Supporting Information for

Stereodivergent Alkyne Hydrofluorination Using Protic Tetrafluoroborates as Tunable Reagents

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Contents

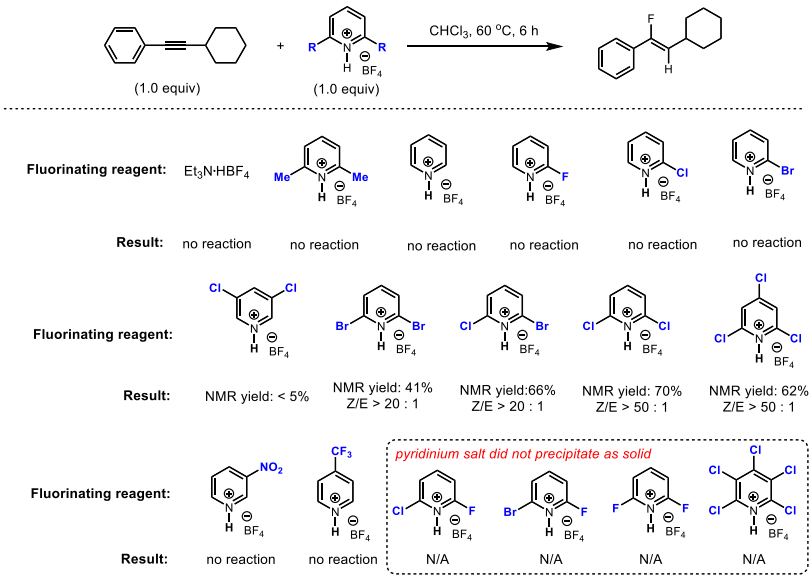
1. General Information

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.

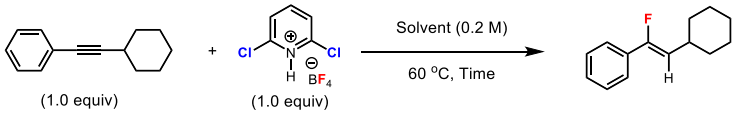
General Analytical Information: New compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 500 MHz instruments. All ^{1}H 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 ($CDCl_3$) or 5.32 ppm (CD_2Cl_2). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 39.52 ppm (DMSO-*d*6), 77.00 ppm ($CDCl_3$) or 53.84 ppm (CD_2Cl_2). 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

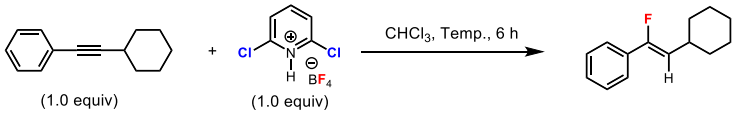


2. Optimization of solvent



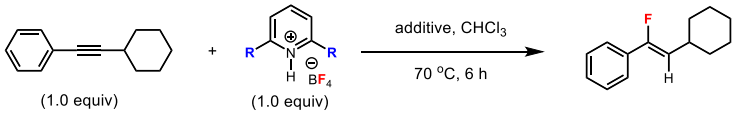
Entry	Solvent	Time (h)	NMR Yield (%)	*Z*/*E*
1	THF	6	0	—
2	*t*Butyl methyl ether	6	0	—
3	Toluene	6	21	*Z*/*E* = 1 : 1
4	PhCl	6	52	*Z*/*E* > 20 : 1
5	$PhCF_3$	6	53	*Z*/*E* > 20 : 1
6	$PhCF_3$	12	65	*Z*/*E* > 20 : 1
7	$CHCl_3$	6	70	*Z*/*E* > 50 : 1
8	DCE	6	34	*Z*/*E* > 50 : 1
9	CH_3CN	6	trace	—

3. Optimization of temperature



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

4. Optimization of additives

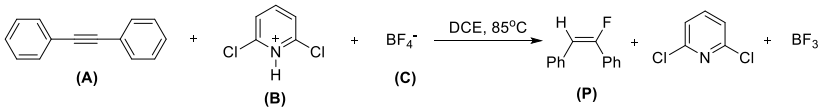


Entry	Additive	NMR Yield (%)	*Z*/*E*
1	$NaBF_4$ (1.0 eq.)	80	*Z*/*E* > 20 : 1
2	$LiBF_4$ (1.0 eq.)	81	*Z*/*E* > 20 : 1
3	$N(n\text{-}Bu)_4BF_4$ (1.0 eq.)	79	*Z*/*E* > 20 : 1
4	$N(Et)_4BF_4$ (1.0 eq.)	77	*Z*/*E* > 20 : 1
5	$LiBF_4$ (0.5 eq.)	83	*Z*/*E* > 20 : 1
6	$LiBF_4$ (0.25 eq.)	82	*Z*/*E* > 50 : 1
7	$LiBF_4$ (0.1 eq.)	79	*Z*/*E* > 50 : 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 NBu_4BF_4 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 CH_2Cl_2. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ^{19}F-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_4BF_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 concentration being varied is shown in red					

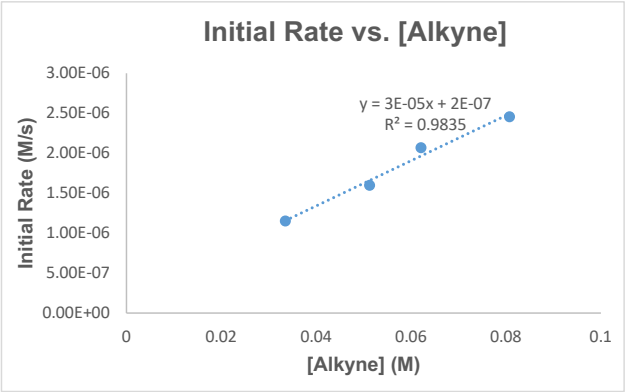


Figure S1: Plot of the initial rate of hydrofluoronation vs. the concentration of **Alkyne**.

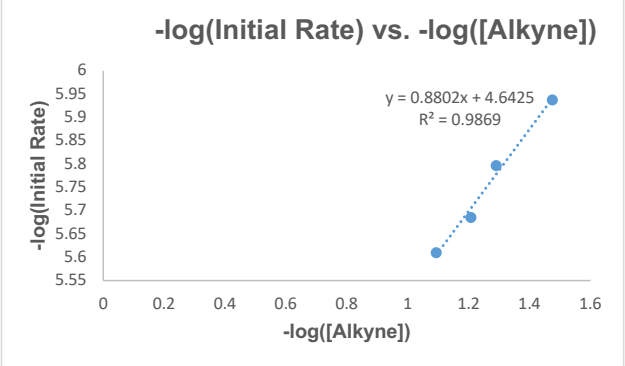


Figure S2: Plot of the minus logarithm of the initial rate of hydrofluoronation vs. the minus logarithm of the concentration of **alkyne**.

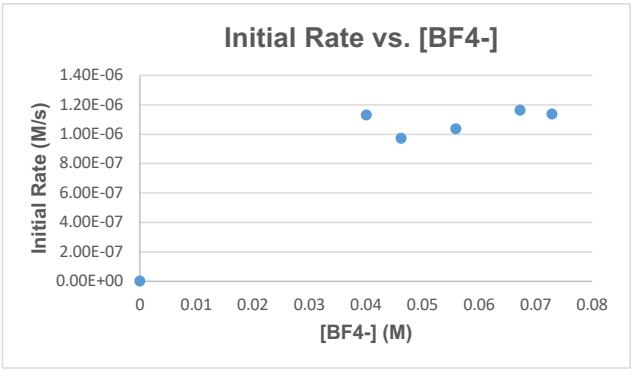


Figure S3: Plot of the initial rate of hydrofluoronation vs. the concentration of BF_4^-.

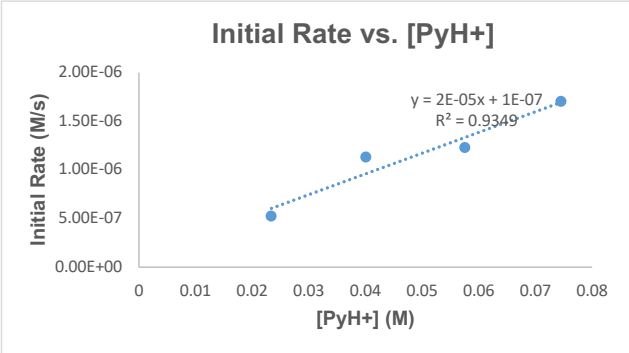


Figure S4: Plot of the initial rate of hydrofluoronation vs. the concentration of **2,6-dichloropyridine cation**.

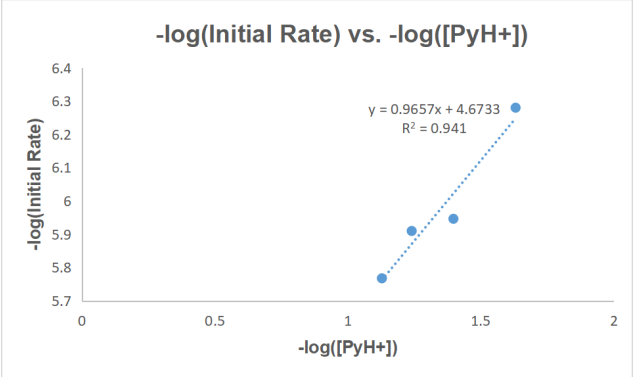
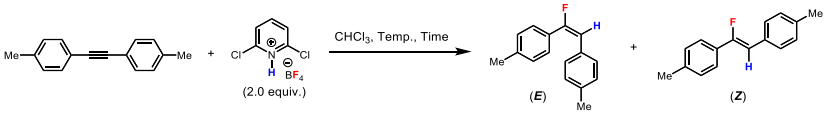


Figure S5: Plot of the minus logarithm of the initial rate of hydrofluoronation vs. the minus logarithm of the concentration of **2,6-dichloropyridine cation.**

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 $CHCl_3$ (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 CH_2Cl_2. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ^{19}F-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

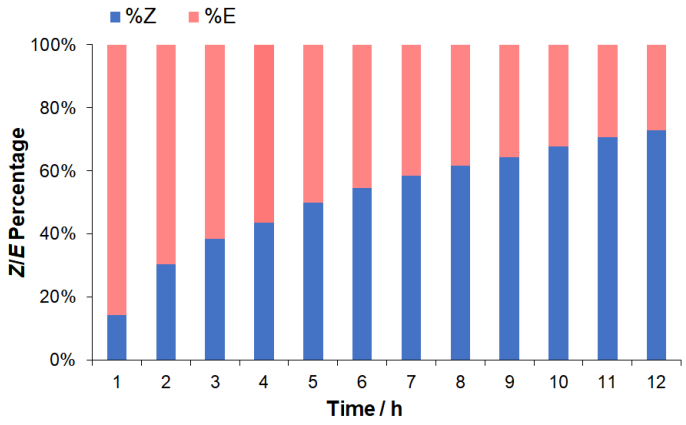


Figure S6: The *Z*/*E*-ratio of the hydrofluorination product over the course of reaction time.

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 $CHCl_3$ (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 CH_2Cl_2. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ^{19}F-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

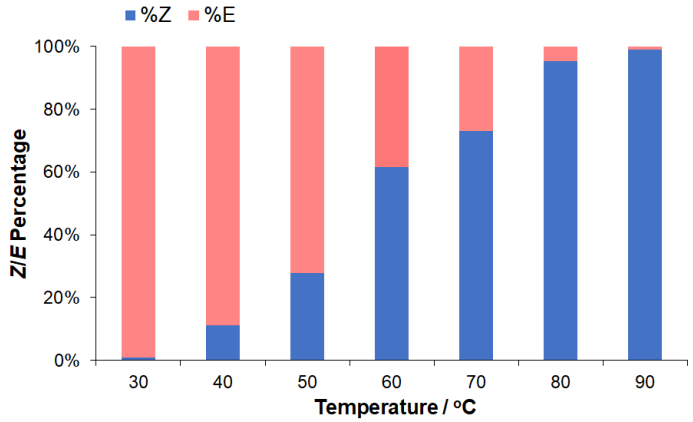
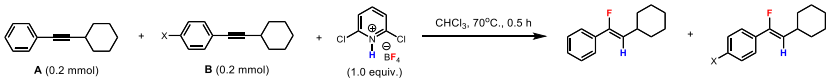


Figure S7: The *Z*/*E*-ratio of the hydrofluorination product over the course of reaction temperature.

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 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 $CHCl_3$ (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 CH_2Cl_2. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ^{19}F-NMR spectroscopy.

R	σ_p	k_X/k_H	$\log(k_X/k_H)$
4-*t*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

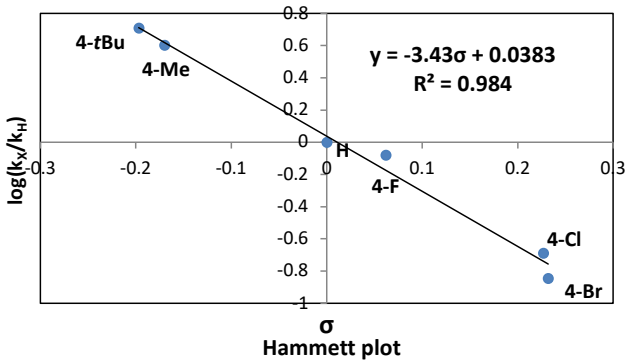
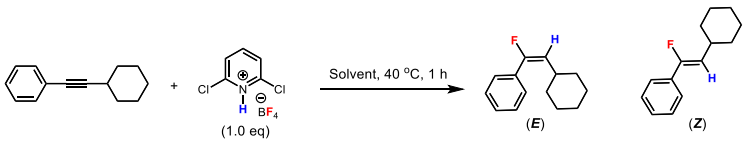


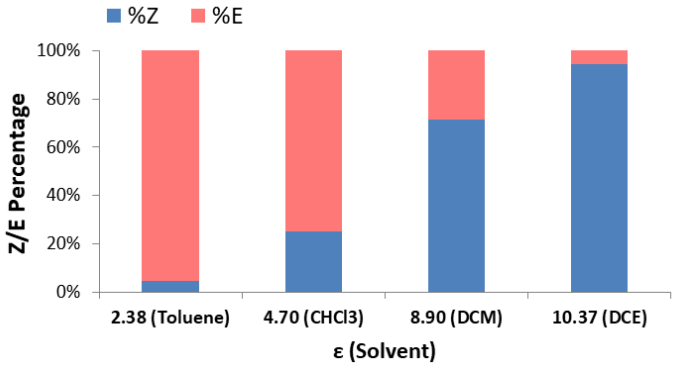
Figure S8: Hammett-plot analysis for *para*-substituted (cyclohexylethynyl)benzene.

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 CH_2Cl_2. The filtrate was concentrated *in vacuo* and benzotrifluoride was added as the internal standard for subsequent quantitative ^{19}F-NMR spectroscopy.

Solvent	**ε**	***E*/*Z***
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 16[21] software package on Pitt CRC and XSEDE[22] supercomputers. Geometries were optimized in chloroform ($CHCl_3$, ε = 4.7) with the SMD solvation model[23] using the M06-2X[24] 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 corrections[25] were applied for entropy calculations with a frequency cut-off of 100 cm^{-1} using the GoodVibes[26] program. Single point energies were calculated using M06-2X and 6-311+G(d,p) basis set in $CHCl_3$ using the SMD solvation model.

Unless otherwise noted, all the energies discussed in the main text and SI were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory. Because dichloroethane (DCE, $\varepsilon = 10.1$) was also used as the solvent in experiment, the free energy profile of the hydrofluorination of diphenylacetylene was also calculated in DCE using the same basis set and solvation model to investigate the solvent effect. In these calculations, which are summarized in Figure S15, all structures were optimized in DCE and energies were calculated at the M06-2X/6-311+G(d,p)/SMD(DCE)//M06-2X/6-31+G(d)/SMD(DCE) level of theory.

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

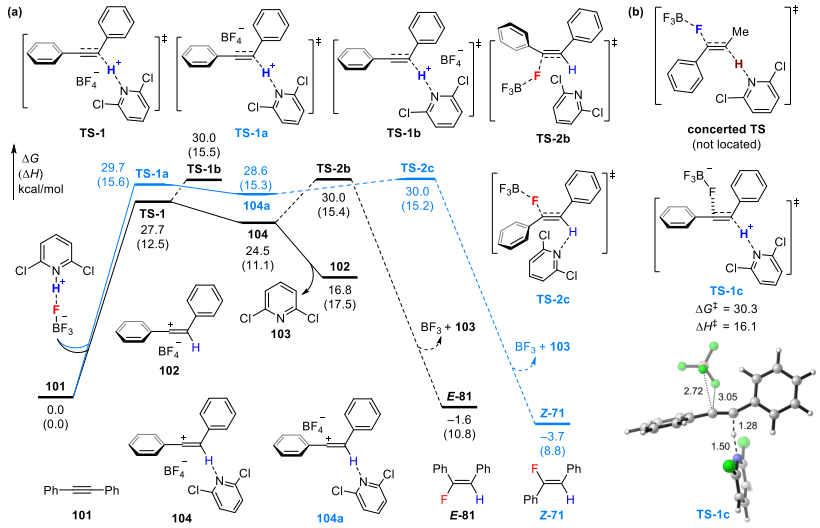


Figure S9. Free energy profiles of disfavored pathways of the hydrofluorination of 1,2-diphenylacetylene **101**. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory.

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. 1) are thus thermodynamically favored. Besides the fluorination transition states from **102** and **102a** (Fig. 1), **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 BF_4^-/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 BF_4^-, 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

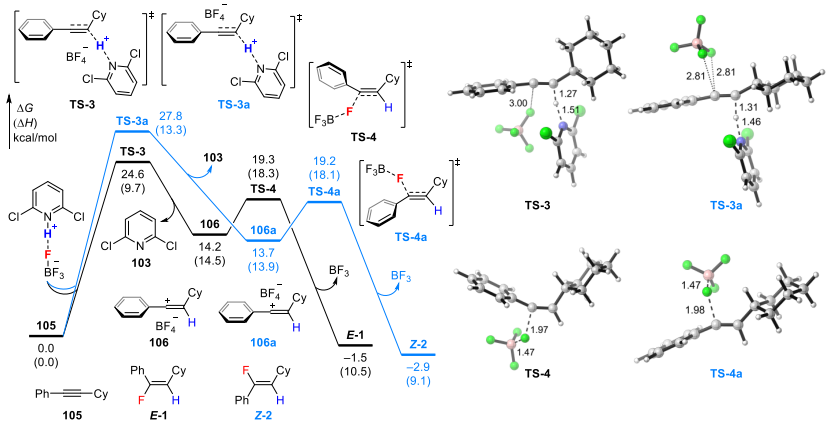


Figure S10. Reaction energy profiles of the hydrofluorination of cyclohexylphenylacetylene **105** with 2,6-dichloropyridinium tetrafluoroborate. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory.

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 BF_4^-/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 BF_4^-/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 BF_3-mediated *E*-to-*Z* vinyl fluoride isomerization is verified by control experiments with fluorinating reagent **F** and $Et_2O \bullet BF_3$ (Fig. S12). Therefore, under thermodynamically controlled conditions, high *Z*-selectivity is observed for the hydrofluorination of cyclohexyl and methyl-substituted phenylacetylene in the experiment.

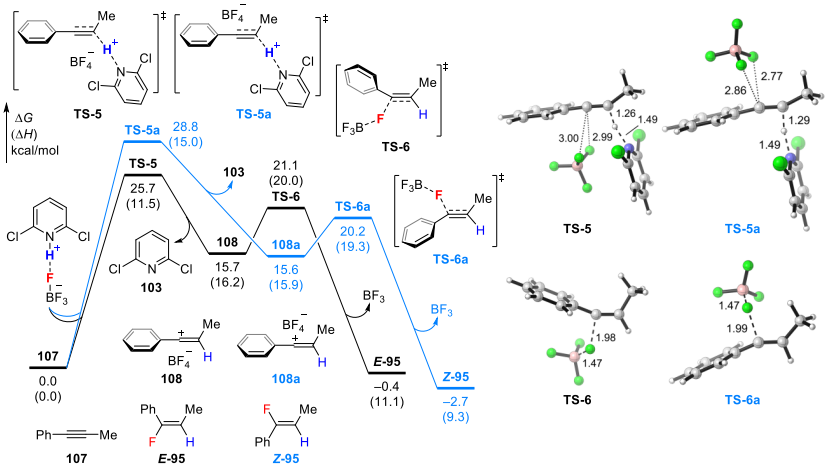


Figure S11. Reaction energy profiles of the hydrofluorination of methyl-substituted phenylacetylene **107** with 2,6-dichloropyridinium tetrafluoroborate. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(chloroform)//M06-2X/6-31+G(d)/SMD(chloroform) level of theory.

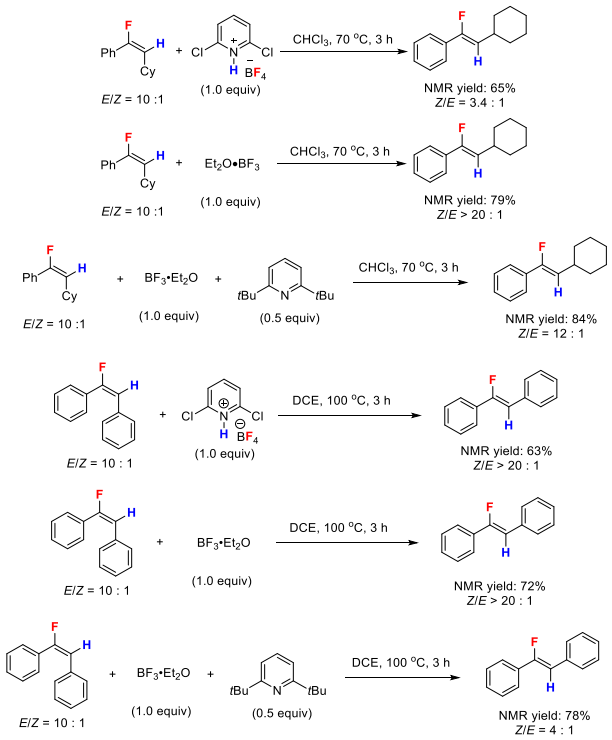


Figure S12. *E*/*Z*-isomerization of vinyl fluoride using fluorinating reagent **F** and $Et_2O{\bullet}BF_3$.

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 Scheme 4D 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. 1 (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.

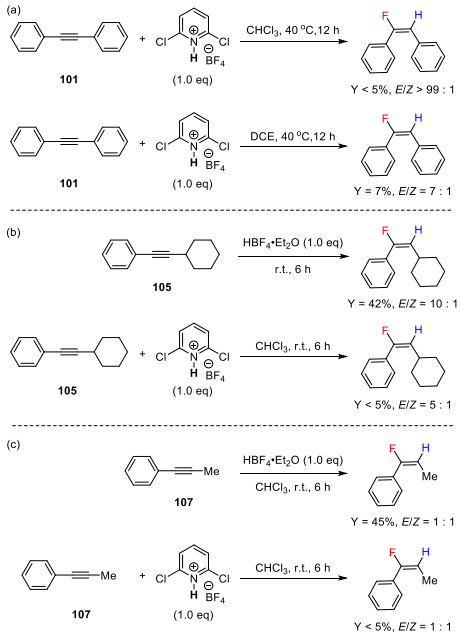


Figure S13. Comparison of *E*/*Z*-alkene ratios for different alkynes under kinetic hydrofluorination conditions.

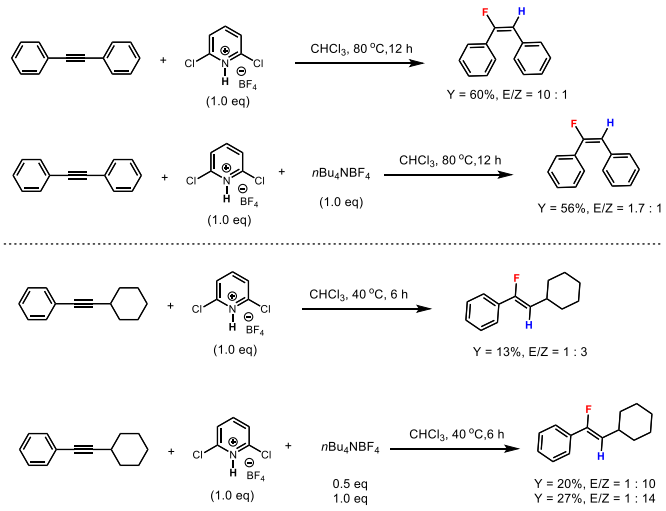


Figure S14. Comparison of *E*/*Z*-alkene ratios for adding excess BF_4^- source conditions.

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.

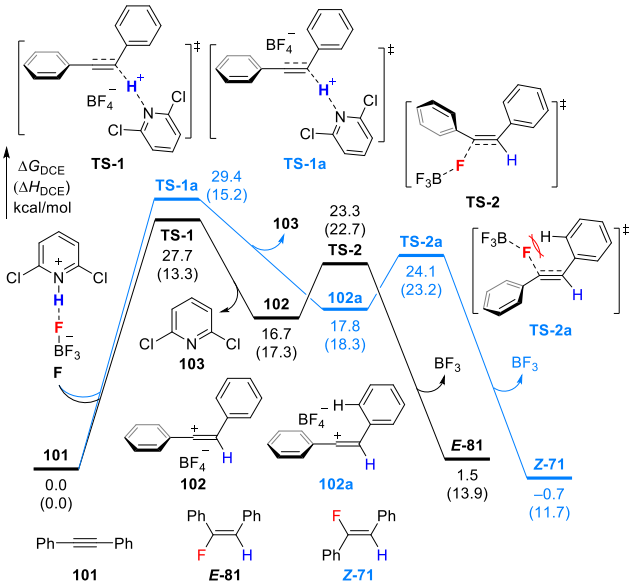


Figure S15. Reaction energy profiles of the hydrofluorination of 1,2-diphenylacetylene **101** with 2,6-dichloropyridinium tetrafluoroborate calculated in DCE. All energies were calculated at the

M06-2X/6-311+G(d,p)/SMD(DCE)//M06-2X/6-31+G(d)/SMD(DCE) level of theory.

In experiment (Table 2), high *Z*-selectivity was obtained for the hydrofluorination of 1,2-diphenylacetylene **101** in a polar solvent (DCE, condition D), while the same reaction in a less polar solvent (chloroform, condition C) favors the *E*-product. We summarized that polar solvent could promote the *E*-to-*Z* isomerization and thus enhance the *Z*-selectivity. We surmised that the more polar solvent (DCE) promotes the *E*-to-*Z* isomerization and thus favors the formation of the Z-product under thermodynamic control. To study the solvent effect, free energy profiles of the hydrofluorination of 1,2-diphenylacetylene **101** with 2,6-dichloropyridinium tetrafluoroborate were calculated in both chloroform (Fig. 1) and in DCE (Fig. S15). The reactions in DCE and chloroform occur via the same mechanism and have the same kinetic selectivity that favors E-products when reactions are under kinetic control. The overall hydrofluorination reaction in DCE was found to be less exothermic than in chloroform. Although the formation of the thermodynamic product ***Z*-71** is only exergonic by 0.7 kcal/mol in DCE, the BF_3 byproduct is expected to be stabilized by coordination with a Lewis base. Our calculations indicate that the complexation of BF_3 with H_2O is highly exothermic. Although water was not added to the experimental system, we expect that the trace amount of water in DCE or other Lewis basic species under the experimental conditions will stabilize the BF_3 byproduct and push the equilibrium towards the product ***Z*-71**.

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It is noteworthy that the reverse reaction of ***E*-81** to generate the vinyl cation **102** has a smaller energy barrier in DCE ($\Delta G^{\ddagger}$ = 21.8 kcal/mol) than that in chloroform (see Fig. 1, $\Delta G^{\ddagger}$ = 23.6 kcal/mol). Therefore, our computational studies suggest that the *E*-to-*Z* isomerization in DCE occurs faster than that in chloroform, which is consistent with the experimental results that polar solvent could increase the *Z*-selectivity in the hydrofluorination of alkynes.

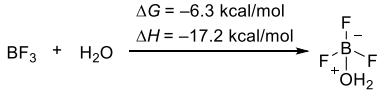


Figure S16. Calculated free energy for the complexation of BF_3 with H_2O. All energies were calculated at the M06-2X/6-311+G(d,p)/SMD(DCE)//M06-2X/6-31+G(d)/SMD(DCE) level of theory.

Several mechanisms for the isomerization of vinyl fluoride were considered besides the reverse fluorination of the vinyl fluoride to regenerate the vinyl cation ion pair intermediate. Figure S17 shows an alternative isomerization pathway, which involves the protonation of vinyl fluoride ***E*-81** with 2,6-dichloropyridinium tetrafluoroborate (**F**) and the deprotonation of alkyl cation intermediate **102b**. This mechanism has an activation free energy of 27.2 kcal/mol, which is higher than that in the reaction of ***E*-81** with BF_3 (via **TS-2**, $\Delta G^{\ddagger}$ = 23.6 kcal/mol) by 3.6 kcal/mol. Therefore, this *E*/*Z*-isomerization mechanism is less likely.

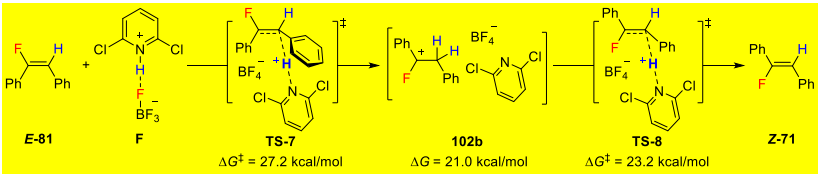
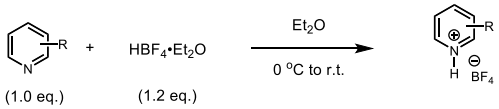
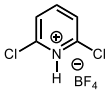


Figure S17. An alternative mechanism for the isomerization between ***E*-81** and ***Z*-71**. All energies are with respect to ***E*-81** and **F**.

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%)

^{1}H 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).

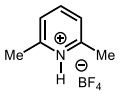
$Et_3N{\cdot}HBF_4$

White solid (9.0 g, 95%)

^{1}H 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).

^{13}C NMR (126 MHz, DMSO) δ 45.8, 8.6.

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



White solid (9.4 g, 96%)

^{1}H 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).

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

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

White solid (7.5 g, 90%)

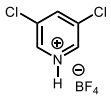
^{1}H NMR (500 MHz, DMSO) δ 15.12 (s, 1H), 8.96 – 8.89 (m, 2H), 8.62 (tt, *J* = 7.9, 1.5 Hz, 1H), 8.08 (dd, *J* = 7.7, 6.7 Hz, 2H).

^{13}C NMR (126 MHz, DMSO) δ 146.4, 142.2, 127.3.
^{19}F NMR (471 MHz, DMSO) δ -148.16 (s), -148.22 (s).

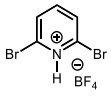
White solid (8.0 g, 86%)
^{1}H NMR (500 MHz, DMSO) δ 12.96 (s, 1H), 8.27 – 8.19 (m, 1H), 8.02 – 7.93 (m, 1H), 7.37 – 7.29 (m, 1H), 7.15 (dd, *J* = 8.3, 2.5 Hz, 1H).
^{13}C NMR (126 MHz, DMSO) δ 163.2 (d, $J_{C\text{-}F}$ = 235.5 Hz), 147.8 (d, $J_{C\text{-}F}$ = 14.6 Hz), 142.3 (d, $J_{C\text{-}F}$ = 7.9 Hz), 122.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 109.8 (d, $J_{C\text{-}F}$ = 37.0 Hz).
^{19}F NMR (471 MHz, DMSO) δ -68.11 (s, 1F), -148.08 (s), -148.14 (s).

White solid (9.0 g, 90%)
^{1}H 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).
^{13}C NMR (126 MHz, DMSO) δ 150.4, 150.1, 140.1, 124.6, 123.3.
^{19}F NMR (471 MHz, DMSO) δ -148.08 (s), -148.13 (s).

White solid (10.7 g, 87%)
^{1}H 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).
^{13}C NMR (126 MHz, DMSO) δ 150.6, 141.5, 139.8, 128.4, 123.6.
^{19}F NMR (471 MHz, DMSO) δ -148.09 (s), -148.14 (s).

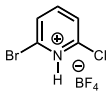


White solid (10.9 g, 93%)
^{1}H NMR (500 MHz, DMSO) δ 13.94 (s, 1H), 8.61 (d, *J* = 2.1 Hz, 2H), 8.23 (t, *J* = 2.1 Hz, 1H).
^{13}C NMR (126 MHz, DMSO) δ 146.8, 136.0, 131.7.
^{19}F NMR (471 MHz, DMSO) δ -148.07 (s), -148.12 (s).

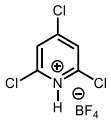


White solid (14.8 g, 92%)

^{1}H NMR (500 MHz, DMSO) δ 13.52 (s, 1H), 7.73 – 7.70 (m, 3H).
^{13}C NMR (126 MHz, DMSO) δ 142.3, 140.1, 127.8.
^{19}F NMR (471 MHz, DMSO) δ -148.12 (s), -148.17 (s).

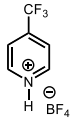


White solid (11.6 g, 83%)
^{1}H NMR (500 MHz, DMSO) δ 12.94 (s, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.62 – 7.57 (m, 1H).
^{13}C NMR (126 MHz, DMSO) δ 149.4, 142.6, 139.9, 127.5, 124.0.
^{19}F NMR (471 MHz, DMSO) δ -148.12 (s), -148.18 (s).



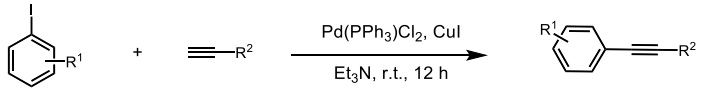
White solid (10.8 g, 80%)
^{1}H NMR (500 MHz, DMSO) δ 10.99 (s, 1H), 7.86 (s, 2H).
^{13}C NMR (126 MHz, DMSO) δ 150.1, 147.2, 123.8.
^{19}F NMR (471 MHz, DMSO) δ -148.09 (s), -148.15 (s).

White solid (9.6 g, 91%)
^{1}H 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).
^{13}C NMR (126 MHz, DMSO) δ 154.8, 144.6, 144.4, 132.1, 124.9.
^{19}F NMR (471 MHz, DMSO) δ -148.10 (s), -148.15 (s).



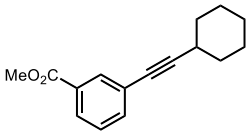
White solid (11.2 g, 95%)
^{1}H NMR (500 MHz, DMSO) δ 14.78 (s, 1H), 9.01 (d, *J* = 6.0 Hz, 2H), 8.05 (d, *J* = 5.9 Hz, 2H).
^{13}C NMR (126 MHz, DMSO) δ 148.8, 139.4 (q, $J_{C\text{-}F}$ = 34.1 Hz), 122.5 (q, $J_{C\text{-}F}$ = 273.7 Hz), 121.1 (q, $J_{C\text{-}F}$ = 3.5 Hz).
^{19}F NMR (471 MHz, DMSO) 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 Et_2O (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



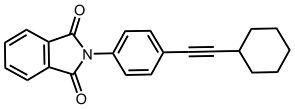
Yellow oil (1.08 g, 89% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380 Found: 243.1377.

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



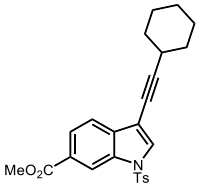
Yellow solid (1.25 g, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{22}H_{20}NO_2$ $[M+H]^+$: 330.1489, Found: 330.1479.

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



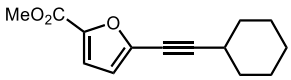
Yellow solid (1.59 g, 73% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{25}H_{26}NO_4S$ $[M+H]^+$: 436.1577, Found: 436.1557.

Methyl 5-(cyclohexylethynyl)furan-2-carboxylate



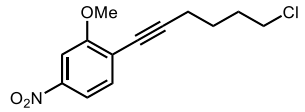
Yellow solid (916 mg, 79% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{14}H_{17}O_3$ $[M+H]^+$: 233.1172, Found: 233.1163.

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

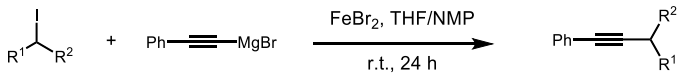


Yellow oil (1.13 g, 85% yield).

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

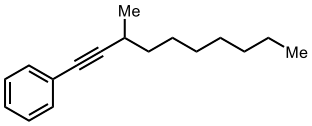
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 147.6, 133.4, 120.1, 115.6, 105.4, 99.3, 76.2, 56.3, 44.4, 31.5, 25.6, 19.2.

HRMS (ESI) calcd for $C_{13}H_{15}ClNO_3$ $[M+H]^+$: 268.0735, Found: 268.0731.



An oven-dried 250 mL flask equipped with a magnetic stir bar was charged with $FeBr_2$ (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 quenched with water (30 mL). The aqueous layer was further extracted with EtOAc (2 x 20 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



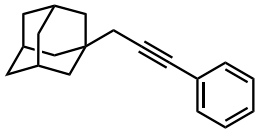
Yellow oil (1.05 g, 46% yield).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{17}H_{24}$ $[M]^+$: 228.1878, Found: 228.1887.

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

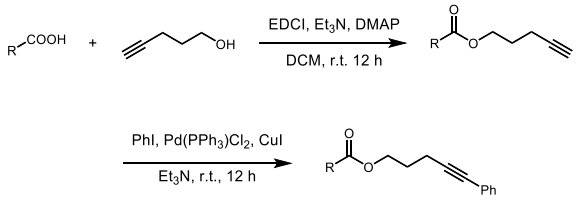


Yellow oil (950 mg, 38% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5, 128.1, 127.4, 124.2, 87.8, 82.6, 42.1, 36.9, 34.6, 33.1, 28.7.

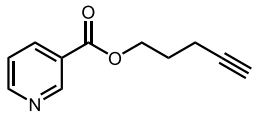
HRMS (ASAP) calcd for $C_{19}H_{23}$ $[M+H]^+$: 251.1800, Found: 251.1811.



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 completed, the resulting mixture was diluted with DCM (50 mL), washed by 1 N HCl (2 x 20 mL), 1 N aqueous $NaHCO_3$ (2 x 20 mL), and brine (1 x 20 mL). The organic layer was dried (Na_2SO_4) and evaporated in vacuo. The resulting residue was purified by column chromatography to afford the desired ester.

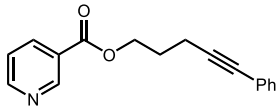
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride (1.0 mol%), copper(I) iodide (3.0 mol%), iodobenzene (2.0 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) 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 completed, the reaction mixture was diluted with Et_2O (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



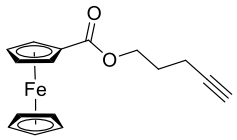
Colorless oil (737 mg, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 1.5 Hz, 1H), 8.75 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.27 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.8, 4.9 Hz, 1H), 4.44 (t, *J* = 6.3 Hz, 2H), 2.36 (td, *J* = 7.0, 2.6 Hz, 2H), 2.04 – 1.93 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{11}H_{12}NO_2$ $[M+H]^+$: 190.0863, Found: 190.0858.

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



Yellow oil (445 mg, 84% yield).
^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, Found: 266.1168.

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



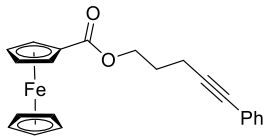
Yellow oil (1.11 g, 75% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{17}FeO_2$ $[M+H]^+$: 297.0578, Found: 297.0590.

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



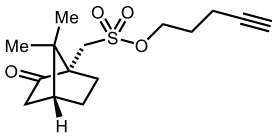
Yellow oil (662 mg, 89% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{22}H_{21}FeO_2$ $[M+H]^+$: 373.0891, Found: 373.0909.

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



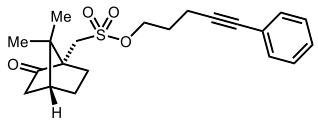
Colorless oil (1.07 g, 72% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{15}H_{23}O_4S$ $[M+H]^+$: 299.1317, Found: 299.1330.

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



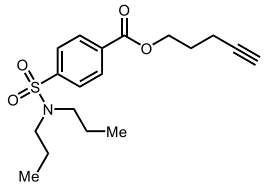
Yellow oil (682 mg, 91% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{21}H_{27}O_4S$ $[M+H]^+$: 375.1630, Found: 375.1647.

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



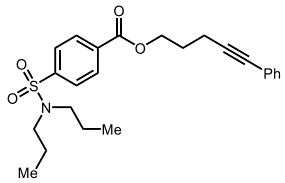
Colorless oil (1.39 g, 79% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{18}H_{26}NO_4S$ $[M+H]^+$: 352.1583, Found: 352.1598.

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



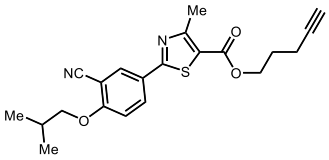
Yellow oil (769 mg, 90% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{24}H_{30}NO_4S$ $[M+H]^+$: 428.1896, Found: 428.1914.

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



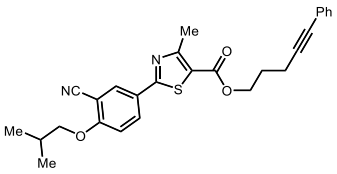
White solid (1.39 g, 73% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{21}H_{23}N_2O_3S$ $[M+H]^+$: 383.1429, Found: 383.1447.

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



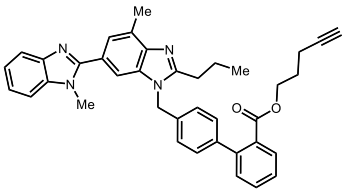
White solid (687 mg, 75% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{27}H_{27}N_2O_3S$ $[M+H]^+$: 459.1742, Found: 459.1764.

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



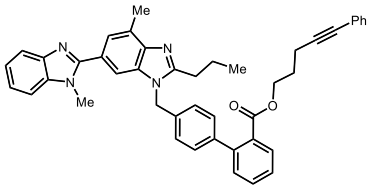
White solid (1.86 g, 64% yield).

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

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{38}H_{37}N_4O_2$ $[M+H]^+$: 581.2917, 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



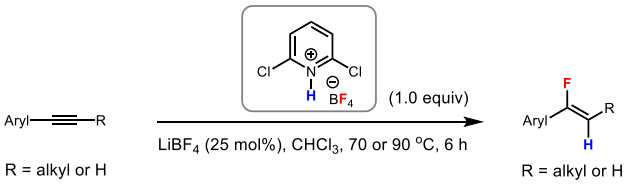
White solid (971 m g, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) 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), 7.47 (s, 1H), 7.43 (s, 1H), 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).

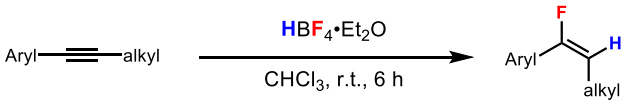
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 156.3, 154.6, 143.1, 142.8, 141.5, 141.2, 136.6, 134.9, 134.8, 131.4, 131.2, 130.7, 130.6, 129.9, 129.4, 128.9, 128.2, 127.7, 127.3, 125.9, 123.83, 123.78, 123.5, 122.4, 122.2, 119.5, 109.4, 108.8, 88.6, 81.2, 63.6, 46.9, 31.7, 29.7, 27.4, 21.8, 16.8, 15.9, 14.0.

HRMS (ESI) calcd for $C_{44}H_{41}N_4O_2$ $[M+H]^+$: 657.3224, Found: 657.3205.

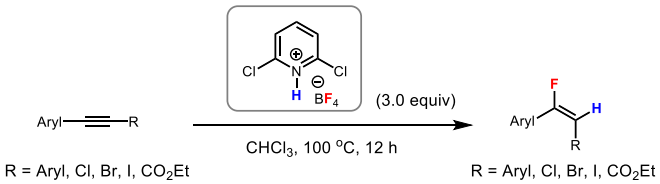
7. General procedure for hydrofluorination of alkynes

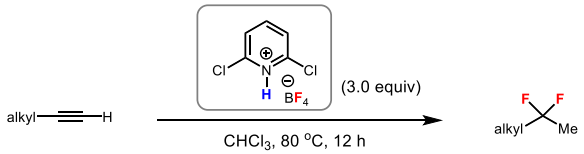


Condition A: A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (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 °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.

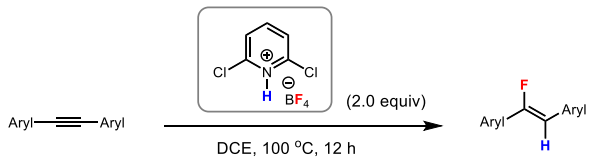


Condition B: A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, dry $CHCl_3$ (1.0 mL), alkyne (0.2 mmol, 1.0 equiv) and $HBF_4{\cdot}Et_2O$ (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 $CHCl_3$ (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 CH_2Cl_2. The filtrate was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product.



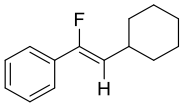
Condition D: A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 97 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 CH_2Cl_2. 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)



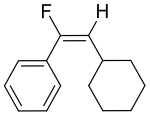
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), (cyclohexylethynyl)benzene (0.2 mmol, 37 mg, 1.0 equiv) at 70 ºC. The reaction mixture was quenched after 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4 (d, $J_{C\text{-}F}$ = 245.3 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.4 Hz), 128.3 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.2, 123.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 112.0 (d, $J_{C\text{-}F}$ = 17.1 Hz), 33.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 33.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 26.0, 25.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.8 (d, *J* = 38.2 Hz).

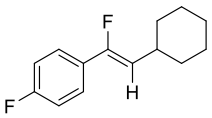
(*E*)-(2-Cyclohexyl-1-fluorovinyl)benzene (2)



Prepared following the general procedure (**condition B**): (cyclohexylethynyl)benzene (0.2 mmol, 37 mg, 1.0 equiv), dry $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **2**. Pale yellow oil (17 mg, 42% yield, *E*/*Z* = 11 : 1).

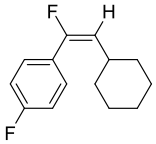
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.43 – 7.32 (m, 3H), 5.26 (dd, J = 23.1, 10.8 Hz, 1H), 2.37 – 2.18 (m, 1H), 1.83 – 1.69 (m, 4H), 1.69 – 1.60 (m, 1H), 1.32 – 1.14 (m, 5H).
^{13}C NMR (126 MHz, $CDCl_3$) δ155.7 (d, $J_{C\text{-}F}$ = 240.1 Hz), 132.4 (d, $J_{C\text{-}F}$ = 30.2 Hz), 128.8 (d, $J_{C\text{-}F}$ = 1.1 Hz), 128.2, 127.5 (d, $J_{C\text{-}F}$ = 5.0 Hz), 114.5 (d, $J_{C\text{-}F}$ = 21.9 Hz), 35.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 33.8 (d, $J_{C\text{-}F}$ = 2.3 Hz), 25.9, 25.6.
^{19}F NMR (471 MHz, $CDCl_3$) δ -103.5 (d, J = 23.1 Hz).
HRMS (APCI) calcd for $C_{14}H_{18}F$ $[M+H]^+$: 205.1387, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 247.9 Hz), 154.7 (d, $J_{C\text{-}F}$ = 245.1 Hz), 129.2 (dd, $J_{C\text{-}F}$ = 30.2, 3.3 Hz), 125.8 (dd, $J_{C\text{-}F}$ = 7.9, 7.2 Hz), 115.3 (dd, $J_{C\text{-}F}$ = 21.8, 1.8 Hz), 111.8 (dd, $J_{C\text{-}F}$ = 17.1, 1.7 Hz), 33.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 33.2 (d, $J_{C\text{-}F}$ = 1.0 Hz), 26.0, 25.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -113.2 – -113.4 (m, 1F), -120.7 (d, J = 38.1 Hz, 1F).
HRMS (ASAP) calcd for $C_{14}H_{16}F_2$ $[M]^+$: 222.1220, Found: 222.1227.

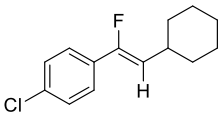
(*E*)-1-(2-Cyclohexyl-1-fluorovinyl)-4-fluorobenzene (4)



Prepared following the general procedure (**condition B**): 1-(cyclohexylethynyl)-4-fluorobenzene (0.2 mmol, 41 mg, 1.0 equiv), dry $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **4**. Pale yellow oil (20 mg, 45% yield, E/Z = 11 : 1).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 248.9 Hz), 154.9 (d, $J_{C\text{-}F}$ = 240.2 Hz), 129.4 (dd, $J_{C\text{-}F}$ = 8.3, 4.8 Hz), 128.6 (dd, $J_{C\text{-}F}$ = 31.0, 3.4 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.7 Hz), 114.4 (d, $J_{C\text{-}F}$ = 21.8 Hz), 35.3 (d, $J_{C\text{-}F}$ = 7.4 Hz), 33.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 25.8, 25.6.

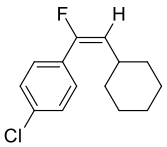
^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -102.5 (d, *J* = 22.8 Hz), -111.6 – -111.9 (m), (*Z*): -113.3 – -113.4 (m), -120.8 (d, *J* = 38.0 Hz).
HRMS (APCI) calcd for $C_{14}H_{16}F_2$ $[M]^+$: 222.1215, Found: 222.1205.

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



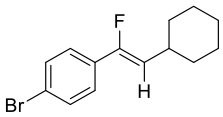
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-chloro-4-(cyclohexylethynyl)benzene (0.2 mmol, 44 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched 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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5 (d, $J_{C\text{-}F}$ = 245.1 Hz), 134.0, 131.4 (d, $J_{C\text{-}F}$ = 30.1 Hz), 128.6 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.2 (d, $J_{C\text{-}F}$ = 7.0 Hz), 112.6 (d, $J_{C\text{-}F}$ = 17.0 Hz), 33.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 33.1 (d, $J_{C\text{-}F}$ = 1.1 Hz), 26.0, 25.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -121.7 (d, *J* = 38.0 Hz).
HRMS (ASAP) calcd for $C_{14}H_{16}ClF$ $[M]^+$: 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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **6**. Pale yellow oil (19 mg, 41% yield, *E*/*Z* = 11 : 1).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7 (d, $J_{C\text{-}F}$ = 240.1 Hz), 134.7, 130.8 (d, $J_{C\text{-}F}$ = 30.9 Hz), 128.8 (d, $J_{C\text{-}F}$ = 4.9 Hz), 128.5, 115.1 (d, $J_{C\text{-}F}$ = 21.7 Hz), 35.3 (d, $J_{C\text{-}F}$ = 7.3 Hz), 33.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 25.8, 25.6.
^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -103.9 (d, *J* = 22.8 Hz), (*Z*): -121.7 (d, *J* = 38.1 Hz).
HRMS (APCI) calcd for $C_{14}H_{16}ClF$ $[M]^+$: 238.0919, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-bromo-4-(cyclohexylethynyl)benzene (0.2 mmol, 53 mg, 1.0 equiv) at 70 ºC. 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).

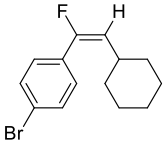
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.37 – 7.32 (m, 2H), 5.27 (dd, J = 38.0, 9.3 Hz, 1H), 2.68 – 2.56 (m, 1H), 1.81 – 1.71 (m, 4H), 1.71 – 1.63 (m, 1H), 1.41 – 1.30 (m, 2H), 1.27 – 1.11 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6 (d, $J_{C\text{-}F}$ = 245.1 Hz), 131.9 (d, $J_{C\text{-}F}$ = 30.0 Hz), 131.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 122.2, 112.7 (d, $J_{C\text{-}F}$ = 17.0 Hz), 33.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 33.0 (d, $J_{C\text{-}F}$ = 1.2 Hz), 26.0, 25.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.8 (d, J = 38.0 Hz).

HRMS (ASAP) calcd for $C_{14}H_{16}BrF$ $[M]^+$: 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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **8**. Pale yellow oil (27 mg, 48% yield, E/Z > 20 : 1).

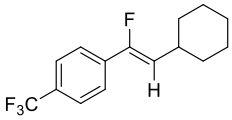
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.28 (dd, J = 22.9, 10.8 Hz, 1H), 2.33 – 2.12 (m, 1H), 1.80 – 1.69 (m, 4H), 1.69 – 1.61 (m, 1H), 1.29 – 1.14 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7 (d, $J_{C\text{-}F}$ = 240.1 Hz), 131.5, 131.3 (d, $J_{C\text{-}F}$ = 30.9 Hz), 129.0 (d, $J_{C\text{-}F}$ = 4.9 Hz), 123.0 (d, $J_{C\text{-}F}$ = 1.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.6 Hz), 35.3 (d, $J_{C\text{-}F}$ = 7.4 Hz), 33.6 (d, $J_{C\text{-}F}$ = 2.2 Hz), 25.8, 25.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -104.2 (d, J = 22.9 Hz), (*Z*): -121.9 (d, J = 37.9 Hz).

HRMS (APCI) calcd for $C_{14}H_{16}BrF$ $[M]^+$: 282.0414, 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 ºC. 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).

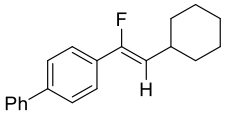
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 4H), 5.40 (dd, *J* = 37.7, 9.3 Hz, 1H), 2.65 (dt, *J* = 20.8, 7.3 Hz, 1H), 1.82 – 1.72 (m, 4H), 1.71 – 1.65 (m, 1H), 1.42 – 1.30 (m, 2H), 1.28 – 1.14 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2 (d, $J_{C\text{-}F}$ = 245.4 Hz), 136.3 (d, $J_{C\text{-}F}$ = 29.7 Hz), 130.1 (q, $J_{C\text{-}F}$ = 32.5 Hz), 125.47 – 125.27 (m), 124.02 (d, $J_{C\text{-}F}$ = 7.0 Hz), 124.01 (q, $J_{C\text{-}F}$ = 273.4 Hz), 114.5 (d, $J_{C\text{-}F}$ = 16.8 Hz), 33.9 (d, $J_{C\text{-}F}$ = 3.4 Hz), 33.0 (d, $J_{C\text{-}F}$ = 1.1 Hz), 25.9, 25.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.7 (s, 3F), -122.2 (d, *J* = 37.7 Hz, 1F).

HRMS (ASAP) calcd for $C_{15}H_{16}F_4$ $[M]^+$: 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 4-(cyclohexylethynyl)-1,1'-biphenyl (0.2 mmol, 52 mg, 1.0 equiv) at 70 ºC. 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).

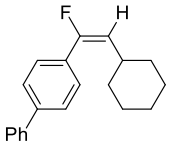
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 6H), 7.45 (m, 2H), 7.36 (m, 1H), 5.32 (dd, *J* = 38.2, 9.2 Hz, 1H), 2.74 – 2.59 (m, 1H), 1.85 – 1.72 (m, 4H), 1.72 – 1.63 (m, 1H), 1.43 – 1.32 (m, 2H), 1.29 – 1.13 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2 (d, $J_{C\text{-}F}$ = 245.0 Hz), 141.0, 140.5, 131.9 (d, $J_{C\text{-}F}$ = 29.7 Hz), 128.8, 127.5, 127.04 (d, $J_{C\text{-}F}$ = 1.9 Hz), 126.97, 124.3 (d, $J_{C\text{-}F}$ = 6.9 Hz), 112.2 (d, $J_{C\text{-}F}$ = 17.2 Hz), 33.9 (d, $J_{C\text{-}F}$ = 3.6 Hz), 33.2, 26.0, 25.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.8 (d, *J* = 38.2 Hz).

HRMS (ASAP) calcd for $C_{20}H_{22}F$ $[M+H]^+$: 281.1706, 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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **11**. Pale yellow oil (18 mg, 32% yield, *E*/*Z* > 20 : 1).

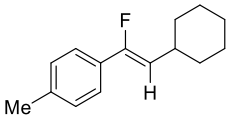
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (t, *J* = 7.5 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.29 (dd, *J* = 23.1, 10.8 Hz, 1H), 2.44 – 2.24 (m, 1H), 1.86 – 1.70 (m, 4H), 1.70 – 1.63 (m, 1H), 1.34 – 1.17 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5 (d, $J_{C\text{-}F}$ = 239.7 Hz), 141.6, 140.4, 131.3 (d, $J_{C\text{-}F}$ = 30.4 Hz), 128.8, 127.8 (d, $J_{C\text{-}F}$ = 5.1 Hz), 127.6, 127.1, 126.9, 114.7 (d, $J_{C\text{-}F}$ = 22.1 Hz), 35.3 (d, $J_{C\text{-}F}$ = 7.6 Hz), 33.8 (d, $J_{C\text{-}F}$ = 2.1 Hz), 25.9, 25.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.1 (d, J = 23.0 Hz).

HRMS (APCI) calcd for $C_{20}H_{21}F$ $[M]^+$: 280.1622, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-(cyclohexylethynyl)-4-methylbenzene (0.2 mmol, 40 mg, 1.0 equiv) at 70 ºC. 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).

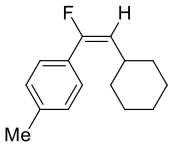
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 5.21 (dd, J = 38.4, 9.2 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.35 (s, 3H), 1.82 – 1.70 (m, 4H), 1.70 – 1.64 (m, 1H), 1.41 – 1.30 (m, 2H), 1.26 – 1.10 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5 (d, $J_{C\text{-}F}$ = 245.1 Hz), 138.1, 130.2 (d, $J_{C\text{-}F}$ = 29.6 Hz), 129.0 (d, $J_{C\text{-}F}$ = 1.8 Hz), 123.8 (d, $J_{C\text{-}F}$ = 6.9 Hz), 111.1 (d, $J_{C\text{-}F}$ = 17.2 Hz), 33.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 33.2 (d, $J_{C\text{-}F}$ = 1.0 Hz), 26.0, 25.9, 21.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.5 (d, J = 38.4 Hz).

HRMS (ASAP) calcd for $C_{15}H_{19}F$ $[M]^+$: 218.1471, Found: 218.1480.

(*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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **13**. Pale yellow oil (16 mg, 36% yield, *E*/*Z* > 20 : 1).

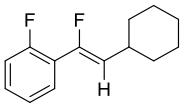
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 5.20 (dd, J = 23.0, 10.7 Hz, 1H), 2.38 (s, 3H), 2.31 – 2.20 (m, 1H), 1.80 – 1.68 (m, 4H), 1.67 – 1.60 (m, 1H), 1.28 – 1.14 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9 (d, $J_{C\text{-}F}$ = 239.9 Hz), 138.8, 129.6 (d, $J_{C\text{-}F}$ = 30.4 Hz), 128.9, 127.4 (d, $J_{C\text{-}F}$ = 4.9 Hz), 113.9 (d, $J_{C\text{-}F}$ = 22.3 Hz), 35.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 33.8 (d, $J_{C\text{-}F}$ = 2.2 Hz), 25.9, 25.7, 21.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -103.1 (d, J = 22.9 Hz).

HRMS (APCI) calcd for $C_{15}H_{19}F$ $[M]^+$: 218.1465, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).

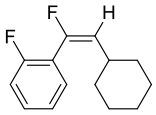
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (td, *J* = 7.8, 1.7 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (m, 1H), 5.48 (dd, *J* = 40.0, 9.3 Hz, 1H), 2.75 – 2.59 (m, 1H), 1.86 – 1.70 (m, 4H), 1.70 – 1.62 (m, 1H), 1.42 – 1.30 (m, 2H), 1.27 – 1.14 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2 (dd, $J_{C\text{-}F}$ = 251.5, 5.4 Hz), 150.0 (dd, $J_{C\text{-}F}$ = 242.9, 5.5 Hz), 129.4 (d, $J_{C\text{-}F}$ = 8.6 Hz), 127.0 (dd, $J_{C\text{-}F}$ = 8.5, 2.4 Hz), 124.0 (dd, $J_{C\text{-}F}$ = 3.6, 1.1 Hz), 121.0 (dd, $J_{C\text{-}F}$ = 31.2, 11.0 Hz), 118.2 (dd, $J_{C\text{-}F}$ = 15.4, 12.3 Hz), 116.0 (dd, $J_{C\text{-}F}$ = 22.8, 2.4 Hz), 34.1 (d, $J_{C\text{-}F}$ = 4.1 Hz), 33.0 (d, $J_{C\text{-}F}$ = 1.1 Hz), 26.0, 25.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.3 – -112.6 (m, 1F), -117.5 (dd, *J* = 40.0, 7.4 Hz, 1F).

HRMS (ASAP) calcd for $C_{14}H_{16}F_2$ $[M]^+$: 222.1220, Found: 222.1217.

(*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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **15**. Pale yellow oil (20 mg, 46% yield, *E*/*Z* > 20 : 1).

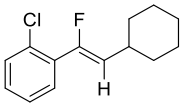
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 2H), 7.15 (dt, *J* = 18.3, 8.2 Hz, 2H), 5.38 (dd, *J* = 20.4, 10.9 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.74 – 1.64 (m, 4H), 1.63 – 1.56 (m, 1H), 1.23 – 1.09 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0 (d, $J_{C\text{-}F}$ = 249.3 Hz), 150.9 (d, $J_{C\text{-}F}$ = 242.7 Hz), 131.1 (dd, $J_{C\text{-}F}$ = 8.3, 1.9 Hz), 130.9 (t, $J_{C\text{-}F}$ = 2.6 Hz), 123.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 120.3 (dd, $J_{C\text{-}F}$ = 30.1, 15.4 Hz), 116.9 (d, $J_{C\text{-}F}$ = 19.8 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.9 Hz), 35.5 (d, $J_{C\text{-}F}$ = 5.6 Hz), 33.4 (d, $J_{C\text{-}F}$ = 2.3 Hz), 25.8, 25.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -100.0 (dd, *J* = 20.3, 7.7 Hz, 1F), -112.2 – -112.3 (m, 1F).

HRMS (ASAP) calcd for $C_{14}H_{17}F_2$ $[M+H]^+$: 223.1298, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-chloro-2-(cyclohexylethynyl)benzene (0.2 mmol, 44 mg, 1.0 equiv) at 90 ºC. 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).

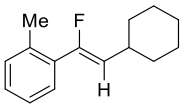
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.36 (m, 2H), 7.30 – 7.25 (m, 2H), 5.22 (dd, *J* = 37.8, 9.3 Hz, 1H), 2.75 – 2.61 (m, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.72 (m, 2H), 1.72 – 1.66 (m, 1H), 1.44 – 1.33 (m, 2H), 1.29 – 1.15 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0 (d, $J_{C\text{-}F}$ = 247.6 Hz), 132.4 (d, $J_{C\text{-}F}$ = 24.1 Hz), 132.2 (d, $J_{C\text{-}F}$ = 2.7 Hz), 130.3, 130.0 (d, $J_{C\text{-}F}$ = 4.9 Hz), 129.7 (d, $J_{C\text{-}F}$ = 1.0 Hz), 126.5, 118.0 (d, $J_{C\text{-}F}$ = 16.3 Hz), 34.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 33.0 (d, $J_{C\text{-}F}$ = 1.4 Hz), 26.0, 25.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.0 (d, *J* = 37.8 Hz).

HRMS (ASAP) calcd for $C_{14}H_{17}ClF$ $[M+H]^+$: 239.1003, Found: 239.0989.

(*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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-(cyclohexylethynyl)-2-methylbenzene (0.2 mmol, 40 mg, 1.0 equiv) at 70 ºC. 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).

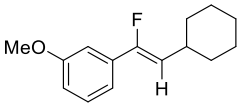
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 (m, 2H), 4.86 (dd, *J* = 37.5, 9.2 Hz, 1H), 2.69 – 2.58 (m, 1H), 2.39 (d, *J* = 3.2 Hz, 3H), 1.86 – 1.70 (m, 4H), 1.70 – 1.63 (m, 1H), 1.42 – 1.32 (m, 2H), 1.20 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ156.4 (d, $J_{C\text{-}F}$ = 249.6 Hz), 136.4, 133.3 (d, $J_{C\text{-}F}$ = 26.7 Hz), 130.5, 128.8 (d, $J_{C\text{-}F}$ = 1.1 Hz), 128.7 (d, $J_{C\text{-}F}$ = 4.8 Hz), 125.5, 116.0 (d, $J_{C\text{-}F}$ = 17.3 Hz), 33.9 (d, $J_{C\text{-}F}$ = 2.6 Hz), 33.3 (d, $J_{C\text{-}F}$ = 1.2 Hz), 26.0, 25.8, 20.5 (d, $J_{C\text{-}F}$ = 3.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.9 (d, *J* = 37.5 Hz).

HRMS (ASAP) calcd for $C_{15}H_{20}F$ $[M+H]^+$: 219.1549, Found: 219.1537.

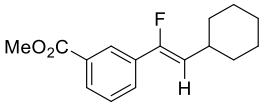
(*Z*)-1-(2-Cyclohexyl-1-fluorovinyl)-3-methoxybenzene (18)



Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-(cyclohexylethynyl)-3-methoxybenzene (0.2 mmol, 43 mg, 1.0 equiv) at 70 ºC. 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).

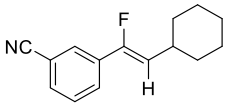
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.05 – 6.99 (m, 1H), 6.84 (ddd, *J* = 8.2, 2.5, 0.7 Hz, 1H), 5.27 (dd, *J* = 38.1, 9.3 Hz, 1H), 3.82 (s, 3H), 2.70 – 2.56 (m, 1H), 1.82 – 1.71 (m, 4H), 1.70 – 1.65 (m, 1H), 1.40 – 1.30 (m, 2H), 1.25 – 1.13 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 155.2 (d, $J_{C\text{-}F}$ = 245.5 Hz), 134.4 (d, $J_{C\text{-}F}$ = 29.3 Hz), 129.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 116.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 114.0, 112.4 (d, $J_{C\text{-}F}$ = 17.2 Hz), 109.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 55.3, 33.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 33.1 (d, $J_{C\text{-}F}$ = 1.1 Hz), 26.0, 25.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -121.2 (d, *J* = 38.1 Hz).
HRMS (APCI) calcd for $C_{15}H_{19}FO$ $[M]^+$: 234.1414, 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).
^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (101 MHz, $CDCl_3$) 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.
^{19}F NMR (376 MHz, $CDCl_3$) δ -121.9 (d, *J* = 38.0 Hz).
HRMS (ESI) calcd for $C_{16}H_{20}FO_2$ $[M+H]^+$: 263.1442, Found: 263.1440.

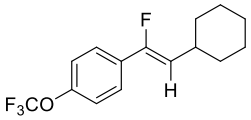
(Z)-3-(2-Cyclohexyl-1-fluorovinyl)benzonitrile (20)



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).
^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (101 MHz, $CDCl_3$) 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.

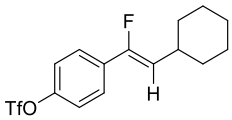
^{19}F NMR (376 MHz, $CDCl_3$) δ (*E*): -105.4 (d, *J* = 22.8 Hz), (*Z*): -122.6 (d, *J* = 37.6 Hz).
HRMS (ESI) calcd for $C_{15}H_{17}FN$ $[M+H]^+$: 230.1340, Found: 230.1339.

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



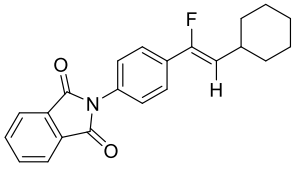
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-(cyclohexylethynyl)-4-(trifluoromethoxy)benzene (0.2 mmol, 54 mg, 1.0 equiv) at 90 °C. The reaction mixture 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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3 (d, $J_{C\text{-}F}$ = 245.2 Hz), 149.0 (d, $J_{C\text{-}F}$ = 1.7 Hz), 131.7 (d, $J_{C\text{-}F}$ = 30.1 Hz), 125.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 120.8, 120.4 (d, $J_{C\text{-}F}$ = 257.0 Hz), 112.9 (d, $J_{C\text{-}F}$ = 16.9 Hz), 33.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 33.1 (d, $J_{C\text{-}F}$ = 1.2 Hz), 26.0, 25.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -57.9 (s, 3F), -121.4 (d, *J* = 37.9 Hz, 1F).
HRMS (ASAP) calcd for $C_{15}H_{16}F_4O$ $[M]^+$: 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).
^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8 (d, $J_{C\text{-}F}$ = 245.3 Hz), 149.1, 133.3 (d, $J_{C\text{-}F}$ = 30.3 Hz), 125.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 121.4, 118.7 (d, $J_{C\text{-}F}$ = 320.9 Hz), 114.0 (d, $J_{C\text{-}F}$ = 16.8 Hz), 33.9 (d, $J_{C\text{-}F}$ = 3.4 Hz), 33.0 (d, $J_{C\text{-}F}$ = 1.3 Hz), 25.9, 25.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -72.8 (s, 3F), -121.7 (d, *J* = 37.7 Hz, 1F).
HRMS (ASAP) calcd for $C_{15}H_{16}F_4O_3S$ $[M]^+$: 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 2-(4-(cyclohexylethynyl)phenyl)isoindoline-1,3-dione (0.2 mmol, 66 mg, 1.0 equiv) at 70 ºC. 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).

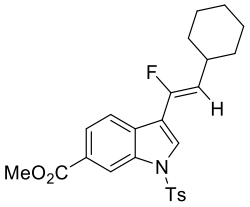
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 5.33 (dd, *J* = 37.9, 9.2 Hz, 1H), 2.75 – 2.56 (m, 1H), 1.84 – 1.62 (m, 5H), 1.41 – 1.30 (m, 2H), 1.27 – 1.13 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 154.7 (d, $J_{C\text{-}F}$ = 245.2 Hz), 134.4, 132.6 (d, $J_{C\text{-}F}$ = 29.8 Hz), 131.7, 131.5, 126.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 124.5 (d, $J_{C\text{-}F}$ = 6.9 Hz), 123.8, 113.1 (d, $J_{C\text{-}F}$ = 16.9 Hz), 33.9 (d, $J_{C\text{-}F}$ = 3.4 Hz), 33.1, 26.0, 25.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.9 (d, *J* = 37.9 Hz).

HRMS (ESI) calcd for $C_{22}H_{21}FNO_2$ $[M+H]^+$: 350.1551, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), methyl 3-(cyclohexylethynyl)-1-tosyl-1H-indole-6-carboxylate (0.2 mmol, 87 mg, 1.0 equiv) at 70 ºC. 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).

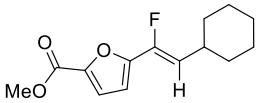
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 1.2 Hz, 1H), 7.97 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.83 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.21 (dd, *J* = 39.0, 9.3 Hz, 1H), 3.97 (s, 3H), 2.72 – 2.61 (m, 1H), 2.35 (s, 3H), 1.84 – 1.71 (m, 4H), 1.42 – 1.31 (m, 2H), 1.28 – 1.15 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 150.0 (d, $J_{C\text{-}F}$ = 241.2 Hz), 145.6, 134.8 (d, $J_{C\text{-}F}$ = 1.0 Hz), 134.7, 130.4 (d, $J_{C\text{-}F}$ = 5.5 Hz), 130.1, 127.0, 126.9, 126.1 (d, $J_{C\text{-}F}$ = 6.3 Hz), 124.8, 120.6, 116.1 (d, $J_{C\text{-}F}$ = 34.0 Hz), 115.4, 114.70 (d, $J_{C\text{-}F}$ = 15.8 Hz), 52.3, 33.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 33.2, 26.0, 25.8, 21.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.1 (d, *J* = 39.0 Hz).

HRMS (ESI) calcd for $C_{25}H_{27}FNO_4S$ $[M+H]^+$: 456.1645, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).

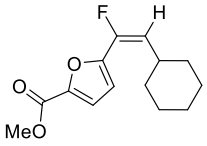
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 3.5 Hz, 1H), 6.48 (d, *J* = 2.9 Hz, 1H), 5.53 (dd, *J* = 38.2, 9.6 Hz, 1H), 3.89 (s, 3H), 2.66 – 2.54 (m, 1H), 1.79 – 1.71 (m, 4H), 1.70 – 1.64 (m, 1H), 1.37 – 1.29 (m, 2H), 1.24 – 1.17 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 150.7 (d, $J_{C\text{-}F}$ = 52.2 Hz), 147.2 (d, $J_{C\text{-}F}$ = 236.2 Hz), 143.9, 119.4, 114.7 (d, $J_{C\text{-}F}$ = 12.0 Hz), 107.8, 52.0, 33.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 32.8 (d, $J_{C\text{-}F}$ = 1.2 Hz), 25.9, 25.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -131.2 (d, *J* = 38.1 Hz).

HRMS (ESI) calcd for $C_{14}H_{18}FO_3$ $[M+H]^+$: 253.1234 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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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/EtOAc = 5 : 1) to provide the title compound **26**. Pale yellow oil (17 mg, 33% yield, *E*/*Z* > 20:1).

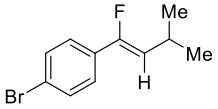
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 3.3 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 5.39 (dd, *J* = 22.8, 10.3 Hz, 1H), 3.90 (s, 3H), 2.90 – 2.76 (m, 1H), 1.86 – 1.72 (m, 4H), 1.72 – 1.64 (m, 1H), 1.46 – 1.32 (m, 2H), 1.24 – 1.12 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 150.2 (d, $J_{C\text{-}F}$ = 50.5 Hz), 146.9 (d, $J_{C\text{-}F}$ = 230.2 Hz), 144.3, 118.7, 117.6 (d, $J_{C\text{-}F}$ = 17.2 Hz), 110.4, 52.0, 34.2 (d, $J_{C\text{-}F}$ = 6.6 Hz), 33.5 (d, $J_{C\text{-}F}$ = 2.1 Hz), 25.9, 25.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -123.6 (d, *J* = 22.7 Hz).

HRMS (ESI) calcd for $C_{14}H_{18}FO_3$ $[M+H]^+$: 253.1234, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene (0.2 mmol, 45 mg, 1.0 equiv) at 70 ºC. 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).

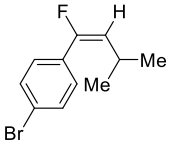
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 5.26 (dd, *J* = 37.7, 9.3 Hz, 1H), 3.02 – 2.85 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4 (d, $J_{C\text{-}F}$ = 245.1 Hz), 131.8 (d, $J_{C\text{-}F}$ = 29.9 Hz), 131.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 122.2, 114.2 (d, $J_{C\text{-}F}$ = 17.0 Hz), 24.4 (d, $J_{C\text{-}F}$ = 4.5 Hz), 22.9 (d, $J_{C\text{-}F}$ = 1.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -122.0 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for $C_{11}H_{12}BrF$ $[M]^+$: 242.0106, Found: 242.0109.

(*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), $HBF_4{\cdot}Et_2O$ (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).

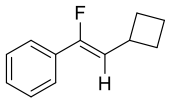
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.25 (dd, *J* = 22.7, 10.9 Hz, 1H), 2.63 – 2.48 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 6H).

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

^{19}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 $C_{11}H_{13}BrF$ $[M+H]^+$: 243.0185, 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 ºC. 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).

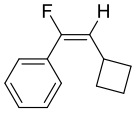
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.35 (m, 2H), 7.29 (m, 1H), 5.50 (dd, *J* = 37.8, 8.8 Hz, 1H), 3.57 – 3.42 (m, 1H), 2.34 – 2.15 (m, 2H), 2.00 – 1.90 (m, 3H), 1.89 – 1.81 (m, 1H).

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

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

HRMS (ASAP) calcd for $C_{12}H_{14}F$ $[M+H]^+$: 177.1080, Found: 177.1078.

(*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), $HBF_4{\cdot}Et_2O$ (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).

