

Supporting Information

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Iron-Catalyzed Decarboxylative Cyanoalkylation of α -Fluoroacrylic Acids

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I. General Information

a. Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity $\geq 99.999\%$). $\text{Fe}(\text{acac})_2$ (CAS:14024-17-0), PhF (CAS:462-06-6) were purchased from Adamas. All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

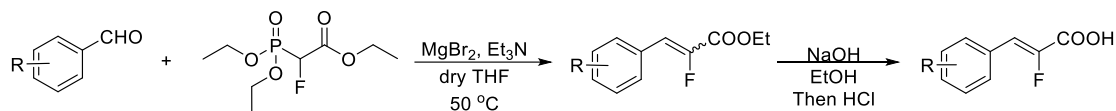
b. Analytical Methods

^1H -NMR, ^{13}C -NMR and ^{19}F -NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in Chloroform- d unless otherwise noted; Data for ^1H -NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C -NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forcedflow chromatography on Silica Gel (200-300 mesh).

II. Preparation of Substrates

Synthesis of α -Fluoroacrylic Acids

Figure S1



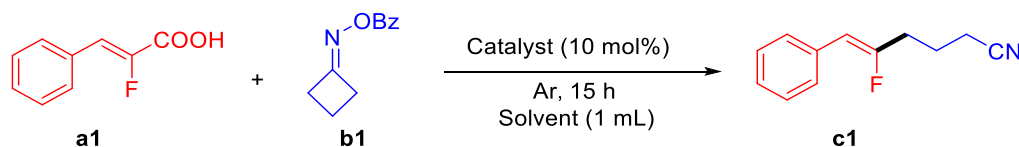
The synthesis of α -fluoroacrylic acids refers to our previous literature, and all compounds have been characterized in our previous work.¹⁻⁹ 2-Fluoro-triethylphosphonoacetate (2.42 g, 10.0 mmol, 1.0 equiv.) was dissolved in dry THF (50 mL, 5 M) at ambient temperature. Triethylamine (2.80 mL, 20.0 mmol, 2.0 equiv.) was added followed by magnesium bromide (1.84 g, 10.0 mmol, 1.0 equiv.). An exotherm is observed, and while the reaction was hot, benzaldehyde (10.0 mmol, 1.0 equiv.) was added. The reaction was stirred and monitored by TLC. Upon completion, the reaction was diluted with 50 mL diethyl ether, then filtered on a medium porosity fritted funnel. The filtrate was washed with saturated ammonium chloride solution, which was then extracted with ether (2×50 mL). The organic layers were combined, washed with brine, dried over magnesium sulfate, filtered, and concentrated to give 1.95 g of colorless oil, ethyl 2-fluoro-3-phenyl acrylate as a mixture of olefin isomers. Spectral data for this compound matched literature, and it was carried over to the next step without further purification.

To a stirred solution of ethyl 2-fluoro-3-phenyl acrylate in EtOH (20 mL) was added 1 M aqueous NaOH (15 mL), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated in vacuo. Then, 50 mL of water was added. The aqueous phase was acidified with 2 N HCl and extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄. The volatile compounds were removed in vacuo to afford 2-fluoro-3-phenylacrylic acid.

III. General Experimental Procedures

Optimization of the reaction conditions

Table S1



Entry	Catalyst	Solvent	T (°C)	Yield (%)
1	Fe(OAc) ₂	CH ₃ CN	100	35
2	Fe(OAc) ₂	PhCF ₃	100	50
3	Fe(OAc) ₂	DMF	100	26
4	Fe(OAc) ₂	DMAc	100	21
5	Fe(OAc) ₂	THF	100	9
6	Fe(OAc) ₂	Dioxane	100	23
7	Fe(OAc) ₂	PhCl	100	37
8	Fe(OAc) ₂	DMSO	100	29
9	Fe(OAc) ₂	NMP	100	8
10	Fe(OAc) ₂	Toluene	100	31
11	Fe(OAc) ₂	DCE	100	34
12	Fe(OAc) ₂	ACE	100	23
13	FeCl ₂	PhCF ₃	100	36
14	FeCl ₂	EtOAc	100	30
15	FeCl ₂	PhF	100	48
16	FeCl ₂	1,2-DCB	100	39
17	FeSO ₄	PhCF ₃	100	10
18	Fe(acac) ₂	PhCF ₃	100	45
19	Fe(OTf) ₂	PhCF ₃	100	3
20	Fe(acac) ₃	PhCF ₃	100	61
21	CuI	PhCF ₃	100	8
22	Mn(OAc) ₂	PhCF ₃	100	11
23	Cu(CH ₃ CN)BF ₄	PhCF ₃	100	10
24	NiCl ₂	PhCF ₃	100	12
25	Fe(acac) ₂	PhCF ₃	60	22
26	Fe(acac) ₂	PhCF ₃	80	57
27	FeBr ₃	PhCF ₃	80	23
28	FeCl ₃	PhCF ₃	80	25
29	Fe(acac) ₂	PhF	80	72
30 ^b	Fe(acac) ₂	PhF	80	82

^a Reaction conditions: **a1** (0.2 mmol), **a2** (0.4 mmol), catalyst (10 mol %), and solvent (1 mL) reacted in an oil bath at the corresponding temperature for 15 h under Ar atmosphere. ^b Reaction conditions:

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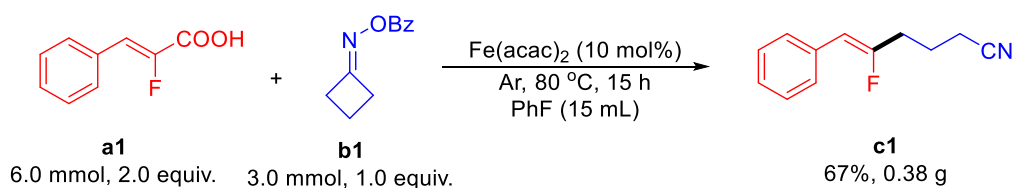
a1 (0.4 mmol), **a2** (0.2 mmol), catalyst (10 mol %), and solvent (1 mL) were heated in an oil bath at 80 °C for 15 h under Ar atmosphere. The reaction yield was determined by GC using biphenyl as internal standard.

IV. General Procedure

a. Standard reaction

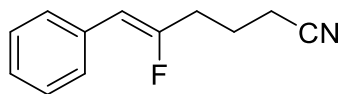
In air, α -fluoroacrylic acids (0.4 mmol, 2.0 equiv.), cyclic Ketoxime Ester (0.2 mmol, 1.0 equiv.) and $\text{Fe}(\text{acac})_2$ (5.1 mg, 10 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles), PhF (1.0 mL, 0.5 M) were added by syringe. The resulting reaction mixture was heated in an oil bath at 80 °C for 15 h under Ar atmosphere. The residue was purified by silica gel (200-300 mesh) column chromatography using petroleum ether (PE) and ethyl acetate (EA). The Z/E ratios were determined by ^1H NMR and ^{19}F NMR analyses. The characteristic signals for the two isomers appeared at approximately 5.5 and 6.3 ppm, respectively.

b. Gram-scale reaction



In air, α -fluoroacrylic acids (6.0 mmol, 2.0 equiv.), cyclic Ketoxime Ester (3.0 mmol, 1.0 equiv.) and $\text{Fe}(\text{acac})_2$ (76.5 mg, 10 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles), PhF (15.0 mL, 0.5 M) were added by syringe. The resulting reaction mixture was heated in an oil bath at 80 °C for 15 h under Ar atmosphere. The residue was purified by silica gel (200-300 mesh) column chromatography using petroleum ether (PE) and ethyl acetate (EtOAc) (PE/EA = 5/1) as an eluent. (381 mg, 3 mmol scale, 67%)

V. Substrate Scope, Spectral Data and NMR Spectra

**(Z)-5-fluoro-6-phenylhex-5-enenitrile**

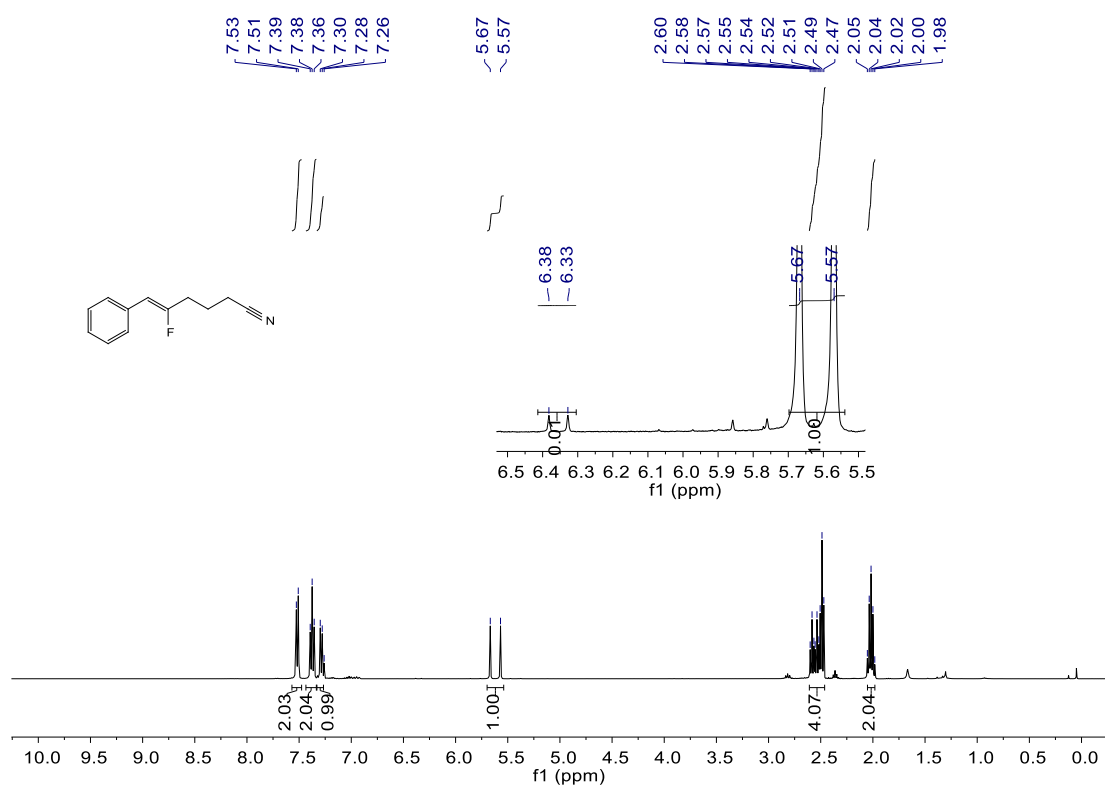
Following the general procedure (**c1**, pale-yellow liquid, 28.8 mg, 76%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 5.62 (d, J = 39.3 Hz, 1H), 2.61 – 2.46 (m, 4H), 2.01 (q, J = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.78.

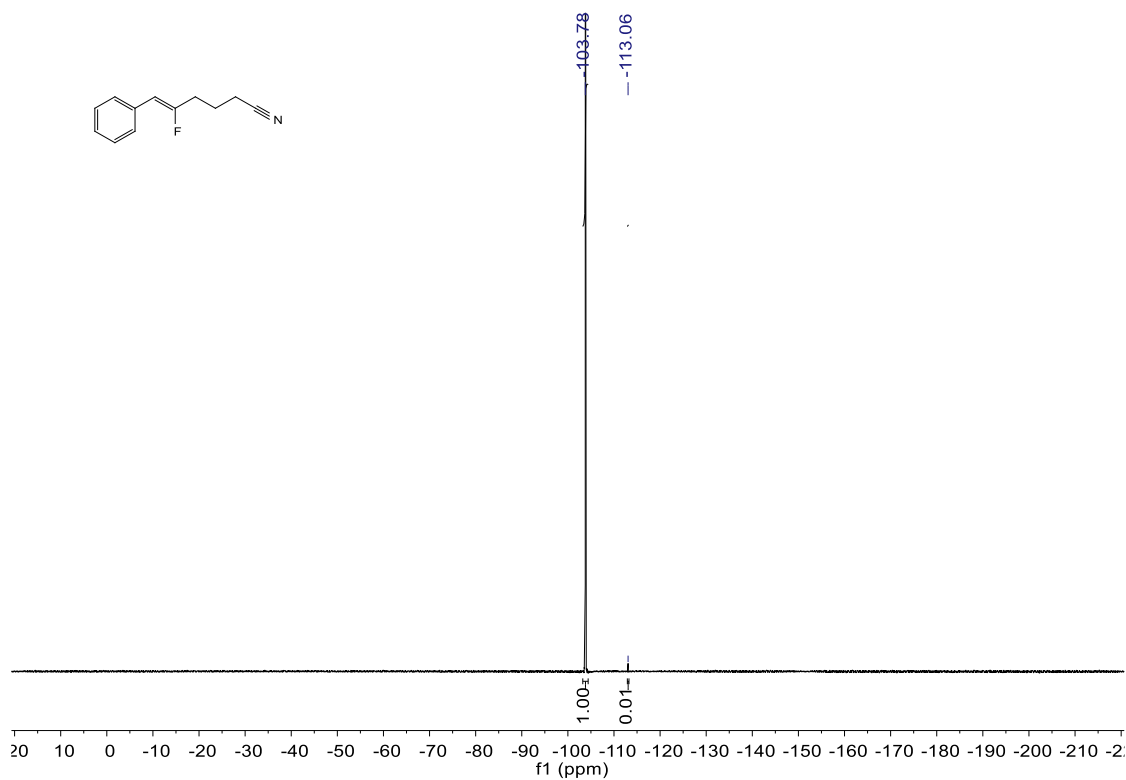
¹³C NMR (101 MHz, Chloroform-*d*) δ 158.11 (d, J = 265.8 Hz), 133.17 (d, J = 2.3 Hz), 128.59, 128.50 (d, J = 7.4 Hz), 127.28 (d, J = 2.2 Hz), 119.17, 107.80 (d, J = 8.1 Hz), 31.89 (d, J = 27.6 Hz), 22.28, 16.33.

HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₂H₁₂FN: 190.1027; found: 190.1026.

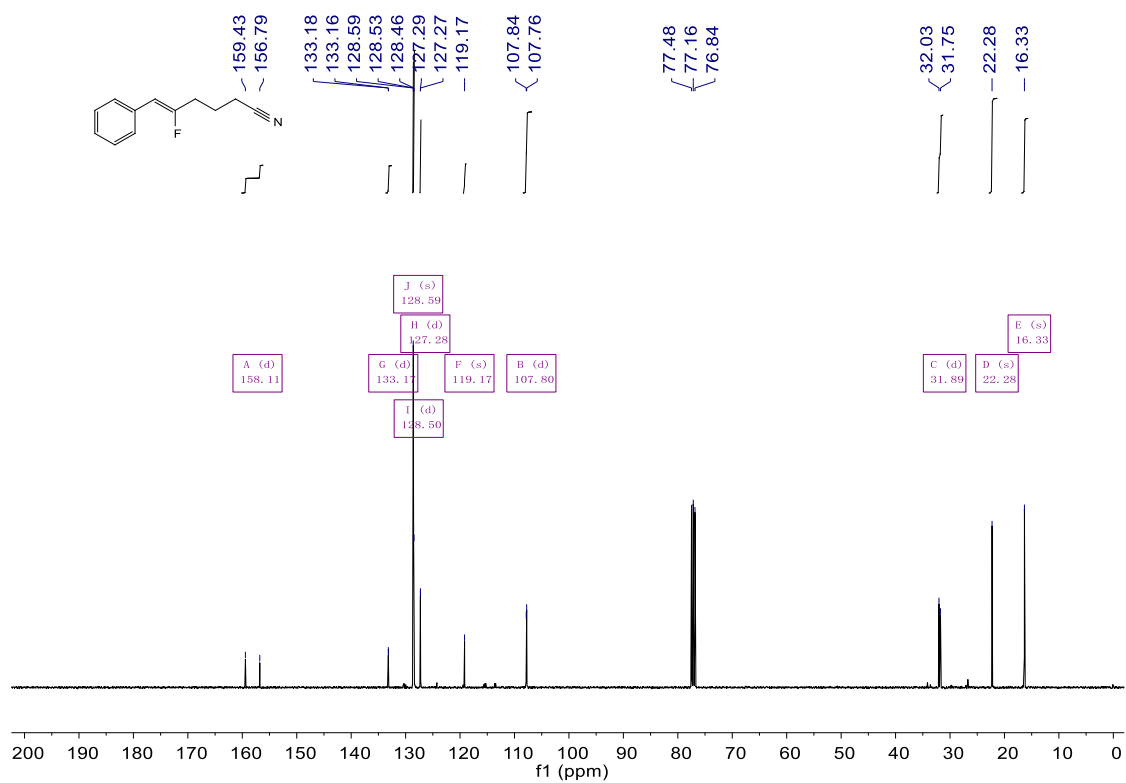
¹H NMR (400 MHz, Chloroform-*d*)

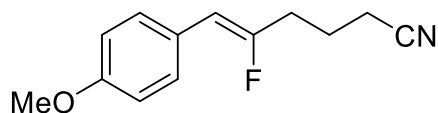
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-6-(4-methoxyphenyl)hex-5-enitrile

Following the general procedure (**c2**, yellow liquid, 25 mg, 57%, *Z/E* > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

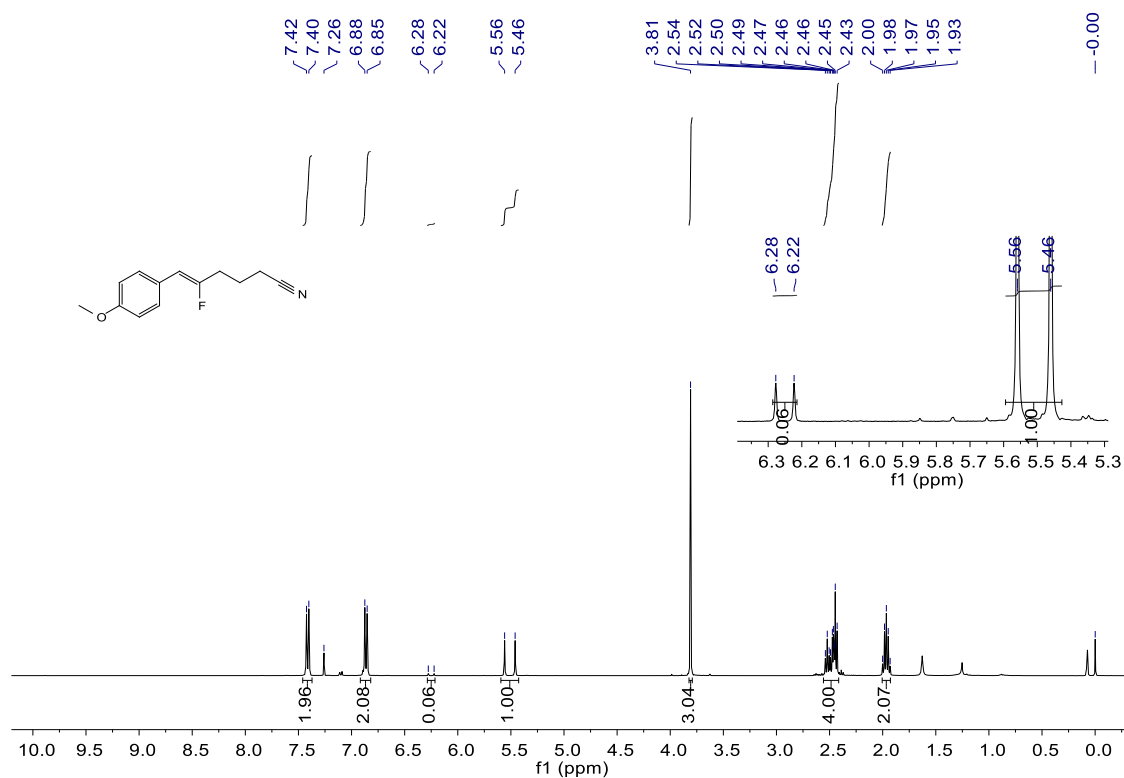
¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.51 (d, *J* = 39.6 Hz, 1H), 3.81 (s, 3H), 2.56 – 2.41 (m, 4H), 1.97 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -106.75.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.68 (d, *J* = 2.7 Hz), 156.70 (d, *J* = 263.6 Hz), 129.77 (d, *J* = 7.5 Hz), 125.89 (d, *J* = 2.4 Hz), 119.27, 113.99, 107.27 (d, *J* = 8.6 Hz), 55.37, 31.86 (d, *J* = 27.5 Hz), 22.35, 16.33.

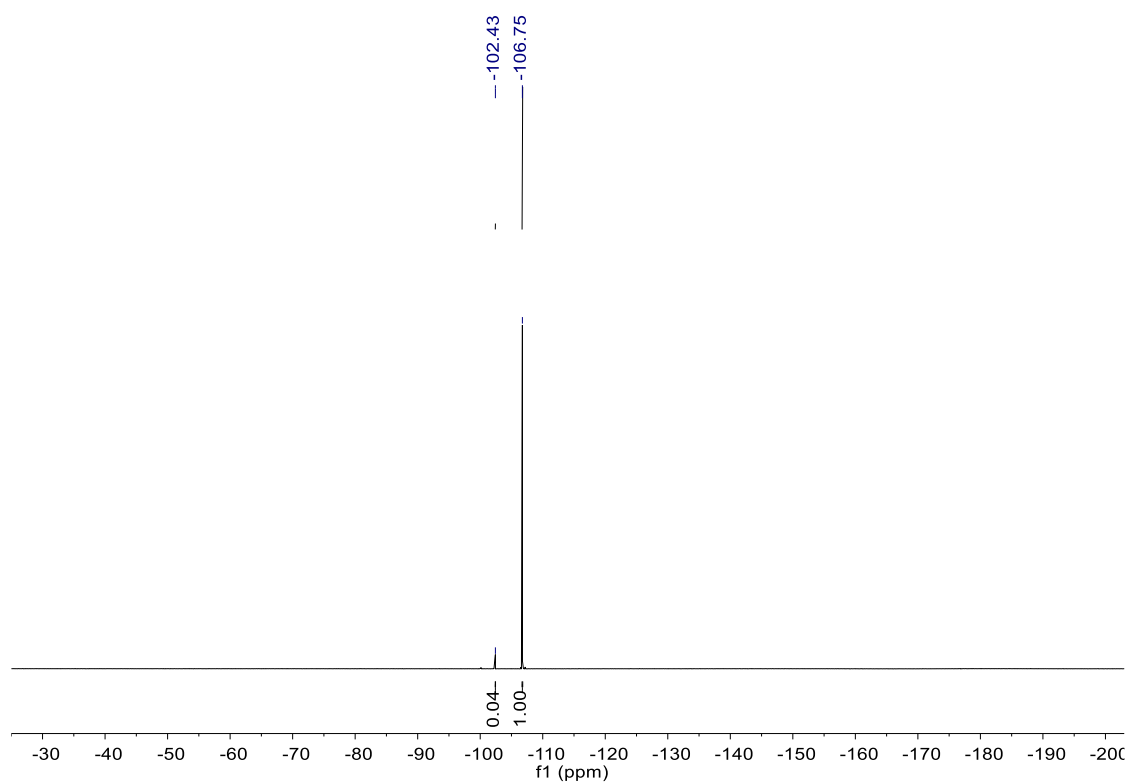
HRMS (ESI) *m/z*: (*M*+*H*)⁺ Calcd for C₁₃H₁₄FNO: 220.1132; found: 220.1122.

¹H NMR (400 MHz, Chloroform-*d*)

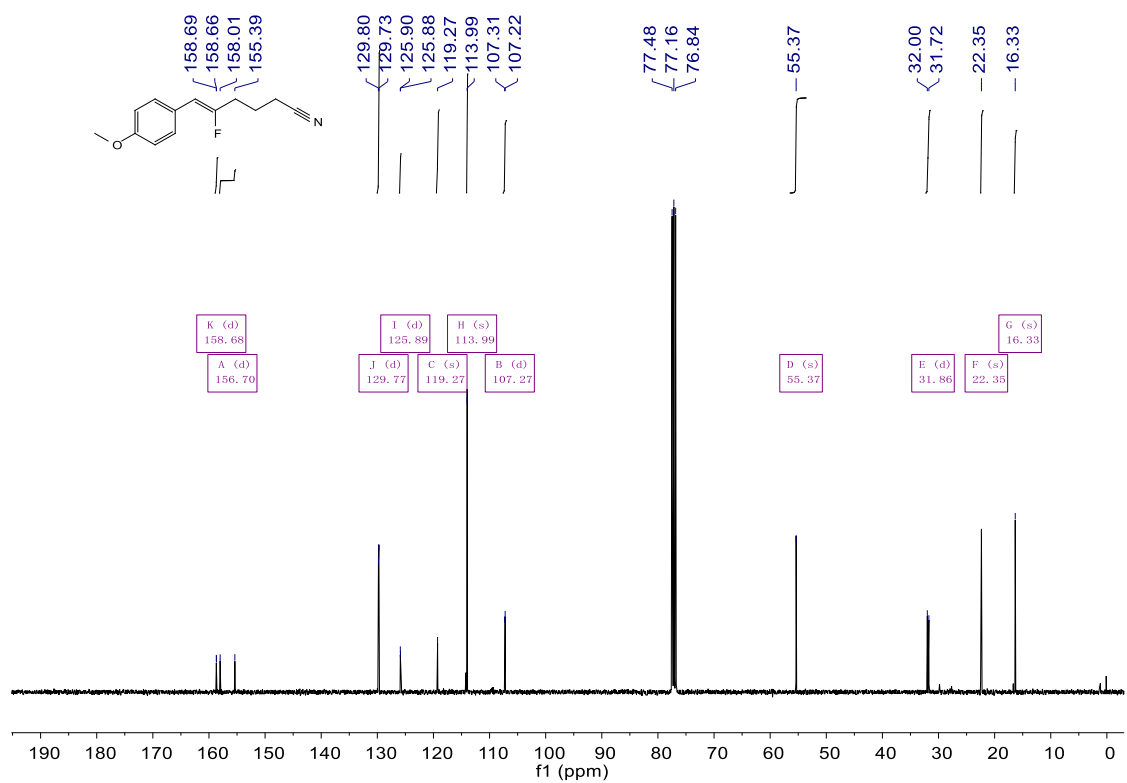


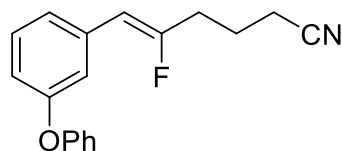
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-6-(3-phenoxyphenyl)hex-5-enitrile

Following the general procedure (**c3**, pale-yellow liquid, 24.2 mg, 43%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

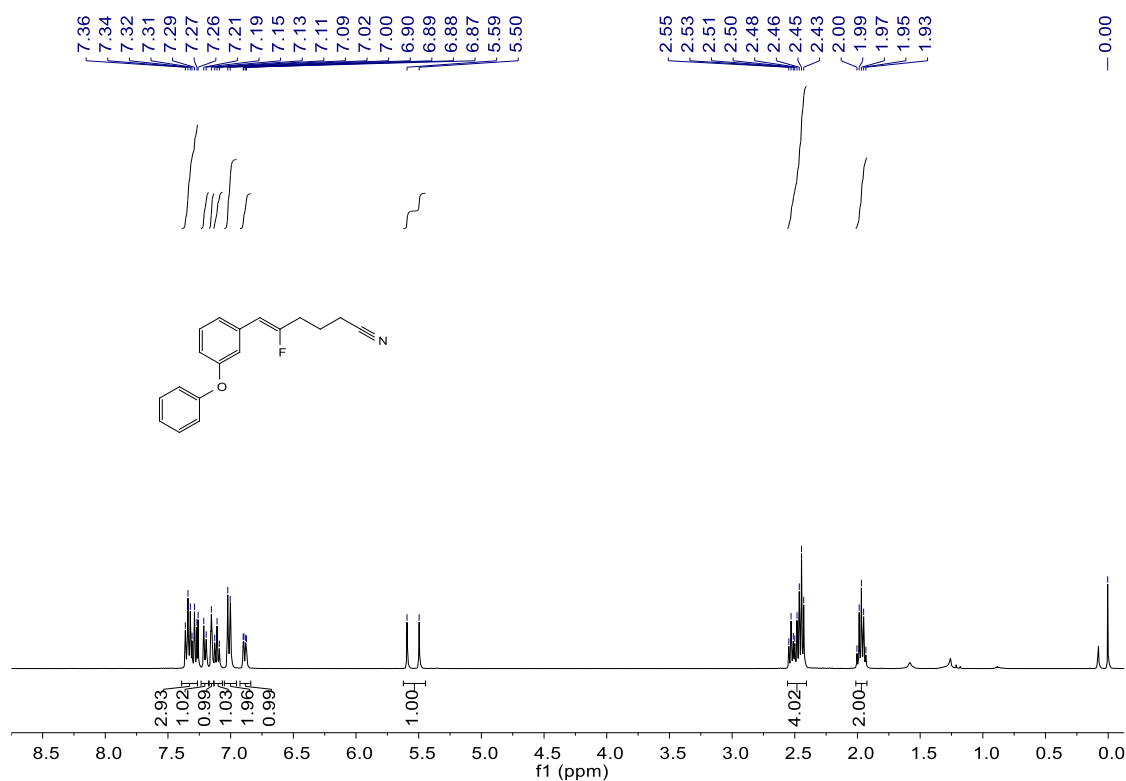
¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dt, *J* = 21.2, 8.2 Hz, 3H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.89 (dd, *J* = 8.0, 2.3 Hz, 1H), 5.54 (d, *J* = 38.7 Hz, 1H), 2.56 – 2.40 (m, 4H), 1.97 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -102.20.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.66 (d, *J* = 267.3 Hz), 157.35 (d, *J* = 13.0 Hz), 134.90 (d, *J* = 2.3 Hz), 129.88, 129.85, 123.57 (d, *J* = 7.2 Hz), 123.40, 119.08, 119.02, 118.97, 118.95, 117.87 (d, *J* = 1.9 Hz), 107.44 (d, *J* = 8.0 Hz), 31.92 (d, *J* = 27.3 Hz), 22.30, 16.40.

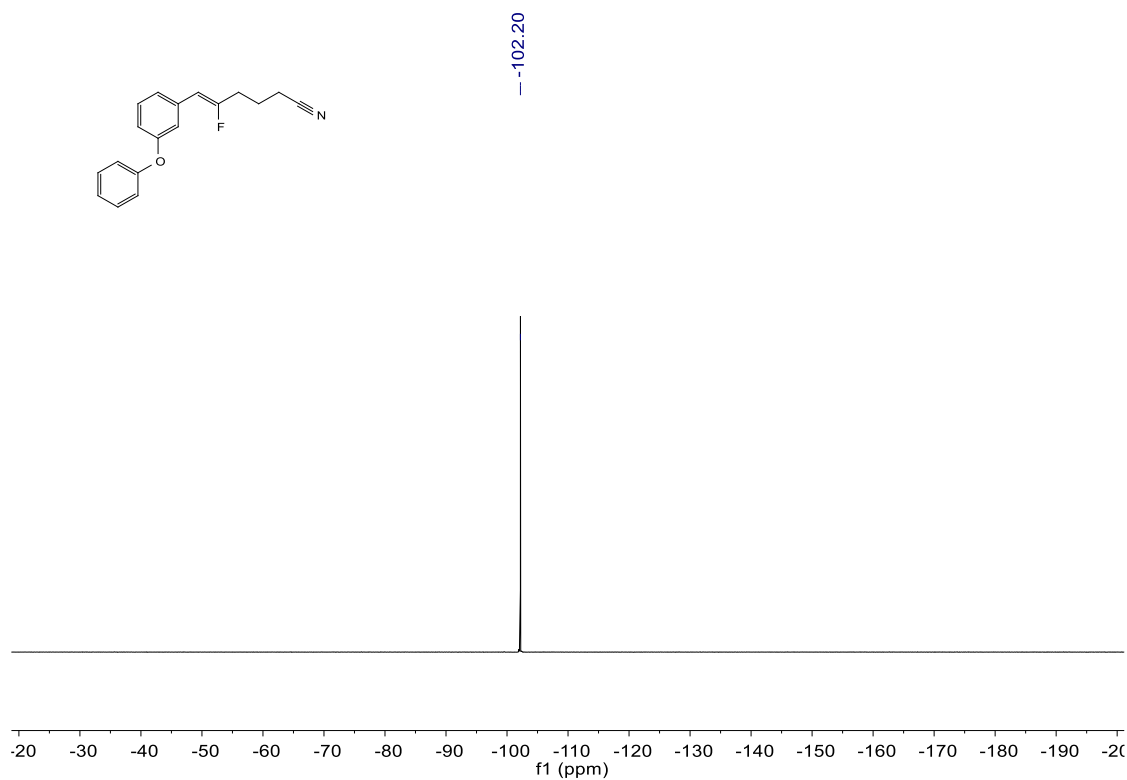
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₈H₁₆FNO: 282.1288; found: 282.1284.

¹H NMR (400 MHz, Chloroform-*d*)

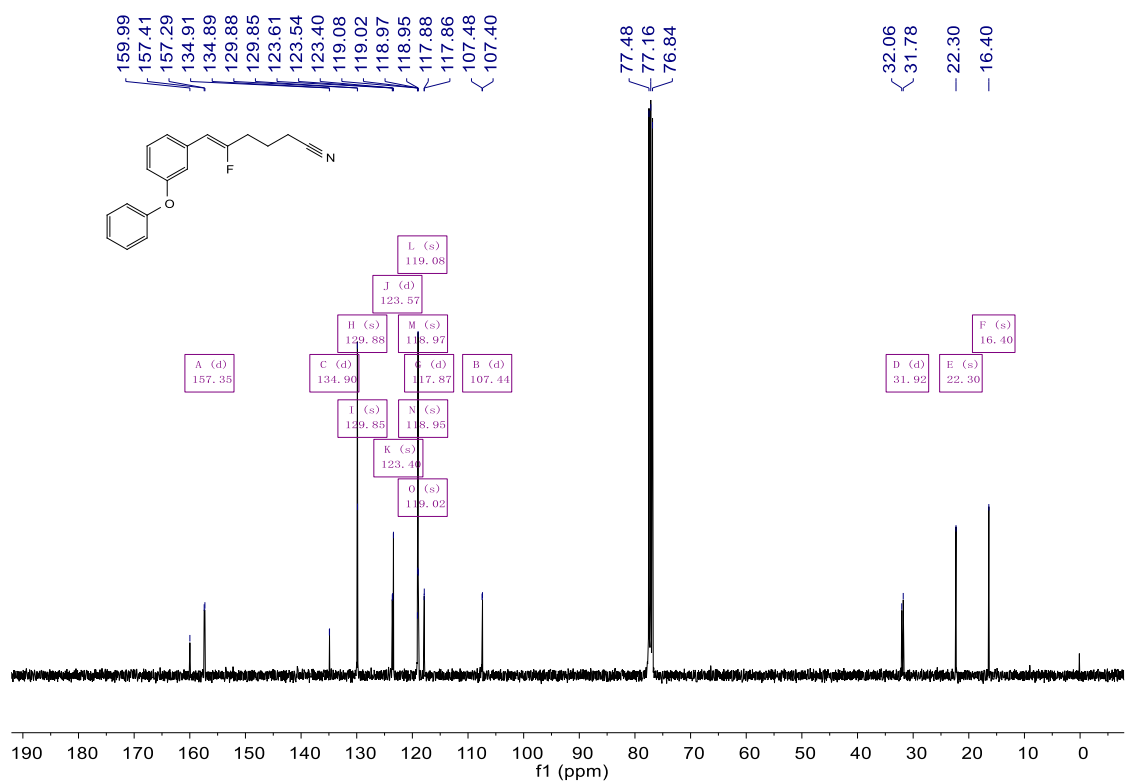


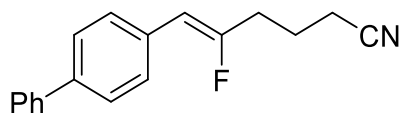
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-6-([1,1'-biphenyl]-4-yl)-5-fluorohex-5-enitrile

Following the general procedure (**c4**, yellow liquid, 24.9 mg, 47%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

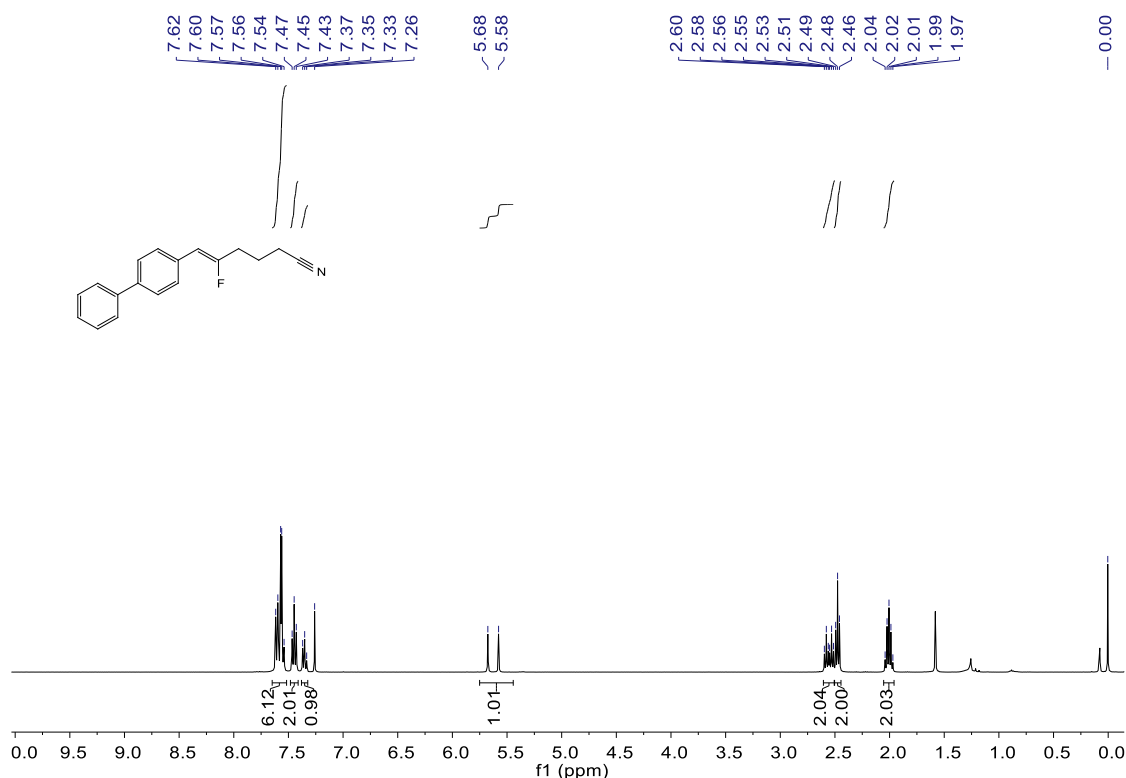
¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.52 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 5.63 (d, *J* = 39.2 Hz, 1H), 2.55 (dt, *J* = 19.1, 7.1 Hz, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.01 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.22.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.32 (d, *J* = 266.3 Hz), 140.72, 139.97 (d, *J* = 2.1 Hz), 132.24 (d, *J* = 2.7 Hz), 128.98, 128.94, 128.91, 127.49, 127.18 (d, *J* = 20.2 Hz), 119.20, 107.55 (d, *J* = 8.1 Hz), 31.99 (d, *J* = 27.4 Hz), 22.33, 16.40.

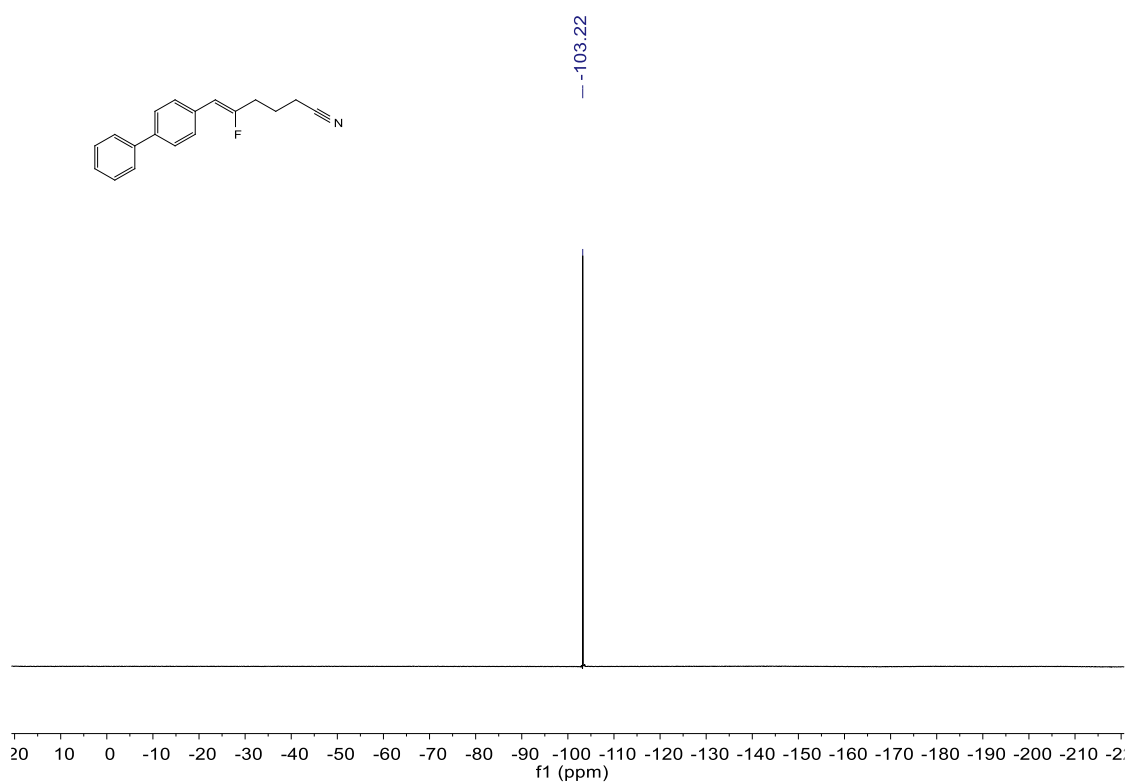
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₈H₁₆FN: 266.1340; found: 266.1346.

¹H NMR (400 MHz, Chloroform-*d*)

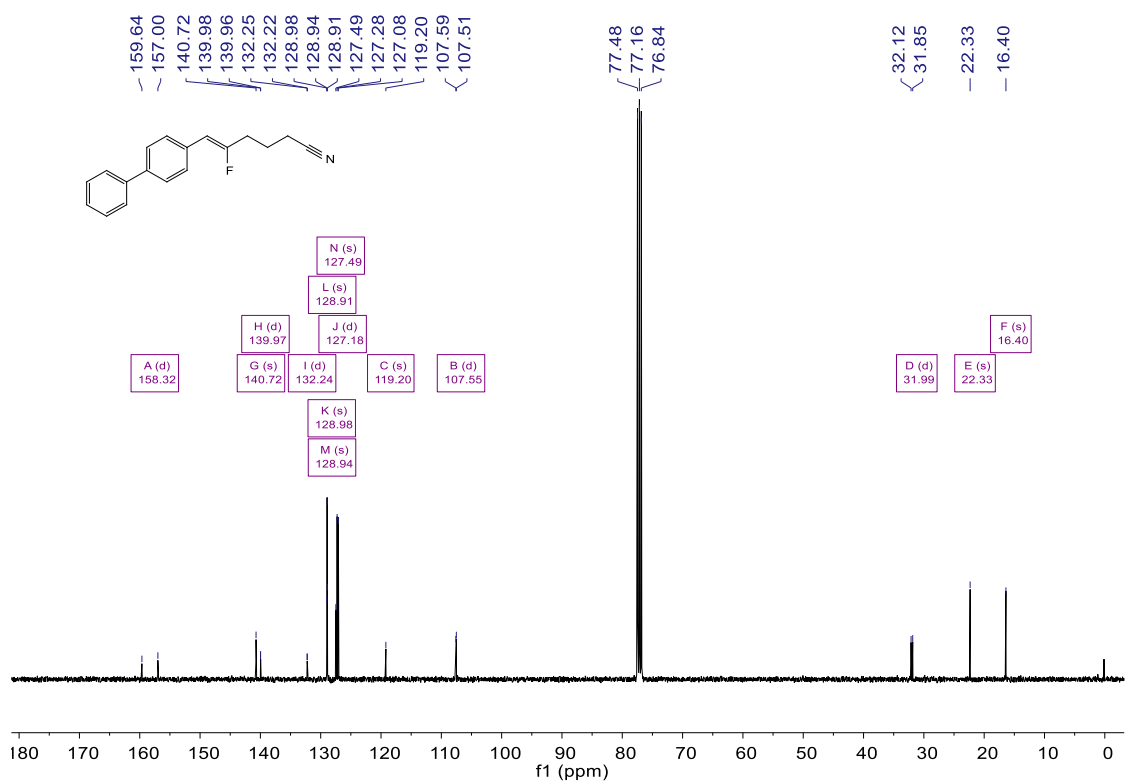


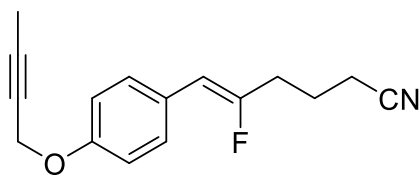
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-6-(4-(but-2-yn-1-yloxy)phenyl)-5-fluorohex-5-enenitrile

Following the general procedure (**c5**, pale-yellow liquid, 42.2 mg, 82%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.54 (d, *J* = 39.5 Hz, 1H), 4.67 (q, *J* = 2.3 Hz, 2H), 2.59 – 2.43 (m, 4H), 1.99 (p, *J* = 7.1 Hz, 2H), 1.89 (t, *J* = 2.3 Hz, 3H).

