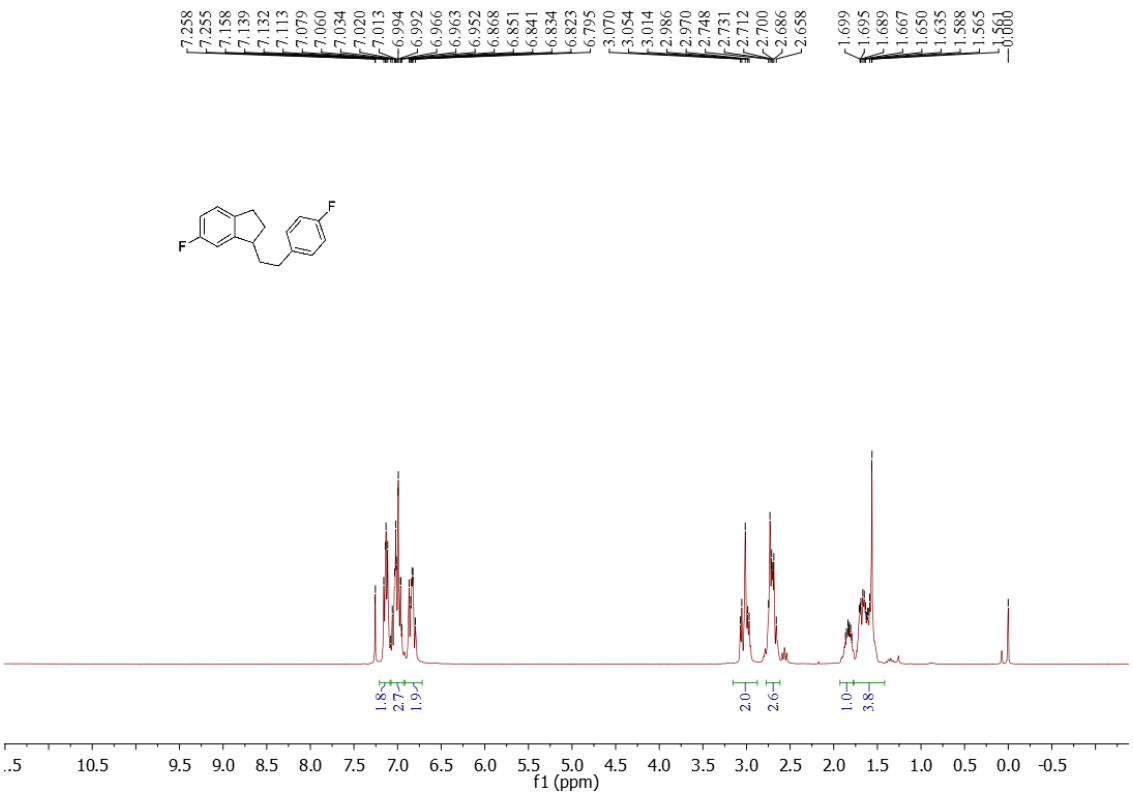


Figure S106. ^{13}C NMR spectrum of **5i**, related to **Figure 3**

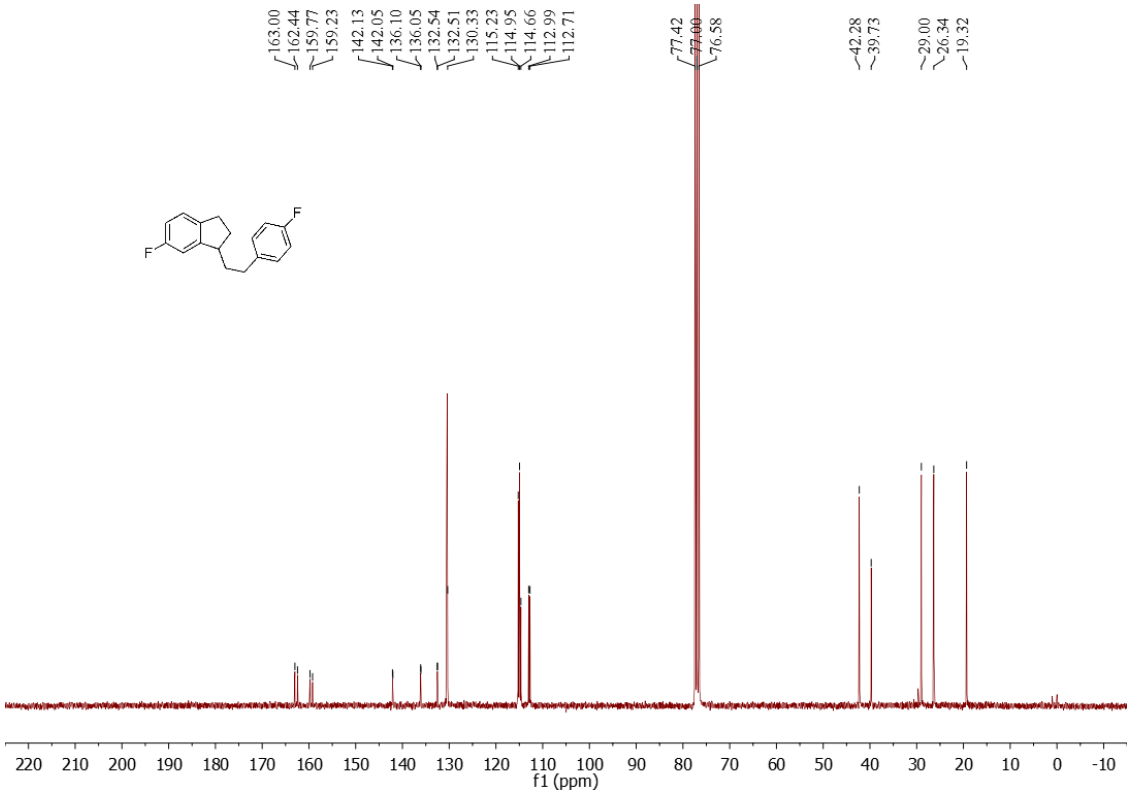


Figure S107. ^{1}H NMR spectrum of **5j**, related to **Figure 3**

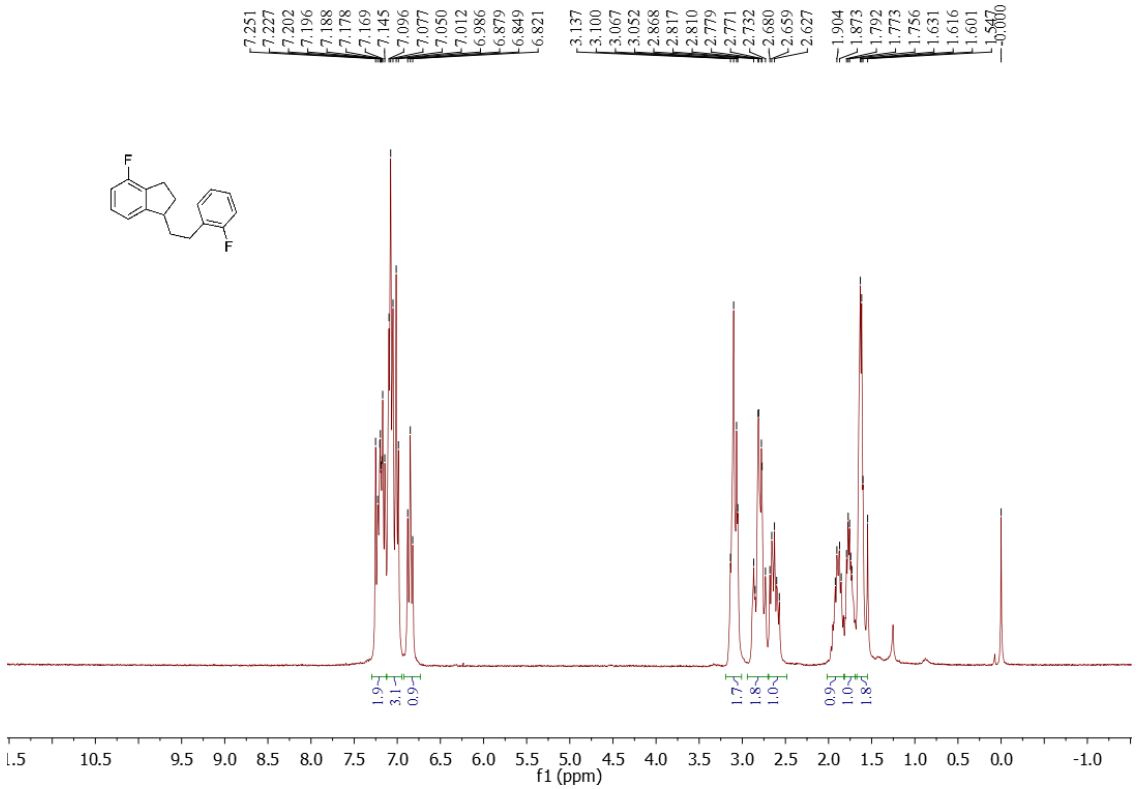


Figure S108. ^{13}C NMR spectrum of **5j**, related to **Figure 3**

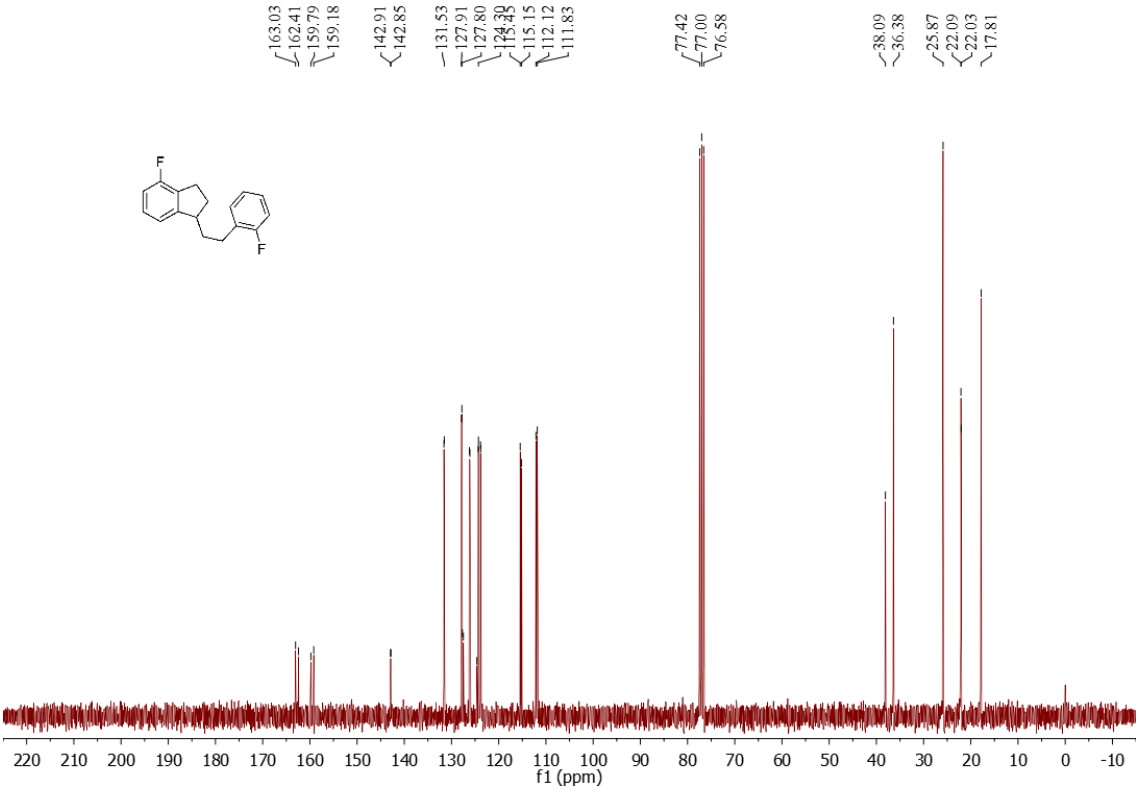


Figure S109. ^{1}H NMR spectrum of **5k**, related to **Figure 3**

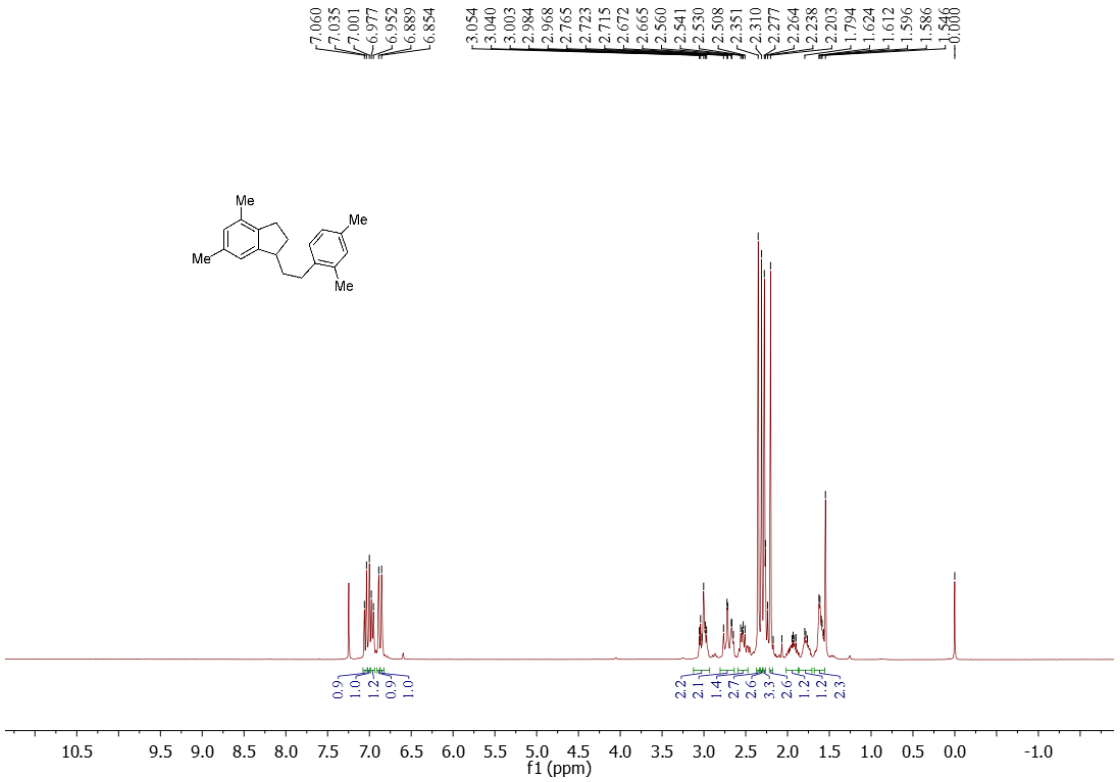


Figure S110. ^{13}C NMR spectrum of **5k**, related to **Figure 3**

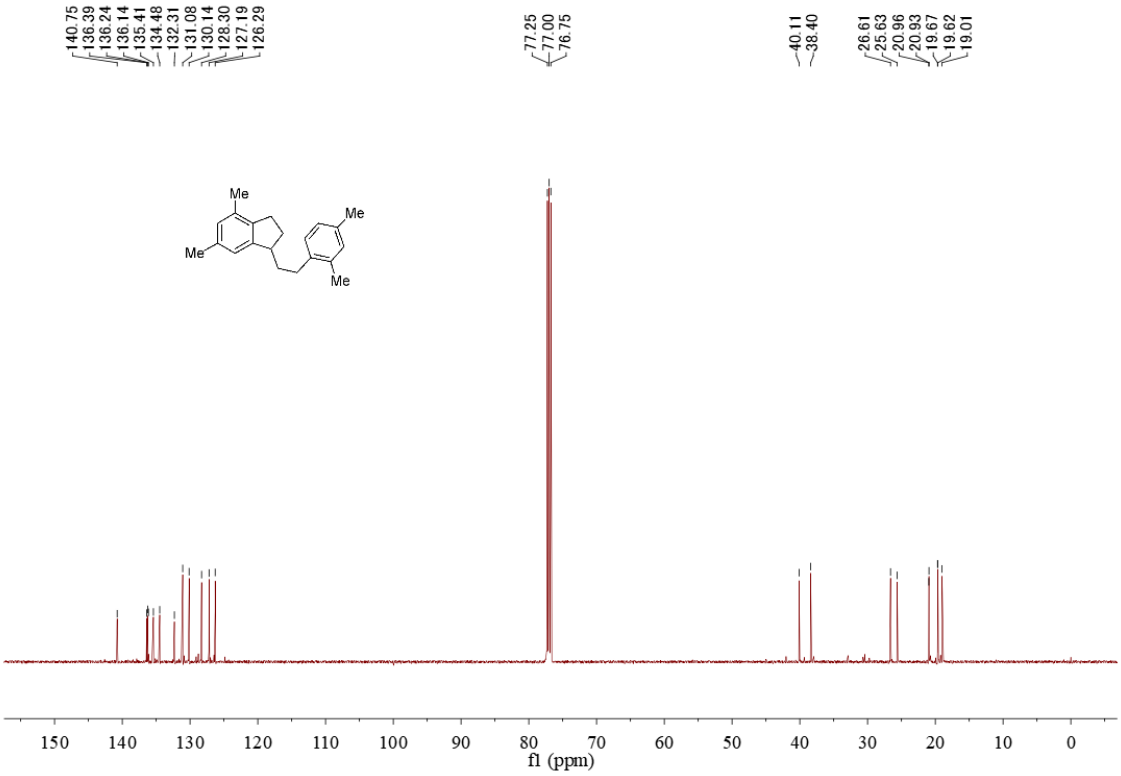


Figure S111. ^{1}H NMR spectrum of **5l**, related to **Figure 3**

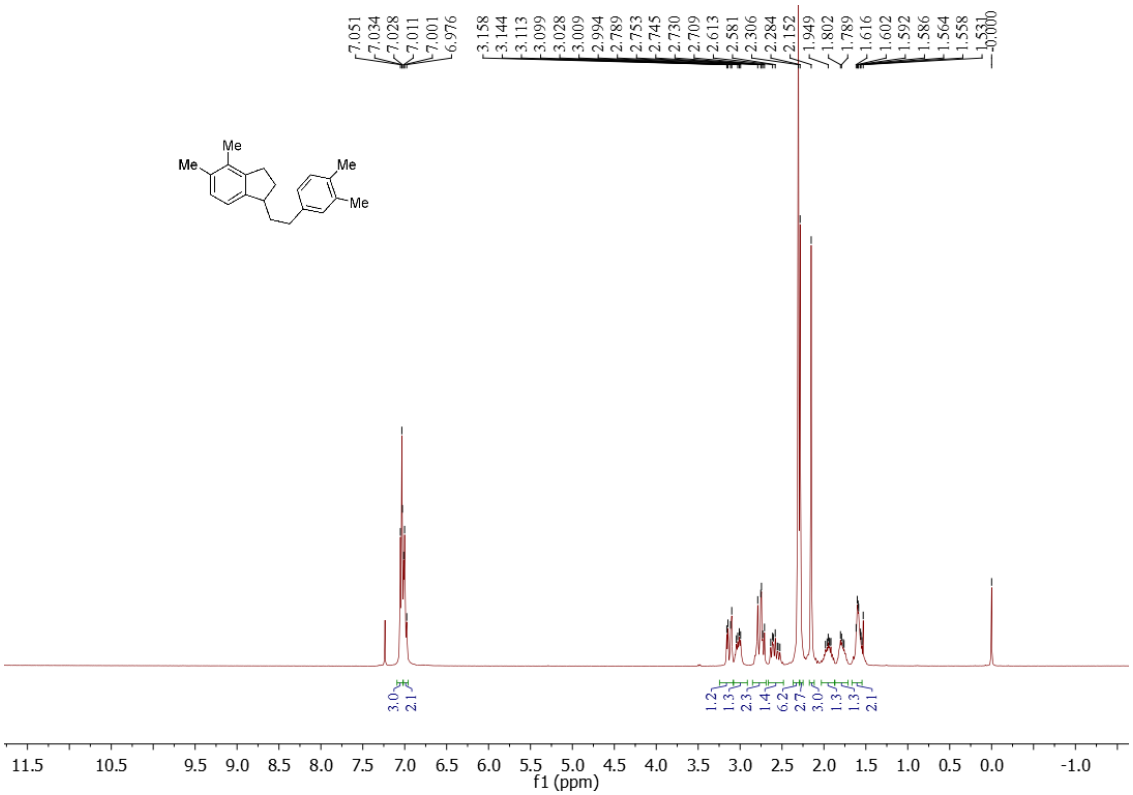


Figure S112. ^{13}C NMR spectrum of **5l**, related to **Figure 3**

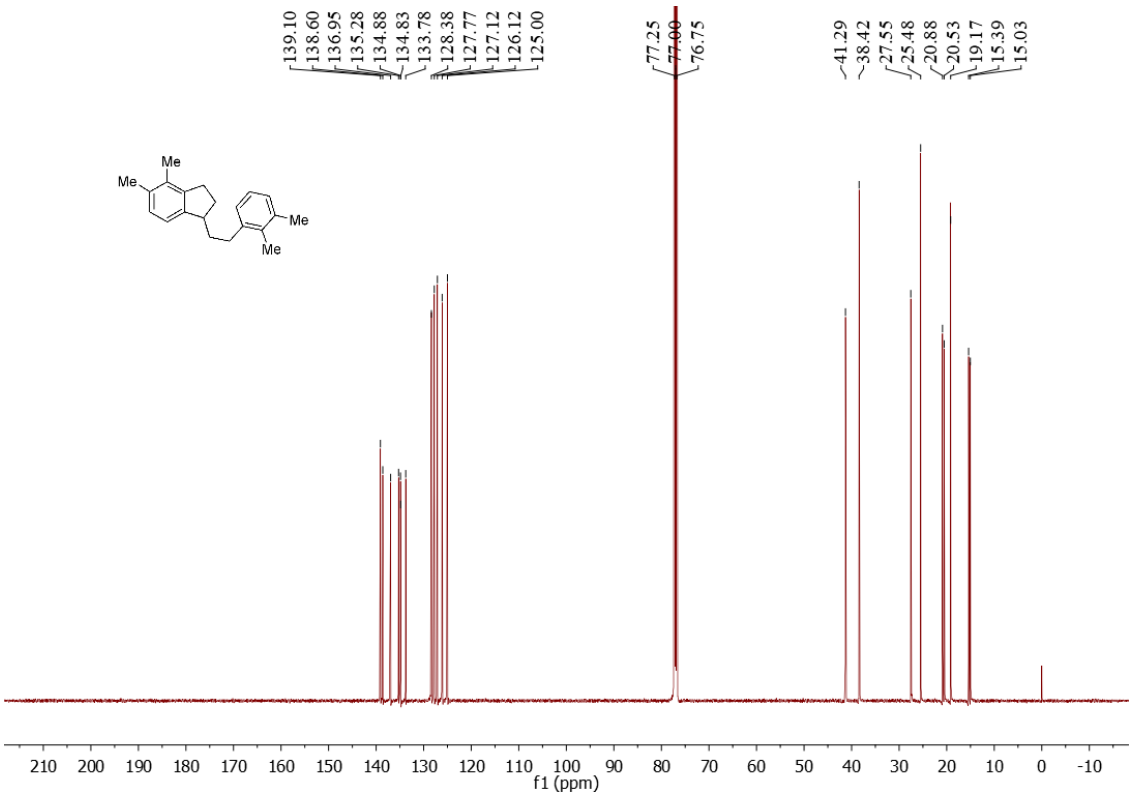


Figure S113. ^{1}H NMR spectrum of **5m**, related to **Figure 3**

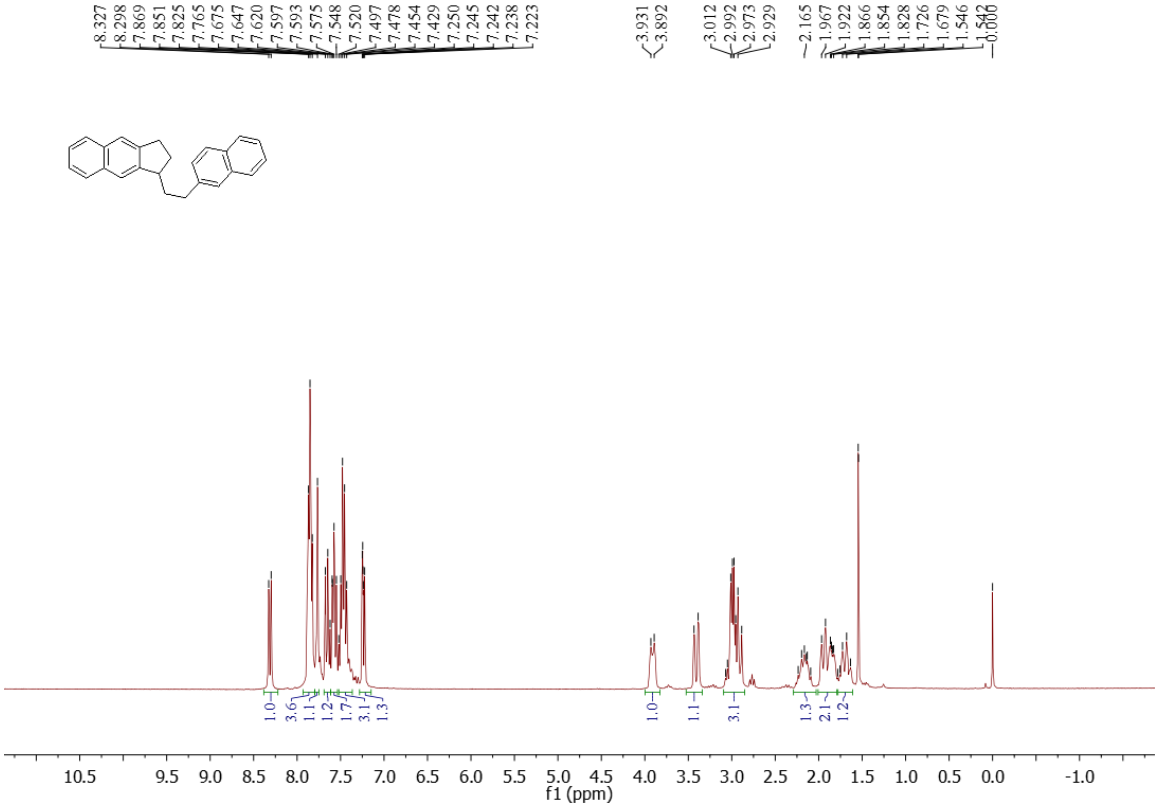


Figure S114. ^{13}C NMR spectrum of **5m**, related to **Figure 3**

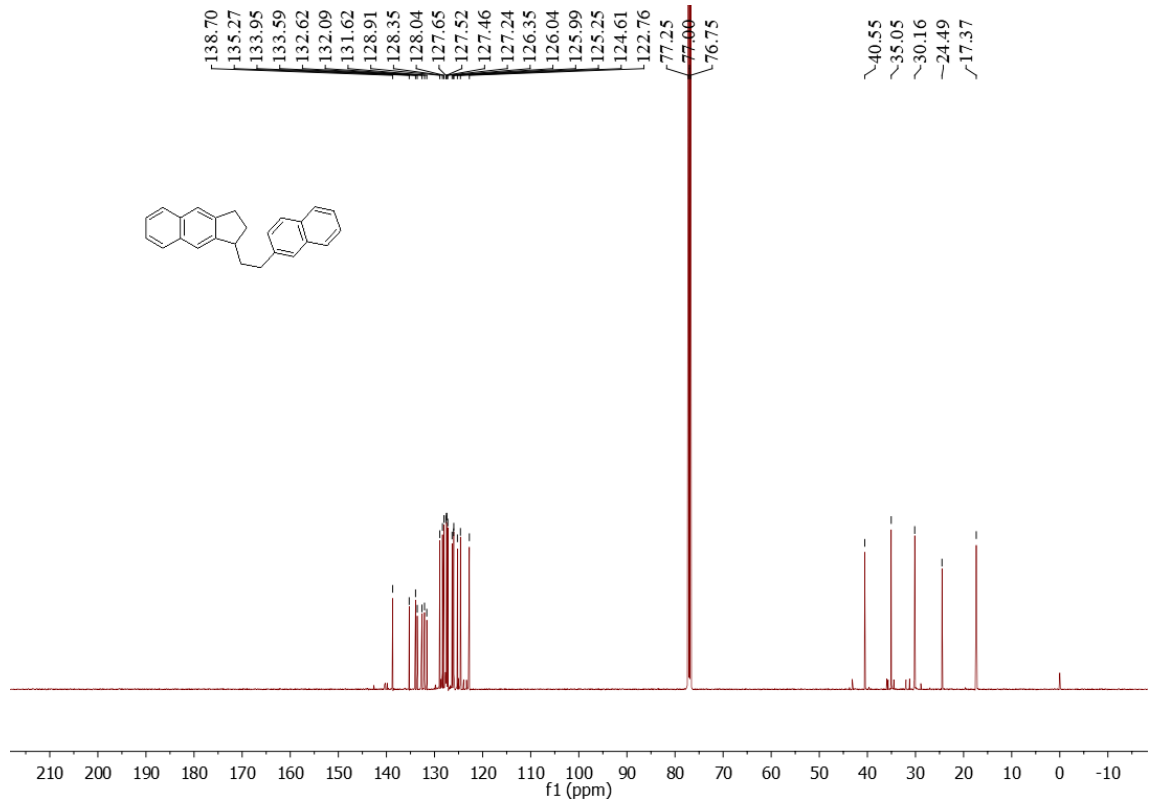


Figure S115. ^{1}H NMR spectrum of **5n**, related to **Figure 3**

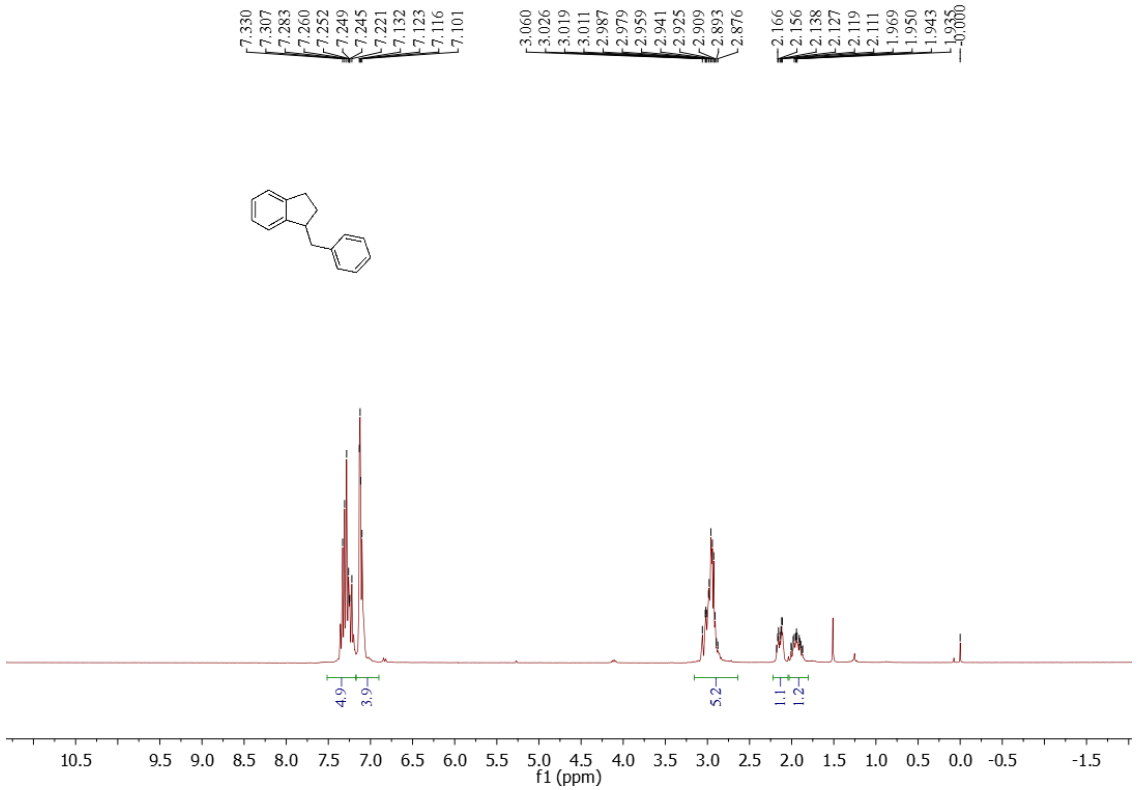


Figure S116. ^{13}C NMR spectrum of **5n**, related to **Figure 3**

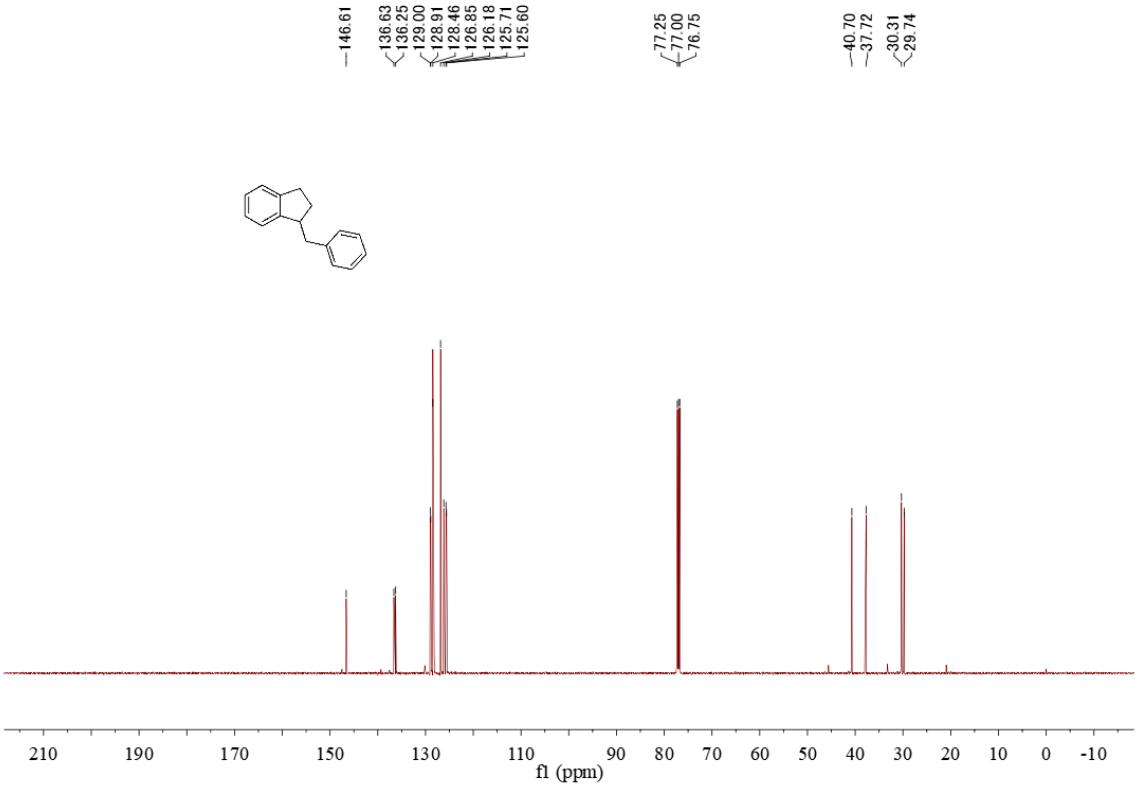


Figure S117. ^{1}H NMR spectrum of **5o**, related to **Figure 3**

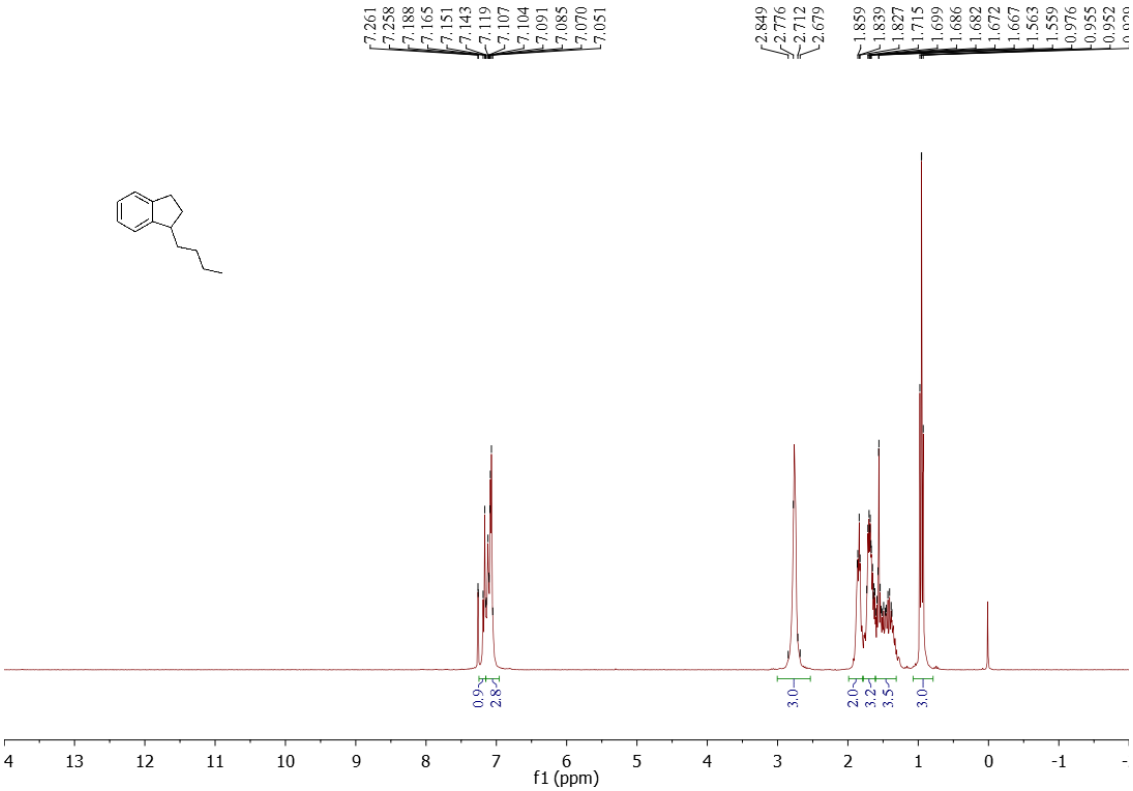


Figure S118. ^{1}H NMR spectrum of **5p**, related to **Figure 3**

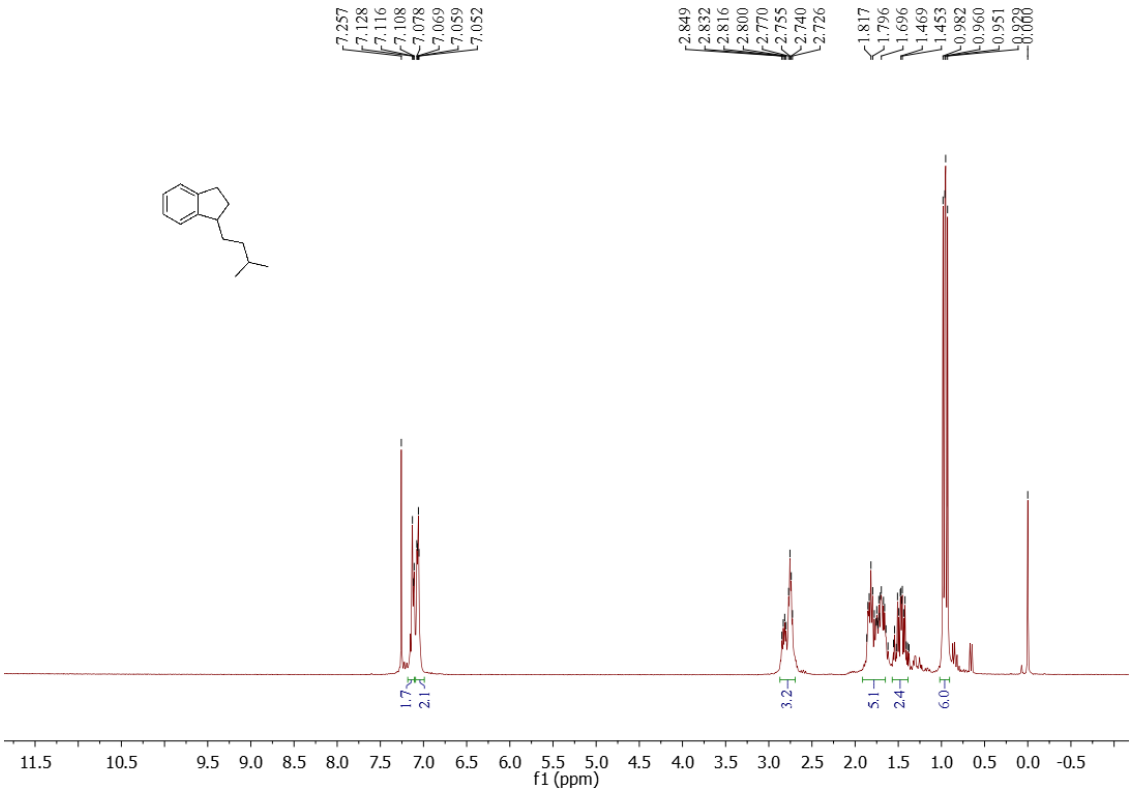


Figure S119. ^{13}C NMR spectrum of **5p**, related to **Figure 3**

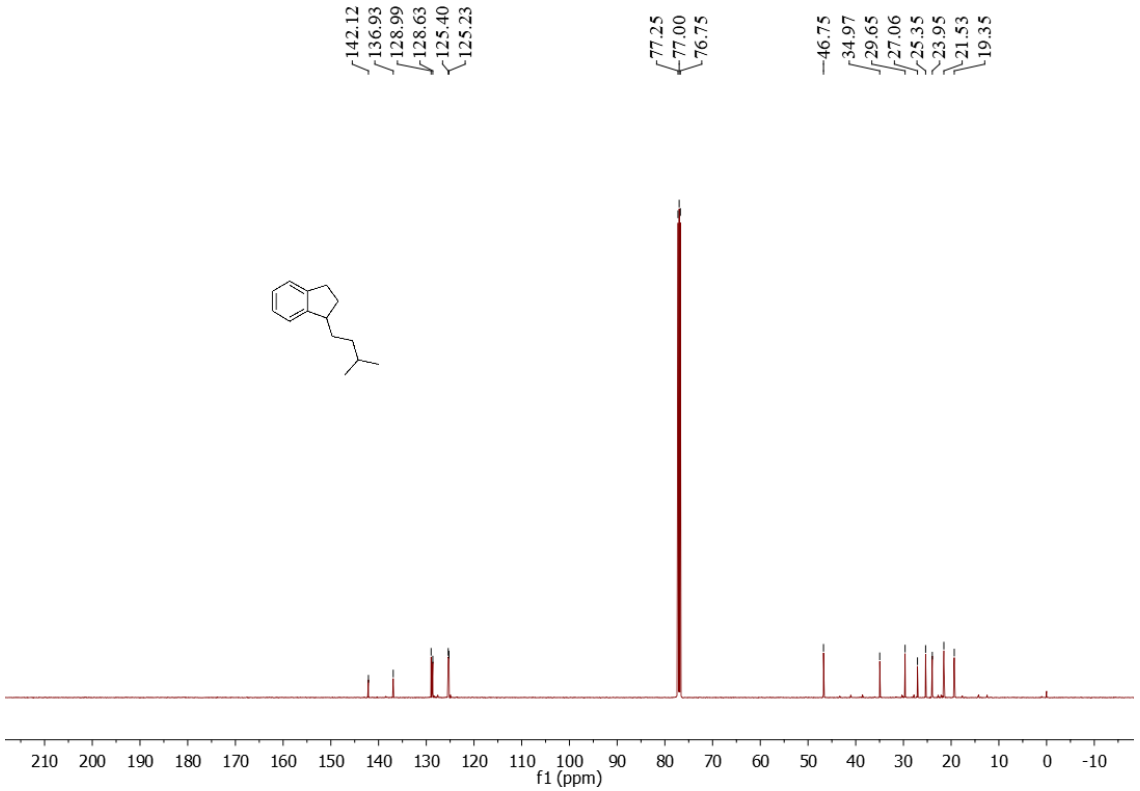


Figure S120. ^{1}H NMR spectrum of **5q**, related to **Figure 3**

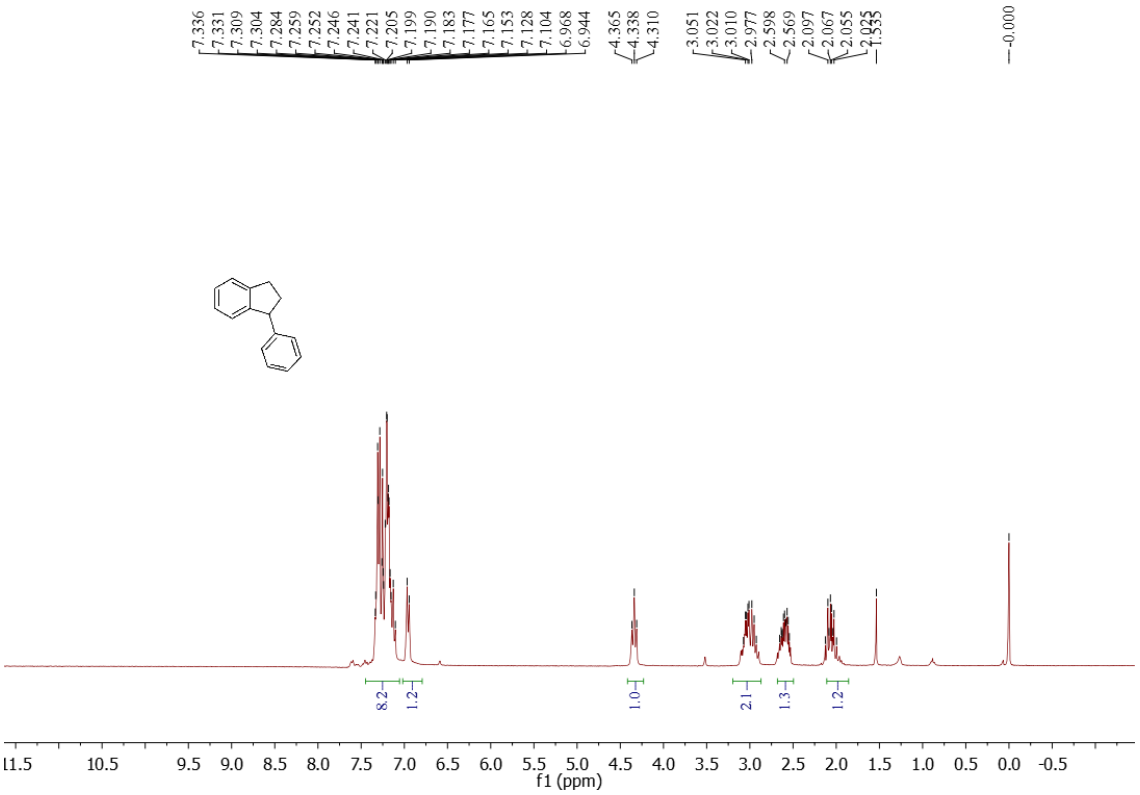


Figure S121. ^{1}H NMR spectrum of **5r**, related to **Figure 3**

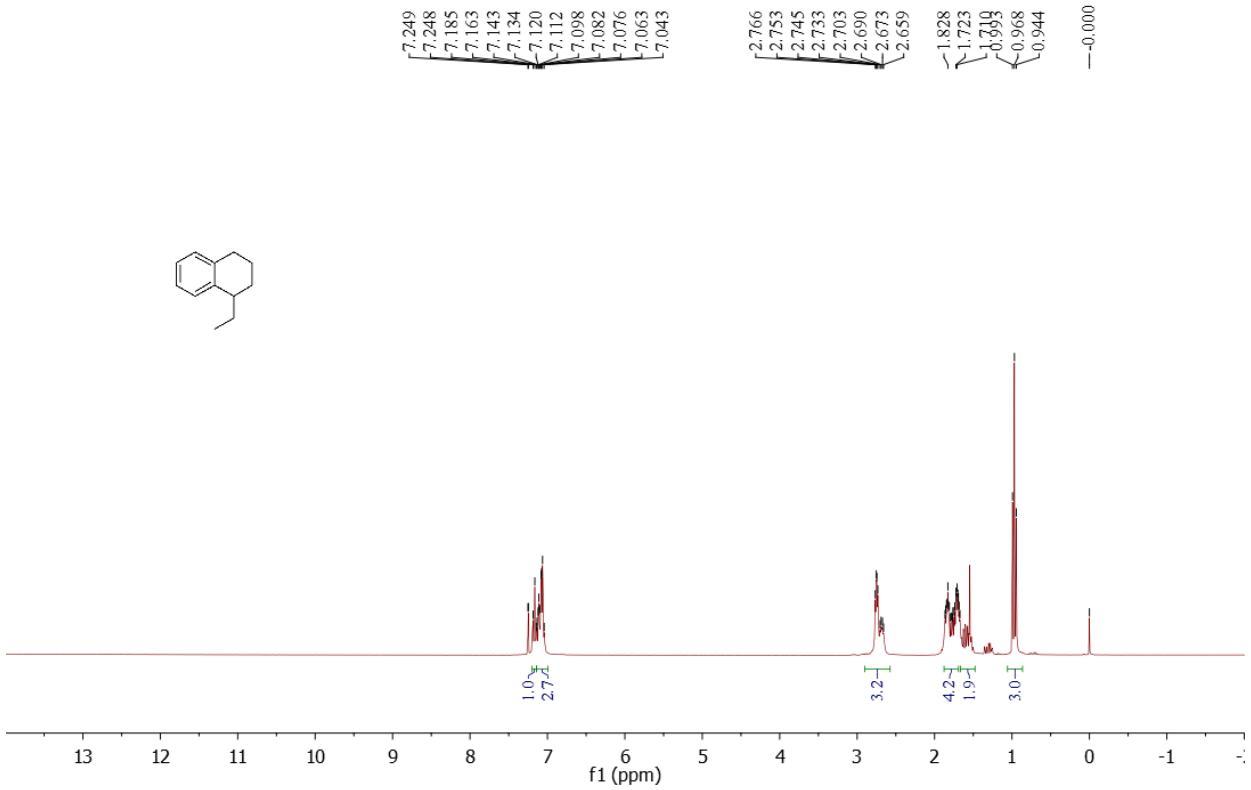


Figure S122. ^{1}H NMR spectrum of **5s**, related to **Figure 3**

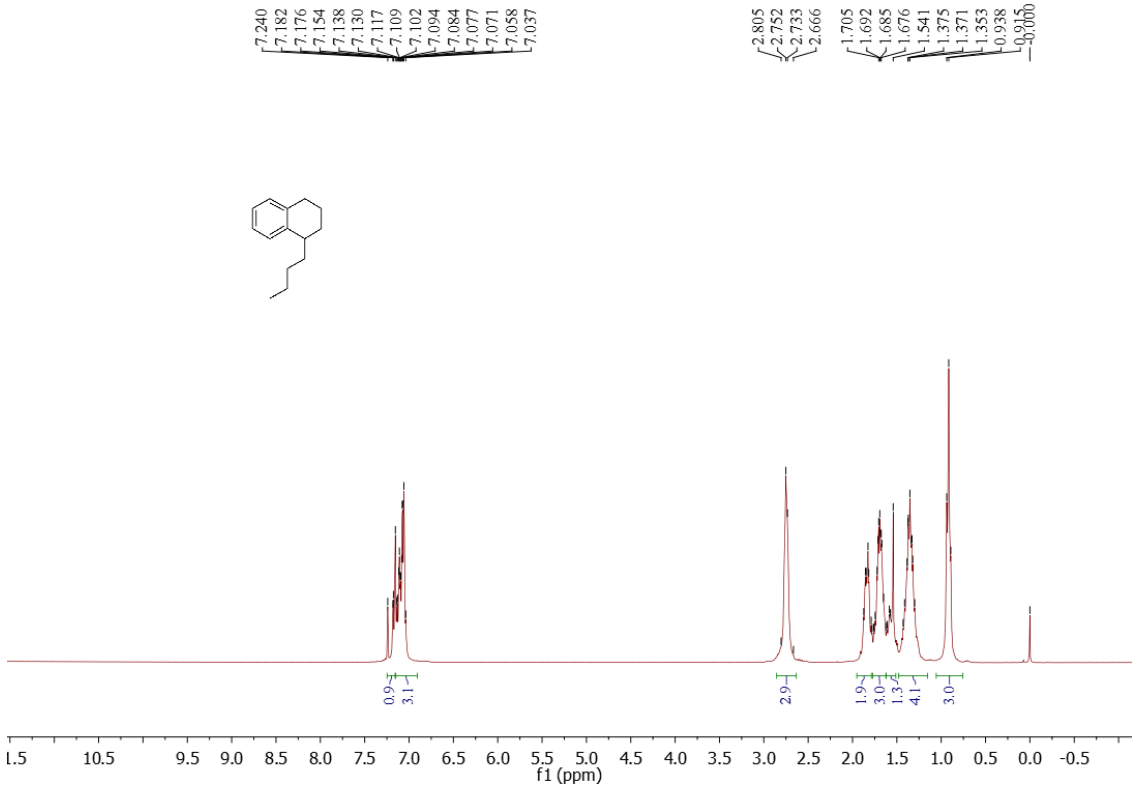


Figure S123. ^{1}H NMR spectrum of unknown *gem*-difluoride **1b**, related to **Figure 2**

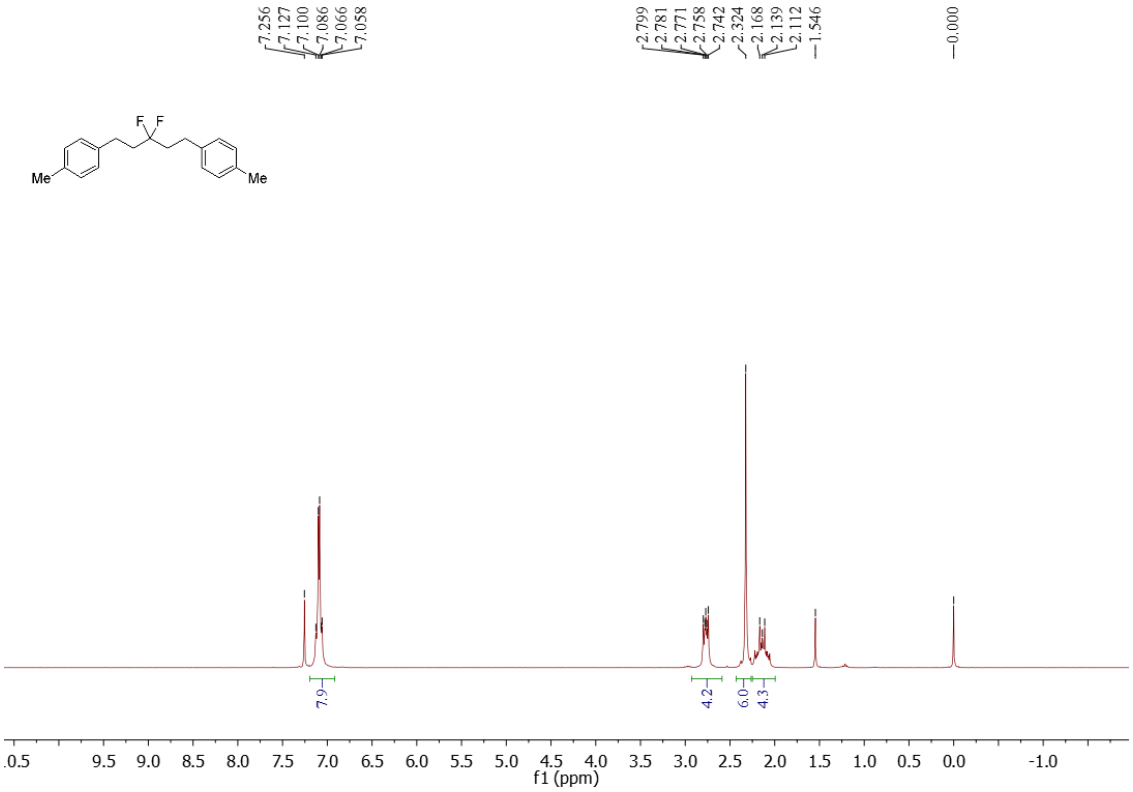


Figure S124. ^{13}C NMR spectrum of unknown *gem*-difluoride **1b**, related to **Figure 2**

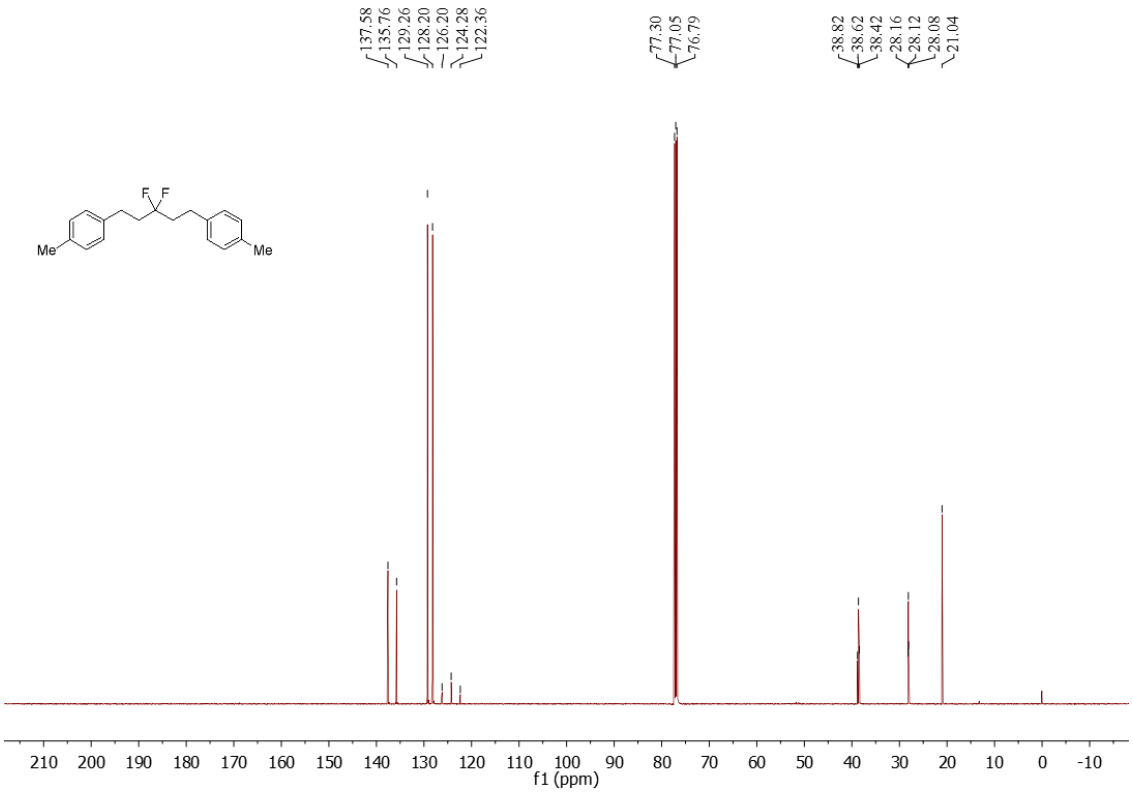


Figure S125. ^{19}F NMR spectrum of unknown *gem*-difluoride **1b**, related to **Figure 2**

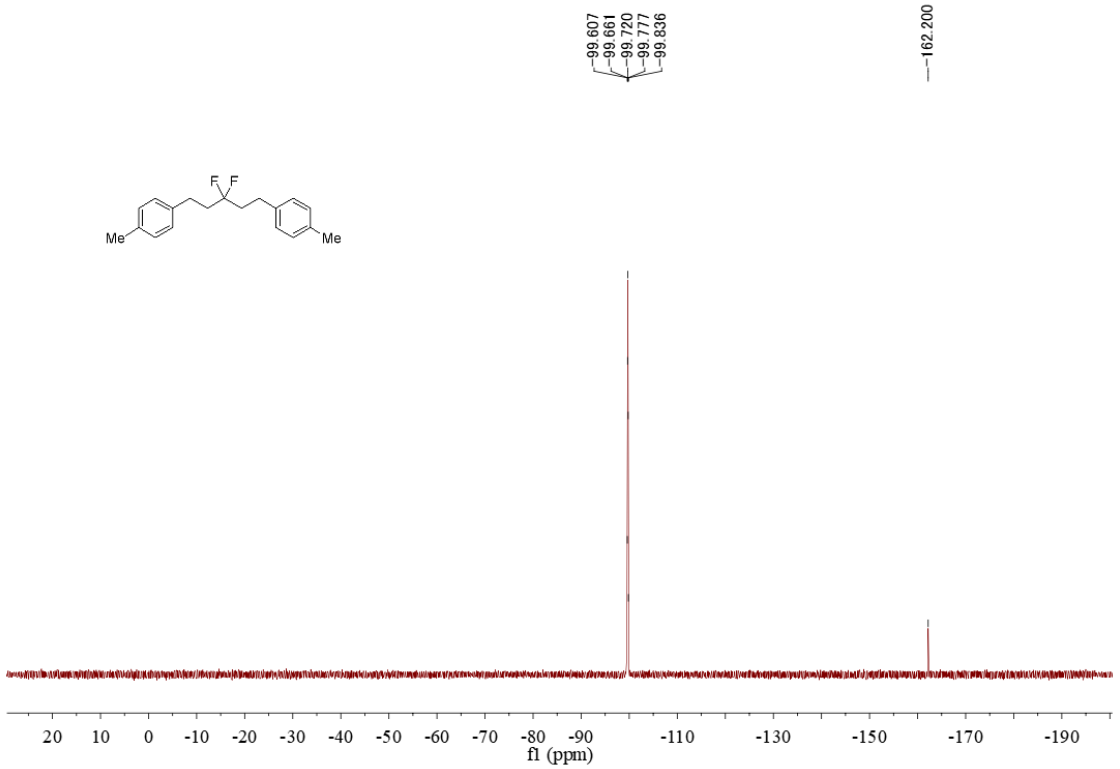


Figure S126. ^{1}H NMR spectrum of unknown *gem*-difluoride **1c**, related to **Figure 2**

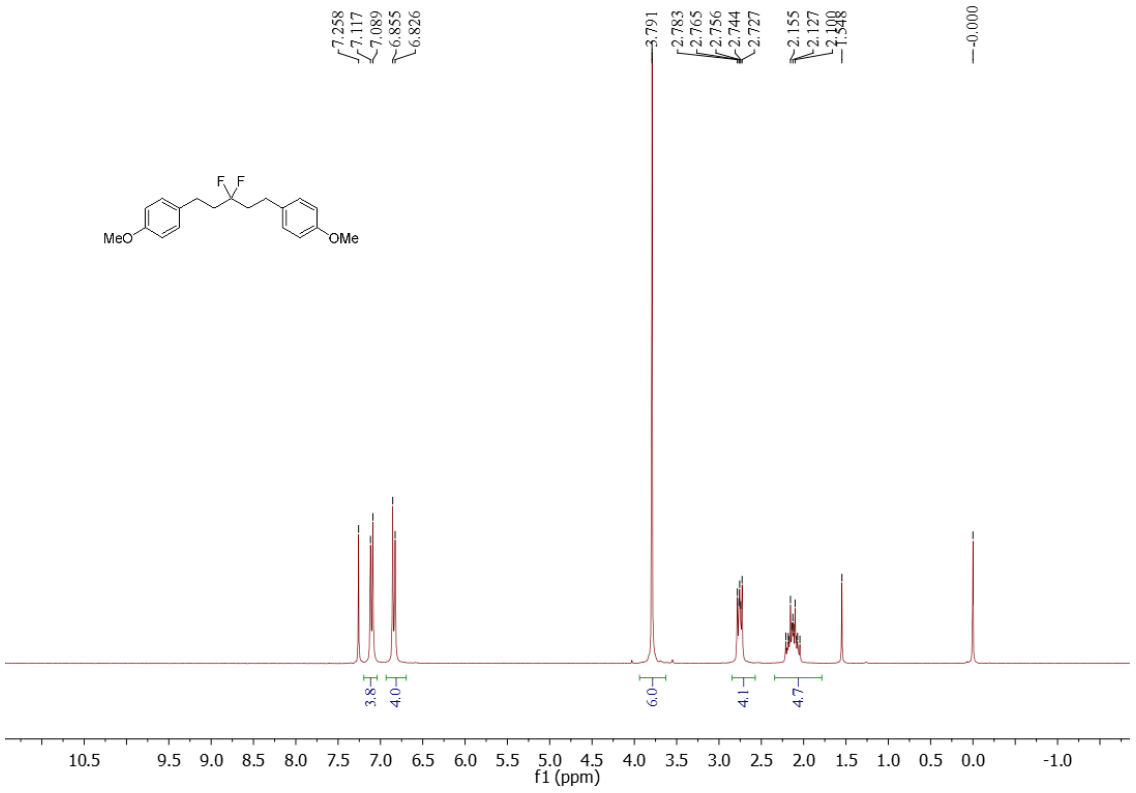


Figure S127. ^{13}C NMR spectrum of unknown *gem*-difluoride **1c**, related to **Figure 2**

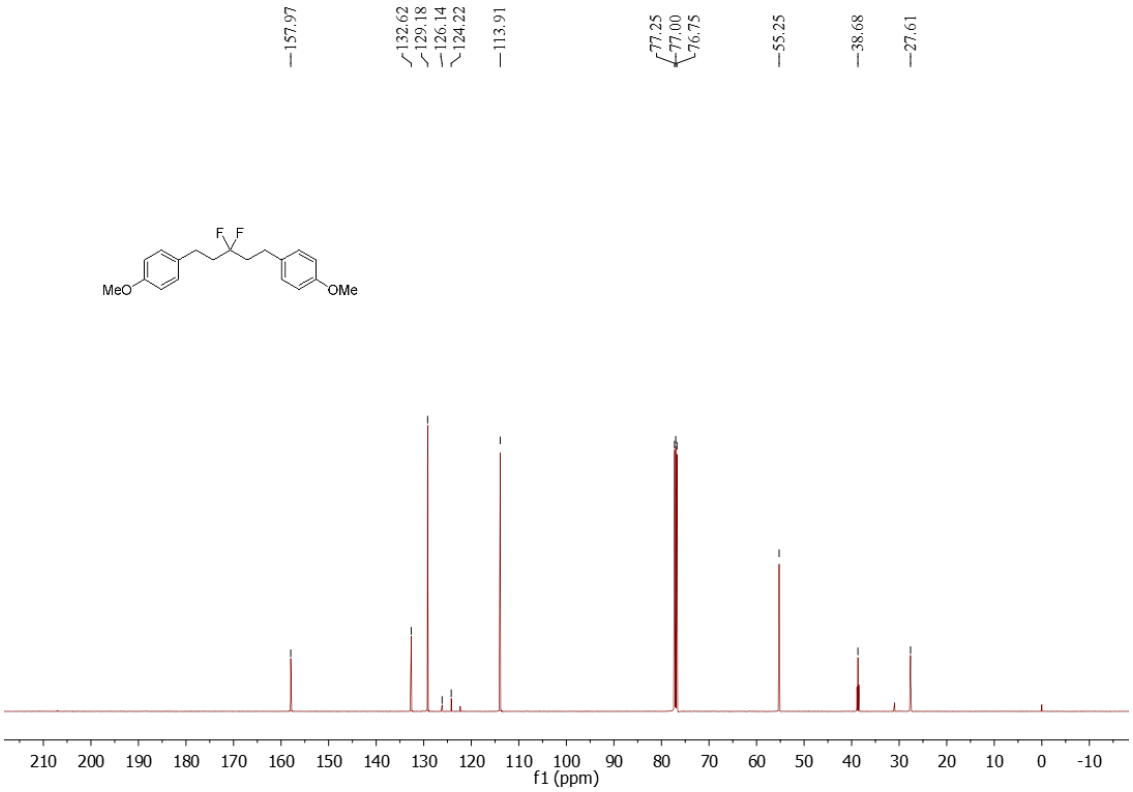


Figure S128. ^{19}F NMR spectrum of unknown *gem*-difluoride **1c**, related to **Figure 2**