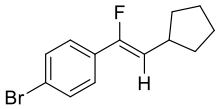
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 5.52 (dd, J = 21.8, 9.8 Hz, 1H), 3.26 – 3.09 (m, 1H), 2.30 – 2.14 (m, 2H), 1.99 – 1.80 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (d, $J_{C\text{-}F}$ = 242.0 Hz), 132.2 (d, $J_{C\text{-}F}$ = 29.8 Hz), 128.9 (d, $J_{C\text{-}F}$ = 0.9 Hz), 128.1, 127.4 (d, $J_{C\text{-}F}$ = 5.1 Hz), 113.8 (d, $J_{C\text{-}F}$ = 22.6 Hz), 32.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 30.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 18.7 (d, $J_{C\text{-}F}$ = 1.2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -105.0 (d, J = 21.8 Hz), (*Z*): -120.8 (d, J = 37.8 Hz).

HRMS (ASAP) calcd for $C_{12}H_{14}F$ $[M+H]^+$: 177.1071, Found: 177.1070.

(*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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-bromo-4-(cyclopentylethynyl)benzene (0.2 mmol, 50 mg, 1.0 equiv) at 70 ºC. 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).

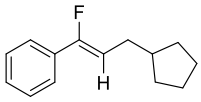
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.38 – 7.32 (m, 2H), 5.35 (dd, J = 37.5, 9.3 Hz, 1H), 3.09 – 2.93 (m, 1H), 1.99 – 1.83 (m, 2H), 1.77 – 1.67 (m, 2H), 1.67 – 1.57 (m, 2H), 1.37 – 1.28 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0 (d, $J_{C\text{-}F}$ = 244.9 Hz), 131.8 (d, $J_{C\text{-}F}$ = 29.9 Hz), 131.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 122.2, 112.2 (d, $J_{C\text{-}F}$ = 17.0 Hz), 35.5 (d, $J_{C\text{-}F}$ = 3.7 Hz), 33.6 (d, $J_{C\text{-}F}$ = 1.1 Hz), 25.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -122.2 (d, J = 37.6 Hz).

HRMS (ASAP) calcd for $C_{13}H_{14}BrF$ $[M]^+$: 268.0263, Found: 268.0275.

(*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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), (3-cyclopentylprop-1-yn-1-yl)benzene (0.2 mmol, 37 mg, 1.0 equiv) at 70 ºC. 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).

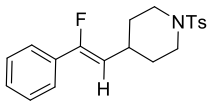
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.38 – 7.32 (m, 2H), 7.30 (ddd, *J* = 7.3, 3.7, 1.3 Hz, 1H), 5.42 (dt, *J* = 37.5, 7.7 Hz, 1H), 2.29 (td, *J* = 7.5, 1.8 Hz, 2H), 2.00 – 1.89 (m, 1H), 1.85 – 1.73 (m, 2H), 1.70 – 1.59 (m, 2H), 1.59 – 1.49 (m, 2H), 1.28 – 1.17 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}F}$ = 245.3 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.4 Hz), 128.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.8 (d, $J_{C\text{-}F}$ = 6.9 Hz), 105.6 (d, $J_{C\text{-}F}$ = 17.7 Hz), 40.1 (d, $J_{C\text{-}F}$ = 1.5 Hz), 32.3, 30.1 (d, $J_{C\text{-}F}$ = 4.2 Hz), 25.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.1 (d, *J* = 37.5 Hz).

HRMS (ASAP) calcd for $C_{14}H_{17}F$ $[M]^+$: 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 4-(phenylethynyl)-1-tosylpiperidine (0.2 mmol, 68 mg, 1.0 equiv) at 70 ºC. 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).

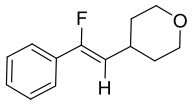
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.48 – 7.43 (m, 2H), 7.36 – 7.29 (m, 5H), 5.21 (dd, *J* = 37.2, 9.0 Hz, 1H), 3.79 (d, *J* = 11.7 Hz, 2H), 2.59 – 2.51 (m, 1H), 2.45 (s, 3H), 2.35 (td, *J* = 11.9, 2.4 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.61 – 1.52 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.68 (d, $J_{C\text{-}F}$ = 247.7 Hz), 143.5, 133.0, 132.1 (d, $J_{C\text{-}F}$ = 28.9 Hz), 129.6, 128.8, 128.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 127.7, 124.0 (d, $J_{C\text{-}F}$ = 7.0 Hz), 109.0 (d, $J_{C\text{-}F}$ = 16.7 Hz), 46.1, 31.4 (d, $J_{C\text{-}F}$ = 1.0 Hz), 31.3 (d, $J_{C\text{-}F}$ = 4.4 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ (*E*): -99.1 (d, *J* = 21.6 Hz), (*Z*): -119.3 (d, *J* = 37.2 Hz).

HRMS (ASAP) calcd for $C_{20}H_{23}FNO_2S$ $[M+H]^+$: 360.1434, 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 $CHCl_3$ (1.0 mL), 4-(phenylethynyl)tetrahydro-2H-pyran (0.2 mmol, 37 mg, 1.0 equiv) and $Et_2O{\bullet}BF_3$ (0.2 mmol, 25 μL, 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).

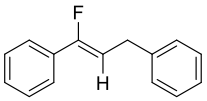
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 3H), 7.30 – 7.21 (m, 2H), 5.30 – 5.07 (m, 1H), 3.94 – 3.84 (m, 2H), 3.43 (td, *J* = 11.7, 1.7 Hz, 1.6H), 3.31 (td, *J* = 11.6, 1.9 Hz, 0.4H), 2.91 – 2.70 (m, 0.8H), 2.48 – 2.39 (m, 0.2H), 1.66 – 1.55 (m, 2H), 1.53 – 1.42 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ156.6 (d, $J_{C\text{-}F}$ = 242.8 Hz), 156.2 (d, $J_{C\text{-}F}$ = 247.0 Hz), 132.5 (d, $J_{C\text{-}F}$ = 29.1 Hz), 132.0 (d, $J_{C\text{-}F}$ = 29.9 Hz), 129.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 128.6, 128.41 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.36, 127.5 (d, $J_{C\text{-}F}$ = 4.7 Hz), 123.9 (d, $J_{C\text{-}F}$ = 7.1 Hz), 112.7 (d, $J_{C\text{-}F}$ = 23.4 Hz), 110.0 (d, $J_{C\text{-}F}$ = 16.7 Hz), 67.6, 67.3, 33.3 (d, $J_{C\text{-}F}$ = 2.3 Hz), 32.7 (d, $J_{C\text{-}F}$ = 1.3 Hz), 32.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 31.2 (d, $J_{C\text{-}F}$ = 4.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) 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 $C_{13}H_{16}FO$ $[M+H]^+$: 207.1180, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), prop-1-yne-1,3-diyldibenzene (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).

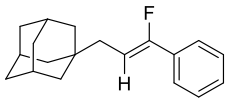
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.26 (m, 7H), 7.25 – 7.20 (m, 1H), 5.60 (dt, *J* = 36.3, 7.7 Hz, 1H), 3.65 (dd, *J* = 7.7, 1.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0 (d, $J_{C\text{-}F}$ = 247.5 Hz), 140.2, 132.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 128.6, 128.5, 128.43, 128.42, 126.2, 124.0 (d, $J_{C\text{-}F}$ = 7.0 Hz), 104.9 (d, $J_{C\text{-}F}$ = 17.3 Hz), 30.4 (d, $J_{C\text{-}F}$ = 5.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.0 (d, *J* = 36.3 Hz).

HRMS (ASAP) calcd for $C_{15}H_{13}F$ $[M]^+$: 212.1001, Found: 212.1008.

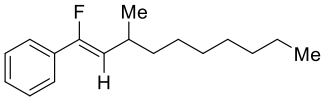
(3r,5r,7r)-1-((*Z*)-3-Fluoro-3-phenylallyl)adamantane (36)



Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), (3r,5r,7r)-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).

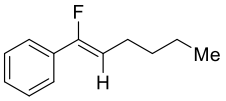
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.29 (m, 1H), 5.48 (dt, *J* = 37.3, 8.2 Hz, 1H), 2.06 (dd, *J* = 8.2, 1.8 Hz, 2H), 1.98 (s, 3H), 1.72 (d, *J* = 12.1 Hz, 3H), 1.68 – 1.62 (m, 3H), 1.58 (d, *J* = 2.5 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3 (d, $J_{C\text{-}F}$ = 245.9 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.6 Hz), 128.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 102.1 (d, $J_{C\text{-}F}$ = 17.4 Hz), 42.3, 38.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 37.1, 33.6 (d, $J_{C\text{-}F}$ = 1.6 Hz), 28.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ -120.4 (d, *J* = 37.3 Hz).
HRMS (ASAP) calcd for $C_{19}H_{23}F$ $[M]^+$: 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (d, $J_{C\text{-}F}$ = 244.9 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.5 Hz), 128.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 112.5 (d, $J_{C\text{-}F}$ = 17.4 Hz), 37.6 (d, $J_{C\text{-}F}$ = 1.4 Hz), 31.9, 29.7, 29.5 (d, $J_{C\text{-}F}$ = 3.9 Hz), 29.3, 27.5, 22.7, 21.1 (d, $J_{C\text{-}F}$ = 1.3 Hz), 14.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -121.9 (d, *J* = 37.8 Hz).
HRMS (ASAP) calcd for $C_{17}H_{25}F$ $[M]^+$: 248.1940, Found: 248.1946.

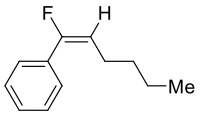
(*Z*)-(1-Fluorohex-1-en-1-yl)benzene (38)



Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6 (d, $J_{C\text{-}F}$ = 245.3 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.4 Hz), 128.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 106.3 (d, $J_{C\text{-}F}$ = 17.8 Hz), 31.6 (d, $J_{C\text{-}F}$ = 1.5 Hz), 23.8 (d, $J_{C\text{-}F}$ = 4.9 Hz), 22.3, 13.9.
^{19}F NMR (471 MHz, $CDCl_3$) δ -121.4 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for $C_{12}H_{15}F$ $[M]^+$: 178.1158, Found: 178.1152.

(*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 $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (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 **39**. Pale yellow oil (14 mg, 40% yield, *E*/*Z* = 6 : 1).

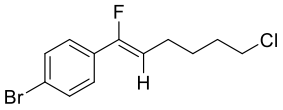
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.29 (m, 5H), 5.39 (dt, *J* = 22.8, 7.9 Hz, 1H), 2.20 (q, *J* = 7.0 Hz, 2H), 1.50 – 1.27 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5 (d, $J_{C\text{-}F}$ = 239.4 Hz), 132.2 (d, $J_{C\text{-}F}$ = 30.1 Hz), 128.8, 128.2, 127.6 (d, $J_{C\text{-}F}$ = 5.0 Hz), 108.6 (d, $J_{C\text{-}F}$ = 24.2 Hz), 32.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 25.7 (d, $J_{C\text{-}F}$ = 7.9 Hz), 22.2, 13.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ (*E*): -102.6 (d, *J* = 22.8 Hz), (*Z*): -121.4 (d, *J* = 37.5 Hz).

HRMS (ASAP) calcd for $C_{12}H_{15}F$ $[M]^+$: 178.1163, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry DCE (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).

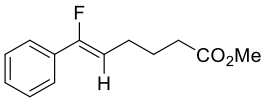
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 5.39 (dt, *J* = 36.9, 7.6 Hz, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.31 (qd, *J* = 7.5, 1.8 Hz, 2H), 1.93 – 1.76 (m, 2H), 1.70 – 1.55 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (d, $J_{C\text{-}F}$ = 246.1 Hz), 131.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 131.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 125.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 122.5, 106.1 (d, $J_{C\text{-}F}$ = 17.6 Hz), 44.8, 32.0, 26.5 (d, $J_{C\text{-}F}$ = 1.7 Hz), 23.4 (d, $J_{C\text{-}F}$ = 4.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -120.6 (d, *J* = 36.9 Hz).

HRMS (ASAP) calcd for $C_{12}H_{13}BrClF$ $[M]^+$: 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), methyl 6-phenylhex-5-ynoate (0.2 mmol, 40 mg, 1.0 equiv) at 70 ºC. 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).

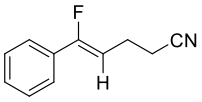
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.42 (m, 2H), 7.41 – 7.27 (m, 3H), 5.37 (dt, *J* = 37.0, 7.7 Hz, 1H), 3.67 (s, 3H), 2.47 – 2.25 (m, 4H), 1.88 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) 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).

^{19}F NMR (282 MHz, $CDCl_3$) δ (*E*): -100.6 (d, *J* = 22.1 Hz), (*Z*): -120.1 (d, *J* = 37.0 Hz).

HRMS (ASAP) calcd for $C_{13}H_{16}FO_2$ $[M+H]^+$: 223.1134, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 5-phenylpent-4-ynenitrile (0.2 mmol, 31 mg, 1.0 equiv) at 70 ºC. 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).

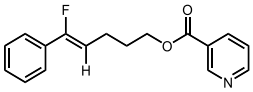
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.46 (m, 2H), 7.45 – 7.30 (m, 3H), 5.47 (dt, *J* = 35.7, 7.5 Hz, 1H), 2.72 – 2.59 (m, 2H), 2.58 – 2.47 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (d, $J_{C\text{-}F}$ = 250.7 Hz), 131.6 (d, $J_{C\text{-}F}$ = 28.5 Hz), 129.2, 128.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 124.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 119.1, 101.3 (d, $J_{C\text{-}F}$ = 16.9 Hz), 20.5 (d, $J_{C\text{-}F}$ = 6.1 Hz), 17.5 (d, $J_{C\text{-}F}$ = 2.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4 (d, *J* = 35.7 Hz).

HRMS (APCI) calcd for $C_{11}H_{11}FN$ $[M+H]^+$: 176.0870, Found: 176.0865.

(*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), $Et_2O \bullet BF_3$ (0.2 mmol, 25 µL, 1.0 equiv), dry $CHCl_3$ (1.0 mL), 5-phenylpent-4-yn-1-yl nicotinate (0.2 mmol, 53 mg, 1.0 equiv) at 70 ºC. 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).

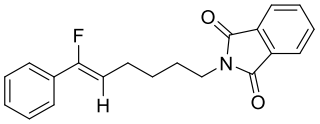
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, *J* = 1.1 Hz, 1H), 8.77 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.30 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.40 – 7.29 (m, 4H), 5.44 (dt, *J* = 36.8, 7.7 Hz, 1H), 4.43 (t, *J* = 6.5 Hz, 2H), 2.47 (qd, *J* = 7.6, 1.6 Hz, 2H), 2.02 – 1.92 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 157.5 (d, $J_{C\text{-}F}$ = 247.3 Hz), 153.4, 150.9, 137.0, 132.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 128.6, 128.4 (d, $J_{C\text{-}F}$ = 1.9 Hz), 126.2, 123.9 (d, $J_{C\text{-}F}$ = 7.0 Hz), 123.2, 104.4 (d, $J_{C\text{-}F}$ = 17.6 Hz), 64.8, 28.4, 20.8 (d, $J_{C\text{-}F}$ = 5.5 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -119.7 (d, J = 36.8 Hz).

HRMS (ESI) calcd for $C_{17}H_{17}FNO_2$ $[M+H]^+$: 286.1238 Found: 286.1229.

(*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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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 $CHCl_3$ (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).

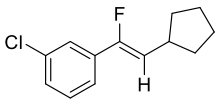
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.4, 3.0 Hz, 2H), 7.71 (dd, J = 5.4, 3.0 Hz, 2H), 7.54 – 7.41 (m, 2H), 7.39 – 7.26 (m, 3H), 5.37 (dt, J = 37.2, 7.6 Hz, 1H), 3.72 (t, J = 7.2 Hz, 2H), 2.33 (qd, J = 7.5, 1.7 Hz, 2H), 1.81 – 1.66 (m, 2H), 1.56 – 1.46 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 157.0 (d, $J_{C\text{-}F}$ = 246.3 Hz), 133.8, 132.62 (d, $J_{C\text{-}F}$ = 29.2 Hz), 132.2, 128.37 (d, $J_{C\text{-}F}$ = 1.7 Hz), 128.35 (d, $J_{C\text{-}F}$ = 2.0 Hz), 123.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 123.2, 105.4 (d, $J_{C\text{-}F}$ = 17.7 Hz), 37.8, 28.2, 26.6, 23.7 (d, $J_{C\text{-}F}$ = 5.1 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -120.6 (d, J = 37.2 Hz).

HRMS (ESI) calcd for $C_{20}H_{19}FNO_2$ $[M+H]^+$: 324.1394, Found: 324.1382.

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

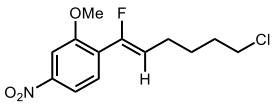


Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-chloro-3-(cyclopentylethynyl)benzene (0.2 mmol, 41 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

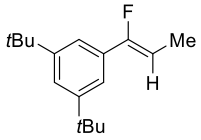
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6 (d, $J_{C\text{-}F}$ = 245.3 Hz), 134.8, 134.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 129.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 124.0 (d, $J_{C\text{-}F}$ = 7.4 Hz), 121.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 112.9 (d, $J_{C\text{-}F}$ = 16.8 Hz), 35.5 (d, $J_{C\text{-}F}$ = 3.7 Hz), 33.6 (d, $J_{C\text{-}F}$ = 1.3 Hz), 25.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -122.2 (d, J = 37.4 Hz).
HRMS (ASAP) calcd for $C_{13}H_{14}ClF$ $[M]^+$: 224.0768, Found: 224.0757.

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



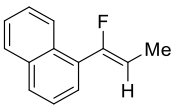
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry DCE (2.0 mL), 1-(6-chlorohex-1-yn-1-yl)-2-methoxy-4-nitrobenzene (0.2 mmol, 53 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 12 h, and the crude residue 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)
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5 (d, $J_{C\text{-}F}$ = 5.6 Hz), 152.0 (d, $J_{C\text{-}F}$ = 242.9 Hz), 147.8, 127.2 (d, $J_{C\text{-}F}$ = 28.7 Hz), 127.0 (d, $J_{C\text{-}F}$ = 11.2 Hz), 115.7 (d, $J_{C\text{-}F}$ = 1.6 Hz), 115.2 (d, $J_{C\text{-}F}$ = 15.6 Hz), 106.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 56.1, 44.8, 32.1, 26.4 (d, $J_{C\text{-}F}$ = 1.5 Hz), 23.9 (d, $J_{C\text{-}F}$ = 6.4 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -98.15 (d, J = 19.6 Hz), (*Z*): -114.11 (d, J = 39.8 Hz).
HRMS (APCI) calcd for $C_{13}H_{15}ClFNO_3$ $[M]^+$: 287.0719, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3 (d, $J_{C\text{-}F}$ = 246.1 Hz), 150.8 (d, $J_{C\text{-}F}$ = 1.6 Hz), 132.2 (d, $J_{C\text{-}F}$ = 28.0 Hz), 122.6, 118.2 (d, $J_{C\text{-}F}$ = 6.6 Hz), 100.1 (d, $J_{C\text{-}F}$ = 18.6 Hz), 34.9, 31.4, 9.4 (d, $J_{C\text{-}F}$ = 6.8 Hz).
^{19}F NMR (471 MHz, $CDCl_3$) δ -120.0 (dd, J = 37.3, 2.2 Hz).
HRMS (ASAP) calcd for $C_{17}H_{26}F$ $[M+H]^+$: 249.2019, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-(prop-1-yn-1-yl)naphthalene (0.2 mmol, 33 mg, 1.0 equiv) at 70 ºC. 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).

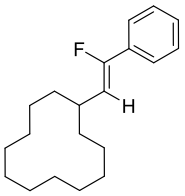
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (m, 1H), 7.86 – 7.74 (m, 2H), 7.49 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 5.15 (dq, *J* = 36.0, 7.0 Hz, 1H), 1.83 (dd, *J* = 7.0, 2.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1 (d, $J_{C\text{-}F}$ = 249.7 Hz), 133.6, 131.5 (d, $J_{C\text{-}F}$ = 26.1 Hz), 131.0, 129.6, 128.3, 127.0 (d, $J_{C\text{-}F}$ = 4.5 Hz), 126.5, 126.0, 125.7 (d, $J_{C\text{-}F}$ = 4.3 Hz), 125.0, 105.6 (d, $J_{C\text{-}F}$ = 18.4 Hz), 9.7 (d, $J_{C\text{-}F}$ = 5.4 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.4 (d, *J* = 36.2 Hz).

HRMS (ASAP) calcd for $C_{13}H_{12}F$ $[M+H]^+$: 187.0923, 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), (phenylethynyl)cyclododecane (0.2 mmol, 54 mg, 1.0 equiv) at 70 ºC. 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).

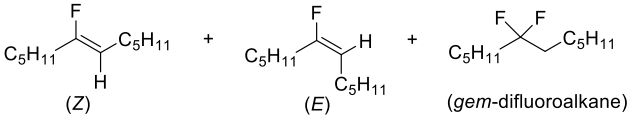
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.28 (m, 1H), 5.26 (dd, *J* = 37.8, 9.8 Hz, 1H), 2.97 – 2.85 (m, 1H), 1.62 (td, *J* = 13.1, 6.4 Hz, 2H), 1.54 – 1.49 (m, 2H), 1.47 – 1.25 (m, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (d, $J_{C\text{-}F}$ = 244.6 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.6 Hz), 128.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 112.0 (d, $J_{C\text{-}F}$ = 17.5 Hz), 30.6 (d, $J_{C\text{-}F}$ = 1.0 Hz), 29.6 (d, $J_{C\text{-}F}$ = 3.1 Hz), 23.9, 23.8, 23.5, 23.3, 22.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.7 (d, *J* = 37.8 Hz).

HRMS (ASAP) calcd for $C_{20}H_{29}F$ $[M]^+$: 288.2253, Found: 288.2251.

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

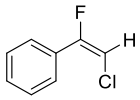


Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), dodec-6-yne (0.2 mmol, 33 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, and the crude 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).

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

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

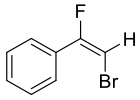


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), (chloroethynyl)benzene (0.2 mmol, 27 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by 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).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.45 – 7.40 (m, 3H), 6.26 (d, *J* = 13.4 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.48 (d, *J* = 13.3 Hz).

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

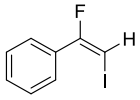


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), (bromoethynyl)benzene (0.2 mmol, 36 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by 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).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2H), 7.45 – 7.41 (m, 3H), 6.24 (d, *J* = 15.8 Hz, 1H).

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

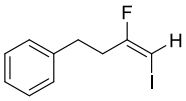
mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), (iodoethynyl)benzene (0.2 mmol, 46 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **53** with spectral properties identical to the reported in the literature[5]. Pale yellow oil (36 mg, 73% yield, *E*/*Z* > 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.46 – 7.39 (m, 3H), 6.14 (d, *J* = 19.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (d, $J_{C\text{-}F}$ = 256.1 Hz), 131.1 (d, $J_{C\text{-}F}$ = 28.6 Hz), 130.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 128.6 (d, $J_{C\text{-}F}$ = 5.2 Hz), 128.2, 53.8 (d, $J_{C\text{-}F}$ = 44.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.9 (d, *J* = 19.5 Hz).

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

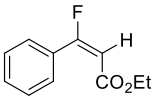


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), (4-iodobut-3-yn-1-yl)benzene (0.2 mmol, 51 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{19}F NMR (471 MHz, $CDCl_3$) δ -82.4 (td, *J* = 21.3, 17.8 Hz).

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

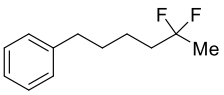


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), ethyl 3-phenylpropiolate (0.2 mmol, 35 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified 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).

^{1}H NMR (300 MHz, $CDCl_3$) 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).

^{19}F NMR (282 MHz, $CDCl_3$) 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 $CHCl_3$ (3.0 mL), hex-5-yn-1-ylbenzene (0.2 mmol, 32 mg, 1.0 equiv) at

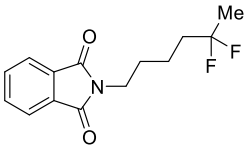
80 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **56** with spectral properties identical to the reported in the literature[7]. Pale yellow oil (20 mg, 51% yield).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 128.35, 128.32, 125.8, 124.3 (t, $J_{C\text{-}F}$ = 237.6 Hz), 37.8 (t, $J_{C\text{-}F}$ = 25.4 Hz), 35.7, 31.1, 23.2 (t, $J_{C\text{-}F}$ = 28.1 Hz), 22.4 (t, $J_{C\text{-}F}$ = 4.7 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) 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 $CHCl_3$ (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).

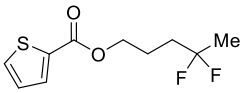
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.69 (m, 2H), 3.70 (t, J = 7.2 Hz, 2H), 1.96 – 1.83 (m, 2H), 1.78 – 1.68 (m, 2H), 1.61 – 1.48 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 133.9, 132.1, 124.0 (t, $J_{C\text{-}F}$ = 237.8 Hz), 123.2, 37.5, 37.4 (t, $J_{C\text{-}F}$ = 25.6 Hz), 28.2, 23.2 (t, $J_{C\text{-}F}$ = 28.0 Hz), 20.0 (t, $J_{C\text{-}F}$ = 4.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -90.6 – -90.9 (m, 2F).

HRMS (ESI) calcd for $C_{14}H_{16}F_2NO_2$ $[M+H]^+$: 268.1144, Found: 268.1142.

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



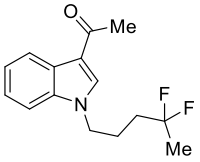
Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), pent-4-yn-1-yl thiophene-2-carboxylate (0.2 mmol, 39 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude residue 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 133.7, 133.5, 132.4, 127.8, 123.8 (t, $J_{C\text{-}F}$ = 238.0 Hz), 64.3, 34.6 (t, $J_{C\text{-}F}$ = 26.1 Hz), 23.4 (t, $J_{C\text{-}F}$ = 27.9 Hz), 22.2 (t, $J_{C\text{-}F}$ = 4.7 Hz).

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

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



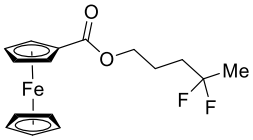
Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), 1-(1-(pent-4-yn-1-yl)-1H-indol-3-yl)ethan-1-one (0.2 mmol, 45 mg, 1.0 equiv) at 80 °C. The reaction mixture was quenched after 12 h, and the crude 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).

^{1}H 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, $J_{C\text{-}F}$ = 238.4 Hz), 123.4, 122.7, 122.6, 117.3, 109.6, 46.3, 34.8 (t, $J_{C\text{-}F}$ = 25.9 Hz), 27.6, 23.6 (t, $J_{C\text{-}F}$ = 27.8 Hz), 23.1 (t, $J_{C\text{-}F}$ = 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).

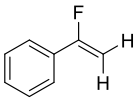
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (s, 2H), 4.40 (s, 2H), 4.26 (t, J = 6.2 Hz, 2H), 4.20 (s, 5H), 2.08 – 1.97 (m, 2H), 1.97 – 1.90 (m, 2H), 1.65 (t, J = 18.3 Hz, 3H).

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

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

HRMS (APCI) calcd for $C_{16}H_{19}F_2FeO_2$ $[M+H]^+$: 337.0697, Found: 337.0681.

(1-Fluorovinyl)benzene (61)



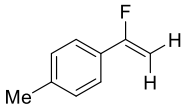
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), phenylacetylene (0.2 mmol, 21 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h,

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[12]. Pale yellow oil (9 mg, 35% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.52 (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).

^{19}F NMR (282 MHz, $CDCl_3$) δ -107.9 (dd, *J* = 49.7, 17.9 Hz).

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

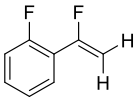


Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 4-ethynyltoluene (0.2 mmol, 23 mg, 1.0 equiv) at 40 °C. The reaction mixture was quenched after 1 h, and 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).

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

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.7 (dd, *J* = 50.1, 18.0 Hz).

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



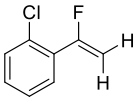
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 2-fluorophenylacetylene (0.2 mmol, 24 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8 (dd, $J_{C\text{-}F}$ = 252.9, 5.9 Hz), 157.3 (dd, $J_{C\text{-}F}$ = 247.1, 4.6 Hz), 130.6 (d, $J_{C\text{-}F}$ = 8.7 Hz), 127.2 (dd, $J_{C\text{-}F}$ = 8.4, 2.0 Hz), 124.1 (dd, $J_{C\text{-}F}$ = 3.7, 1.1 Hz), 120.1 (dd, $J_{C\text{-}F}$ = 31.2, 11.0 Hz), 116.1 (dd, $J_{C\text{-}F}$ = 22.5, 2.8 Hz), 95.6 (dd, $J_{C\text{-}F}$ = 21.0, 13.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) 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)



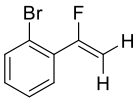
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 2-chlorophenylacetylene (0.2 mmol, 27 mg, 1.0 equiv) at 70 ºC. The reaction mixture was quenched after 6 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) 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).

^{19}F NMR (471 MHz, $CDCl_3$) 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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-bromo-2-ethynylbenzene (0.2 mmol, 36 mg, 1.0 equiv) at 70 ºC. 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).

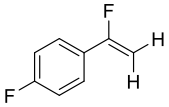
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.33 (tt, *J* = 7.7, 1.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 5.09 (dd, *J* = 16.4, 3.3 Hz, 1H), 4.97 (dd, *J* = 48.4, 3.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, $J_{C\text{-}F}$ = 253.6 Hz), 133.7 (d, $J_{C\text{-}F}$ = 29 Hz, partially superimposed with resonance at 133.6), 133.6, 130.7 (d, $J_{C\text{-}F}$ = 1.1 Hz), 130.5 (d, $J_{C\text{-}F}$ = 4.4 Hz), 127.2, 121.5, 95.6 (d, $J_{C\text{-}F}$ = 21.6 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -91.48 (dd, *J* = 48.4, 16.4 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.74.

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



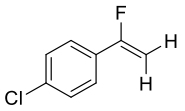
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 4-fluorophenylacetylene (0.2 mmol, 24 mg, 1.0 equiv) at 70 ºC. The reaction mixture was quenched after 6 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).

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

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.0 (dd, *J* = 49.7, 17.9 Hz, 1F), -111.5 – -111.6 (m, 1F).

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



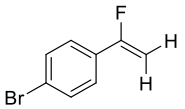
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 4-chlorophenylacetylene (0.2 mmol, 28 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 249.9 Hz), 135.3, 130.5 (d, $J_{C\text{-}F}$ = 29.9 Hz), 128.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 125.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 90.1 (d, $J_{C\text{-}F}$ = 22.4 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -107.9 (dd, *J* = 49.4, 17.7 Hz).

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



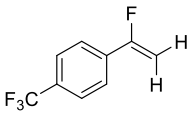
Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 4-bromophenylacetylene (0.2 mmol, 36 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 h, 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 250.2 Hz), 131.7 (d, $J_{C\text{-}F}$ = 1.9 Hz), 130.9 (d, $J_{C\text{-}F}$ = 29.8 Hz), 126.2 (d, $J_{C\text{-}F}$ = 6.9 Hz), 123.6, 90.2 (d, $J_{C\text{-}F}$ = 22.4 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -108.0 (dd, *J* = 49.4, 17.7 Hz).

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

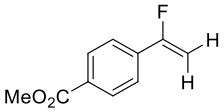


Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), 1-ethynyl-4-(trifluoromethyl)benzene (0.2 mmol, 34 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched 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).

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

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F), -108.4 (dd, *J* = 49.1, 17.6 Hz, 1F).

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

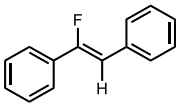


Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.2 mmol, 47 mg, 1.0 equiv), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), methyl 4-ethynylbenzoate (0.2 mmol, 32 mg, 1.0 equiv) at 70 °C. The reaction mixture was quenched after 6 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).

^{1}H NMR (300 MHz, $CDCl_3$) 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).

^{19}F NMR (282 MHz, $CDCl_3$) δ -108.3 (dd, *J* = 49.1, 17.6 Hz).

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



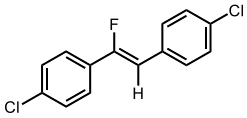
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1,2-diphenylethyne (0.2 mmol, 36 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2 (d, $J_{C\text{-}F}$ = 258.6 Hz), 133.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 132.9 (d, $J_{C\text{-}F}$ = 27.9 Hz), 129.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 128.9, 128.6, 128.6, 127.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 124.3 (d, $J_{C\text{-}F}$ = 7.4 Hz), 105.8 (d, $J_{C\text{-}F}$ = 10.5 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.2 (d, *J* = 39.6 Hz).

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



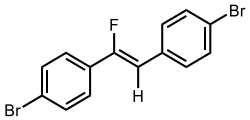
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1,2-bis(4-chlorophenyl)ethyne (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified by 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6 (d, $J_{C\text{-}F}$ = 258.8 Hz), 135.2, 133.2 (d, $J_{C\text{-}F}$ = 3.6 Hz), 131.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.0 (d, $J_{C\text{-}F}$ = 28.4 Hz), 130.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.8, 125.6 (d, $J_{C\text{-}F}$ = 7.4 Hz), 105.2 (d, $J_{C\text{-}F}$ = 10.4 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) 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).

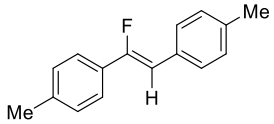
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.51 – 7.41 (m, 6H), 6.24 (d, *J* = 38.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}F}$ = 259.0 Hz), 132.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 131.8, 131.4 (d, $J_{C\text{-}F}$ = 28.4 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 125.8 (d, $J_{C\text{-}F}$ = 7.4 Hz), 123.42, 121.4 (d, $J_{C\text{-}F}$ = 3.7 Hz), 105.4 (d, $J_{C\text{-}F}$ = 10.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -113.5 (d, *J* = 38.8 Hz).

HRMS (ESI) calcd for $C_{14}H_9Br_2F$ $[M]^+$: 353.9050, 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 $CHCl_3$ (2.0 mL), 1,2-di-p-tolylethyne (0.2 mmol, 41 mg, 1.0 equiv) at 90

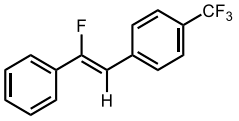
°C. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **74** with spectral properties identical to the reported in the literature[15]. Pale yellow oil (21 mg, 47% yield, *Z*/*E* > 50 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9 (d, $J_{C\text{-}F}$ = 257.1 Hz), 138.9, 137.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 131.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.3 (d, $J_{C\text{-}F}$ = 28.1 Hz), 129.3, 128.7 (d, $J_{C\text{-}F}$ = 7.9 Hz), 124.1 (d, $J_{C\text{-}F}$ = 7.4 Hz), 104.9 (d, $J_{C\text{-}F}$ = 10.8 Hz), 21.28, 21.26.

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.9 (d, *J* = 39.9 Hz).

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



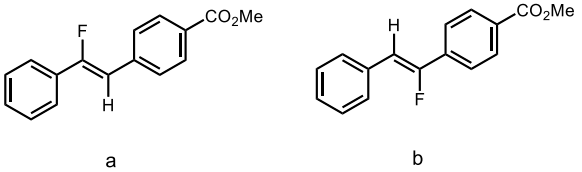
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-(phenylethynyl)-4-(trifluoromethyl)benzene (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7 (d, $J_{C\text{-}F}$ = 261.6 Hz), 137.2, 132.2 (d, $J_{C\text{-}F}$ = 27.6 Hz), 131.8 (d, $J_{C\text{-}F}$ = 6.9 Hz), 129.6, 129.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 124.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 104.6 (d, $J_{C\text{-}F}$ = 10.2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6 (s, 3F), -111.0 (d, *J* = 38.6 Hz, 1F).

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



a b

a : b = 17 : 1

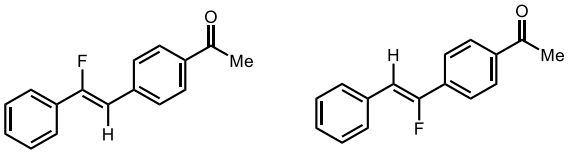
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), methyl 4-(phenylethynyl)benzoate (0.2 mmol, 47 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 158.7 (d, $J_{C\text{-}F}$ = 262.1 Hz), 138.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 132.3 (d, $J_{C\text{-}F}$ = 27.6 Hz), 129.8, 129.6, 128.73, 128.68, 128.67, 124.5 (d, $J_{C\text{-}F}$ = 7.6 Hz), 105.1 (d, $J_{C\text{-}F}$ = 10.1 Hz), 52.0.

^{19}F NMR (471 MHz, $CDCl_3$) 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)



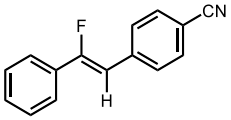
a : b = 15 : 1

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 ºC. 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{19}F NMR (471 MHz, $CDCl_3$) 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)



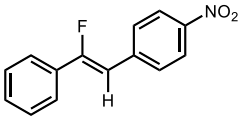
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 4-(phenylethynyl)benzonitrile (0.2 mmol, 41 mg, 1.0 equiv) at 100 ºC. The reaction mixture was quenched after 12 h, and the crude residue was purified by 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5 (d, $J_{C\text{-}F}$ = 263.6 Hz), 138.3 (d, $J_{C\text{-}F}$ = 3.1 Hz), 132.3, 131.9 (d, $J_{C\text{-}F}$ = 27.4 Hz), 130.0, 129.2 (d, $J_{C\text{-}F}$ = 8.6 Hz), 128.8 (d, $J_{C\text{-}F}$ = 2.1 Hz), 124.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 119.0, 110.3 (d, $J_{C\text{-}F}$ = 3.1 Hz), 104.4 (d, $J_{C\text{-}F}$ = 9.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -108.9 (d, J = 38.4 Hz).

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



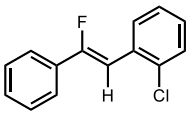
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-nitro-4-(phenylethynyl)benzene (0.2 mmol, 45 mg, 1.0 equiv) at 100 ºC. The reaction mixture was quenched after 12 h, and the crude residue was purified 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9 (d, $J_{C\text{-}F}$ = 264.7 Hz), 146.3, 140.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.8 (d, $J_{C\text{-}F}$ = 27.3 Hz), 130.2, 129.3 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 124.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 123.9, 104.1 (d, $J_{C\text{-}F}$ = 9.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -108.2 (d, *J* = 38.2 Hz).

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



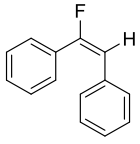
Prepared following the general procedure (**condition D**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv) dry DCE (2.0 mL), 1-chloro-2-(phenylethynyl)benzene (0.2 mmol, 42 mg, 1.0 equiv) at 100 ºC. The reaction mixture was quenched after 12 h, and the crude residue was purified 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2 (d, $J_{C\text{-}F}$ = 260.9 Hz), 133.2(d, $J_{C\text{-}F}$ = 0.6 Hz), 132.6 (d, $J_{C\text{-}F}$ = 27.9 Hz), 131.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 130.5 (d, $J_{C\text{-}F}$ = 13.4 Hz), 129.5, 129.4, 128.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 128.3 (d, $J_{C\text{-}F}$ = 1.6 Hz), 126.8, 124.6 (d, $J_{C\text{-}F}$ = 7.4 Hz), 101.7 (d, $J_{C\text{-}F}$ = 8.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -113.8 (d, *J* = 38.6 Hz).

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



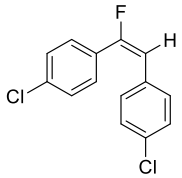
Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), 1,2-diphenylethyne (0.2 mmol, 36 mg, 1.0 equiv) at 80

°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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{19}F NMR (471 MHz, $CDCl_3$) δ -96.0 (d, *J* = 21.6 Hz).

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

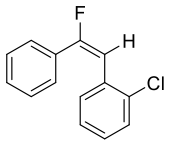


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), 1,2-bis(4-chlorophenyl)ethyne (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was purified 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).

^{1}H 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).

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

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

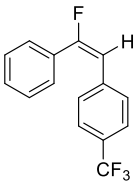


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), 1-chloro-2-(phenylethynyl)benzene (0.2 mmol, 42 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue was 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).

^{1}H 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).

^{19}F 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)

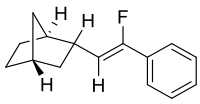


Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (3.0 mL), 1-(phenylethynyl)-4-(trifluoromethyl)benzene (0.2 mmol, 49 mg, 1.0 equiv) at 100 °C. The reaction mixture was quenched after 12 h, and the crude residue 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6 (s, 3F), -91.6 (d, *J* = 20.7 Hz, 1F).

(1*S*,2*R*,4*R*)-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), $LiBF_4$ (0.25 mmol, 4.7 mg, 0.25 equiv), dry $CHCl_3$ (1.0 mL), (1*S*,2*R*,4*R*)-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).

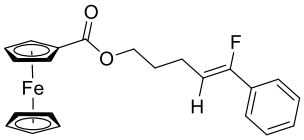
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 5.29 (dd, *J* = 37.6, 9.4 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.33 – 2.26 (m, 1H), 2.15 – 2.08 (m, 1H), 1.73 – 1.64 (m, 1H), 1.60 – 1.48 (m, 2H), 1.46 – 1.41 (m, 1H), 1.37 – 1.26 (m, 2H), 1.25 – 1.18 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7 (d, $J_{C\text{-}F}$ = 245.3 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.2 Hz), 128.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 112.7 (d, $J_{C\text{-}F}$ = 16.9 Hz), 42.9 (d, $J_{C\text{-}F}$ = 1.0 Hz), 39.2 (d, $J_{C\text{-}F}$ = 1.3 Hz), 37.2 (d, $J_{C\text{-}F}$ = 3.7 Hz), 36.5, 36.1, 29.6, 28.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.2 (d, *J* = 37.6 Hz).

HRMS (ASAP) calcd for $C_{15}H_{17}F$ $[M]^+$: 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), $Et_2O \bullet BF_3$ (0.2 mmol, 25 μL, 1.0 equiv), dry $CHCl_3$ (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 (with $Et_2O•BF_3$: 48 mg, 61% yield, *Z*/*E* = 9 : 1; without $Et_2O•BF_3$: 53 mg, 68% yield, Z/E = 3 : 1).

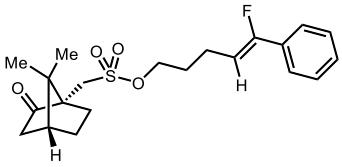
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.43 – 7.29 (m, 3H), 5.46 (dt, *J* = 36.9, 7.6 Hz, 1H), 4.83 (t, *J* = 1.9 Hz, 2H), 4.43 – 4.35 (m, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 4.21 (s, 4H), 4.15 (s, 1H), 2.52 – 2.33 (m, 2H), 1.98 – 1.83 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 157.4 (d, $J_{C\text{-}F}$ = 247.0 Hz), 132.5 (d, $J_{C\text{-}F}$ = 29.1 Hz), 128.5, 128.4 (d, $J_{C\text{-}F}$ = 1.9 Hz), 123.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 104.7 (d, $J_{C\text{-}F}$ = 17.6 Hz), 71.2, 70.1, 69.7, 63.5, 28.7 (d, $J_{C\text{-}F}$ = 1.5 Hz), 20.8 (d, $J_{C\text{-}F}$ = 5.4 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -100.5 (d, *J* = 22.1 Hz), (*Z*): -119.8 (d, *J* = 36.9 Hz).

HRMS (APCI) calcd for $C_{22}H_{21}FFeO_2$ $[M]^+$: 392.0875, Found: 392.0891.

(*Z*)-5-Fluoro-5-phenylpent-4-en-1-yl ((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (87)



Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), $Et_2O \bullet BF_3$ (0.2 mmol, 25 μL, 1.0 equiv), dry $CHCl_3$ (2.0 mL), 5-phenylpent-4-yn-1-yl ((1*S*,4*R*)-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 (with $Et_2O•BF_3$: 50 mg, 64% yield, *Z*/*E* = 9 : 1; without $Et_2O•BF_3$: 55 mg, 70% yield, Z/E = 2.8 : 1).

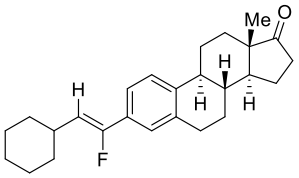
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.40 (dt, *J* = 36.8, 7.6 Hz, 1H), 4.41 – 4.26 (m, 2H), 3.61 (d, *J* = 15.1 Hz, 1H), 2.99 (d, *J* = 15.1 Hz, 1H), 2.52 – 2.35 (m, 4H), 2.11 (t, *J* = 4.3 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.96 – 1.89 (m, 3H), 1.71 – 1.62 (m, 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, $J_{C\text{-}F}$ = 247.6 Hz), 132.2 (d, $J_{C\text{-}F}$ = 29.0 Hz), 128.6, 128.4 (d, $J_{C\text{-}F}$ = 1.9 Hz), 123.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 103.9 (d, $J_{C\text{-}F}$ = 17.5 Hz), 69.8, 57.8, 47.9, 46.6, 42.7, 42.4, 28.9 (d, $J_{C\text{-}F}$ = 1.6 Hz), 26.8, 24.8, 20.2 (d, $J_{C\text{-}F}$ = 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 $C_{21}H_{28}FO_4S$ $[M+H]^+$: 395.1689, Found: 395.1674.

(8*R*,9*S*,13*S*,14*S*)-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), (8*R*,9*S*,13*S*,14*S*)-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).

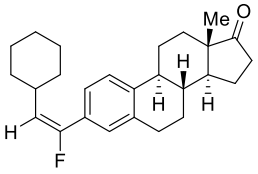
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.22 (s, 1H), 5.21 (dd, *J* = 38.4, 9.2 Hz, 1H), 2.98 – 2.85 (m, 2H), 2.62 (m, 1H), 2.51 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.30 (td, *J* = 10.8, 4.2 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.10 – 2.00 (m, 2H), 1.99 – 1.93 (m, 1H), 1.81 – 1.69 (m, 4H), 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.7, 155.4 (d, $J_{C\text{-}F}$ = 245.2 Hz), 140.0, 136.5, 130.5 (d, $J_{C\text{-}F}$ = 29.5 Hz), 125.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 124.3 (d, $J_{C\text{-}F}$ = 6.6 Hz), 121.4 (d, $J_{C\text{-}F}$ = 6.8 Hz), 111.4 (d, $J_{C\text{-}F}$ = 17.1 Hz), 50.5, 47.9, 44.4, 38.1, 35.8, 33.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 33.2, 31.6, 29.4, 26.4, 26.0, 25.8, 25.7, 21.6, 13.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.8 (d, *J* = 38.3 Hz).

HRMS (ASAP) calcd for $C_{26}H_{34}FO$ $[M+H]^+$: 381.2588, Found: 381.2578.

(8*R*,9*S*,13*S*,14*S*)-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)



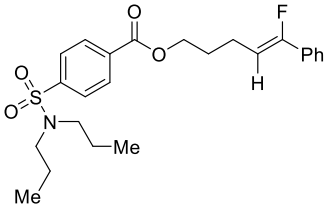
Prepared following the general procedure (**condition B**): (8*R*,9*S*,13*S*,14*S*)-3-(cyclohexylethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (0.2 mmol, 72 mg, 1.0 equiv), dry $CHCl_3$ (1.0 mL), $HBF_4{\cdot}Et_2O$ (27 μL, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was quenched after 6 h, and the crude residue was purified by flash column chromatography (hexanes/EtOAc = 10 : 1) to provide the title compound **89**. Pale yellow oil (37 mg, 49% yield, *E*/*Z* = 13:1).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.6, 155.8 (d, $J_{C\text{-}F}$ = 239.9 Hz), 140.6, 136.4, 123.0 (d, $J_{C\text{-}F}$ = 30.3 Hz), 127.9 (d, $J_{C\text{-}F}$ = 4.7 Hz), 125.2, 124.9 (d, $J_{C\text{-}F}$ = 5.2 Hz), 114.0 (d, $J_{C\text{-}F}$ = 22.2 Hz), 50.5, 47.9, 44.5, 38.0, 35.8, 35.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 33.8 (d, $J_{C\text{-}F}$ = 0.8 Hz), 31.6, 29.4, 26.4, 25.9, 25.7, 25.6, 21.6, 13.8.

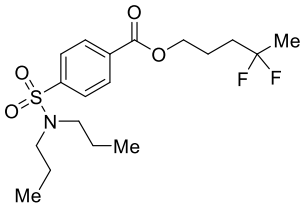
^{19}F NMR (471 MHz, $CDCl_3$) δ (*E*): -103.5 (d, *J* = 23.0 Hz), (*Z*): -121.7 (d, *J* = 38.3 Hz).
HRMS (ESI) calcd for $C_{26}H_{34}FO$ $[M+H]^+$: 381.2594, Found: 381.2577.

(*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 $CHCl_3$ (2.0 mL), 5-phenylpent-4-yn-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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 157.5 (d, $J_{C\text{-}F}$ = 247.3 Hz), 144.2, 133.6, 132.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 130.2, 128.6, 128.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.0, 123.9 (d, $J_{C\text{-}F}$ = 7.0 Hz), 104.5 (d, $J_{C\text{-}F}$ = 17.6 Hz), 65.0, 49.9, 28.4 (d, $J_{C\text{-}F}$ = 1.4 Hz), 21.9, 20.9 (d, $J_{C\text{-}F}$ = 5.5 Hz), 11.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -119.8 (d, *J* = 36.9 Hz).
HRMS (ESI) calcd for $C_{24}H_{31}FNO_4S$ $[M+H]^+$: 448.1952, Found: 448.1934.

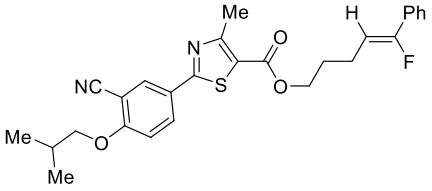
4,4-Difluoropentyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (91)



Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).

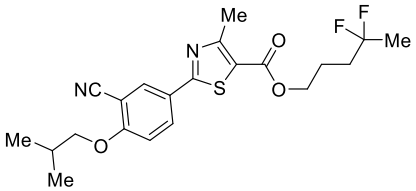
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 144.4, 133.4, 130.2, 127.0, 123.7 (t, $J_{C\text{-}F}$ = 238.1 Hz), 64.8, 49.9, 34.6 (t, $J_{C\text{-}F}$ = 26.1 Hz), 23.5 (t, $J_{C\text{-}F}$ = 27.9 Hz), 22.2 (t, $J_{C\text{-}F}$ = 4.7 Hz), 21.9, 11.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -91.2 – -91.6 (m, 2F).

(*Z*)-5-Fluoro-5-phenylpent-4-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (92)



Prepared following the general procedure (**condition A**): 2,6-dichloropyridinium tetrafluoroborate (0.4 mmol, 94 mg, 2.0 equiv), dry $CHCl_3$ (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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 162.5, 162.0, 161.2, 157.4 (d, $J_{C\text{-}F}$ = 247.2 Hz), 132.5, 132.4 (d, $J_{C\text{-}F}$ = 28.7 Hz), 132.1, 128.6, 128.4 (d, $J_{C\text{-}F}$ = 1.9 Hz), 126.0, 123.9 (d, $J_{C\text{-}F}$ = 7.0 Hz), 121.8, 115.4, 112.6, 104.5 (d, $J_{C\text{-}F}$ = 17.6 Hz), 103.0, 75.7, 64.8, 28.4, 28.2, 21.0 (d, $J_{C\text{-}F}$ = 5.5 Hz), 19.0, 17.5.
^{19}F NMR (471 MHz, $CDCl_3$) δ -119.8 (d, *J* = 36.9 Hz).
HRMS (ESI) calcd for $C_{27}H_{28}FN_2O_3S$ $[M+H]^+$: 479.1799, Found: 479.1784.

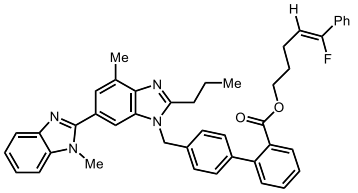
4,4-Difluoropentyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (93)



Prepared following the general procedure (**condition C**): 2,6-dichloropyridinium tetrafluoroborate (0.6 mmol, 141 mg, 3.0 equiv), dry $CHCl_3$ (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).

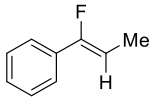
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.3 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.34 (t, *J* = 6.0 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 3H), 2.26 – 2.14 (m, 1H), 2.06 – 1.90 (m, 4H), 1.65 (t, *J* = 18.4 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 162.5, 161.9, 161.4, 132.6, 132.1, 126.0, 123.7 (t, $J_{C\text{-}F}$ = 238.1 Hz), 121.5, 115.4, 112.6, 103.0, 75.7, 64.5, 34.6 (t, $J_{C\text{-}F}$ = 26.0 Hz), 28.2, 23.5 (t, $J_{C\text{-}F}$ = 27.9 Hz), 22.2 (t, $J_{C\text{-}F}$ = 4.6 Hz), 19.0, 17.5.
^{19}F NMR (471 MHz, $CDCl_3$) 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), $Et_2O \bullet BF_3$ (0.2 mmol, 25 μL, 1.0 equiv), dry $CHCl_3$ (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 ºC. 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).
^{1}H NMR (500 MHz, $CDCl_3$) 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).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 157.1 (d, $J_{C\text{-}F}$ = 246.9 Hz), 156.4, 154.7, 143.2, 142.9, 141.7, 141.3, 136.6, 135.0, 134.8, 132.3 (d, $J_{C\text{-}F}$ = 29.0 Hz), 131.3, 130.8, 130.7, 129.9, 129.4, 129.0, 128.6, 128.4 (d, $J_{C\text{-}F}$ = 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, $J_{C\text{-}F}$ = 17.5 Hz), 64.4, 47.0, 31.7, 29.8, 28.0, 21.8, 20.6 (d, $J_{C\text{-}F}$ = 5.3 Hz), 16.8, 14.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ -119.8 (d, *J* = 37.2 Hz).
HRMS (ESI) calcd for $C_{44}H_{42}FN_4O_2$ $[M+H]^+$: 677.3286 Found: 677.3261.

(*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), $LiBF_4$ (1.25 mmol, 117 mg, 0.25 equiv), dry $CHCl_3$ (25 mL), 1-phenyl-1-propyne (5.0 mmol, 580 mg, 1.0 equiv) at 70 ºC. The reaction mixture was quenched after

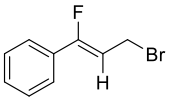
12 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound **95** with spectral properties identical to the reported in the literature[18]. Pale yellow oil (394 mg, 58% yield, *Z*/*E* > 50 : 1).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3 (d, $J_{C\text{-}F}$ = 245.5 Hz), 132.9 (d, $J_{C\text{-}F}$ = 29.1 Hz), 128.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 123.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 100.6 (d, $J_{C\text{-}F}$ = 18.2 Hz), 9.4 (d, $J_{C\text{-}F}$ = 6.7 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -121.6 (d, *J* = 37.2 Hz).

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



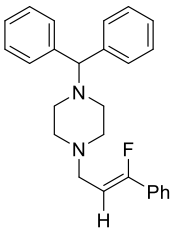
A solution of (*Z*)-(1-fluoroprop-1-en-1-yl)benzene **95** (300 mg, 2.2 mmol, 1.0 equiv), NBS (432 mg, 2.4 mmol, 1.1 equiv) and AIBN (36 mg, 0.22 mmol, 0.1 equiv) in dry CCl_4 (10 mL) was refluxed for 12 h under a nitrogen atmosphere. After completion of the reaction monitored by TLC, the reaction mixture was then cooled to room temperature. The floated succinimide was filtered off and the filtrate was washed with H_2O and brine and dried with Na_2SO_4. 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9 (d, $J_{C\text{-}F}$ = 256.0 Hz), 131.3 (d, $J_{C\text{-}F}$ = 27.8 Hz), 130.0, 128.5, 124.8 (d, $J_{C\text{-}F}$ = 7.2 Hz), 102.7 (d, $J_{C\text{-}F}$ = 15.4 Hz), 24.5 (d, $J_{C\text{-}F}$ = 9.1 Hz,).

^{19}F NMR (471 MHz, $CDCl_3$) 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 Et_2O (10 ml). The organic layer was separated and the aqueous layer was extracted with Et_2O (2×10 ml). The combined organics were washed with brine, dried ($MgSO_4$) 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).

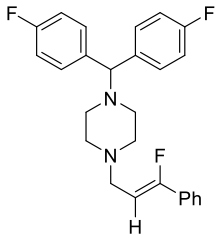
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 4H), 7.31 – 7.22 (m, 3H), 7.18 (dd, *J* = 8.4, 6.8 Hz, 4H), 7.09 (t, *J* = 7.3 Hz, 2H), 5.46 (dt, *J* = 36.7, 7.4 Hz, 1H), 4.16 (s, 1H), 3.22 (dd, *J* = 7.4, 1.8 Hz, 2H), 2.81 – 2.06 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6 (d, $J_{C\text{-}F}$ = 249.9 Hz), 142.7, 132.1 (d, $J_{C\text{-}F}$ = 28.9 Hz), 128.9, 128.5, 128.4, 127.9, 126.9, 124.2(d, $J_{C\text{-}F}$ = 7.1 Hz), 102.0 (d, $J_{C\text{-}F}$ = 15.1 Hz), 76.1, 53.2, 51.9 (d, $J_{C\text{-}F}$ = 4.6 Hz), 51.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.7 (d, *J* = 36.2 Hz).

HRMS (APCI) calcd for $C_{26}H_{28}FN_2$ $[M+H]^+$: 387.2231, 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 Et_2O (10 ml). The organic layer was separated and the aqueous layer was extracted with Et_2O (2×10 ml). The combined organics were washed with brine, dried ($MgSO_4$) 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).

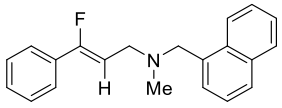
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.9 Hz, 2H), 7.34 (t, *J* = 6.8 Hz, 7H), 6.96 (t, *J* = 8.6 Hz, 4H), 5.53 (dt, *J* = 36.6, 7.3 Hz, 1H), 4.23 (s, 1H), 3.30 (d, *J* = 6.6 Hz, 2H), 2.87 – 2.51 (m, 4H), 2.51 – 2.13 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, $J_{C\text{-}F}$ = 245.5 Hz), 158.7 (d, $J_{C\text{-}F}$ = 250.1 Hz), 138.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 132.0 (d, $J_{C\text{-}F}$ = 28.9 Hz), 129.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 129.0, 128.5 (d, $J_{C\text{-}F}$ = 1.8 Hz), 124.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 101.8 (d, $J_{C\text{-}F}$ = 15.2 Hz), 74.4, 53.1, 51.8 (d, $J_{C\text{-}F}$ = 4.6 Hz), 51.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -115.7 (s, 2F), -117.5 (d, *J* = 35.3 Hz, 1F).

HRMS (ESI) calcd for $C_{26}H_{26}F_3N_2$ $[M+H]^+$: 423.2043, Found: 423.2023.

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



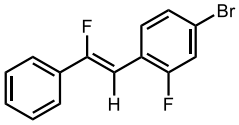
A solution of the (*Z*)-(3-bromo-1-fluoroprop-1-en-1-yl)benzene **96** (43 mg, 0.2 mmol, 1 equiv) in THF (0.5 M) was added dropwise to a solution of 1-methyl-aminomethyl naphthalene (68 mg, 0.4 mmol, 2.0 equiv) in THF (2.5 M) at room temperature. 1 M aq NaOH (0.4 ml, 0.4 mmol, 2 equiv) was then added in one portion, and the reaction was stirred at room temperature for 6 h. The reaction was diluted with Et_2O (10 ml). The organic layer was separated and the aqueous layer was extracted with Et_2O (2×10 ml). The combined organics were washed with brine, dried ($MgSO_4$) 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4 (d, $J_{C\text{-}F}$ = 249.2 Hz), 134.7, 133.8, 132.5, 132.2 (d, $J_{C\text{-}F}$ = 28.9 Hz), 128.9, 128.46, 128.45, 128.0, 127.5, 125.9, 125.6, 125.1, 124.6, 124.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 103.0 (d, $J_{C\text{-}F}$ = 15.3 Hz), 60.0, 51.4 (d, $J_{C\text{-}F}$ = 4.4 Hz), 42.4.

^{19}F NMR (471 MHz, $CDCl_3$) 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).

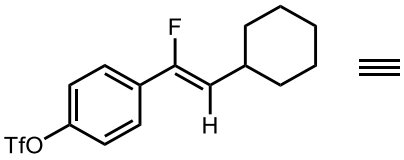
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, *J* = 8.3 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.46 – 7.36 (m, 3H), 7.32 – 7.28 (m, 1H), 7.26 (dd, *J* = 9.8, 1.8 Hz, 1H), 6.50 (d, *J* = 39.0 Hz, 1H).

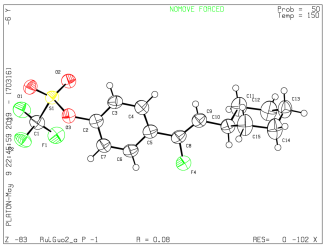
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4 (dd, $J_{C\text{-}F}$ = 253.7, 1.0 Hz), 158.7 (dd, $J_{C\text{-}F}$ = 261.1, 2.3 Hz), 132.3 (d, $J_{C\text{-}F}$ = 27.5 Hz), 130.9 (dd, $J_{C\text{-}F}$ = 14.9, 3.1 Hz), 129.6, 128.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.6 (d, $J_{C\text{-}F}$ = 3.6 Hz), 124.5 (d, $J_{C\text{-}F}$ = 7.6 Hz), 120.9 (dd, $J_{C\text{-}F}$ = 10.0, 3.2 Hz), 120.8 (dd, $J_{C\text{-}F}$ = 11.9, 3.2 Hz), 118.9 (d, $J_{C\text{-}F}$ = 25.6 Hz), 96.2 (dd, $J_{C\text{-}F}$ = 9.4, 7.1 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -111.3 (dd, *J* = 39.0, 3.5 Hz, 1F), -113.9 – -114.1 (m, 1F).

HRMS (APCI) calcd for $C_{14}H_9BrF_2$ $[M]^+$: 293.9850, Found: 293.9864.

