Palladium-catalyzed esterification reaction of arenes/heterocyclic carboxylic acids with difluoroallyl bromide for the efficient preparation of difluoroallyl esters

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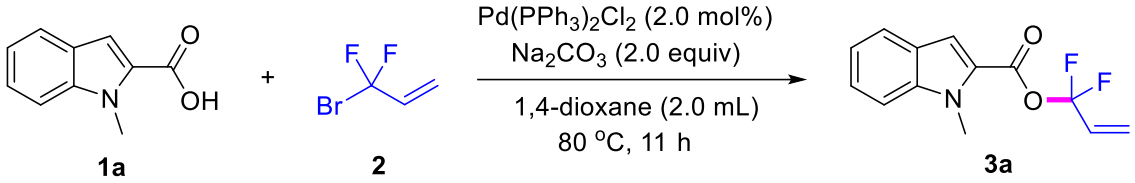
Contents

1. General Information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 600 and 75 MHz spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of the residual prorogated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. ^{19}F NMR chemical shifts were determined relative to *p*-fluoroacetophenone at δ -107.5. Data for ^{1}H, ^{13}C and ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI mode.

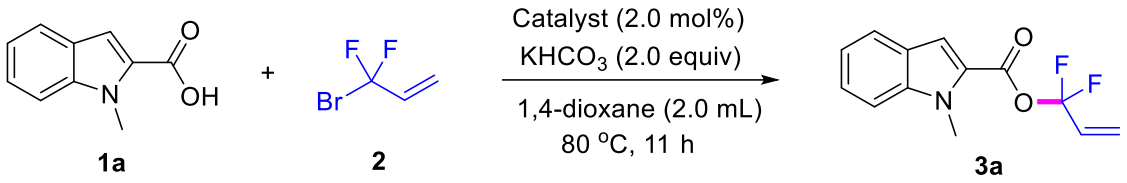
2. General method for the synthesis of products



The reaction was carried out in a 35 mL thick-walled pressure-resistant tube. 1-Methyl-1H-indole-2-carboxylic acid (1.0 mmol), 3-bromo-3,3-difluoropropene (2.0 mmol), bis(triphenylphosphine)palladium dichloride (0.02 mmol), Na_2CO_3 (2.0 mmol), 1,4-dioxane (2.0 mL) and a stirrer were added to the thick-walled pressure-resistant tube. The reaction tube was then heated in an oil bath at 80 °C for 11 hours. At the end of the reaction, the reaction tube was cooled to room temperature and the crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and petroleum ether as the eluent to give the compound 1-methyl-1H-indole-2-carboxylic acid-1,1-difluoroallyl ester.

3. Reaction Optimization

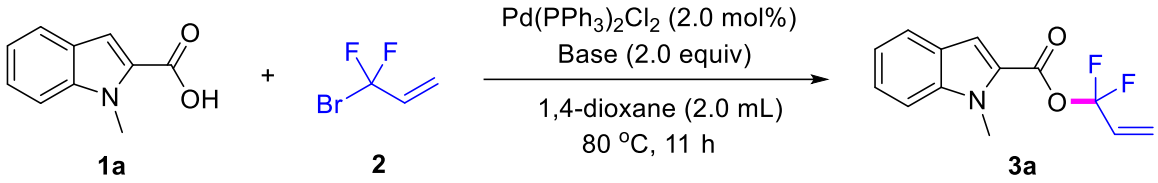
Supplementary Table S1. Screening results on catalyst.



1a + **2** → **3a**

Entry	Catalyst (2.0 mol%)	Yield (%)
1	$FeCl_2$	24
2	CuI	49
3	$CuSO_4$	40
4	$FeBr_3$	13
5	$Pd(OCOCF_3)_2$	51
6	$Pd(PPh_3)_4$	60
7	$Pd(dba)_2$	43
8	$Pd(OAc)_2$	16
9	$PdCl_2(PhCN)_2$	24
10	RuPhos PdG3	65
11	$Pd(PPh_3)_2Cl_2$	80
12	$PdCl_2$	32

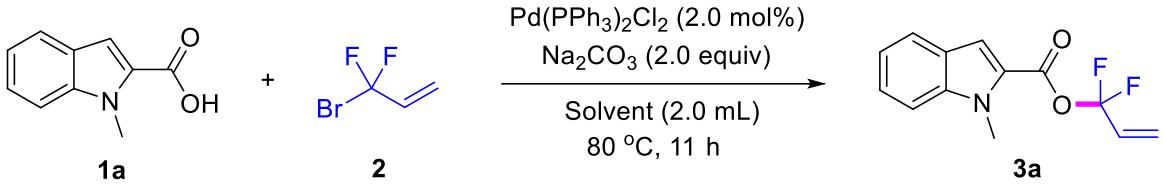
Supplementary Table S2. Screening results on base.



1a + **2** → **3a**

Entry	Base (2.0 equiv)	Yield (%)
1	$KHCO_3$	80
2	DBU	58
3	Na_2CO_3	90
4	K_2CO_3	86
5	Na_2HPO_4	56
6	Na_2SO_4	0
7	$NaHCO_3$	82
8	DMAP	12
9	DABCO	8
10	Et_3N	16

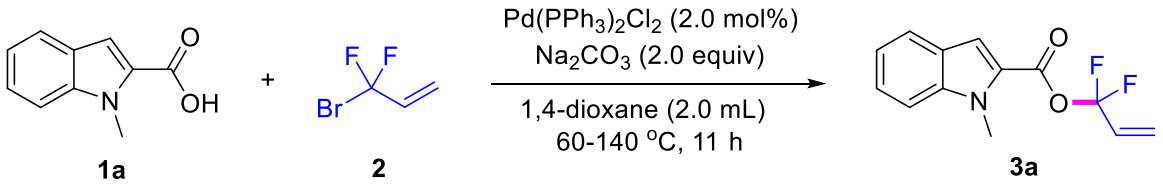
Supplementary Table S3. Screening results on solvents.



1a **2** **3a**

Entry	Solvent (2.0 mL)	Yield (%)
1	1,4-dioxane	90
2	MeCN	85
3	THF	56
4	DMF	87
5	DMSO	<5
6	PhMe	60
7	CyH	23

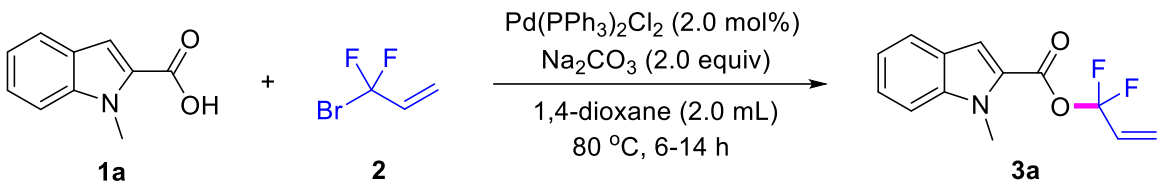
Supplementary Table S4. Screening results on temperature.



1a **2** **3a**

Entry	T (°C)	Yield (%)
1	60	77
2	80	90
3	100	68
4	120	65
5	140	76

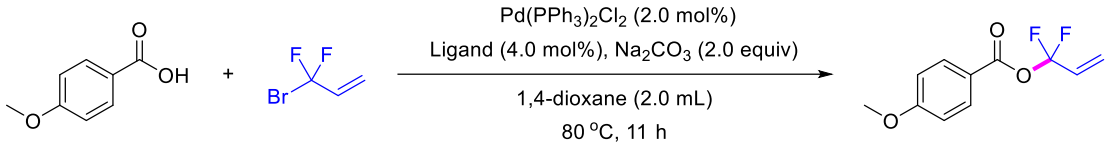
Supplementary Table S5. Screening results on time.



1a **2** **3a**

Entry	t (h)	Yield (%)
1	6	72
2	8	73
3	11	90
4	14	80

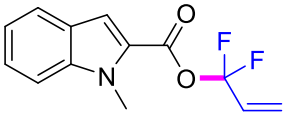
Supplementary Table S6. Screening results on ligand.



Entry	Ligand (4.0 mol%)	Yield (%)
1	PCy_3	0
2	rac-BINAP	<5
3	Brettphos	75
4	Xantphos	82
5	Rutphos	45
6	BINOL	28

4. Analytic data for products

1,1-difluoroallyl-1-methyl-1H-indole-2-carboxylate (3a)



The title compound 3a was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 100:1, 90% yield, 226.0 mg, colourless liquid).

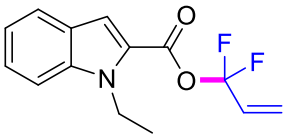
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, 1 H, *J* = 8.4 Hz), 7.26 - 7.23 (m, 2 H), 7.19 (d, 1 H, *J* = 9.0 Hz), 7.04 (t, 1 H, *J* = 7.5 Hz), 6.21 - 6.14 (m, 1 H), 5.85 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.53 (d, 1 H, *J* = 11.4 Hz), 3.84 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.51 (t, *J* = 2.8 Hz), 139.33, 127.82 (t, *J* = 31.9 Hz), 125.06, 124.50, 124.15, 121.94, 121.20 (t, *J* = 7.1 Hz), 119.95, 119.48 (t, *J* = 260.4 Hz), 111.69, 109.24, 30.38.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.72 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + K]^+$ calc. for $C_{13}H_{11}F_2KNO_2$ 290.0395; found: 290.0391.

1,1-difluoroallyl-1-ethyl-1H-indole-2-carboxylate (3b)



The title compound 3b was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 100:1, 83% yield, 220.0 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, 1 H, *J* = 8.4 Hz), 7.44 - 7.40 (m, 3

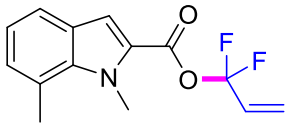
H), 7.21 - 7.18 (m, 1 H), 6.34 - 6.27 (m, 1 H), 5.99 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.68 (d, 1 H, *J* = 10.8 Hz), 4.60 (q, 2 H, *J* = 7.2 Hz), 1.42 (t, 3 H, *J* = 7.2 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.35 (t, *J* = 3.0 Hz), 139.55, 128.96 (t, *J* = 31.8 Hz), 126.18, 125.83, 124.53, 123.21, 122.29 (t, *J* = 7.4 Hz), 121.05, 120.56 (t, *J* = 261.0 Hz), 113.16, 110.39, 39.71, 15.53.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.52 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{14}H_{14}F_2NO_2$ 266.0993; found: 266.0988.

1,1-difluoroallyl-1,7-dimethyl-1H-indole-2-carboxylate (3c)



The title compound 3c was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 50% yield, 132.5 mg, colourless liquid).

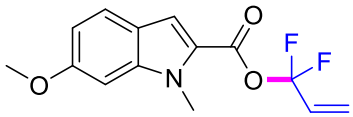
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, 1 H, *J* = 7.8 Hz), 7.41 (s, 1 H), 7.09 (d, 1 H, *J* = 6.6 Hz), 7.03 (t, 1 H, *J* = 7.5 Hz), 6.31 - 6.23 (m, 1 H), 5.96 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.66 (d, 1 H, *J* = 11.4 Hz), 4.33 (s, 3 H), 2.80 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.65 (t, *J* = 2.7 Hz), 140.04, 129.09, 128.96 (t, *J* = 31.9 Hz), 126.56, 125.67, 122.35, 122.24 (t, *J* = 7.1 Hz), 121.19, 121.14, 120.51 (t, *J* = 260.4 Hz), 113.94, 34.37, 20.74.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.58 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{14}H_{14}F_2NO_2$ 266.0993; found: 266.0988.

1,1-difluoroallyl-6-methoxy-1-methyl-1H-indole-2-carboxylate (3d)



The title compound 3d was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 75% yield, 210.8 mg, colourless liquid).

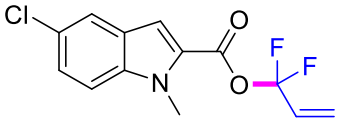
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, 1 H, *J* = 9.0 Hz), 7.26 (s, 1 H), 6.77 (dd, 1 H, *J* = 9.0, 2.4 Hz), 6.60 (s, 1 H), 6.27 - 6.19 (m, 1 H), 5.90 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.59 (d, 1 H, *J* = 10.8 Hz), 3.87 (s, 3 H), 3.81 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.68, 156.48 (t, *J* = 2.8 Hz), 141.77, 129.11 (t, *J* = 31.9 Hz), 124.15, 123.92, 122.12 (t, *J* = 7.2 Hz), 120.59 (t, *J* = 260.2 Hz), 120.03, 113.47, 113.05, 91.75, 55.43, 31.51.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.42 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{14}H_{14}F_2NO_3$ 282.0942; found: 282.0936.

1,1-difluoroallyl-5-chloro-1-methyl-1H-indole-2-carboxylate (3e)



The title compound 3e was synthesized according to General Procedure,

and it was purified by column chromatography on silica gel (PE:EA = 100:1, 81% yield, 230.9 mg, white solid).

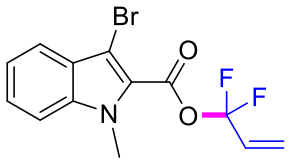
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, 1 H, *J* = 2.4 Hz), 7.33 - 7.28 (m, 3 H), 6.32 - 6.24 (m, 1 H), 5.97 (dt, 1 H, *J* = 16.8, 2.4 Hz), 5.68 (d, 1 H, *J* = 10.8 Hz), 4.02 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.38 (t, *J* = 3.1 Hz), 138.68, 128.72 (t, *J* = 31.9 Hz), 126.76, 126.64, 126.44, 126.32, 122.51 (t, *J* = 7.4 Hz), 122.03, 120.54 (t, *J* = 261.3 Hz), 111.88, 111.56, 31.84.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.78 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{11}ClF_2NO_2$ 286.0446; found: 286.0441.

1,1-difluoroallyl-3-bromo-1-methyl-1H-indole-2-carboxylate (3f)



The title compound 3f was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 90:1, 66% yield, 217.1 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, 1 H, *J* = 8.4 Hz), 7.35 (t, 1 H, *J* = 8.4 Hz), 7.27 (d, 1 H, *J* = 8.4 Hz), 7.16 (t, 1 H, *J* = 7.5 Hz), 6.28 - 6.20 (m, 1 H), 5.96 (dt, 1 H, *J* = 16.8, 2.4 Hz), 5.64 (d, 1 H, *J* = 10.8 Hz), 3.92 (s, 3 H).

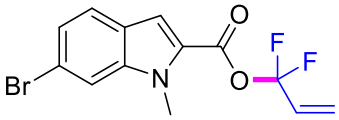
^{13}C NMR (150 MHz, $CDCl_3$) δ 154.83 (t, *J* = 3.0 Hz), 137.75, 127.61 (t,

J = 31.3 Hz), 126.16, 125.49, 122.07, 121.66 (t, J = 7.2 Hz), 120.80, 120.64, 119.57 (t, J = 262.4 Hz), 109.33, 100.21, 31.64.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.62 (d, 2 F, J = 7.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{11}BrF_2NO_2$ 329.9941; found: 329.9936.

1,1-difluoroallyl-6-bromo-1-methyl-1H-indole-2-carboxylate (3g)



The title compound 3g was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 70% yield, 230.3 mg, colourless liquid).

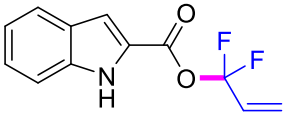
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 1 H), 7.39 (s, 1 H), 7.22 (s, 1 H), 7.13 (dd, 1 H, J = 8.4, 1.8 Hz), 6.21 - 6.13 (m, 1 H), 5.86 (dt, 1 H, J = 17.4, 1.8 Hz), 5.57 (d, 1 H, J = 11.4 Hz), 3.85 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.26 (t, J = 2.7 Hz), 139.86, 127.69 (t, J = 31.6 Hz), 124.84, 123.59, 123.24, 123.14, 121.40 (t, J = 7.2 Hz), 119.47 (t, J = 261.2 Hz), 119.17, 112.33, 111.71, 30.68.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.82 (d, 2 F, J = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{11}BrF_2NO_2$ 329.9941; found: 329.9936.

1,1-difluoroallyl-1H-indole-2-carboxylate (3h)



The title compound 3h was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 60% yield, 142.2 mg, pale yellow solid).

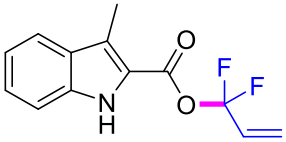
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.39 (s, 1 H), 7.61 (d, 1 H, *J* = 8.4 Hz), 7.34 (d, 1 H, *J* = 8.4 Hz), 7.29 (d, 1 H, *J* = 7.8 Hz), 7.26 (d, 1 H, *J* = 1.2 Hz), 7.09 (t, 1 H, *J* = 8.1 Hz), 6.28 - 6.20 (m, 1 H), 5.92 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.58 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.67 (t, *J* = 2.9 Hz), 137.48, 128.02 (t, *J* = 31.4 Hz), 126.60, 126.03, 124.40, 122.40, 122.12 (t, *J* = 7.2 Hz), 120.76, 120.16 (t, *J* = 261.8 Hz), 117.72, 111.07.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.63 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_{10}F_2NO_2$ 238.0680; found: 238.0675.

1,1-difluoroallyl-3-methyl-1H-indole-2-carboxylate (3i)



The title compound 3i was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 30:1, 87% yield, 218.4 mg, white solid).

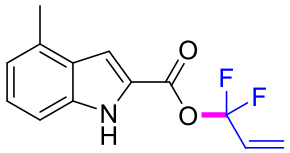
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 1 H), 7.69 (d, 1 H, *J* = 8.4 Hz), 7.38 (s, 2 H), 7.20 - 7.17 (m, 1 H), 6.39 - 6.31 (m, 1 H), 5.99 (dt, 1 H, *J* = 16.8, 2.4 Hz), 5.69 (d, 1 H, *J* = 11.4 Hz), 2.64 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.17 (t, *J* = 3.0 Hz), 135.83, 127.97 (t, *J* = 31.3 Hz), 127.46, 125.99, 122.90, 121.65 (t, *J* = 7.1 Hz), 120.37, 120.28, 119.83 (t, *J* = 261.0 Hz), 119.64, 111.06, 9.29.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.71 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{12}F_2NO_2$ 252.0836; found: 252.0831.

1,1-difluoroallyl-4-methyl-1H-indole-2-carboxylate (3j)



The title compound 3j was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 10:1, 78% yield, 195.8 mg, white solid).

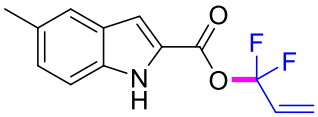
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (s, 1 H), 7.36 (d, 1 H, *J* = 2.4 Hz), 7.24 (t, 2 H, *J* = 5.4 Hz), 6.94 (d, 1 H, *J* = 7.8 Hz), 6.31 - 6.24 (m, 1 H), 5.94 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.65 (d, 1 H, *J* = 10.8 Hz), 2.55 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.62 (t, *J* = 3.0 Hz), 137.51, 132.78, 128.57 (t, *J* = 31.7 Hz), 127.51, 126.75, 124.36, 122.52 (t, *J* = 7.4 Hz), 120.16, 120.54 (t, *J* = 261.5 Hz), 110.11, 109.50, 18.56.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.57 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{12}F_2NO_2$ 252.0836; found: 252.0831.

1,1-difluoroallyl-5-methyl-1H-indole-2-carboxylate (3k)



The title compound 3k was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1, 76% yield, 190.8 mg, white solid).

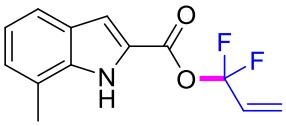
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.22 (s, 1 H), 7.45 (s, 1 H), 7.31 (d, 1 H, *J* = 8.4 Hz), 7.26 (s, 1 H), 7.19 (d, 1 H, *J* = 8.4 Hz), 6.34 - 6.27 (m, 1 H), 5.98 (d, 1 H, *J* = 17.4 Hz), 5.66 (d, 1 H, *J* = 10.8 Hz), 2.44 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.03 (t, *J* = 3.3 Hz), 136.37, 130.66, 128.65, 128.62 (t, *J* = 31.6 Hz), 127.44, 124.91, 122.54 (t, *J* = 7.3 Hz), 122.05, 120.62 (t, *J* = 261.5 Hz), 118.82, 111.01, 21.35.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.75 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{12}F_2NO_2$ 252.0836; found: 252.0831.

1,1-difluoroallyl-7-methyl-1H-indole-2-carboxylate (3l)



The title compound 3l was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1, 65% yield, 163.2 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (s, 1 H), 7.56 (d, 1 H, *J* = 8.4 Hz), 7.37 (d, 1 H, *J* = 2.4 Hz), 7.18 (d, 1 H, *J* = 6.6 Hz), 7.11 (t, 1 H, *J* = 7.5 Hz), 6.34 - 6.27 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.68 (d, 1 H, *J* =

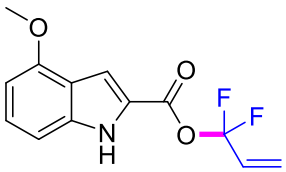
10.8 Hz), 2.53 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.82 (t, *J* = 3.0 Hz), 137.64, 128.64 (t, *J* = 31.6 Hz), 126.87, 126.72, 124.84, 122.59 (t, *J* = 7.3 Hz), 121.63, 121.47, 120.62, 120.62 (t, *J* = 261.5 Hz), 112.07, 16.64.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.69 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{12}F_2NO_2$ 252.0836; found: 252.0831.

1,1-difluoroallyl-4-methoxy-1H-indole-2-carboxylate (3m)



The title compound 3m was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 60% yield, 160.2 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (s, 1 H), 7.48 (s, 1 H), 7.29 (t, 1 H, *J* = 8.1 Hz), 7.02 (d, 1 H, *J* = 8.4 Hz), 6.52 (d, 1 H, *J* = 7.8 Hz), 6.32 - 6.24 (m, 1 H), 5.97 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.67 (d, 1 H, *J* = 11.4 Hz), 3.96 (s, 3 H).

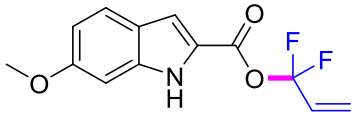
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.65 (t, *J* = 3.0 Hz), 154.85, 139.11, 128.67 (t, *J* = 31.7 Hz), 127.77, 123.78, 122.52 (t, *J* = 7.4 Hz), 120.56 (t, *J* = 261.6 Hz), 119.00, 109.40, 104.88, 100.03, 55.38.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.62 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{12}F_2NO_3$ 268.0785; found:

268.0780.

1,1-difluoroallyl-6-methoxy-1H-indole-2-carboxylate (3n)



The title compound 3n was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 10:1, 72% yield, 192.3 mg, white solid).

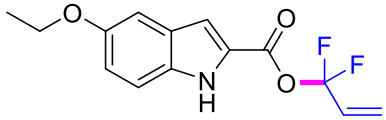
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1 H), 7.56 (d, 1 H, *J* = 8.4 Hz), 7.29 (d, 1 H, *J* = 1.2 Hz), 6.85 (d, 1 H, *J* = 1.8 Hz), 6.84 (d, 1 H, *J* = 1.2 Hz), 6.32 - 6.25 (m, 1 H), 5.95 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.66 (d, 1 H, *J* = 10.8 Hz), 3.87 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.81, 156.58 138.98, 128.75 (t, *J* = 31.9 Hz), 123.88, 123.85, 122.43 (t, *J* = 7.2 Hz), 121.64, 120.56 (t, *J* = 261.0 Hz), 113.35, 112.05, 93.45, 55.50.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.59 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{12}F_2NO_3$ 268.0785; found: 268.0780.

1,1-difluoroallyl-5-ethoxy-1H-indole-2-carboxylate (3o)



The title compound 3o was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 10:1, 59% yield, 165.8 mg, white solid).

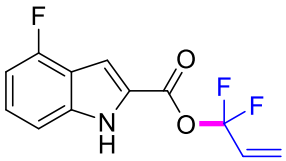
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (s, 1 H), 7.32 (d, 1 H, *J* = 8.4 Hz), 7.25 (s, 1 H), 7.06 (s, 1 H), 7.05 (d, 1 H, *J* = 2.4 Hz), 6.32 - 6.25(m, 1 H), 5.96 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.67 (d, 1 H, *J* = 10.8 Hz), 4.07 (q, 2 H, *J* = 7.0 Hz), 1.45 (t, 3 H, *J* = 6.9 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.55 (t, *J* = 3.0 Hz), 154.31, 133.10, 128.65 (t, *J* = 31.6 Hz), 127.67, 125.31, 122.54 (t, *J* = 7.4 Hz), 120.57 (t, *J* = 261.5 Hz), 119.00, 112.95, 110.96, 103.46, 63.95, 14.91.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.55 (d, 2 F, *J* = 10.2 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{14}H_{14}F_2NO_3$ 282.0942; found: 282.0937.

1,1-difluoroallyl-4-fluoro-1H-indole-2-carboxylate (3p)



The title compound 3p was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 67% yield, 171.0 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.36 (s, 1 H), 7.42 (d, 1 H, *J* = 1.8 Hz), 7.31 - 7.28 (m, 1 H), 7.23 (d, 1 H, *J* = 7.8 Hz), 6.83 (dd, 1 H, *J* = 10.2, 7.8 Hz), 6.33 - 6.26 (m, 1 H), 6.00 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

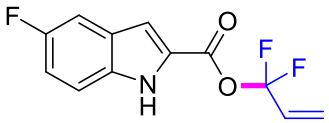
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.31 (d, *J* = 250.5 Hz), 156.67 (t, *J* = 3.0 Hz), 139.79 (d, *J* = 9.3 Hz), 128.40 (t, *J* = 31.3 Hz), 127.22 (d, *J* = 7.6

Hz), 125.19, 122.85 (t, J = 7.3 Hz), 120.63 (t, J = 262.5 Hz), 117.30 (d, J = 22.6 Hz), 108.20 (d, J = 4.0 Hz), 107.51, 105.57 (d, J = 18.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.82 (d, 2 F, J = 7.9 Hz), -121.84 (d, 1 F, J = 4.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9F_3NO_2$ 256.0585; found: 256.0580.

1,1-difluoroallyl-5-fluoro-1H-indole-2-carboxylate (3q)



The title compound 3q was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 30:1, 69% yield, 176.0 mg, white solid).

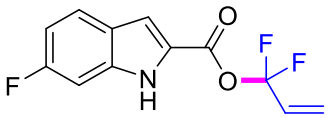
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.25 (s, 1 H), 7.39 (dd, 1 H, J = 9.0, 4.2 Hz), 7.33 (dd, 1 H, J = 8.4, 2.4 Hz), 7.30 (d, 1 H, J = 1.8 Hz), 7.15 (td, 1 H, J = 9.0, 2.4 Hz), 6.33 - 6.25 (m, 1 H), 5.98 (dt, 1 H, J = 17.4, 2.4 Hz), 5.69 (d, 1 H, J = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.35 (d, J = 236.9 Hz), 156.70 (t, J = 3.0 Hz), 134.41, 128.44 (t, J = 31.4 Hz), 127.34 (d, J = 10.4 Hz), 126.51, 122.81 (t, J = 7.4 Hz), 120.63 (t, J = 262.2 Hz), 115.94 (d, J = 27.0 Hz), 113.21 (d, J = 9.3 Hz), 111.23 (d, J = 5.6 Hz), 107.03 (d, J = 23.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.77 (d, 2 F, J = 8.5 Hz), -121.89 (d, 1 F, J = 4.0 Hz).

HRMS (ESI) m/z: [M + H]$^+$ calc. for $C_{12}H_9F_3NO_2$ 256.0585; found: 256.0580.

1,1-difluoroallyl-6-fluoro-1H-indole-2-carboxylate (3r)



The title compound 3r was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 62% yield, 158.1 mg, white solid).

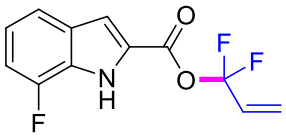
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1 H), 7.64 (dd, 1 H, *J* = 9.0, 5.4 Hz), 7.34 (d, 1 H, *J* = 1.2 Hz), 7.11 (dd, 1 H, *J* = 9.0, 2.4 Hz), 6.96 (td, 1 H, *J* = 9.0, 2.4 Hz), 6.34 - 6.26 (m, 1 H), 6.00 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.41 (d, *J* = 242.9 Hz), 156.88 (t, *J* = 3.0 Hz), 138.10 (d, *J* = 13.1 Hz), 128.50 (t, *J* = 31.4 Hz), 125.61 (d, *J* = 3.6 Hz), 124.35 (d, *J* = 10.4 Hz), 123.86, 122.77 (t, *J* = 7.3 Hz), 120.65 (t, *J* = 262.0 Hz), 111.78, 111.25 (d, *J* = 25.4 Hz), 98.04 (d, *J* = 26.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.82 (d, 2 F, *J* = 7.9 Hz), -121.86 (d, 1 F, *J* = 4.0 Hz).

HRMS (ESI) m/z: [M + H]$^+$ calc. for $C_{12}H_9F_3NO_2$ 256.0585; found: 256.0580.

1,1-difluoroallyl-7-fluoro-1H-indole-2-carboxylate (3s)



The title compound 3s was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 66% yield, 168.3 mg, white solid).

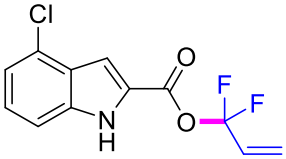
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.16 (s, 1 H), 7.47 (d, 1 H, *J* = 7.8 Hz), 7.37 (t, 1 H, *J* = 3.0 Hz), 7.11 - 7.06 (m, 2 H), 6.35 - 6.27 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.69 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.30 (t, *J* = 3.0 Hz), 149.54 (d, *J* = 245.1 Hz), 130.46 (d, *J* = 4.3 Hz), 128.43 (t, *J* = 31.3 Hz), 126.64 (d, *J* = 13.6 Hz), 126.05, 122.80 (t, *J* = 7.1 Hz), 121.50 (d, *J* = 5.5 Hz), 120.63 (t, *J* = 262.0 Hz), 118.67 (d, *J* = 4.0 Hz), 111.69 (d, *J* = 2.7 Hz), 110.62 (d, *J* = 15.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.73 (d, 2 F, *J* = 8.5 Hz), 121.83 (d, 1 F, *J* = 4.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9F_3NO_2$ 256.0585; found: 256.0580.

1,1-difluoroallyl-4-chloro-1H-indole-2-carboxylate (3t)



The title compound 3t was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1,

65% yield, 176.1 mg, white solid).

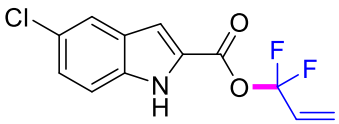
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.26 (s, 1 H), 7.44 (d, 1 H, *J* = 2.4 Hz), 7.35 (d, 1 H, *J* = 8.4 Hz), 7.28 (t, 1 H, *J* = 8.1 Hz), 7.19 (d, 1 H, *J* = 7.8 Hz), 6.33 - 6.26 (m, 1 H), 5.99 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.62 (t, *J* = 3.1 Hz), 138.16, 128.39 (t, *J* = 31.4 Hz), 128.28, 127.02, 126.42, 125.47, 122.88 (t, *J* = 7.1 Hz), 120.99, 120.63 (t, *J* = 262.6 Hz), 110.77, 109.81.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.69 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9ClF_2NO_2$ 272.0290; found: 272.0285.

1,1-difluoroallyl-5-chloro-1H-indole-2-carboxylate (3u)



The title compound 3u was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 74% yield, 200.6 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (s, 1 H), 7.68 (s, 1 H), 7.38 (d, 1 H, *J* = 8.4 Hz), 7.33 (d, 1 H, *J* = 9.0 Hz), 7.28 (s, 1 H), 6.32 - 6.24 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.69 (d, 1 H, *J* = 10.8 Hz).

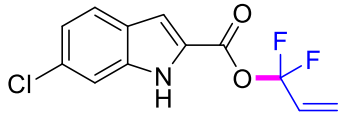
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.57 (t, *J* = 3.0 Hz), 135.94, 128.39 (t, *J* = 31.4 Hz), 128.06, 127.15, 127.07, 126.29, 122.85 (t, *J* = 7.2 Hz), 122.09,

120.62 (t, J = 262.4 Hz), 113.27, 110.70.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.66 (d, 2 F, J = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9ClF_2NO_2$ 272.0290; found: 272.0285.

1,1-difluoroallyl-6-chloro-1H-indole-2-carboxylate (3v)



The title compound 3v was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 66% yield, 178.9 mg, white solid).

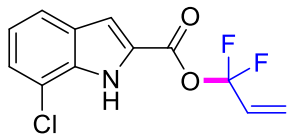
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.36 (s, 1 H), 7.60 (d, 1 H, J = 9.0 Hz), 7.43 (s, 1 H), 7.32 (s, 1 H), 7.14 (dd, 1 H, J = 8.4, 1.8 Hz), 6.34 - 6.26 (m, 1 H), 6.51 (dt, 1 H, J = 16.8, 2.4 Hz), 5.72 (d, 1 H, J = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.92 (t, J = 3.0 Hz), 138.05, 132.63, 128.44 (t, J = 31.3 Hz), 125.71, 125.67, 123.94, 122.89 (t, J = 7.4 Hz), 122.52, 120.65 (t, J = 262.0 Hz), 112.02, 111.54.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.79 (d, 2 F, J = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9ClF_2NO_2$ 272.0290; found: 272.0285.

1,1-difluoroallyl-7-chloro-1H-indole-2-carboxylate (3w)



The title compound 3w was synthesized according to General Procedure,

and it was purified by column chromatography on silica gel (PE:EA = 40:1, 71% yield, 192.4 mg, pale yellow liquid).

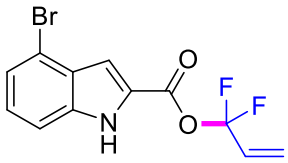
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (s, 1 H), 7.61 (d, 1 H, *J* = 7.8 Hz), 7.38 - 7.37 (m, 2 H), 7.12 (t, 1 H, *J* = 7.8 Hz), 6.33 - 6.26 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.69 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.11 (t, *J* = 2.9 Hz), 133.95, 127.33 (t, *J* = 31.5 Hz), 127.31, 124.78, 124.46, 121.73 (t, *J* = 7.4 Hz), 120.97, 120.49, 119.53 (t, *J* = 262.0 Hz), 116.35, 110.93.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.43 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9ClF_2NO_2$ 272.0290; found: 272.0285.

1,1-difluoroallyl-4-bromo-1H-indole-2-carboxylate (3x)



The title compound 3x was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 50% yield, 157.5 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (s, 1 H), 7.40 - 7.36 (m, 3 H), 7.22 (t, 1 H, *J* = 7.8 Hz), 6.33 - 6.25 (m, 1 H), 5.99 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

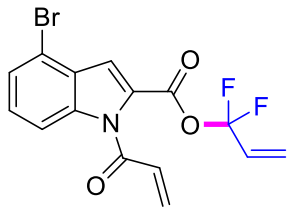
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.54 (t, *J* = 3.0 Hz), 137.70, 128.38 (t, *J* = 31.3 Hz), 128.25, 127.28, 125.45, 124.29, 122.89 (t, *J* = 7.2 Hz), 120.62

(t, J = 262.3 Hz), 116.85, 111.45, 111.30.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.49 (d, 2 F, J = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9BrF_2NO_2$ 315.9785; found: 315.9779.

1,1-difluoroallyl-1-acryloyl-4-bromo-1H-indole-2-carboxylate (3x')



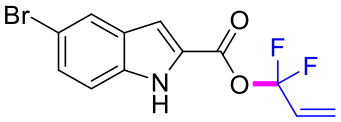
The title compound 3x' was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 20% yield, 74.0 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, 1 H, J = 8.4 Hz), 7.57 (s, 1 H), 7.49 (d, 1 H, J = 7.8 Hz), 7.34 (t, 1 H, J = 8.1 Hz), 6.61 - 6.56 (m, 1 H), 6.40 (d, 1 H, J = 16.8 Hz), 6.27 - 6.20 (m, 1 H), 5.99 (d, 1 H, J = 10.2 Hz), 5.97 (d, 1 H, J = 17.4 Hz), 5.69 (d, 1 H, J = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.01, 153.86 (t, J = 2.8 Hz), 137.73, 130.15, 130.00, 127.97, 126.62 (t, J = 31.3 Hz), 126.24, 125.82, 125.41, 121.63 (t, J = 7.4 Hz), 119.12 (t, J = 263.0 Hz), 117.65, 115.31, 112.12.

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{15}H_{11}BrF_2NO_3$ 369.9890; found: 369.9885.

1,1-difluoroallyl-5-bromo-1H-indole-2-carboxylate (3y)



The title compound 3y was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1, 76% yield, 240.0 mg, white solid).

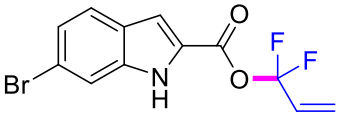
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (s, 1 H), 7.83 (s, 1 H), 7.44 (dd, 1 H, *J* = 8.4, 1.8 Hz), 7.32 (d, 1 H, *J* = 8.4 Hz), 7.26 (s, 1 H), 6.32 - 6.24 (m, 1 H), 5.98 (dd, 1 H, *J* = 17.4, 1.8 Hz), 5.69 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.63, 136.22, 129.60, 128.72, 128.38 (t, *J* = 31.3 Hz), 126.10, 125.28, 122.88 (t, *J* = 7.4 Hz), 120.63 (t, *J* = 262.4 Hz), 114.54, 113.65, 110.57.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.66 (d, 2 F, *J* = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9BrF_2NO_2$ 315.9785; found: 315.9779.

1,1-difluoroallyl-6-bromo-1H-indole-2-carboxylate (3z)



The title compound 3z was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 68% yield, 214.2 mg, white solid).

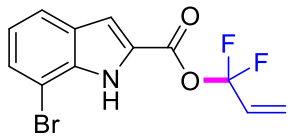
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1 H), 7.55 (s, 1 H), 7.50 (d, 1 H, *J* = 8.4 Hz), 7.26 (s, 1 H), 7.22 (d, 1 H, *J* = 8.4 Hz), 6.29 - 6.23 (m, 1 H), 5.96 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.67 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.92 (t, *J* = 3.1 Hz), 138.38, 128.43 (t, *J* = 31.3 Hz), 125.94, 125.58, 125.02, 124.18, 122.93 (t, *J* = 7.4 Hz), 120.65 (t, *J* = 262.3 Hz), 120.52, 115.52, 111.56.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.58 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9BrF_2NO_2$ 315.9785; found: 315.9779.

1,1-difluoroallyl-7-bromo-1H-indole-2-carboxylate (3aa)



The title compound 3aa was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 56% yield, 176.4 mg, pale yellow liquid).

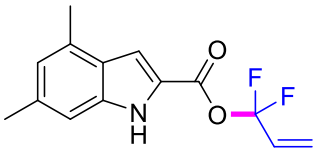
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1 H), 7.65 (d, 1 H, *J* = 7.8 Hz), 7.53 (d, 1 H, *J* = 7.8 Hz), 7.40 (d, 1 H, *J* = 2.4 Hz), 7.07 (t, 1 H, *J* = 7.8 Hz), 6.33 - 6.27 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.69 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.81 (t, *J* = 3.1 Hz), 136.02, 128.27, 128.03 (t, *J* = 31.3 Hz), 127.69, 125.36, 122.43 (t, *J* = 7.4 Hz), 122.06, 121.81, 120.23 (t, *J* = 262.1 Hz), 111.76, 104.87.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.77 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_9BrF_2NO_2$ 315.9785; found: 315.9779.

1,1-difluoroallyl-4,6-dimethyl-1H-indole-2-carboxylate (3ab)



The title compound 3ab was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 72% yield, 191.0 mg, white solid).

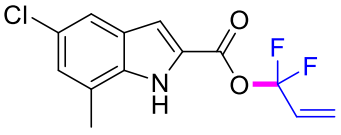
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 1 H), 7.34 (s, 1 H), 7.04 (s, 1 H), 6.82 (s, 1 H), 6.34 - 6.27 (m, 1 H), 5.97 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.67 (d, 1 H, *J* = 10.8 Hz), 2.53 (s, 3 H), 2.44 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.65 (t, *J* = 3.1 Hz), 137.09, 136.23, 131.28, 127.66 (t, *J* = 31.8 Hz), 124.51, 122.74, 122.48, 121.40 (t, *J* = 7.4 Hz), 119.52 (t, *J* = 261.2 Hz), 109.21, 108.06, 20.95, 17.45.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.62 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{14}H_{14}F_2NO_2$ 266.0993; found: 266.0987.

1,1-difluoroallyl-5-chloro-7-methyl-1H-indole-2-carboxylate (3ac)



The title compound 3ac was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1, 70% yield, 200.0 mg, pale yellow solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1 H), 7.51 (s, 1 H), 7.26 (d, 1 H, *J*

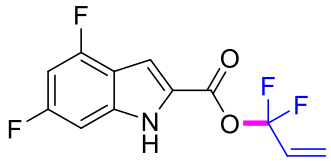
= 1.8 Hz), 7.13 (s, 1 H), 6.32 - 6.24 (m, 1 H), 5.97 (dd, 1 H, *J* = 17.4, 2.4 Hz), 5.68 (dd, 1 H, *J* = 10.8, 1.8 Hz), 2.50 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.58 (t, *J* = 3.0 Hz), 135.96, 128.44 (t, *J* = 31.6 Hz), 127.52, 127.10, 127.00, 125.92, 123.17, 122.77 (t, *J* = 7.4 Hz), 120.59 (t, *J* = 262.4 Hz), 119.55, 111.24, 16.51.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.55 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{11}ClF_2NO_2$ 286.0446; found: 286.0440.

1,1-difluoroallyl-4,6-difluoro-1H-indole-2-carboxylate (3ad)



The title compound 3ad was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 55% yield, 150.2 mg, white solid).

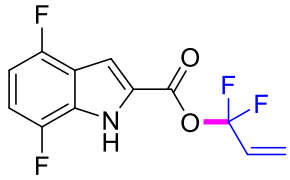
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34 (s, 1 H), 7.39 (d, 1 H, *J* = 1.2 Hz), 6.94 (d, 1 H, *J* = 9.0 Hz), 6.68 (td, 1 H, *J* = 9.6, 1.8 Hz), 6.31 - 6.24 (m, 1 H), 5.99 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.08 (dd, *J* = 244.5, 11.6 Hz), 157.17 (dd, *J* = 248.9, 15.3 Hz), 156.37, 138.77 (dd, *J* = 15.3, 12.0 Hz), 128.31 (t, *J* = 31.3 Hz), 125.62, 122.93 (t, *J* = 7.4 Hz), 120.61 (t, *J* = 262.7 Hz), 114.08 (d, *J* = 22.5 Hz), 107.77, 97.21 (dd, *J* = 244.5, 22.7 Hz), 94.33 (dd, *J* = 26.4, 5.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.97 (d, 2 F, *J* = 8.5 Hz), 124.46 (d, 1 F, *J* = 2.8 Hz), 138.72 (d, 1 F, *J* = 4.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_8F_4NO_2$ 274.0491; found: 274.0486.

1,1-difluoroallyl-4,7-difluoro-1H-indole-2-carboxylate (3ae)



The title compound 3ae was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1, 58% yield, 158.4 mg, white solid).

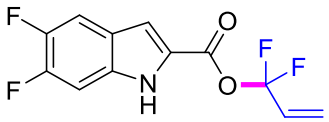
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.12 (s, 1 H), 7.42 (t, 1 H, *J* = 2.4 Hz), 6.98 (td, 1 H, *J* = 10.2, 3.6 Hz), 6.73 (td, 1 H, *J* = 8.4, 3.0 Hz), 6.32 - 6.24 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.83 (t, *J* = 3.1 Hz), 153.02 (dd, *J* = 246.2, 2.9 Hz), 145.67 (dd, *J* = 241.1, 3.8 Hz), 128.23 (t, *J* = 31.3 Hz), 127.65 (dd, *J* = 16.5, 10.1 Hz), 126.17, 123.00 (t, *J* = 7.4 Hz), 120.60 (t, *J* = 262.7 Hz), 119.59 (dd, *J* = 25.2, 4.8 Hz), 110.62 (dd, *J* = 18.8, 8.3 Hz), 107.94, 105.10 (dd, *J* = 21.6, 6.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.04 (d, 2 F, *J* = 8.5 Hz), -124.45 (d, 1 F, *J* = 4.5 Hz), -138.70 (d, 1 F, *J* = 4.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_8F_4NO_2$ 274.0491; found: 274.0486.

1,1-difluoroallyl-5,6-difluoro-1H-indole-2-carboxylate (3af)



The title compound 3af was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 20:1, 57% yield, 155.6 mg, white solid).

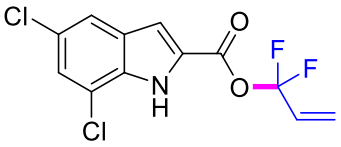
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1 H), 7.44 (dd, 1 H, *J* = 10.2, 7.8 Hz), 7.30 (s, 1 H), 7.23 (dd, 1 H, *J* = 10.2, 6.6 Hz), 6.31 - 6.24 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.36 (t, *J* = 3.1 Hz), 151.07 (dd, *J* = 247.4, 16.5 Hz), 147.68 (dd, *J* = 241.2, 15.5 Hz), 133.21 (d, *J* = 10.5 Hz), 128.37 (t, *J* = 31.4 Hz), 126.52 (d, *J* = 4.4 Hz), 122.86 (t, *J* = 7.2 Hz), 122.46 (d, *J* = 8.9 Hz), 120.61 (t, *J* = 262.4 Hz), 111.51 (dd, *J* = 5.0, 2.3 Hz), 108.99 (d, *J* = 19.4 Hz), 99.79 (d, *J* = 21.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.07 (d, 2 F, *J* = 8.5 Hz), -124.49 (d, 1 F, *J* = 3.4 Hz), -138.74 (d, 1 F, *J* = 4.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_8F_4NO_2$ 274.0491; found: 274.0486.

1,1-difluoroallyl-5,7-dichloro-1H-indole-2-carboxylate (3ag)



The title compound 3ag was synthesized according to General Procedure,

and it was purified by column chromatography on silica gel (PE:EA = 60:1, 65% yield, 198.2 mg, white solid).

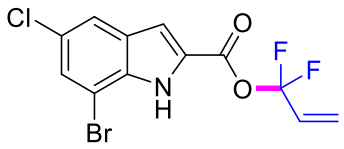
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.08 (s, 1 H), 7.57 (s, 1 H), 7.35 (s, 1 H), 7.27 (d, 1 H, *J* = 1.8 Hz), 6.32 - 6.25 (m, 1 H), 5.98 (d, 1 H, *J* = 17.4 Hz), 5.70 (d, 1 H, *J* = 10.2 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.91 (t, *J* = 3.1 Hz), 133.47, 128.56, 128.24 (t, *J* = 31.3 Hz), 127.04, 127.00, 125.85, 123.00 (t, *J* = 7.4 Hz), 120.82, 120.62 (t, *J* = 262.6 Hz), 118.04, 111.19.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.93 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_8Cl_2F_2NO_2$ 305.9900; found: 305.9895.

1,1-difluoroallyl-7-bromo-5-chloro-1H-indole-2-carboxylate (3ah)



The title compound 3ah was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 63% yield, 219.8 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (s, 1 H), 7.59 (s, 1 H), 7.47 (d, 1 H, *J* = 2.4 Hz), 7.28 (d, 1 H, *J* = 2.4 Hz), 6.31 - 6.25 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 10.8 Hz).

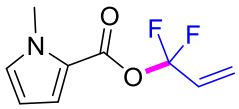
^{13}C NMR (150 MHz, $CDCl_3$) δ 155.87 (t, *J* = 3.0 Hz), 134.85, 128.69, 128.26 (t, *J* = 31.3 Hz), 128.18, 127.23, 126.96, 123.00 (t, *J* = 7.4 Hz),

121.35, 120.63 (t, J = 262.3 Hz), 111.31, 105.54.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.90 (d, 2 F, J = 7.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_8BrClF_2NO_2$ 349.9395; found: 349.9390.

1,1-difluoroallyl-1-methyl-1H-pyrrole-2-carboxylate (5a)



The title compound 5a was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 90:1, 55% yield, 110.6 mg, pale yellow liquid).

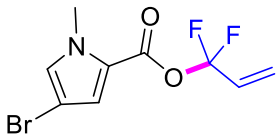
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (dd, 1 H, J = 4.2, 1.8 Hz), 6.88 (t, 1 H, J = 2.1 Hz), 6.27 - 6.20 (m, 1 H), 6.15 (dd, 1 H, J = 4.2, 2.4 Hz), 5.90 (dt, 1 H, J = 16.8, 2.4 Hz), 5.61 (d, 1 H, J = 10.8 Hz), 3.91 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.48 (t, J = 2.8 Hz), 130.69, 128.22 (t, J = 32.2 Hz), 120.77 (t, J = 7.4 Hz), 119.40 (t, J = 259.4 Hz), 119.33, 119.29, 107.58, 35.81.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.29 (d, 2 F, J = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_9H_{10}F_2NO_2$ 202.0680; found: 202.0674.

1,1-difluoroallyl-4-bromo-1-methyl-1H-pyrrole-2-carboxylate (5b)



The title compound 5b was synthesized according to General Procedure,

and it was purified by column chromatography on silica gel (PE:EA = 60:1, 85% yield, 237.1 mg, pale yellow liquid).

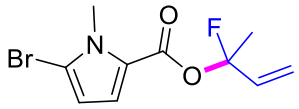
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, 1 H, *J* = 1.8 Hz), 6.86 (d, 1 H, *J* = 1.8 Hz), 6.24 - 6.16 (m, 1 H), 5.89 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.62 (d, 1 H, *J* = 10.8 Hz), 3.88 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.55 (t, *J* = 2.8 Hz), 129.96, 127.84 (t, *J* = 31.9 Hz), 121.14 (t, *J* = 7.4 Hz), 120.38, 119.82, 119.36 (t, *J* = 261.0 Hz), 94.66, 35.99.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.26 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_9H_9BrF_2NO_2$ 279.9785; found: 279.9779.

2-fluorobut-3-en-2-yl-5-bromo-1-methyl-1H-pyrrole-2-carboxylate (5c)



The title compound 5c was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 100:1, 50% yield, 139.5 mg, colourcless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (d, 1 H, *J* = 5.4 Hz), 6.25 (d, 1 H, *J* = 4.8 Hz), 6.23 - 6.18 (m, 1 H), 5.89 (d, 1 H, *J* = 17.4 Hz), 5.61 (d, 1 H, *J* = 10.8 Hz), 3.91 (s, 3 H).

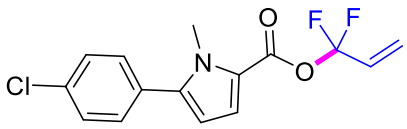
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.28 (t, *J* = 3.1 Hz), 127.71 (t, *J* = 31.8 Hz), 120.64 (t, *J* = 7.1 Hz), 120.12, 119.25, 119.10 (t, *J* = 260.2 Hz), 113.43,

110.53, 33.33.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.38 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_9H_9BrF_2NO_2$ 279.9785; found: 279.9779.

1,1-difluoroallyl-5-(4-chlorophenyl)-1-methyl-1H-pyrrole-2-carboxyl ate (5d)



The title compound 5d was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 90:1, 84% yield, 261.3 mg, white solid).

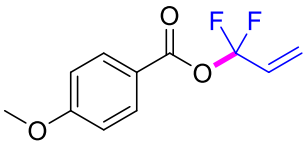
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, 2 H, *J* = 8.4 Hz), 7.33 (d, 2 H, *J* = 8.4 Hz), 7.14 (d, 1 H, *J* = 4.2 Hz), 6.30 - 6.25 (m, 1 H), 6.24 (d, 1 H, *J* = 4.2 Hz), 5.92 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.63 (d, 1 H, *J* = 10.8 Hz), 3.85 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.38 (t, *J* = 3.0 Hz), 141.29, 133.49, 129.33, 128.70, 128.03 (t, *J* = 32.2 Hz), 127.70, 120.61 (t, *J* = 7.5 Hz), 120.36, 119.24 (t, *J* = 259.6 Hz), 119.03, 108.78, 33.19.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.14 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{15}H_{13}ClF_2NO_2$ 312.0603; found: 312.0598.

1,1-difluoroallyl-4-methoxybenzoate (7a)



The title compound 7a was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 82% yield, 187.0 mg, colourless liquid).

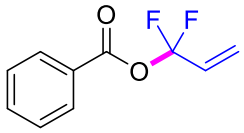
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, 2 H, *J* = 9.0 Hz), 6.94 (d, 2 H, *J* = 9.0 Hz), 6.32 - 6.24 (m, 1 H), 5.91 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.63 (d, 1 H, *J* = 10.8 Hz), 3.87 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.41, 160.10 (t, *J* = 2.8 Hz), 131.38, 127.95 (t, *J* = 31.9 Hz), 121.07 (t, *J* = 7.4 Hz), 119.64, 119.53 (t, *J* = 259.58 Hz), 112.95, 54.50.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.18 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{11}H_{11}F_2O_3$ 229.0676; found: 229.0672.

1,1-difluoroallyl benzoate (7b)



The title compound 7b was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 56% yield, 110.9 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, 2 H, *J* = 8.4, 1.2 Hz), 7.63 (t, 1 H, *J* = 7.5 Hz), 7.48 (t, 2 H, *J* = 7.8 Hz), 6.33-6.25 (m, 1 H), 5.94 (dt, 1 H,

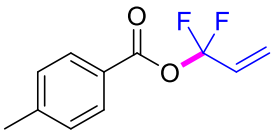
J = 16.8, 2.4 Hz), 5.65 (d, 1 H, J = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.46 (t, J = 2.7 Hz), 134.25, 130.20, 128.75 (t, J = 31.9 Hz), 128.69, 128.38, 122.39 (t, J = 7.7 Hz), 120.71 (t, J = 260.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.15 (d, 2 F, J = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_9F_2O_2$ 199.0571; found: 199.0565.

1,1-difluoroallyl-4-methylbenzoate (7c)



The title compound 7c was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 84% yield, 178.1 mg, colourless liquid).

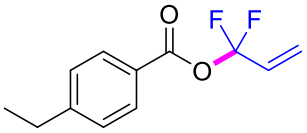
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, 2 H, J = 8.4 Hz), 7.27 (d, 2 H, J = 7.8 Hz), 6.32 - 6.25 (m, 1 H), 5.92 (dt, 1 H, J = 17.4, 1.8 Hz), 5.63 (d, 1 H, J = 10.8 Hz), 2.42 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.00 (t, J = 2.7 Hz), 143.80, 128.76, 127.92, 127.39 (t, J = 31.7 Hz), 124.12, 120.72 (t, J = 7.4 Hz), 119.20 (t, J = 260.2 Hz), 20.27.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.22 (d, 2 F, J = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{11}H_{11}F_2O_2$ 213.0727; found: 213.0722.

1,1-difluoroallyl-4-ethylbenzoate (7d)



The title compound 7d was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 84% yield, 189.9 mg, colourless liquid).