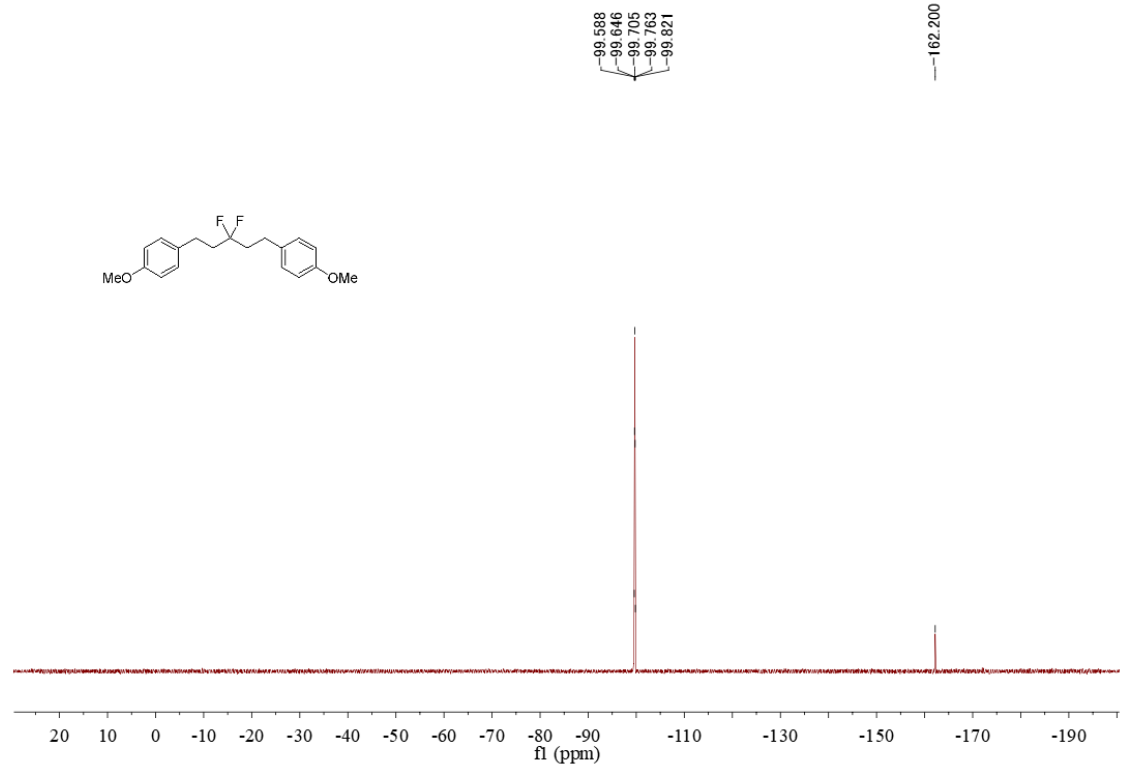


Figure S129. ^{1}H NMR spectrum of unknown *gem*-difluoride **1d**, related to **Figure 2**

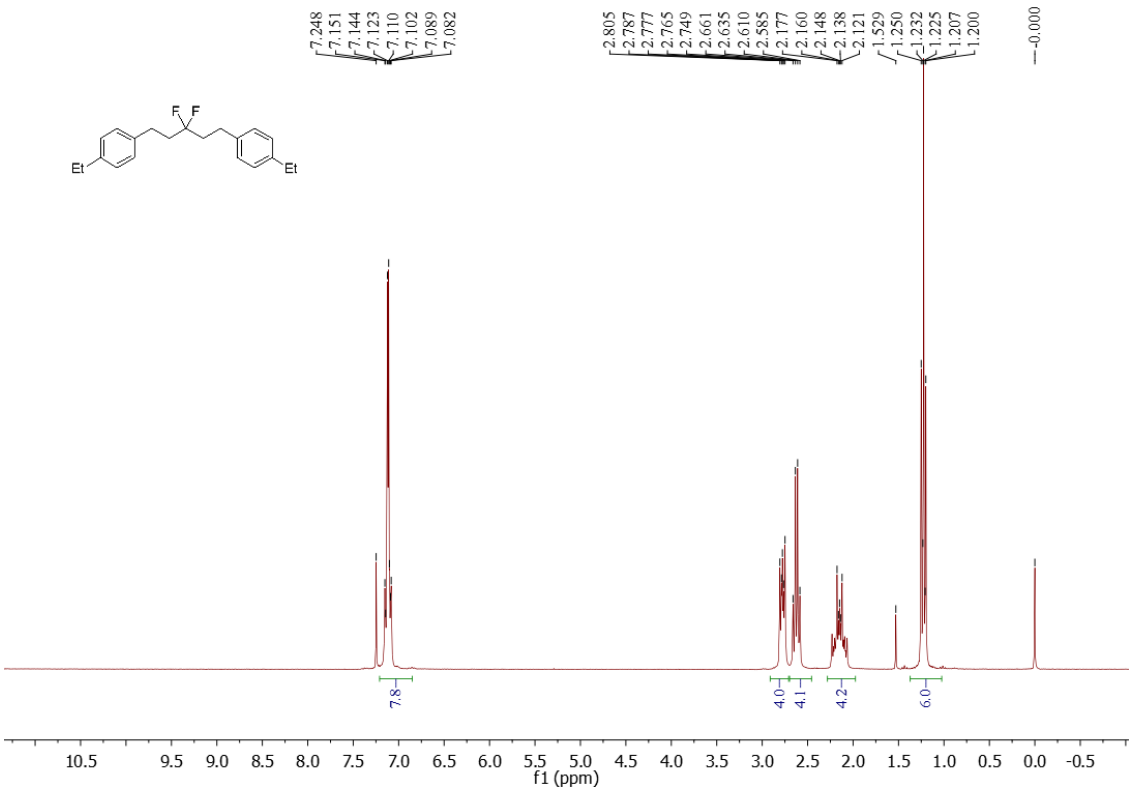


Figure S130. ^{13}C NMR spectrum of unknown *gem*-difluoride **1d**, related to **Figure 2**

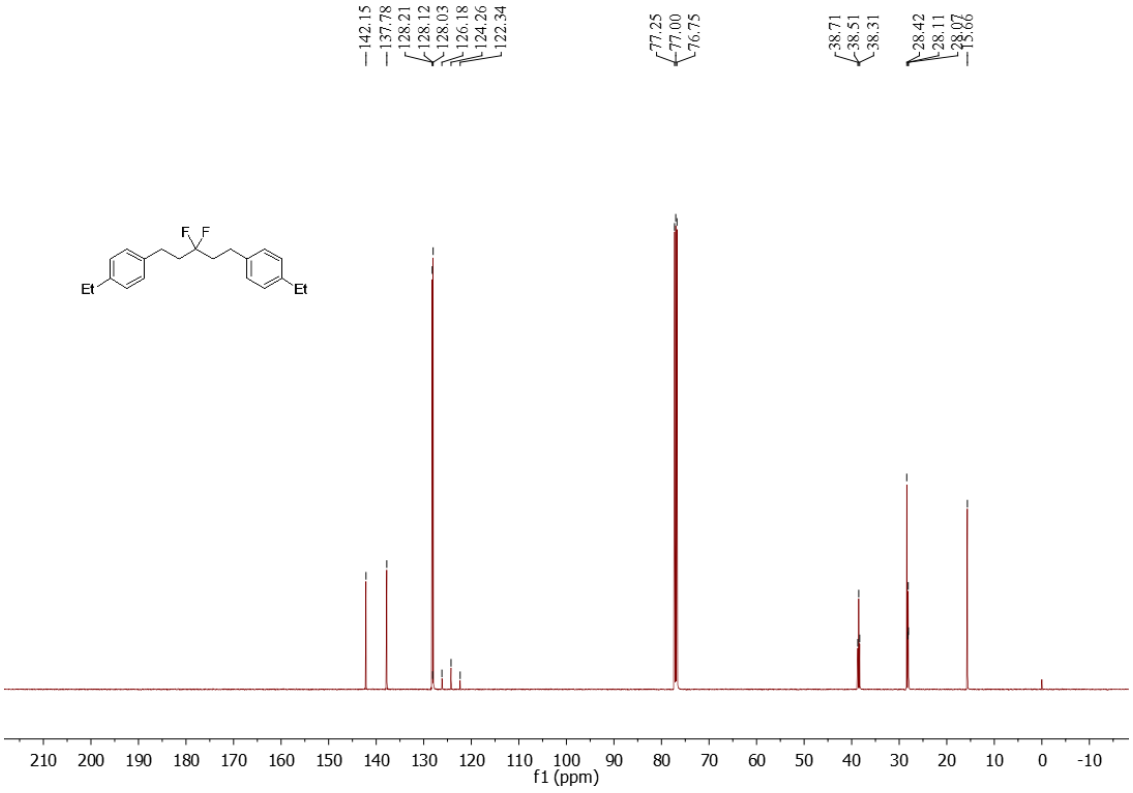


Figure S131. ^{19}F NMR spectrum of unknown *gem*-difluoride **1d**, related to **Figure 2**

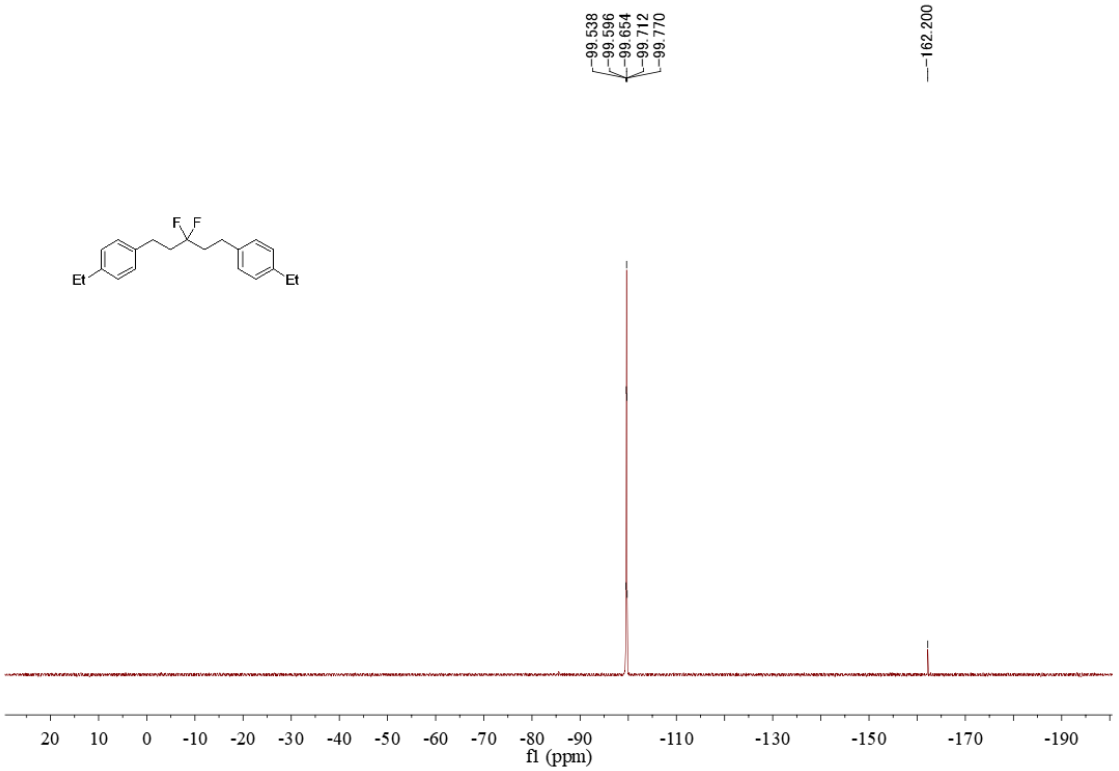


Figure S132. ^{1}H NMR spectrum of unknown *gem*-difluoride **1e**, related to **Figure 2**

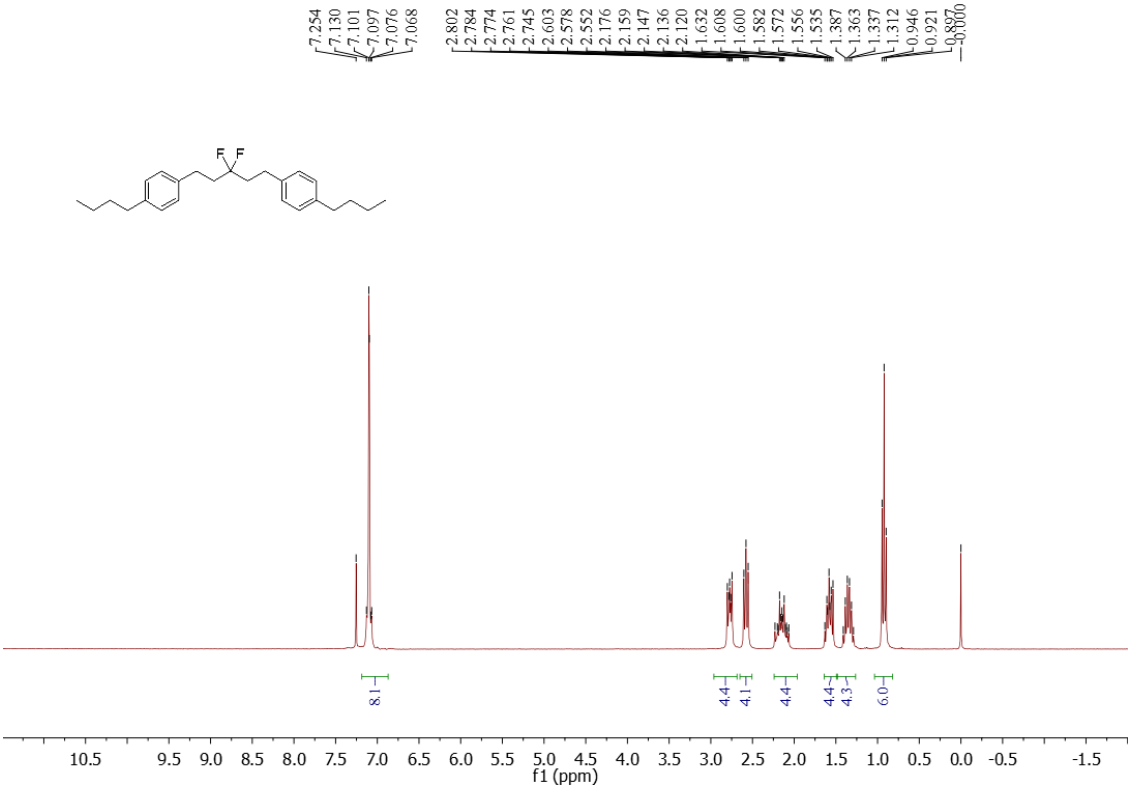


Figure S133. ^{13}C NMR spectrum of unknown *gem*-difluoride **1e**, related to **Figure 2**

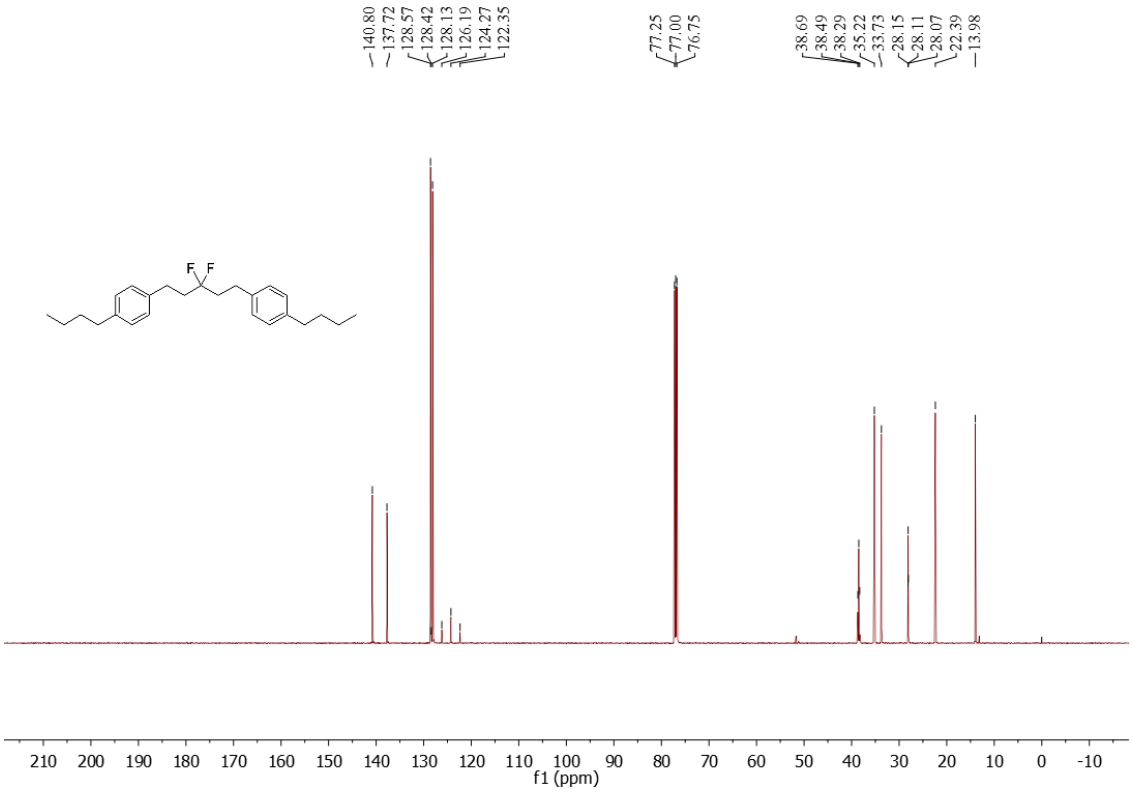


Figure S134. ^{19}F NMR spectrum of unknown *gem*-difluoride **1e**, related to **Figure 2**

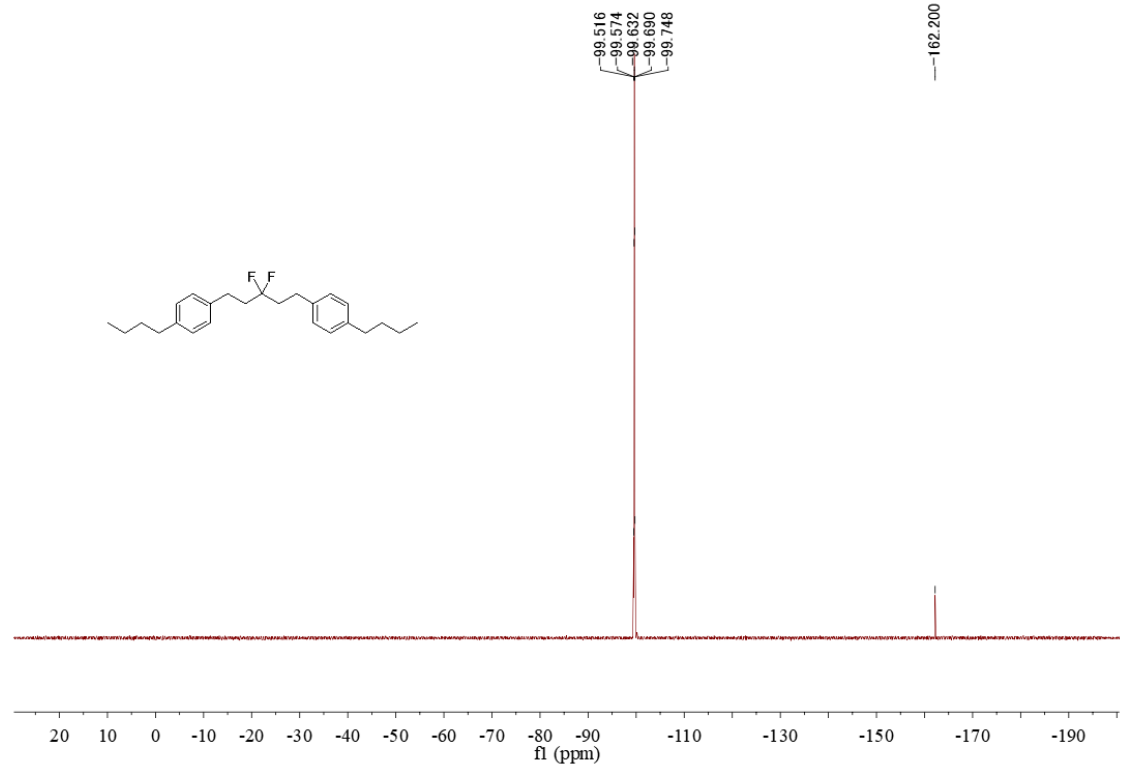


Figure S135. ^{1}H NMR spectrum of unknown *gem*-difluoride **1f**, related to **Figure 2**

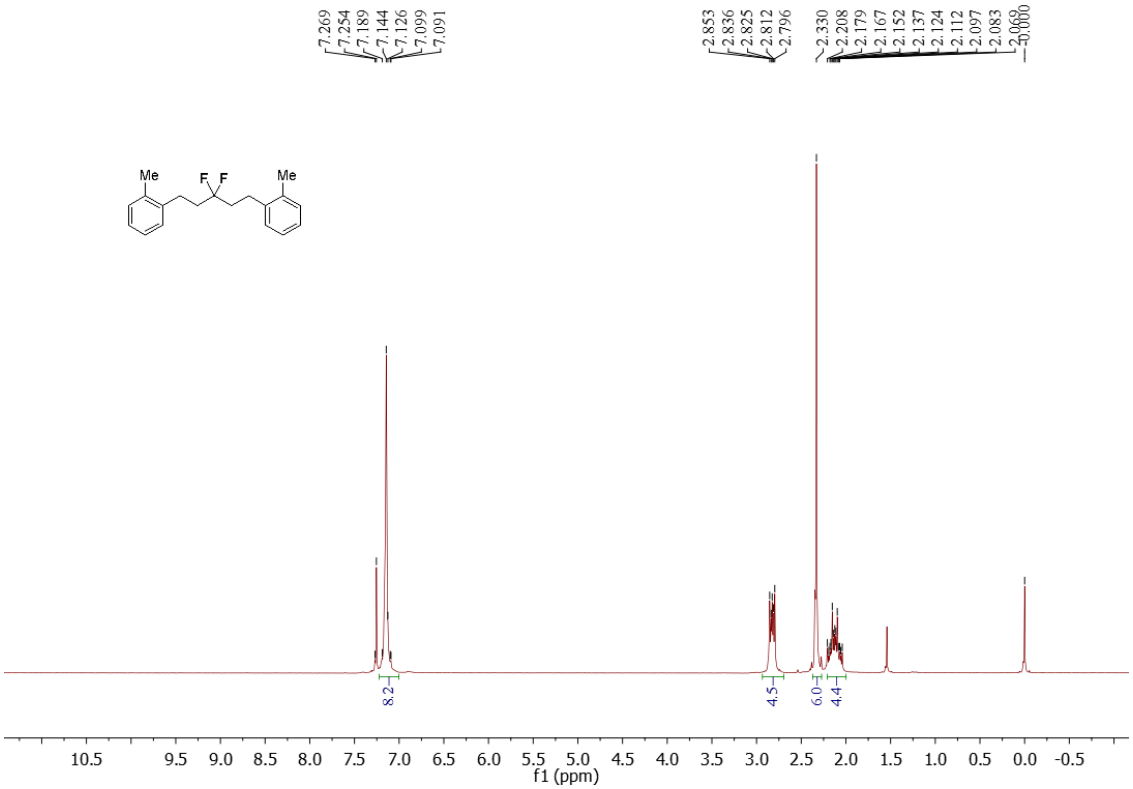


Figure S136. ^{13}C NMR spectrum of unknown *gem*-difluoride **1f**, related to **Figure 2**

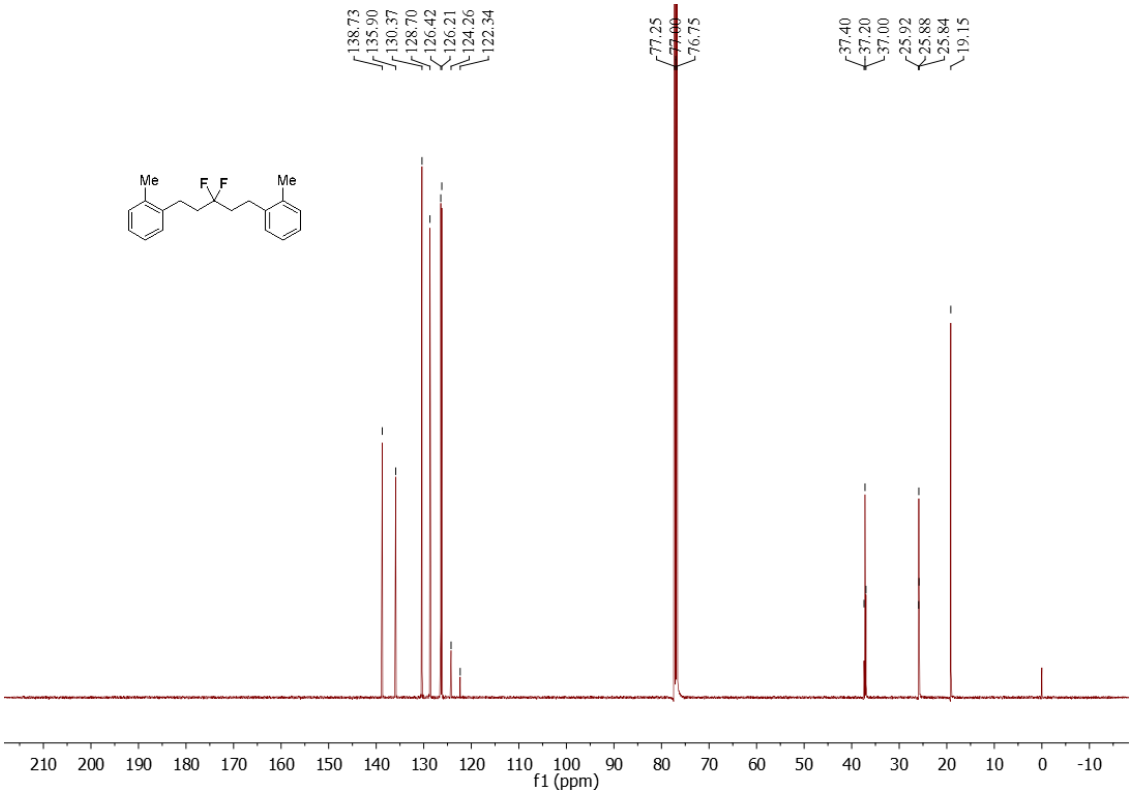


Figure S137. ^{19}F NMR spectrum of unknown *gem*-difluoride **1f**, related to **Figure 2**

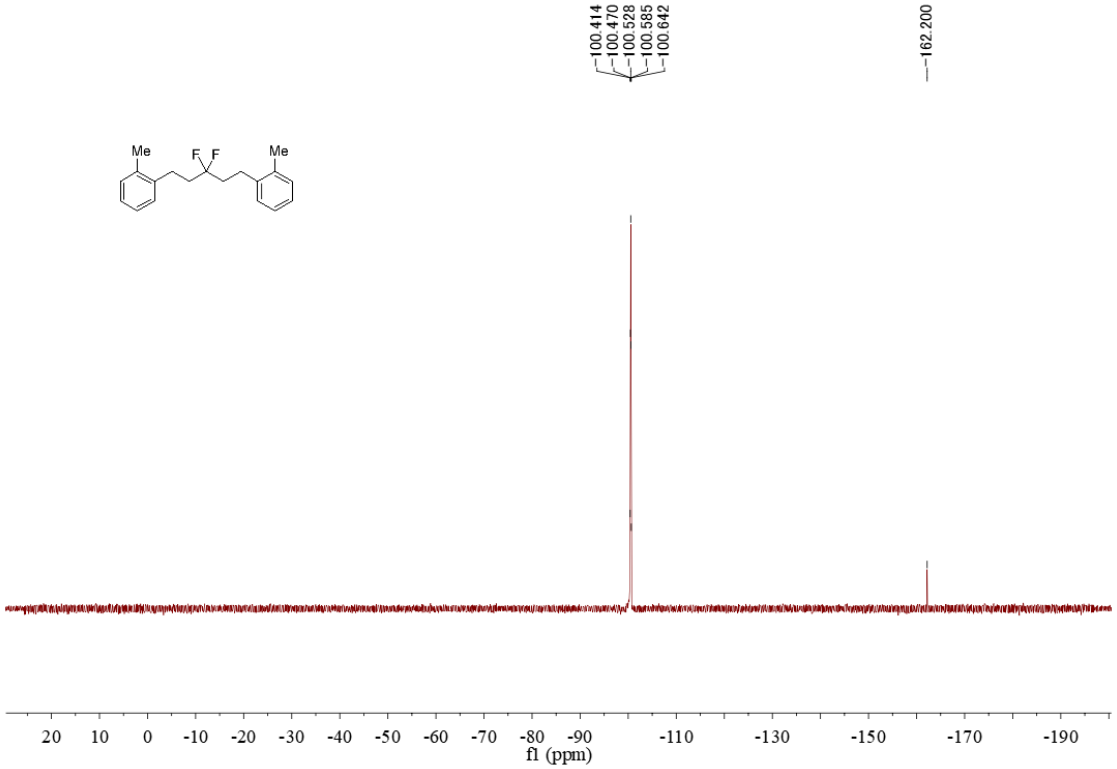


Figure S138. ^{1}H NMR spectrum of unknown *gem*-difluoride **1g**, related to **Figure 2**

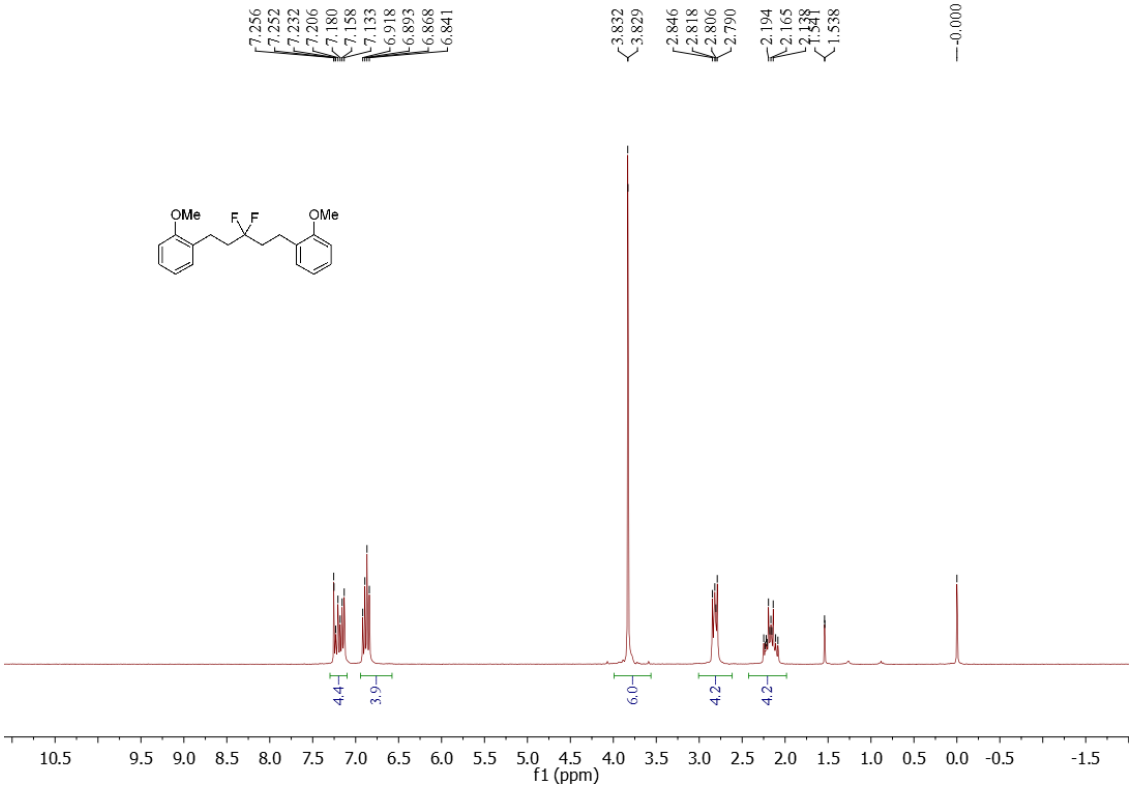


Figure S139. ^{13}C NMR spectrum of unknown *gem*-difluoride **1g**, related to **Figure 2**

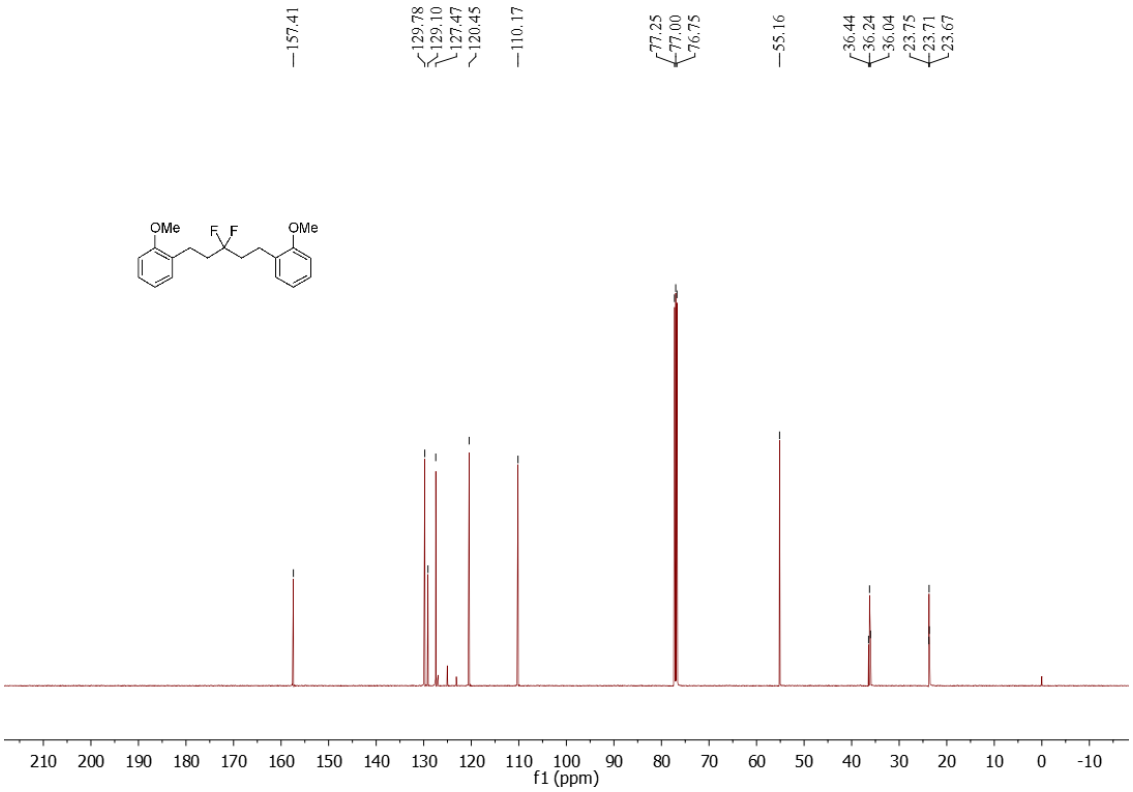


Figure S140. ^{19}F NMR spectrum of unknown *gem*-difluoride **1g**, related to **Figure 2**

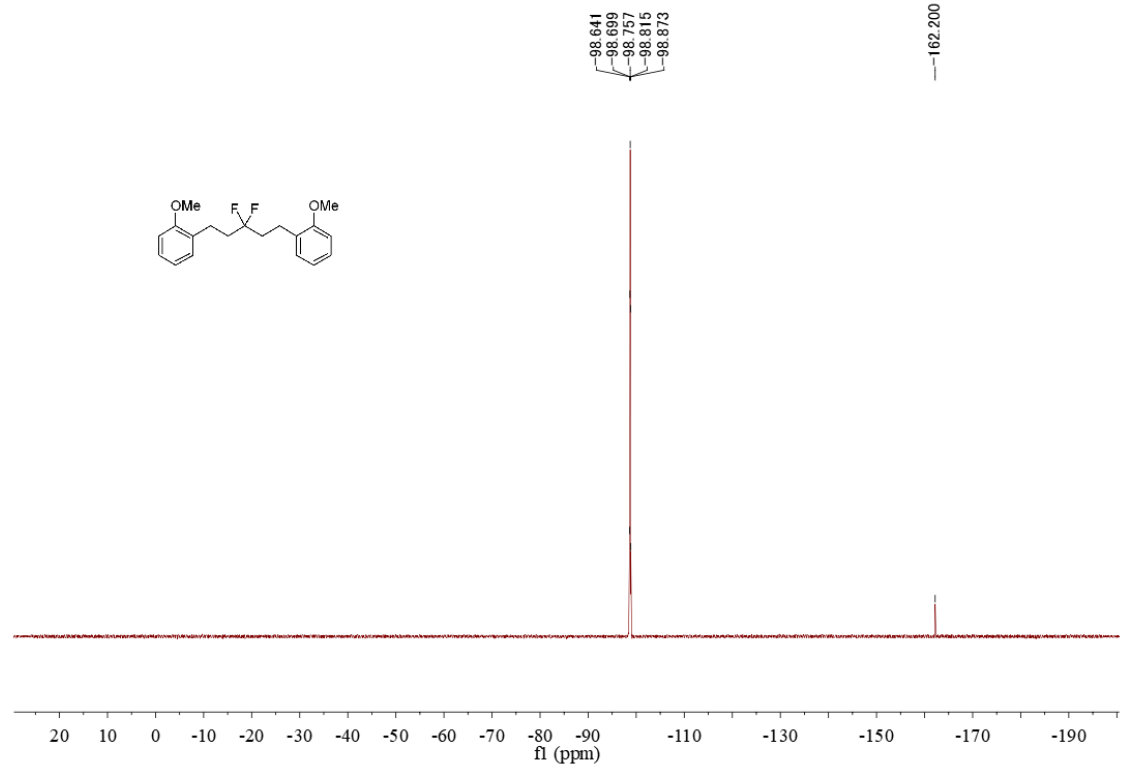


Figure S141. ^{1}H NMR spectrum of unknown *gem*-difluoride **1h**, related to **Figure 2**

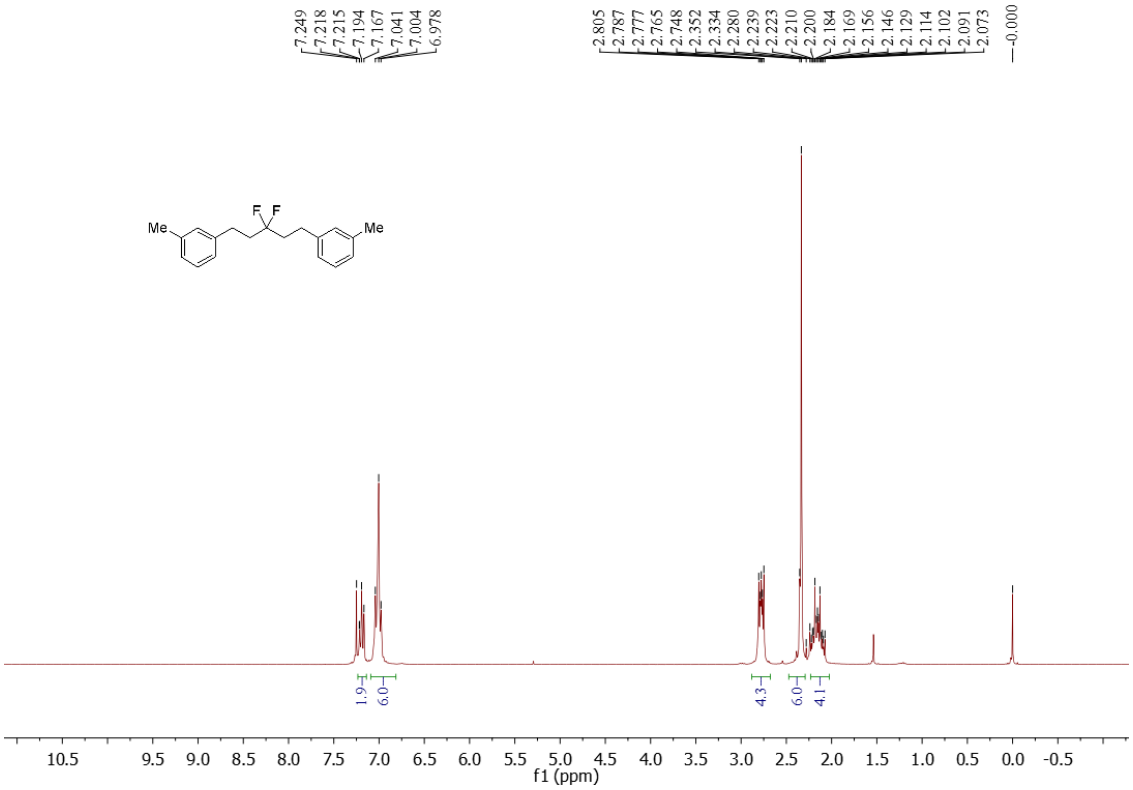


Figure S142. ^{13}C NMR spectrum of unknown *gem*-difluoride **1h**, related to **Figure 2**

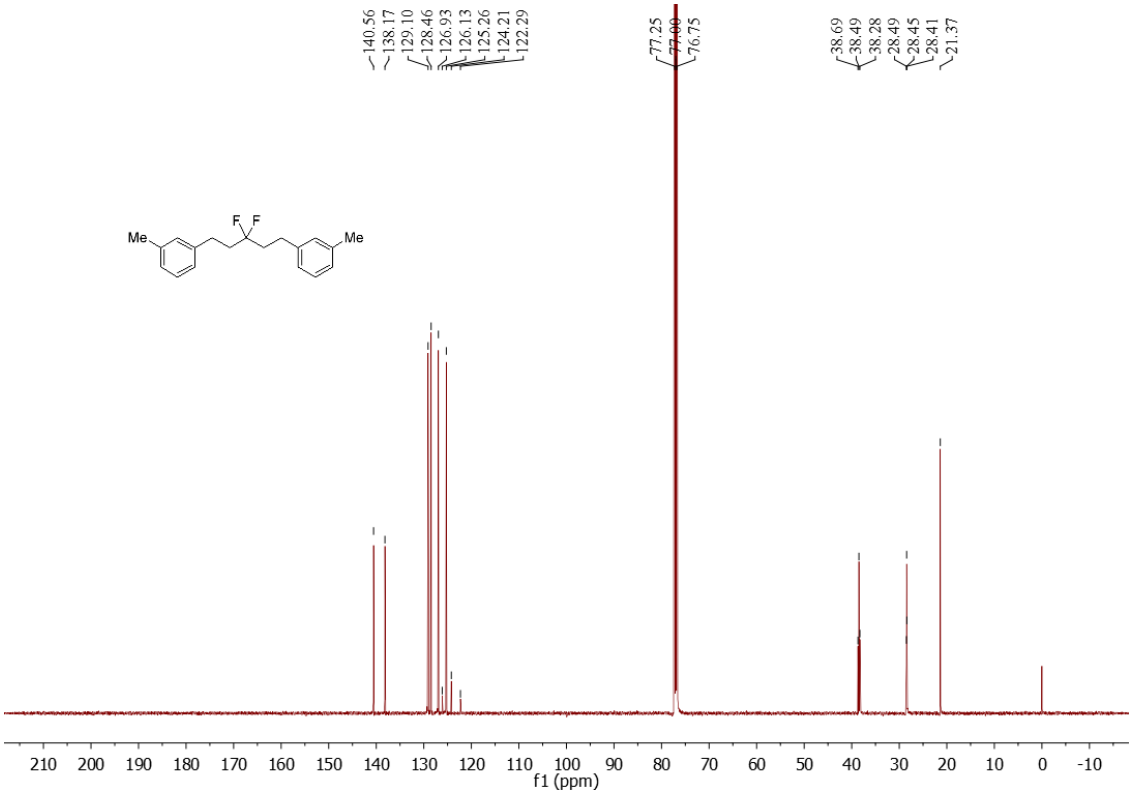


Figure S143. ^{19}F NMR spectrum of unknown *gem*-difluoride **1h**, related to **Figure 2**

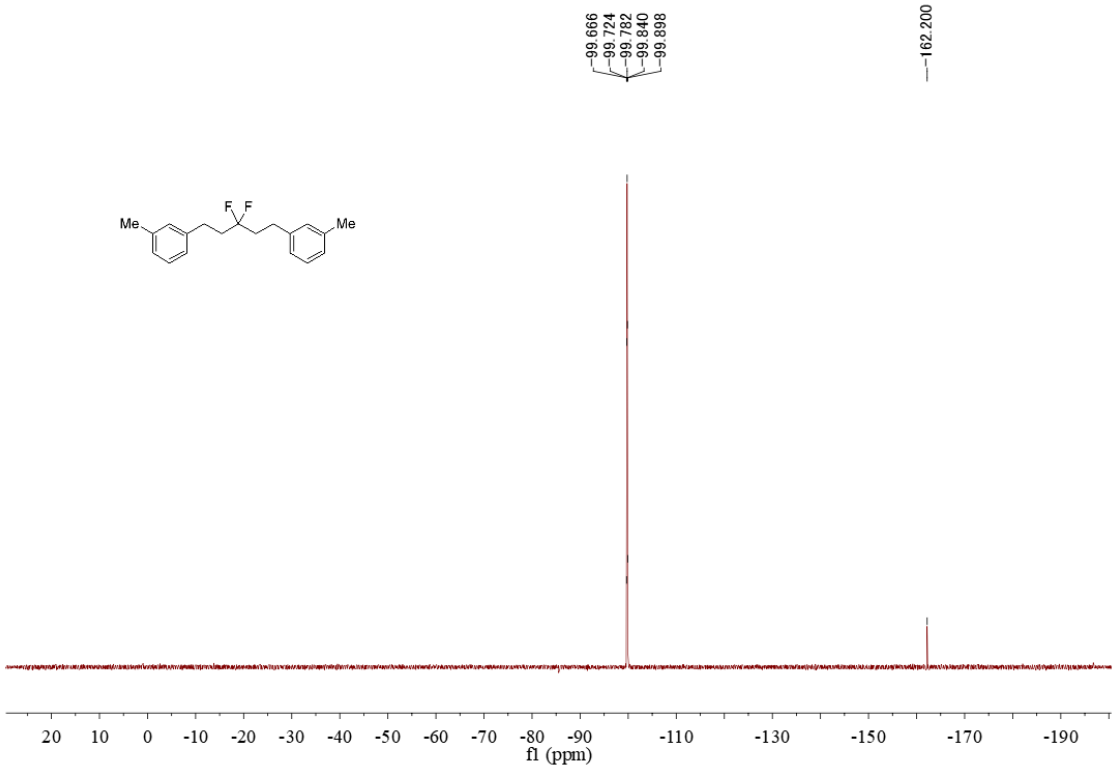


Figure S144. ^{1}H NMR spectrum of unknown *gem*-difluoride **1i**, related to **Figure 2**

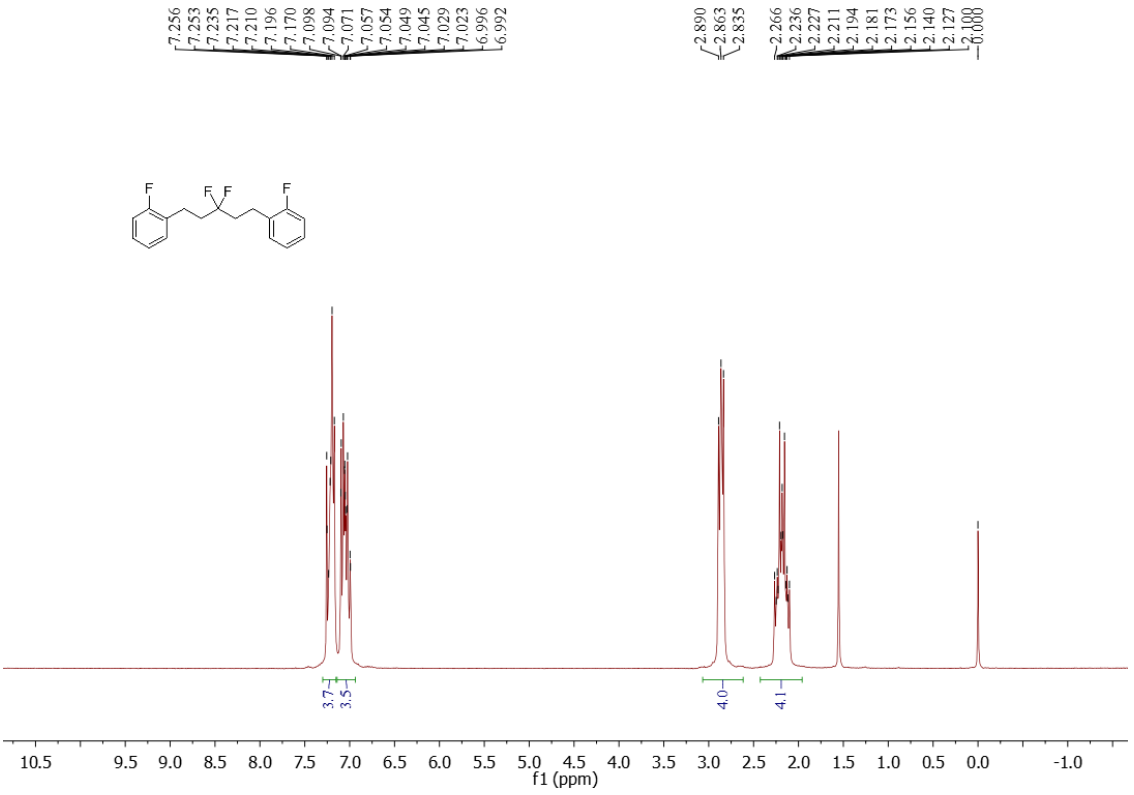


Figure S145. ^{13}C NMR spectrum of unknown *gem*-difluoride **1i**, related to **Figure 2**

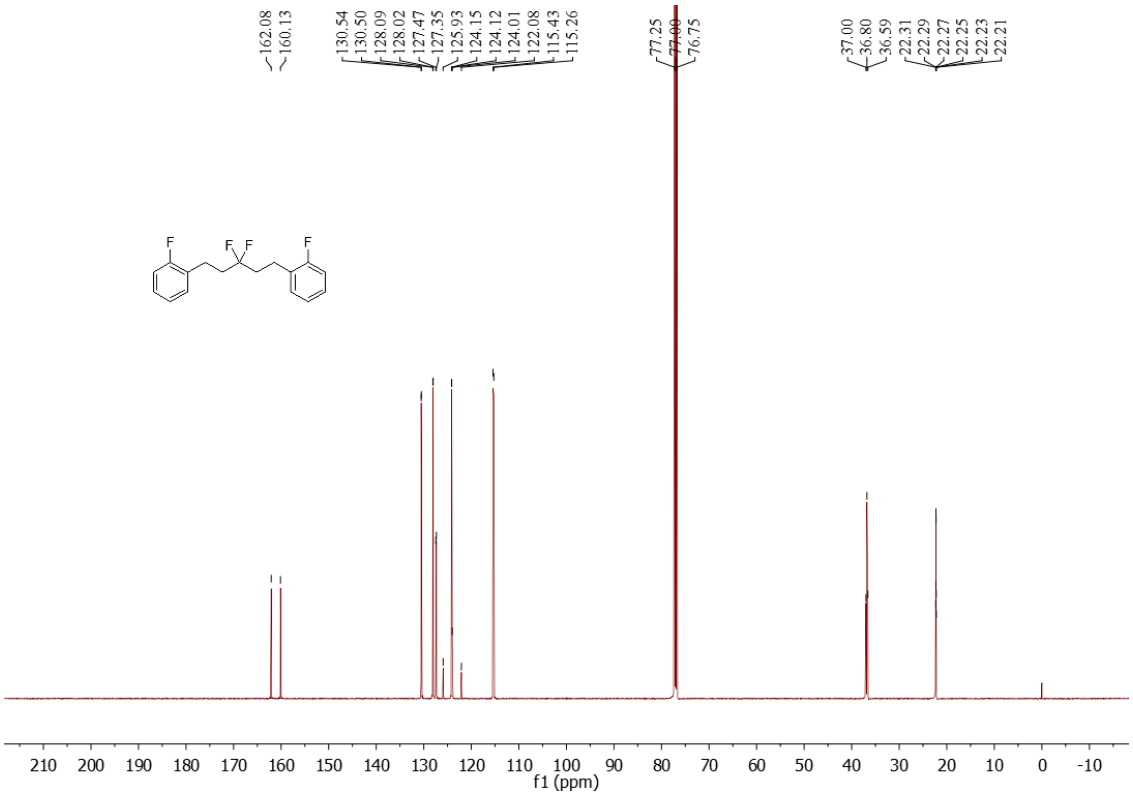


Figure S146. ^{19}F NMR spectrum of unknown *gem*-difluoride **1i**, related to **Figure 2**

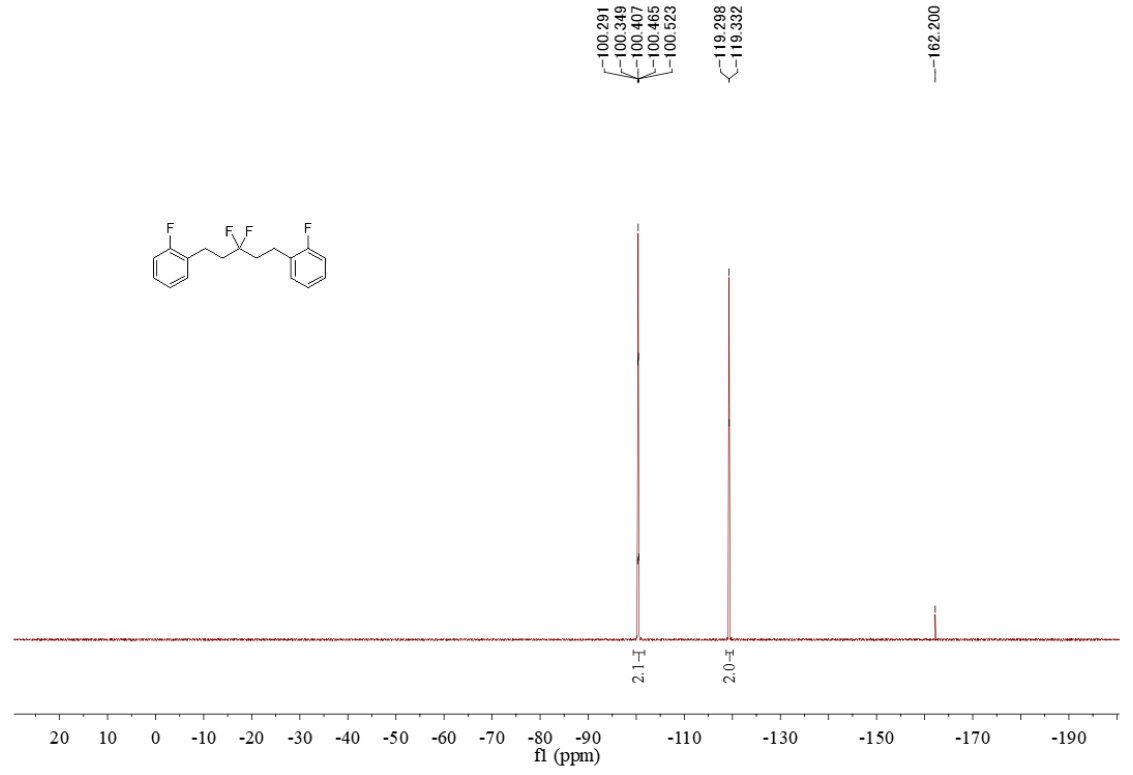


Figure S147. ^{1}H NMR spectrum of unknown *gem*-difluoride **1j**, related to **Figure 2**

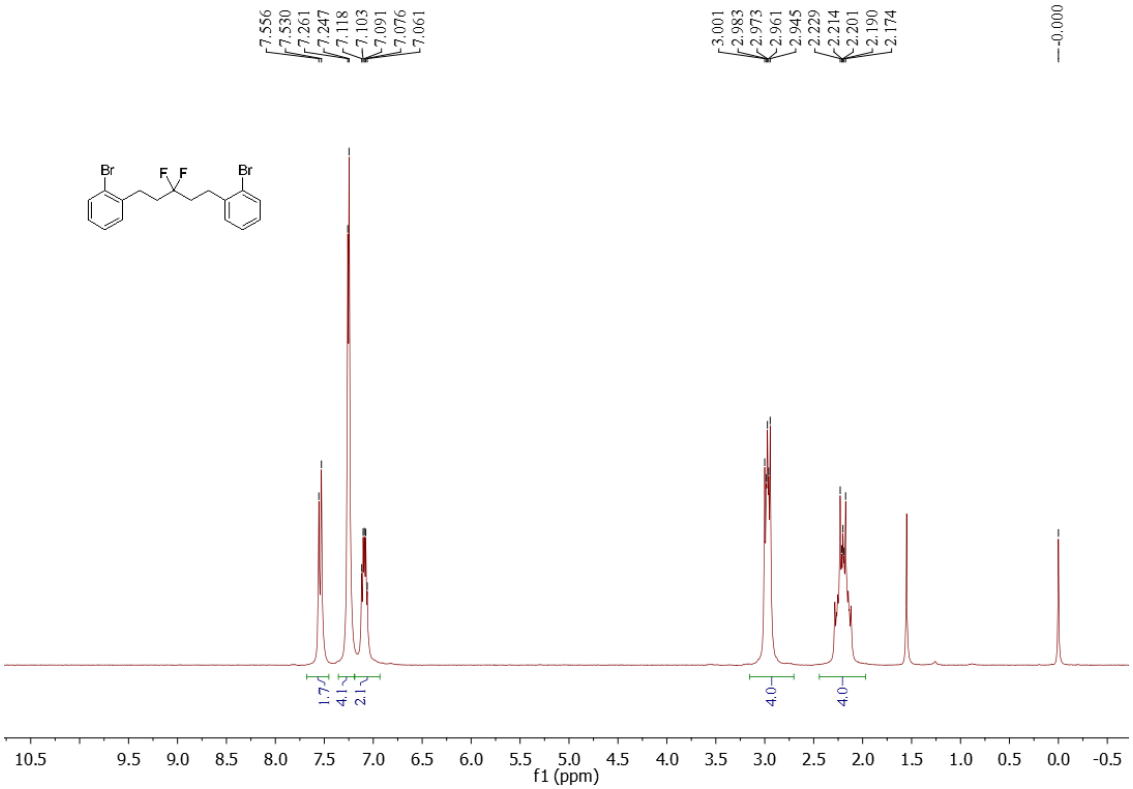


Figure S148. ^{13}C NMR spectrum of unknown *gem*-difluoride **1j**, related to **Figure 2**

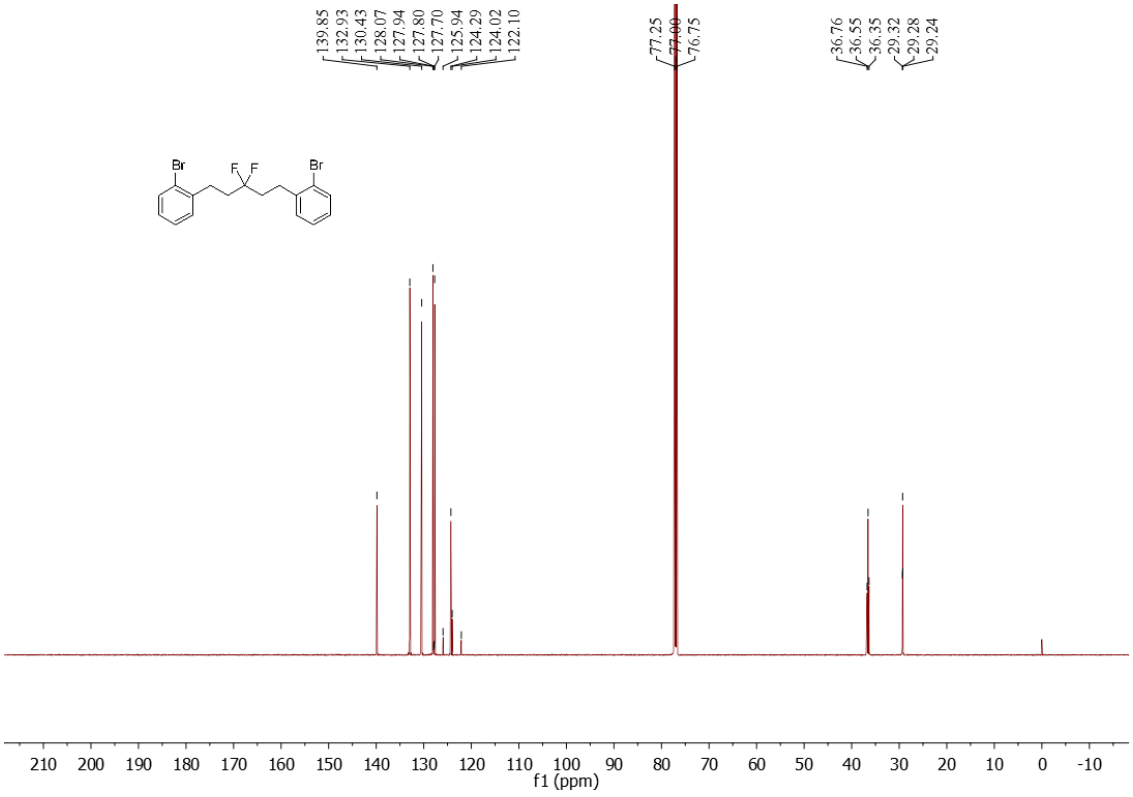


Figure S149. ^{19}F NMR spectrum of unknown *gem*-difluoride **1j**, related to **Figure 2**

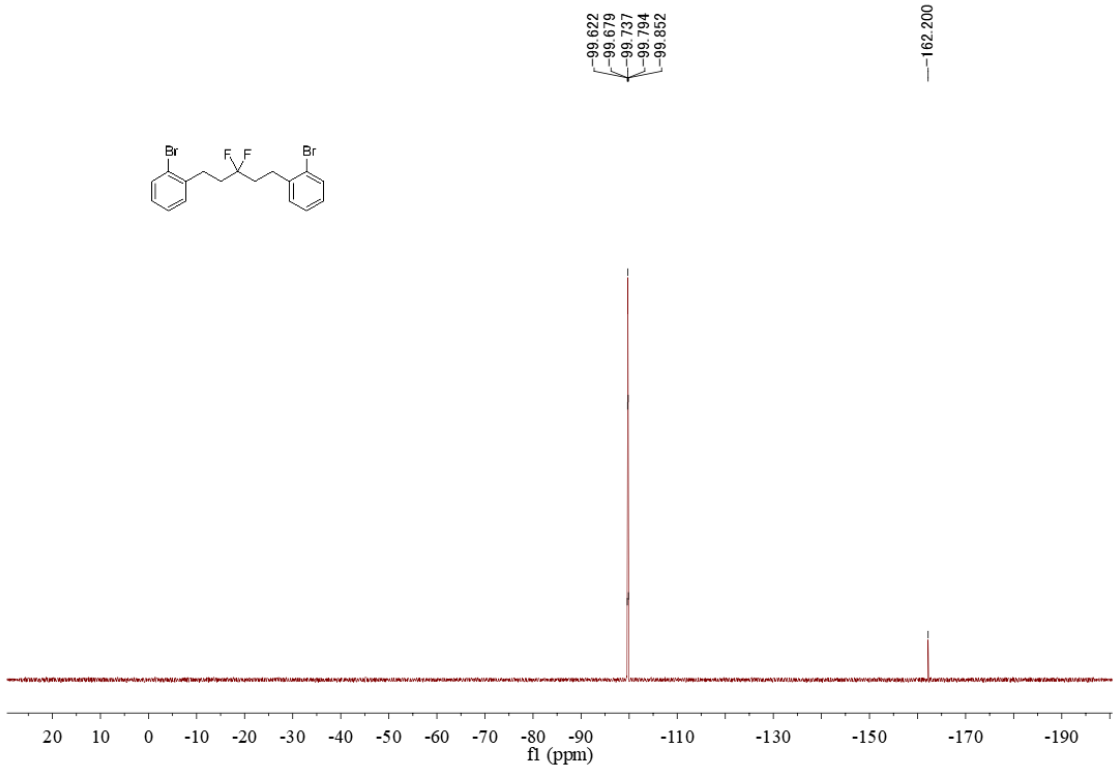


Figure S150. ^{1}H NMR spectrum of unknown *gem*-difluoride **1k**, related to **Figure 2**

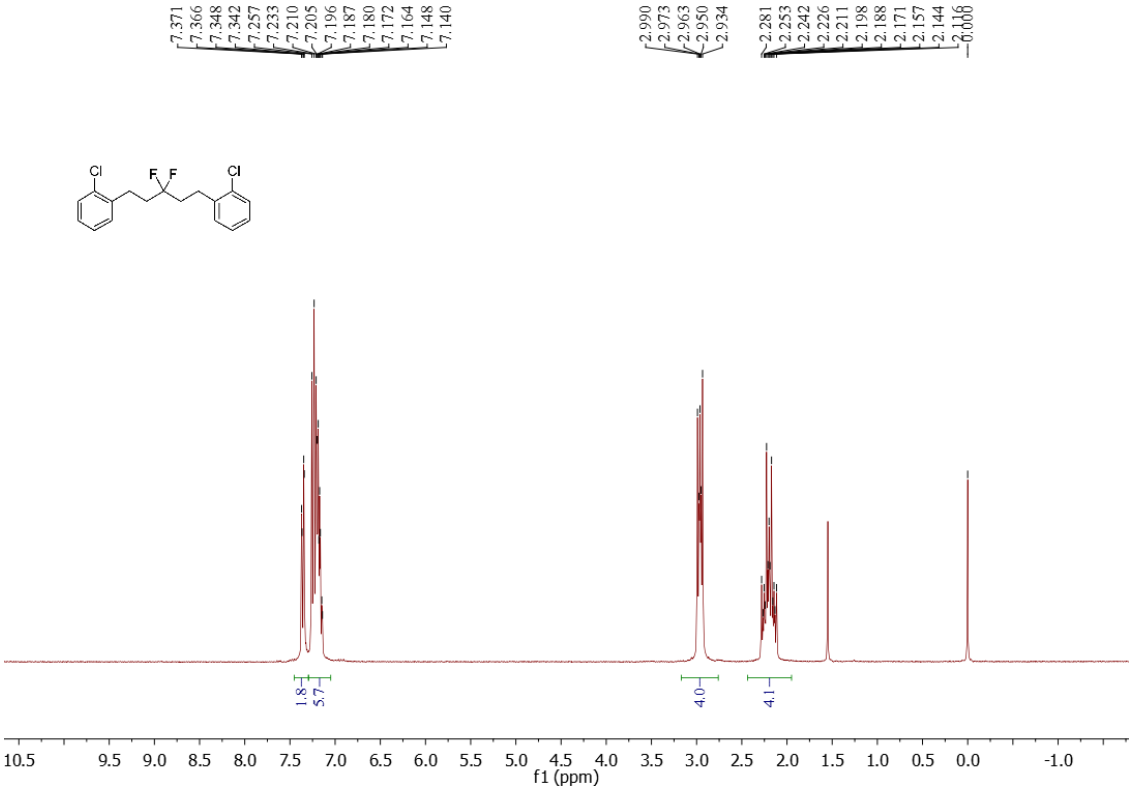


Figure S151. ^{13}C NMR spectrum of unknown *gem*-difluoride **1k**, related to **Figure 2**

