Csp^3–H Monofluoroalkenylation via Stereoselective C–F Bond Cleavage

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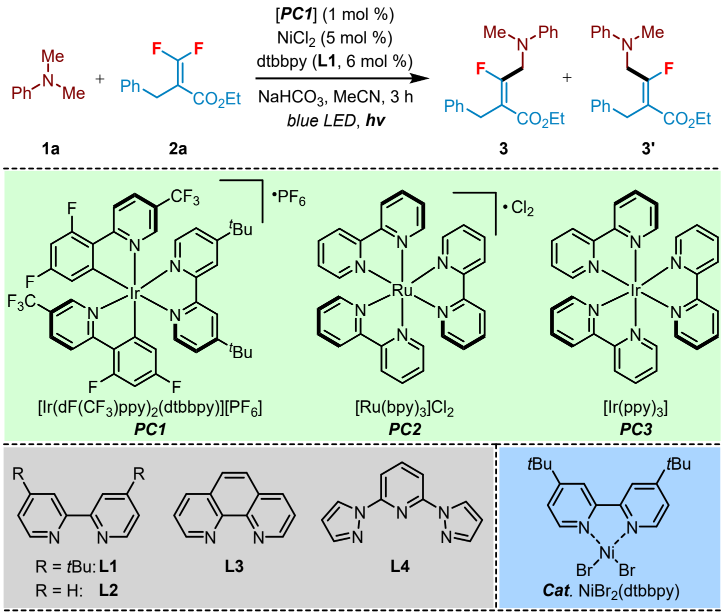
Contents

General Remarks

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under argon. Syringes used to transfer reagents and solvents were purged with N_2 prior to use. The following starting materials were synthesized according to previously described methods: N-aryl amines **1**[1], *gem*-difluoroalkenes **2**[2] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC-analysis. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC were performed using aluminum plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Purification *via* column chromatography was performed using Merck silica gel 60 (40–63 mm 230–400 mesh ASTM from Merck). THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and highresolution mass spectra (HR-MS) were recorded using electro ionization (EI) except where otherwise noted. GCs were recorded on machines of the type Hewlett-Packard 6890 (Hewlett Packard, 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm; film thickness: 0.25 μm).

Optimization Studies

Table S1. Optimization for Stereoselective Alkylation through Csp^3—H/Csp^2—F Bond Cleavage [a]

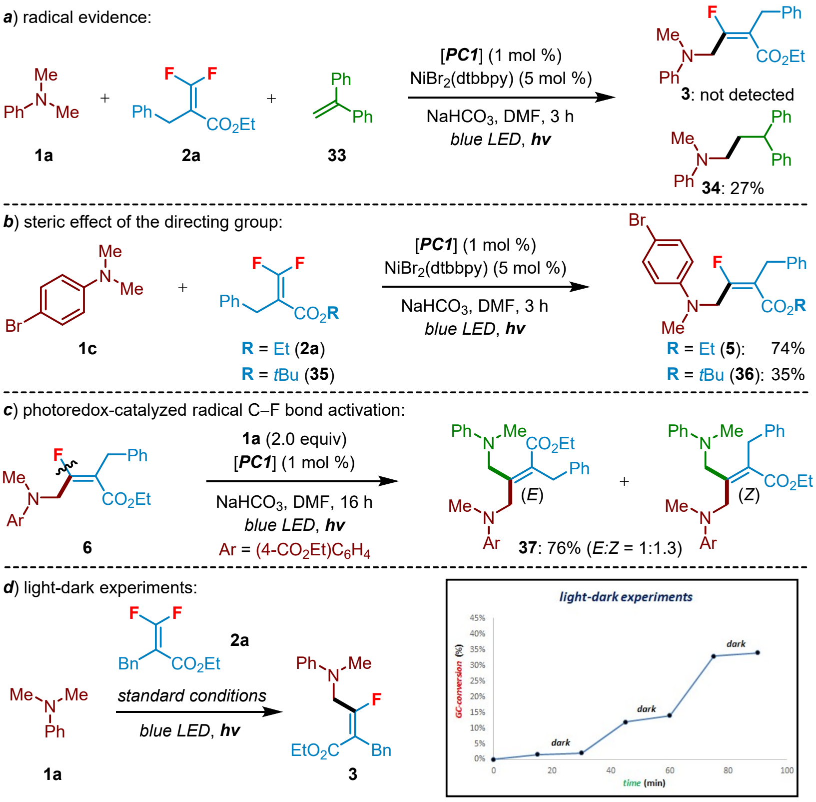


entry	modified conditions	yield (%)[b]
1	*none*	56
2	**PC2** instead of **PC1**	43
3	**PC3** instead of **PC1**	38
4	w/o $NiCl_2$ and **L1**	12
5	w/o $NiCl_2$ and **L1**, DMF instead of MeCN	40 (40)[c]
6	***DMF instead of MeCN***	***78***
7	NMP instead of MeCN	43 (14)[c]
8	DCE instead of MeCN	49
9	1,4-dioxane instead of MeCN	46
10	**L2** instead of **L1**	56[d]
11	**L3** instead of **L1**	60[d]
12	**L4** instead of **L1**	39[d]
13	KOAc instead of $NaHCO_3$	trace[d]
14	K_2HPO_4c instead of $NaHCO_3$	19[d]
15	Na_2CO_3 instead of $NaHCO_3$	67[d]
16	***$NiBr_2$(dtbbpy) instead of $NiCl_2$ and L1***	***80***[d,e]
17	w/o PC1 and light	0[d]

[a] General reaction conditions: **1a** (0.50 mmol, 2.0 equiv), **2a** (0.25 mmol, 1.0 equiv), $NiCl_2$ (5.0 mol %), ligand (6.0 mol %), $NaHCO_3$ (0.50 mmol, 2.0 equiv), anhydrous MeCN (1.0 mL), blue LED (40w, 450–465 nm), 23 °C, 16 h. [b] Isolated yield. [c] Yield of the diaminomethylated product in the parenthess. [d] DMF as the solvent. [e] 3 h.

Additional Experiments

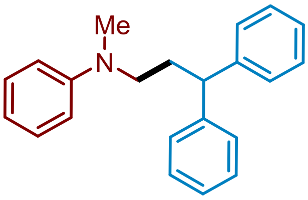
Scheme S2. Mechanistic studies for C–F bond activation.



Procedure for scheme S2a:

(*up*) To a suspension of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)][PF$_6$] (0.01 equiv, 2.8 mg), dtbbpyNiBr$_2$ (0.05 equiv, 5.4 mg), NaHCO$_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **1a** (0.5 mmol, 2 equiv, 60.5 mg), **2a** (0.25 mmol, 1 equiv, 56.5 mg), and TEMPO (0.25 mmol, 1 equiv, 39 mg), then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N$_2$.

(*down*) To a suspension of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)][PF$_6$] (0.01 equiv, 2.8 mg), dtbbpyNiBr$_2$ (0.05 equiv, 5.4 mg), NaHCO$_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **1a** (0.5 mmol, 2 equiv, 60.5 mg), **2a** (0.25 mmol, 1 equiv, 56.5 mg), and **33** (0.25 mmol, 1 equiv, 45 mg), then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N$_2$. Thereafter, the reaction mixture was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (PE/EtOAc 100:1) to isolate **34** (21 mg).



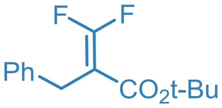
N-(3,3-Diphenylpropyl)-N-methylaniline (34)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.26 (m, 5H), 7.25 (s, 2H), 7.18 (ddd, J = 11.5, 6.5, 3.6 Hz, 5H), 6.66 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 3.92 (t, J = 7.8 Hz, 1H), 3.32 – 3.21 (m, 2H), 2.87 (s, 3H), 2.32 (dd, J = 15.3, 7.7 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.3, 144.7, 129.3, 128.7, 127.9, 126.5, 116.2, 112.4, 51.4, 49.1, 38.4, 32.2. HR-MS (EI) m/z calcd for $C_{22}H_{23}N$ [$M+H^+$] 302.1903, found 302.1908.

Procedure for scheme S2b:

To a suspension of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.01 equiv, 2.8 mg), dtbbpyNiBr_2 (0.05 equiv, 5.4 mg), $NaHCO_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **1c** (0.5 mmol, 2 equiv, 100 mg), **2a** (0.25 mmol, 1 equiv, 56.5 mg), then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N_2. The reaction mixture was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (PE/EtOAc 100:1) to isolate **5** (75 mg, 74%).

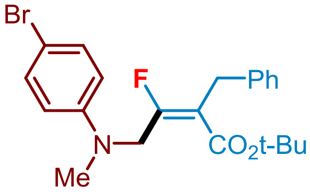
To a suspension of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.01 equiv, 2.8 mg), dtbbpyNiBr_2 (0.05 equiv, 5.4 mg), $NaHCO_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **1c** (0.5 mmol, 2 equiv, 100 mg), **33** (0.25 mmol, 1 equiv, 64 mg), then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N_2. The reaction mixture was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (PE/EtOAc 100:1) to isolate **36** (38 mg, 35%).



***tert*-Butyl 2-benzyl-3,3-difluoroacrylate (35)**

The general procedure **TP1** was followed using *tert*-butyl 3-oxobutanoate (20 mmol) and alkyl bromide (25 mmol). Purification by column chromatography (PE/EtOAc 100:1) yielded **35** (1.8 g, 65%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.09 (m, 5H), 3.53 (t, J = 2.2 Hz, 2H), 1.41 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.6 (dd, J = 12.6, 7.4 Hz), 161.7 (d, J = 294.7 Hz), 158.6 (d, J = 294.8 Hz), 138.8 (T, J = 2.4 Hz), 128.5, 128.4, 126.6, 90.1 (dd, J =

21.0, 5.7 Hz), 82.0, 30.5, 28.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -70.99 (s), -74.74 (d, J = 9.2 Hz). HR-MS (EI) m/z calcd for $C_{14}H_{16}F_2O_2$ [M+H$^+$] 255.1191, found 255.1190.



***tert*-Butyl (*E*)-2-benzyl-4-[(4-bromophenyl)(methyl)amino]-3-fluorobut-2-enoate (36)**

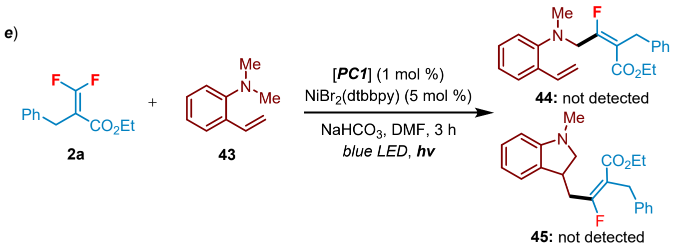
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **36** (38 mg, 35%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.08 (m, 7H), 6.75 – 6.56 (m, 2H), 4.61 (d, J = 19.0 Hz, 2H), 3.62 (d, J = 3.3 Hz, 2H), 3.02 (s, 3H), 1.39 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.1 (d, $^3J_{C–F}$ = 18.2 Hz), 166.0 (d, $^1J_{C–F}$ = 271.9 Hz), 148.1, 139.3 (d, $^4J_{C–F}$ = 1.6 Hz), 131.9, 128.5, 128.4, 126.3, 117.2 (d, $^2J_{C–F}$ = 18.3 Hz), 114.5, 109.4, 82.0, 50.9 (d, $^2J_{C–F}$ = 23.2 Hz), 39.6 (d, $^4J_{C–F}$ = 1.4 Hz), 31.6 (d, $^4J_{C–F}$ = 7.4 Hz), 28.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -94.37 (s). HR-MS (EI) m/z calcd for $C_{22}H_{25}BrFNO_2$ [M+H$^+$] 434.1125, found 434.1129.

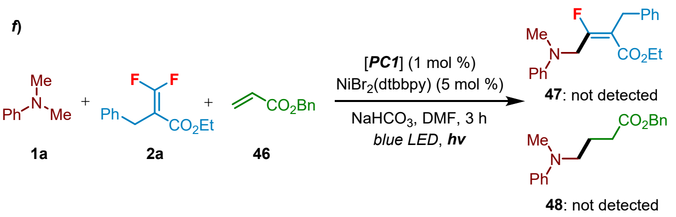
Procedure for scheme S2c:

To a suspension of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.01 equiv, 3.2 mg), $NaHCO_3$ (2 equiv, 46 mg) in anhydrous DMF (1 mL) was added **1a** (0.54 mmol, 2 equiv, 66 mg), **6** (0.27 mmol, 1 equiv, 108 mg), and then the reaction mixture was stirred at 25 °C for 16 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N_2. The reaction mixture was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (PE/EtOAc 20:1) to afford **37** (103 mg, 76%; *E*:*Z* = 1:1.3), .

Procedure for scheme S2d:

To a suspension of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.01 equiv, 2.8 mg), dtbbpyNiBr$_2$ (0.05 equiv, 5.4 mg), $NaHCO_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **1a** (0.5 mmol, 2 equiv, 60.5 mg), **2a** (0.25 mmol, 1 equiv, 56.5 mg), and then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N_2. The reaction conversion was analyzed by GC.





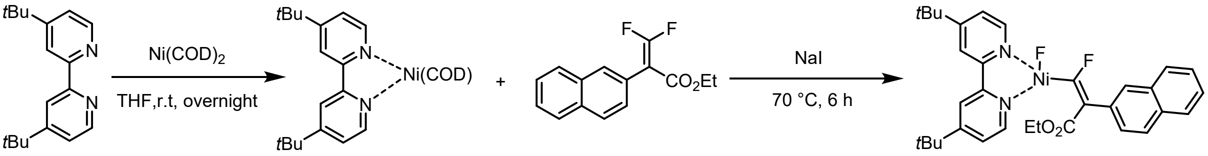
Procedure for scheme S2e:

To a suspension of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)][PF$_6$] (0.01 equiv, 2.8 mg), dtbbpyNiBr$_2$ (0.05 equiv, 5.4 mg), NaHCO$_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **43** (0.5 mmol, 2 equiv, 74 mg), **2a** (0.25 mmol, 1 equiv, 56.5 mg), and then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N$_2$.

Procedure for scheme S2f:

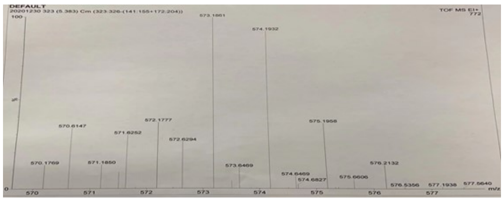
To a suspension of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)][PF$_6$] (0.01 equiv, 2.8 mg), dtbbpyNiBr$_2$ (0.05 equiv, 5.4 mg), NaHCO$_3$ (2 equiv, 42 mg) in anhydrous DMF (1 mL) was added **1a** (0.5 mmol, 2 equiv, 60.5 mg), **2a** (0.25 mmol, 1 equiv, 56.5 mg), **46** (0.25 mmol, 1 equiv, 40.5 mg), and then the reaction mixture was stirred at 25 °C for 3 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N$_2$.

Evidence for oxidative insertion of Ni species to difluoroalkene:[4]



Ni-A $[M]^+$ = 588.2098

MS (EI) m/z calcd for $C_{32}H_{33}F_2N_2NiO_2$ $[M-CH_3]^+$ 573.1864, found 573.1861



In a nitrogen filled glove box, a 25 mL schlenk tube containing a stirring bar was charged with Ni(COD)2 (27.6 mg, 0.1 mmol, 1.0 equiv), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy, 26.8 mg, 0.1 mmol, 1.0 equiv) and dry THF (1 mL) giving a dark purple mixture which was stirred for 12 hours at 25 °C. Ethyl 3,3-difluoro-2-(naphthalen-2-yl)acrylate (26.2 mg, 0.1 mmol, 0.1 equiv) and NaI (30 mg, 0.2 mmol, 2.0 equiv) were added. After sealing this vessel with plug, it was taken out of the glovebox, then stirred at 70 °C for additional 6 h. After cooling the reaction mixture to room temperature, this tube was transferred into the glovebox, then solvent was completely removed to afford crude solid. The obtained solid dissolved in DCM for HR-MS analysis.

Fluorescence Quenching Experiments:

The test conditions for quenching reactions (I_0 and I are respective fluorescence intensities in the absence and presence of the quenchers):

[Ir]: 4.5 mg $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ dissolved in 50 mL DMF

Quenchers:

22.6 mg of **2a** dissolved in 25 mL DMF.

20 mg of **S5** dissolved in 25 mL DMF.

48.6 mg of **dtbbpy • $NiBr_2$** dissolved in 25 mL DMF.

8.4 mg of **$NaHCO_3$** dissolved in 25 mL DMF.

***Procedure*:**

Prepared solution containing **[Ir]**, **Quenchers** and DMF were added to a cuvette as the following table:

	[Ir]	quenchers	DMF	Total volume
a	1 mL	0 mL	3 mL	4 mL
b	1 mL	0.25 mL	2.75 mL	4 mL
c	1 mL	0.5 mL	2.5 mL	4 mL
d	1 mL	0.75 mL	2.25 mL	4 mL
e	1 mL	1 mL	2 mL	4 mL

Stern-Volmer experiments were conducted with a fixed excitation wavelength of 365 nm.

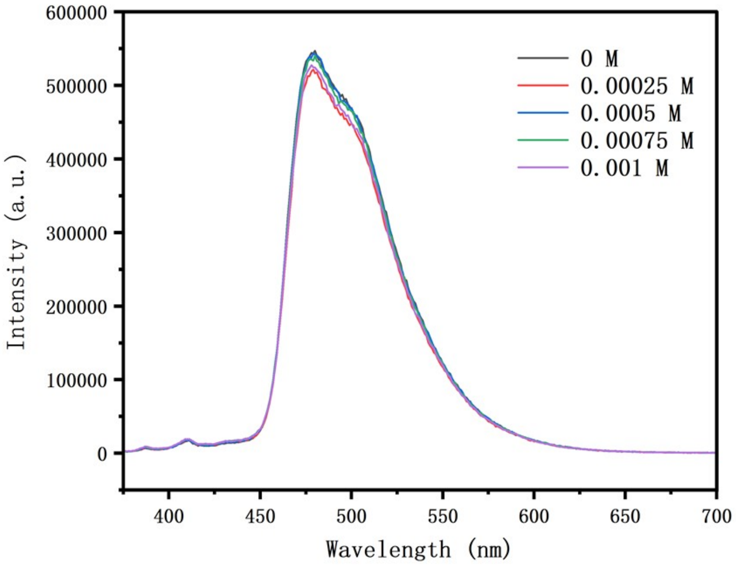


Figure S-1. Fluorescence quenching experiments with ***2a***

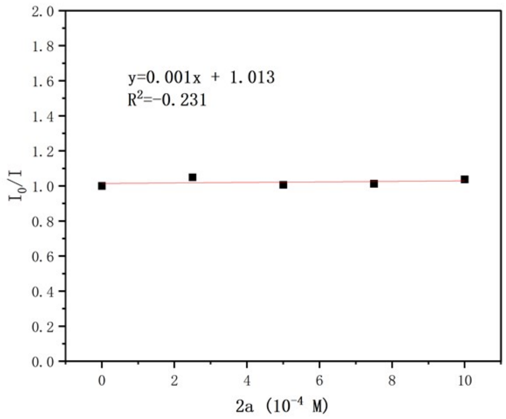


Figure S-2. Stern-Volmer plots of ***2a***

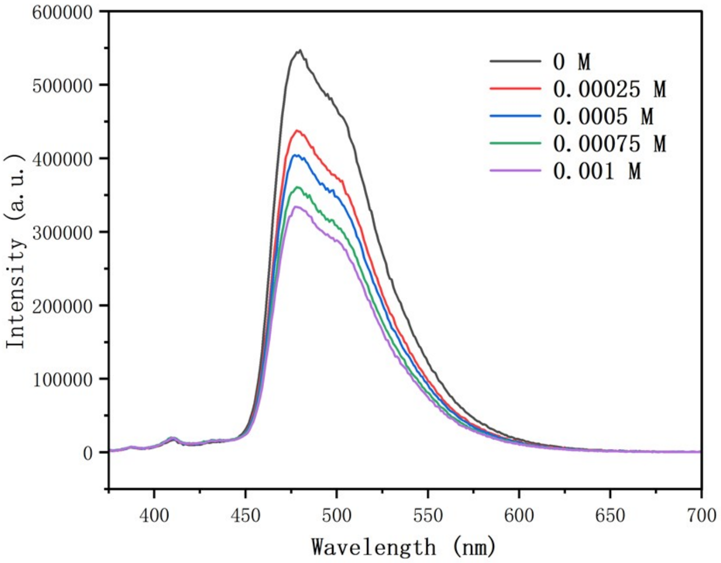


Figure S-3. Fluorescence quenching experiments with ***S5***

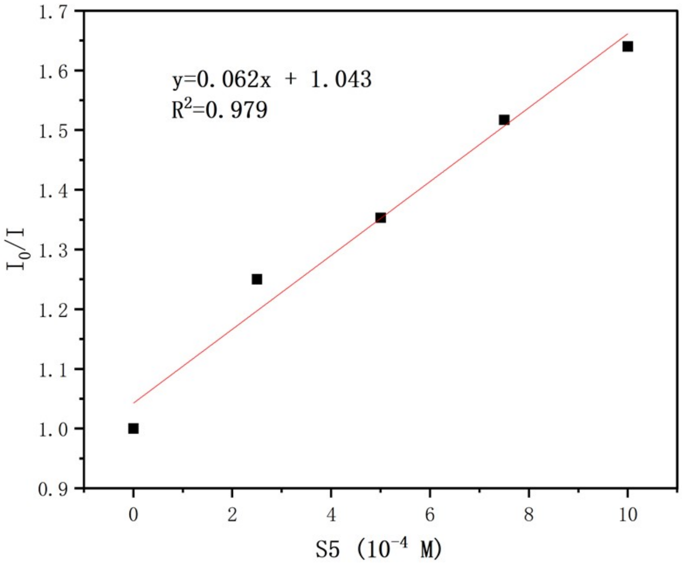


Figure S-4. Stern-Volmer plots of ***S5***

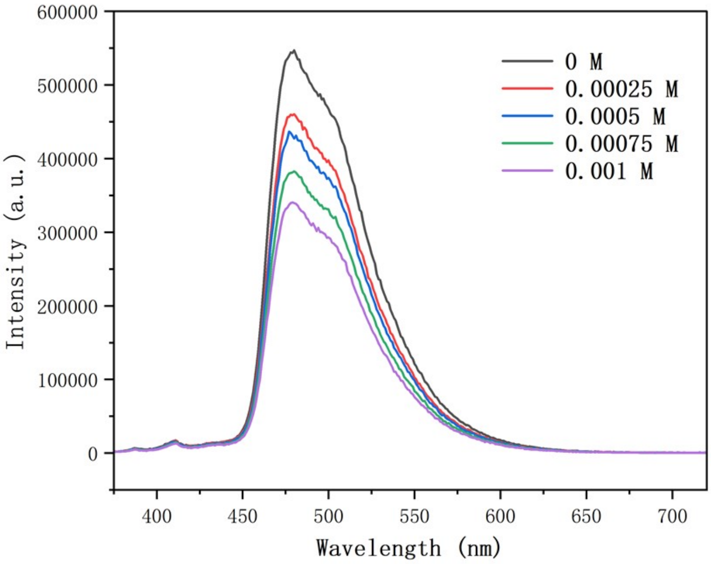


Figure S-5. Fluorescence quenching experiments with ***dtbbpy·NiBr$_2$***

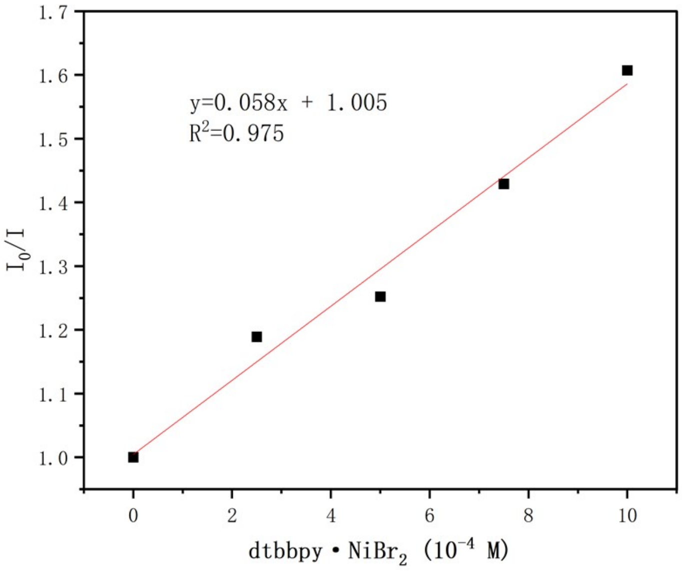


Figure S-6. Stern-Volmer plots of **$NiBr_2$(dtbbpy)**

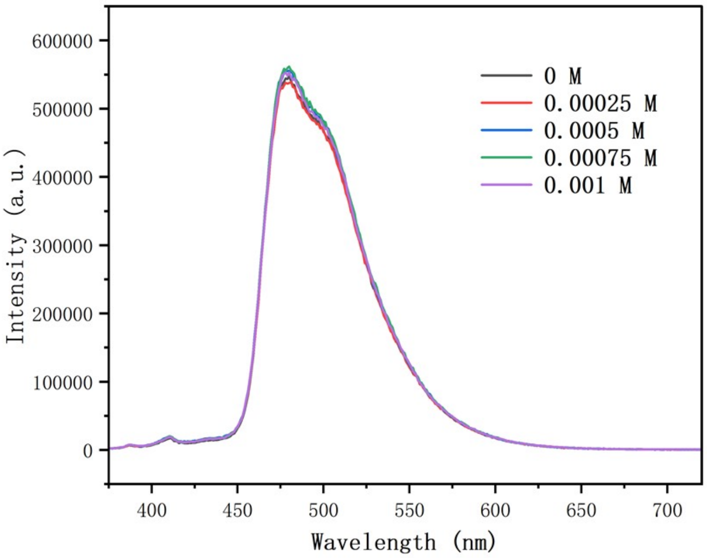


Figure S-7. Fluorescence quenching experiments with ***$NaHCO_3$***

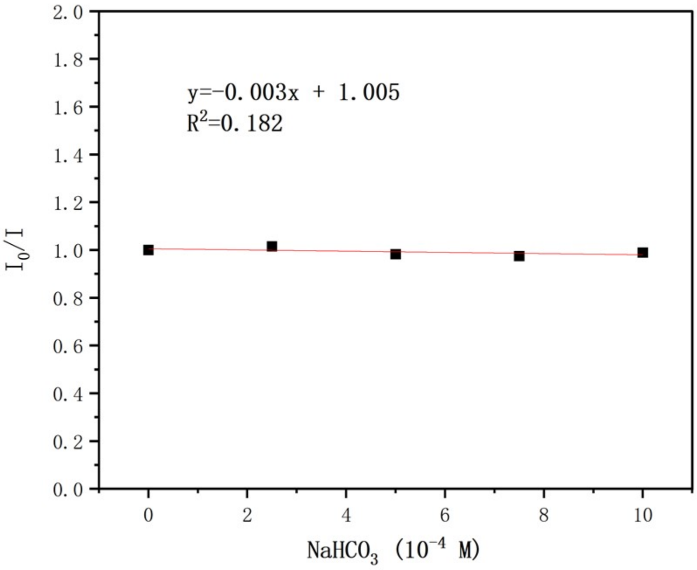


Figure S-8. Stern-Volmer plots of ***$NaHCO_3$***

Inference: Fluorescence quenching was only observed for **[Ir]** given that substrate **S5** and ***dtbbpy·NiBr$_2$*** were present.

Quantum Yield Measurement

The measured method was designed according to a published procedure by Ackermann with slight modifications [3].

Preparation of potassium ferrioxalate solution:

295 mg of solid potassium ferrioxalate, 140 µL H_2SO_4 were diluted with H_2O to a finale volume of 50 mL.

Preparation of buffer solution:

4.95 g NaOAc and 1 mL H_2SO_4 were diluted with H_2O to a finale volume of 100 mL. Using the same setup as for catalytic reactions 0.7 mL of the potassium ferrioxalate solution were irradiated for 20 sec. The sample solution was added to of 1.4 mL of the buffer solution containing 10 mg 1,10-phenanthroline. The solution was diluted with H_2O to a finale volume of 3.5 mL. Subsequently the absorbance of this solution was determined at 510 nm. The same procedure was followed for a nonirradiated sample.

Calculation Number of Photons:

Abs of Fe^{2+} (at 510 nm) = 5.455 (after irradiation of 20 sec)

Abs of Fe^{2+} (at 510 nm) = 0.043 (no irradiation)

ΔAbs of Fe^{2+} (at 510 nm) = 5.455-0.043 = 5.412

$$[Fe^{2+}] = \frac{\text{Abs of } Fe^{2+} (\text{at } 510 \text{ nm})}{e_{510nm} \text{ X } 1}$$

$$[Fe^{2+}] = \frac{5.412}{11100 M^{-1}cm^{-1} \times 1} = 4.876 \times 10^{-4} M$$

$$n_{(Fe2+)} = 4.876 \text{ M} \times 0.0035 \text{ L} = 1.707 \times 10^{-6}$$

with quantum yield of 0.9 for the absorption of Fe^{3+}:

$$n_{(photons)} = 1.897 \times 10^{-6}$$

$$n_{(photons)} = 9.485 \times 10^{-8} \text{ mol/s}$$

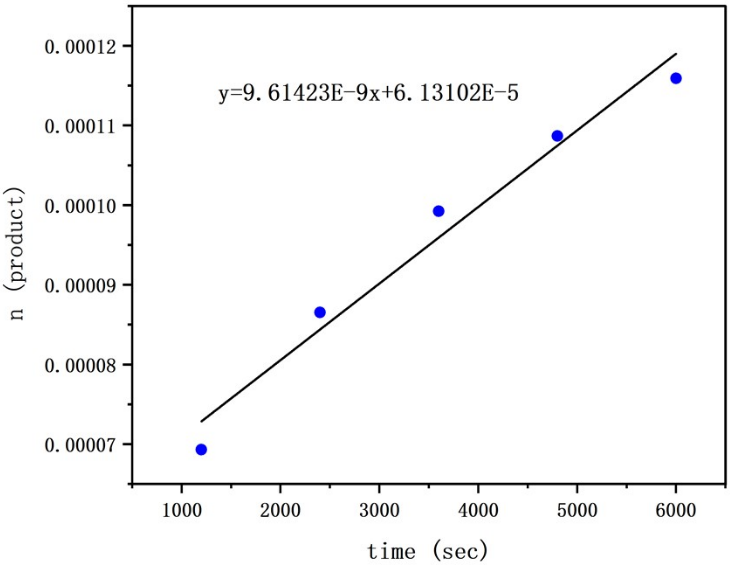
The initial rate of the alkenylation was determined to be 9.614 × 10^{-9} mol/s.

$$\text{Quantum Yield} = \frac{n_{product} / s}{n_{photons} / s} = \frac{9.614 \times 10^{-9}}{9.485 \times 10^{-8}} = 0.101$$

Determination Initial Rate:

Product formation was monitored by GC using dodecane as internal standard.

Time in s	1200	2400	3600	4800	6000
Yield by GC [%]	27.7	34.6	39.7	43.5	46.4
N(product) x 10^{-5}	6.92893	8.65212	9.92194	10.86836	11.58935



Representative Procedures

Typical procedure 1 (*TP1*) for the synthesis of *gem*-difluoroalkenes 2[2]:

Step 1: To a solution of *t*-BuOK (21 mmol) in THF (40 mL) was added ethyl acetoacetate (20 mmol) at 0 °C. Then the solution was stirred for 30min, and alkyl bromide (25 mmol) in THF (10 mL) was added. The resulting mixture was heated under reflux conditions (85 °C) overnight. The mixture was quenched with saturated aqueous NH_4Cl, then the aqueous layer was extracted with ethyl acetate and the organic phase was washed with water. Afterwards the organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel to yield desired product.

Step 2: The previous product and *p*-ABSA (1.5 equiv.) were dissolved in CH_3CN (30 mL), then DBU (1.5 equiv.) was added dropwise at ambient temperature. After stirring for 5h, the reaction mixture was extracted with ethyl acetate and the organic phase was washed with water. Afterwards the organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel to yield desired product.

Step 3: To an oven-dried 100 mL flask equipped with a stir bar was added NaI (2.2 equiv.), the solid was heated at 60 °C under vacuo for 30 min to remove H_2O. Then NaI was cooled down to room temperature followed by the addition of the product of the Step 2, and $TMSCF_3$ (2.4 equiv.) in 48 mL anhydrous THF under argon. The resulting mixture was heated at 60 °C with an oil bath for 5 h with sharp stirring. After cooling to room temperature, the reaction mixture was extracted with Et_2O three times, washed with H_2O then brine (80 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford *gem*-difluoroalkenes.

Typical Procedure 2 (*TP2*) for the Nickel- and Photoredox-Catalyzed Stereoselective Monofluoroalkenylation:

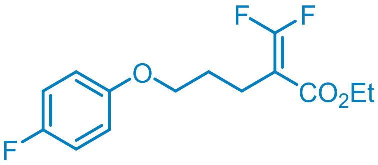
To a suspension of $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (0.01 equiv), $dtbbpyNiBr_2$ (0.05 equiv), $NaHCO_3$ (2.0 equiv) in anhydrous DMF was added N-aryl amines **1** (0.5 mmol, 2.0 equiv) and *gem*-difluoroalkenes **2** (0.25 mmol, 1.0 equiv), then the reaction mixture was stirred at 25 °C for 6 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (PE/EtOAc) to yield products **3–32**, **37**.

Typical Procedure 3 (*TP3*) for the Photoredox-Catalyzed Twofold Csp^2–F Bond-Diaminomethylation:

To a suspension of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)][PF$_6$] (0.01 equiv), NaHCO$_3$ (2.0 equiv) in anhydrous DMF was added N-aryl amines **1** (0.75 mmol, 3.0 equiv) and *gem*-difluoroalkenes **2** (0.25 mmol, 1.0 equiv), then the reaction mixture was stirred at 25 °C for 6 h with *Blue LED* (40 W, 450–465 nm) under an atmosphere of N$_2$. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (PE/EtOAc) to yield products **38–42**.

Diethyl 2-(difluoromethylene)octanedioate (2g)

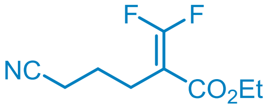
The general procedure **TP1** was followed using ethyl acetoacetate (21 mmol) and alkyl bromide (25.2 mmol). Purification by column chromatography (PE/EtOAc 50:1) yielded **2g** (1.37 g, 81%) as an oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 4.24 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 2.26 – 2.19 (m, 2H), 1.64 (dt, J = 15.2, 7.5 Hz, 2H), 1.51 – 1.43 (m, 2H), 1.36 (dd, J = 8.9, 6.3 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$) : δ = 173.8, 165.0 (dd, J = 13.3, 7.7 Hz), 160.0 (dd, J = 309.9, 294.6 Hz), 88.9 (dd, J = 23.3, 4.9 Hz), 61.2, 60.3, 34.3, 28.6, 28.3, 24.7, 24.4, 14.4, 14.3. ^{19}F-NMR (376 MHz, CDCl$_3$) : δ = -69.71 (s), -74.55 (s). HR-MS (EI) m/z calcd for $C_{13}H_{20}F_2O_4$ [M+H$^+$] 279.1402, found 279.1412.



Ethyl 2-(difluoromethylene)-5-(4-fluorophenoxy)pentanoate (2h)

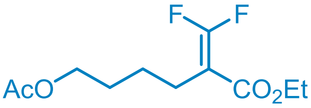
The general procedure **TP1** was followed using ethyl acetoacetate (10 mmol) and alkyl bromide (12 mmol) for Purification by column chromatography (PE/EtOAc 50:1) yielded **2h** (0.8 g, 79%) as an oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.00 – 6.90 (m, 2H), 6.85 – 6.78 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.92 (dd, J = 7.7, 4.5 Hz, 2H), 2.44 (ddt, J = 8.3, 6.2, 2.4 Hz, 2H), 1.98 –

1.90 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.9 (dd, *J* = 13.3, 7.5 Hz), 160.0 (dd, *J* = 310.2, 295.5 Hz), 158.6, 156.2, 155.1 (d, *J* = 1.9 Hz), 115.9 (d, *J* = 22.9 Hz), 115.5 (d, *J* = 7.9 Hz), 88.4 (dd, *J* = 23.2, 5.8 Hz), 67.6, 61.3, 28.2, 21.6, 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -68.89 (s), -73.84 (s), -124.10 – -124.23 (m). HR-MS (EI) m/z calcd for $C_{14}H_{15}F_3O_3$ [M+H$^+$] 289.1046, found 289.1046.



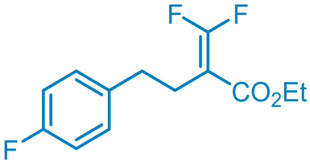
Ethyl 5-cyano-2-(difluoromethylene)pentanoate (2i)

The general procedure **TP2** was followed using ethyl acetoacetate (10 mmol) and alkyl bromide (12 mmol). Purification by column chromatography (PE/EtOAc 20:1) yielded **2i** (0.7g, 85%) as a oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.23 (q, *J* = 7.1 Hz, 2H), 2.40 – 2.34 (m, 4H), 1.84 (dd, *J* = 14.9, 7.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.3 (dd, *J* = 13.0, 7.7 Hz), 160.1 (dd, *J* = 311.3, 296.0 Hz), 119.1, 87.4 (dd, *J* = 22.5, 6.4 Hz), 61.4, 24.4, 23.7, 16.6, 14.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -67.57 (s), -72.72 (dd, *J* = 5.1, 2.4 Hz). HR-MS (EI) m/z calcd for $C_9H_{11}F_2NO_2$ [M+H$^+$] 204.0831, found 204.0831.



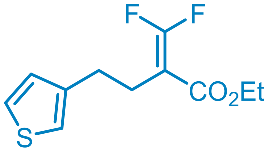
Ethyl 6-acetoxy-2-(difluoromethylene)hexanoate (2j)

The general procedure **TP1** was followed using ethyl acetoacetate (10 mmol) and alkyl bromide (12 mmol). Purification by column chromatography (PE/EtOAc 20:1) yielded **2j** (0.65g, 83%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.24 (q, *J* = 7.1 Hz, 2H), 4.07 (dd, *J* = 7.9, 5.2 Hz, 2H), 2.50 – 2.22 (m, 2H), 2.04 (s, 3H), 1.65 (dd, *J* = 10.2, 4.8 Hz, 2H), 1.53 (dd, *J* = 9.3, 6.4 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.3, 164.9 (dd, *J* = 13.4, 7.3 Hz), 160.0 (dd, *J* = 310.3, 294.7 Hz), 88.7 (dd, *J* = 23.2, 5.4 Hz), 64.2, 61.2, 28.1, 25.1, 24.3, 21.1, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -69.16 (s), -74.11 (s). HR-MS (EI) m/z calcd for $C_{11}H_{16}F_2O_4$ [M+H$^+$] 251.1089, found 251.1091.



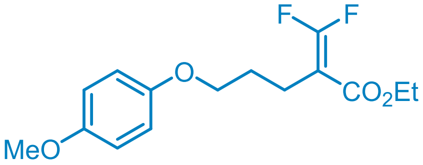
Ethyl 2-(difluoromethylene)-4-(4-fluorophenyl)butanoate (2k)

The general procedure **TP1** was followed using ethyl acetoacetate (10 mmol) and alkyl bromide (12 mmol). Purification by column chromatography (PE/EtOAc 200:1) yielded **2k** (0.97g, 90%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 (ddd, J = 8.7, 5.6, 2.8 Hz, 2H), 7.01 – 6.95 (m, 2H), 4.40 – 4.19 (m, 2H), 2.86 – 2.65 (m, 4H), 1.36 – 1.29 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.6, 163.0, 160.6, 135.5, 130.1, 130.1, 119.9 (dd, J = 8.6, 6.4 Hz), 115.6 (s), 115.4, 62.3, 34.2, 28.6, 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -66.34 (s), -68.26 (t, J = 9.3 Hz), -116.31 – -117.37 (m). HR-MS (EI) m/z calcd for $C_{13}H_{13}F_3O_2$ [M+H$^+$] 259.0940, found 259.0949.



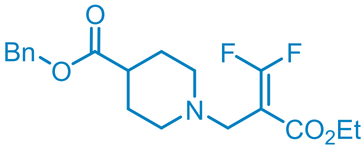
Ethyl 2-(difluoromethylene)-4-(thiophen-3-yl)butanoate (2l)

The general procedure **TP1** was followed using ethyl acetoacetate (20 mmol) and alkyl bromide (25 mmol). Purification by column chromatography (PE/EtOAc 100:1) yielded **2l** (1.75g, 78%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (dd, J = 4.7, 2.8 Hz, 1H), 6.95 (dd, J = 5.9, 3.9 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 2.89 – 2.74 (m, 2H), 2.54 (ddd, J = 9.5, 4.6, 2.2 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.8 (dd, J = 13.2, 7.7 Hz), 160.1 (dd, J = 310.2, 295.4 Hz), 141.1, 128.2, 125.6, 120.9, 88.4 (dd, J = 23.1, 5.6 Hz), 61.3, 29.2, 26.0, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -69.00 (d, J = 2.7 Hz), -73.83 (d, J = 3.2 Hz). HR-MS (EI) m/z calcd for $C_{11}H_{12}F_2O_2S$ [M+H$^+$] 247.0599, found 247.0599.



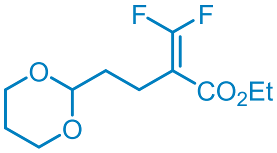
Ethyl 2-(difluoromethylene)-5-(4-methoxyphenoxy)pentanoate (2m)

The general procedure **TP1** was followed using ethyl acetoacetate (10 mmol) and alkyl bromide (12 mmol). Purification by column chromatography (PE/EtOAc 50:1) yielded **2m** (0.87g, 73%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 4H), 4.22 (q, J = 7.1 Hz, 2H), 3.91 (t, J = 6.1 Hz, 2H), 3.76 (s, 3H), 2.44 (dd, J = 9.9, 4.8 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.9 (dd, J = 13.0, 7.5 Hz), 160.0 (dd, J = 310.0, 295.2 Hz), 154.0, 153.2, 115.6 (2C), 114.7 (2C), 88.5 (dd, J = 23.0, 5.6 Hz), 67.7, 61.2, 55.8, 28.3, 21.6, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -69.02 (d, J = 2.4 Hz), -73.83 (d, J = 2.5 Hz). HR-MS (EI) m/z calcd for $C_{15}H_{18}F_2O_4$ [M+H$^+$] 301.1246, found 301.1251.



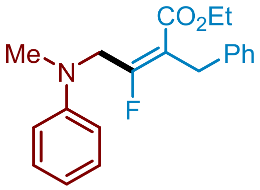
Benzyl 1-(2-(ethoxycarbonyl)-3,3-difluoroallyl)piperidine-4-carboxylate (2n)

The general procedure **TP1** was followed using ethyl acetoacetate (15 mmol) and alkyl bromide (18 mmol). Purification by column chromatography (PE/EtOAc 10:1) yielded **2n** (1.62g, 70%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.27 (m, 5H), 5.12 (s, 2H), 4.34 – 4.21 (m, 2H), 4.19 (d, J = 13.8 Hz, 2H), 2.74 (t, J = 11.0 Hz, 2H), 2.19 (dd, J = 4.2, 2.3 Hz, 2H), 1.65 (d, J = 12.5 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.15 (d, J = 10.4 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.0 (dd, J = 13.2, 7.4 Hz), 160.3 (dd, J = 310.5, 294.9 Hz), 155.4, 137.0, 128.6 (2C), 128.1, 128.0 (2C), 87.0 (dd, J = 23.3, 5.7 Hz), 67.1, 61.3, 44.2 (2C), 35.4, 31.6, 31.2 (2C), 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -68.40 (d, J = 2.3 Hz), -72.71 (s). HR-MS (EI) m/z calcd for $C_{19}H_{23}F_2NO_4$ [M+H$^+$] 368.1668, found 368.1674.



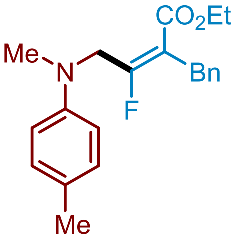
Ethyl 2-(difluoromethylene)-4-(1,3-dioxan-2-yl)butanoate (2o)

The general procedure **TP1** was followed using ethyl acetoacetate (10 mmol) and alkyl bromide (12 mmol). Purification by column chromatography (PE/EtOAc 20:1) yielded **2o** (0.98g, 70%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.52 (t, J = 5.1 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.10 (ddd, J = 11.7, 4.9, 1.1 Hz, 2H), 3.74 (ddd, J = 7.5, 6.7, 1.4 Hz, 2H), 2.43 – 2.28 (m, 2H), 2.15 – 1.81 (m, 2H), 1.78 – 1.67 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.9 (dd, J = 13.4, 7.7 Hz), 159.8 (dd, J = 309.5, 295.2 Hz), 101.5, 88.6 (dd, J = 23.2, 5.8 Hz), 67.0 (2C), 61.2, 33.8, 25.9, 19.5, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -69.40 (s), -74.01 (s). HR-MS (EI) m/z calcd for $C_{11}H_{16}F_2O_4$ [M+H$^+$] 251.1089, found 251.1093.



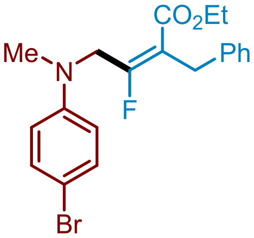
Ethyl (*E*)-2-benzyl-3-fluoro-4-[methyl(phenyl)amino]but-2-enoate (3)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **3** (65.4 mg, 80%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 (ddd, J = 9.7, 5.7, 2.0 Hz, 4H), 7.16 (t, J = 8.4 Hz, 3H), 6.77 (dd, J = 17.2, 7.8 Hz, 3H), 4.68 (d, J = 18.3 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.68 (d, J = 3.5 Hz, 2H), 3.03 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.8 (d, $^1J_{C–F}$ = 275.4 Hz), 166.8 (d, $^3J_{C–F}$ = 18.5 Hz), 149.1, 139.2, 129.2, 128.5, 128.3, 126.2, 117.3, 115.4 (d, $^2J_{C–F}$ = 19.7 Hz), 112.8, 61.1, 51.1 (d, $^2J_{C–F}$ = 22.7 Hz), 39.1, 31.2 (d, $^3J_{C–F}$ = 7.1 Hz), 14.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -90.57 (s). HR-MS (EI) m/z calcd for $C_{20}H_{22}FNO_2$ [M+H$^+$] 328.1707, found 328.1710.



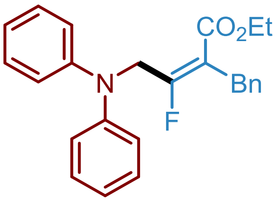
Ethyl (*E*)-2-benzyl-3-fluoro-4-[methyl(*p*-tolyl)amino]but-2-enoate (4)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 6 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **4** (51 mg, 59%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.10 (m, 5H), 7.05 (d, J = 8.4 Hz, 2H), 6.72 (t, J = 5.7 Hz, 2H), 4.64 (d, J = 18.6 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.67 (d, J = 3.5 Hz, 2H), 3.00 (s, 3H), 2.26 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.0 (d, $^1J_{C–F}$ = 274.6 Hz), 166.9 (d, $^3J_{C–F}$ = 18.5 Hz), 147.1, 139.2 (d, $^4J_{C–F}$ = 2.0 Hz), 129.7, 128.5, 128.3, 126.6, 126.2, 115.4 (d, $^2J_{C–F}$ = 19.7 Hz), 113.1, 61.0, 51.4 (d, $^2J_{C–F}$ = 22.5 Hz), 39.3 (d, $^4J_{C–F}$ = 1.3 Hz), 31.2 (d, $^3J_{C–F}$ = 7.1 Hz), 20.3, 14.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -90.20 (s), -104.81 (s). HR-MS (EI) m/z calcd for $C_{21}H_{24}FNO_2$ [M+H$^+$] 342.1864, found 342.1869.



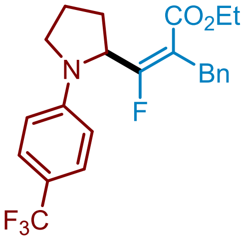
Ethyl (*E*)-2-benzyl-4-[(4-bromophenyl)(methyl)amino]-3-fluorobut-2-enoate (5)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **5** (75 mg, 74%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.09 (m, 3H), 6.69 – 6.62 (m, 2H), 4.66 (d, J = 18.3 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.67 (d, J = 3.5 Hz, 2H), 3.01 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.3 (d, $^1J_{C\text{–}F}$ = 274.1), 166.7 (d, $^3J_{C\text{–}F}$ = 18.6 Hz), 165.9, 148.0, 139.0 (d, $^4J_{C\text{–}F}$ = 1.7 Hz), 131.8, 128.4, 128.3, 126.3, 115.7 (d, $^2J_{C\text{–}F}$ = 19.6 Hz), 114.4, 109.4, 61.1, 51.0 (d, $^2J_{C\text{–}F}$ = 22.6 Hz), 39.4, 31.2 (d, $^4J_{C\text{–}F}$ = 7.0 Hz), 14.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -91.10 (s). HR-MS (EI) m/z calcd for $C_{20}H_{21}BrFNO_2$ [M+H$^+$] 406.0812, found 406.0817.



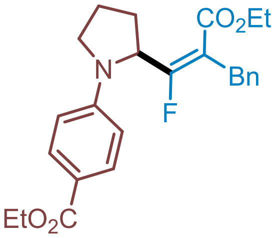
Ethyl (*E*)-2-benzyl-4-(diphenylamino)-3-fluorobut-2-enoate (6)

The general procedure **TP3** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 4 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **6** (50 mg, 51%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.29 – 7.23 (m, 4H), 7.19 (dt, J = 14.3, 6.8 Hz, 3H), 7.06 (dd, J = 12.7, 7.6 Hz, 6H), 6.98 (t, J = 7.3 Hz, 2H), 5.10 (d, J = 15.7 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.66 (d, J = 3.4 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.4 (d, $^1J_{C\text{–}F}$ = 274.3 Hz), 166.68 (d, $^3J_{C\text{–}F}$ = 18.5 Hz), 147.6, 139.1 (d, $^4J_{C\text{–}F}$ = 1.8 Hz), 129.3, 128.4, 128.3, 126.1, 121.9, 121.0, 115.4 (d, $^2J_{C\text{–}F}$ = 20.1 Hz), 61.0, 50.8 (d, $^2J_{C\text{–}F}$ = 22.3 Hz), 31.3 (d, $^3J_{C\text{–}F}$ = 6.8 Hz), 14.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -90.27 (s). HR-MS (EI) m/z calcd for $C_{25}H_{24}FNO_2$ [M+H$^+$] 390.1846, found 390.1849.



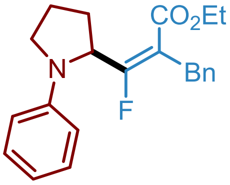
Ethyl (*E*)-2-benzyl-3-fluoro-3-{1-[4-(trifluoromethyl)phenyl]pyrrolidin-2-yl}acrylate (7)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 50:1) yielded **7** (61 mg, 58%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.44 (d, J = 8.6 Hz, 2H), 7.28 – 7.18 (m, 3H), 7.15 (t, J = 10.8 Hz, 2H), 6.64 (t, J = 21.2 Hz, 2H), 5.62 (dd, J = 27.8, 8.4 Hz, 1H), 4.24 (p, J = 7.0 Hz, 2H), 3.79 – 3.60 (m, 2H), 3.60 – 3.53 (m, 1H), 3.46 (dt, J = 20.3, 10.3 Hz, 1H), 2.56 – 2.35 (m, 1H), 2.26 – 2.08 (m, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 170.4 (d, $^1J_{C\text{–}F}$ = 275.2 Hz), 166.7 (d, $^2J_{C\text{–}F}$ = 18.4 Hz), 148.8, 139.0 (d, $^4J_{C\text{–}F}$ = 2.0 Hz), 128.4, 128.3, 126.4 (q, $^3J_{C\text{–}F}$ = 3.7 Hz), 126.3, 125.2 (q, $^1J_{C\text{–}F}$ = 271.2 Hz), 118.1 (q, $^2J_{C\text{–}F}$ = 32.6 Hz), 114.5 (d, $^2J_{C\text{–}F}$ = 20.5 Hz), 111.7, 61.1, 56.7 (d, $^2J_{C\text{–}F}$ = 21.7 Hz), 48.8, 32.0 (d, $^4J_{C\text{–}F}$ = 1.9 Hz), 31.3 (d, $^3J_{C\text{–}F}$ = 7.1 Hz), 24.1, 14.1. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -60.88 (s), -98.49 (d, J = 27.6 Hz). HR-MS (EI) m/z calcd for $C_{23}H_{23}F_4NO_2$ [M+H$^+$] 422.1738, found 422.1738.



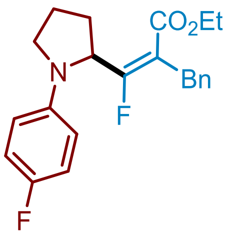
Ethyl (*E*)-4-[2-(2-benzyl-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)pyrrolidin-1-yl]benzoate (8)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 2.5 h. Purification by column chromatography (PE/EtOAc 50:1) yielded **8** (93 mg, 87%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.89 (t, J = 5.8 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.17 (t, J = 5.0 Hz, 1H), 7.13 (t, J = 6.9 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 5.61 (ddd, J = 27.4, 8.4, 2.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.66 (qd, J = 14.8, 3.5 Hz, 2H), 3.60 – 3.54 (m, 1H), 3.52 – 3.41 (m, 1H), 2.50 – 2.35 (m, 1H), 2.27 – 2.03 (m, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 170.5 (d, $^1J_{C\text{–}F}$ = 275.1 Hz), 167.1, 166.8 (d, $^3J_{C\text{–}F}$ = 18.5 Hz), 150.1, 139.1 (d, $^4J_{C\text{–}F}$ = 2.0 Hz), 131.4, 128.5, 128.4, 126.3, 118.2, 114.5 (d, $^2J_{C\text{–}F}$ = 20.4 Hz), 111.5, 61.2, 60.2, 56.9 (d, $^2J_{C\text{–}F}$ = 21.7 Hz), 48.9, 32.2 (d, $^4J_{C\text{–}F}$ = 1.6 Hz), 31.4 (d, $^4J_{C\text{–}F}$ = 7.1 Hz), 24.2, 14.6, 14.2. ^{19}F-NMR (376 MHz, CDCl$_3$) δ = -98.29 (s). HR-MS (EI) m/z calcd for $C_{25}H_{28}FNO_4$ [M+H$^+$] 426.2075, found 426.2075.



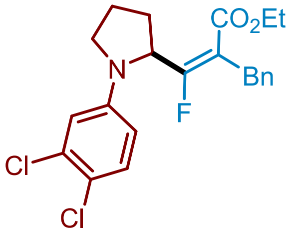
Ethyl (*E*)-2-benzyl-3-fluoro-3-(1-phenylpyrrolidin-2-yl)acrylate (9)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **9** (62 mg, 70%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.08 (m, 7H), 6.70 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.9 Hz, 2H), 5.50 (ddd, J = 27.4, 8.4, 2.6 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.65 (qd, J = 14.7, 3.5 Hz, 2H), 3.52 (td, J = 8.3, 4.0 Hz, 1H), 3.41 (dd, J = 15.8, 7.1 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.25 – 1.99 (m, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.7 (d, $^{1}J_{C–F}$ = 276.1 Hz), 167.0 (d, $^{3}J_{C–F}$ = 18.3 Hz), 146.9, 139.4 (d, $^{4}J_{C–F}$ = 2.0 Hz), 129.3, 128.6, 128.4, 126.2, 116.6, 114.0 (d, $^{2}J_{C–F}$ = 20.5 Hz), 112.3, 61.1, 56.9 (d, $^{2}J_{C–F}$ = 21.7 Hz), 48.8, 32.3 (d, $^{4}J_{C–F}$ = 2.0 Hz), 31.5, 24.3, 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -97.43 (d, J = 27.3 Hz). HR-MS (EI) m/z calcd for $C_{22}H_{24}FNO_2$ [M+H$^+$] 354.1864, found 354.1866.



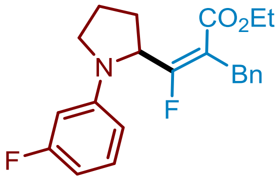
Ethyl (*E*)-2-benzyl-3-fluoro-3-[1-(4-fluorophenyl)pyrrolidin-2-yl]acrylate (10)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 2 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **10** (48 mg, 51%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.13 (m, 3H), 7.09 (d, J = 7.1 Hz, 2H), 6.95 – 6.85 (m, 2H), 6.60 – 6.51 (m, 2H), 5.47 (ddd, J = 28.1, 8.4, 2.8 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.64 (ddd, J = 35.2, 14.7, 3.5 Hz, 2H), 3.48 (td, J = 8.2, 4.4 Hz, 1H), 3.36 (dd, J = 15.4, 7.0 Hz, 1H), 2.48 – 2.32 (m, 1H), 2.19 (ddd, J = 15.0, 11.8, 7.8 Hz, 1H), 2.13 – 2.03 (m, 2H), 1.26 – 1.20 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.5 (d, $^{1}J_{C–F}$ = 276.0 Hz), 167.0 (d, $^{3}J_{C–F}$ = 18.5 Hz), 155.5 (d, $^{1}J_{C–F}$ = 234.4 Hz), 143.4 (d, $^{4}J_{C–F}$ = 1.2 Hz), 139.3 (d, $^{4}J_{C–F}$ = 1.9 Hz), 128.6, 128.4, 126.3, 115.7 (d, $^{2}J_{C–F}$ = 22.1 Hz), 114.3 (d, $^{2}J_{C–F}$ = 20.5 Hz), 113.0 (d, $^{4}J_{C–F}$ = 7.3 Hz), 61.1, 57.2 (d, $^{2}J_{C–F}$ = 21.7 Hz), 49.3, 32.2 (d, $^{4}J_{C–F}$ = 1.5 Hz), 31.5 (d, $^{4}J_{C–F}$ = 7.2 Hz), 24.4, 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -98.26 (s), -129.58 (s). HR-MS (EI) m/z calcd for $C_{22}H_{23}F_2NO_2$ [M+H$^+$] 372.1770, found 372.1770.



Ethyl (*E*)-2-benzyl-3-[1-(3,4-dichlorophenyl)pyrrolidin-2-yl]-3-fluoroacrylate (11)

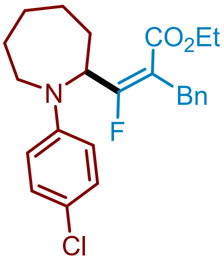
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **11** (91 mg, 86%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (dt, J = 14.4, 8.2 Hz, 4H), 7.13 (d, J = 7.2 Hz, 2H), 6.77 (d, J = 2.8 Hz, 1H), 6.49 (dd, J = 8.9, 2.8 Hz, 1H), 5.54 (ddd, J = 28.4, 8.4, 2.8 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.69 (ddd, J = 40.3, 14.8, 3.4 Hz, 2H), 3.50 (td, J = 8.4, 4.5 Hz, 1H), 3.39 (dd, J = 15.6, 7.0 Hz, 1H), 2.50 – 2.33 (m, 1H), 2.24 – 2.08 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.2 (d, $^{1}J_{C\text{–}F}$ = 275.1 Hz), 166.9 (d, $^{3}J_{C\text{–}F}$ = 18.4 Hz), 146.2, 139.1, 132.9, 130.6, 128.5, 128.4, 126.4, 119.4, 114.9 (d, $^{2}J_{C\text{–}F}$ = 20.4 Hz), 113.9, 112.1, 61.3, 56.8 (d, $^{2}J_{C\text{–}F}$ = 21.8 Hz), 49.0, 32.0 (d, $^{4}J_{C\text{–}F}$ = 1.6 Hz), 31.4 (d, $^{4}J_{C\text{–}F}$ = 7.2 Hz), 24.3, 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -99.40 (s). HR-MS (EI) m/z calcd for $C_{22}H_{22}Cl_2FNO_2$ [M+H^{+}] 422.1084, found 422.1089.



Ethyl (*E*)-2-benzyl-3-fluoro-3-[1-(3-fluorophenyl)pyrrolidin-2-yl]acrylate (12)

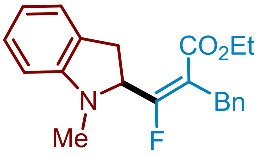
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 8 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **12** (53 mg, 57%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.15 (m, 2H), 7.11 (dd, J = 13.9, 7.0 Hz, 4H), 6.43 – 6.35 (m, 2H), 6.33 (t, J = 2.3 Hz, 1H), 5.49 (ddd, J = 27.6, 8.4, 2.7 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.66 (qd, J = 14.7, 3.5 Hz, 2H), 3.50 (td, J = 8.4, 4.1 Hz, 1H), 3.39 (dd, J = 15.9, 7.1 Hz, 1H), 2.48 – 2.34 (m, 1H), 2.19 (dq, J = 7.6, 4.8 Hz, 1H), 2.14 – 2.01 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.0 (d, $^{1}J_{C\text{–}F}$ = 275.4 Hz), 166.9 (d, $^{3}J_{C\text{–}F}$ = 18.6 Hz), 164.2 (d, $^{1}J_{C\text{–}F}$ = 242.3 Hz), 148.5 (d, $^{3}J_{C\text{–}F}$ = 10.9 Hz), 139.3, 130.3 (d, $^{3}J_{C\text{–}F}$ = 10.3 Hz), 128.5, 128.4, 126.3, 114.4 (d, $^{2}J_{C\text{–}F}$ = 20.5 Hz), 108.1 (d, $^{4}J_{C\text{–}F}$ = 2.1 Hz), 103.1 (d, $^{2}J_{C\text{–}F}$ = 21.7 Hz), 99.5 (d, $^{2}J_{C\text{–}F}$ = 26.0 Hz), 61.2, 57.0 (d, $^{2}J_{C\text{–}F}$ = 21.7 Hz), 49.0, 32.2 (d, $^{4}J_{C\text{–}F}$ = 1.8 Hz), 31.5 (d, $^{4}J_{C\text{–}F}$ = 7.1 Hz), 24.2, 14.2. ^{19}F-NMR

(376 MHz, $CDCl_3$): δ = -98.27 (s), -112.69 (s). HR-MS (EI) m/z calcd for $C_{22}H_{23}F_2NO_2$ [M+H$^+$] 372.1770, found 372.1770.



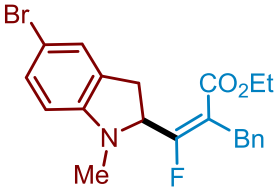
Ethyl (*E*)-2-benzyl-3-[1-(4-chlorophenyl)azepan-2-yl]-3-fluoroacrylate (13)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE) yielded **13** (75 mg, 72%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.21 (m, 3H), 7.20 – 7.11 (m, 4H), 6.60 (d, *J* = 9.0 Hz, 2H), 5.29 (ddd, *J* = 27.4, 11.9, 5.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.66 (dd, *J* = 12.9, 9.1 Hz, 3H), 3.51 (dd, *J* = 15.9, 11.5 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.04 – 1.93 (m, 1H), 1.93 – 1.83 (m, 2H), 1.77 (d, *J* = 14.2 Hz, 1H), 1.59 (d, *J* = 9.4 Hz, 1H), 1.35 (dd, *J* = 14.7, 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.0 (d, $^1J_{C\text{–}F}$ = 274.9 Hz), 166.9, 166.7, 147.5, 139.4 (d, $^4J_{C\text{–}F}$ = 1.9 Hz), 129.2, 128.5, 126.3, 120.9, 113.2 (d, $^2J_{C\text{–}F}$ = 20.7 Hz), 112.4, 61.2, 57.5 (d, $^2J_{C\text{–}F}$ = 20.6 Hz), 46.1 (d, $^4J_{C\text{–}F}$ = 3.2 Hz), 33.0 (d, $^4J_{C\text{–}F}$ = 2.1 Hz), 31.2 (d, $^4J_{C\text{–}F}$ = 7.3 Hz), 29.8, 28.4, 26.5, 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -101.20 (s). HR-MS (EI) m/z calcd for $C_{24}H_{27}ClFNO_2$ [M+H$^+$] 416.1787, found 416.1797.



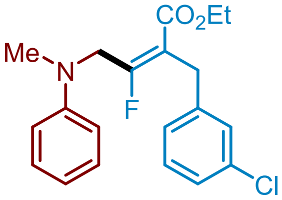
Ethyl (*E*)-2-benzyl-3-fluoro-3-(1-methylindolin-2-yl)acrylate (14)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **14** (45 mg, 53%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.15 (m, 5H), 7.14 – 7.02 (m, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.11 (dt, *J* = 27.6, 9.4 Hz, 1H), 4.19 – 4.10 (m, 2H), 3.76 (qd, *J* = 14.6, 3.4 Hz, 2H), 3.21 (ddd, *J* = 36.8, 15.6, 9.4 Hz, 2H), 2.76 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.8 (d, $^3J_{C\text{–}F}$ = 17.8 Hz), 166.5 (d, $^1J_{C\text{–}F}$ = 272.7 Hz), 152.5, 139.2 (d, $^4J_{C\text{–}F}$ = 1.9 Hz), 128.6, 127.9, 126.5, 124.2, 118.4, 117.0 (d, $^2J_{C\text{–}F}$ = 20.3 Hz), 107.4, 64.1 (d, $^2J_{C\text{–}F}$ = 22.4 Hz), 61.3, 34.3, 32.8 (d, ${}^4J_{C\text{–}F}$ = 1.0 Hz), 31.9 (d, ${}^4J_{C\text{–}F}$ = 6.7 Hz), 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -102.55 (s). HR-MS (EI) m/z calcd for $C_{21}H_{22}FNO_2$ [M+H$^+$] 340.1707, found 340.1707.



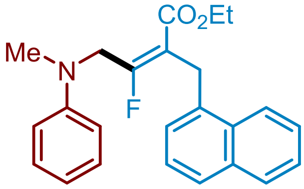
Ethyl (*E*)-2-benzyl-3-(5-bromo-1-methylindolin-2-yl)-3-fluoroacrylate (15)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **15** (42 mg, 40%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.24 (m, 2H), 7.23 – 7.09 (m, 5H), 6.34 (dd, *J* = 22.6, 9.4 Hz, 1H), 5.17 (dt, *J* = 27.9, 9.1 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.75 (qd, *J* = 14.5, 2.8 Hz, 2H), 3.24 (dd, *J* = 15.9, 9.6 Hz, 1H), 3.13 (dd, *J* = 15.9, 8.8 Hz, 1H), 2.73 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6 (d, ${}^3J_{C\text{–}F}$ = 17.6 Hz), 166.1 (d, ${}^1J_{C\text{–}F}$ = 272.9 Hz), 151.6, 139.0 (d, ${}^4J_{C\text{–}F}$ = 1.9 Hz), 130.4, 130.1, 128.6, 128.6, 127.2, 126.5, 117.2 (d, ${}^2J_{C\text{–}F}$ = 20.1 Hz), 109.8, 108.4, 63.9 (d, ${}^2J_{C\text{–}F}$ = 22.5 Hz), 61.3, 33.9, 32.5, 31.8 (d, ${}^4J_{C\text{–}F}$ = 6.7 Hz), 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -103.32 (s). HR-MS (EI) m/z calcd for $C_{21}H_{21}BrFNO_2$ [M+H$^+$] 418.0812, found 418.0823.



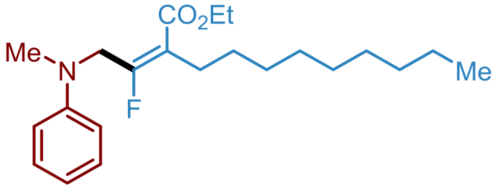
Ethyl (*E*)-2-(3-chlorobenzyl)-3-fluoro-4-[methyl(phenyl)amino]but-2-enoate (16)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **16** (46 mg, 51%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.21 (m, 2H), 7.15 (d, *J* = 5.1 Hz, 3H), 7.01 (dd, *J* = 6.8, 3.2 Hz, 1H), 6.77 (dd, *J* = 12.6, 7.8 Hz, 3H), 4.69 (d, *J* = 18.2 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.64 (d, *J* = 3.4 Hz, 2H), 3.04 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.5 (d, ${}^1J_{C\text{–}F}$ = 275.1 Hz), 166.7 (d, ${}^3J_{C\text{–}F}$ = 18.4 Hz), 149.1, 141.4 (d, ${}^4J_{C\text{–}F}$ = 2.1 Hz), 134.2, 129.7, 129.3, 128.8, 126.8, 126.6, 117.6, 114.9 (d, ${}^2J_{C\text{–}F}$ = 19.6 Hz), 112.9, 61.3, 51.2 (d, ${}^2J_{C\text{–}F}$ = 22.2 Hz), 39.4, 31.1 (d, $4J_{C\text{–}F}$ = 7.3 Hz), 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -89.46 (s). HR-MS (EI) m/z calcd for $C_{20}H_{21}ClFNO_2$ [M+H$^+$] 362.1318, found 362.1318.



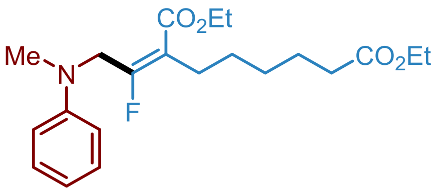
Ethyl (*E*)-3-fluoro-4-[methyl(phenyl)amino]-2-(naphthalen-1-ylmethyl)but-2-enoate (17)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3.5 h. Purification by column chromatography (PE/EtOAc 50:1) yielded **17** (51 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 – 8.02 (m, 1H), 7.83 (dd, J = 6.6, 2.7 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.37 – 7.29 (m, 1H), 7.25 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 7.1 Hz, 1H), 6.82 (d, J = 8.3 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 4.70 (d, J = 18.6 Hz, 2H), 4.17 – 4.08 (m, 4H), 3.06 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 167.5 (d, $^{1}J_{C\text{–}F}$ = 273.4 Hz), 167.1 (d, $^{3}J_{C\text{–}F}$ = 18.5 Hz), 149.2, 134.6 (d, $^{4}J_{C\text{–}F}$ = 1.8 Hz), 133.9, 132.1, 129.3, 128.8, 127.1, 126.1, 125.6, 125.5, 123.6 (d, $^{4}J_{C\text{–}F}$ = 1.1 Hz), 117.5, 115.0 (d, $^{2}J_{C\text{–}F}$ = 19.5 Hz), 113.0, 61.2, 51.2 (d, $^{2}J_{C\text{–}F}$ = 22.8 Hz), 39.4 (d, $^{4}J_{C\text{–}F}$ = 1.2 Hz), 28.3 (d, $^{4}J_{C\text{–}F}$ = 7.6 Hz), 14.2. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -91.21 (s). HR-MS (EI) m/z calcd for $C_{24}H_{24}FNO_2$ [M+H$^+$] 378.1864, found 378.1864.