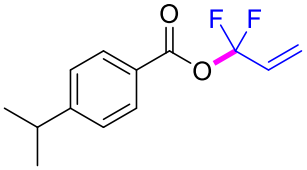
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, 2 H, *J* = 8.4 Hz), 7.30 (d, 2 H, *J* = 8.4 Hz), 6.34 - 6.26 (m, 1 H), 5.93 (dt, 1 H, *J* = 16.8, 2.4 Hz), 5.64 (d, 1 H, *J* = 10.8 Hz), 2.72 (q, 2 H, *J* = 7.6 Hz), 1.27 (t, 3 H, *J* = 7.5 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.07 (t, *J* = 2.8 Hz), 150.03, 128.95, 127.48 (t, *J* = 31.8 Hz), 126.81, 124.39, 120.76 (t, *J* = 7.4 Hz), 119.29 (t, *J* = 260.2 Hz), 27.62, 13.68.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.63 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_{13}F_2O_2$ 227.0884; found: 227.0879.

1,1-difluoroallyl-4-isopropylbenzoate (7e)



The title compound 7e was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 83% yield, 199.3 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98(d, 2 H, *J* = 8.4 Hz), 7.33 (d, 2 H, *J* =

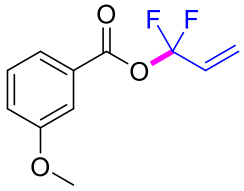
7.8 Hz), 6.33 - 6.25 (m, 1 H), 5.93 (d, 1 H, *J* = 17.4 Hz), 5.64 (d, 1 H, *J* = 11.4 Hz), 3.02-2.95 (m, 1 H), 1.28 (d, 6 H, *J* = 7.2 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.48 (t, *J* = 2.6 Hz), 156.00, 130.44, 128.92 (t, *J* = 31.8 Hz), 126.84, 125.95, 122.20 (t, *J* = 7.4 Hz), 120.70 (t, *J* = 260.2 Hz), 34.38, 23.62.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.18 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{15}F_2O_2$ 241.1040; found: 241.1035.

1,1-difluoroallyl-3-methoxybenzoate (7f)



The title compound 7f was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 79% yield, 180.2 mg, yellow liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, 1 H, *J* = 7.8 Hz), 7.54 (s, 1 H), 7.37 (t, 1 H, *J* = 8.7 Hz), 7.16 (d, 1 H, *J* = 7.8 Hz), 6.32 - 6.25 (m, 1 H), 5.93 (d, 1 H, *J* = 18.6 Hz), 5.65 (d, 1 H, *J* = 10.8 Hz), 3.84 (s, 3 H).

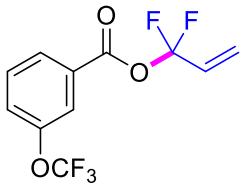
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.28 (t, *J* = 2.8 Hz), 158.71, 128.68, 128.55, 127.68 (t, *J* = 31.6 Hz), 121.52, 121.36 (t, *J* = 7.4 Hz), 119.72, 119.69 (t, *J* = 260.4 Hz), 113.47, 54.41.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.19 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{11}H_{11}F_2O_3$ 229.0676; found:

229.0672.

1,1-difluoroallyl-3-(trifluoromethoxy)benzoate (7g)



The title compound 7g was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 78% yield, 220.0 mg, colourless liquid).

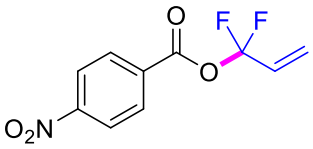
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dt, 1 H, *J* = 7.2, 1.8 Hz), 7.88 (s, 1 H), 7.53 (t, 1 H, *J* = 7.8 Hz), 7.49 (d, 1 H, *J* = 7.8 Hz), 6.32 - 6.24 (m, 1 H), 5.95 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.68 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.09 (t, *J* = 2.7 Hz), 148.35 (d, *J* = 2.3 Hz), 129.41, 129.29, 127.45, 127.34 (t, *J* = 31.4 Hz), 125.62, 121.73 (t, *J* = 7.4 Hz), 121.53, 119.70 (t, *J* = 261.8 Hz), 119.36 (q, *J* = 256.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -58.08 (s, 3 F), -71.80 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{11}H_8F_5O_3$ 283.0394; found: 283.0389.

1,1-difluoroallyl-4-nitrobenzoate (7h)



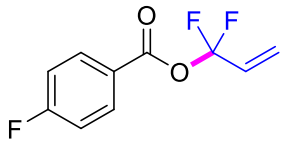
The title compound 7h was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 40:1, 78% yield, 189.6 mg, yellow liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, 2 H, *J* = 9.0 Hz), 8.23 (d, 2 H, *J* = 9.0 Hz), 6.31 - 6.24 (m, 1 H), 5.98 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.61 (t, *J* = 2.7 Hz), 150.17, 132.62, 130.29, 127.00 (t, *J* = 31.1 Hz), 122.76, 122.13 (t, *J* = 7.4 Hz), 119.73 (t, *J* = 262.7 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_8F_2NO_4$ 244.0421; found: 244.0415.

1,1-difluoroallyl-4-fluorobenzoate (7i)



The title compound 7i was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 78% yield, 168.5 mg, colourless liquid).

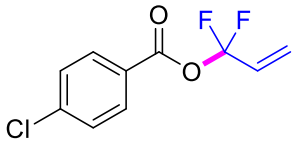
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, 2 H, *J* = 9.0, 5.4 Hz), 7.15 (t, 2 H, *J* = 8.4 Hz), 6.32 - 6.24 (m, 1 H), 5.93 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.66 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.54 (d, *J* = 255.0 Hz), 160.49 (t, *J* = 2.7 Hz), 132.93 (d, *J* = 9.6 Hz), 128.64 (t, *J* = 31.5 Hz), 124.66, 122.52 (t, *J* = 7.4 Hz), 120.70 (t, *J* = 260.7 Hz), 116.02 (d, *J* = 22.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.54 (d, 2 F, *J* = 8.5 Hz), -103.02 (s, 1 F).

HRMS (ESI) m/z: [M + H]$^+$ calc. for $C_{10}H_8F_3O_2$ 217.0476; found: 217.0471.

1,1-difluoroallyl-4-chlorobenzoate (7j)



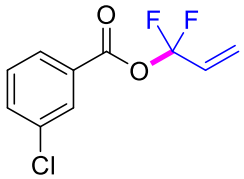
The title compound 7j was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (Pure PE, 73% yield, 169.4 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, 2 H, *J* = 8.4 Hz), 7.44 (d, 2 H, *J* = 8.4 Hz), 6.31 - 6.24 (m, 1 H), 5.93 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.66 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.57 (t, *J* = 2.8 Hz), 140.89, 131.51, 129.08, 128.53 (t, *J* = 31.6 Hz), 126.82, 122.56 (t, *J* = 7.4 Hz), 120.70 (t, *J* = 261.2 Hz).

HRMS (ESI) m/z: [M + H]$^+$ calc. for $C_{10}H_8ClF_2O_2$ 233.0181; found: 233.0176.

1,1-difluoroallyl-3-chlorobenzoate (7k)



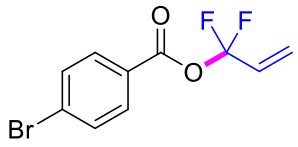
The title compound 7k was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 60% yield, 139.2 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1 H), 7.93 (d, 1 H, *J* = 8.4 Hz), 7.59 (d, 1 H, *J* = 8.4 Hz), 7.42 (t, 1 H, *J* = 7.8 Hz), 6.32 - 6.24 (m, 1 H), 5.94 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.67 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.28 (t, *J* = 3.0 Hz), 134.95, 134.29, 130.15, 130.05, 128.45 (t, *J* = 31.4 Hz), 128.31, 122.74, 122.74 (t, *J* = 7.4 Hz), 120.74 (t, *J* = 261.6 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_8ClF_2O_2$ 233.0181; found: 233.0176.

1,1-difluoroallyl-4-bromobenzoate (7l)



The title compound 7l was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 65% yield, 179.4 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, 2 H, *J* = 8.4 Hz), 7.62 (d, 2 H, *J* = 8.4 Hz), 6.31 - 6.23 (m, 1 H), 5.94 (dt, 1 H, *J* = 16.8, 2.4 Hz), 5.66 (d, 1 H, *J* = 10.8 Hz).

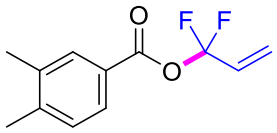
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.74 (t, *J* = 2.8 Hz), 131.08, 130.57, 127.68, 127.47 (t, *J* = 31.4 Hz), 126.24, 121.59 (t, *J* = 7.4 Hz), 119.65 (t, *J* = 261.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.61 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_8BrF_2O_2$ 276.9676; found:

276.9671.

1,1-difluoroallyl-3,4-dimethylbenzoate (7m)



The title compound 7m was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 90:1, 88% yield, 199.0 mg, colourless liquid).

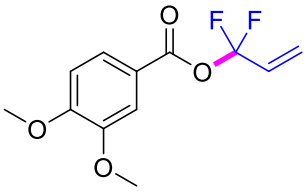
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1 H), 7.78 (d, 1 H, *J* = 7.8 Hz), 7.22 (d, 1 H, *J* = 8.4 Hz), 6.33 - 6.25 (m, 1 H), 5.92 (dt, 1 H, *J* = 16.8, 2.4 Hz), 5.64 (d, 1 H, *J* = 10.8 Hz), 2.32 (d, 6 H, *J* = 10.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.61 (t, *J* = 2.7 Hz), 142.93, 136.11, 130.08, 128.89, 127.87 (t, *J* = 31.9 Hz), 126.77, 124.80, 121.09 (t, *J* = 7.3 Hz), 119.62 (t, *J* = 260.0 Hz), 19.07, 18.59.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.21 (d, 2 F, *J* = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_{13}F_2O_2$ 277.0884; found: 277.0879.

1,1-difluoroallyl-3,4-dimethoxybenzoate (7n)



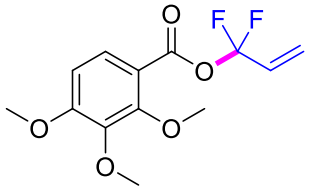
The title compound 7n was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 8:1, 86% yield, 221.9 mg, pale yellow liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, 1 H, *J* = 8.4, 2.0 Hz), 7.50 (d, 1 H, *J* = 2.0 Hz), 6.89 (d, 1 H, *J* = 8.4 Hz), 6.34 - 6.22 (m, 1 H), 5.91 (dt, 1 H, *J* = 17.6, 2.0 Hz), 5.63 (d, 1 H, *J* = 11.2 Hz), 3.94 (s, 3 H), 3.92 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.21 (t, *J* = 2.8 Hz), 154.14, 148.88, 128.91 (t, *J* = 32.2 Hz), 124.68, 122.17 (t, *J* = 7.6 Hz), 120.69 (t, *J* = 262.5 Hz), 120.61, 112.19, 110.38, 56.12, 56.04.

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{12}H_{13}F_2O_4$ 259.0782; found: 259.0777.

1,1-difluoroallyl-2,3,4-trimethoxybenzoate (7o)



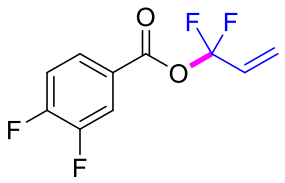
The title compound 7o was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 10:1, 90% yield, 259.3 mg, colourless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 1 H, *J* = 8.8 Hz), 6.69 (d, 1 H, *J* = 9.2 Hz), 6.31 - 6.19 (m, 1 H), 5.89 (dt, 1 H, *J* = 17.6, 2.0 Hz), 5.59 (d, 1 H, *J* = 11.2 Hz), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.83 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66 (t, *J* = 2.8 Hz), 158.44, 155.65, 143.11, 128.99 (t, *J* = 32.2 Hz), 127.74, 122.08 (t, *J* = 7.5 Hz), 120.60 (t, *J* = 262.1 Hz), 115.51, 107.01, 61.76, 60.95, 56.11.

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{15}F_2O_5$ 289.0888; found: 289.0883.

1,1-difluoroallyl-3,4-difluorobenzoate (7p)



The title compound 7p was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 64% yield, 149.8 mg, colourless liquid).

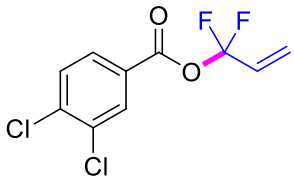
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 - 7.85(m, 2 H), 7.30 - 7.27 (m, 1 H), 6.31 - 6.23 (m, 1 H), 5.95 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.68 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.50 (d, *J* = 2.9 Hz), 153.40 (dd, *J* = 257.3, 12.8 Hz), 149.20 (dd, *J* = 249.6, 12.9 Hz), 127.27 (t, *J* = 31.4 Hz), 126.32 (dd, *J* = 7.7, 3.8 Hz), 124.32, 121.77 (t, *J* = 7.4 Hz), 119.62 (t, *J* = 261.9 Hz), 118.53 (dd, *J* = 18.8, 2.1 Hz), 116.77 (d, *J* = 18.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.72 (d, 2 F, *J* = 8.5 Hz), -82.50 (d, 1 F, *J* = 28.8 Hz), -84.12 (dd, 1 F, *J* = 28.3, 23.2 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_7F_4O_2$ 235.0382; found: 235.0377.

1,1-difluoroallyl-3,4-dichlorobenzoate (7q)



The title compound 7q was synthesized according to General Procedure,

and it was purified by column chromatography on silica gel (PE:EA = 80:1, 65% yield, 172.9 mg, colourless liquid).

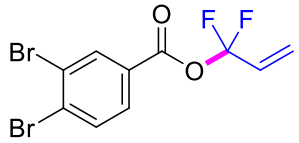
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, 1 H, *J* = 1.8 Hz), 7.86 (dd, 1 H, *J* = 8.4, 1.8 Hz), 7.55 (d, 1 H, *J* = 8.4 Hz), 6.30 - 6.22 (m, 1 H), 5.94 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.67 (d, 1 H, *J* = 11.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.60 (t, *J* = 2.9 Hz), 139.10, 133.40, 131.92, 130.86, 129.09, 128.26 (t, *J* = 31.3 Hz), 128.17, 122.87 (t, *J* = 7.4 Hz), 120.70 (t, *J* = 262.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.66 (d, 2 F, *J* = 8.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_7Cl_2F_2O_2$ 266.9791; found: 266.9786.

1,1-difluoroallyl-3,4-dibromobenzoate (7r)



The title compound 7r was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 80:1, 74% yield, 261.9 mg, colourless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, 1 H, *J* = 1.8 Hz), 7.80 (dd, 1 H, *J* = 8.4, 2.4 Hz), 7.72 (d, 1 H, *J* = 8.4 Hz), 6.30 - 6.22 (m, 1 H), 5.94 (dt, 1 H, *J* = 17.4, 2.4 Hz), 5.67 (d, 1 H, *J* = 10.8 Hz).

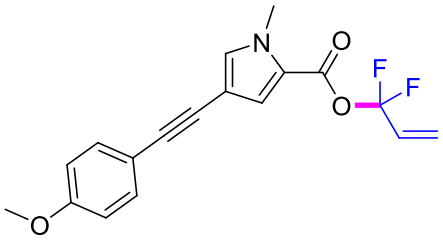
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.60 (t, *J* = 2.9 Hz), 134.93, 134.06, 132.00, 129.61, 128.79, 128.22 (t, *J* = 31.3 Hz), 125.47, 122.89 (t, *J* = 7.4

Hz), 120.68 (t, J = 262.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.64 (d, 2 F, J = 9.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{10}H_7Br_2F_2O_2$ 356.8760; found: 356.8755.

1,1-difluoroallyl-4-((4-methoxyphenyl)ethynyl)-1-methyl-1H-pyrrole-2-carboxylate (9a)



The title compound 9a was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 10:1, 40% yield, 132.4 mg, colourcless liquid).

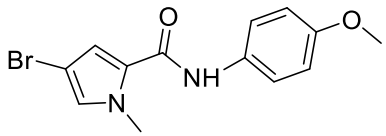
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, 2 H, J = 9.0 Hz), 7.16 (d, 1 H, J = 1.8 Hz), 7.07 (d, 1 H, J = 1.8 Hz), 6.86 (d, 2 H, J = 9.0 Hz), 6.25 - 6.17 (m, 1 H), 5.91 (dt, 1 H, J = 17.4, 2.4 Hz), 5.62 (d, 1 H, J = 10.8 Hz), 3.91 (s, 3 H), 3.82 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.39, 154.07 (t, J = 2.8 Hz), 133.00, 131.76, 127.96 (t, J = 32.1 Hz), 121.75, 121.05 (t, J = 7.1 Hz), 119.35 (t, J = 260.4 Hz), 119.32, 114.51, 112.96, 104.25, 87.51, 80.03, 54.28, 36.07.

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{18}H_{16}F_2NO_3$ 332.1098; found: 332.1093.

4-bromo-*N*-(4-methoxyphenyl)-1-methyl-1H-pyrrole-2-carboxamide

(11a)



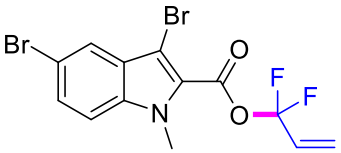
The title compound 11a was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 8:1, 51% yield, 157.1 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1 H), 7.41 (d, 2 H, *J* = 9.0 Hz), 6.86 (d, 2 H, *J* = 9.0 Hz), 6.73 (s, 1 H), 6.64 (s, 1 H), 3.91 (s, 3 H), 3.79 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.95, 156.55, 130.63, 127.81, 126.43, 122.18, 114.25, 113.73, 94.62, 55.52, 36.91.

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{14}BrN_2O_2$ 309.0239; found: 309.0234.

1,1-difluoroallyl-3,4-dibromo-1-methyl-1H-indole-2-carboxylate (13a)



The title compound 13a was synthesized according to General Procedure, and it was purified by column chromatography on silica gel (PE:EA = 60:1, 55% yield, 223.8 mg, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, 1 H, *J* = 1.8 Hz), 7.50 (dd, 1 H, *J* = 9.0, 1.8 Hz), 7.27 (s, 1 H), 6.32 - 6.24 (m, 1 H), 6.02 (dt, 1 H, *J* = 17.4, 1.8 Hz), 5.70 (d, 1 H, *J* = 11.4 Hz), 4.02 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.72 (t, *J* = 3.0 Hz), 137.44, 130.34, 128.52 (t, *J* = 31.1 Hz), 128.08, 124.34, 124.24, 122.95 (t, *J* = 7.2 Hz), 120.67 (t, *J* = 263.5 Hz), 115.07, 112.11, 100.04, 33.04.

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{13}H_{10}Br_2F_2NO_2$ 409.9026; found: 409.9020.

5. Spectra data for the compounds

Figure S1. Compound 3a ^{1}H NMR (600 MHz, $CDCl_3$)

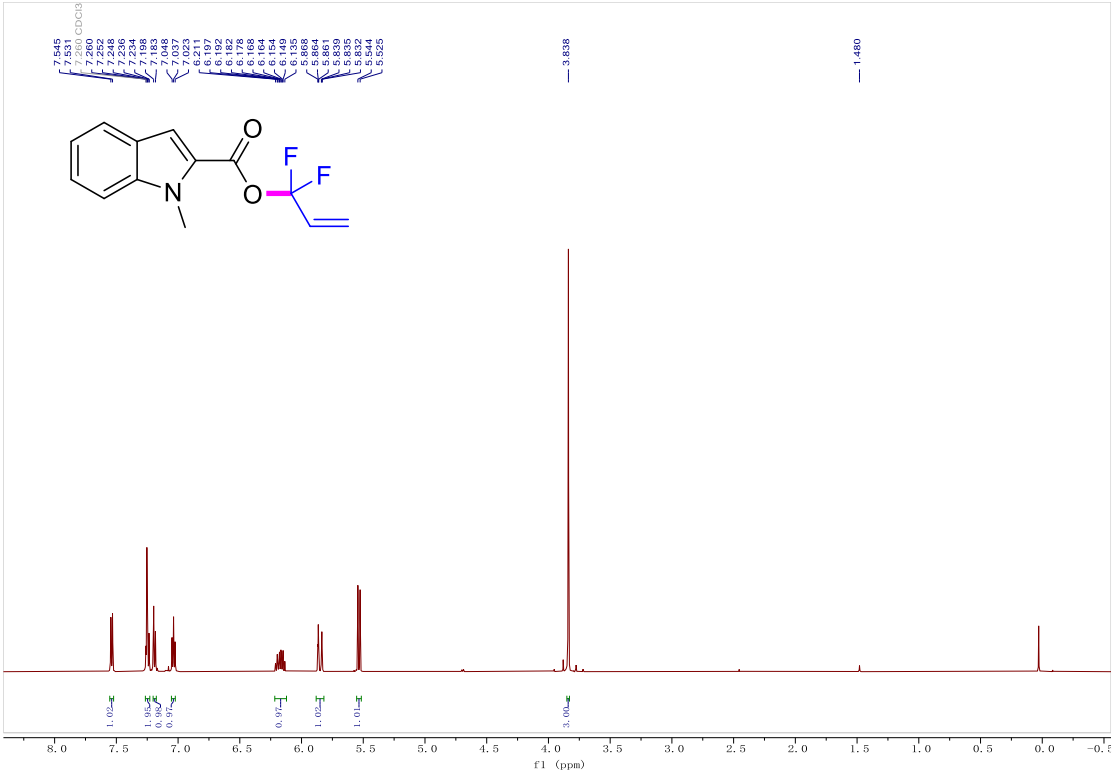


Figure S2. Compound 3a ^{13}C NMR (150 MHz, $CDCl_3$)

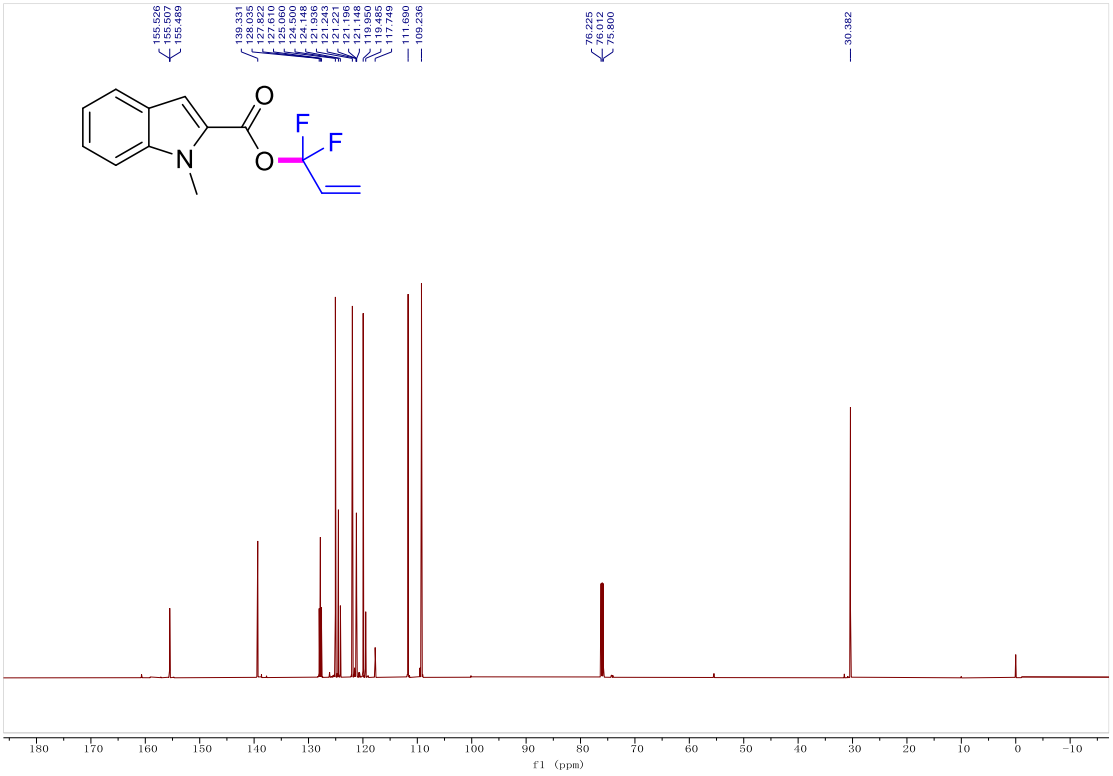


Figure S3. Compound 3a **^{19}F NMR (565 MHz, $CDCl_3$)**

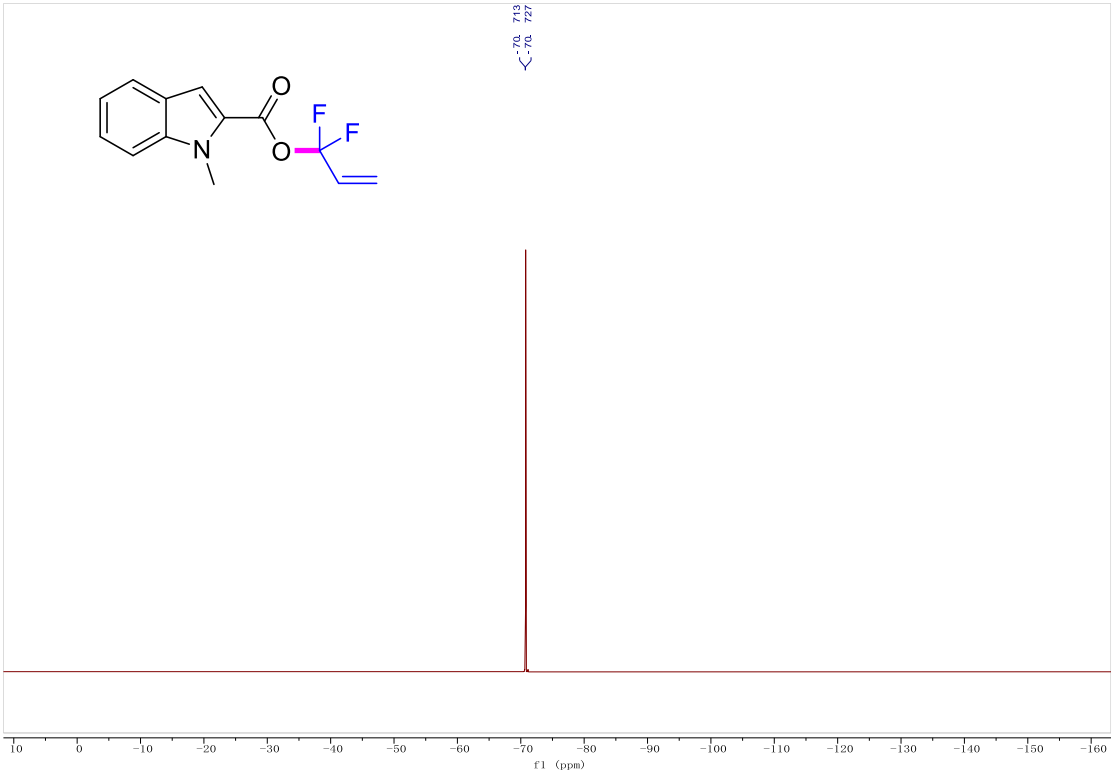


Figure S4. Compound 3b **^{1}H NMR (600 MHz, $CDCl_3$)**

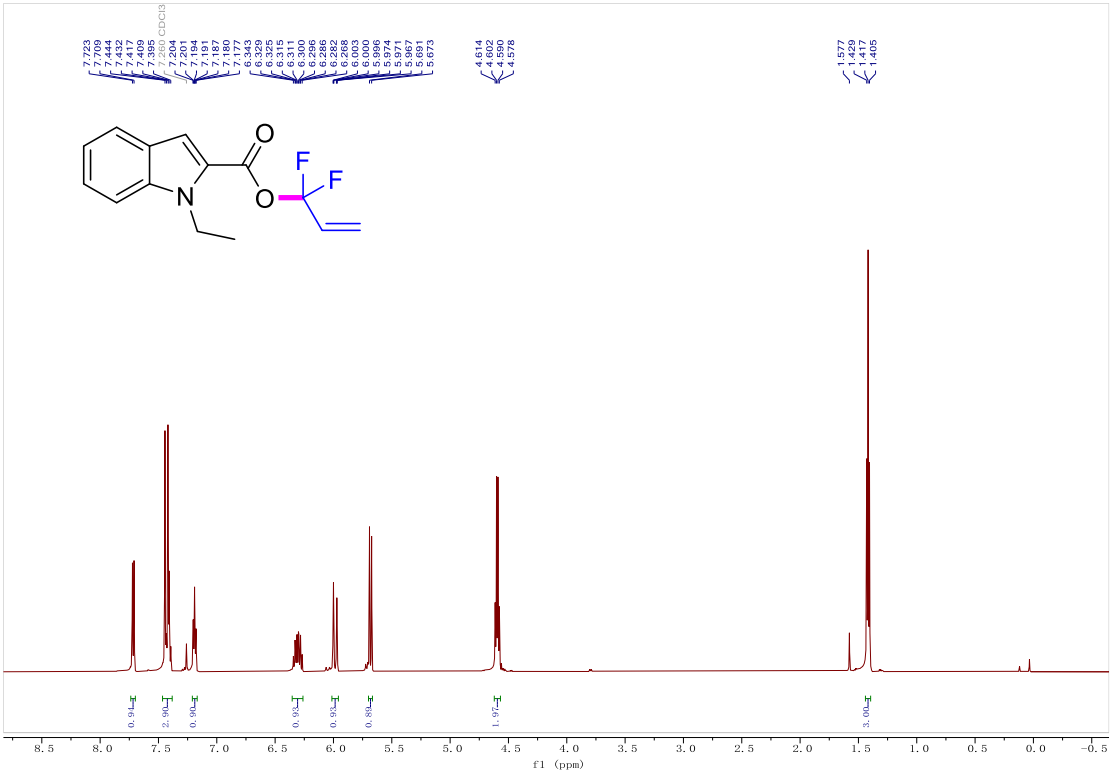


Figure S5. Compound 3b ^{13}C NMR (150 MHz, $CDCl_3$)

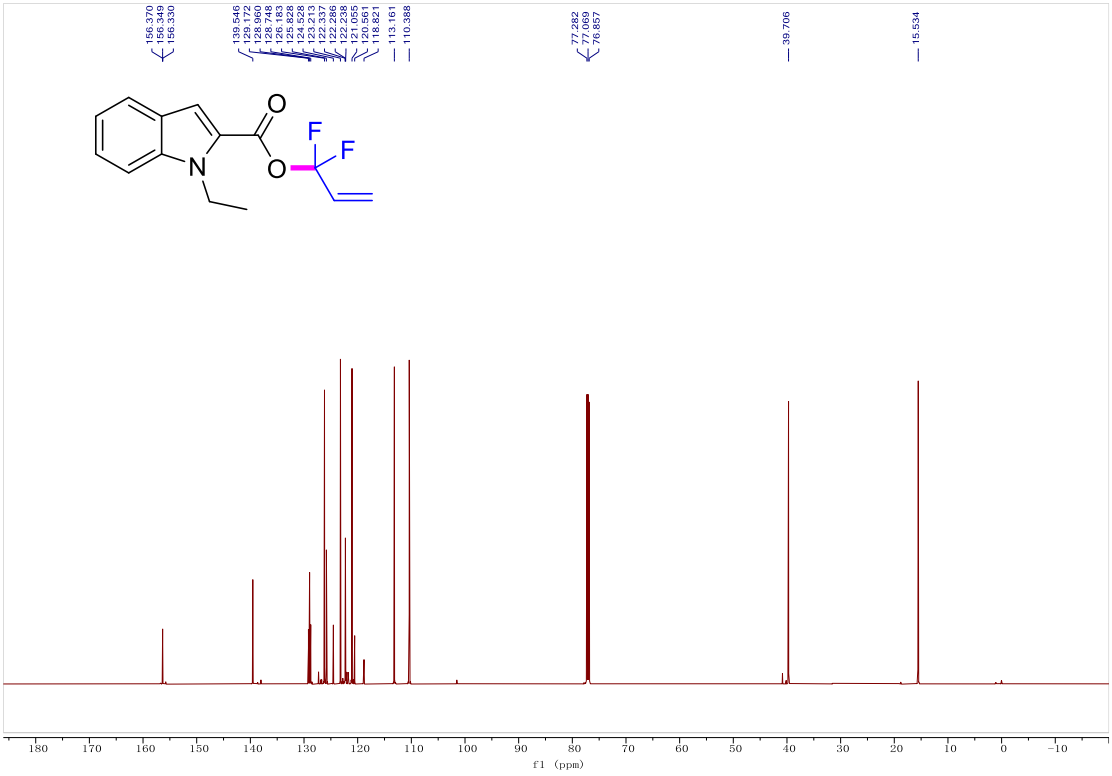


Figure S6. Compound 3b ^{19}F NMR (565 MHz, $CDCl_3$)

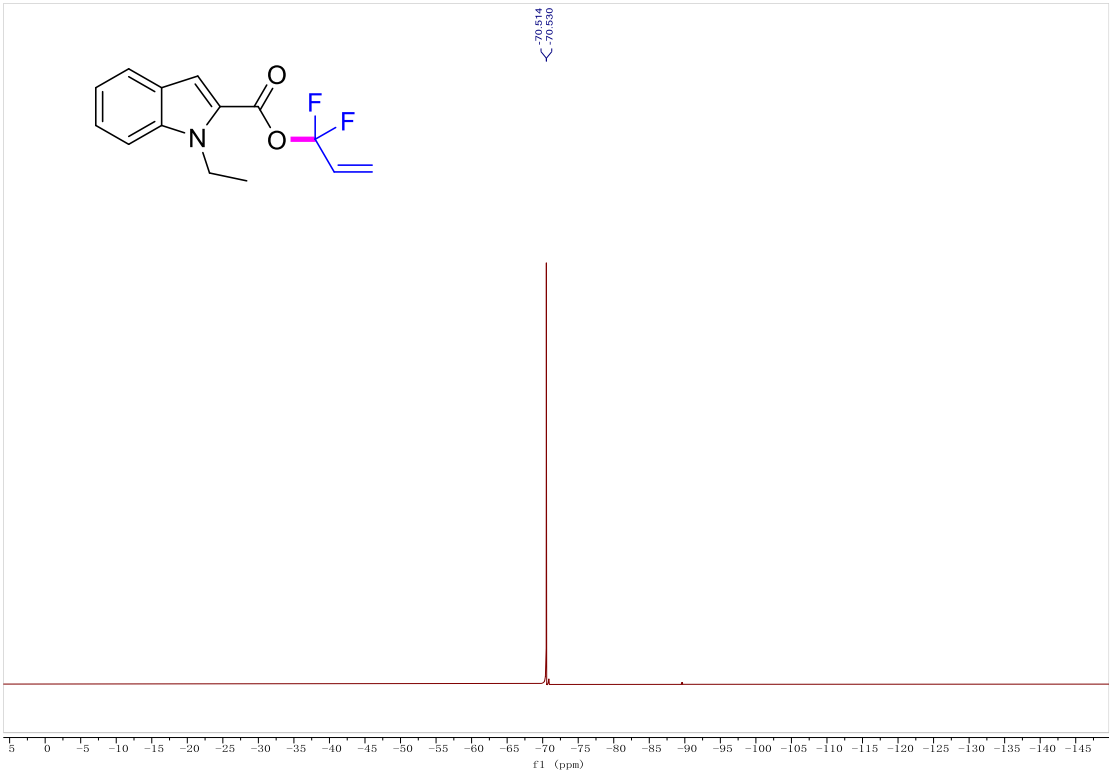


Figure S7. Compound 3c ^{1}H NMR (600 MHz, $CDCl_3$)

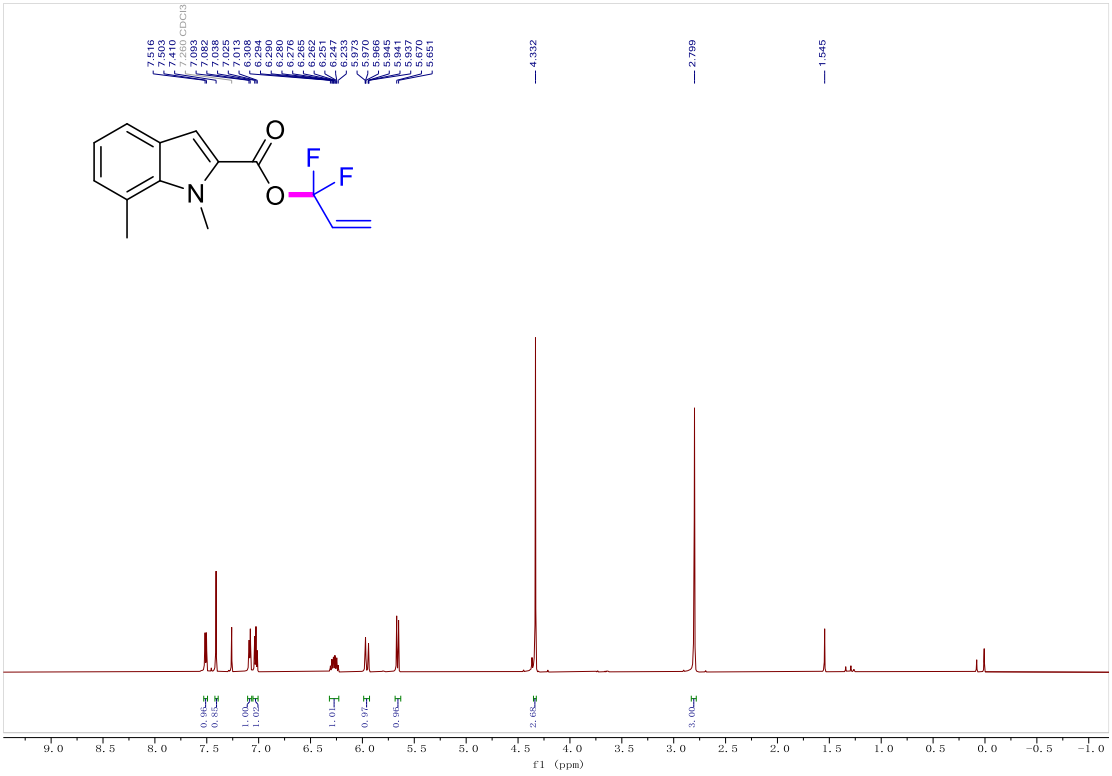


Figure S8. Compound 3c ^{13}C NMR (150 MHz, $CDCl_3$)

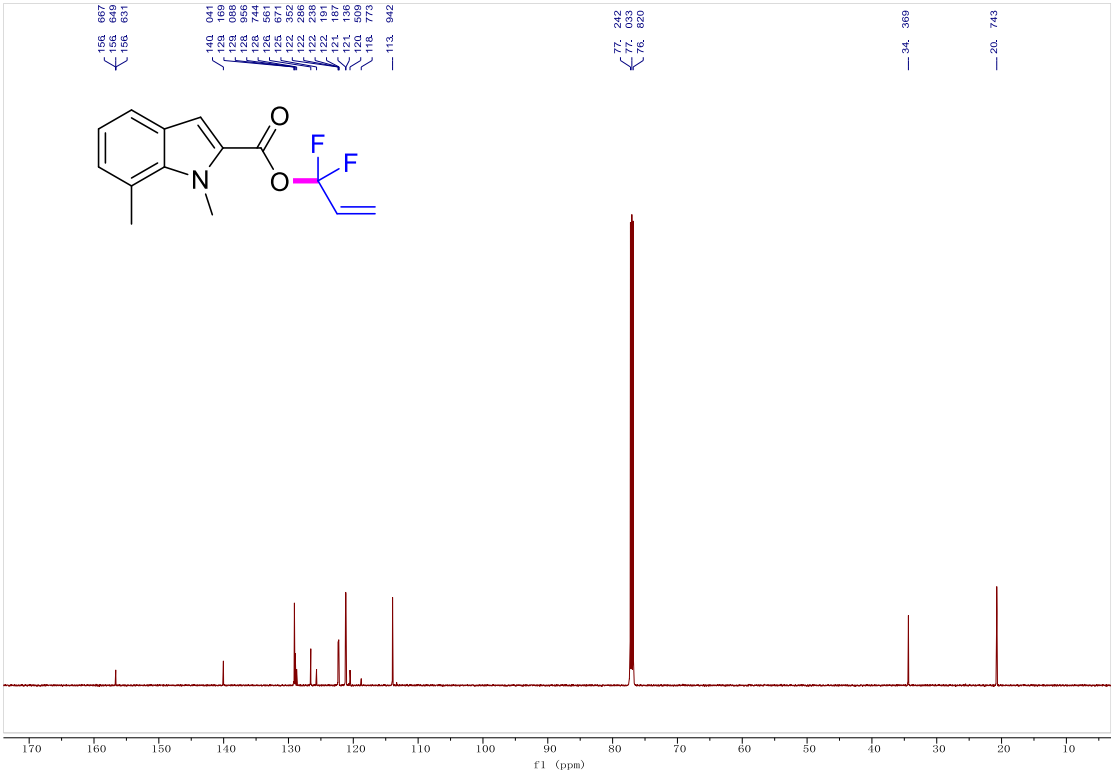


Figure S9. Compound 3c ^{19}F NMR (565 MHz, $CDCl_3$)

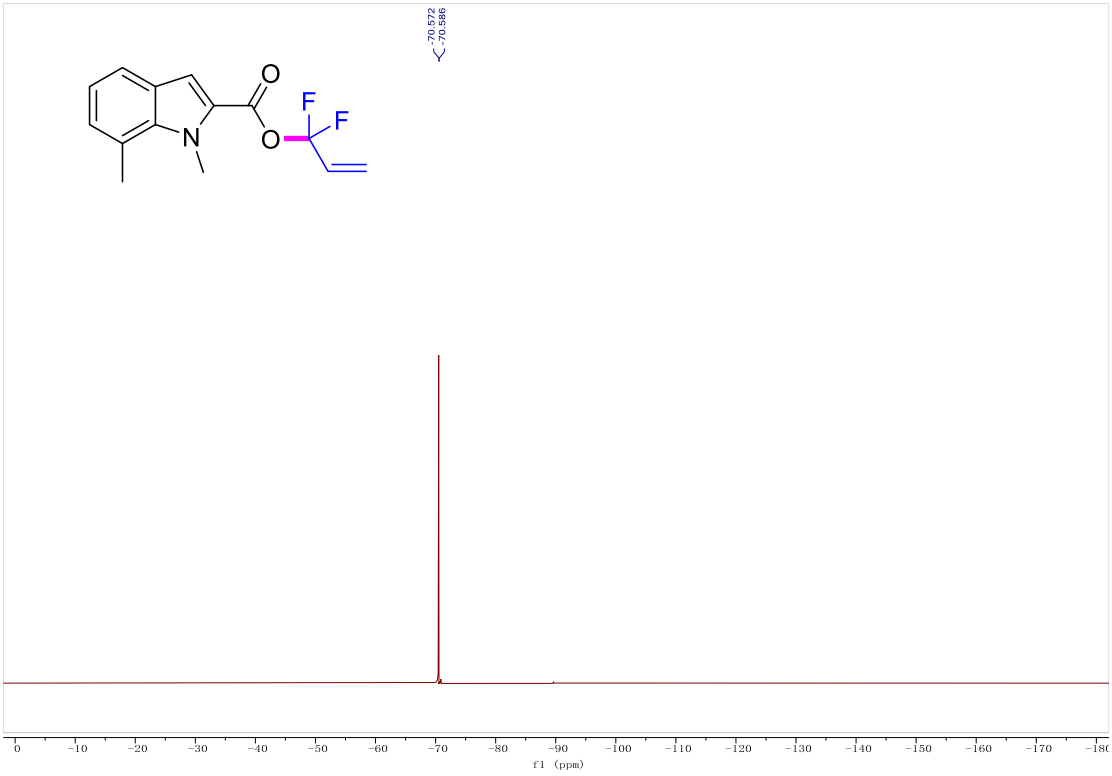


Figure S10. Compound 3d ^{1}H NMR (600 MHz, $CDCl_3$)

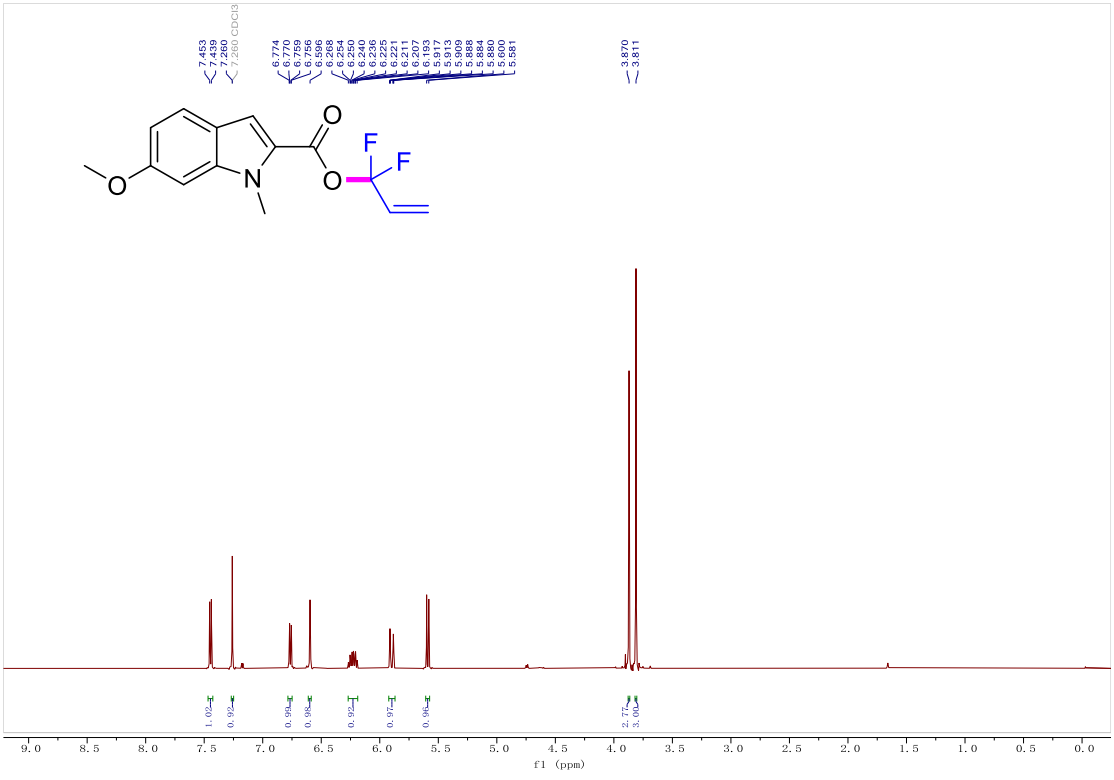


Figure S11. Compound 3d **^{13}C NMR (150 MHz, $CDCl_3$)**

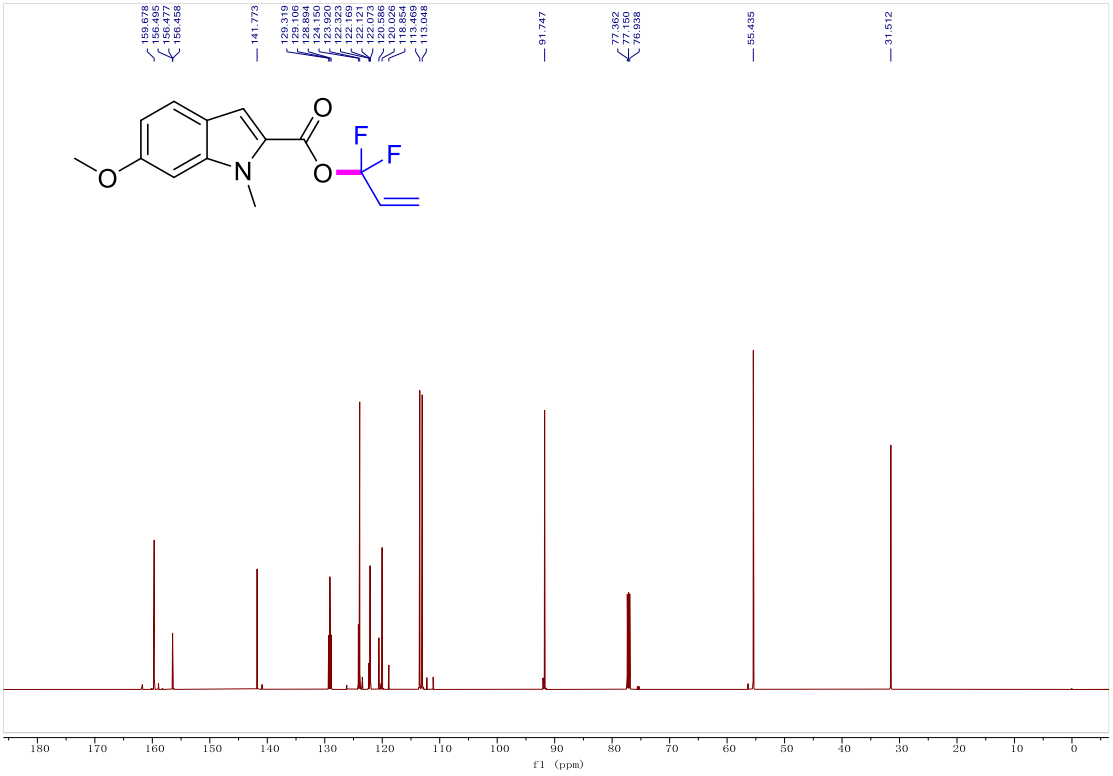


Figure S12. Compound 3d **^{19}F NMR (565 MHz, $CDCl_3$)**

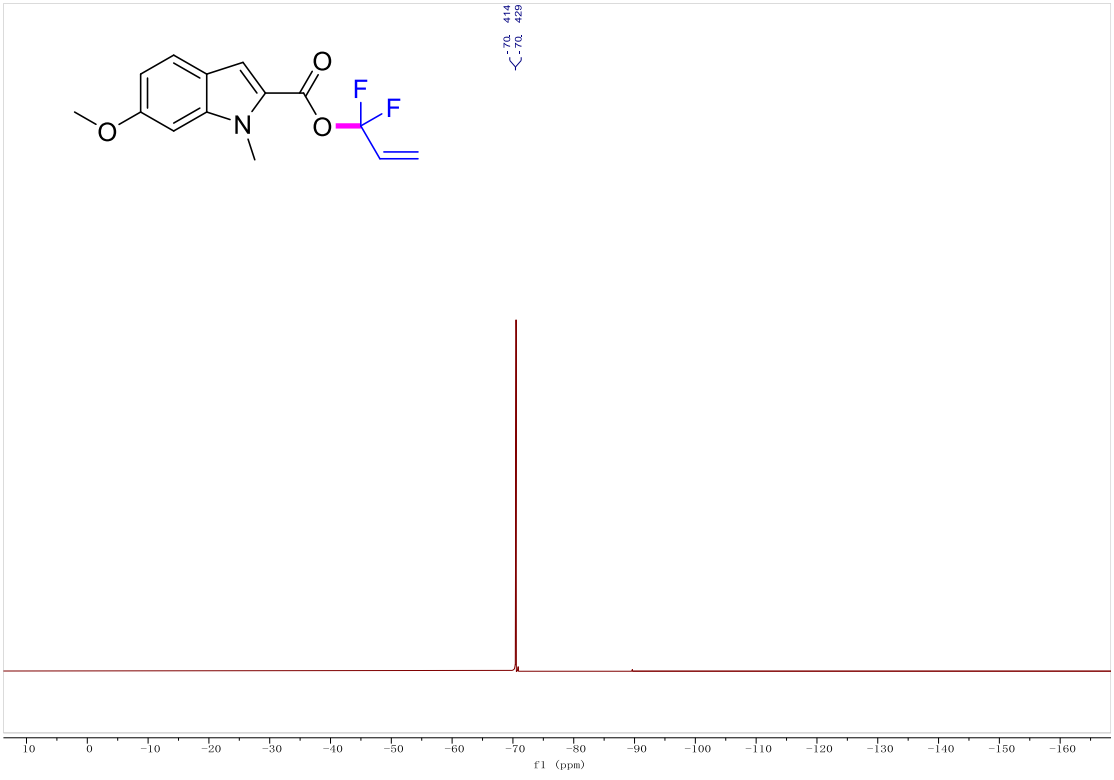


Figure S13. Compound 3e **^{1}H NMR (600 MHz, $CDCl_3$)**

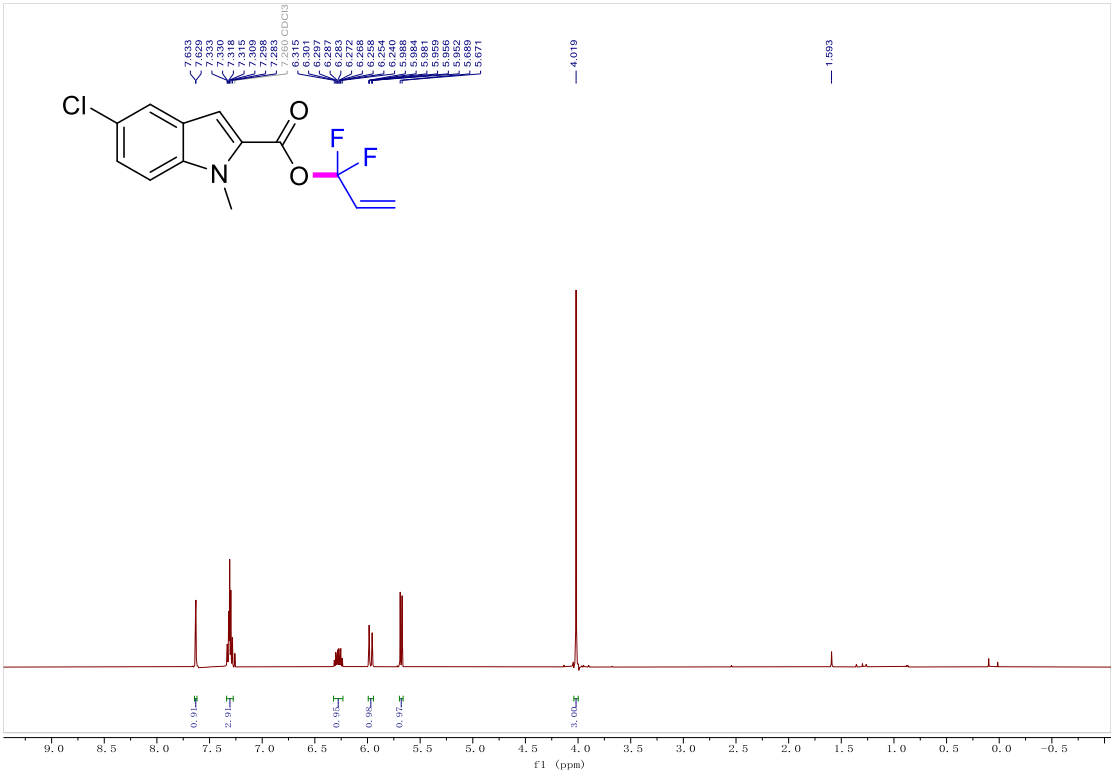


Figure S14. Compound 3e **^{13}C NMR (150 MHz, $CDCl_3$)**

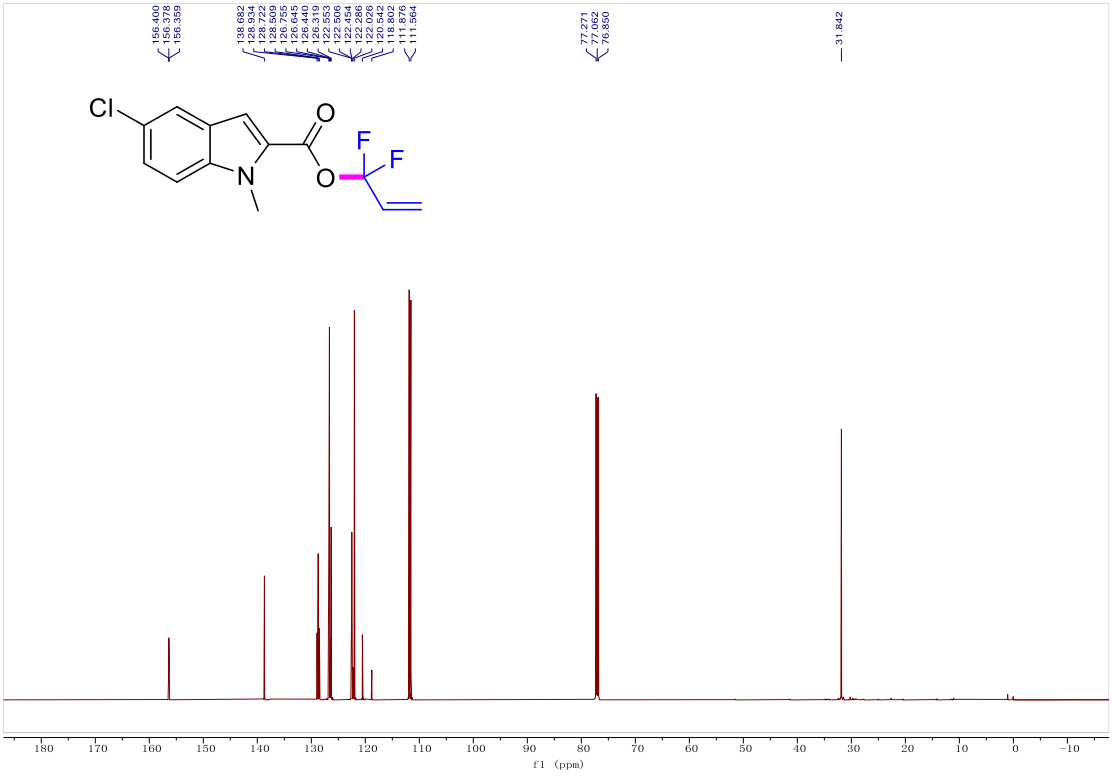


Figure S15. Compound 3e ^{19}F NMR (565 MHz, $CDCl_3$)