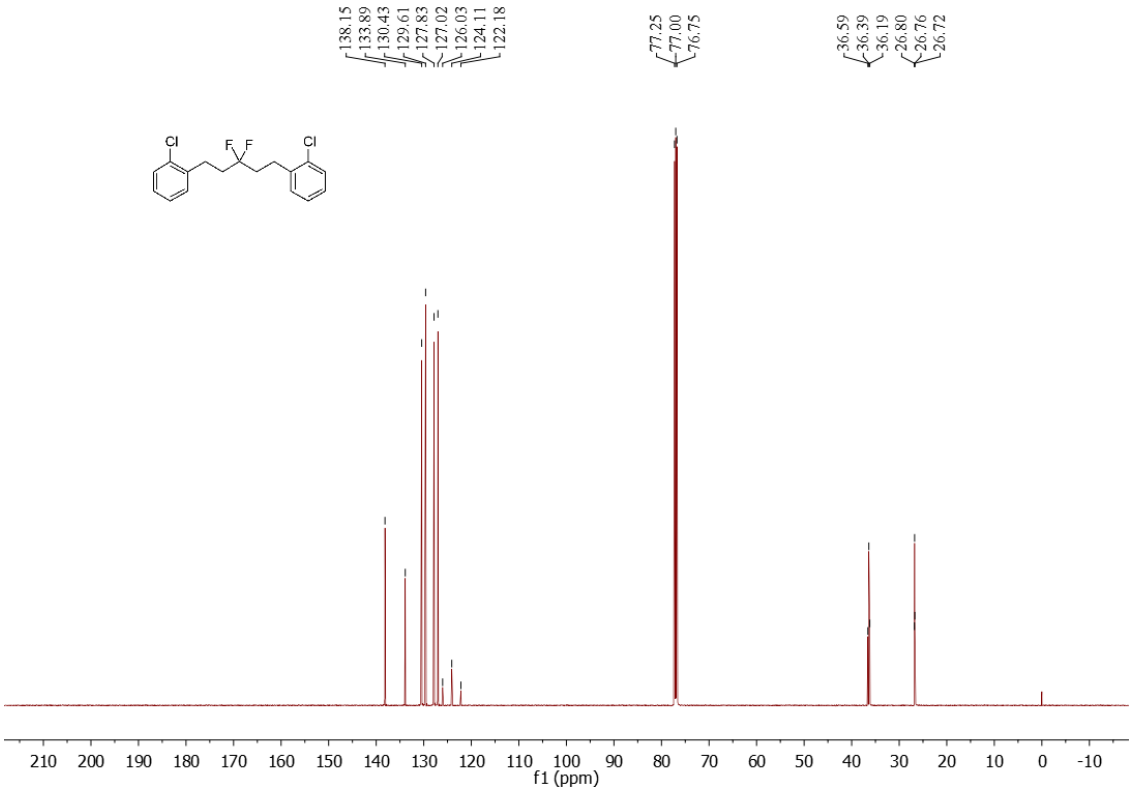


Figure S152. ^{19}F NMR spectrum of unknown *gem*-difluoride **1k**, related to **Figure 2**

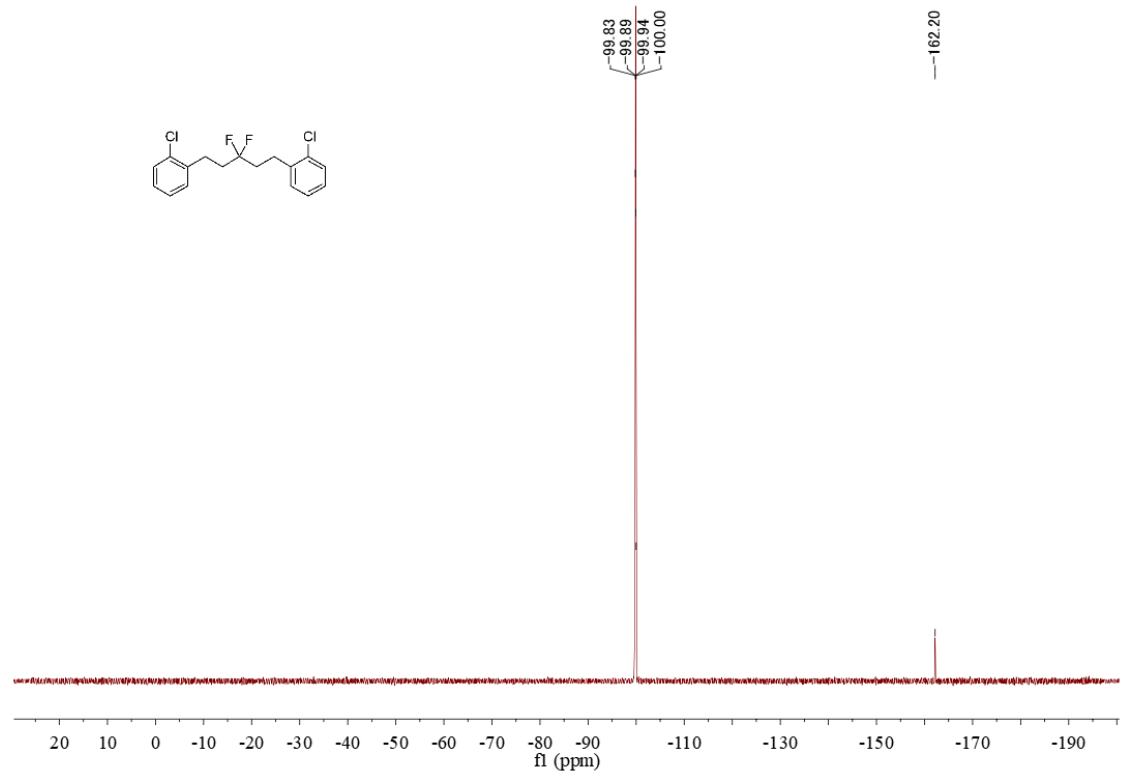


Figure S153. ^{1}H NMR spectrum of unknown *gem*-difluoride **1l**, related to **Figure 2**

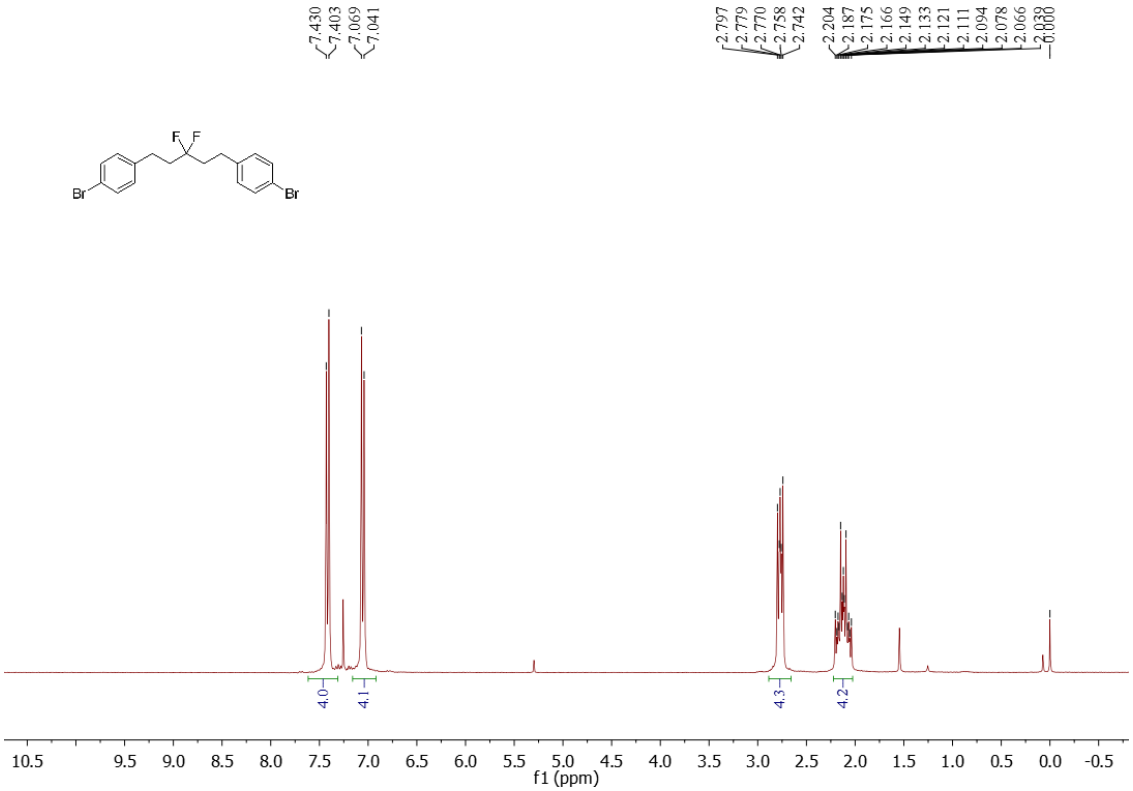


Figure S154. ^{13}C NMR spectrum of unknown *gem*-difluoride **1l**, related to **Figure 2**

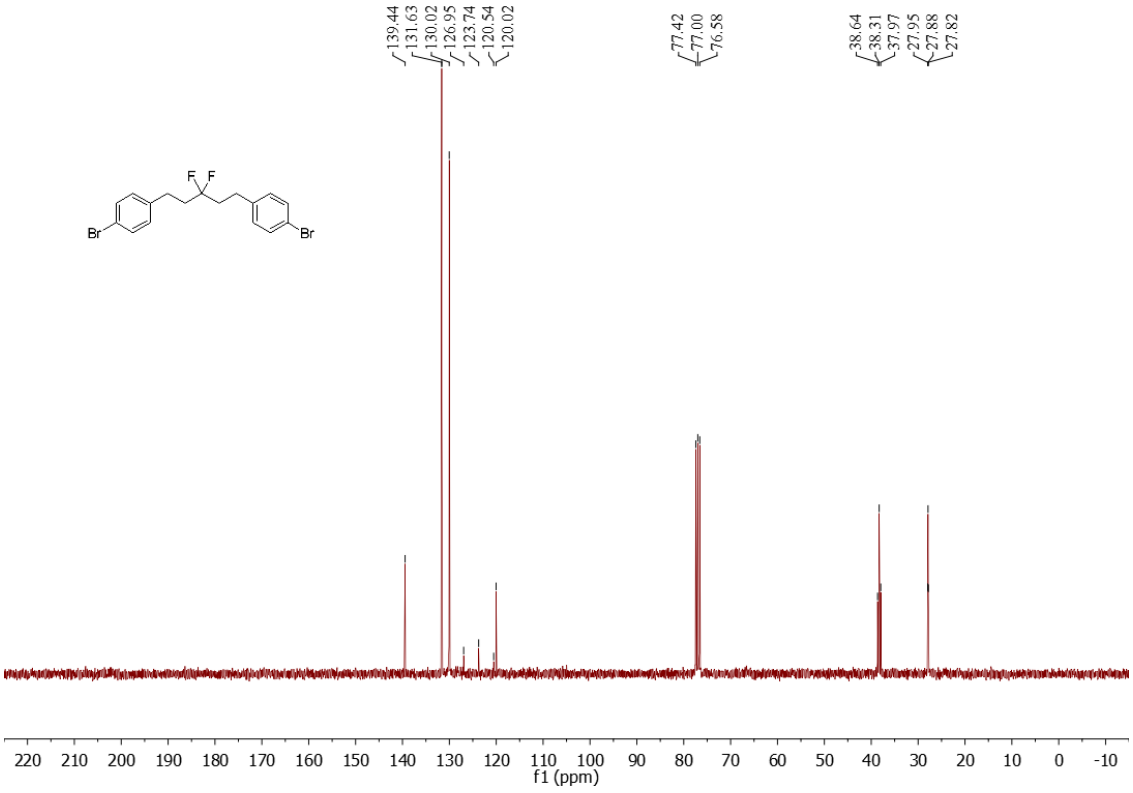


Figure S155. ^{19}F NMR spectrum of unknown *gem*-difluoride **1l**, related to **Figure 2**

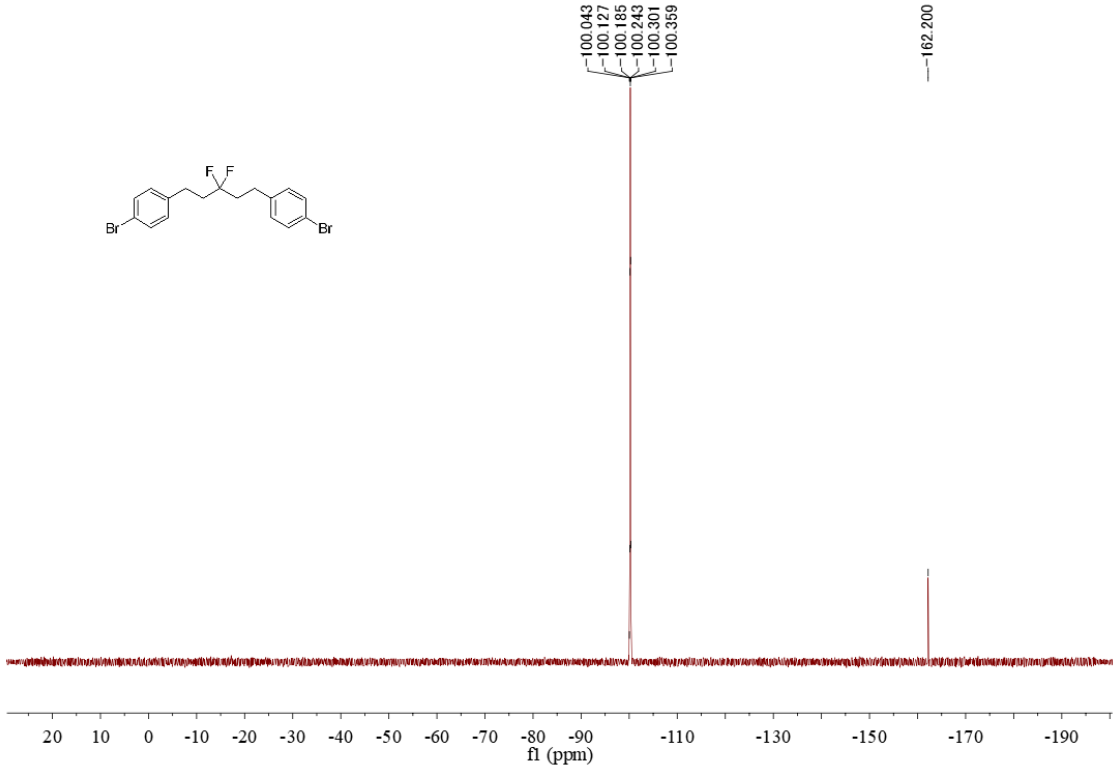


Figure S156. ^{1}H NMR spectrum of unknown *gem*-difluoride **1m**, related to **Figure 2**

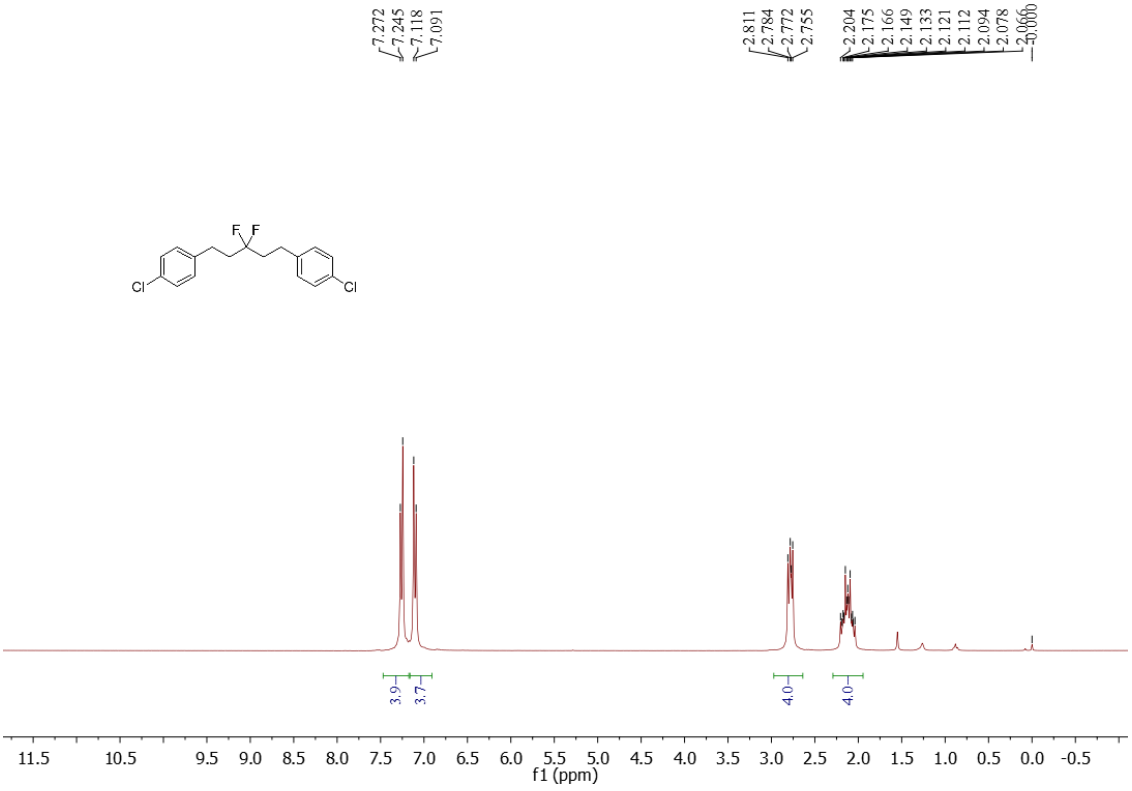


Figure S157. ^{13}C NMR spectrum of unknown *gem*-difluoride **1m**, related to **Figure 2**

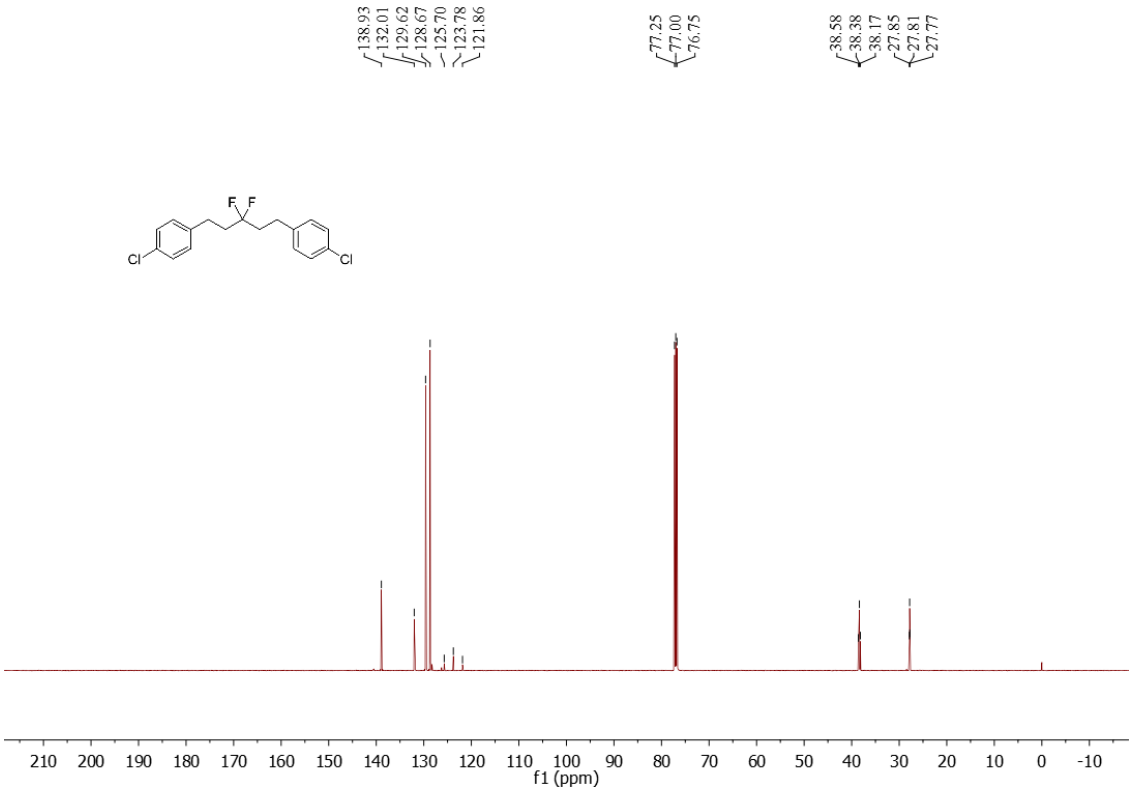


Figure S158. ^{19}F NMR spectrum of unknown *gem*-difluoride **1m**, related to **Figure 2**

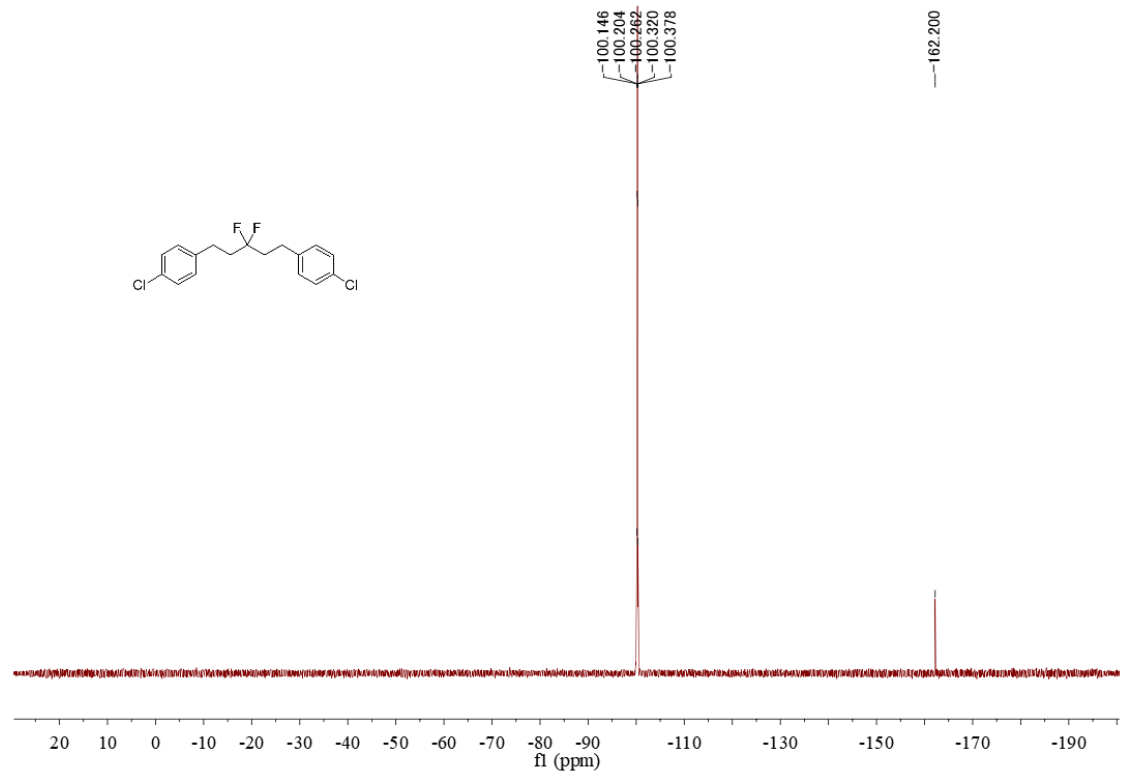


Figure S159. ^{1}H NMR spectrum of unknown *gem*-difluoride **1n**, related to **Figure 2**

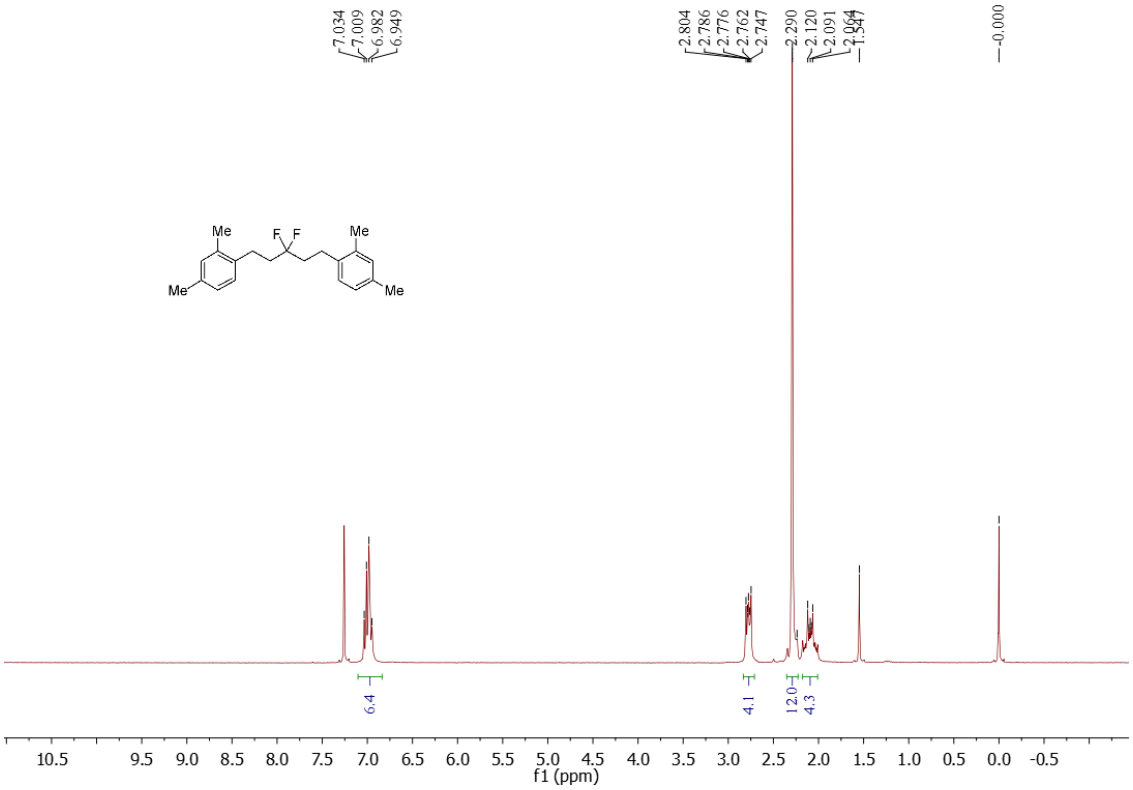


Figure S160. ^{13}C NMR spectrum of unknown *gem*-difluoride **1n**, related to **Figure 2**

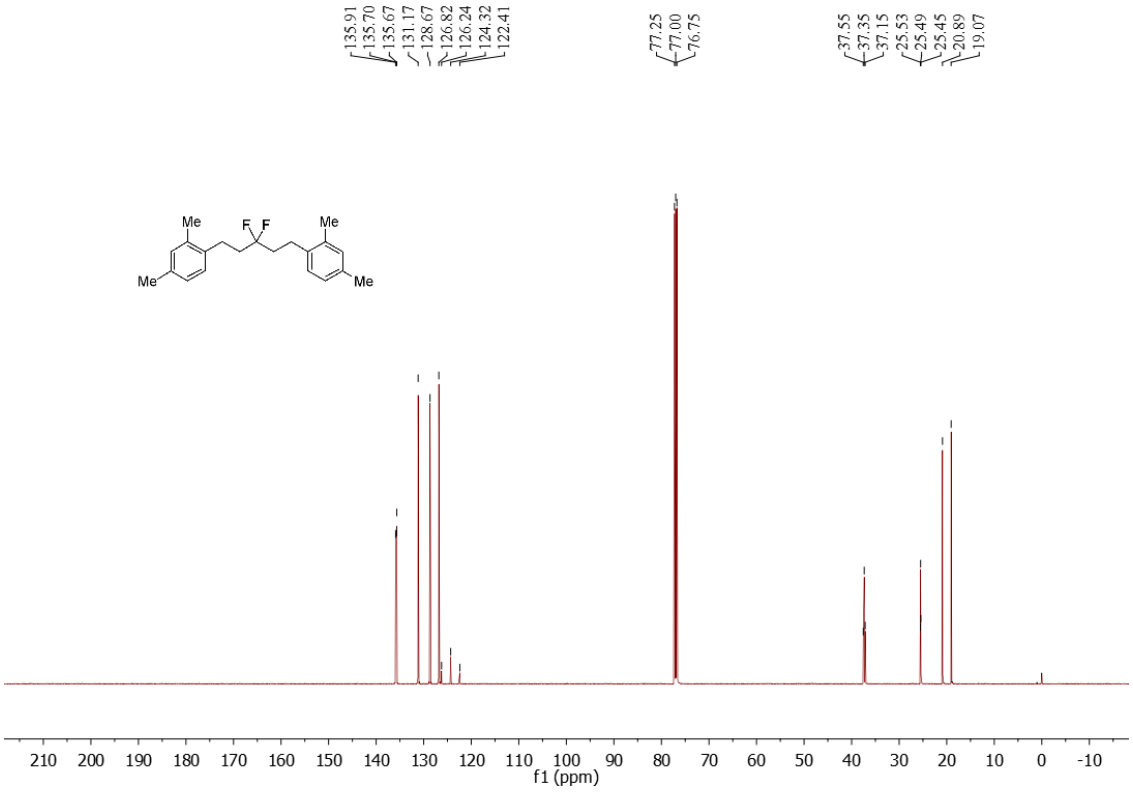


Figure S161. ^{19}F NMR spectrum of unknown *gem*-difluoride **1n**, related to **Figure 2**

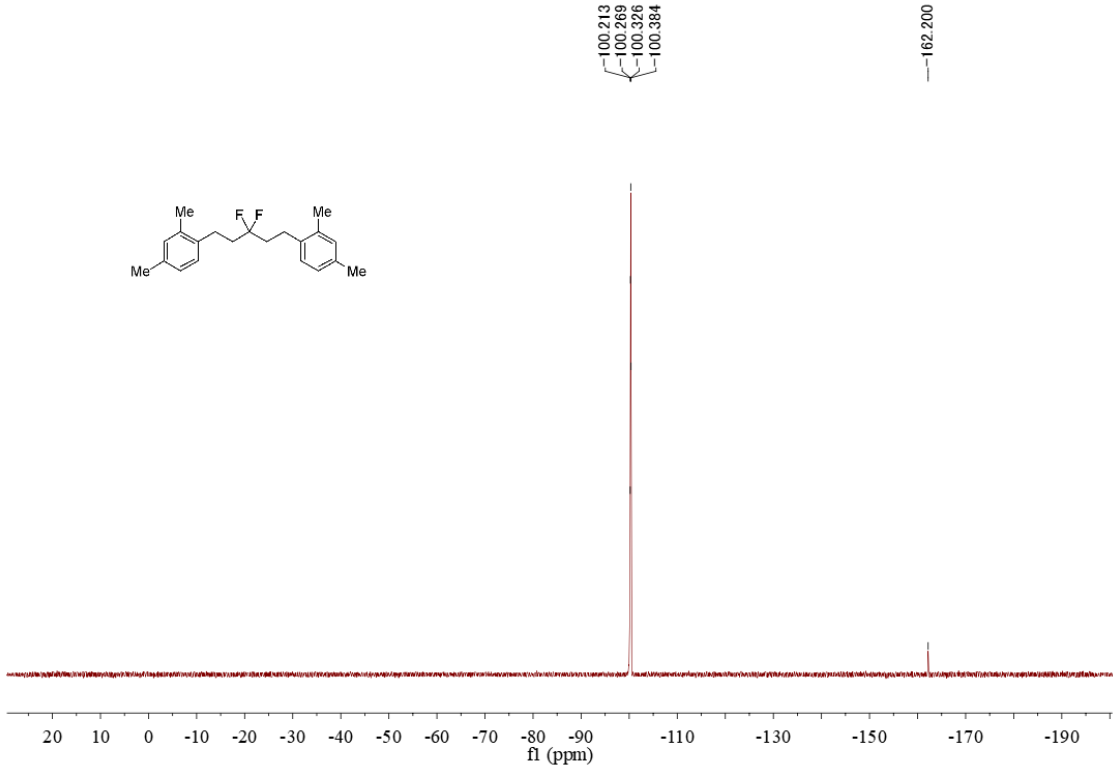


Figure S162. ^{1}H NMR spectrum of unknown *gem*-difluoride **1o**, related to **Figure 2**

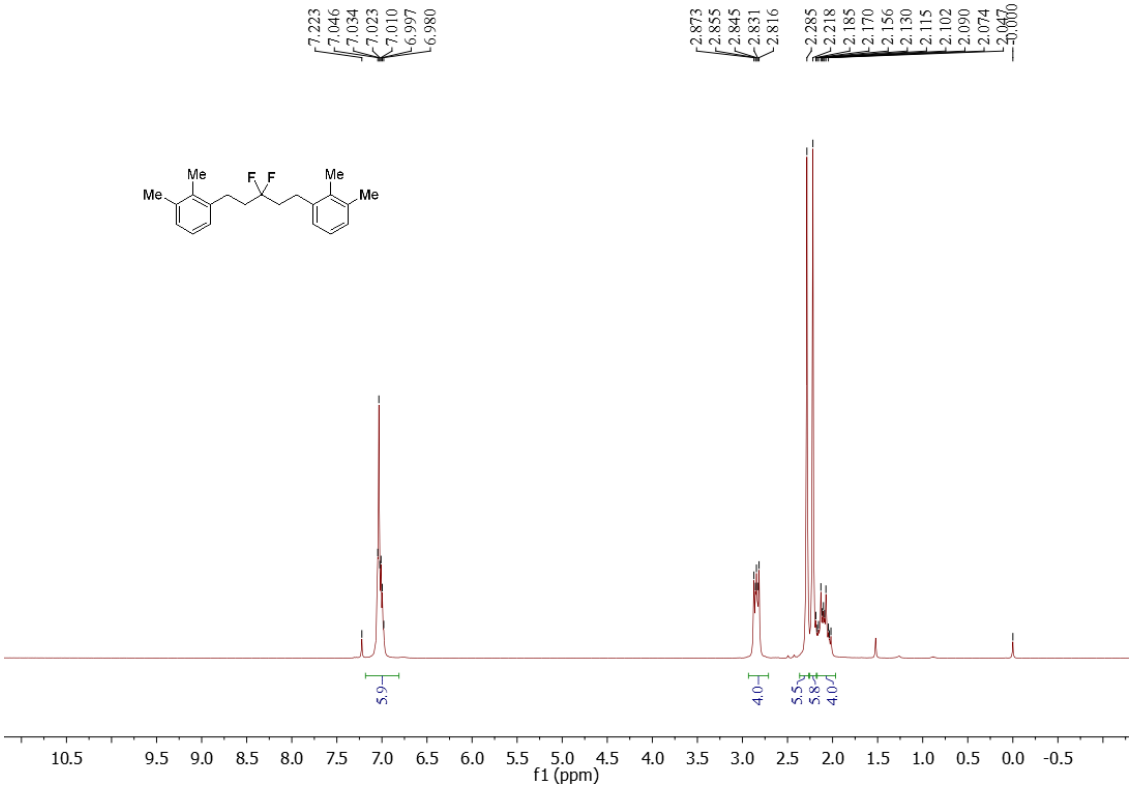


Figure S163. ^{13}C NMR spectrum of unknown *gem*-difluoride **1o**, related to **Figure 2**

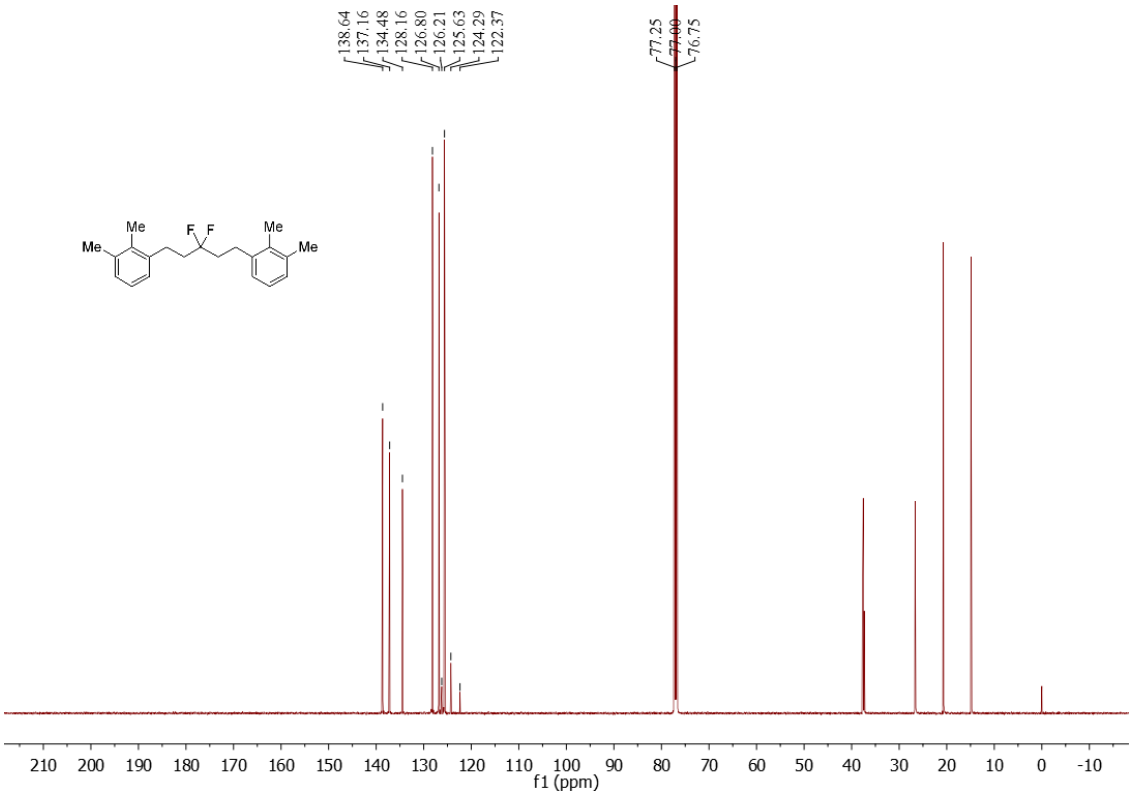


Figure S164. ^{19}F NMR spectrum of unknown *gem*-difluoride **1o**, related to **Figure 2**

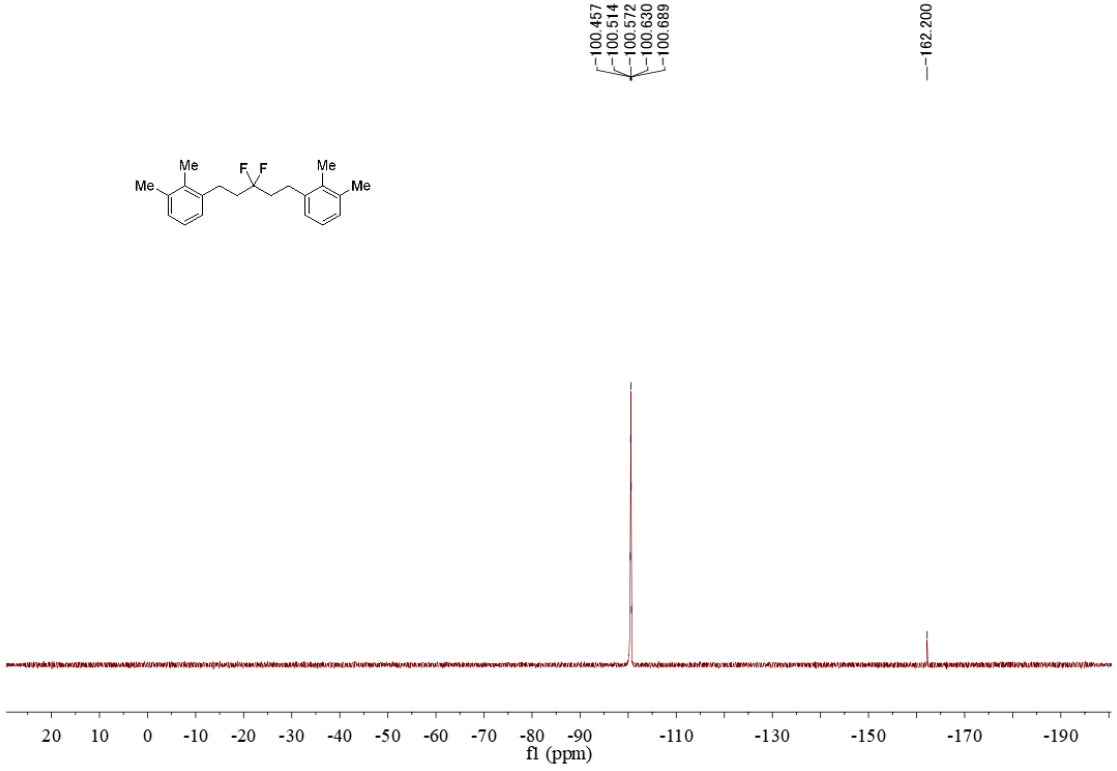


Figure S165. ^{1}H NMR spectrum of unknown *gem*-difluoride **1p**, related to **Figure 2**

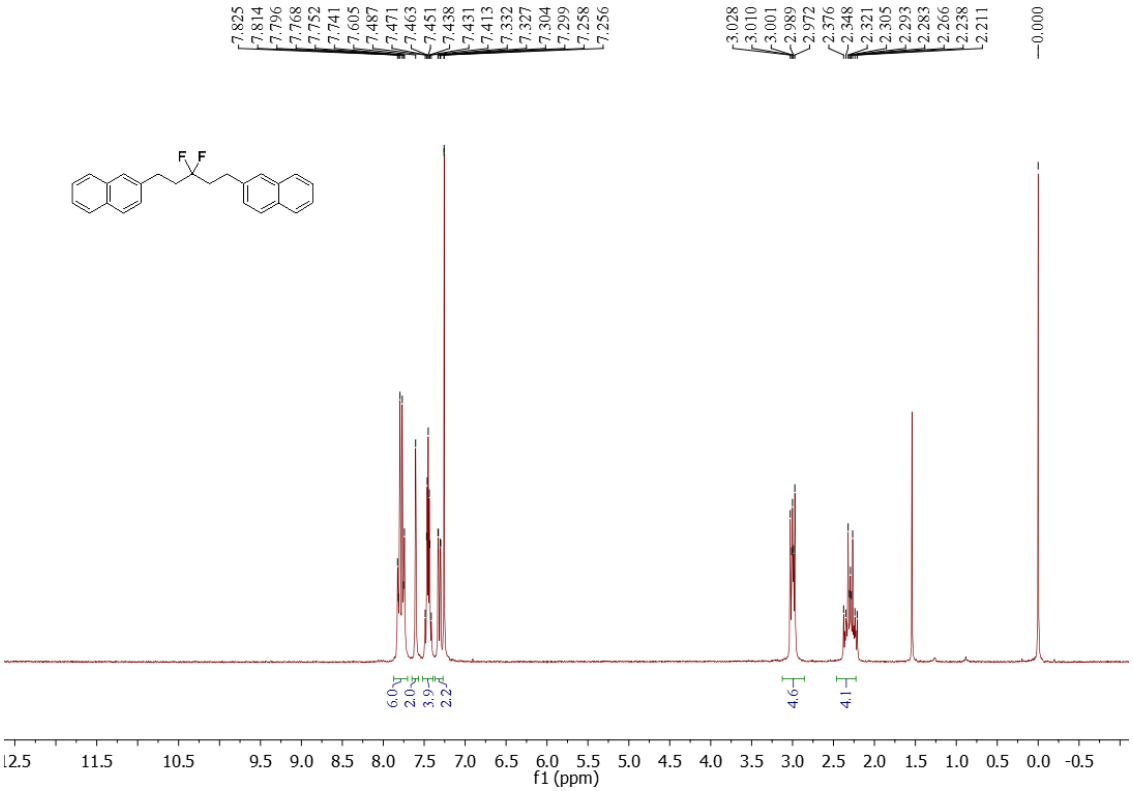


Figure S166. ^{13}C NMR spectrum of unknown *gem*-difluoride **1p**, related to **Figure 2**

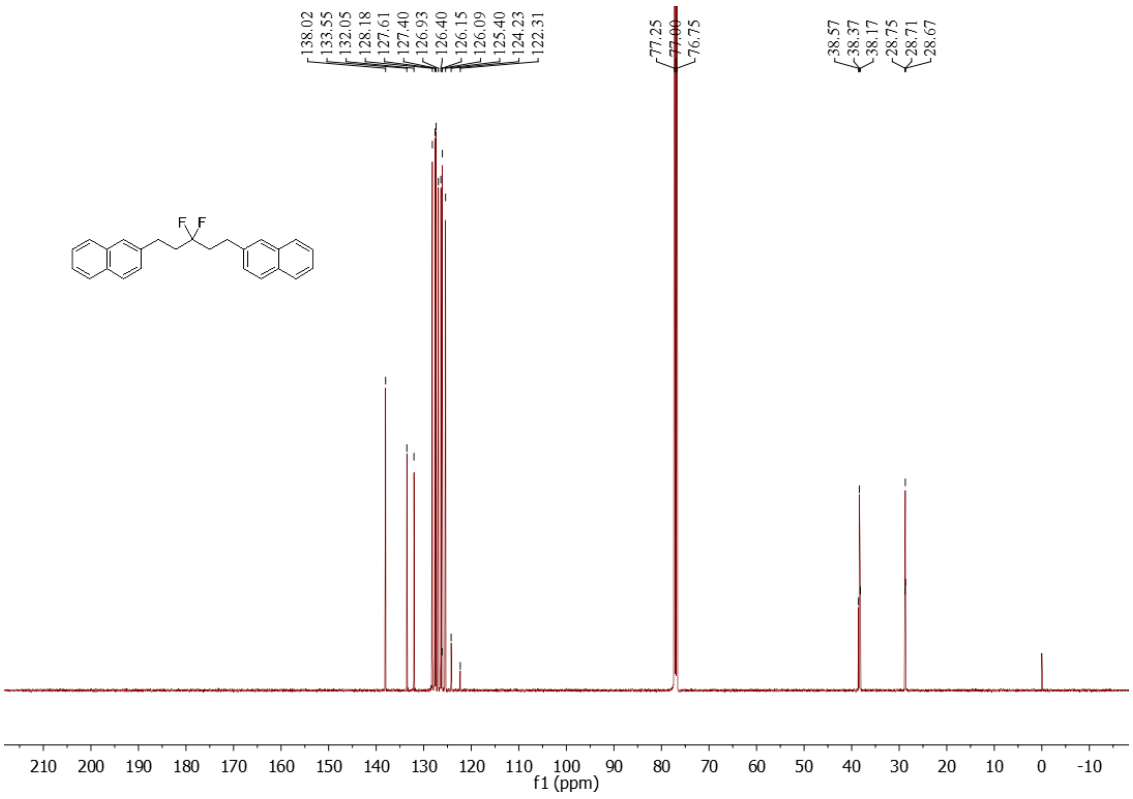


Figure S167. ^{19}F NMR spectrum of unknown *gem*-difluoride **1p**, related to **Figure 2**

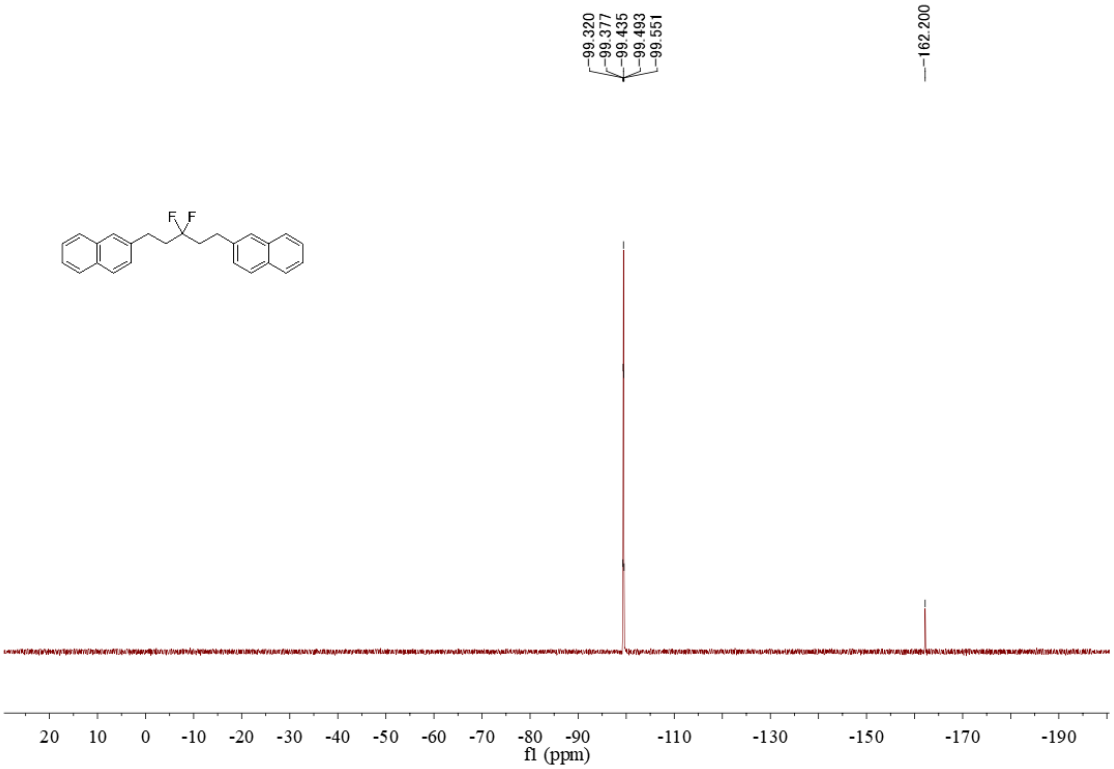


Figure S168. ^{1}H NMR spectrum of unknown *gem*-difluoride **1q**, related to **Figure 2**

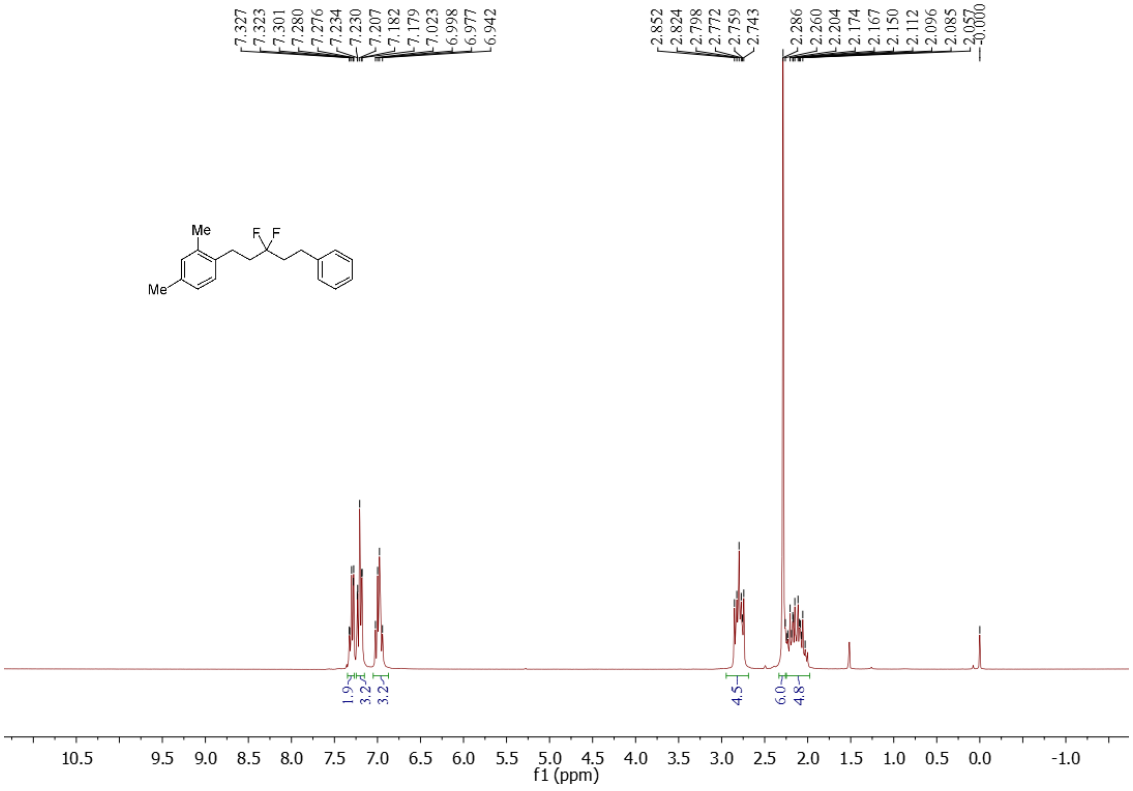


Figure S169. ^{13}C NMR spectrum of unknown *gem*-difluoride **1q**, related to **Figure 2**

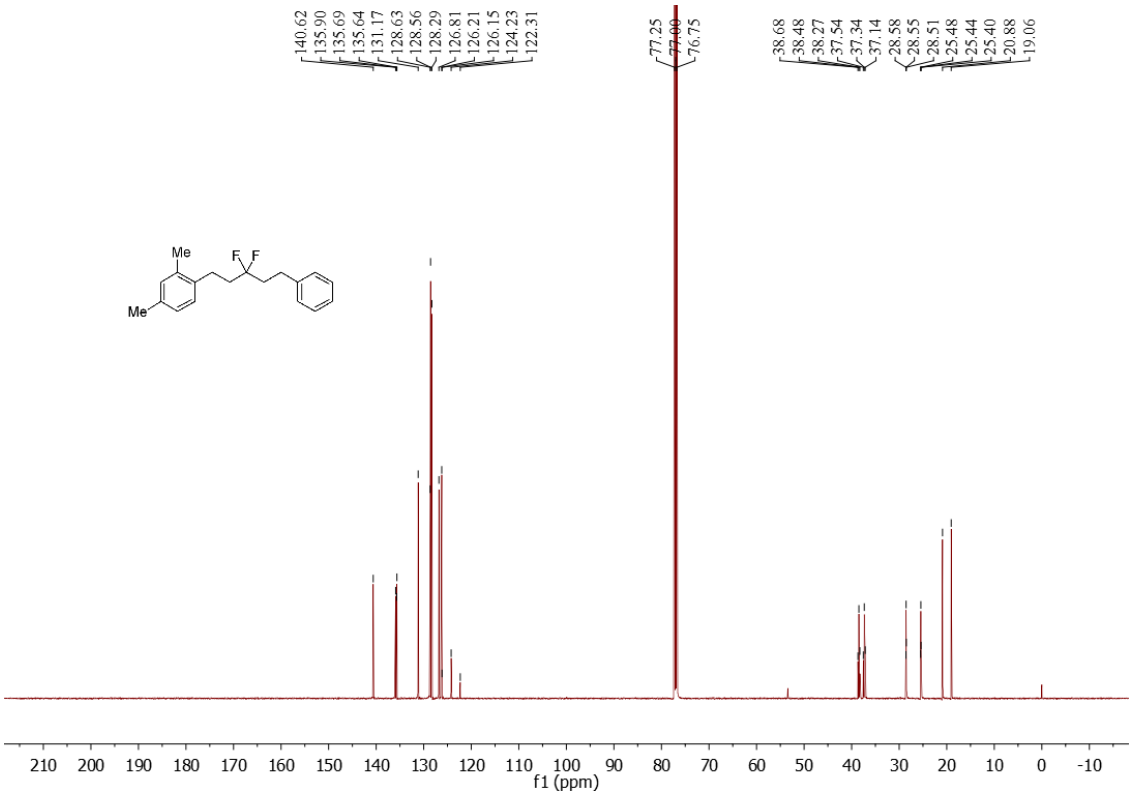


Figure S170. ^{19}F NMR spectrum of unknown *gem*-difluoride **1q**, related to **Figure 2**

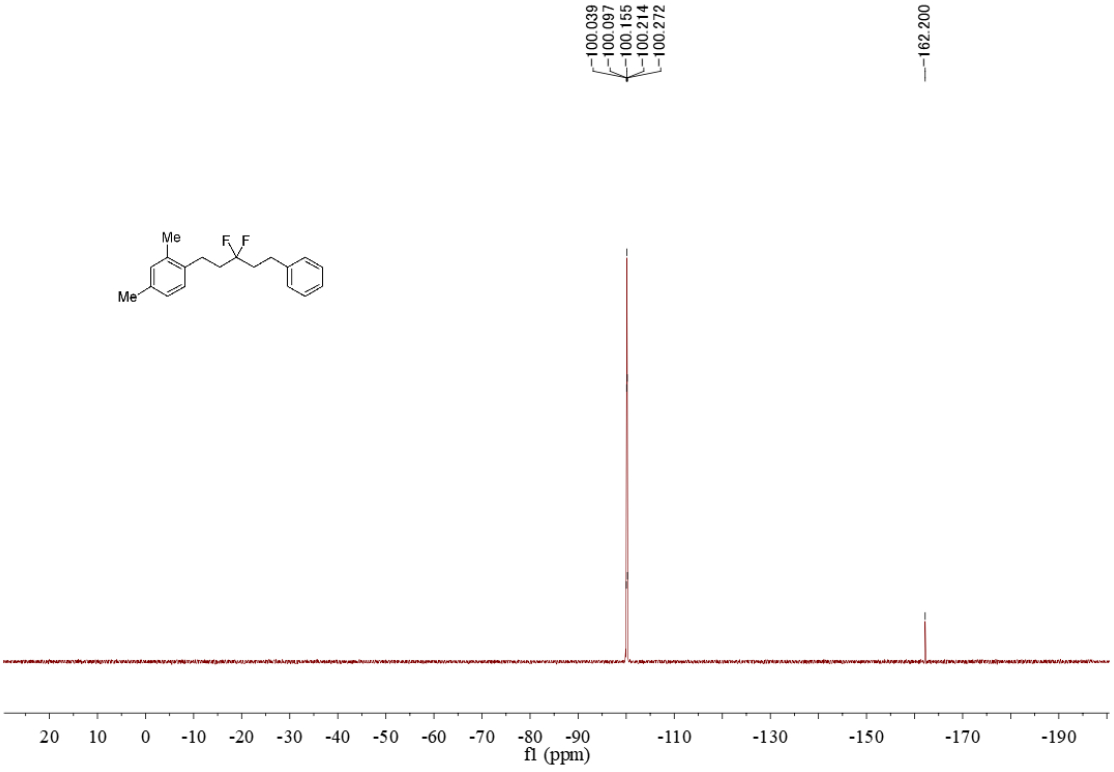


Figure S171. ^{1}H NMR spectrum of unknown *gem*-difluoride **1r**, related to **Figure 2**

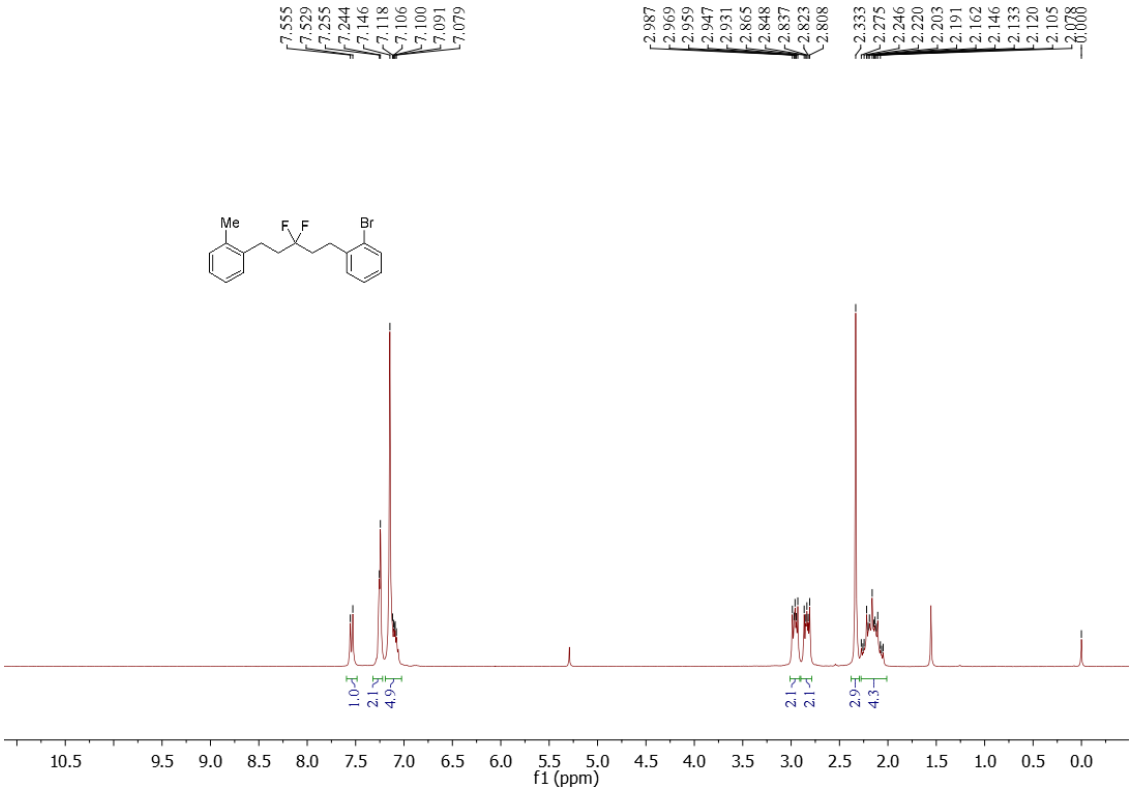


Figure S172. ^{13}C NMR spectrum of unknown *gem*-difluoride **1r**, related to **Figure 2**

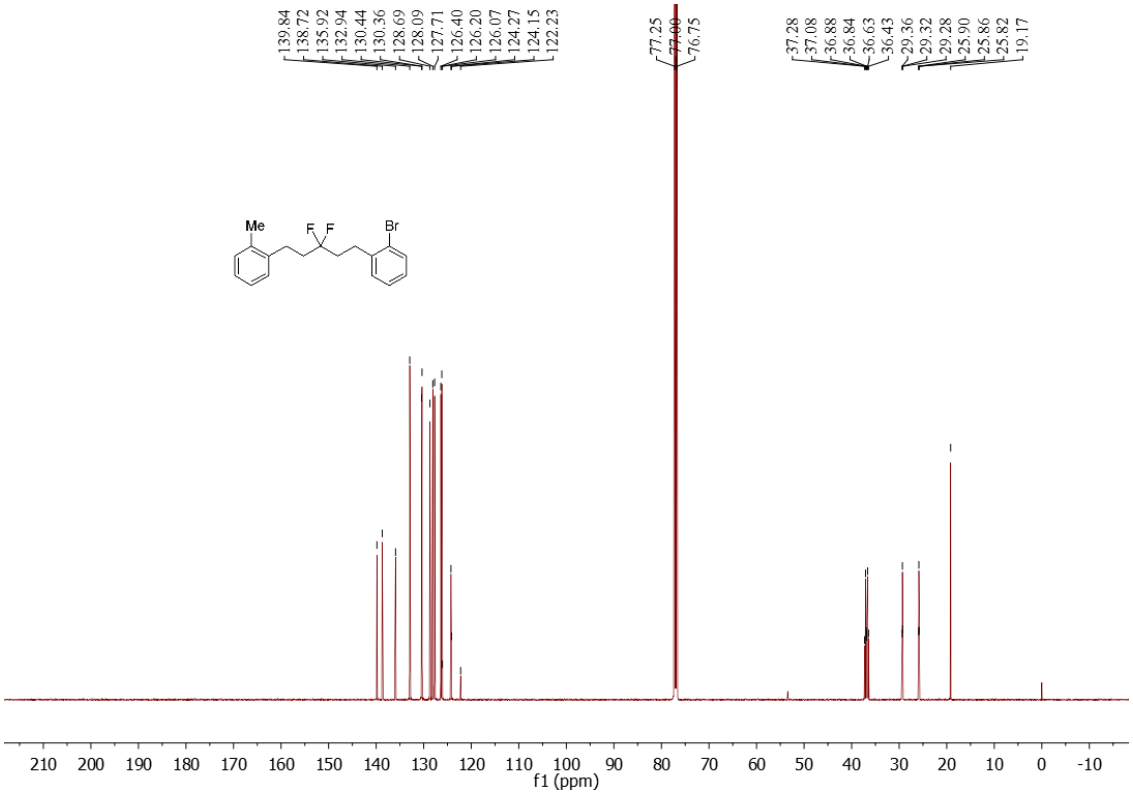


Figure S173. ^{19}F NMR spectrum of unknown *gem*-difluoride **1r**, related to **Figure 2**

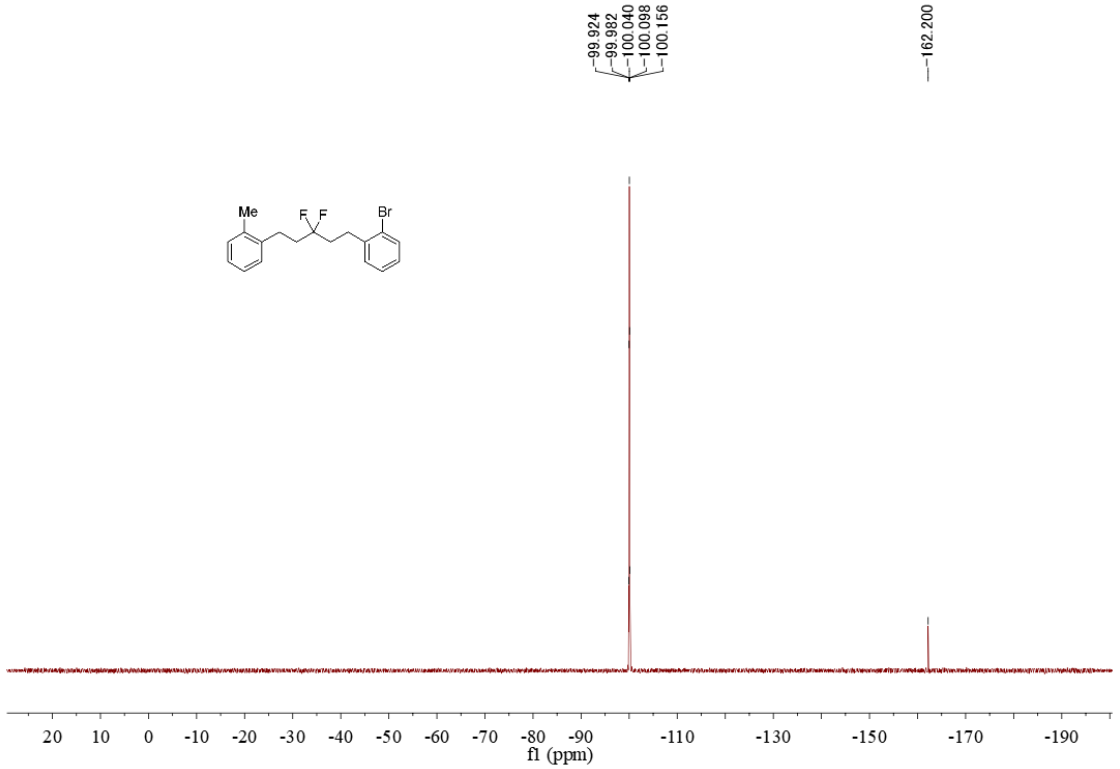


Figure S174. ^{1}H NMR spectrum of unknown *gem*-difluoride **1s**, related to **Figure 2**