9. X-ray structures of product 22





Datablock: RuiGuo2_a

```
Bond precision:  C-C = 0.0077 A          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.

M06-2X free energy in solution after quasi-harmonic correction: -1592.456444 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.

M06-2X free energy in solution after quasi-harmonic correction: -539.221504 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.633758 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.63056 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

102

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.

M06-2X free energy in solution after quasi-harmonic correction: -964.2347879 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: -964.40841636 a.u.

M06-2X enthalpy in solution: -964.170289 a.u.

M06-2X free energy in solution: -964.238669 a.u.

M06-2X free energy in solution after quasi-harmonic correction: -964.2324213 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	1.478305	-1.428117	-0.197537
C	2.035789	-1.881843	1.039504
C	2.273646	-0.687091	-1.126087
C	3.350140	-1.592611	1.330074
H	1.405208	-2.431783	1.731124
C	3.588960	-0.417445	-0.815897
H	1.819793	-0.336883	-2.046329
C	4.115072	-0.862307	0.405661
H	3.792175	-1.913897	2.266738
H	4.207586	0.154952	-1.498042
H	5.148404	-0.629429	0.647903
C	0.158235	-1.637238	-0.443671
C	-1.095488	-1.884721	-0.645270
B	0.736519	2.048952	-0.121072
F	1.895632	2.621236	-0.666029
F	-0.158830	3.047805	0.281013
F	0.121880	1.227579	-1.091671
F	1.083953	1.254095	0.993110
H	-1.288470	-2.810495	-1.199009
C	-2.260152	-1.084094	-0.216385
C	-3.531160	-1.473008	-0.653033
C	-2.112861	0.032329	0.617394
C	-4.651901	-0.741754	-0.265432
H	-3.638204	-2.341599	-1.297320
C	-3.235862	0.757641	0.998194
H	-1.125608	0.335987	0.954761
C	-4.505146	0.373672	0.558188
H	-5.636963	-1.043582	-0.608517
H	-3.117151	1.629271	1.634664
H	-5.378535	0.945761	0.857355

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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.

M06-2X free energy in solution after quasi-harmonic correction: -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.

M06-2X free energy in solution after quasi-harmonic correction: -964.226443 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.

M06-2X free energy in solution after quasi-harmonic correction: -964.2250332 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.

M06-2X free energy in solution after quasi-harmonic correction: -639.6874278 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.

M06-2X free energy in solution after quasi-harmonic correction: -639.6907399 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.

M06-2X free energy in solution after quasi-harmonic correction: -324.5767052 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.630094 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.629656 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.638942 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

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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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.632398 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.630141 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.

M06-2X free energy in solution after quasi-harmonic correction: -2131.630167 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.

M06-2X free energy in solution after quasi-harmonic correction: -542.7671996 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

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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.

M06-2X free energy in solution after quasi-harmonic correction: -967.7847027 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.

M06-2X free energy in solution after quasi-harmonic correction: -967.785393 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.

M06-2X free energy in solution after quasi-harmonic correction: -2135.184517 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.

M06-2X free energy in solution after quasi-harmonic correction: -2135.179334 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.

M06-2X free energy in solution after quasi-harmonic correction: -967.7764615 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.

M06-2X free energy in solution after quasi-harmonic correction: -967.7766189 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.

M06-2X free energy in solution after quasi-harmonic correction: -643.2329134 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.

M06-2X free energy in solution after quasi-harmonic correction: -643.2351597 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

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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.

M06-2X free energy in solution after quasi-harmonic correction: -347.5572986 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

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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.

M06-2X free energy in solution after quasi-harmonic correction: -772.5723547 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.

M06-2X free energy in solution after quasi-harmonic correction: -772.5725091 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.

M06-2X free energy in solution after quasi-harmonic correction: -1939.972733 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.

M06-2X free energy in solution after quasi-harmonic correction: -1939.967893 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.

M06-2X free energy in solution after quasi-harmonic correction: -772.5638336 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.

M06-2X free energy in solution after quasi-harmonic correction: -772.5652408 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.

M06-2X free energy in solution after quasi-harmonic correction: -448.0212987 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.

M06-2X free energy in solution after quasi-harmonic correction: -448.0249025 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

TS-7

M06-2X SCF energy in solution: -2232.35208945 a.u.

M06-2X enthalpy in solution: -2232.021755 a.u.

M06-2X free energy in solution: -2232.107110 a.u.

M06-2X free energy in solution after quasi-harmonic correction: -2232.100588 a.u.

Imaginary frequency: -1319.4377 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.935099	1.515827	-0.393332
C	-2.771342	0.964956	0.597934
C	-1.912878	2.910412	-0.590884
C	-3.573727	1.799516	1.364127
H	-2.796074	-0.103486	0.774269
C	-2.718328	3.734430	0.182764
H	-1.252594	3.341187	-1.335079
C	-3.550046	3.180761	1.157678
H	-4.218385	1.372120	2.125492
H	-2.692478	4.808555	0.030696
H	-4.179970	3.827387	1.761808
C	-1.060293	0.698387	-1.209458
C	-0.736014	-0.660326	-1.166690
F	-0.426031	1.381123	-2.139330
H	-0.175625	-0.945805	-2.062358

C	-1.713564	-1.701003	-0.686420
C	-1.435403	-2.555644	0.383685
C	-2.926983	-1.846690	-1.373072
C	-2.362030	-3.524258	0.773839
H	-0.497777	-2.470731	0.925018
C	-3.851896	-2.811575	-0.983321
H	-3.146160	-1.191123	-2.212988
C	-3.572806	-3.651876	0.096173
H	-2.133296	-4.178123	1.610444
H	-4.789605	-2.908071	-1.523046
H	-4.293290	-4.404465	0.402877
B	2.293307	1.796819	-0.888554
F	2.415470	2.964794	-1.649310
F	1.142333	1.882902	-0.071648
F	2.166186	0.681016	-1.737392
F	3.420633	1.627306	-0.068236
C	1.471486	-0.305549	1.714211
C	2.475341	-1.541993	0.058824
C	3.686460	-1.567355	0.733237
C	3.754050	-0.906208	1.955995
C	2.629551	-0.271550	2.475184
H	4.539119	-2.084688	0.309934
H	4.685946	-0.893955	2.512110
H	2.643829	0.237804	3.431268
N	1.402618	-0.909640	0.530348
H	0.300674	-0.664398	-0.309022
Cl	0.006208	0.401571	2.296186
Cl	2.280535	-2.398904	-1.429167

102b

M06-2X SCF energy in solution: -2232.36525031 a.u.

M06-2X enthalpy in solution: -2232.029260 a.u.

M06-2X free energy in solution: -2232.121761 a.u.

