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Rui Guo, Xiaotian Qi, Hengye Xiang, Paul Geaneates, Ruihan Wang, Peng Liu, Yiming Wang

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Vinyl fluorides play an important role in drug development as they serve as bioisosteres for peptide bonds and are found in a range of biologically active molecules. The discovery of safe, general and practical procedures to prepare vinyl fluorides remains an important goal and challenge for synthetic chemistry. Here we introduce an inexpensive and easily-handled reagent and report simple, scalable, and metal-free protocols for the regioselective and stereodivergent hydrofluorination of alkynes to access both the E and Z isomers of vinyl fluorides. These conditions were suitable for a diverse collection of alkynes, including several highly-functionalized pharmaceutical derivatives. Mechanistic and DFT studies support C–F bond formation through a vinyl cation intermediate, with the (E)- and (Z)-hydrofluorination products forming under kinetic and thermodynamic control, respectively.

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1Stereodivergent alkyne hydrofluorination using a simple practical reagent

2Rui Guo[#], Xiaotian Qi[#], Hengye Xiang, Paul Geaneotes, Ruihan Wang, Peng Liu* and

3Yi-Ming Wang*

4

5Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260,

6United States

7*Corresponding author. E-mail: ym.wang@pitt.edu, pengliu@pitt.edu

8

9**Abstract: Vinyl fluorides play an important role in drug development as they**
10**serve as bioisosteres for peptide bonds and are found in a range of biologically**
11**active molecules. The discovery of safe, general and practical procedures to**
12**prepare vinyl fluorides remains an important goal and challenge for synthetic**
13**chemistry. Here we introduce an inexpensive and easily-handled reagent and**
14**report simple, scalable, and metal-free protocols for the regioselective and**
15**stereodivergent hydrofluorination of alkynes to access both the *E* and *Z* isomers**
16**of vinyl fluorides. These conditions were suitable for a diverse collection of**
17**alkynes, including several highly-functionalized pharmaceutical derivatives.**
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19**cation intermediate, with the (*E*)- and (*Z*)-hydrofluorination products forming**
20**under kinetic and thermodynamic control, respectively.**

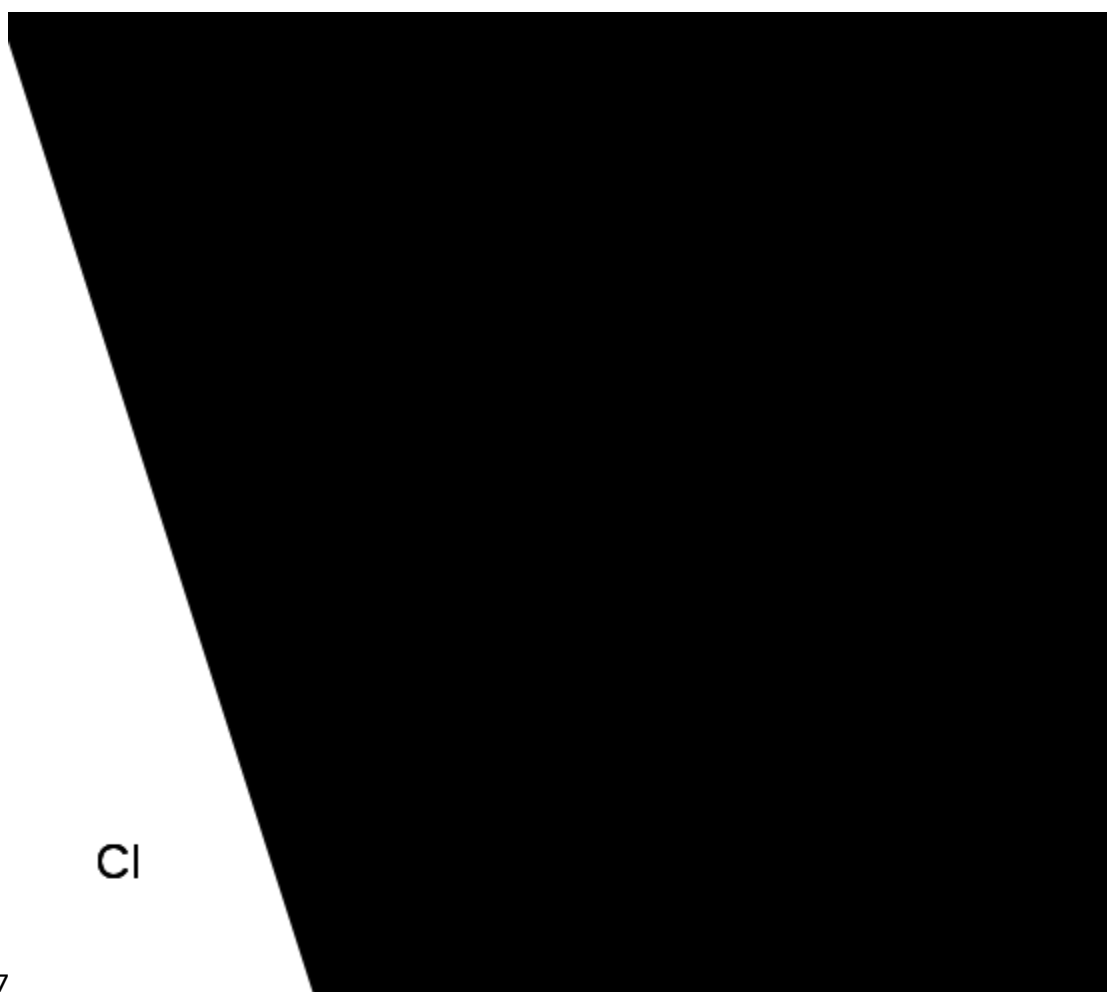
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22 The incorporation of fluorine into organic compounds plays a significant role in the
23pharmaceutical and agrochemical sciences, due to its distinctive capability for
24modulating the physical and chemical properties of a biologically active scaffold,
25including solubility, metabolic stability, potency, and bioavailability^{1,2}. Among them,
26vinyl fluorides are privileged structures that notably serve as bioisosteres of peptide
27bonds, mimicking their charge distribution and dipole moment (Fig. 1A)³.

28 Previous synthetic approaches to vinyl fluorides have primarily employed
29olefination reactions and elimination reactions which require multistep
30transformations and the preparation of prefunctionalized fluorinated substrates^{4,5}. One
31direct approach for vinyl fluoride synthesis involves the coupling of fluoride ion with
32vinyl triflates catalyzed by biaryldialkylphosphine complexes of palladium (Fig. 1B,
33a)⁶. The metal-catalyzed and noncatalytic fluorination of vinyl metal species under
34oxidative conditions constitutes another approach (Fig. 1B, b)⁷⁻¹⁶. Finally, the
35dehydrative fluorination of ketones using difluorosulfur(IV) reagents has been
36reported in the patent literature (Fig. 1B, c)¹⁷. A more direct method to access vinyl
37fluorides is the hydrofluorination of alkynes, substrates that are easily accessed from a
38variety of commercially available starting materials. Several strategies for the
39hydrofluorination of alkynes have been developed in recent years¹⁸⁻²⁶. These have
40included the coinage metal-catalyzed hydrofluorination of alkynes using various
41Lewis base adducts of hydrogen fluoride (Fig. 1B, d)¹⁸⁻²⁵. Although these approaches
42allow for the preparation of various vinyl fluorides, the corrosivity of HF-based
43reagents, the inaccessibility or complexity of metal-based catalysts and ligands, and
44challenges in controlling *E/Z*-selectivity and regioselectivity may limit their
45applicability and scalability. Consequently, the development of operationally simple
46methods and practical reagents for accessing vinyl fluorides with control of regio- and
47stereochemistry remains an ongoing challenge.

48 Considering their low cost, high fluoride content, as well as excellent safety,
49stability, and handling profiles, tetrafluoroborate (BF_4^-) salts are particularly attractive
50and efficient sources of nucleophilic fluoride²⁷. However, aside from the well-
51developed Balz-Schiemann process, they have seldom been employed in the
52formation of $\text{C}(\text{sp}^2)\text{-F}$ bonds due to the weak nucleophilicity of the species, and
53known methods often require the use of exotic functional groups or strongly oxidizing
54conditions²⁸. Given previous reports of alkyne hydrohalogenation that proceed via
55either the concerted $\text{Ad}_\text{E}3$ mechanism or an $\text{Ad}_\text{E}2$ mechanism featuring a vinyl cation

intermediate²⁹, we hypothesized that a partially or wholly protonated alkyne could be sufficiently electrophilic to enable the use of tetrafluoroborate as a nucleophilic fluorinating reagent. Therefore, we posited that an acidic source of tetrafluoroborate could serve as a general hydrofluorinating reagent for alkynes. Indeed, the hydrofluorination of alkynes using a base-modulated acidic source of nucleophilic fluorine was already investigated by Olah and coworkers in the 1970s using the Olah reagent³⁰, C₅H₅N•9HF, and this process was recently improved by Hammond, Xu, and coworkers using designer base-complexed sources of hydrogen fluoride³¹. However, both reports reveal that even under very mild conditions (0 to 50 °C), these reagents deliver the *gem*-difluoride bis(hydrofluorination) product, without allowing for the isolation of the presumed vinyl fluoride intermediate (Fig. 1B, e).



67

68Fig. 1. Strategies for the synthesis of vinyl fluorides. a, Representative bioactive organic molecules

69demonstrating the ubiquitous nature of vinyl fluorides. **b**, Previous synthetic approaches to vinyl
70fluorides through the formation of C–F bond. **c**, This work: stereodivergent alkyne hydrofluorination and
71Mechanistic studies. **d**, Applications in the late-stage functionalization of drug derivatives.

72 An acidic reagent based on the tetrafluoroborate ion, formally equivalent to the
73nonexistent HBF_4 , would serve as a controlled source of nucleophilic fluorine.
74Moreover, we expect the acidity, and thus, the reactivity of such a reagent to be
75tunable through the variation of the protonated weak base. From the point of view of
76cost and availability, such a reagent would be nearly ideal for the hydrofluorination of
77alkynes, provided that the hydrofluorination reactions would proceed with functional
78group tolerance and control over the regiochemical and stereochemical outcomes.
79Here, we report the discovery and development of a simple and practical reagent for
80the stereodivergent hydrofluorination of alkynes, in many cases with excellent control
81of the regio- and stereoselectivity (Fig. 1C). Thus, for certain substitution patterns, we
82report complementary conditions for the synthesis of either the *E* or *Z* isomer of the
83hydrofluorination product with good to excellent *E/Z* ratios. The conditions reported
84here are tolerant of a variety of functional groups, and we applied them to the late-
85stage functionalization of drug derivatives (Fig. 1D). A mechanistic study of the
86process was performed through kinetics experiments and density functional theory
87(DFT) calculations. These studies support the intermediacy of vinyl cations in the
88hydrofluorination. They also provide insight into the excellent stereochemical control
89and accounts for the ability to selectively obtain the *E* or *Z* isomer through the
90variation of reagent and reaction conditions. Previously, vinyl cations have been
91generated through several approaches³², including metal catalysis^{33,34}, photochemical
92processes³⁵, ionization of vinyl iodonium³⁶ and diazonium species³⁷, (pseudo)halide
93abstraction with Lewis acids^{38,39}, as well as protonation of alkynes with strong
94Brønsted acid^{40–42}. In spite of the challenging and specialized conditions that are often
95required for their generation, the versatility of this intermediate has led to a recent
96renaissance in their synthetic applications⁴³. In this context, the hydrofluorination

97conditions reported here represent an unprecedentedly mild, stereocontrolled, and
98functional group compatible approach for utilizing these intermediates.

99Results and discussion

100**Reaction development.** We commenced the exploration of our hydrofluorination
101strategy using (cyclohexylethynyl)benzene as a starting material, considering the lack
102of literature precedent employing secondary alkyl-substituted phenylacetylenes as
103substrates for hydrofluorination (Table 1). We anticipated that the corresponding
104amine salts of HBF₄ could adjust the acidity and release HBF₄ slowly to avoid the
105decomposition of alkynes or the generation of ketone side product. A diverse range of
106amine salts of HBF₄ was evaluated. While it was found that reagents based on
107triethylamine (**A**), pyridine (**B**), and 2-chloropyridine (**C**) were unreactive in CHCl₃ at
108room temperature or 70 °C (entries 1-3), we found that the more electron-poor 3,5-
109dichloropyridinium salt provided a trace of the desired product (entry 4). Continuing
110with more electron-deficient pyridinium salts, we found that the 2,6-dihalopyridinium
111salts (**E** and **F**) were more efficient reagents, with the more electron-deficient
112chlorinated reagent providing the desired product with good yield and excellent
113stereoselectivity (*Z/E* > 50:1, entry 6). We did not detect any *gem*-difluoride product
114from continued hydrofluorination of the monofluoroalkene, a process that could not
115be avoided under previous conditions using pyridine/HF or DMPU/HF^{30,31}. Further
116improving upon these promising results, we found that yields could be enhanced by
117using LiBF₄ (25 mol %) as an inexpensive additive (entry 7 vs. entry 8). Among a
118collection of pyridinium salts examined, we found that 2,6-dichloropyridinium
119tetrafluoroborate (**F**), prepared on large scale (50 mmol) by protonation of the
120pyridine with commercially available HBF₄•Et₂O, possessed the best reactivity and
121handling properties, including excellent crystallinity and low hygroscopicity. In
122particular, **F** could be stored as a colorless solid in the desiccator for at least a week or
123in the glovebox indefinitely (> 3 months) without noticeable deterioration or loss of

124activity. Lastly, we examined $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ as another potential reagent. Surprisingly,
 125we found that treatment of the model substrate with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (1.0 equiv) at room
 126temperature for 6 hours resulted in the formation of desired hydrofluorination product
 127**1** in moderate yield (42% yield) and good selectivity for the *opposite* stereoisomer
 128($E/Z = 11:1$).

129**Table 1. Optimization of reaction conditions for hydrofluorination**

130

| Entr y | Fluorinating reagent | Temp./°C | Yield/% | Z/E |
|-----------|--|----------|---------|----------|
| 1 | A | 70 | 0 | — |
| 2 | B | 70 | 0 | — |
| 3 | C | 70 | 0 | — |
| 4 | D | 70 | < 5 | 1 : 5 |
| 5 | E | 70 | 45 | > 50 : 1 |
| 6 | F | 70 | 74 | > 50 : 1 |
| 7 | F | 70 | 82(76) | > 50 : 1 |
| 8 | $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ | r.t. | 42 | 1 : 11 |

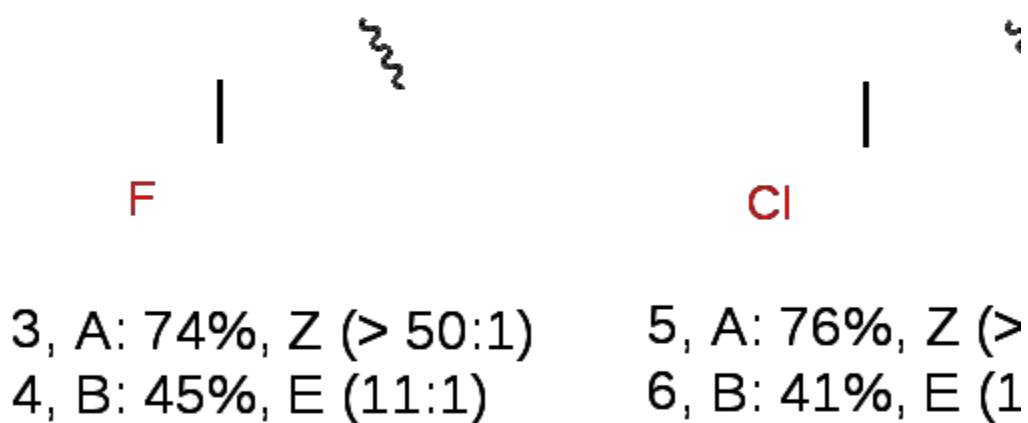
131**The substrate scope.** Under these optimized conditions, we set out to investigate the
 132scope of this hydrofluorination reaction (Table 2). Using reagent **F** for
 133hydrofluorination, aryl alkyl acetylenes bearing electron-withdrawing (e.g., products
 134**9**, **19**, **20**, **22**) to electron-donating (e.g., products **23**, **24**, **25**) aryl substituents reacted
 135effectively to afford the (*Z*)-configured fluoroalkene products in moderate to good
 136yields and excellent regio- and stereoselectivities. Moreover, several common
 137functional groups on the aryl ring including methyl ester (**19**), cyano group (**20**),

trifluoromethanesulfonyl ester (**22**), and phthalimide (**23**) were tolerated. Heteroaryl alkyl acetylenes, including an indole and a furan likewise delivered the desired product (**24**, **25**). We determined the structure of the product **22** by X-ray single-crystal diffraction structure analysis for confirmation of the alkene stereochemistry.

Table 2. Substrate scope of alkynes



$R^1 = \text{Aryl}, R^2 = \text{Cyclohexyl}$ (Condition A)



Condition A: fluorinating reagent **F** (1.0 equiv), LiBF₄ (25 mol%), CHCl₃ (0.2 M), 70 to 90 °C. Condition B: HBF₄·Et₂O (1.0 equiv), CHCl₃ (0.2 M), r.t., 6 h. Condition C: fluorinating reagent **F** (3.0 equiv), CHCl₃, 80 to 100 °C, 12 h. Condition D: fluorinating reagent **F** (2.0 equiv), DCE, 70 to 100 °C, 12 h. ^a*gem*-difluoroalkane. See supporting information for detailed conditions.

We next explored the scope of alkyl substituents on the substrate. A range of primary, secondary, cyclic or acyclic alkyl-substituted alkynes could be employed in

the hydrofluorination to furnish respective products again with moderate to good yields and excellent regio- and stereoselectivities (**27-39**). Remarkably, substrates with several functional groups including primary chloro, carboxymethyl, cyano, pyridyl, and phthalimido groups could also be used to deliver monofluoroalkene products which highlighted the mildness of the conditions and the good functional group tolerance of this protocol (**40-46**). This process was also demonstrated by the gram-scale preparation of **44** with unchanged regio- and stereoselectivities and only slightly reduced yield (1.65 g, 64%). The protocol was insensitive to steric effects on the alkyl substituent, with a methyl group (**47, 48**) and a cyclododecyl (**49**) group giving similar yields, with no loss in regio- and stereoselectivities. It is noteworthy that in all reactions employing aryl-substituted alkynes, the monofluoroalkene products were delivered with exclusive regioselectivity, with C–F bond formation occurring adjacent to the aryl group. These results were complementary to the gold-catalyzed hydrofluorination which delivers the fluorine to the carbon adjacent to the alkyl group¹⁸⁻²³. However, a reduction in selectivity was observed for a dialkylacetylene substrate, which gave the *gem*-difluoroalkane in addition to the monofluorinated product (**50**). A variety of 1-haloalkynes (I > Br > Cl in reactivity) and ethyl phenylpropiolate were also suitable substrates for this reaction, in which a single regio- and stereoisomer was produced in each case (**51-55**). During the course of optimization, we found that tetrafluoroboric acid in diethyl ether (HBF₄•Et₂O) could also deliver hydrofluorination product. However, the predominant stereoisomer formed under these conditions was the *E* isomer. With commercially available reagent, we briefly explored the substrate scope of these conditions (condition B). Substrates bearing mildly electron-withdrawing or electron-donating substituents could afford the monofluoroalkene products with moderate to good *E*-selectivity (*E/Z* ratio from 4:1 to > 20:1).

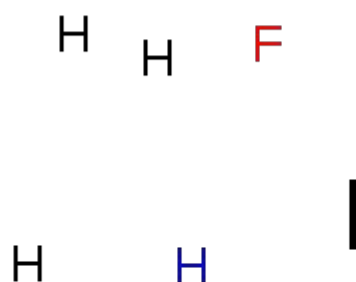
The hydrofluorination reaction could also be applied to terminal alkynes and diarylacetylenes. When using terminal alkyl-substituted alkynes as substrate *gem*-

178difluorides were obtained as the primary product with exclusive internal
179regioselectivity. A variety of functional groups such as an amide, an ester, an indole,
180as well as a ferrocene derivative were well tolerated (**56-60**). On the other hand,
181terminal aryl-substituted alkynes could be employed in this hydrofluorination to give
182the corresponding monofluoroalkene as the major product with moderate yields (**61-**
183**70**). With 1,2-dichloroethane as the solvent, diarylacetylenes could give
184corresponding monofluoroalkene products in modest to good yields and excellent *Z*-
185selectivities (**71-74**). For unsymmetrical substrates, when one of the benzene rings
186was substituted by an electron-withdrawing group (e.g., 4-CO₂Me, 2-Cl), the
187hydrofluorination product proceeded with excellent *Z*-selectivities and regioselectivity
188for fluorination nearer to the more electron-rich aryl group (**75-80**). Finally, it was
189found that by switching to chloroform as the solvent, the monofluoroalkene product
190could be formed with *E*-selectivity (**81-84**).

191**Synthetic applications.** To demonstrate the potential applicability of this new
192hydrofluorination method to the late-stage modification of biologically active
193molecules or complex natural products, we explored several readily available alkynes
194derived from the complex structure molecules *exo*-norborneol (**85**) and ferrocene (**86**),
195natural products (1*S*)-(+)-10-camphorsulfonic acid (**87**) and estrone (**88, 89**), as well
196as drug molecules probenecid (**90**), febuxostat (**92**) and telmisartan (**94**) to afford
197monofluoroalkene products with moderate to good yields and high regio- and
198stereoselectivities (Fig. 2a). In addition, terminal alkyl-substituted alkynes derived
199from drug molecules probenecid and febuxostat could also be employed in the
200dihydrofluorination to form *gem*-difluorides with moderate yields and exclusive
201regioselectivity (**91, 93**). These examples demonstrated that our hydrofluorination and
202difluorination protocols were suitable for the late-stage, protecting-group-free
203modification of biologically active molecules and could tolerate a range of functional
204groups and heterocycles including ketones (**87-89**), esters (**90-94**), a ferrocene (**86**), a

sulfonate (**87**), a sulfonamide (**90**, **91**), a nitrile (**92**, **93**), a thiazole (**92**, **93**), and benzimidazoles (**94**).

a



**85, 77%, Z (> 50:1)
exo -Norborneol derivative**

207

Fig. 2. Synthetic applications of stereodivergent alkyne hydrofluorination. **a**, The late-stage modification of biologically active molecules or complex natural products. **b**, The synthesis of different fluorinated analog of drug molecules. **c**, The preparation of key intermediate for the synthesis of antimicrobial agents with high regio- and *Z/E*-selectivities. See supporting information for detailed conditions.

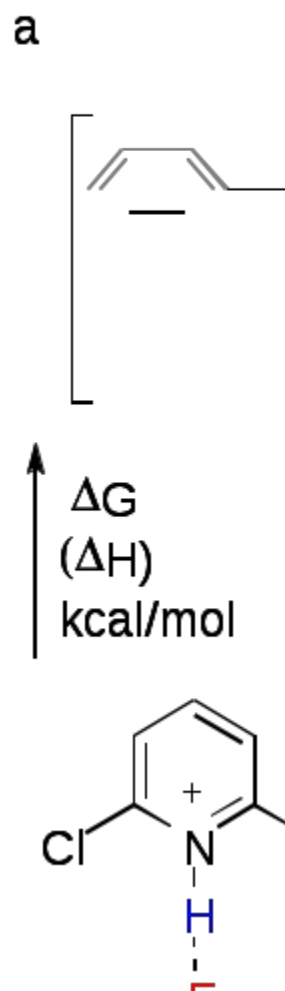
To explore other applications of this chemistry, we prepared **95** on 5-mmol scale to access fluorinated analogues of antihistamines cinnarizine (**97**), flunarizine (**98**) and antifungal drug naftifine (**99**) (Fig. 2b). Via bromination of **95**, we prepared a common brominated intermediate **96**, which could be applied to synthesize all three analogues. Moreover, we also prepared vinyl fluoride **100**, a known precursor for the synthesis of antimicrobial agents (protein synthesis inhibitors) through the coupling

219with 2-oxazolidone (Fig. 2c)^{44,45}. These transformations illustrated in above study
220demonstrated the great potential of this method for industrial applications in the
221future.

222**Mechanistic discussion.** The experimental results have demonstrated that 2,6-
223dichloropyridinium tetrafluoroborate is an effective fluorinating reagent for
224stereodivergent alkyne hydrofluorination. As shown in Table 2, high levels of *Z*-
225selectivity are obtained in a polar solvent (*i.e.* DCE, condition D), while reactions in a
226less polar solvent (*i.e.* chloroform, condition C) or under lower temperatures (see SI)
227completely switch the stereoselectivity to favor *E*-products. Mechanistic studies were
228then performed to investigate whether the hydrofluorination occurs through a
229concerted or stepwise mechanism and the origin of the divergent stereoselectivity.
230DFT calculations⁴⁶ of the hydrofluorination of 1,2-diphenylacetylene **101** indicated a
231stepwise Ad_E2-type protonation-fluorination mechanism with a BF₄[−]/vinyl cation ion-
232pair intermediate (Fig. 3a). Prior to the alkyne protonation, the H⋯F hydrogen bond
233in the fluorinating reagent **F** dissociates to release a free pyridinium cation as the
234proton source. Two protonation transition states were located (**TS-1** and **TS-1a**), in
235which the tetrafluoroborate anion is *syn* and *anti* to the pyridinium, respectively.
236Bonding interactions between BF₄[−] and the alkyne were not observed in either
237protonation transition state, which is likely due to the weak nucleophilicity of BF₄[−].
238The stepwise hydrofluorination mechanism is confirmed by the intrinsic reaction
239coordinate (IRC) calculations, which indicated that **TS-1** and **TS-1a** lead to BF₄[−]/vinyl
240cation ion pairs **102** and **102a**, respectively, rather than the hydrofluorination
241products. Fluorination of the highly electrophilic vinyl cation with BF₄[−] (via **TS-2** and
242**TS-2a**) is very facile, which makes protonation (**TS-1**) the rate-determining step. This
243mechanistic picture is consistent with experimental Hammett analysis and kinetics
244studies, which indicated a ρ value of −3.43 consistent with previously reported vinyl
245cation-mediated reactions³² and first-order kinetics in alkyne and H⁺ and zero-order
246kinetics in excess BF₄[−] (Fig. 3d, see SI for details). The *E*-selective pathway (shown in

black in Fig. 3a) is kinetically favored in both protonation and fluorination steps. The *syn*-protonation transition state **TS-1** is more stable than the *anti*-TS (**TS-1a**) due to more favorable electrostatic interactions between BF_4^- and the pyridinium cation. The *E*-selective fluorination transition state **TS-2** is 0.9 kcal/mol more stable than the *Z*-selective fluorination (**TS-2a**) because of steric repulsions between BF_4^- and the β -phenyl group in **TS-2a**⁴⁷. Therefore, regardless of whether ion pairs **102** and **102a** have sufficient lifetime to interconvert prior to the fluorination, kinetic *E*-selectivity is expected. The relatively low barrier for the reverse reaction of *E*-**81** (via **TS-2**, $\Delta G^\ddagger = 23.6$ kcal/mol) to generate the vinyl cation indicates the *E*-to-*Z* vinyl fluoride isomerization may occur at elevated temperatures through BF_3 -mediated fluoride anion elimination followed by fluorination of the vinyl cation via **TS-2a**. A polar solvent would also promote such isomerization by stabilizing ion-pair intermediates **102** and **102a**. Because the *Z*-stereoisomer *Z*-**71** is 2.3 kcal/mol more stable than *E*-**71**, high *Z*-selectivity is expected under these thermodynamically controlled conditions.

The BF_3 -mediated *E/Z*-vinyl fluoride isomerization is verified experimentally under conditions with either 2,6-dichloropyridinium tetrafluoroborate or $\text{Et}_2\text{O} \cdot \text{BF}_3$ (Fig. 3b). The addition of 2,6-di-*tert*-butylpyridine did not shut down the $\text{Et}_2\text{O} \cdot \text{BF}_3$ -mediated isomerization, which excludes the possibility of Brønsted acid-promoted pathway. In addition, the increase of the *Z*-product ratio over a reaction time of 12 h at 70 °C further confirmed the isomerization of the kinetic *E*-isomer to *Z*-vinyl fluoride in the hydrofluorination of di-*p*-tolylacetylene (Fig. 3c). In certain cases, we also observed that better *Z*-selectivity could be obtained by addition of exogenous $\text{Et}_2\text{O} \cdot \text{BF}_3$ to promote *E*-to-*Z*-isomerization (*e.g.*, product **86** and **87** in Fig. 2, *Z/E* ratio from 3:1 to 19:1).



272

273**Fig. 3. Mechanistic studies.** **a.** Reaction energy profiles of the hydrofluorination of 1,2-
 274diphenylacetylene **101** with 2,6-dichloropyridinium tetrafluoroborate. All energies were calculated at the
 275M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory. See Fig.
 276S10 and S11 in SI for the computational results with the cyclohexyl and methyl-substituted alkynes. **b.**
 277*E/Z*-isomerization of vinyl fluoride with fluorinating reagent **F** and Et₂O•BF₃. **c.** Change of the *Z/E*-ratio of
 278the hydrofluorination product over the course of reaction. **d.** Proposed mechanism for the
 279stereodivergent hydrofluorination of alkyne.

280 Based on these mechanistic studies, a general mechanism is proposed to elucidate
 281the stereoselectivity control in the alkyne hydrofluorination (Fig. 3d). The rate-

determining *syn*-protonation of alkyne (k_1) leads to an ion pair intermediate (**I**), which then undergoes fluorination (k_2) to afford the kinetically favored *E*-vinyl fluoride. The thermodynamically more stable *Z*-product is formed from the isomerization of the *E*-vinyl fluoride, which takes place via BF_3 -mediated fluoride dissociation (k_2) and isomerization of the ion pair intermediate (k_3) followed by *Z*-selective fluorination with BF_4^- (k_4). Higher temperatures and polar solvents (*e.g.* DCE) promote such *E*-to-*Z* isomerization, and thus enhance the *Z*-selectivity. Experimentally, excess BF_4^- (condition A) was also found to favor formation of the *Z*-isomer (see SI), an effect which may be ascribed to increased availability of BF_4^- for *anti*-attack (k_4) or a change in the solvent polarity due to higher ionic content. On the other hand, lower temperatures, polar solvent, and bulkier alkyne substituents (*e.g.* aryl) that suppress ion pair isomerization (k_3) and the *Z*-selective fluorination (k_4) would lead to higher *E*-selectivity under kinetic control.

Conclusion

We have developed a simple, practical, and metal-free strategy for the regio- and stereoselective controlled mono- and dihydrofluorination of alkynes by employing 2,6-dichloropyridinium tetrafluoroborate as a new, safe, and stable fluorinating reagent. Mechanistic and DFT studies reveal that the stereoselectivity of hydrofluorination results from either kinetic or thermodynamic control in a stepwise protonation-fluorination pathway. We anticipate that this hydrofluorination protocol will find wide applications in drug discovery and related fields by facilitating the preparation of fluorinated drug candidates. Studies further exploiting the synthetic applications of vinyl cation intermediates generated under similar mild conditions are ongoing.

Data availability

308The data supporting the findings of this study are available within the paper and its
309Supplementary Information. The x-ray crystallographic coordinates for the structure
310of **22** are available free of charge from the Cambridge Crystallographic Data Centre
311under deposition number CCDC 1988001.

312

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459

460 **Author contributions** Y.-M.W. conceived and directed the project. R.G., H.X., P.G.,
 461 and R.W. carried out all experiments. X.Q. performed the computational studies with

462P.L. providing guidance. Y.-M.W., P.L., R.G. and X.Q. wrote the manuscript with
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465**Additional information**

466**Supplementary information** is available in the online version of the paper.

467**Correspondence and requests for materials** should be addressed to Y.-M.W. or P.L.

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Supporting Information for

Stereodivergent alkyne hydrofluorination with a simple practical reagent

Rui Guo[#], Xiaotian Qi[#], Hengye Xiang, Paul Geaneotes, Ruihan Wang, Peng Liu* and Yi-Ming Wang*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

E-mail: ym.wang@pitt.edu, pengliu@pitt.edu

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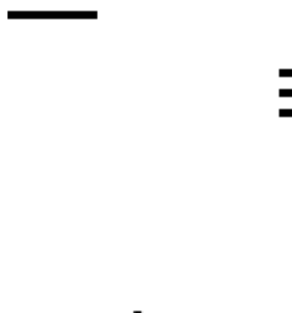
1. General Information

General Reagent Information: Anhydrous chloroform, 1,2-dichloroethane, tetrahydrofuran, and trifluorotoluene were purchased from Acros (AcroSeal packaging), Sigma Aldrich (Sure/Seal packaging), and Frontier Scientific (J&KSeal packaging), respectively, and were transferred into an argon-filled glovebox and used as received. Other dry solvents were obtained by distillation and storage over 3Å or 4Å molecular sieves. All other reagents were purchased from Oakwood, Acros, Alfa Aesar, or Sigma Aldrich and used as received. Compounds were purified by flash column chromatography using SiliCycle *SiliaFlash® F60* silica gel, unless otherwise indicated.

General Analytical Information: New compounds were characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. Copies of the ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra can be found at the end of the Supporting Information. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 500 MHz instruments. All ^1H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 2.50 ppm (DMSO-*d*₆), 7.26 ppm (CDCl₃) or 5.32 ppm (CD₂Cl₂). All ^{13}C NMR spectra are ^1H decoupled and reported in ppm relative to the solvent signal at 39.52 ppm (DMSO-*d*₆), 77.00 ppm (CDCl₃) or 53.84 ppm (CD₂Cl₂). Thin-layer chromatography (TLC) was performed on Silicycle 250 μm (analytical) or 1000 μm (preparative) silica gel plates. Compounds were visualized by irradiation with UV light, or by staining with iodine/silica gel, potassium permanganate, or phosphomolybdic acid (PMA). Yields refer to isolated compounds, unless otherwise indicated. High resolution mass spectra were recorded on a Thermo Scientific Q-Exactive mass spectrometer. NMR yield was determined by using trifluorotoluene as internal standard for ^{19}F NMR spectroscopy.

2. Optimization of reaction conditions

1. Optimization of fluorinating reagents



2. Optimization of solvent

| Entry | Solvent | Time (h) | NMR Yield (%) | Z/E |
|-------|-----------------------------|----------|---------------|--------------|
| 1 | THF | 6 | 0 | — |
| 2 | <i>t</i> Butyl methyl ether | 6 | 0 | — |
| 3 | Toluene | 6 | 21 | Z/E = 1 : 1 |
| 4 | PhCl | 6 | 52 | Z/E > 20 : 1 |
| 5 | PhCF ₃ | 6 | 53 | Z/E > 20 : 1 |
| 6 | PhCF ₃ | 12 | 65 | Z/E > 20 : 1 |
| 7 | CHCl ₃ | 6 | 70 | Z/E > 99 : 1 |
| 8 | DCE | 6 | 34 | Z/E > 99 : 1 |

| | | | | |
|---|--------------------|---|-------|---|
| 9 | CH ₃ CN | 6 | trace | — |
|---|--------------------|---|-------|---|

3. Optimization of temperature

| Entry | <i>T</i> (°C) | NMR Yield (%) | <i>Z/E</i> |
|-------|---------------|---------------|---------------------|
| 1 | 25 | trace | <i>Z/E</i> = 1 : 5 |
| 2 | 40 | 13 | <i>Z/E</i> = 3 : 1 |
| 3 | 50 | 39 | <i>Z/E</i> > 20 : 1 |
| 4 | 60 | 70 | <i>Z/E</i> > 99 : 1 |
| 5 | 70 | 74 | <i>Z/E</i> > 99 : 1 |
| 6 | 80 | 63 | <i>Z/E</i> > 99 : 1 |

4. Optimization of additives

| Entry | Additive | NMR Yield (%) | <i>Z/E</i> |
|-------|---|---------------|---------------------|
| 1 | NaBF ₄ (1.0 eq.) | 80 | <i>Z/E</i> > 20 : 1 |
| 2 | LiBF ₄ (1.0 eq.) | 81 | <i>Z/E</i> > 20 : 1 |
| 3 | N(<i>n</i> -Bu) ₄ BF ₄ (1.0 eq.) | 79 | <i>Z/E</i> > 20 : 1 |
| 4 | N(Et) ₄ BF ₄ (1.0 eq.) | 77 | <i>Z/E</i> > 20 : 1 |
| 5 | LiBF ₄ (0.5 eq.) | 83 | <i>Z/E</i> > 20 : 1 |
| 6 | LiBF ₄ (0.25 eq.) | 82 | <i>Z/E</i> > 99 : 1 |
| 7 | LiBF ₄ (0.1 eq.) | 79 | <i>Z/E</i> > 99 : 1 |

3. Mechanistic studies

3.1 Kinetic study

General Procedure for Initial Rate Kinetics

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, diphenylacetylene, 2,6-dichloropyridinium tetrafluoroborate NBu₄BF₄ and dry DCE were added in succession. The reaction tube was sealed and removed from the glovebox. After stirred at 85 °C for 1 h, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ¹⁹F-NMR spectroscopy. In all cases, conversions were under 15% and in the initial rate kinetics regime.

Table S1: Amounts and Volumes Used for Kinetic Experiments

| | Alkyne (A) | Pyridine Salt | NBu ₄ BF ₄ | DCE |
|--|-------------|---------------|----------------------------------|-------------|
| Entry | Amount (mg) | Amount (mg) | Amount (mg) | Volume (uL) |
| 1 | 3.4 | 5.5 | 0 | 581 |
| 2 | 5.2 | 5.5 | 0 | 581 |
| 3 | 6.3 | 5.5 | 0 | 581 |
| 4 | 8.2 | 5.5 | 0 | 581 |
| 5 | 3.4 | 5.5 | 0 | 581 |
| 6 | 3.4 | 5.5 | 1.5 | 575 |
| 7 | 3.4 | 5.5 | 3.1 | 578 |
| 8 | 3.4 | 5.5 | 4.9 | 555 |
| 9 | 3.4 | 5.5 | 6.5 | 590 |
| 10 | 3.4 | 3.2 | 0 | 580 |
| 11 | 3.4 | 5.5 | 0 | 581 |
| 12 | 3.4 | 7.8 | 0 | 574 |
| 13 | 3.4 | 9.9 | 0 | 563 |
| The reagent being varied is shown in red | | | | |

Table S2: Molarities of Each Reagent and Initial Rates for Each Kinetic Experiment

| Entry | Alkyne (A) /M | Cation (B) /M | BF ₄ ⁻ (C) /M | Temperature /K | Initial Rate /(M/s) |
|-------|---------------|---------------|-------------------------------------|----------------|---------------------|
| 1 | 0.0328 | 0.0400 | 0.0400 | 358.15 | 1.13E-06 |
| 2 | 0.0502 | 0.0400 | 0.0400 | 358.15 | 1.56E-06 |
| 3 | 0.0608 | 0.0400 | 0.0400 | 358.15 | 2.03E-06 |
| 4 | 0.0792 | 0.0400 | 0.0400 | 358.15 | 2.41E-06 |
| 5 | 0.0328 | 0.0400 | 0.0400 | 358.15 | 1.13E-06 |
| 6 | 0.0328 | 0.0400 | 0.0462 | 358.15 | 9.72E-07 |
| 7 | 0.0328 | 0.0400 | 0.0559 | 358.15 | 1.04E-06 |
| 8 | 0.0328 | 0.0400 | 0.0672 | 358.15 | 1.16E-06 |

| | | | | | |
|--|--------|--------|--------|--------|----------|
| 9 | 0.0328 | 0.0400 | 0.0729 | 358.15 | 1.14E-06 |
| 10 | 0.0328 | 0.0234 | 0.0234 | 358.15 | 5.25E-07 |
| 11 | 0.0328 | 0.0400 | 0.0400 | 358.15 | 1.13E-06 |
| 12 | 0.0328 | 0.0575 | 0.0575 | 358.15 | 1.23E-06 |
| 13 | 0.0328 | 0.0745 | 0.0745 | 358.15 | 1.71E-06 |
| The reagent being varied is shown in red | | | | | |

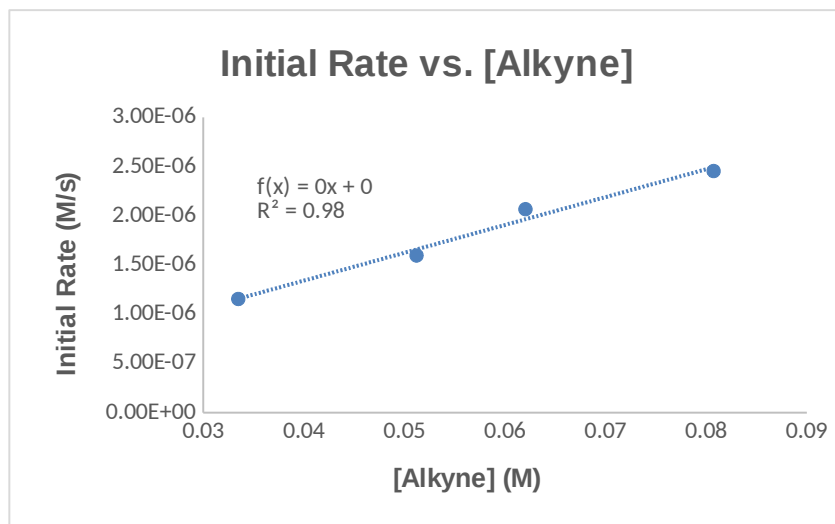


Figure S1: Plot of the initial rate of hydrofluorination vs. the concentration of **Alkyne**.

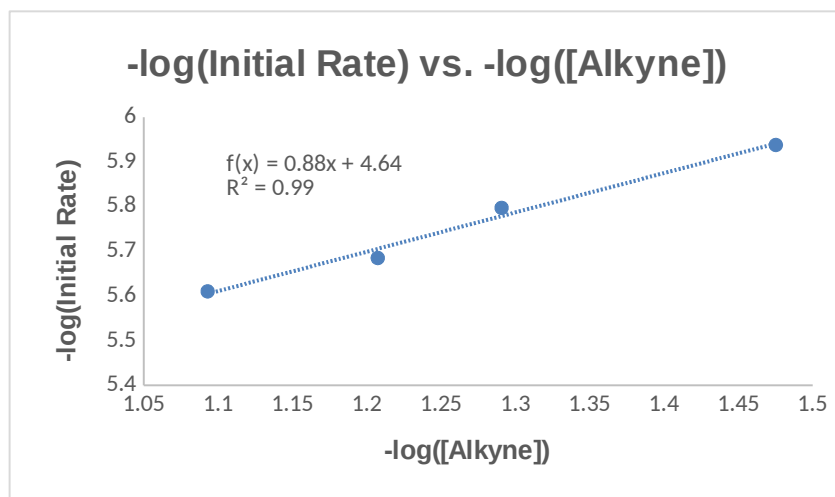


Figure S2: Plot of the minus logarithm of the initial rate of hydrofluorination vs. the minus logarithm of the concentration of **alkyne**.

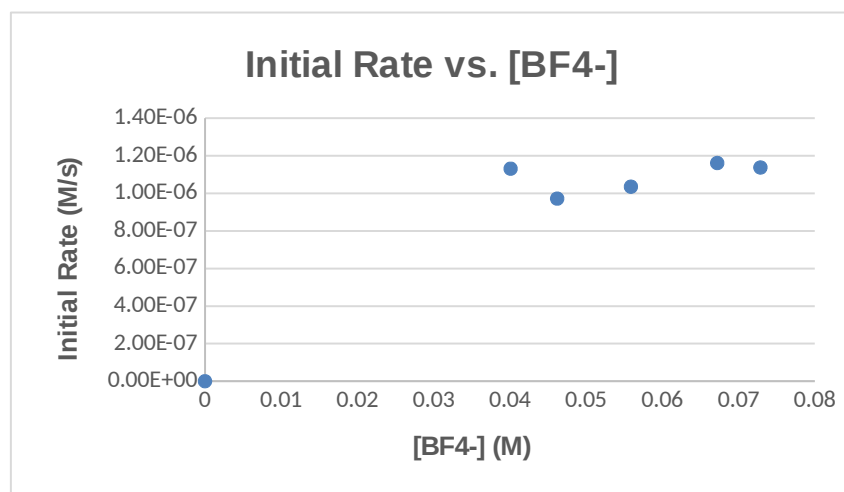


Figure S3: Plot of the initial rate of hydrofluorination vs. the concentration of BF_4^- .

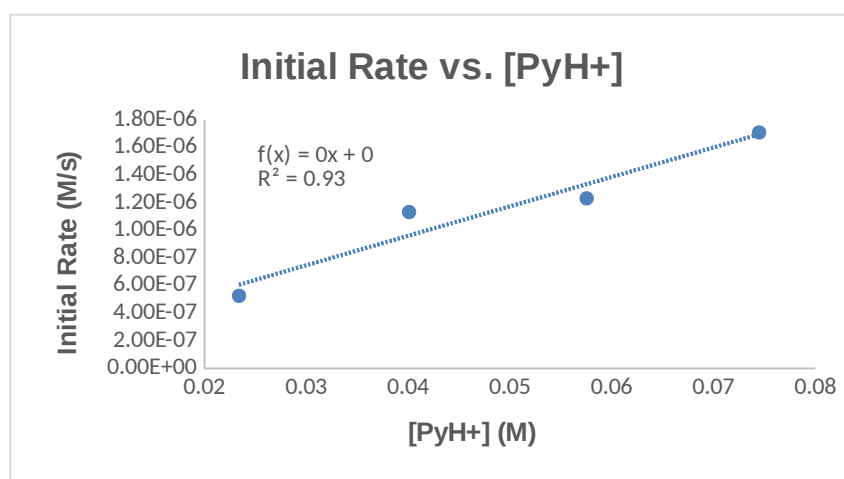


Figure S4: Plot of the initial rate of hydrofluorination vs. the concentration of 2,6-dichloropyridine cation.

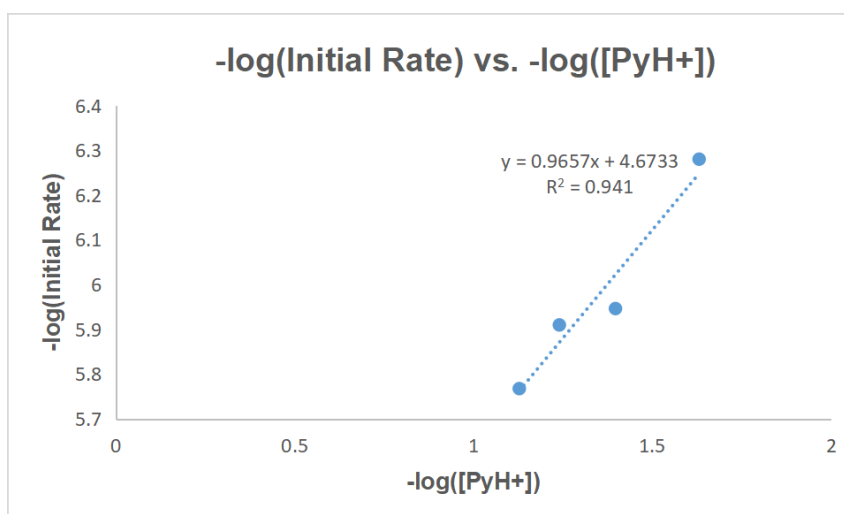


Figure S5: Plot of the minus logarithm of the initial rate of hydrofluorination vs. the minus

logarithm of the concentration of **2,6-dichloropyridine cation**.

Although pyridinium concentration and tetrafluoroborate concentration could not be varied independently, the rate order of tetrafluoroborate was ascertained to be zero by addition of tetrabutylammonium tetrafluoroborate as a source of excess tetrafluoroborate (Figure S3).

3.2 Stereoselectivity study

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), 1,2-Bis(4-methylphenyl)acetylene (0.2 mmol, 41 mg, 1.0 equiv) and dry CHCl₃ (1.0 mL) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirring at 70 °C for the given reaction time, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and benzonitrile was added as the internal standard for subsequent quantitative ¹⁹F-NMR spectroscopy.

| Entry | Temp./ °C | Time/h | E/Z | Yield/% | E/% | Z/% |
|-------|-----------|--------|---------|---------|-------|-------|
| 1 | 70 | 1 | 6 : 1 | 23 | 19.71 | 3.29 |
| 2 | 70 | 2 | 2.3 : 1 | 30 | 20.91 | 9.09 |
| 3 | 70 | 3 | 1.6 : 1 | 37 | 22.77 | 14.23 |
| 4 | 70 | 4 | 1.3 : 1 | 43 | 24.30 | 18.70 |
| 5 | 70 | 5 | 1 : 1 | 49 | 24.50 | 24.50 |
| 6 | 70 | 6 | 1: 1.2 | 53 | 24.09 | 28.91 |
| 7 | 70 | 7 | 1 : 1.4 | 58 | 24.17 | 33.83 |
| 8 | 70 | 8 | 1 : 1.6 | 61 | 23.46 | 37.54 |
| 9 | 70 | 9 | 1 : 1.8 | 59 | 21.07 | 37.93 |
| 10 | 70 | 10 | 1 : 2.1 | 55 | 17.74 | 37.26 |
| 11 | 70 | 11 | 1 : 2.4 | 51 | 15.00 | 36.00 |
| 12 | 70 | 12 | 1 : 2.4 | 45 | 12.16 | 32.84 |

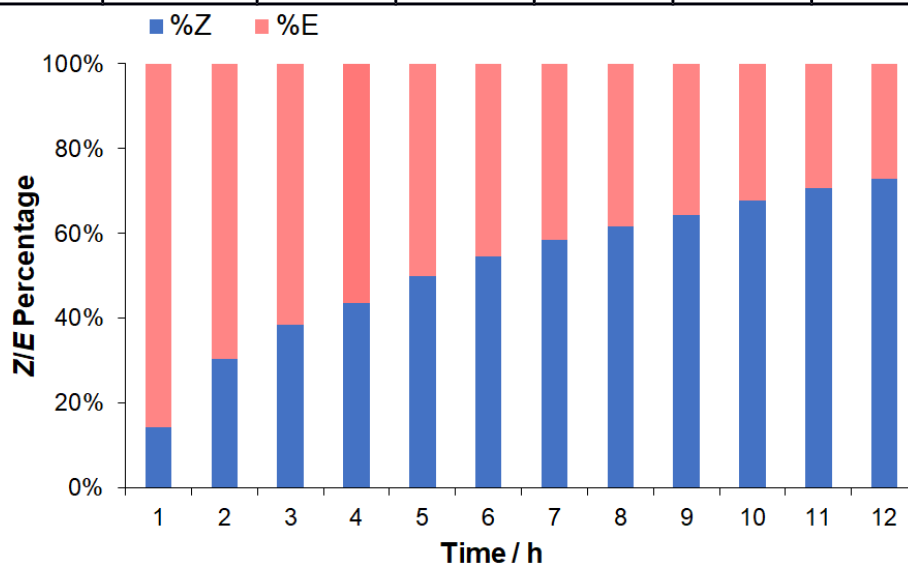


Figure S6: The Z/E-ratio of the hydrofluorination product over the course of reaction time.

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), 1,2-Bis(4-methylphenyl)acetylene (0.2 mmol, 41 mg, 1.0 equiv) and dry CHCl₃ (1.0 mL) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirring at the given temperature for 12 h, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and benzonitrifluoride was added as the internal standard for subsequent quantitative ¹⁹F-NMR spectroscopy.

| Entry | Temp./ °C | Time/h | E/Z | Yield/% | E/% | Z/% |
|-------|-----------|--------|---------|---------|-------|-------|
| 1 | 30 | 12 | 99 : 1 | 5 | 4.95 | 0.05 |
| 2 | 40 | 12 | 8 : 1 | 22 | 19.56 | 2.44 |
| 3 | 50 | 12 | 2.6 : 1 | 40 | 28.89 | 11.11 |
| 4 | 60 | 12 | 1 : 1.6 | 50 | 19.23 | 30.77 |
| 5 | 70 | 12 | 1 : 2.7 | 45 | 12.16 | 32.84 |
| 6 | 80 | 12 | 1 : 20 | 43 | 2.05 | 40.95 |
| 7 | 90 | 12 | 1 : 99 | 36 | 0.36 | 35.64 |

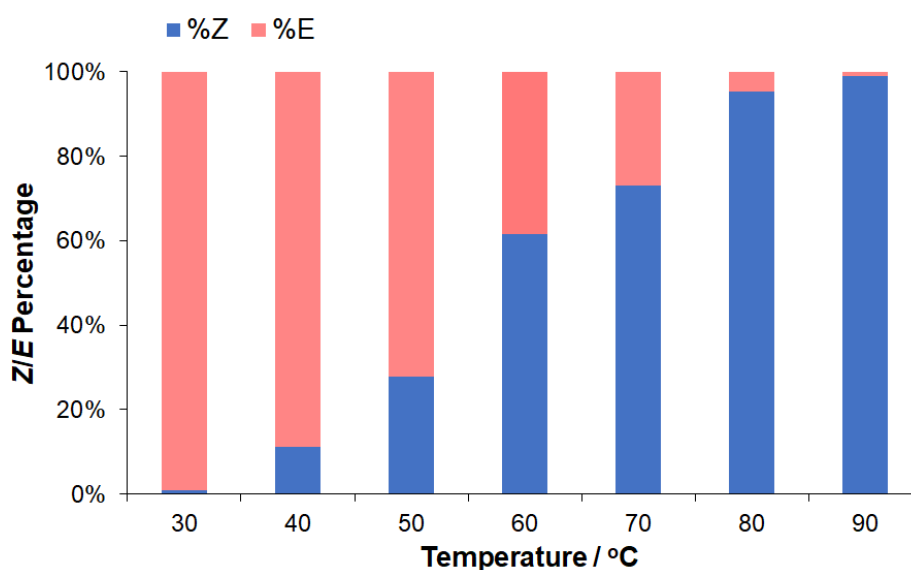


Figure S7: The Z/E-ratio of the hydrofluorination product over the course of reaction temperature.

These mechanistic studies all support that the C–F bond formation is a reversible step, and the generation of *E*-alkene in the hydrofluorination of aryl-substituted phenylacetylene is kinetically controlled while the formation of *Z*-alkene is thermodynamically controlled.

3.3 Hammett-plot analysis for para-substituted alkynes

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), (cyclohexylethynyl)benzene **A** (0.2 mmol, 37 mg) and substituted alkyne **B** (0.2 mmol,) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirred at 70 °C for 30 min, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ¹⁹F-NMR spectroscopy.

| R | σ_p | k_X/k_H | $\log(k_X/k_H)$ |
|----------------|------------|-----------|-----------------|
| 4- <i>t</i> Bu | -0.197 | 5.120 | 0.709 |
| 4-Me | -0.170 | 4.001 | 0.602 |
| H | 0.000 | 1.000 | 0.000 |
| 4-F | 0.062 | 0.833 | -0.079 |
| 4-Cl | 0.227 | 0.205 | -0.689 |
| 4-Br | 0.232 | 0.143 | -0.845 |

Hammett plot

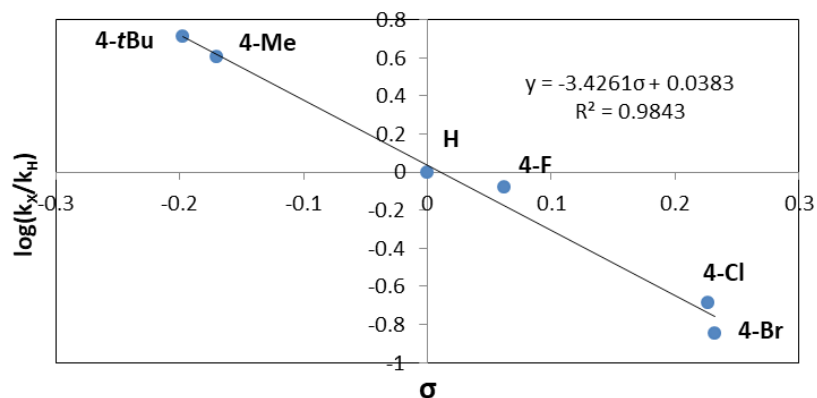


Figure S8: Hammett-plot analysis for *para*-substituted (cyclohexylethynyl)benzene.

3.4 Dielectric constant study

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), (cyclohexylethynyl)benzene (0.2 mmol, 37 mg, 1.0 equiv) and corresponding dry solvent (1.0 mL) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirring at 40 °C for 1 h, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and benzonitrile was added as the internal standard for subsequent quantitative ¹⁹F-NMR spectroscopy.

| Solvent | ε | <i>E/Z</i> |
|-------------------|-------|------------|
| CCl ₄ | 2.23 | NR |
| Toluene | 2.38 | 20 : 1 |
| CHCl ₃ | 4.7 | 3 : 1 |
| DCM | 8.9 | 1 : 2.5 |
| DCE | 10.37 | 1 : 16.2 |

4. DFT studies and control experiments

Computational methods

All density functional theory (DFT) calculations were performed using Gaussian 16²¹ software package on Pitt CRC and XSEDE²² supercomputers. Geometries were optimized in chloroform (CHCl₃) with the SMD solvation model²³ using the M06-2X²⁴ functional and a basis set of 6-31+G(d). Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure. Intrinsic reaction coordinate (IRC) calculations have demonstrated that the transition state connects two corresponding intermediates along the reaction coordinate. Truhlar's quasi-harmonic corrections²⁵ were applied for entropy calculations with a frequency cut-off of 100 cm⁻¹ using the GoodVibes²⁶ program. Single point energies were calculated using M06-2X and 6-311+G(d,p) basis set in CHCl₃ using the SMD solvation model.

Free energy profiles of disfavored pathways of the hydrofluorination of 1,2-diphenylacetylene **101**

(a)

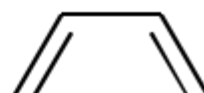


Figure S9. Free energy profiles of disfavored pathways of the hydrofluorination of 1,2-diphenylacetylene **101**. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-311+G(d,p)/SMD(chloroform) level of theory.

In the computational study of hydrofluorination of 1,2-diphenylacetylene **101**, two protonation transition states were located (**TS-1** and **TS-1a**), in which the tetrafluoroborate anion is *syn* and *anti* to the pyridinium, respectively. Besides, another possible conformer of **TS-1** was located as **TS-1b**. This transition state has a higher activation free energy than **TS-1** by 2.3 kcal/mol due to the less stabilizing electrostatic interaction. Therefore, this transition state structure could be rule out. After the protonation transition states, ion-pair intermediates **104** and **104a**, which contain the hydrogen bonding interaction between 2,6-dichloropyridine and vinyl hydrogen, could be located in calculations (Fig. S9a). The dissociation of 2,6-dichloropyridine from these two intermediates is found to be exergonic. The formation of intermediates **102** and **102a** (Fig. 3a) are thus thermodynamically favored. Besides the fluorination transition states from **102** and **102a** (Fig. 3a), **TS-2b** and **TS-2c** were also located, which involve fluorination from the 2,6-dichloropyridine-bound ion pairs **104** and **104a**. However, these transition states are kinetically disfavored because of the entropy loss caused by 2,6-dichloropyridine complexation. Therefore, the fluorination of vinyl cation occurs after the dissociation of 2,6-dichloropyridine.

The concerted hydrofluorination mechanism is also considered in mechanistic studies. Nevertheless, all attempts toward locating the concerted hydrofluorination transition state have failed. An isomer of the *anti*-protonation transition state **TS-1c** (Fig. S9b) was located, which involves a

shorter C–F bond distance (2.72 Å) than those in **TS-1** and **TS-1a** (3.00 and 2.80 Å, respectively). **TS-1c** has a higher energy barrier than those of **TS-1a** and **TS-1**. IRC calculations showed that **TS-1c** also leads to the formation of BF₄[−]/vinyl cation intermediate instead of the hydrofluorination product. Therefore, the higher energy **TS-1c** is still a stepwise protonation transition state. Because the experimental Hammett analysis revealed a ρ value of −3.43 and kinetic studies revealed first-order kinetics in alkyne and H⁺ and zero-order kinetics in excess BF₄[−], which are consistent with the stepwise protonation-fluorination mechanism, the concerted hydrofluorination mechanism could be ruled out.

Free energy profiles of the hydrofluorination of cyclohexylphenylacetylene and methylphenylacetylene

Figure S10. Reaction energy profiles of the hydrofluorination of cyclohexylphenylacetylene **105** with 2,6-dichloropyridinium tetrafluoroborate. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory.

Computational results suggested that the hydrofluorination of cyclohexyl and methyl-substituted phenylacetylene with 2,6-dichloropyridinium tetrafluoroborate also occurs through a stepwise Ad_E2-type protonation-fluorination mechanism with a BF₄[−]/vinyl cation ion-pair intermediate (Fig. S10 and S11). The intrinsic reaction coordinate (IRC) calculations have confirmed that protonation transition states **TS-3**, **TS-3a**, **TS-5**, and **TS-5a** lead to BF₄[−]/vinyl cation ion-pair intermediates rather than the hydrofluorination products. The protonation is still the rate-determining step and the fluorination of vinyl cation is a facile process. The protonation step still favors *syn*-protonation that leads to ion pairs **106** and **108**. The *Z*-vinyl fluoride products are thermodynamically more stable than the corresponding *E*-isomer. The BF₃-mediated *E*-to-*Z* vinyl fluoride isomerization is verified by control experiments with fluorinating reagent **F** and Et₂O•BF₃ (Fig. S12). Therefore, under thermodynamically controlled conditions, high *Z*-selectivity is observed for the hydrofluorination of cyclohexyl and methyl-substituted phenylacetylene in the experiment.

Figure S11. Reaction energy profiles of the hydrofluorination of methyl-substituted phenylacetylene **107** with 2,6-dichloropyridinium tetrafluoroborate. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory.

Figure S12. *E/Z*-isomerization of vinyl fluoride with fluorinating reagent **F** and Et₂O•BF₃.

We summarized that a relatively bulky alkyne substituent (*e.g.* R = Ph or Cy) could suppress the isomerization from ion-pair **I** to **II** (k_3) and the *Z*-selective fluorination (k_4) by steric effects (see Fig. 3a in main text). As shown in Figure S10, the *E*-selective fluorination (via **TS-4**) and *Z*-selective fluorination (via **TS-4a**) has comparable energy barriers. While in Figure S11, the *E*-selective fluorination (via **TS-6**) has a slightly higher energy barrier than that of *Z*-selective fluorination (via **TS-6a**). Combined with the computational results in Fig. 3a (hydrofluorination of 1,2-diphenylacetylene), we found that the *Z*-selective fluorination is slower than the *E*-selective fluorination in the cases of Ph and Cy substituted phenylacetylene.

Moreover, control experiments with different alkynes were performed under kinetic hydrofluorination condition (lower temperature) to study the substituent effects on the *E/Z*-selectivity. As shown in Figure S13, the *E*-product ratios generated from the hydrofluorination of **101** and **105** (Fig. S13a and S13b) are higher than that of **107** (Fig. S13c), which is consistent with the hypothesis that the isomerization rate (k_3) is faster with the methyl-substituted vinyl cation ion pair. Besides, the comparison of solvents in Figure S13a indicates that less polar solvent (chloroform) could enhance the *E*-selectivity. In summary, these computational and experimental studies show that bulkier alkyne substituents and less polar solvent in this hydrofluorination reaction could enhance the kinetic *E*-selectivity.

Figure S13. Comparison of *E/Z*-alkene ratios for different alkynes under kinetic hydrofluorination conditions.

Figure S14. Comparison of *E/Z*-alkene ratios for adding excess BF_4^- source conditions.

Excess BF_4^- was also found to favor formation of the *Z*-isomer (Fig. S14), an effect which may be ascribed to increased availability of BF_4^- for *anti*-attack or a change in the solvent polarity due to higher ionic content.

5. Characterization data of pyridinium tetrafluoroborates

To a solution of the corresponding pyridine (50 mmol, 1.0 equiv) in dry Et_2O (60 mL) was added a solution of HBF_4 in Et_2O (54 wt %, 8.0 mL, 60 mmol, 1.2 equiv) at 0 °C to give a white precipitate. After the mixture was allowed to reach room temperature, the solid was collected by filtration, the solid was washed twice with Et_2O and then dried under vacuum.

White solid (10.8 g, 92%)

^1H NMR (500 MHz, DMSO) δ 14.02 (s, 1H), 7.92 (t, J = 7.9 Hz, 1H), 7.56 (d, J = 7.9 Hz, 2H).

^{13}C NMR (126 MHz, DMSO) δ 149.3, 142.9, 123.8.

^{19}F NMR (471 MHz, DMSO) δ -148.11 (s), -148.16 (s).

White solid (9.0 g, 95%)

¹H NMR (500 MHz, DMSO) δ 8.82 (s, 1H), 3.10 (qd, J = 7.3, 4.8 Hz, 6H), 1.17 (t, J = 7.3 Hz, 9H).

¹³C NMR (126 MHz, DMSO) δ 45.8, 8.6.

¹⁹F NMR (471 MHz, DMSO) δ -148.32 (s), -148.37 (s).

White solid (9.4 g, 96%)

¹H NMR (300 MHz, DMSO) δ 15.21 (s, 1H), 8.36 (t, J = 7.9 Hz, 1H), 7.73 (d, J = 7.9 Hz, 2H), 2.69 (s, 6H).

¹³C NMR (126 MHz, DMSO) δ 153.0, 145.6, 124.6, 19.2.

¹⁹F NMR (471 MHz, DMSO) δ -148.22 (s), -148.28 (s).

White solid (7.5 g, 90%)

¹H NMR (500 MHz, DMSO) δ 15.12 (s, 1H), 8.96 – 8.89 (m, 2H), 8.62 (tt, J = 7.9, 1.5 Hz, 1H), 8.08 (dd, J = 7.7, 6.7 Hz, 2H).

¹³C NMR (126 MHz, DMSO) δ 146.4, 142.2, 127.3.

¹⁹F NMR (471 MHz, DMSO) δ -148.16 (s), -148.22 (s).

White solid (8.0 g, 86%)

¹H NMR (500 MHz, DMSO) δ 12.96 (s, 1H), 8.27 – 8.19 (m, 1H), 8.02 – 7.93 (m, 1H), 7.37 – 7.29 (m, 1H), 7.15 (dd, J = 8.3, 2.5 Hz, 1H).

¹³C NMR (126 MHz, DMSO) δ 163.2 (d, J_{C-F} = 235.5 Hz), 147.8 (d, J_{C-F} = 14.6 Hz), 142.3 (d, J_{C-F} = 7.9 Hz), 122.2 (d, J_{C-F} = 4.0 Hz), 109.8 (d, J_{C-F} = 37.0 Hz).

¹⁹F NMR (471 MHz, DMSO) δ -68.11 (s, 1F), -148.08 (s), -148.14 (s).

White solid (9.0 g, 90%)

¹H NMR (500 MHz, DMSO) δ 13.98 (s, 1H), 8.40 (ddd, J = 4.8, 2.0, 0.6 Hz, 1H), 7.85 (ddd, J = 8.0, 7.5, 2.0 Hz, 1H), 7.49 (dt, J = 8.1, 0.7 Hz, 1H), 7.40 (ddd, J = 7.4, 4.9, 0.9 Hz, 1H).

¹³C NMR (126 MHz, DMSO) δ 150.4, 150.1, 140.1, 124.6, 123.3.

¹⁹F NMR (471 MHz, DMSO) δ -148.08 (s), -148.13 (s).

White solid (10.7 g, 87%)

¹H NMR (500 MHz, DMSO) δ 14.21 (s, 1H), 8.38 (ddd, J = 4.8, 2.0, 0.6 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.64 (dt, J = 8.1, 0.8 Hz, 1H), 7.44 (ddd, J = 7.4, 4.8, 1.0 Hz, 1H).

¹³C NMR (126 MHz, DMSO) δ 150.6, 141.5, 139.8, 128.4, 123.6.

¹⁹F NMR (471 MHz, DMSO) δ -148.09 (s), -148.14 (s).



White solid (10.9 g, 93%)

¹H NMR (500 MHz, DMSO) δ 13.94 (s, 1H), 8.61 (d, J = 2.1 Hz, 2H), 8.23 (t, J = 2.1 Hz, 1H).

¹³C NMR (126 MHz, DMSO) δ 146.8, 136.0, 131.7.

¹⁹F NMR (471 MHz, DMSO) δ -148.07 (s), -148.12 (s).

White solid (14.8 g, 92%)

¹H NMR (500 MHz, DMSO) δ 13.52 (s, 1H), 7.73 – 7.70 (m, 3H).

¹³C NMR (126 MHz, DMSO) δ 142.3, 140.1, 127.8.

¹⁹F NMR (471 MHz, DMSO) δ -148.12 (s), -148.17 (s).

White solid (11.6 g, 83%)

¹H NMR (500 MHz, DMSO) δ 12.94 (s, 1H), 7.82 (t, J = 7.8 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.62 – 7.57 (m, 1H).

¹³C NMR (126 MHz, DMSO) δ 149.4, 142.6, 139.9, 127.5, 124.0.

¹⁹F NMR (471 MHz, DMSO) δ -148.12 (s), -148.18 (s).

White solid (10.8 g, 80%)

¹H NMR (500 MHz, DMSO) δ 10.99 (s, 1H), 7.86 (s, 2H).

¹³C NMR (126 MHz, DMSO) δ 150.1, 147.2, 123.8.

¹⁹F NMR (471 MHz, DMSO) δ -148.09 (s), -148.15 (s).

White solid (9.6 g, 91%)

¹H NMR (500 MHz, DMSO) δ 14.10 (s, 1H), 9.39 (d, J = 2.6 Hz, 1H), 8.97 (dd, J = 4.8, 1.3 Hz, 1H), 8.63 (ddd, J = 8.4, 2.6, 1.4 Hz, 1H), 7.75 (dd, J = 8.4, 4.8 Hz, 1H).

¹³C NMR (126 MHz, DMSO) δ 154.8, 144.6, 144.4, 132.1, 124.9.

¹⁹F NMR (471 MHz, DMSO) δ -148.10 (s), -148.15 (s).

White solid (11.2 g, 95%)

¹H NMR (500 MHz, DMSO) δ 14.78 (s, 1H), 9.01 (d, J = 6.0 Hz, 2H), 8.05 (d, J = 5.9 Hz, 2H).

¹³C NMR (126 MHz, DMSO) δ 148.8, 139.4 (q, J_{C-F} = 34.1 Hz), 122.5 (q, J_{C-F} = 273.7 Hz), 121.1 (q, J_{C-F} = 3.5 Hz).

¹⁹F NMR (471 MHz, DMSO) δ -63.81 (s, 3F), -148.15 (s), -148.21 (s).

6. Characterization data of unreported starting materials

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride (1.0 mol%), copper(I) iodide (3.0 mol%), and aryl iodide or aryl bromide (5.0 mmol, 1.0 equiv), sealed with a septum, and degassed by evacuation and backfilling with argon (repeated three times) before triethylamine (25 ml) was added. The corresponding terminal alkyne (5.0 mmol, 1.0 equiv) was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature or 80 °C for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et₂O (30 mL) and filtered through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography to give the corresponding pure alkynes.

Methyl 3-(cyclohexylethynyl)benzoate

Yellow oil (1.08 g, 89% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 2.63 – 2.51 (m, 1H), 1.91 – 1.81 (m, 2H), 1.79 – 1.69 (m, 2H), 1.59 – 1.46 (m, 3H), 1.41 – 1.26 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.4, 135.6, 132.6, 130.1, 128.3, 128.1, 124.5, 95.4, 79.5, 52.0, 32.5, 29.5, 25.8, 24.8.

HRMS (ESI) calcd for C₁₆H₁₈O₂ [M+H]⁺: 243.1307 Found: 243.1377.

2-(4-(Cyclohexylethynyl)phenyl)isoindoline-1,3-dione

Yellow solid (1.25 g, 76% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.93 (dd, *J* = 5.2, 3.0 Hz, 2H), 7.77 (dd, *J* = 5.2, 3.0 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 2.60 (s, 1H), 1.95 – 1.82 (m, 2H), 1.81 – 1.70 (m, 2H), 1.62 – 1.47 (m, 3H), 1.42 – 1.30 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.0, 134.4, 132.1, 131.6, 130.6, 126.0, 124.0, 123.7, 95.5, 79.9, 32.6, 29.6, 25.8, 24.8.

HRMS (ESI) calcd for C₂₂H₁₉NO₂ [M+H]⁺: 330.1416 Found: 330.1479

Methyl 3-(cyclohexylethynyl)-1-tosyl-1H-indole-6-carboxylate

Yellow solid (1.59 g, 73% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 2.73 – 2.55 (m, 1H), 2.32 (s, 3H), 1.97 – 1.84 (m, 2H), 1.80 – 1.70 (m, 2H), 1.63 – 1.48 (m, 3H), 1.43 – 1.29 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.0, 145.5, 134.8, 134.7, 133.6, 130.5, 130.0, 127.1, 126.9, 124.6, 120.3, 115.2, 105.9, 99.4, 70.4, 52.2, 32.6, 29.8, 25.8, 24.8, 21.5.

HRMS (ESI) calcd for C₂₅H₂₅NO₄S [M+H]⁺: 436.1504, Found: 436.1556.

Methyl 5-(cyclohexylethynyl)furan-2-carboxylate

Yellow solid (916 mg, 79% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 3.6 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 3.87 (s, 3H), 2.66 – 2.52 (m, 1H), 1.91 – 1.79 (m, 2H), 1.76 – 1.65 (m, 2H), 1.58 – 1.44 (m, 3H), 1.38 – 1.25 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.4, 143.5, 141.0, 118.8, 115.1, 100.8, 70.2, 51.9, 31.9, 29.6, 25.6, 24.7.

HRMS (ESI) calcd for C₁₄H₁₆O₃ [M+H]⁺: 233.1099, Found: 233.1163.

1-(6-Chlorohex-1-yn-1-yl)-2-methoxy-4-nitrobenzene

Yellow oil (1.13 g, 85% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.77 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.69 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 6.9 Hz, 2H), 2.02 – 1.94 (m, 2H), 1.84 – 1.75 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 160.1, 147.6, 133.4, 120.1, 115.6, 105.4, 99.3, 76.2, 56.3, 44.4, 31.5, 25.6, 19.2.

HRMS (ESI) calcd for C₁₃H₁₄ClNO₃ [M+H]⁺: 268.0662, Found: 268.0730.

An oven-dried 250 mL flask equipped with a magnetic stir bar was charged with FeBr₂ (216 mg, 1.0 mmol, 0.1 equiv), secondary alkyl halide (10.0 mmol, 1.0 equiv), and NMP solvent (40 mL) under argon atmosphere. Phenylethynylmagnesium bromide solution (0.5 M in THF, 30 mL, 1.5 equiv, prepared by addition of ethylmagnesium bromide and phenylacetylene) was then added by syringe. The reaction mixture was stirred at room temperature for 16 h to form a deep brown or black solution. After the reaction was complete (24 h), the crude product was washed with EtOAc (10 mL) and water (30 mL). The aqueous layer was further extracted with EtOAc (2 x 10 mL). The combined organic layer were concentrated in vacuo with the aid of a rotary evaporator, and the residue was purified by flash column chromatography (hexanes as an eluent) to provide the substituted alkylated alkyne product.

(3-Methyldec-1-yn-1-yl)benzene

Yellow oil (1.05 g, 46% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.37 (m, 2H), 7.30 – 7.23 (m, 3H), 2.71 – 2.57 (m, 1H), 1.56 – 1.43 (m, 4H), 1.34 – 1.28 (m, 8H), 1.25 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 131.6, 128.1, 127.4, 124.1, 94.9, 80.6, 37.0, 31.9, 29.4, 29.3, 27.4, 26.5, 22.7, 21.1, 14.1.

HRMS (ASAP) calcd for C₁₇H₂₄ [M]⁺: 228.1878, Found: 228.1897.

(3r,5r,7r)-1-(3-Phenylprop-2-yn-1-yl)adamantane

Yellow oil (950 mg, 38% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.38 (m, 2H), 7.31 – 7.22 (m, 3H), 2.16 (s, 2H), 2.03 – 1.97 (m, 3H), 1.76 – 1.72 (m, 1H), 1.72 – 1.69 (m, 2H), 1.68 – 1.65 (m, 2H), 1.64 (d, *J* = 2.4 Hz, 7H).

¹³C NMR (101 MHz, CDCl₃) δ 131.5, 128.1, 127.4, 124.2, 87.8, 82.6, 42.1, 36.9, 34.6, 33.1, 28.7.

HRMS (ASAP) calcd for C₁₉H₂₂ [M+H]⁺: 251.1722, Found: 251.1811.

A 50-mL flask fitted with a stirring bar was charged with a solution of alcohol (5 mmol), EDCI (1.2 equiv), triethylamine (1.5 equiv), and DMAP (0.1 equiv) in dichloromethane (25 mL). The corresponding acid (1 equiv) was then added at 0 °C, and the reaction mixture was stirred overnight at room temperature. After the reaction was complete, the resulting mixture was diluted with DCM (50 mL), washed by 1 N HCl (2 x 20 mL), 1 N aqueous NaHCO₃ (2 x 20 mL), and brine (1 x 20 mL). The organic layer was dried (Na₂SO₄) and evaporated in vacuo. The resulting residue was purified by column chromatography to afford the desired ester.

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride (1.0 mol%), copper(I) iodide (3.0 mol%), iodobenzene (2.0 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before triethylamine (10 ml) was added. The corresponding terminal alkyne (2.0 mmol, 1.0 equiv) was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et₂O (20 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography to give the corresponding pure alkyne.

Pent-4-yn-1-yl nicotinate

Colorless oil (737 mg, 78% yield).

¹H NMR (400 MHz, CDCl₃) δ 9.20 (d, *J* = 1.5 Hz, 1H), 8.75 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.27 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.8, 4.9 Hz, 1H), 4.44 (t, *J* = 6.3 Hz, 2H), 2.36 (td, *J* = 7.0, 2.6 Hz, 2H), 2.04 – 1.93 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.1, 153.4, 150.8, 136.9, 126.0, 123.2, 82.7, 69.2, 63.9, 27.4, 15.2.

HRMS (ESI) calcd for C₁₁H₁₁NO₂ [M+H]⁺: 190.0790, Found: 190.0858.

5-Phenylpent-4-yn-1-yl nicotinate

Yellow oil (445 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 1H), 8.78 (d, *J* = 3.8 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.32 – 7.24 (m, 3H), 4.54 (t, *J* = 6.2 Hz, 2H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.17 – 2.05 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 165.2, 153.4, 150.9, 137.0, 131.5, 128.2, 127.7, 126.1, 123.5, 123.2, 88.3, 81.5, 64.2, 27.8, 16.3.

HRMS (ESI) calcd for C₁₇H₁₅NO₂ [M+H]⁺: 266.1103, Found: 266.1168.

(Pent-4-yn-1-yloxy)carbonyl ferrocene

Yellow oil (1.11 g, 75% yield).

¹H NMR (400 MHz, CDCl₃) δ 4.81 (s, 2H), 4.40 (s, 2H), 4.32 (t, *J* = 6.1 Hz, 2H), 4.21 (s, 5H), 2.39 (t, *J* = 5.6 Hz, 2H), 2.04 – 1.89 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.6, 83.0, 71.2, 71.0, 70.0, 69.7, 69.1, 62.5, 27.7, 15.2.

HRMS (APCI) calcd for C₁₆H₁₆FeO₂ [M+H]⁺: 297.0500, Found: 297.0590.

(5-Phenylpent-4-yn-1-yloxy)carbonyl ferrocene

Yellow oil (662 mg, 89% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.36 (m, 2H), 7.34 – 7.22 (m, 3H), 4.83 (s, 2H), 4.47 – 4.31 (m, 4H), 4.22 (s, 5H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.13 – 1.95 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 171.6, 131.6, 128.2, 127.7, 123.6, 88.6, 81.4, 71.2, 71.1, 70.1, 69.7, 62.8, 28.0, 16.2.

HRMS (APCI) calcd for C₂₂H₂₀FeO₂ [M+H]⁺: 373.0813 Found: 373.0908.

Pent-4-yn-1-yl((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate

Colorless oil (1.07 g, 72% yield).

¹H NMR (400 MHz, CDCl₃) δ 4.51 – 4.29 (m, 2H), 3.59 (d, *J* = 15.1 Hz, 1H), 2.98 (d, *J* = 15.1 Hz, 1H), 2.53 – 2.27 (m, 4H), 2.20 – 1.85 (m, 6H), 1.72 – 1.59 (m, 1H), 1.49 – 1.37 (m, 1H), 1.09 (s, 3H), 0.86 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 214.4, 82.2, 69.6, 68.7, 57.8, 47.9, 46.6, 42.6, 42.4, 27.9, 26.8, 24.8, 19.7, 19.6, 14.7.

HRMS (APCI) calcd for C₁₅H₂₂O₄S [M+H]⁺: 299.1239, Found: 299.1330.

5-Phenylpent-4-yn-1-yl((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate

Yellow oil (682 mg, 91% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.35 (m, 2H), 7.30 – 7.24 (m, 3H), 4.52 – 4.41 (m, 2H), 3.63 (d, *J* = 15.1 Hz, 1H), 3.01 (d, *J* = 15.1 Hz, 1H), 2.57 (t, *J* = 6.9 Hz, 2H), 2.53 – 2.43 (m, 1H), 2.42 – 2.32 (m, 1H), 2.13 – 1.89 (m, 5H), 1.67 (ddd, *J* = 14.0, 9.4, 4.7 Hz, 1H), 1.42 (ddd, *J* = 13.0, 9.4, 3.9 Hz, 1H), 1.10 (s, 3H), 0.84 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 214.2, 131.4, 128.0, 127.6, 123.3, 87.6, 81.6, 68.8, 57.7, 47.8, 46.4, 42.5, 42.3, 28.1, 26.7, 24.7, 19.53, 19.42, 15.6.

HRMS (APCI) calcd for C₂₁H₂₆O₄S [M+H]⁺: 375.1552, Found: 375.1647.

Pent-4-yn-1-yl 4-(N,N-dipropylsulfamoyl)benzoate

Colorless oil (1.39 g, 79% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 4.46 (t, *J* = 6.3 Hz, 2H), 3.16 – 3.02 (m, 4H), 2.39 (td, *J* = 7.0, 2.6 Hz, 2H), 2.07 – 1.93 (m, 3H), 1.61 – 1.47 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 165.1, 144.3, 133.4, 130.2, 127.0, 82.8, 69.2, 64.1, 49.9, 27.5, 21.9, 15.3, 11.1.

HRMS (APCI) calcd for C₁₈H₂₅NO₄S [M+H]⁺: 352.1504 Found: 352.1598.

5-Phenylpent-4-yn-1-yl 4-(N,N-dipropylsulfamoyl)benzoate

Yellow oil (769 mg, 90% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.31 – 7.23 (m, 3H), 4.52 (t, *J* = 6.2 Hz, 2H), 3.14 – 3.02 (m, 4H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.15 – 2.04 (m, 2H), 1.60 – 1.48 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 165.0, 144.1, 133.4, 131.4, 130.1, 128.1, 127.6, 126.8, 123.4, 88.3, 81.3, 64.3, 49.8, 27.7, 21.8, 16.3, 11.0.

HRMS (APCI) calcd for C₂₄H₂₉NO₄S [M+H]⁺: 428.1817 Found: 428.1914.

Pent-4-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate

White solid (1.39 g, 73% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 2.2 Hz, 1H), 8.09 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.41 (t, *J* = 6.2 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.76 (s, 3H), 2.38 (td, *J* = 7.0, 2.6 Hz, 2H), 2.27 – 2.14 (m, 1H), 2.04 – 1.92 (m, 3H), 1.09 (d, *J* = 6.7 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 167.3, 162.5, 161.9, 161.3, 132.5, 132.1, 126.0, 121.6, 115.4, 112.6, 103.0, 82.7, 75.7, 69.3, 63.8, 28.1, 27.5, 19.0, 17.5, 15.3.

HRMS (APCI) calcd for C₂₁H₂₂N₂O₃S [M+H]⁺: 383.1351, Found: 383.1447.

5-Phenylpent-4-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate

White solid (687 mg, 75% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 1.5 Hz, 1H), 8.02 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.49 – 7.32 (m, 2H), 7.31 – 7.12 (m, 3H), 6.97 (d, *J* = 8.9 Hz, 1H), 4.45 (t, *J* = 6.0 Hz, 2H), 3.87 (d, *J* = 6.4 Hz, 2H), 2.75 (s, 3H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.28 – 2.12 (m, 1H), 2.12 – 1.94 (m, 2H), 1.08 (d, *J* = 6.6 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 167.1, 162.4, 161.8, 161.1, 132.4, 131.9, 131.4, 128.1, 127.6, 125.8, 123.5, 121.5, 115.3, 112.5, 102.8, 88.3, 81.4, 75.6, 64.0, 28.0, 27.7, 18.9, 17.4, 16.3.

HRMS (APCI) calcd for C₂₇H₂₆N₂O₃S [M+H]⁺: 459.1664 Found: 459.1763.

Pent-4-yn-1-yl 4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxylate

White solid (1.86 g, 64% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.15 (m, 6H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.38 (s, 2H), 4.04 (t, *J* = 5.7 Hz, 2H), 3.67 (s, 3H), 2.95 – 2.81 (m, 2H), 2.73 (s, 3H), 1.89 (t, *J* = 2.4 Hz, 1H), 1.87 – 1.73 (m, 4H), 1.55 – 1.43 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.1, 156.2, 154.3, 142.9, 142.6, 141.2, 141.0, 136.4, 134.7, 134.6, 131.1, 130.5, 130.4, 129.7, 129.1, 128.7, 127.1, 125.7, 123.6, 122.2, 122.0, 119.2, 109.3, 108.6, 82.8, 68.8, 63.2, 46.7, 31.5, 29.5, 27.0, 21.6, 16.6, 14.6, 13.8.

HRMS (ESI) calcd for C₃₈H₃₆N₄O₂ [M+H]⁺: 581.2838, Found: 581.2901.

5-Phenylpent-4-yn-1-yl 4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxylate

White solid (971 m g, 74% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 6.9 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.50 (td, *J* = 7.6, 1.1 Hz, 1H), 7.45 (d, *J* = 18.2 Hz, 2H), 7.39 (td, *J* = 7.7, 0.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.29 – 7.25 (m, 8H),

7.09 (d, $J = 8.0$ Hz, 2H), 5.42 (s, 2H), 4.17 (t, $J = 6.0$ Hz, 2H), 3.79 (s, 3H), 2.97 – 2.87 (m, 2H), 2.76 (s, 3H), 2.10 (t, $J = 7.0$ Hz, 2H), 1.93 – 1.81 (m, 2H), 1.69 – 1.62 (m, 2H), 1.05 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 168.3, 156.3, 154.6, 143.1, 142.8, 141.5, 141.2, 136.6, 134.9, 134.8, 131.4, 131.2, 130.7, 130.6, 129.9, 129.4, 128.9, 128.2, 127.7, 127.3, 125.9, 123.8, 123.8, 123.5, 122.4, 122.2, 119.5, 109.4, 108.8, 88.6, 81.2, 63.6, 46.9, 31.7, 29.7, 27.4, 21.8, 16.8, 15.9, 14.0.

HRMS (ESI) calcd for $\text{C}_{44}\text{H}_{40}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 657.3151, Found: 657.3204.

7. General procedure for hydrofluorination of alkynes

Condition A: A reaction tube (13 mm \times 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF_4 (0.05 mmol, 4.7 mg, 25 mol%), dry CHCl_3 (1.0 mL) and alkyne (0.2 mmol, 1.0 equiv) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirred at 70 or 90 $^\circ\text{C}$ for 6 hours, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH_2Cl_2 . The filtrate was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product.

Condition B: A reaction tube (13 mm \times 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, dry CHCl_3 (1.0 mL), alkyne (0.2 mmol, 1.0 equiv) and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (27 μl , 0.2 mmol, 1.0 equiv) were added in succession. The reaction tube was sealed and removed from the glovebox and stirred at room temperature for 6 hours. The resulting mixture was passed through a pad of silica gel and eluted with CH_2Cl_2 . The filtrate was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product.

Condition C: A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL) and alkyne (0.2 mmol, 1.0 equiv) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirred at 80 or 100 °C for 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product.

Condition D: A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 97 mg, 2.0 equiv), dry DCE (2.0 mL) and alkyne (0.2 mmol, 1.0 equiv) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirred at 100 °C for 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product.

Condition A (reaction under air): A sample (~1 g) of 2,6-dichloropyridinium tetrafluoroborate was removed from the glovebox and condition **A** was repeated outside of the glovebox for (cyclohexylethynyl)benzene (0.2 mmol) by charging an oven-dried reaction tube with fluorinating reagent, dried solvent, and substrate sequentially. The reaction tube was sealed under air and placed in an oil bath at 70 °C. After a reaction time of 6 h, the NMR yield of the desired product (**1**) was determined to be 78% using trifluorotoluene as the internal standard

8. Characterization data of products

(Z)-(2-Cyclohexyl-1-fluorovinyl)benzene (1)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), (cyclohexylethynyl)benzene (0.2 mmol, 37 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **1** with spectral properties identical to the reported in the literature^[1]. Pale yellow oil (31 mg, 76% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 5.29 (dd, *J* = 38.2, 9.2 Hz, 1H), 2.73 – 2.59 (m, 1H), 1.84 – 1.73 (m, 4H), 1.72 – 1.65 (m, 1H), 1.42 – 1.32 (m, 2H), 1.28 – 1.14 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 155.4 (d, *J*_{C-F} = 245.3 Hz), 132.9 (d, *J*_{C-F} = 29.4 Hz), 128.3 (d, *J*_{C-F} = 1.9 Hz), 128.2, 123.8 (d, *J*_{C-F} = 7.0 Hz), 112.0 (d, *J*_{C-F} = 17.1 Hz), 33.8 (d, *J*_{C-F} = 3.6 Hz), 33.2 (d, *J*_{C-F} = 1.2 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.8 (d, *J* = 38.2 Hz).

(E)-(2-Cyclohexyl-1-fluorovinyl)benzene (2)

Prepared following the general procedure (**condition B**): (cyclohexylethynyl)benzene (0.2 mmol, 37 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **2**. Pale yellow oil (17 mg, 42% yield, *E/Z* = 11 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.51 – 7.43 (m, 2H), 7.43 – 7.32 (m, 3H), 5.26 (dd, *J* = 23.1, 10.8 Hz, 1H), 2.37 – 2.18 (m, 1H), 1.83 – 1.69 (m, 4H), 1.69 – 1.60 (m, 1H), 1.32 – 1.14 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 155.7 (d, *J*_{C-F} = 240.1 Hz), 132.4 (d, *J*_{C-F} = 30.2 Hz), 128.8 (d, *J*_{C-F} = 1.1 Hz), 128.2, 127.5 (d, *J*_{C-F} = 5.0 Hz), 114.5 (d, *J*_{C-F} = 21.9 Hz), 35.2 (d, *J*_{C-F} = 7.6 Hz), 33.8 (d, *J*_{C-F} = 2.3 Hz), 25.9, 25.6.

¹⁹F NMR (471 MHz, CDCl₃) δ -103.5 (d, *J* = 23.1 Hz).

HRMS (APCI) calcd for C₁₄H₁₇F [M+H]⁺: 205.1314, Found: 205.1377.

(Z)-1-(2-Cyclohexyl-1-fluorovinyl)-4-fluorobenzene (3)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-(cyclohexylethynyl)-4-fluorobenzene (0.2 mmol, 41 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **3**. Pale yellow oil (33 mg, 74% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.43 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.19 (dd, *J* = 38.1, 9.2 Hz, 1H), 2.68 – 2.56 (m, 1H), 1.81 – 1.71 (m, 4H), 1.71 – 1.64 (m, 1H), 1.41 – 1.30 (m, 2H), 1.28 – 1.11 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 162.7 (d, *J*_{C-F} = 247.9 Hz), 154.7 (d, *J*_{C-F} = 245.1 Hz), 129.2 (dd, *J*_{C-F} = 30.2, 3.3 Hz), 125.8 (dd, *J*_{C-F} = 7.9, 7.2 Hz), 115.3 (dd, *J*_{C-F} = 21.8, 1.8 Hz), 111.8 (dd, *J*_{C-F} = 17.1, 1.7 Hz), 33.8 (d, *J*_{C-F} = 3.6 Hz), 33.2 (d, *J*_{C-F} = 1.0 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -113.2 – -113.4 (m, 1F), -120.7 (d, *J* = 38.1 Hz, 1F).

HRMS (ASAP) calcd for C₁₄H₁₆F₂ [M]⁺: 222.1220, Found: 222.1237.

(*E*)-1-(2-Cyclohexyl-1-fluorovinyl)-4-fluorobenzene (**4**)

Prepared following the general procedure (**condition B**): 1-(cyclohexylethynyl)-4-fluorobenzene (0.2 mmol, 41 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **4**. Pale yellow oil (20 mg, 45% yield, *E/Z* = 11 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.42 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 5.24 (dd, *J* = 22.8, 10.8 Hz, 1H), 2.28 – 2.12 (m, 1H), 1.78 – 1.69 (m, 4H), 1.68 – 1.61 (m, 1H), 1.29 – 1.15 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 162.8 (d, *J*_{C-F} = 248.9 Hz), 154.9 (d, *J*_{C-F} = 240.2 Hz), 129.4 (dd, *J*_{C-F} = 8.3, 4.8 Hz), 128.6 (dd, *J*_{C-F} = 31.0, 3.4 Hz), 115.3 (d, *J*_{C-F} = 21.7 Hz), 114.4 (d, *J*_{C-F} = 21.8 Hz), 35.3 (d, *J*_{C-F} = 7.4 Hz), 33.7 (d, *J*_{C-F} = 2.2 Hz), 25.8, 25.6.

¹⁹F NMR (471 MHz, CDCl₃) δ (*E*): -102.5 (d, *J* = 22.8 Hz), -111.6 – -111.9 (m), (*Z*): -113.3 – -113.4 (m), -120.8 (d, *J* = 38.0 Hz).

HRMS (APCI) calcd for C₁₄H₁₆F₂ [M]⁺: 222.1220, Found: 222.1205.

(*Z*)-1-Chloro-4-(2-cyclohexyl-1-fluorovinyl)benzene (**5**)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2

mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-chloro-4-(cyclohexylethynyl)benzene (0.2 mmol, 44 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **5**. Pale yellow oil (36 mg, 76% yield, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.38 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.26 (dd, *J* = 38.0, 9.2 Hz, 1H), 2.68 – 2.56 (m, 1H), 1.82 – 1.71 (m, 4H), 1.71 – 1.64 (m, 1H), 1.41 – 1.30 (m, 2H), 1.27 – 1.11 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.5 (d, *J*_{C-F} = 245.1 Hz), 134.0, 131.4 (d, *J*_{C-F} = 30.1 Hz), 128.6 (d, *J*_{C-F} = 1.9 Hz), 125.2 (d, *J*_{C-F} = 7.0 Hz), 112.6 (d, *J*_{C-F} = 17.0 Hz), 33.8 (d, *J*_{C-F} = 3.4 Hz), 33.1 (d, *J*_{C-F} = 1.1 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.7 (d, *J* = 38.0 Hz).

HRMS (ASAP) calcd for C₁₄H₁₆ClF [M]⁺: 238.0925, Found: 238.0936.

(E)-1-Chloro-4-(2-cyclohexyl-1-fluorovinyl)benzene (6)

Prepared following the general procedure (**condition B**): 1-chloro-4-(cyclohexylethynyl)benzene (0.2 mmol, 44 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **6**. Pale yellow oil (19 mg, 41% yield, E/Z = 11 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.27 (m, 4H), 5.27 (dd, *J* = 22.9, 10.8 Hz, 1H), 2.31 – 2.13 (m, 1H), 1.79 – 1.69 (m, 4H), 1.68 – 1.61 (m, 1H), 1.29 – 1.13 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 154.7 (d, *J*_{C-F} = 240.1 Hz), 134.7, 130.8 (d, *J*_{C-F} = 30.9 Hz), 128.8 (d, *J*_{C-F} = 4.9 Hz), 128.5, 115.1 (d, *J*_{C-F} = 21.7 Hz), 35.3 (d, *J*_{C-F} = 7.3 Hz), 33.7 (d, *J*_{C-F} = 2.1 Hz), 25.8, 25.6.

¹⁹F NMR (471 MHz, CDCl₃) δ (*E*): -103.9 (d, *J* = 22.8 Hz), (*Z*): -121.7 (d, *J* = 38.1 Hz).

HRMS (APCI) calcd for C₁₄H₁₆ClF [M]⁺: 238.0925, Found: 238.0909.

(Z)-1-Bromo-4-(2-cyclohexyl-1-fluorovinyl)benzene (7)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-bromo-4-(cyclohexylethynyl)benzene (0.2 mmol, 53 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **7**. Pale yellow oil (39 mg, 70% yield, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.32 (m, 2H), 5.27 (dd, *J* = 38.0, 9.3 Hz, 1H), 2.68 – 2.56 (m, 1H), 1.81 – 1.71 (m, 4H), 1.71 – 1.63 (m, 1H), 1.41 – 1.30 (m, 2H), 1.27 – 1.11 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.6 (d, J_{C-F} = 245.1 Hz), 131.9 (d, J_{C-F} = 30.0 Hz), 131.5 (d, J_{C-F} = 1.9 Hz), 125.4 (d, J_{C-F} = 6.9 Hz), 122.2, 112.7 (d, J_{C-F} = 17.0 Hz), 33.8 (d, J_{C-F} = 3.5 Hz), 33.0 (d, J_{C-F} = 1.2 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.8 (d, J = 38.0 Hz).

HRMS (ASAP) calcd for C₁₄H₁₆BrF [M]⁺: 282.0419, Found: 282.0432.

(E)-1-Bromo-4-(2-cyclohexyl-1-fluorovinyl)benzene (8)

Prepared following the general procedure (**condition B**): 1-bromo-4-(cyclohexylethynyl)benzene (0.2 mmol, 53 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **8**. Pale yellow oil (27 mg, 48% yield, $E/Z > 20 : 1$).

¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.28 (dd, J = 22.9, 10.8 Hz, 1H), 2.33 – 2.12 (m, 1H), 1.80 – 1.69 (m, 4H), 1.69 – 1.61 (m, 1H), 1.29 – 1.14 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 154.7 (d, J_{C-F} = 240.1 Hz), 131.5, 131.3 (d, J_{C-F} = 30.9 Hz), 129.0 (d, J_{C-F} = 4.9 Hz), 123.0 (d, J_{C-F} = 1.5 Hz), 115.2 (d, J_{C-F} = 21.6 Hz), 35.3 (d, J_{C-F} = 7.4 Hz), 33.6 (d, J_{C-F} = 2.2 Hz), 25.8, 25.6.

¹⁹F NMR (471 MHz, CDCl₃) δ (*E*): -104.18 (d, J = 22.9 Hz), (*Z*): -121.89 (d, J = 37.9 Hz).

HRMS (APCI) calcd for C₁₄H₁₆BrF [M]⁺: 282.0419, Found: 282.0403.

(Z)-1-(2-Cyclohexyl-1-fluorovinyl)-4-(trifluoromethyl)benzene (9)

Prepared following general **condition D**: 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry DCE (2.0 mL), 1-(cyclohexylethynyl)-4-(trifluoromethyl)benzene (0.2 mmol, 50 mg, 1.0 equiv) at 90 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **9**. Pale yellow oil (39 mg, 72% yield, $Z/E > 50 : 1$).

¹H NMR (500 MHz, CDCl₃) δ 7.59 (s, 4H), 5.40 (dd, J = 37.7, 9.3 Hz, 1H), 2.65 (dt, J = 20.8, 7.3 Hz, 1H), 1.82 – 1.72 (m, 4H), 1.71 – 1.65 (m, 1H), 1.42 – 1.30 (m, 2H), 1.28 – 1.14 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.2 (d, J_{C-F} = 245.4 Hz), 136.3 (d, J_{C-F} = 29.7 Hz), 130.1 (q, J_{C-F} = 32.5 Hz), 125.47 – 125.27 (m), 124.02 (d, J_{C-F} = 7.0 Hz), 124.01 (q, J_{C-F} = 273.4 Hz), 114.5 (d, J_{C-F} = 16.8 Hz), 33.9 (d, J_{C-F} = 3.4 Hz), 33.0 (d, J_{C-F} = 1.1 Hz), 25.9, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -62.7 (s, 3F), -122.2 (d, J = 37.7 Hz, 1F).

HRMS (ASAP) calcd for C₁₅H₁₆F₄ [M]⁺: 272.1188, Found: 272.1198.

(Z)-4-(2-Cyclohexyl-1-fluorovinyl)-1,1'-biphenyl (10)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-(cyclohexylethynyl)-1,1'-biphenyl (0.2 mmol, 52 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **10**. Pale yellow oil (39 mg, 70% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.52 (m, 6H), 7.45 (m, 2H), 7.36 (m, 1H), 5.32 (dd, *J* = 38.2, 9.2 Hz, 1H), 2.74 – 2.59 (m, 1H), 1.85 – 1.72 (m, 4H), 1.72 – 1.63 (m, 1H), 1.43 – 1.32 (m, 2H), 1.29 – 1.13 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 155.2 (d, *J*_{C-F} = 245.0 Hz), 141.0, 140.5, 131.9 (d, *J*_{C-F} = 29.7 Hz), 128.8, 127.5, 127.04 (d, *J*_{C-F} = 1.9 Hz), 126.97, 124.3 (d, *J*_{C-F} = 6.9 Hz), 112.2 (d, *J*_{C-F} = 17.2 Hz), 33.9 (d, *J*_{C-F} = 3.6 Hz), 33.2, 26.0, 25.9.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.8 (d, *J* = 38.2 Hz).

HRMS (ASAP) calcd for C₂₀H₂₁F [M+H]⁺: 281.1627, Found: 281.1695.

(*E*)-4-(2-Cyclohexyl-1-fluorovinyl)-1,1'-biphenyl (**11**)

Prepared following the general procedure (**condition B**): 4-(cyclohexylethynyl)-1,1'-biphenyl (0.2 mmol, 52 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **11**. Pale yellow oil (18 mg, 32% yield, *E/Z* > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.63 (t, *J* = 7.5 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.29 (dd, *J* = 23.1, 10.8 Hz, 1H), 2.44 – 2.24 (m, 1H), 1.86 – 1.70 (m, 4H), 1.70 – 1.63 (m, 1H), 1.34 – 1.17 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 155.5 (d, *J*_{C-F} = 239.7 Hz), 141.6, 140.4, 131.3 (d, *J*_{C-F} = 30.4 Hz), 128.8, 127.8 (d, *J*_{C-F} = 5.1 Hz), 127.6, 127.1, 126.9, 114.7 (d, *J*_{C-F} = 22.1 Hz), 35.3 (d, *J*_{C-F} = 7.6 Hz), 33.8 (d, *J*_{C-F} = 2.1 Hz), 25.9, 25.7.

¹⁹F NMR (471 MHz, CDCl₃) δ -104.1 (d, *J* = 23.0 Hz).

HRMS (APCI) calcd for C₂₀H₂₁F [M]⁺: 280.1627, Found: 280.1610.

(*Z*)-1-(2-Cyclohexyl-1-fluorovinyl)-4-methylbenzene (**12**)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2

mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-(cyclohexylethynyl)-4-methylbenzene (0.2 mmol, 40 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **12**. Pale yellow oil (34 mg, 78% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.21 (dd, *J* = 38.4, 9.2 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.35 (s, 3H), 1.82 – 1.70 (m, 4H), 1.70 – 1.64 (m, 1H), 1.41 – 1.30 (m, 2H), 1.26 – 1.10 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 155.5 (d, *J*_{C-F} = 245.1 Hz), 138.1, 130.2 (d, *J*_{C-F} = 29.6 Hz), 129.0 (d, *J*_{C-F} = 1.8 Hz), 123.8 (d, *J*_{C-F} = 6.9 Hz), 111.1 (d, *J*_{C-F} = 17.2 Hz), 33.8 (d, *J*_{C-F} = 3.7 Hz), 33.2 (d, *J*_{C-F} = 1.0 Hz), 26.0, 25.9, 21.2.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.5 (d, *J* = 38.4 Hz).

HRMS (ASAP) calcd for C₁₅H₁₉F [M]⁺: 218.1471, Found: 218.1485.

(E)-1-(2-Cyclohexyl-1-fluorovinyl)-4-methylbenzene (13)

Prepared following the general procedure (**condition B**): 1-(cyclohexylethynyl)-4-methylbenzene (0.2 mmol, 40 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **13**. Pale yellow oil (16 mg, 36% yield, *E/Z* > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.20 (dd, *J* = 23.0, 10.7 Hz, 1H), 2.38 (s, 3H), 2.31 – 2.20 (m, 1H), 1.80 – 1.68 (m, 4H), 1.67 – 1.60 (m, 1H), 1.28 – 1.14 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 155.9 (d, *J*_{C-F} = 239.9 Hz), 138.8, 129.6 (d, *J*_{C-F} = 30.4 Hz), 128.9, 127.4 (d, *J*_{C-F} = 4.9 Hz), 113.9 (d, *J*_{C-F} = 22.3 Hz), 35.2 (d, *J*_{C-F} = 7.6 Hz), 33.8 (d, *J*_{C-F} = 2.2 Hz), 25.9, 25.7, 21.3.

¹⁹F NMR (471 MHz, CDCl₃) δ -103.1 (d, *J* = 22.9 Hz).

HRMS (APCI) calcd for C₁₅H₁₉F [M]⁺: 218.1471, Found: 218.1456.

(Z)-1-(2-Cyclohexyl-1-fluorovinyl)-2-fluorobenzene (14)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-(cyclohexylethynyl)-2-fluorobenzene (0.2 mmol, 41 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **14**. Pale yellow oil (34 mg, 77% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.51 (td, *J* = 7.8, 1.7 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (m, 1H), 5.48 (dd, *J* = 40.0, 9.3 Hz, 1H), 2.75 – 2.59 (m, 1H), 1.86 – 1.70 (m, 4H), 1.70 – 1.62 (m, 1H), 1.42 – 1.30 (m, 2H), 1.27 – 1.14 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 159.2 (dd, *J*_{C-F} = 251.5, 5.4 Hz), 150.0 (dd, *J*_{C-F} = 242.9, 5.5 Hz), 129.4 (d, *J*_{C-F} = 8.6 Hz), 127.0 (dd, *J*_{C-F} = 8.5, 2.4 Hz), 124.0 (dd, *J*_{C-F} = 3.6, 1.1 Hz), 121.0 (dd, *J*_{C-F} = 31.2, 11.0 Hz), 118.2 (dd, *J*_{C-F} = 15.4, 12.3 Hz), 116.0 (dd, *J*_{C-F} = 22.8, 2.4 Hz), 34.1 (d, *J*_{C-F} = 4.1 Hz), 33.0 (d, *J*_{C-F} = 1.1 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -112.3 – -112.6 (m, 1F), -117.5 (dd, *J* = 40.0, 7.4 Hz, 1F).

HRMS (ASAP) calcd for C₁₄H₁₆F₂ [M]⁺: 222.1220, Found: 222.1237.

(*E*)-1-(2-Cyclohexyl-1-fluorovinyl)-2-fluorobenzene (15)

Prepared following the general procedure (**condition B**): 1-(cyclohexylethynyl)-2-fluorobenzene (0.2 mmol, 41 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **15**. Pale yellow oil (20 mg, 46% yield, *E/Z* > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.30 (m, 2H), 7.15 (dt, *J* = 18.3, 8.2 Hz, 2H), 5.38 (dd, *J* = 20.4, 10.9 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.74 – 1.64 (m, 4H), 1.63 – 1.56 (m, 1H), 1.23 – 1.09 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 160.0 (d, *J*_{C-F} = 249.3 Hz), 150.9 (d, *J*_{C-F} = 242.7 Hz), 131.1 (dd, *J*_{C-F} = 8.3, 1.9 Hz), 130.9 (t, *J*_{C-F} = 2.6 Hz), 123.9 (d, *J*_{C-F} = 3.5 Hz), 120.3 (dd, *J*_{C-F} = 30.1, 15.4 Hz), 116.9 (d, *J*_{C-F} = 19.8 Hz), 116.0 (d, *J*_{C-F} = 21.9 Hz), 35.5 (d, *J*_{C-F} = 5.6 Hz), 33.4 (d, *J*_{C-F} = 2.3 Hz), 25.8, 25.6.

¹⁹F NMR (471 MHz, CDCl₃) δ -100.0 (dd, *J* = 20.3, 7.7 Hz, 1F), -112.2 – -112.3 (m, 1F).

HRMS (ASAP) calcd for C₁₄H₁₆F₂ [M+H]⁺: 223.1220, Found: 223.1304.

(*Z*)-1-Chloro-2-(2-cyclohexyl-1-fluorovinyl)benzene (16)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-chloro-2-(cyclohexylethynyl)benzene (0.2 mmol, 44 mg, 1.0 equiv) at 90 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **16**. Pale yellow oil (32 mg, 68% yield, *Z/E* > 20 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.36 (m, 2H), 7.30 – 7.25 (m, 2H), 5.22 (dd, *J* = 37.8, 9.3 Hz, 1H), 2.75 – 2.61 (m, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.72 (m, 2H), 1.72 – 1.66 (m, 1H), 1.44 – 1.33 (m, 2H), 1.29 – 1.15 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.0 (d, *J*_{C-F} = 247.6 Hz), 132.4 (d, *J*_{C-F} = 24.1 Hz), 132.2 (d, *J*_{C-F} = 2.7 Hz), 130.3, 130.0 (d, *J*_{C-F} = 4.9 Hz), 129.7 (d, *J*_{C-F} = 1.0 Hz), 126.5, 118.0 (d, *J*_{C-F} = 16.3 Hz), 34.0 (d, *J*_{C-F} = 2.7 Hz), 33.0 (d, *J*_{C-F} = 1.4 Hz), 26.0, 25.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -108.0 (d, *J* = 37.8 Hz).

HRMS (ASAP) calcd for C₁₄H₁₆ClF [M+H]⁺: 239.0925, Found: 239.0979.

(Z)-1-(2-Cyclohexyl-1-fluorovinyl)-2-methylbenzene (17)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-(cyclohexylethynyl)-2-methylbenzene (0.2 mmol, 40 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **17**. Pale yellow oil (33 mg, 76% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 (m, 2H), 4.86 (dd, *J* = 37.5, 9.2 Hz, 1H), 2.69 – 2.58 (m, 1H), 2.39 (d, *J* = 3.2 Hz, 3H), 1.86 – 1.70 (m, 4H), 1.70 – 1.63 (m, 1H), 1.42 – 1.32 (m, 2H), 1.20 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.4 (d, *J*_{C-F} = 249.6 Hz), 136.4, 133.3 (d, *J*_{C-F} = 26.7 Hz), 130.5, 128.8 (d, *J*_{C-F} = 1.1 Hz), 128.7 (d, *J*_{C-F} = 4.8 Hz), 125.5, 116.0 (d, *J*_{C-F} = 17.3 Hz), 33.9 (d, *J*_{C-F} = 2.6 Hz), 33.3 (d, *J*_{C-F} = 1.2 Hz), 26.0, 25.8, 20.5 (d, *J*_{C-F} = 3.3 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -104.9 (d, *J* = 37.5 Hz).

HRMS (ASAP) calcd for C₁₅H₁₉F [M+H]⁺: 219.1471, Found: 219.1537.

(Z)-1-(2-Cyclohexyl-1-fluorovinyl)-3-methoxybenzene (18)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-(cyclohexylethynyl)-3-methoxybenzene (0.2 mmol, 43 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **18**. Pale yellow oil (18 mg, 39% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.25 (t, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.05 – 6.99 (m, 1H), 6.84 (ddd, *J* = 8.2, 2.5, 0.7 Hz, 1H), 5.27 (dd, *J* = 38.1, 9.3 Hz, 1H), 3.82 (s, 3H), 2.70 – 2.56 (m, 1H), 1.82 – 1.71 (m, 4H), 1.70 – 1.65 (m, 1H), 1.40 – 1.30 (m, 2H), 1.25 – 1.13 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 159.6 (d, *J*_{C-F} = 2.1 Hz), 155.2 (d, *J*_{C-F} = 245.5 Hz), 134.4 (d, *J*_{C-F} = 29.3 Hz), 129.4 (d, *J*_{C-F} = 2.0 Hz), 116.4 (d, *J*_{C-F} = 6.9 Hz), 114.0, 112.4 (d, *J*_{C-F} = 17.2 Hz), 109.4 (d, *J*_{C-F} = 7.5 Hz), 55.3, 33.8 (d, *J*_{C-F} = 3.7 Hz), 33.1 (d, *J*_{C-F} = 1.1 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.2 (d, *J* = 38.1 Hz).

HRMS (APCI) calcd for C₁₅H₁₉FO [M]⁺: 234.1420, Found: 234.1411.

Methyl (Z)-3-(2-cyclohexyl-1-fluorovinyl)benzoate (19)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry DCE (2.0 mL), methyl 3-(cyclohexylethynyl)benzoate (0.2 mmol, 48 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **19**. Pale yellow oil (35 mg, 67% yield, *Z/E* > 50 : 1).

¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 5.37 (dd, *J* = 38.0, 9.3 Hz, 1H), 3.93 (s, 3H), 2.73 – 2.56 (m, 1H), 1.81 – 1.65 (m, 5H), 1.40 – 1.31 (m, 2H), 1.26 – 1.13 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.8, 154.5 (d, *J* = 245.3 Hz), 133.3 (d, *J* = 30.0 Hz), 130.4 (d, *J* = 2.2 Hz), 129.2, 128.5 (d, *J* = 1.8 Hz), 128.0 (d, *J* = 6.8 Hz), 125.0 (d, *J* = 7.1 Hz), 113.2 (d, *J* = 16.8 Hz), 52.2, 33.8 (d, *J* = 3.6 Hz), 33.0, 26.0, 25.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -121.9 (d, *J* = 38.0 Hz).

HRMS (ESI) calcd for C₁₆H₁₉FO₂ [M+H]⁺: 263.1369, Found: 263.1439.

(*Z*)-3-(2-Cyclohexyl-1-fluorovinyl)benzonitrile (**20**)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry DCE (2.0 mL), 3-(cyclohexylethynyl)benzonitrile (0.2 mmol, 42 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **20**. Pale yellow oil (25 mg, 54% yield, *Z/E* = 13 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 5.37 (dd, *J* = 37.6, 9.3 Hz, 1H), 2.73 – 2.55 (m, 1H), 1.82 – 1.63 (m, 5H), 1.44 – 1.29 (m, 2H), 1.27 – 1.14 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.4 (d, *J* = 245.4 Hz), 134.2 (d, *J* = 30.6 Hz), 131.5, 129.2 (d, *J* = 2.0 Hz), 127.8 (d, *J* = 6.8 Hz), 127.4 (d, *J* = 7.4 Hz), 118.5, 114.5 (d, *J* = 16.6 Hz), 112.8 (d, *J* = 2.3 Hz), 33.9 (d, *J* = 3.4 Hz), 32.9 (d, *J* = 1.3 Hz), 25.9, 25.7.

¹⁹F NMR (376 MHz, CDCl₃) δ (*E*): -105.4 (d, *J* = 22.8 Hz), (*Z*): -122.6 (d, *J* = 37.6 Hz).

HRMS (ESI) calcd for C₁₅H₁₆FN [M+H]⁺: 230.1267, Found: 230.1338.

(*Z*)-1-(2-Cyclohexyl-1-fluorovinyl)-4-(trifluoromethoxy)benzene (**21**)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-

(cyclohexylethynyl)-4-(trifluoromethoxy)benzene (0.2 mmol, 54 mg, 1.0 equiv) at 90 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **21**. Pale yellow oil (41 mg, 71% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.48 (m, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 5.27 (dd, *J* = 37.9, 9.3 Hz, 1H), 2.71 – 2.58 (m, 1H), 1.82 – 1.71 (m, 4H), 1.68 (m, 1H), 1.42 – 1.31 (m, 2H), 1.27 – 1.12 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.3 (d, *J*_{C-F} = 245.2 Hz), 149.0 (d, *J*_{C-F} = 1.7 Hz), 131.7 (d, *J*_{C-F} = 30.1 Hz), 125.4 (d, *J*_{C-F} = 6.9 Hz), 120.8, 120.4 (d, *J*_{C-F} = 257.0 Hz), 112.9 (d, *J*_{C-F} = 16.9 Hz), 33.9 (d, *J*_{C-F} = 3.5 Hz), 33.1 (d, *J*_{C-F} = 1.2 Hz), 26.0, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -57.9 (s, 3F), -121.4 (d, *J* = 37.9 Hz, 1F).

HRMS (ASAP) calcd for C₁₅H₁₆F₄O [M]⁺: 288.1137, Found: 288.1122.

(Z)-4-(2-Cyclohexyl-1-fluorovinyl)phenyl trifluoromethanesulfonate (22)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-(cyclohexylethynyl)phenyl trifluoromethanesulfonate (0.2 mmol, 67 mg, 1.0 equiv) at 90 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **22**. White solid (52 mg, 74% yield, *Z/E* > 50 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.32 (dd, *J* = 37.7, 9.3 Hz, 1H), 2.72 – 2.57 (m, 1H), 1.82 – 1.65 (m, 5H), 1.41 – 1.30 (m, 2H), 1.27 – 1.13 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8 (d, *J*_{C-F} = 245.3 Hz), 149.1, 133.3 (d, *J*_{C-F} = 30.3 Hz), 125.6 (d, *J*_{C-F} = 7.0 Hz), 121.4, 118.7 (d, *J*_{C-F} = 320.9 Hz), 114.0 (d, *J*_{C-F} = 16.8 Hz), 33.9 (d, *J*_{C-F} = 3.4 Hz), 33.0 (d, *J*_{C-F} = 1.3 Hz), 25.9, 25.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -72.8 (s, 3F), -121.7 (d, *J* = 37.7 Hz, 1F).

HRMS (ASAP) calcd for C₁₅H₁₆F₄O₃S [M]⁺: 352.0756, Found: 352.0769.

(Z)-2-(4-(2-Cyclohexyl-1-fluorovinyl)phenyl)isoindoline-1,3-dione (23)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 2-(4-(cyclohexylethynyl)phenyl)isoindoline-1,3-dione (0.2 mmol, 66 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **23**. Yellow solid (43 mg, 62% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.96 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 5.33 (dd, *J* = 37.9, 9.2 Hz, 1H), 2.74 – 2.54 (m, 1H), 1.83 – 1.71 (m, 4H), 1.71 – 1.63 (m, 1H), 1.42 – 1.31 (m, 2H), 1.25 – 1.14 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 167.1, 154.7 (d, *J*_{C-F} = 245.2 Hz), 134.4, 132.6 (d, *J*_{C-F} = 29.8 Hz), 131.7, 131.5, 126.3 (d, *J*_{C-F} = 1.7 Hz), 124.5 (d, *J*_{C-F} = 6.9 Hz), 123.8, 113.1 (d, *J*_{C-F} = 16.9 Hz), 33.9 (d, *J*_{C-F} = 3.4 Hz), 33.1, 26.0, 25.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -121.9 (d, *J* = 37.9 Hz).

HRMS (ESI) calcd for C₂₂H₂₀FNO₂ [M+H]⁺: 350.1478, Found: 350.1539.

Methyl (Z)-3-(2-cyclohexyl-1-fluorovinyl)-1-tosyl-1H-indole-6-carboxylate (24)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), methyl 3-(cyclohexylethynyl)-1-tosyl-1H-indole-6-carboxylate (0.2 mmol, 87 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **24**. Yellow solid (42 mg, 46% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 8.69 (d, *J* = 1.2 Hz, 1H), 7.97 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.83 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.21 (dd, *J* = 39.0, 9.3 Hz, 1H), 3.97 (s, 3H), 2.72 – 2.61 (m, 1H), 2.35 (s, 3H), 1.84 – 1.71 (m, 4H), 1.42 – 1.31 (m, 2H), 1.28 – 1.15 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 167.0, 150.0 (d, *J*_{C-F} = 241.2 Hz), 145.6, 134.8 (d, *J*_{C-F} = 1.0 Hz), 134.7, 130.4 (d, *J*_{C-F} = 5.5 Hz), 130.1, 127.0, 126.9, 126.1 (d, *J*_{C-F} = 6.3 Hz), 124.8, 120.6, 116.1 (d, *J*_{C-F} = 34.0 Hz), 115.4, 114.70 (d, *J*_{C-F} = 15.8 Hz), 52.3, 33.8 (d, *J*_{C-F} = 3.2 Hz), 33.2, 26.0, 25.8, 21.6.

¹⁹F NMR (282 MHz, CDCl₃) δ -114.1 (d, *J* = 39.0 Hz).

HRMS (ESI) calcd for C₂₅H₂₆FNO₄S [M+H]⁺: 456.1567, Found: 456.1633.

Methyl (Z)-5-(2-cyclohexyl-1-fluorovinyl)furan-2-carboxylate (25)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), methyl 5-(cyclohexylethynyl)furan-2-carboxylate (0.2 mmol, 46 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **25**. Pale yellow oil (18 mg, 35% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, *J* = 3.5 Hz, 1H), 6.48 (d, *J* = 2.9 Hz, 1H), 5.53 (dd, *J* = 38.2, 9.6 Hz, 1H), 3.89 (s, 3H), 2.66 – 2.54 (m, 1H), 1.79 – 1.71 (m, 4H), 1.70 – 1.64 (m, 1H), 1.37 – 1.29 (m, 2H), 1.24 – 1.17 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.9, 150.7 (d, *J*_{C-F} = 52.2 Hz), 147.2 (d, *J*_{C-F} = 236.2 Hz), 143.9, 119.4, 114.7 (d, *J*_{C-F} = 12.0 Hz), 107.8, 52.0, 33.6 (d, *J*_{C-F} = 2.0 Hz), 32.8 (d, *J*_{C-F} = 1.2 Hz), 25.9, 25.7.

¹⁹F NMR (471 MHz, CDCl₃) δ -131.2 (d, *J* = 38.1 Hz).

HRMS (ESI) calcd for C₁₄H₁₇FO₃ [M+H]⁺: 253.1162 Found: 253.1227.

Methyl (*E*)-5-(2-cyclohexyl-1-fluorovinyl)furan-2-carboxylate (26**)**

Prepared following the general procedure (**condition B**): methyl 5-(cyclohexylethynyl)furan-2-carboxylate (0.2 mmol, 46 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **26**. Pale yellow oil (17 mg, 33% yield, *E/Z* > 20:1).

¹H NMR (500 MHz, CDCl₃) δ 7.19 (d, *J* = 3.3 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 5.39 (dd, *J* = 22.8, 10.3 Hz, 1H), 3.90 (s, 3H), 2.90 – 2.76 (m, 1H), 1.86 – 1.72 (m, 4H), 1.72 – 1.64 (m, 1H), 1.46 – 1.32 (m, 2H), 1.24 – 1.12 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.8, 150.2 (d, *J*_{C-F} = 50.5 Hz), 146.9 (d, *J*_{C-F} = 230.2 Hz), 144.3, 118.7, 117.6 (d, *J*_{C-F} = 17.2 Hz), 110.4, 52.0, 34.2 (d, *J*_{C-F} = 6.6 Hz), 33.5 (d, *J*_{C-F} = 2.1 Hz), 25.9, 25.7.

¹⁹F NMR (471 MHz, CDCl₃) δ -123.6 (d, *J* = 22.7 Hz).

HRMS (ESI) calcd for C₁₄H₁₇FO₃ [M+H]⁺: 253.1162, Found: 253.1230.

(*Z*)-1-Bromo-4-(1-fluoro-3-methylbut-1-en-1-yl)benzene (27**)**

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene (0.2 mmol, 45 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **27**. Pale yellow oil (35 mg, 73% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 5.26 (dd, *J* = 37.7, 9.3 Hz, 1H), 3.02 – 2.85 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 154.4 (d, *J*_{C-F} = 245.1 Hz), 131.8 (d, *J*_{C-F} = 29.9 Hz), 131.5 (d, *J*_{C-F} = 1.9 Hz), 125.4 (d, *J*_{C-F} = 6.9 Hz), 122.2, 114.2 (d, *J*_{C-F} = 17.0 Hz), 24.4 (d, *J*_{C-F} = 4.5 Hz), 22.9 (d, *J*_{C-F} = 1.3 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -122.0 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for C₁₁H₁₂BrF [M]⁺: 242.0106, Found: 242.0069.

(E)-1-Bromo-4-(1-fluoro-3-methylbut-1-en-1-yl)benzene (28)

Prepared following the general procedure (**condition B**): 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene (0.2 mmol, 45 mg, 1.0 equiv), dry CHCl_3 (1.0 mL), $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (27 μL , 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **28**. Pale yellow oil (23 mg, 47% yield, $E/Z = 4 : 1$).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.53 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 5.25 (dd, $J = 22.7$, 10.9 Hz, 1H), 2.63 – 2.48 (m, 1H), 1.07 (d, $J = 6.8$ Hz, 6H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 154.4 (d, $J_{\text{C-F}} = 240.1$ Hz), 131.5, 131.2 (d, $J_{\text{C-F}} = 30.7$ Hz), 129.1 (d, $J_{\text{C-F}} = 4.8$ Hz), 123.0, 116.5 (d, $J_{\text{C-F}} = 21.6$ Hz), 25.9 (d, $J_{\text{C-F}} = 7.9$ Hz), 23.5 (d, $J_{\text{C-F}} = 2.2$ Hz).

$^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ (E): -104.47 (d, $J = 22.6$ Hz), (Z): -122.04 (d, $J = 37.7$ Hz).

HRMS (ASAP) calcd for $\text{C}_{11}\text{H}_{12}\text{BrF}$ $[\text{M}+\text{H}]^+$: 243.0106, Found: 243.0174.

(Z)-(2-Cyclobutyl-1-fluorovinyl)benzene (29)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF_4 (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl_3 (1.0 mL), (cyclobutylethynyl)benzene (0.2 mmol, 31 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **29**. Pale yellow oil (24 mg, 68% yield, $Z/E > 50 : 1$).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.52 – 7.46 (m, 2H), 7.35 (m, 2H), 7.29 (m, 1H), 5.50 (dd, $J = 37.8$, 8.8 Hz, 1H), 3.57 – 3.42 (m, 1H), 2.34 – 2.15 (m, 2H), 2.00 – 1.90 (m, 3H), 1.89 – 1.81 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.0 (d, $J_{\text{C-F}} = 246.0$ Hz), 132.7 (d, $J_{\text{C-F}} = 29.1$ Hz), 128.4 (d, $J_{\text{C-F}} = 2.0$ Hz), 128.3, 123.8 (d, $J_{\text{C-F}} = 7.0$ Hz), 111.3 (d, $J_{\text{C-F}} = 17.2$ Hz), 31.1 (d, $J_{\text{C-F}} = 4.0$ Hz), 29.8 (d, $J_{\text{C-F}} = 2.2$ Hz), 19.1.

$^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -120.9 (d, $J = 37.8$ Hz).

HRMS (ASAP) calcd for $\text{C}_{12}\text{H}_{13}\text{F}$ $[\text{M}+\text{H}]^+$: 177.1001, Found: 177.1068.

(E)-(2-Cyclobutyl-1-fluorovinyl)benzene (30)

Prepared following the general procedure (**condition B**): (cyclobutylethynyl)benzene (0.2 mmol, 31 mg, 1.0 equiv), dry CHCl_3 (1.0 mL), $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (27 μL , 0.2 mmol, 1.0 equiv) at room temperature. The

reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **30**. Pale yellow oil (14 mg, 40% yield, *E/Z* = 10 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.31 (m, 5H), 5.52 (dd, *J* = 21.8, 9.8 Hz, 1H), 3.26 – 3.09 (m, 1H), 2.30 – 2.14 (m, 2H), 1.99 – 1.80 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 155.8 (d, *J*_{C-F} = 242.0 Hz), 132.2 (d, *J*_{C-F} = 29.8 Hz), 128.9 (d, *J*_{C-F} = 0.9 Hz), 128.1, 127.4 (d, *J*_{C-F} = 5.1 Hz), 113.8 (d, *J*_{C-F} = 22.6 Hz), 32.6 (d, *J*_{C-F} = 7.5 Hz), 30.1 (d, *J*_{C-F} = 2.2 Hz), 18.7 (d, *J*_{C-F} = 1.2 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ (*E*): -105.0 (d, *J* = 21.8 Hz), (*Z*): -120.8 (d, *J* = 37.8 Hz).

HRMS (ASAP) calcd for C₁₂H₁₃F [M+H]⁺: 177.1001, Found: 177.1060.

(Z)-1-Bromo-4-(2-cyclopentyl-1-fluorovinyl)benzene (31)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-bromo-4-(cyclopentylethynyl)benzene (0.2 mmol, 50 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **31**. Pale yellow oil (41 mg, 76% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 2H), 5.35 (dd, *J* = 37.5, 9.3 Hz, 1H), 3.09 – 2.93 (m, 1H), 1.99 – 1.83 (m, 2H), 1.77 – 1.67 (m, 2H), 1.67 – 1.57 (m, 2H), 1.37 – 1.28 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 155.0 (d, *J*_{C-F} = 244.9 Hz), 131.8 (d, *J*_{C-F} = 29.9 Hz), 131.5 (d, *J*_{C-F} = 1.9 Hz), 125.4 (d, *J*_{C-F} = 6.9 Hz), 122.2, 112.2 (d, *J*_{C-F} = 17.0 Hz), 35.5 (d, *J*_{C-F} = 3.7 Hz), 33.6 (d, *J*_{C-F} = 1.1 Hz), 25.2.

¹⁹F NMR (471 MHz, CDCl₃) δ -122.2 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for C₁₃H₁₄BrF [M]⁺: 268.0263, Found: 268.0185

(Z)-(3-Cyclopentyl-1-fluoroprop-1-en-1-yl)benzene (32)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), (3-cyclopentylprop-1-yn-1-yl)benzene (0.2 mmol, 37 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **32**. Pale yellow oil (30 mg, 73% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.47 (m, 2H), 7.38 – 7.32 (m, 2H), 7.30 (ddd, *J* = 7.3, 3.7, 1.3 Hz, 1H), 5.42 (dt, *J* = 37.5, 7.7 Hz, 1H), 2.29 (td, *J* = 7.5, 1.8 Hz, 2H), 2.00 – 1.89 (m, 1H), 1.85 – 1.73 (m, 2H), 1.70 – 1.59 (m, 2H), 1.59 – 1.49 (m, 2H), 1.28 – 1.17 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.7 (d, J_{C-F} = 245.3 Hz), 132.9 (d, J_{C-F} = 29.4 Hz), 128.4 (d, J_{C-F} = 2.0 Hz), 128.2, 123.8 (d, J_{C-F} = 6.9 Hz), 105.6 (d, J_{C-F} = 17.7 Hz), 40.1 (d, J_{C-F} = 1.5 Hz), 32.3, 30.1 (d, J_{C-F} = 4.2 Hz), 25.2.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.1 (d, J = 37.5 Hz).

HRMS (ASAP) calcd for C₁₄H₁₇F [M]⁺: 204.1314, Found: 204.1326.

(Z)-4-(2-Fluoro-2-phenylvinyl)-1-tosylpiperidine (33)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-(phenylethynyl)-1-tosylpiperidine (0.2 mmol, 68 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **33**. Pale yellow oil (43 mg, 60% yield, *Z/E* = 33 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.69 – 7.64 (m, 2H), 7.48 – 7.43 (m, 2H), 7.36 – 7.29 (m, 5H), 5.21 (dd, J = 37.2, 9.0 Hz, 1H), 3.79 (d, J = 11.7 Hz, 2H), 2.59 – 2.51 (m, 1H), 2.45 (s, 3H), 2.35 (td, J = 11.9, 2.4 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.61 – 1.52 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.68 (d, J_{C-F} = 247.7 Hz), 143.5, 133.0, 132.1 (d, J_{C-F} = 28.9 Hz), 129.6, 128.8, 128.4 (d, J_{C-F} = 1.8 Hz), 127.7, 124.0 (d, J_{C-F} = 7.0 Hz), 109.0 (d, J_{C-F} = 16.7 Hz), 46.1, 31.4 (d, J_{C-F} = 1.0 Hz), 31.3 (d, J_{C-F} = 4.4 Hz), 21.5.

¹⁹F NMR (376 MHz, CDCl₃) δ (*E*): -99.1 (d, J = 21.6 Hz), (*Z*): -119.3 (d, J = 37.2 Hz).

HRMS (ASAP) calcd for C₂₀H₂₂FNO₂S [M+H]⁺: 360.1355 Found: 360.1423.

(Z)-4-(2-Fluoro-2-phenylvinyl)tetrahydro-2H-pyran (34)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), 4-(phenylethynyl)tetrahydro-2H-pyran (0.2 mmol, 37 mg, 1.0 equiv) and BF₃•Et₂O (0.2 mmol, 25 ul, 1.0 equiv) at 90 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **34**. Pale yellow oil (26 mg, 64% yield, *Z/E* = 3.6 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.31 (m, 3H), 7.30 – 7.21 (m, 2H), 5.30 – 5.07 (m, 1H), 3.94 – 3.84 (m, 2H), 3.43 (td, J = 11.7, 1.7 Hz, 1.5H), 3.31 (td, J = 11.6, 1.9 Hz, 0.6H), 2.91 – 2.70 (m, 0.8H), 2.48 – 2.39 (m, 0.3H), 1.66 – 1.55 (m, 2H), 1.53 – 1.42 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.6 (d, J_{C-F} = 242.8 Hz), 156.2 (d, J_{C-F} = 247.0 Hz), 132.5 (d, J_{C-F} = 29.1 Hz), 132.0 (d, J_{C-F} = 29.9 Hz), 129.2 (d, J_{C-F} = 1.2 Hz), 128.6, 128.41 (d, J_{C-F} = 2.0 Hz), 128.36, 127.5 (d, J_{C-F} = 4.7 Hz), 123.9 (d, J_{C-F} = 7.1 Hz), 112.7 (d, J_{C-F} = 23.4 Hz), 110.0 (d, J_{C-F} = 16.7 Hz), 67.6, 67.3, 33.3 (d, J_{C-F} = 2.3 Hz), 32.7 (d, J_{C-F} = 1.3 Hz), 32.6 (d, J_{C-F} = 8.1 Hz), 31.2 (d, J_{C-F} = 4.3 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ (*E*): -100.9 (dd, *J* = 22.2, 1.7 Hz, 0.22F), (*Z*): -120.2 (d, *J* = 37.5 Hz, 0.79F).

HRMS (ESI) calcd for C₁₃H₁₅FO [M+H]⁺: 207.1107 Found: 207.1174.

(*Z*)-(1-Fluoroprop-1-ene-1,3-diyl)dibenzene (35)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), prop-1-yne-1,3-diyl dibenzene (0.2 mmol, 39 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **35**. Pale yellow oil (32 mg, 76% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.26 (m, 7H), 7.25 – 7.20 (m, 1H), 5.60 (dt, *J* = 36.3, 7.7 Hz, 1H), 3.65 (dd, *J* = 7.7, 1.1 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 157.0 (d, *J*_{C-F} = 247.5 Hz), 140.2, 132.4 (d, *J*_{C-F} = 29.0 Hz), 128.6, 128.5, 128.43, 128.42, 126.2, 124.0 (d, *J*_{C-F} = 7.0 Hz), 104.9 (d, *J*_{C-F} = 17.3 Hz), 30.4 (d, *J*_{C-F} = 5.8 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -121.0 (d, *J* = 36.3 Hz).

HRMS (ASAP) calcd for C₁₅H₁₃F [M]⁺: 212.1001, Found: 212.1008.