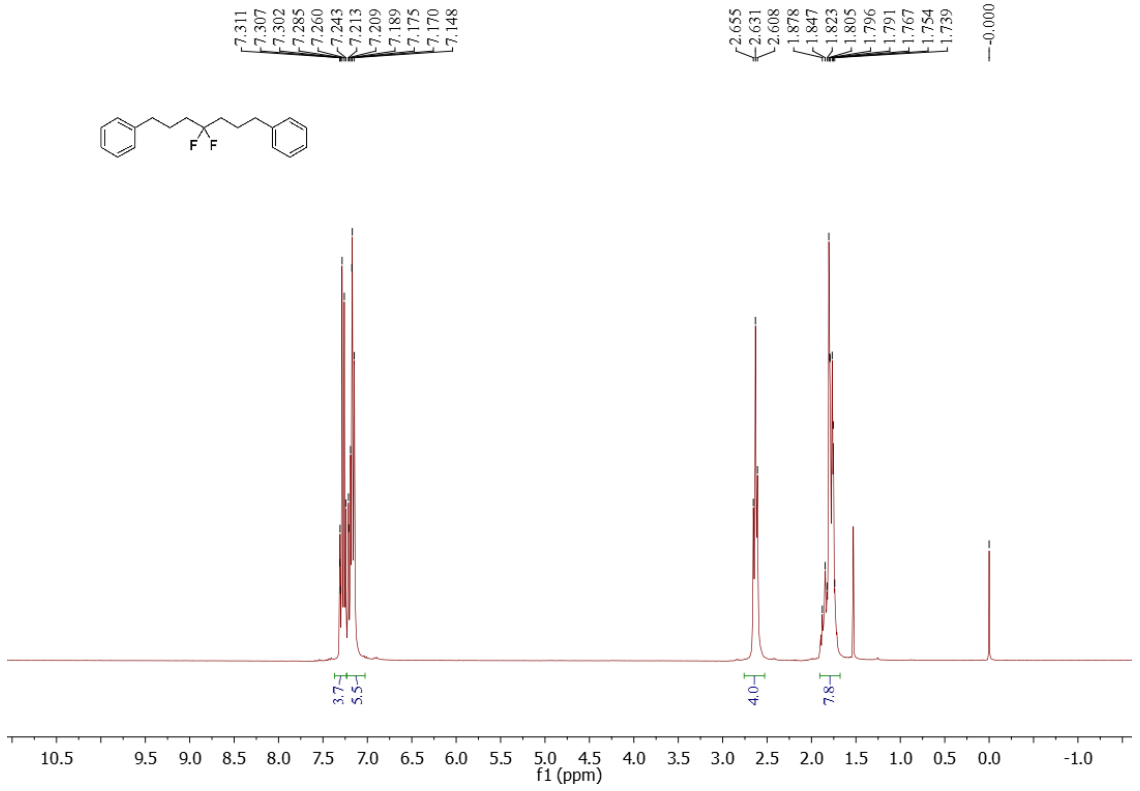


Figure S175. ^{13}C NMR spectrum of unknown *gem*-difluoride **1s**, related to **Figure 2**

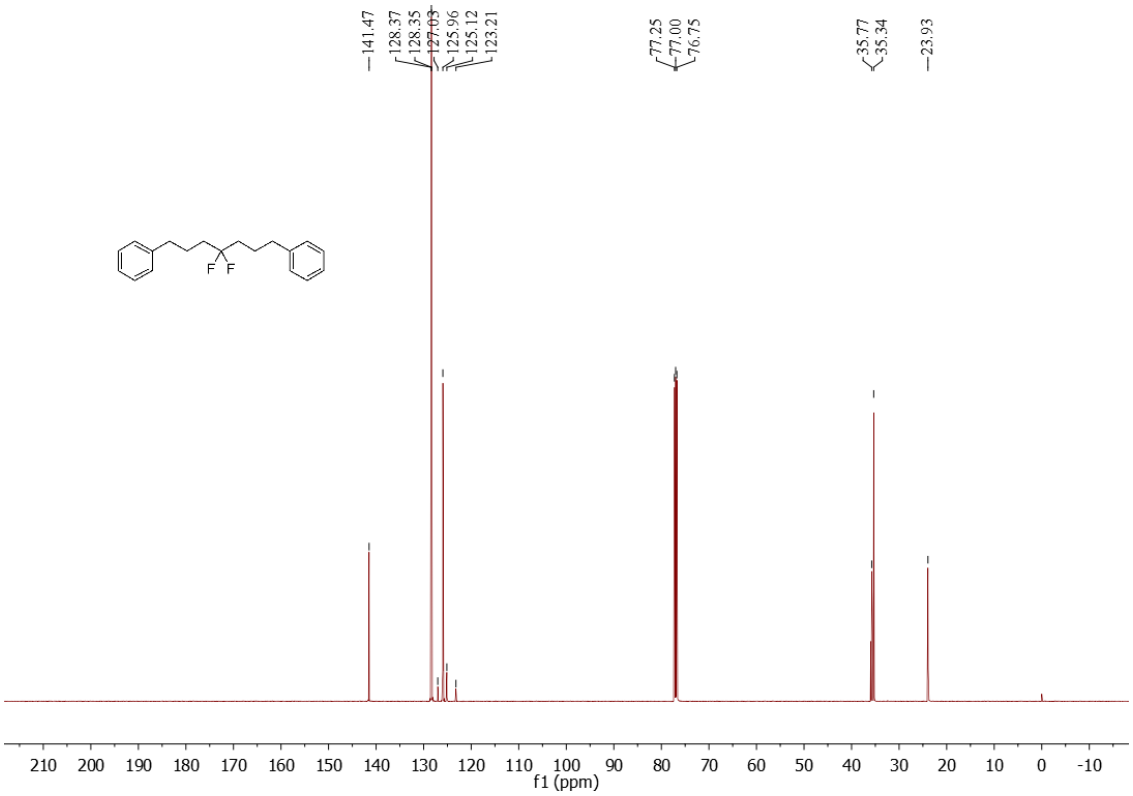


Figure S176. ^{19}F NMR spectrum of unknown *gem*-difluoride **1s**, related to **Figure 2**

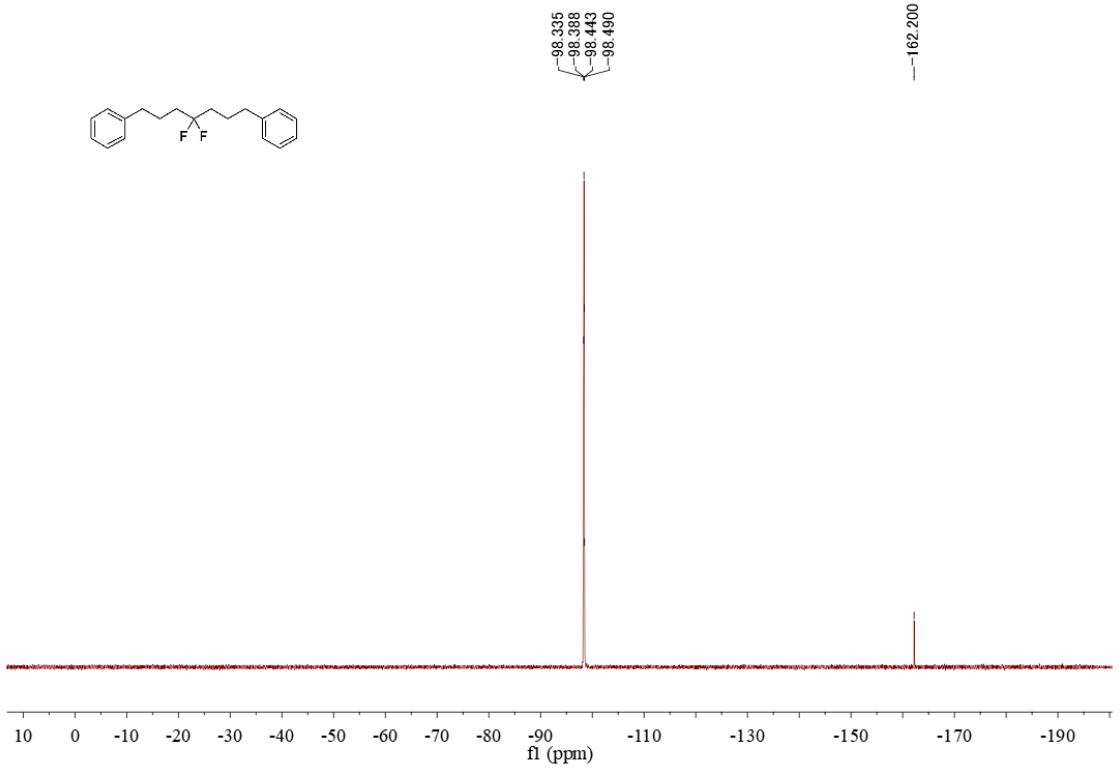


Figure S177. ^{1}H NMR spectrum of unknown *gem*-difluoride **1t**, related to **Figure 2**

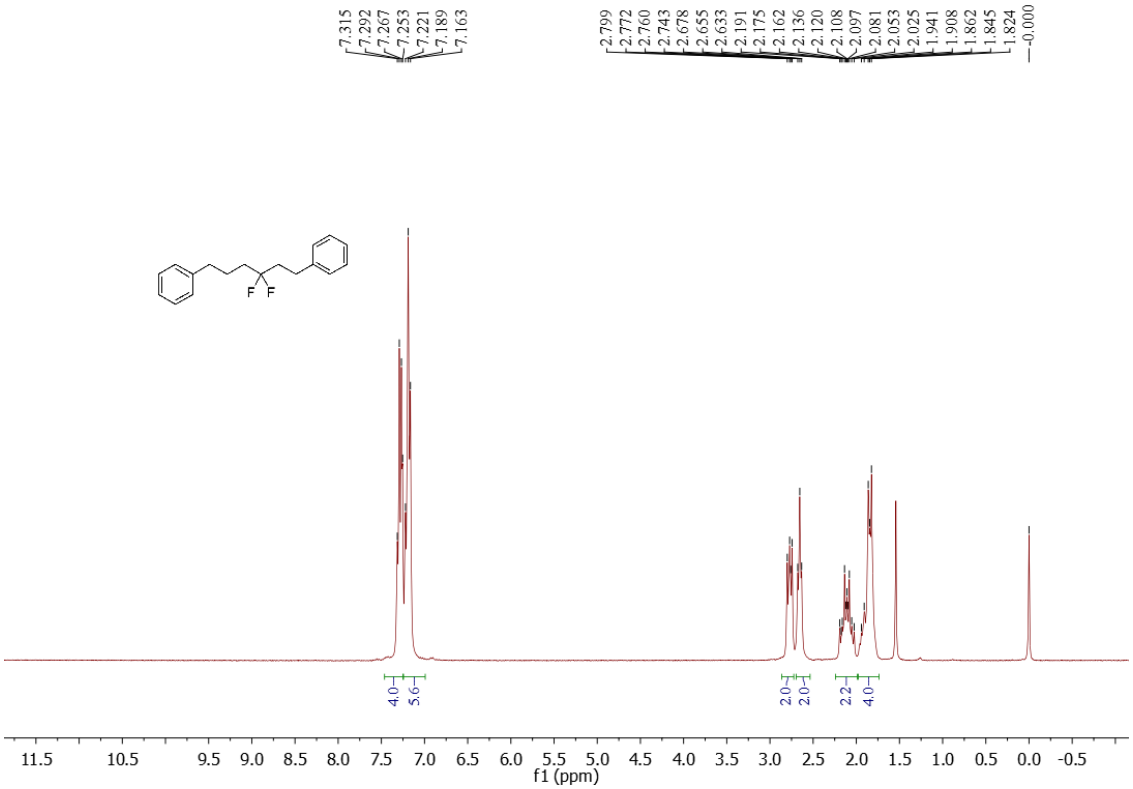


Figure S178. ^{13}C NMR spectrum of unknown *gem*-difluoride **1t**, related to **Figure 2**

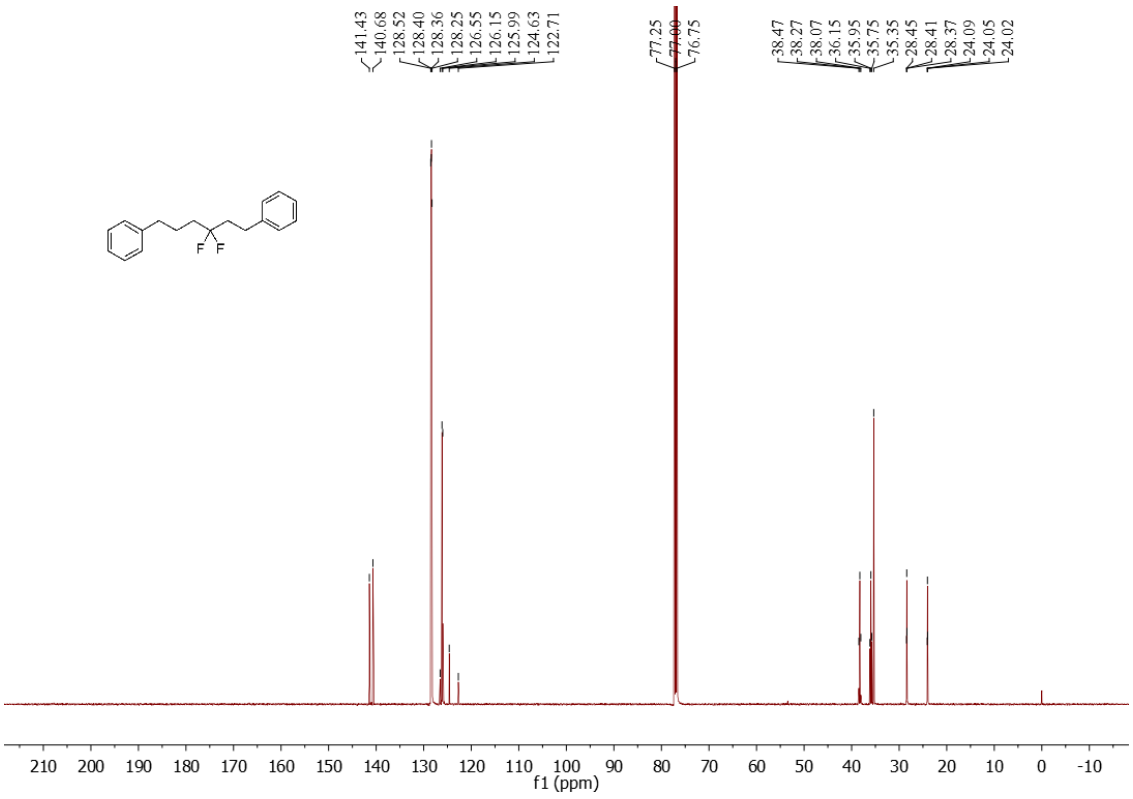


Figure S179. ^{19}F NMR spectrum of unknown *gem*-difluoride **1t**, related to **Figure 2**

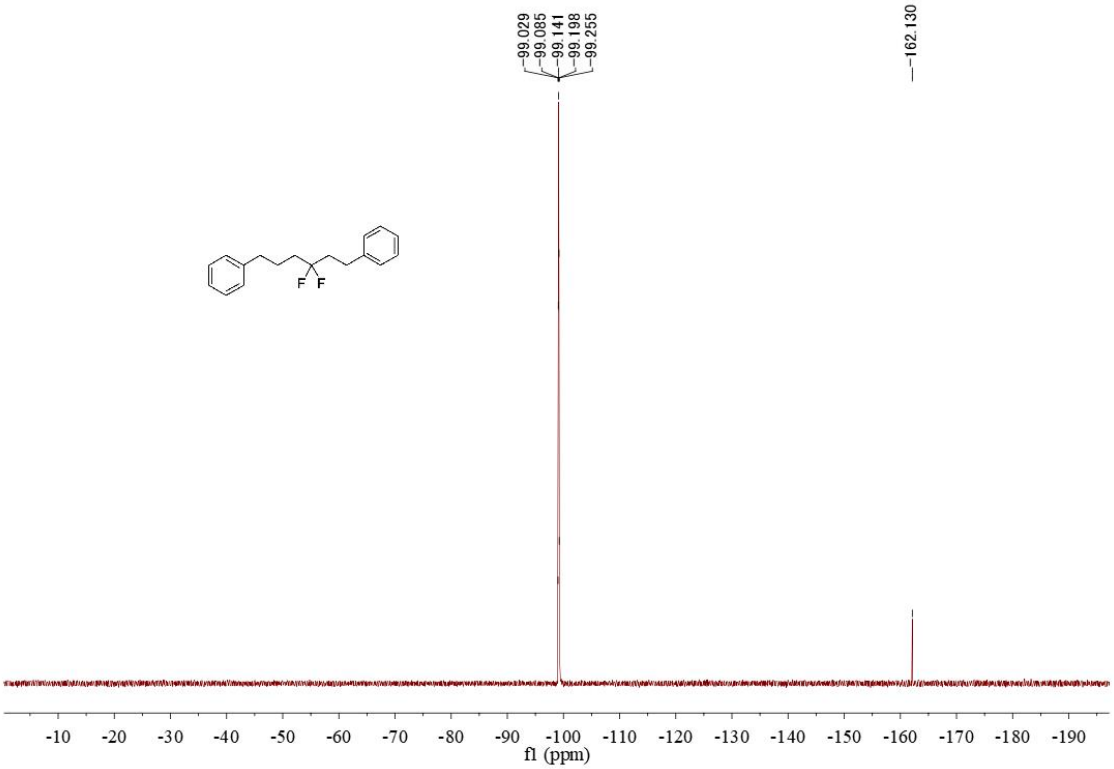


Figure S180. ^{1}H NMR spectrum of unknown *gem*-difluoride **1u**, related to **Figure 2**

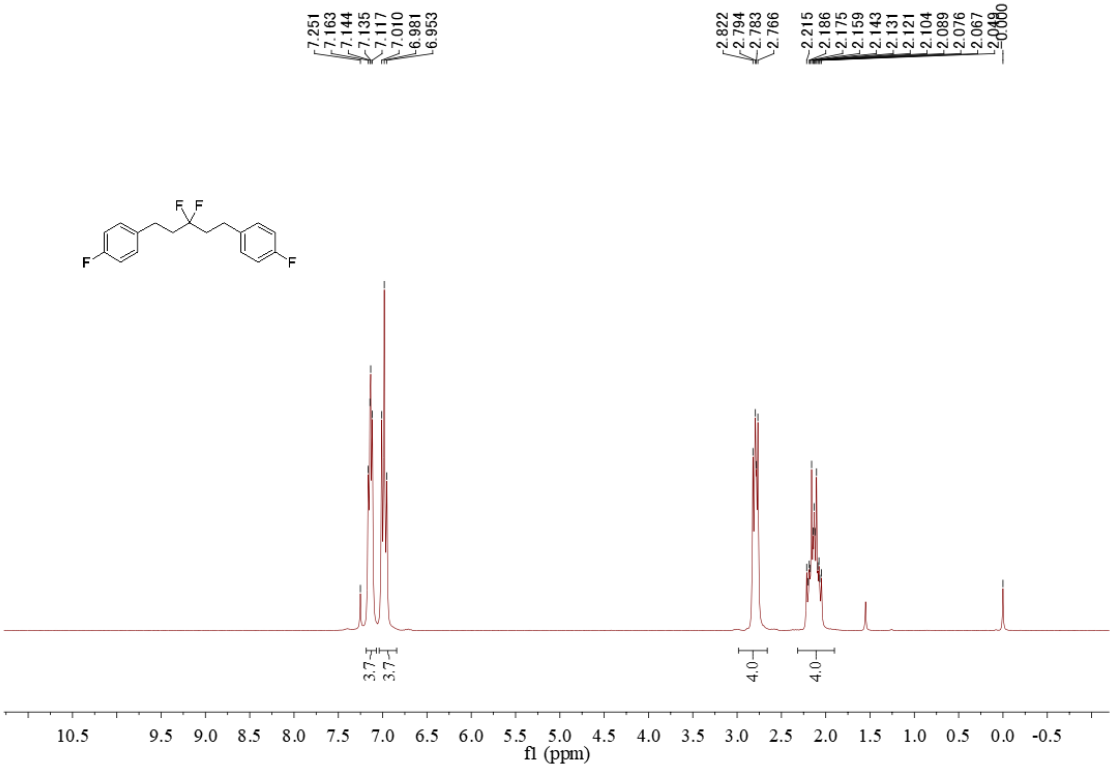


Figure S181. ^{13}C NMR spectrum of unknown *gem*-difluoride **1u**, related to **Figure 2**

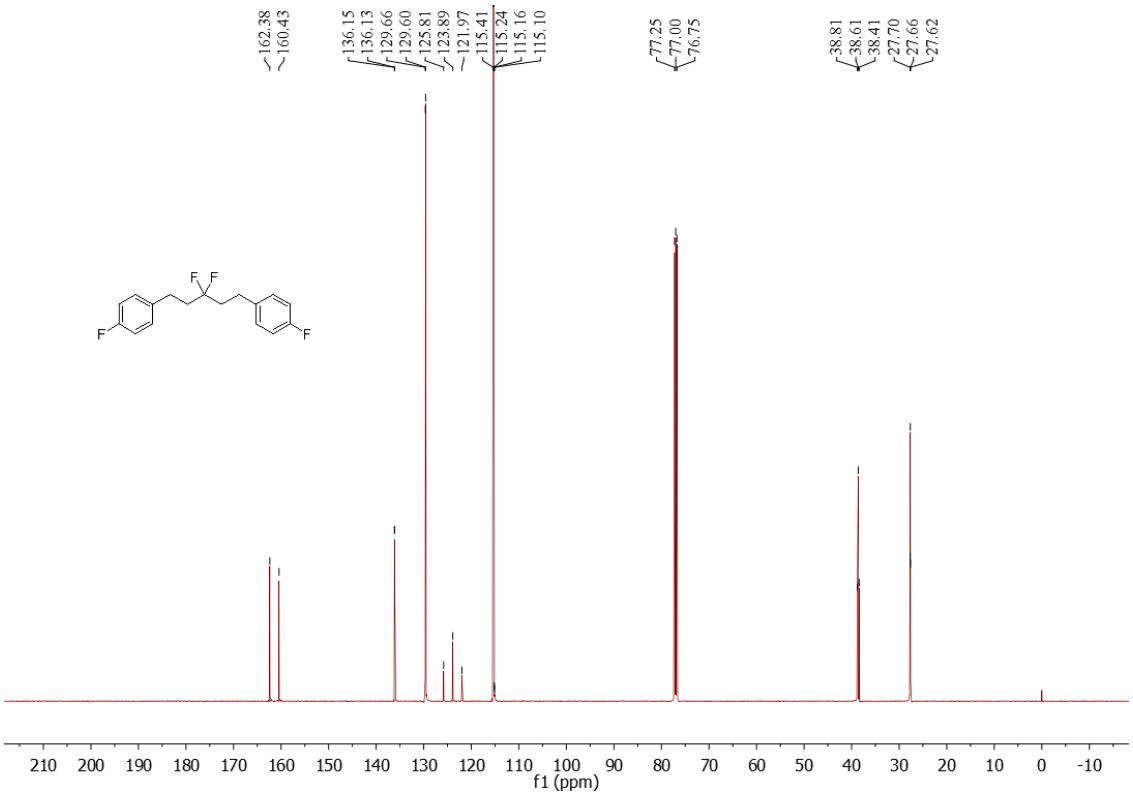


Figure S182. ^{19}F NMR spectrum of unknown *gem*-difluoride **1u**, related to **Figure 2**

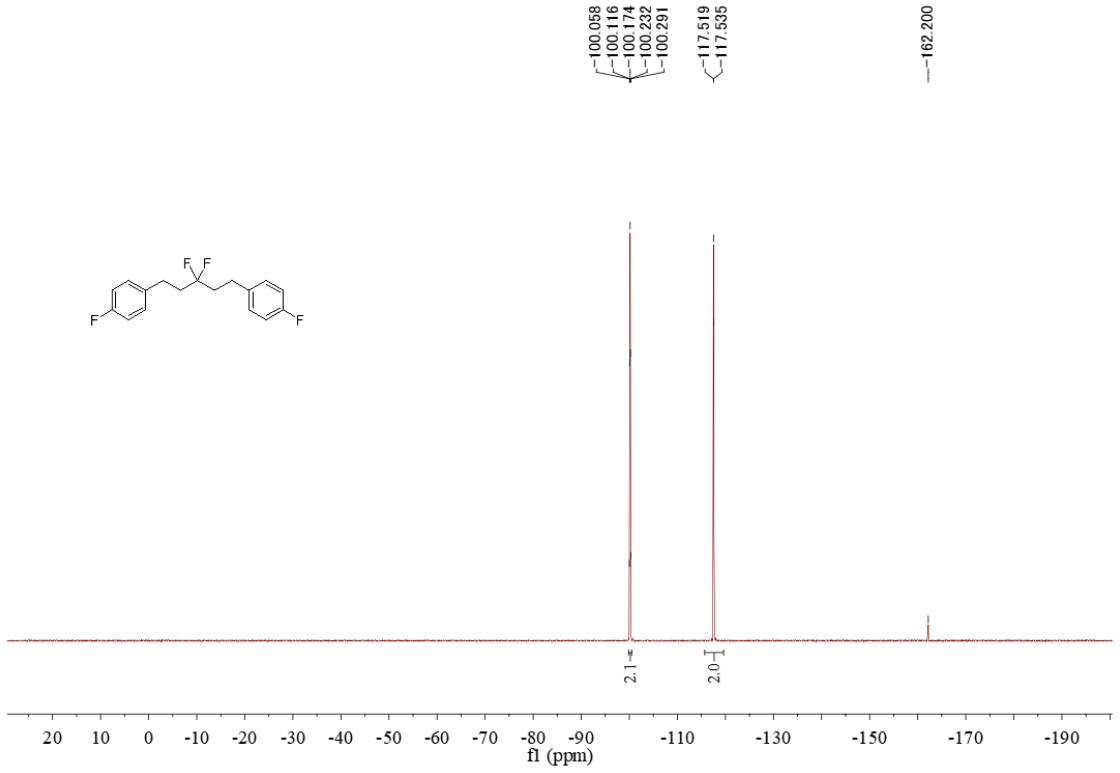


Figure S183. ^{1}H NMR spectrum of unknown *gem*-difluoride **1cc**, related to **Figure 2**

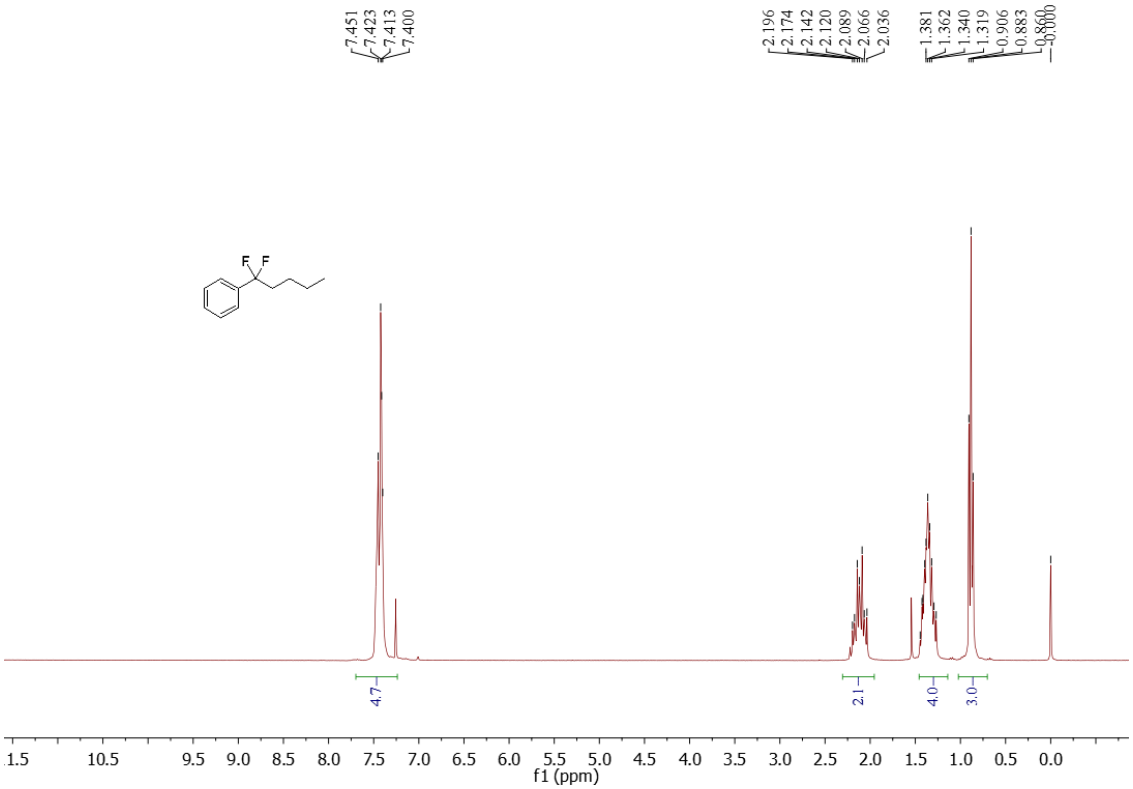


Figure S184. ^{13}C NMR spectrum of unknown *gem*-difluoride **1cc**, related to **Figure 2**

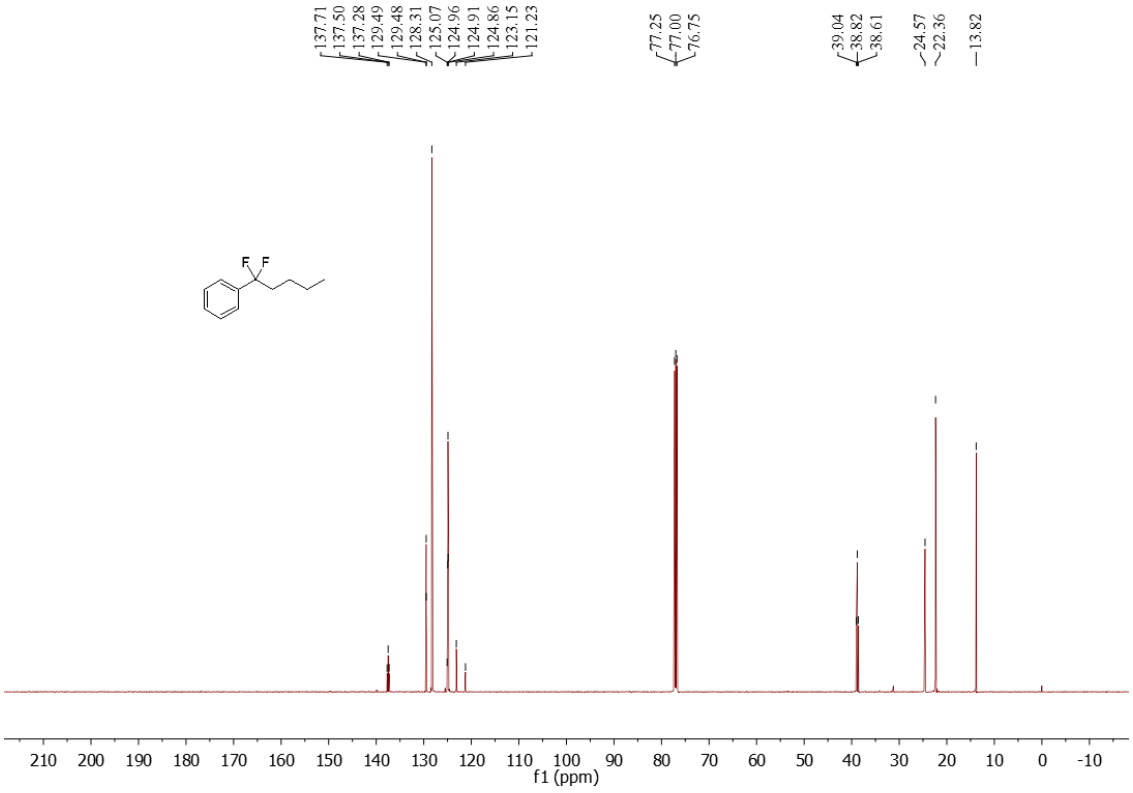


Figure S185. ^{19}F NMR spectrum of unknown *gem*-difluoride **1cc**, related to **Figure 2**

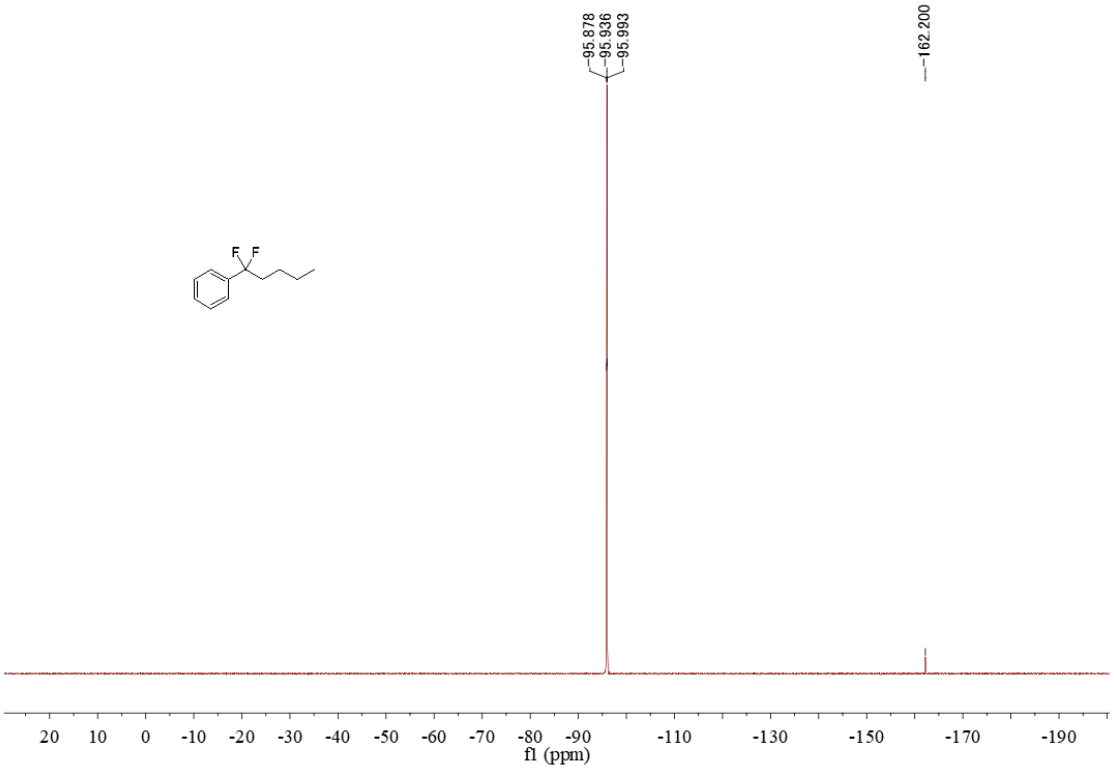


Figure S186. ^{1}H NMR spectrum of unknown *gem*-difluoride **1ee**, related to **Figure 2**

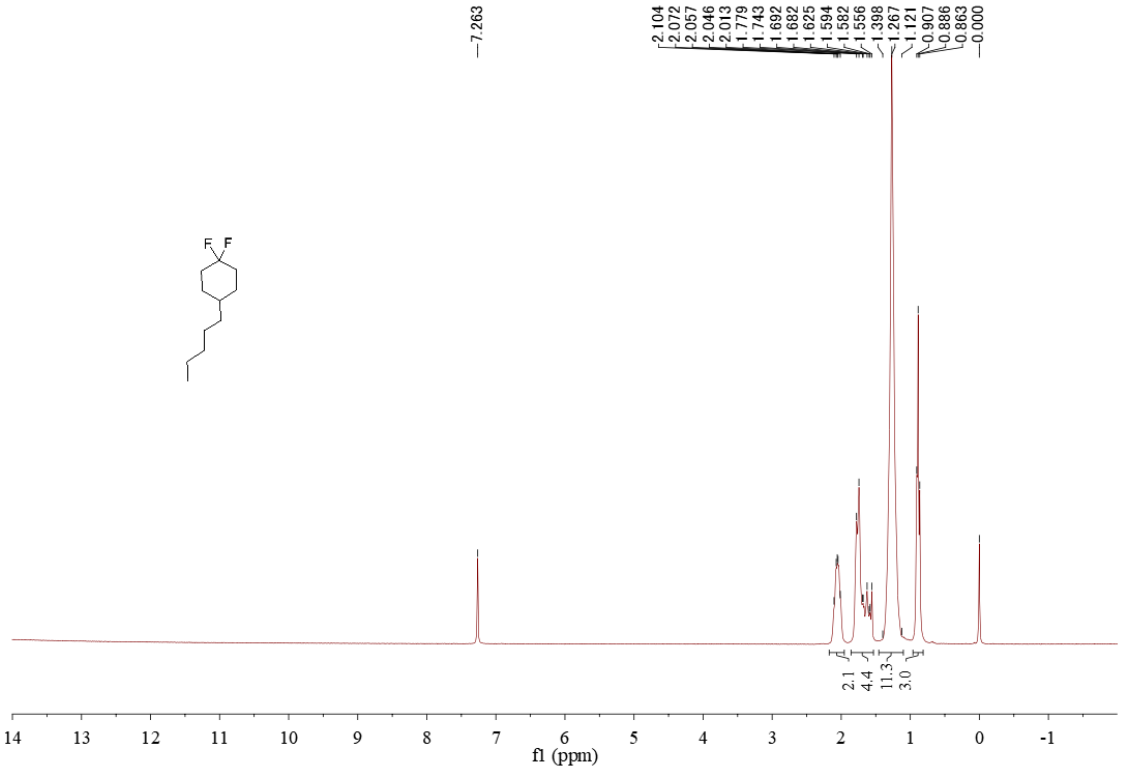


Figure S187. ^{13}C NMR spectrum of unknown *gem*-difluoride **1ee**, related to **Figure 2**

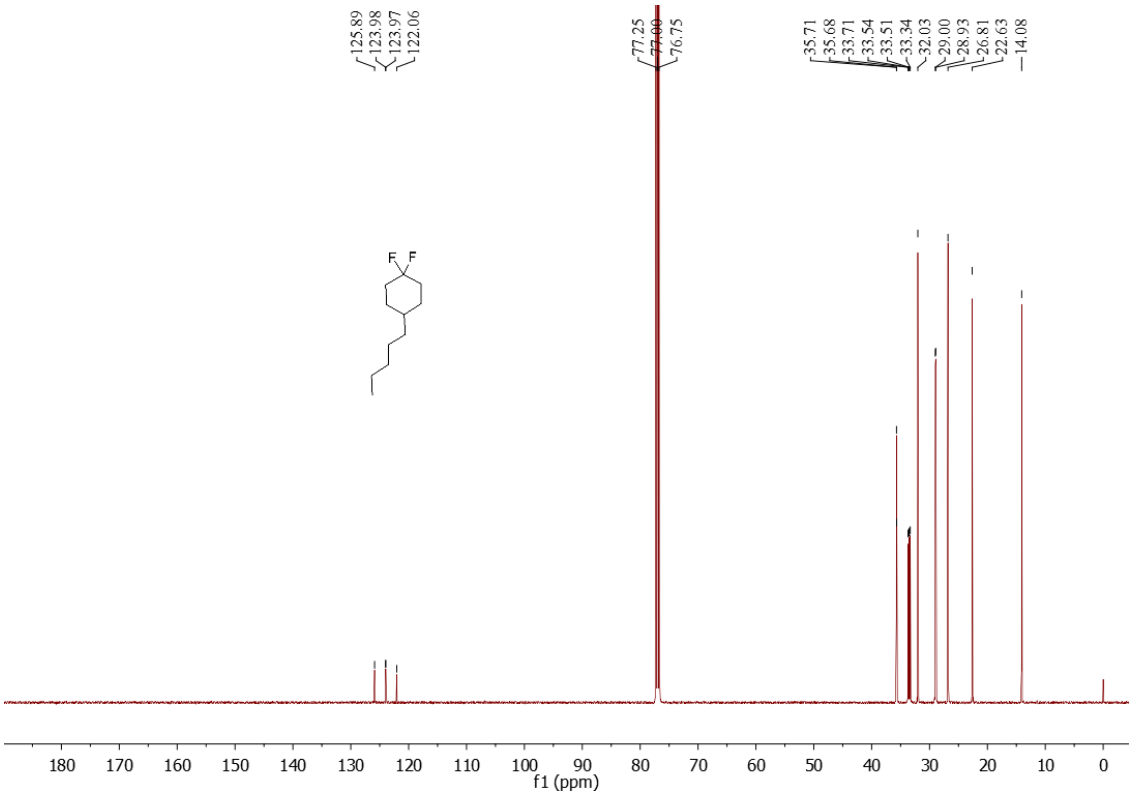


Figure S188. ^{19}F NMR spectrum of unknown *gem*-difluoride **1ee**, related to **Figure 2**

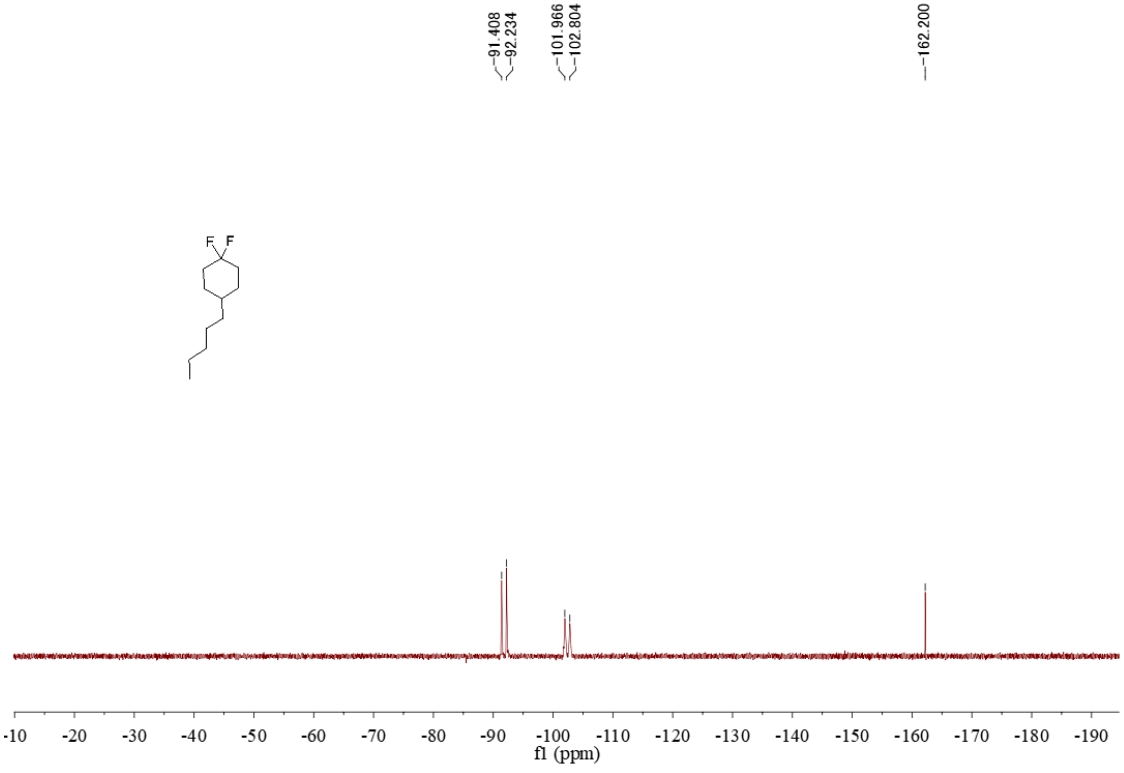


Figure S189. ^{1}H NMR spectrum of unknown *gem*-difluoride **1hh**, related to **Figure 2**

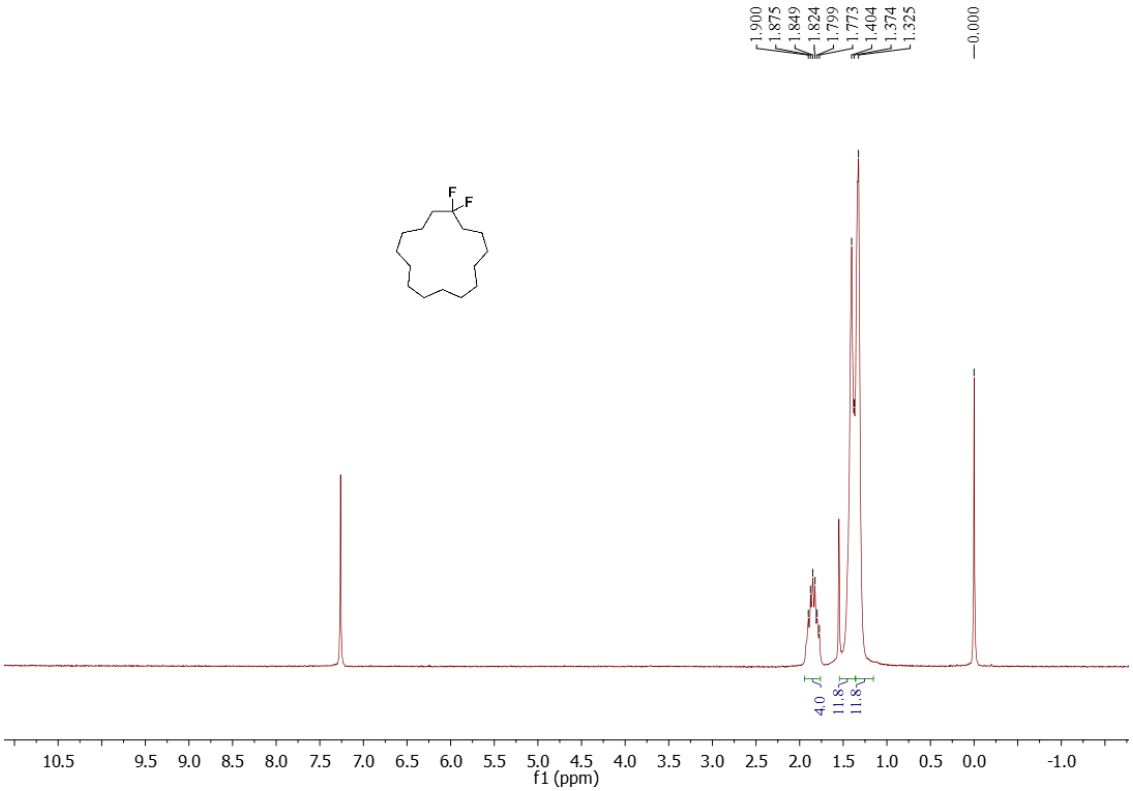


Figure S190. ^{13}C NMR spectrum of unknown *gem*-difluoride **1hh**, related to **Figure 2**

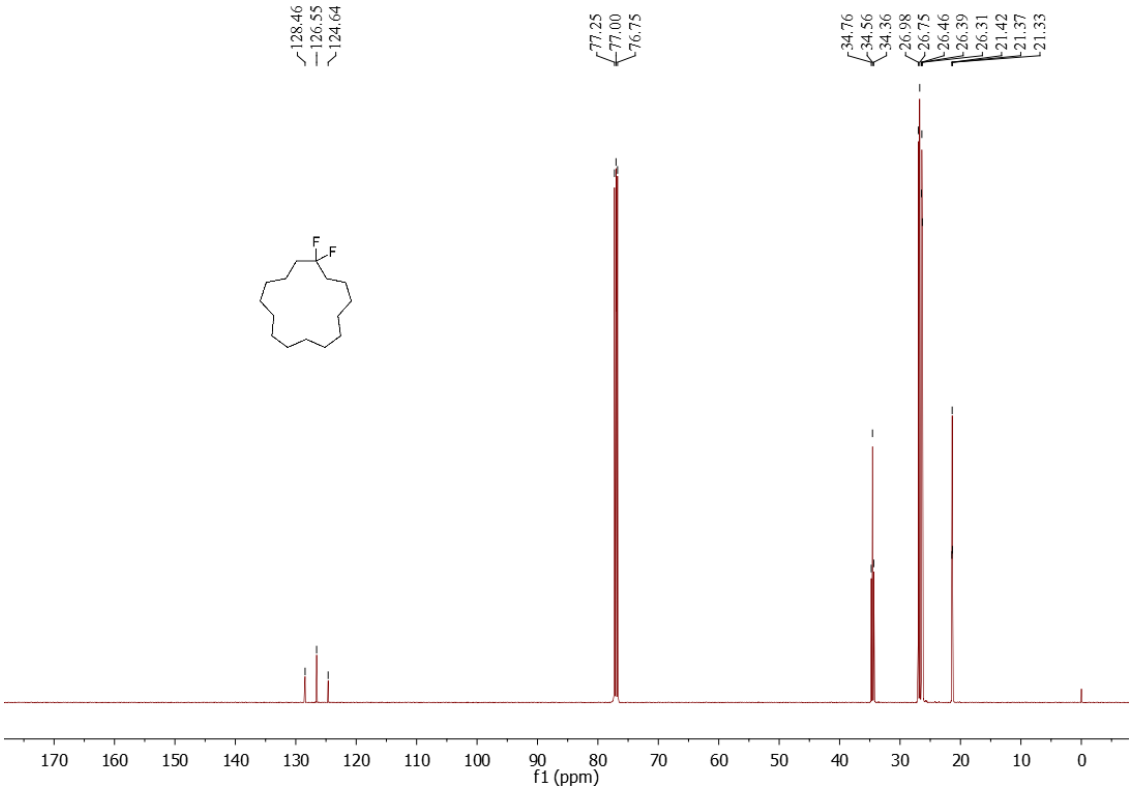


Figure S191. ^{19}F NMR spectrum of unknown *gem*-difluoride **1hh**, related to **Figure 2**

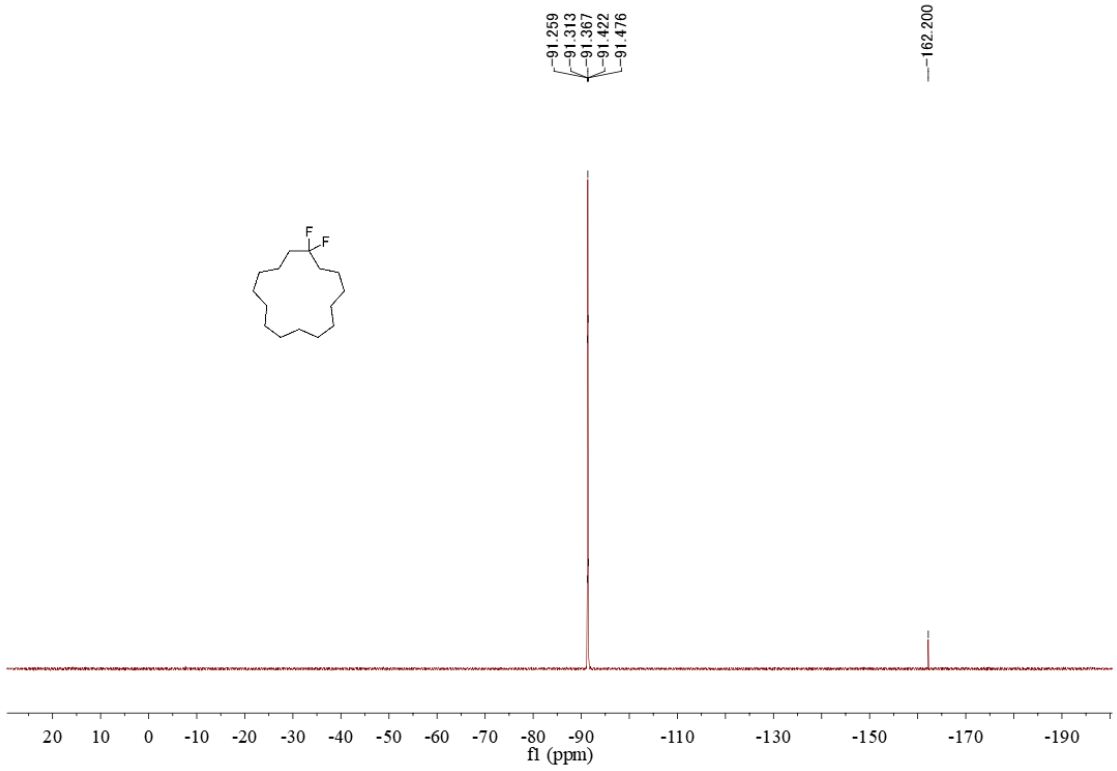


Figure S192. ^{1}H NMR spectrum of unknown secondary monofluoride **4a**, related to **Figure 3**

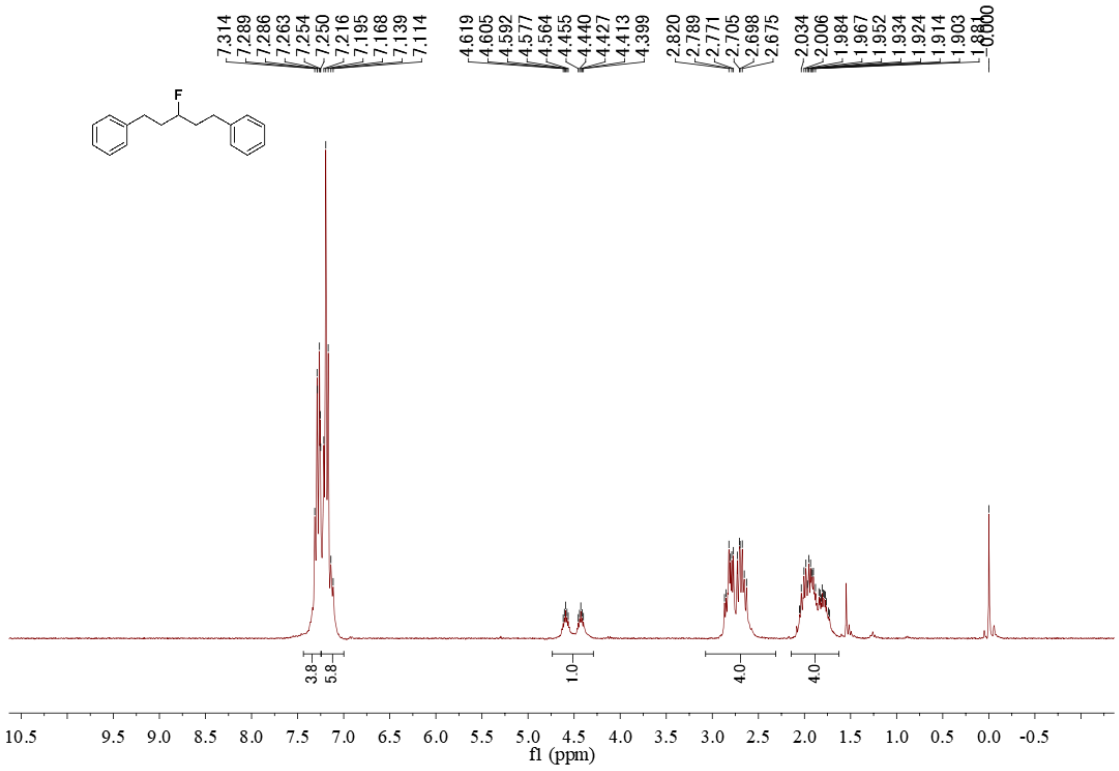


Figure S193. ^{13}C NMR spectrum of unknown secondary monofluoride **4a**, related to **Figure 3**

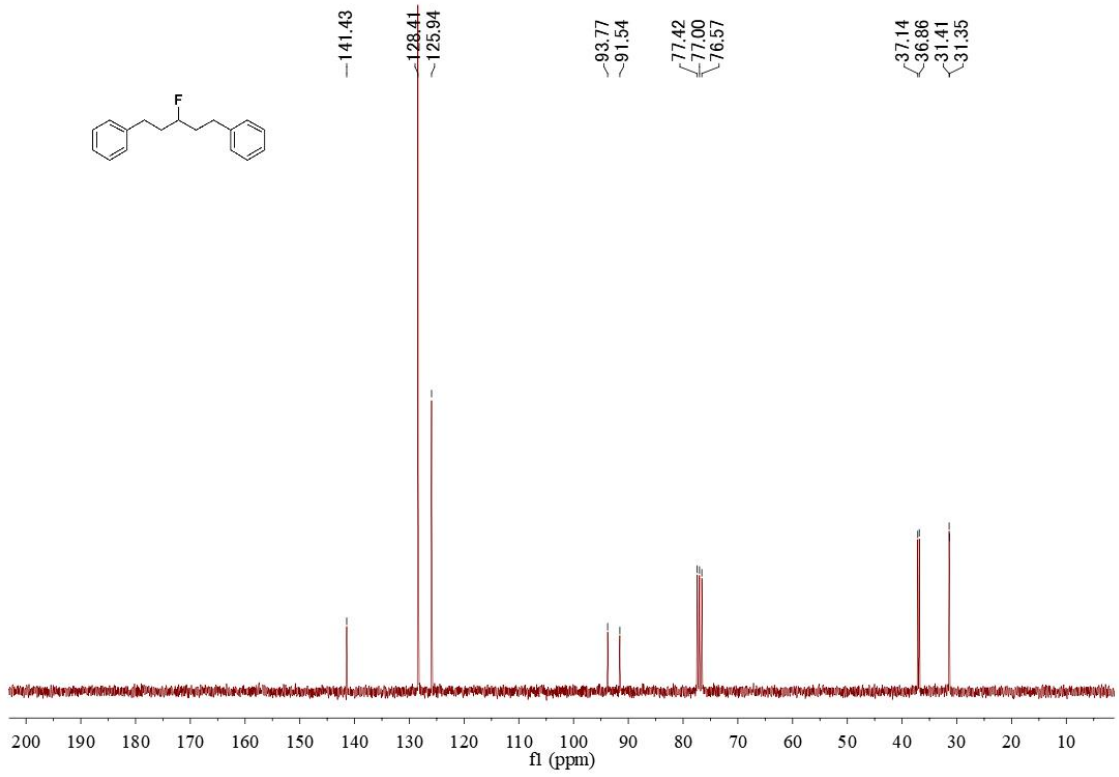


Figure S194. ^{19}F NMR spectrum of unknown secondary monofluoride **4a**, related to **Figure 3**

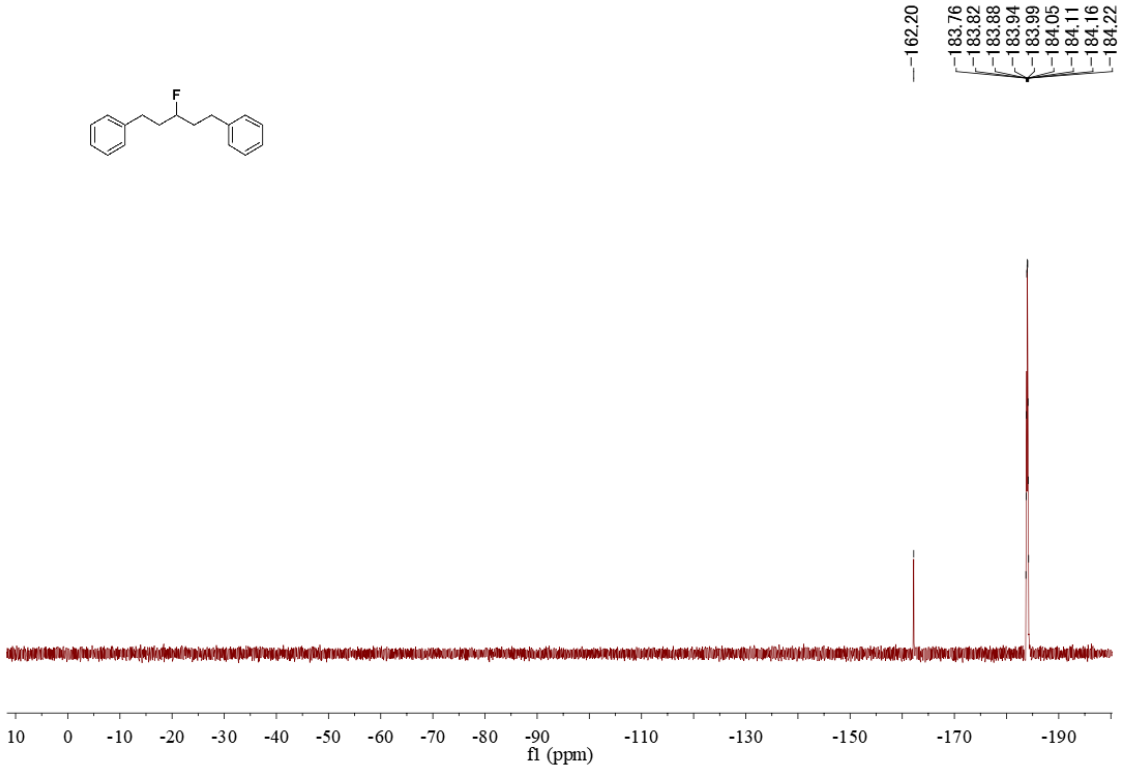


Figure S195. ^{1}H NMR spectrum of unknown secondary monofluoride **4b**, related to **Figure 3**

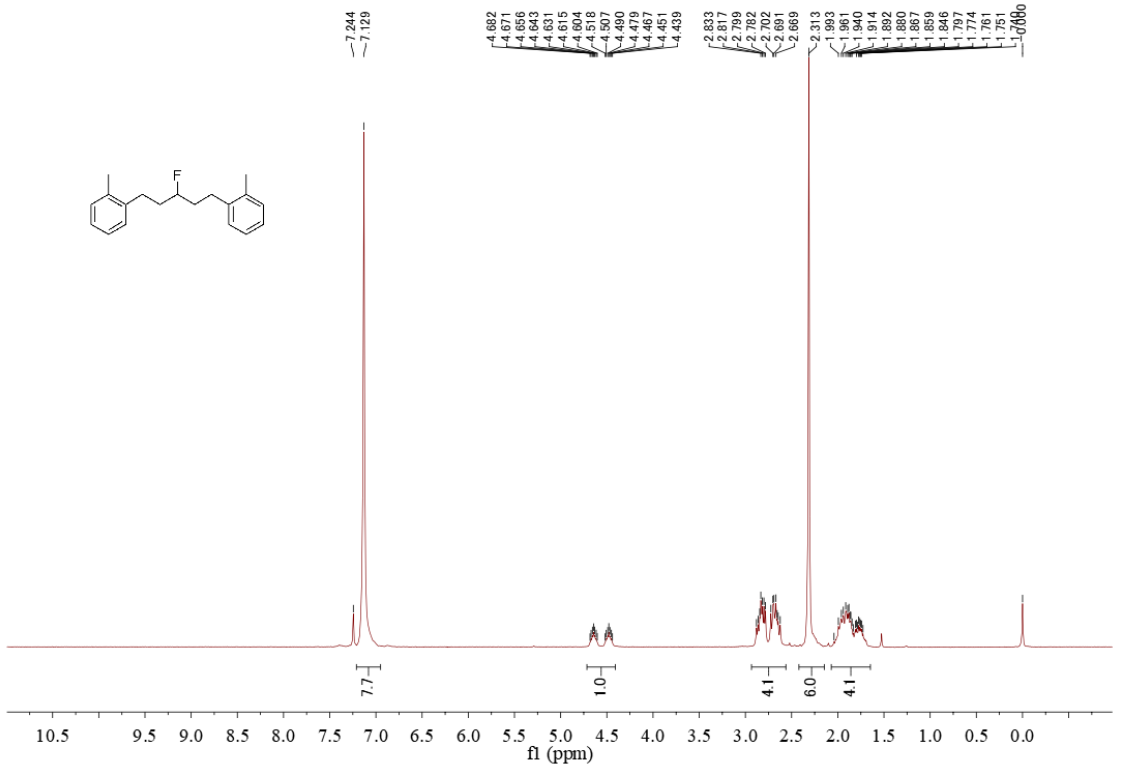


Figure S196. ^{13}C NMR spectrum of unknown secondary monofluoride **4b**, related to **Figure 3**

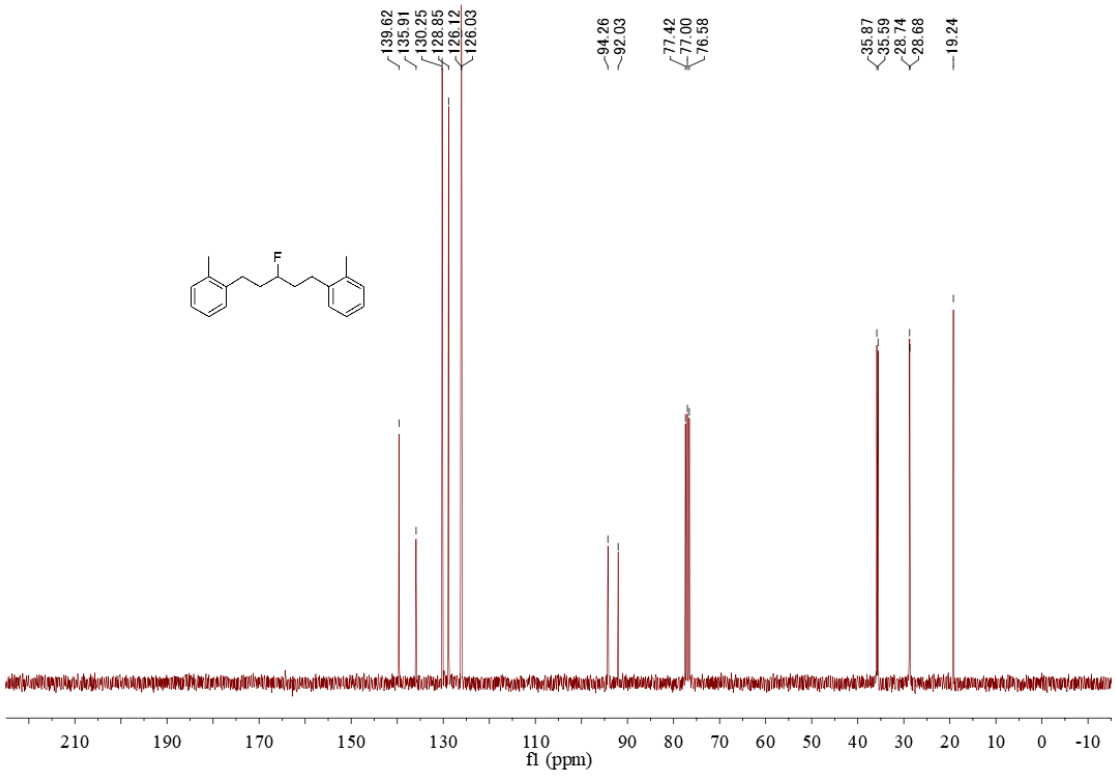


Figure S197. ^{19}F NMR spectrum of unknown secondary monofluoride **4b**, related to **Figure 3**

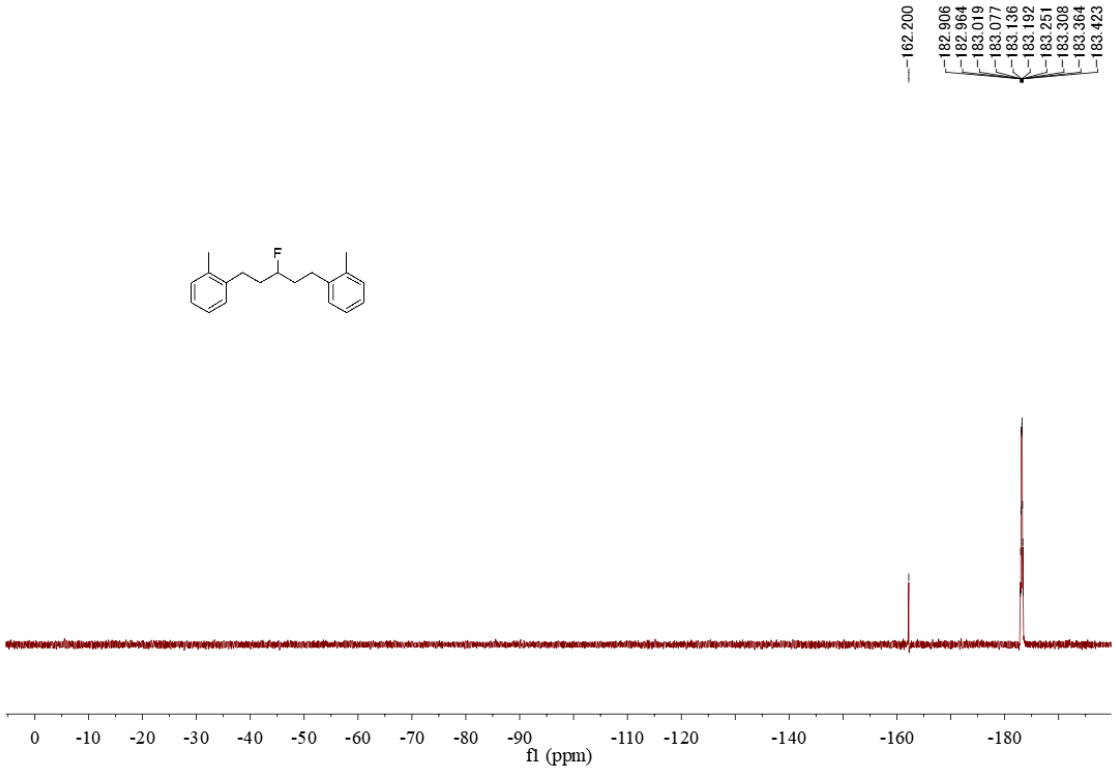


Figure S198. ^{1}H NMR spectrum of unknown secondary monofluoride **4c**, related to **Figure 3**