M06-2X free energy in solution after quasi-harmonic correction: -2232.110398 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.656846	-1.017866	0.673368
C	2.404991	-1.426273	-0.661258
C	3.791098	-1.502191	1.377389
C	3.284375	-2.300133	-1.275529
H	1.527090	-1.072139	-1.193109
C	4.654208	-2.375262	0.747203
H	3.973426	-1.184727	2.398654
C	4.400639	-2.769414	-0.575264
H	3.102371	-2.622072	-2.295069
H	5.525442	-2.754525	1.270103
H	5.084767	-3.457355	-1.063984
C	1.771145	-0.121914	1.301461
C	0.610751	0.586970	0.749825
F	2.048904	0.196475	2.536694
H	0.173349	0.059945	-0.099405
C	1.161144	1.948457	0.306434
C	1.278331	2.997019	1.221348
C	1.554602	2.125023	-1.021259
C	1.774332	4.229888	0.800431
H	0.965098	2.855804	2.253099
C	2.044633	3.360595	-1.439248
H	1.447956	1.308763	-1.731606

C	2.158892	4.411691	-0.528634
H	1.852742	5.049130	1.509084
H	2.327598	3.502178	-2.478012
H	2.540170	5.374470	-0.856276
B	-1.247770	0.226617	-2.462285
F	-2.338223	-0.359396	-3.115274
F	-1.671523	0.896002	-1.302868
F	-0.330255	-0.789366	-2.080378
F	-0.597525	1.123267	-3.322456
C	-2.050139	-1.771990	0.554197
C	-3.306008	-0.055850	1.285674
C	-4.249401	-0.215972	0.277320
C	-4.021986	-1.237725	-0.638631
C	-2.895271	-2.045464	-0.512110
H	-5.107643	0.441535	0.205741
H	-4.712344	-1.395546	-1.460878
H	-2.670832	-2.836052	-1.218088
N	-2.231699	-0.809001	1.440715
H	-0.140527	0.704047	1.537088
Cl	-0.616235	-2.751938	0.786166
Cl	-3.511378	1.224649	2.458029

TS-8

M06-2X SCF energy in solution: -2232.35818854 a.u.

M06-2X enthalpy in solution: -2232.027955 a.u.

M06-2X free energy in solution: -2232.113587 a.u.

M06-2X free energy in solution after quasi-harmonic correction: -2232.106919 a.u.

Imaginary frequency: -939.0572 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.840685	1.903294	-0.088014
C	2.282758	2.010613	-1.420040
C	2.771591	1.883222	0.967668
C	3.641145	2.085249	-1.687416
H	1.573696	2.056386	-2.239817
C	4.127736	1.952065	0.687016
H	2.427928	1.772993	1.990214
C	4.561792	2.049197	-0.636842
H	3.986092	2.170467	-2.712687
H	4.848533	1.911228	1.497044
H	5.625264	2.096602	-0.852485
C	0.438365	1.788624	0.214284
C	-0.601869	1.413543	-0.645491
F	0.123813	2.004121	1.471165
H	-0.304247	1.388729	-1.693923
C	-2.044006	1.758931	-0.423087
C	-2.490253	2.719033	0.491406
C	-2.985781	1.067799	-1.196824
C	-3.854602	2.971147	0.631700
H	-1.783990	3.279631	1.094438
C	-4.347491	1.320664	-1.054186
H	-2.645689	0.326906	-1.917885
C	-4.787266	2.271281	-0.132802
H	-4.187278	3.721088	1.343559
H	-5.063620	0.774951	-1.661784
H	-5.848632	2.469760	-0.015926
B	2.011184	-1.399121	0.968438

F	1.507329	-2.705489	1.079207
F	1.084838	-0.500377	1.545570
F	3.237952	-1.295917	1.637608
F	2.172744	-1.075966	-0.389540
C	-0.497914	-2.138465	-1.314700
C	-1.422041	-1.829945	0.756345
C	-1.583591	-3.193845	0.953237
C	-1.151405	-4.042554	-0.060447
C	-0.600863	-3.518681	-1.226346
H	-2.023646	-3.568262	1.869603
H	-1.247663	-5.117328	0.056515
H	-0.261762	-4.149680	-2.039196
N	-0.887265	-1.316187	-0.346999
H	-0.579772	0.145353	-0.413607
Cl	0.114403	-1.400467	-2.760274
Cl	-1.954537	-0.701551	1.954032

The following coordinates are obtained through geometry optimization in dichloroethane (DCE):

2,6-dichloropyridinium tetrafluoroborate F (optimized in DCE)

M06-2X SCF energy in DCE: -1592.52187456 a.u.

M06-2X enthalpy in DCE: -1592.409256 a.u.

M06-2X free energy in DCE: -1592.465853 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -1592.462163 a.u.

Cartesian coordinates

ATOM	X	Y	Z
B	2.506561	0.127879	0.247439
F	1.522610	-0.044584	1.236201
F	3.356696	-0.973233	0.204039

F	1.816307	0.230873	-1.009585
F	3.219356	1.303303	0.465158
C	-1.535368	1.092640	-0.102509
C	-1.265241	-1.244577	-0.121615
C	-2.531810	-1.432048	0.398262
C	-3.302143	-0.301868	0.664686
C	-2.810399	0.978544	0.417273
H	-2.896368	-2.434490	0.587913
H	-4.300269	-0.420184	1.073822
H	-3.392863	1.868490	0.623326
N	-0.802474	-0.004660	-0.361882
H	0.169121	0.106239	-0.720170
Cl	-0.797378	2.595346	-0.443893
Cl	-0.206156	-2.532418	-0.489509

101 (optimized in DCE)

M06-2X SCF energy in DCE: -539.37941602 a.u.

M06-2X enthalpy in DCE: -539.173959 a.u.

M06-2X free energy in DCE: -539.224576 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -539.2217063 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 (optimized in DCE)

M06-2X SCF energy in DCE: -2131.87485070 a.u.

M06-2X enthalpy in DCE: -2131.561986 a.u.

M06-2X free energy in DCE: -2131.647965 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -2131.639669 a.u.

Imaginary frequency: -1004.9973 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.493253	-2.134346	-0.010655
C	-2.157009	-2.372219	1.214119
C	-2.147839	-2.361869	-1.242337
C	-3.461396	-2.838785	1.198435
H	-1.637949	-2.176108	2.147187
C	-3.452270	-2.828513	-1.240498
H	-1.621639	-2.158079	-2.169730
C	-4.103062	-3.063393	-0.024435
H	-3.986207	-3.020972	2.130464
H	-3.970003	-3.002812	-2.177978
H	-5.128051	-3.423031	-0.029793
C	-0.171127	-1.684143	-0.004795
C	0.986182	-1.199161	-0.003357
B	-2.452546	1.100911	-0.006759
F	-3.720830	0.498861	-0.014103
F	-1.734678	0.708018	-1.151885
F	-2.589893	2.500304	-0.003897
F	-1.745557	0.701769	1.142947
C	0.719369	2.181291	1.163810
C	0.733511	2.189313	-1.130686
C	0.489642	3.553119	-1.189849
C	0.350472	4.227452	0.020887
C	0.474478	3.544807	1.228556
H	0.411418	4.060126	-2.144245
H	0.151395	5.294421	0.023322
H	0.384199	4.045512	2.185230
N	0.832522	1.523200	0.014932
H	0.797367	0.065249	0.004787
Cl	0.943395	1.247337	2.603501

Cl	0.976416	1.263548	-2.573086
C	2.399545	-1.590743	-0.002068
C	3.402562	-0.619596	-0.095391
C	2.747575	-2.947057	0.090433
C	4.743065	-1.001591	-0.099185
H	3.139975	0.432359	-0.165319
C	4.087097	-3.320442	0.087194
H	1.965564	-3.697535	0.165814
C	5.087436	-2.349456	-0.008445
H	5.516884	-0.243452	-0.173427
H	4.351677	-4.371273	0.159174
H	6.132426	-2.644986	-0.011211

TS-1a (optimized in DCE)

M06-2X SCF energy in DCE: -2131.87151209 a.u.

M06-2X enthalpy in DCE: -2131.558930 a.u.

M06-2X free energy in DCE: -2131.649741 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -2131.636975 a.u.

Imaginary frequency: -728.9253 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.126706	-1.576244	-0.001026
C	1.349981	-2.217664	1.235336
C	1.383950	-2.241332	-1.218174
C	1.815589	-3.523923	1.245821
H	1.164327	-1.676881	2.158364
C	1.850320	-3.547025	-1.190665

H	1.223771	-1.718380	-2.156118
C	2.064599	-4.181947	0.037004
H	1.995347	-4.029815	2.188803
H	2.057125	-4.070412	-2.118447
H	2.436896	-5.202277	0.051952
C	0.660393	-0.251611	-0.020011
C	0.015532	0.817943	-0.035619
B	3.959162	0.256967	0.023593
F	4.407667	-1.072429	0.033095
F	3.185959	0.487557	-1.132194
F	3.162337	0.496170	1.161458
F	5.058778	1.130163	0.031837
C	-3.104338	-0.575178	1.163831
C	-3.100638	-0.699430	-1.124867
C	-4.377281	-1.240768	-1.160334
C	-5.016000	-1.445962	0.060288
C	-4.380030	-1.112355	1.253755
H	-4.848275	-1.489260	-2.104184
H	-6.016026	-1.867082	0.081233
H	-4.852576	-1.259986	2.217774
N	-2.480830	-0.376238	0.006269
H	-1.101699	0.199677	-0.022812
Cl	-2.229572	-0.117562	2.587850
Cl	-2.217616	-0.403937	-2.585875
C	-0.030216	2.272959	-0.052148
C	-1.262721	2.934760	-0.107392
C	1.165349	3.004396	-0.012350
C	-1.299561	4.326923	-0.123518
H	-2.186332	2.361690	-0.137291
C	1.117541	4.394711	-0.028316

H	2.113320	2.477844	0.031451
C	-0.111219	5.056891	-0.083928
H	-2.255322	4.840210	-0.166797
H	2.042632	4.962434	0.002814
H	-0.141382	6.142530	-0.096057

102 (optimized in DCE)

M06-2X SCF energy in DCE: -964.41617572 a.u.

M06-2X enthalpy in DCE: -964.178142 a.u.

M06-2X free energy in DCE: -964.247052 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -964.240557 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.861073	-1.074337	-0.009951
C	-1.438581	-1.458425	1.238886
C	-1.425431	-1.519973	-1.244351
C	-2.545066	-2.279959	1.240485
H	-0.997837	-1.087664	2.158792
C	-2.532809	-2.339557	-1.217137
H	-0.974237	-1.196125	-2.176944
C	-3.084903	-2.711356	0.018839
H	-3.005691	-2.582613	2.174367