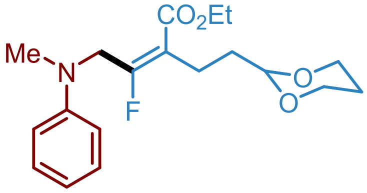
Ethyl (*E*)-2-{1-fluoro-2-[methyl(phenyl)amino]ethylidene}undecanoate (18)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 4 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **18** (58 mg, 64%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, J = 8.6, 7.3 Hz, 2H), 6.74 (dd, J = 16.6, 7.9 Hz, 3H), 4.57 (d, J = 18.3 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.00 (s, 3H), 2.31 (td, J = 7.8, 3.7 Hz, 2H), 1.34 (dt, J = 14.3, 7.2 Hz, 5H), 1.24 (s, 12H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.5 (d, $^{3}J_{C\text{–}F}$ = 19.1 Hz), 166.6 (d, $^{1}J_{C\text{–}F}$ = 272.4 Hz), 149.2, 129.1, 117.2, 116.4 (d, $^{2}J_{C\text{–}F}$ = 20.5 Hz), 112.7, 60.9, 51.1 (d, $^{2}J_{C\text{–}F}$ = 23.3 Hz), 38.9 (d, $^{4}J_{C\text{–}F}$ = 1.2 Hz), 31.9, 29.5, 29.3, 29.3, 29.2, 28.8 (d, $^{4}J_{C\text{–}F}$ = 1.6 Hz), 25.5 (d, $^{4}J_{C\text{–}F}$ = 6.4 Hz), 22.7, 14.2, 14.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -92.80 (s). HR-MS (EI) m/z calcd for $C_{22}H_{34}FNO_2$ [M+H$^+$] 364.2646, found 364.2650.



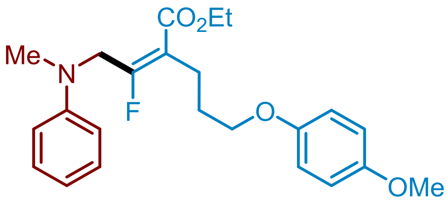
Diethyl (*E*)-2-{1-fluoro-2-[methyl(phenyl)amino]ethylidene}octanedioate (19)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 4 h. Purification by column chromatography (PE/EtOAc 50:1) yielded **19** (59 mg, 62%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.19 (m, 2H), 6.74 (dd, J = 14.1, 7.6 Hz, 3H), 4.58 (d, J = 18.3 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.00 (s, 3H), 2.32 (td, J = 7.6, 3.7 Hz, 2H), 2.24 (t, J = 7.6 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.46 – 1.36 (m, 2H), 1.36 – 1.19 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.9, 167.5 (d, $^3J_{C–F}$ = 19.4 Hz), 167.02 (d, $^1J_{C–F}$ = 272.4 Hz), 149.3, 129.2, 117.3, 116.2 (d, $^2J_{C–F}$ = 20.4 Hz), 112.8, 61.1, 60.3, 51.3, 51.1, 39.1 (d, $^4J_{C–F}$ = 0.9 Hz), 34.4, 28.8, 28.5 (d, $^4J_{C–F}$ = 1.1 Hz), 25.4 (d, $^4J_{C–F}$ = 6.5 Hz), 24.8, 14.4. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -92.28 (t, J = 18.4 Hz). HR-MS (EI) m/z calcd for $C_{21}H_{30}FNO_4$ [M+H$^+$] 380.2232, found 380.2236.



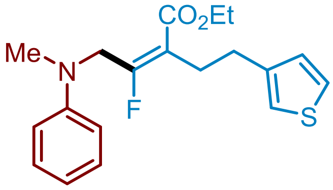
Ethyl (*E*)-2-[2-(1,3-dioxan-2-yl)ethyl]-3-fluoro-4-[methyl(phenyl)amino]but-2-enoate (20)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **20** (51 mg, 58%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, J = 8.7, 7.3 Hz, 2H), 6.74 (dd, J = 15.9, 7.8 Hz, 3H), 4.60 (d, J = 18.1 Hz, 2H), 4.38 (t, J = 5.2 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.03 (dd, J = 10.8, 4.9 Hz, 2H), 3.62 (td, J = 12.3, 2.3 Hz, 2H), 3.01 (s, 3H), 2.43 (td, J = 7.7, 3.6 Hz, 2H), 2.02 (ddd, J = 17.7, 12.6, 7.6 Hz, 1H), 1.69 (dd, J = 12.8, 7.4 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.27 (dt, J = 13.3, 1.5 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.5 (d, $^1J_{C–F}$ = 273.7 Hz), 167.32 (d, $^3J_{C–F}$ = 18.9 Hz), 149.2, 129.2, 117.3, 115.6 (d, $^2J_{C–F}$ = 20.2 Hz), 112.8, 101.8, 66.9, 61.1, 51.2 (d, $^2J_{C–F}$ = 22.9 Hz), 39.3, 34.1 (d, $^4J_{C–F}$ = 1.3 Hz), 25.9, 20.4 (d, $^4J_{C–F}$ = 7.3 Hz), 14.4. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -91.21 (t, J = 18.1 Hz). HR-MS (EI) m/z calcd for $C_{19}H_{26}FNO_4$ [M+H$^+$] 352.1919, found 352.1919.



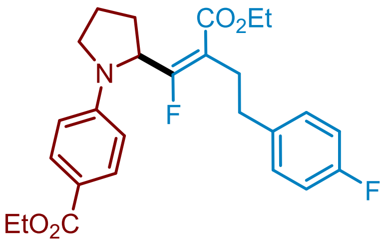
Ethyl (*E*)-2-{1-fluoro-2-[methyl(phenyl)amino]ethylidene}-5-(4-methoxyphenoxy)pentanoate (21)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 6 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **21** (58 mg, 58%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.22 (t, J = 7.8 Hz, 2H), 6.88 – 6.69 (m, 7H), 4.60 (d, J = 18.1 Hz, 2H), 4.22 (p, J = 7.0 Hz, 2H), 3.83 (t, J = 6.4 Hz, 2H), 3.76 (s, 3H), 2.99 (s, 3H), 2.58 – 2.46 (m, 2H), 1.91 – 1.83 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 167.6 (d, $^1J_{C–F}$ = 273.4 Hz), 167.3 (d, $^3J_{C–F}$ = 19.1 Hz), 153.8, 153.2, 149.1, 129.3, 129.0 (d, $^3J_{C–F}$ = 19.9 Hz), 117.4, 115.5, 114.7, 112.8, 67.9, 61.1, 55.9, 51.2 (d, $^2J_{C–F}$ = 22.8 Hz), 39.2, 28.6 (d, $^4J_{C–F}$ = 1.2 Hz), 22.44 (d, $^4J_{C–F}$ = 6.9 Hz), 14.3. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -91.13 (s). HR-MS (EI) m/z calcd for $C_{23}H_{28}FNO_4$ [M+H$^+$] 402.2075, found 402.2075.



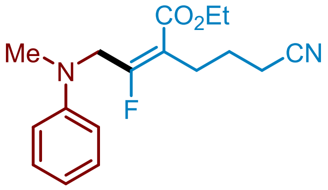
Ethyl (*E*)-3-fluoro-4-[methyl(phenyl)amino]-2-[2-(thiophen-3-yl)ethyl]but-2-enoate (22)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **22** (45 mg, 52%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.24 – 7.18 (m, 3H), 6.89 (dd, J = 8.0, 3.8 Hz, 2H), 6.75 (t, J = 8.2 Hz, 3H), 4.58 (d, J = 18.3 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 2.97 (s, 3H), 2.76 – 2.71 (m, 2H), 2.64 (dd, J = 8.0, 3.2 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 167.65 (d, $^1J_{C–F}$ = 273.7 Hz), 167.24 (d, $^3J_{C–F}$ = 19.1 Hz), 149.2, 141.6, 129.3, 128.4, 125.4, 120.7, 117.4, 115.5 (d, $^2J_{C–F}$ = 20.7 Hz), 112.8, 61.1, 51.2 (d, $^2J_{C–F}$ = 22.8 Hz), 39.1, 29.6, 26.8 (d, $^4J_{C–F}$ = 6.3 Hz), 14.4. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -91.07 (s). HR-MS (EI) m/z calcd for $C_{19}H_{22}FNO_2S$ [M+H$^+$] 348.1428, found 348.1430.



Ethyl (*E*)-4-{2-[2-(ethoxycarbonyl)-1-fluoro-4-(4-fluorophenyl)but-1-en-1-yl]pyrrolidin-1-yl}benzoate (23)

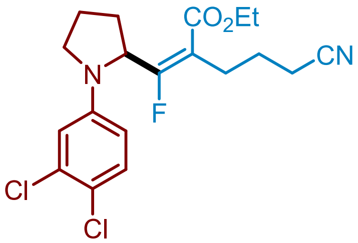
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 7.5 h. Purification by column chromatography (PE/EtOAc 50:1) yielded **23** (64 mg, 56%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.91 (d, J = 8.7 Hz, 2H), 7.09 (dd, J = 8.3, 5.6 Hz, 2H), 6.93 (t, J = 8.7 Hz, 2H), 6.57 (d, J = 8.8 Hz, 2H), 5.49 (ddd, J = 27.2, 8.5, 2.5 Hz, 1H), 4.41 – 4.23 (m, 4H), 3.56 – 3.49 (m, 1H), 3.44 (dd, J = 16.5, 7.8 Hz, 1H), 2.73 – 2.67 (m, 2H), 2.65 – 2.57 (m, 2H), 2.35 (dq, J = 12.4, 8.6 Hz, 1H), 2.08 (dt, J = 13.9, 6.8 Hz, 2H), 2.01 – 1.92 (m, 1H), 1.37 (dd, J = 12.3, 7.1 Hz, 6H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 170.4 (d, $^1J_{C\text{–}F}$ = 274.8 Hz), 167.1, 166.9, 161.5 (d, $^1J_{C\text{–}F}$ = 243.5 Hz), 150.0, 136.8 (d, $^4J_{C\text{–}F}$ = 3.1 Hz), 131.4, 130.1 (d, $^4J_{C\text{–}F}$ = 7.9 Hz), 118.1, 115.1 (d, $^2J_{C\text{–}F}$ = 21.2 Hz), 114.0 (d, $^2J_{C\text{–}F}$ = 20.9 Hz), 111.3, 61.2, 60.3, 56.8 (d, $^2J_{C\text{–}F}$ = 22.0 Hz), 48.8, 34.3, 32.2 (d, $^4J_{C\text{–}F}$ = 1.7 Hz), 27.7 (d, $^4J_{C\text{–}F}$ = 5.6 Hz), 24.0, 14.6, 14.4. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -97.99 (s), -117.44 (s). HR-MS (EI) m/z calcd for $C_{26}H_{29}F_2NO_4$ [M+H$^+$] 458.2137, found 458.2140.



Ethyl (*E*)-5-cyano-2-{1-fluoro-2-[methyl(phenyl)amino]ethylidene}pentanoate (24)

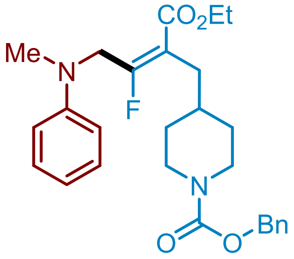
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3.5 h. Purification by column chromatography (PE/EtOAc 10:1) yielded **24** (46 mg, 60%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.26 (t, J = 7.9 Hz, 2H), 6.82 – 6.76 (m, 3H), 4.66 (d, J = 18.3 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.05 (s, 3H), 2.49 (td, J = 7.3, 3.7 Hz, 2H), 2.24 (t, J = 7.3 Hz, 2H), 1.80 (p, J = 7.3 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 168.8 (d, $^1J_{C\text{–}F}$ = 275.0 Hz), 166.8 (d, $^3J_{C\text{–}F}$ = 18.9 Hz), 148.9, 129.3, 119.5, 117.7, 114.2 (d, $^2J_{C\text{–}F}$ = 19.6 Hz), 112.9, 61.4, 51.3 (d, $^2J_{C\text{–}F}$ = 22.6 Hz), 39.5 (d, $^4J_{C\text{–}F}$ = 1.3 Hz), 24.8 (d, $^4J_{C\text{–}F}$ = 1.6 Hz), 24.7 (d, $^4J_{C\text{–}F}$ = 7.1 Hz), 16.6, 14.4.

^{19}F-NMR (376 MHz, CDCl$_3$): δ = -89.27 (s). HR-MS (EI) m/z calcd for $C_{17}H_{21}FN_2O_2$ [M+H$^+$] 305.1660, found 305.1665.



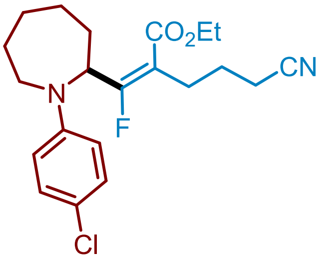
Ethyl (*E*)-5-cyano-2-{2-[(3,4-dichlorophenyl)(methyl)amino]-1-fluoroethylidene}pentanoate (**25**)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 6.5 h. Purification by column chromatography (PE/EtOAc 10:1) yielded **25** (47 mg, 44%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.20 (d, J = 8.9 Hz, 1H), 6.67 (d, J = 2.8 Hz, 1H), 6.42 (dd, J = 8.9, 2.8 Hz, 1H), 5.42 (ddd, J = 28.3, 8.6, 2.8 Hz, 1H), 4.37 – 4.27 (m, 2H), 3.44 (td, J = 8.5, 4.4 Hz, 1H), 3.39 – 3.31 (m, 1H), 2.46 (dtd, J = 11.0, 7.4, 3.5 Hz, 2H), 2.40 – 2.34 (m, 1H), 2.25 (q, J = 7.2 Hz, 2H), 2.07 (ddd, J = 14.9, 7.2, 3.8 Hz, 3H), 1.77 (tq, J = 13.8, 6.9 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 170.8 (d, $^1J_{C\text{–}F}$ = 275.8 Hz), 166.7 (d, $^3J_{C\text{–}F}$ = 18.6 Hz), 146.1, 132.9, 130.7, 119.4 (d, $^4J_{C\text{–}F}$ = 7.4 Hz), 113.8, 113.7, 113.6, 111.9, 61.6, 56.8 (d, $^2J_{C\text{–}F}$ = 22.0 Hz), 49.0, 31.8 (d, $^4J_{C\text{–}F}$ = 1.1 Hz), 24.8, 24.7, 24.2 (d, $^4J_{C\text{–}F}$ = 0.8 Hz), 16.7, 14.4. ^{19}F-NMR (377 MHz, CDCl$_3$): δ = -98.07 (s). HR-MS (EI) m/z calcd for $C_{19}H_{21}Cl_2FN_2O_2$ [M+H$^+$] 399.1037, found 399.1048.



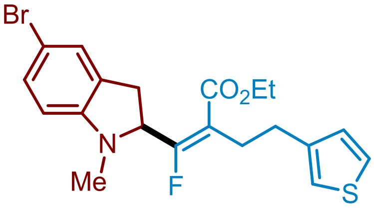
Benzyl (*E*)-4-{2-(ethoxycarbonyl)-3-fluoro-4-[methyl(phenyl)amino]but-2-en-1-yl}piperidine-1-carboxylate (**26**)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 3.5 h. Purification by column chromatography (PE/EtOAc 10:1) yielded **26** (78 mg, 66%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.35 (d, J = 3.0 Hz, 5H), 7.21 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 9.1 Hz, 3H), 5.11 (s, 2H), 4.61 (d, J = 18.4 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 4.06 (d, J = 35.8 Hz, 2H), 3.01 (s, 3H), 2.71 (d, J = 24.0 Hz, 3H), 2.27 (dd, *J* = 6.2, 3.9 Hz, 2H), 1.61 – 1.47 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 167.8 (d, $^1J_{C–F}$ = 272.2 Hz), 167.4 (d, $^3J_{C–F}$ = 19.1 Hz), 155.4, 149.0, 137.1, 129.2, 128.6, 128.1, 128.0, 117.6, 114.3 (d, $^2J_{C–F}$ = 20.1 Hz), 113.0, 67.1, 61.2, 51.4 (d, $^2J_{C–F}$ = 23.0 Hz), 44.2, 39.4 (d, $^4J_{C–F}$ = 1.1 Hz), 35.8 (d, $^4J_{C–F}$ = 1.8 Hz), 32.1 (d, $^4J_{C–F}$ = 5.4 Hz), 19.3, 14.4. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -89.60 (s). HR-MS (EI) m/z calcd for $C_{27}H_{33}FN_2O_4$ [M+H$^+$] 469.2497, found 469.2497.



Ethyl (*E*)-2-{[1-(4-chlorophenyl)azepan-2-yl]fluoromethylene}-5-cyanopentanoate (27)

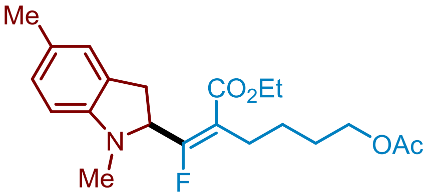
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 4.5 h. Purification by column chromatography (PE/EtOAc 10:1) yielded **27** (57 mg, 58%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.15 (d, *J* = 9.1 Hz, 2H), 6.57 (d, *J* = 9.1 Hz, 2H), 5.24 (ddd, *J* = 27.5, 11.9, 5.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.42 (m, 2H), 2.50 (d, *J* = 3.4 Hz, 2H), 2.35 – 2.25 (m, 3H), 2.04 – 1.94 (m, 2H), 1.88 (dd, *J* = 17.0, 9.4 Hz, 2H), 1.84 – 1.79 (m, 2H), 1.59 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 172.7 (d, $^1J_{C–F}$ = 275.4 Hz), 166.7 (d, $^3J_{C–F}$ = 19.1 Hz), 147.4, 129.2, 121.0, 119.5, 112.2 112.0 (d, $^2J_{C–F}$ = 20.5 Hz), 61.5, 57.4 (d, $^2J_{C–F}$ = 20.5 Hz), 46.0 (d, $^4J_{C–F}$ = 3.2 Hz), 32.9, 29.8, 28.3, 26.5, 24.9 (d, $^4J_{C–F}$ = 1.6 Hz), 24.5 (d, $^4J_{C–F}$ = 7.3 Hz), 16.8, 14.4. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -99.81 (s). HR-MS (EI) m/z calcd for $C_{21}H_{26}ClFN_2O_2$ [M+H$^+$] 393.1740, found 393.1743.



Ethyl (*E*)-2-[(5-bromo-1-methylindolin-2-yl)fluoromethylene]-4-(thiophen-3-yl)butano-ate (28)

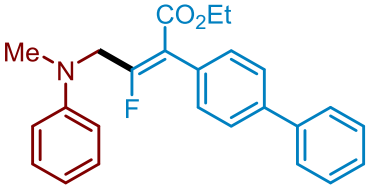
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **28** (42 mg, 38%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.25 – 7.22

(m, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.11 (s, 1H), 6.94 (d, *J* = 3.9 Hz, 2H), 6.28 (d, *J* = 8.3 Hz, 1H), 5.02 (dt, *J* = 27.6, 9.2 Hz, 1H), 4.24 – 4.17 (m, 2H), 3.08 (ddd, *J* = 65.6, 15.9, 9.2 Hz, 2H), 2.80 (d, *J* = 7.1 Hz, 2H), 2.72 (dd, *J* = 15.7, 8.1 Hz, 2H), 2.63 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 167.0 (d, $^3J_{C–F}$ = 18.1 Hz), 165.8 (d, $^1J_{C–F}$ = 272.2 Hz), 151.6, 141.3, 130.4, 130.2, 128.4, 127.1, 125.5, 120.9, 116.8 (d, $^2J_{C–F}$ = 20.2 Hz), 109.7, 108.3, 64.0 (d, $^2J_{C–F}$ = 22.7 Hz), 61.3, 33.8, 32.4, 29.4 (d, $^4J_{C–F}$ = 1.5 Hz), 27.1 (d, $^4J_{C–F}$ = 5.9 Hz), 14.3. ^{19}F-NMR (376 MHz, CDCl$_3$): δ =-104.00 (s). HR-MS (EI) m/z calcd for $C_{20}H_{21}BrFNO_2S$ [M+H$^+$] 438.0533, found 438.0532.



Ethyl (*E*)-6-acetoxy-2-[(1,5-dimethylindolin-2-yl)fluoromethylene]hexanoate (29)

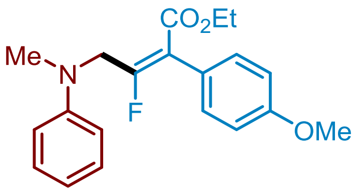
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 5 h. Purification by column chromatography (PE/EtOAc 50:1) yielded **29** (21 mg, 22%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 6.90 (d, *J* = 8.5 Hz, 2H), 6.40 (d, *J* = 7.7 Hz, 1H), 4.90 (dt, *J* = 27.1, 9.5 Hz, 1H), 4.26 – 4.18 (m, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.13 (qd, *J* = 15.5, 9.5 Hz, 2H), 2.71 (s, 3H), 2.50 – 2.40 (m, 2H), 2.25 (s, 3H), 2.04 (s, 3H), 1.74 – 1.62 (m, 2H), 1.53 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 171.3, 167.3 (d, $^3J_{C–F}$ = 18.1 Hz), 165.8 (d, $^1J_{C–F}$ = 270.8 Hz), 150.4, 128.2, 128.0, 127.9, 125.1, 117.2 (d, $^2J_{C–F}$ = 20.7 Hz), 107.6, 64.7 (d, $^2J_{C–F}$ = 22.8 Hz), 64.3, 61.2, 34.9, 32.8, 28.3, 25.8 (d, $^4J_{C–F}$ = 6.2 Hz), 25.3 (d, $^4J_{C–F}$ = 1.3 Hz), 21.1, 20.9, 14.3. ^{19}F-NMR (376 MHz, CDCl$_3$): δ =-103.93 (s). HR-MS (EI) m/z calcd for $C_{21}H_{28}FNO_4$ [M+H$^+$] 378.2075, found 378.2075.



Ethyl (*E*)-2-[(1,1'-biphenyl)-4-yl]-3-fluoro-4-[methyl(phenyl)amino]but-2-enoate (30)

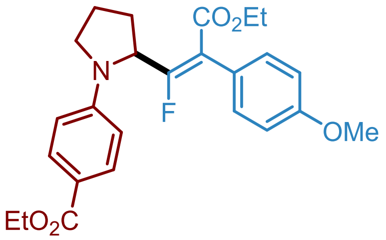
The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 6 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **30** (28 mg, 28%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ =7.57 (dd, *J*

= 10.3, 8.0 Hz, 3H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (dd, J = 11.2, 7.8 Hz, 3H), 7.25 (t, J = 8.0 Hz, 3H), 6.83 (d, J = 8.3 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 4.66 (d, J = 16.7 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.07 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, $^{3}J_{C–F}$ = 19.4 Hz), 165.7 (d, $^{1}J_{C–F}$ = 273.2 Hz), 149.2, 140.8 (d, $^{4}J_{C–F}$ = 4.9 Hz), 130.9 (d, J = 1.0 Hz), 130.1, 130.0, 129.3, 128.9, 127.6, 127.2, 126.9, 117.7, 117.5 (d, $^{2}J_{C–F}$ = 17.9 Hz), 113.0, 61.7, 51.8 (d, $^{2}J_{C–F}$ = 23.7 Hz), 39.2 (d, $^{4}J_{C–F}$ = 1.0 Hz), 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ =-92.35 (s). HR-MS (EI) m/z calcd for $C_{25}H_{24}FNO_2$ [M+H$^+$] 390.1864, found 390.1865.



Ethyl (*E*)-3-fluoro-2-(4-methoxyphenyl)-4-[methyl(phenyl)amino]but-2-enoate (31)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 8 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **31** (30 mg, 35%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 (dd, J = 9.4, 6.5 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.84 (dd, J = 17.8, 8.5 Hz, 4H), 6.76 (t, J = 7.3 Hz, 1H), 4.61 (d, J = 16.9 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 3.04 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.3 (d, $^{3}J_{C–F}$ = 16.3 Hz), 165.0 (d, $^{1}J_{C–F}$ = 274.9 Hz), 159.2, 149.2, 130.8 (d, $^{4}J_{C–F}$ = 3.0 Hz), 129.3, 124.1 (d, $^{4}J_{C–F}$ = 1.1 Hz), 117.6, 117.4 (d, $^{2}J_{C–F}$ = 18.0 Hz), 113.6, 112.9, 61.5, 55.3, 51.8 (d, $^{2}J_{C–F}$ = 24.1 Hz), 39.1 (d, $^{4}J_{C–F}$ = 1.1 Hz), 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -93.84 (s). HR-MS (EI) m/z calcd for $C_{20}H_{22}FNO_3$ [M+H$^+$] 344.1656, found 344.1658.

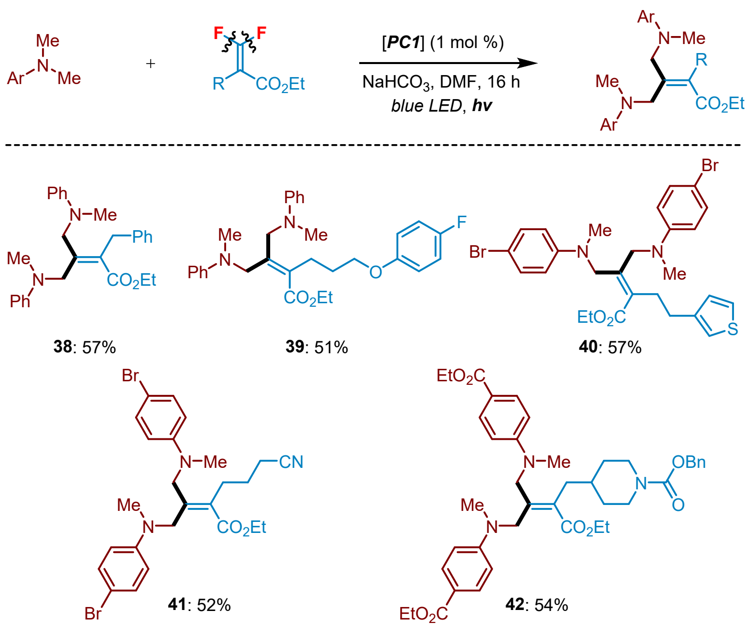


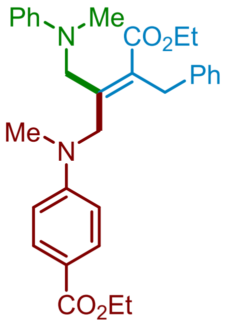
Ethyl (*E*)-4-{2-[3-ethoxy-1-fluoro-2-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl]pyrrolidin-1-yl}benzoate (32)

The general procedure **TP2** was followed using **N-aryl amines** (0.5 mmol) and **gem-difluoroalkenes** (0.25 mmol) for 24 h. Purification by column chromatography (PE) yielded

32 (34 mg, 30%) as a colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.95 (d, J = 8.9 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 6.89 (t, J = 11.7 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 5.42 – 5.23 (m, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.24 (dddd, J = 25.0, 10.8, 7.1, 3.7 Hz, 2H), 3.82 (s, 3H), 3.56 (td, J = 8.6, 4.3 Hz, 1H), 3.47 (dd, J = 15.3, 8.1 Hz, 1H), 2.57 – 2.35 (m, 1H), 2.34 – 2.19 (m, 2H), 2.16 – 2.00 (m, 1H), 1.39 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 167.1 (d, $J_{C\text{–}F}$ = 18.4 Hz), 166.6 (d, J = 274.9 Hz), 159.3, 150.2, 131.5, 130.7, 130.7, 124.0, 118.4, 116.5 (d, $^2J_{C\text{–}F}$ = 18.7 Hz), 113.7, 111.5, 61.6, 60.3, 57.7 (d, $^2J_{C\text{–}F}$ = 24.3 Hz), 55.4, 48.9, 32.1 (d, $^4J_{C\text{–}F}$ = 1.9 Hz), 24.0, 14.6, 14.2. ^{19}F-NMR (376 MHz, CDCl$_3$): δ = -102.32 (s). HR-MS (EI) m/z calcd for $C_{25}H_{28}FNO_5$ [M+H$^+$] 442.2024, found 442.2034.

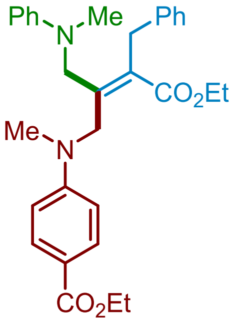
Scheme S3. Photoredox-Catalyzed Twofold Csp^3–H/Csp^2–F Bond-Diaminomethylation.





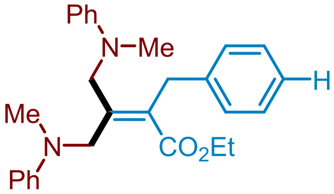
Ethyl (*E*)-4-{[3-benzyl-4-ethoxy-2-((methyl(phenyl)amino)methyl)-4-oxobut-2-en-1-yl](methyl)amino}benzoate (37)

The general procedure **TP3** was followed using **6** (0.27 mmol) and **1a** (0.54 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **37** (38 mg, 35%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 9.0 Hz, 2H), 7.29 (dd, J = 9.9, 4.8 Hz, 2H), 7.24 – 7.15 (m, 5H), 6.75 (t, J = 7.2 Hz, 1H), 6.70 – 6.59 (m, 4H), 4.34 – 4.29 (m, 2H), 4.19 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.88 (d, J = 6.9 Hz, 4H), 2.88 (s, 3H), 2.72 (s, 3H), 1.36 (dd, J = 8.0, 6.2 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 167.1 153.3, 150.3, 141.2, 138.3, 133.6, 131.2, 129.3, 128.7, 128.6, 126.7, 118.3, 118.1, 113.8, 111.7, 61.1, 60.3, 52.6, 51.8, 38.3, 38.2, 36.1, 14.6, 14.2. HR-MS (EI) m/z calcd for $C_{31}H_{36}N_2O_4$ [M+H$^+$] 501.2748, found 501.2749.



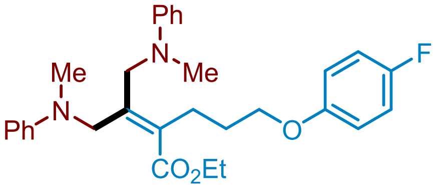
Ethyl (*Z*)-4-{[3-benzyl-4-ethoxy-2-((methyl(phenyl)amino)methyl)-4-oxobut-2-en-1-yl](methyl)amino}benzoate (37')

The general procedure **TP3** was followed using **6** (0.27 mmol) and **1a** (0.54 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **37'** (38 mg, 35%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 9.0 Hz, 2H), 7.40 – 7.12 (m, 7H), 6.80 – 6.66 (m, 3H), 6.61 (t, J = 13.0 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 4.20 – 4.03 (m, 4H), 3.93 (d, J = 27.2 Hz, 2H), 3.87 (s, 2H), 2.86 (d, J = 21.2 Hz, 3H), 2.74 (d, J = 12.5 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.13 (dd, J = 8.0, 6.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.3, 167.0, 153.1, 150.4, 140.9, 138.2, 133.5, 131.3, 129.2, 128.7, 128.6, 126.7, 118.5, 117.8, 113.8, 111.6, 61.0, 60.3, 53.1, 51.2, 38.4, 38.1, 36.1, 14.6, 14.2. HR-MS (EI) m/z calcd for $C_{31}H_{36}N_2O_4$ [M+H$^+$] 501.2748, found 501.2749.



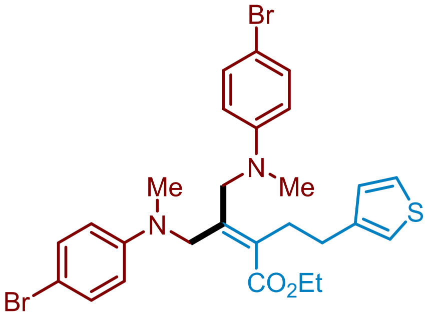
Ethyl 2-benzyl-4-[methyl(phenyl)amino]-3-{[methyl(phenyl)amino]methyl}but-2-enoate (38)

The general procedure **TP3** was followed using **N-aryl amines** (0.75 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **38** (61 mg, 57%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.24 (m, 2H), 7.24 – 7.15 (m, 7H), 6.77 – 6.68 (m, 6H), 4.08 – 4.00 (m, 4H), 3.96 (s, 2H), 3.87 (s, 2H), 2.79 (s, 3H), 2.76 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.5, 150.5, 150.5, 141.6, 138.5, 133.0, 129.2, 129.1, 128.6, 126.5, 117.7, 117.4, 113.8, 113.7, 60.9, 53.5, 52.0, 38.3, 38.1, 36.1, 14.1. HR-MS (EI) m/z calcd for $C_{28}H_{32}N_2O_2$ [M+H$^+$] 429.2537, found 429.2540.



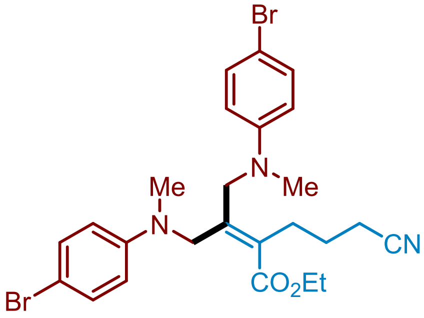
Ethyl 2-{1,3-bis[methyl(phenyl)amino]propan-2-ylidene}-5-(4-fluorophenoxy)pentanoate (39)

The general procedure **TP3** was followed using **N-aryl amines** (0.75 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **39** (62.5 mg, 51%) as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17 (td, *J* = 7.5, 4.6 Hz, 4H), 6.93 (t, *J* = 8.6 Hz, 2H), 6.85 – 6.64 (m, 8H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 3.92 (t, *J* = 5.9 Hz, 2H), 3.87 (s, 2H), 2.76 (s, 3H), 2.74 (s, 3H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.95 (dt, *J* = 13.3, 6.5 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.1, 157.3 (d, $^1J_{C-F}$ = 238.2 Hz), 155.0 (d, $^4J_{C-F}$ = 1.6 Hz), 150.6, 150.4, 139.7, 133.5, 129.2, 129.1, 117.7, 117.4, 115.9 (d, $^2J_{C-F}$ = 23.2 Hz), 115.4 (d, $^3J_{C-F}$ = 8.0 Hz), 113.8, 113.7, 67.1, 61.0, 53.9, 51.1, 38.4, 37.9, 28.1, 26.7, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -124.13 (s). HR-MS (EI) m/z calcd for $C_{30}H_{35}FN_2O_3$ [M+H$^+$] 491.2704, found 491.2704.



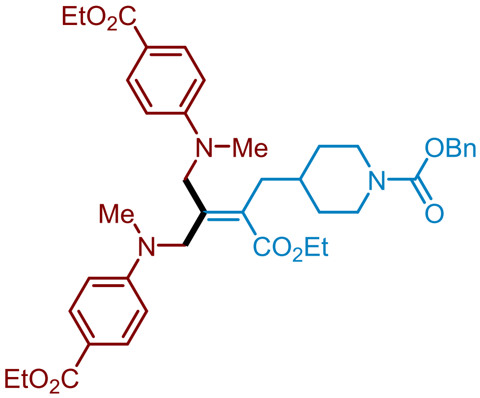
Ethyl 4-[(4-bromophenyl)(methyl)amino]-3-{[(4-bromophenyl)(methyl)amino]methyl}-2-[2-(thiophen-3-yl)ethyl]but-2-enoate (40)

The general procedure **TP3** was followed using **N-aryl amines** (0.75 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **40** (86 mg, 57%) as an oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.22 (ddd, J = 6.6, 4.2, 1.7 Hz, 5H), 7.00 – 6.90 (m, 2H), 6.55 – 6.45 (m, 4H), 4.17 (q, J = 7.1 Hz, 2H), 3.85 (s, 2H), 3.62 (s, 2H), 2.83 – 2.74 (m, 4H), 2.68 (s, 3H), 2.64 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 169.7, 149.2 (d, J = 1.5 Hz), 140.9, 139.1, 134.0, 131.9, 131.7, 128.4, 125.7, 121.3, 115.1, 115.0, 109.7, 109.4, 61.1, 53.6, 50.8, 38.1, 37.8, 31.6, 29.0, 14.4. HR-MS (EI) m/z calcd for $C_{27}H_{30}Br_2N_2O_2S$ [M+H$^+$] 605.0468, found 605.0468.



Ethyl 2-{1,3-bis[(4-bromophenyl)(methyl)amino]propan-2-ylidene}-5-cyanopentanoate (41)

The general procedure **TP3** was followed using **N-aryl amines** (0.75 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **41** (73 mg, 52%) as an oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.27 (d, J = 6.8 Hz, 2H), 7.24 (d, J = 9.1 Hz, 2H), 6.56 (dd, J = 9.1, 7.0 Hz, 4H), 4.19 – 4.14 (m, 2H), 3.91 (s, 2H), 3.87 (s, 2H), 2.76 (s, 3H), 2.72 (s, 3H), 2.65 – 2.59 (m, 2H), 2.40 (t, J = 7.0 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.27 (d, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 169.3, 149.3, 149.2, 140.2, 132.8, 132.0, 131.8, 119.2, 115.4, 115.2, 110.2, 109.8, 61.3, 53.7, 51.2, 38.5, 38.1, 28.9, 24.5, 16.8, 14.3. HR-MS (EI) m/z calcd for $C_{25}H_{29}Br_2N_3O_2$ [M+H$^+$] 562.0699, found 562.0690.



Diethyl 4,4'-{[2-(3-(1-((benzyloxy)carbonyl)piperidin-4-yl)-1-ethoxy-1-oxopropan-2-ylidene)propane-1,3-diyl]bis(methylazanediyl)dibenzoate (42)

The general procedure **TP3** was followed using **N-aryl amines** (0.75 mmol) and ***gem*-difluoroalkenes** (0.25 mmol) for 16 h. Purification by column chromatography (PE/EtOAc 100:1) yielded **42** (96.3 mg, 54%) as an oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.85 (dd, J = 13.3, 9.0 Hz, 4H), 7.39 – 7.27 (m, 5H), 6.60 (dd, J = 12.2, 9.1 Hz, 4H), 5.12 (s, 2H), 4.31 (qd, J = 7.1, 3.6 Hz, 4H), 4.19 (q, J = 7.1 Hz, 4H), 3.97 (d, J = 19.9 Hz, 4H), 2.82 (s, 3H), 2.80 (s, 3H), 2.76 (d, J = 3.6 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.74 (d, J = 11.7 Hz, 2H), 1.67 – 1.58 (m, 1H), 1.36 (td, J = 7.1, 2.9 Hz, 6H), 1.28 (t, J = 7.1 Hz, 3H), 1.20 – 1.10 (m, 2H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 169.6, 166.9, 166.8, 155.3, 153.0, 153.0, 138.6, 136.9, 134.1, 131.3, 131.2, 128.5, 128.0, 128.0, 118.9, 118.6, 111.8, 111.6, 67.1, 61.2, 60.3, 60.3, 52.4, 50.5, 44.2, 38.0, 37.9, 37.1, 35.8, 32.0, 27.0, 14.5, 14.3. HR-MS (EI) m/z calcd for $C_{41}H_{51}N_3O_8$ [M+H$^+$] 714.3749, found 714.3755.

References:

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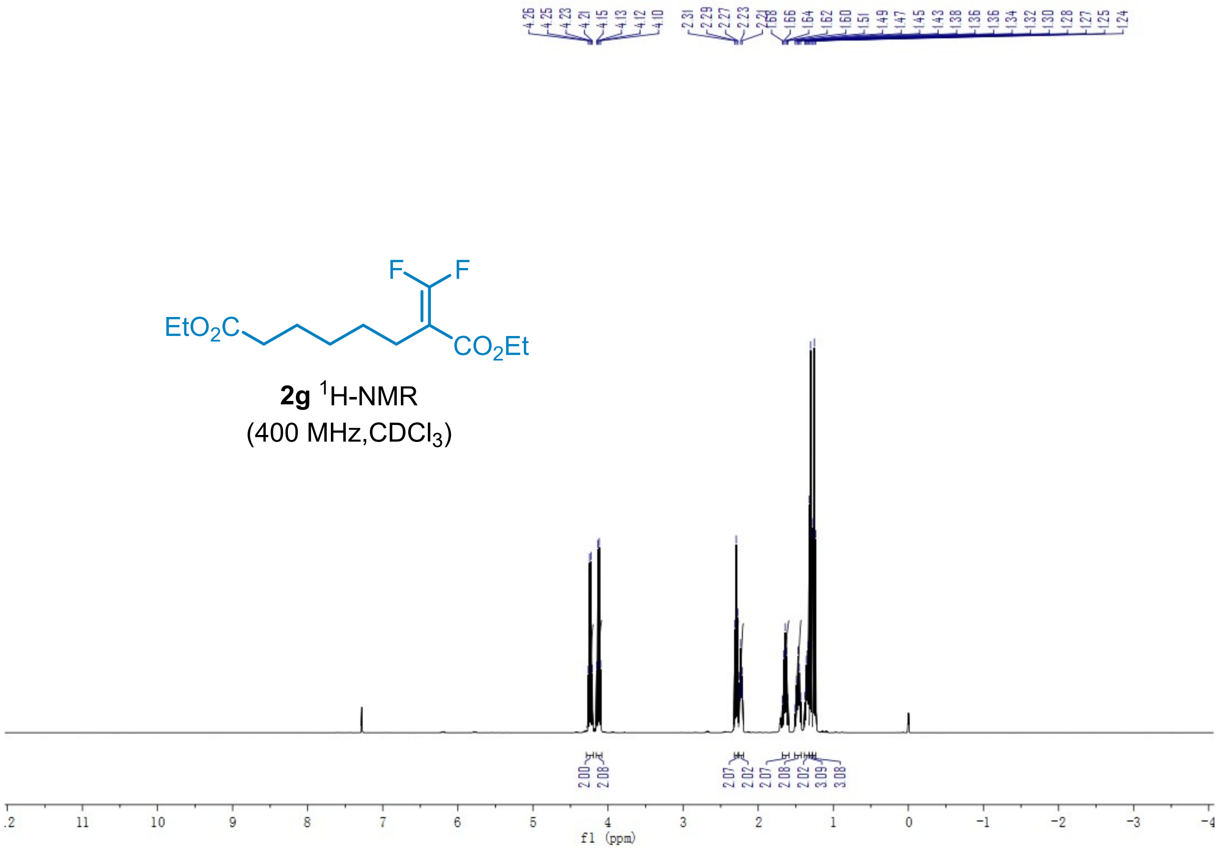
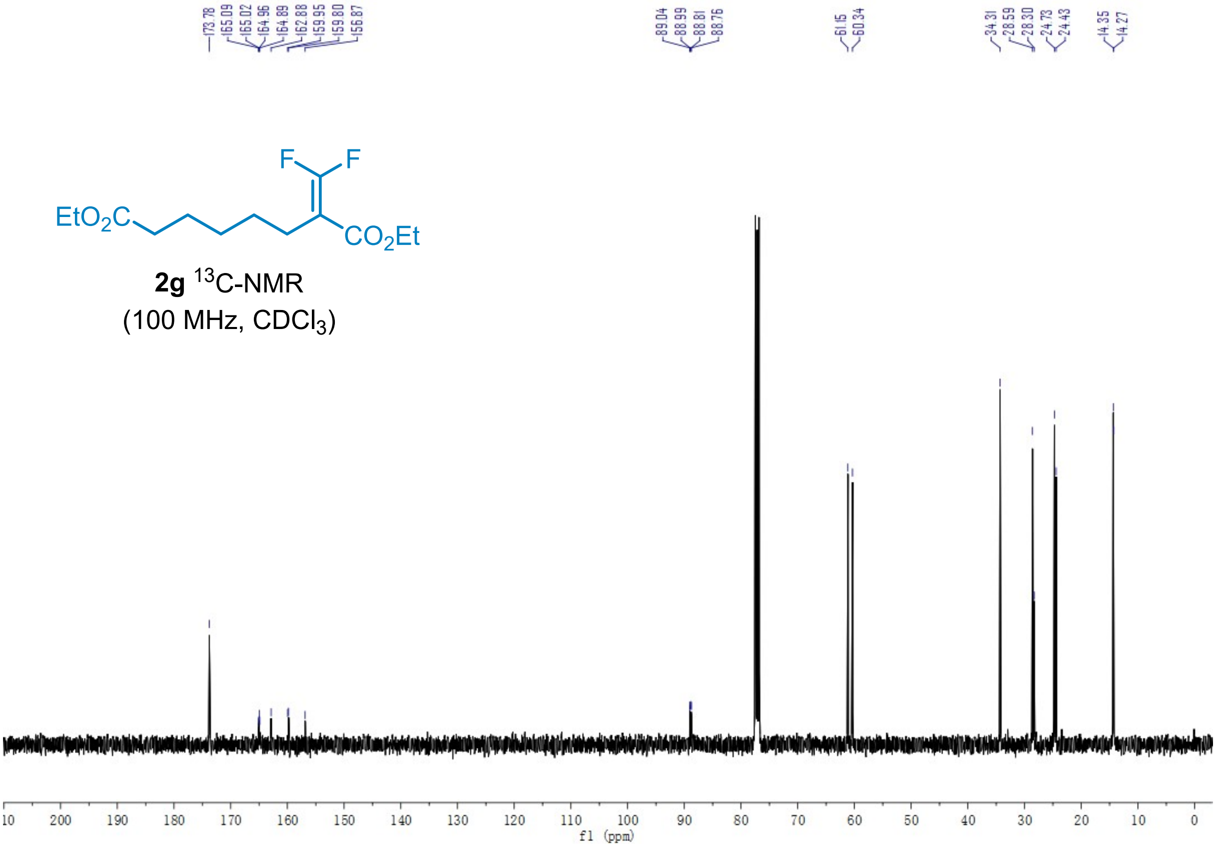
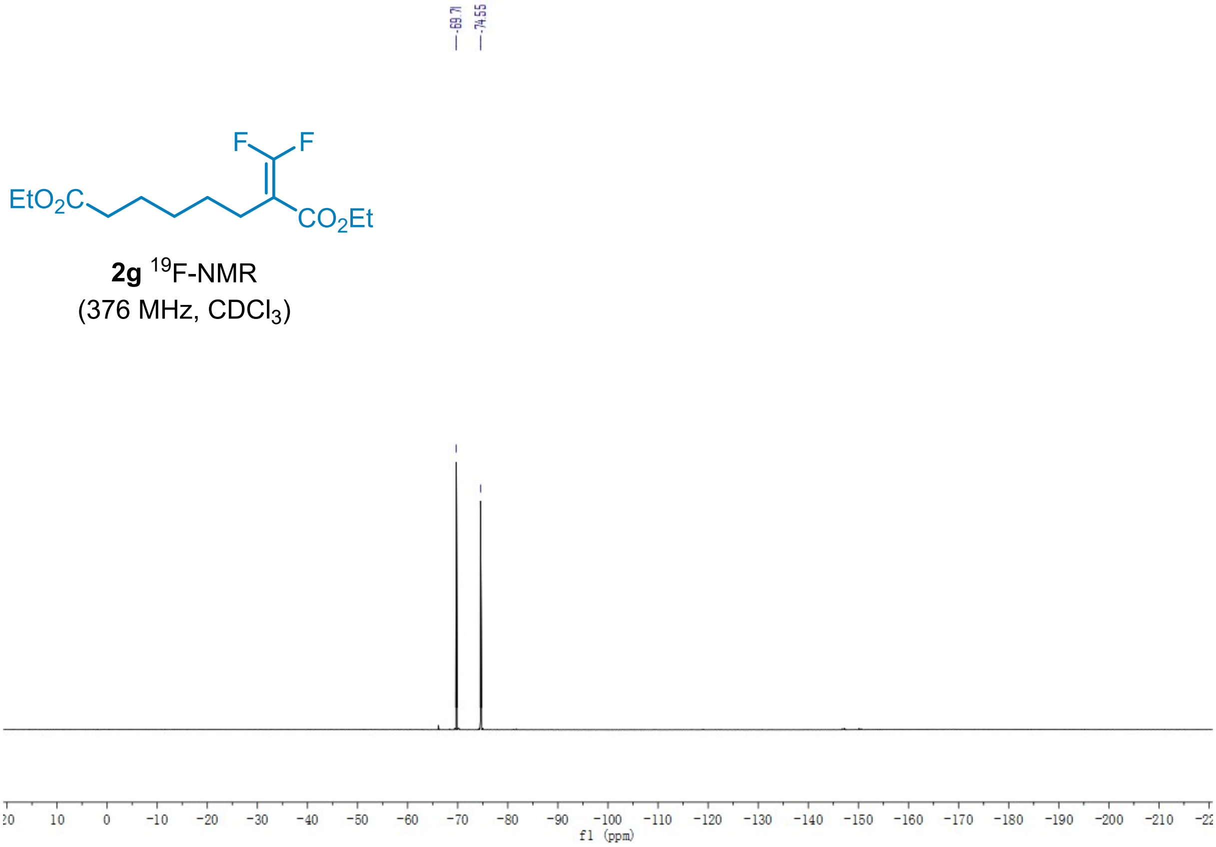
2g ^{1}H-NMR
(400 MHz,CDCl$_3$)

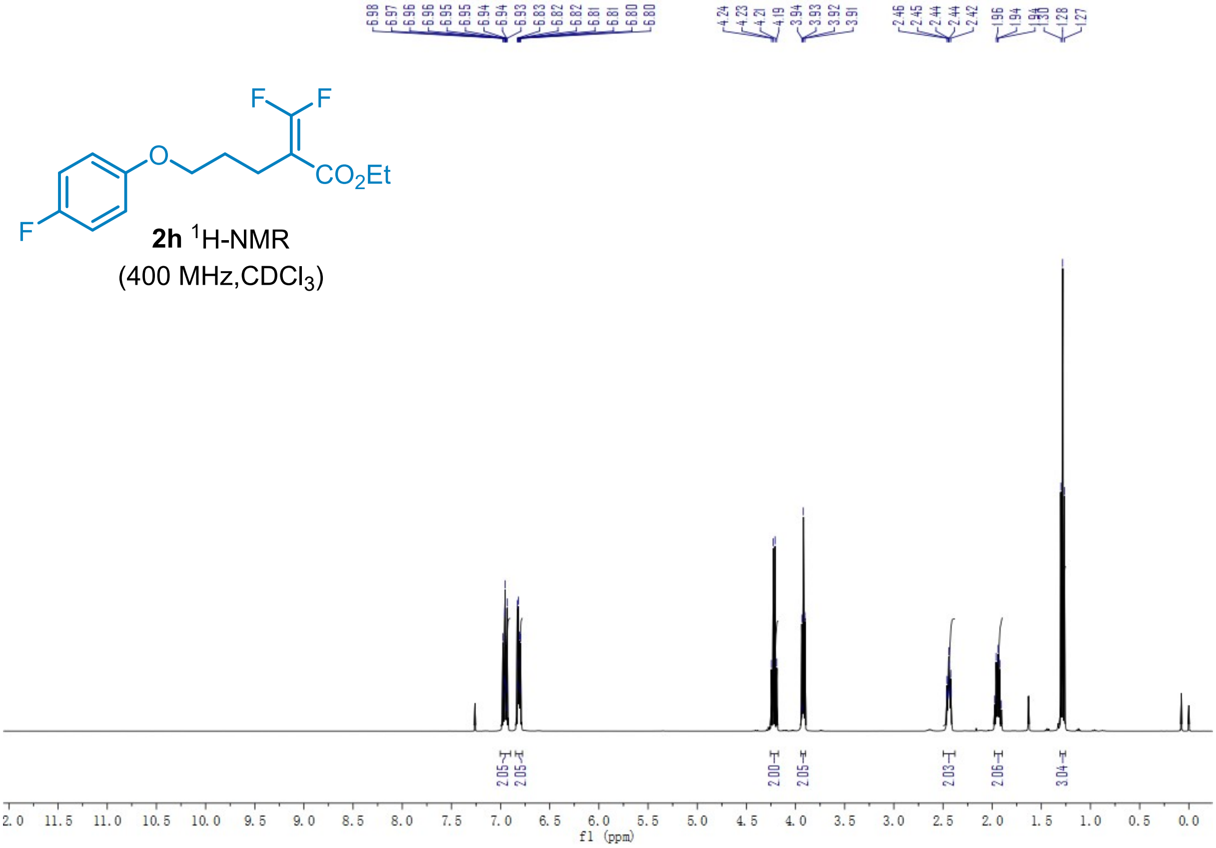


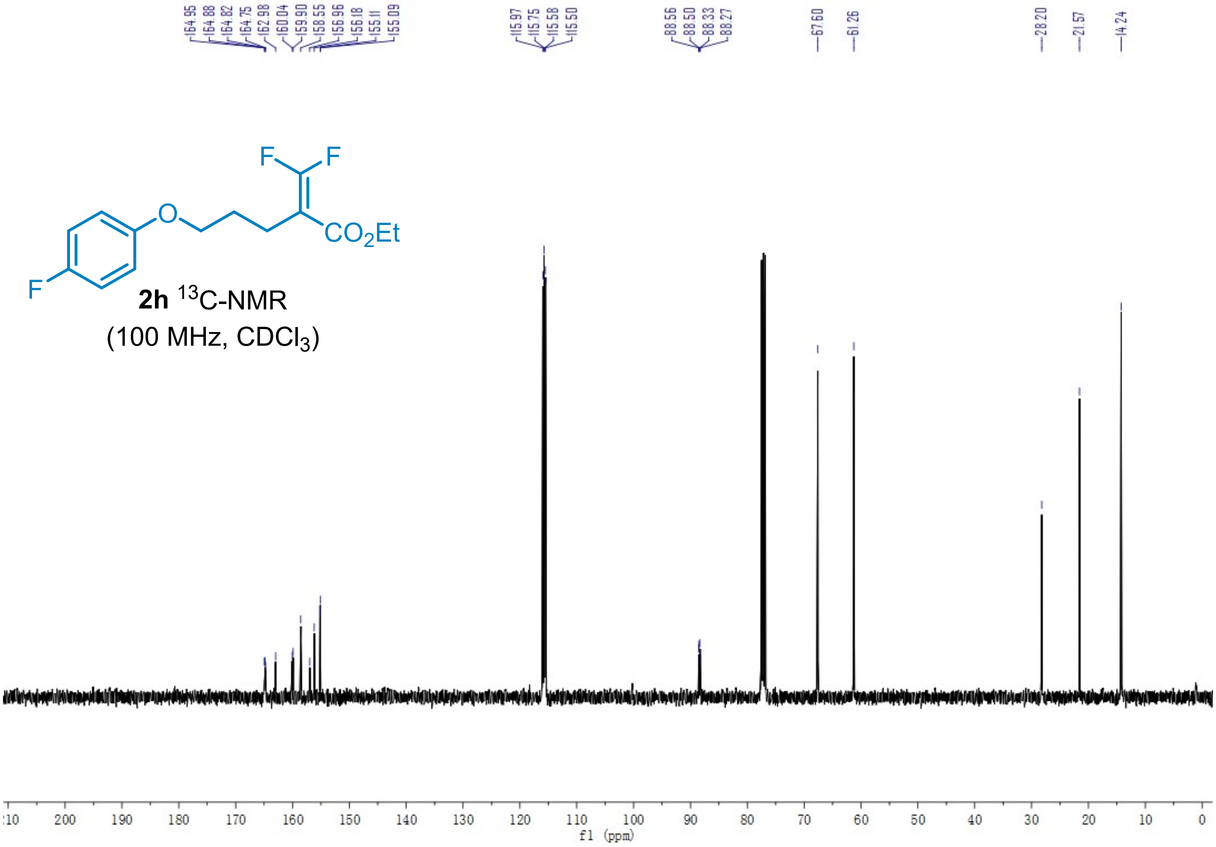


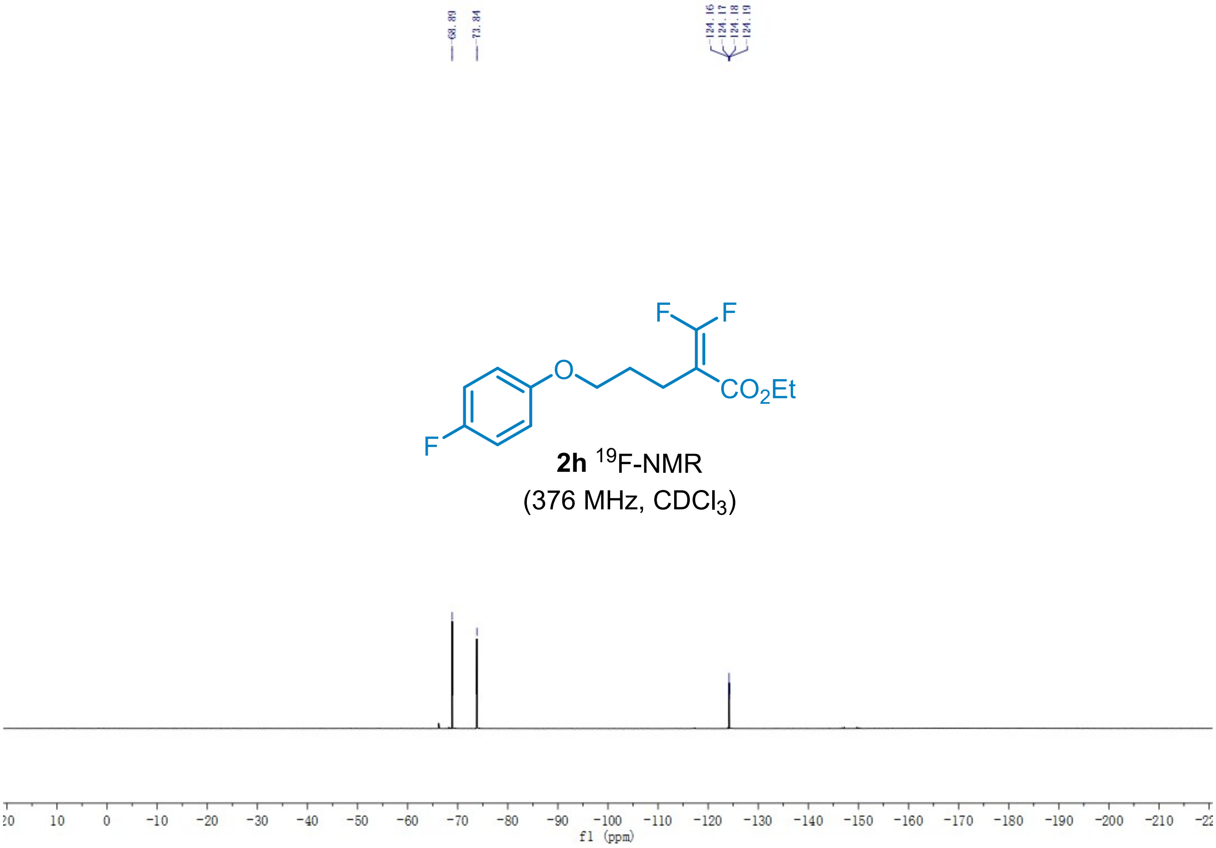
2g ^{13}C-NMR
(100 MHz, $CDCl_3$)



2g ^{19}F-NMR
(376 MHz, $CDCl_3$)

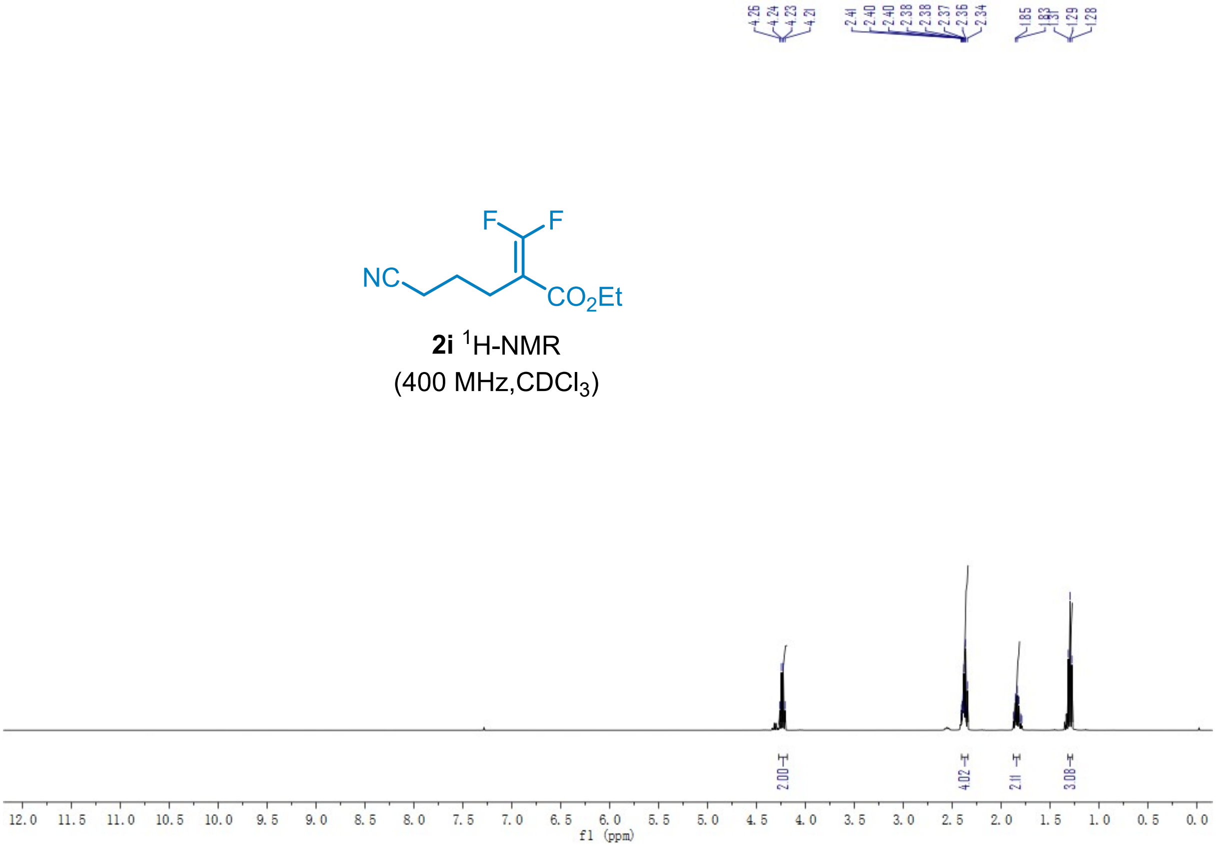

2h ^{1}H-NMR
(400 MHz,CDCl$_3$)


2h ^{13}C-NMR
(100 MHz, CDCl$_3$)



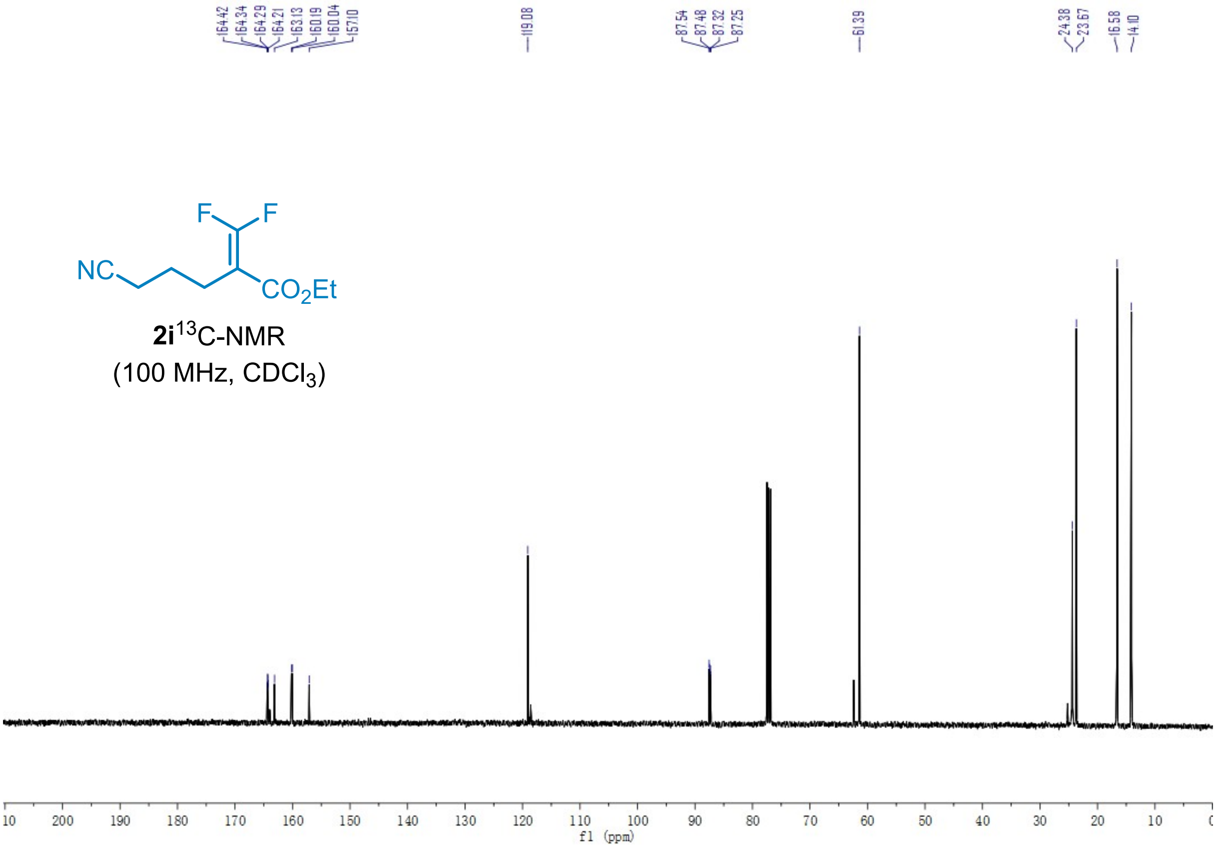
2h ^{19}F-NMR

(376 MHz, $CDCl_3$)

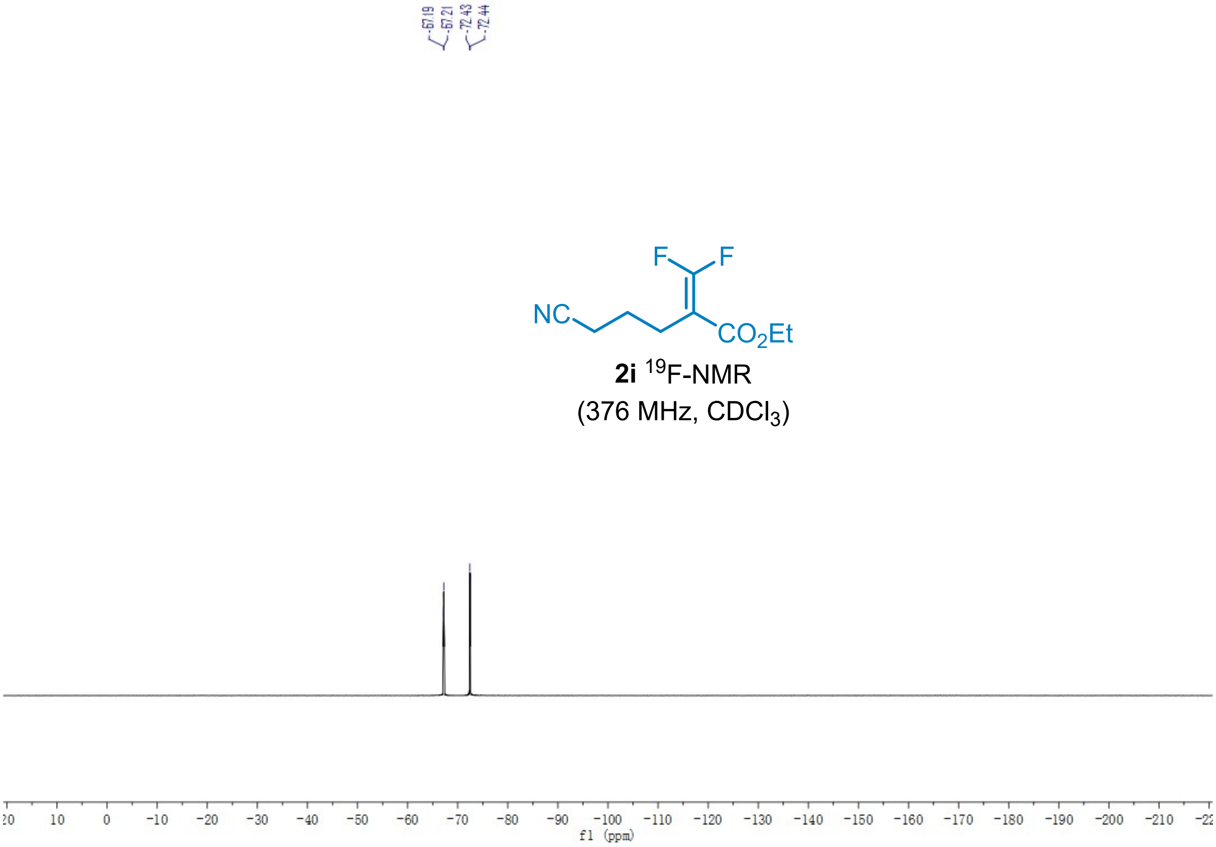


2i ^{1}H-NMR

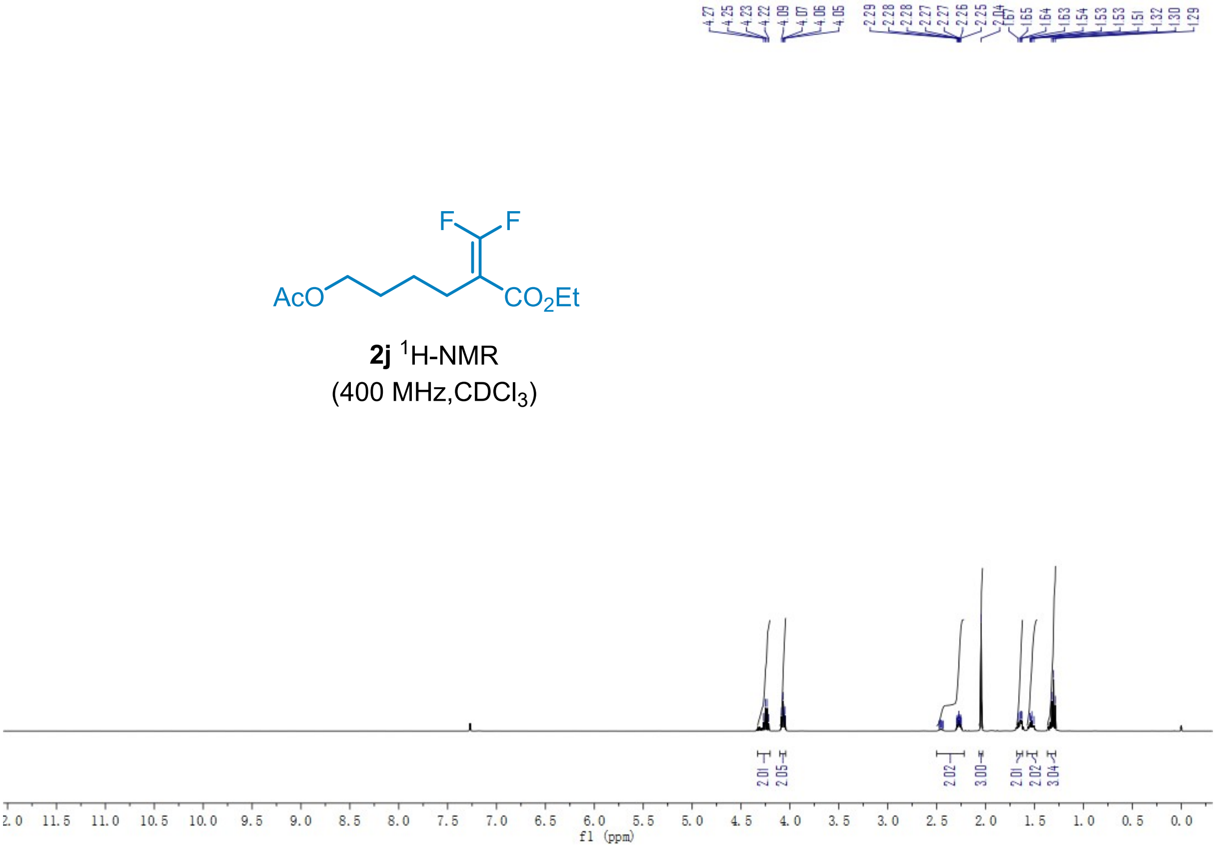
(400 MHz,$CDCl_3$)