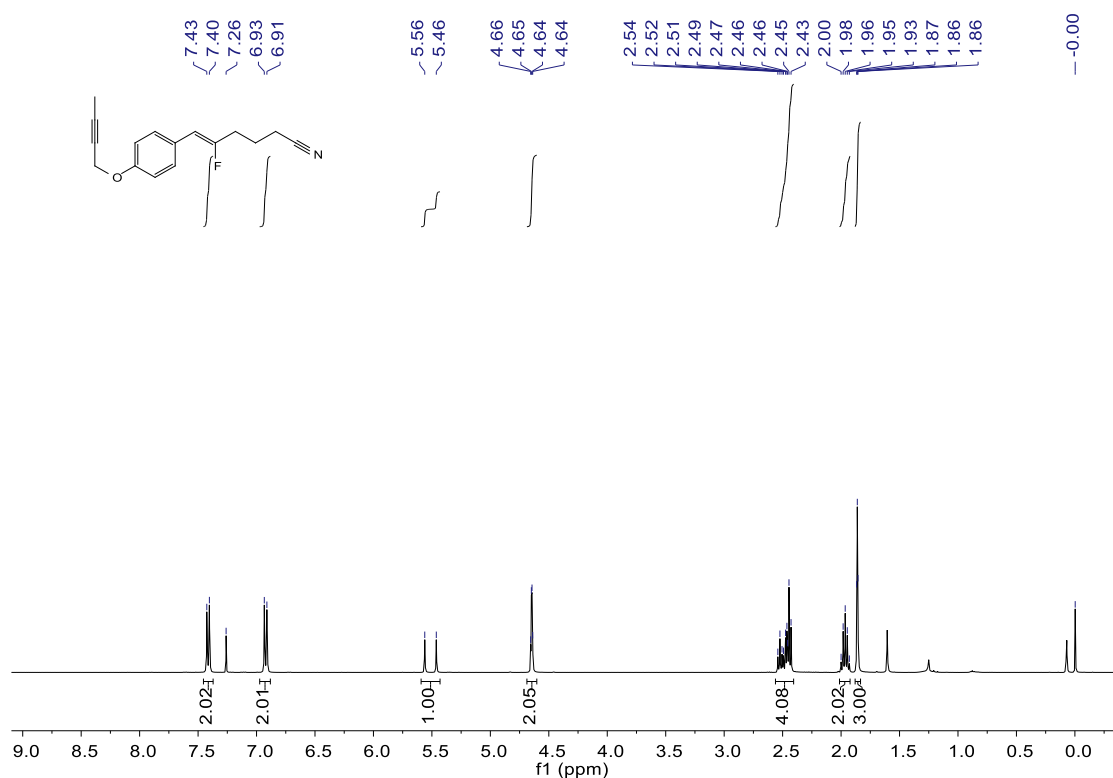
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -106.43.

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.90 (d, *J* = 2.8 Hz), 156.87 (d, *J* = 263.7 Hz), 129.72 (d, *J* = 7.7 Hz), 126.43 (d, *J* = 2.8 Hz), 119.25, 114.91, 107.24 (d, *J* = 8.6 Hz), 84.00, 73.97, 56.49, 31.86 (d, *J* = 27.5 Hz), 22.35, 16.34, 3.85.

156.87 (d, *J* = 263.7 Hz)

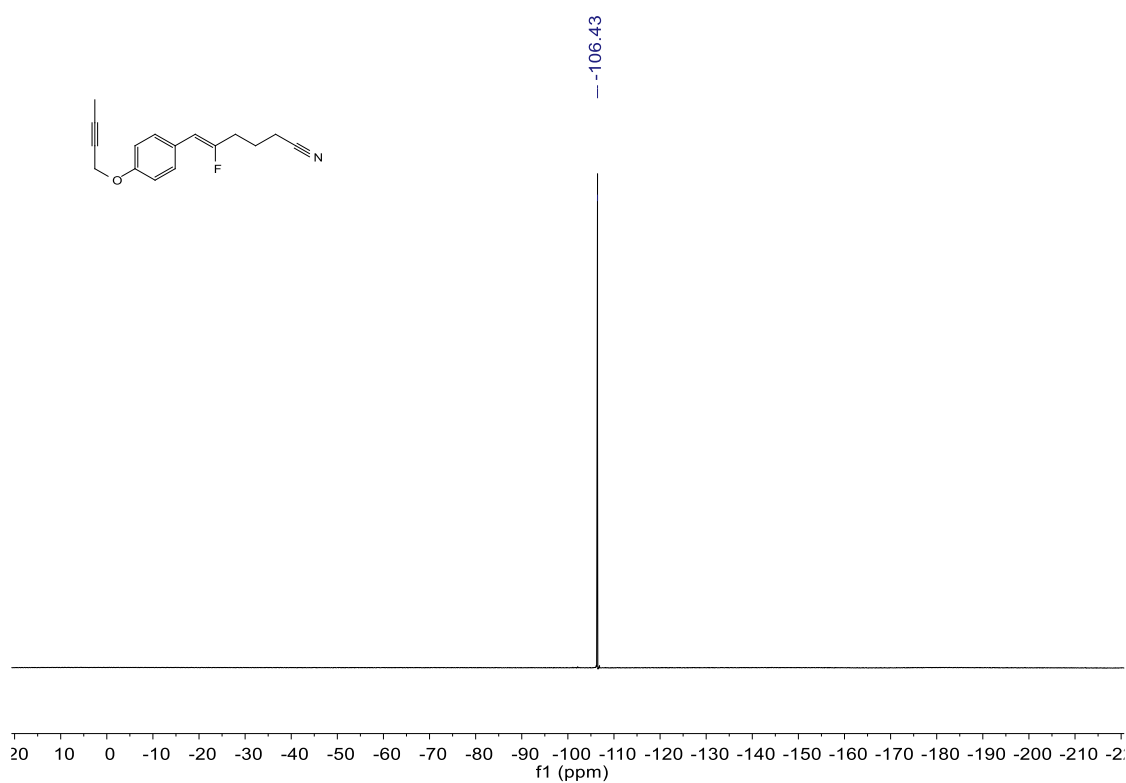
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₆H₁₆FNO: 258.1288; found: 258.1285.

¹H NMR (400 MHz, Chloroform-*d*)

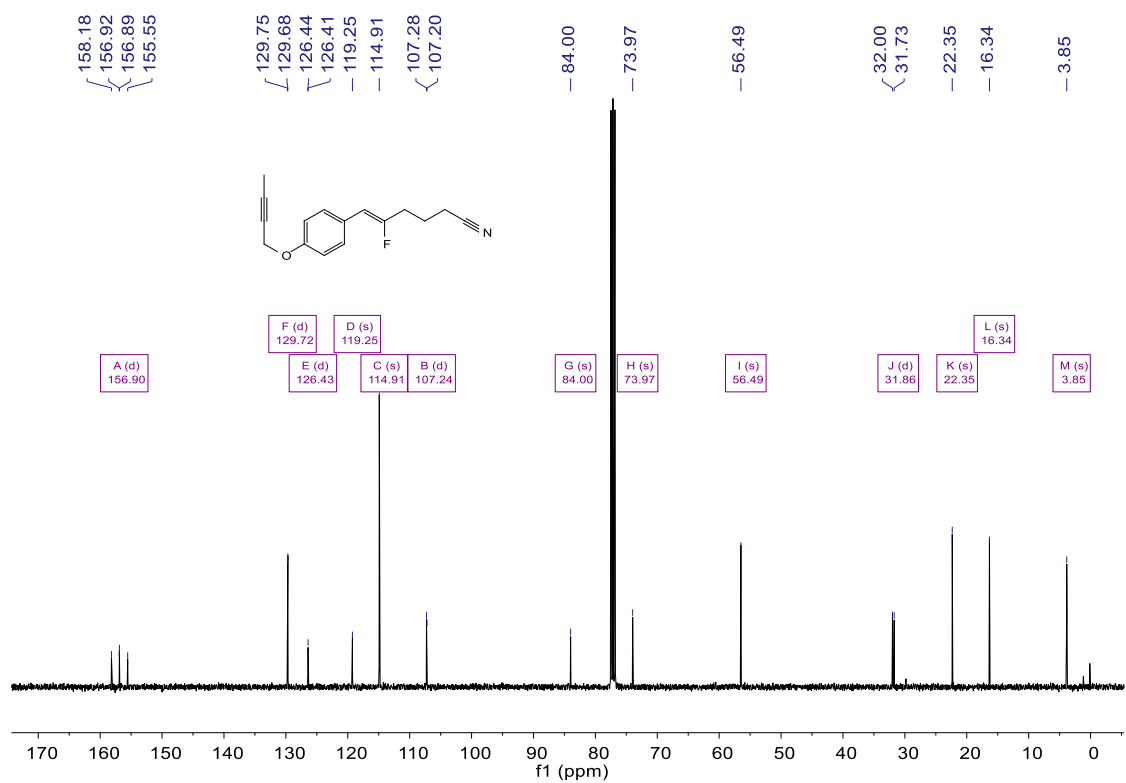


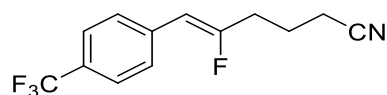
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-6-(4-(trifluoromethyl)phenyl)hex-5-enenitrile

Following the general procedure (**c6**, pale-yellow solid, 23.7 mg, 46%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

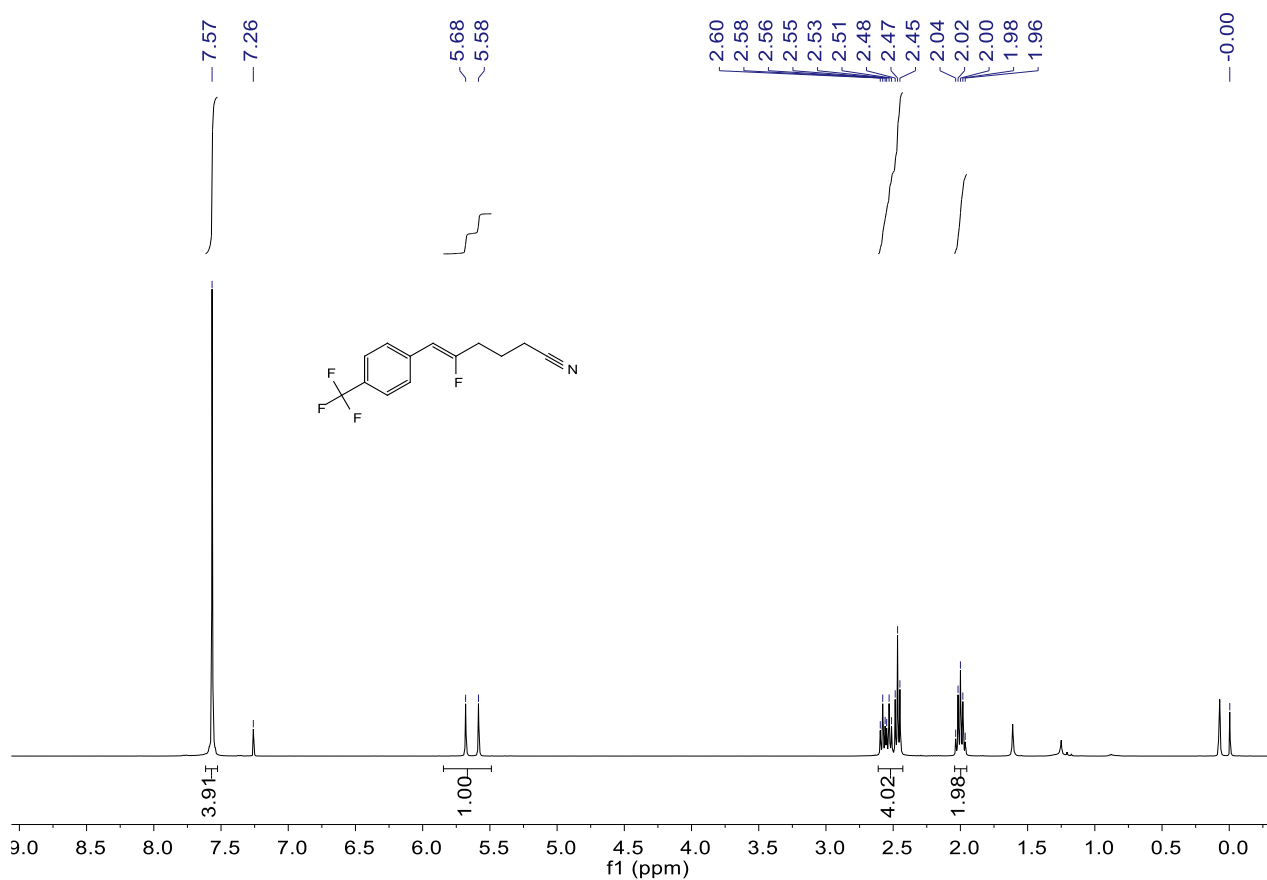
¹H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 4H), 5.63 (d, J = 38.4 Hz, 1H), 2.61 – 2.43 (m, 4H), 2.00 (p, J = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.56, -100.30.

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.94 (d, J = 269.4 Hz), 136.68, 128.69, 128.61, 125.51 (q, J = 3.8 Hz), 121.52 (q, J = 271.8 Hz), 119.02, 106.88 (d, J = 7.9 Hz), 31.93 (d, J = 26.9 Hz), 22.18, 16.43.

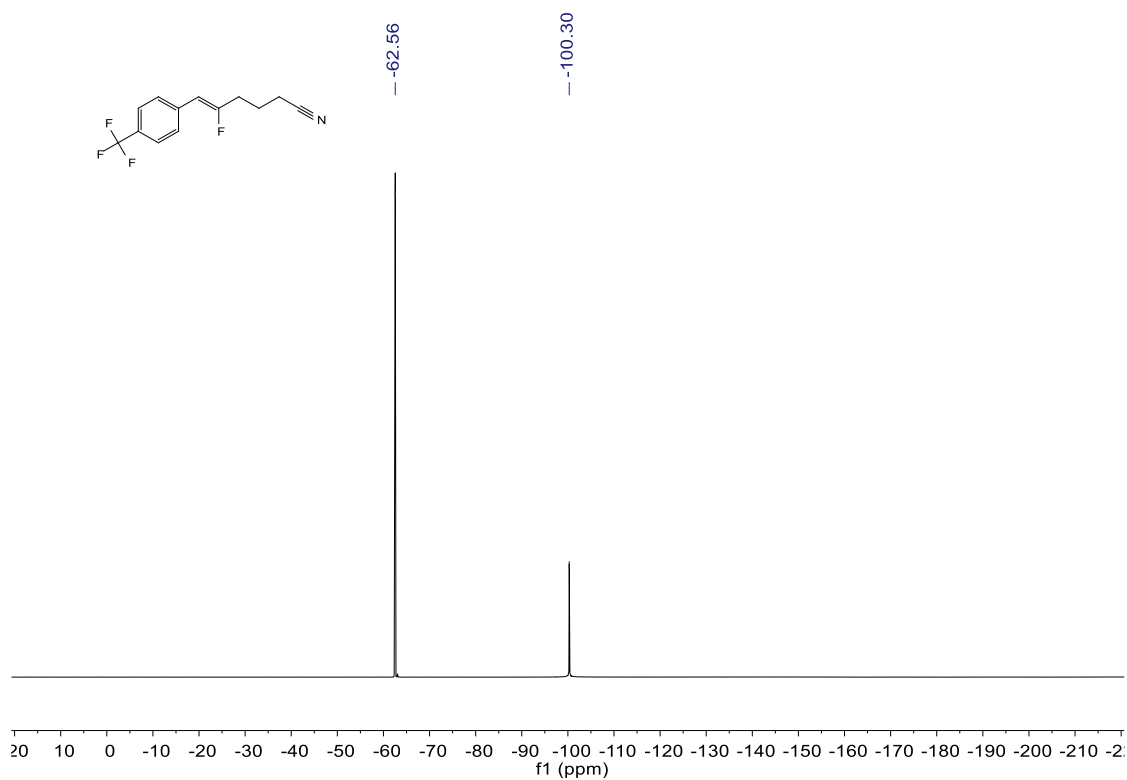
HRMS (ESI) m/z : (M+Na)⁺ Calcd for C₁₃H₁₁F₄N: 280.0719; found: 280.0711.

¹H NMR (400 MHz, Chloroform-*d*)

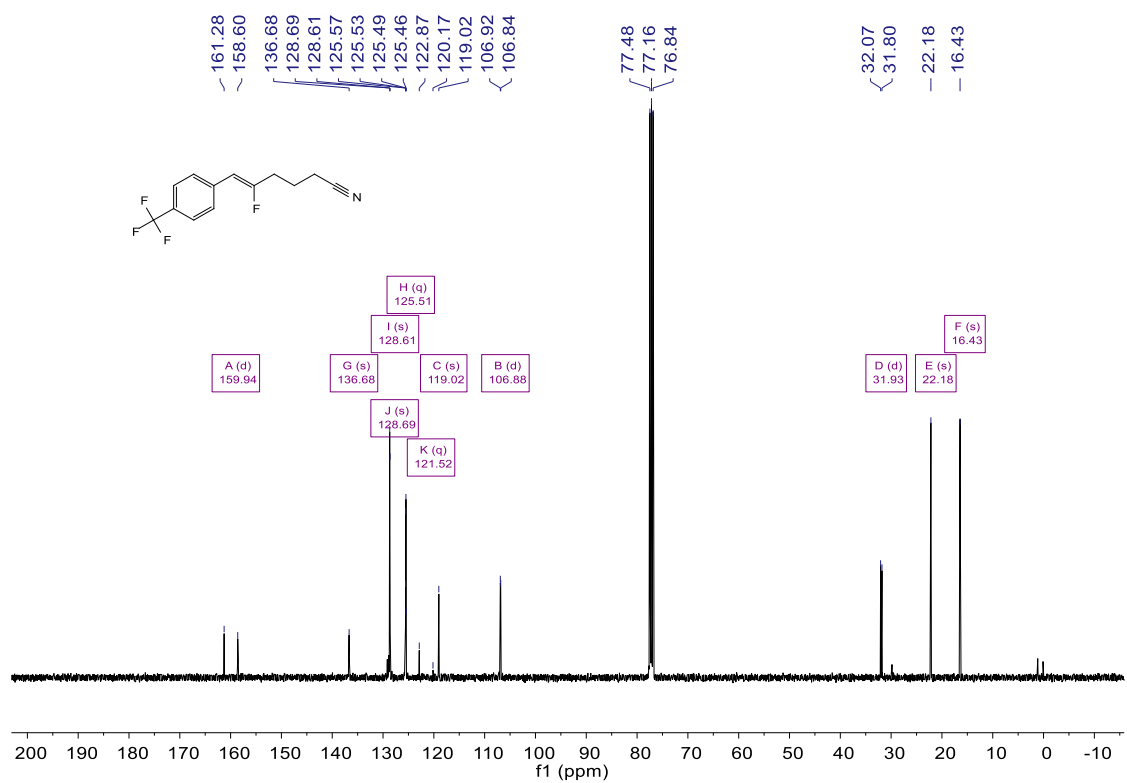


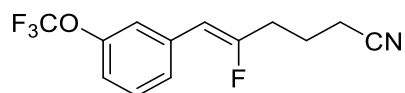
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-6-(3-(trifluoromethoxy)phenyl)hex-5-enitrile

Following the general procedure (**c7**, brown liquid, 38.8 mg, 71%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

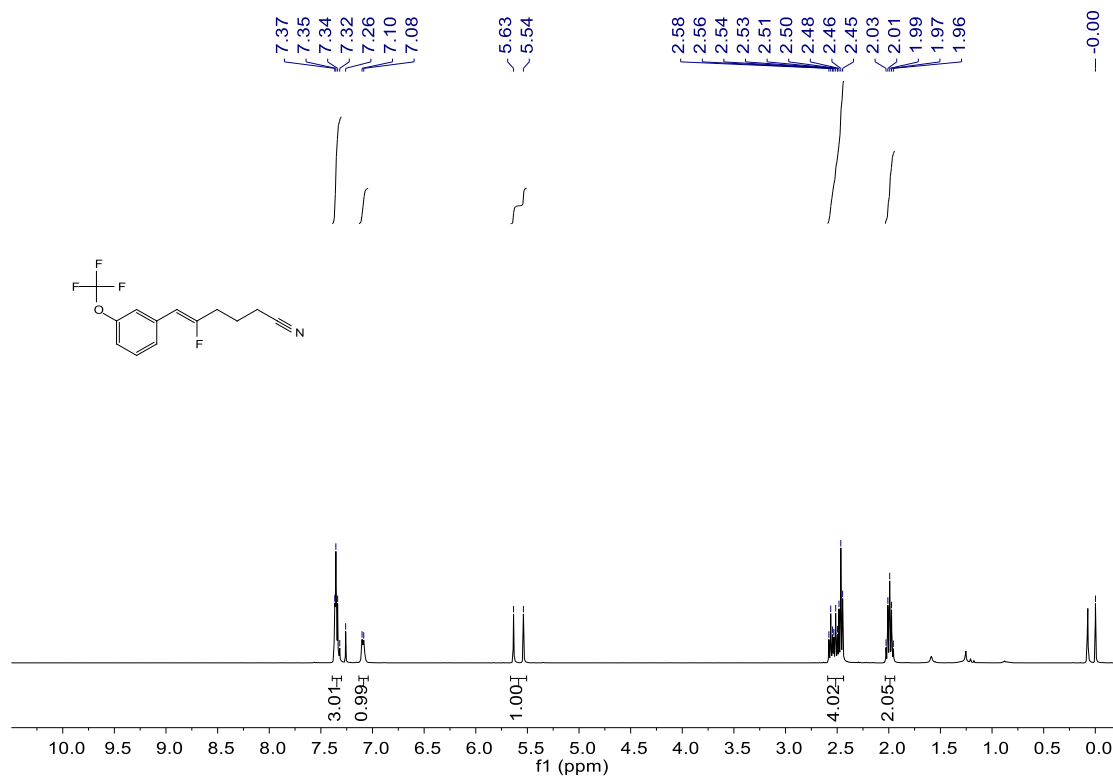
¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 3H), 7.09 (d, *J* = 6.5 Hz, 1H), 5.59 (d, *J* = 38.2 Hz, 1H), 2.59 – 2.44 (m, 4H), 1.99 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -57.74, -101.16.

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.40 (d, *J* = 268.2 Hz), 149.47, 135.09 (d, *J* = 2.6 Hz), 129.87, 126.90 (d, *J* = 7.1 Hz), 120.96 (d, *J* = 8.6 Hz), 120.59 (q, *J* = 257.2 Hz), 119.69, 119.03, 106.82 (d, *J* = 7.9 Hz), 31.89 (d, *J* = 27.0 Hz), 22.21, 16.43.

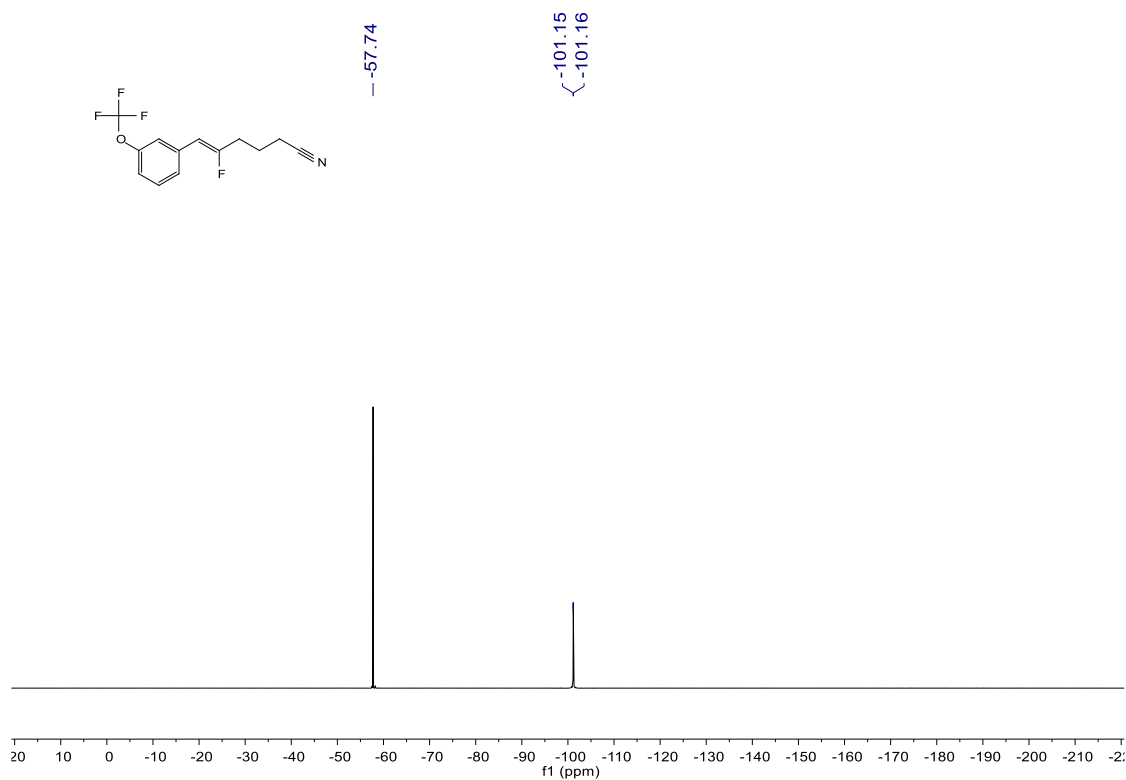
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₃H₁₁F₄NO: 274.0850; found: 274.0839.

¹H NMR (400 MHz, Chloroform-*d*)

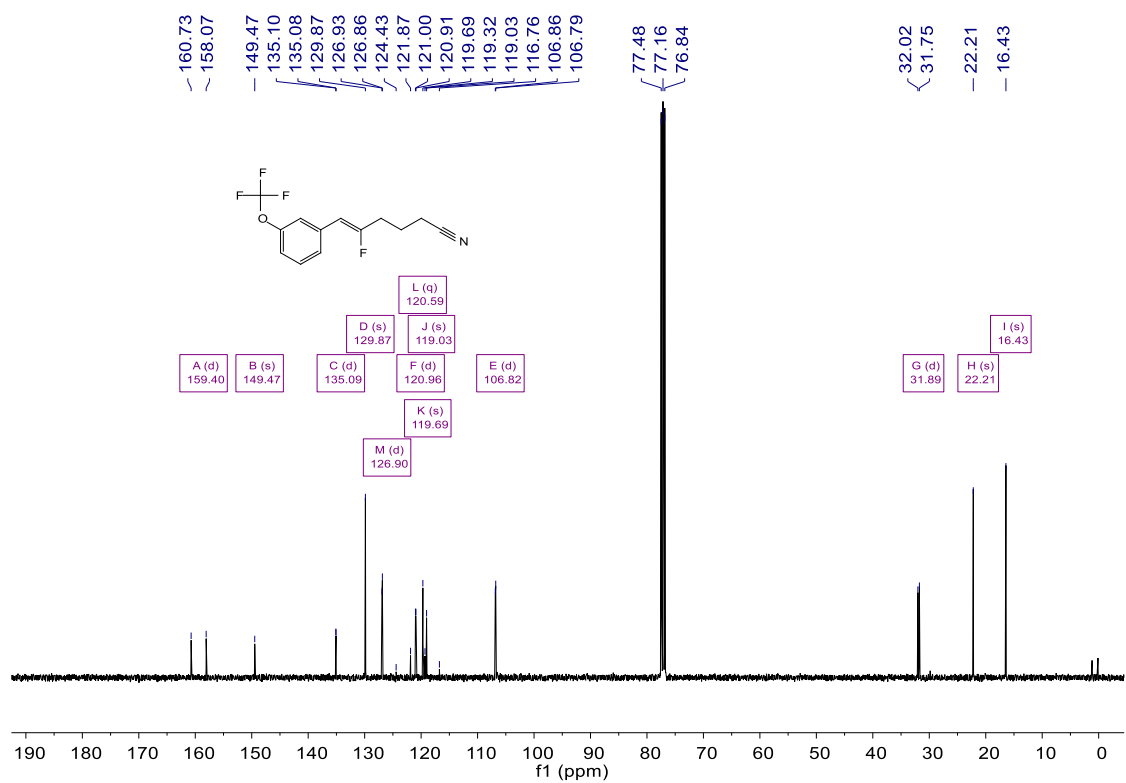


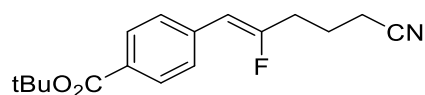
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^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)




tert-butyl (Z)-4-(5-cyano-2-fluoropent-1-en-1-yl)benzoate

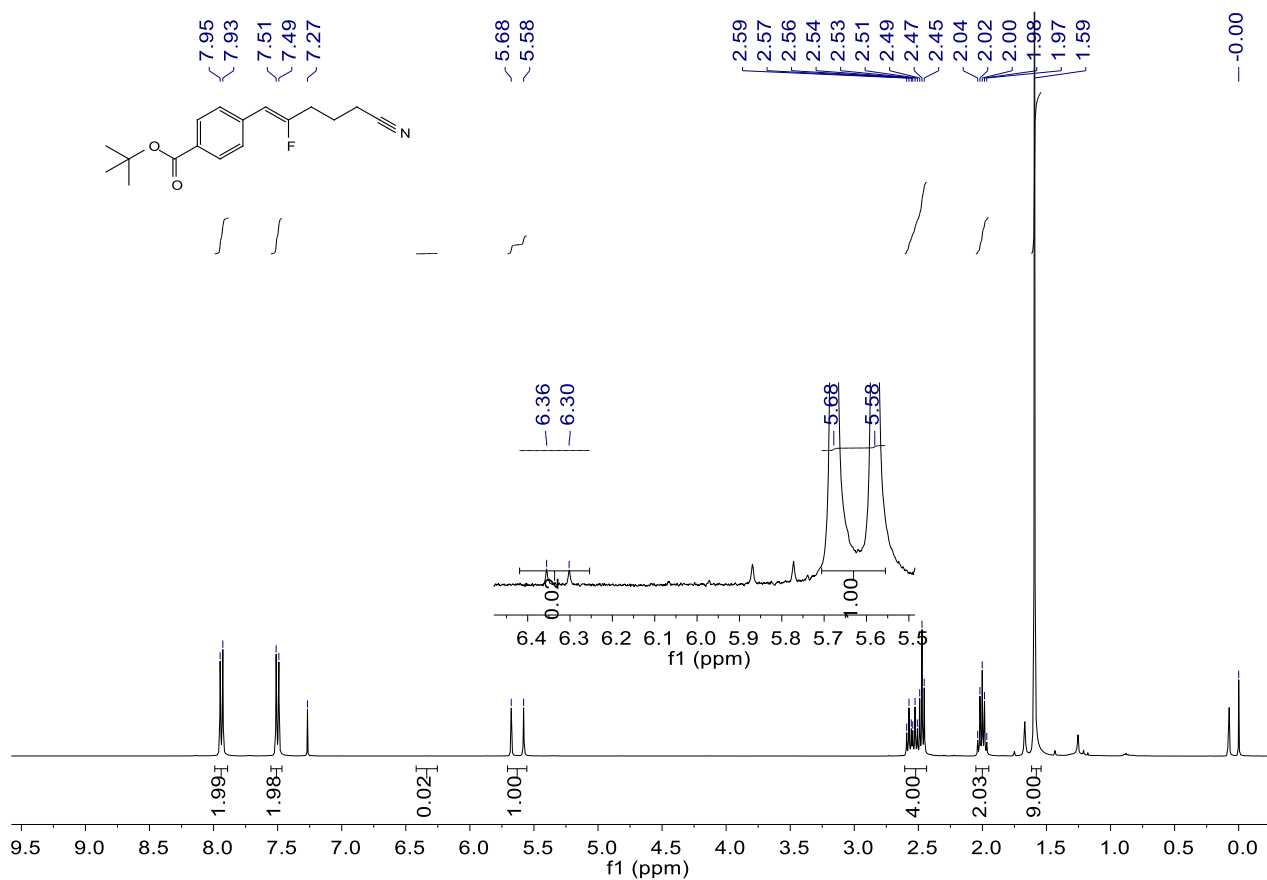
Following the general procedure (**c8**, pale-yellow liquid, 24.3 mg, 42%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 5.62 (d, J = 38.7 Hz, 1H), 2.60 – 2.43 (m, 4H), 1.99 (p, J = 7.1 Hz, 2H), 1.59 (s, 9H).

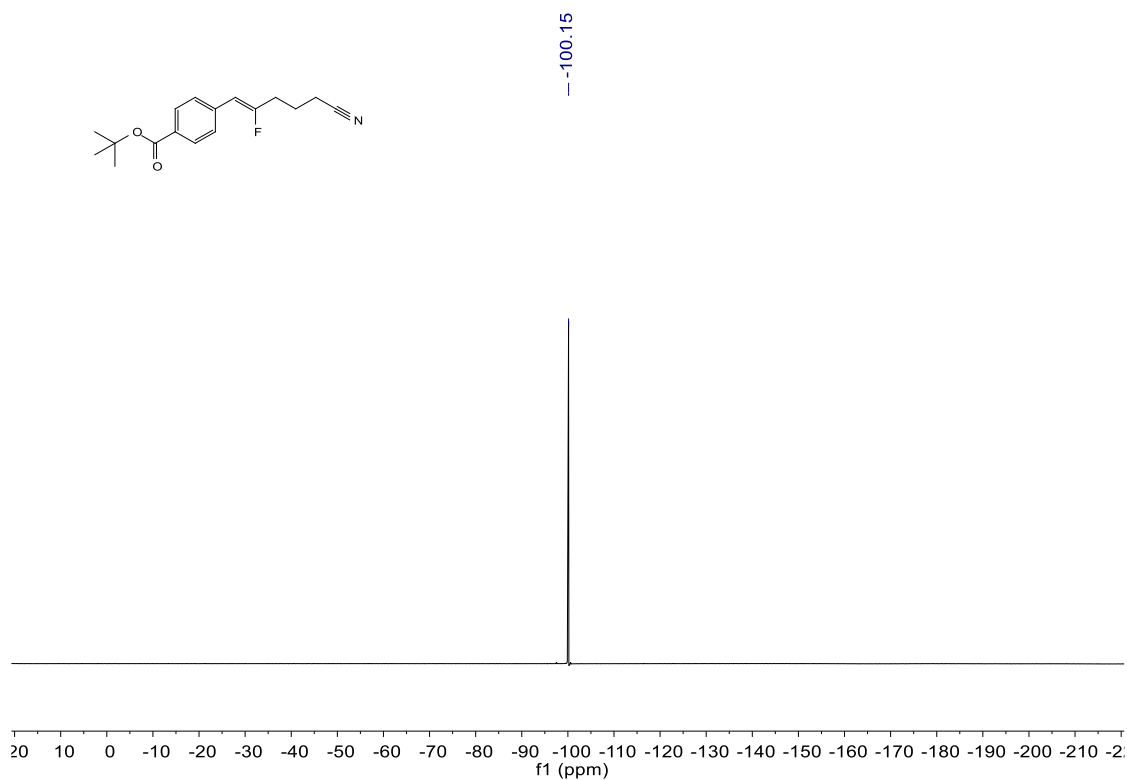
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -100.15.

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.52, 159.57 (d, J = 269.1 Hz), 137.13 (d, J = 2.6 Hz), 130.42 (d, J = 2.4 Hz), 129.63, 128.12 (d, J = 7.4 Hz), 118.98, 107.29 (d, J = 7.6 Hz), 81.03, 31.91 (d, J = 27.3 Hz), 28.22, 22.14, 16.36.

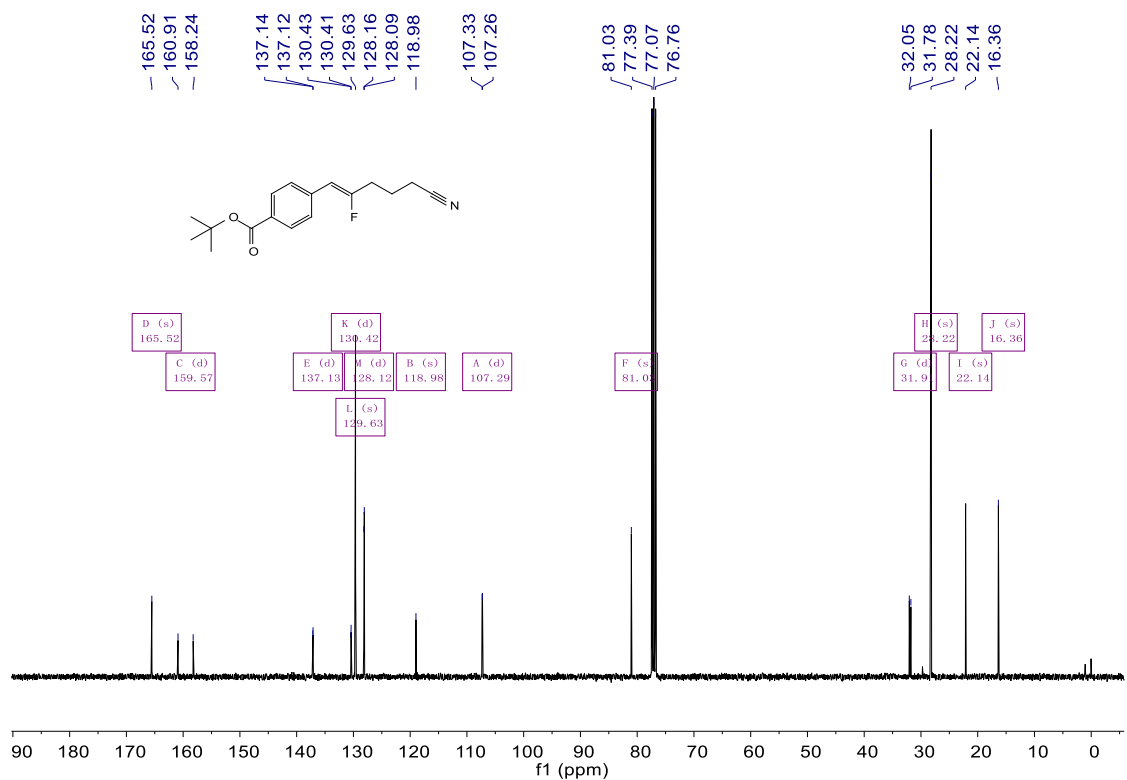
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₇H₂₀FNO₂: 290.1551; found: 290.1555.

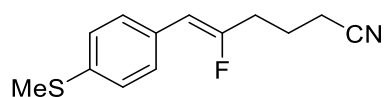
¹H NMR (400 MHz, Chloroform-*d*)


Supporting Information



¹³C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-6-(4-(methylthio)phenyl)hex-5-enitrile

Following the general procedure (**c9**, yellow liquid, 16 mg, 34%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

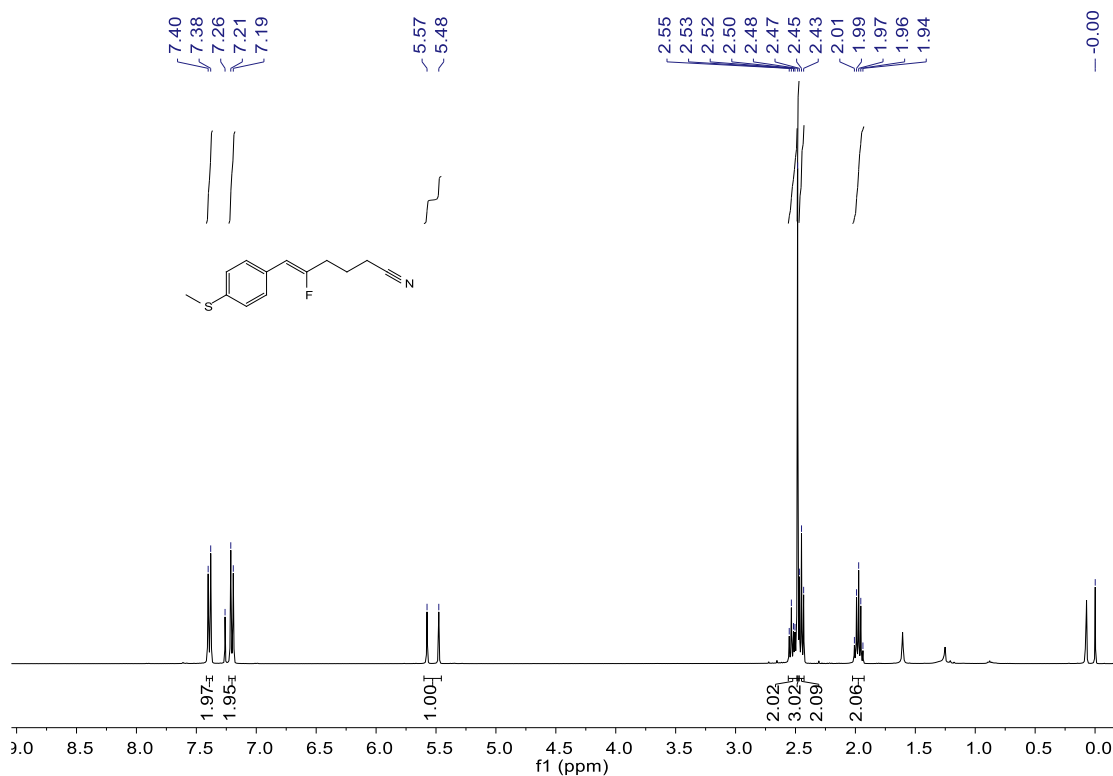
¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 5.53 (d, *J* = 39.3 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.48 (s, 3H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.97 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.75.

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.93 (d, *J* = 265.8 Hz), 137.49 (d, *J* = 2.9 Hz), 130.00 (d, *J* = 2.8 Hz), 128.88 (d, *J* = 7.7 Hz), 126.51, 119.18, 107.34 (d, *J* = 8.1 Hz), 31.92 (d, *J* = 27.5 Hz), 22.30, 16.37, 15.80.

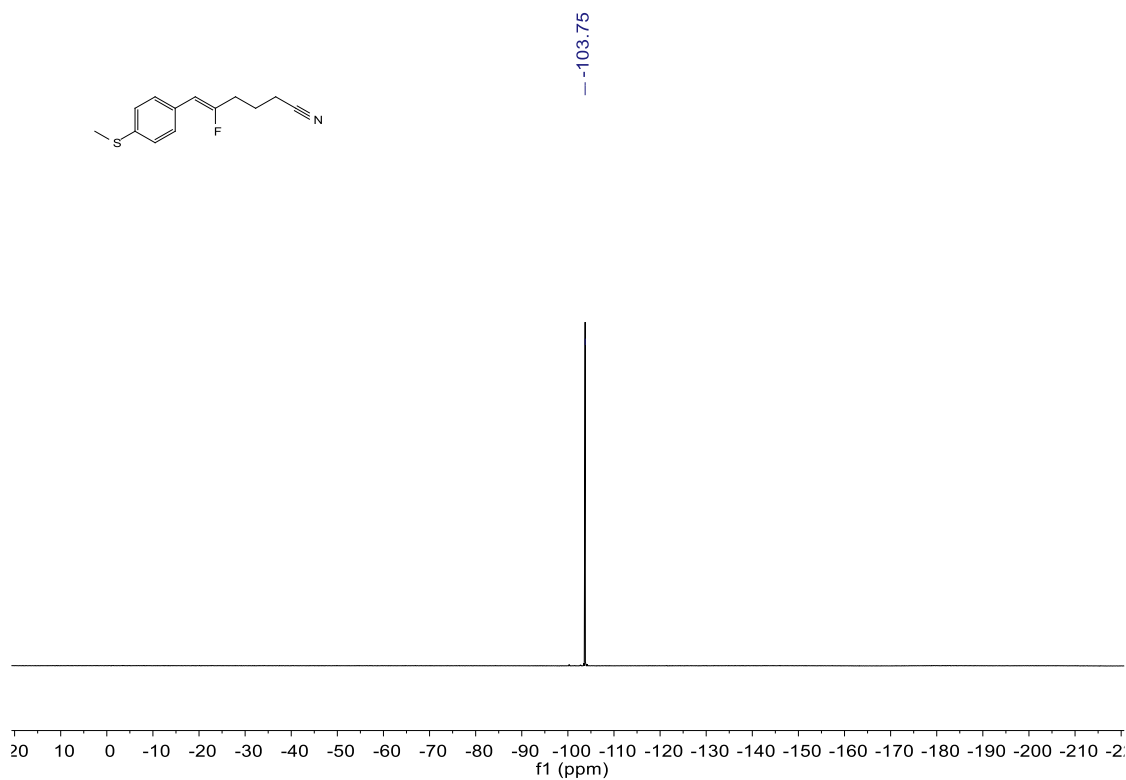
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₃H₁₄FNS: 236.0903; found: 236.0898.