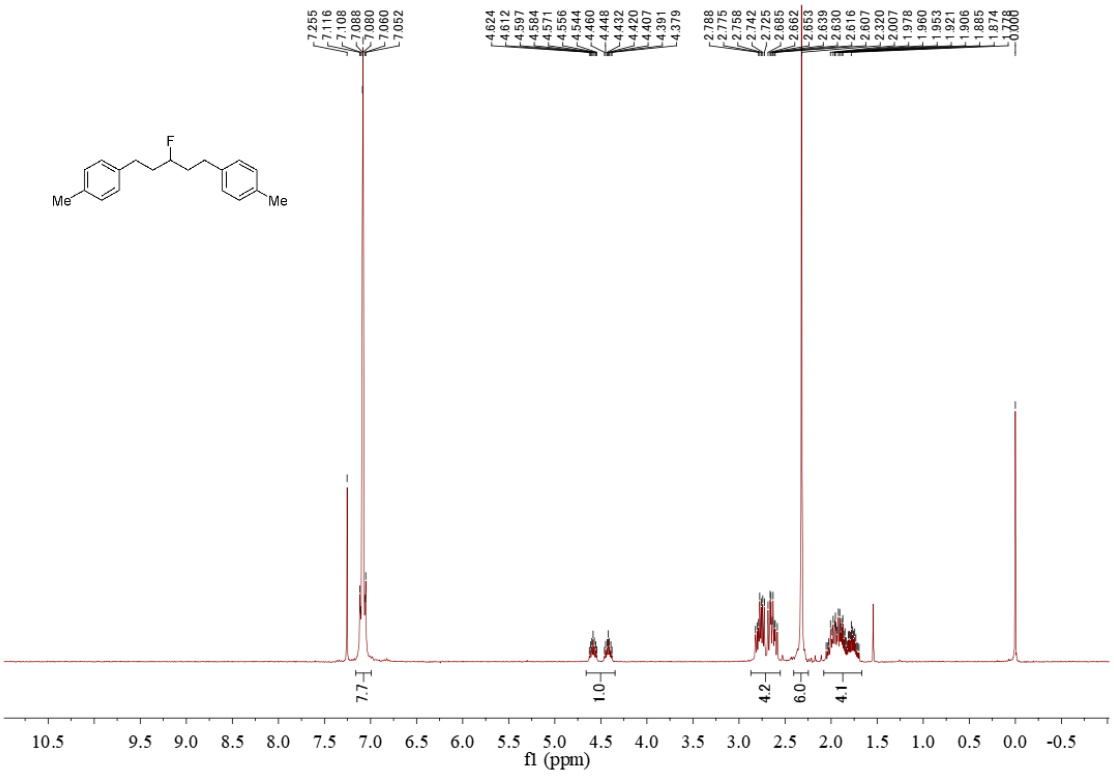


Figure S199. ^{13}C NMR spectrum of unknown secondary monofluoride **4c**, related to **Figure 3**

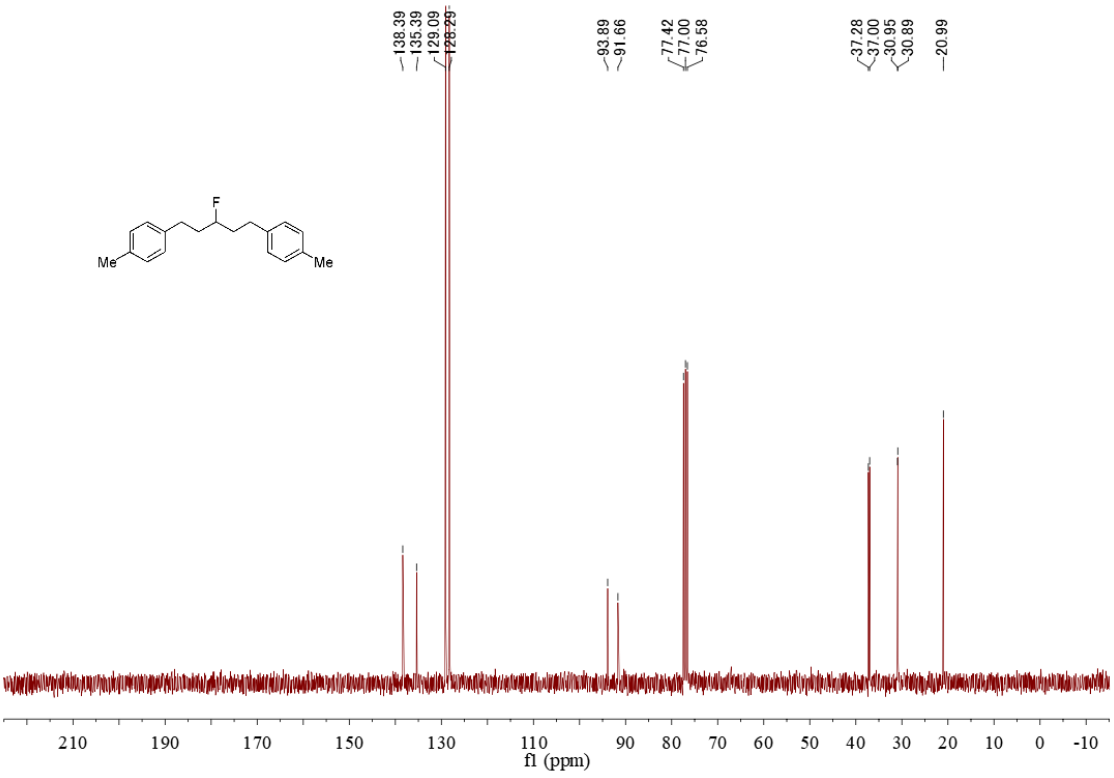


Figure S200. ^{19}F NMR spectrum of unknown secondary monofluoride **4c**, related to **Figure 3**

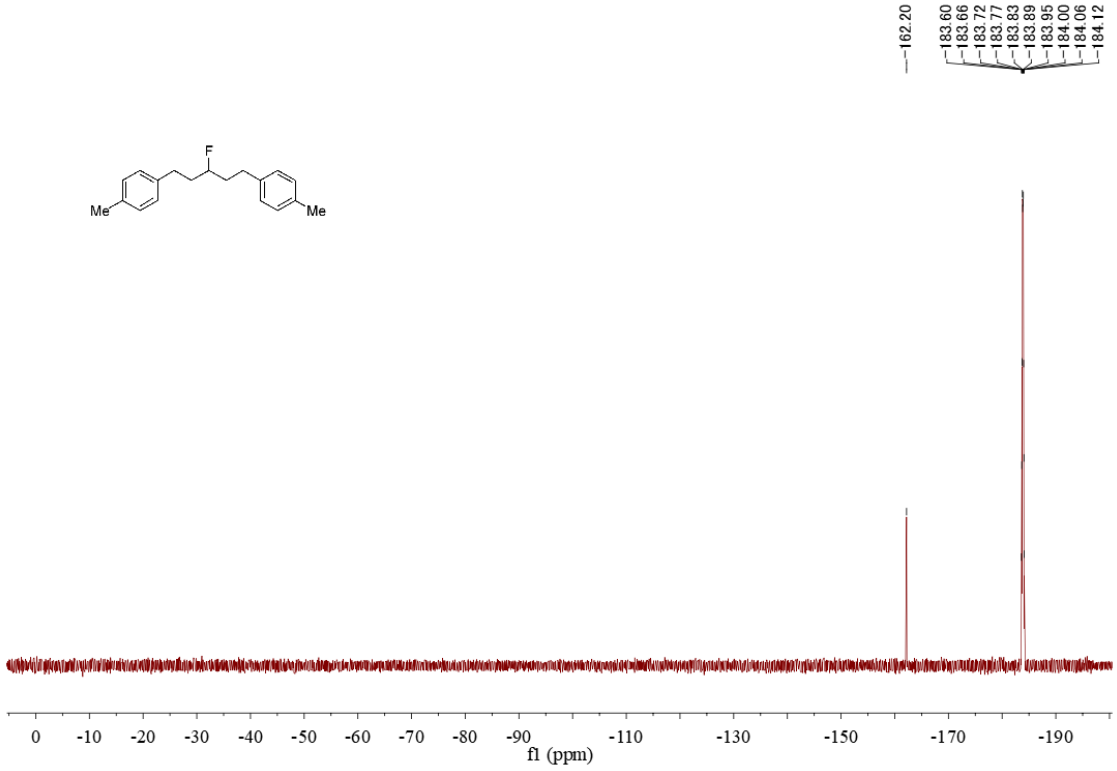


Figure S201. ^{1}H NMR spectrum of unknown secondary monofluoride **4d**, related to **Figure 3**

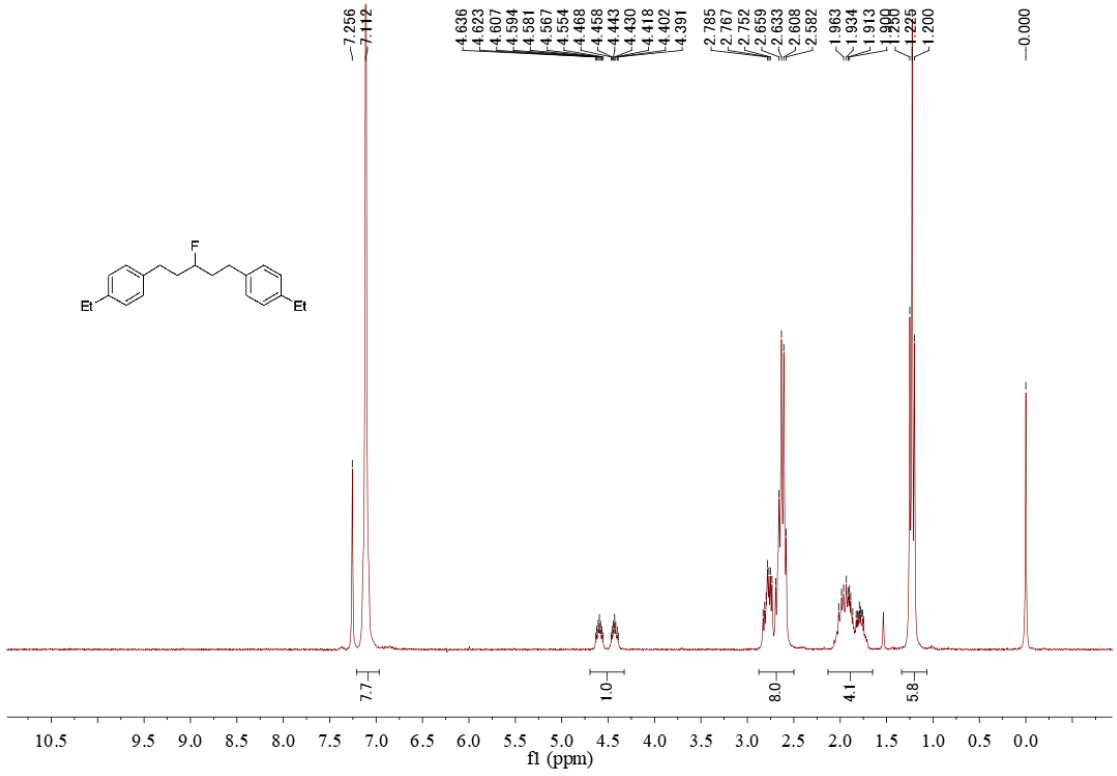


Figure S202. ^{13}C NMR spectrum of unknown secondary monofluoride **4d**, related to **Figure 3**

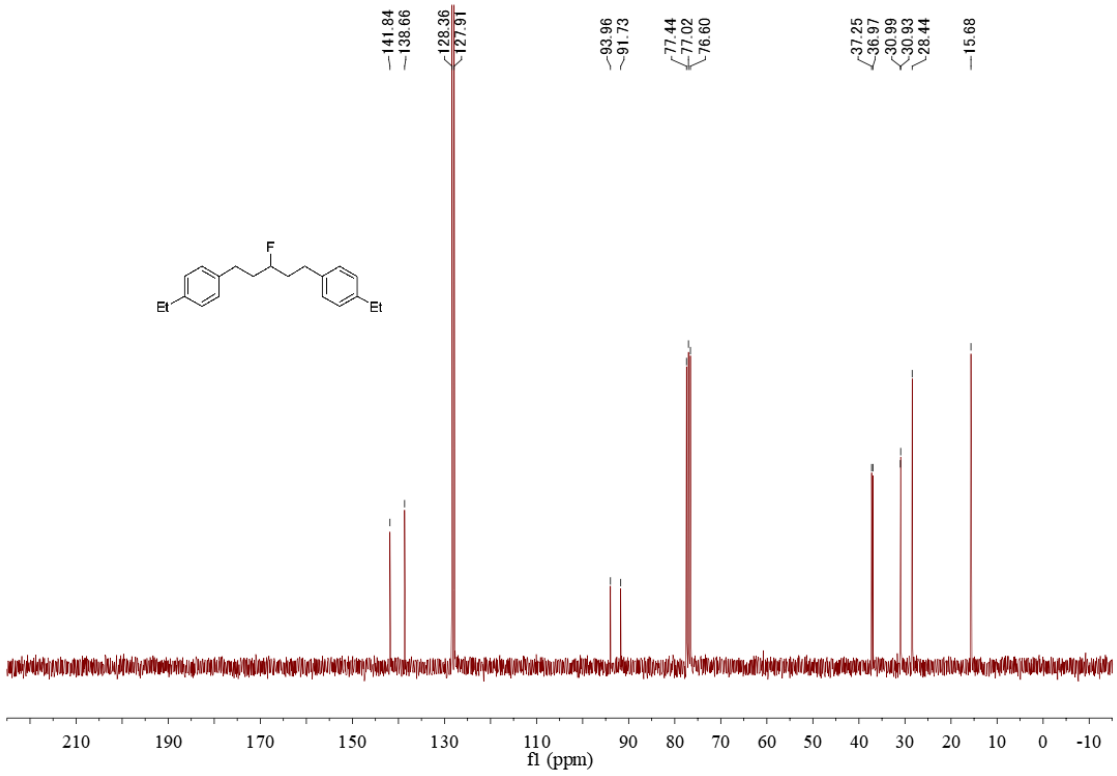


Figure S203. ^{19}F NMR spectrum of unknown secondary monofluoride **4d**, related to **Figure 3**

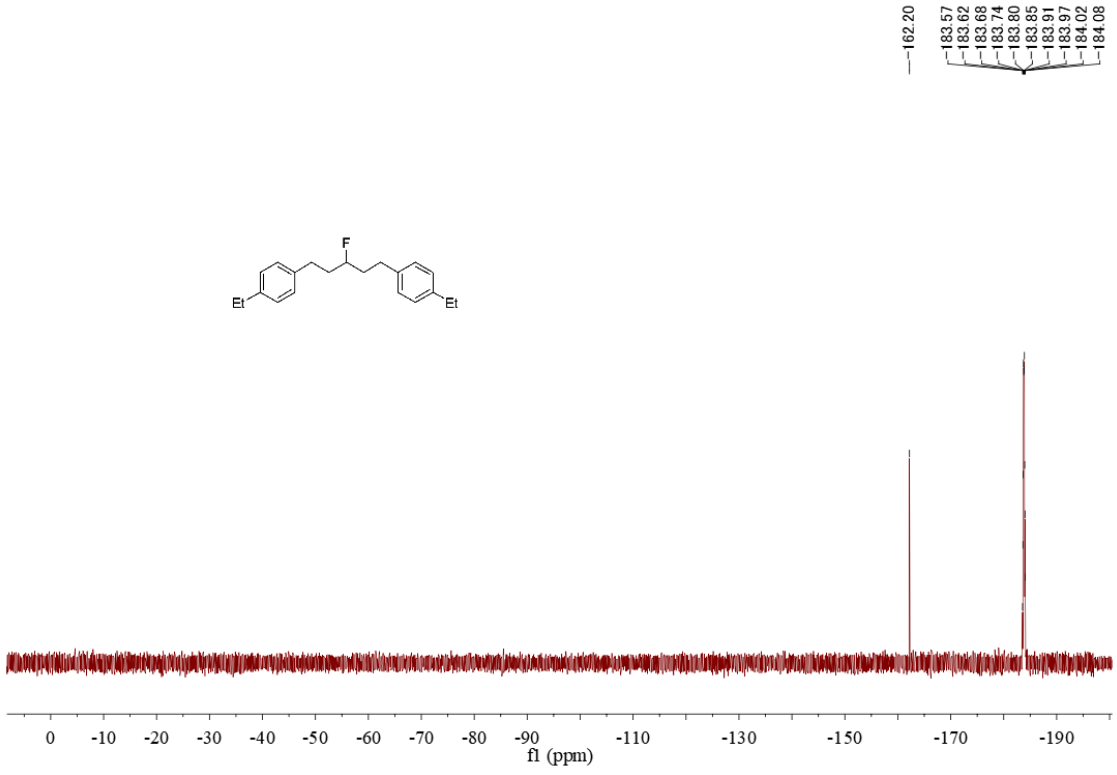


Figure S204. ^{1}H NMR spectrum of unknown secondary monofluoride **4e**, related to **Figure 3**

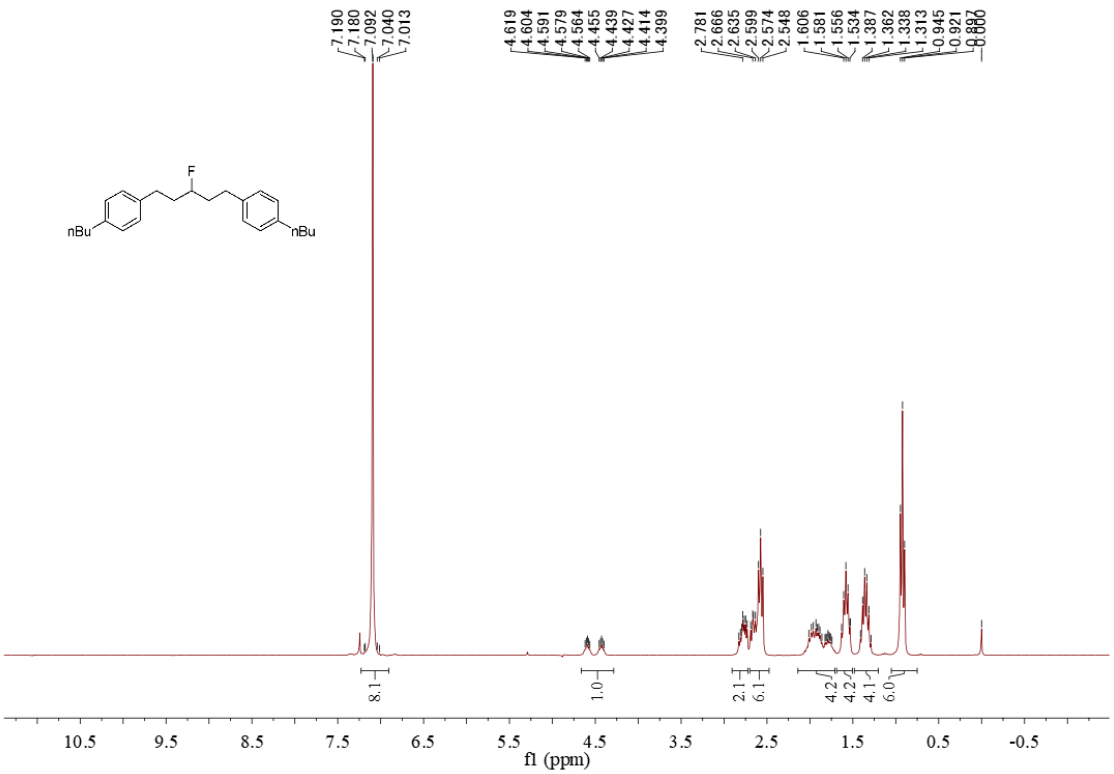


Figure S205. ^{13}C NMR spectrum of unknown secondary monofluoride **4e**, related to **Figure 3**

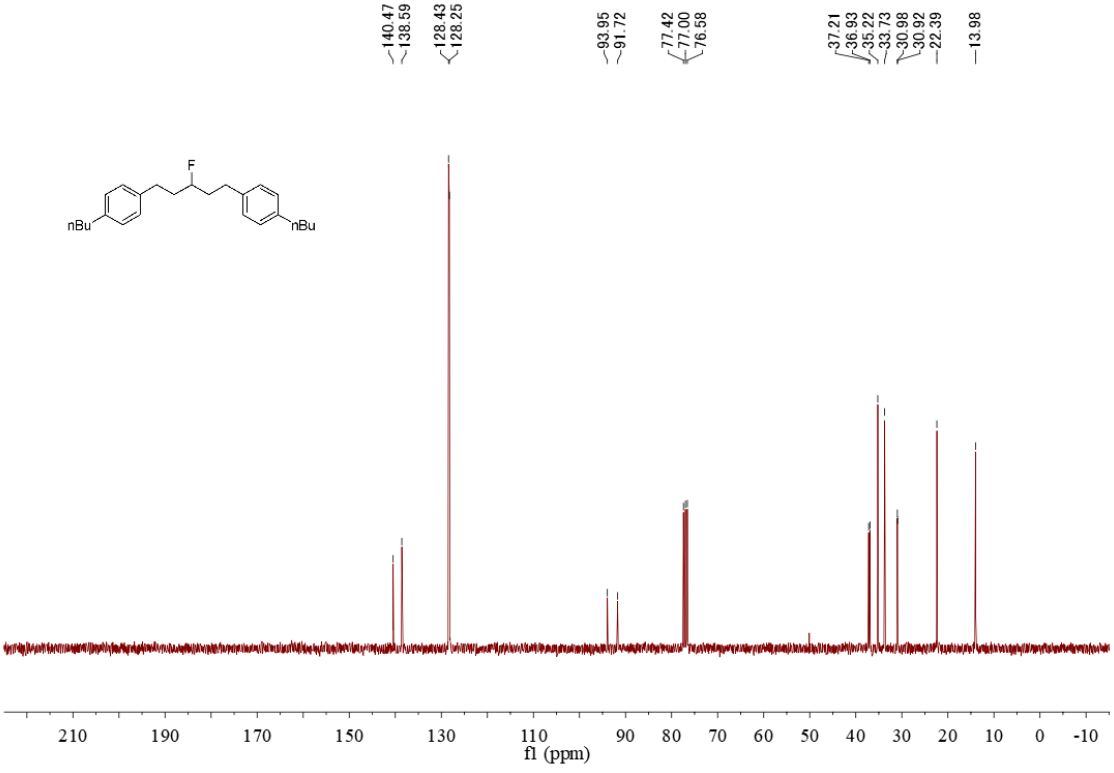


Figure S206 ^{19}F NMR spectrum of unknown secondary monofluoride **4e**, related to **Figure 3**

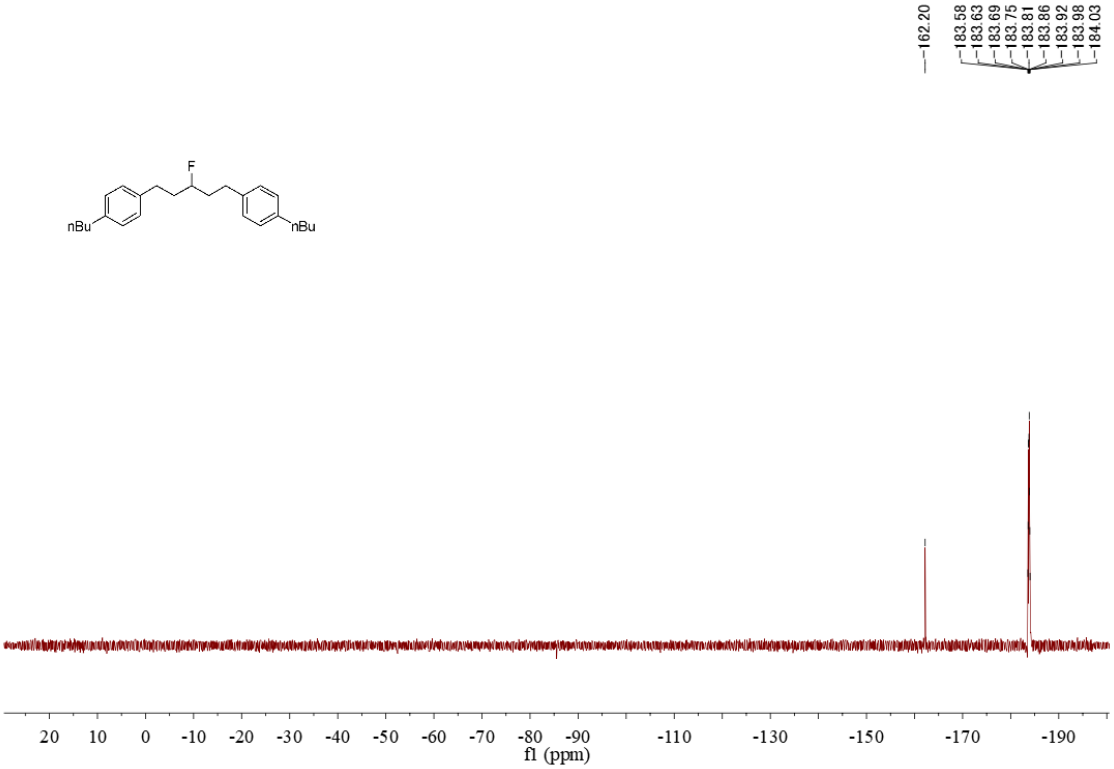


Figure S207. ^{1}H NMR spectrum of unknown secondary monofluoride **4f**, related to **Figure 3**

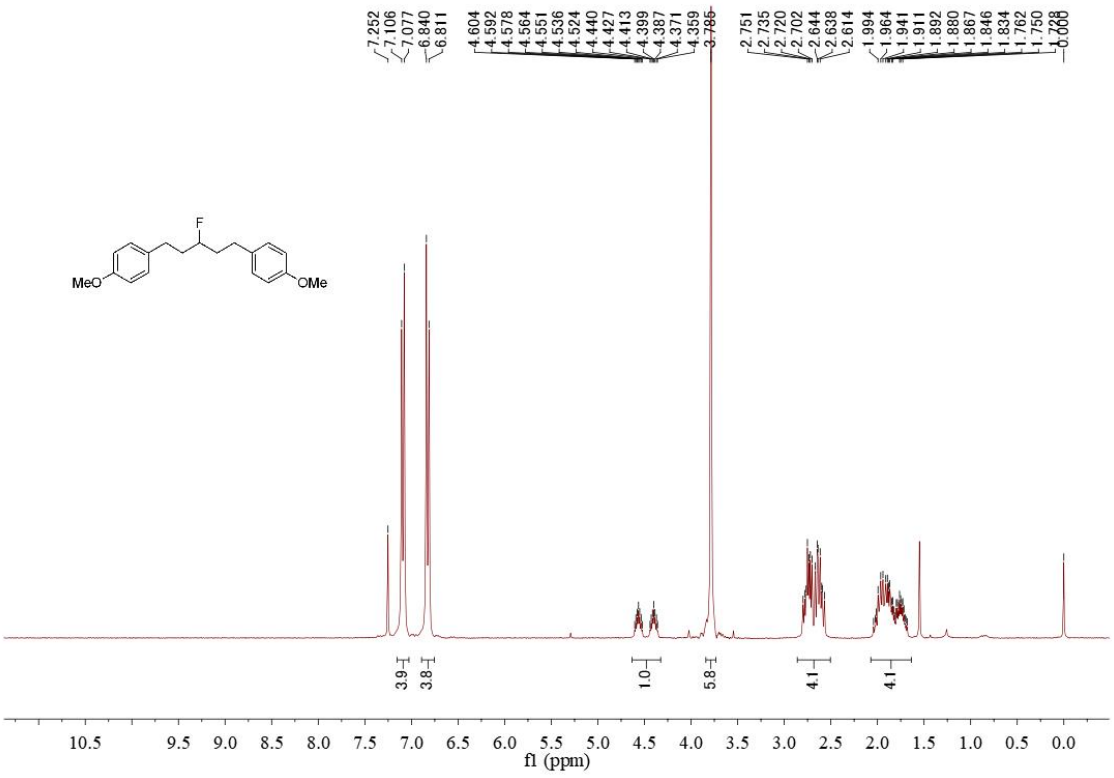


Figure S208. ^{13}C NMR spectrum of unknown secondary monofluoride **4f**, related to **Figure 3**

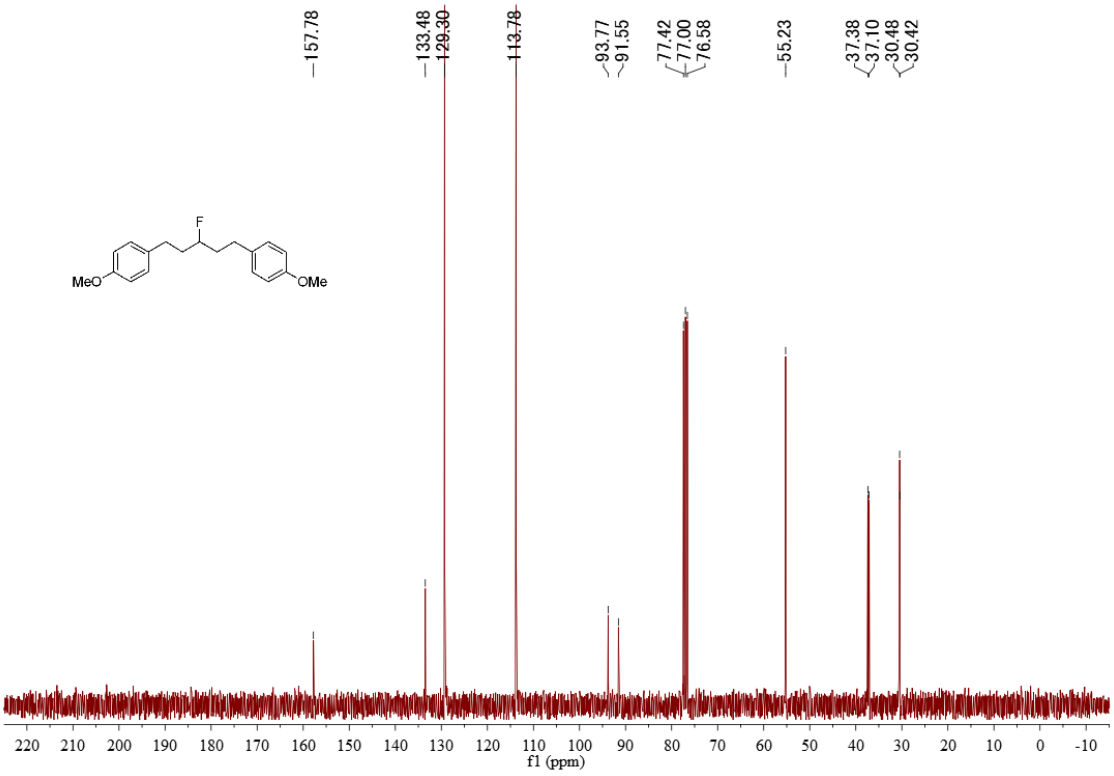


Figure S209. ^{19}F NMR spectrum of unknown secondary monofluoride **4f**, related to **Figure 3**

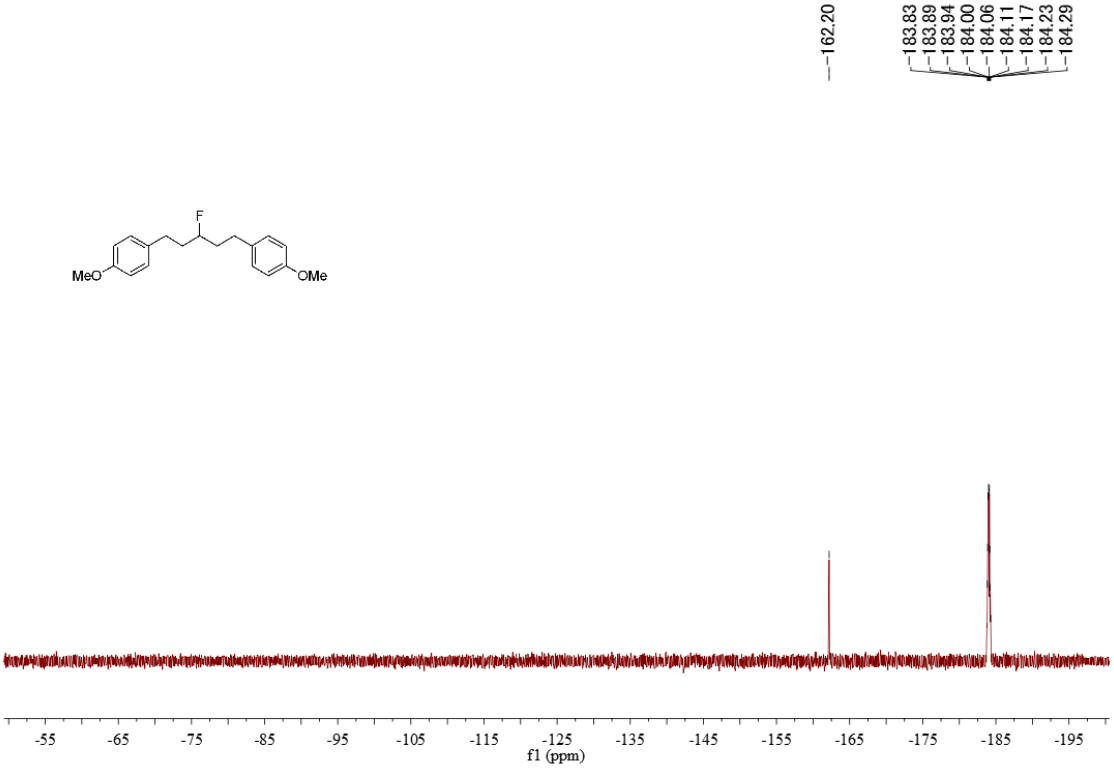


Figure S210. ^{1}H NMR spectrum of unknown secondary monofluoride **4g**, related to **Figure 3**

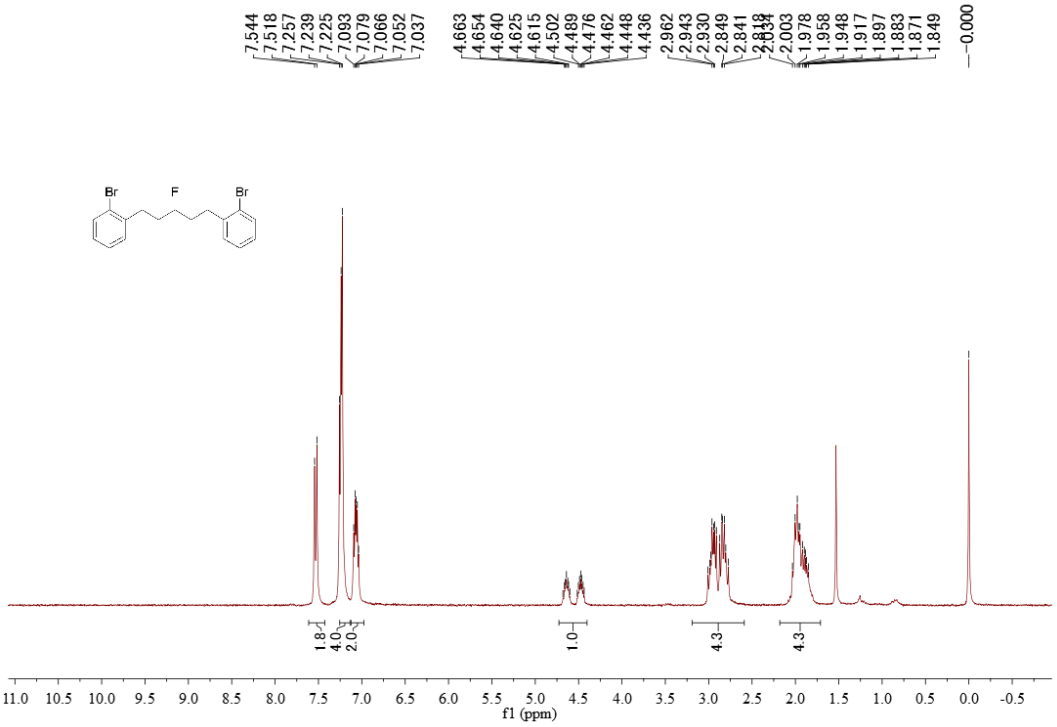


Figure S211. ^{13}C NMR spectrum of unknown secondary monofluoride **4g**, related to **Figure 3**

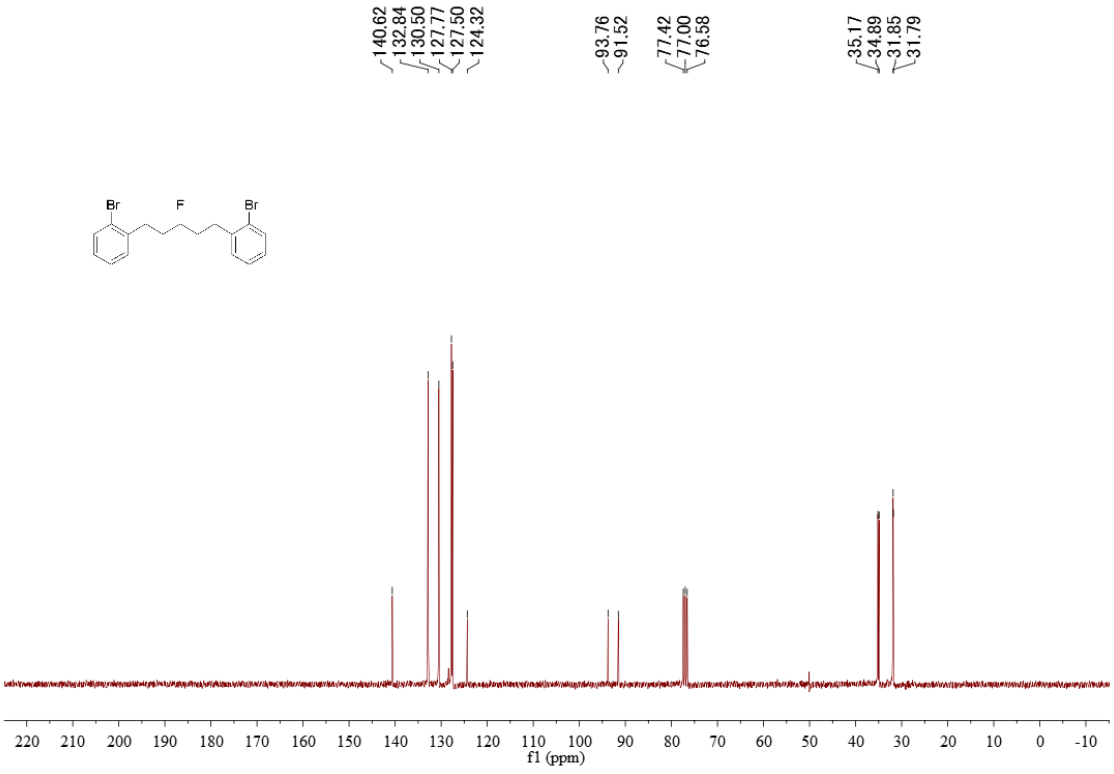


Figure S212. ^{19}F NMR spectrum of unknown secondary monofluoride **4g**, related to **Figure 3**

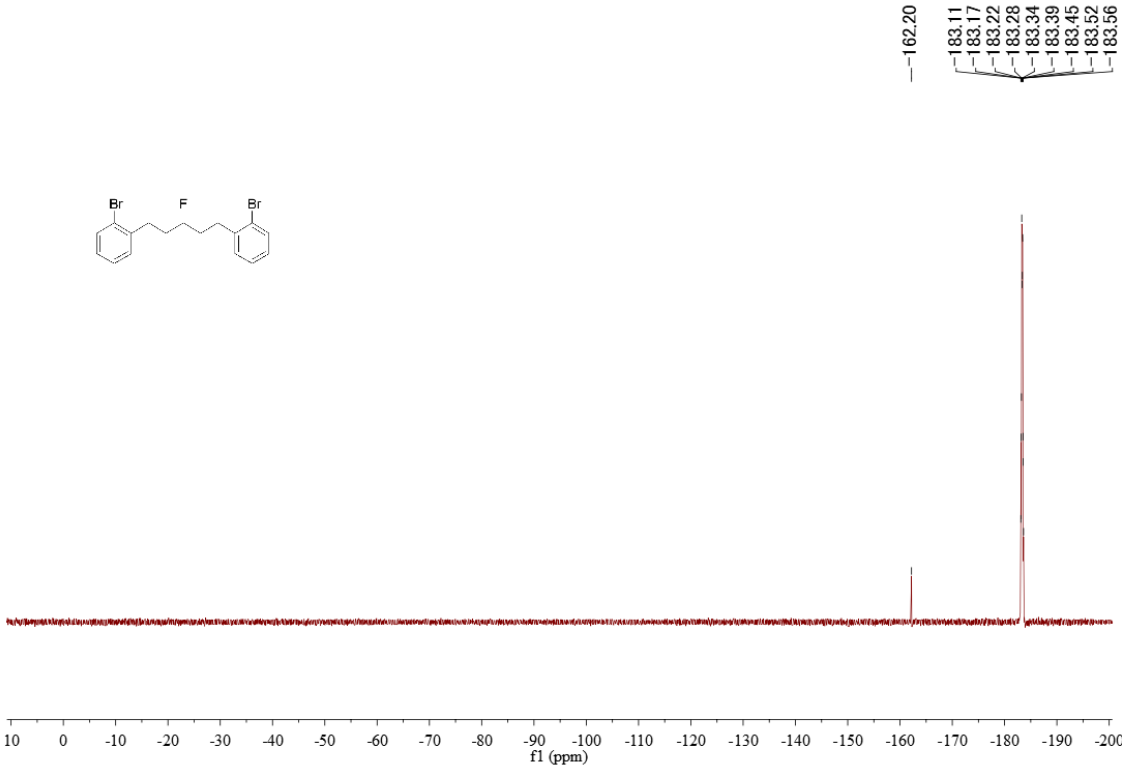


Figure S213. ^{1}H NMR spectrum of unknown secondary monofluoride **4h**, related to **Figure 3**

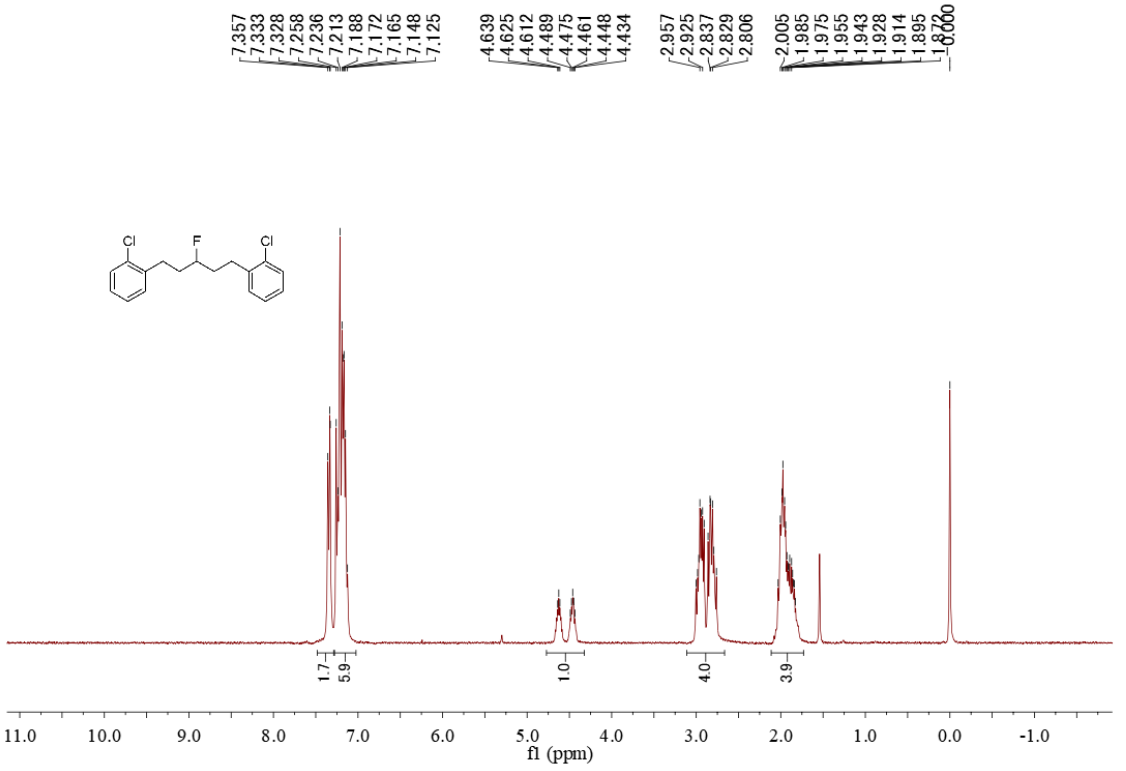


Figure S214. ^{13}C NMR spectrum of unknown secondary monofluoride **4h**, related to **Figure 3**

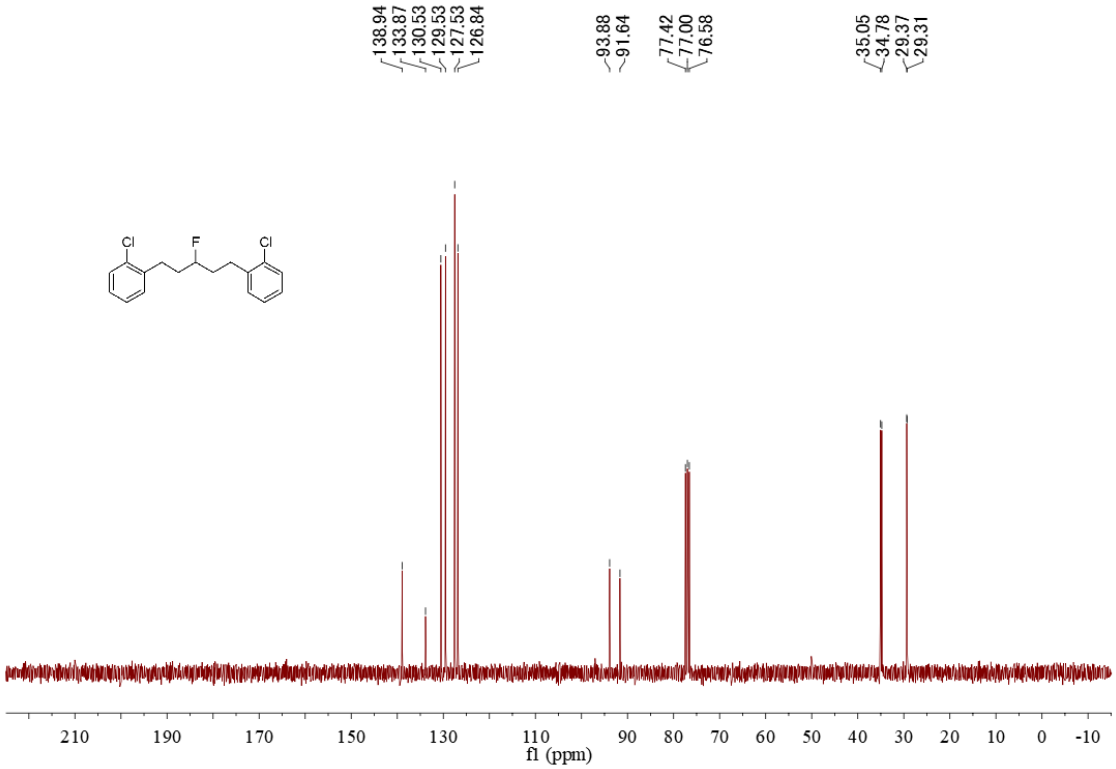


Figure S215. ^{19}F NMR spectrum of unknown secondary monofluoride **4h**, related to **Figure 3**

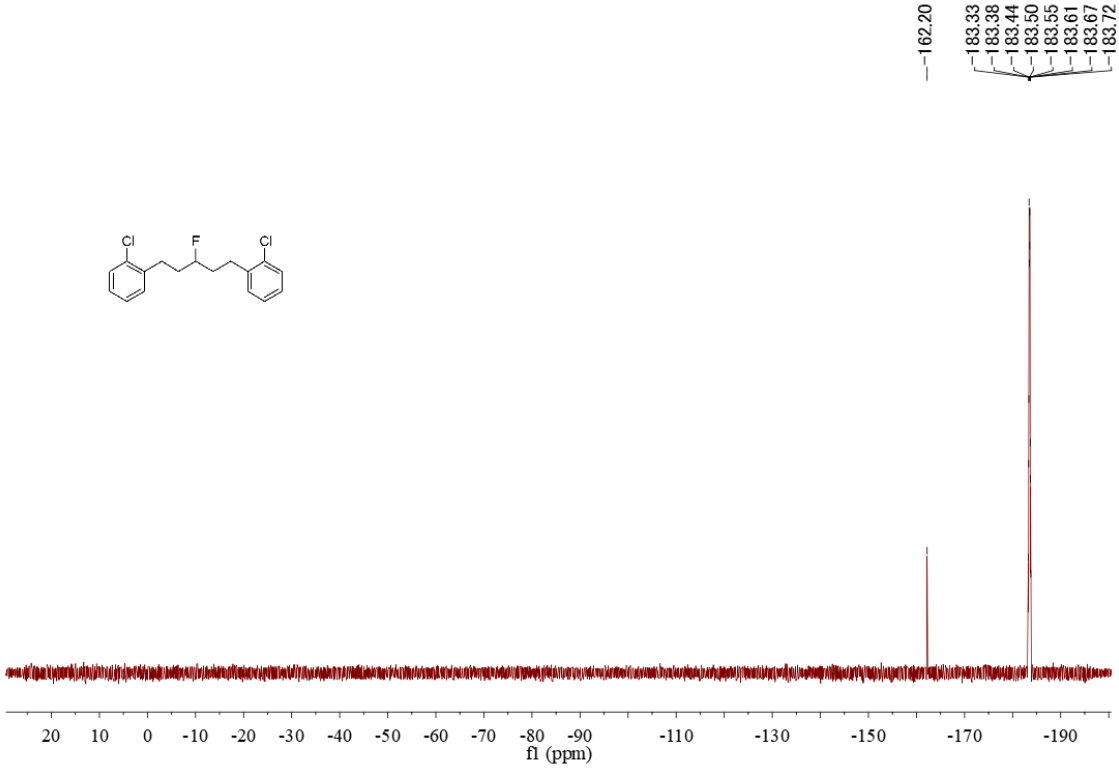


Figure S216. ^{1}H NMR spectrum of unknown secondary monofluoride **4i**, related to **Figure 3**

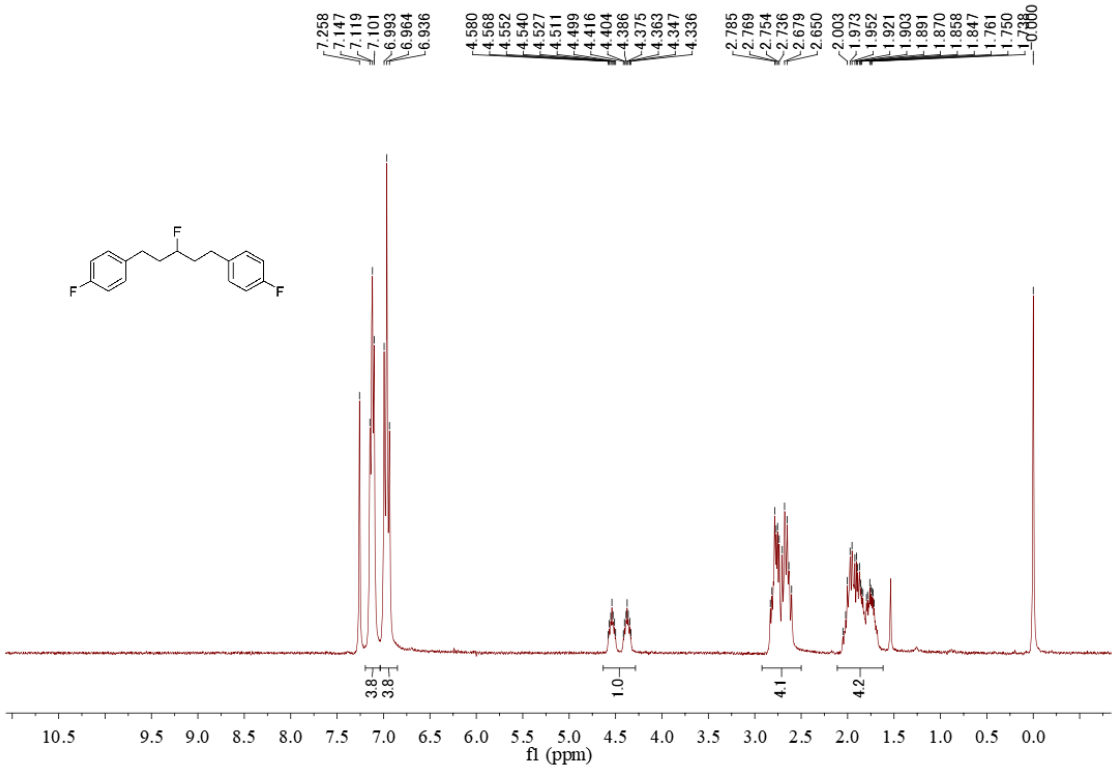


Figure S217. ^{13}C NMR spectrum of unknown secondary monofluoride **4i**, related to **Figure 3**

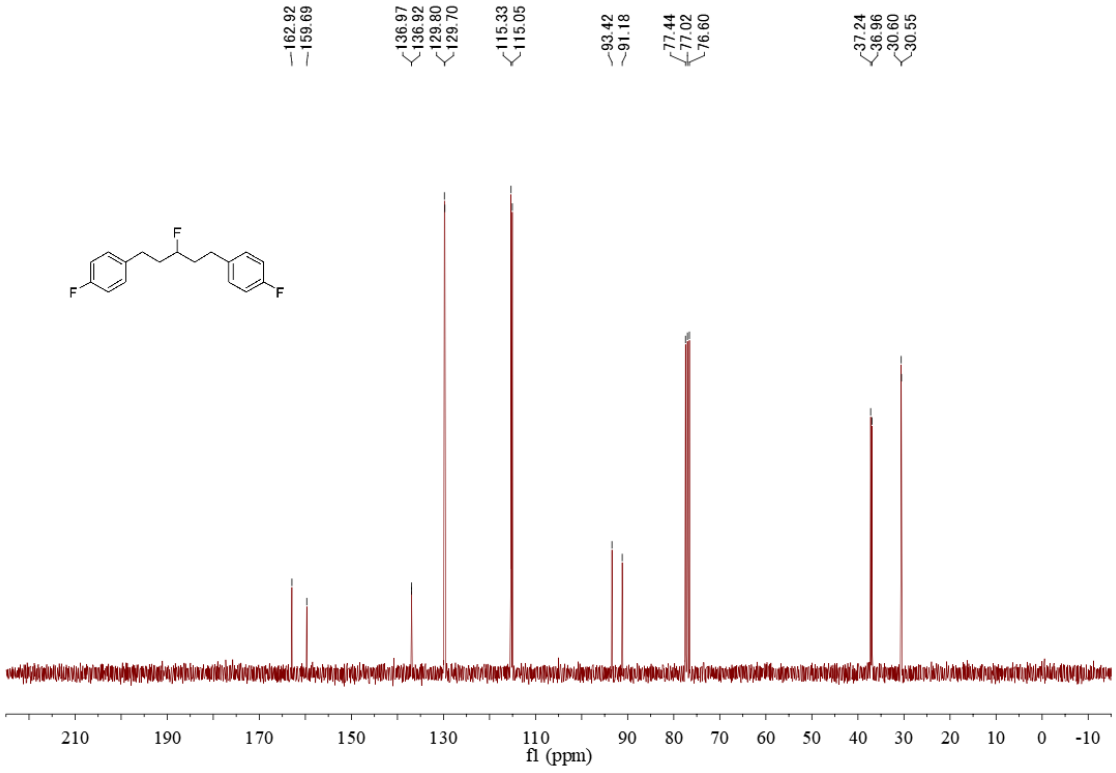


Figure S218. ^{19}F NMR spectrum of unknown secondary monofluoride **4i**, related to **Figure 3**

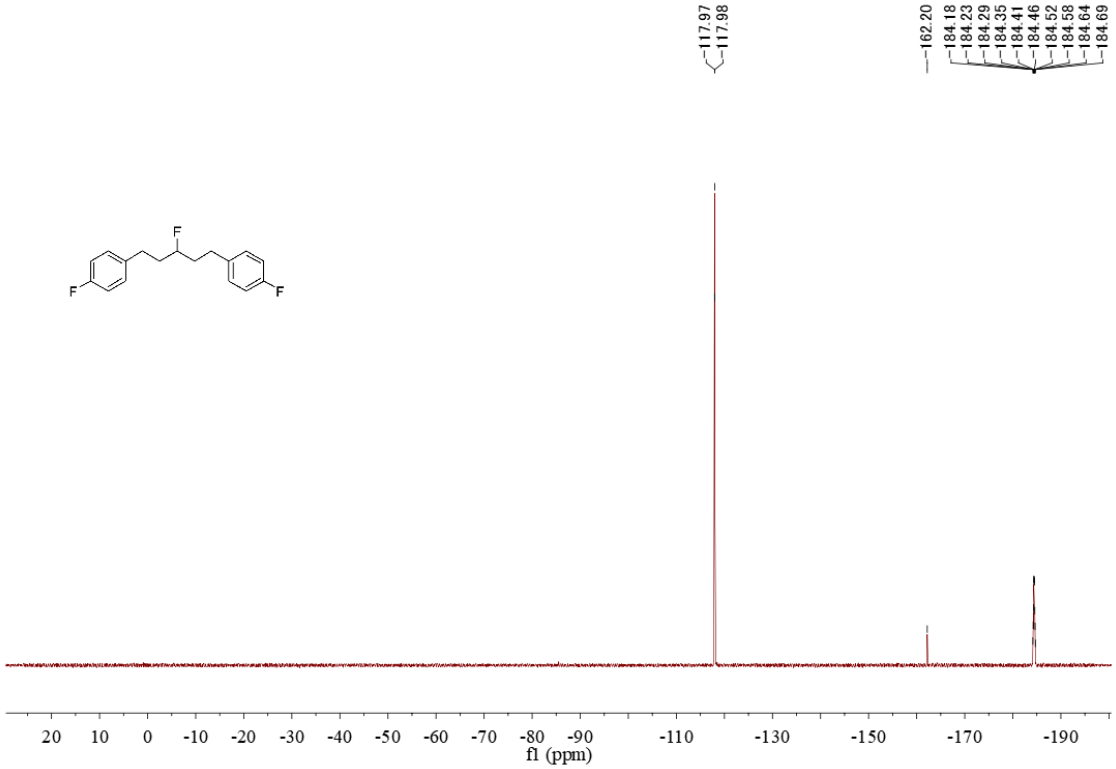


Figure S219. ^{1}H NMR spectrum of unknown secondary monofluoride **4j**, related to **Figure 3**

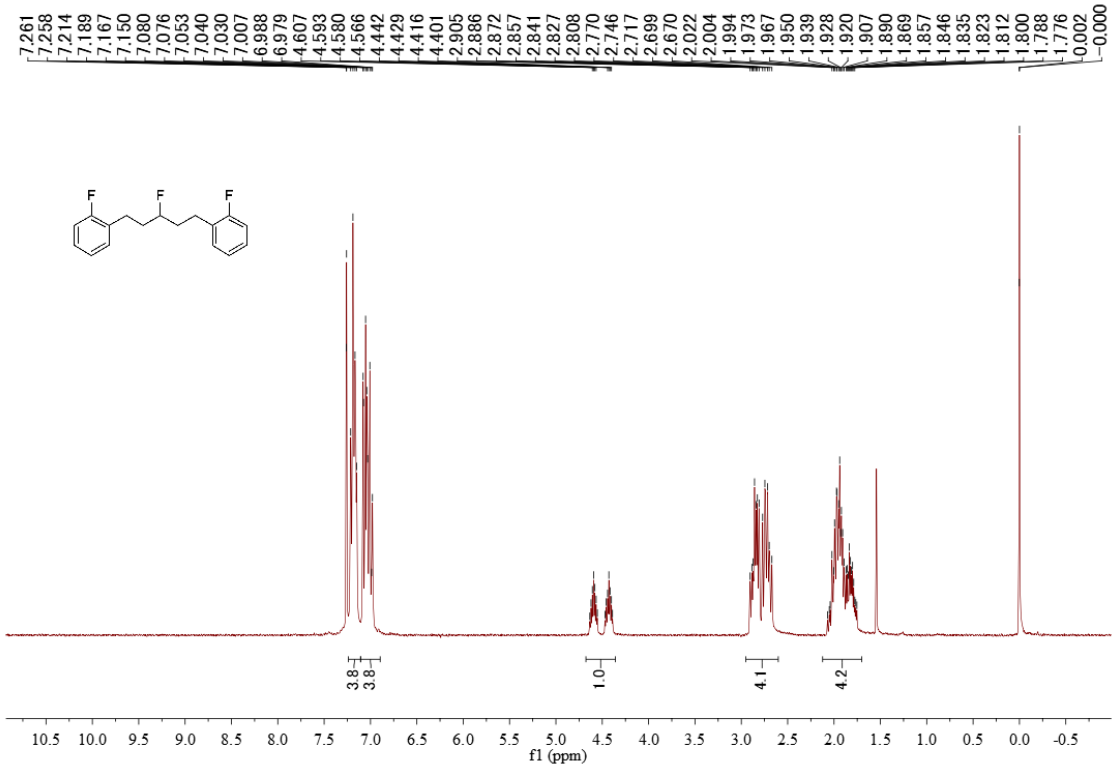


Figure S220. ^{13}C NMR spectrum of unknown secondary monofluoride **4j**, related to **Figure 3**

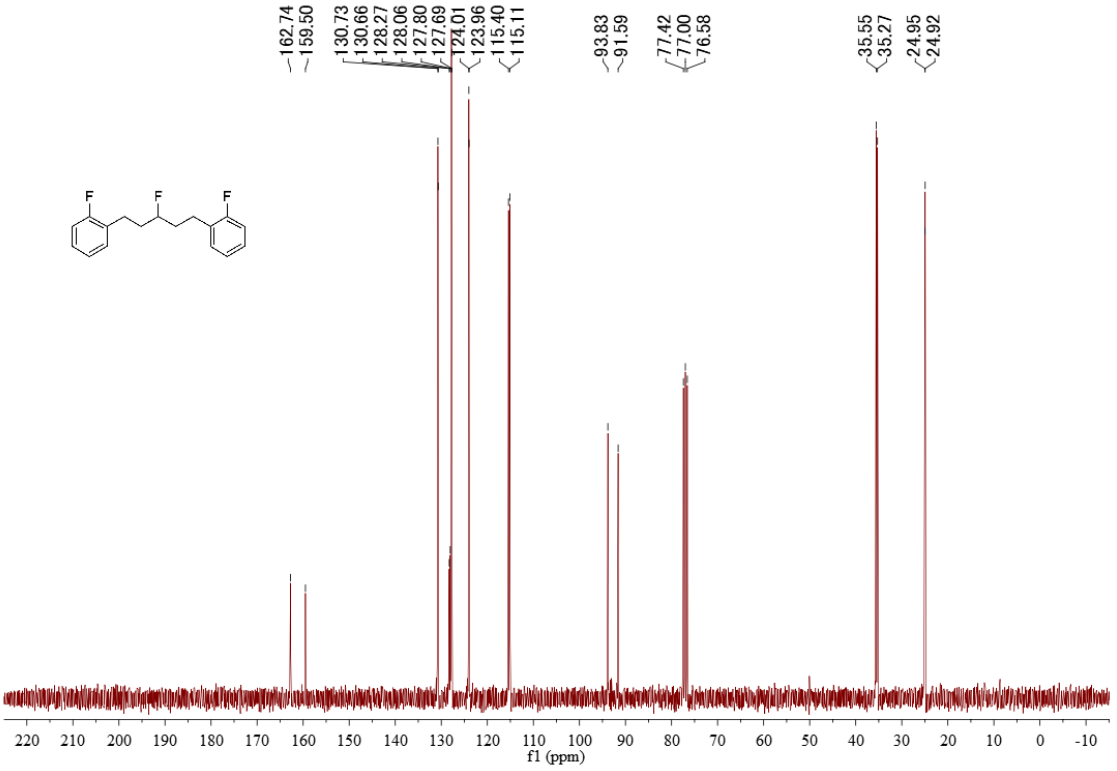


Figure S221. ^{19}F NMR spectrum of unknown secondary monofluoride **4j**, related to **Figure 3**

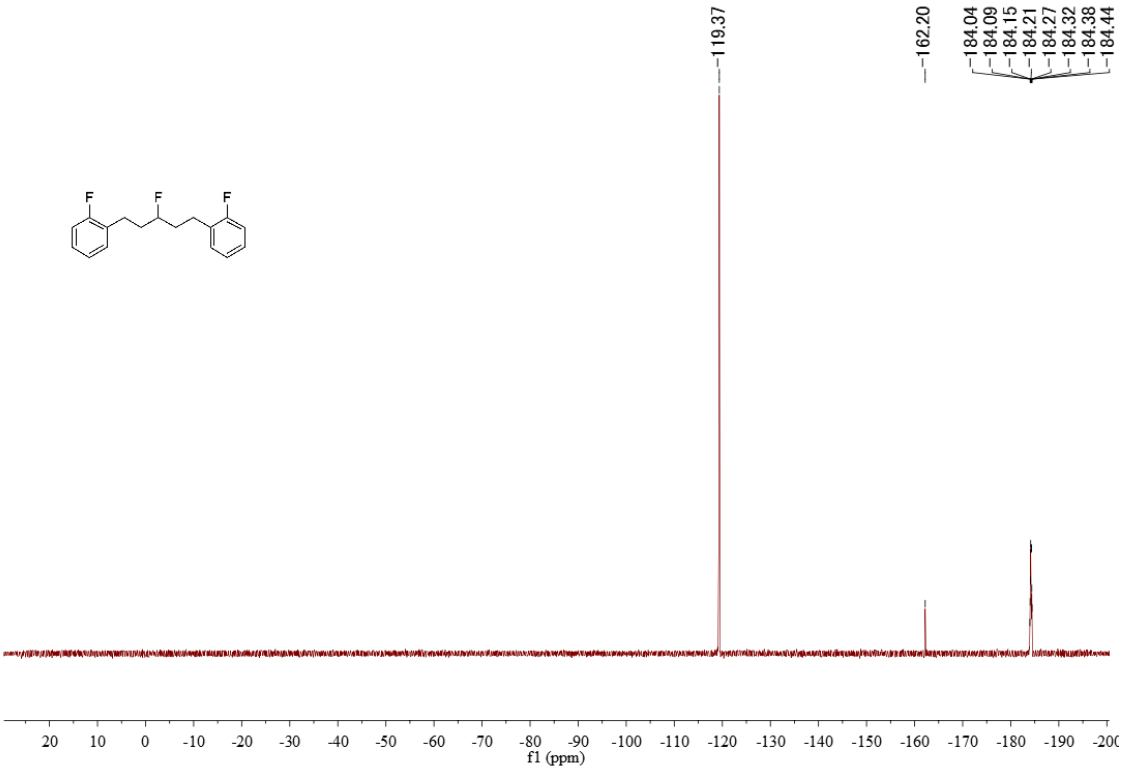


Figure S222. ^{1}H NMR spectrum of unknown secondary monofluoride **4k**, related to **Figure 3**