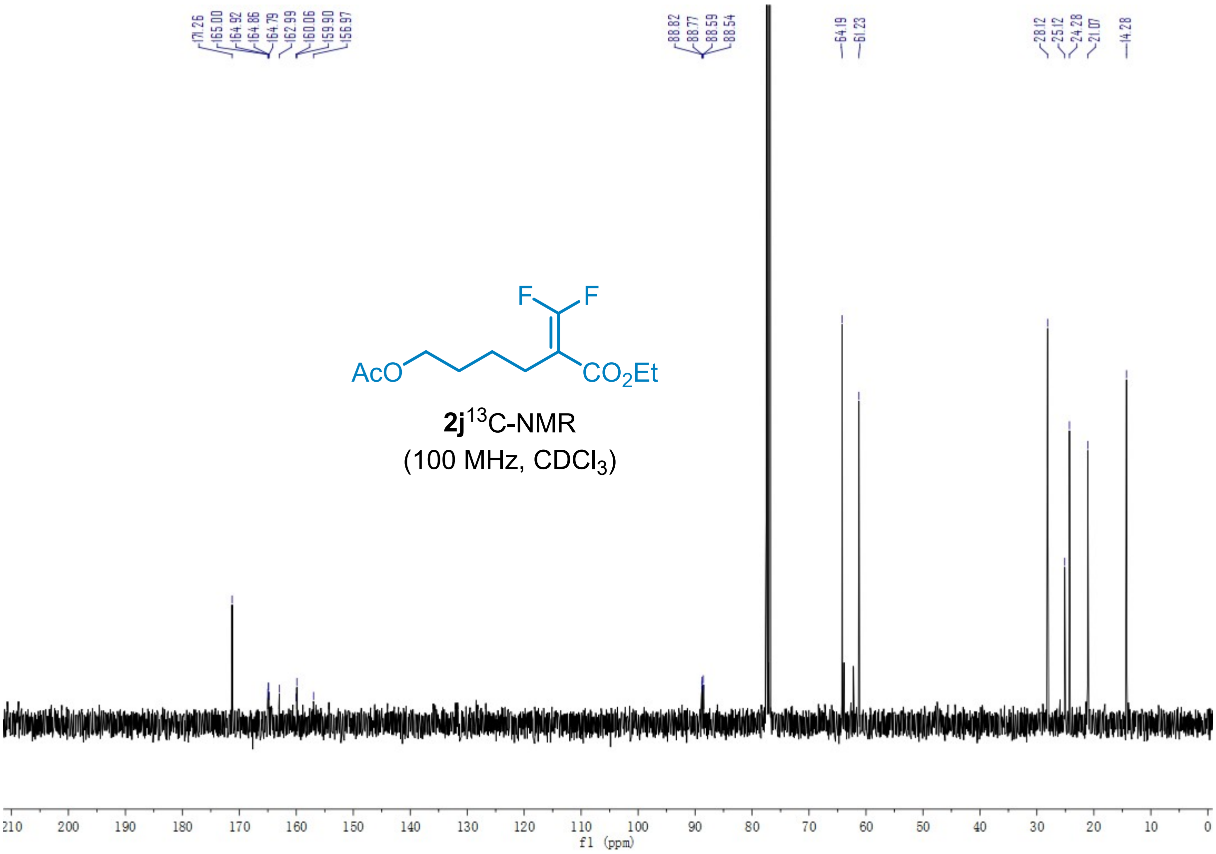
2i ^{13}C-NMR
(100 MHz, CDCl$_3$)



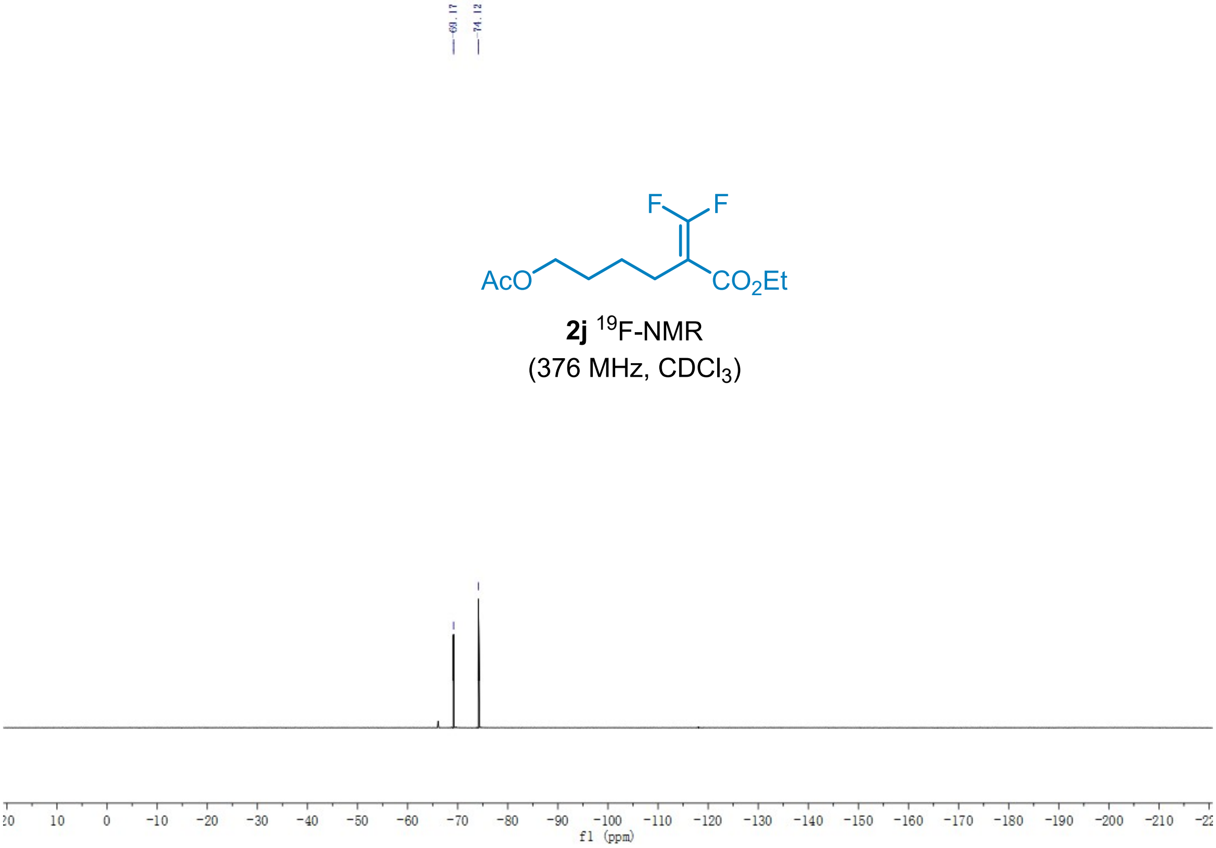
2i ^{19}F-NMR
(376 MHz, CDCl$_3$)



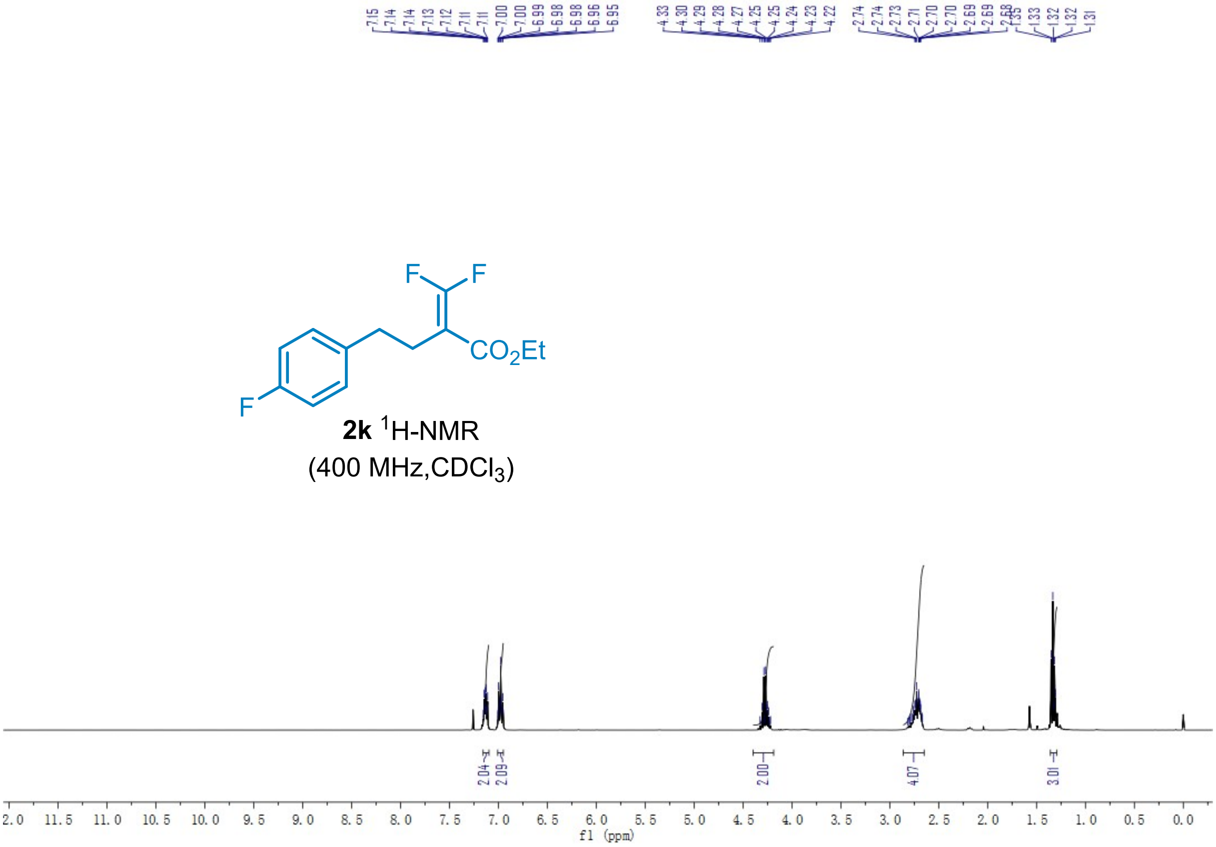
2j ^{1}H-NMR
(400 MHz,CDCl$_3$)



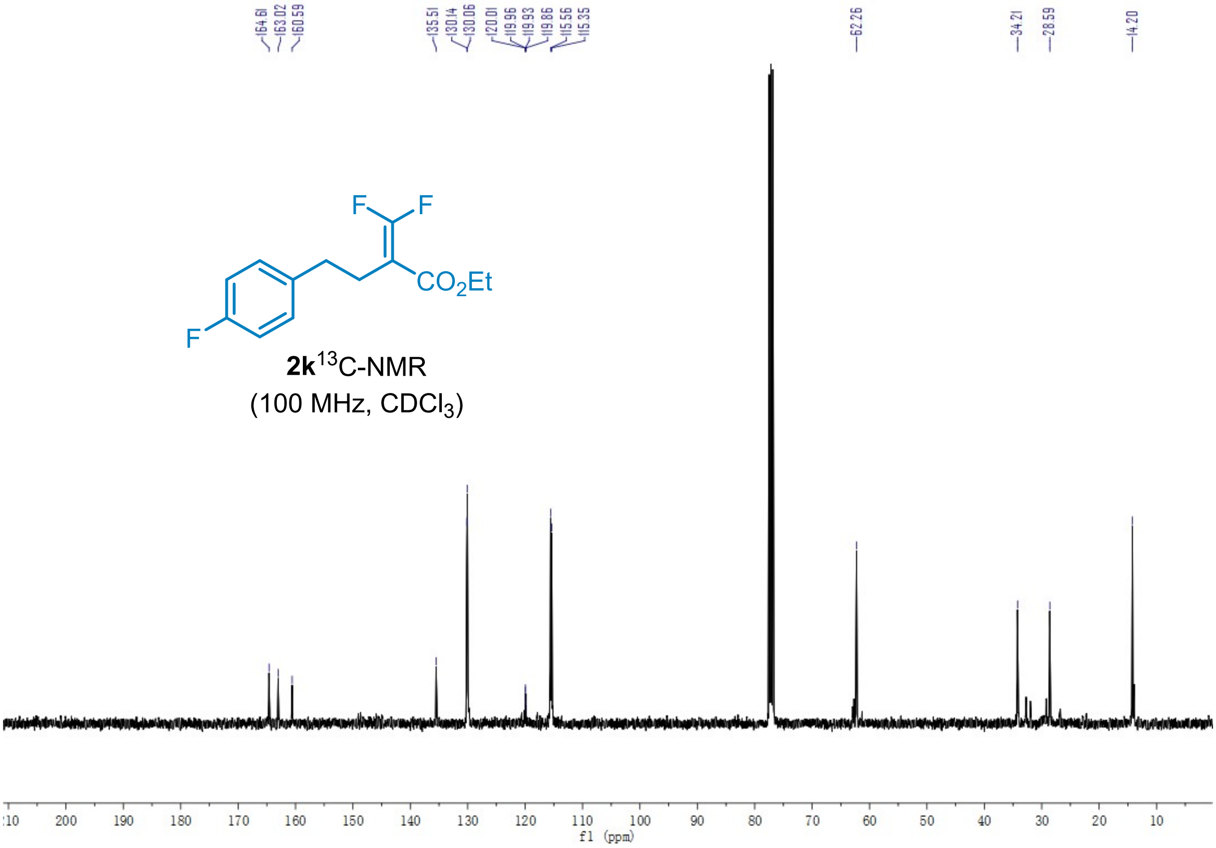
2j ^{13}C-NMR
(100 MHz, CDCl$_3$)



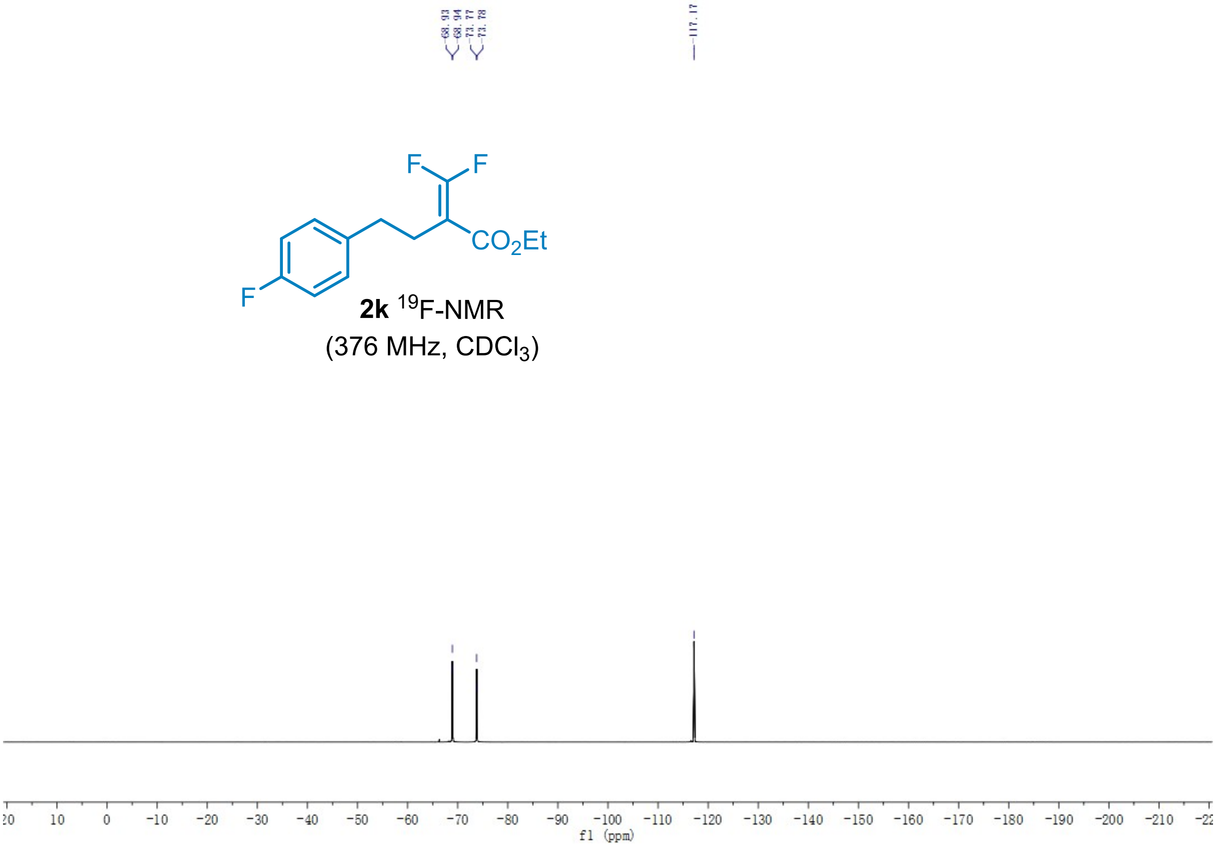
2j ^{19}F-NMR
(376 MHz, $CDCl_3$)



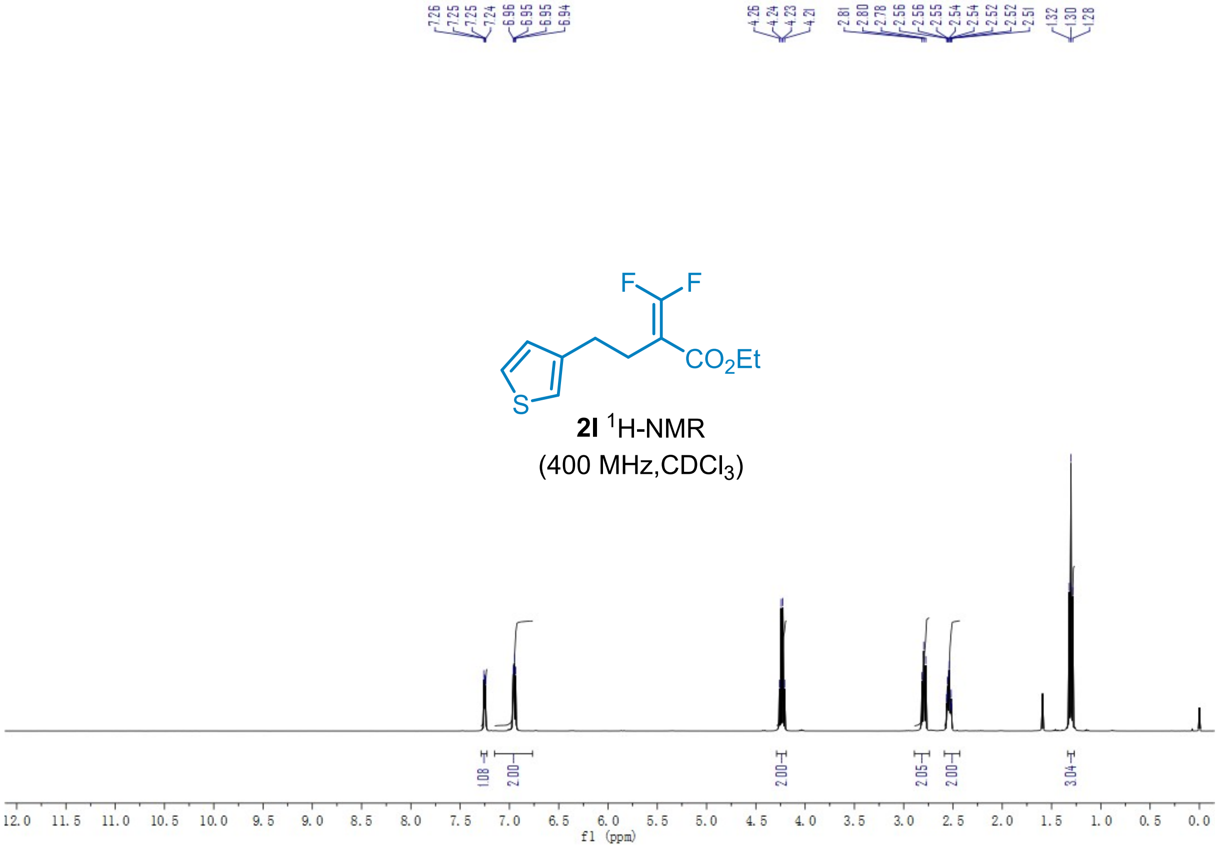
2k ^{1}H-NMR
(400 MHz,$CDCl_3$)



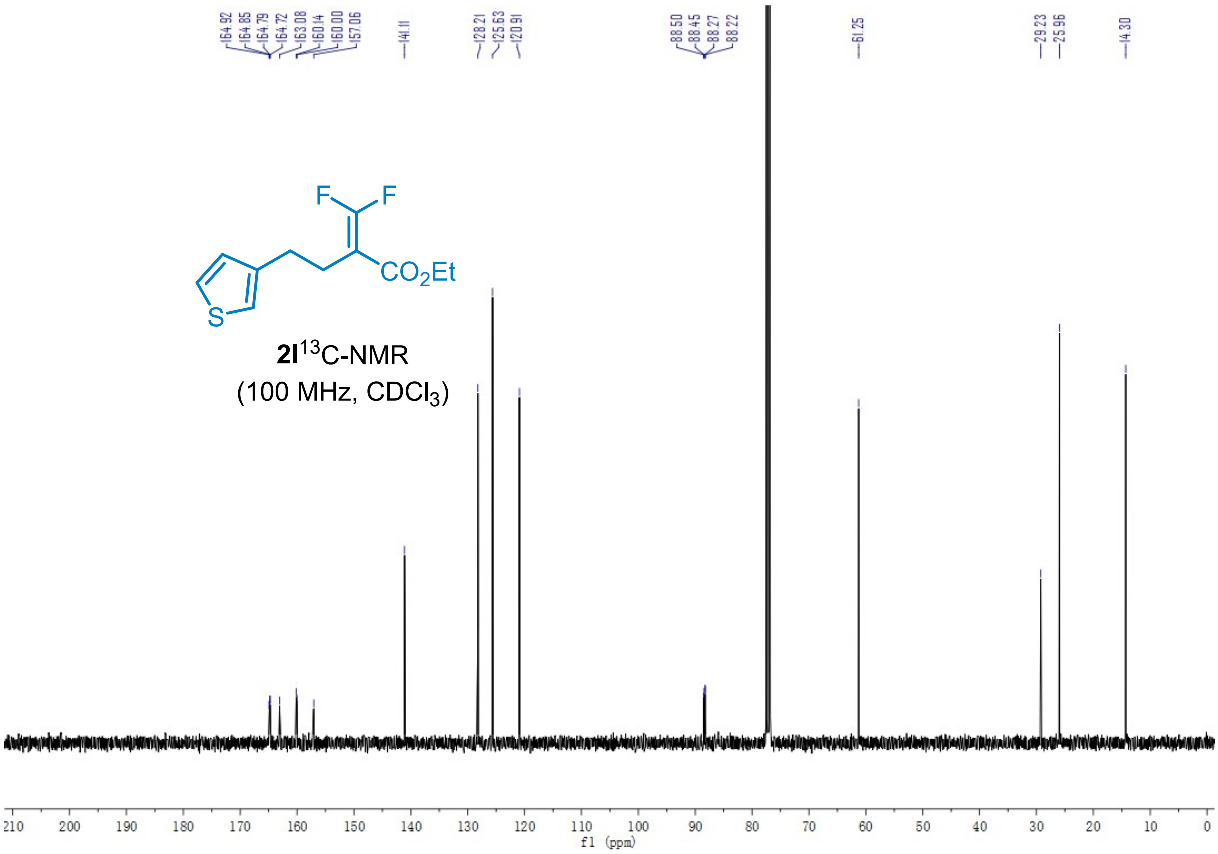
2k ^{13}C-NMR
(100 MHz, $CDCl_3$)



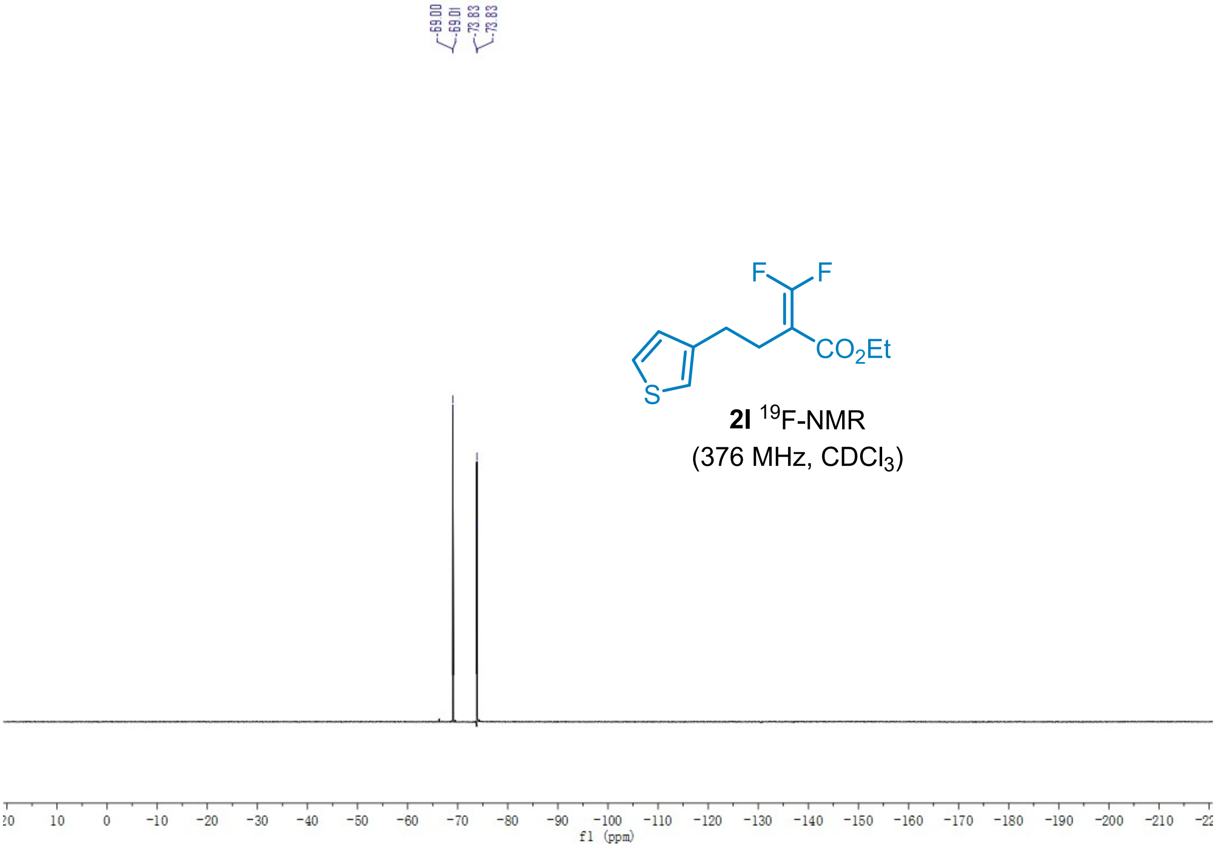
2k ^{19}F-NMR
(376 MHz, $CDCl_3$)



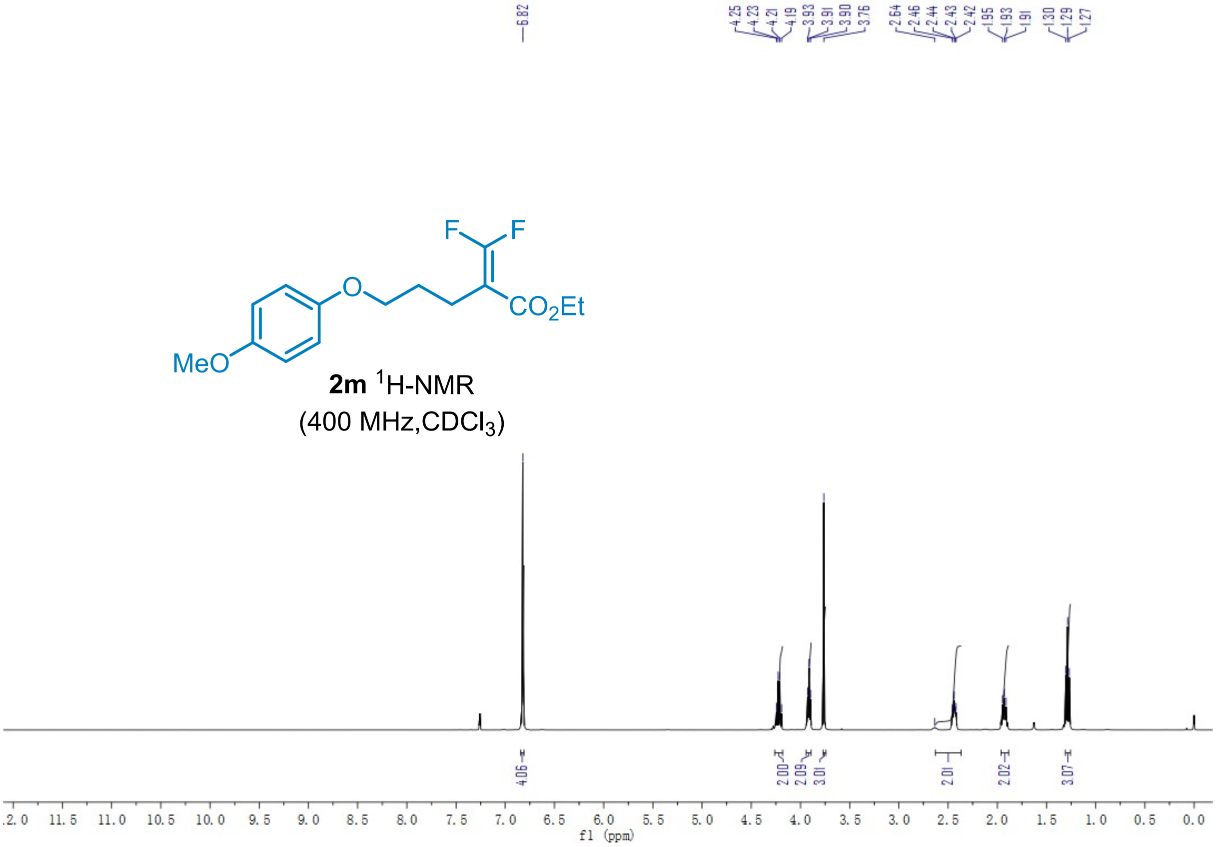
2l ^{1}H-NMR
(400 MHz,CDCl$_3$)



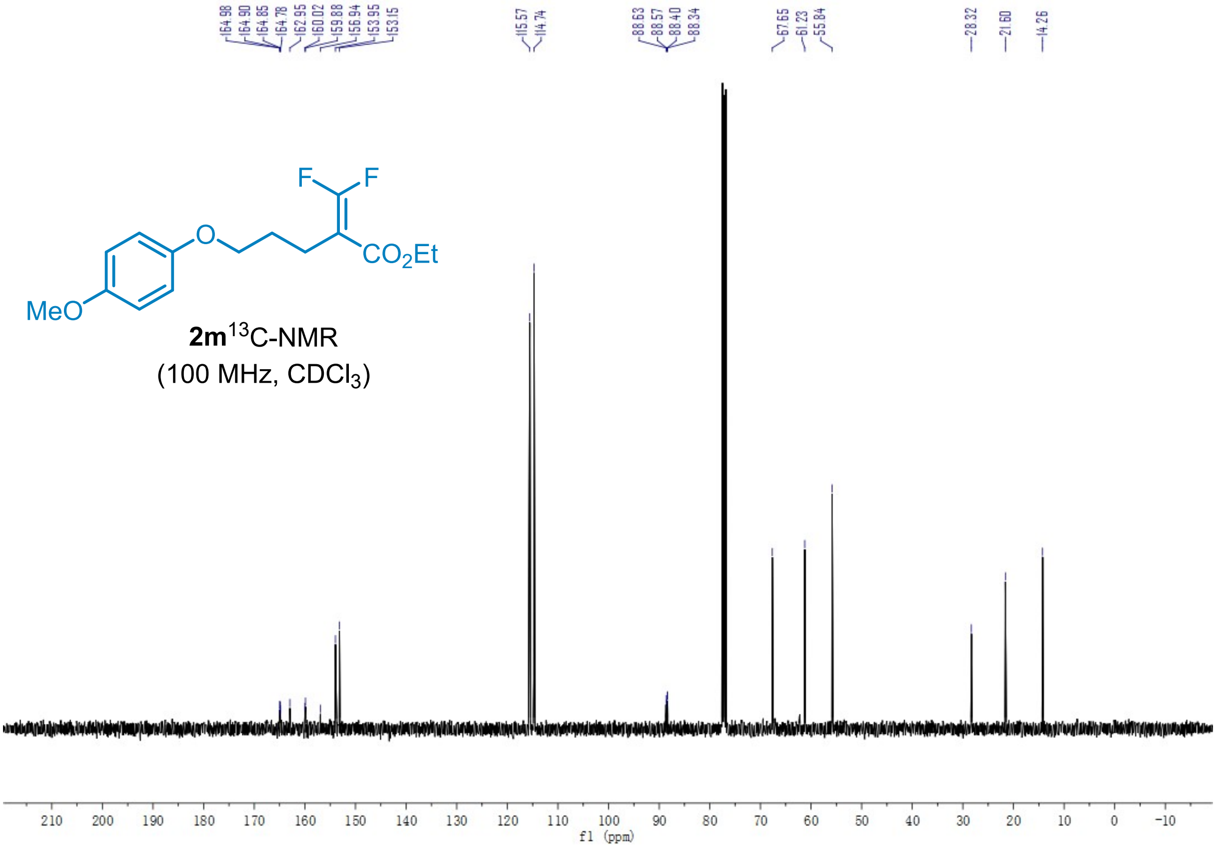
2l ^{13}C-NMR
(100 MHz, CDCl$_3$)



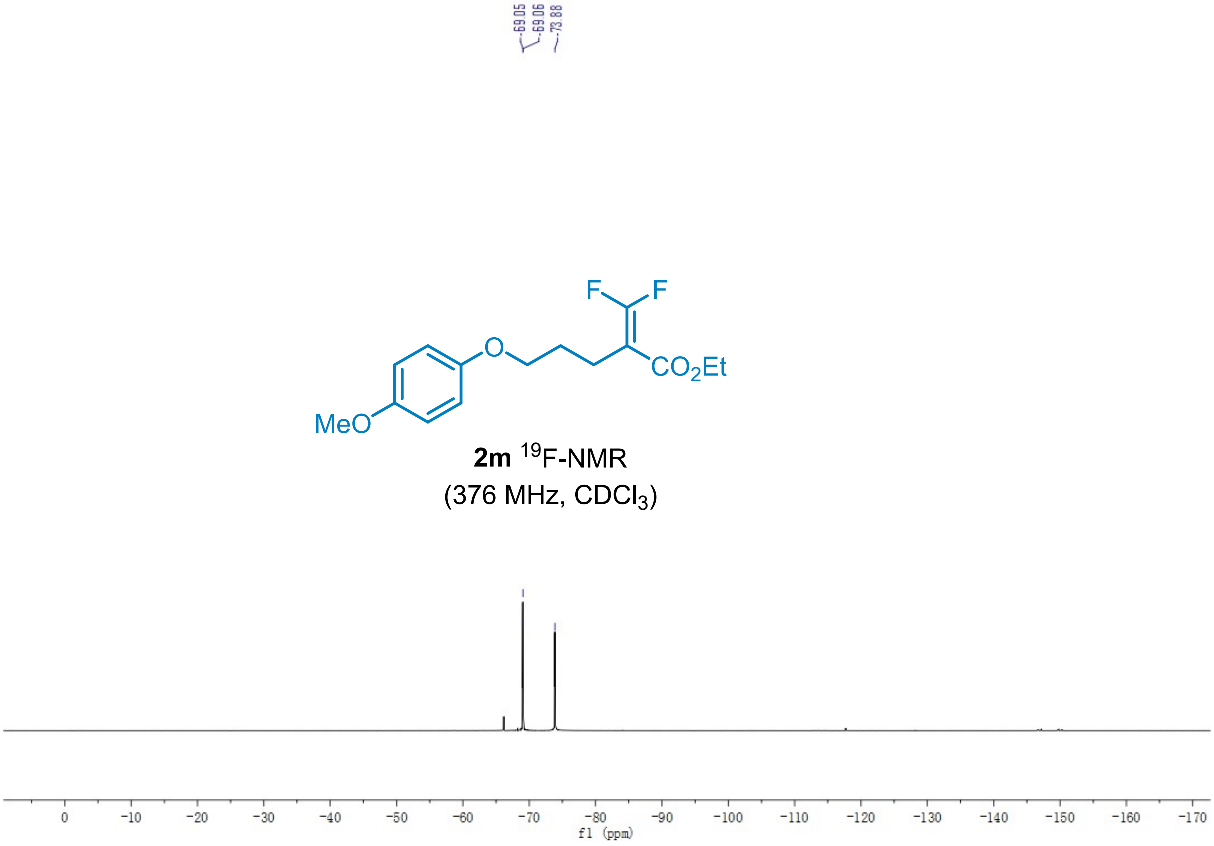
2l ^{19}F-NMR
(376 MHz, $CDCl_3$)



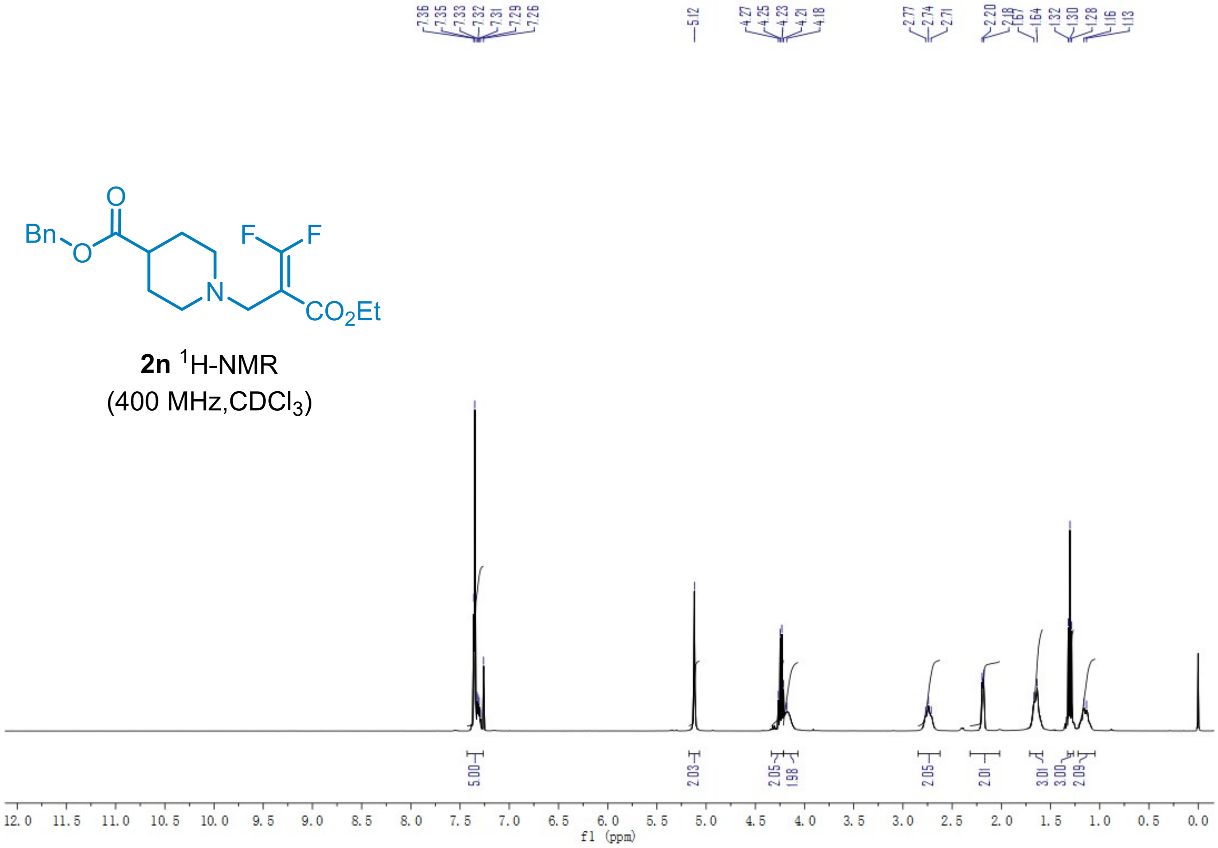
2m ^{1}H-NMR
(400 MHz,$CDCl_3$)



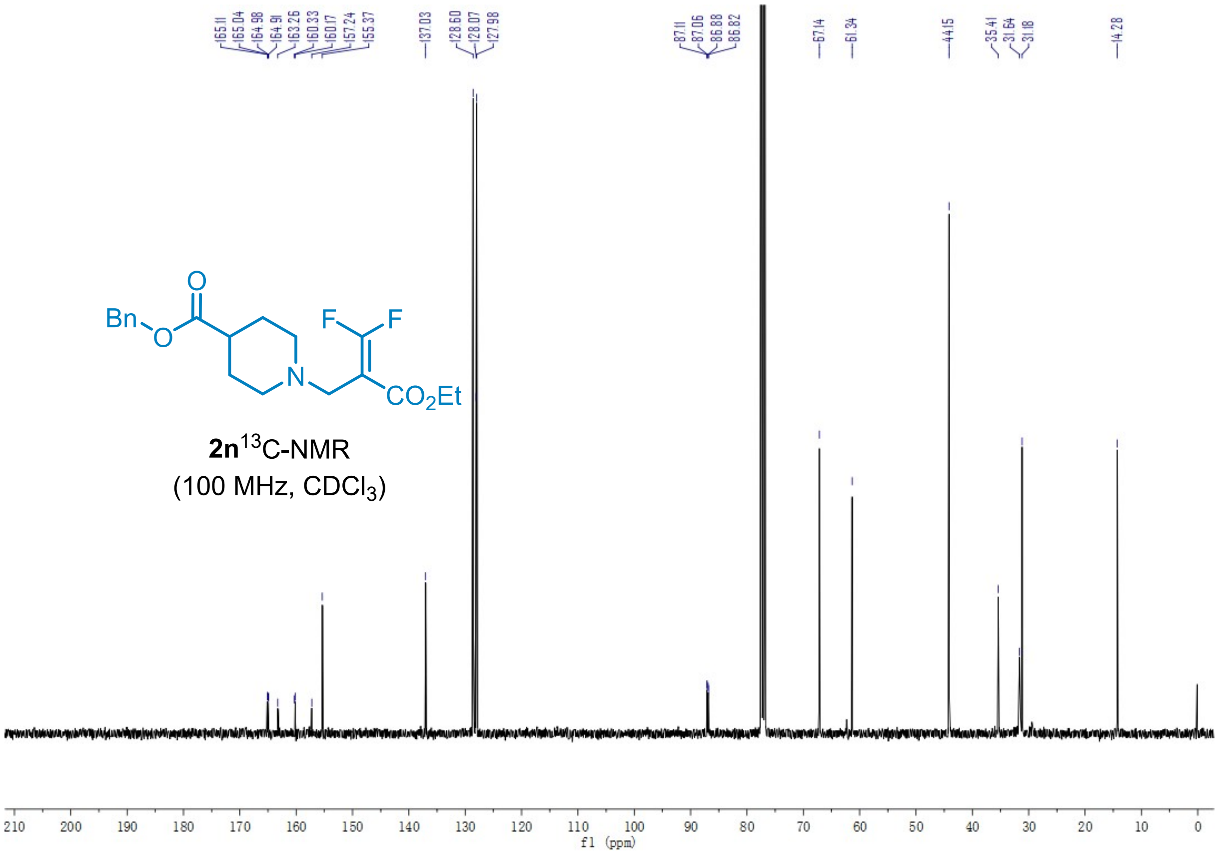
2m ^{13}C-NMR
(100 MHz, $CDCl_3$)



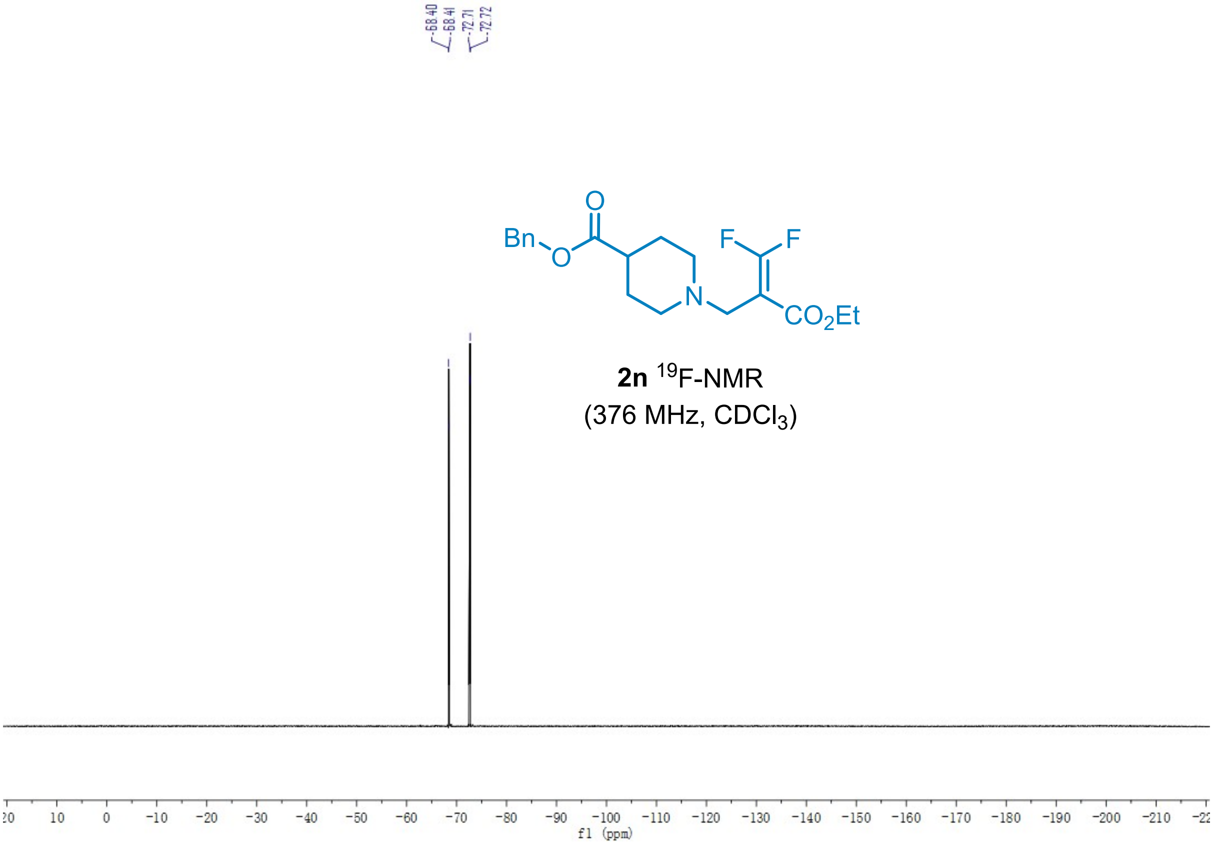
2m ^{19}F-NMR
(376 MHz, $CDCl_3$)



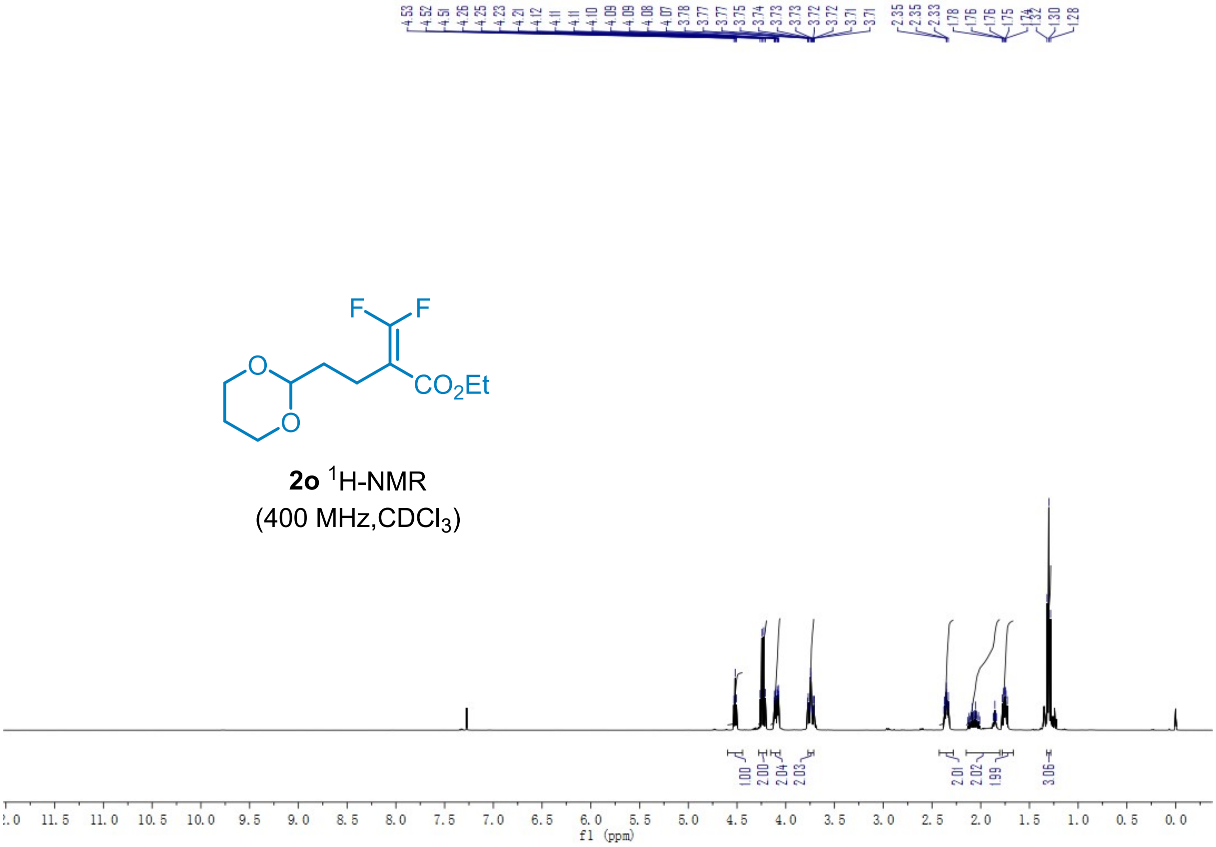
2n ^{1}H-NMR
(400 MHz,CDCl$_3$)



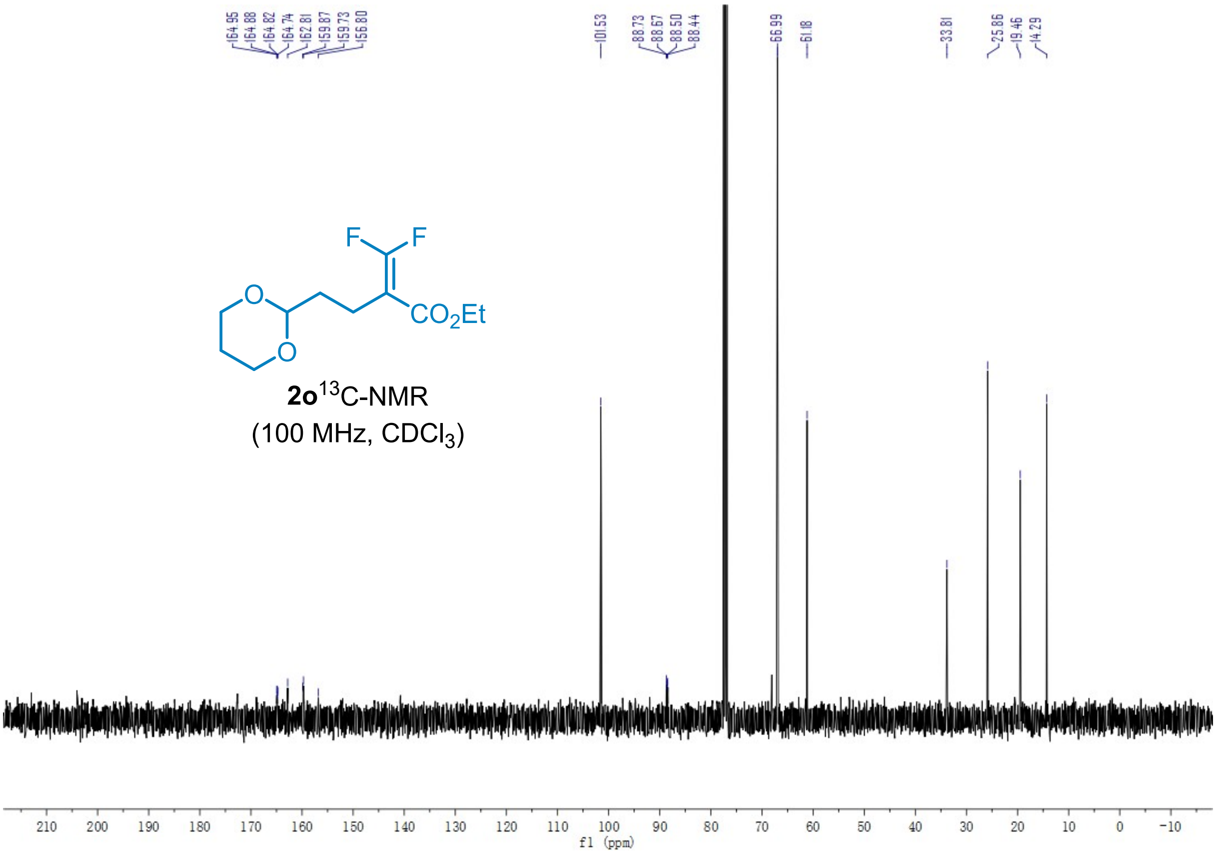
2n ^{13}C-NMR
(100 MHz, CDCl$_3$)



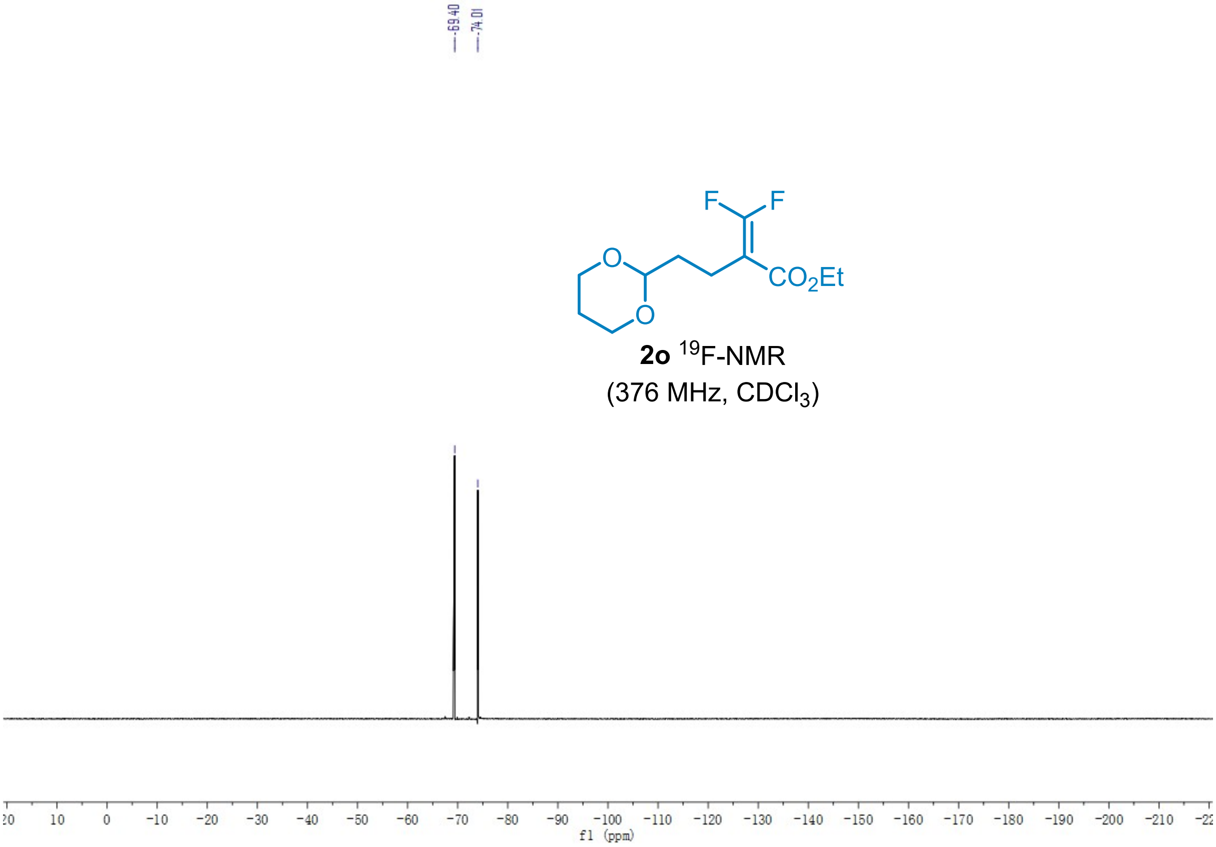
2n ^{19}F-NMR
(376 MHz, $CDCl_3$)



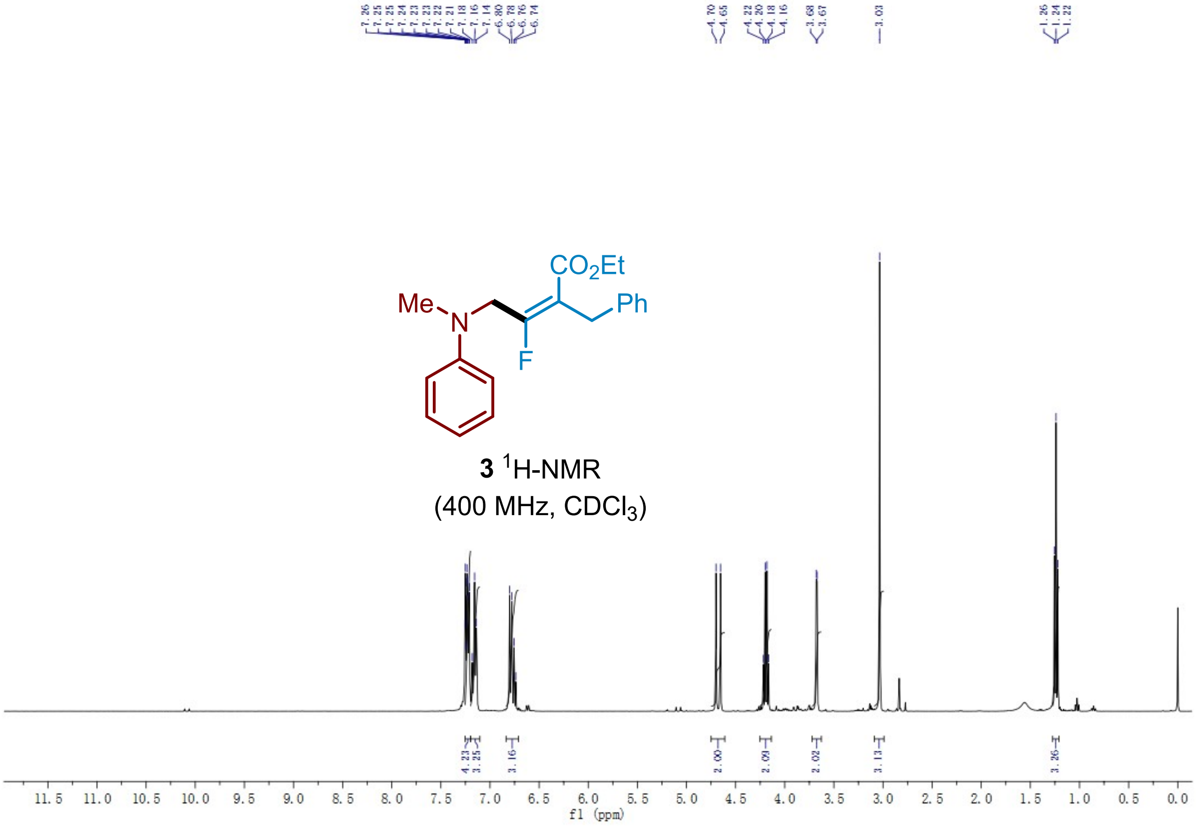
2o ^{1}H-NMR
(400 MHz,$CDCl_3$)



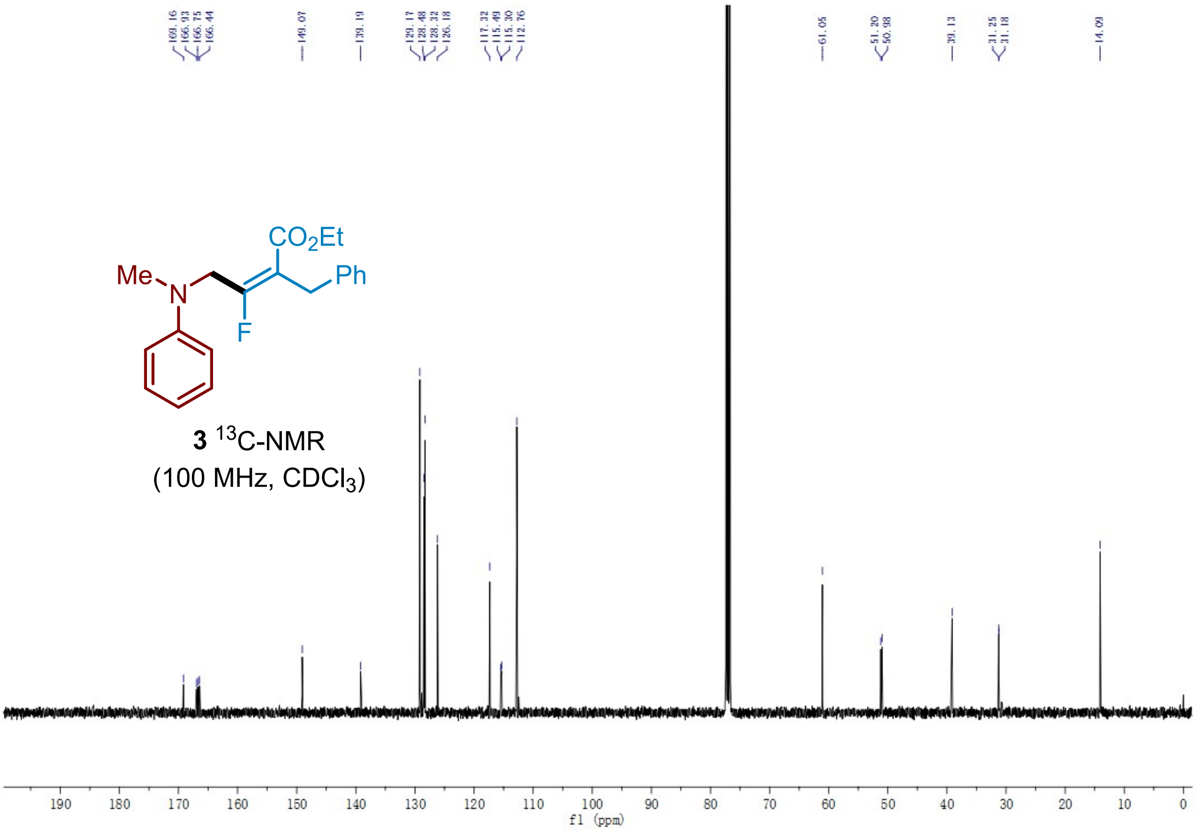
2o ^{13}C-NMR
(100 MHz, CDCl$_3$)



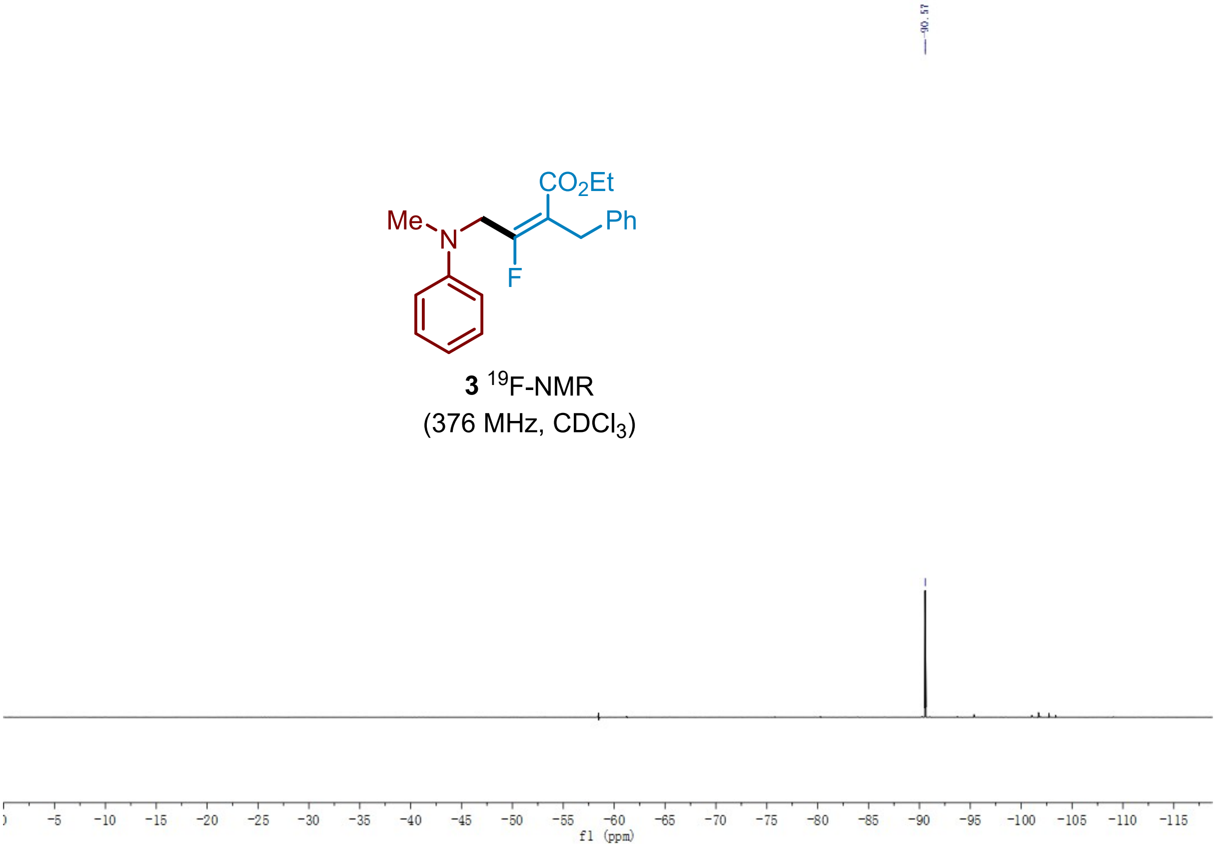
2o ^{19}F-NMR
(376 MHz, CDCl$_3$)



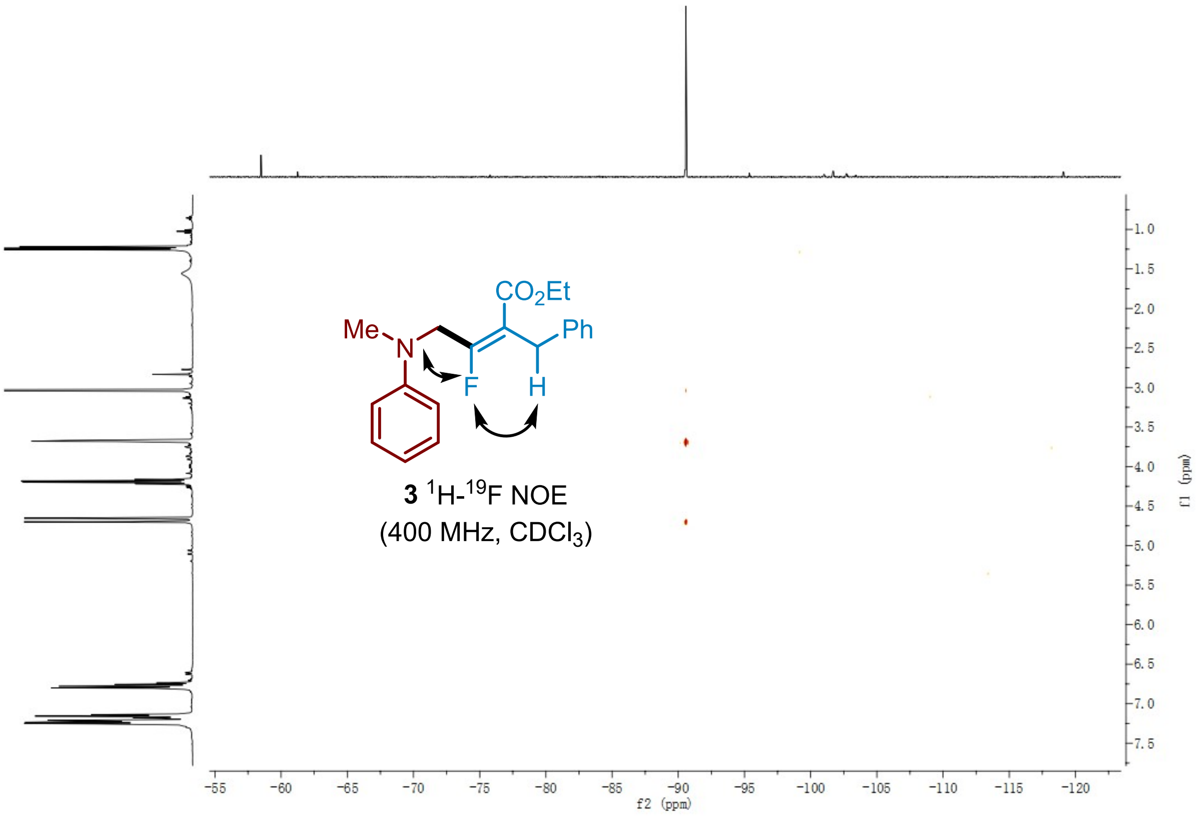
3 ^{1}H-NMR
(400 MHz, $CDCl_3$)