¹H NMR (400 MHz, Chloroform-*d*)

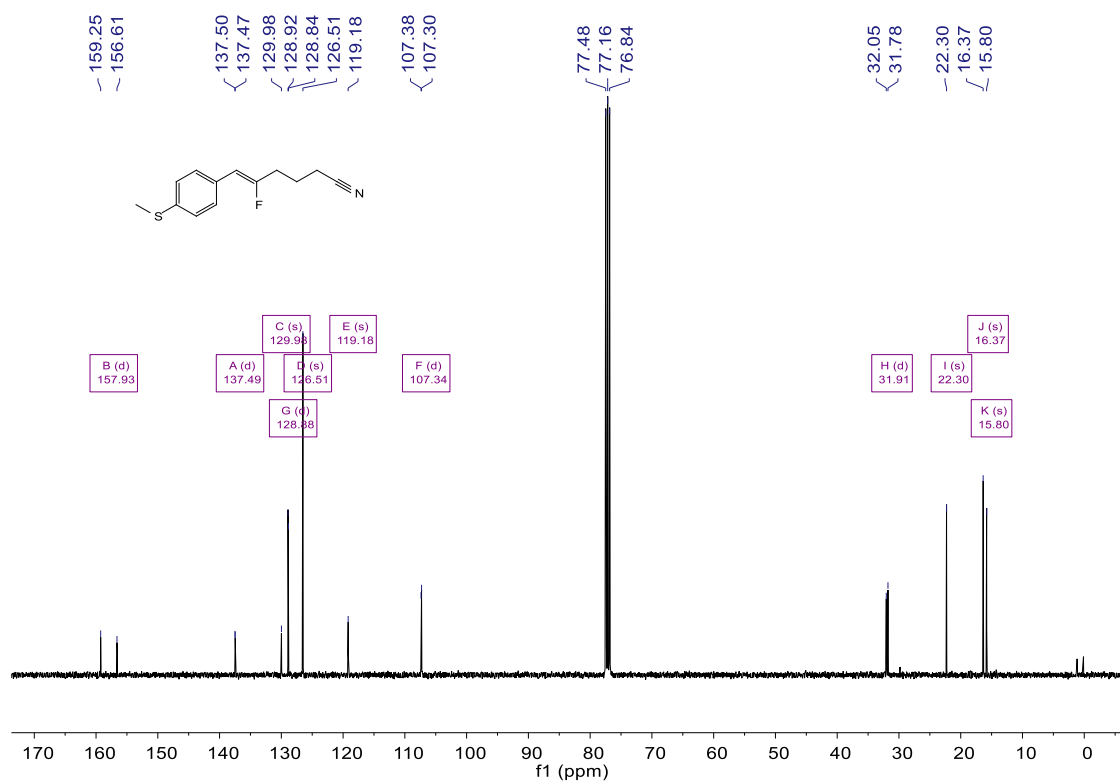


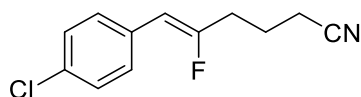
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(Z)-6-(4-chlorophenyl)-5-fluorohex-5-enitrile

Following the general procedure (**c10**, yellow solid, 39.3 mg, 88%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

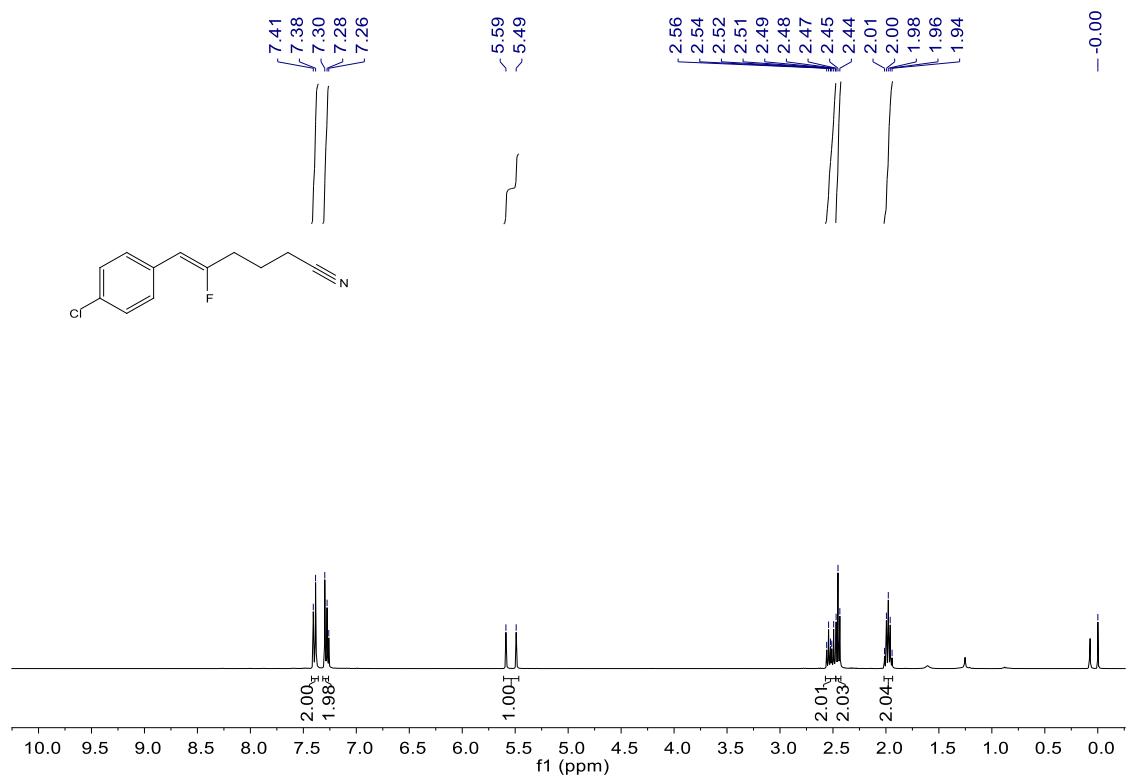
¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 5.54 (d, *J* = 38.7 Hz, 1H), 2.52 (dt, *J* = 19.1, 7.2 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.98 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -102.76.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.61 (d, *J* = 267.2 Hz), 132.87 (d, *J* = 3.5 Hz), 131.64 (d, *J* = 2.8 Hz), 129.76 (d, *J* = 7.5 Hz), 128.76, 119.09, 106.86 (d, *J* = 8.5 Hz), 31.90 (d, *J* = 27.0 Hz), 22.24, 16.40.

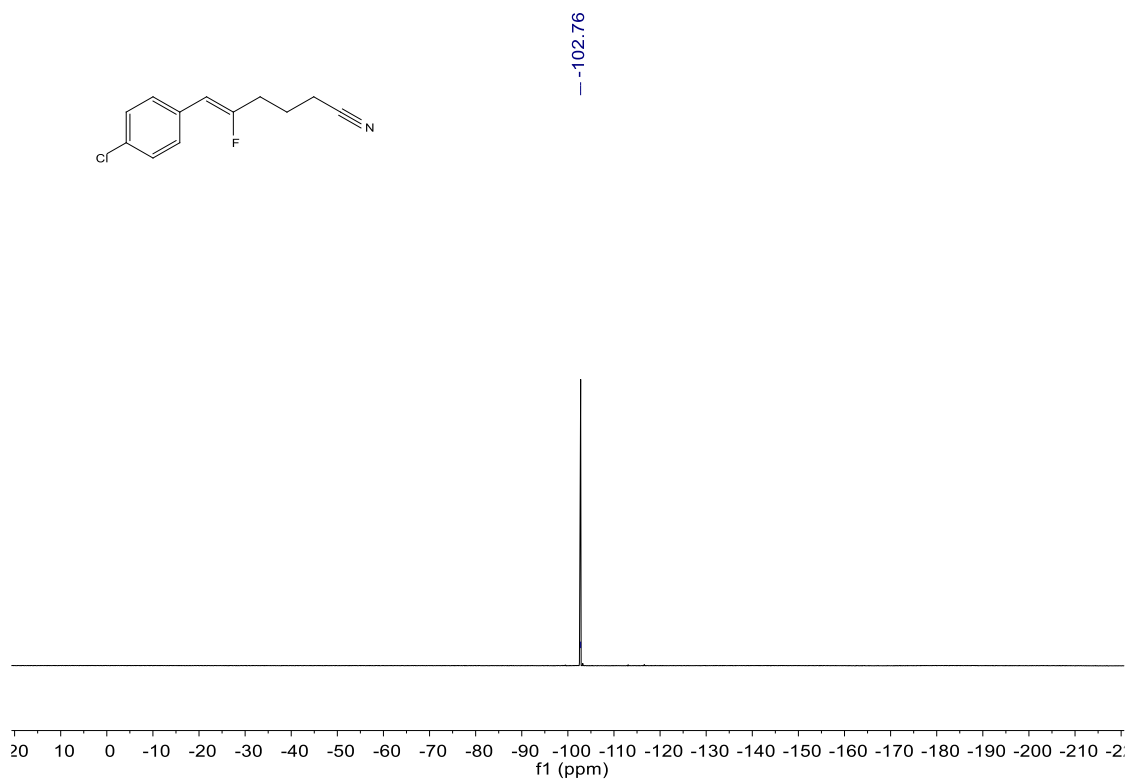
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₂H₁₁ClFN: 224.0637; found: 224.0636.

¹H NMR (400 MHz, Chloroform-*d*)

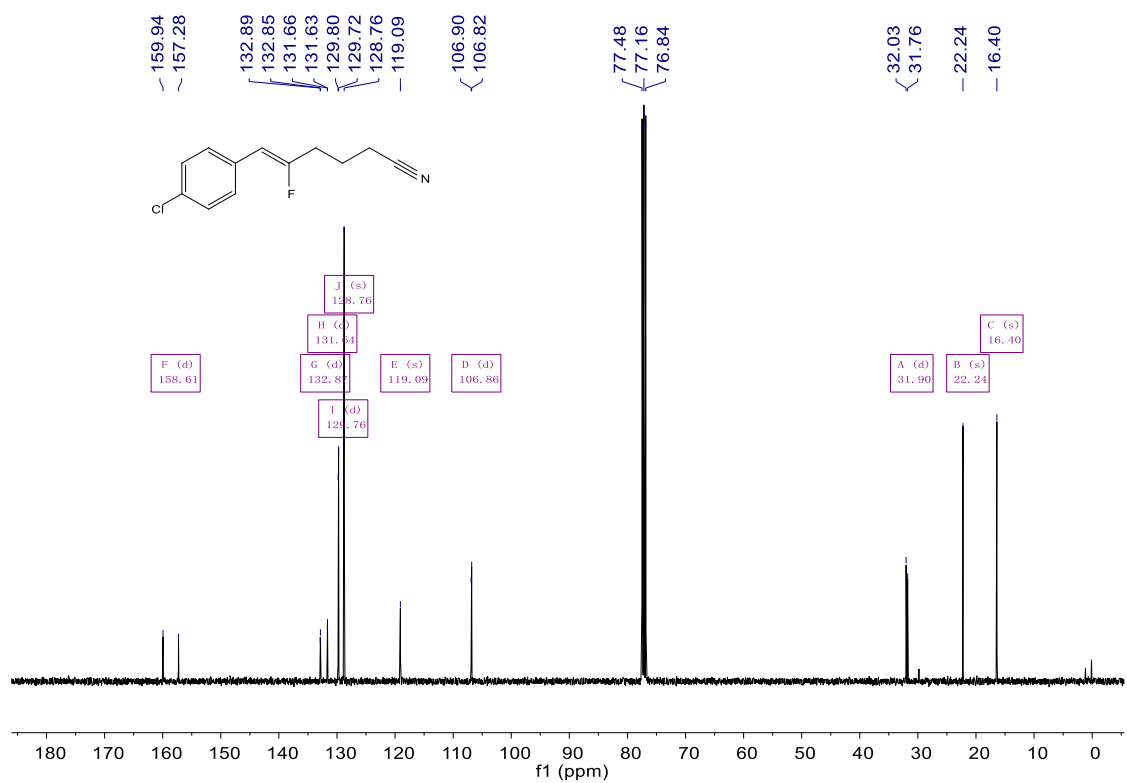


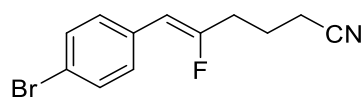
Supporting Information

^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-6-(4-bromophenyl)-5-fluorohex-5-enenitrile

Following the general procedure (**c11**, yellow liquid, 29.4 mg, 55%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

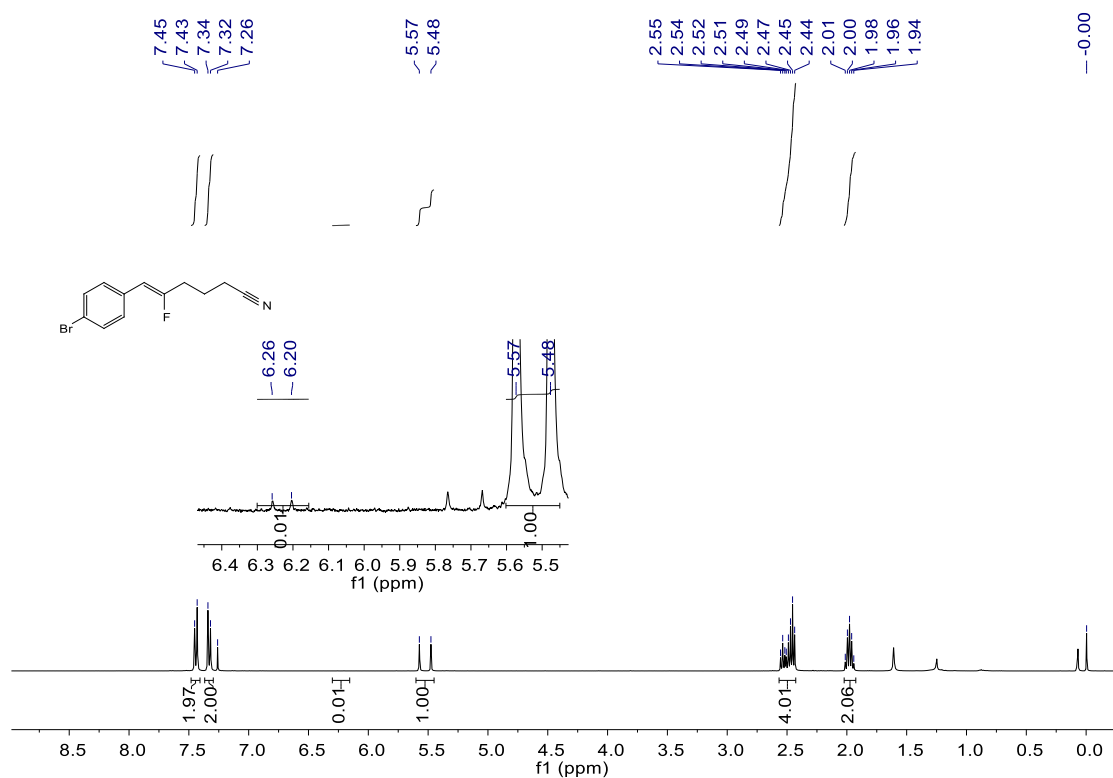
¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 5.52 (d, J = 38.7 Hz, 1H), 2.57 – 2.43 (m, 4H), 1.98 (p, J = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -102.38.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.73 (d, J = 267.2 Hz), 132.07 (d, J = 2.3 Hz), 131.72, 130.06 (d, J = 7.4 Hz), 121.04 (d, J = 3.6 Hz), 119.10, 106.92 (d, J = 8.5 Hz), 31.92 (d, J = 27.0 Hz), 22.19, 16.41.

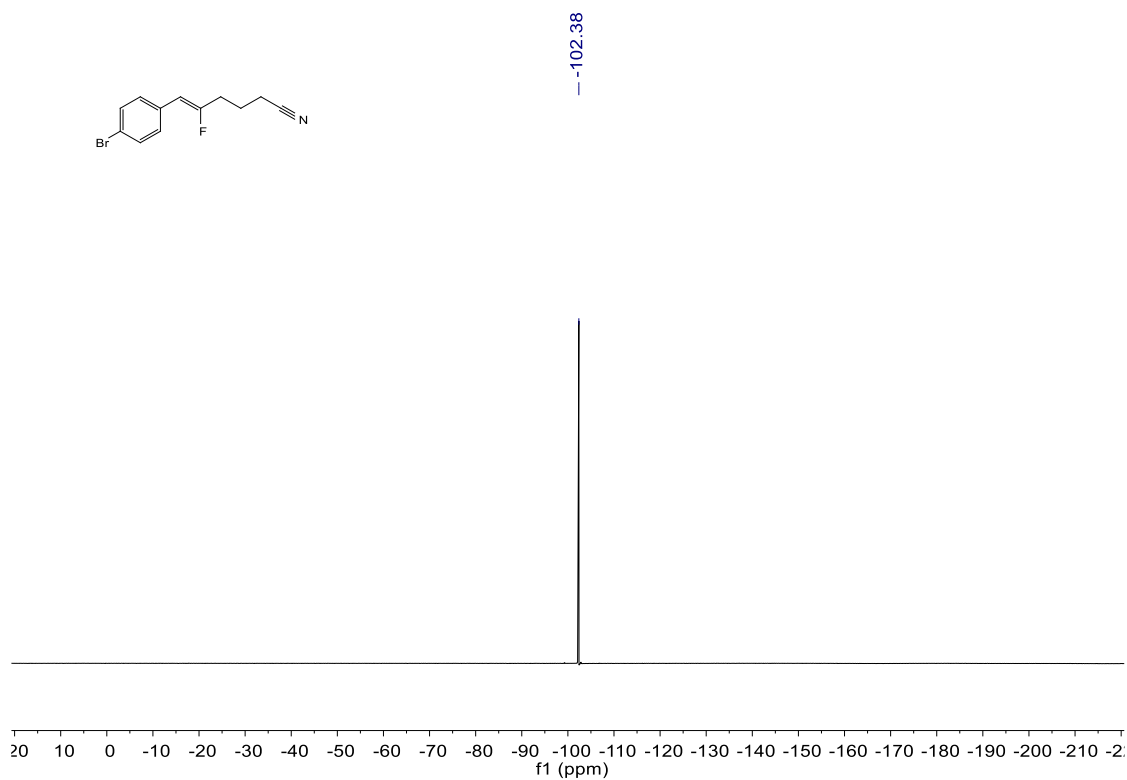
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₂H₁₁BrFN: 268.0132; found: 268.0135.

¹H NMR (400 MHz, Chloroform-*d*)

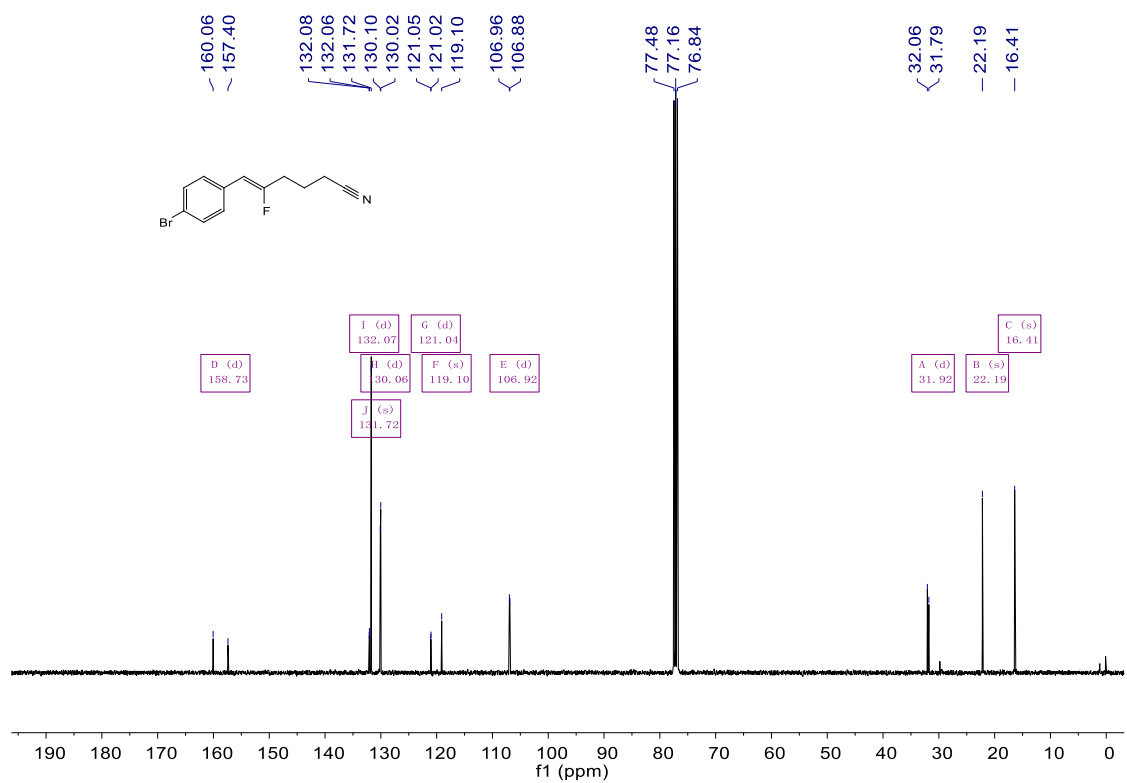


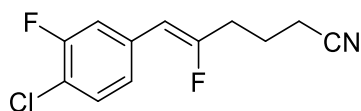
Supporting Information

^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z)-6-(4-chloro-3-fluorophenyl)-5-fluorohex-5-enitrile

Following the general procedure (**c12**, pale-yellow liquid, 32.3 mg, 67%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

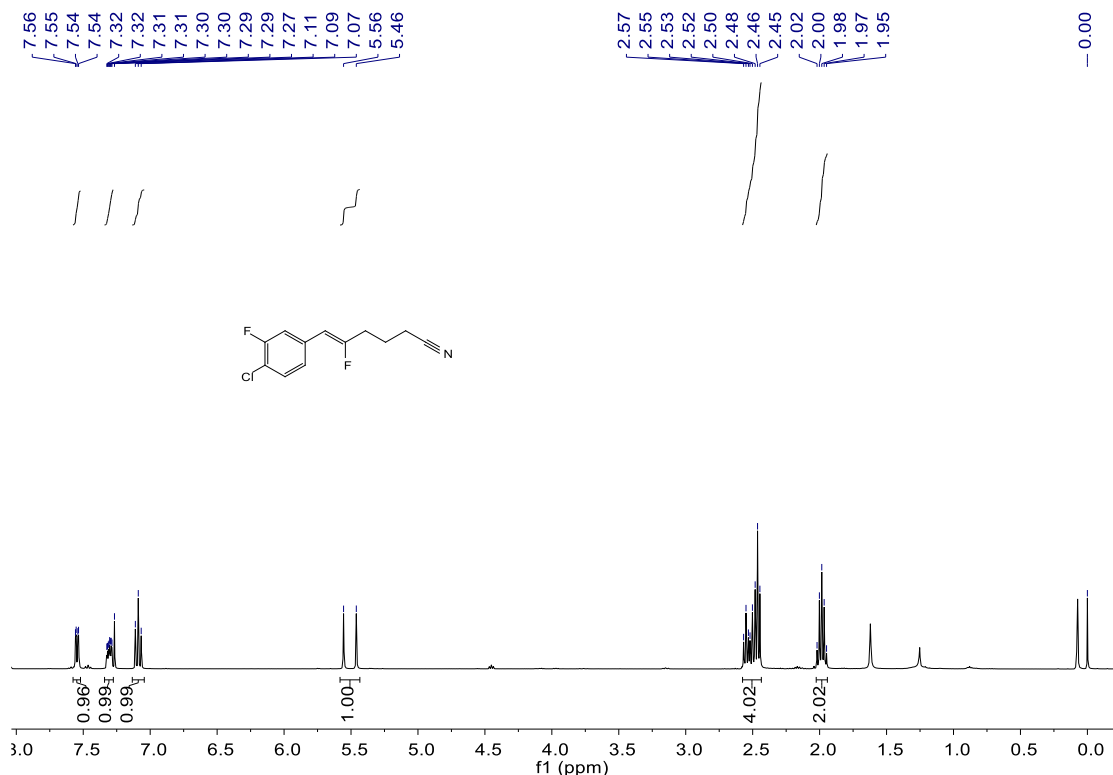
¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, J = 7.1, 2.1 Hz, 1H), 7.30 (ddd, J = 8.5, 4.6, 2.2 Hz, 1H), 7.08 (t, J = 8.7 Hz, 1H), 5.50 (d, J = 38.1 Hz, 1H), 2.57 – 2.43 (m, 4H), 1.98 (p, J = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -102.96, -116.72.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.79 (dd, J = 267.2, 2.3 Hz), 157.03 (dd, J = 249.7, 3.3 Hz), 130.47 (d, J = 8.7 Hz), 130.40 (d, J = 3.6 Hz), 128.28 (t, J = 7.2 Hz), 121.07 (d, J = 18.1 Hz), 119.04, 116.65 (d, J = 21.4 Hz), 105.93 (d, J = 8.1 Hz), 31.81 (d, J = 26.9 Hz), 22.17, 16.41.

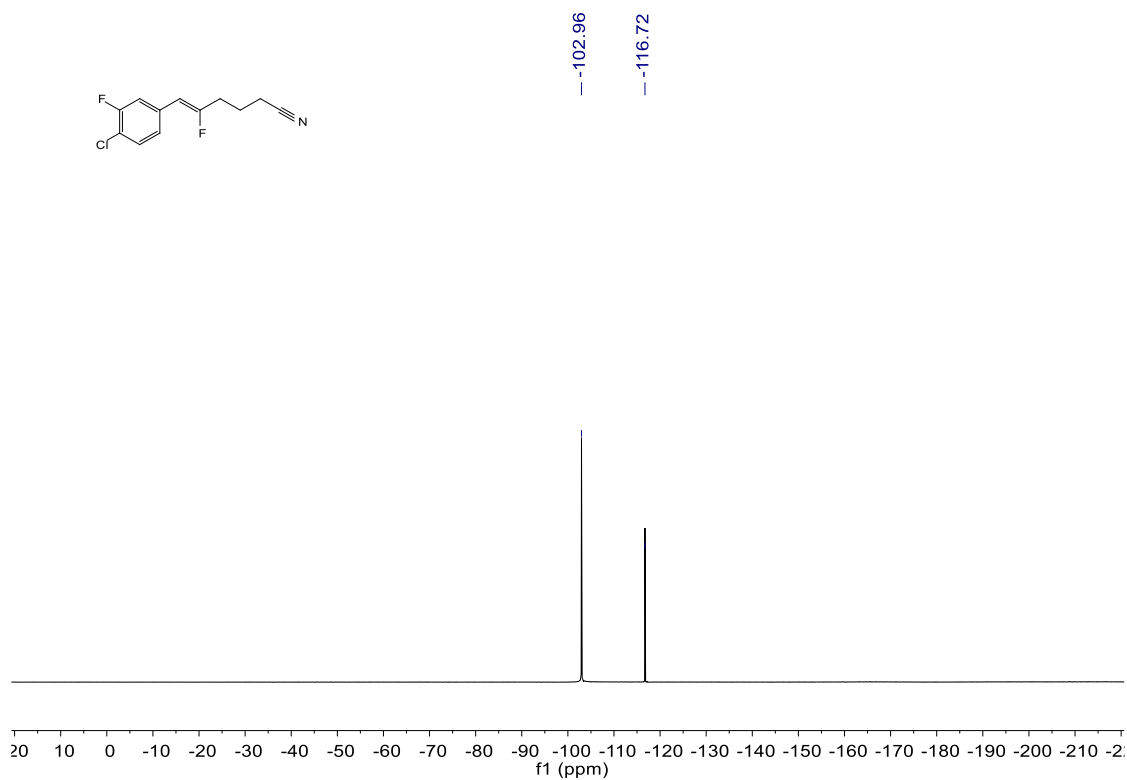
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₂H₁₀ClF₂N: 242.0543; found: 242.0542.

¹H NMR (400 MHz, Chloroform-*d*)

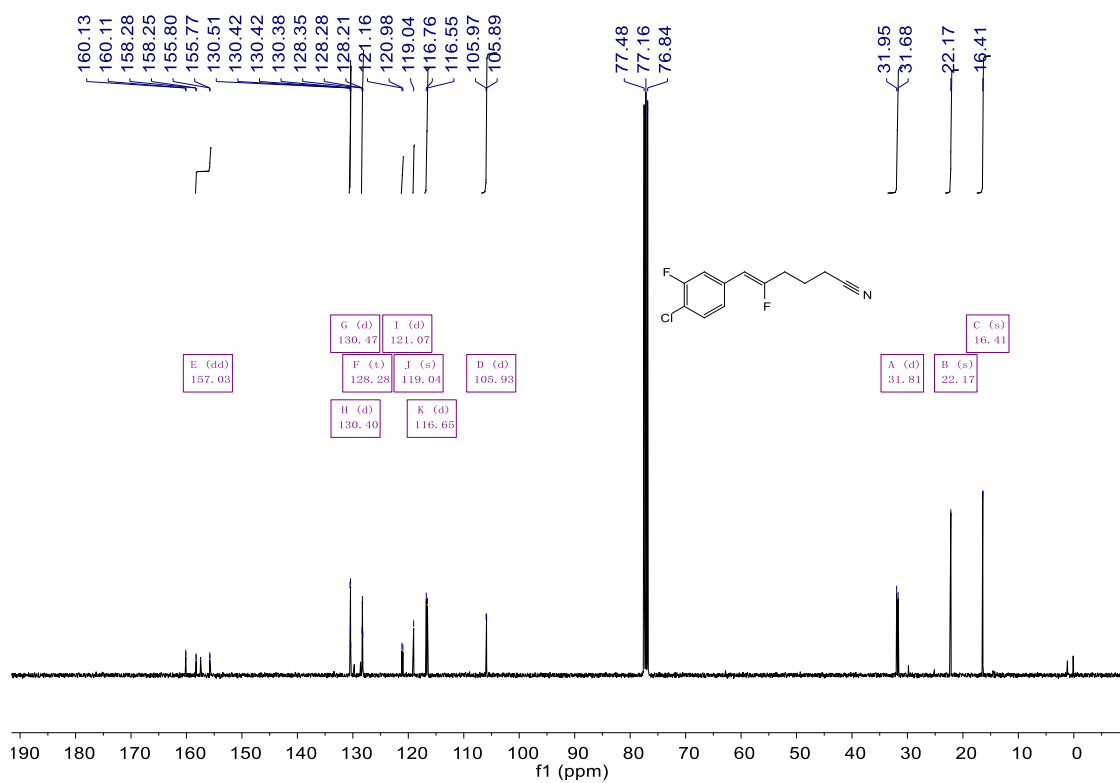


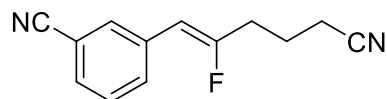
Supporting Information

^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





(Z) -3-(5-cyano-2-fluoropent-1-en-1-yl)benzonitrile

Following the general procedure (**c13**, yellow liquid, 12.8mg, 30%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

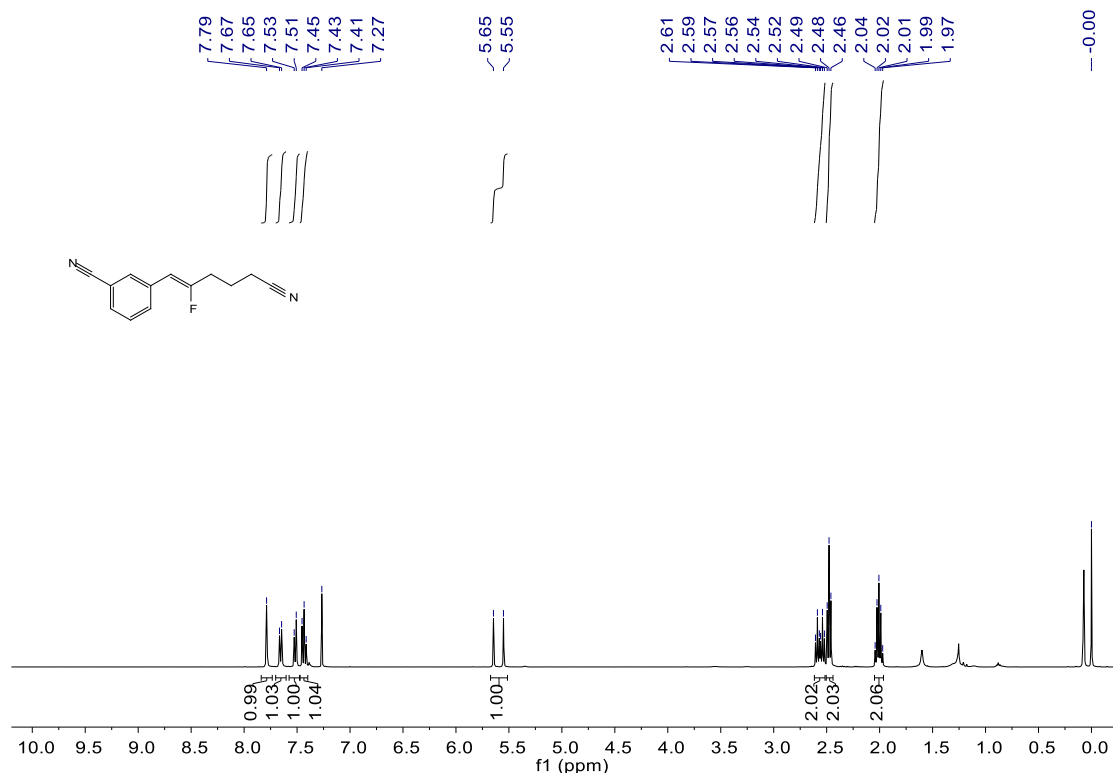
¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 5.59 (d, *J* = 37.9 Hz, 1H), 2.56 (dt, *J* = 19.2, 7.2 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.00 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -100.04.

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.18 (d, *J* = 269.1 Hz), 134.36 (d, *J* = 2.5 Hz), 132.65 (d, *J* = 7.2 Hz), 131.89 (d, *J* = 8.6 Hz), 130.61 (d, *J* = 2.1 Hz), 129.45, 118.95, 118.88, 112.86, 106.16 (d, *J* = 7.9 Hz), 31.88 (d, *J* = 26.4 Hz), 22.13, 16.47.

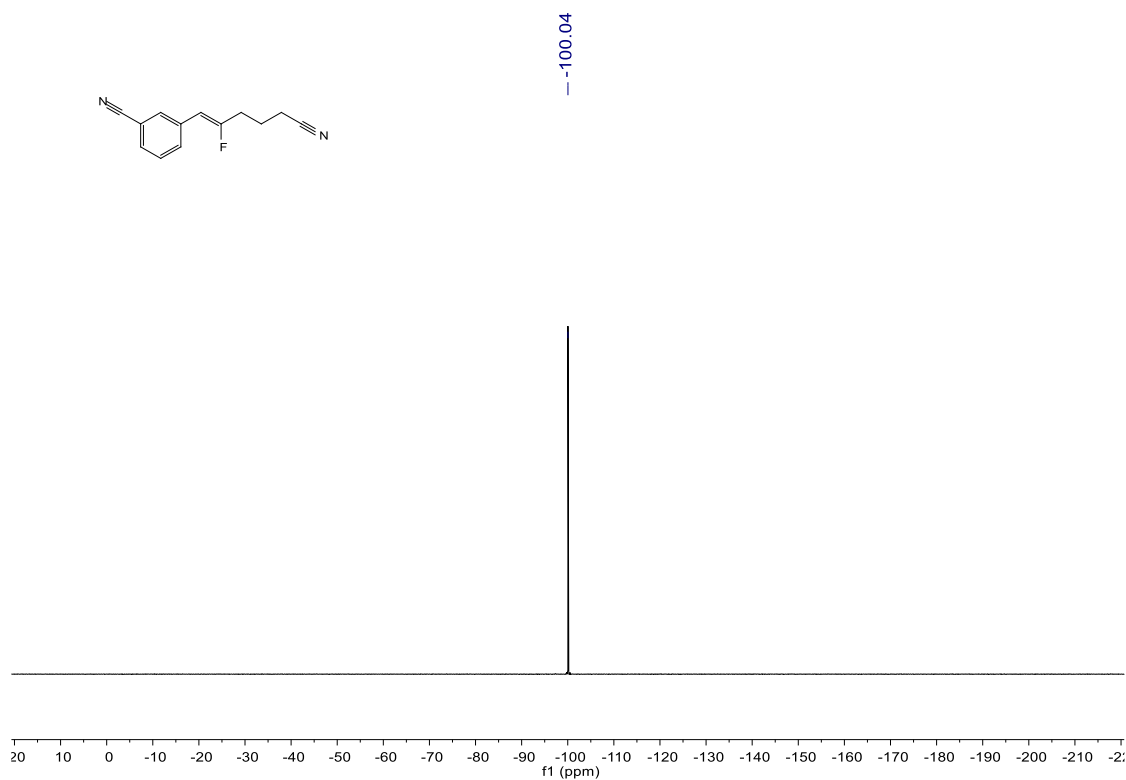
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₃H₁₁FN₂: 215.0979; found: 215.0978.

¹H NMR (400 MHz, Chloroform-*d*)

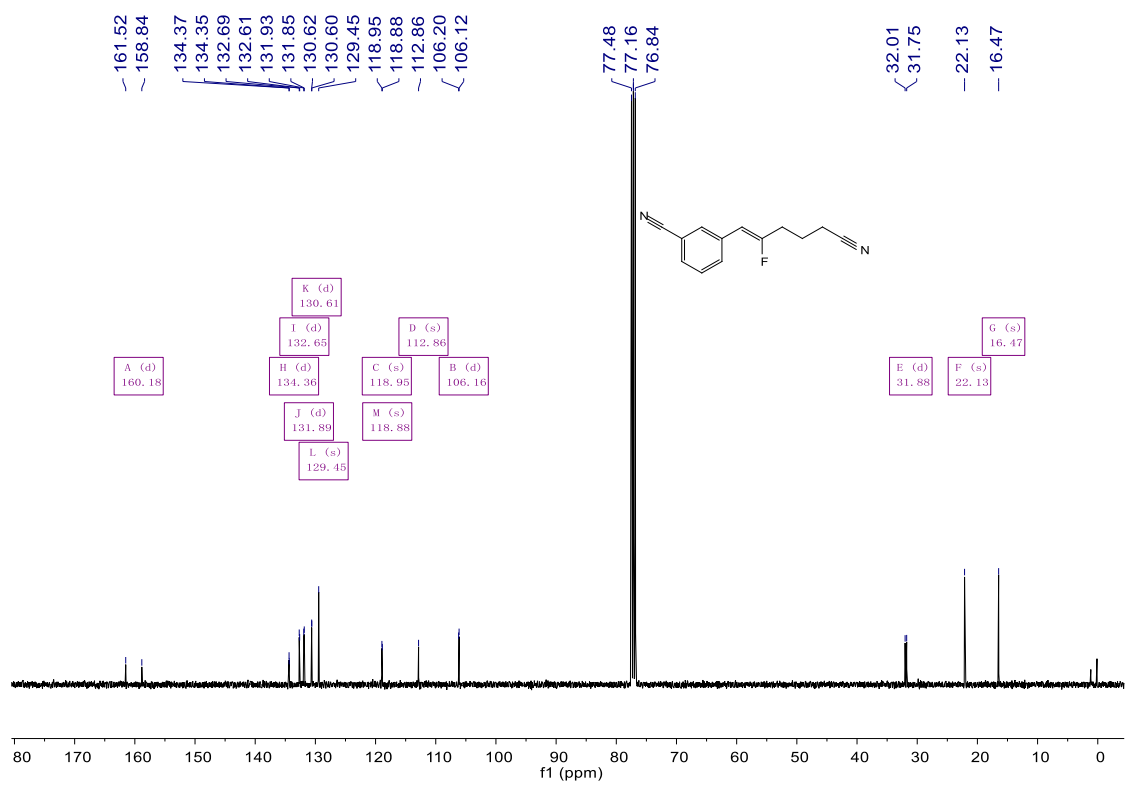


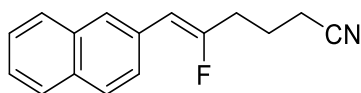
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(Z)-5-fluoro-6-(naphthalen-2-yl)hex-5-enitrile

Following the general procedure (**c14**, yellow liquid, 31.1 mg, 65%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

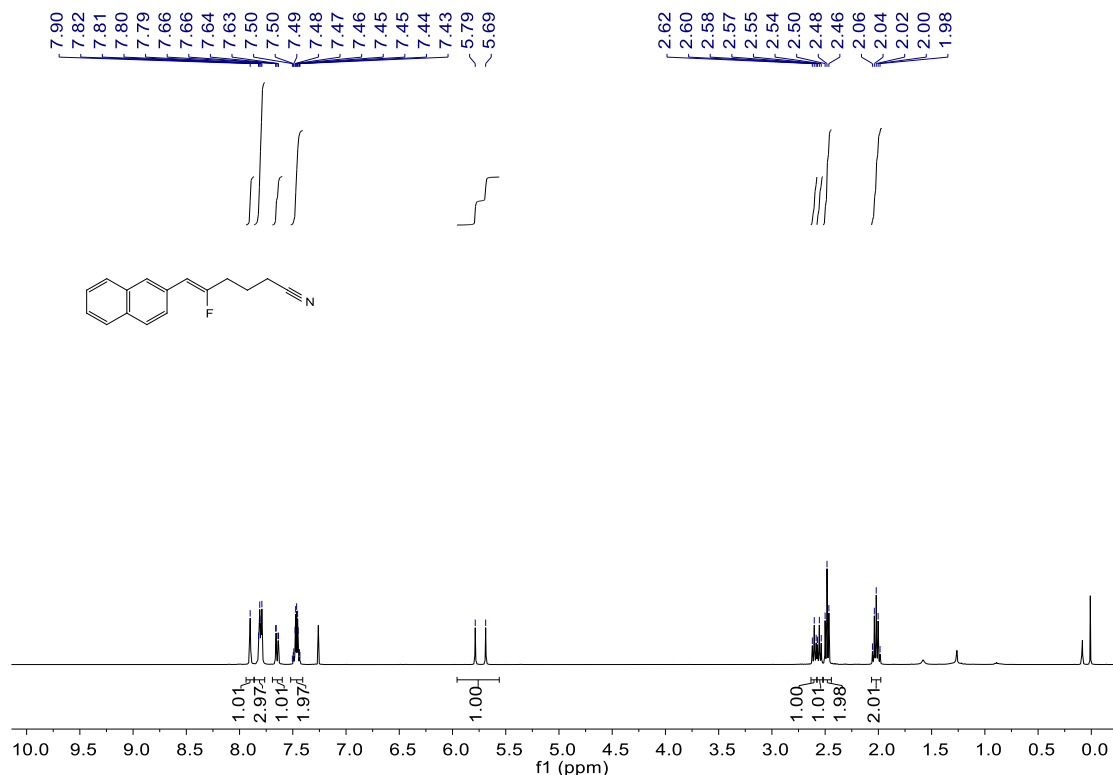
¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.7 Hz, 1H), 7.86 – 7.76 (m, 3H), 7.65 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 – 7.42 (m, 2H), 5.74 (d, *J* = 39.2 Hz, 1H), 2.60 (t, *J* = 7.2 Hz, 1H), 2.55 (t, *J* = 7.1 Hz, 1H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.02 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.22.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.45 (d, *J* = 266.6 Hz), 133.52, 132.53 (d, *J* = 1.7 Hz), 130.74 (d, *J* = 2.9 Hz), 128.14, 127.03 (d, *J* = 93.8 Hz), 127.02 (d, *J* = 108.8 Hz), 126.90 (d, *J* = 156.5 Hz), 126.33, 119.19, 108.01 (d, *J* = 8.1 Hz), 32.05 (d, *J* = 27.5 Hz), 22.37, 16.42.