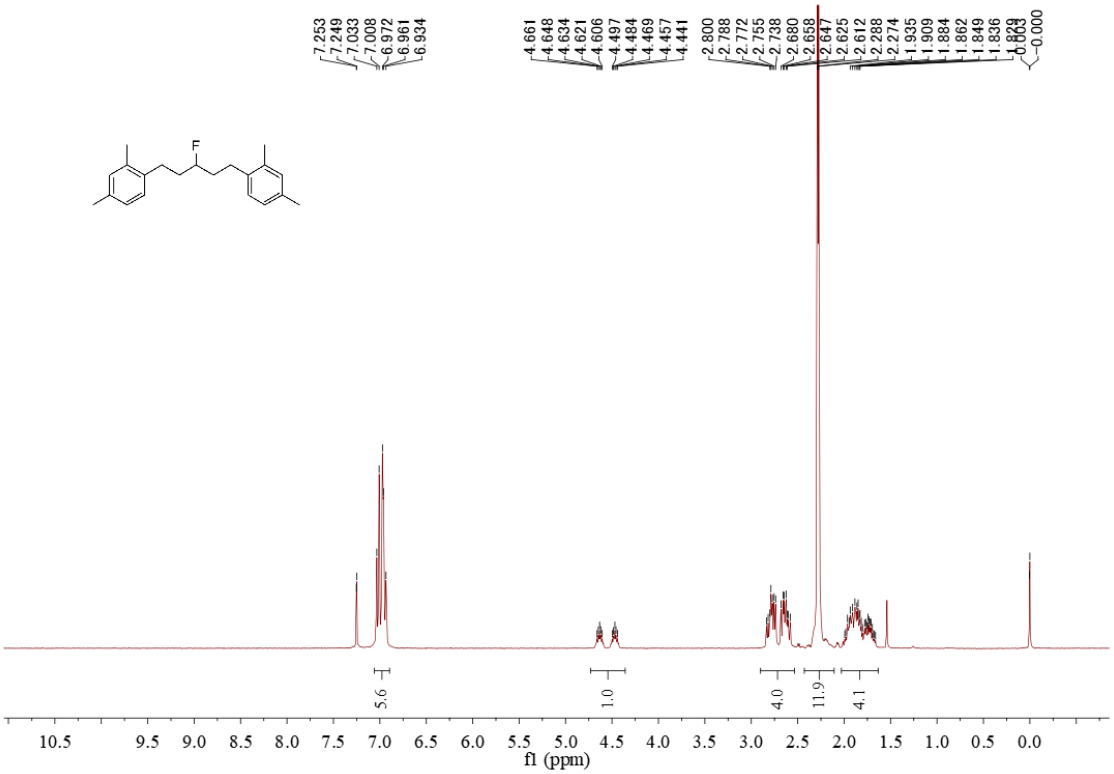


Figure S223. ^{13}C NMR spectrum of unknown secondary monofluoride **4k**, related to **Figure 3**

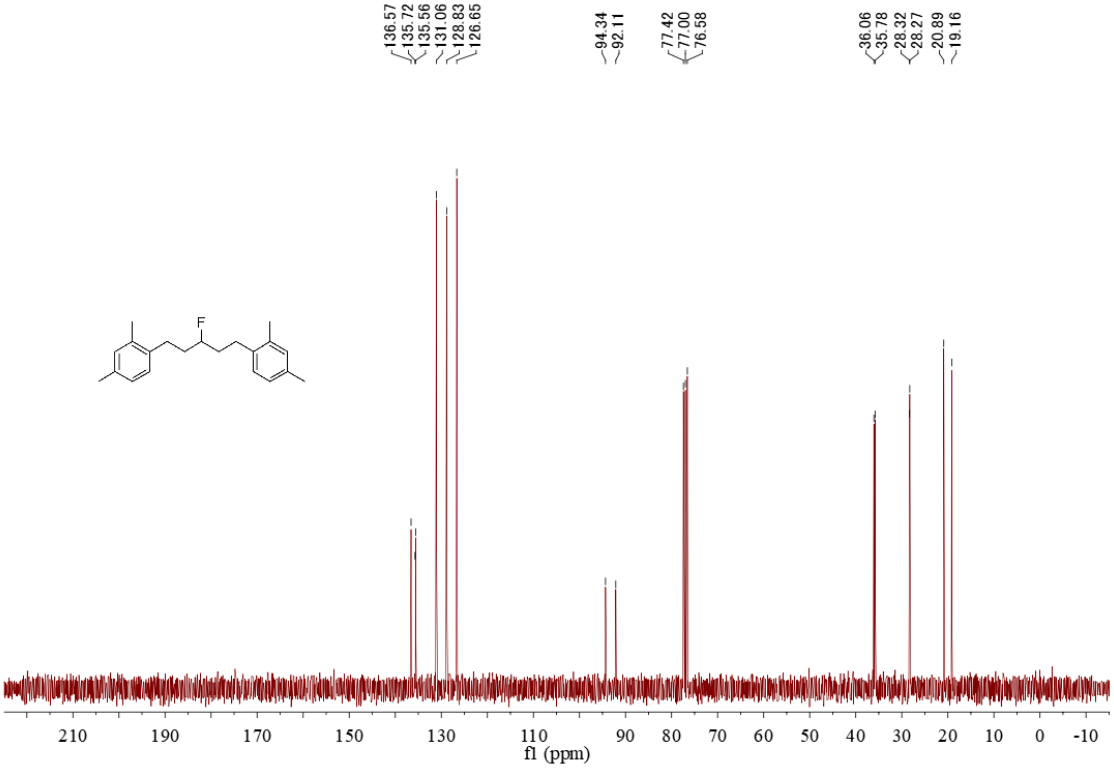


Figure S224. ^{19}F NMR spectrum of unknown secondary monofluoride **4k**, related to **Figure 3**

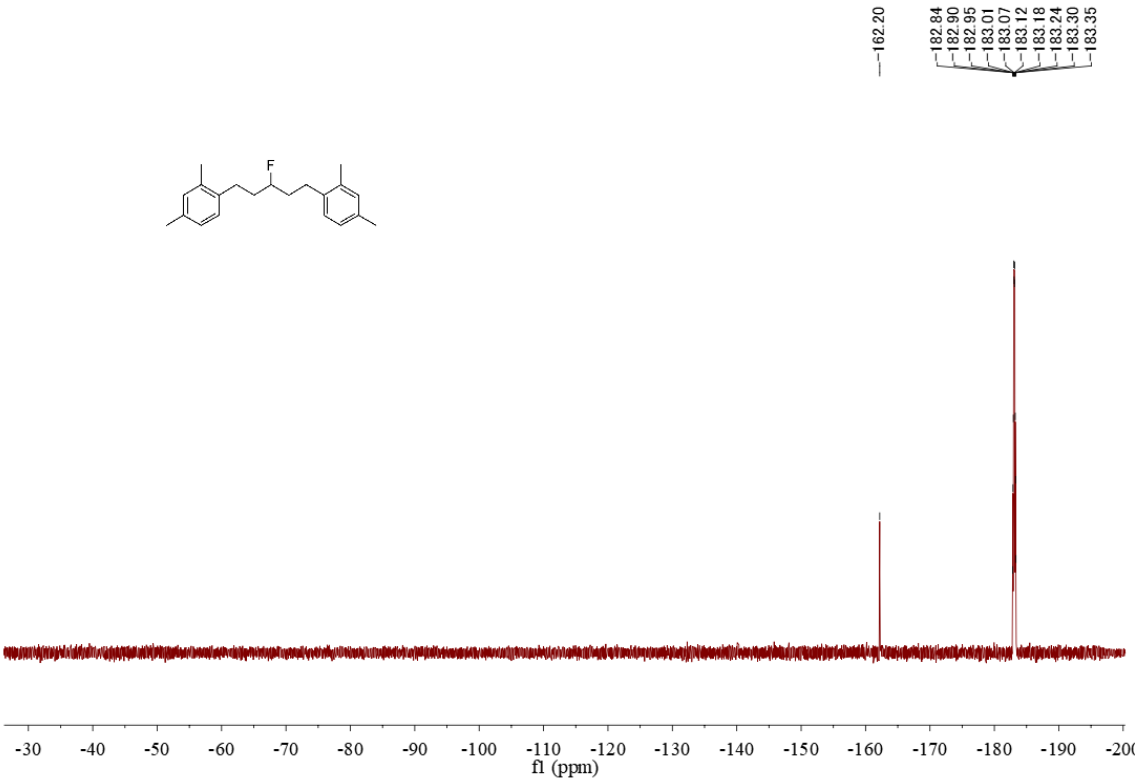


Figure S225. ^{1}H NMR spectrum of unknown secondary monofluoride **4l**, related to **Figure 3**

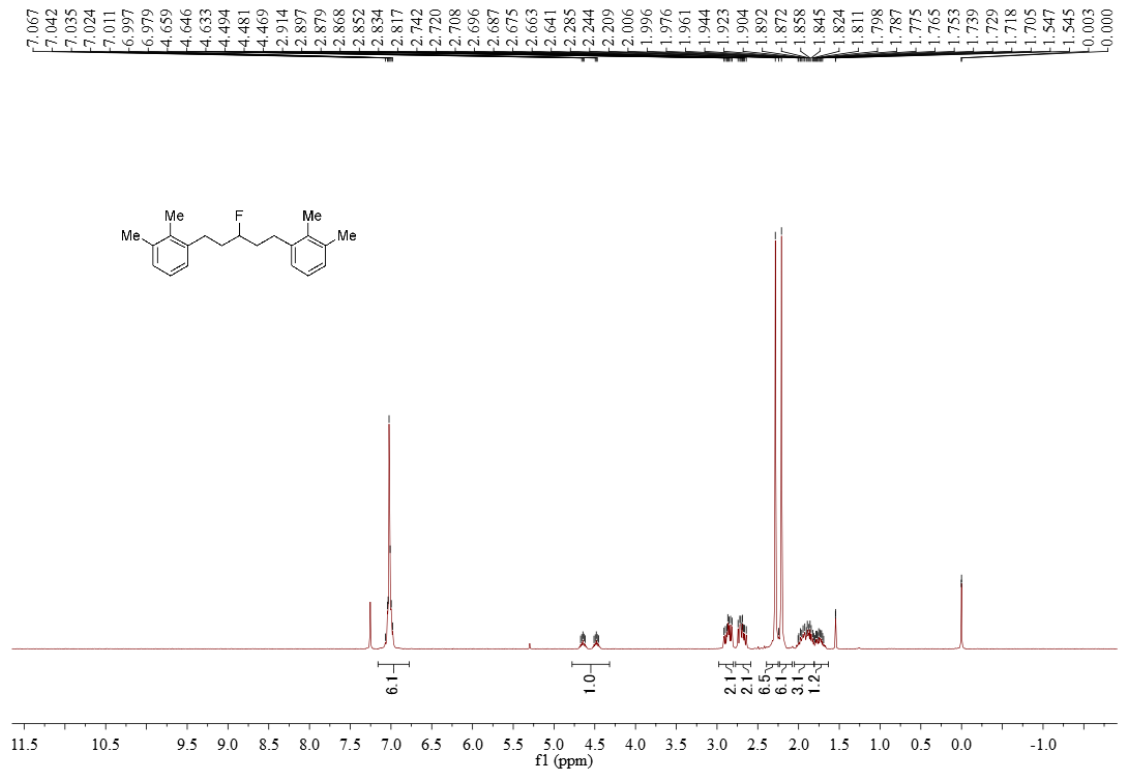


Figure S226. ^{13}C NMR spectrum of unknown secondary monofluoride **4l**, related to **Figure 3**

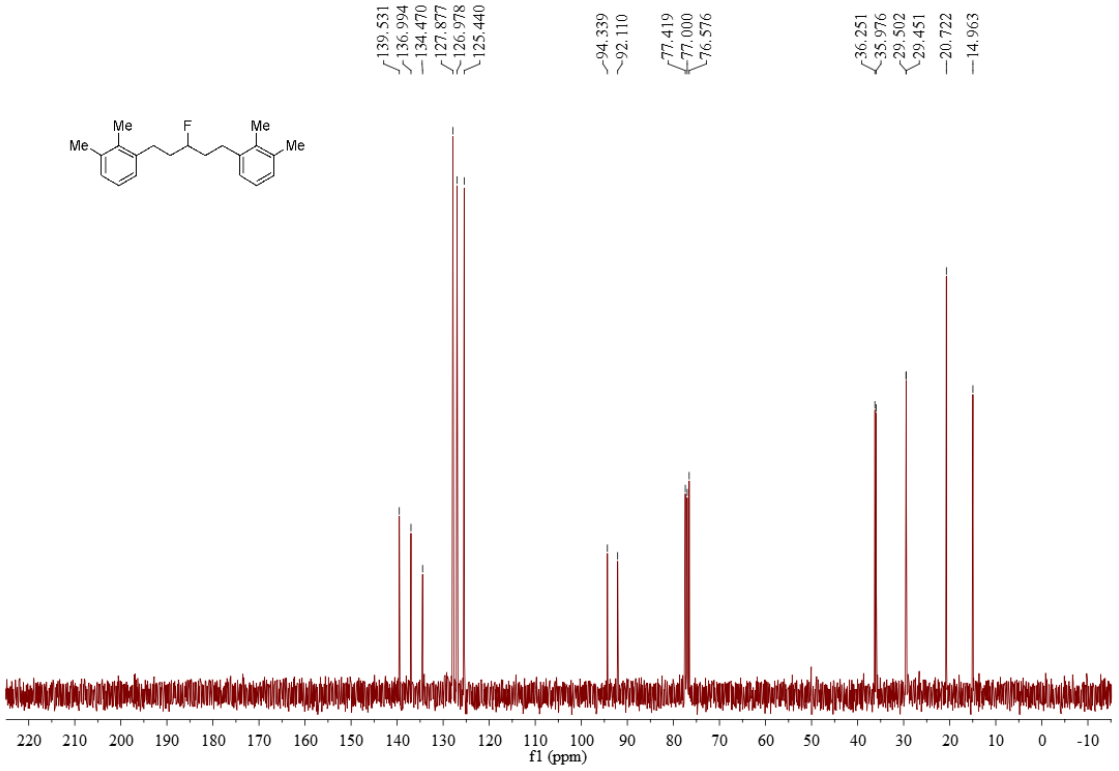


Figure S227. ^{19}F NMR spectrum of unknown secondary monofluoride **4l**, related to **Figure 3**

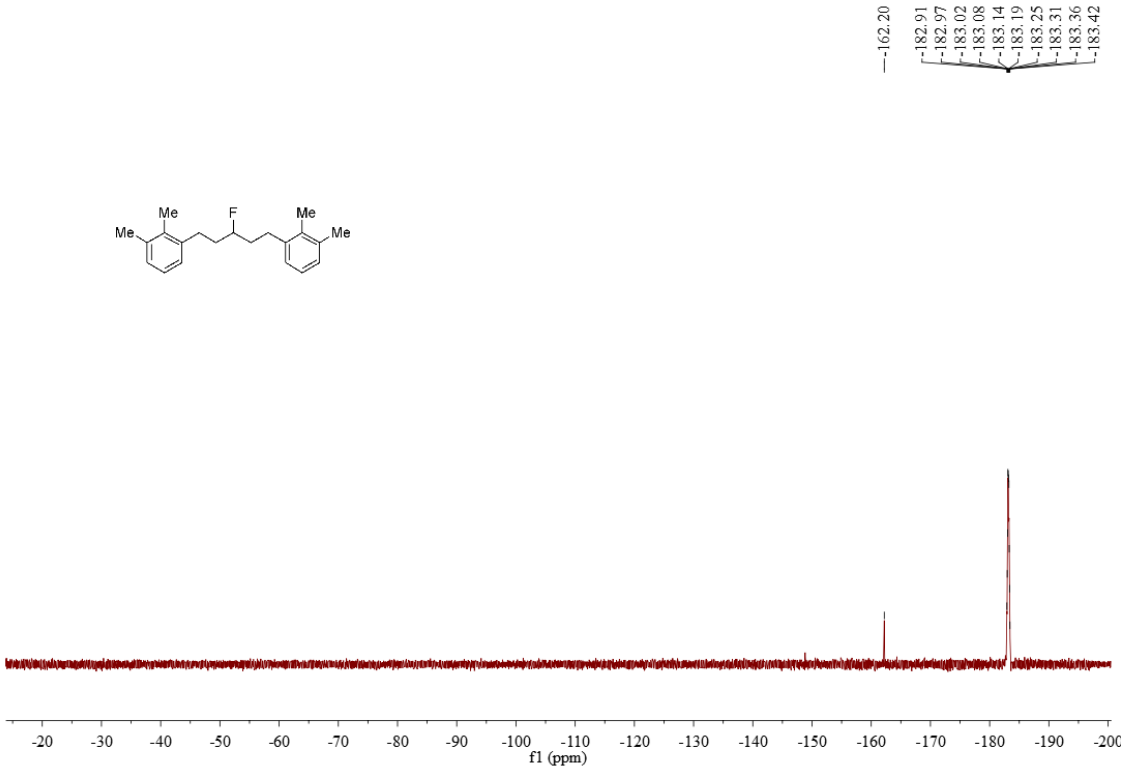


Figure S228. ^{1}H NMR spectrum of unknown secondary monofluoride **4m**, related to **Figure 3**

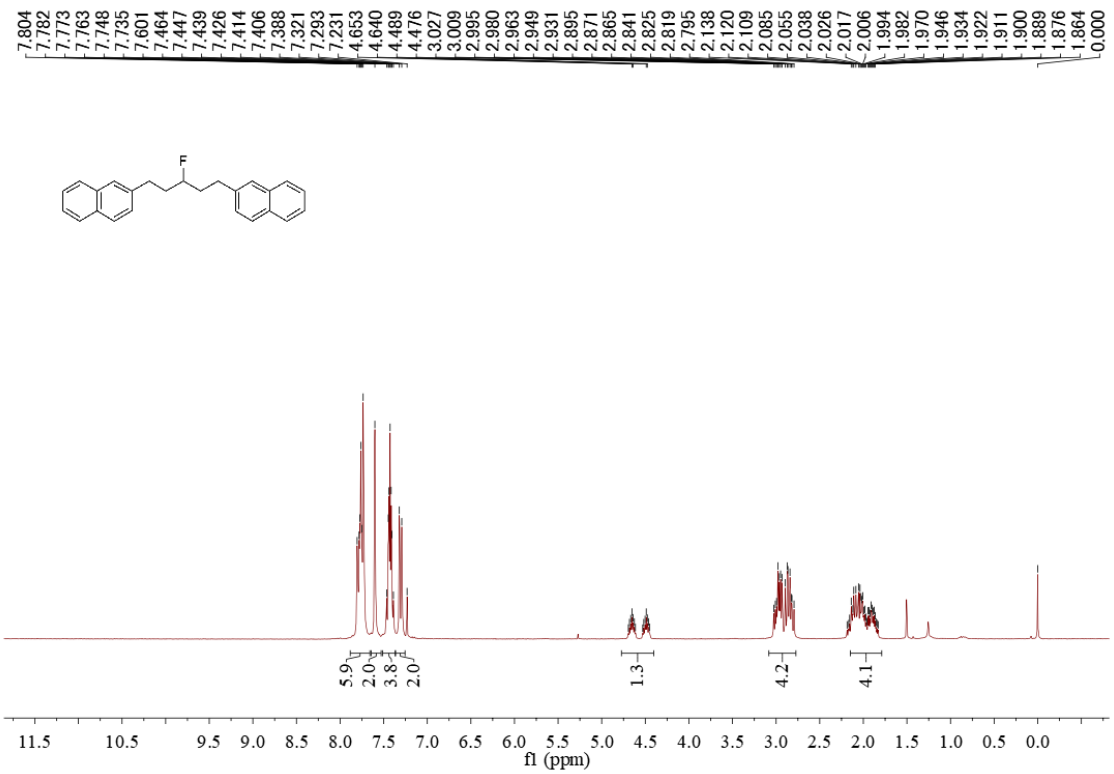


Figure S229. ^{13}C NMR spectrum of unknown secondary monofluoride **4m**, related to **Figure 3**

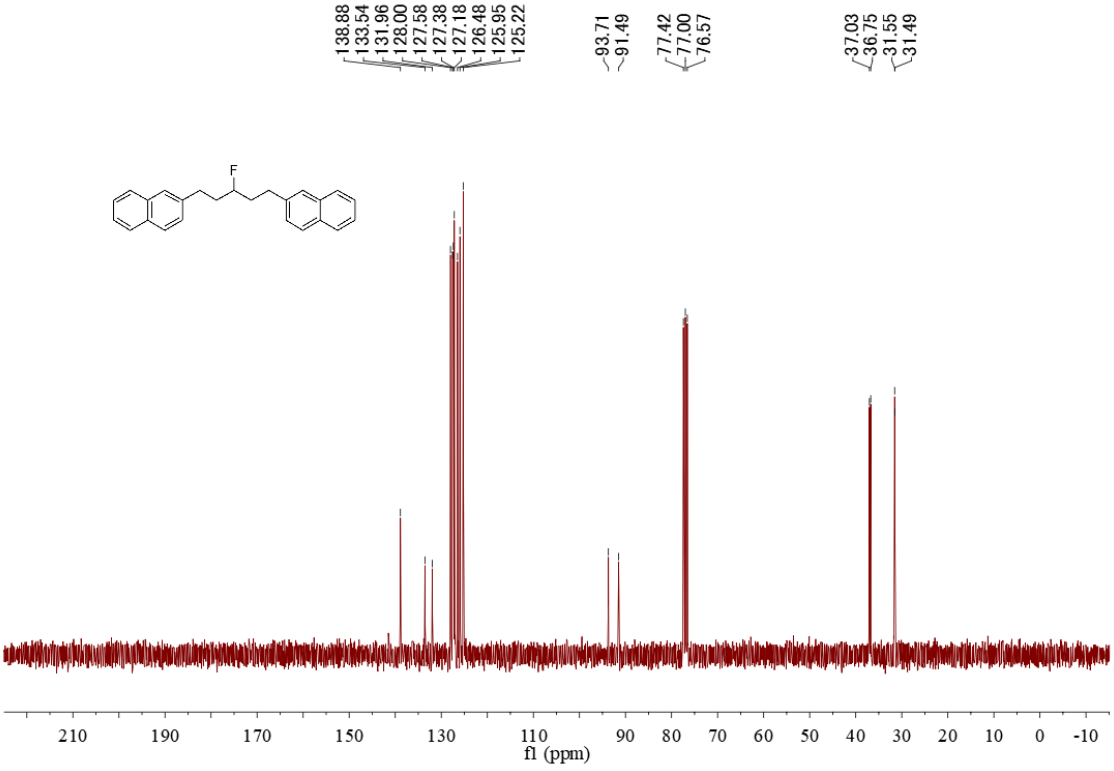


Figure S230. ^{19}F NMR spectrum of unknown secondary monofluoride **4m**, related to **Figure 3**

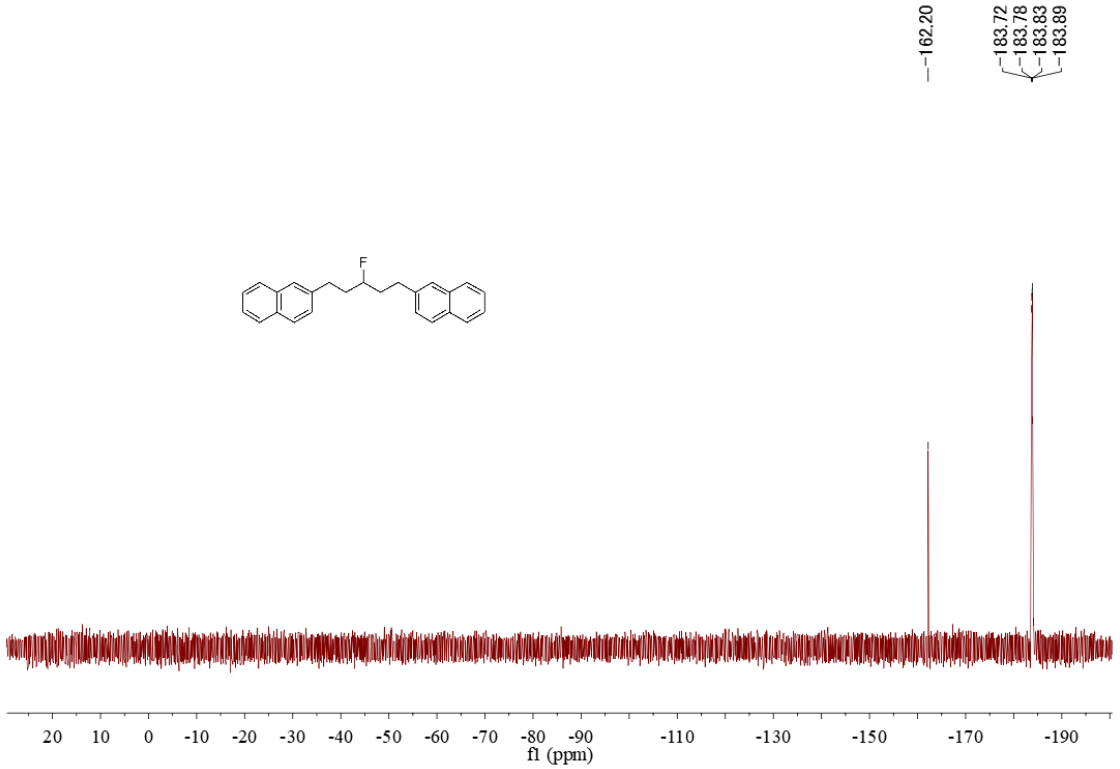


Figure S231. ^{1}H NMR spectrum of unknown secondary monofluoride **4n**, related to **Figure 3**

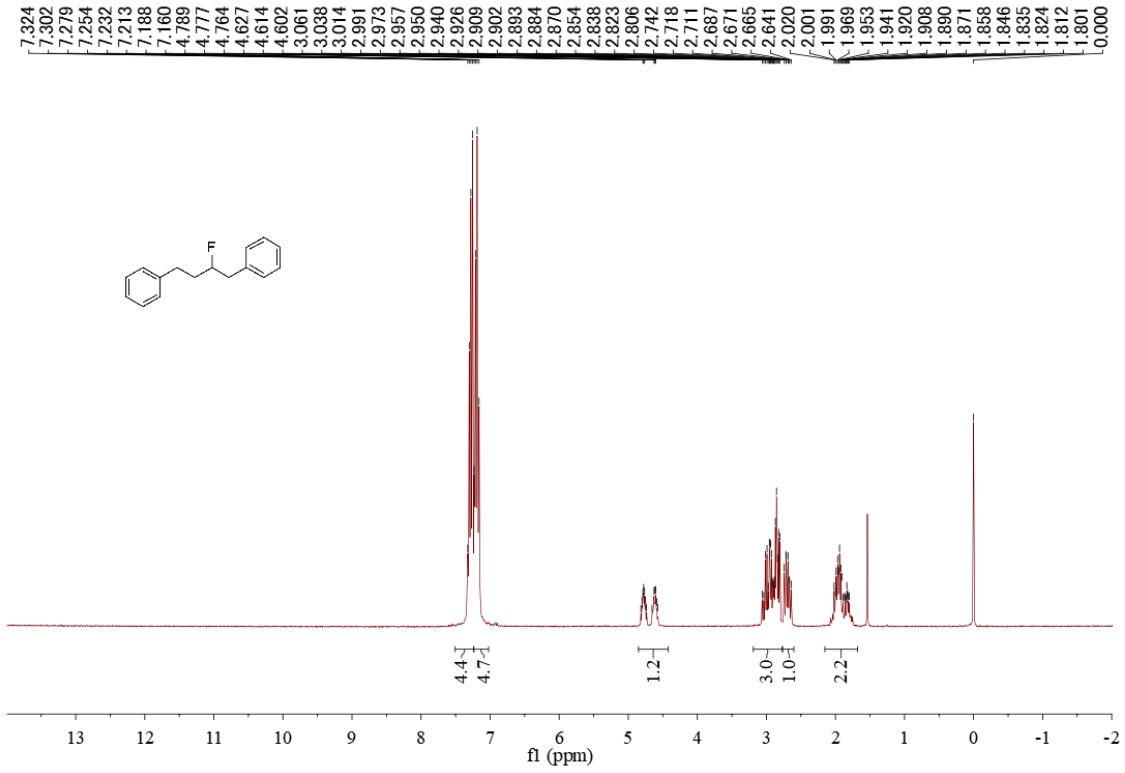


Figure S232. ^{13}C NMR spectrum of unknown secondary monofluoride **4n**, related to **Figure 3**

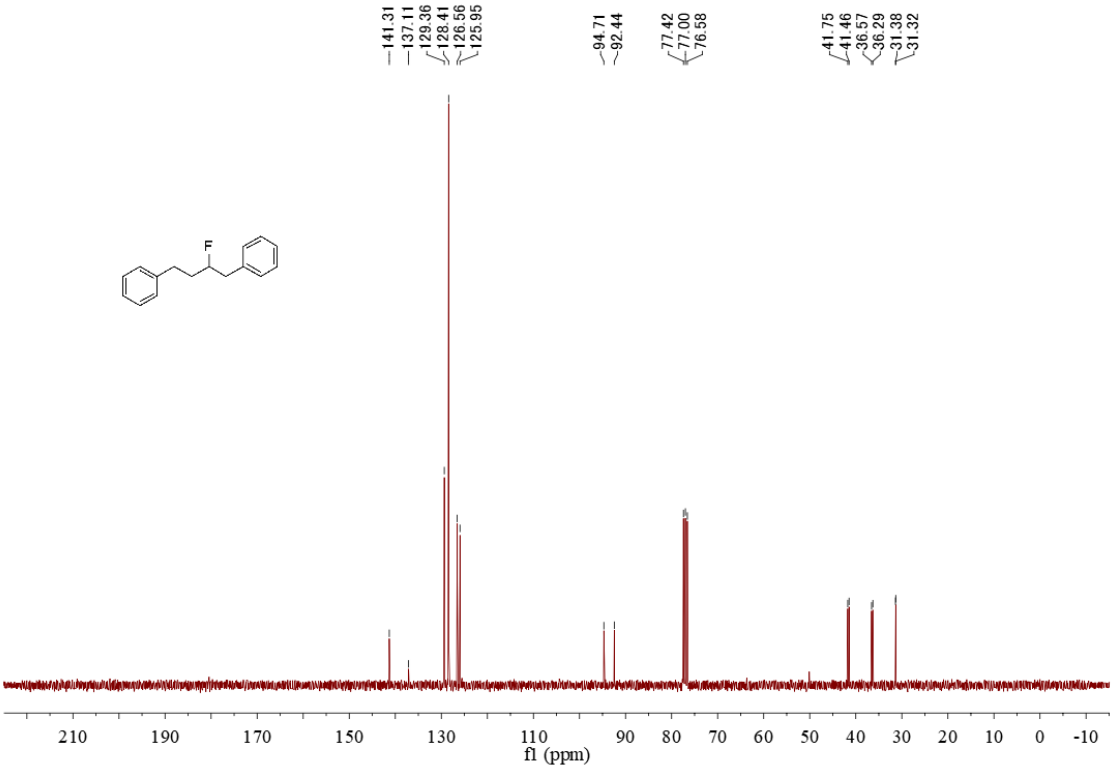


Figure S233. ^{19}F NMR spectrum of unknown secondary monofluoride **4n**, related to **Figure 3**

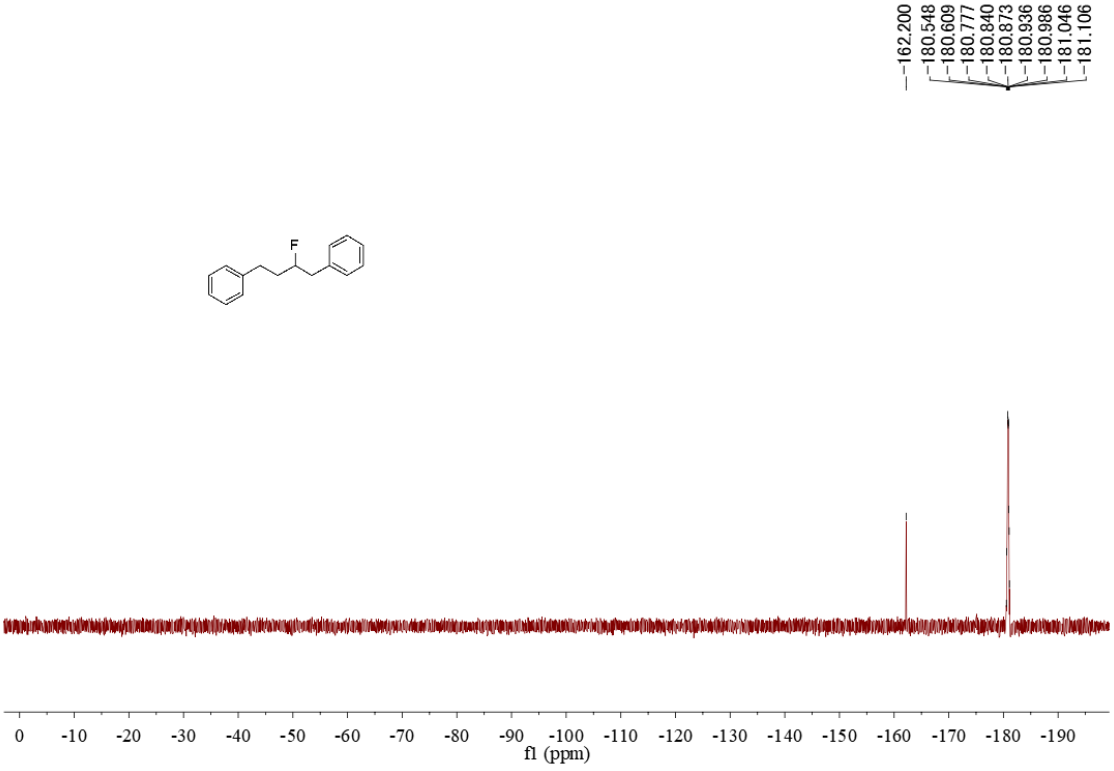


Figure S234. ^{1}H NMR spectrum of unknown secondary monofluoride **4p**, related to **Figure 3**

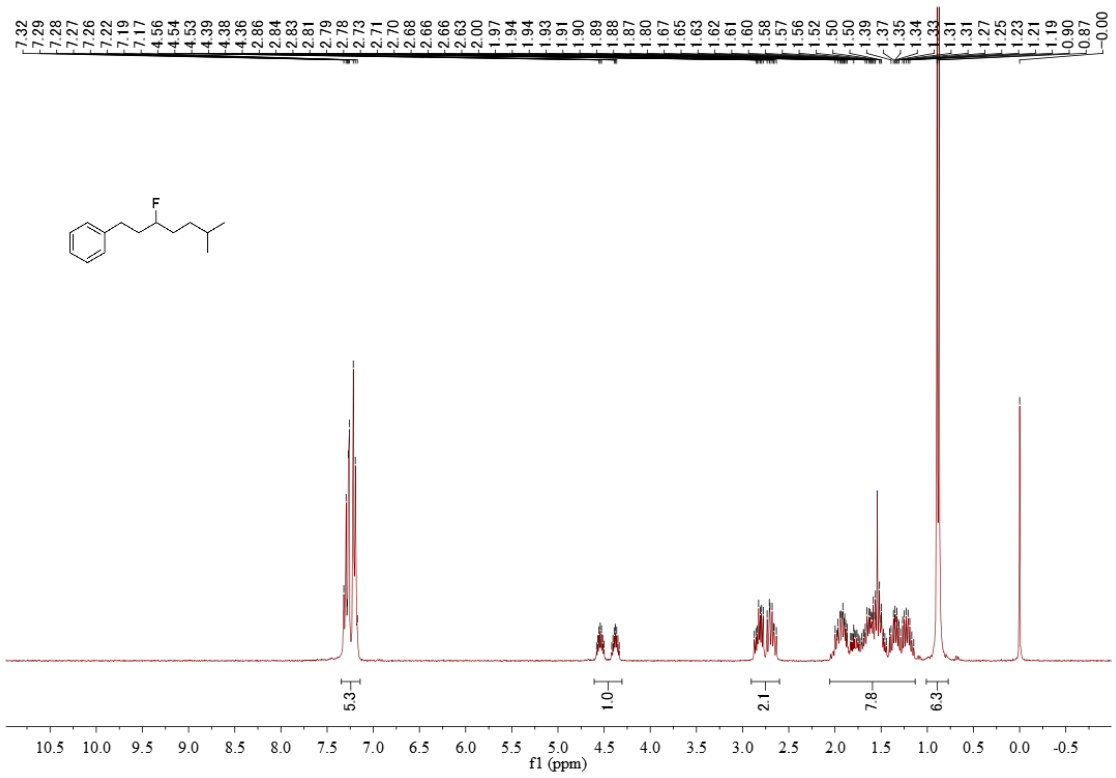


Figure S235. ^{13}C NMR spectrum of unknown secondary monofluoride **4p**, related to **Figure 3**

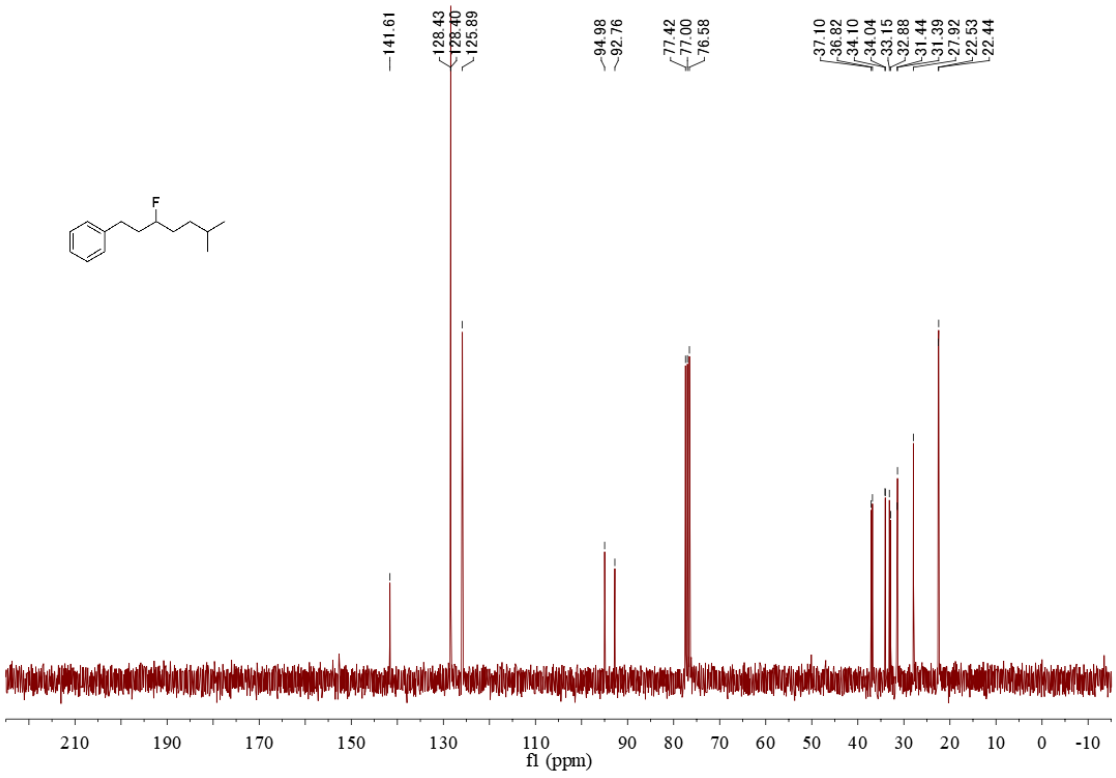


Figure S236. ^{19}F NMR spectrum of unknown secondary monofluoride **4p**, related to **Figure 3**

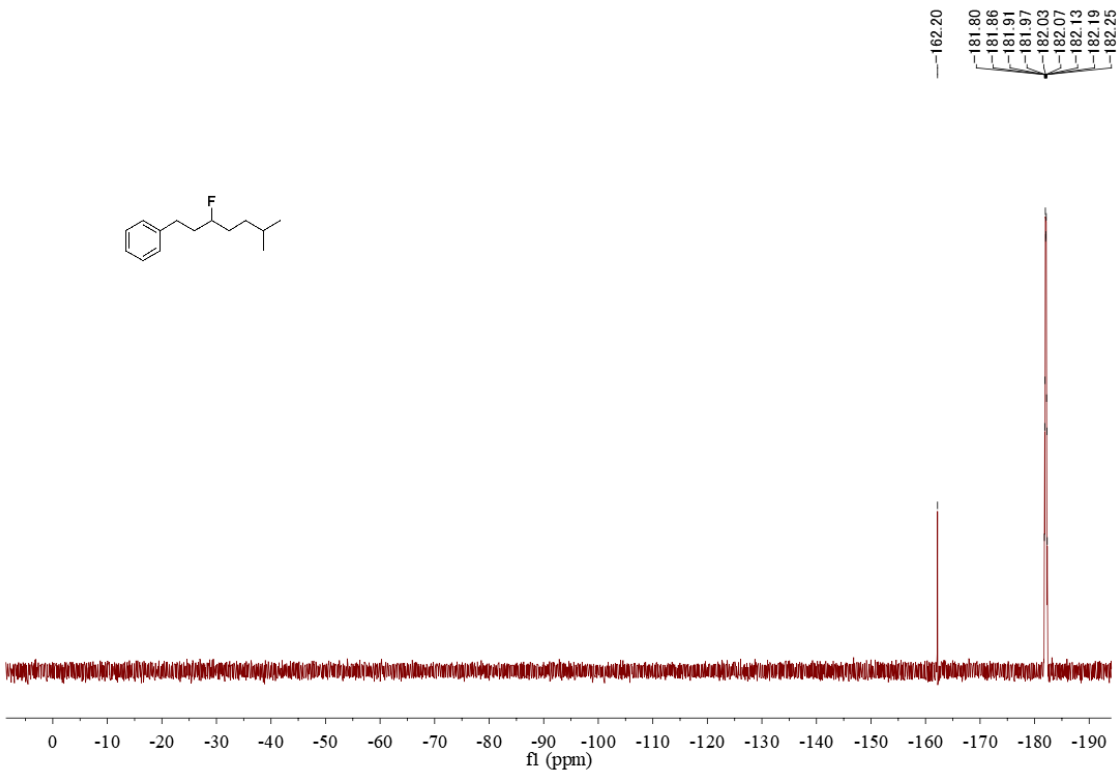


Figure S237. ^{1}H NMR spectrum of unknown secondary monofluoride **4r**, related to **Figure 3**

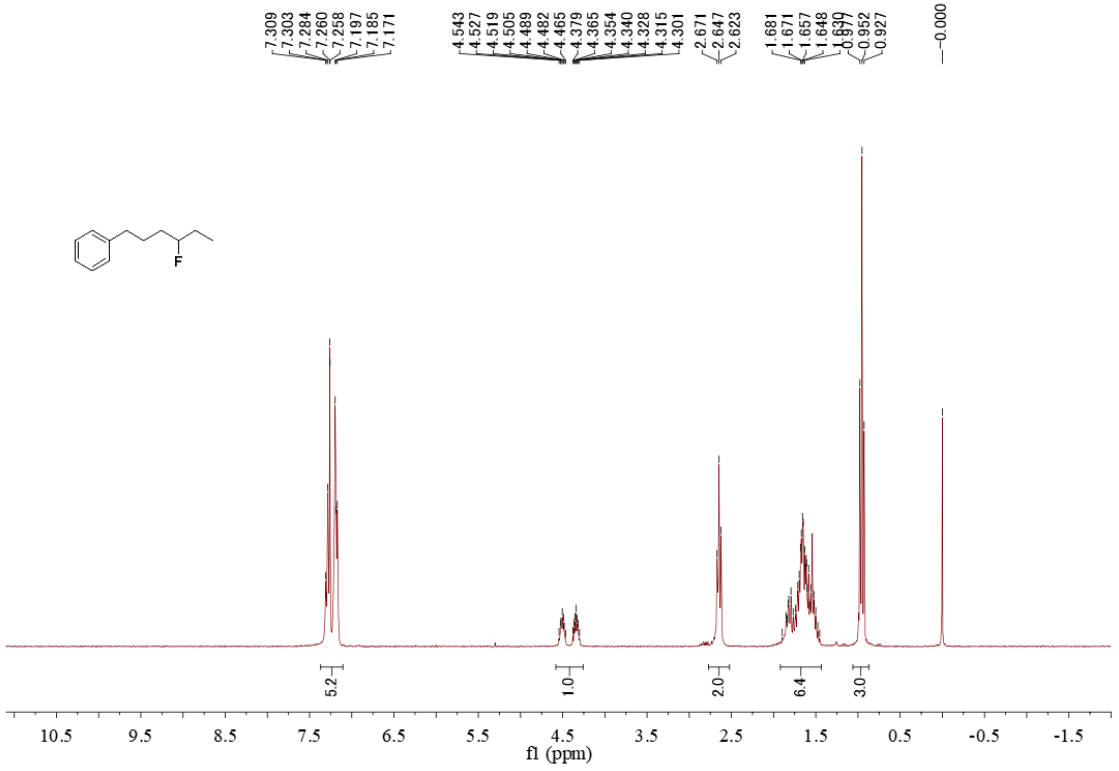


Figure S238. ^{13}C NMR spectrum of unknown secondary monofluoride **4r**, related to **Figure 3**

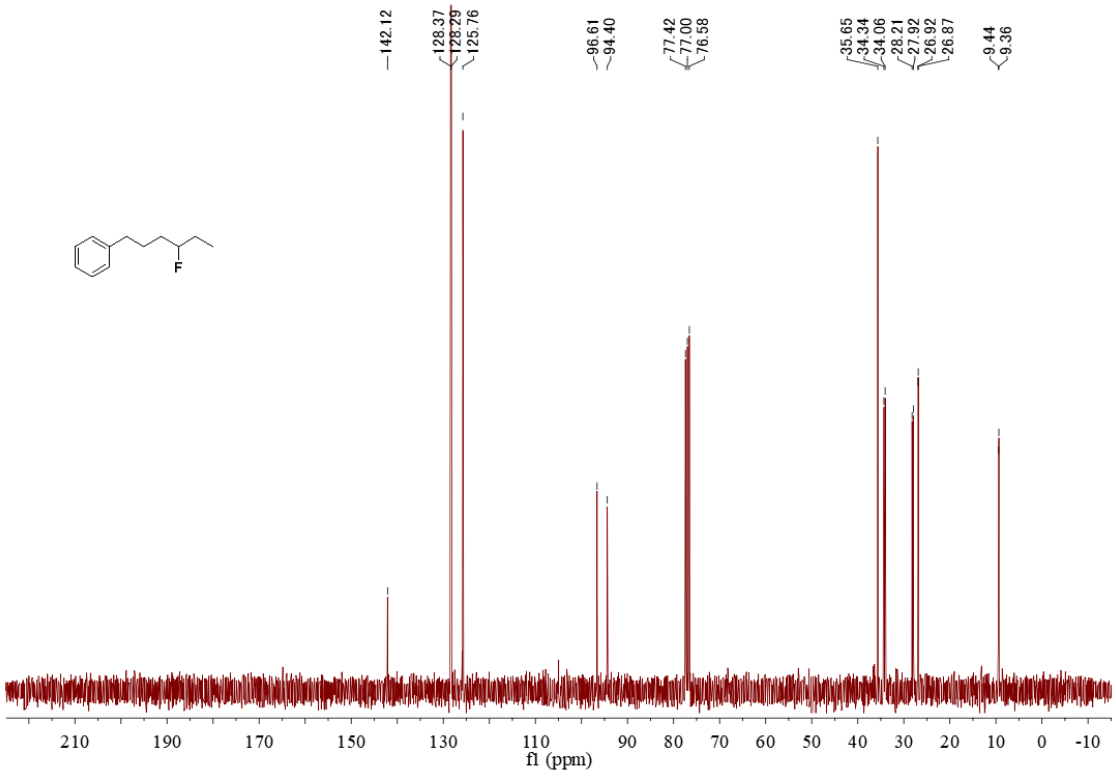


Figure S239. ^{19}F NMR spectrum of unknown secondary monofluoride **4r**, related to **Figure 3**

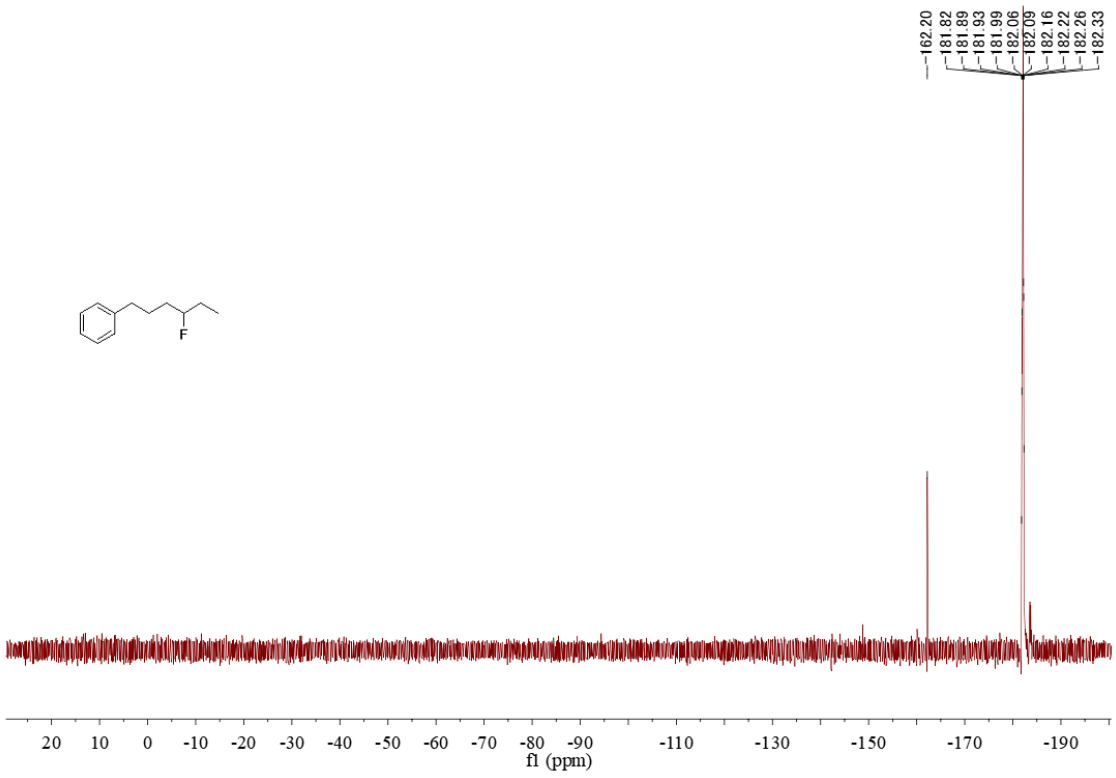


Figure S240. ^{1}H NMR spectrum of unknown secondary monofluoride **4s**, related to **Figure 3**

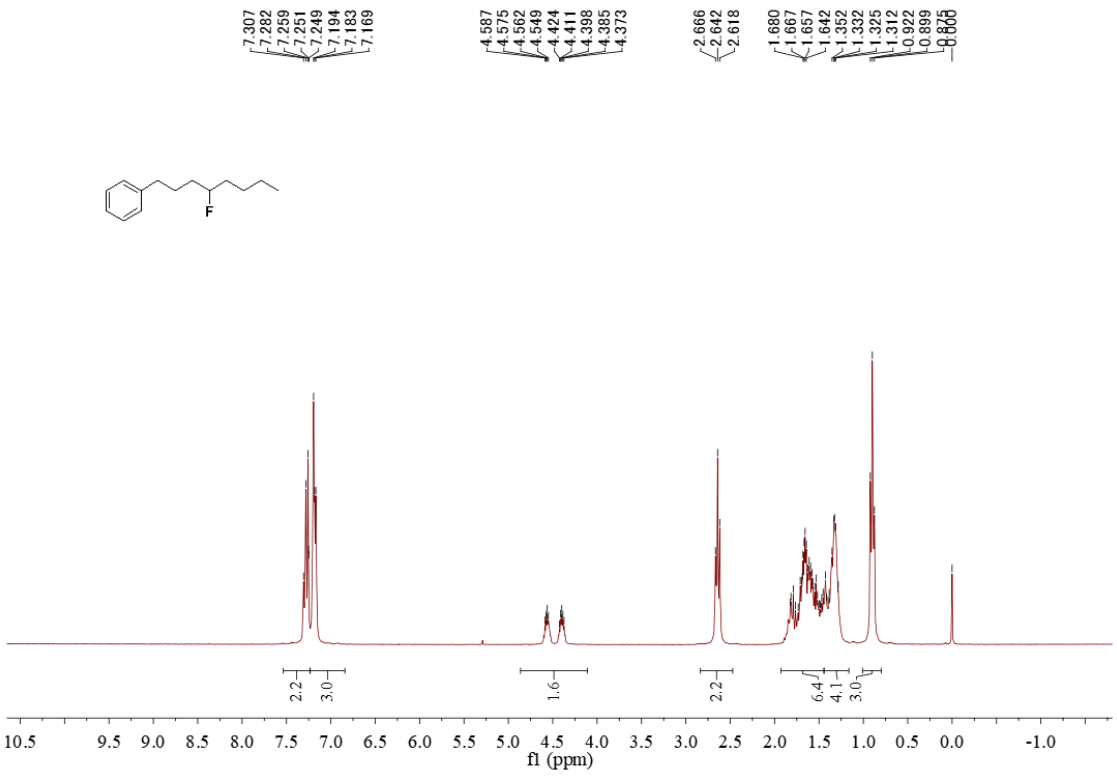


Figure S241. ^{13}C NMR spectrum of unknown secondary monofluoride **4s**, related to **Figure 3**

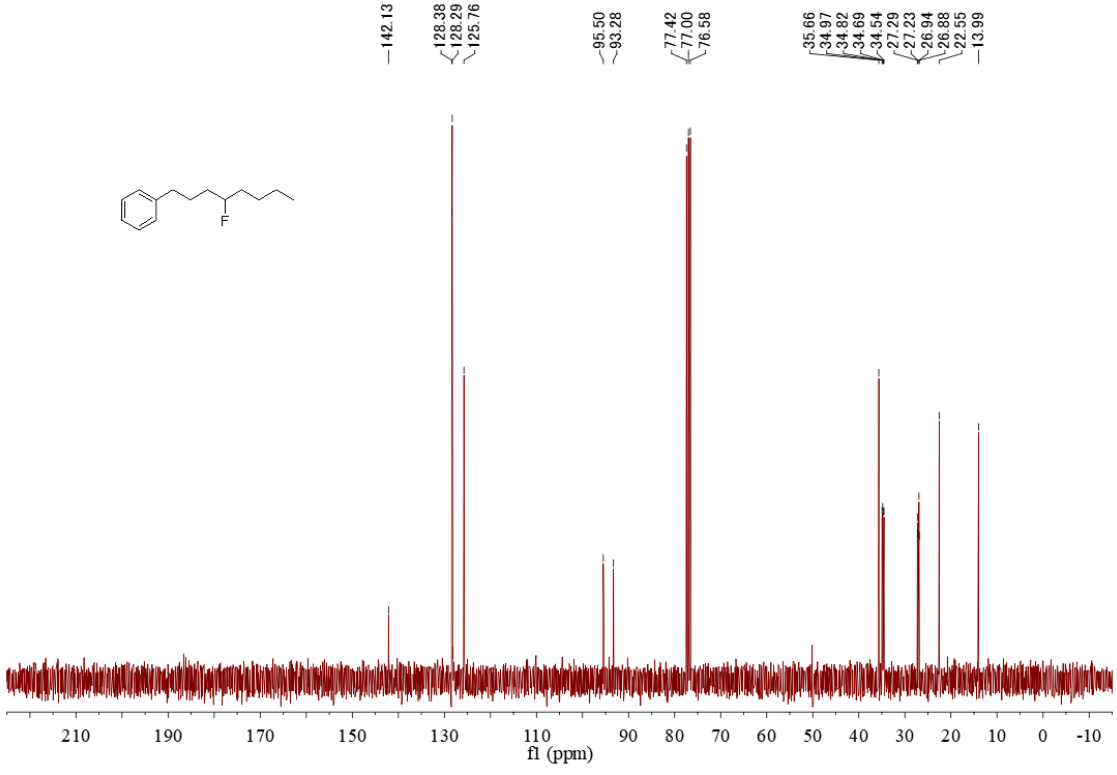


Figure S242. ^{19}F NMR spectrum of unknown secondary monofluoride **4s**, related to **Figure 3**

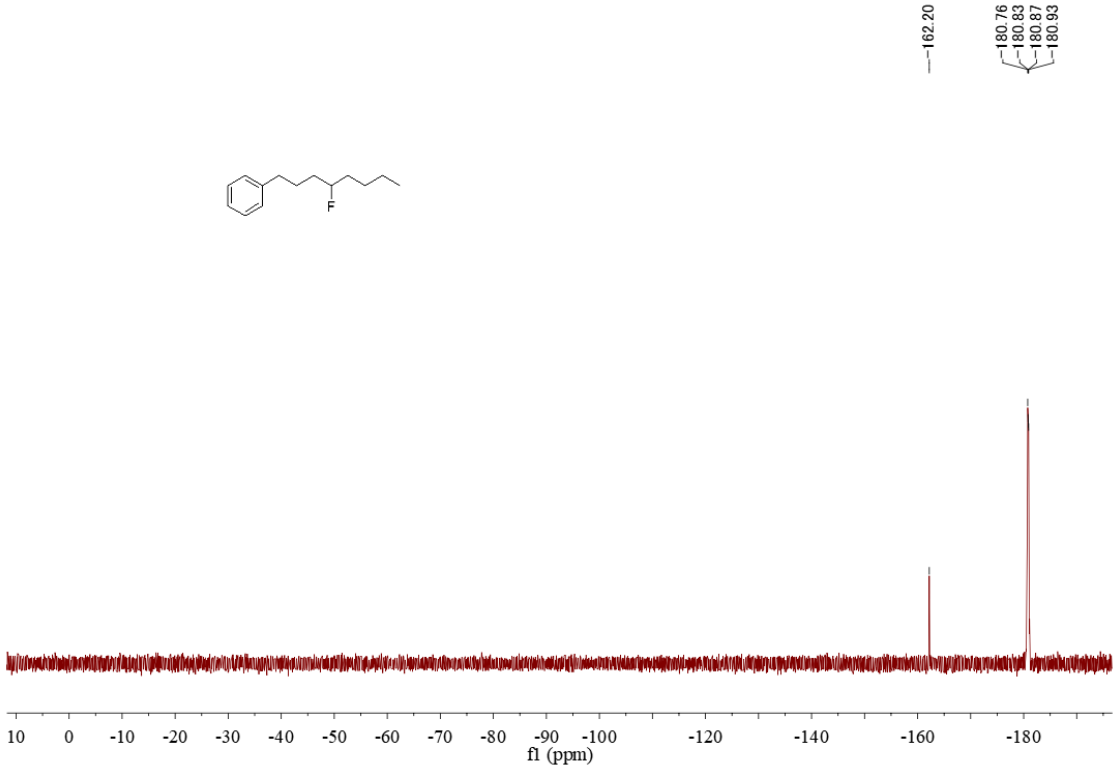


Figure S243. ^{1}H-NMR spectra copy of crude reaction mixture: Using $(CF_3)_2CHOH$ as purchased without precaution to exclude moisture, related to **Table 1** (entry 7)