(3*r*,5*r*,7*r*)-1-((*Z*)-3-Fluoro-3-phenylallyl)adamantane (36)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), (3*r*,5*r*,7*r*)-1-(3-phenylprop-2-yn-1-yl)adamantane (0.2 mmol, 50 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **36**. Pale yellow oil (36 mg, 67% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.50 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.29 (m, 1H), 5.48 (dt, *J* = 37.3, 8.2 Hz, 1H), 2.06 (dd, *J* = 8.2, 1.8 Hz, 2H), 1.98 (s, 3H), 1.72 (d, *J* = 12.1 Hz, 3H), 1.68 – 1.62 (m, 3H), 1.58 (d, *J* = 2.5 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 157.3 (d, *J*_{C-F} = 245.9 Hz), 132.9 (d, *J*_{C-F} = 29.6 Hz), 128.4 (d, *J*_{C-F} = 2.0 Hz), 128.2, 123.9 (d, *J*_{C-F} = 6.9 Hz), 102.1 (d, *J*_{C-F} = 17.4 Hz), 42.3, 38.6 (d, *J*_{C-F} = 3.3 Hz), 37.1, 33.6 (d, *J*_{C-F} = 1.6 Hz), 28.7.

¹⁹F NMR (471 MHz, CDCl₃) δ -120.4 (d, *J* = 37.3 Hz).

HRMS (ASAP) calcd for C₁₉H₂₃F [M]⁺: 270.1784, Found: 270.1774.

(*Z*)-(1-Fluoro-3-methyldec-1-en-1-yl)benzene (37)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), (3-methyldec-1-yn-1-yl)benzene (0.2 mmol, 46 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **37**. Pale yellow oil (36 mg, 73% yield, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.48 (m, 2H), 7.36 (dd, *J* = 11.0, 4.4 Hz, 2H), 7.33 – 7.28 (m, 1H), 5.21 (dd, *J* = 37.8, 9.7 Hz, 1H), 2.88 – 2.74 (m, 1H), 1.44 – 1.22 (m, 12H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 155.8 (d, *J*_{C-F} = 244.9 Hz), 132.9 (d, *J*_{C-F} = 29.5 Hz), 128.3 (d, *J*_{C-F} = 2.0 Hz), 128.2, 123.8 (d, *J*_{C-F} = 7.0 Hz), 112.5 (d, *J*_{C-F} = 17.4 Hz), 37.6 (d, *J*_{C-F} = 1.4 Hz), 31.9, 29.7, 29.5 (d, *J*_{C-F} = 3.9 Hz), 29.3, 27.5, 22.7, 21.1 (d, *J*_{C-F} = 1.3 Hz), 14.1.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.9 (d, *J* = 37.8 Hz).

HRMS (ASAP) calcd for C₁₇H₂₅F [M]⁺: 248.1940, Found: 248.1946.

(Z)-(1-Fluorohex-1-en-1-yl)benzene (38)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), hex-1-yn-1-ylbenzene (0.2 mmol, 32 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **38**. Pale yellow oil (24 mg, 66% yield, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.52 – 7.47 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 5.40 (dt, *J* = 37.6, 7.6 Hz, 1H), 2.33 – 2.25 (m, 2H), 1.49 – 1.34 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.6 (d, *J*_{C-F} = 245.3 Hz), 132.9 (d, *J*_{C-F} = 29.4 Hz), 128.4 (d, *J*_{C-F} = 2.0 Hz), 128.2, 123.8 (d, *J*_{C-F} = 7.0 Hz), 106.3 (d, *J*_{C-F} = 17.8 Hz), 31.6 (d, *J*_{C-F} = 1.5 Hz), 23.8 (d, *J*_{C-F} = 4.9 Hz), 22.3, 13.9.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.4 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for C₁₂H₁₅F [M]⁺: 178.1158, Found: 178.1172.

(E)-(1-Fluorohex-1-en-1-yl)benzene (39)

Prepared following the general procedure (**condition B**): hex-1-yn-1-ylbenzene (0.2 mmol, 32 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction

mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **39**. Pale yellow oil (14 mg, 40% yield, *E/Z* = 6 : 1).

¹H NMR (300 MHz, CDCl₃) δ 7.53 – 7.29 (m, 5H), 5.39 (dt, *J* = 22.8, 7.9 Hz, 1H), 2.20 (q, *J* = 7.0 Hz, 2H), 1.50 – 1.27 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.5 (d, *J*_{C-F} = 239.4 Hz), 132.2 (d, *J*_{C-F} = 30.1 Hz), 128.8, 128.2, 127.6 (d, *J*_{C-F} = 5.0 Hz), 108.6 (d, *J*_{C-F} = 24.2 Hz), 32.3 (d, *J*_{C-F} = 1.7 Hz), 25.7 (d, *J*_{C-F} = 7.9 Hz), 22.2, 13.8.

¹⁹F NMR (282 MHz, CDCl₃) δ (*E*): -102.6 (d, *J* = 22.8 Hz), (*Z*): -121.4 (d, *J* = 37.5 Hz).

HRMS (ASAP) calcd for C₁₂H₁₅F [M]⁺: 178.1158, Found: 178.1167.

(Z)-1-Bromo-4-(6-chloro-1-fluorohex-1-en-1-yl)benzene (40)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-bromo-4-(6-chlorohex-1-yn-1-yl)benzene (0.2 mmol, 54 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **40**. Pale yellow oil (39 mg, 67% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 5.31 (dt, *J* = 36.9, 7.7 Hz, 1H), 3.50 (t, *J* = 6.6 Hz, 2H), 2.24 (qd, *J* = 7.5, 1.8 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.59 – 1.50 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.3 (d, *J*_{C-F} = 246.1 Hz), 131.6 (d, *J*_{C-F} = 2.0 Hz), 131.4 (d, *J*_{C-F} = 3.2 Hz), 125.4 (d, *J*_{C-F} = 6.9 Hz), 122.5, 106.1 (d, *J*_{C-F} = 17.6 Hz), 44.8, 32.0, 26.5 (d, *J*_{C-F} = 1.7 Hz), 23.4 (d, *J*_{C-F} = 4.9 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -120.6 (d, *J* = 36.9 Hz).

HRMS (ASAP) calcd for C₁₂H₁₃BrClF [M]⁺: 289.9873, Found: 289.9860.

Methyl (Z)-6-fluoro-6-phenylhex-5-enoate (41)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), methyl 6-phenylhex-5-ynoate (0.2 mmol, 40 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **41**. Pale yellow oil (23 mg, 52% yield, *Z/E* = 33 : 1).

¹H NMR (300 MHz, CDCl₃) δ 7.55 – 7.42 (m, 2H), 7.41 – 7.27 (m, 3H), 5.37 (dt, *J* = 37.0, 7.7 Hz, 1H), 3.67 (s, 3H), 2.47 – 2.25 (m, 4H), 1.88 – 1.75 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 173.9, 157.3 (d, *J* = 246.8 Hz), 132.5 (d, *J* = 29.1 Hz), 128.5, 128.4 (d, *J* = 2.0 Hz), 123.9 (d, *J* = 7.0 Hz), 104.8 (d, *J* = 17.6 Hz), 51.5, 33.4, 24.6 (d, *J* = 1.8 Hz), 23.5 (d, *J* = 5.1 Hz).

¹⁹F NMR (282 MHz, CDCl₃) δ (*E*): -100.6 (d, *J* = 22.1 Hz), (*Z*): -120.1 (d, *J* = 37.0 Hz).

HRMS (ASAP) calcd for C₁₃H₁₅FO₂ [M+H]⁺: 223.1056, Found: 223.1122.

(Z)-5-Fluoro-5-phenylpent-4-enenitrile (42)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 5-phenylpent-4-ynenitrile (0.2 mmol, 31 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **42**. Pale yellow oil (18 mg, 50% yield, *Z/E* > 50 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.46 (m, 2H), 7.45 – 7.30 (m, 3H), 5.47 (dt, *J* = 35.7, 7.5 Hz, 1H), 2.72 – 2.59 (m, 2H), 2.58 – 2.47 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 158.8 (d, *J*_{C-F} = 250.7 Hz), 131.6 (d, *J*_{C-F} = 28.5 Hz), 129.2, 128.5 (d, *J*_{C-F} = 1.9 Hz), 124.2 (d, *J*_{C-F} = 7.1 Hz), 119.1, 101.3 (d, *J*_{C-F} = 16.9 Hz), 20.5 (d, *J*_{C-F} = 6.1 Hz), 17.5 (d, *J*_{C-F} = 2.2 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -116.4 (d, *J* = 35.7 Hz).

HRMS (APCI) calcd for C₁₁H₁₀FN [M+H]⁺: 176.0797 Found: 176.0864.

(Z)-5-Fluoro-5-phenylpent-4-en-1-yl nicotinate (43)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), BF₄•Et₂O (0.2 mmol, 28 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), 5-phenylpent-4-yn-1-yl nicotinate (0.2 mmol, 53 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **43**. Pale yellow oil (19 mg, 33% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 9.25 (d, *J* = 1.1 Hz, 1H), 8.77 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.30 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.40 – 7.29 (m, 4H), 5.44 (dt, *J* = 36.8, 7.7 Hz, 1H), 4.43 (t, *J* = 6.5 Hz, 2H), 2.47 (qd, *J* = 7.6, 1.6 Hz, 2H), 2.02 – 1.92 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 165.3, 157.5 (d, *J*_{C-F} = 247.3 Hz), 153.4, 150.9, 137.0, 132.4 (d, *J*_{C-F} = 29.0 Hz), 128.6, 128.4 (d, *J*_{C-F} = 1.9 Hz), 126.2, 123.9 (d, *J*_{C-F} = 7.0 Hz), 123.2, 104.4 (d, *J*_{C-F} = 17.6 Hz), 64.8, 28.4, 20.8 (d, *J*_{C-F} = 5.5 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -119.7 (d, *J* = 36.8 Hz).

HRMS (ESI) calcd for C₁₇H₁₆FNO₂ [M+H]⁺: 286.1165 Found: 286.1228

(Z)-2-(6-Fluoro-6-phenylhex-5-en-1-yl)isoindoline-1,3-dione (44)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 2-(6-phenylhex-5-yn-1-yl)isoindoline-1,3-dione (0.2 mmol, 61 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **44**. Yellow solid (47 mg, 72% yield, Z/E > 50 : 1).

Gram scale: 2,6-dichloropyridinium tetrafluoroborate (16 mmol, 3.76 g, 2.0 equiv), dry CHCl₃ (80 mL), 2-(6-phenylhex-5-yn-1-yl)isoindoline-1,3-dione (8.0 mmol, 2.42 g, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **44**. Yellow solid (1.65g, 64% yield, Z/E > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.54 – 7.41 (m, 2H), 7.39 – 7.26 (m, 3H), 5.37 (dt, *J* = 37.2, 7.6 Hz, 1H), 3.72 (t, *J* = 7.2 Hz, 2H), 2.33 (qd, *J* = 7.5, 1.7 Hz, 2H), 1.81 – 1.66 (m, 2H), 1.56 – 1.46 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 168.4, 156.98 (d, *J*_{C-F} = 246.3 Hz), 133.8, 132.62 (d, *J*_{C-F} = 29.2 Hz), 132.2, 128.37 (d, *J*_{C-F} = 1.7 Hz), 128.35 (d, *J*_{C-F} = 2.0 Hz), 123.9 (d, *J*_{C-F} = 6.9 Hz), 123.2, 105.4 (d, *J*_{C-F} = 17.7 Hz), 37.8, 28.2, 26.6, 23.7 (d, *J*_{C-F} = 5.1 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -120.6 (d, *J* = 37.2 Hz).

HRMS (ESI) calcd for C₂₀H₁₈FNO₂ [M+H]⁺: 324.1322, Found: 324.1381.

(Z)-1-Chloro-3-(2-cyclopentyl-1-fluorovinyl)benzene (**45**)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-chloro-3-(cyclopentylethynyl)benzene (0.2 mmol, 41 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **45**. Pale yellow oil (35 mg, 79% yield, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.47 (s, 1H), 7.38 – 7.34 (m, 1H), 7.29 – 7.22 (m, 2H), 5.37 (dd, *J* = 37.4, 9.3 Hz, 1H), 3.08 – 2.94 (m, 1H), 1.98 – 1.87 (m, 2H), 1.76 – 1.68 (m, 2H), 1.67 – 1.57 (m, 2H), 1.38 – 1.28 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.6 (d, *J*_{C-F} = 245.3 Hz), 134.8, 134.5 (d, *J*_{C-F} = 2.4 Hz), 129.6 (d, *J*_{C-F} = 2.0 Hz), 128.2, 124.0 (d, *J*_{C-F} = 7.4 Hz), 121.9 (d, *J*_{C-F} = 6.9 Hz), 112.9 (d, *J*_{C-F} = 16.8 Hz), 35.5 (d, *J*_{C-F} = 3.7 Hz), 33.6 (d, *J*_{C-F} = 1.3 Hz), 25.2.

¹⁹F NMR (471 MHz, CDCl₃) δ -122.2 (d, *J* = 37.4 Hz).

HRMS (ASAP) calcd for C₁₃H₁₄ClF [M]⁺: 224.0768, Found: 224.0757.

(Z)-1-(6-Chloro-1-fluorohex-1-en-1-yl)-2-methoxy-4-nitrobenzene (46)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry DCE (2.0 mL), 1-(6-chlorohex-1-yn-1-yl)-2-methoxy-4-nitrobenzene (0.2 mmol, 53 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **46**. Pale yellow oil (28 mg, 49% yield, *Z/E* = 13 : 1)

¹H NMR (500 MHz, CDCl₃) δ 7.86 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 6.04 (dt, *J* = 39.7, 7.7 Hz, 1H), 4.00 (s, 3H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.38 (qd, *J* = 7.5, 1.7 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.70 – 1.61 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.5 (d, *J*_{C-F} = 5.6 Hz), 152.0 (d, *J*_{C-F} = 242.9 Hz), 147.8, 127.2 (d, *J*_{C-F} = 28.7 Hz), 127.0 (d, *J*_{C-F} = 11.2 Hz), 115.7 (d, *J*_{C-F} = 1.6 Hz), 115.2 (d, *J*_{C-F} = 15.6 Hz), 106.0 (d, *J*_{C-F} = 2.5 Hz), 56.1, 44.8, 32.1, 26.4 (d, *J*_{C-F} = 1.5 Hz), 23.9 (d, *J*_{C-F} = 6.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ (E): -98.15 (d, *J* = 19.6 Hz), (Z): -114.11 (d, *J* = 39.8 Hz).

HRMS (APCI) calcd for C₁₃H₁₅ClFNO₃ [M]⁺: 287.0724, Found: 287.0715.

(Z)-1,3-Di-tert-butyl-5-(1-fluoroprop-1-en-1-yl)benzene (47)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1,3-di-tert-butyl-5-(prop-1-yn-1-yl)benzene (0.2 mmol, 46 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **47**. Pale yellow oil (26 mg, 52% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.39 (t, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 2H), 5.41 (dq, *J* = 37.3, 7.0 Hz, 1H), 1.82 (dd, *J* = 7.0, 2.4 Hz, 3H), 1.34 (s, 18H).

¹³C NMR (126 MHz, CDCl₃) δ 158.3 (d, *J*_{C-F} = 246.1 Hz), 150.8 (d, *J*_{C-F} = 1.6 Hz), 132.2 (d, *J*_{C-F} = 28.0 Hz), 122.6, 118.2 (d, *J*_{C-F} = 6.6 Hz), 100.1 (d, *J*_{C-F} = 18.6 Hz), 34.9, 31.4, 9.4 (d, *J*_{C-F} = 6.8 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -120.0 (dd, *J* = 37.3, 2.2 Hz).

HRMS (ASAP) calcd for C₁₇H₂₅F [M+H]⁺: 249.1940, Found: 249.2025.

(Z)-1-(1-Fluoroprop-1-en-1-yl)naphthalene (48)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-(prop-1-yn-1-

yl)naphthalene (0.2 mmol, 33 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **48**. Pale yellow oil (18 mg, 47% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 8.10 (m, 1H), 7.86 – 7.74 (m, 2H), 7.49 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 5.15 (dq, *J* = 36.0, 7.0 Hz, 1H), 1.83 (dd, *J* = 7.0, 2.5 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.1 (d, *J*_{C-F} = 249.7 Hz), 133.6, 131.5 (d, *J*_{C-F} = 26.1 Hz), 131.0, 129.6, 128.3, 127.0 (d, *J*_{C-F} = 4.5 Hz), 126.5, 126.0, 125.7 (d, *J*_{C-F} = 4.3 Hz), 125.0, 105.6 (d, *J*_{C-F} = 18.4 Hz), 9.7 (d, *J*_{C-F} = 5.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -102.4 (d, *J* = 36.2 Hz).

HRMS (ASAP) calcd for C₁₃H₁₁F [M+H]⁺: 187.0845, Found: 187.0934.

(Z)-(2-Fluoro-2-phenylvinyl)cyclododecane (49)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), (phenylethynyl)cyclododecane (0.2 mmol, 54 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **49**. Pale yellow oil (36 mg, 62% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.49 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.28 (m, 1H), 5.26 (dd, *J* = 37.8, 9.8 Hz, 1H), 2.97 – 2.85 (m, 1H), 1.62 (td, *J* = 13.1, 6.4 Hz, 2H), 1.54 – 1.49 (m, 2H), 1.47 – 1.25 (m, 18H).

¹³C NMR (126 MHz, CDCl₃) δ 155.8 (d, *J*_{C-F} = 244.6 Hz), 132.9 (d, *J*_{C-F} = 29.6 Hz), 128.3 (d, *J*_{C-F} = 2.0 Hz), 128.2, 123.8 (d, *J*_{C-F} = 7.0 Hz), 112.0 (d, *J*_{C-F} = 17.5 Hz), 30.6 (d, *J*_{C-F} = 1.0 Hz), 29.6 (d, *J*_{C-F} = 3.1 Hz), 23.9, 23.8, 23.5, 23.3, 22.6.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.7 (d, *J* = 37.8 Hz).

HRMS (ASAP) calcd for C₂₀H₂₉F [M]⁺: 288.2253, Found: 288.2251.

(Z)-6-Fluorododec-6-ene (50)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), dodec-6-yne (0.2 mmol, 33 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **50** with spectral properties identical to the reported in the literature^[2]. Pale yellow oil (26 mg, 70% yield, *Z/E/gem*-difluoroalkane = 4 : 1 : 3).

¹H NMR (400 MHz, CDCl₃) δ 4.99 (dt, *J* = 22.4, 7.9 Hz, 0.2H), 4.45 (dt, *J* = 38.3, 7.4 Hz, 0.8H), 2.26 – 2.18 (m, 0.4H), 2.16 – 2.08 (m, 1.6H), 2.07 – 2.00 (m, 1.6H), 1.93 – 1.88 (m, 0.4H), 1.52 – 1.44 (m, 2H), 1.35 – 1.28 (m, 10H), 0.91 – 0.87 (m, 6H).

¹⁹F NMR (376 MHz, CDCl₃) δ (*gem*-difluoroalkane): -97.6 (p, *J* = 16.7 Hz), (*E*): -105.3 (qd, *J* = 23.1, 5.7 Hz), (*Z*): -110.1 – -110.4 (m).

(*E*)-(2-Chloro-1-fluorovinyl)benzene (51)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), (chloroethynyl)benzene (0.2 mmol, 27 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **51** with spectral properties identical to the reported in the literature^[3]. Pale yellow oil (5 mg, 16% yield, *E/Z* > 50 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 2H), 7.45 – 7.40 (m, 3H), 6.26 (d, *J* = 13.4 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -110.48 (d, *J* = 13.3 Hz).

(*E*)-(2-Bromo-1-fluorovinyl)benzene (52)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), (bromoethynyl)benzene (0.2 mmol, 36 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **52** with spectral properties identical to the reported in the literature^[4]. Pale yellow oil (16 mg, 41% yield, *E/Z* > 50 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.78 (m, 2H), 7.45 – 7.41 (m, 3H), 6.24 (d, *J* = 15.8 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -96.20 (d, *J* = 15.7 Hz).

(*E*)-(1-Fluoro-2-iodovinyl)benzene (53)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), (iodoethynyl)benzene (0.2 mmol, 46 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **53** with spectral properties identical to the reported in the literature^[5]. Pale yellow oil (36 mg, 73% yield, *E/Z* > 50 : 1).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.77 (m, 2H), 7.46 – 7.39 (m, 3H), 6.14 (d, *J* = 19.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 158.9 (d, *J*_{C-F} = 256.1 Hz), 131.1 (d, *J*_{C-F} = 28.6 Hz), 130.2 (d, *J*_{C-F} = 1.2 Hz), 128.6 (d, *J*_{C-F} = 5.2 Hz), 128.2, 53.8 (d, *J*_{C-F} = 44.7 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -75.9 (d, *J* = 19.5 Hz).

(*E*)-(3-Fluoro-4-iodobut-3-en-1-yl)benzene (54)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), (4-iodobut-3-yn-1-yl)benzene (0.2 mmol, 51 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **54** with spectral properties identical to the reported in the literature^[5]. Pale yellow oil (18 mg, 32% yield, *E/Z* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 5.71 (d, *J* = 17.6 Hz, 1H), 2.89 – 2.76 (m, 4H).

¹⁹F NMR (471 MHz, CDCl₃) δ -82.4 (td, *J* = 21.3, 17.8 Hz).

Ethyl (*E*)-3-fluoro-3-phenylacrylate (55)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), ethyl 3-phenylpropionate (0.2 mmol, 35 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **55** with spectral properties identical to the reported in the literature^[6]. Pale yellow oil (14 mg, 36% yield, *E/Z* > 50 : 1).

¹H NMR (300 MHz, CDCl₃) δ 7.73 – 7.66 (m, 2H), 7.50 – 7.43 (m, 3H), 5.86 (d, *J* = 20.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -76.3 (d, *J* = 20.6 Hz).

(5,5-Difluorohexyl)benzene (56)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), hex-5-yn-1-ylbenzene (0.2 mmol, 32 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **56** with spectral properties identical to the reported in the literature^[7]. Pale yellow oil (20 mg, 51% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.80 (m, 2H), 1.73 – 1.63 (m, 2H), 1.63 – 1.44 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 142.1, 128.35, 128.32, 125.8, 124.3 (t, J_{C-F} = 237.6 Hz), 37.8 (t, J_{C-F} = 25.4 Hz), 35.7, 31.1, 23.2 (t, J_{C-F} = 28.1 Hz), 22.4 (t, J_{C-F} = 4.7 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -90.2 – -90.5 (m, 2F).

2-(5,5-Difluorohexyl)isoindoline-1,3-dione (57)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), 2-(hex-5-yn-1-yl)isoindoline-1,3-dione (0.2 mmol, 45 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **57**. Pale yellow oil (36 mg, 67% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.69 (m, 2H), 3.70 (t, J = 7.2 Hz, 2H), 1.96 – 1.83 (m, 2H), 1.78 – 1.68 (m, 2H), 1.61 – 1.48 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 168.4, 133.9, 132.1, 124.0 (t, J_{C-F} = 237.8 Hz), 123.2, 37.5, 37.4 (t, J_{C-F} = 25.6 Hz), 28.2, 23.2 (t, J_{C-F} = 28.0 Hz), 20.0 (t, J_{C-F} = 4.8 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -90.6 – -90.9 (m, 2F).

HRMS (ESI) calcd for C₁₄H₁₅F₂NO₂ [M+H]⁺: 268.1071, Found: 268.1141.

4,4-Difluoropentyl thiophene-2-carboxylate (58)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), pent-4-yn-1-yl thiophene-2-carboxylate (0.2 mmol, 39 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **58** with spectral properties identical to the reported in the literature^[7]. Pale yellow oil (29 mg, 62% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.81 (dd, J = 3.7, 1.2 Hz, 1H), 7.56 (dd, J = 5.0, 1.1 Hz, 1H), 7.11 (dd, J = 4.9, 3.8 Hz, 1H), 4.34 (t, J = 6.0 Hz, 2H), 2.05 – 1.92 (m, 4H), 1.63 (t, J = 18.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 162.1, 133.7, 133.5, 132.4, 127.8, 123.8 (t, J_{C-F} = 238.0 Hz), 64.3, 34.6 (t, J_{C-F} = 26.1 Hz), 23.4 (t, J_{C-F} = 27.9 Hz), 22.2 (t, J_{C-F} = 4.7 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -91.2 – -91.4 (m, 2F).

1-(1-(4,4-Difluoropentyl)-1H-indol-3-yl)ethan-1-one (59)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl_3 (3.0 mL), 1-(1-(pent-4-yn-1-yl)-1H-indol-3-yl)ethan-1-one (0.2 mmol, 45 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **59** with spectral properties identical to the reported in the literature^[7]. Pale yellow oil (39 mg, 73% yield).

^1H NMR (500 MHz, CDCl_3) δ 8.45 – 8.33 (m, 1H), 7.73 (s, 1H), 7.39 – 7.26 (m, 3H), 4.23 (t, J = 7.1 Hz, 2H), 2.53 (s, 3H), 2.18 – 2.06 (m, 2H), 1.94 – 1.79 (m, 2H), 1.59 (t, J = 18.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 192.9, 136.6, 134.44, 126.4, 123.6 (t, $J_{\text{C-F}}$ = 238.4 Hz), 123.4, 122.7, 122.6, 117.3, 109.6, 46.3, 34.8 (t, $J_{\text{C-F}}$ = 25.9 Hz), 27.6, 23.6 (t, $J_{\text{C-F}}$ = 27.8 Hz), 23.1 (t, $J_{\text{C-F}}$ = 4.1 Hz).

^{19}F NMR (471 MHz, CDCl_3) δ -91.2 – -91.4 (m, 2F).

(4,4-Difluoropentyloxy)carbonyl ferrocene (**60**)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl_3 (3.0 mL), (pent-4-yn-1-yloxy)carbonyl ferrocene (0.2 mmol, 59 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **60**. Pale yellow oil (32 mg, 48% yield).

^1H NMR (500 MHz, CDCl_3) δ 4.81 (s, 2H), 4.40 (s, 2H), 4.26 (t, J = 6.2 Hz, 2H), 4.20 (s, 5H), 2.08 – 1.97 (m, 2H), 1.97 – 1.90 (m, 2H), 1.65 (t, J = 18.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 171.6, 123.9 (t, $J_{\text{C-F}}$ = 237.9 Hz), 71.3, 71.1, 70.1, 69.7, 63.3, 34.7 (t, $J_{\text{C-F}}$ = 26.0 Hz), 23.5 (t, $J_{\text{C-F}}$ = 28.0 Hz), 22.4 (t, $J_{\text{C-F}}$ = 4.7 Hz).

^{19}F NMR (471 MHz, CDCl_3) δ -91.0 – -91.3 (m, 2F).

HRMS (APCI) calcd for $\text{C}_{16}\text{H}_{18}\text{F}_2\text{FeO}_2$ $[\text{M}+\text{H}]^+$: 337.0624, Found: 337.0680.

(1-Fluorovinyl)benzene (**61**)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF_4 (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl_3 (1.0 mL), phenylacetylene (0.2 mmol, 21 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude

residue was purified by flash column chromatography (hexanes) to provide the title compound **61** with spectral properties identical to the reported in the literature^[2]. Pale yellow oil (9 mg, 35% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.60 – 6.52 (m, 2H), 7.40 – 7.31 (m, 3H), 5.03 (dd, *J* = 49.8, 3.5 Hz, 1H), 4.84 (dd, *J* = 17.9, 3.5 Hz, 1H).

¹⁹F NMR (282 MHz, CDCl₃) δ -107.9 (dd, *J* = 49.7, 17.9 Hz).

1-(1-Fluorovinyl)-4-methylbenzene (62)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-ethynyltoluene (0.2 mmol, 23 mg, 1.0 equiv) at 40 °C. The reaction mixture was quenched after 1 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **62** with spectral properties identical to the reported in the literature^[8]. Pale yellow oil (7 mg, 27% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.96 (dd, *J* = 50.0, 3.4 Hz, 1H), 4.77 (dd, *J* = 18.0, 3.4 Hz, 1H), 2.35 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -107.7 (dd, *J* = 50.1, 18.0 Hz).

1-Fluoro-2-(1-fluorovinyl)benzene (63)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 2-fluorophenylacetylene (0.2 mmol, 24 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **63** with spectral properties identical to the reported in the literature^[9]. Pale yellow oil (15 mg, 52% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.57 (td, *J* = 7.8, 1.5 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (dd, *J* = 11.5, 8.3 Hz, 1H), 5.26 (dd, *J* = 52.1, 3.3 Hz, 1H), 5.11 (dt, *J* = 19.9, 3.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 159.8 (dd, *J*_{C-F} = 252.9, 5.9 Hz), 157.3 (dd, *J*_{C-F} = 247.1, 4.6 Hz), 130.6 (d, *J*_{C-F} = 8.7 Hz), 127.2 (dd, *J*_{C-F} = 8.4, 2.0 Hz), 124.1 (dd, *J*_{C-F} = 3.7, 1.1 Hz), 120.1 (dd, *J*_{C-F} = 31.2, 11.0 Hz), 116.1 (dd, *J*_{C-F} = 22.5, 2.8 Hz), 95.6 (dd, *J*_{C-F} = 21.0, 13.0 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -103.6 (ddd, *J* = 52.3, 19.9, 6.7 Hz, 1F), -112.0 – -112.1 (m, 1F).

1-Chloro-2-(1-fluorovinyl)benzene (64)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 2-chlorophenylacetylene (0.2 mmol, 27 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **64** with spectral properties identical to the reported in the literature^[10]. Pale yellow oil (18 mg, 58% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.52 (dd, *J* = 7.1, 2.4 Hz, 1H), 7.43 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.34 – 7.27 (m, 2H), 5.14 (q, 3.3 Hz, 1H), 5.07 (dd, *J* = 37.6, 3.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 160.5 (d, *J* = 252.0 Hz), 132.2 (d, *J* = 2.1 Hz), 131.4 (d, *J* = 28.3 Hz), 130.5, 130.4 (d, *J* = 0.7 Hz), 129.8 (d, *J* = 5.6 Hz), 126.7, 95.9 (d, *J* = 21.8 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -93.6 (dd, *J* = 49.1, 17.9 Hz).

1-Bromo-2-(1-fluorovinyl)benzene (65)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-bromo-2-ethynylbenzene (0.2 mmol, 36 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **65** with spectral properties identical to the reported in the literature^[11]. Pale yellow oil (22 mg, 54% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.33 (tt, *J* = 7.7, 1.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 5.09 (dd, *J* = 16.4, 3.3 Hz, 1H), 4.97 (dd, *J* = 48.4, 3.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 161.8 (d, *J*_{C-F} = 253.6 Hz), 133.7 (d, *J*_{C-F} = 29 Hz, partially superimposed with resonance at 133.6), 133.6, 130.7 (d, *J*_{C-F} = 1.1 Hz), 130.5 (d, *J*_{C-F} = 4.4 Hz), 127.2, 121.5, 95.6 (d, *J*_{C-F} = 21.6 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -91.48 (dd, *J* = 48.4, 16.4 Hz).

¹³C NMR (126 MHz, CDCl₃) δ 133.74.

1-Fluoro-4-(1-fluorovinyl)benzene (66)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-fluorophenylacetylene (0.2 mmol, 24 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **66** with spectral properties identical to the reported in the literature^[8]. Pale yellow oil (12 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.06 (t, *J* = 8.8 Hz, 2H), 4.96 (dd, *J* = 49.7, 3.6 Hz, 1H), 4.83 (dd, *J* = 17.9, 3.6 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -107.0 (dd, *J* = 49.7, 17.9 Hz, 1F), -111.5 – -111.6 (m, 1F).

1-Chloro-4-(1-fluorovinyl)benzene (67)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-chlorophenylacetylene (0.2 mmol, 28 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **67** with spectral properties identical to the reported in the literature^[8]. Pale yellow oil (17 mg, 55% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.02 (dd, *J* = 49.4, 3.7 Hz, 1H), 4.87 (dd, *J* = 17.7, 3.6 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 162.0 (d, *J*_{C-F} = 249.9 Hz), 135.3, 130.5 (d, *J*_{C-F} = 29.9 Hz), 128.7 (d, *J*_{C-F} = 2.0 Hz), 125.9 (d, *J*_{C-F} = 6.9 Hz), 90.1 (d, *J*_{C-F} = 22.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -107.9 (dd, *J* = 49.4, 17.7 Hz).

1-Bromo-4-(1-fluorovinyl)benzene (68)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 4-bromophenylacetylene (0.2 mmol, 36 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **68** with spectral properties identical to the reported in the literature^[12]. Pale yellow oil (24 mg, 59% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.51 (t, *J* = 5.7 Hz, 2H), 7.44 – 7.39 (m, 2H), 5.04 (dd, *J* = 49.4, 3.7 Hz, 1H), 4.88 (dd, *J* = 17.7, 3.7 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 162.0 (d, *J*_{C-F} = 250.2 Hz), 131.7 (d, *J*_{C-F} = 1.9 Hz), 130.9 (d, *J*_{C-F} = 29.8 Hz), 126.2 (d, *J*_{C-F} = 6.9 Hz), 123.6, 90.2 (d, *J*_{C-F} = 22.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -108.0 (dd, *J* = 49.4, 17.7 Hz).

1-(1-Fluorovinyl)-4-(trifluoromethyl)benzene (69)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), 1-ethynyl-4-(trifluoromethyl)benzene (0.2 mmol, 34 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched

after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **69** with spectral properties identical to the reported in the literature^[13]. Pale yellow oil (14 mg, 38% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.60 (m, 4H), 5.15 (dd, J = 49.1, 3.8 Hz, 1H), 4.98 (dd, J = 17.5, 3.8 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 3F), -108.4 (dd, J = 49.1, 17.6 Hz, 1F).

Methyl 4-(1-fluorovinyl)benzoate (70)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), methyl 4-ethynylbenzoate (0.2 mmol, 32 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **70** with spectral properties identical to the reported in the literature^[14]. Pale yellow oil (12 mg, 34% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 5.16 (dd, J = 49.1, 3.7 Hz, 1H), 4.97 (dd, J = 17.6, 3.7 Hz, 1H), 3.93 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -108.3 (dd, J = 49.1, 17.6 Hz).

(Z)-(1-Fluoroethene-1,2-diyl)dibenzene (71)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1,2-diphenylethyne (0.2 mmol, 36 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **71** with spectral properties identical to the reported in the literature^[2]. Pale yellow oil (23 mg, 59% yield, $Z/E > 50 : 1$).

¹H NMR (500 MHz, CDCl₃) δ 7.73 – 7.58 (m, 4H), 7.50 – 7.32 (m, 5H), 7.28 (t, J = 7.4 Hz, 1H), 6.33 (d, J = 39.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 157.2 (d, J_{C-F} = 258.6 Hz), 133.7 (d, J_{C-F} = 3.0 Hz), 132.9 (d, J_{C-F} = 27.9 Hz), 129.0 (d, J_{C-F} = 2.3 Hz), 128.9, 128.6, 128.6, 127.3 (d, J_{C-F} = 2.5 Hz), 124.3 (d, J_{C-F} = 7.4 Hz), 105.8 (d, J_{C-F} = 10.5 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -114.2 (d, J = 39.6 Hz).

(Z)-4,4'-(1-Fluoroethene-1,2-diyl)bis(chlorobenzene) (72)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1,2-bis(4-chlorophenyl)ethyne (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **72** with spectral properties identical to the reported in the literature^[2]. Pale yellow oil (34 mg, 64% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.55 (dd, *J* = 8.6, 2.7 Hz, 4H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.24 (d, *J* = 38.9 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 156.6 (d, *J*_{C-F} = 258.8 Hz), 135.2, 133.2 (d, *J*_{C-F} = 3.6 Hz), 131.8 (d, *J*_{C-F} = 3.1 Hz), 131.0 (d, *J*_{C-F} = 28.4 Hz), 130.1 (d, *J*_{C-F} = 8.3 Hz), 128.9 (d, *J*_{C-F} = 2.0 Hz), 128.8, 125.6 (d, *J*_{C-F} = 7.4 Hz), 105.2 (d, *J*_{C-F} = 10.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -113.7 (d, *J* = 38.9 Hz).

(Z)-4,4'-(1-Fluoroethene-1,2-diyl)bis(bromobenzene) (73)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1,2-bis(4-bromophenyl)ethyne (0.2 mmol, 67 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **73**. Pale yellow oil (48 mg, 68% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.59 – 7.52 (m, 2H), 7.51 – 7.41 (m, 6H), 6.24 (d, *J* = 38.8 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 156.7 (d, *J*_{C-F} = 259.0 Hz), 132.2 (d, *J*_{C-F} = 3.0 Hz), 131.9 (d, *J*_{C-F} = 2.0 Hz), 131.8, 131.4 (d, *J*_{C-F} = 28.4 Hz), 130.4 (d, *J*_{C-F} = 8.3 Hz), 125.8 (d, *J*_{C-F} = 7.4 Hz), 123.42, 121.4 (d, *J*_{C-F} = 3.7 Hz), 105.4 (d, *J*_{C-F} = 10.3 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -113.5 (d, *J* = 38.8 Hz).

HRMS (ESI) calcd for C₁₄H₉Br₂F [M]⁺: 353.9055, Found: 353.9046.

(Z)-4,4'-(1-Fluoroethene-1,2-diyl)bis(methylbenzene) (74)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry CHCl₃ (2.0 mL), 1,2-di-p-tolyne (0.2 mmol, 41 mg, 1.0 equiv) at 90 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **74** with spectral properties identical to the reported in the literature^[15]. Pale yellow oil (21 mg, 47% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 8.1 Hz, 4H), 7.20 (dd, *J* = 14.3, 8.0 Hz, 4H), 6.24 (d, *J* = 39.9 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.9 (d, J_{C-F} = 257.1 Hz), 138.9, 137.0 (d, J_{C-F} = 2.5 Hz), 131.0 (d, J_{C-F} = 2.9 Hz), 130.3 (d, J_{C-F} = 28.1 Hz), 129.3, 128.7 (d, J_{C-F} = 7.9 Hz), 124.1 (d, J_{C-F} = 7.4 Hz), 104.9 (d, J_{C-F} = 10.8 Hz), 21.28, 21.26.

¹⁹F NMR (471 MHz, CDCl₃) δ -114.9 (d, J = 39.9 Hz).

(Z)-1-(2-Fluoro-2-phenylvinyl)-4-(trifluoromethyl)benzene (75)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-(phenylethynyl)-4-(trifluoromethyl)benzene (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **75** with spectral properties identical to the reported in the literature^[1]. Pale yellow oil (29 mg, 55% yield, r.r. > 50 : 1, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 6.9 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.48 – 7.37 (m, 3H), 6.35 (d, J = 38.7 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 158.7 (d, J_{C-F} = 261.6 Hz), 137.2, 132.2 (d, J_{C-F} = 27.6 Hz), 131.8 (d, J_{C-F} = 6.9 Hz), 129.6, 129.0 (d, J_{C-F} = 8.3 Hz), 128.7 (d, J_{C-F} = 2.0 Hz), 125.4 (q, J_{C-F} = 3.7 Hz), 124.6 (d, J_{C-F} = 7.6 Hz), 124.2 (q, J_{C-F} = 271.7 Hz), 104.6 (d, J_{C-F} = 10.2 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -62.6 (s, 3F), -111.0 (d, J = 38.6 Hz, 1F).

Methyl (Z)-4-(2-fluoro-2-phenylvinyl)benzoate (76)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), methyl 4-(phenylethynyl)benzoate (0.2 mmol, 47 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **76** with spectral properties identical to the reported in the literature^[16]. Pale yellow oil (22 mg, 43% yield, r.r. = 17 : 1, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 2H), 7.73 – 7.63 (m, 4H), 7.46 – 7.36 (m, 3H), 6.35 (d, J = 38.9 Hz, 1H), 3.93 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 166.8, 158.7 (d, J_{C-F} = 262.1 Hz), 138.2 (d, J_{C-F} = 3.1 Hz), 132.3 (d, J_{C-F} = 27.6 Hz), 129.8, 129.6, 128.7, 128.7, 128.7, 124.5 (d, J_{C-F} = 7.6 Hz), 105.1 (d, J_{C-F} = 10.1 Hz), 52.0.

¹⁹F NMR (471 MHz, CDCl₃) δ (a): -110.5 (d, J = 38.9 Hz), (b): -115.1 (d, J = 39.2 Hz).

(Z)-1-(4-(2-Fluoro-2-phenylvinyl)phenyl)ethan-1-one (77)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-(4-(phenylethynyl)phenyl)ethan-1-one (0.2 mmol, 44 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **77** with spectral properties identical to the reported in the literature^[2]. Pale yellow oil (15 mg, 32% yield, r.r. = 15 : 1, Z/E = 17 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 6.9 Hz, 2H), 7.46 – 7.39 (m, 3H), 6.37 (d, *J* = 38.9 Hz, 1H), 2.62 (s, 3H).

¹⁹F NMR (471 MHz, CDCl₃) δ (a-*E*): -91.0 (d, *J* = 20.7 Hz), (a-*Z*): -110.2 (d, *J* = 38.9 Hz), (b): -115.2 (d, *J* = 39.1 Hz).

(*Z*)-4-(2-Fluoro-2-phenylvinyl)benzonitrile (**78**)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 4-(phenylethynyl)benzonitrile (0.2 mmol, 41 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **78** with spectral properties identical to the reported in the literature^[1]. Pale yellow oil (24 mg, 54% yield, r.r. > 50 : 1, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.60 (m, 4H), 7.51 – 7.37 (m, 3H), 6.33 (d, *J* = 38.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 159.5 (d, *J*_{C-F} = 263.6 Hz), 138.3 (d, *J*_{C-F} = 3.1 Hz), 132.3, 131.9 (d, *J*_{C-F} = 27.4 Hz), 130.0, 129.2 (d, *J*_{C-F} = 8.6 Hz), 128.8 (d, *J*_{C-F} = 2.1 Hz), 124.7 (d, *J*_{C-F} = 7.7 Hz), 119.0, 110.3 (d, *J*_{C-F} = 3.1 Hz), 104.4 (d, *J*_{C-F} = 9.9 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -108.9 (d, *J* = 38.4 Hz).

(*Z*)-1-(2-Fluoro-2-phenylvinyl)-4-nitrobenzene (**79**)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4

mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-nitro-4-(phenylethynyl)benzene (0.2 mmol, 45 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **79** with spectral properties identical to the reported in the literature^[2]. Pale yellow oil (19 mg, 38% yield, r.r. > 50 : 1, Z/E > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.51 – 7.38 (m, 3H), 6.39 (d, *J* = 38.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 159.9 (d, *J*_{C-F} = 264.7 Hz), 146.3, 140.4 (d, *J*_{C-F} = 3.1 Hz), 131.8 (d, *J*_{C-F} = 27.3 Hz), 130.2, 129.3 (d, *J*_{C-F} = 8.8 Hz), 128.8 (d, *J*_{C-F} = 2.0 Hz), 124.8 (d, *J*_{C-F} = 7.7 Hz), 123.9, 104.1 (d, *J*_{C-F} = 9.9 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -108.2 (d, *J* = 38.2 Hz).

(Z)-1-Chloro-2-(2-fluoro-2-phenylvinyl)benzene (80)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-chloro-2-(phenylethynyl)benzene (0.2 mmol, 42 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **80** with spectral properties identical to the reported in the literature^[1]. Pale yellow oil (24 mg, 51% yield, r.r. > 20 : 1, Z/E > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.50 – 7.34 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.20 (td, *J* = 7.8, 1.5 Hz, 1H), 6.76 (d, *J* = 38.6 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 158.2 (d, *J*_{C-F} = 260.9 Hz), 133.2 (d, *J*_{C-F} = 0.6 Hz), 132.6 (d, *J*_{C-F} = 27.9 Hz), 131.5 (d, *J*_{C-F} = 3.4 Hz), 130.5 (d, *J*_{C-F} = 13.4 Hz), 129.5, 129.4, 128.6 (d, *J*_{C-F} = 2.1 Hz), 128.3 (d, *J*_{C-F} = 1.6 Hz), 126.8, 124.6 (d, *J*_{C-F} = 7.4 Hz), 101.7 (d, *J*_{C-F} = 8.9 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -113.8 (d, *J* = 38.6 Hz).

(E)-(1-Fluoroethene-1,2-diyl)dibenzene (81)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), 1,2-diphenylethyne (0.2 mmol, 36 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **81** with spectral properties identical to the reported in the literature^[15]. Pale yellow oil (24 mg, 60% yield, E/Z = 10 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.24 – 7.13 (m, 5H), 6.46 (d, *J* = 21.6 Hz, 1H).

¹⁹F NMR (471 MHz, CDCl₃) δ -96.0 (d, *J* = 21.6 Hz).

(E)-4,4'-(1-Fluoroethene-1,2-diyl)bis(chlorobenzene) (82)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl_3 (3.0 mL), 1,2-bis(4-chlorophenyl)ethyne (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **82** with spectral properties identical to the reported in the literature^[17]. Pale yellow oil (22 mg, 41% yield, *E/Z* = 10 : 1).

¹H NMR (500 MHz, CDCl_3) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.41 (d, *J* = 20.8 Hz, 1H).

¹⁹F NMR (471 MHz, CDCl_3) δ -95.9 (d, *J* = 20.8 Hz).

(E)-1-Chloro-2-(2-fluoro-2-phenylvinyl)benzene (83)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl_3 (3.0 mL), 1-chloro-2-(phenylethynyl)benzene (0.2 mmol, 42 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **83** with spectral properties identical to the reported in the literature^[1]. Pale yellow oil (19 mg, 40% yield, r.r. = 9 : 1, *E/Z* = 4 : 1).

¹H NMR (500 MHz, CDCl_3) δ 7.98 (dd, *J* = 7.9, 1.6 Hz, 0.2H), 7.73 – 7.66 (m, 0.8H), 7.48 – 7.23 (m, 6H), 7.23 – 7.12 (m, 1H), 7.11 – 7.01 (m, 1H), 6.75 (d, *J* = 38.6 Hz, 0.2H), 6.54 (d, *J* = 20.5 Hz, 0.8H).

¹⁹F NMR (471 MHz, CDCl_3) δ (*E*): -96.4 (d, *J* = 20.5 Hz, 0.8F), (*Z*): -113.9 (d, *J* = 38.5 Hz, 0.2F).

(E)-1-(2-Fluoro-2-phenylvinyl)-4-(trifluoromethyl)benzene (84)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl_3 (3.0 mL), 1-(phenylethynyl)-4-(trifluoromethyl)benzene (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **84** with spectral properties identical to the reported in the literature^[1]. Pale yellow oil (12 mg, 23% yield, r.r. > 20 : 1, *E/Z* > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.46 (d, *J* = 20.6 Hz, 1H).

¹⁹F NMR (471 MHz, CDCl₃) δ -62.6 (s, 3F), -91.6 (d, *J* = 20.7 Hz, 1F).

(1S,2R,4R)-2-((Z)-2-Fluoro-2-phenylvinyl)bicyclo[2.2.1]heptane (85)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF₄ (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl₃ (1.0 mL), (1S,2R,4R)-2-(phenylethynyl)bicyclo[2.2.1]heptane (0.2 mmol, 39 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **85**. Pale yellow oil (33 mg, 77% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.45 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 5.29 (dd, *J* = 37.6, 9.4 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.33 – 2.26 (m, 1H), 2.15 – 2.08 (m, 1H), 1.73 – 1.64 (m, 1H), 1.60 – 1.48 (m, 2H), 1.46 – 1.41 (m, 1H), 1.37 – 1.26 (m, 2H), 1.25 – 1.18 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.7 (d, *J*_{C-F} = 245.3 Hz), 132.9 (d, *J*_{C-F} = 29.2 Hz), 128.3 (d, *J*_{C-F} = 2.0 Hz), 128.2, 123.8 (d, *J*_{C-F} = 7.0 Hz), 112.7 (d, *J*_{C-F} = 16.9 Hz), 42.9 (d, *J*_{C-F} = 1.0 Hz), 39.2 (d, *J*_{C-F} = 1.3 Hz), 37.2 (d, *J*_{C-F} = 3.7 Hz), 36.5, 36.1, 29.6, 28.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.2 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for C₁₅H₁₇F [M]⁺: 216.1314, Found: 216.1326.

((Z)-5-Fluoro-5-phenylpent-4-en-1-yloxy)carbonyl ferrocene (86)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), BF₄•Et₂O (0.2 mmol, 28 mg, 1.0 equiv), dry CHCl₃ (2.0 mL), (5-phenylpent-4-yn-1-yloxy)carbonyl ferrocene (0.2 mmol, 74 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **86**. Pale yellow oil (48 mg, 61% yield, *Z/E* = 9 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.55 – 7.47 (m, 2H), 7.43 – 7.29 (m, 3H), 5.46 (dt, *J* = 36.9, 7.6 Hz, 1H), 4.83 (t, *J* = 1.9 Hz, 2H), 4.43 – 4.35 (m, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 4.21 (s, 4H), 4.15 (s, 1H), 2.52 – 2.33 (m, 2H), 1.98 – 1.83 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 171.7, 157.4 (d, *J*_{C-F} = 247.0 Hz), 132.5 (d, *J*_{C-F} = 29.1 Hz), 128.5, 128.4 (d, *J*_{C-F} = 1.9 Hz), 123.9 (d, *J*_{C-F} = 6.9 Hz), 104.7 (d, *J*_{C-F} = 17.6 Hz), 71.2, 70.1, 69.7, 63.5, 28.7 (d, *J*_{C-F} = 1.5 Hz), 20.8 (d, *J*_{C-F} = 5.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ (*E*): -100.5 (d, *J* = 22.1 Hz), (*Z*): -119.8 (d, *J* = 36.9 Hz).

HRMS (APCI) calcd for C₂₂H₂₁FFeO₂ [M]⁺: 392.0875 Found: 392.0891.

**(Z)-5-Fluoro-5-phenylpent-4-en-1-yl
yl)methanesulfonate (87)**

((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), $\text{BF}_4 \cdot \text{Et}_2\text{O}$ (0.2 mmol, 28 mg, 1.0 equiv), dry CHCl_3 (2.0 mL), 5-phenylpent-4-yn-1-yl ((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (0.2 mmol, 75 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **87**. Pale yellow oil (50 mg, 64% yield, *Z/E* = 9 : 1).

^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.40 (dt, *J* = 36.8, 7.6 Hz, 1H), 4.41 – 4.26 (m, 2H), 3.61 (d, *J* = 15.1 Hz, 1H), 2.99 (d, *J* = 15.1 Hz, 1H), 2.52 – 2.35 (m, 4H), 2.11 (t, *J* = 4.3 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.96 – 1.89 (m, 3H), 1.71 – 1.62 (m, 1H), 1.47 – 1.38 (m, 1H), 1.10 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 214.4, 157.6 (d, $J_{\text{C-F}}$ = 247.6 Hz), 132.2 (d, $J_{\text{C-F}}$ = 29.0 Hz), 128.6, 128.4 (d, $J_{\text{C-F}}$ = 1.9 Hz), 123.9 (d, $J_{\text{C-F}}$ = 6.9 Hz), 103.9 (d, $J_{\text{C-F}}$ = 17.5 Hz), 69.8, 57.8, 47.9, 46.6, 42.7, 42.4, 28.9 (d, $J_{\text{C-F}}$ = 1.6 Hz), 26.8, 24.8, 20.2 (d, $J_{\text{C-F}}$ = 5.5 Hz), 19.7, 19.6.

^{19}F NMR (282 MHz, CDCl_3) δ (*E*): -99.9 (d, *J* = 21.7 Hz), (*Z*): -119.2 (d, *J* = 36.8 Hz).

HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{27}\text{FO}_4\text{S}$ [$\text{M}+\text{H}$] $^+$: 395.1614 Found: 395.1673

(8R,9S,13S,14S)-3-((Z)-2-Cyclohexyl-1-fluorovinyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (88)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), LiBF_4 (0.25 mmol, 4.7 mg, 0.25 equiv), dry CHCl_3 (1.0 mL), (8R,9S,13S,14S)-3-(cyclohexylethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (0.2 mmol, 72 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **88**. Pale yellow oil (55 mg, 72% yield, *Z/E* > 50 : 1).

^1H NMR (500 MHz, CDCl_3) δ 7.26 (m, 2H), 7.22 (s, 1H), 5.21 (dd, *J* = 38.4, 9.2 Hz, 1H), 2.98 – 2.85 (m, 2H), 2.62 (m, 1H), 2.51 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.30 (td, *J* = 10.8, 4.2 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.10 – 2.00 (m, 2H), 1.99 – 1.93 (m, 1H), 1.81 – 1.69 (m, 4H), 1.68 – 1.57 (m, 3H), 1.55 – 1.42 (m, 4H), 1.40 – 1.30 (m, 2H), 1.23 – 1.11 (m, 3H), 0.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 220.7, 155.4 (d, J_{C-F} = 245.2 Hz), 140.0, 136.5, 130.5 (d, J_{C-F} = 29.5 Hz), 125.4 (d, J_{C-F} = 1.8 Hz), 124.3 (d, J_{C-F} = 6.6 Hz), 121.4 (d, J_{C-F} = 6.8 Hz), 111.4 (d, J_{C-F} = 17.1 Hz), 50.5, 47.9, 44.4, 38.1, 35.8, 33.8 (d, J_{C-F} = 3.8 Hz), 33.2, 31.6, 29.4, 26.4, 26.0, 25.8, 25.7, 21.6, 13.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -121.8 (d, J = 38.3 Hz).

HRMS (ASAP) calcd for C₂₆H₃₃FO [M+H]⁺: 381.2515, Found: 381.2577.

(8R,9S,13S,14S)-3-((E)-2-Cyclohexyl-1-fluorovinyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (89)

Prepared following the general procedure (**condition B**): (8R,9S,13S,14S)-3-(cyclohexylethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (0.2 mmol, 72 mg, 1.0 equiv), dry CHCl₃ (1.0 mL), HBF₄·Et₂O (27 ul, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **89**. Pale yellow oil (37 mg, 49% yield, *E/Z* = 13:1).

¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.19 (s, 1H), 5.21 (dd, J = 23.0, 10.7 Hz, 1H), 2.94 (dd, J = 8.7, 3.9 Hz, 2H), 2.52 (dd, J = 19.0, 8.7 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.37 – 2.24 (m, 2H), 2.18 – 2.11 (m, 1H), 2.09 – 2.02 (m, 2H), 2.01 – 1.96 (m, 1H), 1.78 – 1.69 (m, 4H), 1.67 – 1.61 (m, 3H), 1.57 – 1.46 (m, 4H), 1.27 – 1.16 (m, 5H), 0.92 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 220.6, 155.8 (d, J_{C-F} = 239.9 Hz), 140.6, 136.4, 123.0 (d, J_{C-F} = 30.3 Hz), 127.9 (d, J_{C-F} = 4.7 Hz), 125.2, 124.9 (d, J_{C-F} = 5.2 Hz), 114.0 (d, J_{C-F} = 22.2 Hz), 50.5, 47.9, 44.5, 38.0, 35.8, 35.2 (d, J_{C-F} = 7.6 Hz), 33.8 (d, J_{C-F} = 0.8 Hz), 31.6, 29.4, 26.4, 25.9, 25.7, 25.6, 21.6, 13.8.

¹⁹F NMR (471 MHz, CDCl₃) δ (E): -103.5 (d, J = 23.0 Hz), (Z): -121.7 (d, J = 38.3 Hz).

HRMS (ESI) calcd for C₂₆H₃₃FO [M+H]⁺: 381.2515 Found: 381.2577

(Z)-5-Fluoro-5-phenylpent-4-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (90)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry CHCl₃ (2.0 mL), 5-phenylpent-4-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (0.2 mmol, 85 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **90**. Pale yellow oil (63 mg, 70% yield, *Z/E* = 33 : 1).

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.44 (m, 2H), 7.39 – 7.29 (m, 3H), 5.44 (dt, *J* = 36.8, 7.7 Hz, 1H), 4.42 (t, *J* = 6.4 Hz, 2H), 3.14 – 3.05 (m, 4H), 2.47 (qd, *J* = 7.5, 1.5 Hz, 2H), 2.03 – 1.92 (m, 2H), 1.58 – 1.52 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 165.3, 157.5 (d, *J*_{C-F} = 247.3 Hz), 144.2, 133.6, 132.4 (d, *J*_{C-F} = 29.0 Hz), 130.2, 128.6, 128.4 (d, *J*_{C-F} = 2.0 Hz), 127.0, 123.9 (d, *J*_{C-F} = 7.0 Hz), 104.5 (d, *J*_{C-F} = 17.6 Hz), 65.0, 49.9, 28.4 (d, *J*_{C-F} = 1.4 Hz), 21.9, 20.9 (d, *J*_{C-F} = 5.5 Hz), 11.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -119.8 (d, *J* = 36.9 Hz).

HRMS (ESI) calcd for C₂₄H₃₀FNO₄S [M+H]⁺: 448.1880 Found: 448.1934.

4,4-Difluoropentyl 4-(N,N-dipropylsulfamoyl)benzoate (91)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), pent-4-yn-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (0.2 mmol, 70 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **91** with spectral properties identical to the reported in the literature^[7]. Pale yellow oil (44 mg, 56% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 4.40 (t, *J* = 6.0 Hz, 2H), 3.15 – 3.05 (m, 4H), 2.09 – 1.92 (m, 4H), 1.64 (t, *J* = 18.4 Hz, 3H), 1.58 – 1.51 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 165.1, 144.4, 133.4, 130.2, 127.0, 123.7 (t, *J*_{C-F} = 238.1 Hz), 64.8, 49.9, 34.6 (t, *J*_{C-F} = 26.1 Hz), 23.5 (t, *J*_{C-F} = 27.9 Hz), 22.2 (t, *J*_{C-F} = 4.7 Hz), 21.9, 11.1.

¹⁹F NMR (471 MHz, CDCl₃) δ -91.2 – -91.6 (m, 2F).

(Z)-5-Fluoro-5-phenylpent-4-en-1-yl carboxylate (92)

2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry CHCl₃ (2.0 mL), 5-phenylpent-4-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (0.2 mmol, 92 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **92**. Pale yellow oil (50 mg, 52% yield, *Z/E* > 20

: 1).

¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 2.2 Hz, 1H), 8.06 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 2H), 7.40 – 7.27 (m, 3H), 7.00 (d, *J* = 8.9 Hz, 1H), 5.44 (dt, *J* = 36.8, 7.7 Hz, 1H), 4.37 (t, *J* = 6.3 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 3H), 2.46 (dd, *J* = 13.4, 7.1 Hz, 2H), 2.28 – 2.14 (m, 1H), 2.01 – 1.86 (m, 2H), 1.09 (d, *J* = 6.7 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 167.2, 162.5, 162.0, 161.2, 157.4 (d, *J*_{C-F} = 247.2 Hz), 132.5, 132.4 (d, *J*_{C-F} = 28.7 Hz), 132.1, 128.6, 128.4 (d, *J*_{C-F} = 1.9 Hz), 126.0, 123.9 (d, *J*_{C-F} = 7.0 Hz), 121.8, 115.4, 112.6, 104.5 (d, *J*_{C-F} = 17.6 Hz), 103.0, 75.7, 64.8, 28.4, 28.2, 21.0 (d, *J*_{C-F} = 5.5 Hz), 19.0, 17.5.

¹⁹F NMR (471 MHz, CDCl₃) δ -119.8 (d, *J* = 36.9 Hz).

HRMS (ESI) calcd for C₂₇H₂₇FN₂O₃S [M+H]⁺: 479.1726 Found: 479.1783.

4,4-Difluoropentyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (93)

Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry CHCl₃ (3.0 mL), pent-4-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (0.2 mmol, 76 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 5 : 1) to provide the title compound **93** with spectral properties identical to the reported in the literature^[7]. Pale yellow oil (36 mg, 43% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 2.3 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.34 (t, *J* = 6.0 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 3H), 2.26 – 2.14 (m, 1H), 2.06 – 1.90 (m, 4H), 1.65 (t, *J* = 18.4 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 167.4, 162.5, 161.9, 161.4, 132.6, 132.1, 126.0, 123.7 (t, *J*_{C-F} = 238.1 Hz), 121.5, 115.4, 112.6, 103.0, 75.7, 64.5, 34.6 (t, *J*_{C-F} = 26.0 Hz), 28.2, 23.5 (t, *J*_{C-F} = 27.9 Hz), 22.2 (t, *J*_{C-F} = 4.6 Hz), 19.0, 17.5.

¹⁹F NMR (471 MHz, CDCl₃) δ -91.3 – -91.6 (m, 2F).

(Z)-5-Fluoro-5-phenylpent-4-en-1-yl

4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-

bibenzo[d]imidazol-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxylate (94)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), BF₄•Et₂O (0.2 mmol, 28 mg, 1.0 equiv), dry CHCl₃ (2.0 mL), 5-phenylpent-

4-yn-1-yl4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxylate (0.2 mmol, 131 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (EtOAc) to provide the title compound **94**. Pale yellow oil (43 mg, 32% yield, *Z/E* > 20 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.83 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.80 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.38 (td, *J* = 7.6, 1.0 Hz, 1H), 7.35 – 7.25 (m, 9H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.41 (s, 2H), 5.22 (dt, *J* = 37.2, 7.6 Hz, 1H), 4.06 (t, *J* = 6.3 Hz, 2H), 3.76 (s, 3H), 2.94 – 2.89 (m, 2H), 2.76 (s, 3H), 2.10 – 2.03 (m, 2H), 1.90 – 1.82 (m, 2H), 1.60 – 1.49 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.3, 157.1 (d, *J*_{C-F} = 246.9 Hz), 156.4, 154.7, 143.2, 142.9, 141.7, 141.3, 136.6, 135.0, 134.8, 132.3 (d, *J*_{C-F} = 29.0 Hz), 131.3, 130.8, 130.7, 129.9, 129.4, 129.0, 128.6, 128.4 (d, *J*_{C-F} = 1.9 Hz), 127.4, 125.9, 123.9, 123.8, 123.8, 122.4, 122.2, 119.6, 109.5, 108.9, 104.6 (d, *J*_{C-F} = 17.5 Hz), 64.4, 47.0, 31.7, 29.8, 28.0, 21.8, 20.6 (d, *J*_{C-F} = 5.3 Hz), 16.8, 14.0.

¹⁹F NMR (471 MHz, CDCl₃) δ -119.8 (d, *J* = 37.2 Hz).

HRMS (ESI) calcd for C₄₄H₄₁FN₄O₂ [M+H]⁺: 677.3214 Found: 677.3260

(Z)-(1-Fluoroprop-1-en-1-yl)benzene (95)

Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (5.0 mmol, 1.18 g, 1.0 equiv), LiBF₄ (1.25 mmol, 117 mg, 0.25 equiv), dry CHCl₃ (25 mL), 1-phenyl-1-propyne (5.0 mmol, 580 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **95** with spectral properties identical to the reported in the literature^[18]. Pale yellow oil (394 mg, 58% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 5.44 (dq, *J* = 37.2, 7.1 Hz, 1H), 1.82 (dd, *J* = 7.1, 2.5 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.3 (d, *J*_{C-F} = 245.5 Hz), 132.9 (d, *J*_{C-F} = 29.1 Hz), 128.4 (d, *J*_{C-F} = 2.0 Hz), 128.2, 123.7 (d, *J*_{C-F} = 6.9 Hz), 100.6 (d, *J*_{C-F} = 18.2 Hz), 9.4 (d, *J*_{C-F} = 6.7 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -121.6 (d, *J* = 37.2 Hz).

(Z)-(3-Bromo-1-fluoroprop-1-en-1-yl)benzene (96)

A solution of (Z)-(1-fluoroprop-1-en-1-yl)benzene **95** (300 mg, 2.2 mmol, 1.0 equiv), NBS (432 mg, 2.4 mmol, 1.1 equiv) and AIBN (36 mg, 0.22 mmol, 0.1 equiv) in dry CCl₄ (10 mL) was refluxed for 12 h under a nitrogen atmosphere. After completion of the reaction monitored by TLC, the reaction mixture was then cooled to room temperature. The floated succinimide was filtered off and the filtrate was washed with H₂O and brine and dried with Na₂SO₄. The solution was filtered and concentrated. The residue was purified by column chromatography on

silica gel (hexanes) to provide product **96** with spectral properties identical to the reported in the literature^[19]. Pale yellow oil (433 mg, 92% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.60 – 7.50 (m, 2H), 7.46 – 7.34 (m, 3H), 5.79 (dt, *J* = 33.0, 8.6 Hz, 1H), 4.27 (dd, *J* = 8.6, 1.7 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 159.9 (d, *J*_{C-F} = 256.0 Hz), 131.3 (d, *J*_{C-F} = 27.8 Hz), 130.0, 128.5, 124.8 (d, *J*_{C-F} = 7.2 Hz), 102.7 (d, *J*_{C-F} = 15.4 Hz), 24.5 (d, *J*_{C-F} = 9.1 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -115.0 (d, *J* = 33.0 Hz)

(Z)-1-Benzhydryl-4-(3-fluoro-3-phenylallyl)piperazine (97)

A solution of the (Z)-(3-bromo-1-fluoroprop-1-en-1-yl)benzene **96** (43 mg, 0.2 mmol, 1 equiv) in THF (0.5 M) was added dropwise to a solution of 1-(diphenylmethyl)piperazine (101 mg, 0.4 mmol, 2.0 equiv) in THF (2.5 M) at room temperature. 1 M aq NaOH (0.4 ml, 0.4 mmol, 2 equiv) was then added in one portion, and the reaction was stirred at room temperature for 6 h. The reaction was diluted with Et₂O (10 ml). The organic layer was separated and the aqueous layer was extracted with Et₂O (2×10 ml). The combined organics were washed with brine, dried (MgSO₄) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 5 : 1) to afford the product **97**. Pale yellow oil (68 mg, 88% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.47 – 7.40 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 4H), 7.31 – 7.22 (m, 3H), 7.18 (dd, *J* = 8.4, 6.8 Hz, 4H), 7.09 (t, *J* = 7.3 Hz, 2H), 5.46 (dt, *J* = 36.7, 7.4 Hz, 1H), 4.16 (s, 1H), 3.22 (dd, *J* = 7.4, 1.8 Hz, 2H), 2.81 – 2.06 (m, 8H).

¹³C NMR (126 MHz, CDCl₃) δ 158.6 (d, *J*_{C-F} = 249.9 Hz), 142.7, 132.1 (d, *J*_{C-F} = 28.9 Hz), 128.9, 128.5, 128.4, 127.9, 126.9, 124.2 (d, *J*_{C-F} = 7.1 Hz), 102.0 (d, *J*_{C-F} = 15.1 Hz), 76.1, 53.2, 51.9 (d, *J*_{C-F} = 4.6 Hz), 51.8.

¹⁹F NMR (471 MHz, CDCl₃) δ -117.7 (d, *J* = 36.2 Hz).

HRMS (APCI) calcd for C₂₆H₂₇FN₂ [M+H]⁺: 387.2158, Found: 387.2212.

(Z)-1-(Bis(4-fluorophenyl)methyl)-4-(3-fluoro-3-phenylallyl)piperazine (98)

A solution of the (Z)-(3-bromo-1-fluoroprop-1-en-1-yl)benzene **96** (43 mg, 0.2 mmol, 1 equiv) in THF (0.5 M) was added dropwise to a solution of 4,4'-difluorobenzhydrylpiperazine (115 mg, 0.4 mmol, 2.0 equiv) in THF (2.5 M) at room temperature. 1 M aq NaOH (0.4 ml, 0.4 mmol, 2 equiv) was then added in one portion, and the reaction was stirred at room temperature for 6 h. The reaction was diluted with Et₂O (10 ml). The organic layer was separated and the aqueous layer was extracted with Et₂O (2×10 ml). The combined organics were washed with brine, dried (MgSO₄) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 1 : 1) to afford the product **98**. Pale yellow oil (73 mg, 86% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 6.9 Hz, 2H), 7.34 (t, *J* = 6.8 Hz, 7H), 6.96 (t, *J* = 8.6 Hz, 4H), 5.53 (dt, *J* = 36.6, 7.3 Hz, 1H), 4.23 (s, 1H), 3.30 (d, *J* = 6.6 Hz, 2H), 2.87 – 2.51 (m, 4H), 2.51 – 2.13 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 161.8 (d, *J*_{C-F} = 245.5 Hz), 158.7 (d, *J*_{C-F} = 250.1 Hz), 138.2 (d, *J*_{C-F} = 3.1 Hz), 132.0 (d, *J*_{C-F} = 28.9 Hz), 129.2 (d, *J*_{C-F} = 7.8 Hz), 129.0, 128.5 (d, *J*_{C-F} = 1.8 Hz), 124.2 (d, *J*_{C-F} = 7.1 Hz), 115.4 (d, *J*_{C-F} = 21.2 Hz), 101.8 (d, *J*_{C-F} = 15.2 Hz), 74.4, 53.1, 51.8 (d, *J*_{C-F} = 4.6 Hz), 51.6.

¹⁹F NMR (471 MHz, CDCl₃) δ -115.7 (s, 2F), -117.5 (d, *J* = 35.3 Hz, 1F).

HRMS (ESI) calcd for C₂₆H₂₅F₃N₂ [M+H]⁺: 423.1970 Found: 423.2023.

(Z)-3-Fluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine (99)

A solution of the (Z)-(3-bromo-1-fluoroprop-1-en-1-yl)benzene **96** (43 mg, 0.2 mmol, 1 equiv) in THF (0.5 M) was added dropwise to a solution of 1-methyl-aminomethyl naphthalene (68 mg, 0.4 mmol, 2.0 equiv) in THF (2.5 M) at room temperature. 1 M aq NaOH (0.4 ml, 0.4 mmol, 2 equiv) was then added in one portion, and the reaction was stirred at room temperature for 6 h. The reaction was diluted with Et₂O (10 ml). The organic layer was separated and the aqueous layer was extracted with Et₂O (2×10 ml). The combined organics were washed with brine, dried (MgSO₄) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 5 : 1) to afford the product **99** with spectral properties identical to the reported in the literature^[20]. Pale yellow oil (48 mg, 79% yield, *Z/E* > 50 : 1).

¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 35.1, 8.0 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.51 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.31 (m, 3H), 5.64 (dt, *J* = 37.1, 7.3 Hz, 1H), 3.99 (s, 2H), 3.43 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.32 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.4 (d, *J*_{C-F} = 249.2 Hz), 134.7, 133.8, 132.5, 132.2 (d, *J*_{C-F} = 28.9 Hz), 128.9, 128.46, 128.45, 128.0, 127.5, 125.9, 125.6, 125.1, 124.6, 124.2 (d, *J*_{C-F} = 7.1 Hz), 103.0 (d, *J*_{C-F} = 15.3 Hz), 60.0, 51.4 (d, *J*_{C-F} = 4.4 Hz), 42.4.

¹⁹F NMR (471 MHz, CDCl₃) δ -117.8 (d, *J* = 37.0 Hz).

(Z)-4-Bromo-2-fluoro-1-(2-fluoro-2-phenylvinyl)benzene (100)

Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 4-bromo-2-fluoro-1-(phenylethynyl)benzene (0.2 mmol, 55 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **100**. Pale yellow oil (28 mg, 47% yield, r.r. > 50 : 1, *Z/E* > 50 : 1).

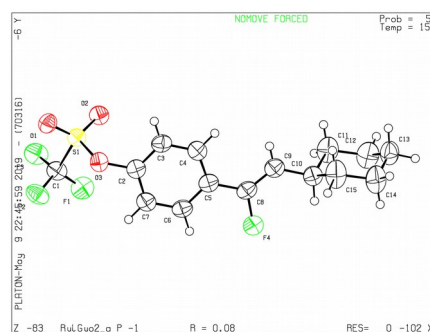
¹H NMR (500 MHz, CDCl₃) δ 7.85 (t, *J* = 8.3 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.46 – 7.36 (m, 3H), 7.32 – 7.28 (m, 1H), 7.26 (dd, *J* = 9.8, 1.8 Hz, 1H), 6.50 (d, *J* = 39.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 159.4 (dd, *J*_{C-F} = 253.7, 1.0 Hz), 158.7 (dd, *J*_{C-F} = 261.1, 2.3 Hz), 132.3 (d, *J*_{C-F} = 27.5 Hz), 130.9 (dd, *J*_{C-F} = 14.9, 3.1 Hz), 129.6, 128.7 (d, *J*_{C-F} = 2.1 Hz), 127.6 (d, *J*_{C-F} = 3.6 Hz), 124.5 (d, *J*_{C-F} = 7.6 Hz), 120.9 (dd, *J*_{C-F} = 10.0, 3.2 Hz), 120.8 (dd, *J*_{C-F} = 11.9, 3.2 Hz), 118.9 (d, *J*_{C-F} = 25.6 Hz), 96.2 (dd, *J*_{C-F} = 9.4, 7.1 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -111.3 (dd, *J* = 39.0, 3.5 Hz, 1F), -113.9 – -114.1 (m, 1F).

HRMS (APCI) calcd for C₁₄H₉BrF₂ [M]⁺: 293.9856, Found: 293.9864.

9. X-ray structures of product 22



Datablock: RuiGuo2_a

Bond precision: C-C = 0.0077 Å Wavelength=1.54178

Cell: a=5.6338(4) b=9.0435(7) c=16.2254(14)
 alpha=74.325(6) beta=89.146(6) gamma=82.210(5)

Temperature: 150 K

| | Calculated | Reported |
|----------------|-----------------|-----------------|
| Volume | 788.38(11) | 788.38(11) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | C15 H16 F4 O3 S | ? |
| Sum formula | C15 H16 F4 O3 S | C15 H16 F4 O3 S |
| Mr | 352.34 | 352.34 |
| Dx,g cm-3 | 1.484 | 1.484 |
| Z | 2 | 2 |
| Mu (mm-1) | 2.342 | 2.342 |
| F000 | 364.0 | 364.0 |
| F000' | 366.06 | |
| h,k,lmax | 6,10,19 | 6,10,19 |
| Nref | 2886 | 2770 |
| Tmin,Tmax | 0.932,0.988 | 0.650,0.880 |
| Tmin' | 0.626 | |

Correction method= # Reported T Limits: Tmin=0.650 Tmax=0.880
AbsCorr = MULTI-SCAN

Data completeness= 0.960 Theta(max)= 68.331

R(reflections)= 0.0791(1917) wR2(reflections)= 0.2040(2770)

S = 1.223 Npar= 212

10. Cartesian coordinates (Å) and energies of optimized structures

2,6-dichloropyridinium-tetrafluoroborate F

M06-2X SCF energy in solution: -1592.51622503 a.u.

M06-2X enthalpy in solution: -1592.403628 a.u.

M06-2X free energy in solution: -1592.460383 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|----------|----------|
| B | 2.487699 | 0.129212 | 0.252608 |

| | | | |
|----|-----------|-----------|-----------|
| F | 1.493814 | -0.045602 | 1.233381 |
| F | 3.334145 | -0.970251 | 0.207487 |
| F | 1.791677 | 0.230042 | -1.010268 |
| F | 3.190017 | 1.307244 | 0.467682 |
| C | -1.520308 | 1.091930 | -0.103642 |
| C | -1.249743 | -1.244879 | -0.122188 |
| C | -2.518176 | -1.432283 | 0.395625 |
| C | -3.289382 | -0.302808 | 0.660825 |
| C | -2.797156 | 0.977225 | 0.413716 |
| H | -2.881153 | -2.435343 | 0.584860 |
| H | -4.287998 | -0.421090 | 1.069025 |
| H | -3.378836 | 1.867929 | 0.618481 |
| N | -0.787377 | -0.005114 | -0.361583 |
| H | 0.194316 | 0.106720 | -0.706423 |
| Cl | -0.784128 | 2.594186 | -0.443721 |
| Cl | -0.193016 | -2.532802 | -0.488542 |

101

M06-2X SCF energy in solution: -539.37926831 a.u.

M06-2X enthalpy in solution: -539.173770 a.u.

M06-2X free energy in solution: -539.224038 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -2.040586 | 0.000084 | 0.000022 |
| C | -2.748722 | 1.213047 | 0.000020 |
| C | -2.748722 | -1.212879 | -0.000006 |
| C | -4.140432 | 1.208276 | -0.000010 |
| H | -2.200056 | 2.150201 | 0.000042 |
| C | -4.140432 | -1.208108 | -0.000033 |
| H | -2.200056 | -2.150034 | -0.000003 |
| C | -4.839484 | 0.000084 | -0.000037 |

| | | | |
|---|-----------|-----------|-----------|
| H | -4.680914 | 2.150316 | -0.000011 |
| H | -4.680914 | -2.150148 | -0.000054 |
| H | -5.925634 | 0.000084 | -0.000060 |
| C | -0.606903 | 0.000083 | 0.000058 |
| C | 0.606903 | -0.000083 | 0.000058 |
| C | 2.040586 | -0.000084 | 0.000022 |
| C | 2.748722 | 1.212879 | -0.000006 |
| C | 2.748722 | -1.213047 | 0.000020 |
| C | 4.140432 | 1.208108 | -0.000033 |
| H | 2.200056 | 2.150034 | -0.000003 |
| C | 4.140432 | -1.208276 | -0.000010 |
| H | 2.200056 | -2.150201 | 0.000042 |
| C | 4.839484 | -0.000084 | -0.000037 |
| H | 4.680914 | 2.150148 | -0.000054 |
| H | 4.680914 | -2.150316 | -0.000011 |
| H | 5.925634 | -0.000084 | -0.000060 |

TS-1

M06-2X SCF energy in solution: -2131.87055224 a.u.

M06-2X enthalpy in solution: -2131.557413 a.u.

M06-2X free energy in solution: -2131.639127 a.u.

Imaginary frequency: -993.3685 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.532541 | -2.115855 | -0.016755 |
| C | -2.198126 | -2.334267 | 1.210115 |
| C | -2.196589 | -2.332192 | -1.244902 |
| C | -3.512896 | -2.770210 | 1.200245 |
| H | -1.673821 | -2.141177 | 2.140707 |
| C | -3.511150 | -2.768639 | -1.237640 |
| H | -1.670806 | -2.137634 | -2.174331 |

| | | | |
|----|-----------|-----------|-----------|
| C | -4.165669 | -2.979712 | -0.019276 |
| H | -4.039770 | -2.931906 | 2.134854 |
| H | -4.036585 | -2.929231 | -2.173249 |
| H | -5.200836 | -3.308835 | -0.020215 |
| C | -0.204926 | -1.680022 | -0.015860 |
| C | 0.957912 | -1.209016 | -0.016658 |
| B | -2.382163 | 1.102267 | -0.009443 |
| F | -3.659601 | 0.527631 | -0.019374 |
| F | -1.663934 | 0.684970 | -1.148974 |
| F | -2.478413 | 2.503368 | -0.013867 |
| F | -1.684854 | 0.689476 | 1.144483 |
| C | 0.731777 | 2.158340 | 1.172569 |
| C | 0.739209 | 2.192094 | -1.122331 |
| C | 0.479405 | 3.553432 | -1.164534 |
| C | 0.334436 | 4.212160 | 0.053528 |
| C | 0.471359 | 3.517970 | 1.252549 |
| H | 0.389206 | 4.068303 | -2.113522 |
| H | 0.118494 | 5.275760 | 0.068436 |
| H | 0.375051 | 4.005048 | 2.215496 |
| N | 0.848776 | 1.514491 | 0.015806 |
| H | 0.786221 | 0.060607 | -0.006863 |
| Cl | 0.975731 | 1.213012 | 2.600293 |
| Cl | 0.993019 | 1.287808 | -2.575244 |
| C | 2.367483 | -1.613430 | -0.013466 |
| C | 3.378938 | -0.651787 | -0.111538 |
| C | 2.705315 | -2.971547 | 0.086929 |
| C | 4.716089 | -1.044396 | -0.112281 |
| H | 3.124185 | 0.401394 | -0.188593 |
| C | 4.041495 | -3.355992 | 0.086555 |
| H | 1.917564 | -3.715564 | 0.166465 |
| C | 5.049682 | -2.394089 | -0.013734 |
| H | 5.496031 | -0.292929 | -0.190342 |

| | | | |
|---|----------|-----------|-----------|
| H | 4.297470 | -4.408527 | 0.164505 |
| H | 6.092231 | -2.698081 | -0.014113 |

TS-1a

M06-2X SCF energy in solution: -2131.86519752 a.u.

M06-2X enthalpy in solution: -2131.552472 a.u.

M06-2X free energy in solution: -2131.642231 a.u.

Imaginary frequency: -892.0643 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 1.123860 | -1.560260 | 0.045977 |
| C | 1.345068 | -2.230780 | 1.265563 |
| C | 1.387896 | -2.193690 | -1.184427 |
| C | 1.808387 | -3.537909 | 1.246268 |
| H | 1.165105 | -1.709496 | 2.200726 |
| C | 1.851532 | -3.501078 | -1.187707 |
| H | 1.242482 | -1.643882 | -2.109116 |
| C | 2.059457 | -4.167366 | 0.023339 |
| H | 1.989644 | -4.064066 | 2.177860 |
| H | 2.066592 | -3.998915 | -2.127633 |
| H | 2.433145 | -5.187302 | 0.014514 |
| C | 0.662128 | -0.230700 | 0.057083 |
| C | 0.023221 | 0.839001 | 0.060703 |
| B | 3.911111 | 0.248584 | -0.048835 |
| F | 4.336287 | -1.086892 | -0.078427 |
| F | 3.092520 | 0.509786 | -1.168896 |
| F | 3.157382 | 0.480364 | 1.122140 |
| F | 5.018720 | 1.107922 | -0.069252 |
| C | -3.084184 | -0.707696 | 1.097975 |
| C | -3.032975 | -0.605010 | -1.195717 |
| C | -4.295402 | -1.168926 | -1.309678 |

| | | | |
|----|-----------|-----------|-----------|
| C | -4.953498 | -1.505226 | -0.129341 |
| C | -4.349967 | -1.275497 | 1.104573 |
| H | -4.740203 | -1.333575 | -2.284091 |
| H | -5.944008 | -1.947004 | -0.170588 |
| H | -4.838676 | -1.524427 | 2.039191 |
| N | -2.444279 | -0.382901 | -0.022790 |
| H | -1.104692 | 0.192035 | 0.028985 |
| Cl | -2.248894 | -0.377426 | 2.576204 |
| Cl | -2.135129 | -0.143363 | -2.600023 |
| C | -0.041385 | 2.291920 | 0.072133 |
| C | -1.279410 | 2.943998 | 0.115850 |
| C | 1.148531 | 3.032436 | 0.038345 |
| C | -1.328148 | 4.335499 | 0.127375 |
| H | -2.198516 | 2.363422 | 0.140861 |
| C | 1.088652 | 4.422222 | 0.049868 |
| H | 2.100262 | 2.512141 | 0.002534 |
| C | -0.145371 | 5.074562 | 0.094513 |
| H | -2.288167 | 4.841532 | 0.162018 |
| H | 2.009630 | 4.996738 | 0.023781 |
| H | -0.184359 | 6.159976 | 0.103340 |

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M06-2X SCF energy in solution: -964.41616323 a.u.

M06-2X enthalpy in solution: -964.177906 a.u.

M06-2X free energy in solution: -964.246903 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|-----------|-----------|
| C | 0.869874 | -1.054748 | 0.025923 |
| C | 1.465178 | -1.379205 | -1.230569 |
| C | 1.432237 | -1.536403 | 1.246857 |
| C | 2.583115 | -2.185075 | -1.253991 |

| | | | |
|---|-----------|-----------|-----------|
| H | 1.031248 | -0.973074 | -2.138409 |
| C | 2.552265 | -2.337260 | 1.198494 |
| H | 0.972343 | -1.249241 | 2.187185 |
| C | 3.119303 | -2.654232 | -0.045736 |
| H | 3.058639 | -2.440150 | -2.194603 |
| H | 3.004175 | -2.709047 | 2.111379 |
| H | 4.008891 | -3.277568 | -0.072814 |
| C | -0.212005 | -0.229672 | 0.062640 |
| C | -1.230384 | 0.565282 | 0.090988 |
| B | 2.282216 | 1.885826 | -0.002658 |
| F | 3.229446 | 0.852947 | 0.084687 |
| F | 1.392770 | 1.795076 | 1.092940 |
| F | 2.918600 | 3.129745 | 0.006759 |
| F | 1.535447 | 1.735784 | -1.190594 |
| H | -0.947044 | 1.621759 | 0.164594 |
| C | -2.664780 | 0.219186 | 0.038004 |
| C | -3.104187 | -1.111077 | -0.012759 |
| C | -3.597066 | 1.261753 | 0.040525 |
| C | -4.465363 | -1.388374 | -0.062783 |
| H | -2.384304 | -1.926206 | -0.010755 |
| C | -4.960375 | 0.976978 | -0.010135 |
| H | -3.251632 | 2.291004 | 0.081006 |
| C | -5.395971 | -0.345805 | -0.061981 |
| H | -4.802844 | -2.419695 | -0.101754 |
| H | -5.679585 | 1.790443 | -0.008579 |
| H | -6.458381 | -0.567423 | -0.100945 |

102a

M06-2X SCF energy in solution: -964.40820249 a.u.

M06-2X enthalpy in solution: -964.169875 a.u.

M06-2X free energy in solution: -964.236020 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 1.356547 | -1.312063 | 0.008884 |
| C | 2.059431 | -1.241228 | 1.251635 |
| C | 2.064244 | -1.254675 | -1.231766 |
| C | 3.433803 | -1.154699 | 1.241027 |
| H | 1.493144 | -1.259139 | 2.177108 |
| C | 3.438828 | -1.171428 | -1.216502 |
| H | 1.501399 | -1.280887 | -2.159181 |
| C | 4.112453 | -1.122467 | 0.013247 |
| H | 3.989479 | -1.099547 | 2.170543 |
| H | 3.998374 | -1.128667 | -2.144354 |
| H | 5.196532 | -1.048462 | 0.014956 |
| C | 0.006184 | -1.476082 | 0.006542 |
| C | -1.251620 | -1.780962 | 0.002606 |
| B | 1.119017 | 1.937497 | -0.022556 |
| F | 2.476116 | 1.585123 | -0.061885 |
| F | 0.535267 | 1.413346 | 1.152012 |
| F | 0.978842 | 3.329265 | -0.037653 |
| F | 0.460524 | 1.380153 | -1.140525 |
| H | -1.399076 | -2.869260 | -0.004732 |
| C | -2.469243 | -0.950137 | 0.006567 |
| C | -2.413761 | 0.448122 | 0.063693 |
| C | -3.706283 | -1.603939 | -0.045775 |
| C | -3.596377 | 1.180322 | 0.065777 |
| H | -1.453730 | 0.951703 | 0.107564 |
| C | -4.885201 | -0.862891 | -0.044609 |
| H | -3.740711 | -2.689479 | -0.087746 |
| C | -4.831167 | 0.529625 | 0.011057 |
| H | -3.551537 | 2.264294 | 0.110625 |
| H | -5.842838 | -1.372927 | -0.086597 |
| H | -5.749879 | 1.108918 | 0.012766 |

103

M06-2X SCF energy in solution: -1167.45474965 a.u.

M06-2X enthalpy in solution: -1167.377050 a.u.

M06-2X free energy in solution: -1167.416368 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.000107 | 0.007883 | 1.126557 |
| C | -0.000107 | 0.007883 | -1.126557 |
| C | 0.000225 | 1.396731 | -1.204520 |
| C | 0.000384 | 2.093988 | 0.000000 |
| C | 0.000225 | 1.396731 | 1.204520 |
| H | 0.000382 | 1.903073 | -2.162426 |
| H | 0.000656 | 3.179640 | 0.000000 |
| H | 0.000382 | 1.903073 | 2.162426 |
| N | -0.000215 | -0.683646 | 0.000000 |
| Cl | -0.000107 | -0.929987 | 2.598735 |
| Cl | -0.000107 | -0.929987 | -2.598735 |

TS-2

M06-2X SCF energy in solution: -964.40352766 a.u.

M06-2X enthalpy in solution: -964.166138 a.u.

M06-2X free energy in solution: -964.230824 a.u.

Imaginary frequency: -298.9906 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|----------|-----------|
| C | 0.781630 | 0.881718 | -0.188517 |
| C | 1.171834 | 1.306299 | 1.102188 |
| C | 1.178676 | 1.599151 | -1.340710 |
| C | 1.934316 | 2.456137 | 1.231802 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.869345 | 0.725922 | 1.967745 |
| C | 1.949519 | 2.739012 | -1.193105 |
| H | 0.878038 | 1.241144 | -2.320612 |
| C | 2.323707 | 3.161232 | 0.088637 |
| H | 2.239940 | 2.799117 | 2.214615 |
| H | 2.266732 | 3.300345 | -2.065632 |
| H | 2.931999 | 4.054760 | 0.196733 |
| C | -0.011899 | -0.261181 | -0.319628 |
| C | -1.081828 | -1.004849 | -0.328497 |
| B | 2.476120 | -1.784826 | 0.126614 |
| F | 3.375219 | -0.769400 | -0.165824 |
| F | 1.333334 | -1.638444 | -0.788220 |
| F | 3.015654 | -3.038585 | -0.099135 |
| F | 1.972012 | -1.659898 | 1.417697 |
| H | -0.960552 | -2.072620 | -0.497195 |
| C | -2.456380 | -0.494592 | -0.129199 |
| C | -3.505332 | -1.415920 | -0.230995 |
| C | -2.739587 | 0.849185 | 0.152602 |
| C | -4.823577 | -0.999758 | -0.055917 |
| H | -3.283831 | -2.457519 | -0.447364 |
| C | -4.056871 | 1.258858 | 0.326594 |
| H | -1.934865 | 1.574421 | 0.239911 |
| C | -5.101650 | 0.337049 | 0.222760 |
| H | -5.630472 | -1.721899 | -0.136566 |
| H | -4.269746 | 2.300861 | 0.545815 |
| H | -6.128495 | 0.662499 | 0.360719 |

TS-2a

M06-2X SCF energy in solution: -964.40227439 a.u.

M06-2X enthalpy in solution: -964.165129 a.u.

M06-2X free energy in solution: -964.228789 a.u.

Imaginary frequency: -292.5851 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 1.712099 | -0.998451 | 0.056276 |
| C | 2.392291 | -0.746661 | 1.267958 |
| C | 2.424716 | -1.214180 | -1.144658 |
| C | 3.778516 | -0.742189 | 1.275884 |
| H | 1.820884 | -0.557336 | 2.170830 |
| C | 3.808272 | -1.197686 | -1.121002 |
| H | 1.876399 | -1.379196 | -2.067063 |
| C | 4.478123 | -0.961887 | 0.085813 |
| H | 4.317001 | -0.553958 | 2.198682 |
| H | 4.371522 | -1.358621 | -2.034142 |
| H | 5.564321 | -0.944501 | 0.096004 |
| C | 0.311570 | -1.006421 | 0.046051 |
| C | -0.879740 | -1.483084 | 0.244170 |
| B | 0.598209 | 1.935971 | -0.178101 |
| F | -0.024945 | 0.772315 | -0.815334 |
| F | 1.918346 | 1.994878 | -0.599582 |
| F | -0.123748 | 3.051378 | -0.567077 |
| F | 0.515525 | 1.726623 | 1.199247 |
| H | -0.780189 | -2.536038 | 0.541233 |
| C | -2.250681 | -0.950152 | 0.147460 |
| C | -2.564010 | 0.378318 | 0.458797 |
| C | -3.267954 | -1.839470 | -0.221545 |
| C | -3.884092 | 0.811912 | 0.373011 |
| H | -1.786159 | 1.060601 | 0.780987 |
| C | -4.583988 | -1.395279 | -0.317019 |
| H | -3.023892 | -2.875501 | -0.441874 |
| C | -4.893248 | -0.067655 | -0.021465 |
| H | -4.122542 | 1.842688 | 0.617193 |
| H | -5.366123 | -2.086882 | -0.615280 |

H -5.920118 0.279451 -0.089737

E-81

M06-2X SCF energy in solution: -639.85885185 a.u.

M06-2X enthalpy in solution: -639.637084 a.u.

M06-2X free energy in solution: -639.689604 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.535580 | 0.403490 | -0.099976 |
| C | -1.183347 | -0.686935 | -0.906020 |
| C | -2.739908 | 0.373415 | 0.614401 |
| C | -2.013365 | -1.802157 | -0.973266 |
| H | -0.264636 | -0.655223 | -1.484799 |
| C | -3.567119 | -0.745736 | 0.544972 |
| H | -3.023047 | 1.223768 | 1.228000 |
| C | -3.204045 | -1.836648 | -0.244682 |
| H | -1.735263 | -2.641970 | -1.603299 |
| H | -4.495739 | -0.764446 | 1.107859 |
| H | -3.850289 | -2.707986 | -0.299509 |
| C | -0.671683 | 1.595066 | -0.021181 |
| C | 0.657490 | 1.727658 | 0.002226 |
| F | -1.402725 | 2.748116 | 0.012455 |
| H | 1.037153 | 2.747046 | -0.039612 |
| C | 1.658269 | 0.646449 | 0.092359 |
| C | 1.479199 | -0.472682 | 0.919214 |
| C | 2.853893 | 0.762791 | -0.630422 |
| C | 2.455877 | -1.462294 | 0.992828 |
| H | 0.574323 | -0.561531 | 1.514459 |
| C | 3.831200 | -0.228584 | -0.557507 |
| H | 3.012630 | 1.635788 | -1.259136 |
| C | 3.633254 | -1.347702 | 0.250822 |

| | | | |
|---|----------|-----------|-----------|
| H | 2.301360 | -2.321438 | 1.639576 |
| H | 4.748405 | -0.124005 | -1.130216 |
| H | 4.394812 | -2.119838 | 0.311974 |

Z-71

M06-2X SCF energy in solution: -639.86258720 a.u.

M06-2X enthalpy in solution: -639.640351 a.u.

M06-2X free energy in solution: -639.694215 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.943555 | -0.076036 | -0.023333 |
| C | -2.846005 | -1.113410 | 0.249923 |
| C | -2.442233 | 1.210332 | -0.281575 |
| C | -4.216762 | -0.864521 | 0.282062 |
| H | -2.474406 | -2.114207 | 0.443527 |
| C | -3.811003 | 1.453246 | -0.245017 |
| H | -1.764488 | 2.021334 | -0.530564 |
| C | -4.704649 | 0.418062 | 0.038618 |
| H | -4.903311 | -1.677669 | 0.499079 |
| H | -4.182678 | 2.452953 | -0.450194 |
| H | -5.773203 | 0.610778 | 0.061982 |
| C | -0.499371 | -0.355748 | -0.035126 |
| C | 0.513423 | 0.517344 | 0.041938 |
| F | -0.231310 | -1.684999 | -0.112165 |
| H | 0.222964 | 1.558359 | 0.149014 |
| C | 1.959902 | 0.271347 | 0.023037 |
| C | 2.558255 | -0.984935 | -0.186329 |
| C | 2.801702 | 1.380387 | 0.221841 |
| C | 3.945134 | -1.114290 | -0.190038 |
| H | 1.946315 | -1.862968 | -0.351026 |
| C | 4.186807 | 1.247158 | 0.219377 |

| | | | |
|---|----------|-----------|-----------|
| H | 2.355459 | 2.359190 | 0.380789 |
| C | 4.766514 | -0.004829 | 0.013650 |
| H | 4.386793 | -2.093171 | -0.354760 |
| H | 4.812392 | 2.121109 | 0.377393 |
| H | 5.847003 | -0.115349 | 0.010075 |

BF3

M06-2X SCF energy in solution: -324.56269572 a.u.

M06-2X enthalpy in solution: -324.546035 a.u.

M06-2X free energy in solution: -324.576705 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| B | -0.000001 | 0.000130 | -0.000102 |
| F | -1.150308 | 0.643185 | 0.000019 |
| F | 1.132233 | 0.674490 | 0.000019 |
| F | 0.018076 | -1.317747 | 0.000019 |

TS-1b

M06-2X SCF energy in solution: -2131.86614792 a.u.

M06-2X enthalpy in solution: -2131.552661 a.u.

M06-2X free energy in solution: -2131.639469 a.u.

Imaginary frequency: -202.0959 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -3.724356 | 0.200553 | 0.100745 |
| C | -4.425915 | -0.183080 | -1.067397 |
| C | -4.277210 | -0.029735 | 1.383520 |
| C | -5.663200 | -0.792903 | -0.944519 |
| H | -3.981950 | 0.005316 | -2.040251 |
| C | -5.515933 | -0.640137 | 1.487490 |

| | | | |
|----|-----------|-----------|-----------|
| H | -3.720032 | 0.272979 | 2.264995 |
| C | -6.201828 | -1.018494 | 0.327537 |
| H | -6.212563 | -1.095081 | -1.829937 |
| H | -5.952523 | -0.825406 | 2.463302 |
| H | -7.172621 | -1.497603 | 0.416748 |
| C | -2.474886 | 0.810204 | -0.010714 |
| C | -1.274679 | 1.179146 | -0.094706 |
| B | 3.958708 | -0.255703 | -0.019658 |
| F | 2.925417 | -0.408662 | -0.968858 |
| F | 3.400730 | 0.201404 | 1.187848 |
| F | 4.588252 | -1.495056 | 0.189270 |
| F | 4.892890 | 0.678445 | -0.492047 |
| C | 0.398775 | -1.972067 | -1.021661 |
| C | 0.860373 | -1.454351 | 1.152568 |
| C | 1.809590 | -2.458923 | 1.258098 |
| C | 2.025609 | -3.249054 | 0.133247 |
| C | 1.305654 | -3.019831 | -1.036093 |
| H | 2.369285 | -2.596012 | 2.175423 |
| H | 2.770972 | -4.037239 | 0.163826 |
| H | 1.458824 | -3.608177 | -1.932673 |
| N | 0.171238 | -1.214000 | 0.042891 |
| H | -0.739550 | 0.079232 | -0.045525 |
| Cl | -0.516838 | -1.575087 | -2.444943 |
| Cl | 0.498507 | -0.431193 | 2.505729 |
| C | -0.378631 | 2.329117 | -0.199312 |
| C | 1.003643 | 2.122671 | -0.251904 |
| C | -0.905537 | 3.628675 | -0.238692 |
| C | 1.859798 | 3.217985 | -0.344773 |
| H | 1.416664 | 1.117697 | -0.228970 |
| C | -0.042996 | 4.714483 | -0.331349 |
| H | -1.980867 | 3.777057 | -0.196389 |
| C | 1.339170 | 4.510502 | -0.383816 |

| | | | |
|---|-----------|----------|-----------|
| H | 2.932094 | 3.052384 | -0.384572 |
| H | -0.447484 | 5.721866 | -0.361862 |
| H | 2.008934 | 5.362531 | -0.454961 |

TS-1c

M06-2X SCF energy in solution: -2131.86454140 a.u.

M06-2X enthalpy in solution: -2131.551715 a.u.

M06-2X free energy in solution: -2131.640038 a.u.

Imaginary frequency: -636.7487 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.873374 | -1.821826 | -0.650960 |
| C | 1.343452 | -2.414239 | 0.538662 |
| C | 0.668886 | -2.594885 | -1.812600 |
| C | 1.593917 | -3.779017 | 0.560073 |
| H | 1.519424 | -1.790928 | 1.409402 |
| C | 0.921819 | -3.957854 | -1.773294 |
| H | 0.321610 | -2.112206 | -2.721043 |
| C | 1.383077 | -4.544232 | -0.590158 |
| H | 1.965527 | -4.246639 | 1.465991 |
| H | 0.770239 | -4.564740 | -2.660059 |
| H | 1.587973 | -5.610826 | -0.567502 |
| C | 0.610115 | -0.438942 | -0.680865 |
| C | 0.130394 | 0.711014 | -0.644915 |
| B | 3.739834 | 0.081124 | 0.631857 |
| F | 4.330637 | -1.143129 | 0.975408 |
| F | 3.289686 | 0.026962 | -0.707202 |
| F | 2.635112 | 0.323578 | 1.472484 |
| F | 4.668867 | 1.122560 | 0.764131 |
| C | -2.553426 | -0.012731 | 1.609912 |
| C | -3.326285 | -0.534418 | -0.485064 |

| | | | |
|----|-----------|-----------|-----------|
| C | -4.583973 | -0.871667 | -0.007291 |
| C | -4.795035 | -0.758636 | 1.364861 |
| C | -3.770465 | -0.323838 | 2.200875 |
| H | -5.360383 | -1.208095 | -0.683957 |
| H | -5.763398 | -1.011691 | 1.784729 |
| H | -3.903673 | -0.226999 | 3.271777 |
| N | -2.338737 | -0.115385 | 0.300596 |
| H | -0.994506 | 0.235859 | -0.263196 |
| Cl | -1.218676 | 0.536098 | 2.561948 |
| Cl | -2.960512 | -0.645478 | -2.174600 |
| C | 0.227579 | 2.160182 | -0.731545 |
| C | -0.934618 | 2.931140 | -0.856672 |
| C | 1.485223 | 2.776173 | -0.676178 |
| C | -0.838718 | 4.317668 | -0.936351 |
| H | -1.906448 | 2.446038 | -0.897916 |
| C | 1.568920 | 4.162849 | -0.754768 |
| H | 2.376392 | 2.166463 | -0.570723 |
| C | 0.412067 | 4.933774 | -0.884914 |
| H | -1.739582 | 4.915463 | -1.036908 |
| H | 2.542585 | 4.641280 | -0.710662 |
| H | 0.485926 | 6.015731 | -0.944532 |

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M06-2X SCF energy in solution: -2131.87748267 a.u.

M06-2X enthalpy in solution: -2131.559682 a.u.

M06-2X free energy in solution: -2131.649353 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|-----------|-----------|
| C | 2.744147 | 0.306918 | -0.069280 |
| C | 3.294321 | -0.057903 | 1.194608 |
| C | 3.437273 | 0.010769 | -1.279548 |

| | | | |
|----|-----------|-----------|-----------|
| C | 4.522159 | -0.684612 | 1.235982 |
| H | 2.727686 | 0.154329 | 2.095690 |
| C | 4.661844 | -0.619695 | -1.214497 |
| H | 2.978342 | 0.275228 | -2.227046 |
| C | 5.194284 | -0.962927 | 0.037133 |
| H | 4.958940 | -0.977412 | 2.184409 |
| H | 5.204556 | -0.863710 | -2.121178 |
| H | 6.155115 | -1.468520 | 0.078350 |
| C | 1.515198 | 0.898358 | -0.120489 |
| C | 0.336204 | 1.415802 | -0.156497 |
| B | 0.765807 | -2.308978 | -0.080416 |
| F | 2.126852 | -2.654944 | -0.141328 |
| F | 0.435107 | -1.510674 | -1.196183 |
| F | -0.020038 | -3.466881 | -0.074054 |
| F | 0.525986 | -1.558019 | 1.089011 |
| C | -2.373800 | -0.928543 | 1.237836 |
| C | -2.635012 | -1.208355 | -0.987526 |
| C | -3.117878 | -2.502885 | -0.845609 |
| C | -3.213774 | -2.998652 | 0.451781 |
| C | -2.837933 | -2.204927 | 1.531173 |
| H | -3.392246 | -3.094556 | -1.710713 |
| H | -3.573064 | -4.009014 | 0.620464 |
| H | -2.890676 | -2.559045 | 2.553713 |
| N | -2.271677 | -0.429262 | 0.017865 |
| H | -0.456363 | 0.648390 | -0.220702 |
| Cl | -1.889228 | 0.134601 | 2.533614 |
| Cl | -2.496351 | -0.507429 | -2.578590 |
| C | -0.078254 | 2.830793 | -0.117821 |
| C | 0.853830 | 3.873020 | -0.023987 |
| C | -1.445938 | 3.117321 | -0.177175 |
| C | 0.414657 | 5.191533 | 0.008484 |
| H | 1.917129 | 3.650401 | 0.023806 |

| | | | |
|---|-----------|----------|-----------|
| C | -1.879168 | 4.441713 | -0.144318 |
| H | -2.159877 | 2.300587 | -0.246201 |
| C | -0.951975 | 5.478387 | -0.051946 |
| H | 1.138071 | 5.998212 | 0.081182 |
| H | -2.941651 | 4.660985 | -0.190681 |
| H | -1.290683 | 6.509908 | -0.026305 |

104a

M06-2X SCF energy in solution: -2131.87108908 a.u.

M06-2X enthalpy in solution: -2131.553028 a.u.

M06-2X free energy in solution: -2131.645117 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 1.661303 | -1.458025 | 0.291382 |
| C | 2.131365 | -1.873821 | 1.571205 |
| C | 2.008164 | -2.187866 | -0.883454 |
| C | 2.905924 | -3.010705 | 1.664852 |
| H | 1.872466 | -1.284043 | 2.444720 |
| C | 2.777434 | -3.326130 | -0.765529 |
| H | 1.657830 | -1.830163 | -1.846507 |
| C | 3.221764 | -3.728074 | 0.501919 |
| H | 3.278400 | -3.344660 | 2.627031 |
| H | 3.052495 | -3.897688 | -1.645191 |
| H | 3.837093 | -4.619756 | 0.585086 |
| C | 0.856711 | -0.358851 | 0.183869 |
| C | -0.041240 | 0.559920 | 0.077666 |
| B | 4.233708 | 0.474692 | -0.107926 |
| F | 4.675977 | -0.855471 | -0.063914 |
| F | 3.602287 | 0.797284 | 1.114195 |
| F | 5.314496 | 1.337908 | -0.320805 |
| F | 3.294646 | 0.622177 | -1.152220 |

| | | | |
|----|-----------|-----------|-----------|
| C | -3.978964 | -0.308873 | 1.022932 |
| C | -3.567107 | -1.160612 | -1.030068 |
| C | -4.881805 | -1.576494 | -1.205498 |
| C | -5.767888 | -1.315898 | -0.163443 |
| C | -5.321834 | -0.667120 | 0.985013 |
| H | -5.191873 | -2.078854 | -2.114176 |
| H | -6.807037 | -1.618659 | -0.246551 |
| H | -5.982403 | -0.447130 | 1.815394 |
| N | -3.114345 | -0.543593 | 0.049024 |
| H | -1.049702 | 0.106087 | 0.147984 |
| Cl | -3.338181 | 0.507819 | 2.423199 |
| Cl | -2.394311 | -1.444930 | -2.289291 |
| C | 0.003403 | 2.018381 | -0.123595 |
| C | 1.195431 | 2.747747 | -0.036072 |
| C | -1.203401 | 2.670600 | -0.404650 |
| C | 1.170791 | 4.124336 | -0.236923 |
| H | 2.126378 | 2.238928 | 0.190004 |
| C | -1.217938 | 4.048225 | -0.607331 |
| H | -2.123816 | 2.094450 | -0.465410 |
| C | -0.030825 | 4.775819 | -0.524023 |
| H | 2.095555 | 4.689420 | -0.168904 |
| H | -2.154546 | 4.551563 | -0.827909 |
| H | -0.040999 | 5.850644 | -0.680348 |

TS-2b

M06-2X SCF energy in solution: -2131.86995998 a.u.

M06-2X enthalpy in solution: -2131.552879 a.u.

M06-2X free energy in solution: -2131.639721 a.u.

Imaginary frequency: -286.3257 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|---|---|---|
|------|---|---|---|

| | | | |
|----|-----------|-----------|-----------|
| C | 0.871012 | 1.932124 | 0.051591 |
| C | 1.166765 | 3.003822 | -0.820408 |
| C | 0.675614 | 2.155349 | 1.433573 |
| C | 1.277529 | 4.284555 | -0.303122 |
| H | 1.297986 | 2.807879 | -1.879564 |
| C | 0.786163 | 3.441302 | 1.933922 |
| H | 0.445021 | 1.314119 | 2.080416 |
| C | 1.082392 | 4.498306 | 1.065213 |
| H | 1.504790 | 5.118837 | -0.958313 |
| H | 0.640403 | 3.630628 | 2.992249 |
| H | 1.162074 | 5.506276 | 1.462405 |
| C | 0.771497 | 0.631446 | -0.453836 |
| C | 1.141211 | -0.564590 | -0.812697 |
| B | -1.956042 | 1.547313 | -1.327322 |
| F | -2.118035 | 2.487234 | -0.316934 |
| F | -1.168479 | 0.438677 | -0.773143 |
| F | -3.167904 | 1.016792 | -1.736069 |
| F | -1.231000 | 2.065979 | -2.394213 |
| C | -2.485428 | -2.061762 | 0.032986 |
| C | -1.115083 | -1.454767 | 1.711391 |
| C | -2.017877 | -0.528621 | 2.219445 |
| C | -3.232506 | -0.402302 | 1.549271 |
| C | -3.489855 | -1.186233 | 0.430311 |
| H | -1.781750 | 0.061341 | 3.097635 |
| H | -3.972988 | 0.312248 | 1.894856 |
| H | -4.415097 | -1.108330 | -0.127352 |
| N | -1.324057 | -2.209493 | 0.646685 |
| H | 0.380221 | -1.260822 | -1.160244 |
| Cl | -2.723183 | -3.042071 | -1.391314 |
| Cl | 0.427170 | -1.674613 | 2.508610 |
| C | 2.537382 | -1.047325 | -0.721926 |
| C | 3.636518 | -0.180499 | -0.673762 |

| | | | |
|---|----------|-----------|-----------|
| C | 2.739373 | -2.431989 | -0.683171 |
| C | 4.923713 | -0.699399 | -0.573366 |
| H | 3.488843 | 0.894994 | -0.730918 |
| C | 4.030369 | -2.944936 | -0.580233 |
| H | 1.882931 | -3.100157 | -0.725301 |
| C | 5.123301 | -2.080579 | -0.523397 |
| H | 5.773752 | -0.024311 | -0.541768 |
| H | 4.180850 | -4.019821 | -0.547777 |
| H | 6.130030 | -2.480894 | -0.448023 |

TS-2c

M06-2X SCF energy in solution: -2131.86989076 a.u.

M06-2X enthalpy in solution: -2131.553127 a.u.

M06-2X free energy in solution: -2131.640090 a.u.

Imaginary frequency: -285.2250 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.568602 | 1.175429 | 0.307291 |
| C | -1.161784 | 1.442510 | -0.945304 |
| C | -1.064264 | 1.772048 | 1.487373 |
| C | -2.259056 | 2.288716 | -1.006475 |
| H | -0.745633 | 0.987297 | -1.839137 |
| C | -2.158391 | 2.617332 | 1.408463 |
| H | -0.575841 | 1.564539 | 2.434612 |
| C | -2.748267 | 2.873807 | 0.164817 |
| H | -2.728647 | 2.502177 | -1.961379 |
| H | -2.551245 | 3.085708 | 2.304910 |
| H | -3.600776 | 3.545189 | 0.109278 |
| C | 0.535590 | 0.310690 | 0.370158 |
| C | 1.146519 | -0.832698 | 0.374350 |
| B | 2.095035 | 2.701262 | -0.406134 |

| | | | |
|----|-----------|-----------|-----------|
| F | 1.995760 | 1.656158 | 0.616367 |
| F | 1.178228 | 3.693105 | -0.090141 |
| F | 3.397844 | 3.170134 | -0.387311 |
| F | 1.786937 | 2.096210 | -1.625107 |
| C | -2.806100 | -1.285213 | 0.887963 |
| C | -2.254426 | -1.822239 | -1.233530 |
| C | -3.398432 | -1.233196 | -1.762126 |
| C | -4.271849 | -0.635090 | -0.858450 |
| C | -3.980718 | -0.648026 | 0.503248 |
| H | -3.588421 | -1.238883 | -2.829030 |
| H | -5.176546 | -0.152467 | -1.215507 |
| H | -4.633291 | -0.188459 | 1.236513 |
| N | -1.954401 | -1.860175 | 0.054140 |
| H | 0.365319 | -1.609648 | 0.419476 |
| Cl | -2.379946 | -1.354561 | 2.577797 |
| Cl | -1.092718 | -2.558916 | -2.305351 |
| C | 2.546537 | -1.287203 | 0.347141 |
| C | 2.844215 | -2.499579 | 0.982488 |
| C | 3.554950 | -0.584084 | -0.323118 |
| C | 4.148625 | -2.986106 | 0.983787 |
| H | 2.052336 | -3.052631 | 1.480974 |
| C | 4.854353 | -1.083485 | -0.327856 |
| H | 3.322501 | 0.333931 | -0.849586 |
| C | 5.156204 | -2.276799 | 0.330072 |
| H | 4.375071 | -3.920557 | 1.488457 |
| H | 5.633067 | -0.536170 | -0.850503 |
| H | 6.173480 | -2.657342 | 0.325014 |

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M06-2X SCF energy in solution: -542.99356576 a.u.
M06-2X enthalpy in solution: -542.716477 a.u.
M06-2X free energy in solution: -542.770712 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.388307 | -0.281549 | -0.282741 |
| C | 0.815604 | -0.175611 | -0.179298 |
| C | 2.243893 | -0.058579 | -0.063999 |
| C | 2.814938 | 1.031509 | 0.611840 |
| C | 3.083277 | -1.033746 | -0.626065 |
| C | 4.198550 | 1.141001 | 0.721320 |
| H | 2.166622 | 1.786420 | 1.047013 |
| C | 4.465978 | -0.917591 | -0.512623 |
| H | 2.642665 | -1.877586 | -1.148877 |
| C | 5.027575 | 0.168384 | 0.160476 |
| H | 4.630525 | 1.988303 | 1.246056 |
| H | 5.106624 | -1.677370 | -0.951012 |
| H | 6.106621 | 0.256522 | 0.247627 |
| C | -1.848687 | -0.384011 | -0.380431 |
| C | -2.465194 | -0.837442 | 0.957689 |
| C | -2.470589 | 0.950015 | -0.837386 |
| H | -2.085469 | -1.146042 | -1.137970 |
| C | -3.987582 | -0.943497 | 0.849541 |
| H | -2.197585 | -0.103761 | 1.730807 |
| H | -2.029727 | -1.797126 | 1.257250 |
| C | -3.992975 | 0.837104 | -0.938204 |
| H | -2.203045 | 1.726979 | -0.107684 |
| H | -2.039090 | 1.246899 | -1.799696 |
| C | -4.606420 | 0.377339 | 0.386338 |
| H | -4.406513 | -1.243642 | 1.817004 |
| H | -4.244241 | -1.735838 | 0.131523 |
| H | -4.415681 | 1.802127 | -1.240887 |
| H | -4.250020 | 0.115244 | -1.726922 |
| H | -5.692960 | 0.272391 | 0.285098 |

H -4.429094 1.146522 1.151932

106

M06-2X SCF energy in solution: -968.02975983 a.u.

M06-2X enthalpy in solution: -967.719948 a.u.

M06-2X free energy in solution: -967.791208 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.171873 | -1.109432 | 0.003127 |
| C | -1.795030 | -1.301123 | 1.269409 |
| C | -1.753179 | -1.641921 | -1.183242 |
| C | -2.964401 | -2.030448 | 1.338988 |
| H | -1.343516 | -0.858802 | 2.151309 |
| C | -2.926692 | -2.360680 | -1.092045 |
| H | -1.268324 | -1.457801 | -2.136913 |
| C | -3.523707 | -2.549437 | 0.163219 |
| H | -3.459823 | -2.185420 | 2.291148 |
| H | -3.393752 | -2.767427 | -1.982254 |
| H | -4.452755 | -3.109421 | 0.224580 |
| C | -0.031335 | -0.357966 | -0.080295 |
| C | 1.058878 | 0.317199 | -0.142442 |
| B | -2.323901 | 1.965338 | -0.077933 |
| F | -3.376354 | 1.042369 | -0.182710 |
| F | -1.411448 | 1.748703 | -1.136950 |
| F | -2.815908 | 3.272225 | -0.138915 |
| F | -1.643435 | 1.765535 | 1.141298 |
| C | 2.451458 | -0.279877 | -0.000541 |
| C | 3.243787 | -0.032310 | -1.292267 |
| C | 3.152294 | 0.351534 | 1.211165 |
| H | 2.360075 | -1.361400 | 0.162351 |
| C | 4.676136 | -0.555501 | -1.153739 |

| | | | |
|---|----------|-----------|-----------|
| H | 3.263011 | 1.048462 | -1.492664 |
| H | 2.736847 | -0.510080 | -2.138171 |
| C | 4.584962 | -0.173846 | 1.337878 |
| H | 3.168946 | 1.442827 | 1.080079 |
| H | 2.580790 | 0.143318 | 2.122610 |
| C | 5.380538 | 0.067527 | 0.053352 |
| H | 5.232176 | -0.344667 | -2.074140 |
| H | 4.652978 | -1.648376 | -1.037551 |
| H | 5.076206 | 0.308010 | 2.190632 |
| H | 4.557873 | -1.251764 | 1.552073 |
| H | 6.392793 | -0.340548 | 0.152951 |
| H | 5.485876 | 1.149757 | -0.108605 |
| H | 0.963409 | 1.394842 | -0.307685 |

106a

M06-2X SCF energy in solution: -968.03079736 a.u.

M06-2X enthalpy in solution: -967.720899 a.u.

M06-2X free energy in solution: -967.793033 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|-----------|-----------|
| C | 1.800695 | -1.186699 | 0.001977 |
| C | 2.490618 | -1.054081 | 1.240664 |
| C | 2.494912 | -1.061099 | -1.235039 |
| C | 3.850570 | -0.822923 | 1.231078 |
| H | 1.930123 | -1.128526 | 2.166992 |
| C | 3.854763 | -0.829614 | -1.222038 |
| H | 1.937600 | -1.140809 | -2.162846 |
| C | 4.522136 | -0.710353 | 0.005363 |
| H | 4.396022 | -0.713003 | 2.161925 |
| H | 4.403409 | -0.724764 | -2.151594 |
| H | 5.591354 | -0.517208 | 0.006657 |

| | | | |
|---|-----------|-----------|-----------|
| C | 0.451049 | -1.413499 | 0.000348 |
| C | -0.803941 | -1.685638 | -0.000226 |
| B | 0.798636 | 1.898808 | -0.007144 |
| F | 2.200922 | 1.892130 | 0.000482 |
| F | 0.317717 | 3.211897 | -0.013933 |
| F | 0.333750 | 1.215828 | -1.154121 |
| F | 0.321384 | 1.223015 | 1.138957 |
| H | -1.061603 | -2.751243 | 0.003936 |
| C | -1.952958 | -0.687460 | -0.003996 |
| C | -2.803731 | -0.896524 | -1.263693 |
| C | -2.786288 | -0.868856 | 1.271658 |
| H | -1.530259 | 0.319569 | -0.017630 |
| C | -3.997993 | 0.062185 | -1.259717 |
| H | -3.164183 | -1.935699 | -1.289630 |
| H | -2.187727 | -0.738765 | -2.156256 |
| C | -3.980717 | 0.089593 | 1.263042 |
| H | -3.145667 | -1.907349 | 1.325468 |
| H | -2.157799 | -0.691080 | 2.151637 |
| C | -4.837394 | -0.101222 | 0.009402 |
| H | -4.611059 | -0.112340 | -2.151322 |
| H | -3.627696 | 1.094691 | -1.321594 |
| H | -4.581444 | -0.065204 | 2.166600 |
| H | -3.609462 | 1.123040 | 1.297343 |
| H | -5.668182 | 0.613649 | 0.007314 |
| H | -5.280885 | -1.107691 | 0.023334 |

TS-3

M06-2X SCF energy in solution: -2135.48898352 a.u.

M06-2X enthalpy in solution: -2135.104668 a.u.

M06-2X free energy in solution: -2135.191873 a.u.

Imaginary frequency: -634.7545 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 1.010856 | -2.386669 | -0.027562 |
| C | 1.863932 | -2.551474 | -1.139204 |
| C | 1.360140 | -2.917915 | 1.233179 |
| C | 3.056530 | -3.240422 | -0.981670 |
| H | 1.586884 | -2.115306 | -2.092690 |
| C | 2.554806 | -3.605622 | 1.374118 |
| H | 0.688525 | -2.778975 | 2.074929 |
| C | 3.399264 | -3.760732 | 0.269625 |
| H | 3.729553 | -3.358319 | -1.824498 |
| H | 2.838116 | -4.014427 | 2.338539 |
| H | 4.340071 | -4.290764 | 0.388052 |
| C | -0.185118 | -1.668425 | -0.164901 |
| C | -1.174035 | -0.909672 | -0.242352 |
| B | 2.613959 | 0.729450 | -0.972443 |
| F | 3.713717 | 0.199605 | -1.664600 |
| F | 2.577629 | 0.210714 | 0.334003 |
| F | 2.713728 | 2.130491 | -0.911099 |
| F | 1.424264 | 0.380859 | -1.644574 |
| C | -0.309457 | 2.580566 | -0.464181 |
| C | 0.421852 | 1.812976 | 1.562510 |
| C | 0.994101 | 3.033746 | 1.889152 |
| C | 0.882837 | 4.059432 | 0.954756 |
| C | 0.211656 | 3.846907 | -0.245509 |
| H | 1.504383 | 3.167737 | 2.835500 |
| H | 1.320176 | 5.030440 | 1.164629 |
| H | 0.104658 | 4.624192 | -0.992652 |
| N | -0.204079 | 1.589757 | 0.413491 |
| H | -0.612731 | 0.190094 | 0.033202 |
| Cl | -1.181695 | 2.225880 | -1.917906 |
| Cl | 0.456088 | 0.494939 | 2.687700 |

| | | | |
|---|-----------|-----------|-----------|
| C | -2.653032 | -0.810768 | -0.467059 |
| C | -3.284383 | -2.202482 | -0.610499 |
| C | -3.321261 | -0.008434 | 0.660706 |
| H | -2.789805 | -0.259505 | -1.408347 |
| C | -4.792728 | -2.088544 | -0.841689 |
| H | -3.091435 | -2.770260 | 0.310723 |
| H | -2.803584 | -2.741564 | -1.434658 |
| C | -4.830339 | 0.093050 | 0.425936 |
| H | -3.124957 | -0.513890 | 1.617146 |
| H | -2.877196 | 0.992251 | 0.725628 |
| C | -5.466758 | -1.290807 | 0.277010 |
| H | -5.230041 | -3.090717 | -0.915684 |
| H | -4.974058 | -1.589717 | -1.804394 |
| H | -5.295255 | 0.641938 | 1.252499 |
| H | -5.012057 | 0.676938 | -0.487870 |
| H | -6.540335 | -1.193534 | 0.079087 |
| H | -5.364058 | -1.839371 | 1.224394 |

TS-3a

M06-2X SCF energy in solution: -2135.48335228 a.u.

M06-2X enthalpy in solution: -2135.098994 a.u.

M06-2X free energy in solution: -2135.189850 a.u.

Imaginary frequency: -851.6812 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.723587 | -1.322367 | 0.000005 |
| C | -2.147255 | -1.873810 | -1.223691 |
| C | -2.147242 | -1.873947 | 1.223644 |
| C | -2.979135 | -2.984716 | -1.216234 |
| H | -1.834064 | -1.410891 | -2.154447 |
| C | -2.979122 | -2.984852 | 1.216071 |

| | | | |
|----|-----------|-----------|-----------|
| H | -1.834037 | -1.411138 | 2.154450 |
| C | -3.390480 | -3.536982 | -0.000110 |
| H | -3.319529 | -3.414000 | -2.152978 |
| H | -3.319506 | -3.414242 | 2.152770 |
| H | -4.049716 | -4.400404 | -0.000155 |
| C | -0.903487 | -0.171844 | 0.000061 |
| C | -0.025162 | 0.701907 | 0.000113 |
| B | -3.793834 | 1.371053 | 0.000078 |
| F | -4.634865 | 0.247127 | -0.000049 |
| F | -2.973523 | 1.344960 | 1.147796 |
| F | -2.973413 | 1.345142 | -1.147568 |
| F | -4.561624 | 2.545073 | 0.000134 |
| C | 2.642926 | -1.445468 | -1.147765 |
| C | 2.642972 | -1.445500 | 1.147740 |
| C | 3.834100 | -2.154288 | 1.207914 |
| C | 4.432535 | -2.502953 | -0.000063 |
| C | 3.834052 | -2.154256 | -1.208006 |
| H | 4.267969 | -2.421998 | 2.164036 |
| H | 5.365973 | -3.056602 | -0.000088 |
| H | 4.267880 | -2.421941 | -2.164154 |
| N | 2.068698 | -1.091457 | 0.000003 |
| H | 0.887143 | -0.242251 | 0.000055 |
| Cl | 1.810762 | -0.992703 | -2.595508 |
| Cl | 1.810861 | -0.992777 | 2.595525 |
| C | 0.458652 | 2.110255 | 0.000111 |
| C | 1.279173 | 2.411602 | 1.263777 |
| C | 1.278776 | 2.411689 | -1.263793 |
| H | -0.442996 | 2.737522 | 0.000274 |
| C | 1.743025 | 3.869820 | 1.262127 |
| H | 2.156274 | 1.747105 | 1.283234 |
| H | 0.682797 | 2.192402 | 2.156196 |
| C | 1.742629 | 3.869906 | -1.262196 |

| | | | |
|---|----------|----------|-----------|
| H | 2.155870 | 1.747191 | -1.283558 |
| H | 0.682122 | 2.192538 | -2.156039 |
| C | 2.544558 | 4.196930 | -0.000149 |
| H | 2.341634 | 4.066993 | 2.158645 |
| H | 0.862805 | 4.525487 | 1.314846 |
| H | 2.340957 | 4.067136 | -2.158888 |
| H | 0.862393 | 4.525577 | -1.314596 |
| H | 2.835916 | 5.253459 | -0.000158 |
| H | 3.474078 | 3.608691 | -0.000315 |

TS-4

M06-2X SCF energy in solution: -968.02286715 a.u.

M06-2X enthalpy in solution: -967.713853 a.u.

M06-2X free energy in solution: -967.781386 a.u.

Imaginary frequency: -299.5191 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.068905 | -0.946393 | -0.154582 |
| C | -1.444630 | -1.273913 | 1.165141 |
| C | -1.574170 | -1.672938 | -1.253573 |
| C | -2.302622 | -2.342786 | 1.378389 |
| H | -1.060550 | -0.683016 | 1.990556 |
| C | -2.440322 | -2.729360 | -1.024974 |
| H | -1.284901 | -1.387847 | -2.260570 |
| C | -2.800065 | -3.059774 | 0.286873 |
| H | -2.597586 | -2.610613 | 2.387540 |
| H | -2.841961 | -3.295602 | -1.858788 |
| H | -3.482749 | -3.887004 | 0.459211 |
| C | -0.184942 | 0.126682 | -0.365456 |
| C | 0.946383 | 0.754619 | -0.400975 |
| B | -2.510044 | 1.880705 | 0.023646 |

| | | | |
|---|-----------|-----------|-----------|
| F | -3.513844 | 0.942982 | -0.168758 |
| F | -1.417989 | 1.558270 | -0.908982 |
| F | -2.931253 | 3.163326 | -0.279380 |
| F | -1.976397 | 1.797381 | 1.306278 |
| H | 0.989751 | 1.819902 | -0.617121 |
| C | 2.240770 | 0.009335 | -0.125934 |
| C | 3.179797 | 0.149313 | -1.333233 |
| C | 2.889187 | 0.570154 | 1.149209 |
| H | 2.019023 | -1.054927 | 0.029946 |
| C | 4.523130 | -0.530757 | -1.055053 |
| H | 3.342860 | 1.218468 | -1.531922 |
| H | 2.706603 | -0.278168 | -2.224651 |
| C | 4.233800 | -0.112189 | 1.415972 |
| H | 3.043311 | 1.651477 | 1.023011 |
| H | 2.210573 | 0.436932 | 1.999618 |
| C | 5.172810 | 0.022481 | 0.215290 |
| H | 5.187366 | -0.395642 | -1.916065 |
| H | 4.363908 | -1.612403 | -0.940684 |
| H | 4.692257 | 0.320262 | 2.312392 |
| H | 4.062837 | -1.177493 | 1.626478 |
| H | 6.117569 | -0.496323 | 0.413834 |
| H | 5.415921 | 1.083992 | 0.063997 |

TS-4a

M06-2X SCF energy in solution: -968.02320645 a.u.

M06-2X enthalpy in solution: -967.714204 a.u.

M06-2X free energy in solution: -967.781631 a.u.

Imaginary frequency: -302.9303 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|-----------|----------|
| C | 2.119698 | -0.843507 | 0.123053 |

| | | | |
|---|-----------|-----------|-----------|
| C | 2.805227 | -0.197033 | 1.172490 |
| C | 2.825886 | -1.523163 | -0.891646 |
| C | 4.190624 | -0.253181 | 1.210346 |
| H | 2.239508 | 0.335447 | 1.929753 |
| C | 4.210517 | -1.567146 | -0.841669 |
| H | 2.275729 | -2.002200 | -1.695772 |
| C | 4.886417 | -0.933270 | 0.206221 |
| H | 4.732162 | 0.235953 | 2.013252 |
| H | 4.767161 | -2.087928 | -1.613862 |
| H | 5.971687 | -0.968106 | 0.238993 |
| C | 0.711254 | -0.825760 | 0.092547 |
| C | -0.490703 | -1.235083 | 0.339284 |
| B | 0.269785 | 2.086445 | -0.392599 |
| F | 0.435856 | 0.774918 | -1.036467 |
| F | 1.209320 | 2.937772 | -0.947577 |
| F | -1.027994 | 2.506672 | -0.646310 |
| F | 0.484862 | 1.900891 | 0.970588 |
| H | -0.457609 | -2.146097 | 0.952379 |
| C | -1.850998 | -0.697702 | -0.018329 |
| C | -2.714101 | -1.815698 | -0.622293 |
| C | -2.515400 | -0.109189 | 1.238162 |
| H | -1.726513 | 0.099702 | -0.755869 |
| C | -4.117027 | -1.295664 | -0.945239 |
| H | -2.786392 | -2.642747 | 0.099665 |
| H | -2.233898 | -2.211881 | -1.524588 |
| C | -3.919465 | 0.403591 | 0.908500 |
| H | -2.578828 | -0.889886 | 2.010668 |
| H | -1.894308 | 0.699949 | 1.637012 |
| C | -4.786020 | -0.698214 | 0.294658 |
| H | -4.725617 | -2.109535 | -1.355790 |
| H | -4.044190 | -0.525027 | -1.725324 |
| H | -4.387671 | 0.799062 | 1.817050 |

| | | | |
|---|-----------|-----------|----------|
| H | -3.835879 | 1.240323 | 0.201218 |
| H | -5.775138 | -0.302631 | 0.036771 |
| H | -4.942994 | -1.492794 | 1.038833 |

E-1

M06-2X SCF energy in solution: -643.47375760 a.u.

M06-2X enthalpy in solution: -643.180238 a.u.

M06-2X free energy in solution: -643.234627 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.431752 | 1.469311 | -0.315552 |
| C | -0.899881 | 1.431676 | -0.342161 |
| C | -1.846309 | 0.322825 | -0.120693 |
| C | -1.581734 | -0.968203 | -0.595605 |
| C | -3.046807 | 0.568647 | 0.560661 |
| C | -2.488715 | -2.001120 | -0.366135 |
| H | -0.678651 | -1.159146 | -1.167971 |
| C | -3.951613 | -0.465322 | 0.785853 |
| H | -3.265152 | 1.570868 | 0.917531 |
| C | -3.673072 | -1.753973 | 0.327726 |
| H | -2.275216 | -2.997065 | -0.743301 |
| H | -4.875853 | -0.264479 | 1.319929 |
| H | -4.380739 | -2.559344 | 0.501912 |
| C | 1.367592 | 0.344153 | 0.021668 |
| C | 2.121787 | -0.145851 | -1.227364 |
| C | 2.370707 | 0.798769 | 1.096156 |
| H | 0.796459 | -0.499312 | 0.433135 |
| C | 3.116185 | -1.257260 | -0.883134 |
| H | 2.661380 | 0.705786 | -1.668510 |
| H | 1.405575 | -0.490390 | -1.983625 |
| C | 3.366431 | -0.311091 | 1.441485 |

| | | | |
|---|-----------|-----------|-----------|
| H | 2.917986 | 1.676234 | 0.719516 |
| H | 1.828418 | 1.120812 | 1.993319 |
| C | 4.103778 | -0.803073 | 0.194024 |
| H | 3.652910 | -1.571670 | -1.785980 |
| H | 2.562737 | -2.135403 | -0.519156 |
| H | 4.081308 | 0.048827 | 2.190767 |
| H | 2.824715 | -1.152643 | 1.896934 |
| H | 4.786492 | -1.620897 | 0.453175 |
| H | 4.721390 | 0.014468 | -0.205658 |
| F | -1.554896 | 2.611281 | -0.586646 |
| H | 0.889701 | 2.434903 | -0.533782 |

Z-2

M06-2X SCF energy in solution: -643.47617263 a.u.

M06-2X enthalpy in solution: -643.182459 a.u.

M06-2X free energy in solution: -643.238851 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.340134 | -0.303439 | 0.067806 |
| C | 0.735753 | 0.460501 | -0.121442 |
| C | 2.163855 | 0.104346 | -0.038108 |
| C | 2.573209 | -1.232284 | 0.086914 |
| C | 3.138257 | 1.109643 | -0.083425 |
| C | 3.923828 | -1.550092 | 0.175573 |
| H | 1.837039 | -2.030200 | 0.104631 |
| C | 4.491982 | 0.785551 | 0.003650 |
| H | 2.838012 | 2.147112 | -0.184477 |
| C | 4.890789 | -0.542570 | 0.135093 |
| H | 4.223835 | -2.589804 | 0.269799 |
| H | 5.234583 | 1.577530 | -0.031860 |
| H | 5.945213 | -0.794273 | 0.201534 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.766667 | 0.147186 | -0.044626 |
| C | -2.503118 | -0.660260 | -1.128503 |
| C | -2.488202 | -0.000032 | 1.307042 |
| H | -1.788456 | 1.206752 | -0.331455 |
| C | -3.975993 | -0.256066 | -1.228178 |
| H | -2.434823 | -1.730256 | -0.879089 |
| H | -2.001024 | -0.524312 | -2.093800 |
| C | -3.961098 | 0.403671 | 1.205451 |
| H | -2.418722 | -1.049448 | 1.632021 |
| H | -1.975424 | 0.603753 | 2.065216 |
| C | -4.683273 | -0.399230 | 0.121241 |
| H | -4.478889 | -0.863441 | -1.990004 |
| H | -4.040801 | 0.789879 | -1.561170 |
| H | -4.453692 | 0.266198 | 2.175289 |
| H | -4.025056 | 1.474696 | 0.964792 |
| H | -5.727505 | -0.075064 | 0.039692 |
| H | -4.699729 | -1.460688 | 0.409023 |
| H | -0.173201 | -1.345638 | 0.332765 |
| F | 0.549281 | 1.777296 | -0.430425 |

107

M06-2X SCF energy in solution: -347.66381256 a.u.

M06-2X enthalpy in solution: -347.515112 a.u.

M06-2X free energy in solution: -347.557987 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|-----------|-----------|
| C | 0.042875 | -0.000006 | 0.000164 |
| C | 0.752427 | 1.211413 | 0.000032 |
| C | 0.752407 | -1.211428 | 0.000067 |
| C | 2.144780 | 1.207463 | -0.000003 |
| H | 0.204739 | 2.149250 | 0.000103 |

| | | | |
|---|-----------|-----------|-----------|
| C | 2.144778 | -1.207476 | -0.000006 |
| H | 0.204712 | -2.149260 | 0.000129 |
| C | 2.844598 | -0.000015 | -0.000049 |
| H | 2.684738 | 2.149932 | 0.000000 |
| H | 2.684731 | -2.149947 | -0.000054 |
| H | 3.930834 | -0.000019 | -0.000056 |
| C | -1.395057 | 0.000039 | -0.000023 |
| C | -2.606953 | 0.000059 | -0.000370 |
| C | -4.069785 | -0.000001 | -0.000012 |
| H | -4.457182 | -0.154210 | 1.012081 |
| H | -4.456272 | 0.953647 | -0.371995 |
| H | -4.456722 | -0.799682 | -0.639004 |

108

M06-2X SCF energy in solution: -772.69740850 a.u.