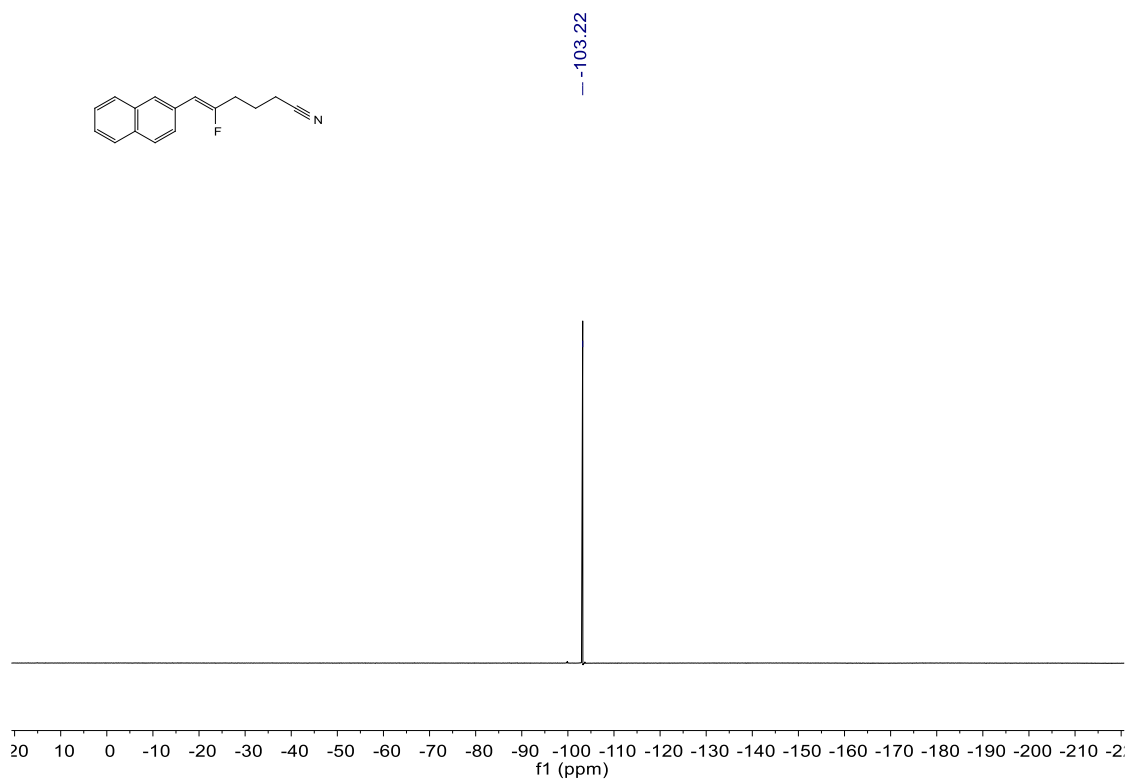
HRMS (ESI) *m/z*: (M+Na)⁺ Calcd for C₁₆H₁₄FN: 262.1003; found: 262.1003.

¹H NMR (400 MHz, Chloroform-*d*)

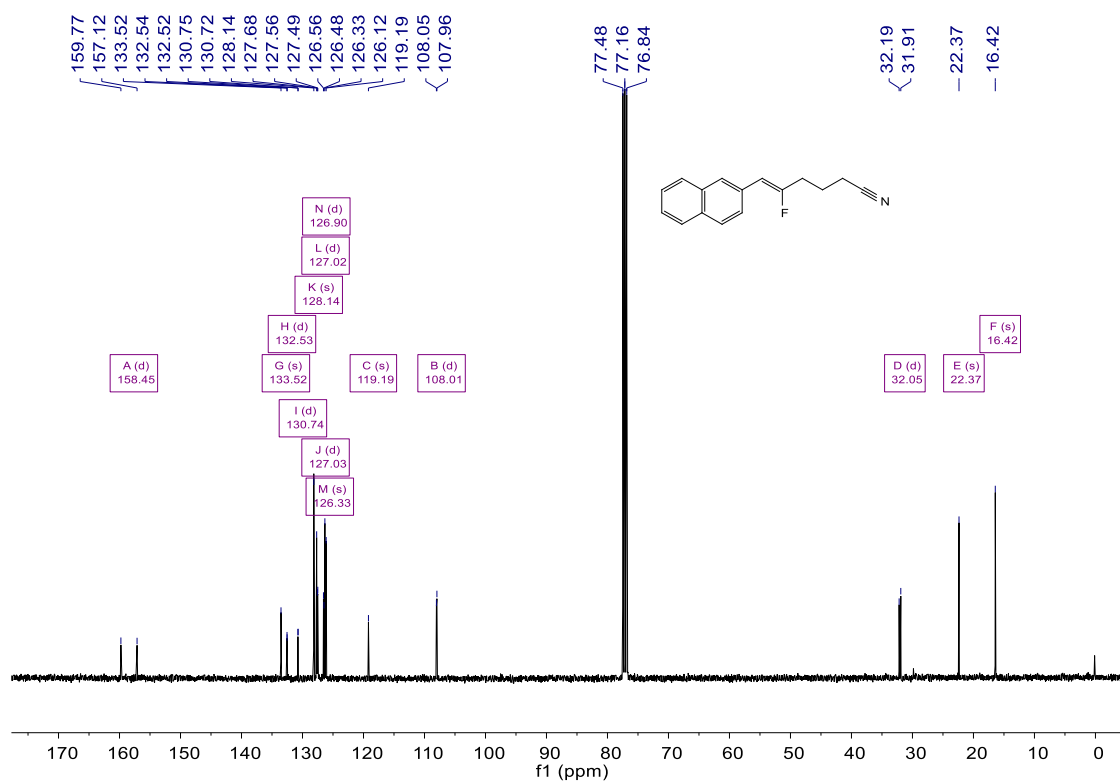


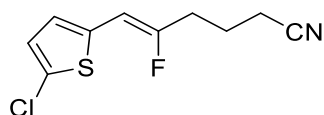
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)





(Z)-6-(5-chlorothiophen-2-yl)-5-fluorohex-5-enitrile

Following the general procedure (**c15**, yellow solid, 35.7 mg, 78%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

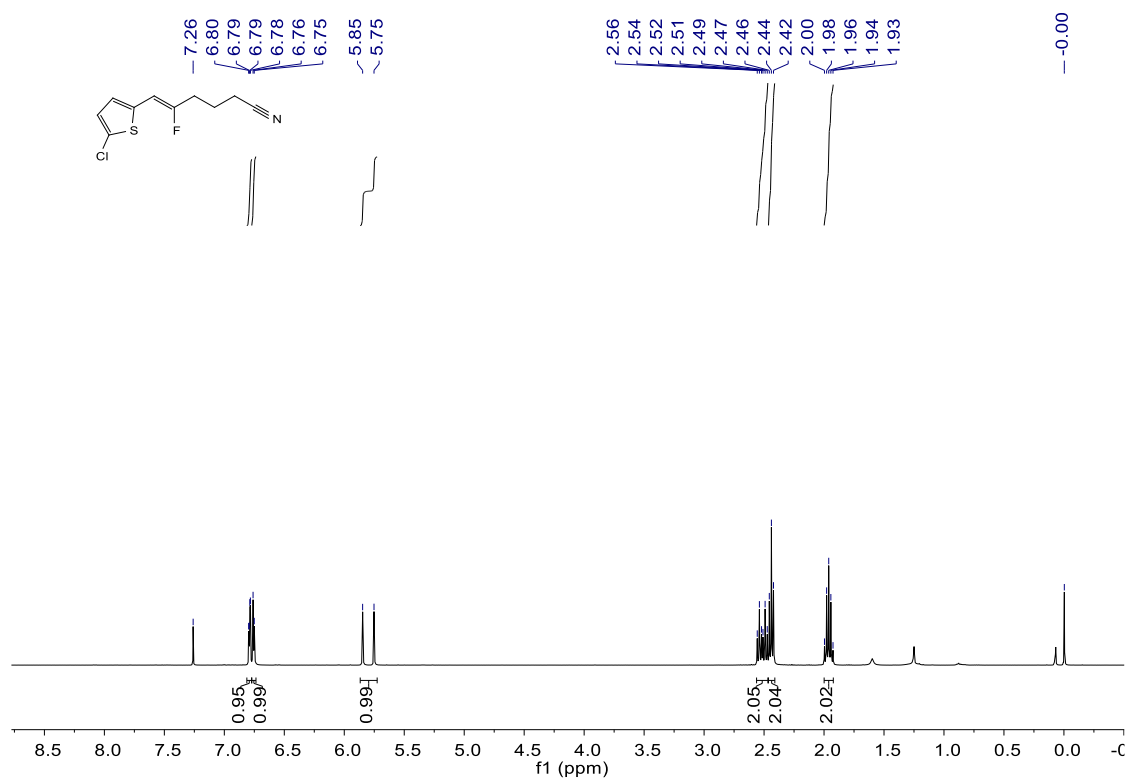
¹H NMR (400 MHz, Chloroform-*d*) δ 6.79 (dd, $J = 3.9, 2.0$ Hz, 1H), 6.76 (d, $J = 4.0$ Hz, 1H), 5.80 (d, $J = 38.0$ Hz, 1H), 2.52 (dt, $J = 19.1, 7.2$ Hz, 2H), 2.44 (t, $J = 7.0$ Hz, 2H), 1.96 (p, $J = 7.1$ Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -100.13.

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.99 (d, $J = 265.2$ Hz), 134.09 (d, $J = 3.6$ Hz), 130.09 (d, $J = 11.5$ Hz), 125.73, 125.48 (d, $J = 3.0$ Hz), 118.99, 102.58 (d, $J = 12.3$ Hz), 31.03 (d, $J = 26.1$ Hz), 22.12, 16.38.

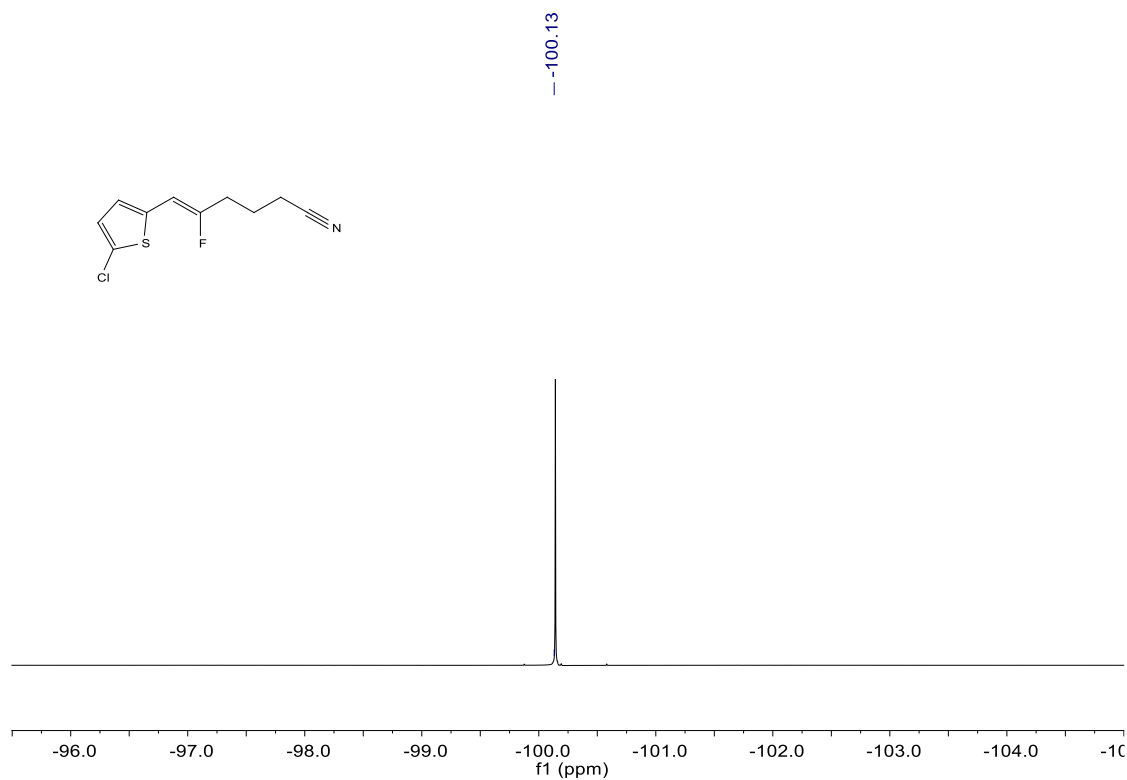
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₀H₉ClFNS: 230.0201; found: 230.0205.

¹H NMR (400 MHz, Chloroform-*d*)

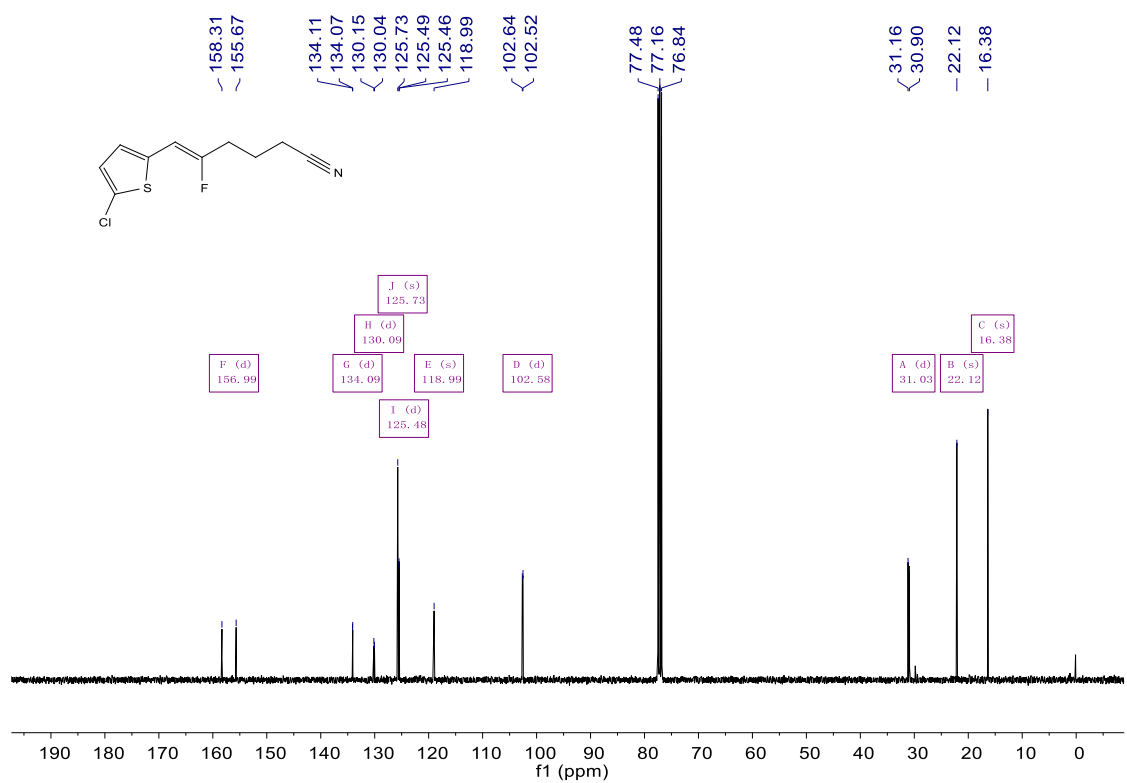


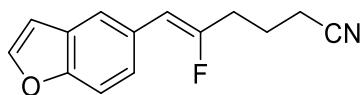
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(Z)-6-(benzofuran-5-yl)-5-fluorohex-5-enitrile

Following the general procedure (**c16**, pale-yellow solid, 25.2 mg, 55%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

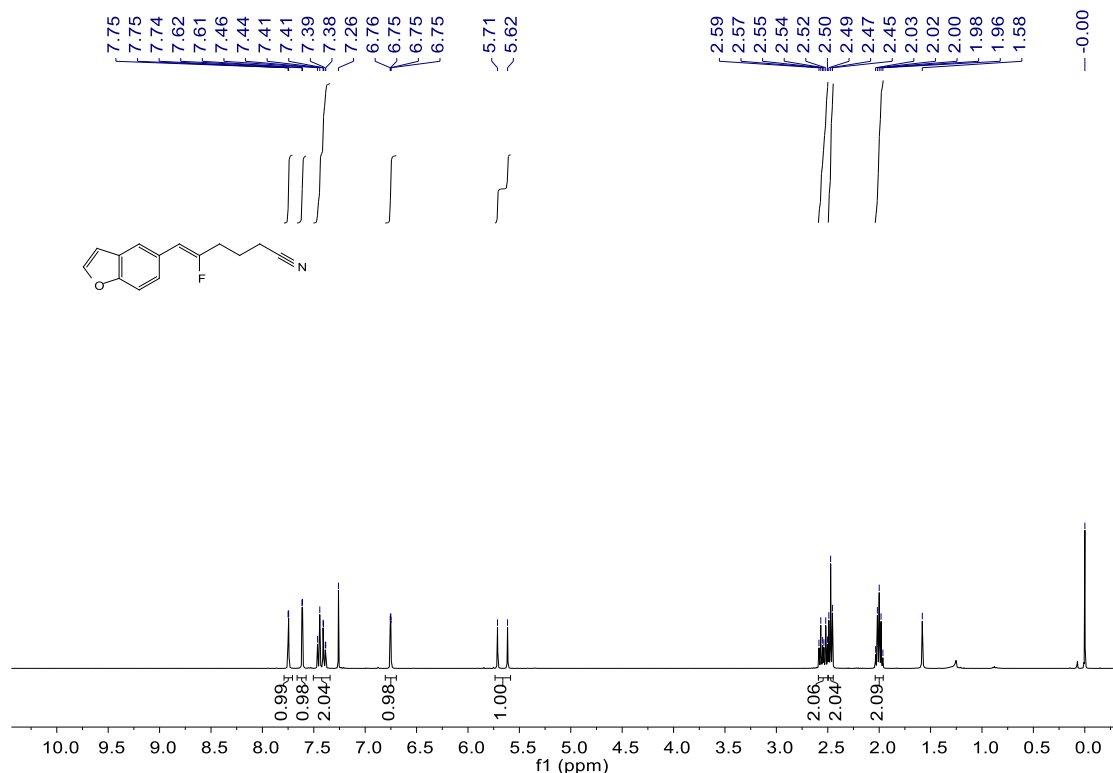
¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.71 (m, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.50 – 7.34 (m, 2H), 6.75 (dd, *J* = 2.2, 0.8 Hz, 1H), 5.66 (d, *J* = 39.2 Hz, 1H), 2.54 (dt, *J* = 19.2, 7.1 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 2.00 (p, *J* = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -106.09.

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.12 (d, *J* = 264.1 Hz), 154.05, 145.60, 128.05 (d, *J* = 2.8 Hz), 127.80, 125.23 (d, *J* = 6.6 Hz), 121.18 (d, *J* = 8.1 Hz), 119.26, 111.42, 107.92 (d, *J* = 8.1 Hz), 106.81, 31.95 (d, *J* = 27.5 Hz), 22.37, 16.39.

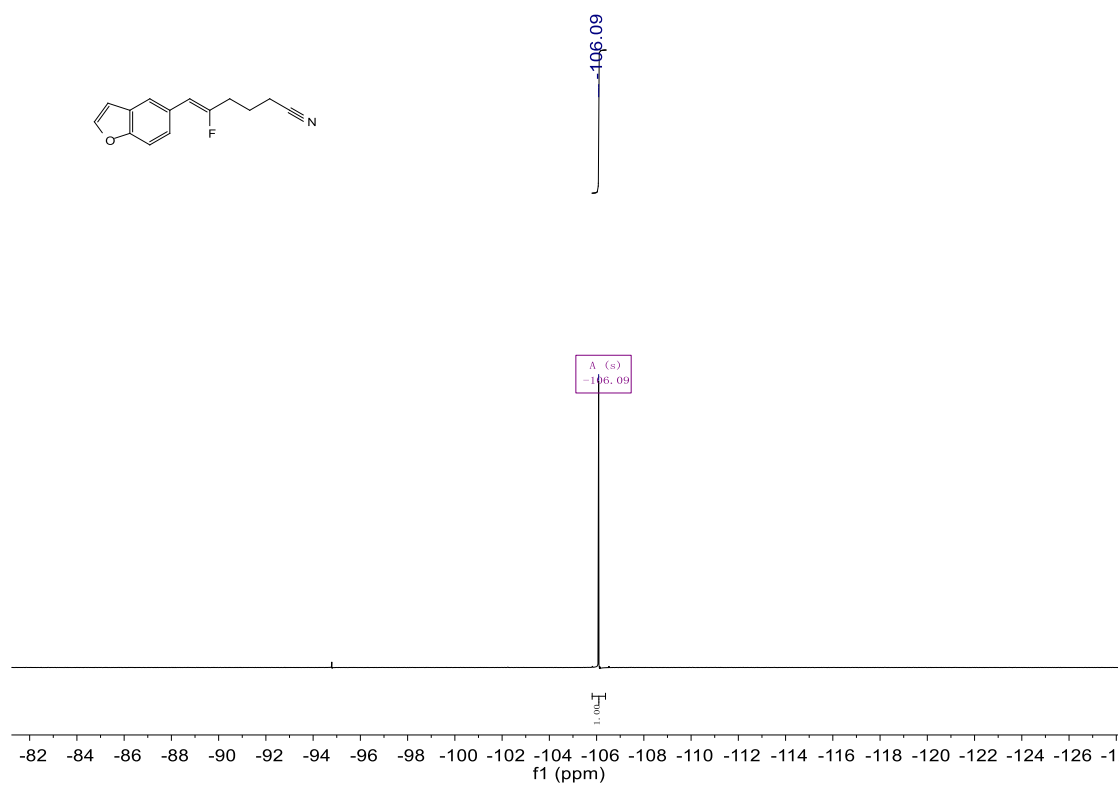
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₄H₁₂FNO: 230.0975; found: 230.0966.

¹H NMR (400 MHz, Chloroform-*d*)

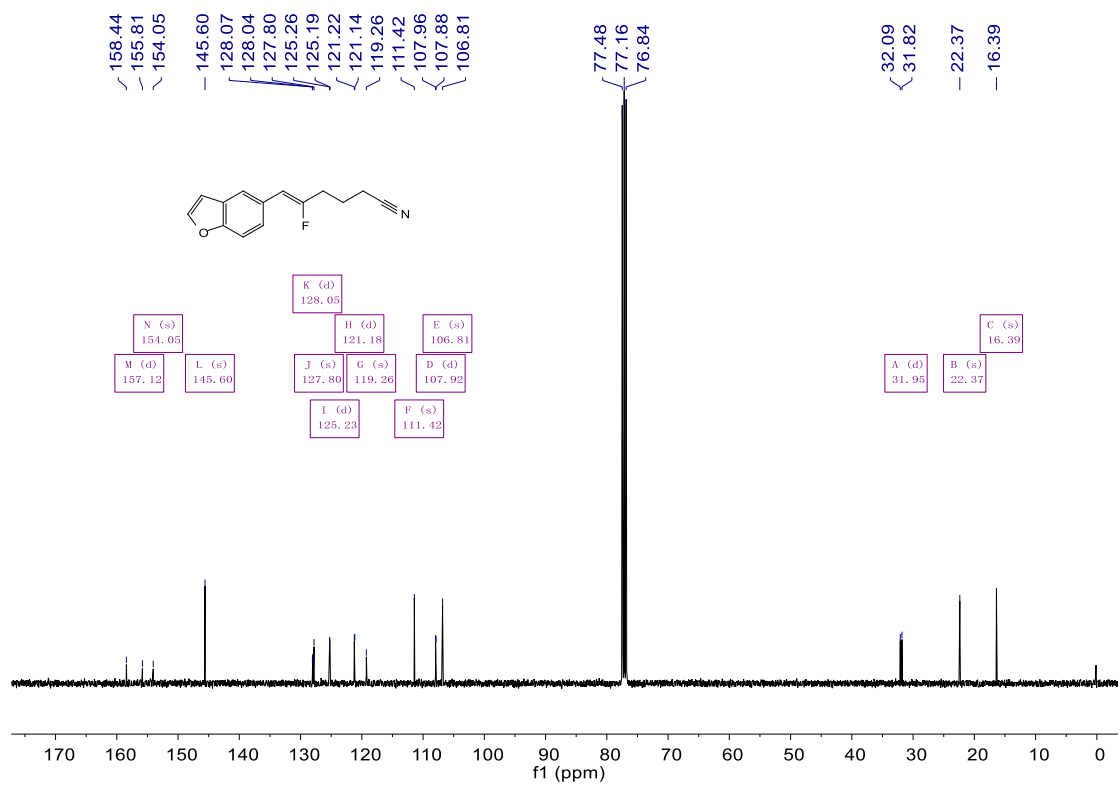


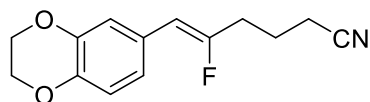
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(Z)-6-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-fluorohex-5-enenitrile

Following the general procedure (**c17**, yellow liquid, 28.2 mg, 57%, Z/E > 14:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (3:1) as an eluent.

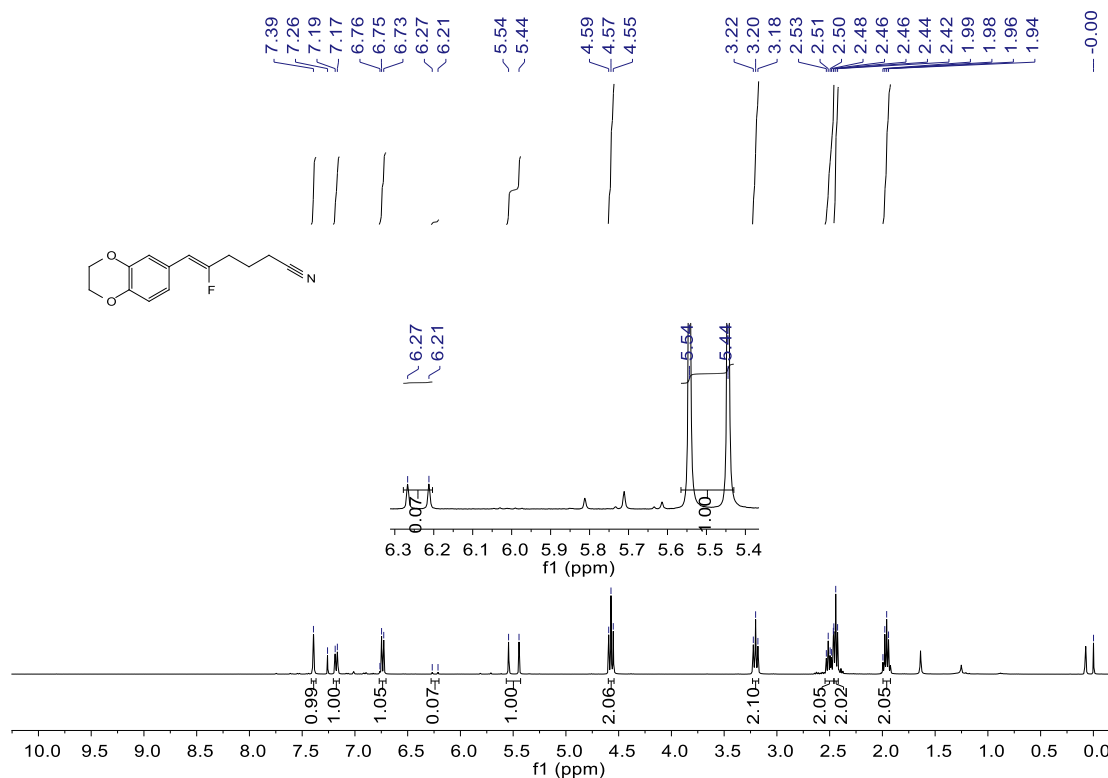
¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.49 (d, *J* = 39.6 Hz, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.20 (t, *J* = 8.7 Hz, 2H), 2.54 – 2.46 (m, 2H), 2.43 (d, *J* = 7.1 Hz, 2H), 1.99 – 1.92 (m, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -107.27.

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.29 (d, *J* = 2.8 Hz), 156.26 (d, *J* = 262.9 Hz), 128.69 (d, *J* = 6.5 Hz), 127.45, 125.77 (d, *J* = 2.9 Hz), 125.10 (d, *J* = 8.4 Hz), 119.27, 109.28, 107.61 (d, *J* = 8.2 Hz), 71.53, 31.87 (d, *J* = 27.6 Hz), 29.73, 22.37, 16.31.

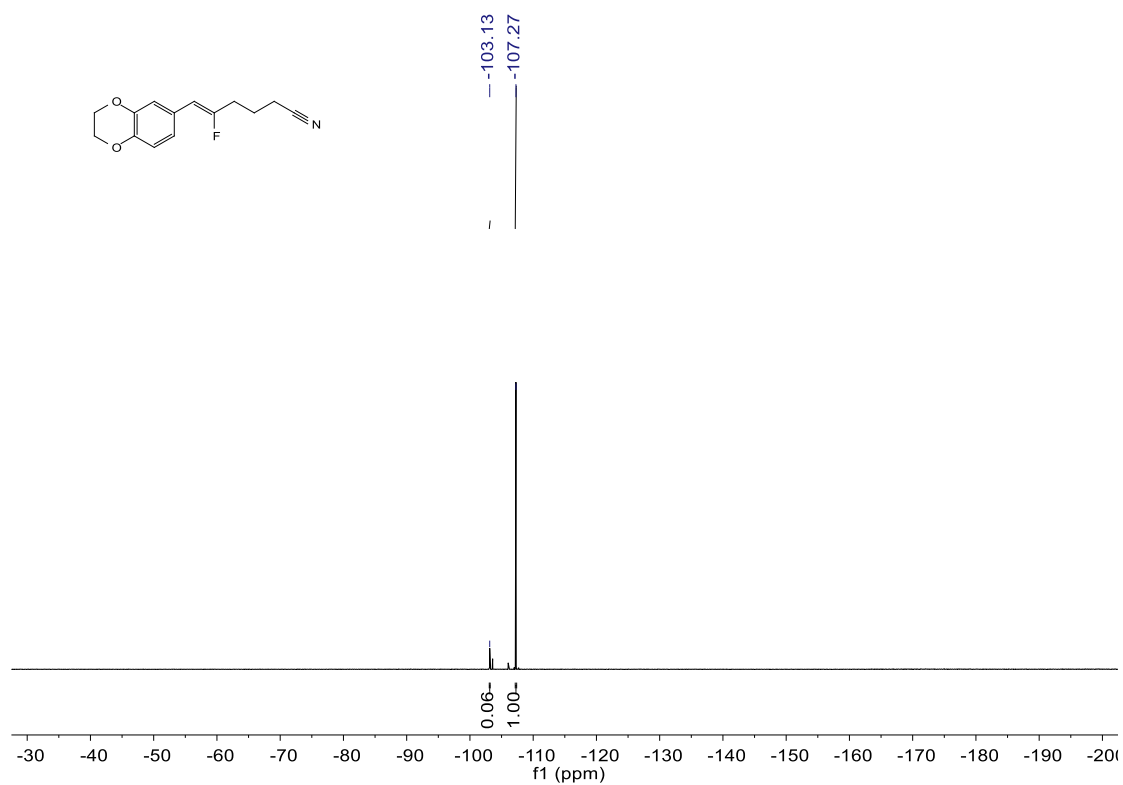
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₄H₁₄FNO₂: 248.1081; found: 248.1068.

¹H NMR (400 MHz, Chloroform-*d*)

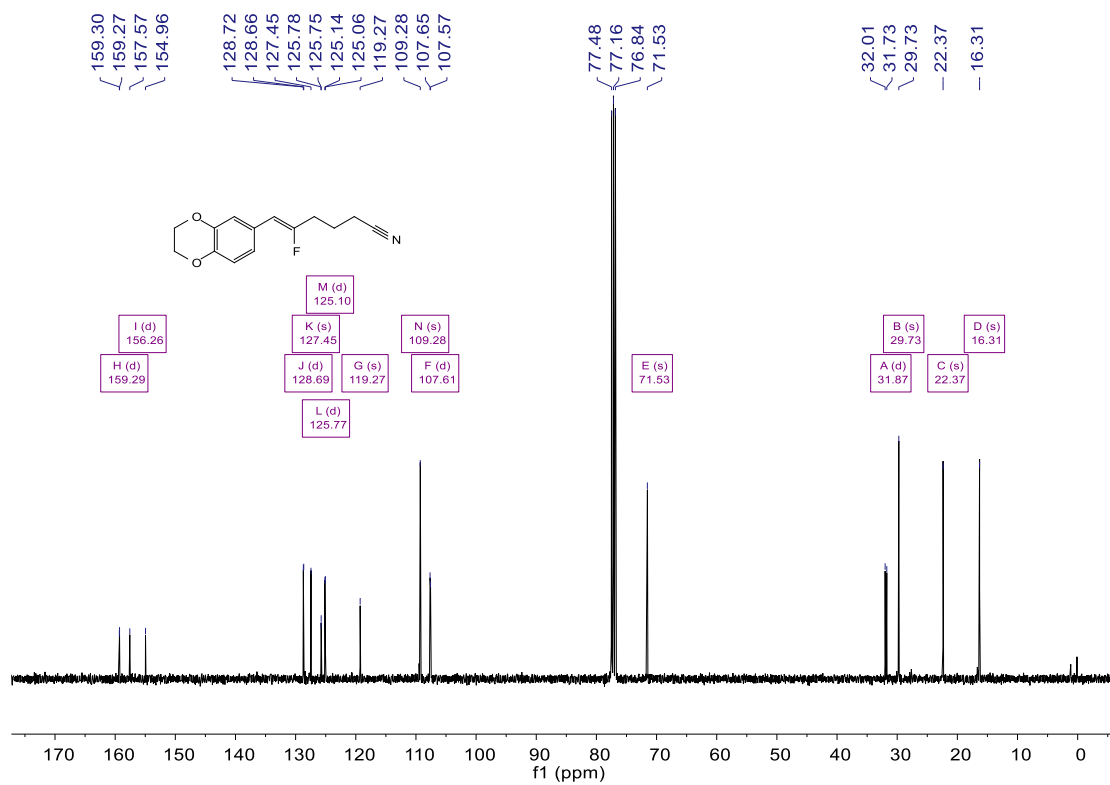


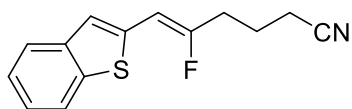
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(Z)-6-(benzo[b]thiophen-2-yl)-5-fluorohex-5-enenitrile

Following the general procedure (**c18**, pale-yellow liquid, 35.3 mg, 72%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

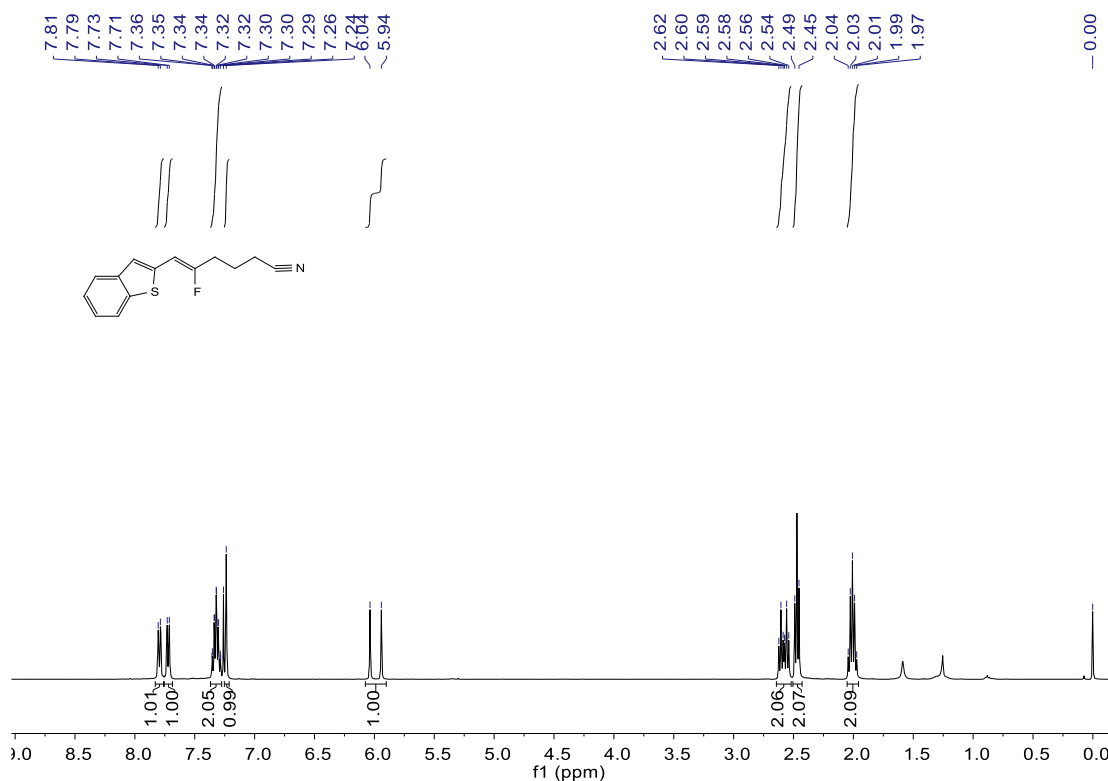
¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 7.0 Hz, 1H), 7.32 (pd, J = 7.1, 1.4 Hz, 2H), 7.24 (s, 1H), 5.99 (d, J = 37.9 Hz, 1H), 2.58 (dt, J = 18.9, 7.2 Hz, 2H), 2.47 (d, J = 14.0 Hz, 2H), 2.01 (p, J = 7.1 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -98.86.

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.39 (d, J = 267.6 Hz), 140.11 (d, J = 7.9 Hz), 139.22, 135.46 (d, J = 4.3 Hz), 124.56, 124.52, 123.44 (d, J = 1.3 Hz), 123.01 (d, J = 4.2 Hz), 122.15, 119.05, 103.11 (d, J = 11.6 Hz), 31.36 (d, J = 26.1 Hz), 22.17, 16.44.

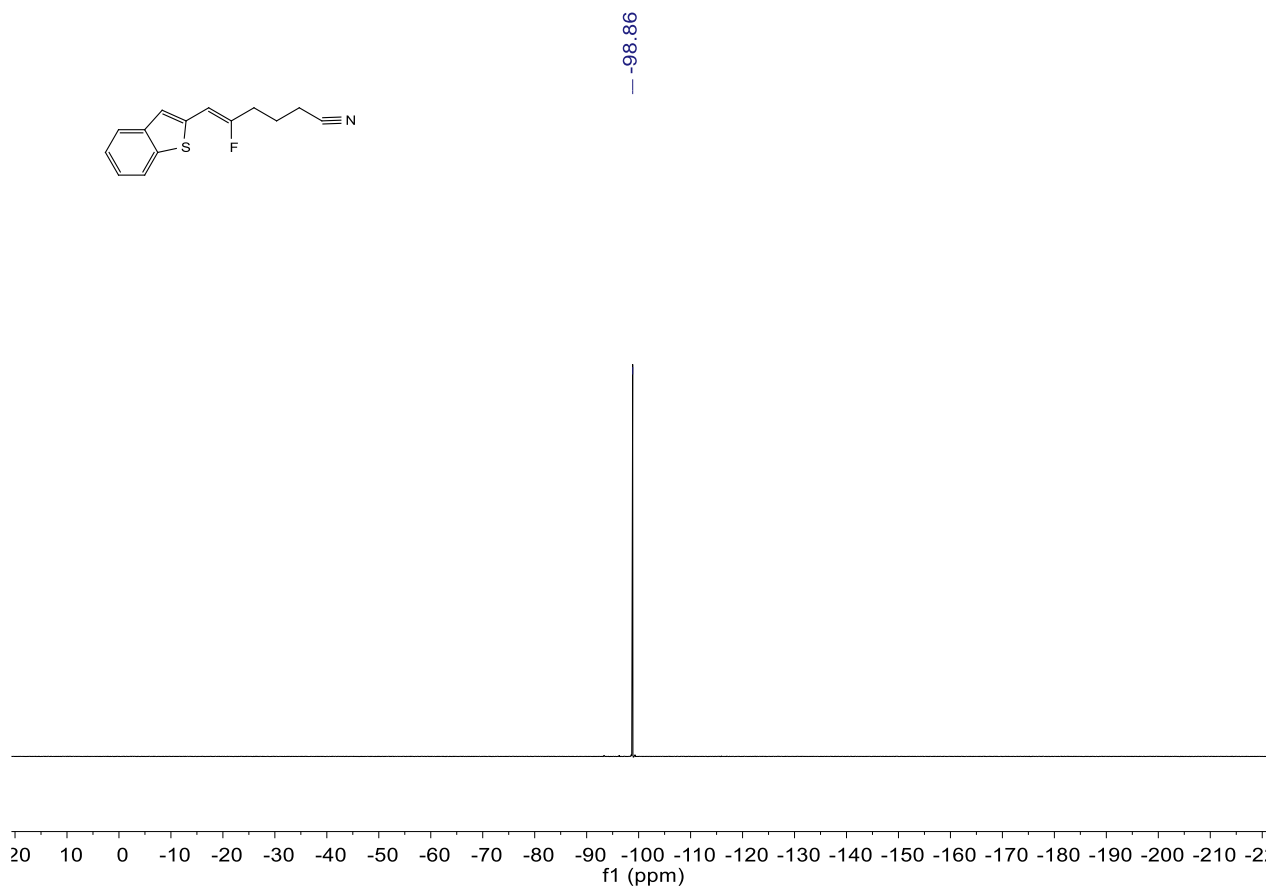
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₄H₁₂FNS: 246.0747; found: 246.0750.