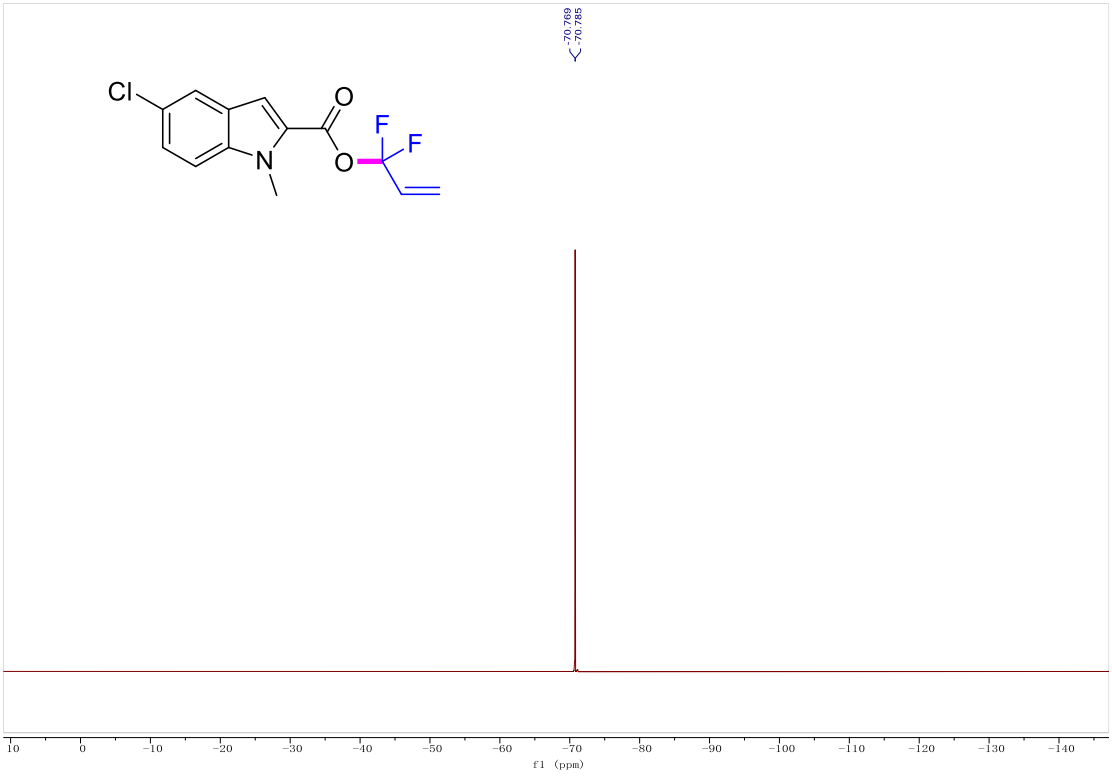


Figure S16. Compound 3f ^{1}H NMR (600 MHz, $CDCl_3$)

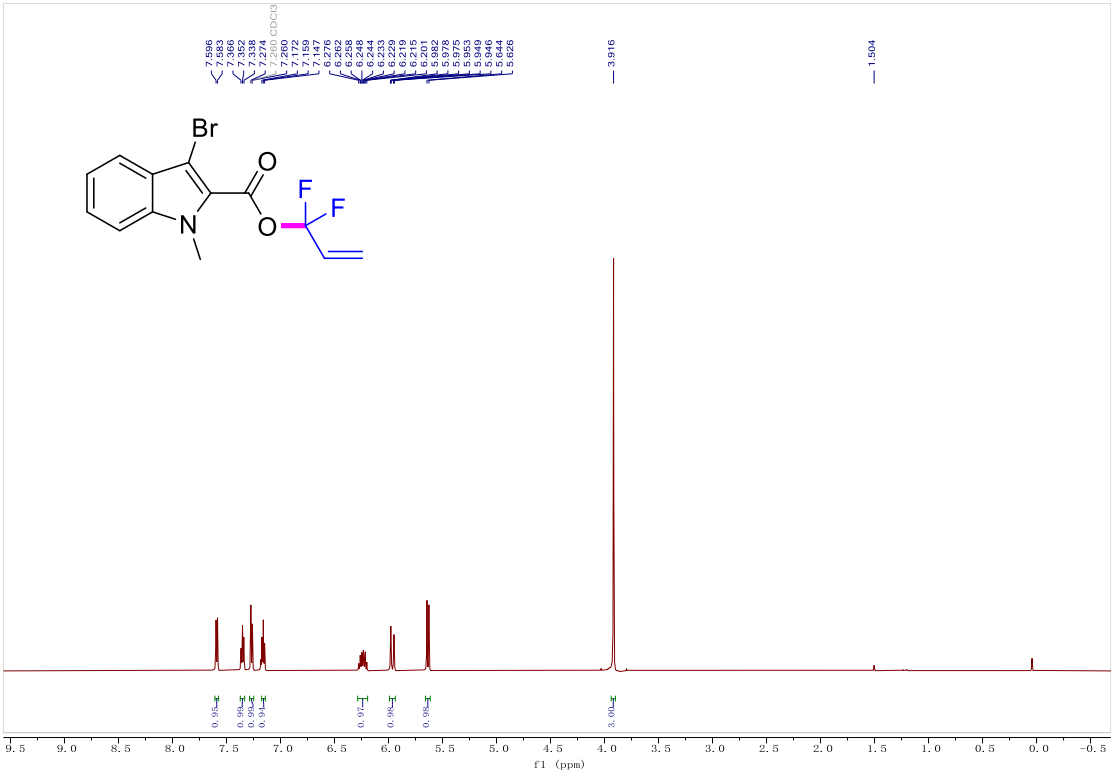


Figure S17. Compound 3f **^{13}C NMR (150 MHz, $CDCl_3$)**

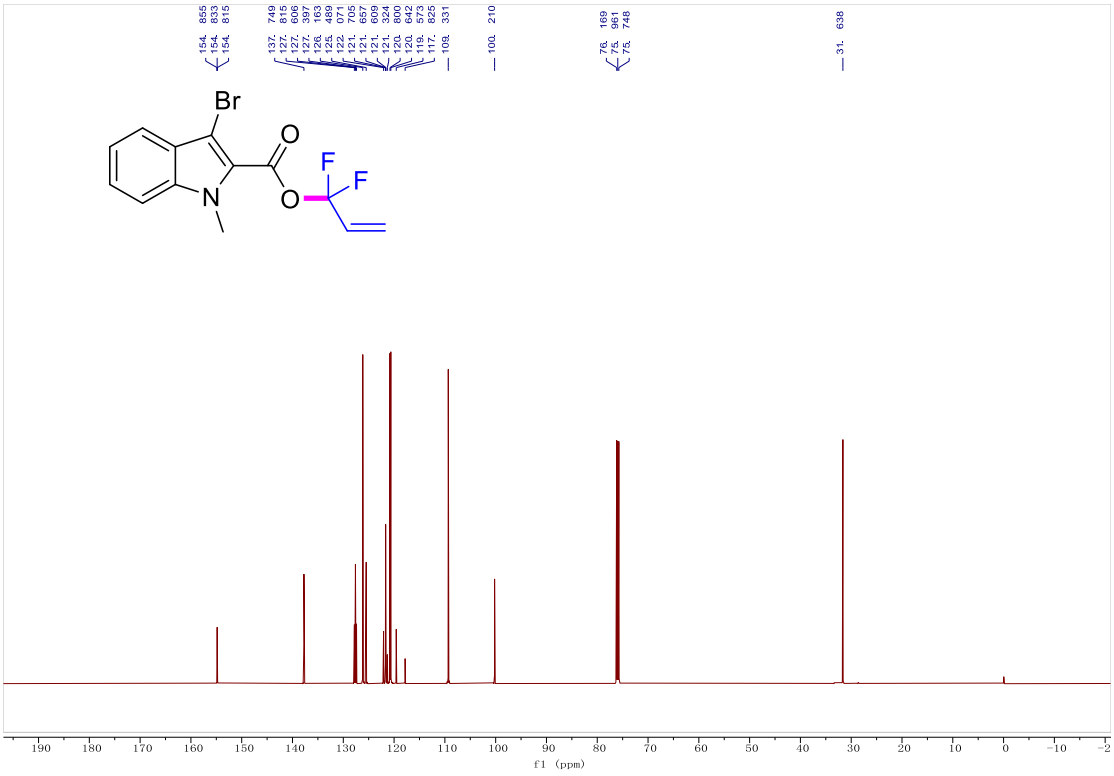


Figure S18. Compound 3f **^{19}F NMR (565 MHz, $CDCl_3$)**

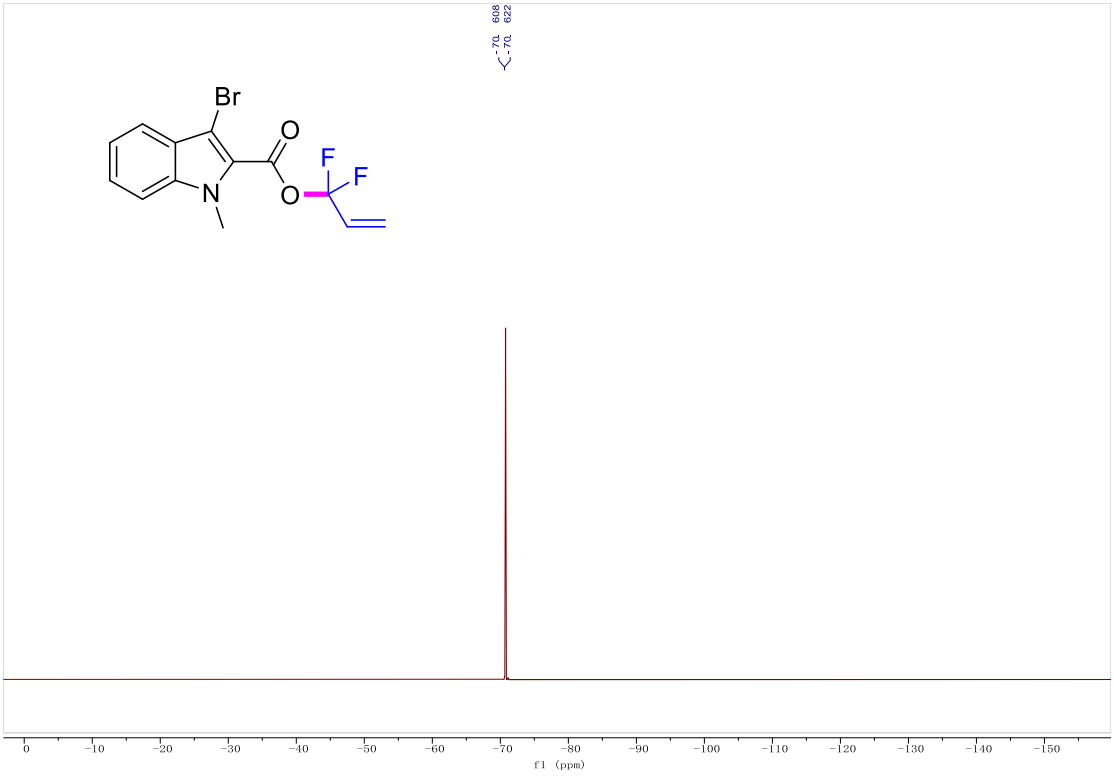


Figure S19. Compound 3g ^{1}H NMR (600 MHz, $CDCl_3$)

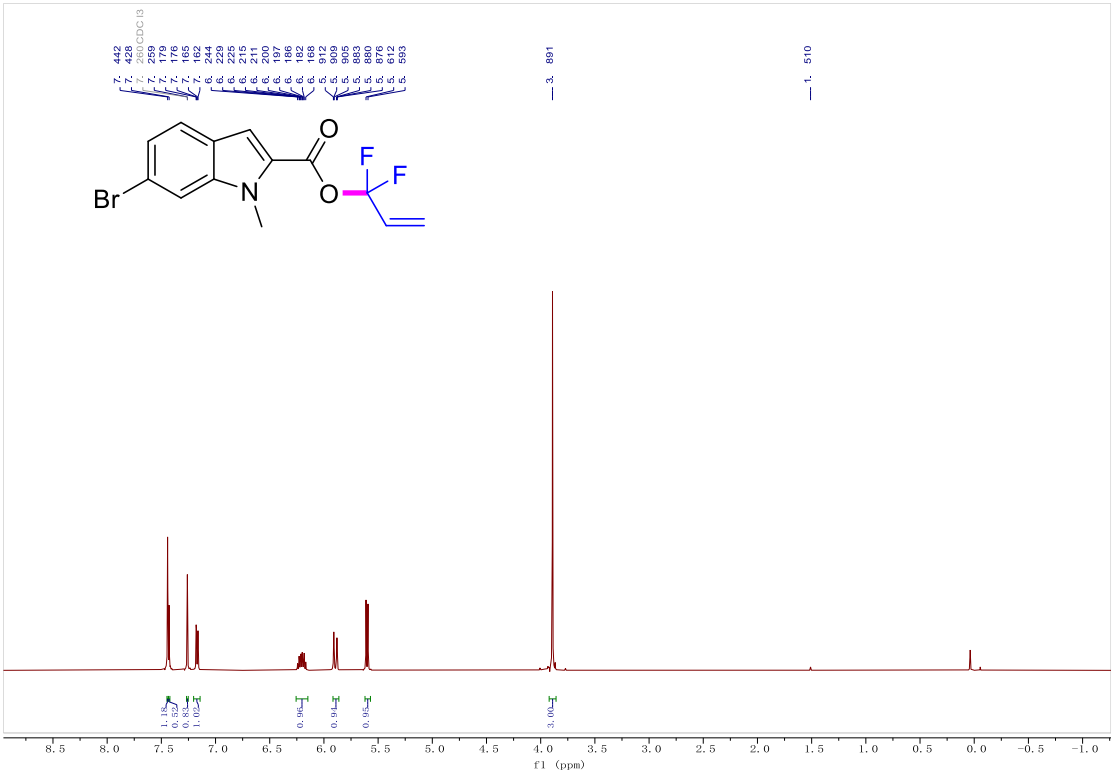


Figure S20. Compound 3g ^{13}C NMR (150 MHz, $CDCl_3$)

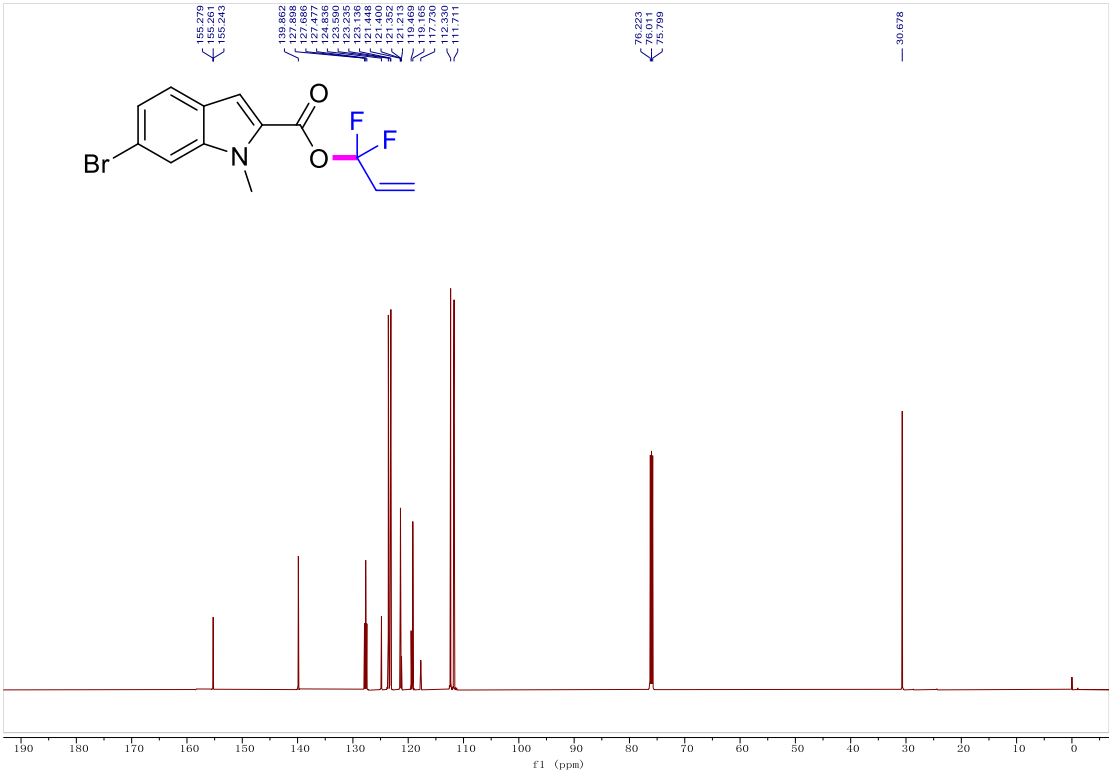


Figure S21. Compound 3g **^{19}F NMR (565 MHz, $CDCl_3$)**

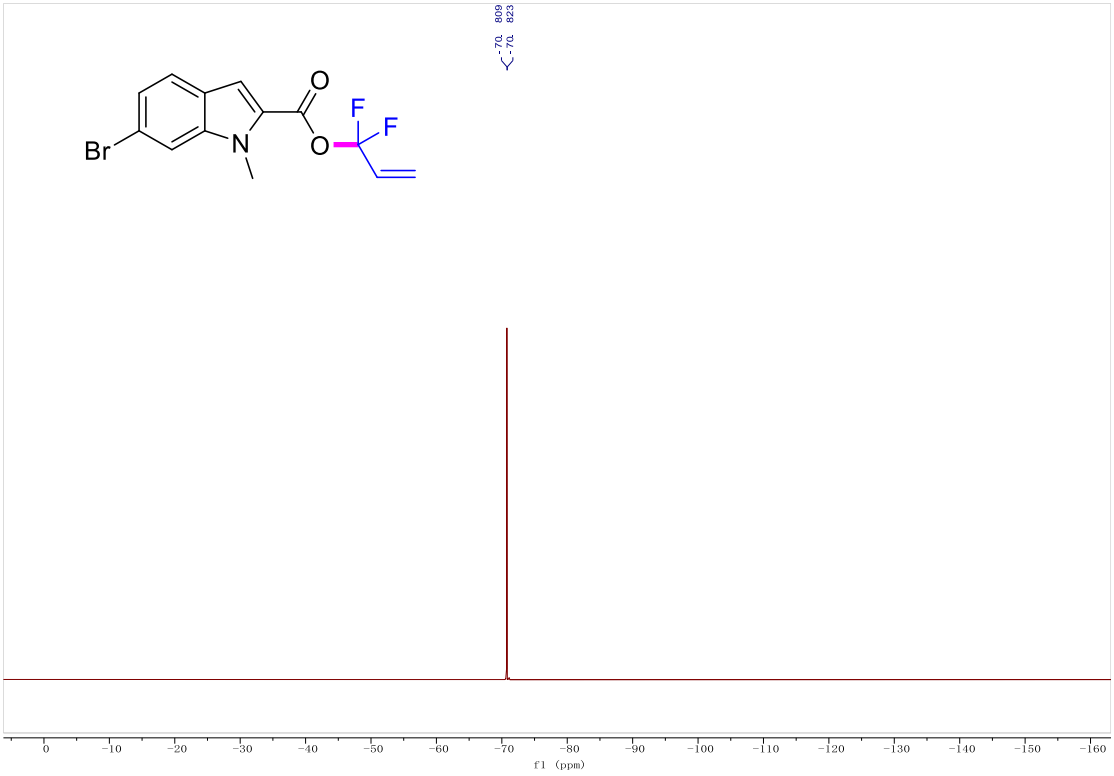


Figure S22. Compound 3h **^{1}H NMR (600 MHz, $CDCl_3$)**

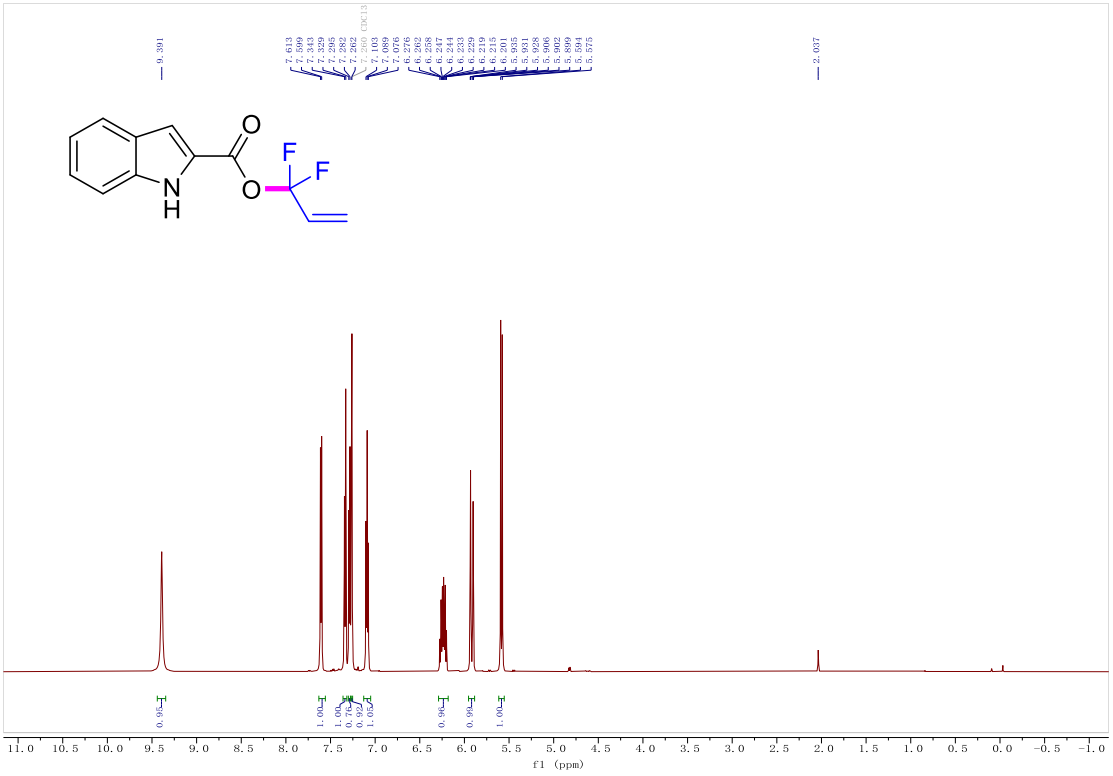


Figure S23. Compound 3h ^{13}C NMR (150 MHz, $CDCl_3$)

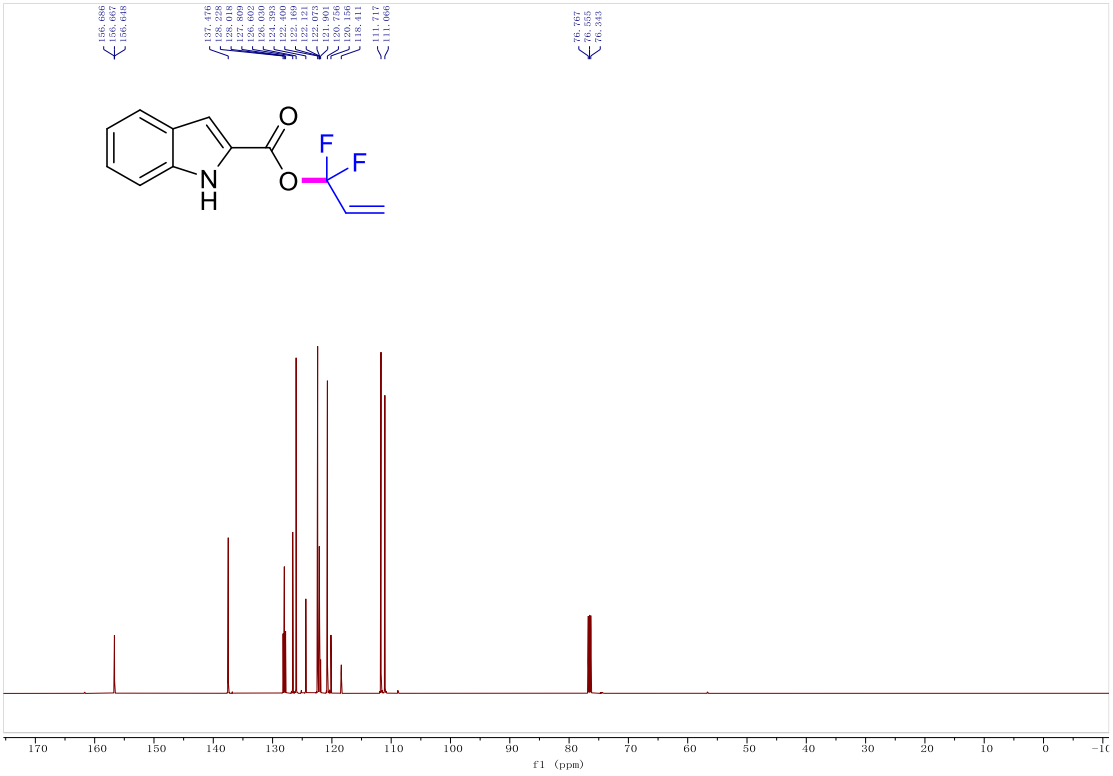


Figure S24. Compound 3h ^{19}F NMR (565 MHz, $CDCl_3$)

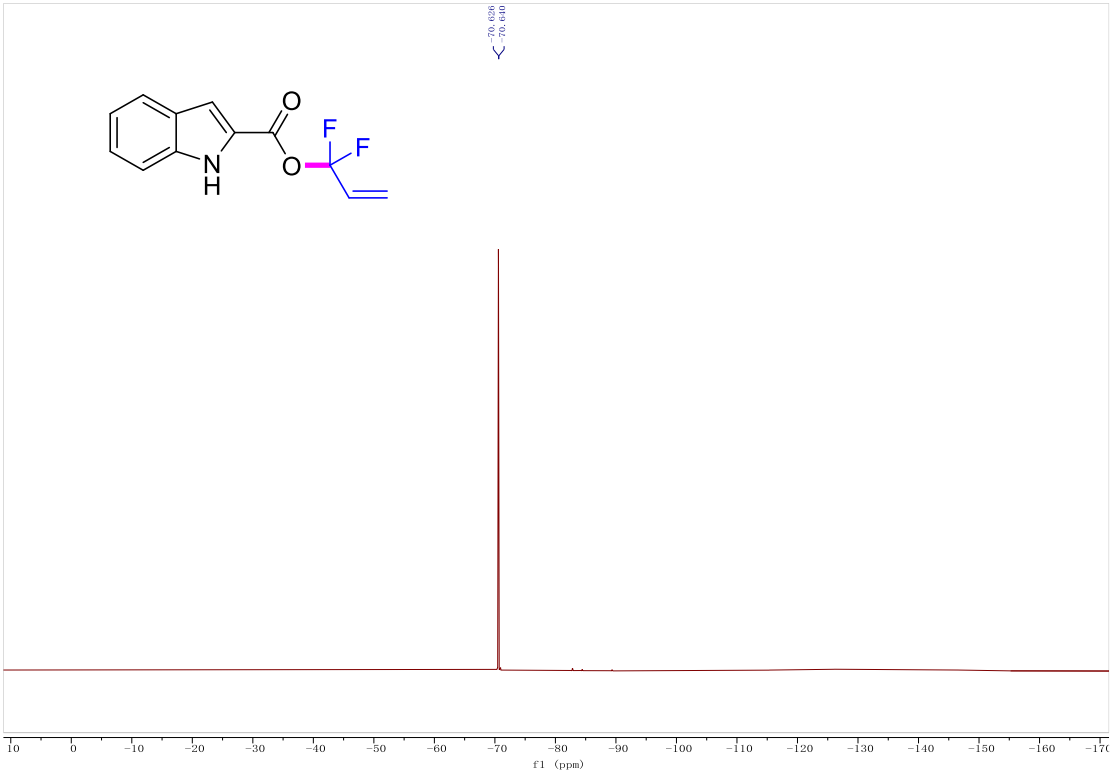


Figure S25. Compound 3i **^{1}H NMR (600 MHz, $CDCl_3$)**

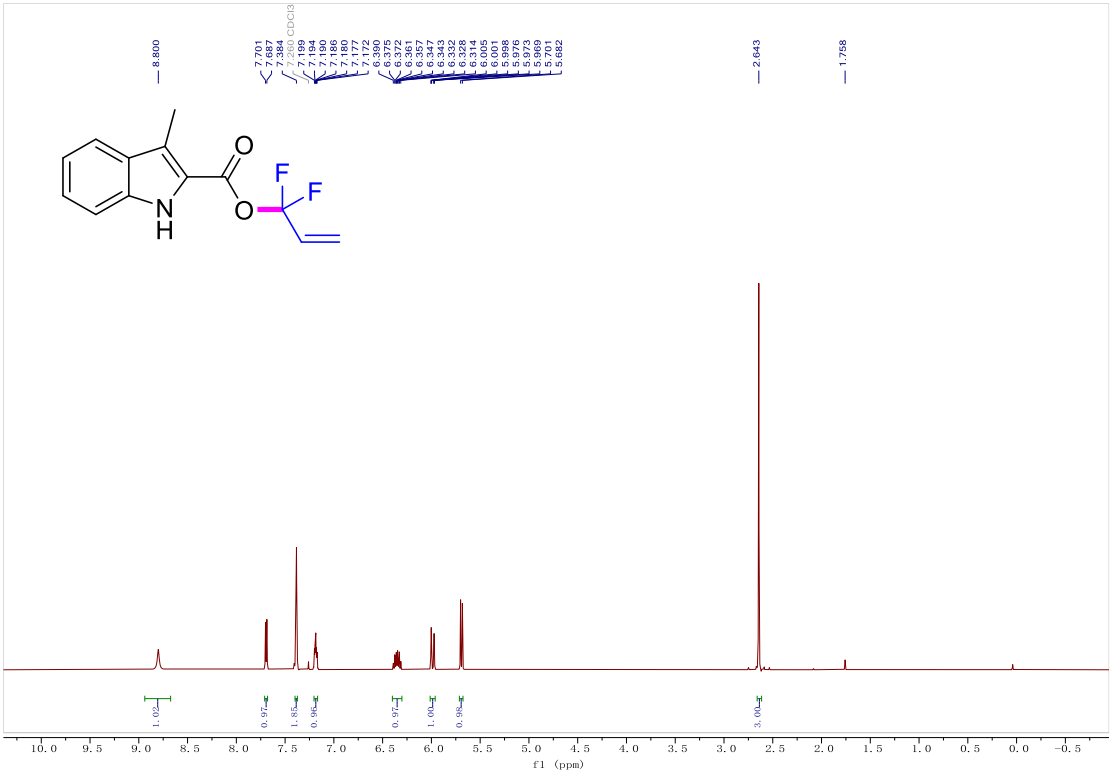


Figure S26. Compound 3i **^{13}C NMR (150 MHz, $CDCl_3$)**

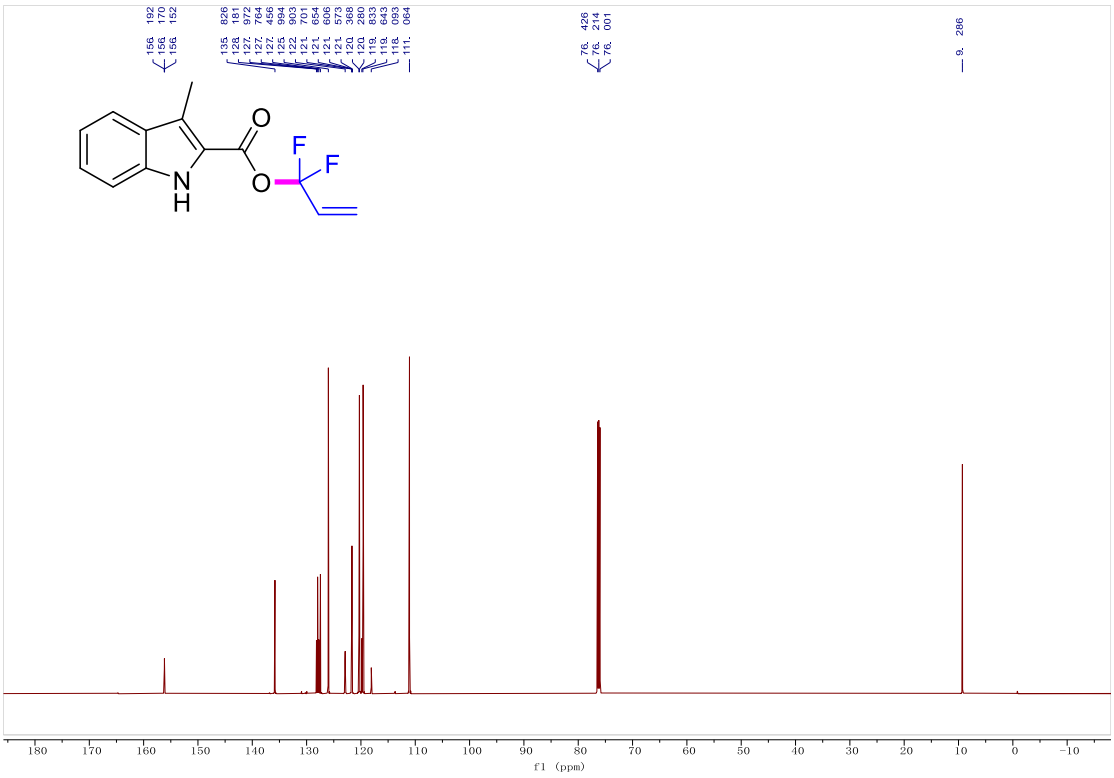


Figure S27. Compound 3i **^{19}F NMR (565 MHz, $CDCl_3$)**

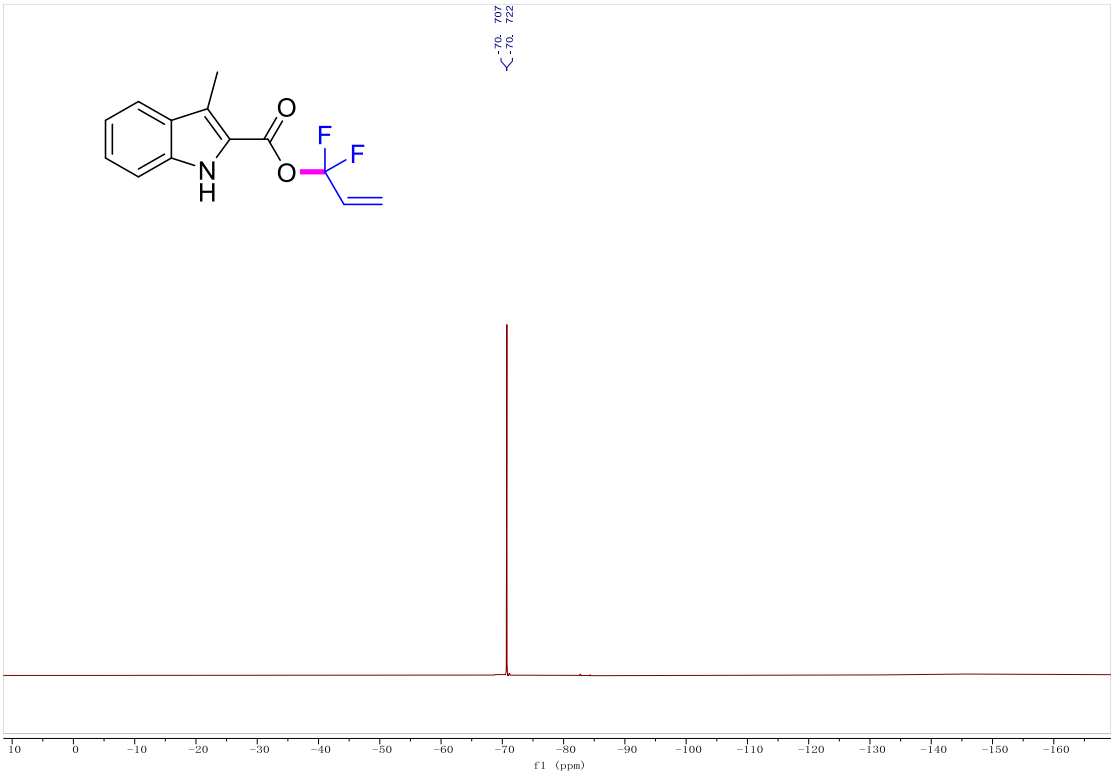


Figure S28. Compound 3j **^{1}H NMR (600 MHz, $CDCl_3$)**

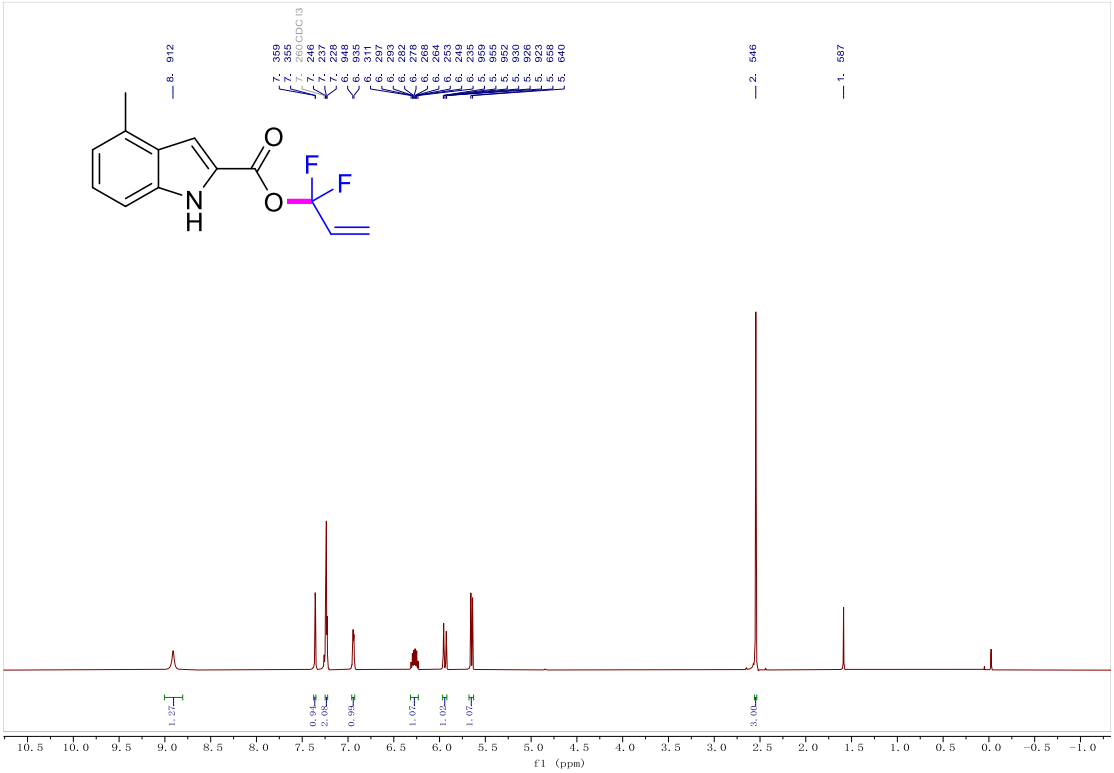


Figure S29. Compound 3j **^{13}C NMR (150 MHz, $CDCl_3$)**

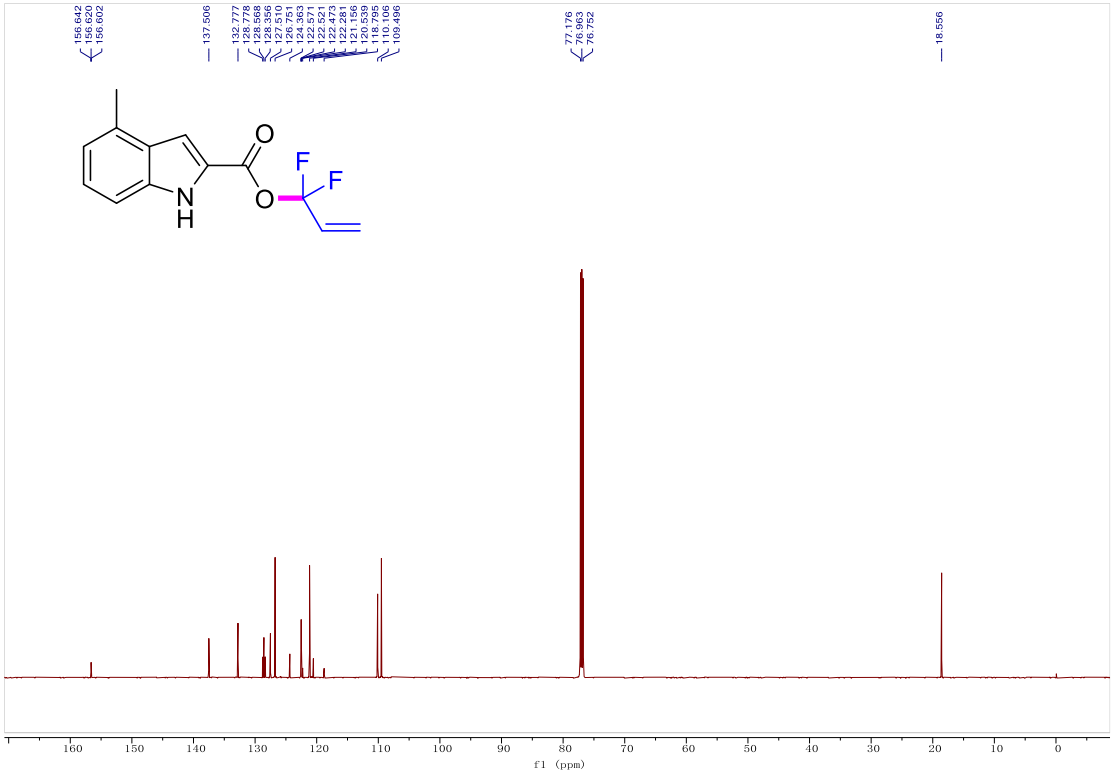


Figure S30. Compound 3j **^{19}F NMR (565 MHz, $CDCl_3$)**

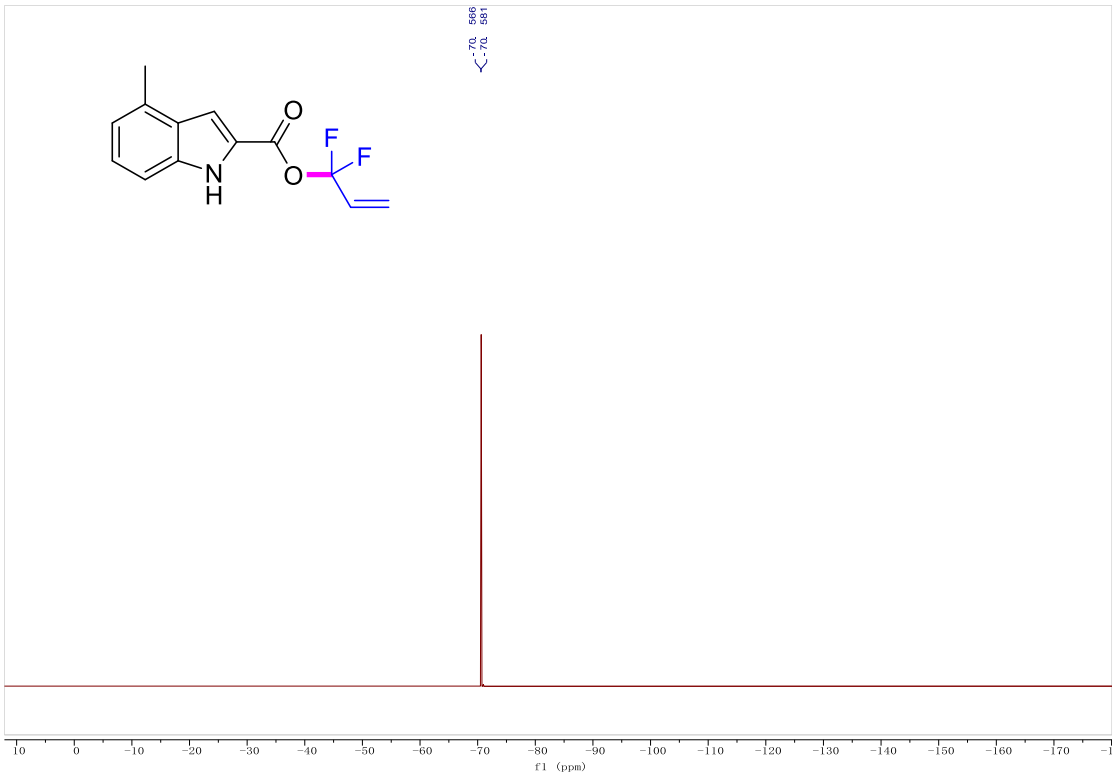


Figure S31. Compound 3k ^{1}H NMR (600 MHz, $CDCl_3$)

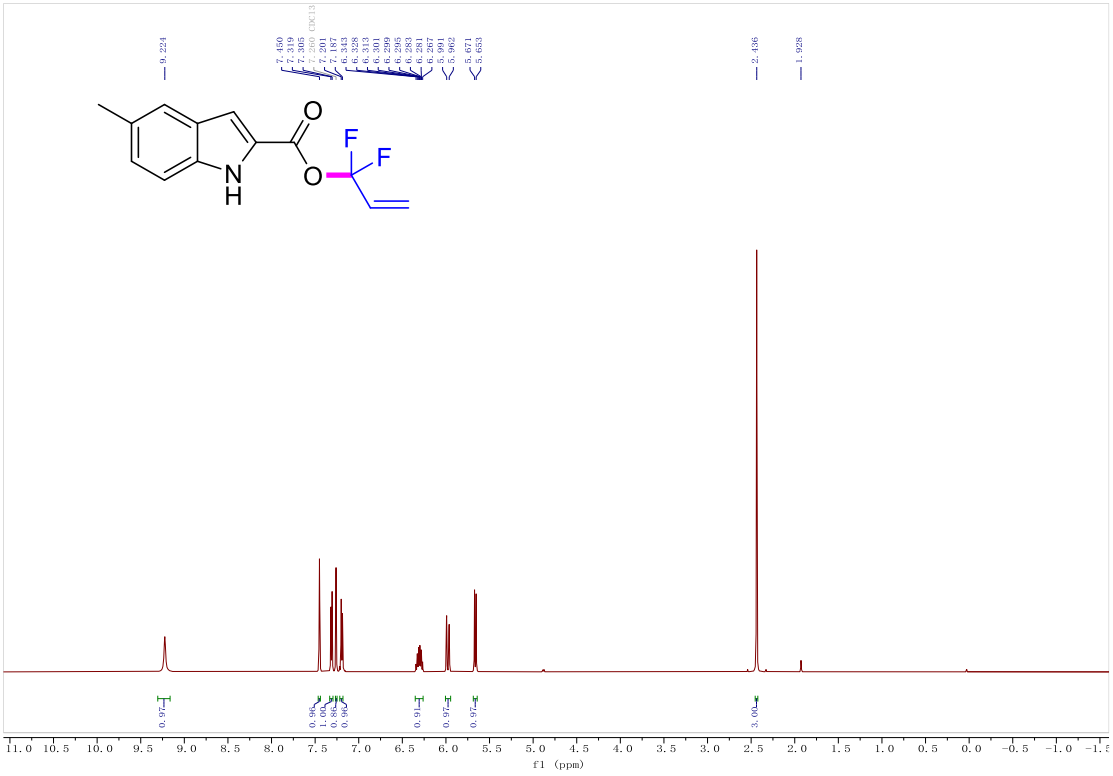


Figure S32. Compound 3k ^{13}C NMR (150 MHz, $CDCl_3$)