H	-2.983860	-2.687870	-2.139673
H	-3.962788	-3.351513	0.029792
C	0.214324	-0.241012	-0.024670
C	1.224674	0.564588	-0.037109
B	-2.300540	1.910103	0.000692
F	-3.248879	0.874779	-0.018926

F	-1.469411	1.805626	-1.134118
F	-2.948105	3.152733	-0.001659
F	-1.501524	1.792391	1.156112
H	0.937519	1.622143	-0.067090
C	2.662325	0.226509	-0.016157
C	3.109716	-1.102102	0.002043
C	3.588228	1.275006	-0.014452
C	4.473442	-1.371850	0.022813
H	2.394223	-1.921048	-0.000946
C	4.954097	0.997472	0.006682
H	3.235990	2.302631	-0.029073
C	5.398163	-0.323682	0.025393
H	4.817199	-2.401739	0.036752
H	5.668474	1.815252	0.008338
H	6.462354	-0.539679	0.041673

102a (optimized in DCE)

M06-2X SCF energy in DCE: -964.41458078 a.u.

M06-2X enthalpy in DCE: -964.176562 a.u.

M06-2X free energy in DCE: -964.244189 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -964.2387448 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.497944	-1.425317	-0.203080
C	2.059290	-1.913449	1.018976
C	2.289611	-0.657725	-1.113352
C	3.374433	-1.629805	1.313921

H	1.432689	-2.487821	1.694155
C	3.605689	-0.395918	-0.800072
H	1.834721	-0.289195	-2.026102
C	4.136563	-0.874905	0.407267
H	3.820804	-1.980012	2.238041
H	4.224569	0.189410	-1.471109
H	5.171914	-0.652323	0.650301
C	0.180413	-1.640610	-0.458396
C	-1.069966	-1.890100	-0.674489
B	0.692856	2.090231	-0.119152
F	1.836286	2.671395	-0.692078
F	-0.201388	3.092407	0.287910
F	0.066150	1.259853	-1.069814
F	1.069793	1.317562	0.997377
H	-1.254741	-2.799438	-1.257945
C	-2.240205	-1.107774	-0.226207
C	-3.504996	-1.470930	-0.701322
C	-2.104750	-0.033435	0.663536
C	-4.630296	-0.754667	-0.297337
H	-3.602830	-2.307880	-1.387462
C	-3.231978	0.676379	1.061678
H	-1.122556	0.247721	1.034047
C	-4.495125	0.318911	0.582175
H	-5.610357	-1.036837	-0.670131
H	-3.123706	1.512716	1.745864
H	-5.372118	0.877630	0.895757

103 (optimized in DCE)

M06-2X SCF energy in DCE: -1167.45510816 a.u.

M06-2X enthalpy in DCE: -1167.377451 a.u.

M06-2X free energy in DCE: -1167.416780 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -1167.41678 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000076	0.008688	1.126415
C	0.000076	0.008688	-1.126415
C	-0.000161	1.397277	-1.204782
C	-0.000275	2.094506	0.000000
C	-0.000161	1.397277	1.204782
H	-0.000275	1.904281	-2.162393
H	-0.000468	3.180063	0.000000
H	-0.000275	1.904281	2.162393
N	0.000155	-0.683456	0.000000
Cl	0.000076	-0.930678	2.598721
Cl	0.000076	-0.930678	-2.598721

TS-2 (optimized in DCE)

M06-2X SCF energy in DCE: -964.40696850 a.u.

M06-2X enthalpy in DCE: -964.169660 a.u.

M06-2X free energy in DCE: -964.234826 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -964.2299108 a.u.

Imaginary frequency: -319.0149 cm-1

Cartesian coordinates

ATOM	X	Y	Z

C	0.767894	0.877235	-0.186249
C	1.133168	1.322112	1.103843
C	1.153116	1.597368	-1.339589
C	1.863589	2.493562	1.231883
H	0.834415	0.743744	1.972338
C	1.891632	2.759697	-1.193927
H	0.867831	1.226974	-2.319558
C	2.243621	3.201731	0.087284
H	2.147783	2.853368	2.215171
H	2.197621	3.324695	-2.068171
H	2.824384	4.113495	0.194121
C	0.003606	-0.290115	-0.316241
C	-1.066556	-1.035173	-0.323925
B	2.504831	-1.767134	0.128198
F	3.388755	-0.738420	-0.161299
F	1.346039	-1.621588	-0.769341
F	3.055644	-3.010420	-0.133042
F	2.022419	-1.675111	1.427712
H	-0.951634	-2.104083	-0.490333
C	-2.440294	-0.521333	-0.127209
C	-3.489208	-1.444309	-0.218989
C	-2.723748	0.825579	0.140460
C	-4.807748	-1.026880	-0.047262
H	-3.266734	-2.487665	-0.425712
C	-4.041473	1.236309	0.311186
H	-1.919828	1.552626	0.218597
C	-5.086204	0.312932	0.217851
H	-5.614480	-1.750063	-0.120425
H	-4.254490	2.280600	0.519166
H	-6.113113	0.639540	0.352861

TS-2a (optimized in DCE)

M06-2X SCF energy in DCE: -964.40586170 a.u.

M06-2X enthalpy in DCE: -964.168836 a.u.

M06-2X free energy in DCE: -964.232826 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -964.2287611 a.u.

Imaginary frequency: -321.5740 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.719640	-0.984530	0.051822
C	2.399066	-0.747586	1.265655
C	2.431676	-1.206018	-1.147125
C	3.786084	-0.759340	1.277152
H	1.828324	-0.561145	2.169746
C	3.816160	-1.205521	-1.120429
H	1.884378	-1.366791	-2.071002
C	4.486751	-0.982050	0.088257
H	4.323975	-0.585135	2.203146
H	4.379095	-1.373641	-2.032570
H	5.572997	-0.979495	0.101436
C	0.314707	-0.977091	0.039311
C	-0.869375	-1.469348	0.246756
B	0.589447	1.949625	-0.175351
F	-0.025390	0.766832	-0.792408
F	1.904402	2.019384	-0.609680
F	-0.150424	3.047001	-0.584760
F	0.517452	1.766835	1.202888

H	-0.755670	-2.519408	0.548294
C	-2.245820	-0.951138	0.149661
C	-2.575240	0.372486	0.466518
C	-3.252779	-1.849520	-0.226037
C	-3.899768	0.793063	0.379489
H	-1.806150	1.061237	0.796780
C	-4.573496	-1.418579	-0.323141
H	-2.996342	-2.881904	-0.448713
C	-4.898436	-0.095612	-0.022412
H	-4.150938	1.819414	0.629903
H	-5.347328	-2.117428	-0.626178
H	-5.928947	0.240400	-0.091314

***E*-81** (optimized in DCE)

M06-2X SCF energy in DCE: -639.85890833 a.u.

M06-2X enthalpy in DCE: -639.637213 a.u.

M06-2X free energy in DCE: -639.689786 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -639.6875768 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.536071	0.405861	-0.099797
C	-1.192460	-0.678741	-0.917563
C	-2.733126	0.371569	0.626792
C	-2.024134	-1.793069	-0.984927
H	-0.279295	-0.643441	-1.505029
C	-3.562056	-0.746634	0.557174
H	-3.009093	1.216391	1.251343

C	-3.207678	-1.832027	-0.244477
H	-1.753074	-2.628477	-1.623824
H	-4.484654	-0.769148	1.129732
H	-3.855009	-2.702552	-0.299108
C	-0.669254	1.595229	-0.021376
C	0.659979	1.725827	0.001465
F	-1.398696	2.750900	0.010627
H	1.042810	2.743993	-0.042787
C	1.658778	0.642887	0.092064
C	1.473446	-0.482609	0.909323
C	2.860332	0.765451	-0.620243
C	2.450161	-1.472558	0.983266
H	0.564638	-0.576454	1.497840
C	3.837478	-0.226458	-0.547196
H	3.024035	1.643954	-1.239930
C	3.633430	-1.352101	0.251013
H	2.291078	-2.336536	1.622461
H	4.759185	-0.117057	-1.111738
H	4.394695	-2.124536	0.312293

***Z*-71** (optimized in DCE)

M06-2X SCF energy in DCE: -639.86286416 a.u.

M06-2X enthalpy in DCE: -639.640694 a.u.

M06-2X free energy in DCE: -639.694316 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -639.6910937 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	-1.943630	-0.075727	-0.022660
C	-2.845166	-1.112782	0.256239
C	-2.443043	1.209329	-0.287516
C	-4.216476	-0.864961	0.286716
H	-2.473715	-2.112465	0.456146
C	-3.812386	1.450900	-0.252568
H	-1.766050	2.020270	-0.538694
C	-4.705431	0.416147	0.036113
H	-4.902227	-1.677595	0.508135
H	-4.184786	2.449345	-0.462497
H	-5.774153	0.608119	0.058323
C	-0.499075	-0.353689	-0.032913
C	0.513369	0.520692	0.033650
F	-0.229478	-1.684231	-0.095115
H	0.224068	1.563161	0.129737
C	1.959816	0.272608	0.017871
C	2.557658	-0.982044	-0.204343
C	2.801832	1.378949	0.232200
C	3.944722	-1.113049	-0.204380
H	1.946075	-1.857689	-0.383444
C	4.187112	1.243886	0.233787
H	2.355348	2.356087	0.400218
C	4.766486	-0.006584	0.015870
H	4.386100	-2.090248	-0.379588
H	4.813031	2.115280	0.404189
H	5.846885	-0.118212	0.015108

BF3 (optimized in DCE)

M06-2X SCF energy in DCE: -324.56306263 a.u.

M06-2X enthalpy in DCE: -324.546476 a.u.

M06-2X free energy in DCE: -324.577164 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -324.5771643 a.u.

Cartesian coordinates

ATOM	X	Y	Z
B	0.000042	-0.000047	-0.000150
F	-0.458337	-1.236108	0.000028
F	1.299718	0.221162	0.000028
F	-0.841404	1.014973	0.000028

H2O (optimized in DCE)

M06-2X SCF energy in DCE: -76.42887078 a.u.

M06-2X enthalpy in DCE: -76.404022 a.u.

M06-2X free energy in DCE: -76.425467 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -76.425467 a.u.

Cartesian coordinates

ATOM	X	Y	Z
O	0.000000	0.000000	0.117933
H	0.000000	0.770127	-0.471733
H	0.000000	-0.770127	-0.471733

BF3-H2O (optimized in DCE)

M06-2X SCF energy in DCE: -401.02217209 a.u.

M06-2X enthalpy in DCE: -400.977854 a.u.

M06-2X free energy in DCE: -401.012686 a.u.

M06-2X free energy in DCE after quasi-harmonic correction: -401.0126861 a.u.