¹H NMR (400 MHz, Chloroform-*d*)

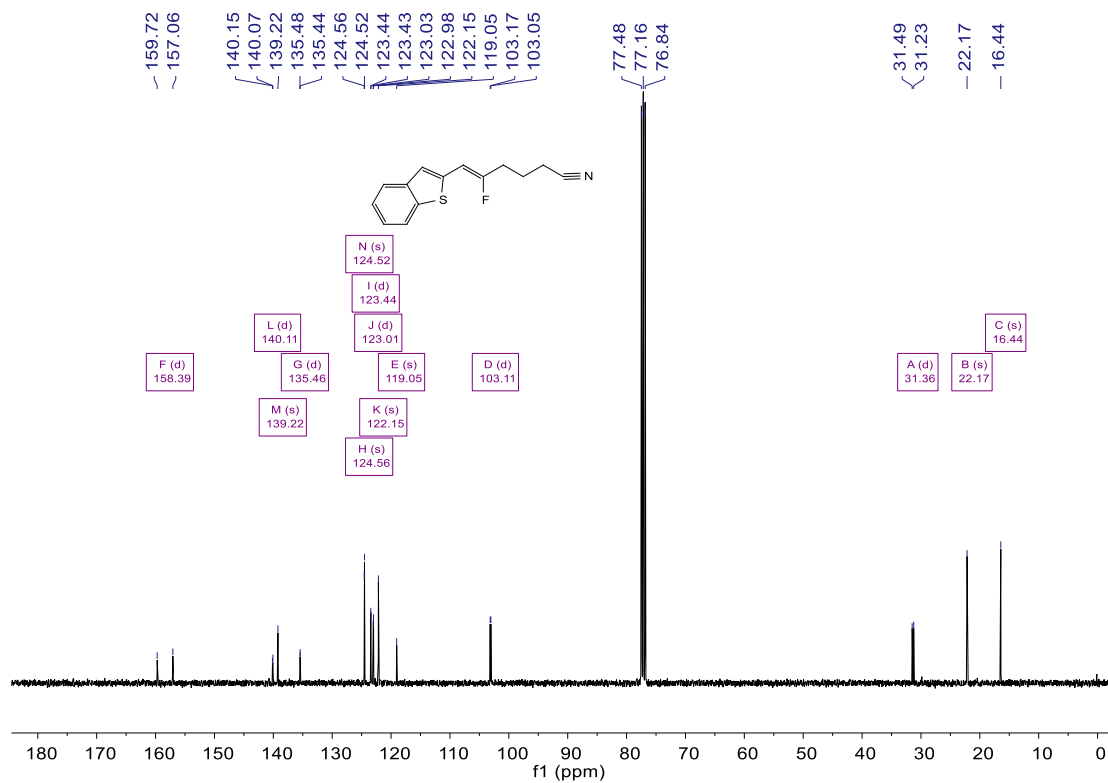


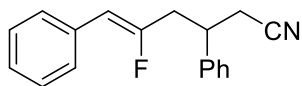
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-3,6-diphenylhex-5-enitrile

Following the general procedure (**d1**, yellow liquid, 39.8 mg, 75%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

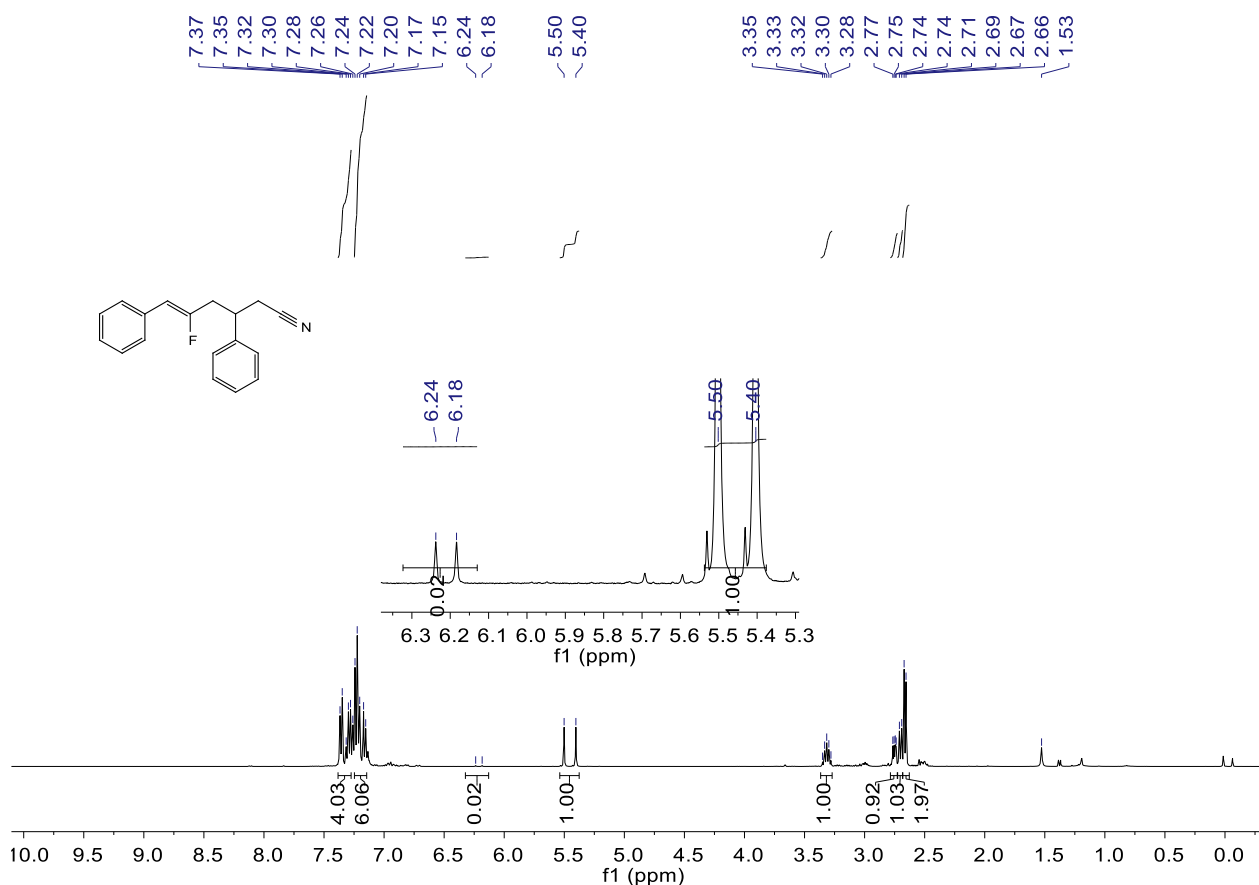
¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 4H), 7.25 – 7.14 (m, 6H), 5.45 (d, *J* = 39.2 Hz, 1H), 3.32 (p, *J* = 6.9 Hz, 1H), 2.75 (dd, *J* = 7.5, 3.6 Hz, 1H), 2.70 (d, *J* = 7.6 Hz, 1H), 2.66 (d, *J* = 6.4 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.22.

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.05 (d, *J* = 265.7 Hz), 140.49, 133.03 (d, *J* = 2.4 Hz), 129.11, 128.57, 128.51, 127.95, 127.36 (d, *J* = 2.3 Hz), 127.14, 118.10, 109.08 (d, *J* = 8.1 Hz), 39.07, 38.75 (d, *J* = 26.5 Hz), 23.86.

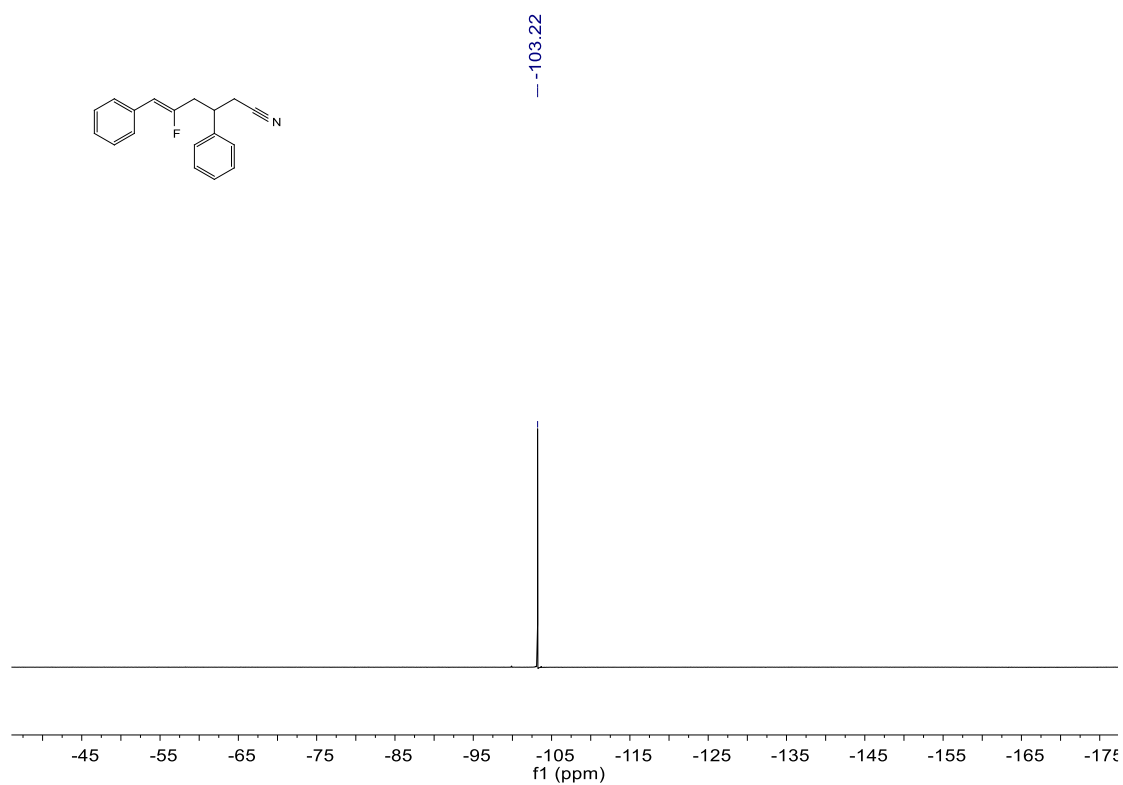
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₈H₁₆FN: 266.1340; found: 266.1334.

¹H NMR (400 MHz, Chloroform-*d*)

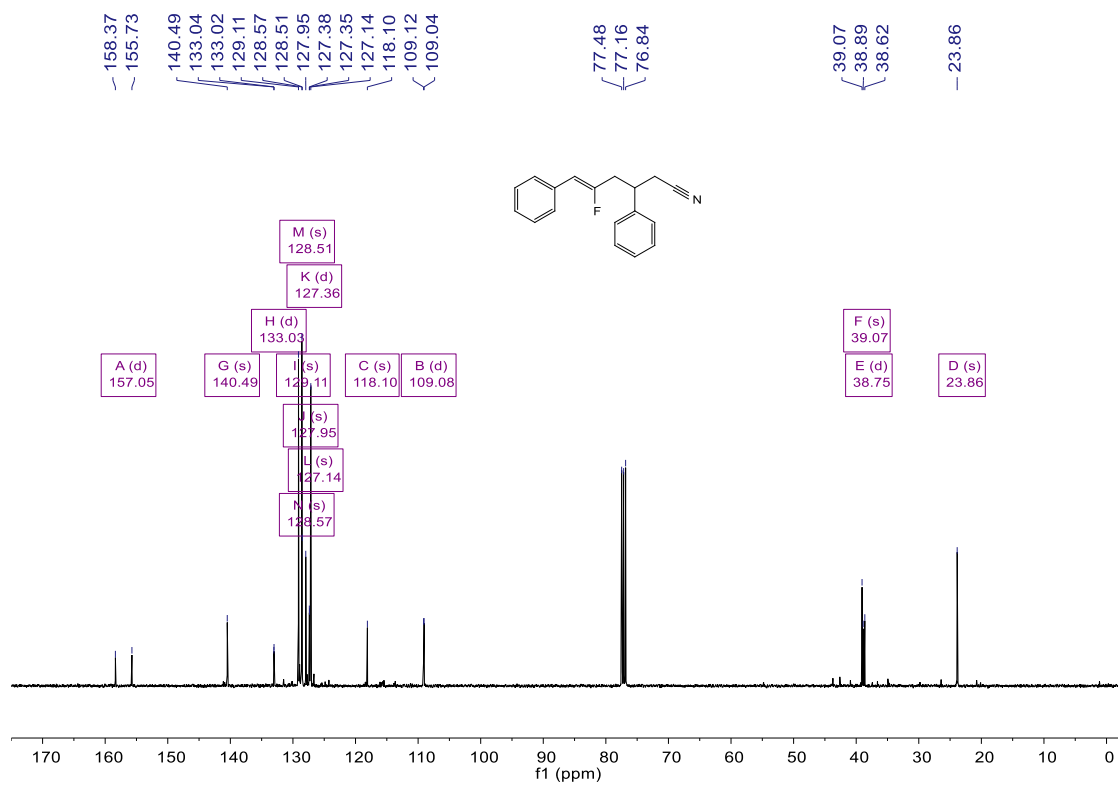


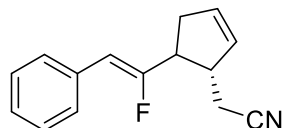
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)




2-((1S)-5-((Z)-1-fluoro-2-phenylvinyl)cyclopent-2-en-1-yl)acetonitrile

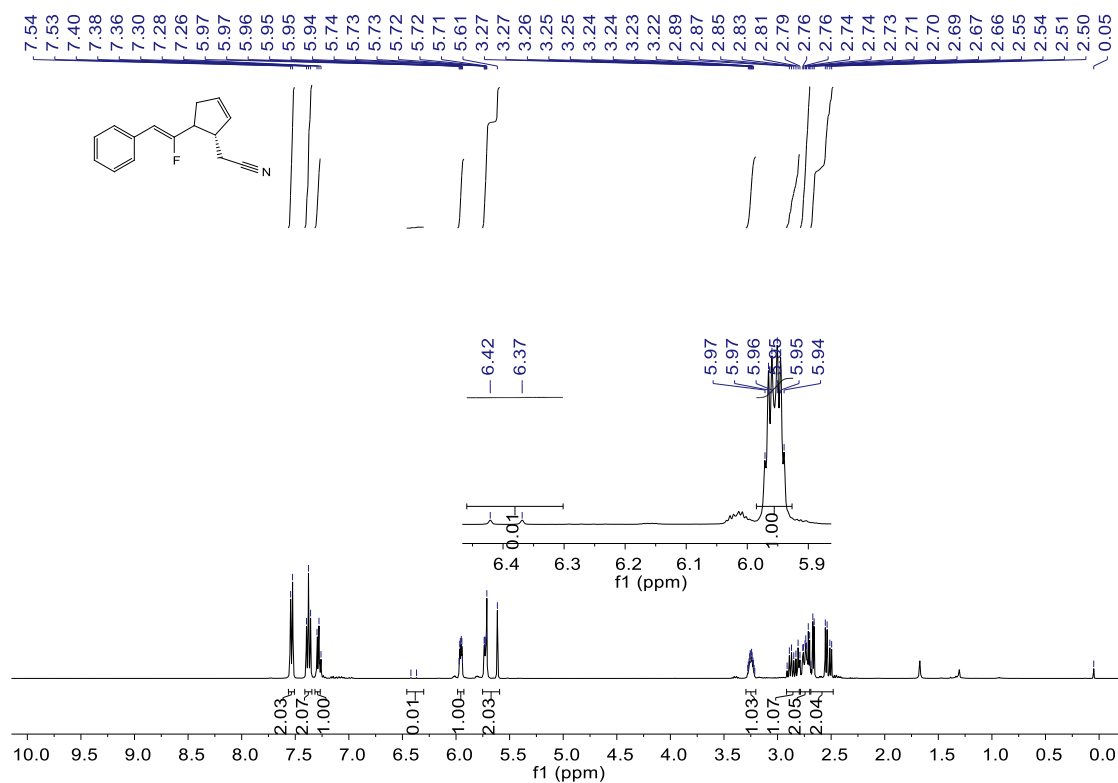
Following the general procedure (**d2**, pale-yellow liquid, 34.5 mg, 76%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 5.96 (dq, *J* = 4.5, 2.3 Hz, 1H), 5.75 – 5.59 (m, 2H), 3.25 (dtq, *J* = 9.9, 4.9, 2.4 Hz, 1H), 2.92 – 2.80 (m, 1H), 2.79 – 2.70 (m, 2H), 2.69 – 2.48 (m, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -100.14.

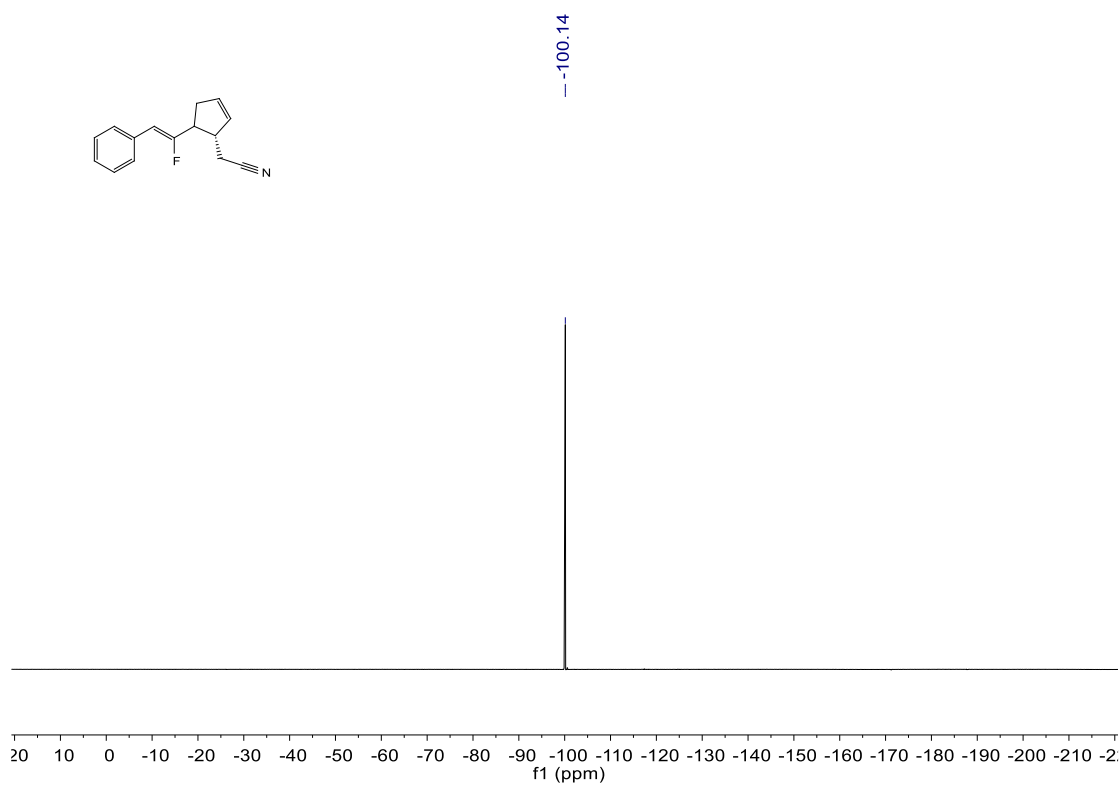
¹³C NMR (101 MHz, Chloroform-*d*) δ 159.57 (d, *J* = 266.4 Hz), 133.18 (d, *J* = 2.8 Hz), 132.41, 130.40, 128.59, 128.53, 127.28 (d, *J* = 2.2 Hz), 118.20, 106.96 (d, *J* = 8.8 Hz), 47.81 (d, *J* = 25.7 Hz), 45.54, 36.55 (d, *J* = 2.5 Hz), 22.22.

HRMS (ESI) *m/z*: (*M*+Na)⁺ Calcd for C₁₅H₁₄FN: 250.1002; found: 250.1005.

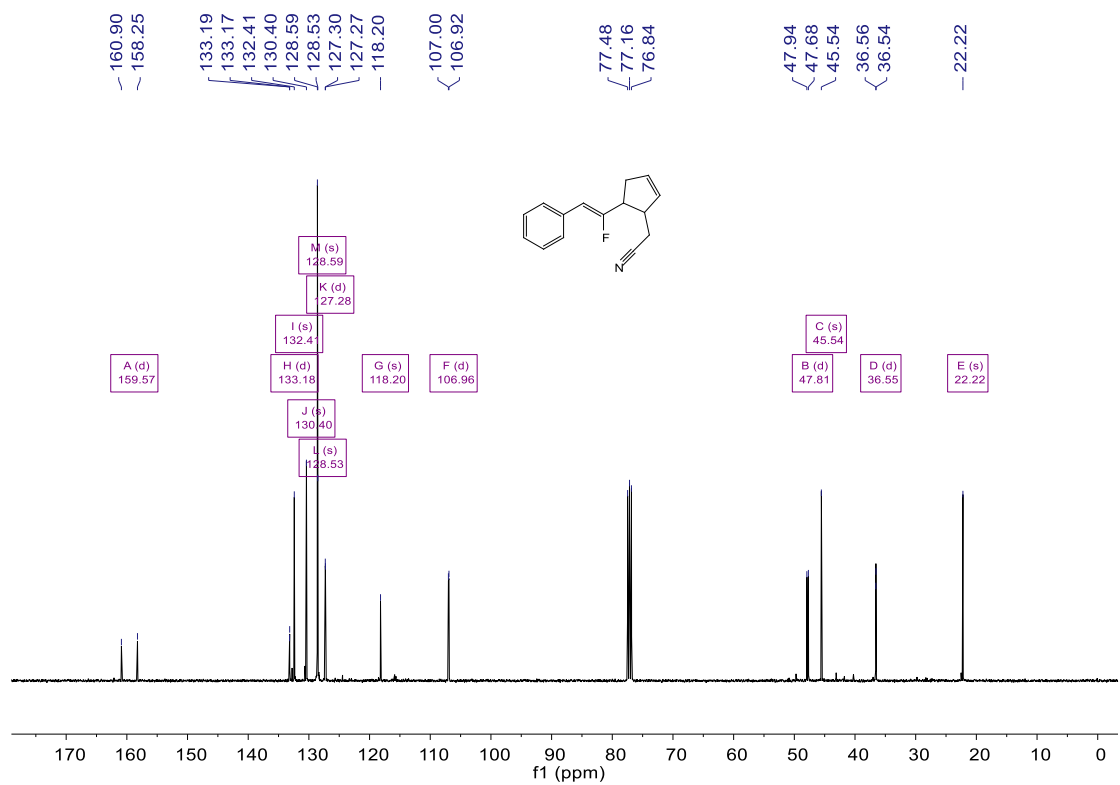
¹H NMR (400 MHz, Chloroform-*d*)


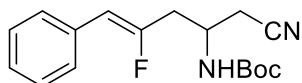
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





tert-butyl (Z)-(1-cyano-4-fluoro-5-phenylpent-4-en-2-yl)carbamate

Following the general procedure (**d3**, yellow solid, 27.4 mg, 45%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

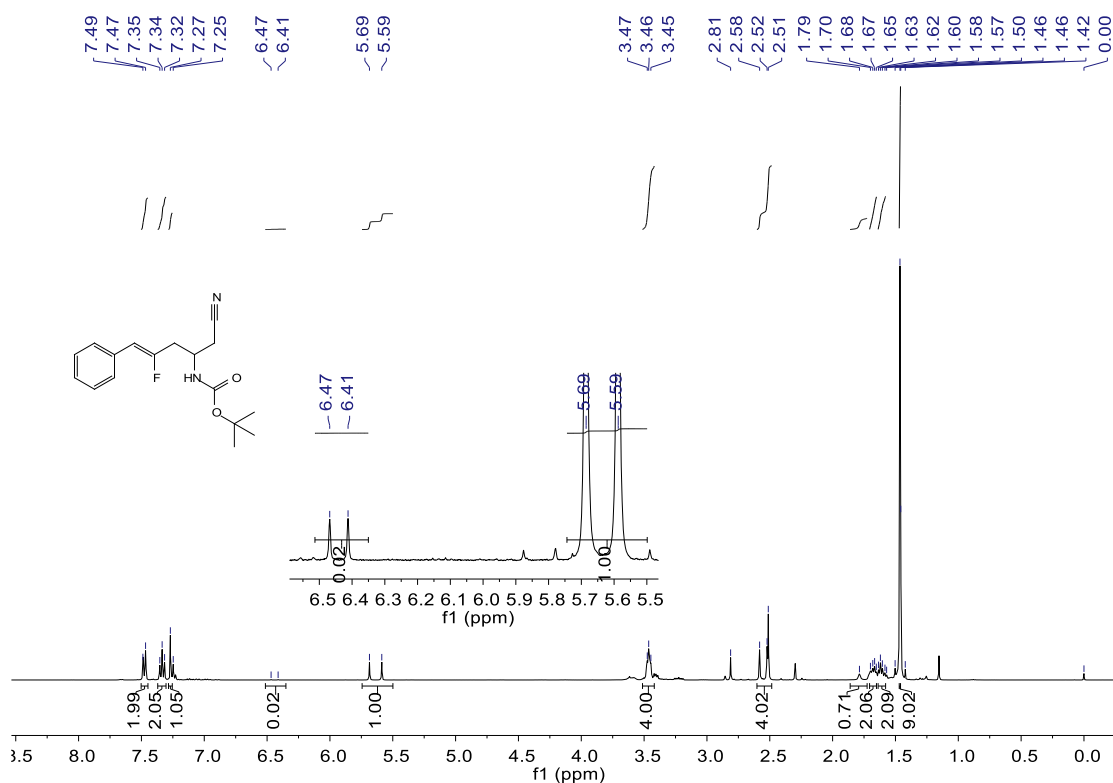
¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 5.69 (d, *J* = 39.1 Hz, 1H), 4.94 (d, *J* = 7.3 Hz, 1H), 4.19 (d, *J* = 6.6 Hz, 1H), 2.75 (ddd, *J* = 37.0, 19.6, 6.0 Hz, 4H), 1.46 (s, 9H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -105.12.

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.54 (d, *J* = 265.5 Hz), 154.93, 132.72 (d, *J* = 2.8 Hz), 128.72, 128.66, 127.68 (d, *J* = 2.4 Hz), 117.16, 110.04 (d, *J* = 7.5 Hz), 80.67, 45.37, 37.19 (d, *J* = 26.7 Hz), 28.36, 22.94.

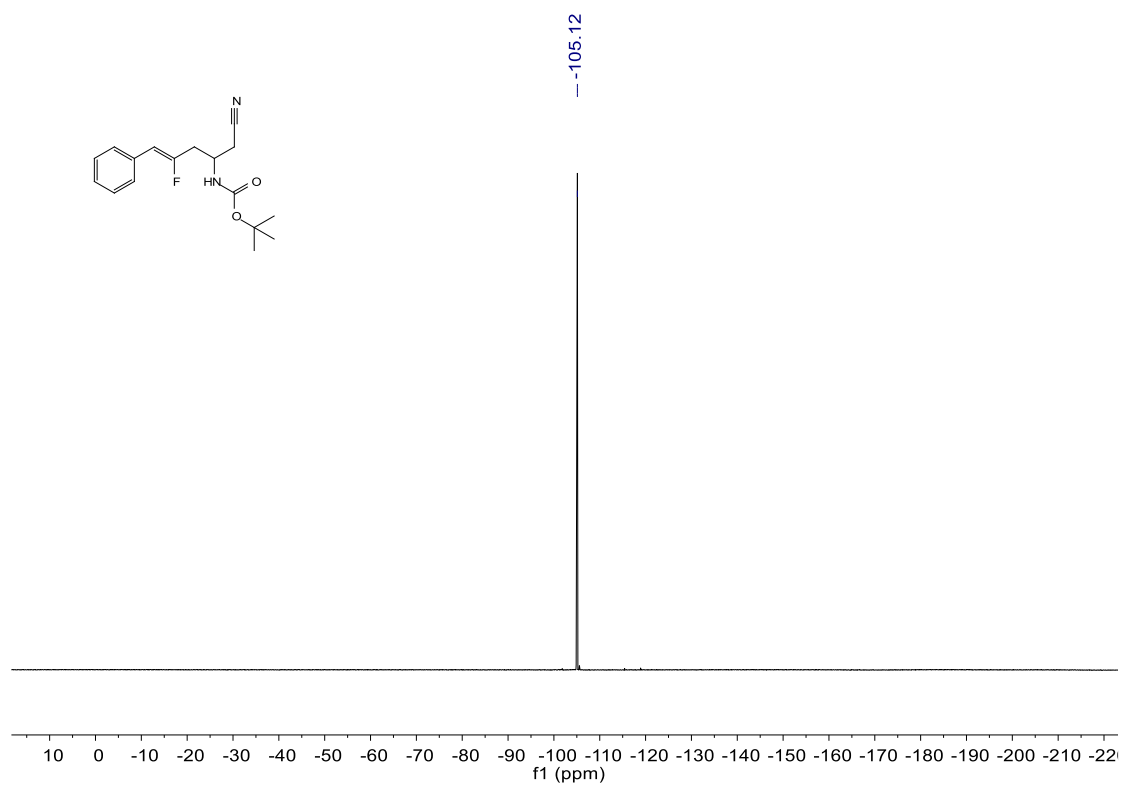
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₇H₂₁FN₂O₂: 305.1659; found: 305.1659.

¹H NMR (400 MHz, Chloroform-*d*)

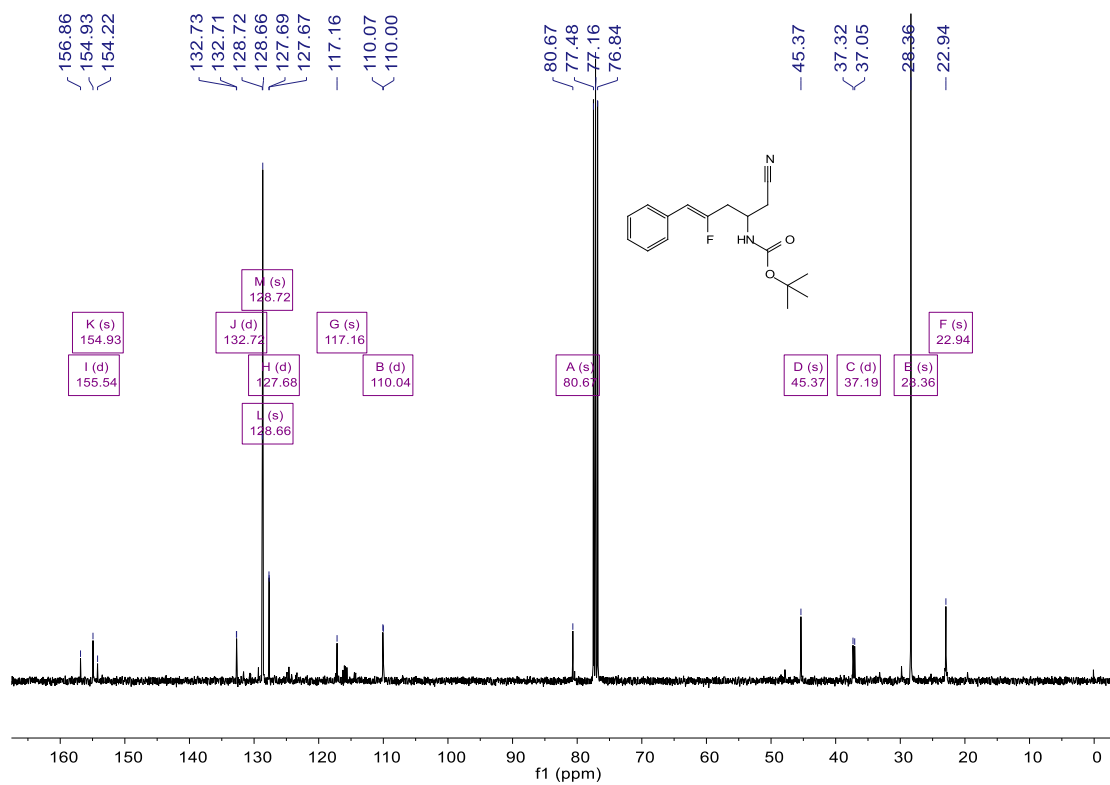


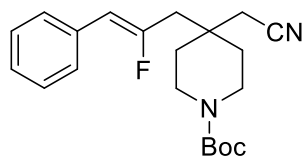
Supporting Information

^{19}F NMR (376 MHz, Chloroform- d)



^{13}C NMR (101 MHz, Chloroform- d)





tert-butyl (Z)-4-(cyanomethyl)-4-(2-fluoro-3-phenylallyl)piperidine-1-carboxylate

Following the general procedure (**d4**, yellow liquid, 54.4 mg, 76%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

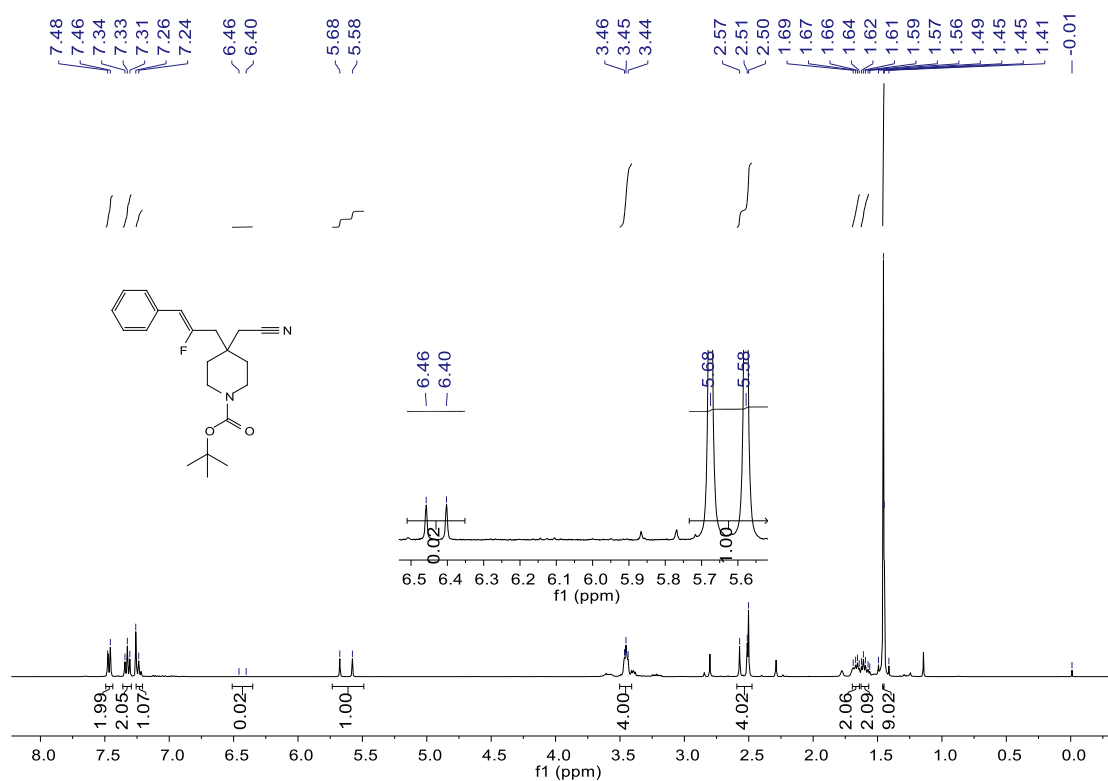
¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, J = 8.5 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (s, 1H), 5.63 (d, J = 39.2 Hz, 1H), 3.45 (t, J = 5.7 Hz, 4H), 2.59 – 2.47 (m, 4H), 1.70 – 1.64 (m, 2H), 1.63 – 1.57 (m, 2H), 1.45 (s, 9H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.10.

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.86 (d, J = 266.9 Hz), 154.77 (d, J = 3.5 Hz), 132.85 (d, J = 2.8 Hz), 128.62, 128.57, 127.55 (d, J = 2.2 Hz), 117.44, 110.66 (d, J = 8.2 Hz), 80.02, 56.45, 40.07 (d, J = 25.1 Hz), 35.04 (d, J = 4.3 Hz), 34.30, 28.48, 26.51 (d, J = 2.0 Hz).

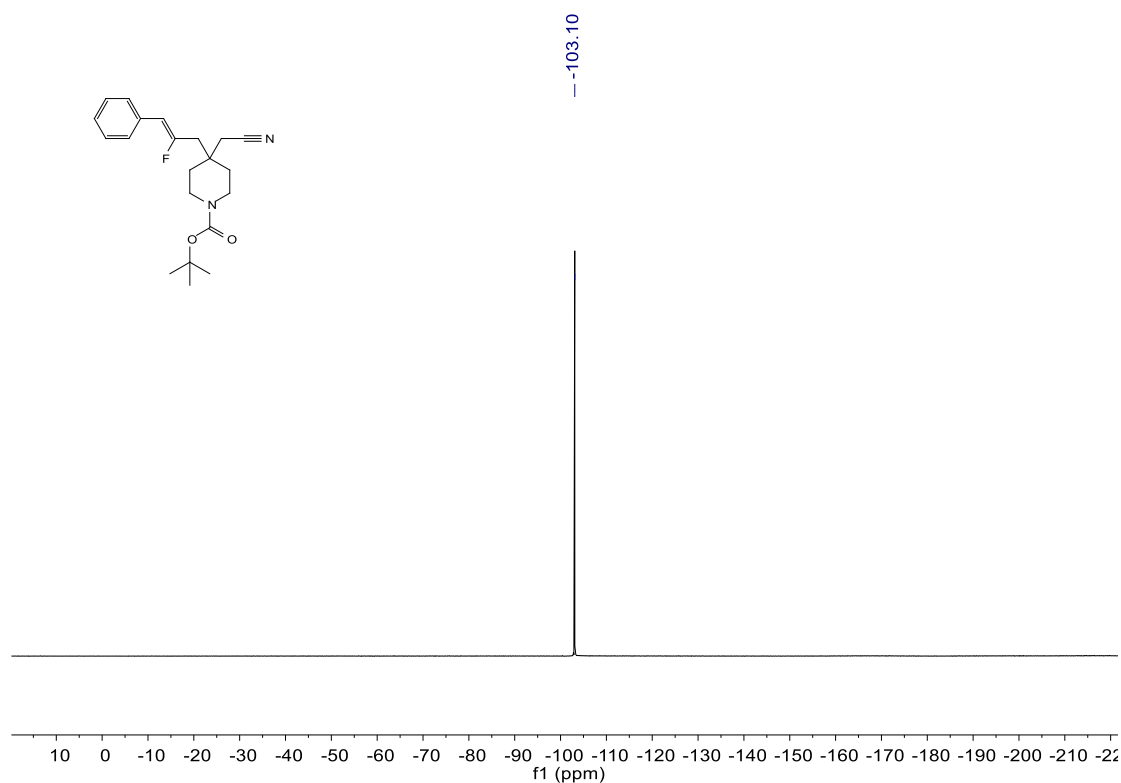
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₂₁H₂₇FN₂O₂: 359.2129; found: 359.2128.

¹H NMR (400 MHz, Chloroform-*d*)

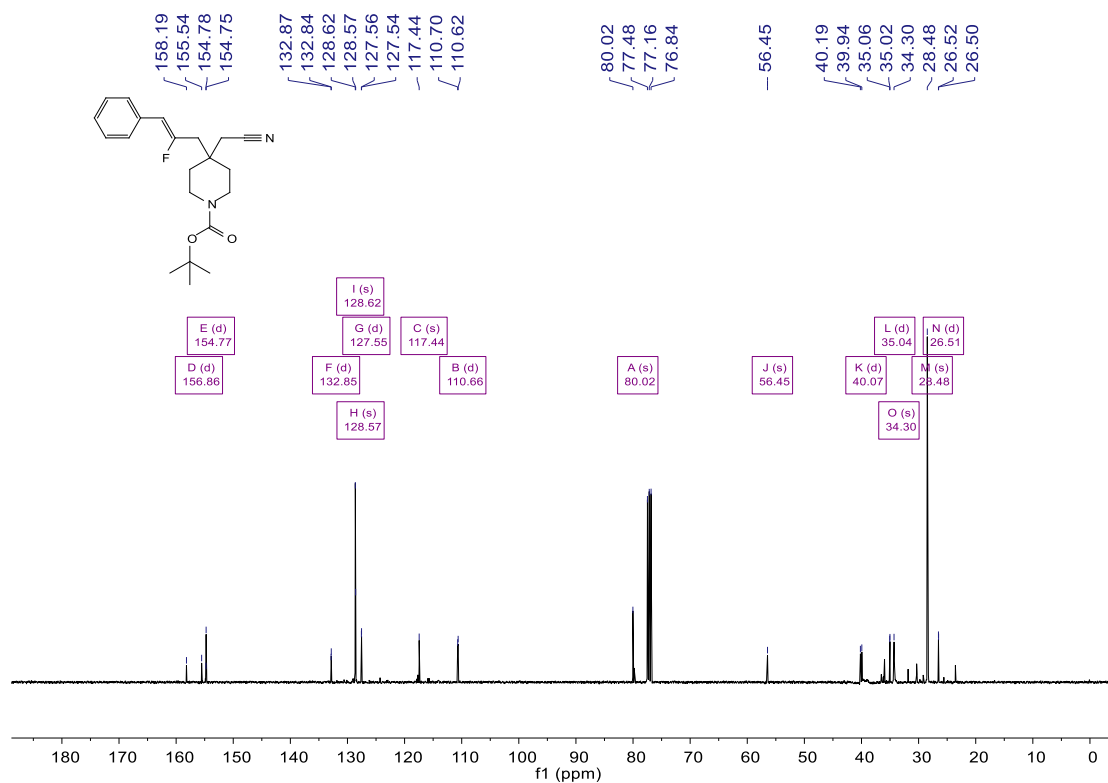


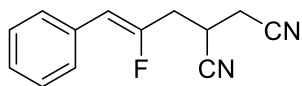
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)





(Z)-2-(2-fluoro-3-phenylallyl)succinonitrile

Following the general procedure (**d5**, yellow liquid, 28.3 mg, 66%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (3:1) as an eluent.

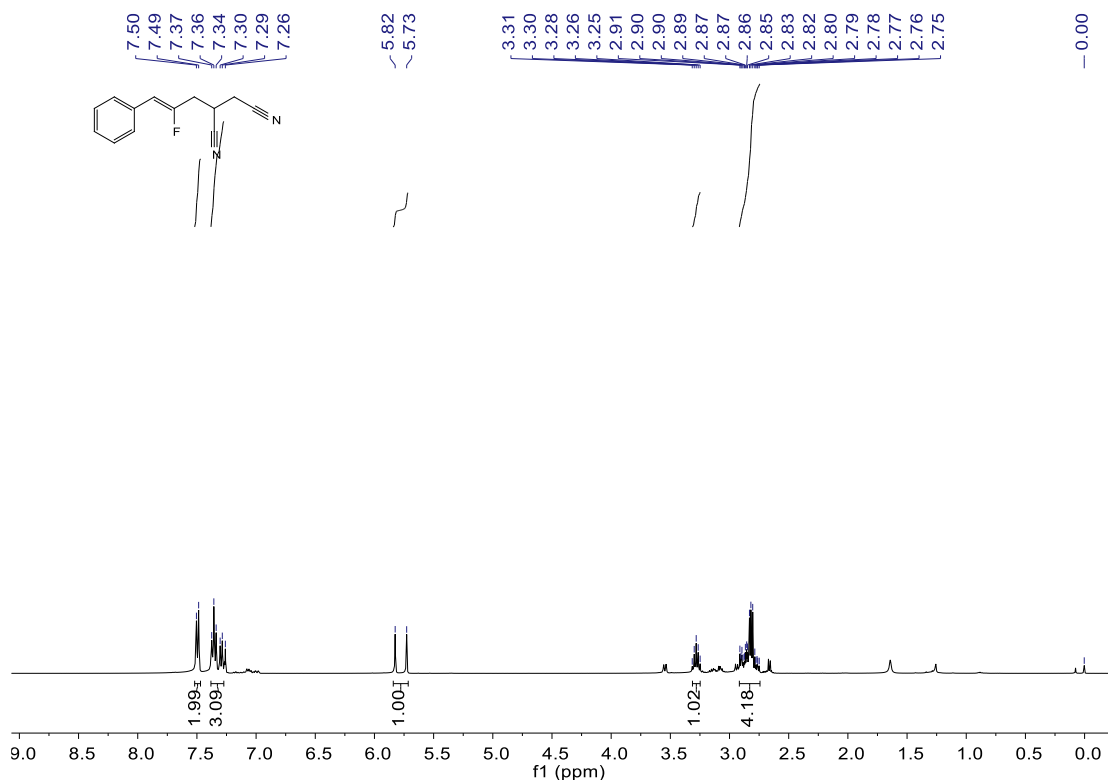
¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 7.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.78 (d, J = 38.9 Hz, 1H), 3.27 (q, J = 6.6 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.79 (dd, J = 14.0, 6.9 Hz, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -101.87.

¹³C NMR (101 MHz, Chloroform-*d*) δ 153.22 (d, J = 264.4 Hz), 132.05 (d, J = 2.9 Hz), 128.87 (d, J = 7.3 Hz), 128.74, 128.15 (d, J = 2.2 Hz), 117.92, 115.23, 111.28 (d, J = 7.3 Hz), 35.21 (d, J = 27.2 Hz), 26.17 (d, J = 2.0 Hz), 20.27.

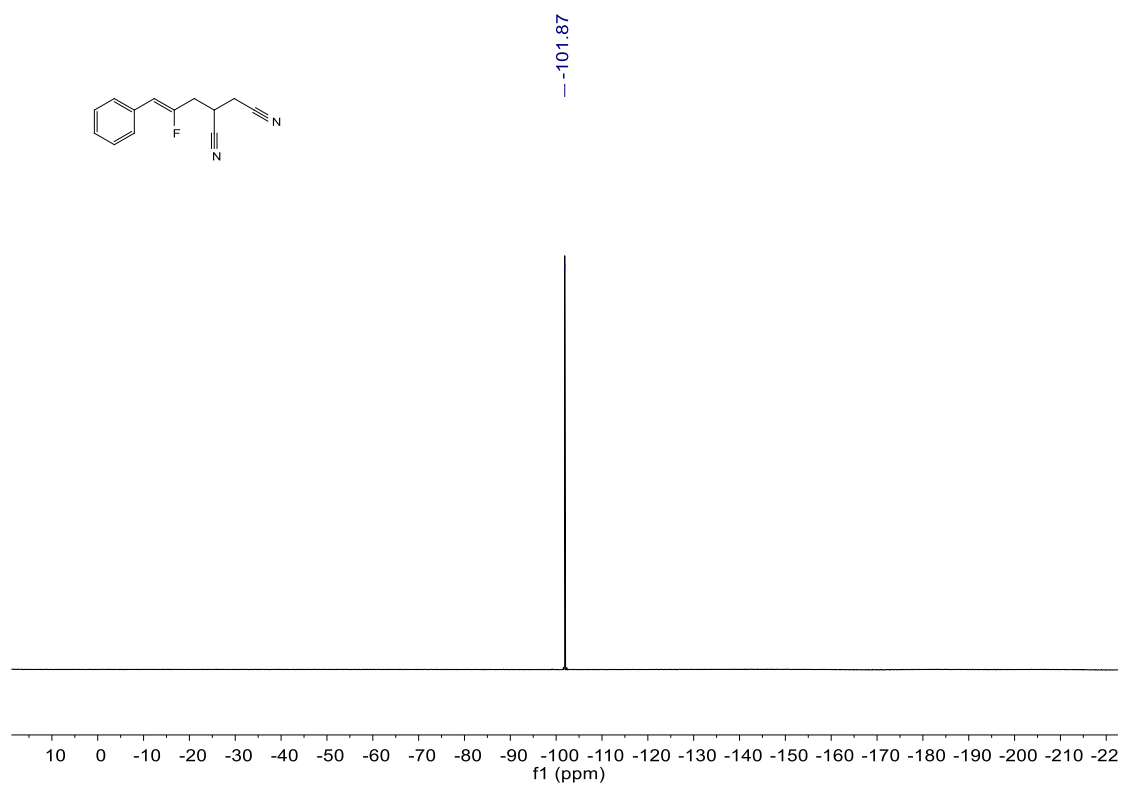
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₁₃H₁₁FN₂: 215.0979; found: 215.0978.