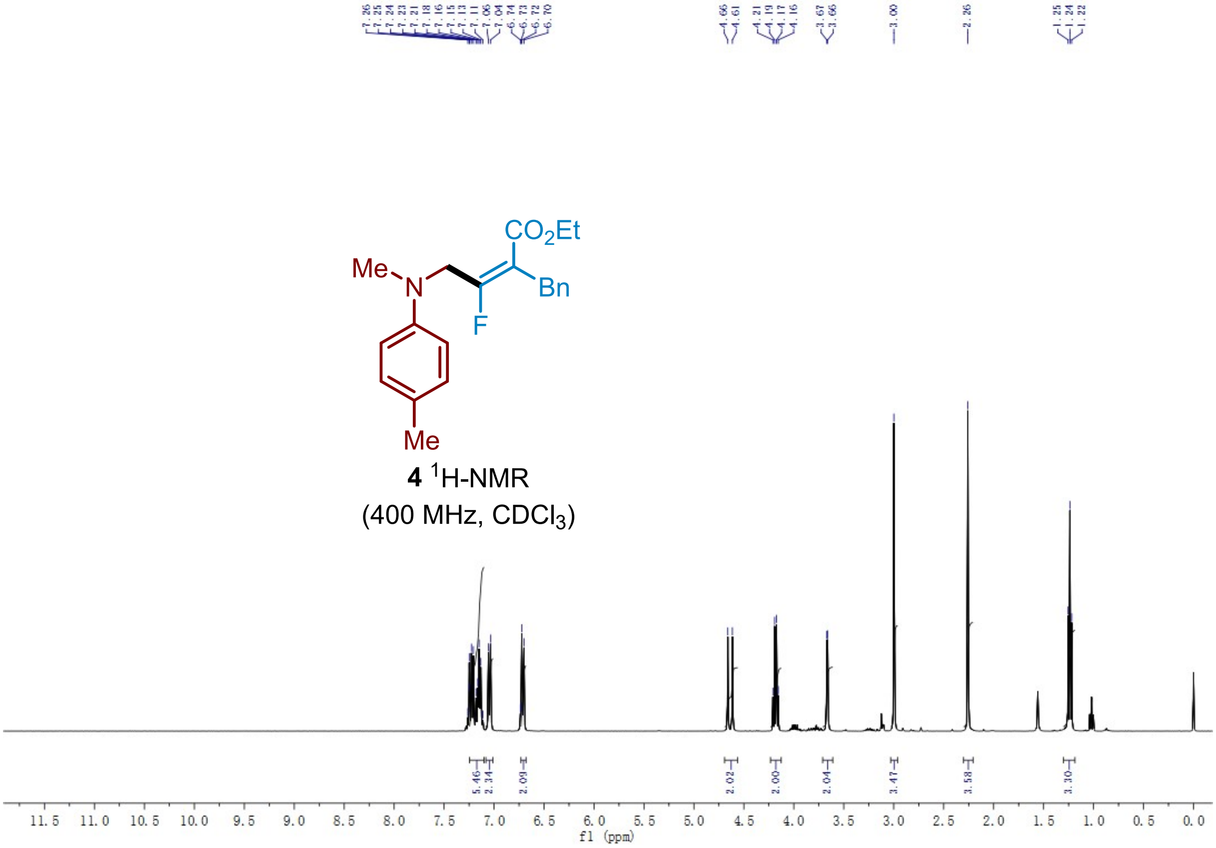
3 ^{13}C-NMR
(100 MHz, $CDCl_3$)



3 ^{19}F-NMR
(376 MHz, $CDCl_3$)

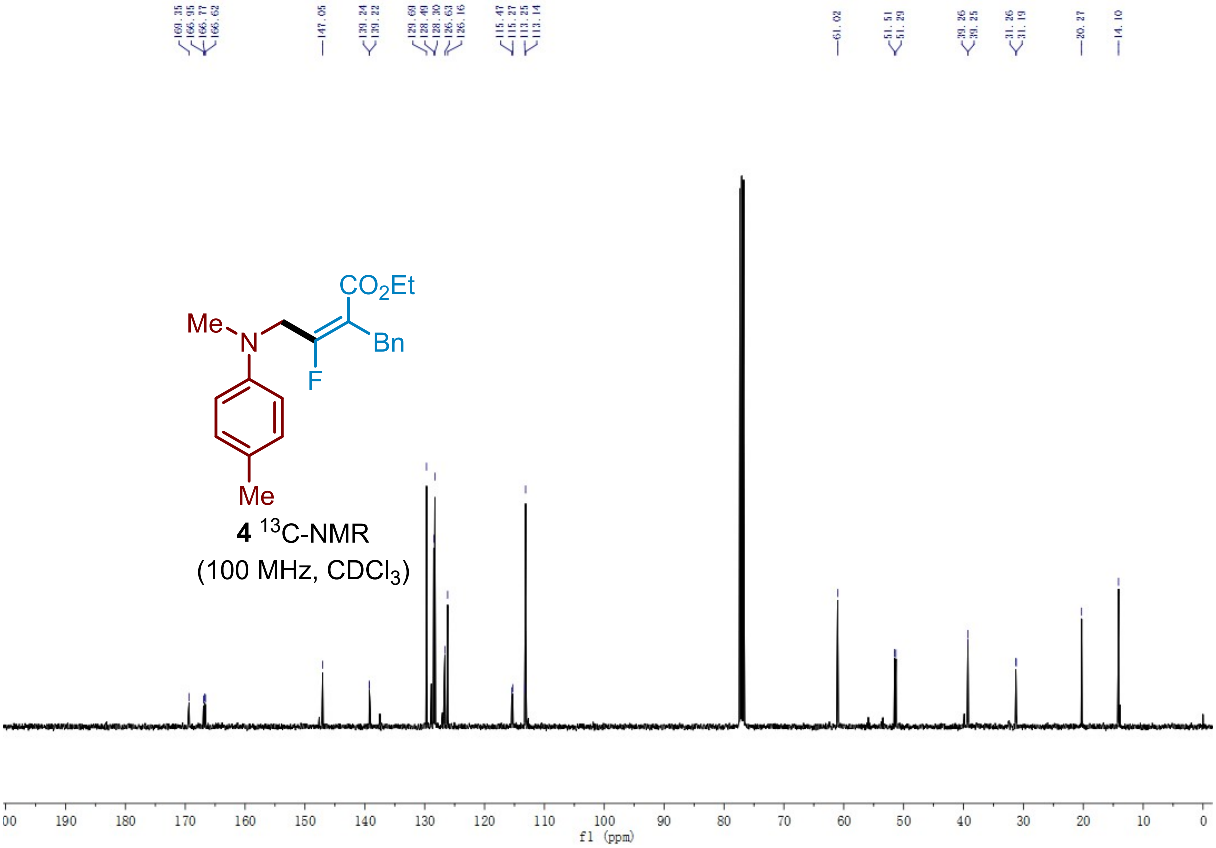


3 ^{1}H-^{19}F NOE
(400 MHz, $CDCl_3$)



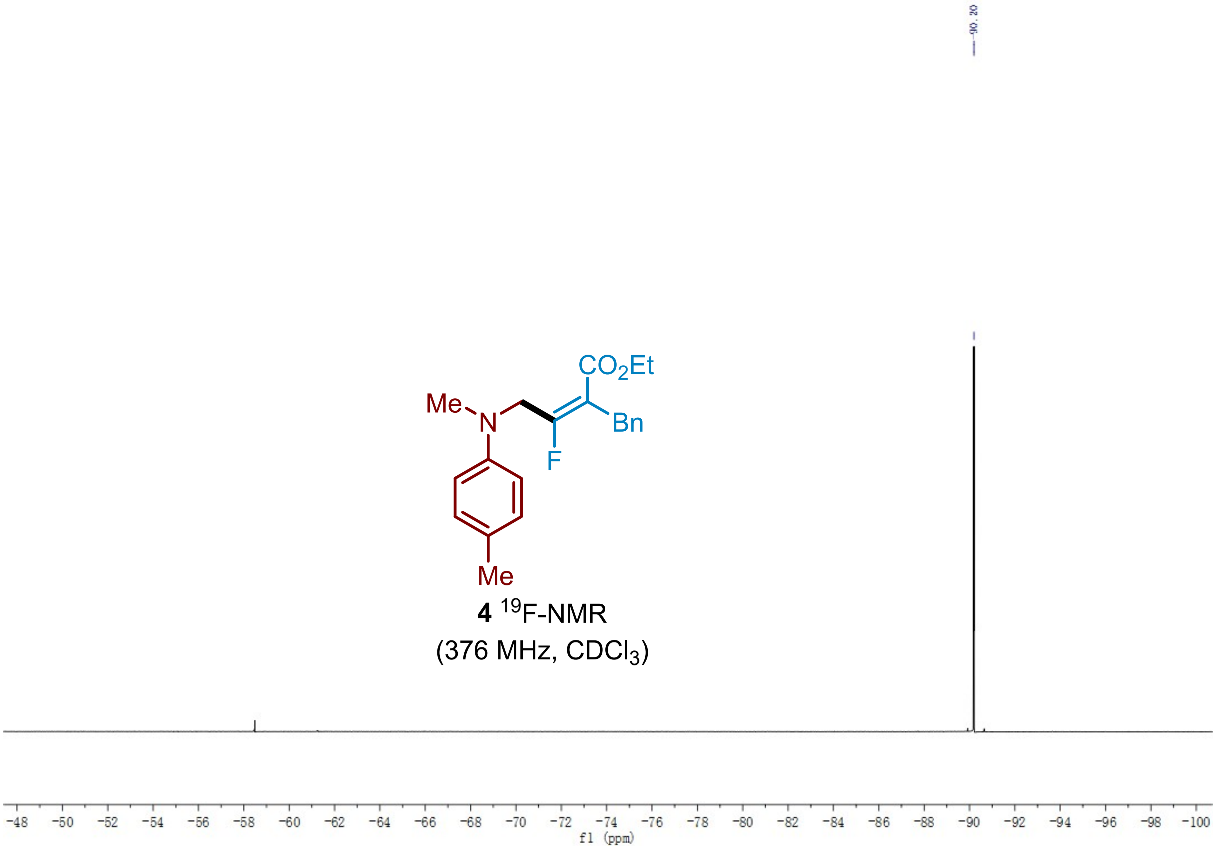
4 ^{1}H-NMR

(400 MHz, CDCl$_3$)

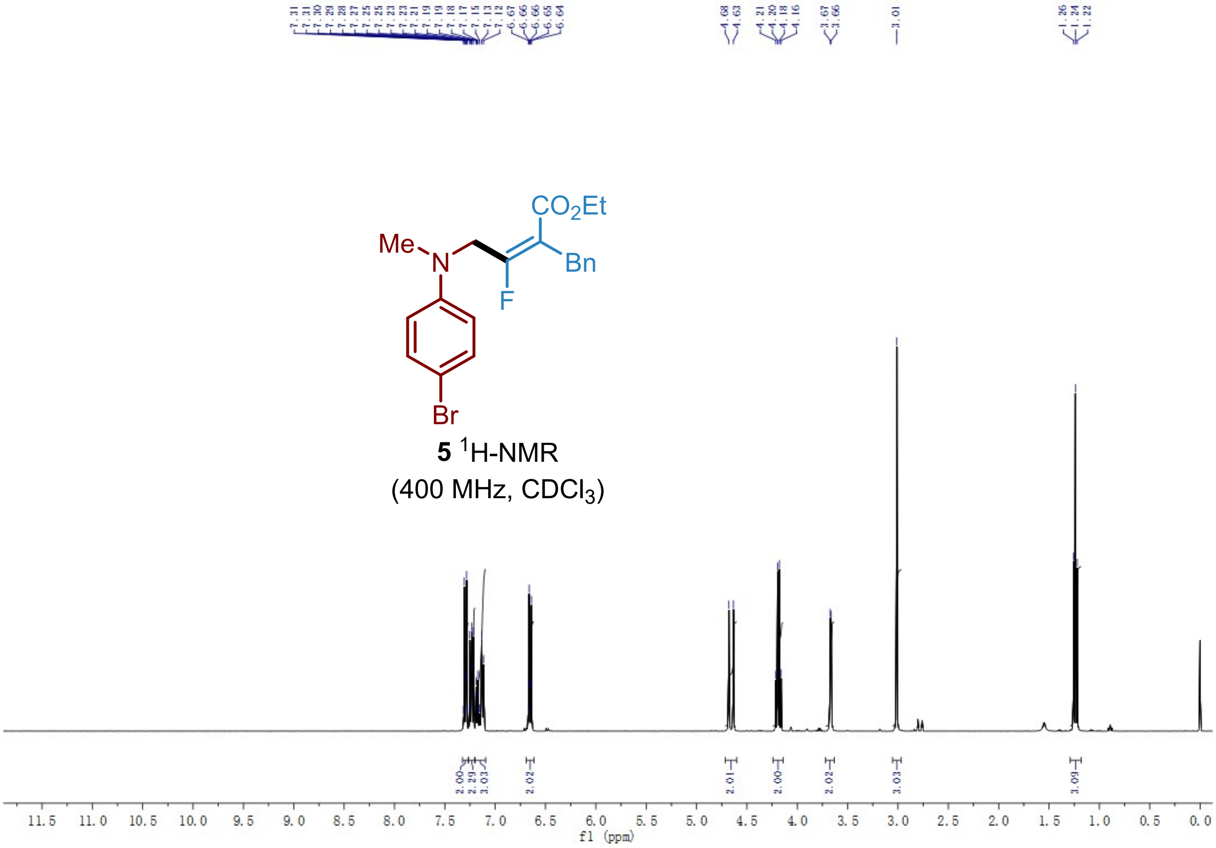


4 ^{13}C-NMR

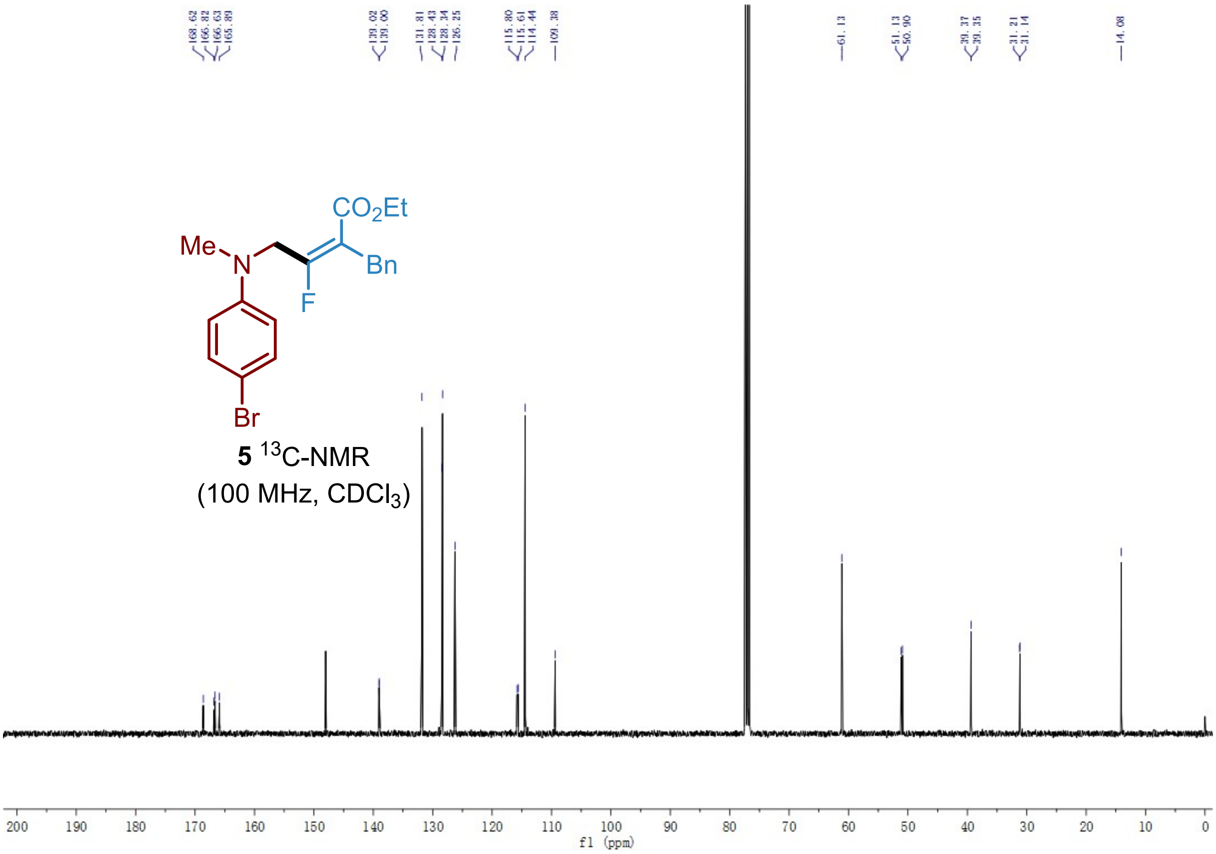
(100 MHz, CDCl$_3$)



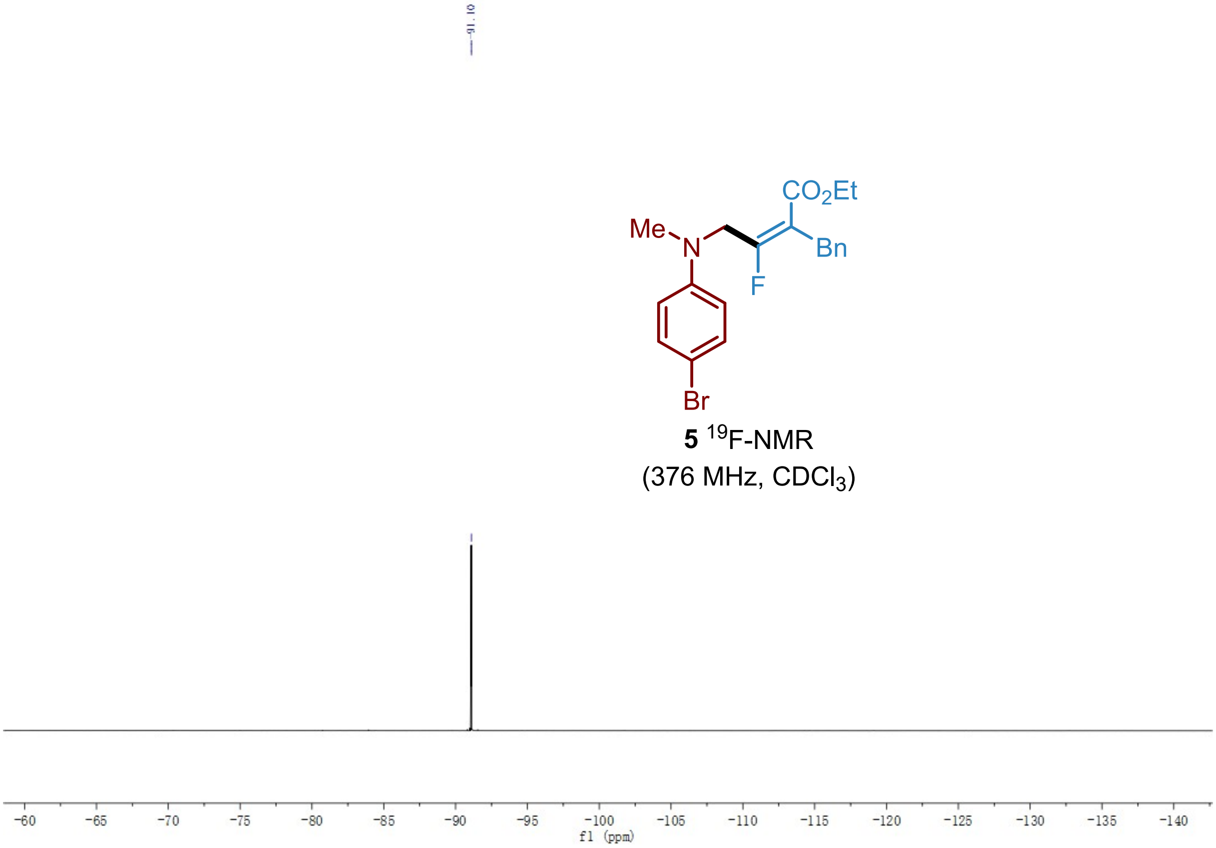
4 ^{19}F-NMR
(376 MHz, CDCl$_3$)



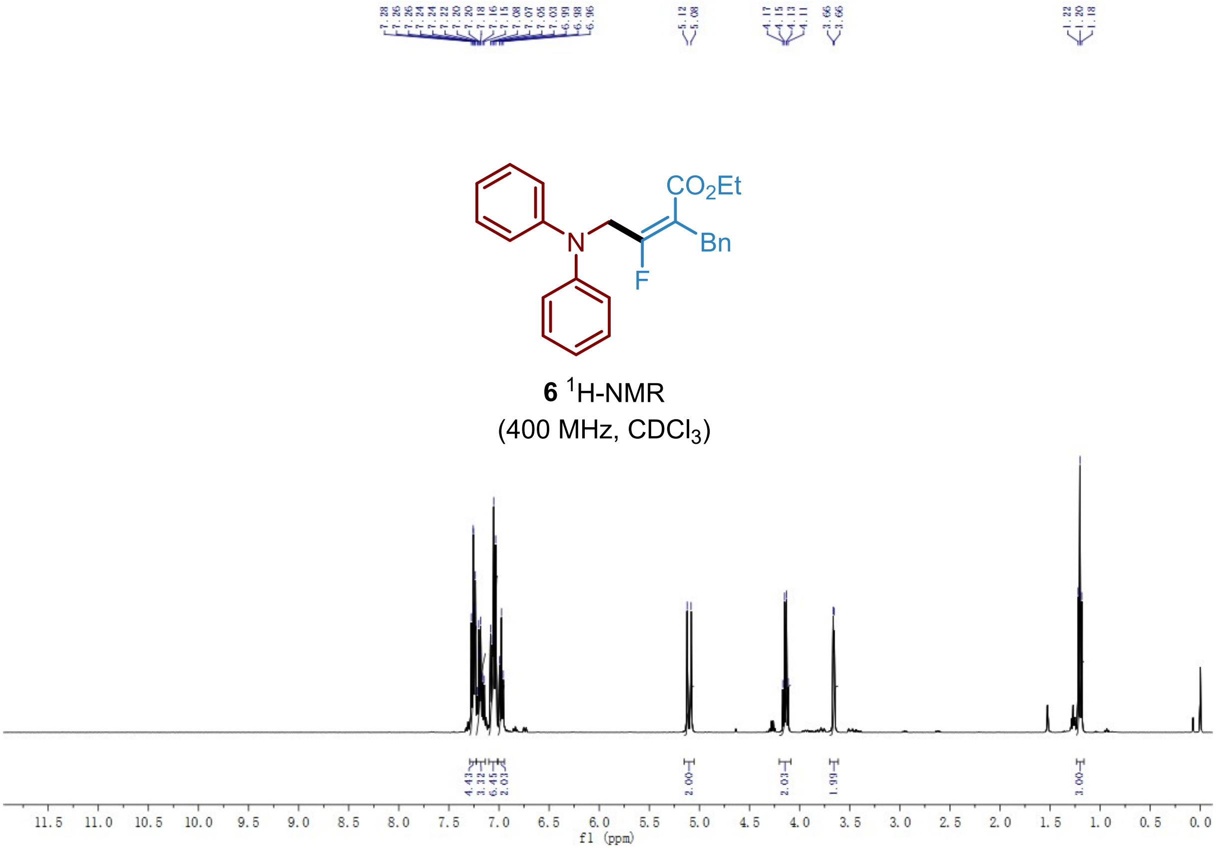
5 ^{1}H-NMR
(400 MHz, CDCl$_3$)



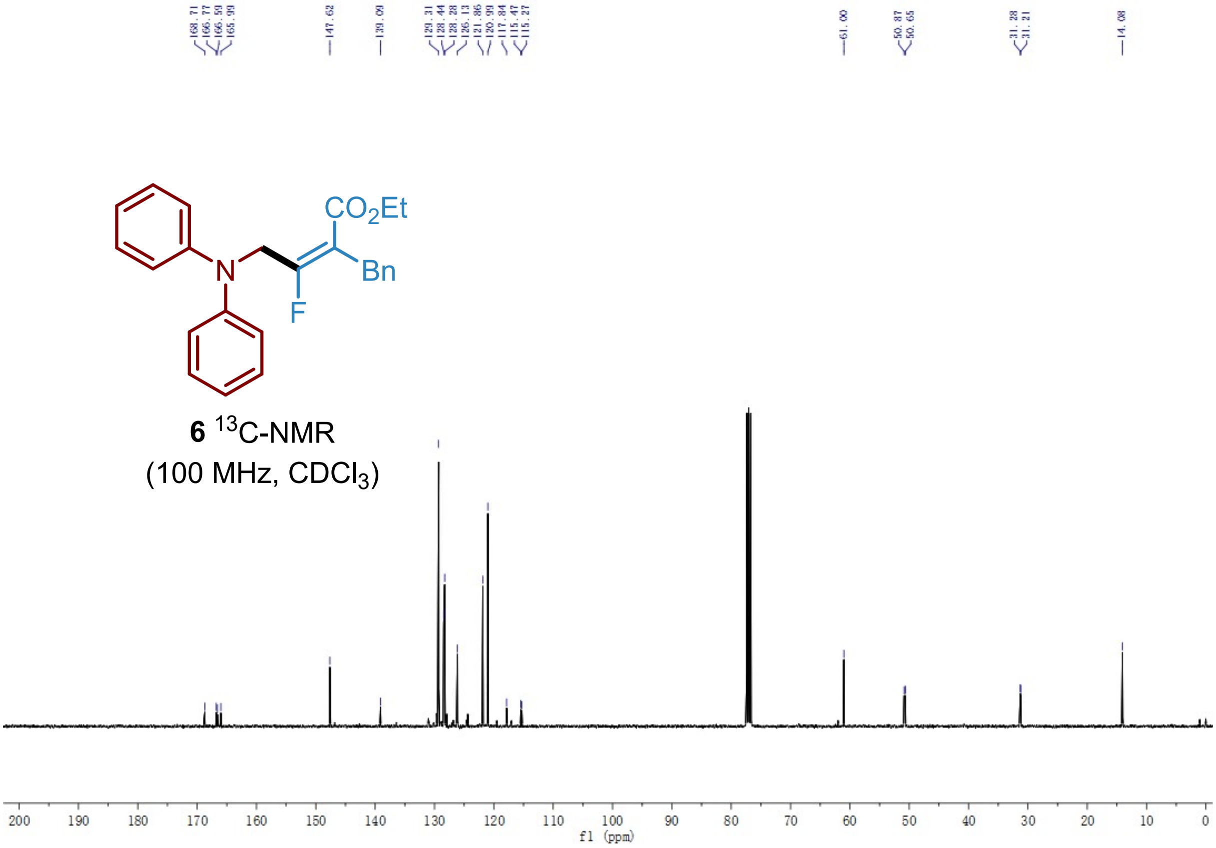
5 ^{13}C-NMR
(100 MHz, $CDCl_3$)



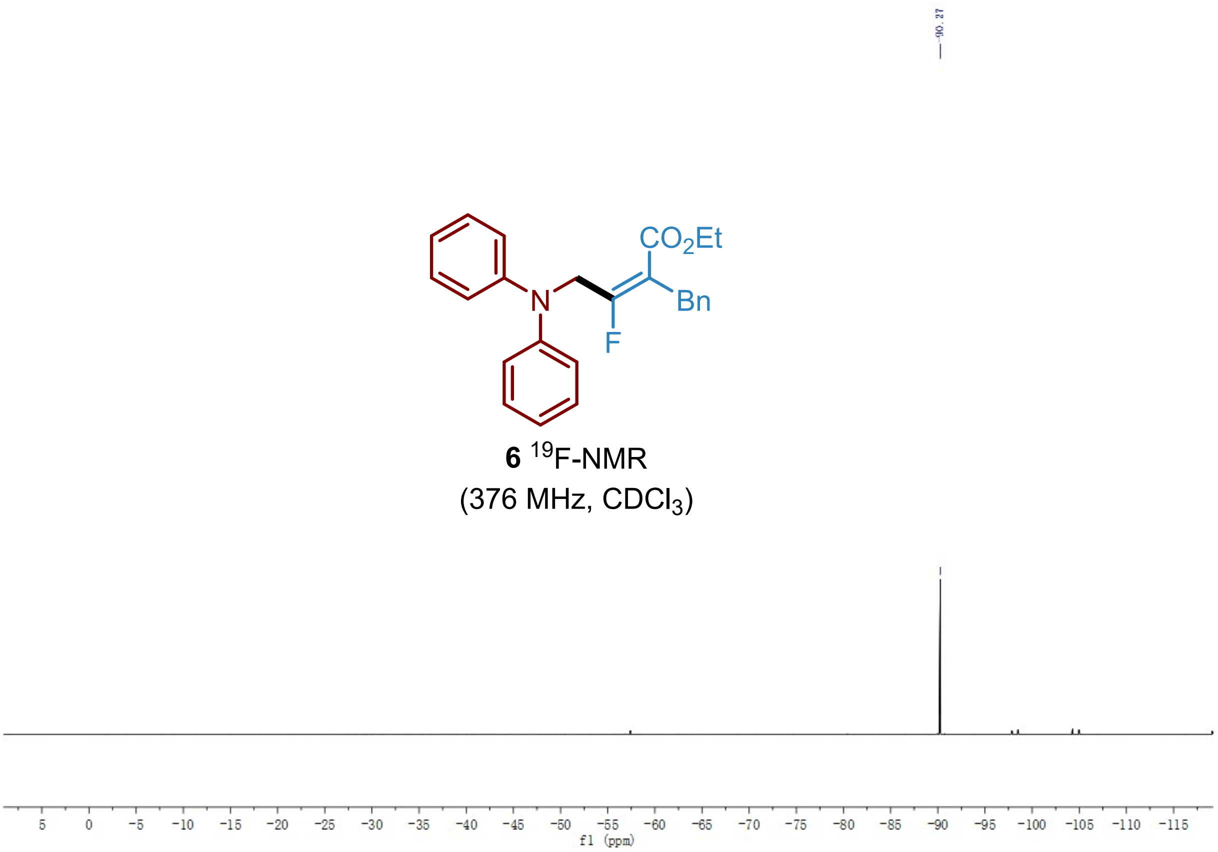
5 ^{19}F-NMR
(376 MHz, $CDCl_3$)



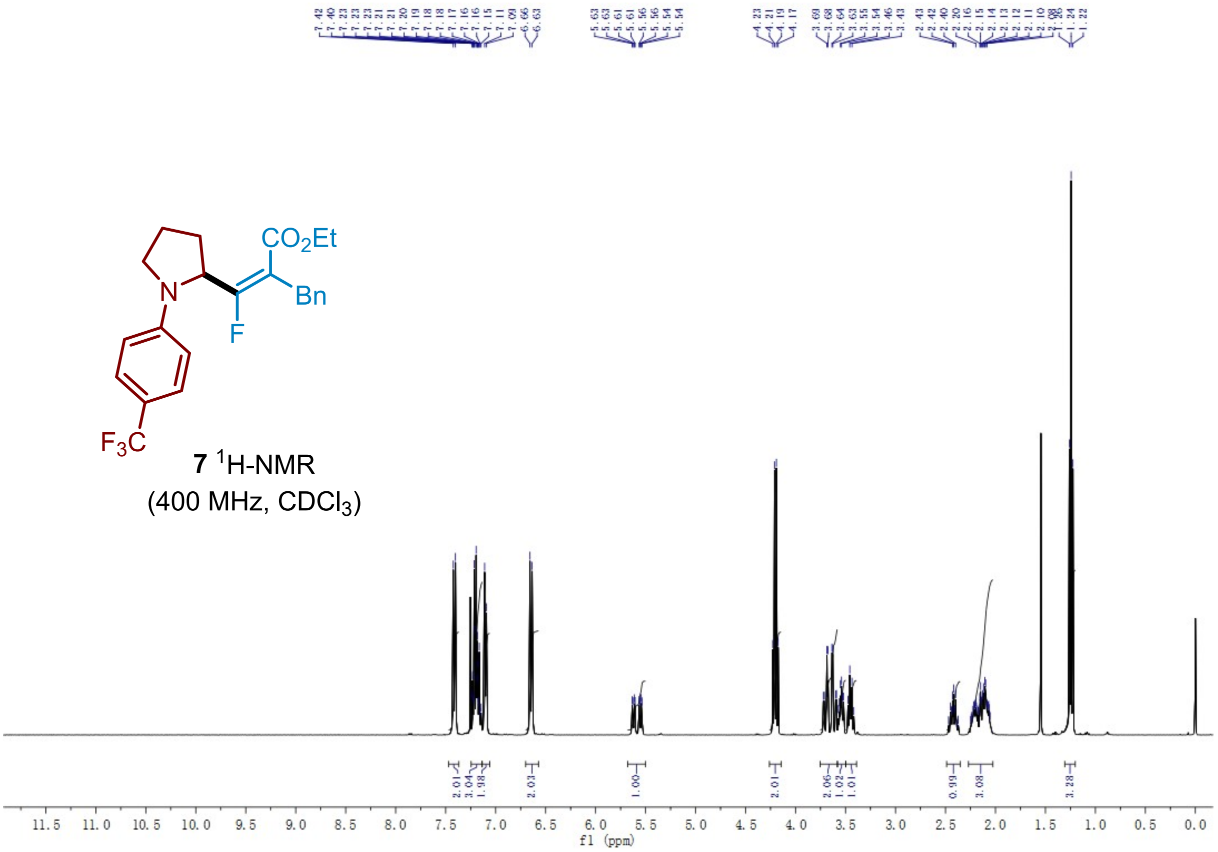
6 ^{1}H-NMR
(400 MHz, $CDCl_3$)



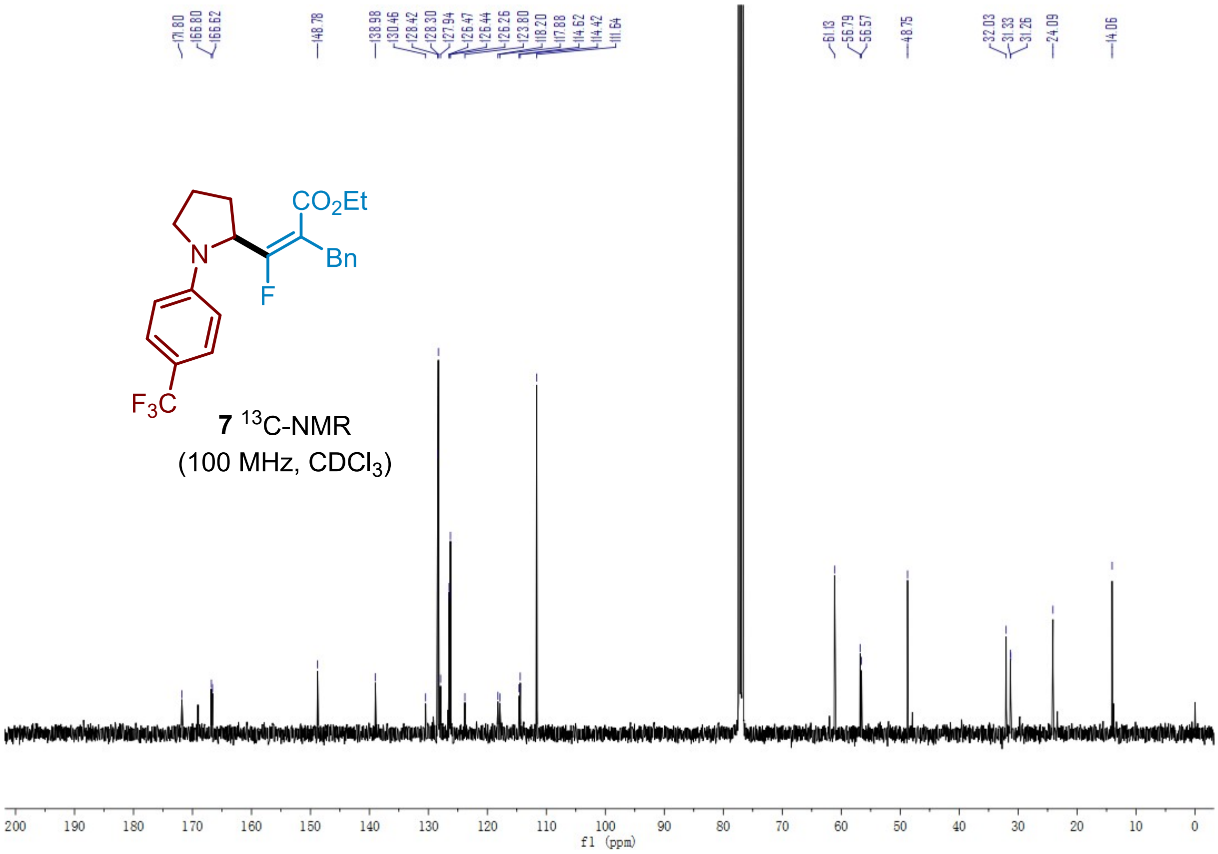
6 ^{13}C-NMR
(100 MHz, $CDCl_3$)



6 ^{19}F-NMR
(376 MHz, $CDCl_3$)

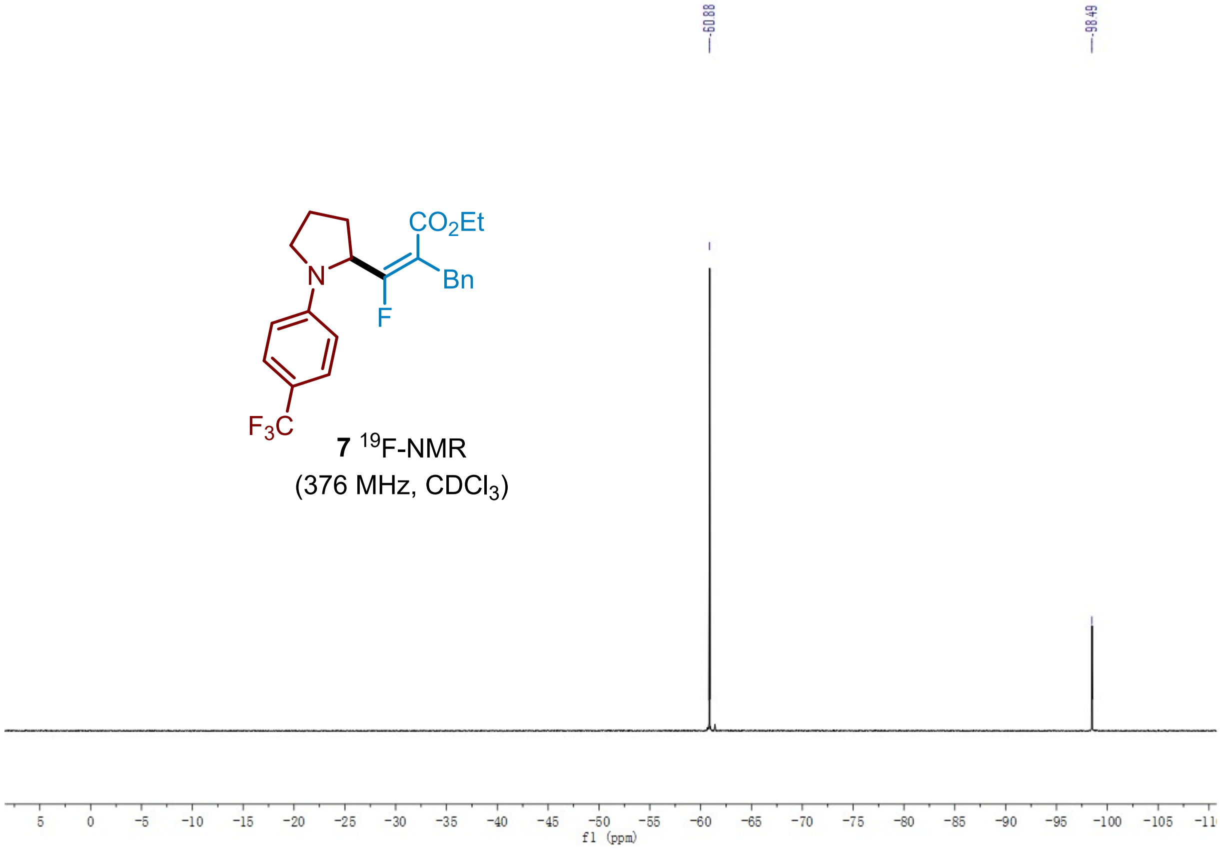


7 ^{1}H-NMR
(400 MHz, $CDCl_3$)



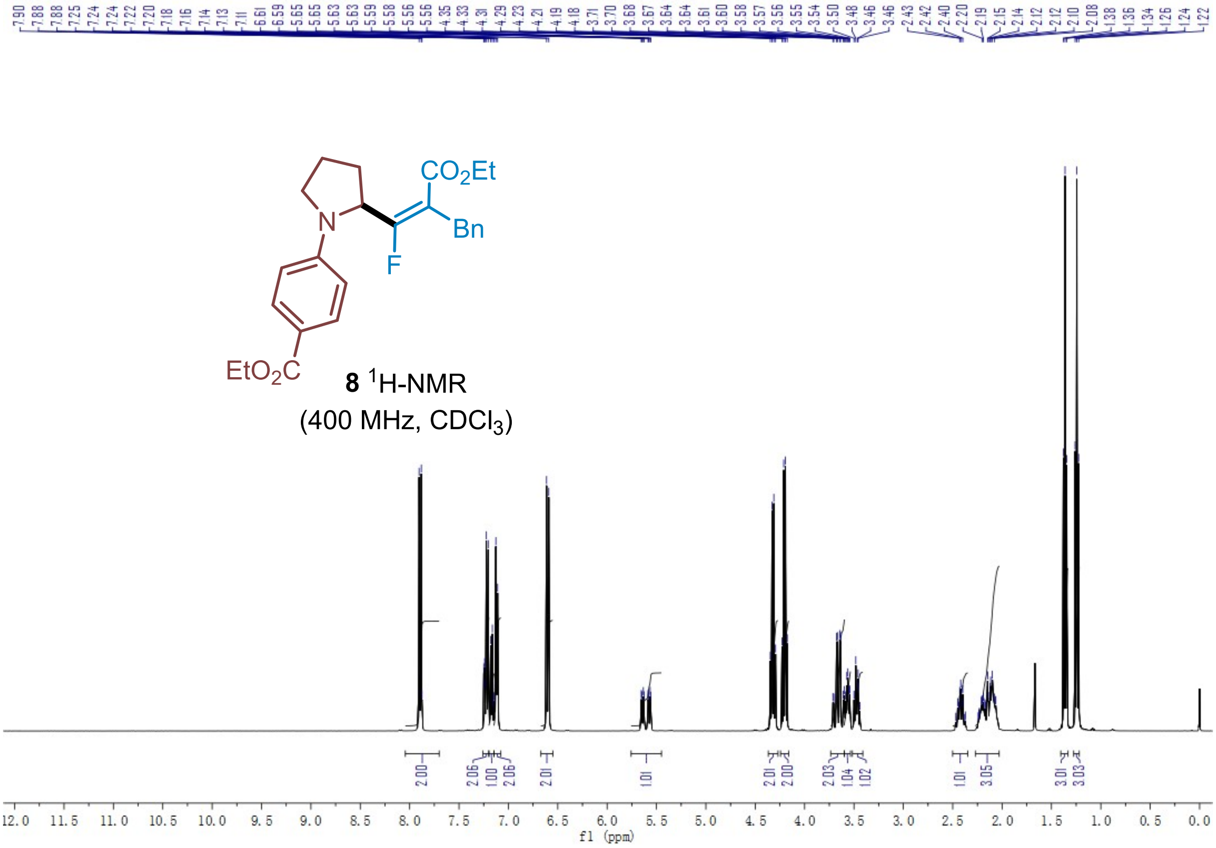
7 ^{13}C-NMR

(100 MHz, $CDCl_3$)

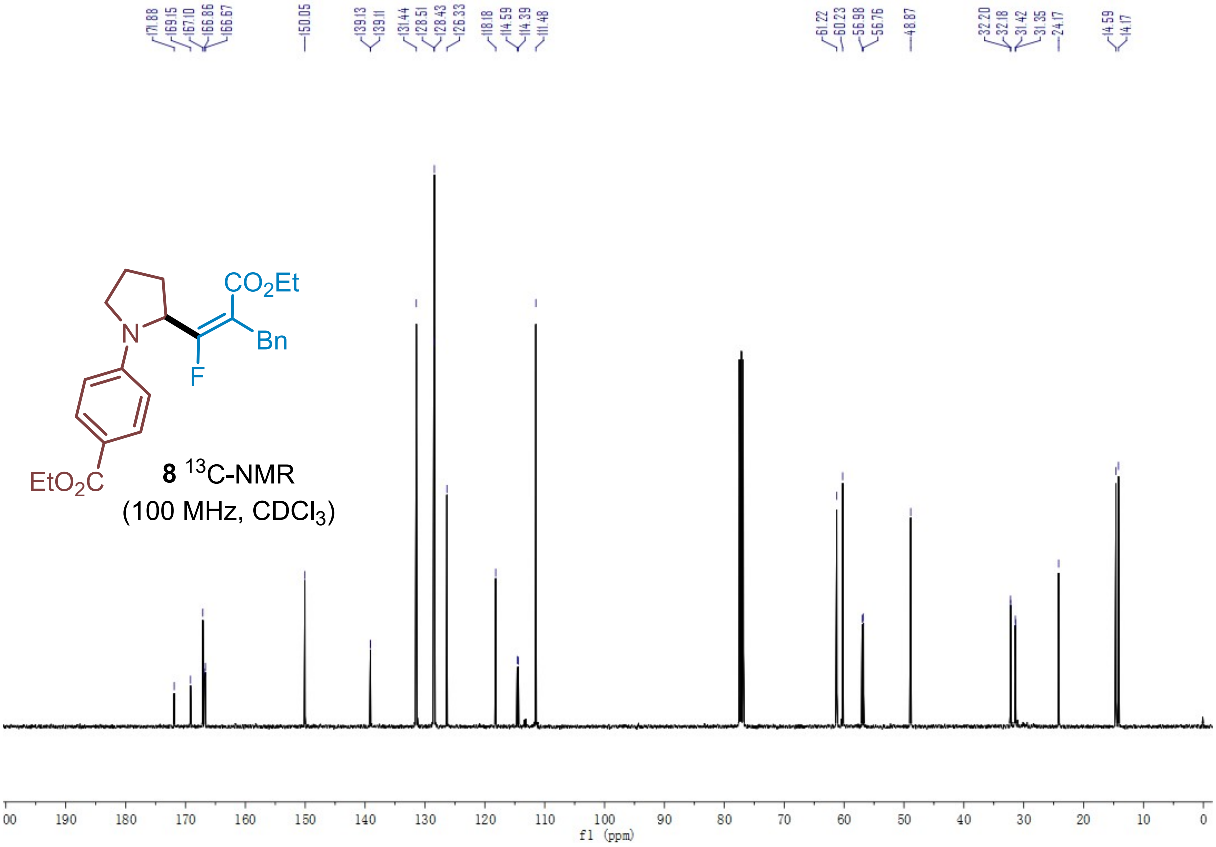


7 ^{19}F-NMR

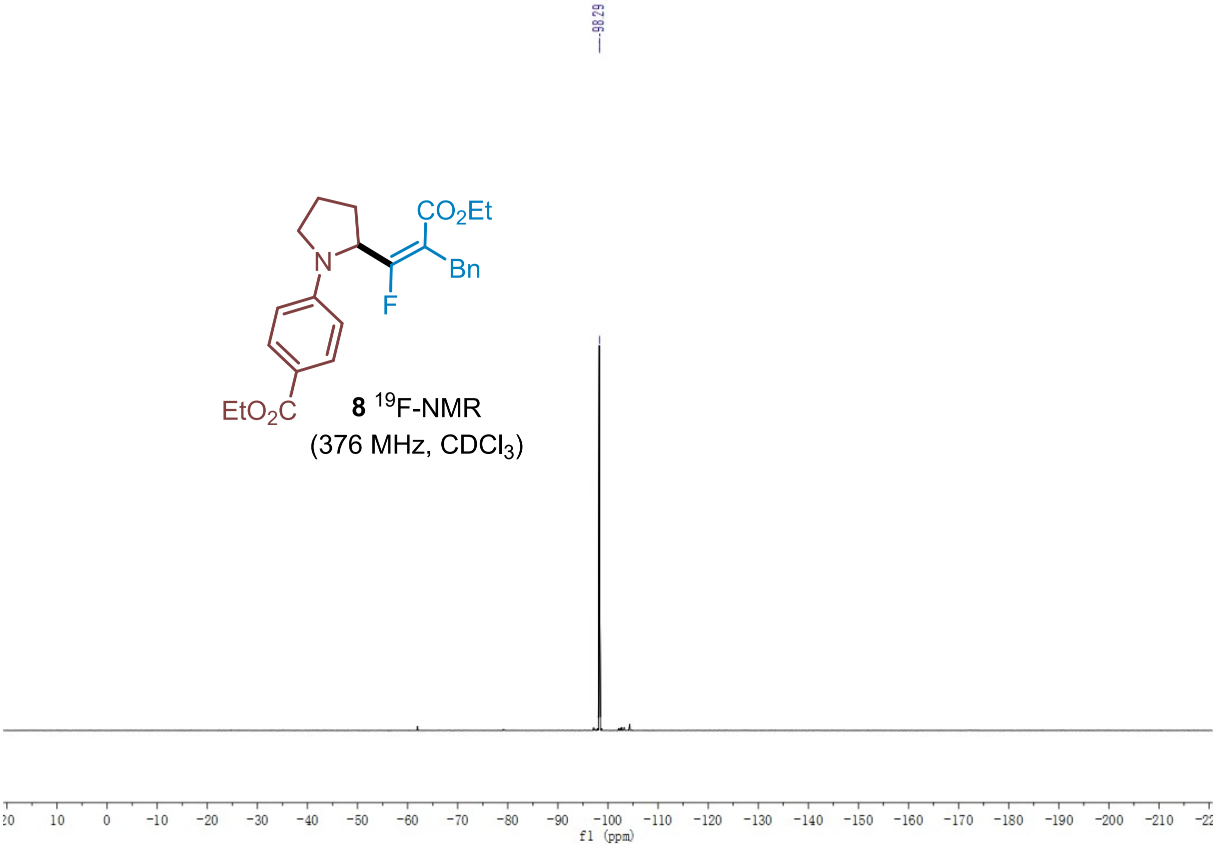
(376 MHz, $CDCl_3$)



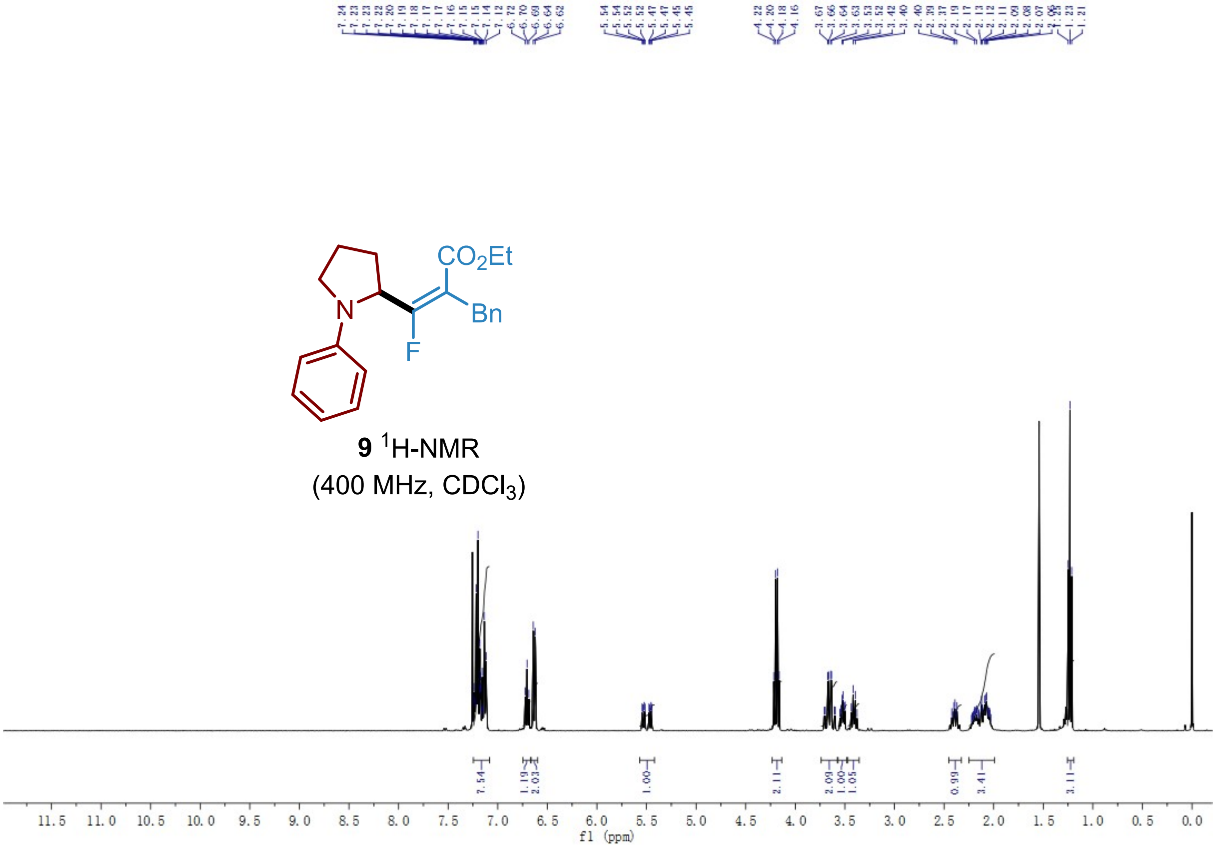
8 ^{1}H-NMR
(400 MHz, $CDCl_3$)



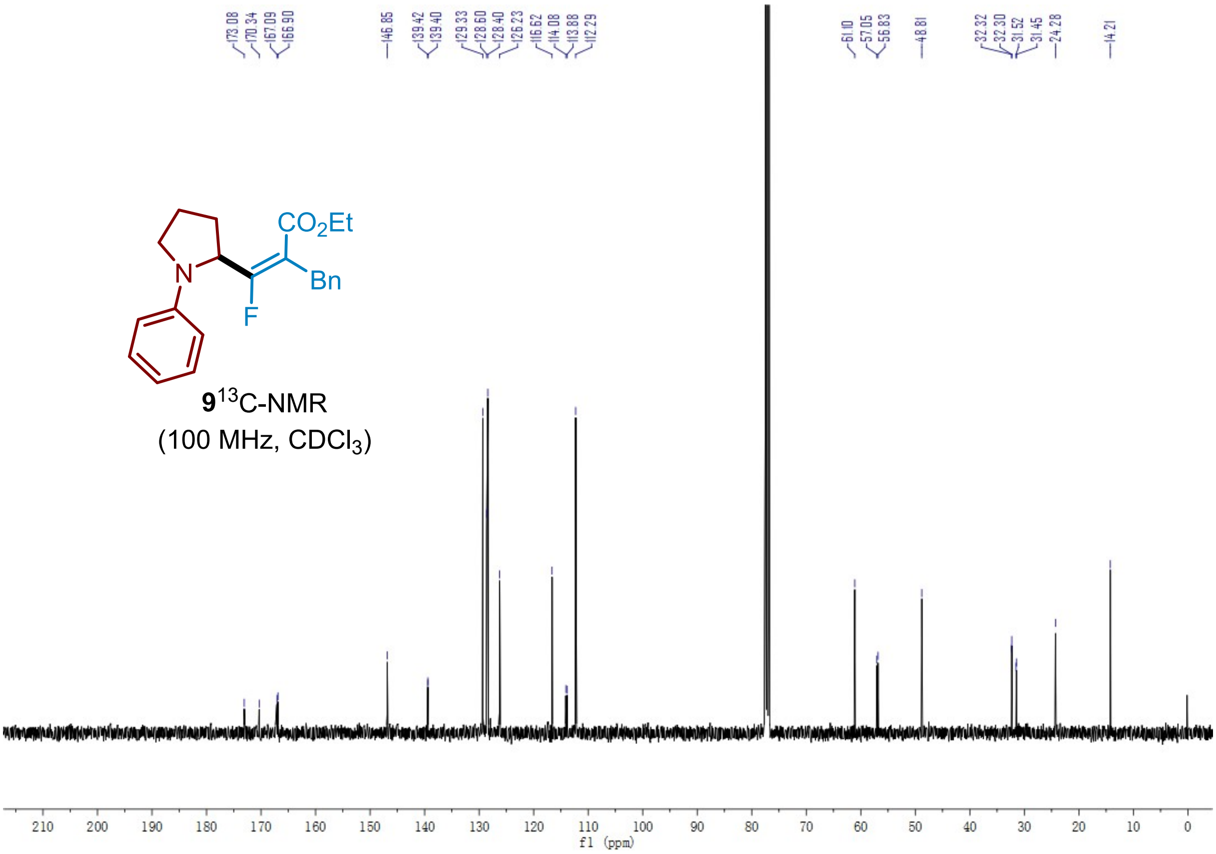
8 ^{13}C-NMR
(100 MHz, $CDCl_3$)



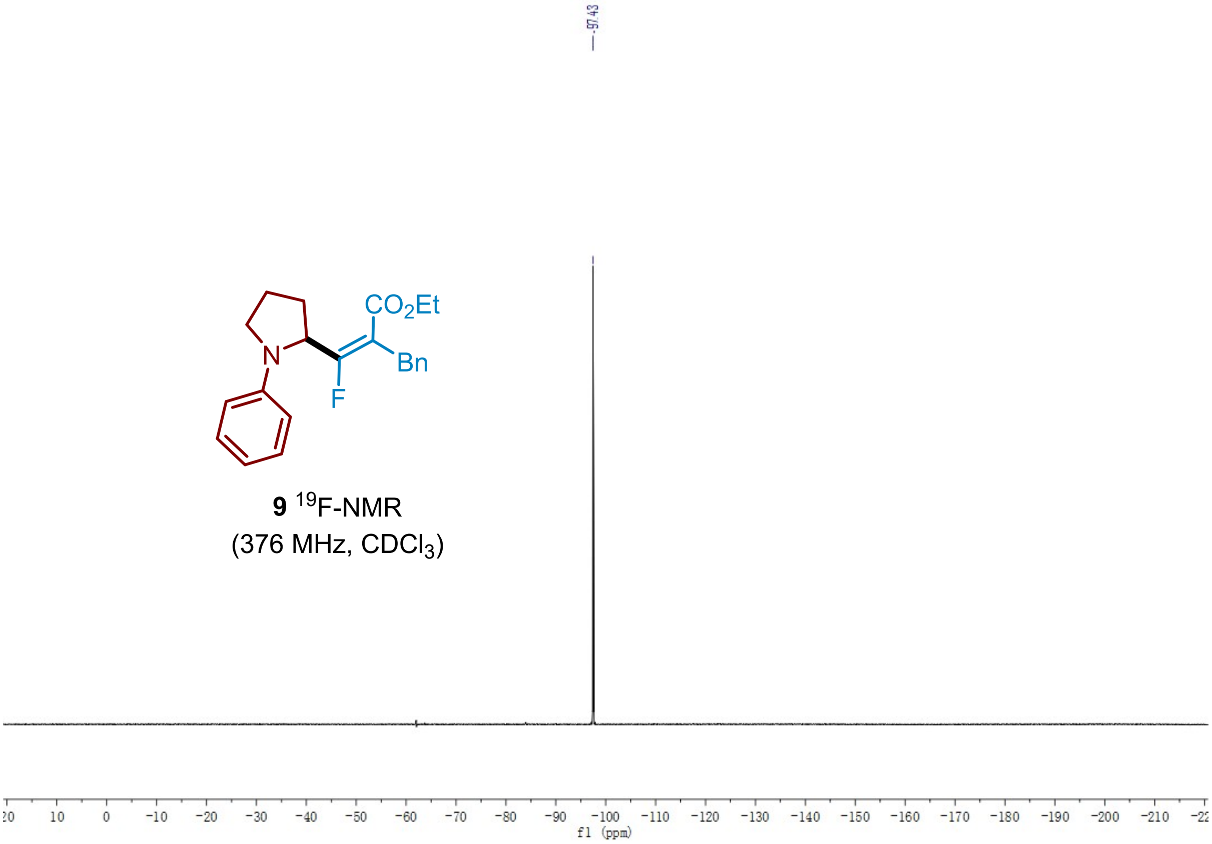
8 ^{19}F-NMR
(376 MHz, $CDCl_3$)



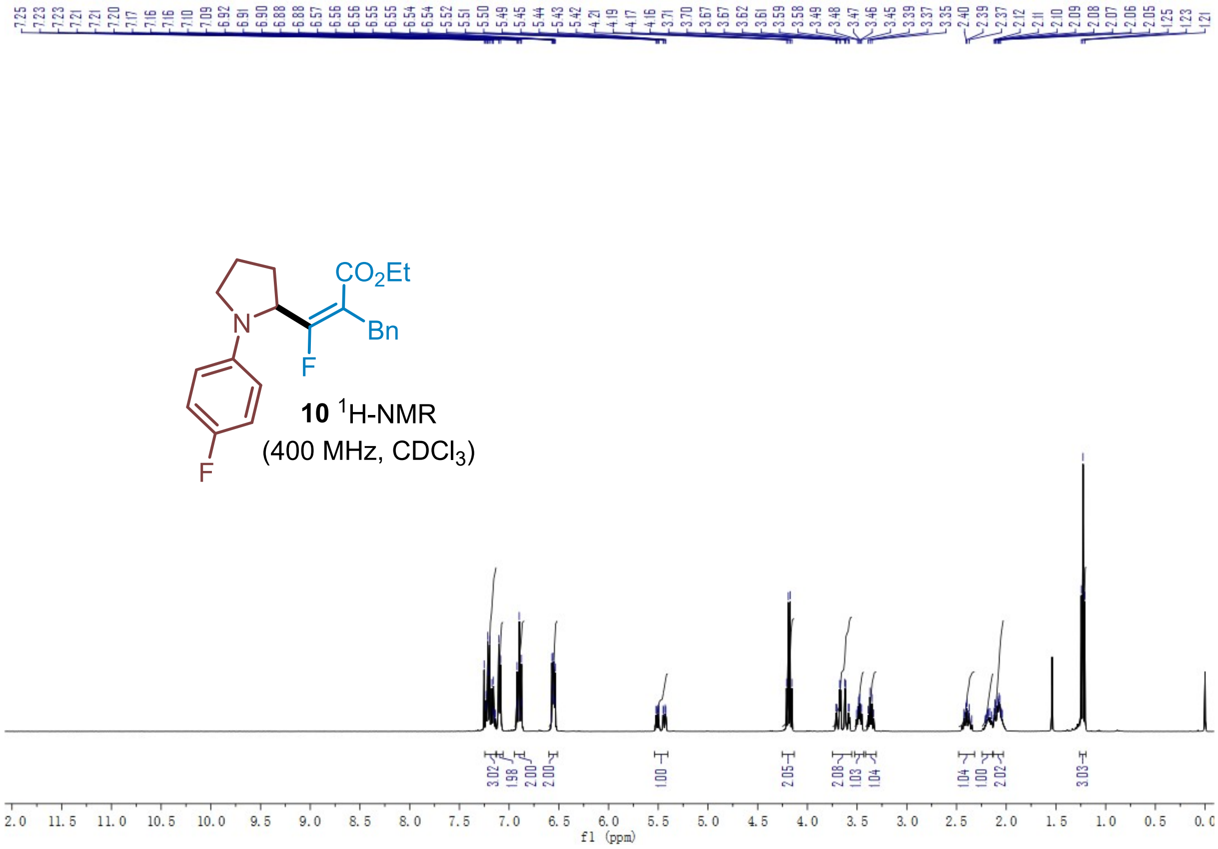
9 ^{1}H-NMR
(400 MHz, $CDCl_3$)



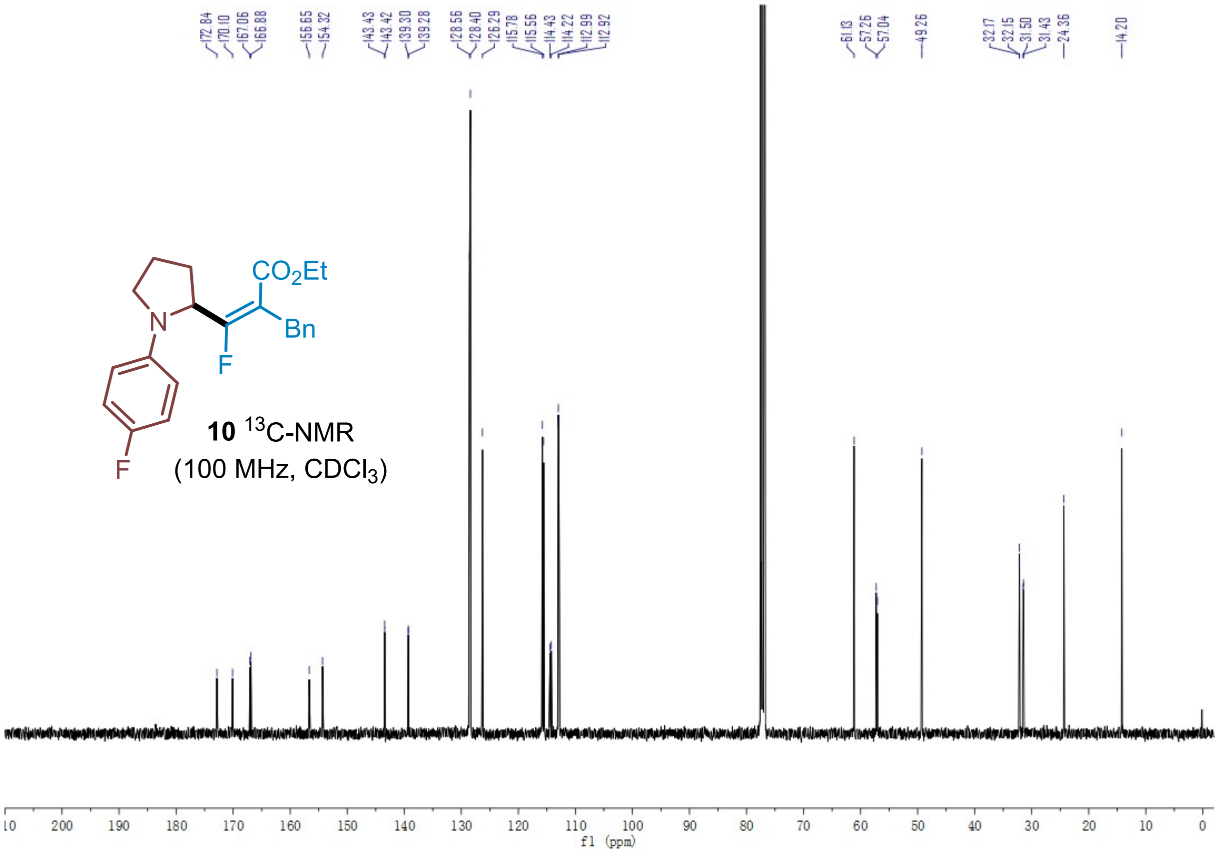
9 ^{13}C-NMR (100 MHz, $CDCl_3$)



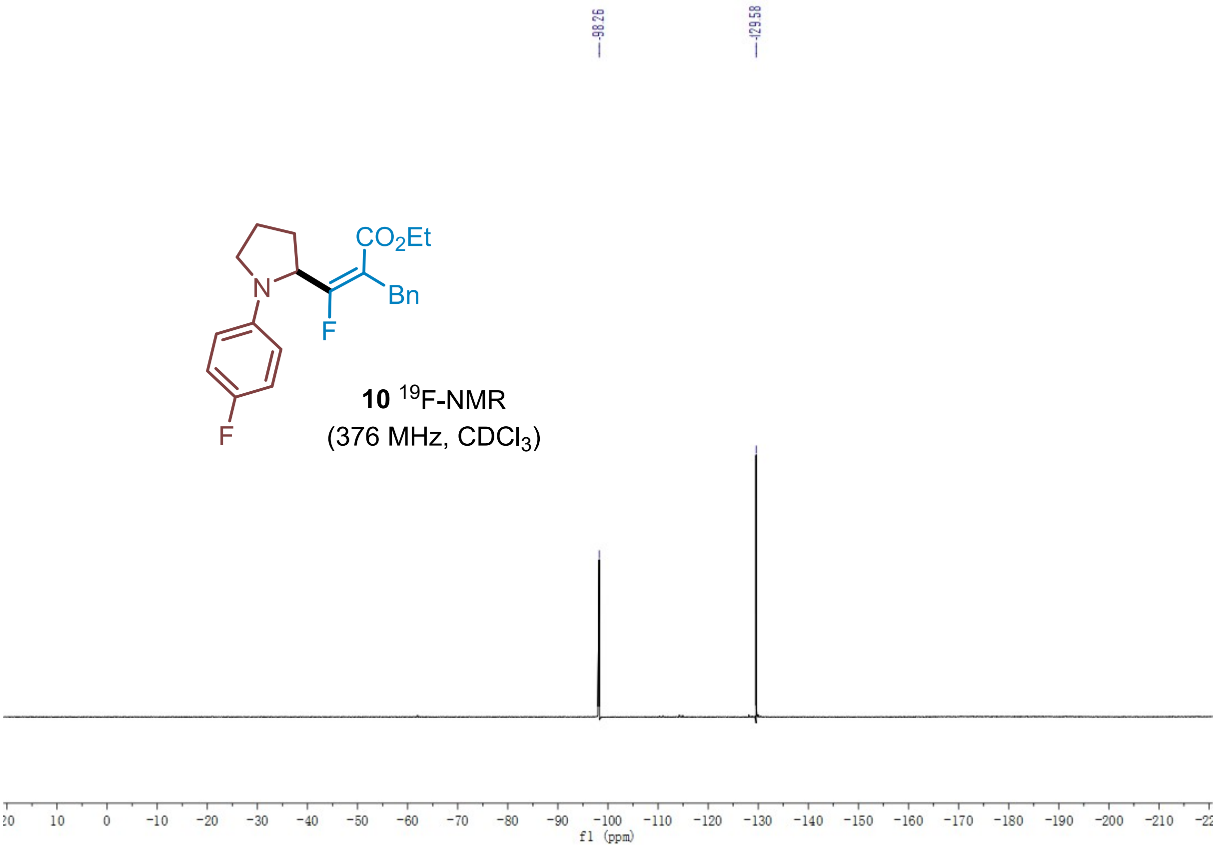
9 ^{19}F-NMR (376 MHz, $CDCl_3$)