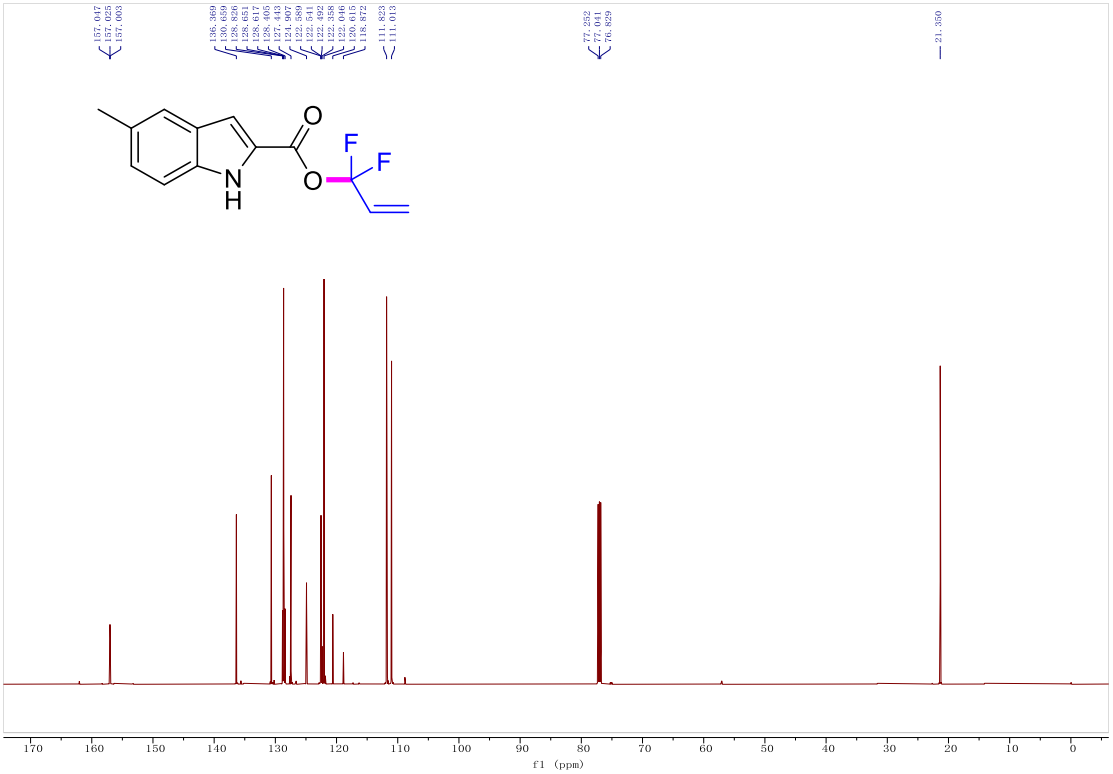


Figure S33. Compound 3k **^{19}F NMR (565 MHz, $CDCl_3$)**

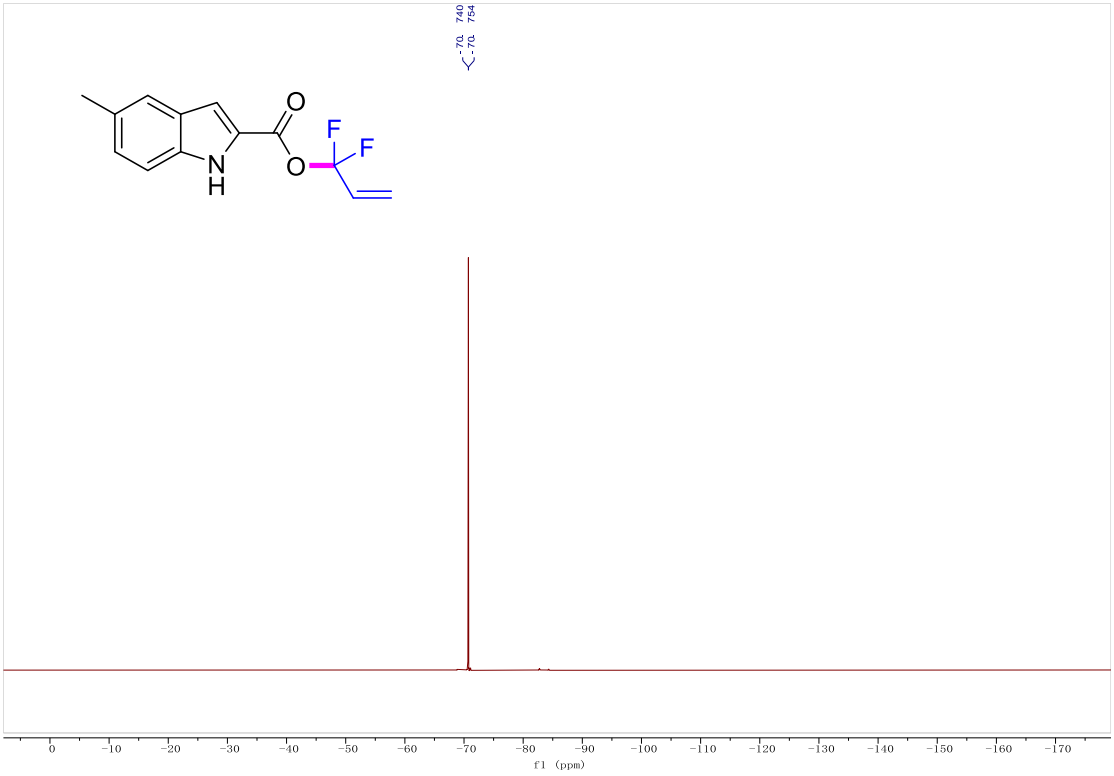


Figure S34. Compound 31 **^{1}H NMR (600 MHz, $CDCl_3$)**

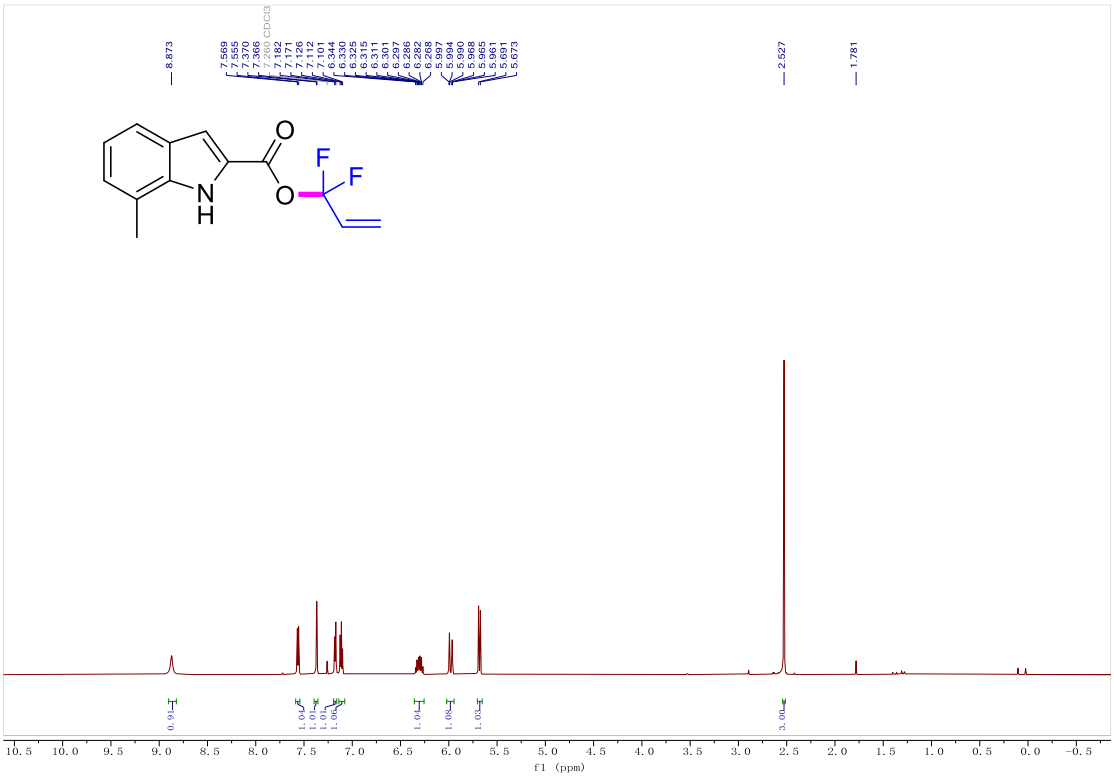


Figure S35. Compound 31 **^{13}C NMR (150 MHz, $CDCl_3$)**

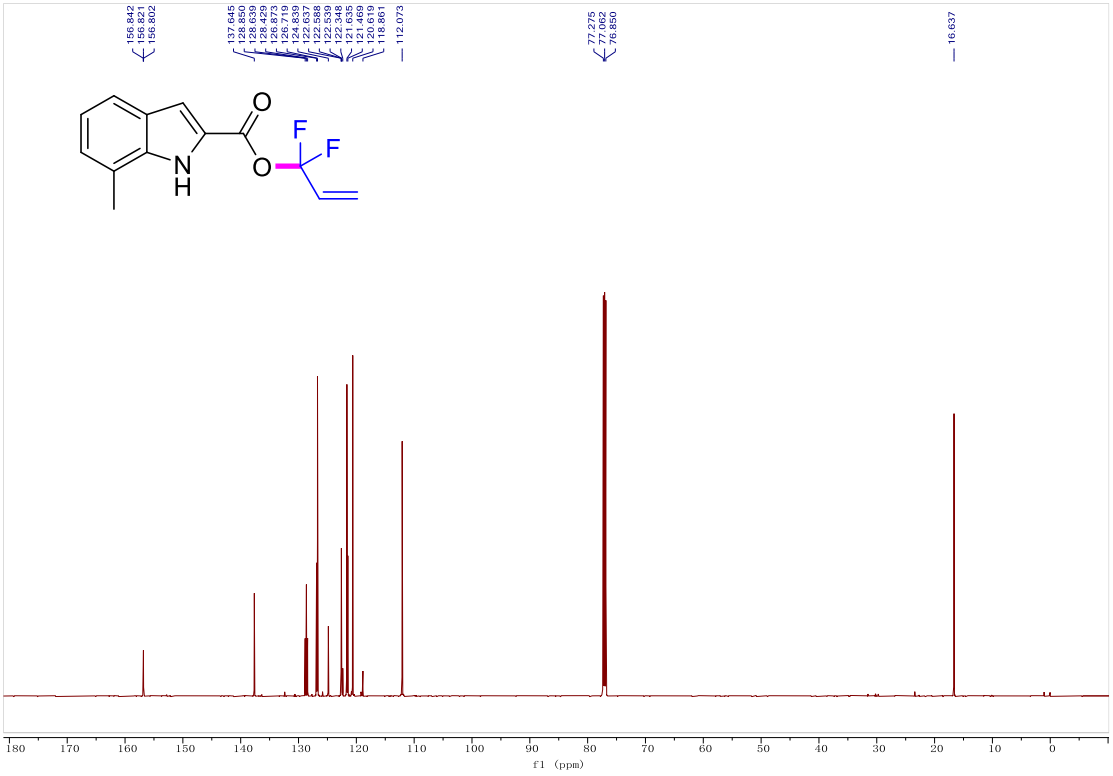


Figure S36. Compound 31 **^{19}F NMR (565 MHz, $CDCl_3$)**

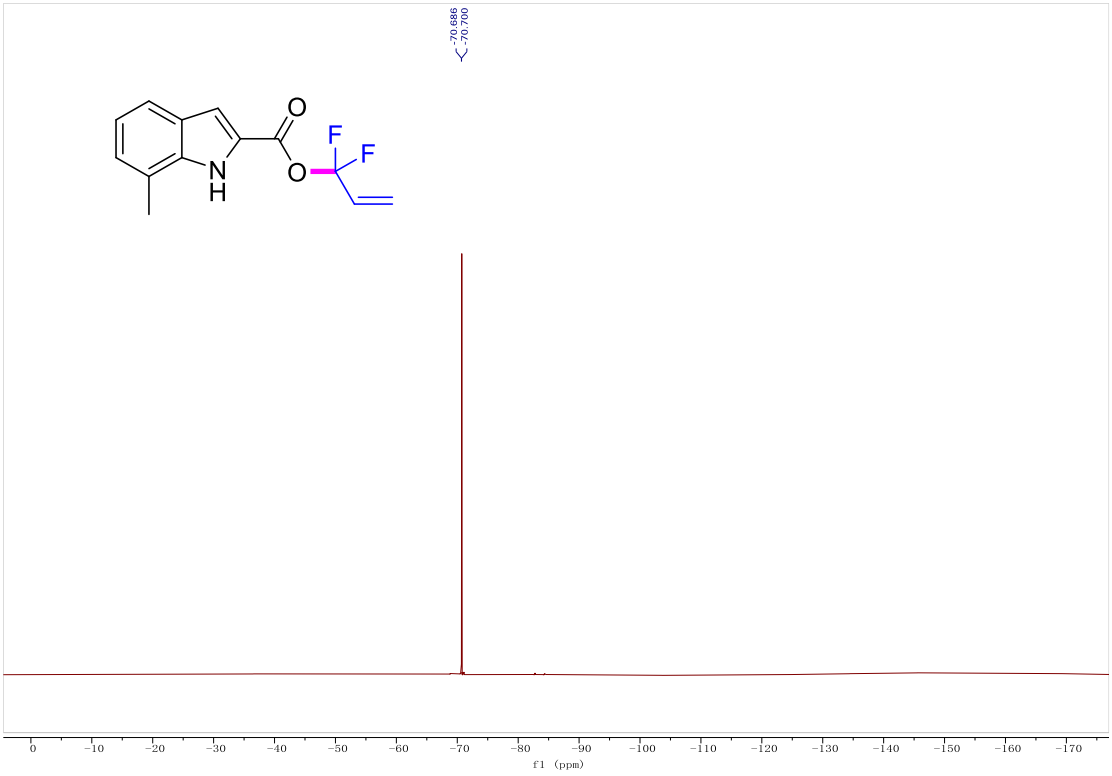


Figure S37. Compound 3m **^{1}H NMR (600 MHz, $CDCl_3$)**

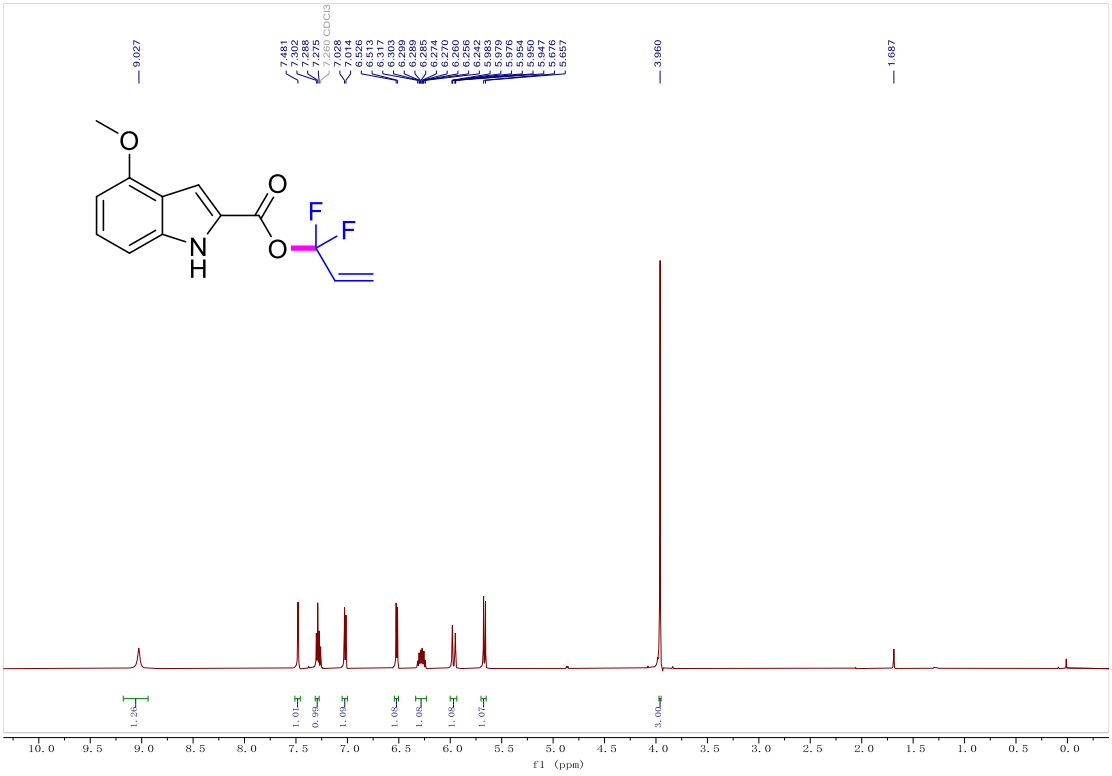


Figure S38. Compound 3m **^{13}C NMR (150 MHz, $CDCl_3$)**

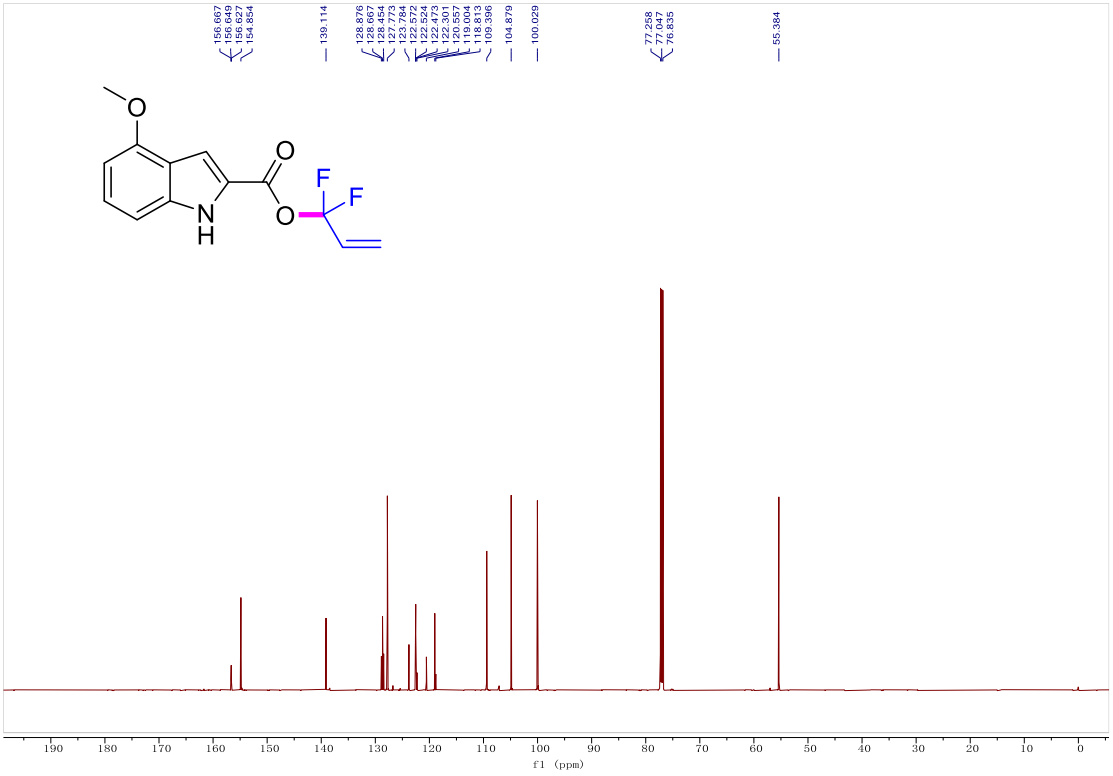


Figure S39. Compound 3m ^{19}F NMR (565 MHz, $CDCl_3$)

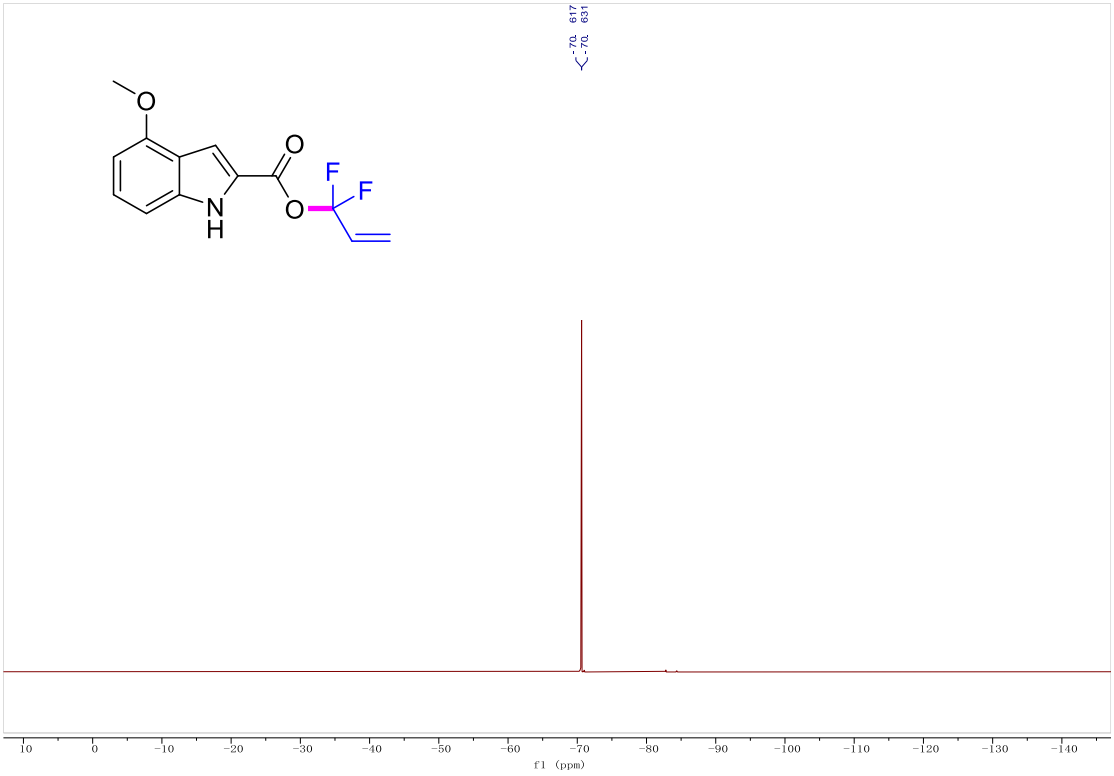


Figure S40. Compound 3n ^{1}H NMR (600 MHz, $CDCl_3$)

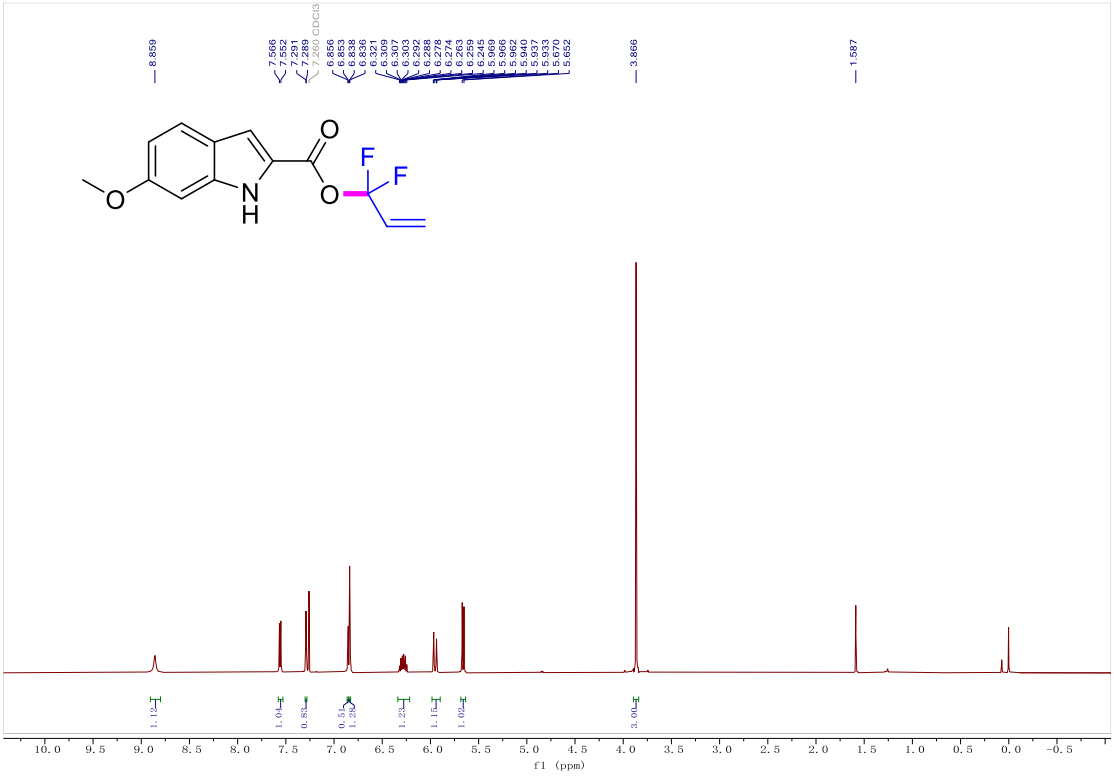


Figure S41. Compound 3n ^{13}C NMR (150 MHz, $CDCl_3$)

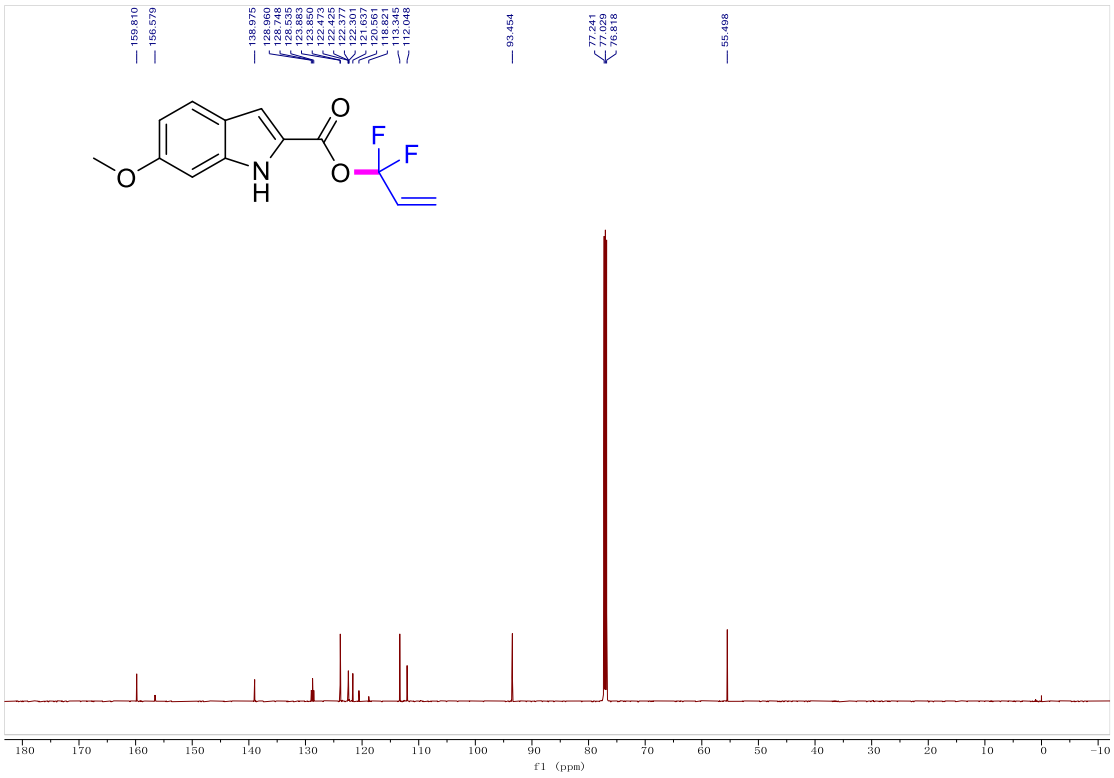


Figure S42. Compound 3n ^{19}F NMR (565 MHz, $CDCl_3$)

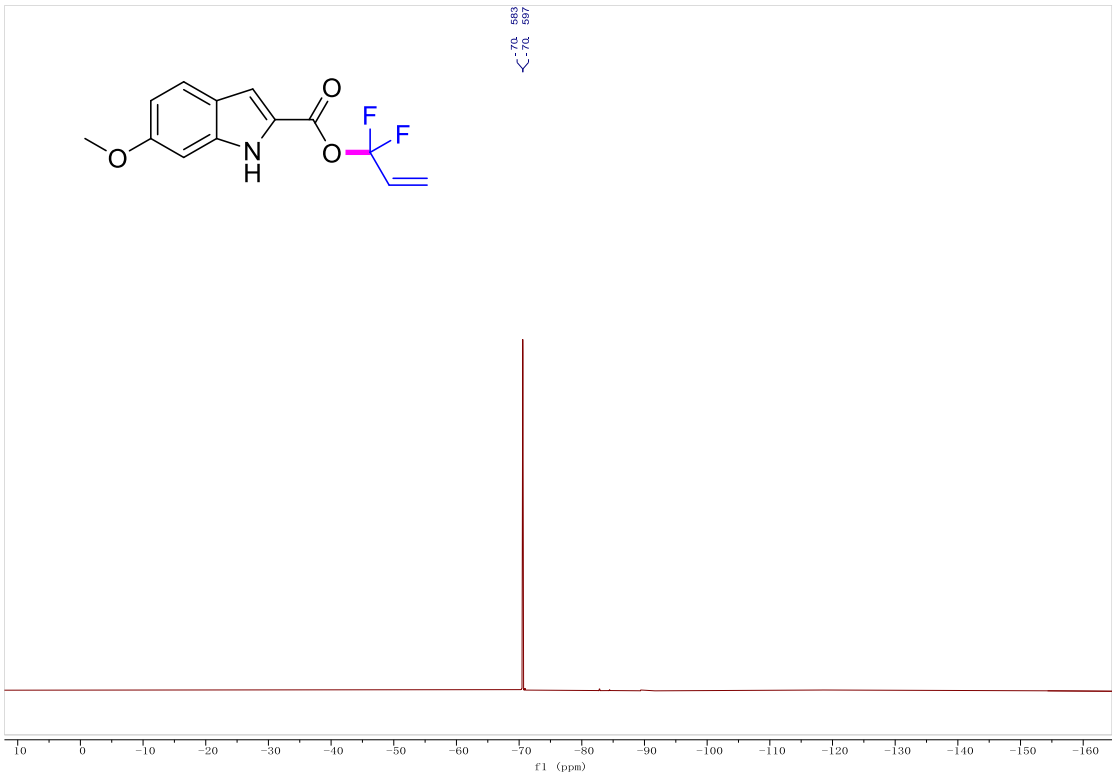


Figure S43. Compound 3o ^{1}H NMR (600 MHz, $CDCl_3$)

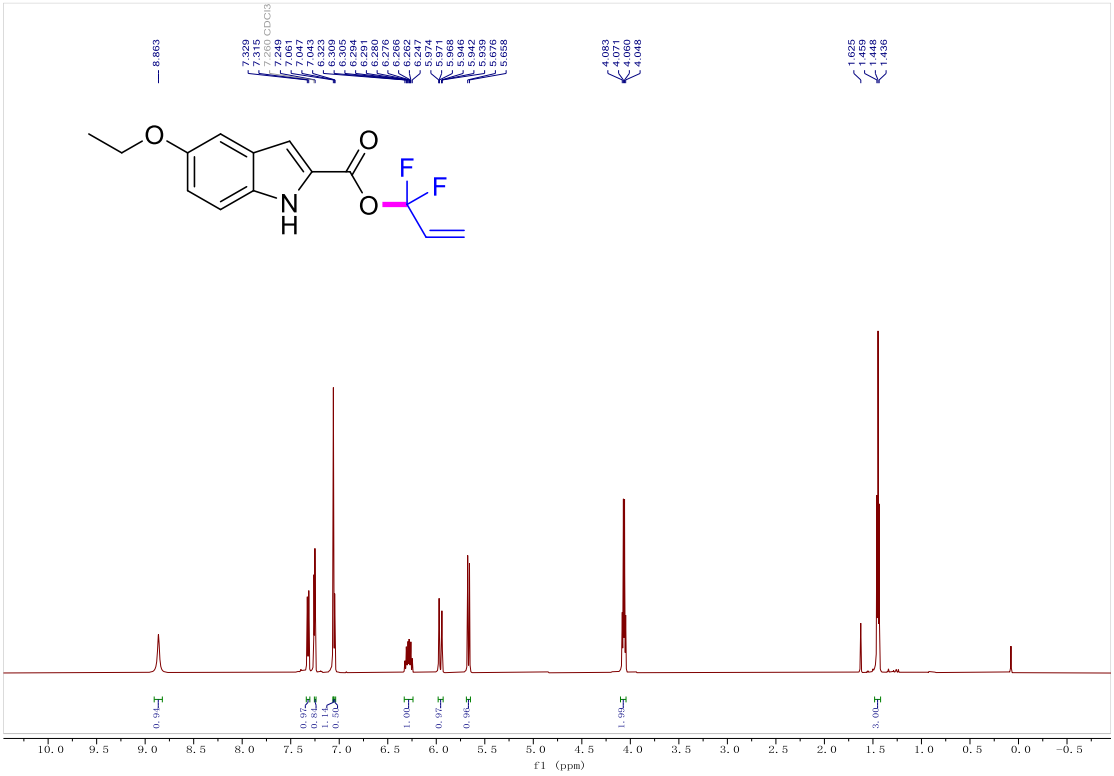


Figure S44. Compound 3o ^{13}C NMR (150 MHz, $CDCl_3$)

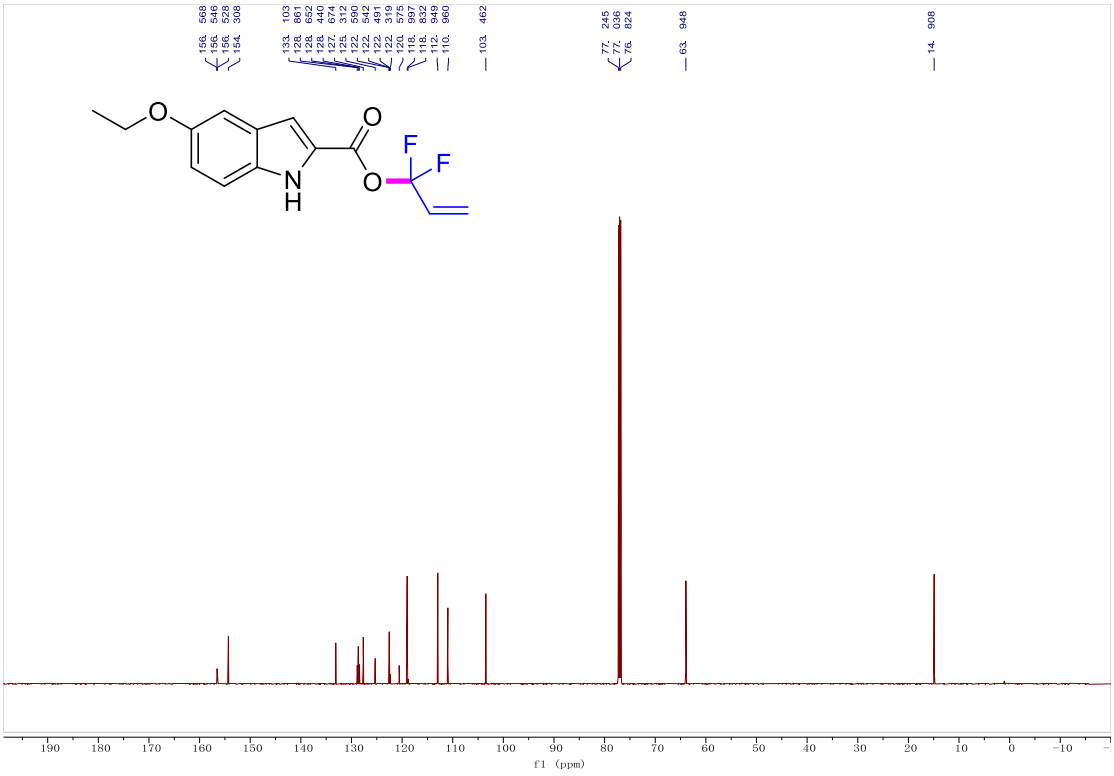


Figure S45. Compound 3o ^{19}F NMR (565 MHz, $CDCl_3$)

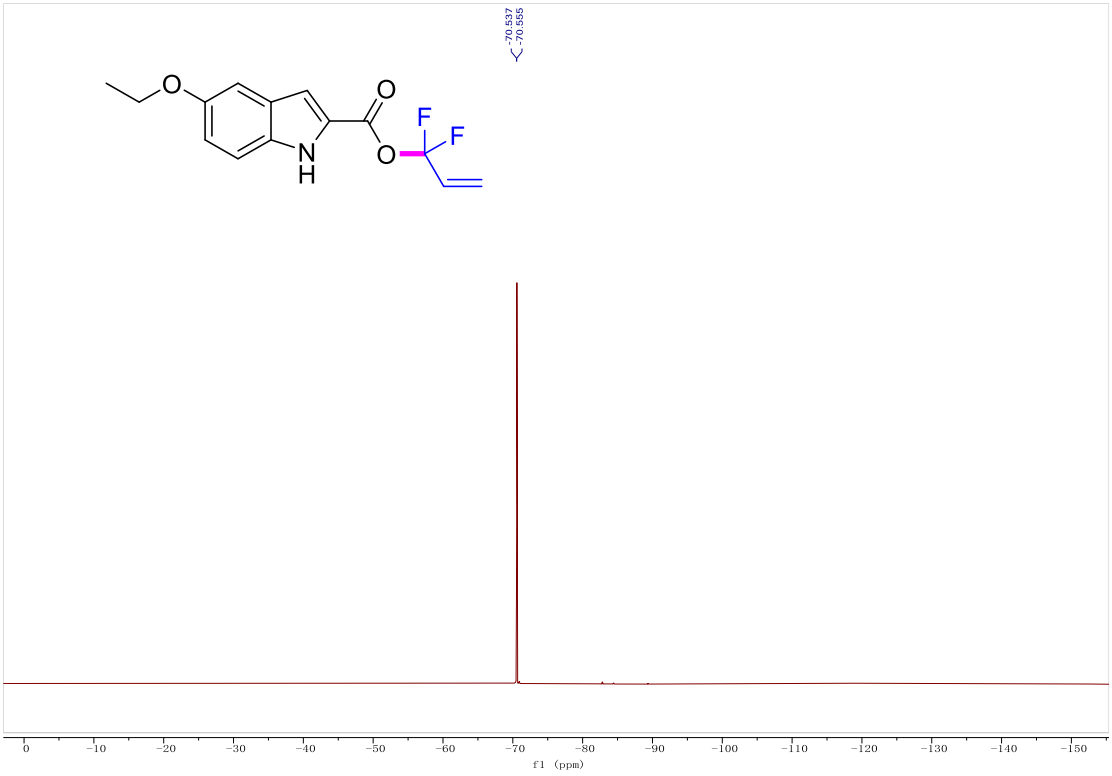


Figure S46. Compound 3p ^{1}H NMR (600 MHz, $CDCl_3$)

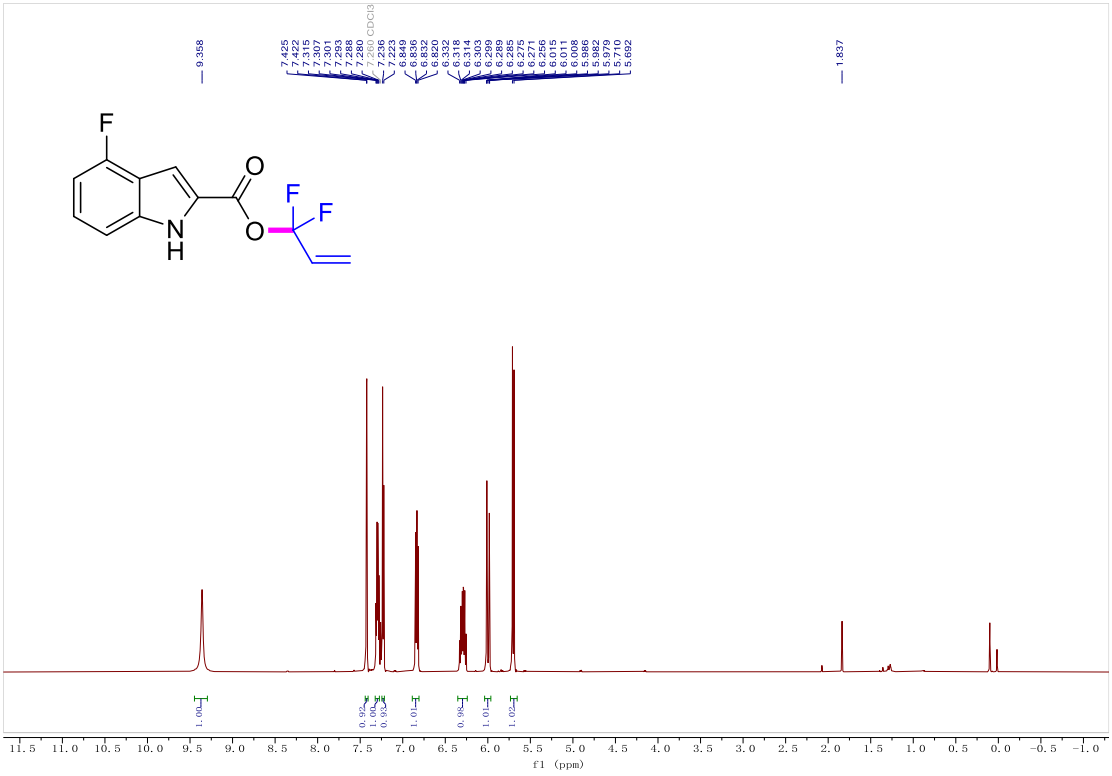


Figure S47. Compound 3p ^{13}C NMR (150 MHz, $CDCl_3$)

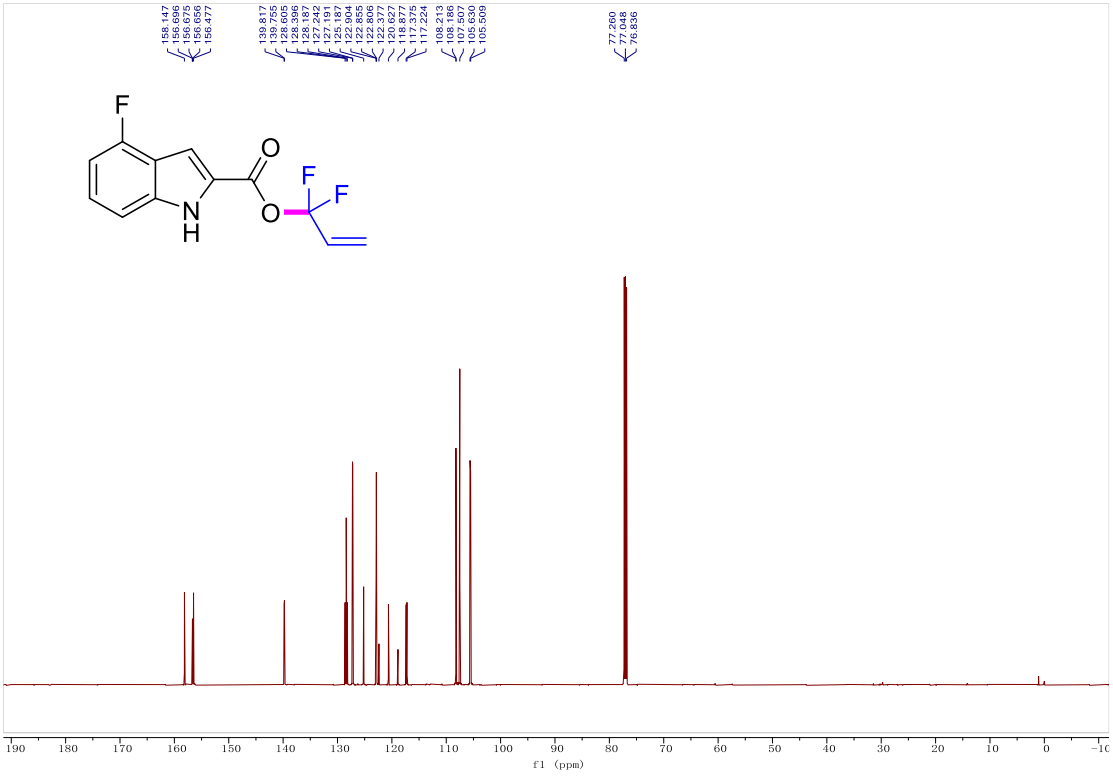


Figure S48. Compound 3p ^{19}F NMR (565 MHz, $CDCl_3$)

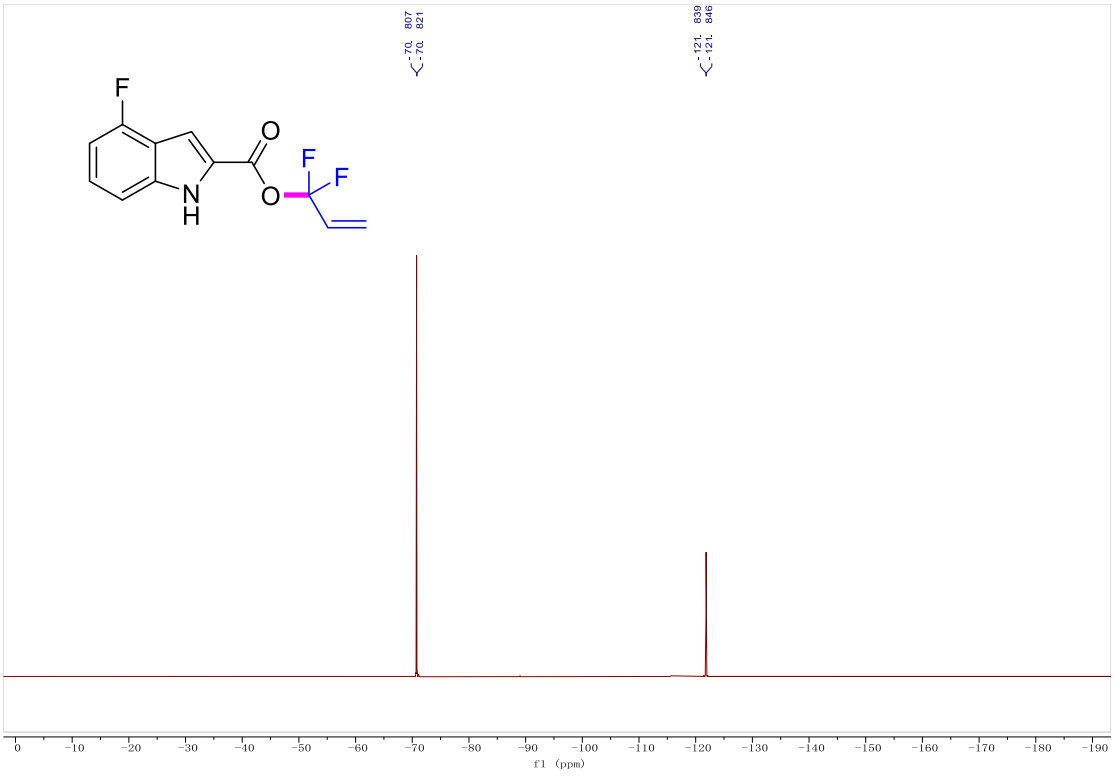


Figure S49. Compound 3q **^{1}H NMR (600 MHz, $CDCl_3$)**

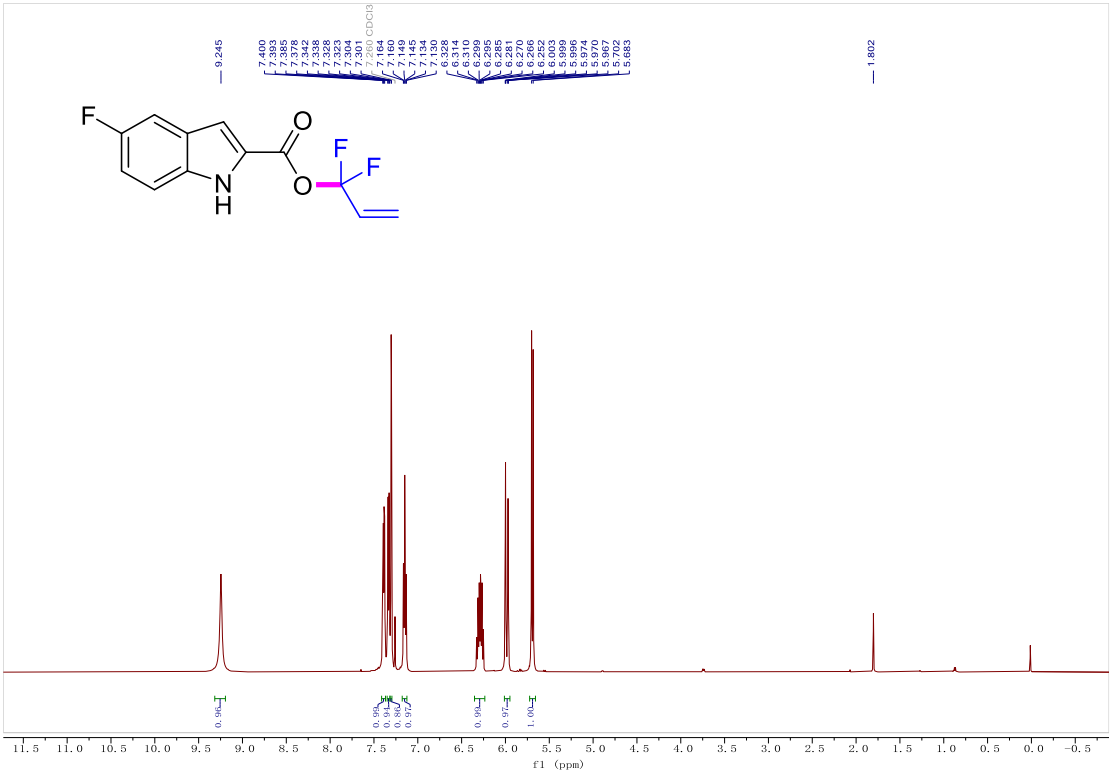


Figure S50. Compound 3q **^{13}C NMR (150 MHz, $CDCl_3$)**

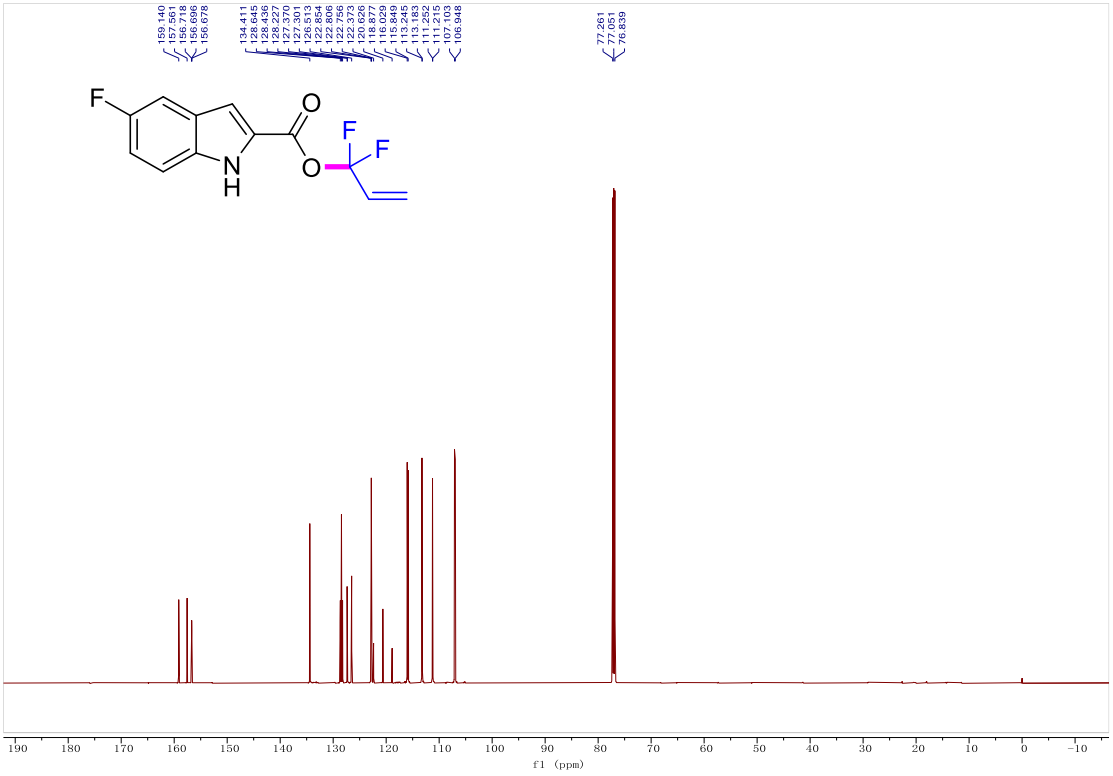


Figure S51. Compound 3q **^{19}F NMR (565 MHz, $CDCl_3$)**

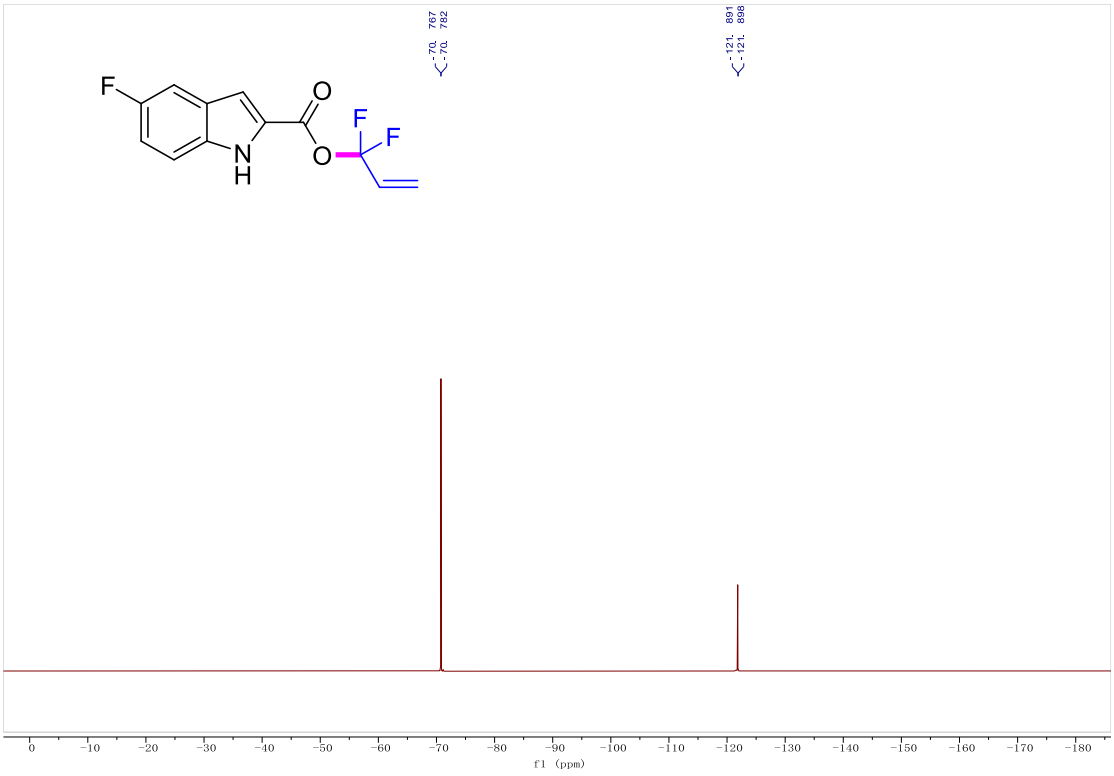


Figure S52. Compound 3r **^{1}H NMR (600 MHz, $CDCl_3$)**

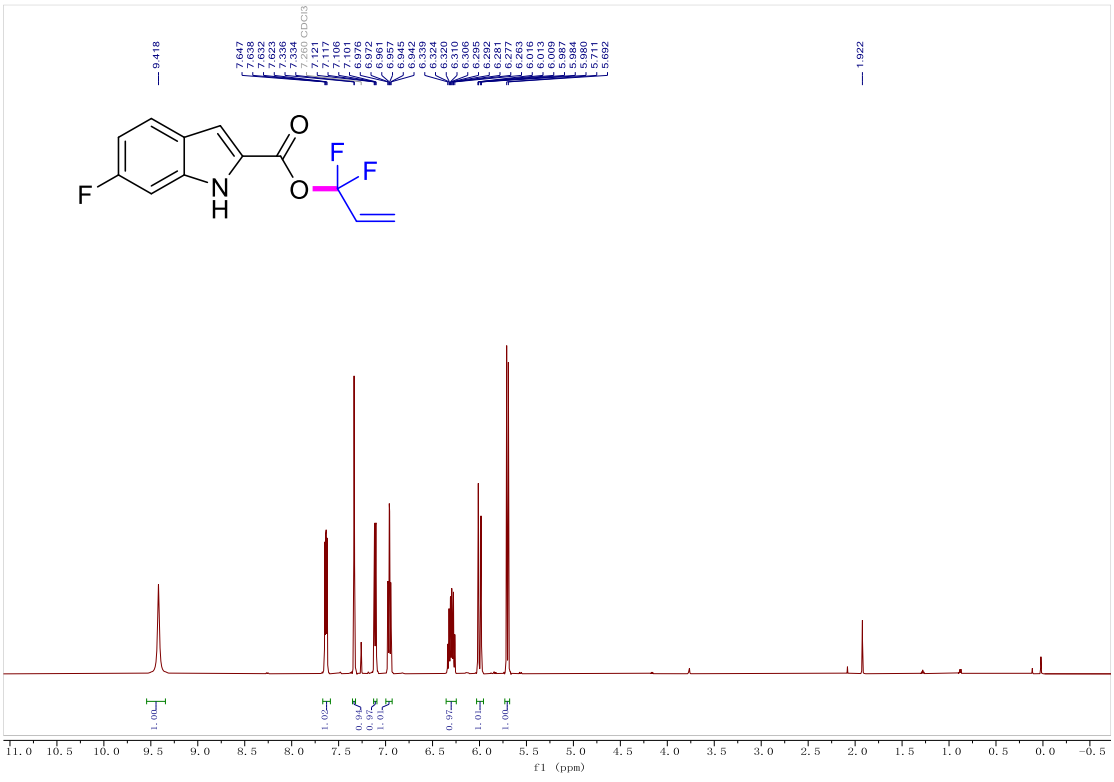


Figure S53. Compound 3r ^{13}C NMR (150 MHz, $CDCl_3$)