¹H NMR (400 MHz, Chloroform-*d*)

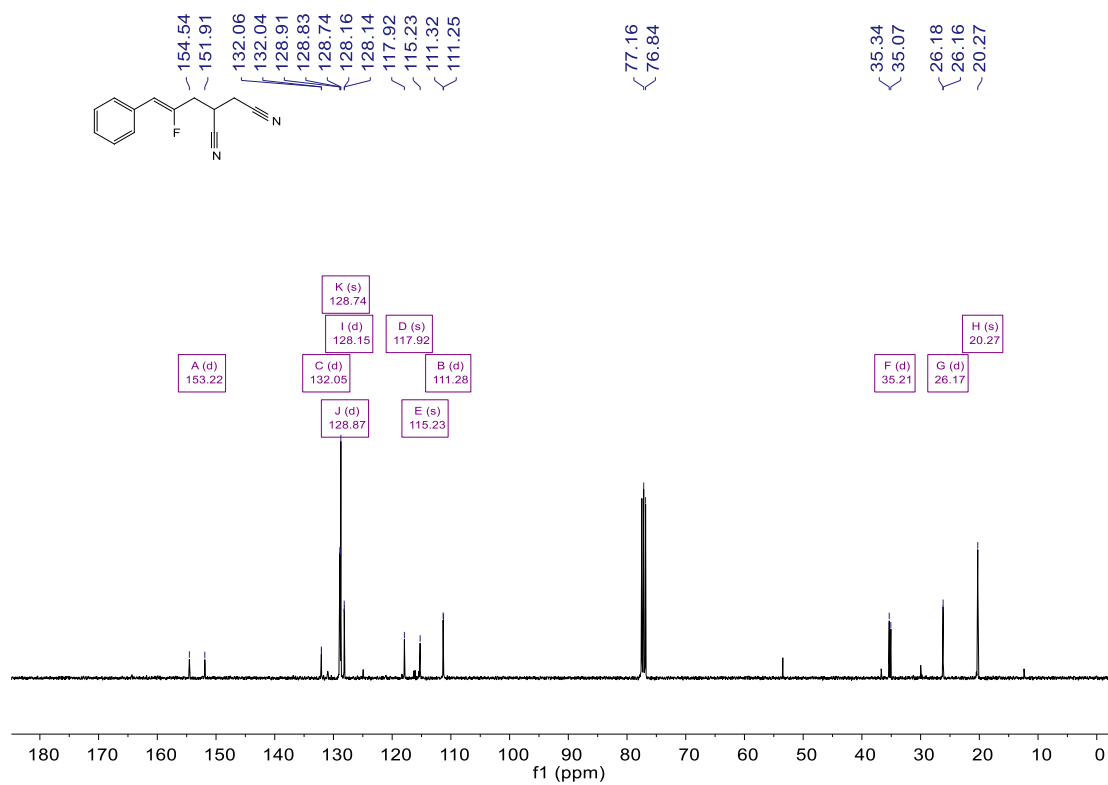


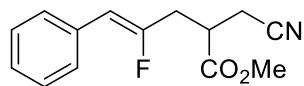
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





methyl (Z)-2-(cyanomethyl)-4-fluoro-5-phenylpent-4-enoate

Following the general procedure (**d6**, pale-yellow liquid, 34.1 mg, 69%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (3:1) as an eluent.

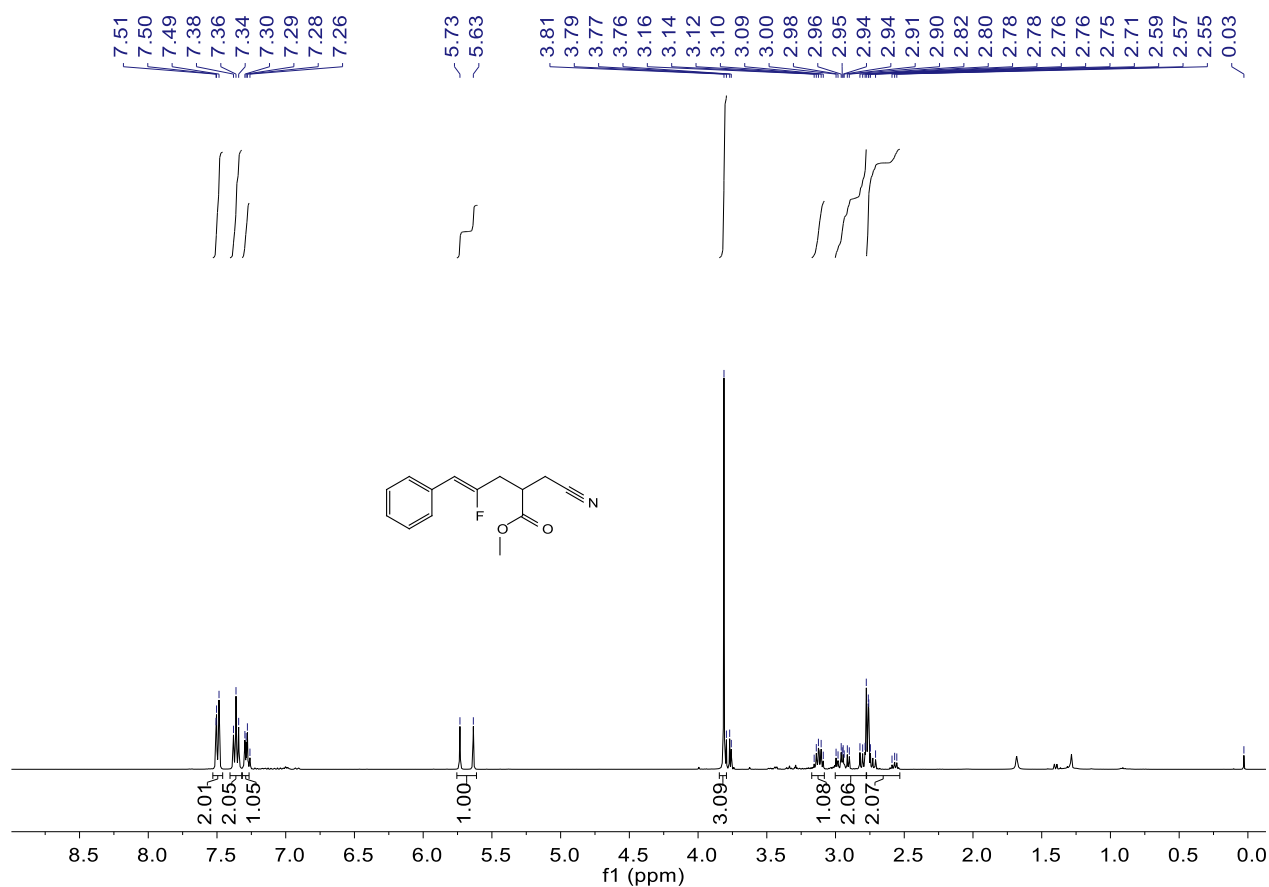
¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 5.68 (d, *J* = 39.0 Hz, 1H), 3.81 (s, 3H), 3.18 – 3.08 (m, 1H), 3.01 – 2.78 (m, 2H), 2.77 – 2.54 (m, 2H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ 103.02.

¹³C NMR (101 MHz, Chloroform-*d*) δ 171.79, 155.60 (d, *J* = 265.5 Hz), 132.67 (d, *J* = 2.7 Hz), 128.70, 128.64, 127.67 (d, *J* = 2.7 Hz), 117.37, 109.80 (d, *J* = 7.9 Hz), 52.87, 38.90 (d, *J* = 1.6 Hz), 34.62 (d, *J* = 27.1 Hz), 18.55.

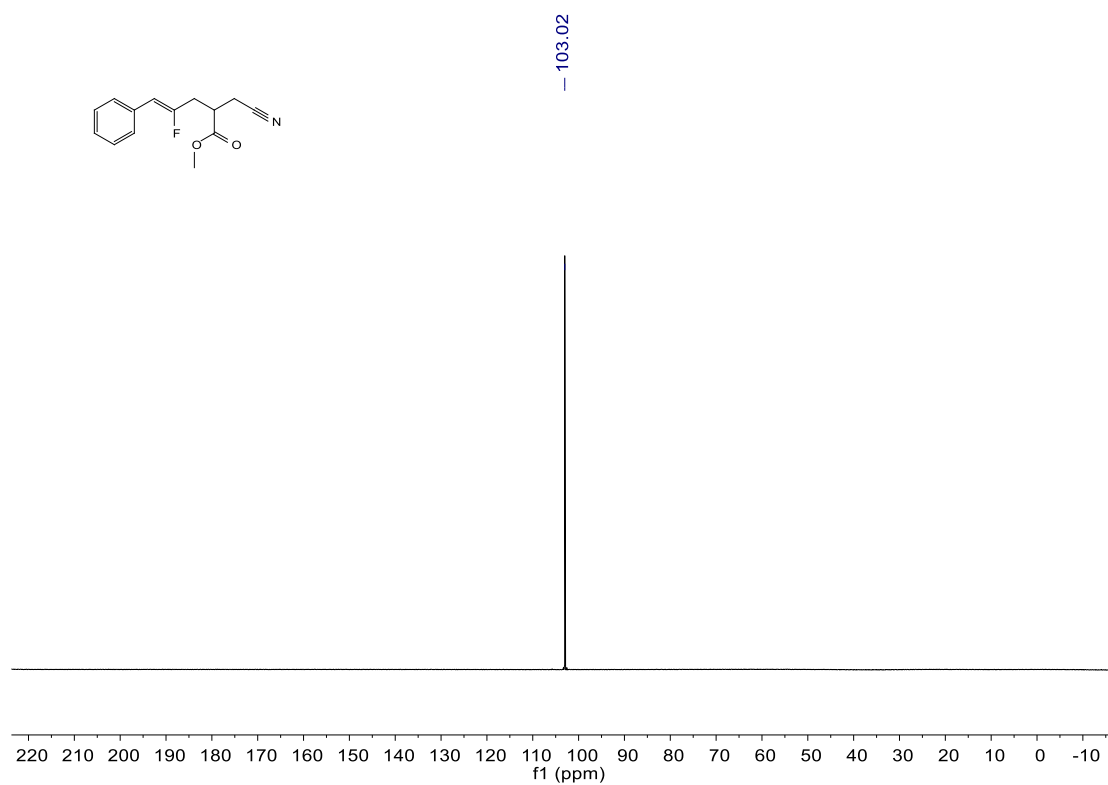
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₄H₁₄FNO₂: 248.1081; found: 248.1080.

¹H NMR (400 MHz, Chloroform-*d*)

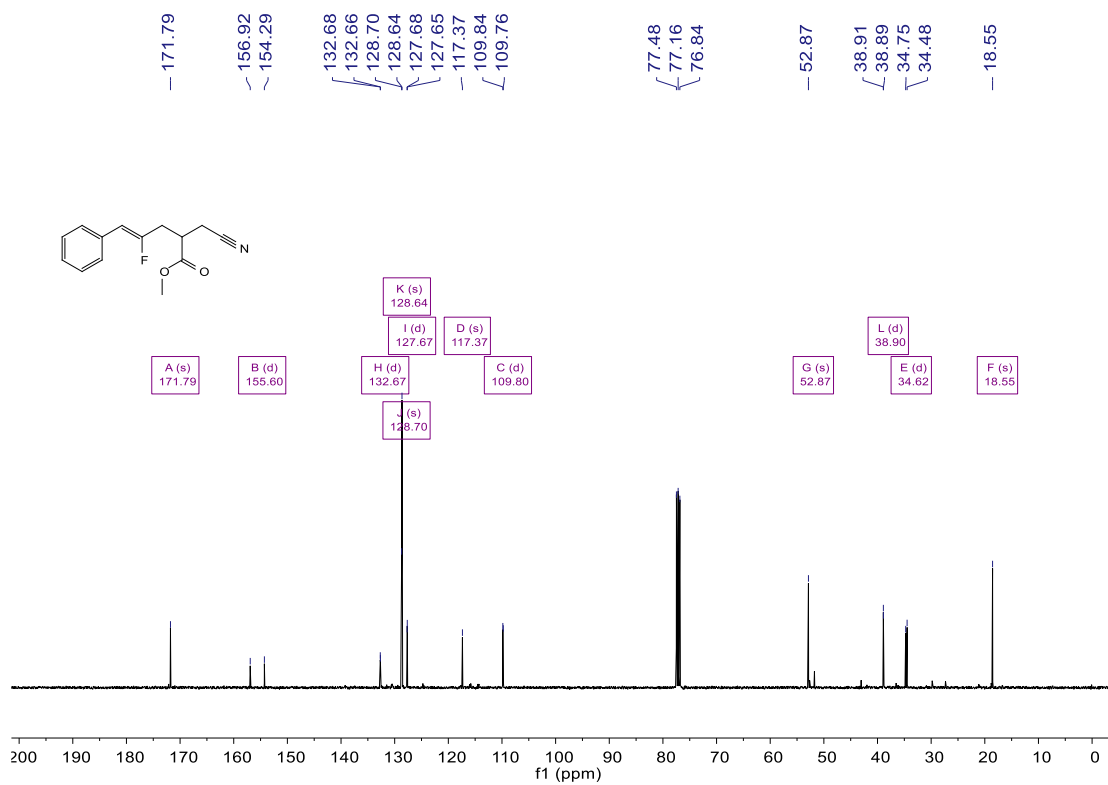


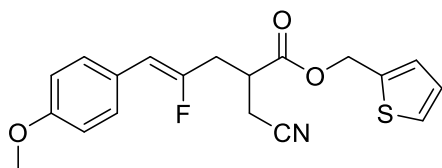
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





thiophen-2-ylmethyl (Z)-2-(cyanomethyl)-4-fluoro-5-(4-methoxyphenyl)pent-4-enoate

Following the general procedure (**d7**, pale-yellow liquid, 37.3 mg, 52%, Z/E > 14:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (4:1) as an eluent.

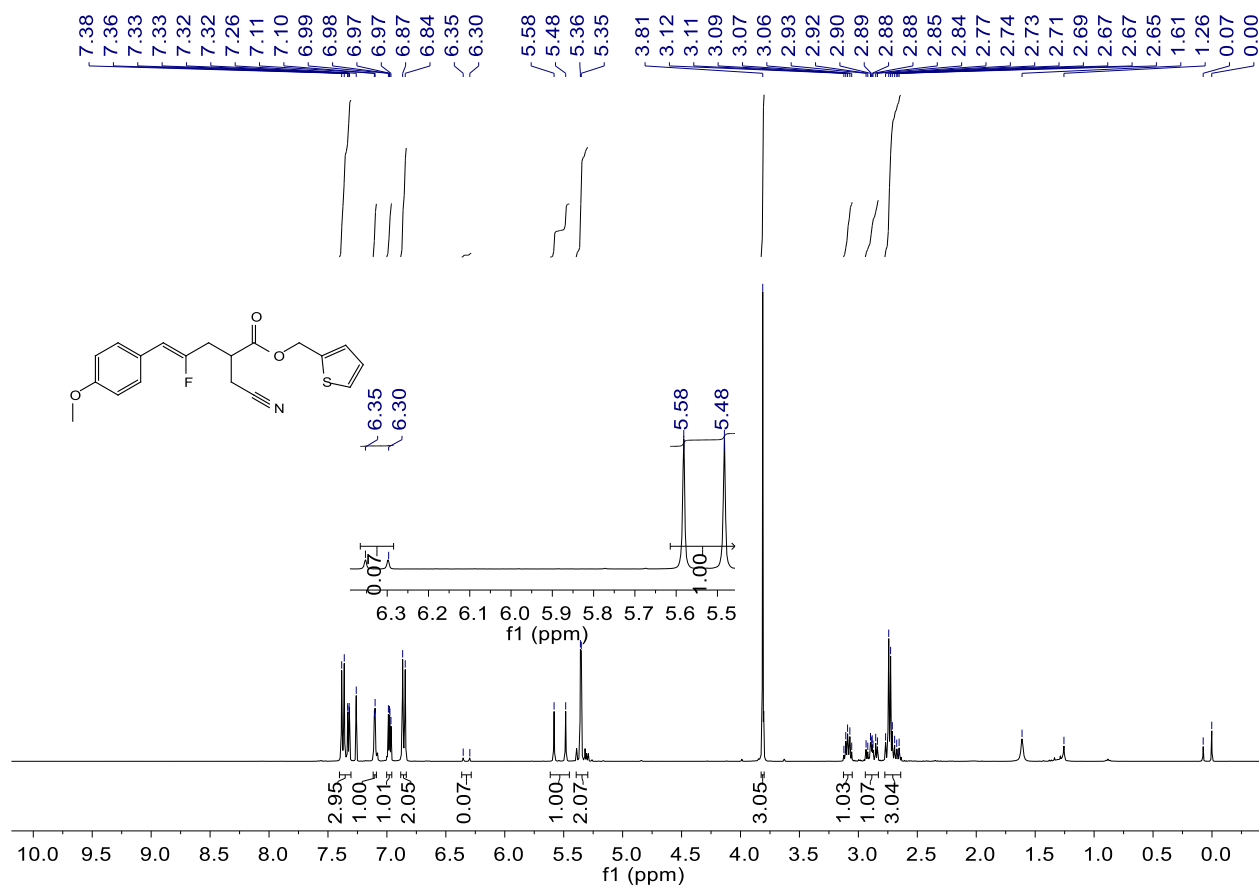
¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 3H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.53 (d, *J* = 39.4 Hz, 1H), 5.35 (d, *J* = 3.1 Hz, 2H), 3.81 (s, 3H), 3.09 (p, *J* = 6.3 Hz, 1H), 2.89 (ddd, *J* = 17.7, 15.0, 5.8 Hz, 1H), 2.78 – 2.64 (m, 3H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -107.42.

¹³C NMR (101 MHz, Chloroform-*d*) δ 171.13, 158.96 (d, *J* = 2.5 Hz), 154.04 (d, *J* = 262.7 Hz), 136.91, 130.02 (d, *J* = 7.3 Hz), 128.96, 127.46, 127.07, 125.38 (d, *J* = 2.9 Hz), 117.36, 113.99, 109.36 (d, *J* = 8.0 Hz), 61.74, 55.39, 39.01 (d, *J* = 1.6 Hz), 34.52 (d, *J* = 27.1 Hz), 18.49.

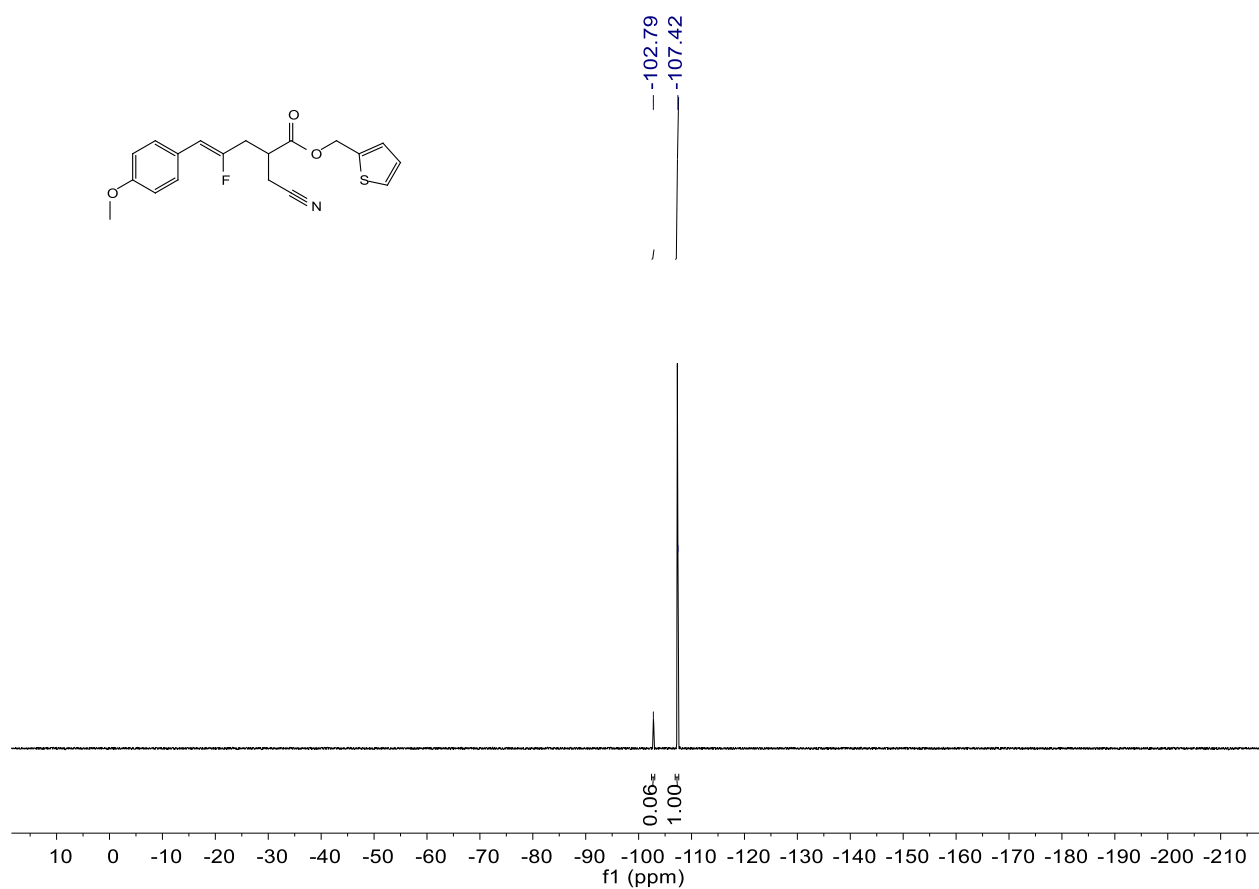
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₉H₁₈FNO₃S: 360.1064; found: 360.1061.

¹H NMR (400 MHz, Chloroform-*d*)

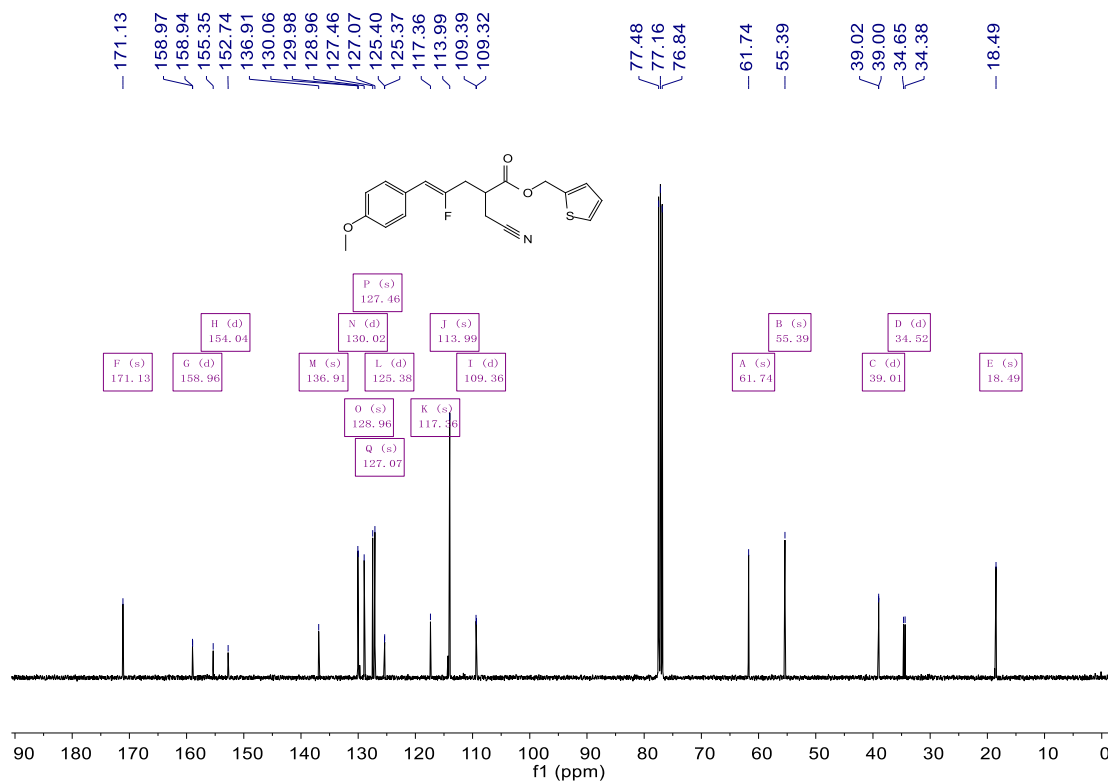


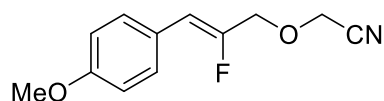
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)





(Z)-2-((2-fluoro-3-(4-methoxyphenyl)allyl)oxy)acetonitrile

Following the general procedure (**d8**, yellow liquid, 27.4 mg, 62%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

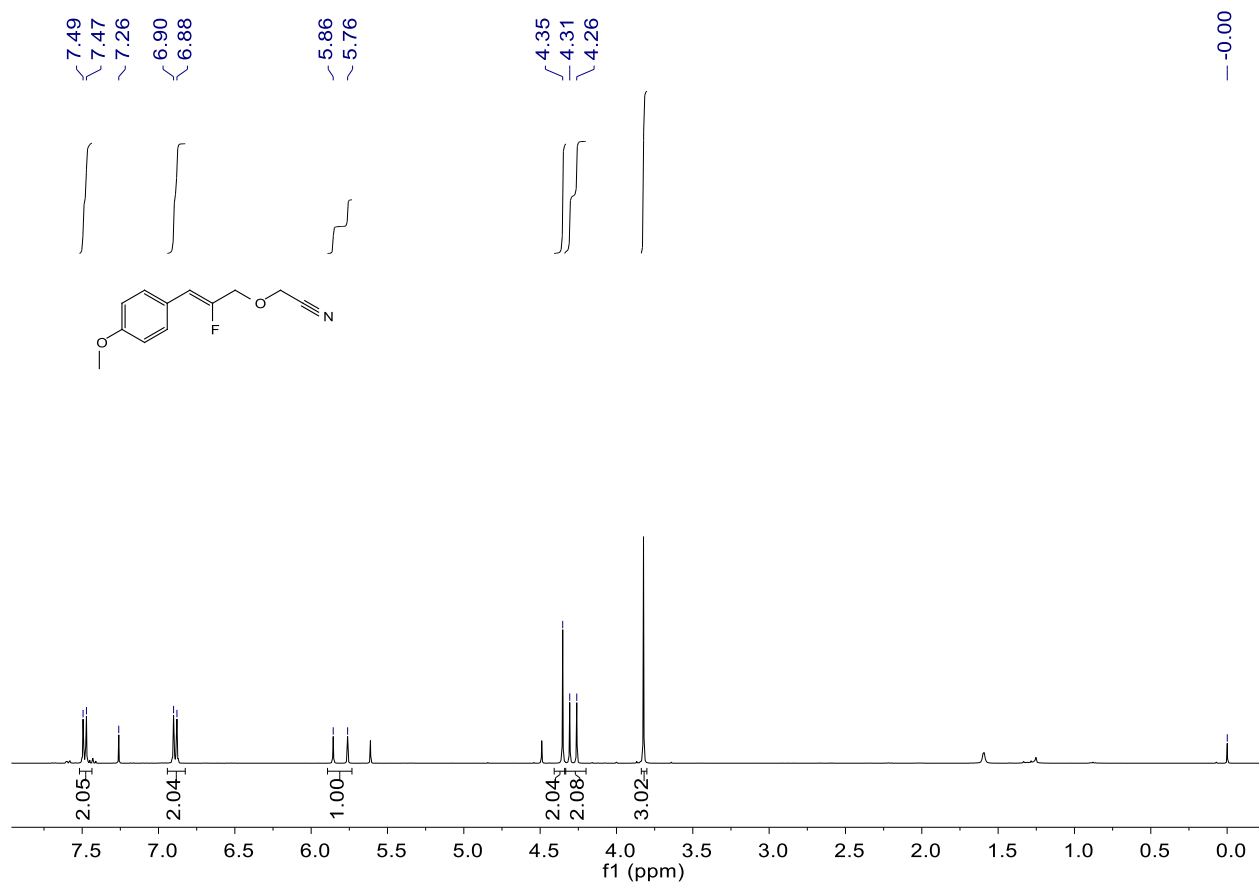
¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.81 (d, *J* = 37.8 Hz, 1H), 4.35 (s, 1H), 4.28 (d, *J* = 18.4 Hz, 1H), 3.82 (s, 3H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.29.

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.51 (d, *J* = 2.9 Hz), 152.10 (d, *J* = 264.8 Hz), 130.52 (d, *J* = 7.4 Hz), 130.13 (d, *J* = 3.7 Hz), 115.63, 114.15, 111.92 (d, *J* = 6.6 Hz), 69.82 (d, *J* = 29.9 Hz), 55.41, 54.68.

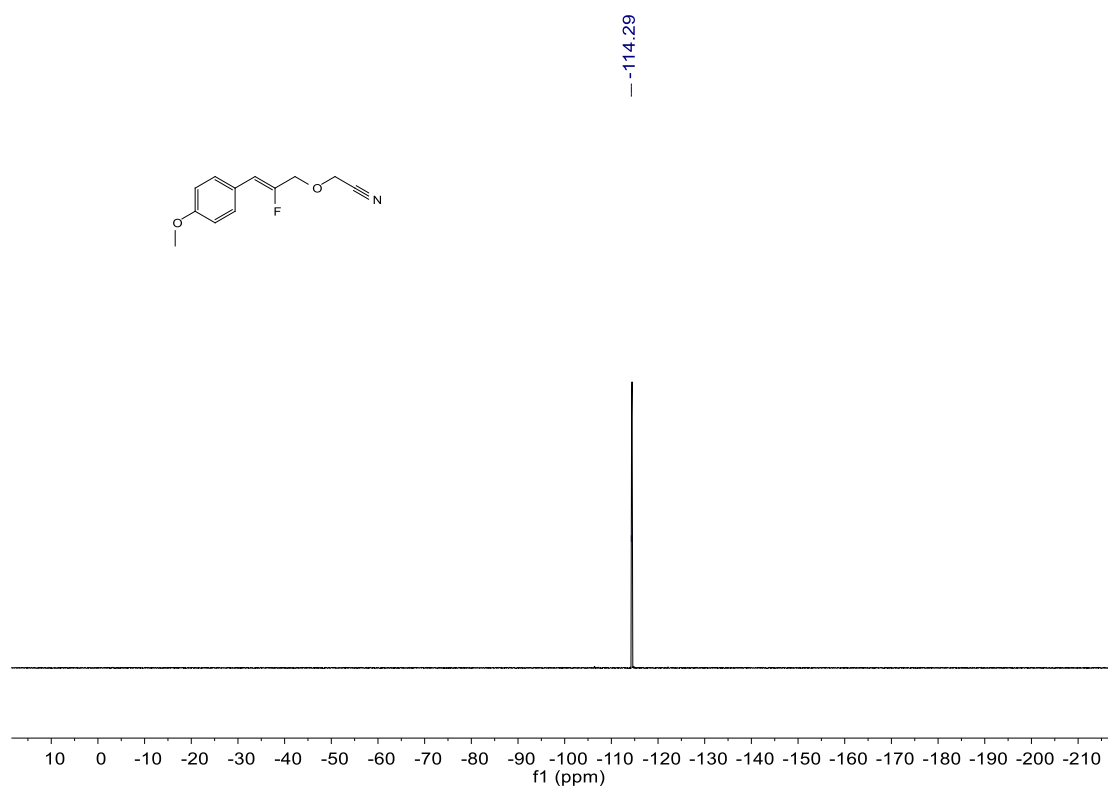
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₂H₁₂FNO₂: 222.0925; found: 222.0925.

¹H NMR (400 MHz, Chloroform-*d*)

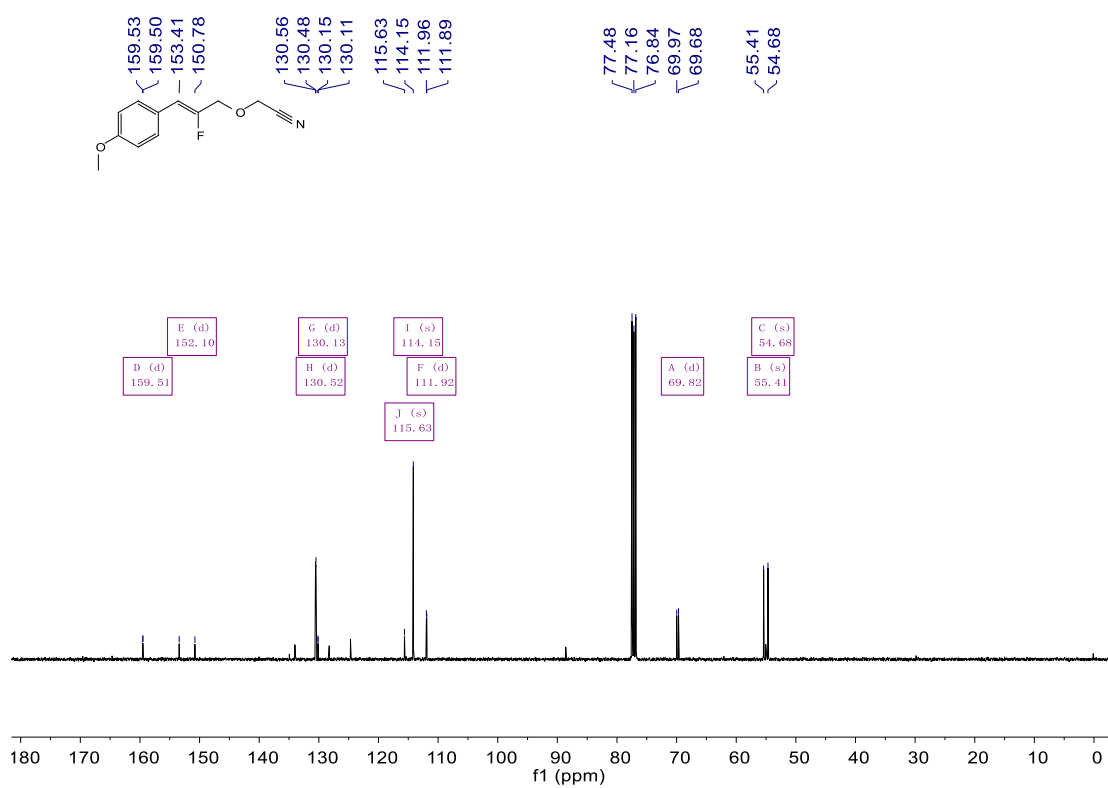


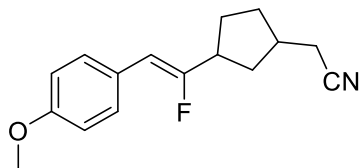
Supporting Information

^{19}F NMR (376 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)





2-((3S)-3-((Z)-1-fluoro-2-(4-methoxyphenyl)vinyl)cyclopentyl)acetonitrile

Following the general procedure (**d9**, pale-yellow liquid, 22.8 mg, 44%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

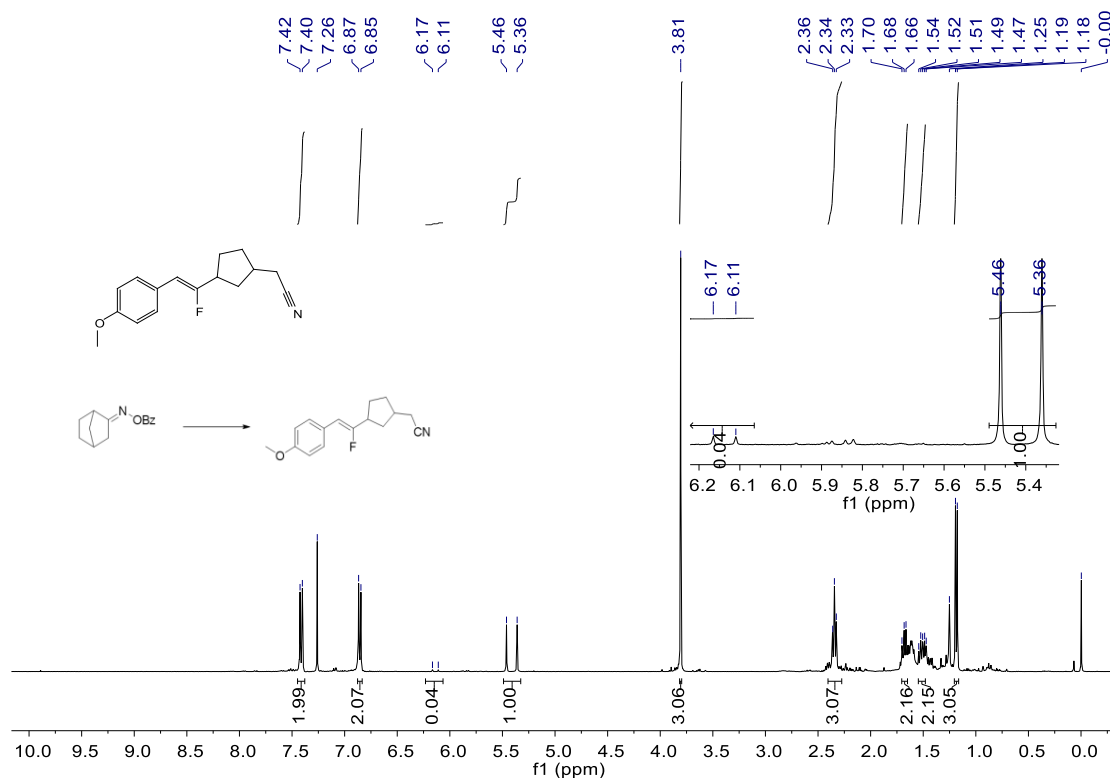
¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.41 (d, *J* = 40.4 Hz, 1H), 3.81 (s, 3H), 2.34 (t, *J* = 6.9 Hz, 3H), 1.67 (d, *J* = 7.1 Hz, 2H), 1.52 – 1.46 (m, 2H), 1.18 (d, *J* = 6.9 Hz, 3H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.47.

¹³C NMR (101 MHz, Chloroform-*d*) δ 162.33 (d, *J* = 266.6 Hz), 158.42 (d, *J* = 2.9 Hz), 129.69 (d, *J* = 7.4 Hz), 126.48 (d, *J* = 2.6 Hz), 119.84, 113.96, 104.71 (d, *J* = 9.2 Hz), 55.39, 37.69 (d, *J* = 25.5 Hz), 33.06, 26.51, 25.54, 18.13 (d, *J* = 2.5 Hz), 17.25.

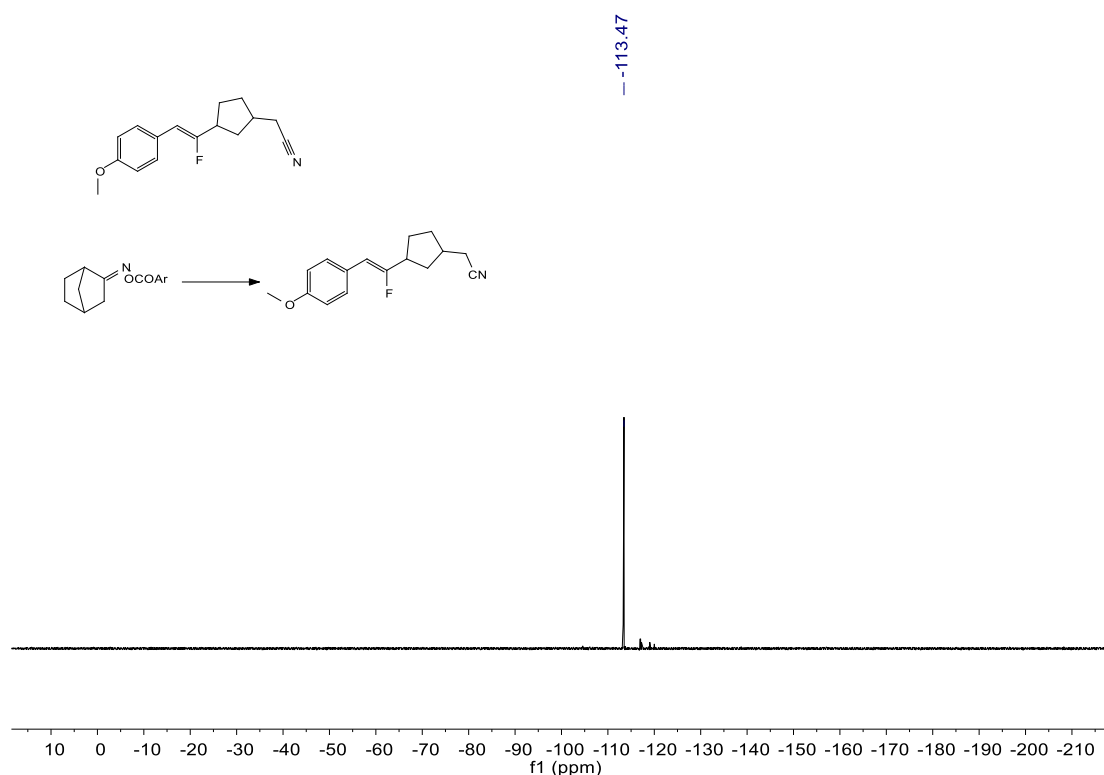
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₆H₁₈FNO: 260.1445; found: 260.1443.