M06-2X enthalpy in solution: -772.515862 a.u.

M06-2X free energy in solution: -772.575496 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.650503 | -1.008706 | -0.002891 |
| C | -1.230239 | -0.625626 | 1.241608 |
| C | -1.376631 | -0.863572 | -1.220977 |
| C | -2.517041 | -0.128731 | 1.257967 |
| H | -0.642703 | -0.721380 | 2.148683 |
| C | -2.658930 | -0.358801 | -1.181970 |
| H | -0.898622 | -1.139624 | -2.155647 |
| C | -3.219238 | 0.004790 | 0.051980 |
| H | -2.977895 | 0.174274 | 2.191660 |
| H | -3.227768 | -0.229581 | -2.096148 |
| H | -4.227118 | 0.410074 | 0.072192 |
| C | 0.634224 | -1.472414 | -0.032704 |

| | | | |
|---|-----------|-----------|-----------|
| C | 1.837721 | -1.925352 | -0.046632 |
| C | 2.234034 | -3.373470 | 0.104642 |
| H | 2.792211 | -3.681885 | -0.783472 |
| H | 2.890580 | -3.469972 | 0.973583 |
| H | 1.364576 | -4.019522 | 0.231360 |
| B | 1.072323 | 1.777976 | -0.033451 |
| F | -0.298023 | 2.023745 | -0.213167 |
| F | 1.521971 | 0.900938 | -1.049093 |
| F | 1.791799 | 2.974583 | -0.091838 |
| F | 1.276576 | 1.152381 | 1.214052 |
| H | 2.613815 | -1.165783 | -0.180686 |

108a

M06-2X SCF energy in solution: -772.69800641 a.u.

M06-2X enthalpy in solution: -772.516367 a.u.

M06-2X free energy in solution: -772.574832 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -0.833727 | -1.076037 | -0.000017 |
| C | -1.444101 | -0.724569 | -1.238564 |
| C | -1.443810 | -0.724236 | 1.238588 |
| C | -2.651738 | -0.058636 | -1.227125 |
| H | -0.940383 | -0.980046 | -2.165367 |
| C | -2.651486 | -0.058369 | 1.227268 |
| H | -0.939841 | -0.979437 | 2.165330 |
| C | -3.245343 | 0.270250 | 0.000099 |
| H | -3.133862 | 0.223209 | -2.156751 |
| H | -3.133425 | 0.223665 | 2.156934 |
| H | -4.191678 | 0.804002 | 0.000142 |
| C | 0.370171 | -1.723349 | -0.000016 |
| C | 1.460736 | -2.405402 | 0.000119 |

| | | | |
|---|-----------|-----------|-----------|
| C | 2.878259 | -1.891547 | 0.000050 |
| H | 2.900837 | -0.804163 | -0.000330 |
| H | 3.389150 | -2.276820 | 0.886962 |
| H | 3.389241 | -2.277313 | -0.886604 |
| B | 1.139687 | 1.474394 | -0.000066 |
| F | -0.194090 | 1.907245 | -0.000002 |
| F | 2.005689 | 2.571286 | -0.000216 |
| F | 1.373522 | 0.679510 | 1.145195 |
| F | 1.373311 | 0.679329 | -1.145266 |
| H | 1.301871 | -3.490023 | 0.000212 |

TS-5

M06-2X SCF energy in solution: -1940.15662007 a.u.

M06-2X enthalpy in solution: -1939.900421 a.u.

M06-2X free energy in solution: -1939.977209 a.u.

Imaginary frequency: -751.0513 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -2.478431 | 0.920583 | -0.008104 |
| C | -3.061967 | 0.528361 | -1.231232 |
| C | -3.066251 | 0.553163 | 1.220639 |
| C | -4.232264 | -0.213820 | -1.218041 |
| H | -2.577929 | 0.802390 | -2.163337 |
| C | -4.236735 | -0.188896 | 1.218063 |
| H | -2.585715 | 0.846057 | 2.148744 |
| C | -4.814062 | -0.569536 | 0.002743 |
| H | -4.687627 | -0.528955 | -2.151132 |
| H | -4.695882 | -0.484705 | 2.155606 |
| H | -5.726338 | -1.159278 | 0.006990 |
| C | -1.304293 | 1.686982 | -0.014409 |
| C | -0.212672 | 2.290890 | -0.020838 |

| | | | |
|----|-----------|-----------|-----------|
| C | 0.493570 | 3.603082 | -0.031773 |
| H | -0.220696 | 4.428148 | -0.048668 |
| H | 1.124106 | 3.683820 | 0.858459 |
| H | 1.140365 | 3.661228 | -0.912011 |
| B | -0.462885 | -1.721315 | 0.031851 |
| F | -1.703739 | -2.371366 | 0.036661 |
| F | -0.353456 | -0.895664 | 1.169839 |
| F | 0.580819 | -2.661087 | 0.044024 |
| F | -0.350948 | -0.922090 | -1.124414 |
| C | 2.330988 | 0.036403 | -1.153809 |
| C | 2.344145 | 0.068944 | 1.136417 |
| C | 3.261395 | -0.968610 | 1.208688 |
| C | 3.702803 | -1.512785 | 0.005846 |
| C | 3.247439 | -1.003036 | -1.206930 |
| H | 3.606179 | -1.334406 | 2.168306 |
| H | 4.410763 | -2.335575 | 0.013574 |
| H | 3.581285 | -1.396003 | -2.159610 |
| N | 1.882321 | 0.548251 | -0.013064 |
| H | 0.629903 | 1.347980 | -0.015548 |
| Cl | 1.741625 | 0.771363 | -2.606379 |
| Cl | 1.772710 | 0.846262 | 2.574160 |

TS-5a

M06-2X SCF energy in solution: -1940.15080370 a.u.

M06-2X enthalpy in solution: -1939.894878 a.u.

M06-2X free energy in solution: -1939.976304 a.u.

Imaginary frequency: -638.9062 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|----------|----------|-----------|
| C | 1.091725 | 0.922057 | 0.008436 |
| C | 1.290358 | 1.663609 | -1.171380 |

| | | | |
|----|-----------|-----------|-----------|
| C | 1.350358 | 1.489863 | 1.270127 |
| C | 1.731179 | 2.976501 | -1.081117 |
| H | 1.113419 | 1.193634 | -2.134057 |
| C | 1.791649 | 2.803430 | 1.344939 |
| H | 1.220772 | 0.887285 | 2.163763 |
| C | 1.979994 | 3.541217 | 0.173008 |
| H | 1.896223 | 3.556886 | -1.983076 |
| H | 2.003222 | 3.250740 | 2.310760 |
| H | 2.335679 | 4.565592 | 0.237173 |
| C | 0.665947 | -0.422614 | -0.075032 |
| C | 0.086361 | -1.515412 | -0.133106 |
| C | -0.004450 | -2.987042 | -0.230545 |
| H | 1.003617 | -3.404494 | -0.285702 |
| H | -0.518529 | -3.388993 | 0.646782 |
| H | -0.565640 | -3.268781 | -1.125757 |
| B | 3.881720 | -1.018462 | -0.032069 |
| F | 4.309250 | 0.317775 | -0.050444 |
| F | 3.120272 | -1.254659 | 1.131547 |
| F | 3.072943 | -1.268681 | -1.161394 |
| F | 4.991102 | -1.875866 | -0.050240 |
| C | -3.084039 | -0.074006 | -1.130371 |
| C | -3.055445 | -0.225493 | 1.157222 |
| C | -4.356829 | 0.243121 | 1.266356 |
| C | -5.022567 | 0.558043 | 0.084514 |
| C | -4.387511 | 0.401086 | -1.144858 |
| H | -4.824564 | 0.355044 | 2.237342 |
| H | -6.042468 | 0.927219 | 0.121708 |
| H | -4.879643 | 0.636788 | -2.081140 |
| N | -2.435430 | -0.377717 | -0.009570 |
| H | -1.033220 | -0.870460 | -0.063430 |
| Cl | -2.207194 | -0.303526 | -2.605669 |
| Cl | -2.144096 | -0.650441 | 2.566175 |

TS-6

M06-2X SCF energy in solution: -772.69054680 a.u.

M06-2X enthalpy in solution: -772.509873 a.u.

M06-2X free energy in solution: -772.566737 a.u.

Imaginary frequency: -306.1641 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.912982 | 0.500825 | -0.085483 |
| C | 1.281097 | -0.014209 | 1.176200 |
| C | 1.652516 | 0.177342 | -1.244347 |
| C | 2.400104 | -0.827075 | 1.273951 |
| H | 0.682143 | 0.230547 | 2.047316 |
| C | 2.760028 | -0.645967 | -1.131705 |
| H | 1.336062 | 0.570770 | -2.205498 |
| C | 3.128245 | -1.144173 | 0.123712 |
| H | 2.699449 | -1.227865 | 2.236602 |
| H | 3.336532 | -0.908721 | -2.012469 |
| H | 3.995468 | -1.793376 | 0.204370 |
| C | -0.213197 | 1.332422 | -0.186487 |
| C | -0.919174 | 2.417885 | -0.123390 |
| C | -0.277638 | 3.732783 | 0.246372 |
| H | -0.429659 | 4.444989 | -0.569846 |
| H | -0.768921 | 4.126038 | 1.141046 |
| H | 0.791520 | 3.628146 | 0.439595 |
| B | -1.814499 | -1.135940 | -0.003119 |
| F | -0.805487 | -2.040152 | -0.301667 |
| F | -1.588878 | 0.064820 | -0.821783 |
| F | -3.065086 | -1.623737 | -0.339141 |
| F | -1.755600 | -0.729036 | 1.326668 |
| H | -1.984424 | 2.383123 | -0.335146 |

TS-6a

M06-2X SCF energy in solution: -772.69137669 a.u.

M06-2X enthalpy in solution: -772.510914 a.u.

M06-2X free energy in solution: -772.569025 a.u.

Imaginary frequency: -297.7995 cm⁻¹

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | -1.095505 | 0.719225 | 0.052795 |
| C | -1.516660 | -0.024255 | 1.175663 |
| C | -1.921519 | 0.843856 | -1.084905 |
| C | -2.771566 | -0.614777 | 1.163724 |
| H | -0.852324 | -0.125648 | 2.028158 |
| C | -3.170117 | 0.243836 | -1.083301 |
| H | -1.565514 | 1.404649 | -1.943701 |
| C | -3.589624 | -0.480832 | 0.038333 |
| H | -3.111541 | -1.186827 | 2.020617 |
| H | -3.818214 | 0.330524 | -1.949123 |
| H | -4.568501 | -0.951722 | 0.032218 |
| C | 0.170260 | 1.330623 | 0.069927 |
| C | 1.062725 | 2.227747 | 0.339858 |
| C | 2.544223 | 2.276760 | 0.136921 |
| H | 2.803948 | 3.190999 | -0.404196 |
| H | 3.030885 | 2.315876 | 1.116363 |
| H | 2.901010 | 1.407294 | -0.411123 |
| B | 1.632673 | -1.230573 | -0.126838 |
| F | 1.211162 | -0.059330 | -0.905099 |
| F | 0.621882 | -2.176276 | -0.213617 |
| F | 2.818372 | -1.681388 | -0.682717 |
| F | 1.811008 | -0.799698 | 1.186249 |
| H | 0.581760 | 3.084858 | 0.827546 |

E-95

M06-2X SCF energy in solution: -448.14319944 a.u.

M06-2X enthalpy in solution: -447.977904 a.u.

M06-2X free energy in solution: -448.021817 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.089204 | 0.222236 | -0.079377 |
| C | 0.538236 | -1.039535 | -0.490367 |
| C | 1.019299 | 1.163123 | 0.385067 |
| C | 1.891223 | -1.363976 | -0.409470 |
| H | -0.166952 | -1.757693 | -0.898036 |
| C | 2.370150 | 0.835499 | 0.462537 |
| H | 0.679652 | 2.148609 | 0.689810 |
| C | 2.809260 | -0.430251 | 0.070652 |
| H | 2.229207 | -2.343555 | -0.734994 |
| H | 3.081553 | 1.569461 | 0.829855 |
| H | 3.863756 | -0.683832 | 0.130308 |
| C | -1.337961 | 0.580897 | -0.147834 |
| C | -2.431043 | -0.148001 | 0.073197 |
| C | -2.472743 | -1.575522 | 0.531567 |
| H | -3.285179 | -1.705373 | 1.253566 |
| H | -2.671712 | -2.260389 | -0.302051 |
| H | -1.539709 | -1.884748 | 1.010129 |
| H | -3.381798 | 0.361537 | -0.070600 |
| F | -1.518063 | 1.898796 | -0.475979 |

Z-95

M06-2X SCF energy in solution: -448.14595773 a.u.

M06-2X enthalpy in solution: -447.980767 a.u.

M06-2X free energy in solution: -448.025667 a.u.

Cartesian coordinates

| ATOM | X | Y | Z |
|------|-----------|-----------|-----------|
| C | 0.253328 | 0.035832 | -0.021565 |
| C | 1.065817 | 1.169671 | 0.108504 |
| C | 0.858347 | -1.224942 | -0.133791 |
| C | 2.453887 | 1.042570 | 0.142388 |
| H | 0.611309 | 2.151715 | 0.187921 |
| C | 2.243338 | -1.347020 | -0.094878 |
| H | 0.248421 | -2.113434 | -0.267772 |
| C | 3.047998 | -0.214060 | 0.044954 |
| H | 3.070109 | 1.931019 | 0.246254 |
| H | 2.696997 | -2.329753 | -0.185566 |
| H | 4.129332 | -0.312139 | 0.070254 |
| C | -1.213055 | 0.182029 | -0.035730 |
| C | -2.155007 | -0.741849 | 0.151333 |
| C | -3.629578 | -0.487412 | 0.107650 |
| H | -4.093537 | -0.747826 | 1.065985 |
| H | -3.855909 | 0.557902 | -0.112263 |
| H | -4.103653 | -1.112667 | -0.657825 |
| F | -1.603497 | 1.471212 | -0.257649 |
| H | -1.822052 | -1.754642 | 0.358660 |

11. References

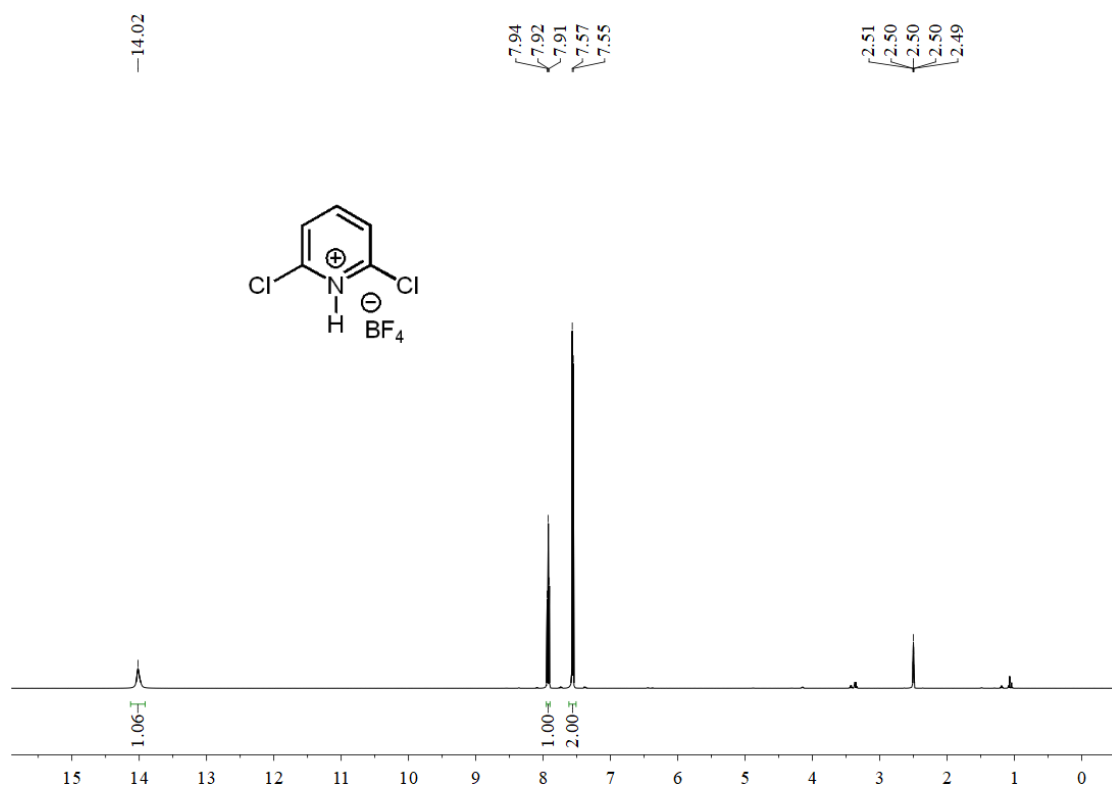
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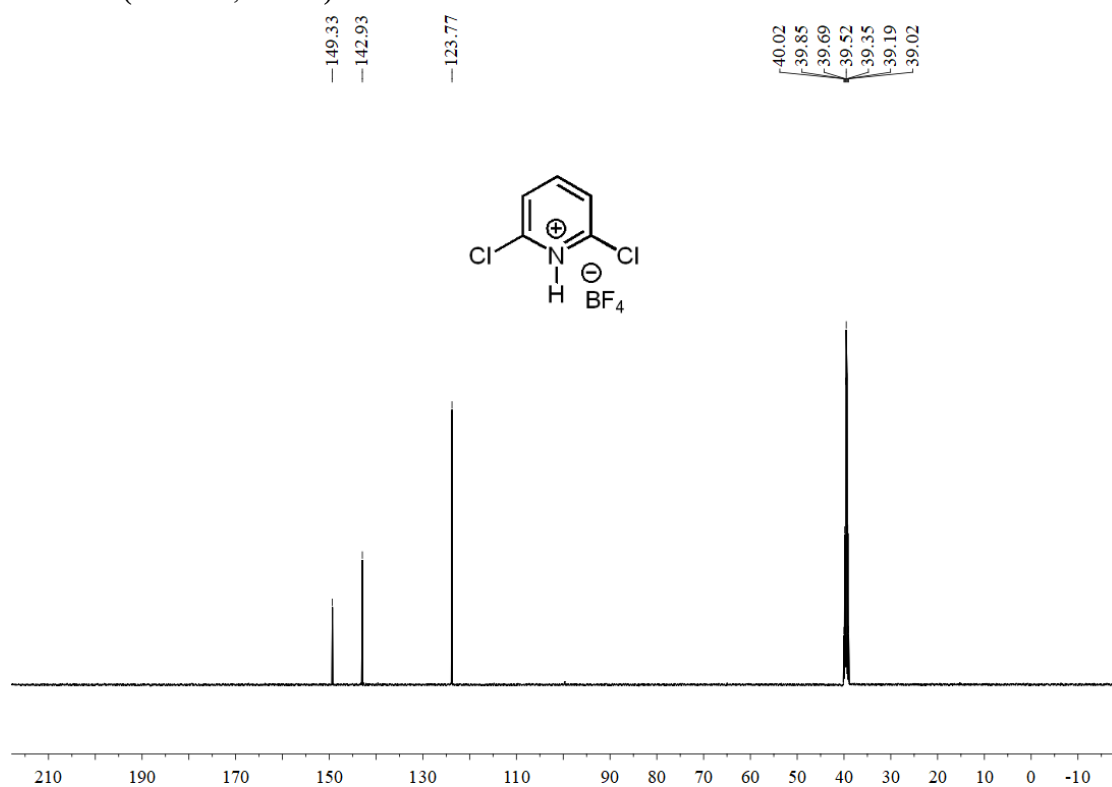
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12. Copies of NMR Spectra

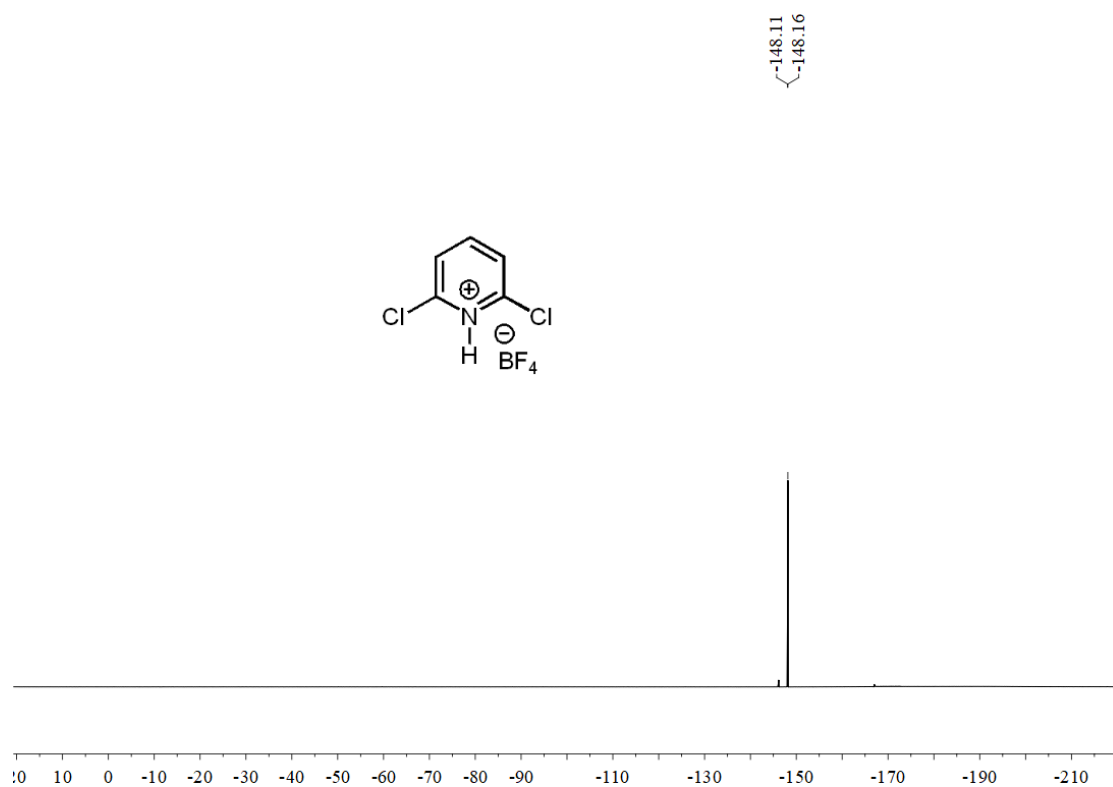
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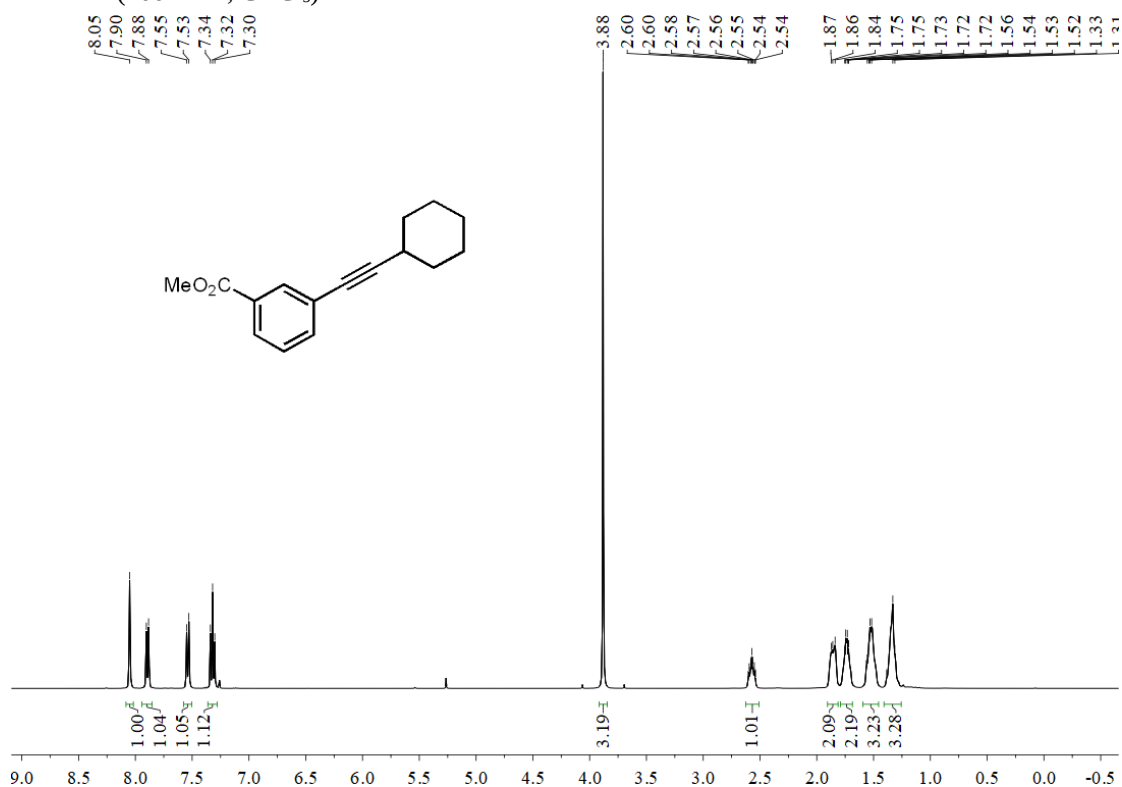
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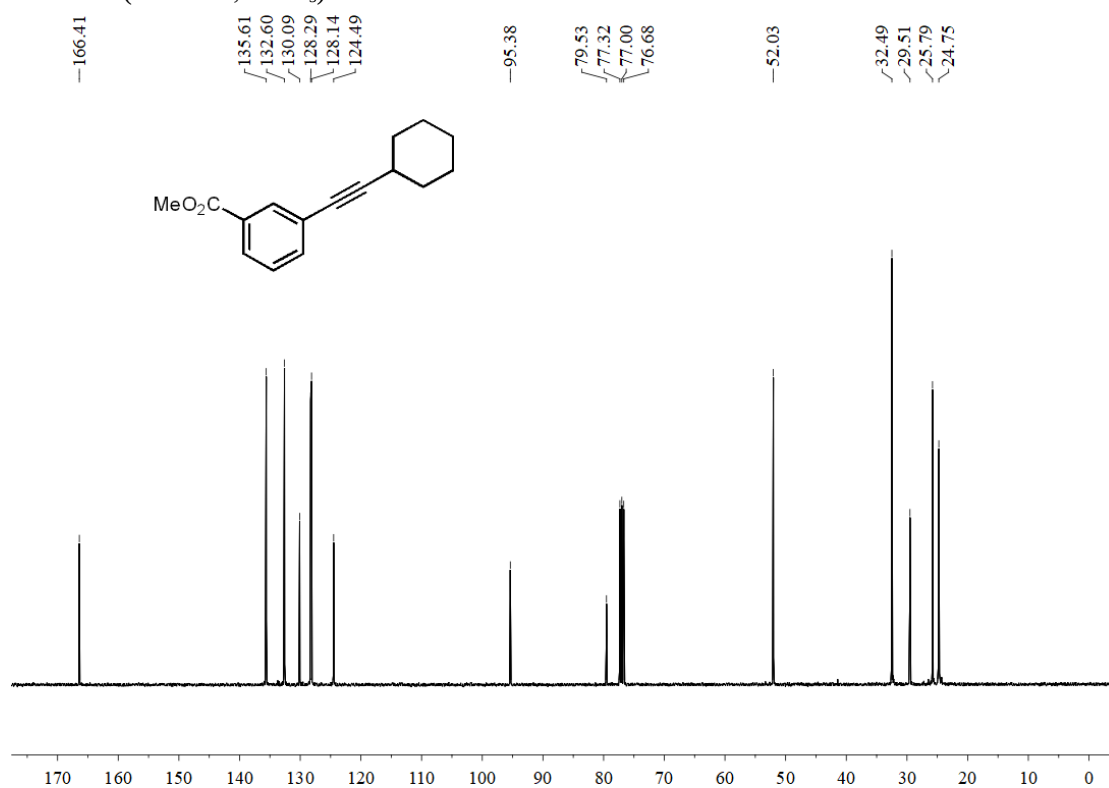
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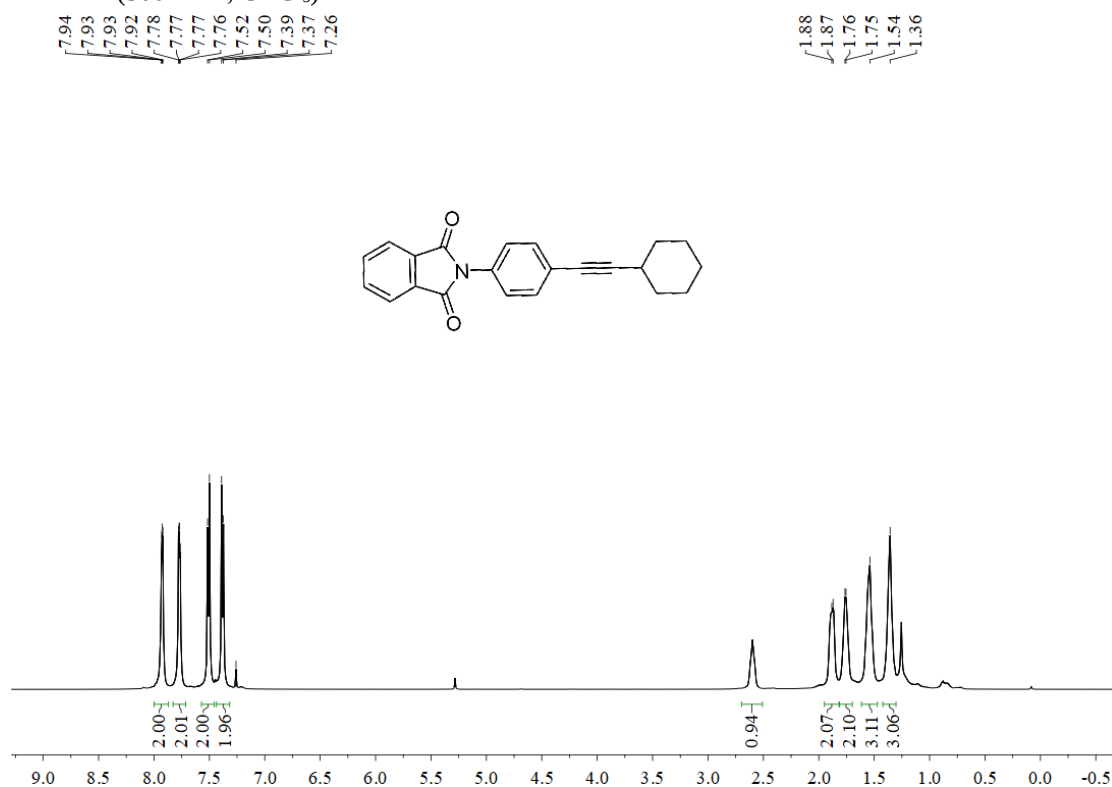
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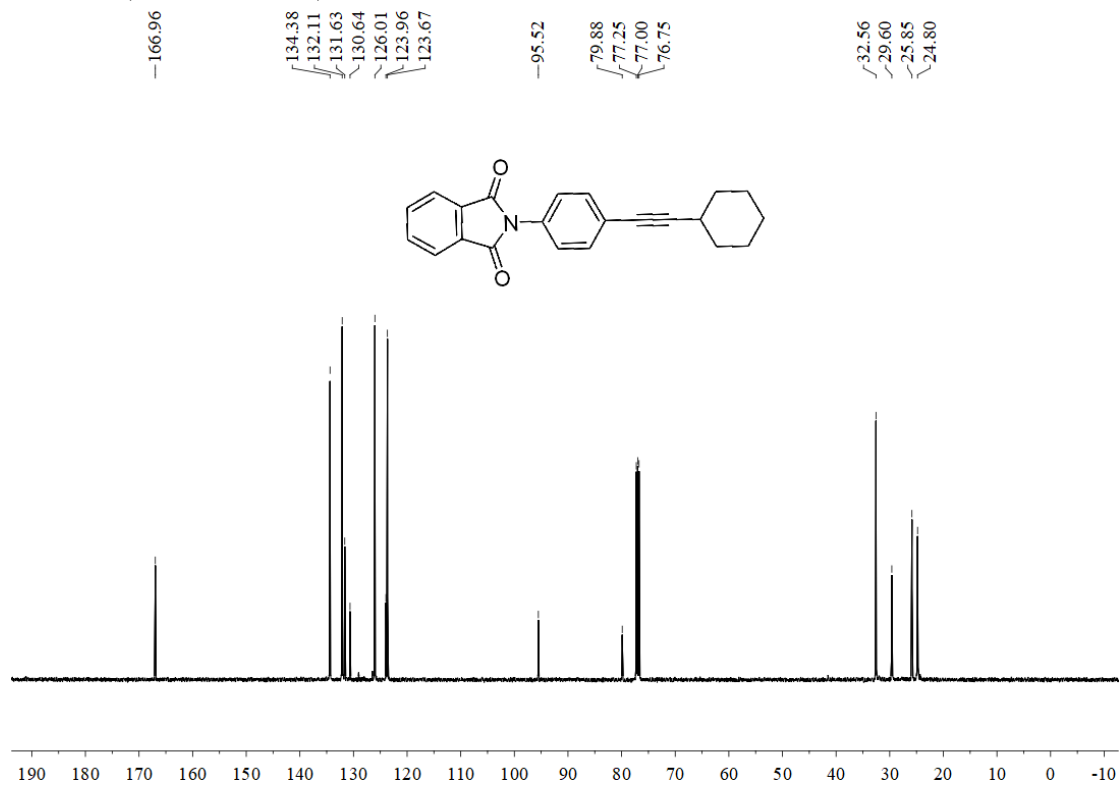
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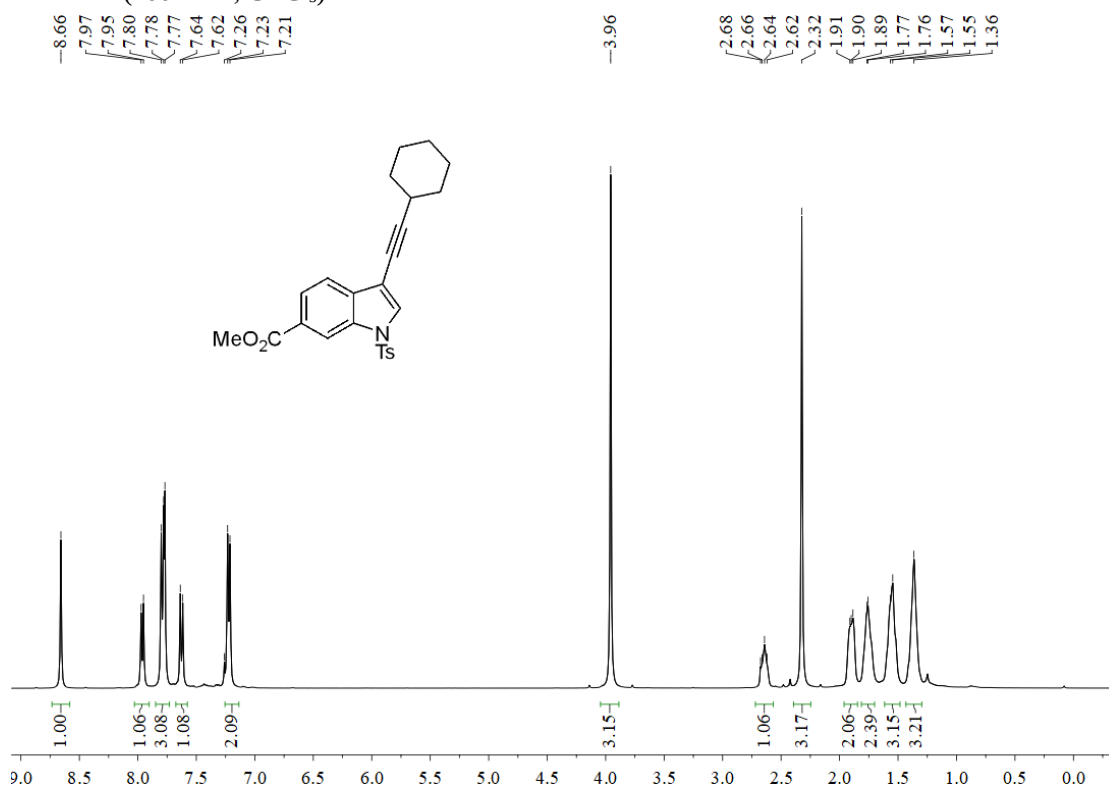
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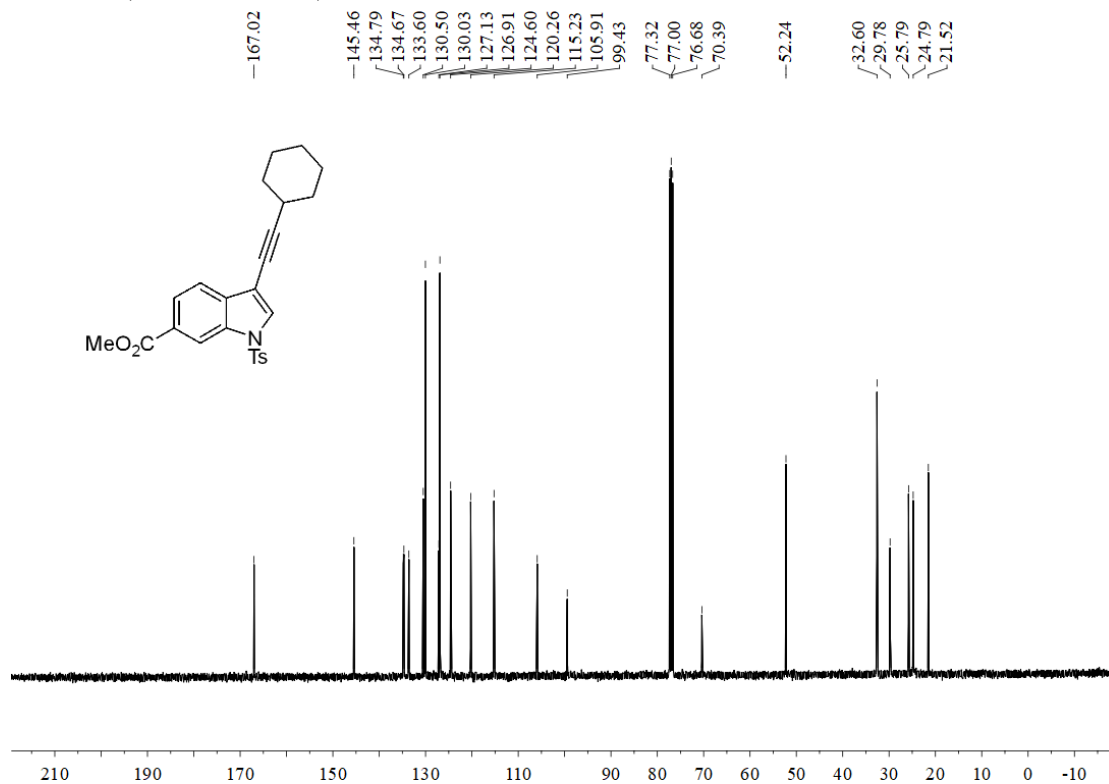
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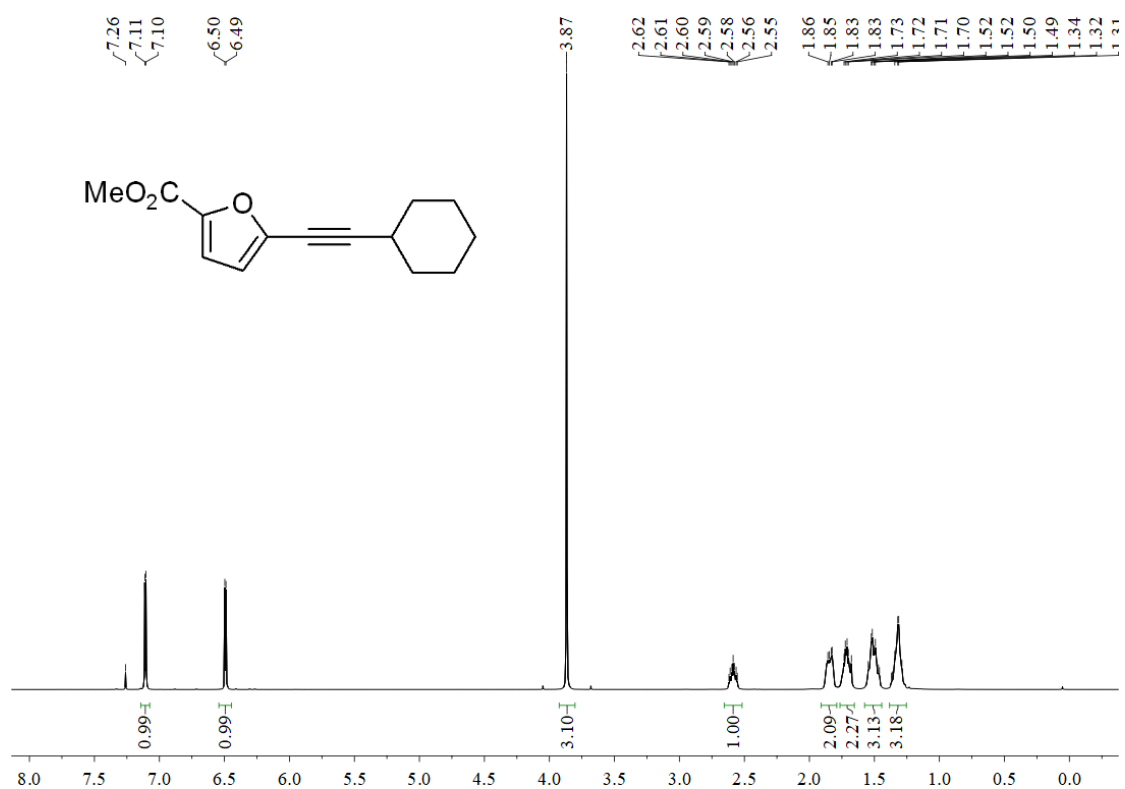
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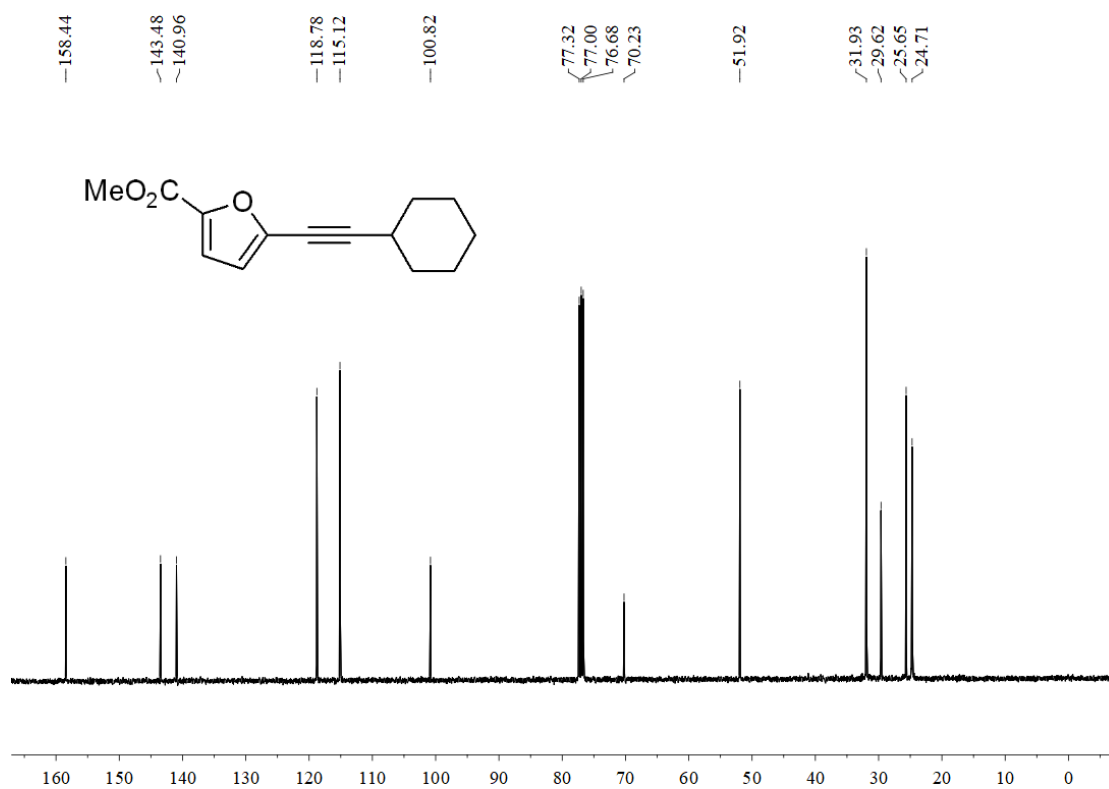
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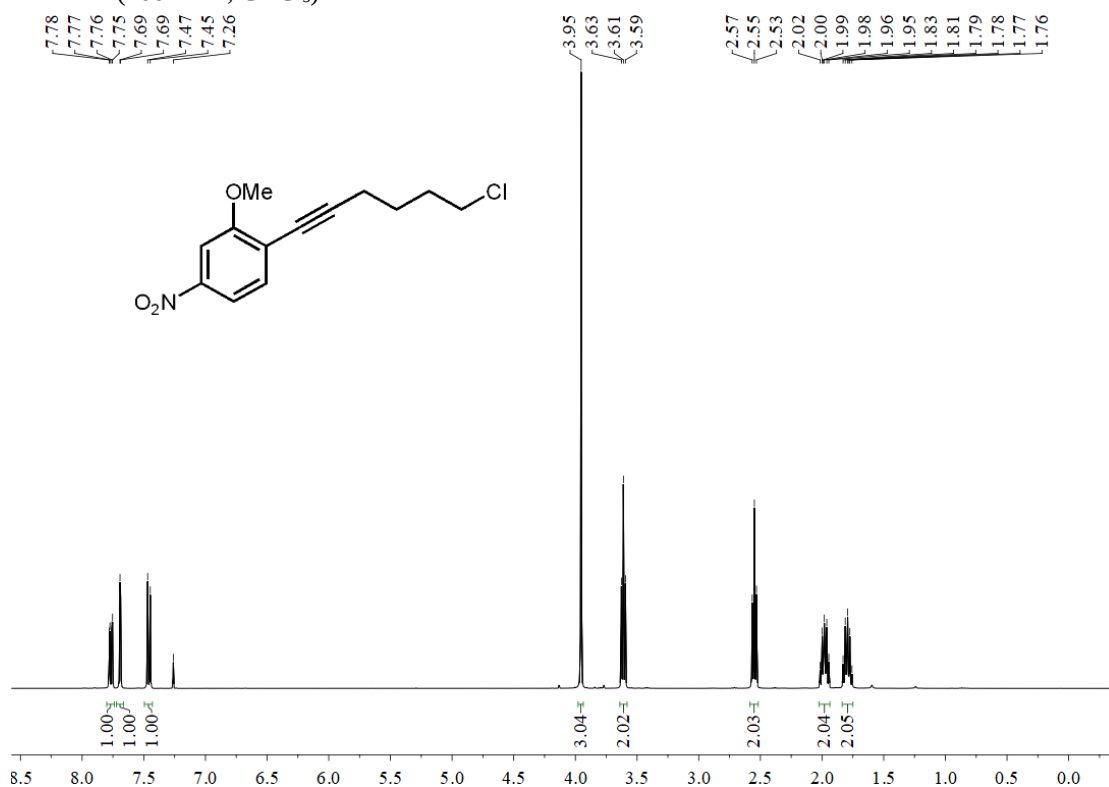
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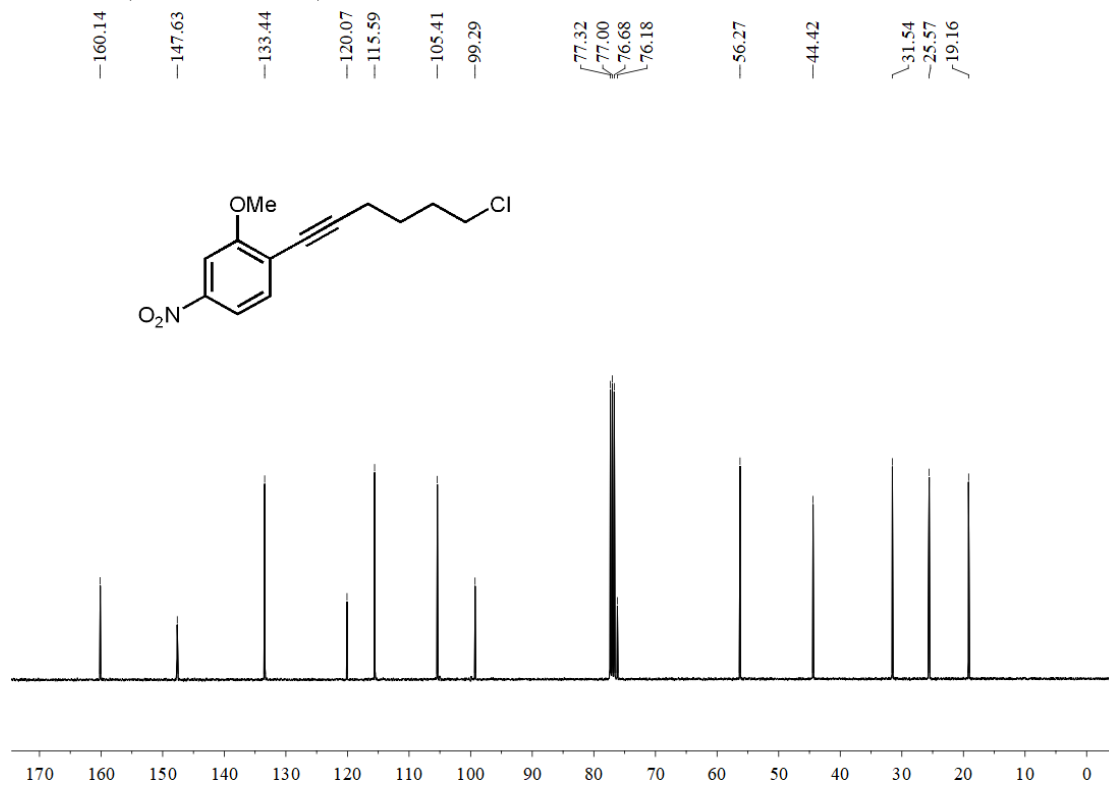
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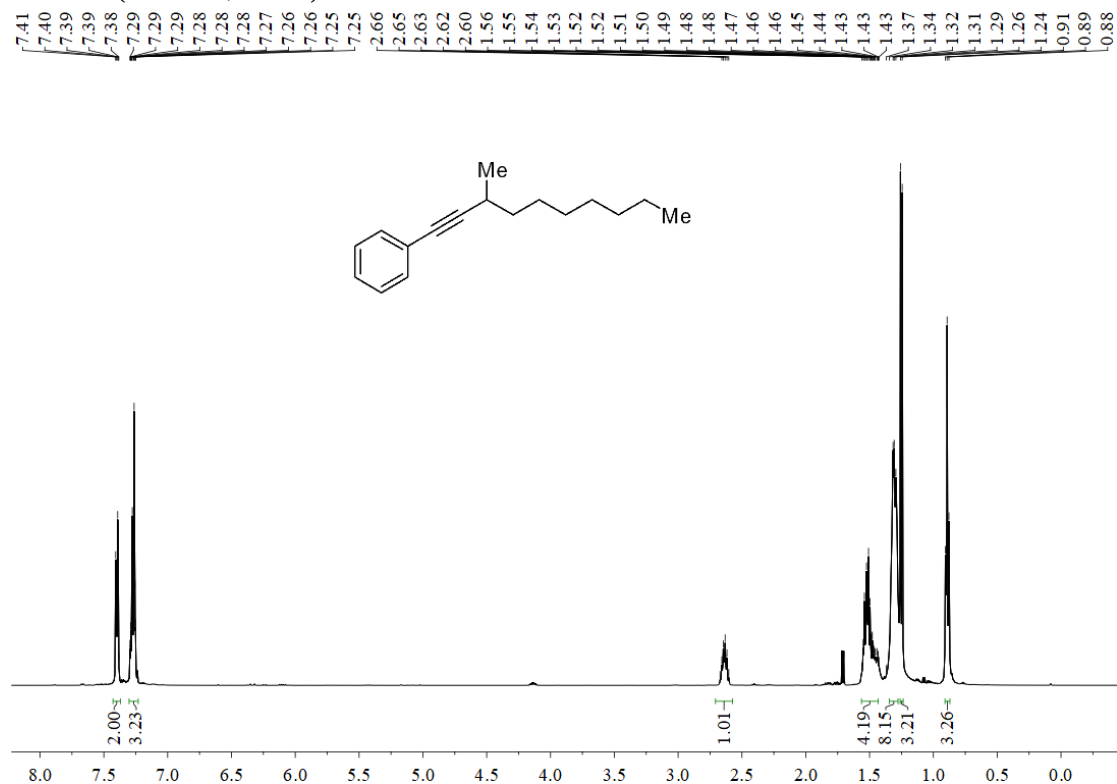
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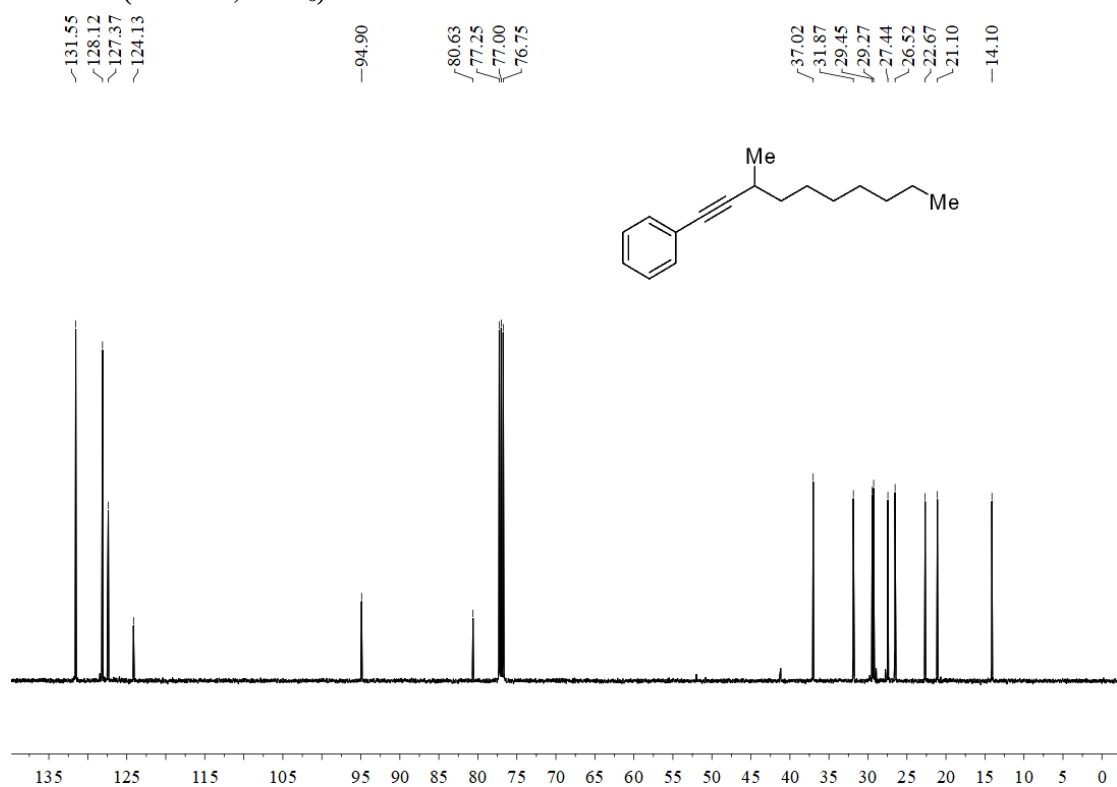
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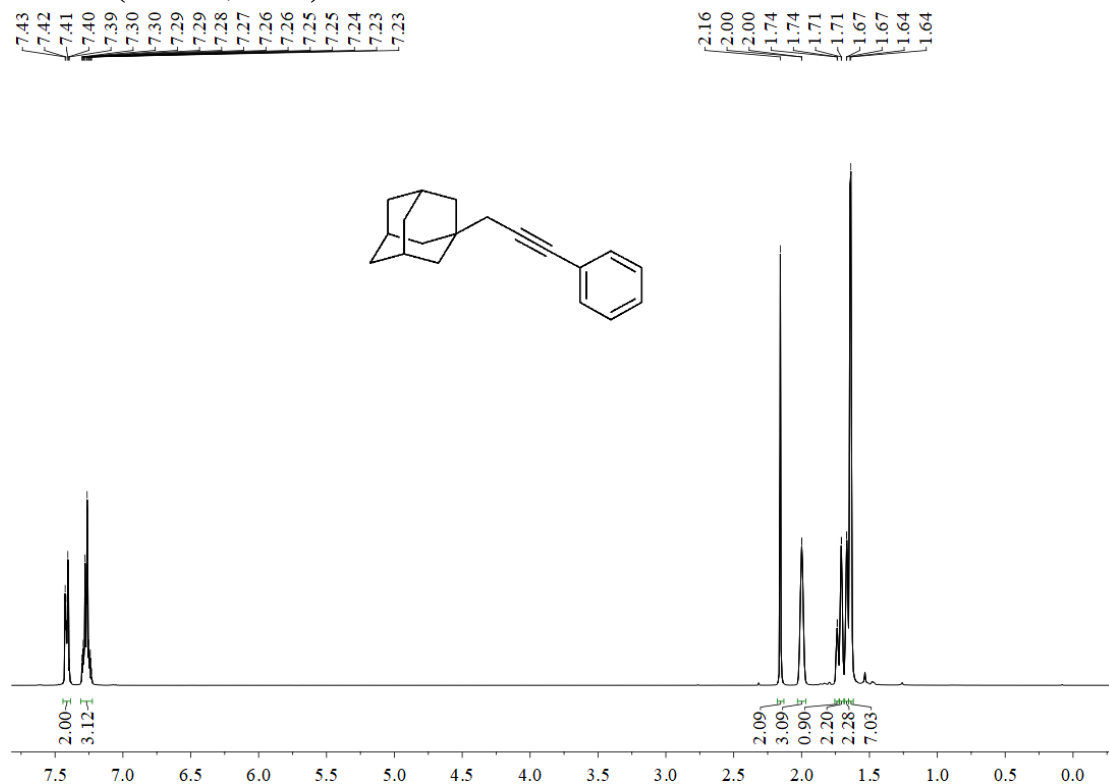
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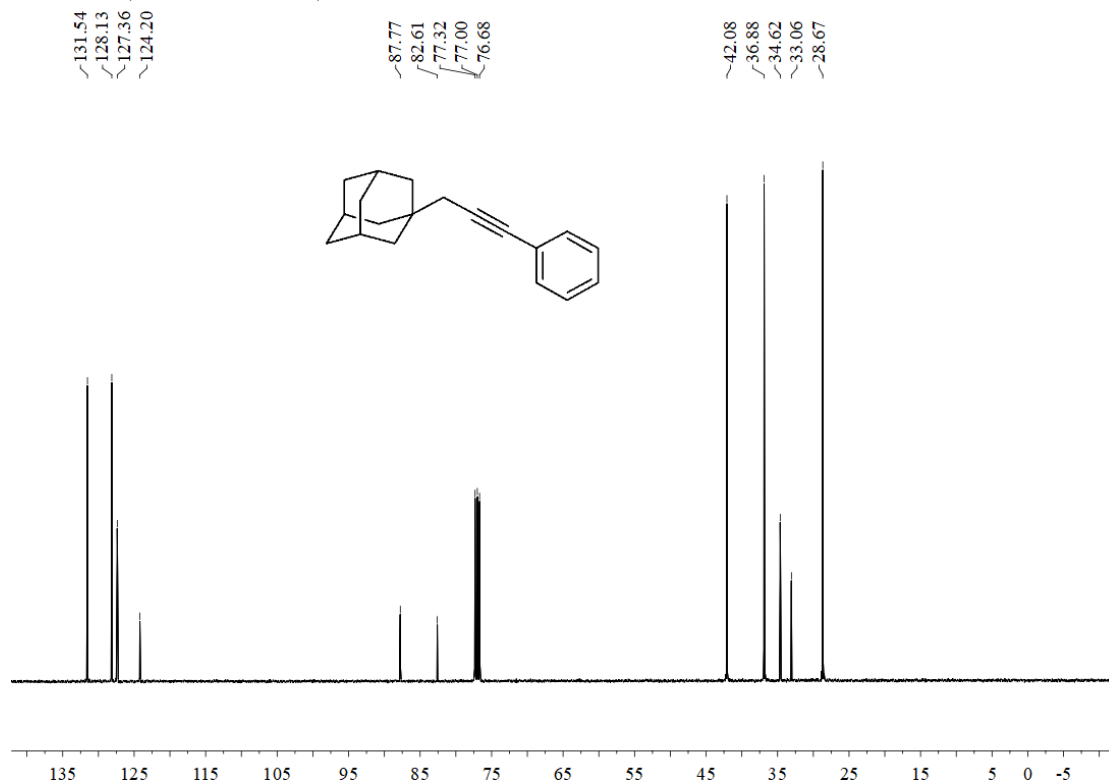
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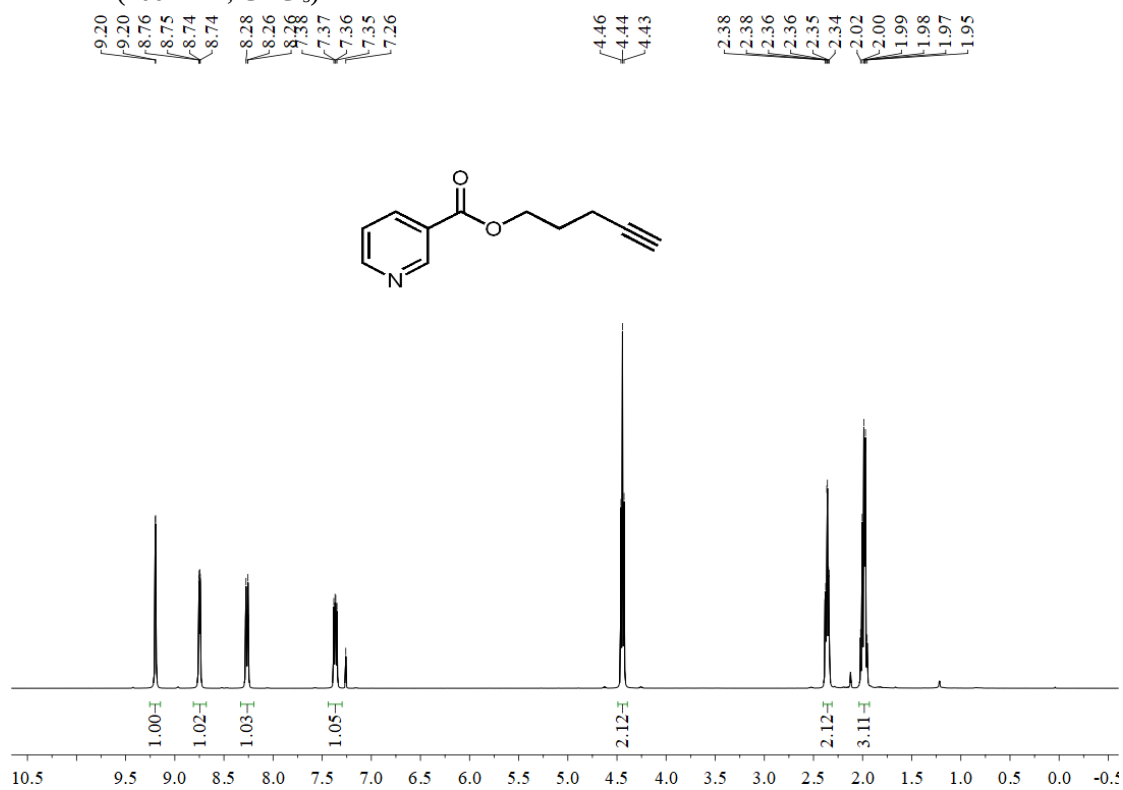
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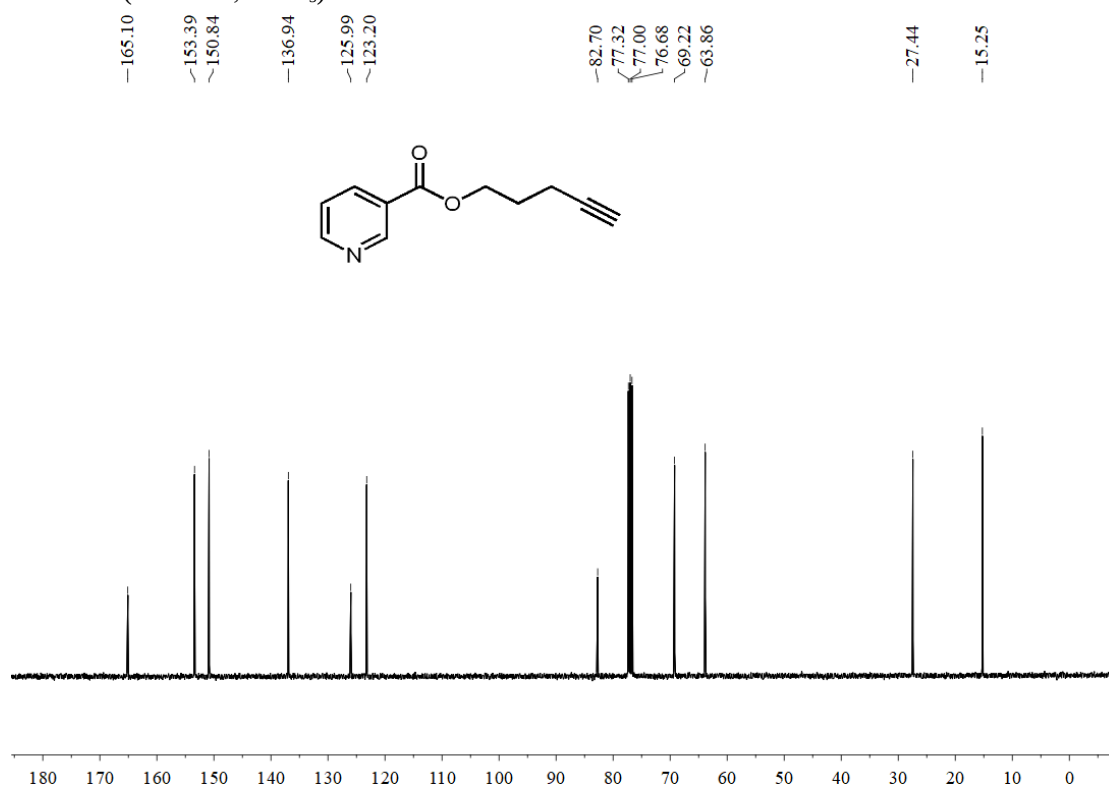
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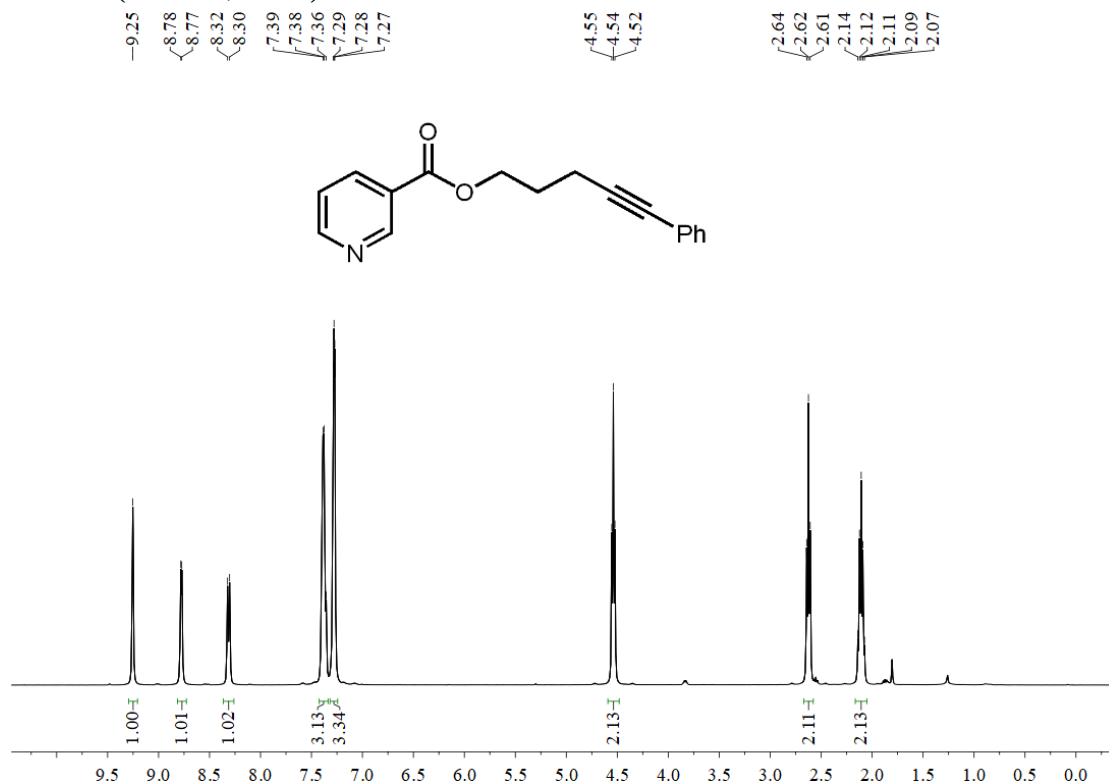
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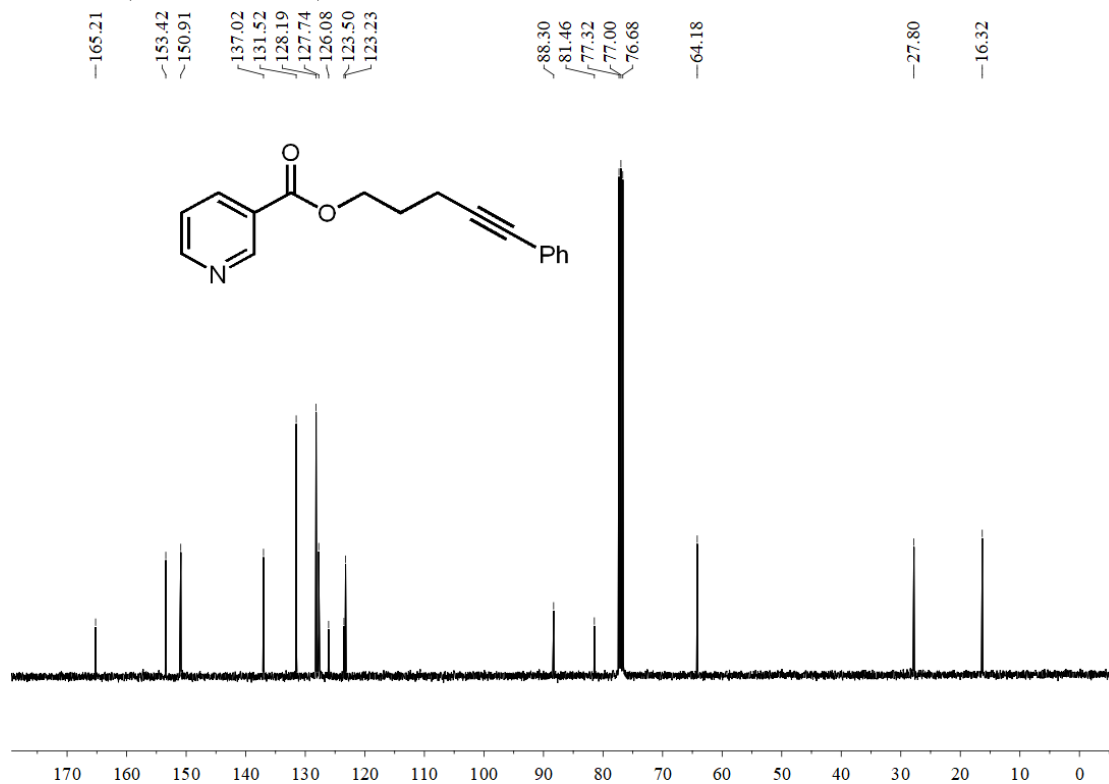
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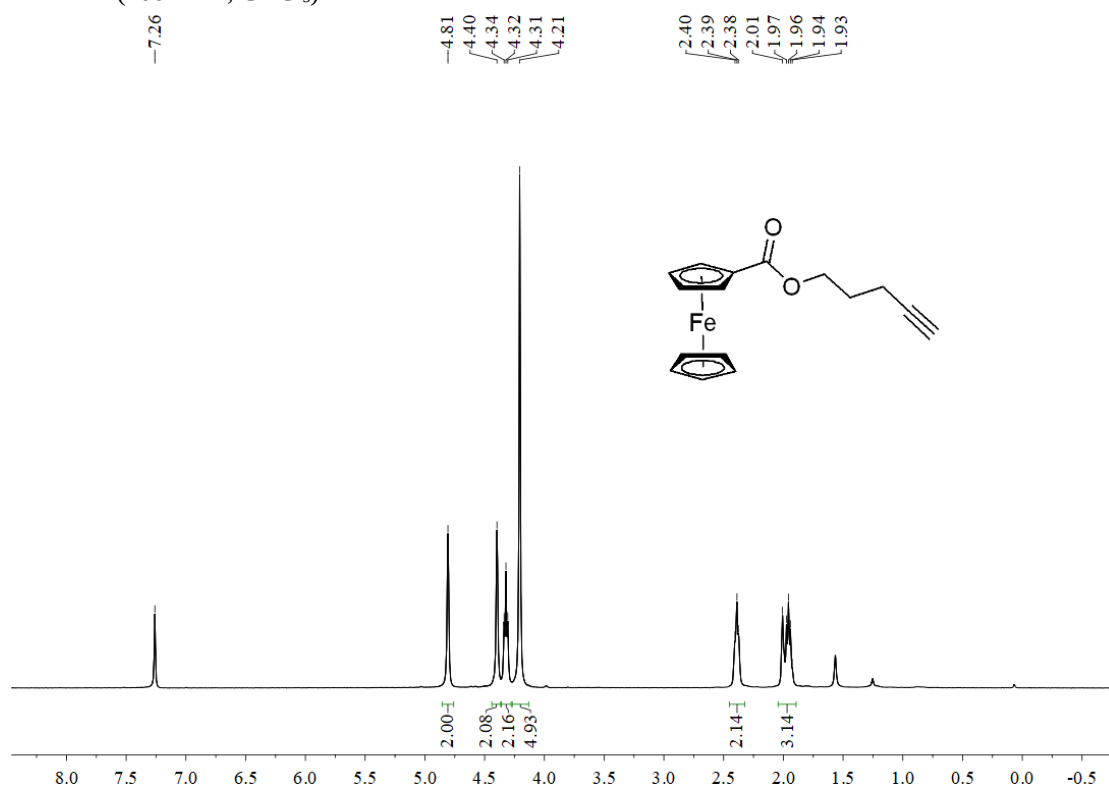
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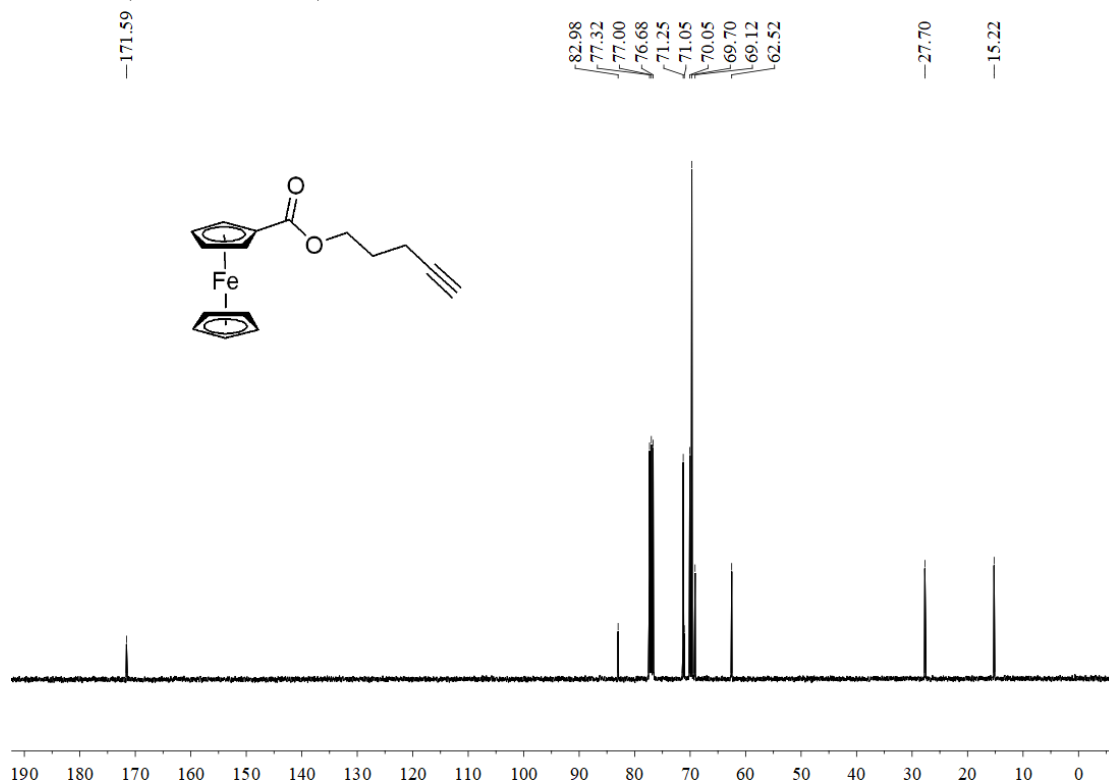
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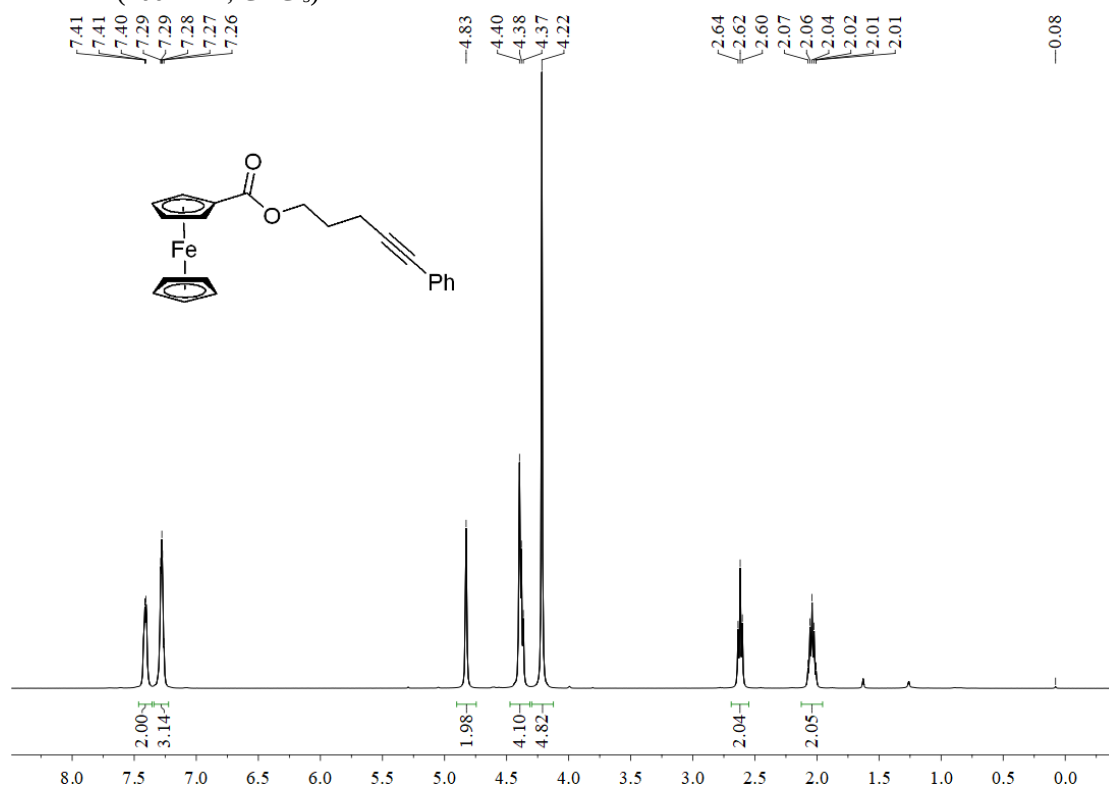
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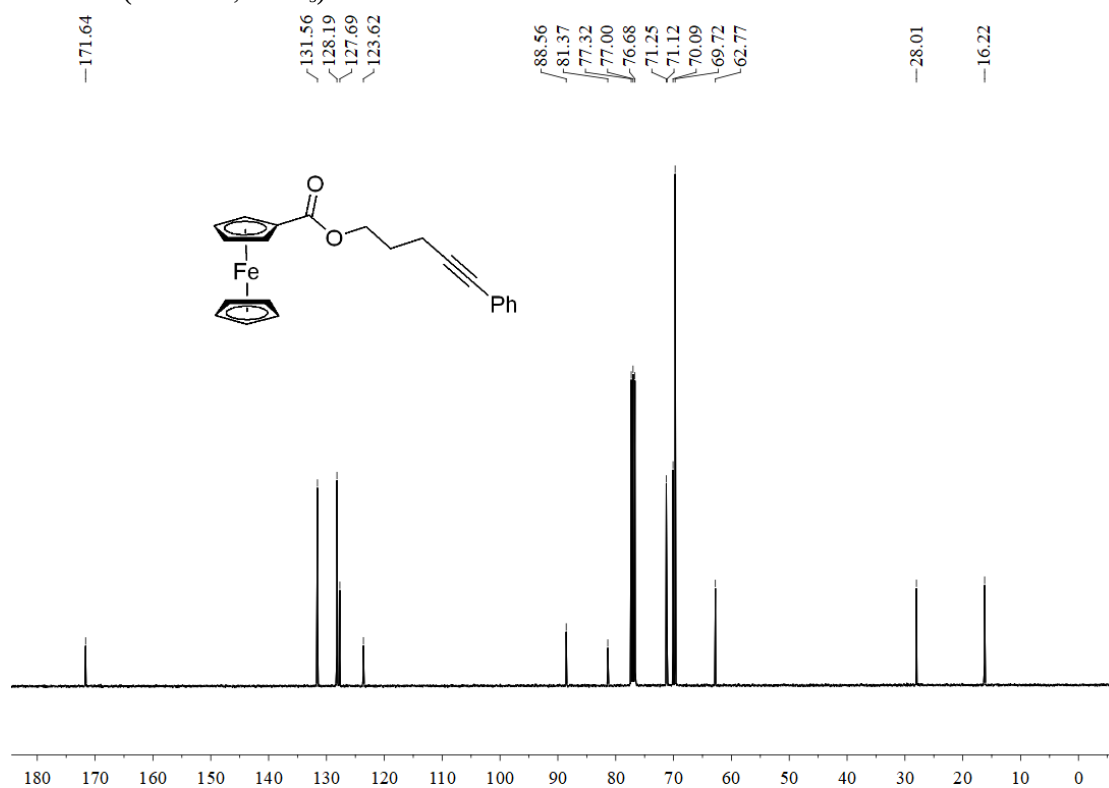
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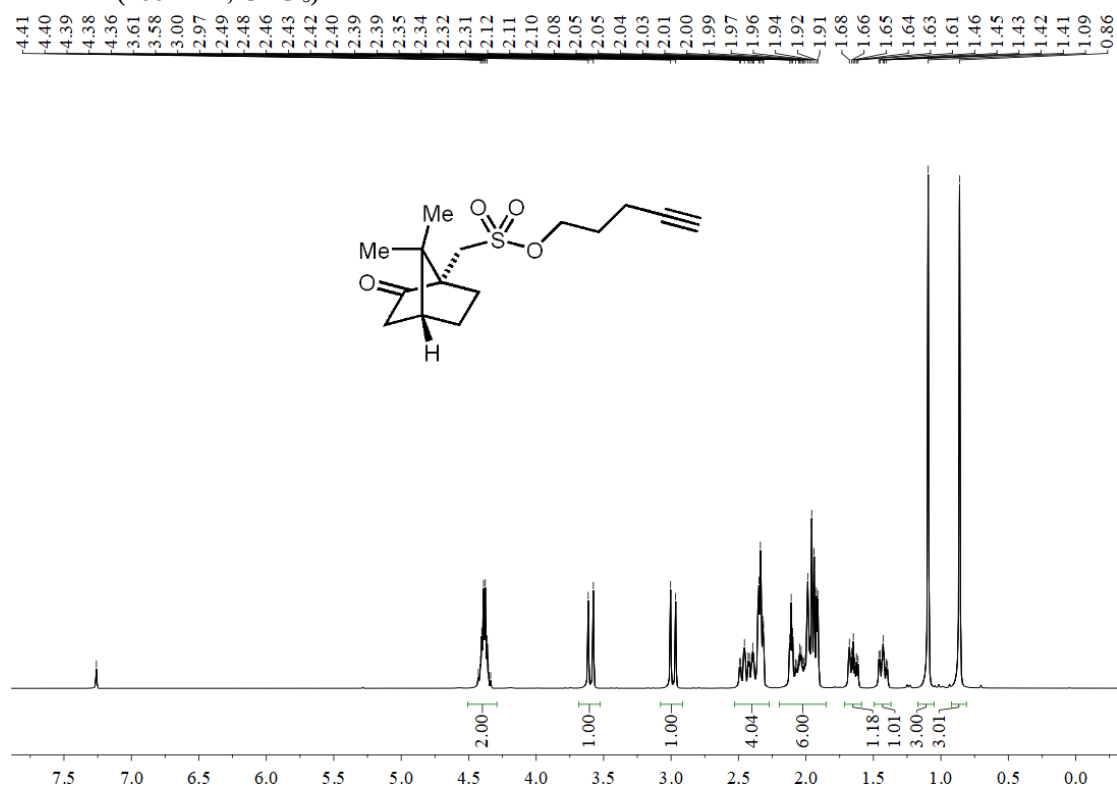
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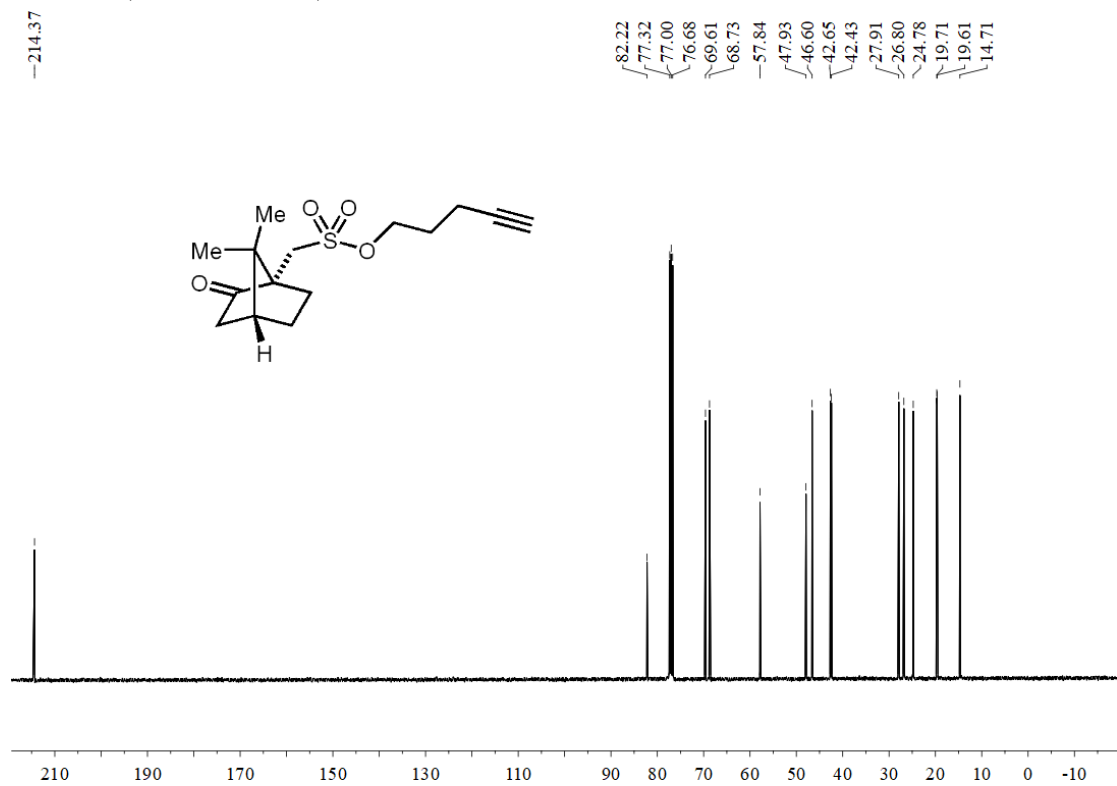
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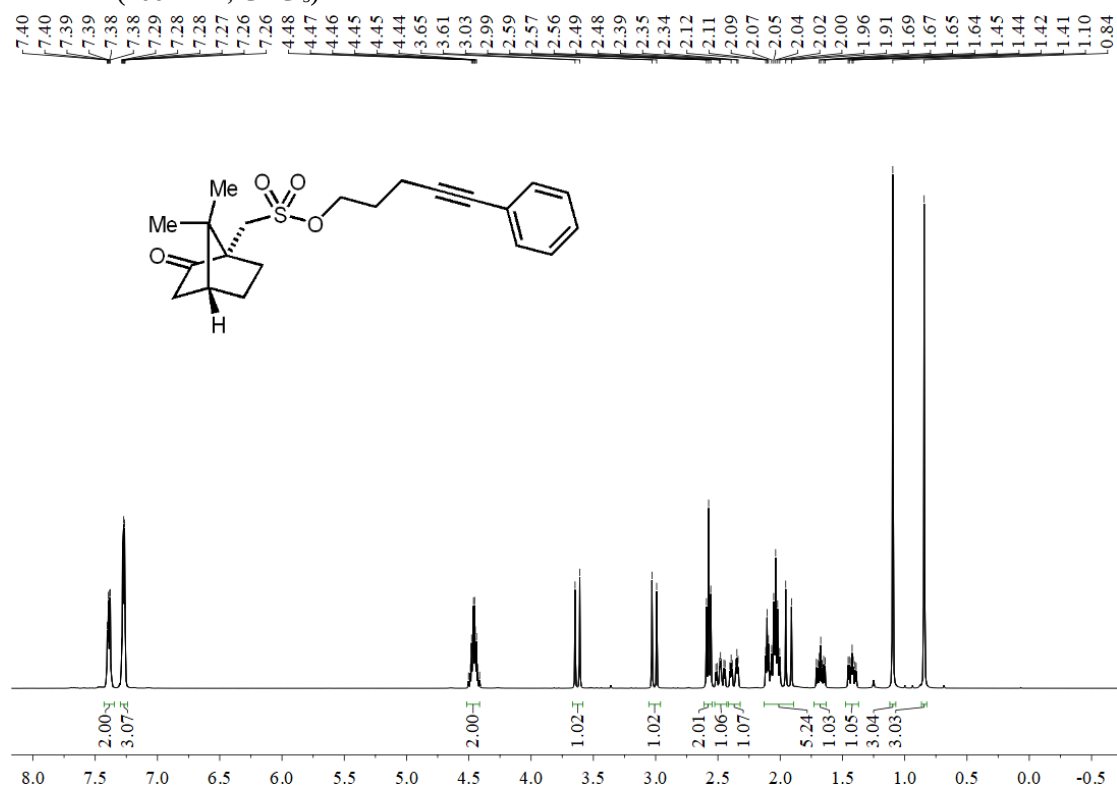
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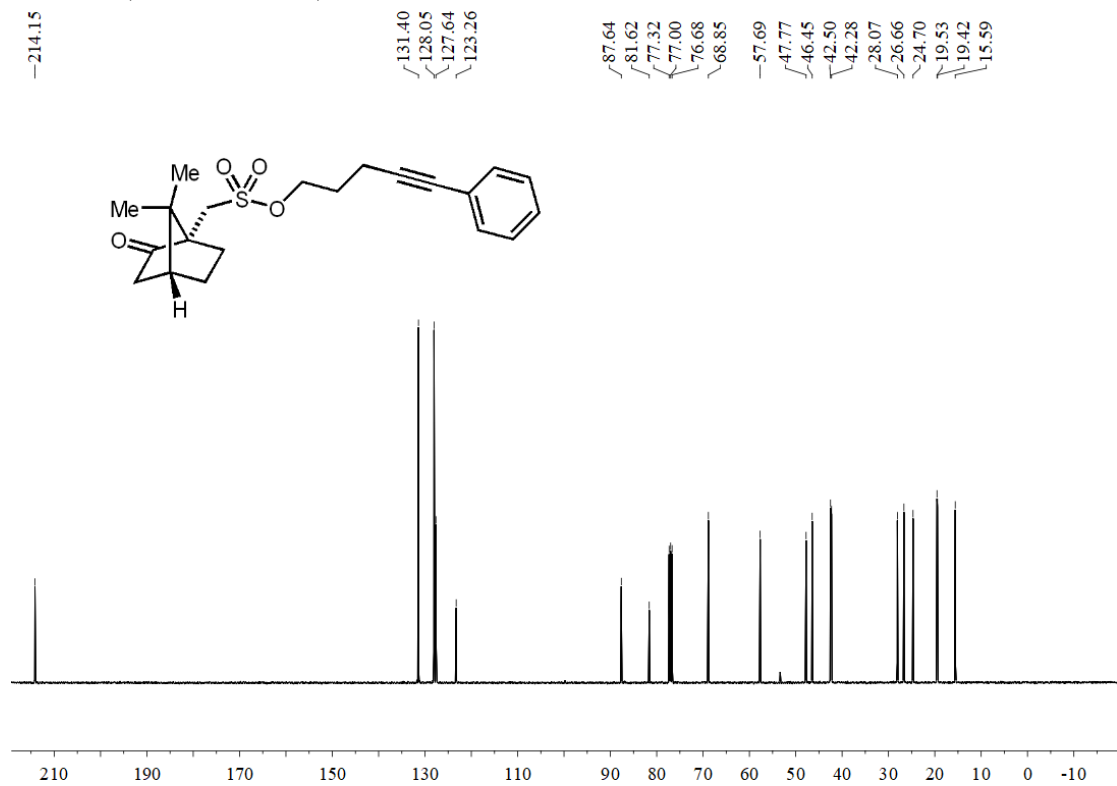
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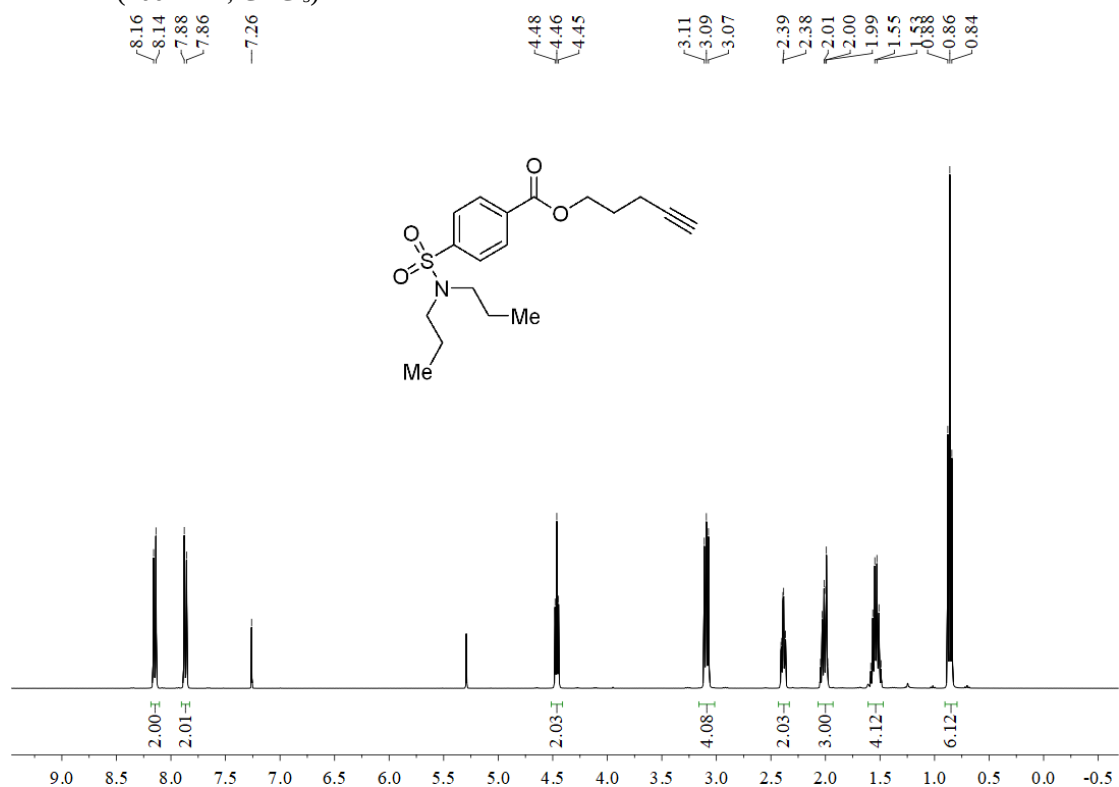
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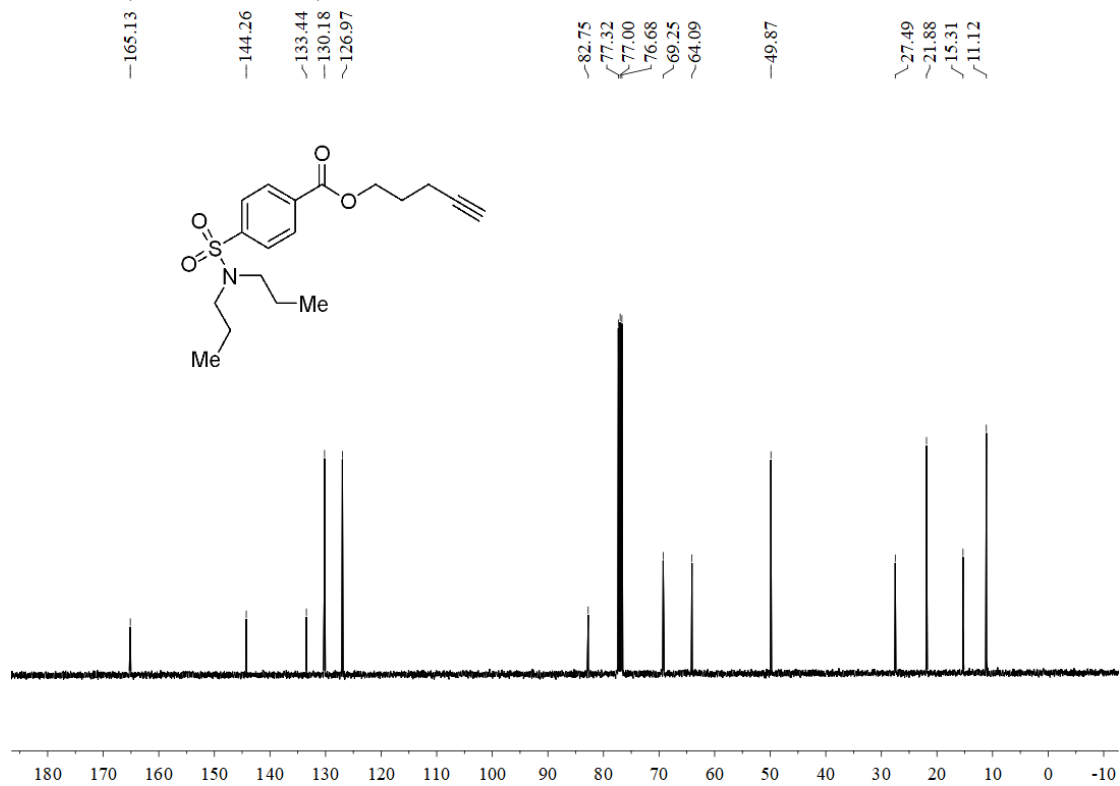
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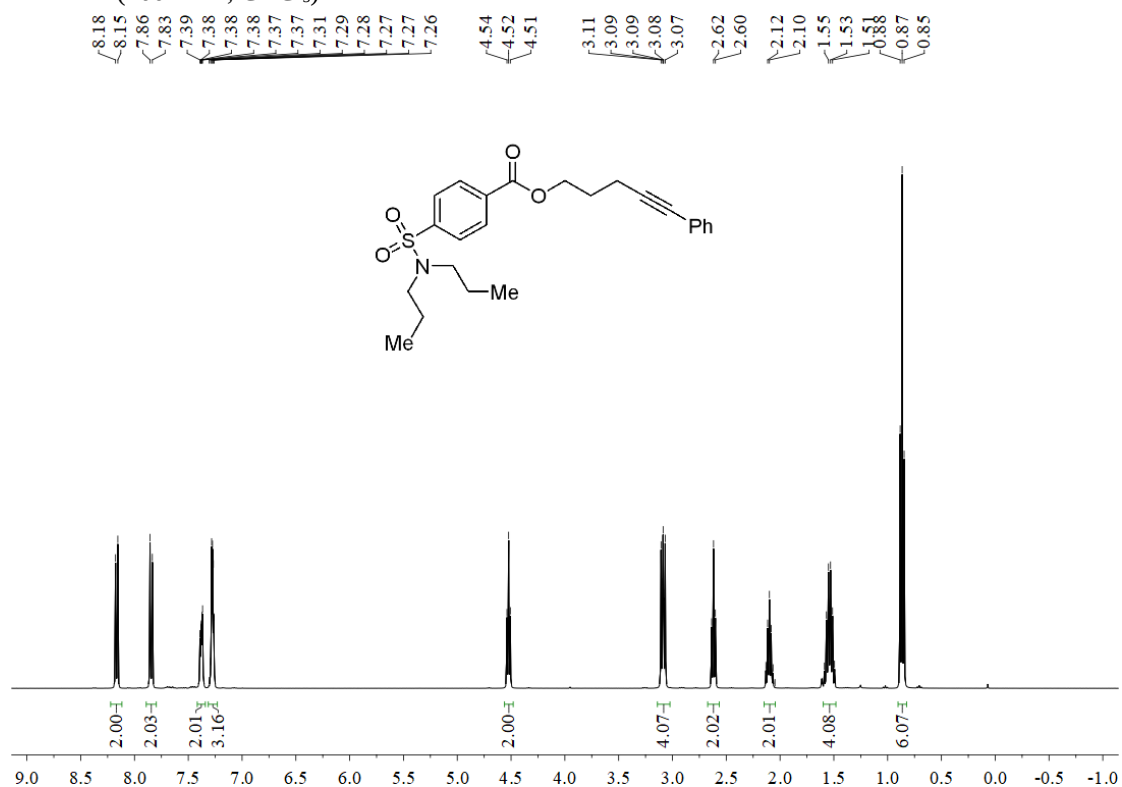
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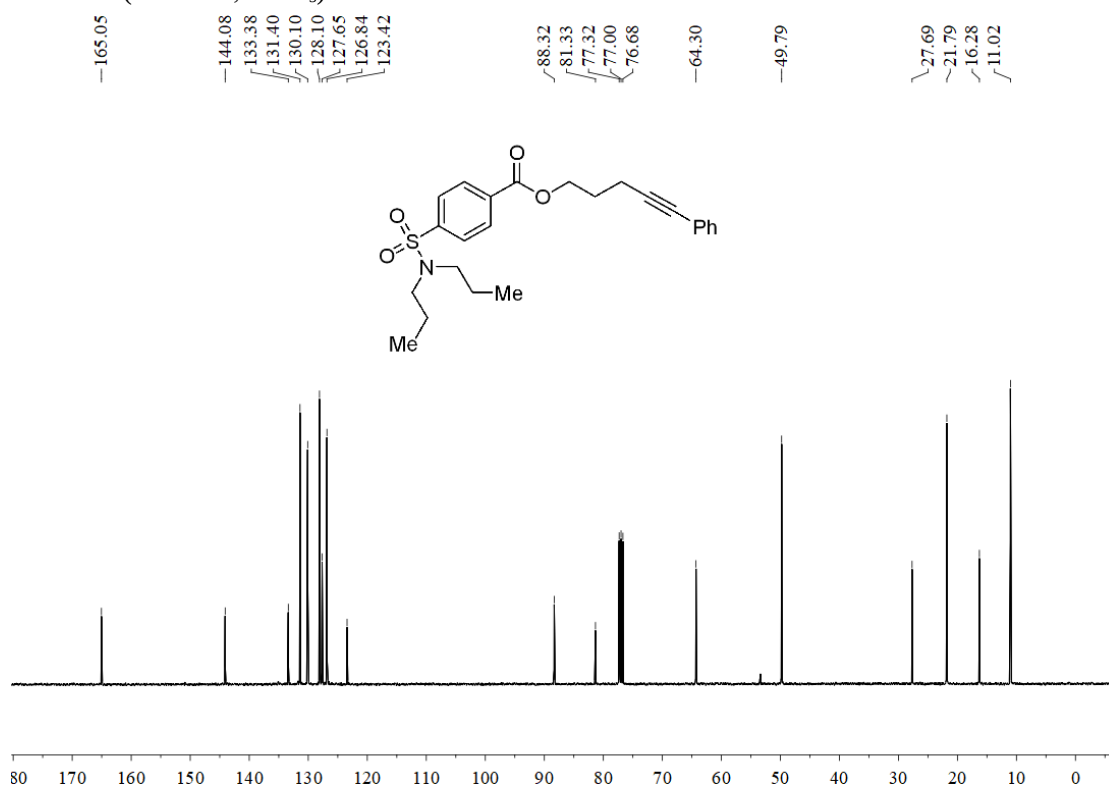
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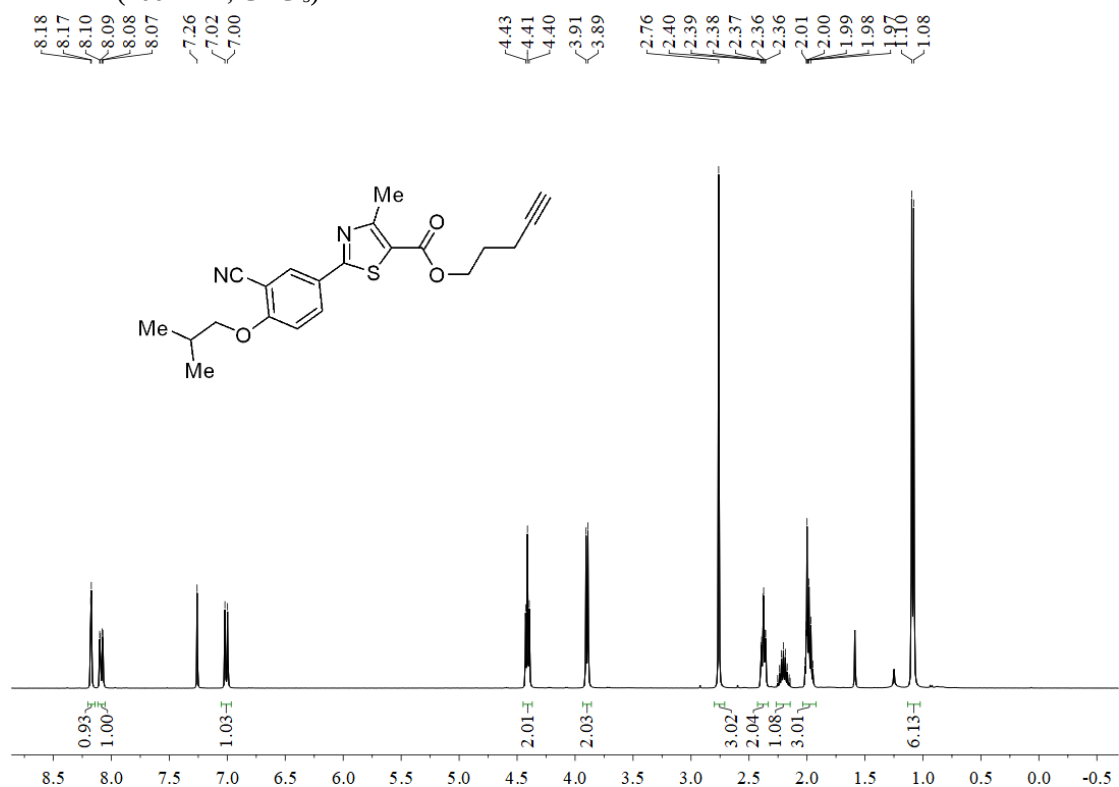
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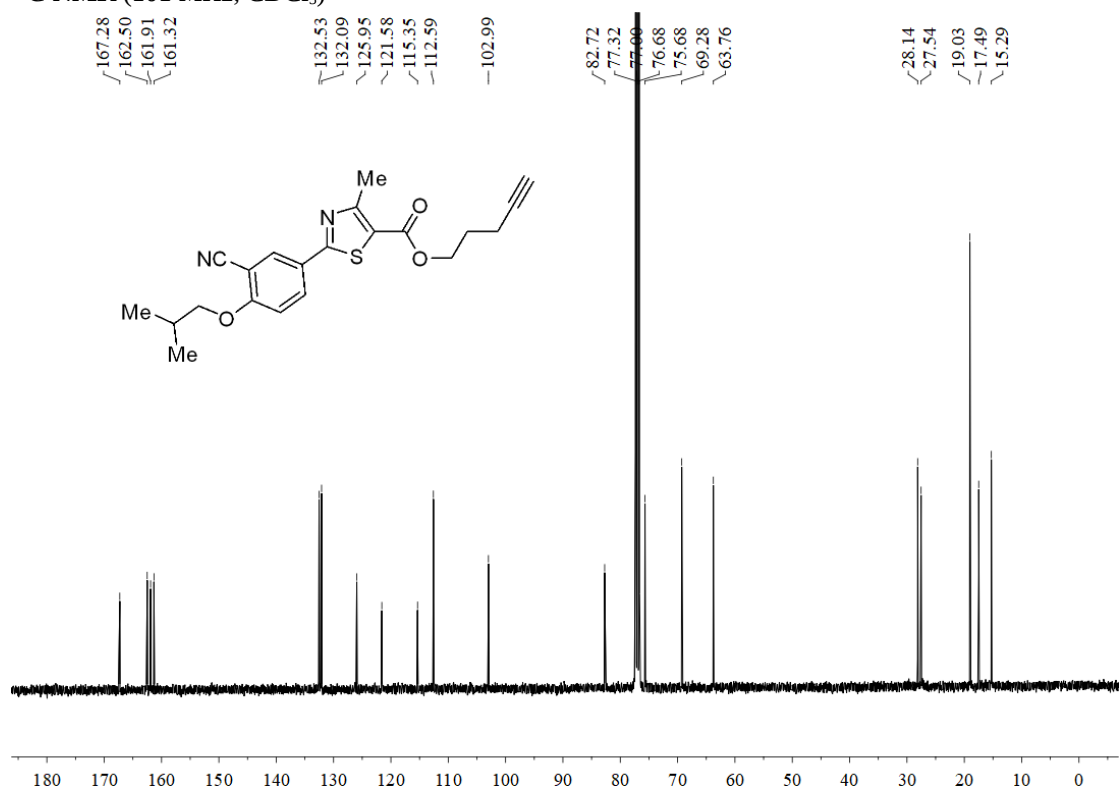
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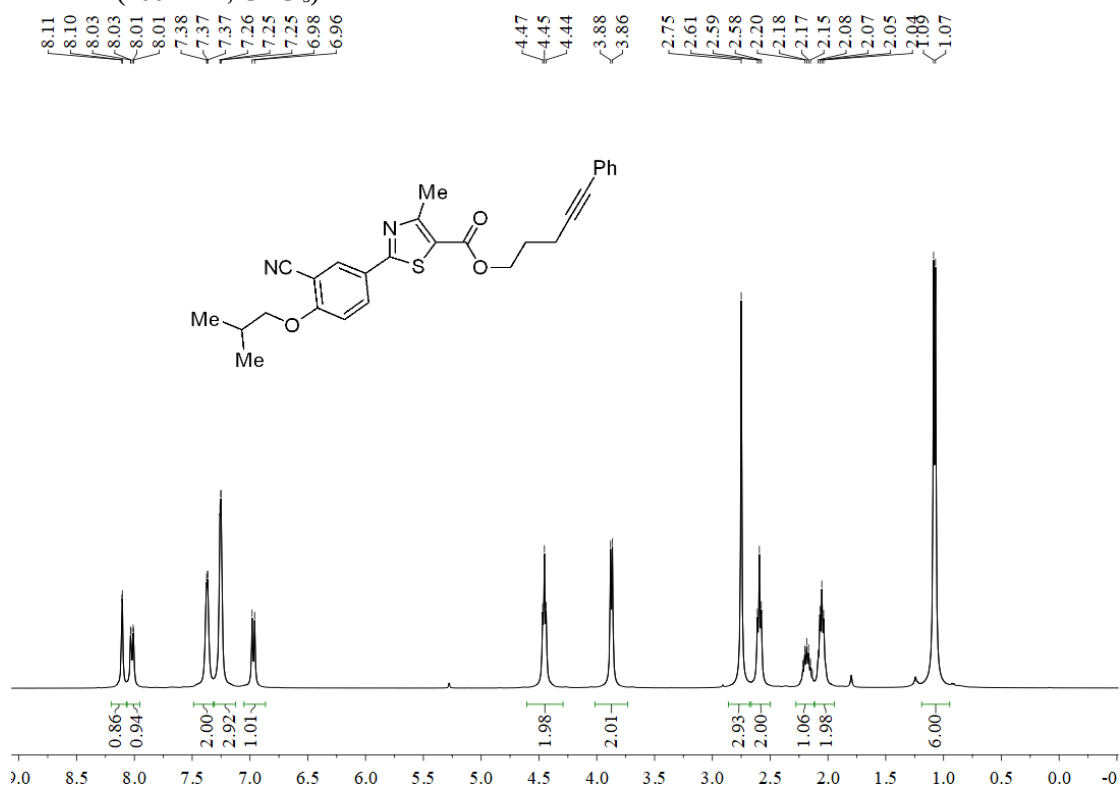
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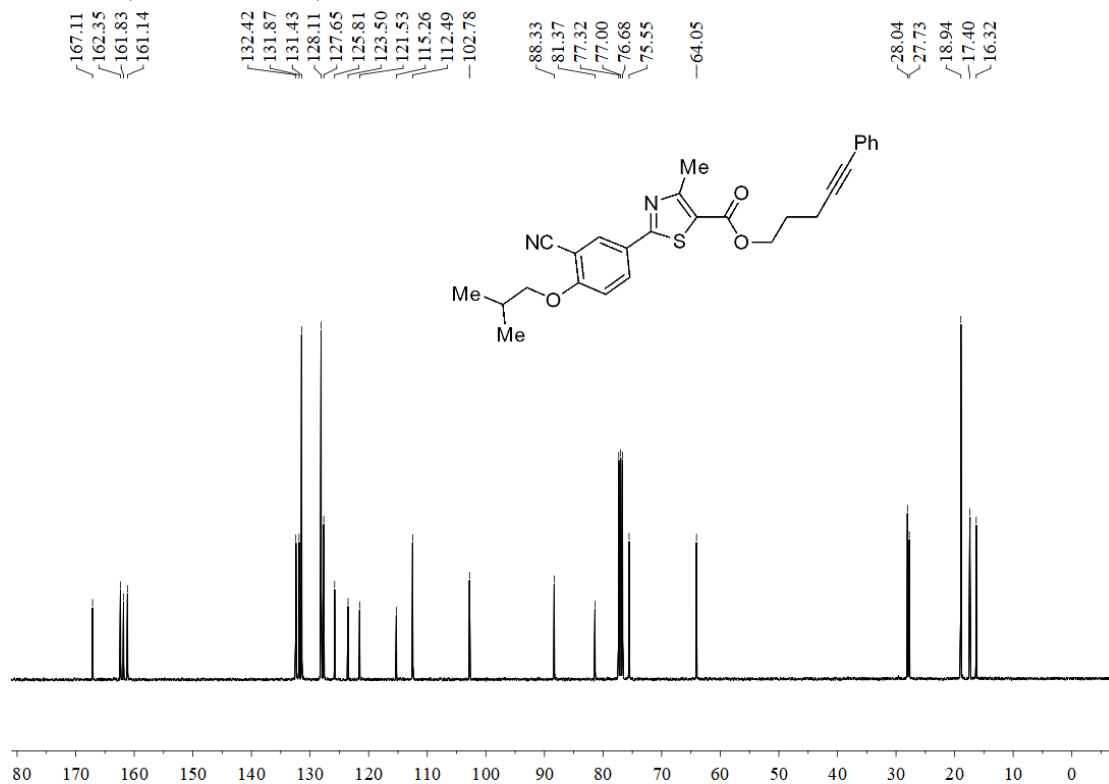
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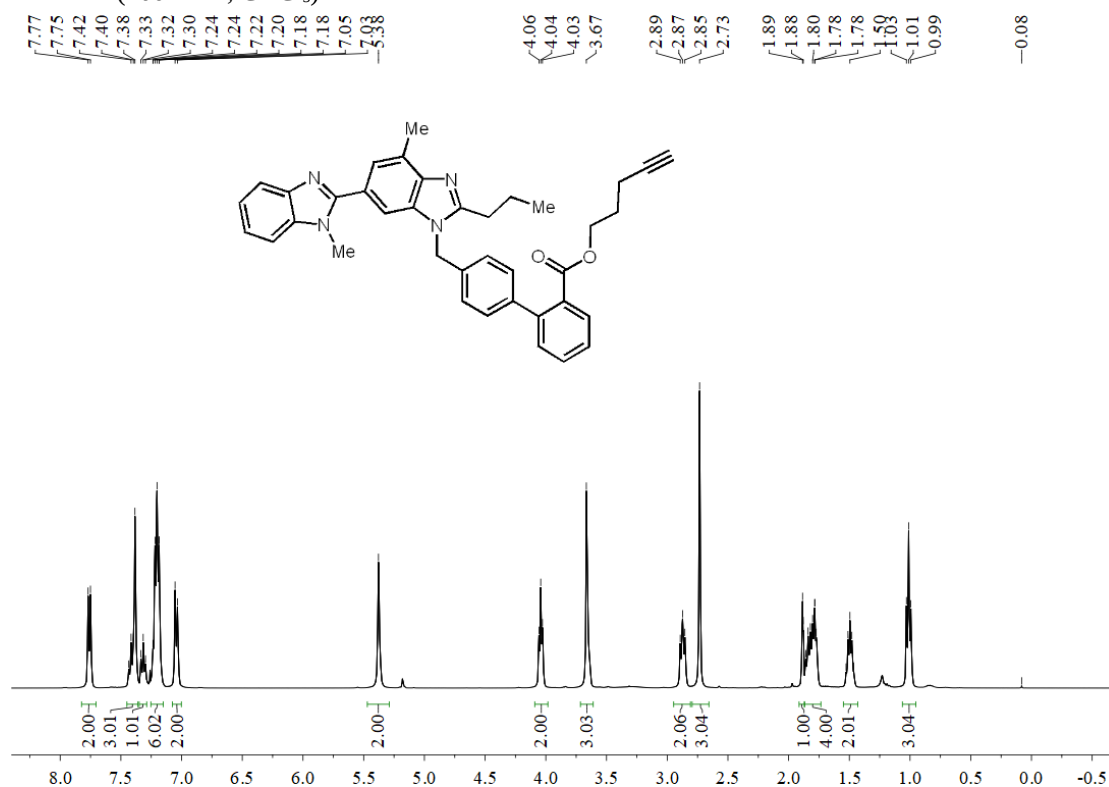
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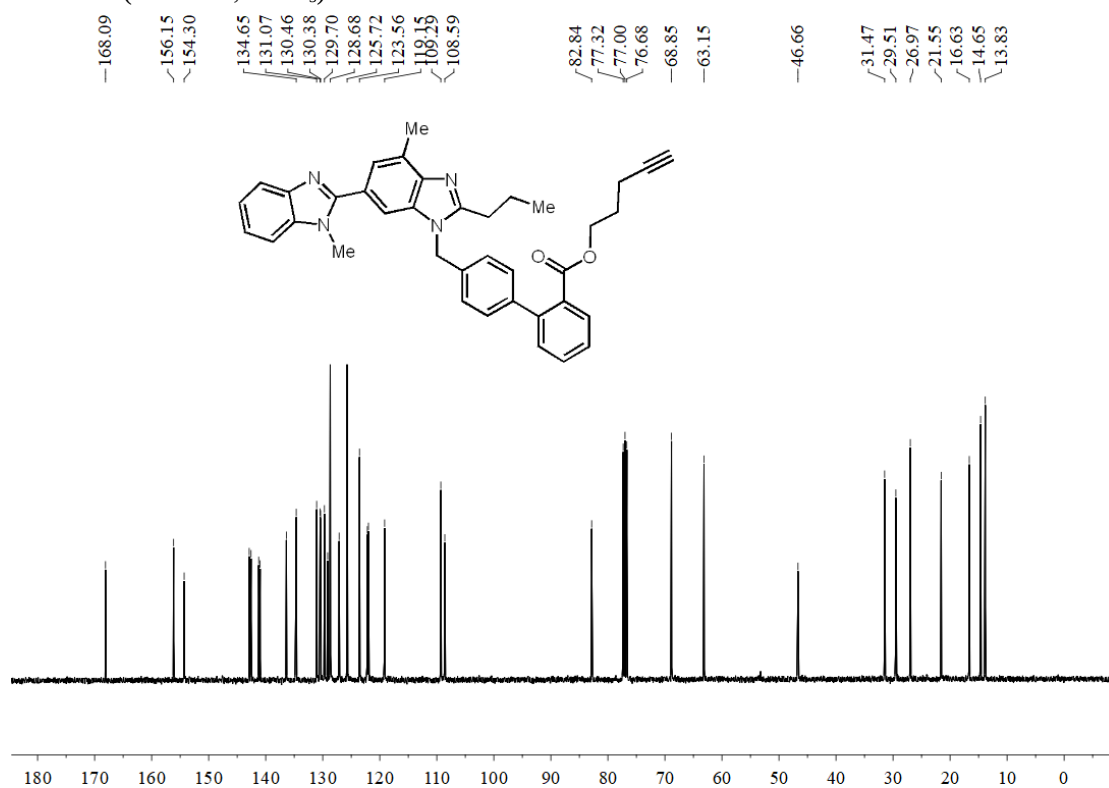
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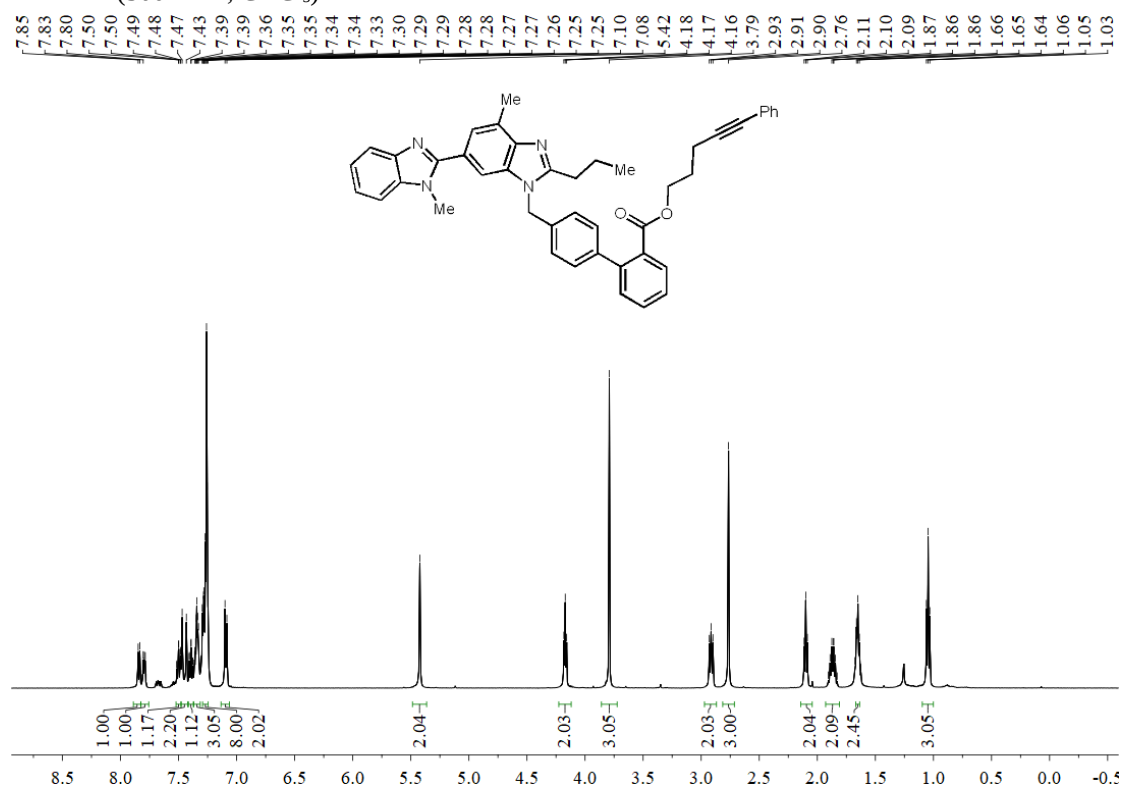
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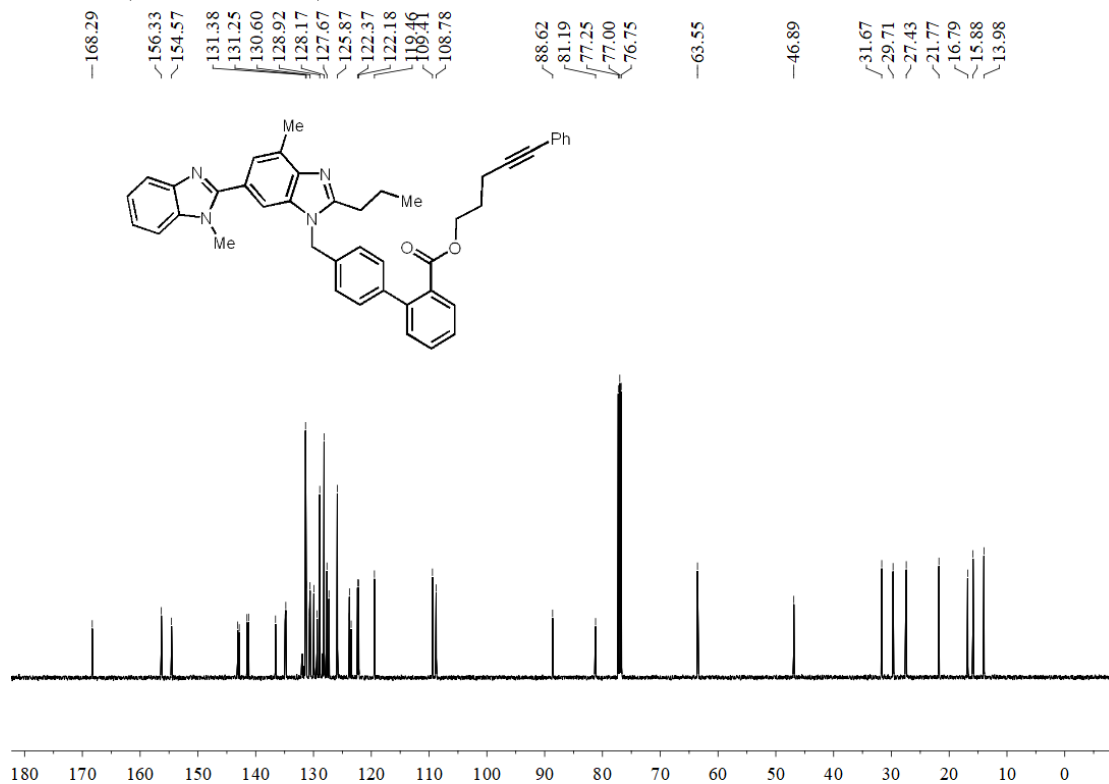
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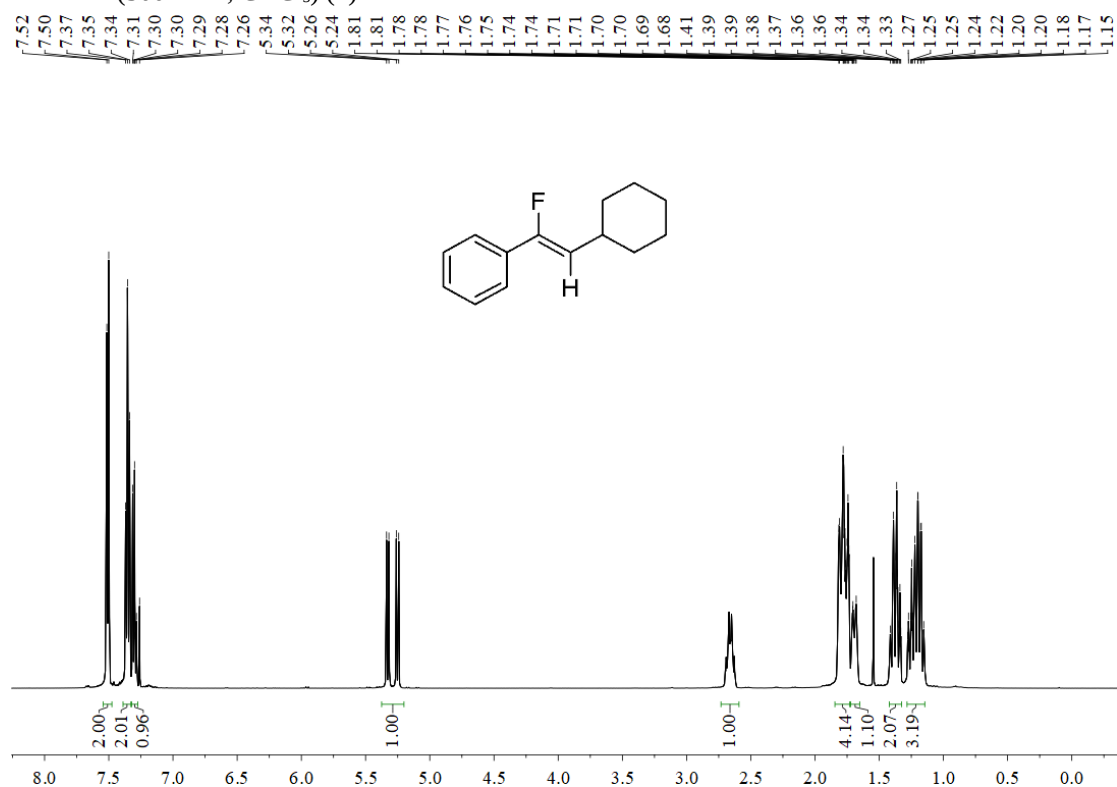
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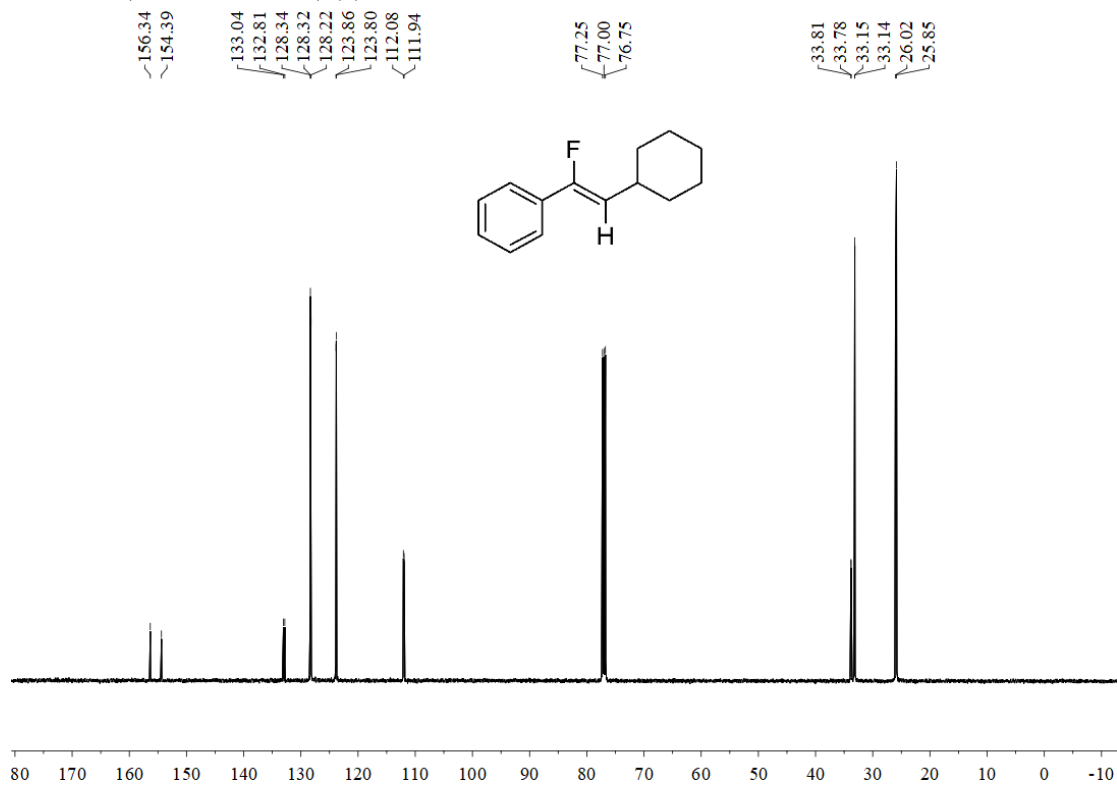
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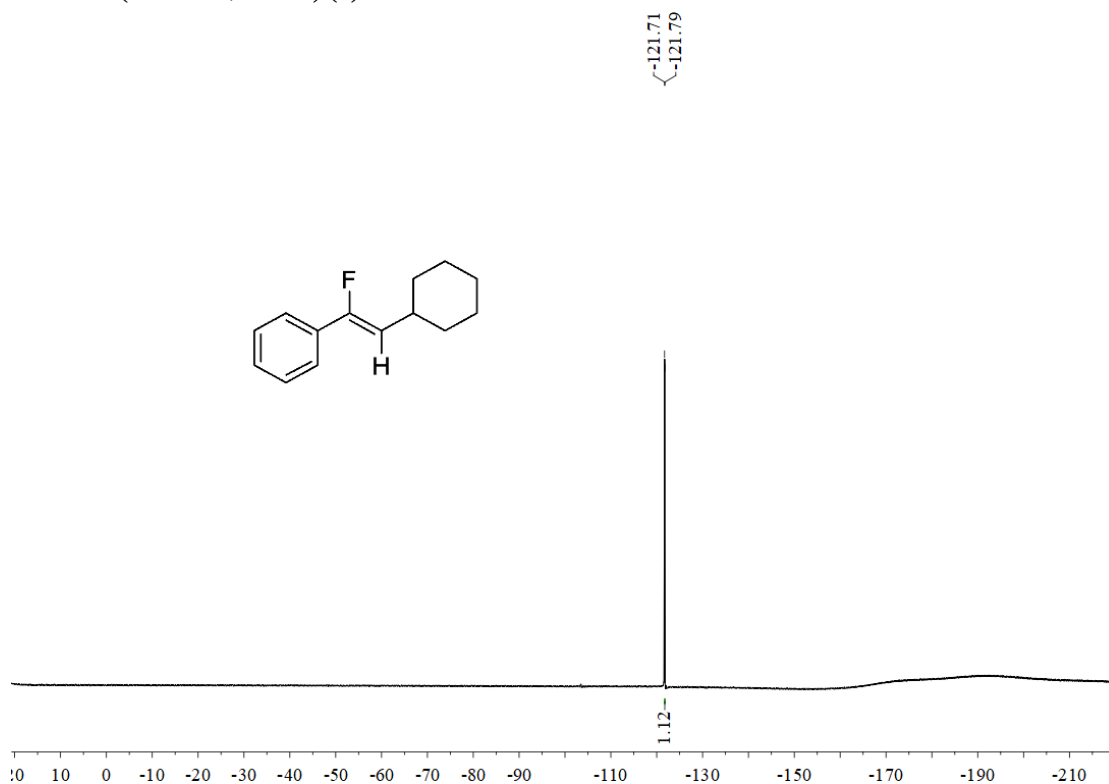
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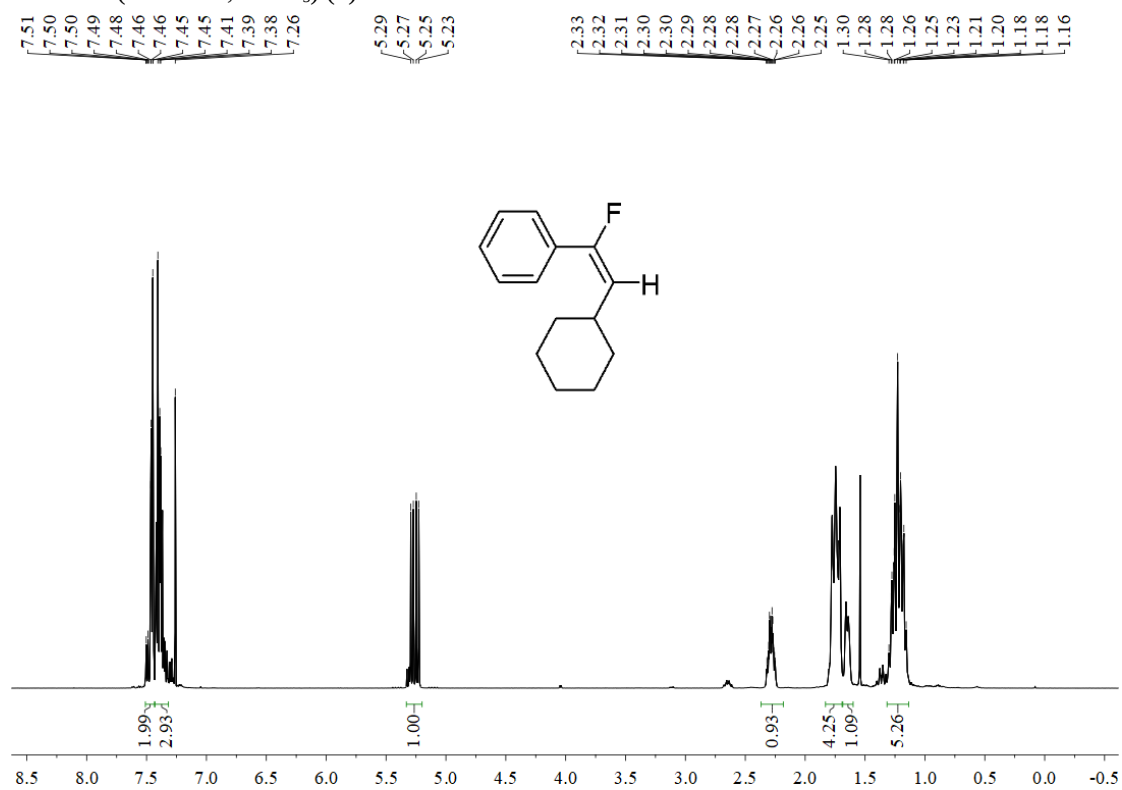
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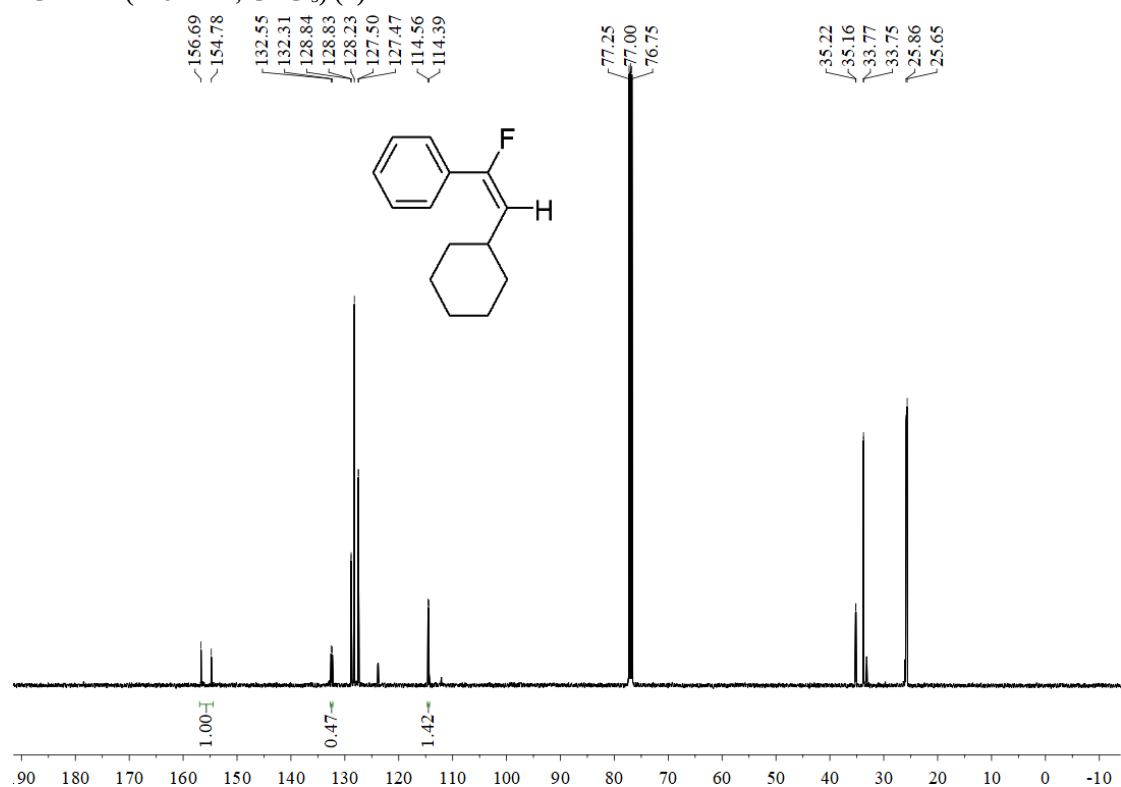
^{19}F NMR (471 MHz, CDCl_3) (1)