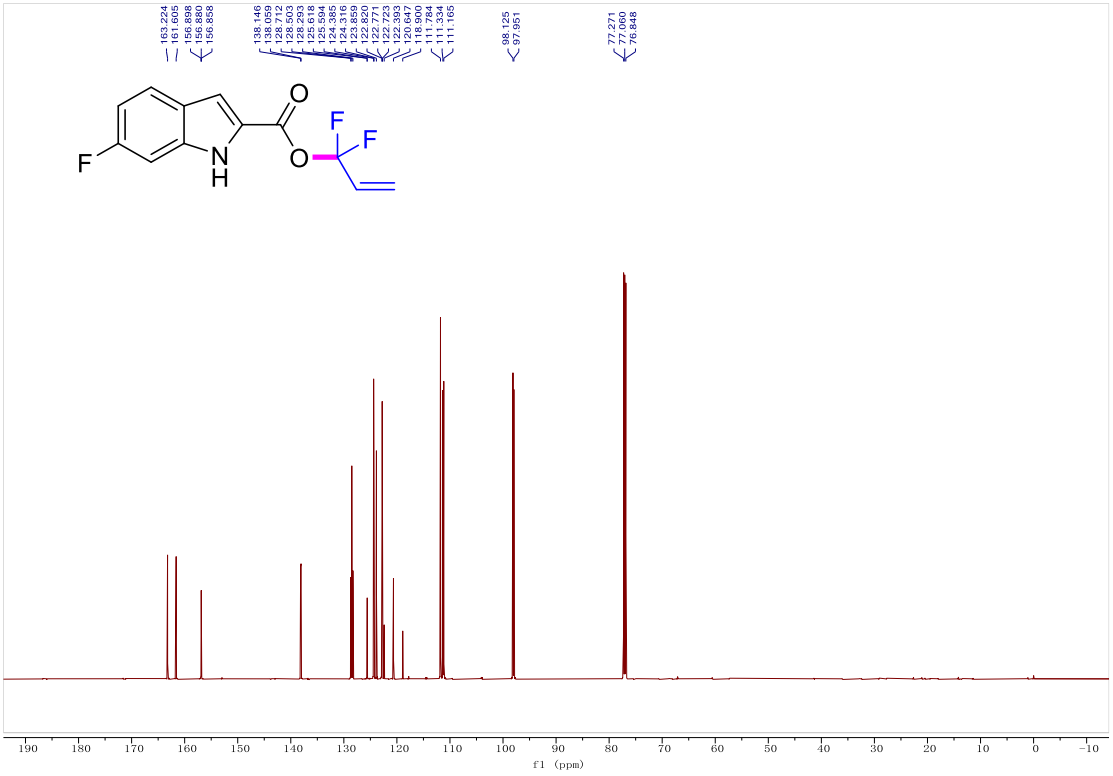


Figure S54. Compound 3r ^{19}F NMR (565 MHz, $CDCl_3$)

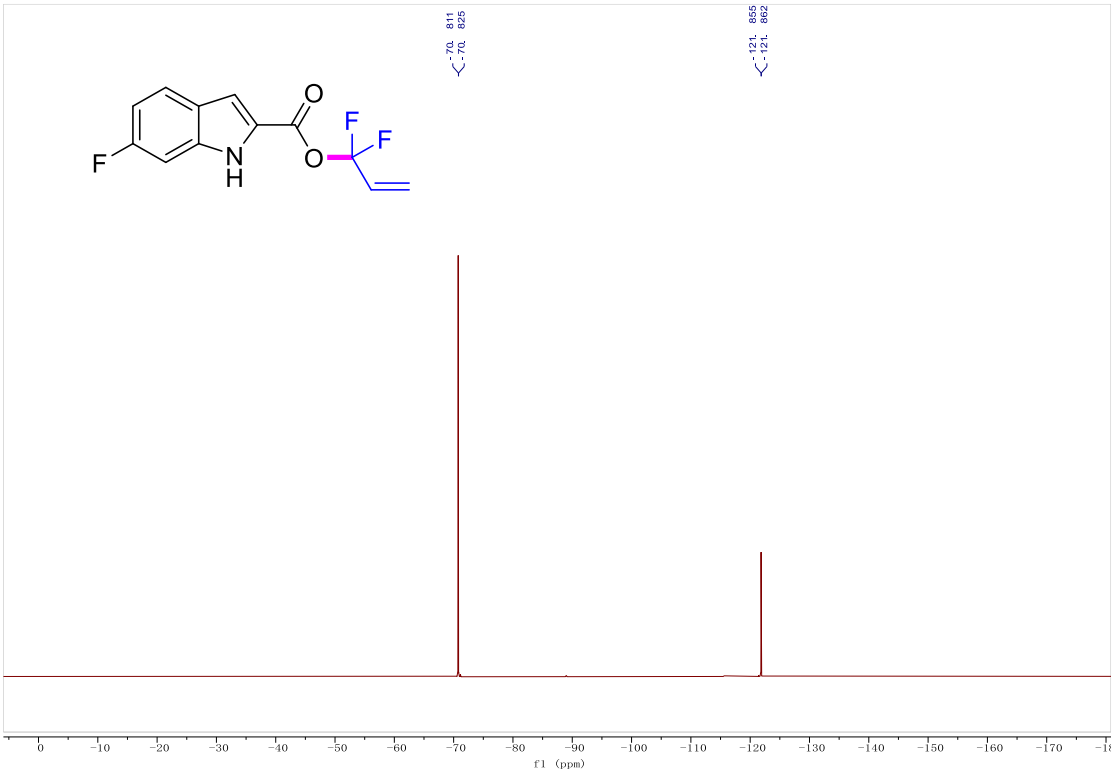


Figure S55. Compound 3s **^{1}H NMR (600 MHz, $CDCl_3$)**

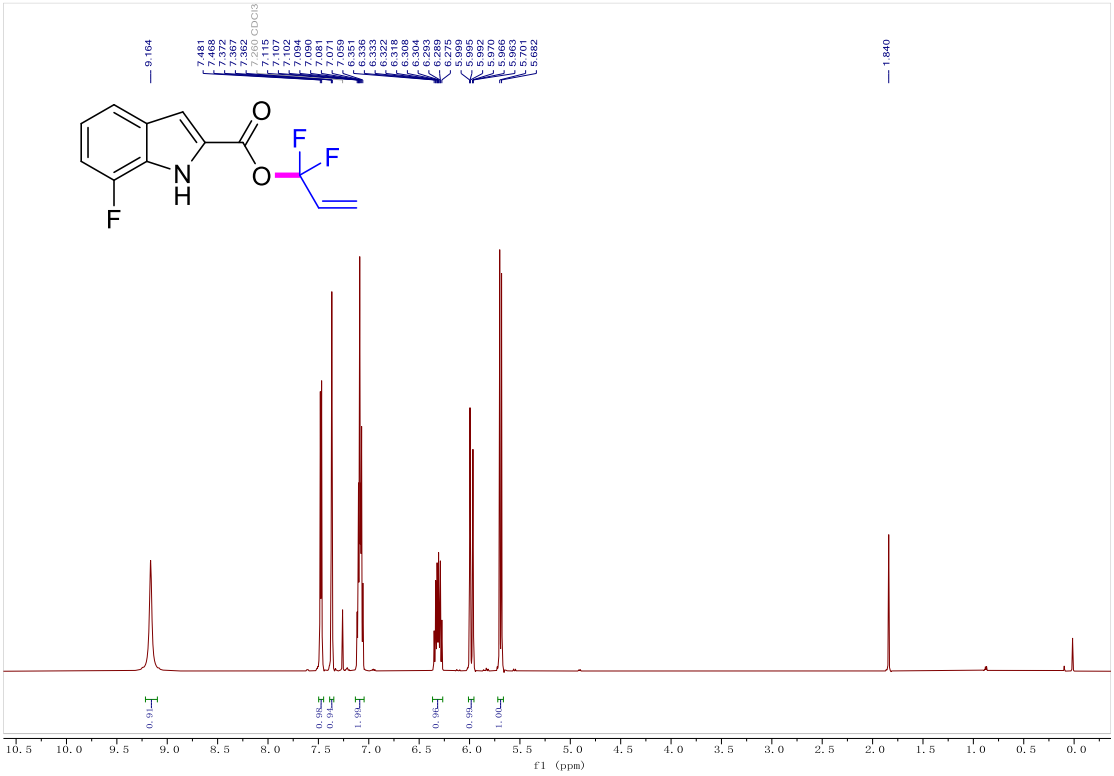


Figure S56. Compound 3s **^{13}C NMR (150 MHz, $CDCl_3$)**

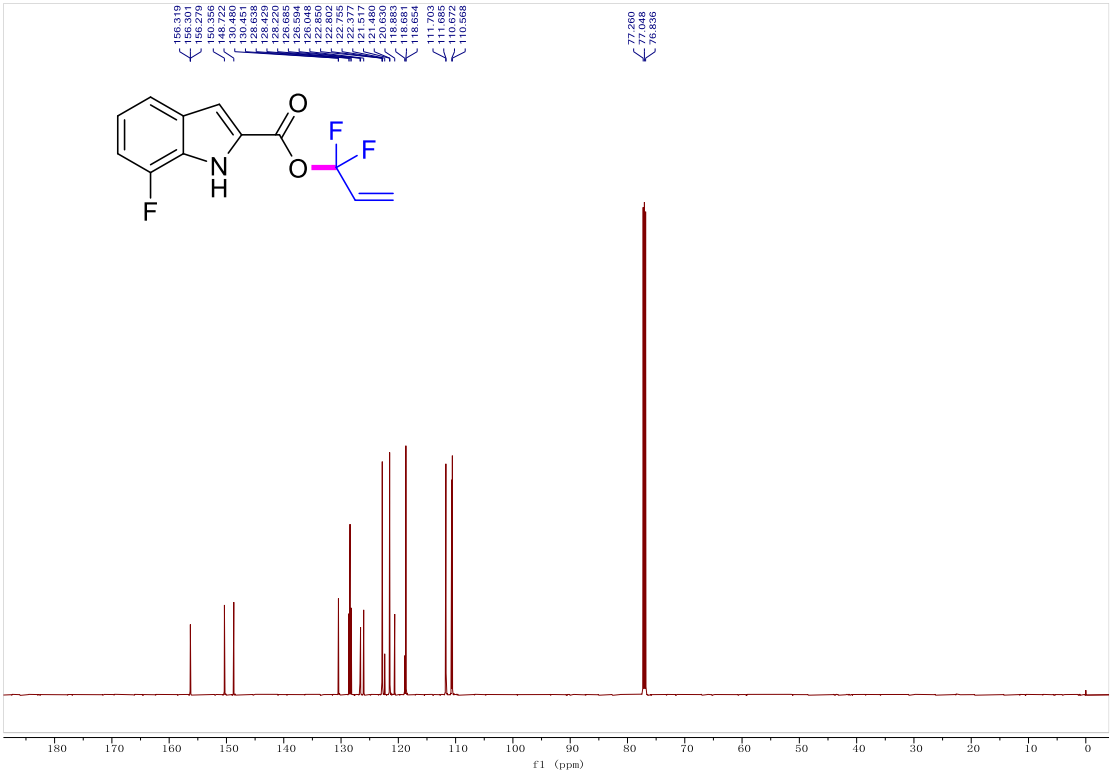


Figure S57. Compound 3s **^{19}F NMR (565 MHz, $CDCl_3$)**

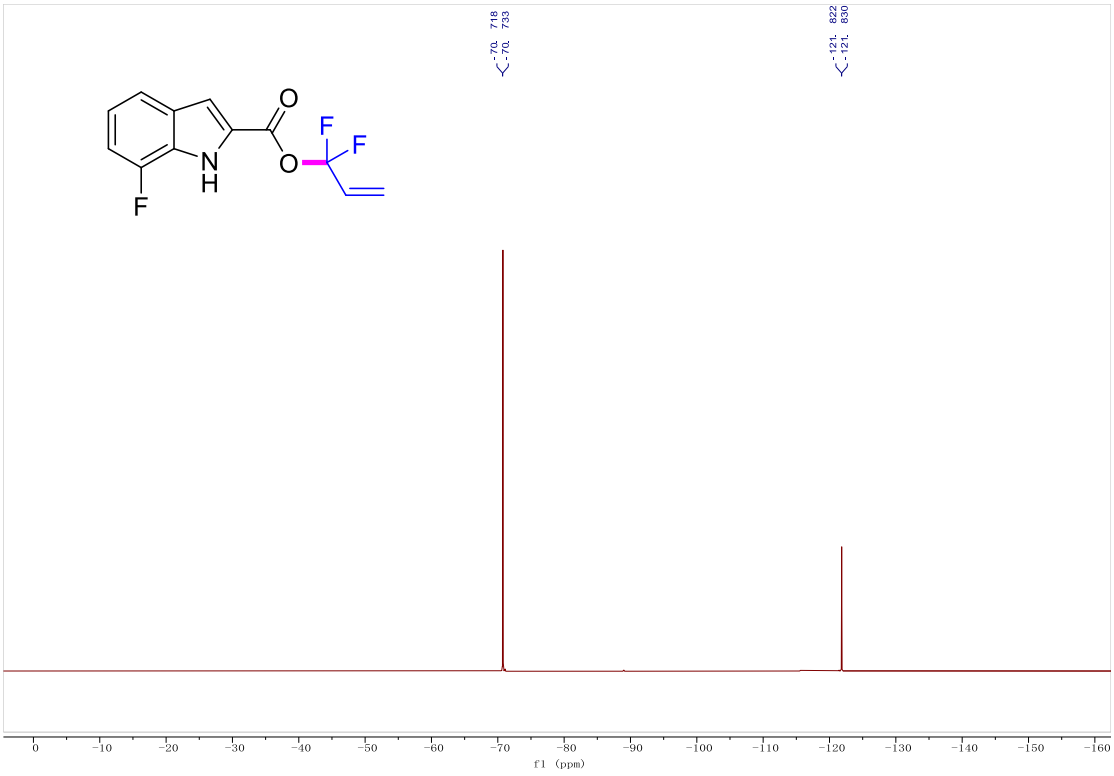


Figure S58. Compound 3t **^{1}H NMR (600 MHz, $CDCl_3$)**

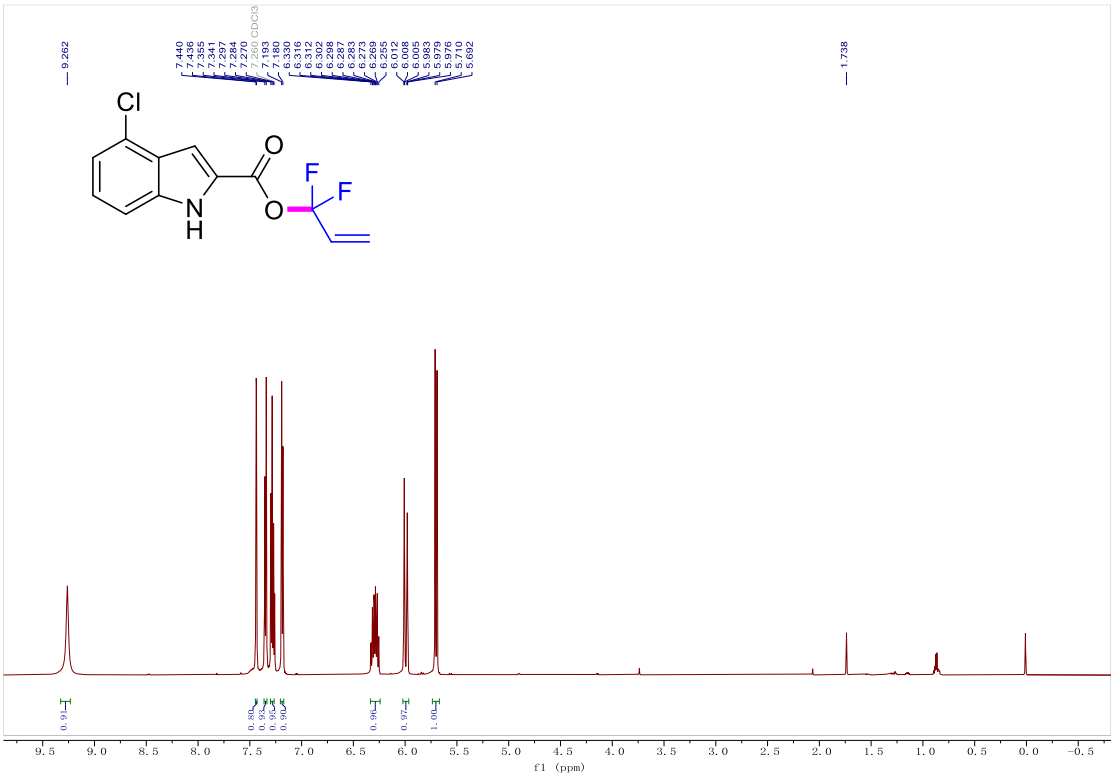


Figure S59. Compound 3t **^{13}C NMR (150 MHz, $CDCl_3$)**

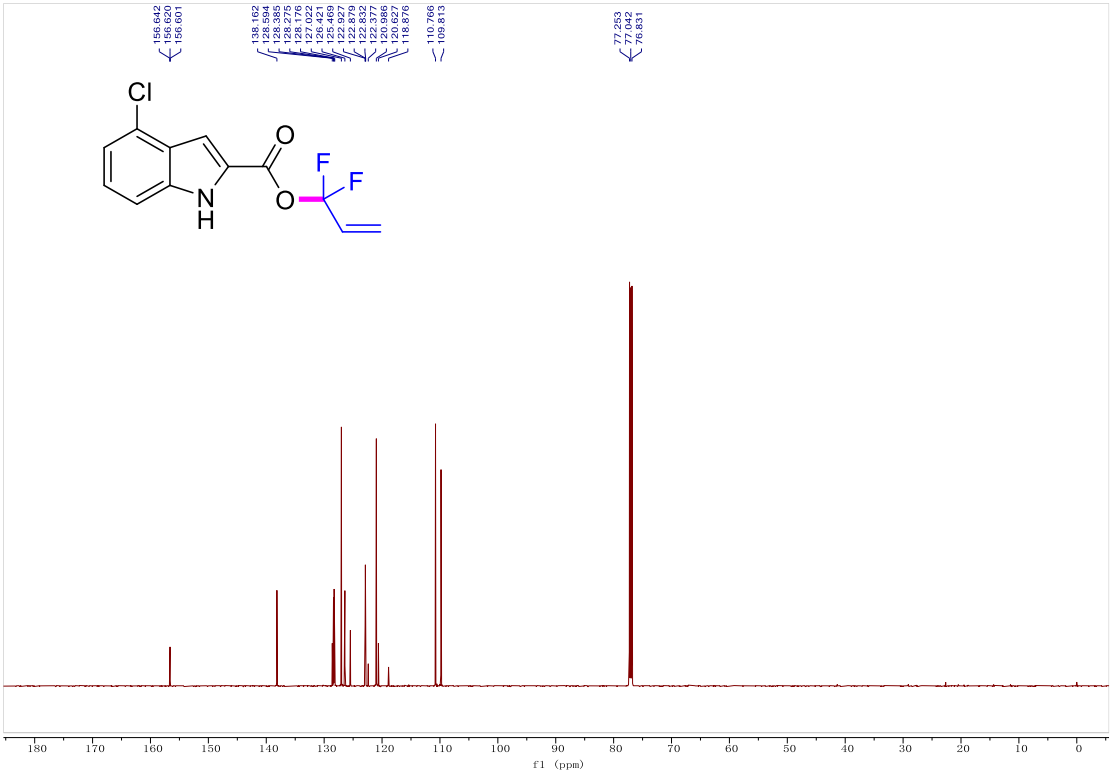


Figure S60. Compound 3t **^{19}F NMR (565 MHz, $CDCl_3$)**

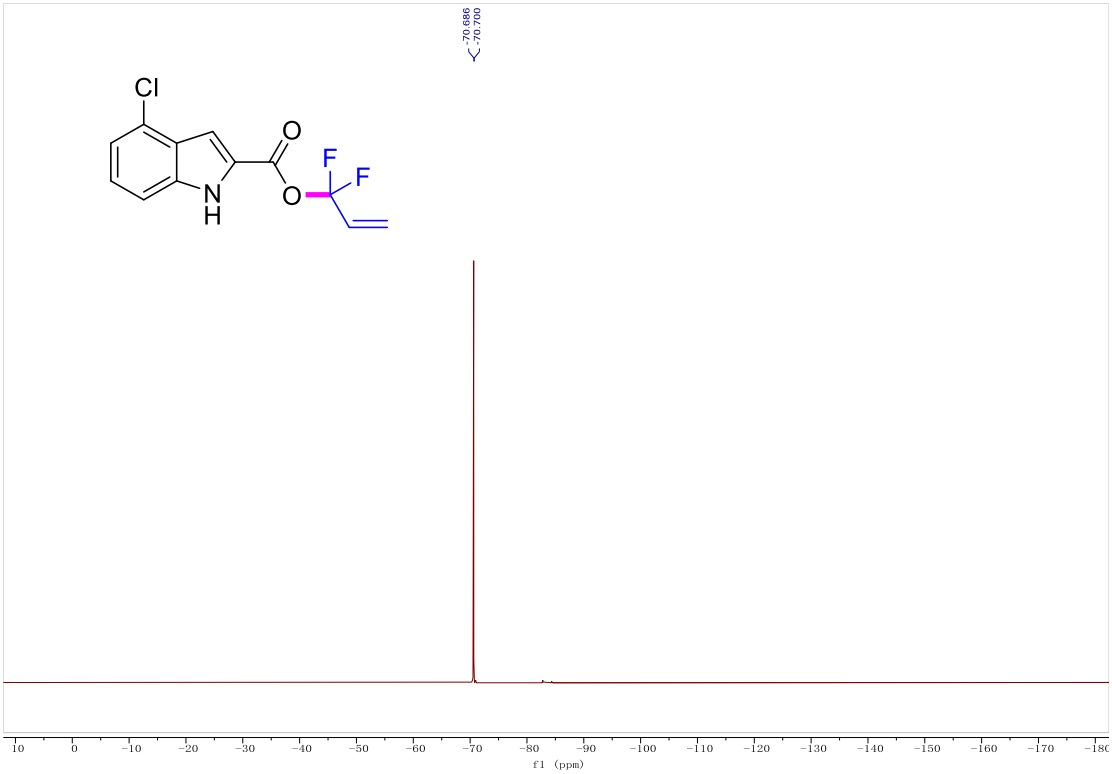


Figure S61. Compound 3u **^{1}H NMR (600 MHz, $CDCl_3$)**

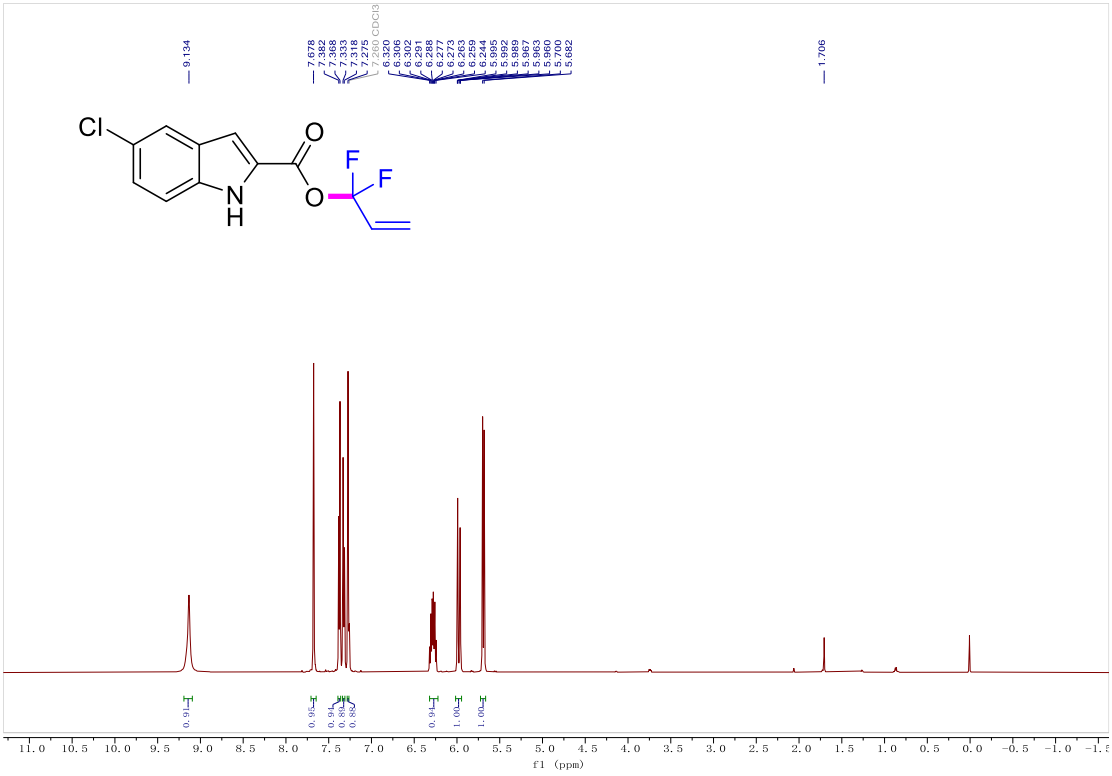


Figure S62. Compound 3u **^{13}C NMR (150 MHz, $CDCl_3$)**

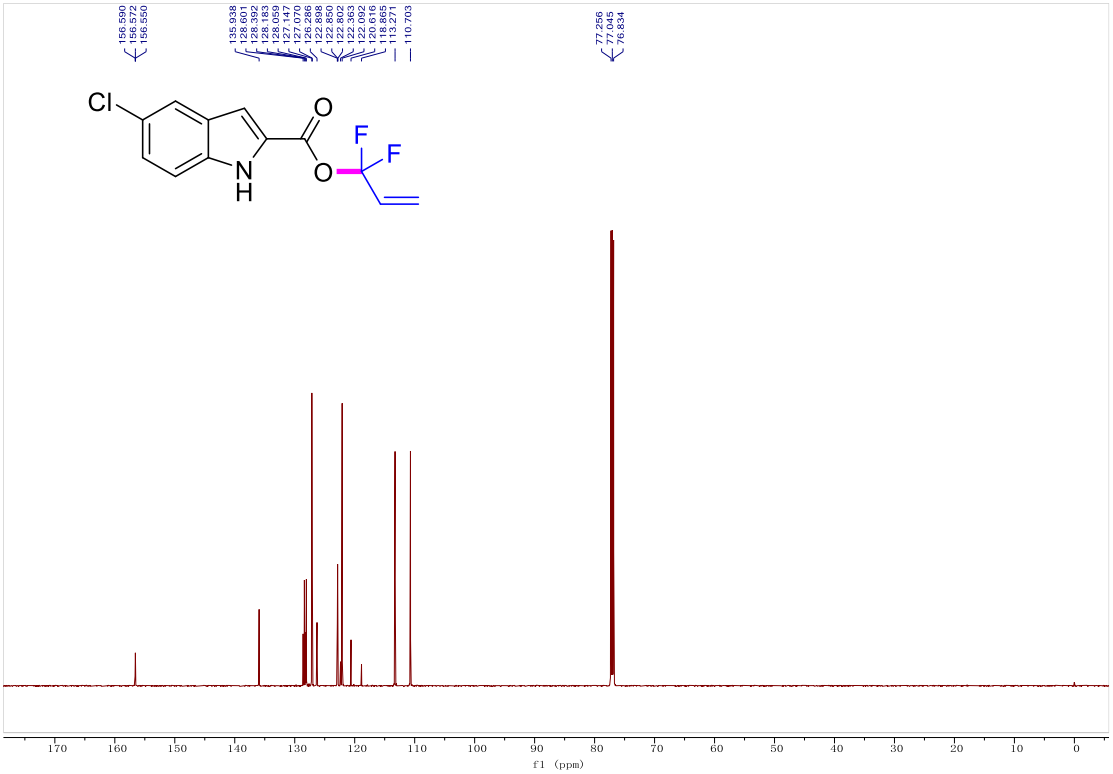


Figure S63. Compound 3u **^{19}F NMR (565 MHz, $CDCl_3$)**

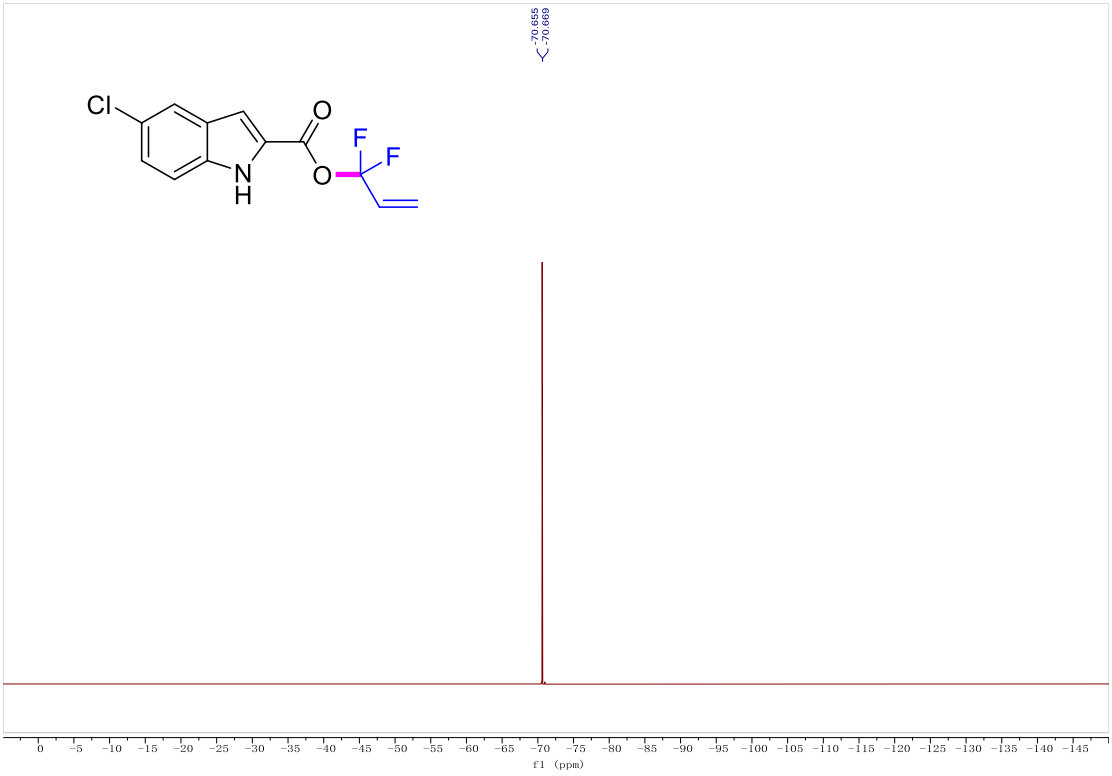


Figure S64. Compound 3v **^{1}H NMR (600 MHz, $CDCl_3$)**

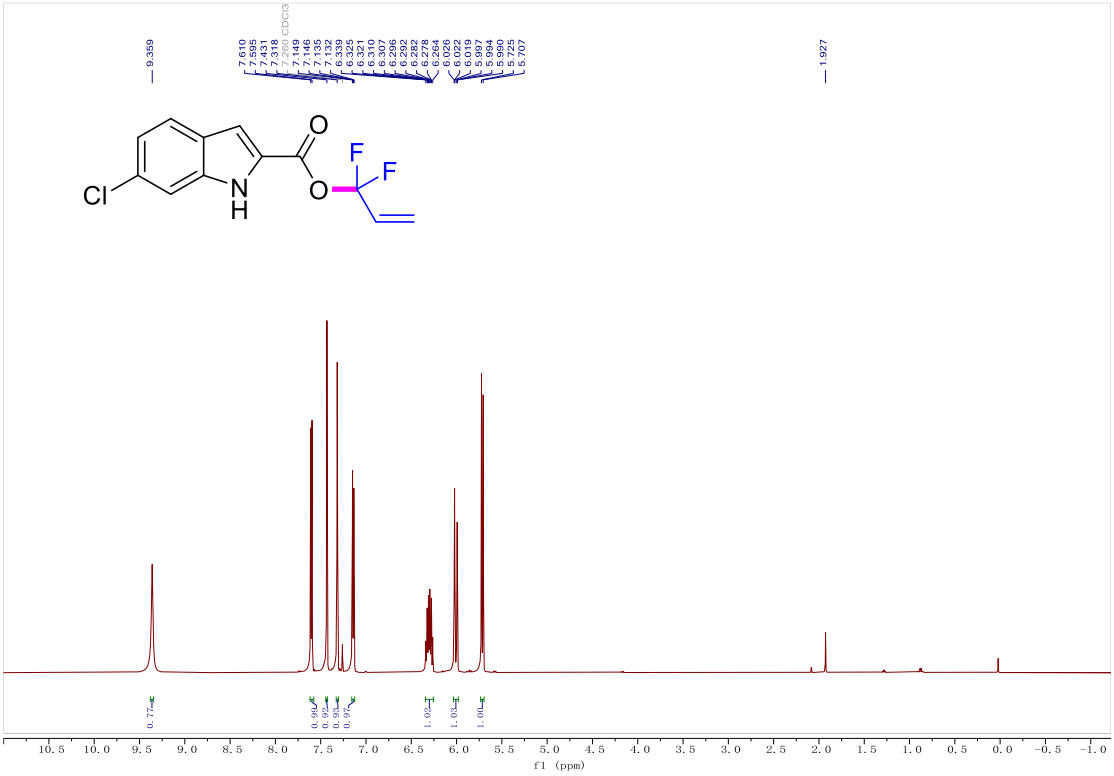


Figure S65. Compound 3v ^{13}C NMR (150 MHz, $CDCl_3$)

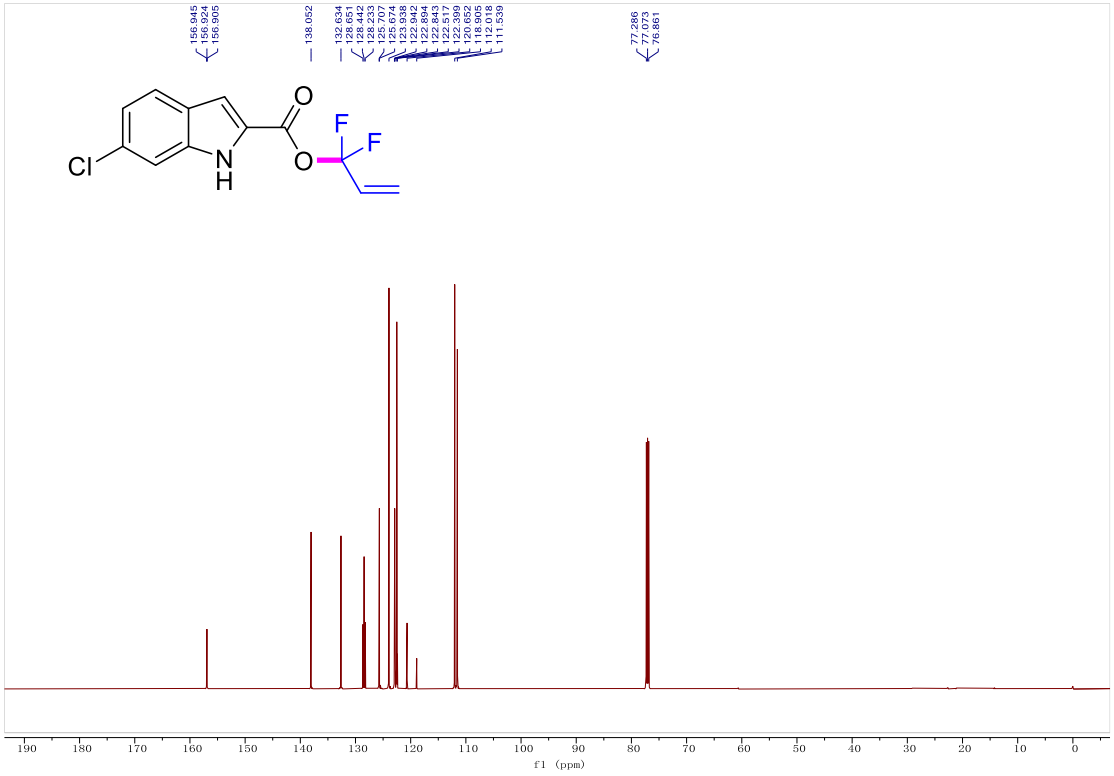


Figure S66. Compound 3v ^{19}F NMR (565 MHz, $CDCl_3$)

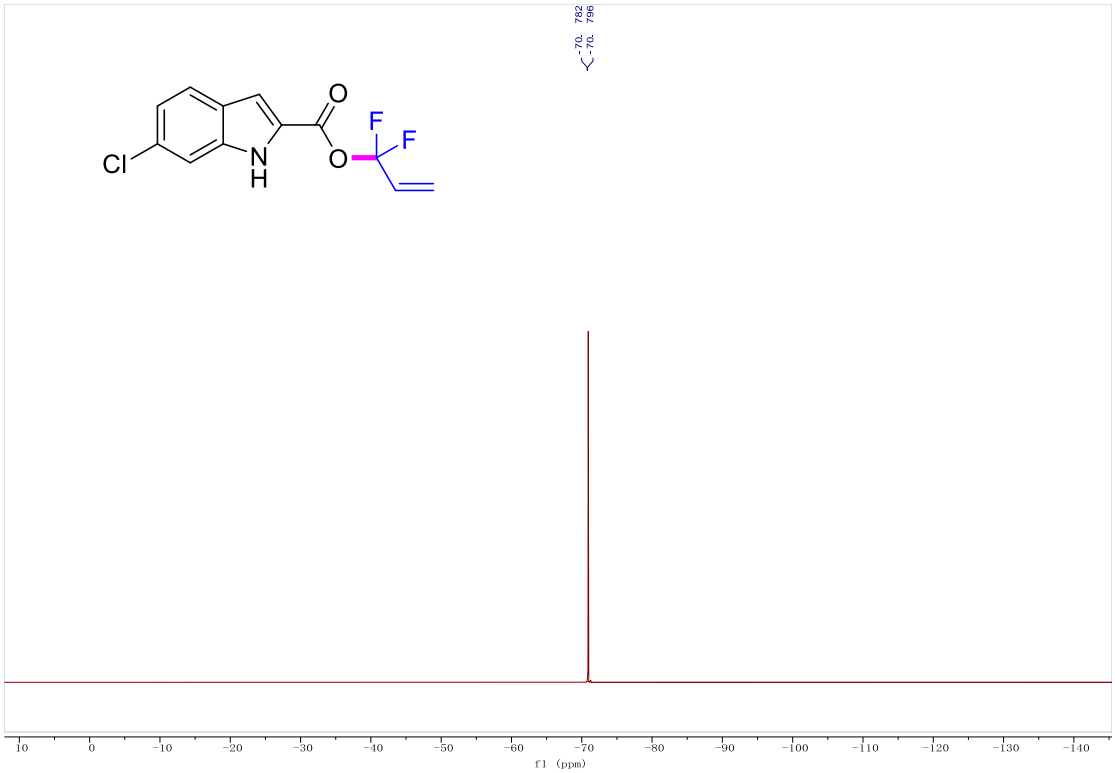


Figure S67. Compound 3w **^{1}H NMR (600 MHz, $CDCl_3$)**

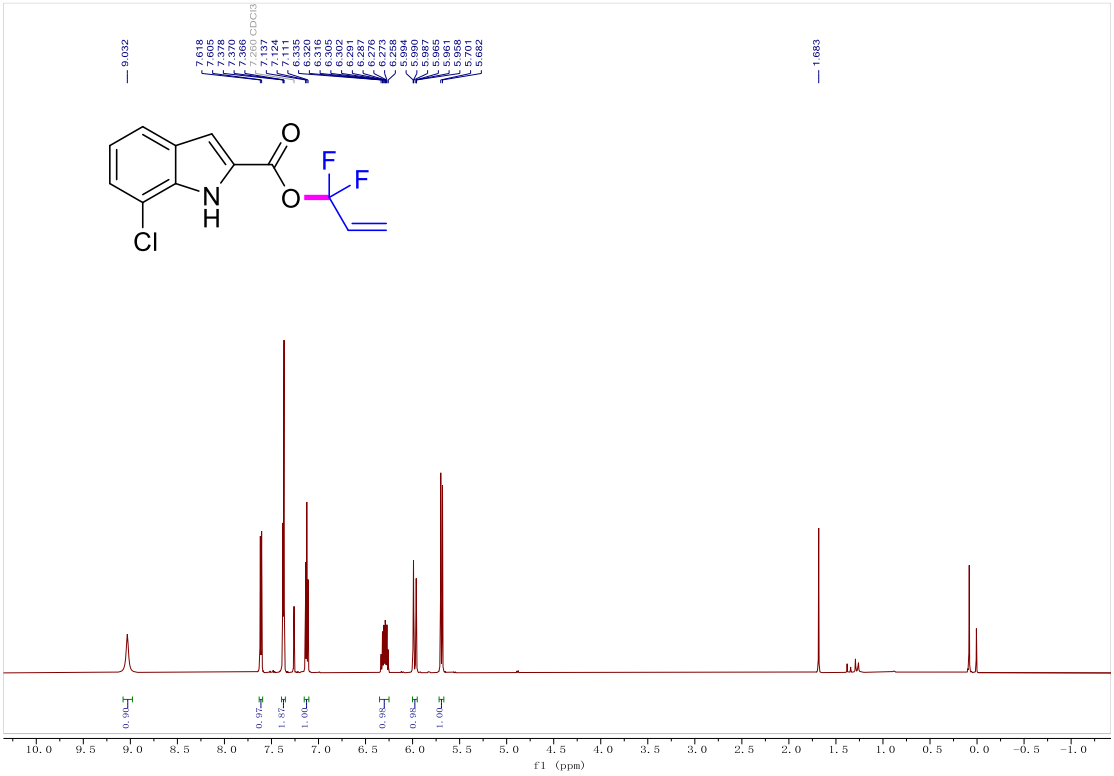


Figure S68. Compound 3w **^{13}C NMR (150 MHz, $CDCl_3$)**

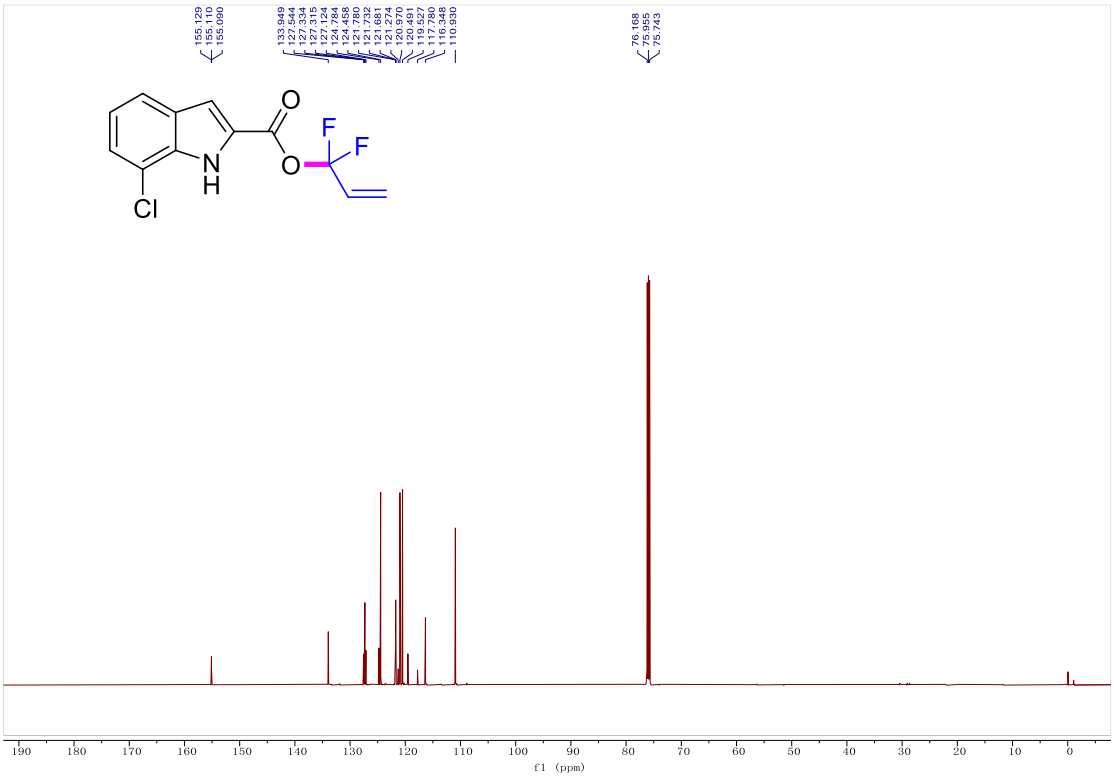


Figure S69. Compound 3w **^{19}F NMR (565 MHz, $CDCl_3$)**

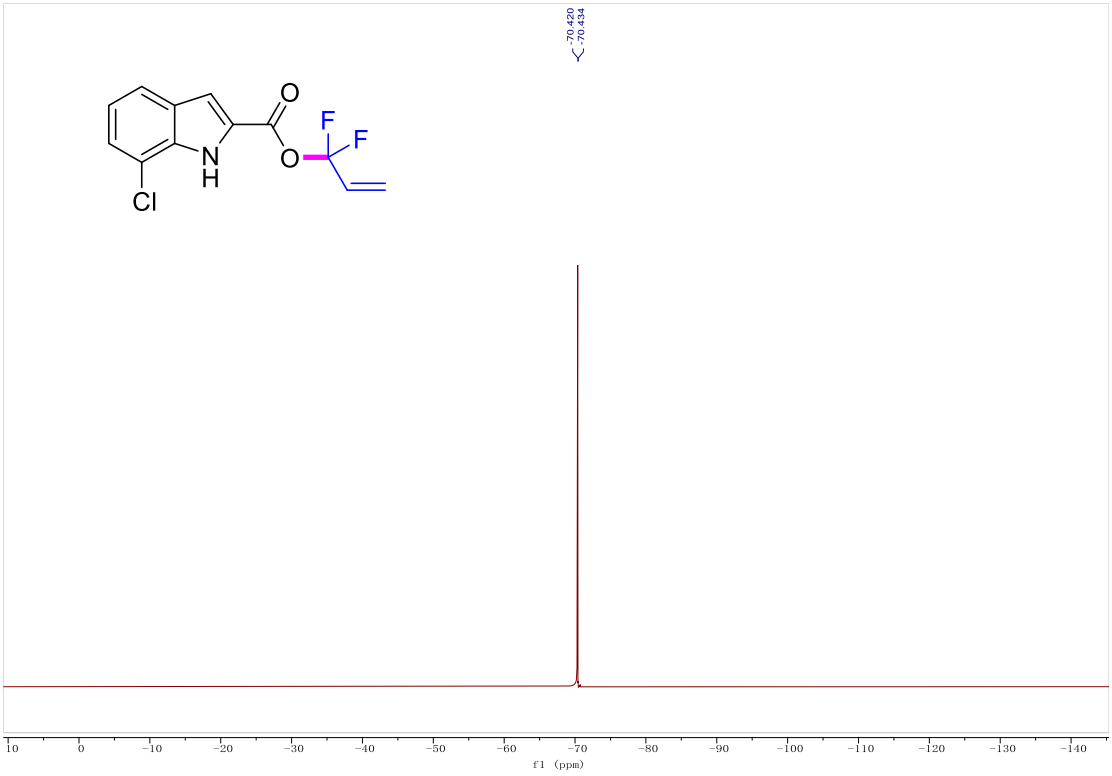


Figure S70. Compound 3x **^{1}H NMR (600 MHz, $CDCl_3$)**

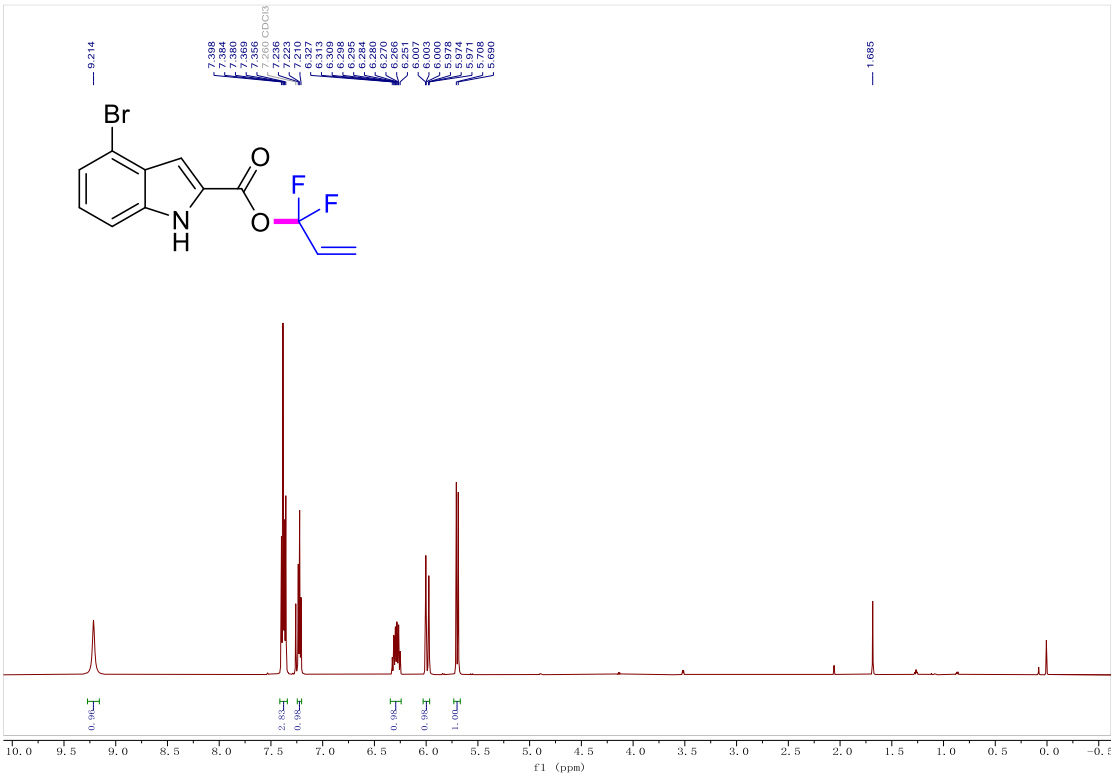


Figure S71. Compound 3x ^{13}C NMR (150 MHz, $CDCl_3$)

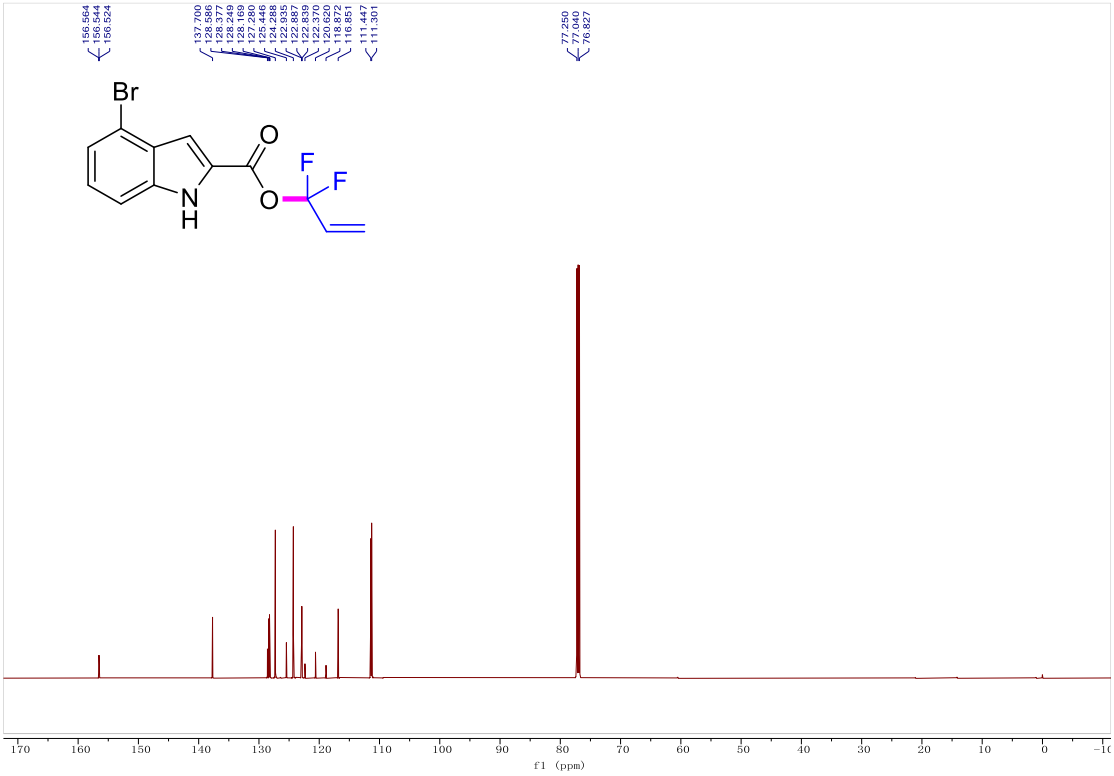


Figure S72. Compound 3x ^{19}F NMR (565 MHz, $CDCl_3$)