Cartesian coordinates

ATOM	X	Y	Z
B	-0.182457	0.000104	0.002762
F	-0.572835	-1.152027	-0.626452
F	-0.426534	-0.003286	1.354724
F	-0.570745	1.156225	-0.620464
O	1.416157	-0.000752	-0.173999
H	1.857619	0.790692	0.204539
H	1.856440	-0.793408	0.203371

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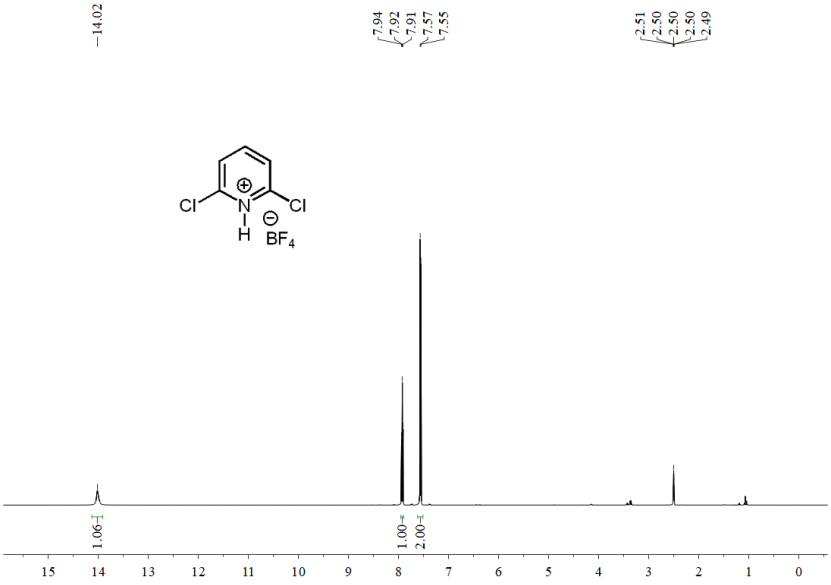
12. Copies of NMR Spectra

^{1}H NMR (500 MHz, DMSO)



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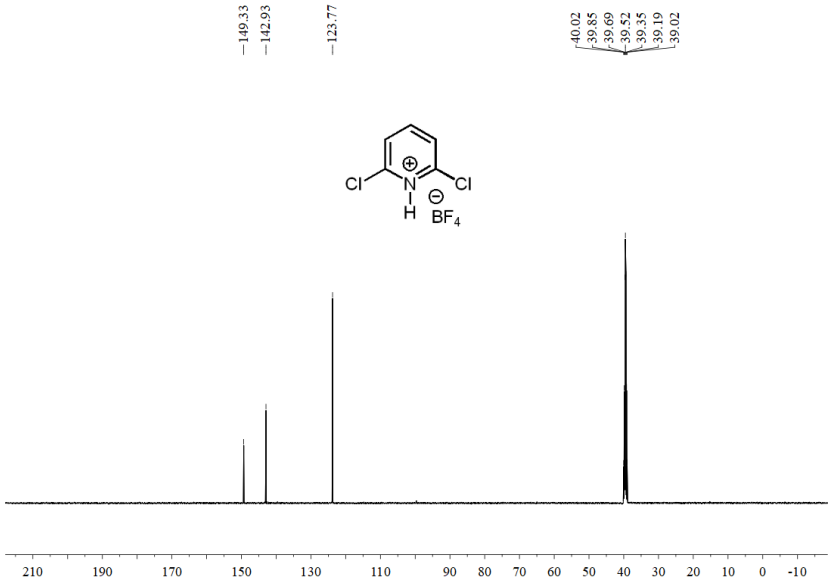

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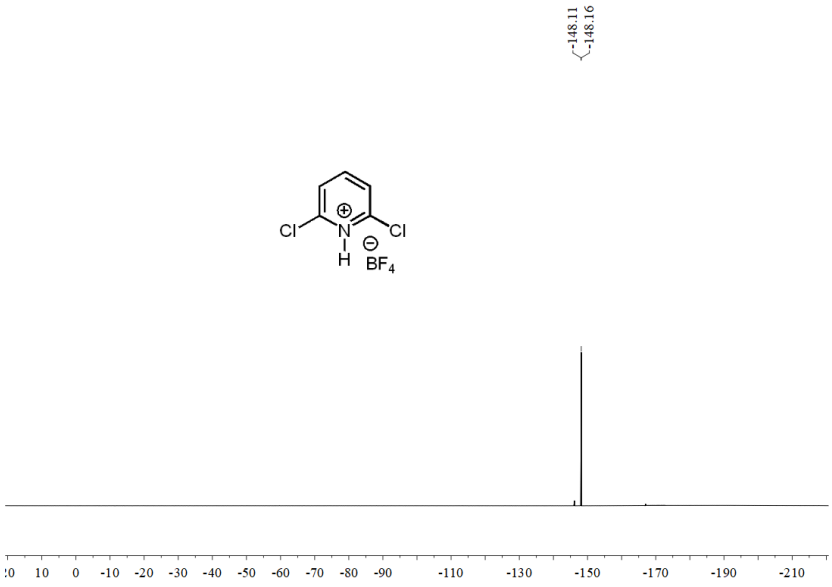

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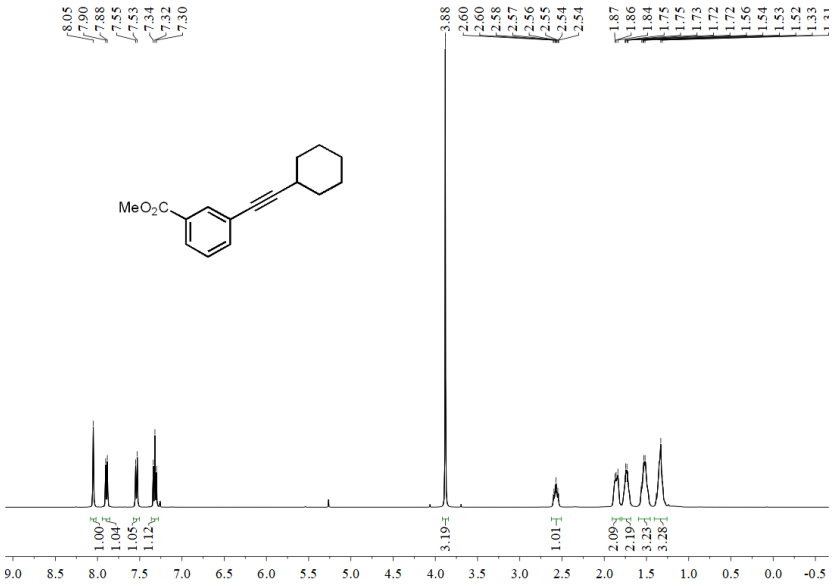

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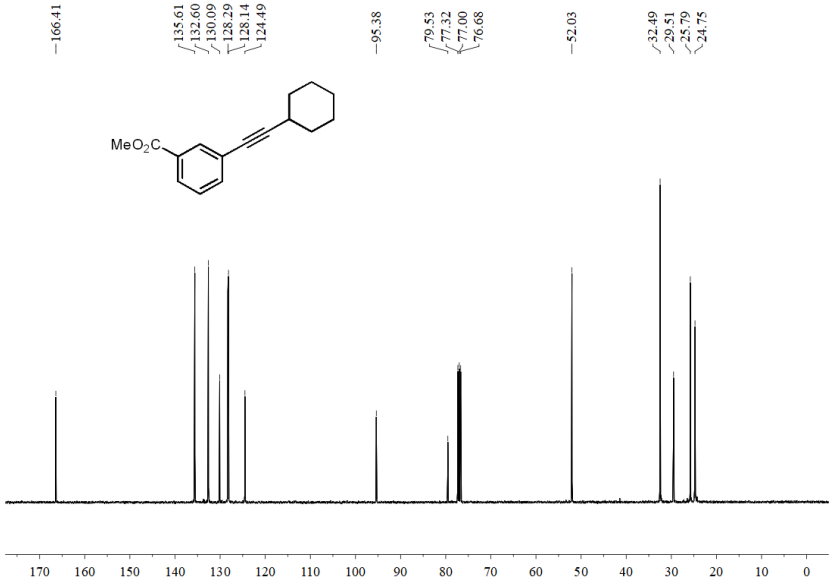

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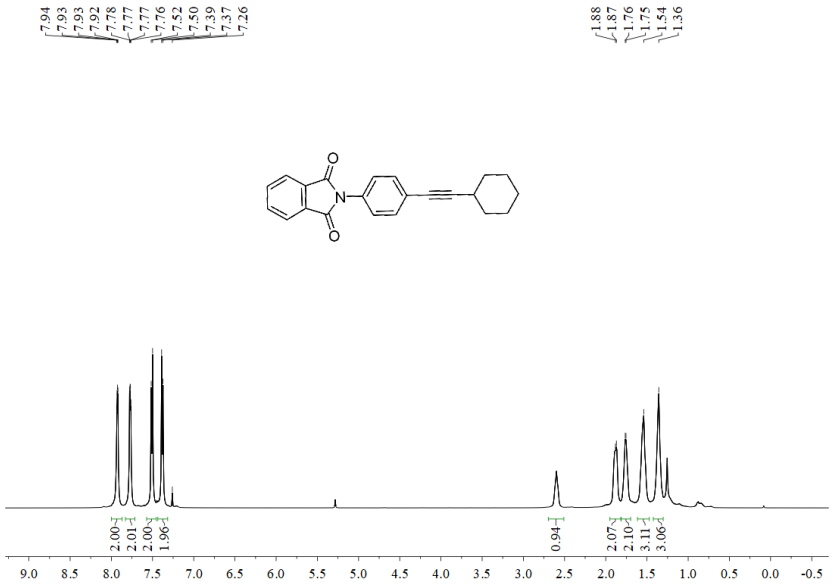

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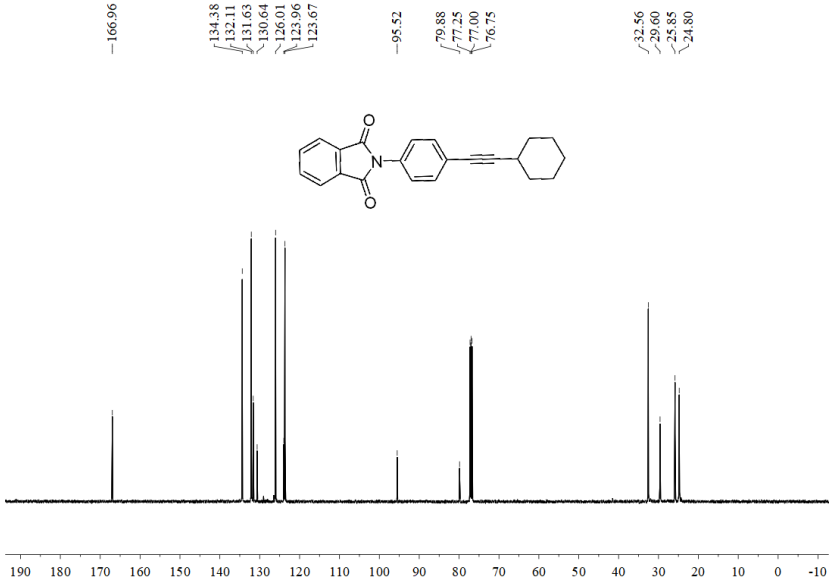

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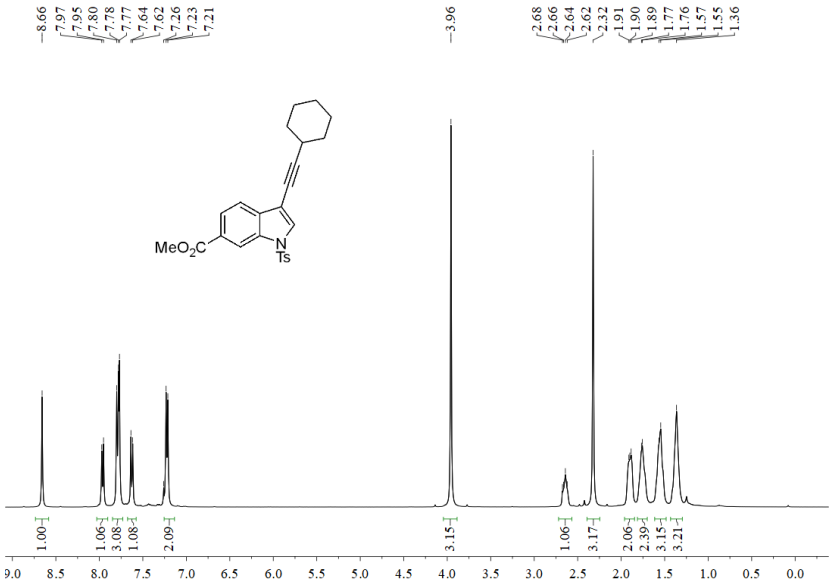

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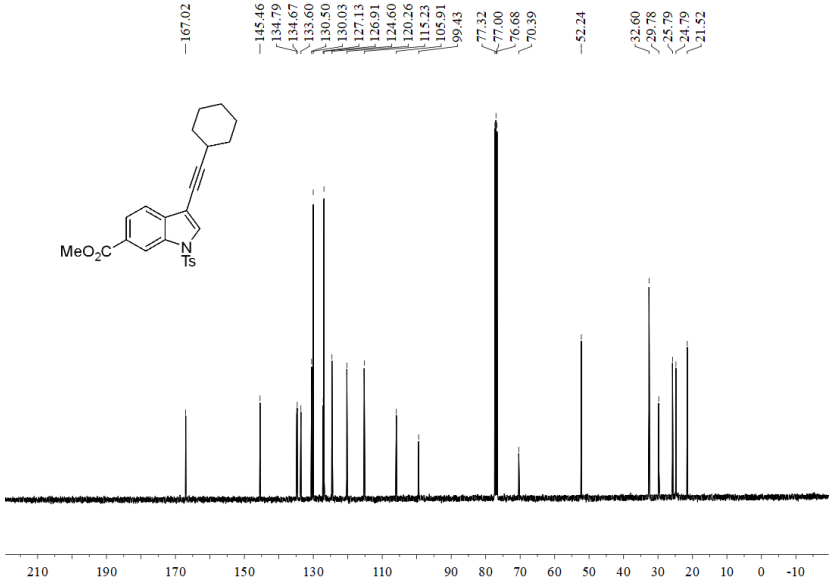

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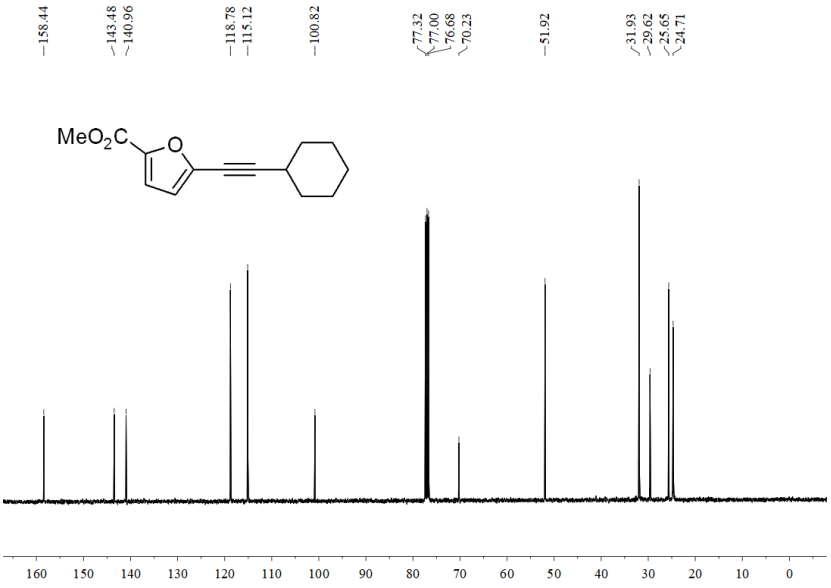

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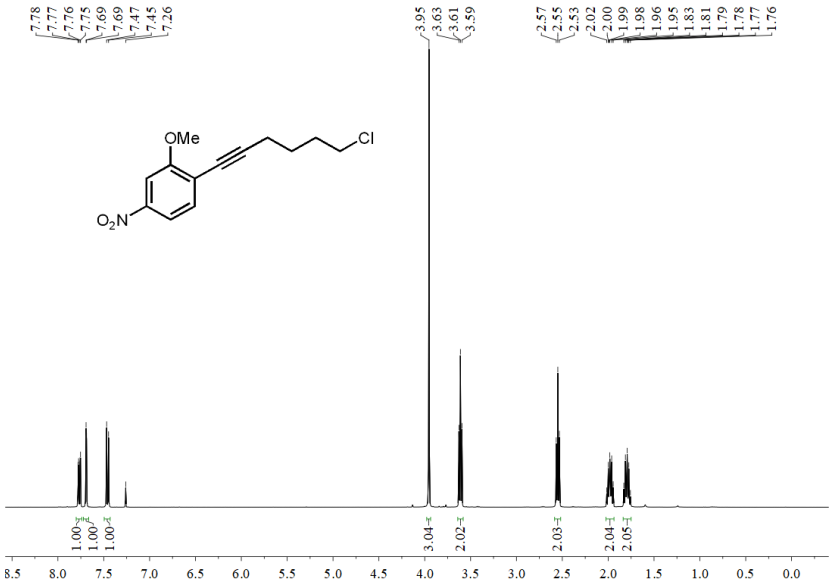

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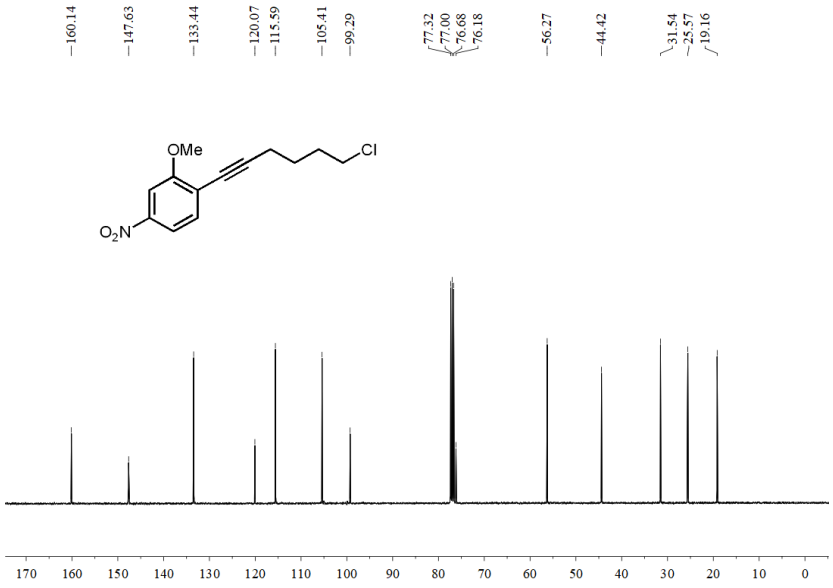

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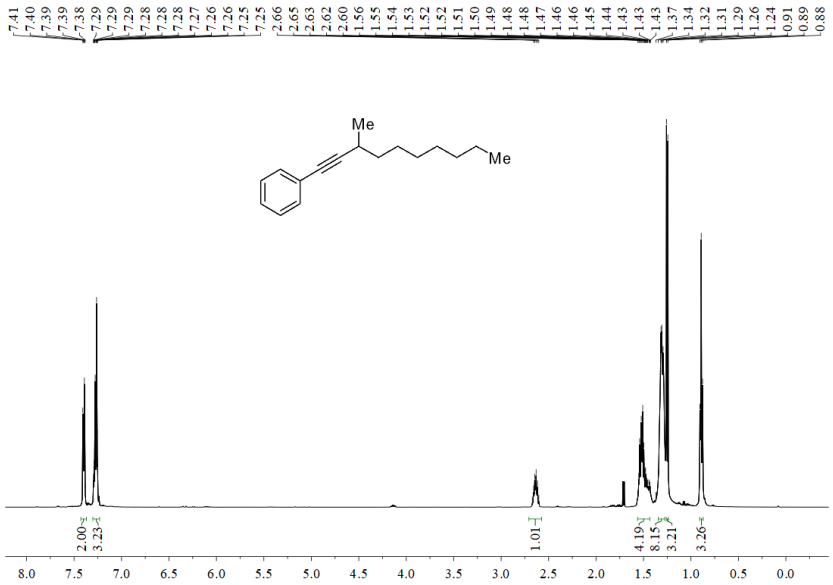

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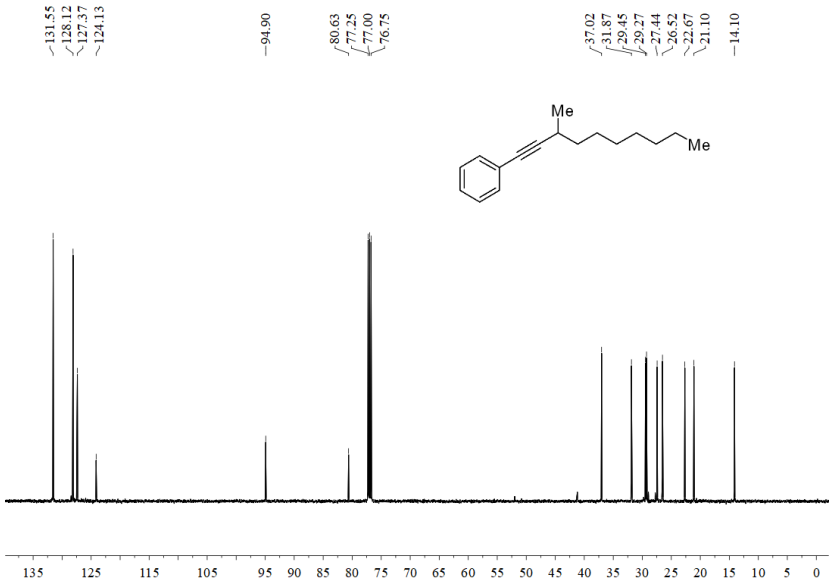

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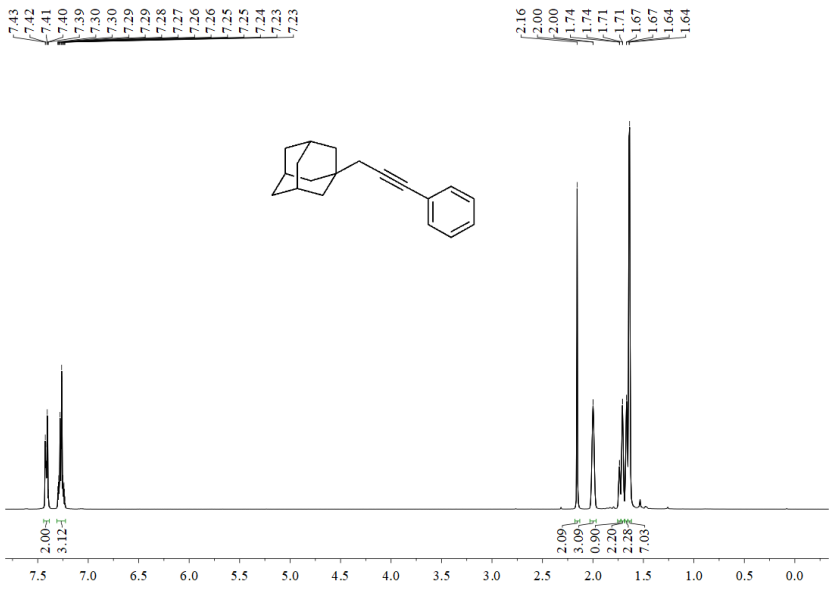

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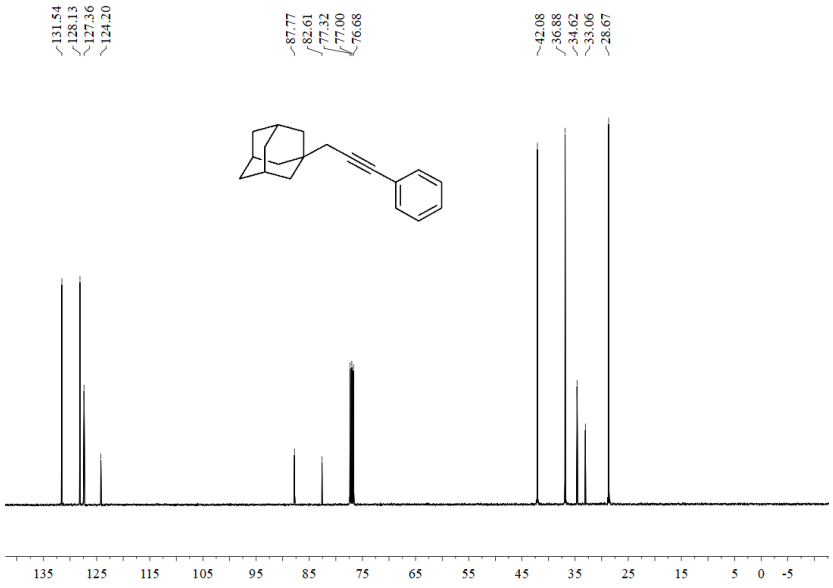

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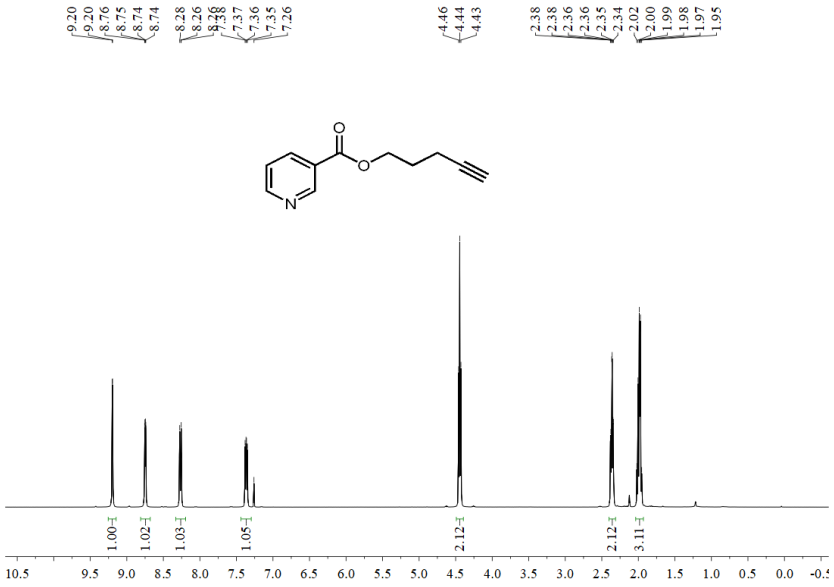

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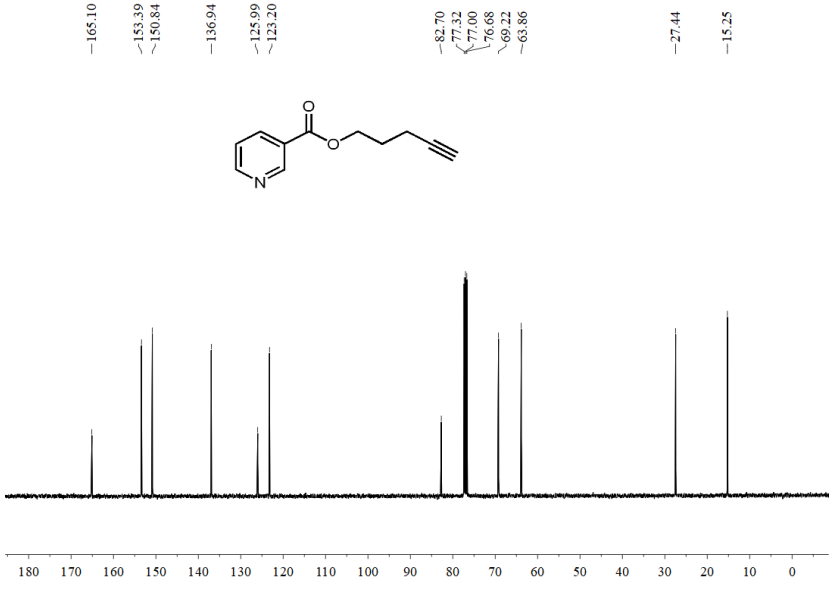

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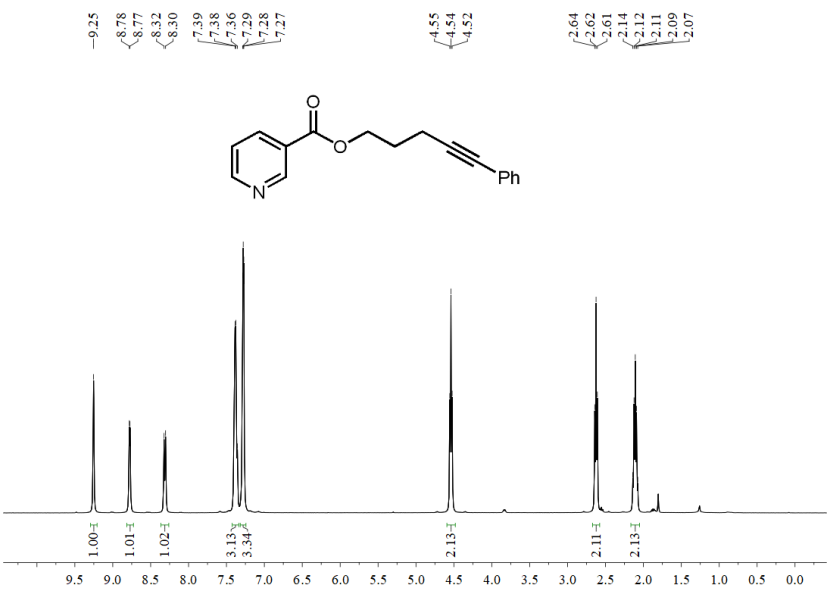

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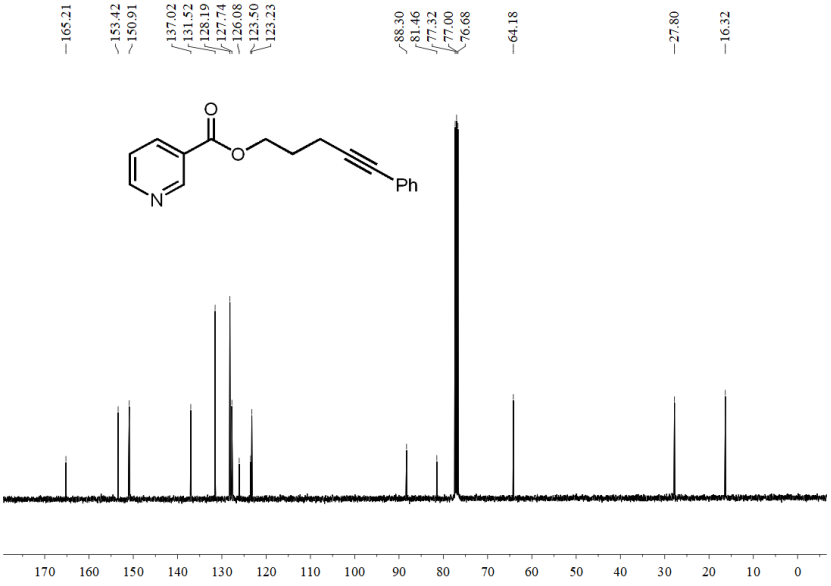

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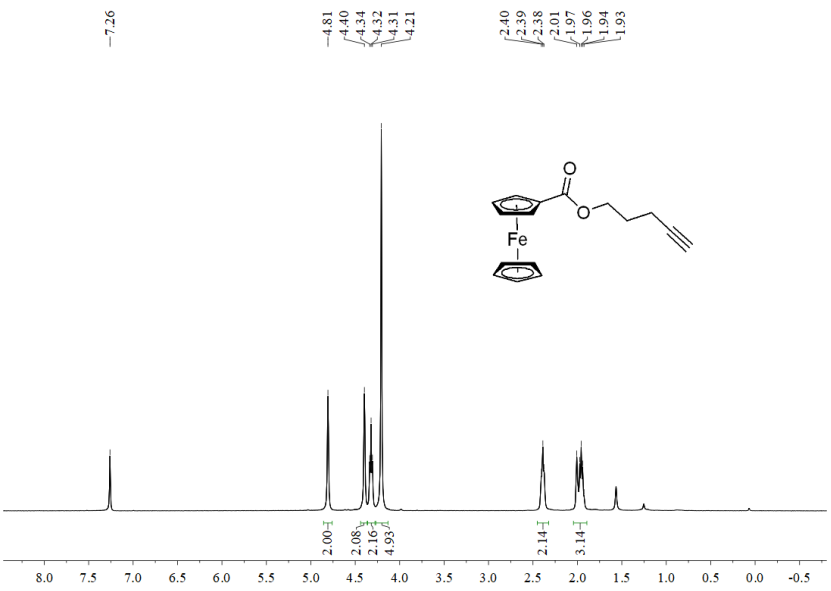

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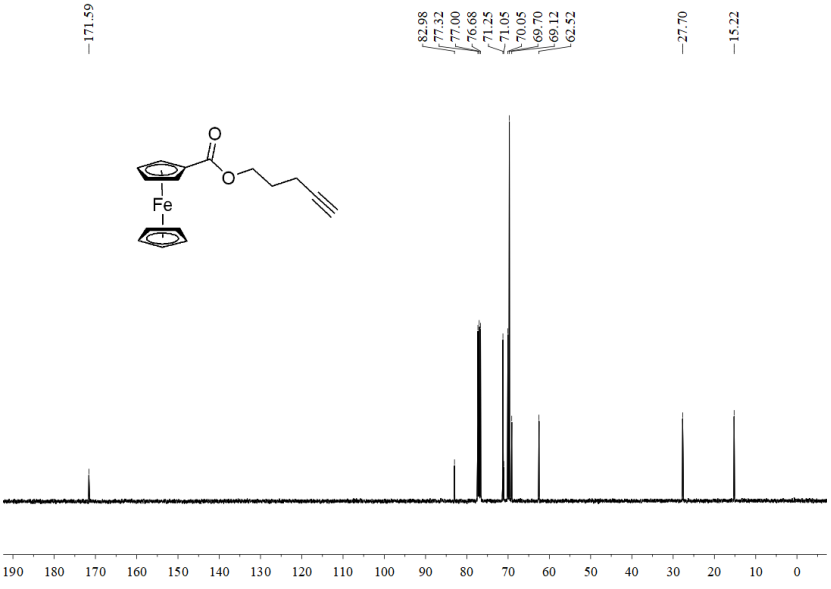

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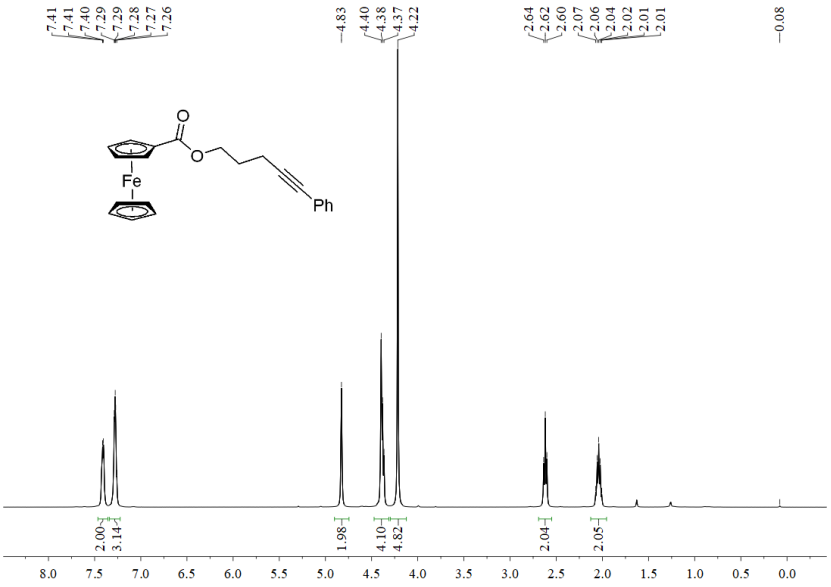

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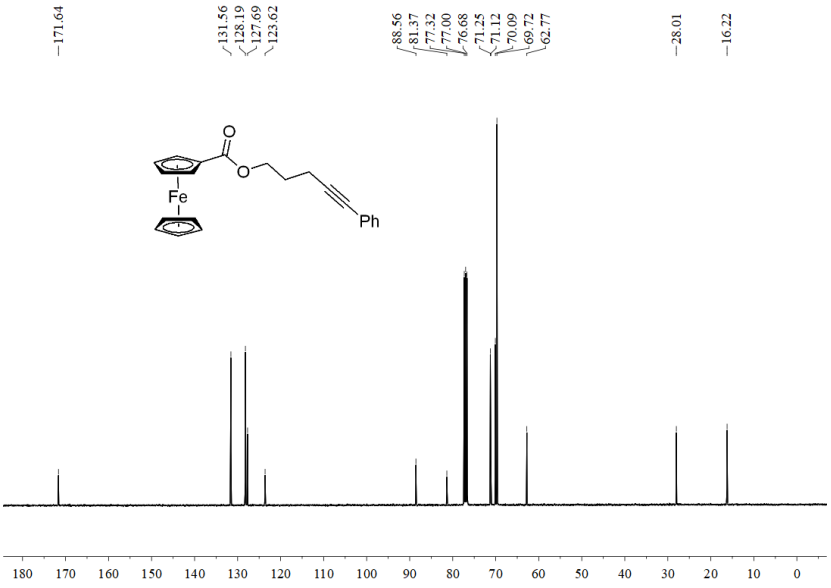

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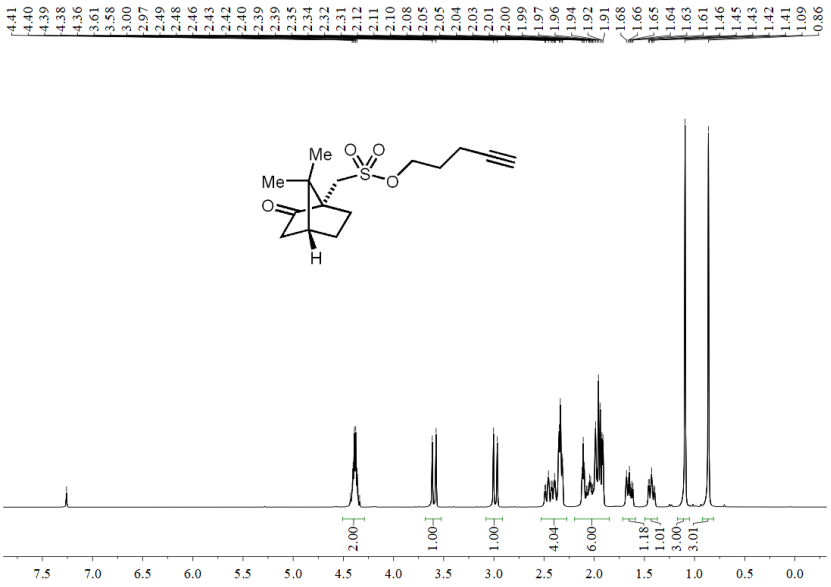

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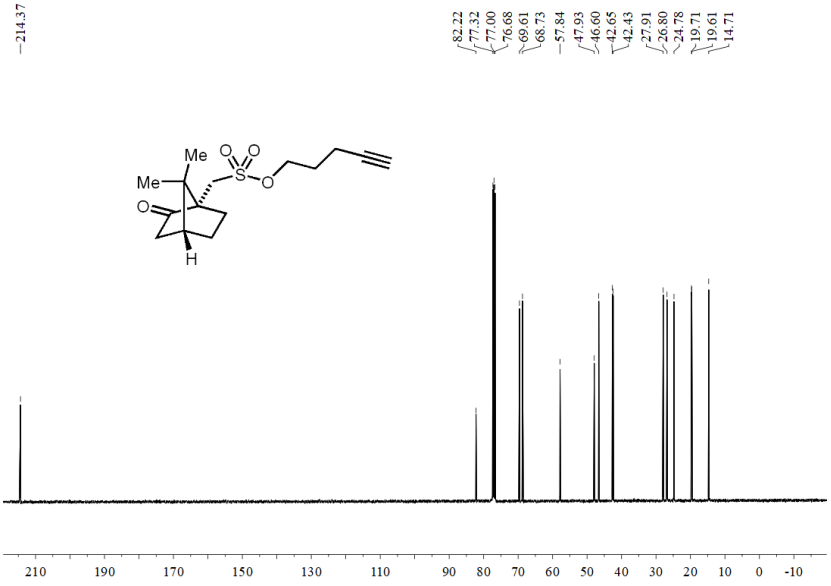

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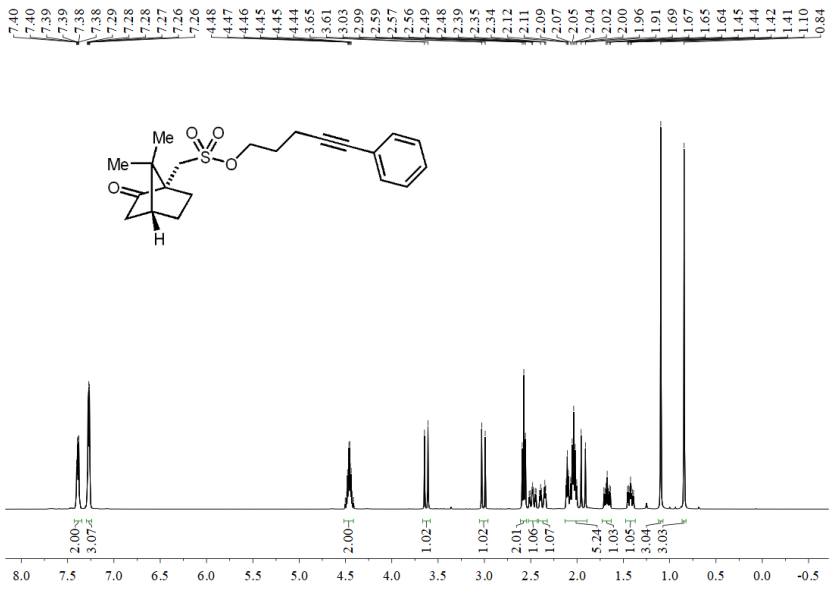

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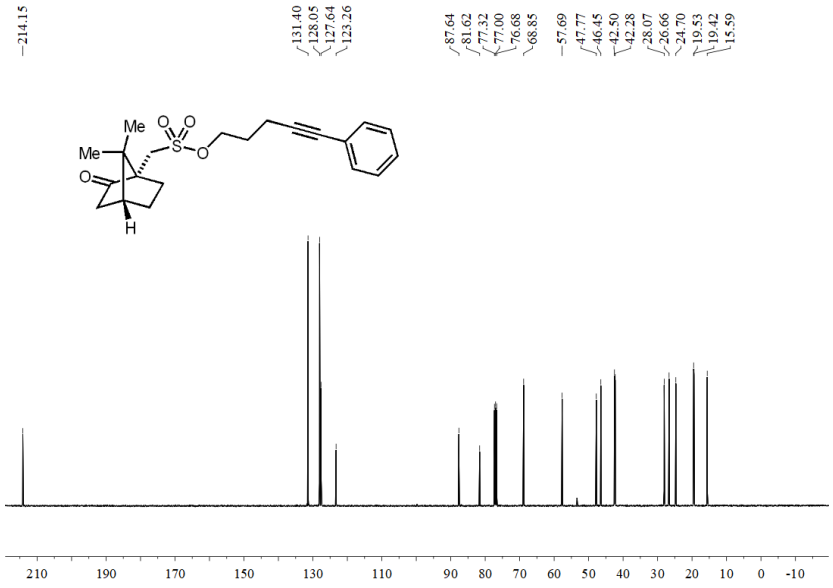

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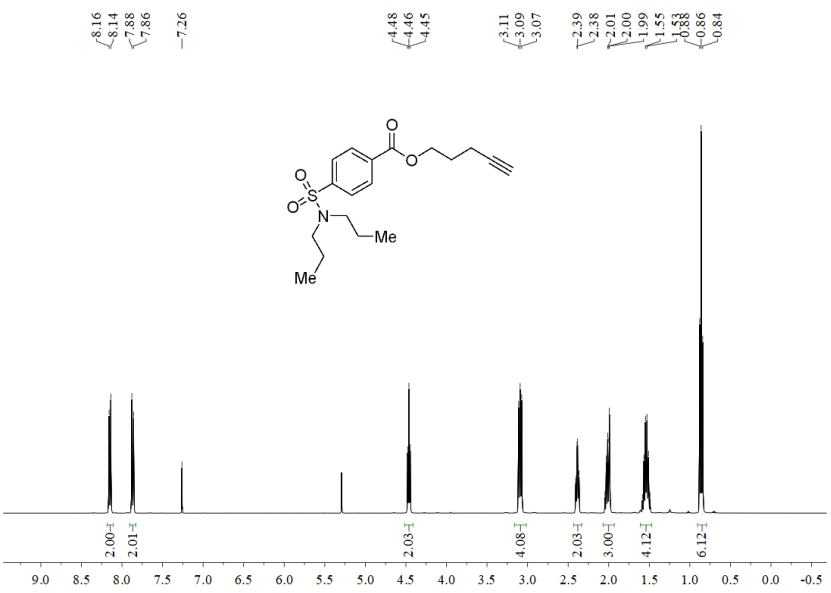

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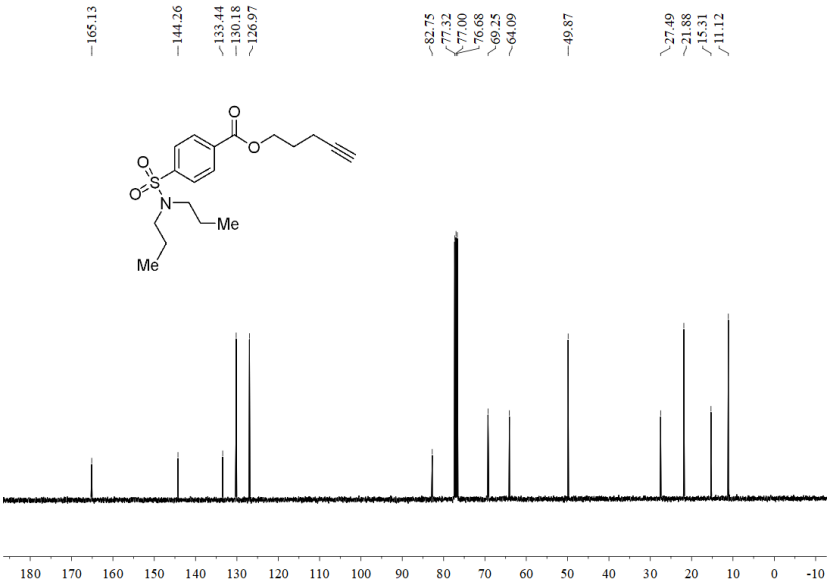

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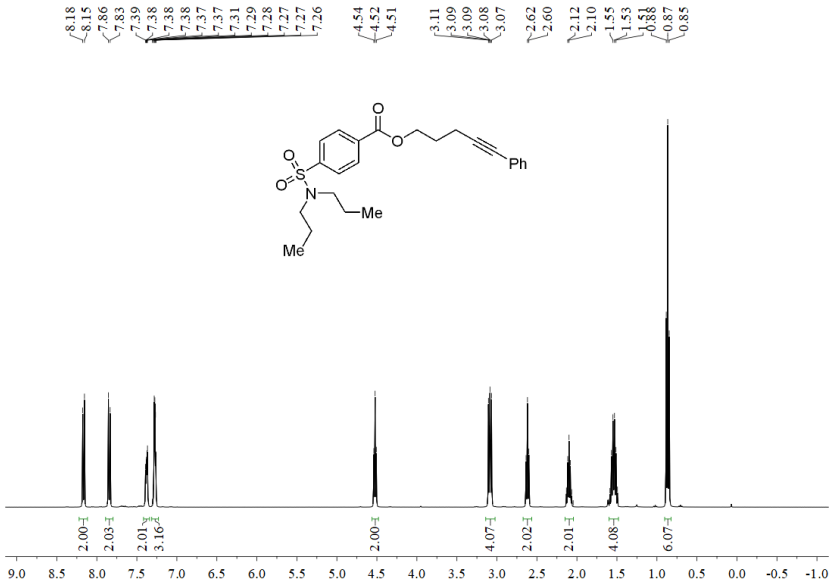

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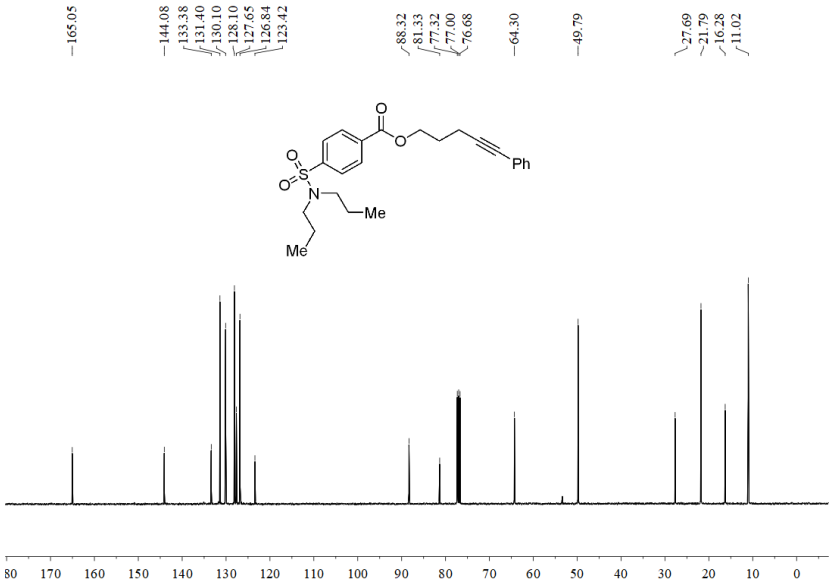

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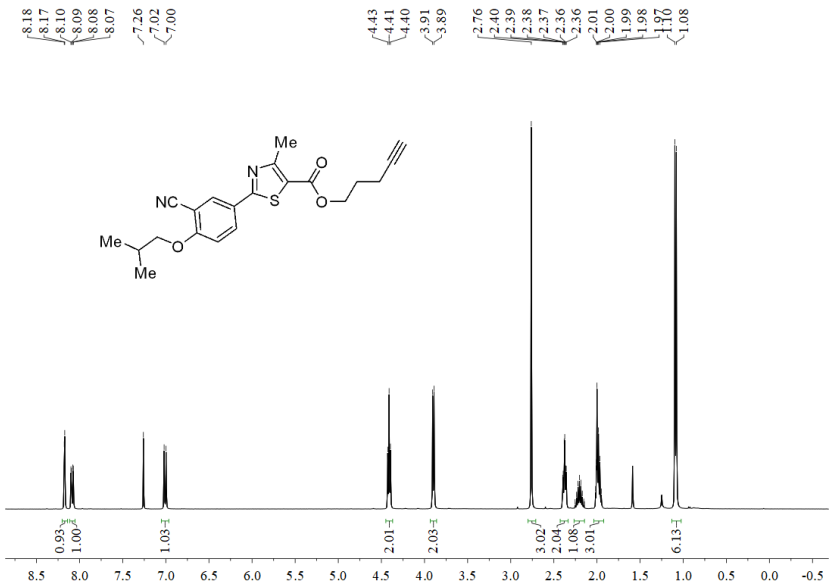

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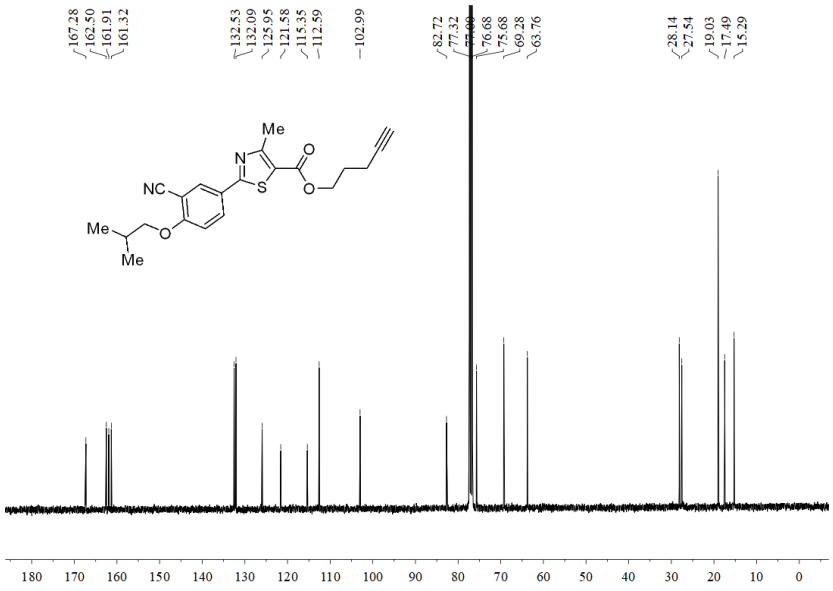

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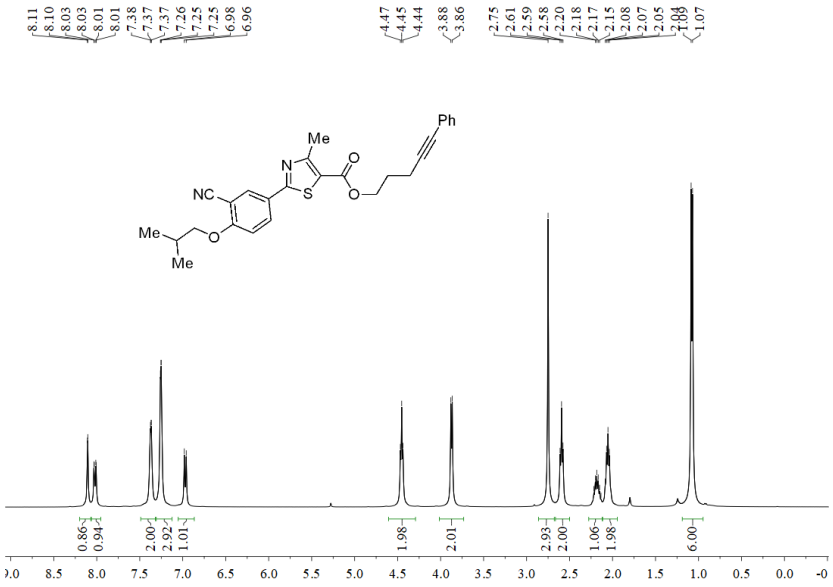

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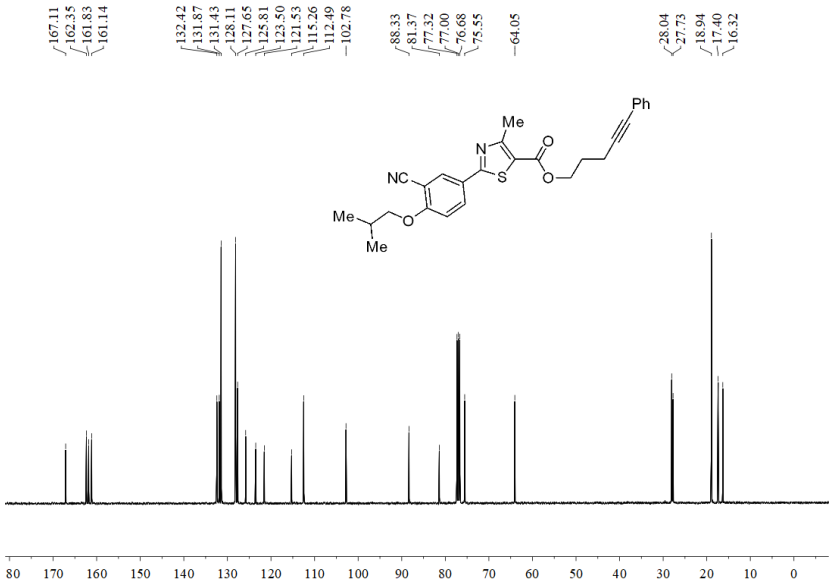

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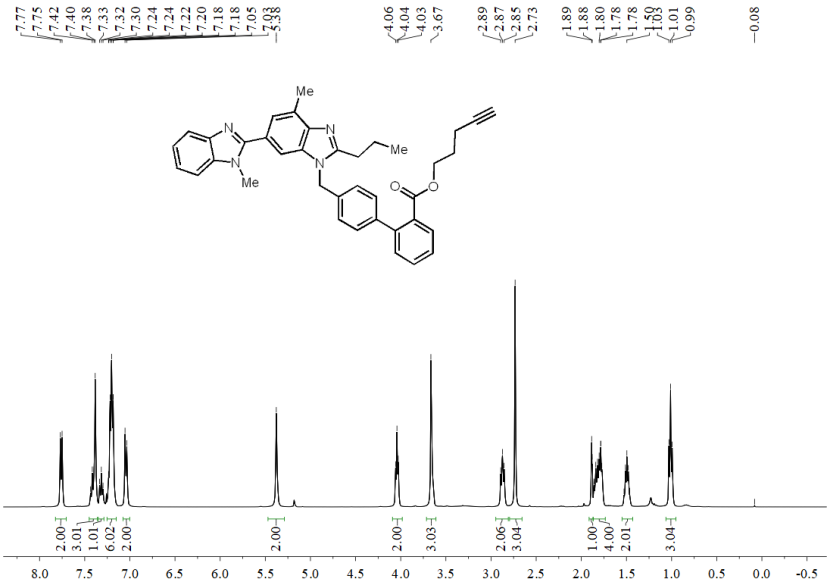

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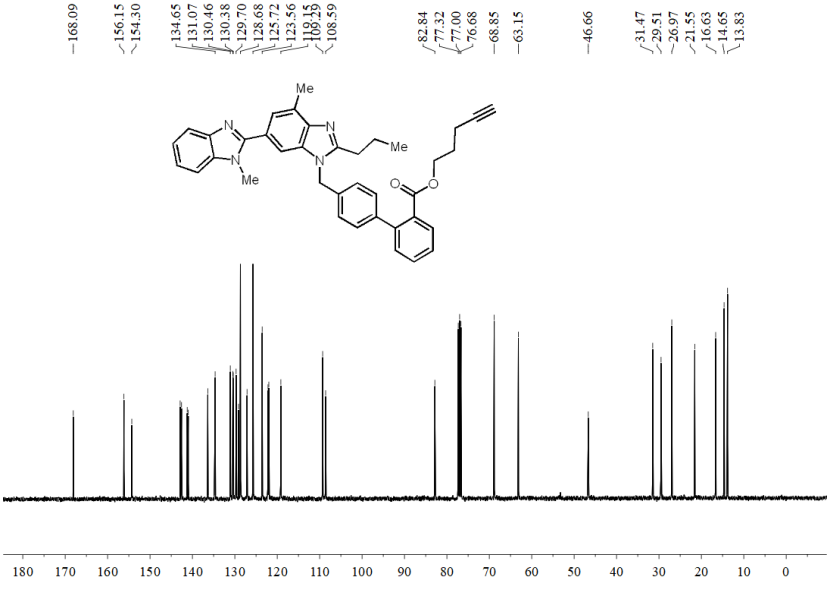

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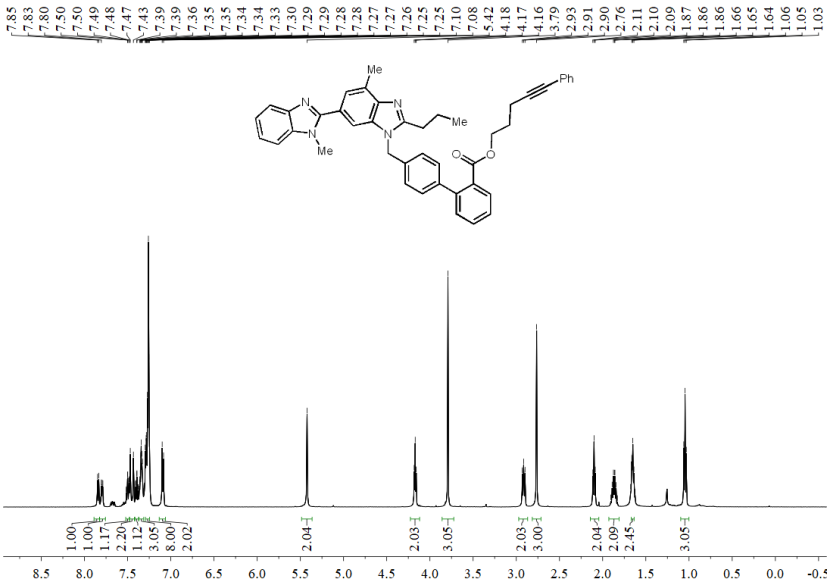
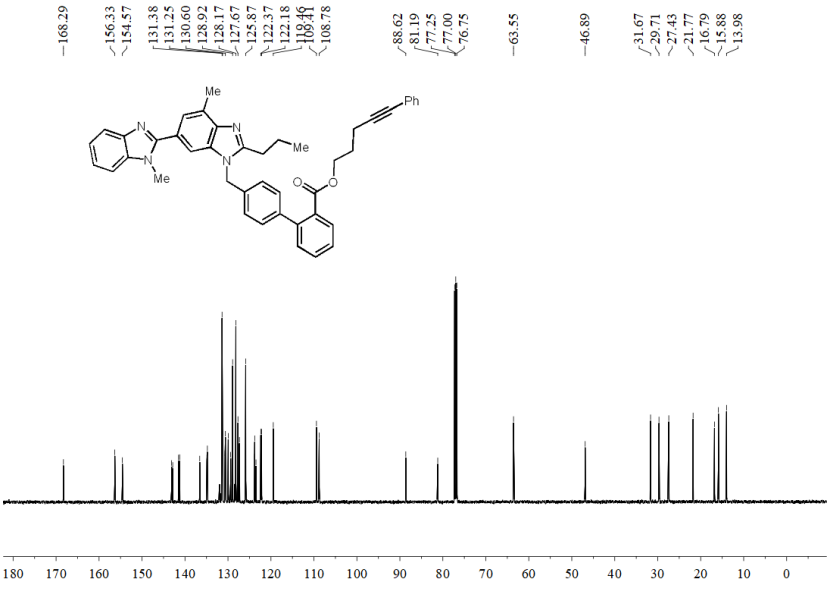
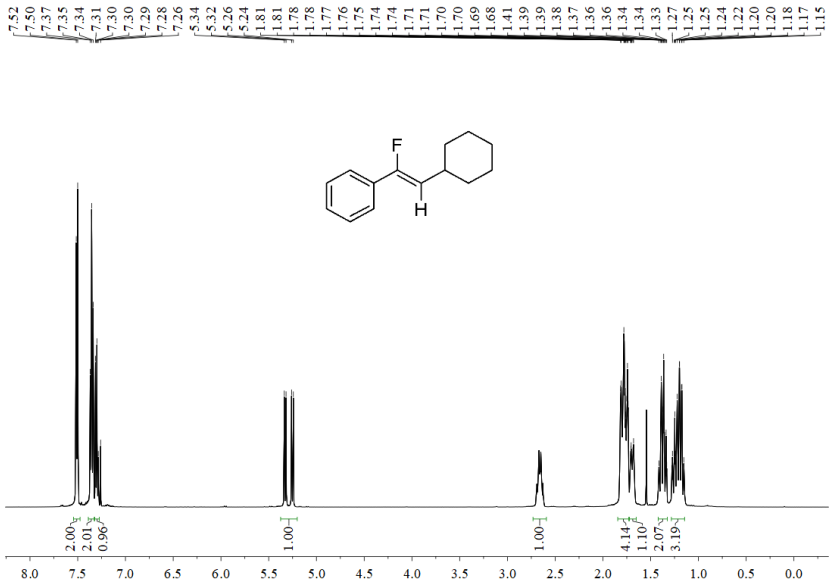


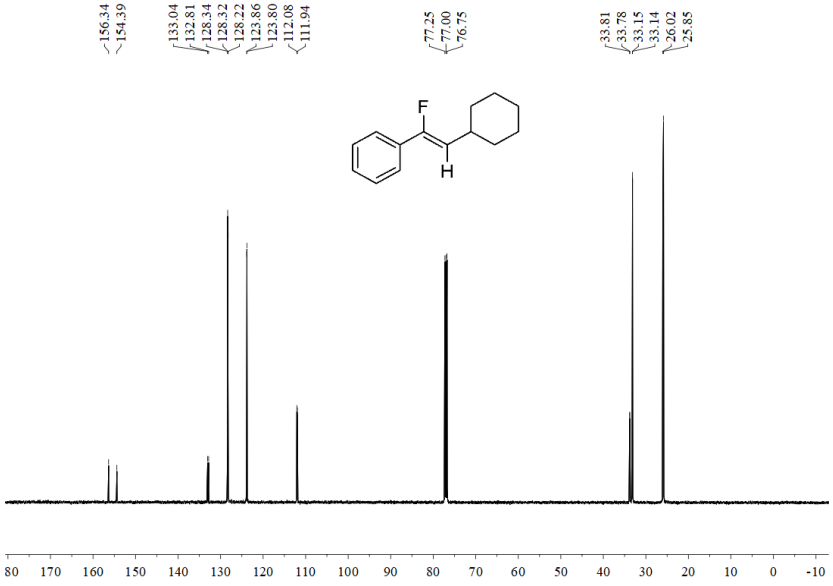
^{13}C NMR (126 MHz, $CDCl_3$)



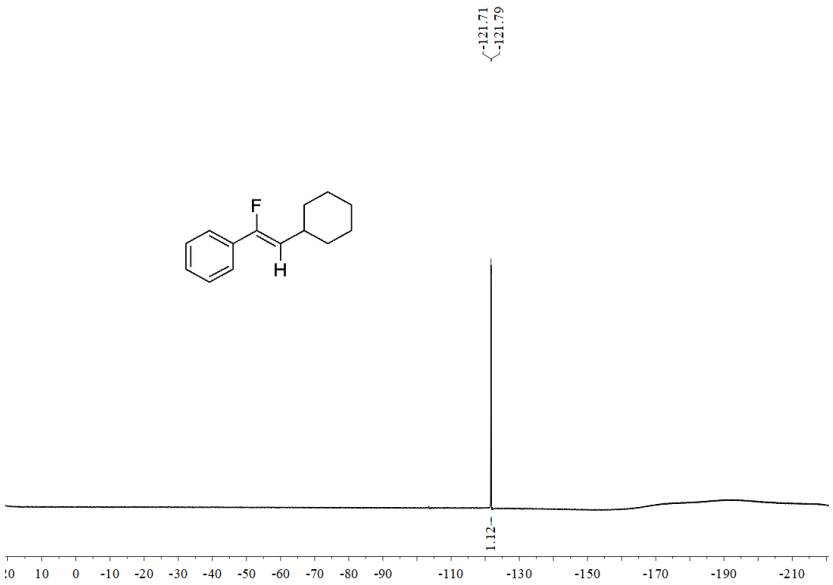
^{1}H NMR (500 MHz, $CDCl_3$) (**1**)



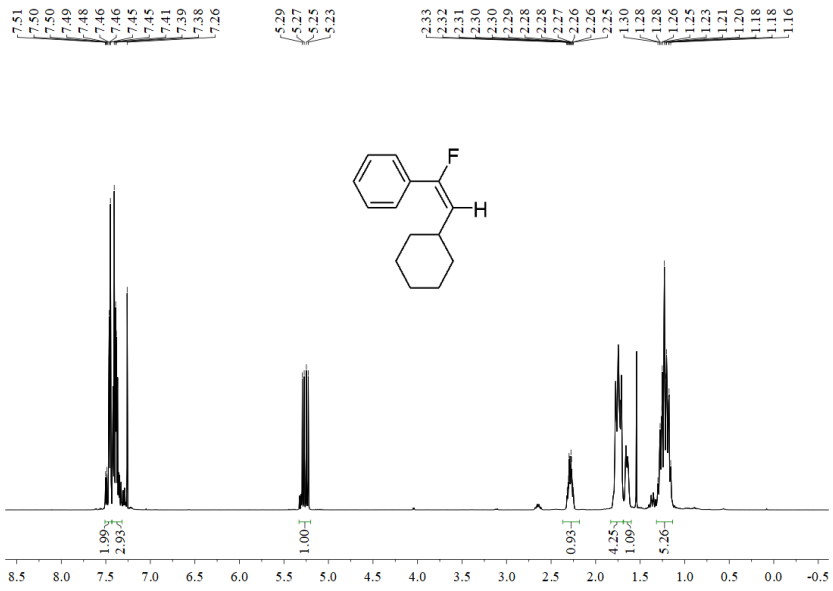
^{13}C NMR (126 MHz, $CDCl_3$) (**1**)



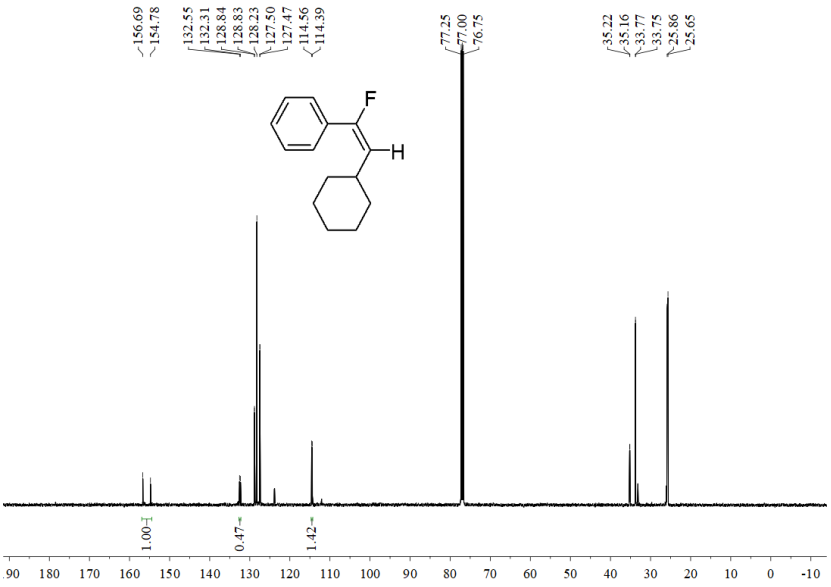
^{19}F NMR (471 MHz, $CDCl_3$) (**1**)



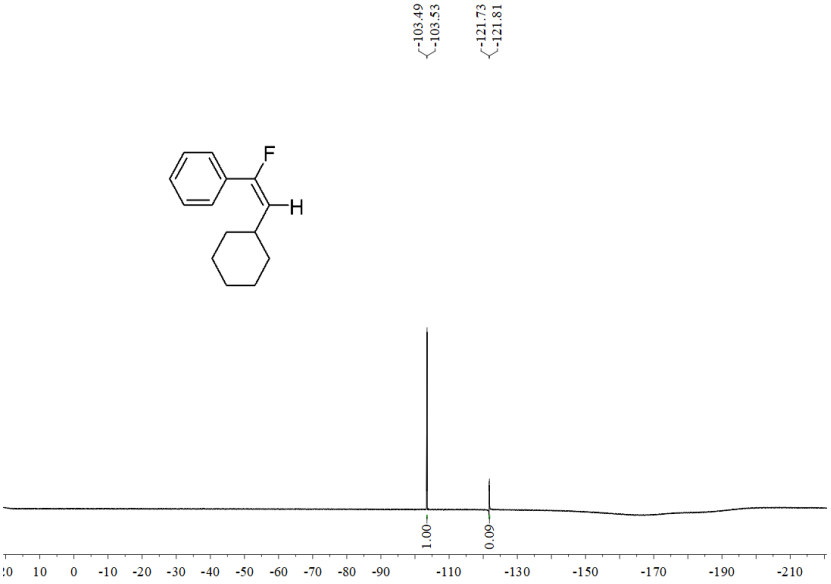
^{1}H NMR (500 MHz, $CDCl_3$) (**2**)



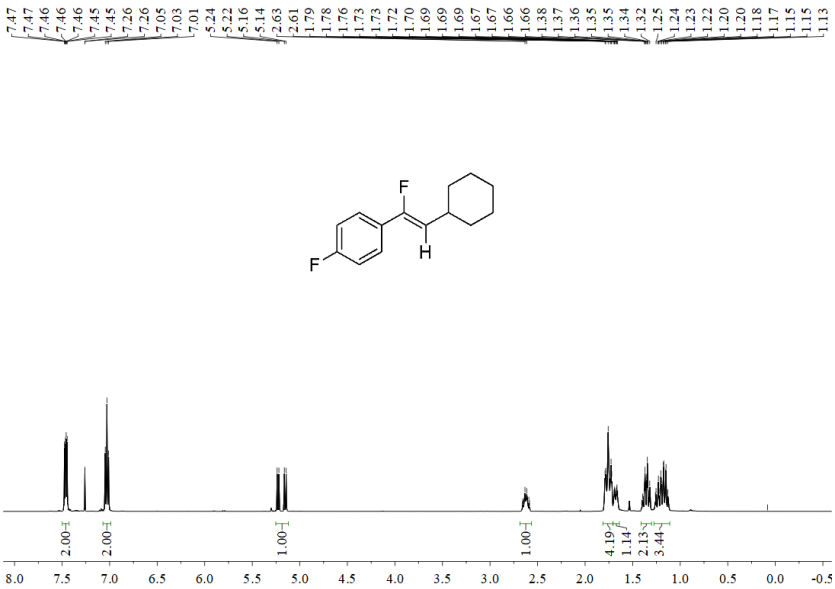
^{13}C NMR (126 MHz, $CDCl_3$) (**2**)



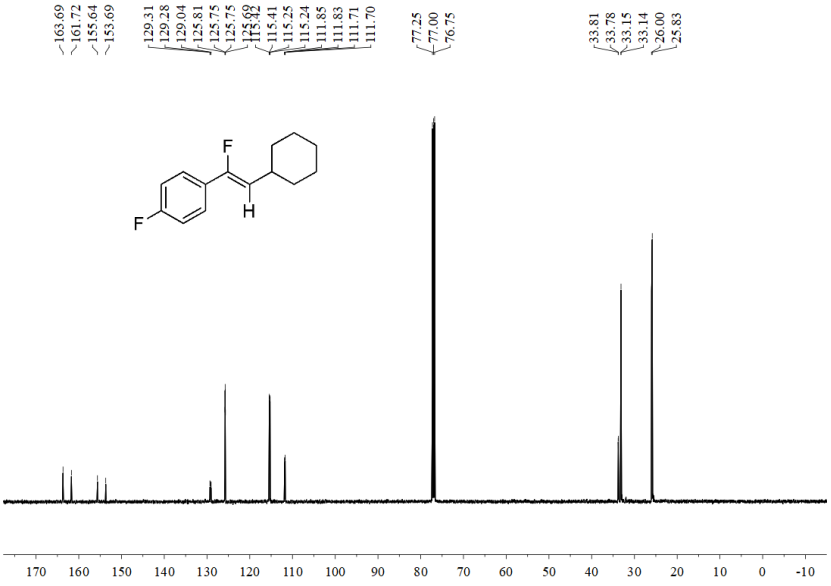
^{19}F NMR (471 MHz, $CDCl_3$) (**2**)



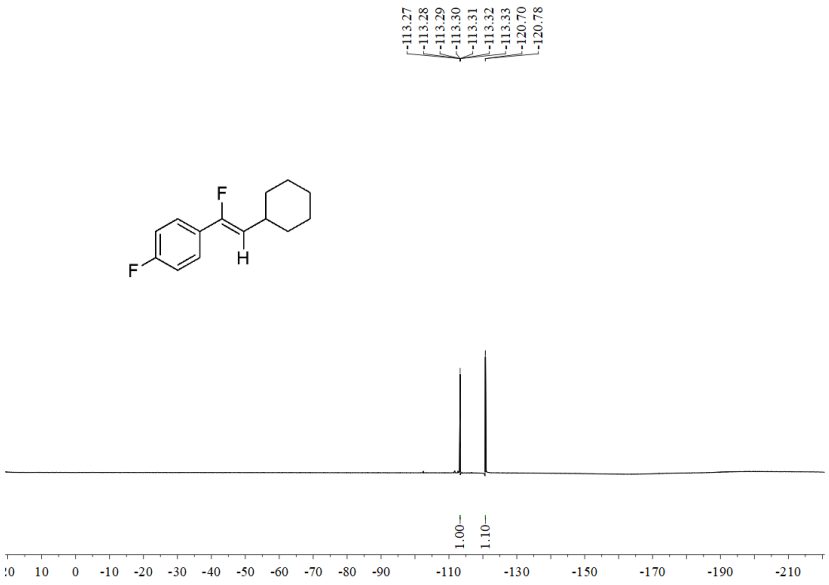
^{1}H NMR (500 MHz, $CDCl_3$) (**3**)



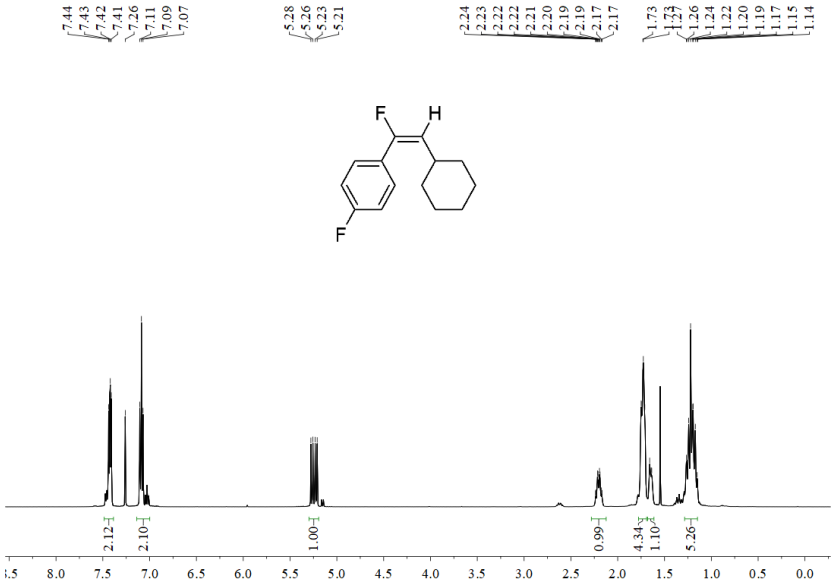
^{13}C NMR (126 MHz, $CDCl_3$) (**3**)



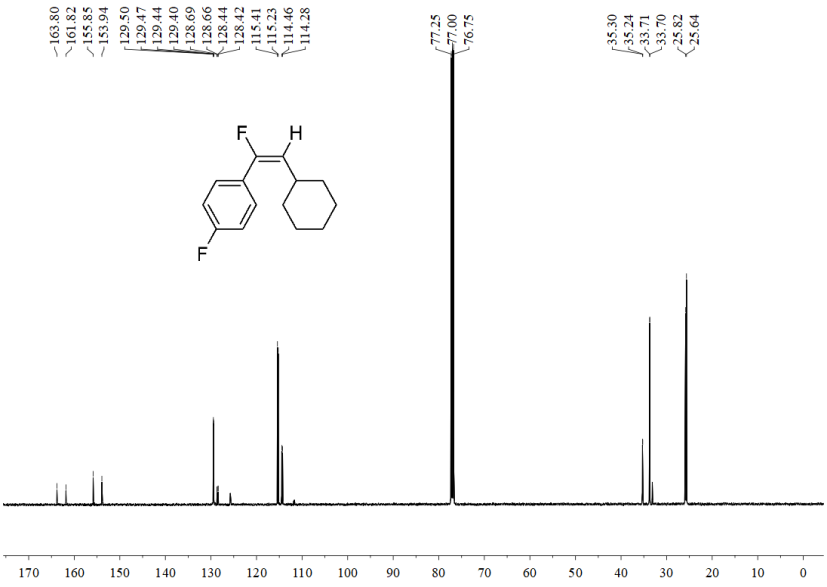
^{19}F NMR (471 MHz, $CDCl_3$) (**3**)



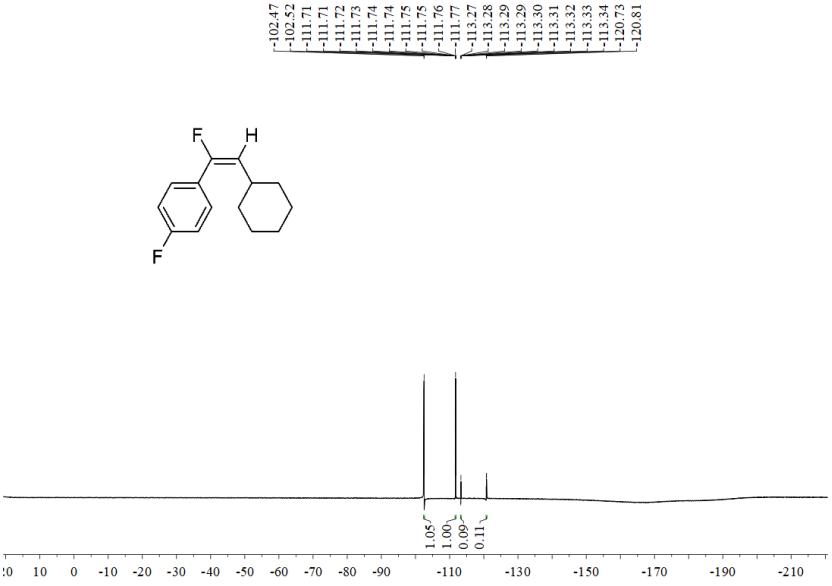
^{1}H NMR (500 MHz, $CDCl_3$) (**4**)



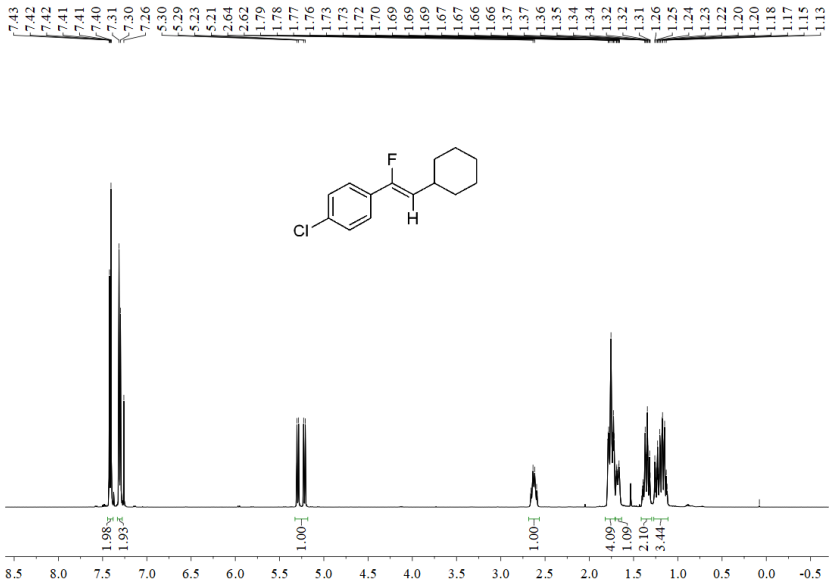
^{13}C NMR (126 MHz, $CDCl_3$) (**4**)



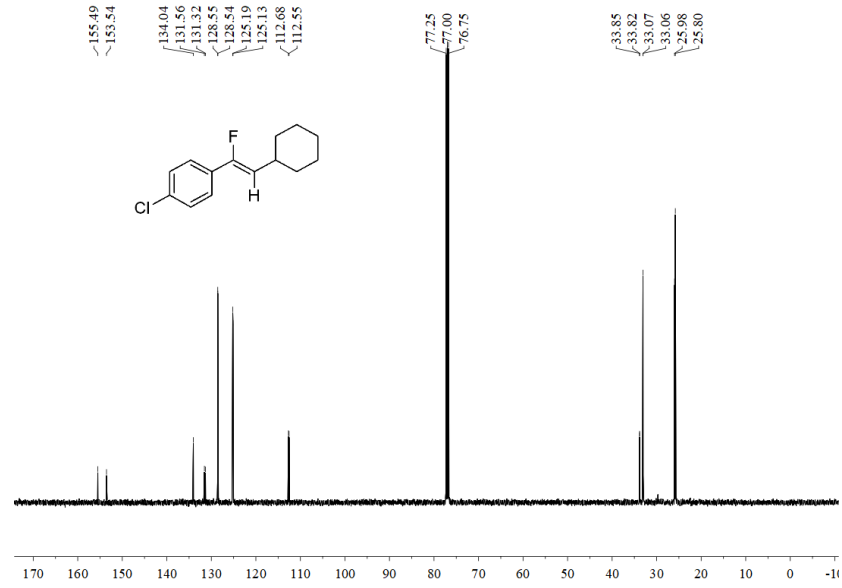
^{19}F NMR (471 MHz, $CDCl_3$) (**4**)



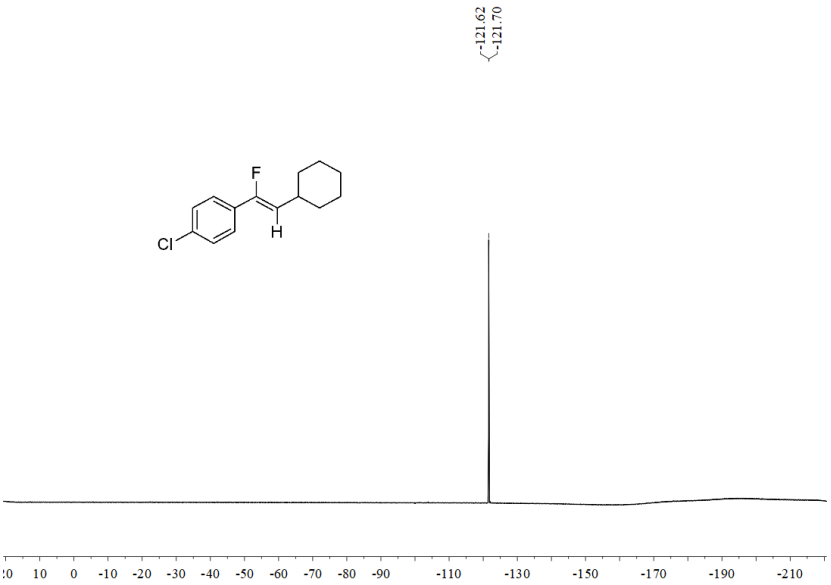
^{1}H NMR (500 MHz, $CDCl_3$) (**5**)



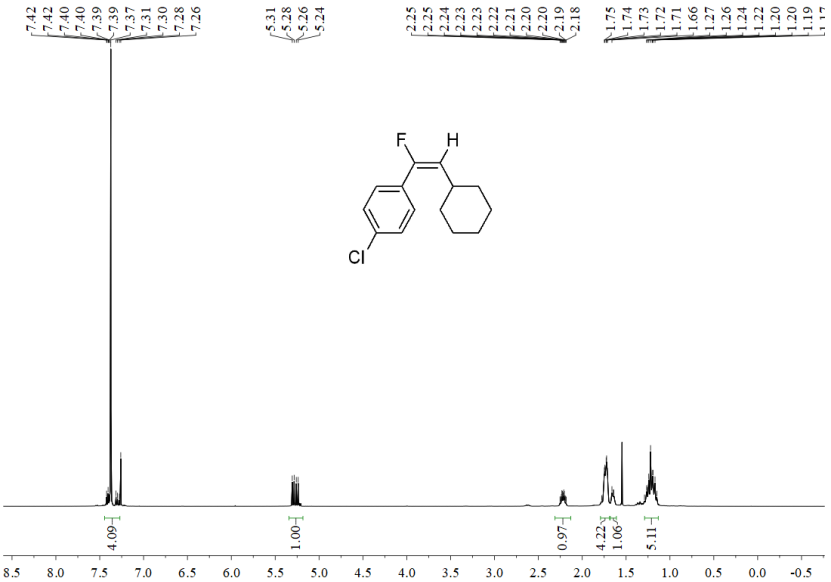
^{13}C NMR (126 MHz, $CDCl_3$) (**5**)



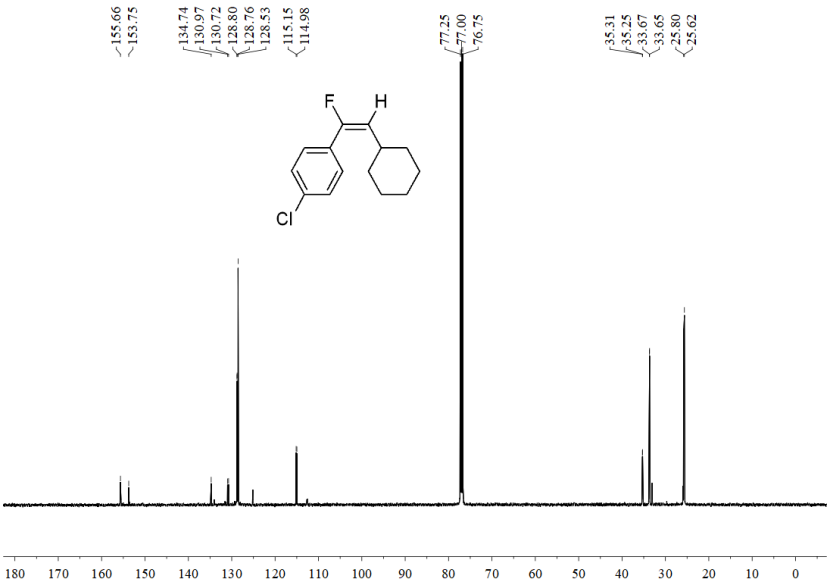
^{19}F NMR (471 MHz, $CDCl_3$) (**5**)



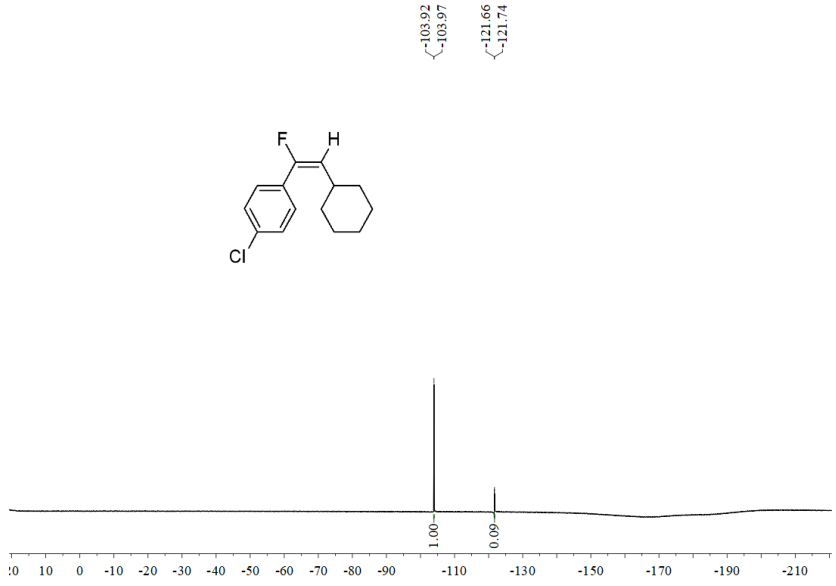
^{1}H NMR (500 MHz, $CDCl_3$) (**6**)



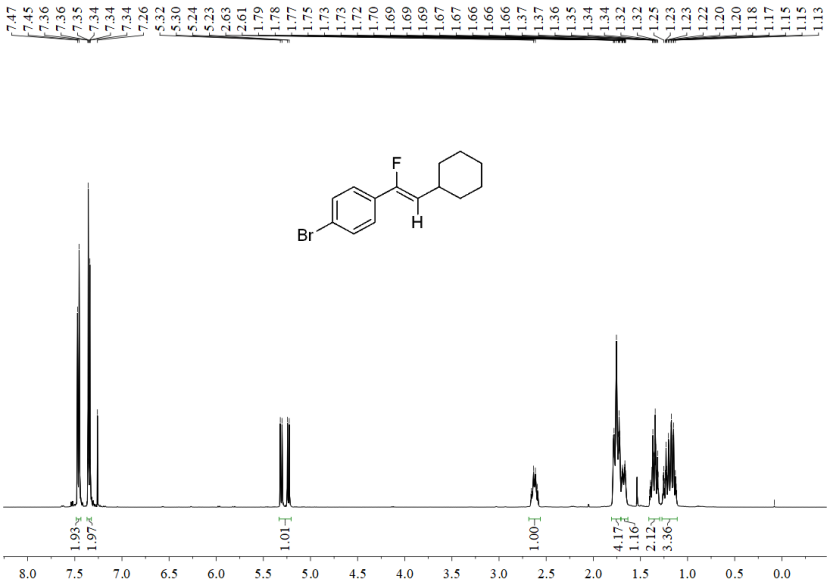
^{13}C NMR (126 MHz, $CDCl_3$) (**6**)



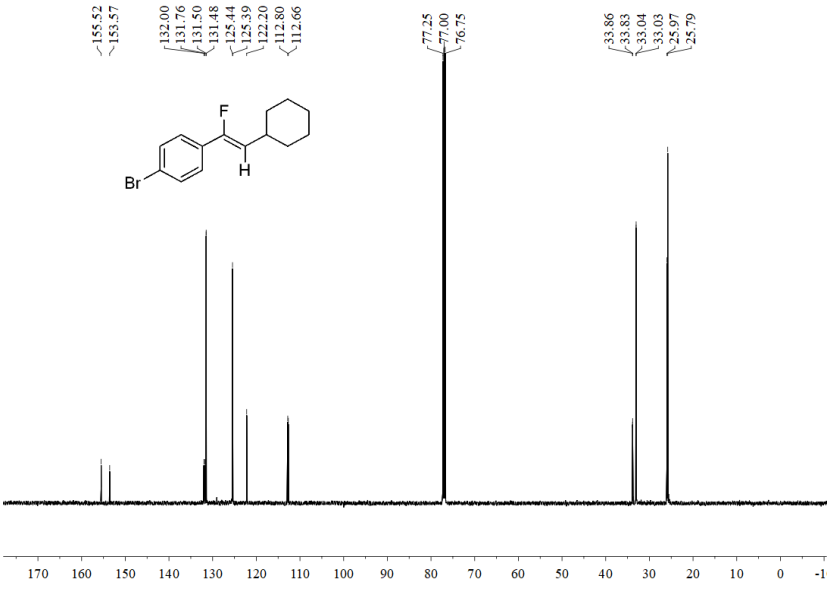
^{19}F NMR (471 MHz, $CDCl_3$) (**6**)



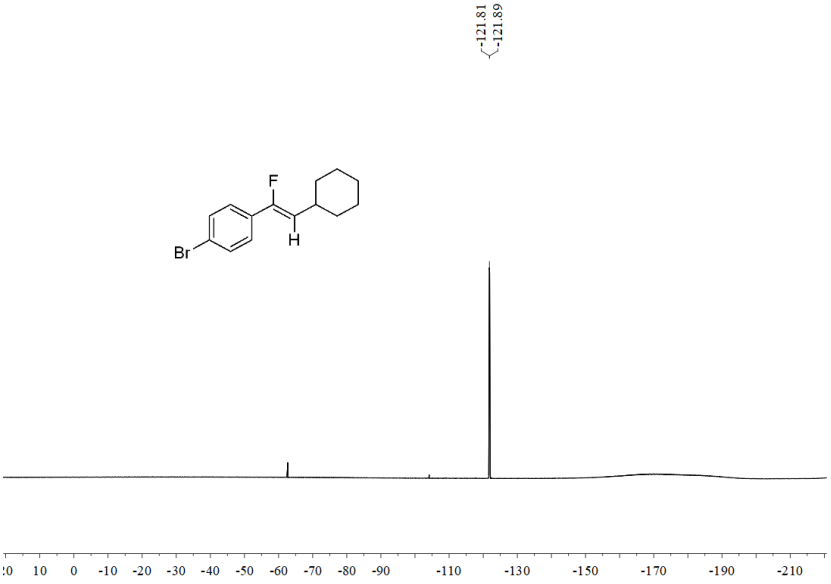
^{1}H NMR (500 MHz, $CDCl_3$) (**7**)



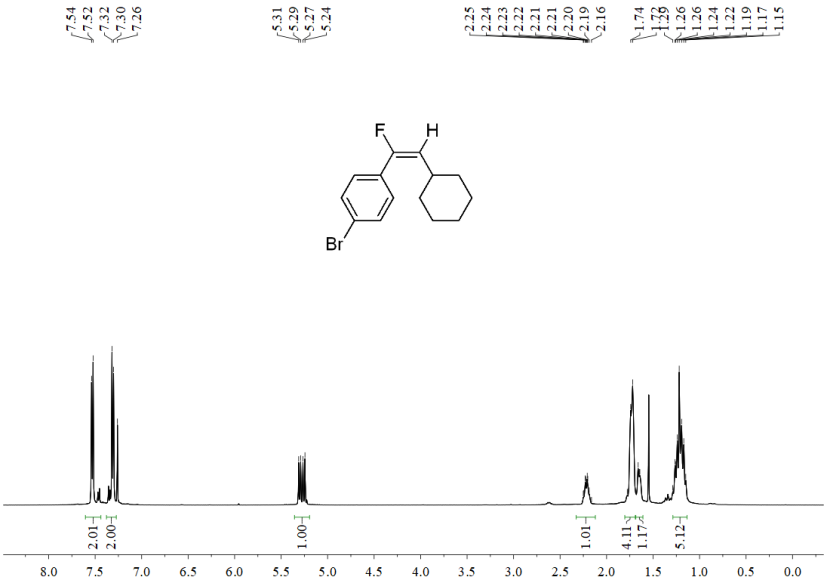
^{13}C NMR (126 MHz, $CDCl_3$) (**7**)



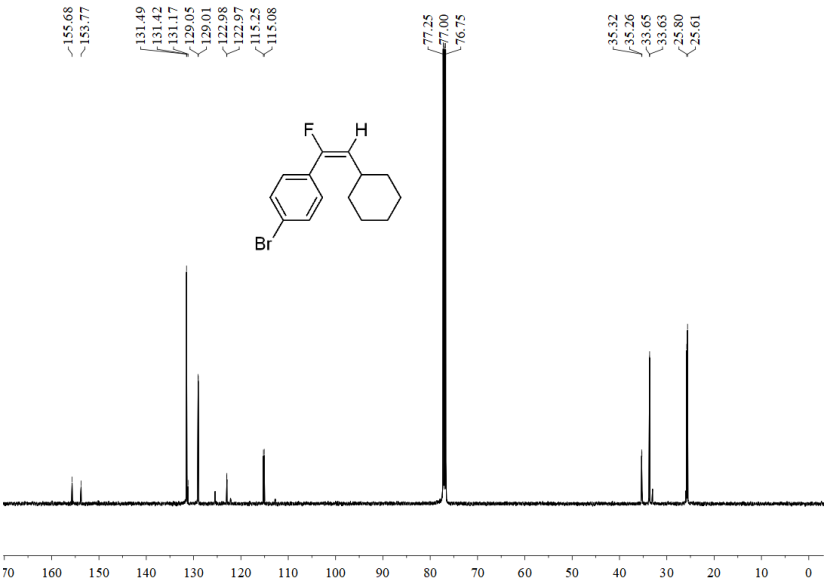
^{19}F NMR (471 MHz, $CDCl_3$) (**7**)



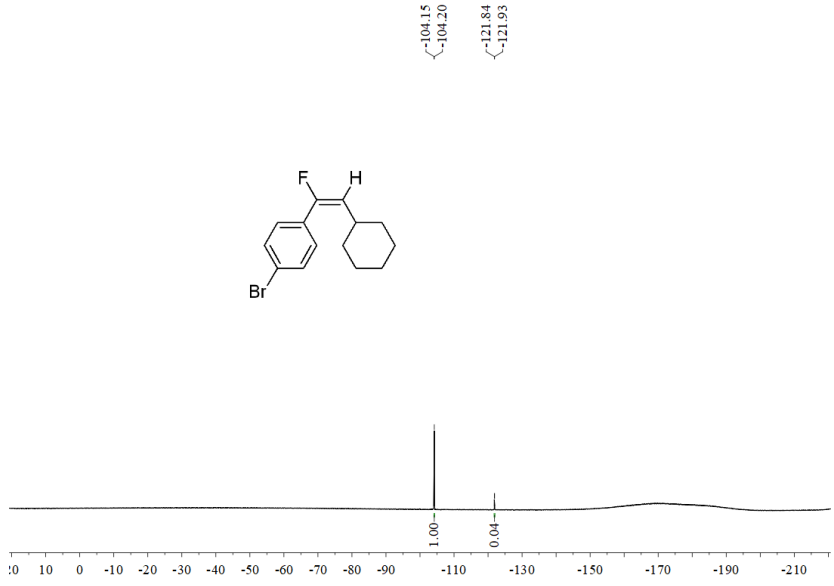
^{1}H NMR (500 MHz, $CDCl_3$) (**8**)



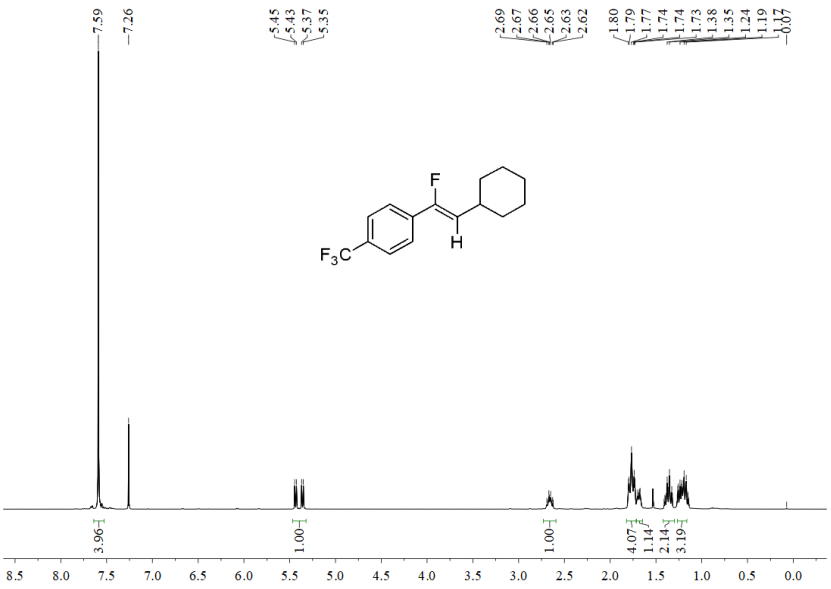
^{13}C NMR (126 MHz, $CDCl_3$) (**8**)



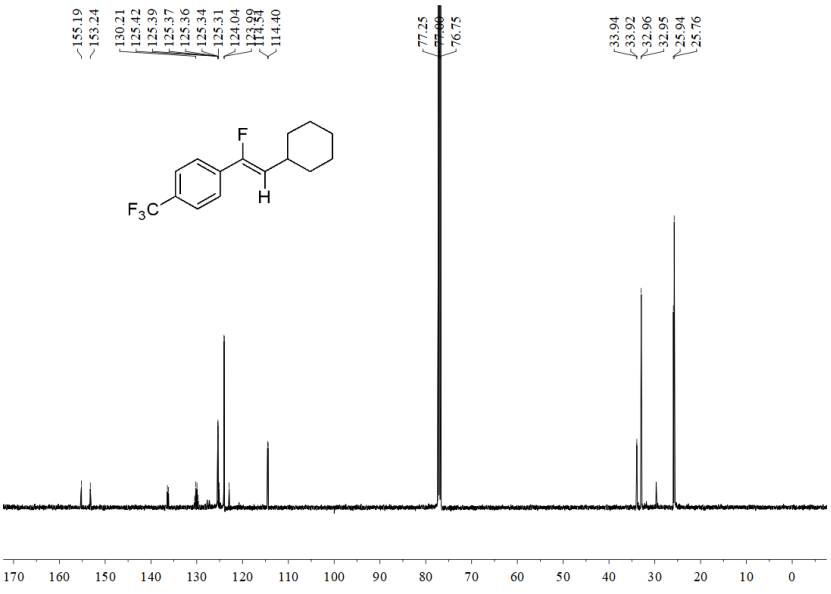
^{19}F NMR (471 MHz, $CDCl_3$) (**8**)



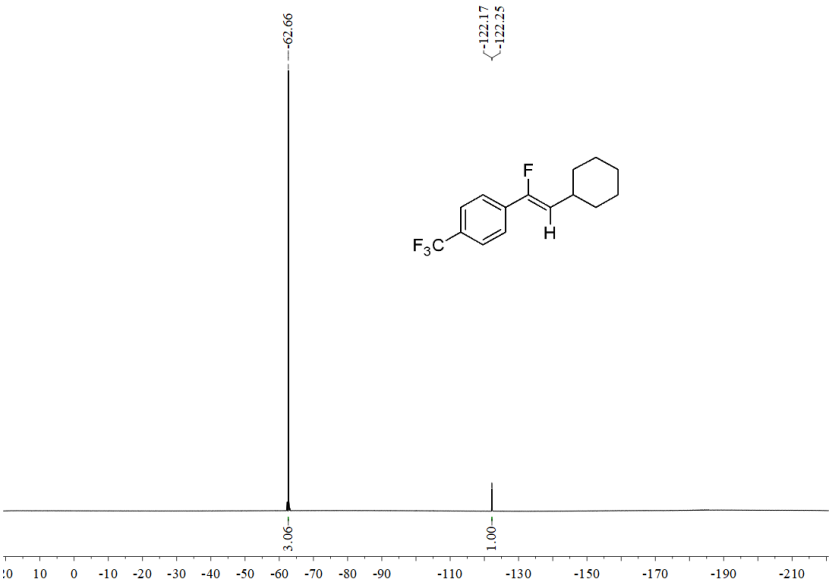
^{1}H NMR (500 MHz, $CDCl_3$) (**9**)



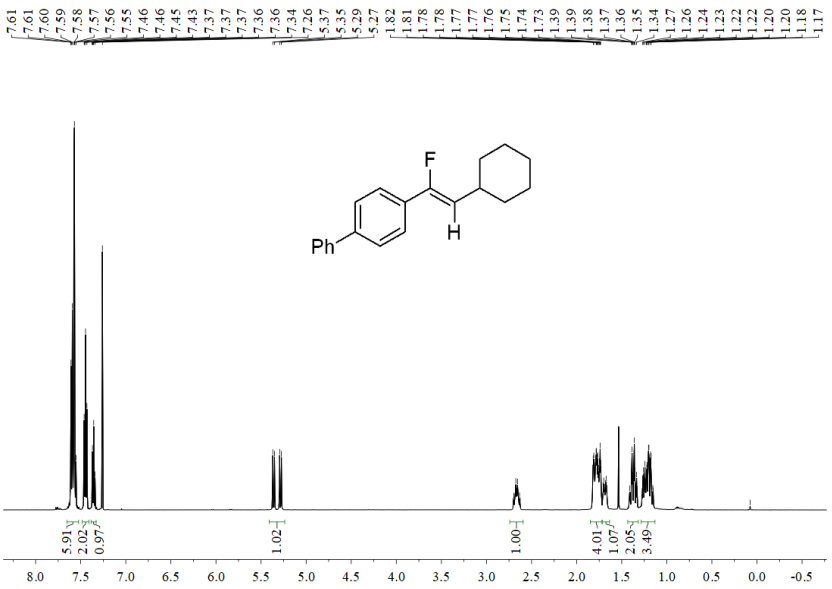
^{13}C NMR (126 MHz, $CDCl_3$) (**9**)



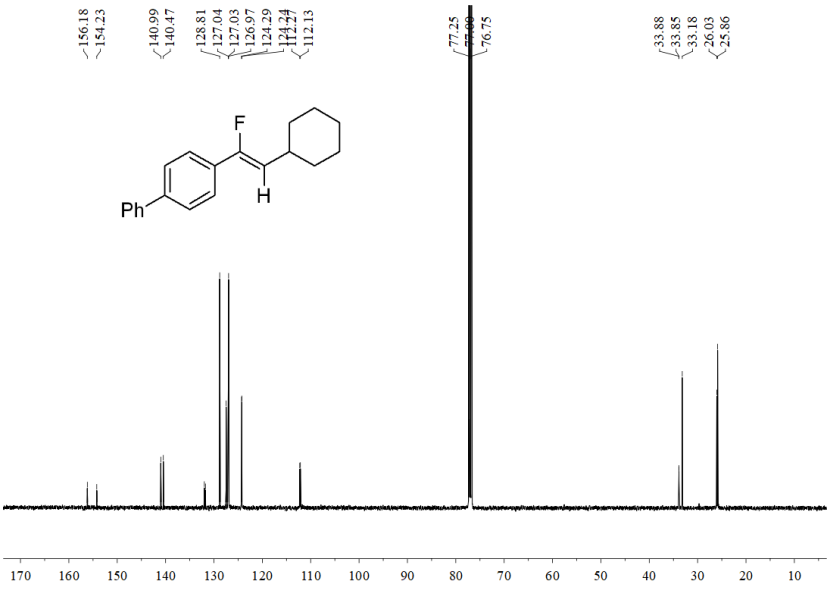
^{19}F NMR (471 MHz, $CDCl_3$) (**9**)



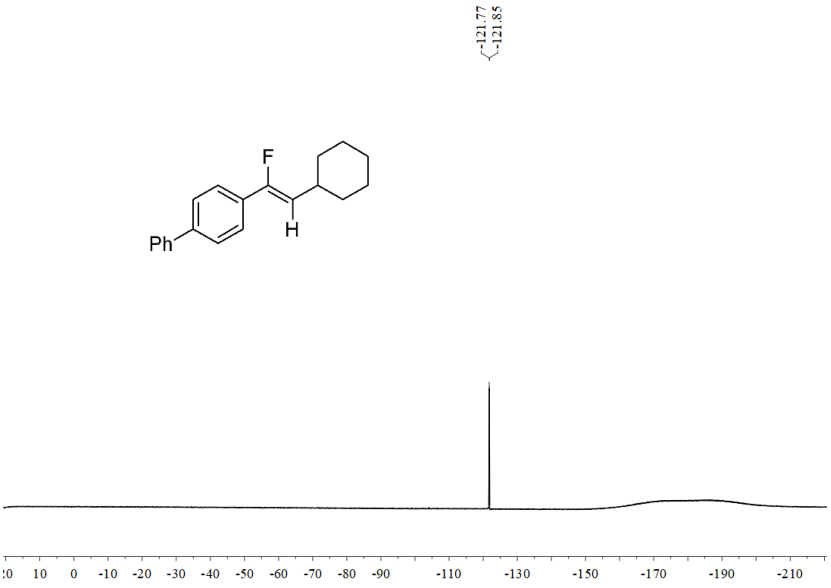
^{1}H NMR (500 MHz, $CDCl_3$) (**10**)



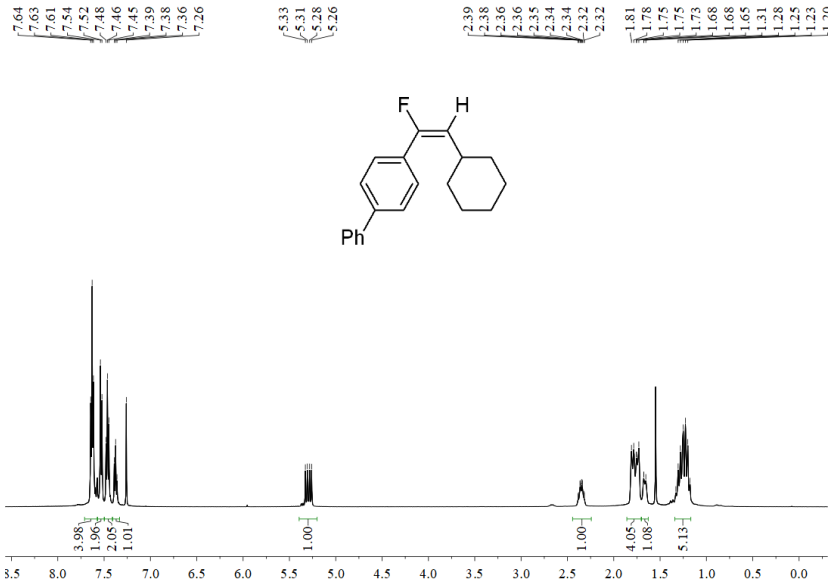
^{13}C NMR (126 MHz, $CDCl_3$) (**10**)



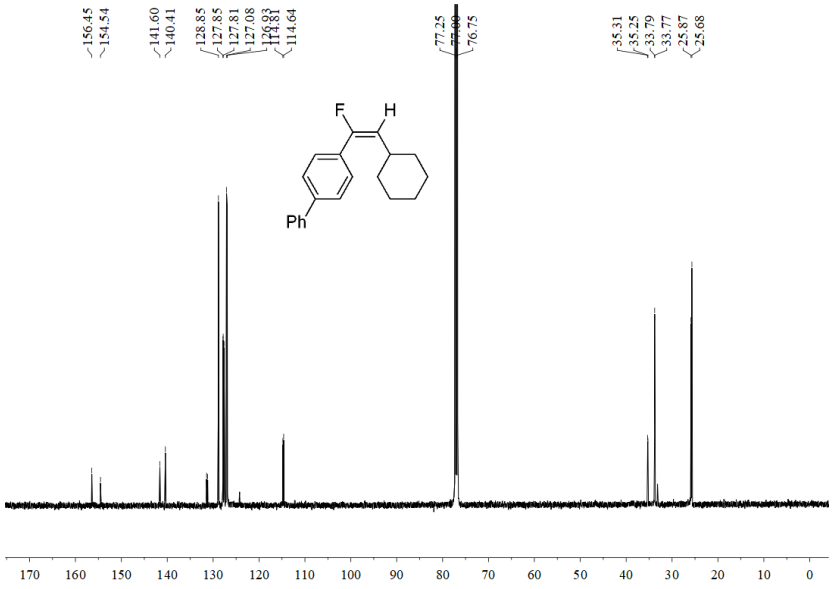
^{19}F NMR (471 MHz, $CDCl_3$) (**10**)



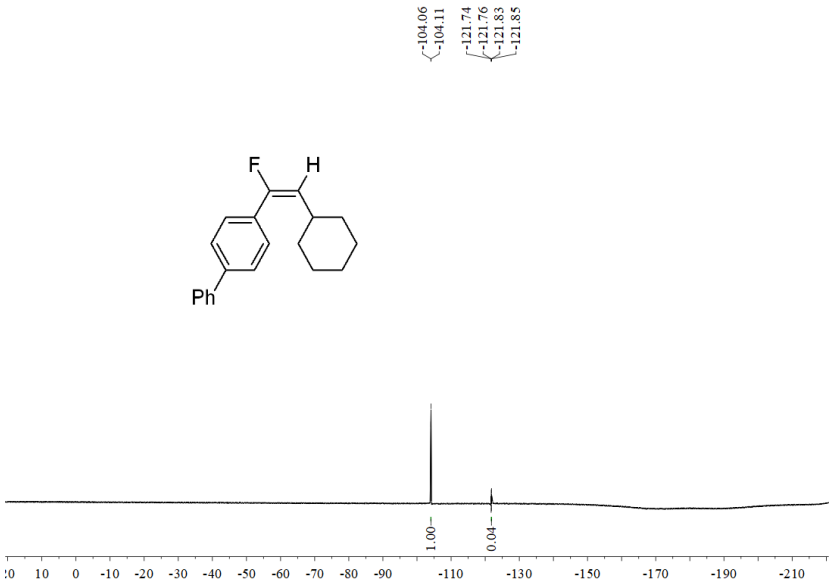
^{1}H NMR (500 MHz, $CDCl_3$) (**11**)



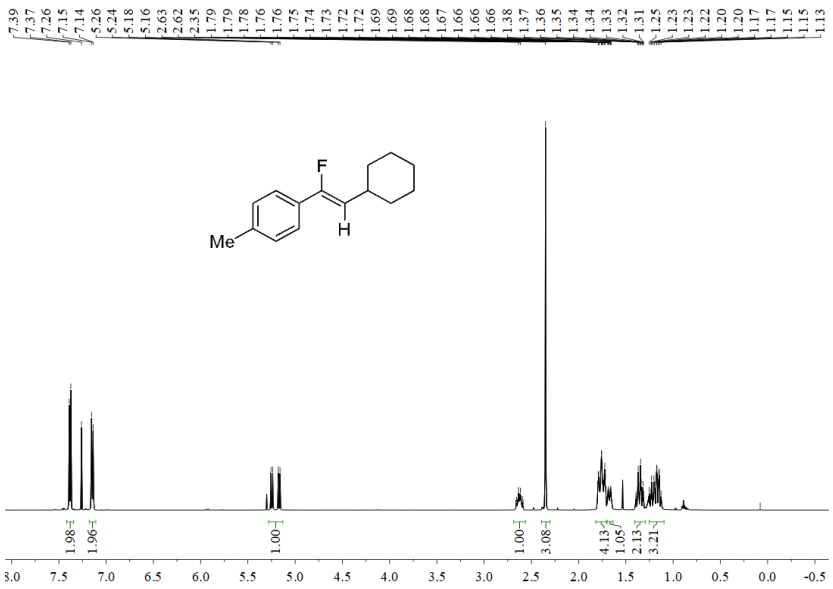
^{13}C NMR (126 MHz, $CDCl_3$) (**11**)



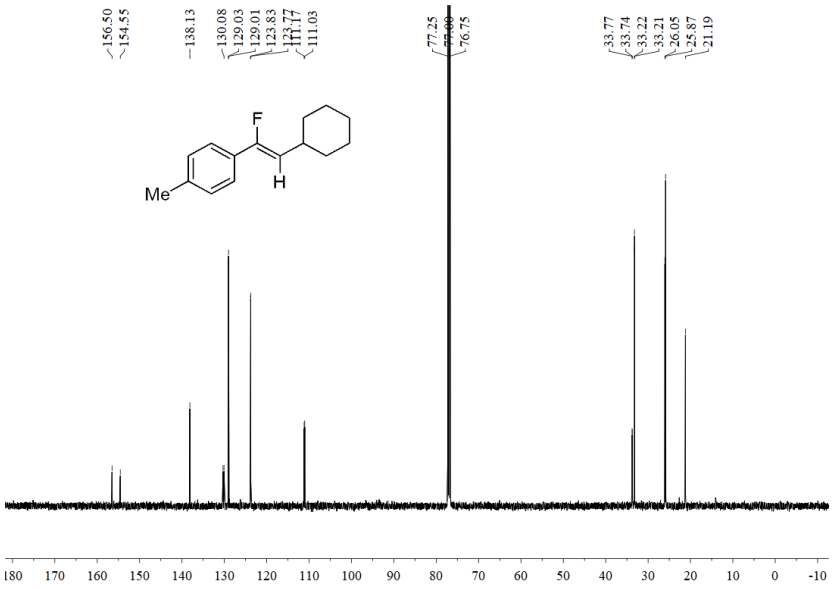
^{19}F NMR (471 MHz, $CDCl_3$) (**11**)



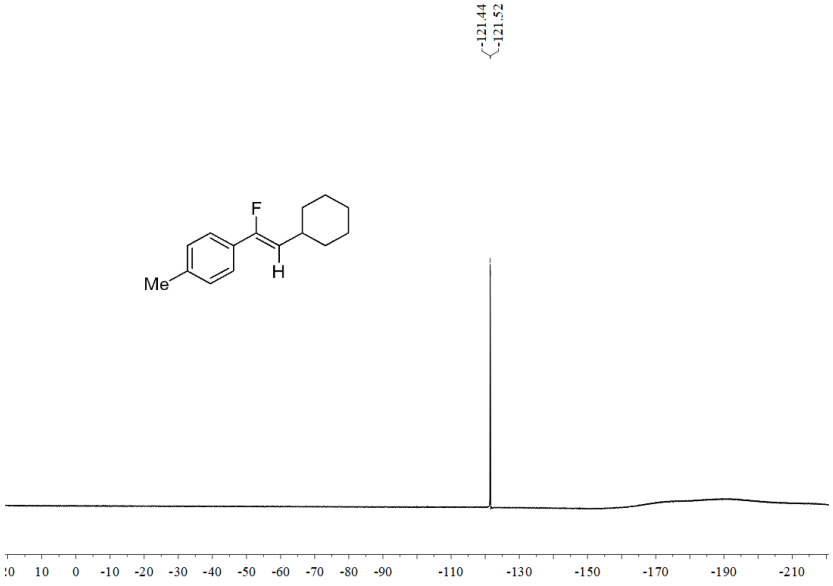
^{1}H NMR (500 MHz, $CDCl_3$) (**12**)



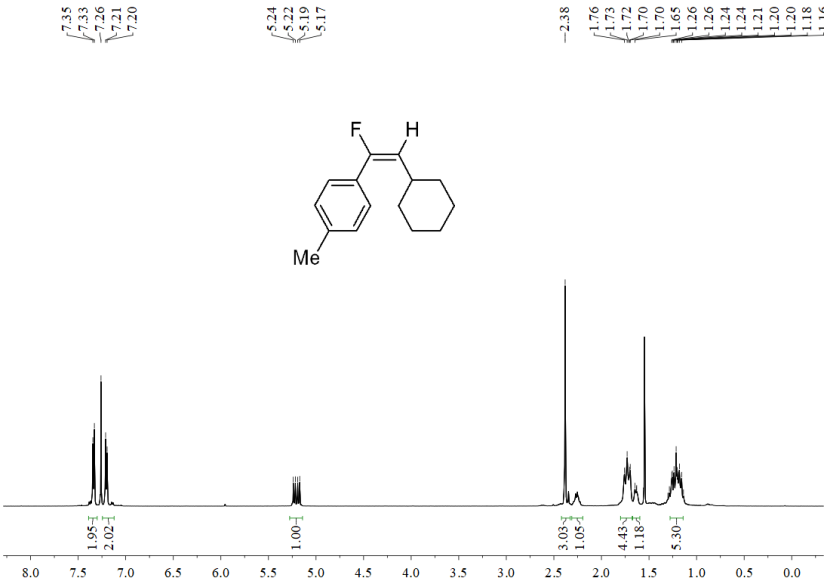
^{13}C NMR (126 MHz, $CDCl_3$) (**12**)



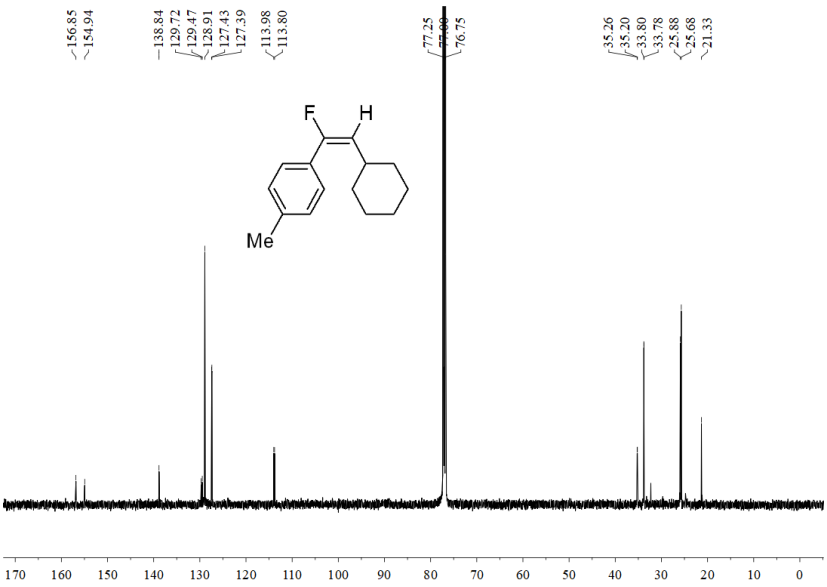
^{19}F NMR (471 MHz, $CDCl_3$) (**12**)



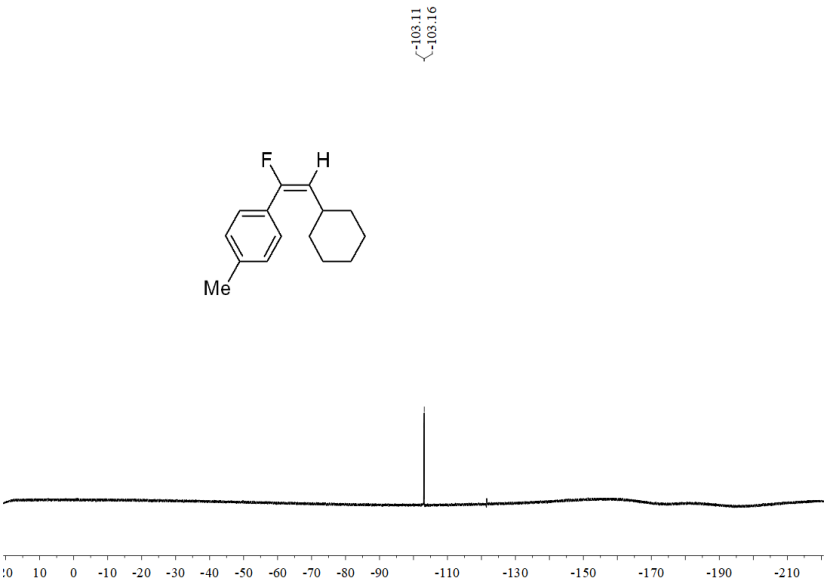
^{1}H NMR (500 MHz, $CDCl_3$) (**13**)



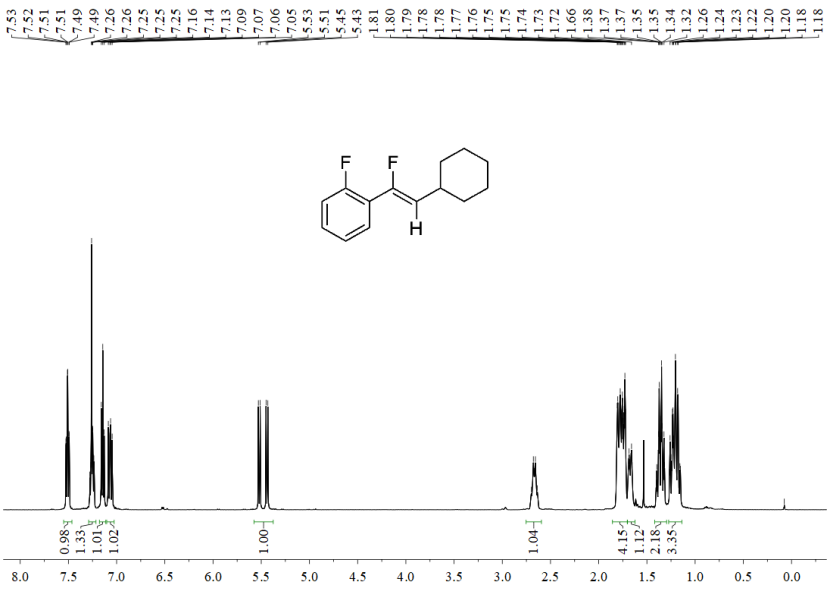
^{13}C NMR (126 MHz, $CDCl_3$) (**13**)



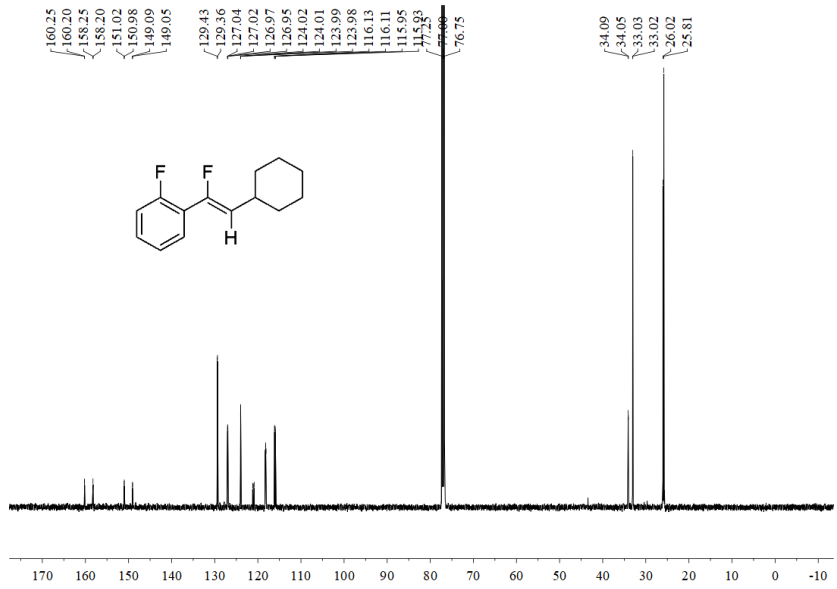
^{19}F NMR (471 MHz, $CDCl_3$) (**13**)



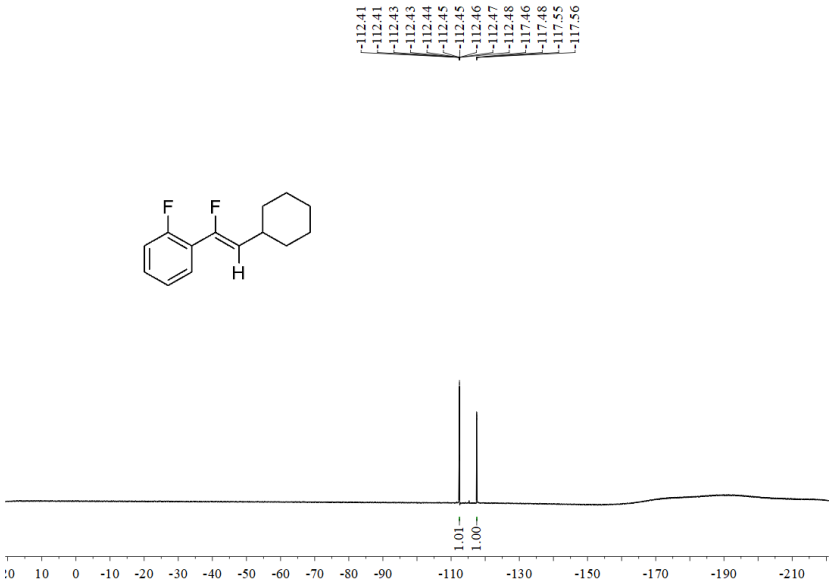
^{1}H NMR (500 MHz, $CDCl_3$) (**14**)



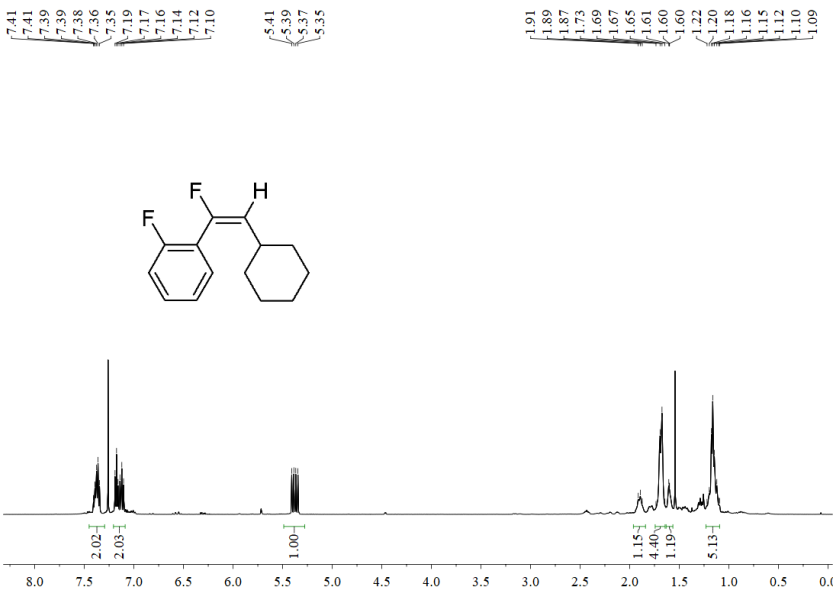
^{13}C NMR (126 MHz, $CDCl_3$) (**14**)



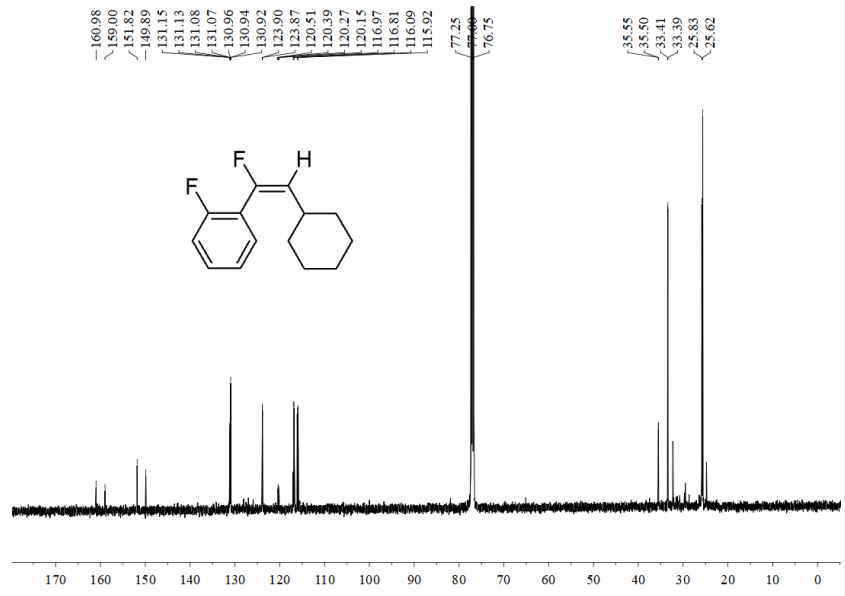
^{19}F NMR (471 MHz, $CDCl_3$) (**14**)



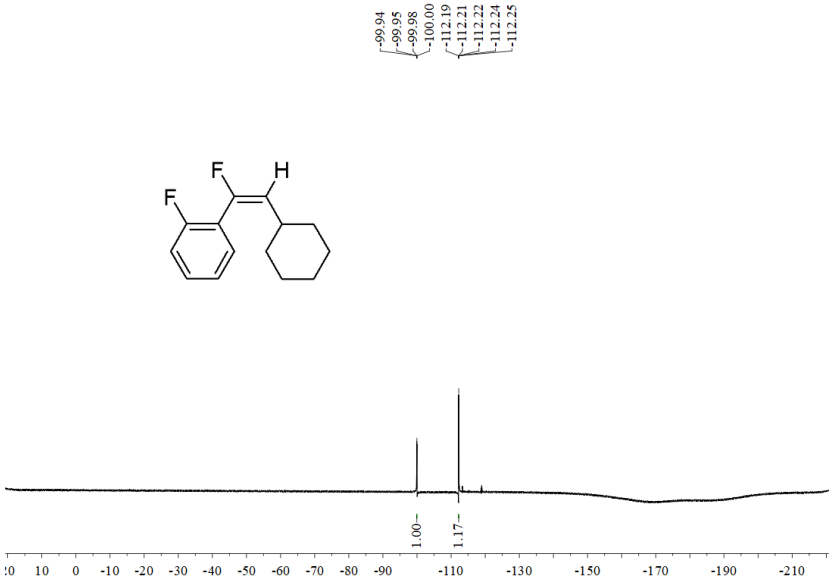
^{1}H NMR (500 MHz, $CDCl_3$) (**15**)



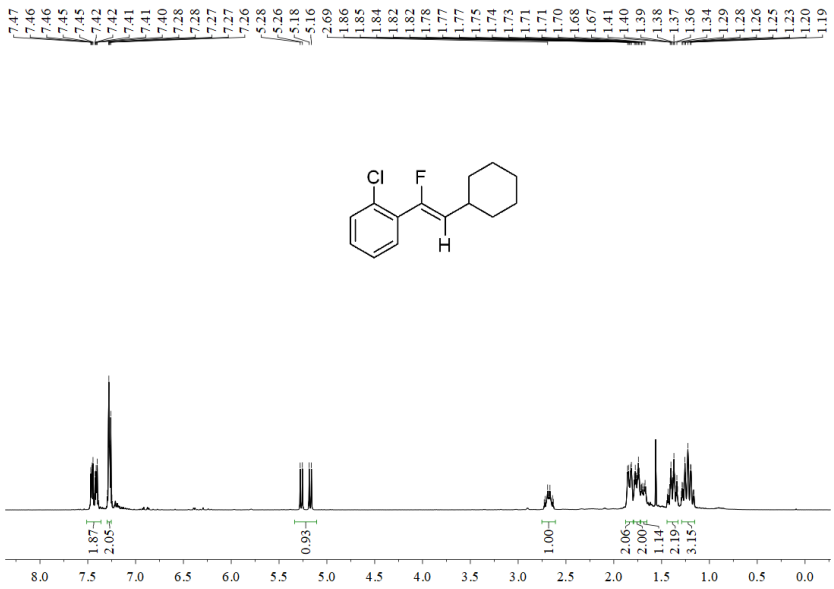
^{13}C NMR (126 MHz, $CDCl_3$) (**15**)



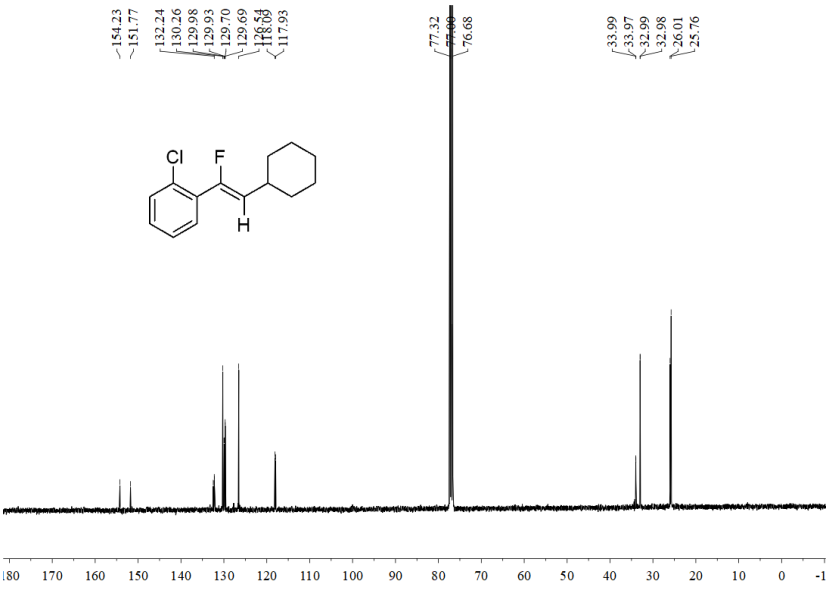
^{19}F NMR (471 MHz, $CDCl_3$) (**15**)