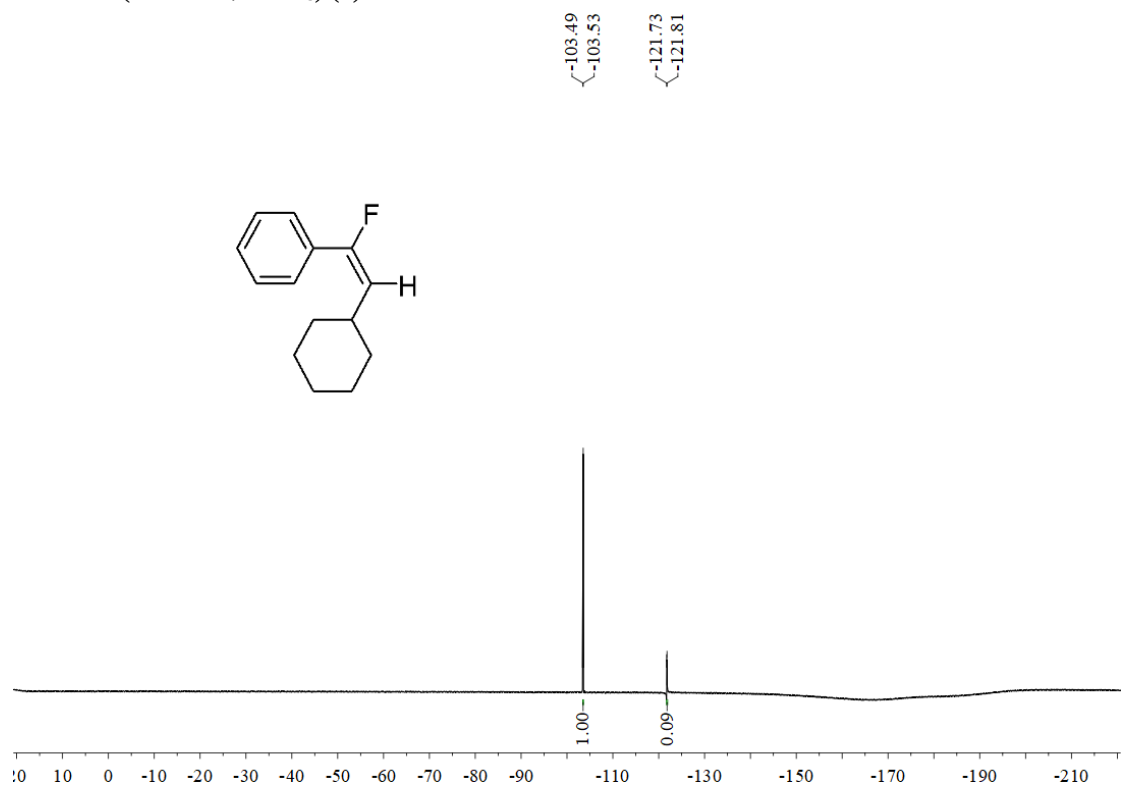
^1H NMR (500 MHz, CDCl_3) (2)



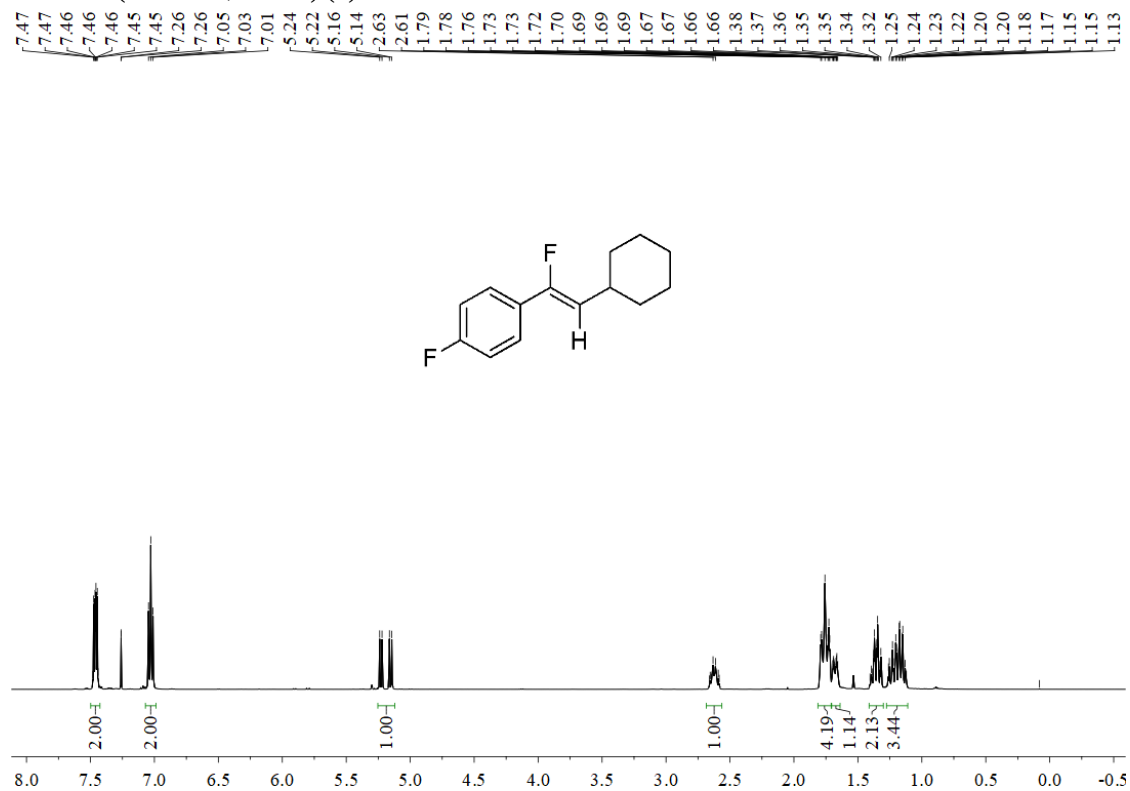
¹³C NMR (126 MHz, CDCl₃) (2)



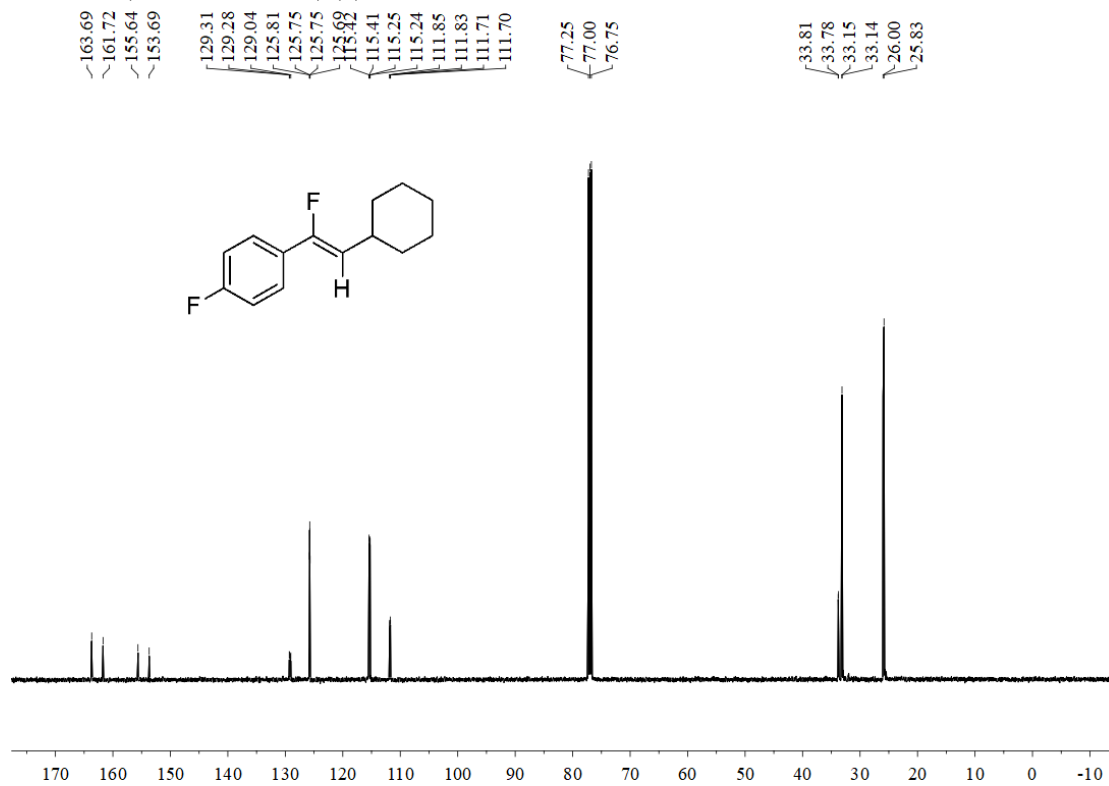
¹⁹F NMR (471 MHz, CDCl₃) (2)



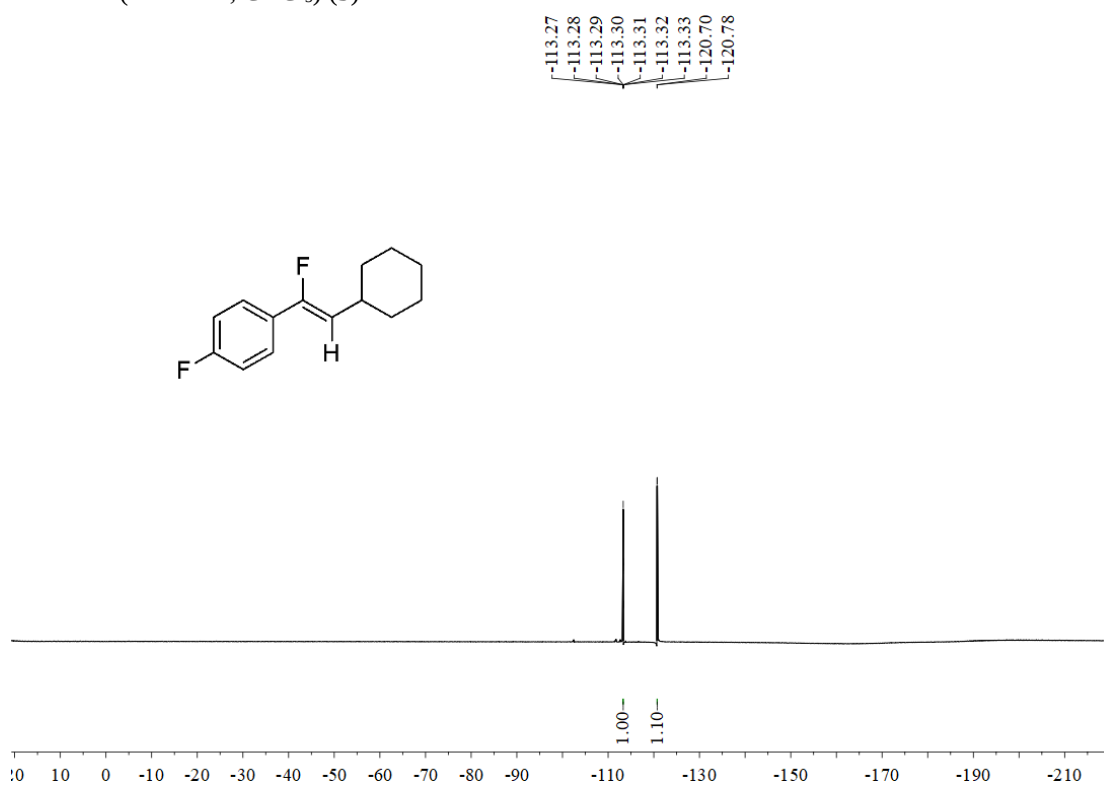
¹H NMR (500 MHz, CDCl₃) (3)



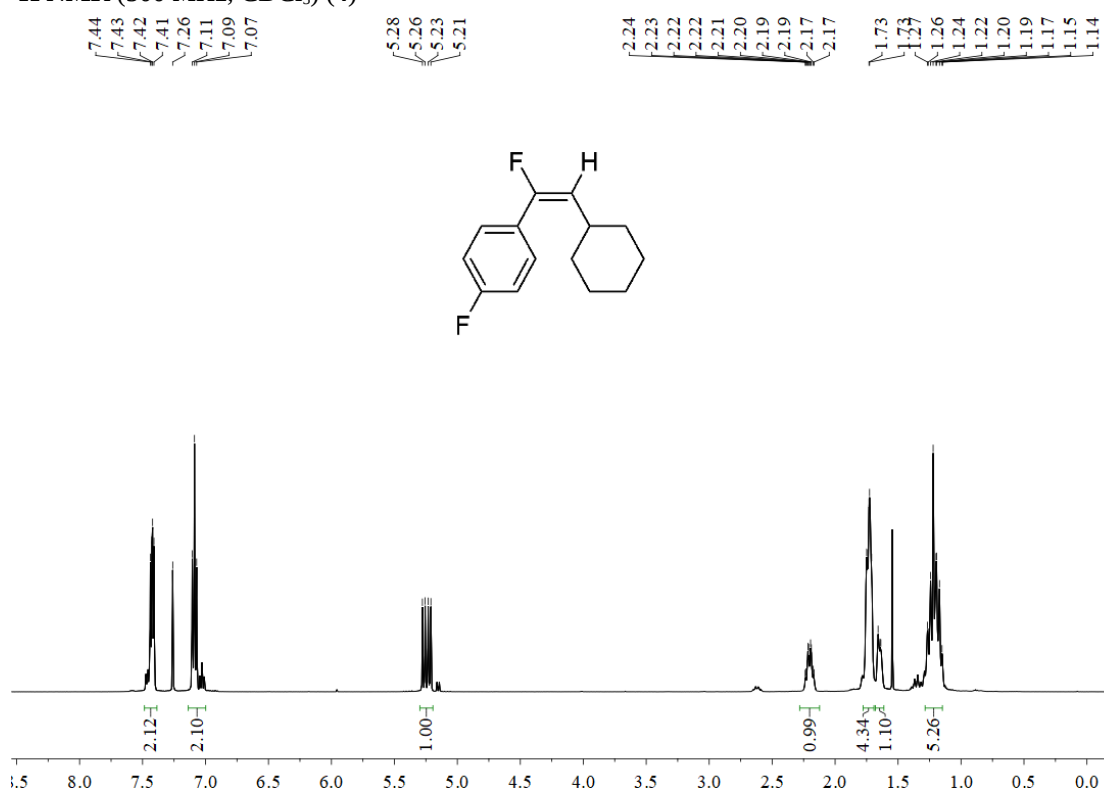
¹³C NMR (126 MHz, CDCl₃) (3)



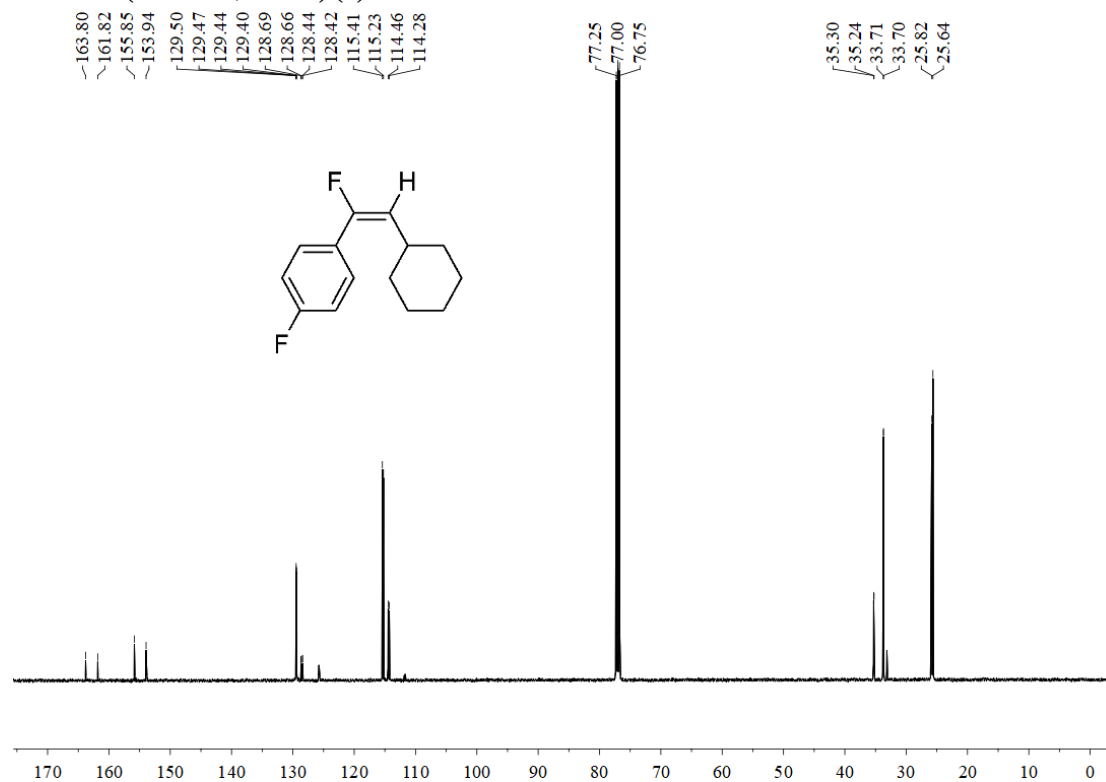
^{19}F NMR (471 MHz, CDCl_3) (3)



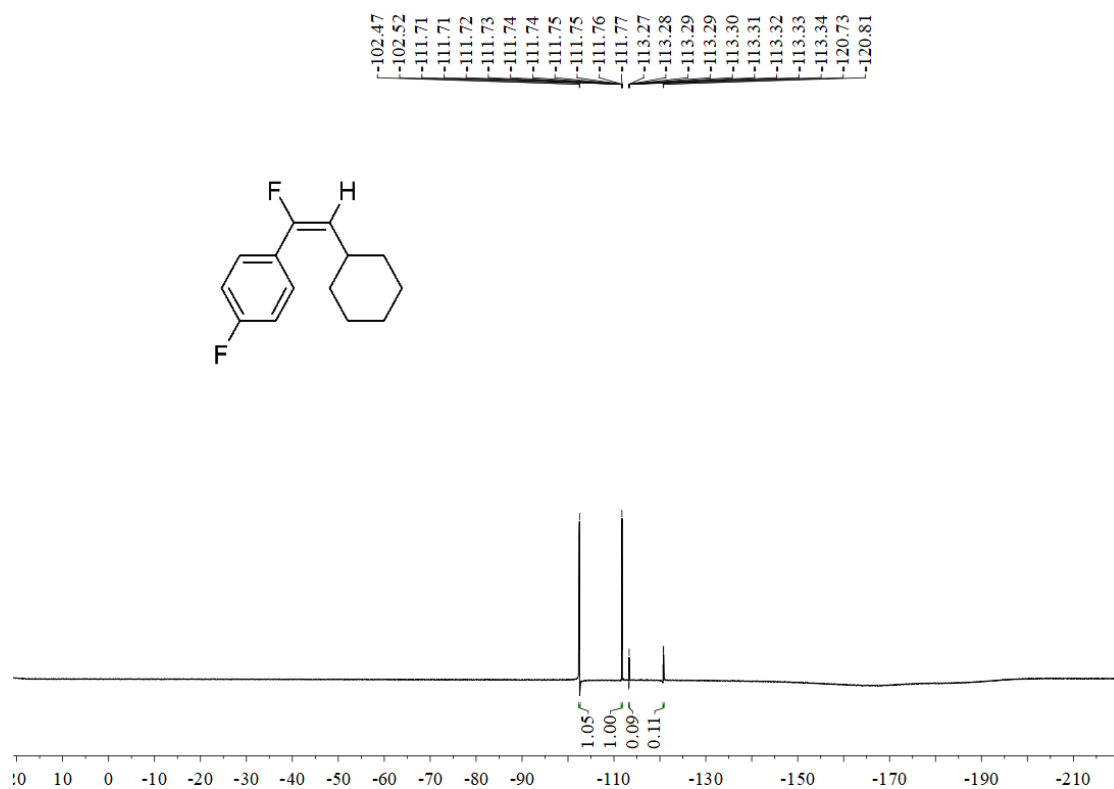
^1H NMR (500 MHz, CDCl_3) (4)



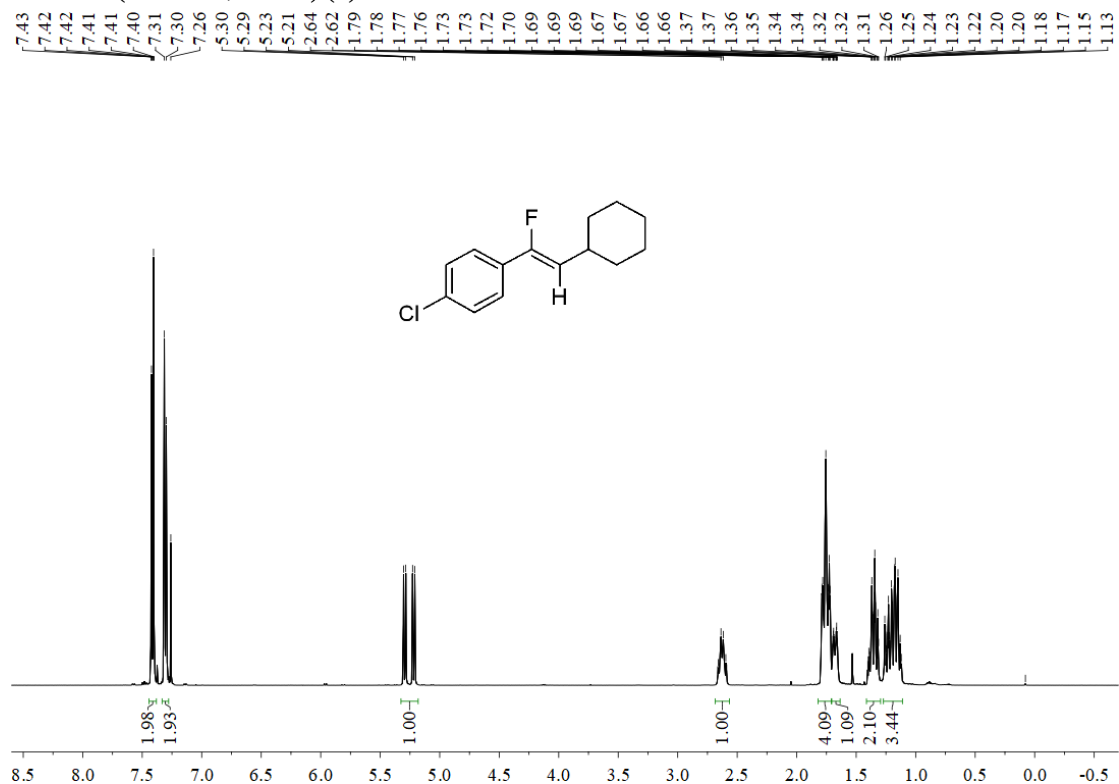
¹³C NMR (126 MHz, CDCl₃) (4)



¹⁹F NMR (471 MHz, CDCl₃) (4)



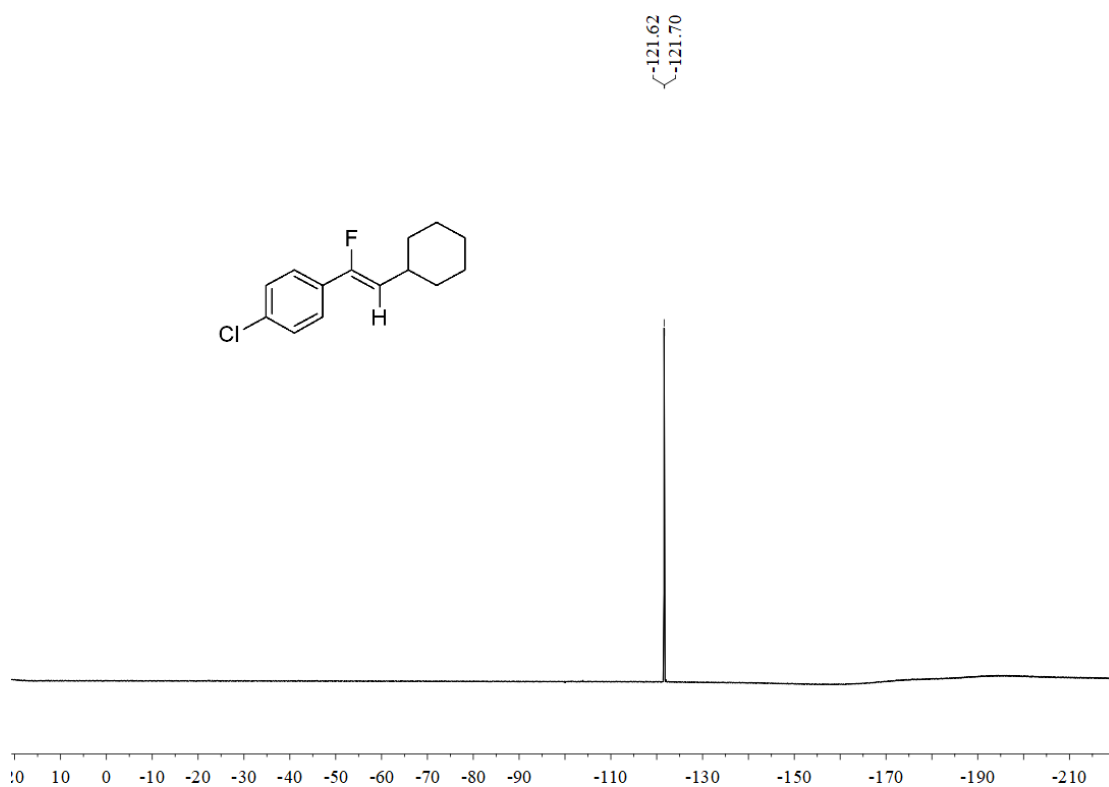
¹H NMR (500 MHz, CDCl₃) (5)



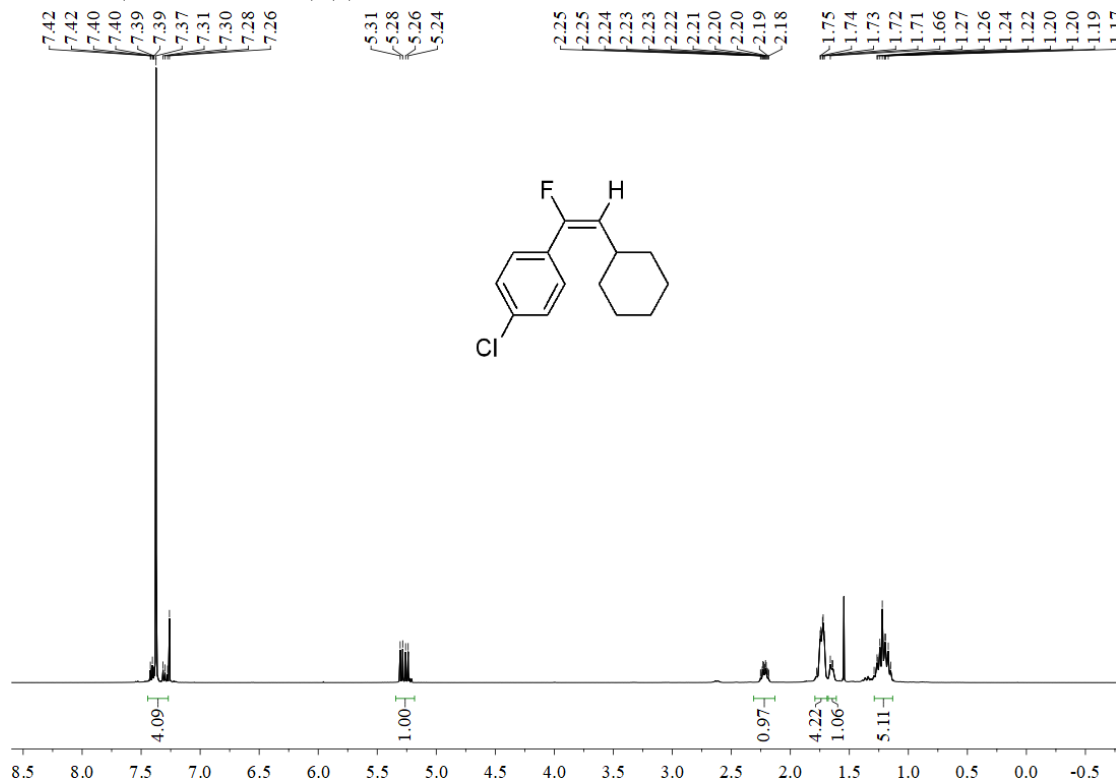
¹³C NMR (126 MHz, CDCl₃) (5)



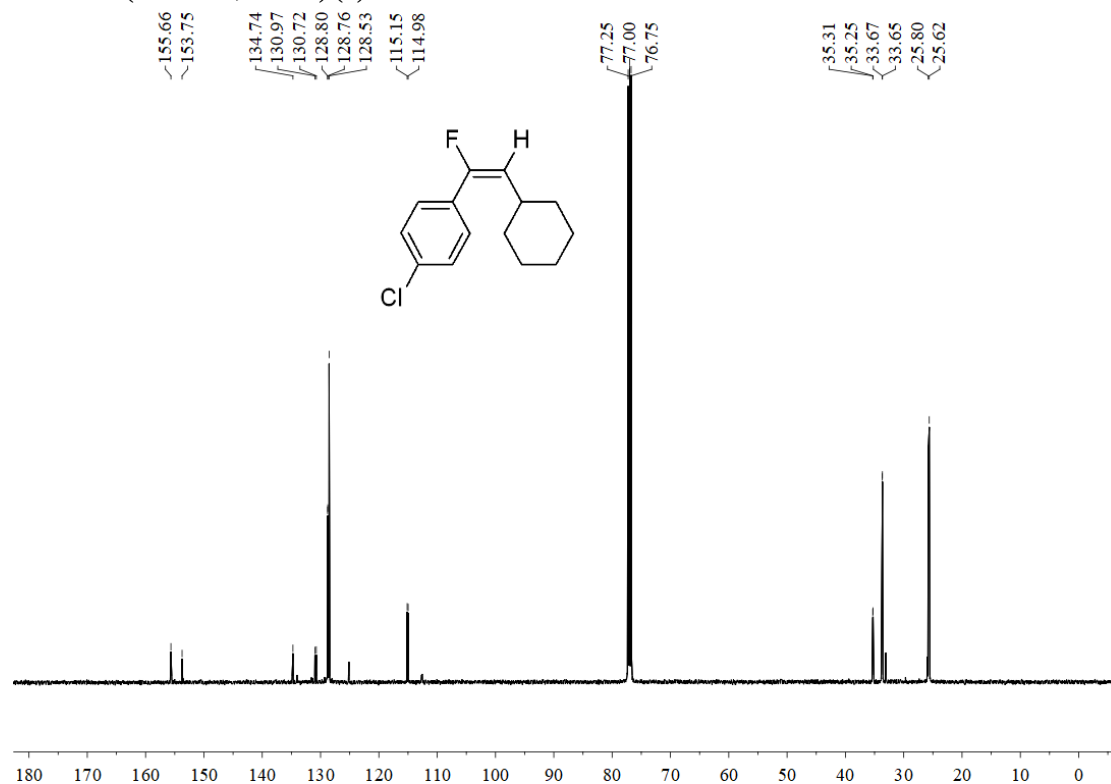
^{19}F NMR (471 MHz, CDCl_3) (5)



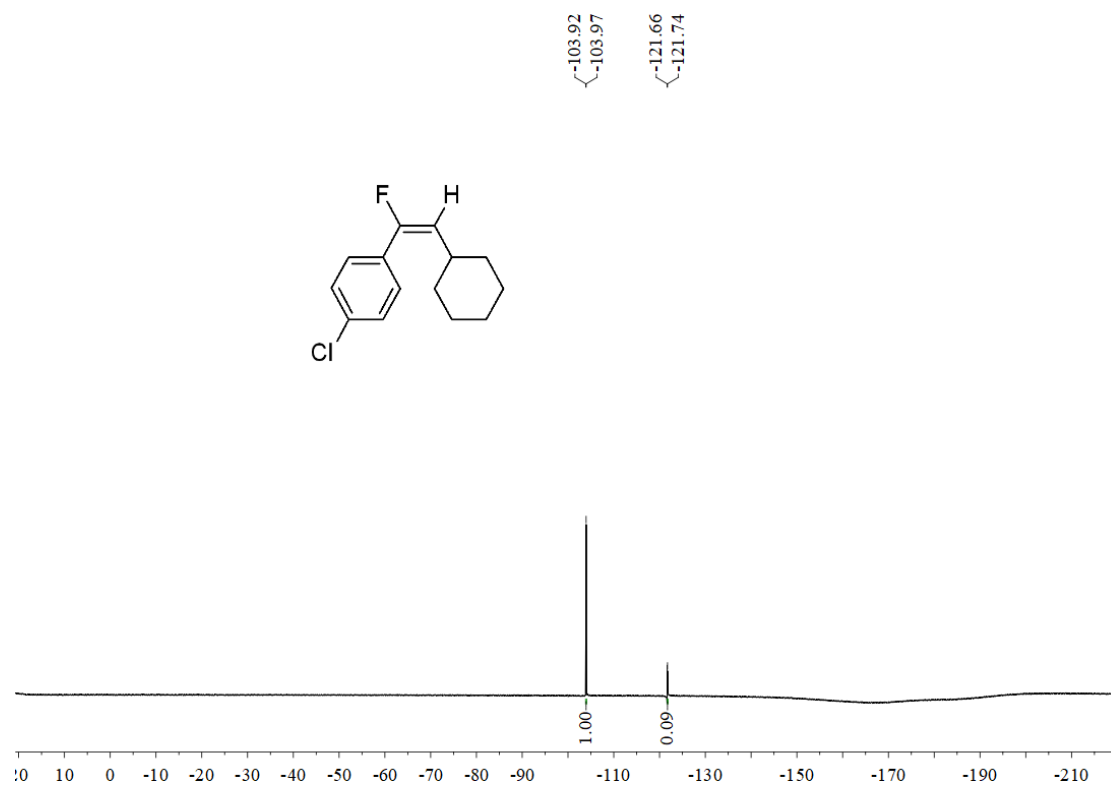
^1H NMR (500 MHz, CDCl_3) (6)



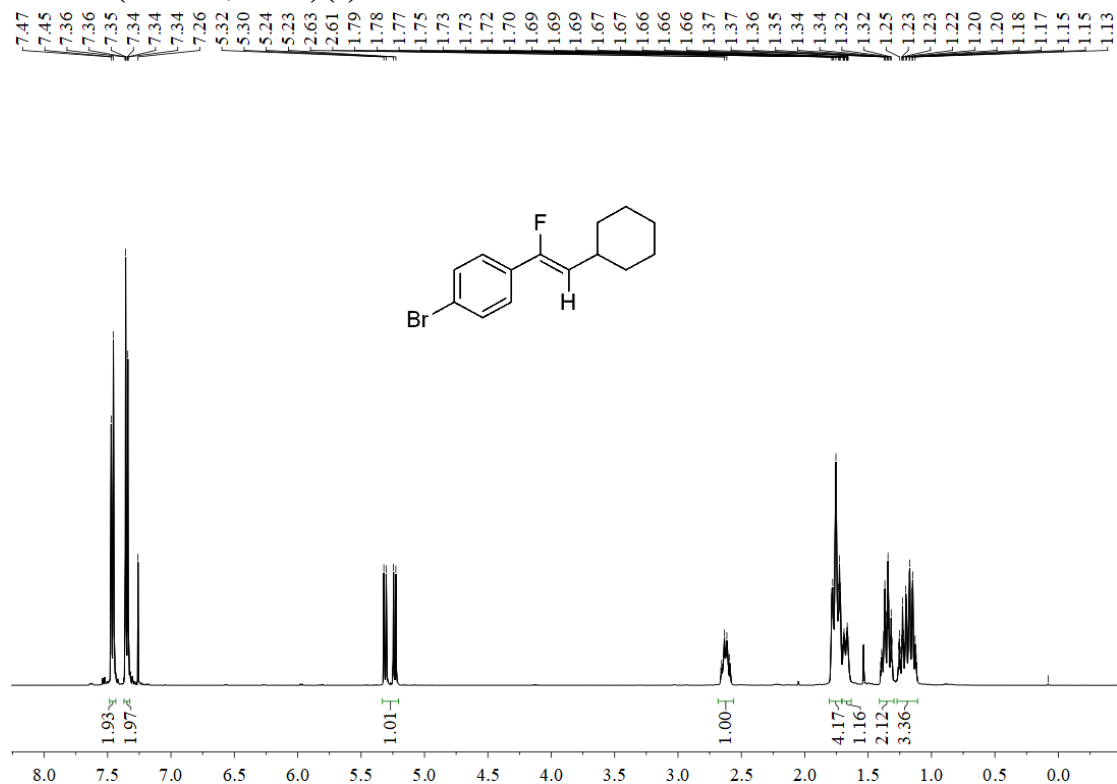
¹³C NMR (126 MHz, CDCl₃) (6)



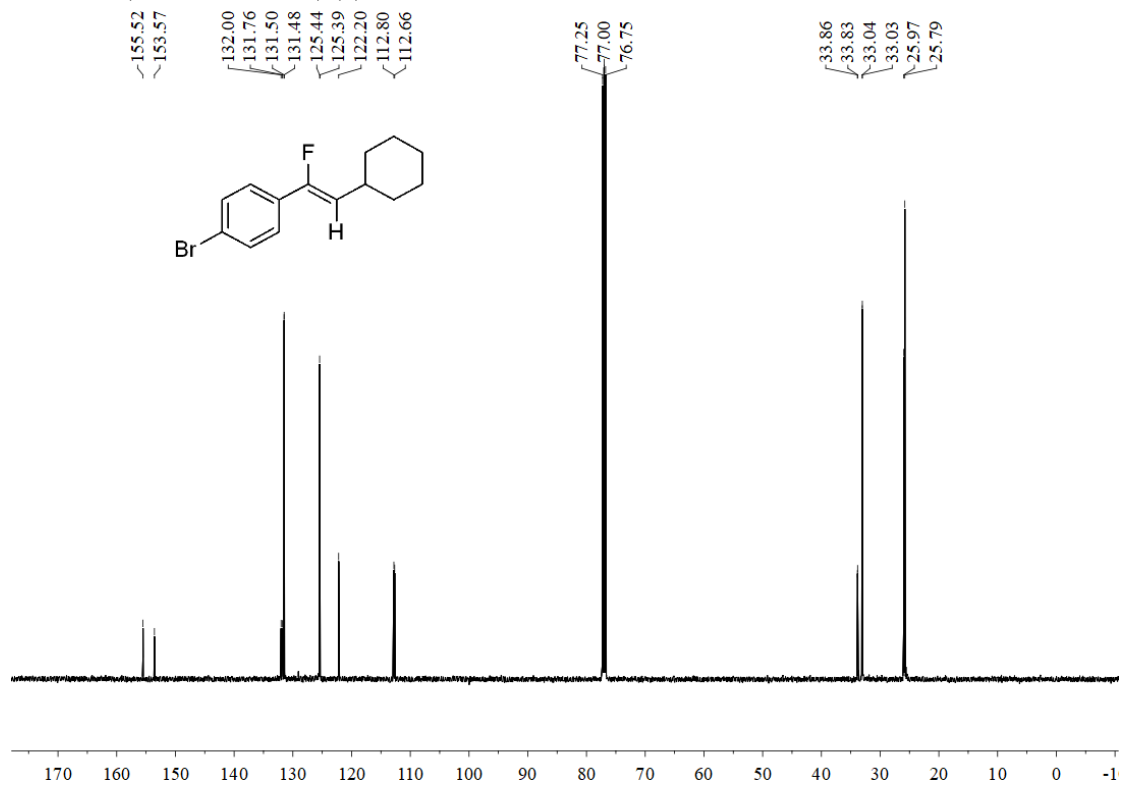
¹⁹F NMR (471 MHz, CDCl₃) (6)



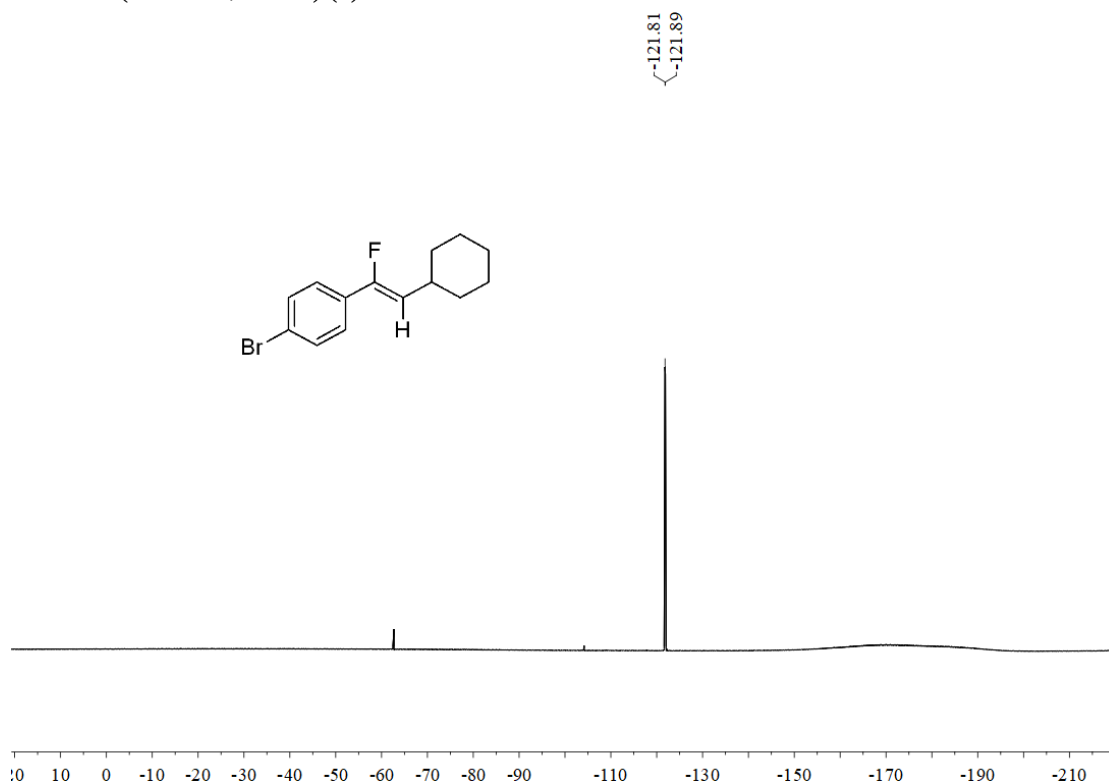
¹H NMR (500 MHz, CDCl₃) (7)



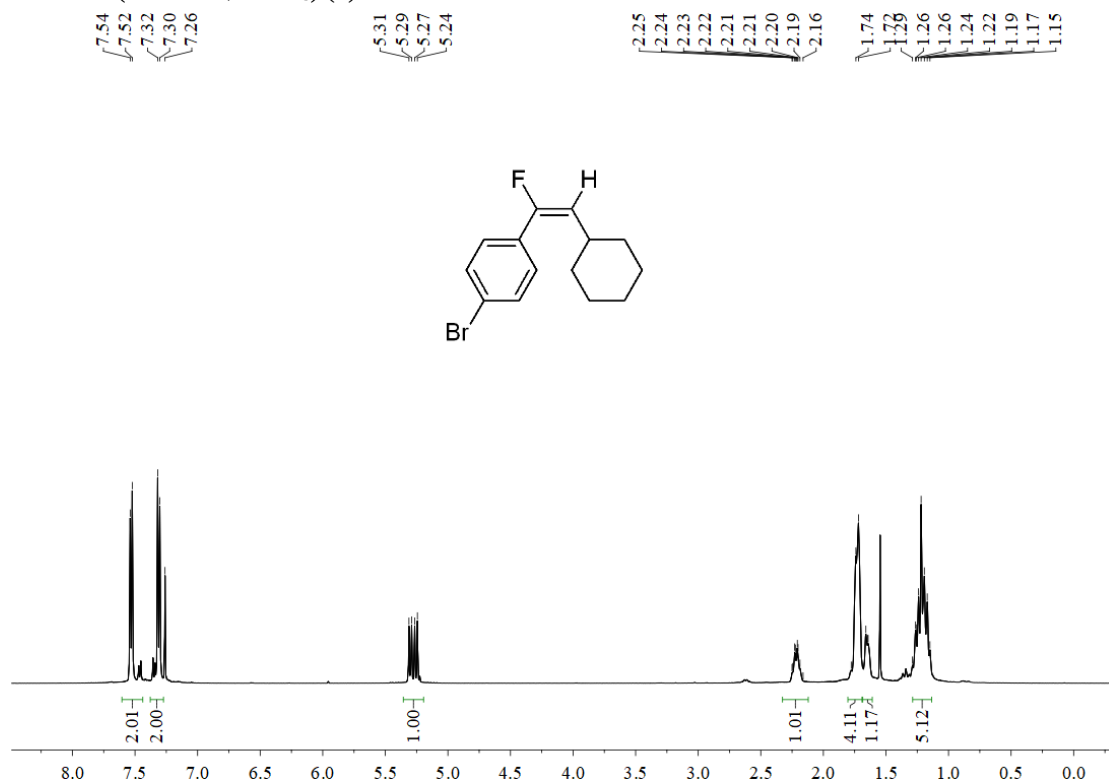
¹³C NMR (126 MHz, CDCl₃) (7)



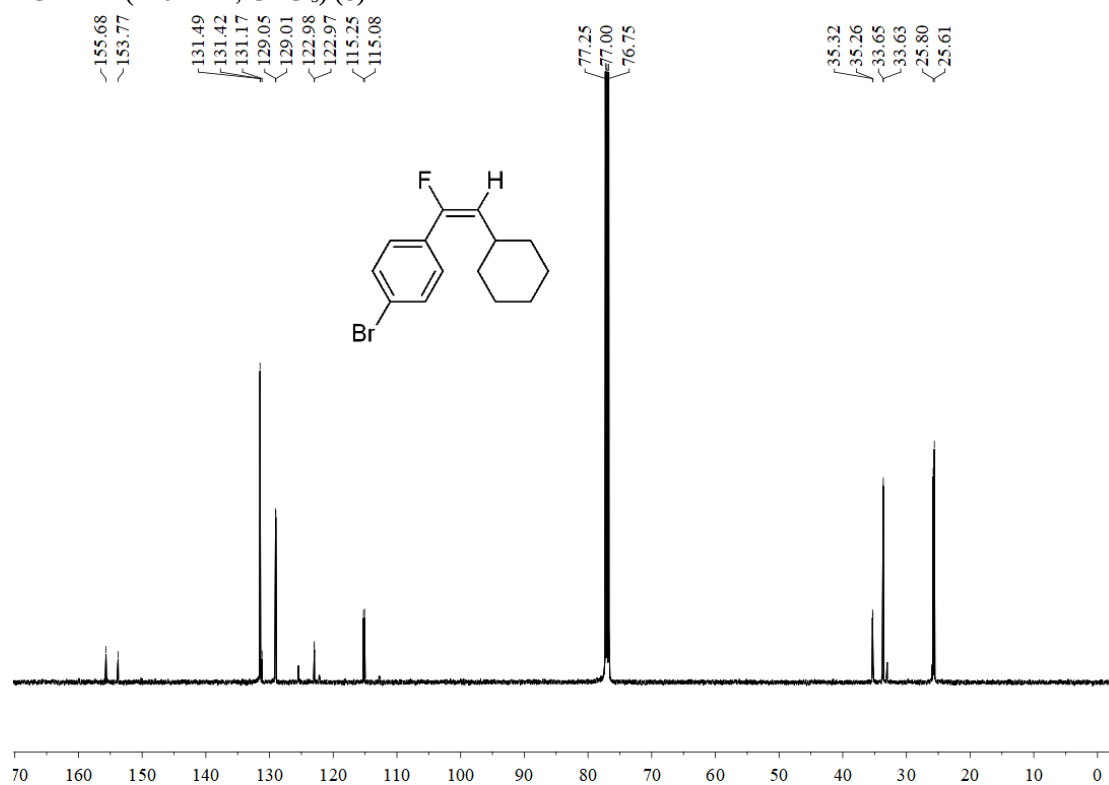
^{19}F NMR (471 MHz, CDCl_3) (7)



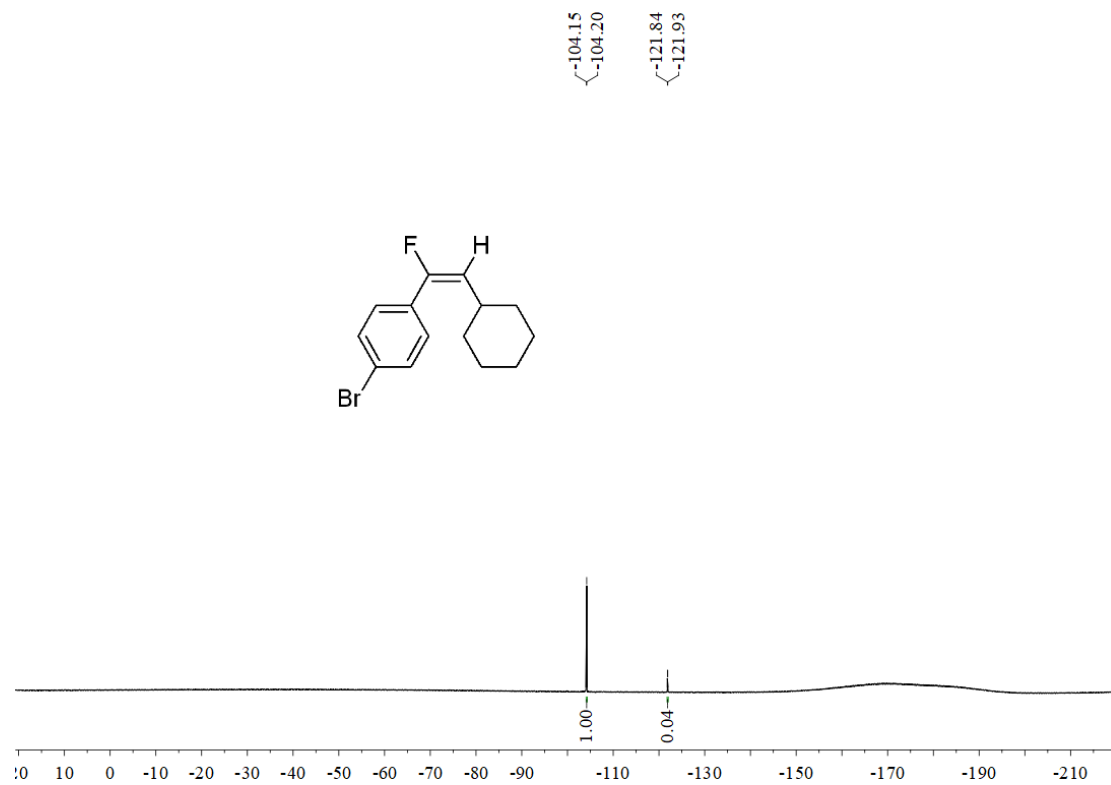
^1H NMR (500 MHz, CDCl_3) (8)



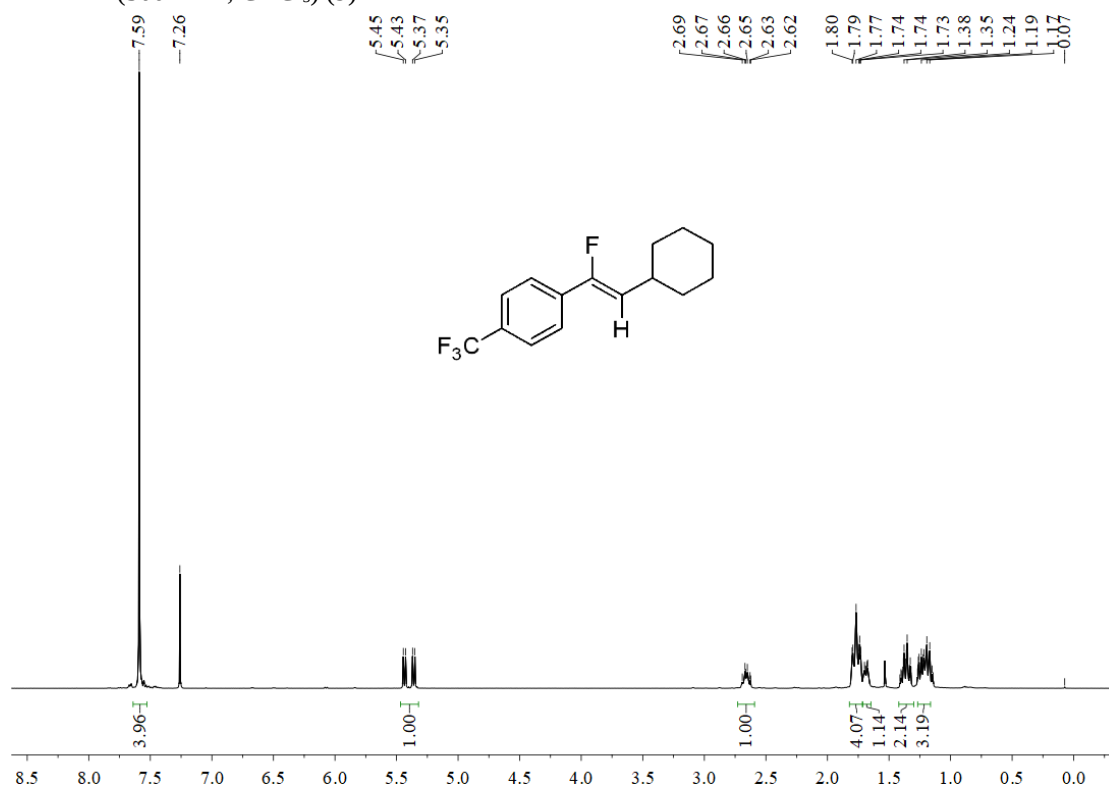
^{13}C NMR (126 MHz, CDCl_3) (8)



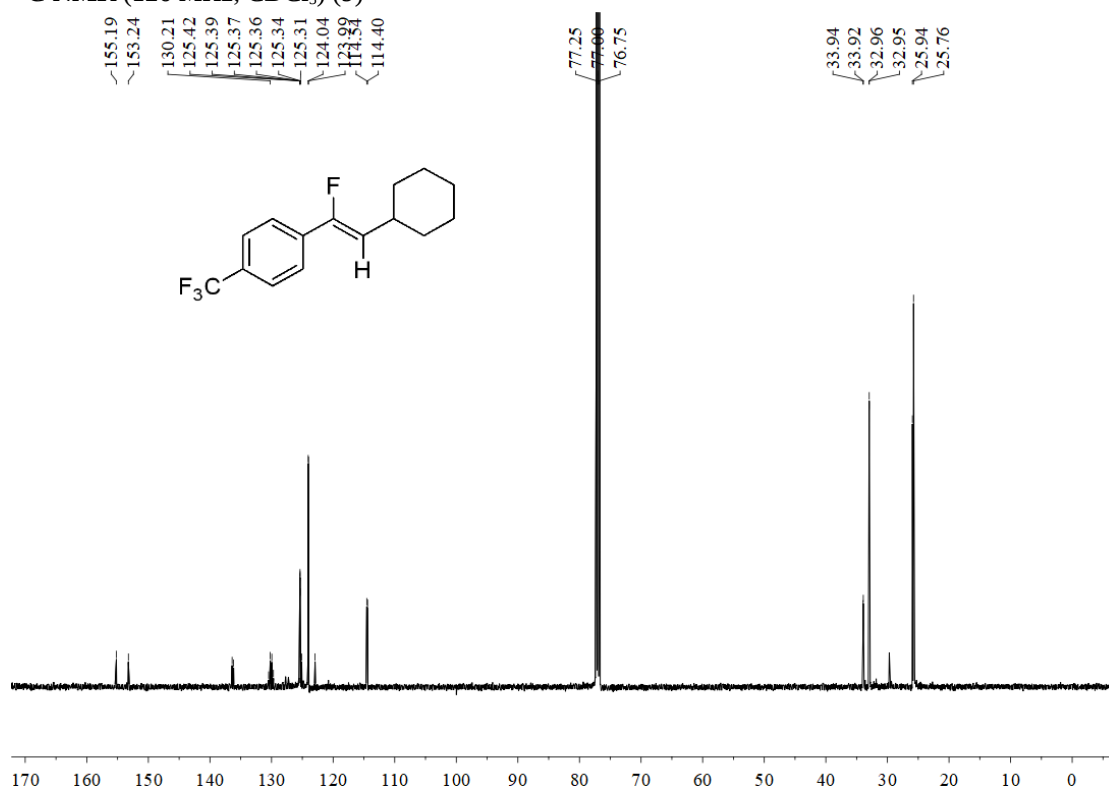
^{19}F NMR (471 MHz, CDCl_3) (8)



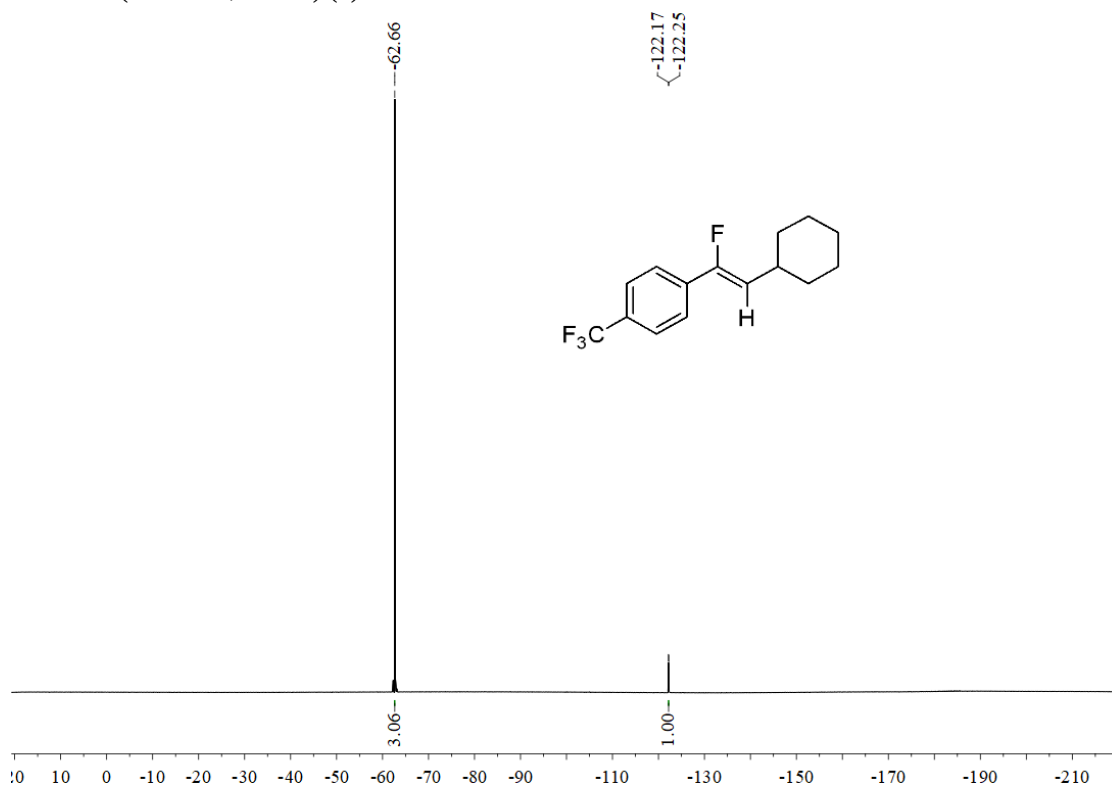
¹H NMR (500 MHz, CDCl₃) (9)



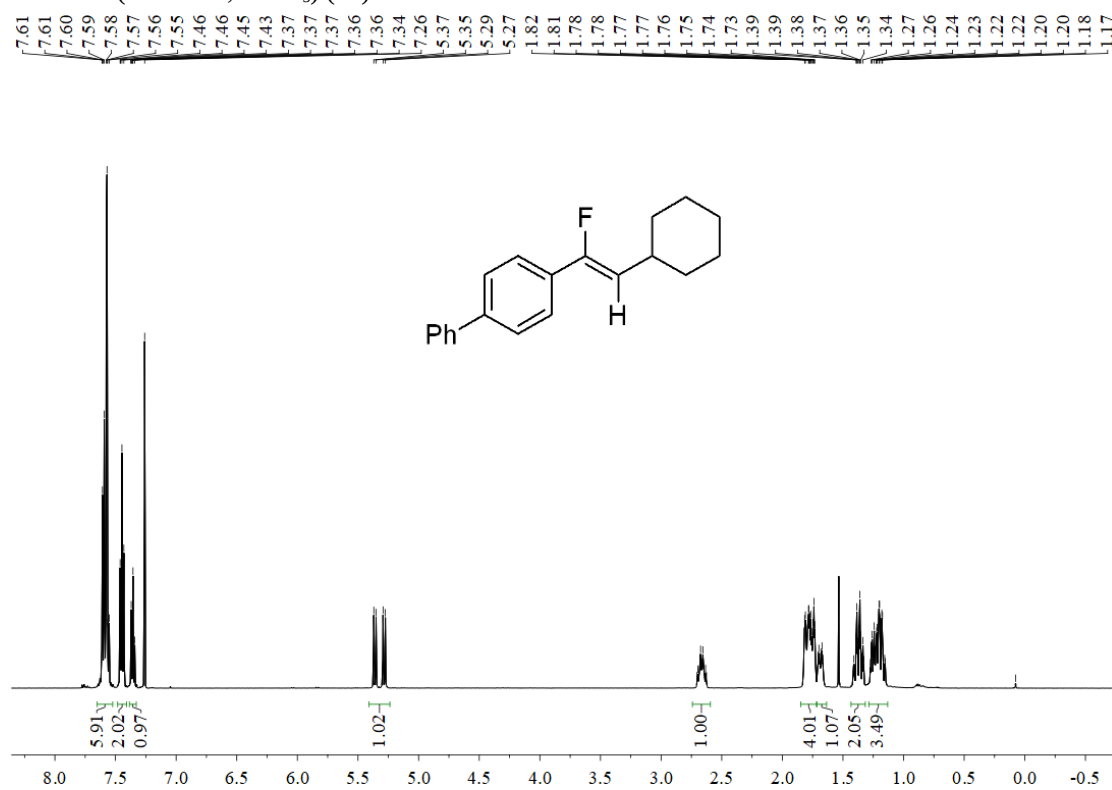
¹³C NMR (126 MHz, CDCl₃) (9)



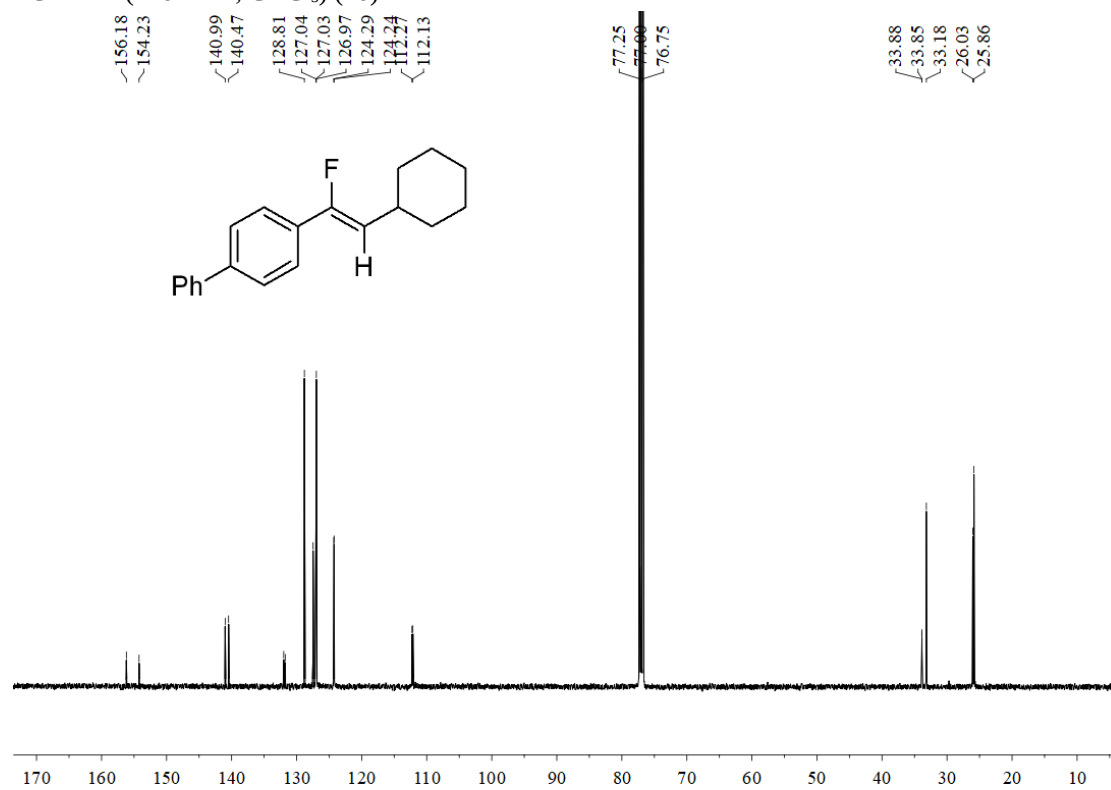
¹⁹F NMR (471 MHz, CDCl₃) (9)



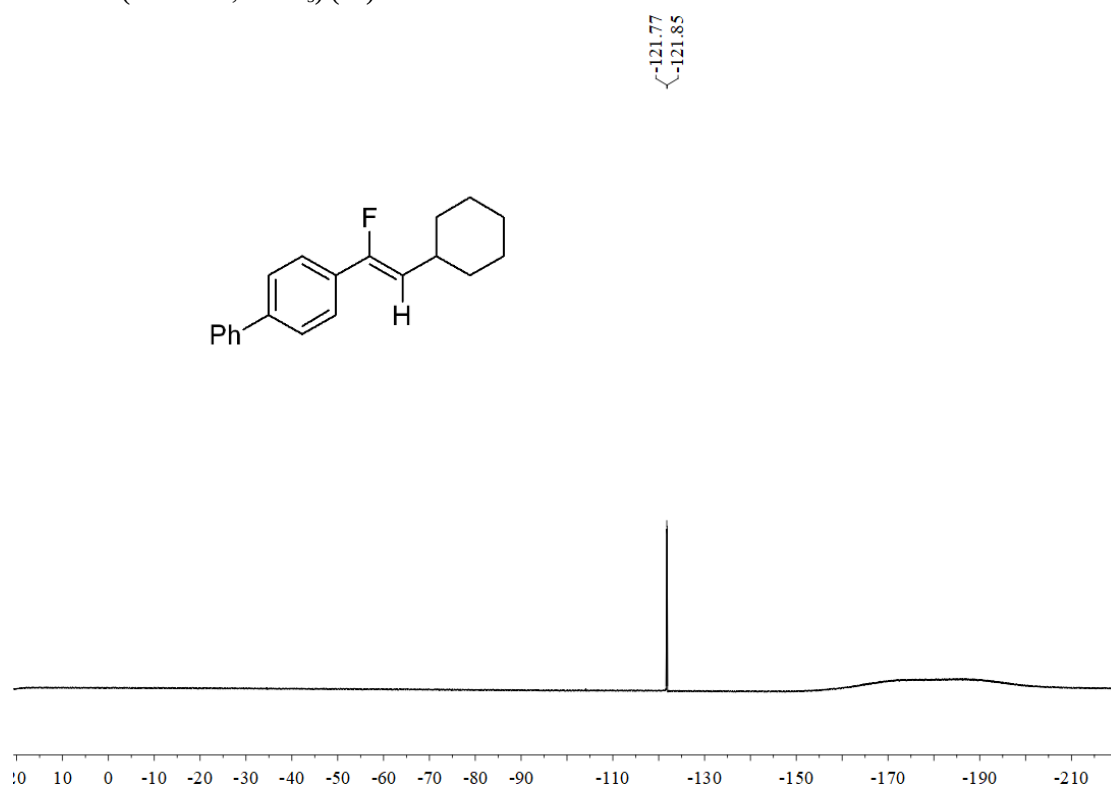
¹H NMR (500 MHz, CDCl₃) (10)



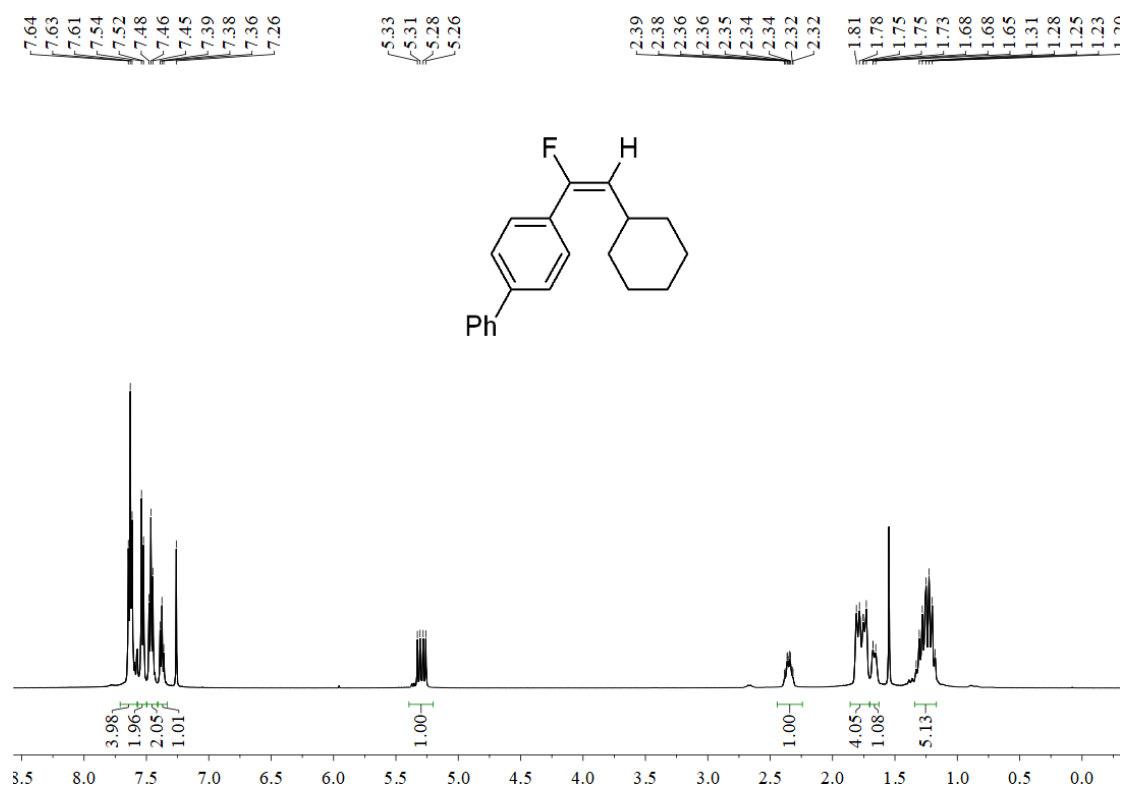
¹³C NMR (126 MHz, CDCl₃) (10)



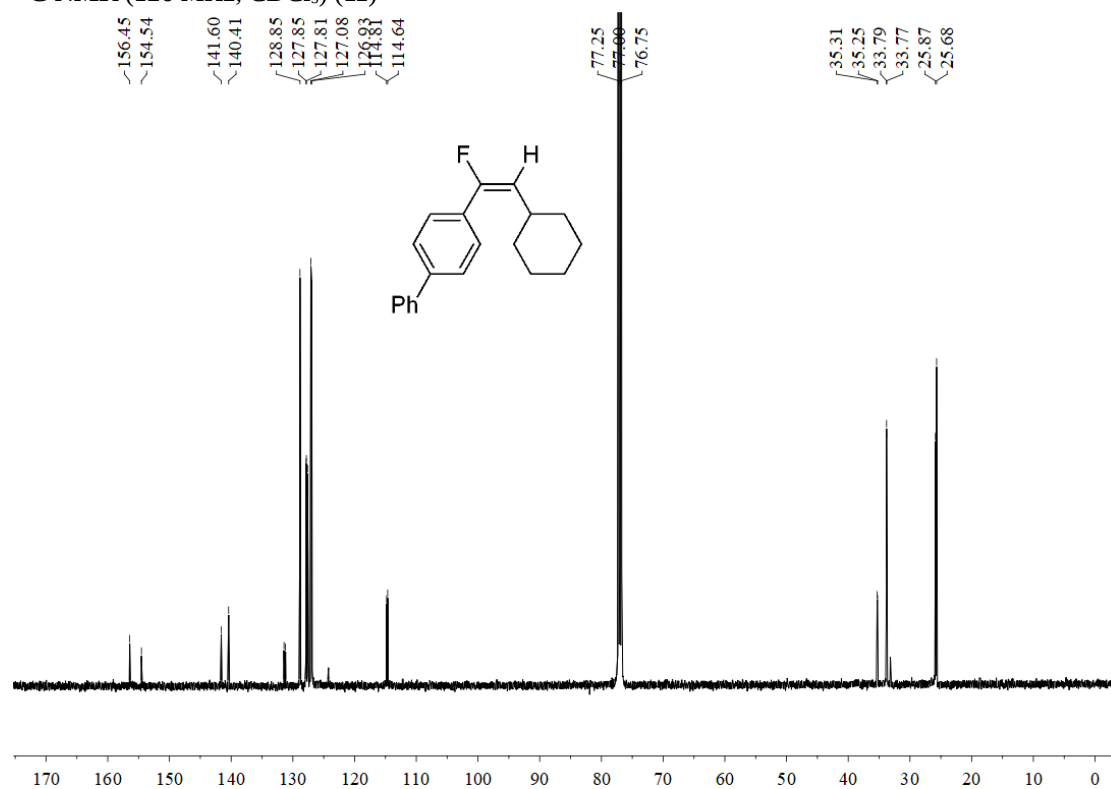
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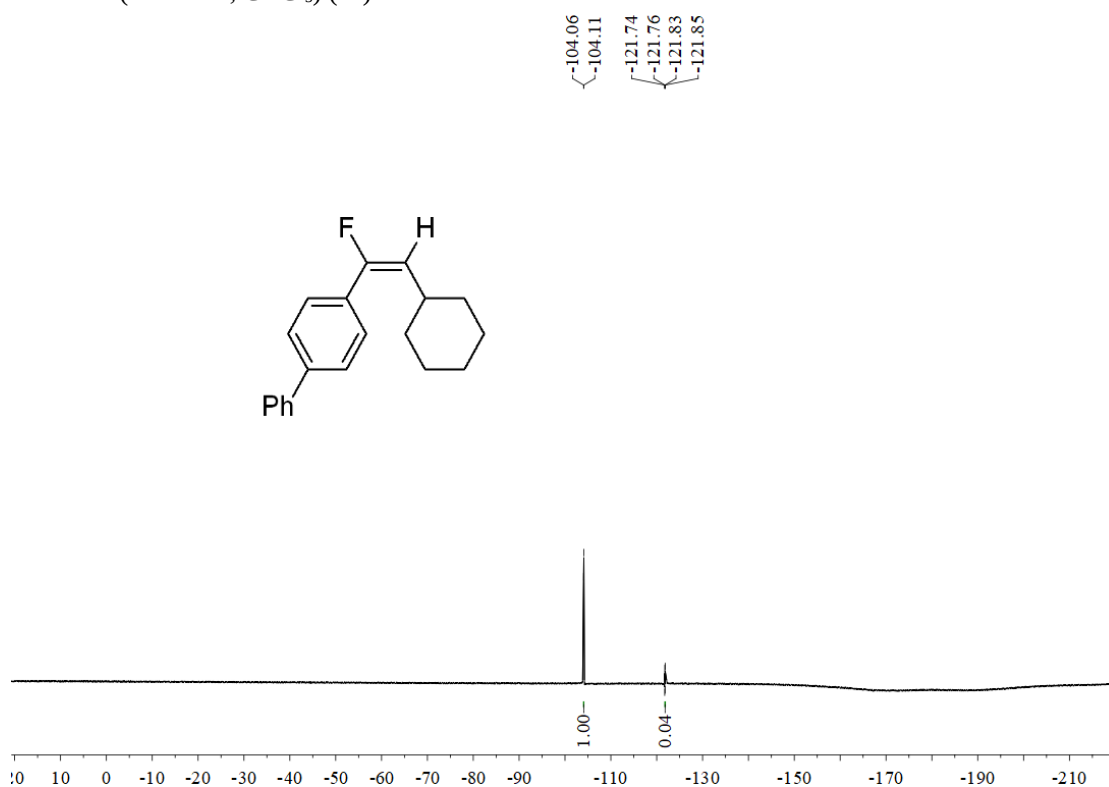
¹H NMR (500 MHz, CDCl₃) (11)



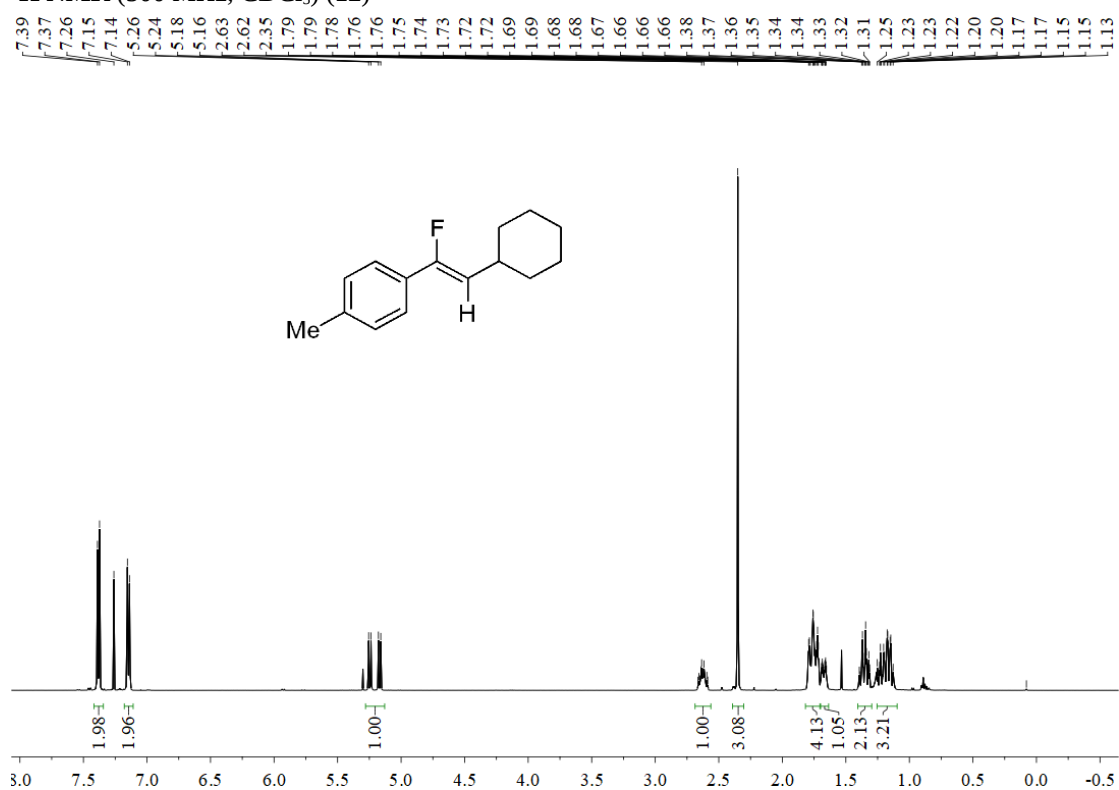
¹³C NMR (126 MHz, CDCl₃) (11)



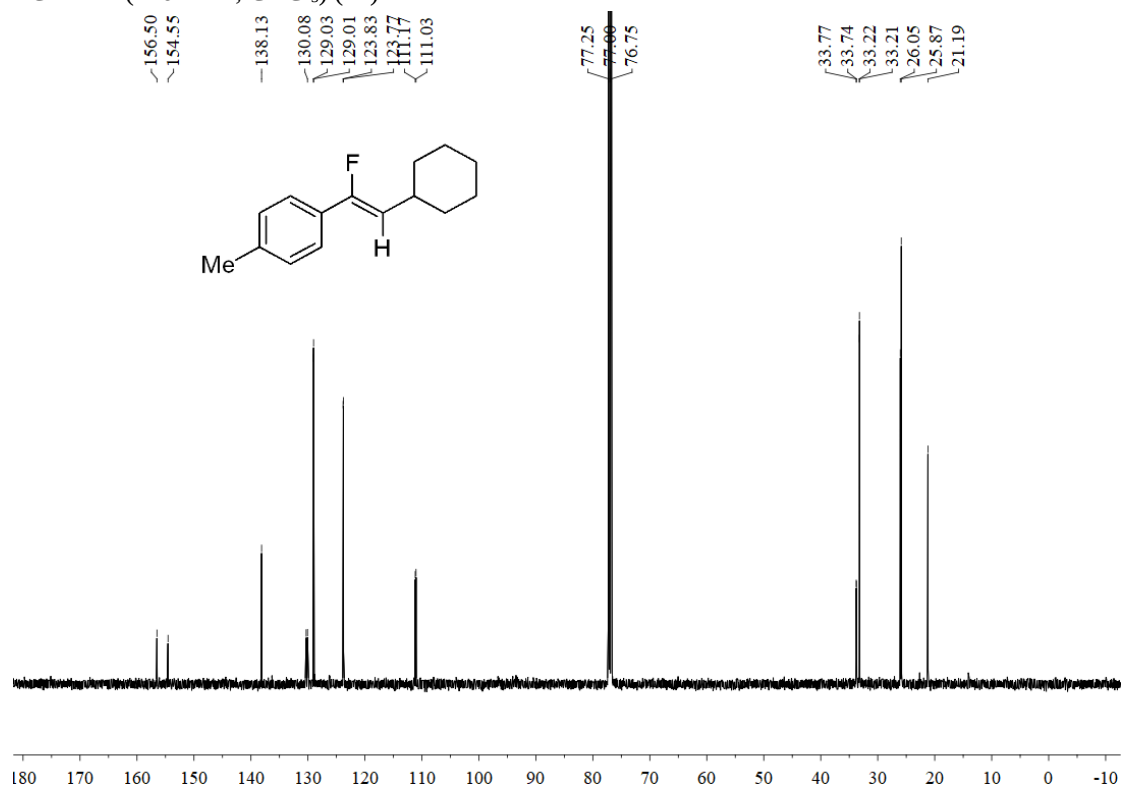
^{19}F NMR (471 MHz, CDCl_3) (11)



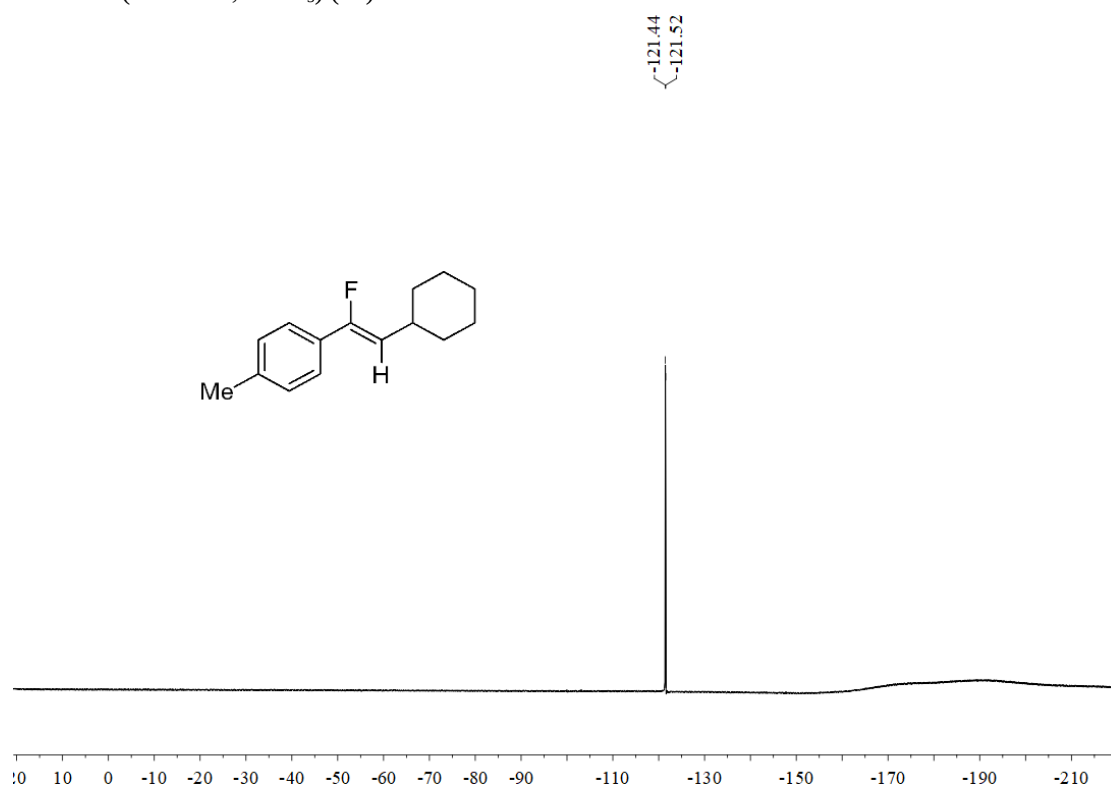
^1H NMR (500 MHz, CDCl_3) (12)



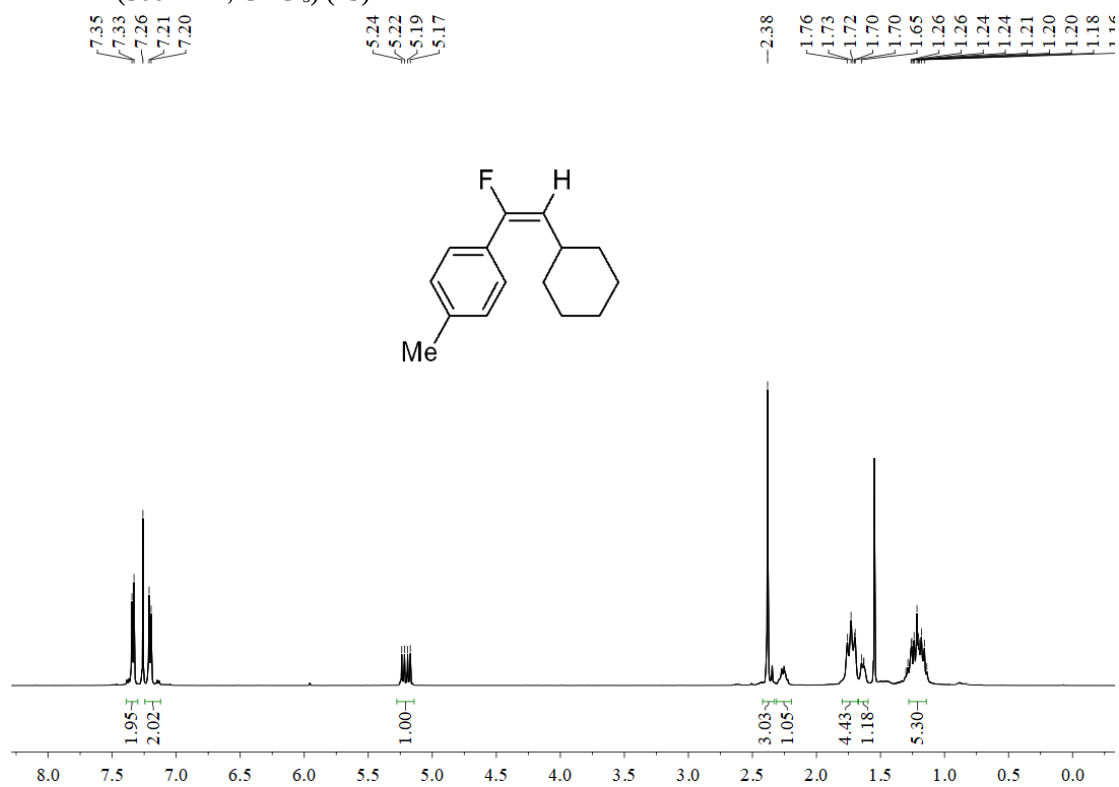
^{13}C NMR (126 MHz, CDCl_3) (12)



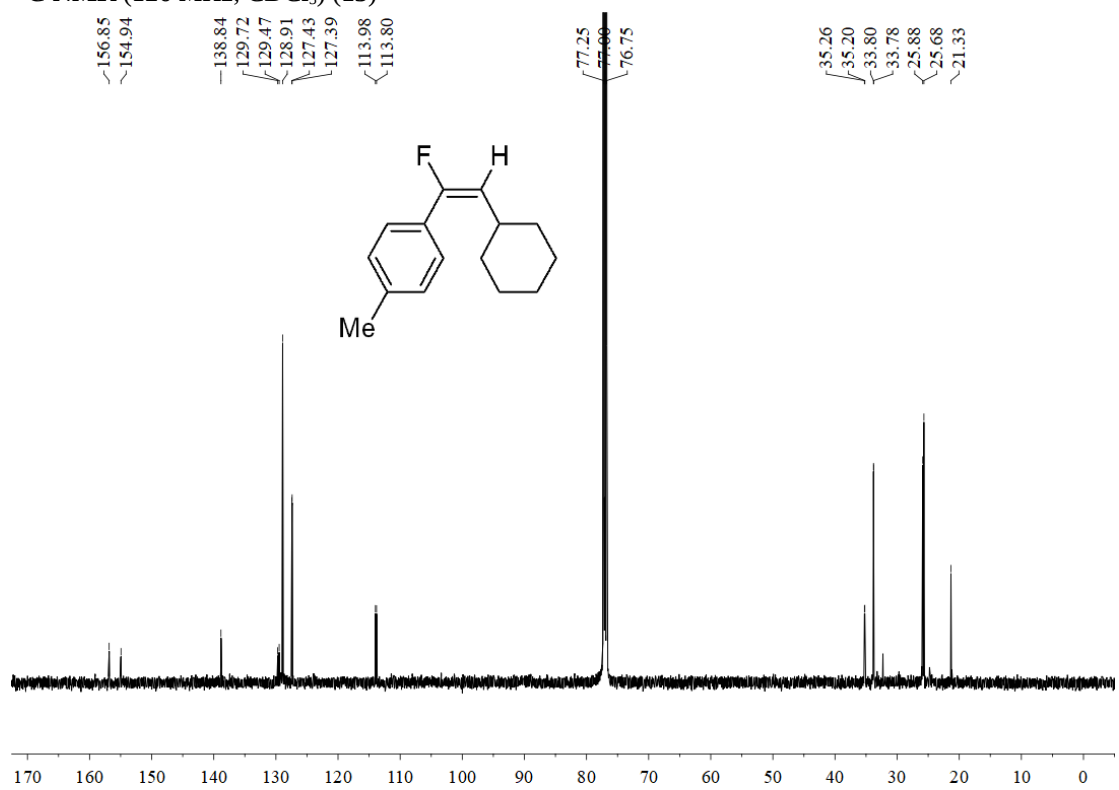
^{19}F NMR (471 MHz, CDCl_3) (12)



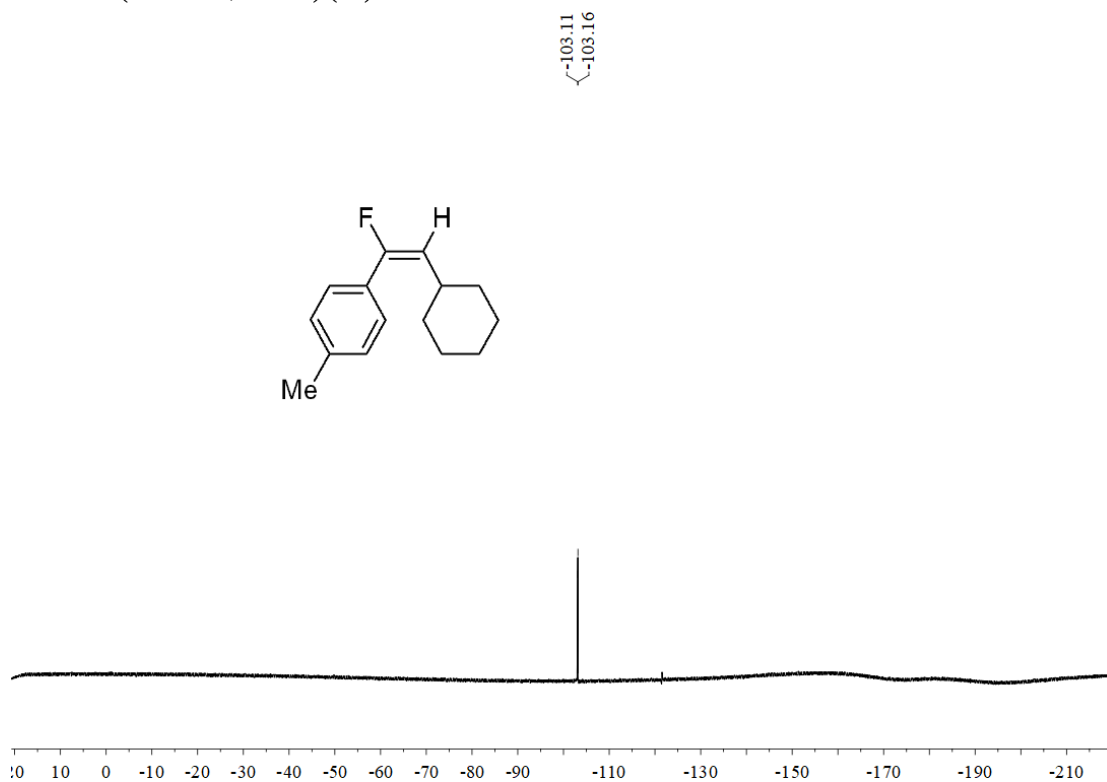
¹H NMR (500 MHz, CDCl₃) (13)



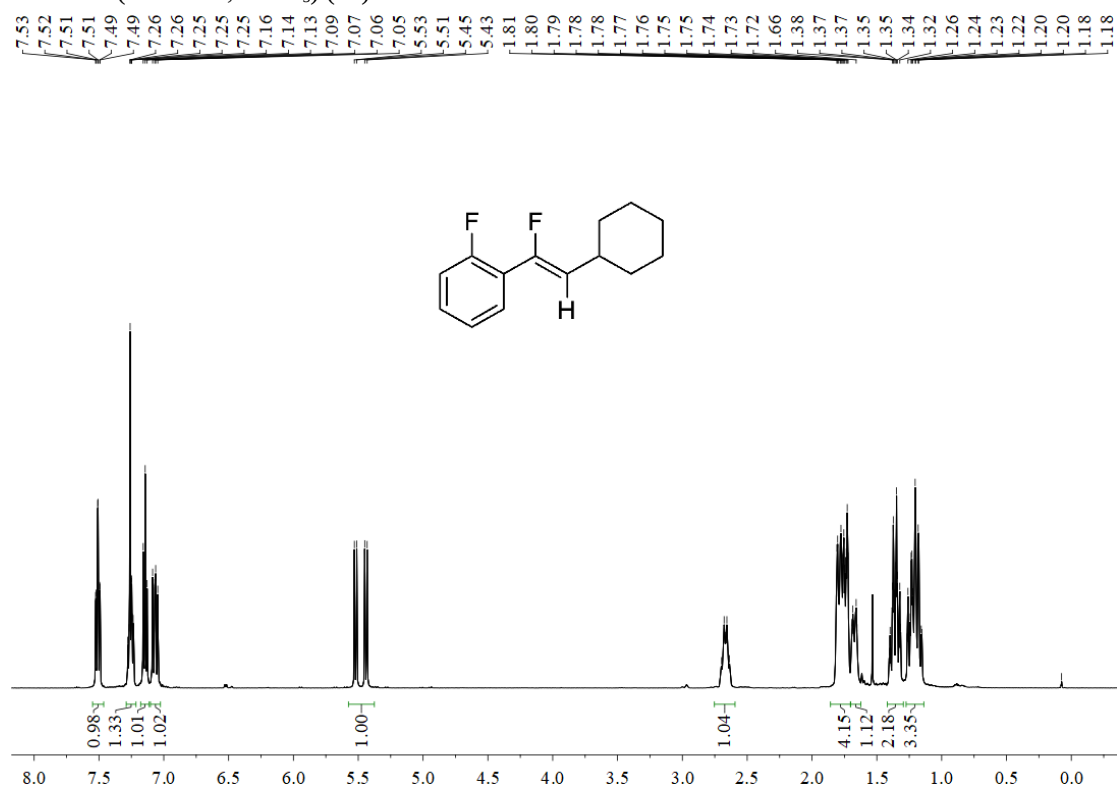
¹³C NMR (126 MHz, CDCl₃) (13)



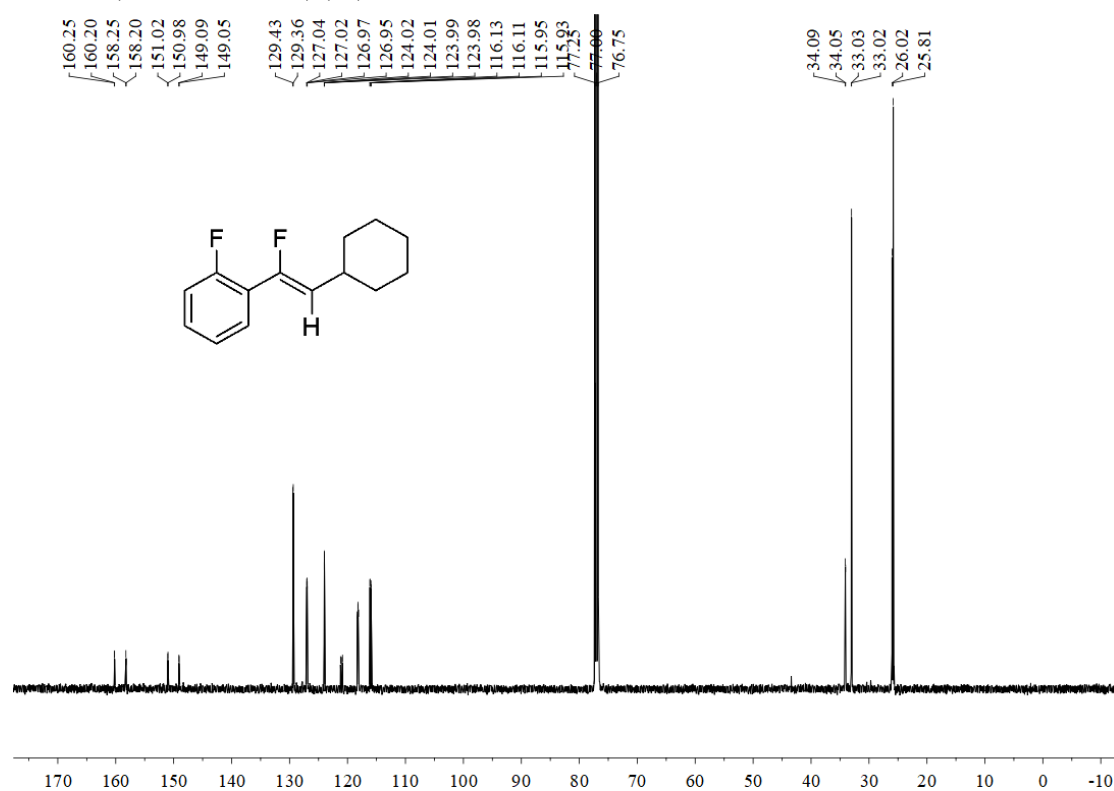
^{19}F NMR (471 MHz, CDCl_3) (13)



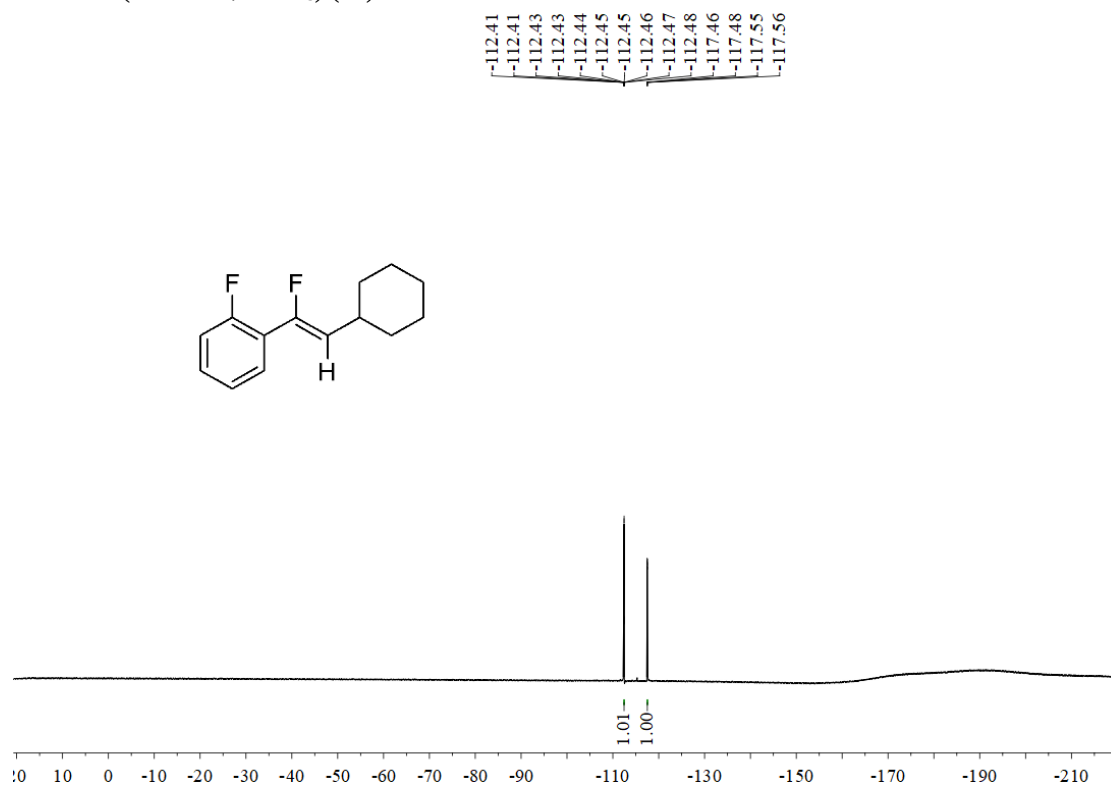
^1H NMR (500 MHz, CDCl_3) (14)



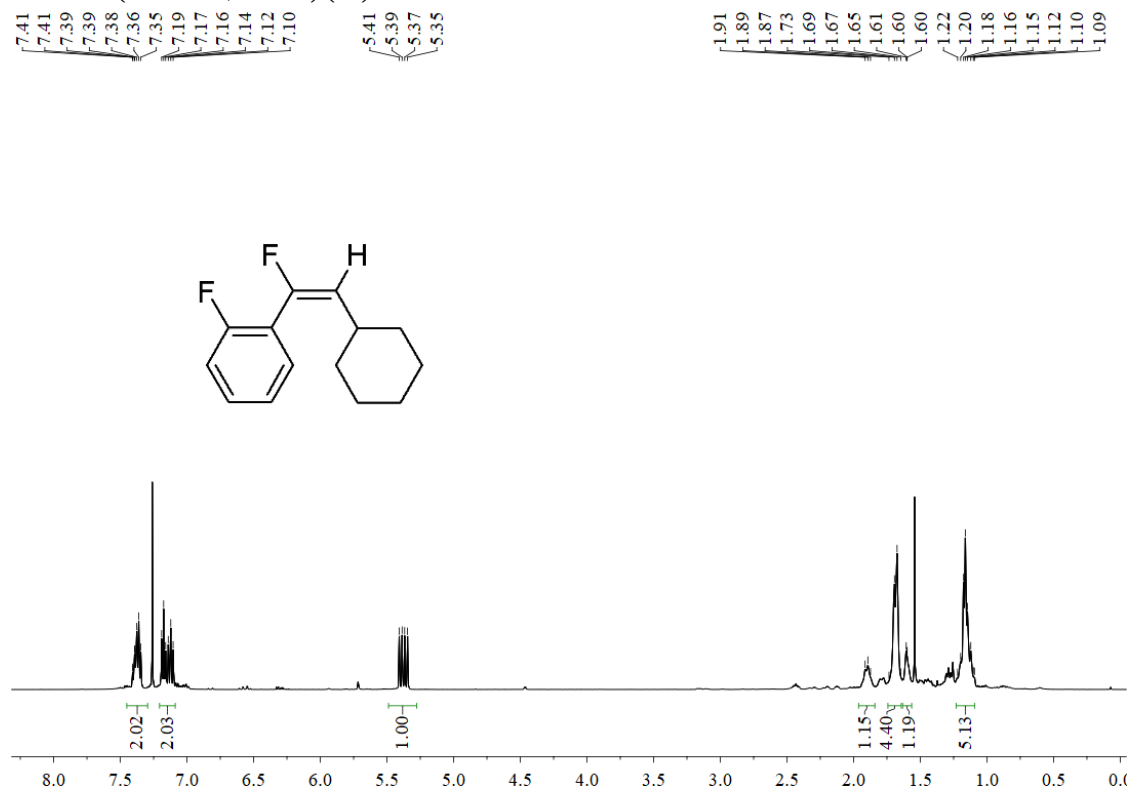
^{13}C NMR (126 MHz, CDCl_3) (14)



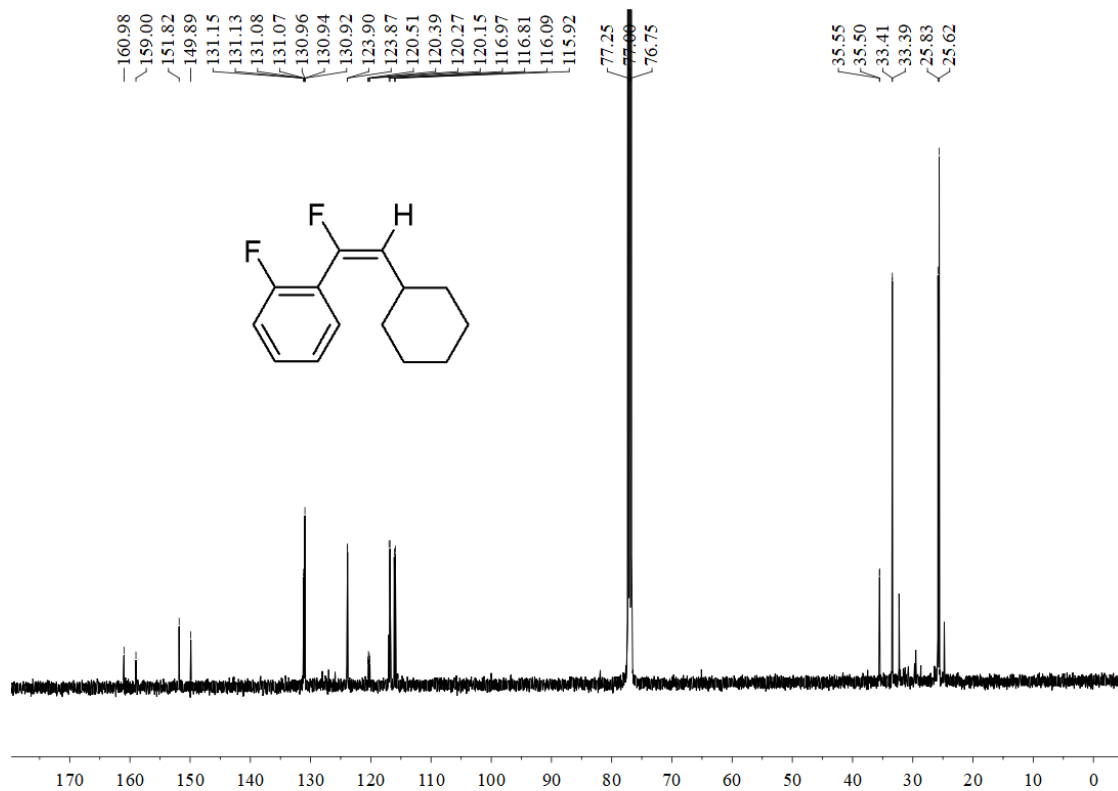
^{19}F NMR (471 MHz, CDCl_3) (14)



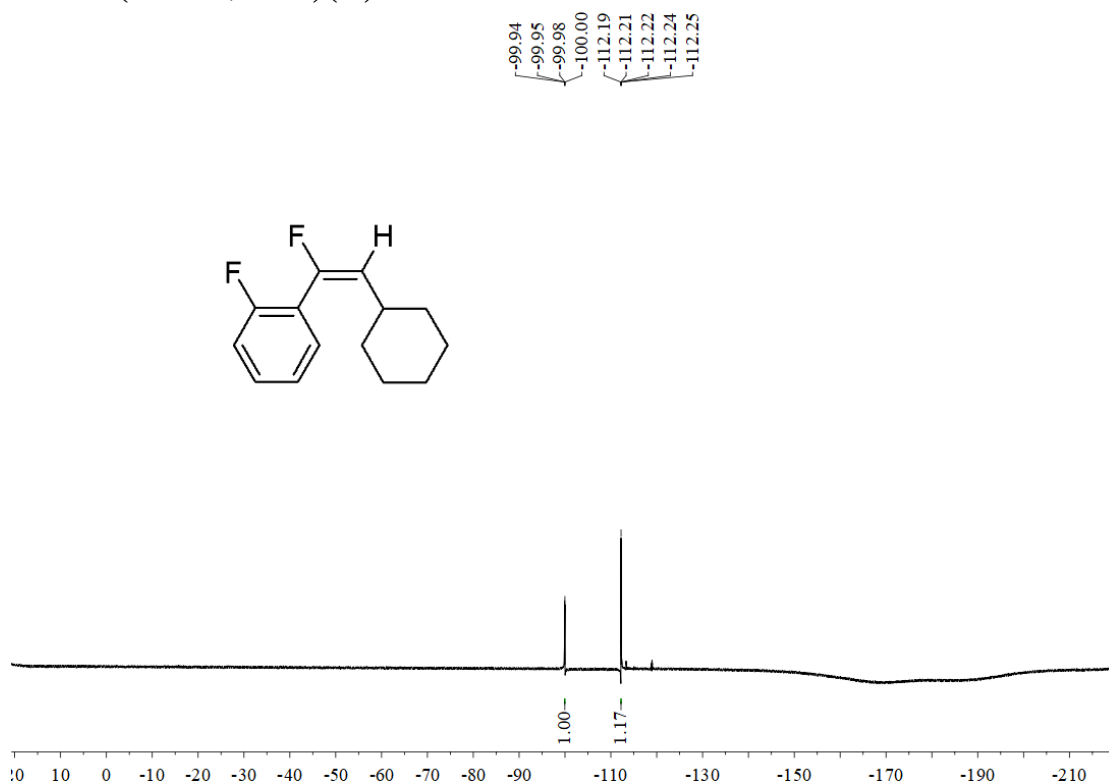
¹H NMR (500 MHz, CDCl₃) (15)



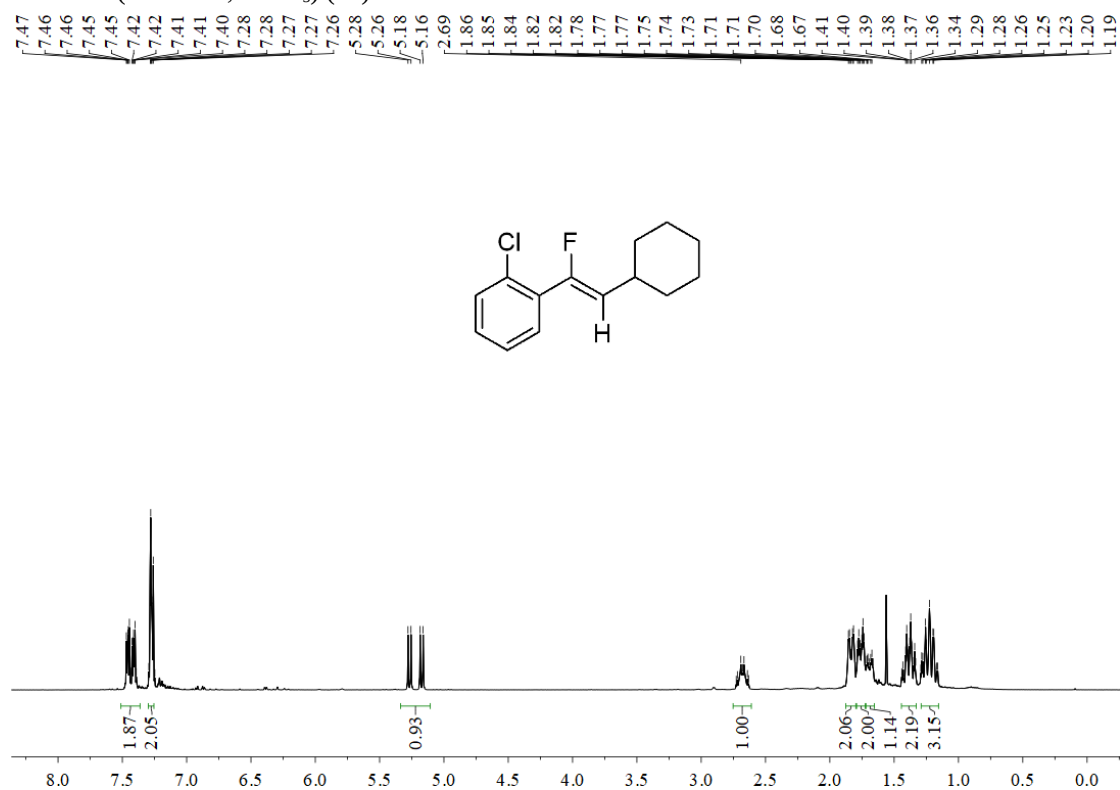
¹³C NMR (126 MHz, CDCl₃) (15)



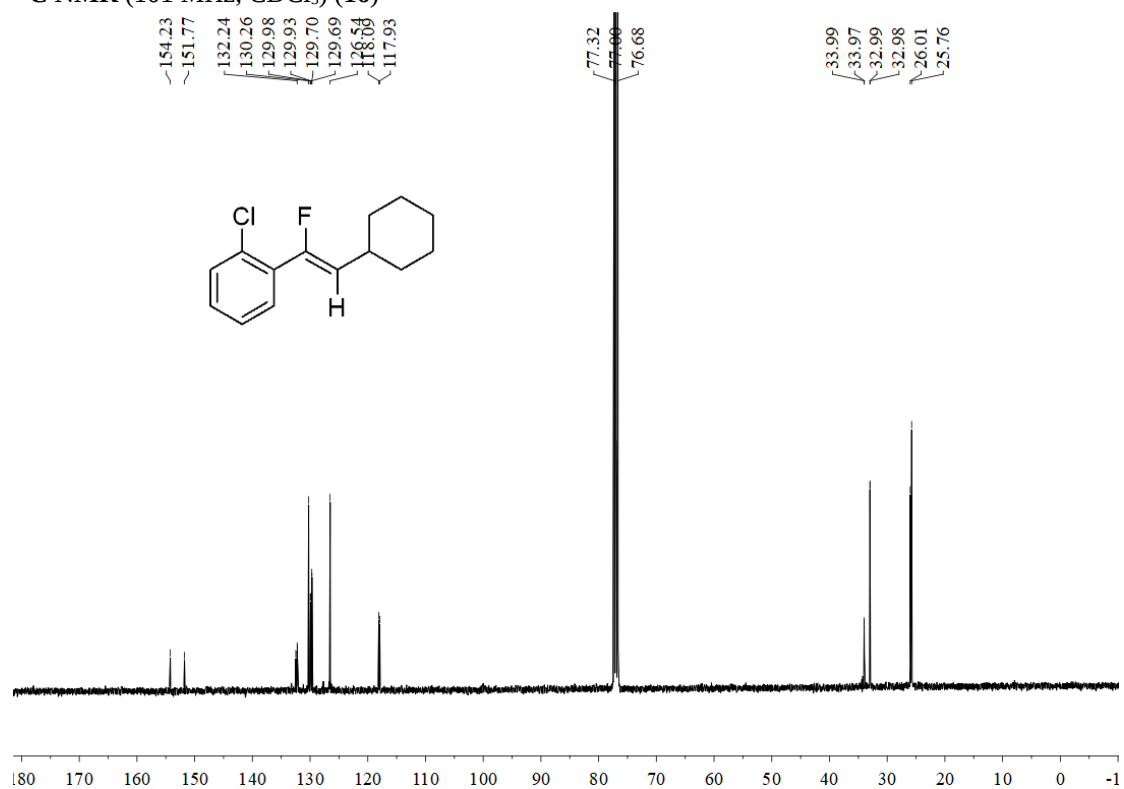
^{19}F NMR (471 MHz, CDCl_3) (15)



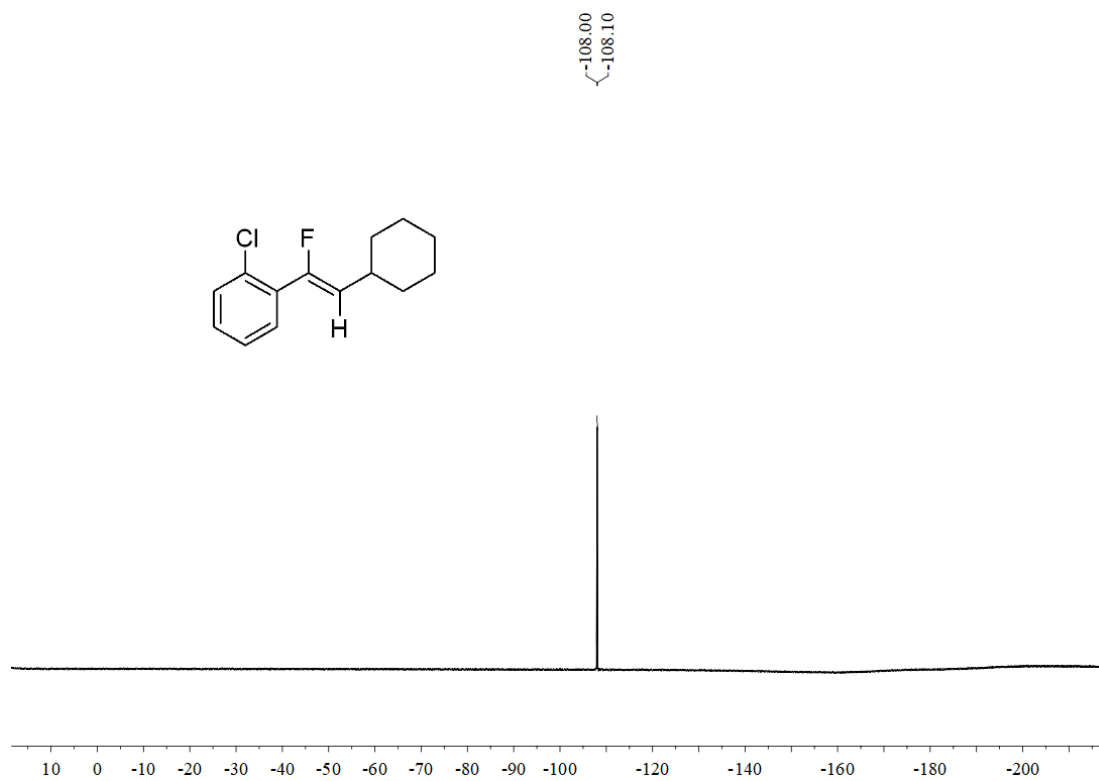
^1H NMR (400 MHz, CDCl_3) (16)



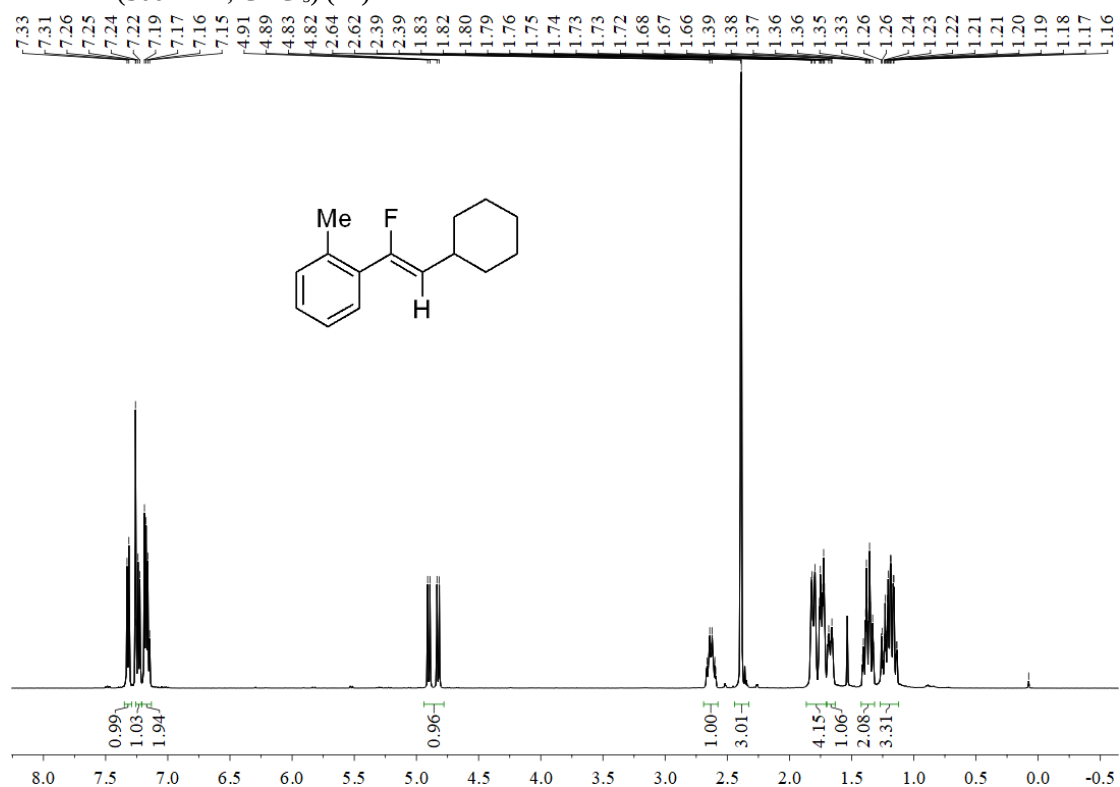
^{13}C NMR (101 MHz, CDCl_3) (16)



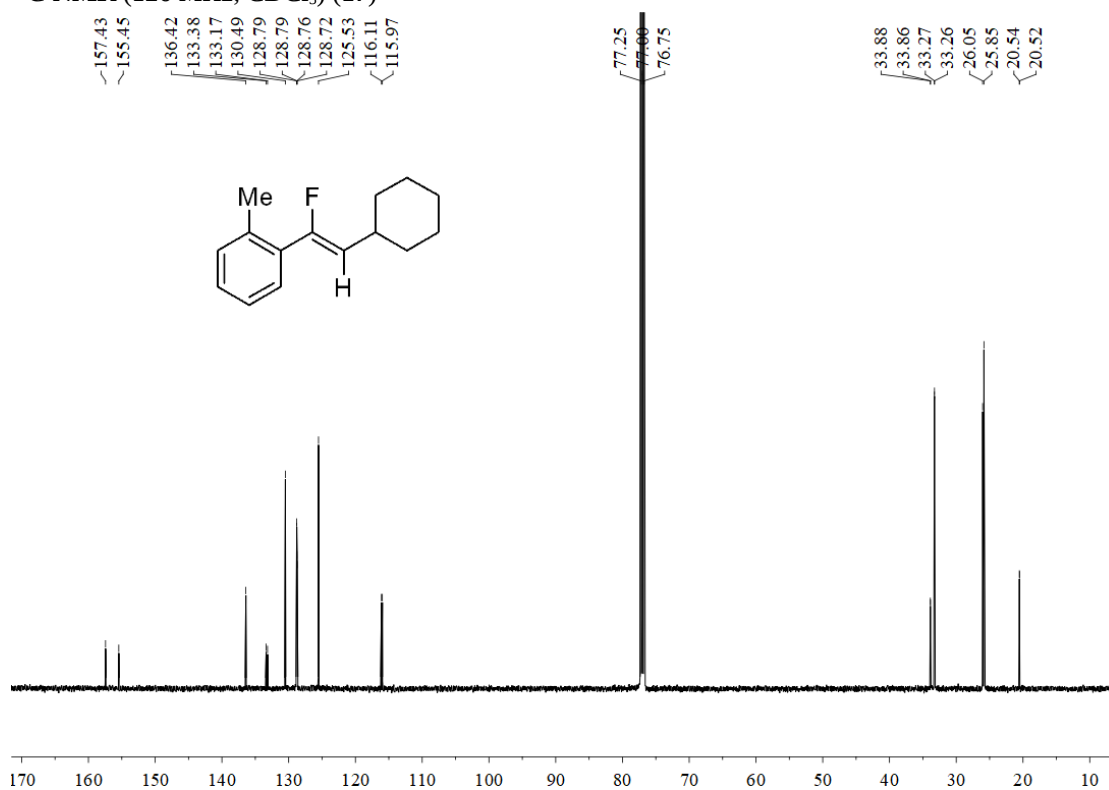
^{19}F NMR (376 MHz, CDCl_3) (16)



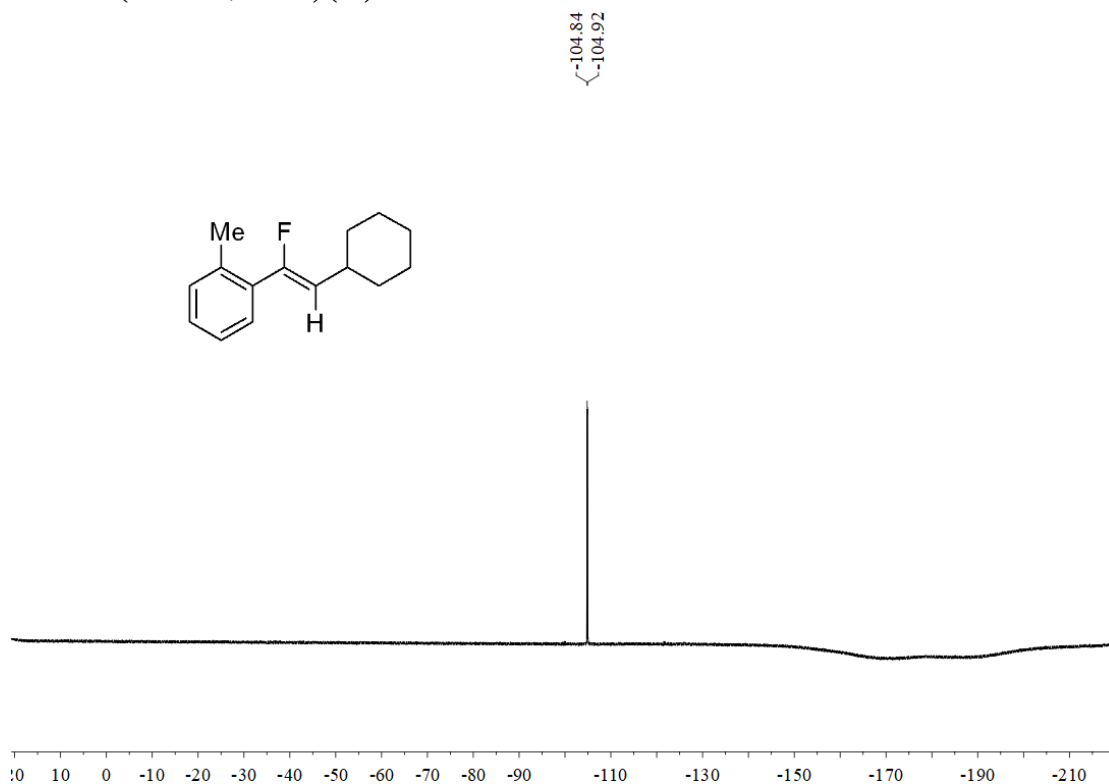
¹H NMR (500 MHz, CDCl₃) (17)