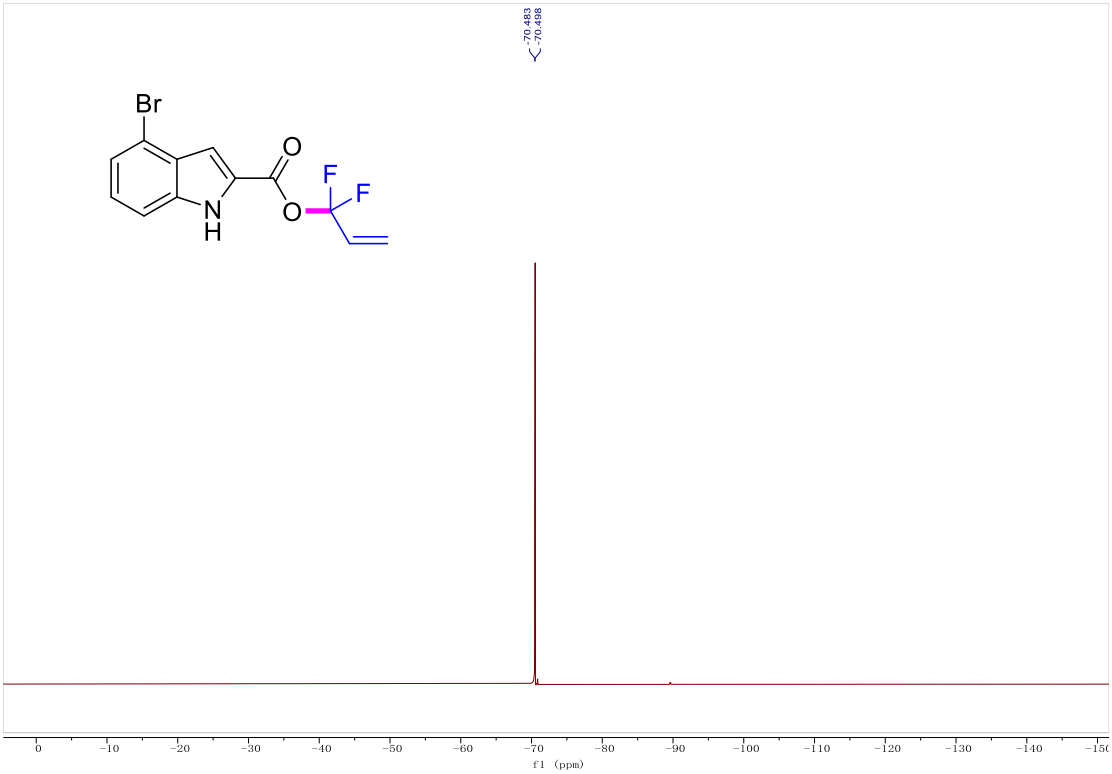


Figure S73. Compound 3x' **^{1}H NMR (600 MHz, $CDCl_3$)**

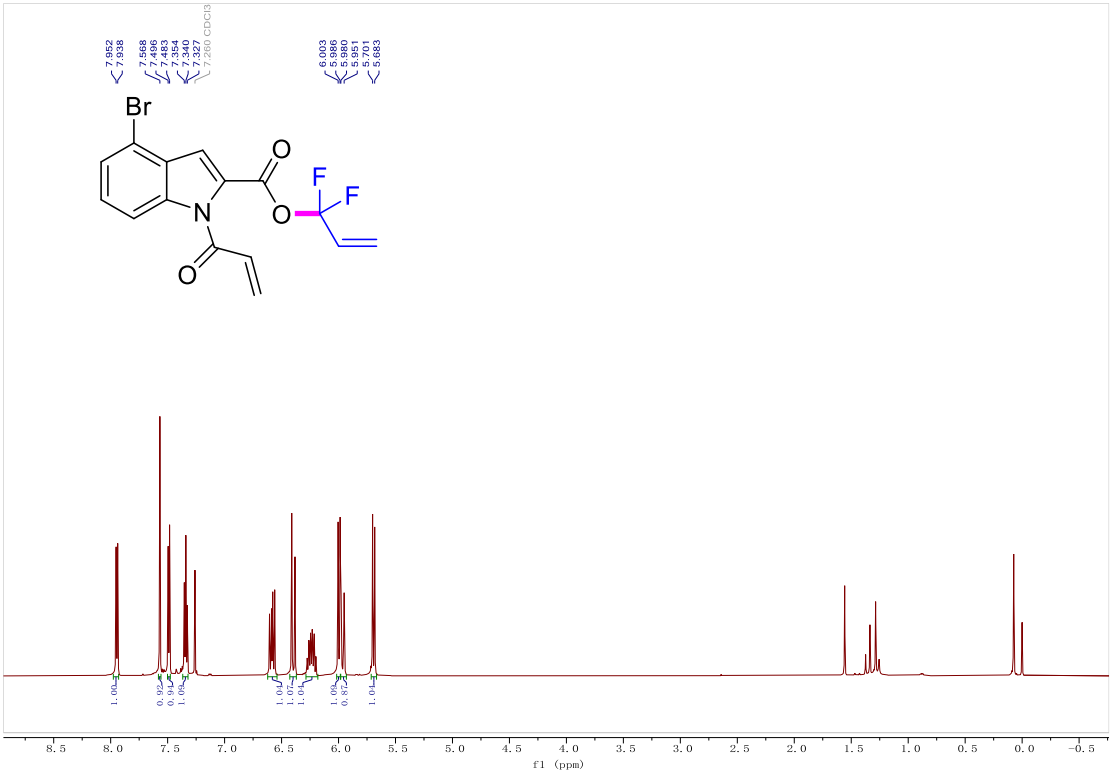


Figure S74. Compound 3x' **^{13}C NMR (150 MHz, $CDCl_3$)**

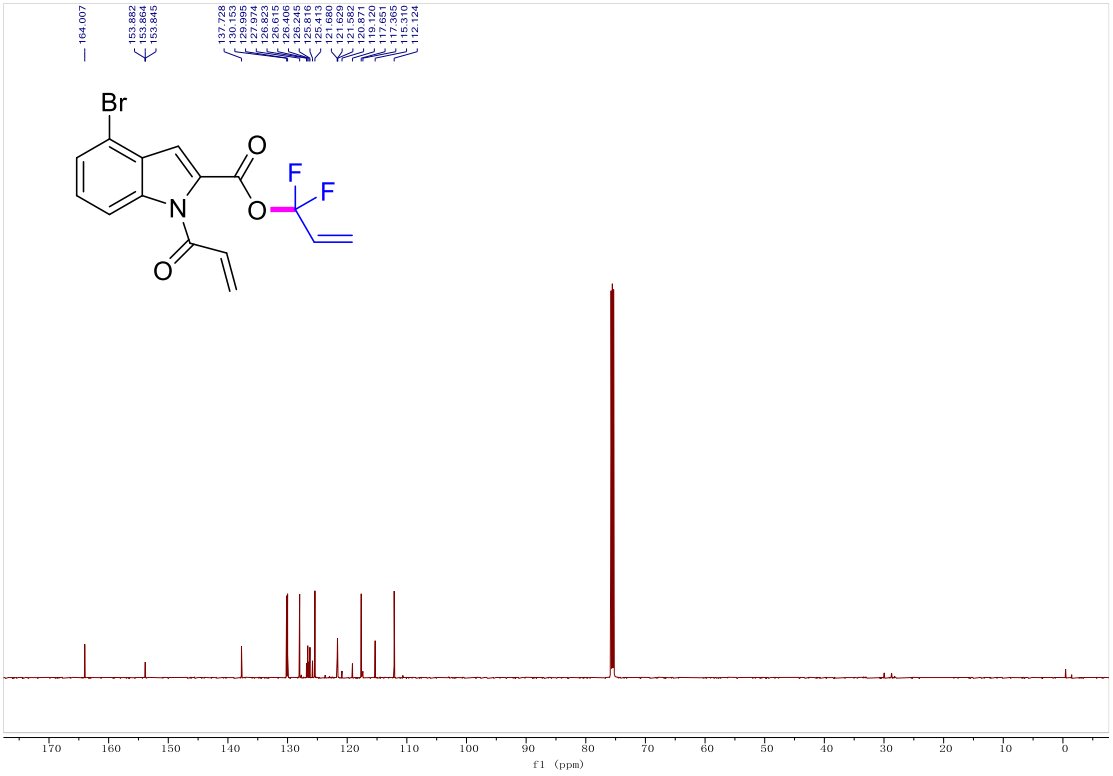


Figure S75. Compound 3y **^{1}H NMR (600 MHz, $CDCl_3$)**

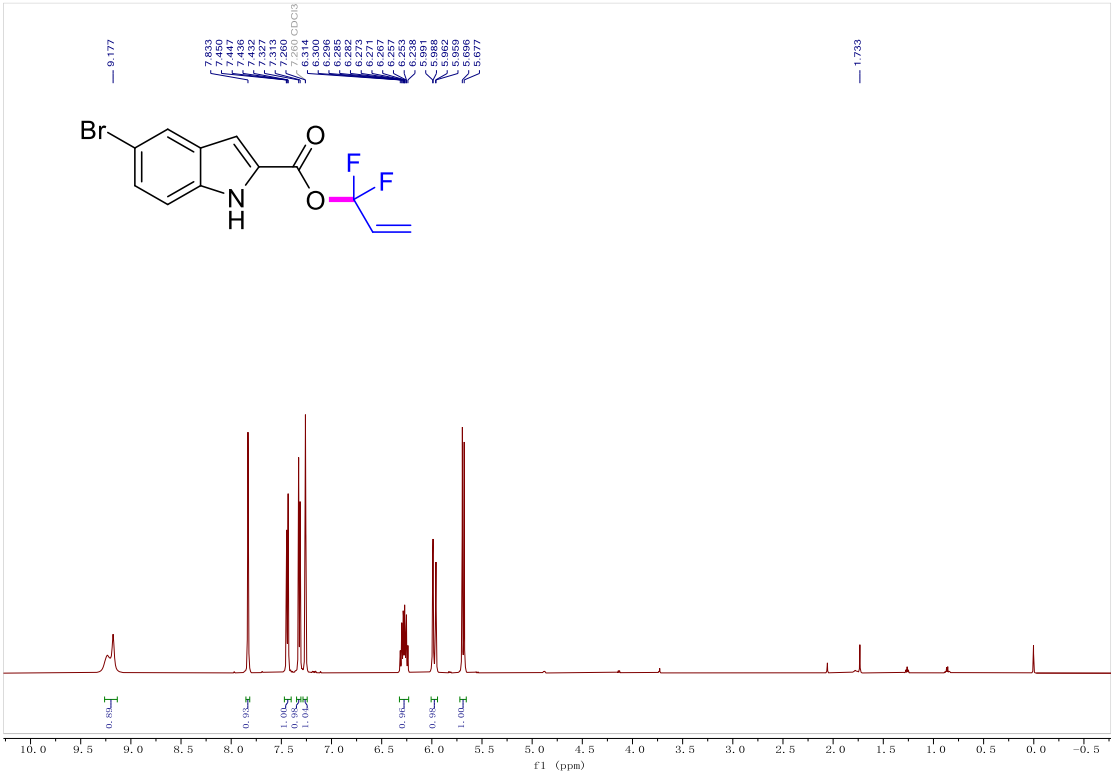


Figure S76. Compound 3y **^{13}C NMR (150 MHz, $CDCl_3$)**

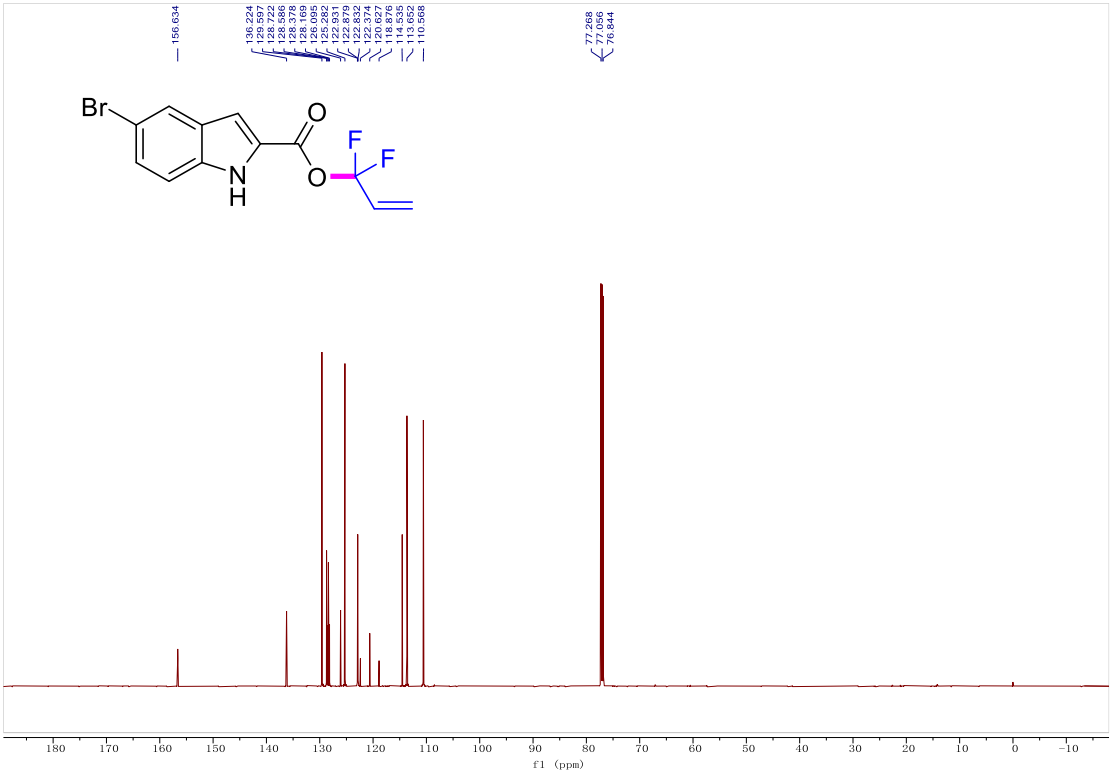


Figure S77. Compound 3y **^{19}F NMR (565 MHz, $CDCl_3$)**

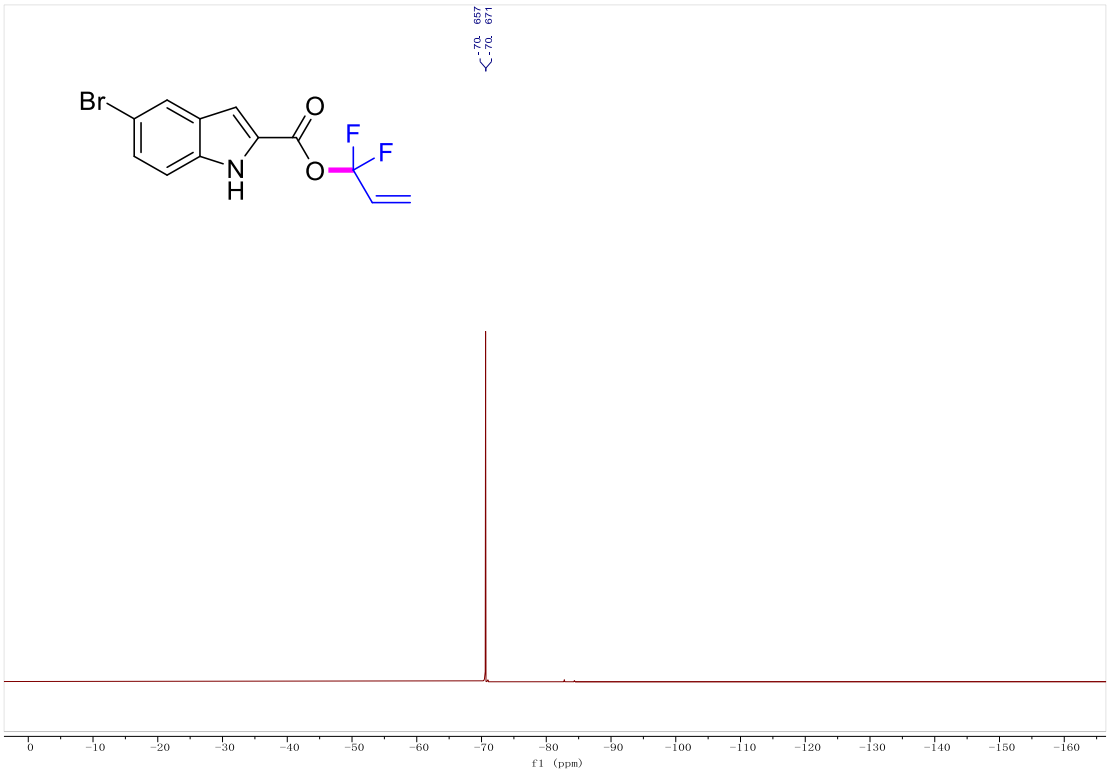


Figure S78. Compound 3z **^{1}H NMR (600 MHz, $CDCl_3$)**

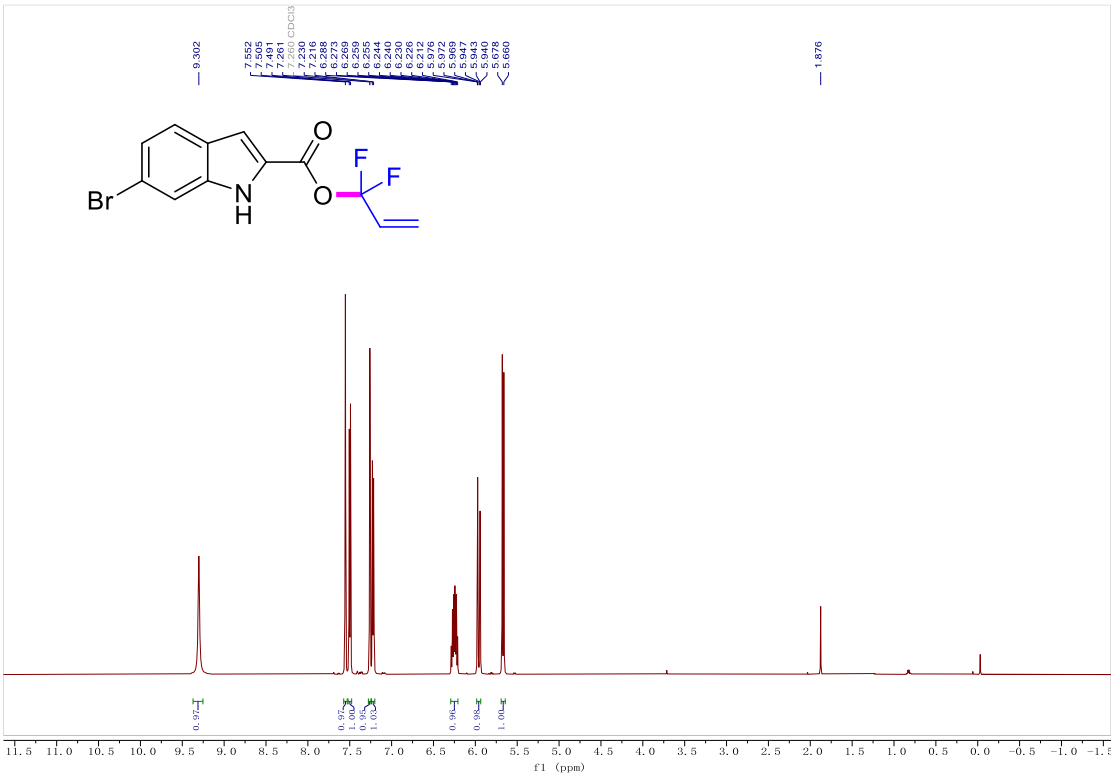


Figure S79. Compound 3z **^{13}C NMR (150 MHz, $CDCl_3$)**

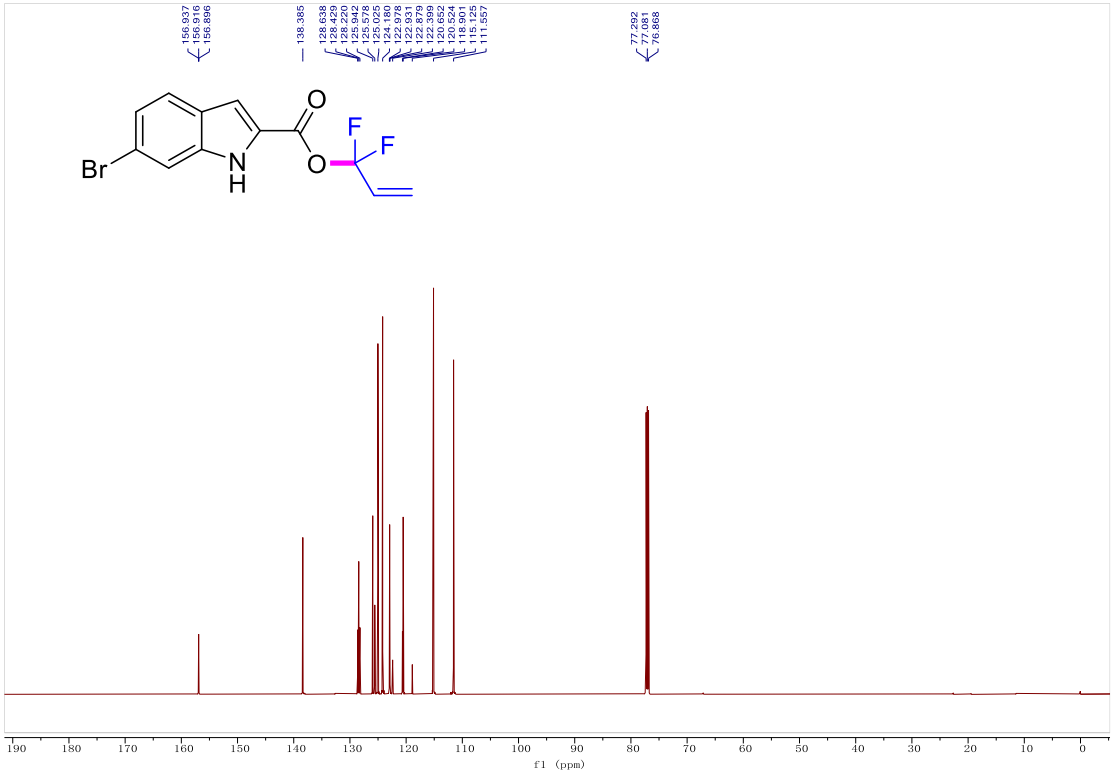


Figure S80. Compound 3z **^{19}F NMR (565 MHz, $CDCl_3$)**

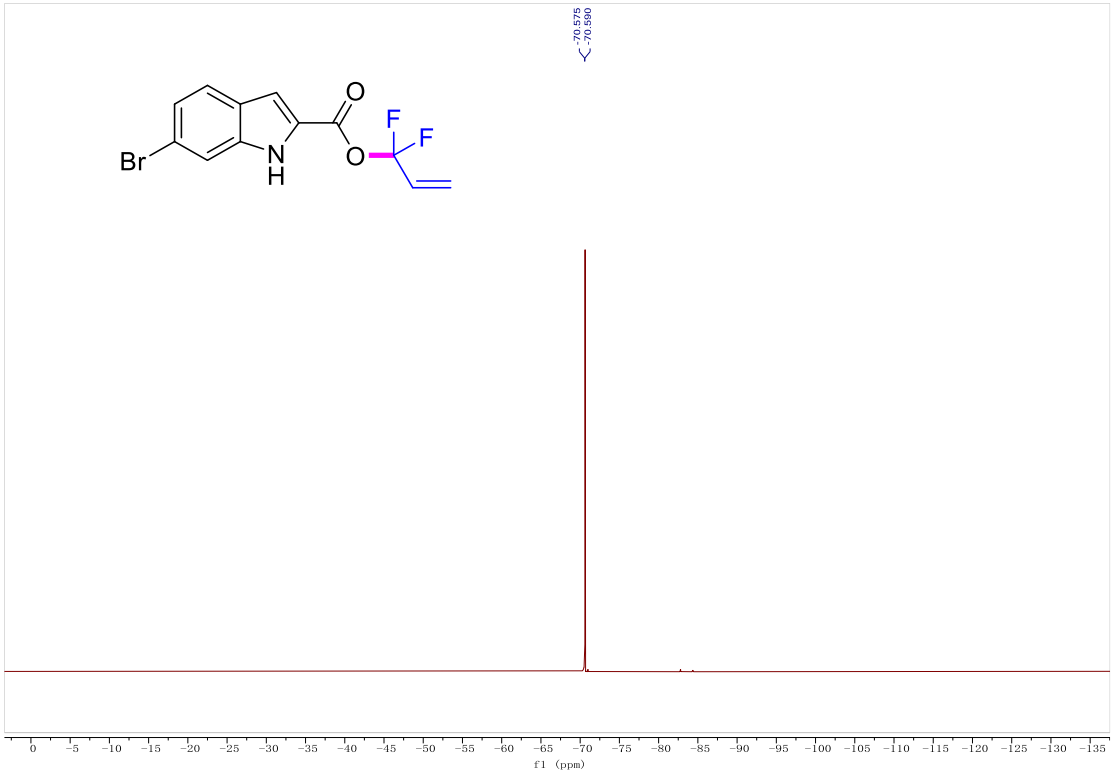


Figure S81. Compound 3aa ^{1}H NMR (600 MHz, $CDCl_3$)

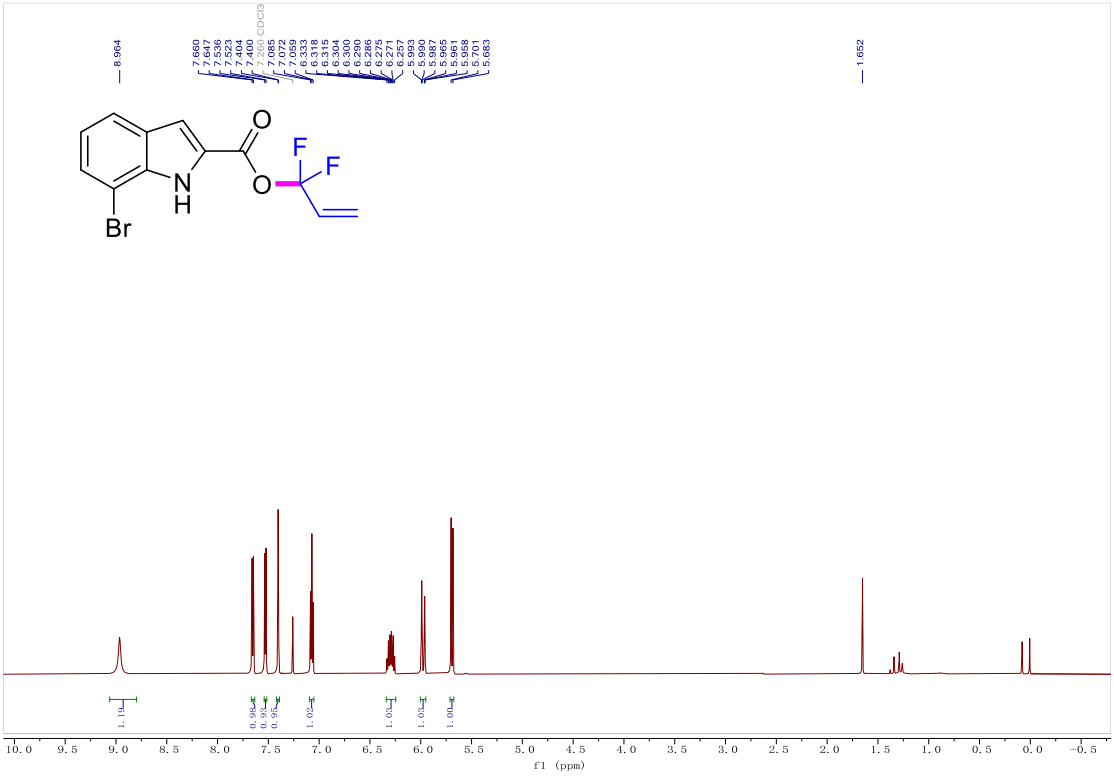


Figure S82. Compound 3aa ^{13}C NMR (150 MHz, $CDCl_3$)

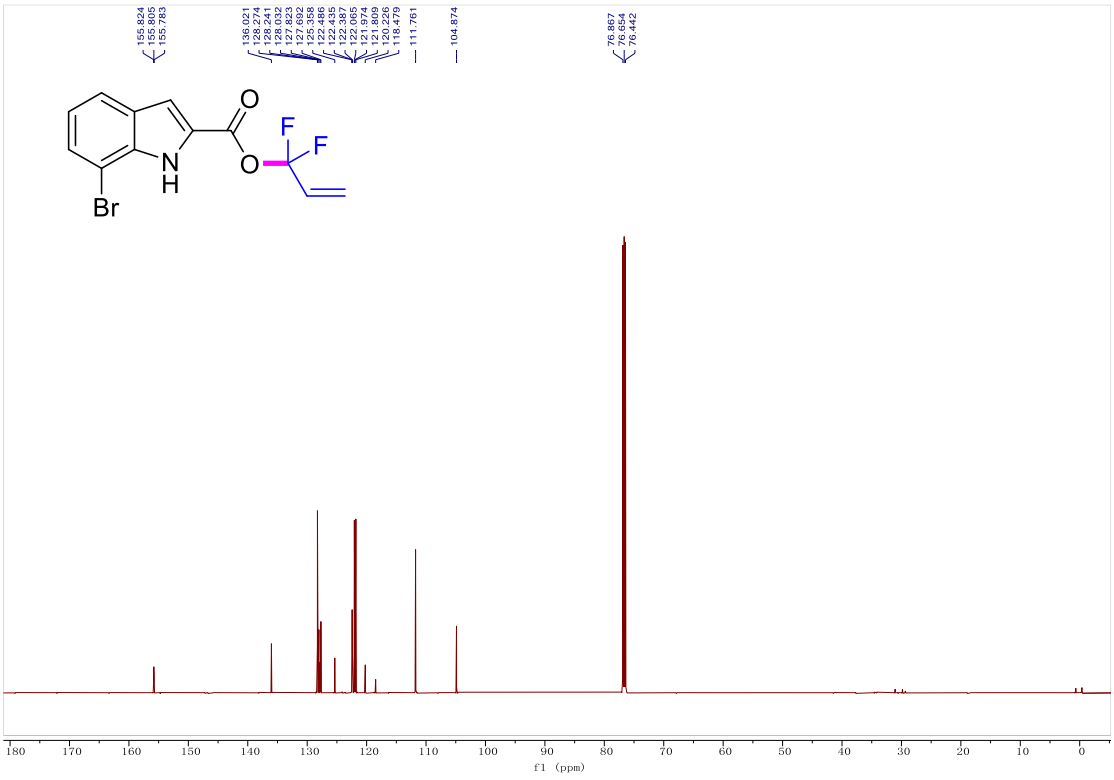


Figure S83. Compound 3aa ^{19}F NMR (565 MHz, $CDCl_3$)

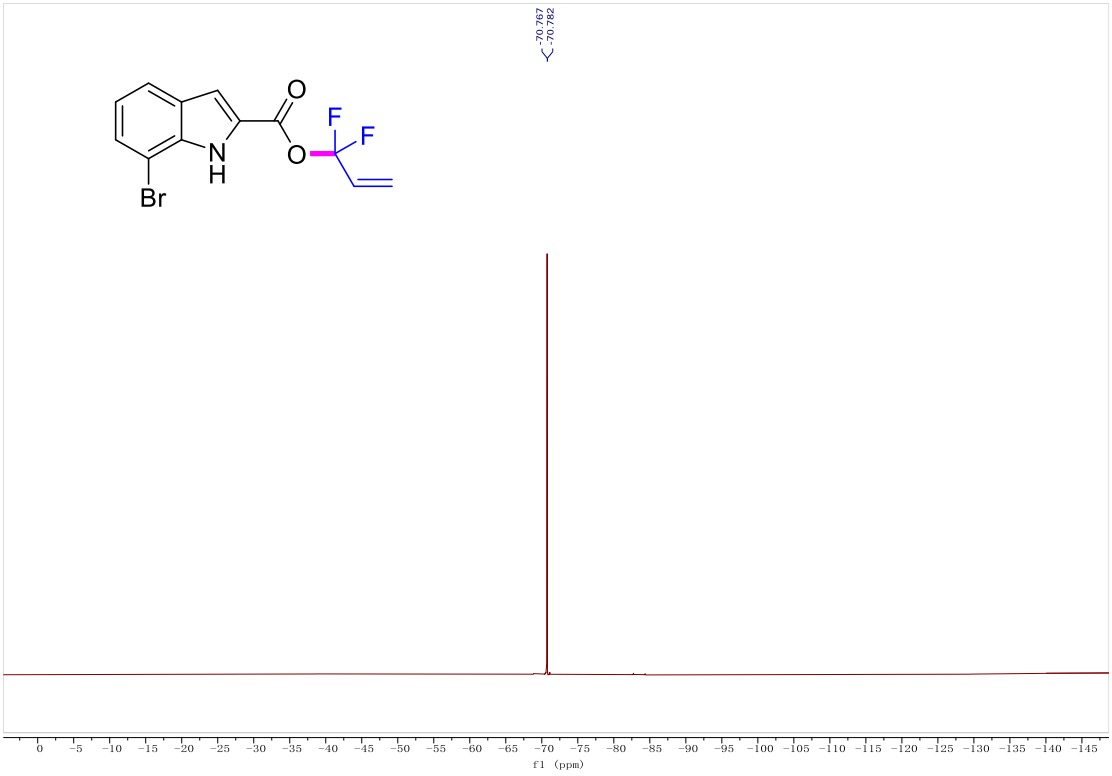


Figure S84. Compound 3ab ^{1}H NMR (600 MHz, $CDCl_3$)

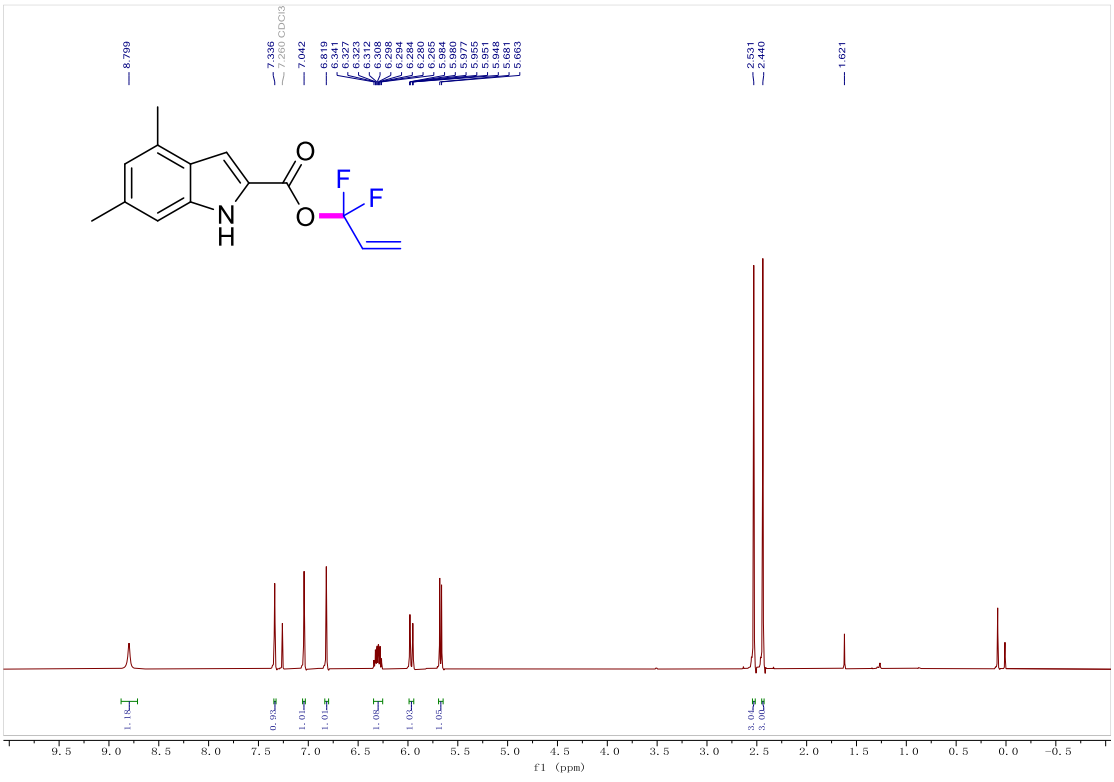


Figure S85. Compound 3ab ^{13}C NMR (150 MHz, $CDCl_3$)

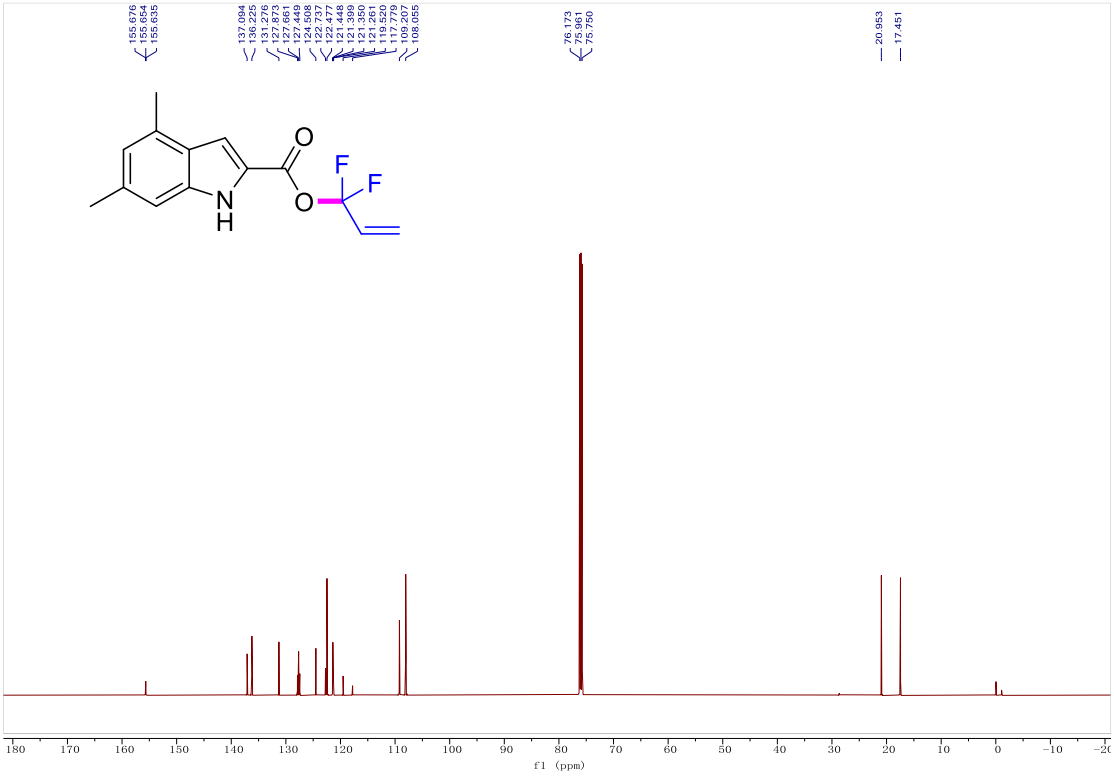


Figure S86. Compound 3ab ^{19}F NMR (565 MHz, $CDCl_3$)

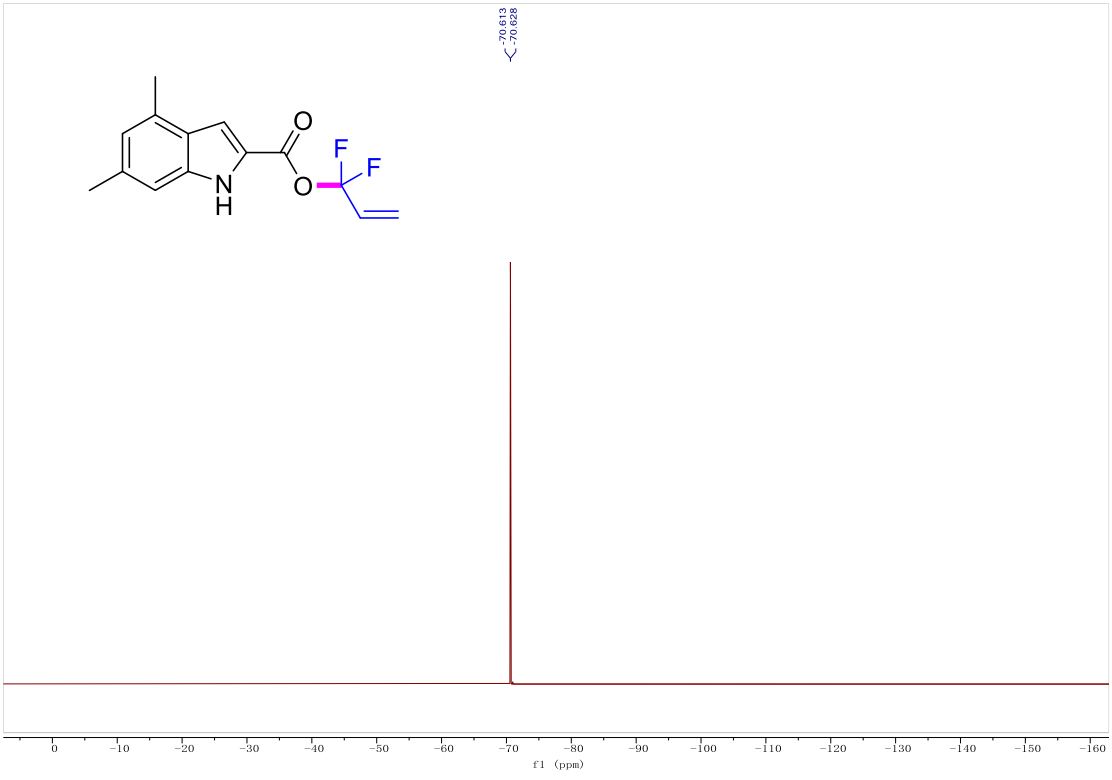


Figure S87. Compound 3ac ^{1}H NMR (600 MHz, $CDCl_3$)

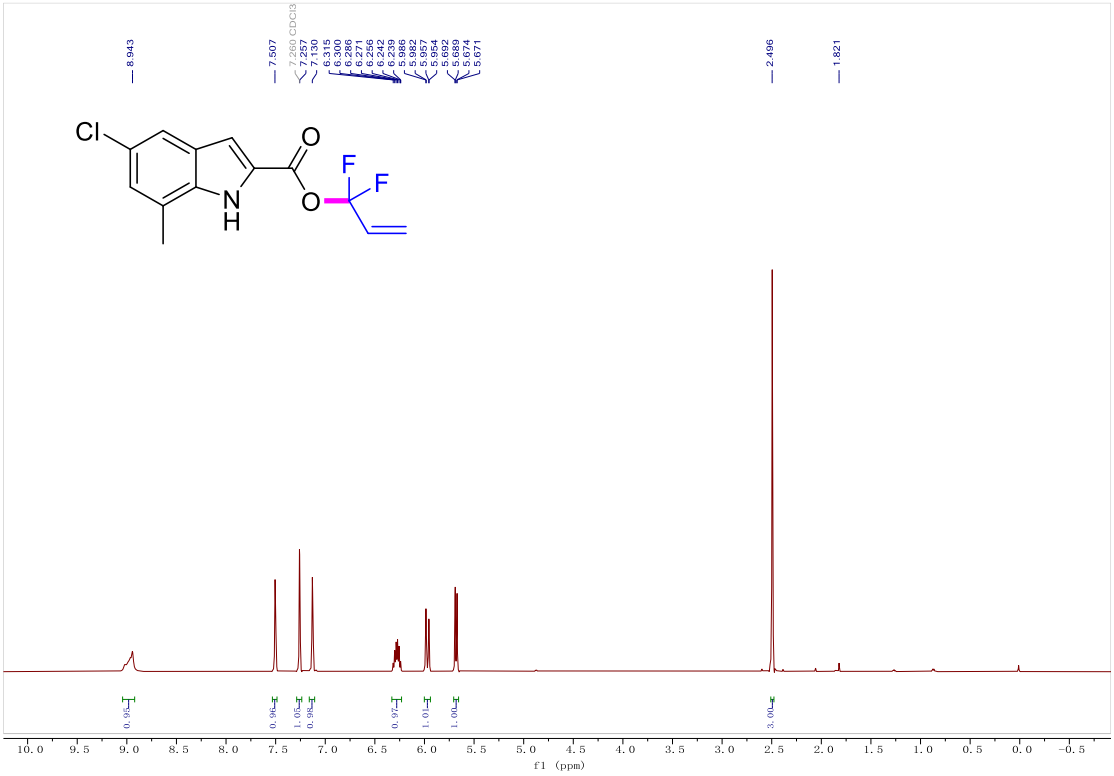


Figure S88. Compound 3ac ^{13}C NMR (150 MHz, $CDCl_3$)

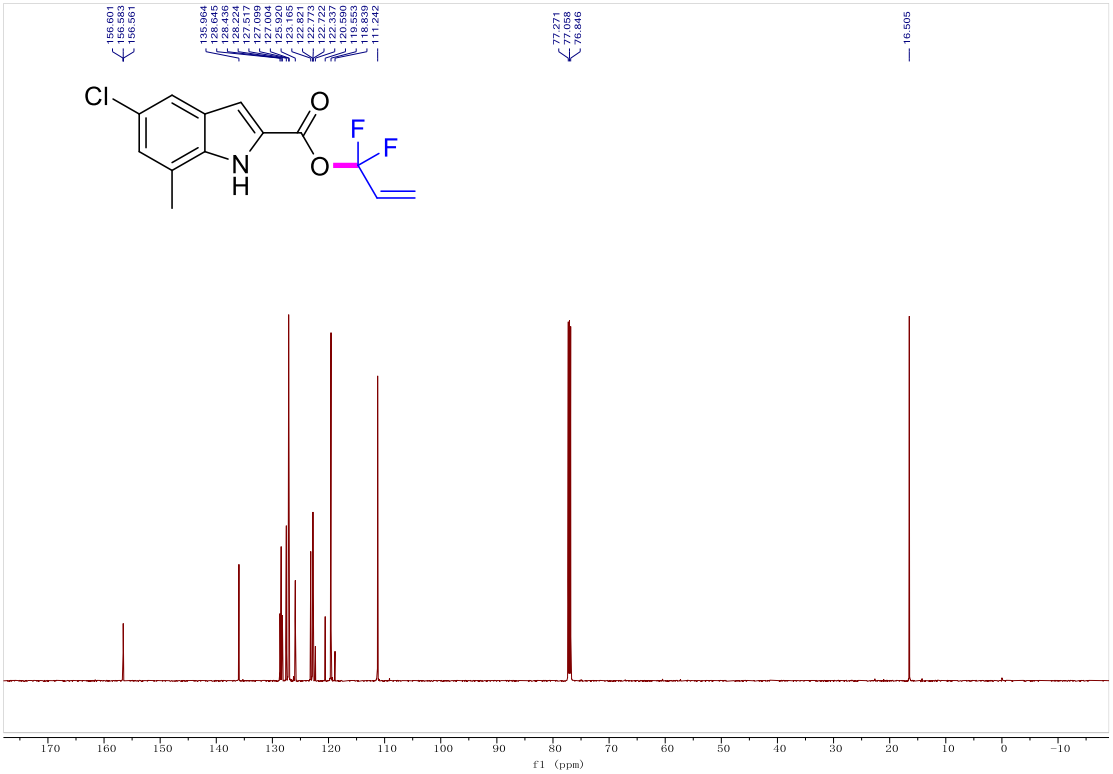


Figure S89. Compound 3ac ^{19}F NMR (565 MHz, $CDCl_3$)

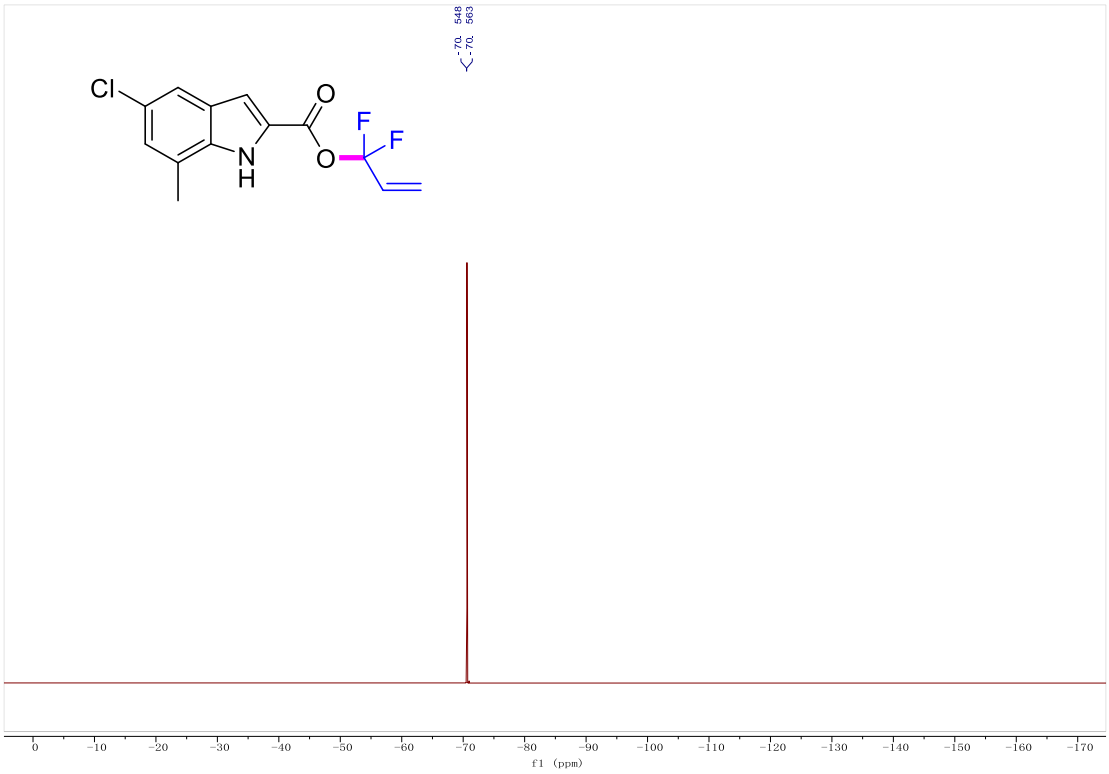


Figure S90. Compound 3ad ^{1}H NMR (600 MHz, $CDCl_3$)

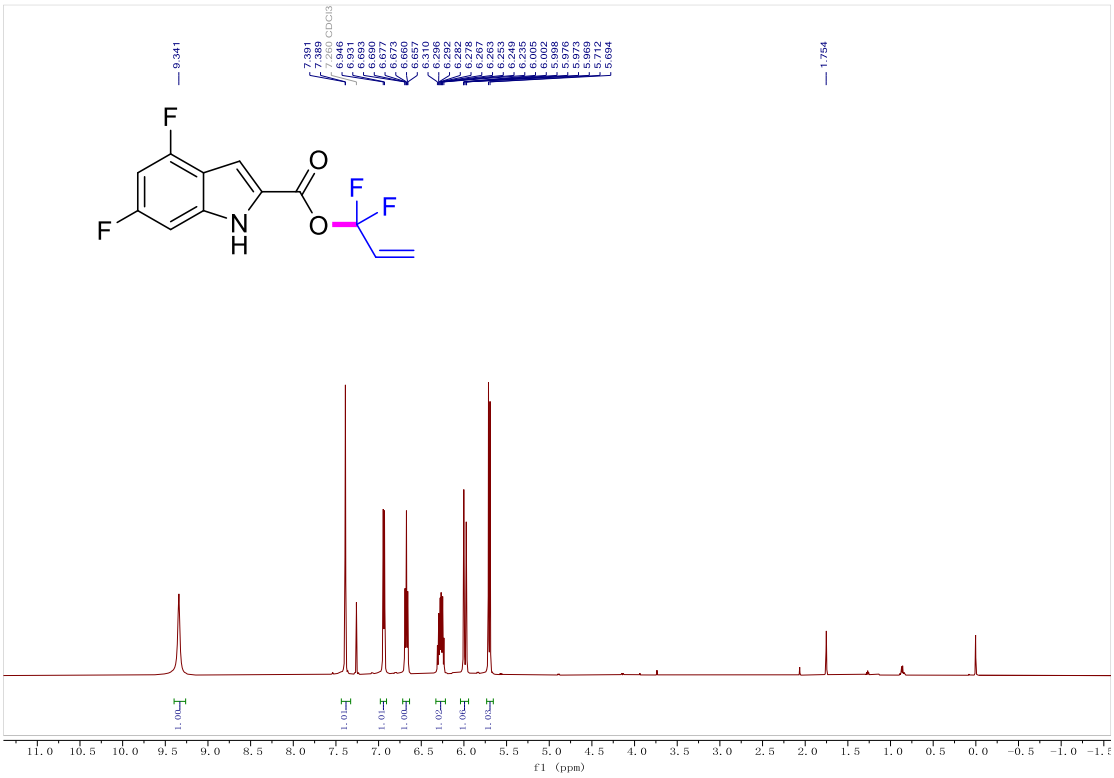


Figure S91. Compound 3ad ^{13}C NMR (150 MHz, $CDCl_3$)

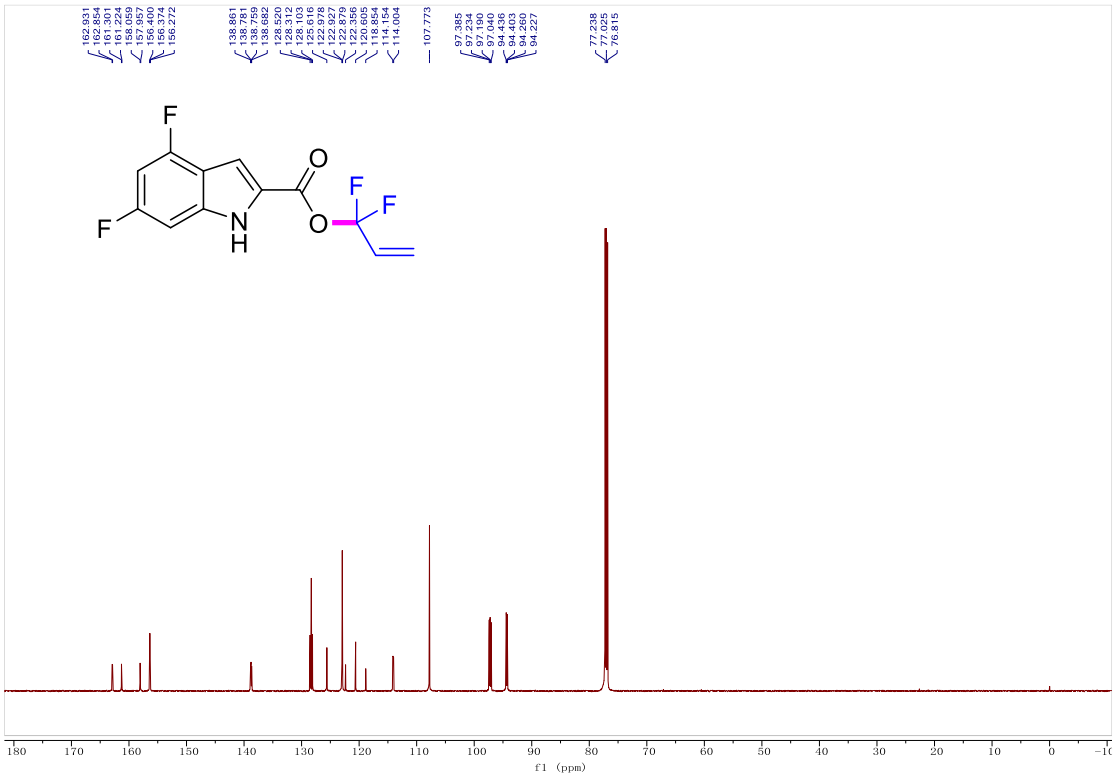


Figure S92. Compound 3ad ^{19}F NMR (565 MHz, $CDCl_3$)