¹H NMR (400 MHz, Chloroform-*d*)

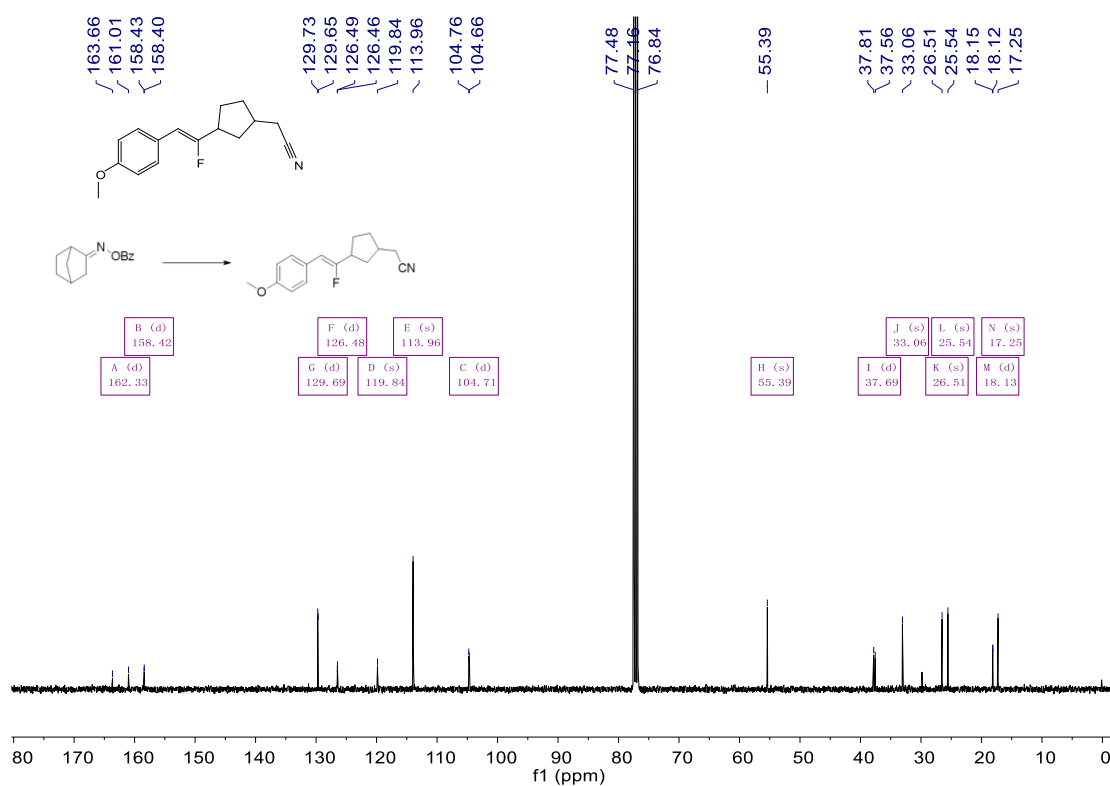


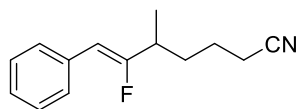
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(S,Z)-6-fluoro-5-methyl-7-phenylhept-6-enitrile

Following the general procedure (**d10**, yellow liquid, 39.1 mg, 90%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

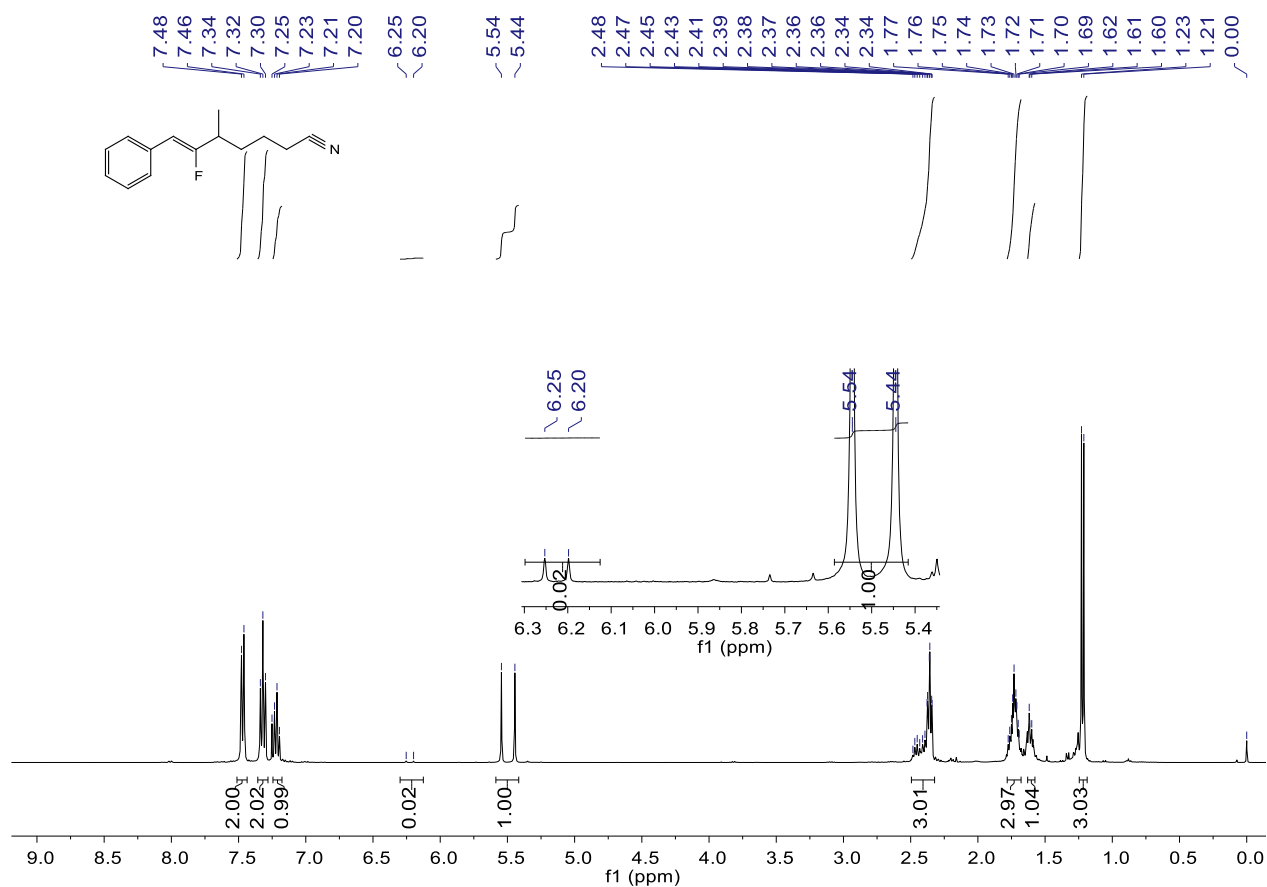
¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.50 (d, *J* = 40.0 Hz, 1H), 2.50 – 2.33 (m, 3H), 1.74 (ddq, *J* = 10.0, 7.0, 3.8, 3.1 Hz, 3H), 1.64 – 1.58 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ 102.55.

¹³C NMR (101 MHz, Chloroform-*d*) δ 162.99 (d, *J* = 269.3 Hz), 133.51 (d, *J* = 2.3 Hz), 128.56, 128.48 (d, *J* = 7.5 Hz), 127.02 (d, *J* = 2.4 Hz), 119.62, 105.71 (d, *J* = 8.7 Hz), 37.42 (d, *J* = 25.6 Hz), 32.76, 23.26, 18.09 (d, *J* = 2.4 Hz), 17.29.

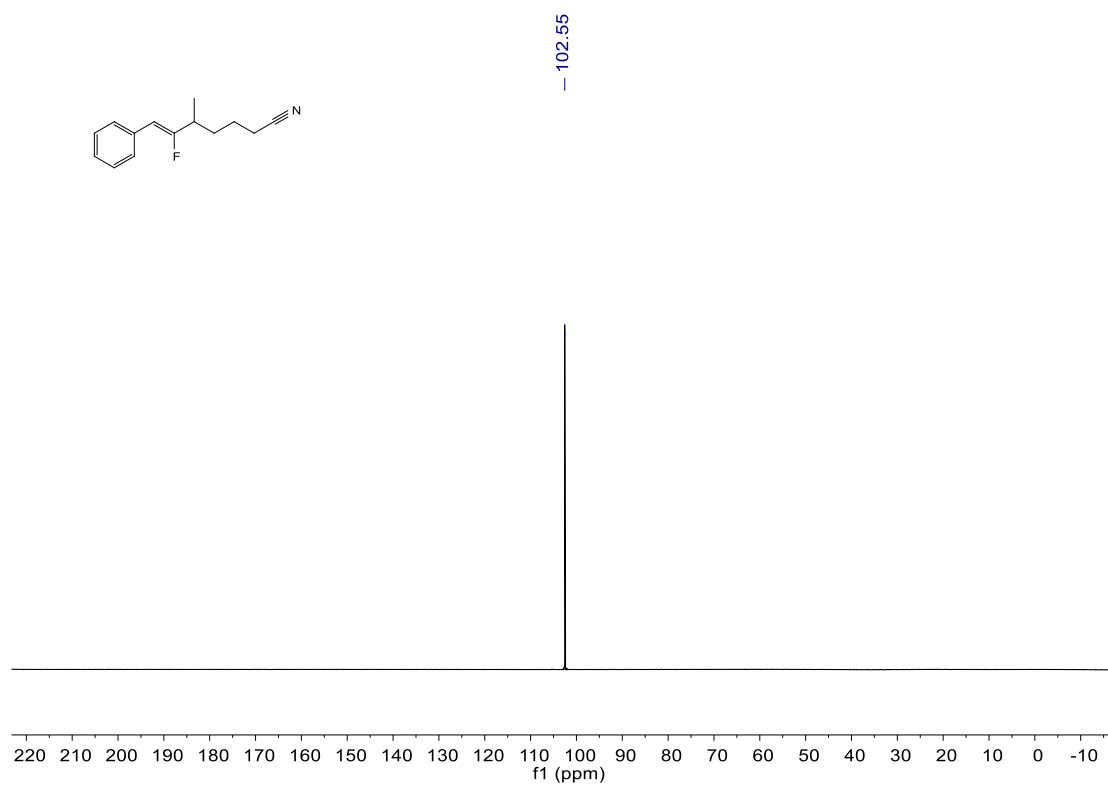
HRMS (ESI) *m/z*: (M+Na)⁺ Calcd for C₁₄H₁₆FN: 240.1159; found: 240.1157.

¹H NMR (400 MHz, Chloroform-*d*)

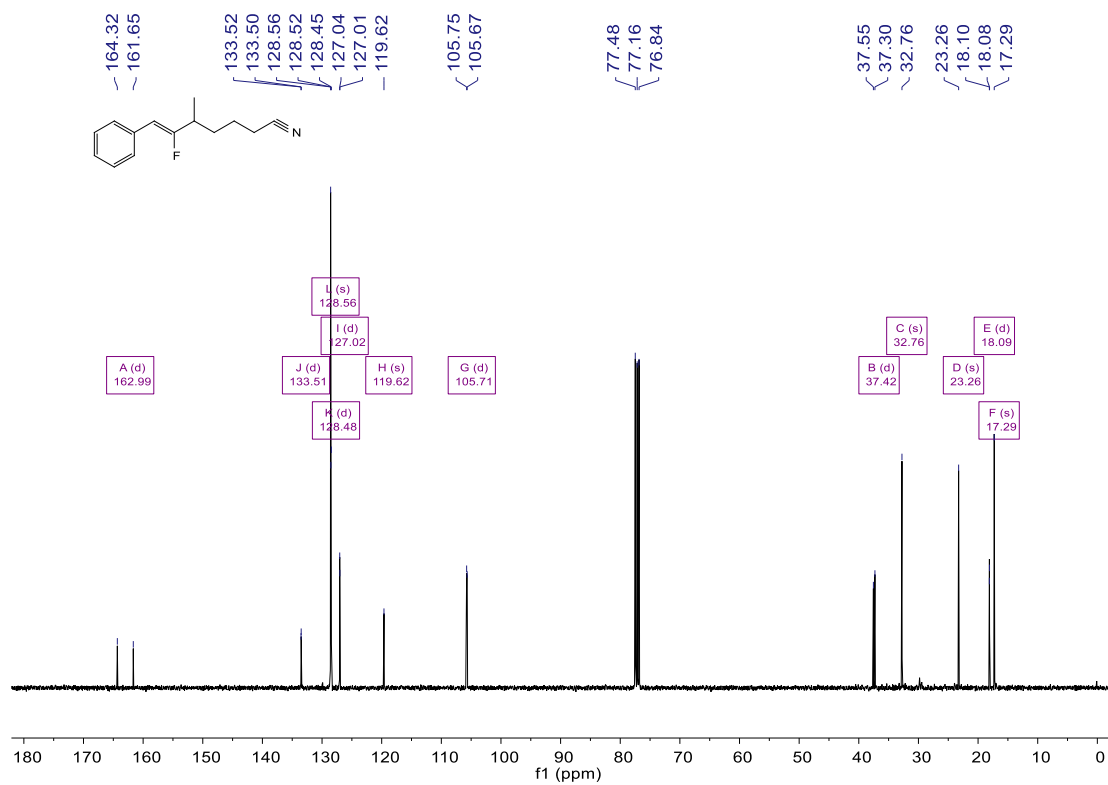


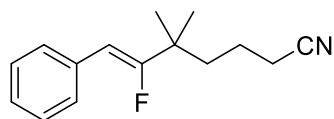
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)





(Z)-6-fluoro-5,5-dimethyl-7-phenylhept-6-enitrile

Following the general procedure (**d11**, yellow liquid, 14.8 mg, 32%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

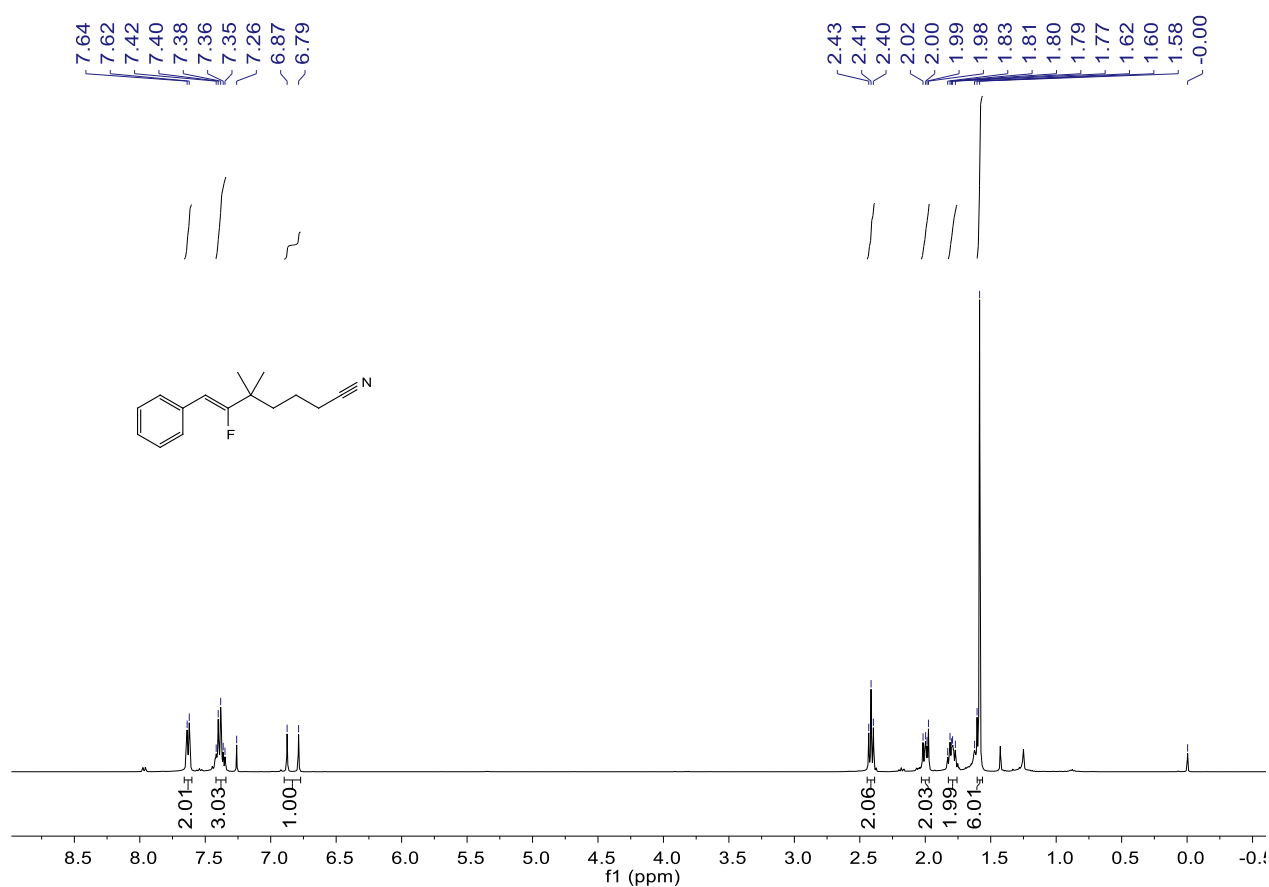
¹H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 6.5 Hz, 2H), 7.39 (q, *J* = 7.8, 7.0 Hz, 3H), 6.83 (d, *J* = 35.1 Hz, 1H), 2.41 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.97 (m, 2H), 1.79 (dd, *J* = 9.9, 6.4 Hz, 2H), 1.58 (s, 6H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ 102.01.

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.49 (d, *J* = 269.0 Hz), 131.28 (d, *J* = 4.4 Hz), 130.37 (d, *J* = 8.1 Hz), 129.76 (d, *J* = 2.7 Hz), 128.92, 119.58, 117.13 (d, *J* = 5.0 Hz), 84.04, 40.10, 26.02, 20.35, 17.54.

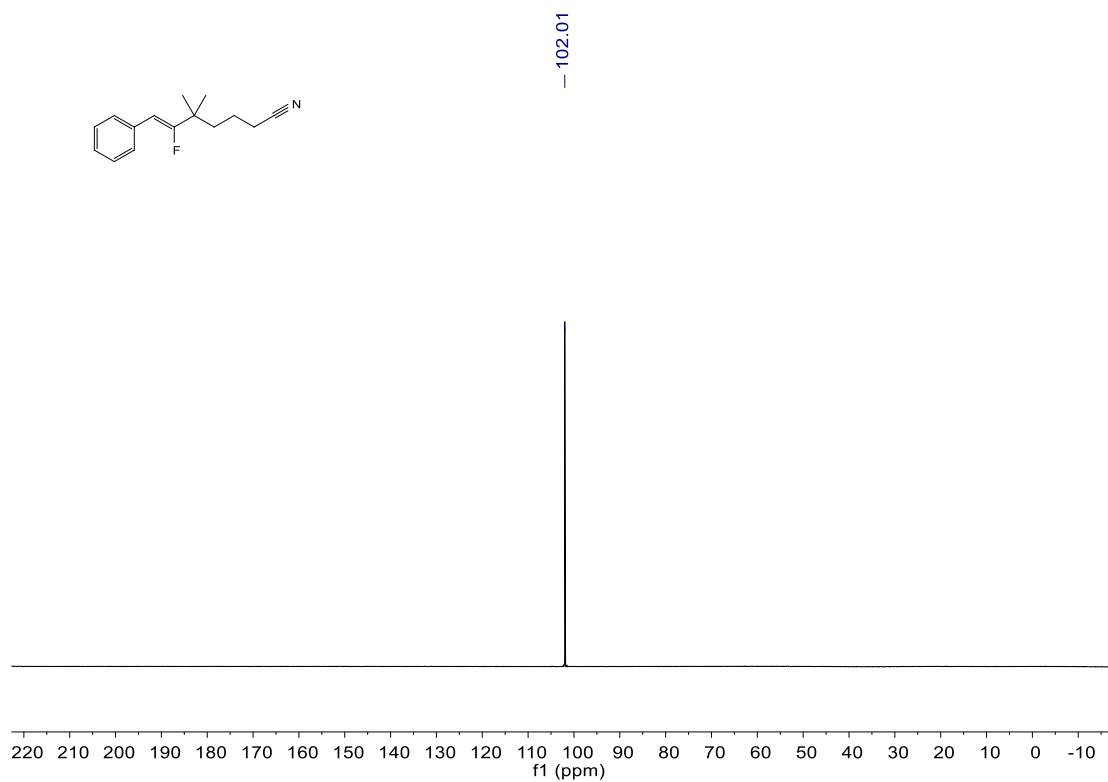
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₅H₁₈FN: 232.1496; found: 232.1499.

¹H NMR (400 MHz, Chloroform-*d*)

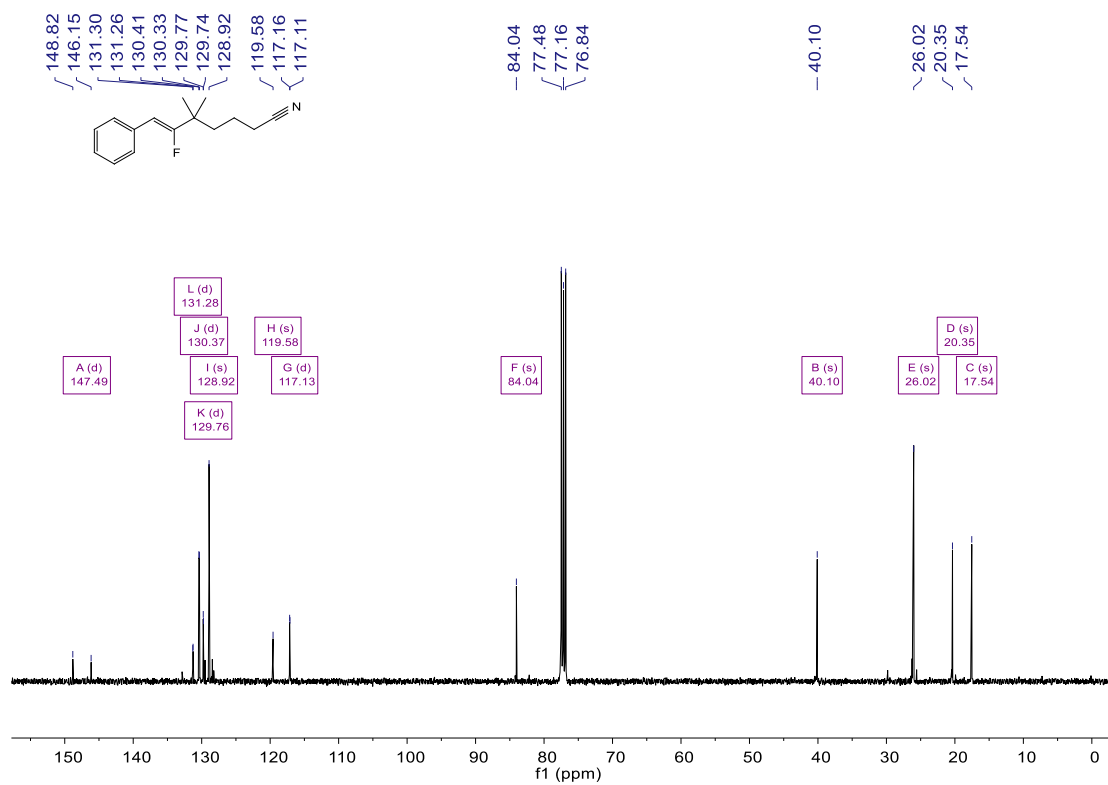


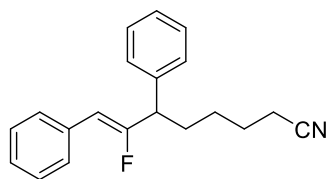
Supporting Information

^{19}F NMR (376 MHz, Chloroform- d)



^{13}C NMR (101 MHz, Chloroform- d)





(R,Z)-7-fluoro-6,8-diphenyloct-7-enenitrile

Following the general procedure (**d12**, yellow liquid, 53.4 mg, 91%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

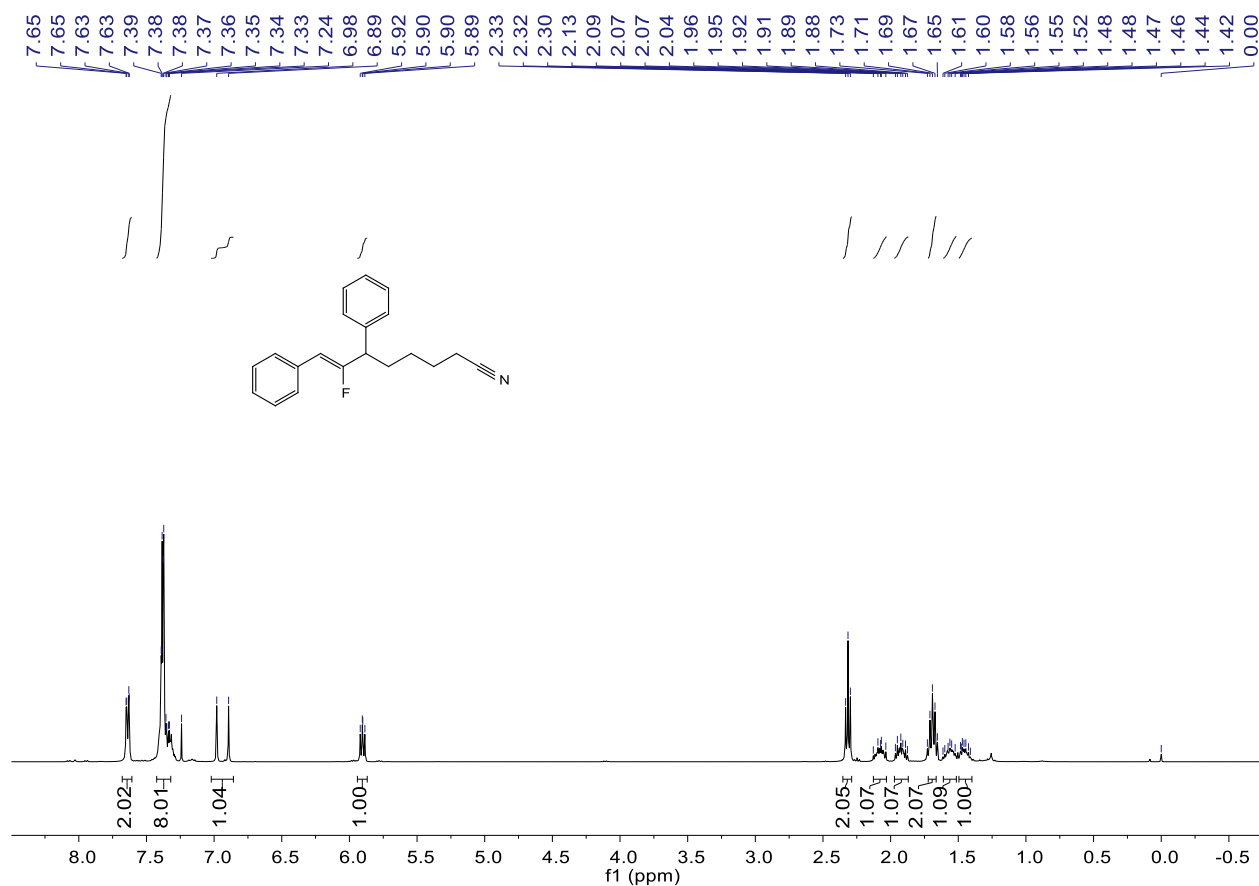
¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.44 – 7.34 (m, 8H), 6.96 (d, J = 35.0 Hz, 1H), 5.92 (dd, J = 7.7, 6.0 Hz, 1H), 2.33 (t, J = 7.1 Hz, 2H), 2.15 – 2.05 (m, 1H), 1.99 – 1.89 (m, 1H), 1.74 – 1.68 (m, 2H), 1.63 – 1.53 (m, 1H), 1.51 – 1.42 (m, 1H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ 103.01.

¹³C NMR (101 MHz, Chloroform-*d*) δ 146.87 (d, J = 267.8 Hz), 139.43, 131.06 (d, J = 4.4 Hz), 130.41 (d, J = 8.1 Hz), 129.88 (d, J = 2.4 Hz), 128.88, 128.76, 128.48, 126.51, 119.51, 118.02 (d, J = 4.8 Hz), 77.26, 35.44, 25.11, 24.67, 17.07.

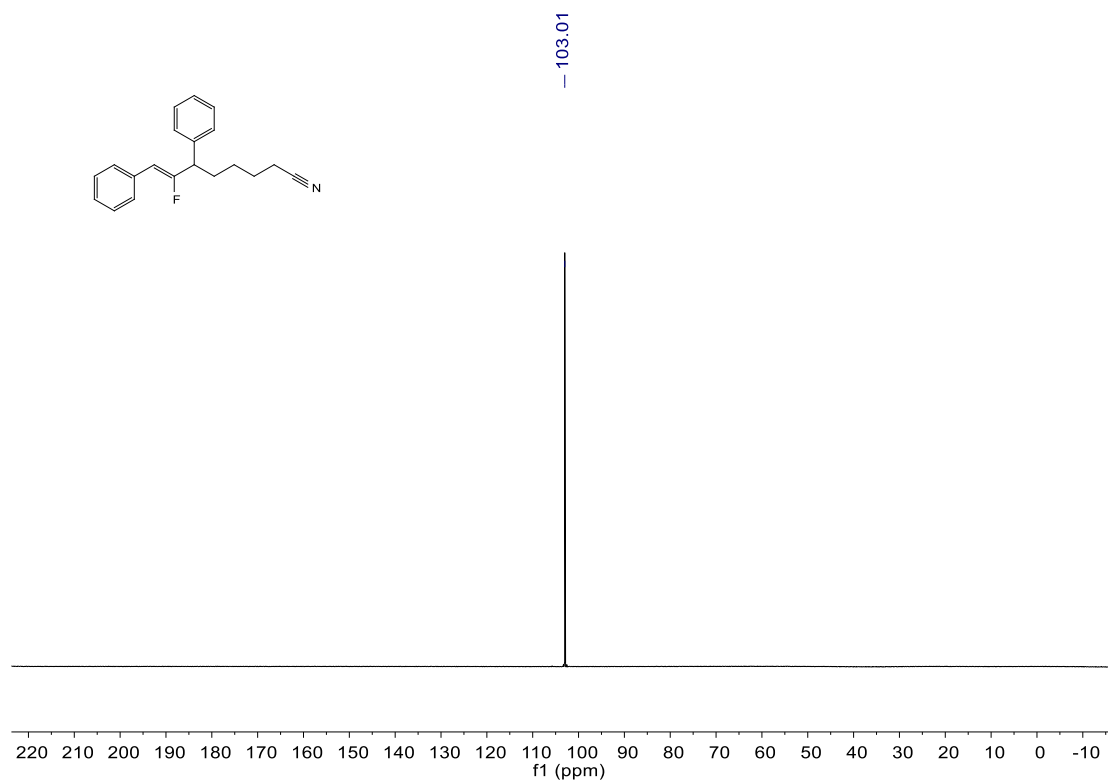
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₂₀H₂₀FN: 294.1653; found: 294.1670.

¹H NMR (400 MHz, Chloroform-*d*)

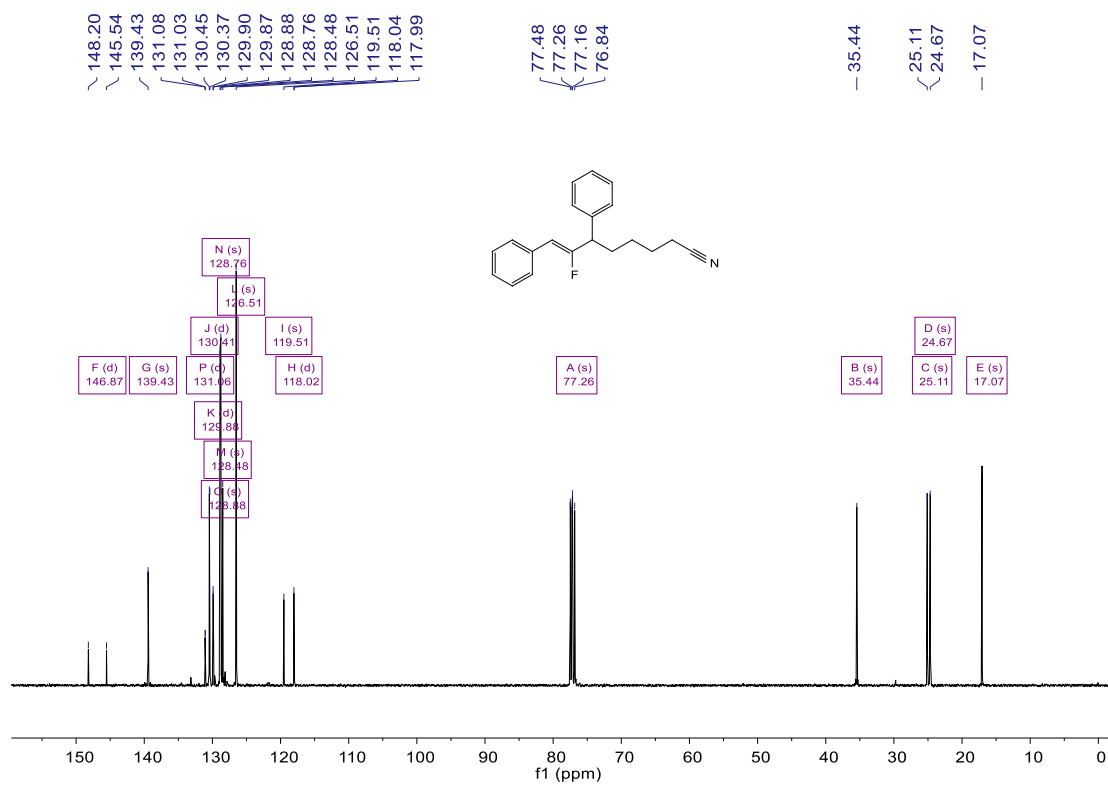


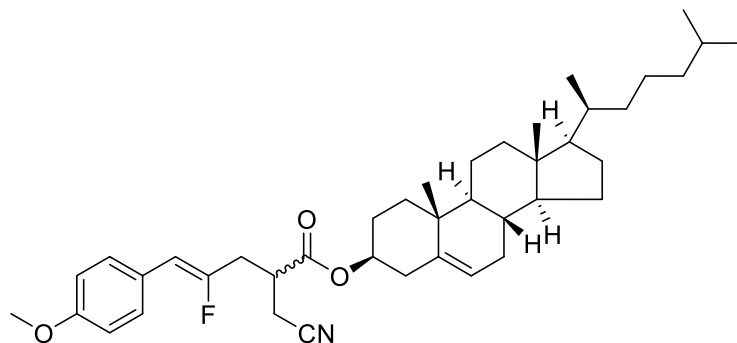
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)





(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (Z)-2-(cyanomethyl)-4-fluoro-5-(4-methoxyphenyl)pent-4-enoate

Following the general procedure (**e1**, pale-yellow liquid, 84.6 mg, 67%, Z/E = 14:1, dr = 1:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (3:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.58 (d, *J* = 39.3 Hz, 1H), 5.36 (dd, *J* = 14.9, 4.6 Hz, 1H), 4.75 – 4.64 (m, 1H), 3.81 (s, 3H), 3.03 (p, *J* = 6.4 Hz, 1H), 2.87 (td, *J* = 19.9, 17.8, 6.3 Hz, 1H), 2.77 – 2.63 (m, 3H), 2.33 (dd, *J* = 12.8, 6.9 Hz, 2H), 2.03 – 1.92 (m, 2H), 1.84 (ddt, *J* = 16.1, 9.4, 3.7 Hz, 3H), 1.54 (ddt, *J* = 35.4, 15.6, 7.4 Hz, 7H), 1.34 (d, *J* = 7.5 Hz, 4H), 1.19 – 1.06 (m, 7H), 1.00 (s, 6H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.67 (s, 3H).

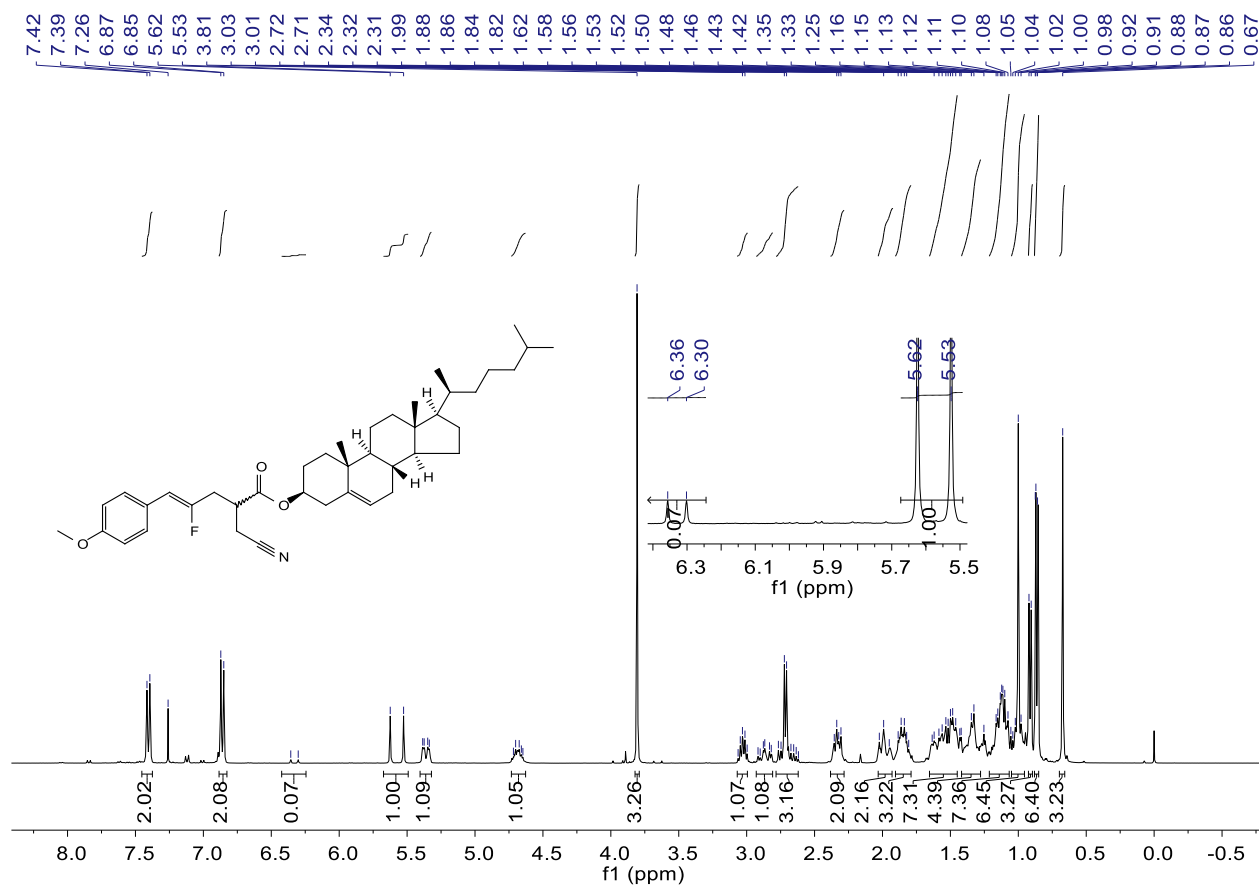
¹⁹F NMR¹⁹ (376 MHz, Chloroform-*d*) δ -102.53, -106.99.

¹³C NMR¹³ (101 MHz, Chloroform-*d*) δ 170.80, 158.94, 154.38 (d, *J* = 263.1 Hz), 139.29, 129.95 (d, *J* = 7.3 Hz), 125.47, 123.14, 117.55, 114.03, 109.19 (d, *J* = 8.0 Hz), 75.75, 56.75, 56.21, 55.37, 50.06, 42.40, 39.79, 39.62, 39.17, 38.01 (d, *J* = 4.1 Hz), 36.97, 36.64, 36.28, 35.90, 34.71 (dd, *J* = 27.1, 3.0 Hz), 31.99, 31.91, 28.34, 28.13, 27.74 (d, *J* = 5.9 Hz), 24.39, 23.93, 22.96, 22.69, 21.13, 19.39, 18.82, 18.59, 11.96.

HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₄₁H₅₈FNO₃: 632.4474; found: 632.4463.

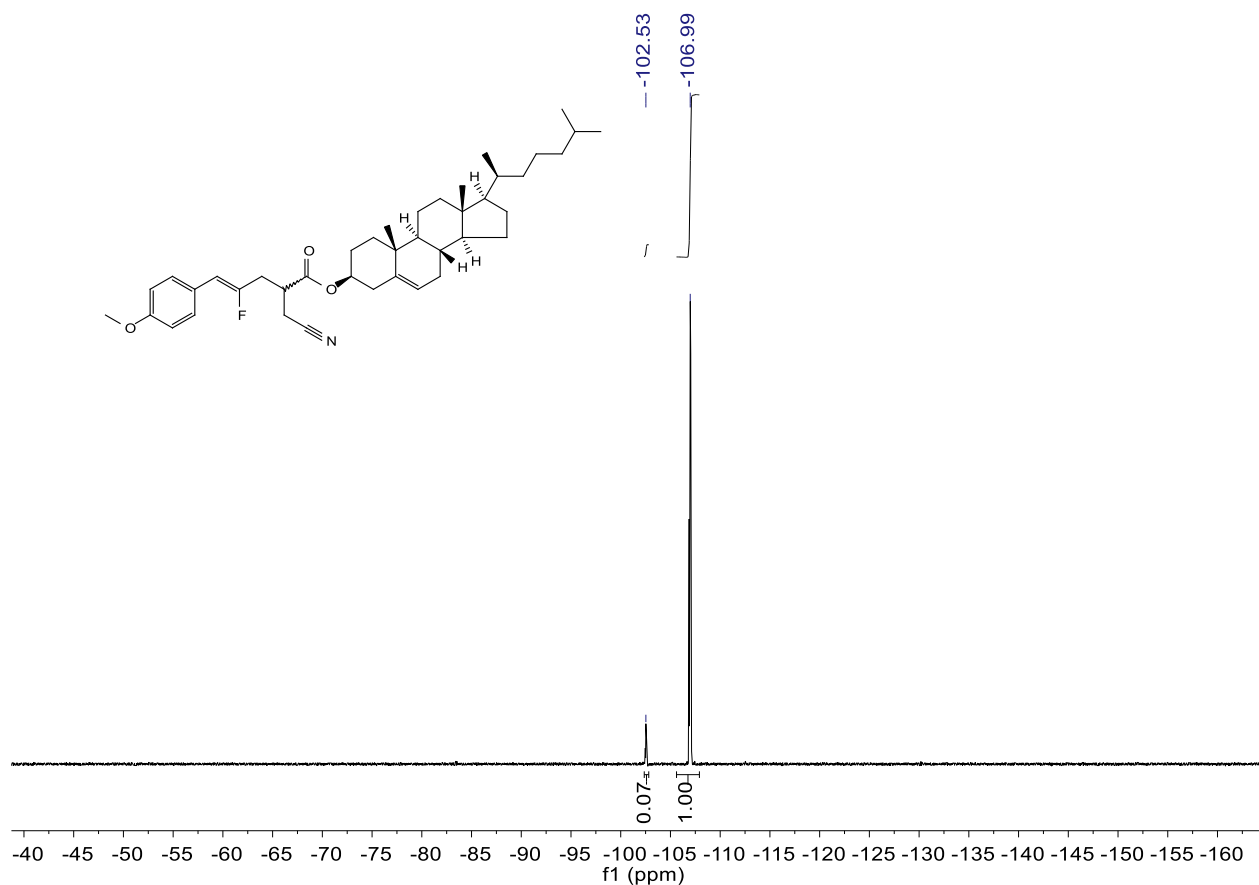
Supporting Information

¹H NMR (400 MHz, Chloroform-*d*)

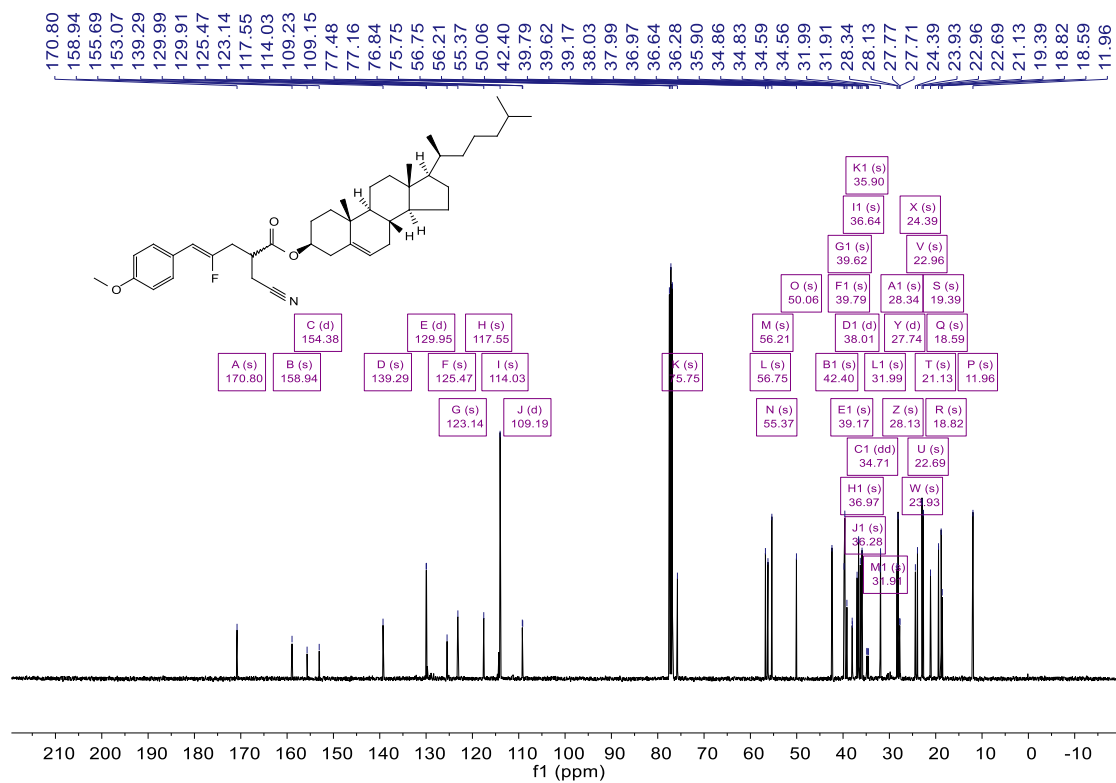


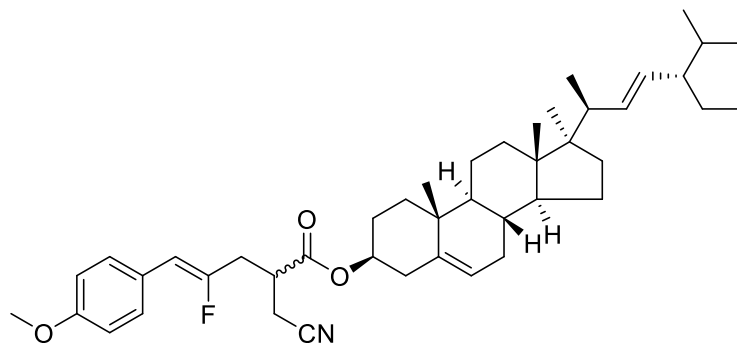
¹⁹F NMR (376 MHz, Chloroform-*d*)

Supporting Information



¹³C NMR (101 MHz, Chloroform-*d*)





(3S,8R,9S,10R,13S,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13,17-trimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (Z)-2-(cyanomethyl)-4-fluoro-5-(4-methoxyphenyl)pent-4-enoate

Following the general procedure (**e2**, pale-yellow liquid, 83.3 mg, 62%, Z/E = 14:1, dr = 1.7:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (3:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.58 (d, *J* = 39.3 Hz, 1H), 5.36 (dd, *J* = 15.0, 4.5 Hz, 1H), 5.15 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.01 (dd, *J* = 15.1, 8.7 Hz, 1H), 4.74 – 4.64 (m, 1H), 3.81 (s, 3H), 3.07 – 2.98 (m, 1H), 2.93 – 2.80 (m, 1H), 2.78 – 2.61 (m, 3H), 2.33 (dd, *J* = 12.7, 7.0 Hz, 2H), 2.01 (tt, *J* = 20.0, 10.0 Hz, 3H), 1.90 – 1.81 (m, 2H), 1.66 (dd, *J* = 23.0, 7.1 Hz, 2H), 1.56 – 1.41 (m, 7H), 1.31 – 1.10 (m, 6H), 1.08 – 0.94 (m, 9H), 0.86 – 0.78 (m, 9H), 0.69 (s, 3H).