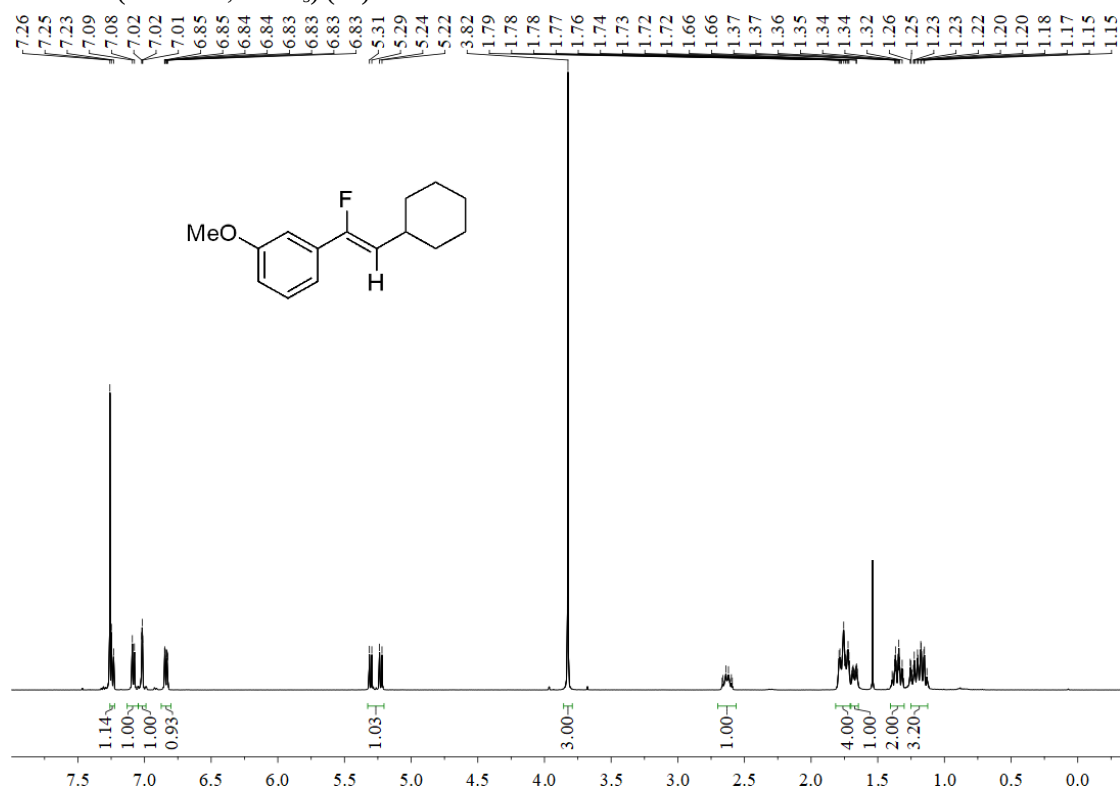
¹³C NMR (126 MHz, CDCl₃) (17)



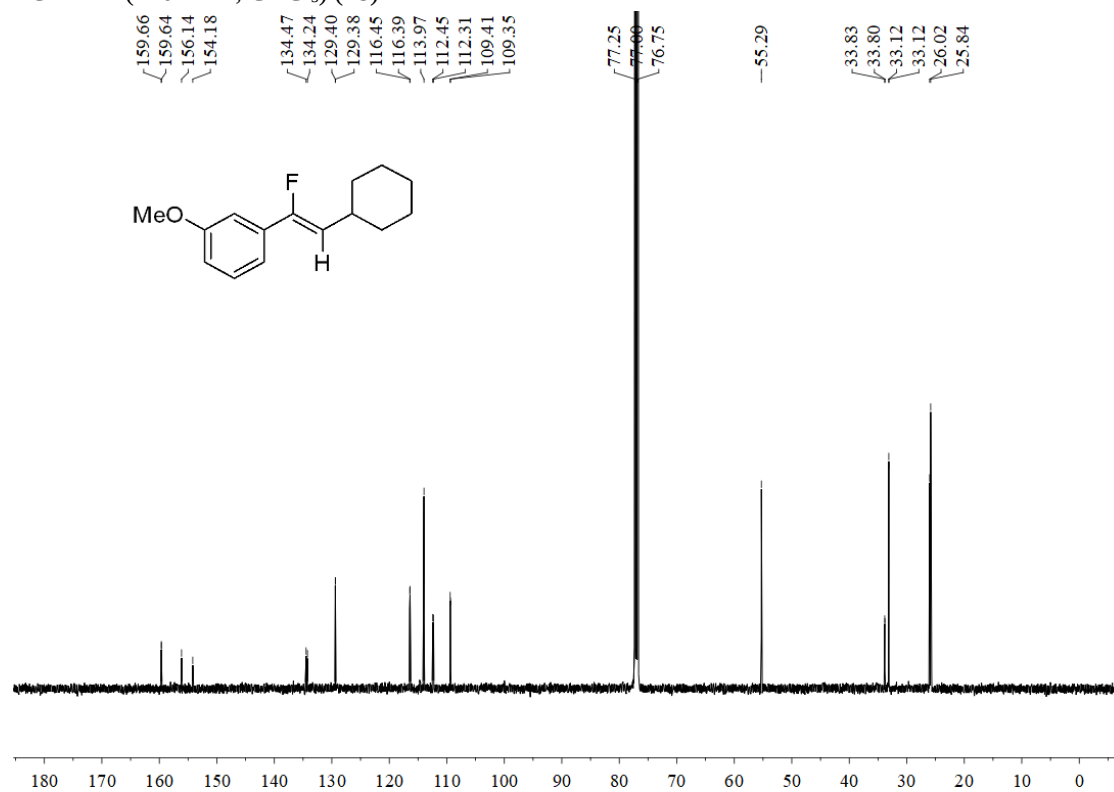
¹⁹F NMR (471 MHz, CDCl₃) (17)



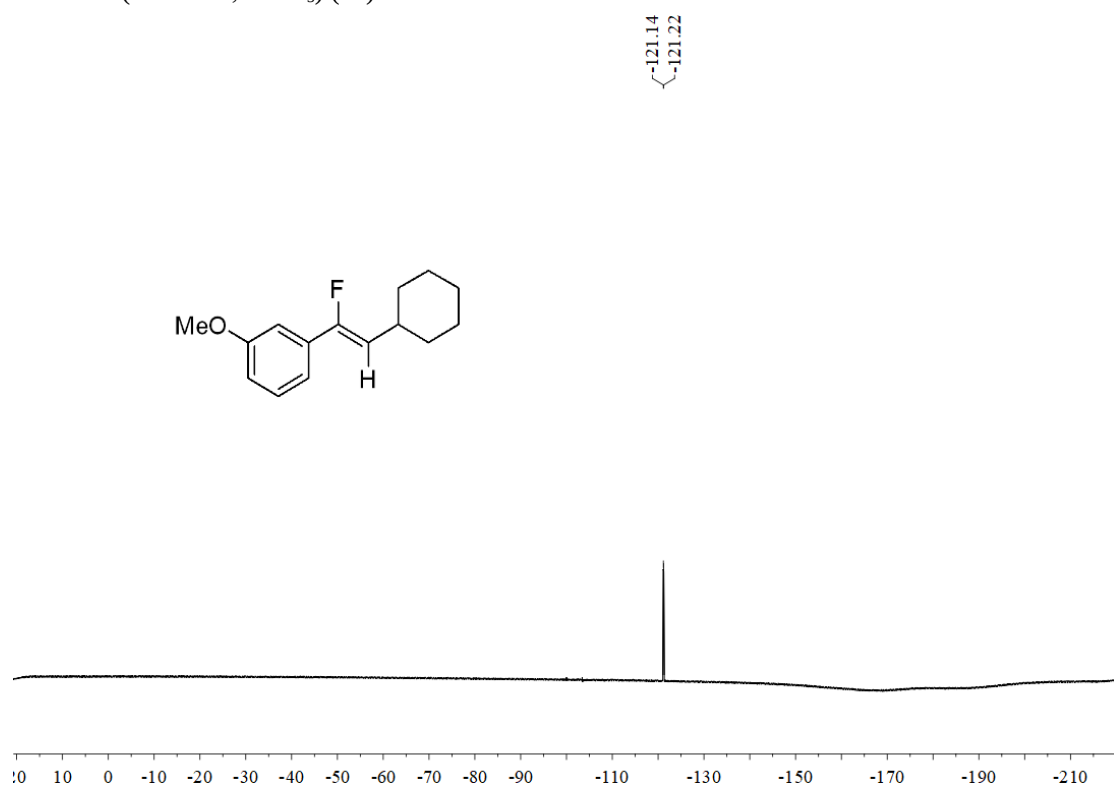
¹H NMR (500 MHz, CDCl₃) (18)



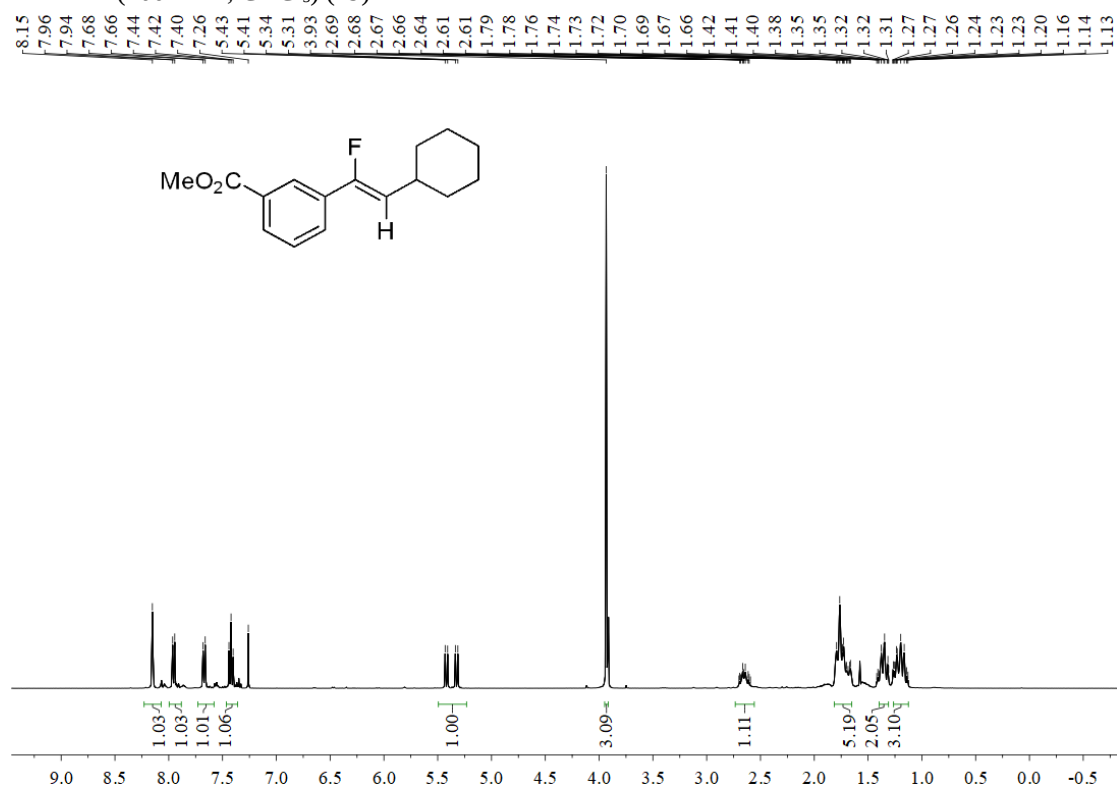
¹³C NMR (126 MHz, CDCl₃) (18)



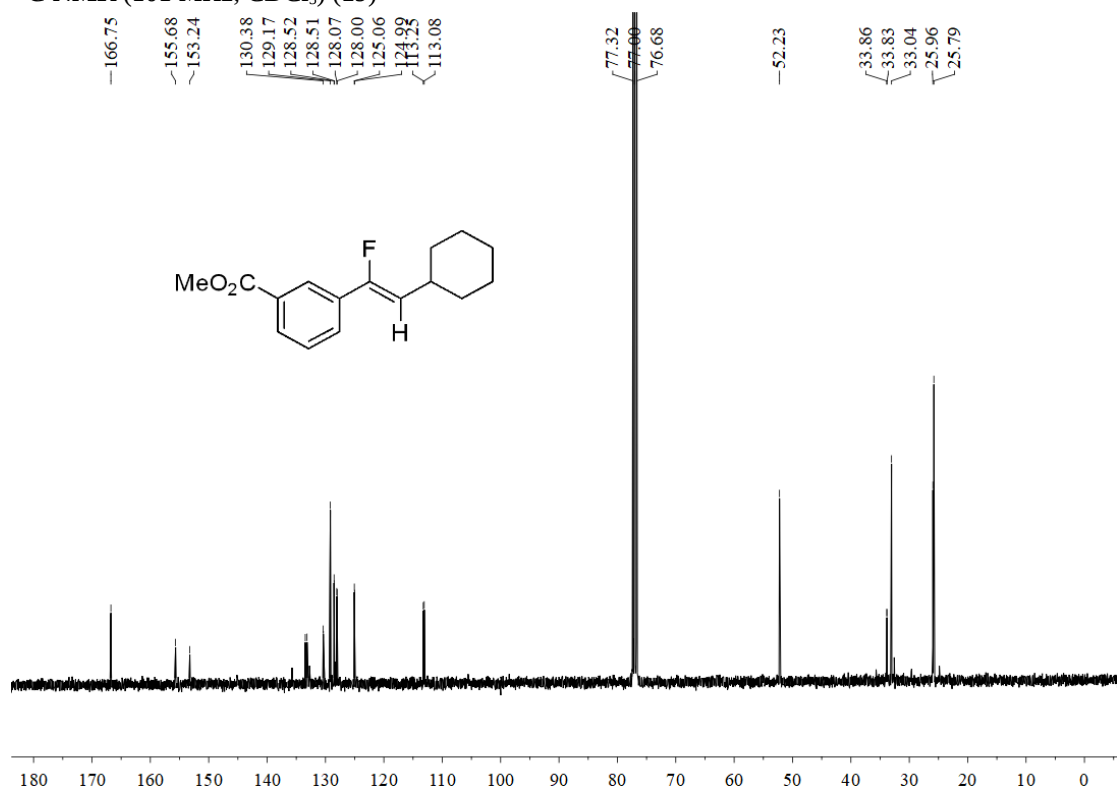
¹⁹F NMR (471 MHz, CDCl₃) (18)



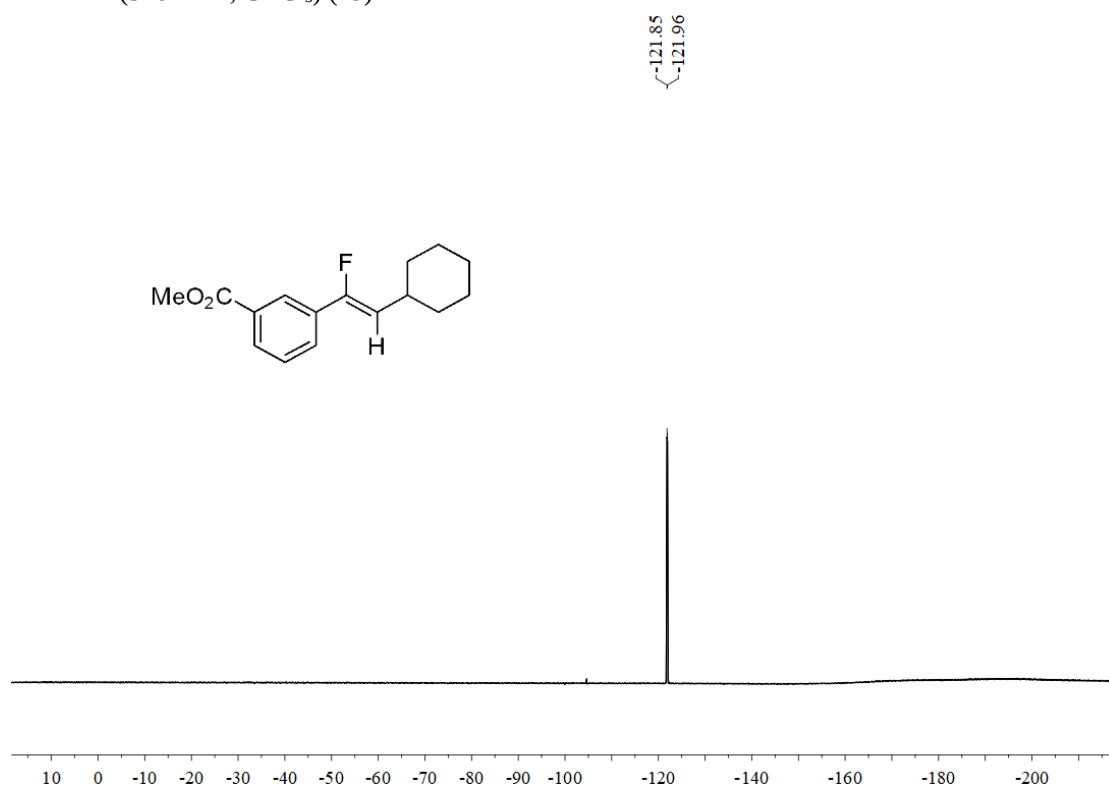
¹H NMR (400 MHz, CDCl₃) (19)



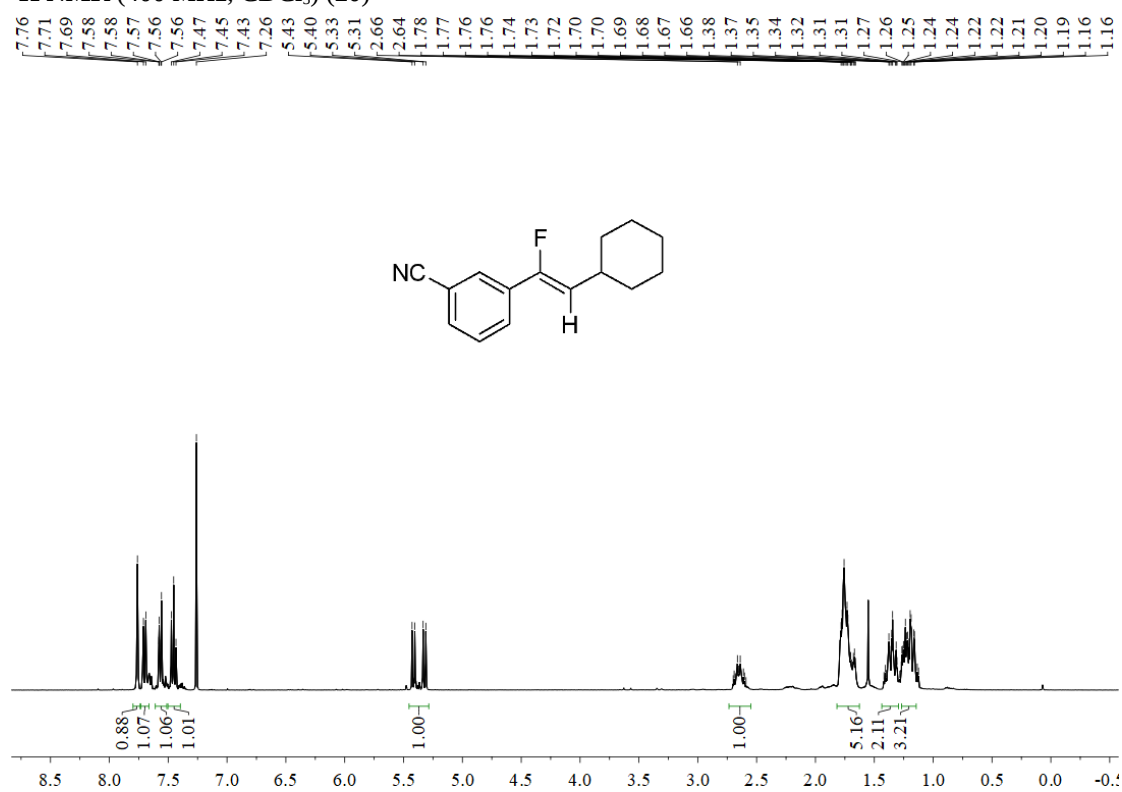
¹³C NMR (101 MHz, CDCl₃) (19)



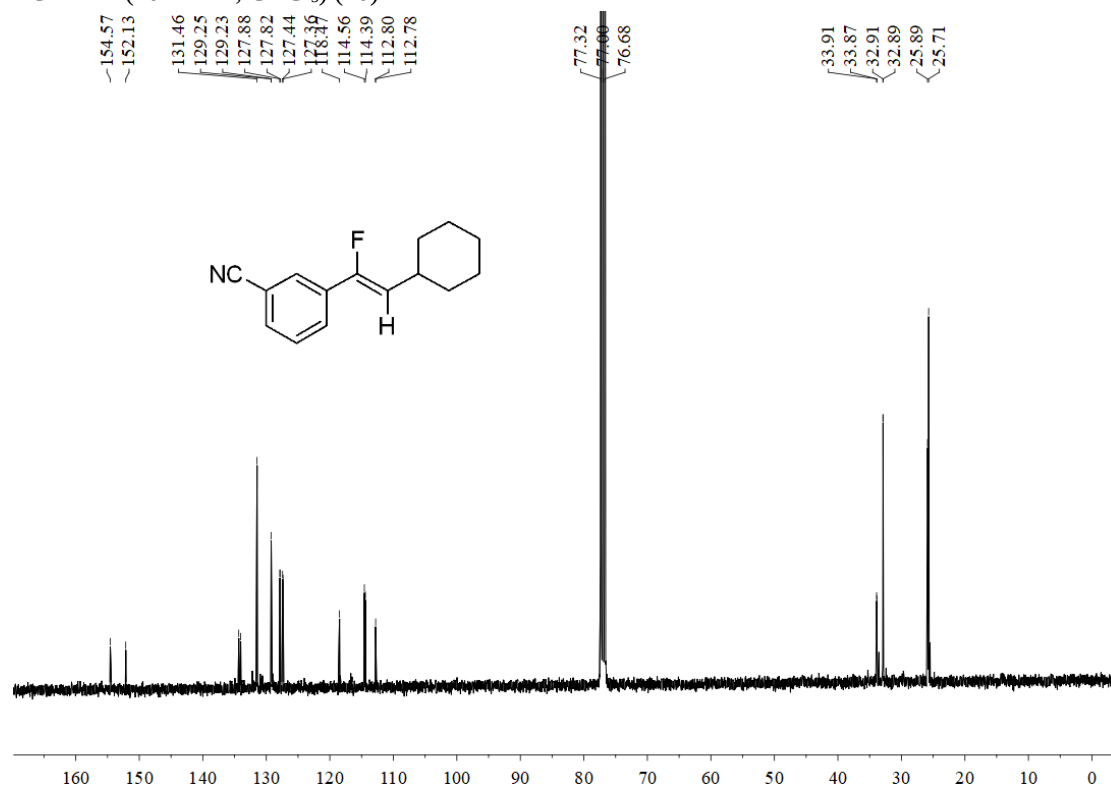
^{19}F NMR (376 MHz, CDCl_3) (19)



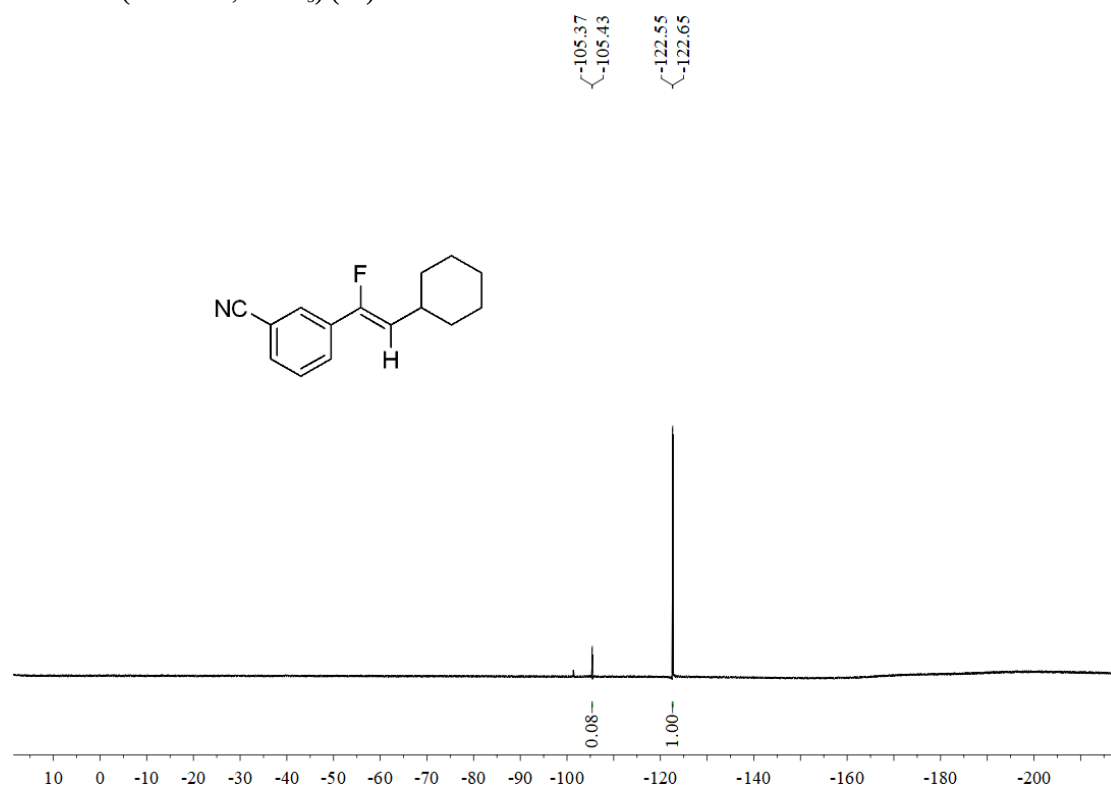
^1H NMR (400 MHz, CDCl_3) (20)



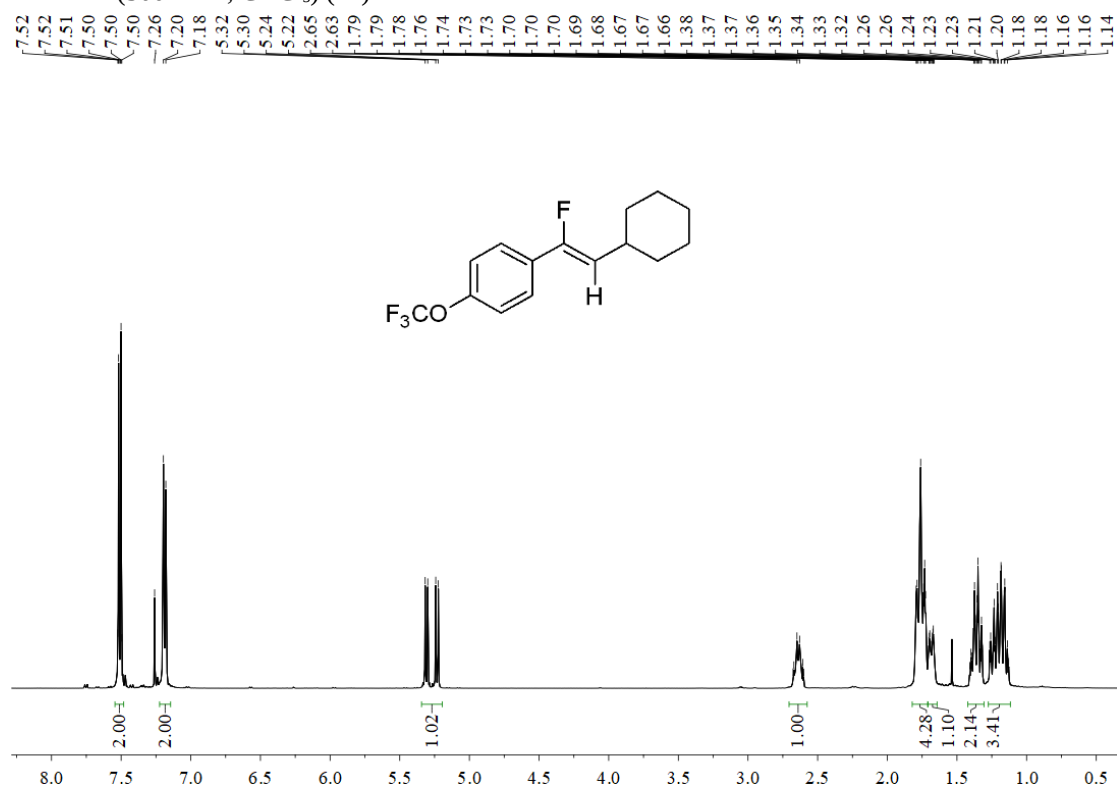
^{13}C NMR (101 MHz, CDCl_3) (20)



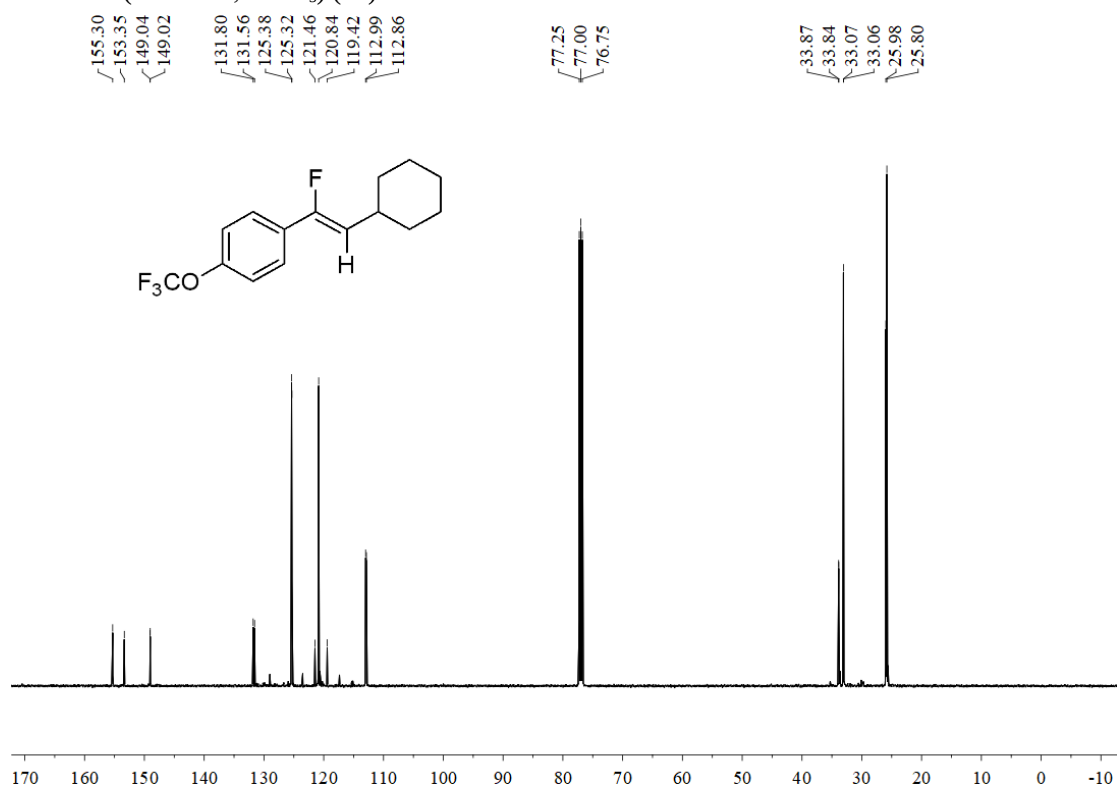
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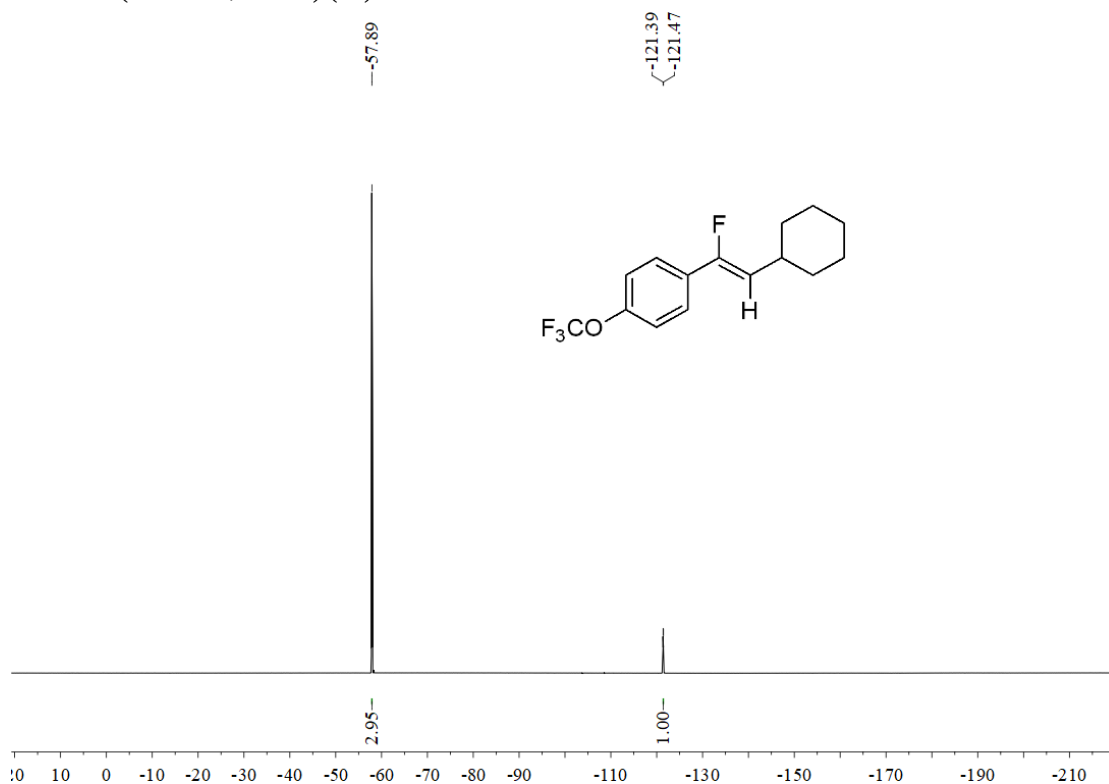
¹H NMR (500 MHz, CDCl₃) (21)



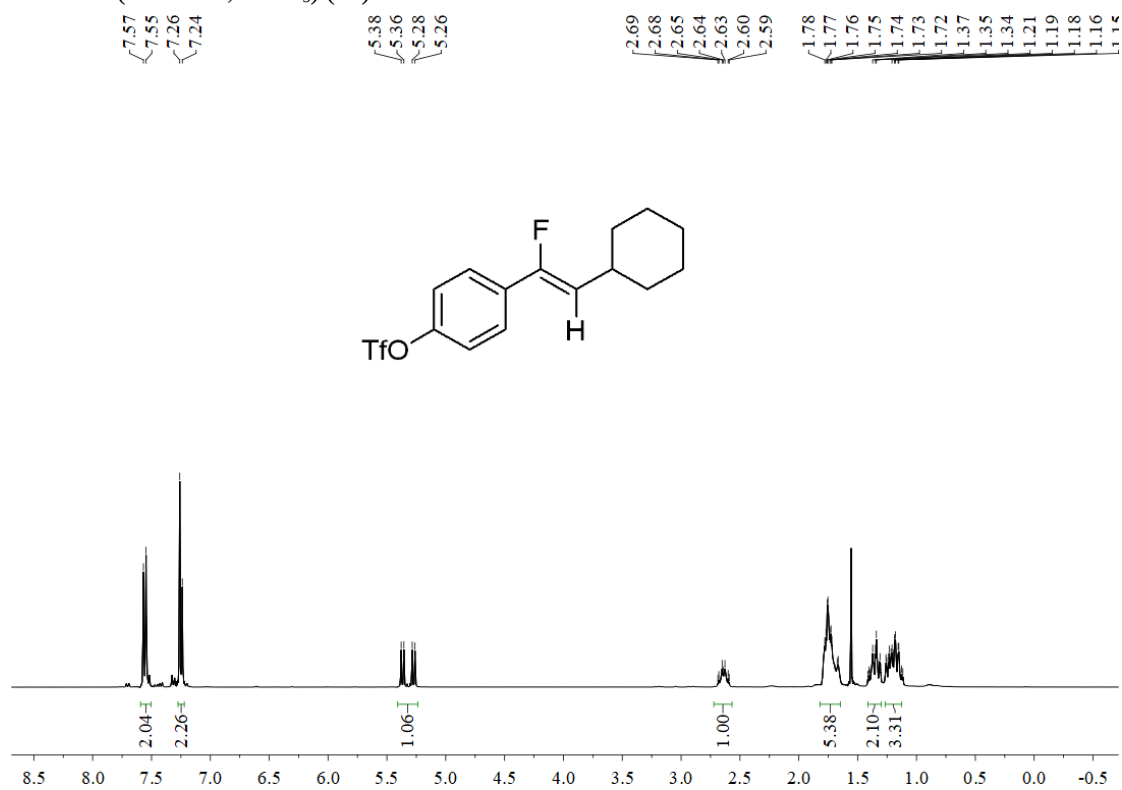
¹³C NMR (126 MHz, CDCl₃) (21)



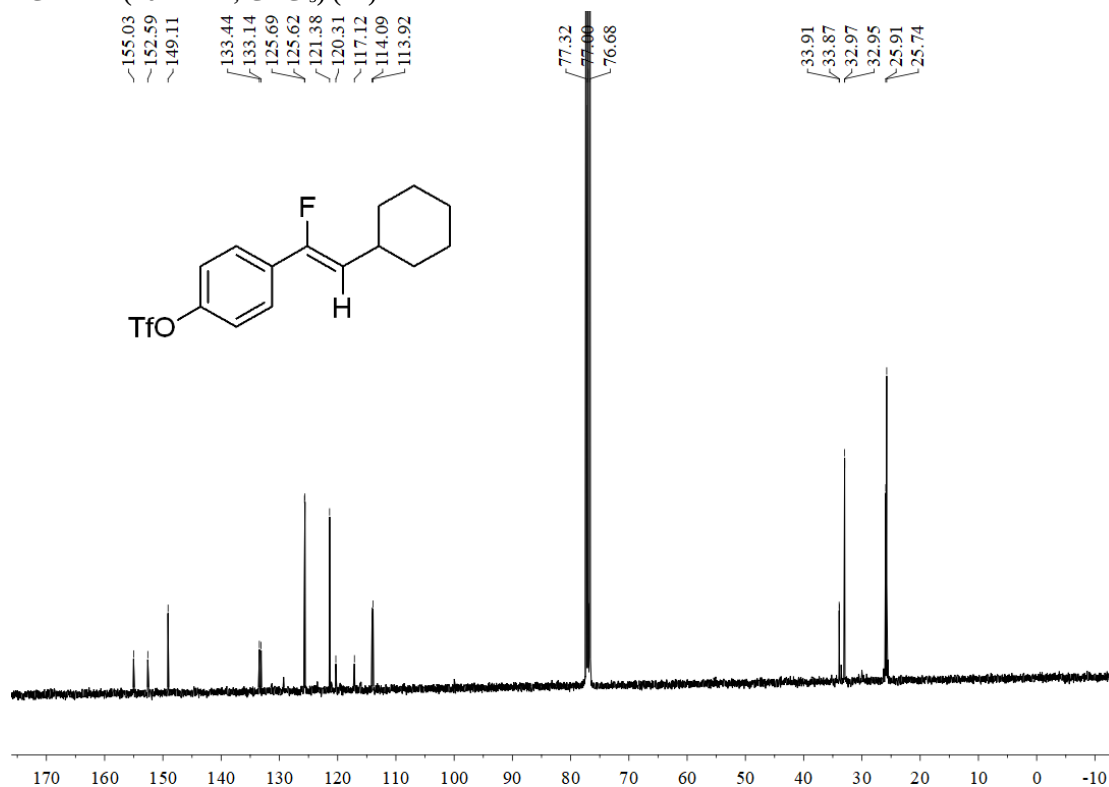
^{19}F NMR (471 MHz, CDCl_3) (21)



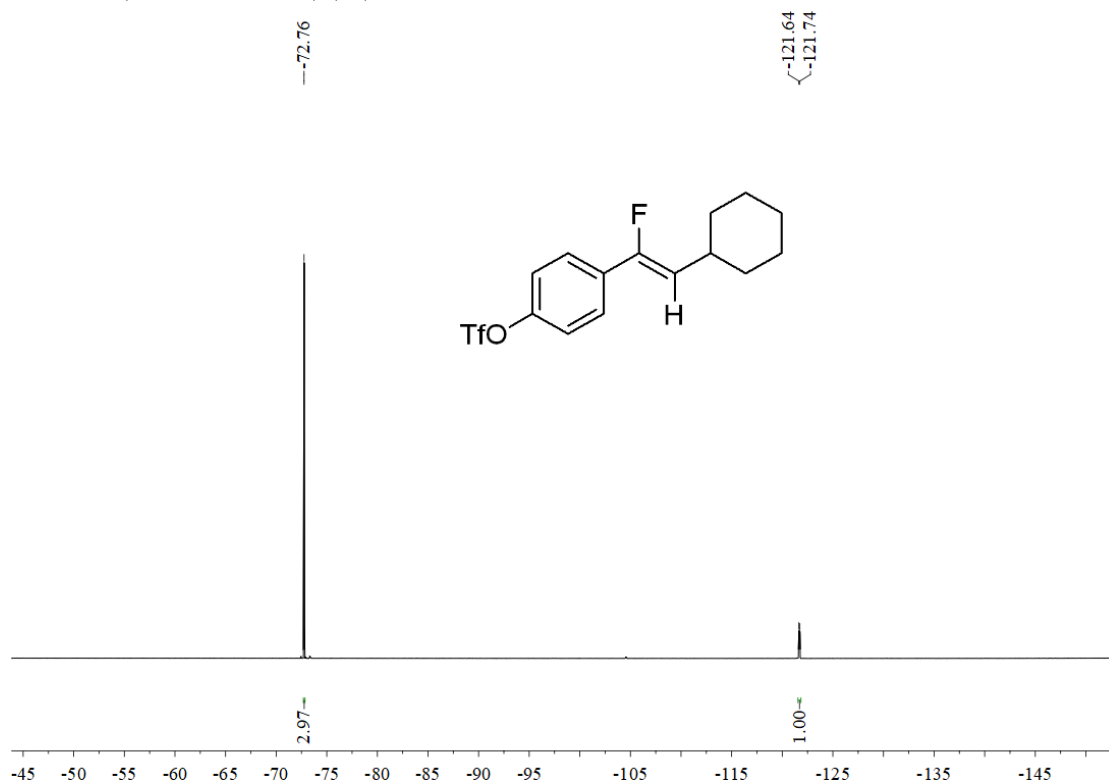
^1H NMR (400 MHz, CDCl_3) (22)



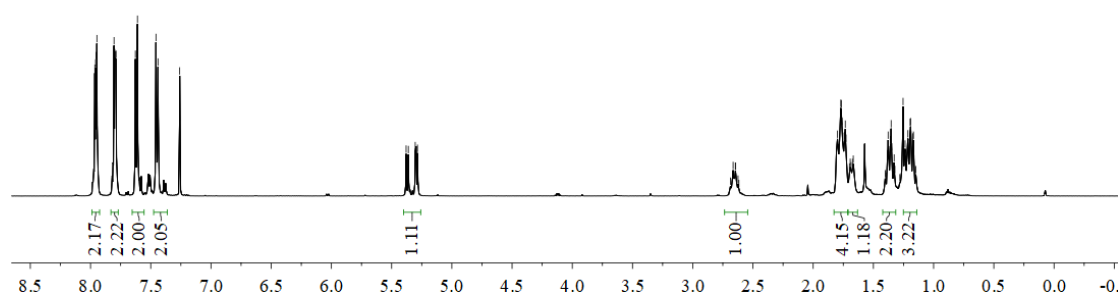
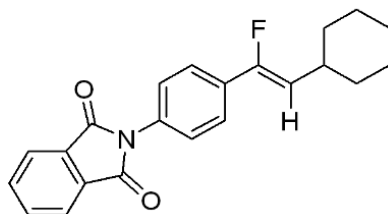
^{13}C NMR (101 MHz, CDCl_3) (22)



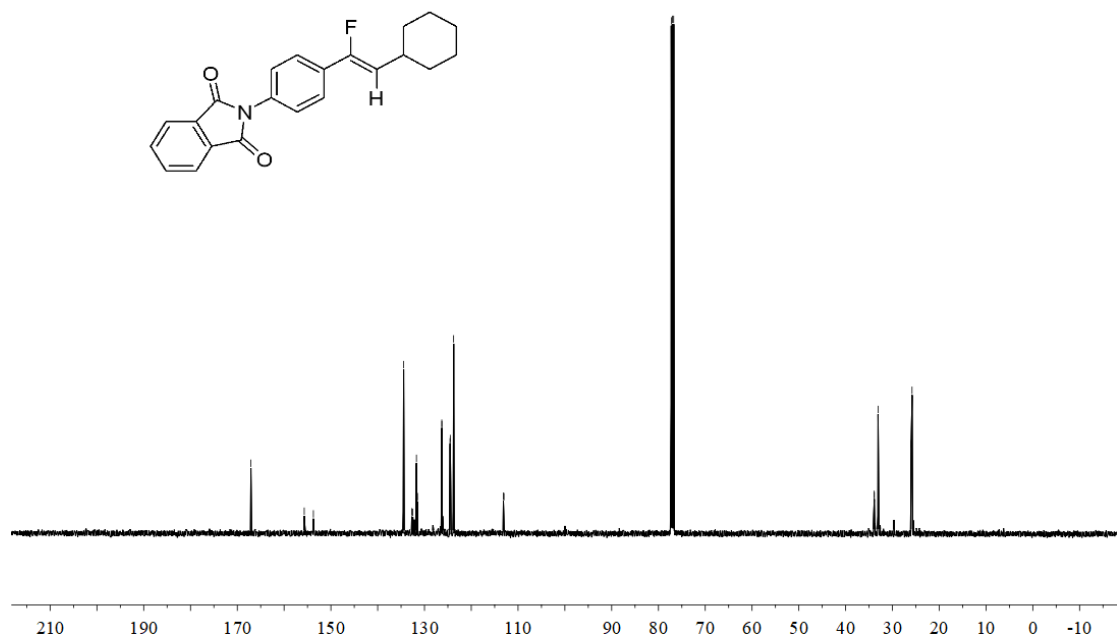
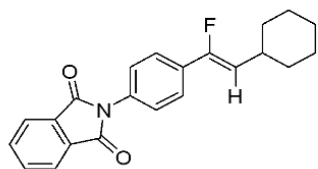
^{19}F NMR (376 MHz, CDCl_3) (22)



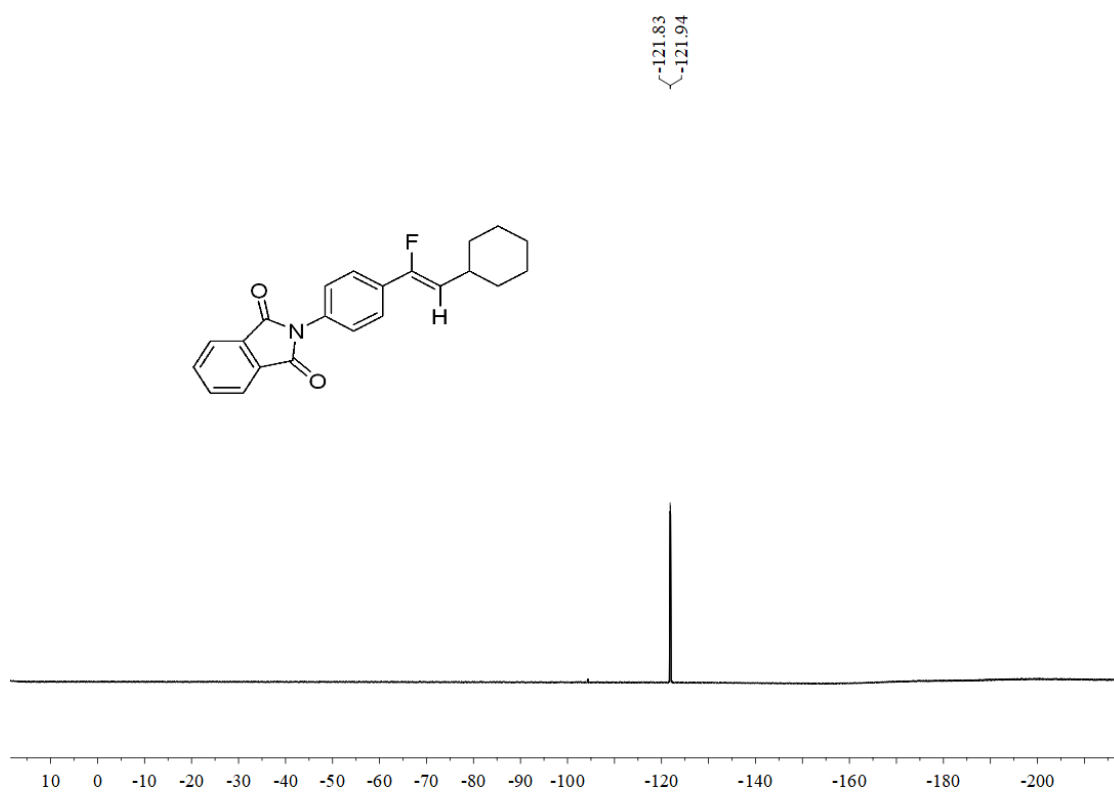
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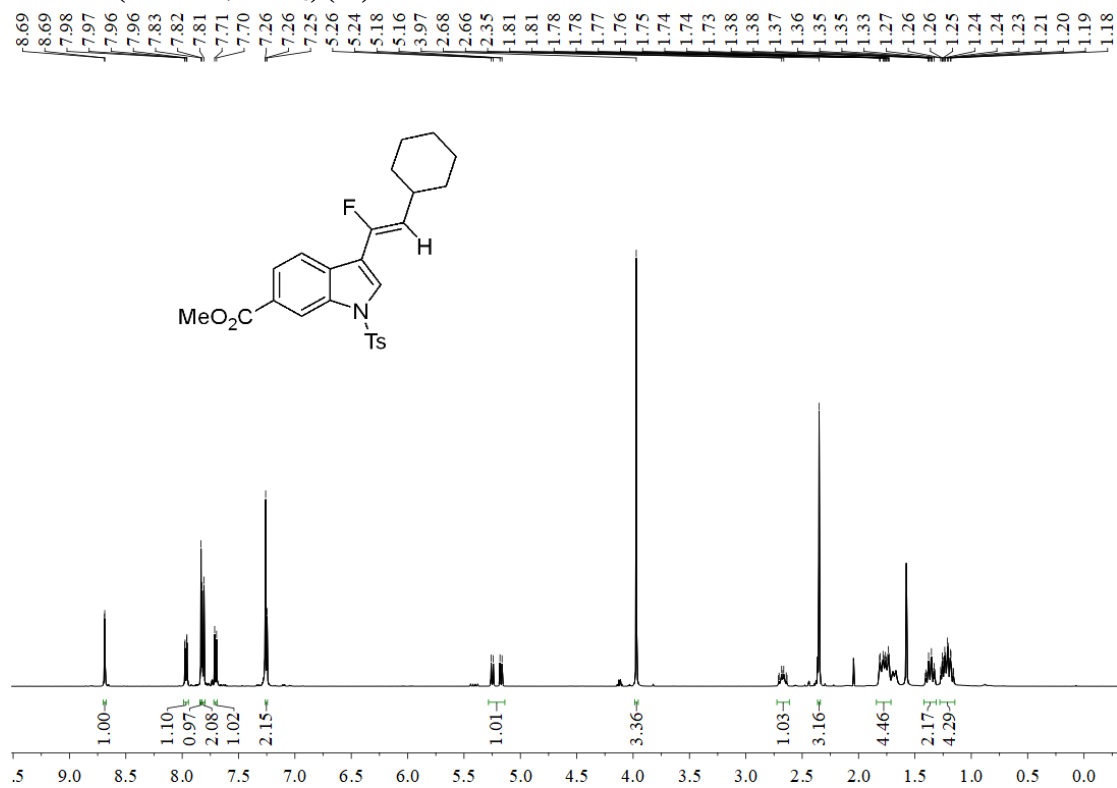
$\begin{array}{r} 155.69 \\ 137.74 \\ 134.45 \\ 126.30 \\ 126.29 \\ 124.54 \\ 124.49 \\ 113.17 \\ 113.00 \end{array}$



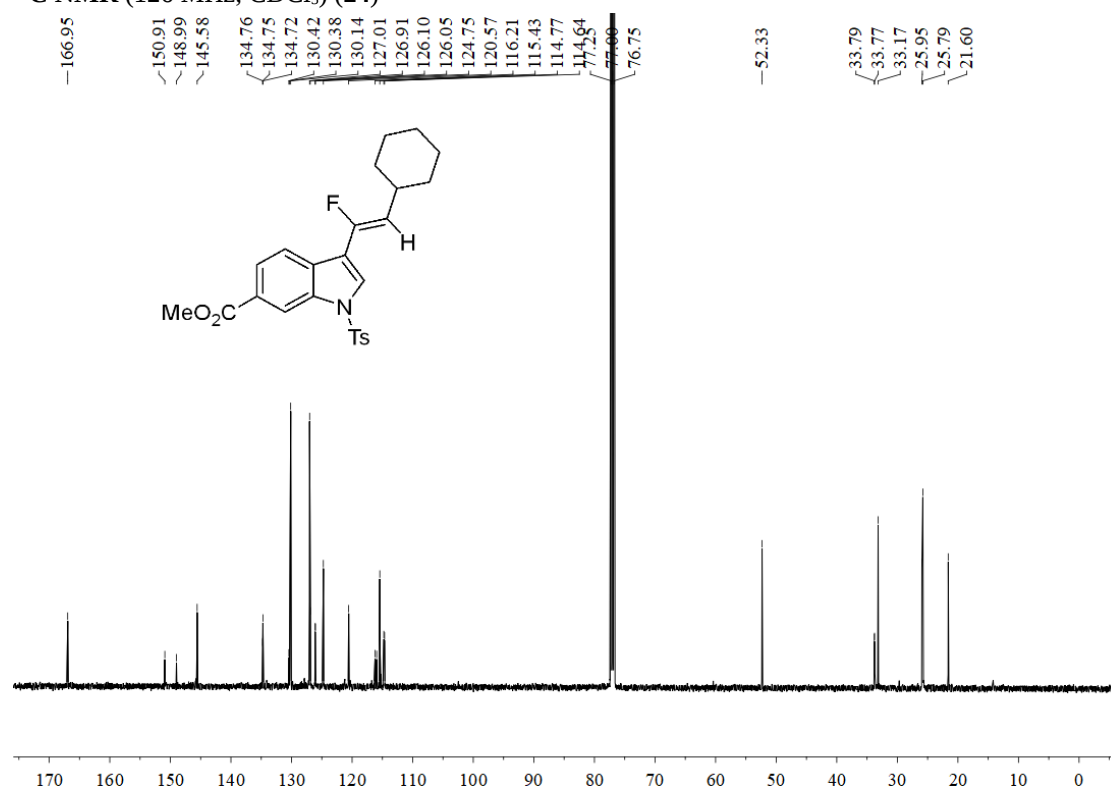
^{19}F NMR (471 MHz, CDCl_3) (23)



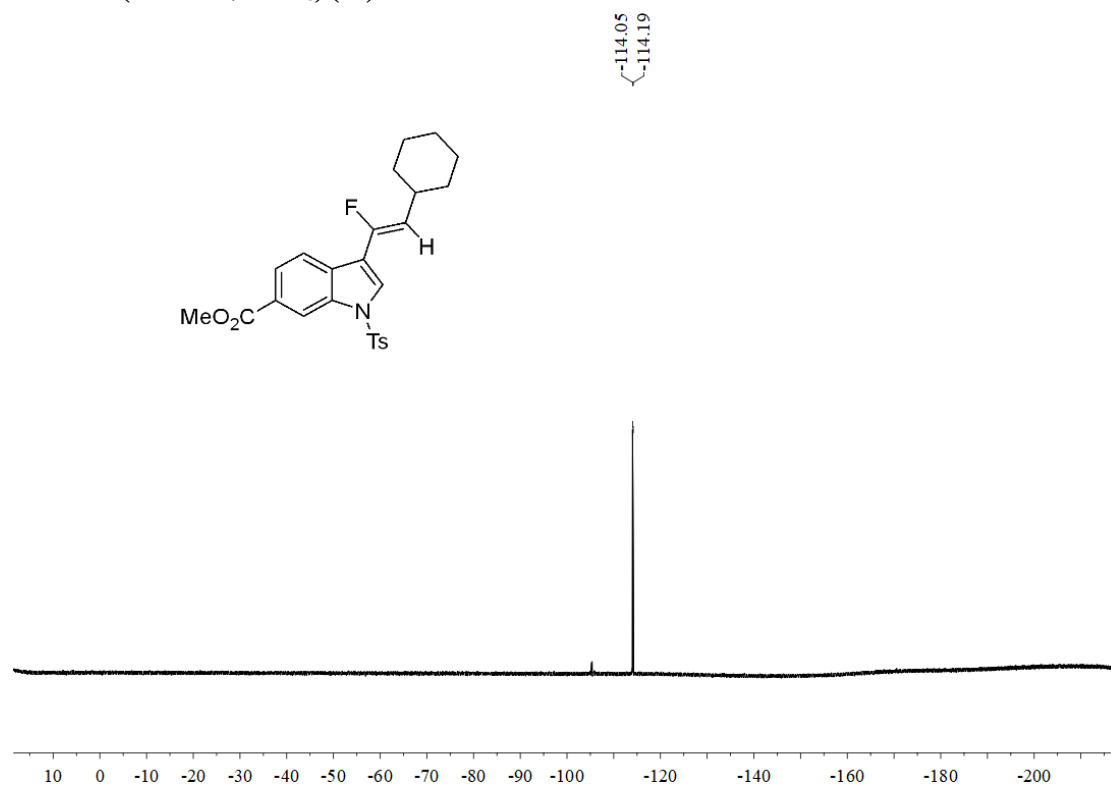
^1H NMR (500 MHz, CDCl_3) (24)



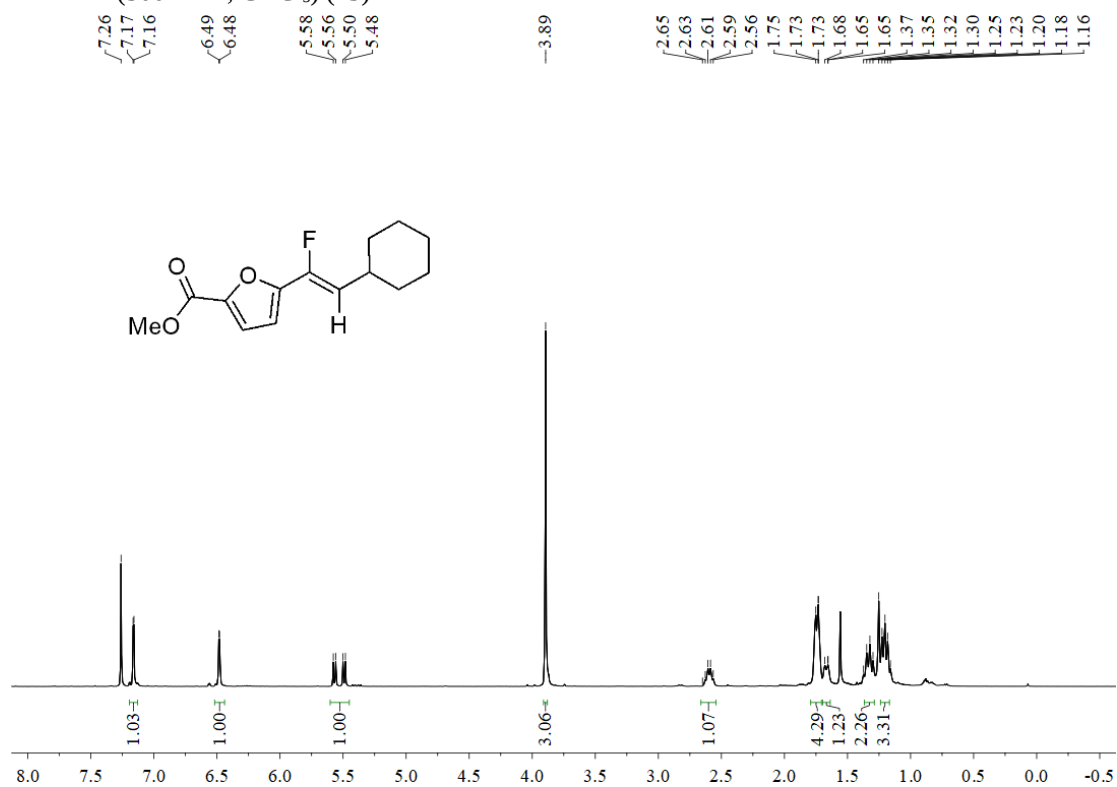
^{13}C NMR (126 MHz, CDCl_3) (24)



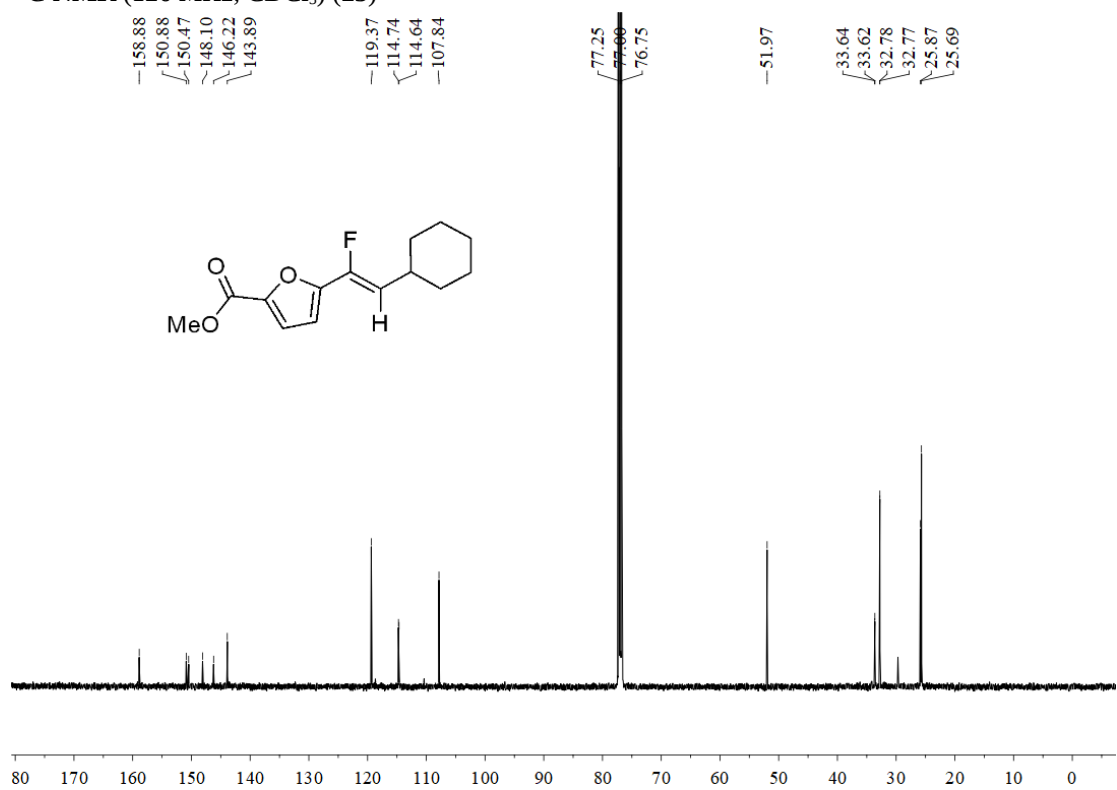
^{19}F NMR (471 MHz, CDCl_3) (24)



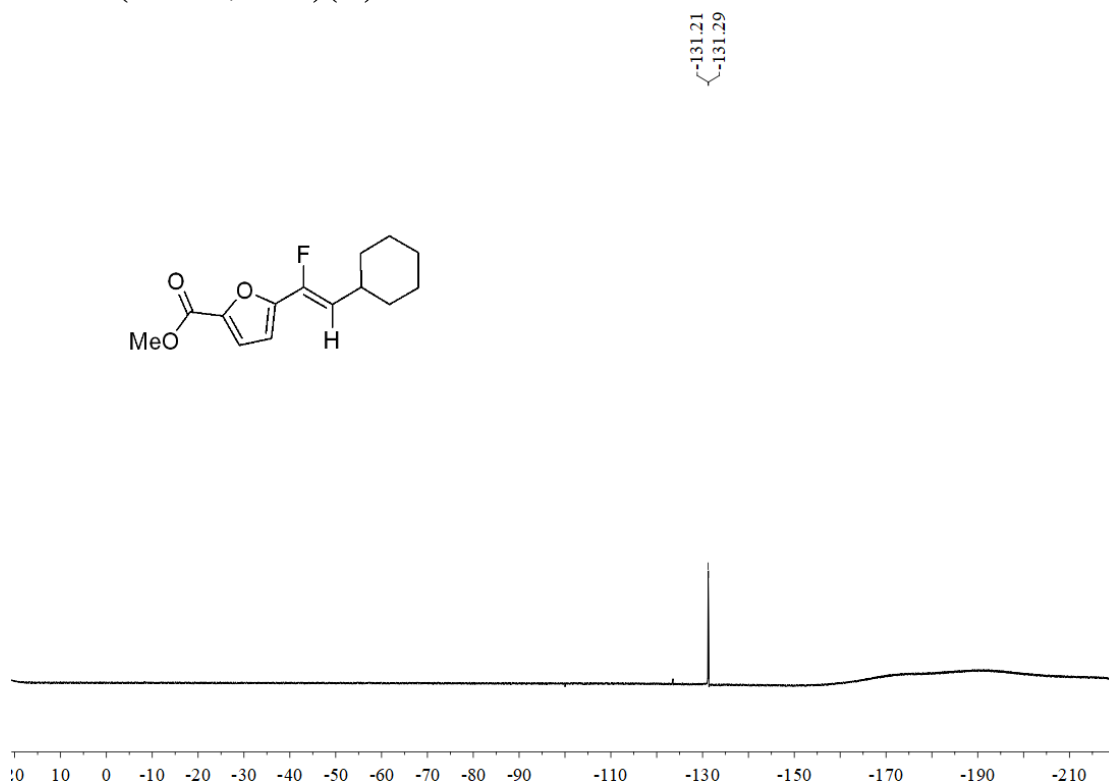
¹H NMR (500 MHz, CDCl₃) (25)



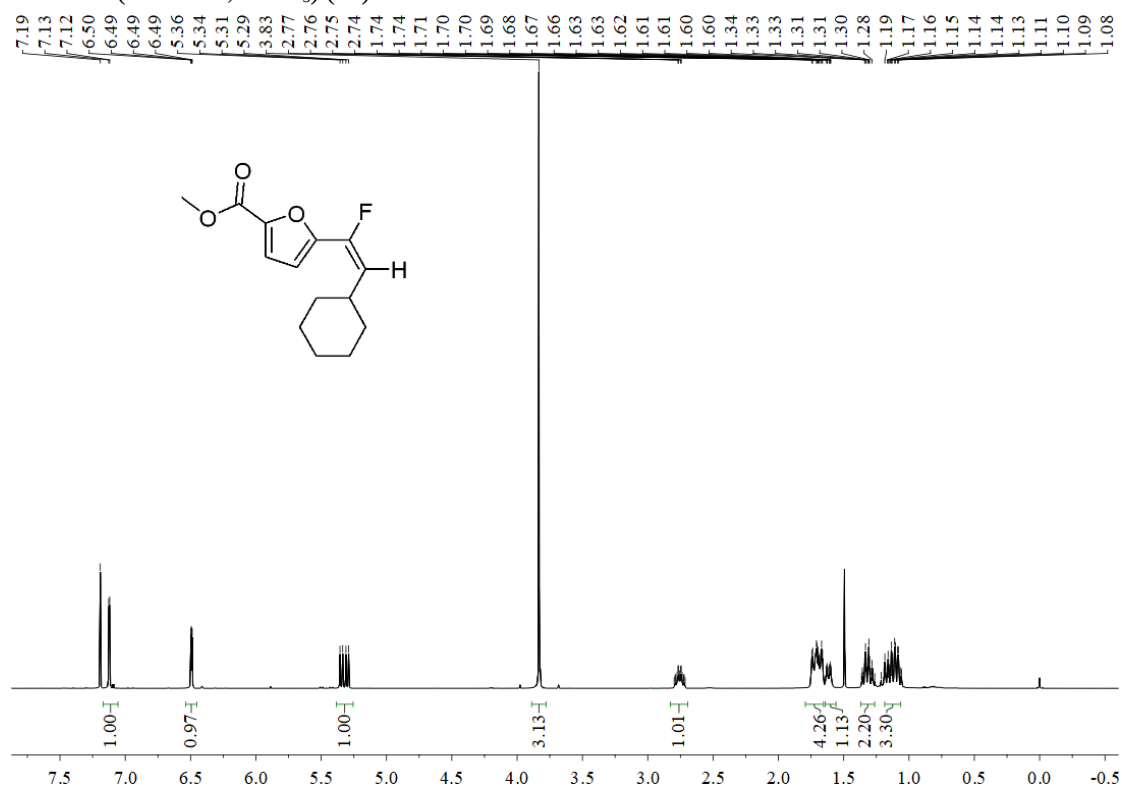
¹³C NMR (126 MHz, CDCl₃) (25)



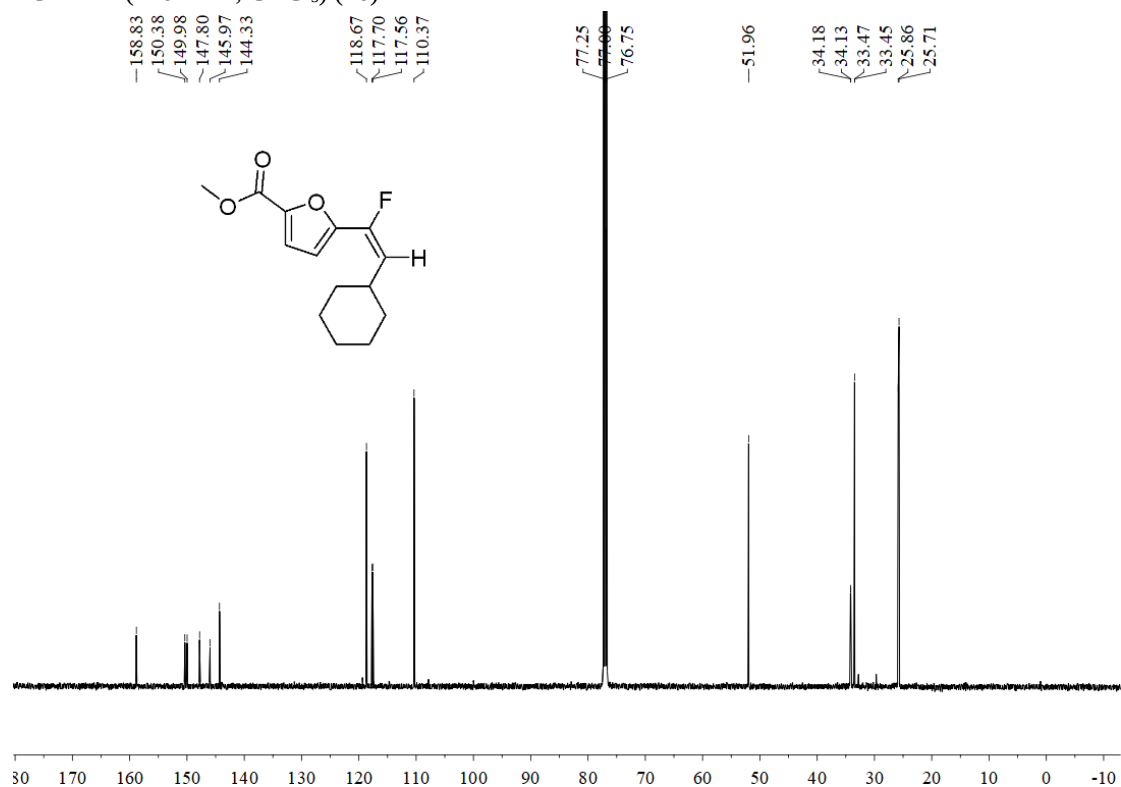
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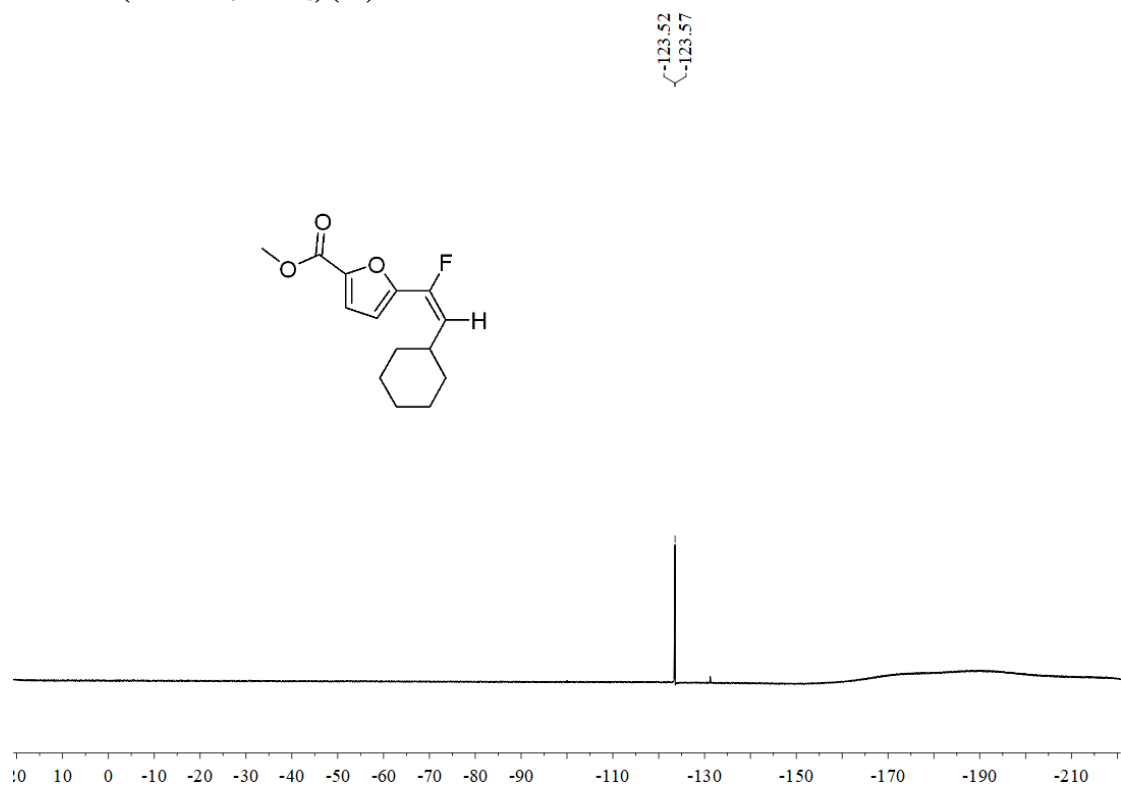
^1H NMR (500 MHz, CDCl_3) (26)



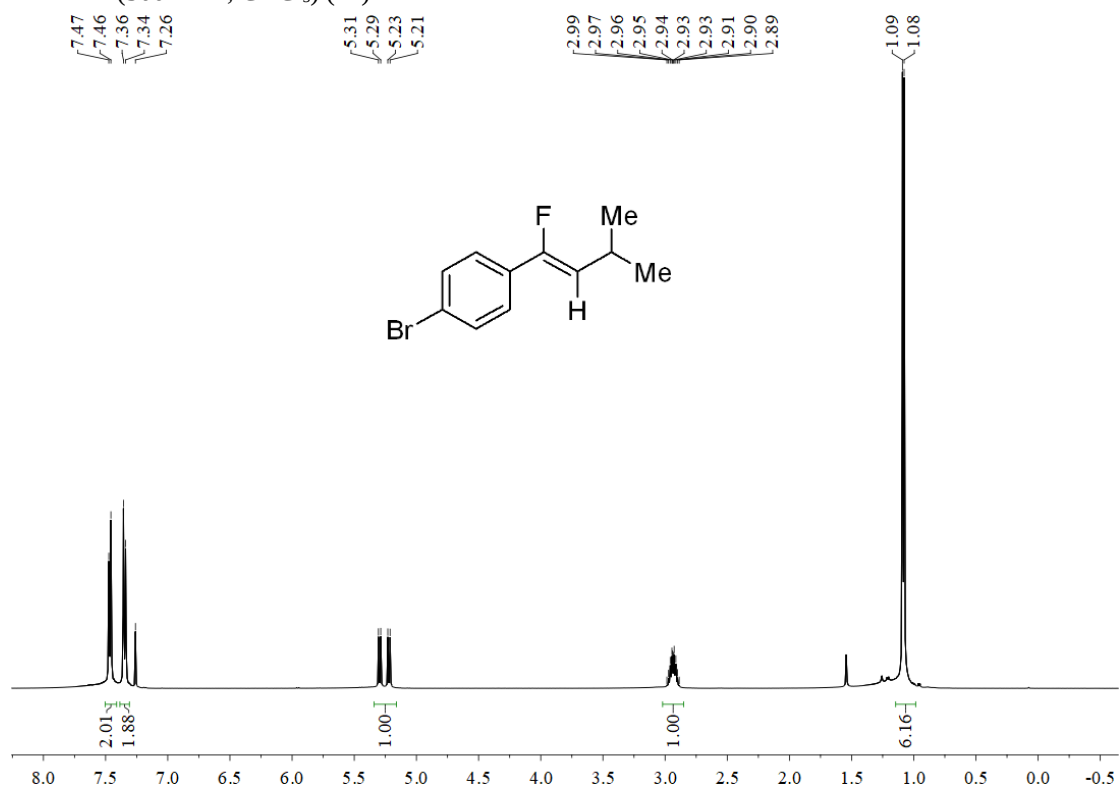
^{13}C NMR (126 MHz, CDCl_3) (26)



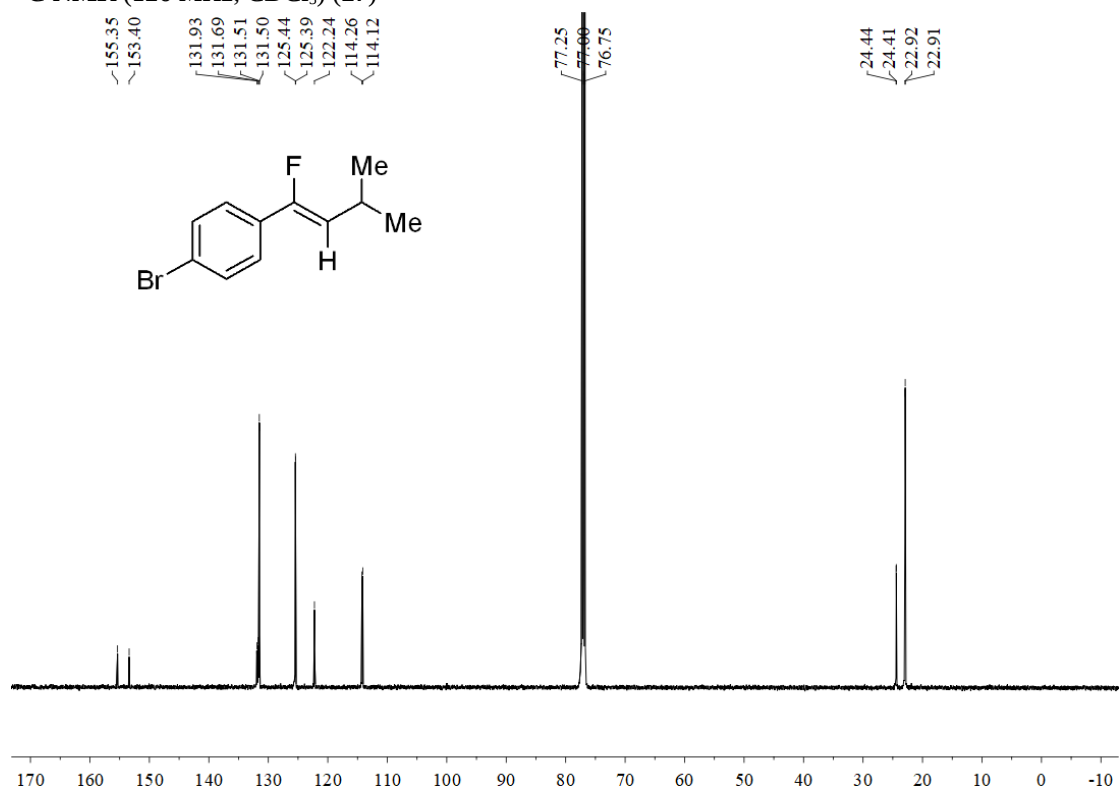
^{19}F NMR (471 MHz, CDCl_3) (26)



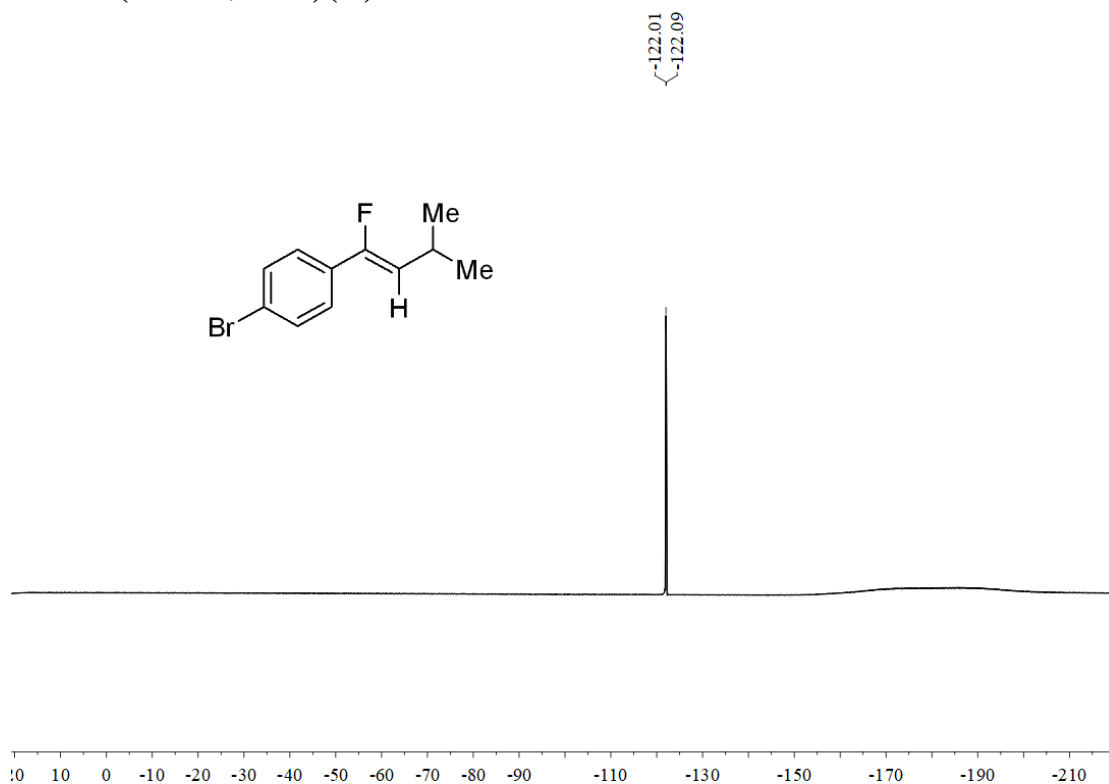
¹H NMR (500 MHz, CDCl₃) (27)



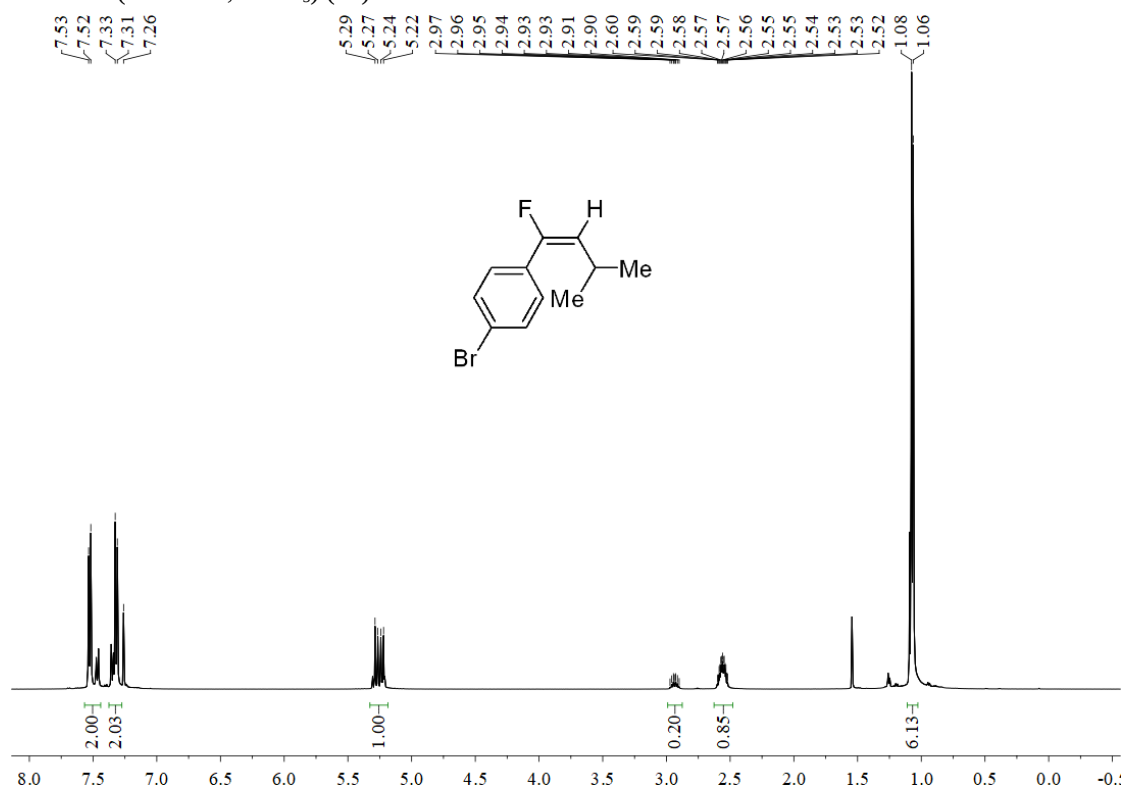
¹³C NMR (126 MHz, CDCl₃) (27)



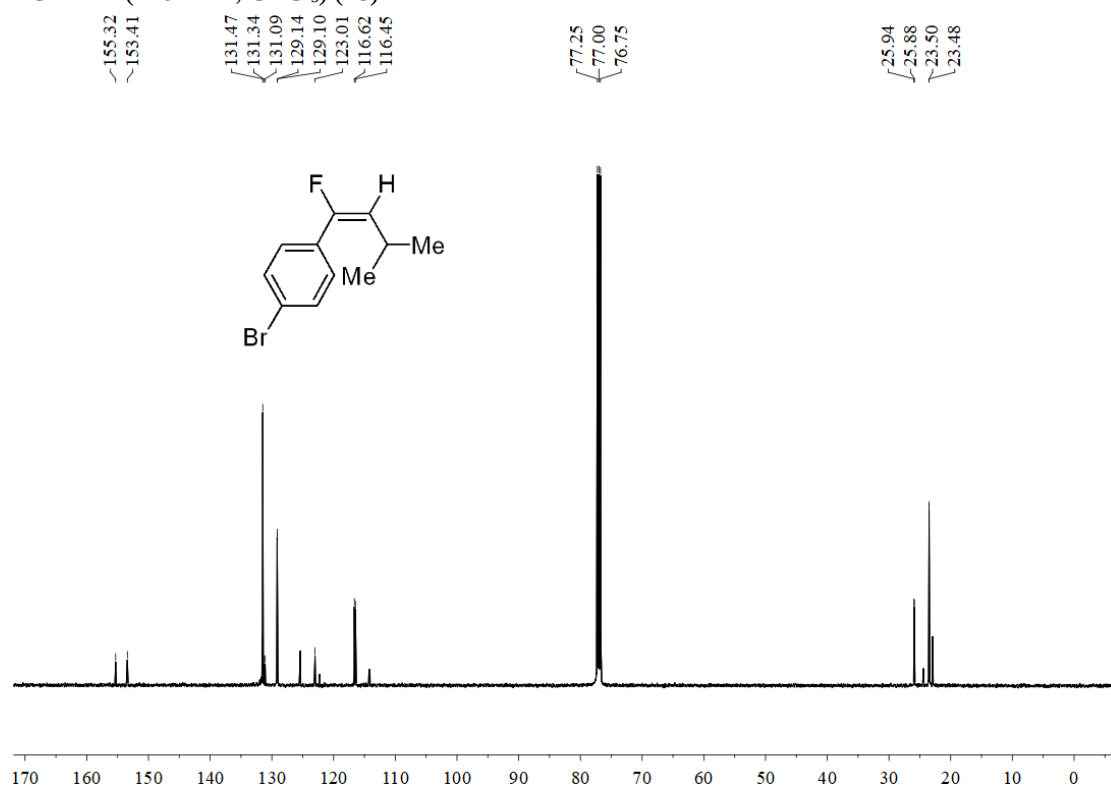
^{19}F NMR (471 MHz, CDCl_3) (27)



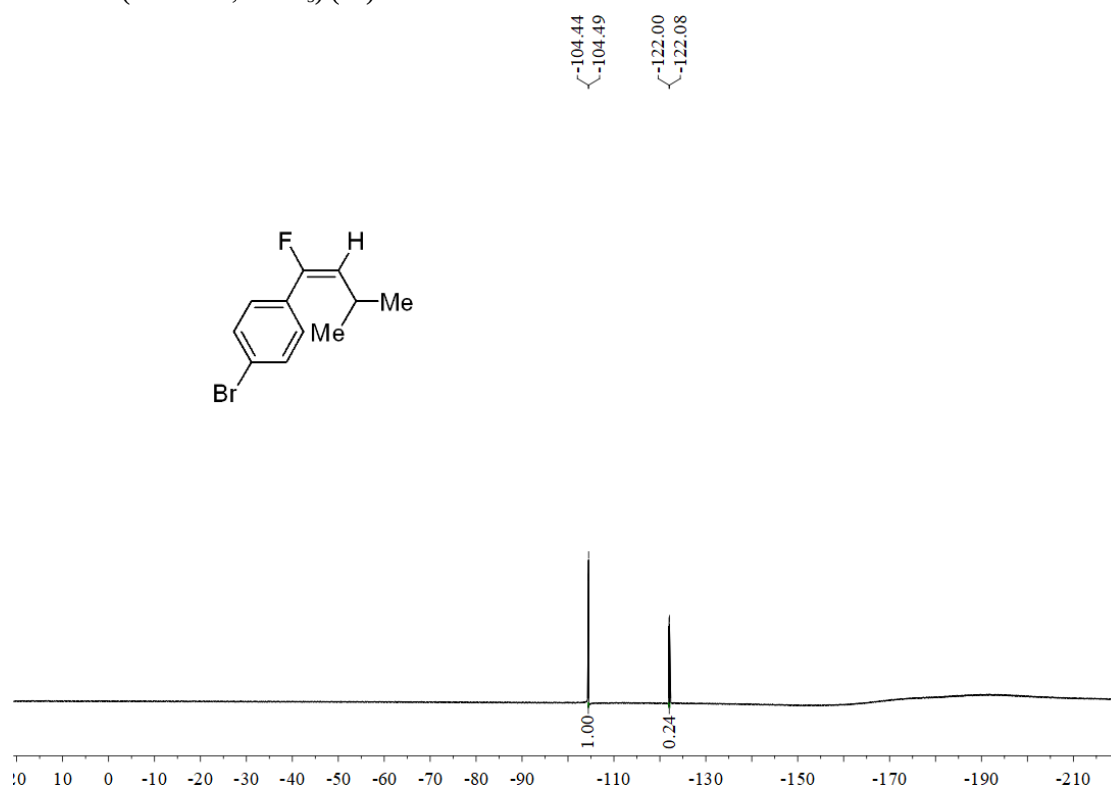
^1H NMR (500 MHz, CDCl_3) (28)



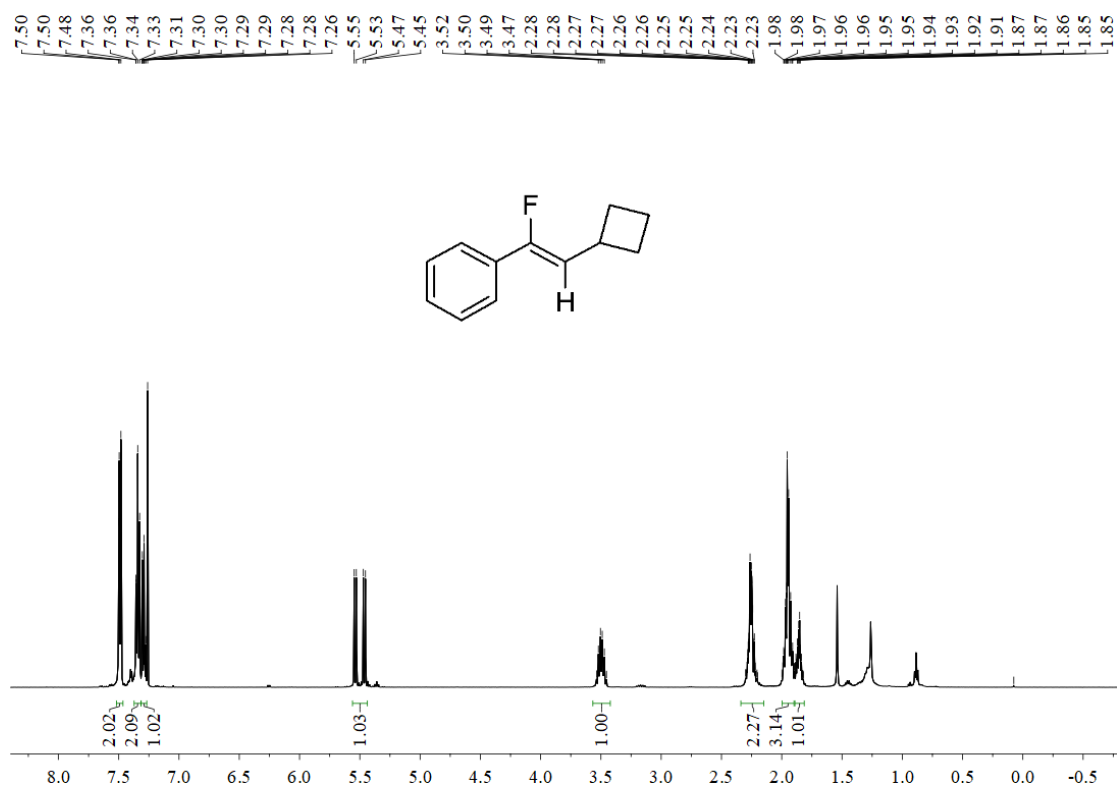
^{13}C NMR (126 MHz, CDCl_3) (28)



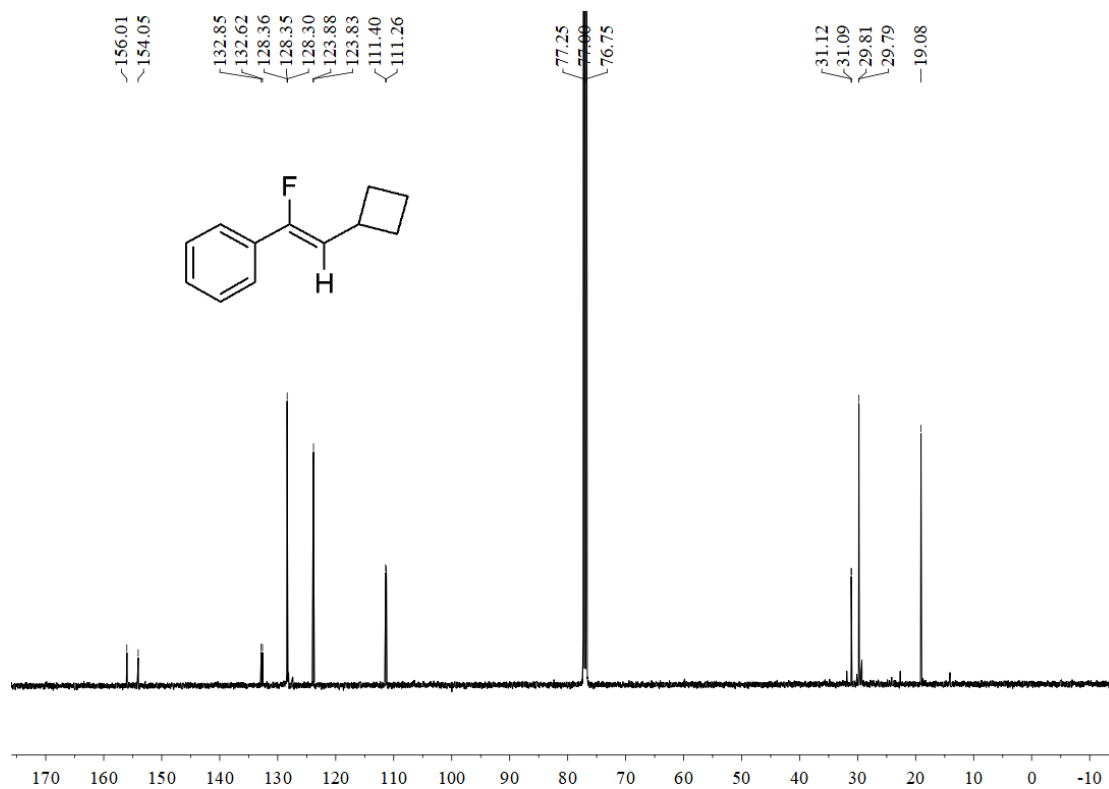
^{19}F NMR (471 MHz, CDCl_3) (28)



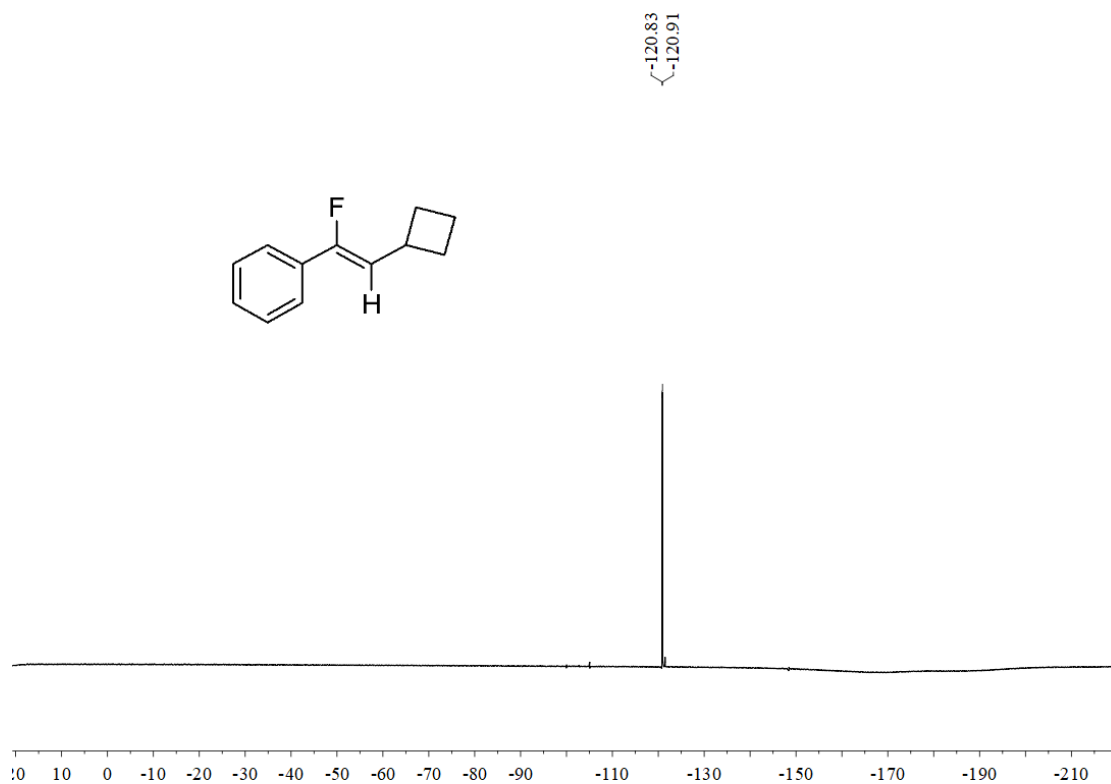
¹H NMR (500 MHz, CDCl₃) (29)



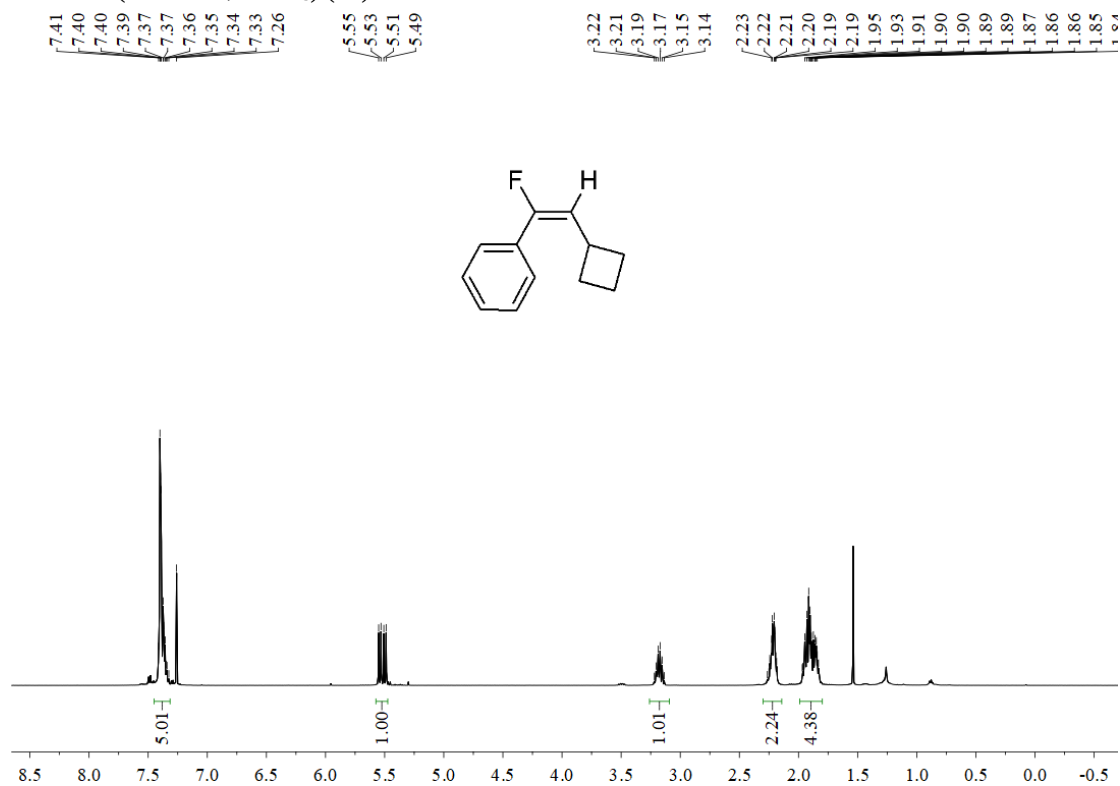
¹³C NMR (126 MHz, CDCl₃) (29)



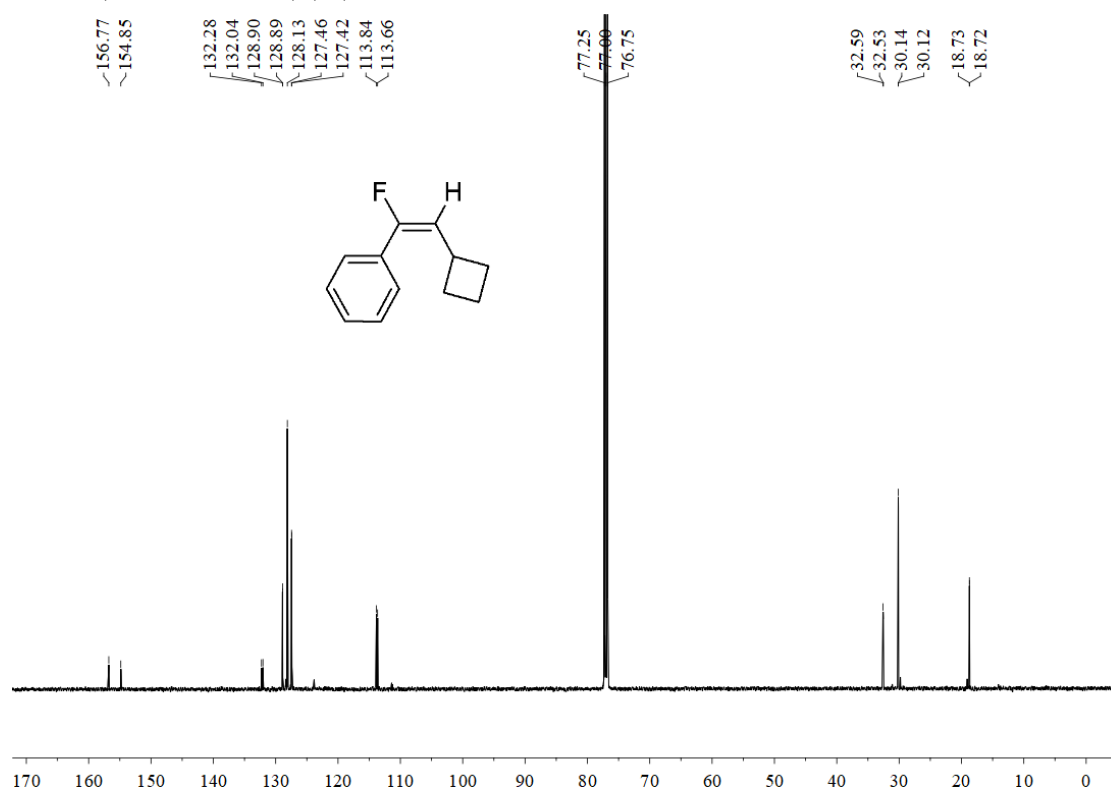
^{19}F NMR (471 MHz, CDCl_3) (29)



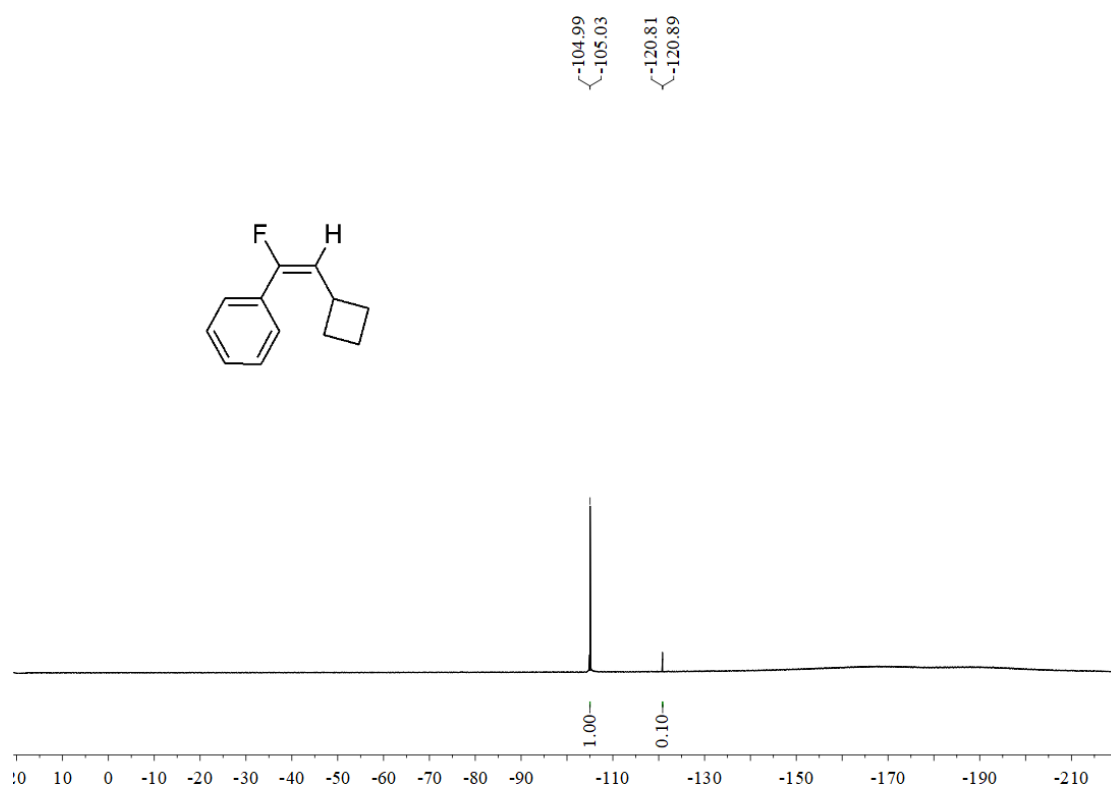
^1H NMR (500 MHz, CDCl_3) (30)



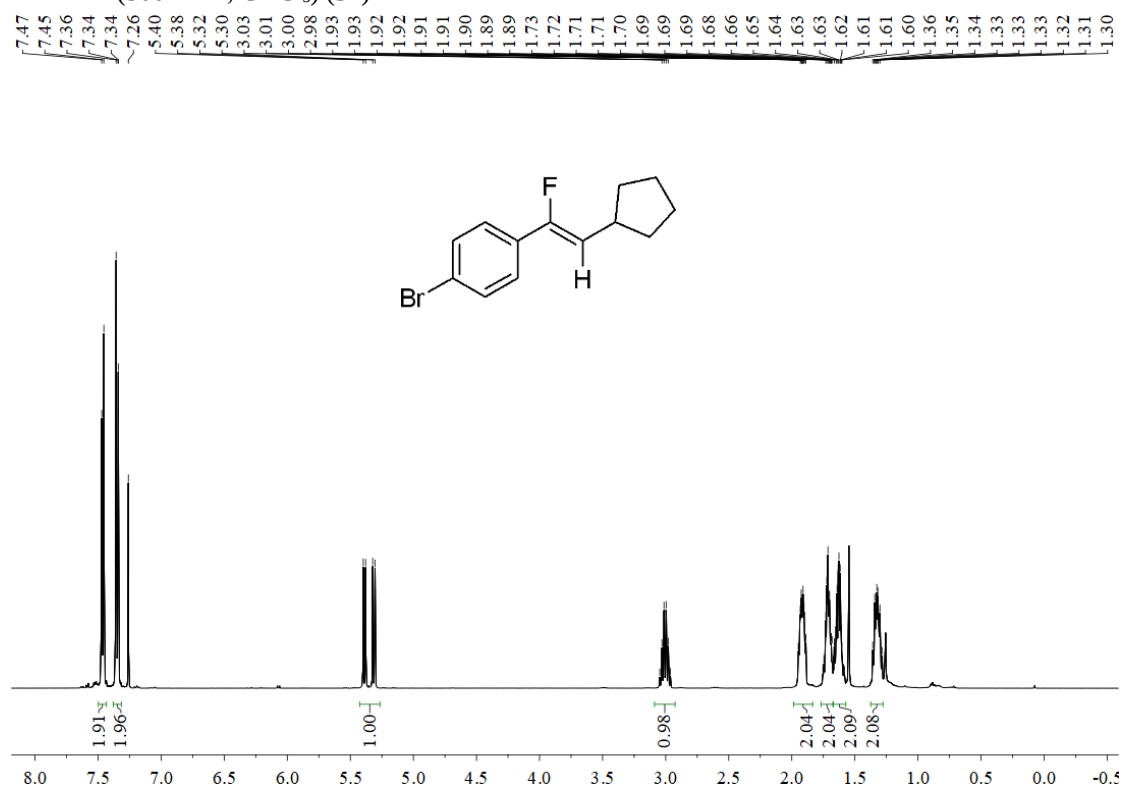
^{13}C NMR (126 MHz, CDCl_3) (30)



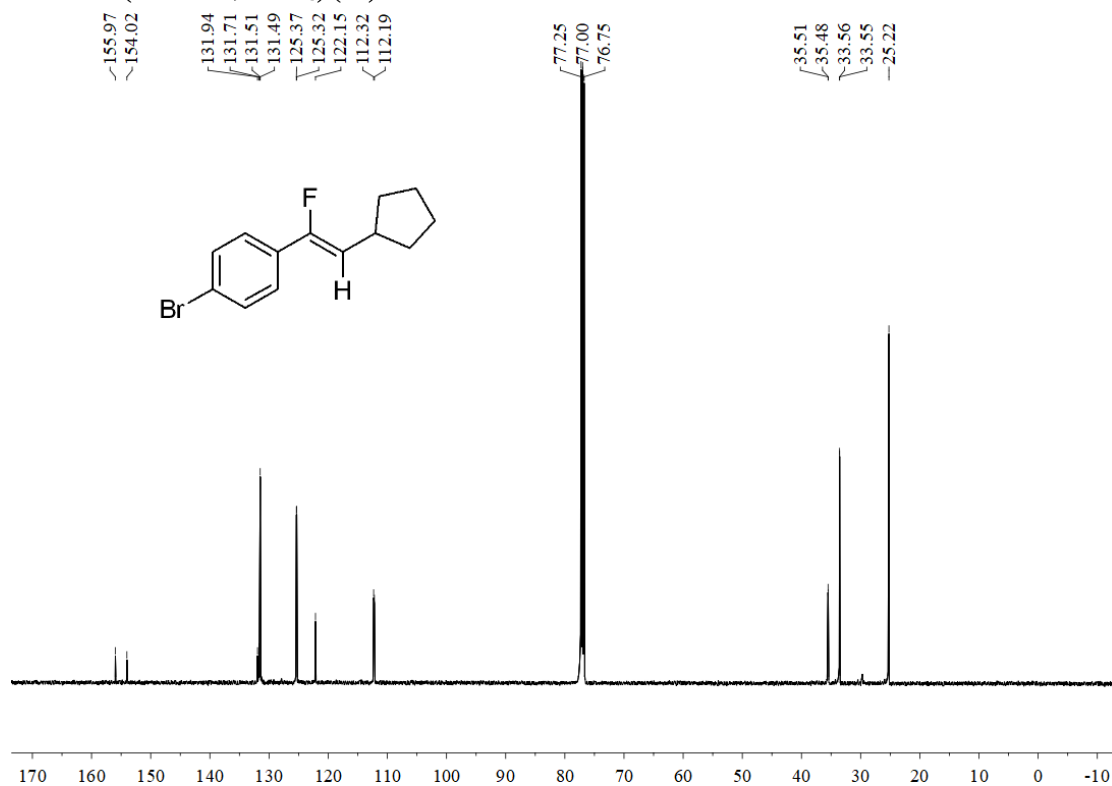
^{19}F NMR (471 MHz, CDCl_3) (30)



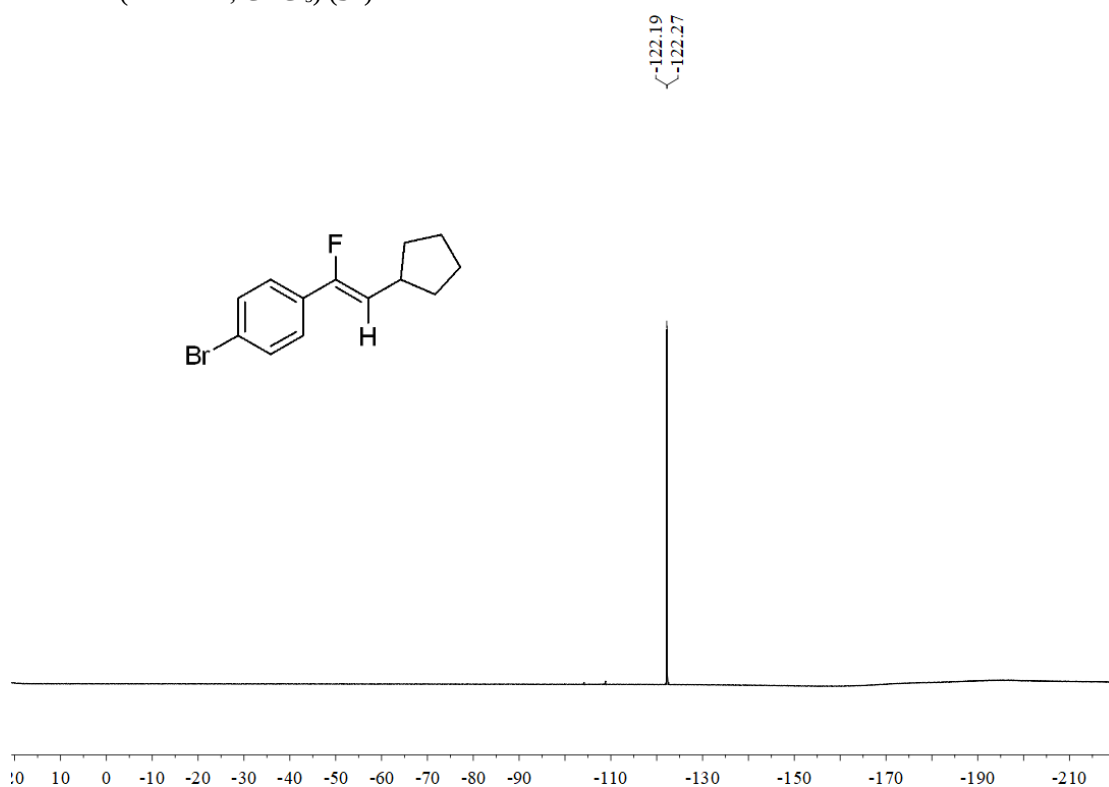
¹H NMR (500 MHz, CDCl₃) (31)



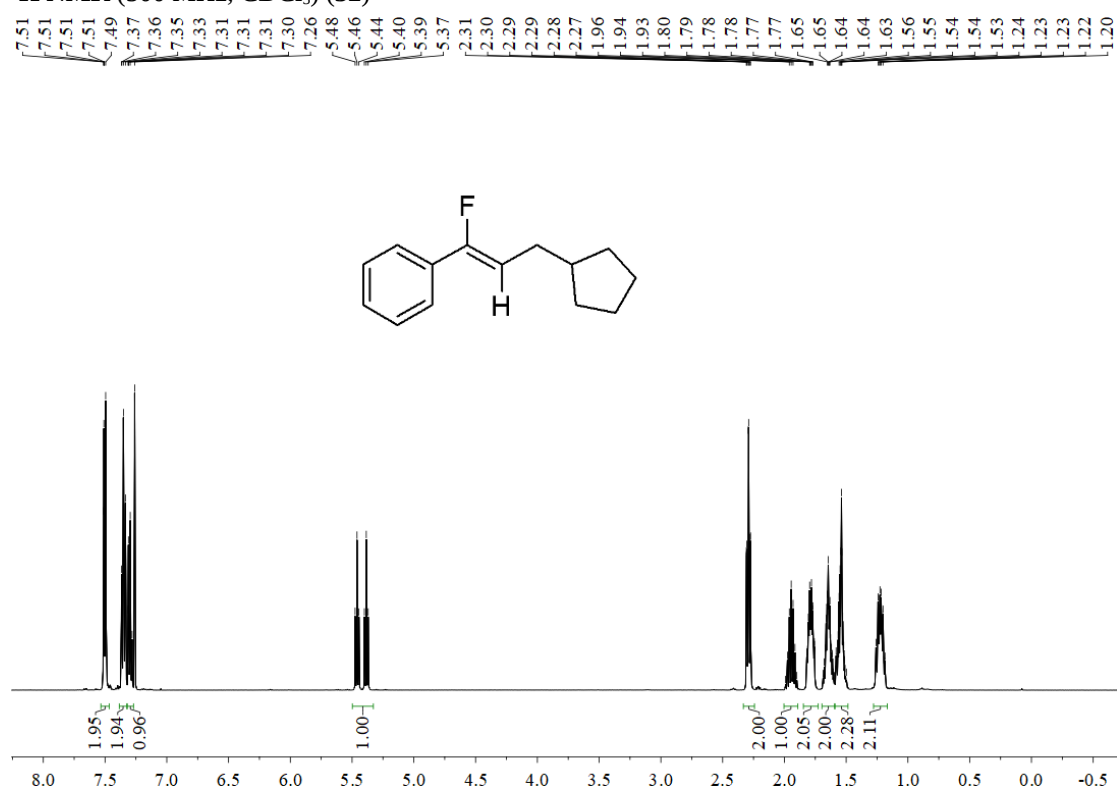
¹³C NMR (126 MHz, CDCl₃) (31)



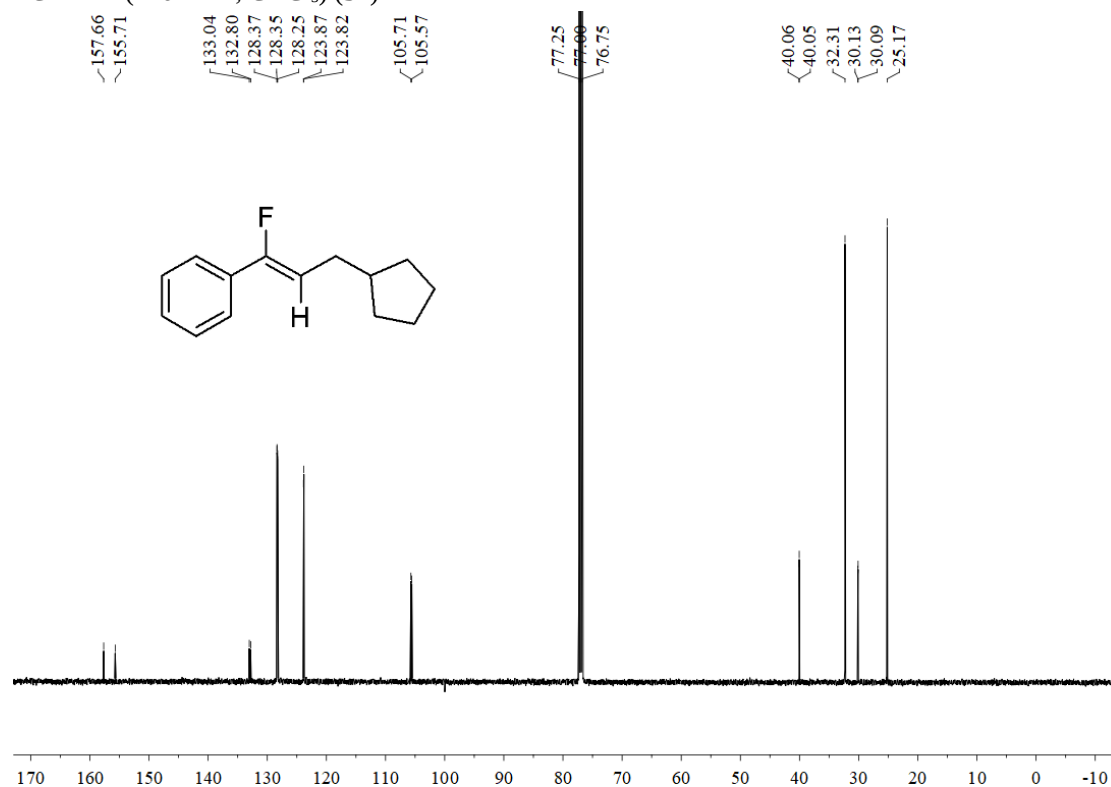
^{19}F NMR (471 MHz, CDCl_3) (31)



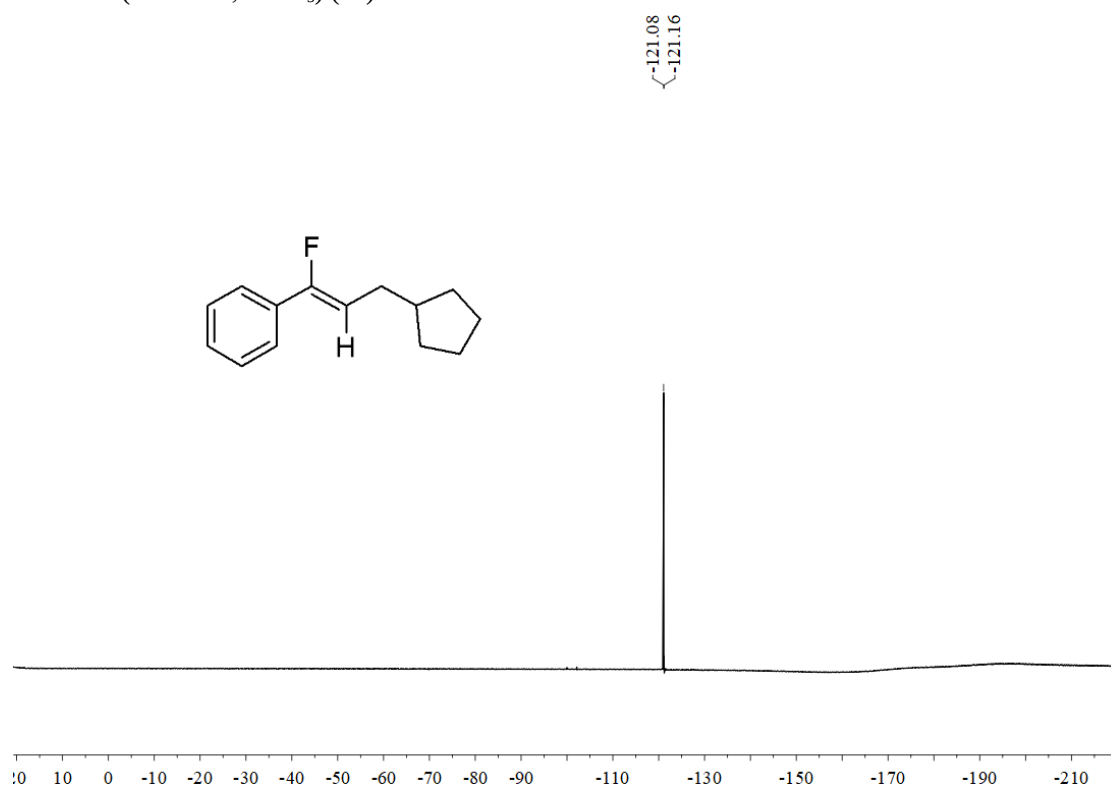
^1H NMR (500 MHz, CDCl_3) (32)



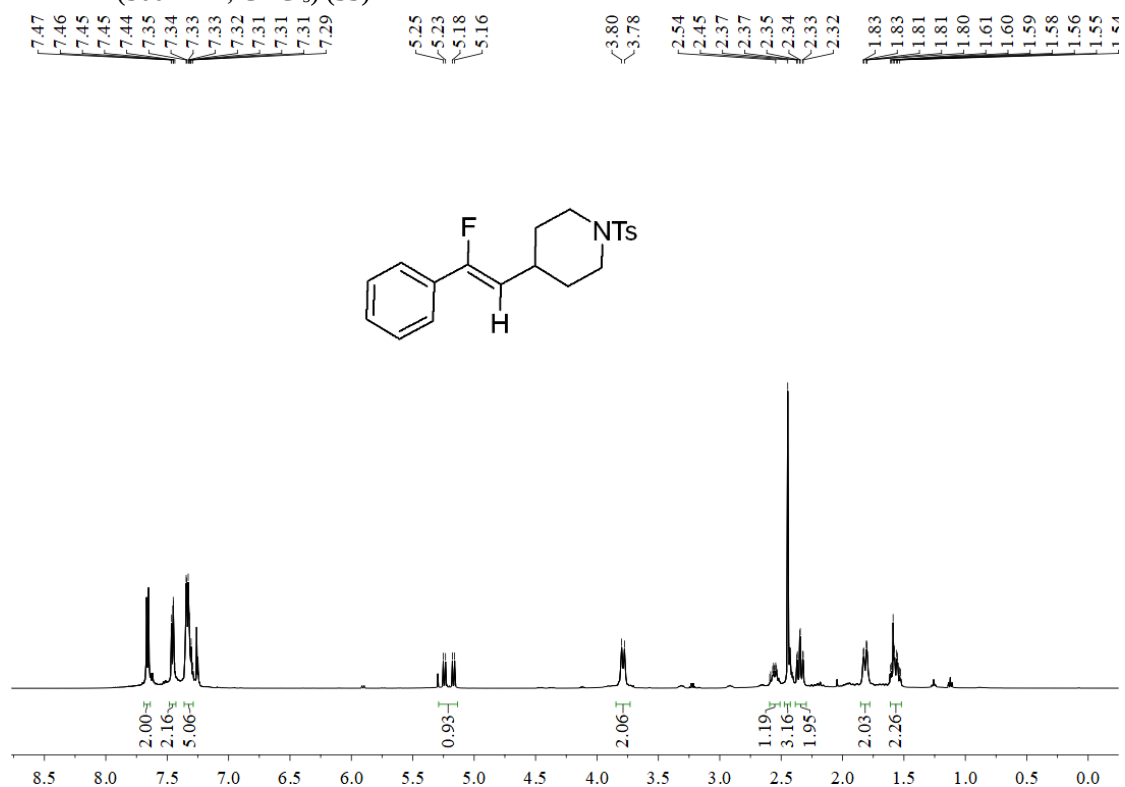
^{13}C NMR (126 MHz, CDCl_3) (32)



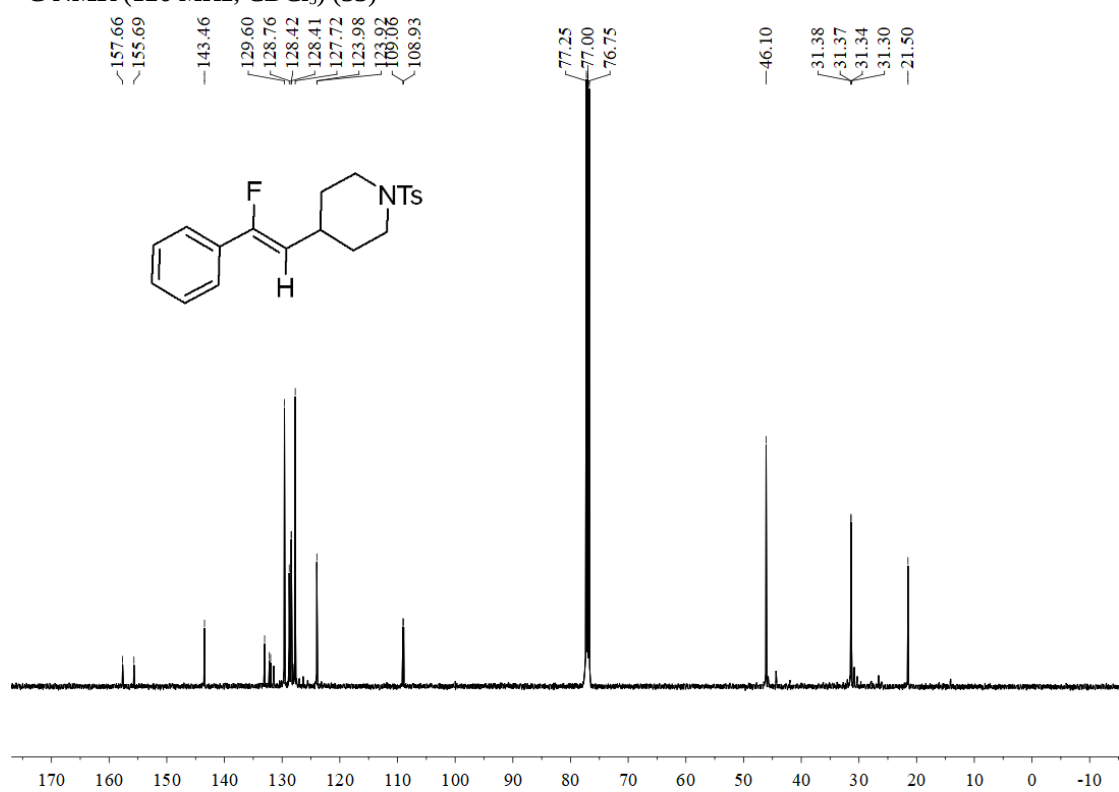
^{19}F NMR (471 MHz, CDCl_3) (32)



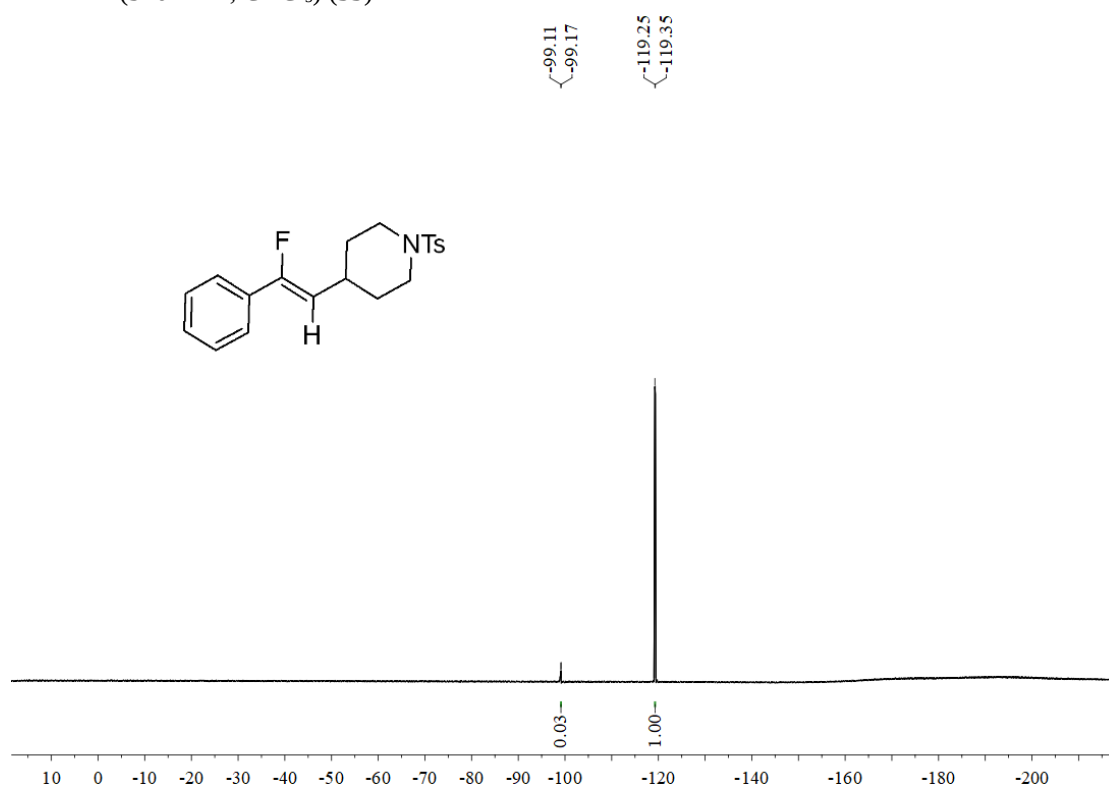
¹H NMR (500 MHz, CDCl₃) (33)



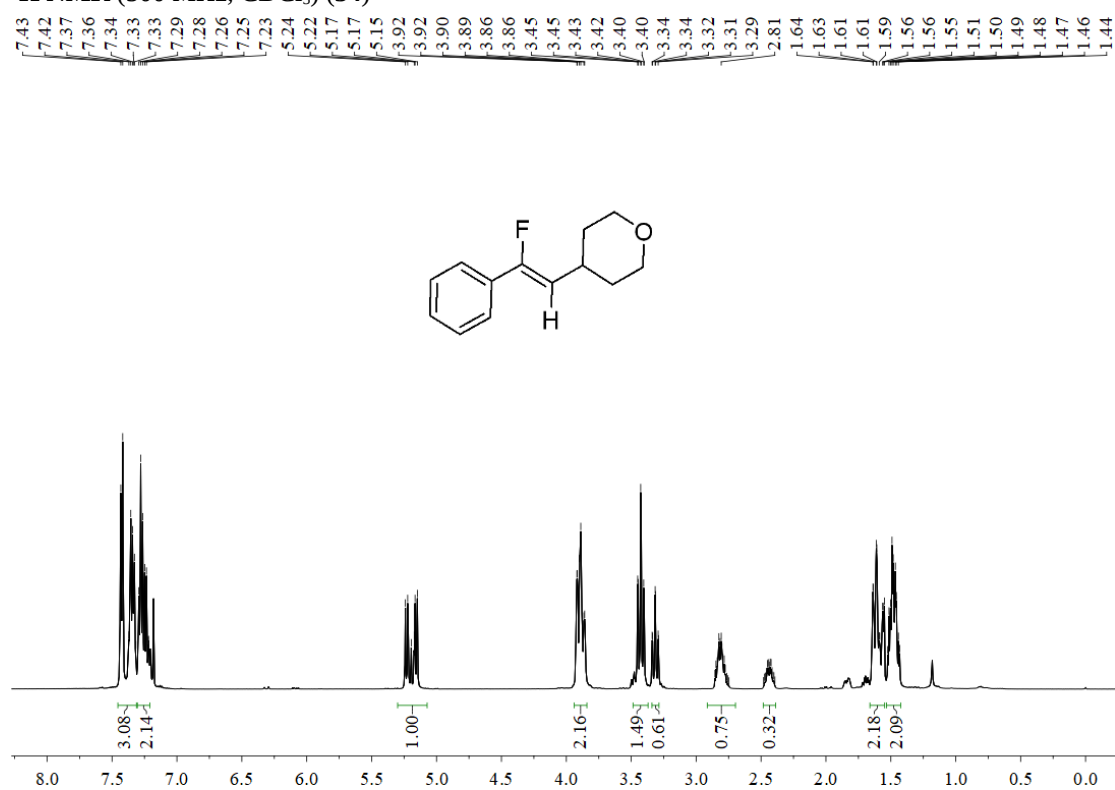
¹³C NMR (126 MHz, CDCl₃) (33)