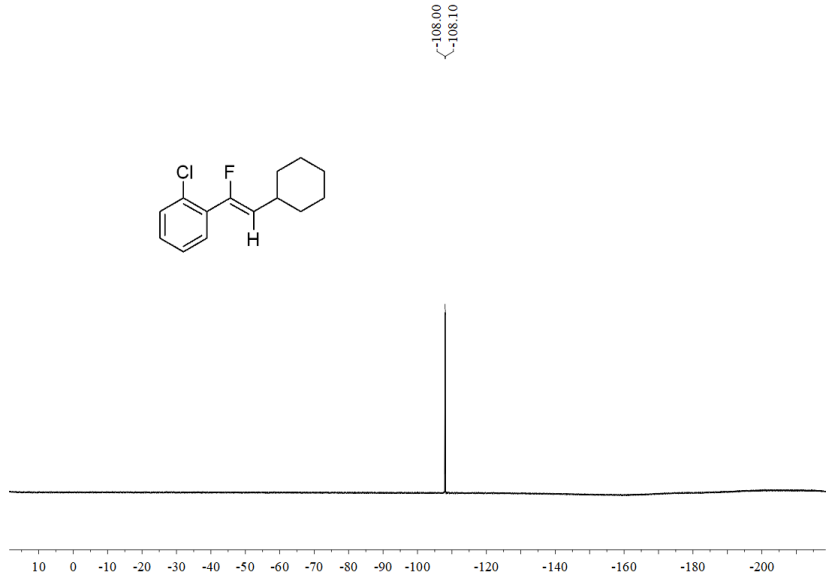
^{1}H NMR (400 MHz, $CDCl_3$) (**16**)



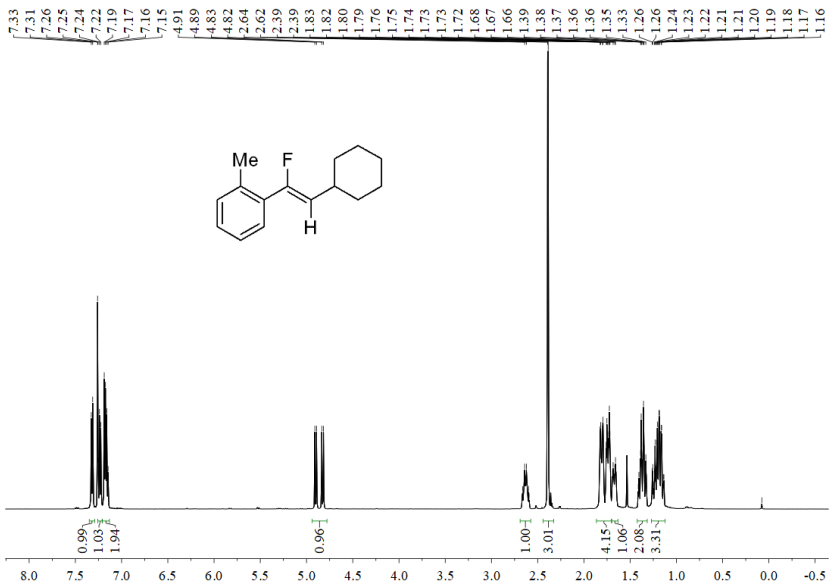
^{13}C NMR (101 MHz, $CDCl_3$) (**16**)



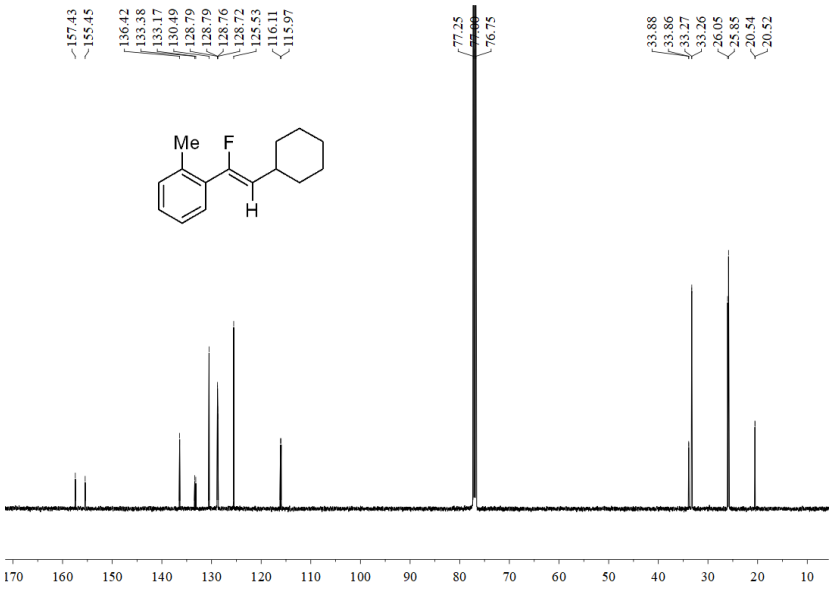
^{19}F NMR (376 MHz, $CDCl_3$) (**16**)



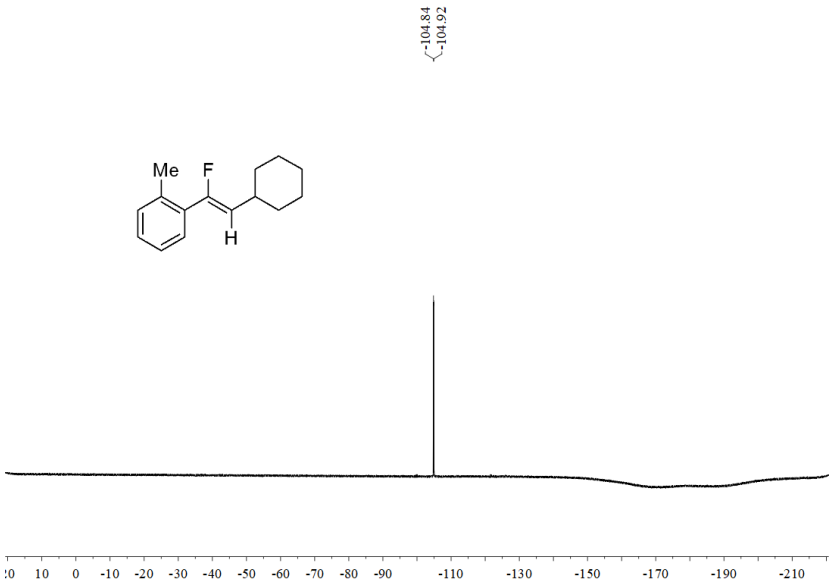
^{1}H NMR (500 MHz, $CDCl_3$) (**17**)



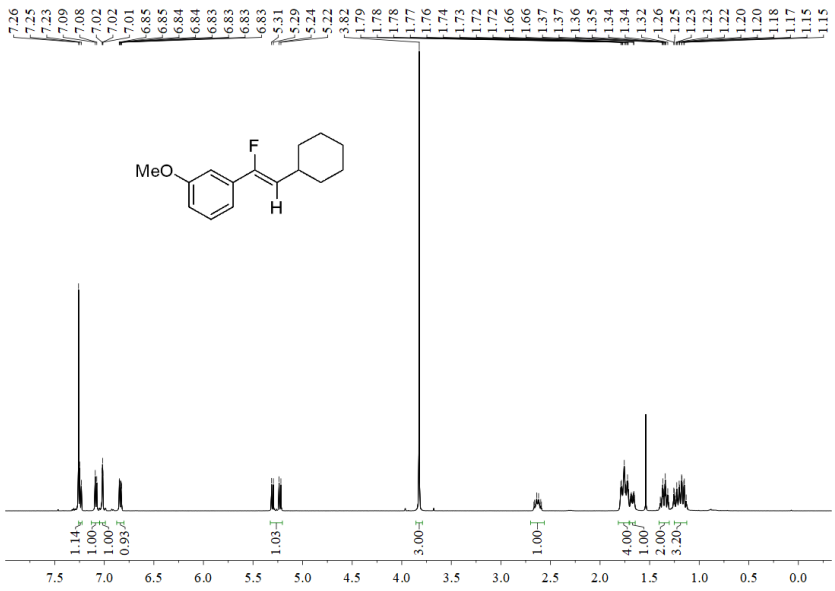
^{13}C NMR (126 MHz, $CDCl_3$) (**17**)



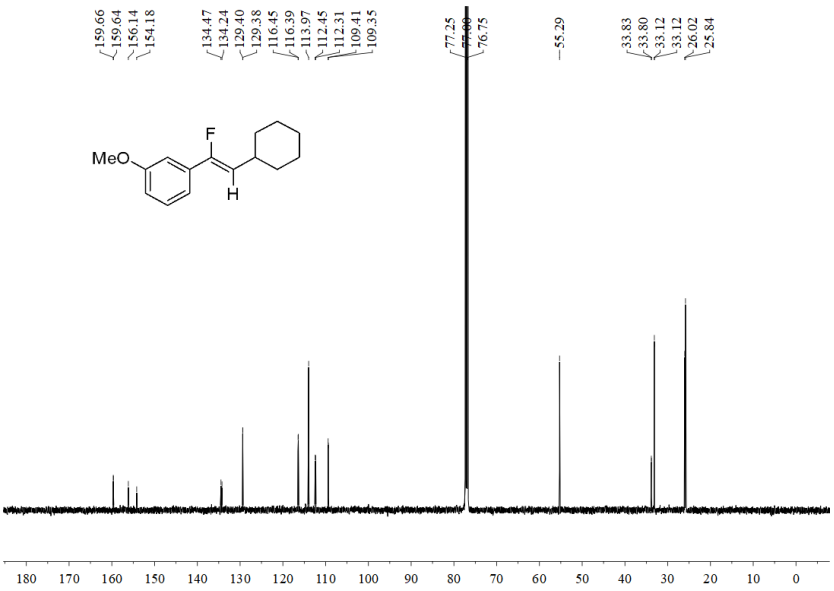
^{19}F NMR (471 MHz, $CDCl_3$) (**17**)



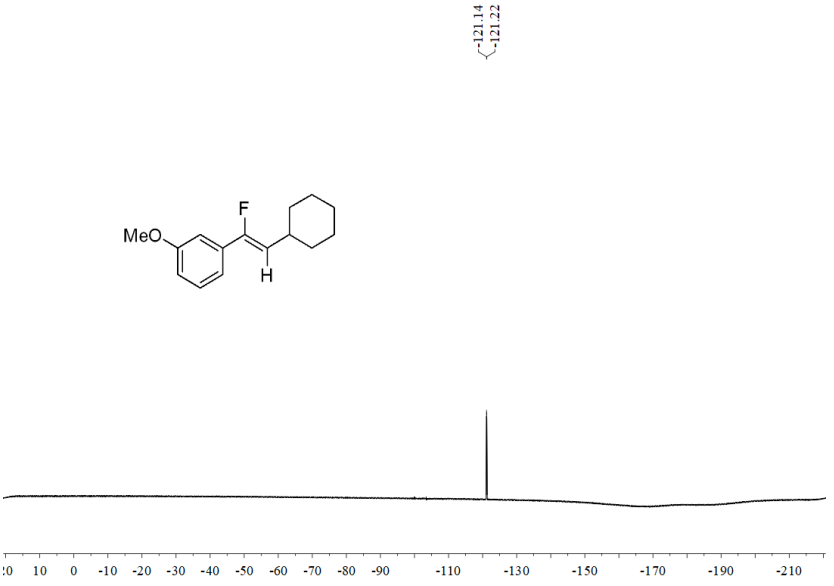
^{1}H NMR (500 MHz, $CDCl_3$) (**18**)



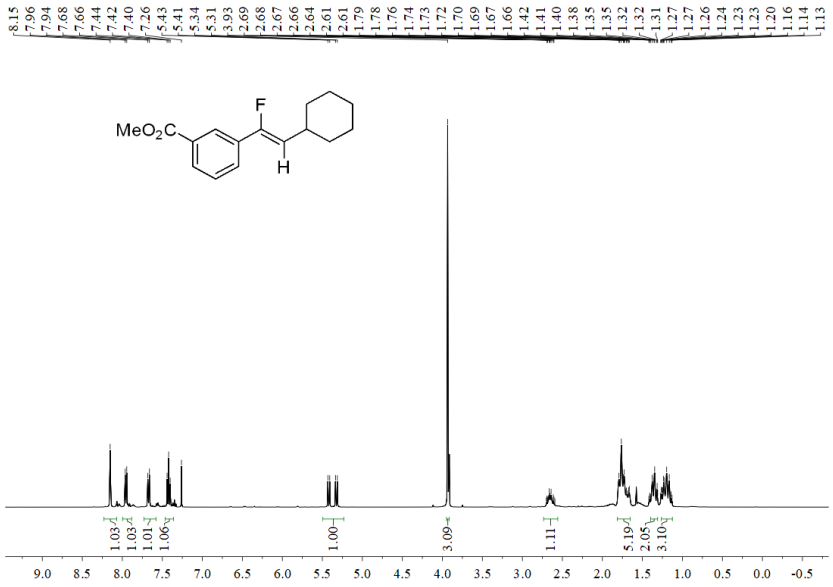
^{13}C NMR (126 MHz, $CDCl_3$) (**18**)



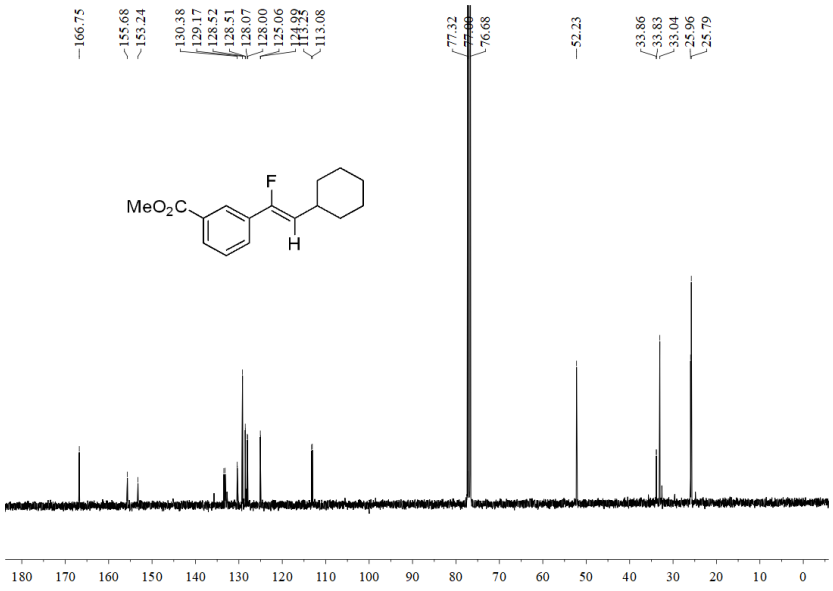
^{19}F NMR (471 MHz, $CDCl_3$) (**18**)



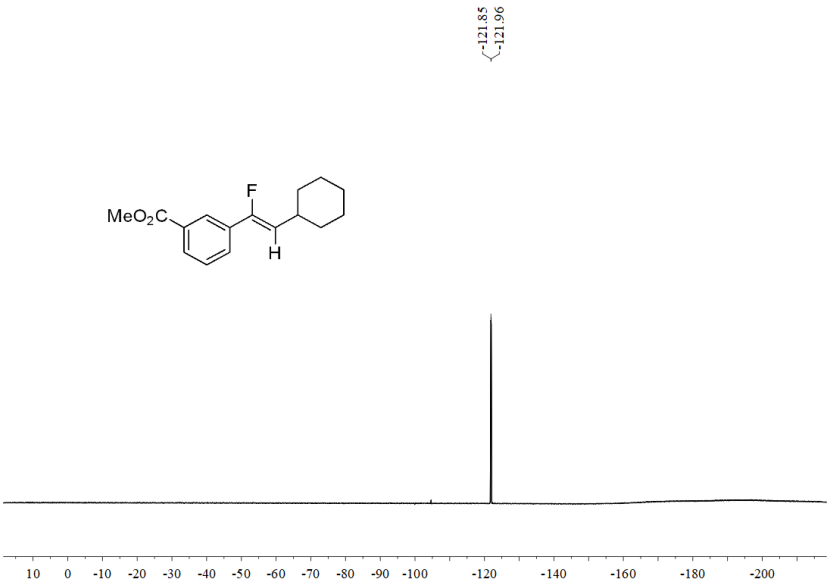
^{1}H NMR (400 MHz, $CDCl_3$) (**19**)



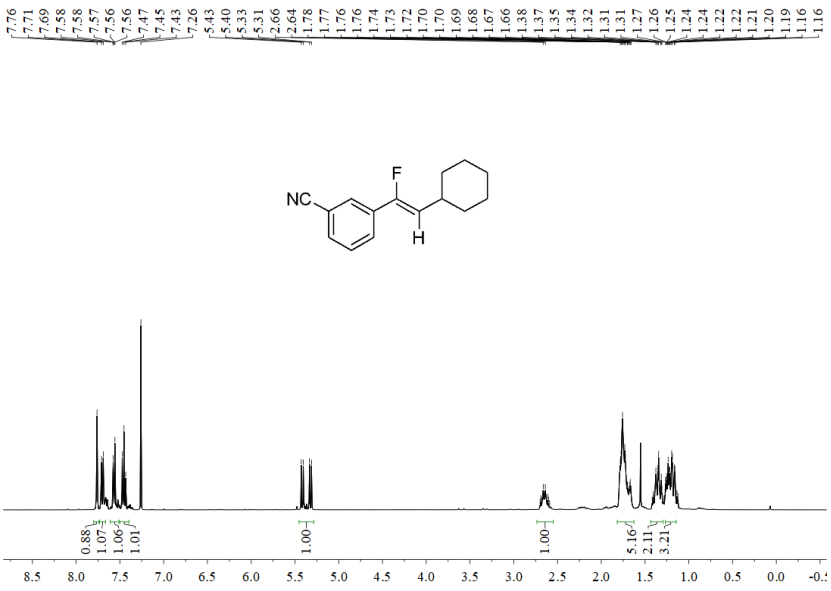
^{13}C NMR (101 MHz, $CDCl_3$) (**19**)



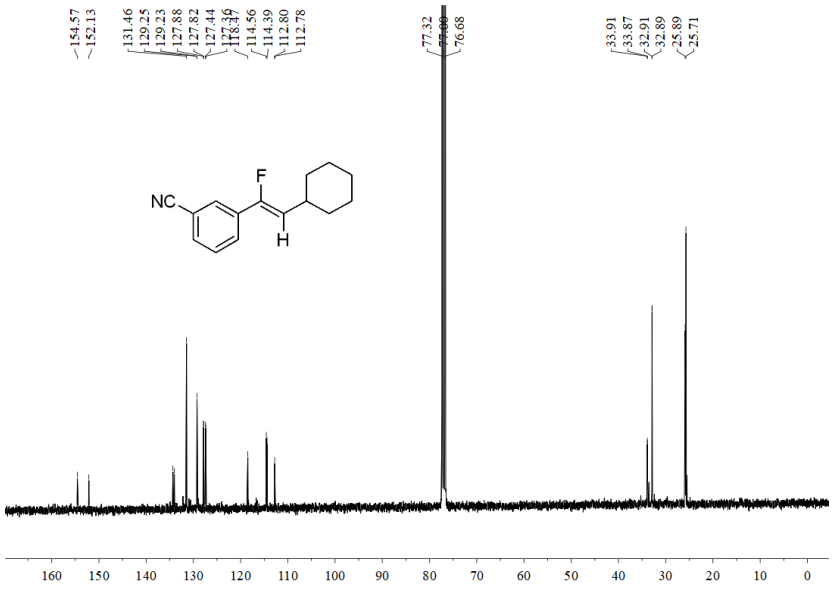
^{19}F NMR (376 MHz, $CDCl_3$) (**19**)



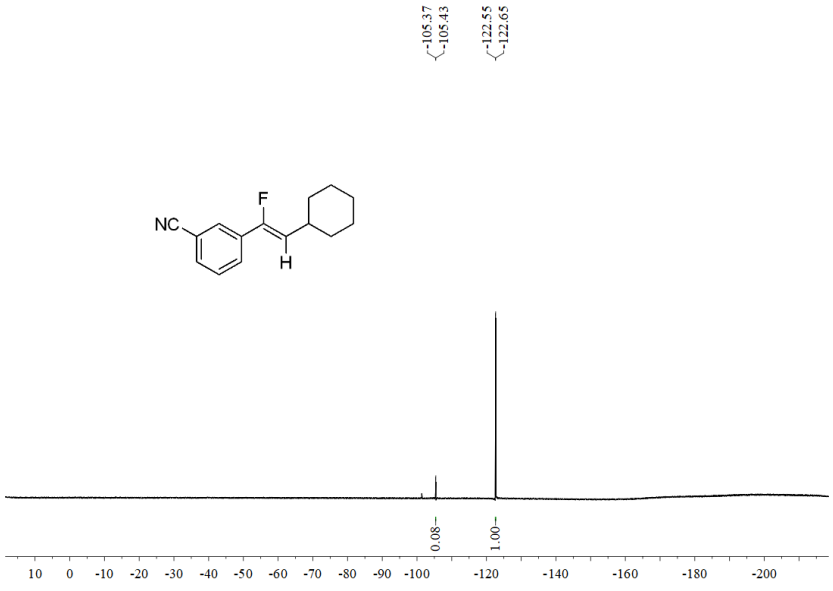
^{1}H NMR (400 MHz, $CDCl_3$) (**20**)



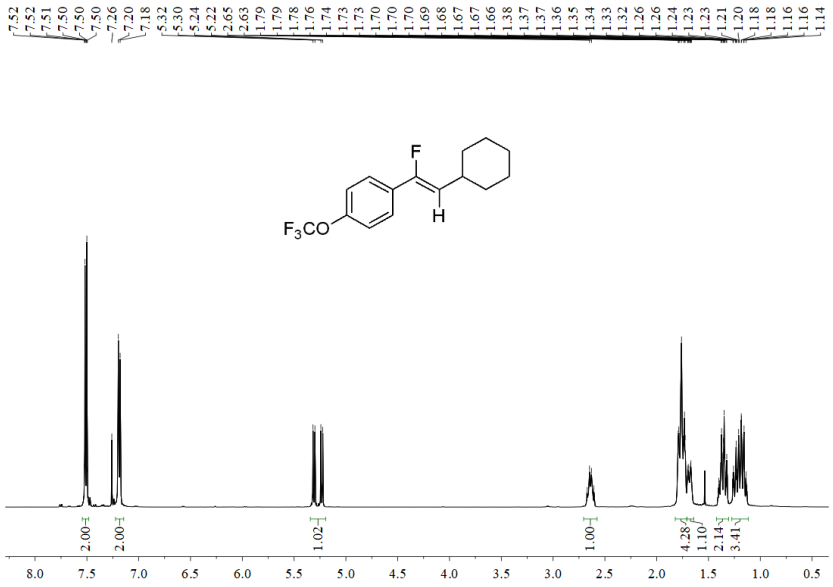
^{13}C NMR (101 MHz, $CDCl_3$) (**20**)



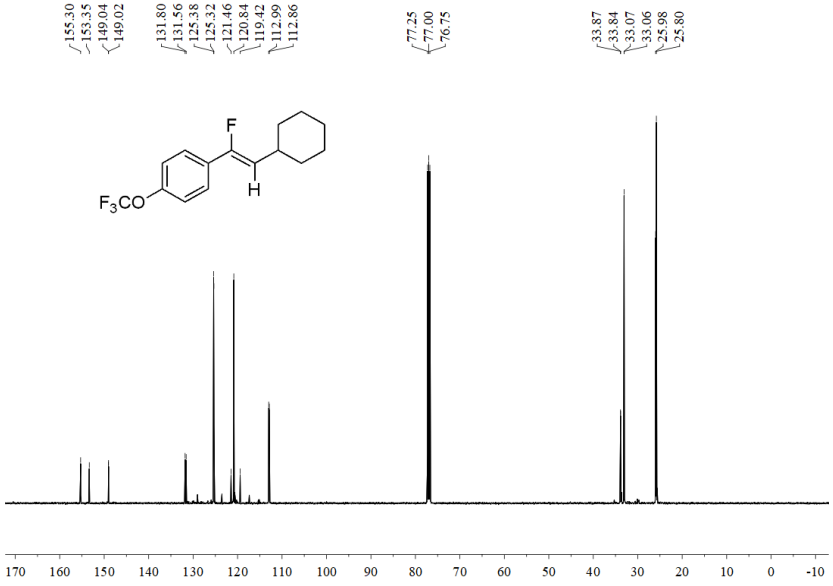
^{19}F NMR (376 MHz, $CDCl_3$) (**20**)



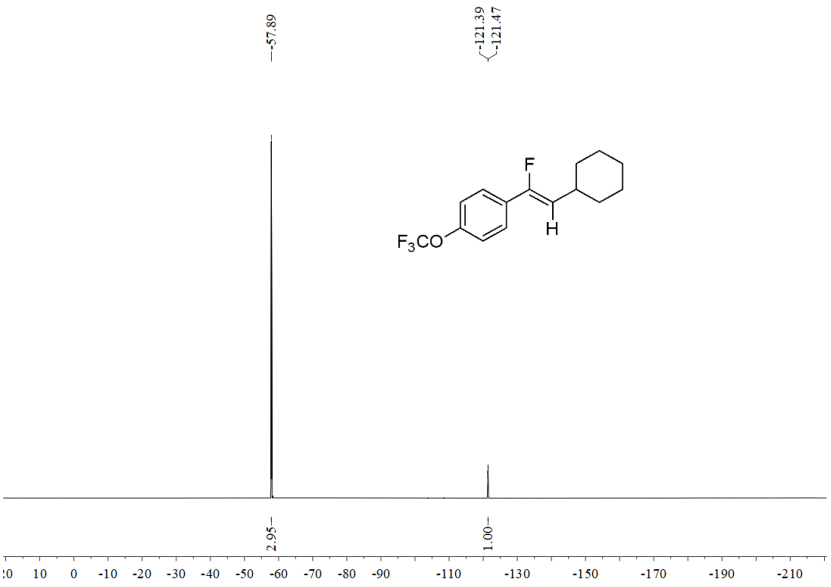
^{1}H NMR (500 MHz, $CDCl_3$) (**21**)



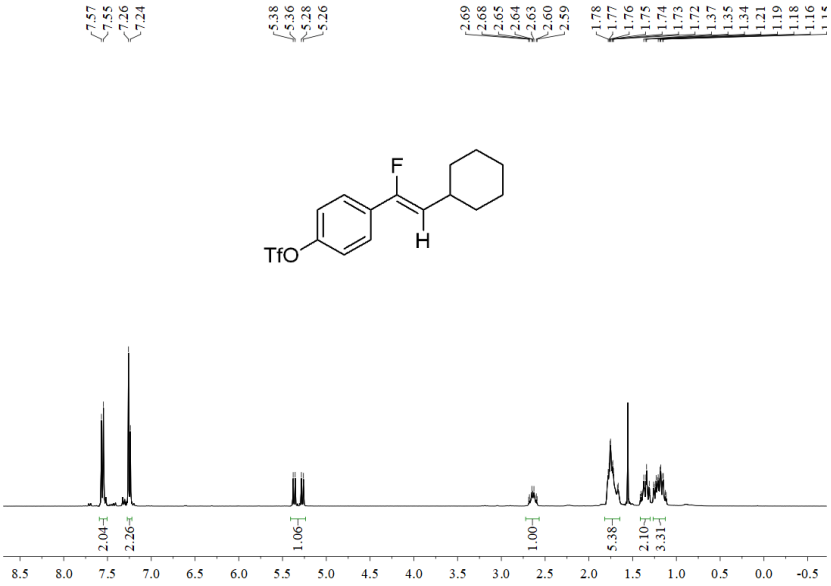
^{13}C NMR (126 MHz, $CDCl_3$) (**21**)



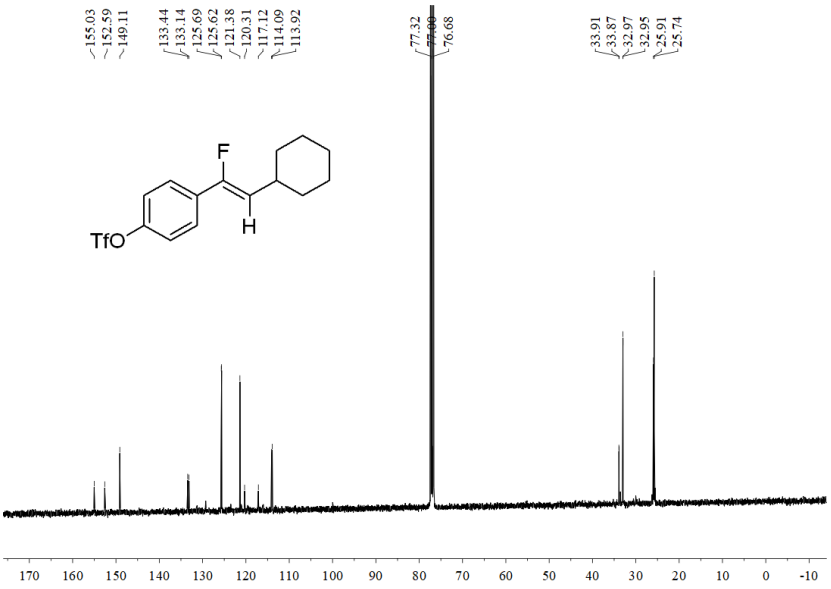
^{19}F NMR (471 MHz, $CDCl_3$) (**21**)



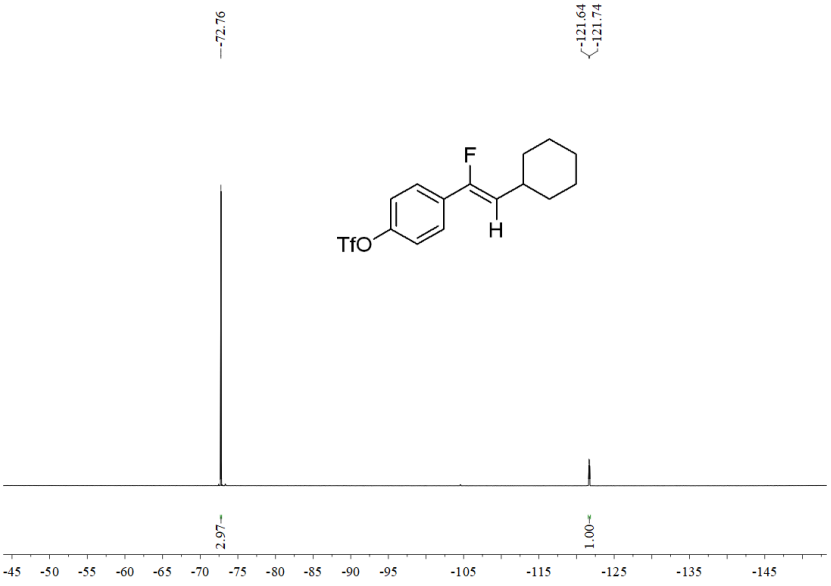
^{1}H NMR (400 MHz, $CDCl_3$) (**22**)



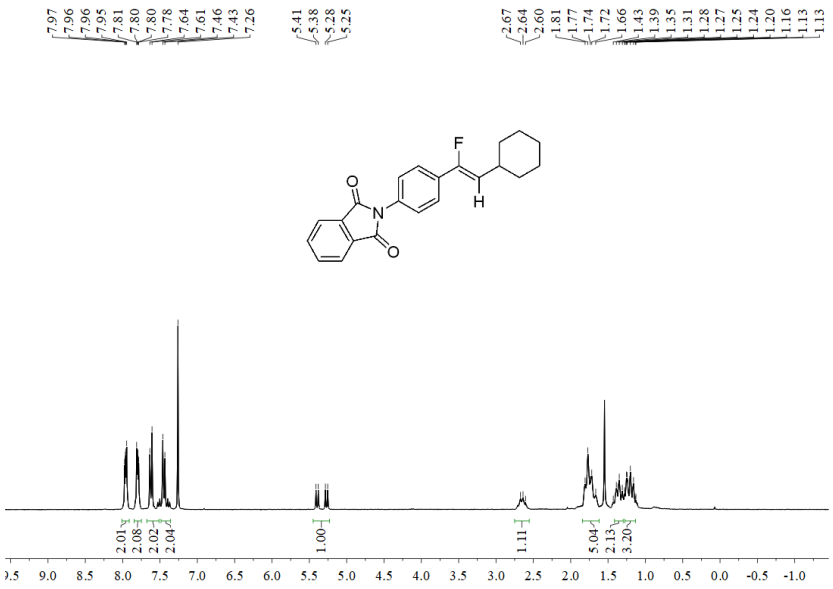
^{13}C NMR (101 MHz, $CDCl_3$) (**22**)



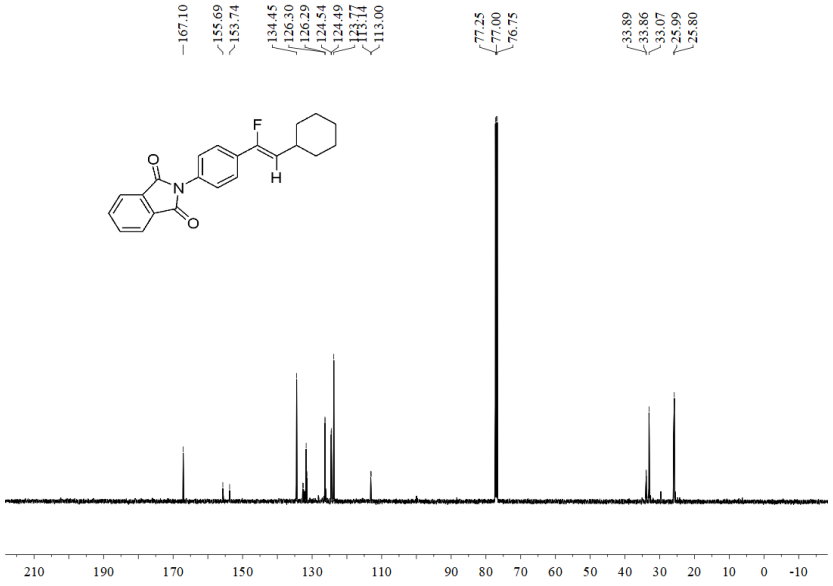
^{19}F NMR (376 MHz, $CDCl_3$) (**22**)



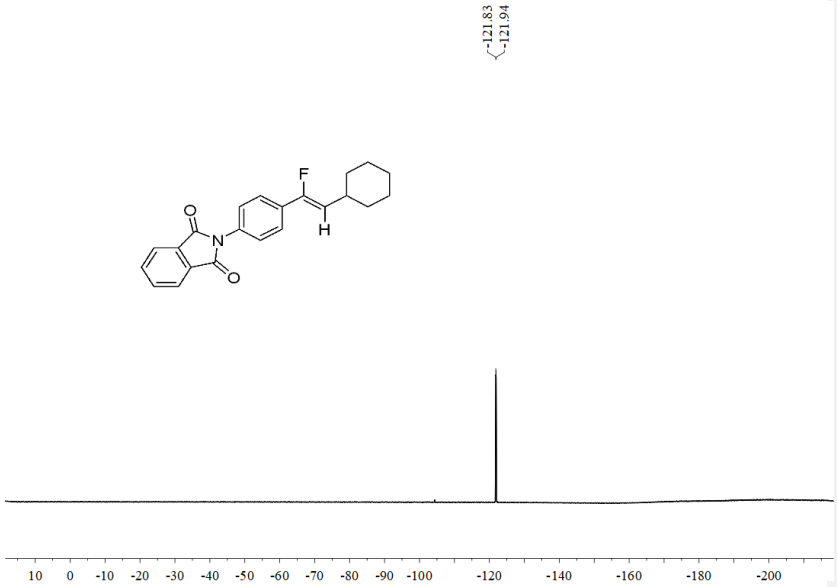
^{1}H NMR (300 MHz, $CDCl_3$) (**23**)



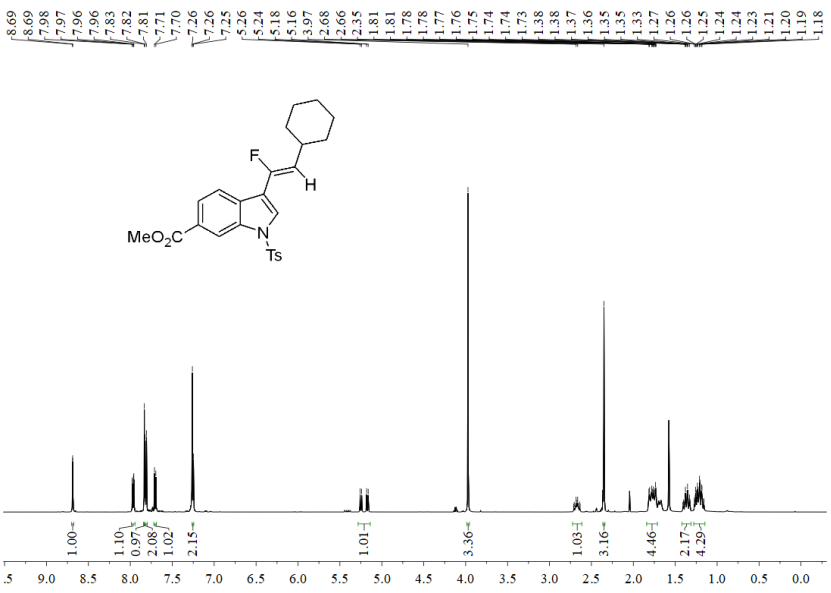
^{13}C NMR (126 MHz, $CDCl_3$) (**23**)



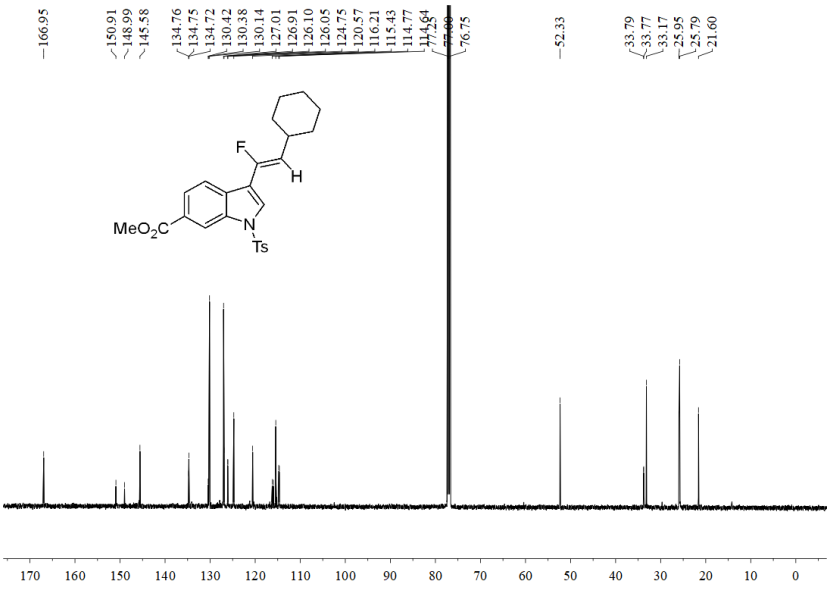
^{19}F NMR (471 MHz, $CDCl_3$) (**23**)



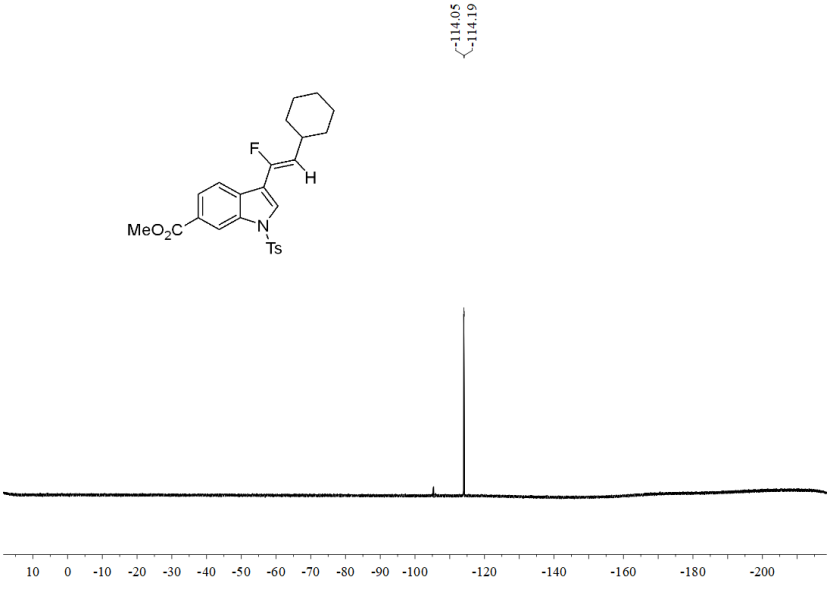
^{1}H NMR (500 MHz, $CDCl_3$) (**24**)



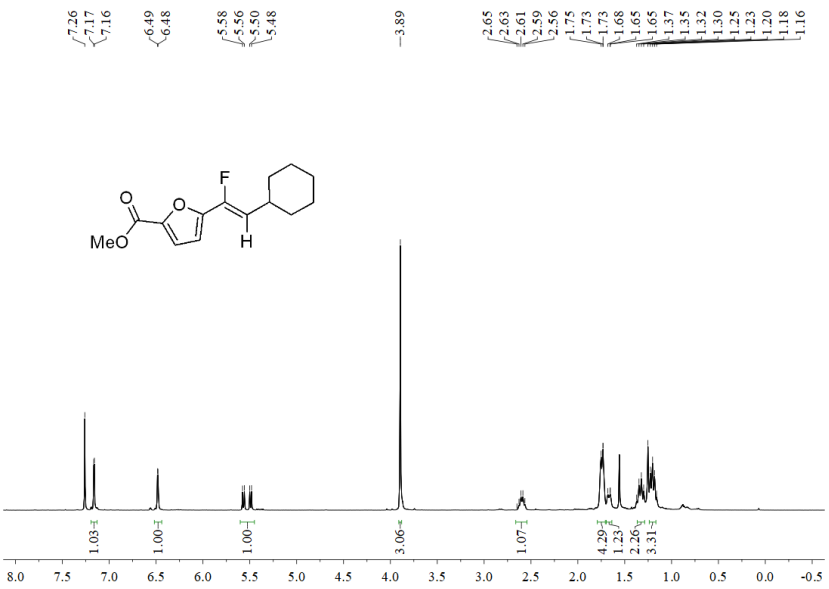
^{13}C NMR (126 MHz, $CDCl_3$) (**24**)



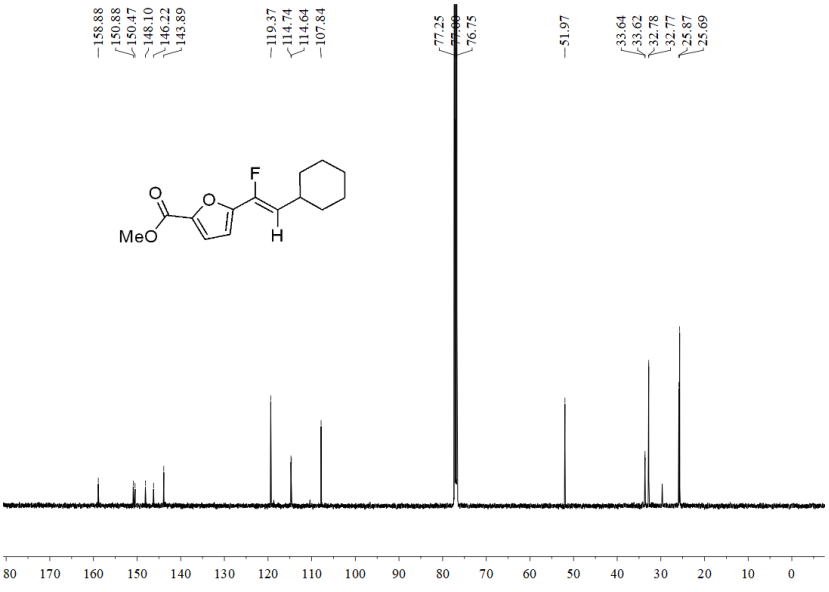
^{19}F NMR (471 MHz, $CDCl_3$) (**24**)



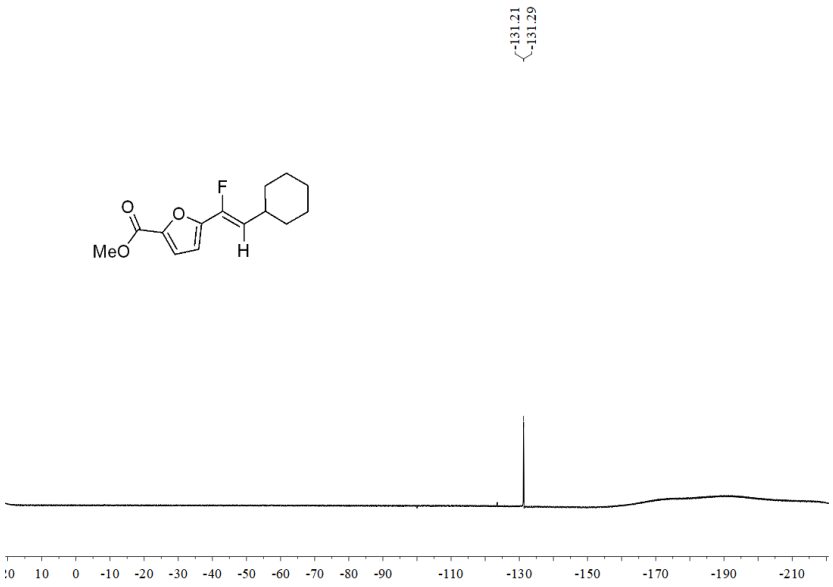
^{1}H NMR (500 MHz, $CDCl_3$) (**25**)



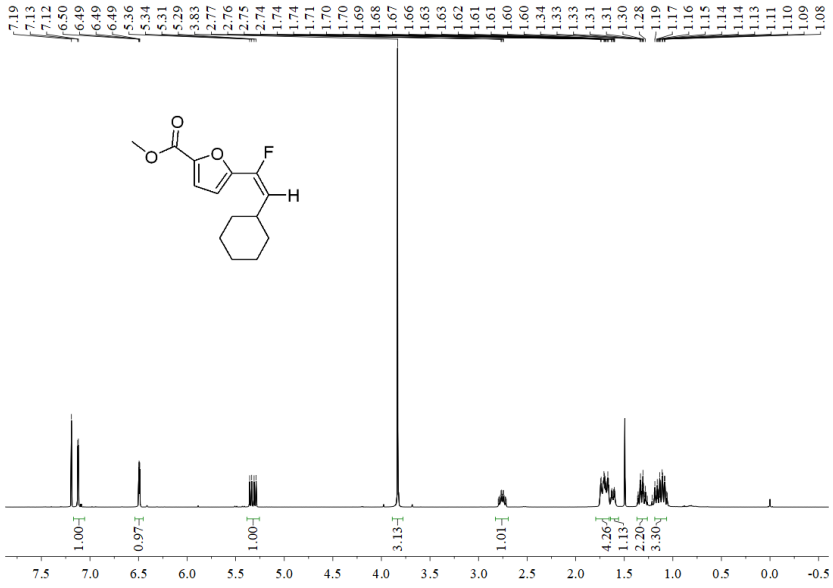
^{13}C NMR (126 MHz, $CDCl_3$) (**25**)



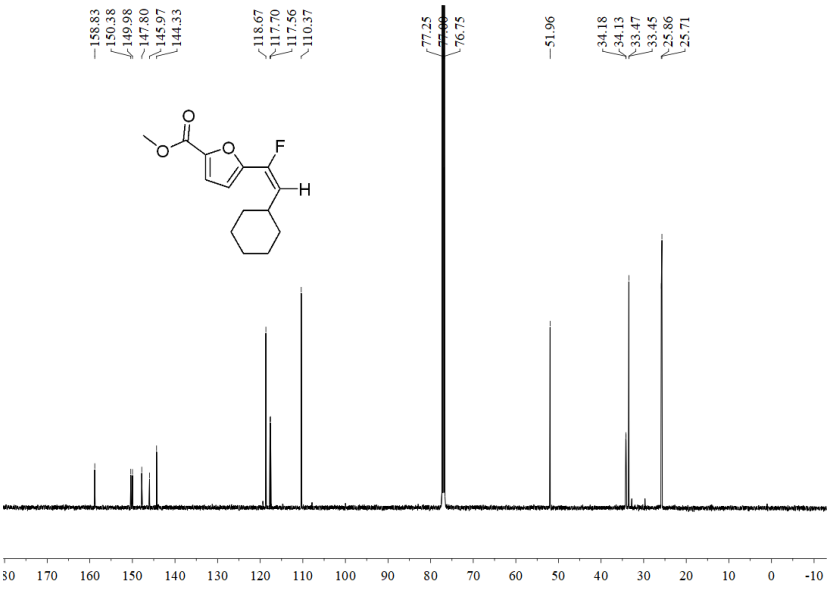
^{19}F NMR (471 MHz, $CDCl_3$) (**25**)



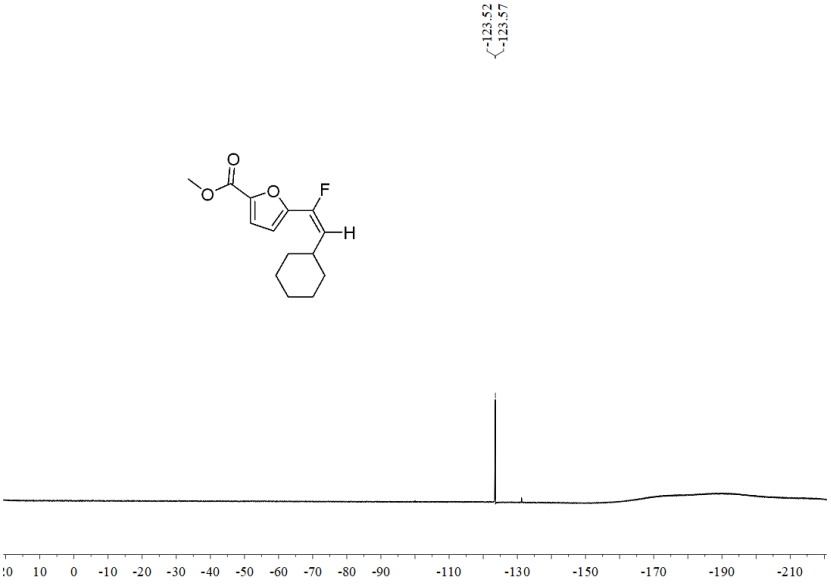
^{1}H NMR (500 MHz, $CDCl_3$) (**26**)



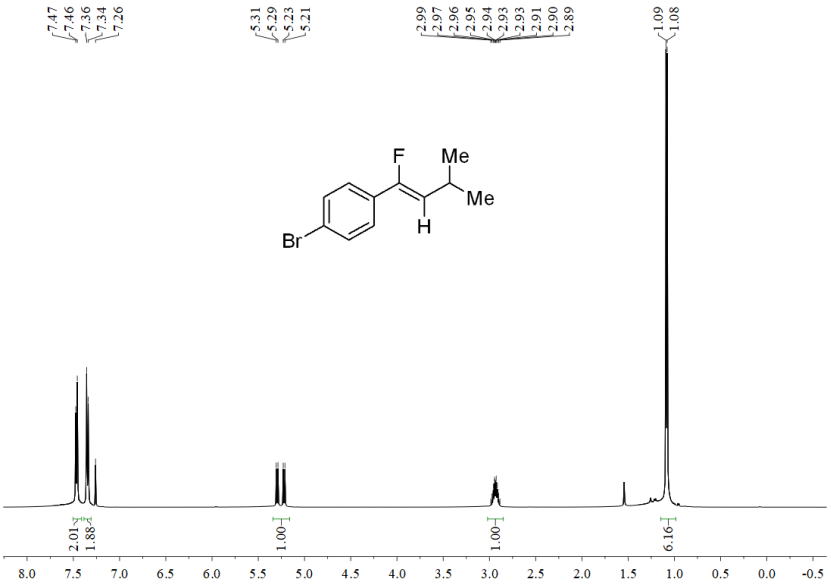
^{13}C NMR (126 MHz, $CDCl_3$) (**26**)



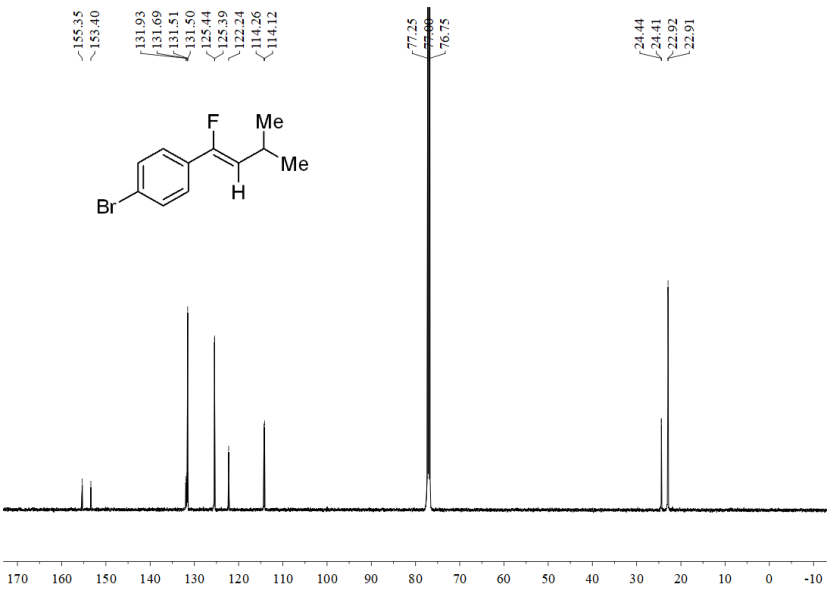
^{19}F NMR (471 MHz, $CDCl_3$) (**26**)



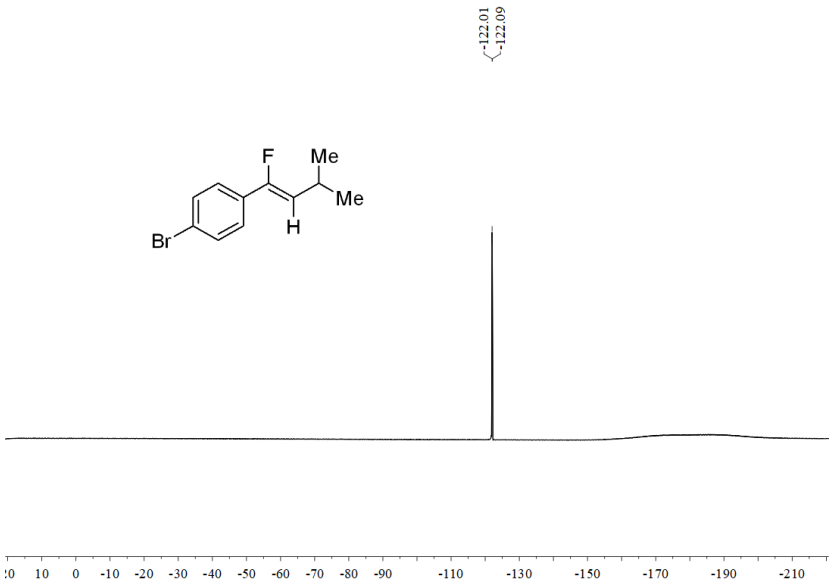
^{1}H NMR (500 MHz, $CDCl_3$) (**27**)



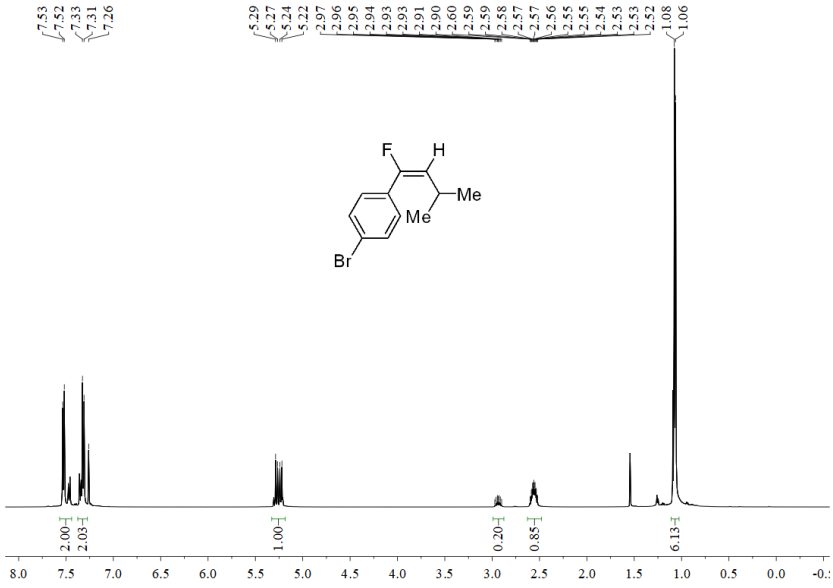
^{13}C NMR (126 MHz, $CDCl_3$) (**27**)



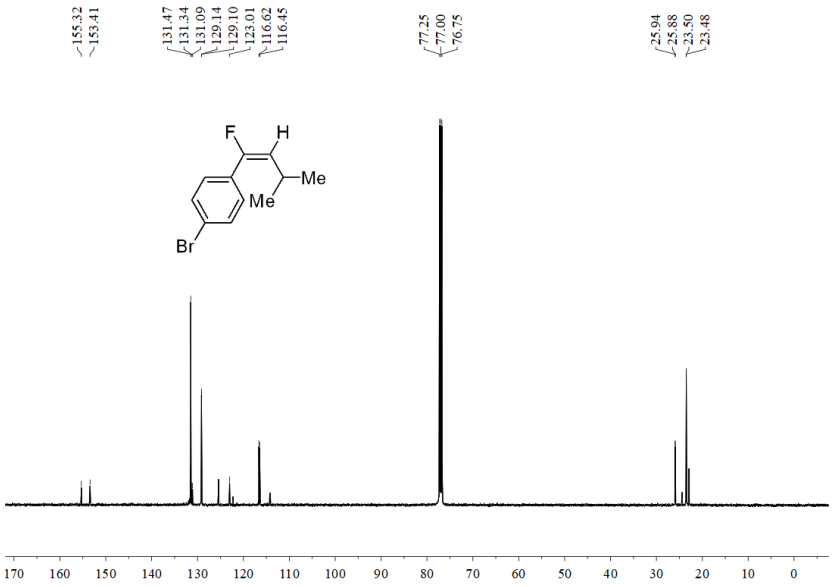
^{19}F NMR (471 MHz, $CDCl_3$) (**27**)



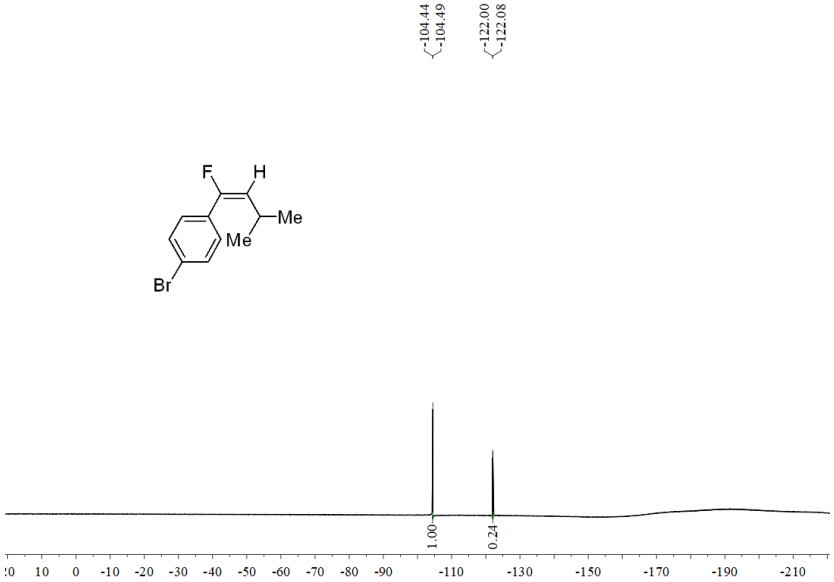
^{1}H NMR (500 MHz, $CDCl_3$) (**28**)



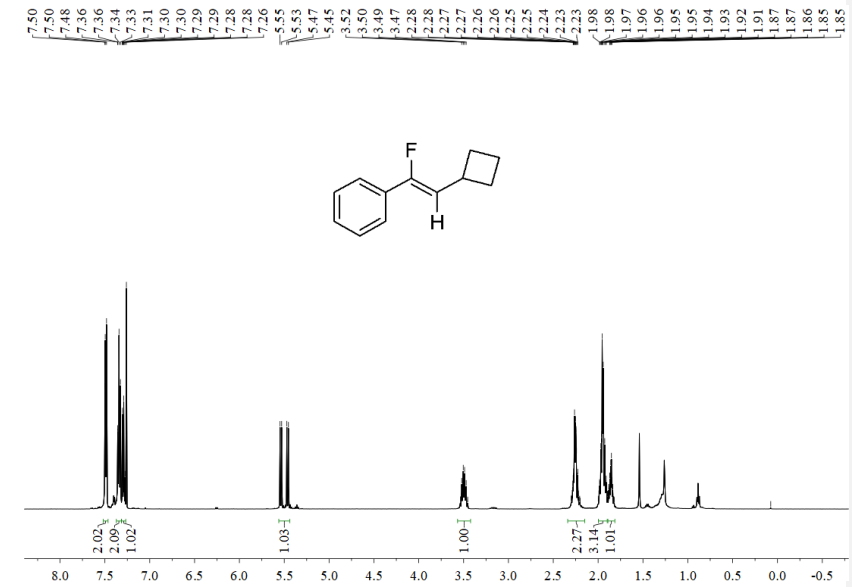
^{13}C NMR (126 MHz, $CDCl_3$) (**28**)



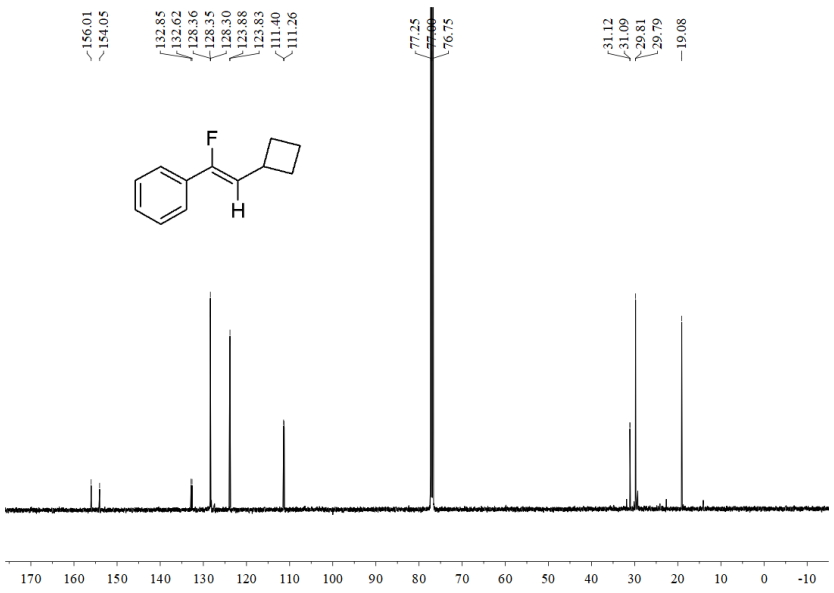
^{19}F NMR (471 MHz, $CDCl_3$) (**28**)



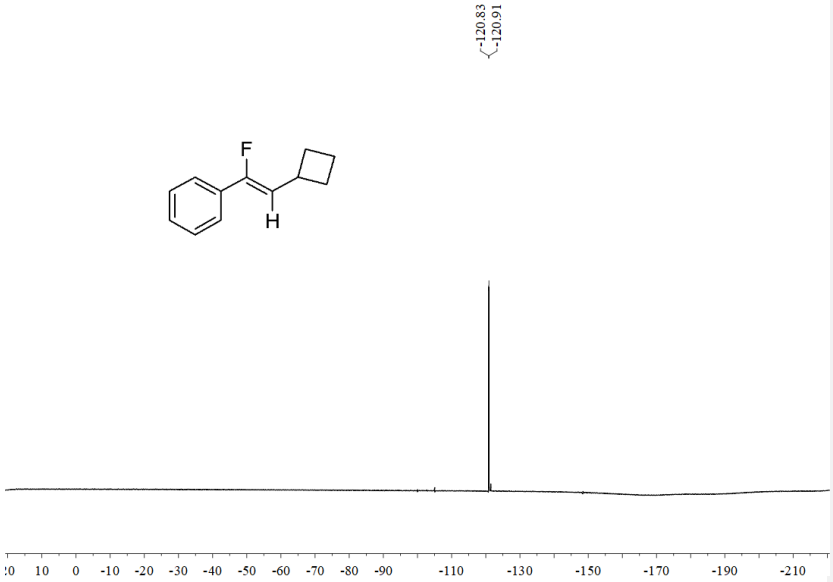
^{1}H NMR (500 MHz, $CDCl_3$) (**29**)



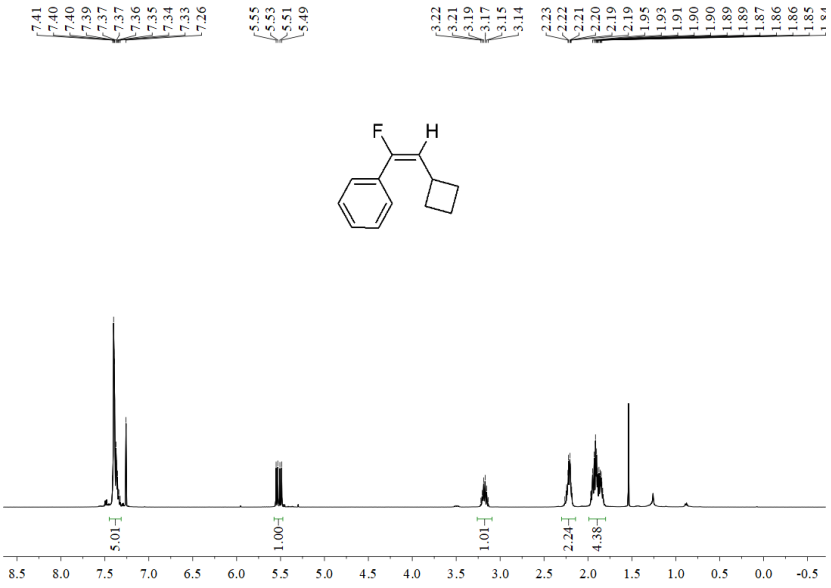
^{13}C NMR (126 MHz, $CDCl_3$) (**29**)



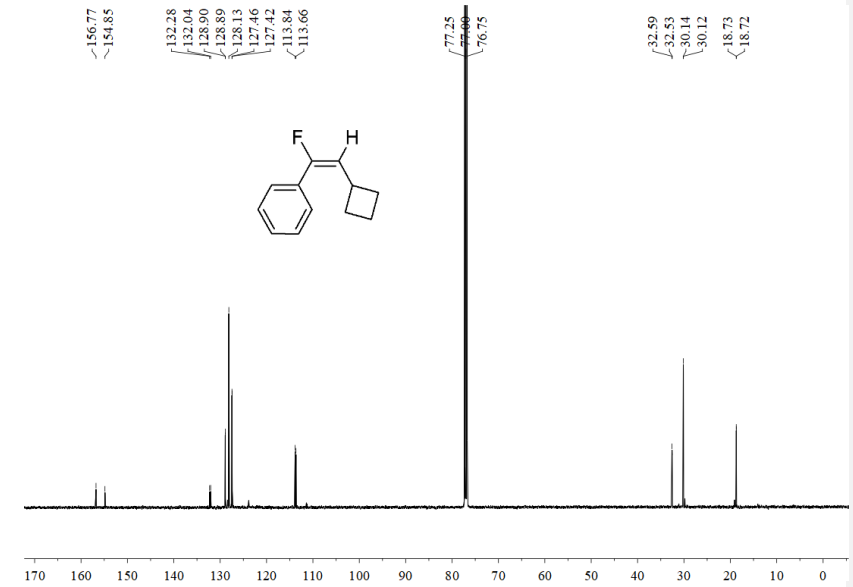
^{19}F NMR (471 MHz, $CDCl_3$) (**29**)



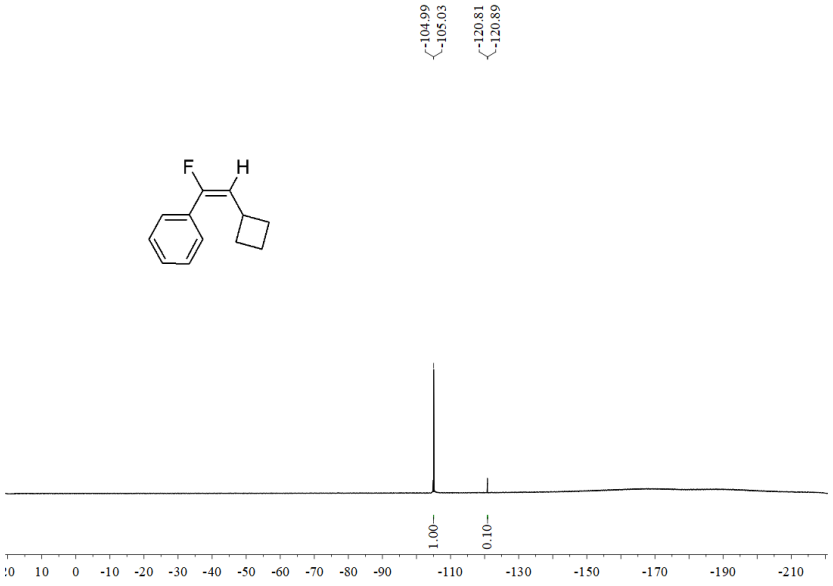
^{1}H NMR (500 MHz, $CDCl_3$) (**30**)



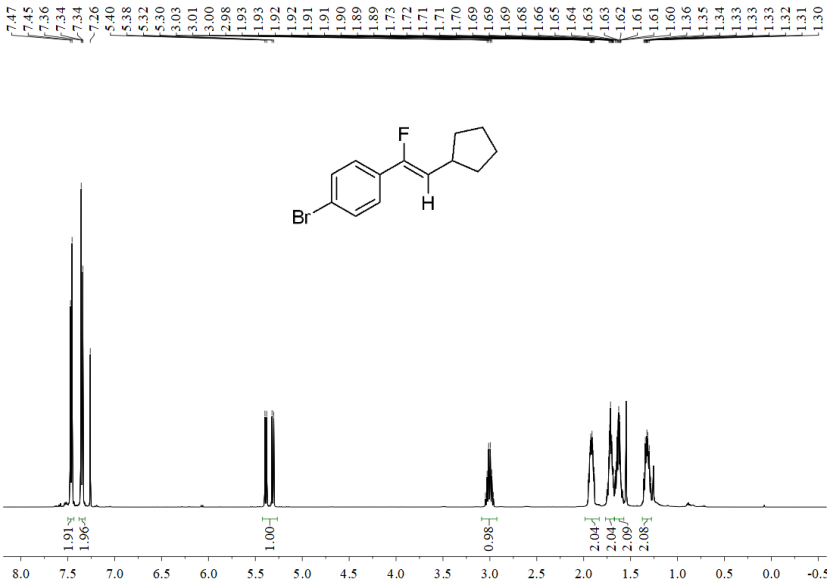
^{13}C NMR (126 MHz, $CDCl_3$) (**30**)



^{19}F NMR (471 MHz, $CDCl_3$) (**30**)

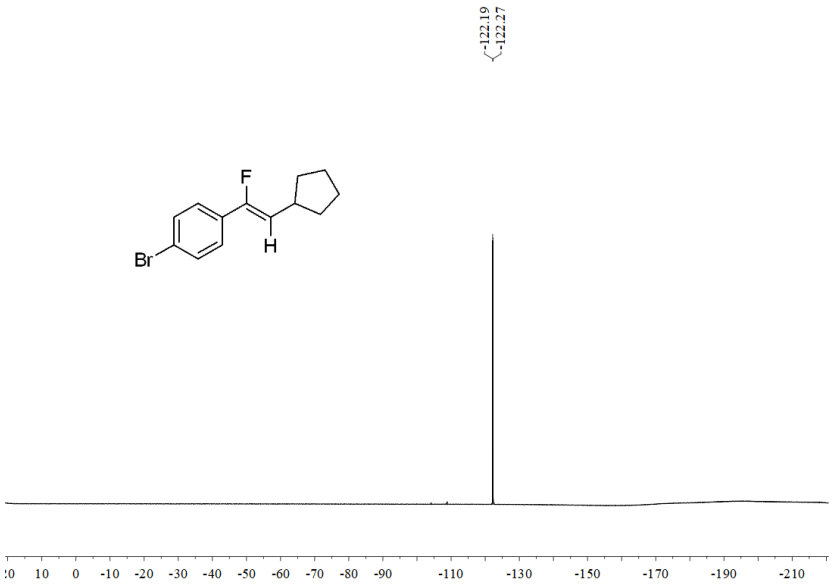


^{1}H NMR (500 MHz, $CDCl_3$) (**31**)

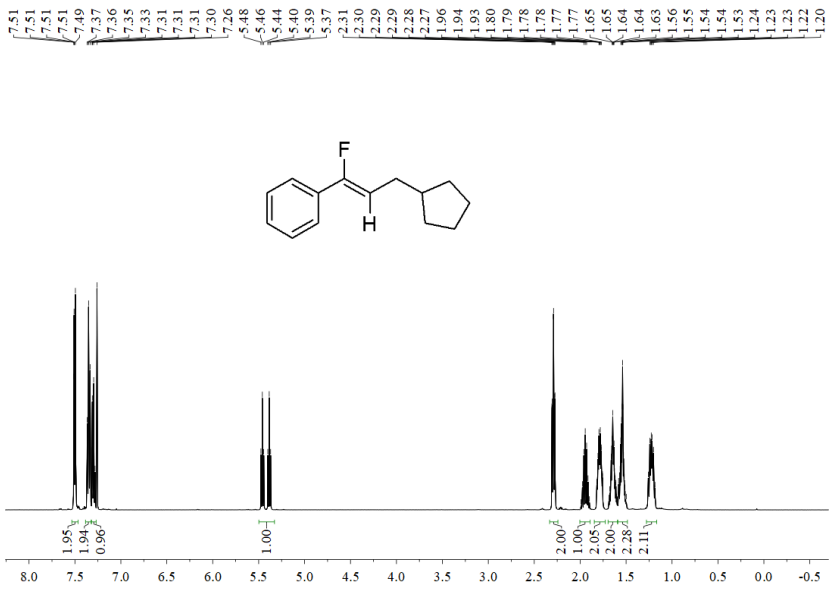


^{13}C NMR (126 MHz, $CDCl_3$) (**31**)

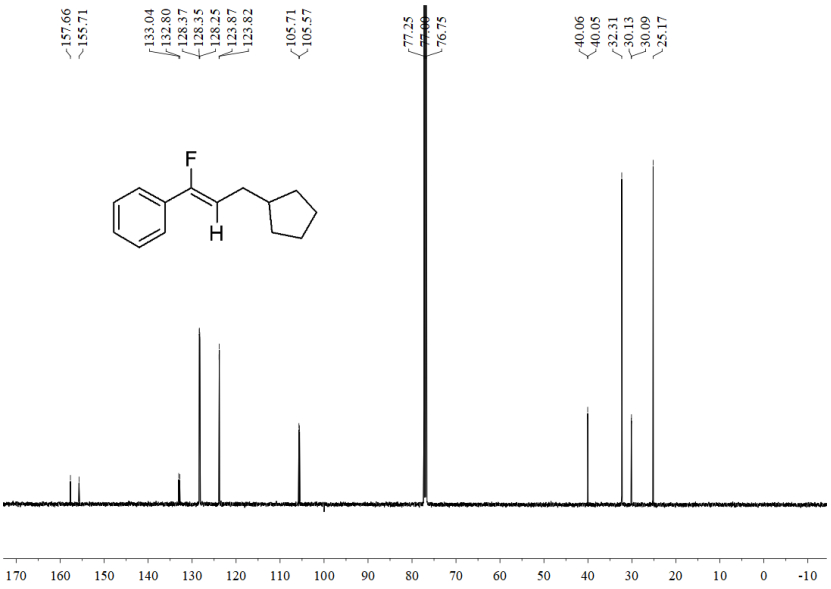
^{19}F NMR (471 MHz, $CDCl_3$) (**31**)



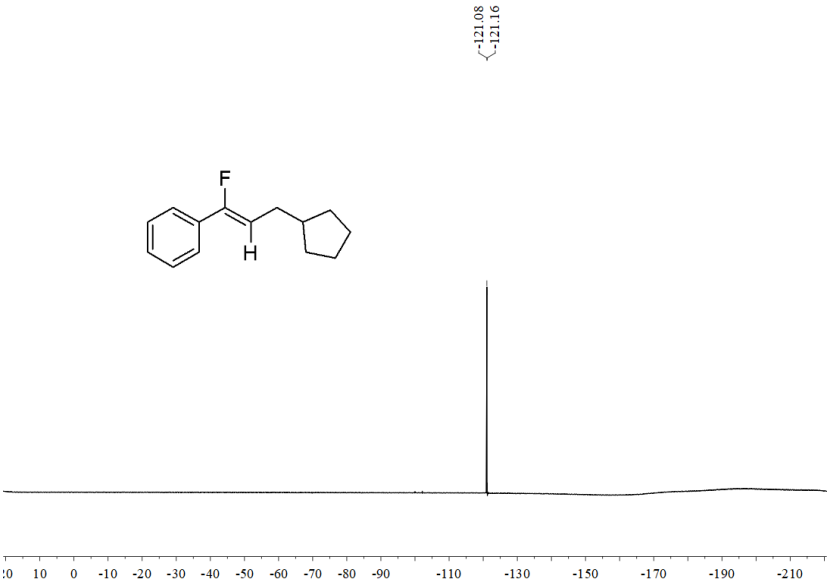
^{1}H NMR (500 MHz, $CDCl_3$) (**32**)



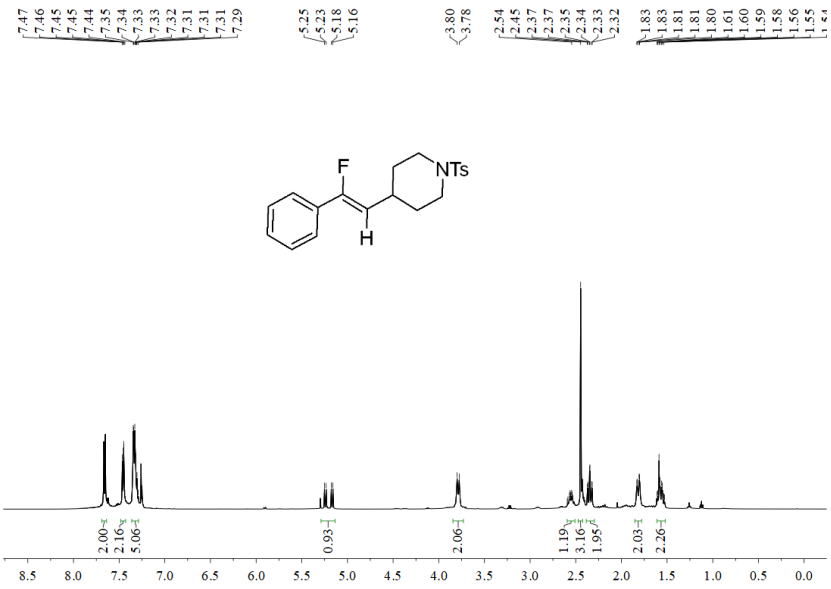
^{13}C NMR (126 MHz, $CDCl_3$) (**32**)



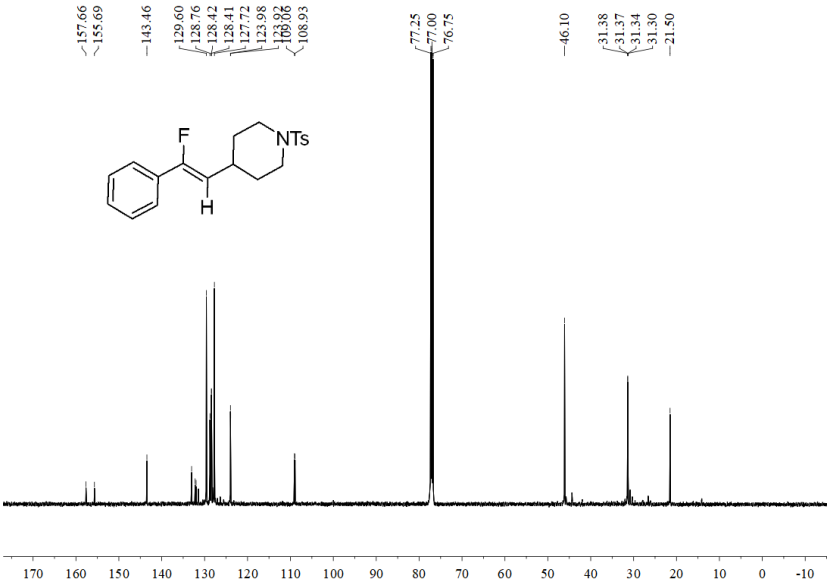
^{19}F NMR (471 MHz, $CDCl_3$) (**32**)



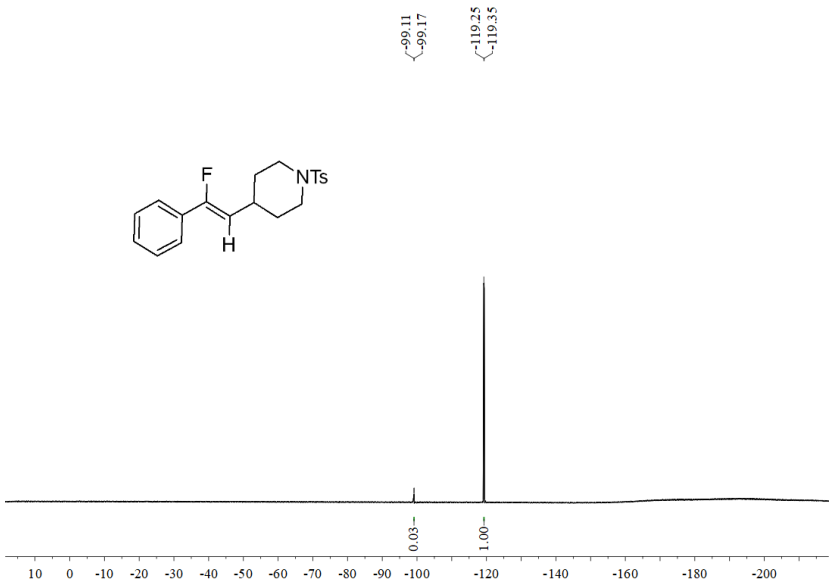
^{1}H NMR (500 MHz, $CDCl_3$) (**33**)



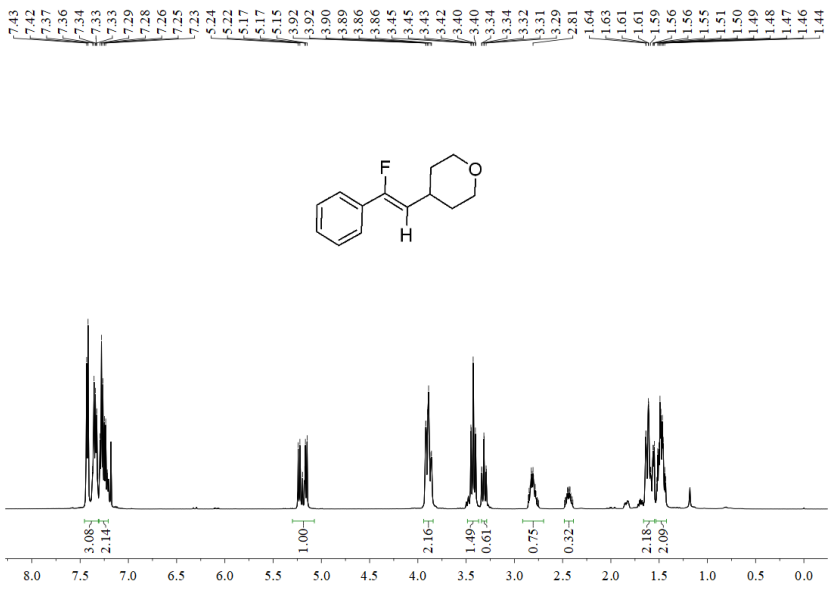
^{13}C NMR (126 MHz, $CDCl_3$) (**33**)



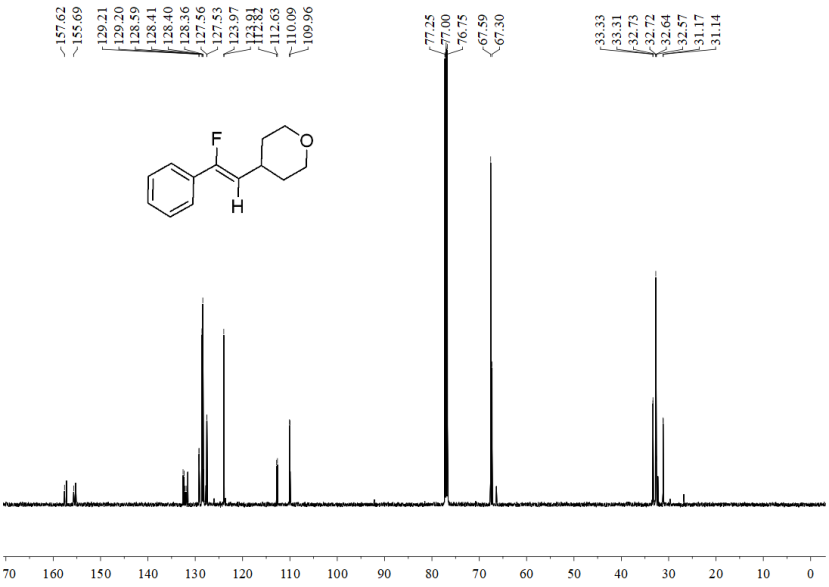
^{19}F NMR (376 MHz, $CDCl_3$) (**33**)



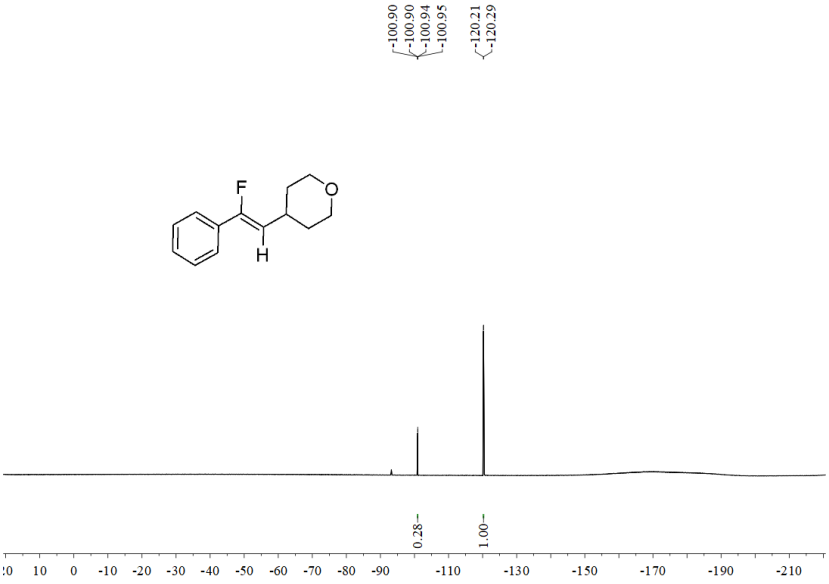
^{1}H NMR (500 MHz, $CDCl_3$) (**34**)



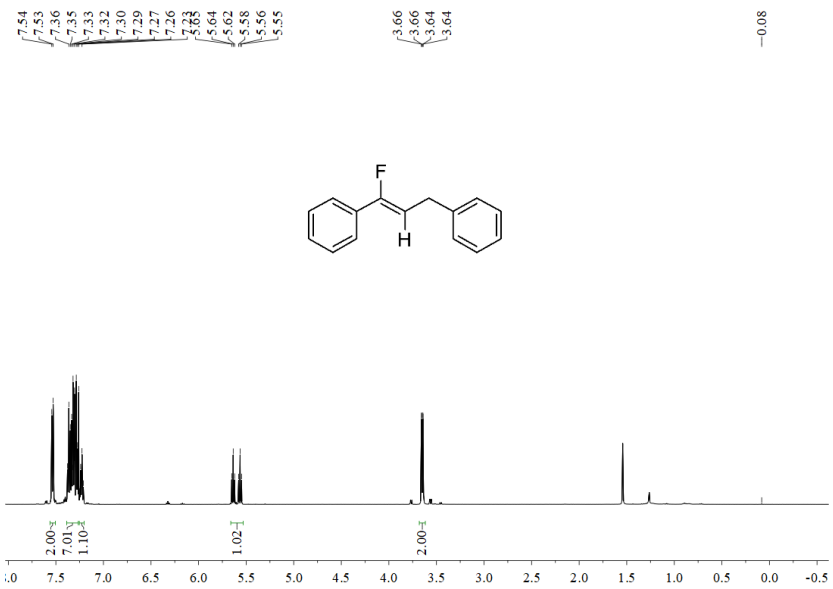
^{13}C NMR (126 MHz, $CDCl_3$) (**34**)



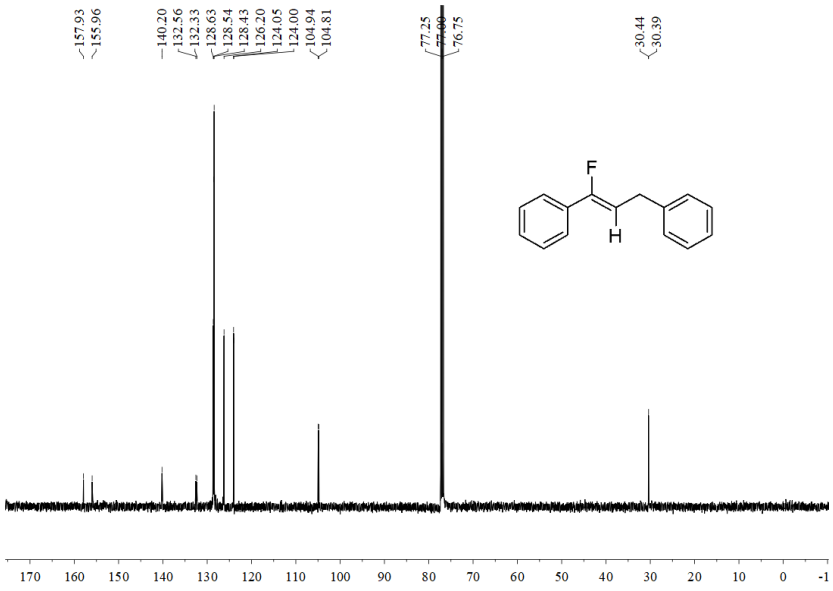
^{19}F NMR (471 MHz, $CDCl_3$) (**34**)



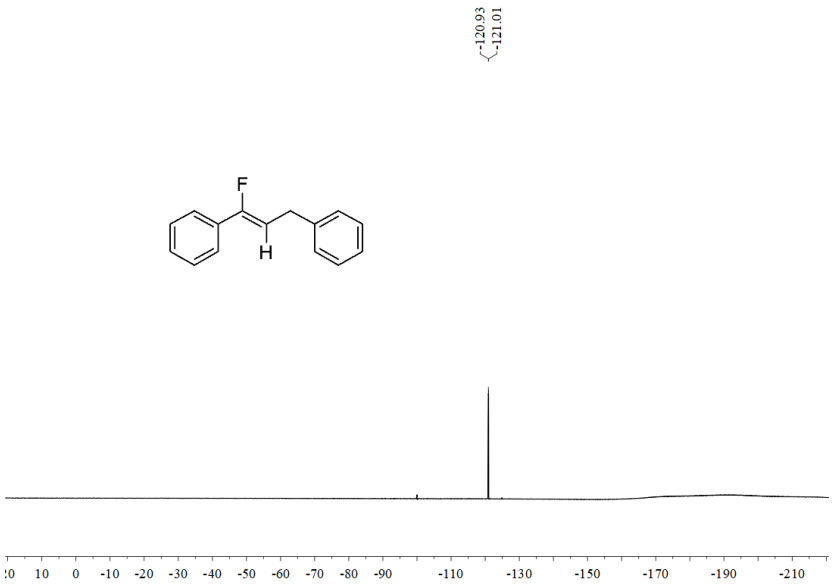
^{1}H NMR (500 MHz, $CDCl_3$) (**35**)



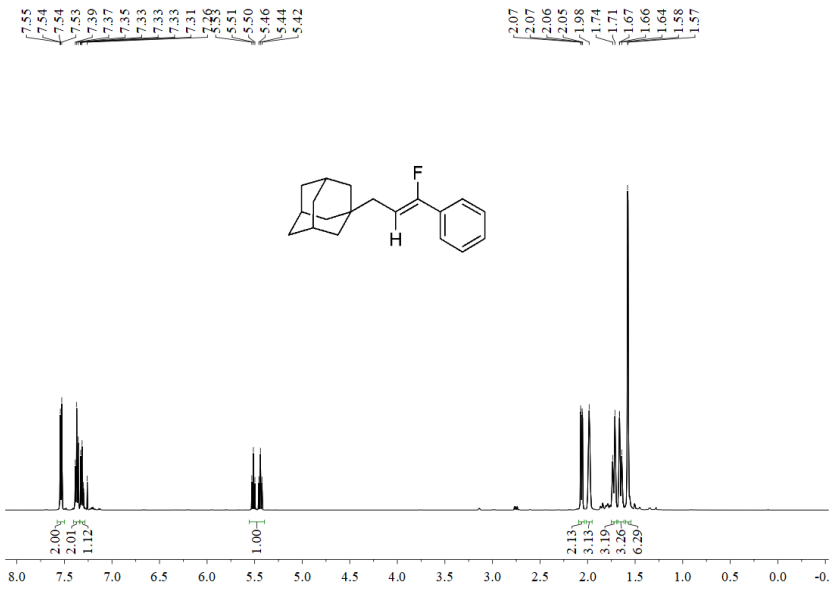
^{13}C NMR (126 MHz, $CDCl_3$) (**35**)



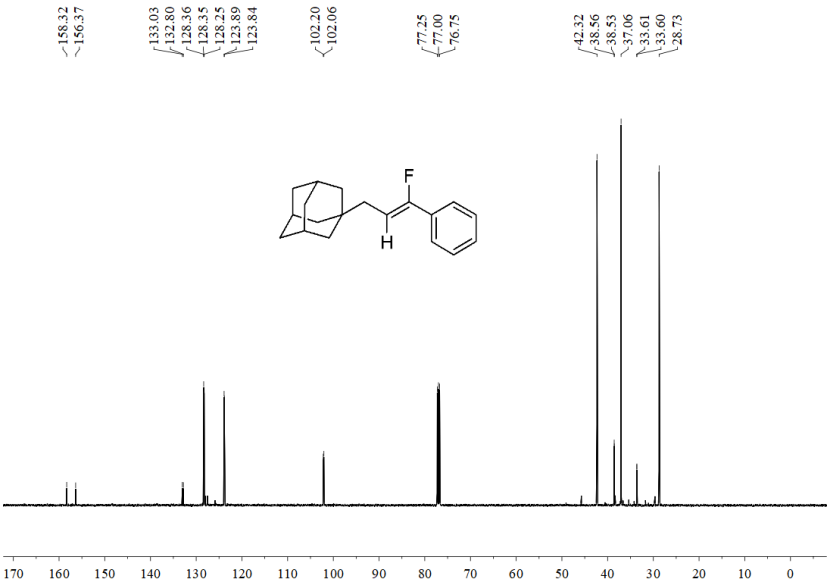
^{19}F NMR (471 MHz, $CDCl_3$) (**35**)



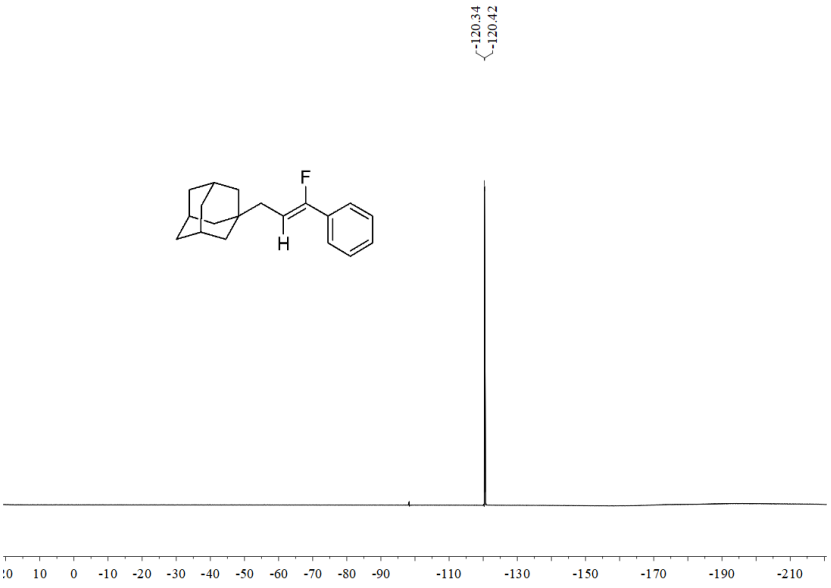
^{1}H NMR (500 MHz, $CDCl_3$) (**36**)



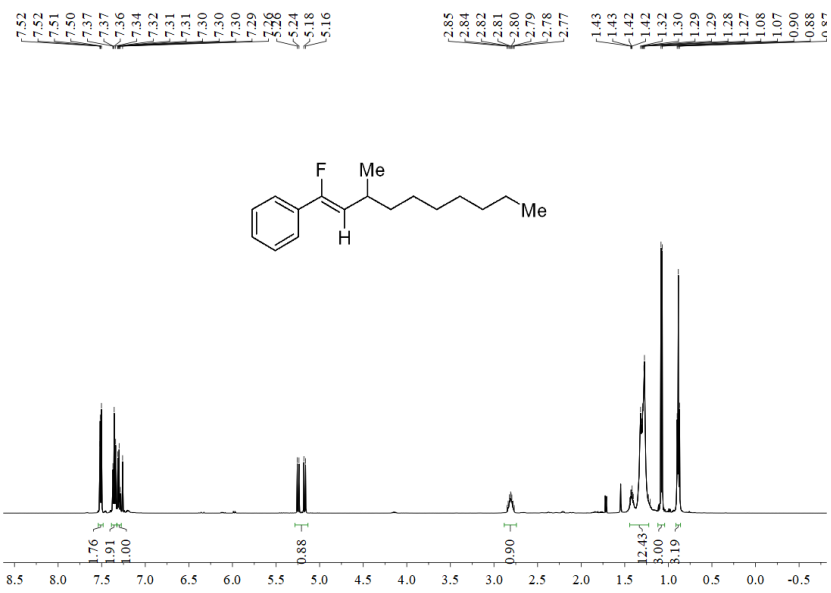
^{13}C NMR (126 MHz, $CDCl_3$) (**36**)



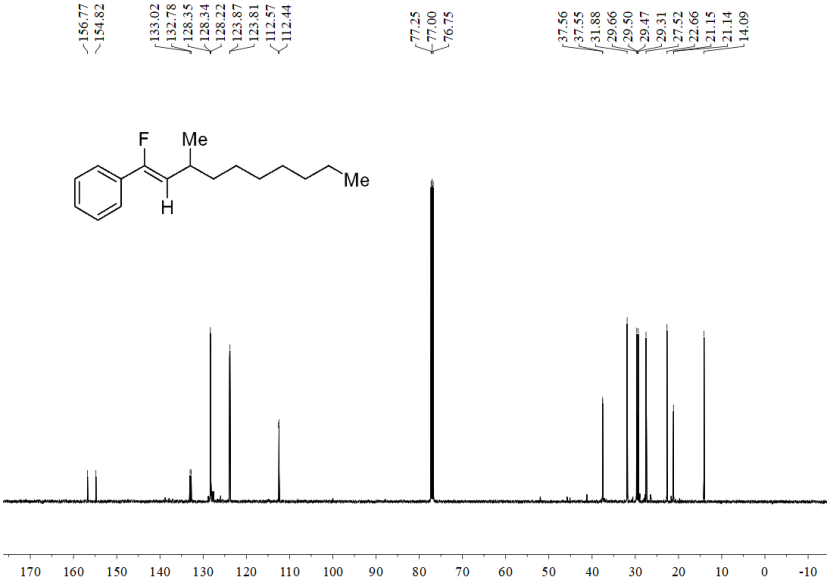
^{19}F NMR (471 MHz, $CDCl_3$) (**36**)



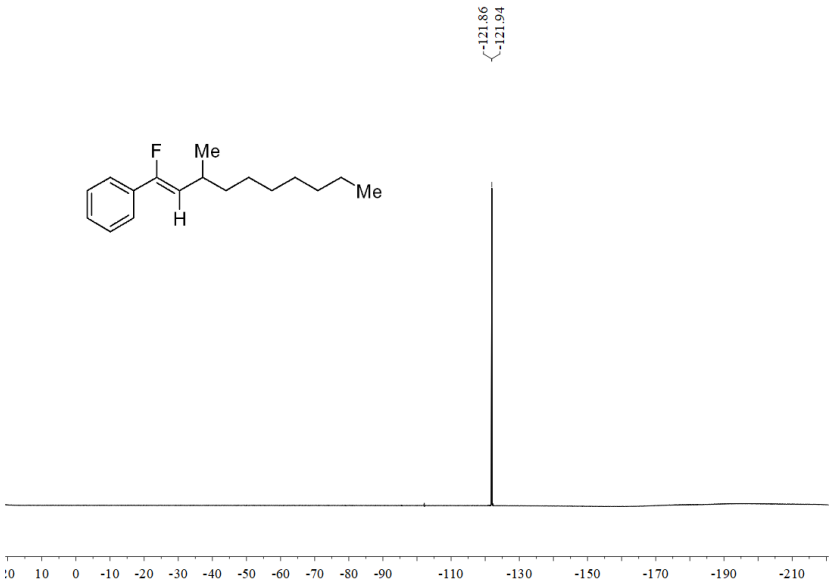
^{1}H NMR (500 MHz, $CDCl_3$) (**37**)



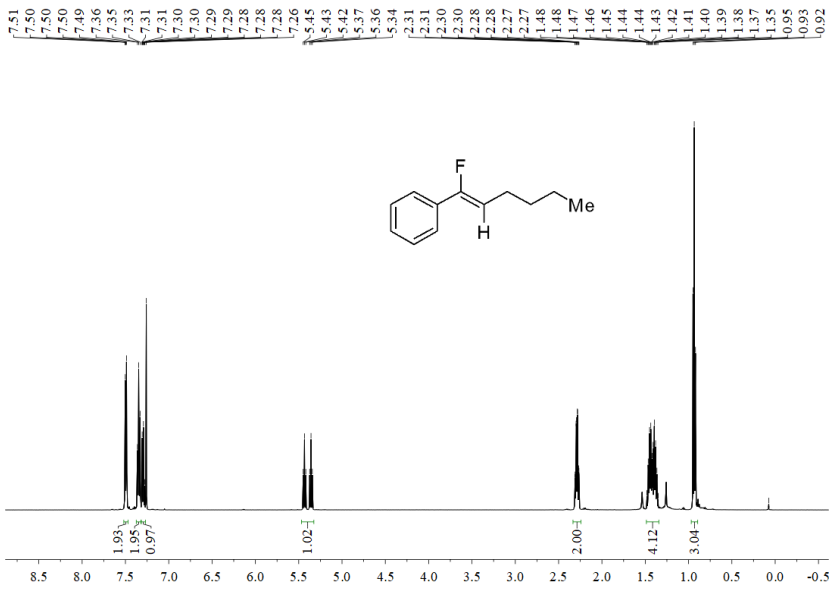
^{13}C NMR (126 MHz, $CDCl_3$) (**37**)



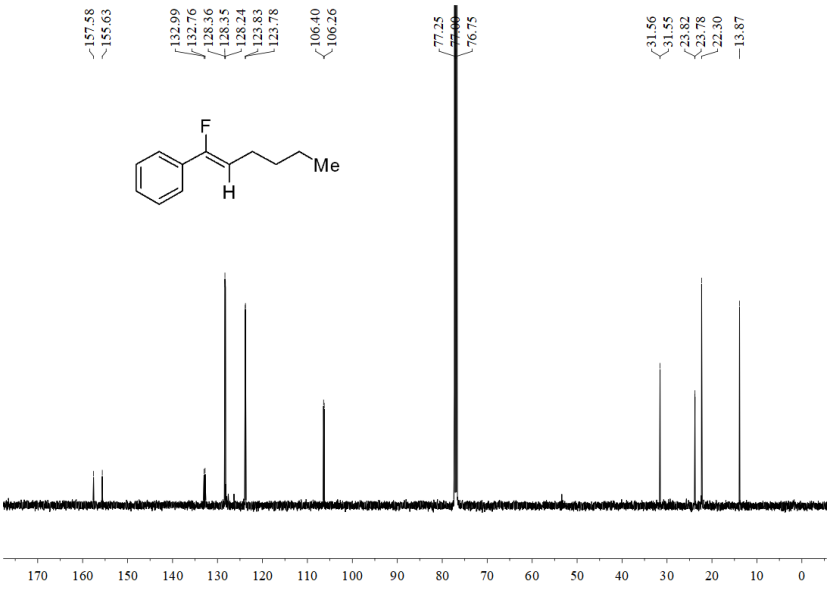
^{19}F NMR (471 MHz, $CDCl_3$) (**37**)



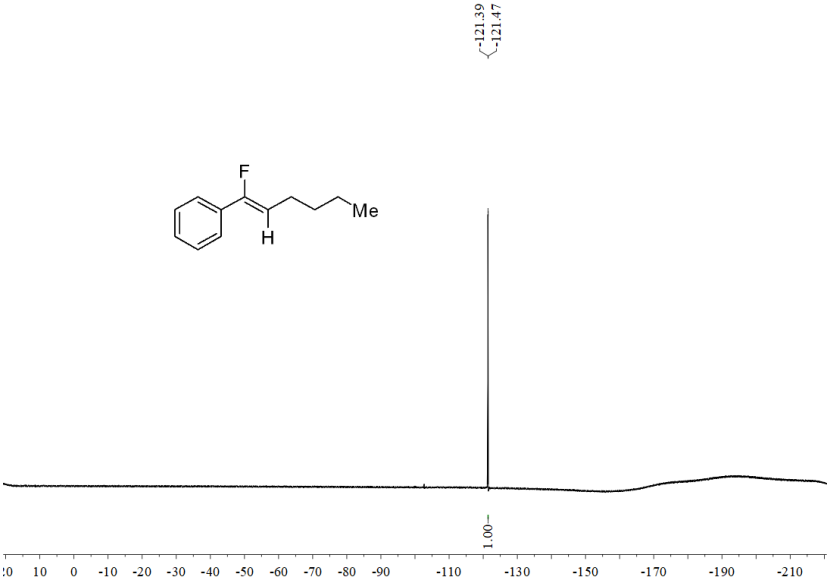
^{1}H NMR (500 MHz, $CDCl_3$) (**38**)



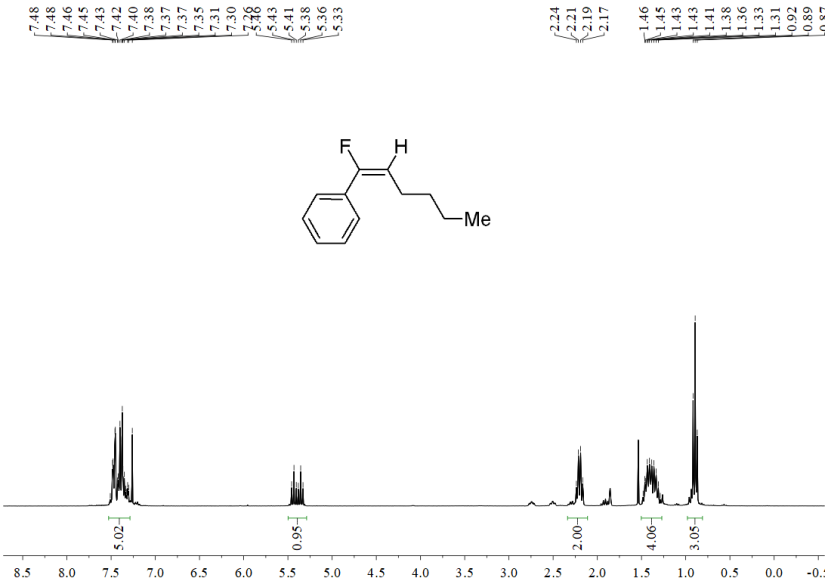
^{13}C NMR (126 MHz, $CDCl_3$) (**38**)



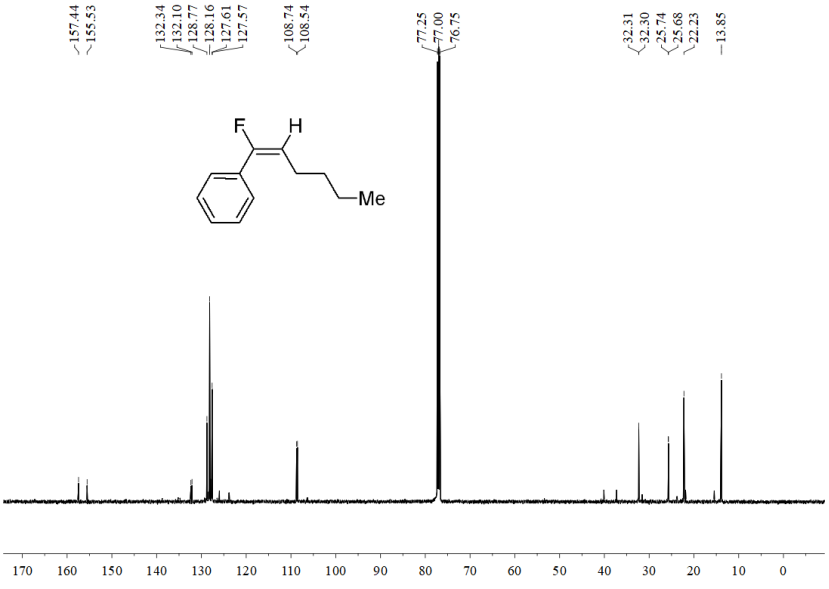
^{19}F NMR (471 MHz, $CDCl_3$) (**38**)



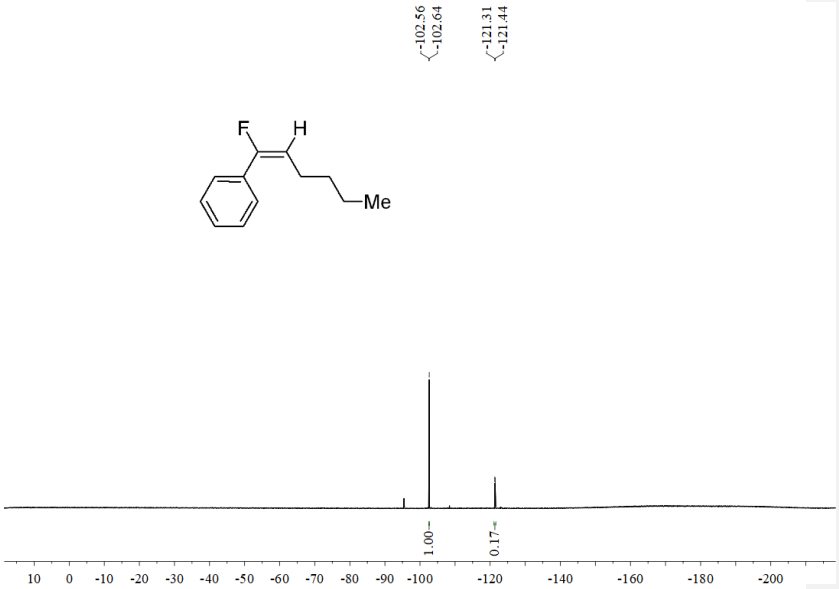
^{1}H NMR (300 MHz, $CDCl_3$) (**39**)



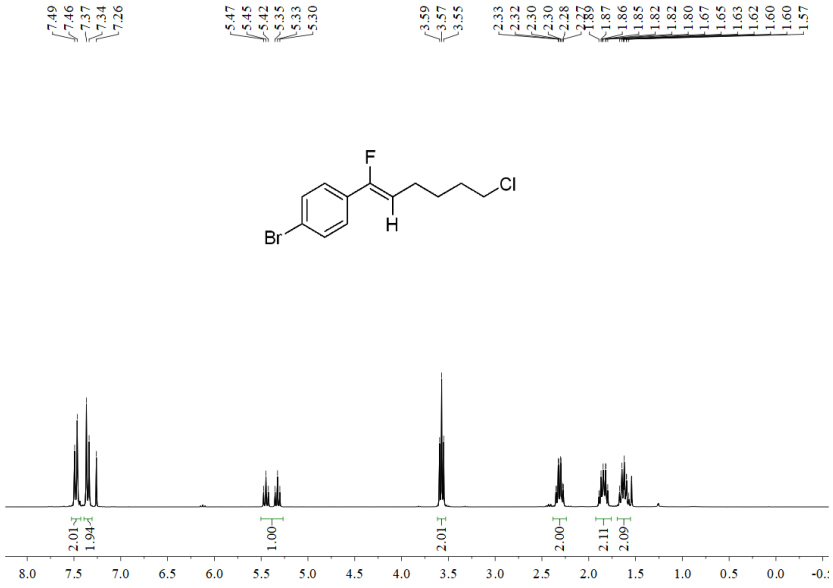
^{13}C NMR (126 MHz, $CDCl_3$) (**39**)



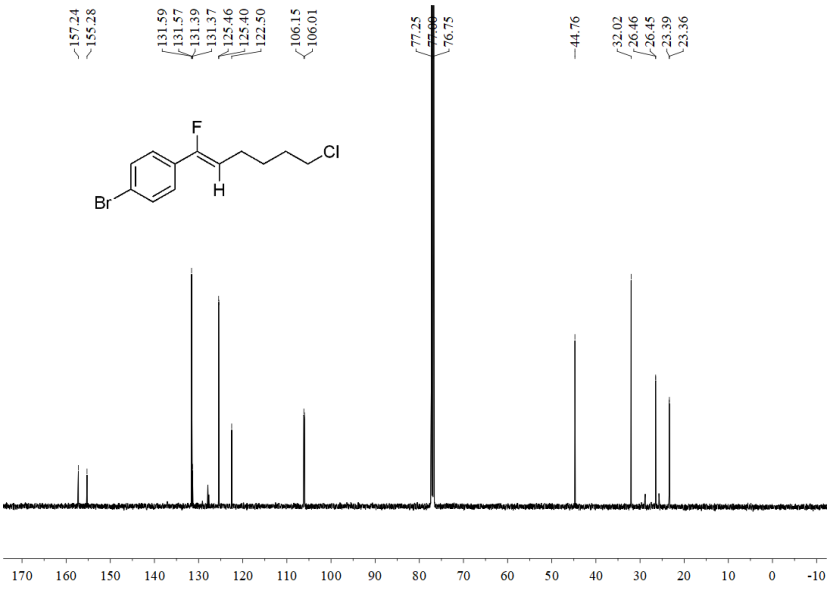
^{19}F NMR (282 MHz, $CDCl_3$) (**39**)



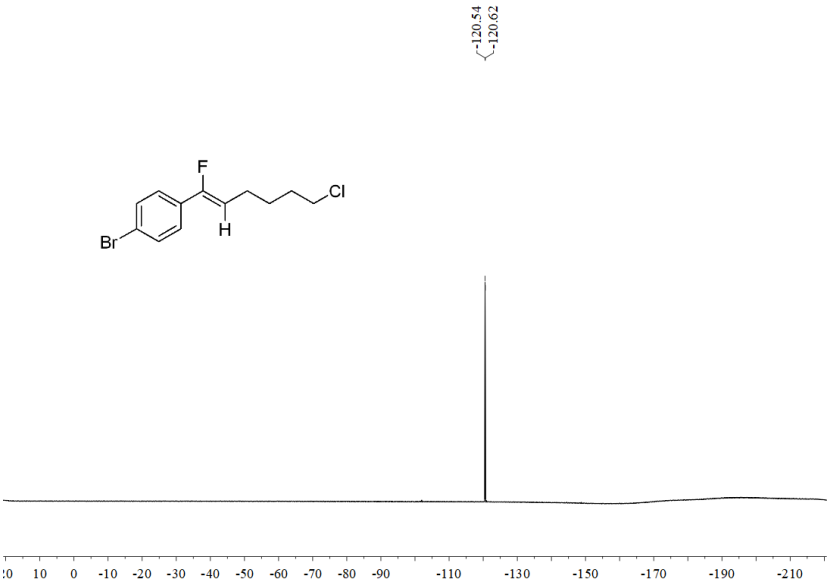
^{1}H NMR (500 MHz, $CDCl_3$) (**40**)



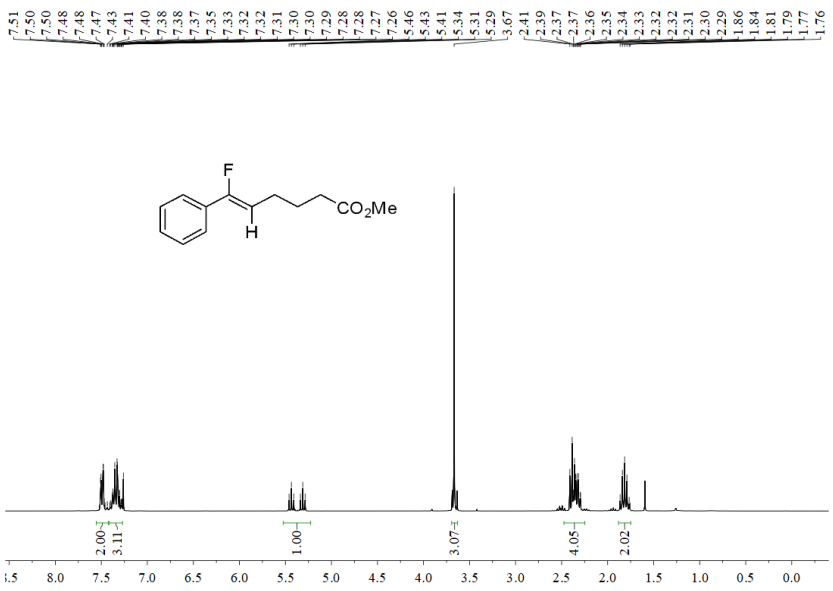
^{13}C NMR (126 MHz, $CDCl_3$) (**40**)



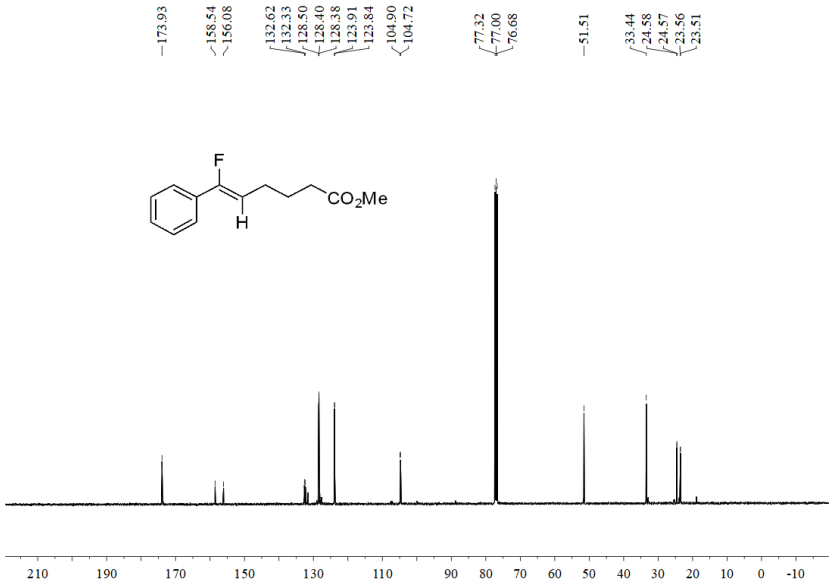
^{19}F NMR (471 MHz, $CDCl_3$) (**40**)



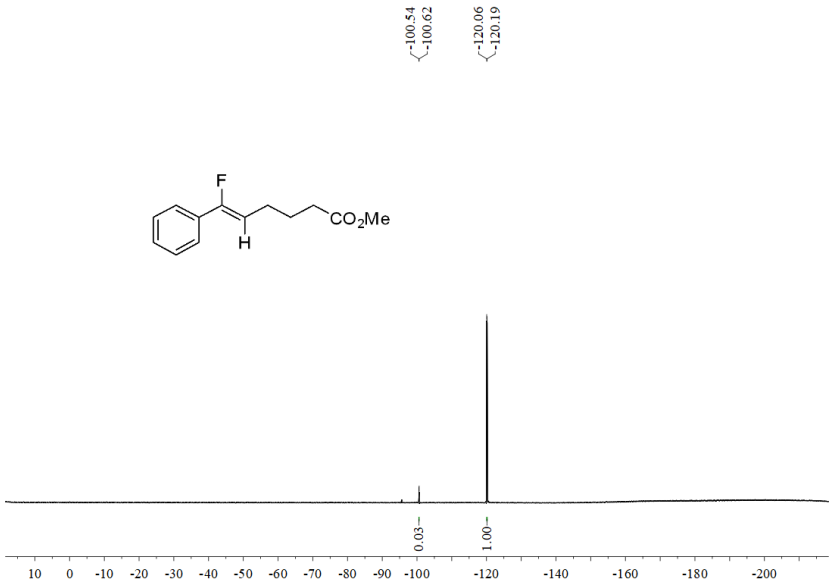
^{1}H NMR (300 MHz, $CDCl_3$) (**41**)



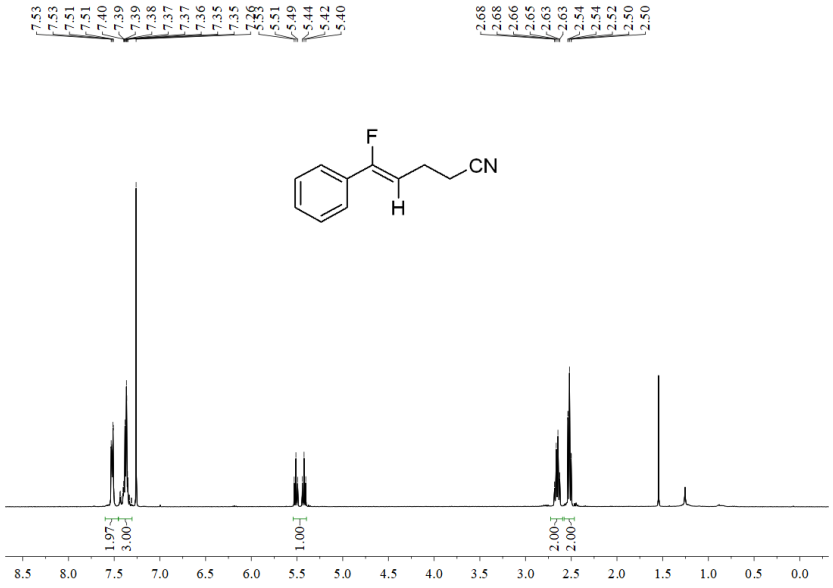
^{13}C NMR (101 MHz, $CDCl_3$) (**41**)



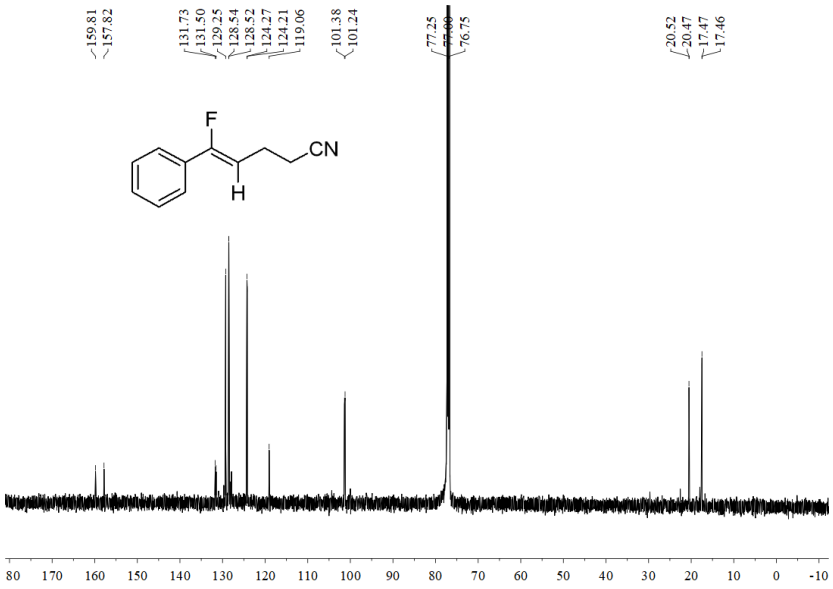
^{19}F NMR (282 MHz, $CDCl_3$) (**41**)



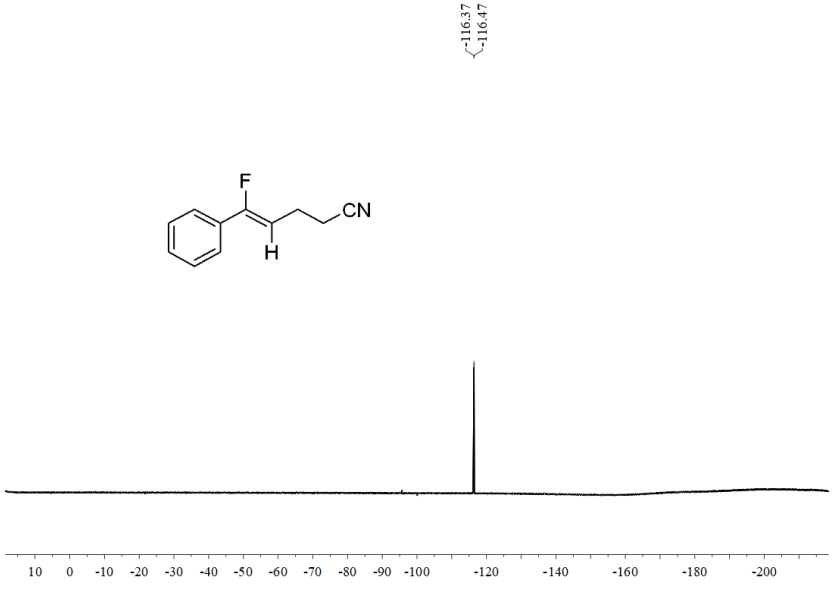
^{1}H NMR (400 MHz, $CDCl_3$) (**42**)



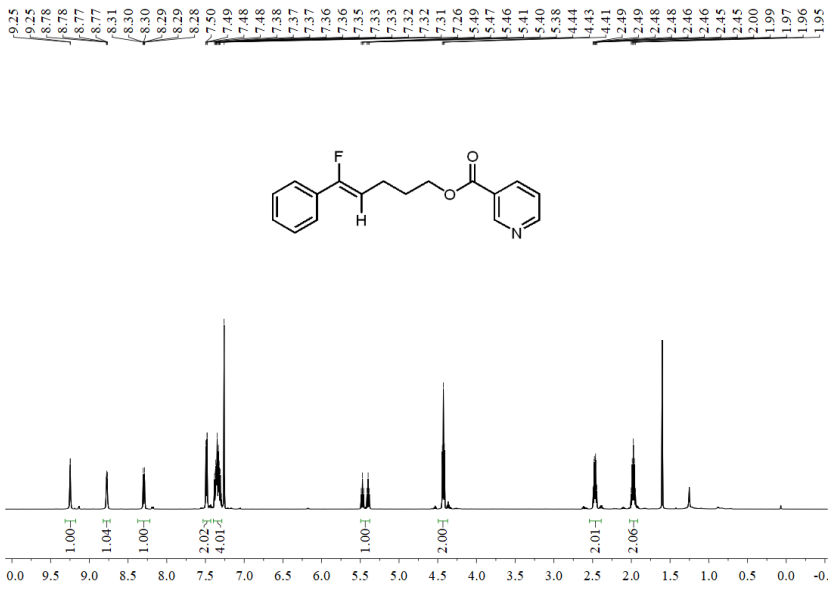
^{13}C NMR (126 MHz, $CDCl_3$) (**42**)



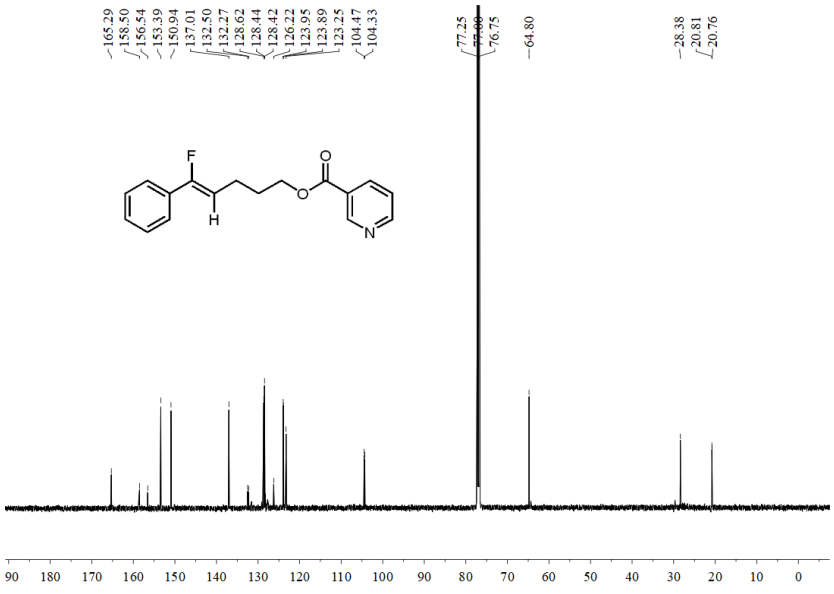
^{19}F NMR (376 MHz, $CDCl_3$) (**42**)



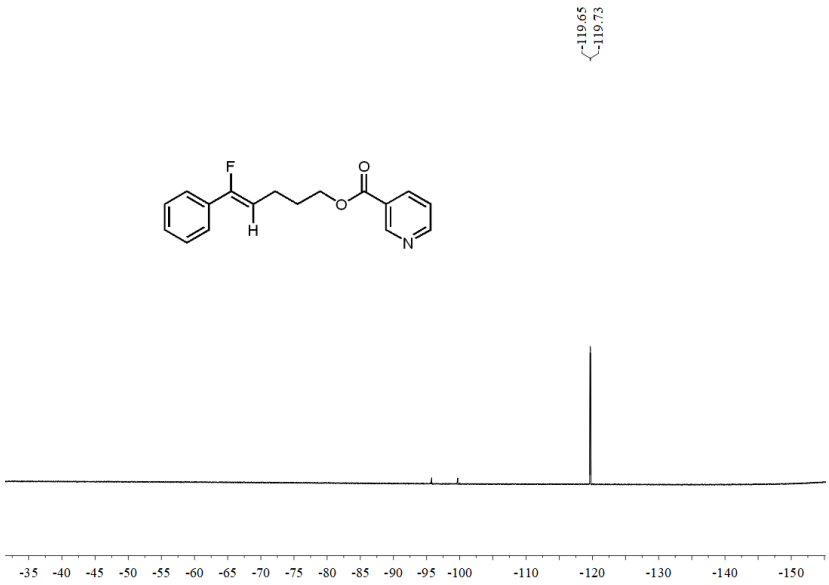
^{1}H NMR (500 MHz, $CDCl_3$) (**43**)



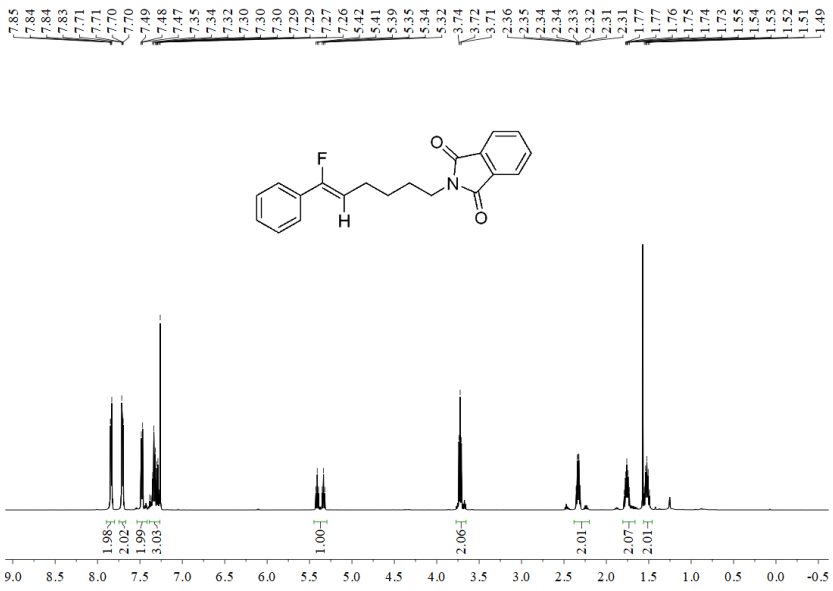
^{13}C NMR (126 MHz, $CDCl_3$) (**43**)



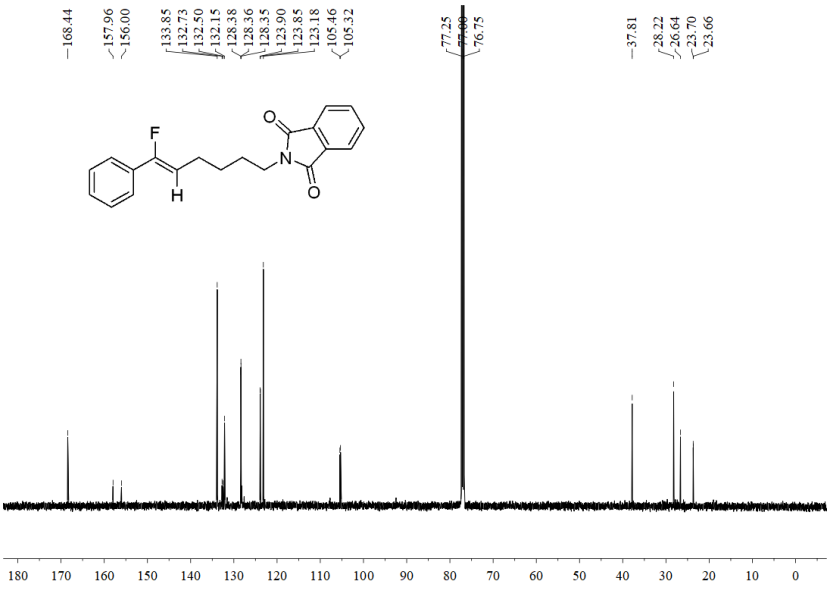
^{19}F NMR (471 MHz, $CDCl_3$) (**43**)



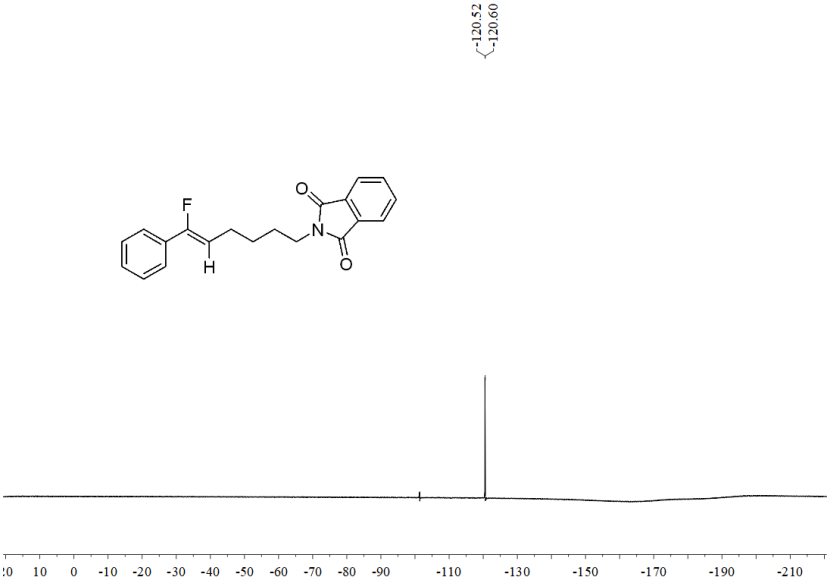
^{1}H NMR (500 MHz, $CDCl_3$) (**44**)



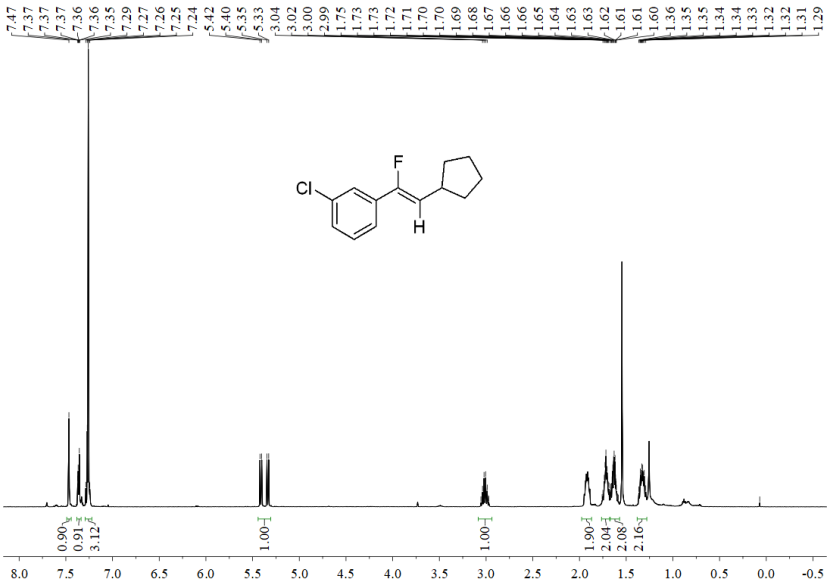
^{13}C NMR (126 MHz, $CDCl_3$) (**44**)



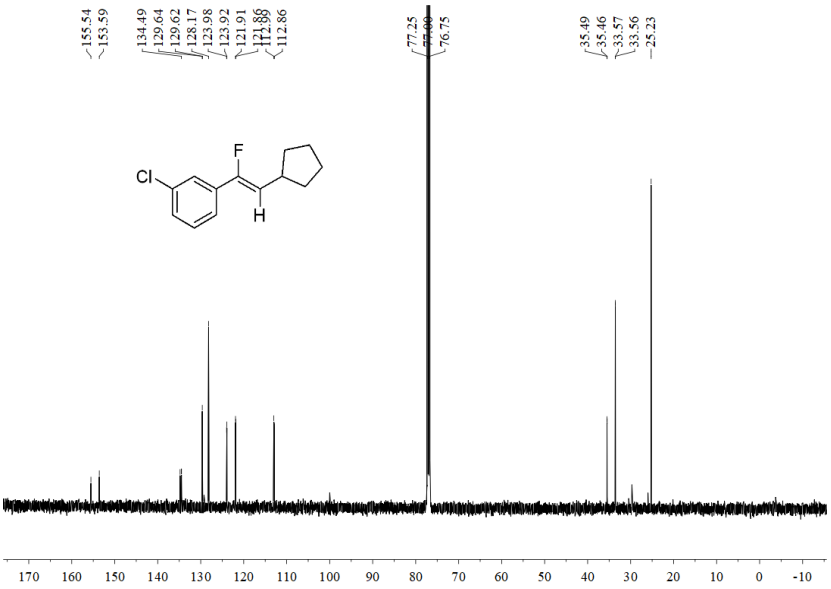
^{19}F NMR (471 MHz, $CDCl_3$) (**44**)



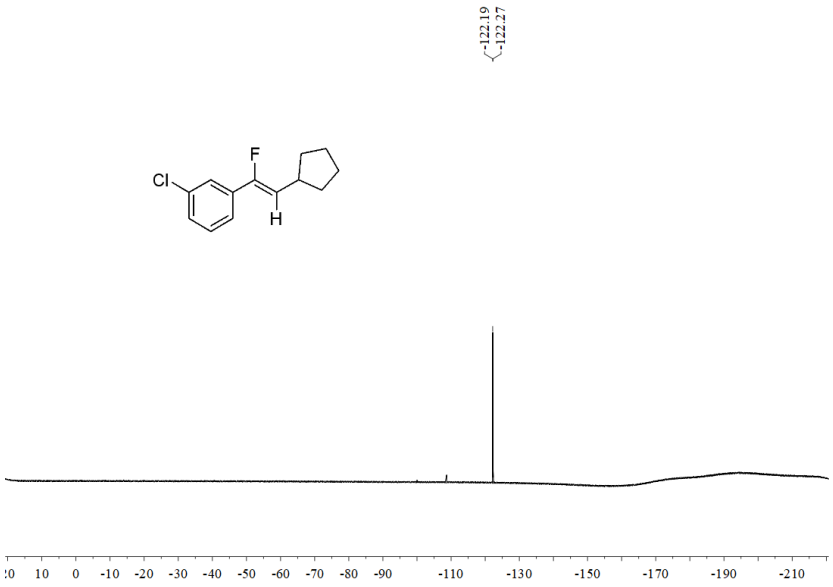
^{1}H NMR (500 MHz, $CDCl_3$) (**45**)



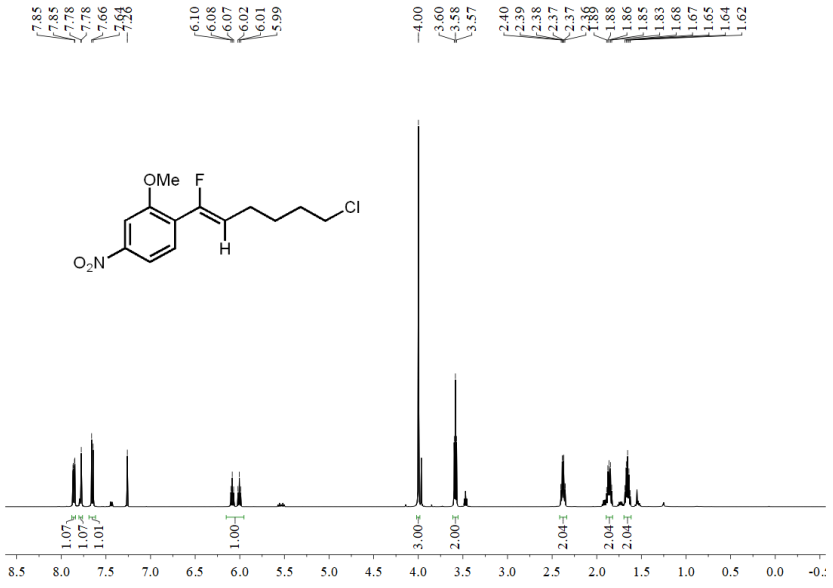
^{13}C NMR (126 MHz, $CDCl_3$) (**45**)



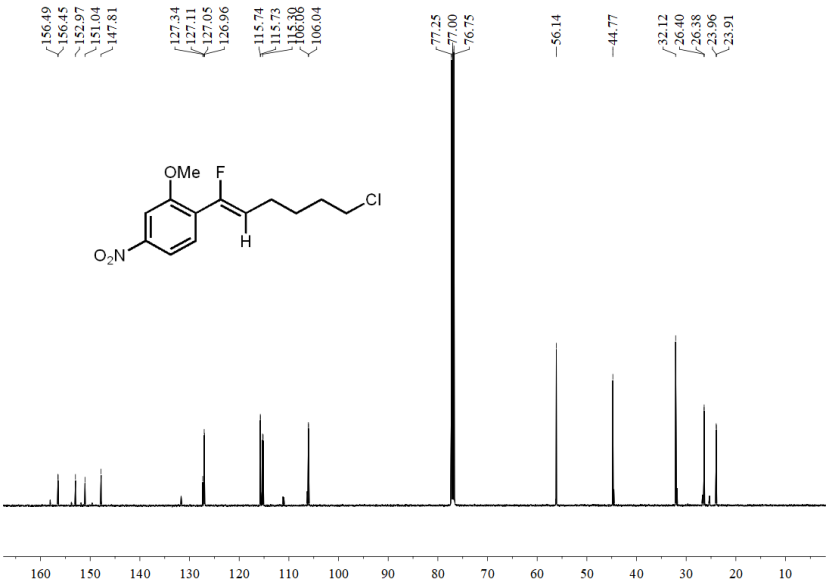
^{19}F NMR (471 MHz, $CDCl_3$) (**45**)



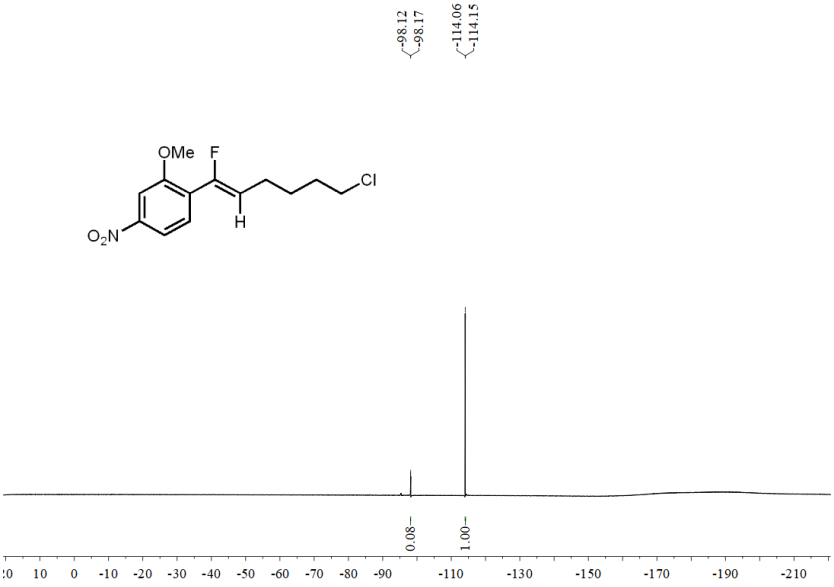
^{1}H NMR (500 MHz, $CDCl_3$) (**46**)



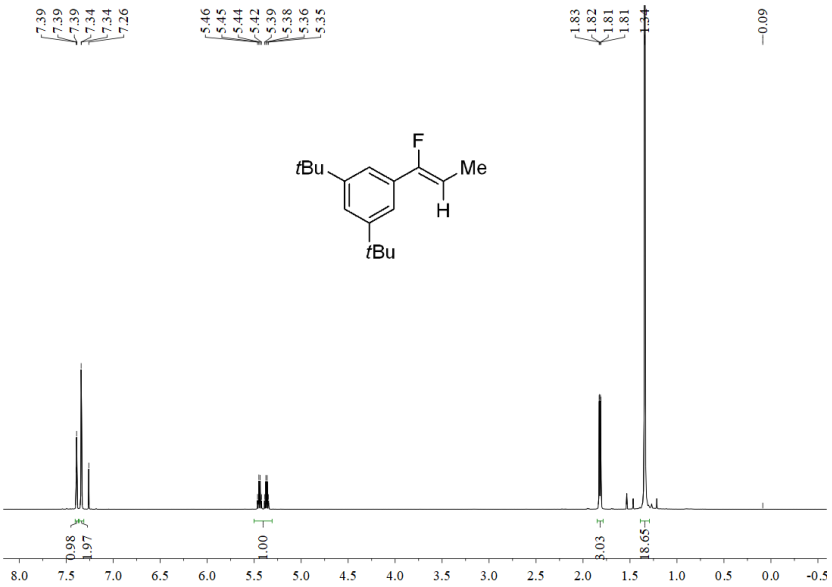
^{13}C NMR (126 MHz, $CDCl_3$) (**46**)



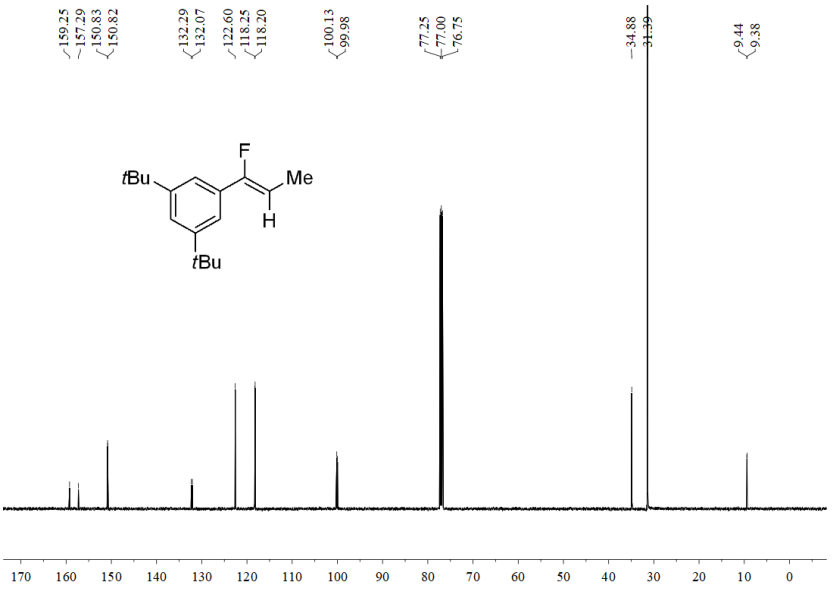
^{19}F NMR (471 MHz, $CDCl_3$) (**46**)



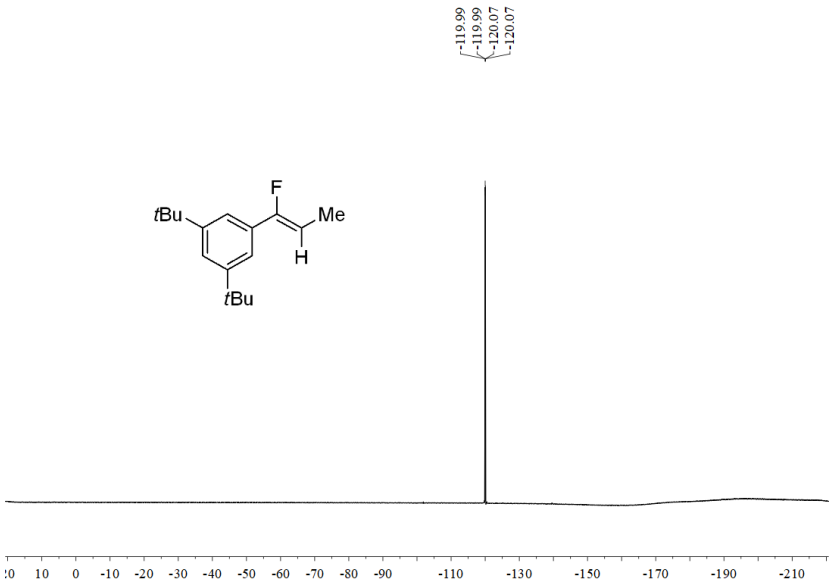
^{1}H NMR (500 MHz, $CDCl_3$) (**47**)



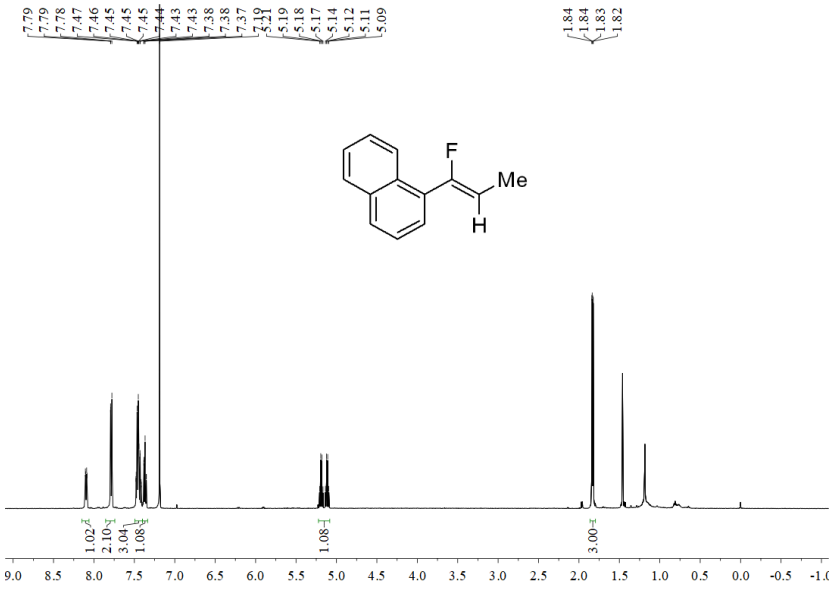
^{13}C NMR (126 MHz, $CDCl_3$) (**47**)



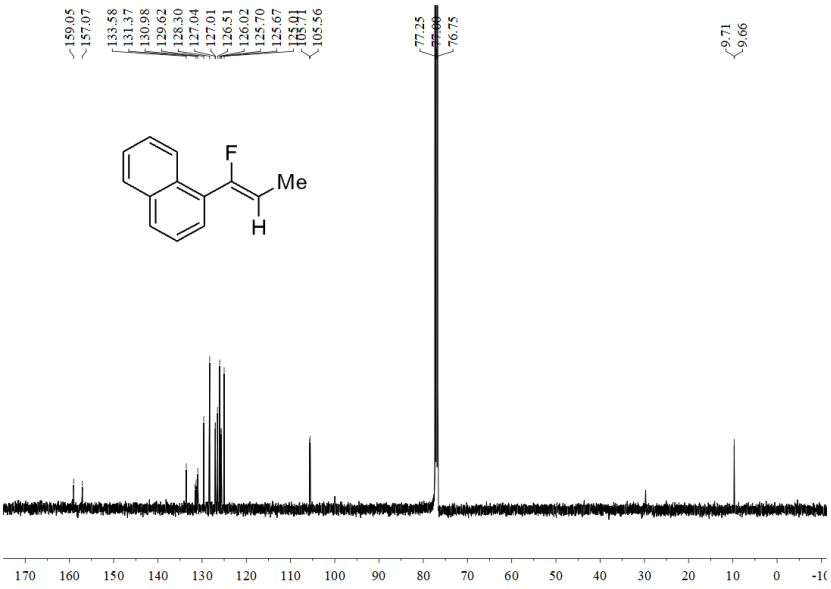