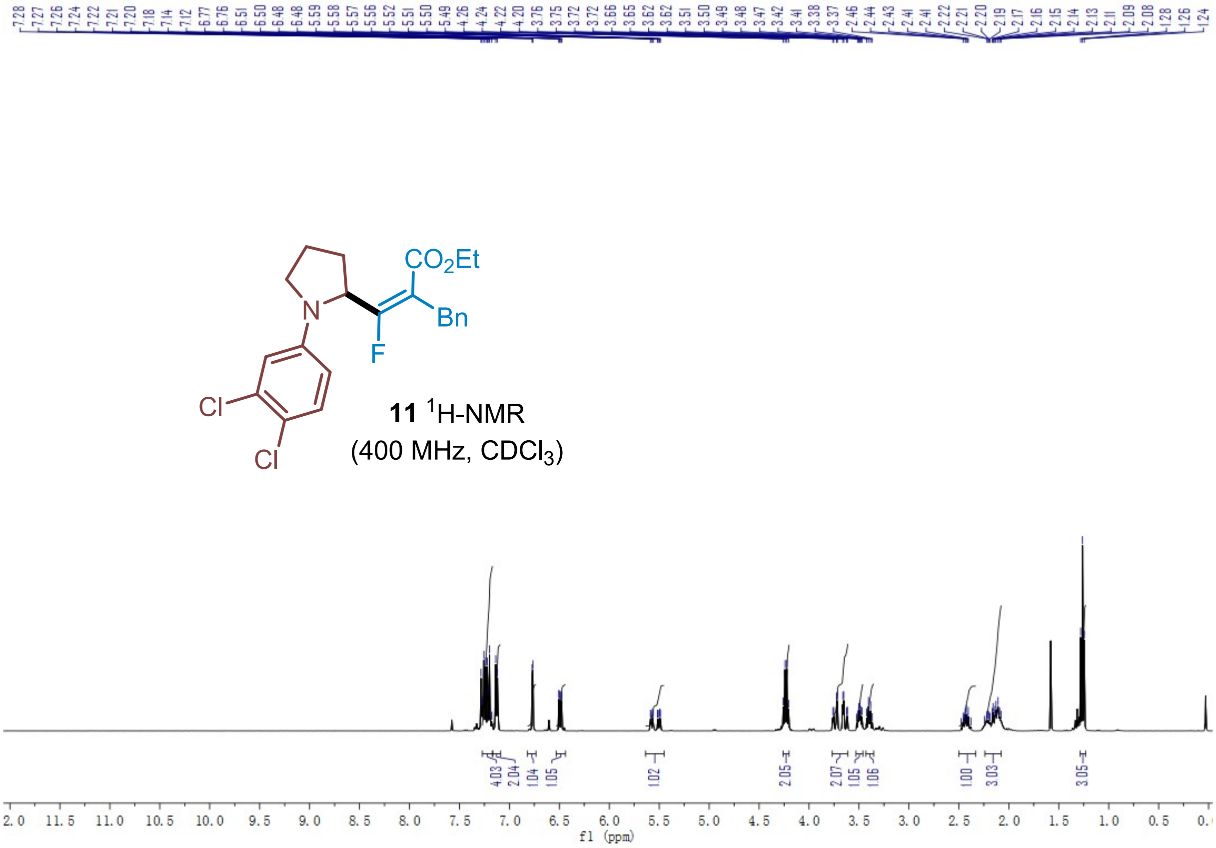
10 ^{1}H-NMR
(400 MHz, CDCl$_3$)



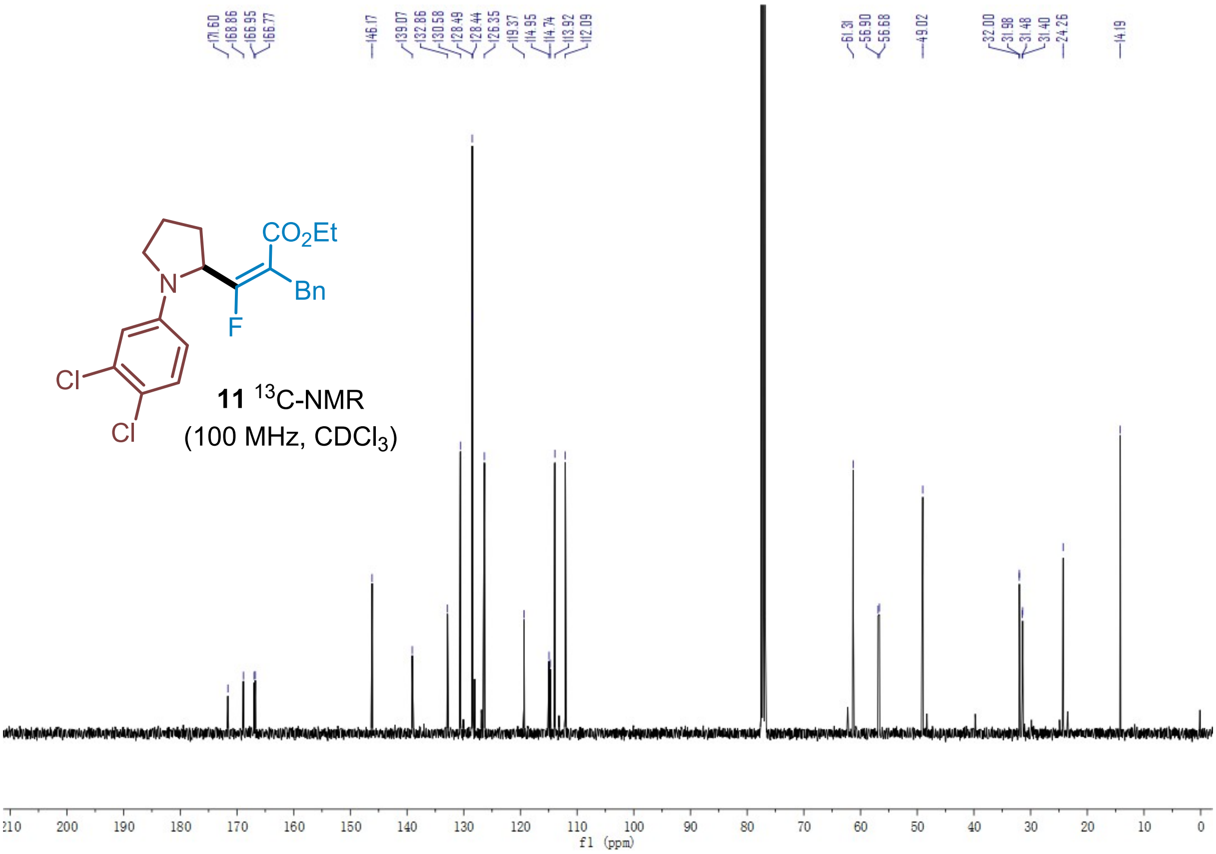
10 ^{13}C-NMR
(100 MHz, CDCl$_3$)



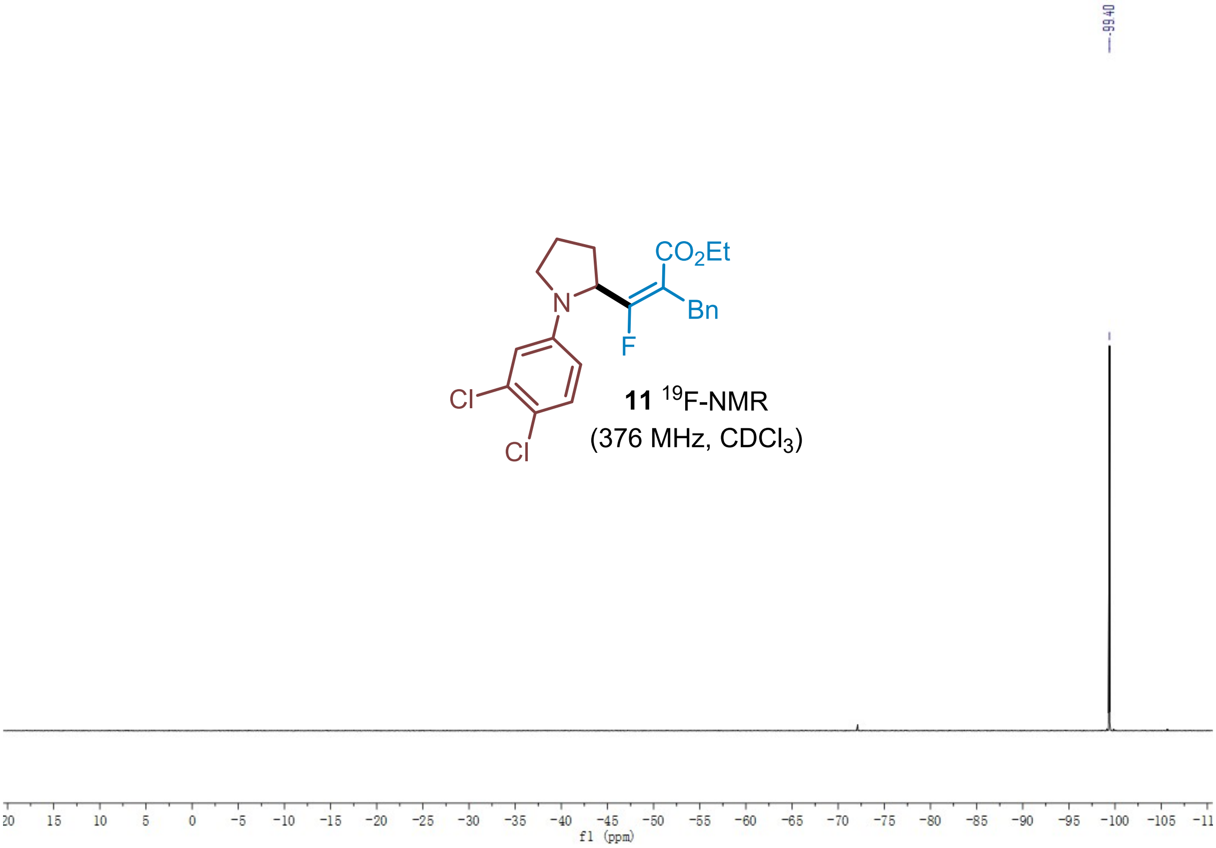
10 ^{19}F-NMR
(376 MHz, CDCl$_3$)



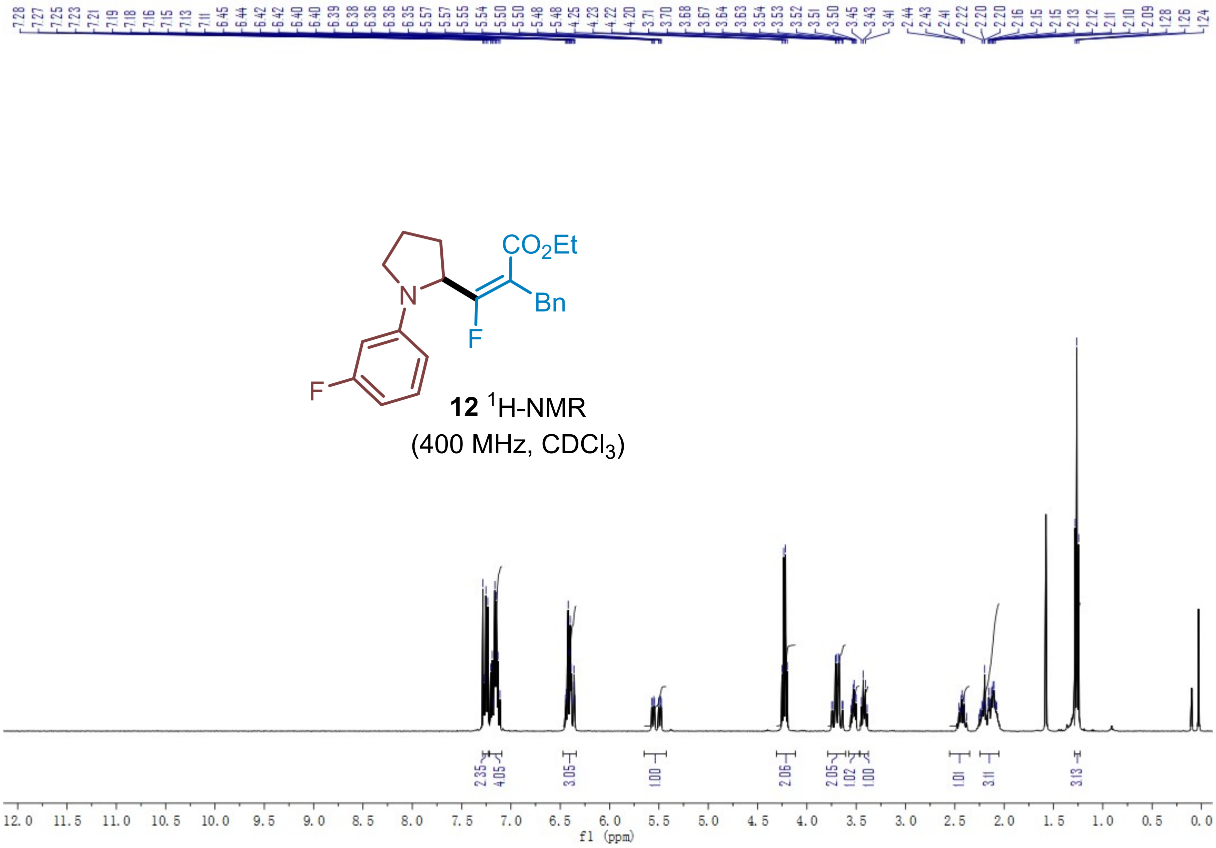
11 ^{1}H-NMR
(400 MHz, CDCl$_3$)



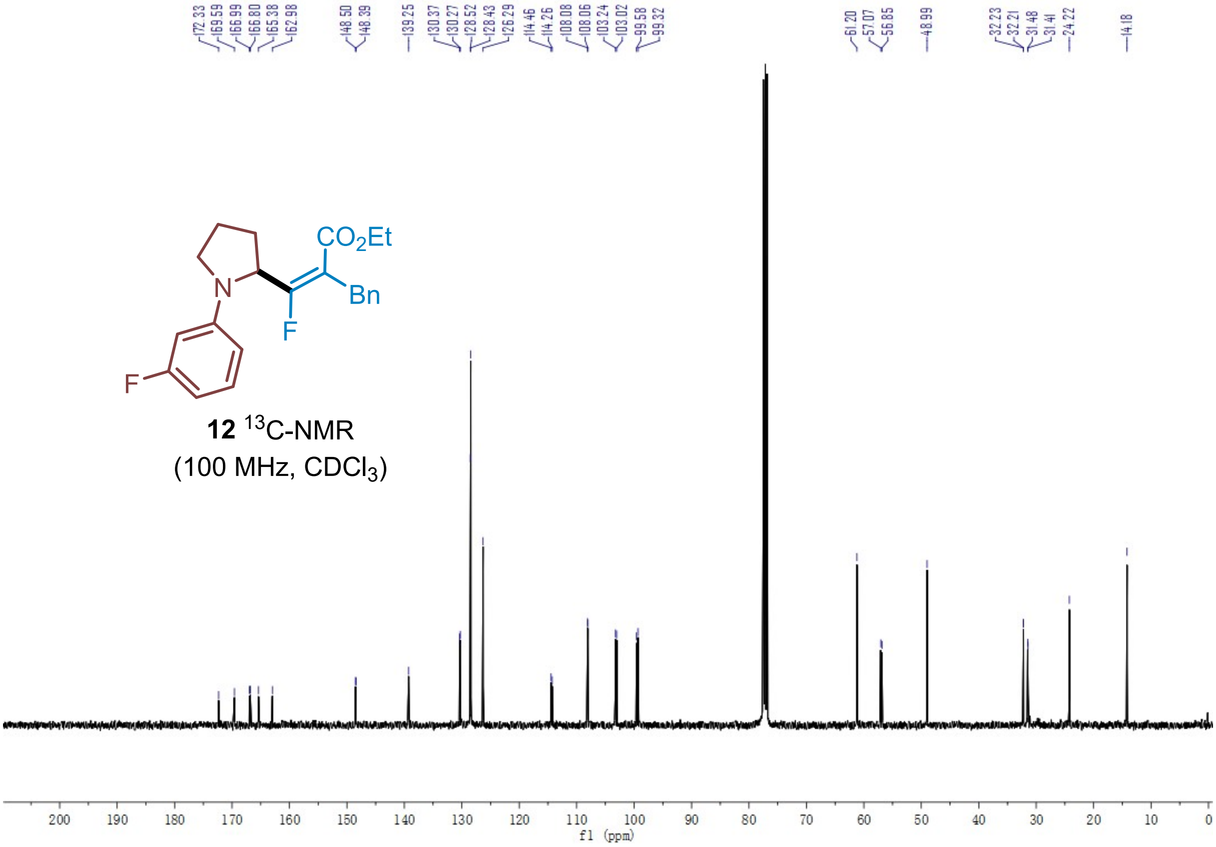
11 ^{13}C-NMR (100 MHz, $CDCl_3$)



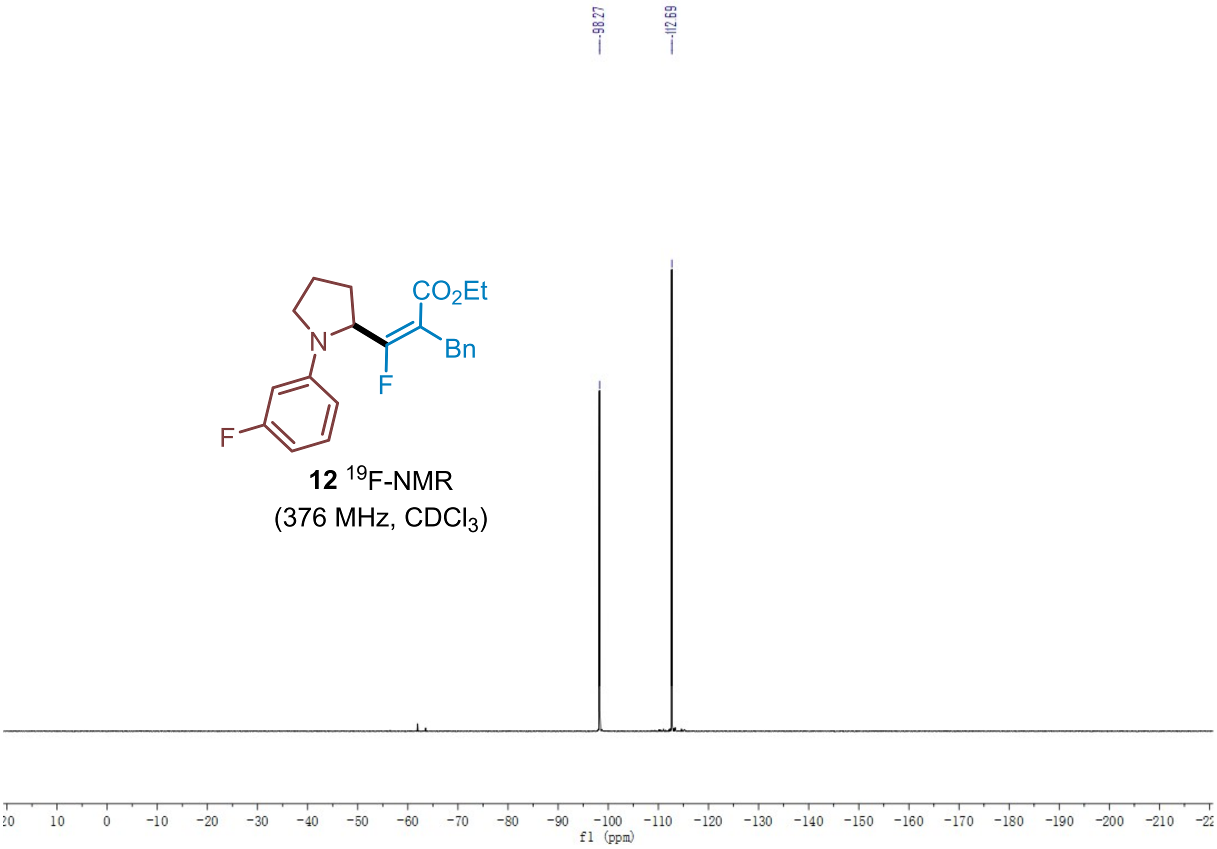
11 ^{19}F-NMR (376 MHz, $CDCl_3$)



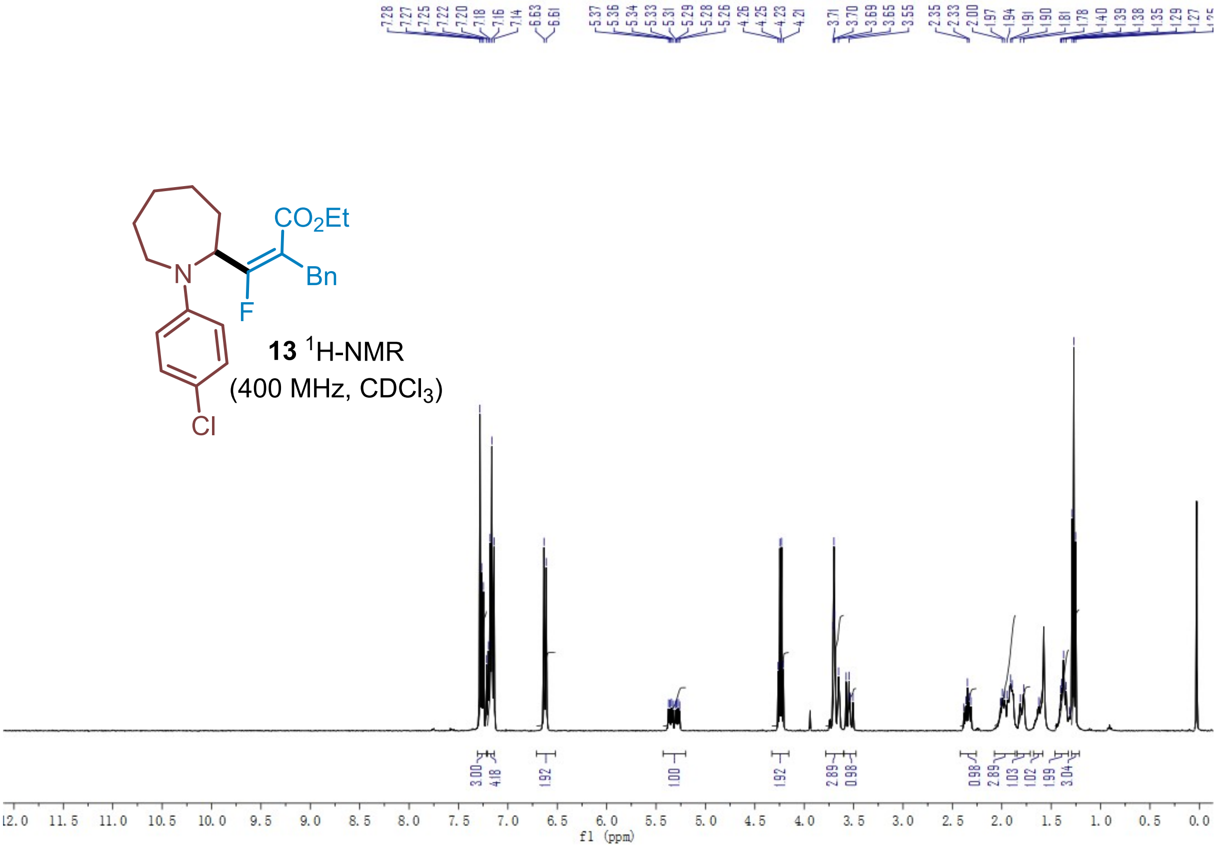
12 ^{1}H-NMR
(400 MHz, $CDCl_3$)



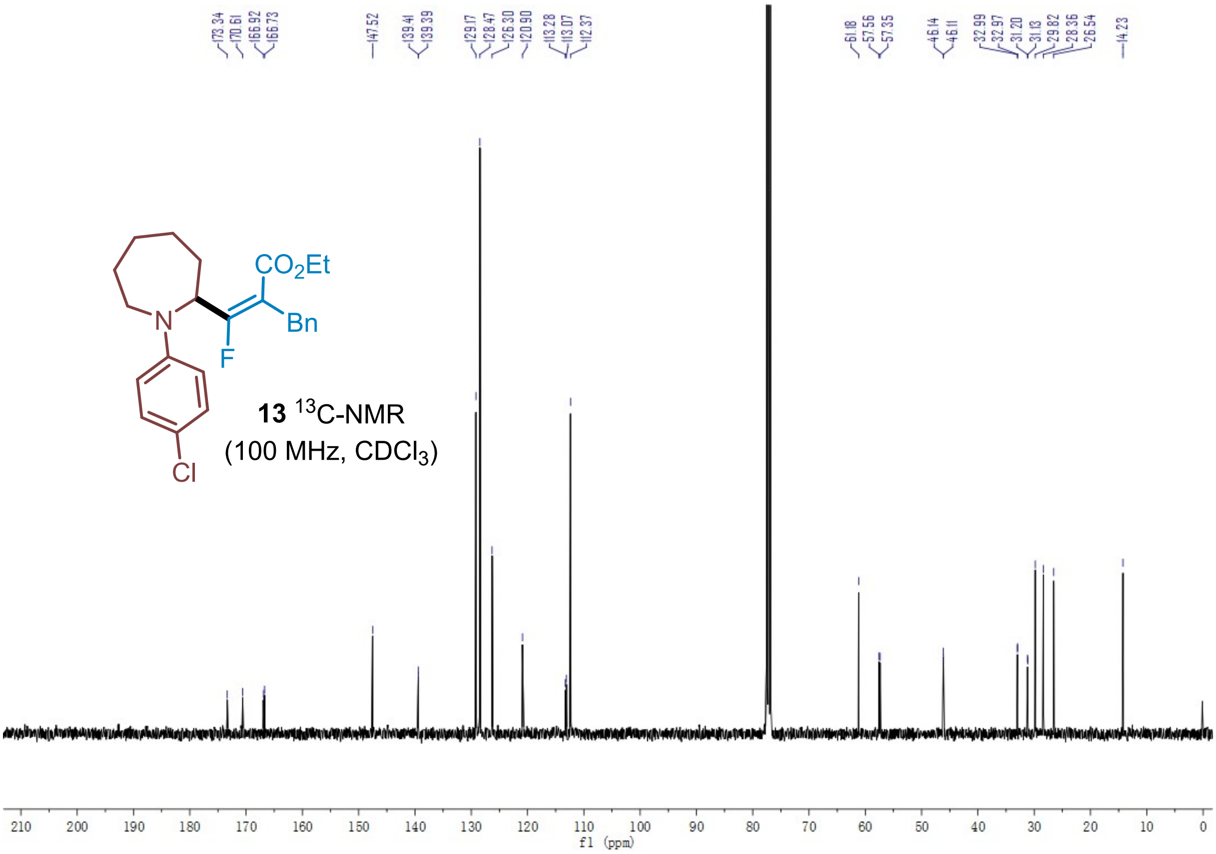
12 ^{13}C-NMR
(100 MHz, $CDCl_3$)

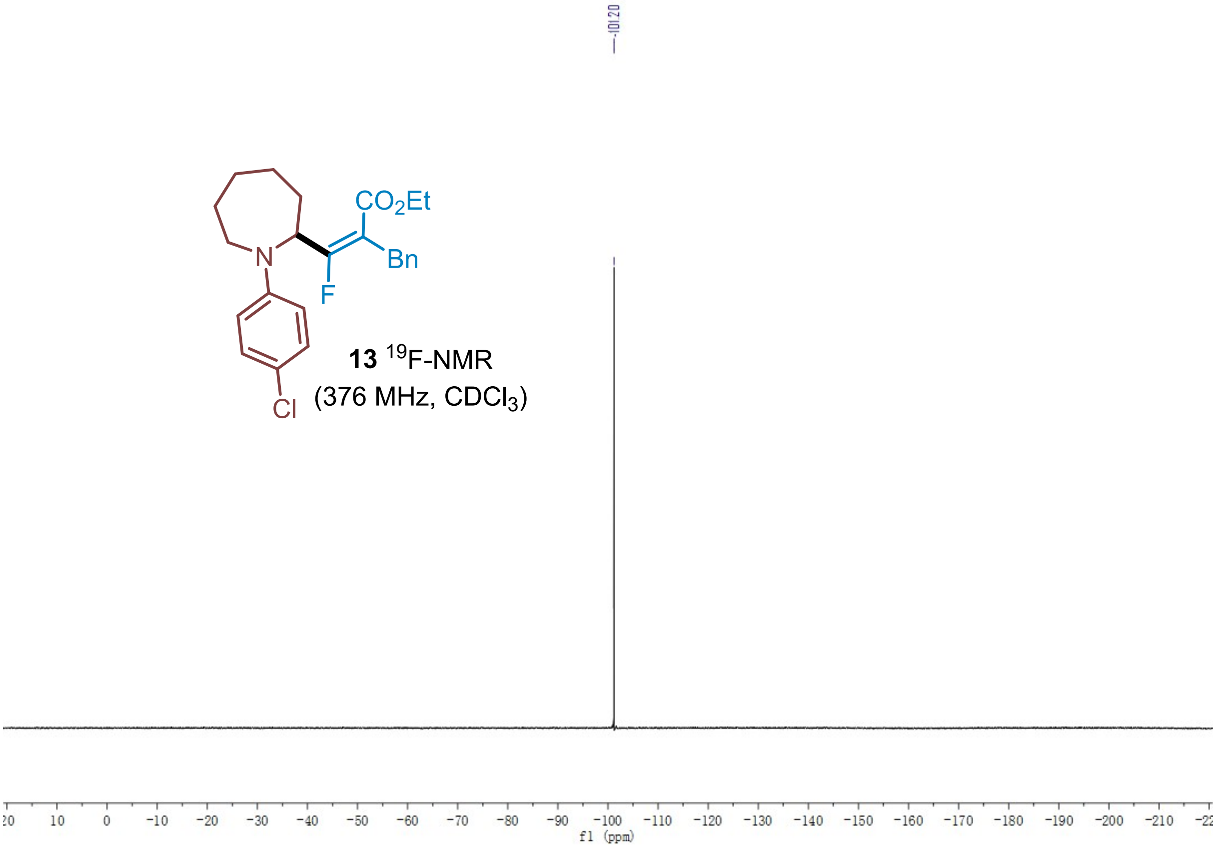


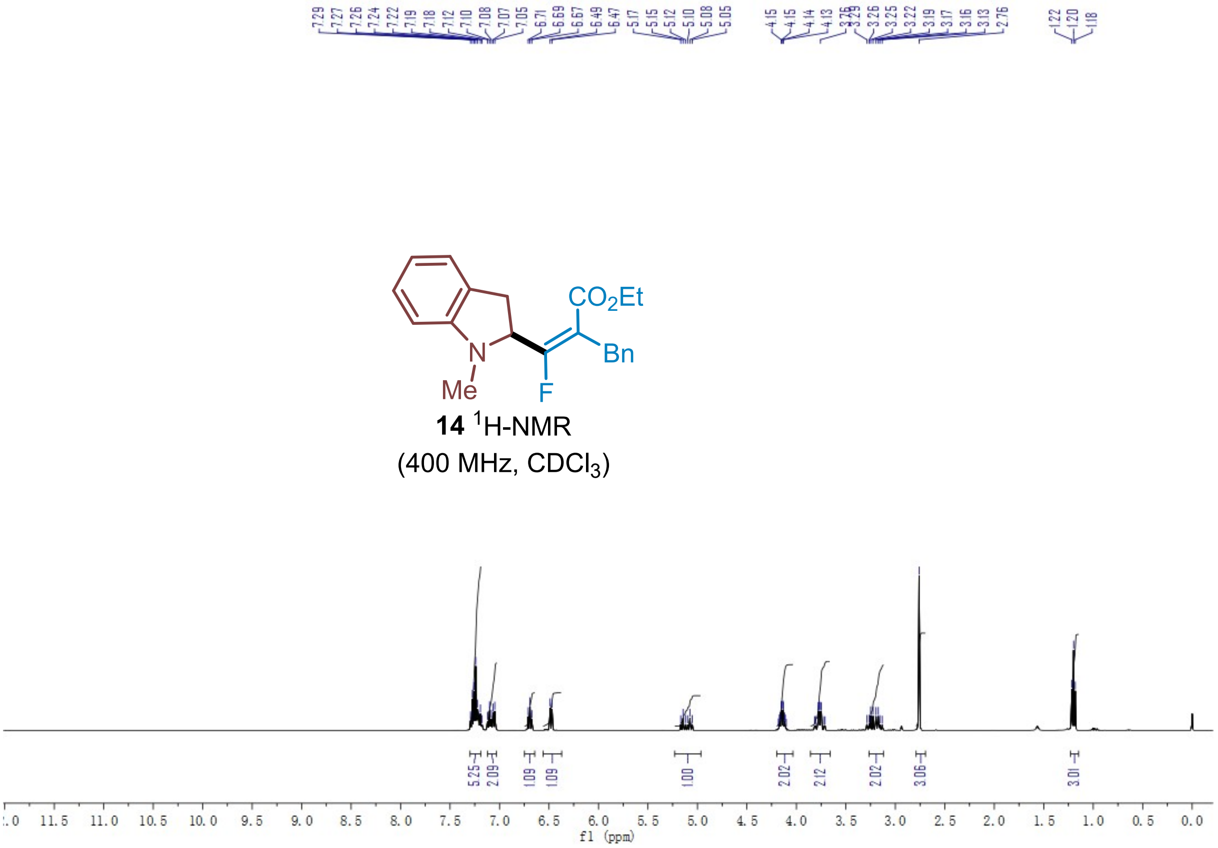
12 ^{19}F-NMR
(376 MHz, $CDCl_3$)



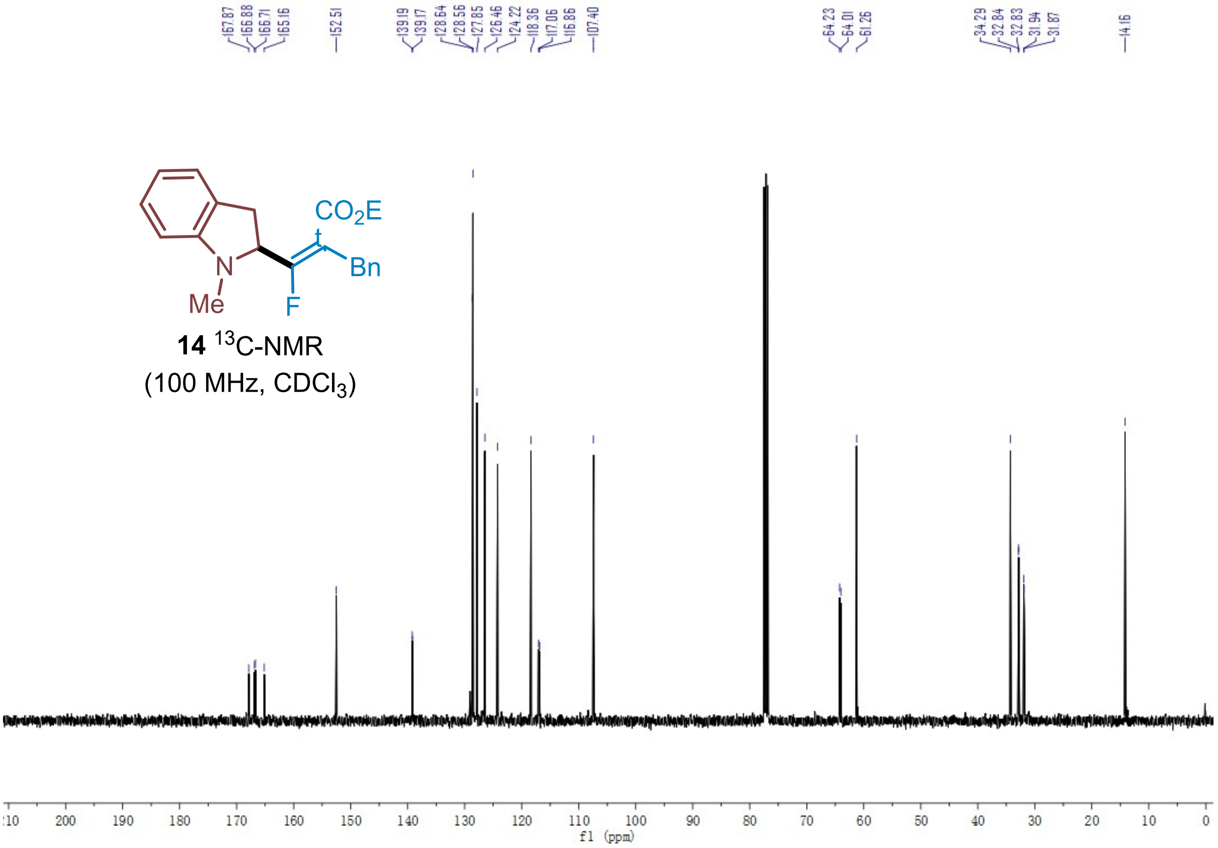
13 ^{1}H-NMR
(400 MHz, $CDCl_3$)


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

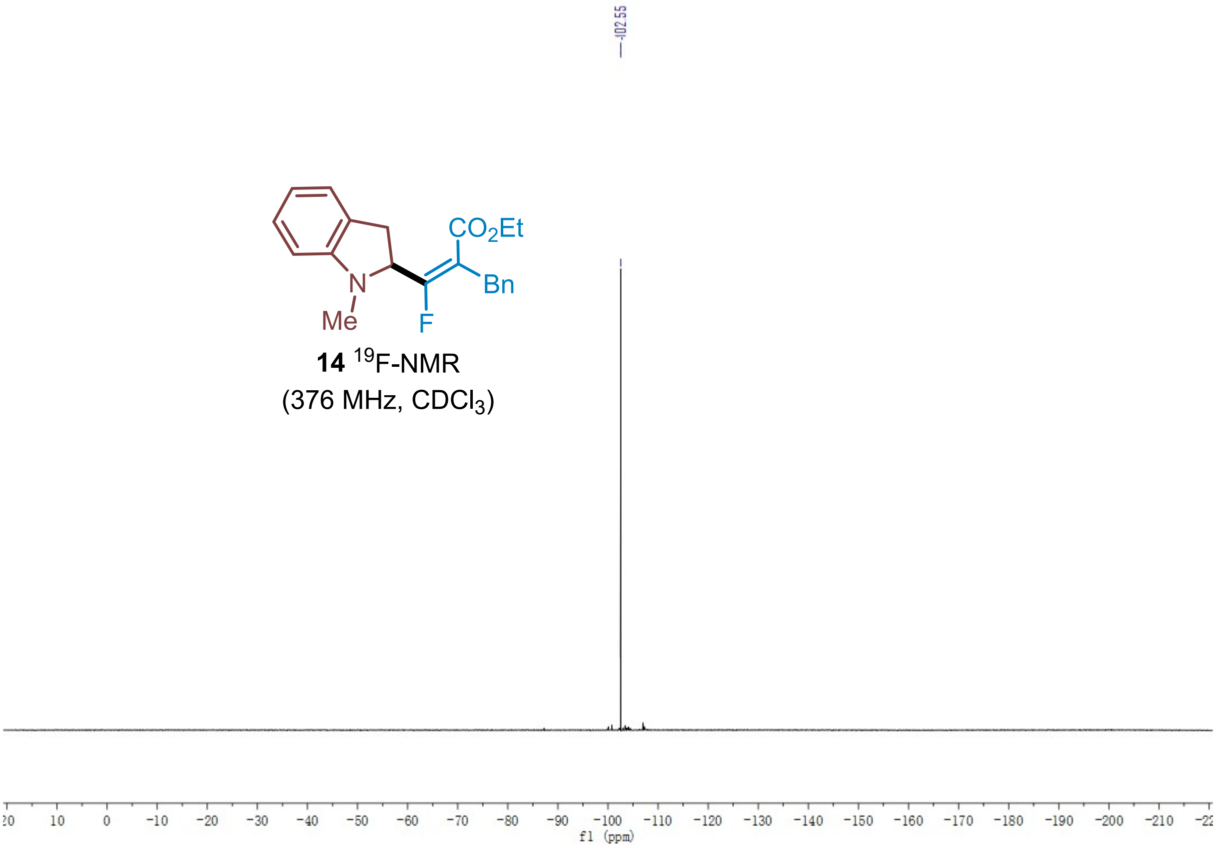

13 ^{19}F-NMR
(376 MHz, $CDCl_3$)



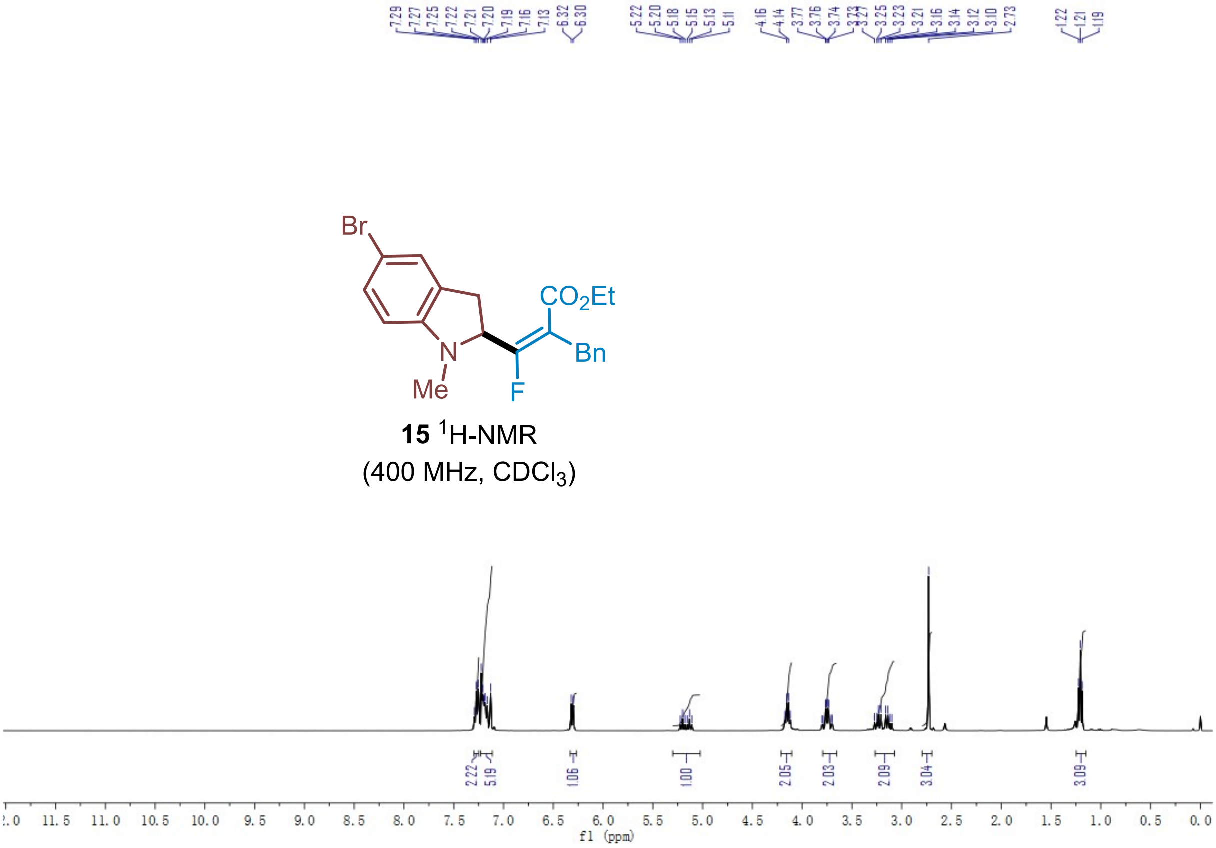
14 ^{1}H-NMR
(400 MHz, $CDCl_3$)



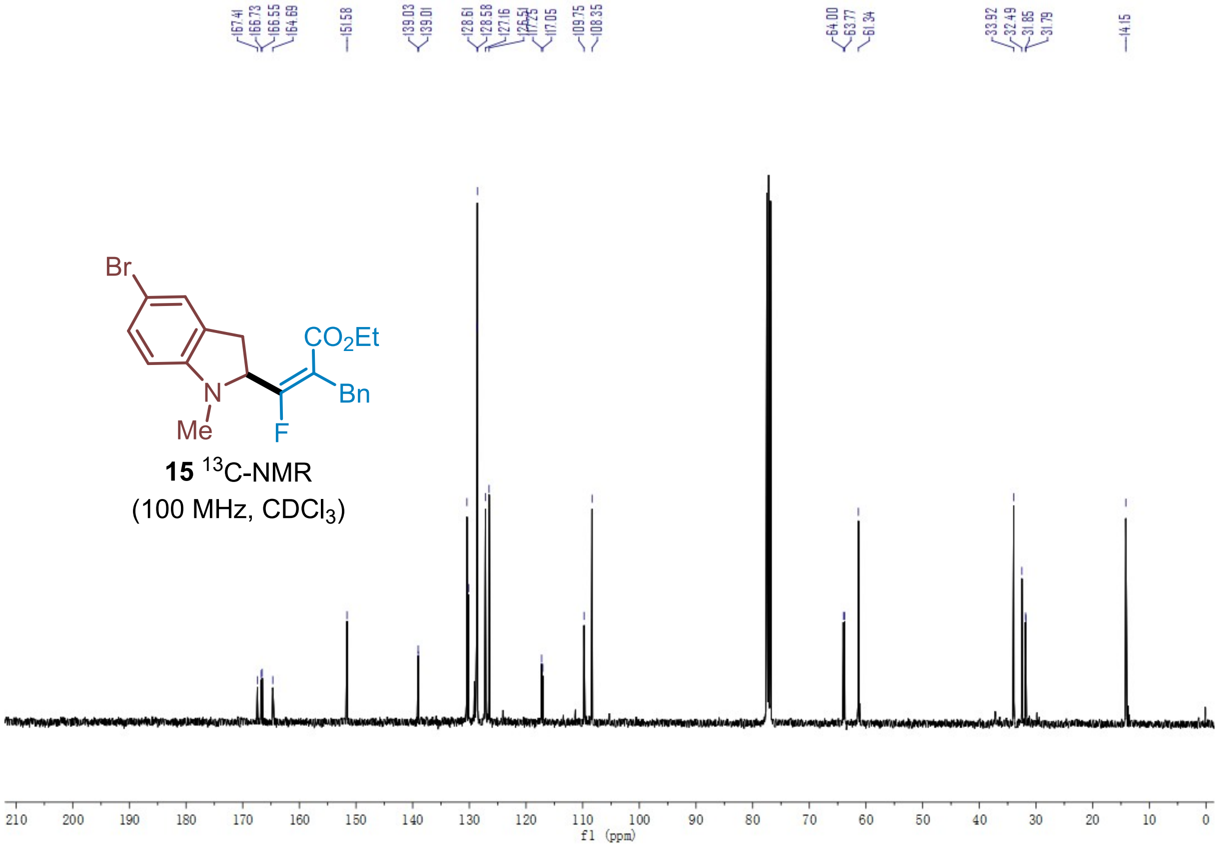
14 ^{13}C-NMR
(100 MHz, $CDCl_3$)



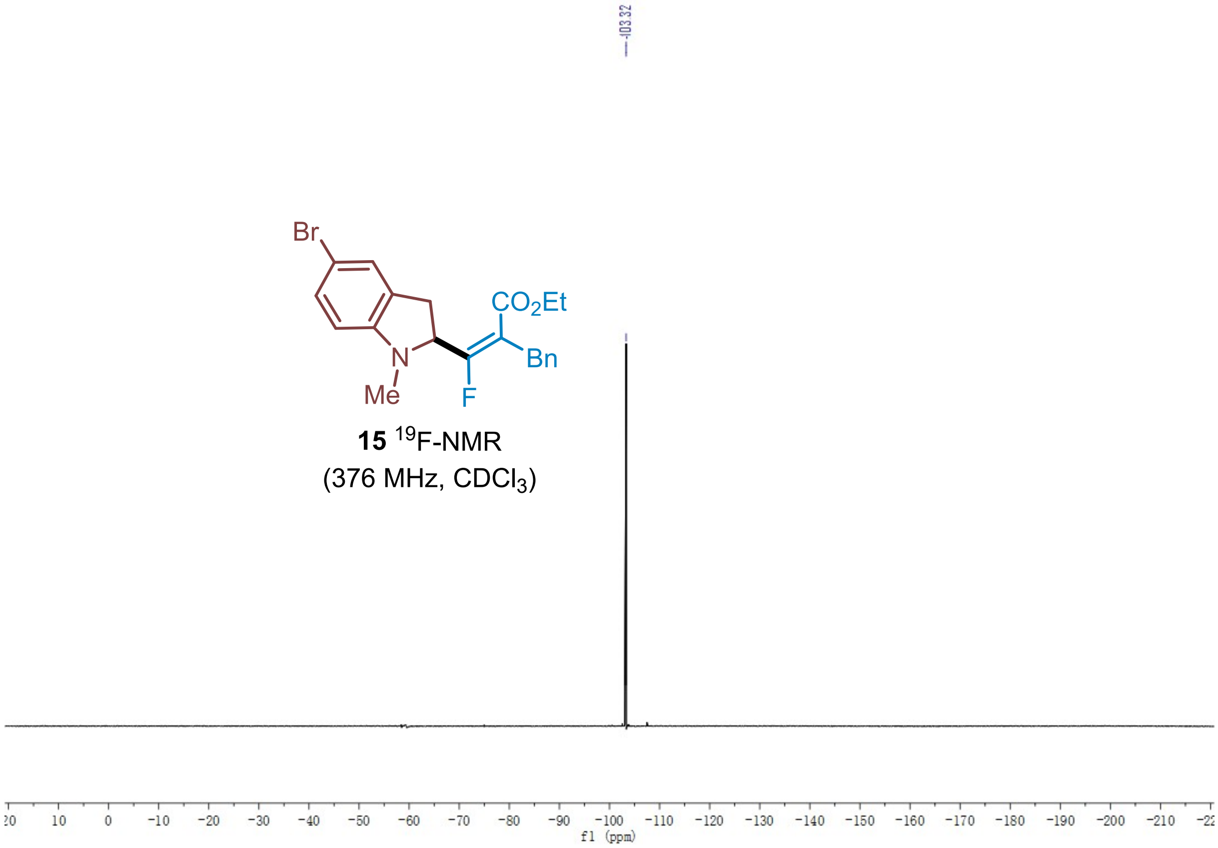
14 ^{19}F-NMR
(376 MHz, $CDCl_3$)



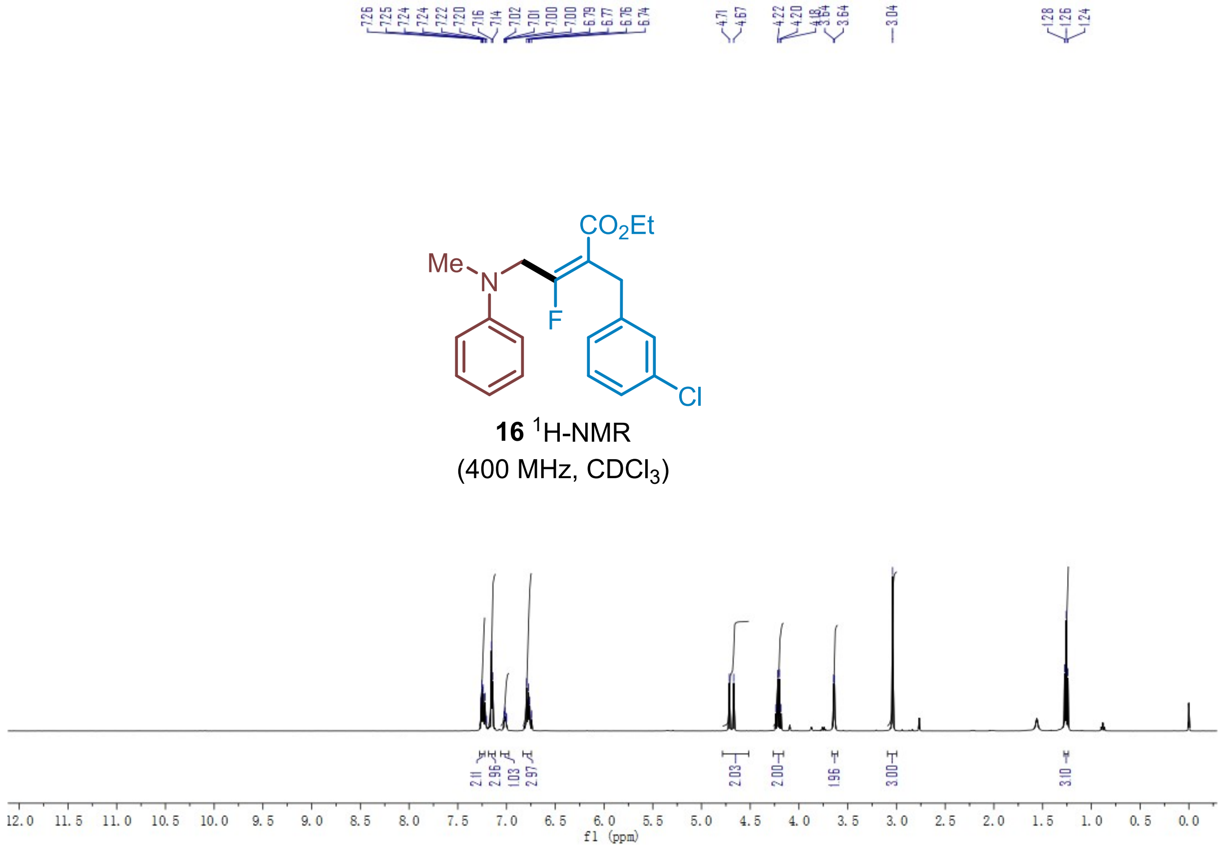
15 ^{1}H-NMR
(400 MHz, $CDCl_3$)



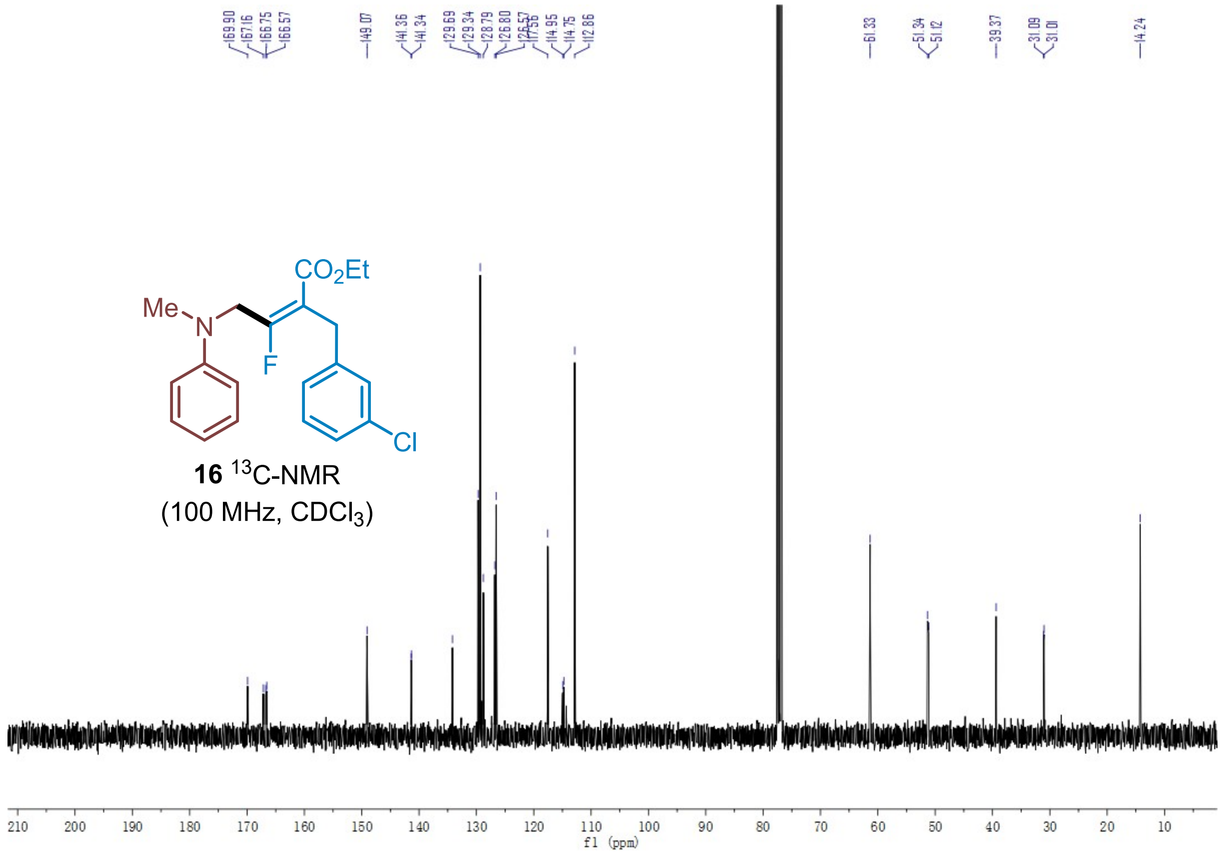
15 ^{13}C-NMR
(100 MHz, $CDCl_3$)



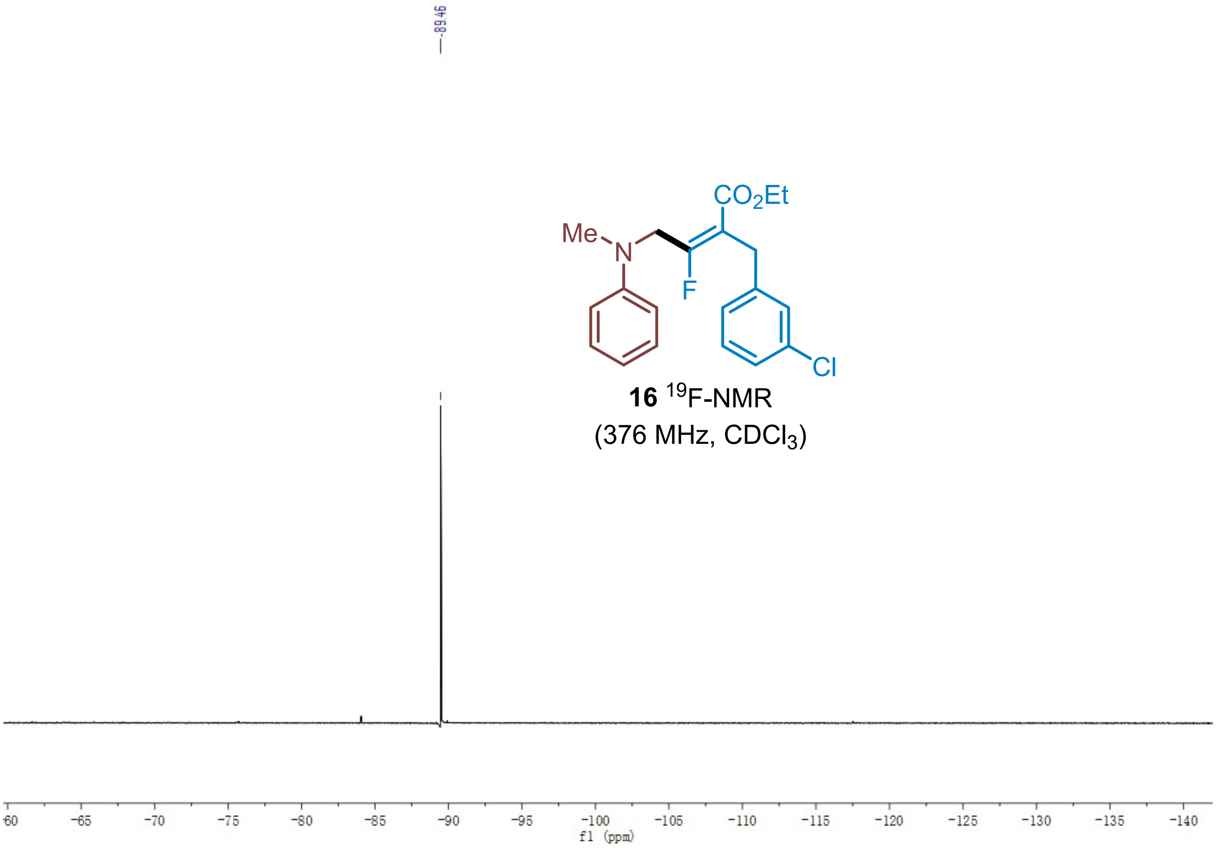
15 ^{19}F-NMR
(376 MHz, $CDCl_3$)



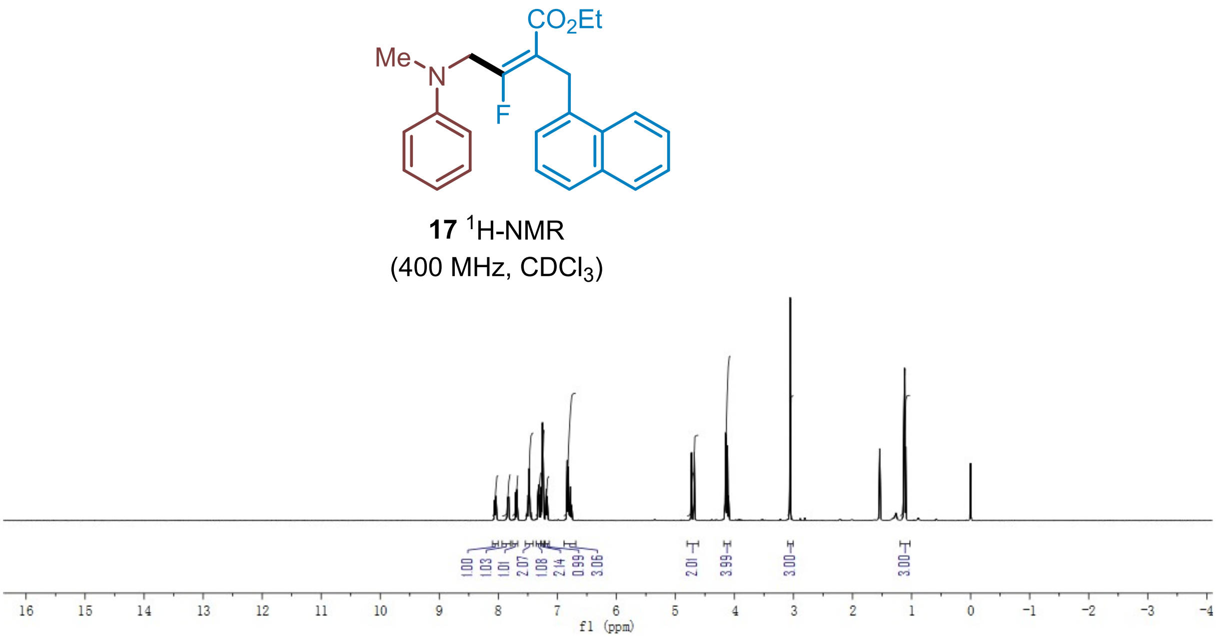
16 ^{1}H-NMR
(400 MHz, $CDCl_3$)



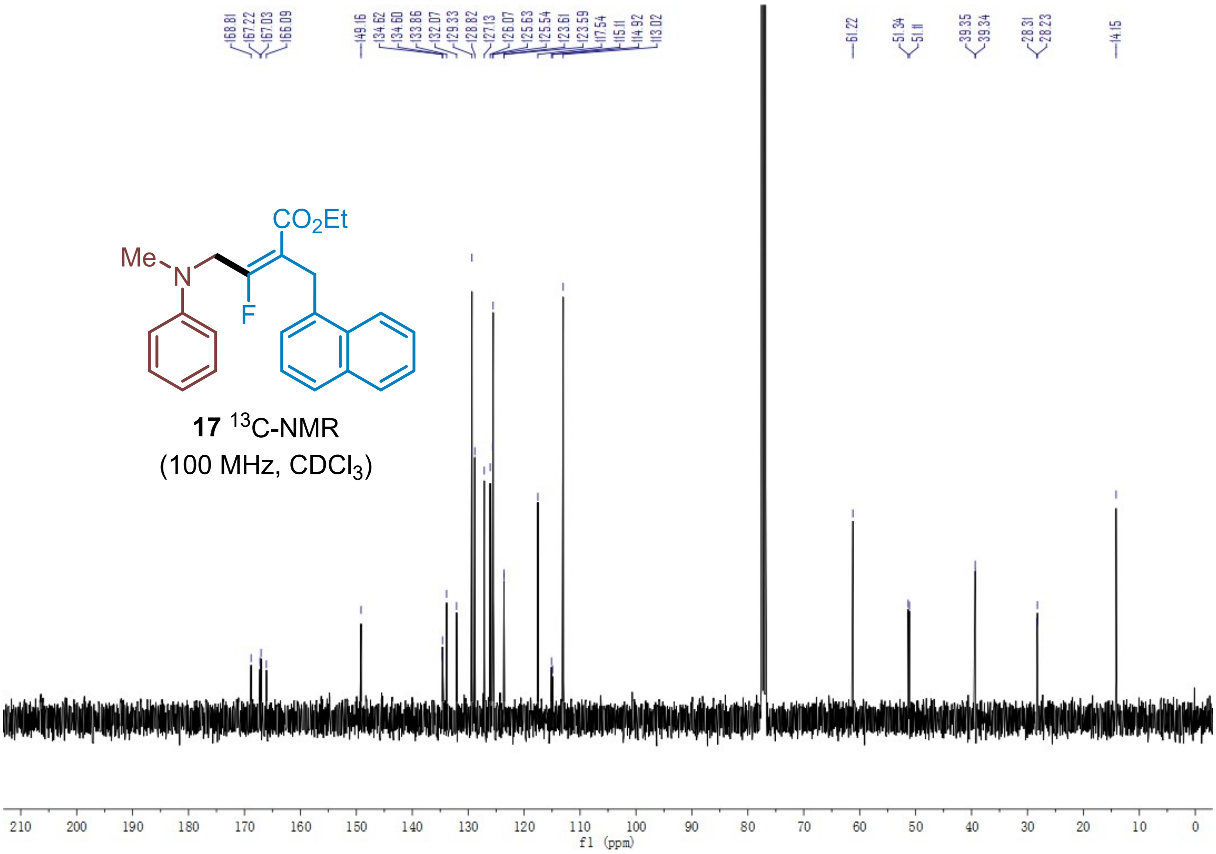
16 ^{13}C-NMR
(100 MHz, $CDCl_3$)



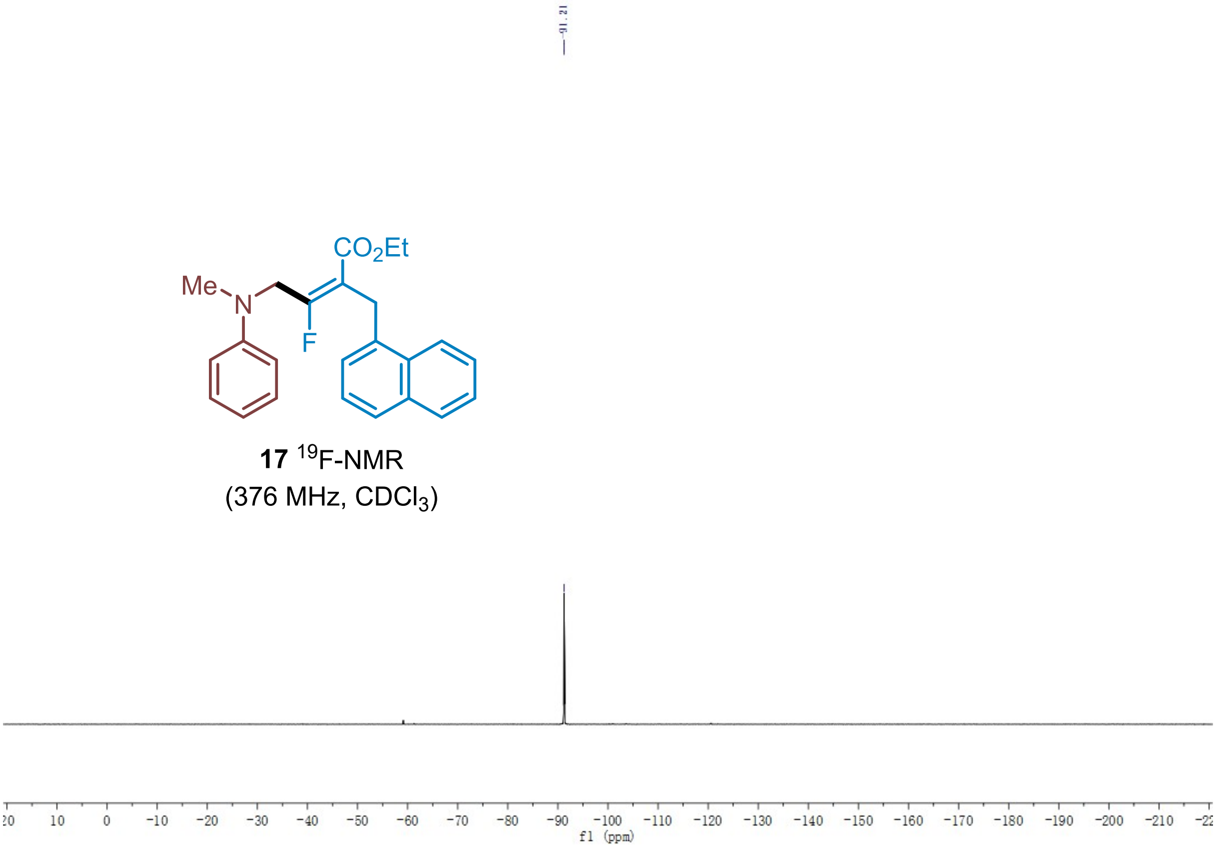
16 ^{19}F-NMR
(376 MHz, $CDCl_3$)



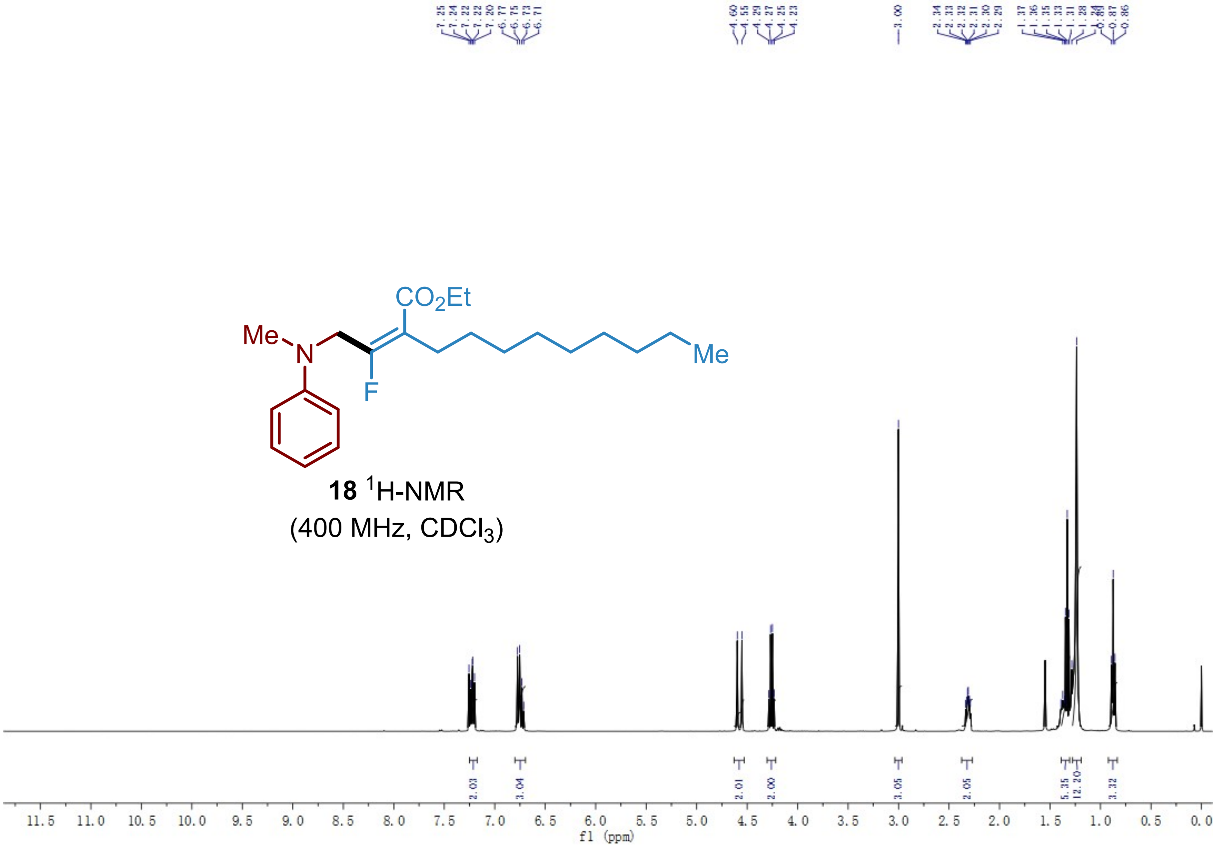
17 ^{1}H-NMR
(400 MHz, $CDCl_3$)