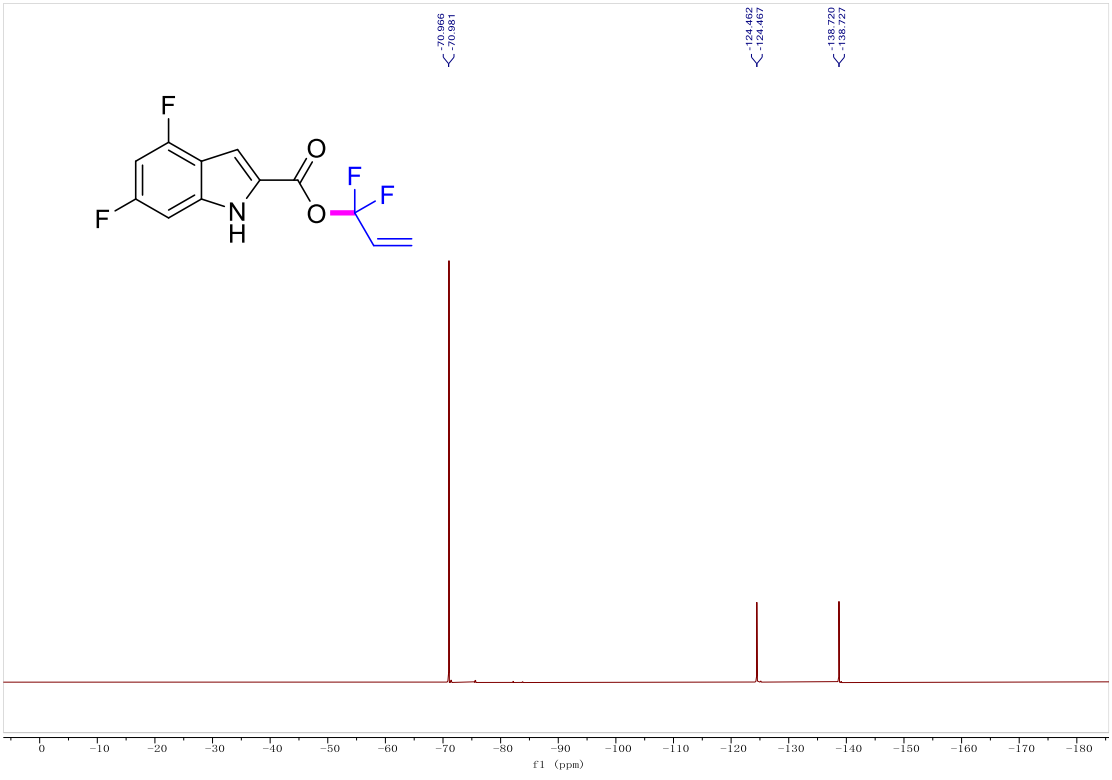


Figure S93. Compound 3ae **^{1}H NMR (600 MHz, $CDCl_3$)**

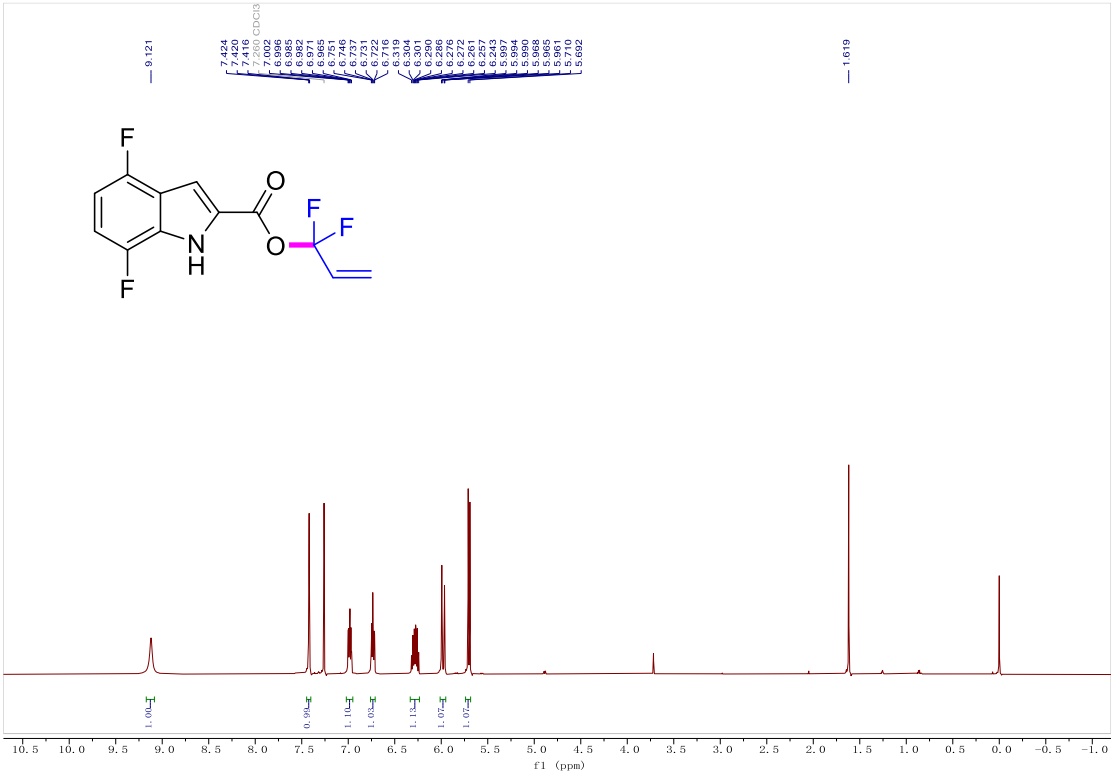


Figure S94. Compound 3ae **^{13}C NMR (150 MHz, $CDCl_3$)**

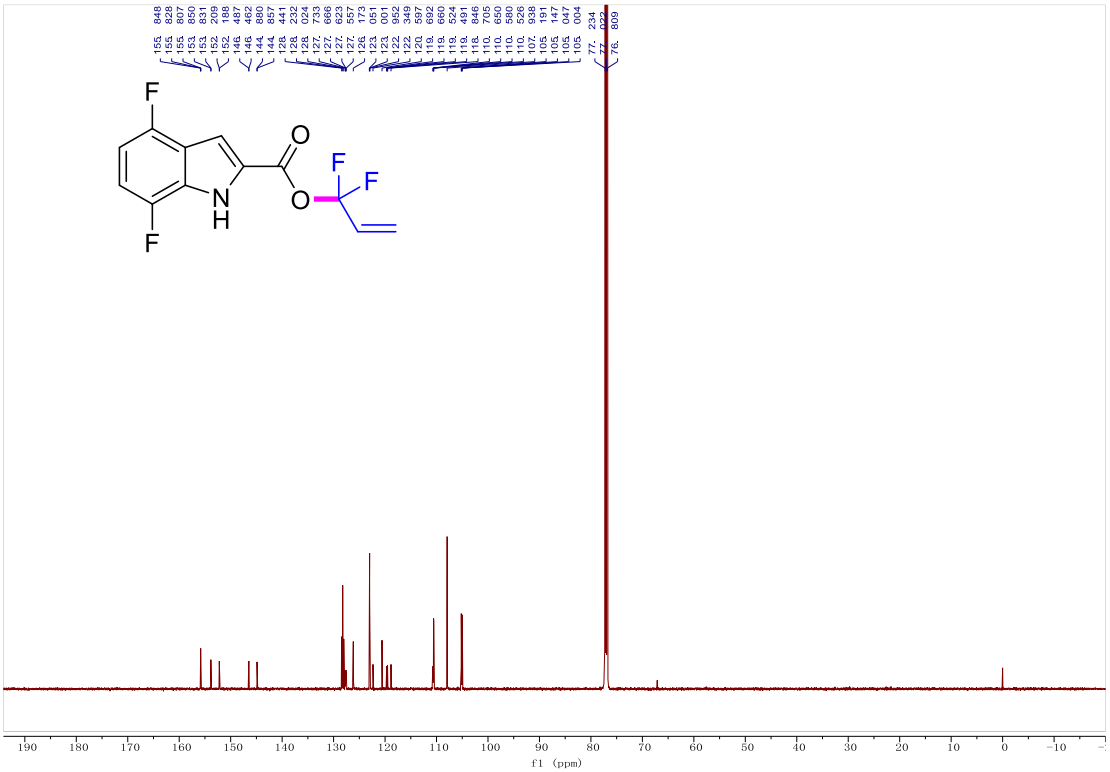


Figure S95. Compound 3ae ^{19}F NMR (565 MHz, $CDCl_3$)

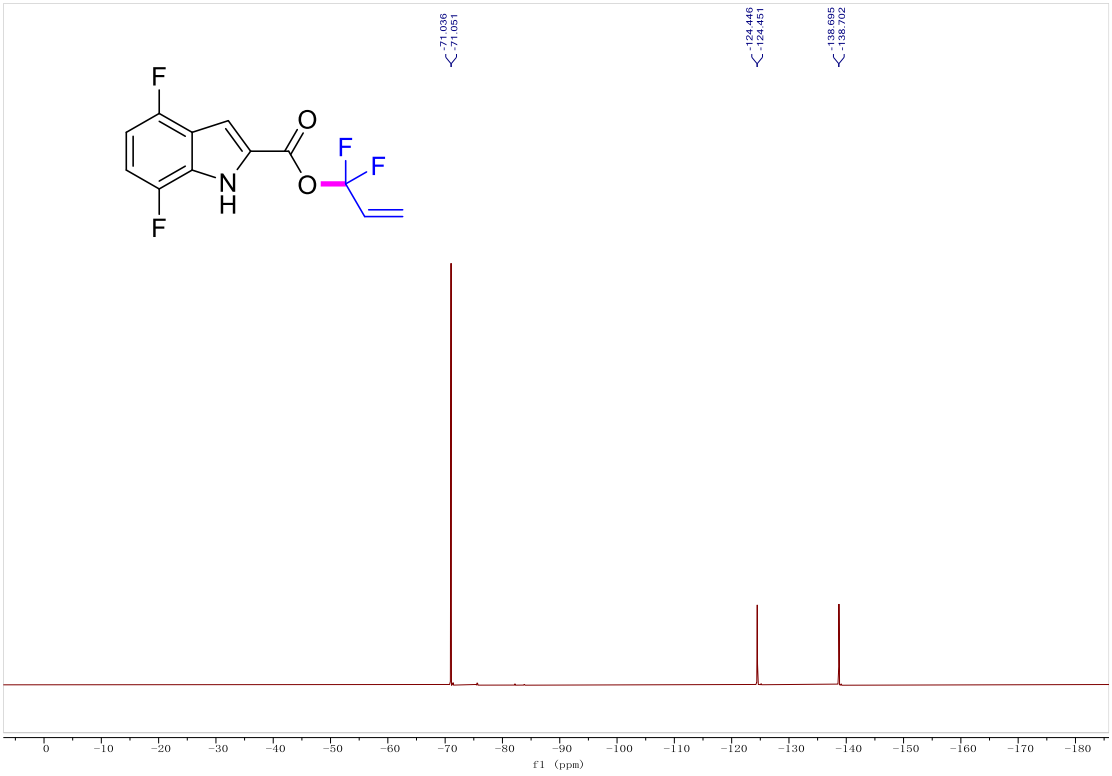


Figure S96. Compound 3af ^{1}H NMR (600 MHz, $CDCl_3$)

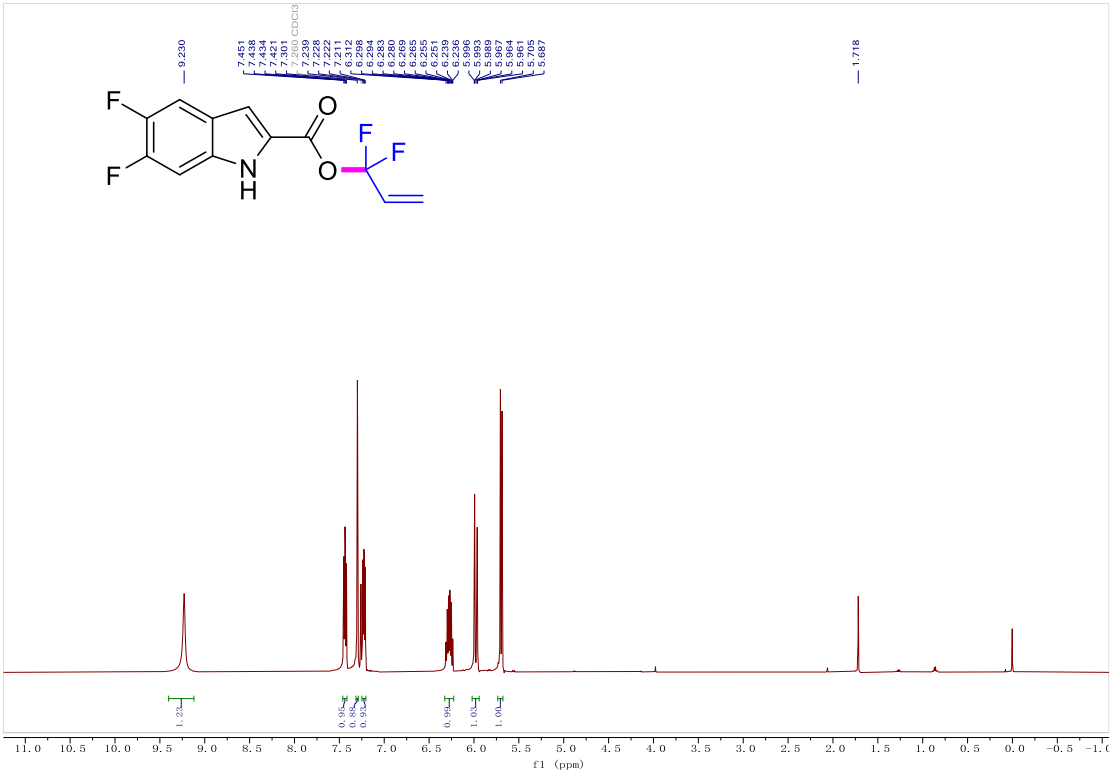


Figure S97. Compound 3af ^{13}C NMR (150 MHz, $CDCl_3$)

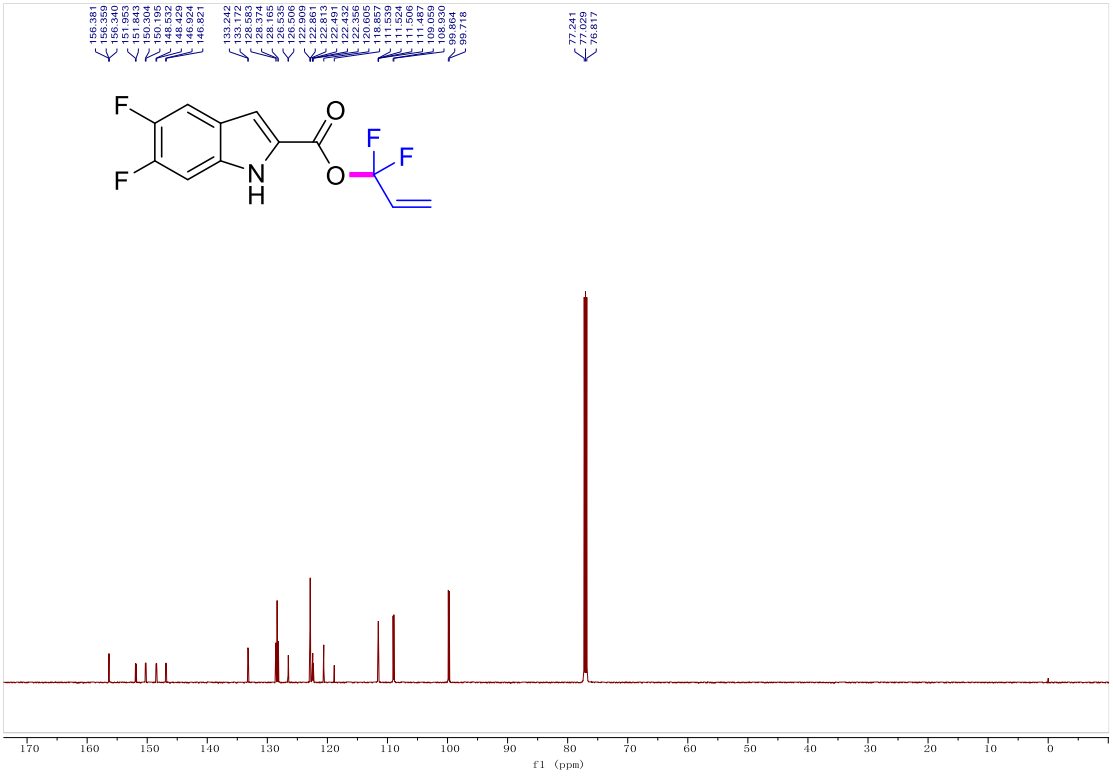


Figure S98. Compound 3af ^{19}F NMR (565 MHz, $CDCl_3$)

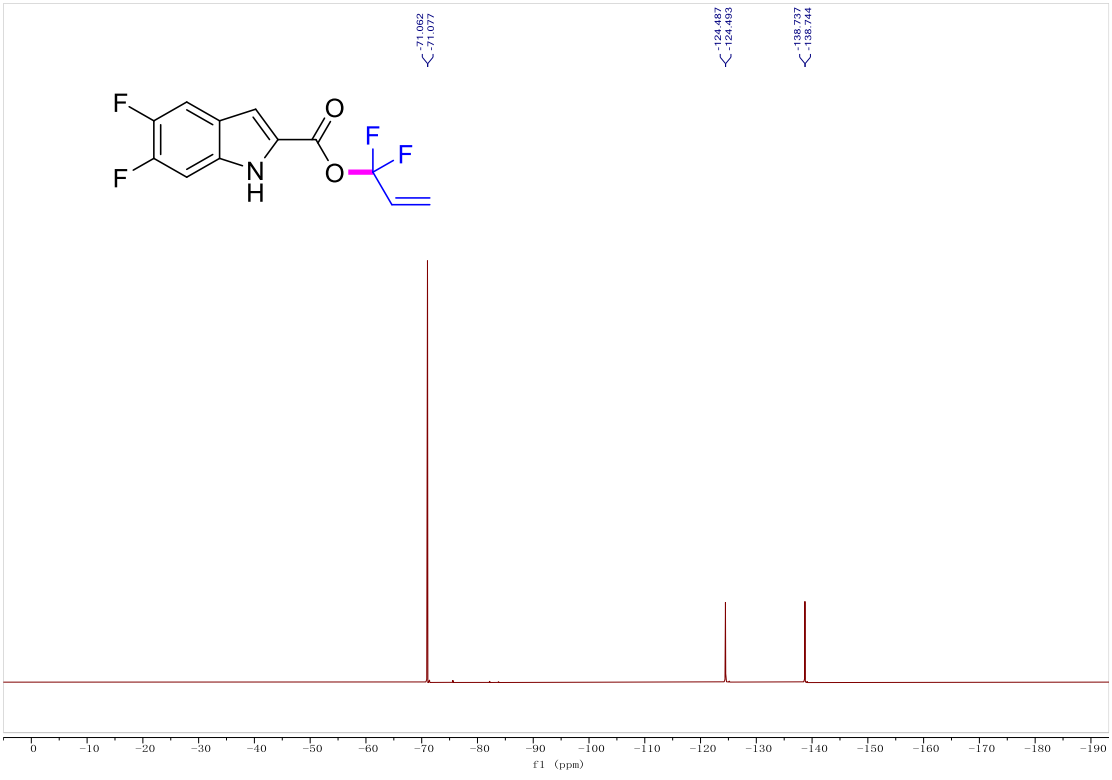


Figure S99. Compound 3ag **^{1}H NMR (600 MHz, $CDCl_3$)**

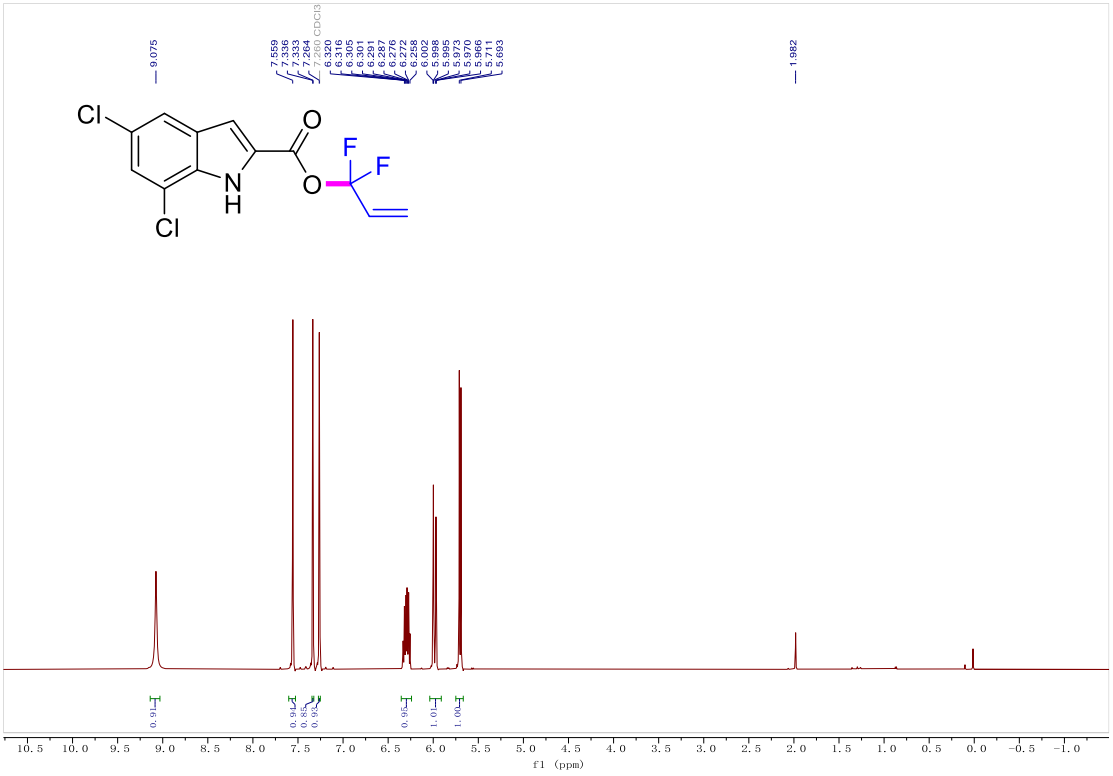


Figure S100. Compound 3ag **^{13}C NMR (150 MHz, $CDCl_3$)**

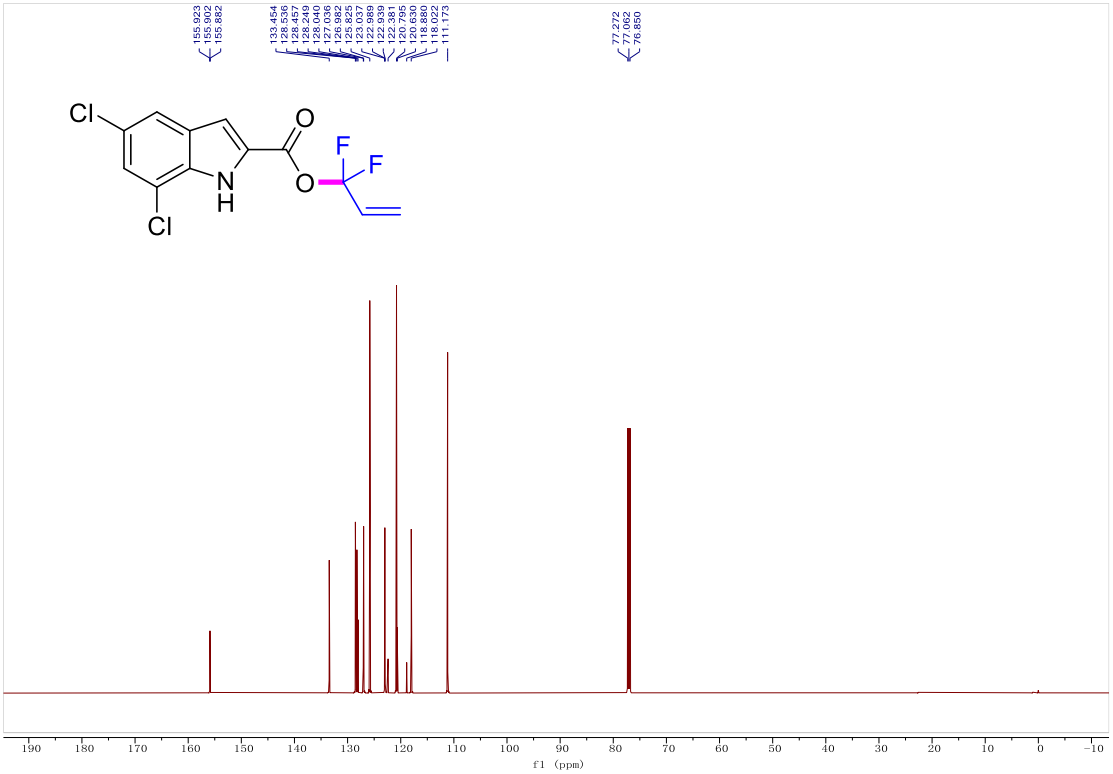


Figure S101. Compound 3ag **^{19}F NMR (565 MHz, $CDCl_3$)**

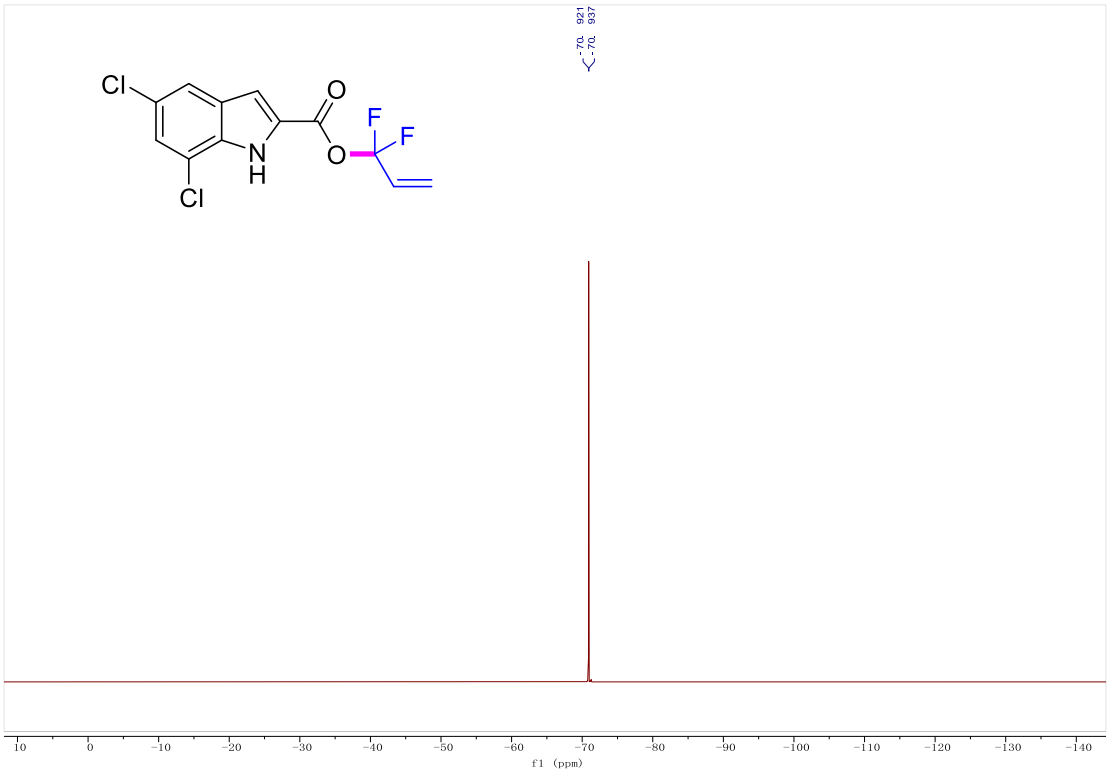


Figure S102. Compound 3ah **^{1}H NMR (600 MHz, $CDCl_3$)**

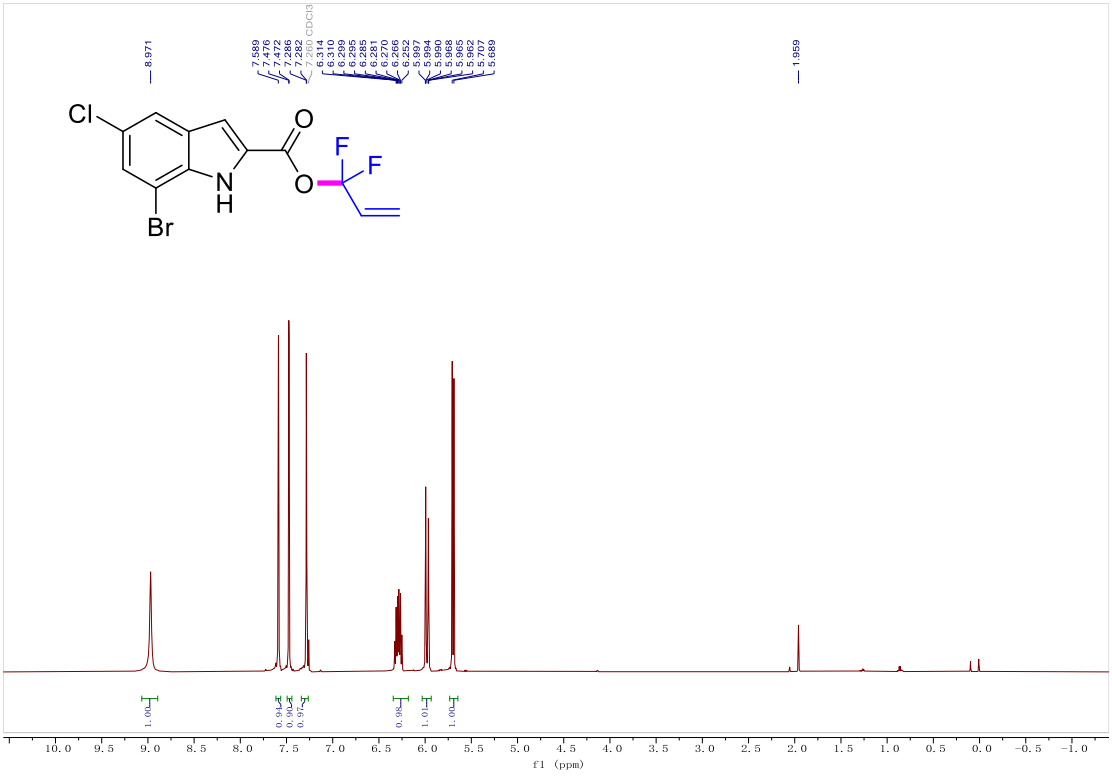


Figure S103. Compound 3ah ^{13}C NMR (150 MHz, $CDCl_3$)

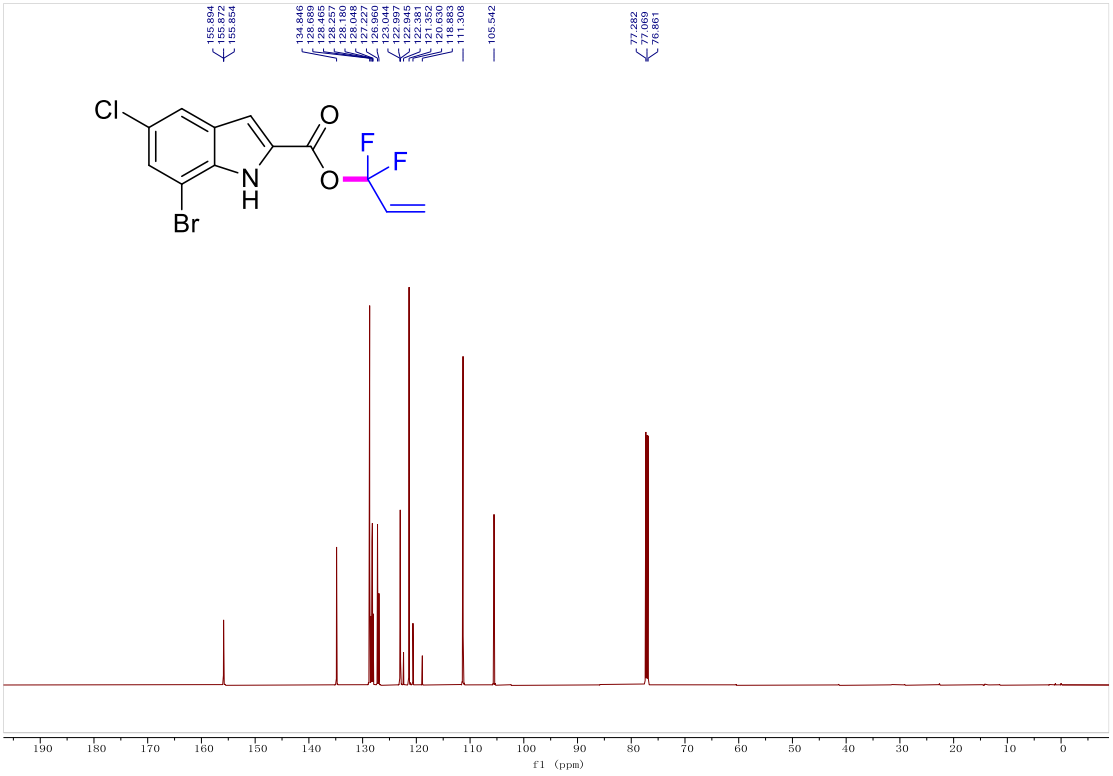


Figure S104. Compound 3ah ^{19}F NMR (565 MHz, $CDCl_3$)

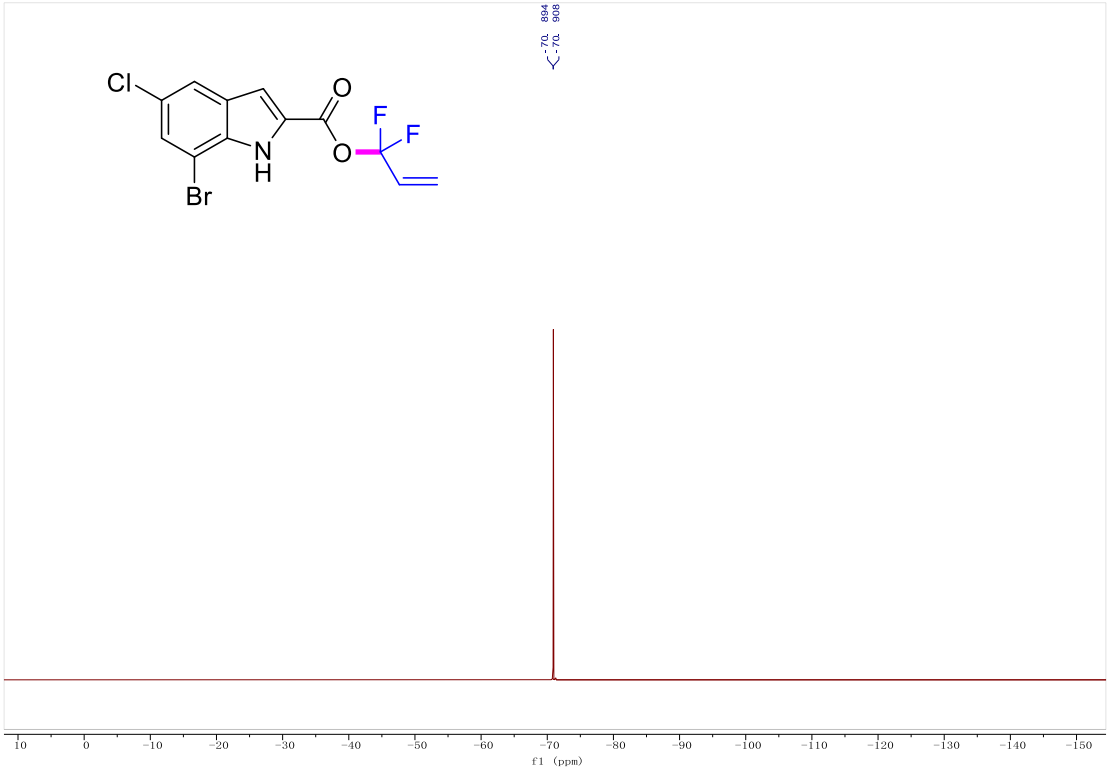


Figure S105. Compound 5a ^{1}H NMR (600 MHz, $CDCl_3$)

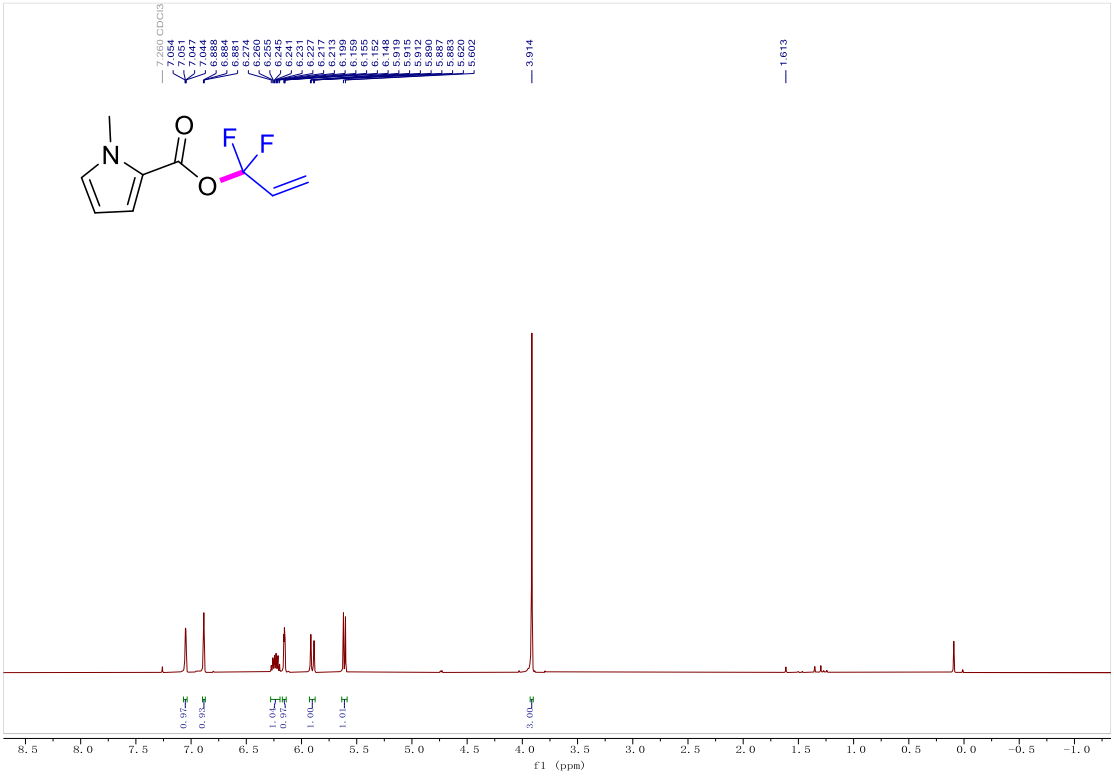


Figure S106. Compound 5a ^{13}C NMR (150 MHz, $CDCl_3$)

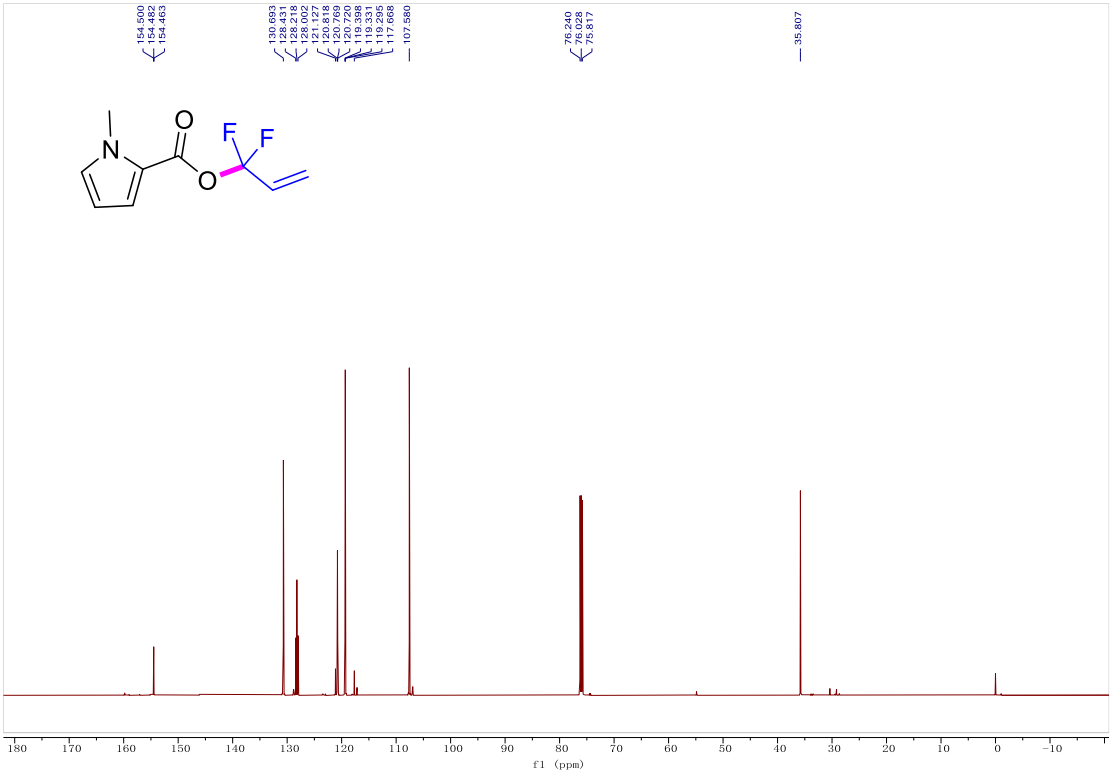


Figure S107. Compound 5a **^{19}F NMR (565 MHz, $CDCl_3$)**

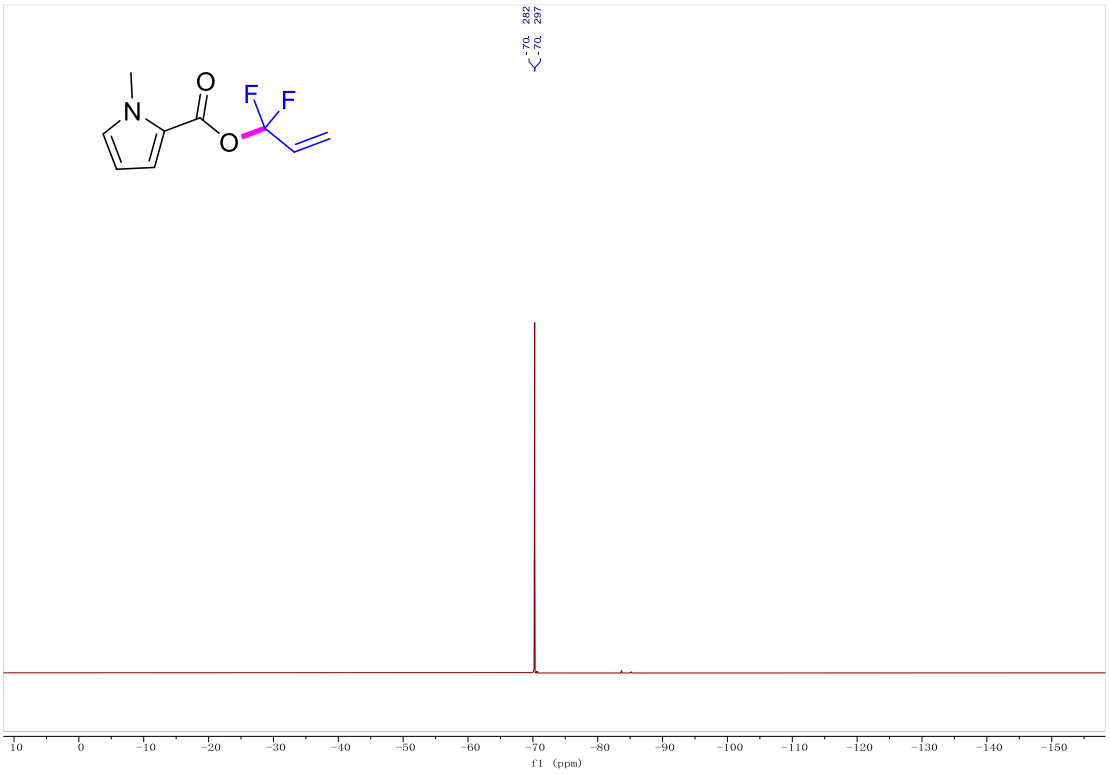


Figure S108. Compound 5b **^{1}H NMR (600 MHz, $CDCl_3$)**

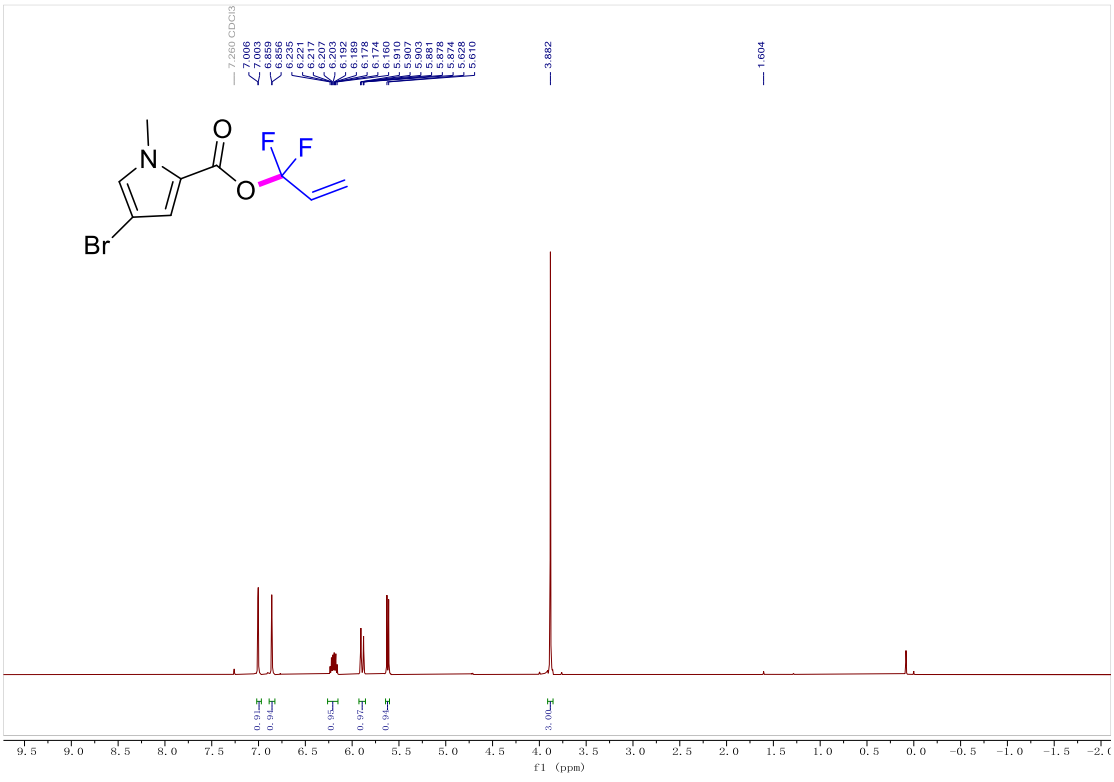


Figure S109. Compound 5b **^{13}C NMR (150 MHz, $CDCl_3$)**

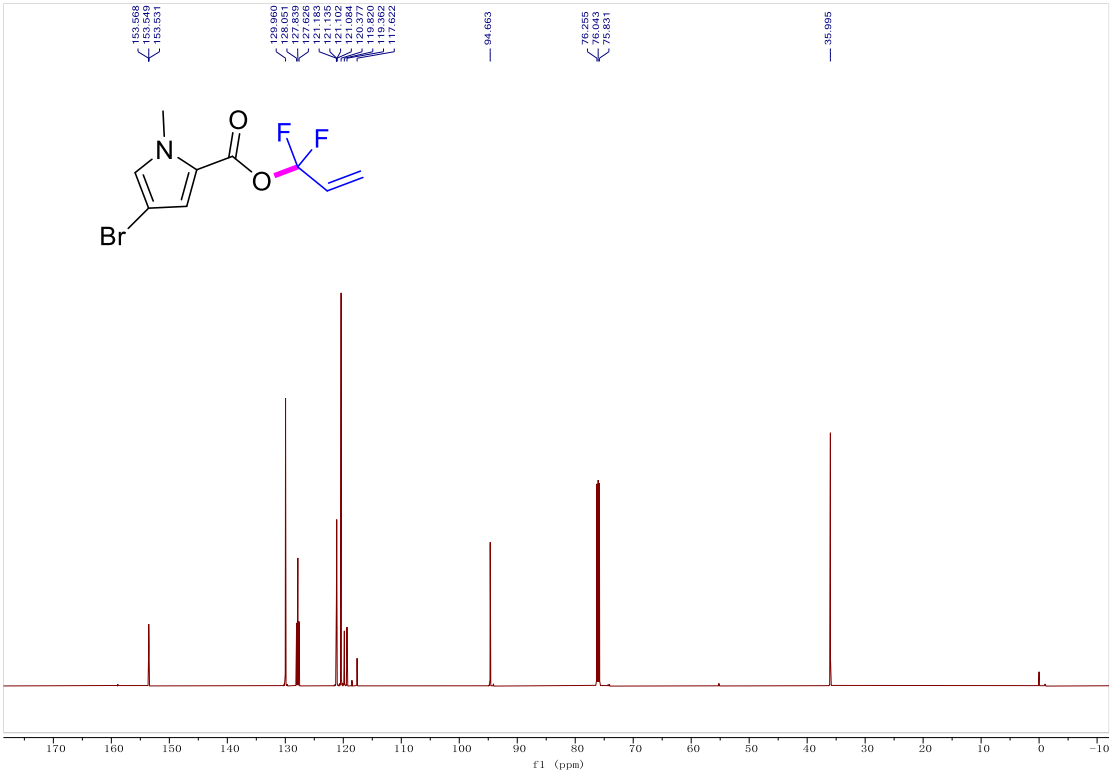


Figure S110. Compound 5b **^{19}F NMR (565 MHz, $CDCl_3$)**

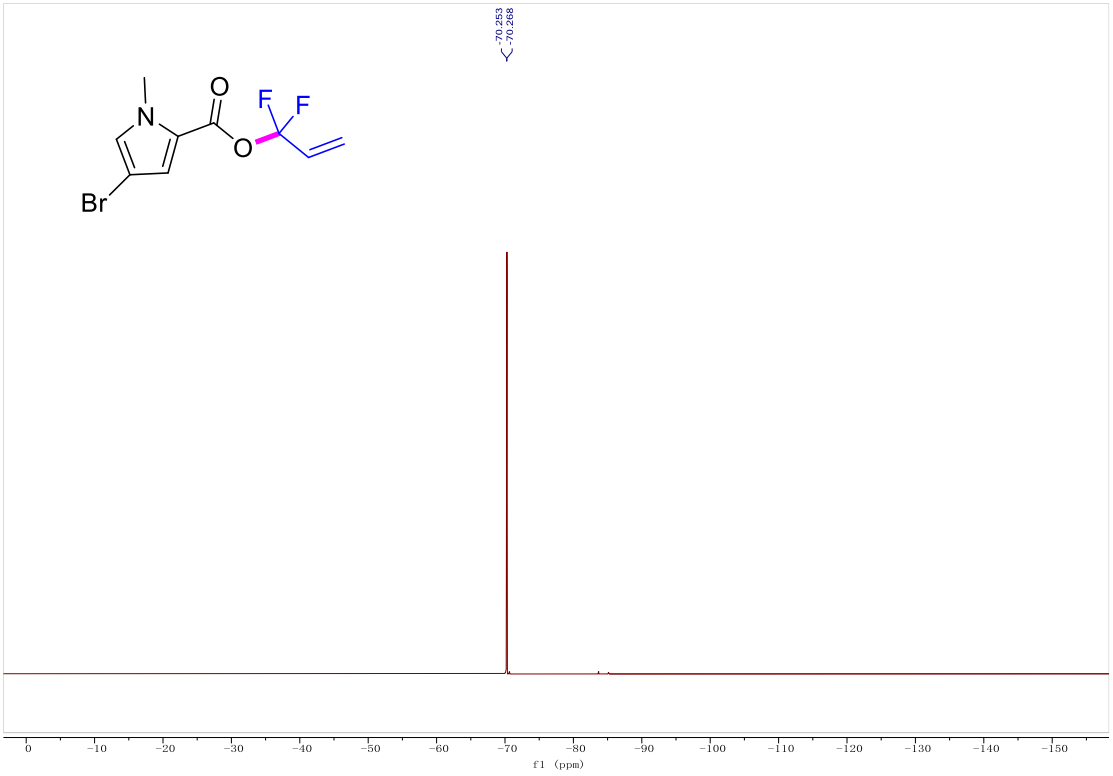


Figure S111. Compound 5c ^{1}H NMR (600 MHz, $CDCl_3$)

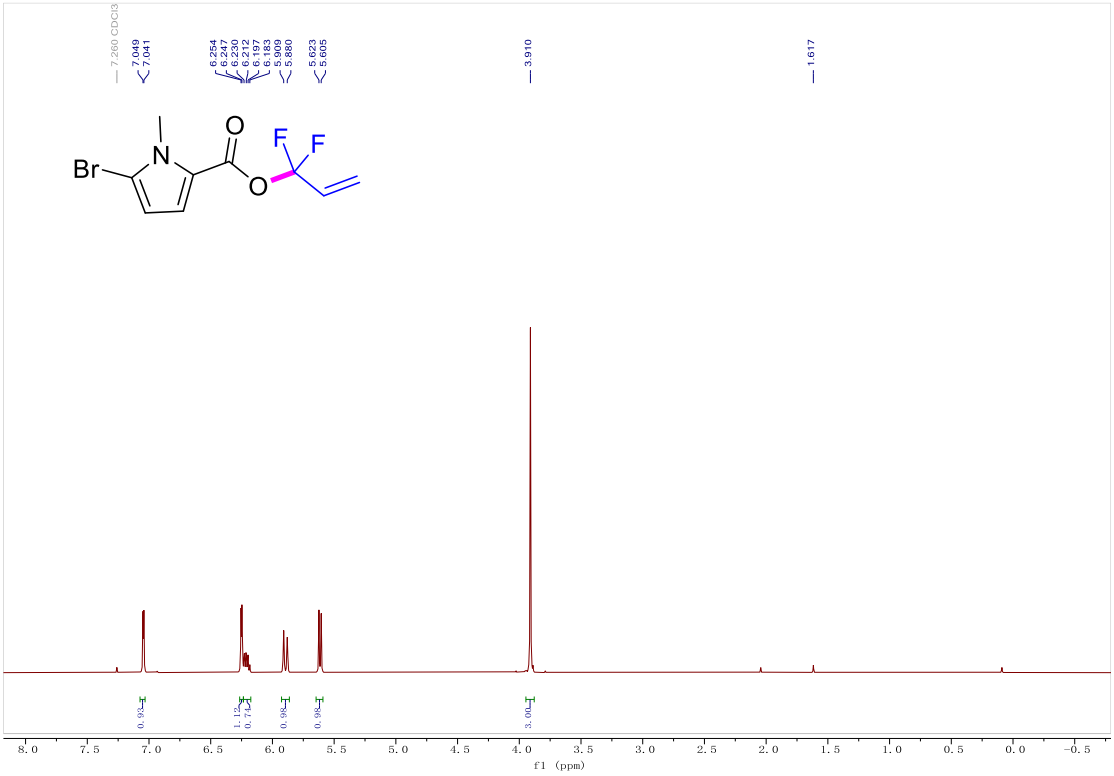


Figure S112. Compound 5c ^{13}C NMR (150 MHz, $CDCl_3$)