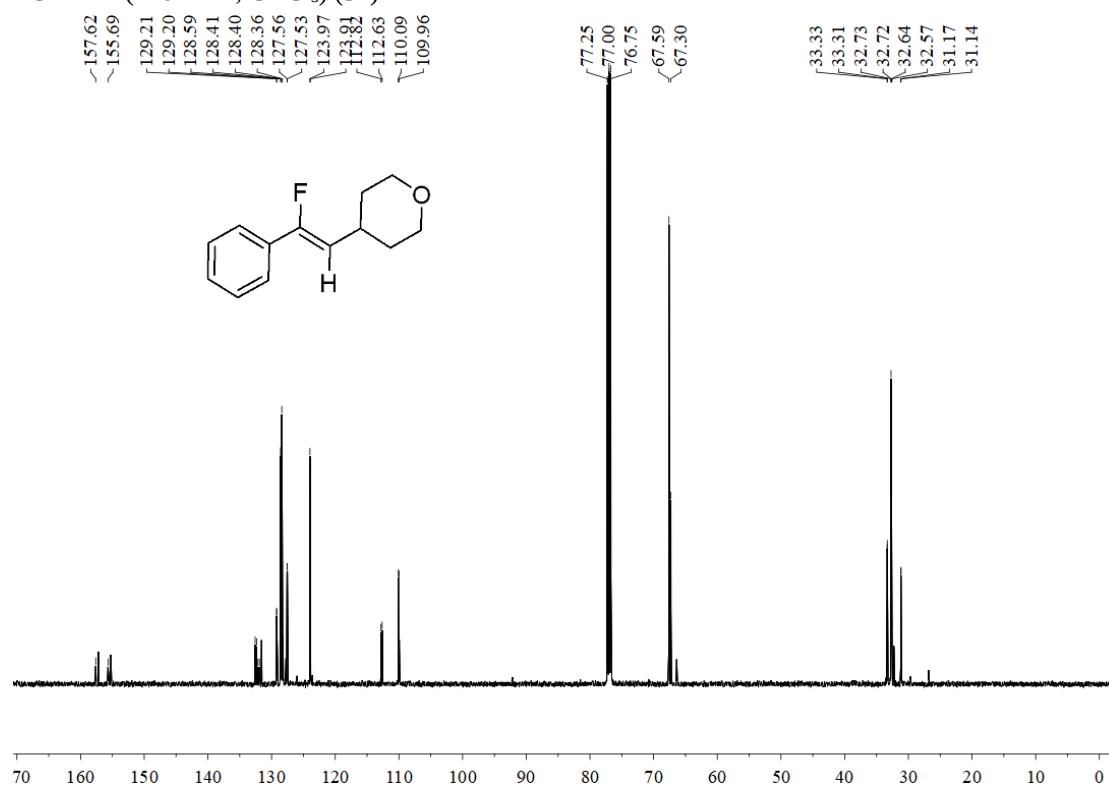
^{19}F NMR (376 MHz, CDCl_3) (33)



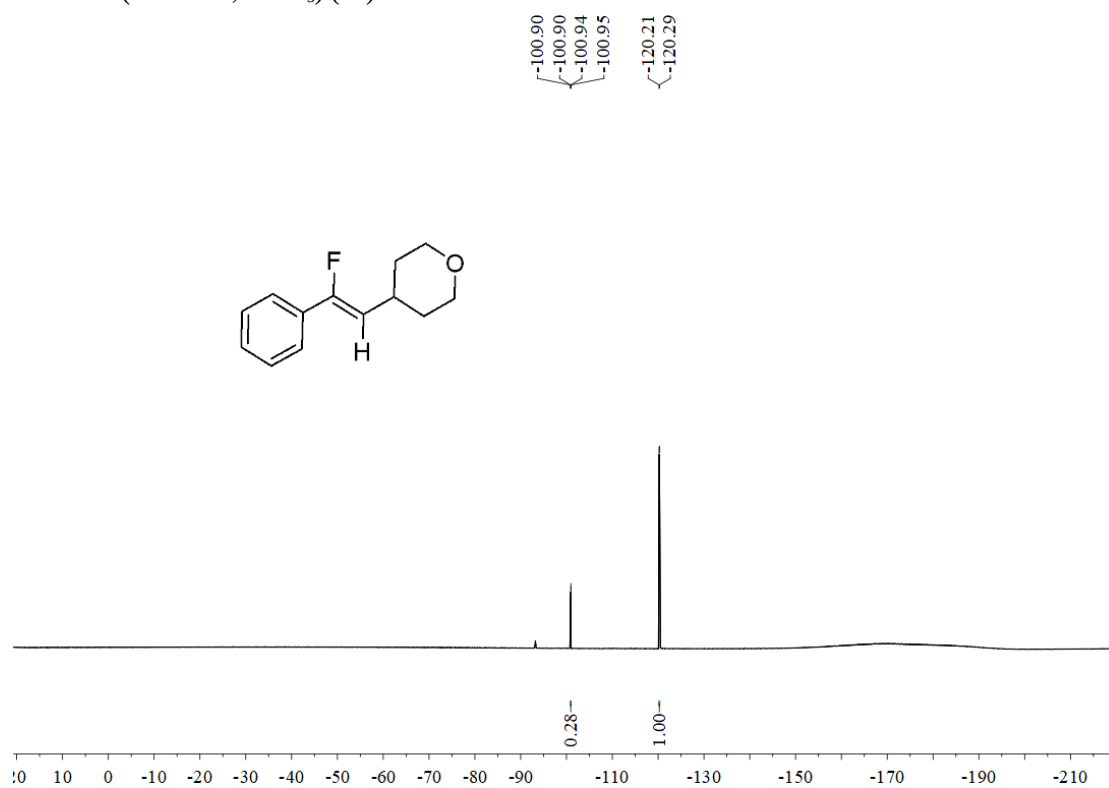
^1H NMR (500 MHz, CDCl_3) (34)



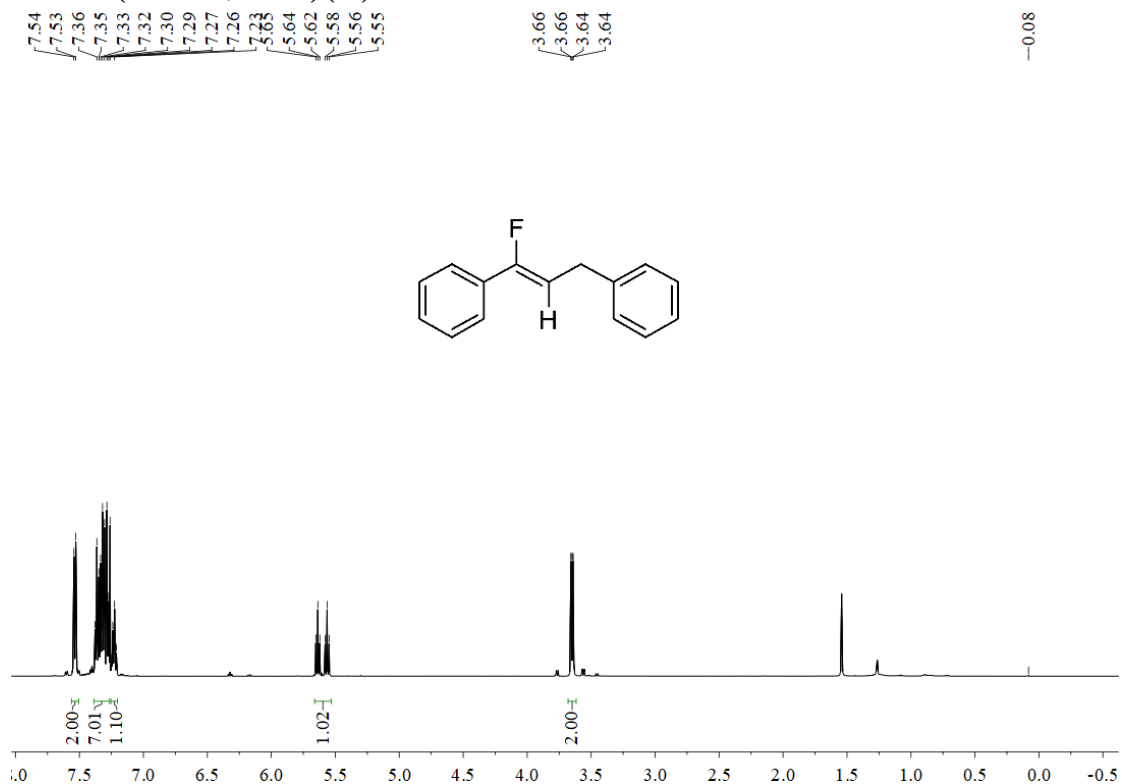
^{13}C NMR (126 MHz, CDCl_3) (34)



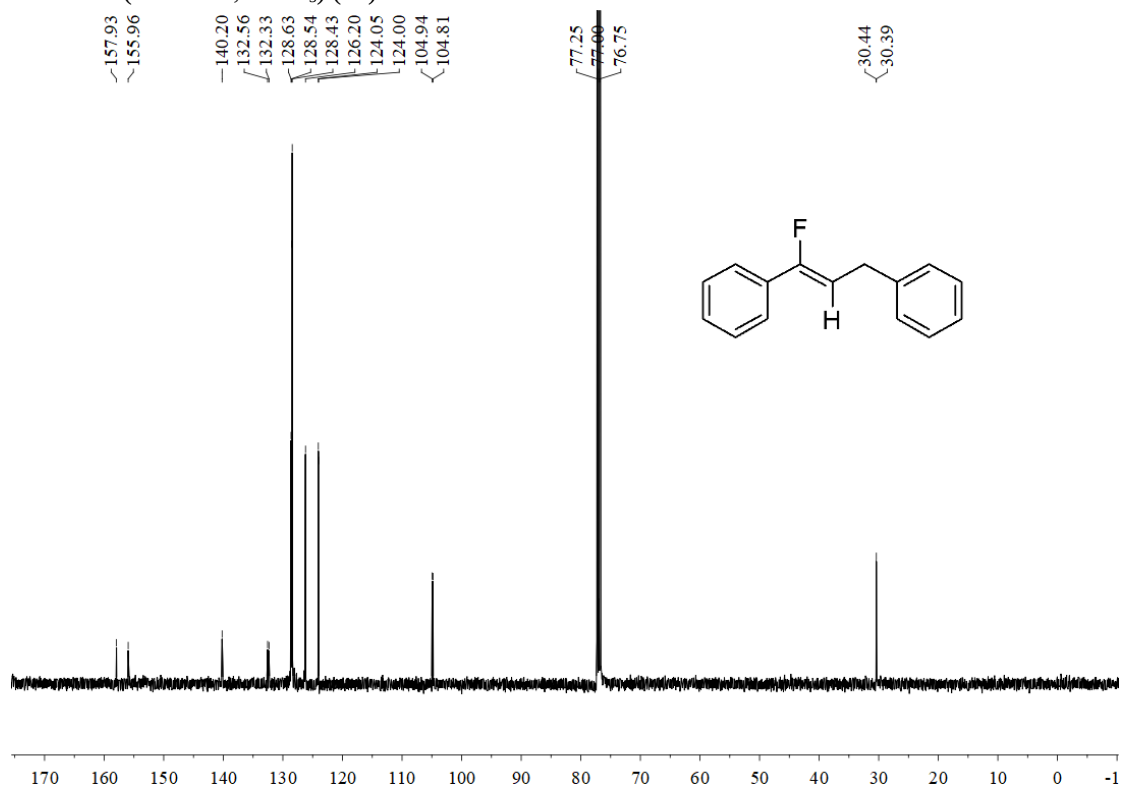
^{19}F NMR (471 MHz, CDCl_3) (34)



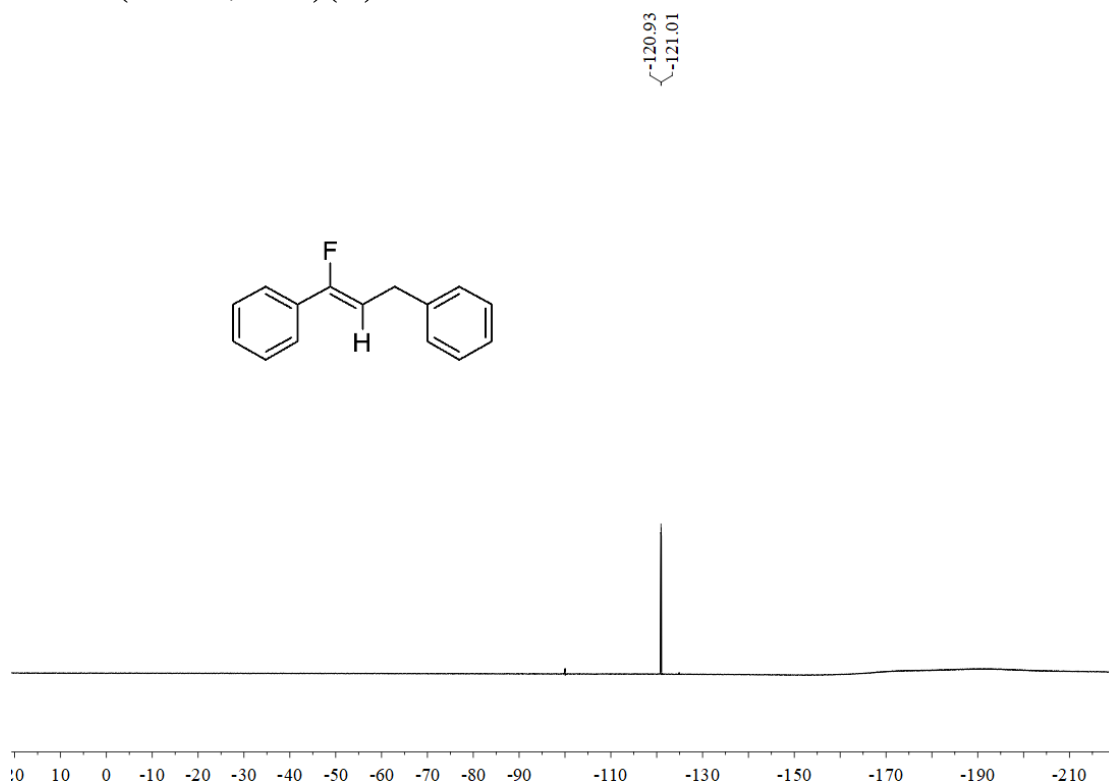
¹H NMR (500 MHz, CDCl₃) (35)



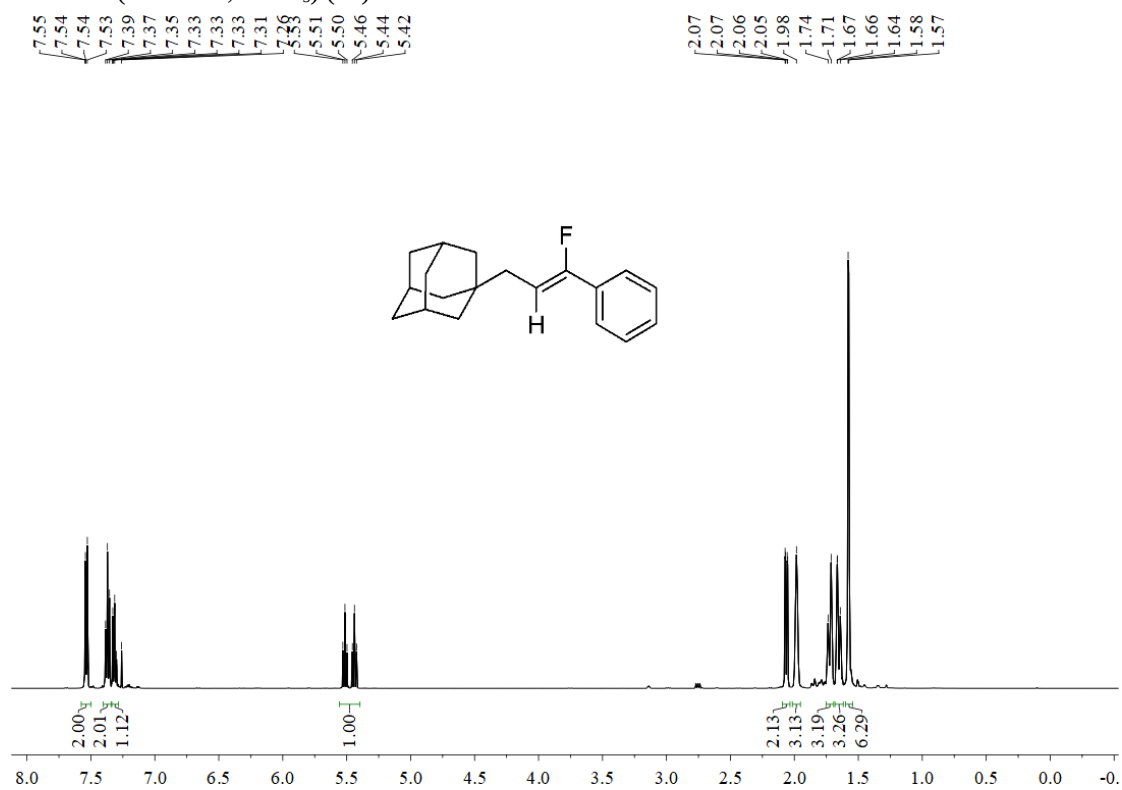
¹³C NMR (126 MHz, CDCl₃) (35)



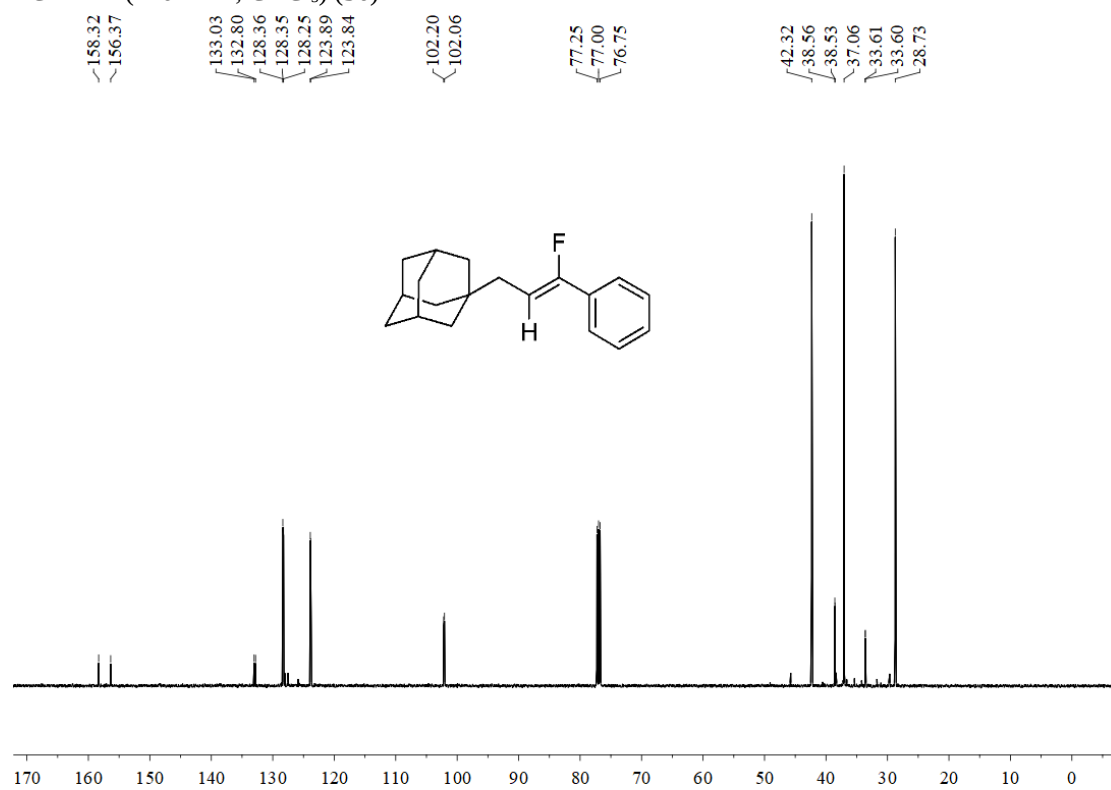
^{19}F NMR (471 MHz, CDCl_3) (35)



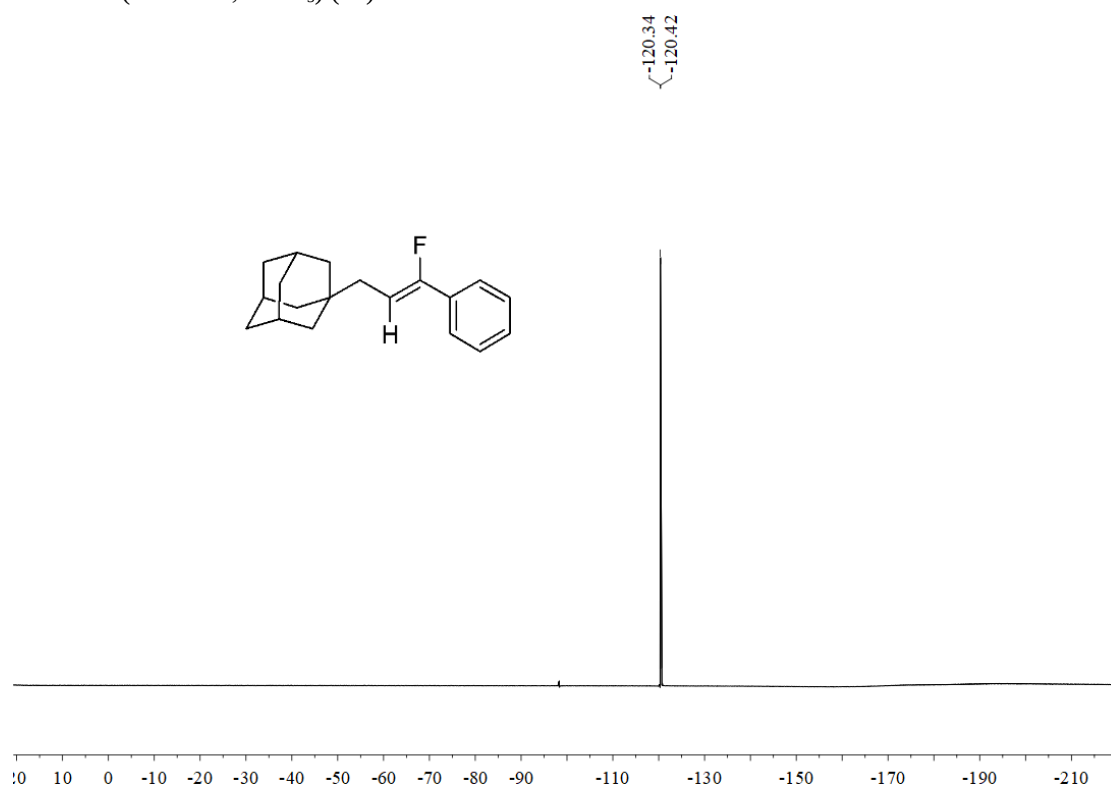
^1H NMR (500 MHz, CDCl_3) (36)



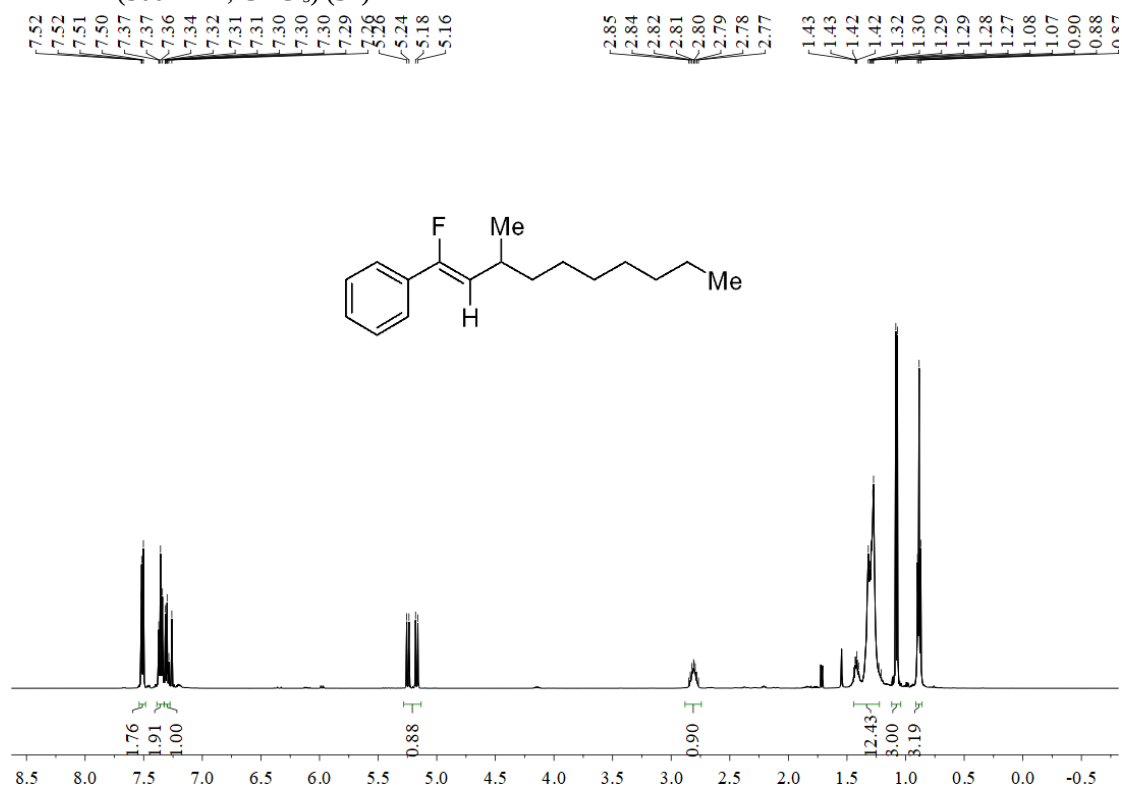
^{13}C NMR (126 MHz, CDCl_3) (36)



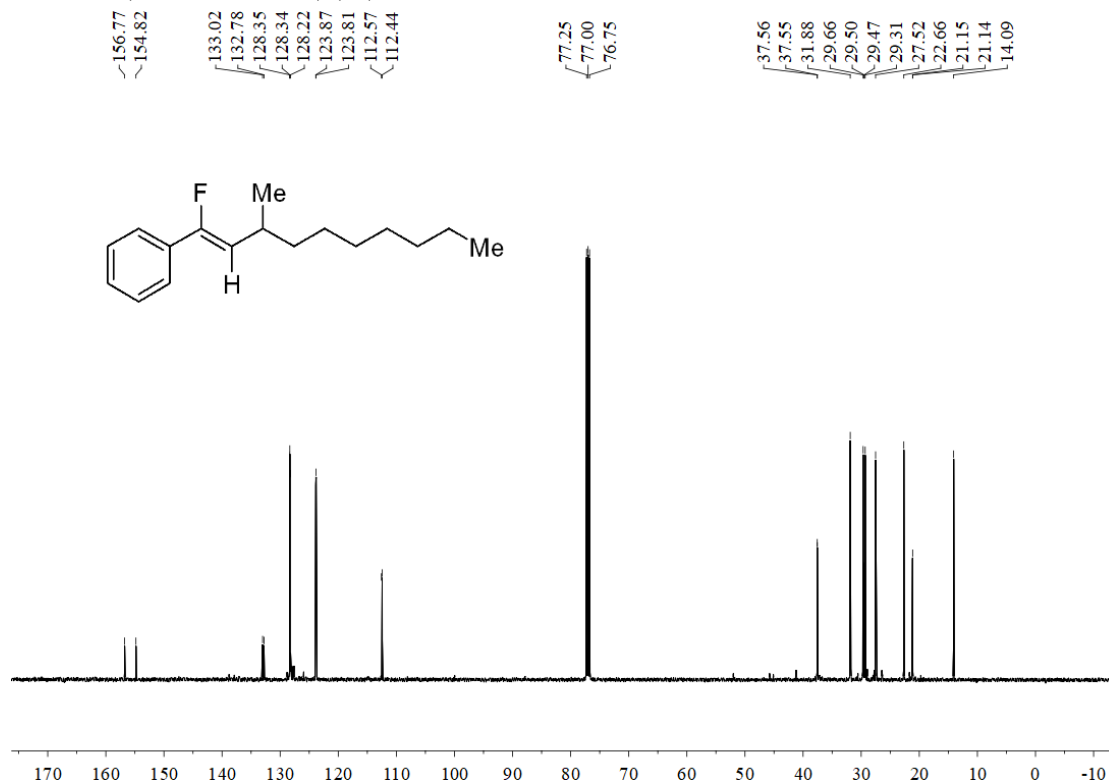
^{19}F NMR (471 MHz, CDCl_3) (36)



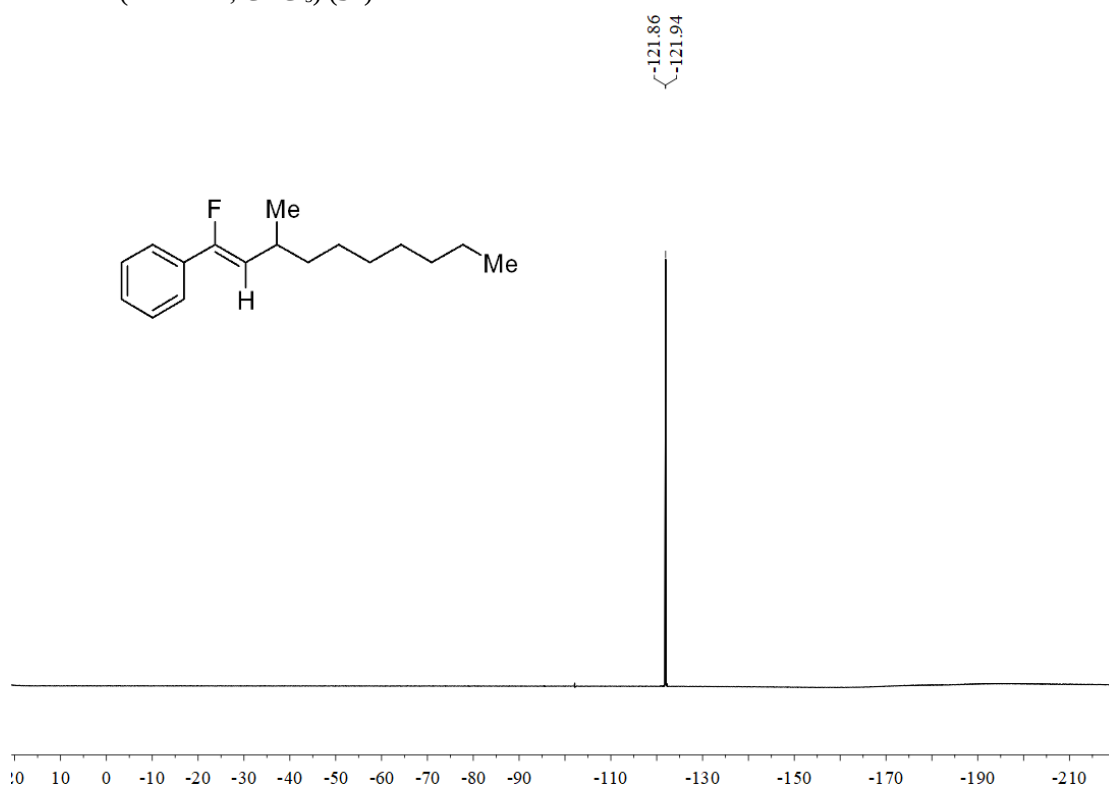
¹H NMR (500 MHz, CDCl₃) (37)



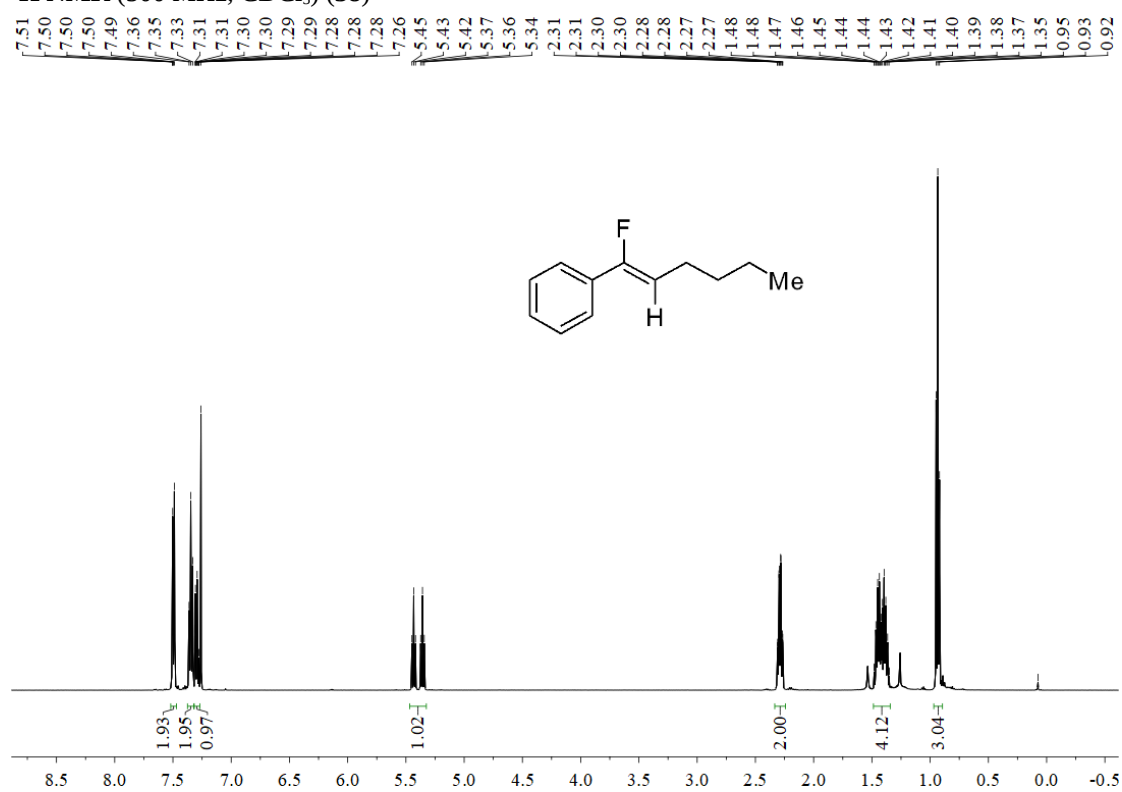
¹³C NMR (126 MHz, CDCl₃) (37)



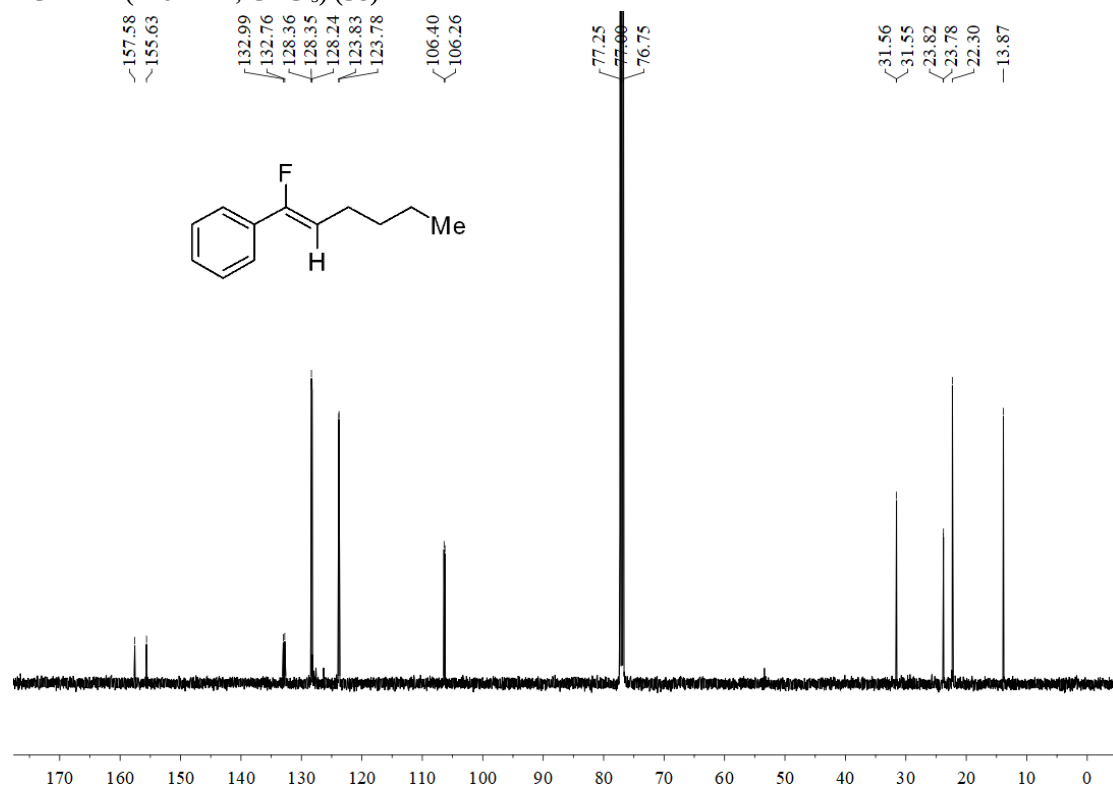
^{19}F NMR (471 MHz, CDCl_3) (37)



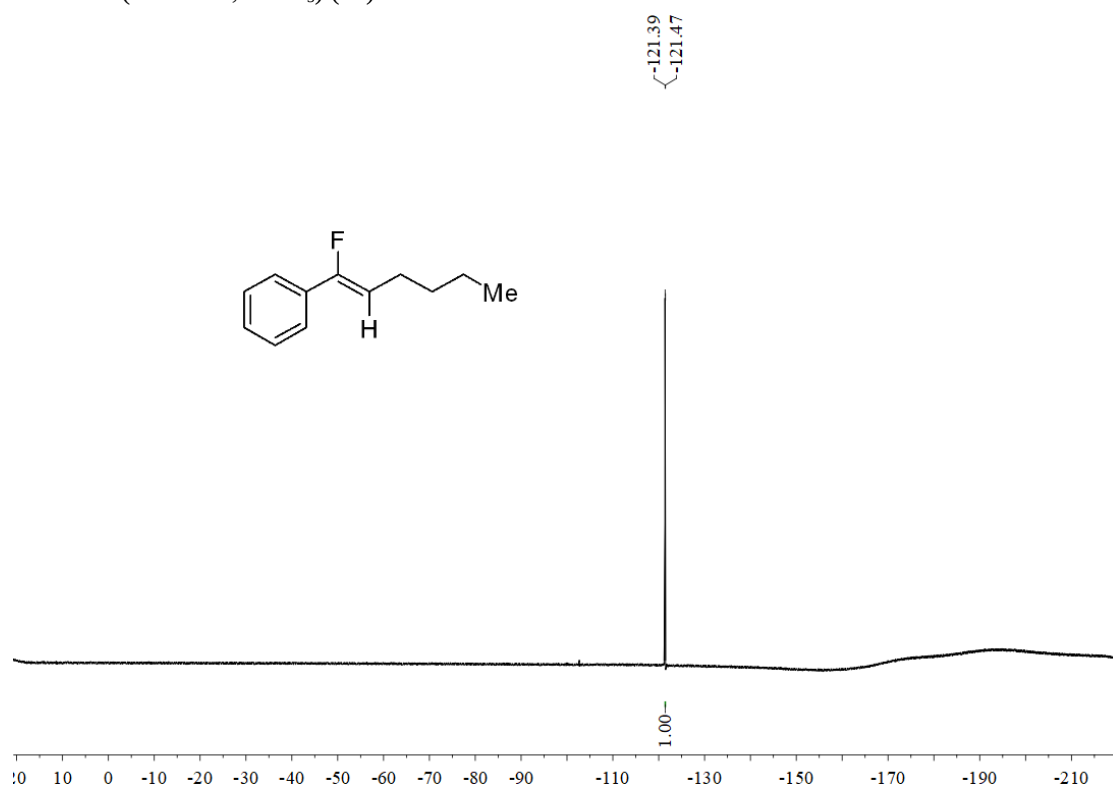
^1H NMR (500 MHz, CDCl_3) (38)



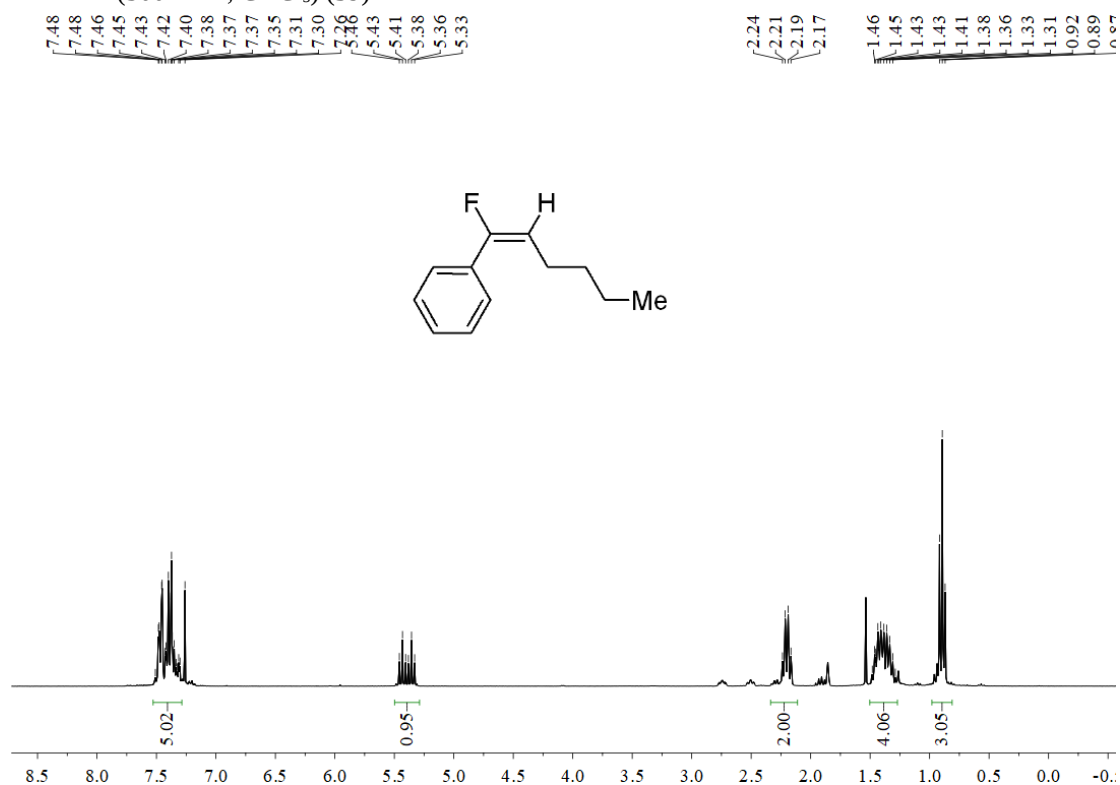
¹³C NMR (126 MHz, CDCl₃) (38)



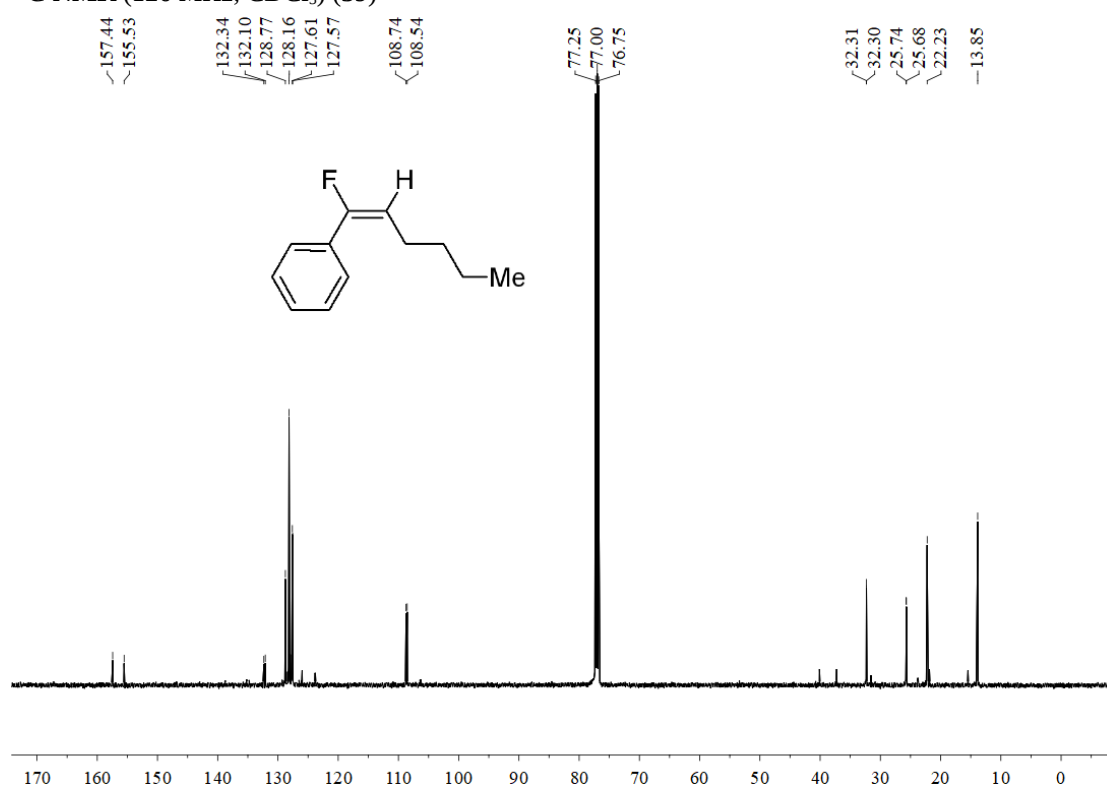
¹⁹F NMR (471 MHz, CDCl₃) (38)



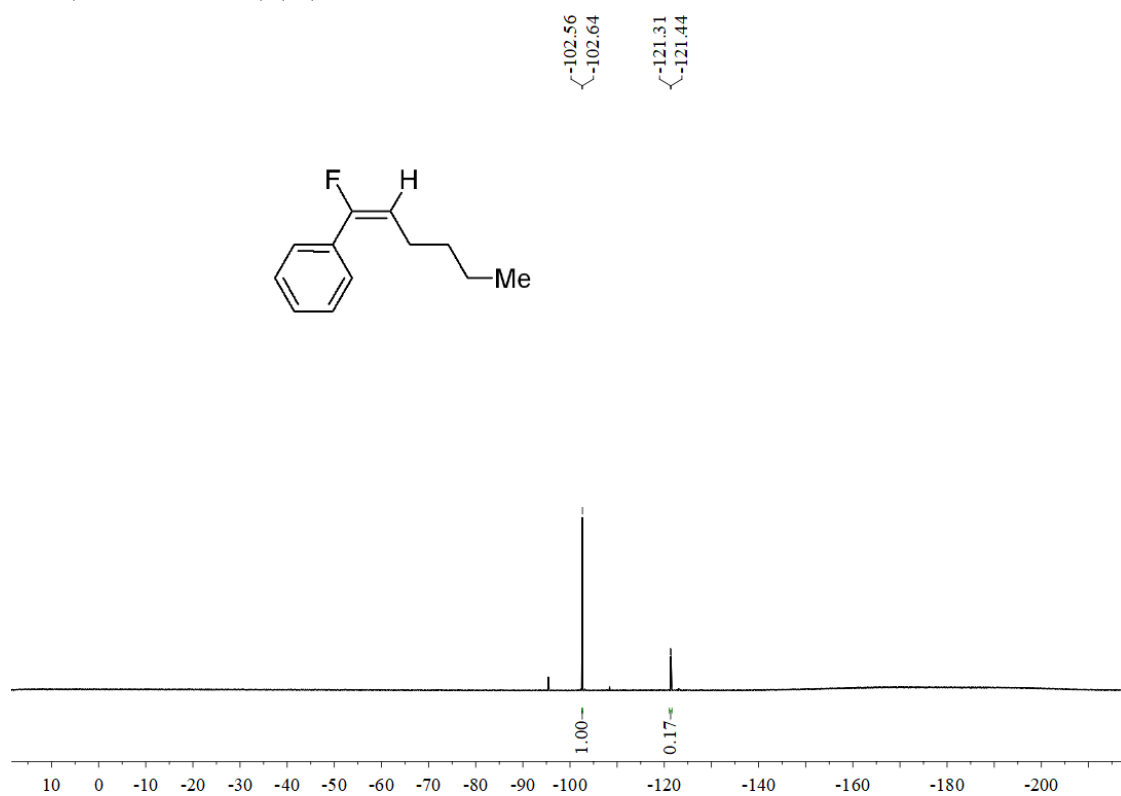
¹H NMR (300 MHz, CDCl₃) (39)



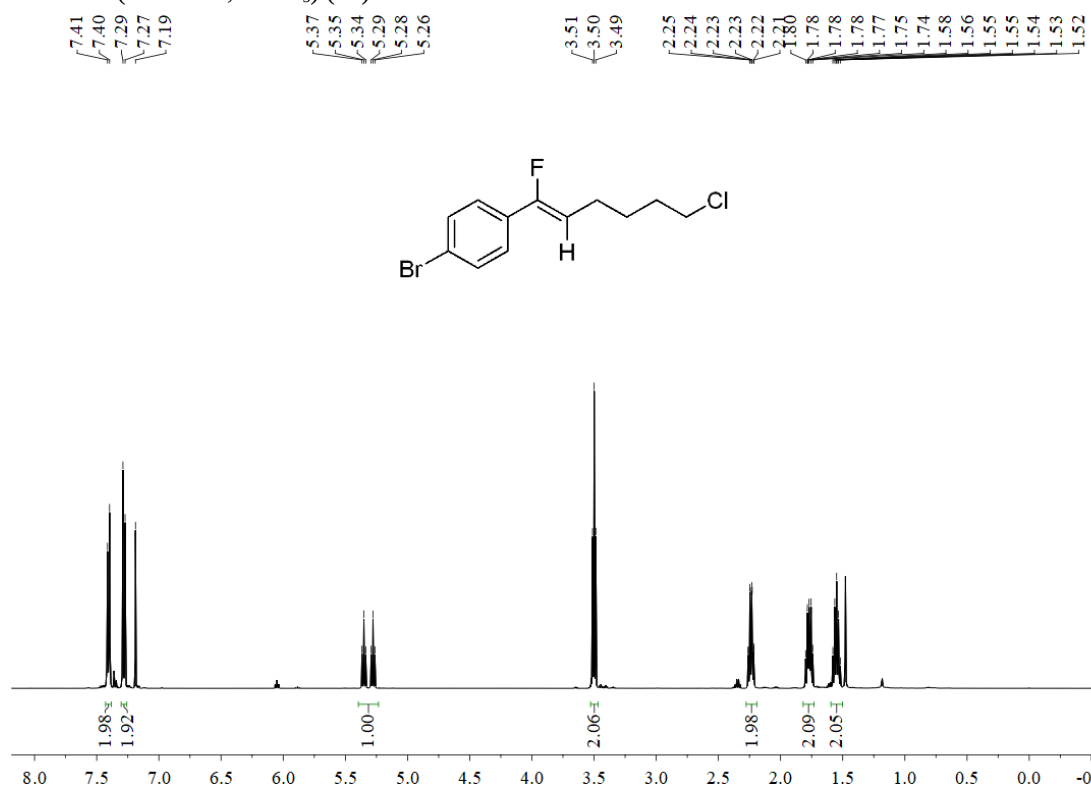
¹³C NMR (126 MHz, CDCl₃) (39)



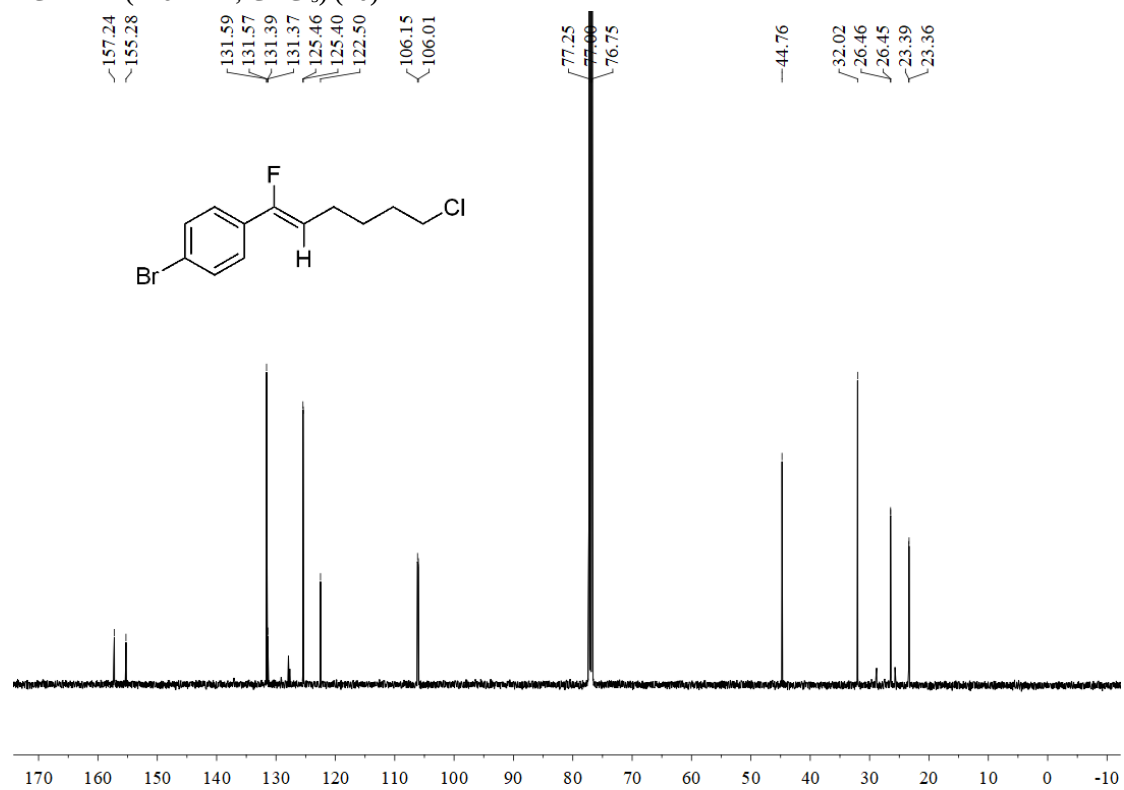
^{19}F NMR (282 MHz, CDCl_3) (39)



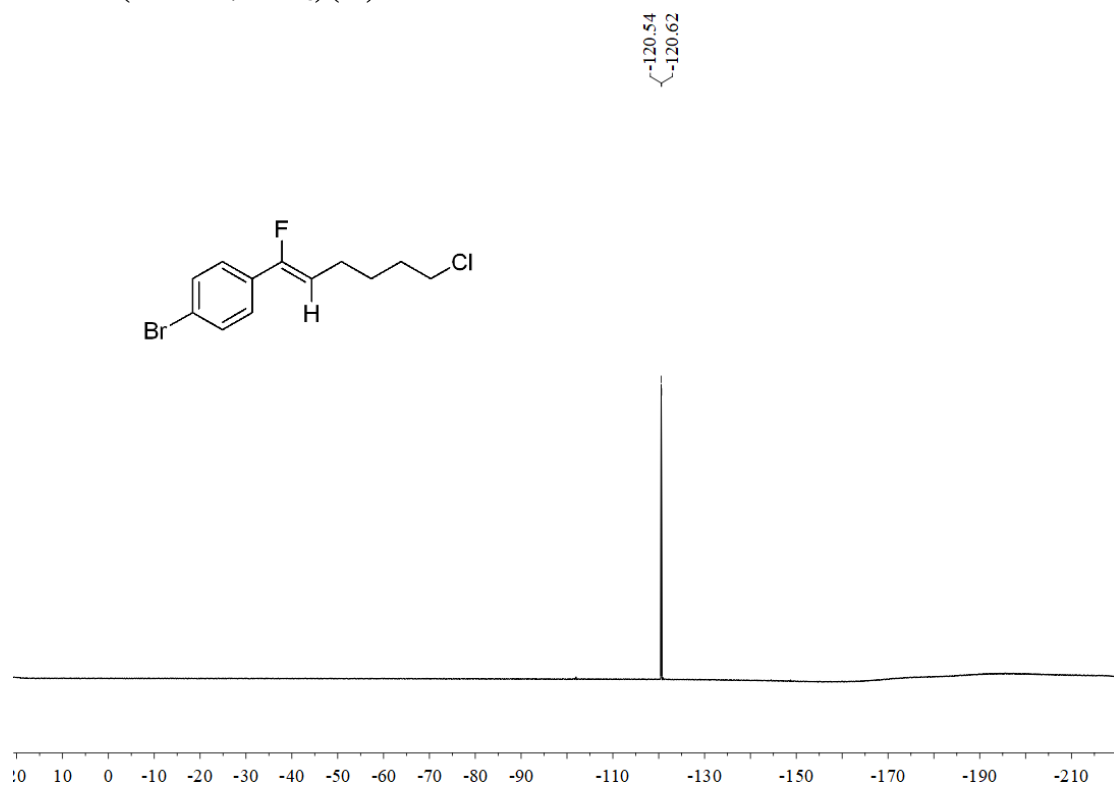
^1H NMR (500 MHz, CDCl_3) (40)



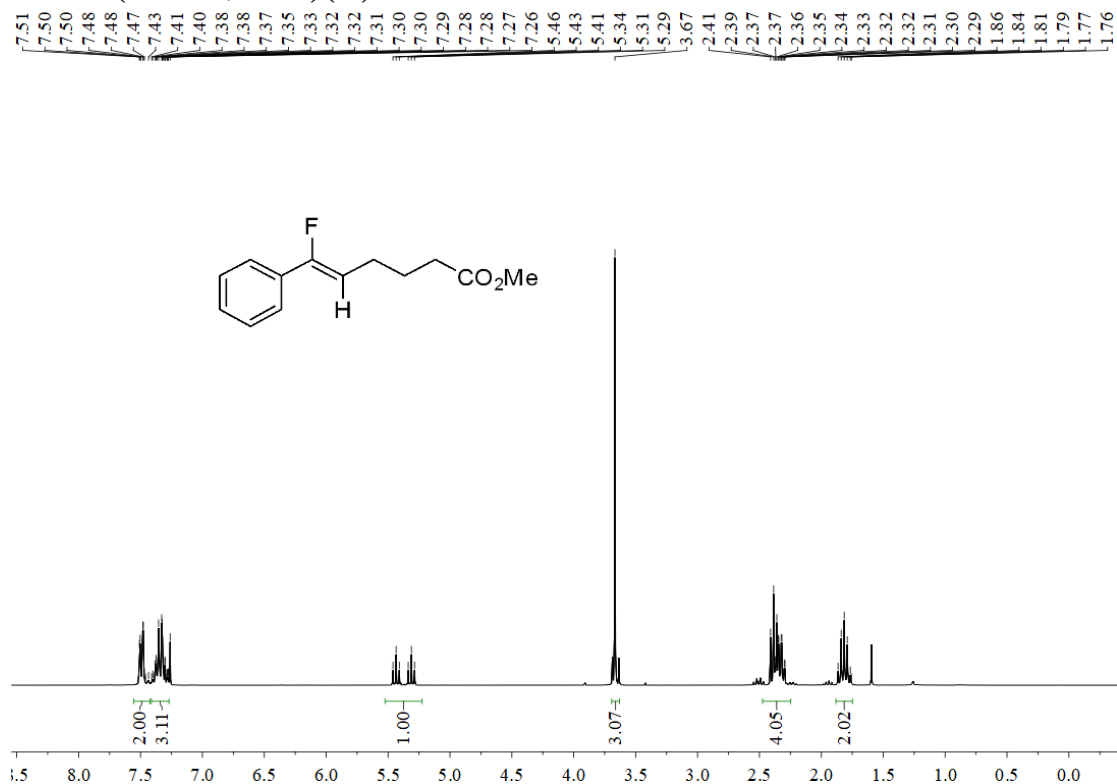
^{13}C NMR (126 MHz, CDCl_3) (40)



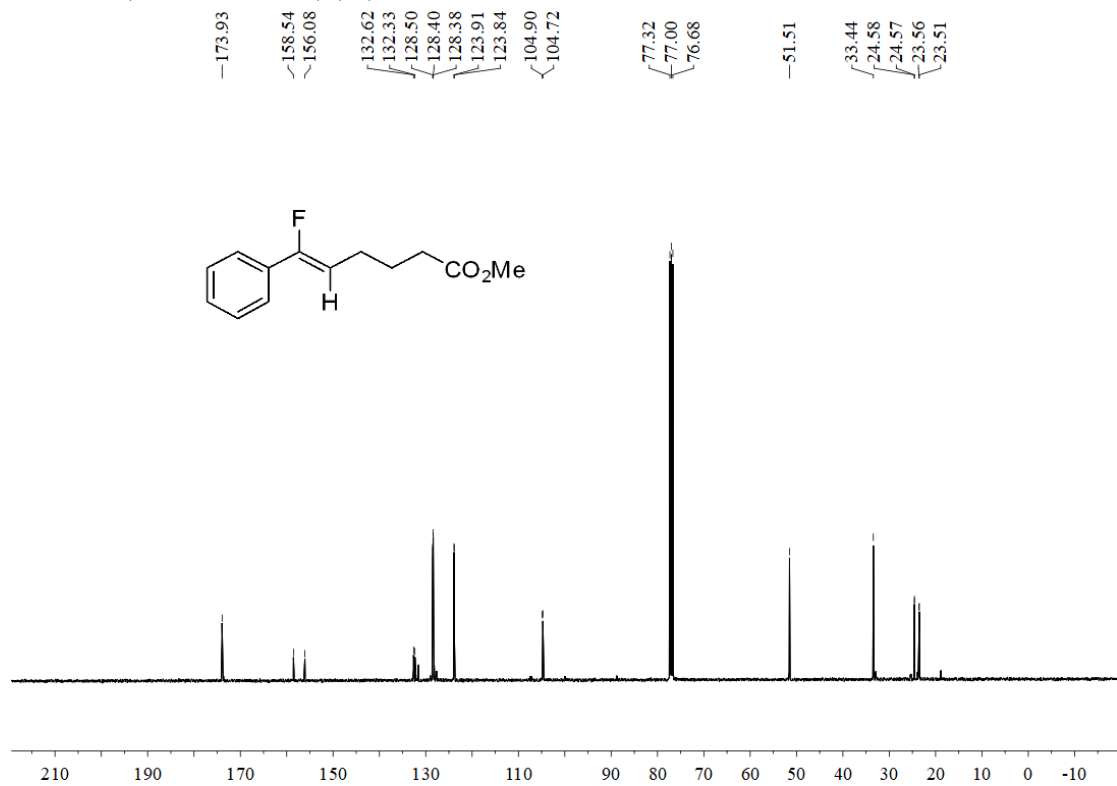
^{19}F NMR (471 MHz, CDCl_3) (40)



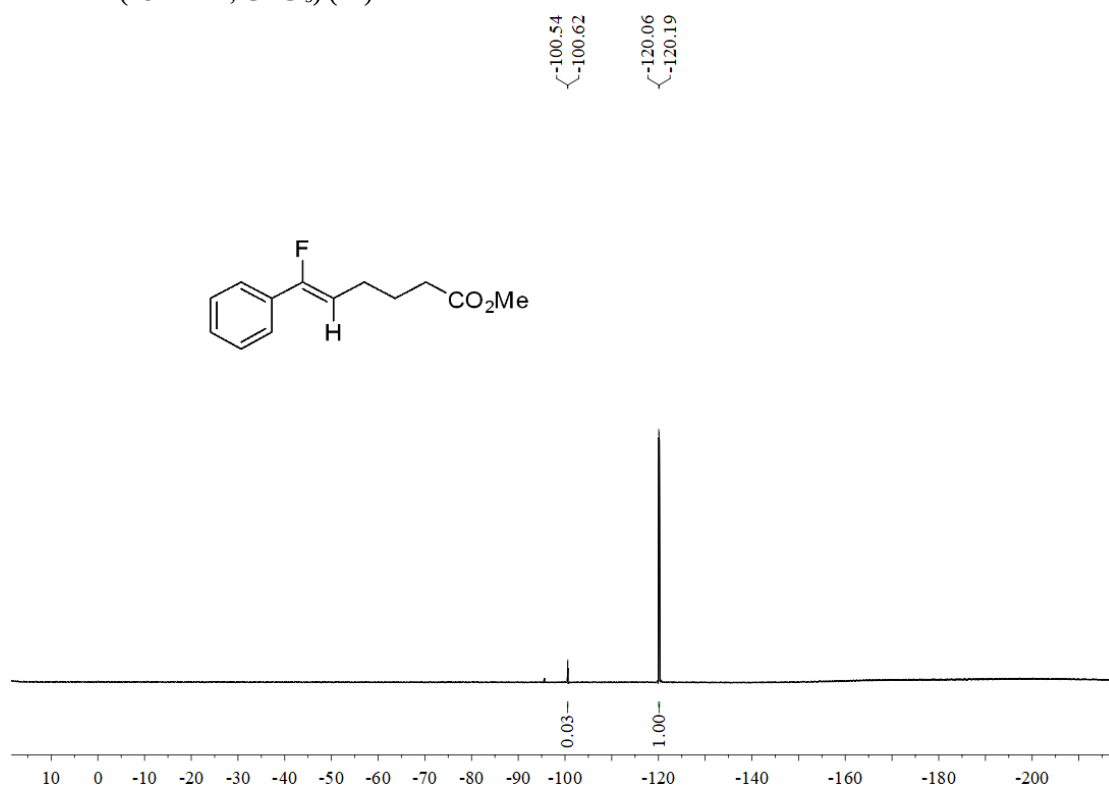
¹H NMR (300 MHz, CDCl₃) (41)



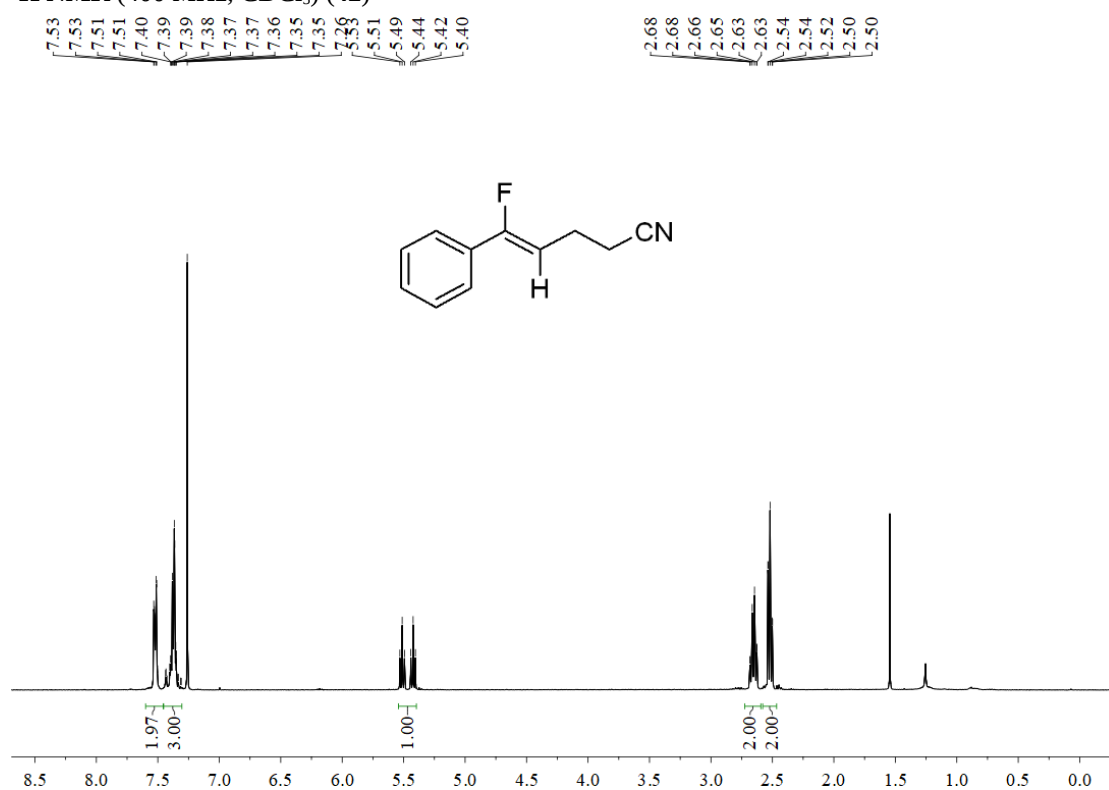
¹³C NMR (101 MHz, CDCl₃) (41)



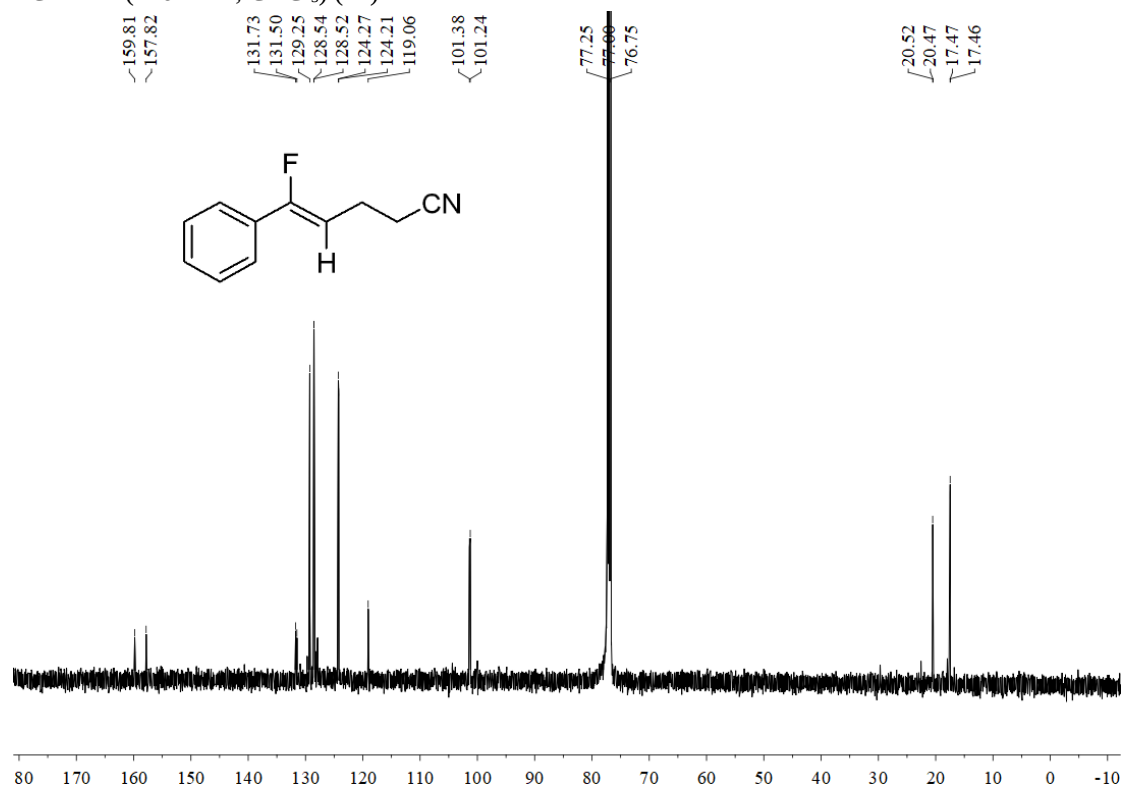
^{19}F NMR (282 MHz, CDCl_3) (41)



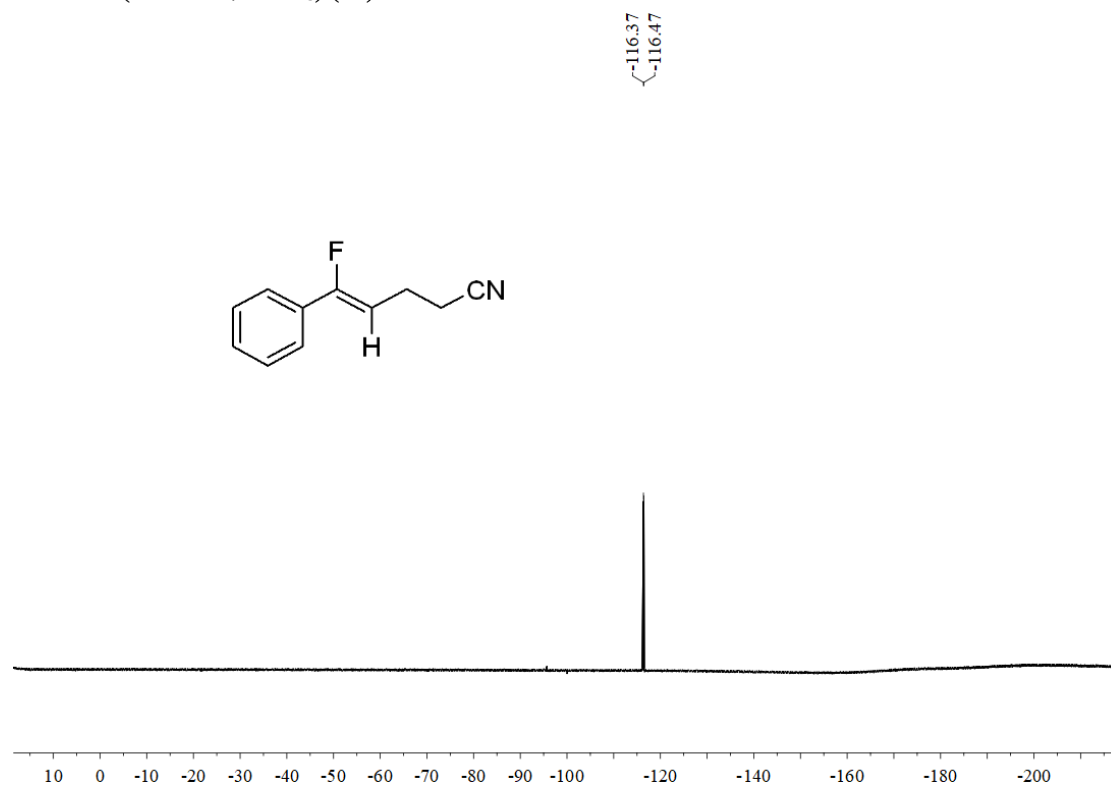
^1H NMR (400 MHz, CDCl_3) (42)



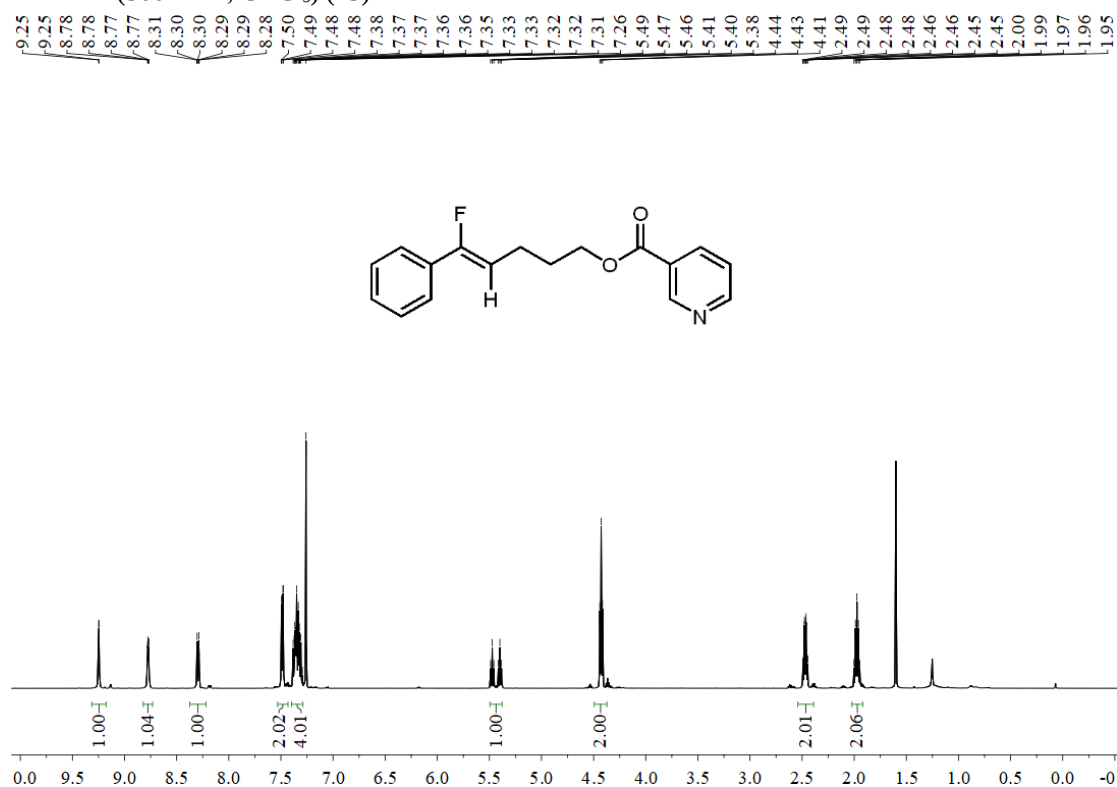
¹³C NMR (126 MHz, CDCl₃) (42)



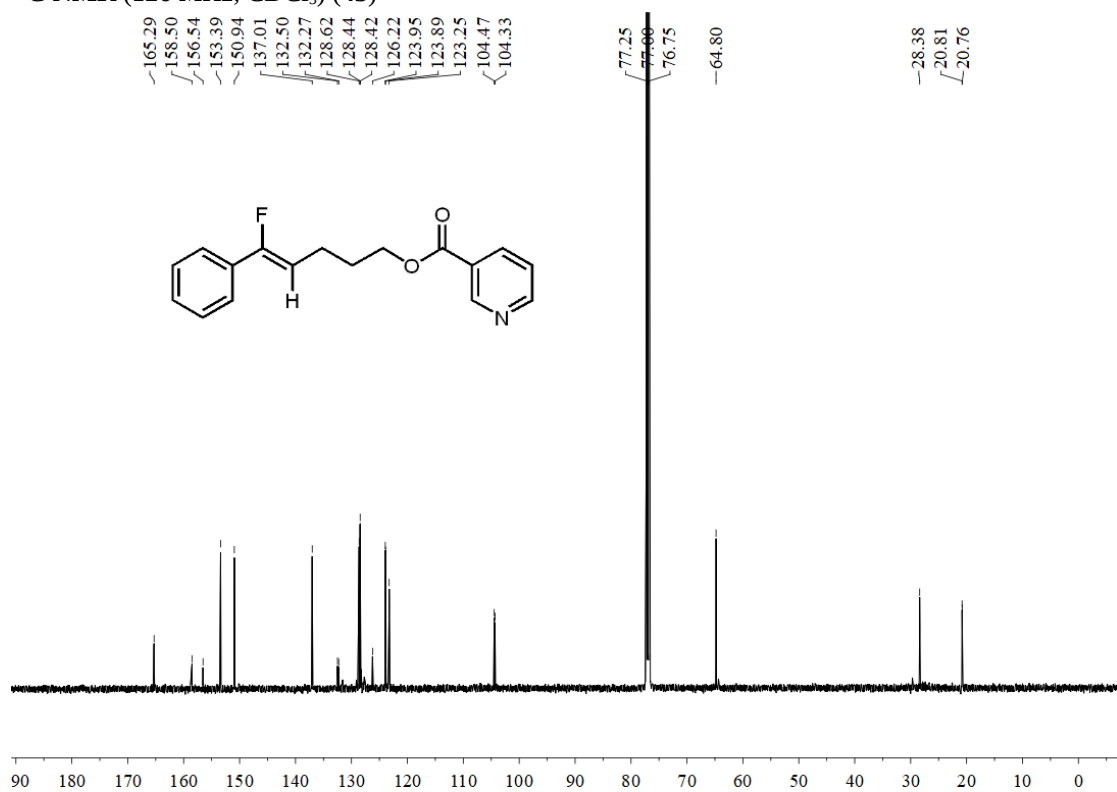
¹⁹F NMR (376 MHz, CDCl₃) (42)



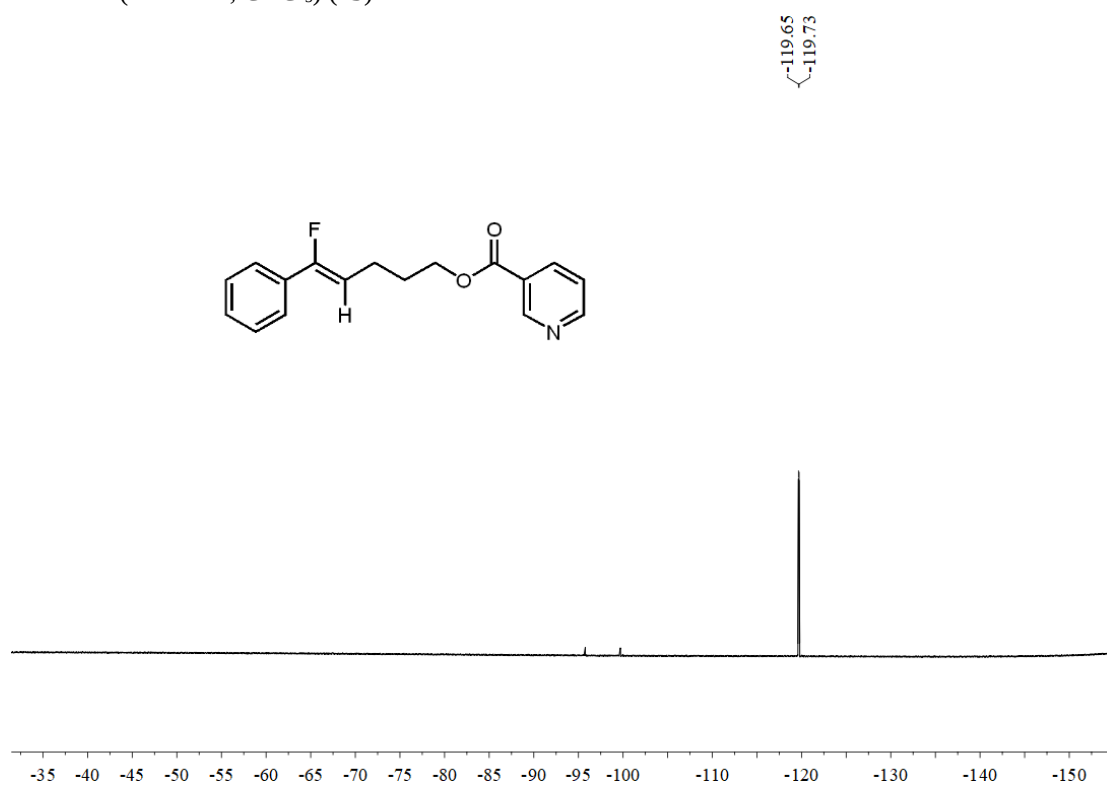
¹H NMR (500 MHz, CDCl₃) (43)



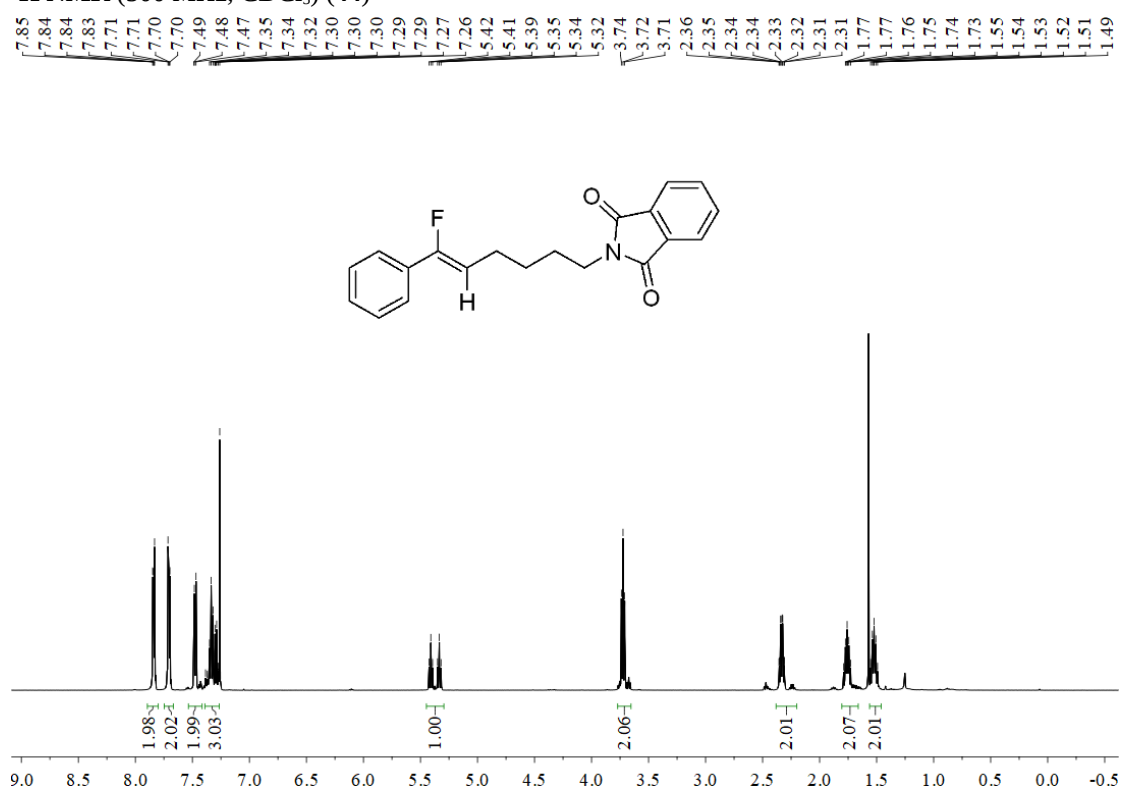
¹³C NMR (126 MHz, CDCl₃) (43)



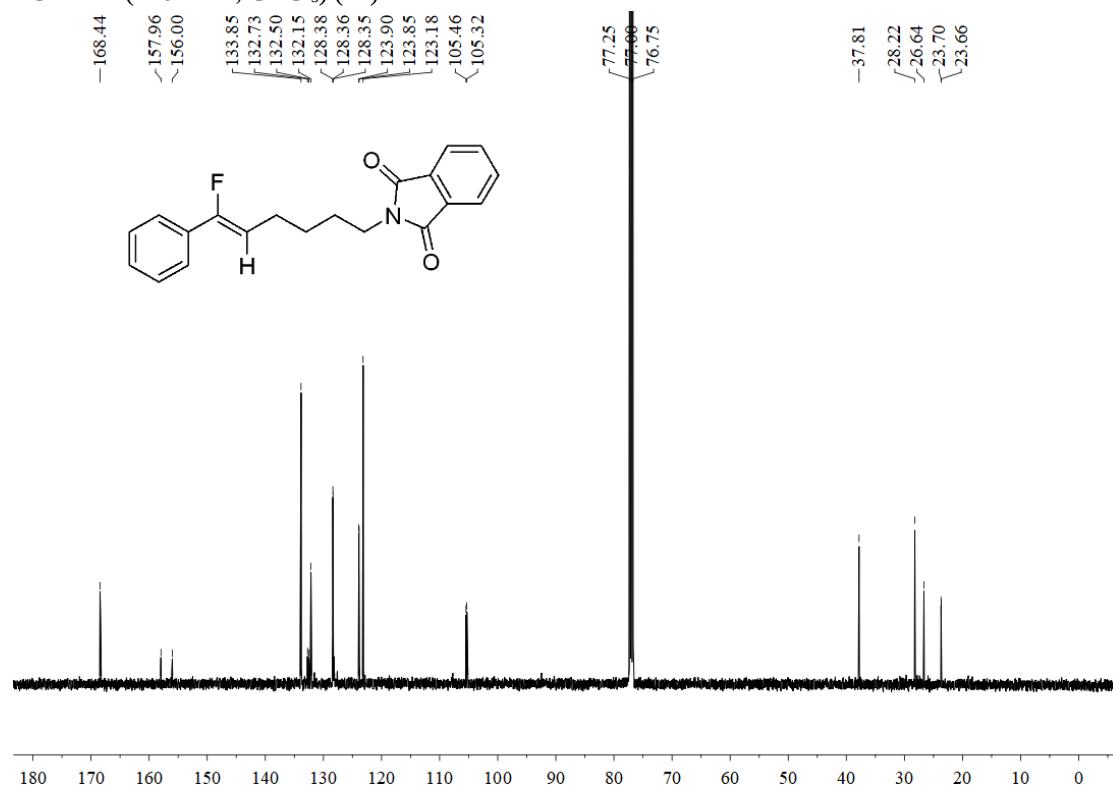
¹⁹F NMR (471 MHz, CDCl₃) (43)



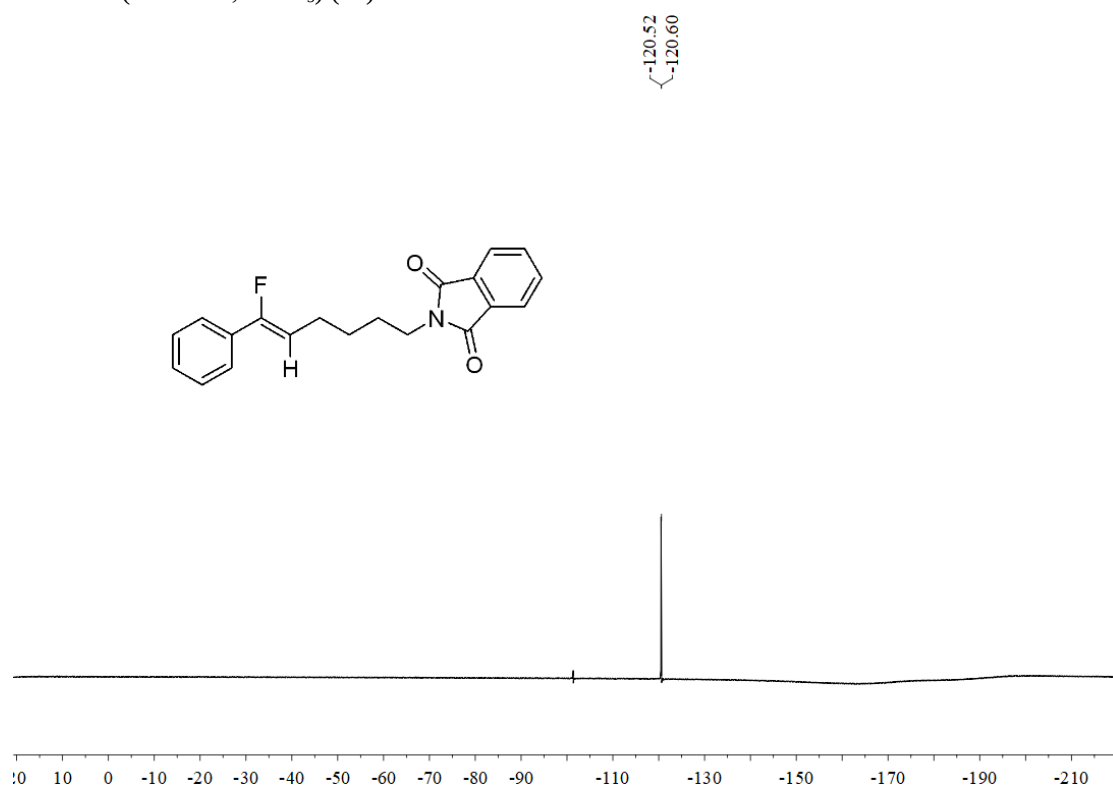
¹H NMR (500 MHz, CDCl₃) (44)



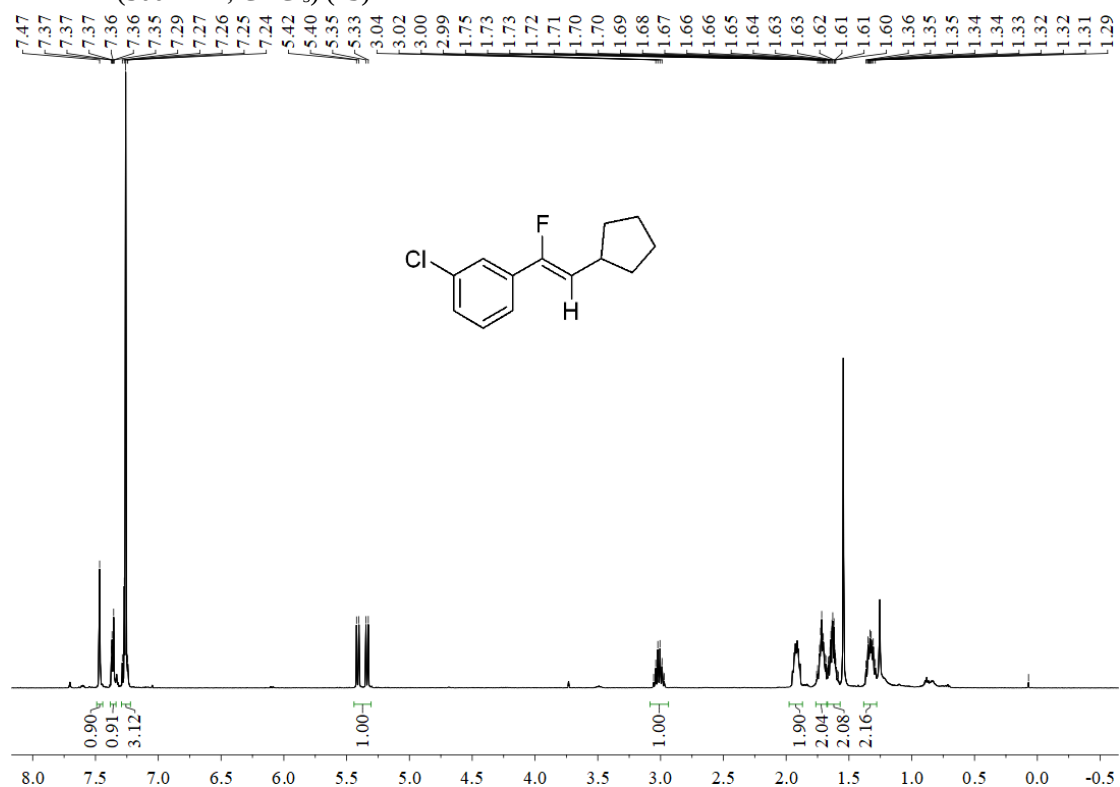
¹³C NMR (126 MHz, CDCl₃) (44)



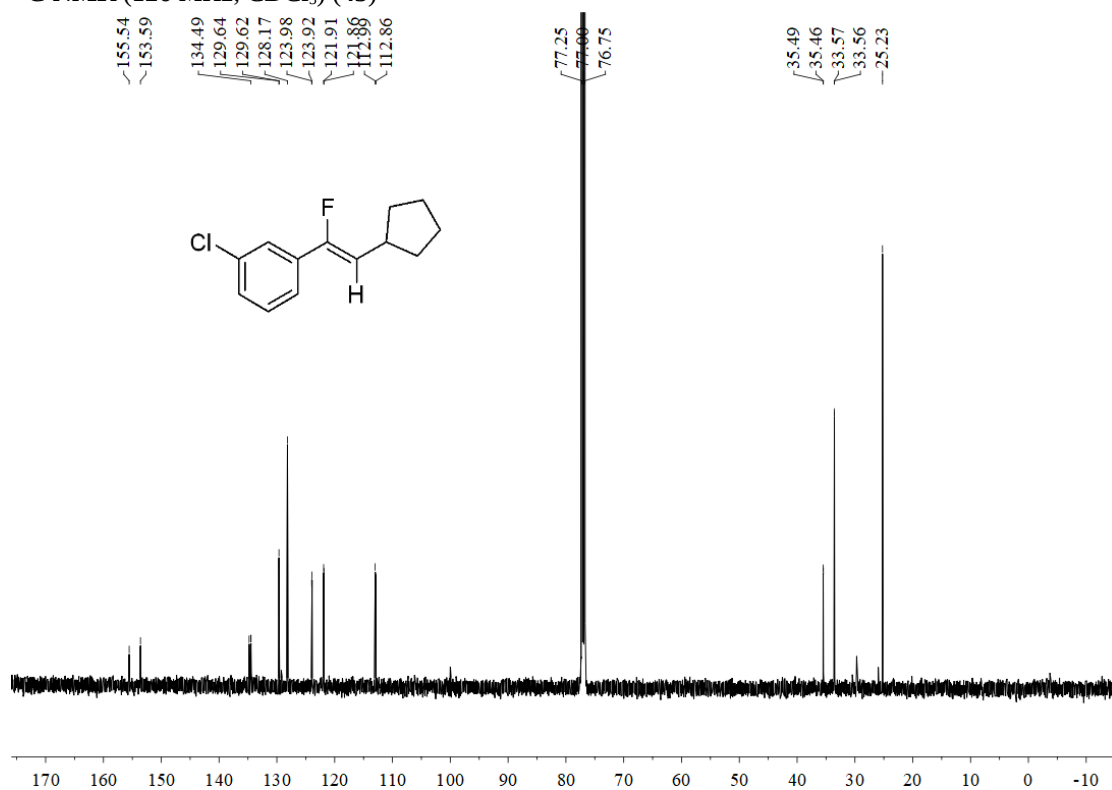
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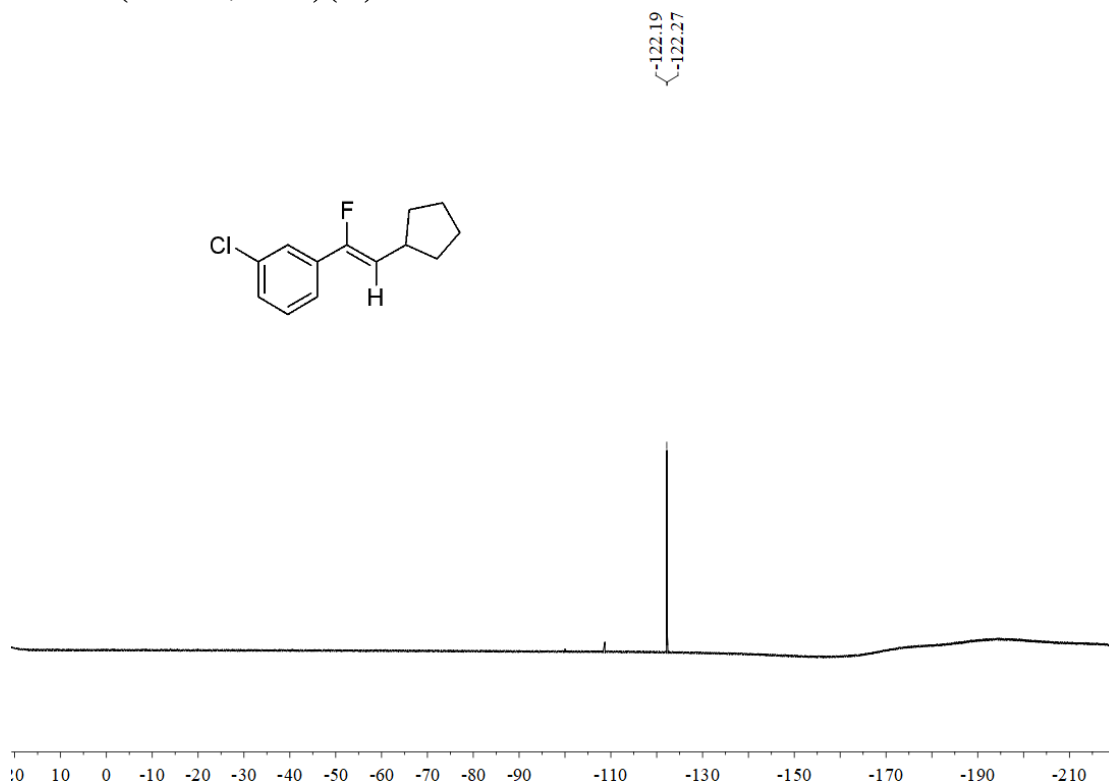
¹H NMR (500 MHz, CDCl₃) (45)



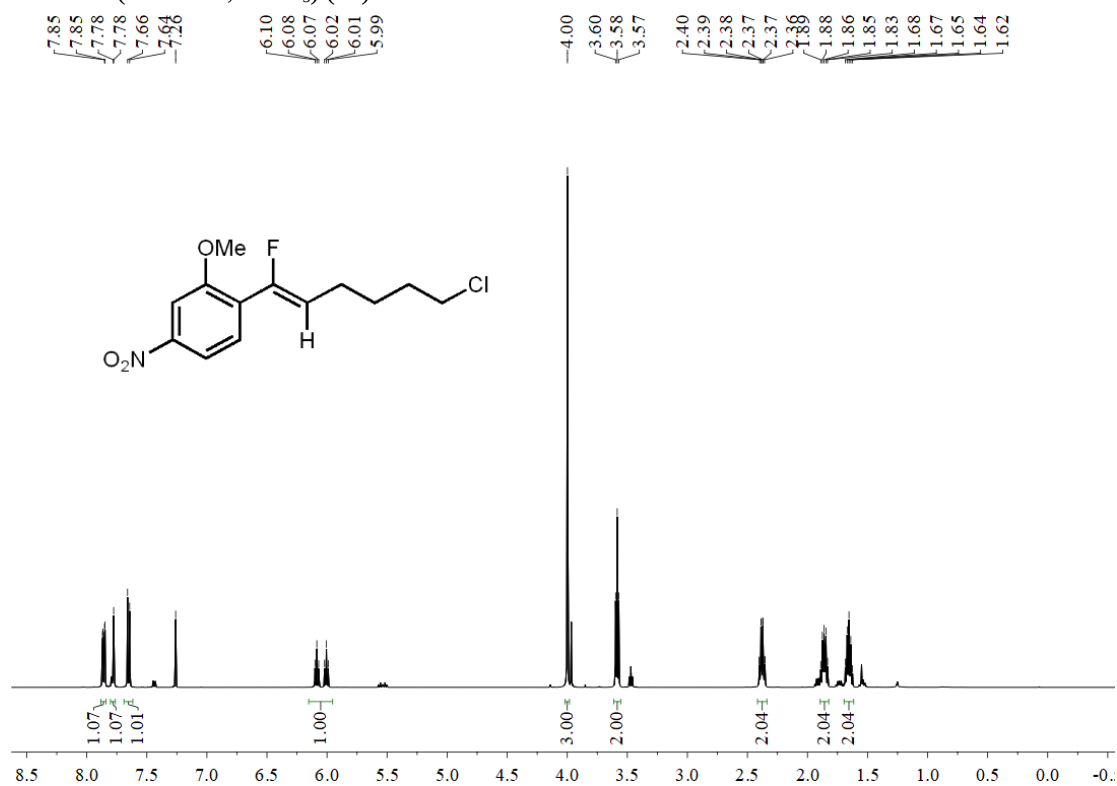
¹³C NMR (126 MHz, CDCl₃) (45)



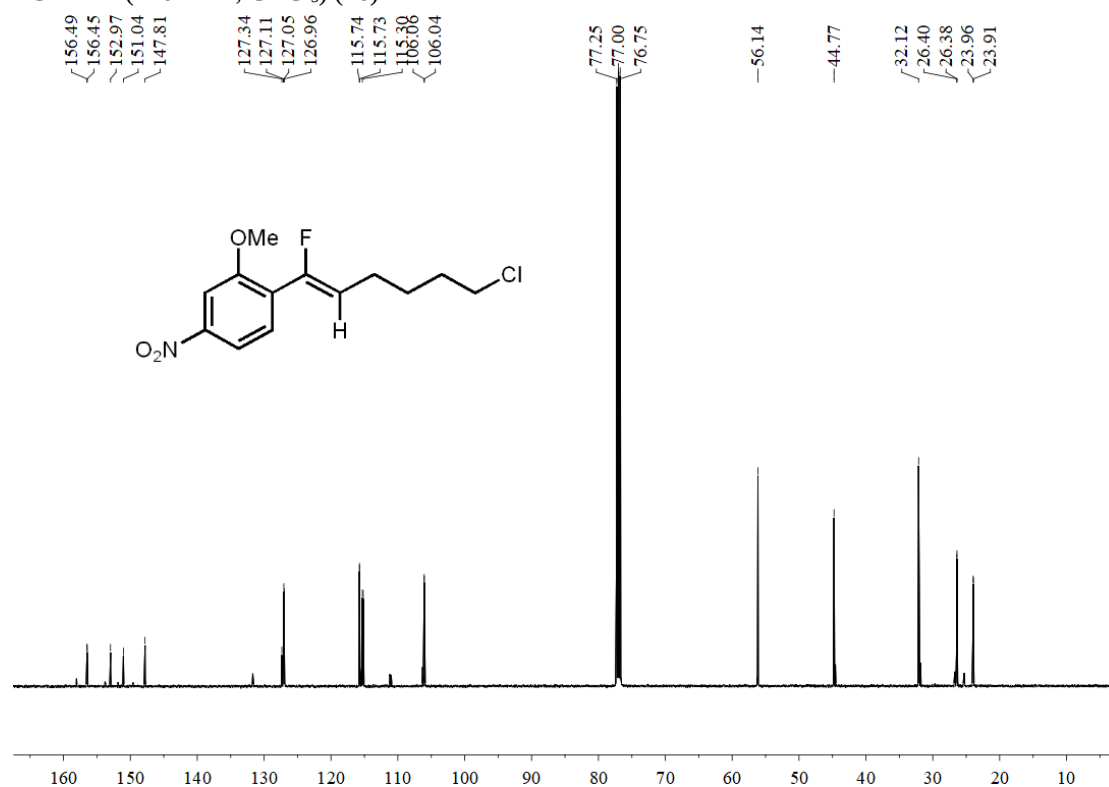
^{19}F NMR (471 MHz, CDCl_3) (45)



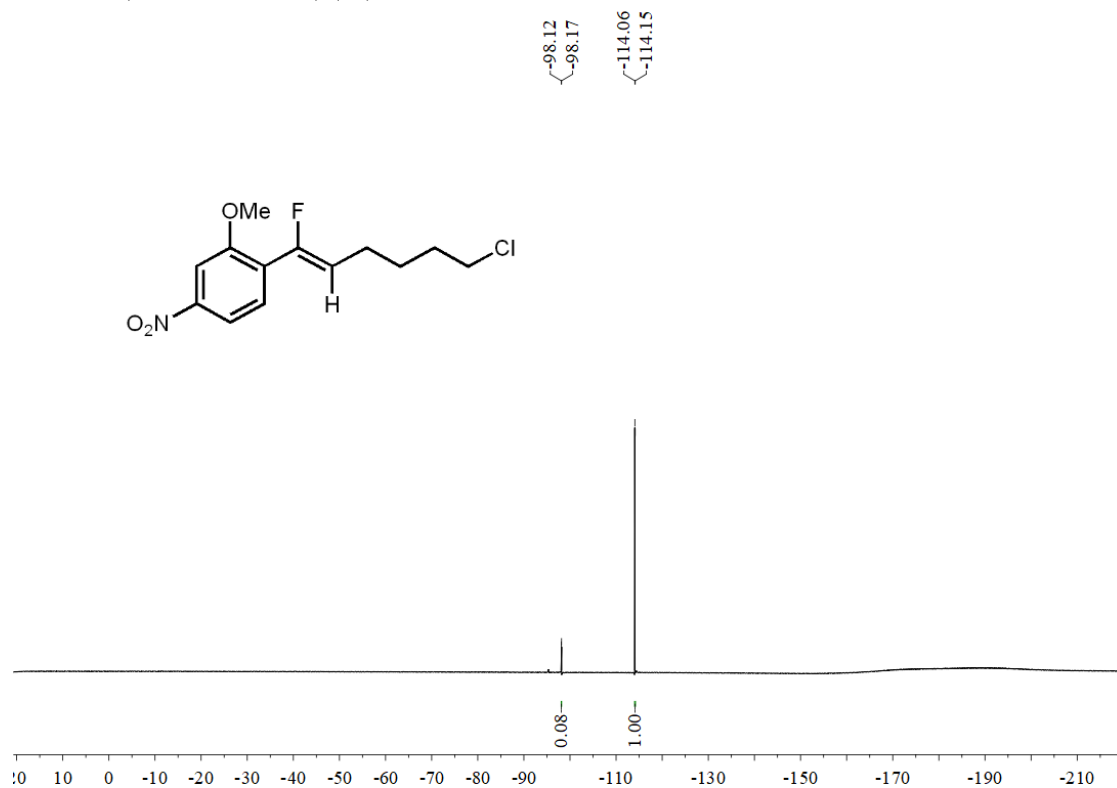
^1H NMR (500 MHz, CDCl_3) (46)



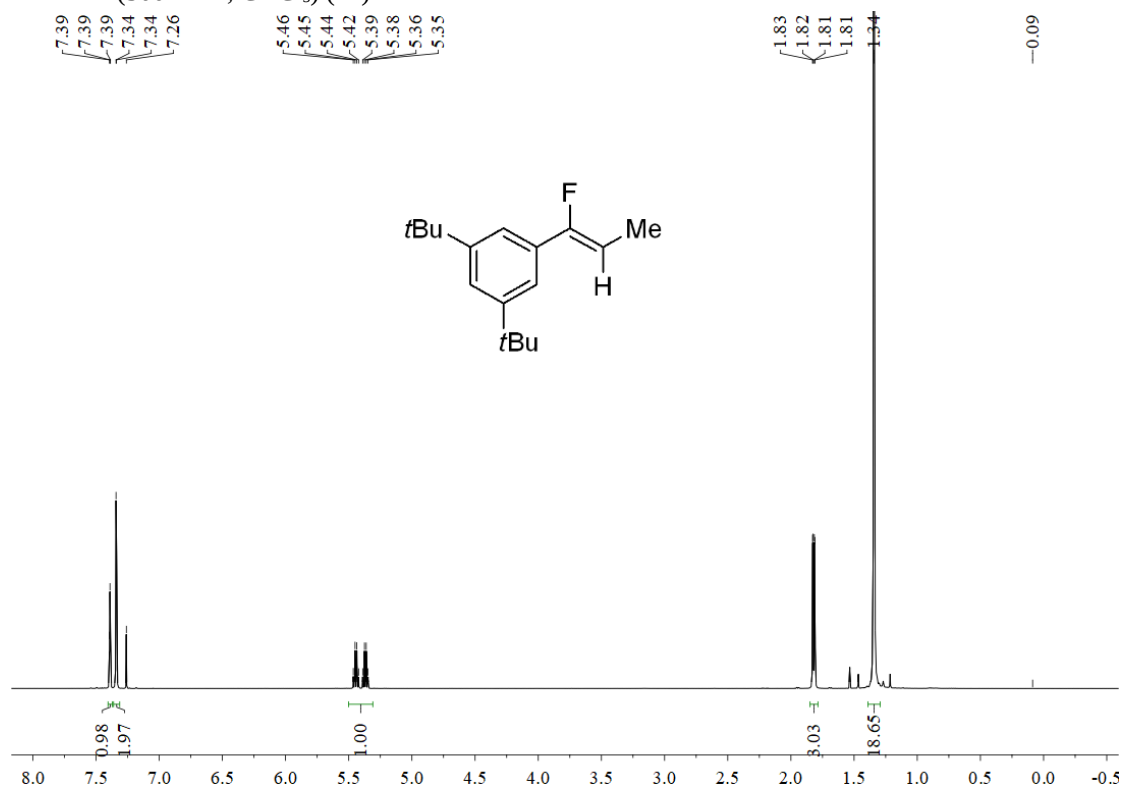
¹³C NMR (126 MHz, CDCl₃) (46)



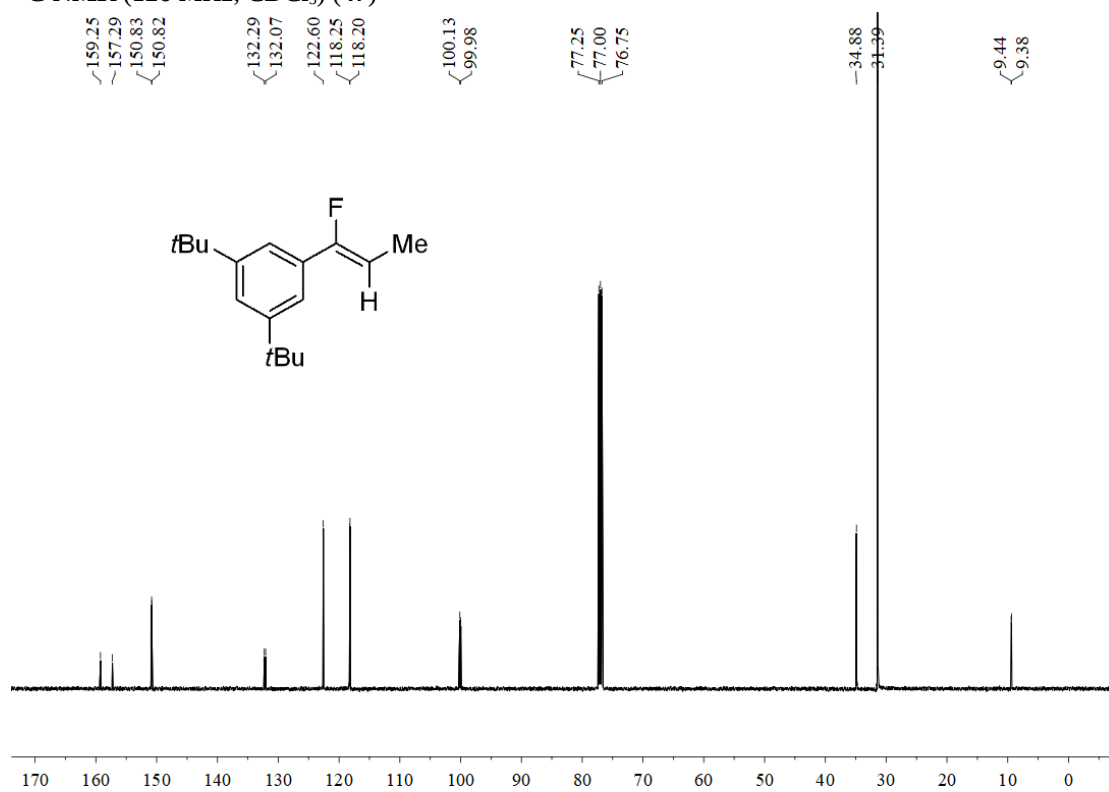
¹⁹F NMR (471 MHz, CDCl₃) (46)



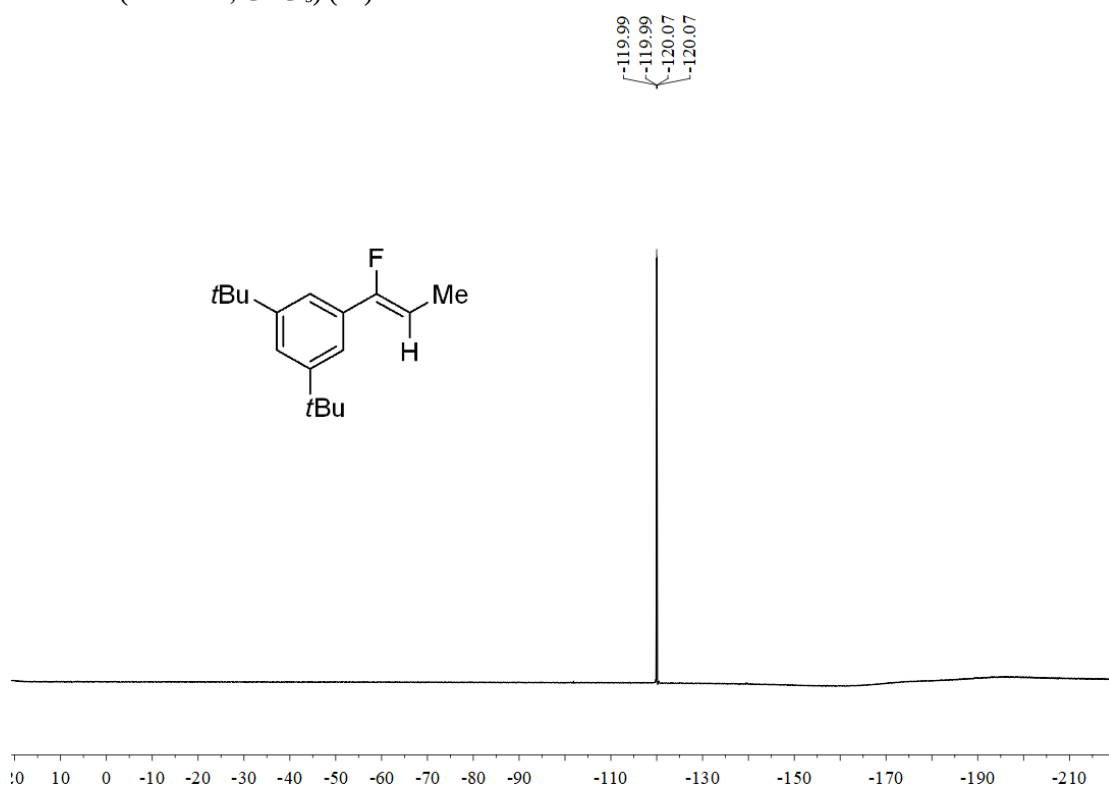
¹H NMR (500 MHz, CDCl₃) (47)



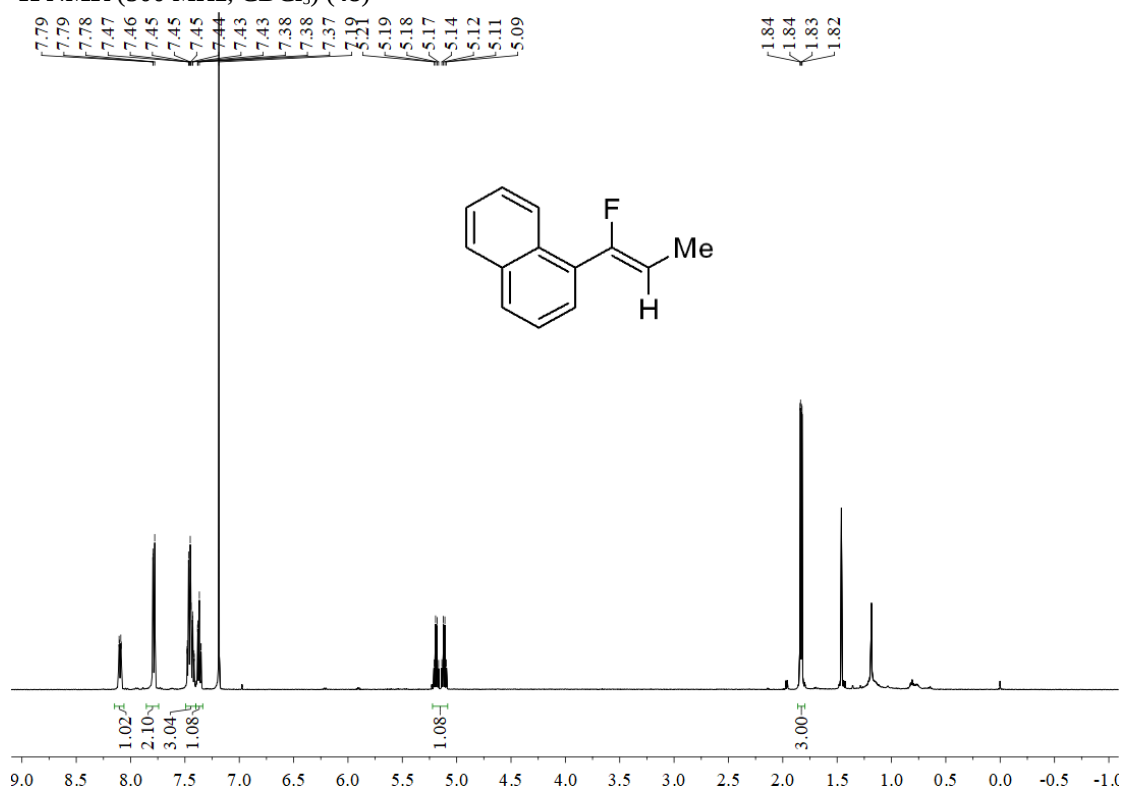
¹³C NMR (126 MHz, CDCl₃) (47)



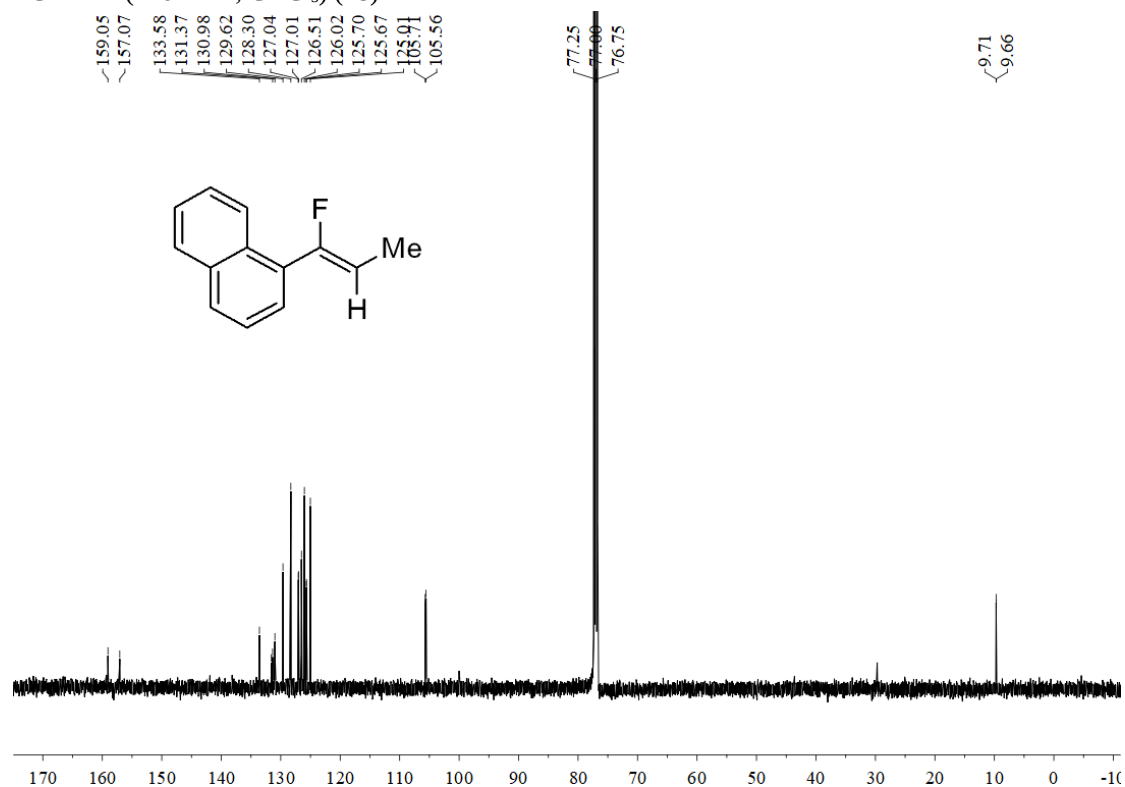
^{19}F NMR (471 MHz, CDCl_3) (47)



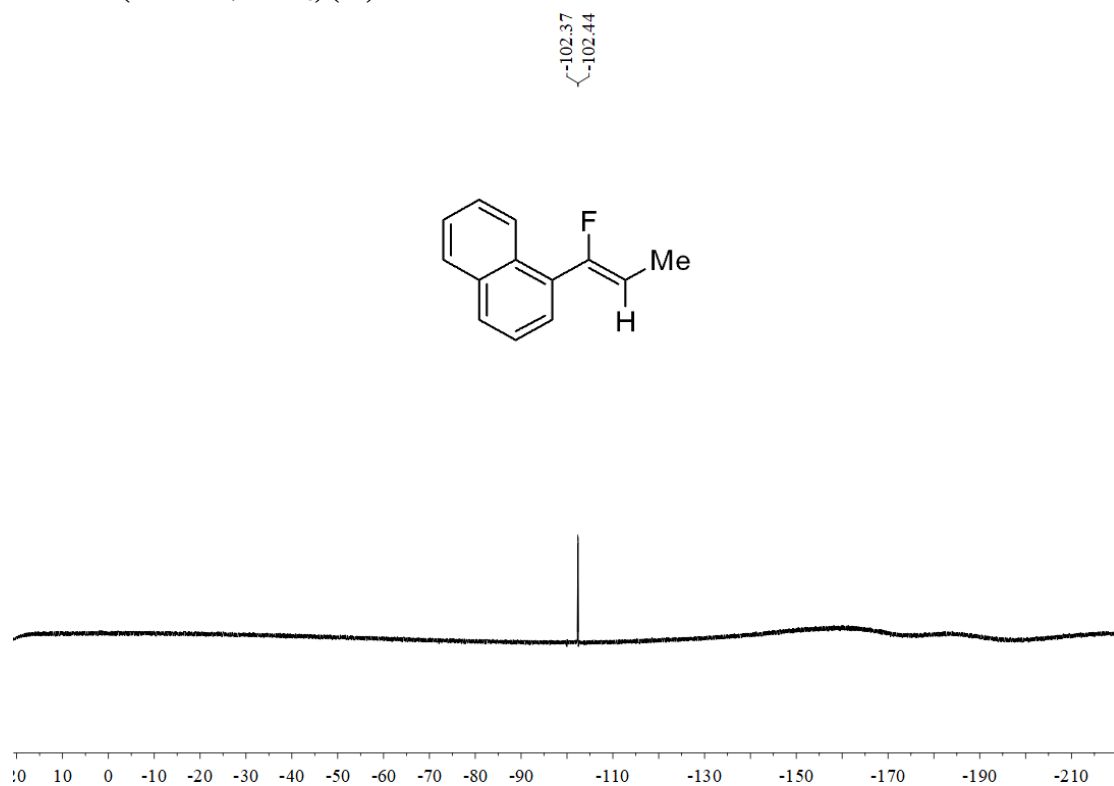
^1H NMR (500 MHz, CDCl_3) (48)



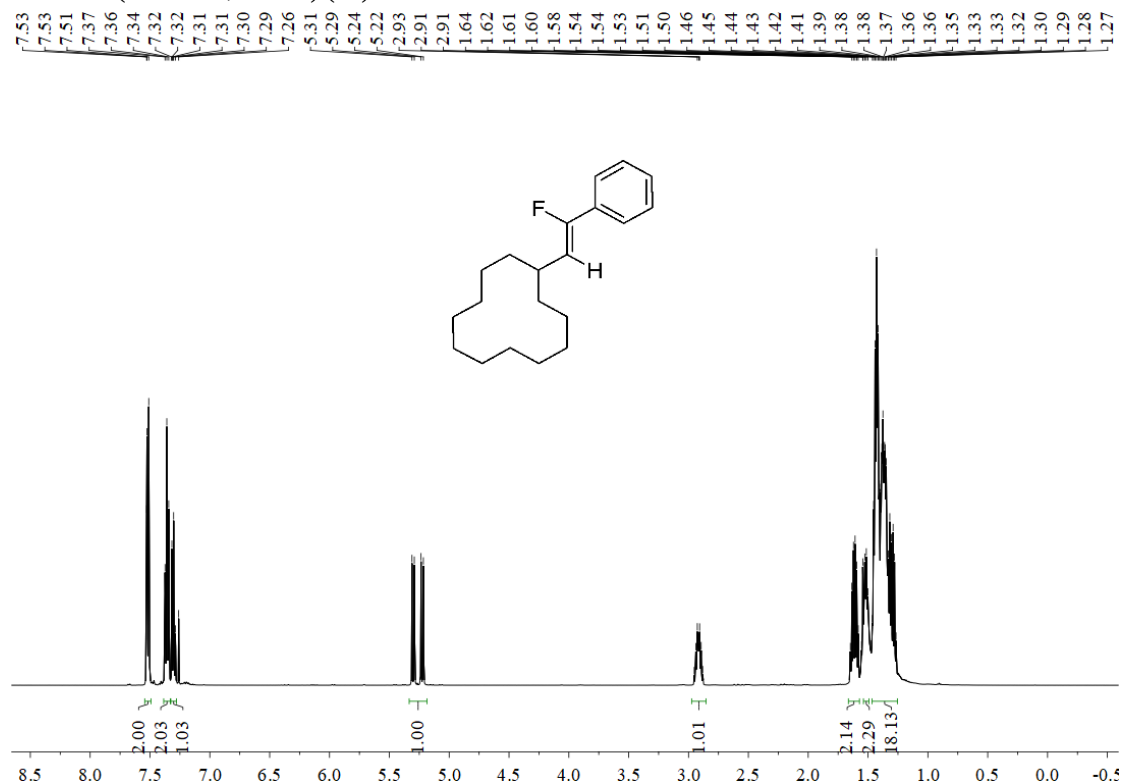
¹³C NMR (126 MHz, CDCl₃) (48)



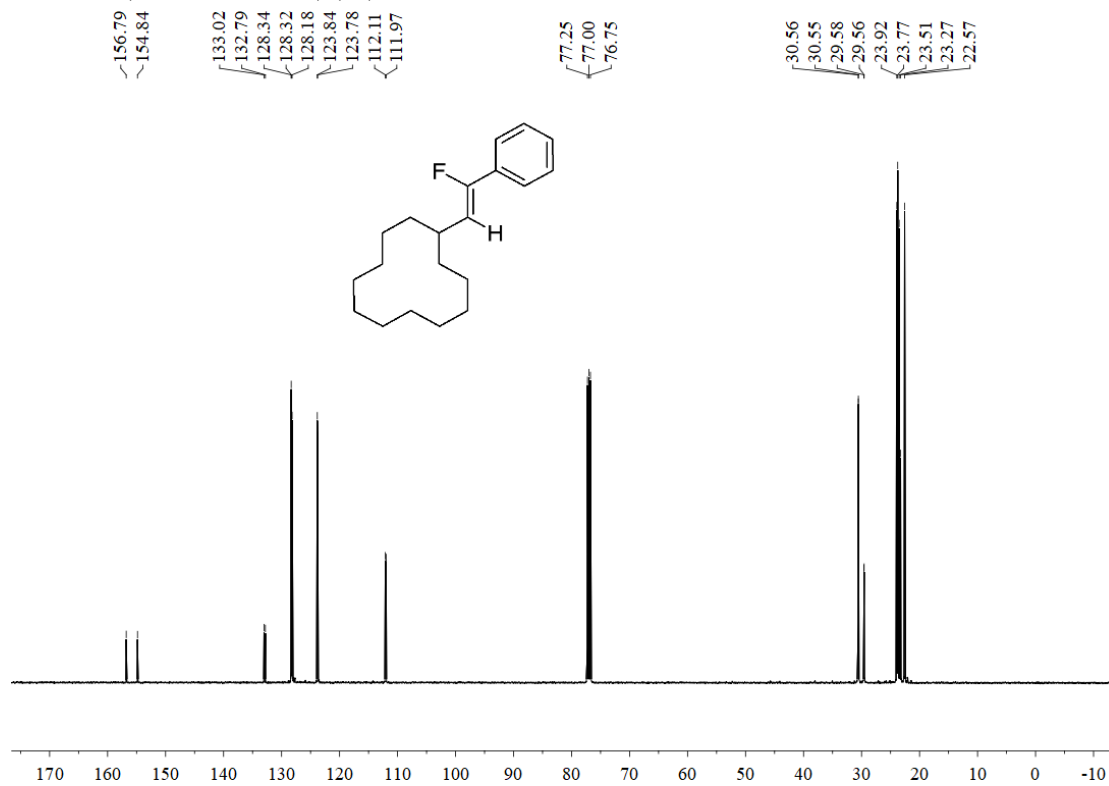
¹⁹F NMR (471 MHz, CDCl₃) (48)



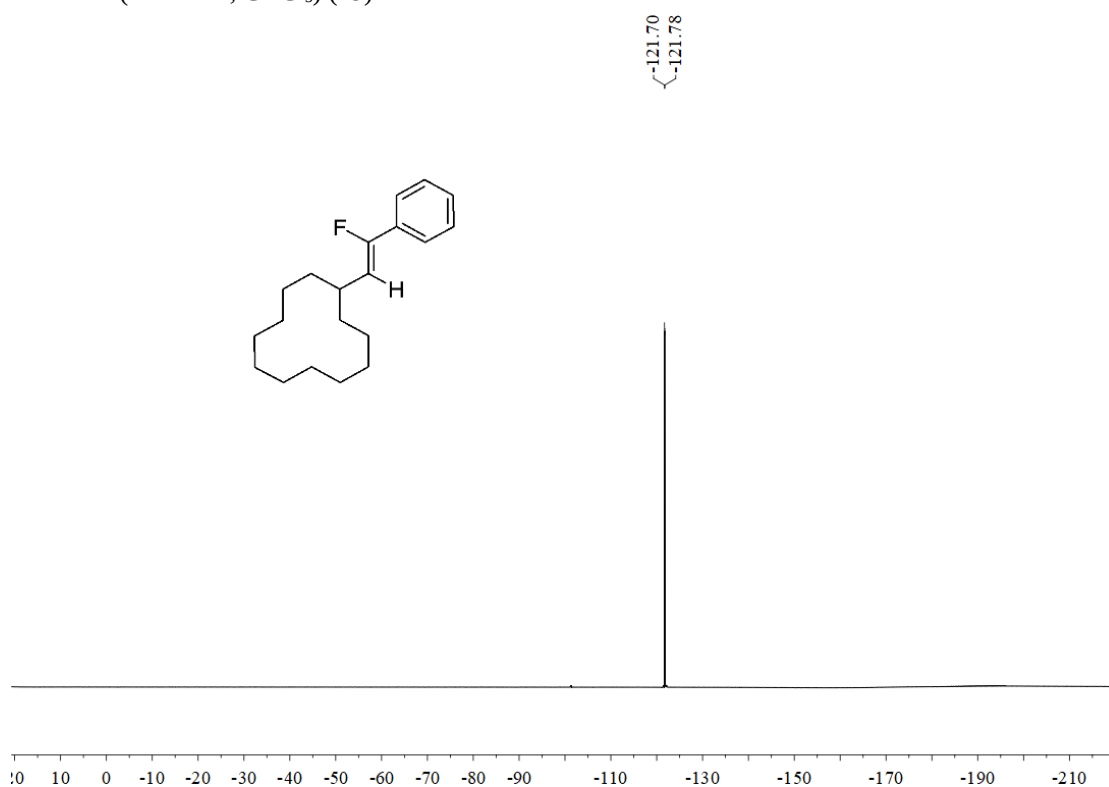
¹H NMR (500 MHz, CDCl₃) (49)