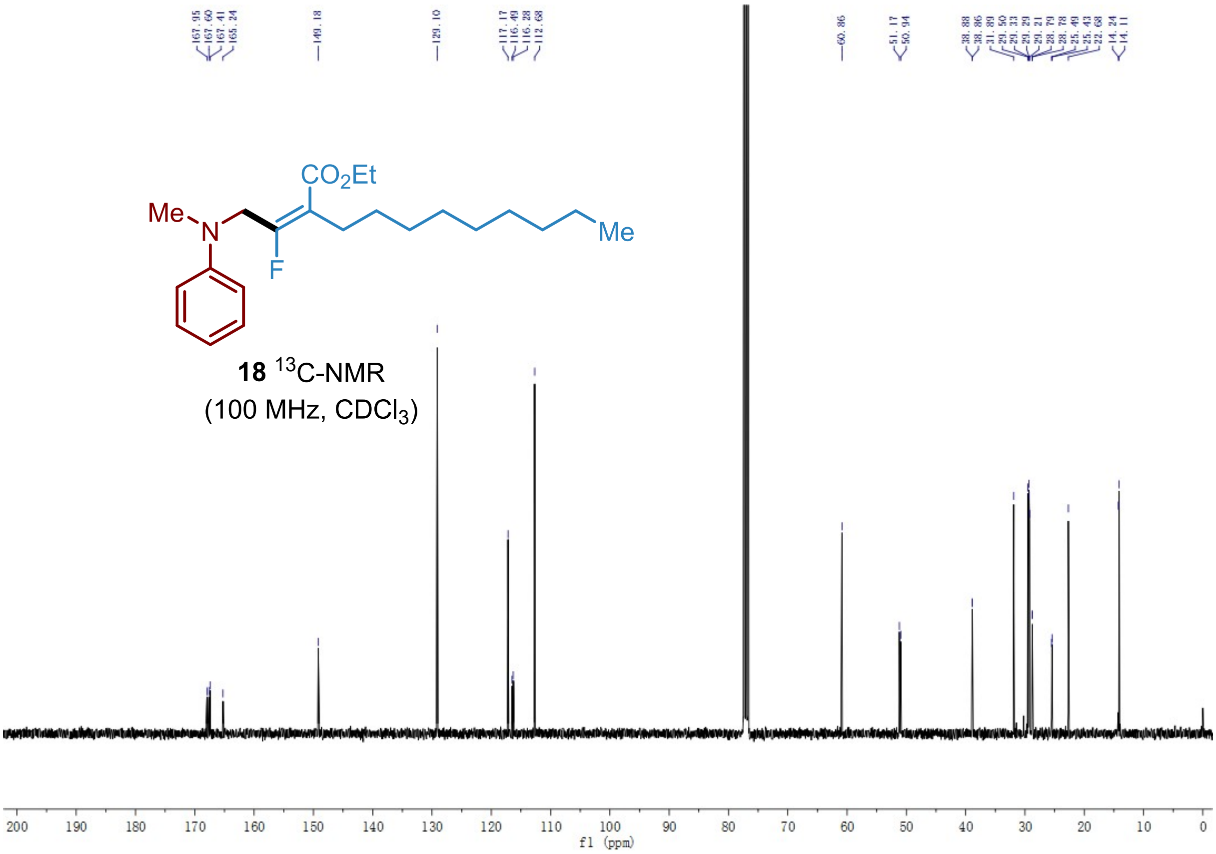
17 ^{13}C-NMR
(100 MHz, $CDCl_3$)



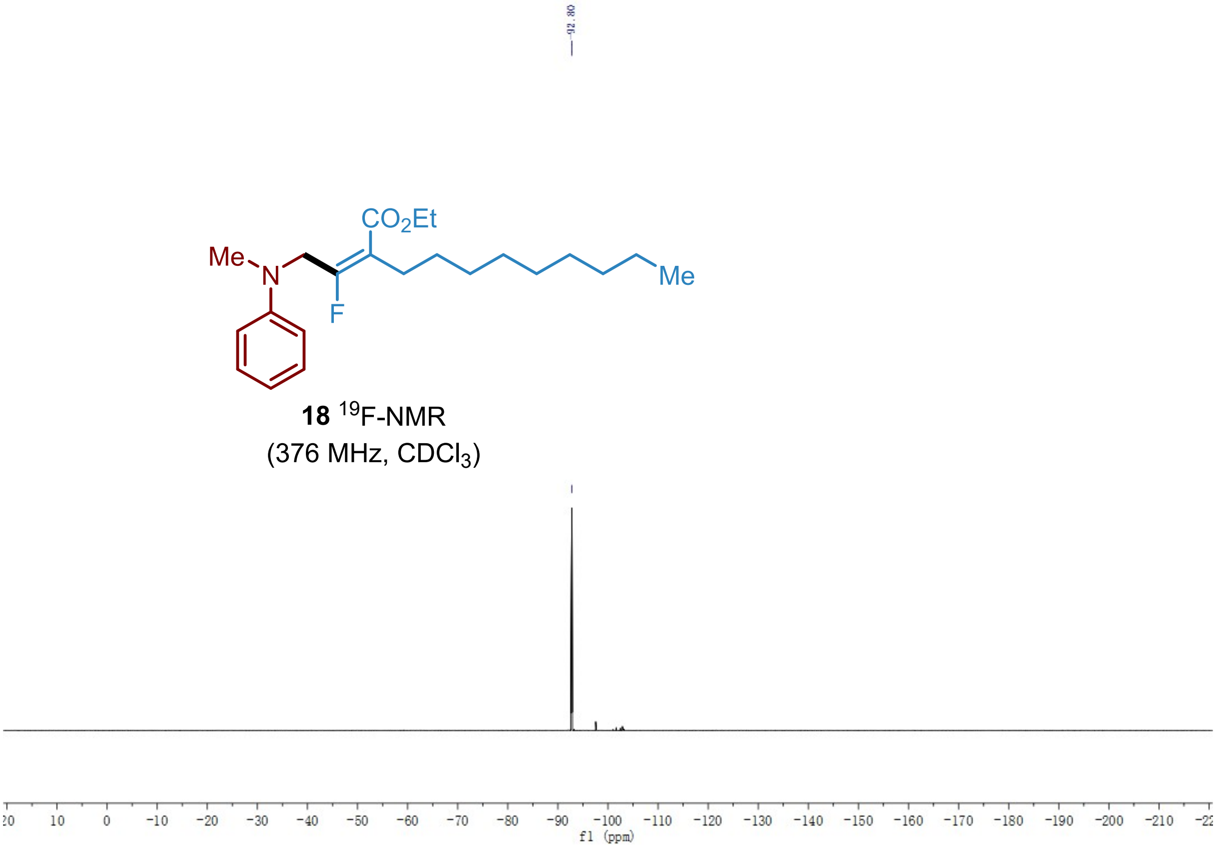
17 ^{19}F-NMR
(376 MHz, $CDCl_3$)



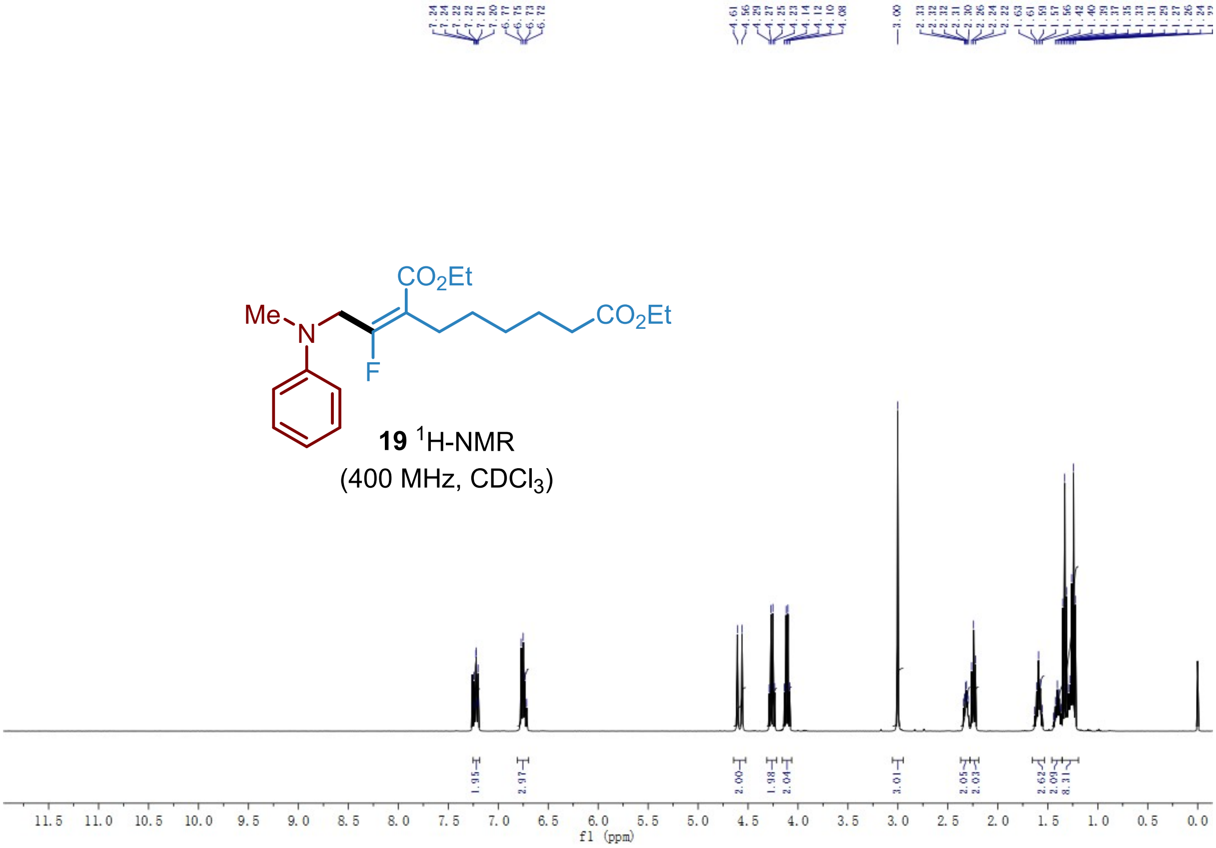
18 ^{1}H-NMR
(400 MHz, $CDCl_3$)



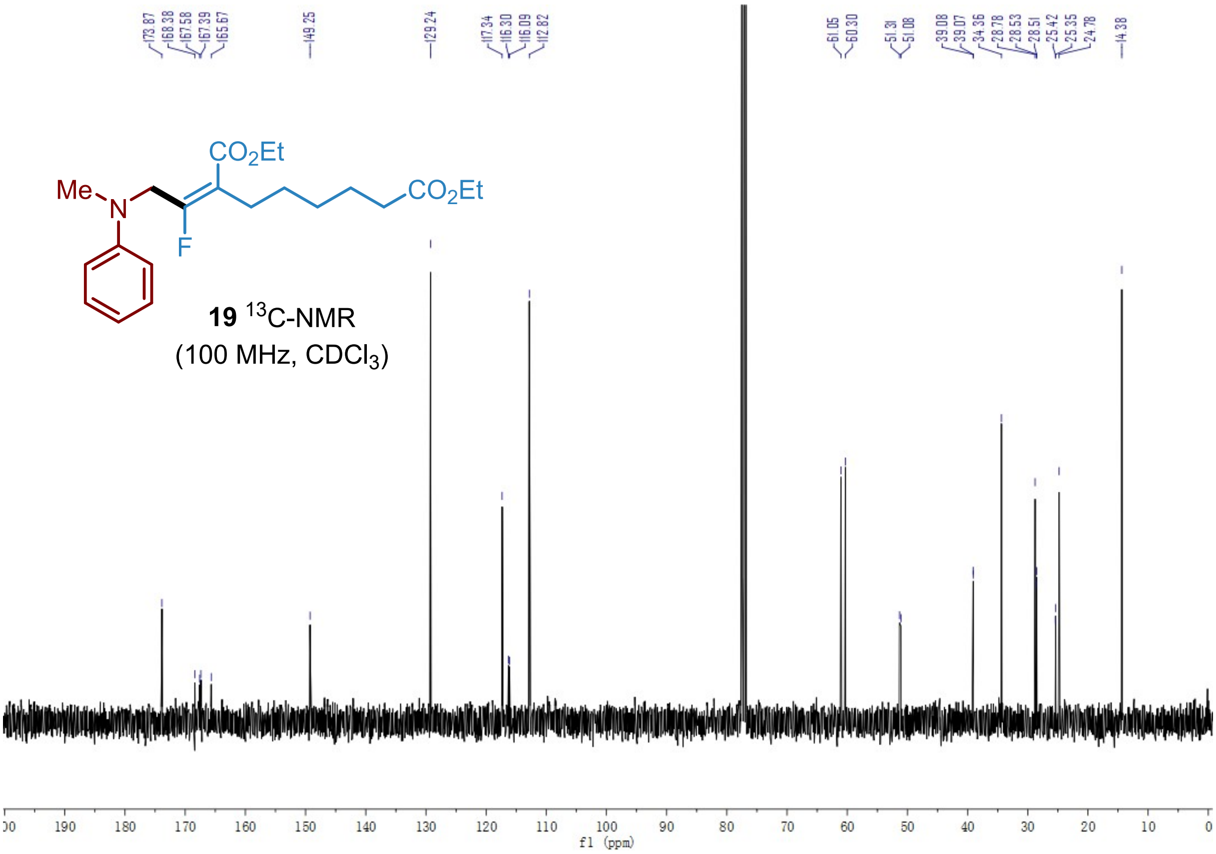
18 ^{13}C-NMR
(100 MHz, $CDCl_3$)



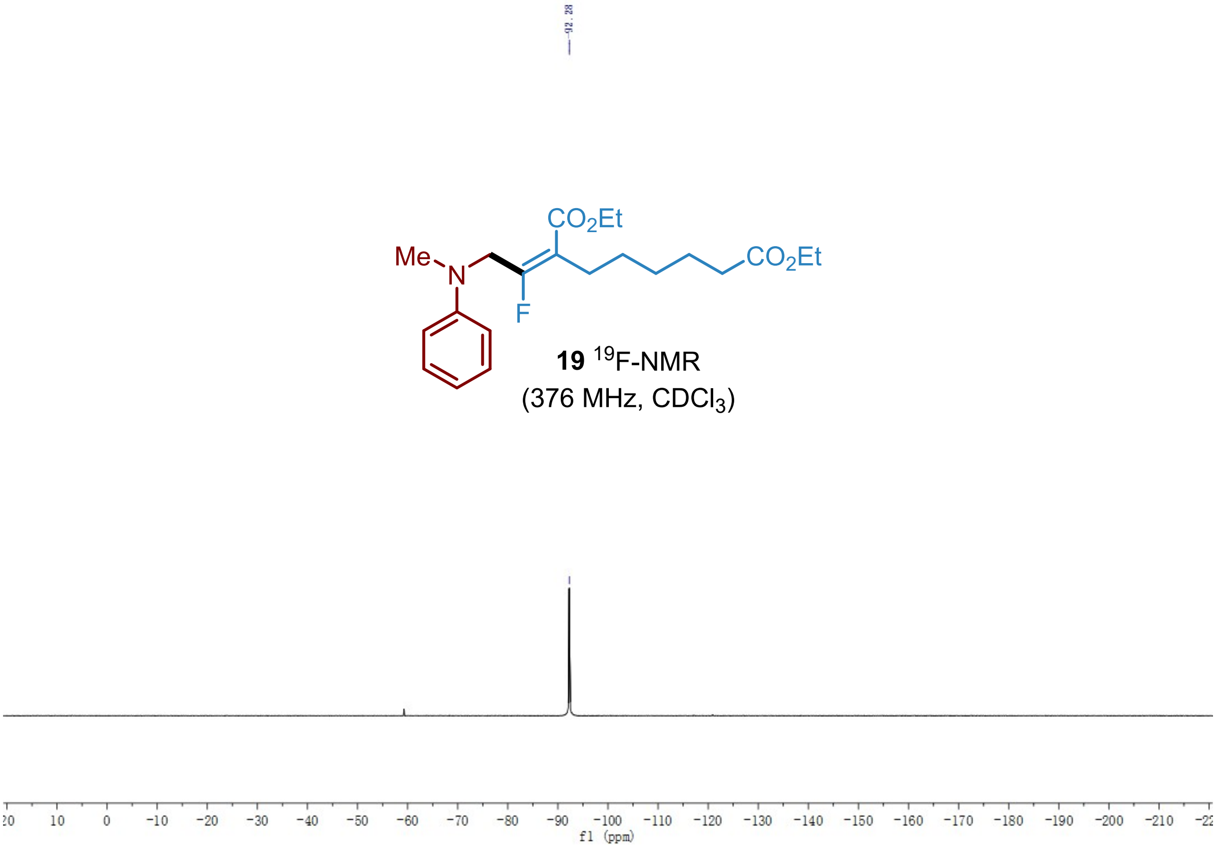
18 ^{19}F-NMR
(376 MHz, $CDCl_3$)



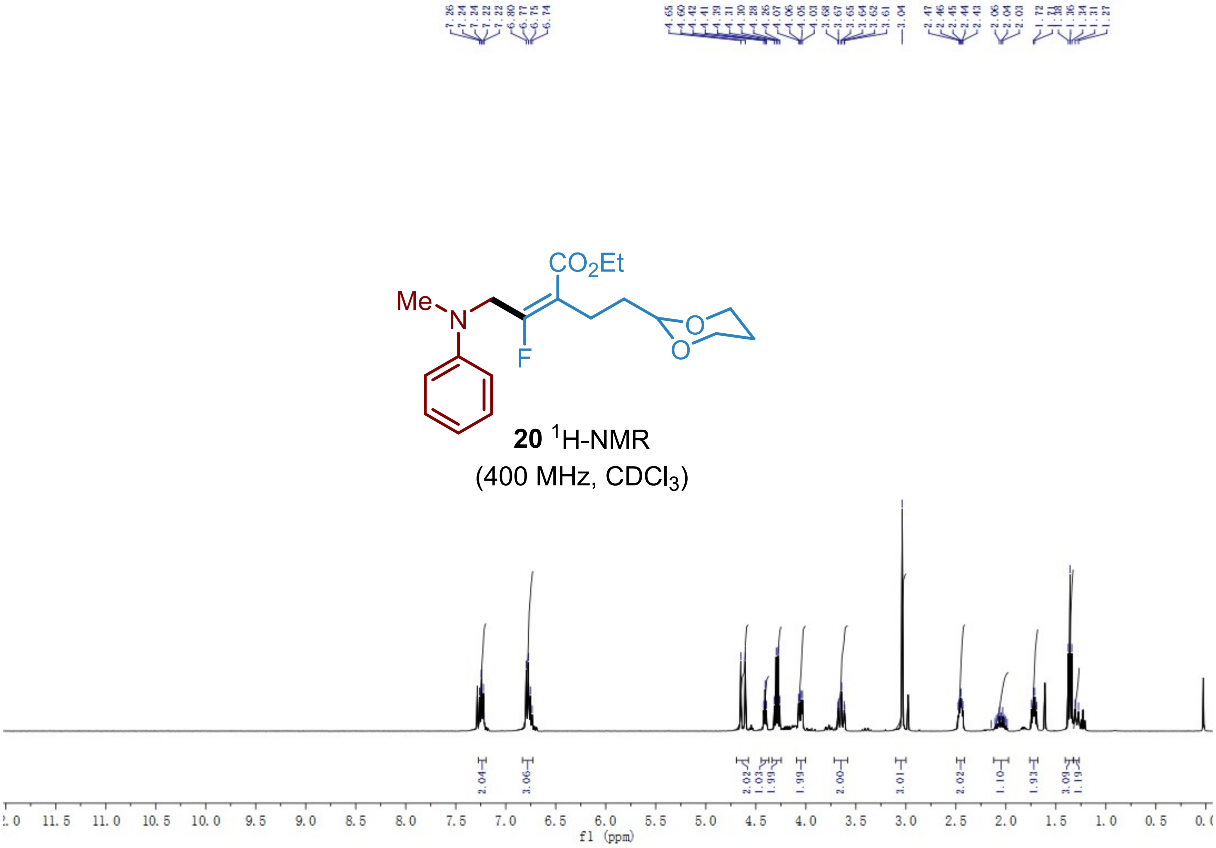
19 ^{1}H-NMR
(400 MHz, $CDCl_3$)



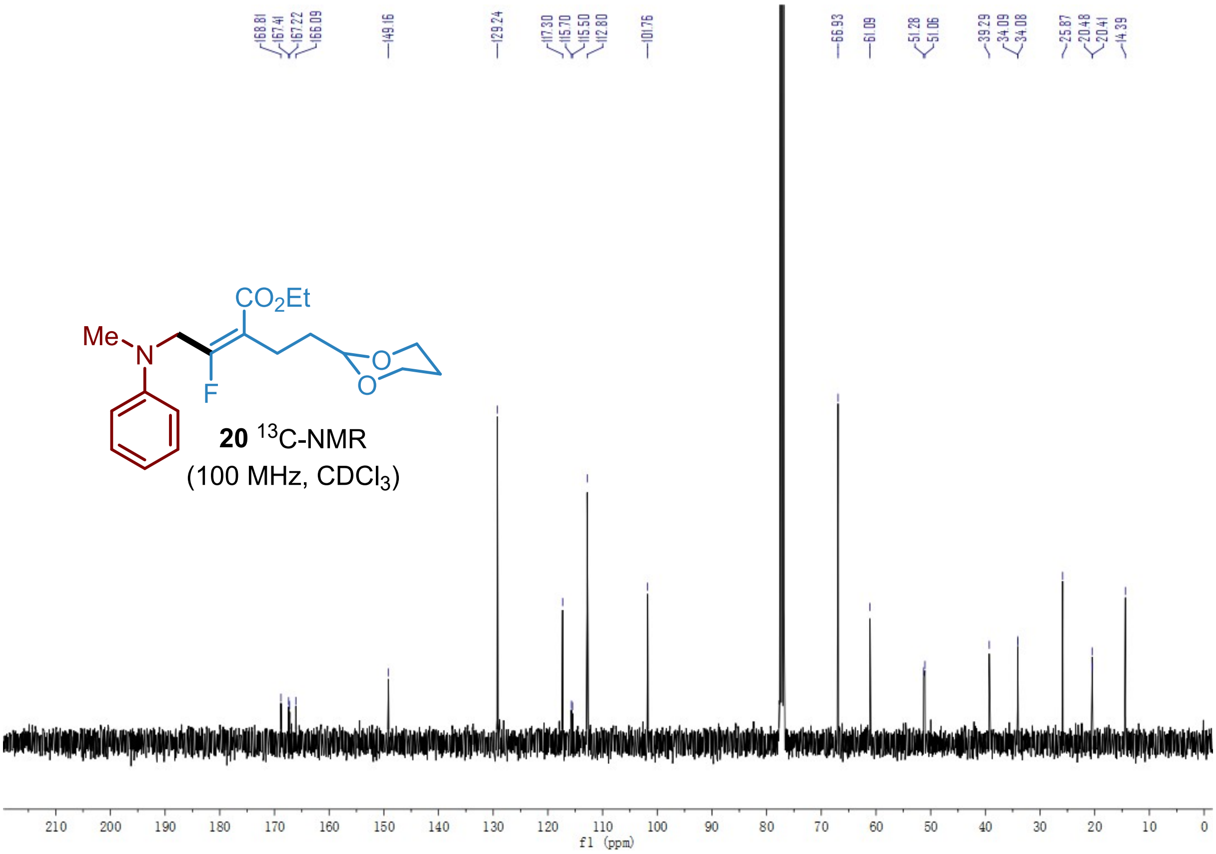
19 ^{13}C-NMR
(100 MHz, $CDCl_3$)



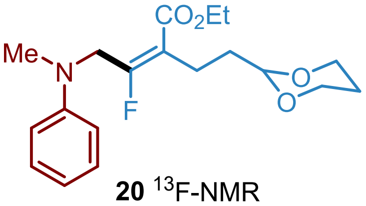
19 ^{19}F-NMR
(376 MHz, $CDCl_3$)



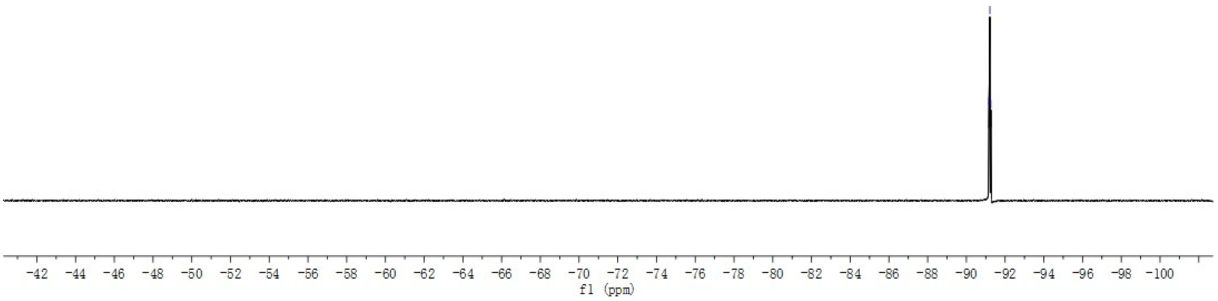
20 ^{1}H-NMR
(400 MHz, $CDCl_3$)

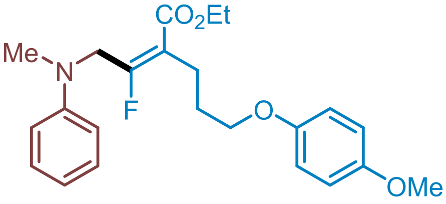


20 ^{13}C-NMR
(100 MHz, $CDCl_3$)

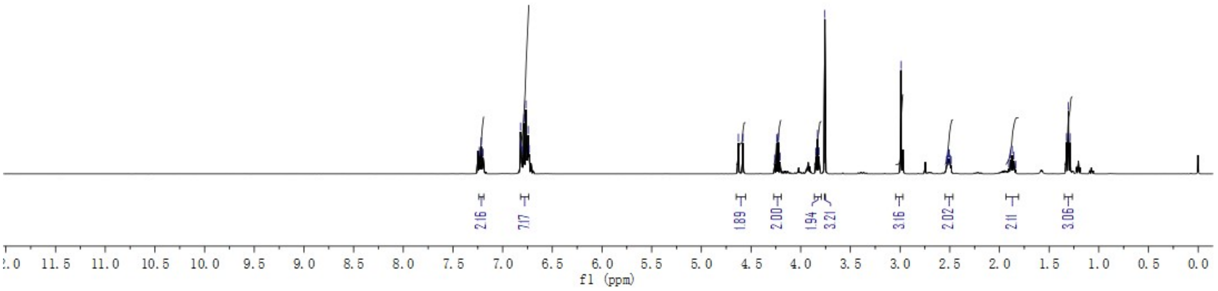


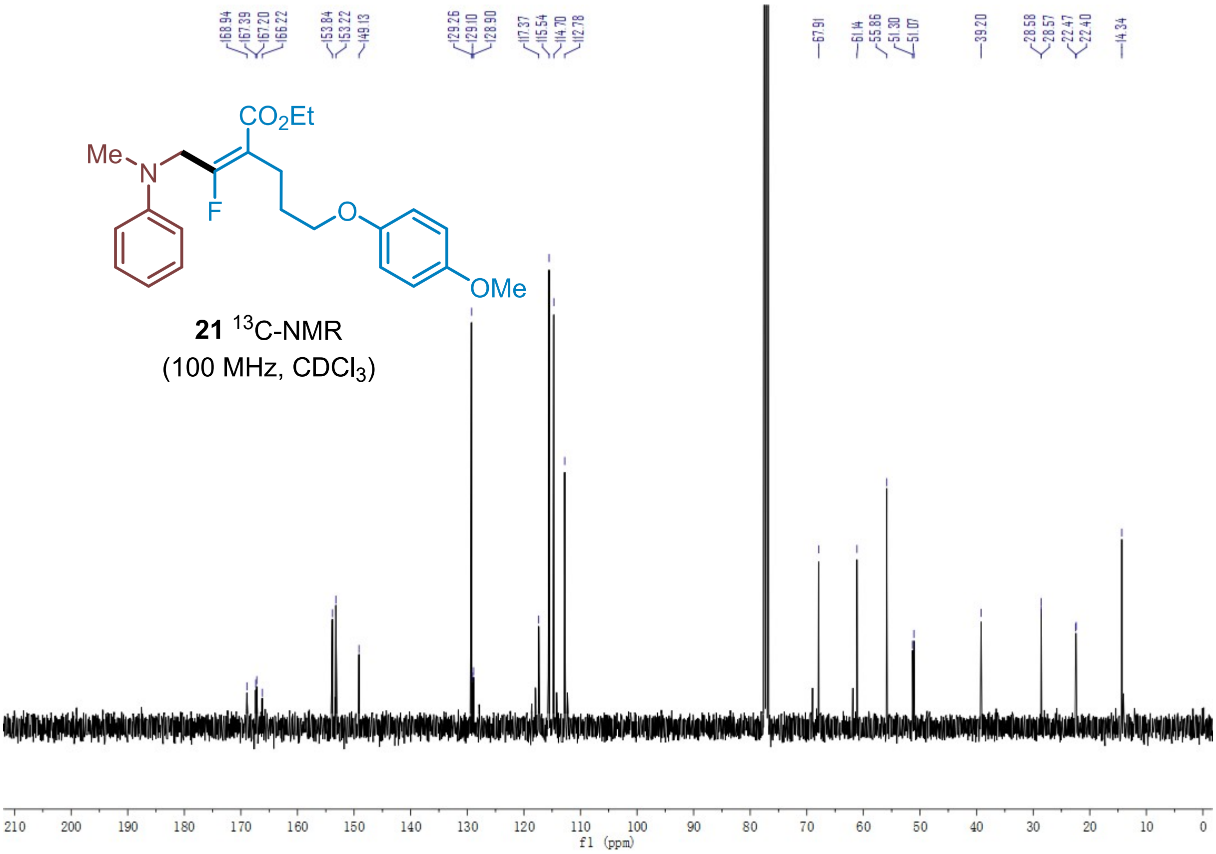
20 ^{13}F-NMR
(376 MHz, $CDCl_3$)

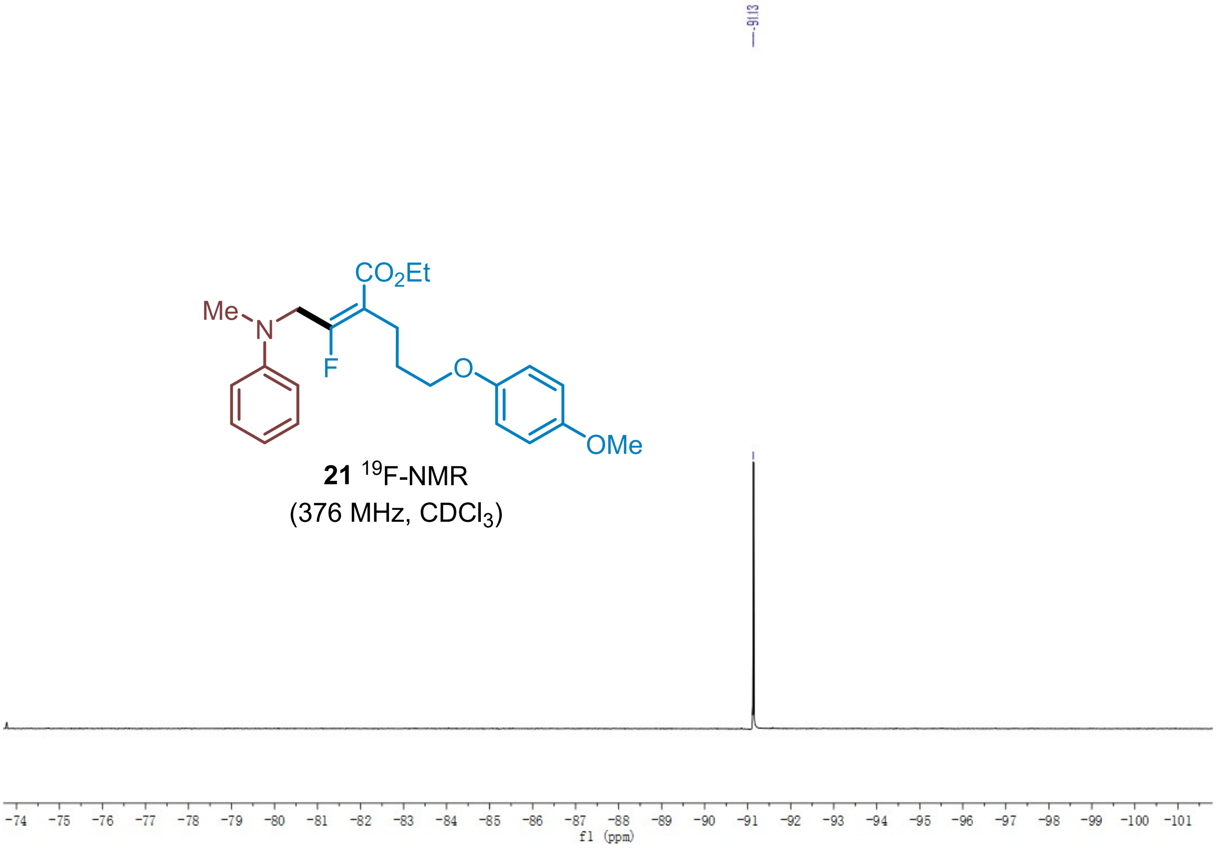


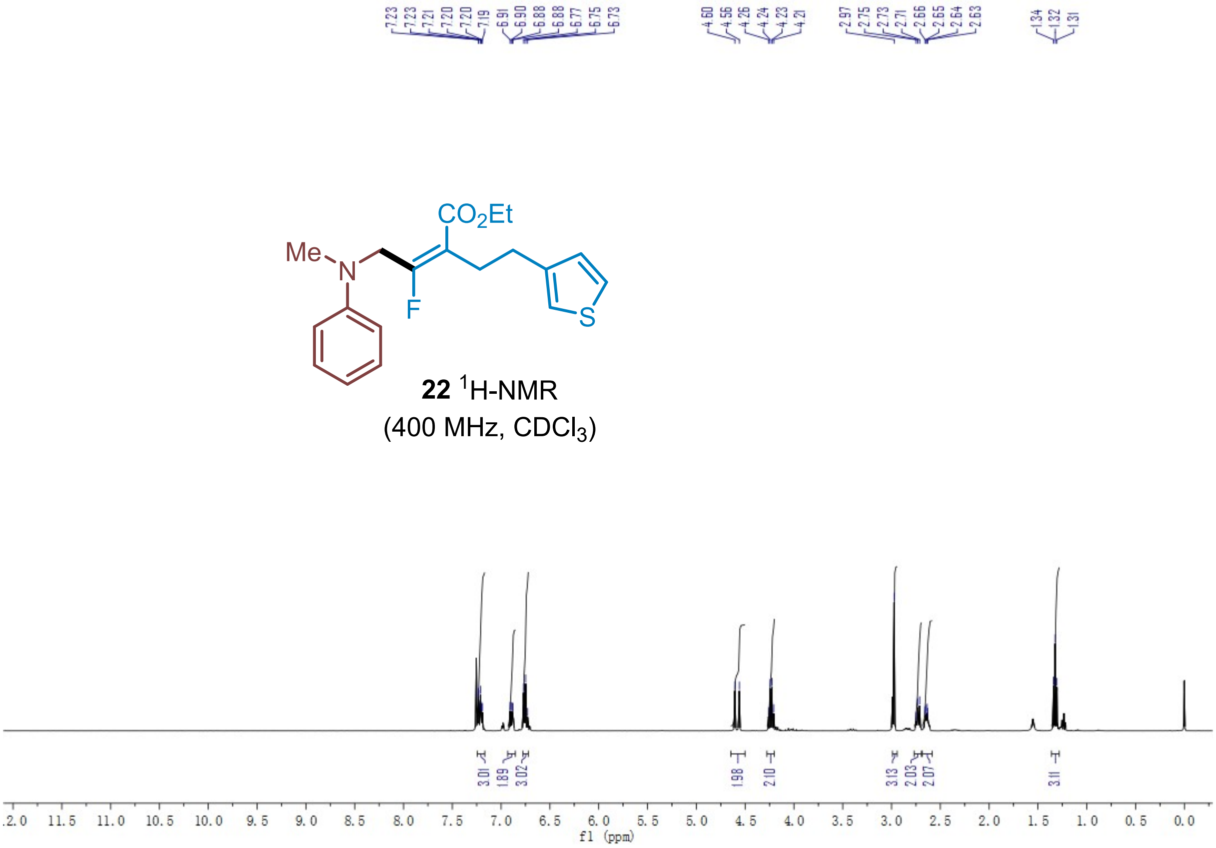


21 ^{1}H-NMR
(400 MHz, $CDCl_3$)

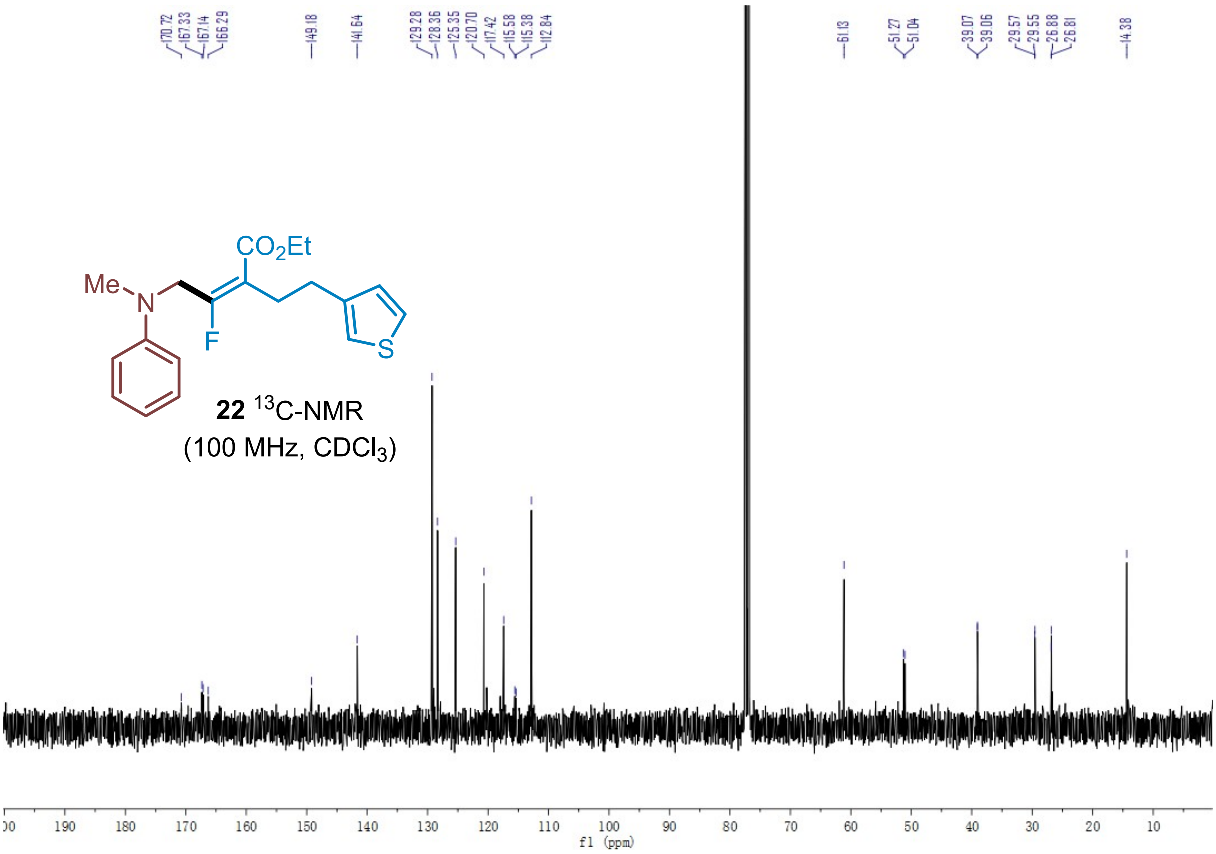



21 ^{13}C-NMR
(100 MHz, $CDCl_3$)

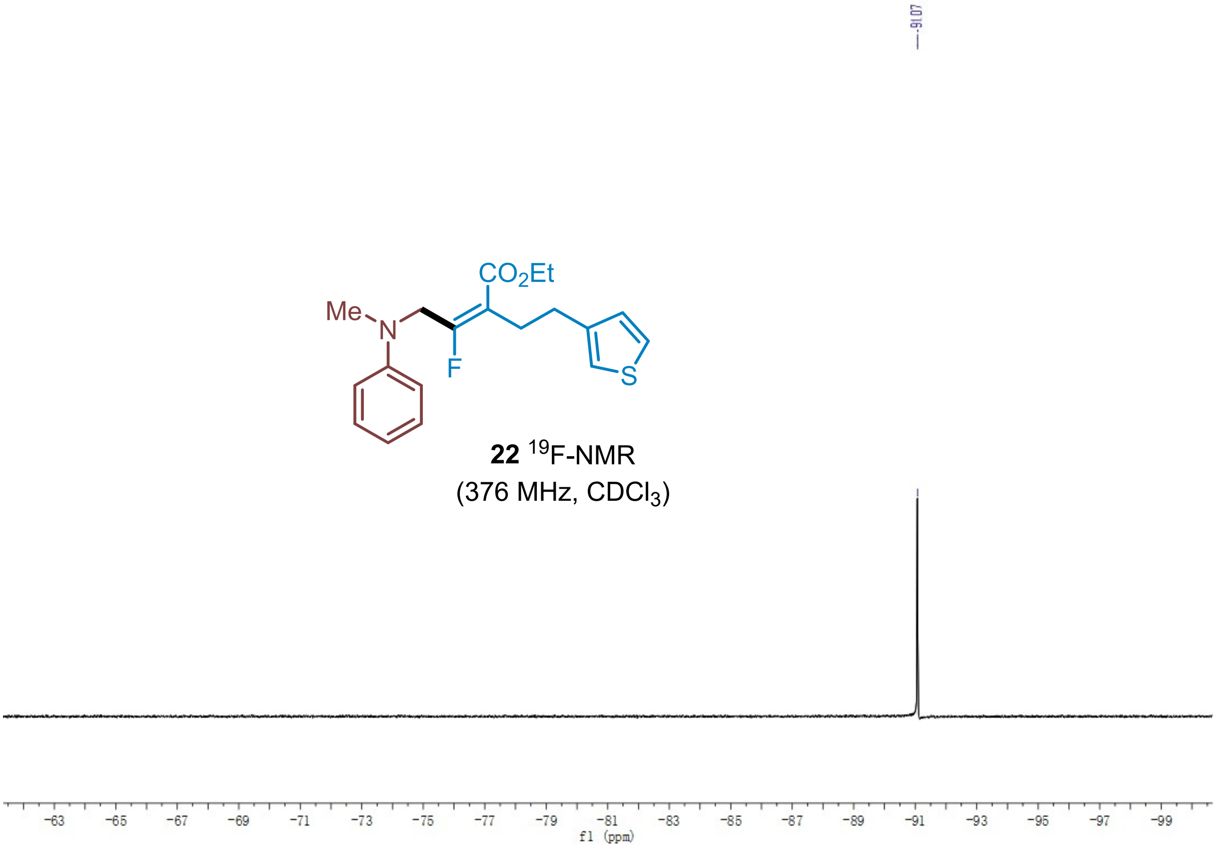

21 ^{19}F-NMR
(376 MHz, $CDCl_3$)



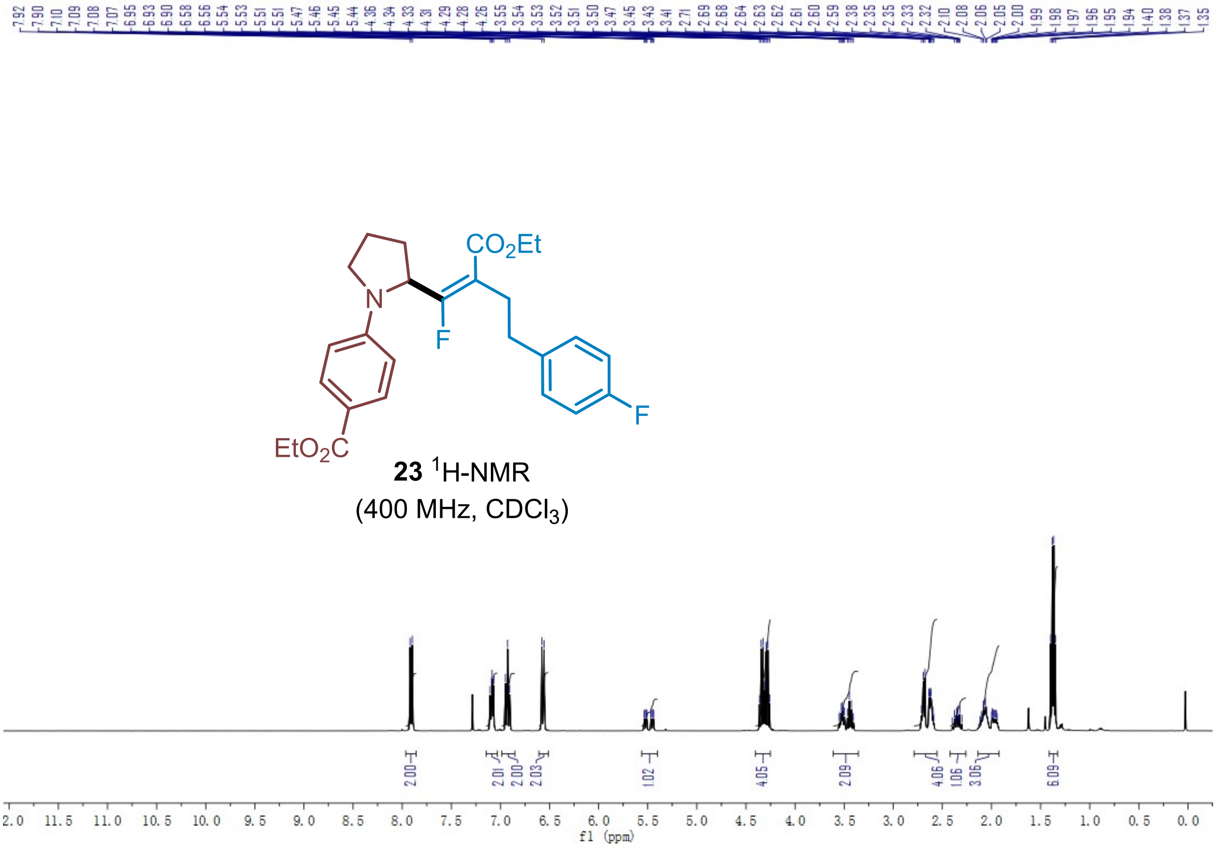
22 ^{1}H-NMR
(400 MHz, CDCl$_3$)



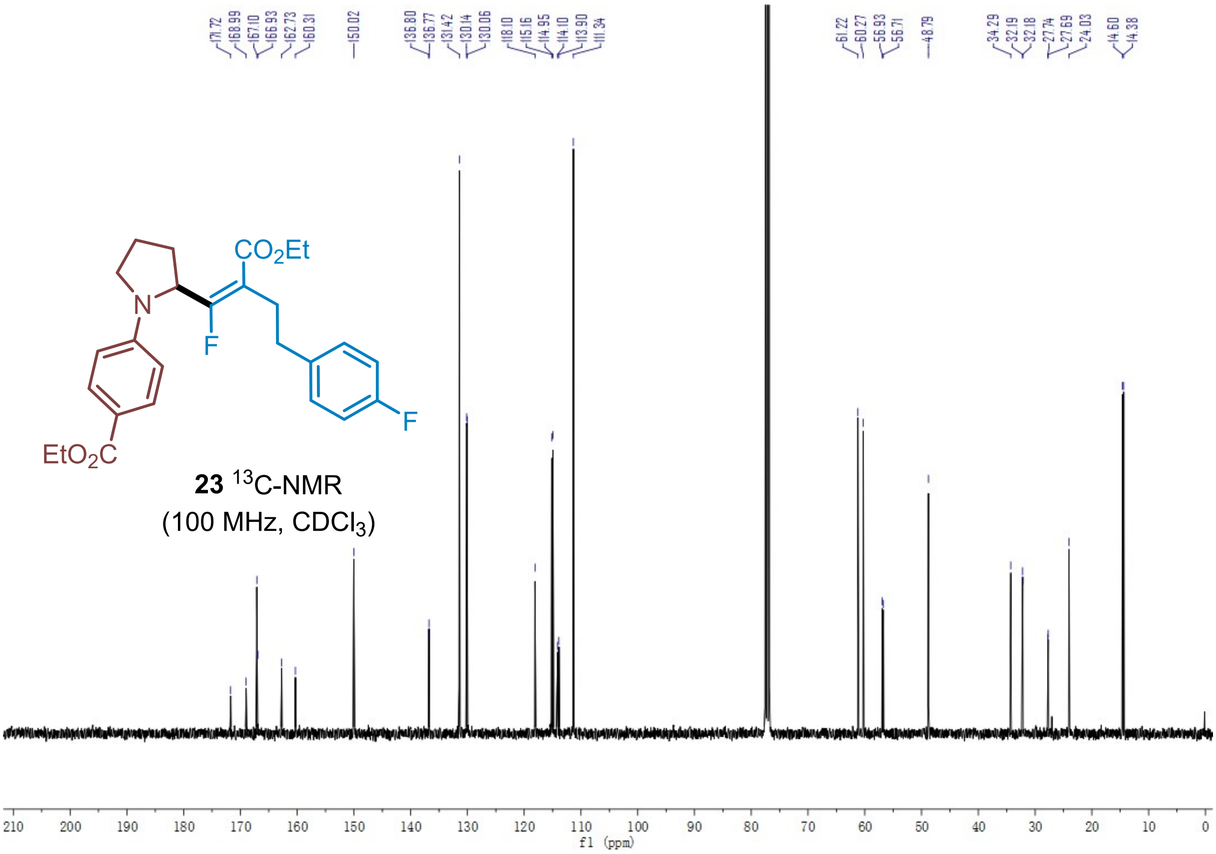
22 ^{13}C-NMR
(100 MHz, CDCl$_3$)



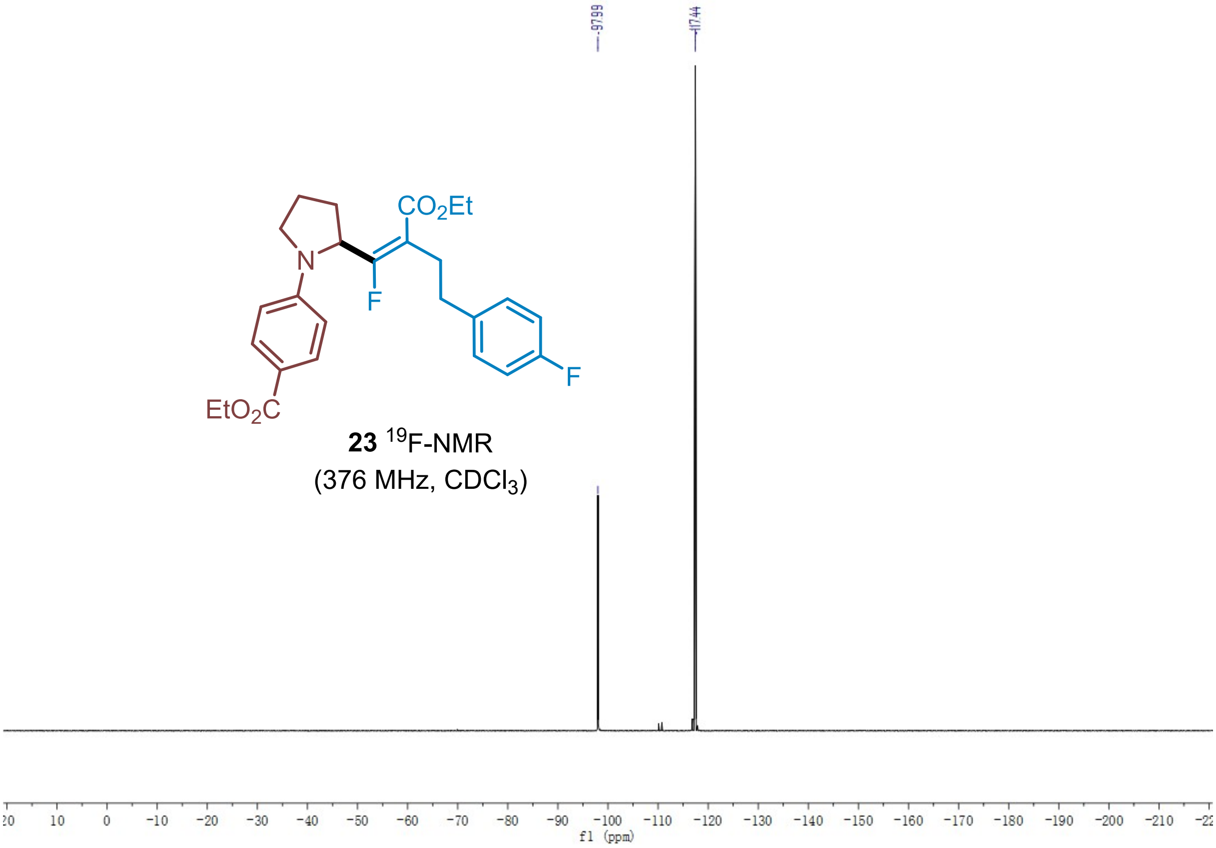
22 ^{19}F-NMR
(376 MHz, $CDCl_3$)



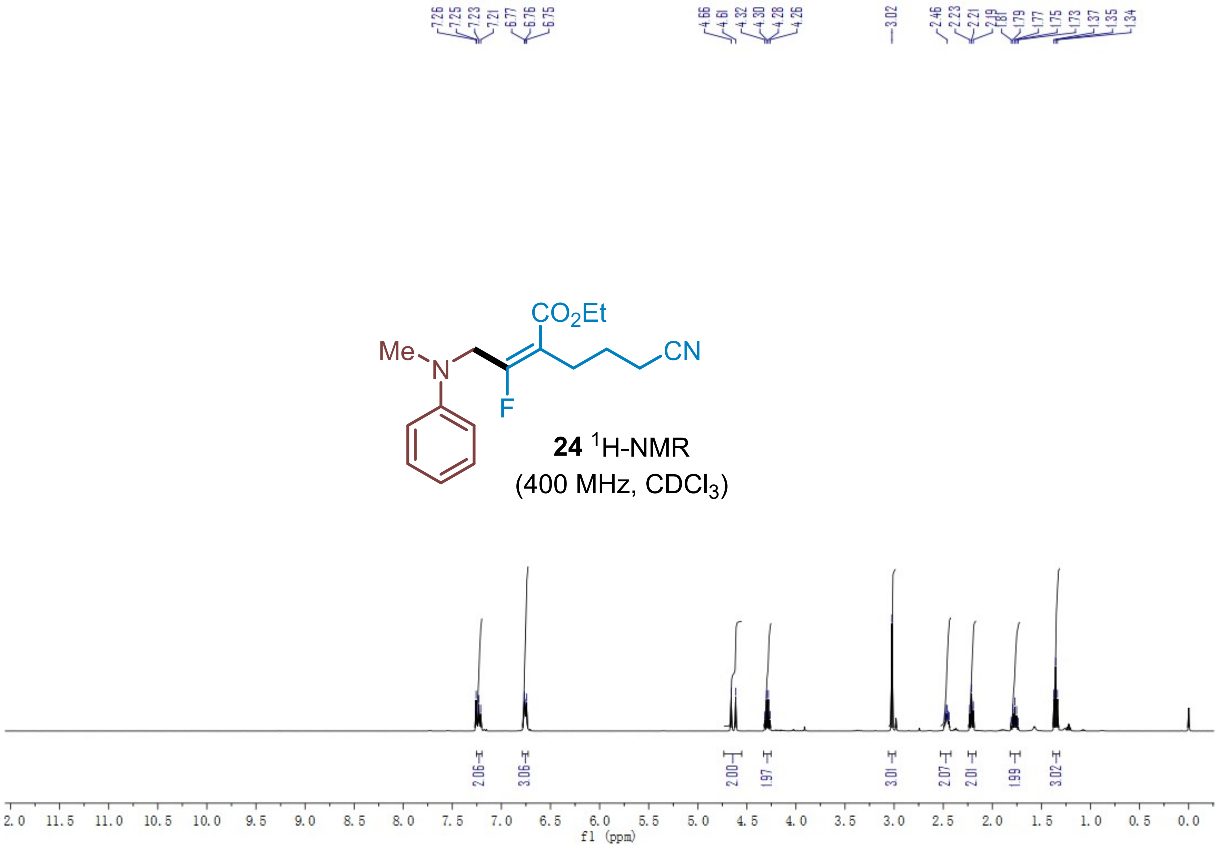
23 ^{1}H-NMR
(400 MHz, $CDCl_3$)



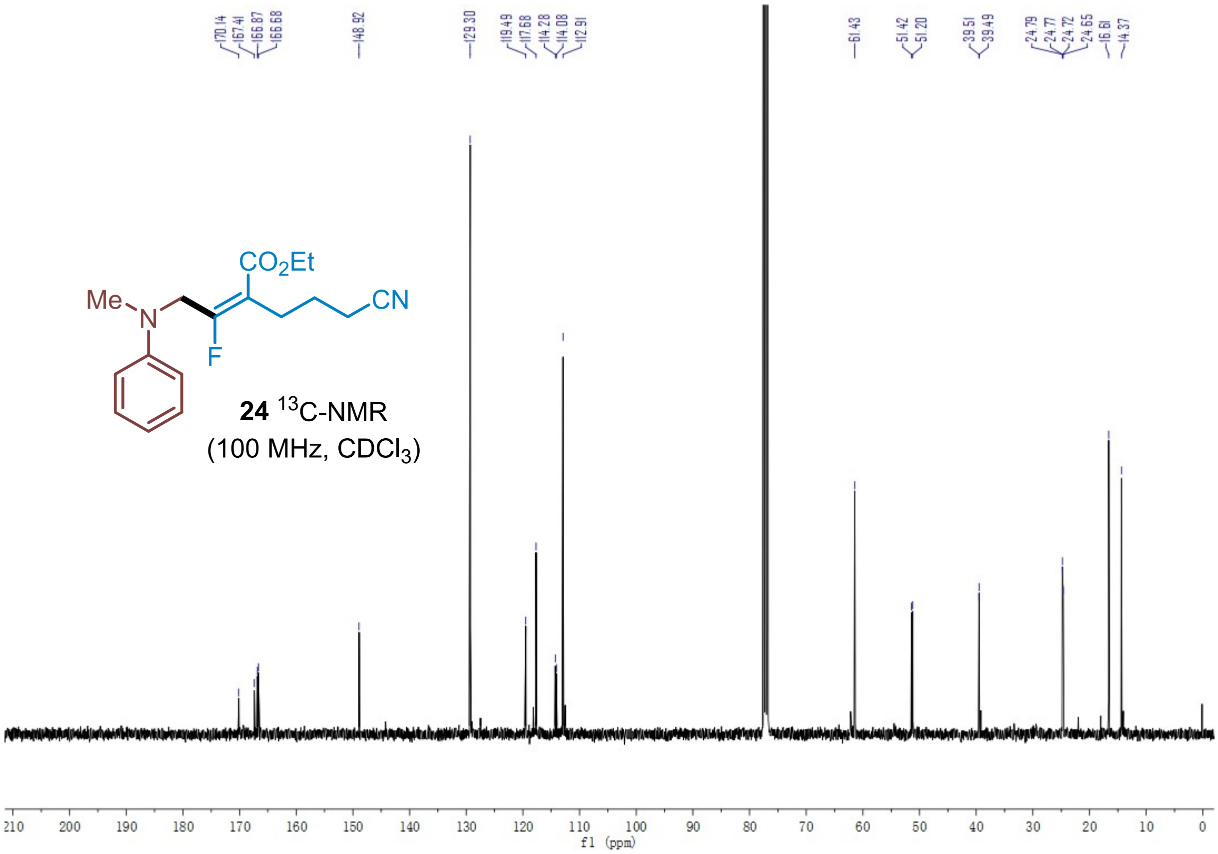
23 ^{13}C-NMR (100 MHz, $CDCl_3$)



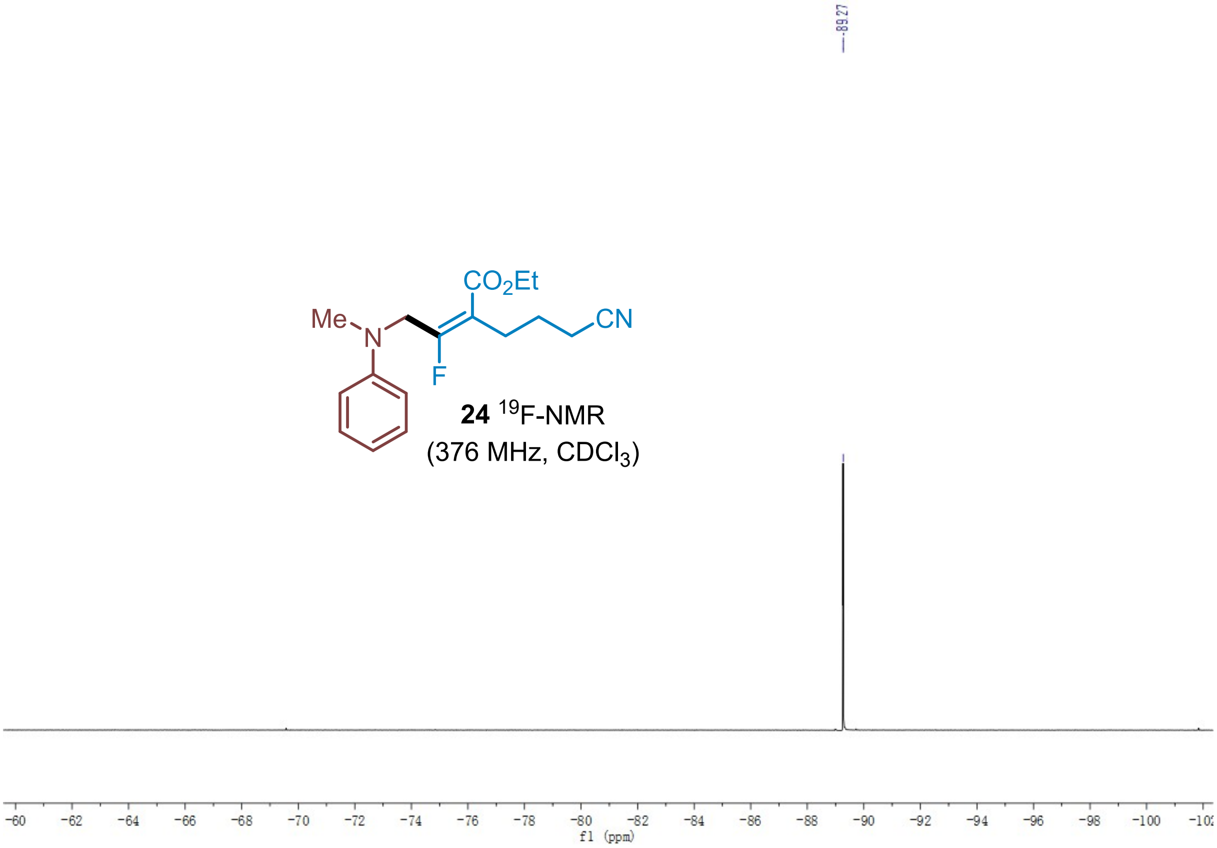
23 ^{19}F-NMR (376 MHz, $CDCl_3$)



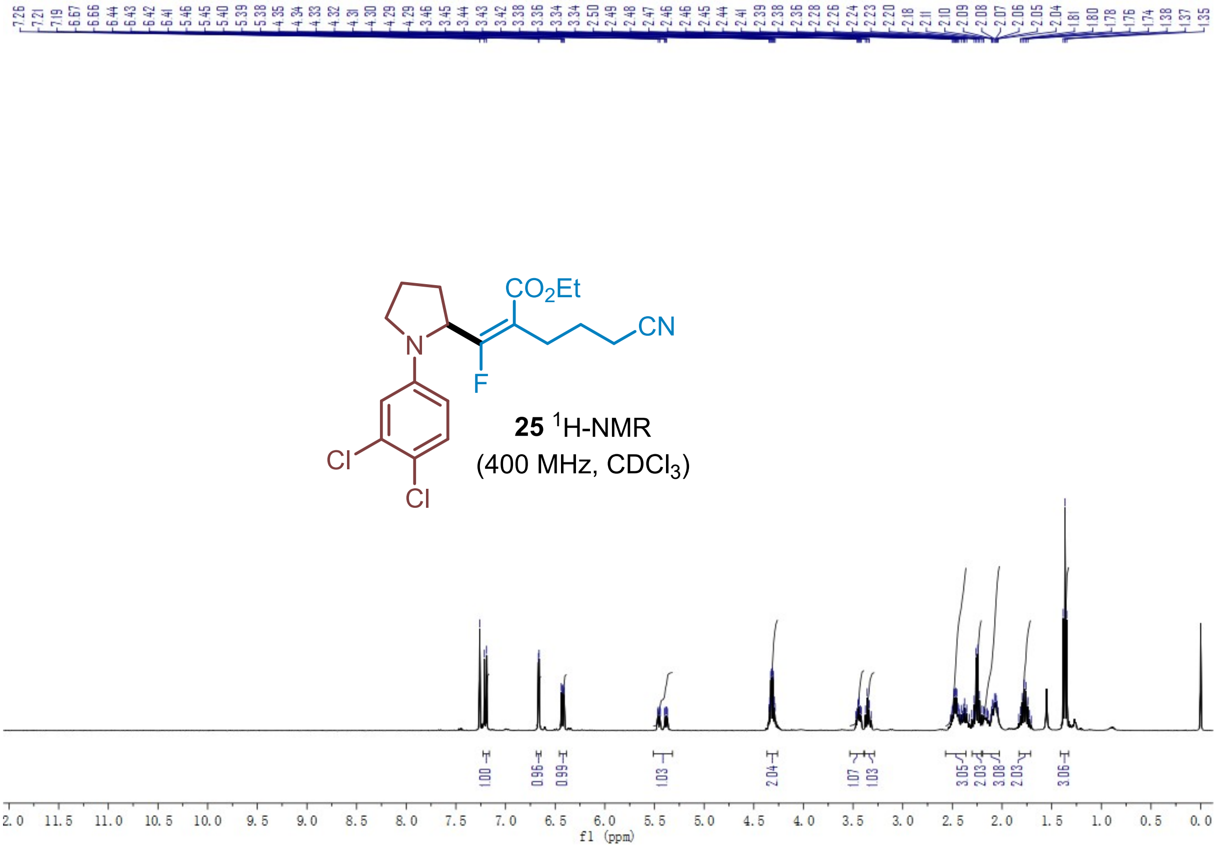
24 ^{1}H-NMR (400 MHz, $CDCl_3$)



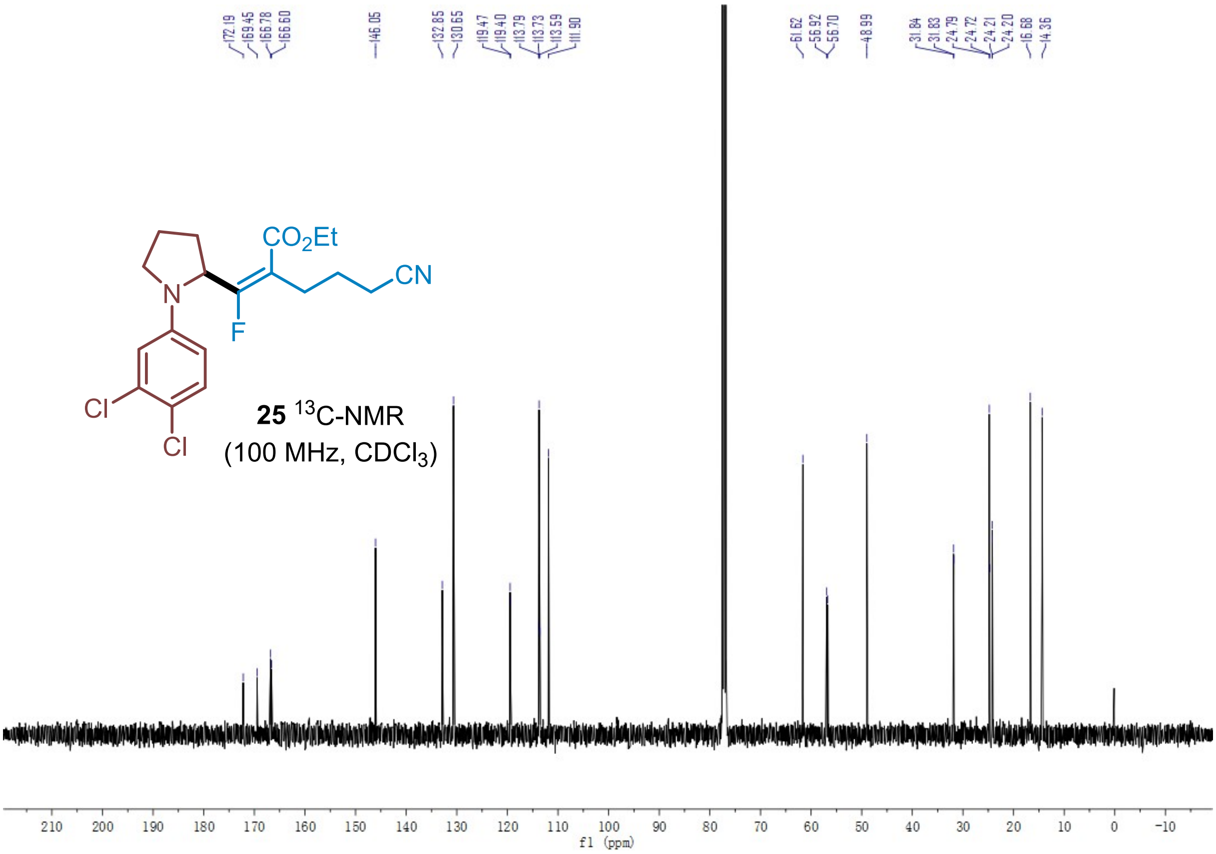
24 ^{13}C-NMR (100 MHz, $CDCl_3$)