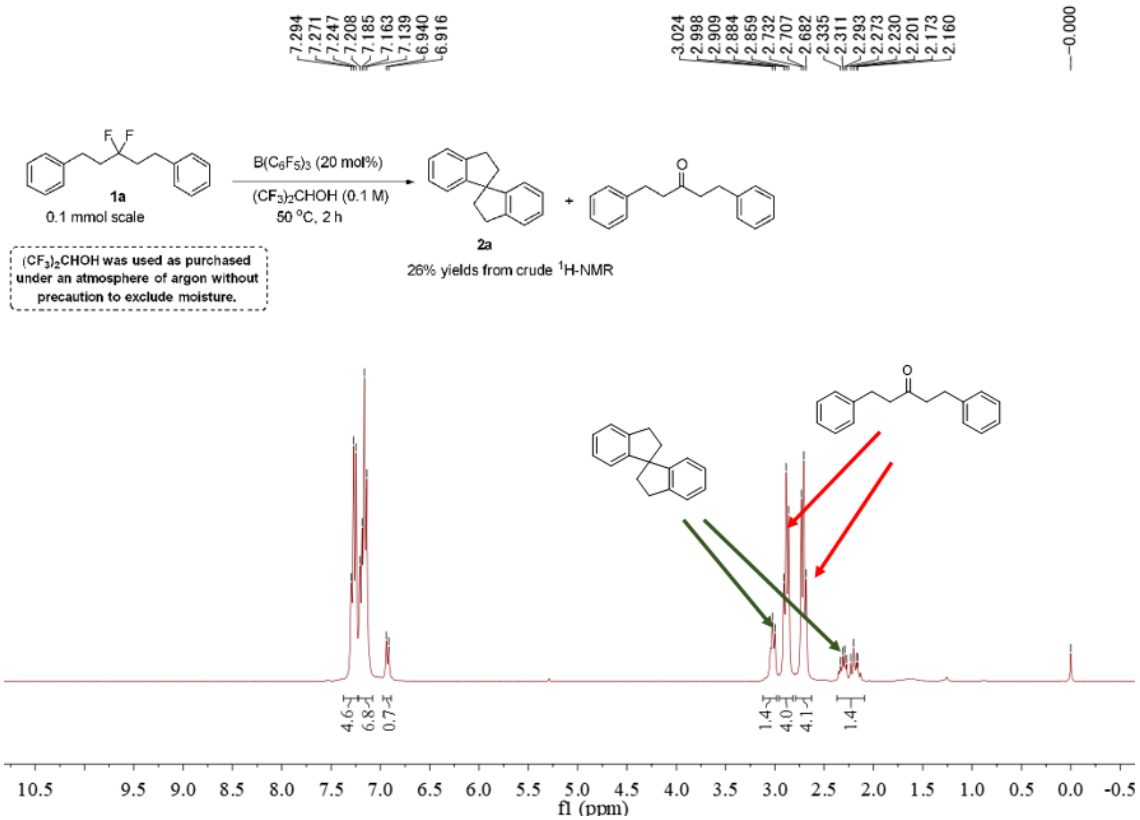


Figure S244. ^{1}H-NMR spectrum of **1v**, related to **Table 2**

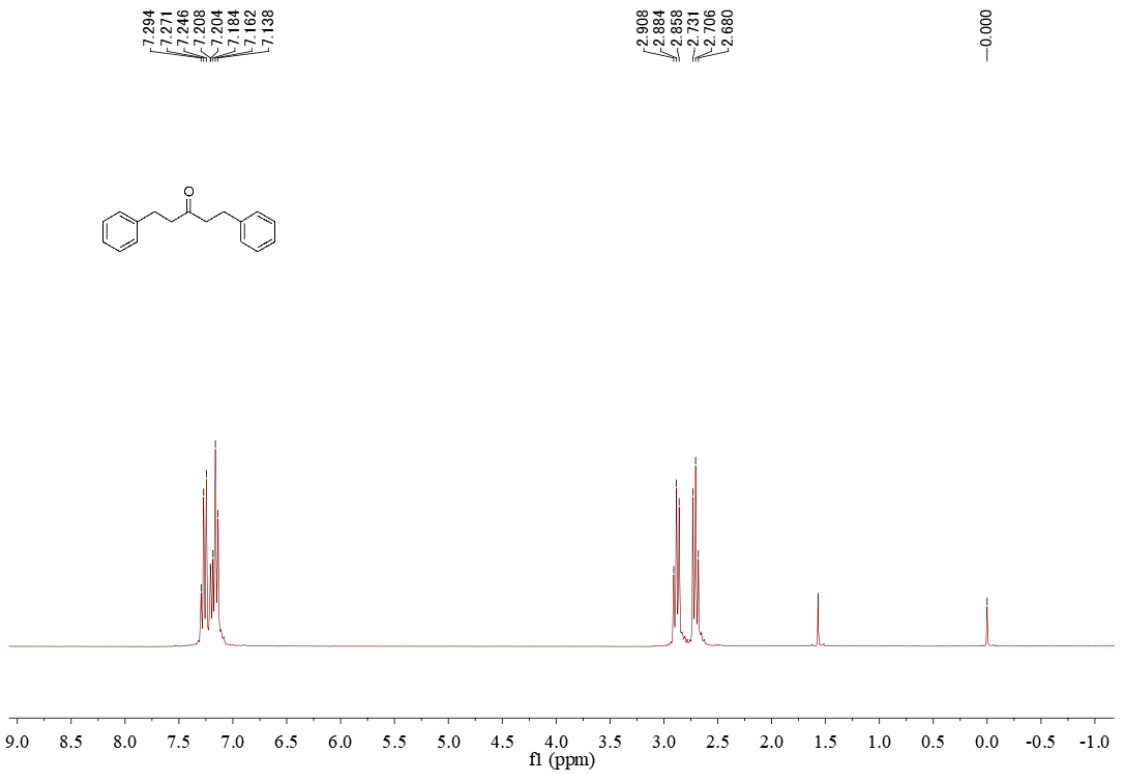


Figure S245. ^{1}H-NMR spectrum of **1w**, related to **Table 2**

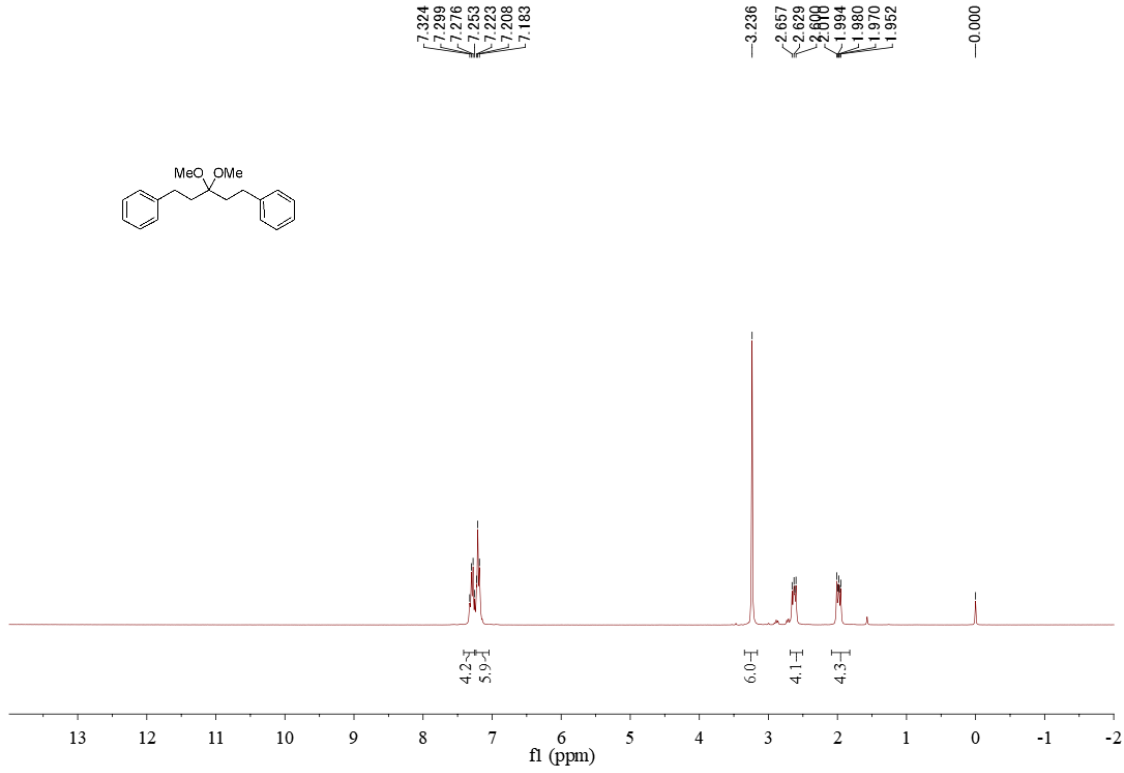


Figure S246. ^{1}H-NMR spectrum of **1x**, related to **Table 2**

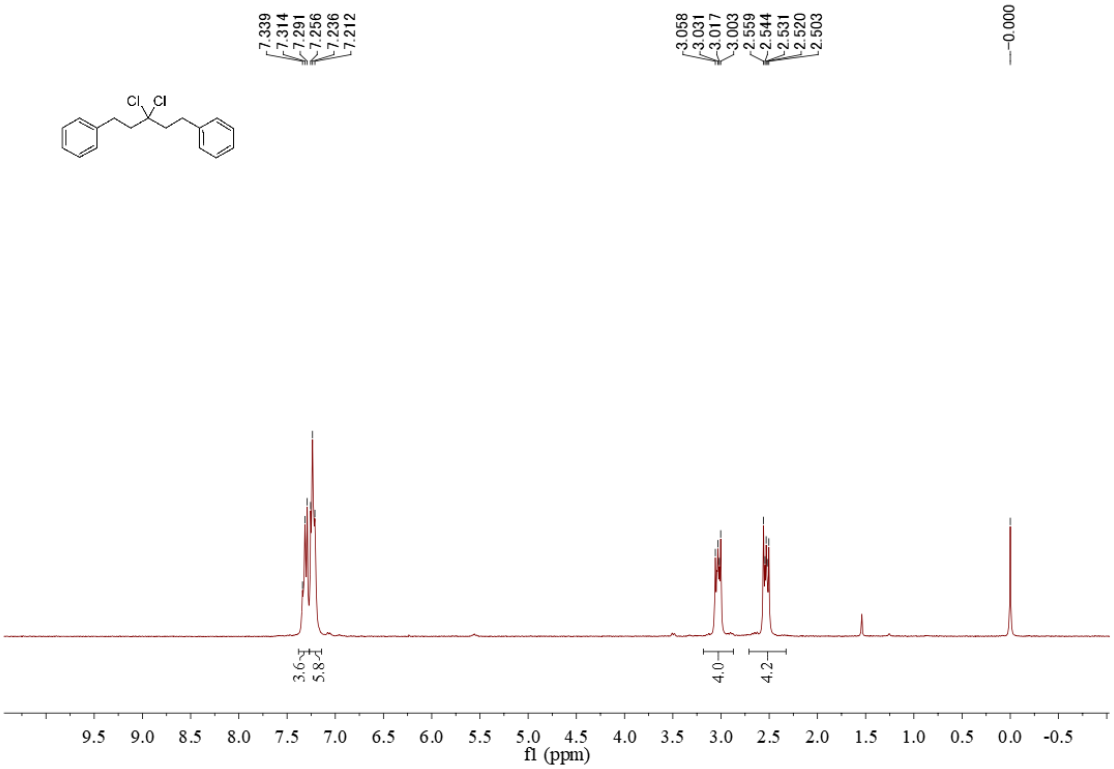


Figure S247. ^{1}H-NMR spectrum of **1y**, related to **Table 2**

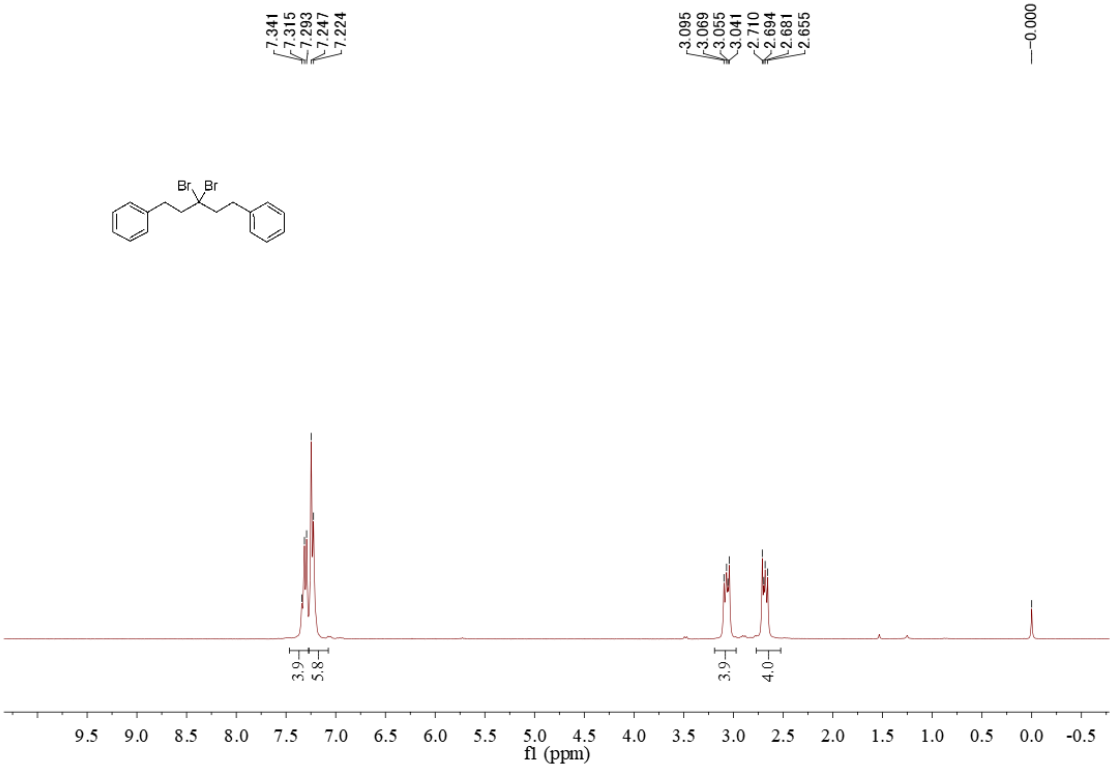


Figure S248. ^{1}H-NMR spectrum of **3x**, related to **Table 2**

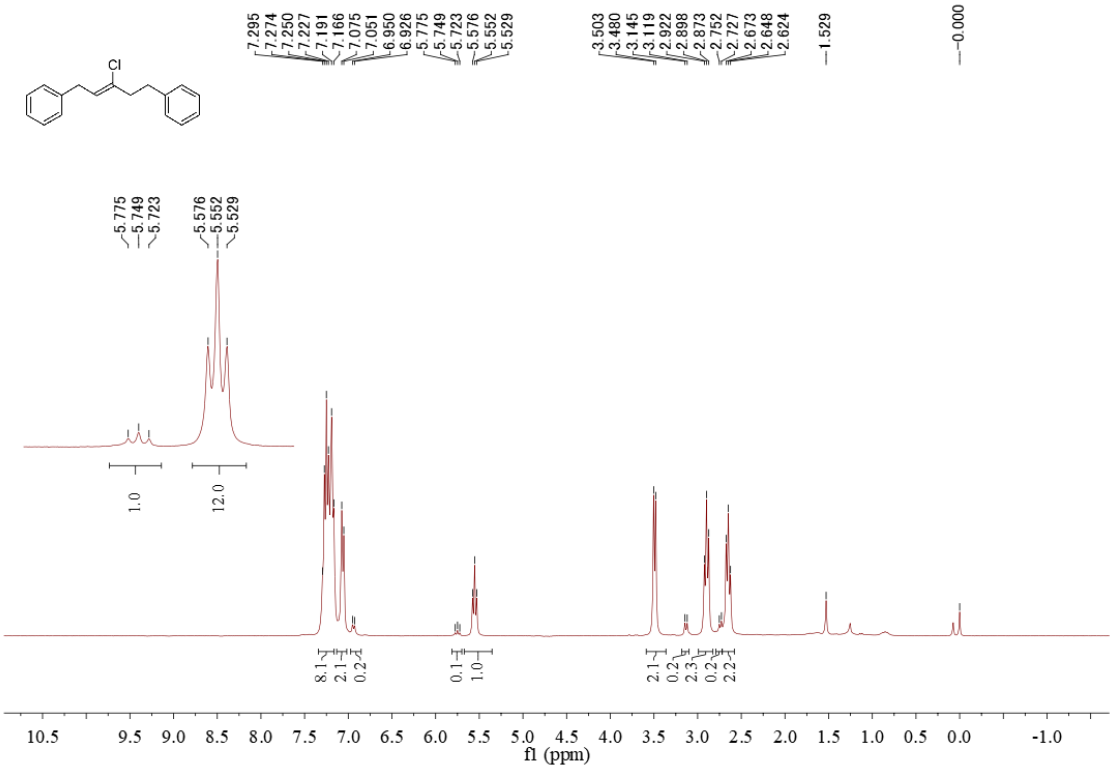


Figure S249. ^{1}H-NMR spectrum of **3y**, related to **Table 2**

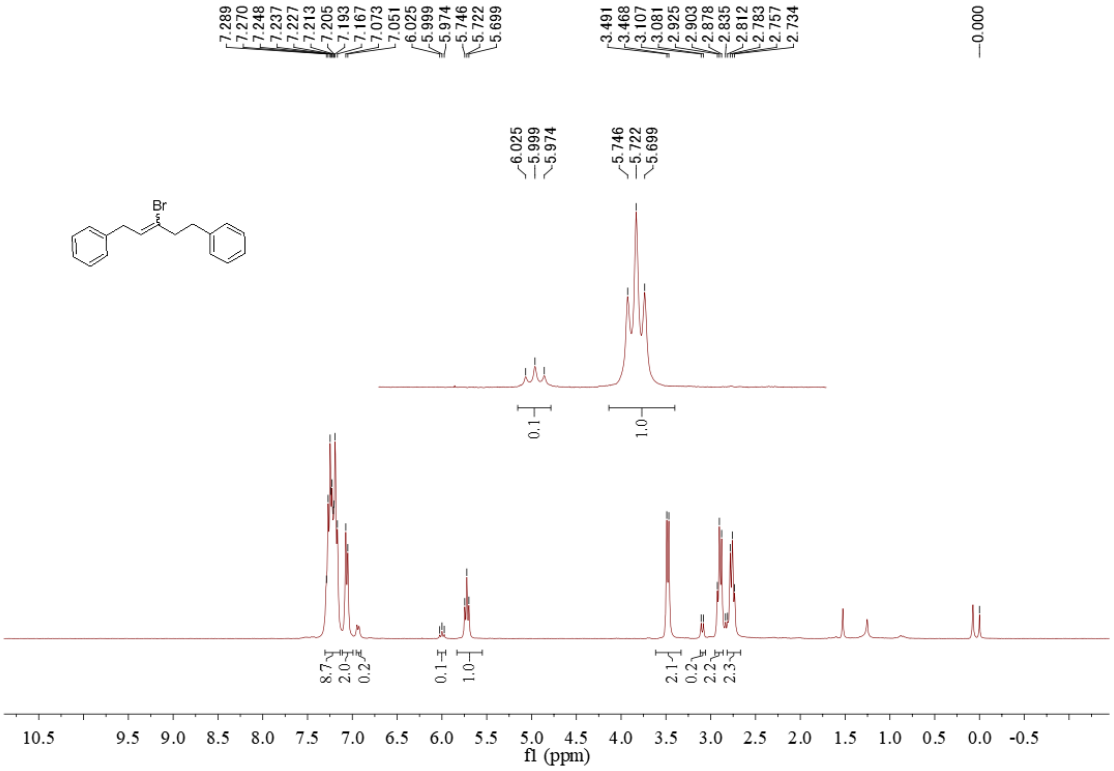


Figure S250. ^{13}C-NMR spectrum of **3y**, related to **Table 2**

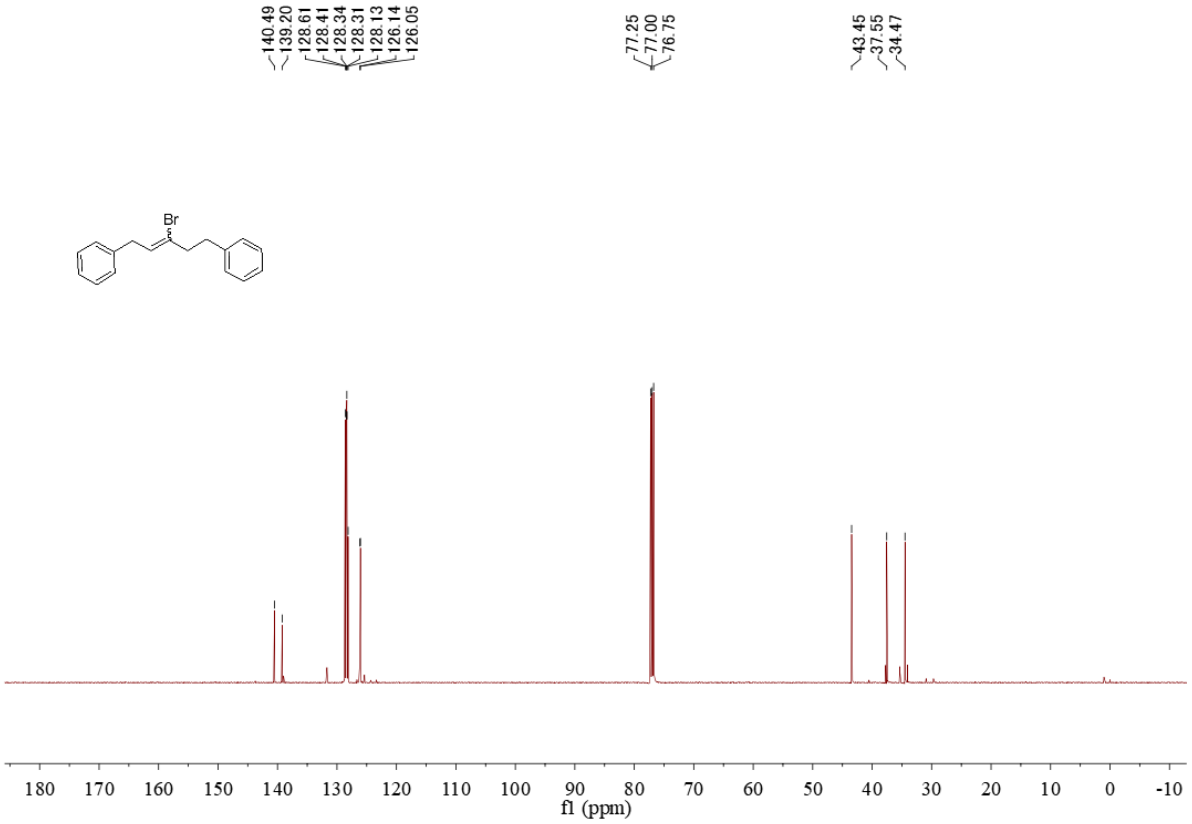


Figure S251. ^{1}H-NMR spectrum of crude reaction mixture of (3,3-dichloropentane-1,5-diyl)dibenzene (**1x**) and $(CF_3)_2CHOH$, related to **Table 2.**

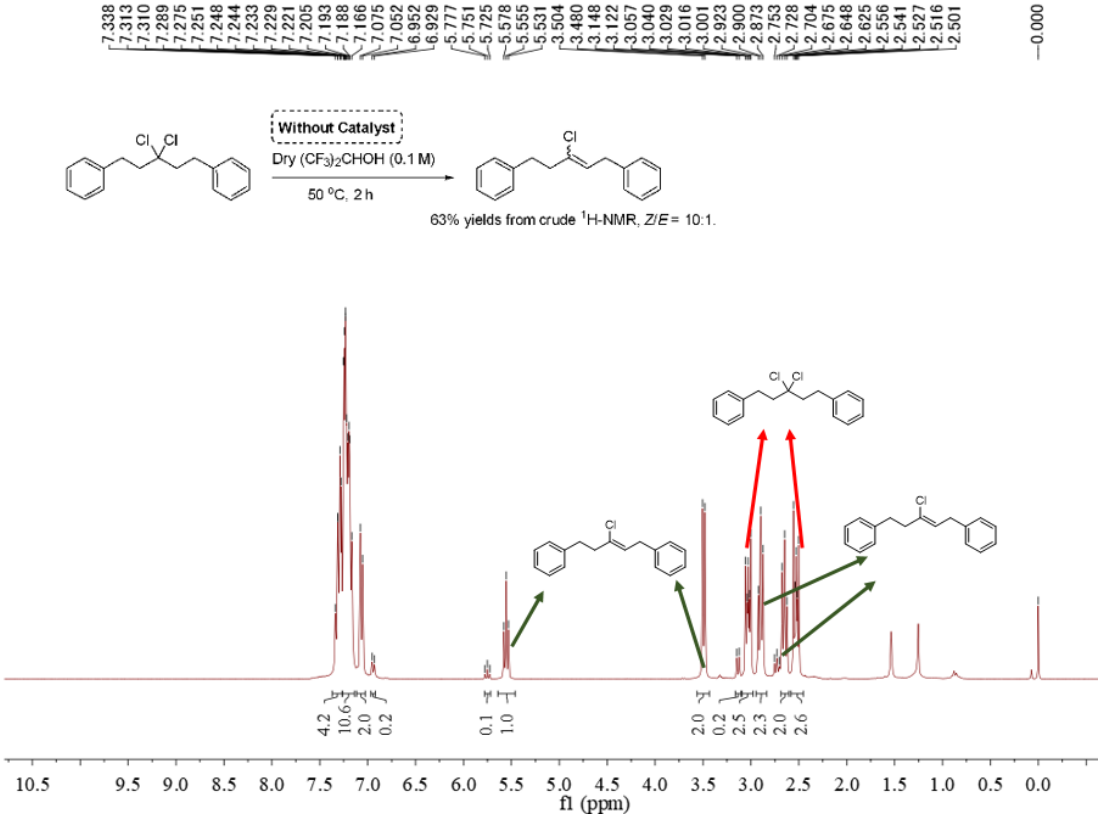


Figure S252. ^{1}H-NMR spectrum of crude reaction mixture of (3,3-dibromopentane-1,5-diyl)dibenzene (**1y**) and $(CF_3)_2CHOH$, related to **Table 2.**

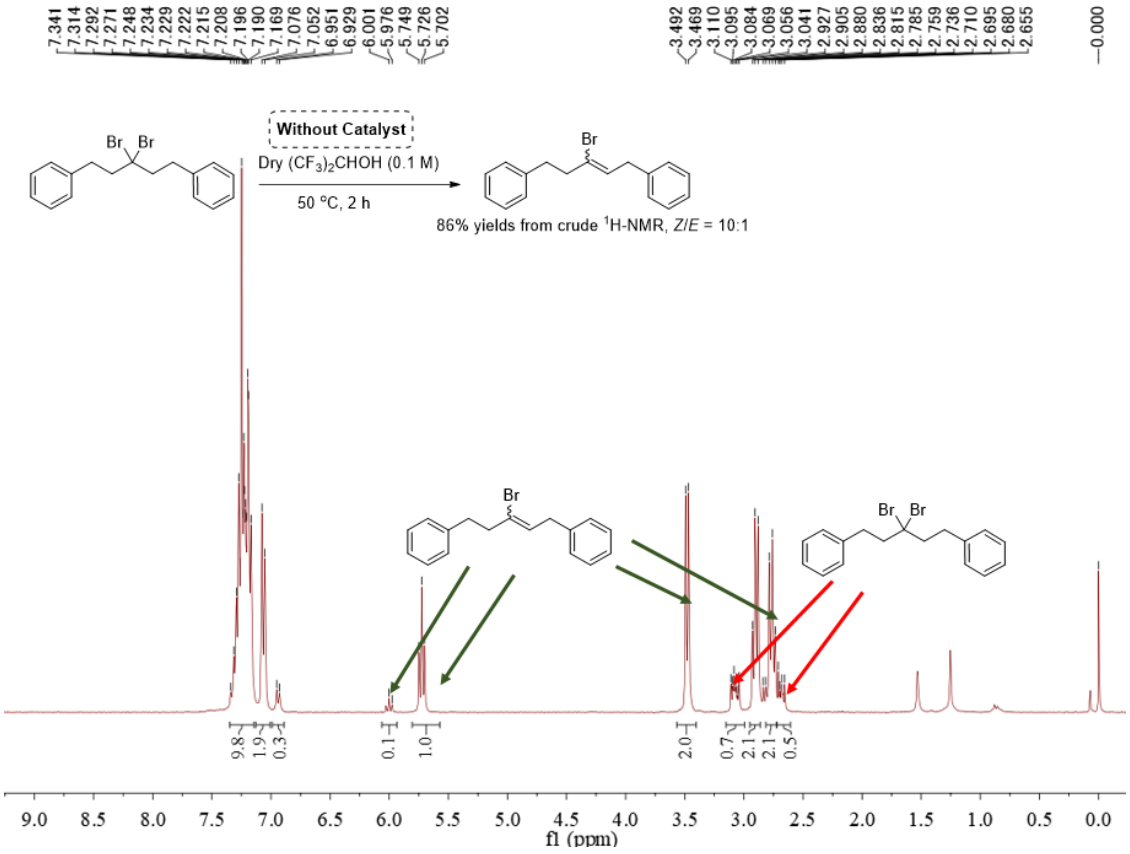
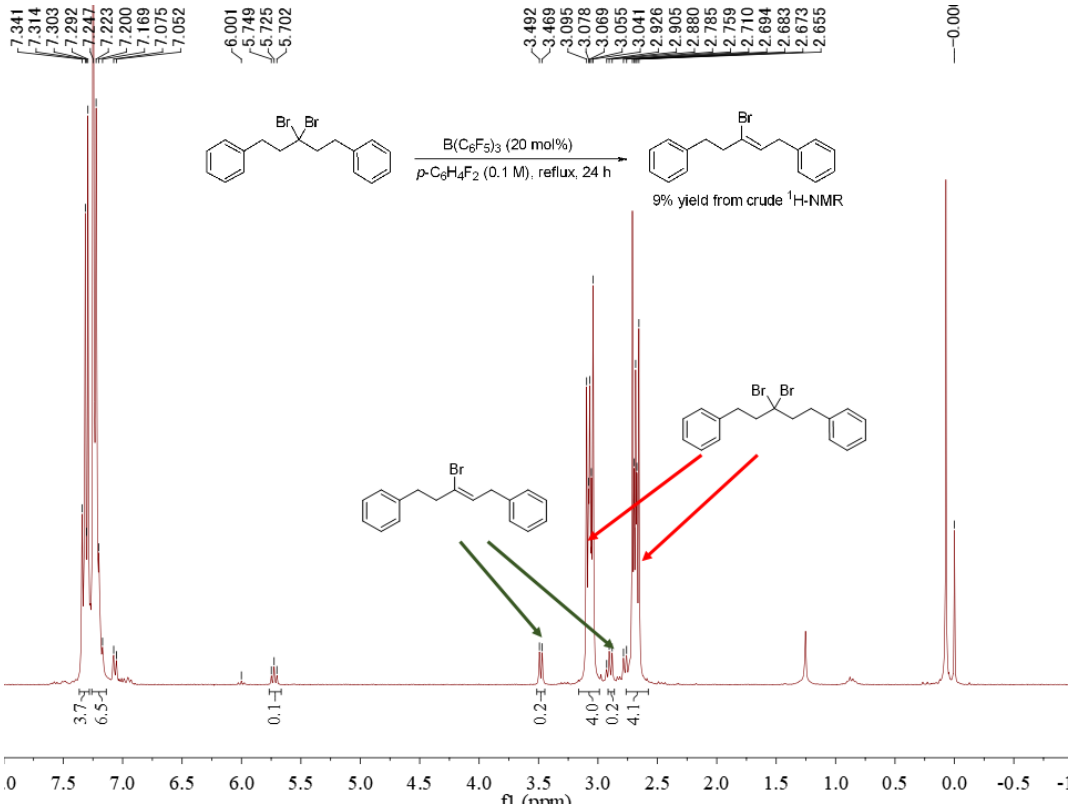
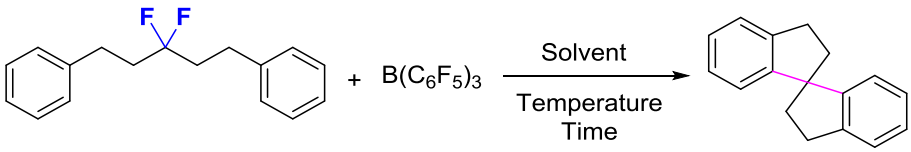


Figure S253 ^{1}H-NMR spectra copy of crude reaction mixture of (3,3-dibromopentane-1,5-diyl)dibenzene(**1y**)/$B(C_6F_5)_3$/*p*-$C_6H_4F_2$, related to **Table 2.**



Supplemental Table

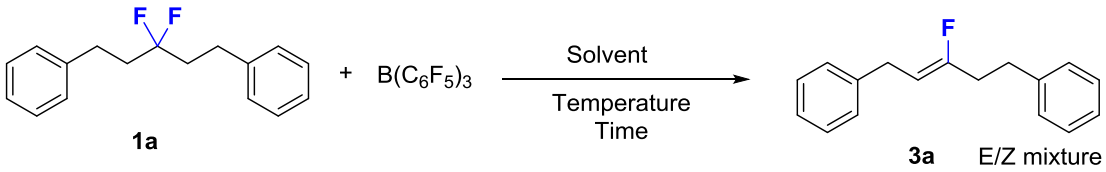
Table S1. Optimization of $B(C_6F_5)_3$ induced defluorinative Friedel-Crafts cyclization, related to **Table 1**.



Entry	$B(C_6F_5)_3$ (equiv)	Solvent	Concentration	Temperature (°C)	Time (h)	Yields (%)
1	2.2	CH_2Cl_2	0.1 M	RT	30	85
2	1.1	CH_2Cl_2	0.1 M	RT	30	31
3	0.2	CH_2Cl_2	0.1 M	RT	30	Trace
4	0.2	CH_2Cl_2	0.2 M	100[a]	2	Trace
5	0.2	CH_2Cl_2	2.0 M	100[a]	2	Trace
6	0.5	$MeNO_2$	2.0 M	RT	30	Trace
7	0.2	$(CF_3)_2CHOH$	2.0 M	100[a]	2	54
8	0.2	$(CF_3)_2CHOH$	0.25 M	100[a]	2	53
9	0.1	$(CF_3)_2CHOH$	0.25 M	100[a]	2	41
10	0.05	$(CF_3)_2CHOH$	0.25 M	100[a]	2	25
11	---	$(CF_3)_2CHOH$	0.25 M	100[a]	2	NR
12	0.2	$(CF_3)_2CHOH$/ DCM (1:9)	0.25 M	100[a]	2	Trace
13	0.2	$(CF_3)_2CHOH$	0.125 M	100[a]	2	71
14	0.2	$(CF_3)_2CHOH$ H_2O (2.2 equiv)	0.125 M	100[a]	2	0[b]
15	0.2	$(CF_3)_2CHOH$	0.125 M	50	2	75
16	0.2	$(CF_3)_2CHOH$	0.1 M	50	2	77
17	0.2	$(CF_3)_2CHOH$	0.1 M	RT	17	28
18	0.1	$(CF_3)_2CHOH$	0.1 M	50	20	16
19	0.2	$(CF_3)_2CHOH$	0.05 M	50	2	84
20	0.2	$(CF_3)_2CHOH$	0.05 M	50[c]	2	83
21	0.2	$(CF_3)_2CHOH$[d]	0.05 M	50	2	27[e]
22	0.2	$(CF_3)_2CHOH$ H_2O (2.2 equiv)	0.05 M	50	12	0[b]
23	---	$(CF_3)_2CHOH$	0.05 M	50	2	NR
24	0.2	Solkane-365	0.05 M	50	2	NR
25	0.2	iPrOH	0.05 M	50	2	NR
26	0.2	1,4-dioxane	0.05 M	50	2	NR
27	0.2	CF_3CH_2OH	0.05 M	50	2	NR
28	0.2	$(CF_3)_2PhOH$	0.05 M	100	2	NR

[a]Sealed tube. [b] The hydrolysis product 1,5-diphenylpentan-3-one was obtained in quantitative yield. [c]The reaction was conducted under microwave conditions. [d]$(CF_3)_2CHOH$ was used as purchased, without any precaution to exclude moisture. [e]1,5-diphenylpentan-3-one was observed as major product.

Table S2. Optimization of conditions for the synthesis of monofluoroalkenes, related to **Table 1.**



1a **3a** E/Z mixture

Entry	$B(C_6F_5)_3$ (equiv)	Solvent	Concentration	Temperature (^oC)	Time (h)	Yield[a] (%)	*Z*/*E*[a]
1	0.2	*o*-$C_6H_4Cl_2$	0.1 M	100	3	45	5.9:1
2	0.2	*o*-$C_6H_4Cl_2$	0.1 M	160	3	70	6.9:1
3	0.1	*o*-$C_6H_4Cl_2$	0.1 M	160	3	30	6.3:1
4	0.2	*o*-$C_6H_4Cl_2$	0.1 M	160	6	64	6.2:1
5	---	*o*-$C_6H_4Cl_2$	0.1 M	160	3	NR	---
6	0.2	*o*-$C_6H_4Cl_2$	0.25 M	180[b]	3	67	5.9:1
7	0.2	*o*-$C_6H_4Cl_2$	0.25 M	160	3	52	6.3:1
8	0.1	*o*-$C_6H_4Cl_2$	0.25 M	160	3	43	7.5:1
9	0.2	*o*-$C_6H_4Cl_2$	0.05 M	160	3	71	5.6:1
10	0.2	*o*-$C_6H_4Cl_2$	0.1 M	220[c]	3	81	7.3:1
11	0.2	*m*-$C_6H_4Cl_2$	0.1 M	160	3	13	---
12	0.2	Nitrobenzene	0.1 M	160	3	23	6.5:1
14	0.2	DMF	0.1 M	reflux	3	NR	---
15	0.2	DMSO	0.1 M	160	3	NR	---
16	0.2	*o*-$C_6H_4F_2$	0.1 M	reflux	3	75	6.9:1
17	0.2	*o*-$C_6H_4F_2$	0.1 M	reflux	24	87	7.1:1

[a]Determined by ^{19}F NMR analysis using $PhCF_3$ as the internal standard. [b]The reaction was conducted under microwave conditions. [c] Sealed tube.

Transparent Methods

General information

All reactions were performed in oven-dried and flame-dried glassware (10 mL) under a positive pressure of argon atmosphere unless mentioned otherwise. Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in ethanol/heat. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63-210 μm). The ^{1}H-NMR (300 MHz), ^{19}F-NMR (282 MHz), ^{13}C-NMR (125 MHz or 75 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker Avance 500, a Varian Mercury 300 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00) for ^{1}H-NMR. C_6F_6 [δ = −162.2 ($CDCl_3$)] was used as an internal standard for ^{19}F-NMR. Mass spectra were recorded on a SHIMAZU LCMS-2010EV (ESI-MS and APCI-MS) and SHIMADZU GCMS-QP5050A (EI-MS) using GC capillary column HYDRODEX-β-TBDAc (length: 25 m, i.d.: 0.25 mm). Helium was used as a carrier gas. Initial temperature: 50 ^{o}C, increase temperature at a rate: 40 ^{o}C/min until final temperature (230 ^{o}C), hold temperature for 15 min at 230 ^{o}C. Solvent delay: 3.0 minutes.High resolution mass spectrometry (HRMS) was recorded on a Waters, GCT Premier (EI-MS) with a TOF analyzer. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Melting points were recorded on a BUCHI M-565.

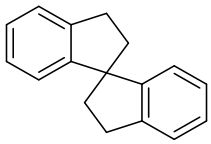
Super dehydrated solvents such as CH_2Cl_2, 1,4-dioxane and 1,2-dichlorobenznene (water max 0.001%) were purchased from Wako Pure Chemical Industries, Ltd. and used under argon atmosphere. 1,4-difluorobenzene and 1,1,1,3,3,3-hexafluoropropan-2-ol was purchased from Tokyo Chemical Industry Co., Ltd., and were dried and distilled from 4Å molecule sieves under argon atmosphere, and were stored in glove box. Tis(pentafluorophenyl)borane was purchased from Tokyo Chemical Industry Co., Ltd. (>98.0%, stored under Ar), and was used and stored in glove box with argon atmosphere.

Experimental Procedures

The preparation of spirobiindanes 2a-2t, related to Figure 2.

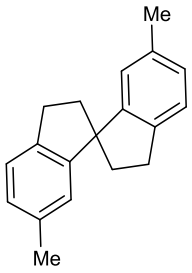
General procedure for the intramolecular Friedel-Craft reaction of *gem*-difluoroalkanes: In a flame-dried test tube (10 mL), *gem*-difluoroalkanes **1** (0.1 mmol) were added to a solution of $B(C_6F_5)_3$ (20 mol%) in dry HFIP (2.0 mL) at room temperature in a glovebox filled with argon. Subsequently, the tube was sealed with a rubber septum, removed from the glovebox and stirred at 50 ^oC for 2-4 h under a positive pressure of argon with a balloon. The resulting mixture was allowed to cool to room temperature and washed with water, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using *n*-hexane as the eluent to afford the desired spirobiindanes **2a**-**2t** in good yields.

2,2',3,3'-Tetrahydro-1,1'-spirobi[indene] **2a**



(3,3-Difluoropentane-1,5-diyl)dibenzene **1a** (26.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 ^oC for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2a** (18.8 mg, 84%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34–7.24 (m, 2H), 7.24–7.08 (m, 4H), 6.99–6.86 (m, 2H), 3.10–2.94 (m, 4H), 2.34-2.23 (m, 2H), 2.25–2.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 143.7, 126.65, 126.63, 124.3, 123.4, 60.7, 40.5, 30.8. MS (EI, *m*/*z*) 220 $[M]^+$

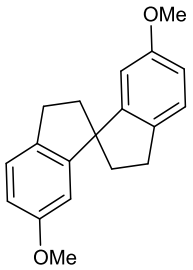
6,6'-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2b**



4,4'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1b** (28.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 ^oC for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2a** (17.3 mg, 69%) as a white solid, mp = 84–86 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.6 Hz, 2H), 7.08–6.98 (m, 2H), 6.78 (s, 2H), 2.99 (dd, *J* = 8.0, 6.0 Hz, 4H), 2.39–2.16 (m, 8H), 2.23–2.08 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 140.7, 136.2, 127.5, 124.1, 124.0, 60.6, 40.8, 30.5, 21.3. IR (KBr): 2929, 2852, 1490, 1459, 1380, 809 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{20}^+$ $[M^+]$: 248.1565 found

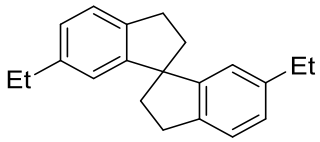
248.1573.

6,6'-Dimethoxy-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2c**



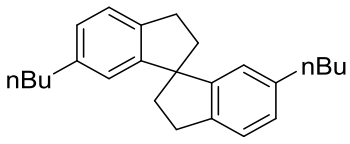
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) **1c** (32.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2c** (9.7 mg, 27%) as a white solid, mp = 129–131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.2 Hz, 2H), 6.75 (dd, *J* = 8.2, 2.5 Hz, 2H), 6.49 (d, *J* = 2.4 Hz, 2H), 3.72 (s, 6H), 2.98–2.83 (m, 4H), 2.34–2.21 (m, 2H), 2.24–1.95 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 151.7, 135.7, 124.8, 112.8, 108.7, 61.2, 55.4, 40.9, 30.1. IR (KBr): 2937, 2832, 1614, 1479, 1364, 1284, 821 cm^{-1}. MS (EI, *m*/*z*) 280 [M$^+$]. HRMS (EI) calcd. for $C_{19}H_{20}O_2^+$ [M$^+$]: 280.1463 found 280.1466.

6,6'-Diethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2d**



4,4'-(3,3-Difluoropentane-1,5-diyl)bis(ethylbenzene) **1d** (31.5 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2d** (17.6 mg, 62%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.16 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.79 (s, 2H), 2.98–2.86 (m, 4H), 2.57 (q, *J* = 7.5 Hz, 4H), 2.31–2.03 (m, 4H), 1.17 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 142.8, 141.1, 126.2, 124.0, 122.9, 60.6, 40.7, 30.4, 28.8, 15.9. IR (KBr): 2960, 2933, 2852, 1482, 1463, 1373, 885, 813 cm^{-1}. MS (EI, *m*/*z*) 276 [M$^+$]. HRMS (EI) calcd. for $C_{21}H_{24}^+$ [M$^+$]: 276.1878 found 276.1884.

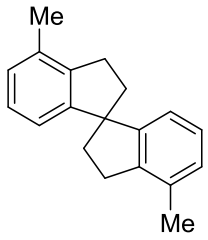
6,6'-Dibutyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2e**



4,4'-(3,3-Difluoropentane-1,5-diyl)bis(butylbenzene) **1e** (37.2 mg, 0.1 mmol) was added to a solution of

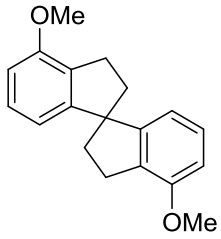
tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2e** (19.7 mg, 59%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.6 Hz, 2H), 7.05–6.96 (m, 2H), 6.77 (s, 2H), 2.99–2.86 (m, 4H), 2.54–2.46 (m, 4H), 2.37–2.24 (m, 2H), 2.21–2.12 (m, 2H), 1.53–1.44 (m, 4H), 1.30 (dq, *J* = 14.5, 7.2 Hz, 4H), 0.88 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 141.5, 141.1, 126.8, 123.9, 123.5, 60.6, 40.8, 35.6, 34.0, 30.5, 22.5, 13.9. IR (KBr): 2948, 2925, 2860, 1606, 1488, 1454, 1378, 829, 732 cm^{-1}. MS (EI, *m*/*z*) 332 [M^+]. HRMS (EI) calcd. for $C_{25}H_{32}^+$ [M^+]: 332.2504 found 332.2519

4,4'-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2f**



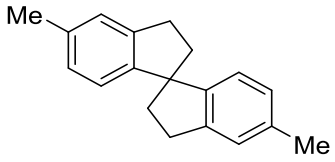
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1f** (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2f** (22.8 mg, 90%) as a white solid, mp = 89–90 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.11–6.99 (m, 4H), 6.76 (d, *J* = 7.2 Hz, 2H), 2.95–2.89 (m, 4H), 2.34–2.25 (m, 8H), 2.22–2.04 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 142.5, 133.5, 127.4, 126.8, 120.7, 61.1, 40.3, 29.3, 19.1. IR (KBr): 2937, 2848, 1590, 1494, 1376, 782, 765 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{20}^+$ [M^+]: 248.1565 found 248.1567.

4,4'-Dimethoxy-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2g**



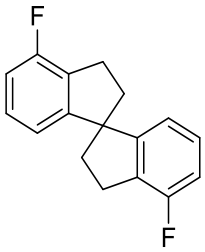
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) **1g** (32.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2g** (10.5 mg, 37%) as a white solid, mp = 107-109 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 7.5 Hz, 2H), 3.87 (s, 6H), 2.99–2.81 (m, 4H), 2.30–2.21 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 152.3, 131.1, 128.2, 115.8, 108.1, 61.7, 55.2, 40.4, 27.4. IR (KBr): 2952, 2840, 1687, 1463, 1315, 1255, 775 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{20}O_2^+$ [M^+]: 280.1463 found 280.1460.

5,5'-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2h**



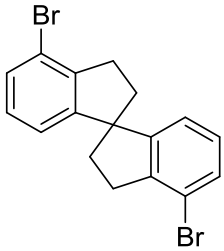
3,3'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1h** (28.8mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2h** (19.6 mg, 78%) as a colorless oil. The isolated **2h** was obtained with impure isomers (ratio about 9:1, based on integrals of methyl peak in ^{1}H-NMR, and GC-MS analysis). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.7 Hz, 2H), 2.99–2.87 (m, 4H), 2.33–2.23 (m, 8H), 2.22–2.16 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 143.9, 136.2, 127.4, 125.0, 123.0, 59.9, 40.7, 30.7, 21.2. IR (KBr): 3004, 2940, 2948, 1610, 1490, 1448, 1376, 809, 771 cm^{-1}. MS (EI, *m*/*z*) 248 [M$^+$]. HRMS (EI) calcd. for $C_{19}H_{20}^+$ [M$^+$]:248.1565 found 248. 1577.

4,4'-Difluoro-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2i**



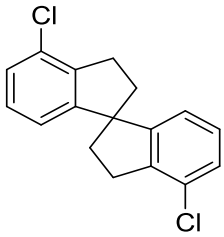
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(fluorobenzene) **1i** (29.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2i** (14.9 mg, 57%) as a white solid, mp = 96–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.08 (m, 2H), 6.96–6.86 (m, 2H), 6.70 (d, *J* = 7.5 Hz, 2H), 3.13–2.97 (m, 4H), 2.35 (ddd, *J* = 11.6, 7.5, 2.0 Hz, 2H), 2.26–2.16 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.19 (d, *J* = 246.6 Hz), 153.50 (d, *J* = 5.6 Hz), 129.55 (d, *J* = 18.3 Hz), 128.75 (d, *J* = 6.9 Hz), 118.96 (d, *J* = 3.3 Hz), 113.43 (d, *J* = 20.6 Hz), 61.6, 40.5, 26.70. IR (KBr): 2944, 1614, 1585, 1455, 1241 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{14}F_2^+$ [M$^+$]: 256.1064 found 256.1057.

4,4'-Dibromo-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2j**



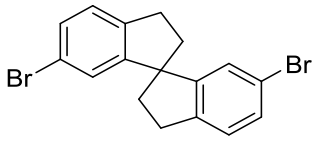
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) **1j** (41.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2j** (30.1 mg, 79%) as a white solid 100-102 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.31 (m, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 3.07–2.99 (m, 4H), 2.33–2.25 (m, 2H), 2.24–2.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 143.9, 130.1, 128.7, 122.2, 119.9, 63.2, 39.8, 32.3. IR (KBr): 2940, 1565, 1442, 1307, 775, 678 cm^{-1}. MS (EI, *m*/*z*) 375 [M^+]. HRMS (EI) calcd. for $C_{17}H_{14}Br_2^+$ [M^+]: 375.9462 found 375. 9452

4,4'-Dichloro-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2k**



2,2'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) **1k** (32.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2k** (23.3 mg, 77%) as a white solid, mp = 116-118 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 2H), 3.15–2.96 (m, 4H), 2.34 (ddd, *J* = 11.7, 7.3, 4.2 Hz, 2H), 2.26–2.17 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 141.7, 130.6, 128.4, 126.9, 121.6, 62.6, 39.9, 30.1. IR (KBr): 2937, 2844, 1590, 1459, 1415, 1099, 817, 725 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{14}Cl_2^+$ [M^+]: 288.0473 found 288.0481.

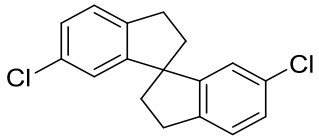
6,6'-Dibromo-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2l**



4,4'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) **1l** (41.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture

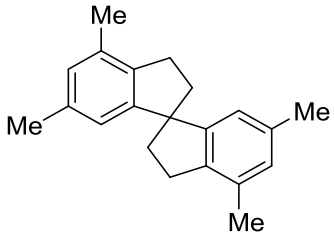
was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2l** (24.4 mg, 64%) as a white solid, mp = 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 1.5 Hz, 2H), 2.96 (dd, *J* = 8.2, 6.0 Hz, 4H), 2.32–2.23 (m, 2H), 2.24–2.16 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 142.5, 129.9, 126.4, 126.0, 120.4, 60.8, 40.6, 30.3. IR (KBr): 2944, 2840, 1583, 1479, 1396, 1064, 809, 638 cm^{-1}. HRMS (EI) calcd. for Chemical Formula: $C_{17}H_{14}Br_2^+$ [M^+]: 375.9462 found 375.9454.

6,6'-Dichloro-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2m**



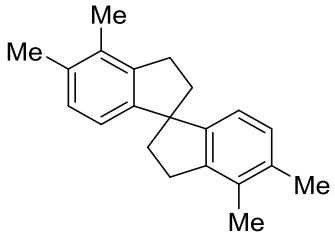
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) **1m** (32.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2m** (18.9 mg, 65%) as a white solid, mp = 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.14 (m, 4H), 6.87 (d, *J* = 1.3 Hz, 2H), 2.97 (dd, *J* = 8.4, 5.9 Hz, 4H), 2.35–2.14 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 141.9, 132.4, 127.1, 125.5, 123.5, 60.8, 40.6, 30.2. IR (KBr): 2937, 2844, 1590, 1415, 1459, 1099, 877, 725 cm^{-1}. MS (EI, *m/z*) 288 [M^+]. HRMS (EI) calcd. for Chemical Formula: $C_{17}H_{14}Cl_2^+$ [M^+]: 288.0473 found 288.0476.

4,4',6,6'-Tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2n**



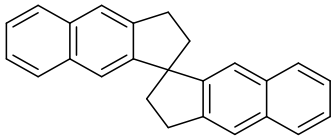
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) **1n** (31.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2n** (26.5 mg, 95%) as a white solid, mp = 149–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 2H), 6.59 (s, 2H), 2.87 (t, *J* = 7.6 Hz, 4H), 2.28 (s, 6H), 2.25–1.94 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 139.5, 136.4, 133.2, 128.4, 121.3, 60.9, 40.6, 28.9, 21.2, 19.0. IR (KBr): 2917, 2848, 1594, 1448, 1471, 1376 cm^{-1}. MS (EI, *m/z*) 276 [$M]^+$. HRMS (EI) calcd. for $C_{21}H_{24}^+$ [M^+]: 276.1878 found 276.1886.

4,4',5,5'-Tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2o**



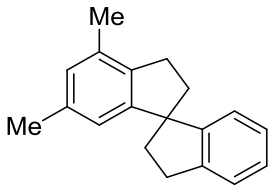
3,3'-(3,3-Difluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) **1o** (31.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 ^oC for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2o** (23.7 mg, 85%) as a white solid, mp = 140–141 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 2.93 (dd, *J* = 11.6, 6.0 Hz, 4H), 2.25–2.24 (m, 8H), 2.22 (s, 6H), 2.19–2.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 142.7, 134.6, 132.1, 128.4, 120.4, 61.1, 40.6, 29.7, 19.6, 15.9. IR (KBr): 2996, 2933, 2857, 1605, 1475, 1452, 1373 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{24}^+$ [M^+]: 276.1878 found 276.1879.

2,2',3,3'-Tetrahydro-1,1'-spirobi[cyclopenta[b]naphthalene] **2p**



2,2'-(3,3-Difluoropentane-1,5-diyl)dinaphthalene **1p** (36.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 ^oC for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2l** (28.6 mg, 84%) as a white solid. M.p 49-51 ^oC ^1H NMR (300 MHz, $CDCl_3$) δ 7.82–7.75 (m, 4H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.38–7.25 (m, 6H), 3.24–3.14 (m, 4H), 2.47–2.33 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 143.0, 133.2, 133.1, 127.8, 127.4, 125.1, 124.9, 122.3, 121.6, 59.9, 41.3, 30.5. IR (KBr): 2933, 2848, 1598, 1448, 1259, 750 cm^{-1}. MS (EI, m/z) 320 [M^+] HRMS (EI) calcd. for $C_{25}H_{20}^+$ [M^+]: 320.1565 found 320.1568.

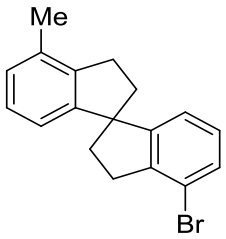
4,6-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2q**



1-(3,3-Difluoro-5-phenylpentyl)-2,4-dimethylbenzene **1q** (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture

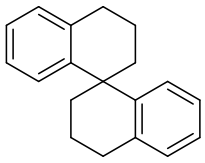
was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2q** (10.8 mg, 42%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 6.6 Hz, 1H), 7.25–7.14 (m, 2H), 6.95 (d, *J* = 6.9 Hz, 1H), 6.85 (s, 1H), 6.58 (s, 1H), 3.03–2.85 (m, 4H), 2.36–2.24 (m, 5H), 2.23 (s, 3H), 2.20–2.12 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 150.4, 143.8, 139.6, 136.6, 133.3, 128.6, 126.6, 126.5, 124.3, 123.5, 121.3, 60.9, 40.7, 40.4, 30.9, 29.1, 21.2, 19.1. IR (KBr): 2937, 2852, 1610, 1479, 1463, 850, 754, 730 cm^{-1}. MS (EI, m/z) 248 [M^+]. HRMS (EI) calcd. for $C_{19}H_{20}^+$ [M^+]: 248.1565 found 248.1567.

4-Bromo-4'-methyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] **2r**



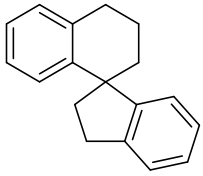
1-Bromo-2-(3,3-difluoro-5-(o-tolyl)pentyl)benzene **1r** (35.3 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2r** (24.3 mg, 69%) as a white solid, mp = 83–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.10–7.03 (m, 3H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.1 Hz, 1H), 3.06–2.98 (m, 2H), 2.98–2.90 (m, 2H), 2.32–2.21 (m, 5H), 2.26–2.16 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 149.6, 143.9, 142.3, 133.7, 129.6, 128.5, 127.7, 127.0, 122.3, 120.6, 119.8, 62.2, 40.3, 39.5, 32.2, 29.3, 19.1. IR (KBr): 3075, 2932, 2848, 1598, 1486, 1438, 750, 615 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{17}Br^+$ [M^+]: 312.0514 found 312.0517.

3,3',4,4'-Tetrahydro-2H,2'H-1,1'-spirobi[naphthalene] **2s**



(4,4-Difluoroheptane-1,7-diyl)dibenzene **1s** (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2s** (22.7 mg, 90%) as a white solid, mp = 56–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–6.99 (m, 6H), 6.77 (d, *J* = 7.5 Hz, 2H), 2.96–2.87 (m, 4H), 2.16–2.10 (m, 2H), 1.94–1.83 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 137.1, 130.2, 128.5, 125.7, 125.2, 42.9, 38.8, 30.3, 19.5. IR (KBr): 2952, 2852, 1579, 1479, 1448 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{20}^+$ [M^+]: 248.1565 found 248.1571.

2,3,3',4'-Tetrahydro-2'H-spiro[indene-1,1'-naphthalene] **2t**

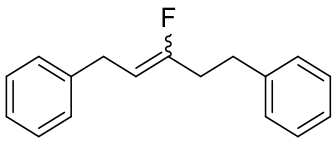


(3,3-Difluorohexane-1,6-diyl)dibenzene **1t** (27.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2t** (21.7 mg, 88%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (t, *J* = 6.9 Hz, 2H), 7.08–6.99 (m, 4H), 6.84 (dd, *J* = 14.5, 7.3 Hz, 2H), 2.94–2.84 (m, 4H), 2.36–2.25 (m, 2H), 1.95–1.84 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 144.2, 143.6, 137.1, 129.0, 128.6, 126.6, 126.4, 125.8, 125.6, 124.2, 124.2, 52.4, 43.1, 36.2, 30.2, 30.1, 20.6. IR (KBr): 2937, 2840, 1592, 1563, 1450, 1307 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{18}^+$ [M$^+$]: 234.1409 found 234.1411.

General procedure for the preparation of monofluoroalkene 3, related to Figure 2.

In a flame-dried test tube, *gem*-difluoroalkanes **1** (0.1 mmol) were added to a solution of $B(C_6F_5)_3$ (20 mol%) in dry 1,4-difluorobenzene (1.0 mL) at room temperature in a glovebox filled with argon. Subsequently, the tube was sealed with a rubber septum, removed from the glovebox and heated to reflux for 24-48 h under a positive pressure of argon with a balloon. The resulting mixture was allowed to cool to room temperature and washed with water, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using *n*-hexane as the eluent to give the desired monofluoroalkene **3**.

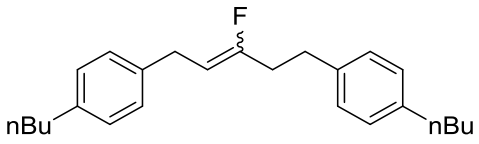
(3-Fluoropent-2-ene-1,5-diyl)dibenzene **3a**



(3,3-Difluoropentane-1,5-diyl)dibenzene **1a** (26.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **2a** (20.3 mg, 84%) as a colorless oil. The ratio for *Z*/*E* isomers (7.1:1) was determined by ^{19}F-NMR. (*Z*)-**3a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.15 (m, 8H), 7.12 (d, *J* = 6.8 Hz, 2H), 4.68 (dt, *J* = 36.8, 7.6 Hz, 1H), 3.41 (d, *J* = 7.5 Hz, 2H), 2.87–2.81 (m, 2H), 2.53 (dt, *J* = 16.2, 6.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (d, *J* = 254.5 Hz), 140.7, 140.5 (d, *J* = 1.7 Hz), 128.4, 128.4, 128.3, 128.2, 126.1, 125.9, 104.6 (d, *J* = 15.2 Hz), 33.9 (d, *J* = 27.5 Hz), 32.5 (d, *J* = 1.0 Hz), 29.8 (d, *J* = 5.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.7 (dt, *J* = 36.2, 17.5 Hz, 1F). IR (KBr): 3087, 3023, 2933, 2852, 1710, 1610, 1486, 1452, 1068, 943 cm^{-1}. MS (EI, *m/z*) 240 [M]$^+$. HRMS (EI) calcd. for $C_{17}H_{17}F^+$ [M$^+$]: 240.1314,

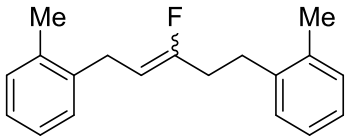
found 240.1325.

4,4'-(3-Fluoropent-2-ene-1,5-diyl)bis(butylbenzene) **3e**



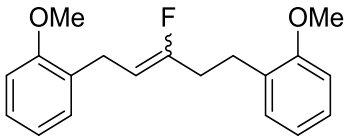
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(butylbenzene) **1e** (37.2, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3e** (24.5 mg, 69%) as a colorless oil. The ratio for *Z*/*E* isomers (10.0:1) was determined by ^{19}F-NMR. (*Z*)-**3e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–6.97 (m, 8H), 4.66 (dt, *J* = 36.9, 7.5 Hz, 1H), 3.36 (d, *J* = 7.4 Hz, 2H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.65–2.54 (m, 6H), 1.58–1.51 (m, 4H), 1.35 (dd, *J* = 14.6, 7.3 Hz, 4H), 0.92 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.02 (d, *J* = 254.2 Hz), 140.6, 140.5, 137.9, 137.74 (d, *J* = 1.5 Hz), 128.41, 128.40, 128.3, 128.1, 104.77 (d, *J* = 15.2 Hz), 35.3, 35.2, 34.07 (d, *J* = 27.4 Hz), 33.75 (d, *J* = 2.3 Hz), 32.1, 29.4, 29.3, 22.42 , 22.40, 14.00, 13.98. ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.3 (dt, *J* = 36.9, 17.2 Hz, 1F). IR (KBr): 3012, 2956, 2925, 2857, 1511, 1452, 1378, 1112, 798 cm^{-1}. HRMS (EI) calcd. for $C_{25}H_{33}F^+$ [M$^+$]: 352.2566, found 352.2569.

2,2'-(3-Fluoropent-2-ene-1,5-diyl)bis(methylbenzene) **3f**



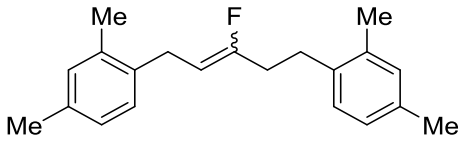
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1f** (28.8, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3f** (17.3 mg, 60%) as a colorless oil. The ratio for *Z*/*E* isomers (9.1:1) was determined by ^{19}F-NMR. (*Z*)-**3f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.06 (m, 8H), 4.64 (dt, *J* = 36.9, 7.4 Hz, 1H), 3.39 (d, *J* = 7.4 Hz, 2H), 2.84–2.77 (m, 2H), 2.49–2.38 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.12 (d, *J* = 254.6 Hz), 138.9, 138.70 (d, *J* = 1.5 Hz), 136.2, 135.9, 130.2, 130.1, 128.8, 128.6, 126.32 (d, *J* = 4.5 Hz), 126.2, 126.07, 126.05, 103.9 (d, *J* = 15.2 Hz), 32.9 (d, *J* = 27.6 Hz), 30.00 (d, *J* = 14.6 Hz), 27.7 (d, *J* = 5.8 Hz), 19.3, 19.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.17 (dt, *J* = 36.2, 17.8 Hz, 1F). IR (KBr): 3056, 2921, 2877, 1710, 1594, 14886, 1255, 1145, 1101, 738 cm^{-1}. MS (EI, *m/z*) 268 [M]$^+$. HRMS (EI) calcd. for $C_{19}H_{21}F^+$ [M$^+$]: 268.1627, found 268.1633.

2,2'-(3-Fluoropent-2-ene-1,5-diyl)bis(methoxybenzene) **3g**



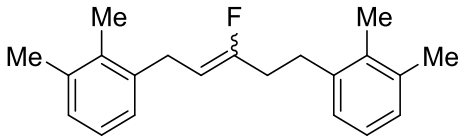
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) **1g** (32.0, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3g** (15.9 mg, 53%) as a colorless oil. The ratio for *Z*/*E* isomers (5.8:1) was determined by ^{19}F-NMR. (*Z*)-**3g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.16 (m, 4H), 6.94–6.72 (m, 4H), 4.69 (dt, *J* = 37.4, 7.5 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.38 (d, *J* = 7.4 Hz, 2H), 2.85–2.79 (m, 2H), 2.51–2.40 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.69 (d, *J* = 254.1 Hz), 157.4, 157.1, 130.0, 129.3, 129.2, 128.9, 127.3, 127.0, 120.39, 120.32, 110.13, 110.03, 103.41 (d, *J* = 15.0 Hz), 55.26, 55.16, 32.22 (d, *J* = 27.4 Hz), 27.44 (d, *J* = 1.4 Hz), 24.01 (d, *J* = 6.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.32 (dt, *J* = 37.4, 17.3 Hz, 1F). IR (KBr): 3019, 2952, 2832, 1702, 1602, 1486, 1459, 1243, 1108, 1025 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{21}FO_2^+$ [M^+]: 300.1526, found 300.1532.

4,4'-(3-Fluoropent-2-ene-1,5-diyl)bis(1,3-dimethylbenzene) **3n**



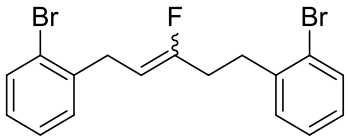
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) **1n** (31.6, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3g** (15.0 mg, 50%) as a colorless oil. The ratio for *Z*/*E* isomers (9.1:1) was determined by ^{19}F-NMR. (*Z*)-**3n**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03–6.84 (m, 6H), 4.60 (dt, *J* = 37.1, 7.4 Hz, 1H), 3.34 (d, *J* = 7.4 Hz, 2H), 2.81–2.74 (m, 2H), 2.45–2.34 (m, 2H), 2.28 (s, 6H), 2.26 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.01 (d, *J* = 254.3 Hz), 136.0, 135.9, 135.68, 135.66, 135.64, 135.63, 131.0, 130.9, 128.7, 128.5, 126.6, 126.5, 103.99 (d, *J* = 15.2 Hz), 32.95 (d, *J* = 27.5 Hz), 29.6, 27.25 (d, *J* = 5.8 Hz), 20.90, 20.89, 19.22, 19.13. ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.37 (dt, *J* = 37.0, 17.7 Hz, 1F). IR (KBr): 3004, 2917, 2869, 1698, 1610, 1496, 1375, 1268, 1089 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{25}F^+$ [M^+]: 296.1940, found 296.1954.

3,3'-(3-Fluoropent-2-ene-1,5-diyl)bis(1,2-dimethylbenzene) **3o**



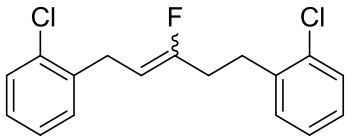
3,3'-(3,3-Difluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) **1o** (31.6, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3o** (20.5 mg, 70%) as a colorless oil. The ratio for *Z*/*E* isomers (8.7:1) was determined by ^{19}F-NMR. (*Z*)-**3o**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02–6.94 (m, 6H), 4.62 (dt, *J* = 37.1, 7.4 Hz, 1H), 3.41 (d, *J* = 7.3 Hz, 2H), 2.86–2.81 (m, 2H), 2.49–2.39 (m, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (d, *J* = 254.3 Hz), 138.8, 138.63 (d, *J* = 1.5 Hz), 136.9, 136.84, 134.81, 134.4, 127.99, 127.98, 126.9, 126.6, 125.44, 125.43, 104.14 (d, *J* = 15.1 Hz), 33.16 (d, *J* = 27.5 Hz), 30.8, 28.40 (d, *J* = 5.6 Hz), 20.7, 20.6, 14.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.43 (dt, *J* = 37.1, 17.7 Hz, 1F). IR (KBr): 3016, 2917, 1702, 1583, 1452, 1382, 1132, 732, 779 cm^{-1}. MS (EI, *m/z*) 296 $[M]^+$. HRMS (EI) calcd. for $C_{21}H_{25}F^+$ $[M^+]$: 296.1940, found 296.1949.

2,2'-(3-Fluoropent-2-ene-1,5-diyl)bis(bromobenzene) **3j**



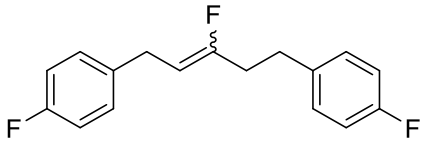
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) **1j** (41.5, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3j** (15.1 mg, 38%) as a colorless oil. The ratio for *Z*/*E* isomers (25:1) was determined by ^{19}F-NMR. (*Z*)-**3j**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 4.5 Hz, 2H), 7.24–7.02 (m, 6H), 4.69 (dt, *J* = 36.6, 7.5 Hz, 1H), 3.49 (d, *J* = 7.5 Hz, 2H), 3.06–2.93 (m, 2H), 2.62–2.46 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.24 (d, *J* = 255.9 Hz), 139.8, 139.78 (d, *J* = 1.8 Hz), 132.8, 132.6, 130.7, 130.1, 127.9, 127.7, 127.4, 124.34, 124.29, 103.31 (d, *J* = 14.8 Hz), 33.1, 32.21 (d, *J* = 27.4 Hz), 30.4 (d, *J* = 5.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.96 (dt, *J* = 36.4, 18.1 Hz). IR (KBr): 3056, 2925, 1714, 1558, 1463, 1438, 1153, 1022, 754, 659 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{15}Br_2F^+$ $[M^+]$: 395.9525, found 395. 9547.

2,2'-(3-Fluoropent-2-ene-1,5-diyl)bis(chlorobenzene) **3k**



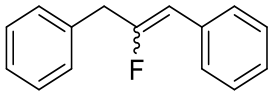
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) **1k** (32.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3k** (18.1 mg, 55%) as a colorless oil. The ratio for *Z*/*E* isomers (8.6:1) was determined by ^{19}F-NMR. (*Z*)-**3k**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.26 (m, 2H), 7.23–7.04 (m, 6H), 4.68 (dt, *J* = 36.5, 7.6 Hz, 1H), 3.49 (d, *J* = 7.5 Hz, 2H), 2.99–2.85 (m, 2H), 2.52 (dt, *J* = 17.9, 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.34 (d, *J* = 255.8 Hz), 138.16, 138.11, 138.0, 133.87, 133.85, 130.7, 130.0, 129.5, 129.3, 127.7, 127.4, 126.8, 103.18 (d, *J* = 14.8 Hz), 32.07 (d, *J* = 27.4 Hz), 30.5, 27.72 (d, *J* = 6.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.22 (dt, *J* = 36.4, 18.1 Hz, 1F). IR (KBr): 3072, 2911, 1706, 1565, 1463, 1438, 1141, 1041, 757 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{15}Cl_2F^+$ [M^+]: 308.0535, found 308.0558.

4,4'-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) **3u**



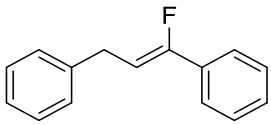
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(fluorobenzene) **1u** (29.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3u** (14.9 mg, 52%) as a colorless oil. The ratio for *Z*/*E* isomers (11.1:1) was determined by ^{19}F-NMR. (*Z*)-**3u**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.07 (m, 2H), 7.02–6.86 (m, 6H), 4.60 (dt, *J* = 36.6, 7.7 Hz, 1H), 3.33 (d, *J* = 7.6 Hz, 2H), 2.82 (dd, *J* = 14.6, 7.3 Hz, 2H), 2.52–2.44 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.43 (d, *J* = 243.8 Hz), 161.32 (d, *J* = 243.6 Hz), 158.78 (d, *J* = 254.9 Hz), 136.22, 136.19, 136.07 (d, *J* = 3.0 Hz), 136.06 (d, *J* = 2.9 Hz), 129.75 (d, *J* = 41.2 Hz), 129.69 (d, *J* = 41.2 Hz), 115.2, 115.1, 115.08, 115.00, 104.95 (d, *J* = 15.1 Hz), 34.05 (d, *J* = 27.4 Hz), 31.6, 28.95 (d, *J* = 6.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.75 (dt, *J* = 36.6, 17.7 Hz, 1F), -117.18–-117.34 (m, 1F), -117.43–-117.68 (m, 1F). IR (KBr): 3045, 2929, 2857, 1710, 1606, 1519, 1430, 1153, 1089, 806 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{15}F_3^+$ [M^+]: 276.1126, found 276.1139.

(2-Fluoroprop-1-ene-1,3-diyl)dibenzene **3aa** (Nahra et al., 2015)



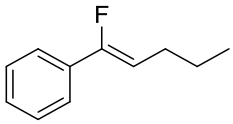
(2,2-Difluoropropane-1,3-diyl)dibenzene **1aa** (23.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3aa** (11.0 mg, 50%) as a colorless oil. The ratio for Z/E isomers (16.6:1) was determined by ^{19}F-NMR. (*Z*)-**3aa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.40 (m, 2H), 7.37–7.17 (m, 8H), 5.52 (d, *J* = 38.8 Hz, 1H), 3.65 (d, *J* = 17.0 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -100.15 (dt, *J* = 38.7, 17.0 Hz); MS (EI, *m/z*) 212 $[M]^+$

(*Z*)-(1-Fluoroprop-1-ene-1,3-diyl)dibenzene **3bb** (Yang et al., 2013)



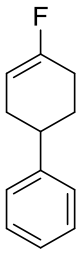
(1,1-Difluoropropane-1,3-diyl)dibenzene **1bb** (23.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give ***Z*-3bb** (8.8 mg, 41%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.44 (m, 2H), 7.37–7.19 (m, 8H), 5.60 (dt, *J* = 36.4, 7.7 Hz, 1H), 3.65 (d, *J* = 7.7 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -121.09 (d, *J* = 36.4 Hz, 1F); MS (EI, *m/z*) 212 $[M]^+$

(*Z*)-(1-Fluoropent-1-en-1-yl)benzene **3cc** (Zhang et al., 2009)



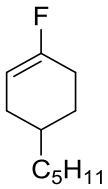
(1,1-Difluoropentyl)benzene **1cc** (18.4 mg, 0.1mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give ***Z*-3cc** (4.2 mg, 25%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.47–7.29 (m, 3H), 5.40 (dt, *J* = 37.6, 7.6 Hz, 1H), 2.27–2.20 (m, 2H), 1.56–1.47 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -121.38 (d, *J* = 37.6 Hz); MS (EI, *m/z*) 164 $[M]^+$

4-Fluoro-1,2,3,6-tetrahydro-1,1'-biphenyl **3dd** (Vandamme and Paquin, 2017)



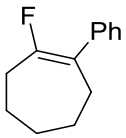
(4,4-Difluorocyclohexyl)benzene **3dd** (19.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give *Z*-**3dd** (15.6 mg, 82%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.28 (m, 2H), 7.28–7.16 (m, 3H), 5.30–5.23 (m, 1H), 2.84–2.74 (m, 1H), 2.29–2.21 (m, 4H), 2.02–1.89 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -103.35–-103.72 (m, 1F); MS (EI, *m/z*) 176 $[M]^+$

1-Fluoro-4-pentylcyclohex-1-ene **3ee** (Vandamme et al., 2017)



1,1-Difluoro-4-pentylcyclohexane **1ee** (19.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give *Z*-**3ee** (11.1 mg, 64%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.17–5.10 (m, 1H), 2.23–2.09 (m, 3H), 1.84–1.80 (m, 1H), 1.71–1.62 (m, 1H), 1.52–1.46 (m, 1H), 1.40–1.20 (m, 9H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$)) δ -103.59–-103.77 (m, 1F); MS (EI, *m/z*) 170 $[M]^+$

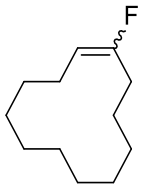
1-Fluoro-2-phenylcyclohept-1-ene **3ff**



1,1-Difluoro-2-phenylcycloheptane **1ff** (21.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3ff** with 1-fluoro-7-phenylcyclohept-1-ene **3ff'** in a 3.3:1 ratio, (9.4 mg, 45%) as a colorless oil. 1-fluoro-2-phenylcyclohept-1-ene **3ff**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5H), 2.63–2.48 (m, 2H), 2.49–2.36 (m, 2H), 1.86–1.70 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.30 (d, *J* = 258.1 Hz), 139.5, 127.97, 127.91, 126.33, 118.73 (d, *J* = 11.5 Hz), 31.79 (d, *J* = 29.6 Hz), 31.54 (d, *J* = 6.3 Hz),

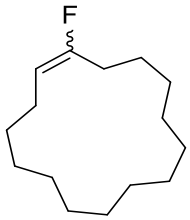
31.2, 26.97 (d, *J* = 1.6 Hz), 24.67 (d, *J* = 3.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -94.81 (t, *J* = 17.0 Hz, 1F). 1-fluoro-7-phenylcyclohept-1-ene **3ff'**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.14 (m, 5H), 5.59 (dt, *J* = 23.9, 6.4 Hz, 1H), 3.86–3.75 (m, 1H), 2.20–2.11 (m, 2H), 2.07–1.92 (m, 2H), 1.63–1.43 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.30 (d, *J* = 246.3 Hz), 141.05 (d, *J* = 1.4 Hz), 128.4, 127.7, 126.4, 108.24 (d, *J* = 23.3 Hz), 47.96 (d, *J* = 28.0 Hz), 32.28 (d, *J* = 9.3 Hz), 27.1, 24.1, 22.22 (d, *J* = 11.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -94.26 (dd, *J* = 23.8, 13.0 Hz, 1F). IR (KBr): 3016, 2933, 2861, 1681, 1594, 1490, 1442, 1351, 1176, 1022, 750, 698 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{15}F^+$ [M^+]: 190.1158, found 190.1168.