^{19}F NMR (471 MHz, $CDCl_3$) (**47**)



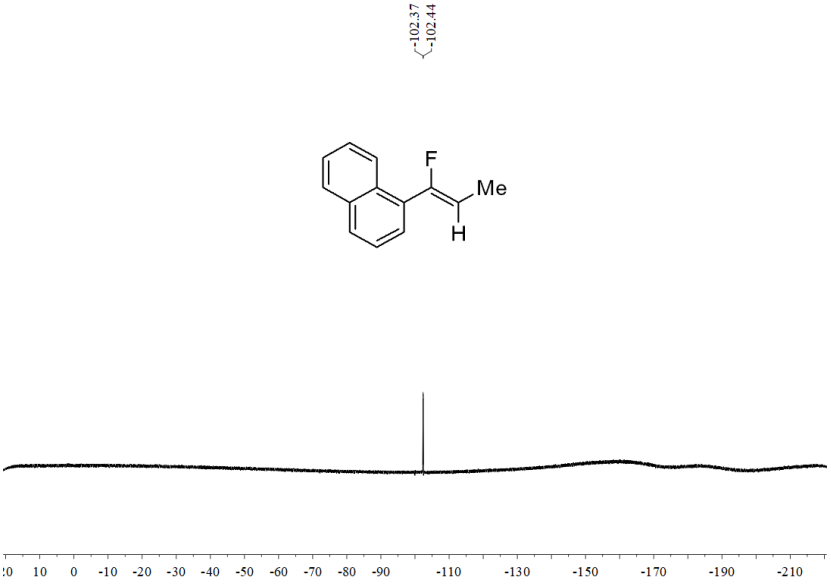
^{1}H NMR (500 MHz, $CDCl_3$) (**48**)



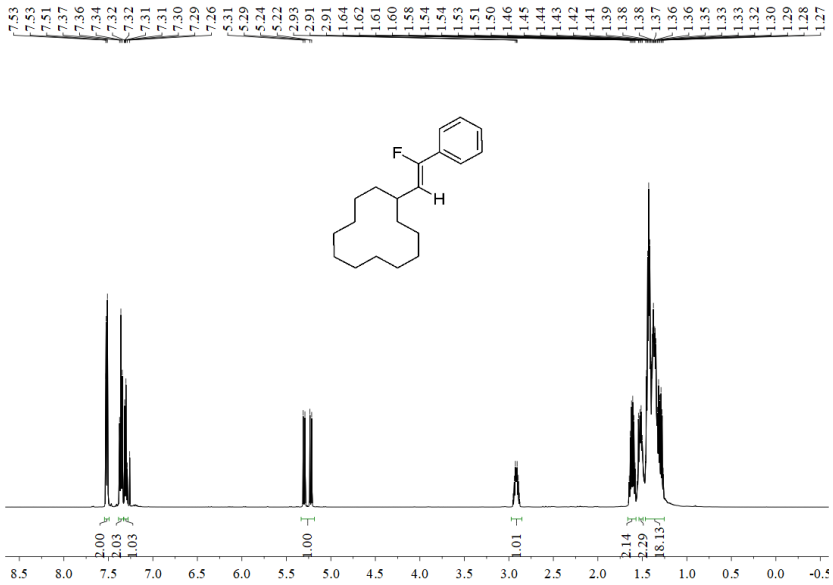
^{13}C NMR (126 MHz, $CDCl_3$) (**48**)



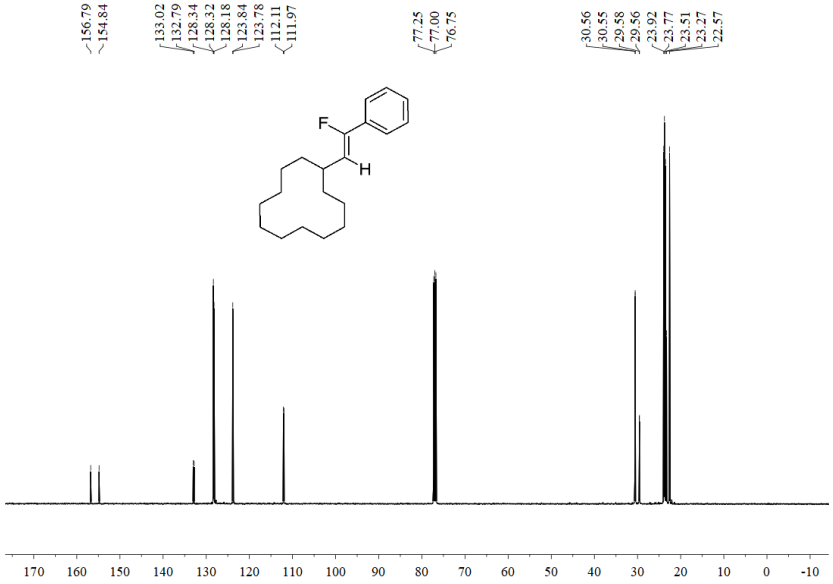
^{19}F NMR (471 MHz, $CDCl_3$) (**48**)



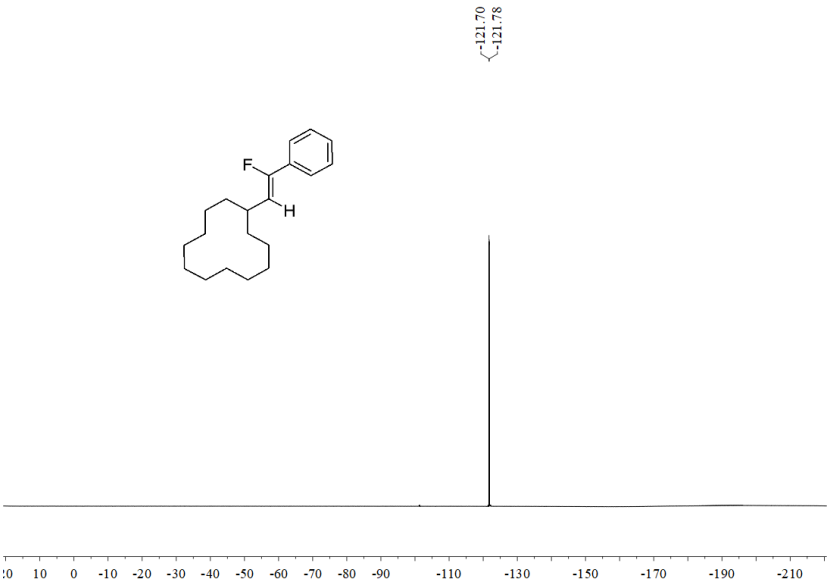
^{1}H NMR (500 MHz, $CDCl_3$) (**49**)



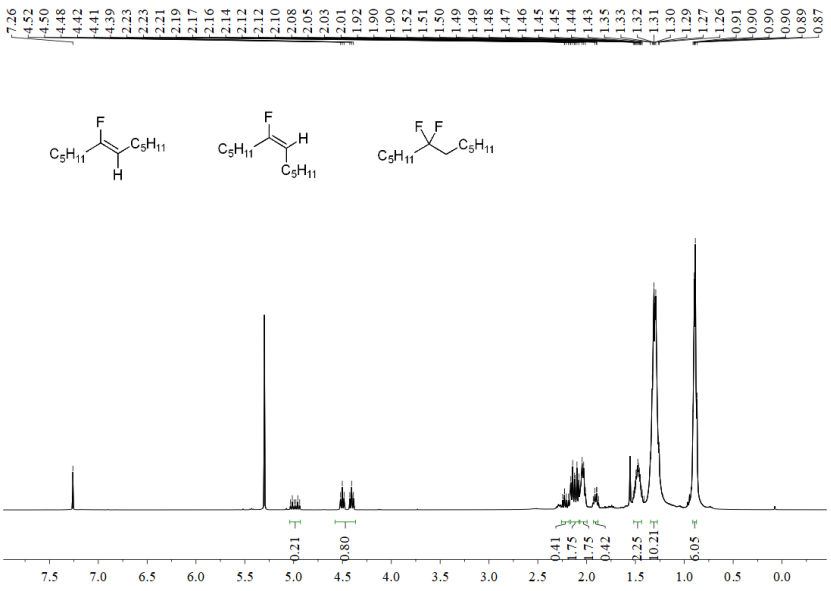
^{13}C NMR (126 MHz, $CDCl_3$) (**49**)



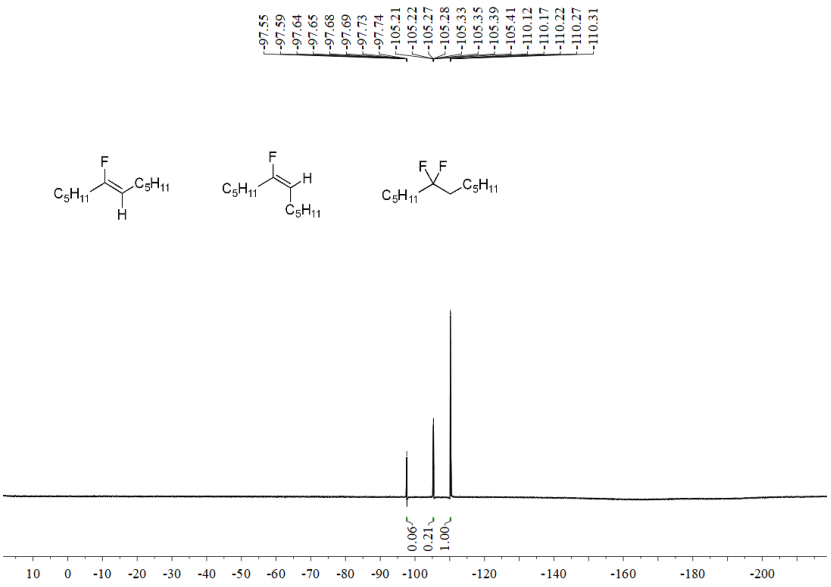
^{19}F NMR (471 MHz, $CDCl_3$) (**49**)



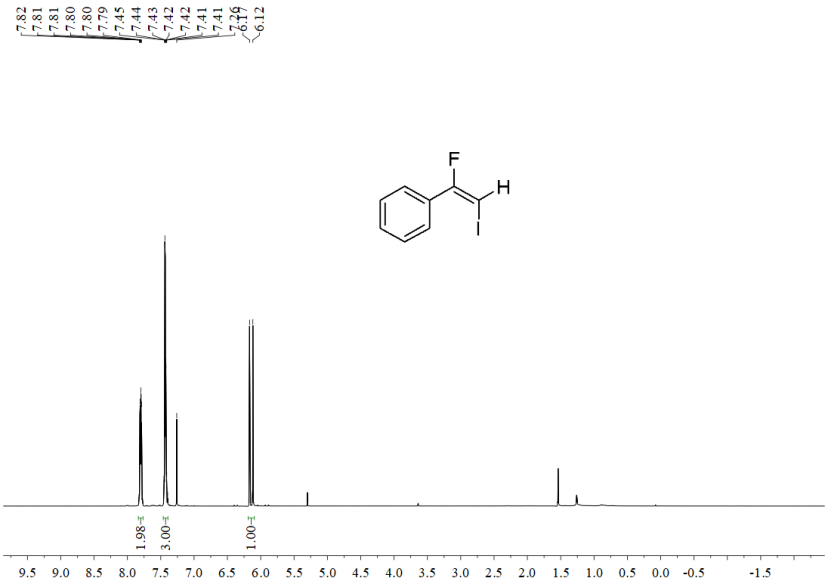
^{1}H NMR (400 MHz, $CDCl_3$) (**50**)



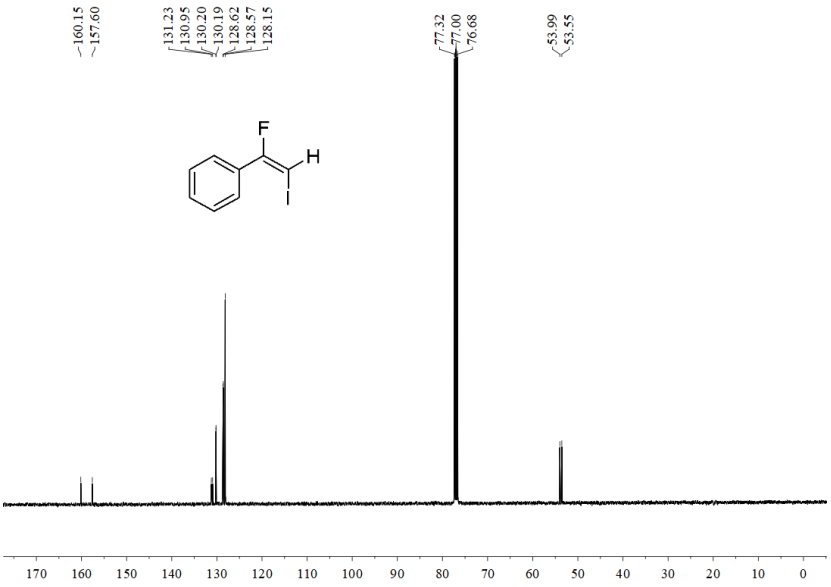
^{19}F NMR (376 MHz, $CDCl_3$) (**50**)



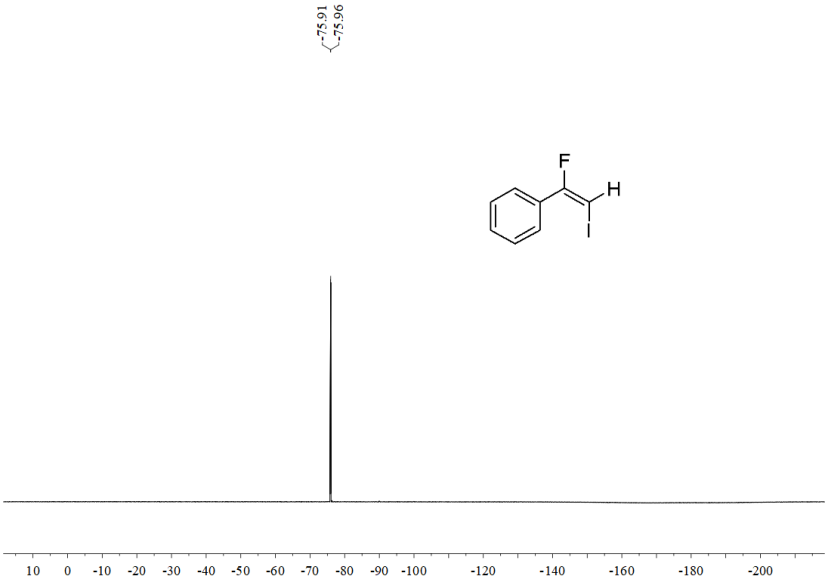
^{1}H NMR (400 MHz, $CDCl_3$) (**53**)



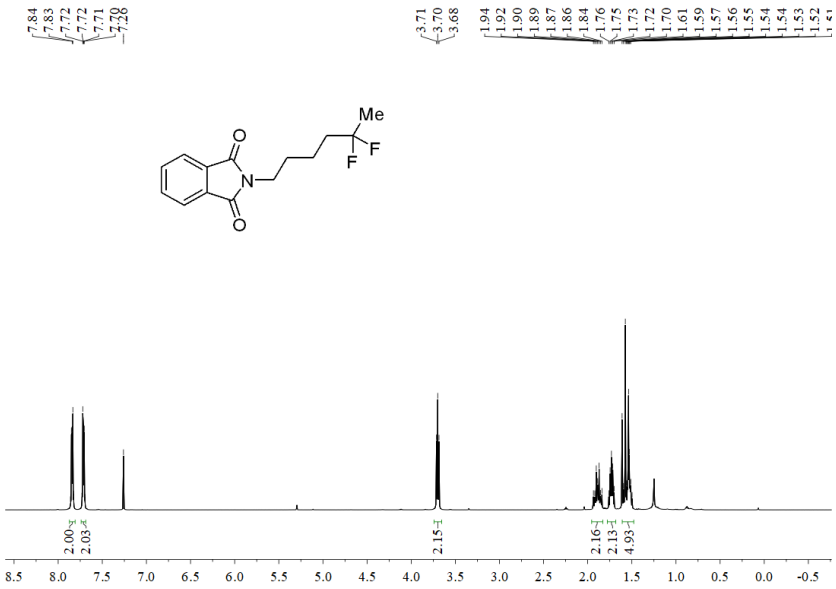
^{13}C NMR (101 MHz, $CDCl_3$) (**53**)



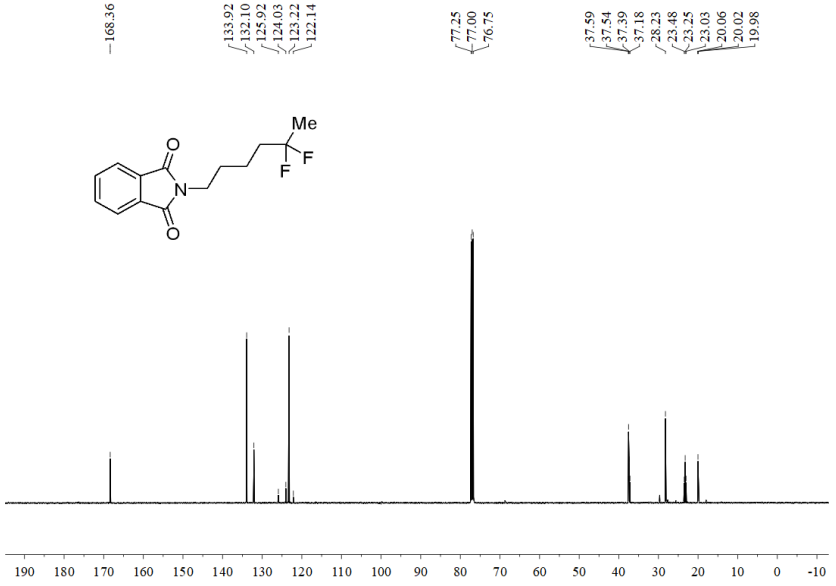
^{19}F NMR (376 MHz, $CDCl_3$) (**53**)



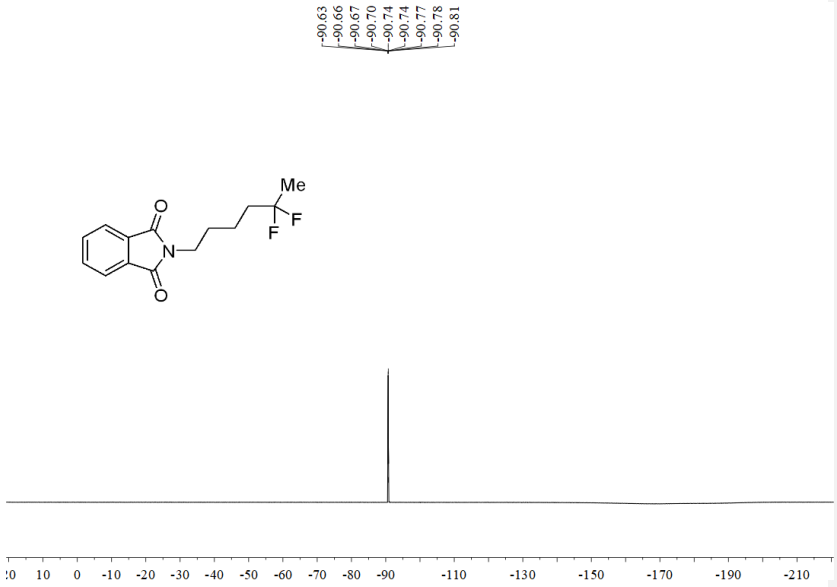
^{1}H NMR (500 MHz, $CDCl_3$) (**57**)



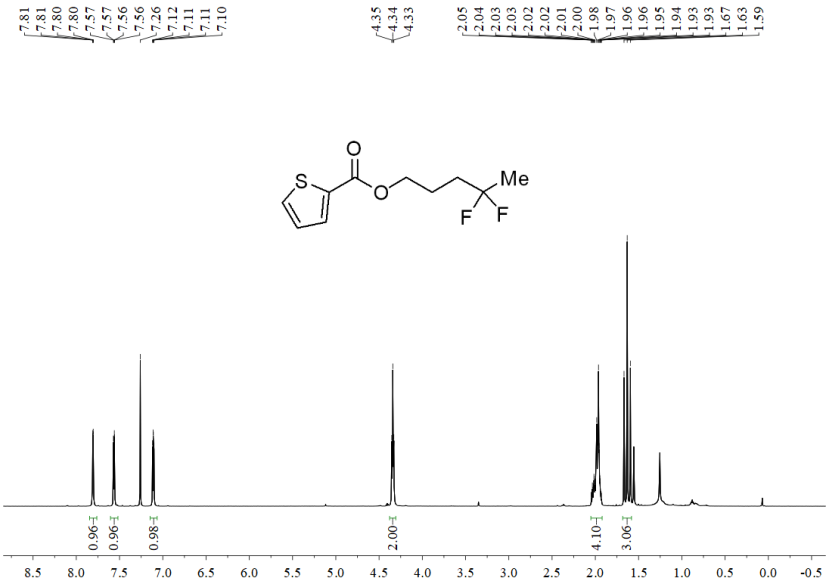
^{13}C NMR (126 MHz, $CDCl_3$) (**57**)



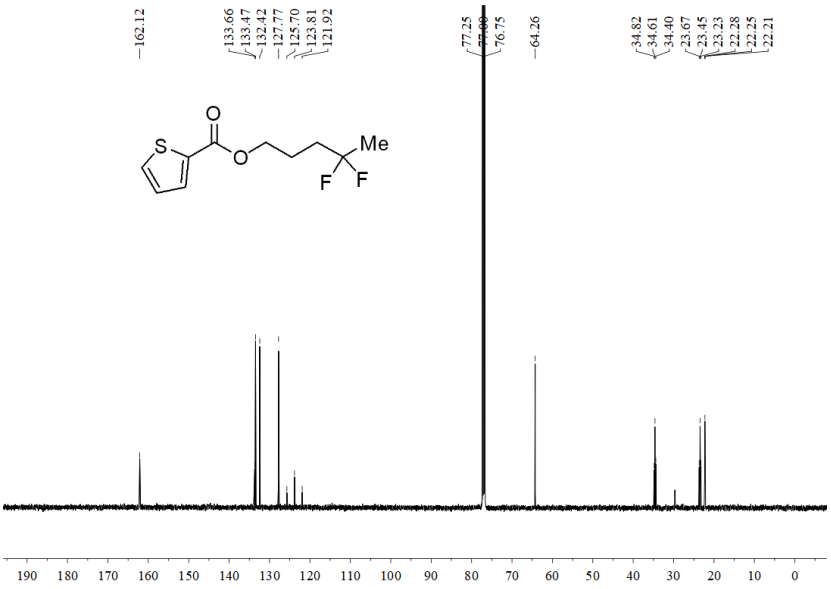
^{19}F NMR (471 MHz, $CDCl_3$) (**57**)



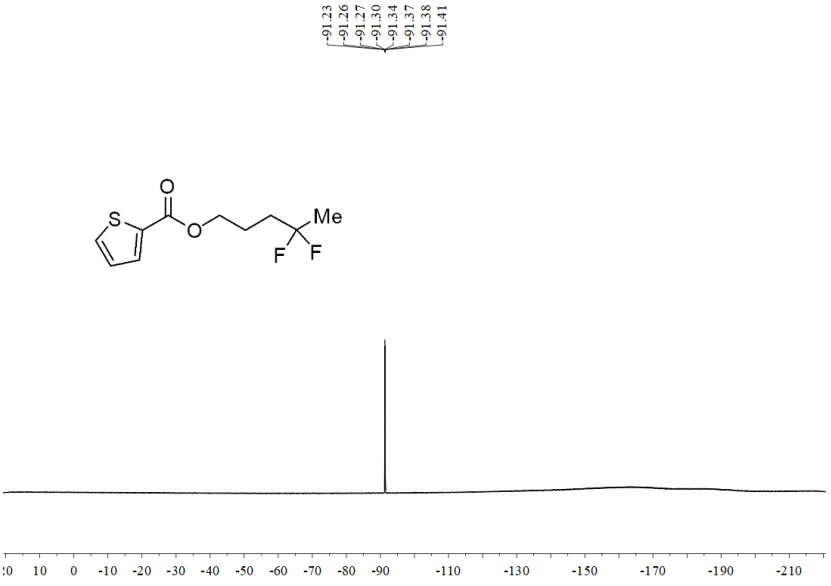
^{1}H NMR (500 MHz, $CDCl_3$) (**58**)



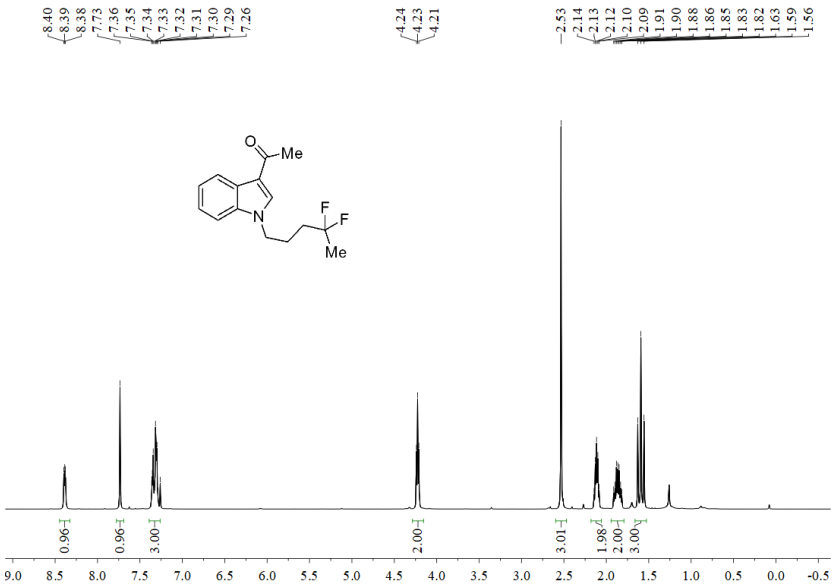
^{13}C NMR (126 MHz, $CDCl_3$) (**58**)



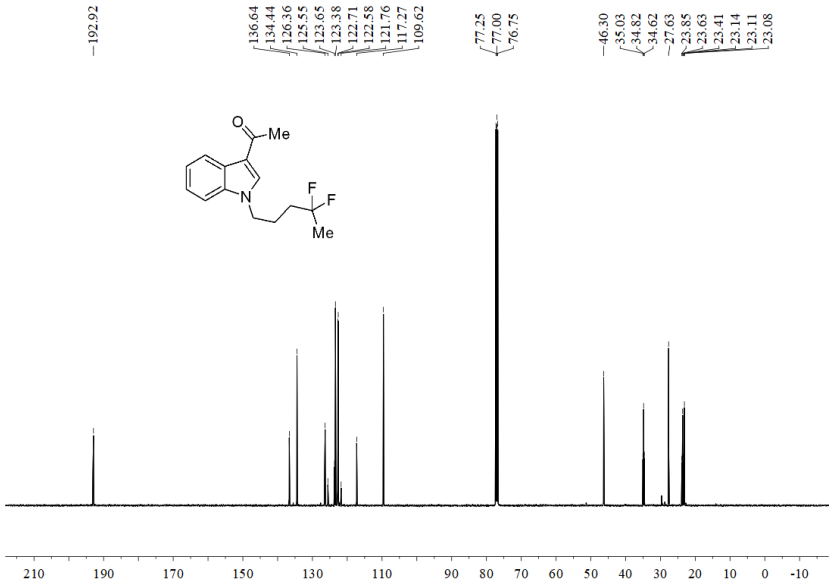
^{19}F NMR (471 MHz, $CDCl_3$) (**58**)



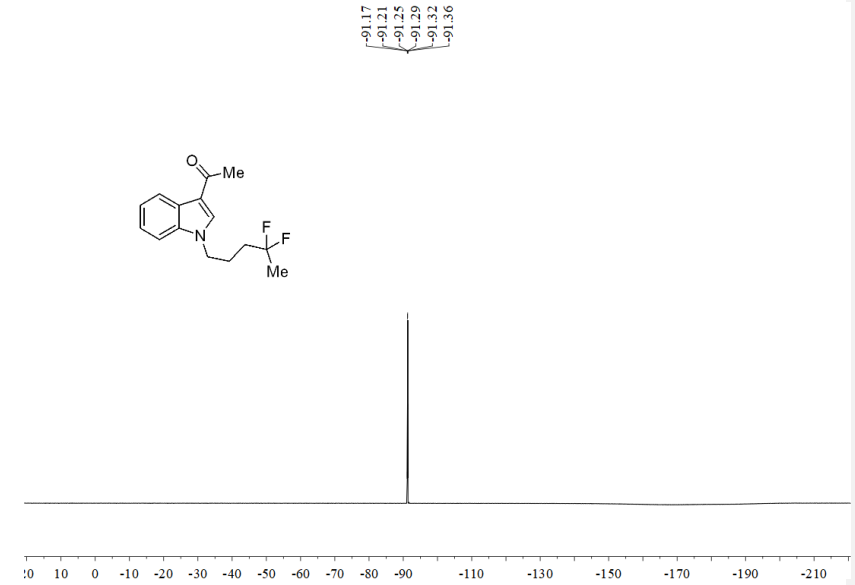
^{1}H NMR (500 MHz, $CDCl_3$) (**59**)



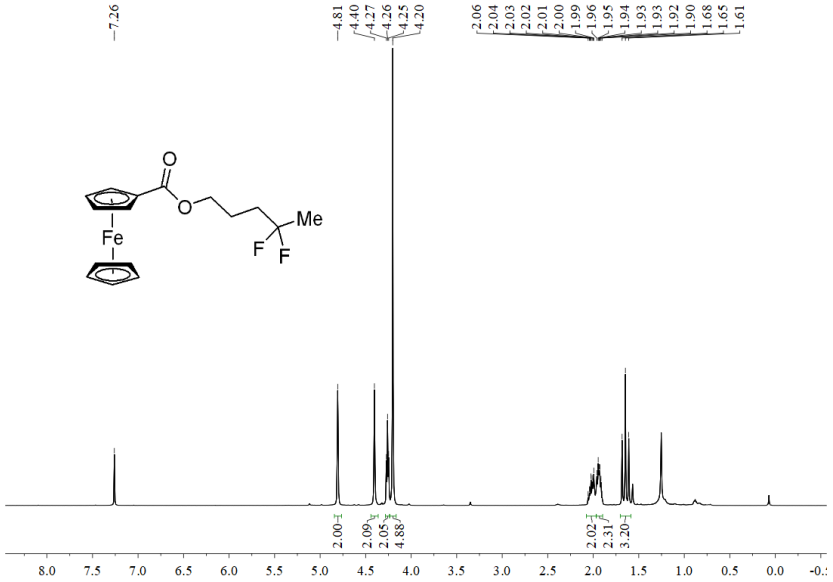
^{13}C NMR (126 MHz, $CDCl_3$) (**59**)



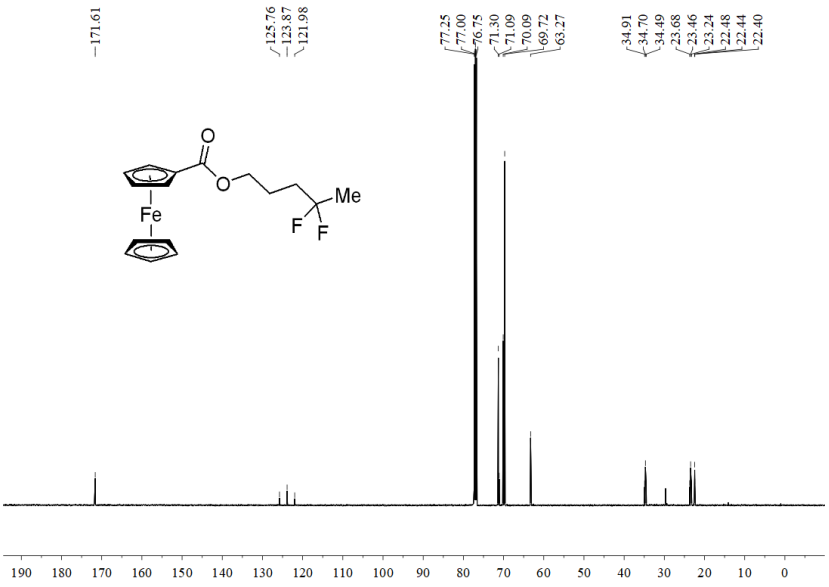
^{19}F NMR (471 MHz, $CDCl_3$) (**59**)



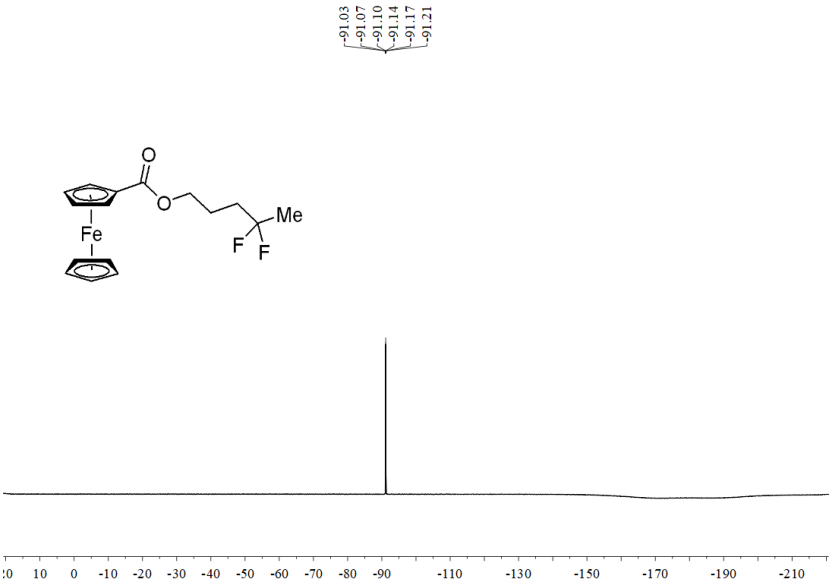
^{1}H NMR (500 MHz, $CDCl_3$) (**60**)



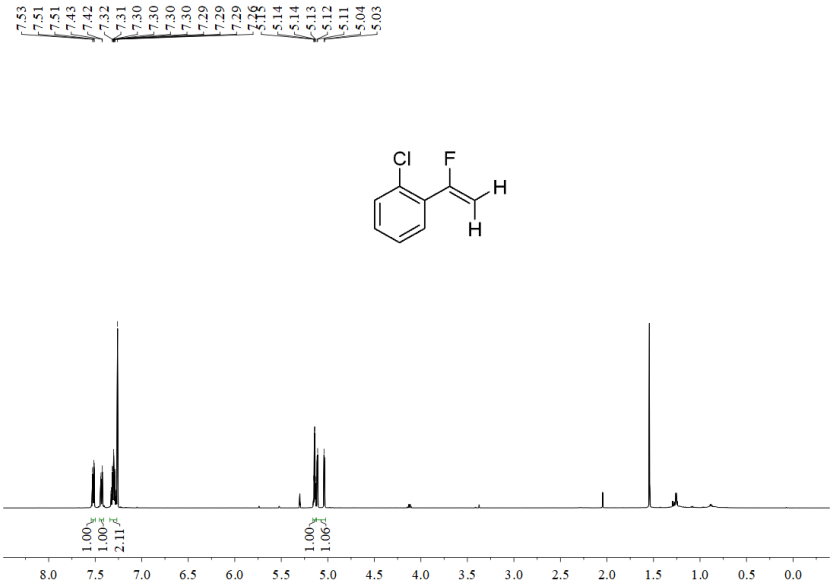
^{13}C NMR (126 MHz, $CDCl_3$) (**60**)



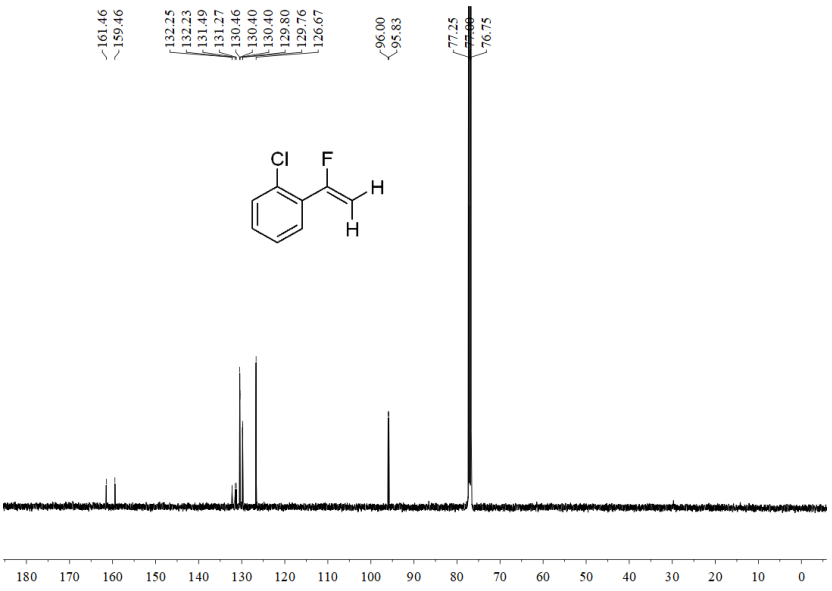
^{19}F NMR (471 MHz, $CDCl_3$) (**60**)



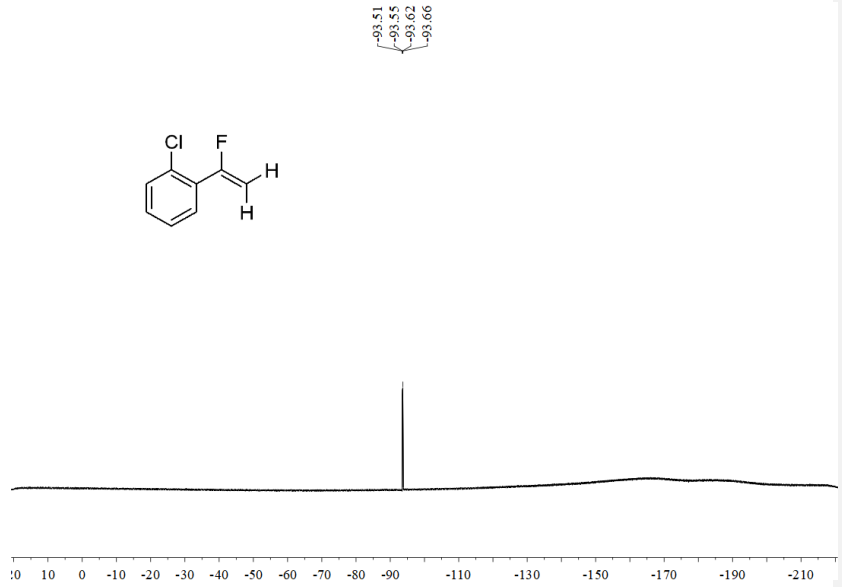
^{1}H NMR (500 MHz, $CDCl_3$) (**64**)



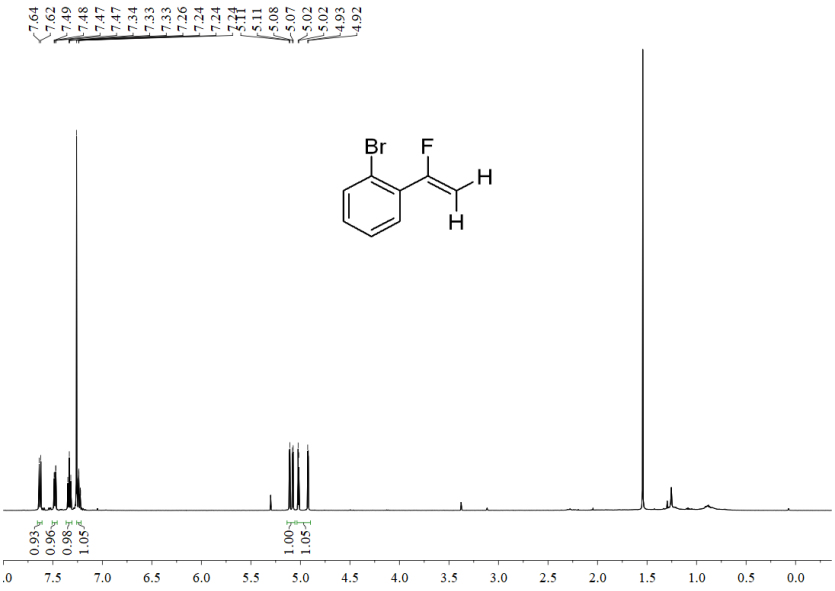
^{13}C NMR (126 MHz, $CDCl_3$) (**64**)



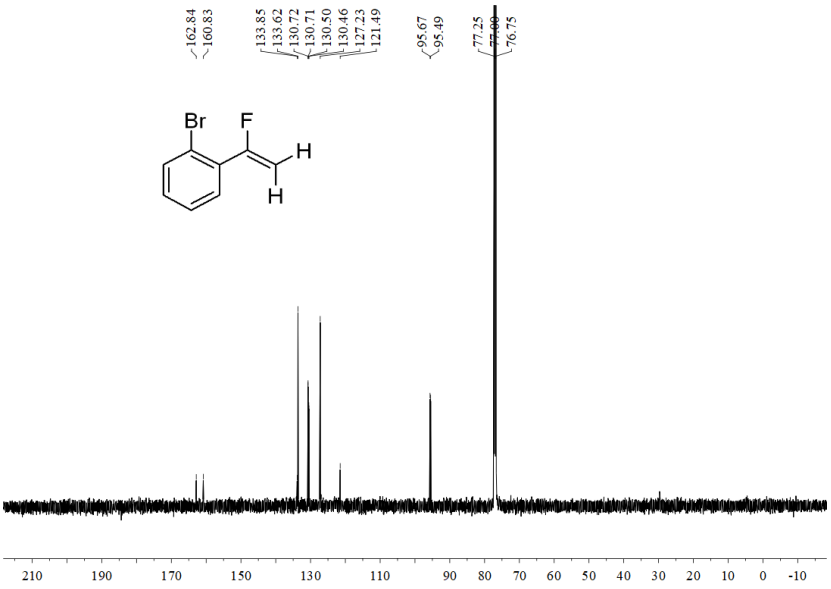
^{19}F NMR (471 MHz, $CDCl_3$) (**64**)



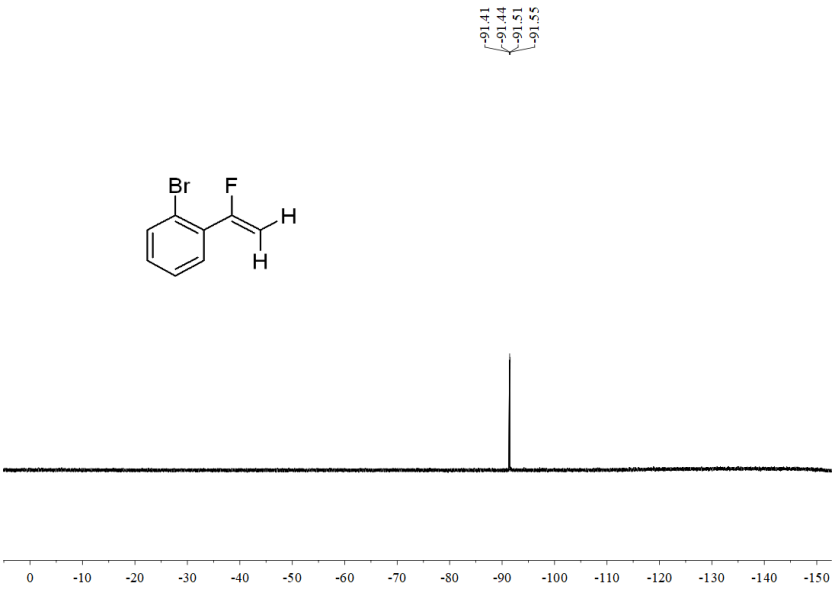
^{1}H NMR (500 MHz, $CDCl_3$) (**65**)



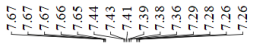
^{13}C NMR (126 MHz, $CDCl_3$) (**65**)

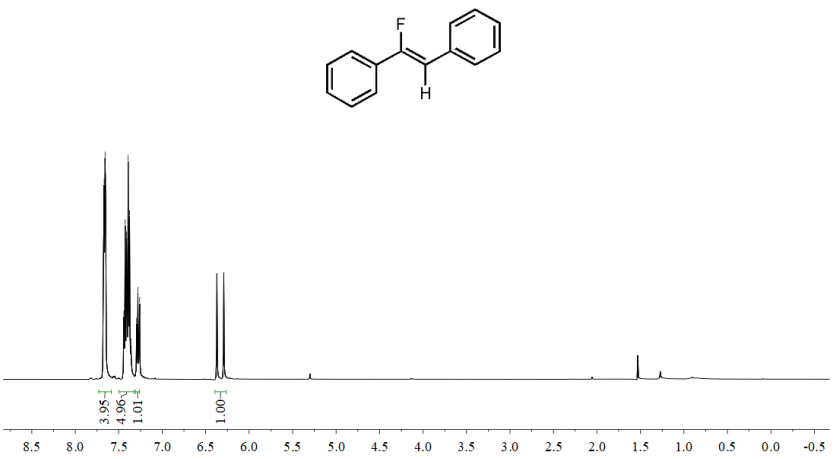


^{19}F NMR (471 MHz, $CDCl_3$) (**65**)

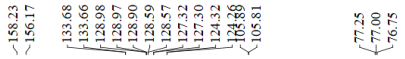


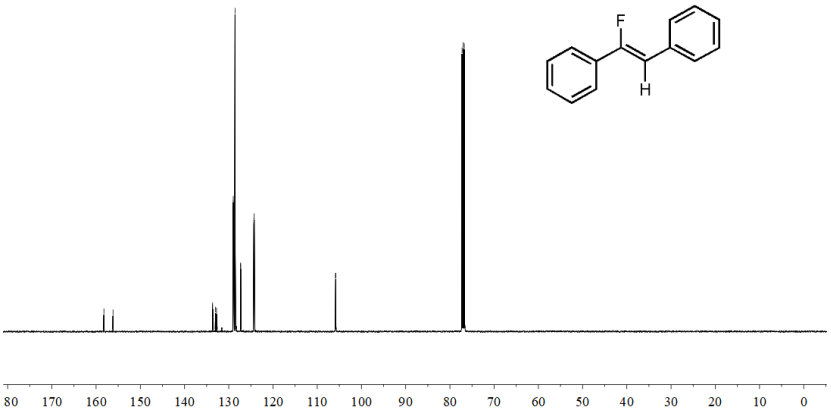
^{1}H NMR (500 MHz, $CDCl_3$) (**71**)



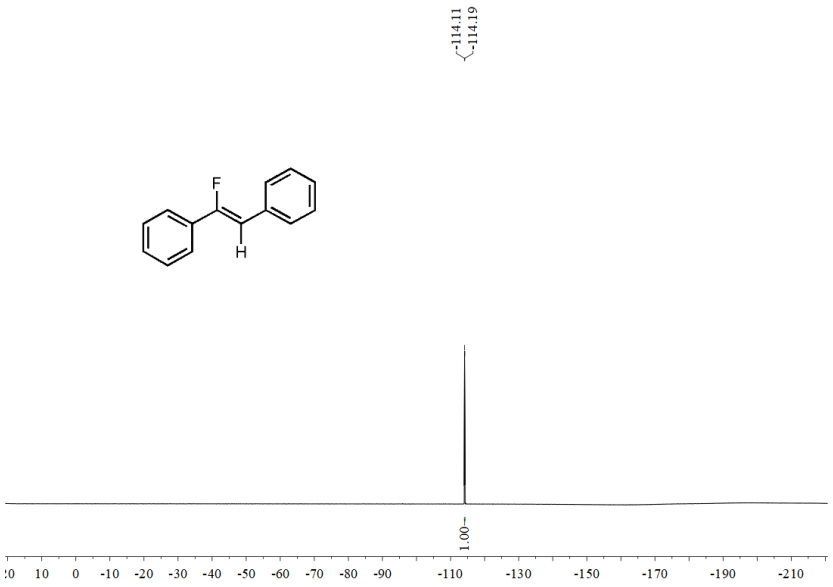


^{13}C NMR (126 MHz, $CDCl_3$) (**71**)



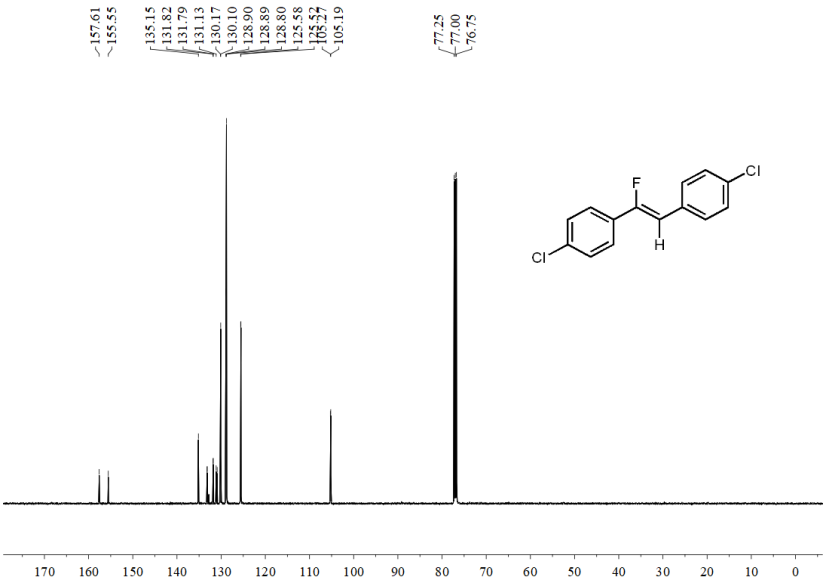


^{19}F NMR (471 MHz, $CDCl_3$) (**71**)

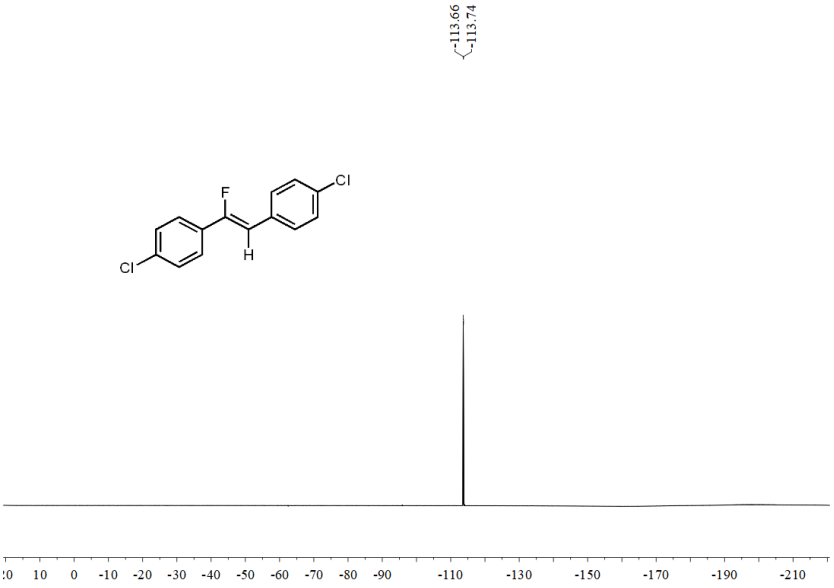


^{1}H NMR (500 MHz, $CDCl_3$) (**72**)

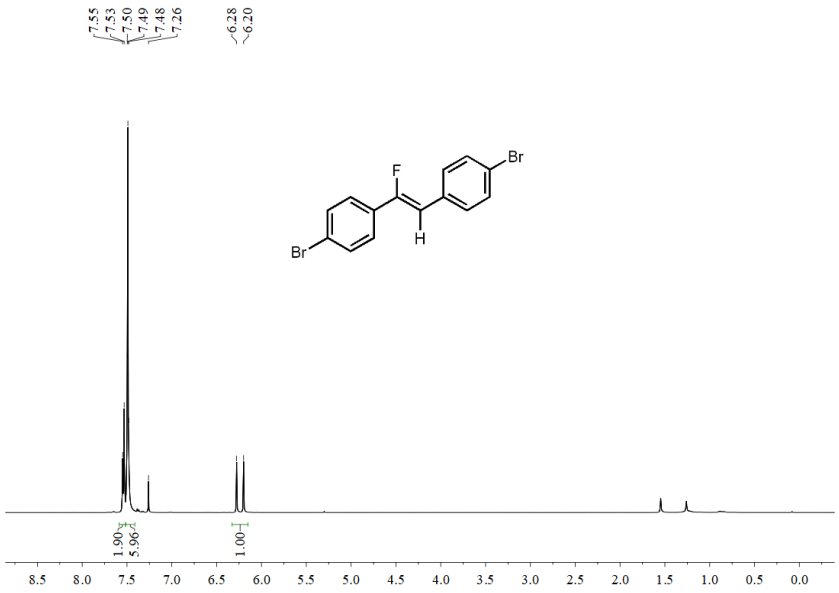
^{13}C NMR (126 MHz, $CDCl_3$) (**72**)



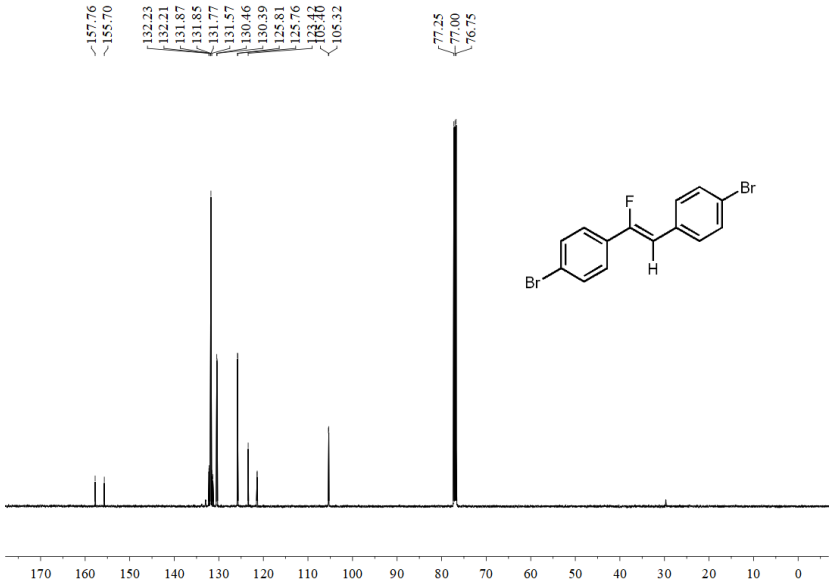
^{19}F NMR (471 MHz, $CDCl_3$) (**72**)



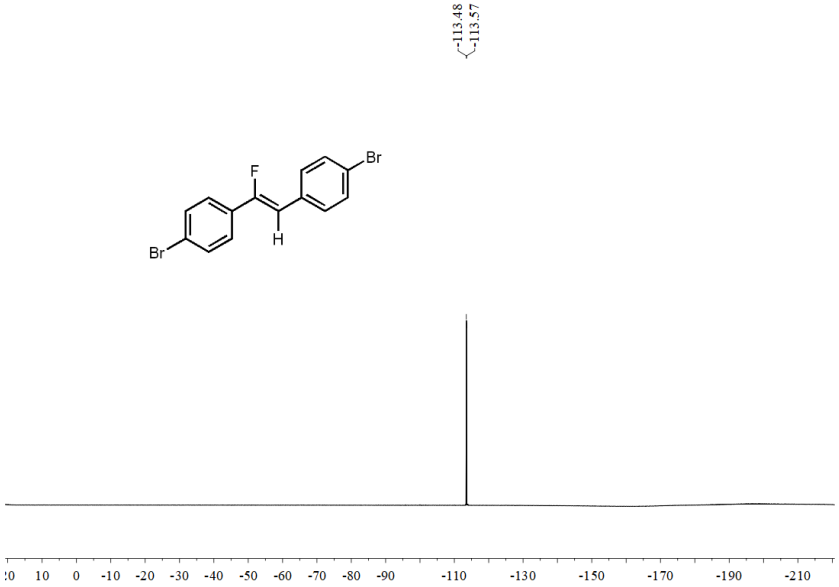
^{1}H NMR (500 MHz, $CDCl_3$) (**73**)



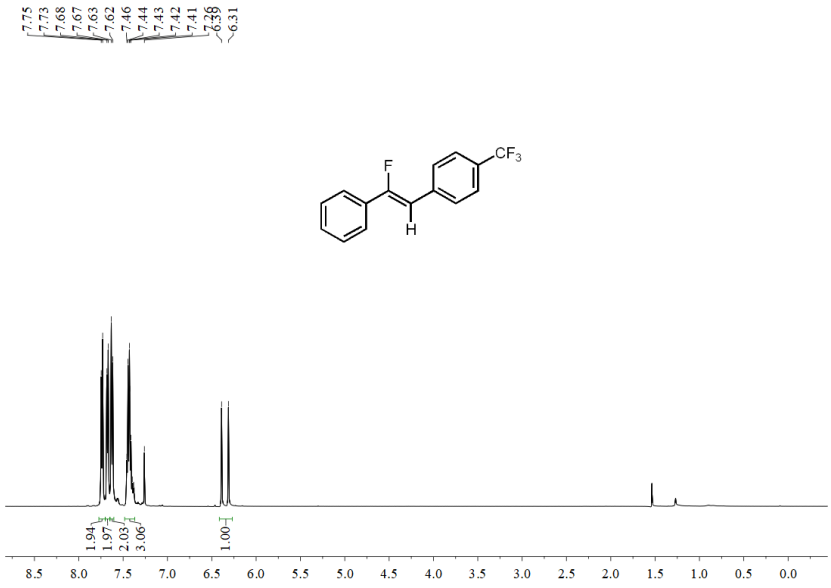
^{13}C NMR (126 MHz, $CDCl_3$) (**73**)



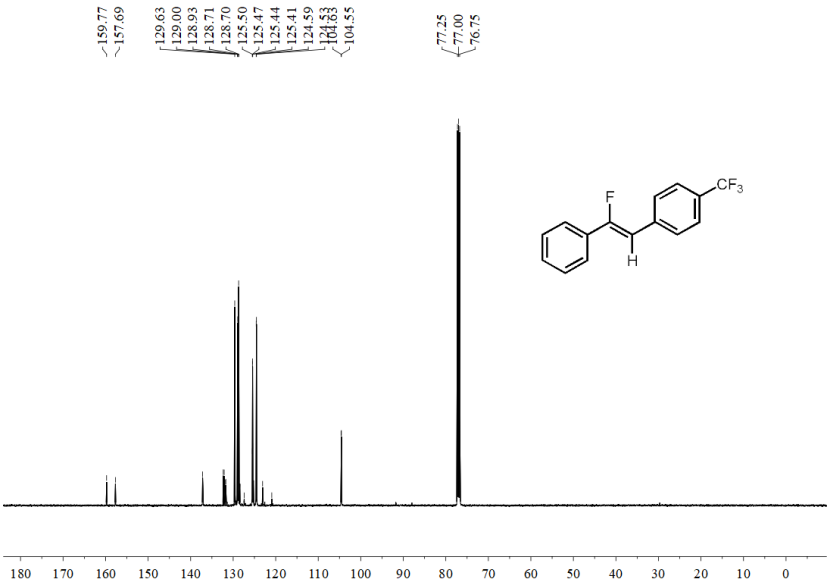
^{19}F NMR (471 MHz, $CDCl_3$) (**73**)



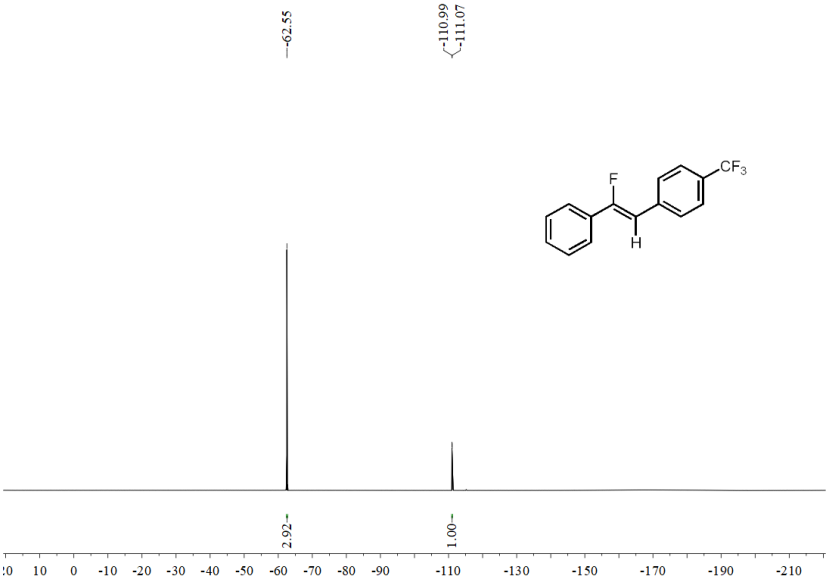
^{1}H NMR (500 MHz, $CDCl_3$) (**75**)



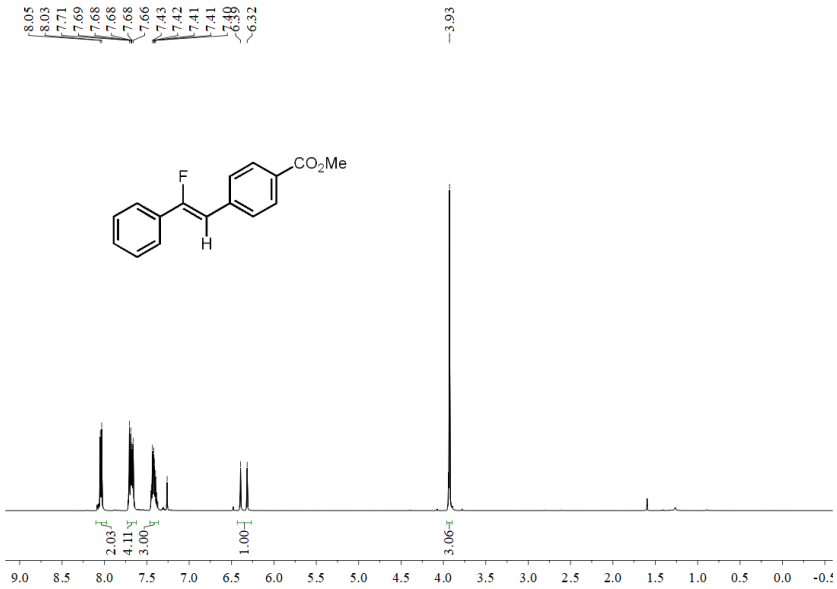
^{13}C NMR (126 MHz, $CDCl_3$) (**75**)



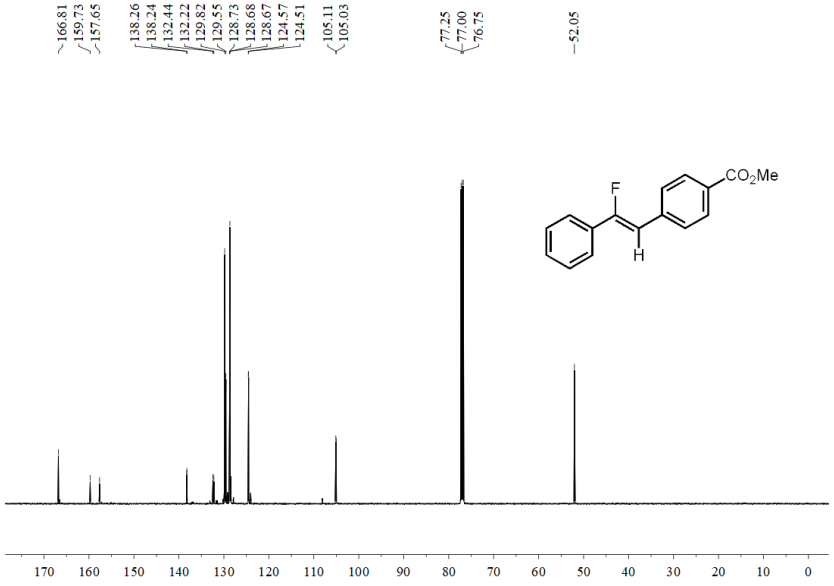
^{19}F NMR (471 MHz, $CDCl_3$) (**75**)



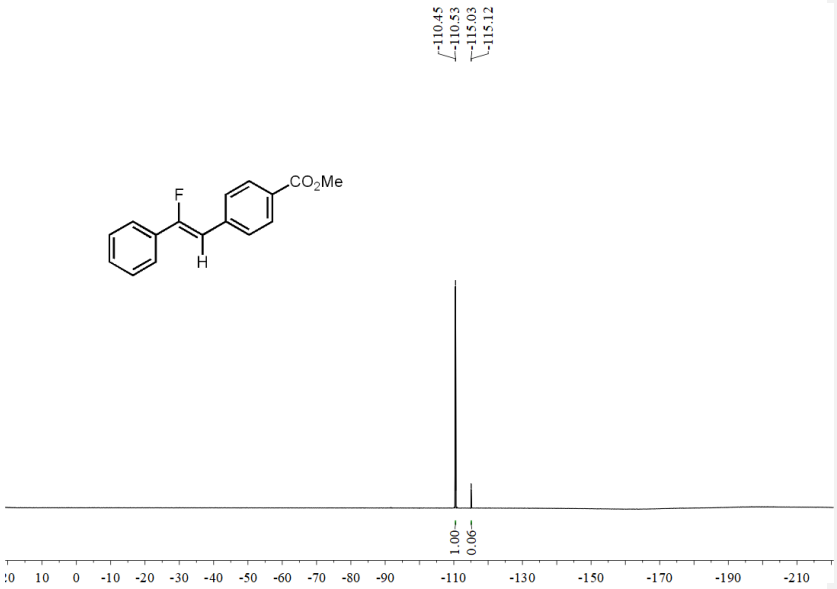
^{1}H NMR (500 MHz, $CDCl_3$) (**76**)



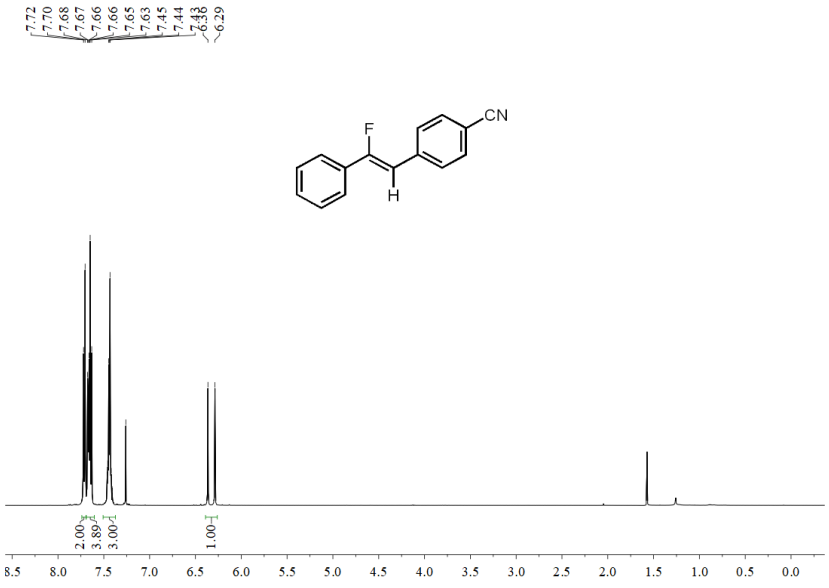
^{13}C NMR (126 MHz, $CDCl_3$) (**76**)



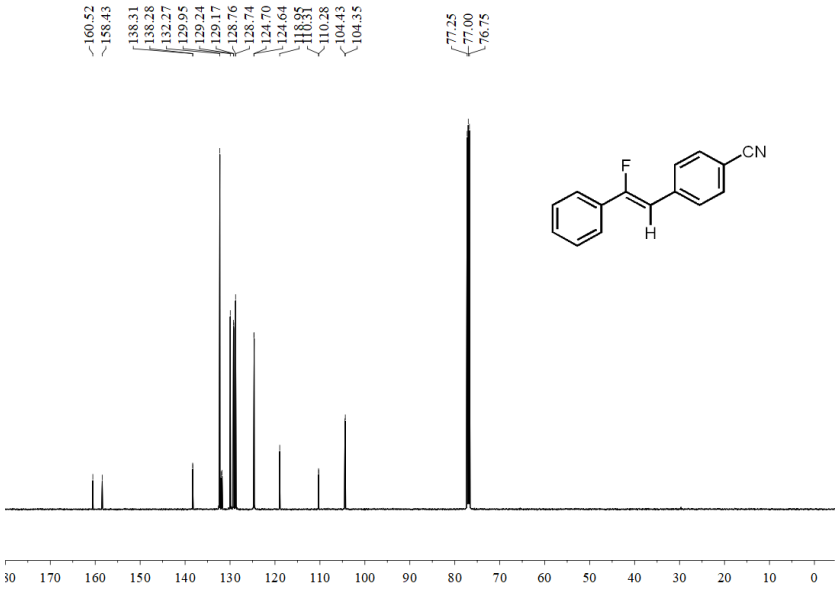
^{19}F NMR (471 MHz, $CDCl_3$) (**76**)



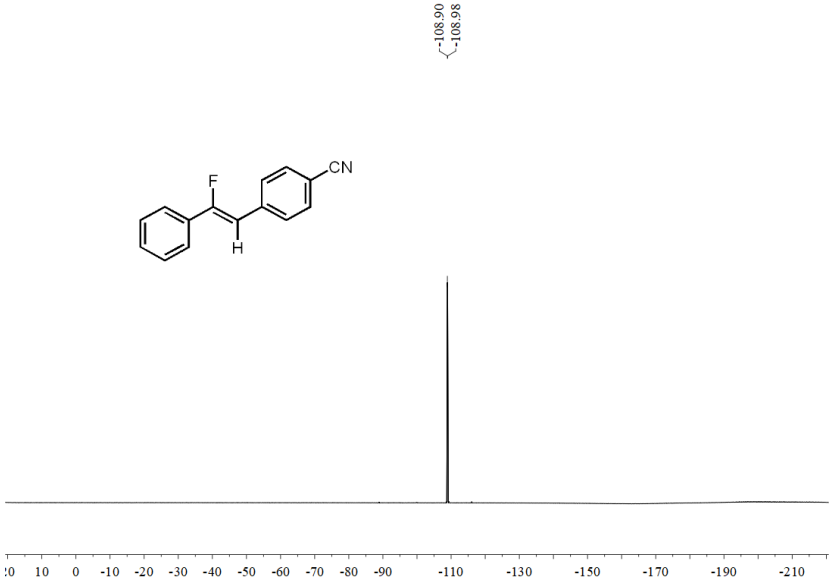
^{1}H NMR (500 MHz, $CDCl_3$) (**78**)



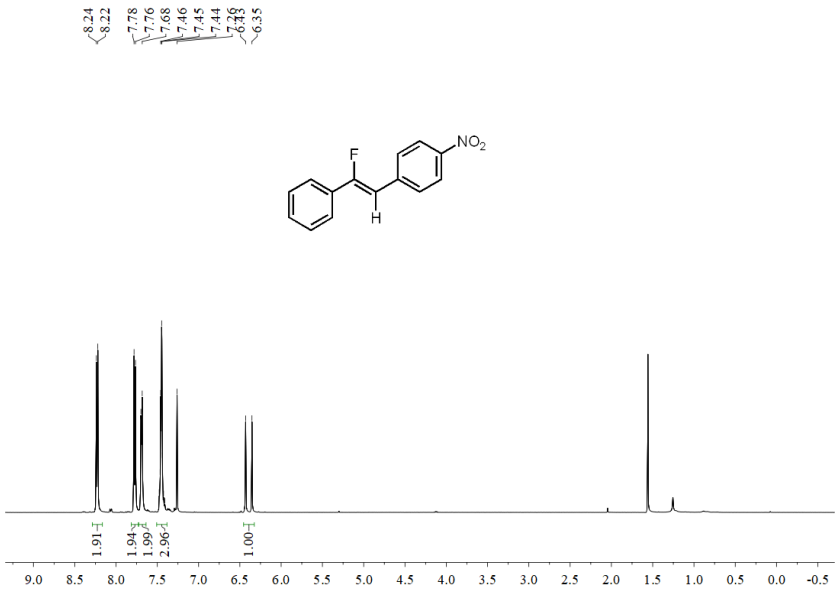
^{13}C NMR (126 MHz, $CDCl_3$) (**78**)



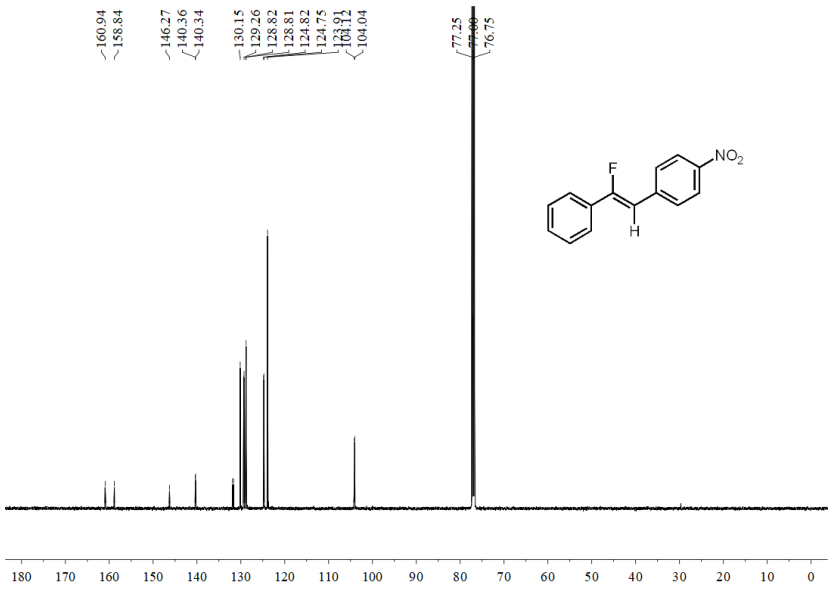
^{19}F NMR (471 MHz, $CDCl_3$) (**78**)



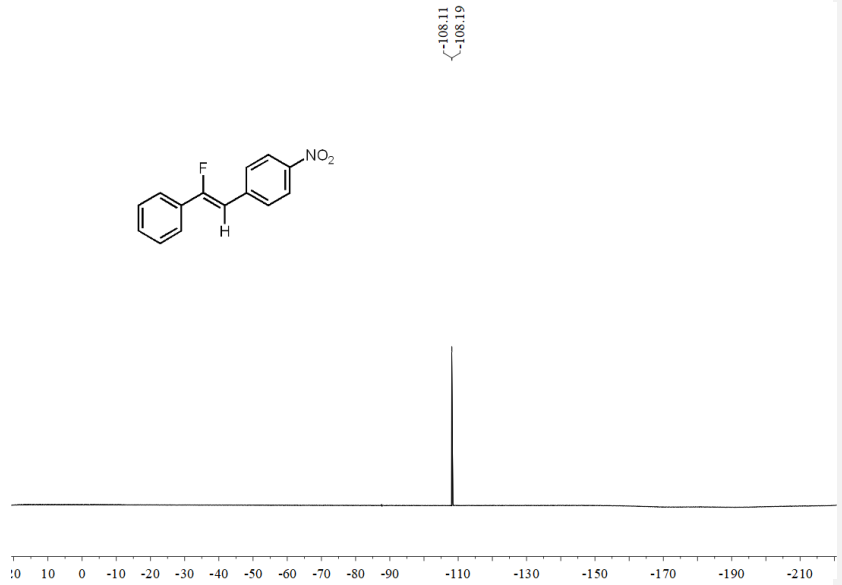
^{1}H NMR (500 MHz, $CDCl_3$) (**79**)



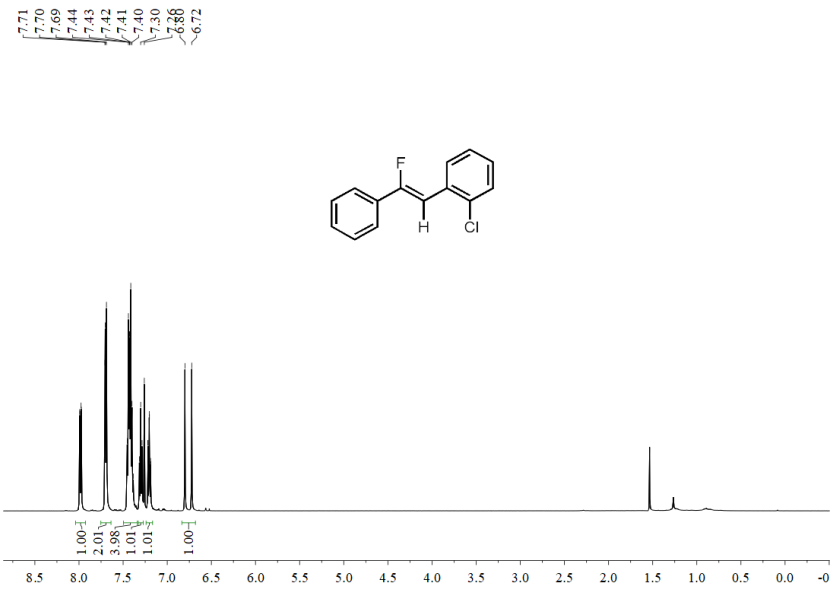
^{13}C NMR (126 MHz, $CDCl_3$) (**79**)



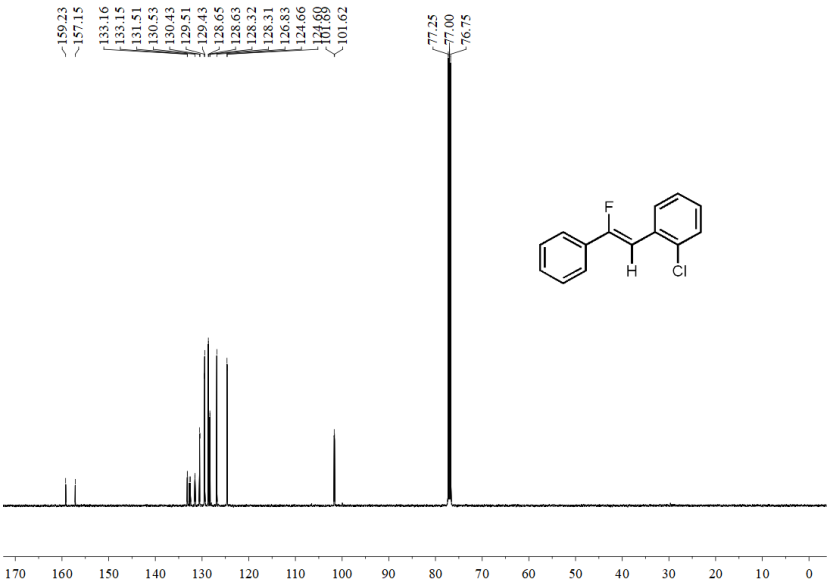
^{19}F NMR (471 MHz, $CDCl_3$) (**79**)



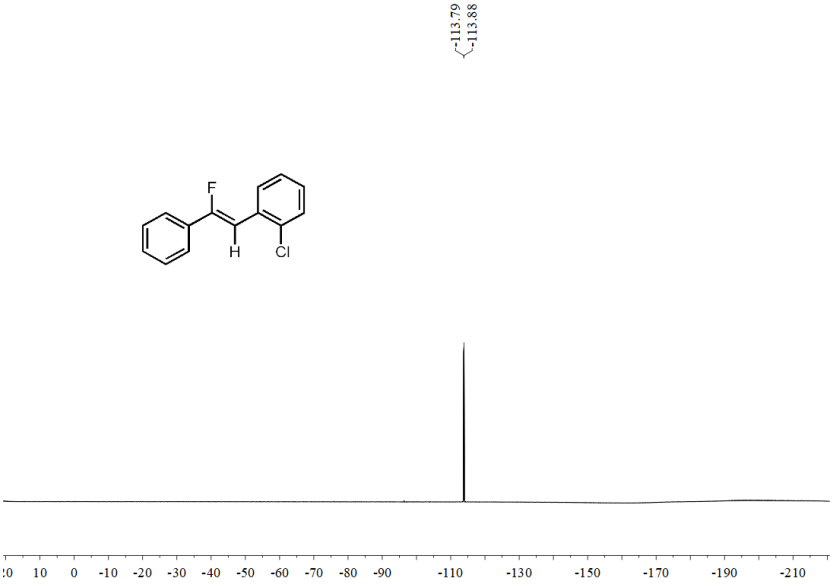
^{1}H NMR (500 MHz, $CDCl_3$) (**80**)



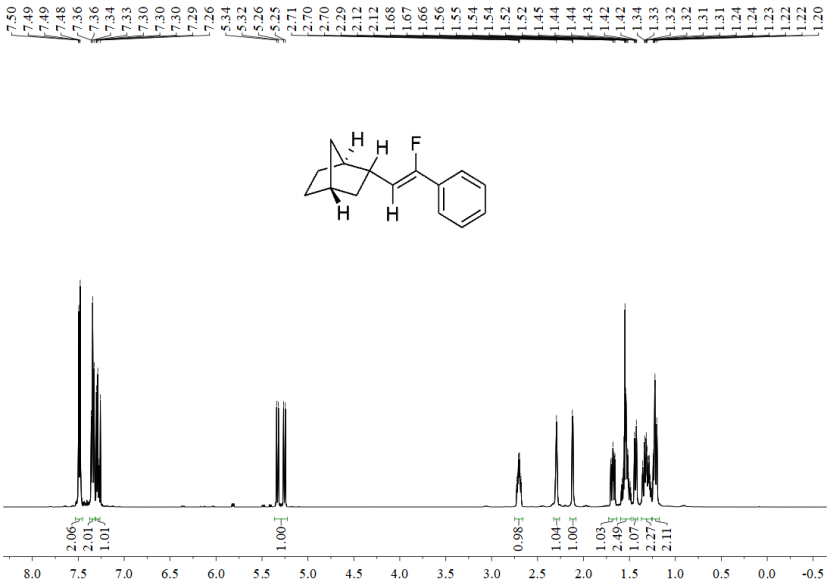
^{13}C NMR (126 MHz, $CDCl_3$) (**80**)



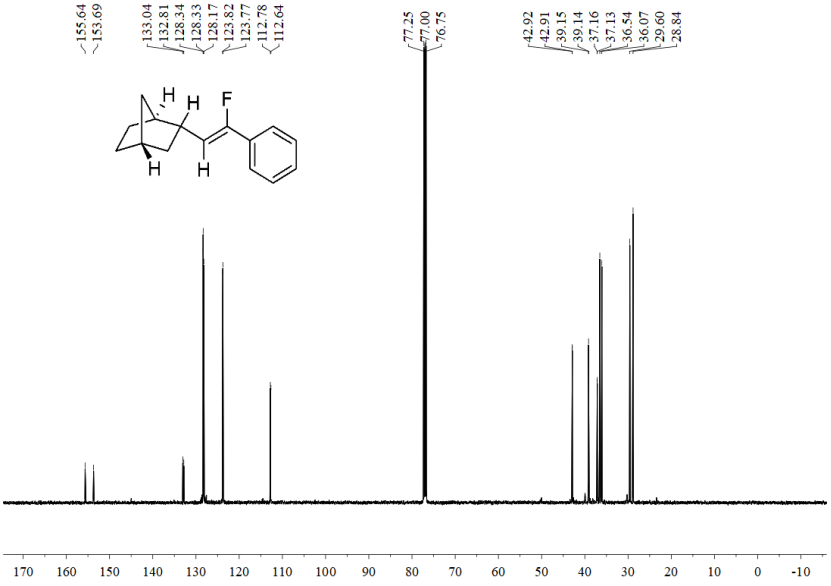
^{19}F NMR (471 MHz, $CDCl_3$) (**80**)



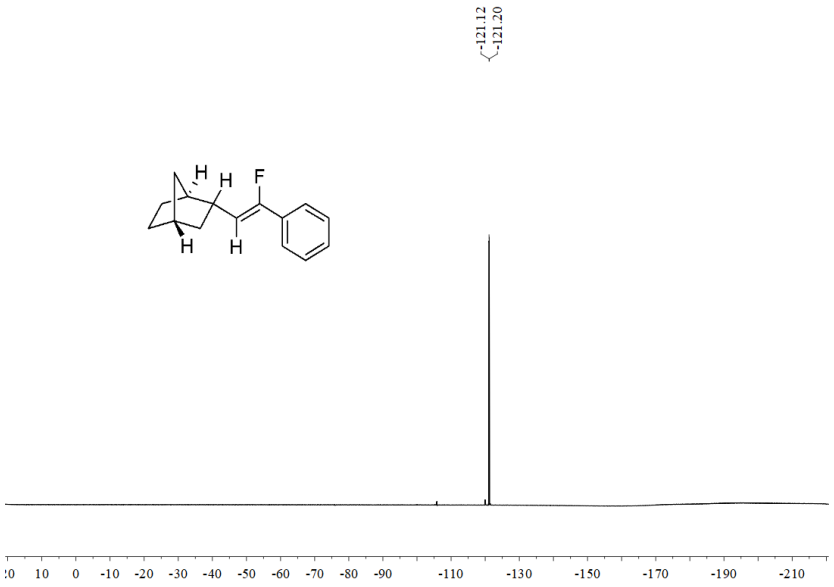
^{1}H NMR (500 MHz, $CDCl_3$) (**85**)



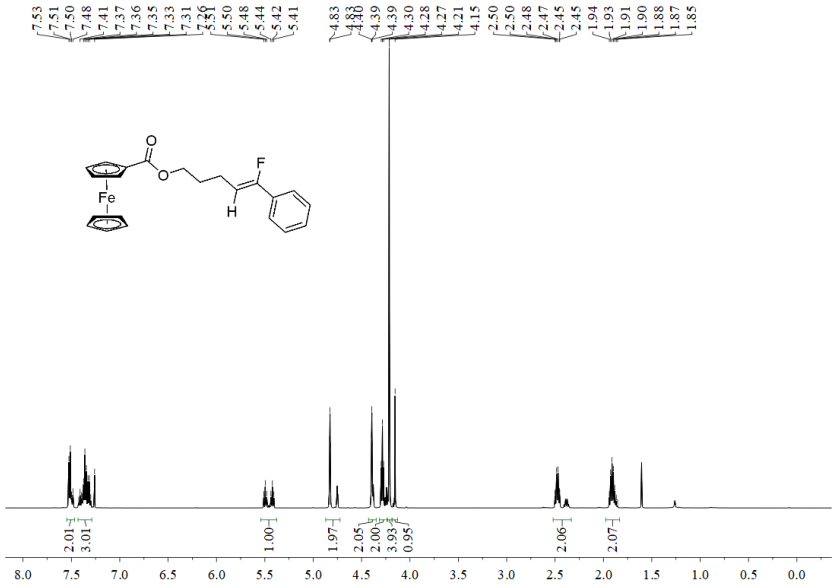
^{13}C NMR (126 MHz, $CDCl_3$) (**85**)



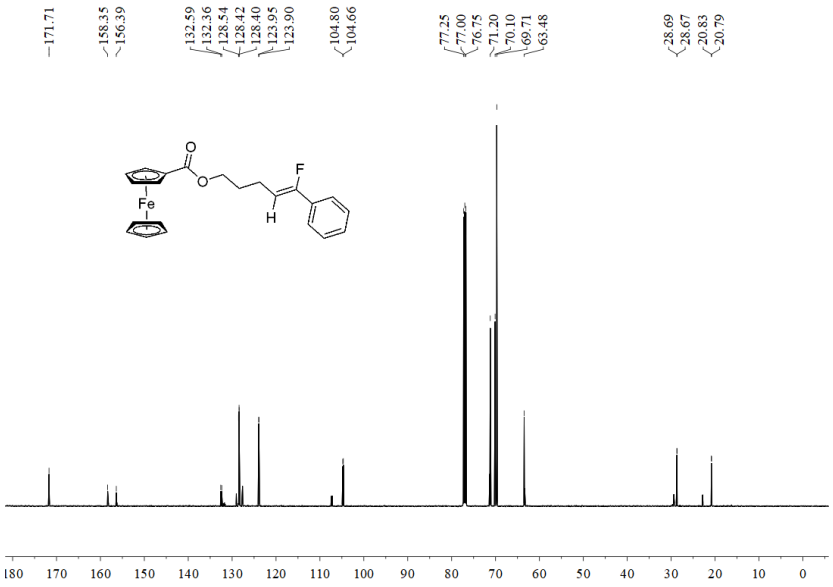
^{19}F NMR (471 MHz, $CDCl_3$) (**85**)



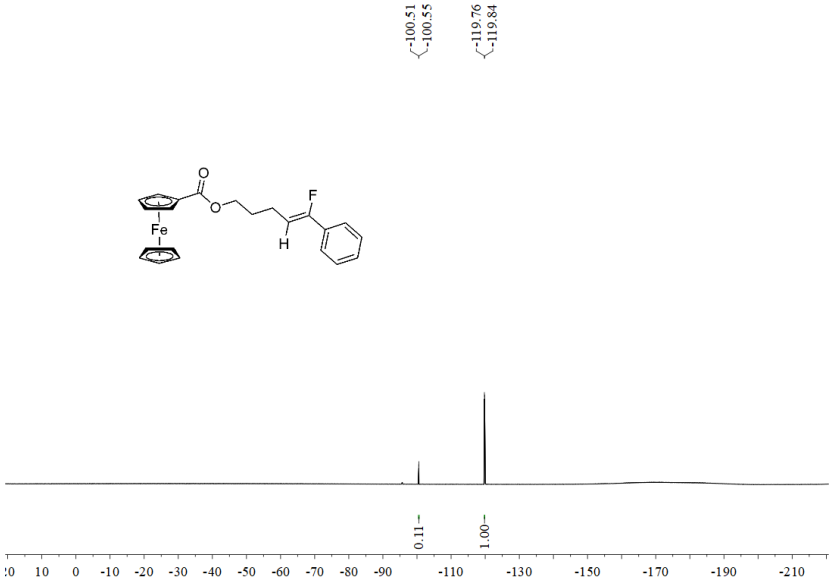
^{1}H NMR (500 MHz, $CDCl_3$) (**86**)



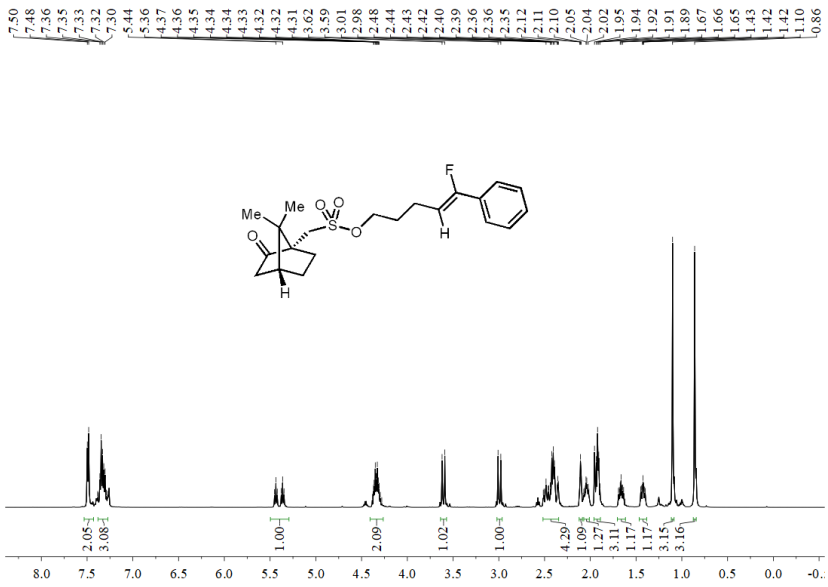
^{13}C NMR (126 MHz, $CDCl_3$) (**86**)



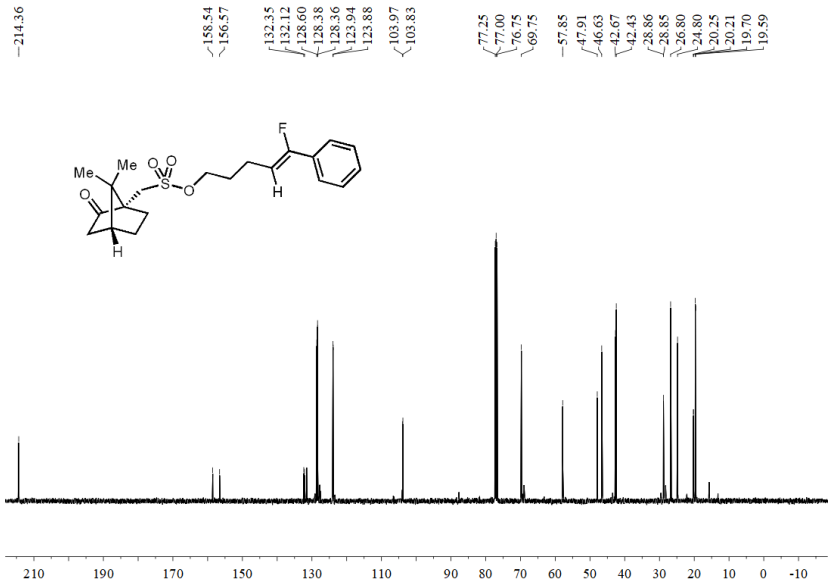
^{19}F NMR (471 MHz, $CDCl_3$) (**86**)



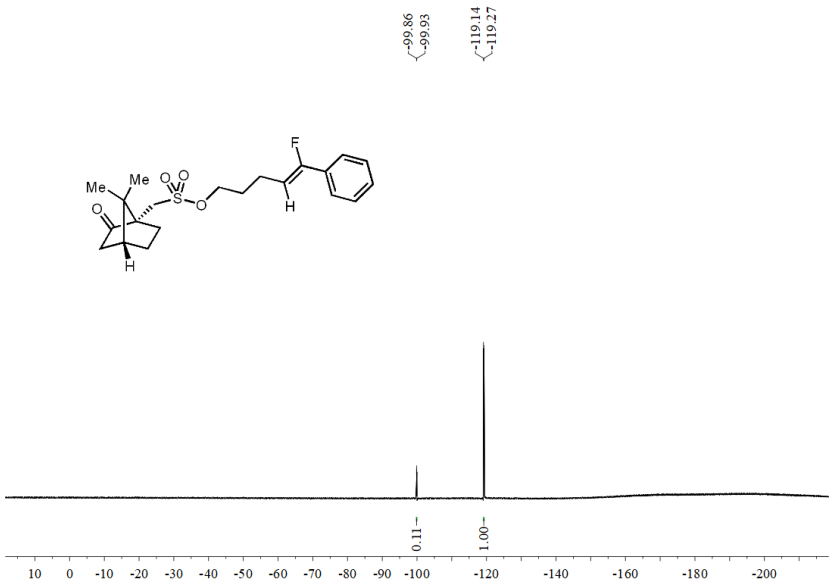
^{1}H NMR (500 MHz, $CDCl_3$) (**87**)



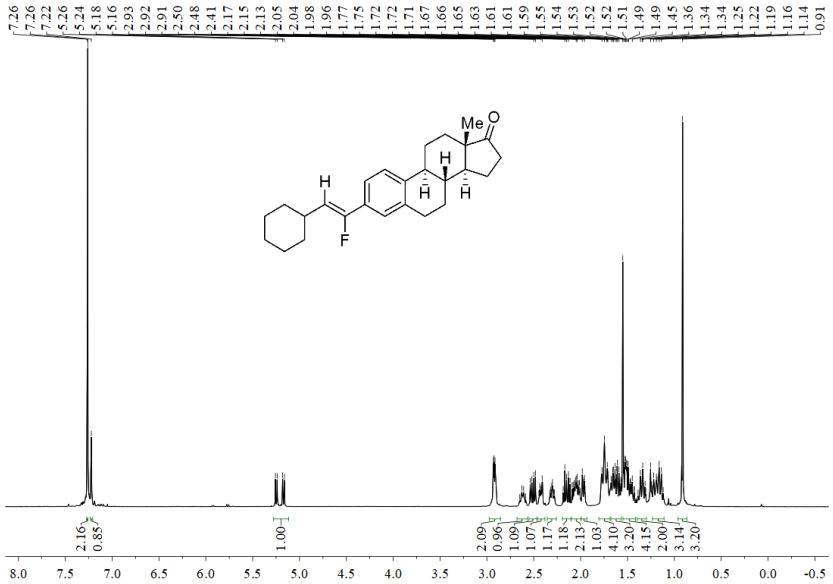
^{13}C NMR (126 MHz, $CDCl_3$) (**87**)



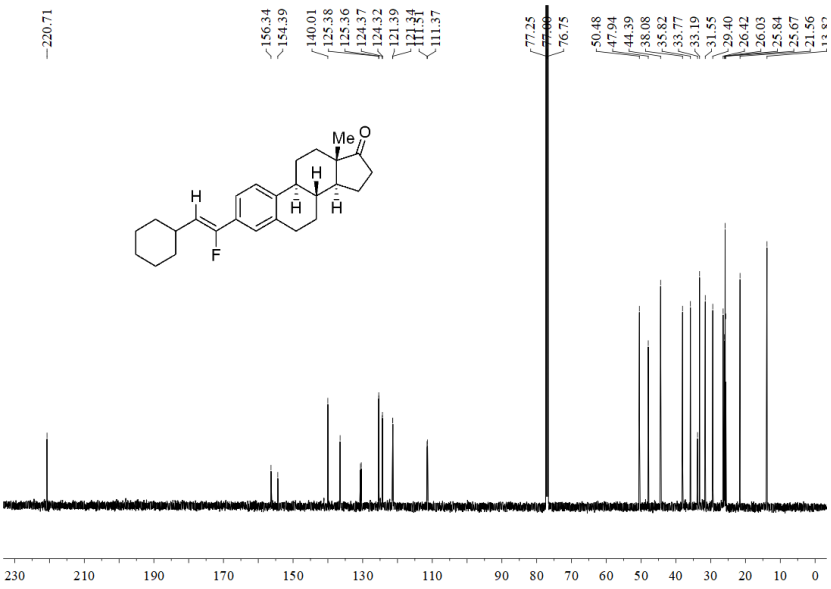
^{19}F NMR (471 MHz, $CDCl_3$) (**87**)



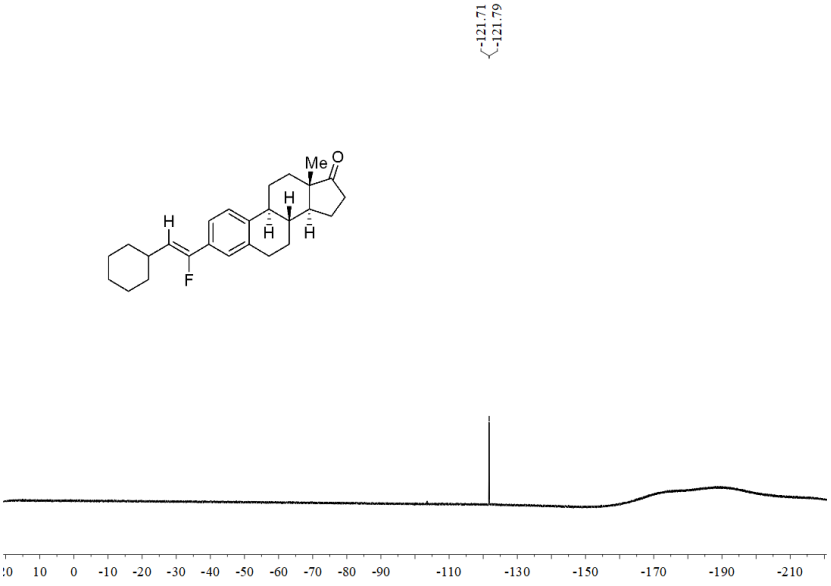
^{1}H NMR (500 MHz, $CDCl_3$) (**88**)



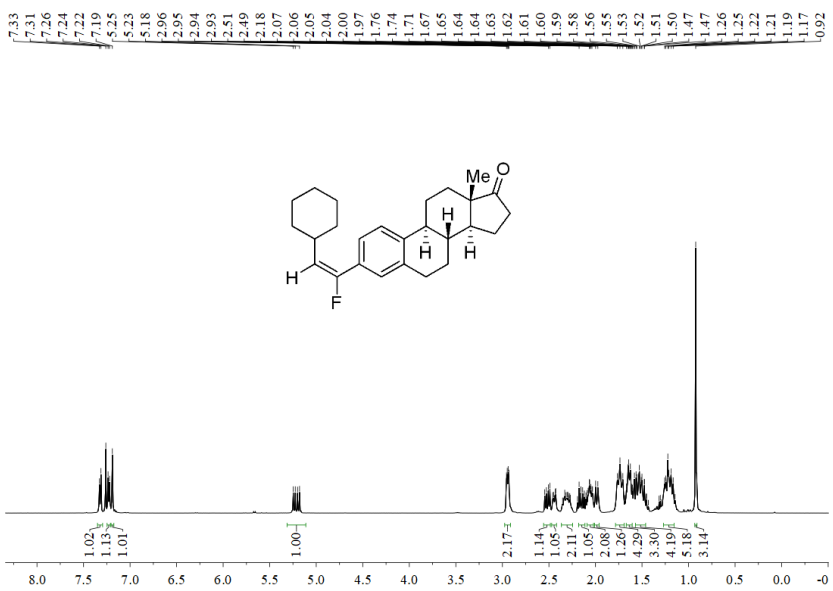
^{13}C NMR (126 MHz, $CDCl_3$) (**88**)



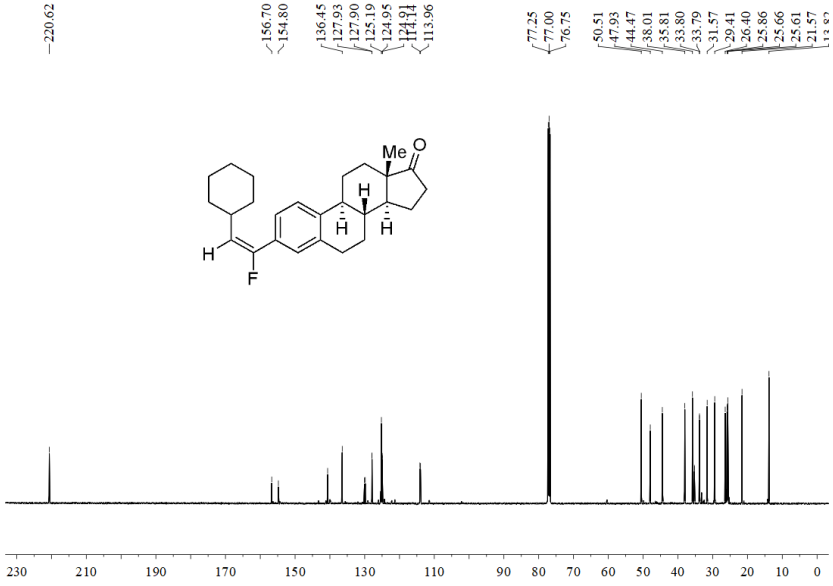
^{19}F NMR (471 MHz, $CDCl_3$) (**88**)



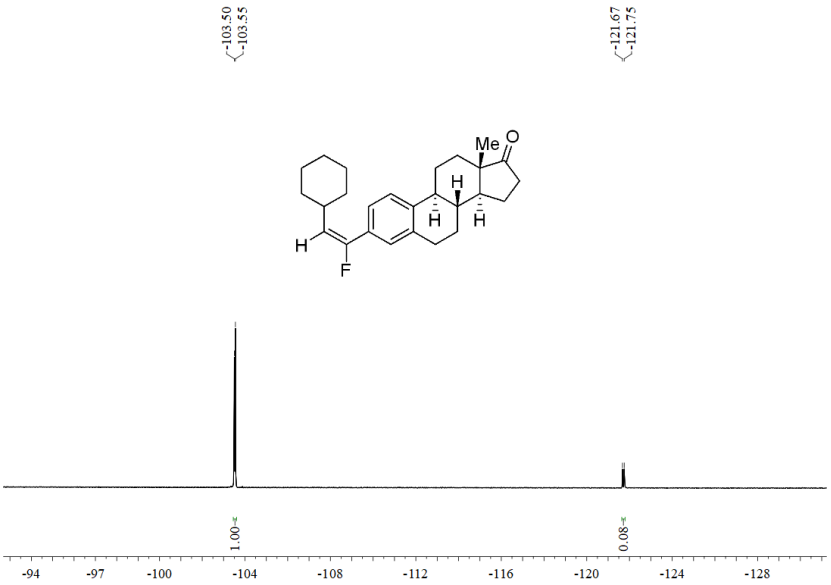
^{1}H NMR (500 MHz, $CDCl_3$) (**89**)



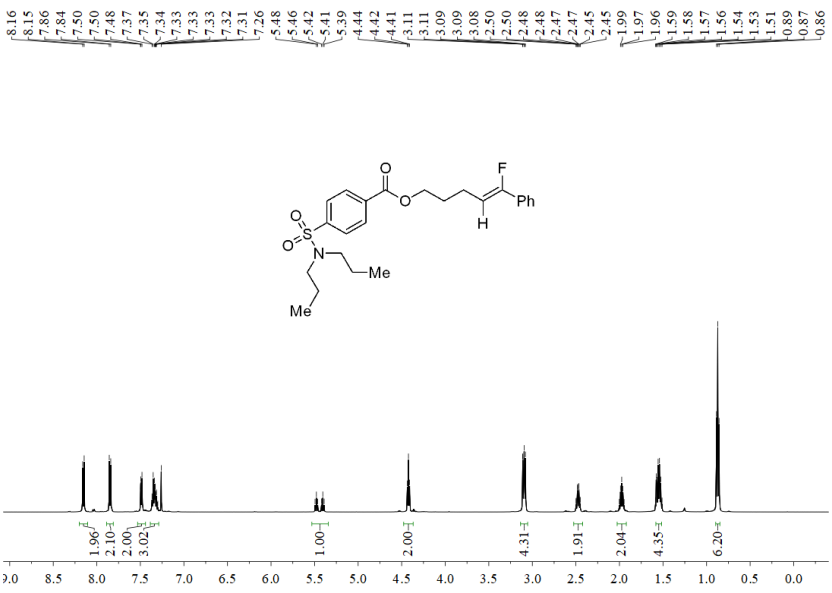
^{13}C NMR (126 MHz, $CDCl_3$) (**89**)



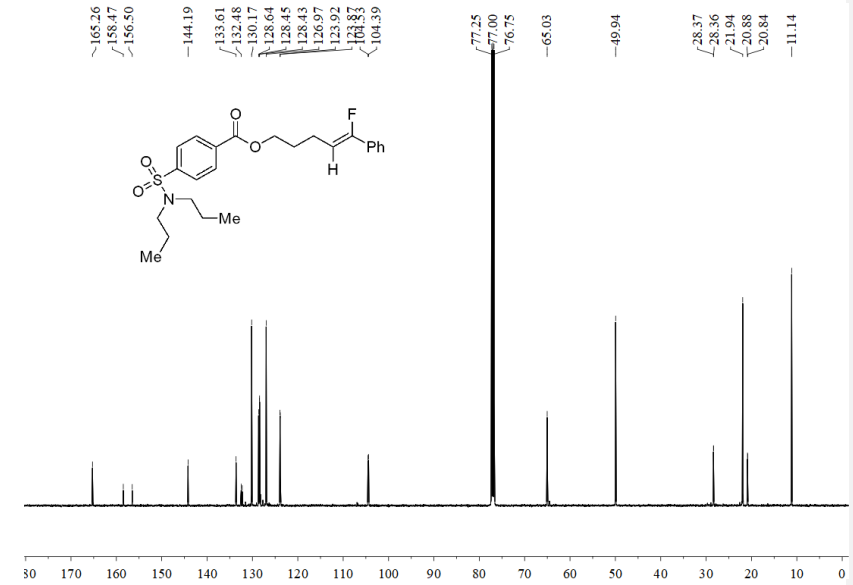
^{19}F NMR (471 MHz, $CDCl_3$) (**89**)



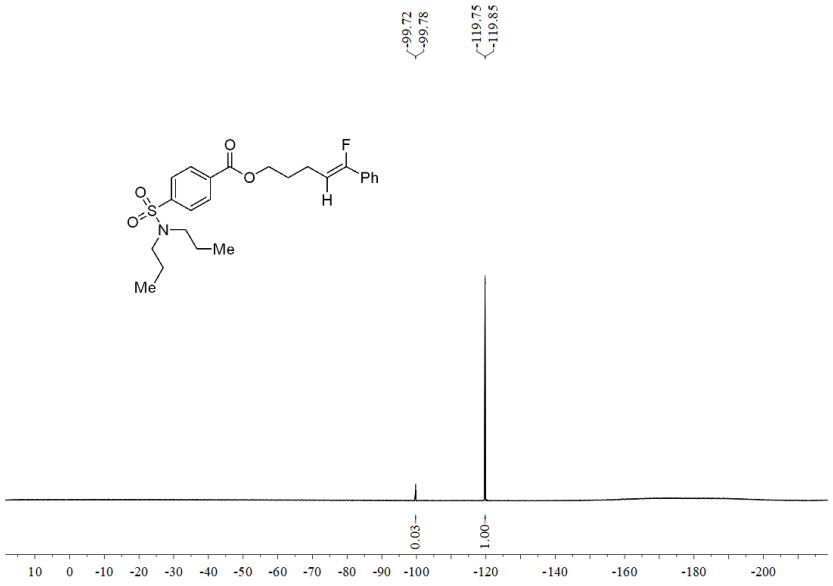
^{1}H NMR (500 MHz, $CDCl_3$) (**90**)



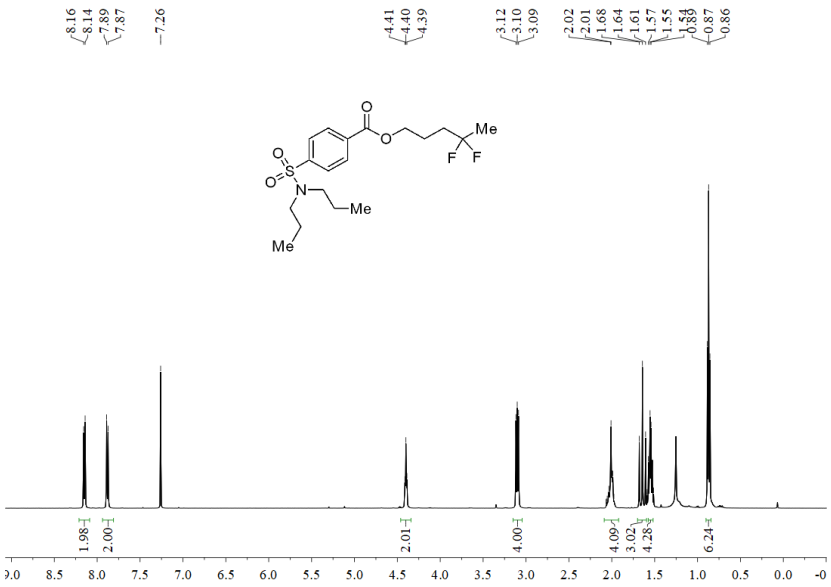
^{13}C NMR (126 MHz, $CDCl_3$) (**90**)



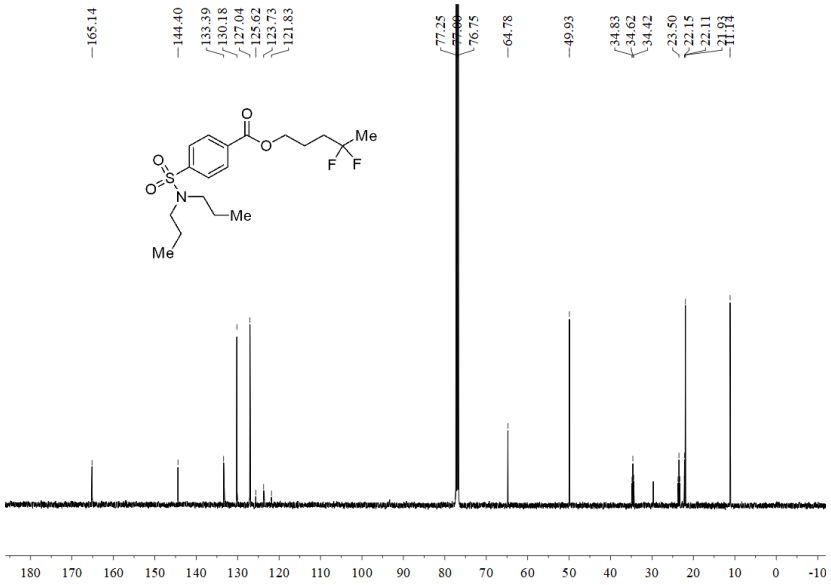
^{19}F NMR (471 MHz, $CDCl_3$) (**90**)



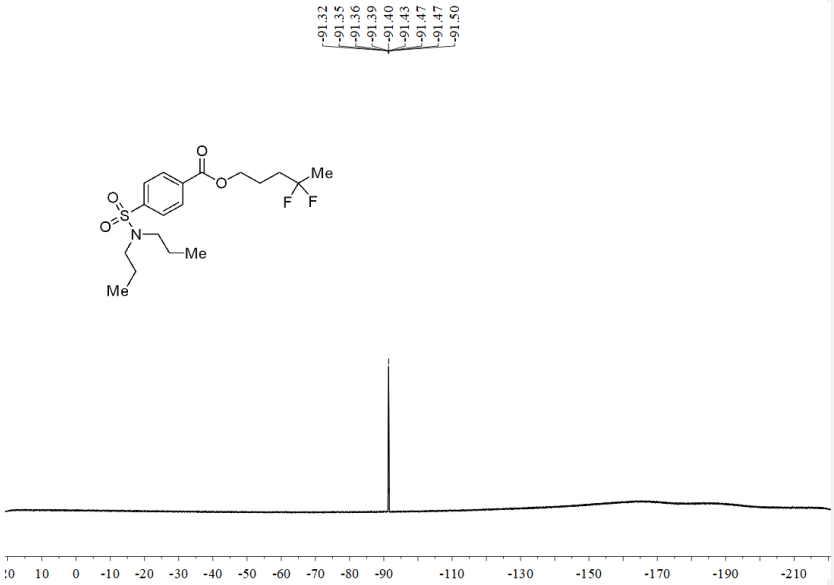
^{1}H NMR (500 MHz, $CDCl_3$) (**91**)



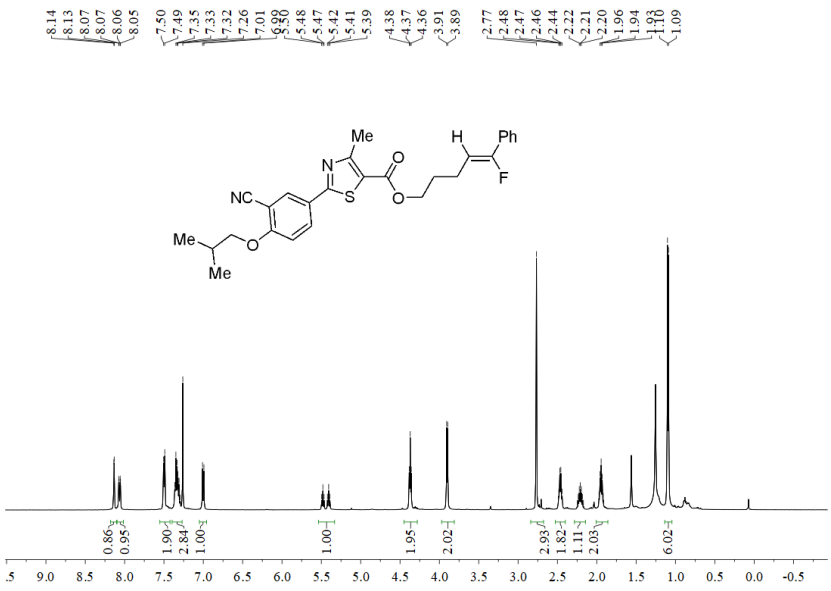
^{13}C NMR (126 MHz, $CDCl_3$) (**91**)



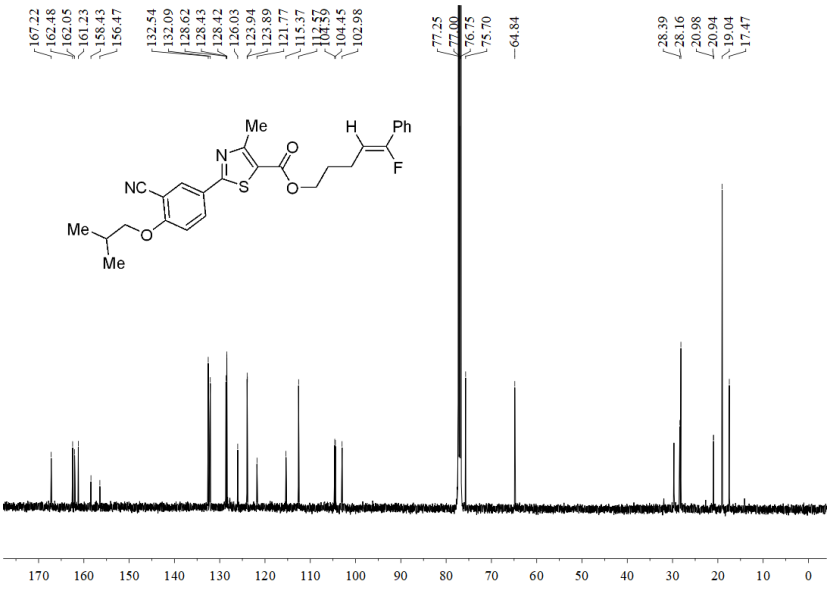
^{19}F NMR (471 MHz, $CDCl_3$) (**91**)



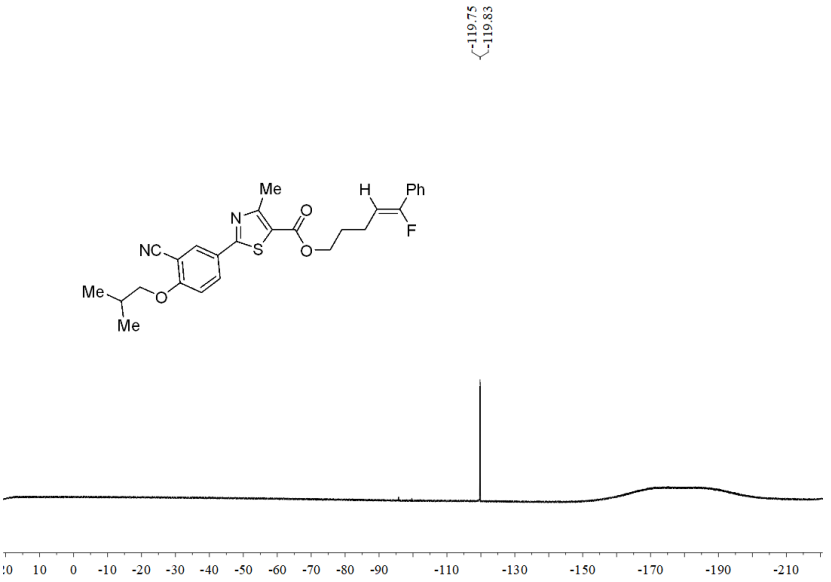
^{1}H NMR (500 MHz, $CDCl_3$) (**92**)



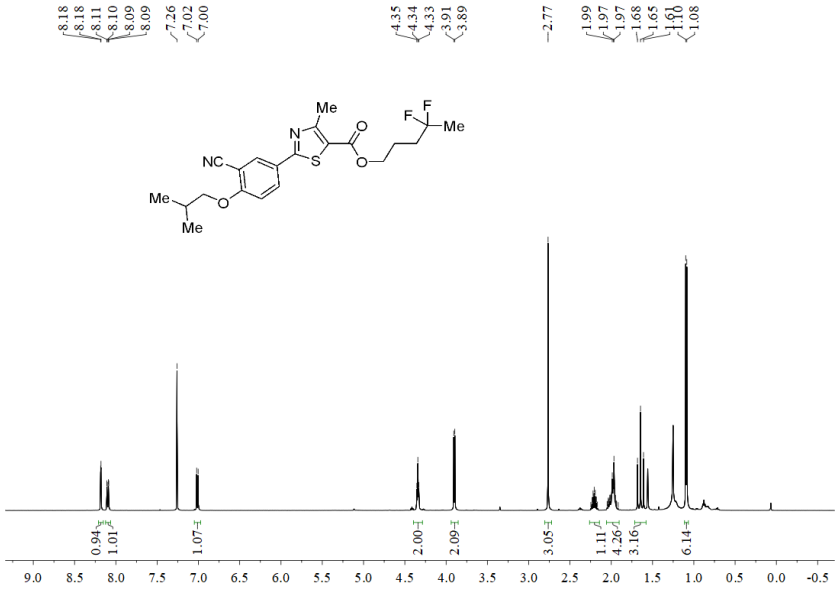
^{13}C NMR (126 MHz, $CDCl_3$) (**92**)



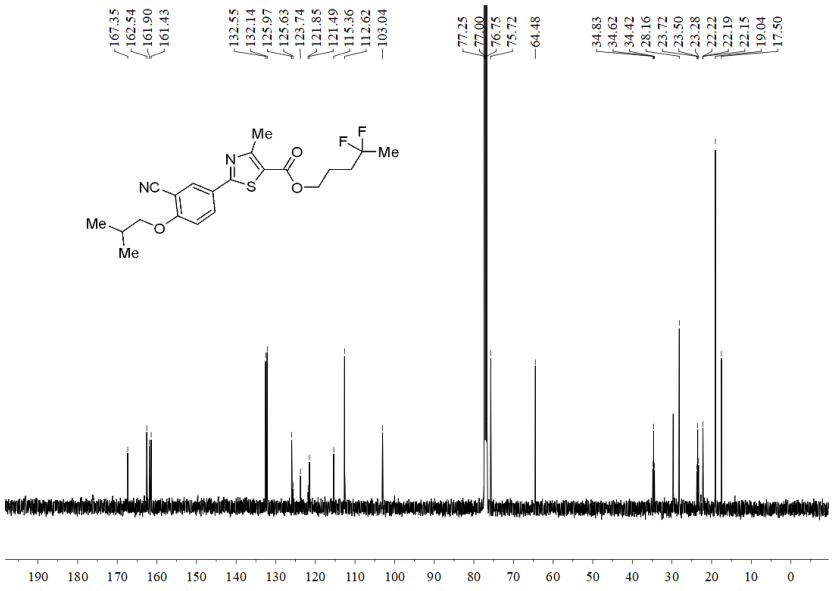
^{19}F NMR (471 MHz, $CDCl_3$) (**92**)



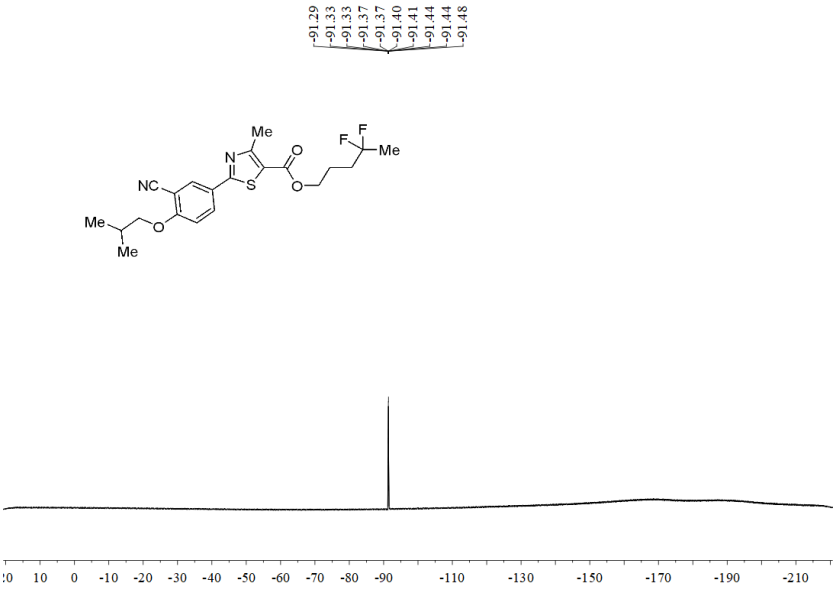
^{1}H NMR (500 MHz, $CDCl_3$) (**93**)



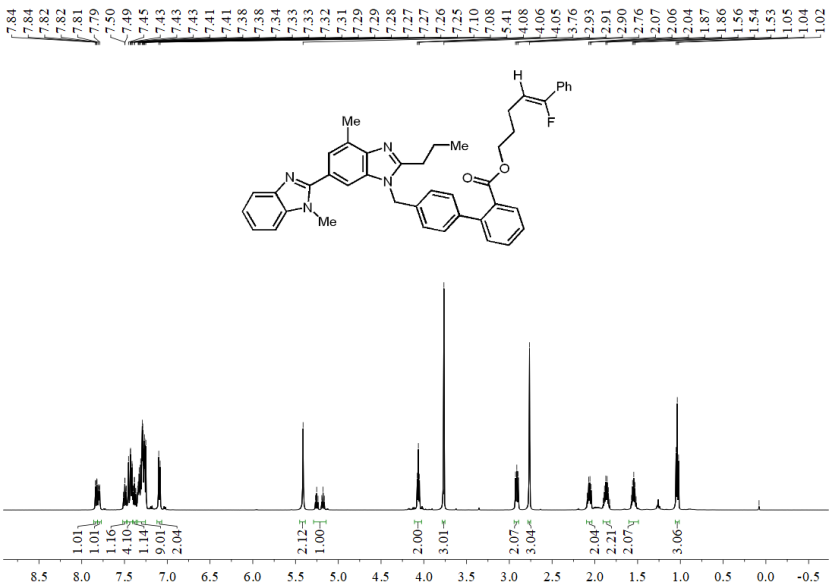
^{13}C NMR (126 MHz, $CDCl_3$) (**93**)



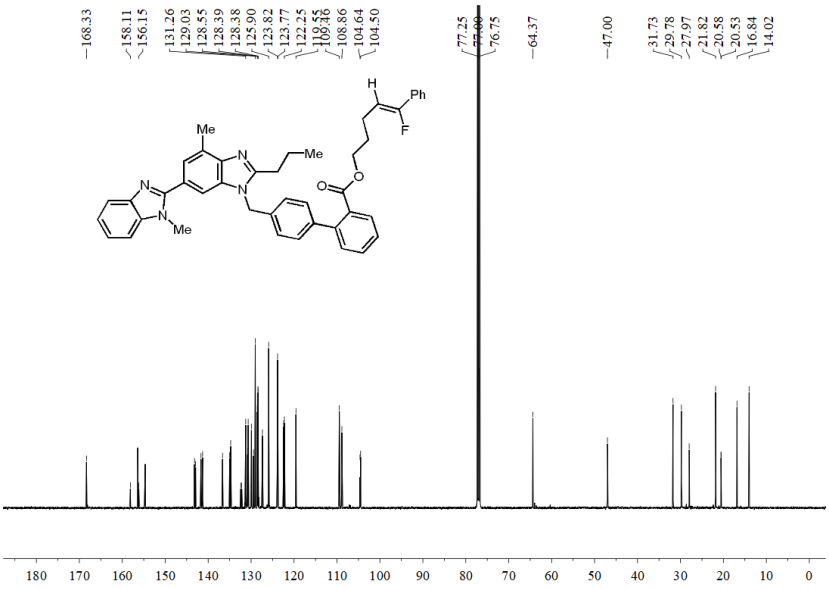
^{19}F NMR (471 MHz, $CDCl_3$) (**93**)



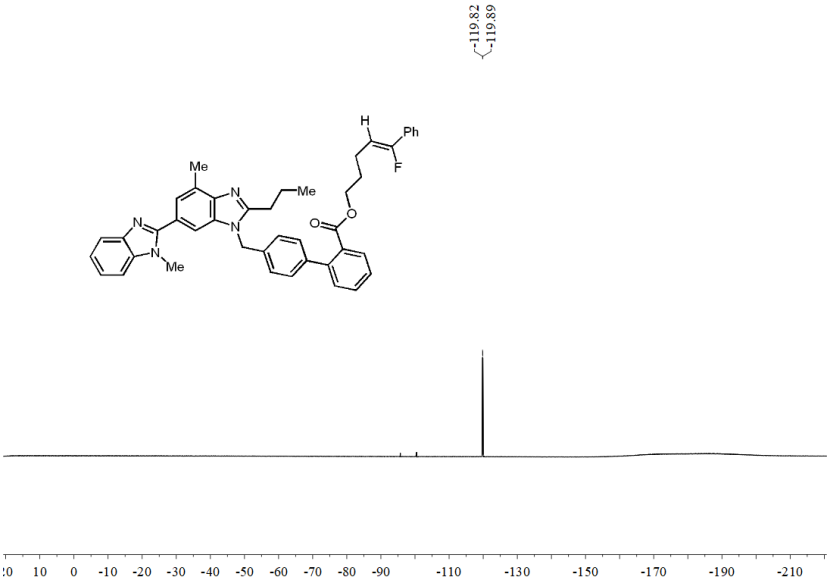
^{1}H NMR (500 MHz, $CDCl_3$) (**94**)



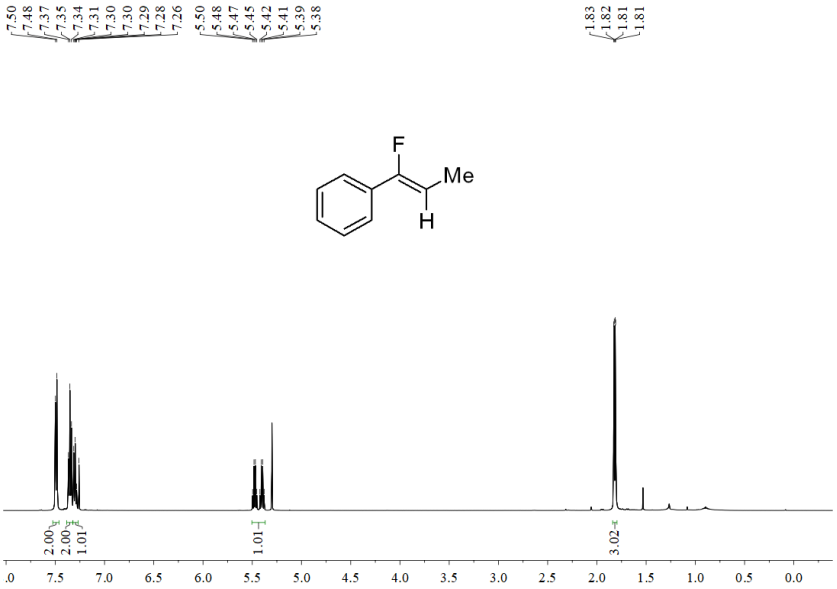
^{13}C NMR (126 MHz, $CDCl_3$) (**94**)



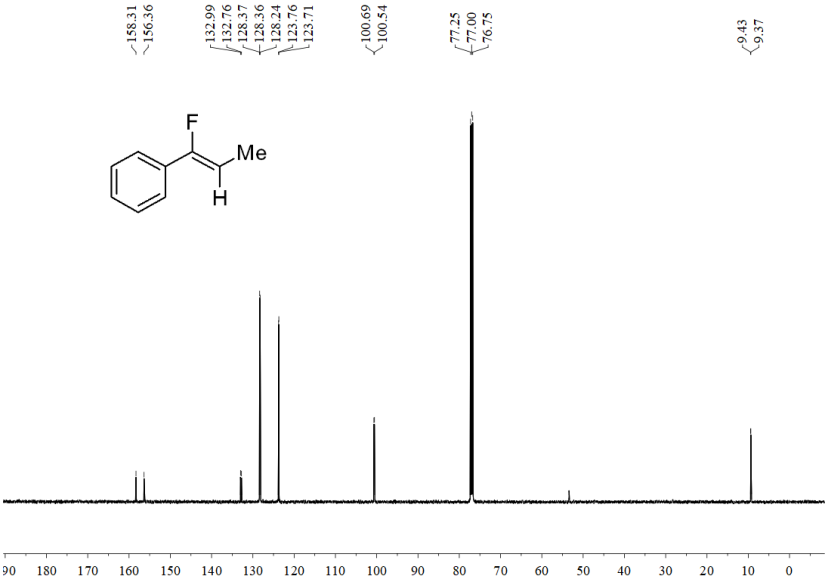
^{19}F NMR (471 MHz, $CDCl_3$) (**94**)



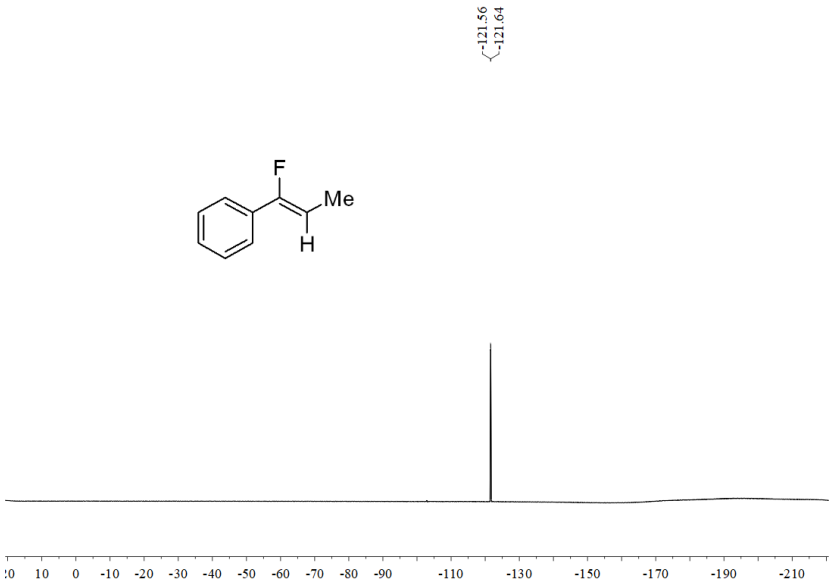
^{1}H NMR (500 MHz, $CDCl_3$) (**95**)



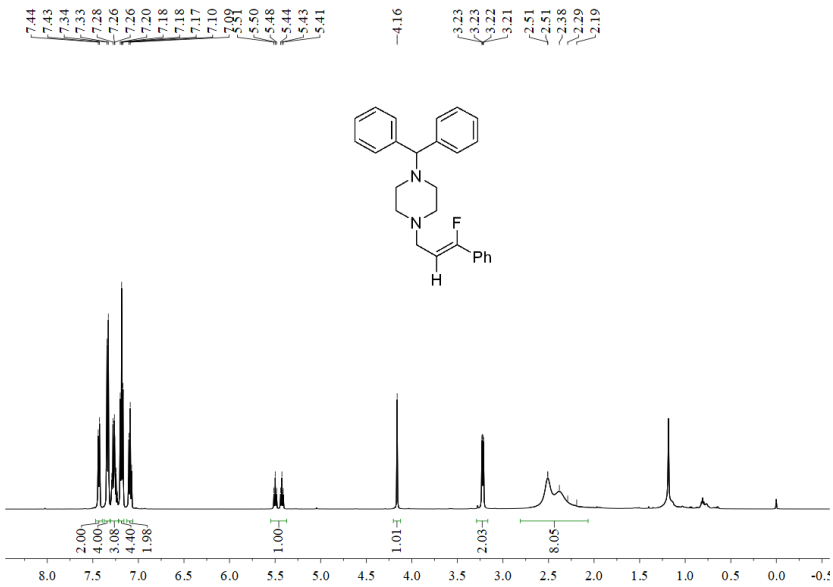
^{13}C NMR (126 MHz, $CDCl_3$) (**95**)



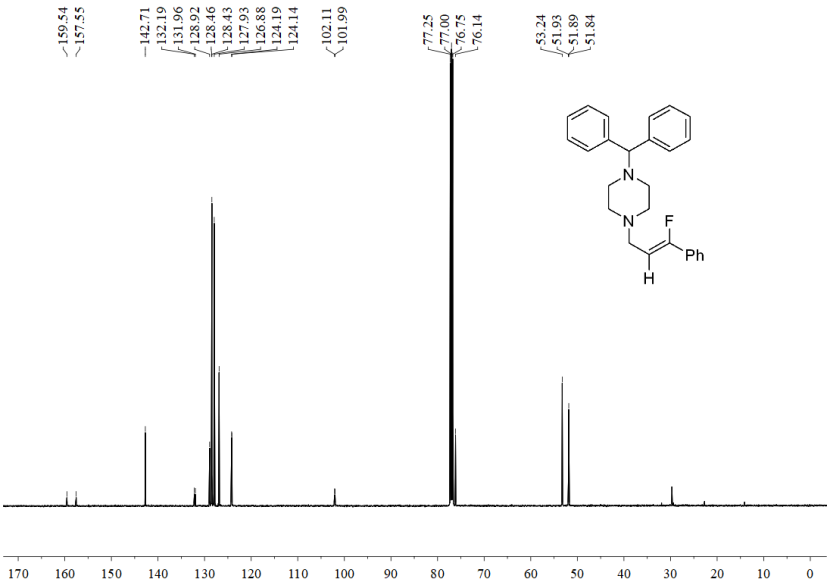
^{19}F NMR (471 MHz, $CDCl_3$) (**95**)



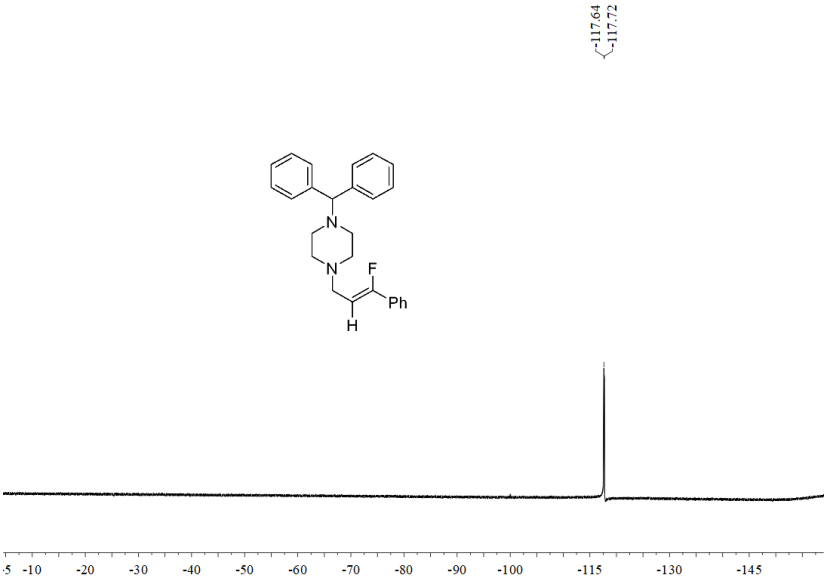
^{1}H NMR (500 MHz, $CDCl_3$) (**97**)



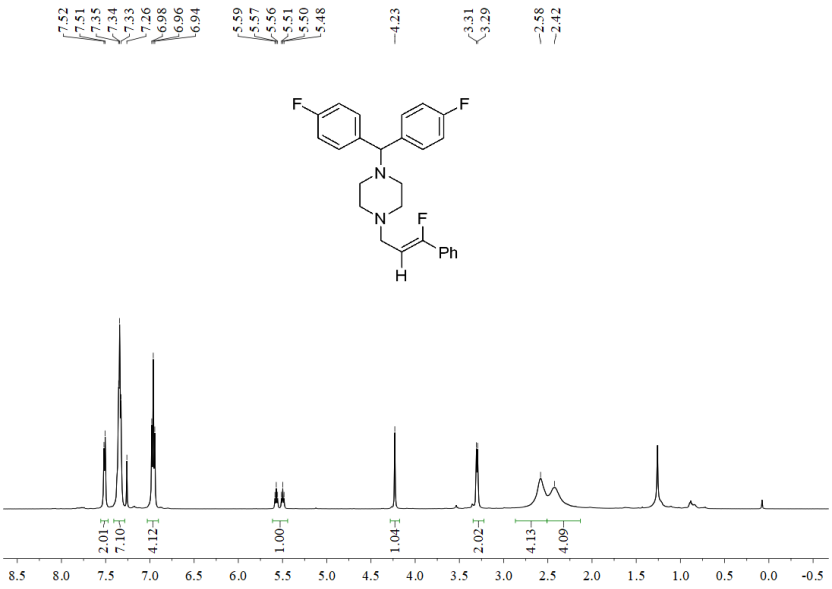
^{13}C NMR (126 MHz, $CDCl_3$) (**97**)



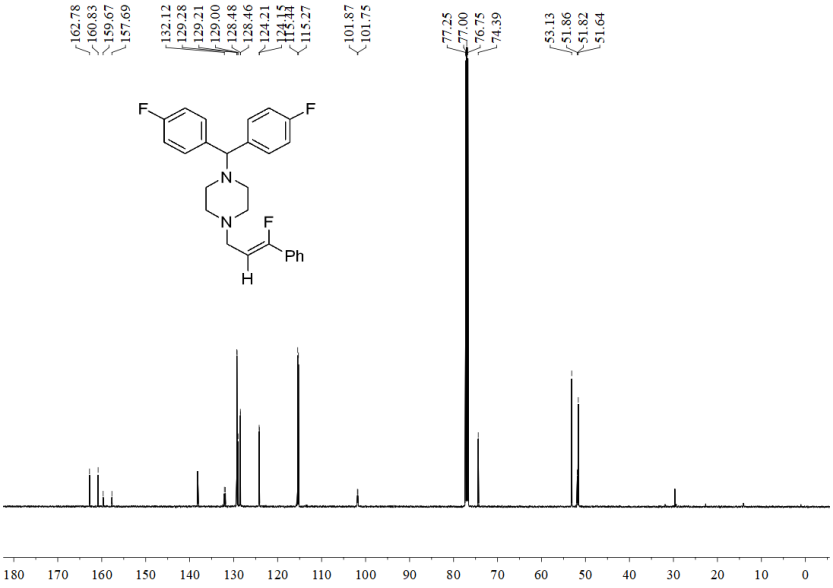
^{19}F NMR (471 MHz, $CDCl_3$) (**97**)



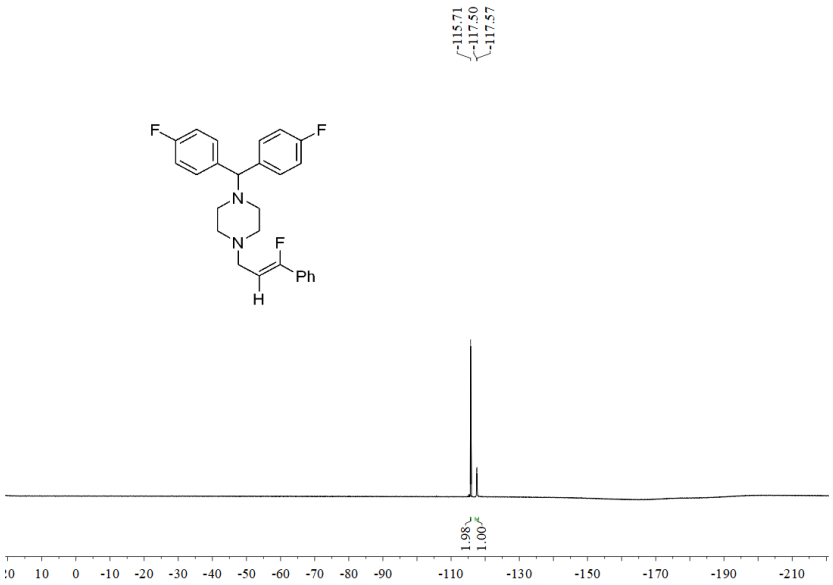
^{1}H NMR (500 MHz, $CDCl_3$) (**98**)



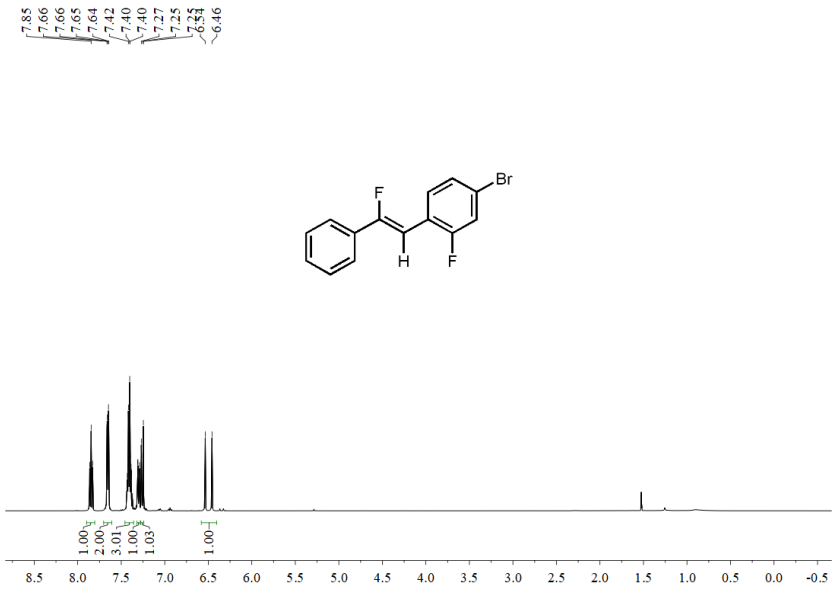
^{13}C NMR (126 MHz, $CDCl_3$) (**98**)



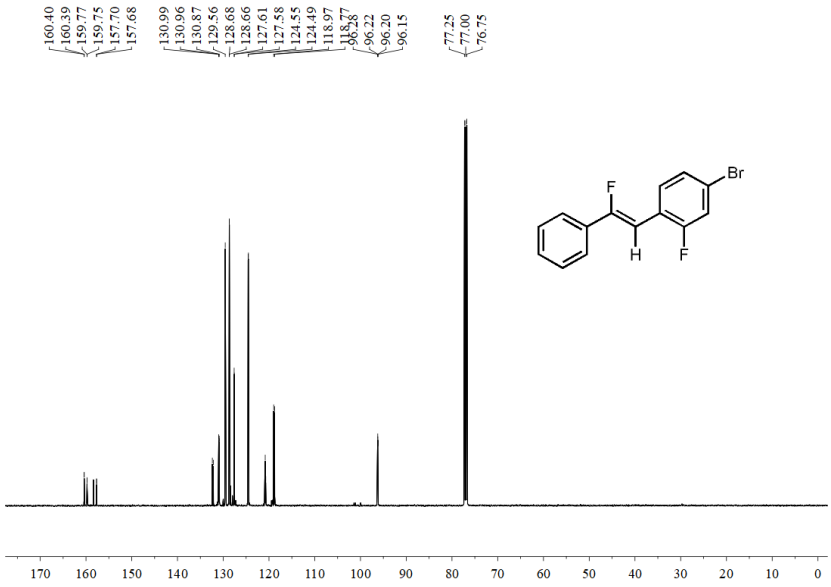
^{19}F NMR (471 MHz, $CDCl_3$) (**98**)



^{1}H NMR (500 MHz, $CDCl_3$) (**100**)



^{13}C NMR (126 MHz, $CDCl_3$) (**100**)



^{19}F NMR (471 MHz, $CDCl_3$) (**100**)