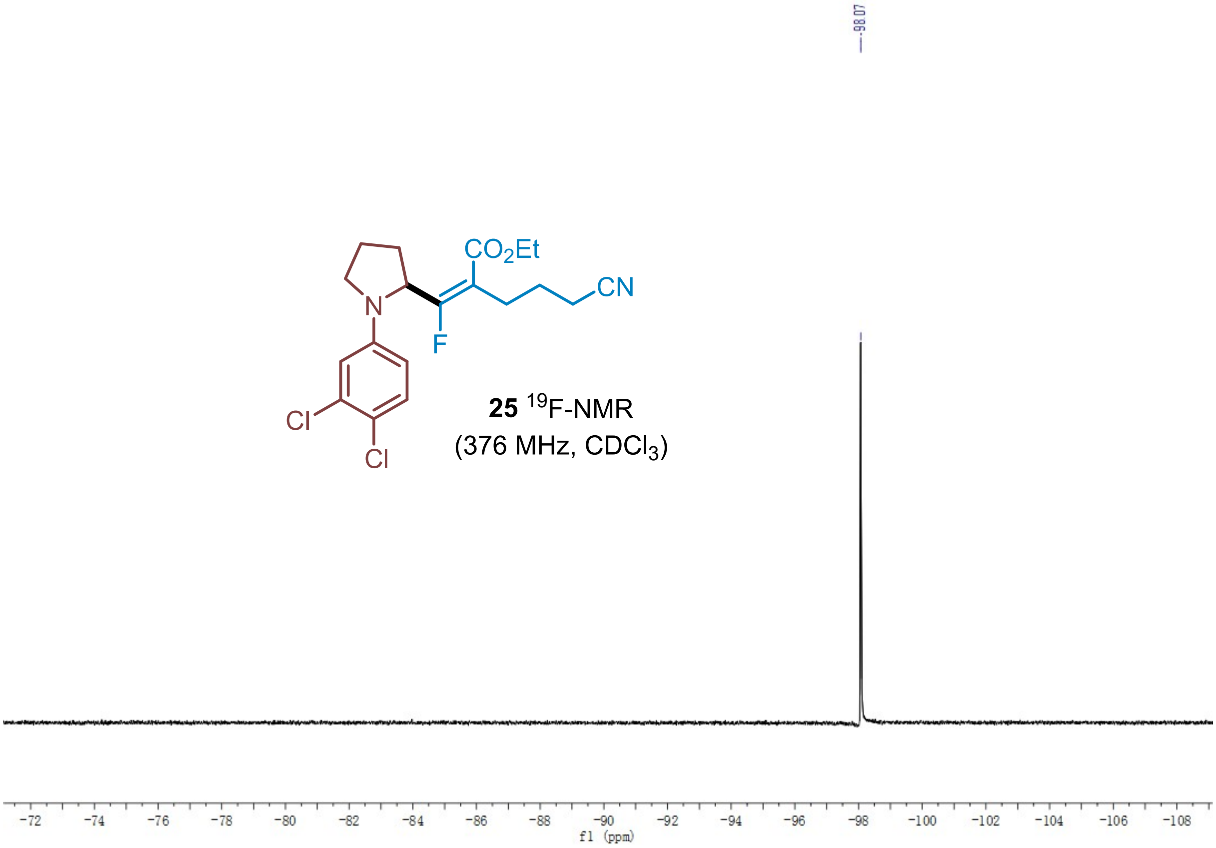
24 ^{19}F-NMR
(376 MHz, $CDCl_3$)



25 ^{1}H-NMR
(400 MHz, $CDCl_3$)



25 ^{13}C-NMR (100 MHz, $CDCl_3$)



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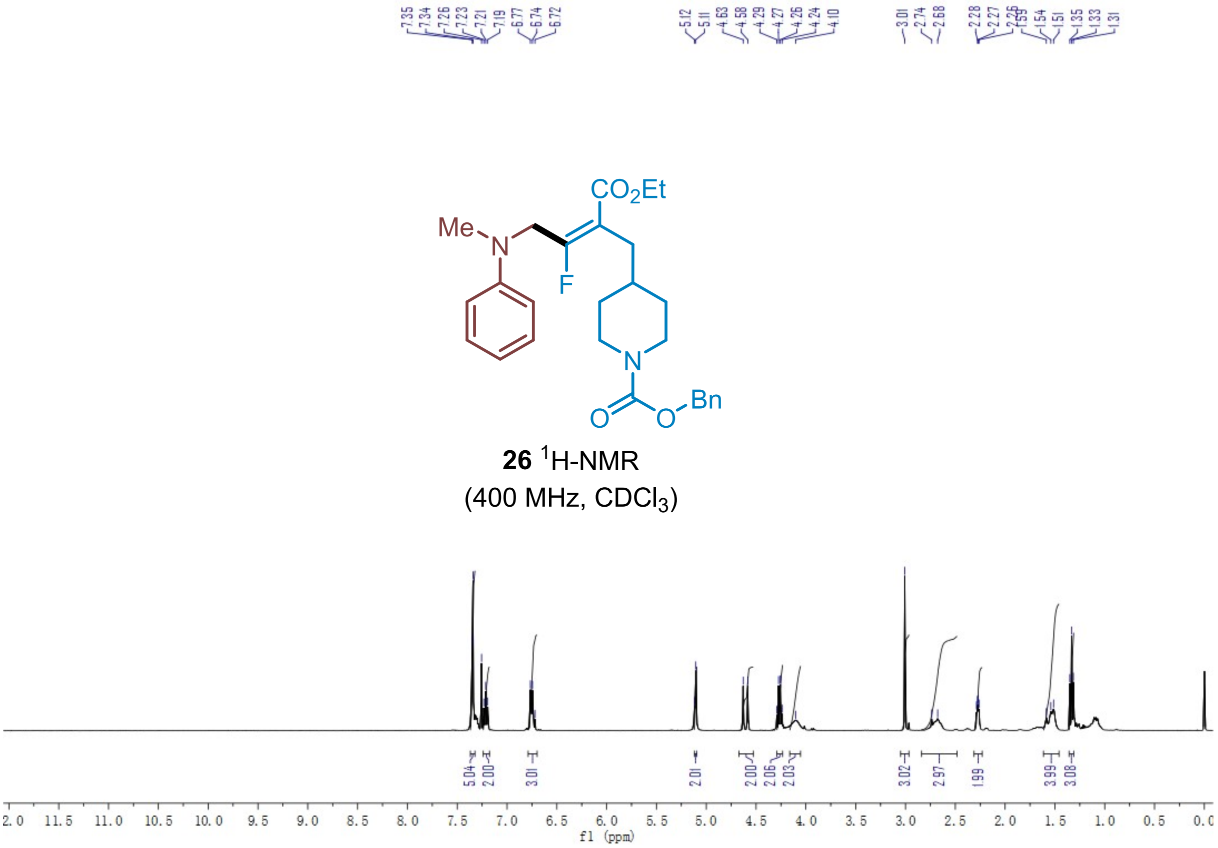
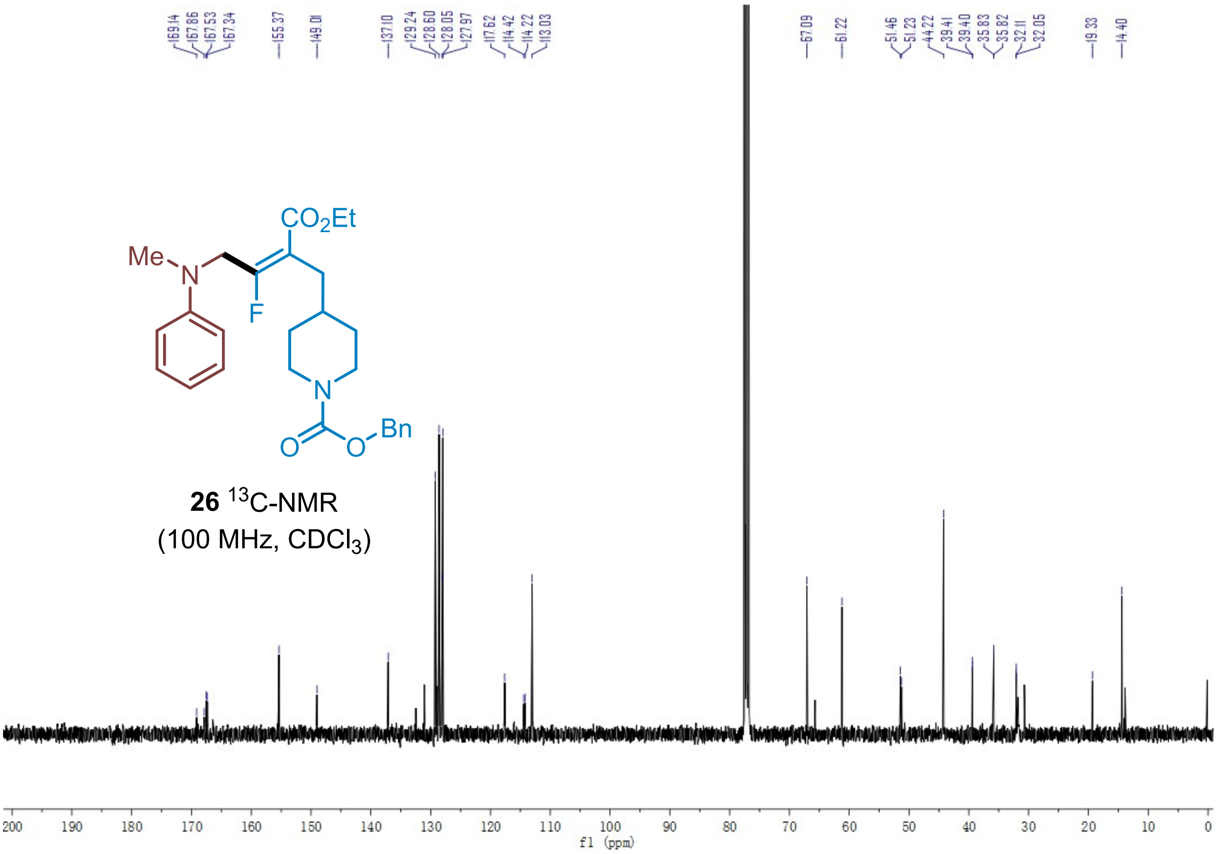
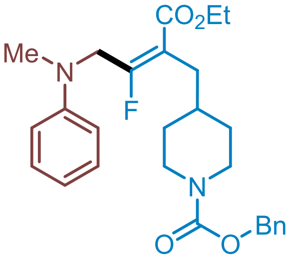


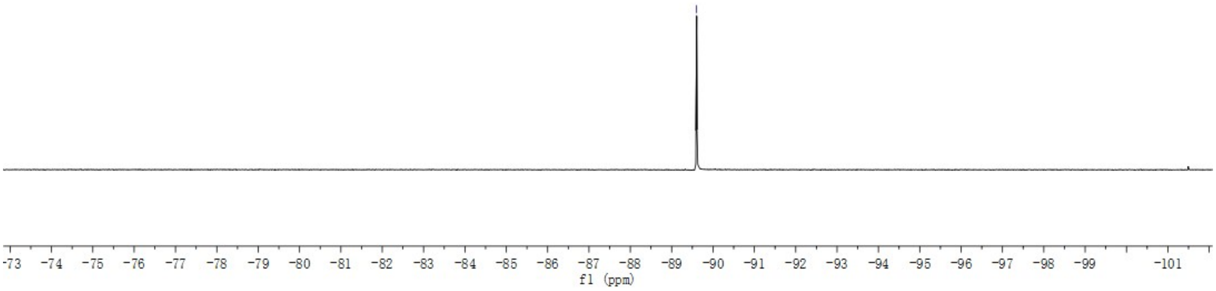
26 ^{1}H-NMR
(400 MHz, $CDCl_3$)

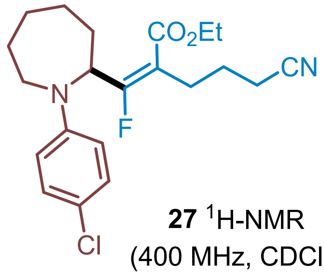


26 ^{13}C-NMR
(100 MHz, $CDCl_3$)

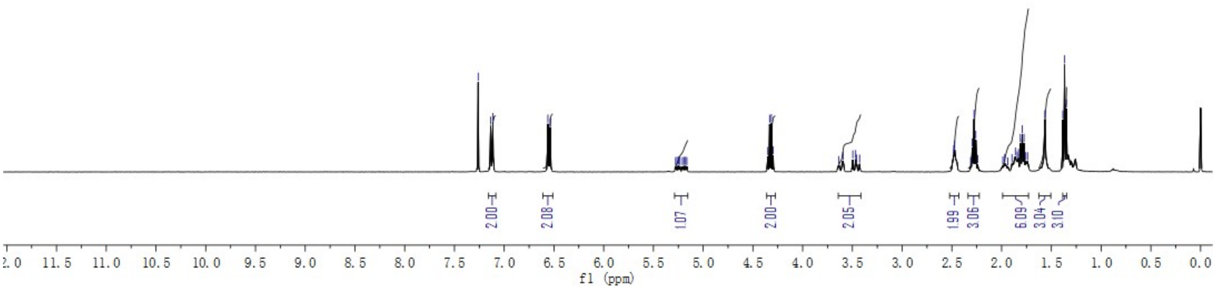


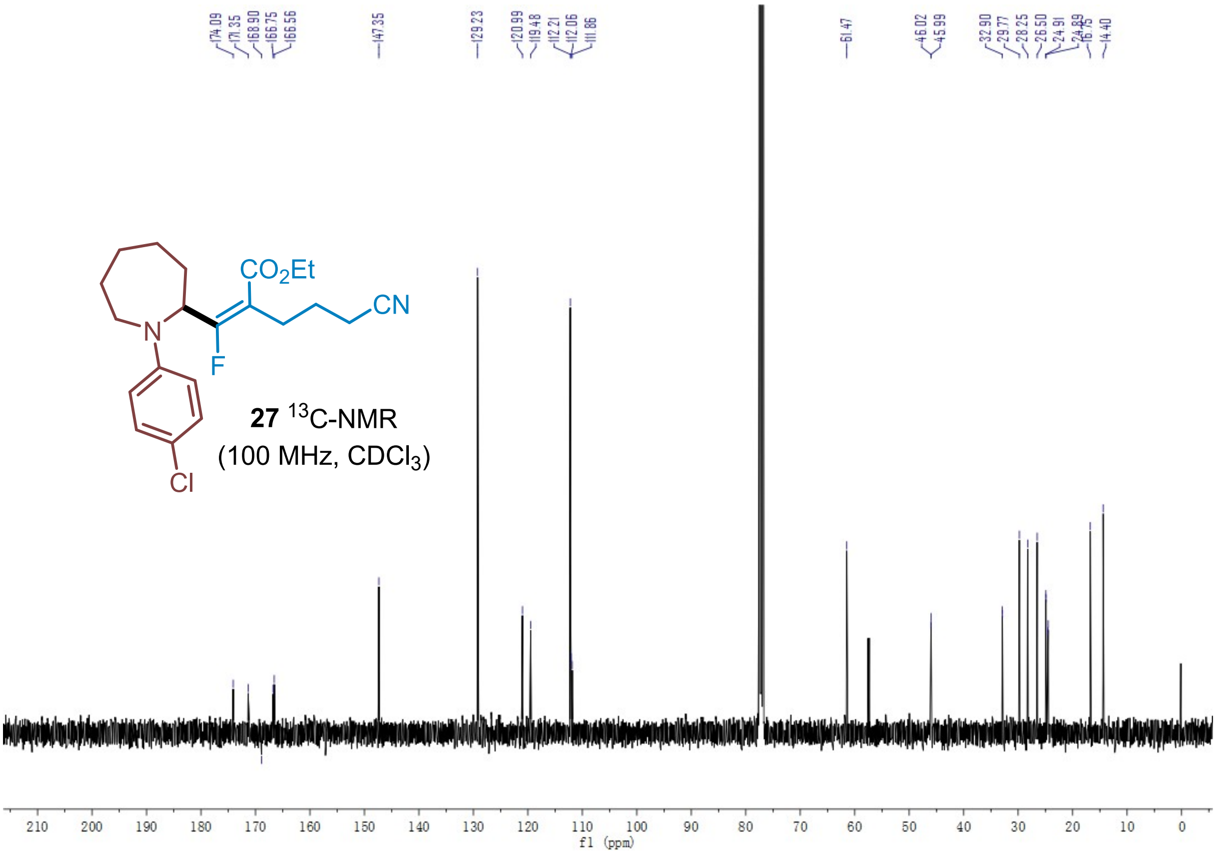
26 ^{19}F-NMR
(376 MHz, $CDCl_3$)

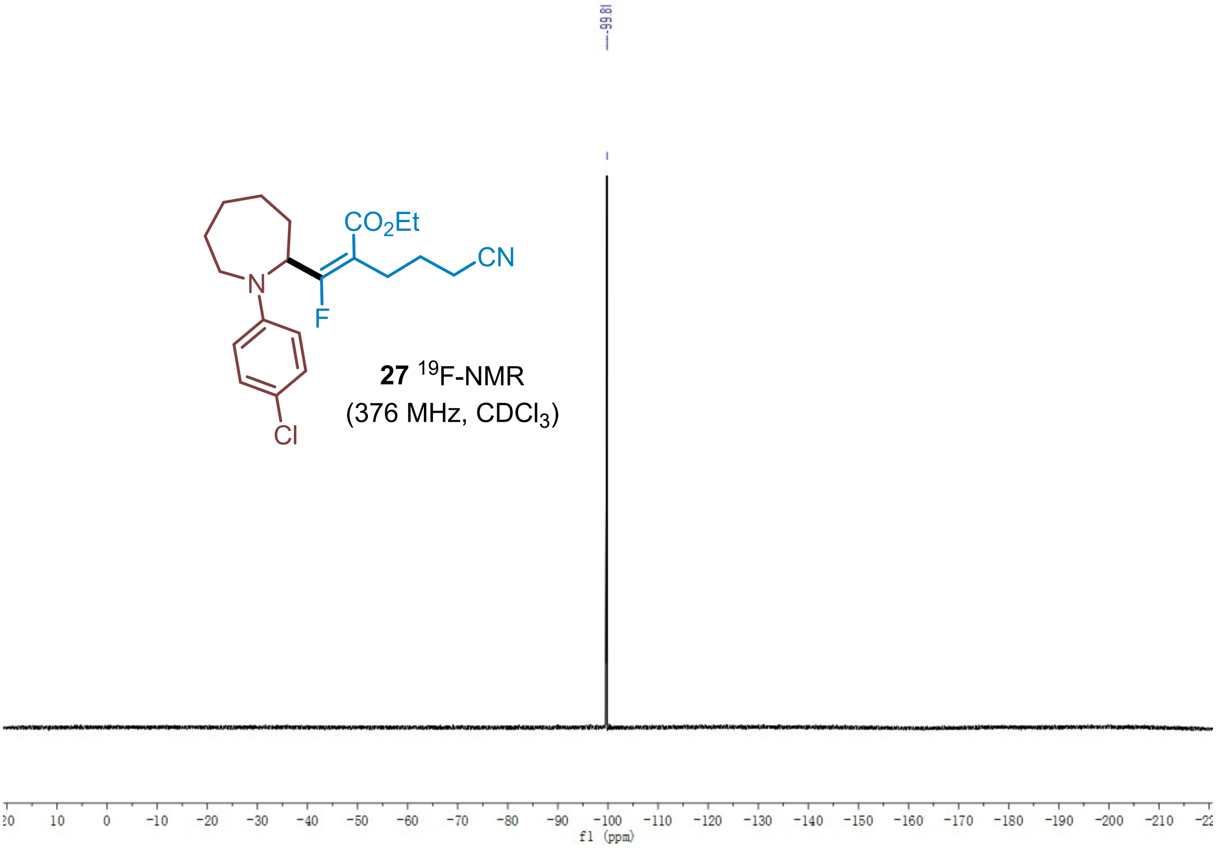


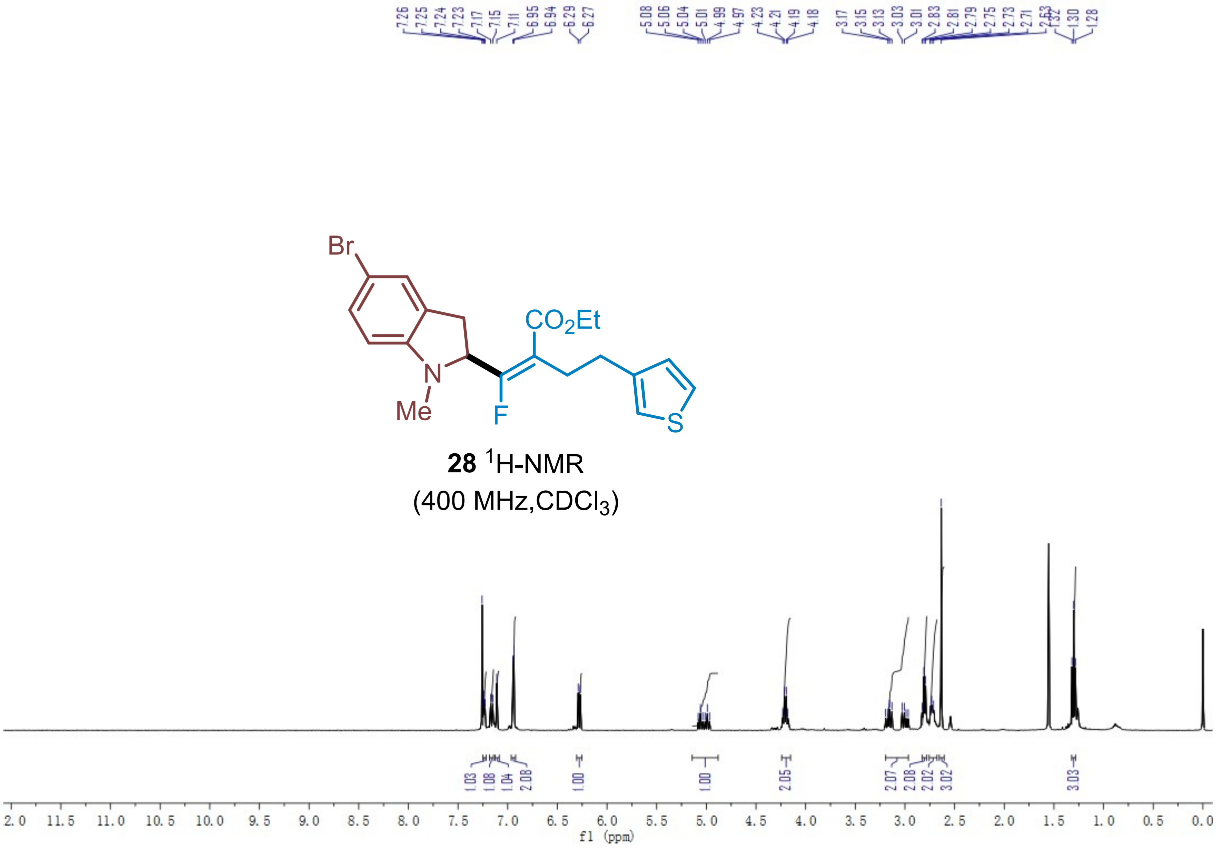


27 ^{1}H-NMR
(400 MHz, $CDCl_3$)

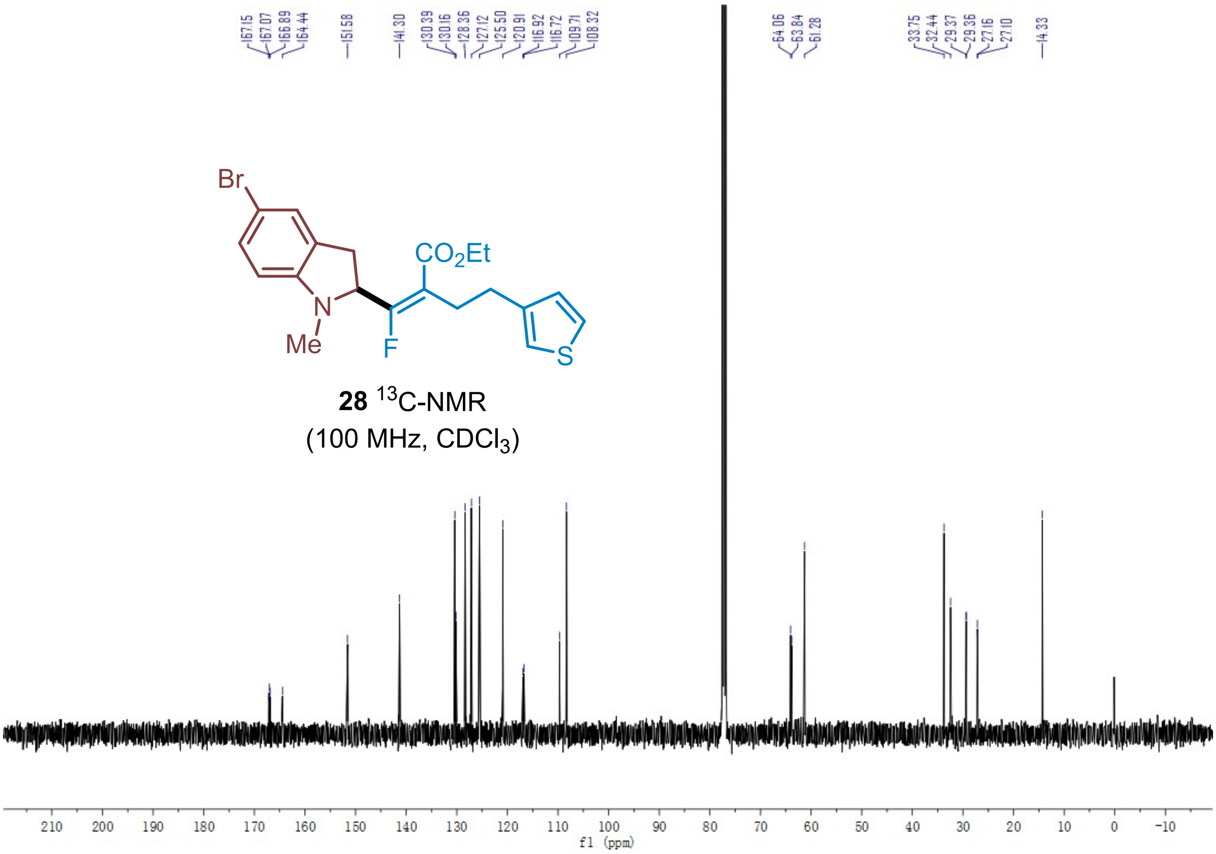



27 ^{13}C-NMR (100 MHz, $CDCl_3$)

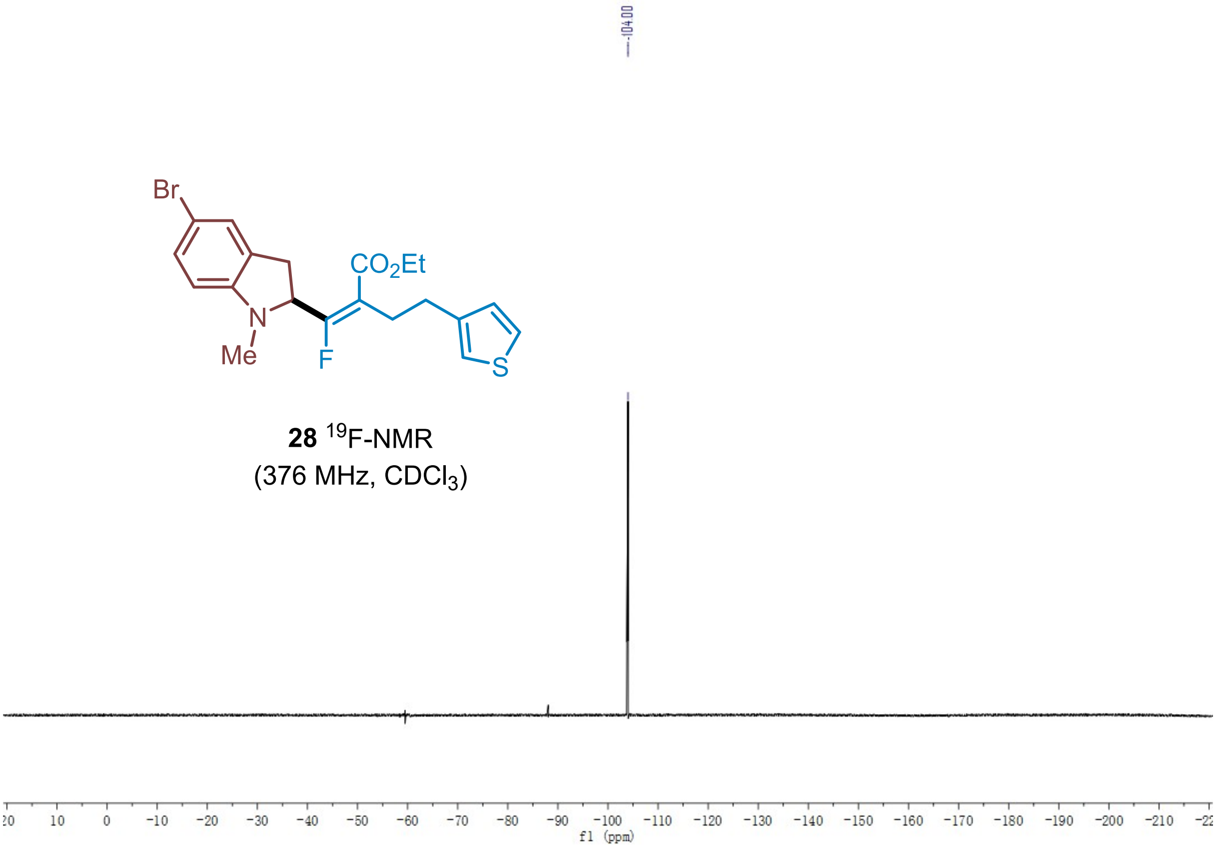

27 ^{19}F-NMR (376 MHz, $CDCl_3$)



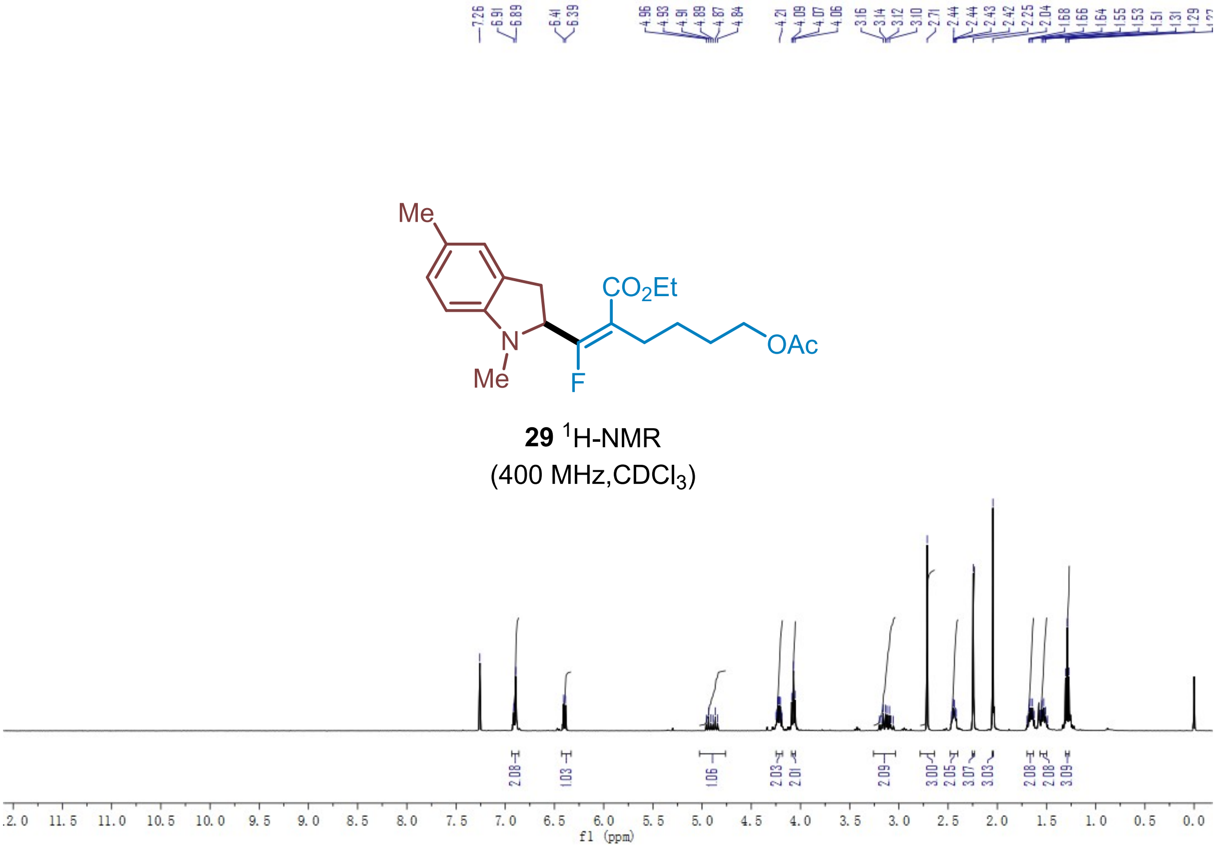
28 ^{1}H-NMR
(400 MHz,CDCl$_3$)



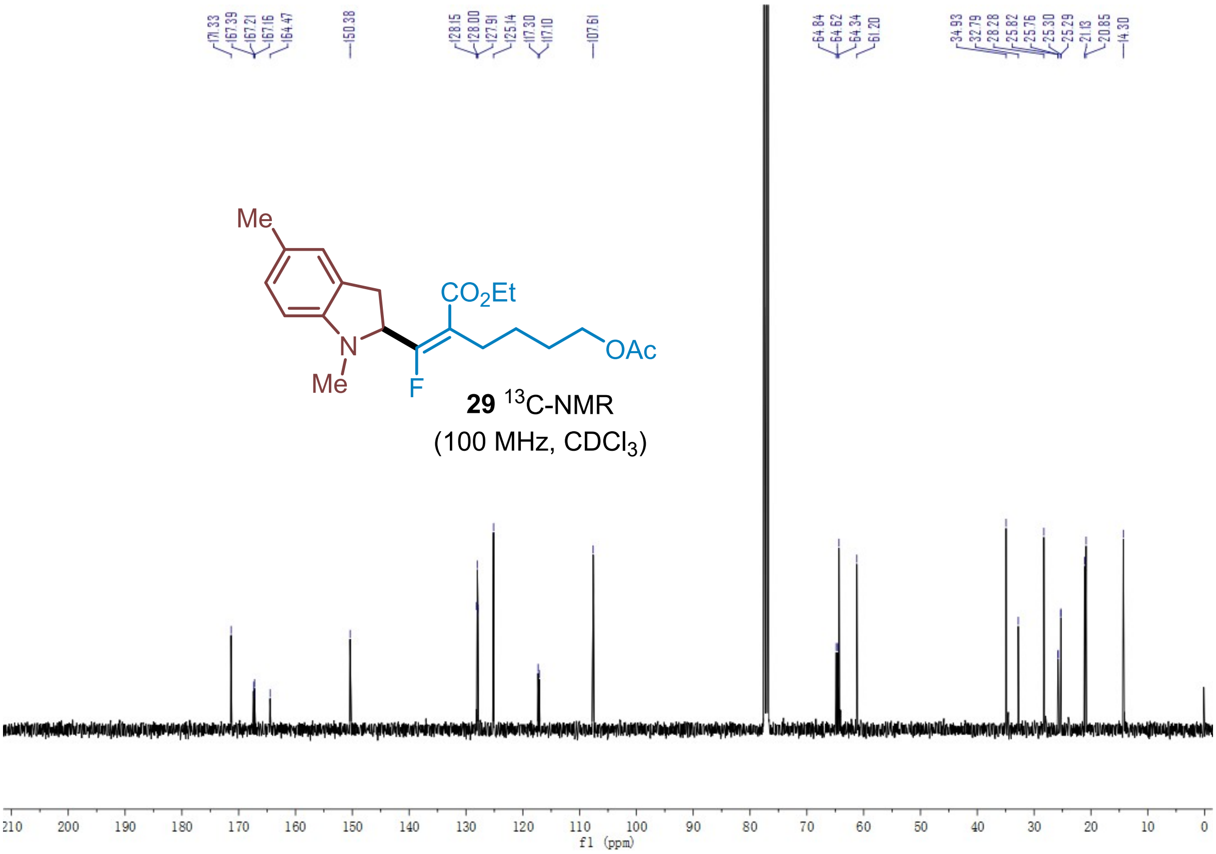
28 ^{13}C-NMR
(100 MHz, CDCl$_3$)



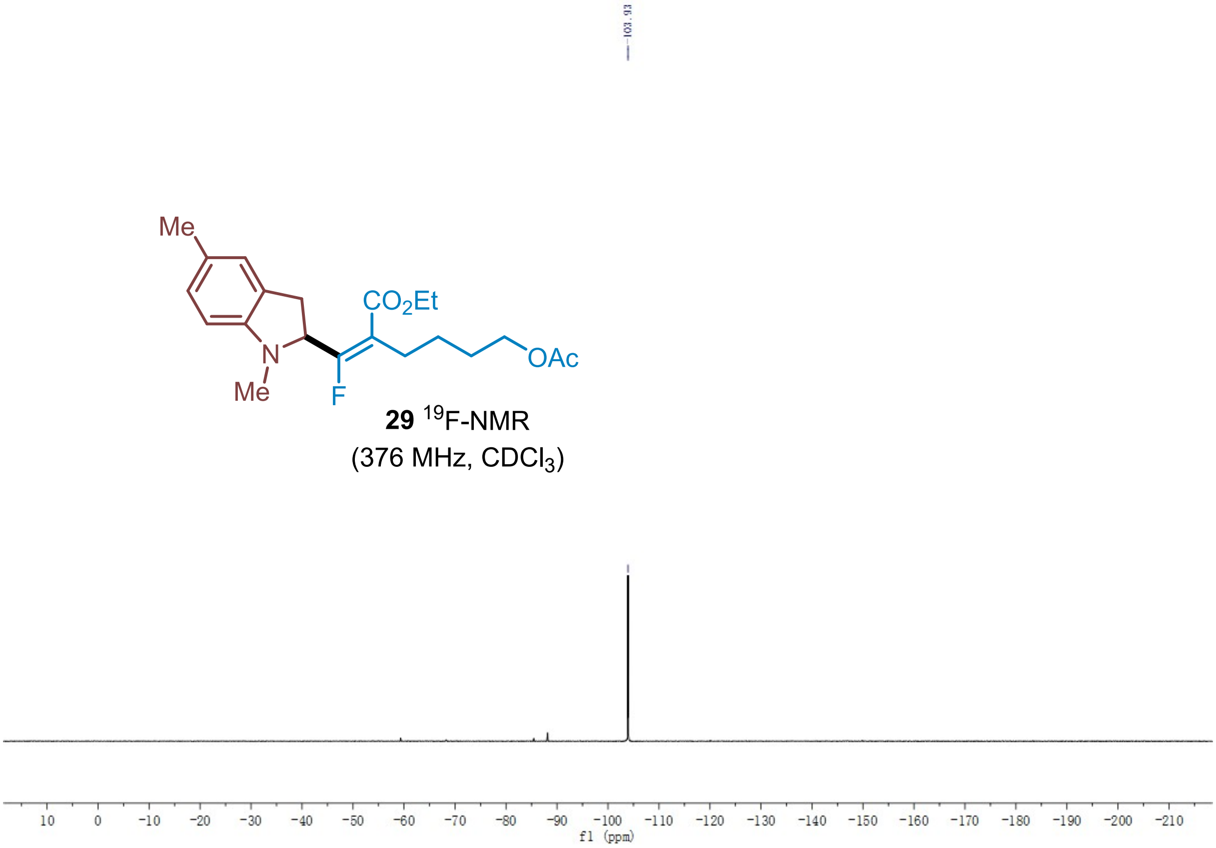
28 ^{19}F-NMR
(376 MHz, $CDCl_3$)



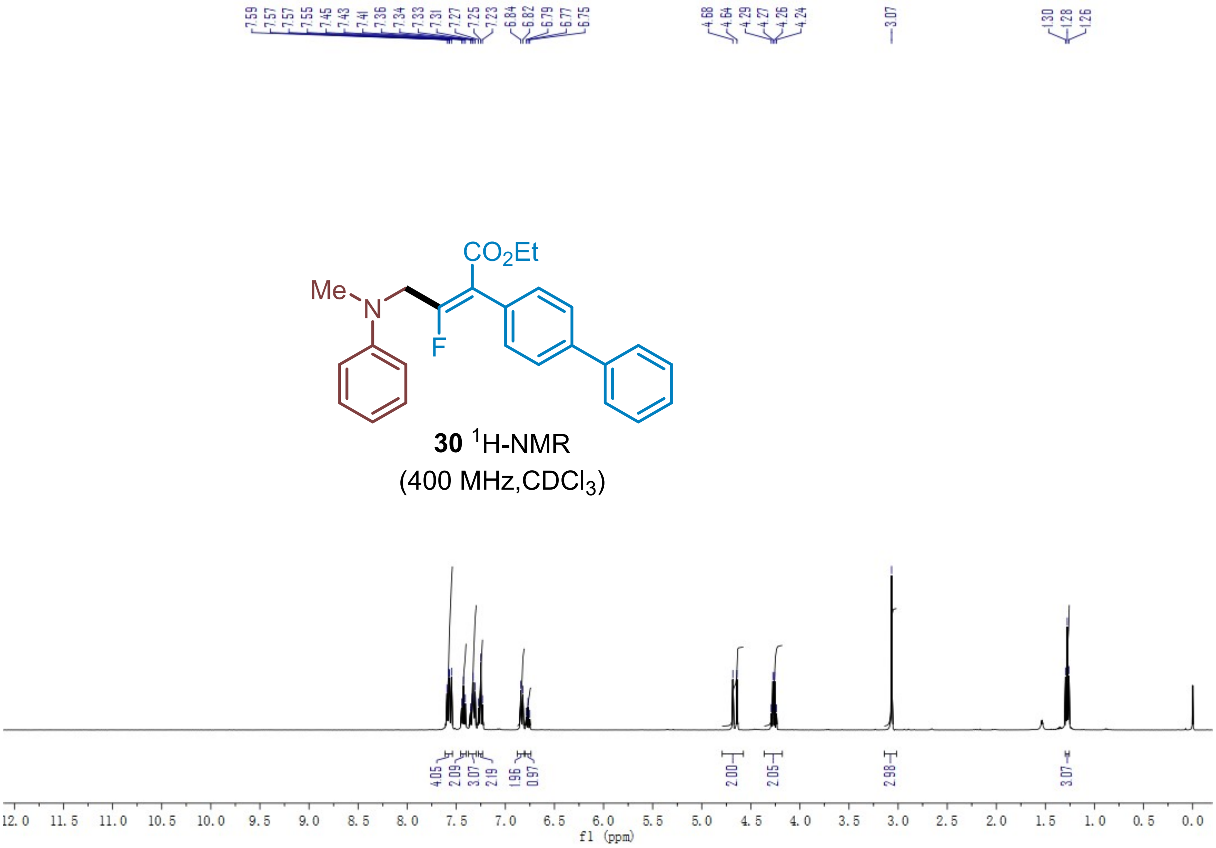
29 ^{1}H-NMR
(400 MHz,$CDCl_3$)



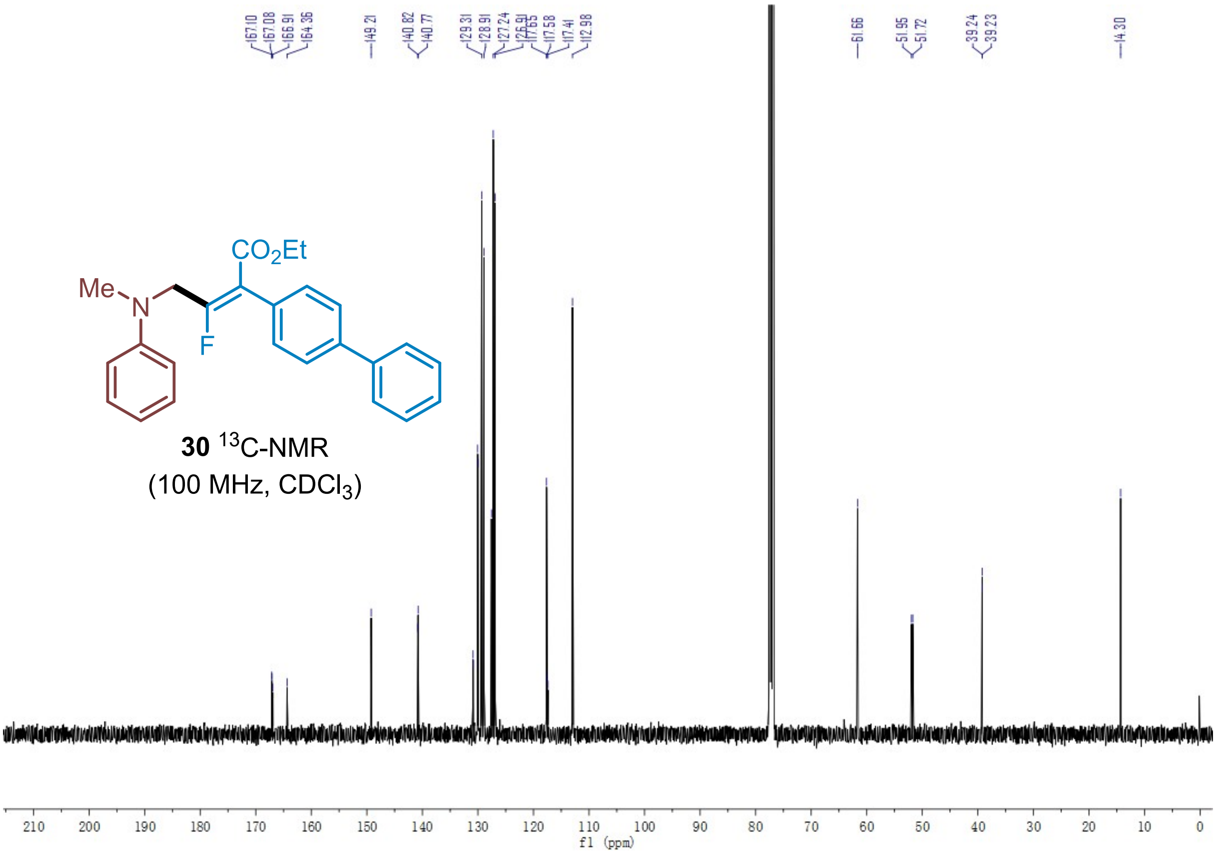
29 ^{13}C-NMR
(100 MHz, $CDCl_3$)



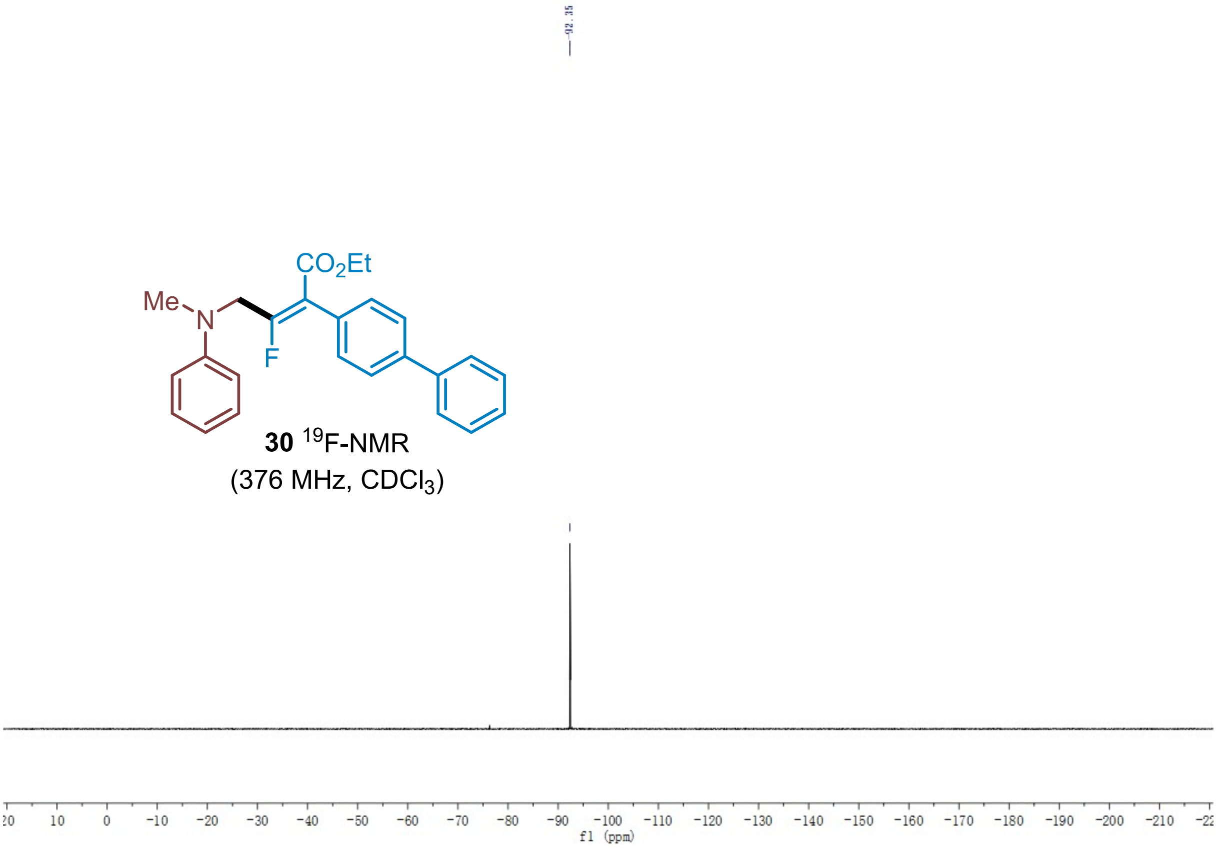
29 ^{19}F-NMR
(376 MHz, $CDCl_3$)



30 ^{1}H-NMR
(400 MHz,CDCl$_3$)

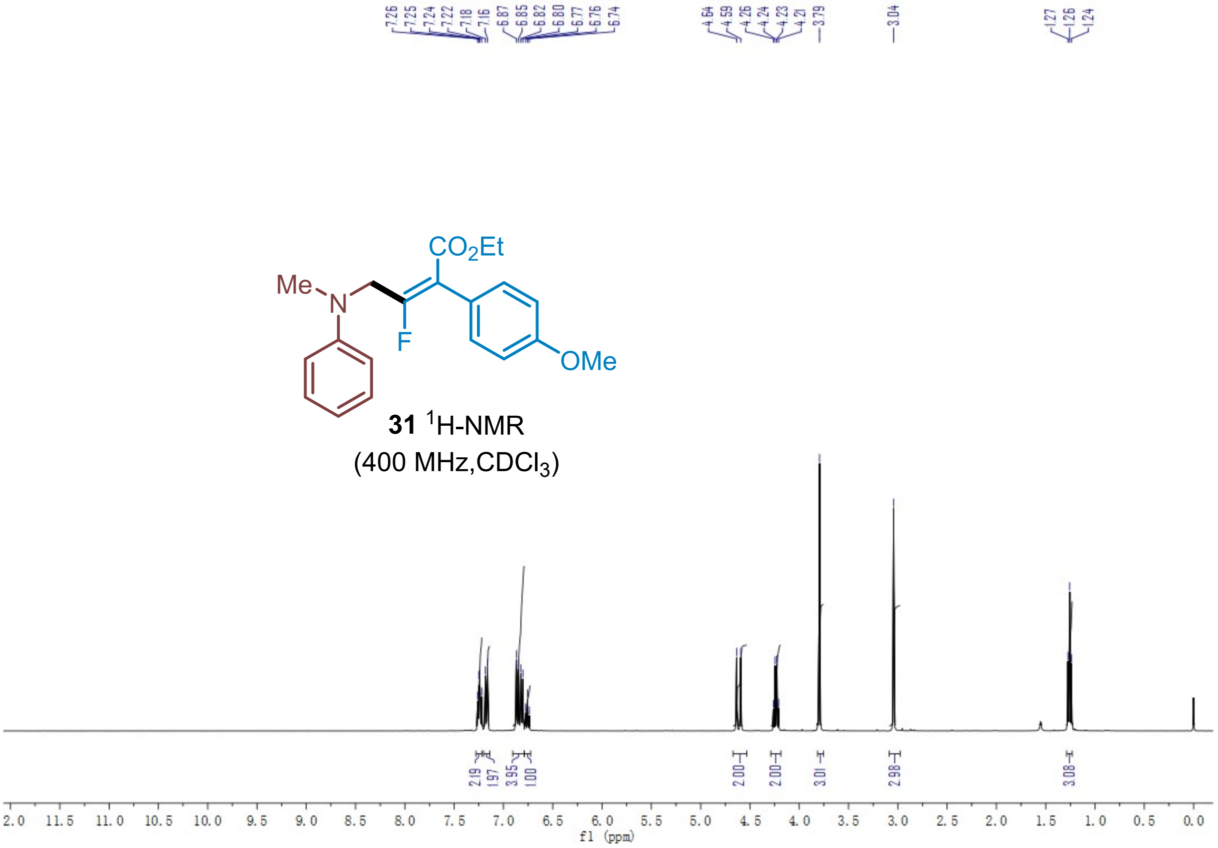


30 ^{13}C-NMR
(100 MHz, CDCl$_3$)



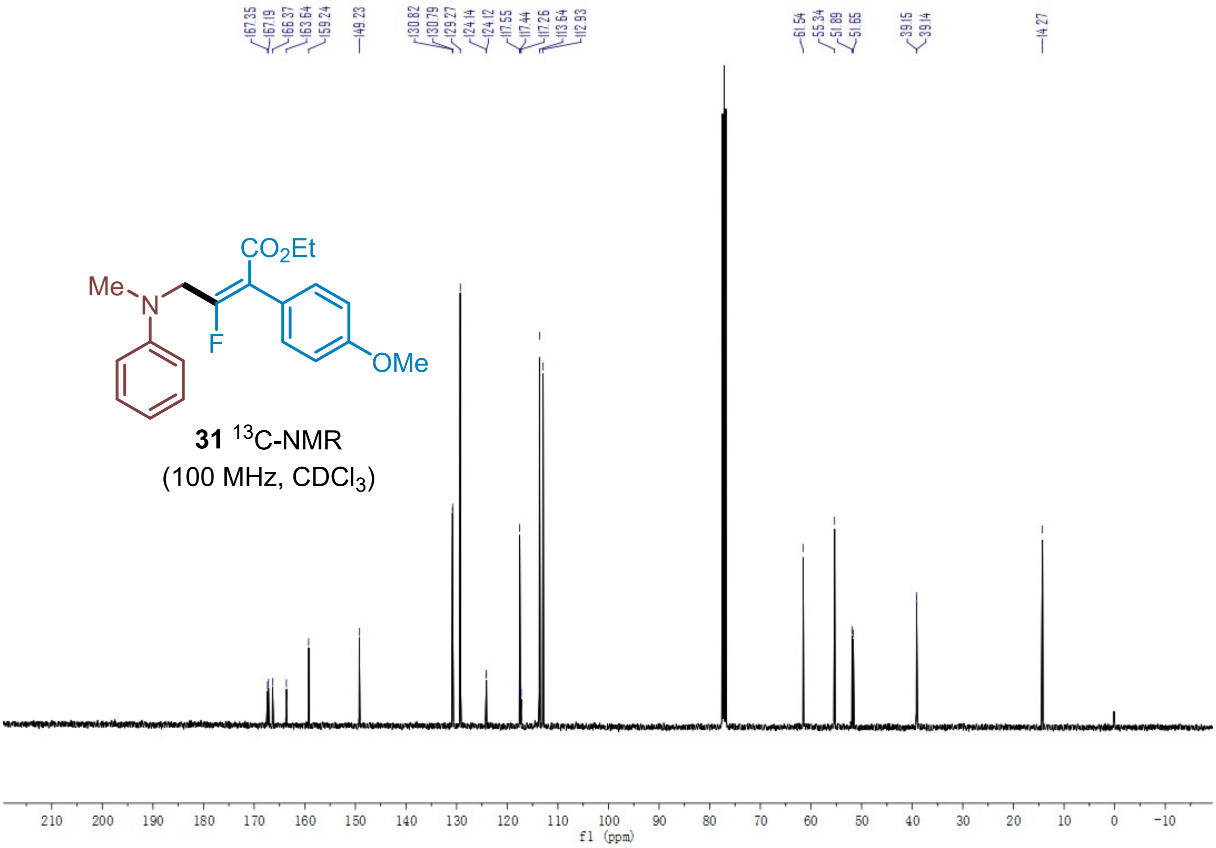
30 ^{19}F-NMR

(376 MHz, $CDCl_3$)

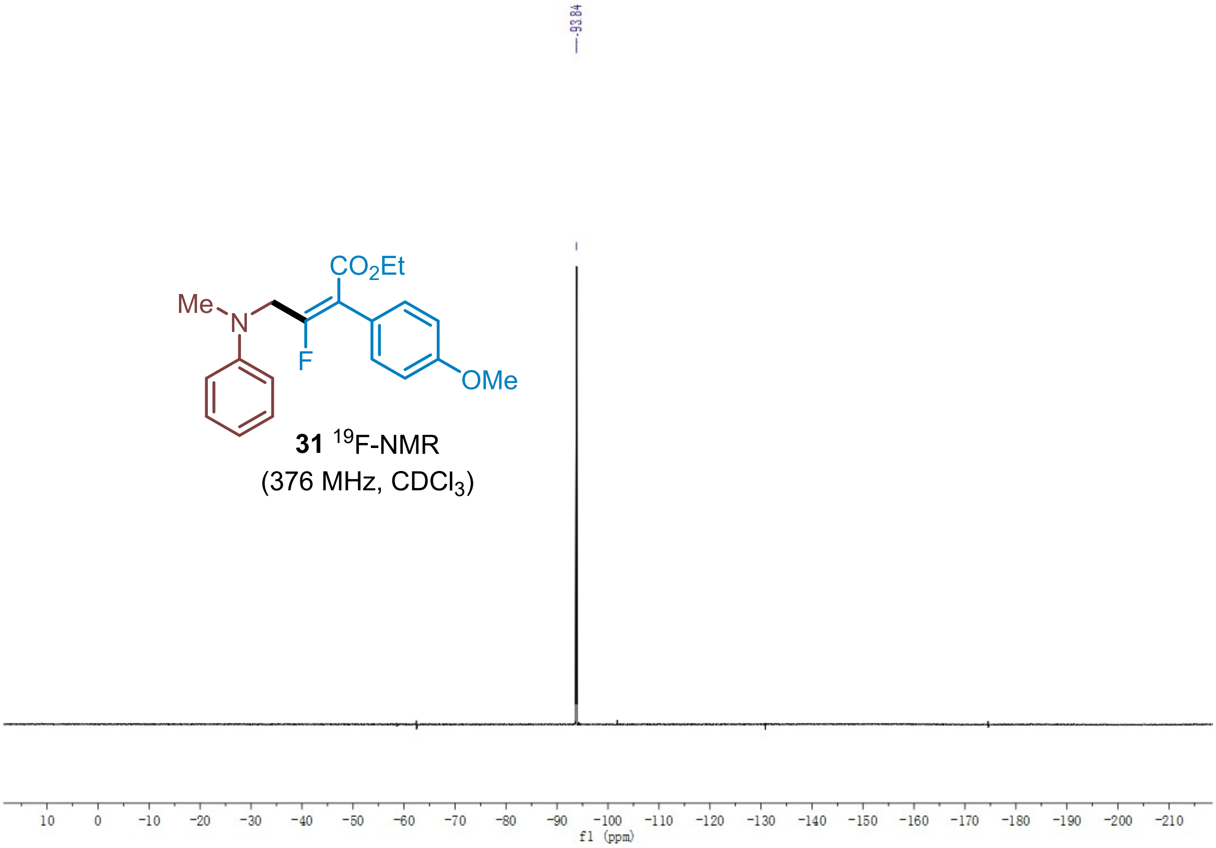


31 ^{1}H-NMR

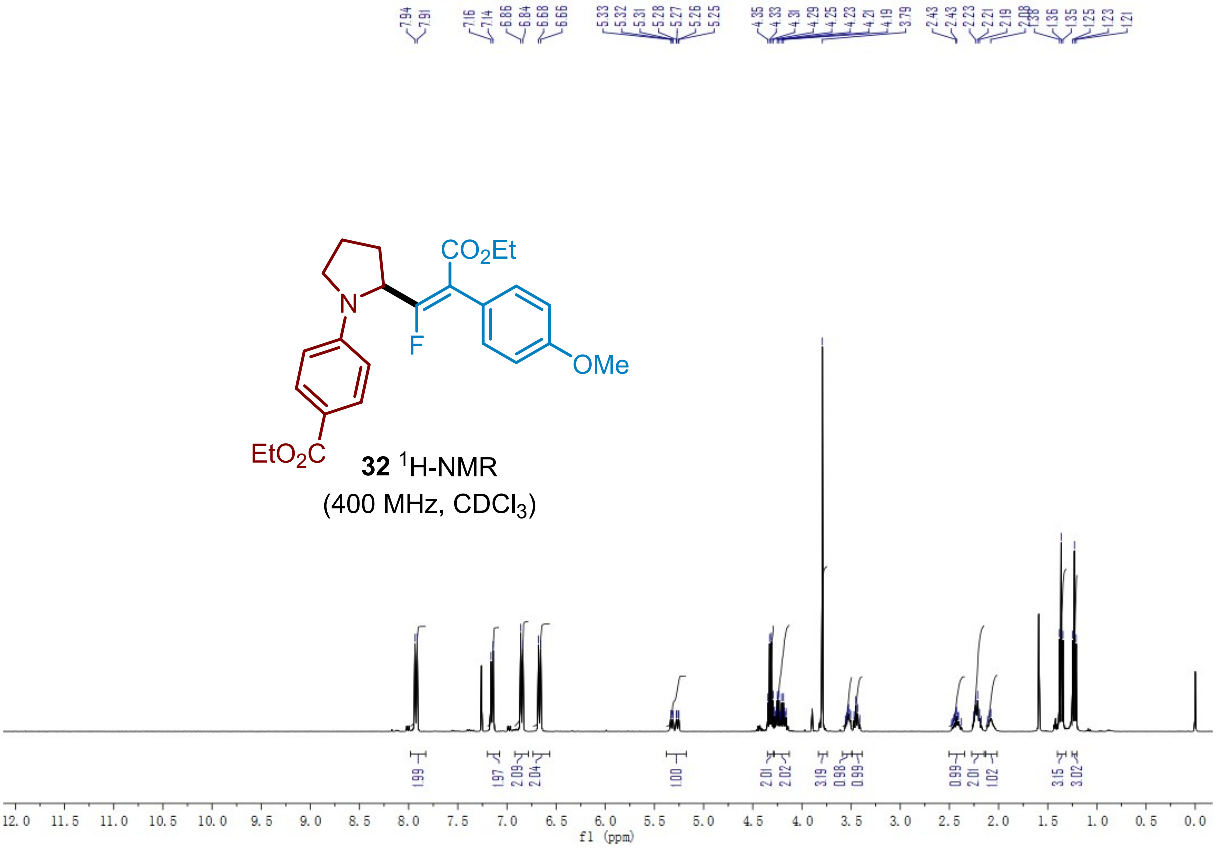
(400 MHz,$CDCl_3$)



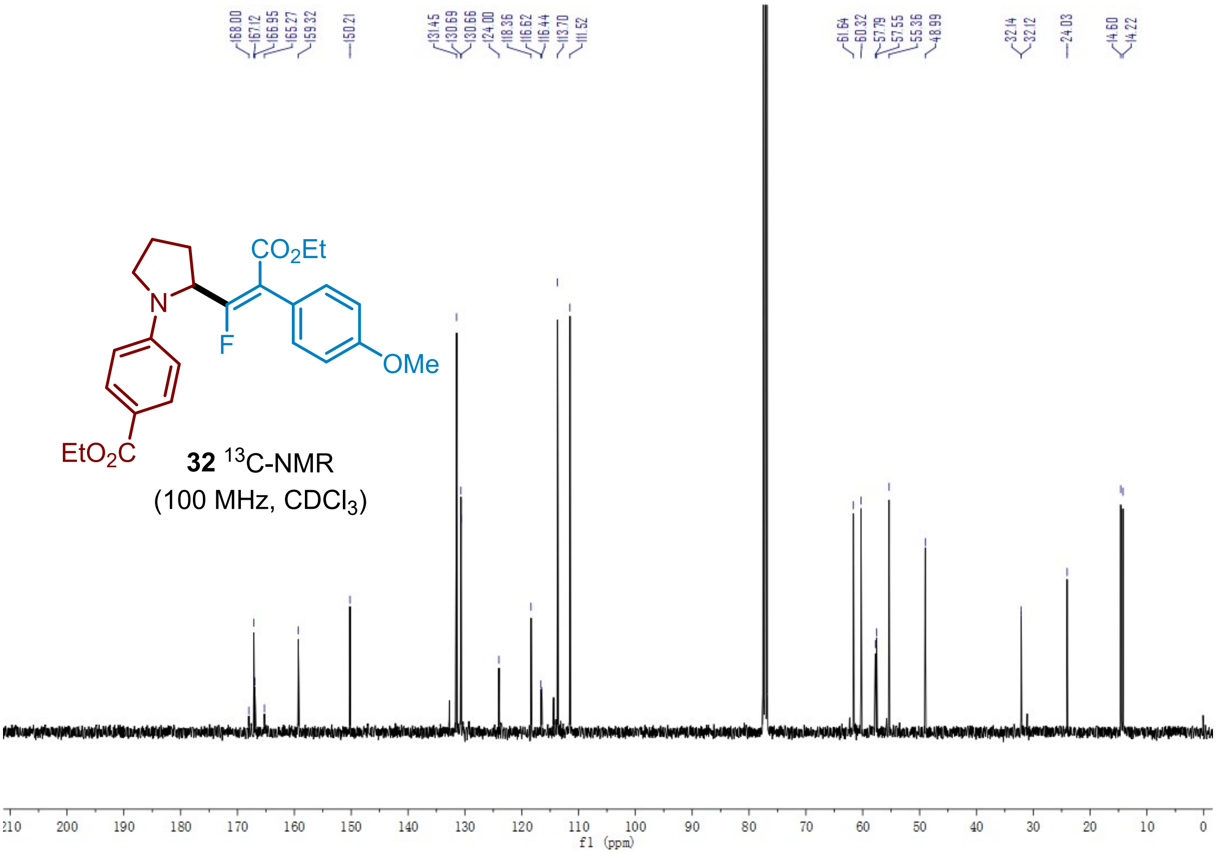
31 ^{13}C-NMR
(100 MHz, $CDCl_3$)



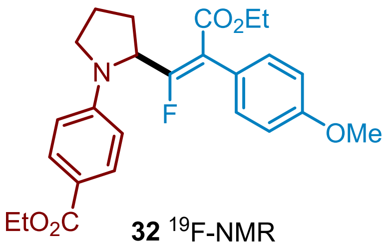
31 ^{19}F-NMR
(376 MHz, $CDCl_3$)



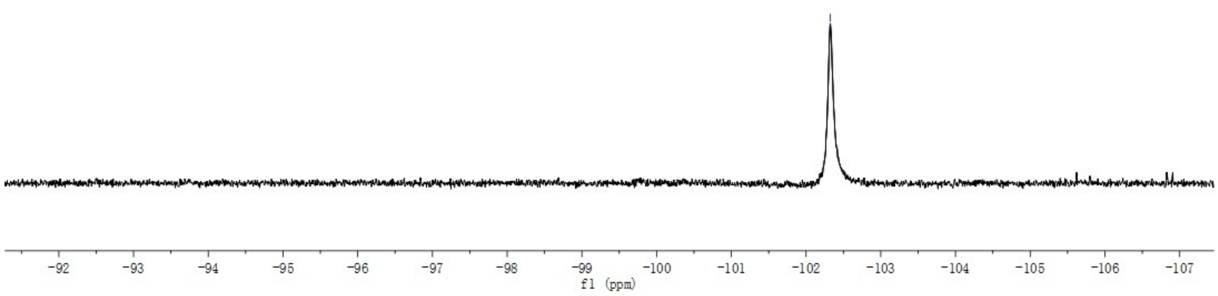
32 ^{1}H-NMR
(400 MHz, $CDCl_3$)

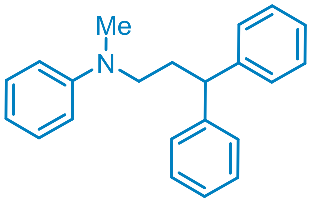


32 ^{13}C-NMR
(100 MHz, $CDCl_3$)

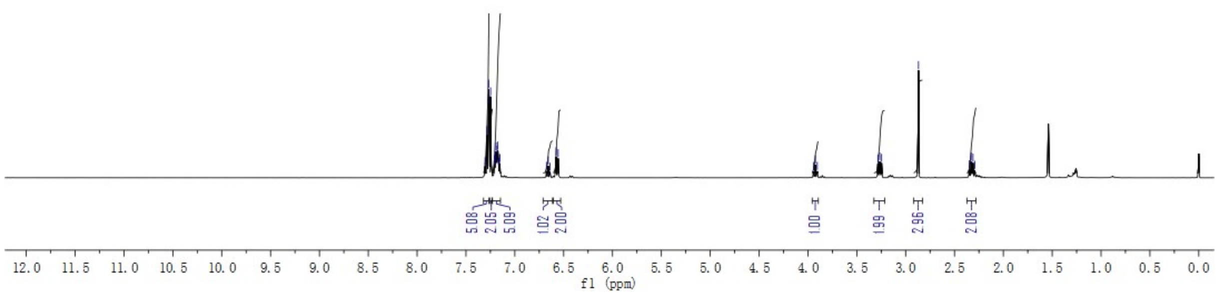


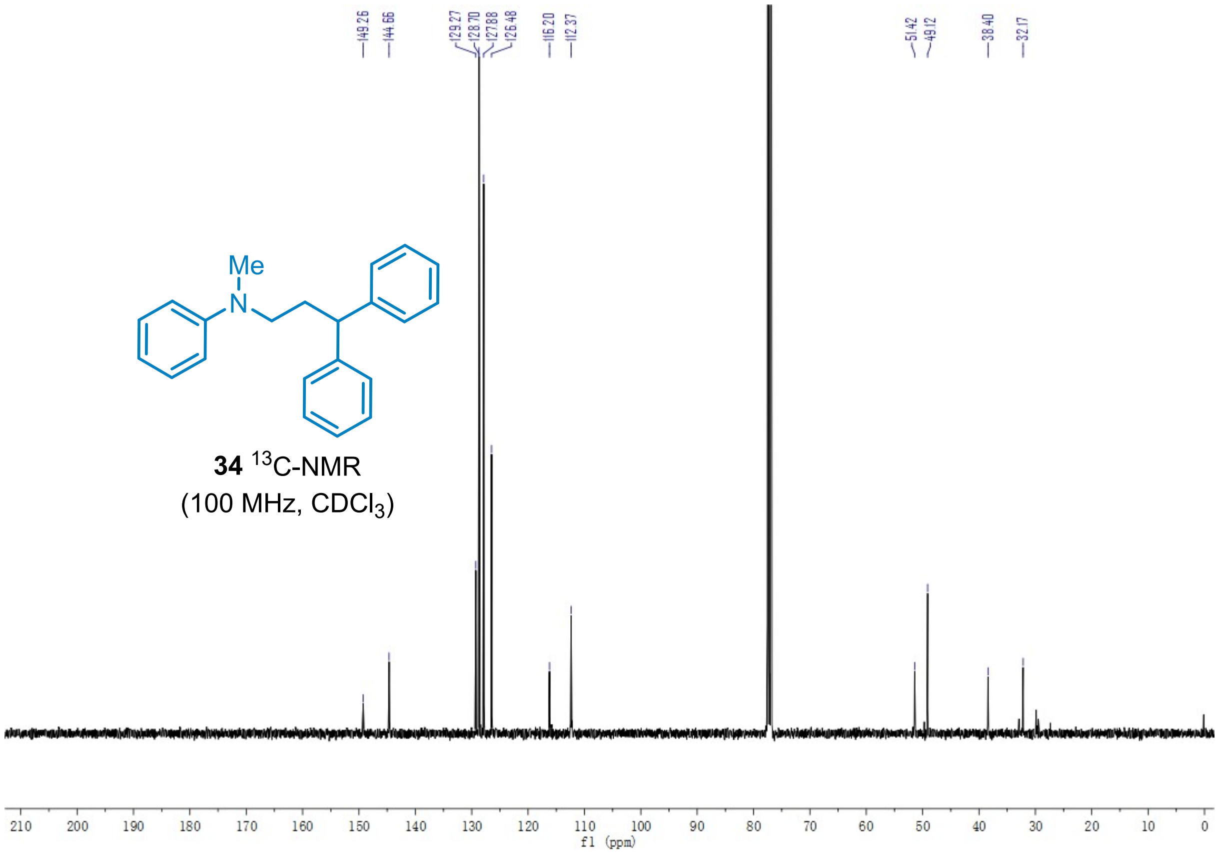
32 ^{19}F-NMR
(376 MHz, $CDCl_3$)