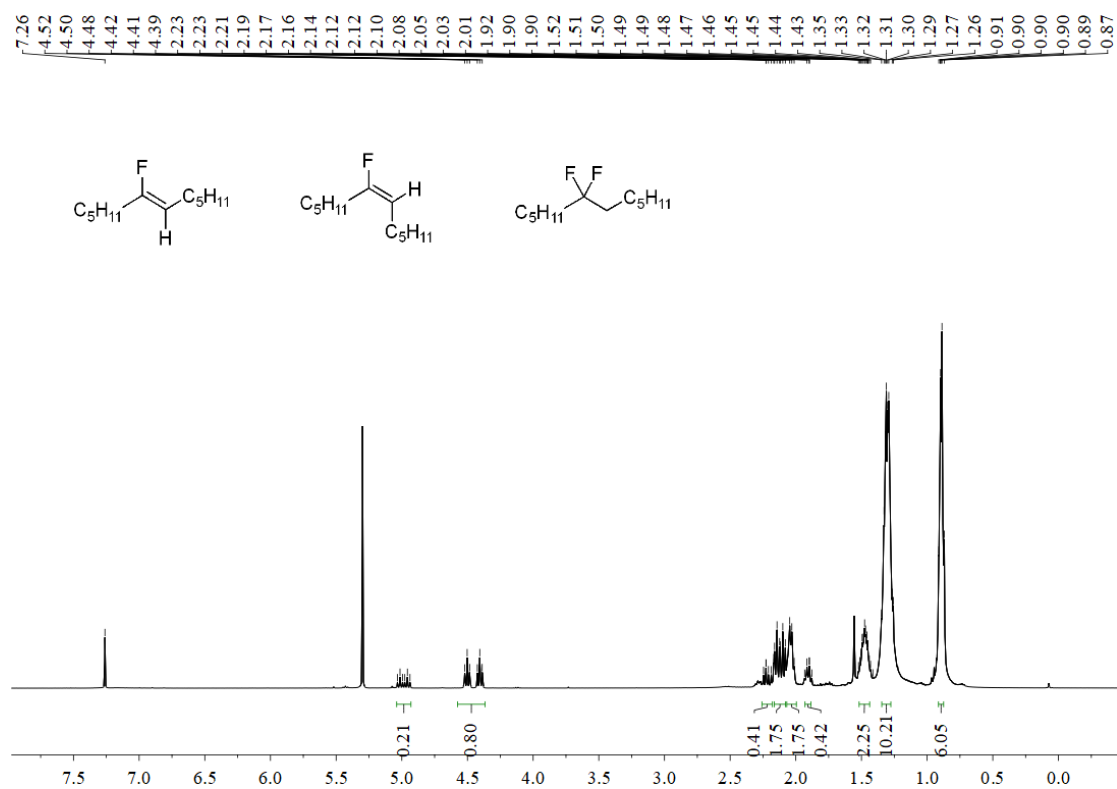
¹³C NMR (126 MHz, CDCl₃) (49)



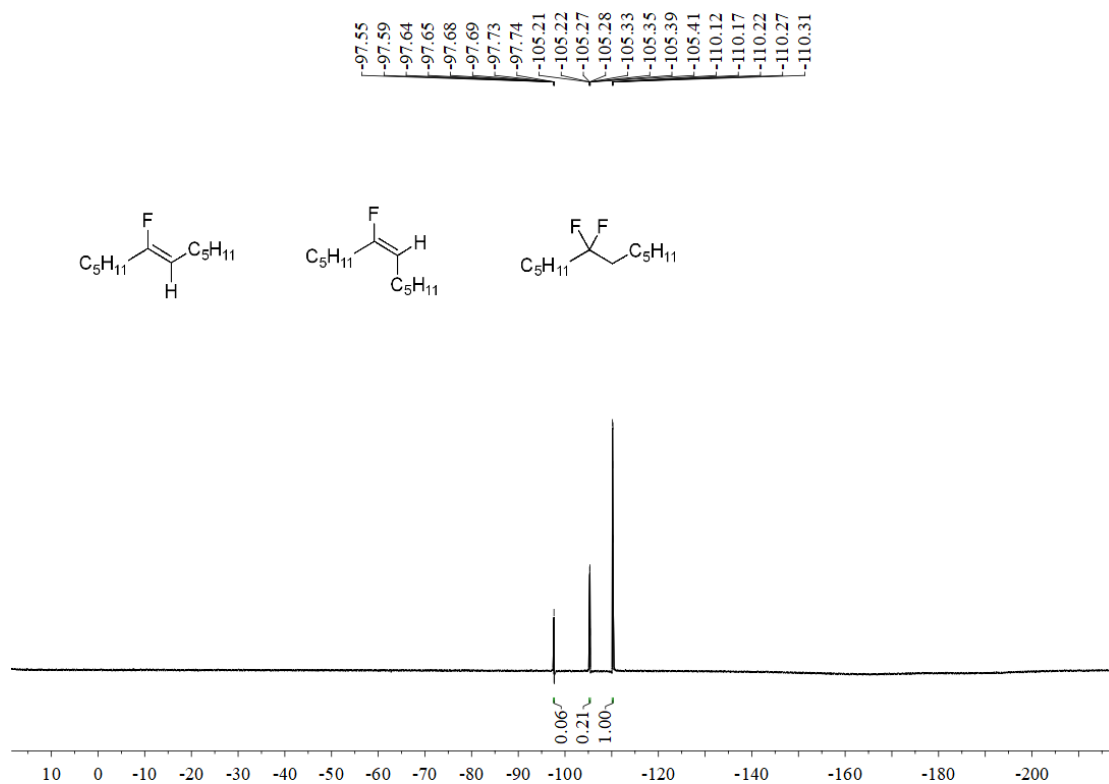
¹⁹F NMR (471 MHz, CDCl₃) (49)



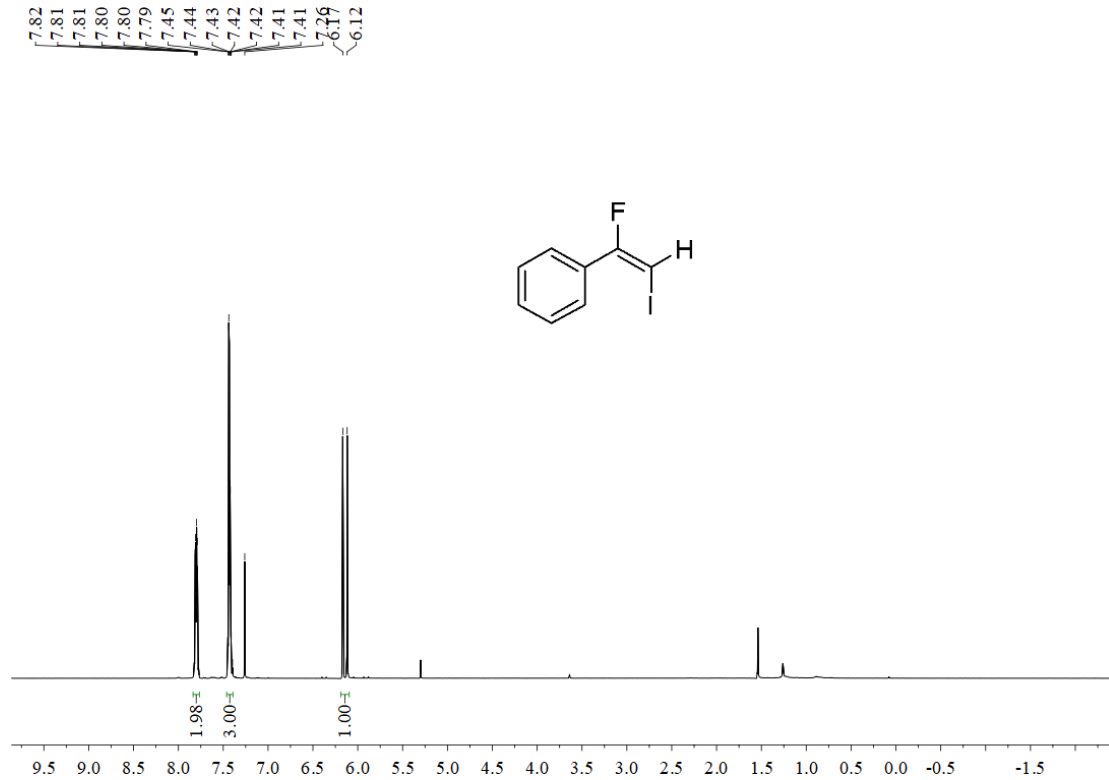
¹H NMR (400 MHz, CDCl₃) (50)



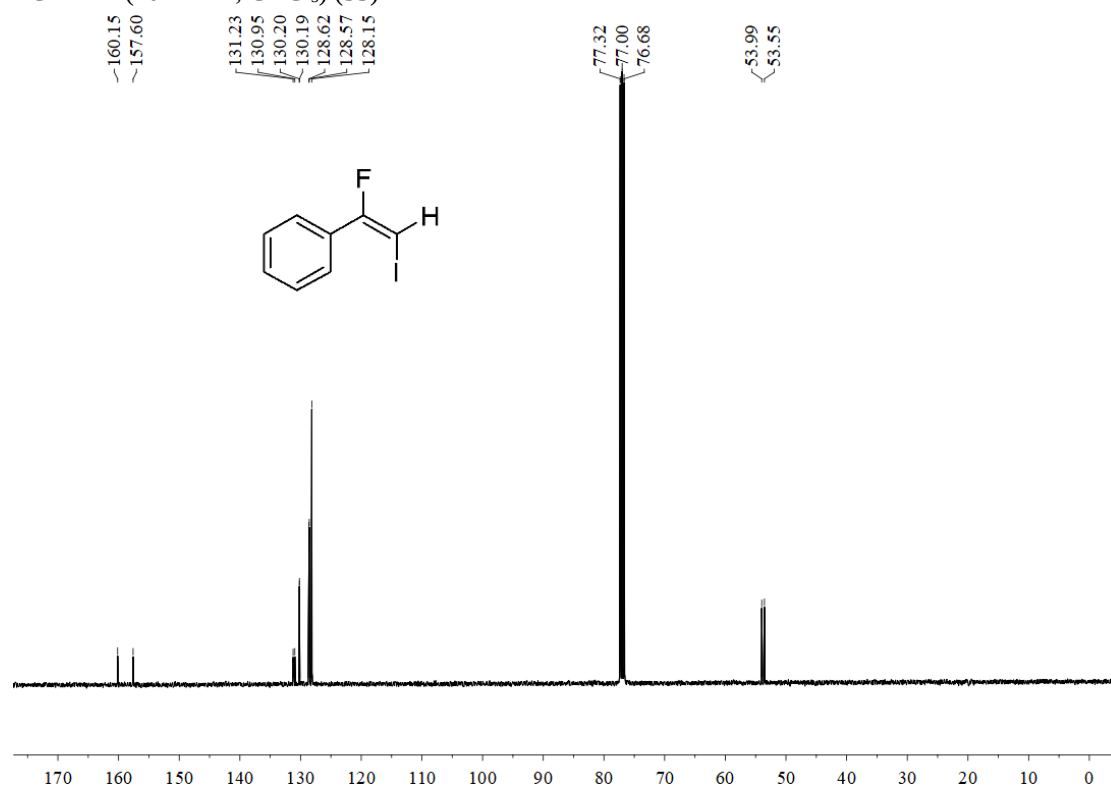
^{19}F NMR (376 MHz, CDCl_3) (50)



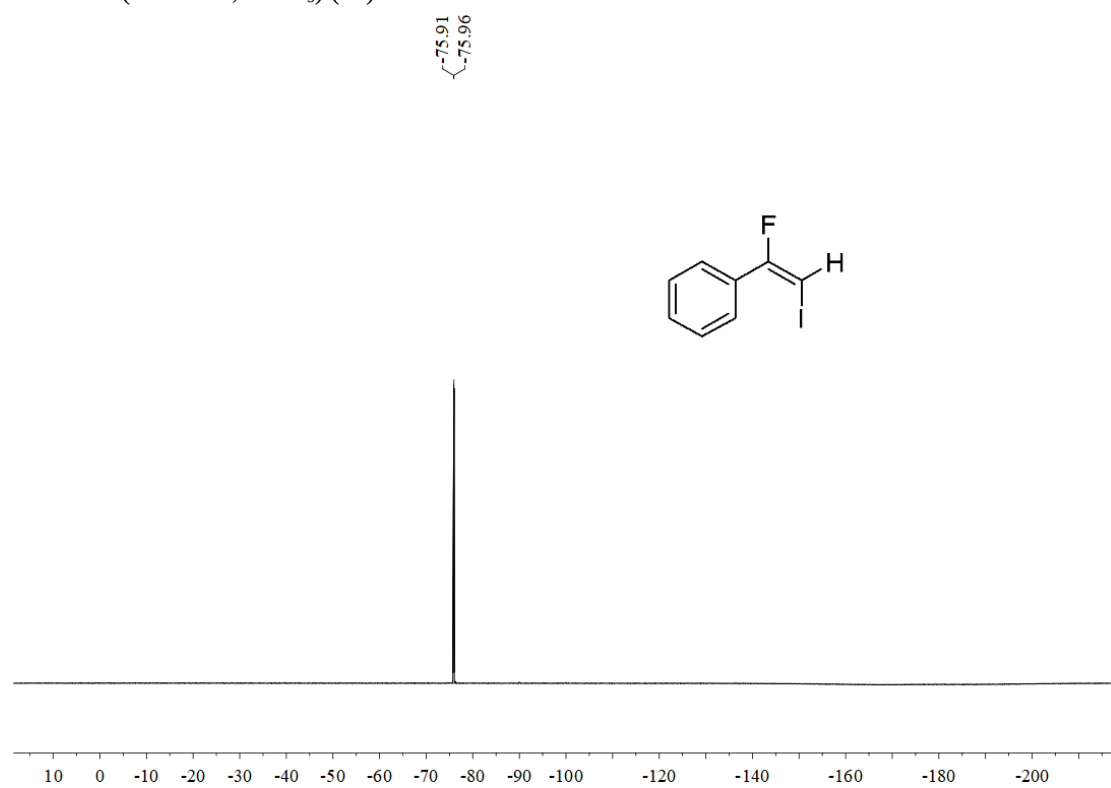
^1H NMR (400 MHz, CDCl_3) (53)



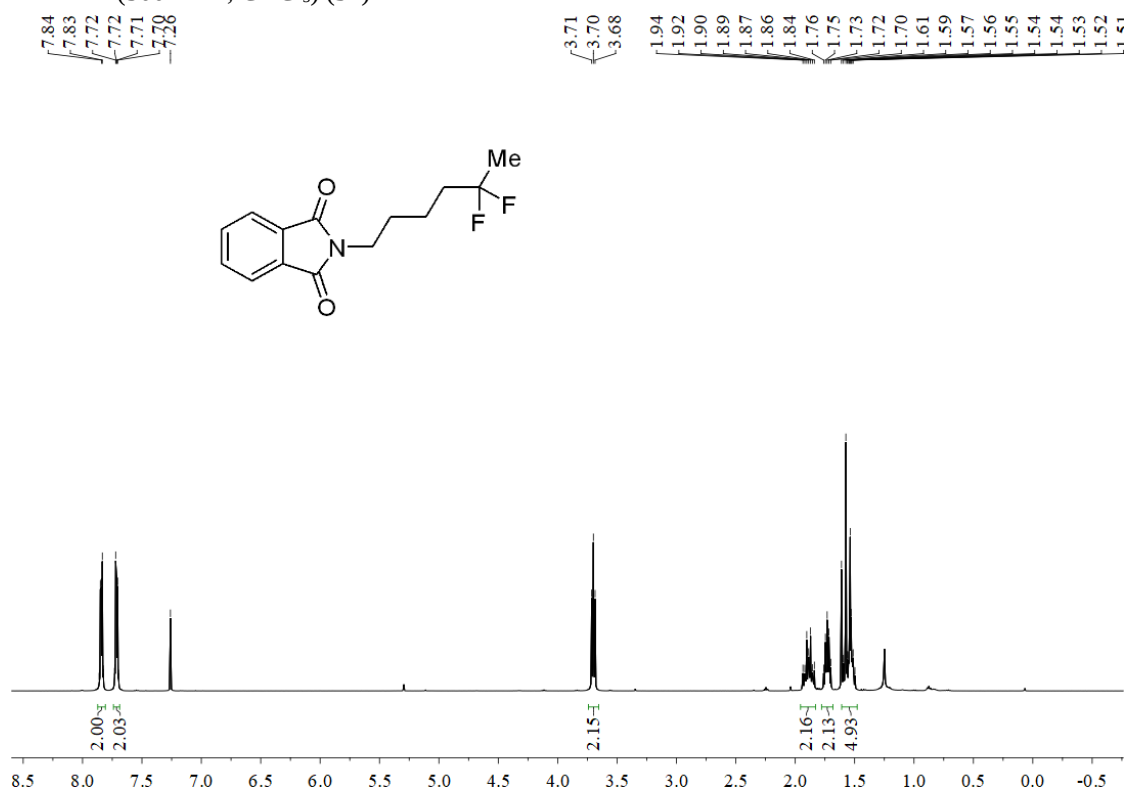
^{13}C NMR (101 MHz, CDCl_3) (53)



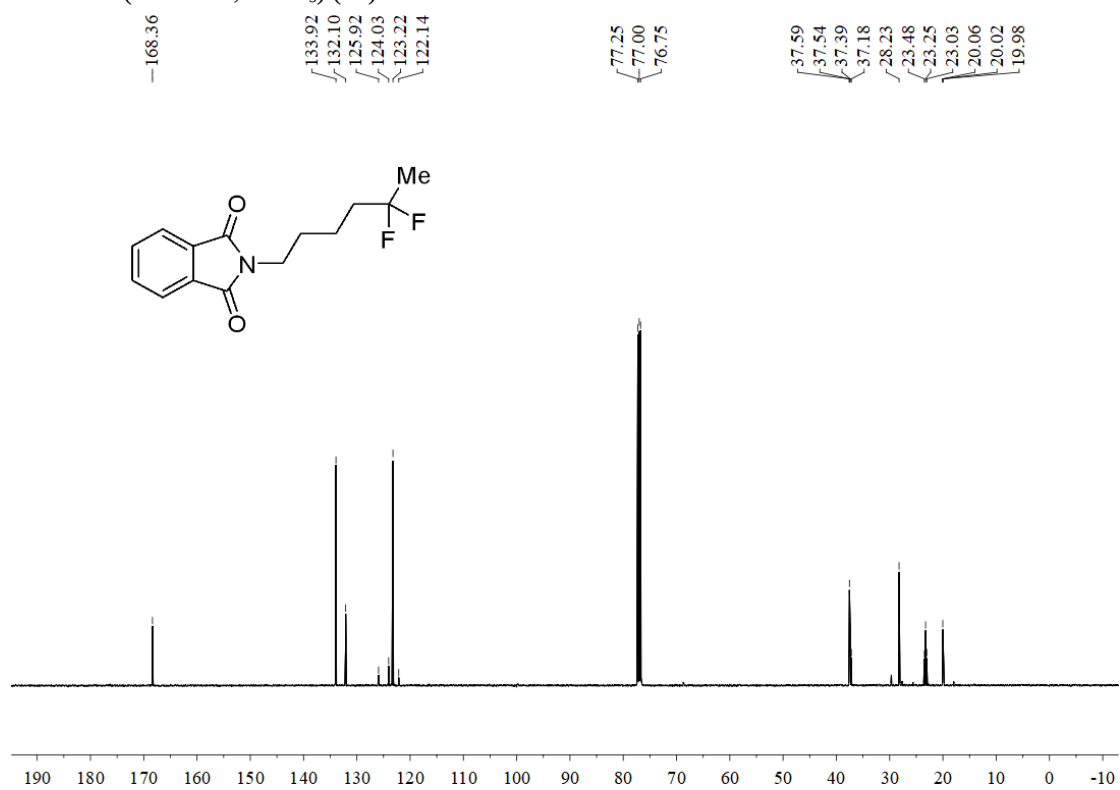
^{19}F NMR (376 MHz, CDCl_3) (53)



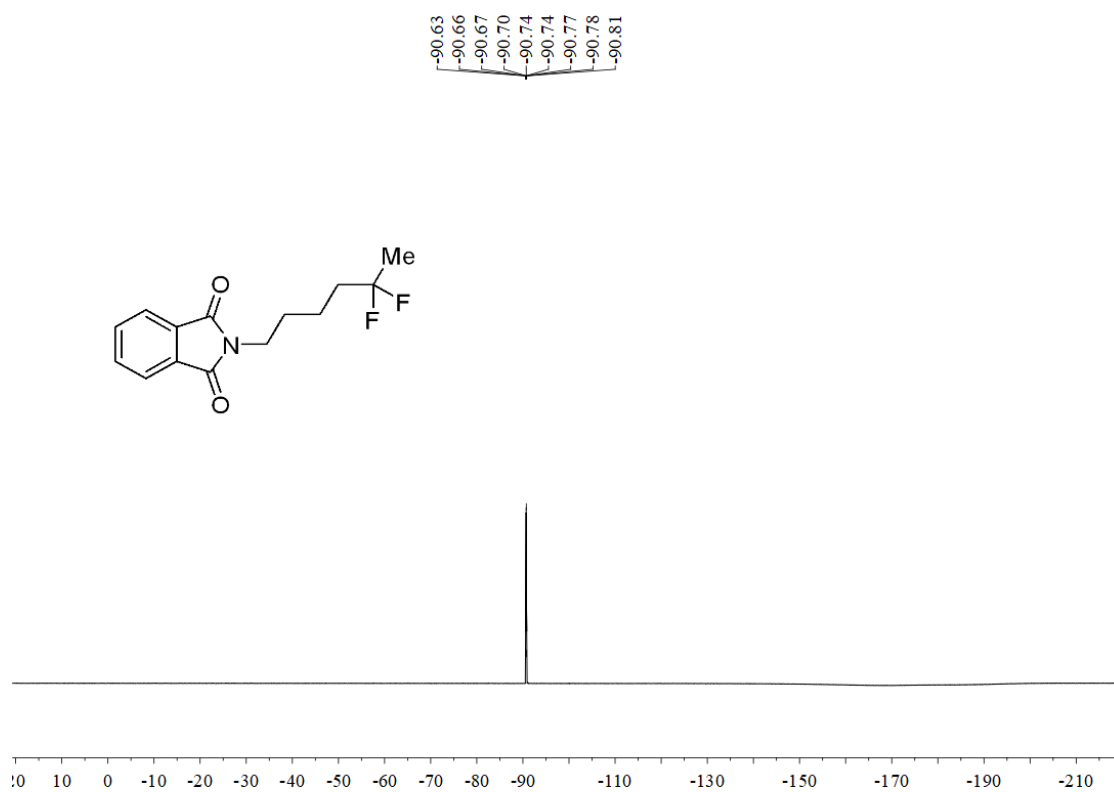
¹H NMR (500 MHz, CDCl₃) (57)



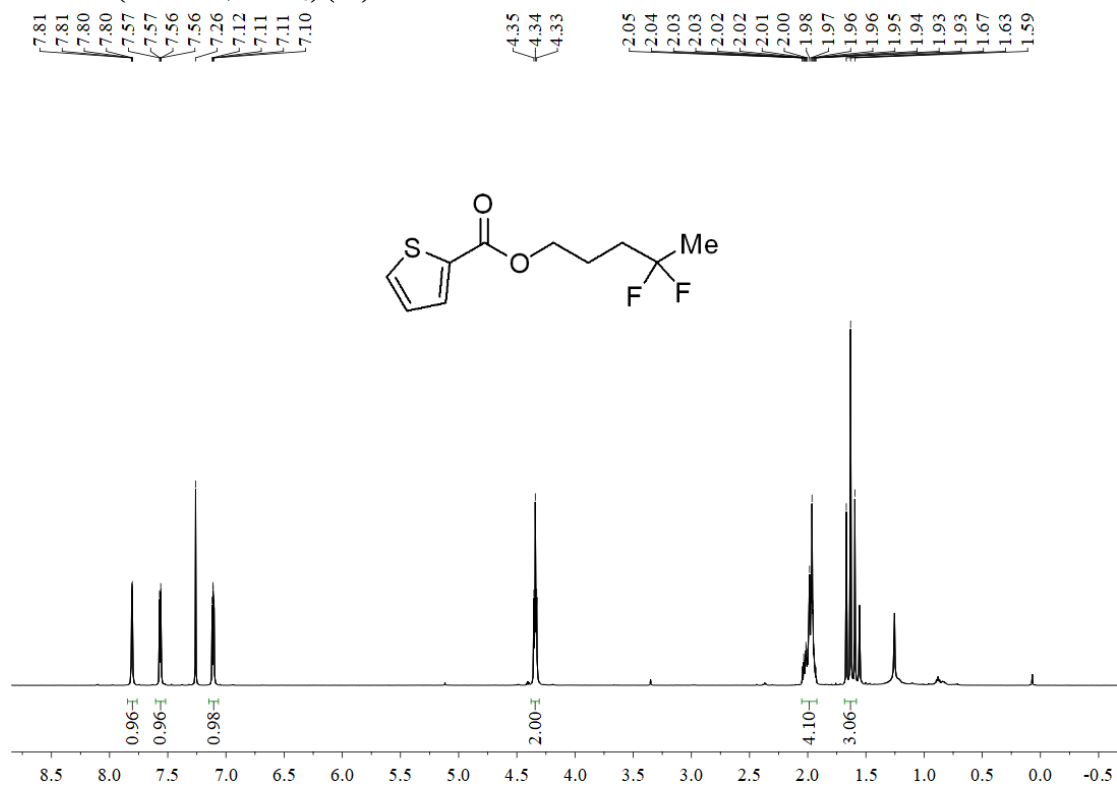
¹³C NMR (126 MHz, CDCl₃) (57)



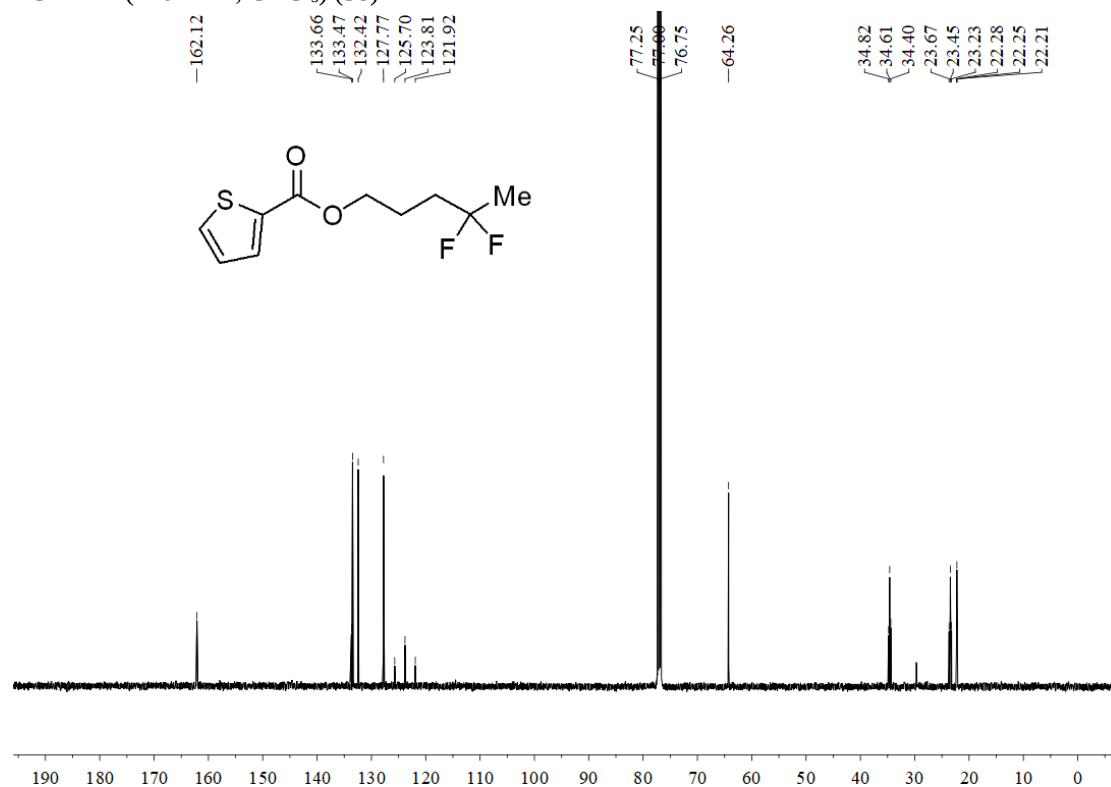
^{19}F NMR (471 MHz, CDCl_3) (57)



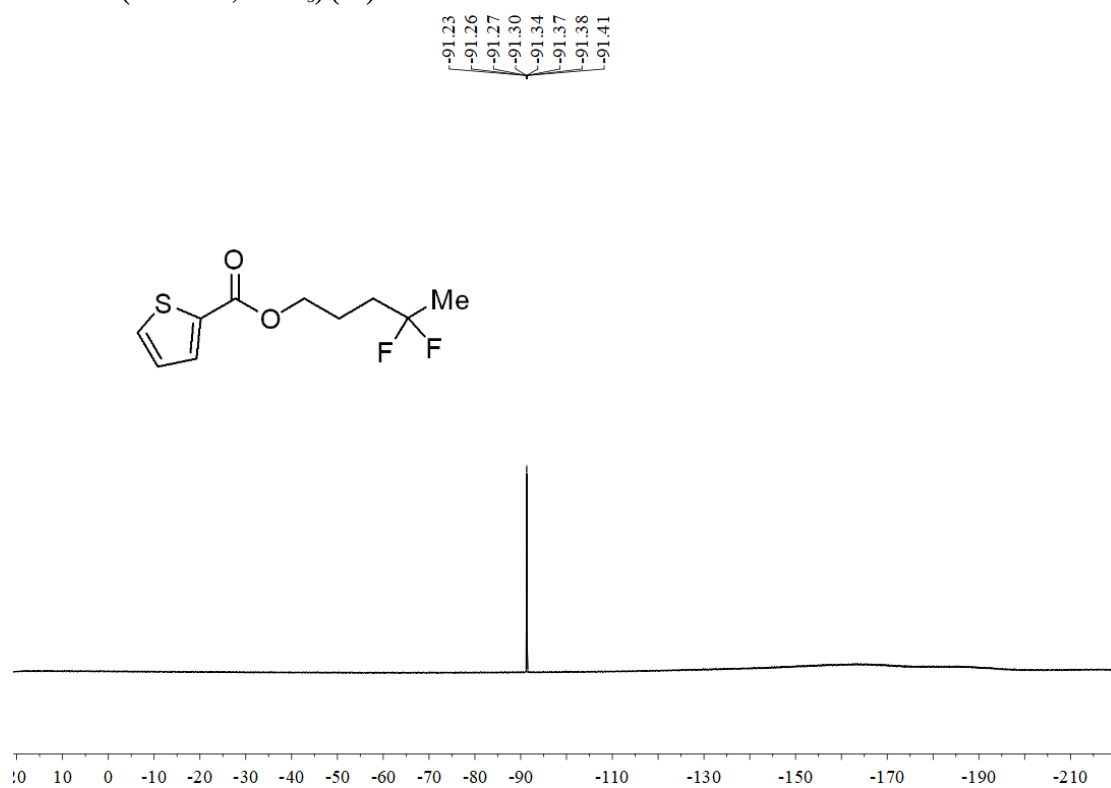
^1H NMR (500 MHz, CDCl_3) (58)



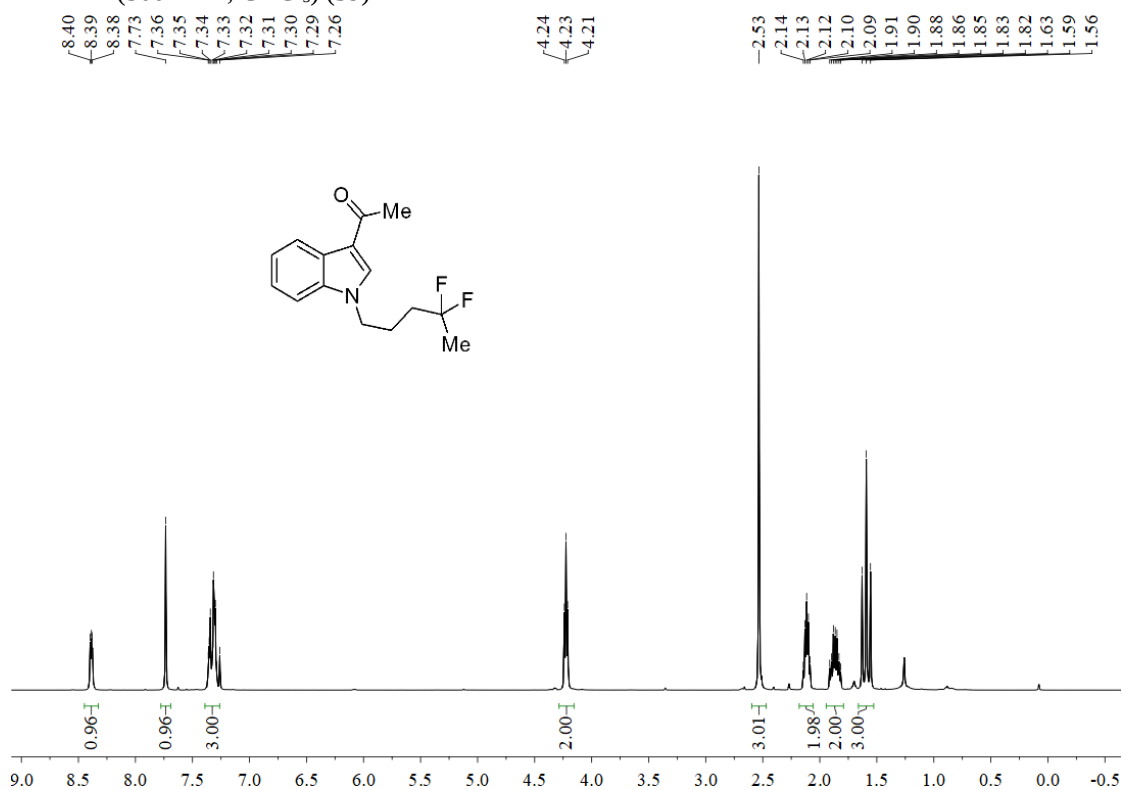
¹³C NMR (126 MHz, CDCl₃) (58)



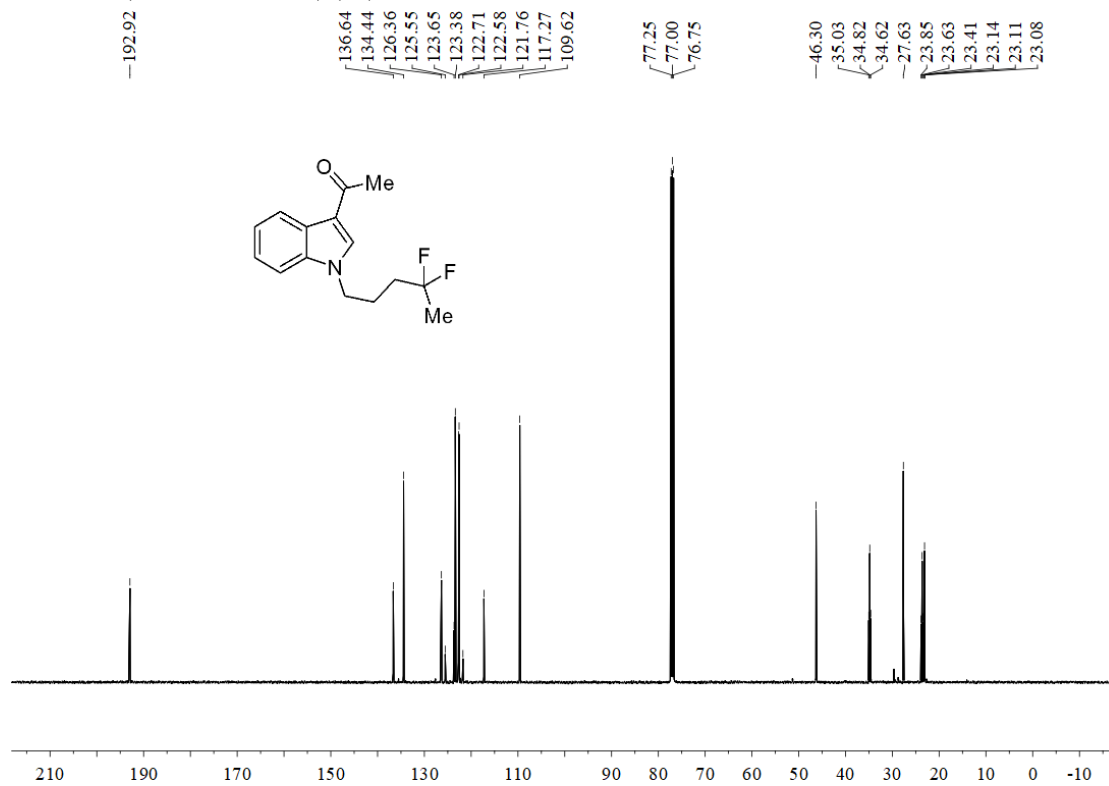
¹⁹F NMR (471 MHz, CDCl₃) (58)



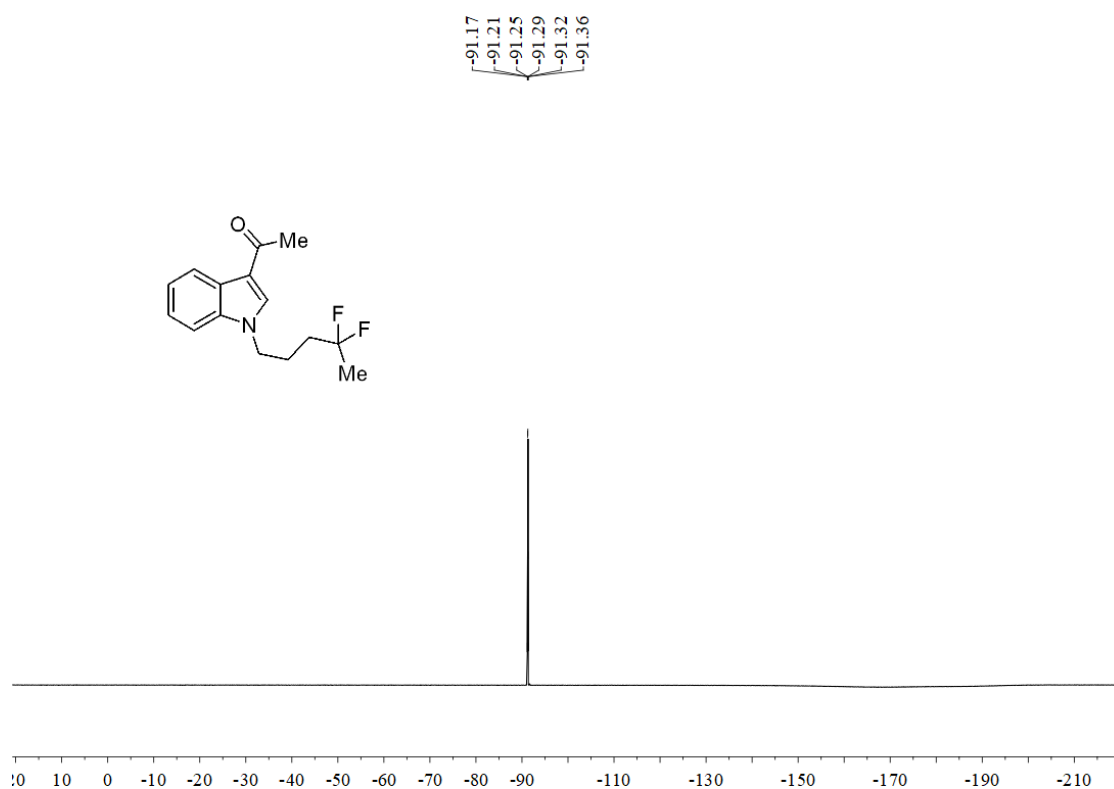
¹H NMR (500 MHz, CDCl₃) (59)



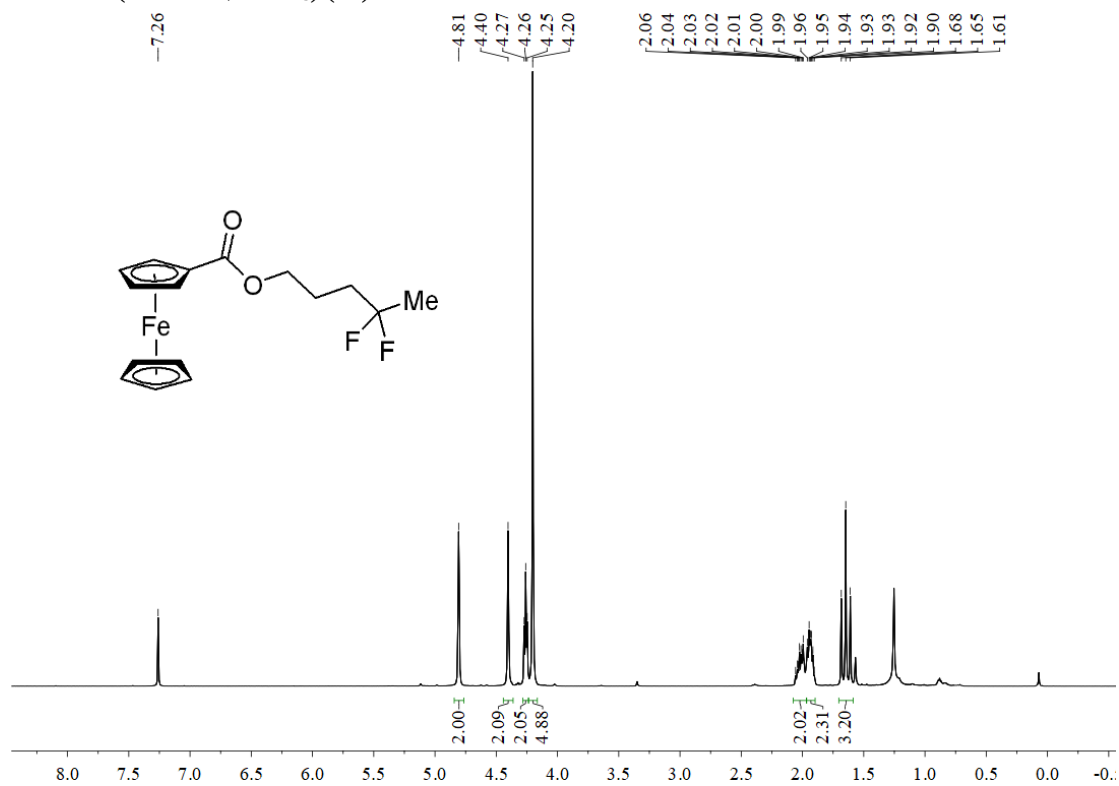
¹³C NMR (126 MHz, CDCl₃) (59)



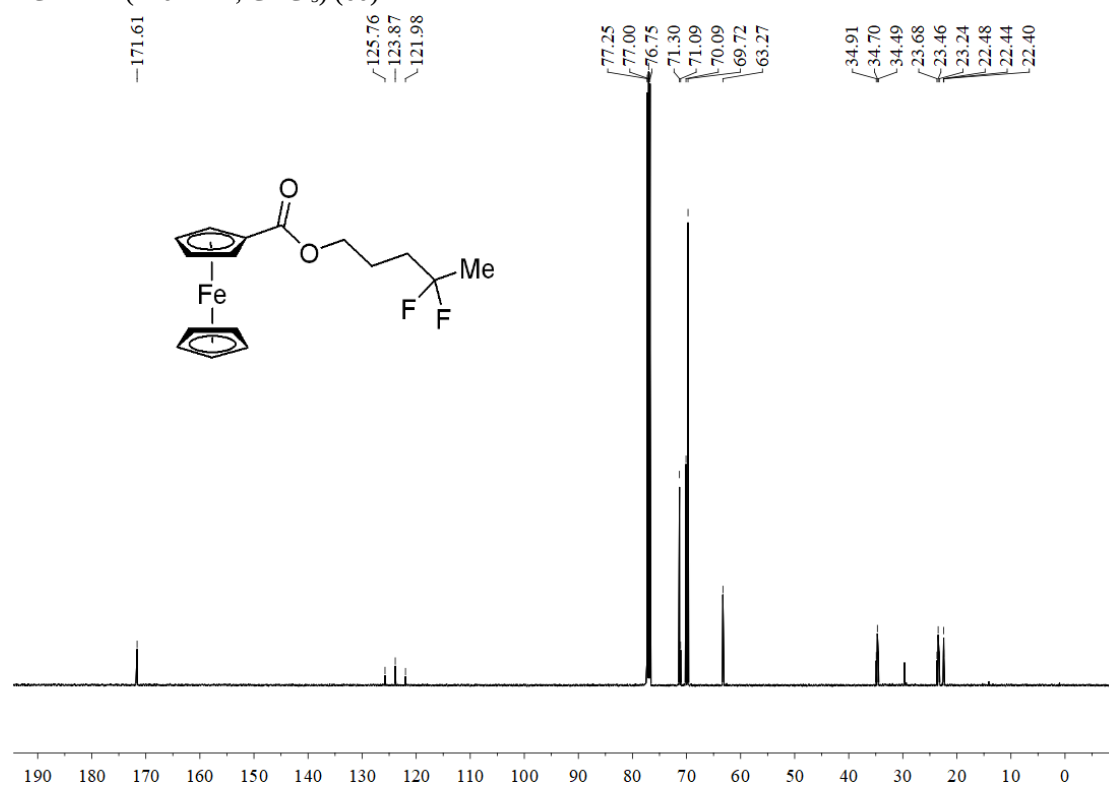
^{19}F NMR (471 MHz, CDCl_3) (59)



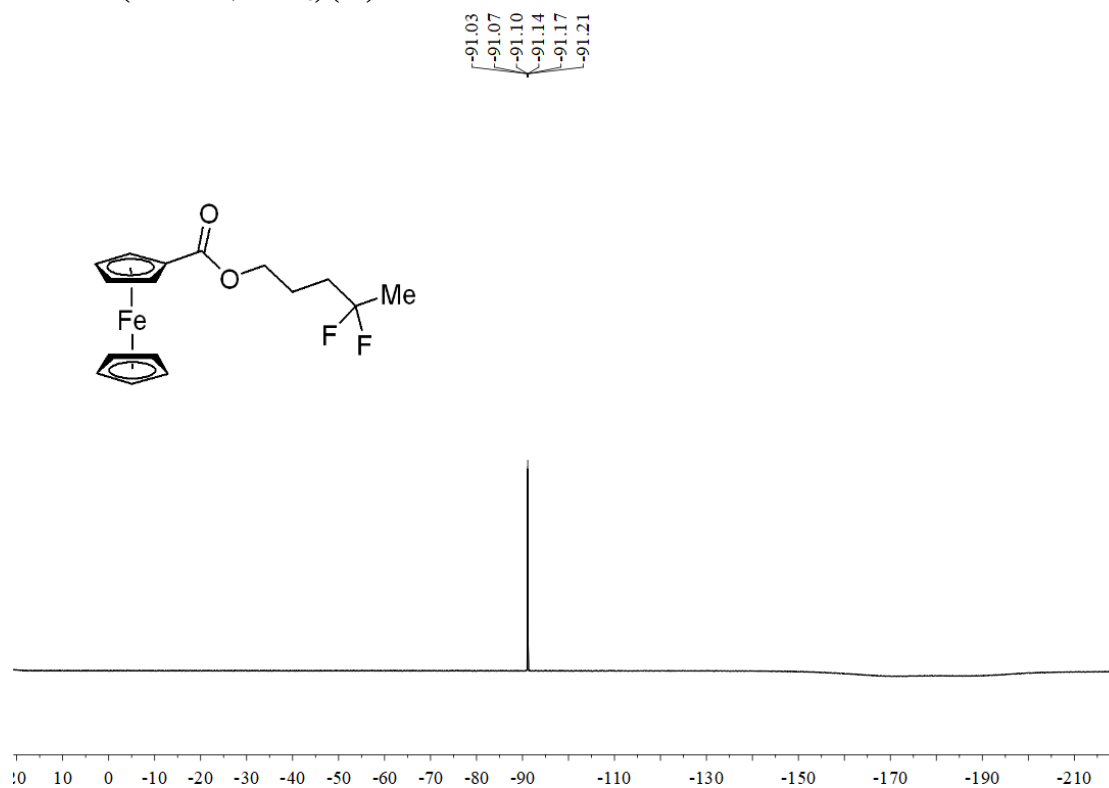
^1H NMR (500 MHz, CDCl_3) (60)



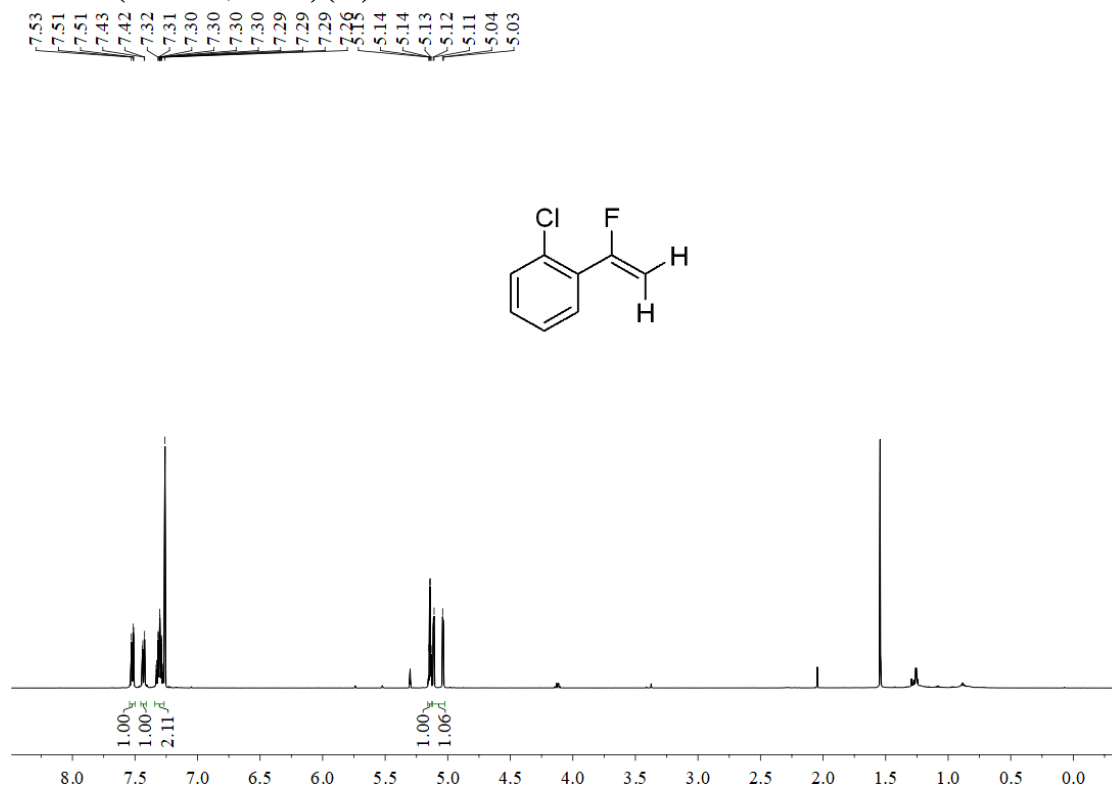
^{13}C NMR (126 MHz, CDCl_3) (60)



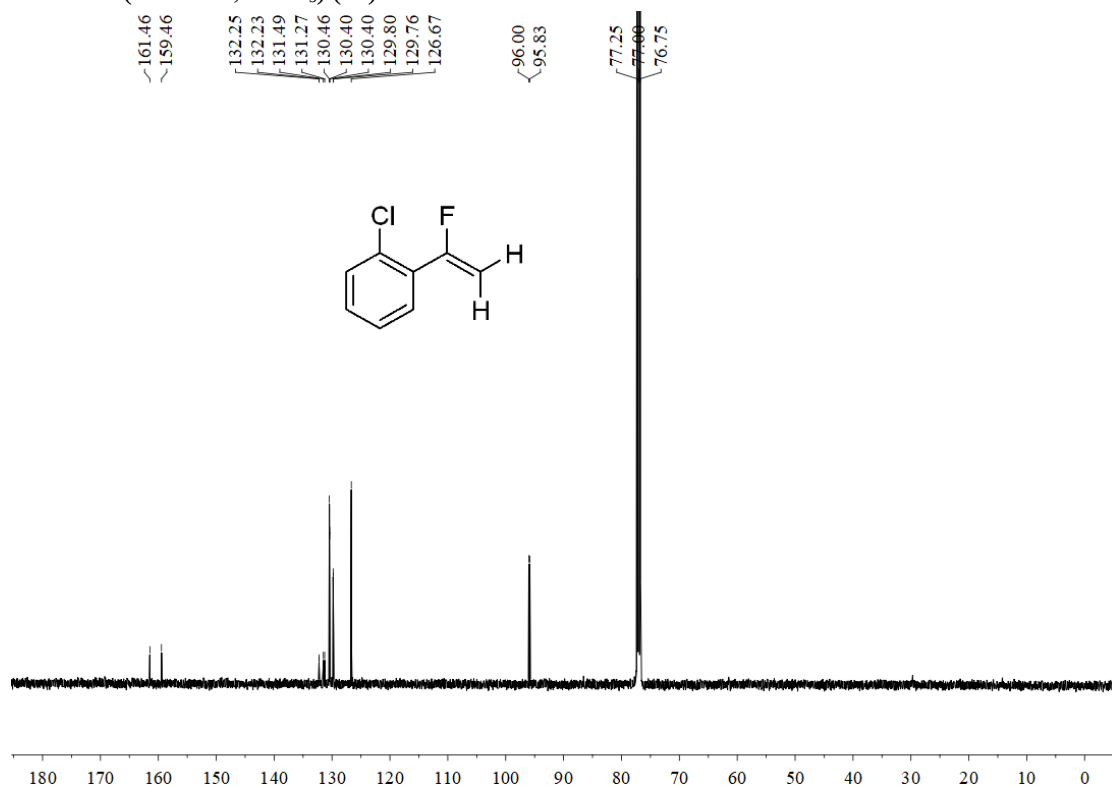
^{19}F NMR (471 MHz, CDCl_3) (60)



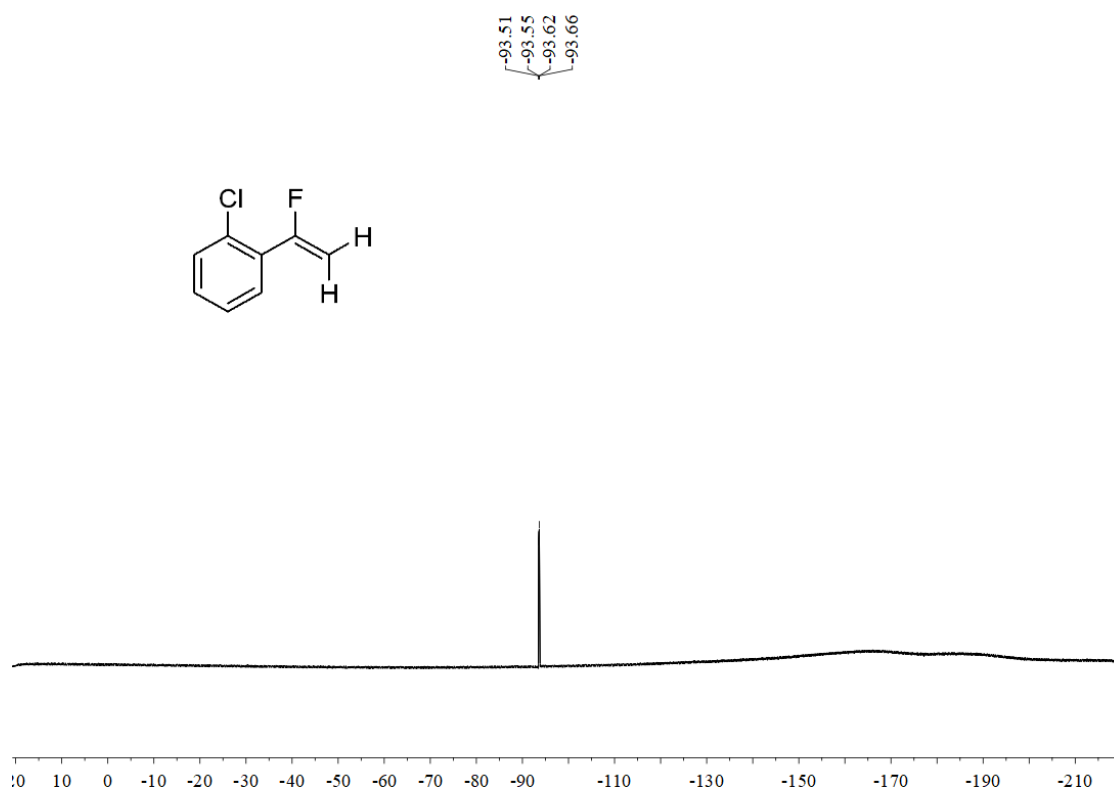
¹H NMR (500 MHz, CDCl₃) (64)



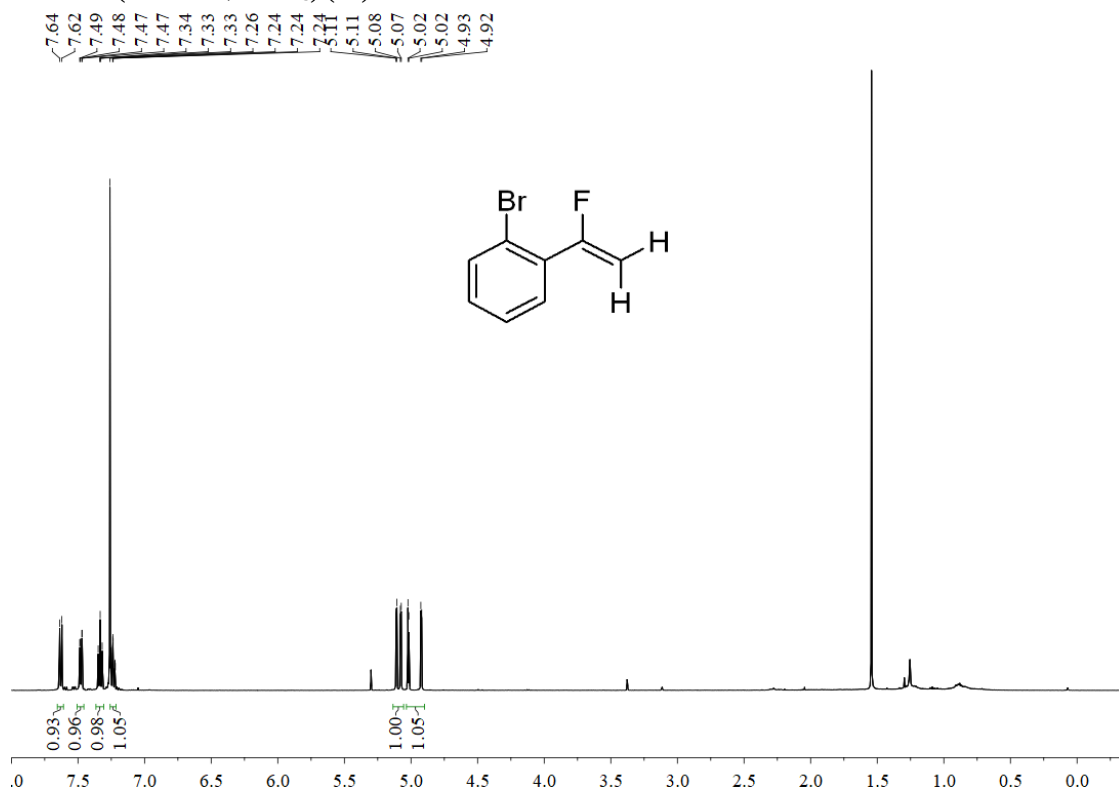
¹³C NMR (126 MHz, CDCl₃) (64)



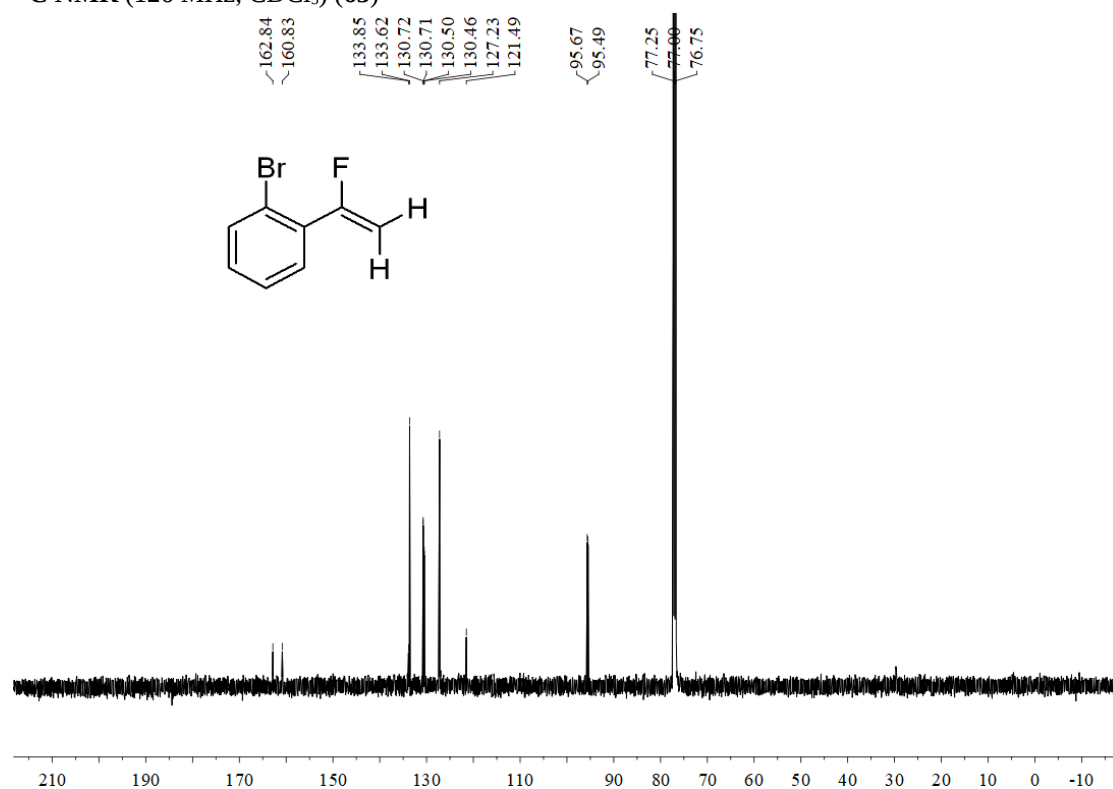
^{19}F NMR (471 MHz, CDCl_3) (**64**)



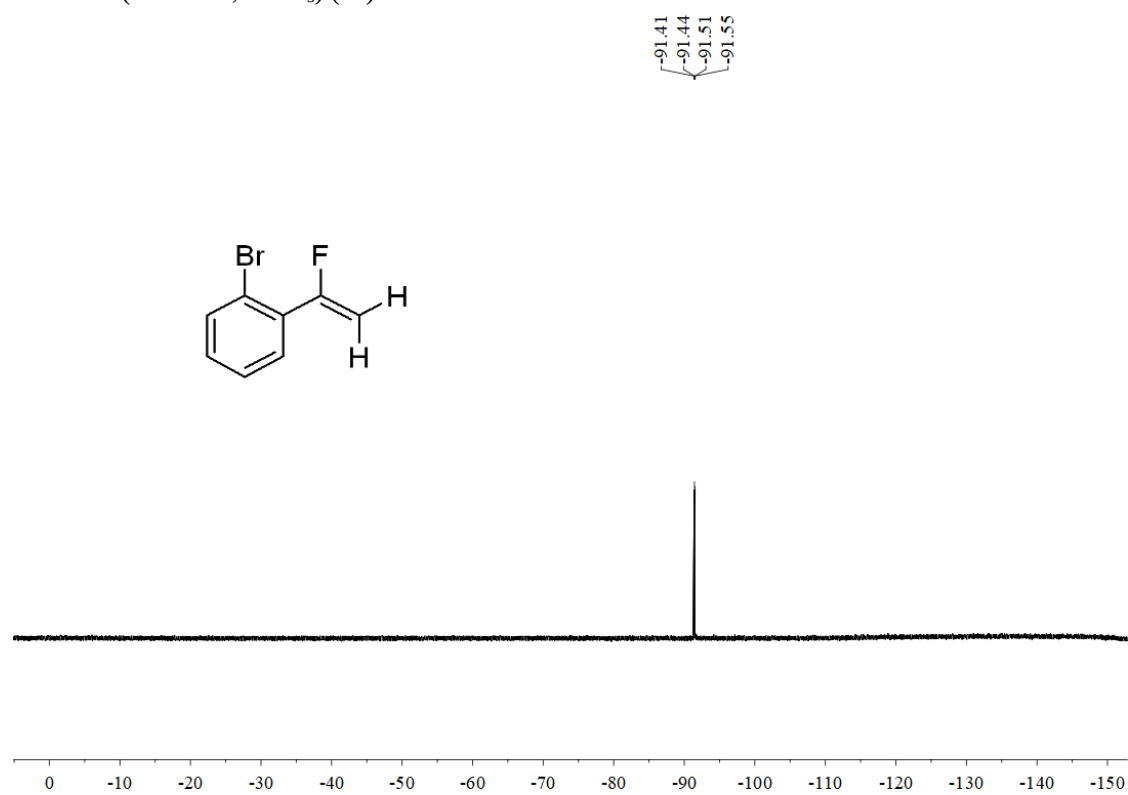
^1H NMR (500 MHz, CDCl_3) (**65**)



¹³C NMR (126 MHz, CDCl₃) (65)

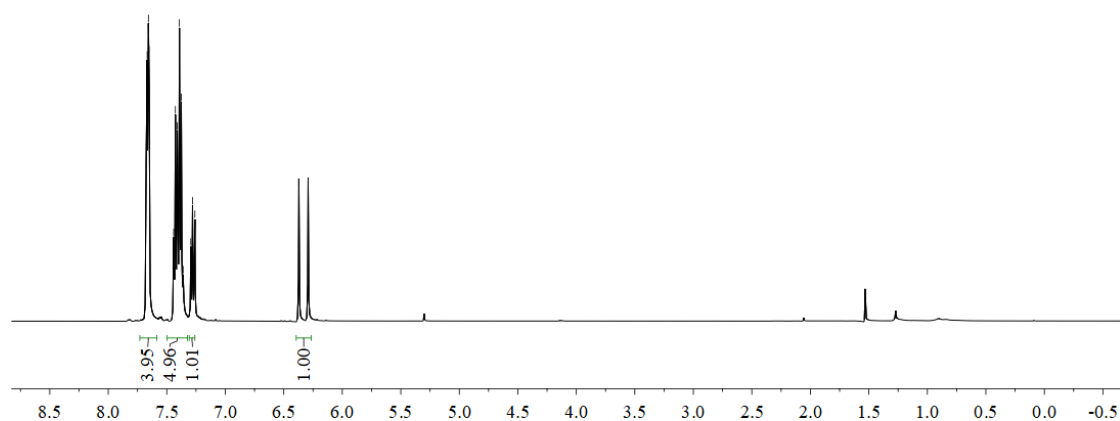
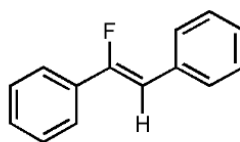


¹⁹F NMR (471 MHz, CDCl₃) (65)



¹H NMR (500 MHz, CDCl₃) (71)

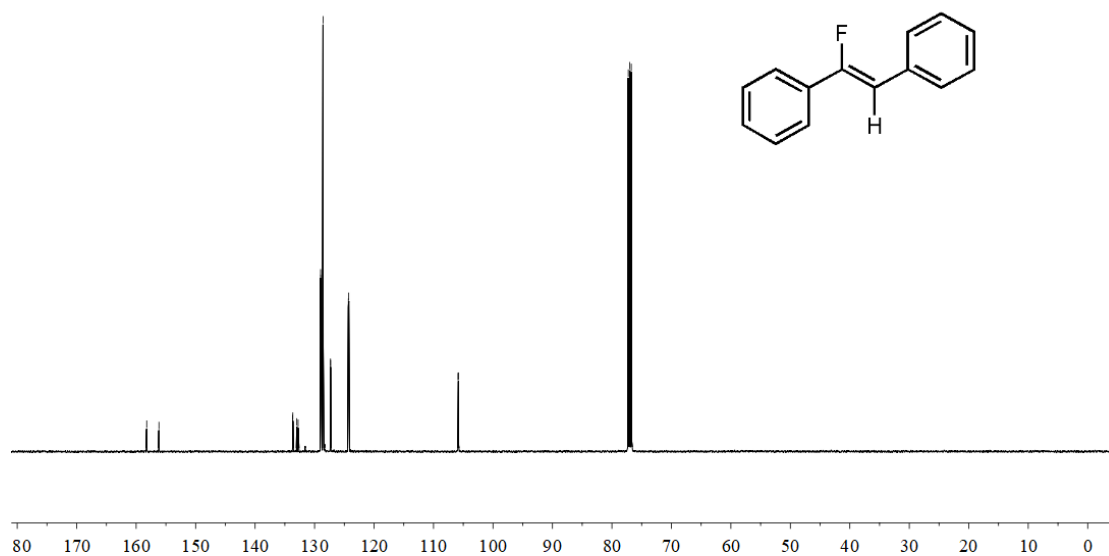
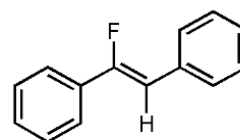
7.67
7.67
7.66
7.65
7.44
7.43
7.41
7.39
7.38
7.36
7.29
7.28
7.26
7.26



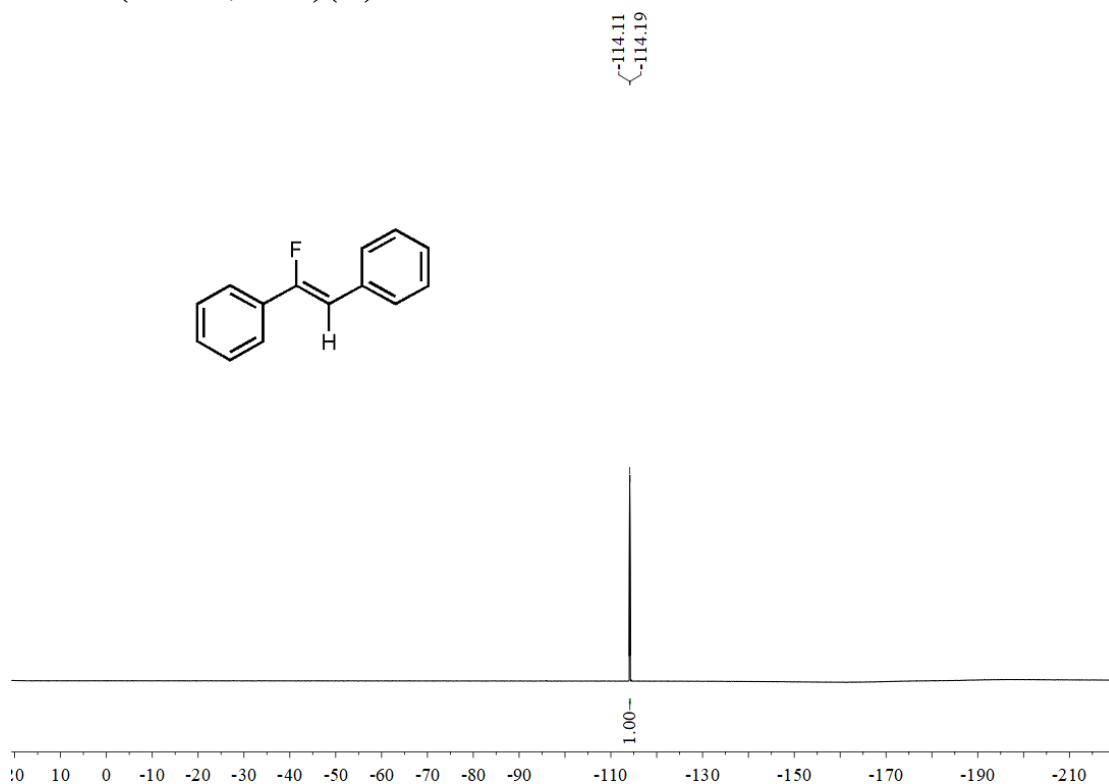
¹³C NMR (126 MHz, CDCl₃) (71)

158.23
156.17
133.68
133.66
128.98
128.97
128.90
128.59
128.57
127.32
127.30
124.32
104.89
105.81

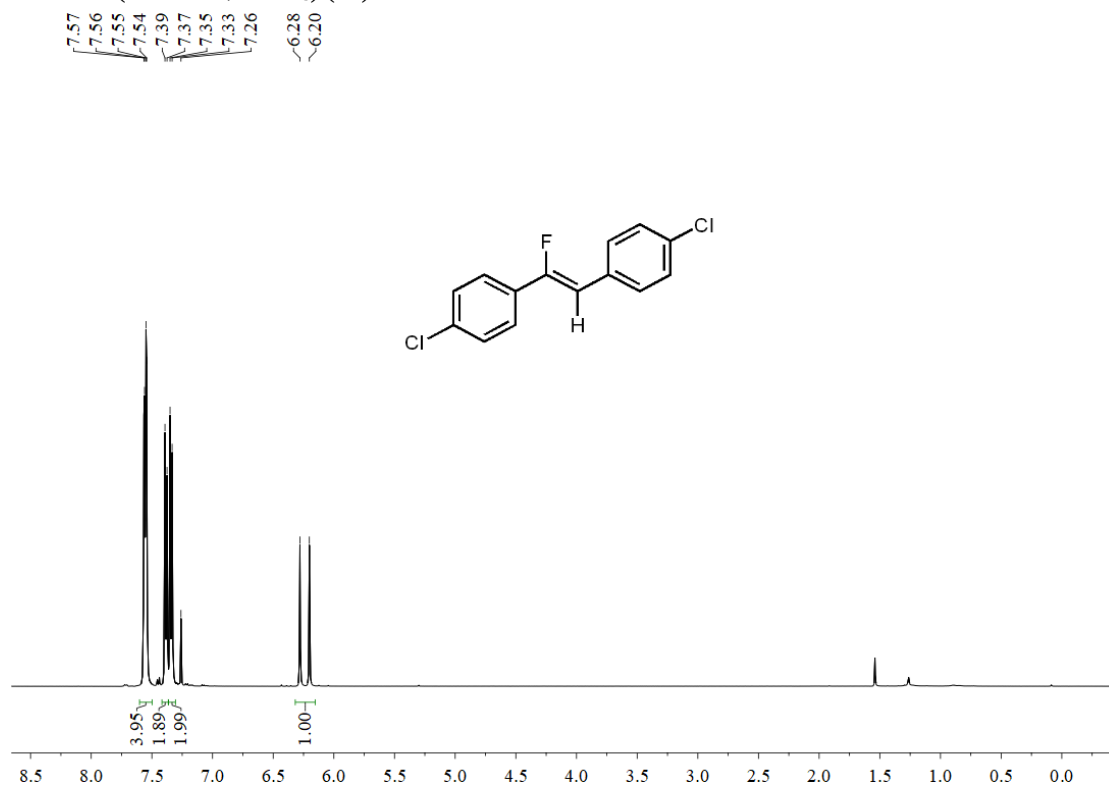
77.25
77.00
76.75



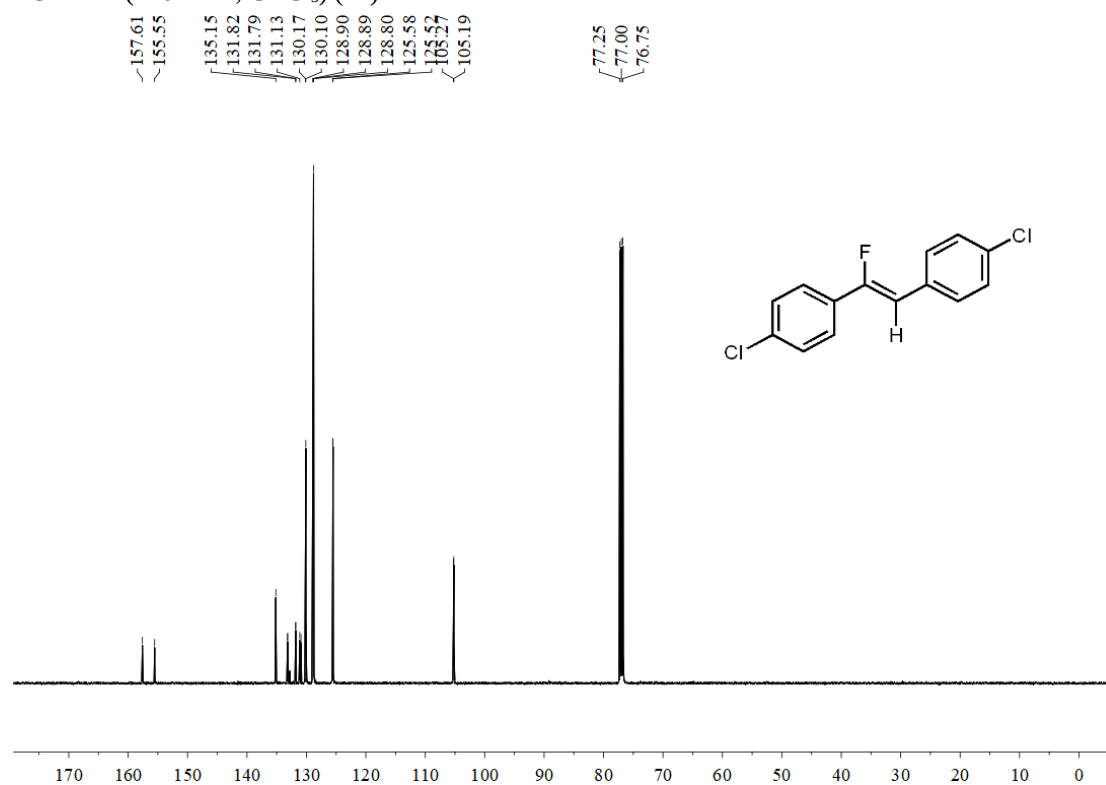
^{19}F NMR (471 MHz, CDCl_3) (71)



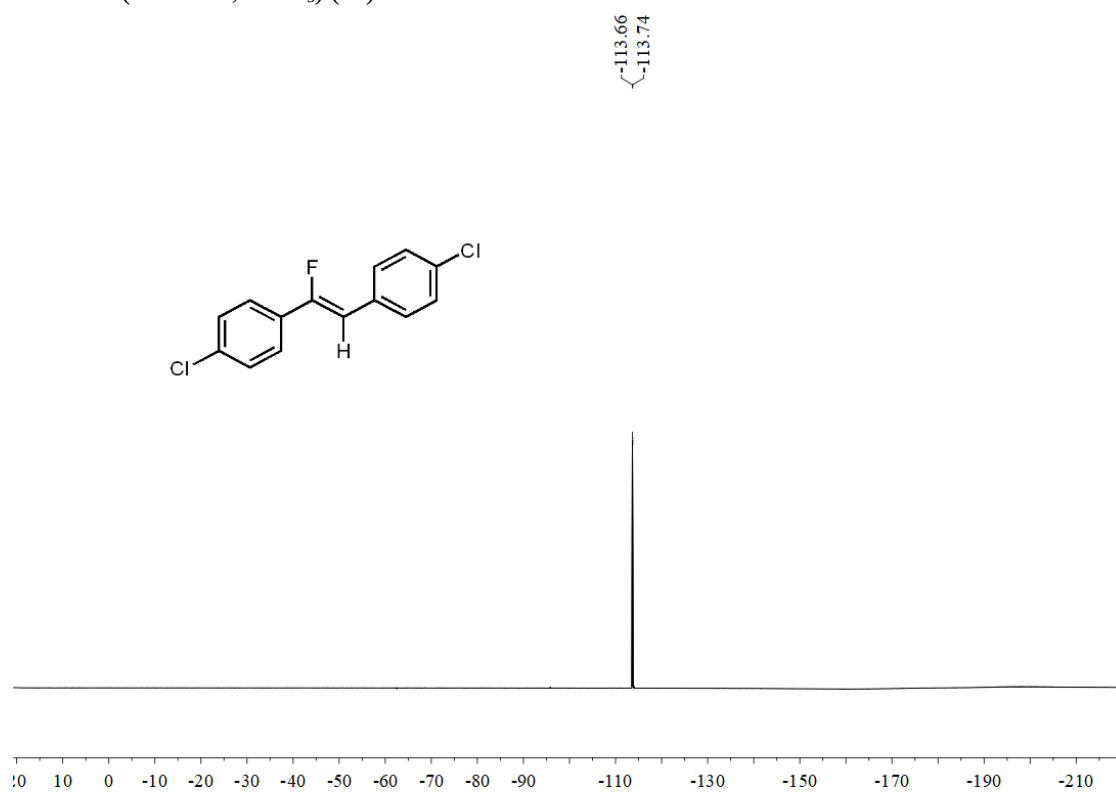
^1H NMR (500 MHz, CDCl_3) (72)



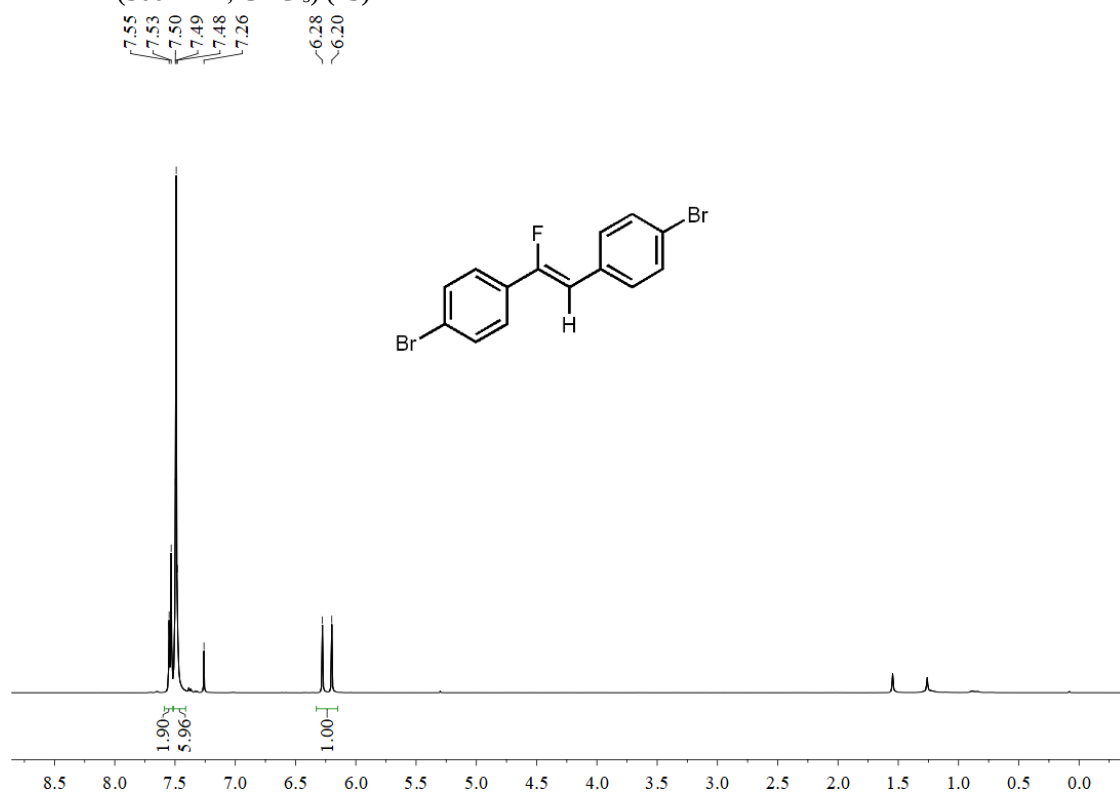
^{13}C NMR (126 MHz, CDCl_3) (72)



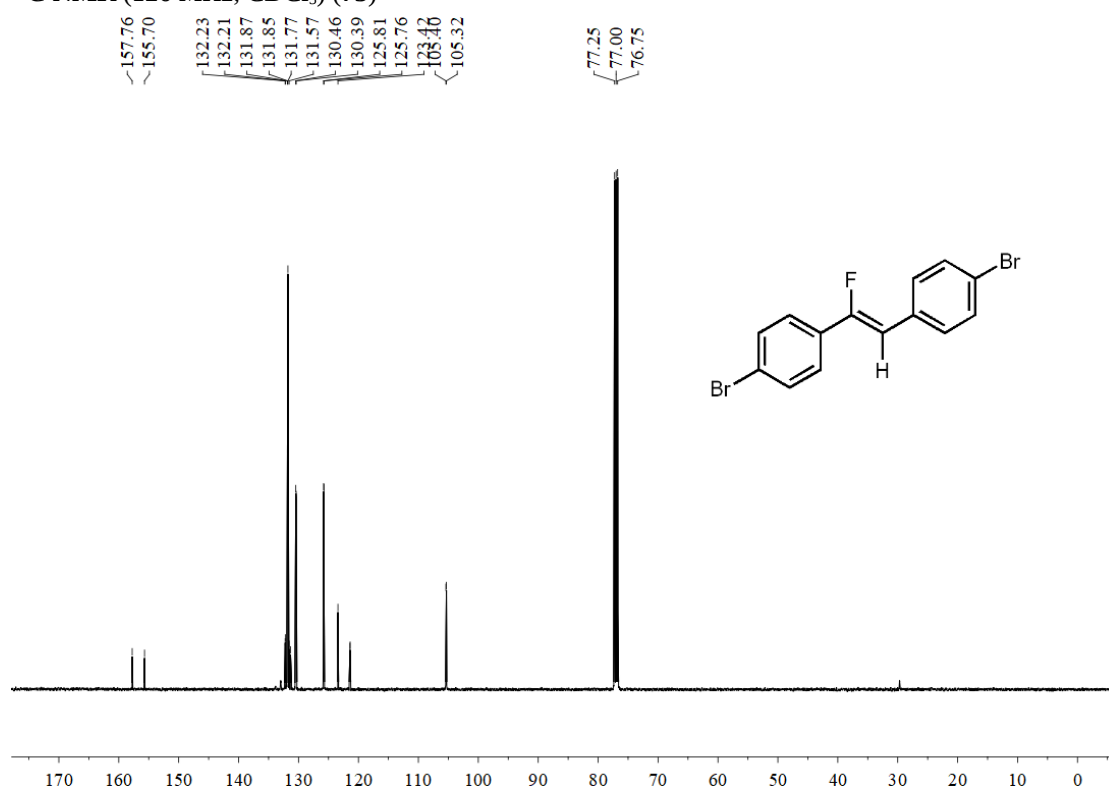
^{19}F NMR (471 MHz, CDCl_3) (72)



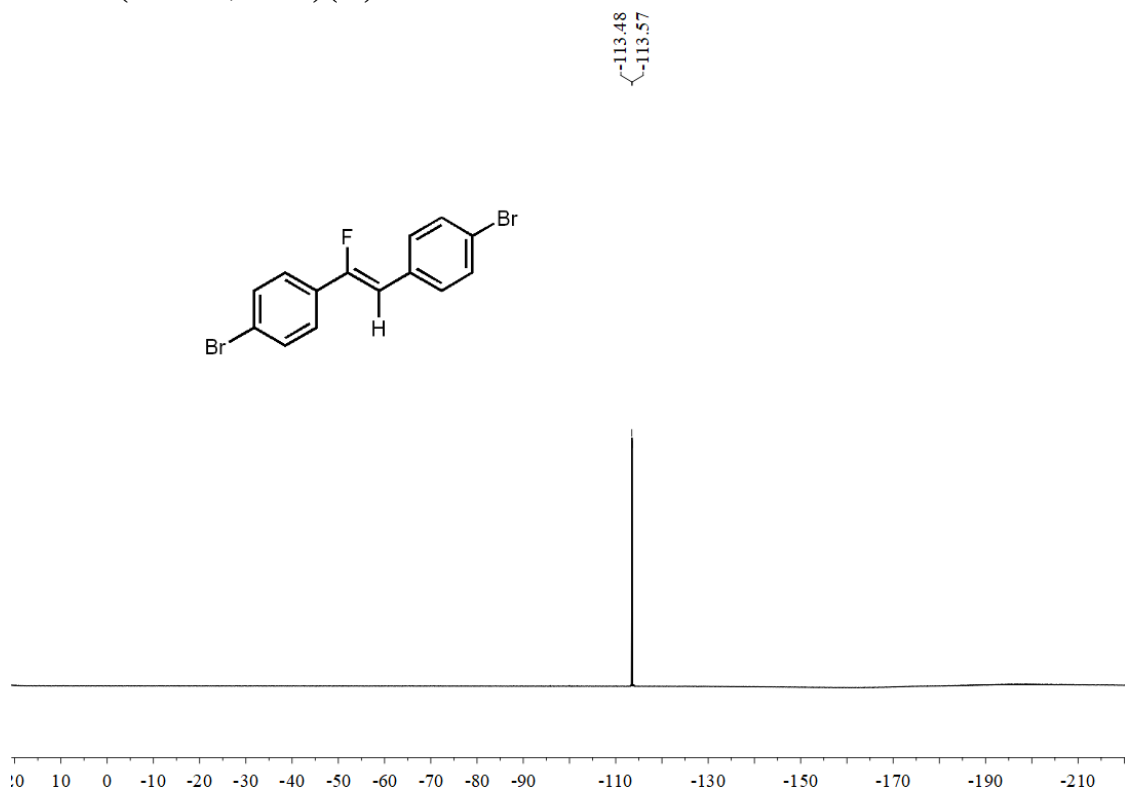
¹H NMR (500 MHz, CDCl₃) (73)



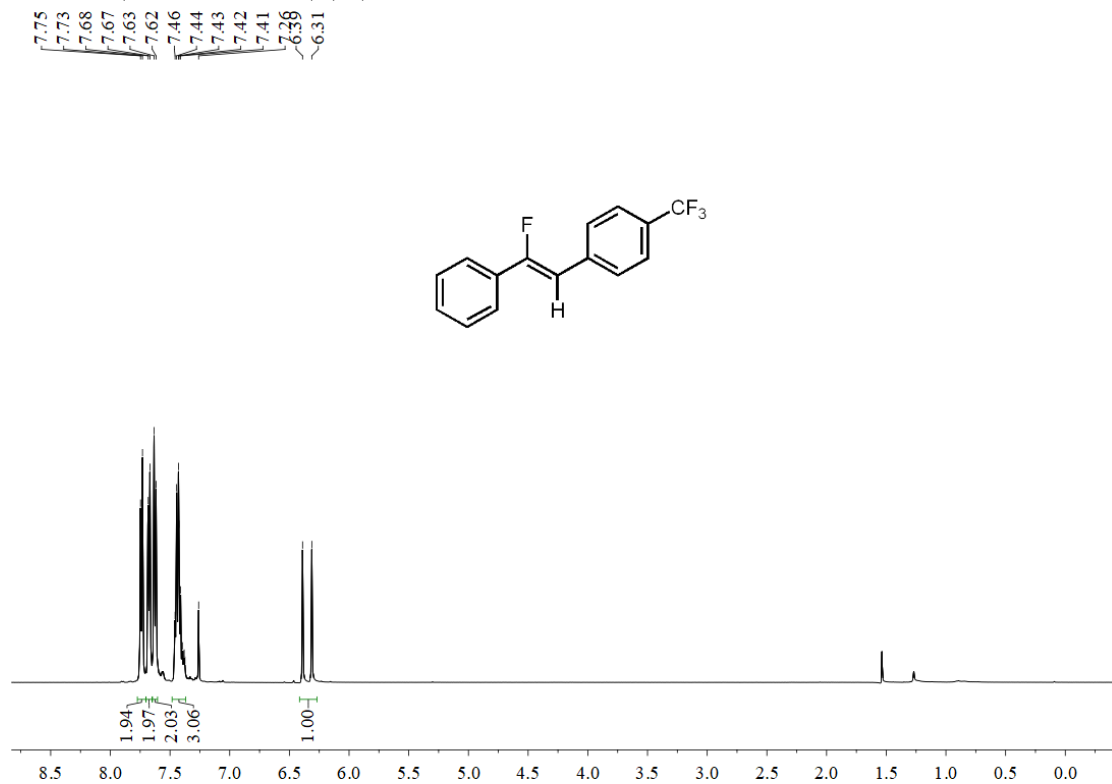
¹³C NMR (126 MHz, CDCl₃) (73)



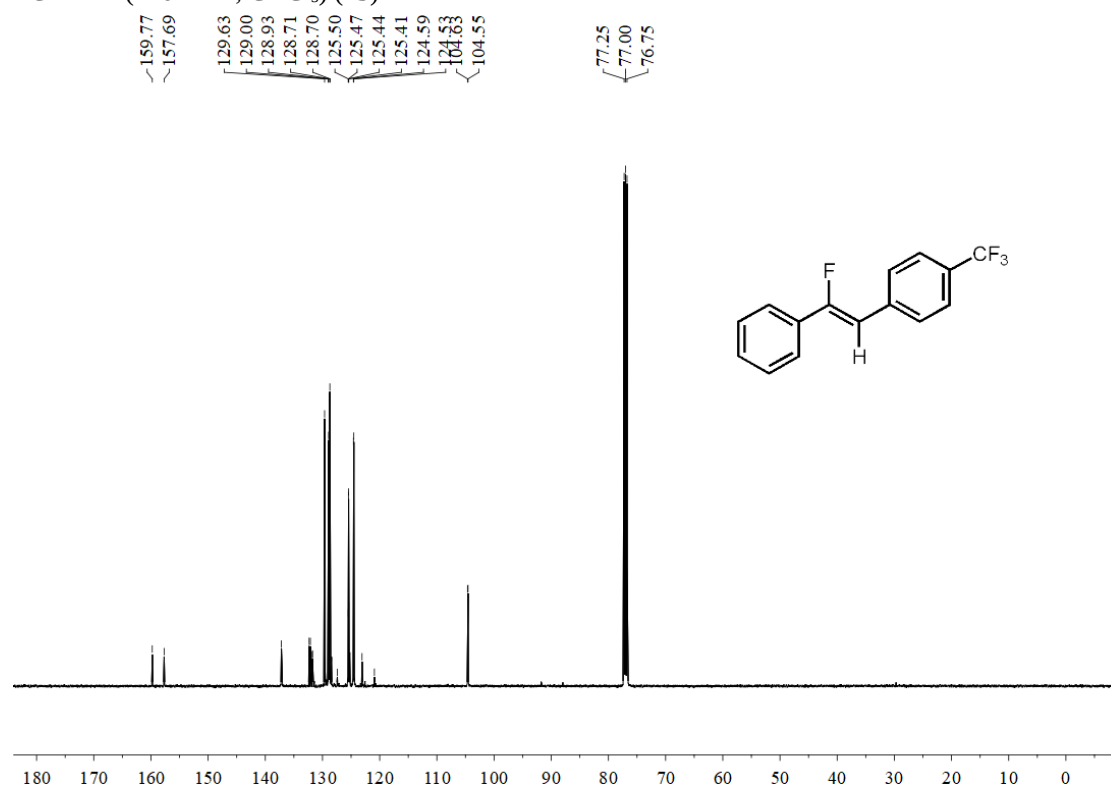
^{19}F NMR (471 MHz, CDCl_3) (73)



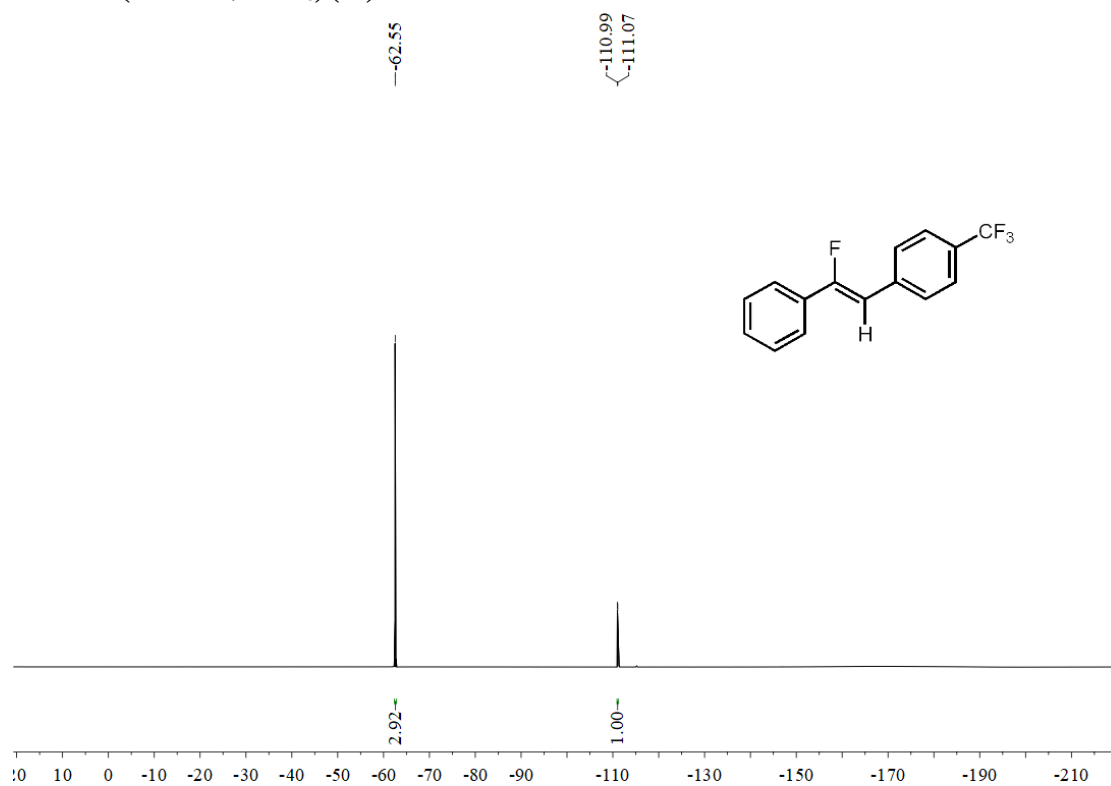
^1H NMR (500 MHz, CDCl_3) (75)



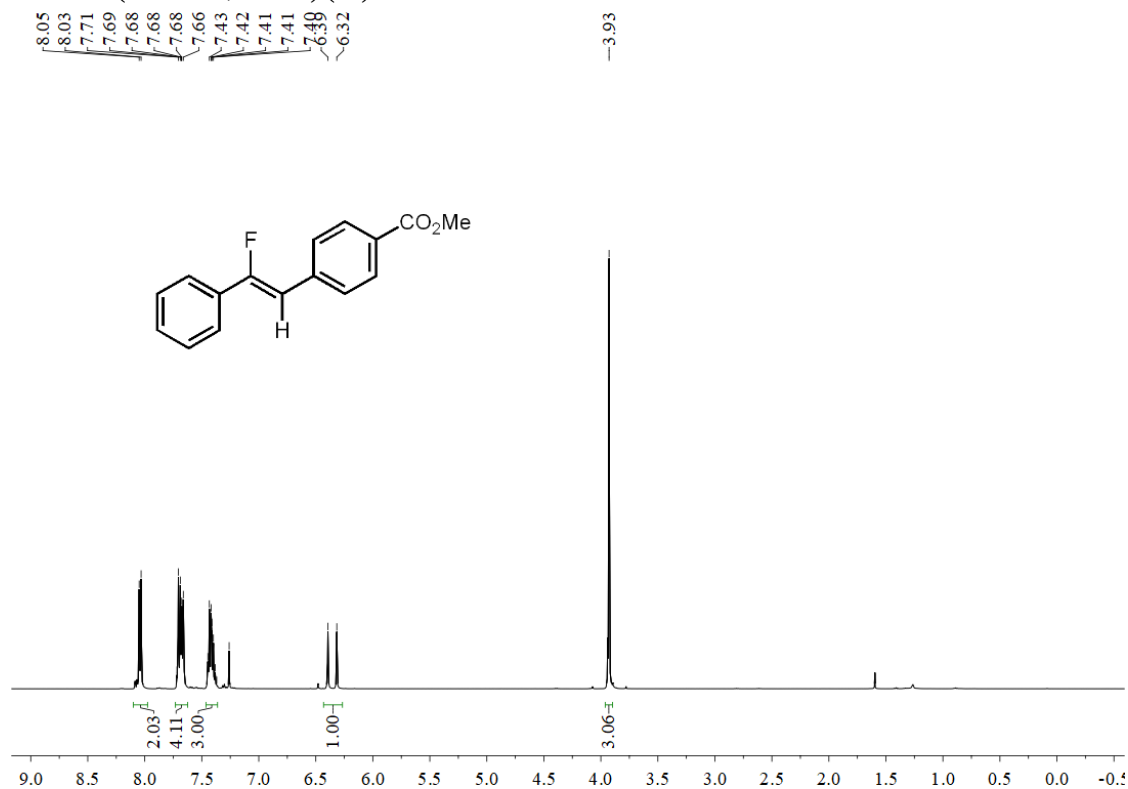
^{13}C NMR (126 MHz, CDCl_3) (75)



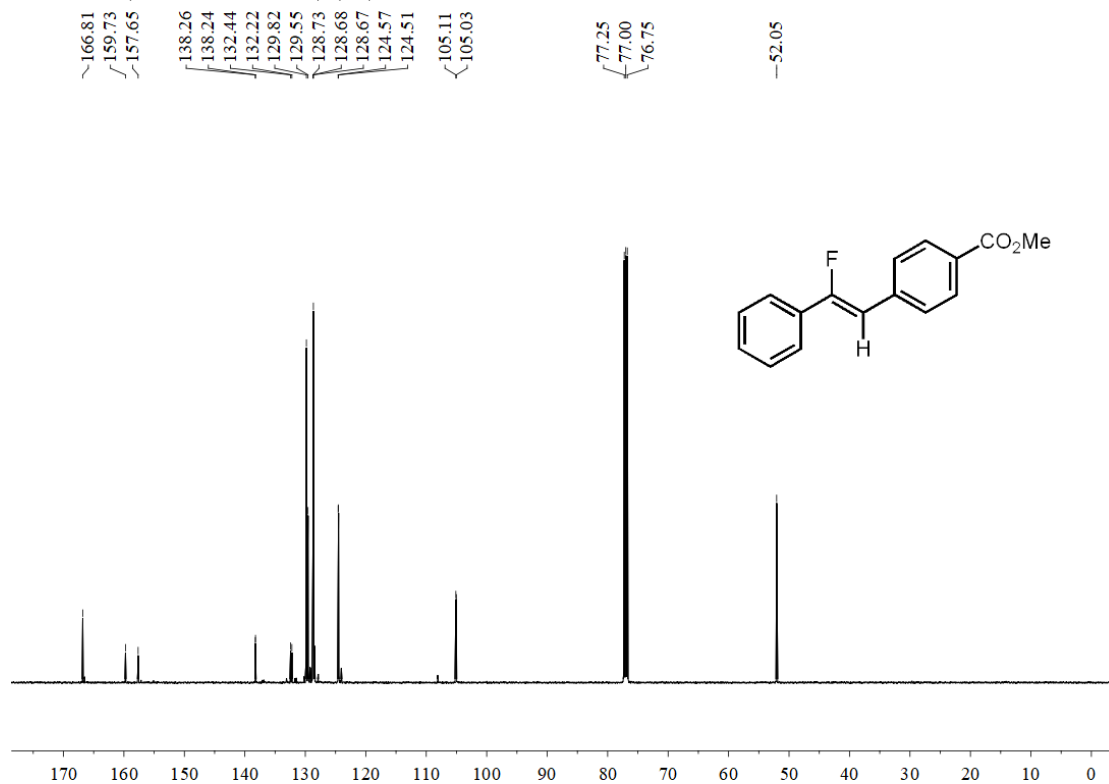
^{19}F NMR (471 MHz, CDCl_3) (75)



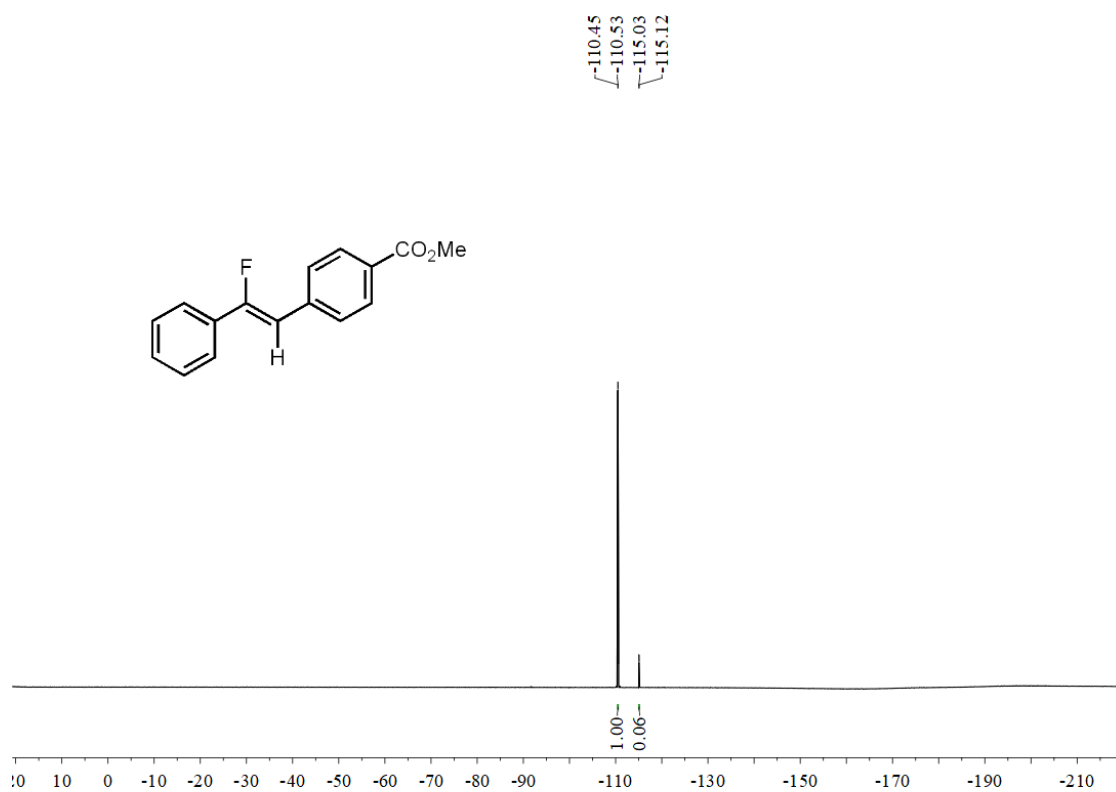
¹H NMR (500 MHz, CDCl₃) (76)



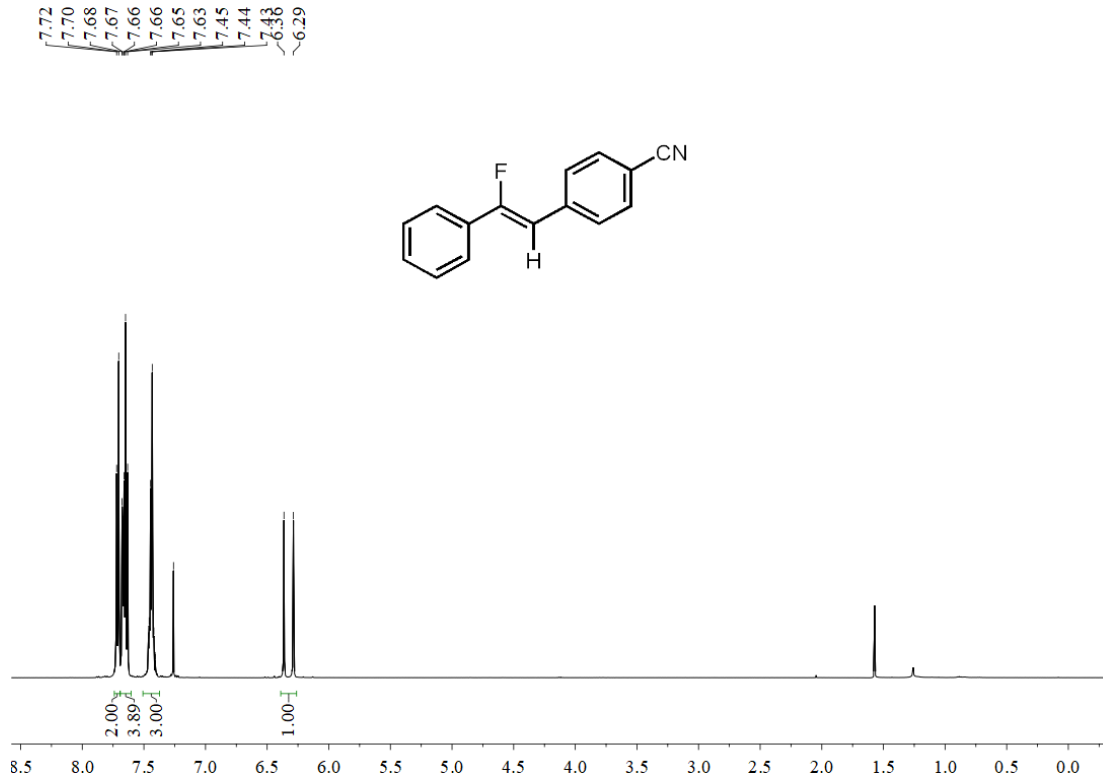
¹³C NMR (126 MHz, CDCl₃) (76)



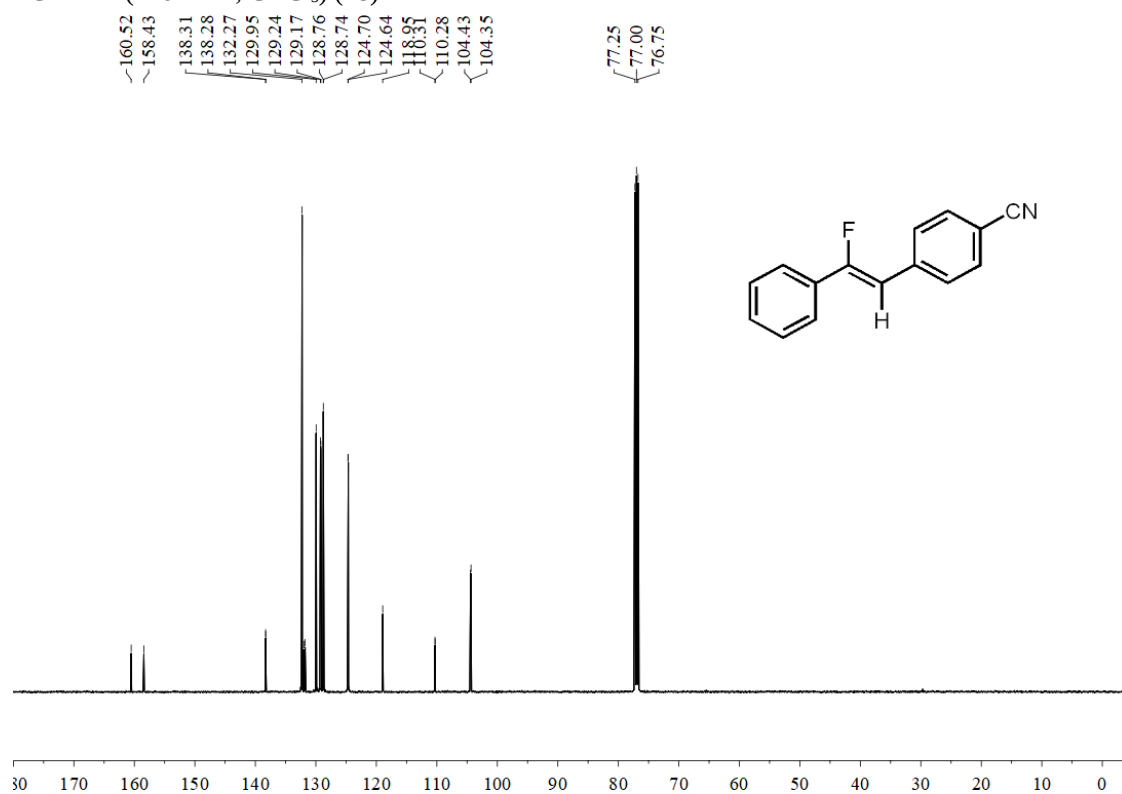
^{19}F NMR (471 MHz, CDCl_3) (76)



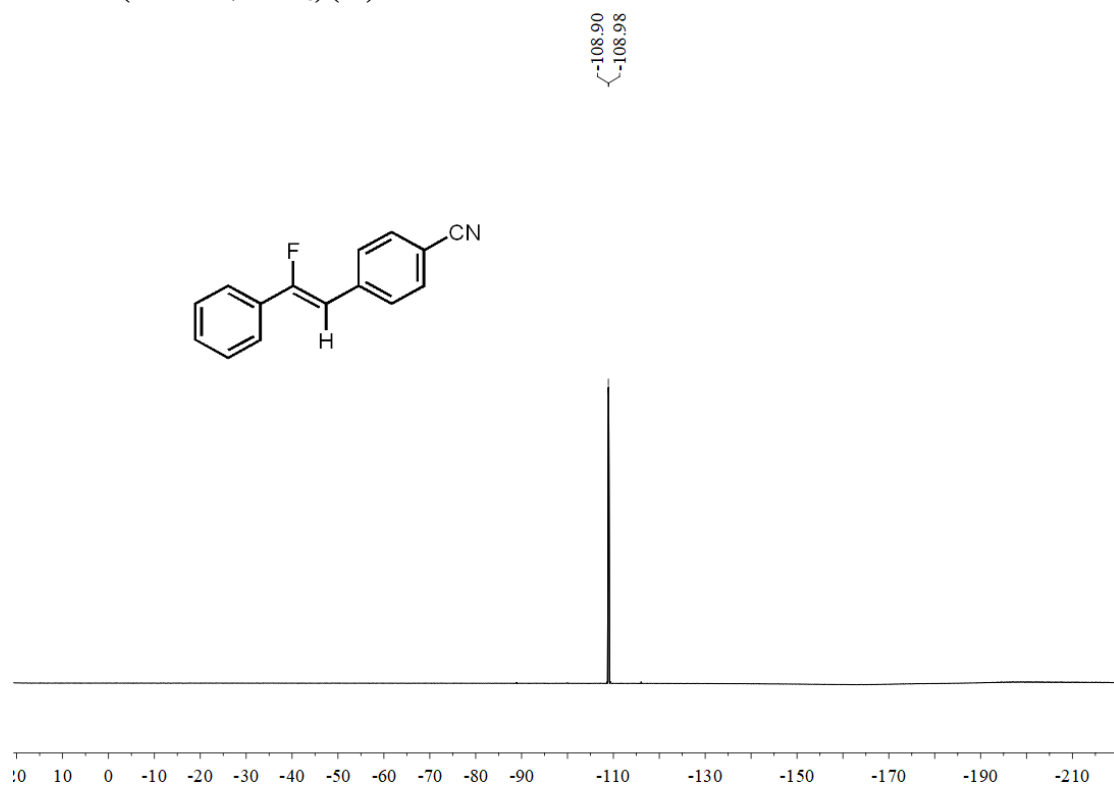
^1H NMR (500 MHz, CDCl_3) (78)



^{13}C NMR (126 MHz, CDCl_3) (78)

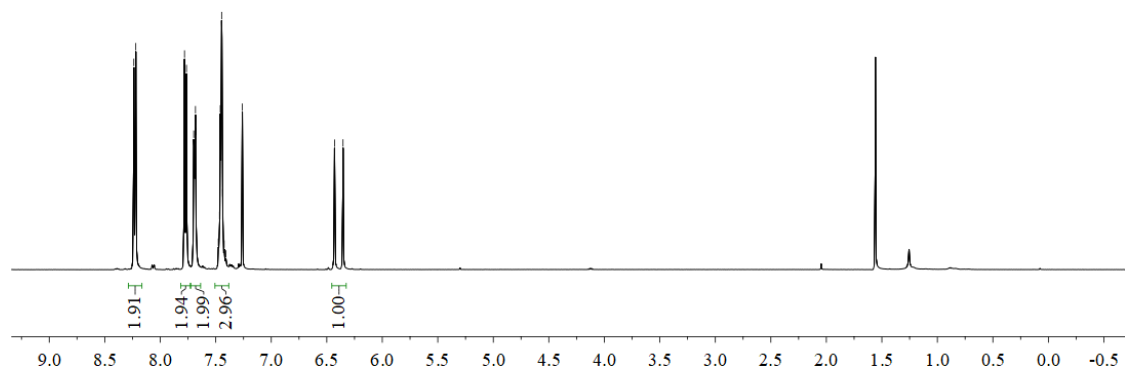
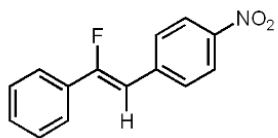


^{19}F NMR (471 MHz, CDCl_3) (78)



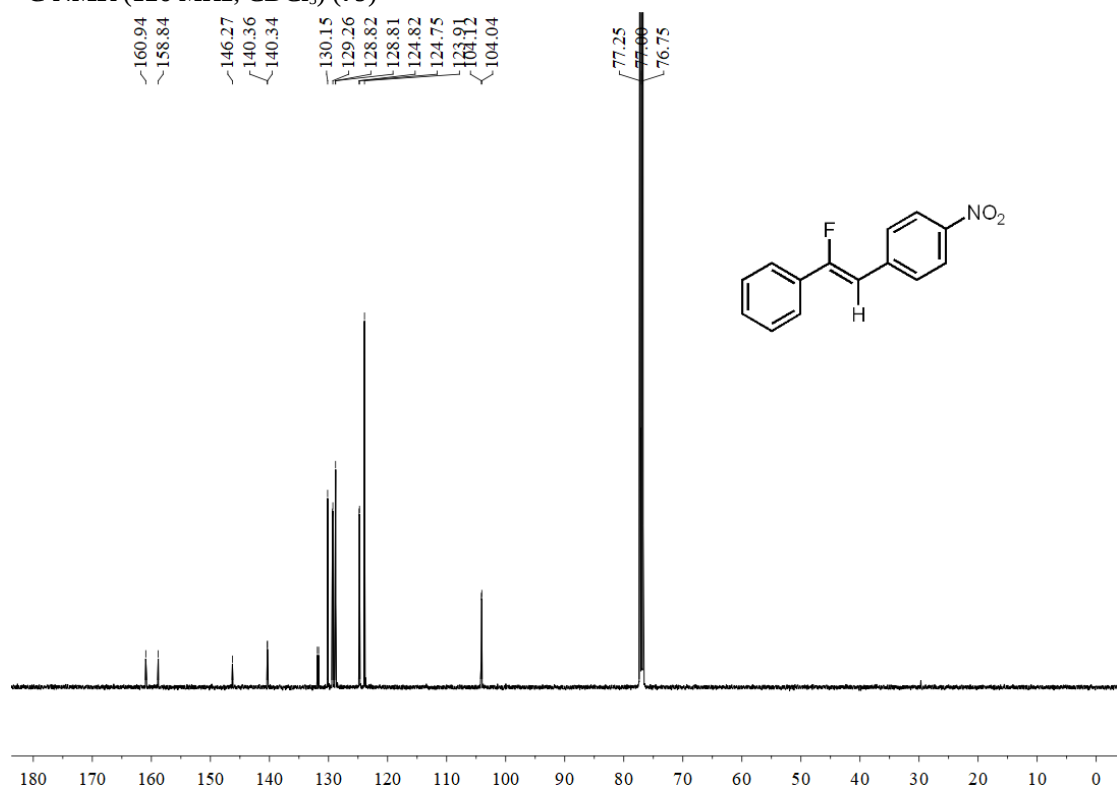
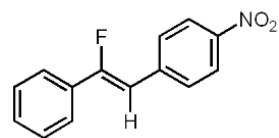
¹H NMR (500 MHz, CDCl₃) (79)

8.24
8.22
7.78
7.76
7.68
7.46
7.45
7.44
7.39
6.35

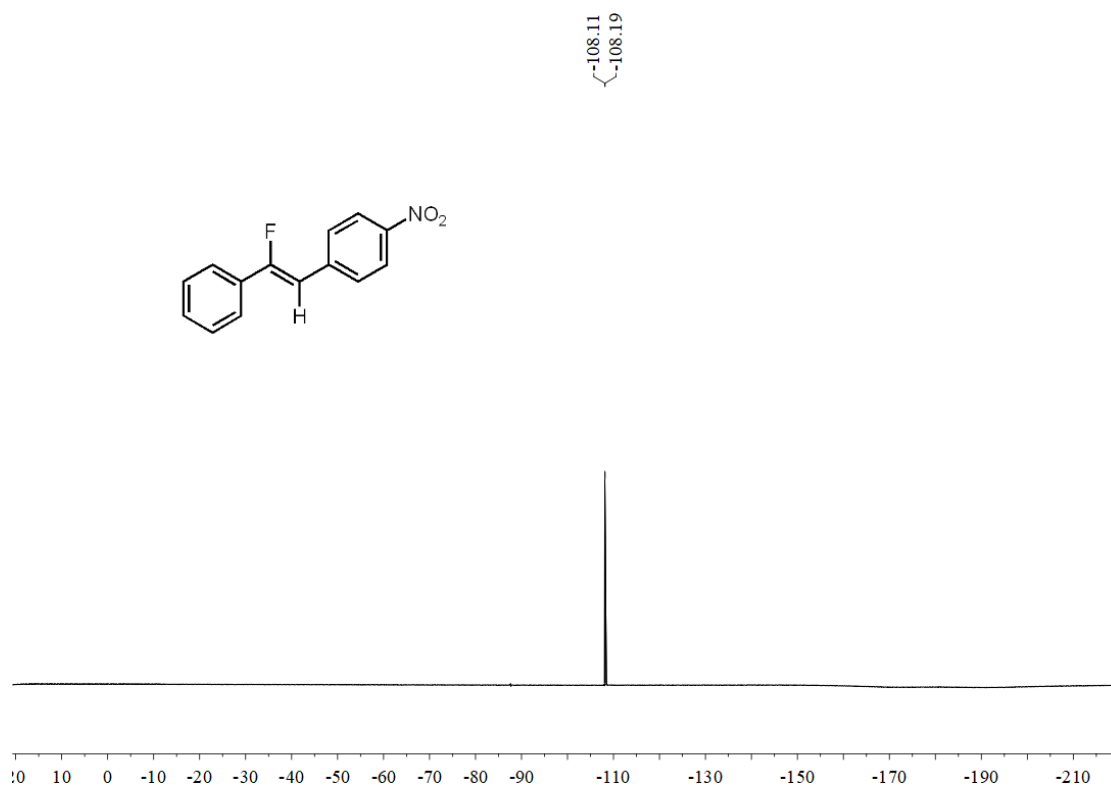


¹³C NMR (126 MHz, CDCl₃) (79)

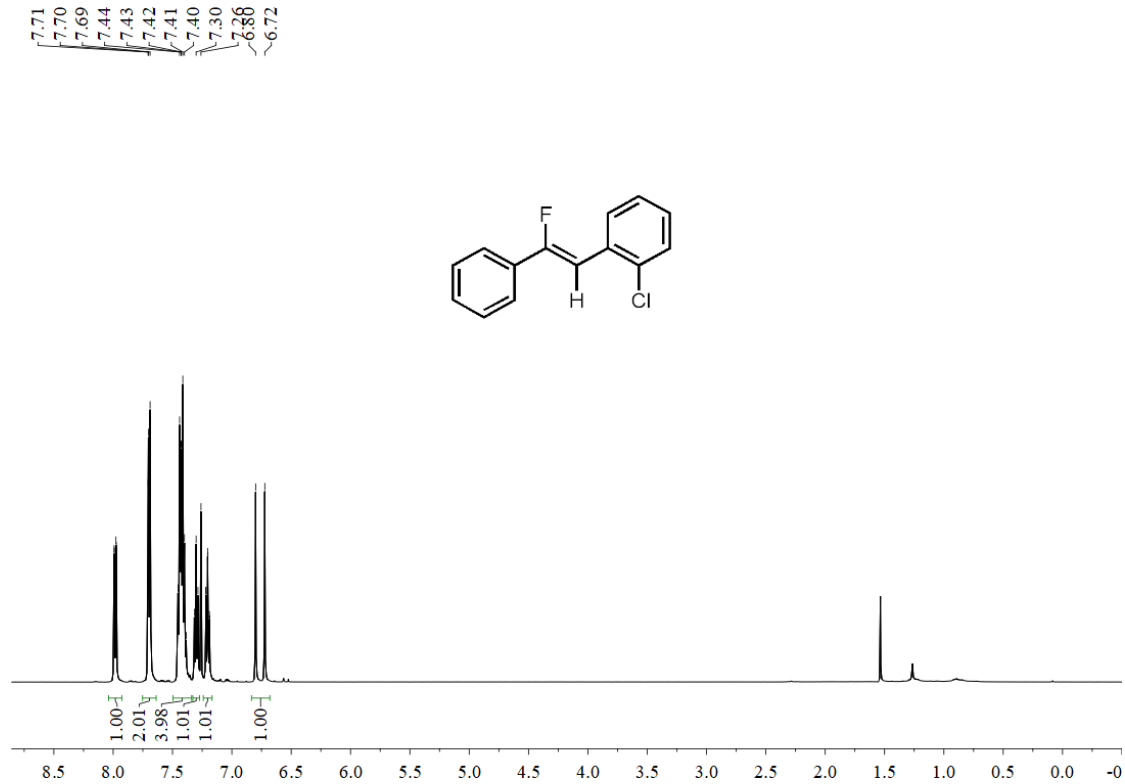
160.94
158.84
146.27
140.36
140.34
130.15
129.26
128.82
128.81
124.82
124.75
123.91
123.12
104.04
77.25
77.00
76.75



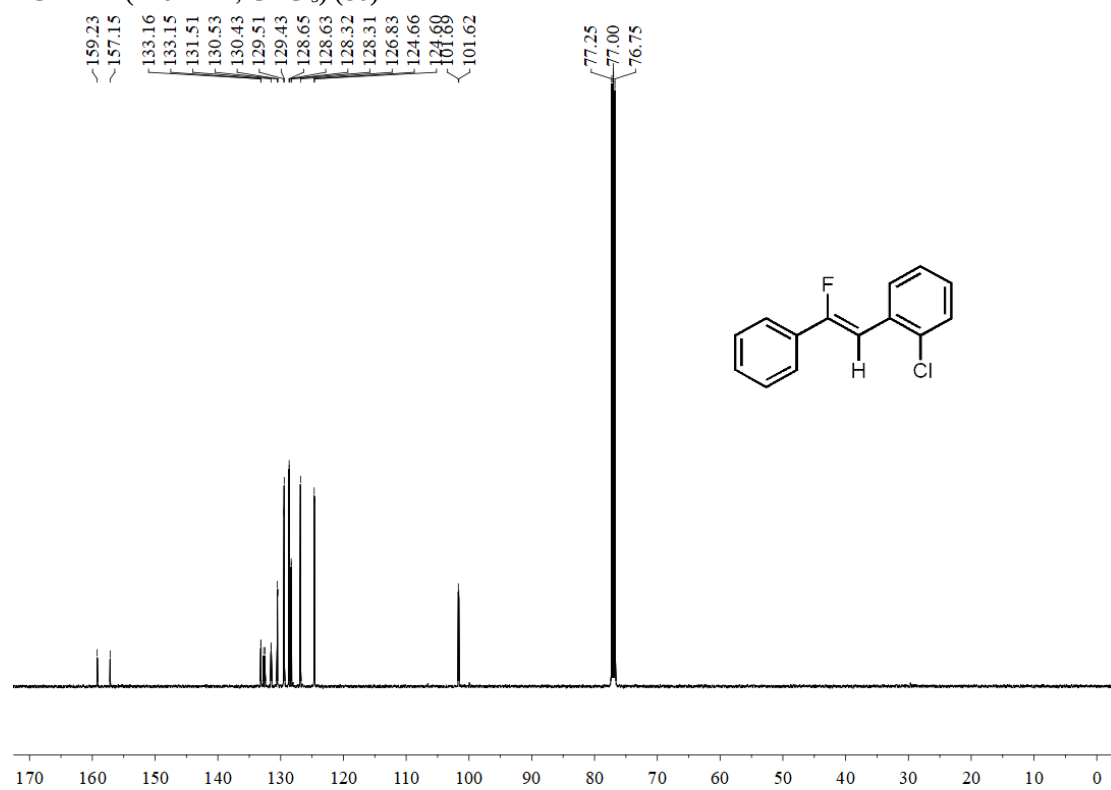
^{19}F NMR (471 MHz, CDCl_3) (79)



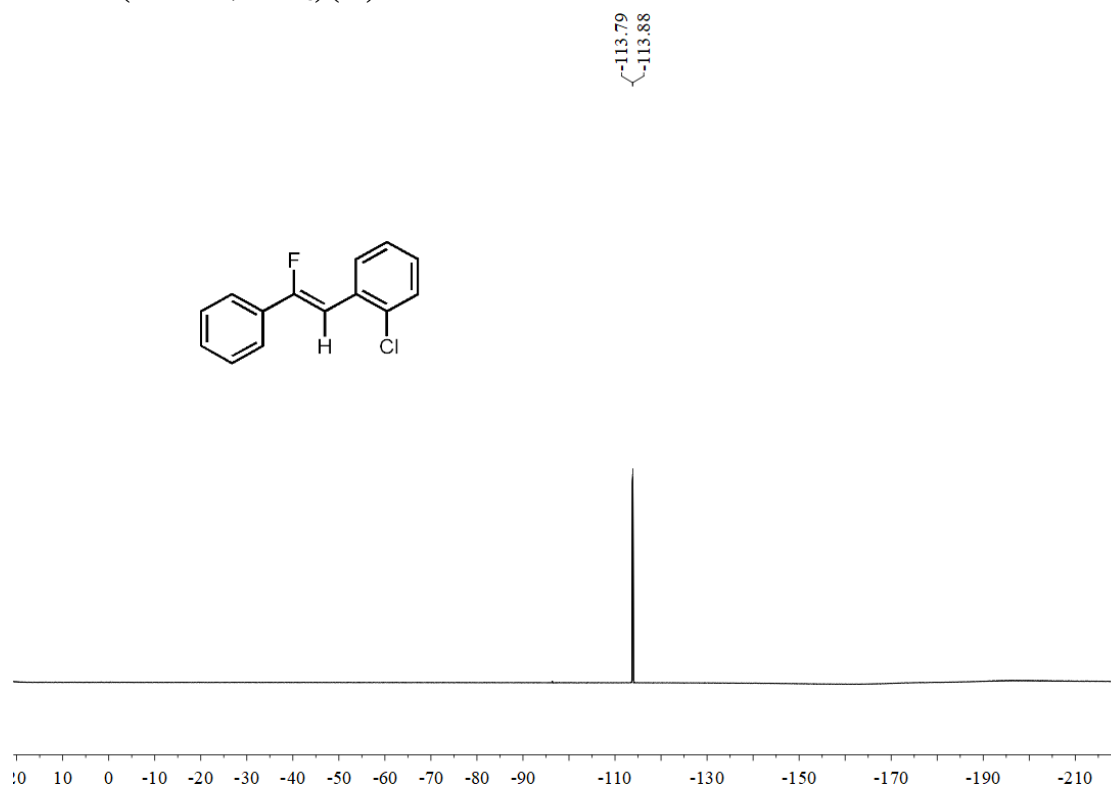
^1H NMR (500 MHz, CDCl_3) (80)



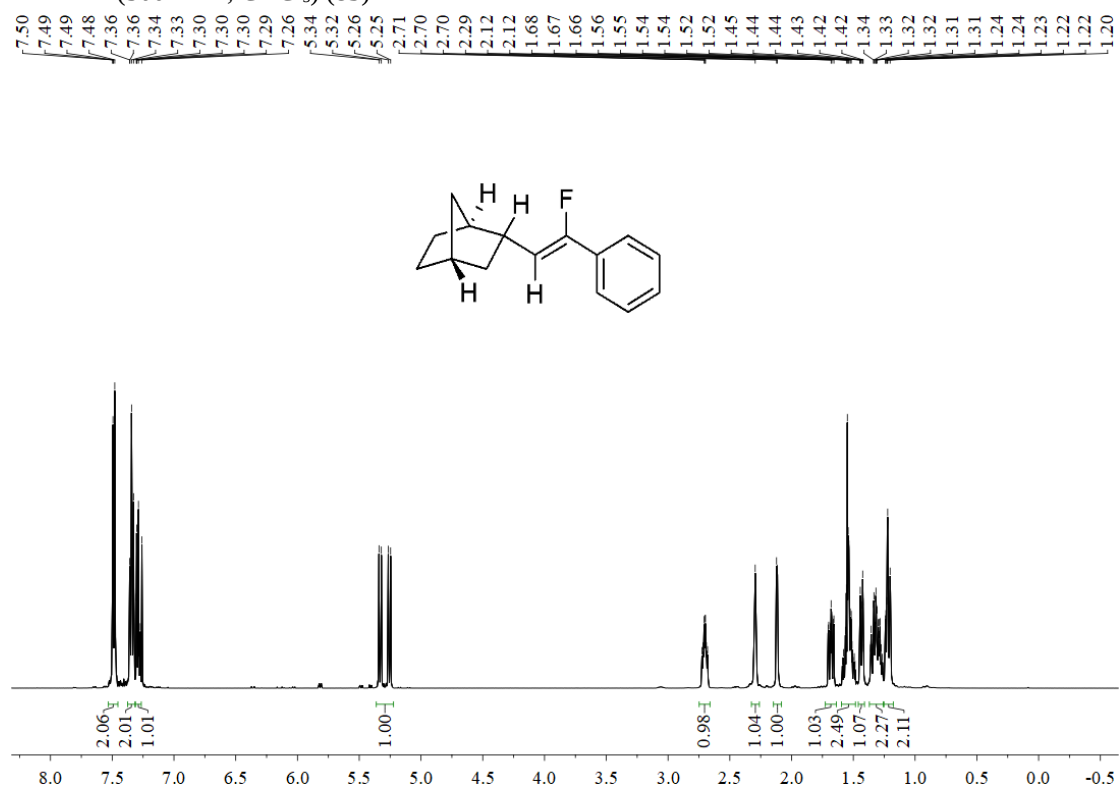
^{13}C NMR (126 MHz, CDCl_3) (80)