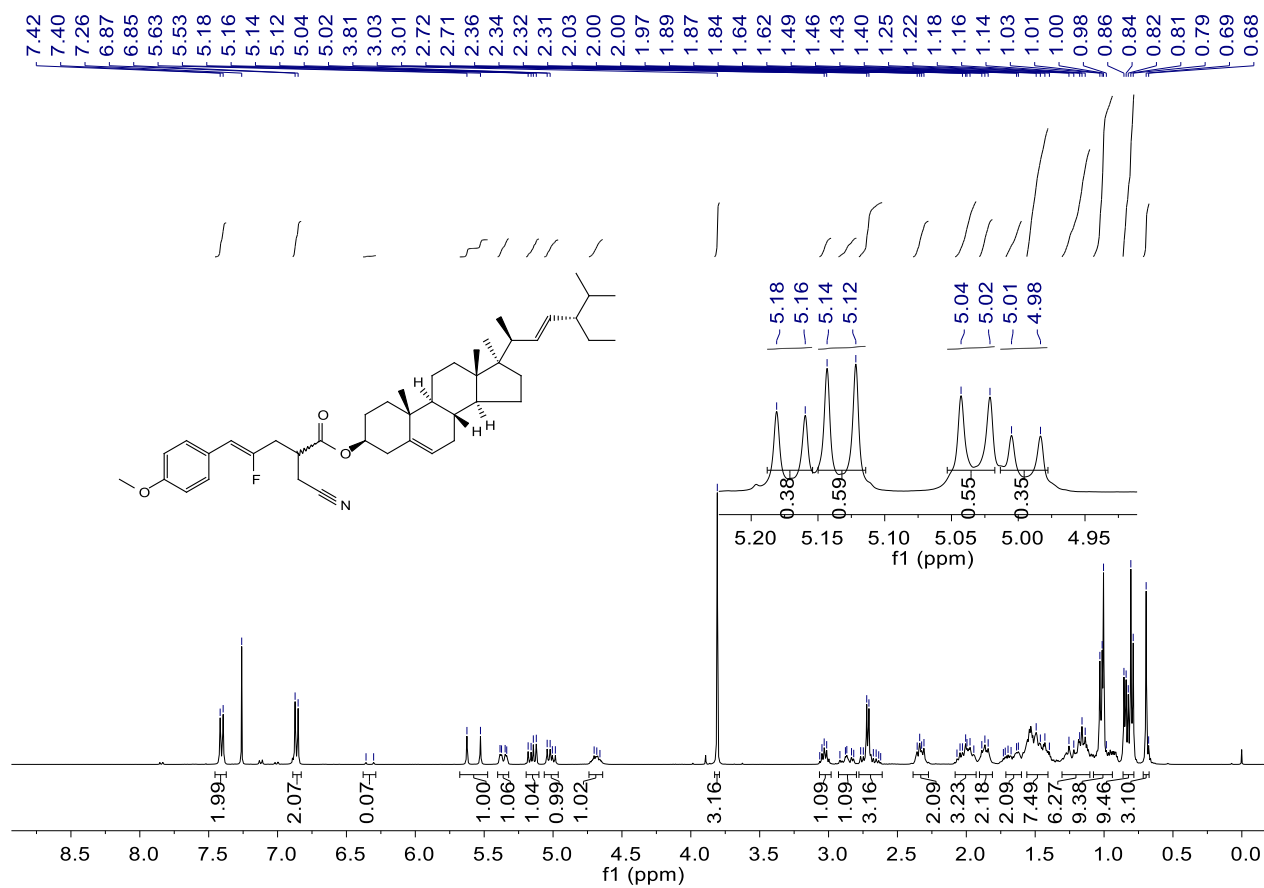
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -102.5, -106.99.

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.80, 158.93, 154.38 (d, *J* = 263.3 Hz), 139.28, 138.43, 129.95 (d, *J* = 7.4 Hz), 129.37, 125.46 (d, *J* = 2.5 Hz), 123.14 (d, *J* = 3.3 Hz), 117.55, 114.02, 109.19 (d, *J* = 8.1 Hz), 75.74, 56.85, 56.00, 55.36, 51.34, 50.07, 42.29, 40.64, 39.69, 39.17, 38.01 (d, *J* = 3.9 Hz), 36.97, 36.66, 34.71 (dd, *J* = 26.9, 2.7 Hz), 32.00, 31.98, 31.91, 29.04, 27.74 (d, *J* = 5.9 Hz), 25.54, 24.46, 21.35, 21.23, 21.11, 19.39, 19.10, 18.59, 12.39, 12.15.

HRMS (ESI) *m/z*: (M+Na)⁺ Calcd for C₄₄H₆₂FNO₃: 694.4605; found: 694.4600.

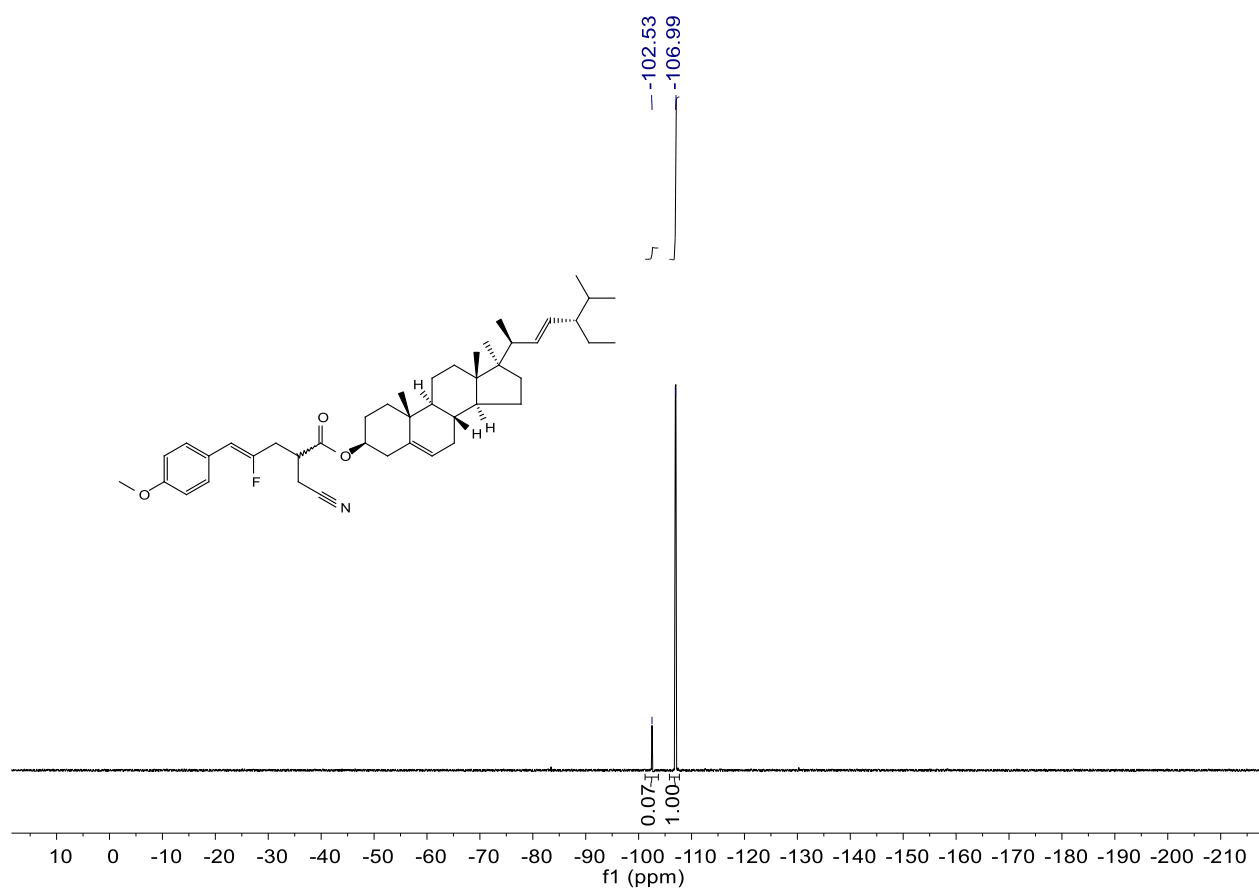
¹H NMR (400 MHz, Chloroform-*d*)

Supporting Information

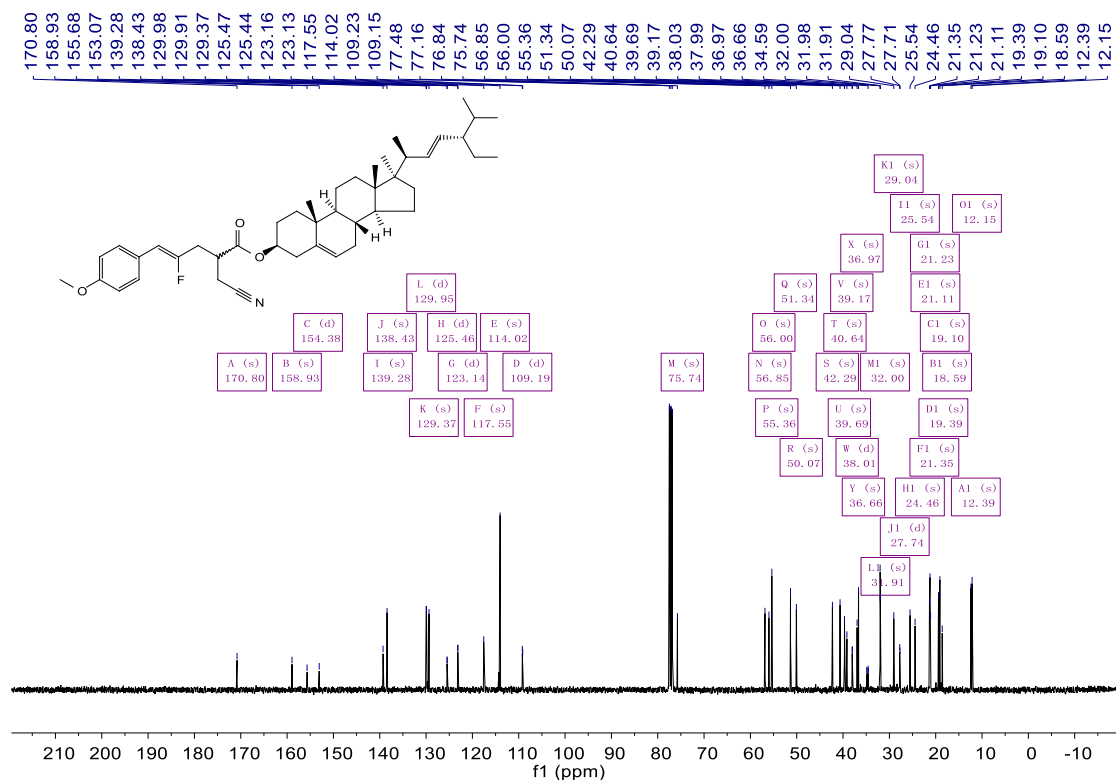


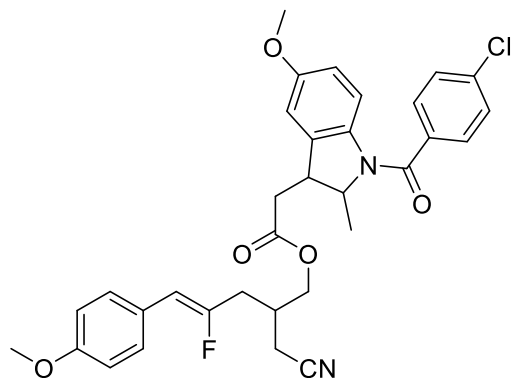
Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)



¹³C NMR (101 MHz, Chloroform-*d*)





(E)-2-(cyanomethyl)-4-fluoro-5-(4-methoxyphenyl)pent-4-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

Following the general procedure (**e3**, pale-yellow liquid, 67.4 mg, 58%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (3:1) as an eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.89 – 6.83 (m, 3H), 6.71 – 6.68 (m, 1H), 5.37 (d, *J* = 39.5 Hz, 1H), 4.27 (d, *J* = 5.6 Hz, 1H), 4.13 (dd, *J* = 11.1, 5.6 Hz, 1H), 3.83 (s, 5H), 3.80 (s, 3H), 3.72 (s, 2H), 2.40 (d, *J* = 2.5 Hz, 8H).

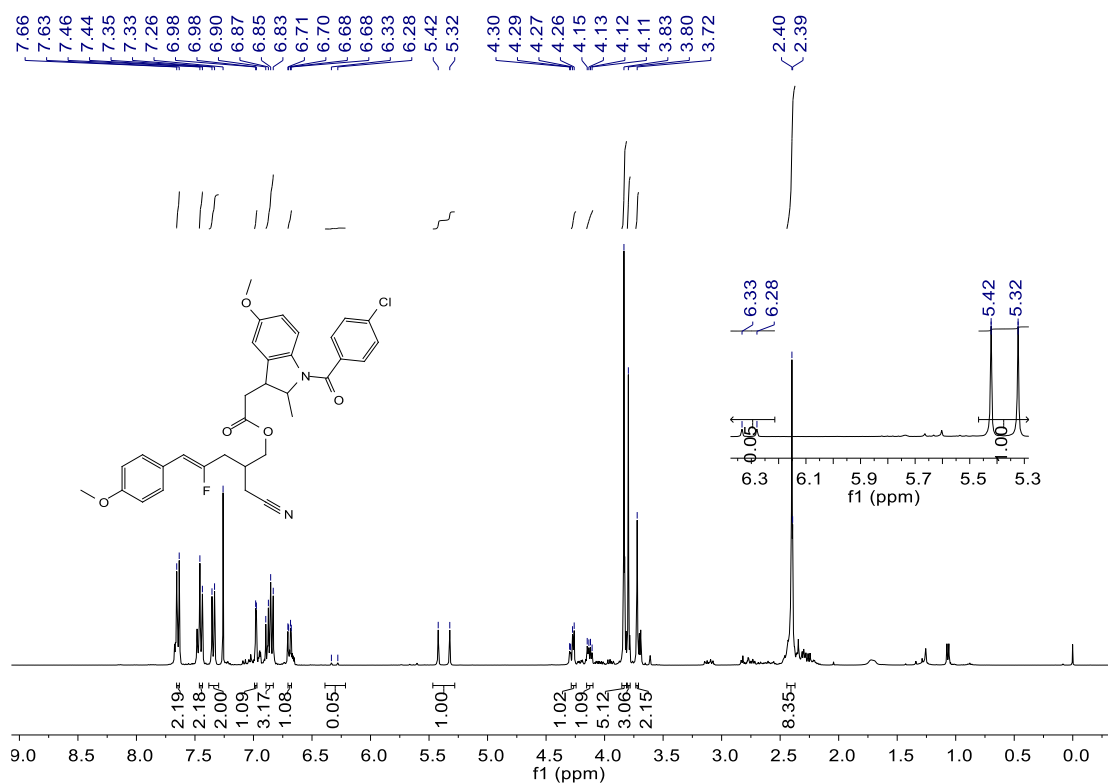
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.43.

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.40, 168.36, 158.85 (d, *J* = 2.9 Hz), 156.18, 154.66 (d, *J* = 262.6 Hz), 139.42, 136.12, 133.81 (d, *J* = 4.8 Hz), 131.25, 130.84, 130.53 (d, *J* = 4.2 Hz), 129.84 (d, *J* = 7.3 Hz), 129.24, 117.51, 115.17, 113.98, 111.76, 108.78 (d, *J* = 8.2 Hz), 101.32, 65.31, 55.82 (d, *J* = 1.5 Hz), 55.33, 49.95, 34.27 (d, *J* = 27.1 Hz), 32.69, 30.28, 22.12 (d, *J* = 141.3 Hz), 19.02, 13.42.

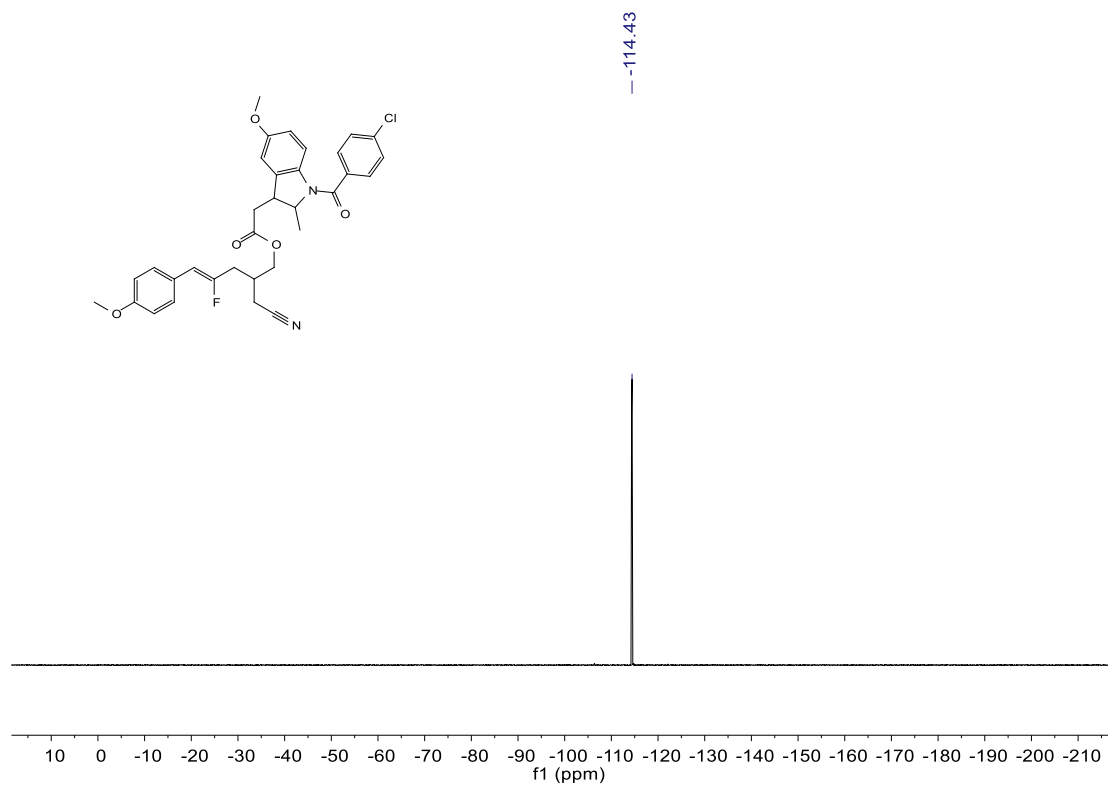
HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₃₃H₃₂ClFN₂O₅: 591.2057; found: 591.2071.

Supporting Information

¹H NMR (400 MHz, Chloroform-*d*)

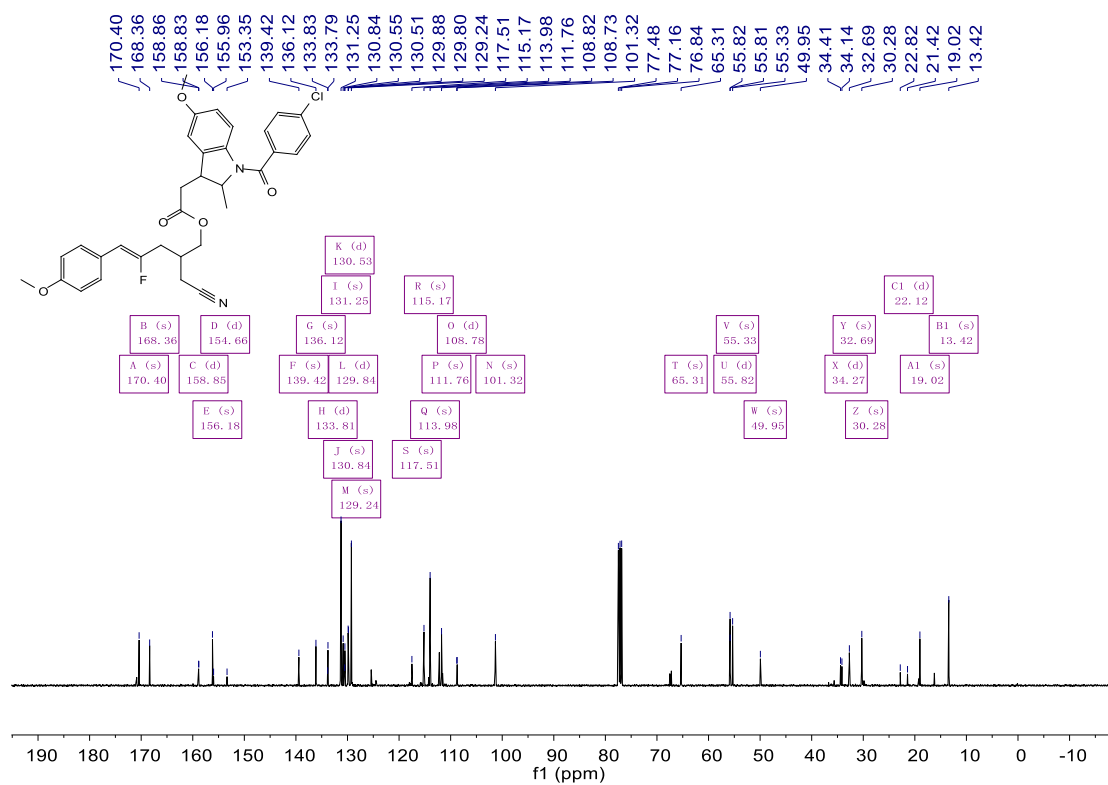


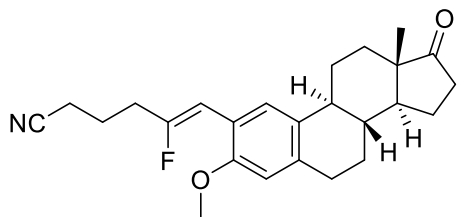
¹⁹F NMR (376 MHz, Chloroform-*d*)



Supporting Information

¹³C NMR (101 MHz, Chloroform-*d*)





(Z)-5-fluoro-6-((8R,9S,13S,14S)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)hex-5-enenitrile

Following the general procedure (**e4**, pale-yellow liquid, 31.6 mg, 40%, Z/E > 15:1). The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (5:1) as an eluent.

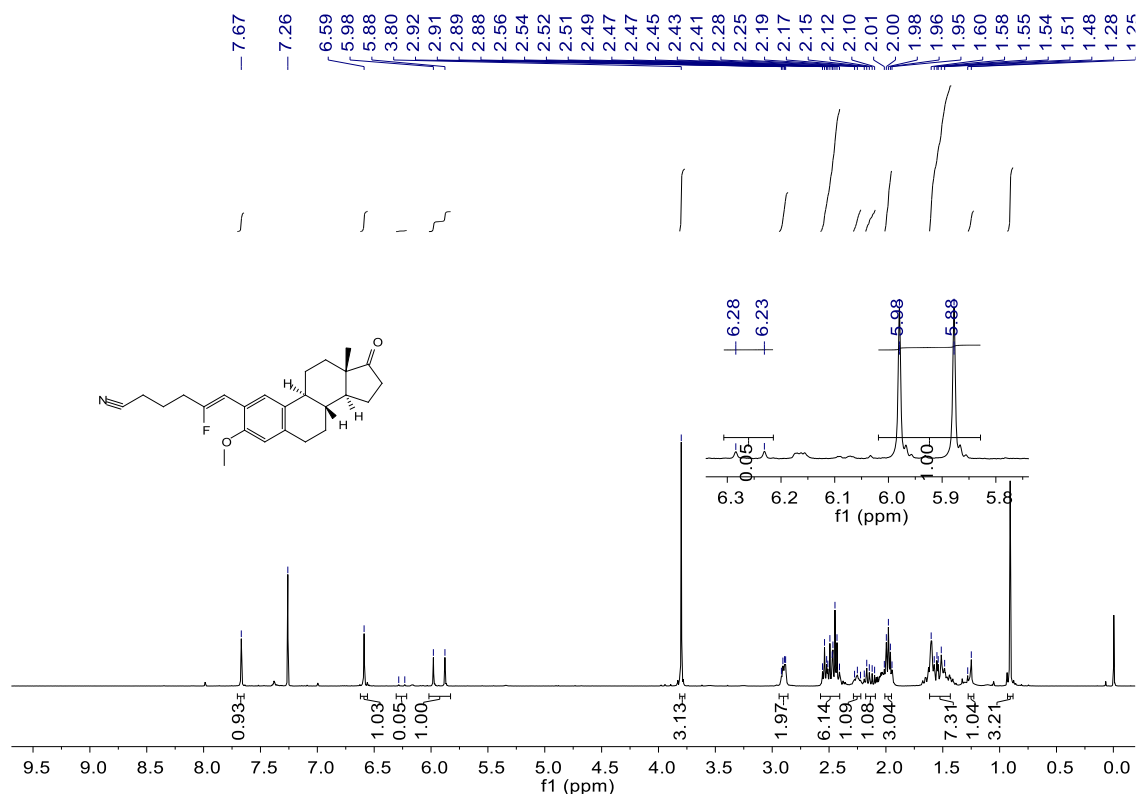
¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 6.59 (s, 1H), 5.93 (d, J = 40.7 Hz, 1H), 3.80 (s, 3H), 2.90 (dd, J = 10.4, 4.5 Hz, 2H), 2.58 – 2.41 (m, 6H), 2.25 (t, J = 10.5 Hz, 1H), 2.13 (dd, J = 18.8, 8.8 Hz, 1H), 1.98 (t, J = 7.1 Hz, 3H), 1.62 – 1.43 (m, 7H), 1.25 (s, 1H), 0.91 (s, 3H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -102.38.

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.59 (d, J = 264.1 Hz), 154.18, 136.96, 131.81, 126.82 (d, J = 12.5 Hz), 119.42 (d, J = 2.9 Hz), 119.34, 110.85, 101.27 (d, J = 6.8 Hz), 55.68, 50.51, 48.16, 44.09, 38.51, 36.03, 32.21 (d, J = 27.9 Hz), 31.68, 29.91, 26.67, 26.06, 22.51, 21.72, 16.38, 13.98.

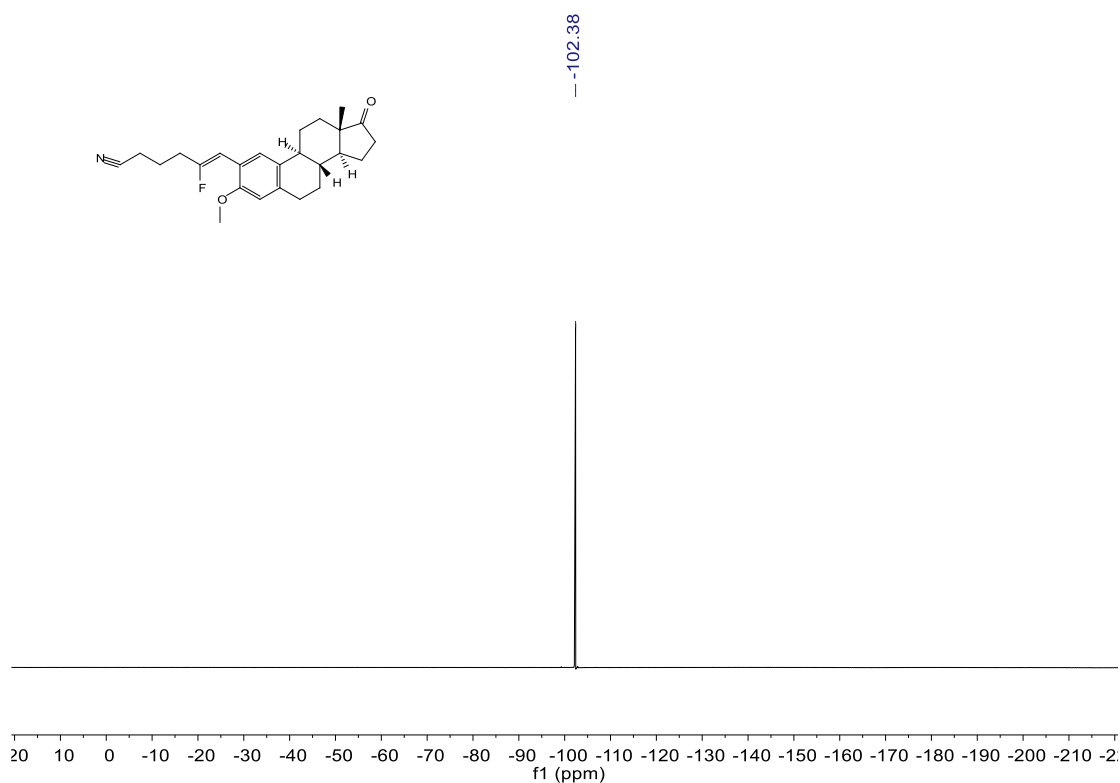
HRMS (ESI) m/z : (M+H)⁺ Calcd for C₂₅H₃₀FNO₂: 396.2333; found: 396.2331.

¹H NMR (400 MHz, Chloroform-*d*)

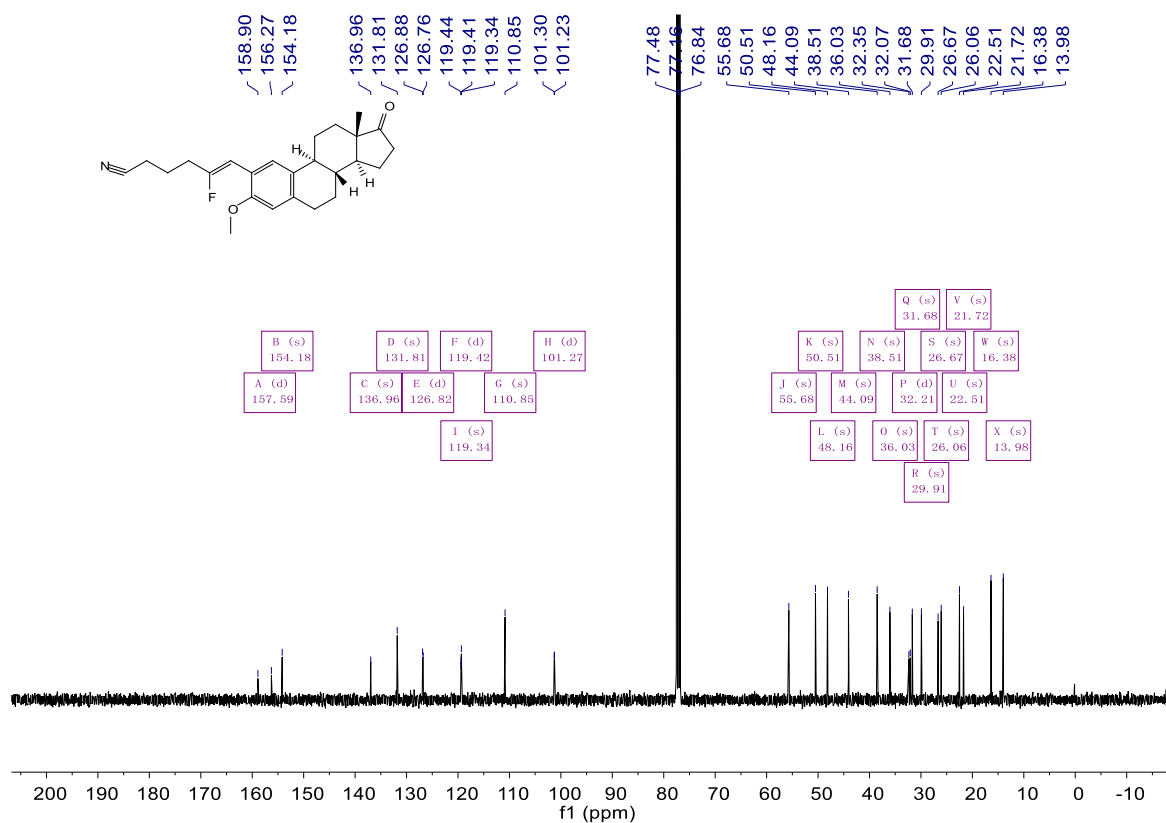


Supporting Information

¹⁹F NMR (376 MHz, Chloroform-*d*)

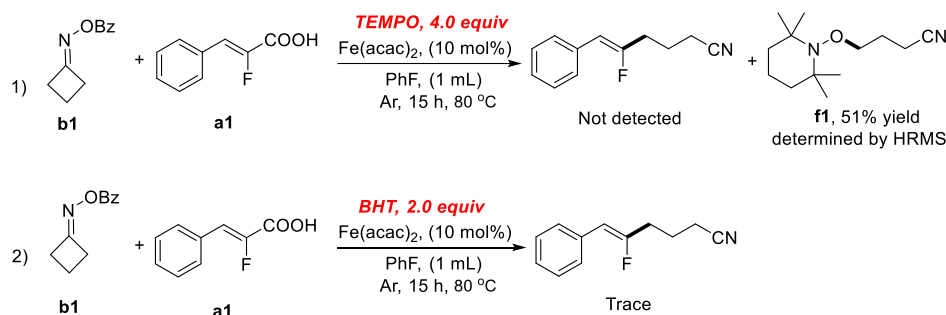


¹³C NMR (101 MHz, Chloroform-*d*)



VI. Radical inhibiting experiment

Figure S2



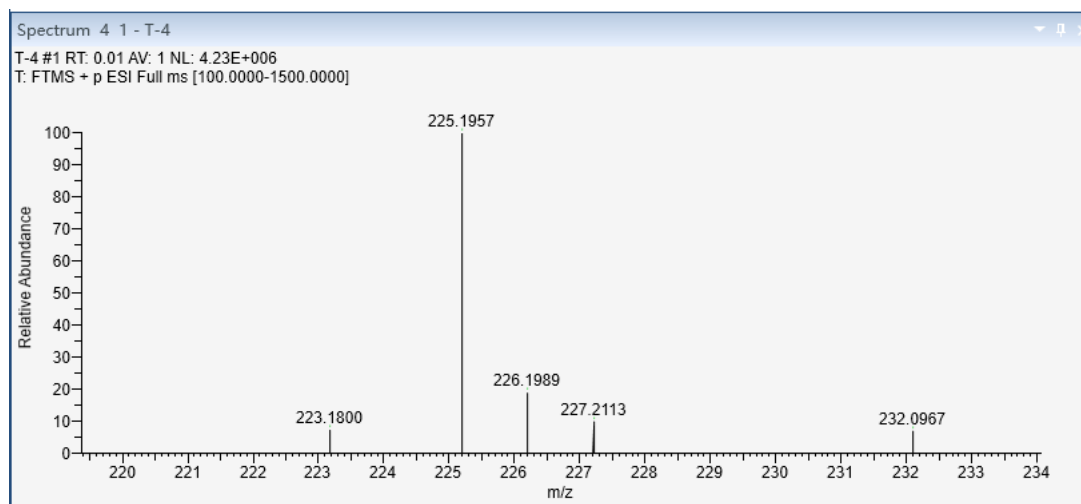
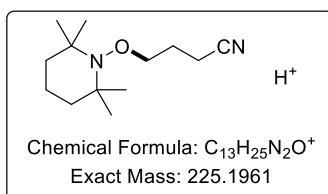
(1) In air, **a1** (0.4 mmol, 2.0 equiv.), **b1** (0.2 mmol, 1.0 equiv.), 2,2,6,6-tetramethyl-1-piperidinyloxy (0.80 mmol, 4.0 equiv) and Fe(acac)₂ (5.1 mg, 10 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles), PhF (1.0 mL, 0.5 M) were added by syringe. The resulting reaction mixture was heated in an oil bath at 80 °C for 15 h under Ar atmosphere. The residue was purified by silica gel (200-300 mesh) column chromatography using PE/EA (10:1) as an eluent.

f1: ¹H NMR (600 MHz, Chloroform-*d*) δ 3.83 (t, *J* = 5.8 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 1.88 (ddd, *J* = 13.1, 7.2, 5.8 Hz, 2H), 1.58 – 1.50 (m, 1H), 1.44 (dd, *J* = 9.0, 4.5 Hz, 4H), 1.36 – 1.28 (m, 1H), 1.14 (s, 6H), 1.08 (s, 6H).

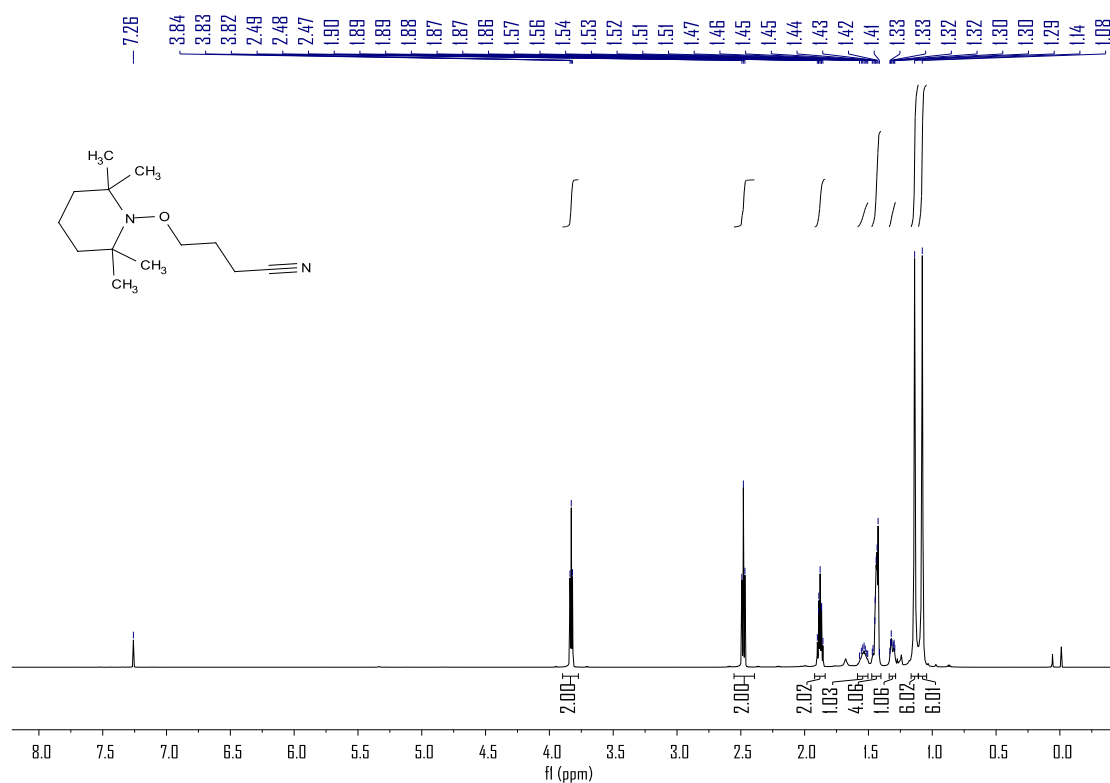
¹³C NMR (151 MHz, Chloroform-*d*) δ 119.82, 73.73, 59.94, 39.70, 33.20, 25.23, 20.19, 17.16, 14.57.

(2) In air, **a1** (0.4 mmol, 2.0 equiv.), **b1** (0.2 mmol, 1.0 equiv.), butylated hydroxytoluene (BHT) (0.40 mmol, 2.0 equiv) and Fe(acac)₂ (5.1 mg, 10 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles), PhF (1.0 mL, 0.5 M) were added by syringe. The resulting reaction mixture was heated in an oil bath at 80 °C for 15 h under Ar atmosphere.

HRMS

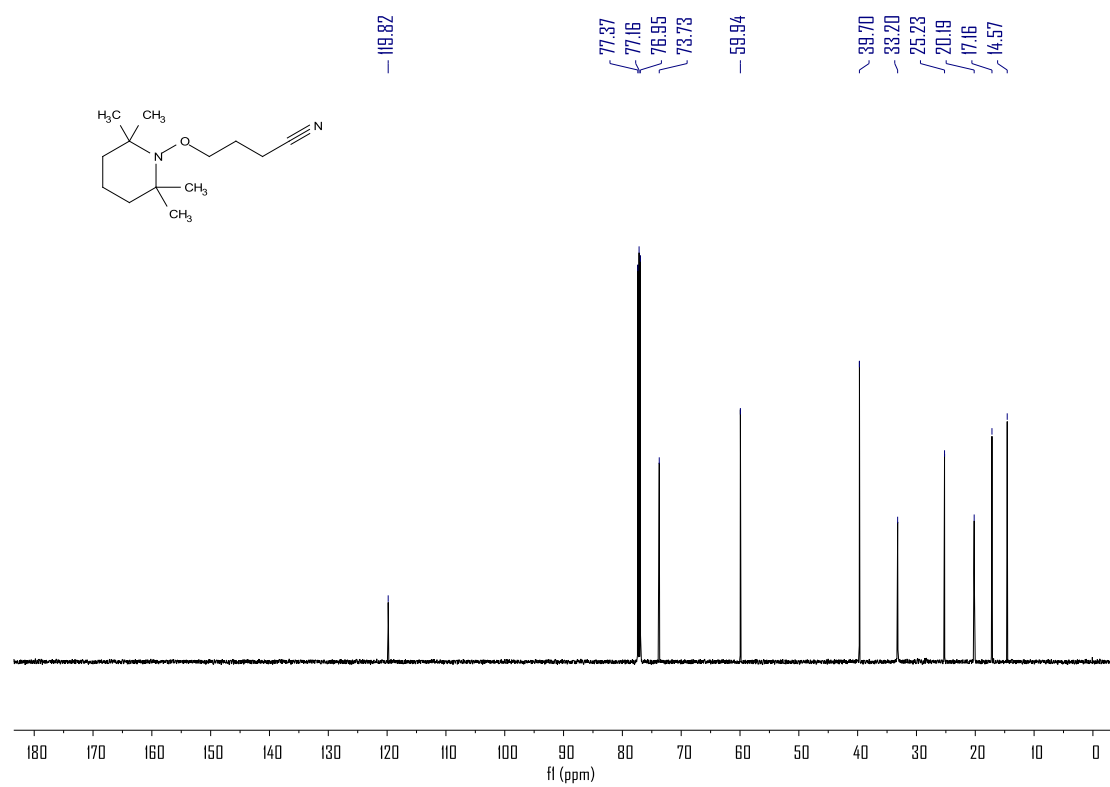


^1H NMR



Supporting Information

^{13}C NMR



References

1. X.-Y. Lu; A. Gao; M.-Y. Ge; Z.-J. Xia; Q.-L. Liu; T.-H. Tao; X.-M. Sun. *J. Org. Chem.* 2022, **87**, 4654–4669.
2. X.-Y. Lu; M.-T. Gao; L.-J. Yu; H.-Y. Pan; X. Zhang; R. Huang; K. Yang; F.-Y. Shui; Y.-W. Song; G.-X. Yang. *Org. Chem. Front.* 2023, **10**, 1788–1795.
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