1-Fluorocyclododec-1-ene **3gg**



1,1-Difluorocyclododecane **1gg** (20.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **3gg** (14.9 mg, 71%) as a colorless oil. The ratio for *Z*/*E* isomers (3.3:1) was determined by ^{19}F-NMR. (*Z*)-**3gg**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (dt, *J* = 37.8, 7.8 Hz, 1H), 2.28–2.19 (m, 1H), 2.19–2.11 (m, 3H), 1.39–1.26 (m, *J* = 12.0 Hz, 16H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1 (d, *J* = 252.5 Hz), 107.2 (d, *J* = 15.9 Hz), 31.7 (d, *J* = 28.4 Hz), 26.2 (d, *J* = 1.7 Hz), 25.9, 25.7, 25.2, 24.6, 24.65, 24.61, 22.9, 22.87 (d, *J* = 4.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.85 (dt, *J* = 37.8, 21.6 Hz, 1F). (*E*)-**3gg**: ^{1}H NMR (300 MHz, CDC_3) δ 4.96 (dt, *J* = 23.4, 8.2 Hz, 1H), 2.35–2.30 (m, 2H), 2.02–1.95 (m, 2H), 1.65–1.41 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0 (d, *J* = 244.9 Hz), 106.7 (d, *J* = 21.7 Hz), 27.1 (d, *J* = 2.1 Hz), 26.9 (d, *J* = 22.7 Hz), 24.6, 24.4, 24.2, 23.9, 23.55, 22.58(d, *J* = 9.4 Hz), 22.13, 21.93. ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.15–-106.71 (m, 1F). IR (KBr): 2921, 2857, 1695, 1452, 1068 cm^{-1}. HRMS (EI) calcd. for $C_{12}H_{21}F^+$ [M^+]: 184.1627, found 184.1646.

1-Fluorocyclopentadec-1-ene **3hh**



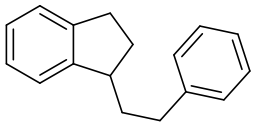
1,1-Difluorocyclopentadecane **1hh** (24.6, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixtuure was refluxed for 48 h under argon atmosphere. The ^{19}F-NMR showed that the *Z*/*E* ratio was 3:1. Then the purification by column chromatography on silica gel (*n*-hexane) to give **3hh** (18.8 mg, 80% yield)

as a colorless oil. The ratio for *Z*/*E* isomers (3.0:1) was determined by ^{19}F-NMR. (*Z*)**-3hh**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (dt, *J* = 38.6, 7.3 Hz, 1H), 2.26–2.17 (m, 1H), 2.20–1.93 (m, 3H), 1.53–1.45 (m, 3H), 1.44–1.30 (m, 19H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.30 (d, *J* = 252.9 Hz), 105.96 (d, *J* = 16.2 Hz), 31.43 (d, *J* = 28.0 Hz), 28.55 (d, *J* = 1.4 Hz), 27.2, 27.1, 27.0, 26.96, 26.90, 26.89, 26.87, 26.8, 25.6, 25.1, 22.7 (d, *J* = 4.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.35 (dt, *J* = 38.7, 19.4 Hz, 1F). IR (KBr): 2925, 2861, 1706, 1448, 1340 cm^{-1}. MS (EI, *m/z*) 226 $[M]^+$. HRMS (EI) calcd. for $C_{15}H_{27}F^+$ $[M^+]$: 226.2097, found 226.2088.

General procedure for Friedel-Crafts reaction of secondary monofluoroalkanes 4, related to Figure 3.

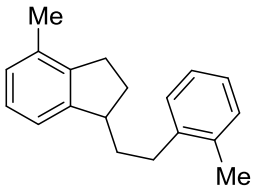
In a flame-dried test tube, monofluoroalkanes **4a-4s** (0.1 mmol) were added to a solution of $B(C_6F_5)_3$ (2 mol%) in dry HFIP (2.0 mL) at room temperature in a glovebox filled with argon. Subsequently, the tube was sealed with a rubber septum, removed from the glovebox and stirred at 50 °C for 2-4 h under a positive pressure of argon with a balloon. The resulting mixture was allowed to cool to room temperature and washed with water, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using *n*-hexane as the eluent to give the desired substituted indane derivatives **5a-5s.**

1-Phenethyl-2,3-dihydro-1*H*-indene **5a** (Khalaf and Roberts, 1972)



(3-Fluoropentane-1,5-diyl)dibenzene 4**a** (24.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5a** (20.5 mg, 91%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.28 (m, 2H), 7.28–7.18 (m, 4H), 7.18–7.07 (m, 3H), 3.15–3.04 (m, 2H), 2.78–2.67 (m, 2H), 1.91–1.80 (m, 1H), 1.74–1.60 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 140.5, 137.0, 129.2, 129.1, 128.8, 128.2, 125.9, 125.6, 125.5, 43.3, 39.5, 29.7, 26.4, 19.1. MS -EI: 222.

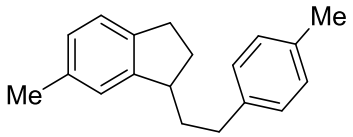
4-Methyl-1-(2-methylphenethyl)-2,3-dihydro-1*H*-indene **5b**



2,2'-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) **4b** (27.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel

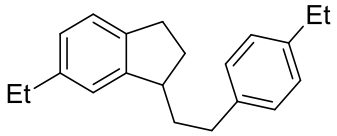
(*n*-hexane) to give **5a** (22.5 mg, 85%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.09 (m, 4H), 7.11–6.99 (m, 3H), 3.08–3.00 (m, 2H), 2.81–2.69 (m, 2H), 2.60–2.55 (m, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 1.96–1.88 (m, 1H), 1.88–1.74 (m, 1H), 1.72–1.64 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 139.2, 136.5, 136.3, 135.4, 130.3, 130.2, 127.2, 126.7, 126.0, 125.6, 125.1, 40.5, 38.3, 26.8, 25.7, 19.7, 19.6, 18.9. IR(KBr): 3016, 2857, 2933, 1587, 1490, 1455, 1371, 1033, 782, 740 cm^{-1}. MS-EI: 250. HRMS (EI) calcd. for $C_{19}H_{22}^{+}$ [M^{+}]: 250.1722, found 250.1720.

6-Methyl-1-(4-methylphenethyl)-2,3-dihydro-1*H*-indene **5c**



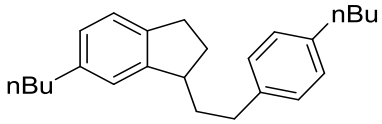
4,4'-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) **4c** (27 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 ^{o}C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5c** (22.9 mg, 90%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–7.03 (m, 5H), 7.03–6.94 (m, 2H), 3.07 (dd, *J* = 13.2, 4.3 Hz, 1H), 2.99 (dt, *J* = 14.8, 4.7 Hz, 1H), 2.75–2.62 (m, 2H), 2.55–2.49 (m, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.92–1.77 (m, 1H), 1.73–1.56 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 138.0, 135.3, 134.8, 133.9, 129.4, 129.09, 129.04, 128.95, 126.56, 42.96, 39.59, 29.37, 26.33, 21.11, 21.07, 19.28. IR(KBr): 3012, 2857, 2937, 1614, 1498, 1442, 802 cm^{-1}. MS-EI: 250, HRMS (EI) calcd. for $C_{19}H_{22}^{+}$ [M^{+}]: 250.1722, found 250.1715.

6-Ethyl-1-(4-ethylphenethyl)-2,3-dihydro-1*H*-indene **5d**



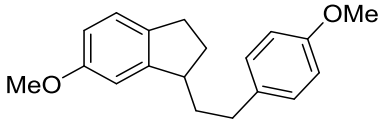
4,4'-(3-Fluoropentane-1,5-diyl)bis(ethylbenzene) **4d** (29.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 ^{o}C for 3 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5c** (26.6 mg, 93%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.06 (m, 4H), 7.08–6.95 (m, 3H), 3.09–3.00 (m, 2H), 2.72–2.55 (m, 7H), 1.92–1.80 (m, 1H), 1.77–1.58 (m, 3H), 1.29–1.17 (m, 6H). ^{13}C NMR (75 MHz, $cdcl_3$) δ 141.7, 141.3, 140.4, 138.2, 134.2, 129.1, 129.0, 128.3, 127.7, 125.3, 43.0, 39.6, 29.4, 28.5, 28.5, 26.5, 19.2, 15.8, 15.7. IR(KBr): 3012, 2933, 2865, 1614, 1508, 1452, 1052, 835, 809 cm^{-1}. EI-MS: 278. HRMS (EI) calcd. for $C_{21}H_{26}^{+}$ [M^{+}]: 278.2035, found 278.2036.

6-Butyl-1-(4-butylphenethyl)-2,3-dihydro-1*H*-indene **5e**



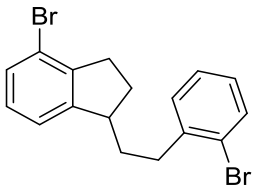
4,4'-(3-Fluoropentane-1,5-diyl)bis(butylbenzene) **4e** (35.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5e** (28.8 mg, 86%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13-7.10 (m, 4H), 7.04-6.98 (m, 3H), 3.13–2.95 (m, 2H), 2.78–2.49 (m, 7H), 1.93–1.81 (m, 1H), 1.74–1.51 (m, 7H), 1.43–1.27 (m, 4H), 0.98-0.85 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 140.3, 140.1, 138.2, 134.2, 129.1, 128.9, 128.8, 128.3, 125.9, 43.1, 39.7, 35.5, 35.3, 35.2, 33.9, 33.8, 29.4, 26.6, 22.5, 22.4, 19.2, 14.1; IR (KBr): 3008, 2937, 2857, 1610, 1508, 1455, 1375, 806, 838 cm^{-1}. MS (EI, *m/z*) 334 $[M]^+$. HRMS (EI) calcd. for $C_{25}H_{34}^+$ $[M^+]$: 334.2661, found 334.2663.

6-Methoxy-1-(4-methoxyphenethyl)-2,3-dihydro-1*H*-indene **5f**



4,4'-(3-Fluoropentane-1,5-diyl)bis(methoxybenzene) **4f** (30.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5f** (12.4 mg, 44%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.5 Hz, 2H), 7.04–7.01 (m, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.74–6.69 (m, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.09–2.95 (m, 2H), 2.73–2.67 (m, 2H), 1.87–1.82 (m, 1H), 1.68–1.59 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 157.2, 141.6, 133.0, 130.1, 129.9, 129.1, 113.7, 113.6, 111.9, 55.3, 55.2, 42.4, 39.9, 28.9, 26.5, 19.4. IR (KBr): 3004, 2915, 2840, 1610, 1579, 1519, 1243, 1033, 846, 794 cm^{-1}. MS-EI: 282. HRMS (EI) calcd. for $C_{19}H_{22}O_2^+$ $[M^+]$: 282.1620, found 282.1622.

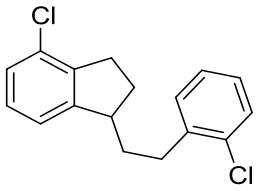
4-Bromo-1-(2-bromophenethyl)-2,3-dihydro-1*H*-indene **5g**



2,2'-(3-Fluoropentane-1,5-diyl)bis(bromobenzene) **4g** (40.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5g** (32.9 mg, 80%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.29–7.18 (m, 2H), 7.09–7.04 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 3.32–3.14 (m,

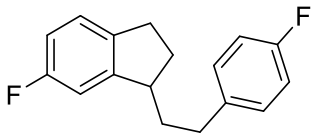
2H), 3.04–2.82 (m, 2H), 2.73–2.57 (m, 1H), 2.06–1.90 (m, 1H), 1.88–1.74 (m, 1H), 1.74–1.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 139.7 136.3, 133.0, 131.9, 130.1, 128.3, 127.9, 127.2, 126.7, 125.7, 124.9, 43.3, 37.7, 30.4, 25.4, 18.7. IR (KBr): 3056, 2933, 2873, 1554, 1434, 1135, 1037, 808, 777, 719 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}Br_2^+$ [M^+]: 377.9619, found 377.9622.

4-Chloro-1-(2-chlorophenethyl)-2,3-dihydro-1*H*-indene **5h**



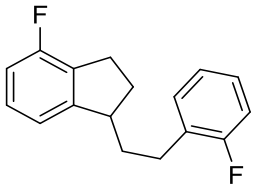
2,2'-(3-Fluoropentane-1,5-diyl)bis(chlorobenzene) **4h** (31.1 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5h** (21.8 mg, 75%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.35 (m, 1H), 7.28–7.12 (m, 5H), 7.07 (t, *J* = 7.7 Hz, 1H), 3.28–3.14 (m, 2H), 2.98–2.79 (m, 2H), 2.70–2.60(m, 1H), 1.99–1.77 (m, 2H), 1.70–1.58 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7 138.1, 134.8, 134.4, 134.3, 131.8, 129.7, 127.7, 127.6, 126.7, 126.5, 126.2, 40.9, 37.7, 27.4, 25.4, 18.4; IR (KBr): 3056, 2933, 2873, 1594, 1563, 1444, 1143, 1051, 773, 682 cm^{-1}. MS (EI, *m/z*) 290 [M]$^+$. HRMS (EI) calcd. for $C_{17}H_{16}Cl_2^+$ [M^+]: 290.0629, found 290.0642.

6-Fluoro-1-(4-fluorophenethyl)-2,3-dihydro-1*H*-indene **5i**



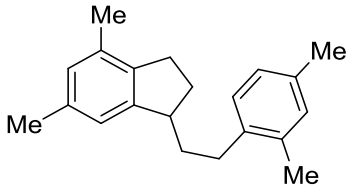
4,4'-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) **4i** (27.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5i** (17.6 mg, 68%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.09 (m, 2H), 7.08–6.94 (m, 3H), 6.87–6.75 (m, 2H), 3.08–2.95 (m, 2H), 2.76–2.65 (m, 2H), 1.93–1.76 (m, 1H), 1.73–1.56 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.8 Hz), 160.8 (d, *J* = 242.8 Hz), 142.1 (d, *J* = 6.5 Hz), 136.1 (d, *J* = 3.3 Hz), 132.5 (d, *J* = 2.9 Hz), 130.49 (d, *J* = 7.7 Hz), 130.3, 115.1 (d, *J* = 21.1 Hz), 114.8 (d, *J* = 21.1 Hz), 112.9 (d, *J* = 21.1 Hz), 42.29, 39.7, 29.0, 26.3, 19.3. IR (KBr): 3041, 2925, 2869, 1602, 1511, 1459, 1153, 1128, 813, 730 cm^{-1}. MS-EI: 258. HRMS (EI) calcd. for $C_{17}H_{16}F_2^+$ [M^+]: 258.1220, found 258.1225.

4-Fluoro-1-(2-fluorophenethyl)-2,3-dihydro-1*H*-indene **5j**



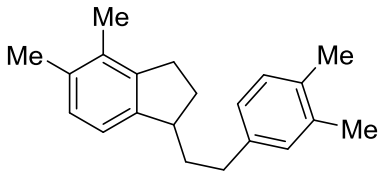
2,2'-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) **4j** (27.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5j** (17.6 mg, 68%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.11 (m, 2H), 7.10–6.99 (m, 4H), 6.85 (t, *J* = 8.6 Hz, 1H), 3.17–3.04 (m, 2H), 2.91–2.75 (m, 2H), 2.65–2.56 (m, 1H), 1.95–1.83 (m, 1H), 1.82–1.74 (m, 1H), 1.63–1.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4 (d, *J* = 244.8 Hz), 160.7 (d, *J* = 243.3 Hz), 142.8 (d, *J* = 4.7 Hz), 131.5 (d, *J* = 5.1 Hz), 127.8 (d, *J* = 8.1 Hz), 127.5 (d, *J* = 16.0 Hz), 126.1 (d, *J* = 8.9 Hz), 124.6, 124.3 (d, *J* = 3.1 Hz), 123.83 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 22.4 Hz), 111.9 (d, *J* = 22.1 Hz), 38.0, 36.3, 25.8, 22.06 (d, *J* = 4.3 Hz), 17.8. IR (KBr): 3031, 2933, 2857, 1579, 1498, 1457, 1234, 879, 773, 755 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}F_2^+$ [M^+]: 258.1220, found 258.1225.

1-(2,4-Dimethylphenethyl)-4,6-dimethyl-2,3-dihydro-1*H*-indene **5k**



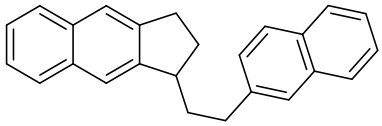
4,4'-(3-Fluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) **4k** (29.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5j** (14.1 mg, 50%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.87 (s, 1H), 3.08–2.95 (m, 2H), 2.73–2.65 (m, 2H), 2.57–2.45 (m, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 2.03–1.87 (m, 1H), 1.85–1.71 (m, 1H), 1.70–1.57 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 136.3, 136.2, 136.1, 135.5, 134.4, 132.3, 131.1, 130.1, 128.2, 127.1, 126.2, 40.1, 38.3, 26.6, 25.5, 20.96, 20.93, 19.68, 19.63, 18.9. IR (KBr): 3004, 2925, 2861, 1612, 1500, 1452, 1027, 852, 813 cm^{-1}. MS-EI: 278. HRMS (EI) calcd. for $C_{21}H_{26}^+$ [M^+]: 278.2035, found 278.2041.

1-(3,4-Dimethylphenethyl)-4,5-dimethyl-2,3-dihydro-1*H*-indene **5l**



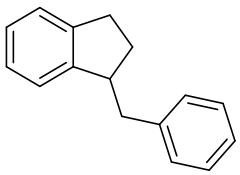
3,3'-(3-Fluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) **4l** (29.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5j** (25.2 mg, 67%) as a white solid, mp = 97-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08–7.02 (m, 3H), 7.02–6.96 (m, 2H), 3.13 (dd, *J* = 13.5, 4.2 Hz, 1H), 3.02 (dd, *J* = 10.3, 4.8 Hz, 1H), 2.80–2.72 (m, 2H), 2.66–2.50 (m, 1H), 2.31 (s, 6H), 2.28 (s, 3H), 2.15 (s, 3H), 2.01–1.89 (m, 1H), 1.86–1.72 (m, 1H), 1.67–1.55 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 138.6, 136.9, 135.2, 134.8, 134.7, 133.7, 128.3, 127.7, 127.1, 126.1, 125.0, 41.2, 38.4, 27.5, 25.4, 20.8, 20.5, 19.1, 15.3, 15.1. IR (KBr): 3016, 2937, 2861, 1590, 1471, 1378, 777, 725 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{26}^+$ [M^+]: 278.2035, found 278.2059.

1-(2-(Naphthalen-2-yl)ethyl)-2,3-dihydro-1*H*-cyclopenta[b]naphthalene **5m**



2,2'-(3-Fluoropentane-1,5-diyl)dinaphthalene 4m (34.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5m** (25.7 mg, 79%) as a sticky semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 1H), 7.94–7.80 (m, 4H), 7.77 (s, 1H), 7.70–7.61 (m, 1H), 7.61–7.53 (m, 2H), 7.52–7.40 (m, 3H), 7.28–7.20 (m, 1H), 3.91 (d, *J* = 11.5 Hz, 1H), 3.41 (d, *J* = 14.2 Hz, 1H), 3.09–2.87 (m, 3H), 2.24–2.06 (m, 1H), 2.02–1.78 (m, 2H), 1.75–1.58 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 135.2, 133.9, 133.5, 132.6, 132.0, 131.6, 128.9, 128.3, 128.0, 127.6, 127.5, 127.4, 127.2, 126.3, 126.0, 125.9, 125.2, 124.6, 122.7, 40.5, 35.0, 30.1, 24.4, 17.3. IR (KBr): 3052, 3012, 2925, 2865, 1673, 1600, 1513, 1450, 1373, 1268, 850, 738 cm^{-1}. HRMS (EI) calcd. for $C_{25}H_{22}^+$ [M^+]: 322.1722, found 322.1718.

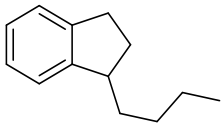
1-Benzyl-2,3-dihydro-1*H*-indene **5n** (Adamczyk et al., 1984)



(2-Fluorobutane-1,4-diyl)dibenzene **4n** (22.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was

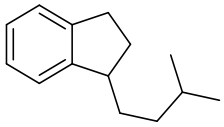
stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5m** (20.0 mg, 91%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 7.22–7.10 (m, 4H), 3.14–2.81 (m, 5H), 2.19–2.08 (m, 1H), 2.03–1.82 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 136.6, 136.2, 129.0, 128.9, 128.4, 126.8, 126.1, 125.7, 125.6, 40.7, 37.7, 30.3, 29.7. MS (EI, *m/z*) 208 $[M]^+$

1-Butyl-2,3-dihydro-1*H*-indene **5o** (Adamczyk et al., 1984)



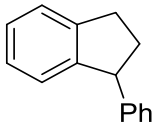
(3-Fluoroheptyl)benzene **4o** (19.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5o** (10.9 mg, 62%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.05 (m, 4H), 2.87–2.68 (m, 3H), 1.97–1.80 (m, 2H), 1.75–1.61 (m, 3H), 1.58–1.28 (m, 3H), 0.95 (t, *J* = 7.6, 3H). MS (EI, *m/z*) 174 $[M]^+$

1-Isopentyl-2,3-dihydro-1*H*-indene **5p**



(3-Fluoro-6-methylheptyl)benzene **4p** (20.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5p** (7.5 mg, 39%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–7.07 (m, 2H), 7.07–6.95 (m, 2H), 2.91–2.68 (m, 3H), 1.92–1.63(m, 5H), 1.58–1.37 (m, 2H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 136.9, 129.1, 128.6, 125.4, 125.3, 46.8, 35.1, 29.7, 27.1, 25.4, 23.9, 21.5, 19.3; IR (KBr): 3006, 2937, 2869, 1725, 1573, 1490, 1454, 1365, 748 cm^{-1}. MS (EI, *m/z*) 188 $[M]^+$. HRMS (EI) calcd. for $C_{14}H_{20}^+$ $[M^+]$: 188.1565 found 188.1564.

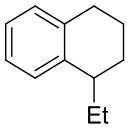
1-Phenyl-2,3-dihydro-1*H*-indene **5q** (Léonard and Chirik, 2018)



(1-Fluoropropane-1,3-diyl)dibenzene **4q** (21.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5q** (5.7 mg, 29%) as a colorless oil. Under the same condition in the absence of tris(pentafluorophenyl)borane, the desired **5q** was isolated in 46% yield (9.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.16 (m, 8H), 6.96 (d, *J* = 7.3 Hz, 1H), 4.35 (t, *J* = 8.3 Hz, 1H), 3.05–2.97 (m, 2H), 2.66–2.56 (m,

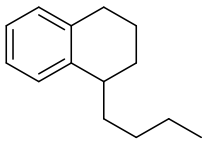
1H), 2.15–1.99 (m, 1H); MS (EI, *m/z*) 194 $[M]^+$

1-Ethyl-1,2,3,4-tetrahydronaphthalene **5r** (Michelet et al., 2014)



(4-Fluorohexyl)benzene **4r** (18.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5q** (13.4 mg, 82%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.25–7.04 (m, 4H), 2.81–2.62 (m, 3H), 1.95–1.67 (m, 4H), 1.65–1.49 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); MS (EI, *m/z*) 160 $[M]^+$

1-Butyl-1,2,3,4-tetrahydronaphthalene **5s** (Adamczyk, et al., 1984)

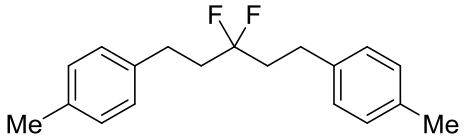


(4-Fluorooctyl)benzene **4s** (20.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry $(CF_3)_2CHOH$ (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (*n*-hexane) to give **5s** (16.1 mg, 85%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20–7.05 (m, 4H), 2.80–2.66 (m, 3H), 1.90–1.78 (m, 2H), 1.73–1.63 (m, 3H), 1.62–1.49 (m, 1H), 1.44–1.25 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 3H); MS (EI, *m/z*) 188 $[M]^+$

Synthesis of unkown *gem*-difluorides 1b-1u, 1cc, 1ee and 1hh, related to Figure 2.

For the preparation of substrates **1b-1u**, to a solution of corresponding ketone (1.0 mmol) in dry1,2-dichloroethane at room temperature, was slowly added (diethylamino)sulfur trifluoride (DAST, 2.5 mmol). The resulting mixture was stirred at 60 °C, monitored by TLC and upon the completion of the reaction at the same temperature. After cooling to room temperature, the mixture was diluted with CH_2Cl_2, and then washed with water and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane/ CH_2Cl_2) to afford desired **1b-1u** in 28% to 57% yields, as shown in the following.

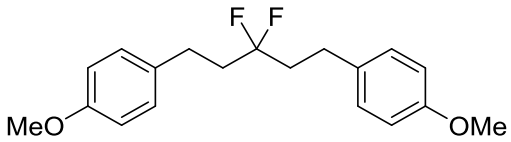
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1b**



White solid, mp = 64–65 °C, 33% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20–6.84 (m, 8H), 2.84–2.68 (m, 4H),

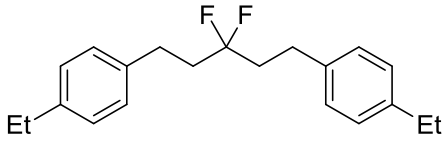
2.32 (s, 6H), 2.23–2.04 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 135.7, 129.2, 128.2, 124.2 (t, *J* = 241.3 Hz), 38.6 (t, *J* = 25.2 Hz), 28.1 (t, *J* = 5.0 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.18 (quintet, *J* = 16.4 Hz, 2F). IR (KBr): 3016, 2937, 2877, 1523, 1434, 1378, 1184, 1052, 908, 815, 742 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}F_2^+$ [M^+] 288.1690, found 288.1688.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) **1c**



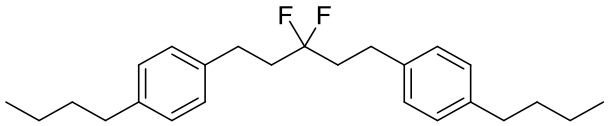
White solid, mp = 54–55 °C, 28% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 3.79 (s, 6H), 2.82–2.72 (m, 4H), 2.17–1.98 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 132.6, 129.1, 124.2 (t, *J* = 241.3 Hz), 113.9, 55.2, 38.6 (t, *J* = 25.2 Hz), 27.6 (t, *J* = 5.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.16 (quintet, *J* = 16.5 Hz, 2F). IR (KBr): 3008, 2937, 2877, 1523, 1434, 1378, 1184, 1052, 908, 815, 742 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}F_2O_2^+$ [M^+] 320.1588, found 320.1587.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(ethylbenzene) **1d**



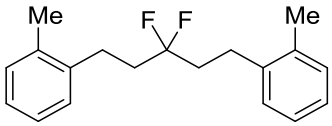
White solid, mp = 35–36 °C, 33% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–6.97 (m, 8H), 2.80–2.71 (m, 4H), 2.62 (q, *J* = 7.6 Hz, 4H), 2.29–2.12 (m, 4H), 1.22 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 137.8, 128.2, 128.0, 124.2 (t, *J* = 241.3 Hz), 38.5 (t, *J* = 25.3 Hz), 28.4, 28.11 (t, *J* = 4.9 Hz), 15.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.09 (quintet, *J* = 16.4 Hz, 2F). IR(KBr): 3008, 2960, 2929, 2837, 1515, 1457, 1375, 1299, 1189, 1151, 1172, 813 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{26}F_2^+$ [M^+] 316.2003, found 316.2000.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(butylbenzene) **1e**



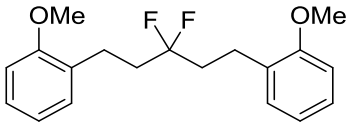
White solid, mp = 30–31 °C, 36% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.06 (m, 8H), 2.80–2.69 (m, 4H), 2.62–2.46 (m, 4H), 2.26–2.07 (m, 4H), 1.67–1.53 (m, 4H), 1.35 (dq, *J* = 14.5, 7.3 Hz, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 137.7, 128.5, 128.1, 124.27 (t, *J* = 241.3 Hz), 38.49 (t, *J* = 25.2 Hz), 35.2, 33.7, 28.11 (t, *J* = 4.6 Hz), 22.3, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.07 (quintet, *J* = 16.4 Hz, 2F). IR (KBr): 3012, 2956, 2861, 1517, 1455, 1375, 1199, 1153, 1056, 813 cm^{-1}. HRMS (EI) calcd. for $C_{25}H_{34}F_2^+$ [M^+] 372.2629, found 372.2625.

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1f**



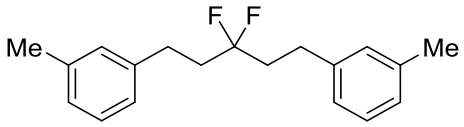
White solid, mp = 52–53 °C, 32% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.09 (m, 8H), 2.87–2.77 (m, 4H), 2.33 (s, 6H), 2.23–2.04 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 135.9, 130.3, 128.7, 126.4, 126.2, 124.2 (t, *J* = 241.5 Hz), 37.2 (t, *J* = 25.3 Hz), 25.8 (t, *J* = 5.0 Hz), 19.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.98 (quintet, *J* = 16.4 Hz, 2F). IR(KBr): 3019, 2937, 2869, 1494, 1461, 1380, 1299, 1199, 1157, 1064, 750 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}F_2^+$ [M^+] 288.1690, found 288.1692.

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) **1g**



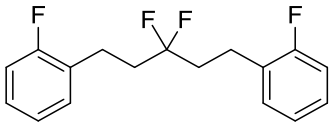
White solid, mp = 89–90 °C, 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.13 (m, 4H), 6.88 (dd, *J* = 15.3, 7.8 Hz, 4H), 3.83 (d, *J* = 0.8 Hz, 6H), 2.87–2.75 (m, 4H), 2.22–2.11 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 129.7, 129.1, 127.4, 125.1 (t, *J* = 241.0 Hz), 120.4, 110.1, 55.1, 36.2 (t, *J* = 25.2 Hz), 23.7 (t, *J* = 5.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -98.23 (quintet, *J* = 16.4 Hz, 2F). IR (KBr): 3019, 2960, 2940, 2844, 1598, 1492, 1457, 1448, 1367, 1243, 1151, 1108, 1052, 1022, 844 cm^{-1}.HRMS (EI) calcd. for $C_{19}H_{22}F_2O_2^+$ [M^+] 320.1588, found 320.1587.

3,3'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) **1h**



White solid, mp = 44–45°C, 30% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.12 (m, 2H), 7.09–6.94 (m, 6H), 2.85–2.73 (m, 4H), 2.33 (s, 6H), 2.28–2.07 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.5, 138.1, 129.1, 128.4, 126.9, 125.2, 124.21 (t, *J* = 241.3 Hz), 38.49 (t, *J* = 25.3 Hz), 28.45 (t, *J* = 5.1 Hz), 21.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.24 (quintet, *J* = 16.3 Hz, 2F). IR(KBr): 3035, 2956, 2929, 1610, 1448, 1378, 1301, 1203, 1151, 1070, 779 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}F_2^+$ [M^+] 288.1690, found 288.1695.

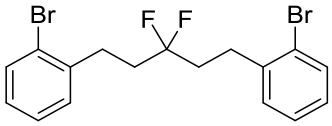
2,2'-(3,3-Difluoropentane-1,5-diyl)bis(fluorobenzene) **1i**



Colorless oil, 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.14 (m, 4H), 7.12–6.99 (m, 4H), 2.92–2.79 (m, 4H), 2.28–2.12 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1 (d, *J* = 245.1 Hz), 130.5 (d, *J* = 4.9 Hz), 128.1 (d, *J* = 8.1 Hz), 127.4 (d, *J* = 15.6 Hz), 124.1 (d, *J* = 3.6 Hz), 124.0 (t, *J* = 241.6 Hz), 115.3 (d, *J* = 21.9 Hz), 36.8 (t, *J* = 25.2 Hz), 22.2 (td, *J* = 5.4, 2.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.87 (quintet, *J* = 16.4 Hz,

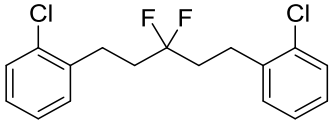
2F), -117.30–-119.91 (m, 2F). IR (KBr): 3052, 2937, 2869, 1589, 1494, 1454, 1228, 1195, 1060, 752 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}F_4^+$ [M^+] 296.1188, found 296.1194.

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) **1j**



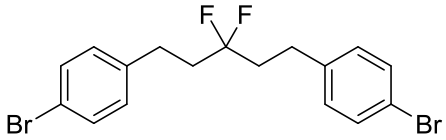
White solid, mp = 58–59 °C, 50% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 4H), 7.09 (dt, *J* = 8.9, 4.4 Hz, 2H), 3.06–2.92 (m, 4H), 2.27–2.13 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 132.9, 130.4, 128.0, 127.7, 124.2, 124.0 (t, *J* = 241.9 Hz), 36.5 (t, *J* = 25.3 Hz), 29.2 (t, *J* = 5.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.18 (quintet, *J* = 16.3 Hz, 2F). IR(KBr): 3060, 2933, 1565, 1475, 1438, 1297, 1211, 1155, 1025, 744 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}Br_2F_2^+$ [M^+] 415.9587, found 415.9598.

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) **1k**



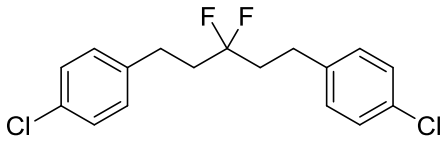
Colorless oil, 56% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.3, 1.6 Hz, 2H), 7.34–7.13 (m, 6H), 3.02–2.93 (m, 4H), 2.28–2.08 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 133.8, 130.4, 129.6, 127.8, 127.0, 124.1 (t, *J* = 241.8 Hz), 36.3 (t, *J* = 25.4 Hz), 26.7 (t, *J* = 5.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.35 (quintet, *J* = 16.3 Hz, 2F). IR(KBr): 3072, 2933, 2869, 1592, 1569, 1477, 1299, 1199, 1126, 1157, 1024, 759 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}Cl_2F_2^+$ [M^+] 328.0597, found 328.0604.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) **1l**



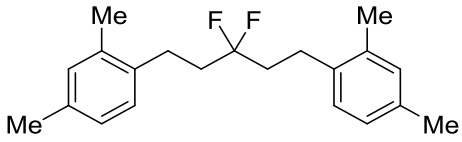
Yellow Solid, mp = 74–76 °C, 26% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 4H), 7.06 (d, *J* = 8.3 Hz, 4H), 2.83–2.64 (m, 4H), 2.27–2.03 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 131.6, 130.0, 123.7 (t, *J* = 241.7 Hz), 120.0, 38.3 (t, *J* = 25.3 Hz), 27.8 (t, *J* = 5.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.70 (quintet, *J* = 16.1 Hz, 2F). IR(KBr): 3025, 2971, 2925, 2867, 1492, 1455, 1402, 1267, 1193, 1068, 1010, 844, 736 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}Br_2F_2^+$ [M^+] 415.9587, found 415.9583.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) **1m**



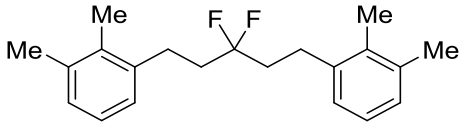
Yellow Solid, mp = 54–55 °C, 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 4H), 7.10 (d, *J* = 8.3 Hz, 4H), 2.86–2.72 (m, 4H), 2.24–1.99 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 132.0, 129.6, 128.6, 123.7 (t, *J* = 241.7 Hz), 38.38 (t, *J* = 25.3 Hz), 27.81 (t, *J* = 5.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.66 (quintet, *J* = 16.4 Hz, 2F). IR (KBr): 3027, 2937, 2889, 1490, 1455, 1407, 1384, 1159, 1095, 1014, 815, 757 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}Cl_2F_2^+$ [M^+] 328.0597, found 328.0606.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) **1n**



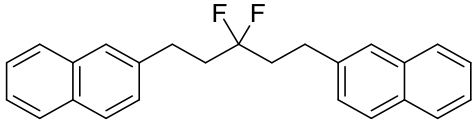
White Solid, mp = 66–68 °C, 29% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08–6.92 (m, 6H), 2.87–2.72 (m, 4H), 2.29 (s, 12H), 2.19–1.98 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.9, 135.7, 135.6, 131.1, 128.6, 126.8, 124.3 (t, *J* = 241.4 Hz), 37.3 (t, *J* = 25.3 Hz), 25.4 (t, *J* = 5.0 Hz), 20.8, 19.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.82 (quintet, *J* = 16.5 Hz, 2F). IR(KBr): 3002, 2948, 2879, 1614, 1502, 1461, 1376, 1270, 1189, 1047, 840, 761 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{26}F_2^+$ [M^+] 316.2003, found 316.2013.

3,3'-(3,3-Difluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) **1o**



White Solid, mp = 76–77 °C, 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–6.98 (m, 6H), 2.87–2.75 (m, 4H), 2.28 (s, 6H), 2.22 (s, 6H), 2.24–2.04 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 137.1, 134.4, 128.1, 126.8, 125.6, 124.29 (t, *J* = 241.4 Hz), 37.56 (t, *J* = 25.3 Hz), 26.65 (t, *J* = 4.9 Hz), 20.7, 14.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.97 (quintet, *J* = 16.5 Hz, 2F).
IR(KBr): 3001, 2948, 2892, 1585, 1467, 1440, 1386, 1186, 1031, 823, 773 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{26}F_2^+$ [M^+] 316.2003, found 316.1998.

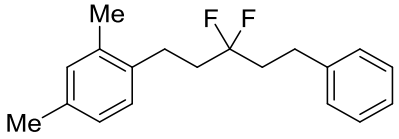
2,2'-(3,3-Difluoropentane-1,5-diyl)dinaphthalene



White Solid, mp = 110–112 °C, 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.70 (m, 6H), 7.60 (s, 2H), 7.52–7.39 (m, 4H), 7.32 (dd, *J* = 8.4, 1.5 Hz, 2H), 3.09–2.97 (m, 4H), 2.50–2.21 (m, 4H). ^{13}C NMR (126

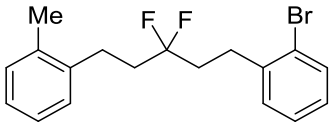
MHz, $CDCl_3$) δ 138.0, 133.5, 132.0, 128.1, 127.6, 127.4, 126.9, 126.4, 126.0, 125.4, 124.23 (t, *J* = 241.5 Hz), 38.37 (t, *J* = 25.3 Hz), 28.71 (t, *J* = 5.0 Hz). ^{19}F NMR (282 MHz, cdcl$_3$) δ -98.91 (quintet, *J* = 16.2 Hz, 2F). IR (KBr): 2937, 1598, 1508, 1458, 1365, 1295, 1155, 1102, 1066, 817 cm^{-1}. HRMS (EI) calcd. for $C_{25}H_{22}F_2^+$ [M^+] 360.1690, found 360.1696.

1-(3,3-Difluoro-5-phenylpentyl)-2,4-dimethylbenzene **1p**



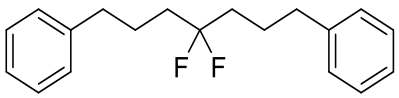
Colorless oil, 48% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.26 (m, 2H), 7.25–7.12 (m, 3H), 7.07–6.94 (m, 3H), 2.85–2.64 (m, 4H), 2.29 (s, 6H), 2.22–1.97 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 135.9, 135.7, 135.6, 131.1, 128.6, 128.5, 128.2, 126.8, 126.2, 124.2 (t, *J* = 241.4 Hz), 38.4 (t, *J* = 25.3 Hz), 37.3 (t, *J* = 25.2 Hz), 28.5 (t, *J* = 5.0 Hz), 25.4 (t, *J* = 5.0 Hz), 20.8, 19.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.53 (m, 2F). IR(KBr): 3027, 2944, 2869, 1504, 1450, 1382, 1305, 1199, 1159, 811 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}F_2^+$ [M^+] 288.1690, found 288.1697.

1-Bromo-2-(3,3-difluoro-5-(o-tolyl)pentyl)benzene **1r**



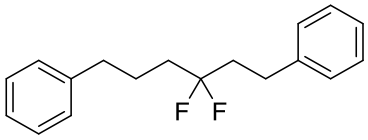
Yellow oil, 44% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.29–7.22 (m, 2H), 7.21–7.07 (m, 5H), 3.04–2.90 (m, 2H), 2.90–2.76 (m, 2H), 2.33 (s, 3H), 2.28–2.00 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 138.7, 135.9, 132.9, 130.4, 130.3, 128.6, 128.1, 127.7, 126.4, 126.2, 124.2, 124.1 (t, *J* = 241.6 Hz), 37.0 (t, *J* = 25.2 Hz), 36.6 (t, *J* = 25.4 Hz), 29.3 (t, *J* = 5.3 Hz), 25.8 (t, *J* = 5.1 Hz), 19.1. ^{19}F NMR (282 MHz, cdcl$_3$) δ -99.51 (quintet, *J* = 16.3 Hz, 2F). HRMS (EI) calcd. for $C_{18}H_{19}BrF_2^+$ [M^+] 352.0638, found 352.0639.

(4,4-Difluoroheptane-1,7-diyl)dibenzene **1s**



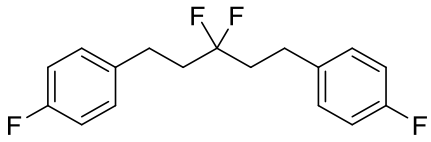
Yellow oil, 35% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.23 (m, 4H), 7.23–7.10 (m, 6H), 2.65–2.50 (m, 4H), 1.95–1.63 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 128.3, 128.3, 125.9, 125.1 (t, *J* = 240.4 Hz), 35.7 (t, *J* = 25.5 Hz), 35.3, 23.9 (t, *J* = 4.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -97.85 (m, 2F).IR(KBr): 3023, 2952, 2857, 1604, 1492, 1454, 1322, 1091, 752 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}F_2^+$ [M^+] 288.1690, found 288.1692.

(3,3-Difluorohexane-1,6-diyl)dibenzene **1t**



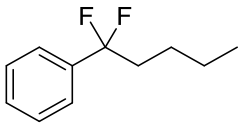
Colorless oil, 29% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.24 (m, 4H), 7.24–7.08 (m, 6H), 2.85–2.72 (m, 2H), 2.71–2.58 (m, 2H), 2.25–2.00 (m, 2H), 1.98–1.70 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 140.6, 128.5, 128.4, 128.3, 128.2, 126.1, 125.9, 124.6 (t, *J* = 240.9 Hz), 38.2 (t, *J* = 25.5 Hz), 35.9 (t, *J* = 25.3 Hz), 35.3, 28.41 (t, *J* = 5.0 Hz), 24.05 (t, *J* = 4.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -98.67 (quintet, *J* = 16.1 Hz, 2F). IR(KBr): 3027, 2952, 2857, 1606, 1496, 1454, 1321, 1205, 1149, 746 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{20}F_2^+$ [M^+] 274.1533, found 274.1539.

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(fluorobenzene) **1u**



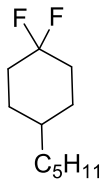
Colorless oil, 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.07 (m, 4H), 7.08–6.95 (m, 4H), 2.87–2.71 (m, 4H), 2.28–2.05 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (d, *J* = 244.0 Hz), 136.1 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.9 Hz), 123.8 (t, *J* = 241.5 Hz), 115.3 (d, *J* = 21.2 Hz), 38.6 (t, *J* = 25.3 Hz), 27.6 (t, *J* = 5.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.66 (qunitet, *J* = 16.4 Hz, 2F), -116.94–-117.21 (m, 1F). IR(KBr): 2877, 2929, 1608, 1517, 1454, 1311, 1228, 1157, 1054, 829 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{16}F_4^+$ [M^+] 296.1188, found 296.1191.

(1,1-Difluoropentyl)benzene **1cc**



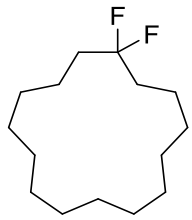
To a solution of 1-phenylpentan-1-one (1.0 mmol) in CH_2Cl_2 (1.0 mL) at room temperature, was slowly added 4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride (Fluolead, 2.0 mmol) and hydrogen fluoride pyridine (around 70% HF, 0.4 equiv). (Umemoto et al., 2010) The resulting mixture was stirred for 36 hours and was diluted with CH_2Cl_2, and then washed with saturated Na_2CO_3 aqueous solution and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane) to afford desired **3cc** in 80% yields, as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.30 (m, 5H), 2.25–2.03 (m, 2H), 1.48–1.31 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5 (t, *J* = 26.7 Hz), 129.4 (d, *J* = 1.6 Hz), 128.3, 124.9 (t, *J* = 6.3 Hz), 123.1 (t, *J* = 241.9 Hz), 38.8 (t, *J* = 27.4 Hz), 24.5 (t, *J* = 4.0 Hz), 22.3, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -95.44 (t, *J* = 16.2 Hz). HRMS (EI) calcd. for $C_{11}H_{14}F_2^+$ [M^+] 184.1064, found 184.1068.

1,1-Difluoro-4-pentylcyclohexane **1ee**



To a solution of 4-pentylcyclohexan-1-one (1.0 mmol) in dry CH_2Cl_2 at -40 ^oC, was slowly added DAST ((diethylamino)sulfur trifluoride, 2.0 mmol). The resulting mixture was slowly warmed to room temperature with 2-3 hours. And the reaction mixture was monitored by TLC and upon the completion of the reaction at the same temperature and was diluted with CH_2Cl_2, and then washed with water and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane/ CH_2Cl_2) to afford desired **3ee** in 72% yield, as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 2.19–1.95 (m, 2H), 1.77–1.54 (m, 4H), 1.35–1.10 (m, 11H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 123.9 (dd, *J* = 241.5, 239.6 Hz), 35.6 (d, *J* = 3.2 Hz), 33.6 (d, *J* = 22.2 Hz), 33.4 (d, *J* = 22.2 Hz), 32.0, 28.9 (d, *J* = 9.5 Hz), 26.8, 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -91.32 (d, *J* = 233.2 Hz, 1F), -101.18–-102.71 (m, 1F). HRMS (EI) calcd. for $C_{11}H_{20}F^+$ $[M\text{-}F]^+$ 171.1544, found 171.1548.

1,1-Difluorocyclopentadecane **1hh**

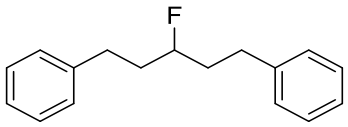


To a solution of cyclopentadecanone (1.0 mmol) in CH_2Cl_2 (1.0 mL) at room temperature, was slowly added 4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride (Fluolead, 2.0 mmol) and hydrogen fluoride pyridine (around 70% HF, 0.4 equiv). (Umemoto et al., 2010) The resulting mixture was stirred for 48 hours and was diluted with CH_2Cl_2, and then washed with saturated Na_2CO_3 aqueous solution and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane) to afford desired **3hh** in 66% yields, as a colorless semi-solid. ^1H NMR (300 MHz, $CDCl_3$) δ 1.93–1.79 (m, 4H), 1.53–1.37 (m, 12H), 1.37–1.24 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.5 (t, *J* = 239.8 Hz), 34.5 (t, *J* = 25.5 Hz), 26.9, 26.7, 26.4, 26.3, 26.3, 21.3 (t, *J* = 5.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -90.88 (quintet, *J* = 15.5 Hz, 2F). IR(KBr): 2929, 2862, 1448, 1085, 1037 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{28}F^+$ $[M\text{-}F]^+$, 227.2170 found 227.2179

General procedure for preparation of aliphatic fluoride 4a-4s, related to Figure 3.

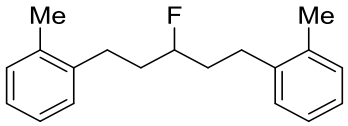
To a solution of aliphatic secondary alcohol (1.0 mmol) in dry CH_2Cl_2 at -78 ^oC, was slowly added (diethylamino)sulfur trifluoride (DAST, 1.3 mmol). The resulting mixture was slowly warmed to room temperature with 2-3 hours. And the reaction mixture was monitored by TLC and upon the completion of the reaction at the same temperature (around 2-3 hours) and was diluted with CH_2Cl_2, and then washed with water and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane/ CH_2Cl_2) to afford desired **4a-4s** in 41% to 90% yields as shown in the following.

(3-Fluoropentane-1,5-diyl)dibenzene **4a**



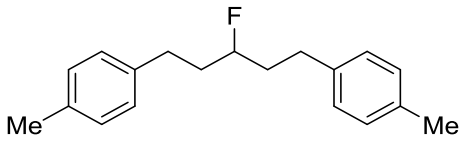
Colorless oil, 82% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.24 (m, 4H), 7.23–7.02 (m, 6H), 4.61–4.39 (m, 1H, $^2J_{H-F}$ = 49.4 Hz), 2.87–2.62 (m, 4H), 2.02–1.76 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 128.4, 125.9, 92.7 (d, *J* = 168.2 Hz), 37.0 (d, *J* = 20.9 Hz), 31.4 (d, *J* = 4.3 Hz). ^{19}F NMR (282 MHz, cdcl$_3$) δ -183.61–-184.34 (m, 1F). IR (KBr): 3031, 2940, 2865, 1606, 1490, 1442, 1164, 1037, 754, 698 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{19}F^+$ [M^+]: 242.1471, found 242.1469.

2,2'-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) **4b**



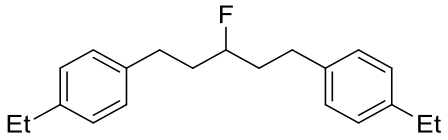
Colorless oil, 87% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.22–7.01 (m, 8H), 4.62–4.37 (m, 1H, $^2J_{H-F}$ = 49.3 Hz), 2.99–2.75 (m, 2H), 2.75–2.55 (m, 2H), 2.31 (s, 6H), 2.06–1.74 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 135.8, 130.2, 128.8, 126.1, 126.0, 93.1 (d, *J* = 168.5 Hz), 35.7 (d, *J* = 21.0 Hz), 28.7 (d, *J* = 4.3 Hz), 19.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -181.50–-185.19 (m, 1F). IR (KBr): 3019, 2937, 2877, 1598, 1486, 1455, 1378, 1168, 1025, 738 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{23}F^+$ [M^+]: 270.1784 found 270.1783.

4,4'-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) **4c**



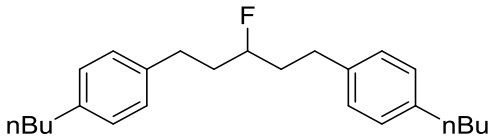
Colorless oil, 80% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18–6.96 (m, 8H), 4.62–4.37 (m, 1H, $^2J_{H-F}$ = 49.3 Hz), 2.87–2.70 (m, 2H), 2.69–2.56 (m, 2H), 2.32 (s, 6H), 2.12–1.77 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 135.3, 129.1, 128.3, 92.8 (d, *J* = 168.0 Hz), 37.1 (d, *J* = 20.9 Hz), 30.9 (d, *J* = 4.4 Hz), 20.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -177.86–-191.48 (m, 1F). IR (KBr): 3008, 2940, 2861, 1515, 1442, 1375, 1041, 892, 806 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{23}F^+$ [M^+]: 270.1784 found 270.1789.

4,4'-(3-Fluoropentane-1,5-diyl)bis(ethylbenzene) **4d**



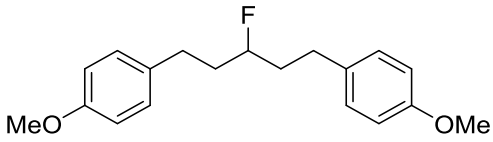
Colorless oil, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–6.98 (m, 8H), 4.68–4.39 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 2.92–2.58 (m, 8H), 2.16–1.79 (m, 4H), 1.23 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 138.6, 128.3, 127.9, 92.8 (d, *J* = 168.0 Hz), 37.1 (d, *J* = 20.9 Hz), 30.9 (d, *J* = 4.4 Hz), 28.4, 15.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -178.72–-187.28 (m, 1F). IR (KBr): 3016, 2498, 2873, 1519, 1438, 1378, 1037, 898, 838 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{27}F^{+}$ [M^{+}]: 298.2097 found 298.2098.

4,4'-(3-Fluoropentane-1,5-diyl)bis(butylbenzene) **4e**



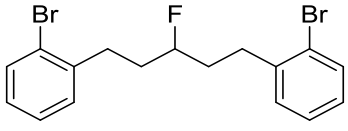
Colorless oil, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–6.97 (m, 8H), 4.62–4.39 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 2.86–2.71 (m, 2H), 2.69–2.49 (m, 6H), 2.01–1.86 (m, 4H), 1.66–1.53 (m, 4H), 1.43–1.21 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 138.5, 128.4, 128.2, 92.8 (d, *J* = 168.0 Hz), 37.0 (d, *J* = 20.9 Hz), 35.2, 33.7, 30.9 (d, *J* = 4.5 Hz), 22.3, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -172.31–-193.10 (m, 1F). IR (KBr): 3019, 2940, 2857, 1511, 1455, 1375, 1045, 902, 825 cm^{-1}. HRMS (EI) calcd. for $C_{25}H_{35}F^{+}$ [M^{+}]: 354.2723 found 354.2726.

4,4'-(3-Fluoropentane-1,5-diyl)bis(methoxybenzene) **4f**



Colorless oi, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.60–4.35 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 3.79 (s, 6H), 2.75–2.61 (m, 4H), 1.99–1.67 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 133.4, 129.3, 113.7, 92.6 (d, *J* = 167.8 Hz), 55.2 (s), 37.2 (d, *J* = 20.8 Hz), 30.4 (d, *J* = 4.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -172.79–-190.80 (m, 1F). IR (KBr): 2940, 2836, 1610, 1587, 1523, 1459, 1303, 1240, 1172, 1033, 829 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{23}FO_2^{+}$ [M^{+}]: 302.1682 found 302.1687.

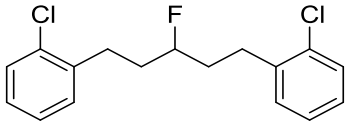
2,2'-(3-Fluoropentane-1,5-diyl)bis(bromobenzene) **4g**



White solid, mp = 36–37 ^{o}C, 52% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.32–7.13

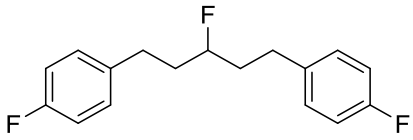
(m, 4H), 7.13–6.97 (m, 2H), 4.68–4.43 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 3.09–2.81 (m, 4H), 2.03–1.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 132.8, 131.8, 127.7, 127.5, 124.3, 92.6 (d, *J* = 169.1 Hz), 35.0 (d, *J* = 20.9 Hz), 31.8 (d, *J* = 4.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -174.86–-190.11 (m, 1F). IR (KBr): 3060, 2944, 2833, 1698, 1562, 1455, 1022, 881, 655 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{17}Br_2F^+$ [M^+]: 397.9681 found 397.9685.

2,2'-(3-Fluoropentane-1,5-diyl)bis(chlorobenzene) **4h**



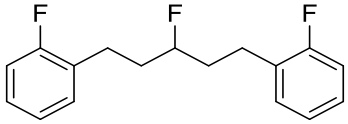
Colorless oil, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.29 (m, 2H), 7.28–7.02 (m, 6H), 4.63–4.41 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 3.03–2.95 (m, 4H), 2.02–1.74 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 133.8, 130.5, 129.5, 127.5, 126.8, 92.7 (d, *J* = 169.0 Hz), 34.9 (d, *J* = 20.9 Hz), 29.3 (d, *J* = 4.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -179.97–-189.12 (m, 1F). IR (KBr): 3068, 2933, 2869, 1575, 1448, 1475, 1378, 1134, 1045, 892, 750, 678 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{17}Cl_2F^+$ [M^+]: 310.0691 found 310.0696.

4,4'-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) **4i**



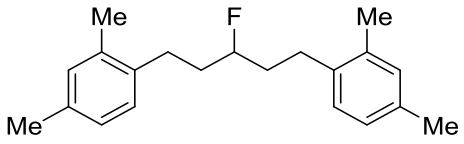
Colorless oil, 75% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.06 (m, 4H), 7.03–6.87 (m, 4H), 4.58–4.33 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.1 Hz), 2.78–2.60 (m, 4H), 2.06–1.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.31 (d, *J* = 243.6 Hz), 136.95 (d, *J* = 3.2 Hz), 129.75 (d, *J* = 7.8 Hz), 115.19 (d, *J* = 21.1 Hz), 92.30 (d, *J* = 168.5 Hz), 37.10 (d, *J* = 21.0 Hz), 30.57 (d, *J* = 4.4 Hz) ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.85 (s, 2F), -180.69–-190.67 (m, 1F). IR (KBr): 3031, 2940, 2861, 1610, 1502, 1438, 1232, 1037, 829 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{17}F_3^+$ [M^+]: 278.1282 found 278.1282.

2,2'-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) 4**j**



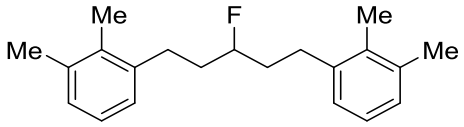
Colorless oil, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.12 (m, 4H), 7.11–6.97 (m, 4H), 4.61–4.40 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 2.90–2.67(m, 4H), 2.02–1.74 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1 (d, *J* = 244.8 Hz), 130.7 (d, *J* = 5.0 Hz), 128.1 (d, *J* = 15.8 Hz), 127.7 (d, *J* = 8.1 Hz), 123.9 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 22.0 Hz), 92.7 (d, *J* = 168.7 Hz), 35.4 (d, *J* = 20.9 Hz), 24.9 (d, *J* = 2.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -119.37 (s, 2F), -179.94–-190.41 (m, 1F). IR (KBr): 2940, 2873, 1587, 1498, 1452, 1232, 1191, 1033, 750 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{17}F_3^+$ [M^+]: 278.1282 found 278.1288.

4,4'-(3-Fluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) **4k**



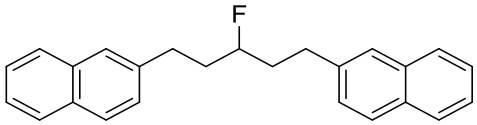
Semi-solid, 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07–6.91 (m, 6H), 4.66–4.41 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.4 Hz), 2.83–2.72 (m, 2H), 2.70–2.56 (m, 2H), 2.29 (s, 6H), 2.27 (s, 6H), 1.99–1.67 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 135.7, 135.5, 131.1, 128.8, 126.6, 93.2 (d, *J* = 168.3 Hz), 35.9 (d, *J* = 21.0 Hz), 28.3 (d, *J* = 4.2 Hz), 20.9, 19.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -182.74–-183.43 (m, 1F). IR (KBr): 3008, 2952, 2819, 1606, 1515, 1448, 1375, 1037, 862, 813 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{27}F^{+}$ [M^{+}]: 298.2097 found 298.2094.

3,3'-(3-Fluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) **4l**



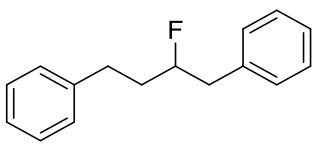
White solid, mp = 36–38 °C, 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06–6.83 (m, 6H), 4.66–4.44 (m, 1H, $^{2}J_{H\text{-}F}$ =49.1 Hz), 3.01–2.80 (m, 2H), 2.75–2.60 (m, 2H), 2.28 (s, 6H), 2.21 (s, 6H), 1.96–1.64 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 136.9, 134.4, 127.9, 126.9, 125.4, 93.2 (d, *J* = 168.2 Hz), 36.1 (d, *J* = 20.8 Hz), 29.4 (d, *J* = 3.8 Hz), 20.7, 14.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -173.12–-190.67 (m, 1F). IR (KBr): 3019, 2937, 1594, 1455, 1375, 1172, 1029, 889 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{27}F^{+}$ [M^{+}]: 298.2097 found 298.2096.

2,2'-(3-Fluoropentane-1,5-diyl)dinaphthalene **4m**



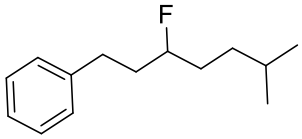
White solid, mp = 90–92 °C, 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.68 (m, 6H), 7.60 (s, 2H), 7.49–7.37 (m, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.65–4.47 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 3.08–2.83 (m, 4H), 2.12–1.87 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 133.5, 131.9, 128.0, 127.5, 127.3, 127.1, 126.4, 125.9, 125.2, 92.6 (d, *J* = 168.2 Hz), 36.8 (d, *J* = 21.0 Hz), 31.5 (d, *J* = 4.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -182.84–-185.18 (m, 1F). IR (KBr): 3062, 2940, 1639, 1587, 1511, 1060, 862, 732 cm^{-1}. HRMS (EI) calcd. for $C_{25}H_{23}F^{+}$ [M^{+}]: 342.1784 found 342.1786.

(2-Fluorobutane-1,4-diyl)dibenzene **4n**



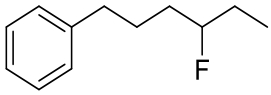
White solid, mp = 30–31 °C, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.23 (m, 4H), 7.24–7.11 (m, 6H), 4.87–4.60 (m, 1H, $^{2}J_{H\text{-}F}$ = 48.8 Hz), 3.06–2.80 (m, 3H), 2.76–2.59 (m, 1H), 2.02–1.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.3, 128.4, 126.5, 125.9, 93.5 (d, *J* = 171.3 Hz), 41.6 (d, *J* = 21.4 Hz), 36.4 (d, *J* = 20.9 Hz), 31.3 (d, *J* = 4.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -180.42–-181.31 (m, 1F). IR (KBr): 3031, 2952, 2865, 1598, 1498, 1442, 1072, 838, 738, 694 cm^{-1}.HRMS (EI) calcd. for $C_{16}H_{17}F^{+}$ [M^{+}]: 228.1314 found 228.1317.

(3-Fluoro-6-methylheptyl)benzene **4p**



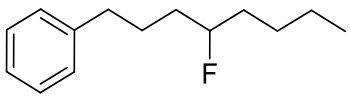
Colorless oil, 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.03 (m, 5H), 4.58–4.34 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 2.87–2.59 (m, 2H), 2.06–1.75 (m, 2H), 1.72–1.44 (m, 3H), 1.42-1.15 (m, 2H), 0.90 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 128.43, 128.40, 125.8, 93.8 (d, *J* = 167.5 Hz), 36.9 (d, *J* = 21.1 Hz), 34.0 (d, *J* = 4.3 Hz), 33.0 (d, *J* = 20.7 Hz), 31.4 (d, *J* = 4.3 Hz), 27.9, 22.4 (d, *J* = 6.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -177.27–-184.97 (m, 1F). IR (KBr): 3023, 2944, 2864, 1590, 1494, 1463, 1382, 1060, 741, 698 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{21}F^{+}$ [M^{+}]: 208.1627 found 208.1635

(4-Fluorohexyl)benzene **4r**



Colorless oil, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.24 (m, 2H), 7.23–7.13 (m, 3H), 4.59–4.28 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 2.65 (t, *J* = 7.3 Hz, 2H), 1.89–1.45 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 128.3, 128.2, 125.7, 95.5 (d, *J* = 167.4 Hz), 35.6, 34.2 (d, *J* = 21.0 Hz), 28.0 (d, *J* = 21.5 Hz), 26.9 (d, *J* = 4.1 Hz), 9.4 (d, *J* = 5.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -181.54–-182.72 (m, 1F). IR(KBr): 3027, 2933, 2819, 1606, 1494, 1463, 1363, 1097, 944, 709 cm^{-1}. HRMS (EI) calcd. for $C_{12}H_{17}F^{+}$ [M^{+}]: 180.1314 found 180.1322.

(4-Fluorooctyl)benzene **4s**



Colorless oil, 53% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.24 (m, 2H), 7.22–7.15 (m, 3H), 4.58–4.37 (m, 1H, $^{2}J_{H\text{-}F}$ = 49.3 Hz), 2.64 (t, *J* = 7.3 Hz, 2H), 1.82–1.45 (m, 6H), 1.44–1.22 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 128.3, 128.2, 125.7, 94.3 (d, *J* = 166.8 Hz), 35.6, 34.8 (d, *J* = 11.5 Hz), 34.6 (d, *J* = 11.7 Hz), 27.2 (d, *J* = 4.4 Hz), 26.9 (d, *J* = 4.2 Hz), 22.5, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -180.40–181.34 (m, 1F). IR (KBr): 3019, 2937, 2865, 1602, 1494, 1448, 1378, 1022, 764, 690 cm^{-1}. HRMS

(EI) calcd. for $C_{14}H_{21}F^+$ [M^+]: 208.1627 found 208.1622

Synthesis of compound 1v-y, 3x and 3y, related to Table 2.

In Table 2, substrates such as 1,5-diphenylpentan-3-one (**1v**), (3,3-dimethoxypentane-1,5-diyl)dibenzene (**1w**), (3,3-dichloropentane-1,5-diyl)dibenzene (**1x**), (3,3-dibromopentane-1,5-diyl)dibenzene (**1y**) and elimination product (3-chloropent-2-ene-1,5-diyl)dibenzene (**3x**), were known compounds, and were synthesized followed literature report (Blümel et al., 2018; Takeda et al., 1997; Mukaiyama et al., 1973).

(3-bromopent-2-ene-1,5-diyl)dibenzene (**3y**) was new compound, as yellow oil. The *Z*/*E* ratio (10:1) was determined by ^{1}H-NMR. HRMS (EI) calcd. for $C_{17}H_{17}Br^+$ [M^+]: 300.0514, found 300.0518. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.15 (m, 8H), 7.06 (d, *J* = 6.8 Hz, 2H), 5.72 (t, *J* = 7.0 Hz, 1H), 3.48 (d, *J* = 6.9 Hz, 2H), 2.93–2.83 (m, 2H), 2.83–2.71 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 139.2, 128.6, 128.4, 128.34, 128.31, 128.13, 128.12, 126.1, 126.0, 43.4, 37.5, 34.4. IR (KBr): 3019, 2921, 2844, 1654, 1598, 1490, 1452, 1081, 686 cm^{-1}.

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