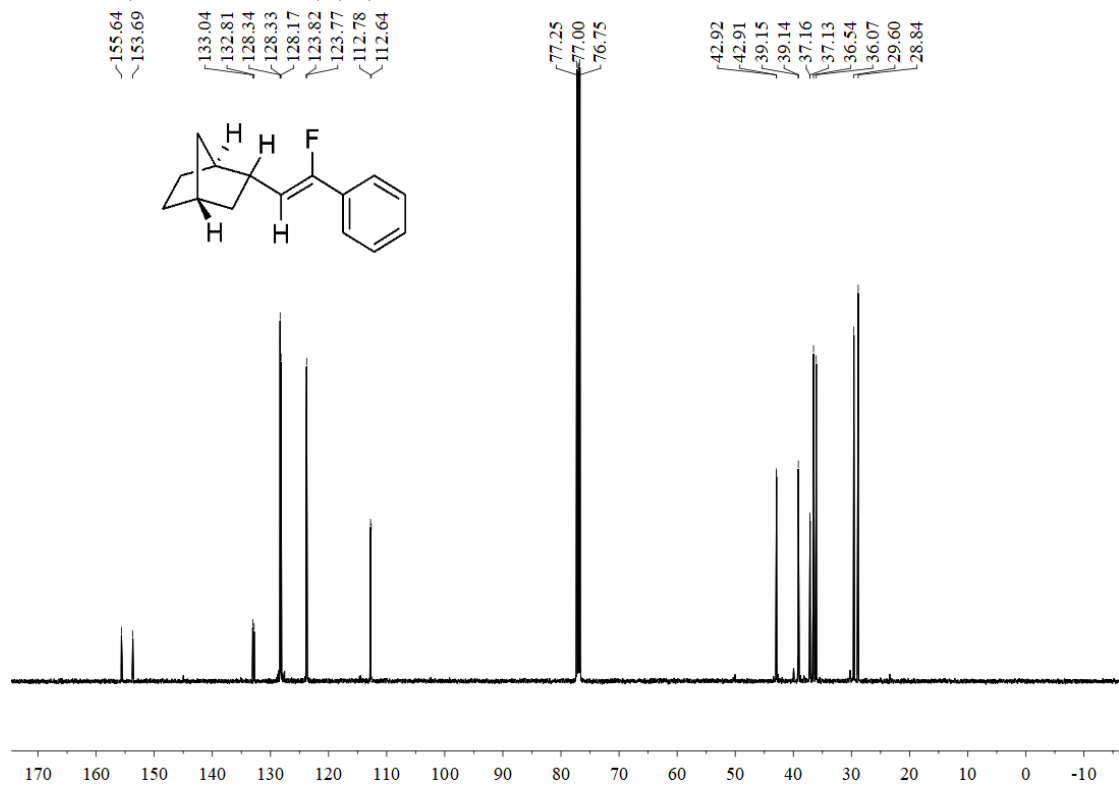
^{19}F NMR (471 MHz, CDCl_3) (80)



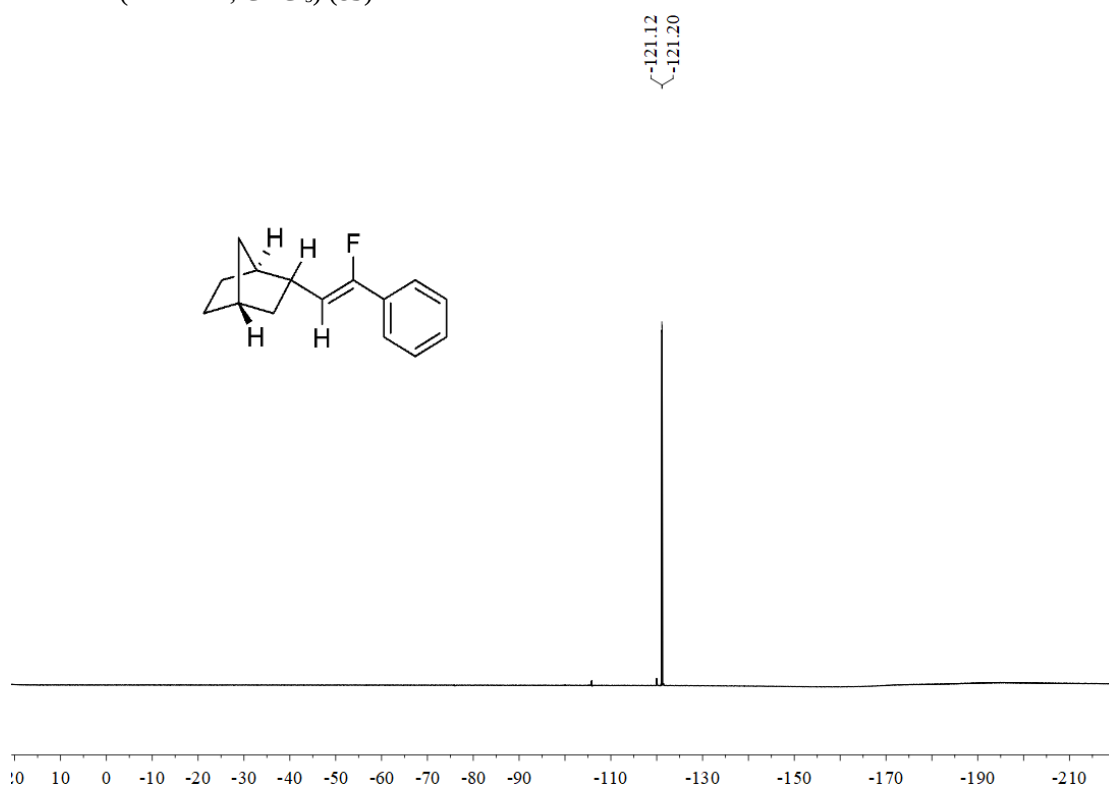
¹H NMR (500 MHz, CDCl₃) (85)



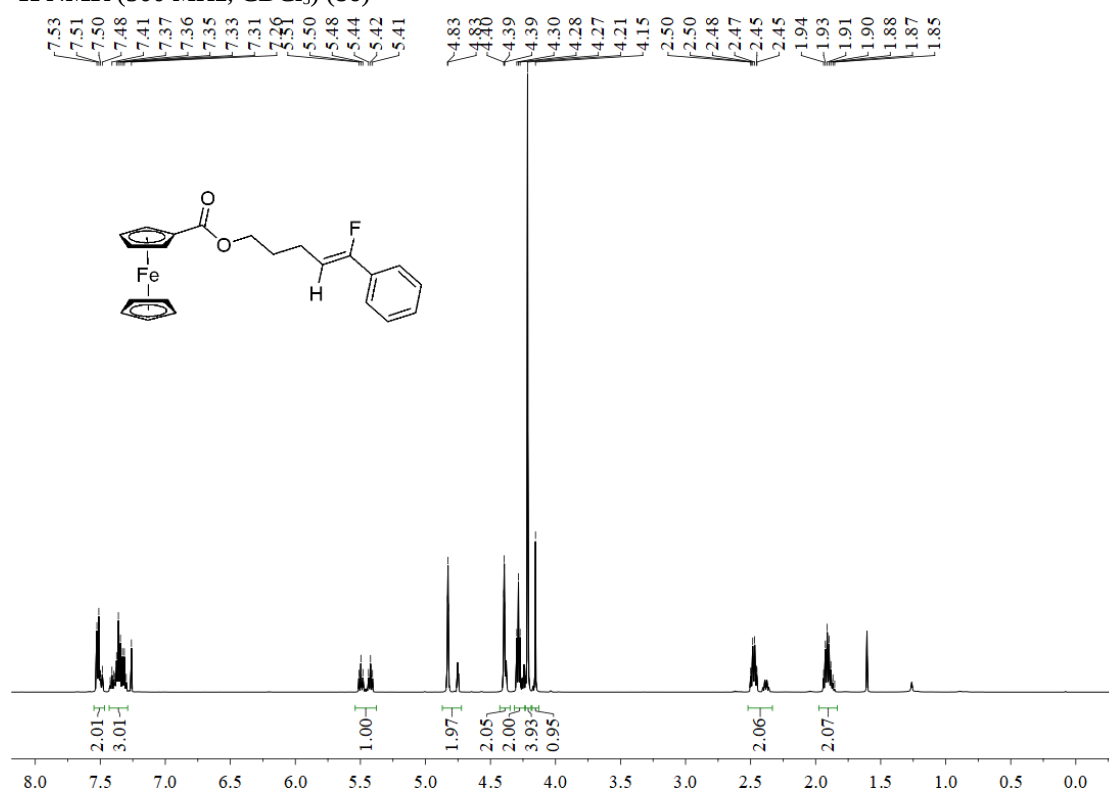
¹³C NMR (126 MHz, CDCl₃) (85)



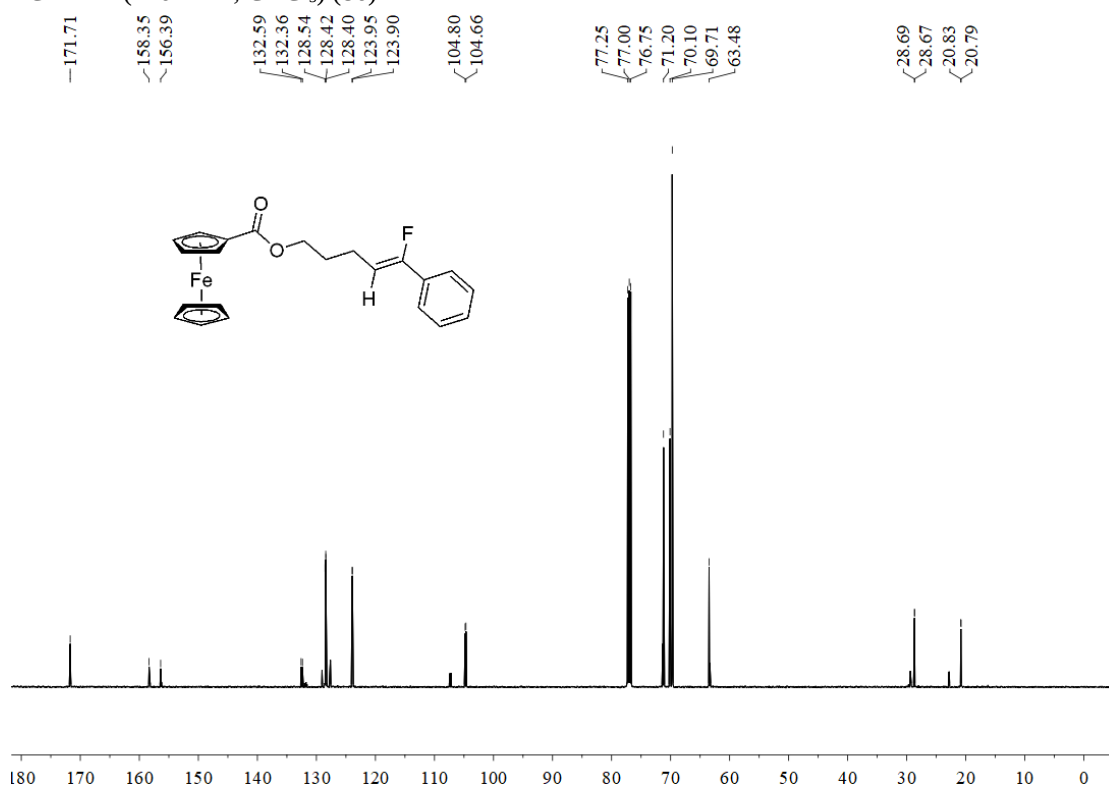
^{19}F NMR (471 MHz, CDCl_3) (85)



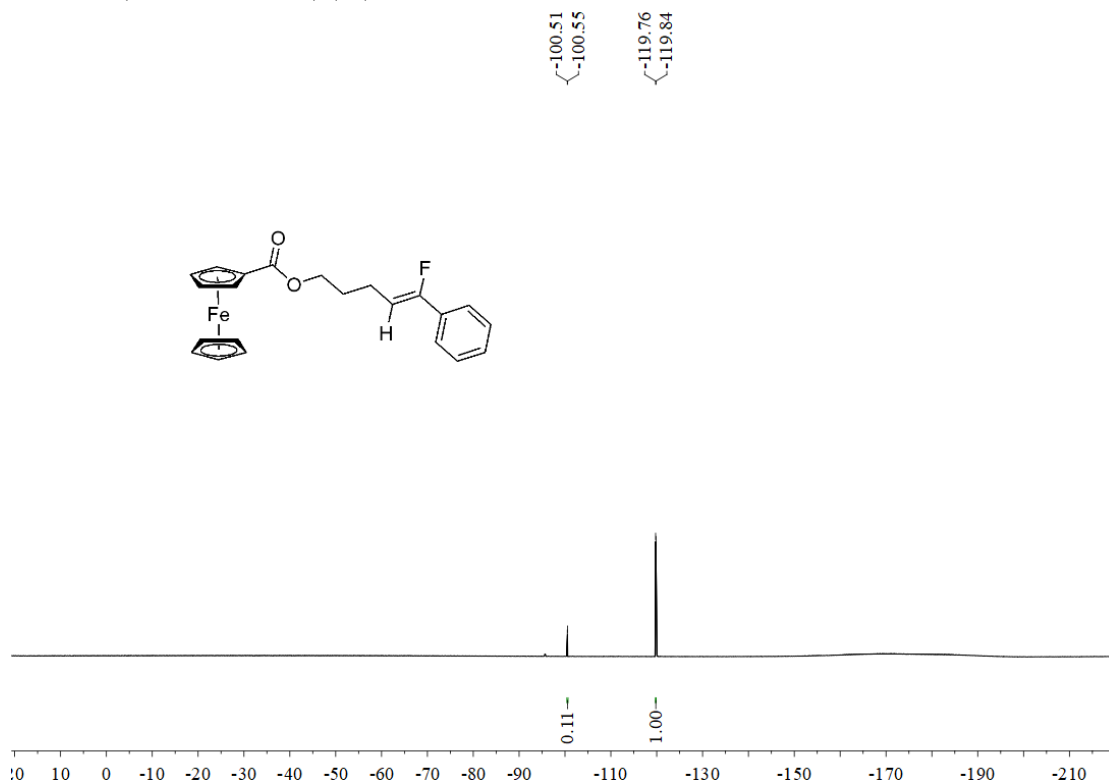
^1H NMR (500 MHz, CDCl_3) (86)



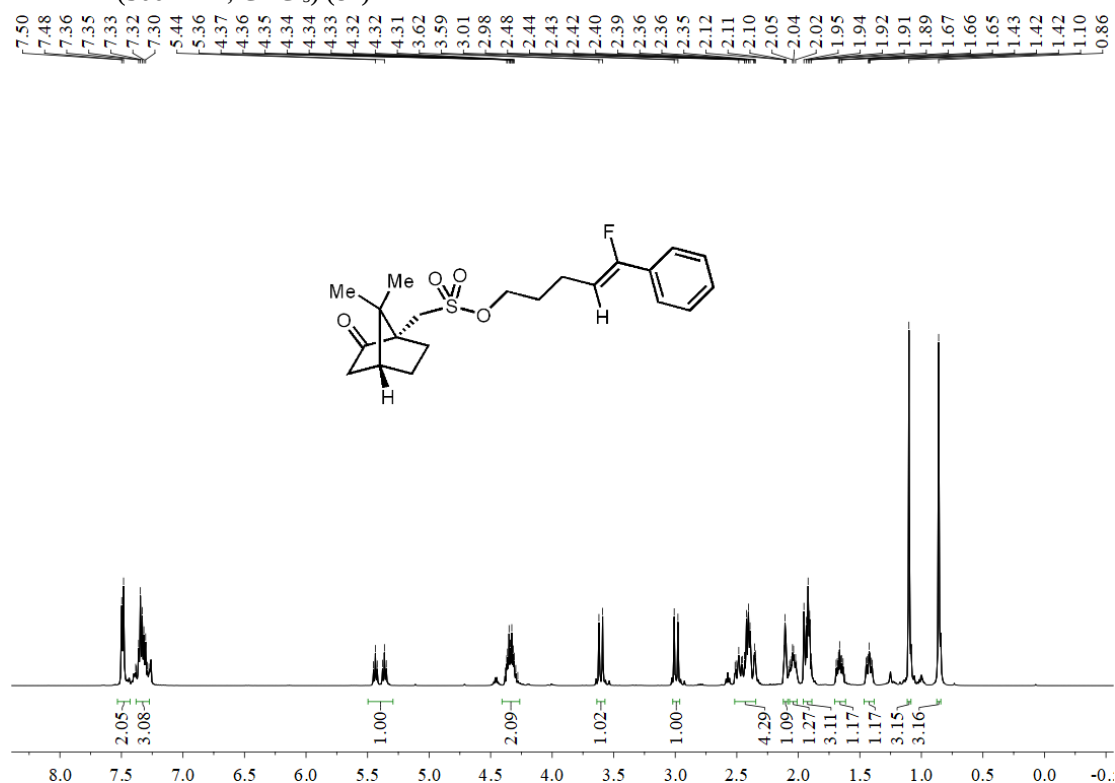
¹³C NMR (126 MHz, CDCl₃) (86)



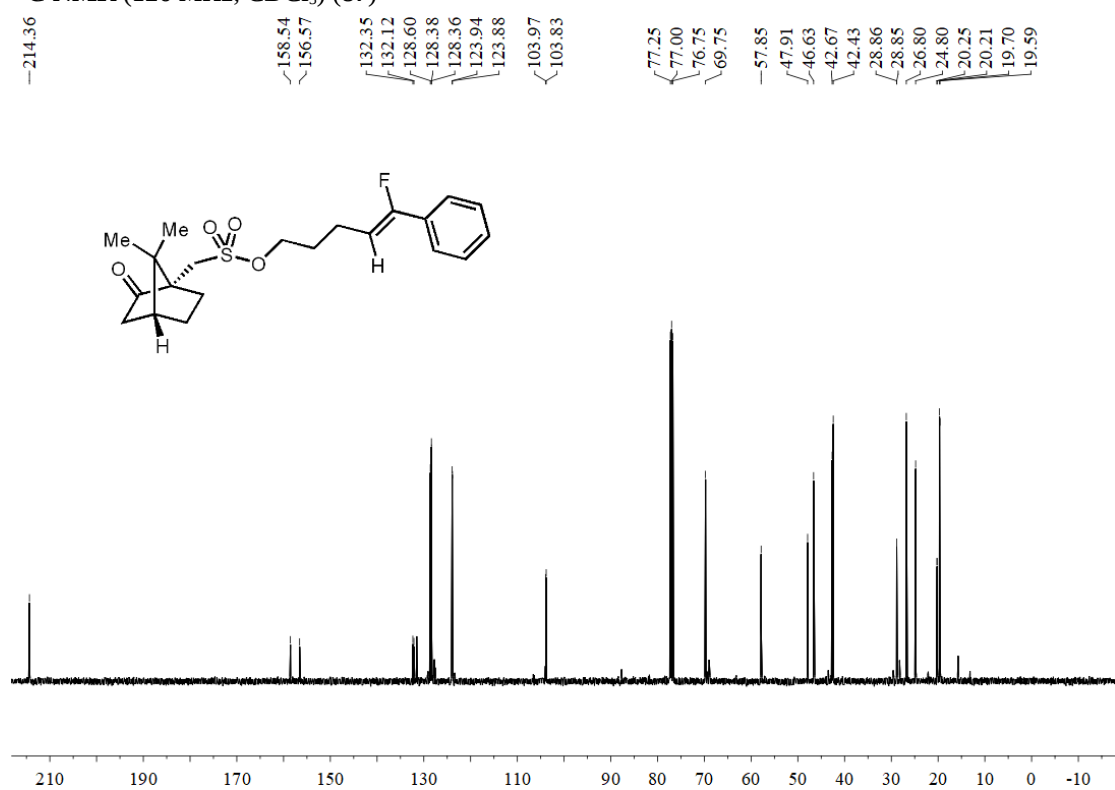
¹⁹F NMR (471 MHz, CDCl₃) (86)



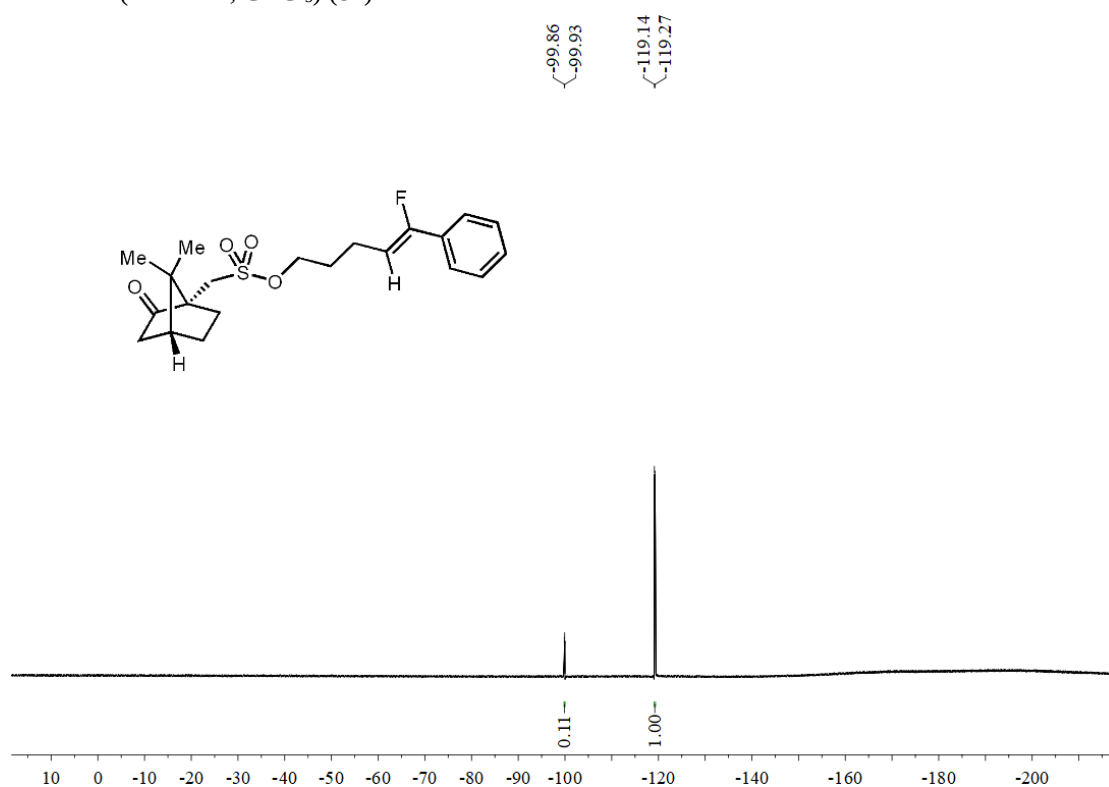
¹H NMR (500 MHz, CDCl₃) (87)



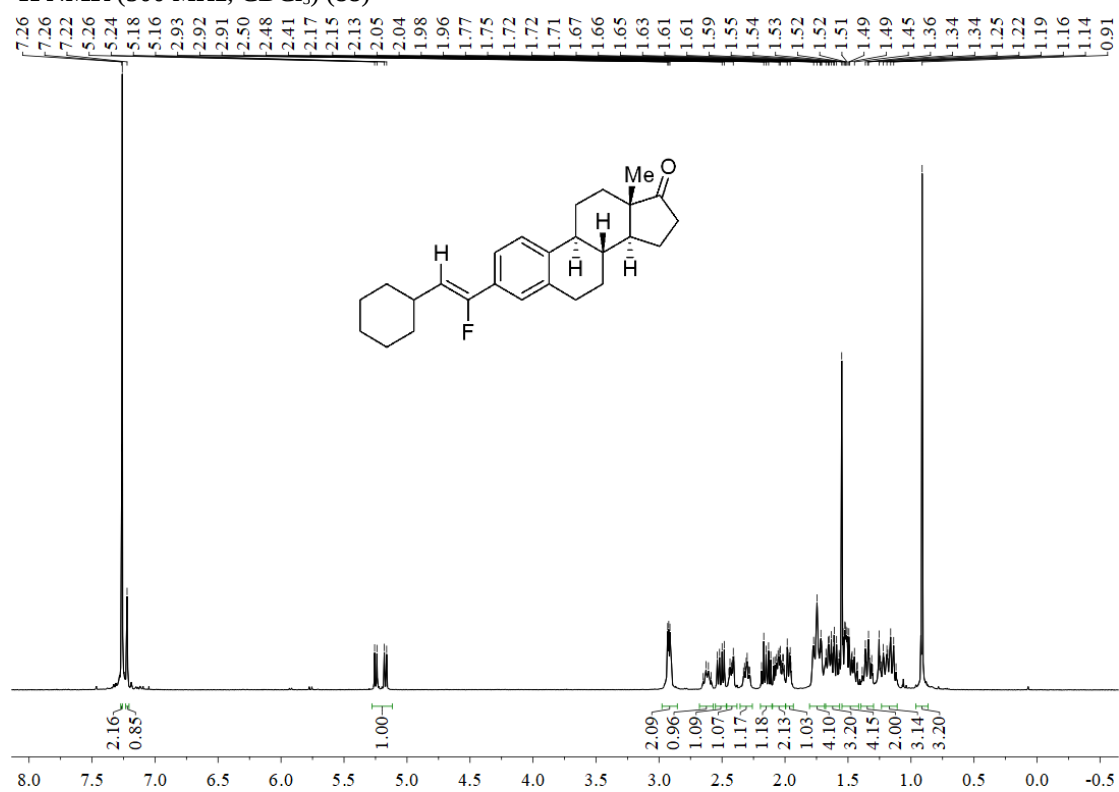
¹³C NMR (126 MHz, CDCl₃) (87)



¹⁹F NMR (471 MHz, CDCl₃) (87)



¹H NMR (500 MHz, CDCl₃) (88)



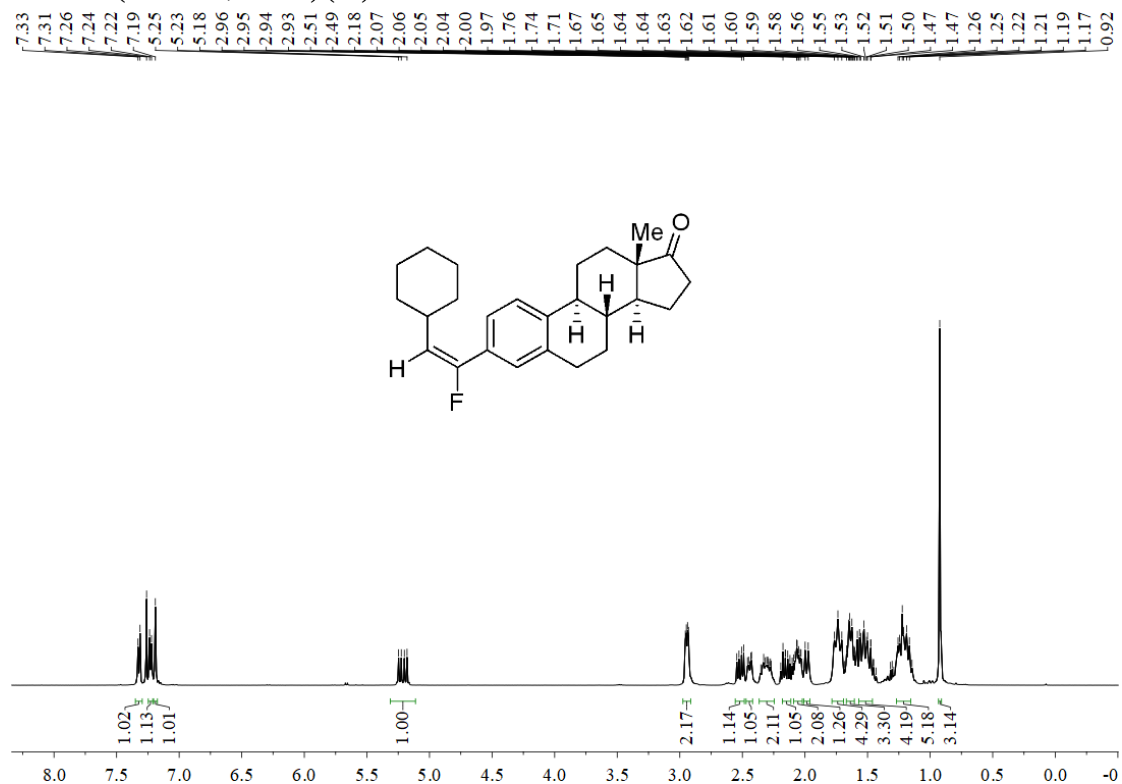
Chemical structure of compound 10 is shown above the spectrum. The structure is a steroid derivative with a cyclohexyl group at C-3, a fluorine atom at C-2, and a methyl ketone at C-17.

¹³C NMR spectrum (CDCl₃) peaks (ppm):

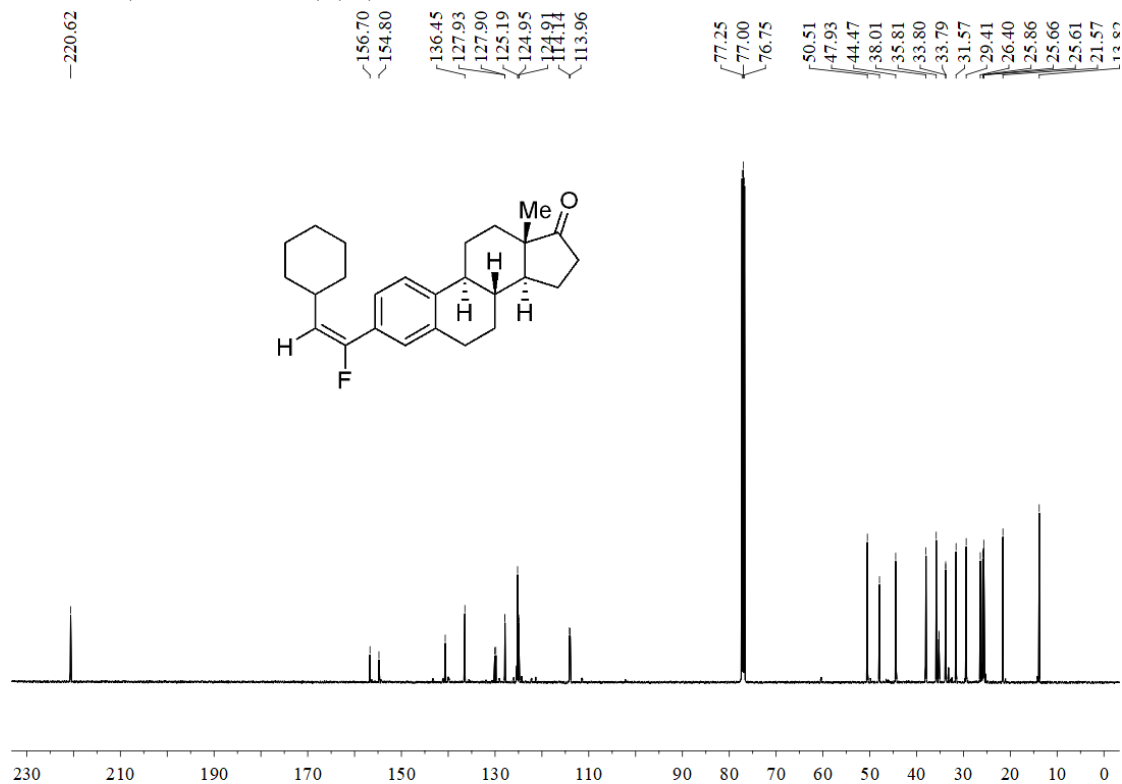
- 220.71
- 156.34
- 154.39
- 140.01
- 125.38
- 125.36
- 124.37
- 124.32
- 121.39
- 121.34
- 121.31
- 111.37
- 77.25
- 77.08
- 76.75
- 50.48
- 47.94
- 44.39
- 38.08
- 35.82
- 33.77
- 33.19
- 31.55
- 29.40
- 26.42
- 26.03
- 25.84
- 25.67
- 21.56
- 12.87

Chemical structure of the compound is shown above the spectrum. The structure is a complex steroid derivative with a cyclohexyl group, a fluorine atom, and a methyl group. The spectrum shows a sharp peak at $\delta = 121.71$ and a broad peak at $\delta = 121.79$.

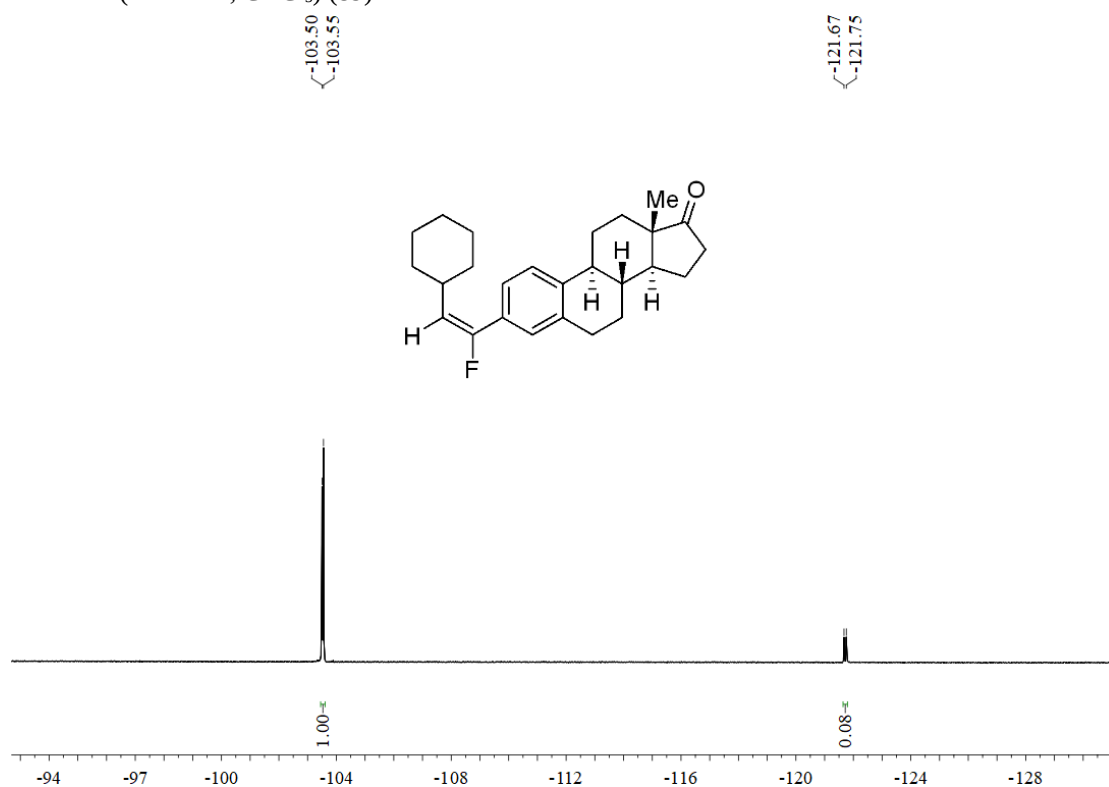
¹H NMR (500 MHz, CDCl₃) (89)



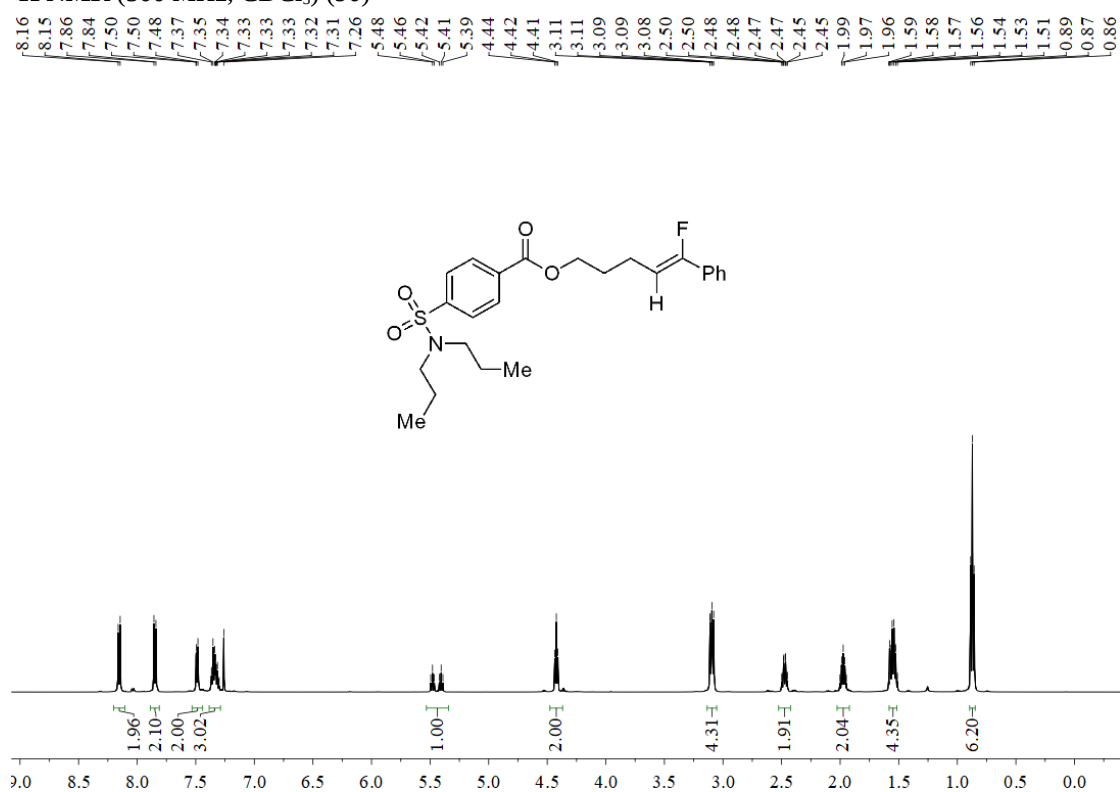
¹³C NMR (126 MHz, CDCl₃) (89)



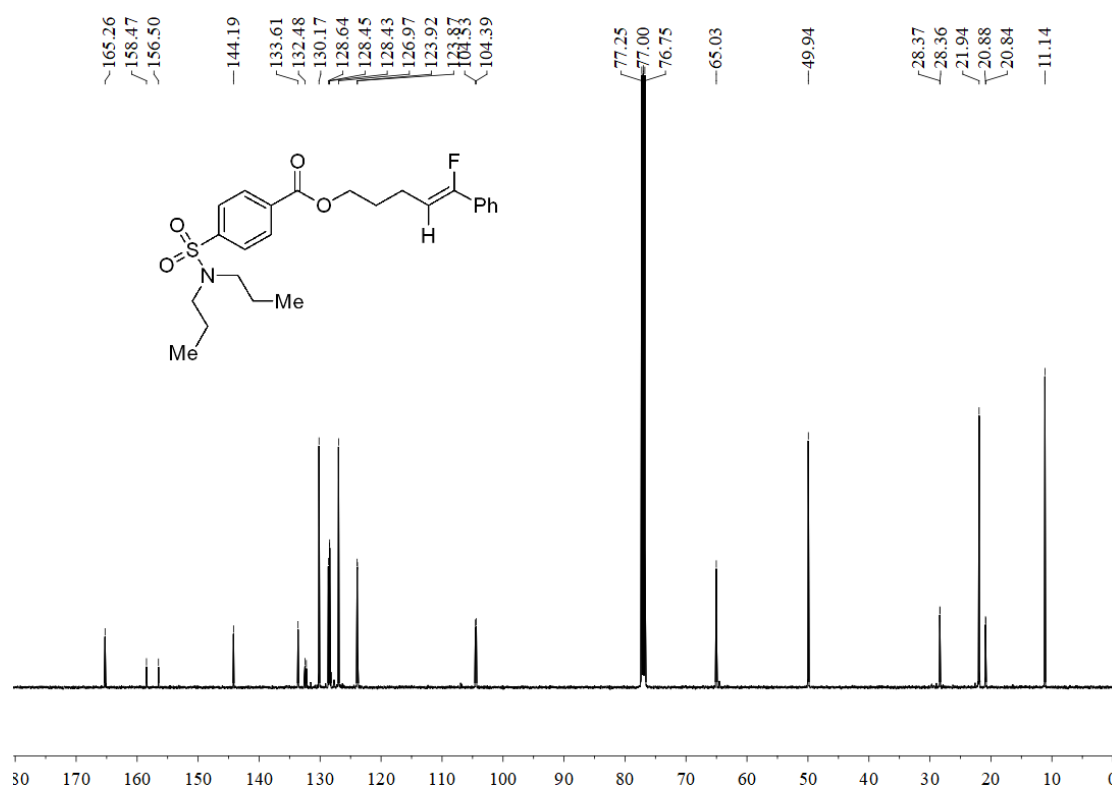
¹⁹F NMR (471 MHz, CDCl₃) (89)



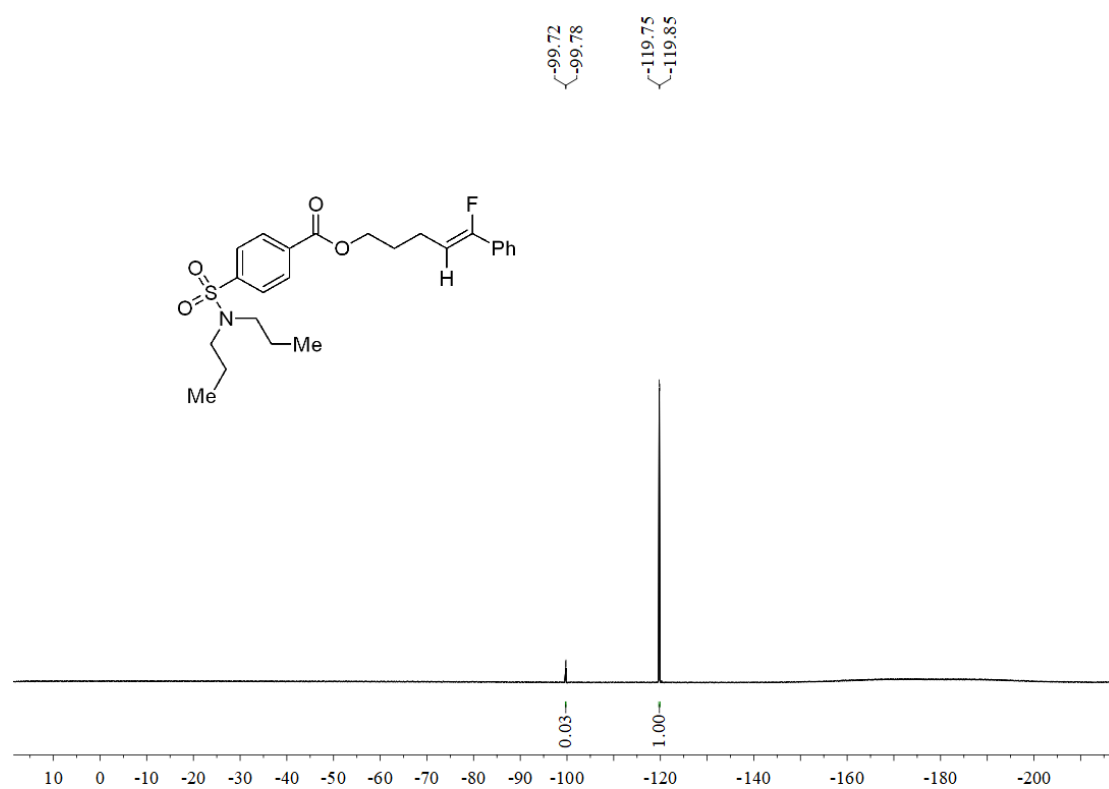
¹H NMR (500 MHz, CDCl₃) (90)



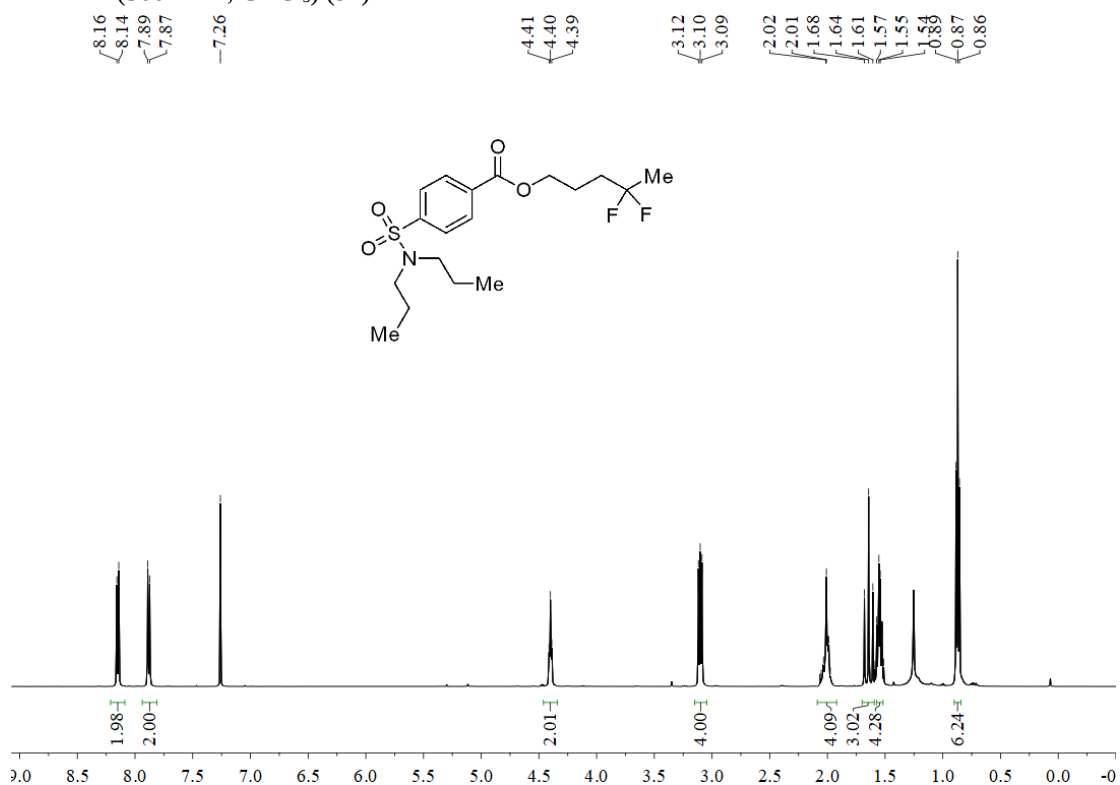
¹³C NMR (126 MHz, CDCl₃) (90)



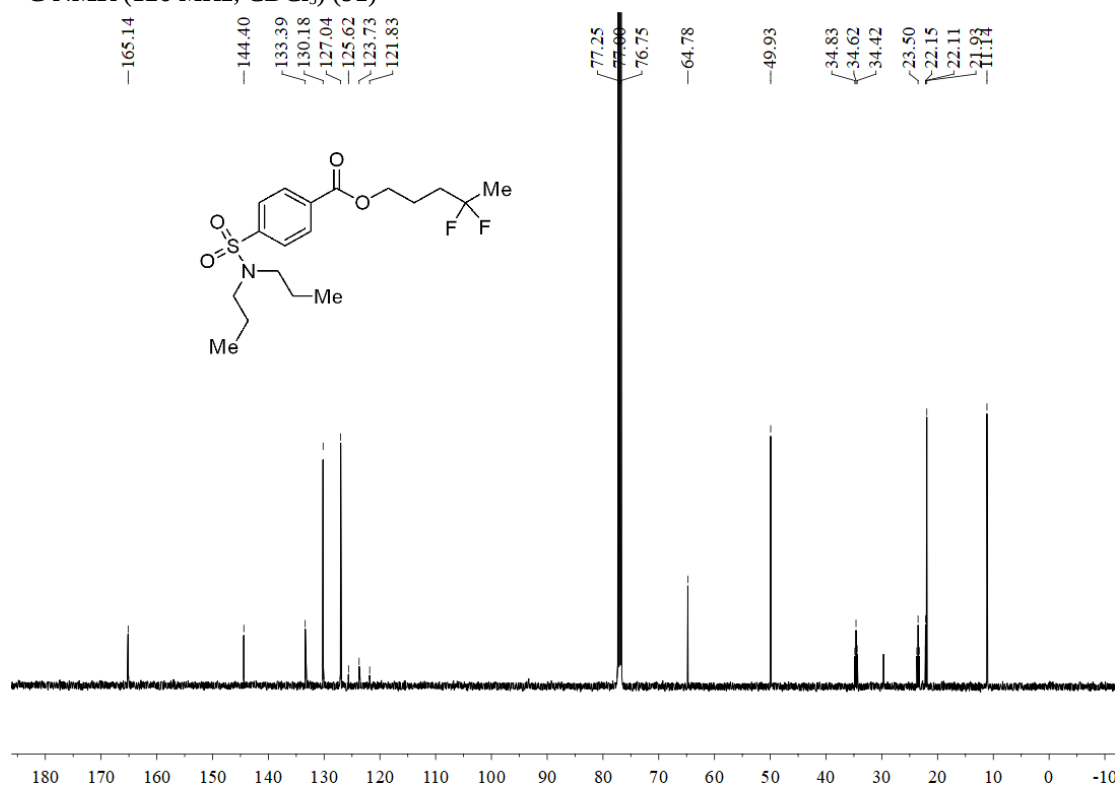
¹⁹F NMR (471 MHz, CDCl₃) (90)



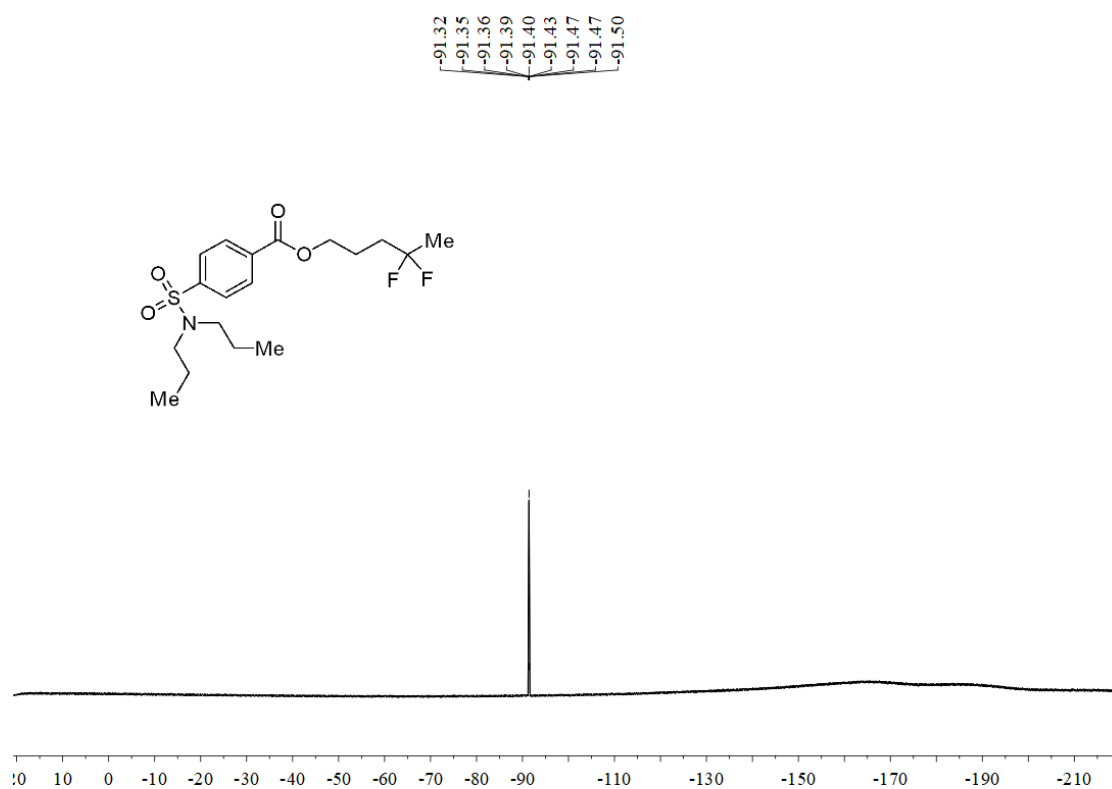
¹H NMR (500 MHz, CDCl₃) (91)



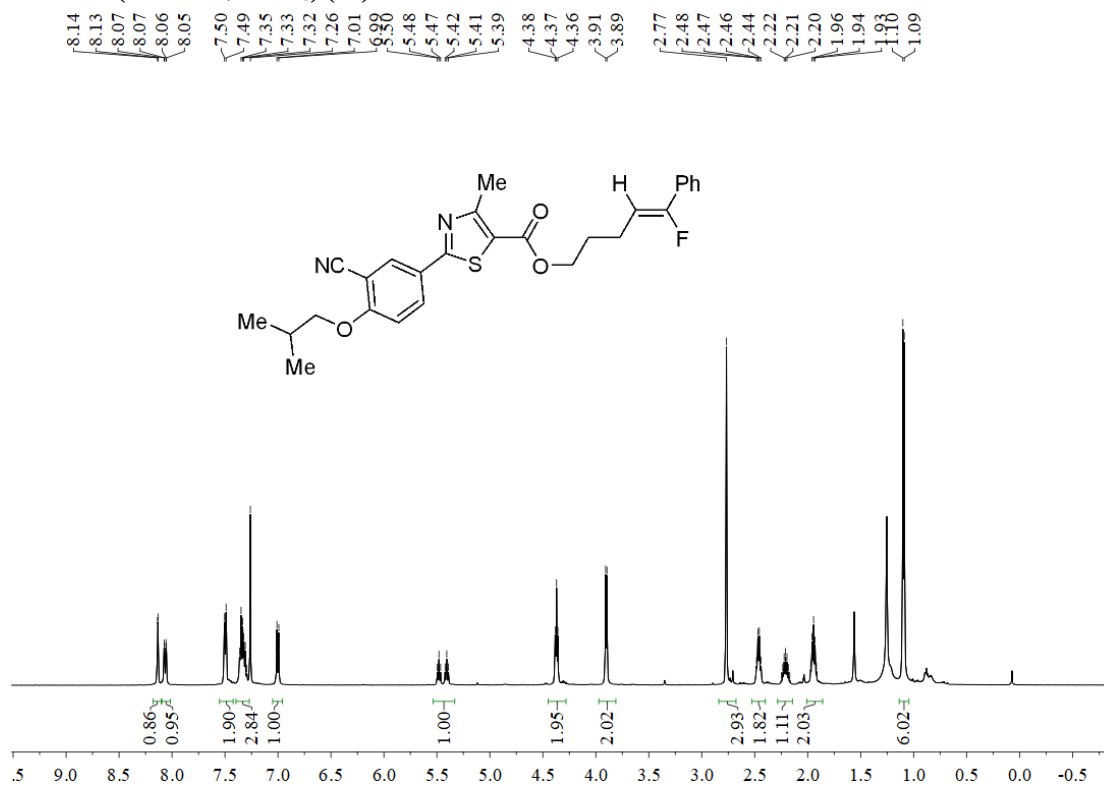
¹³C NMR (126 MHz, CDCl₃) (91)



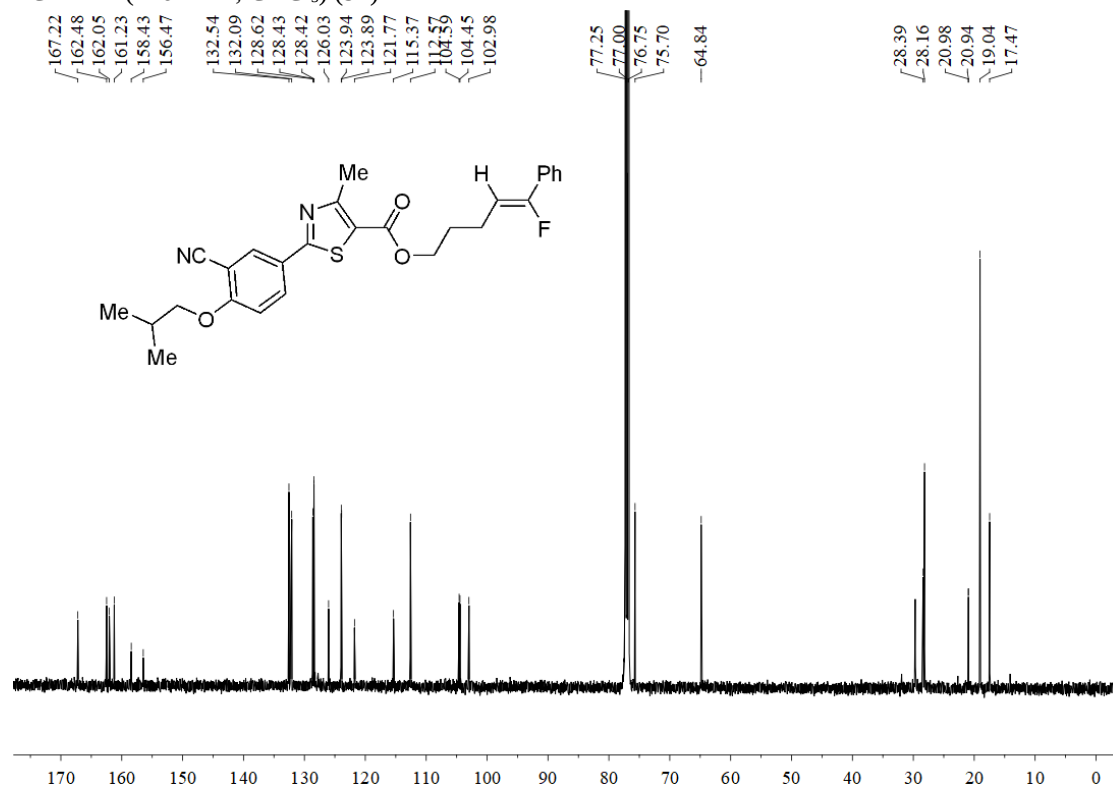
^{19}F NMR (471 MHz, CDCl_3) (91)



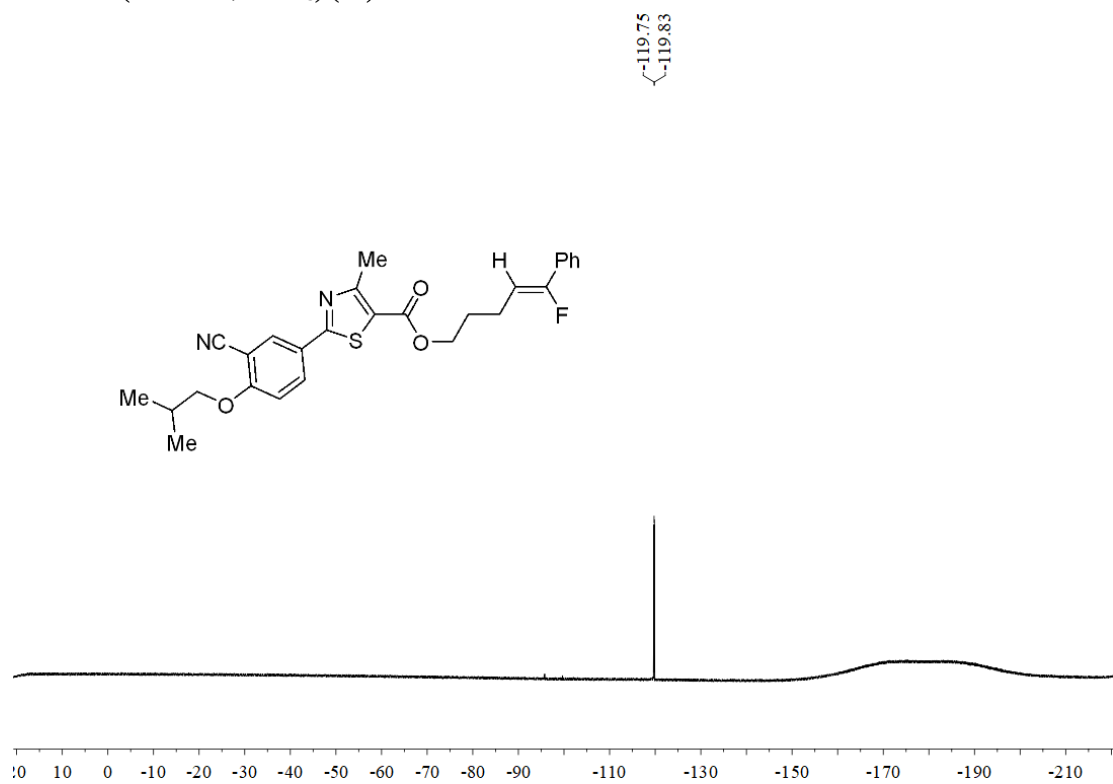
^1H NMR (500 MHz, CDCl_3) (92)



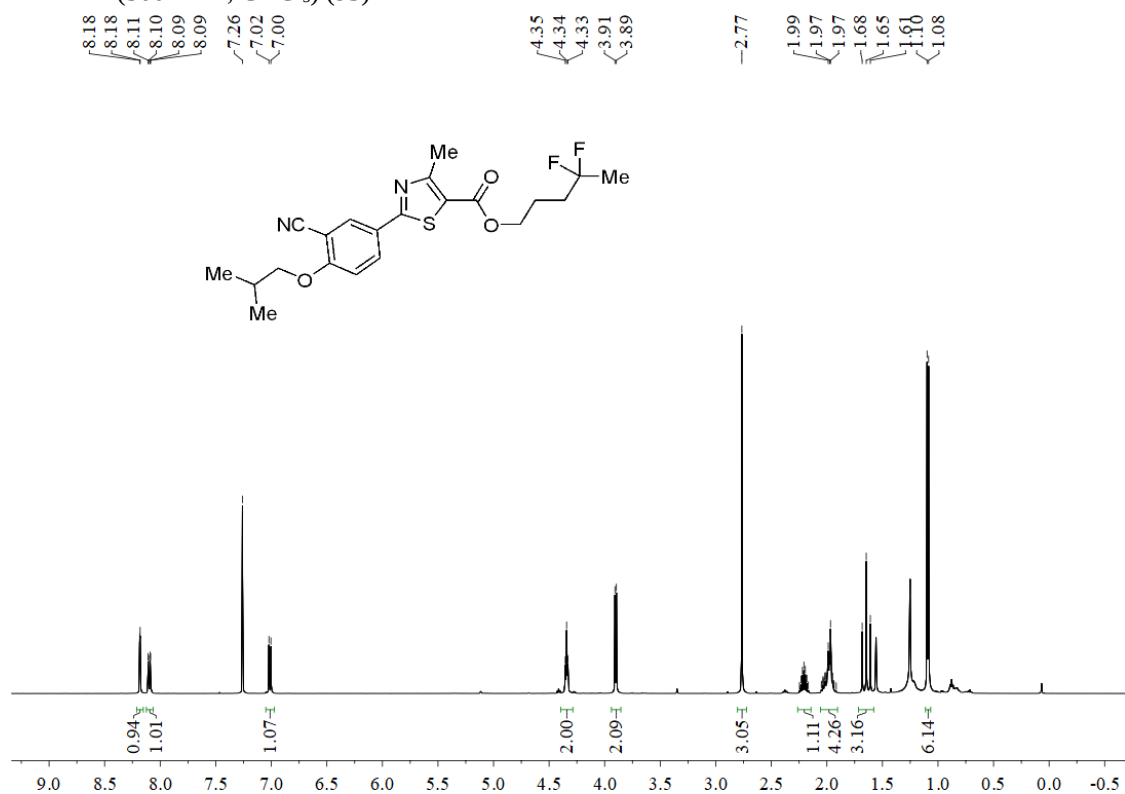
¹³C NMR (126 MHz, CDCl₃) (92)



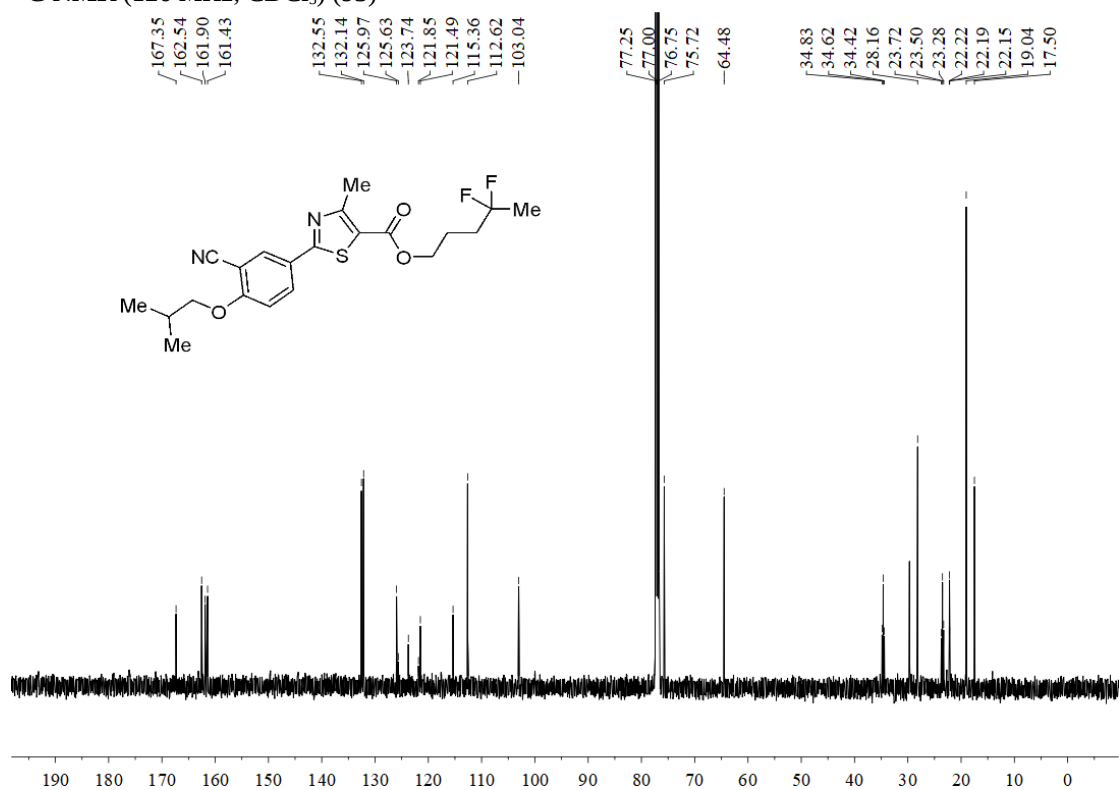
¹⁹F NMR (471 MHz, CDCl₃) (92)



¹H NMR (500 MHz, CDCl₃) (93)



¹³C NMR (126 MHz, CDCl₃) (93)



Chemical structure of the compound is shown above the spectrum. The structure is a thiazole derivative with a nitrile group, a methoxy group, and a trifluoromethyl group.

The spectrum shows a single sharp peak at $\delta = -91.33$ ppm, which is assigned to the methoxy group. The chemical shift of this peak is consistent with the chemical structure.

Chemical structure: CC(C)OC1=CC=C(C#N)C=C1N2C(=S)C(C)=NC2C(=O)OCC(C)(F)F

Chemical shift values (ppm): -91.29, -91.33, -91.33, -91.37, -91.37, -91.40, -91.41, -91.44, -91.44, -91.48.

Chemical structure of compound 10 is shown above the ^1H NMR spectrum. The spectrum displays peaks corresponding to the structure, with integration values provided below the peaks.

Chemical structure of compound 10: Cc1nc2ccccc2n1C3=CC=C(C=C3C4=CC(=CC=C4)C(=O)OCC=C5C=CC(=C5)F)CC

^1H NMR spectrum (CDCl₃) data:

| Chemical Shift (ppm) | Integration |
|--|--|
| 7.84, 7.82, 7.81, 7.79, 7.49, 7.45, 7.43, 7.41, 7.38, 7.36, 7.34, 7.33, 7.32, 7.31, 7.29, 7.27, 7.26, 7.25, 7.10, 7.08, 5.41, 4.08, 4.06, 4.05, 4.05, 3.76, 2.93, 2.91, 2.90, 2.76, 2.07, 2.06, 2.04, 1.87, 1.86, 1.56, 1.54, 1.53, 1.05, 1.04, 1.02 | 1.01, 1.01, 1.16, 4.10, 1.14, 9.01, 2.04, 2.12, 1.00, 2.00, 3.01, 2.07, 3.04, 2.04, 2.21, 2.07, 3.06 |

Chemical structure of the compound is shown above the spectrum. The structure is a complex molecule featuring a benzimidazole core, a 2-methyl-5-(2-methyl-2-((2-oxo-2-phenyl-1-phenylethyl)methyl)-1H-benzimidazol-5-yl)benzene ring, and a 2-(2-(2-fluoro-3-phenylprop-1-en-1-yl)ethoxy)benzoyl group.

¹³C NMR spectrum (CDCl₃) showing chemical shifts (ppm) for the compound. The spectrum displays peaks corresponding to the structure, with the following labeled chemical shifts (ppm):

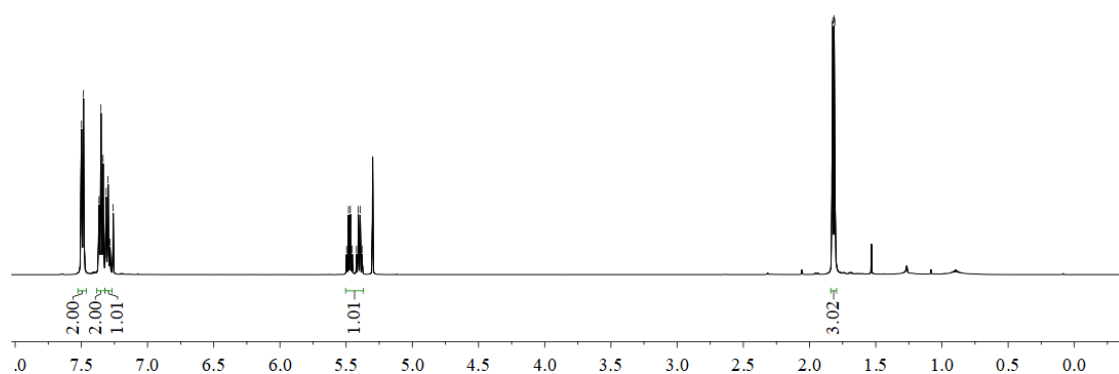
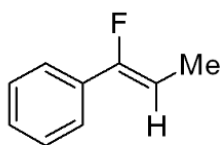
- 168.33
- 158.11
- 156.15
- 131.26
- 129.03
- 128.55
- 128.39
- 128.38
- 125.90
- 123.82
- 123.77
- 122.25
- 109.55
- 109.48
- 108.86
- 104.64
- 104.50
- 77.25
- 77.00
- 76.75
- 64.37
- 47.00
- 31.73
- 29.78
- 27.97
- 21.82
- 20.58
- 20.53
- 16.84
- 14.02

Chemical structure of the compound is shown above the spectrum. The structure is a complex molecule featuring a benzimidazole core substituted with a methyl group, a 2-phenyl-2-fluoroethenyl group, and a 2-methyl-2-phenylethan-1-yl group. The spectrum shows a sharp peak at approximately -119.8 ppm, which is labeled with its chemical shift values: -119.82 and -119.89.

¹H NMR (500 MHz, CDCl₃) (95)

7.50, 7.48, 7.37, 7.35, 7.34, 7.31, 7.30, 7.29, 7.28, 7.26, 5.50, 5.48, 5.47, 5.45, 5.42, 5.41, 5.39, 5.38

1.83, 1.82, 1.81, 1.81



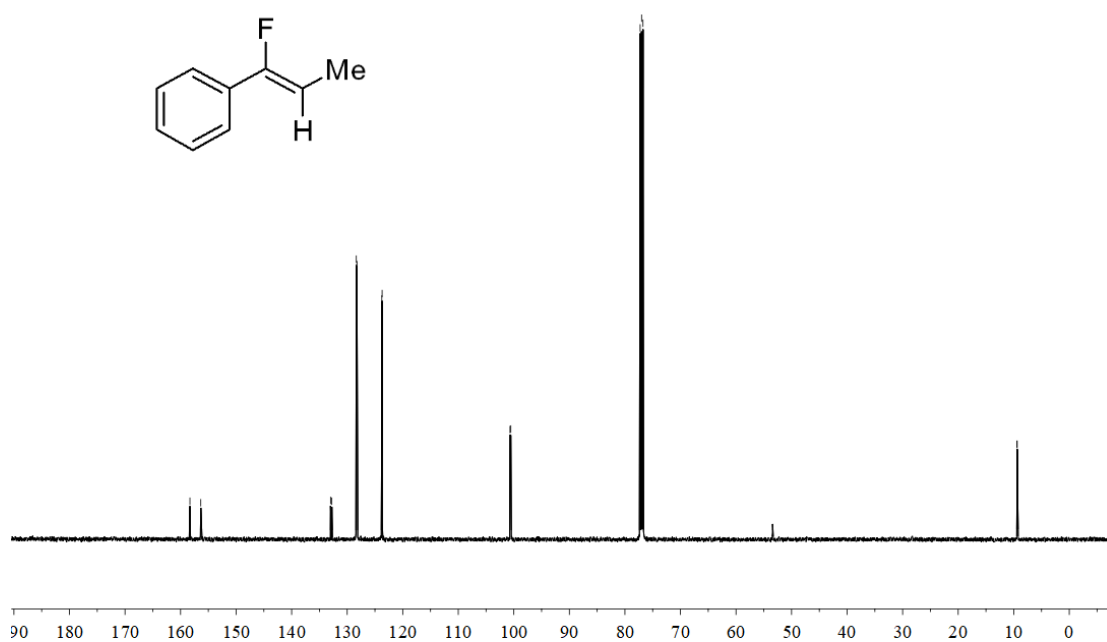
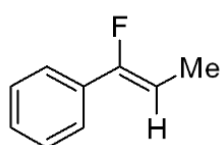
¹³C NMR (126 MHz, CDCl₃) (95)

158.31, 156.36, 132.99, 132.76, 128.37, 128.36, 128.24, 123.76, 123.71

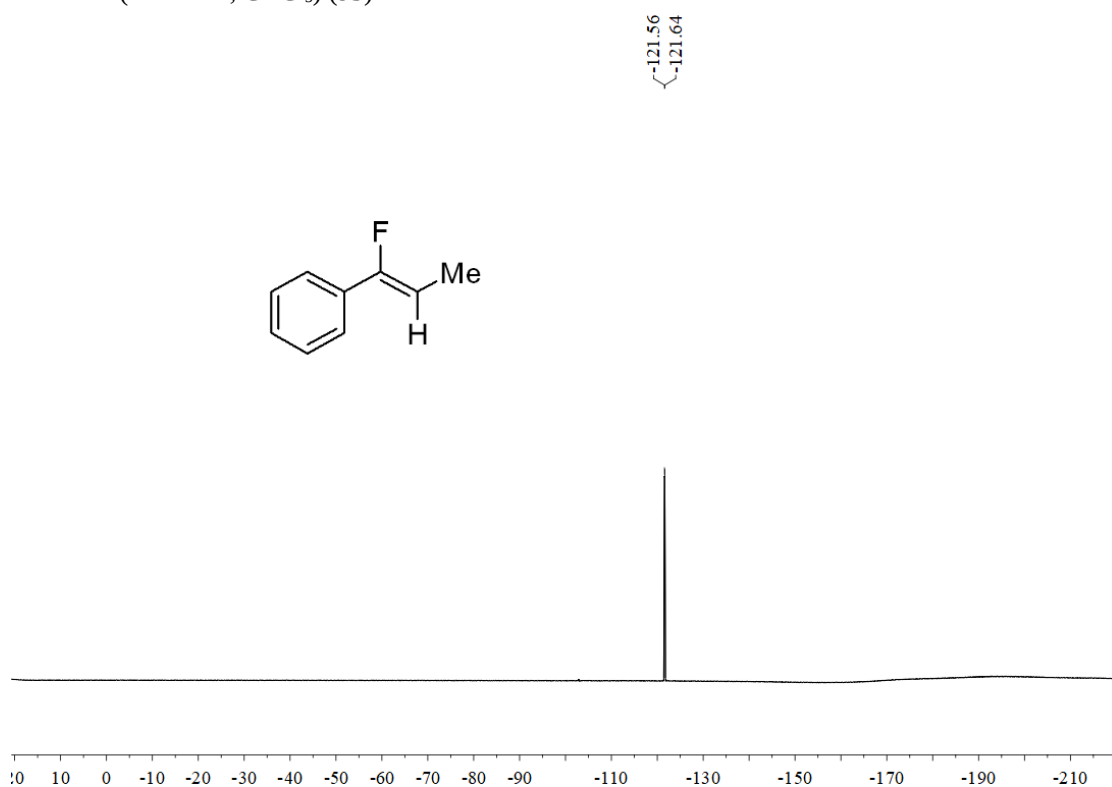
100.69, 100.54

77.25, 77.00, 76.75

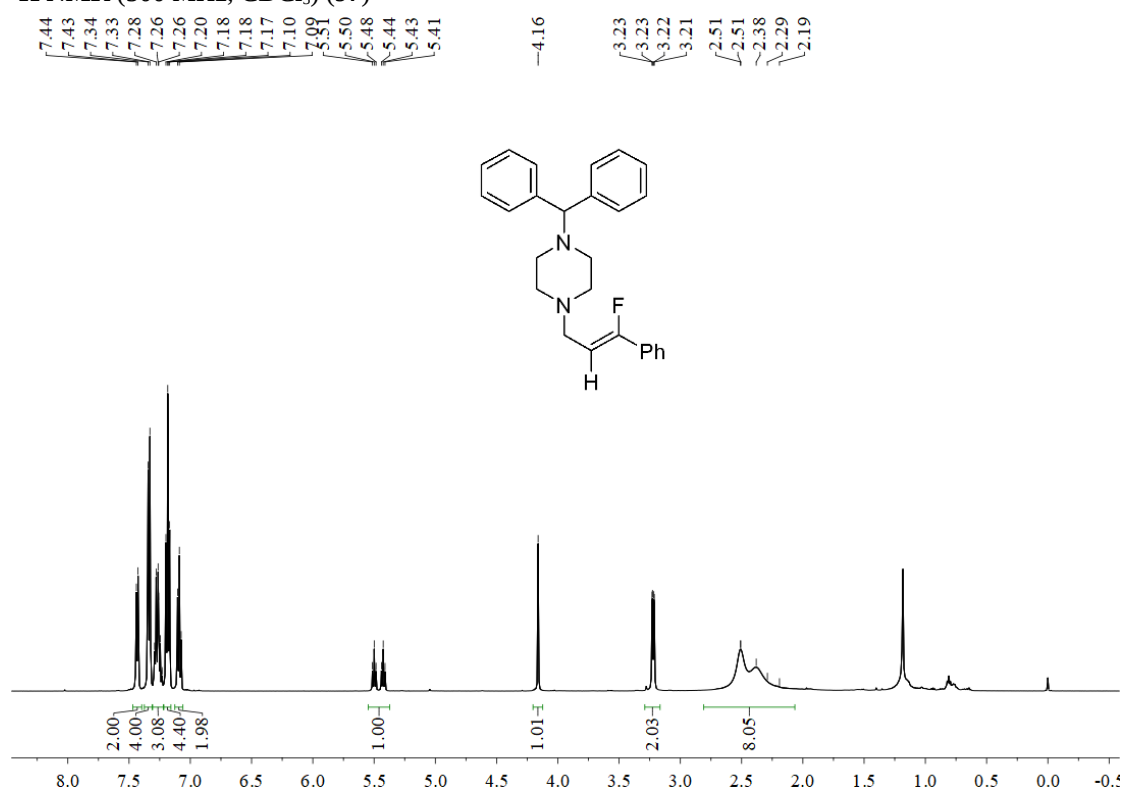
9.43, 9.37



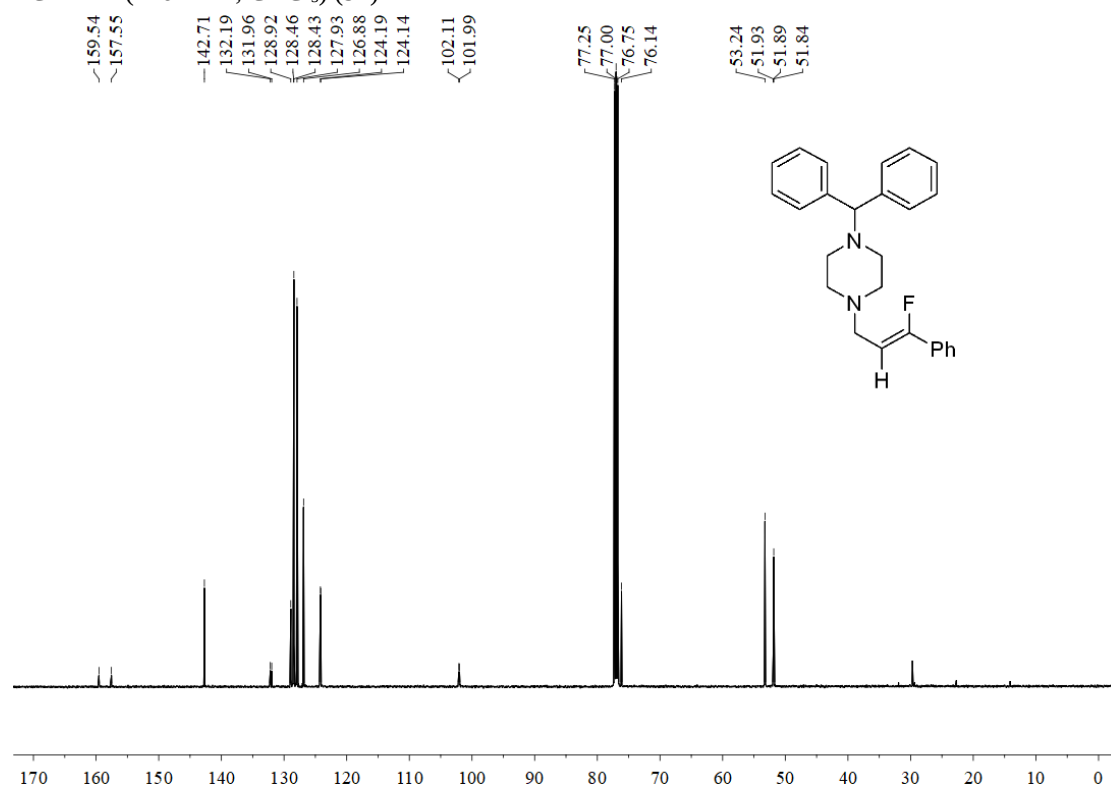
^{19}F NMR (471 MHz, CDCl_3) (95)



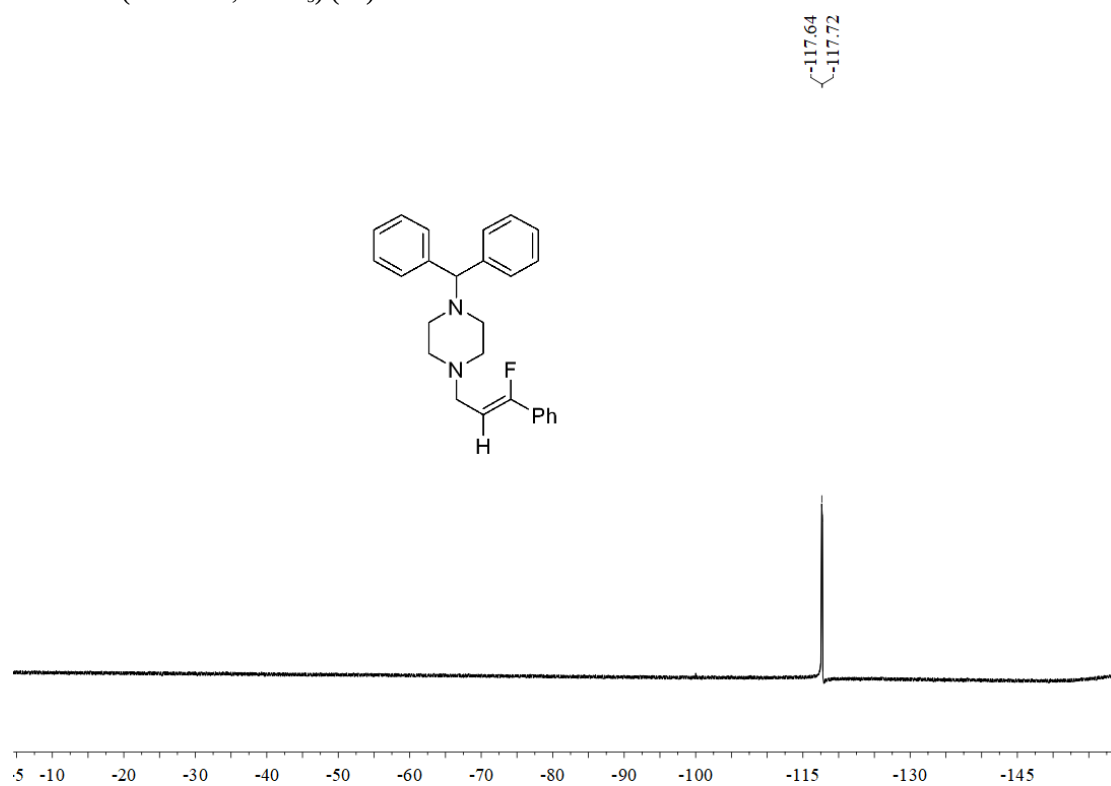
^1H NMR (500 MHz, CDCl_3) (97)



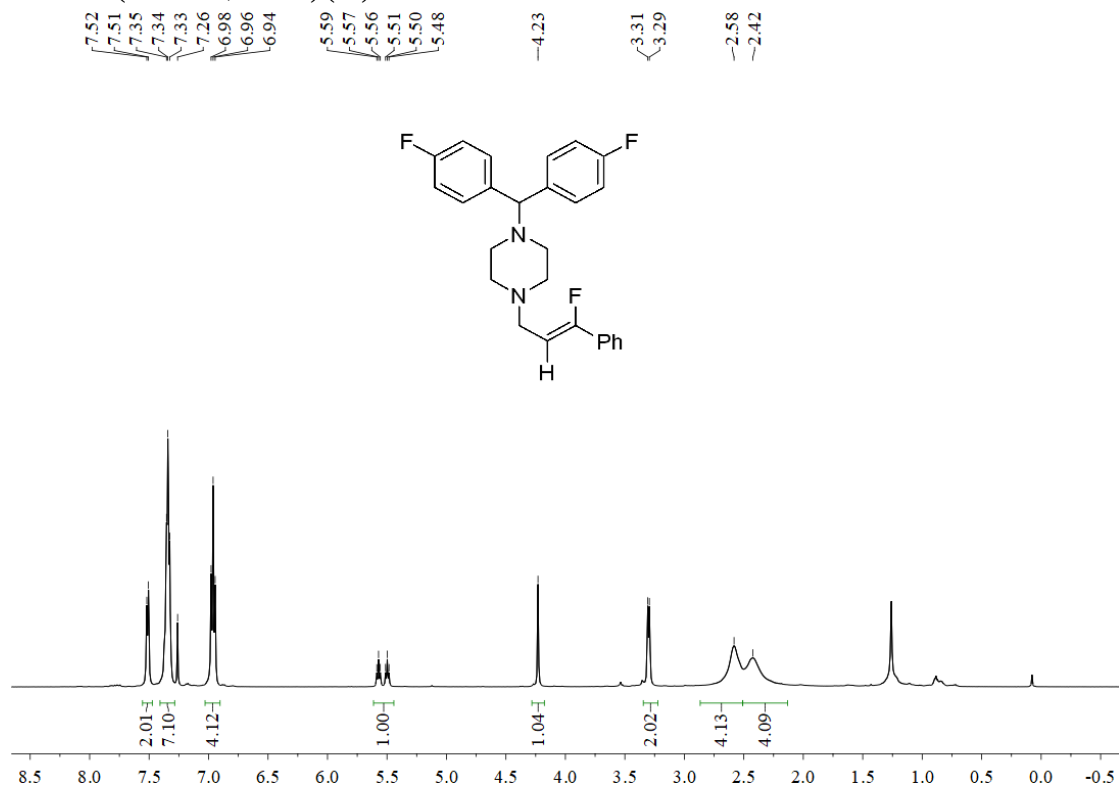
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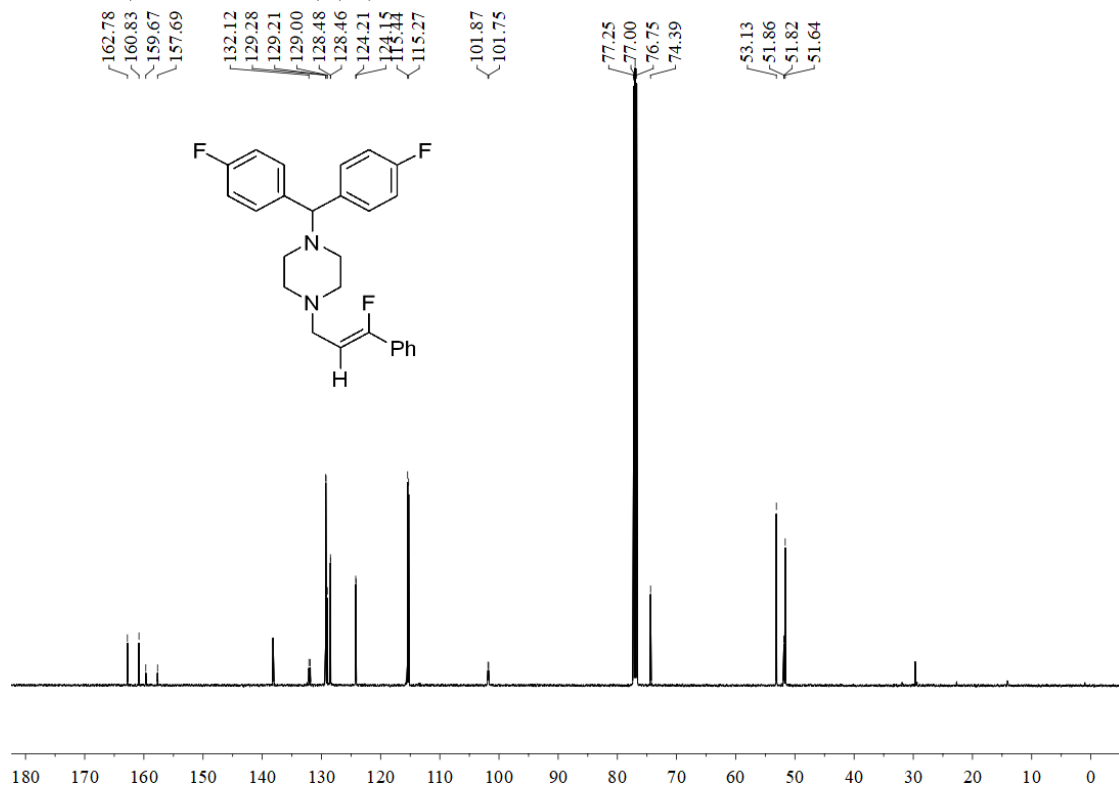
^{19}F NMR (471 MHz, CDCl_3) (97)



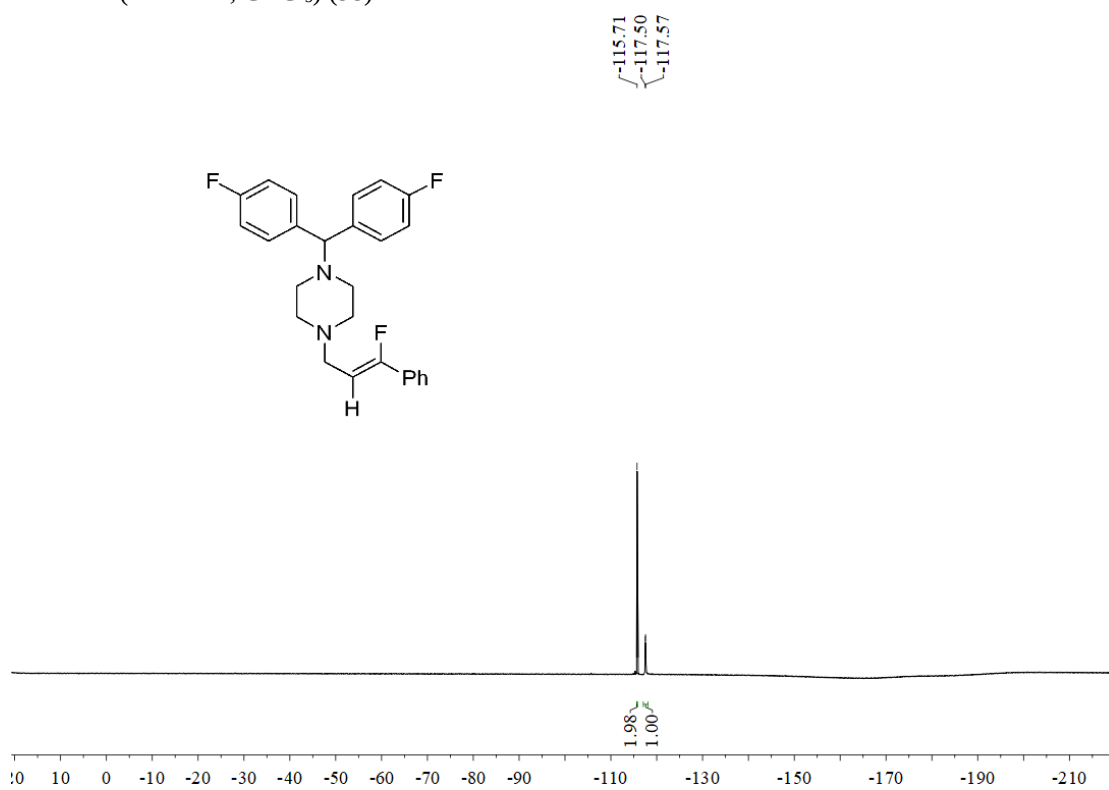
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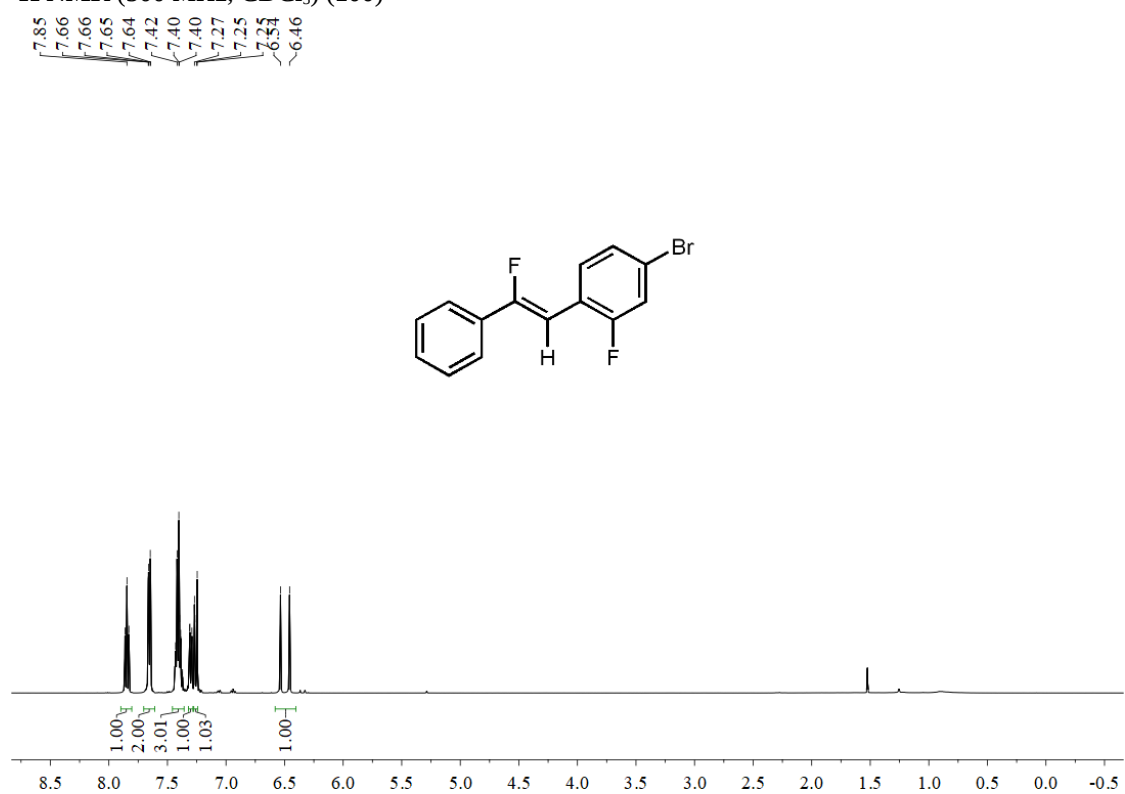
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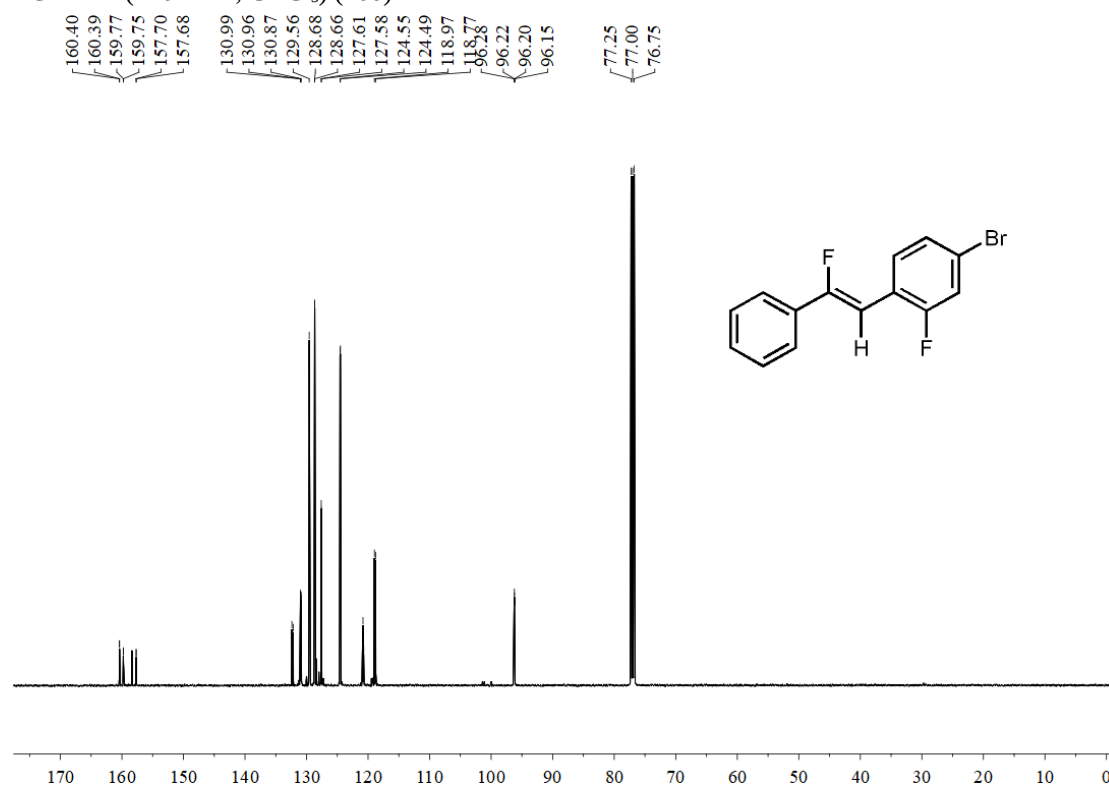
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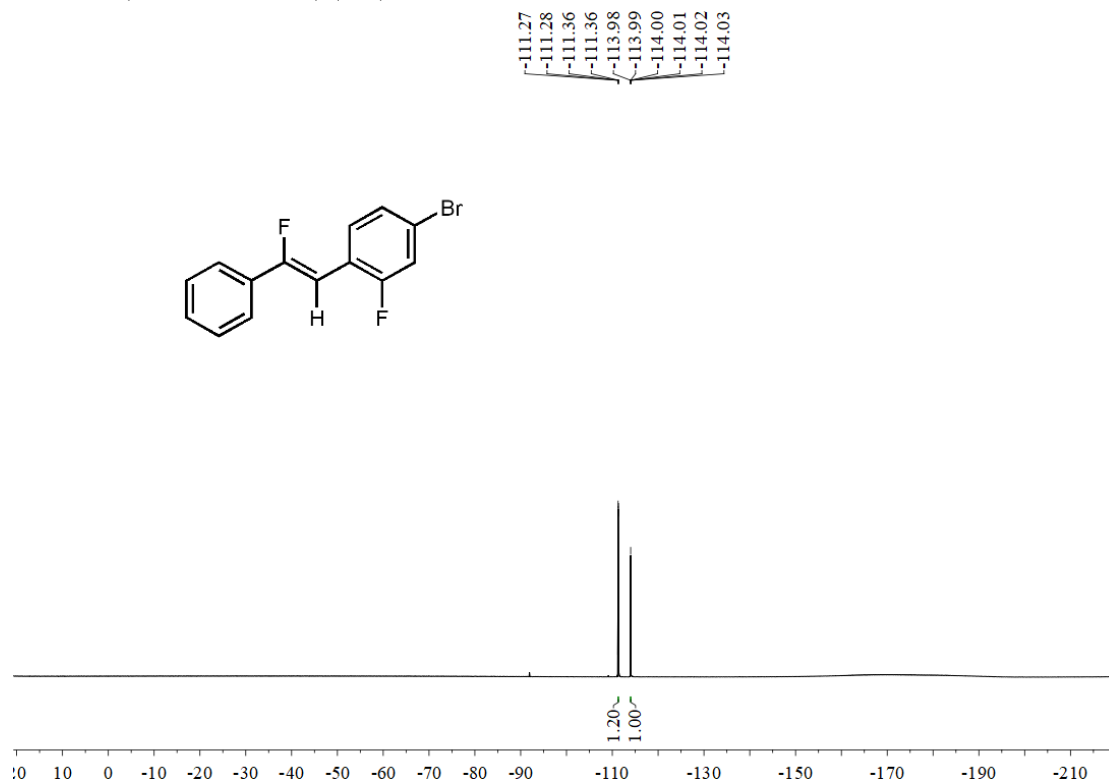
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^{13}C NMR (126 MHz, CDCl_3) (100)



^{19}F NMR (471 MHz, CDCl_3) (100)



SI-exp _ DFT.docx (21.61 MiB)

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1 **Stereodivergent alkyne hydrofluorination using a simple practical reagent**

2 Rui Guo[#], Xiaotian Qi[#], Hengye Xiang, Paul Geaneotes, Ruihan Wang, Peng Liu* and
3 Yi-Ming Wang*

4
5 Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260,
6 United States

7 *Corresponding author. E-mail: ym.wang@pitt.edu, pengliu@pitt.edu
8

9 **Abstract: Vinyl fluorides play an important role in drug development as they**
10 **serve as bioisosteres for peptide bonds and are found in a range of biologically**
11 **active molecules. The discovery of safe, general and practical procedures to**
12 **prepare vinyl fluorides remains an important goal and challenge for synthetic**
13 **chemistry. Here we introduce an inexpensive and easily-handled reagent and**
14 **report simple, scalable, and metal-free protocols for the regioselective and**
15 **stereodivergent hydrofluorination of alkynes to access both the *E* and *Z* isomers**
16 **of vinyl fluorides. These conditions were suitable for a diverse collection of**
17 **alkynes, including several highly-functionalized pharmaceutical derivatives.**
18 **Mechanistic and DFT studies support C–F bond formation through a vinyl**
19 **cation intermediate, with the (*E*)- and (*Z*)-hydrofluorination products forming**
20 **under kinetic and thermodynamic control, respectively.**

21
22 The incorporation of fluorine into organic compounds plays a significant role in the
23 pharmaceutical and agrochemical sciences, due to its distinctive capability for
24 modulating the physical and chemical properties of a biologically active scaffold,
25 including solubility, metabolic stability, potency, and bioavailability^{1,2}. Among them,
26 vinyl fluorides are privileged structures that notably serve as bioisosteres of peptide
27 bonds, mimicking their charge distribution and dipole moment (Fig. 1A)³.

28 Previous synthetic approaches to vinyl fluorides have primarily employed
29 olefination reactions and elimination reactions which require multistep

transformations and the preparation of prefunctionalized fluorinated substrates^{4,5}. One direct approach for vinyl fluoride synthesis involves the coupling of fluoride ion with vinyl triflates catalyzed by biaryldialkylphosphine complexes of palladium (Fig. 1B, a)⁶. The metal-catalyzed and noncatalytic fluorination of vinyl metal species under oxidative conditions constitutes another approach (Fig. 1B, b)⁷⁻¹⁶. Finally, the dehydrative fluorination of ketones using difluorosulfur(IV) reagents has been reported in the patent literature (Fig. 1B, c)¹⁷. A more direct method to access vinyl fluorides is the hydrofluorination of alkynes, substrates that are easily accessed from a variety of commercially available starting materials. Several strategies for the hydrofluorination of alkynes have been developed in recent years¹⁸⁻²⁶. These have included the coinage metal-catalyzed hydrofluorination of alkynes using various Lewis base adducts of hydrogen fluoride (Fig. 1B, d)¹⁸⁻²⁵. Although these approaches allow for the preparation of various vinyl fluorides, the corrosivity of HF-based reagents, the inaccessibility or complexity of metal-based catalysts and ligands, and challenges in controlling *E/Z*-selectivity and regioselectivity may limit their applicability and scalability. Consequently, the development of operationally simple methods and practical reagents for accessing vinyl fluorides with control of regio- and stereochemistry remains an ongoing challenge.

Considering their low cost, high fluoride content, as well as excellent safety, stability, and handling profiles, tetrafluoroborate (BF_4^-) salts are particularly attractive and efficient sources of nucleophilic fluoride²⁷. However, aside from the well-developed Balz-Schiemann process, they have seldom been employed in the formation of $\text{C}(\text{sp}^2)\text{-F}$ bonds due to the weak nucleophilicity of the species, and known methods often require the use of exotic functional groups or strongly oxidizing conditions²⁸. Given previous reports of alkyne hydrohalogenation that proceed via either the concerted $\text{Ad}_{\text{E}3}$ mechanism or an $\text{Ad}_{\text{E}2}$ mechanism featuring a vinyl cation intermediate²⁹, we hypothesized that a partially or wholly protonated alkyne could be sufficiently electrophilic to enable the use of tetrafluoroborate as a nucleophilic fluorinating reagent. Therefore, we posited that an acidic source of tetrafluoroborate

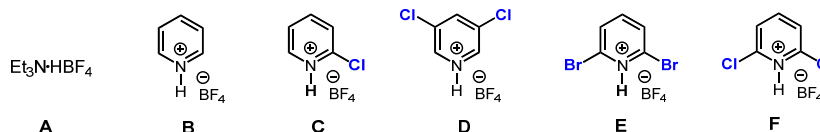
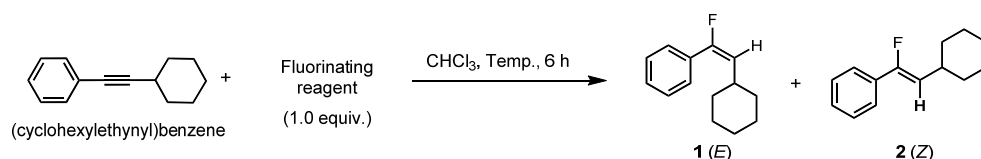
Moreover, we expect the acidity, and thus, the reactivity of such a reagent to be tunable through the variation of the protonated weak base. From the point of view of cost and availability, such a reagent would be nearly ideal for the hydrofluorination of alkynes, provided that the hydrofluorination reactions would proceed with functional group tolerance and control over the regiochemical and stereochemical outcomes. Here, we report the discovery and development of a simple and practical reagent for the stereodivergent hydrofluorination of alkynes, in many cases with excellent control of the regio- and stereoselectivity (Fig. 1C). Thus, for certain substitution patterns, we report complementary conditions for the synthesis of either the *E* or *Z* isomer of the hydrofluorination product with good to excellent *E/Z* ratios. The conditions reported here are tolerant of a variety of functional groups, and we applied them to the late-stage functionalization of drug derivatives (Fig. 1D). A mechanistic study of the process was performed through kinetics experiments and density functional theory (DFT) calculations. These studies support the intermediacy of vinyl cations in the hydrofluorination. They also provide insight into the excellent stereochemical control and accounts for the ability to selectively obtain the *E* or *Z* isomer through the variation of reagent and reaction conditions. Previously, vinyl cations have been generated through several approaches³², including metal catalysis^{33,34}, photochemical processes³⁵, ionization of vinyl iodonium³⁶ and diazonium species³⁷, (pseudo)halide abstraction with Lewis acids^{38,39}, as well as protonation of alkynes with strong Brønsted acid⁴⁰⁻⁴². In spite of the challenging and specialized conditions that are often required for their generation, the versatility of this intermediate has led to a recent renaissance in their synthetic applications⁴³. In this context, the hydrofluorination conditions reported here represent an unprecedentedly mild, stereocontrolled, and functional group compatible approach for utilizing these intermediates.

Results and discussion

Reaction development. We commenced the exploration of our hydrofluorination strategy using (cyclohexylethynyl)benzene as a starting material, considering the lack of literature precedent employing secondary alkyl-substituted phenylacetylenes as

103 substrates for hydrofluorination (Table 1). We anticipated that the corresponding
104 amine salts of HBF_4 could adjust the acidity and release HBF_4 slowly to avoid the
105 decomposition of alkynes or the generation of ketone side product. A diverse range of
106 amine salts of HBF_4 was evaluated. While it was found that reagents based on
107 triethylamine (**A**), pyridine (**B**), and 2-chloropyridine (**C**) were unreactive in CHCl_3 at
108 room temperature or $70\text{ }^\circ\text{C}$ (entries 1-3), we found that the more electron-poor
109 3,5-dichloropyridinium salt provided a trace of the desired product (entry 4).
110 Continuing with more electron-deficient pyridinium salts, we found that the
111 2,6-dihalopyridinium salts (**E** and **F**) were more efficient reagents, with the more
112 electron-deficient chlorinated reagent providing the desired product with good yield
113 and excellent stereoselectivity ($Z/E > 50:1$, entry 6). We did not detect any
114 *gem*-difluoride product from continued hydrofluorination of the monofluoroalkene, a
115 process that could not be avoided under previous conditions using pyridine/HF or
116 DMPU/HF^{30,31}. Further improving upon these promising results, we found that yields
117 could be enhanced by using LiBF_4 (25 mol %) as an inexpensive additive (entry 7 vs.
118 entry 8). Among a collection of pyridinium salts examined, we found that
119 2,6-dichloropyridinium tetrafluoroborate (**F**), prepared on large scale (50 mmol) by
120 protonation of the pyridine with commercially available $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, possessed the
121 best reactivity and handling properties, including excellent crystallinity and low
122 hygroscopicity. In particular, **F** could be stored as a colorless solid in the desiccator
123 for at least a week or in the glovebox indefinitely (> 3 months) without noticeable
124 deterioration or loss of activity. Lastly, we examined $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ as another potential
125 reagent. Surprisingly, we found that treatment of the model substrate with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$
126 (1.0 equiv) at room temperature for 6 hours resulted in the formation of desired
127 hydrofluorination product **1** in moderate yield (42% yield) and good selectivity for the
128 *opposite* stereoisomer ($E/Z = 11:1$).

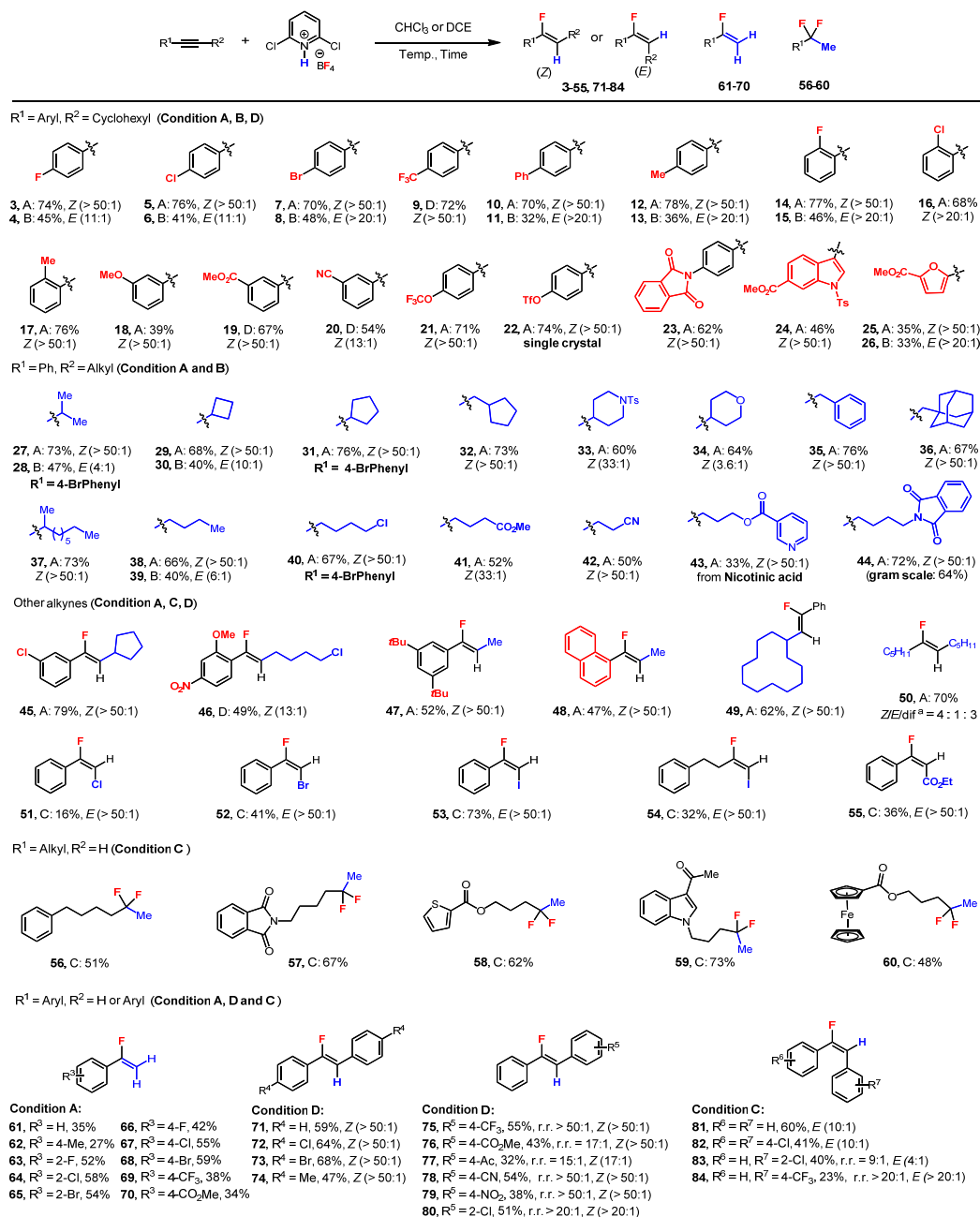
129 **Table 1. Optimization of reaction conditions for hydrofluorination**



| Entry | Fluorinating reagent | Temp./°C | Yield/% | Z/E |
|-------|--|----------|---------|----------|
| 1 | A | 70 | 0 | — |
| 2 | B | 70 | 0 | — |
| 3 | C | 70 | 0 | — |
| 4 | D | 70 | < 5 | 1 : 5 |
| 5 | E | 70 | 45 | > 50 : 1 |
| 6 | F | 70 | 74 | > 50 : 1 |
| 7 | F | 70 | 82(76) | > 50 : 1 |
| 8 | $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ | r.t. | 42 | 1 : 11 |

The substrate scope. Under these optimized conditions, we set out to investigate the scope of this hydrofluorination reaction (Table 2). Using reagent **F** for hydrofluorination, aryl alkyl acetylenes bearing electron-withdrawing (e.g., products **9**, **19**, **20**, **22**) to electron-donating (e.g., products **23**, **24**, **25**) aryl substituents reacted effectively to afford the (Z)-configured fluoroalkene products in moderate to good yields and excellent regio- and stereoselectivities. Moreover, several common functional groups on the aryl ring including methyl ester (**19**), cyano group (**20**), trifluoromethanesulfonyl ester (**22**), and phthalimide (**23**) were tolerated. Heteroaryl alkyl acetylenes, including an indole and a furan likewise delivered the desired product (**24**, **25**). We determined the structure of the product **22** by X-ray single-crystal diffraction structure analysis for confirmation of the alkene stereochemistry.

Table 2. Substrate scope of alkynes



144

145 Condition A: fluorinating reagent **F** (1.0 equiv), LiBF₄ (25 mol%), CHCl₃ (0.2 M), 70 to 90 °C. Condition B:
 146 HBF₄·Et₂O (1.0 equiv), CHCl₃ (0.2 M), r.t., 6 h. Condition C: fluorinating reagent **F** (3.0 equiv), CHCl₃, 80 to
 147 100 °C, 12 h. Condition D: fluorinating reagent **F** (2.0 equiv), DCE, 70 to 100 °C, 12 h.
 148 ^a*gem*-difluoroalkane. See supporting information for detailed conditions.

149 We next explored the scope of alkyl substituents on the substrate. A range of
 150 primary, secondary, cyclic or acyclic alkyl-substituted alkynes could be employed in
 151 the hydrofluorination to furnish respective products again with moderate to good
 152 yields and excellent regio- and stereoselectivities (**27-39**). Remarkably, substrates

153 with several functional groups including primary chloro, carboxymethyl, cyano,
154 pyridyl, and phthalimido groups could also be used to deliver monofluoroalkene
155 products which highlighted the mildness of the conditions and the good functional
156 group tolerance of this protocol (**40-46**). This process was also demonstrated by the
157 gram-scale preparation of **44** with unchanged regio- and stereoselectivities and only
158 slightly reduced yield (1.65 g, 64%). The protocol was insensitive to steric effects on
159 the alkyl substituent, with a methyl group (**47, 48**) and a cyclododecyl (**49**) group
160 giving similar yields, with no loss in regio- and stereoselectivities. It is noteworthy
161 that in all reactions employing aryl-substituted alkynes, the monofluoroalkene
162 products were delivered with exclusive regioselectivity, with C–F bond formation
163 occurring adjacent to the aryl group. These results were complementary to the
164 gold-catalyzed hydrofluorination which delivers the fluorine to the carbon adjacent to
165 the alkyl group¹⁸⁻²³. However, a reduction in selectivity was observed for a
166 dialkylacetylene substrate, which gave the *gem*-difluoroalkane in addition to the
167 monofluorinated product (**50**). A variety of 1-haloalkynes (I > Br > Cl in reactivity)
168 and ethyl phenylpropiolate were also suitable substrates for this reaction, in which a
169 single regio- and stereoisomer was produced in each case (**51-55**). During the course
170 of optimization, we found that tetrafluoroboric acid in diethyl ether (HBF₄•Et₂O)
171 could also deliver hydrofluorination product. However, the predominant stereoisomer
172 formed under these conditions was the *E* isomer. With commercially available reagent,
173 we briefly explored the substrate scope of these conditions (condition B). Substrates
174 bearing mildly electron-withdrawing or electron-donating substituents could afford
175 the monofluoroalkene products with moderate to good *E*-selectivity (*E/Z* ratio from
176 4:1 to > 20:1).

177 The hydrofluorination reaction could also be applied to terminal alkynes and
178 diarylacetylenes. When using terminal alkyl-substituted alkynes as substrate
179 *gem*-difluorides were obtained as the primary product with exclusive internal
180 regioselectivity. A variety of functional groups such as an amide, an ester, an indole,
181 as well as a ferrocene derivative were well tolerated (**56-60**). On the other hand,

terminal aryl-substituted alkynes could be employed in this hydrofluorination to give the corresponding monofluoroalkene as the major product with moderate yields (61-70). With 1,2-dichloroethane as the solvent, diarylacetylenes could give corresponding monofluoroalkene products in modest to good yields and excellent *Z*-selectivities (71-74). For unsymmetrical substrates, when one of the benzene rings was substituted by an electron-withdrawing group (e.g., 4-CO₂Me, 2-Cl), the hydrofluorination product proceeded with excellent *Z*-selectivities and regioselectivity for fluorination nearer to the more electron-rich aryl group (75-80). Finally, it was found that by switching to chloroform as the solvent, the monofluoroalkene product could be formed with *E*-selectivity (81-84).

Synthetic applications. To demonstrate the potential applicability of this new hydrofluorination method to the late-stage modification of biologically active molecules or complex natural products, we explored several readily available alkynes derived from the complex structure molecules *exo*-norborneol (85) and ferrocene (86), natural products (1*S*)-(+)-10-camphorsulfonic acid (87) and estrone (88, 89), as well as drug molecules probenecid (90), febuxostat (92) and telmisartan (94) to afford monofluoroalkene products with moderate to good yields and high regio- and stereoselectivities (Fig. 2a). In addition, terminal alkyl-substituted alkynes derived from drug molecules probenecid and febuxostat could also be employed in the dihydrofluorination to form *gem*-difluorides with moderate yields and exclusive regioselectivity (91, 93). These examples demonstrated that our hydrofluorination and difluorination protocols were suitable for the late-stage, protecting-group-free modification of biologically active molecules and could tolerate a range of functional groups and heterocycles including ketones (87-89), esters (90-94), a ferrocene (86), a sulfonate (87), a sulfonamide (90, 91), a nitrile (92, 93), a thiazole (92, 93), and benzimidazoles (94).

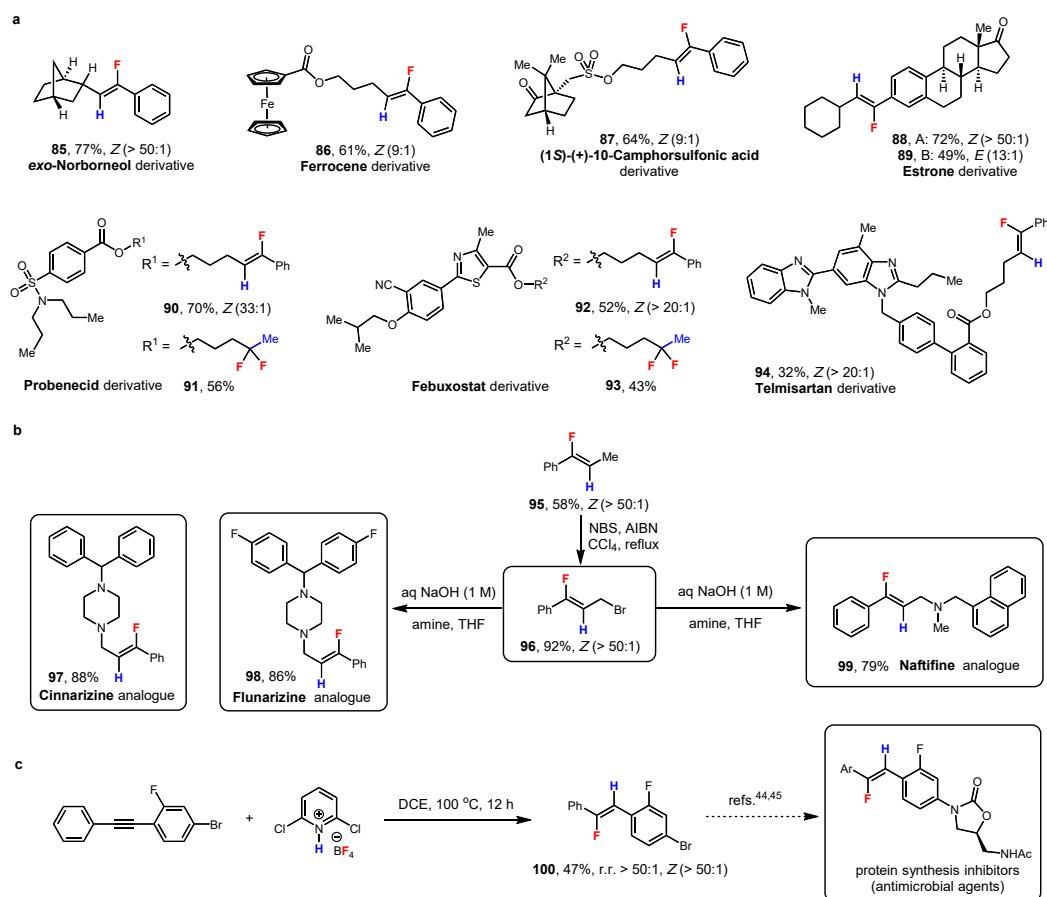


Fig. 2. Synthetic applications of stereodivergent alkyne hydrofluorination. **a**, The late-stage modification of biologically active molecules or complex natural products. **b**, The synthesis of different fluorinated analog of drug molecules. **c**, The preparation of key intermediate for the synthesis of antimicrobial agents with high regio- and *Z/E*-selectivities. See supporting information for detailed conditions.

To explore other applications of this chemistry, we prepared **95** on 5-mmol scale to access fluorinated analogues of antihistamines cinnarizine (**97**), flunarizine (**98**) and antifungal drug naftifine (**99**) (Fig. 2b). Via bromination of **95**, we prepared a common brominated intermediate **96**, which could be applied to synthesize all three analogues. Moreover, we also prepared vinyl fluoride **100**, a known precursor for the synthesis of antimicrobial agents (protein synthesis inhibitors) through the coupling with 2-oxazolidone (Fig. 2c)^{44,45}. These transformations illustrated in above study demonstrated the great potential of this method for industrial applications in the future.

Mechanistic discussion. The experimental results have demonstrated that 2,6-dichloropyridinium tetrafluoroborate is an effective fluorinating reagent for stereodivergent alkyne hydrofluorination. As shown in Table 2, high levels of *Z*-selectivity are obtained in a polar solvent (*i.e.* DCE, condition D), while reactions in a less polar solvent (*i.e.* chloroform, condition C) or under lower temperatures (see SI) completely switch the stereoselectivity to favor *E*-products. Mechanistic studies were then performed to investigate whether the hydrofluorination occurs through a concerted or stepwise mechanism and the origin of the divergent stereoselectivity. DFT calculations⁴⁶ of the hydrofluorination of 1,2-diphenylacetylene **101** indicated a stepwise Ad_E2-type protonation-fluorination mechanism with a BF₄[−]/vinyl cation ion-pair intermediate (Fig. 3a). Prior to the alkyne protonation, the H⋯F hydrogen bond in the fluorinating reagent **F** dissociates to release a free pyridinium cation as the proton source. Two protonation transition states were located (**TS-1** and **TS-1a**), in which the tetrafluoroborate anion is *syn* and *anti* to the pyridinium, respectively. Bonding interactions between BF₄[−] and the alkyne were not observed in either protonation transition state, which is likely due to the weak nucleophilicity of BF₄[−]. The stepwise hydrofluorination mechanism is confirmed by the intrinsic reaction coordinate (IRC) calculations, which indicated that **TS-1** and **TS-1a** lead to BF₄[−]/vinyl cation ion pairs **102** and **102a**, respectively, rather than the hydrofluorination products. Fluorination of the highly electrophilic vinyl cation with BF₄[−] (via **TS-2** and **TS-2a**) is very facile, which makes protonation (**TS-1**) the rate-determining step. This mechanistic picture is consistent with experimental Hammett analysis and kinetics studies, which indicated a ρ value of −3.43 consistent with previously reported vinyl cation-mediated reactions³² and first-order kinetics in alkyne and H⁺ and zero-order kinetics in excess BF₄[−] (Fig. 3d, see SI for details). The *E*-selective pathway (shown in black in Fig. 3a) is kinetically favored in both protonation and fluorination steps. The *syn*-protonation transition state **TS-1** is more stable than the *anti*-TS (**TS-1a**) due to more favorable electrostatic interactions between BF₄[−] and the pyridinium cation. The *E*-selective fluorination transition state **TS-2** is 0.9 kcal/mol more stable than the *Z*-selective fluorination (**TS-2a**) because of

steric repulsions between BF_4^- and the β -phenyl group in **TS-2a**⁴⁷. Therefore, regardless of whether ion pairs **102** and **102a** have sufficient lifetime to interconvert prior to the fluorination, kinetic *E*-selectivity is expected. The relatively low barrier for the reverse reaction of *E*-**81** (via **TS-2**, $\Delta G^\ddagger = 23.6$ kcal/mol) to generate the vinyl cation indicates the *E*-to-*Z* vinyl fluoride isomerization may occur at elevated temperatures through BF_3 -mediated fluoride anion elimination followed by fluorination of the vinyl cation via **TS-2a**. A polar solvent would also promote such isomerization by stabilizing ion-pair intermediates **102** and **102a**. Because the *Z*-stereoisomer *Z*-**71** is 2.3 kcal/mol more stable than *E*-**71**, high *Z*-selectivity is expected under these thermodynamically controlled conditions.

The BF_3 -mediated *E/Z*-vinyl fluoride isomerization is verified experimentally under conditions with either 2,6-dichloropyridinium tetrafluoroborate or $\text{Et}_2\text{O} \cdot \text{BF}_3$ (Fig. 3b). The addition of 2,6-di-*tert*-butylpyridine did not shut down the $\text{Et}_2\text{O} \cdot \text{BF}_3$ -mediated isomerization, which excludes the possibility of Brønsted acid-promoted pathway. In addition, the increase of the *Z*-product ratio over a reaction time of 12 h at 70 °C further confirmed the isomerization of the kinetic *E*-isomer to *Z*-vinyl fluoride in the hydrofluorination of di-*p*-tolylacetylene (Fig. 3c). In certain cases, we also observed that better *Z*-selectivity could be obtained by addition of exogenous $\text{Et}_2\text{O} \cdot \text{BF}_3$ to promote *E*-to-*Z*-isomerization (*e.g.*, product **86** and **87** in Fig. 2, *Z/E* ratio from 3:1 to 9:1).

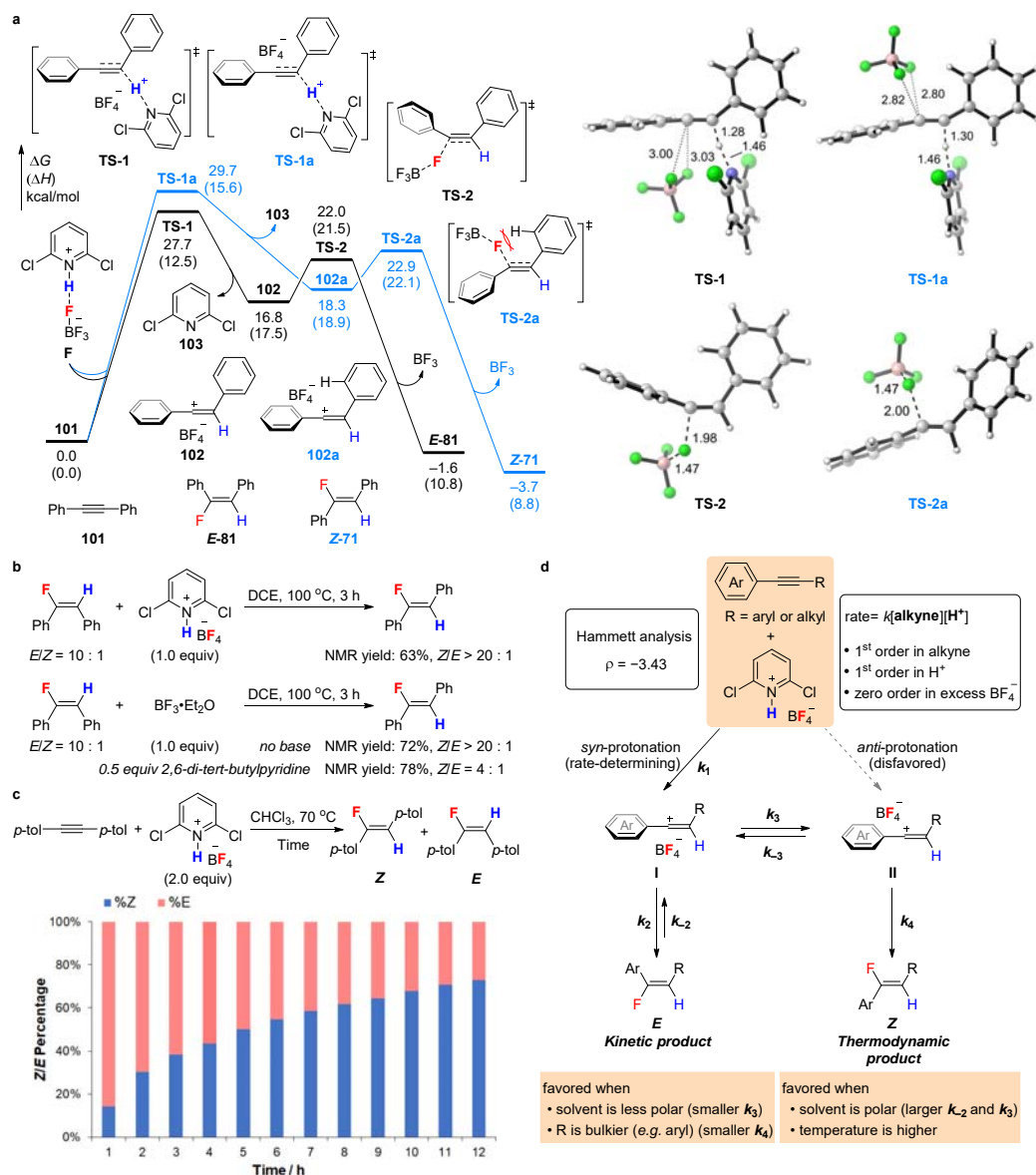


Fig. 3. Mechanistic studies. **a.** Reaction energy profiles of the hydrofluorination of 1,2-diphenylacetylene **101** with 2,6-dichloropyridinium tetrafluoroborate. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-311+G(d,p)/SMD(chloroform) level of theory. See Fig. S10 and S11 in SI for the computational results with the cyclohexyl and methyl-substituted alkynes. **b.** *E/Z*-isomerization of vinyl fluoride with fluorinating reagent **F** and $\text{Et}_2\text{O} \cdot \text{BF}_3$. **c.** Change of the *Z/E*-ratio of the hydrofluorination product over the course of reaction. **d.** Proposed mechanism for the stereodivergent hydrofluorination of alkyne.

Based on these mechanistic studies, a general mechanism is proposed to elucidate the stereoselectivity control in the alkyne hydrofluorination (Fig. 3d). The rate-determining *syn*-protonation of alkyne (k_1) leads to an ion pair intermediate (**I**), which then undergoes fluorination (k_2) to afford the kinetically favored *E*-vinyl

fluoride. The thermodynamically more stable Z-product is formed from the isomerization of the *E*-vinyl fluoride, which takes place via BF₃-mediated fluoride dissociation (k_2) and isomerization of the ion pair intermediate (k_3) followed by Z-selective fluorination with BF₄[−] (k_4). Higher temperatures and polar solvents (*e.g.* DCE) promote such *E*-to-Z isomerization, and thus enhance the Z-selectivity. Experimentally, excess BF₄[−] (condition A) was also found to favor formation of the Z-isomer (see SI), an effect which may be ascribed to increased availability of BF₄[−] for *anti*-attack (k_4) or a change in the solvent polarity due to higher ionic content. On the other hand, lower temperatures, polar solvent, and bulkier alkyne substituents (*e.g.* aryl) that suppress ion pair isomerization (k_3) and the Z-selective fluorination (k_4) would lead to higher *E*-selectivity under kinetic control.

Conclusion

We have developed a simple, practical, and metal-free strategy for the regio- and stereoselective controlled mono- and dihydrofluorination of alkynes by employing 2,6-dichloropyridinium tetrafluoroborate as a new, safe, and stable fluorinating reagent. Mechanistic and DFT studies reveal that the stereoselectivity of hydrofluorination results from either kinetic or thermodynamic control in a stepwise protonation-fluorination pathway. We anticipate that this hydrofluorination protocol will find wide applications in drug discovery and related fields by facilitating the preparation of fluorinated drug candidates. Studies further exploiting the synthetic applications of vinyl cation intermediates generated under similar mild conditions are ongoing.

Data availability

The data supporting the findings of this study are available within the paper and its Supplementary Information. The x-ray crystallographic coordinates for the structure of **22** are available free of charge from the Cambridge Crystallographic Data Centre under deposition number CCDC 1988001.

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Author contributions Y.-M.W. conceived and directed the project. R.G., H.X., P.G., and R.W. carried out all experiments. X.Q. performed the computational studies with P.L. providing guidance. Y.-M.W., P.L., R.G. and X.Q. wrote the manuscript with input of all other authors. #R.G. and X.Q. contributed equally to this work.

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Additional information

Supplementary information is available in the online version of the paper.

Correspondence and requests for materials should be addressed to Y.-M.W. or P.L.

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