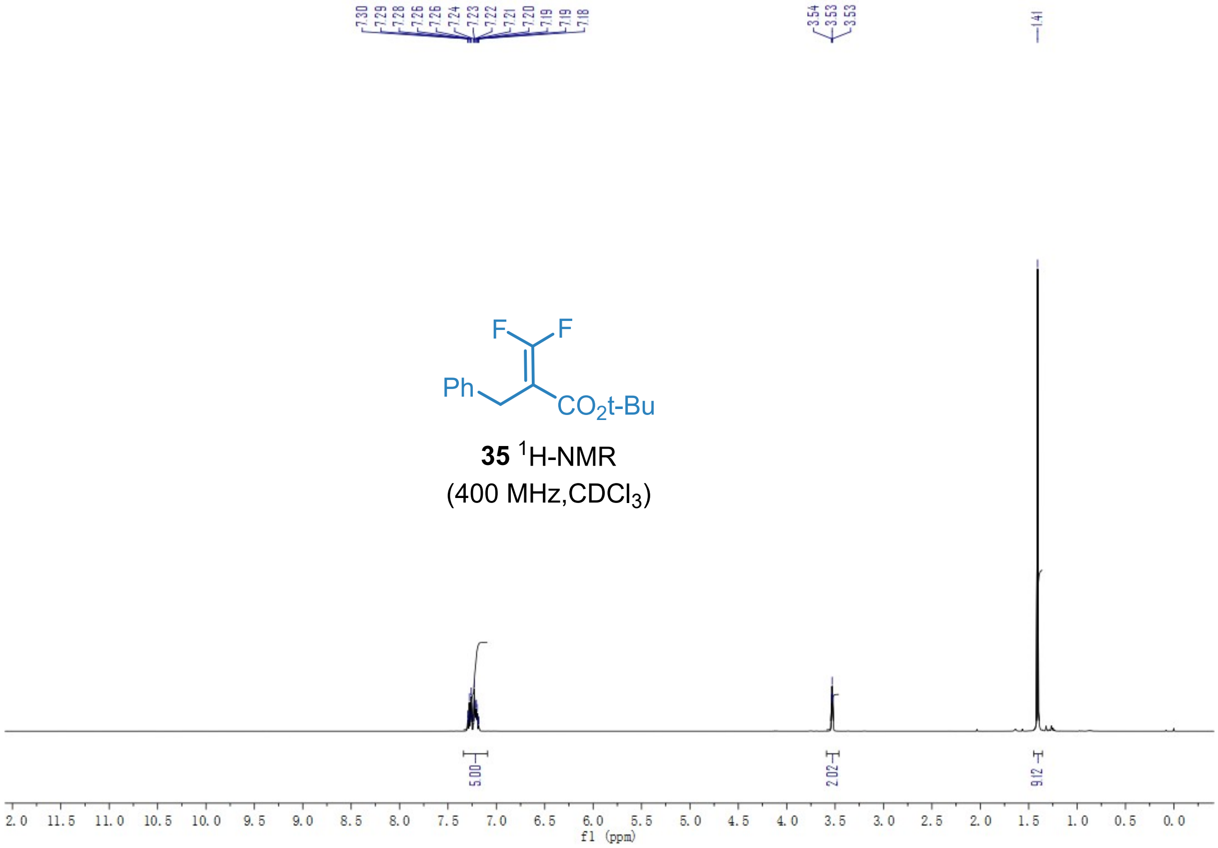


34 ^{1}H-NMR
(400 MHz,$CDCl_3$)

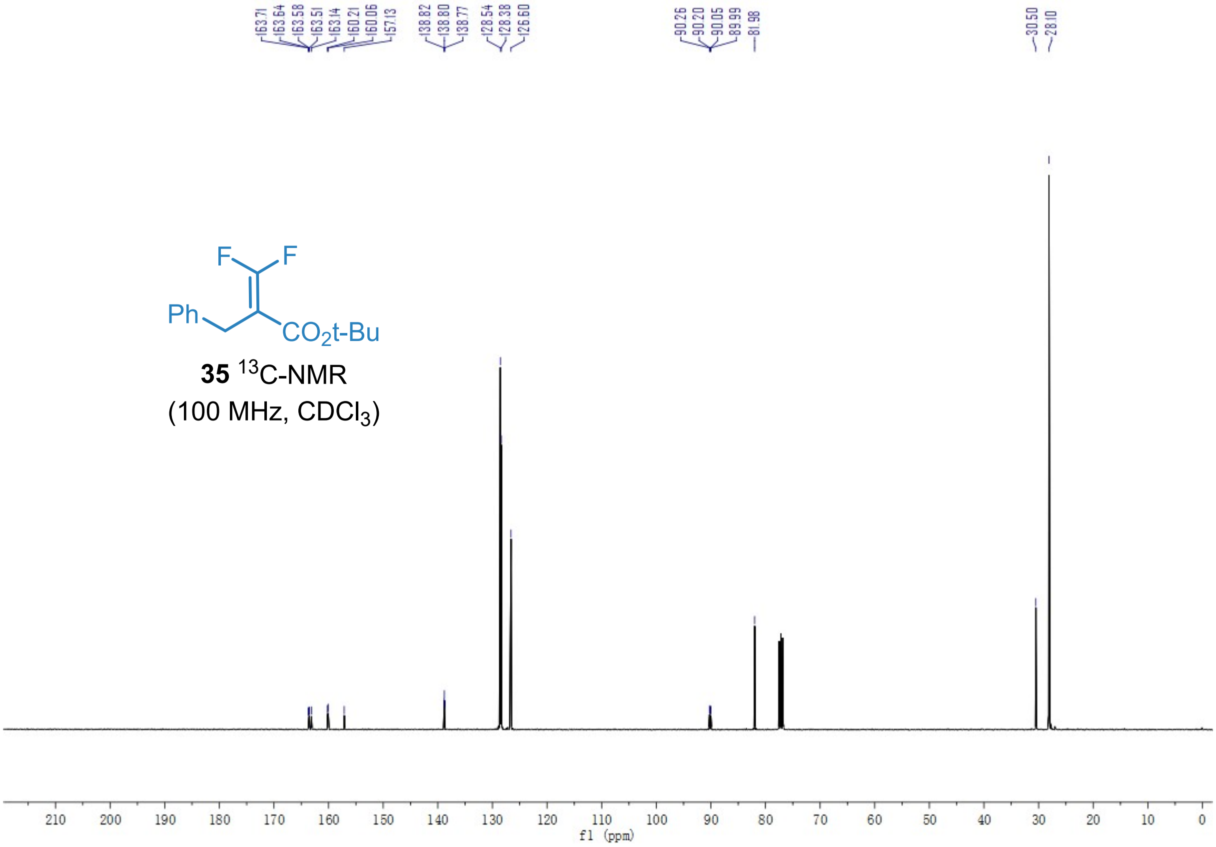




34 ^{13}C-NMR
(100 MHz, $CDCl_3$)

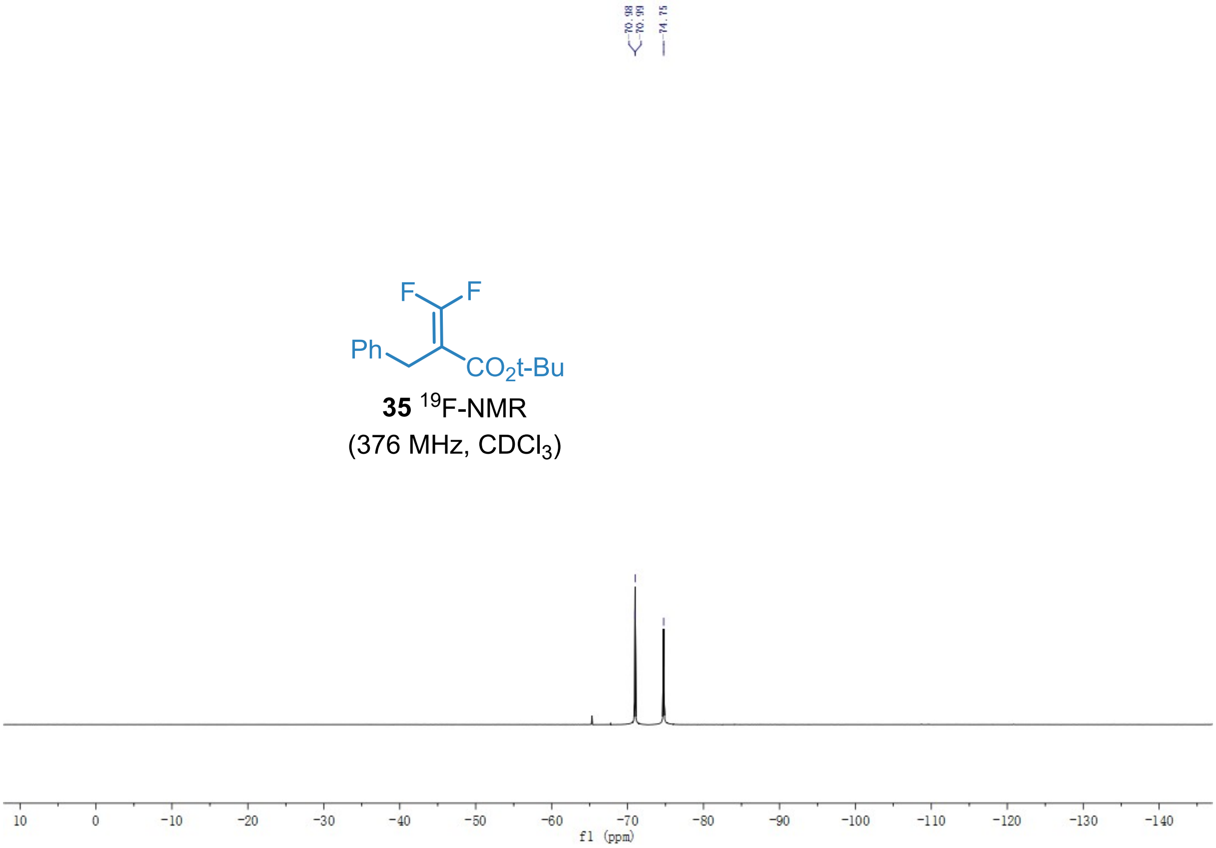


35 ^{1}H-NMR
(400 MHz,$CDCl_3$)



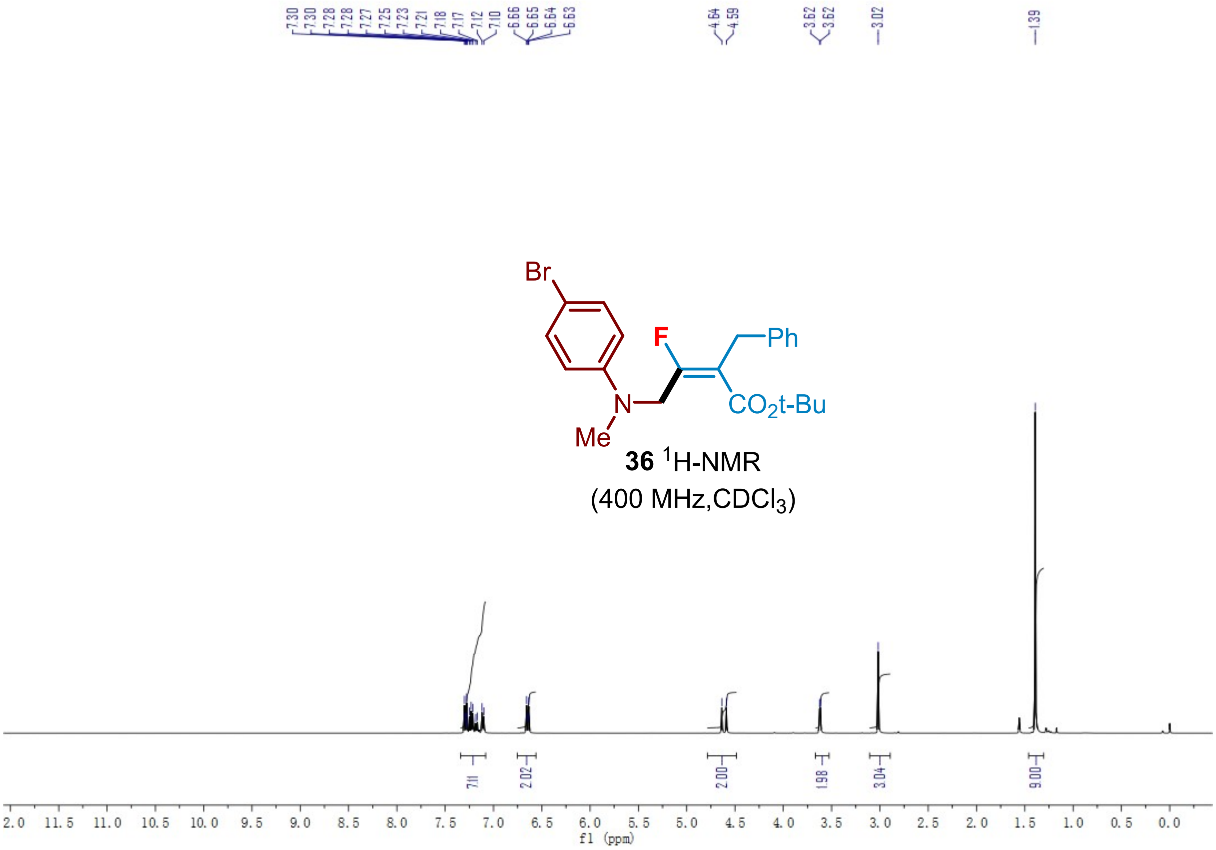
35 ^{13}C-NMR

(100 MHz, CDCl$_3$)

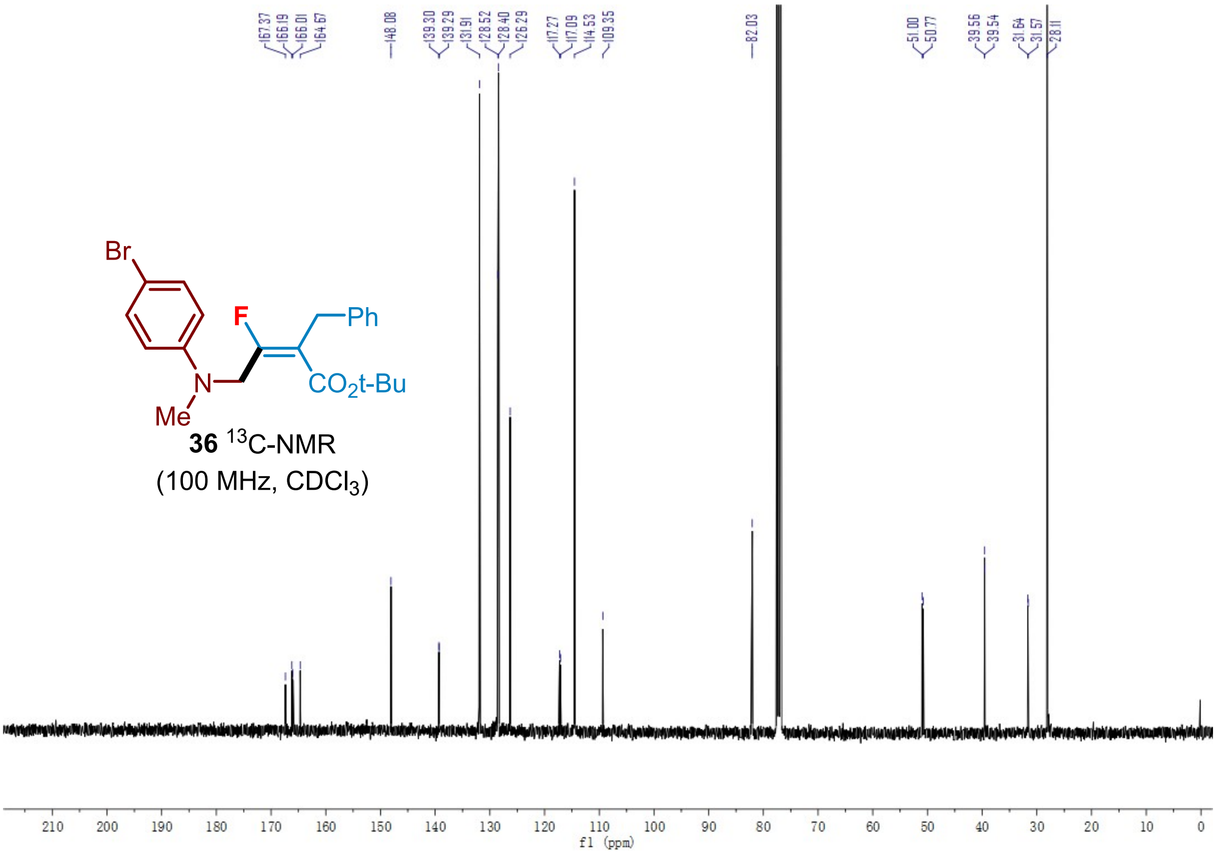


35 ^{19}F-NMR

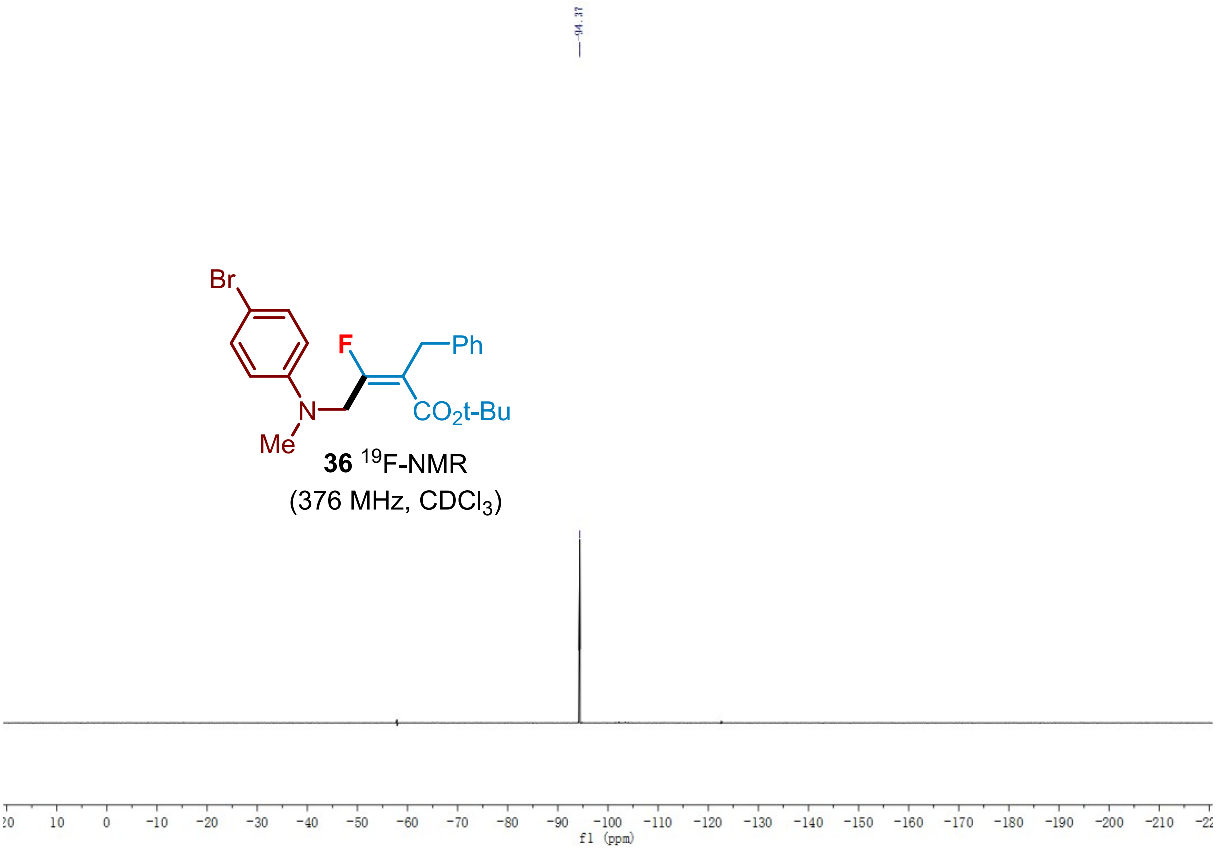
(376 MHz, CDCl$_3$)



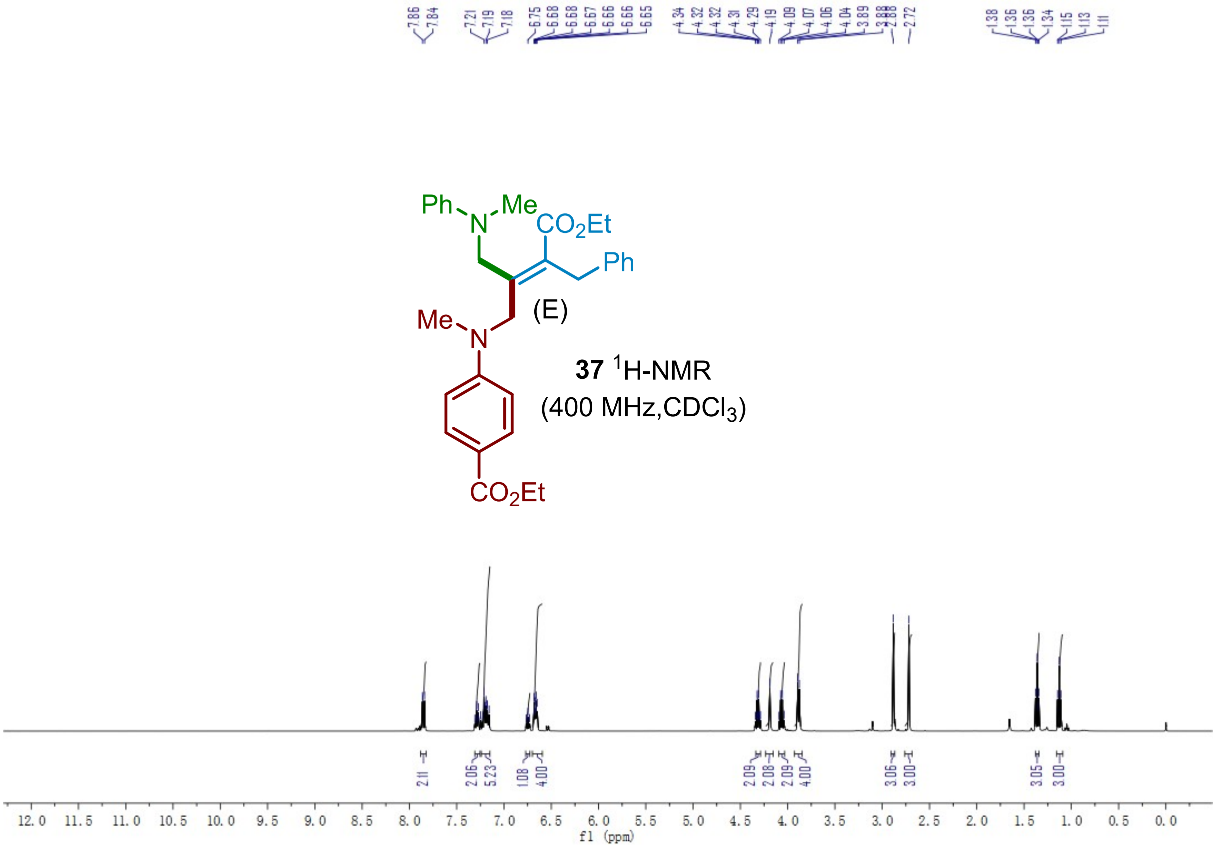
36 ^{1}H-NMR
(400 MHz,CDCl$_3$)



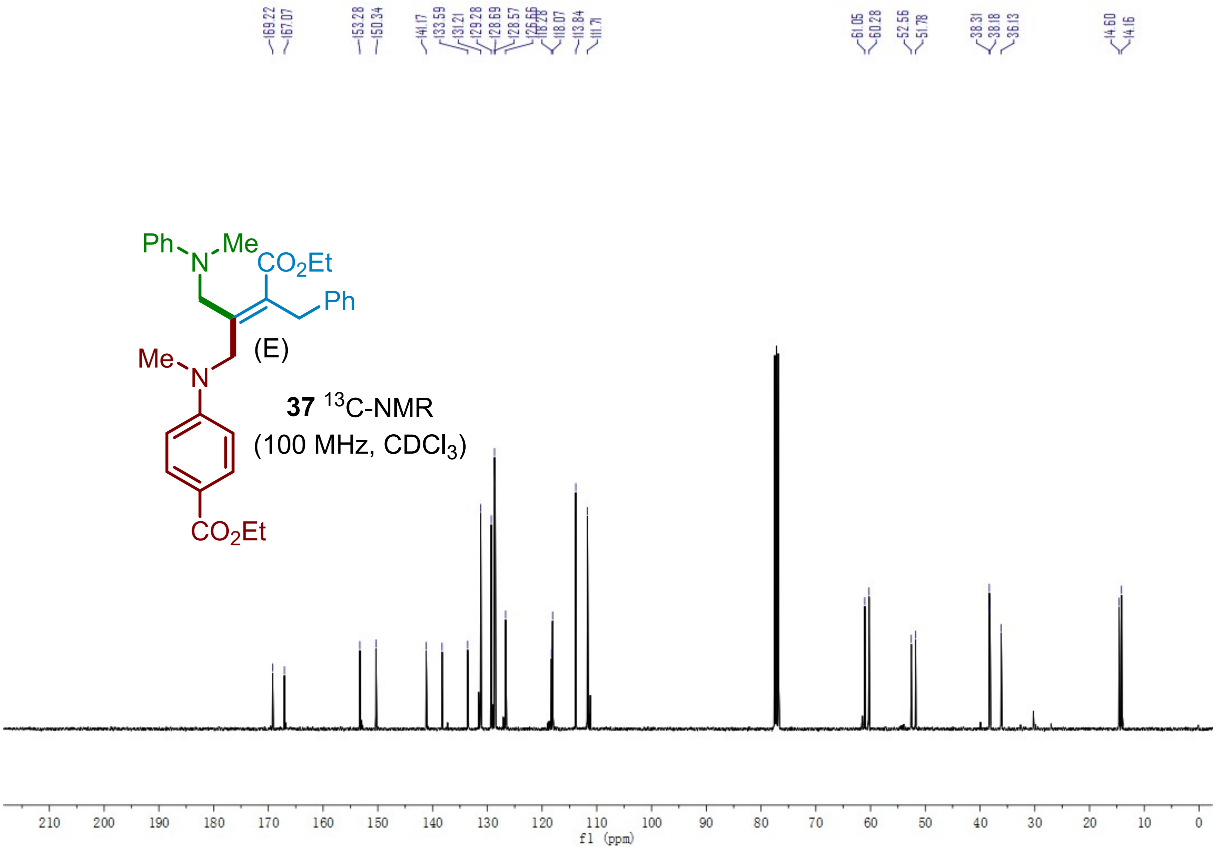
36 ^{13}C-NMR
(100 MHz, CDCl$_3$)



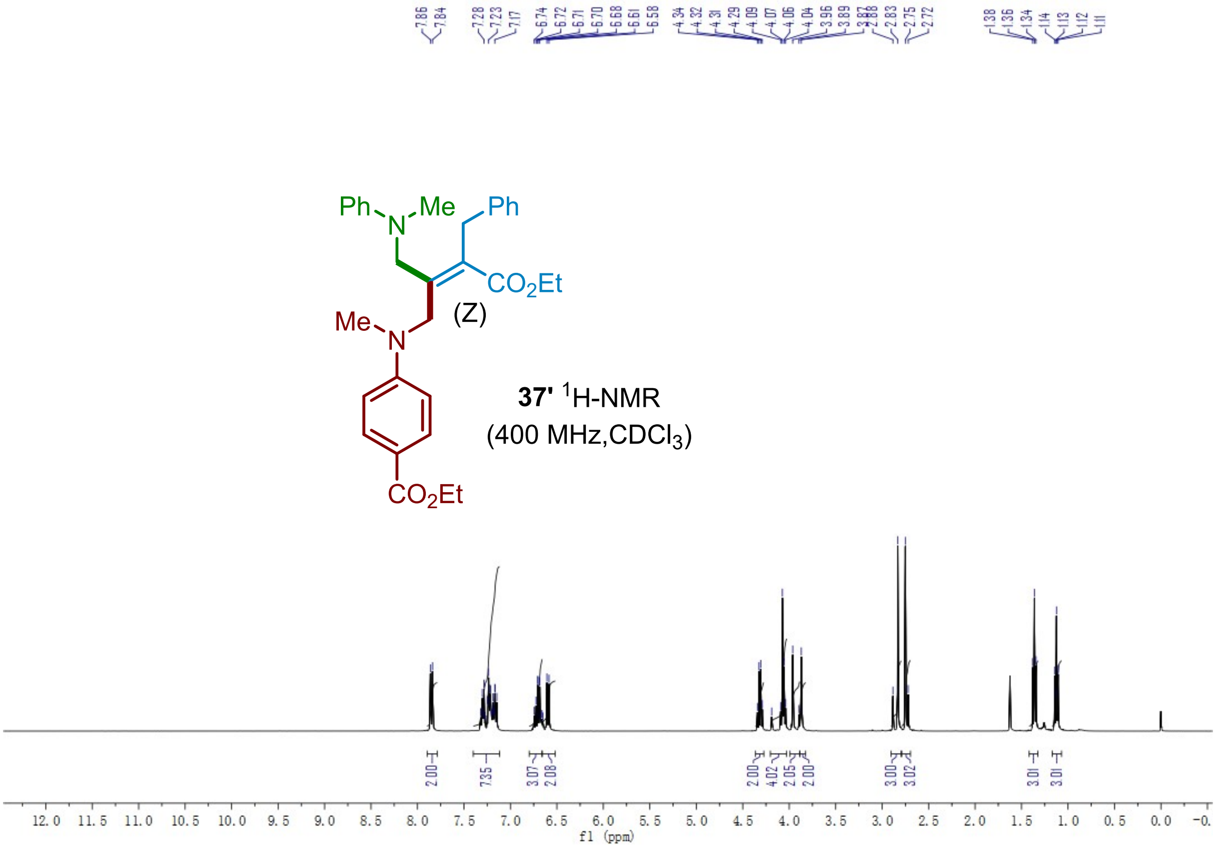
36 ^{19}F-NMR
(376 MHz, $CDCl_3$)



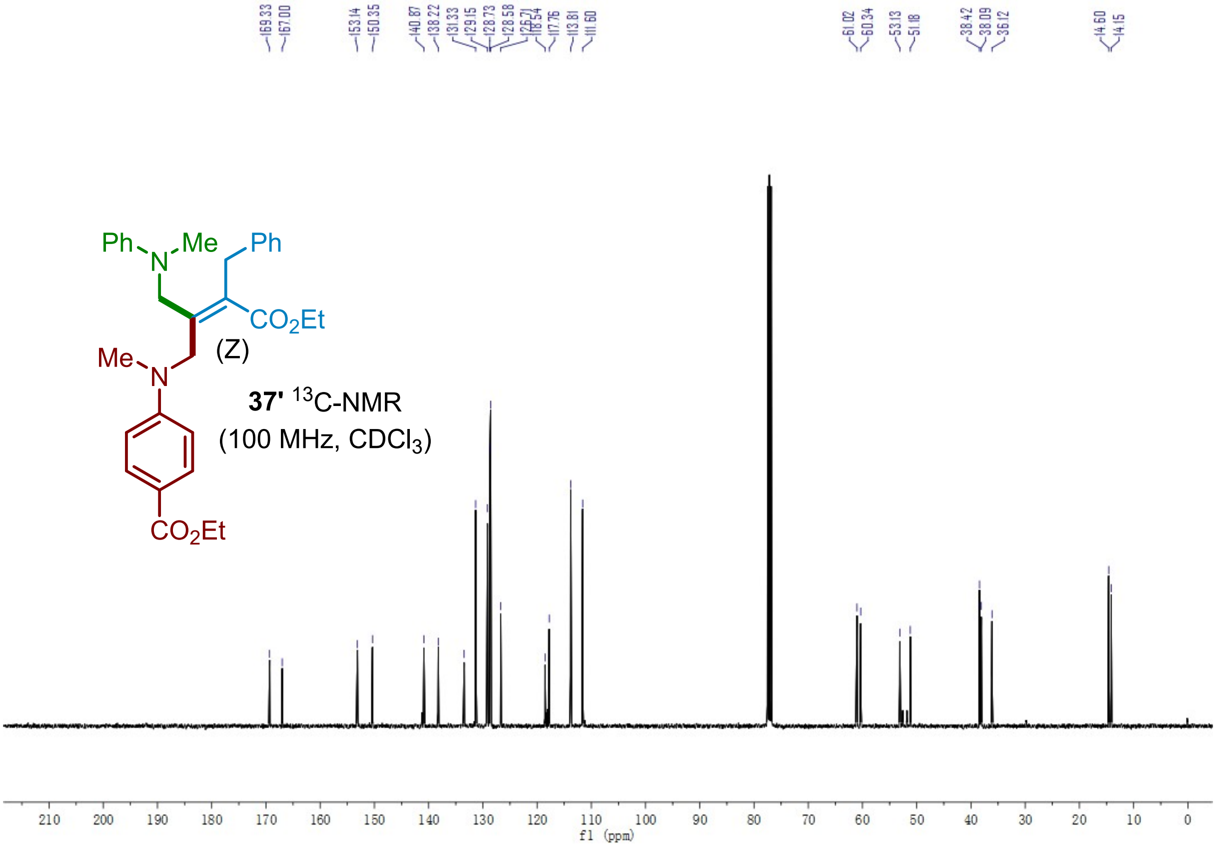
37 ^{1}H-NMR
(400 MHz,$CDCl_3$)



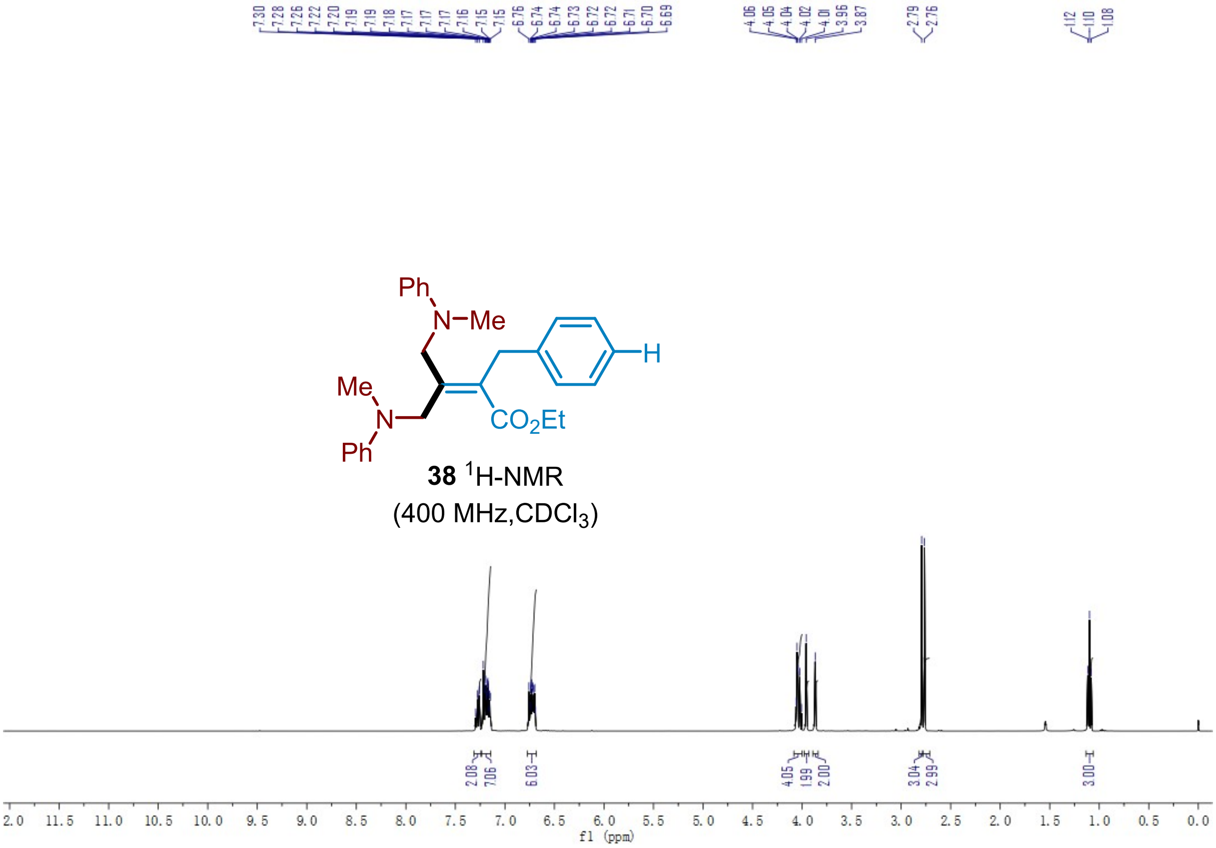
37 ^{13}C-NMR (100 MHz, $CDCl_3$)



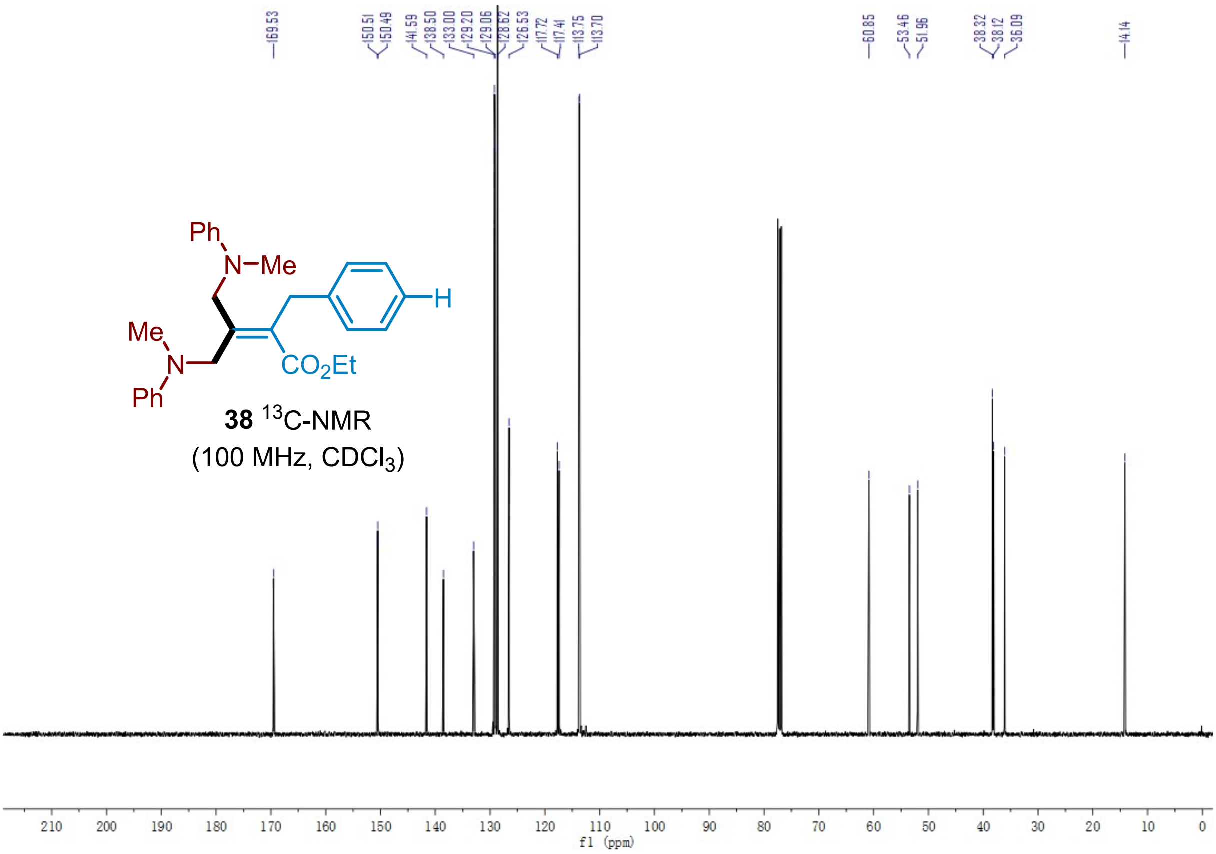
37' ^{1}H-NMR (400 MHz, $CDCl_3$)



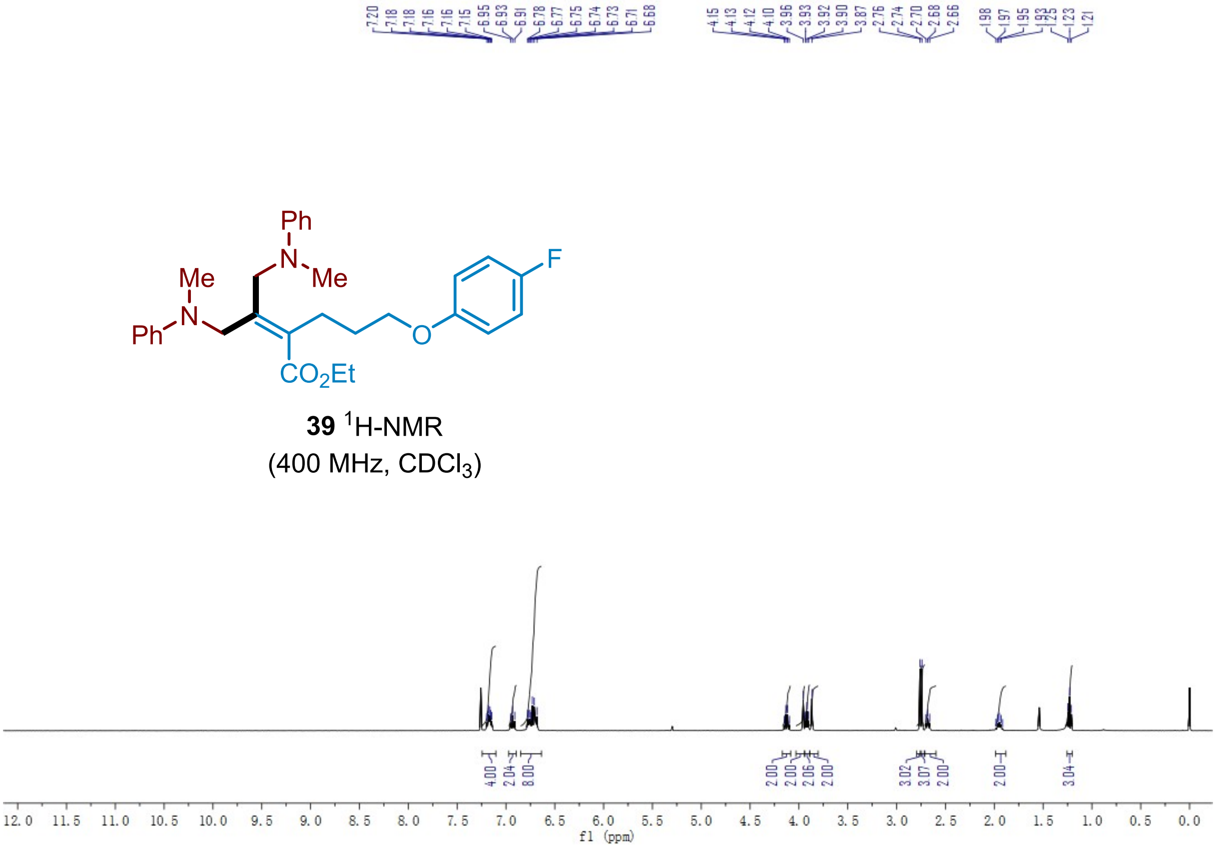
37' ^{13}C-NMR (100 MHz, $CDCl_3$)



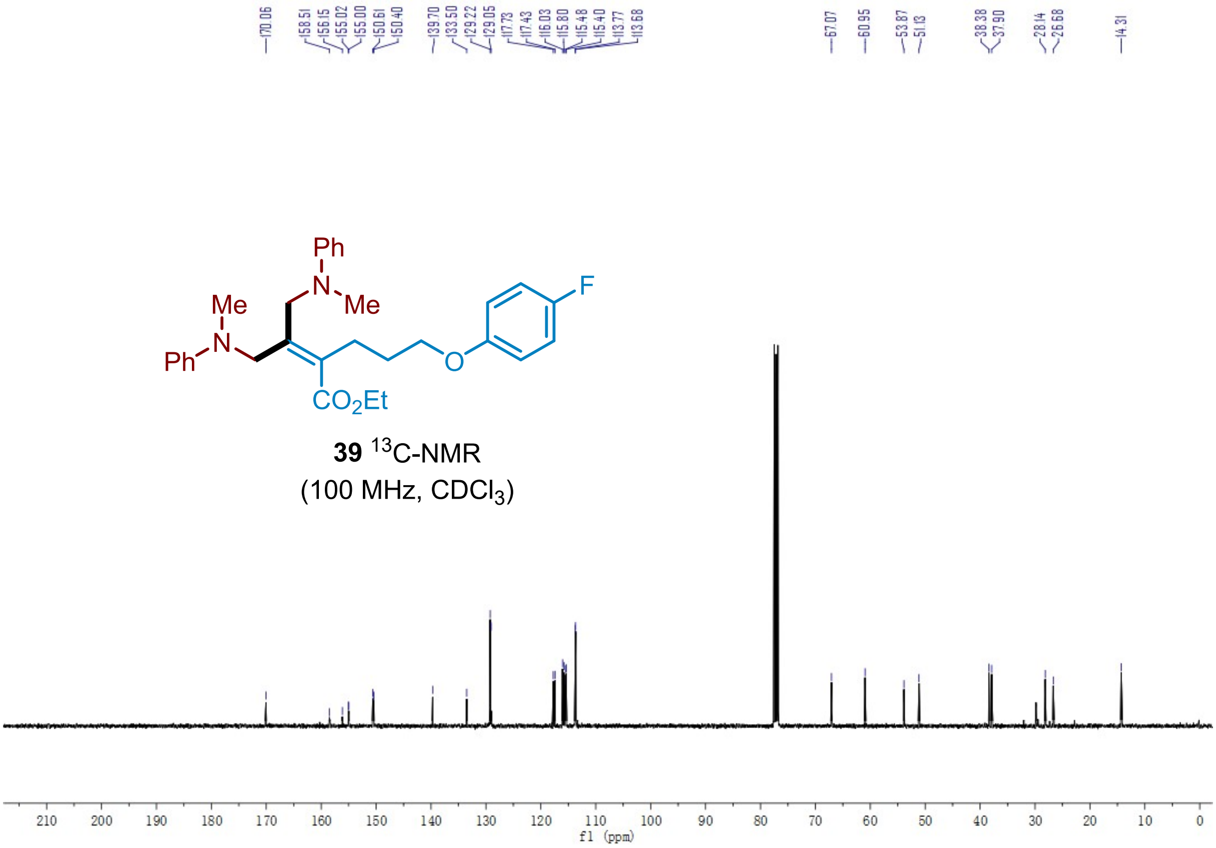
38 ^{1}H-NMR (400 MHz, $CDCl_3$)



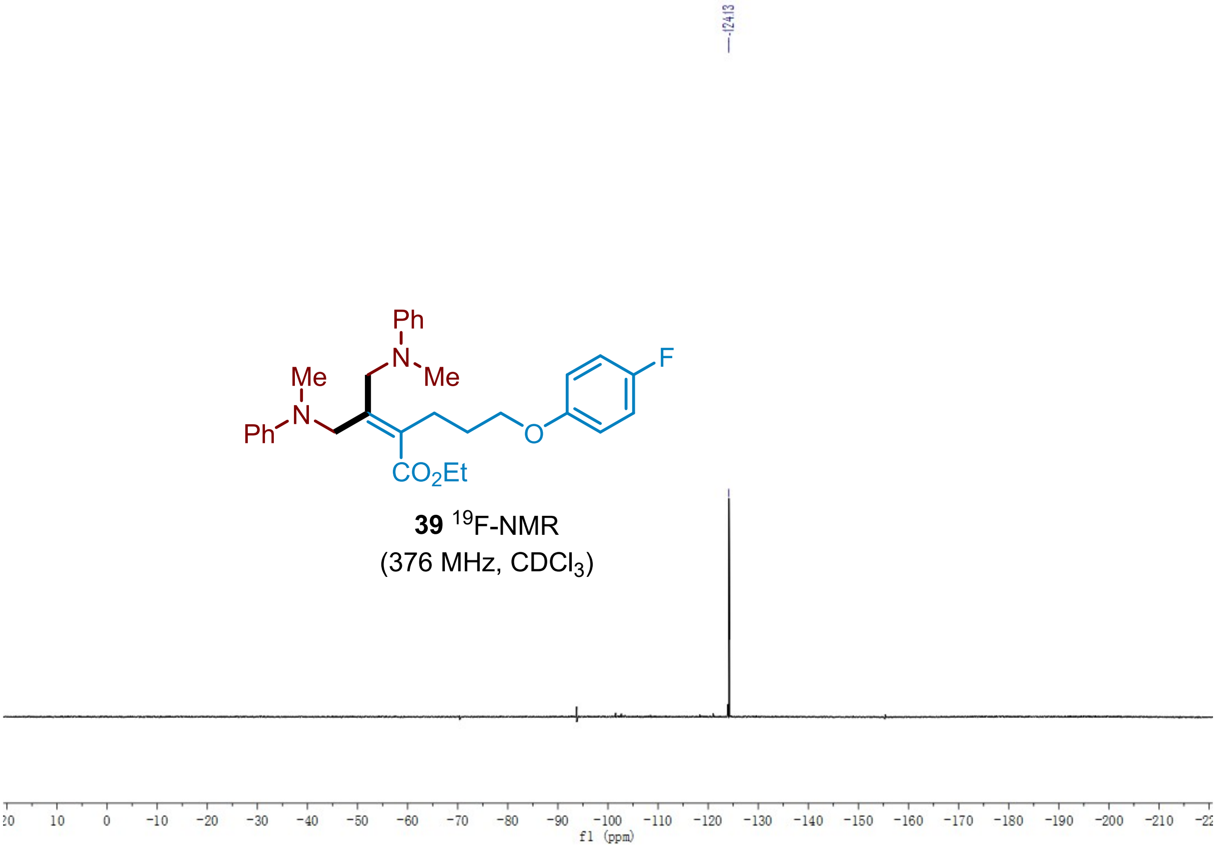
38 ^{13}C-NMR
(100 MHz, CDCl$_3$)



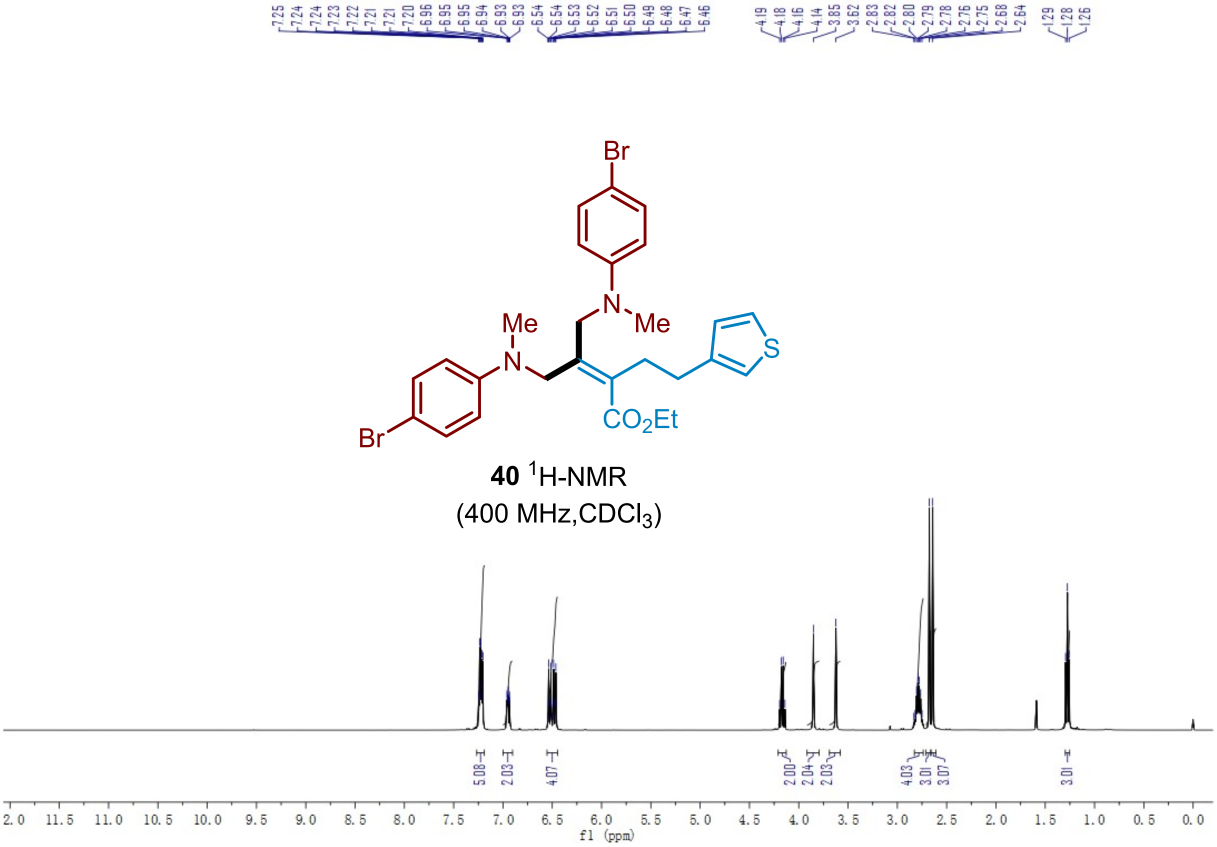
39 ^{1}H-NMR
(400 MHz, CDCl$_3$)



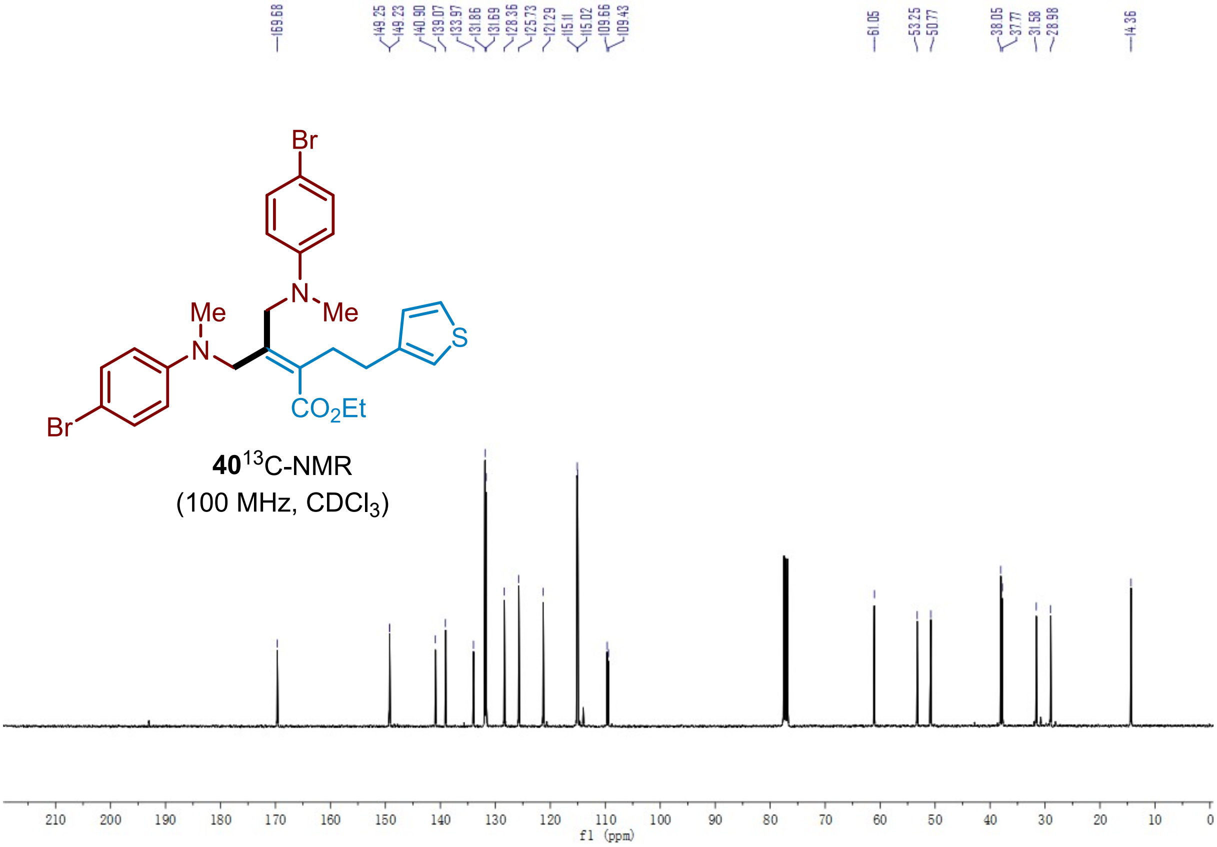
39 ^{13}C-NMR
(100 MHz, $CDCl_3$)



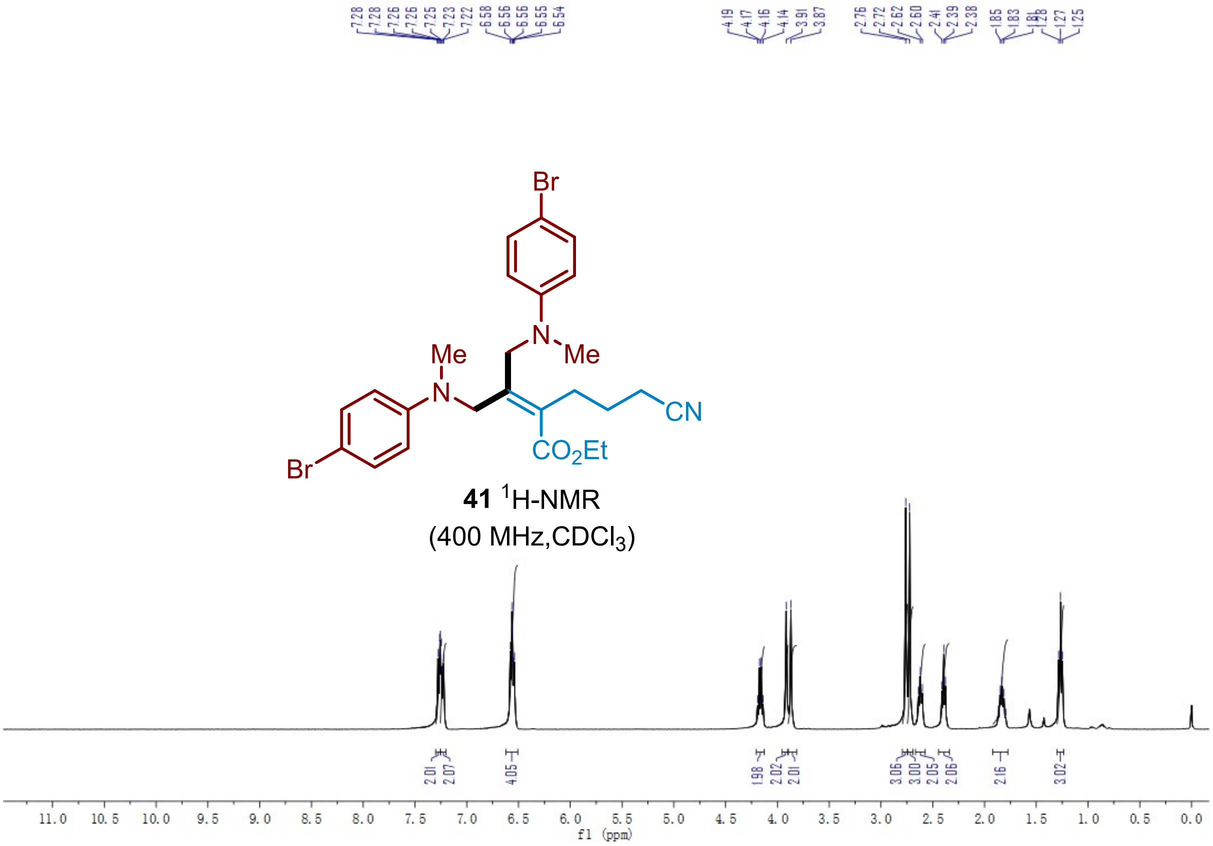
39 ^{19}F-NMR
(376 MHz, $CDCl_3$)



40 ^{1}H-NMR
(400 MHz,CDCl$_3$)

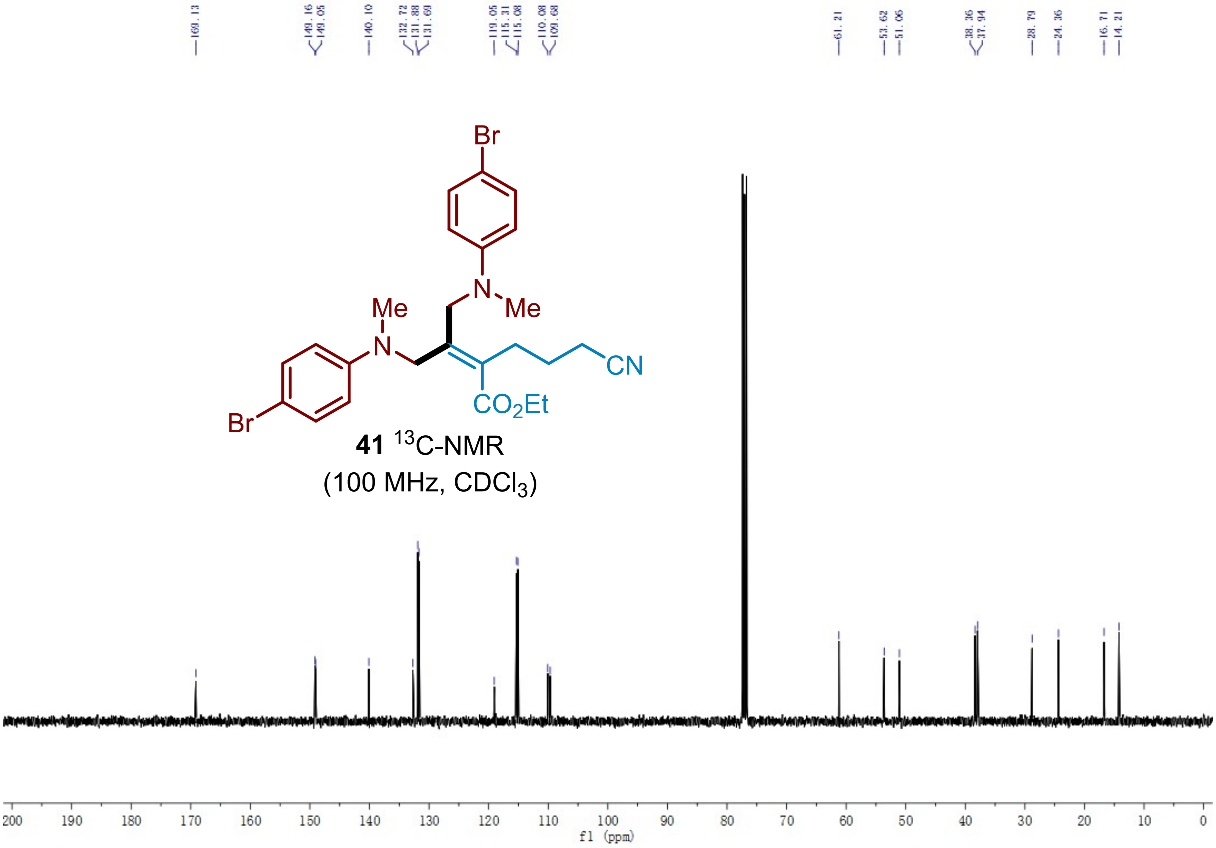


40 ^{13}C-NMR
(100 MHz, CDCl$_3$)



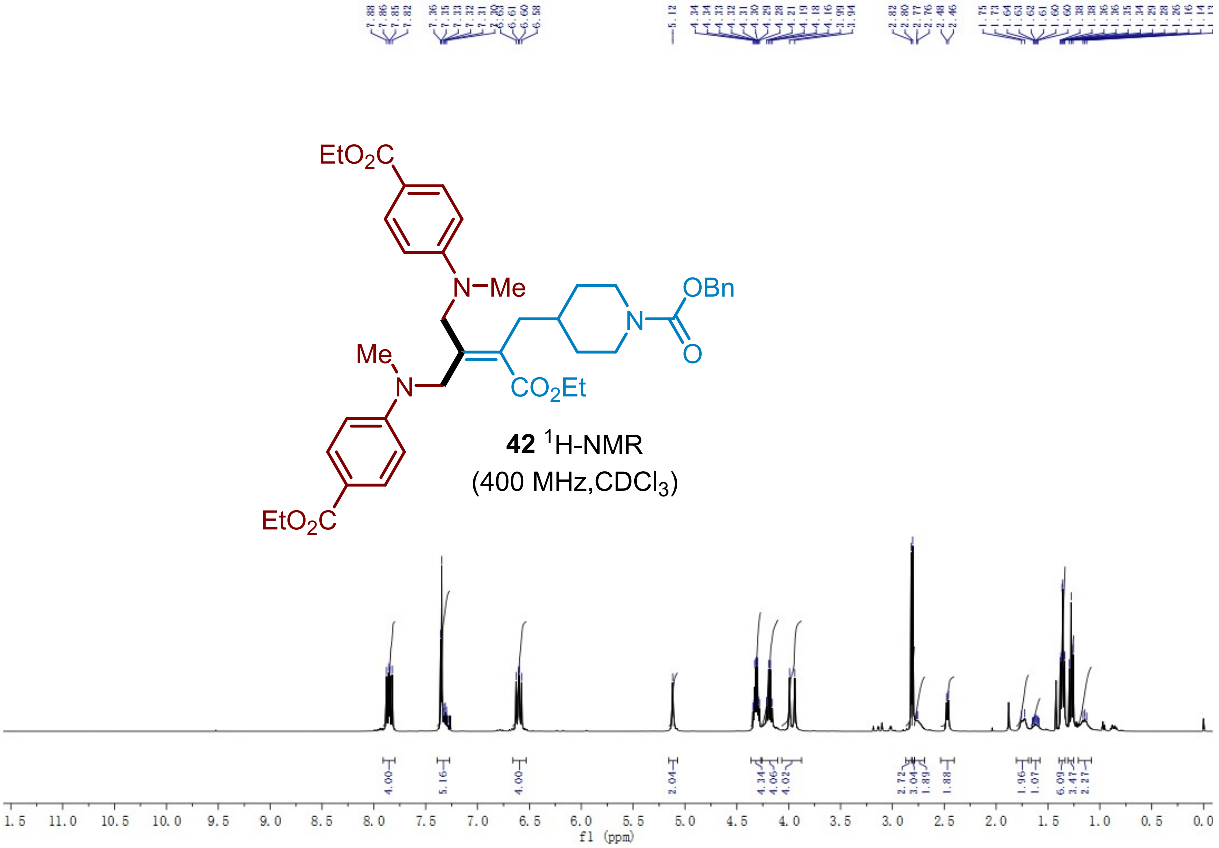
41 ^{1}H-NMR

(400 MHz, $CDCl_3$)

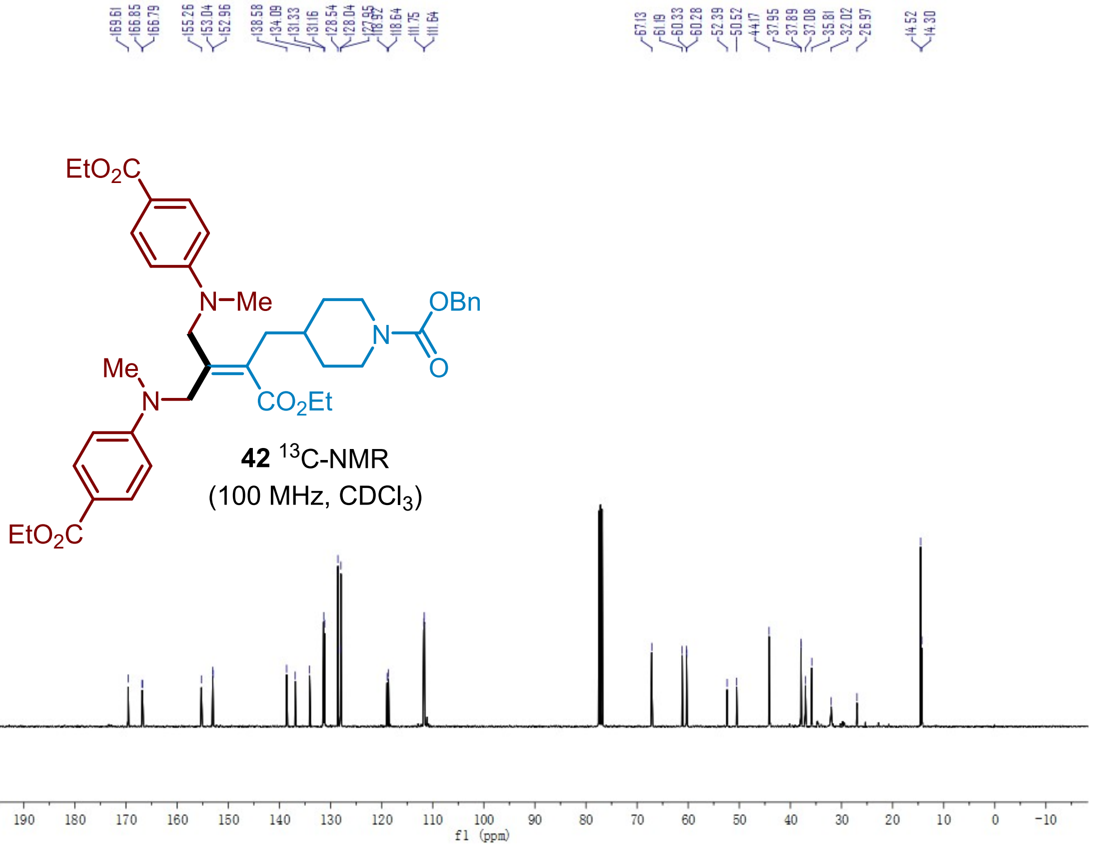


41 ^{13}C-NMR

(100 MHz, $CDCl_3$)



42 ^{1}H-NMR (400 MHz,CDCl$_3$)



42 ^{13}C-NMR (100 MHz, CDCl$_3$)