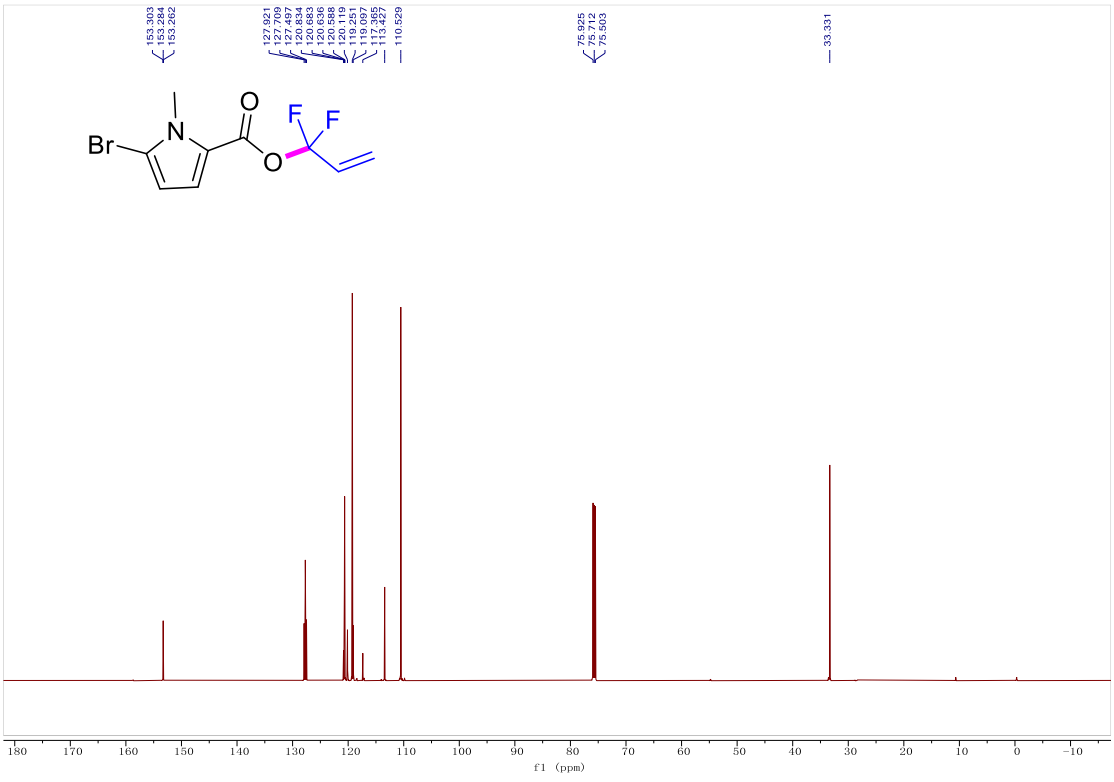


Figure S113. Compound 5c ^{19}F NMR (565 MHz, $CDCl_3$)

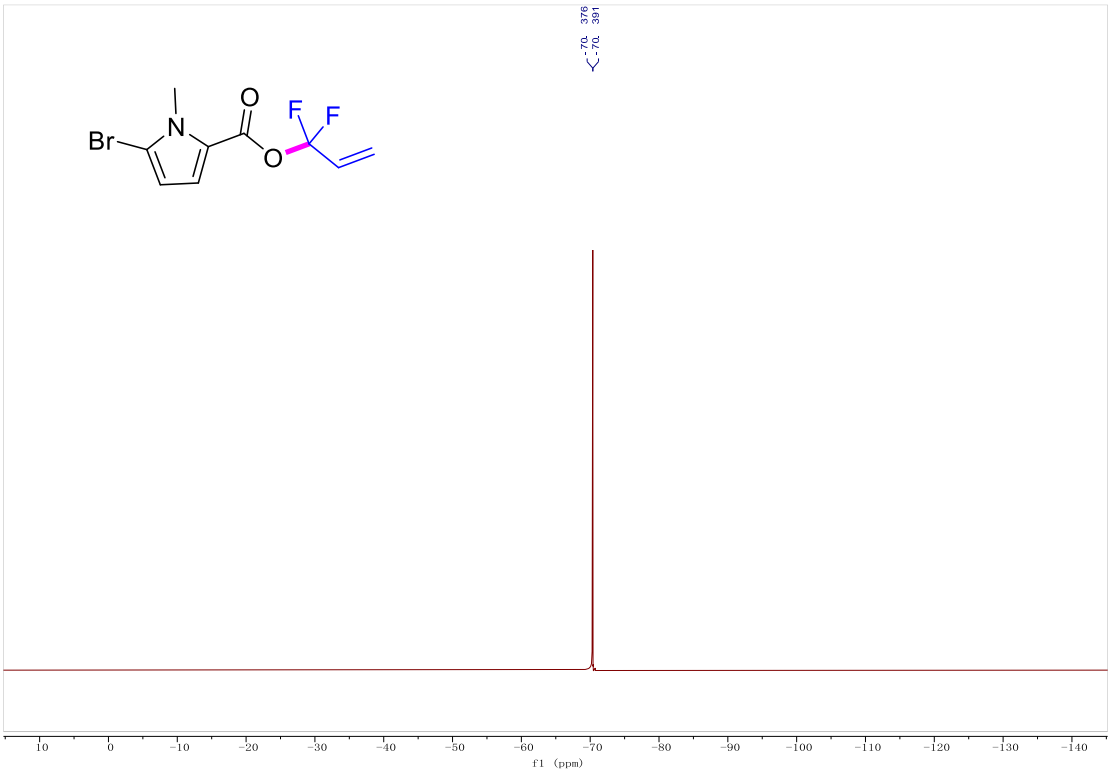


Figure S114. Compound 5d ^{1}H NMR (600 MHz, $CDCl_3$)

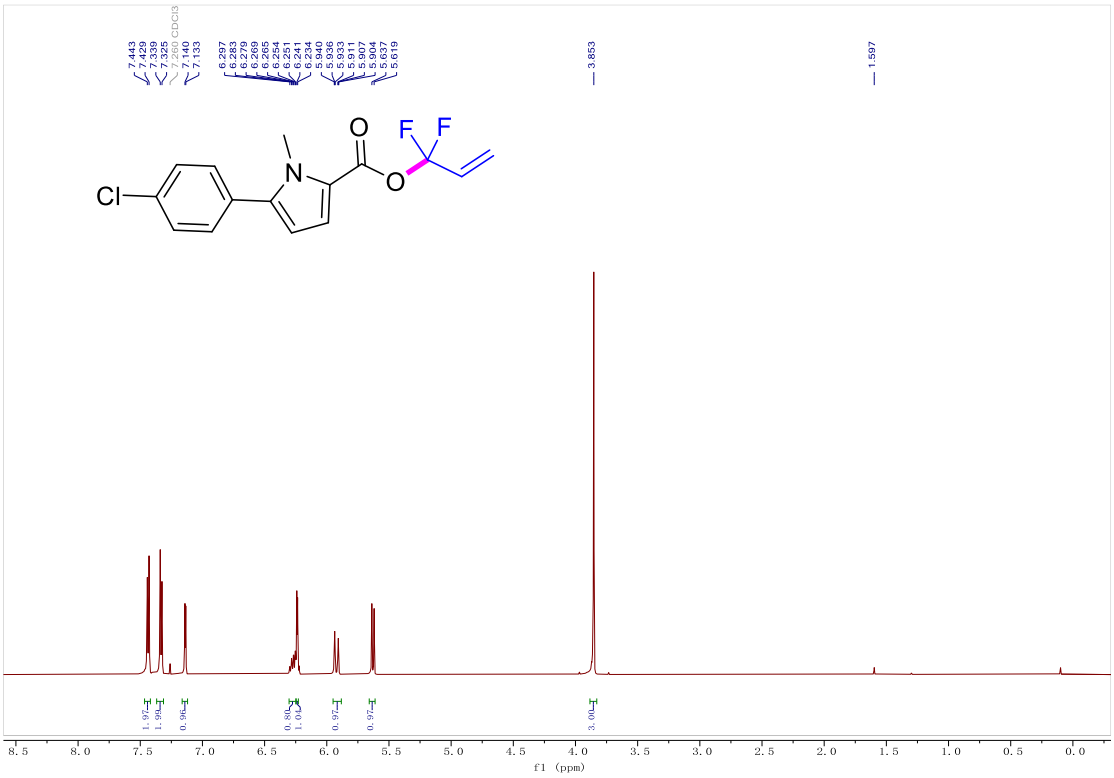


Figure S115. Compound 5d ^{13}C NMR (150 MHz, $CDCl_3$)

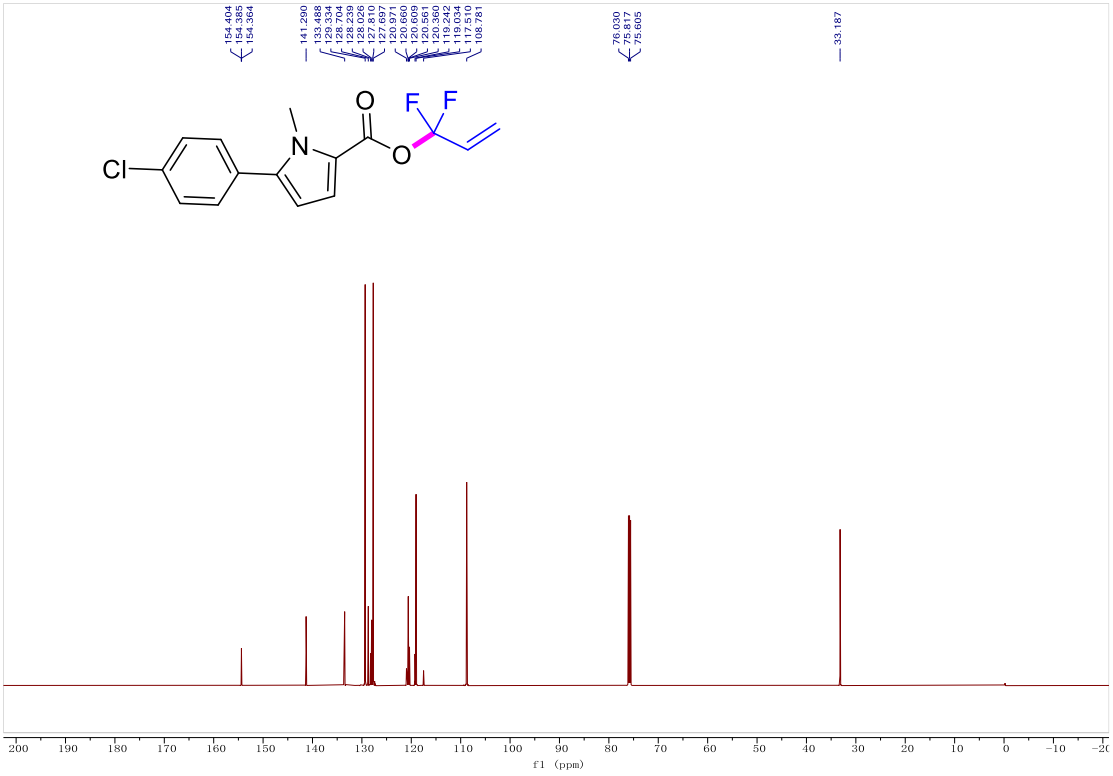


Figure S116. Compound 5d ^{19}F NMR (565 MHz, $CDCl_3$)

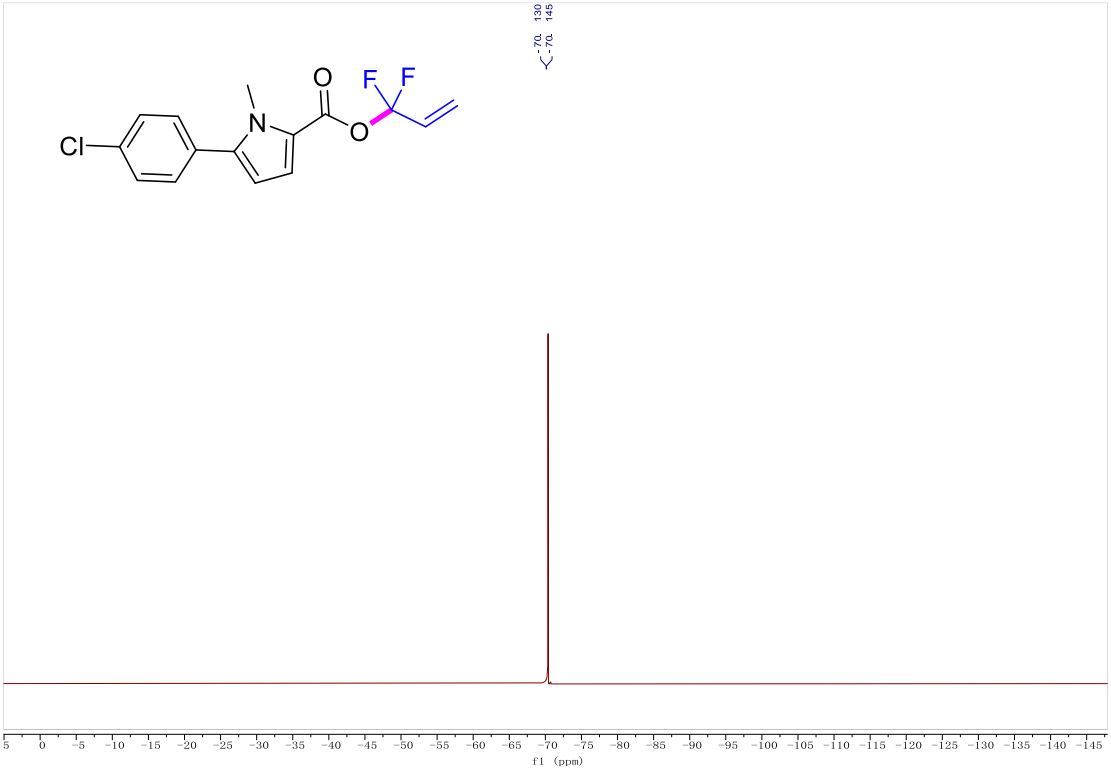


Figure S117. Compound 7a ^{1}H NMR (600 MHz, $CDCl_3$)

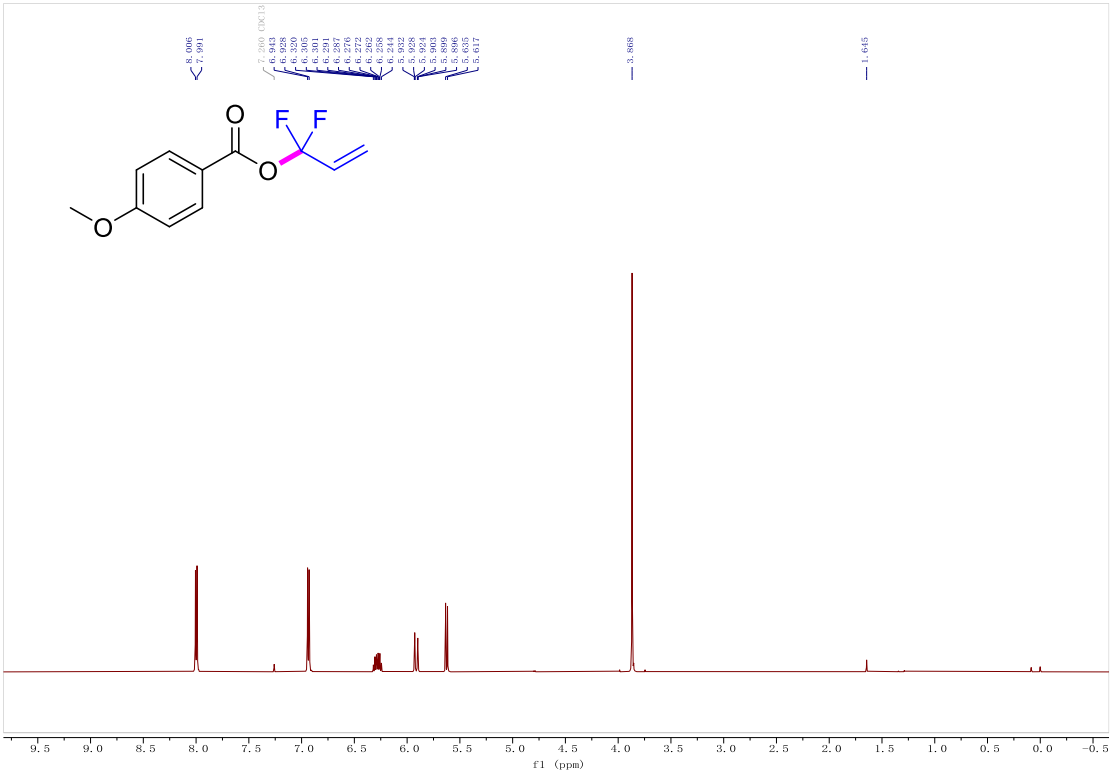


Figure S118. Compound 7a ^{13}C NMR (150 MHz, $CDCl_3$)

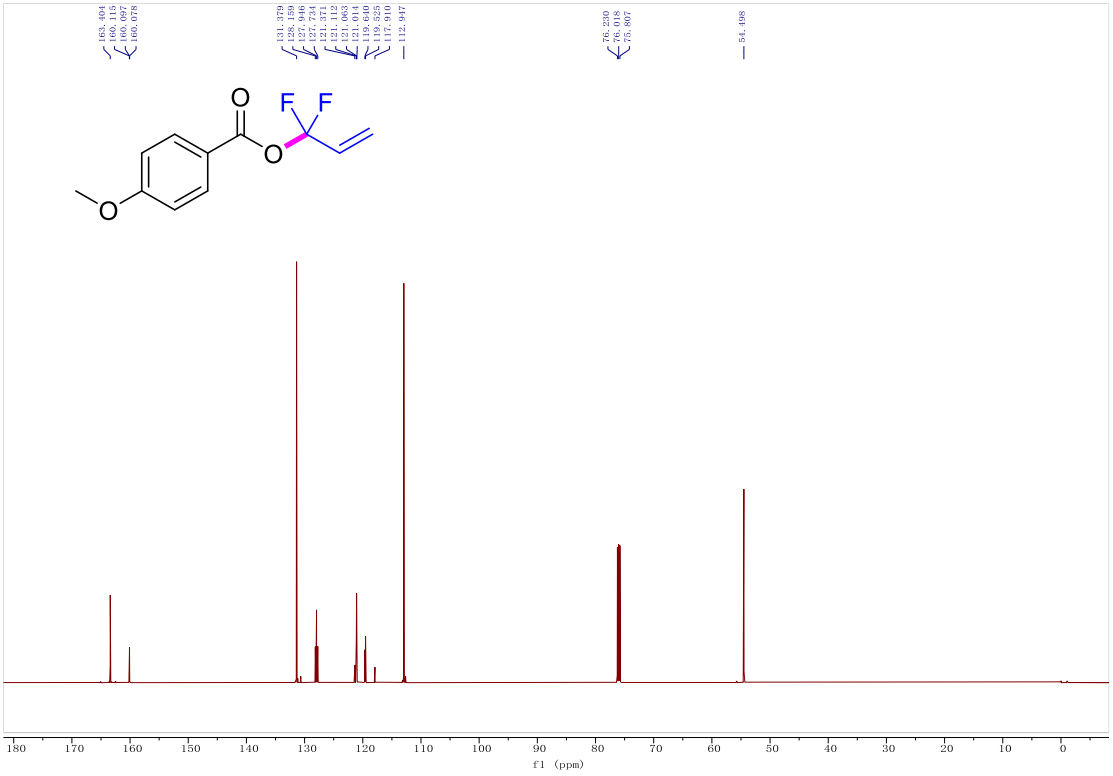


Figure S119. Compound 7a **^{19}F NMR (565 MHz, $CDCl_3$)**

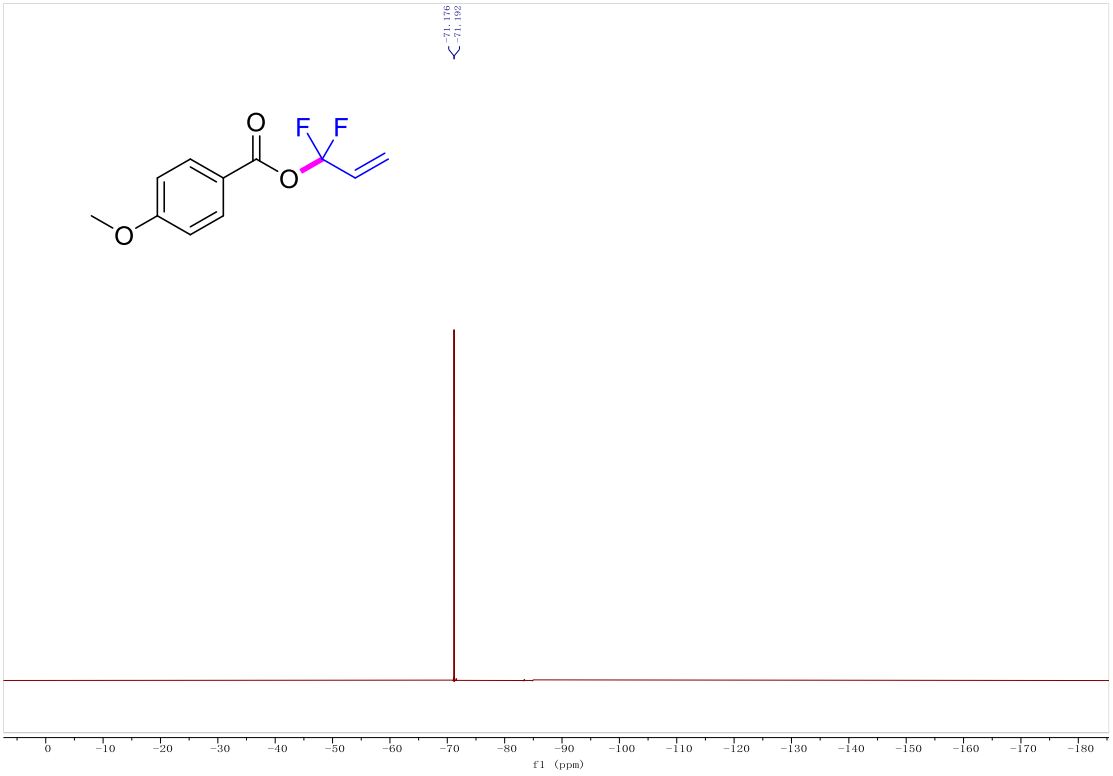


Figure S120. Compound 7b **^{1}H NMR (600 MHz, $CDCl_3$)**

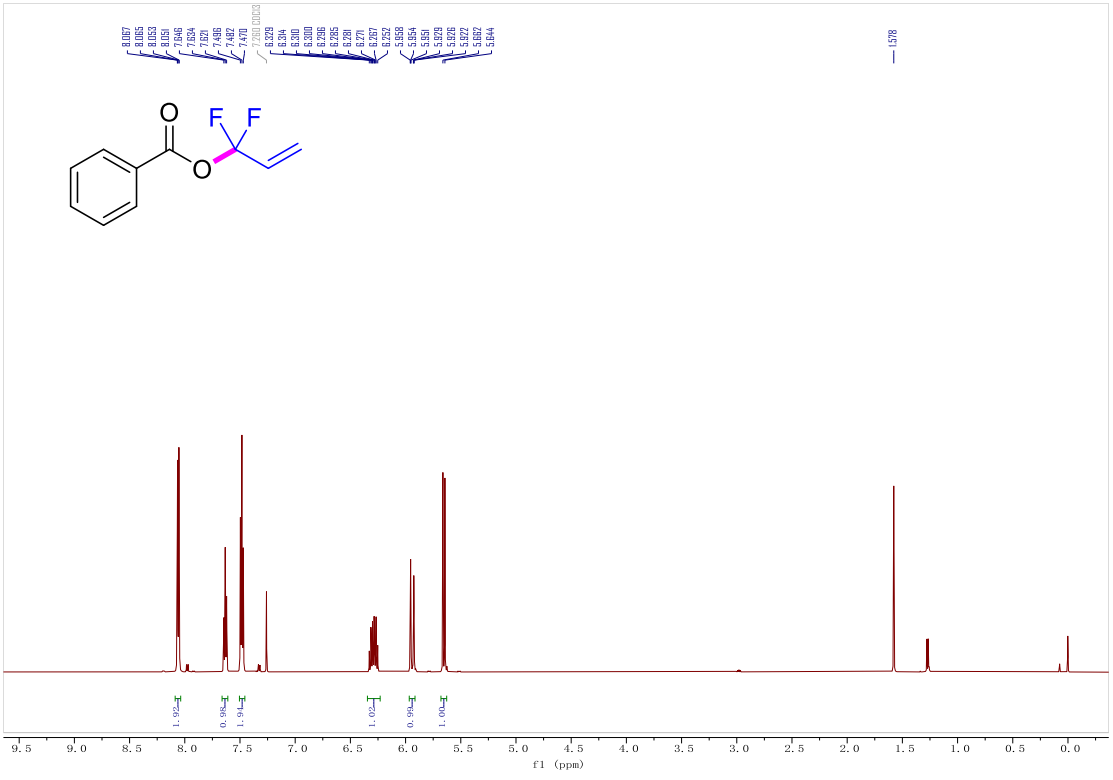


Figure S121. Compound 7b ^{13}C NMR (150 MHz, $CDCl_3$)

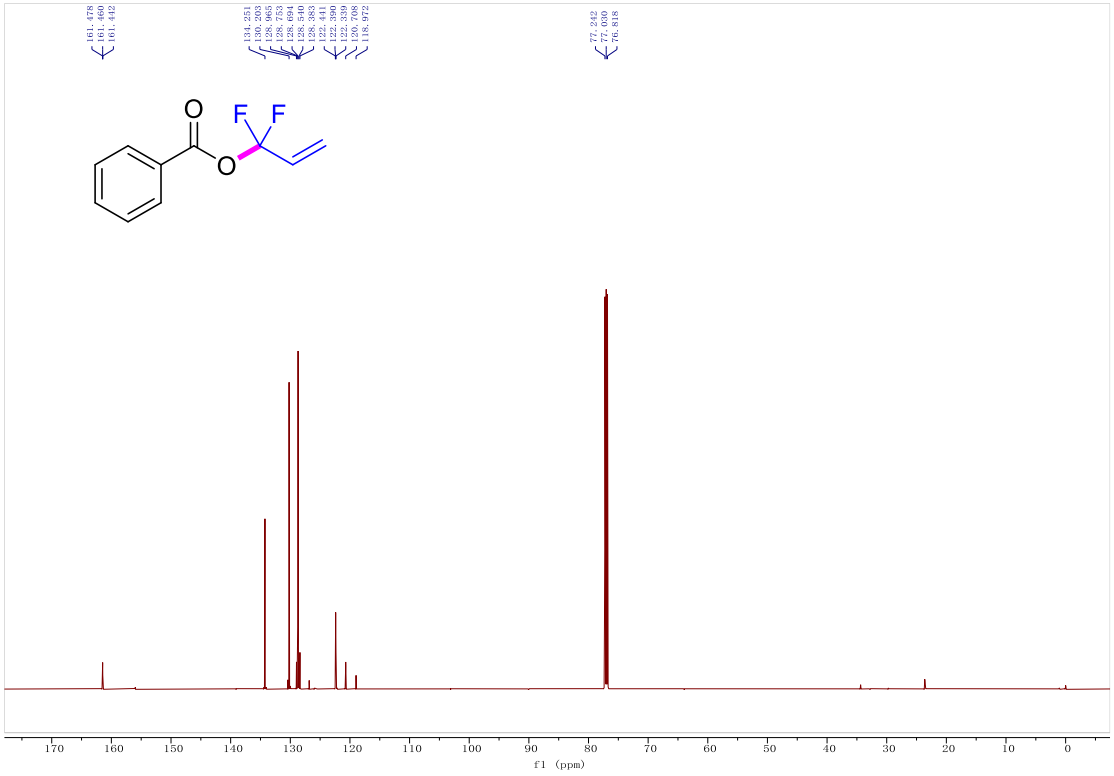


Figure S122. Compound 7b ^{19}F NMR (565 MHz, $CDCl_3$)

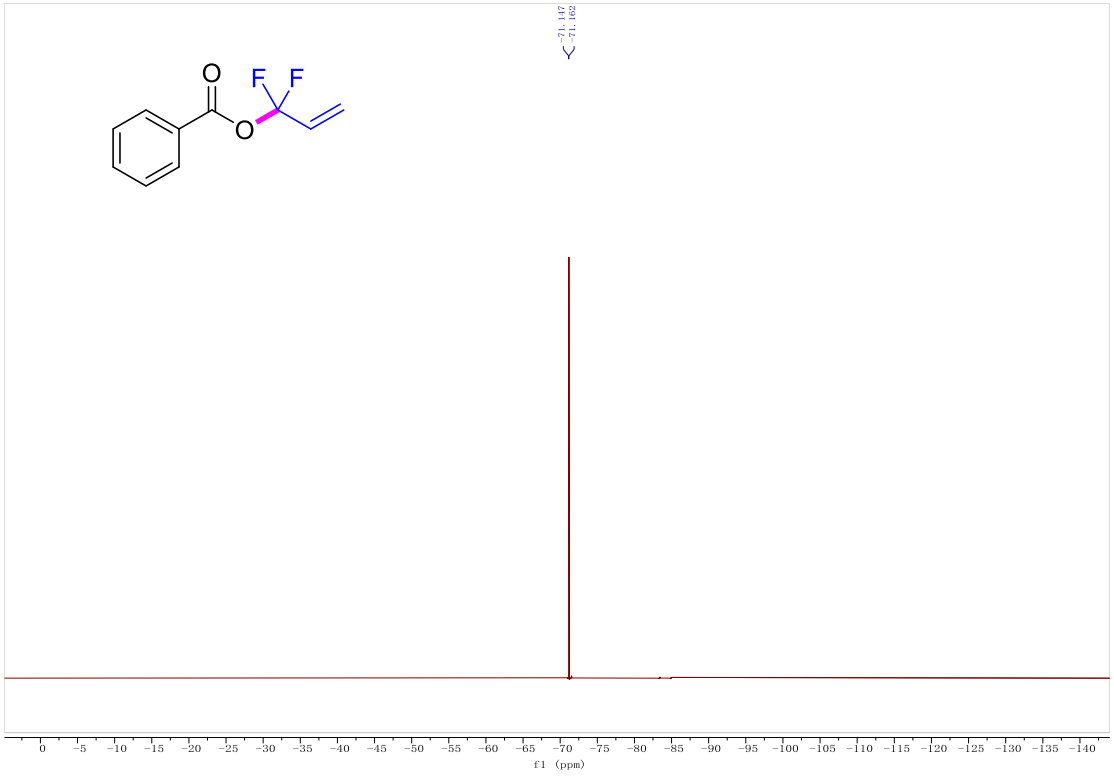


Figure S123. Compound 7c ^{1}H NMR (600 MHz, $CDCl_3$)

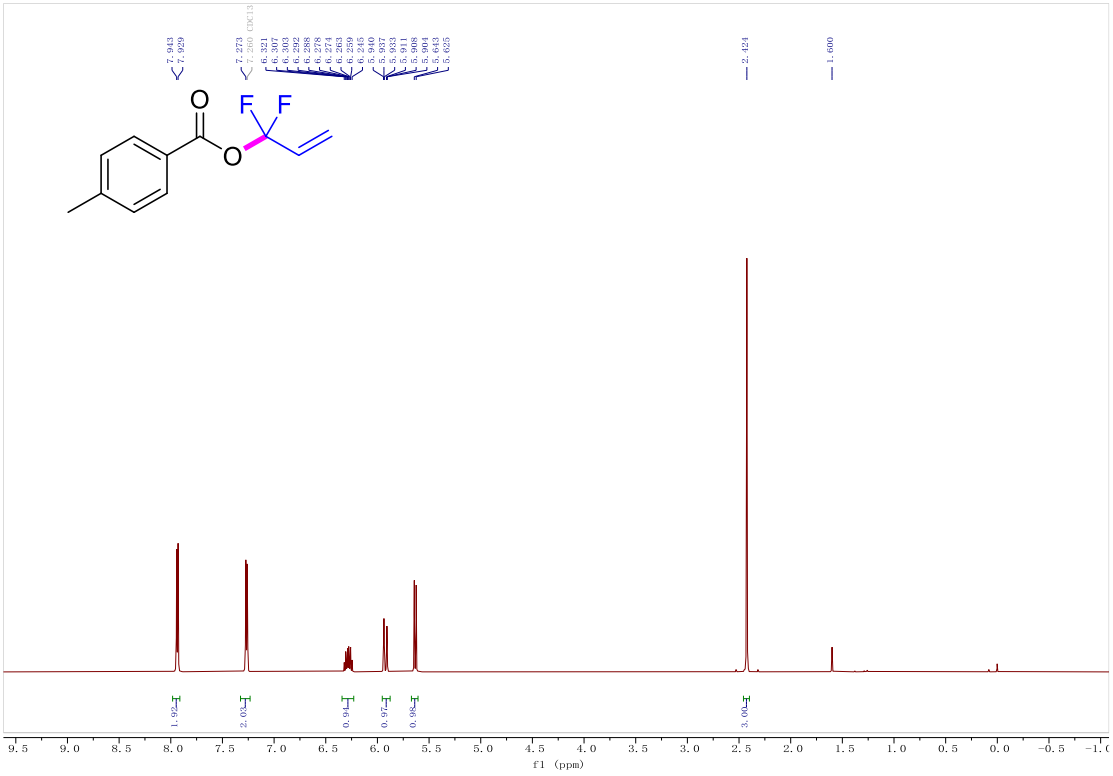


Figure S124. Compound 7c ^{13}C NMR (150 MHz, $CDCl_3$)

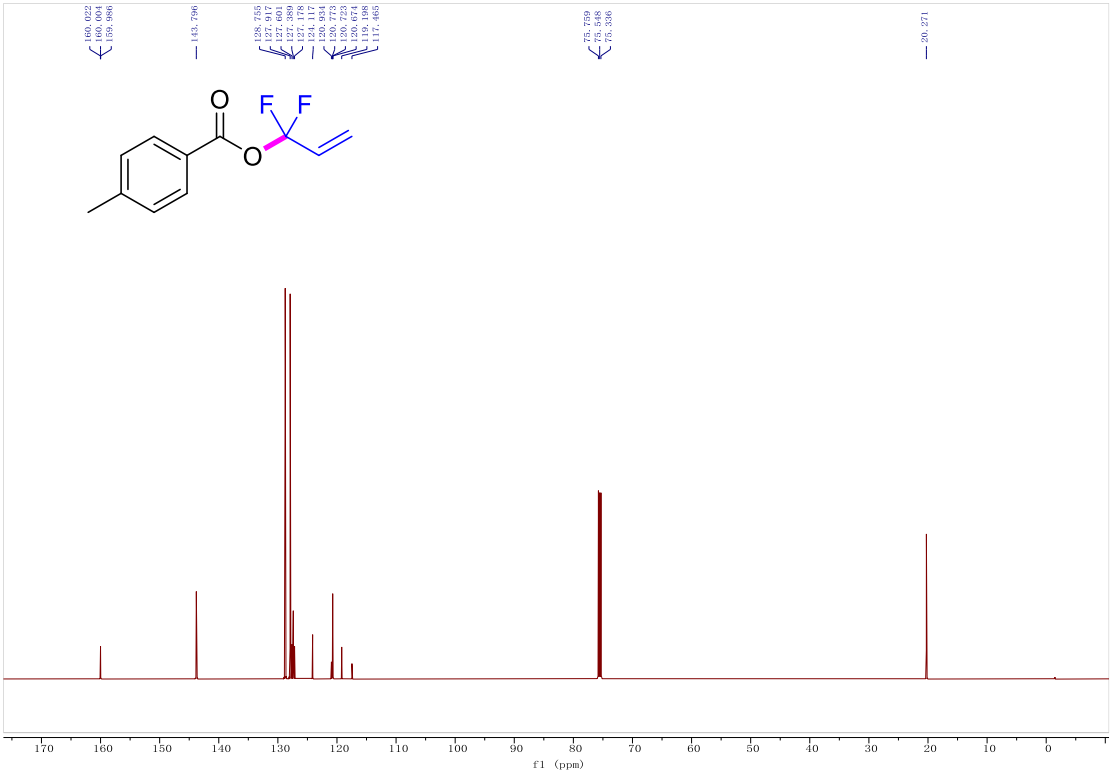


Figure S125. Compound 7c ^{19}F NMR (565 MHz, $CDCl_3$)

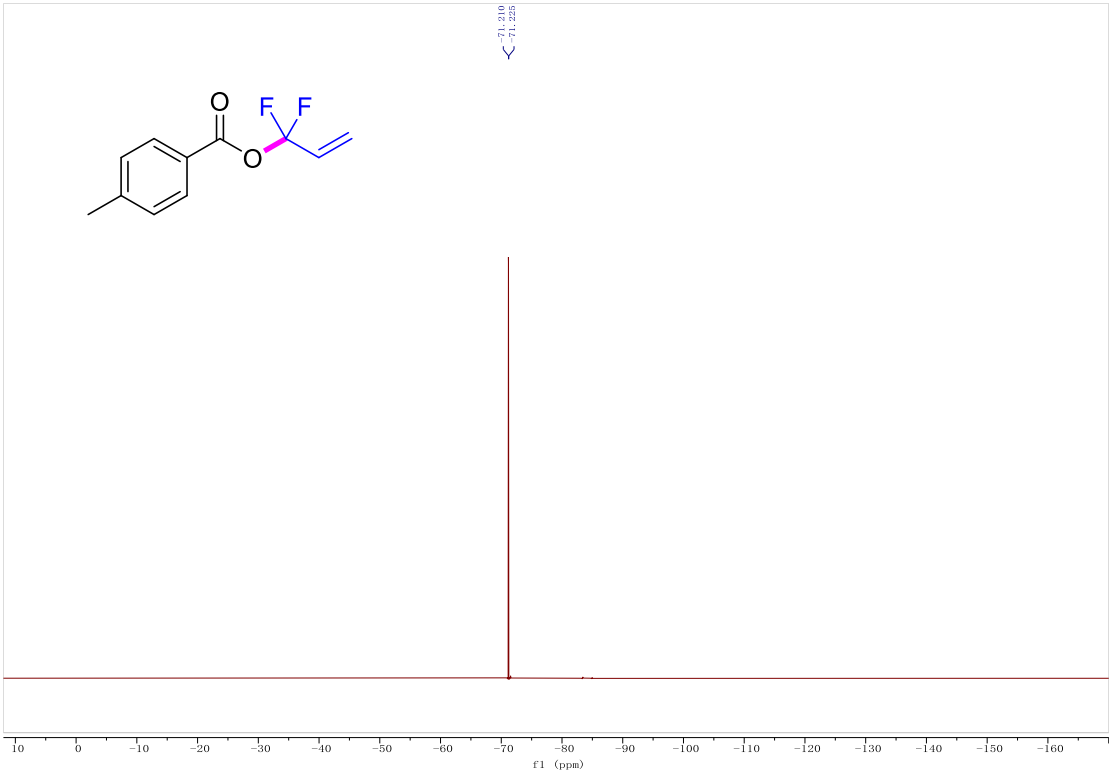


Figure S126. Compound 7d ^{1}H NMR (600 MHz, $CDCl_3$)

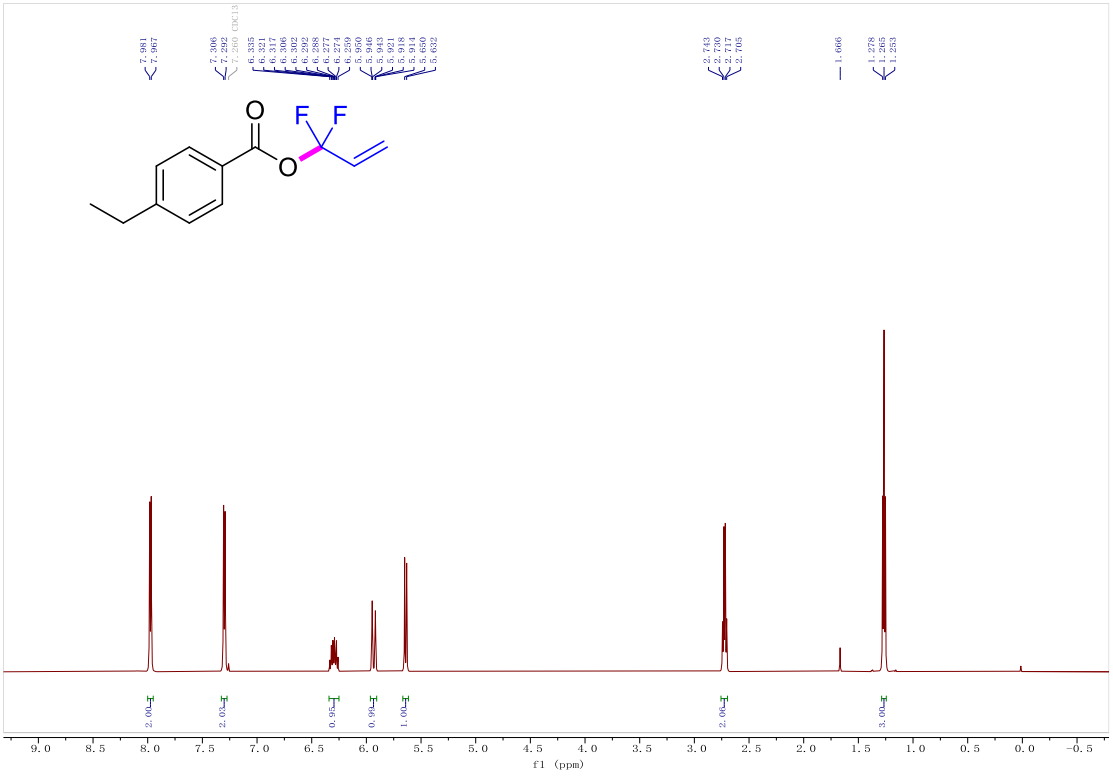


Figure S127. Compound 7d ^{13}C NMR (150 MHz, $CDCl_3$)

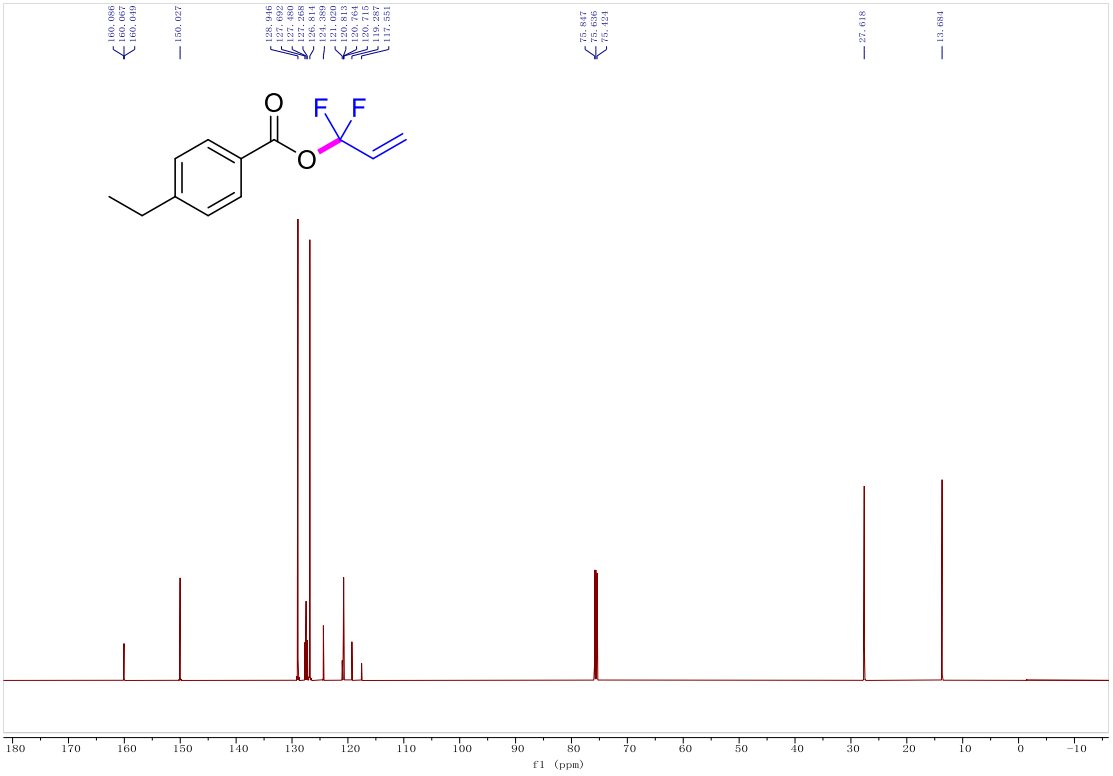


Figure S128. Compound 7d ^{19}F NMR (565 MHz, $CDCl_3$)

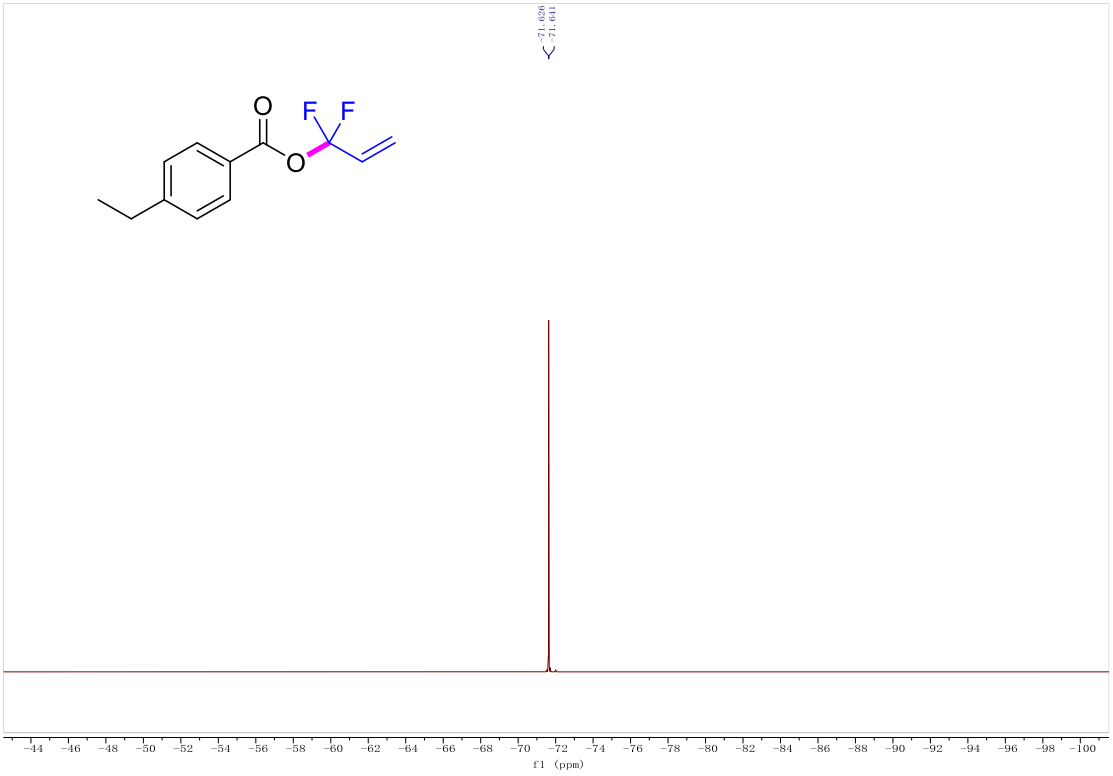


Figure S129. Compound 7e **^{1}H NMR (600 MHz, $CDCl_3$)**

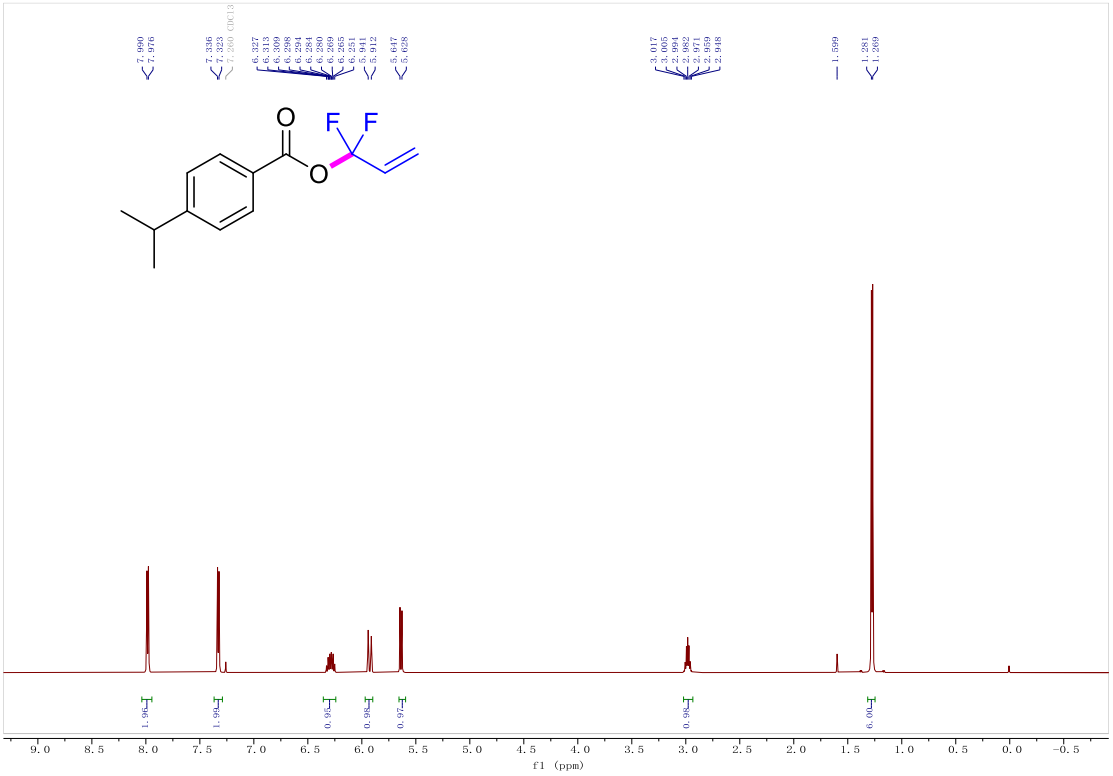


Figure S130. Compound 7e **^{13}C NMR (150 MHz, $CDCl_3$)**

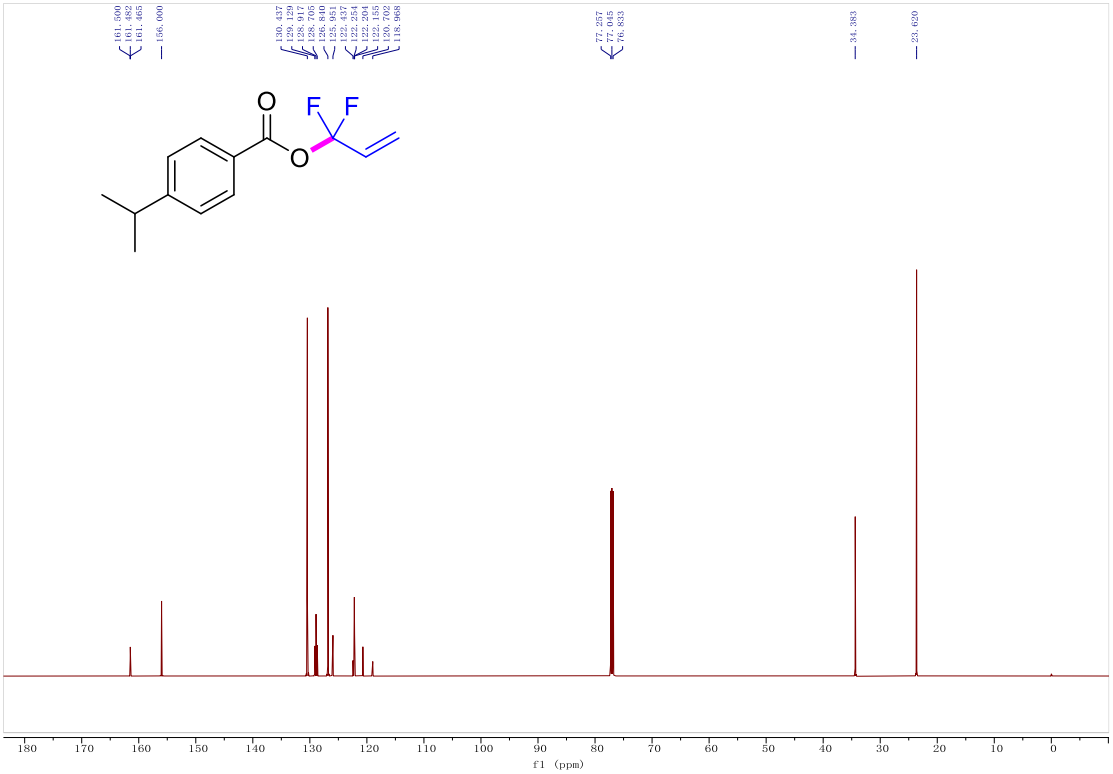


Figure S131. Compound 7e **^{19}F NMR (565 MHz, $CDCl_3$)**

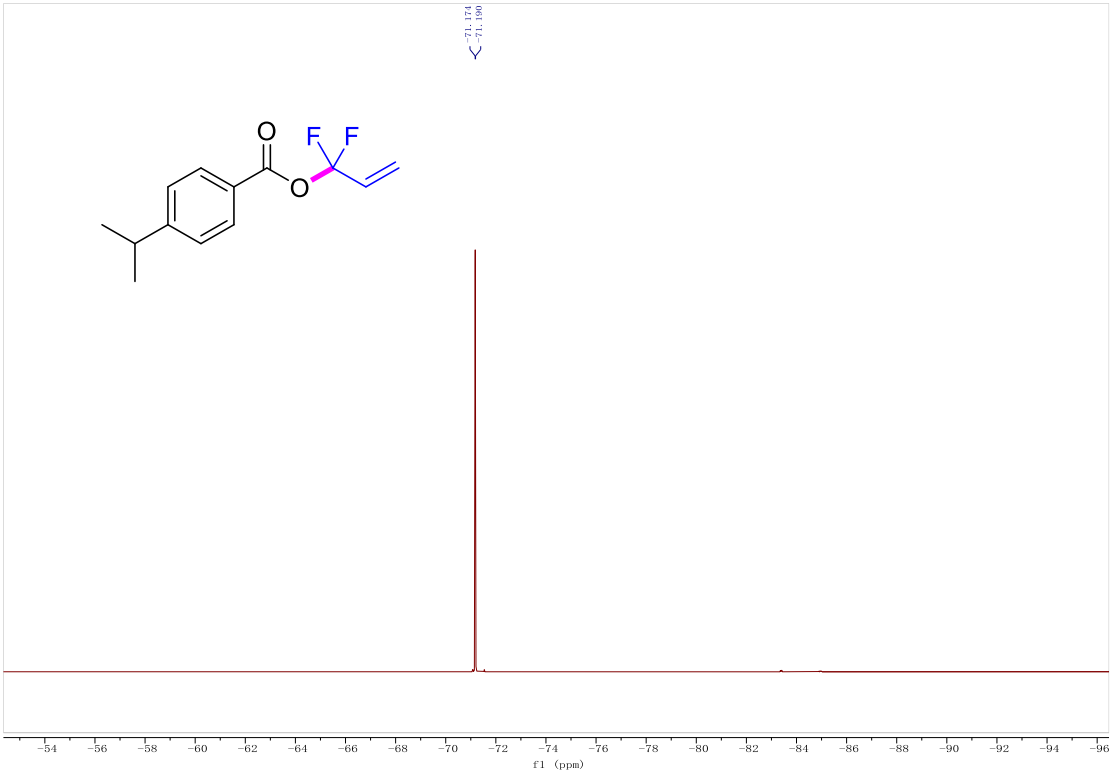


Figure S132. Compound 7f **^{1}H NMR (600 MHz, $CDCl_3$)**

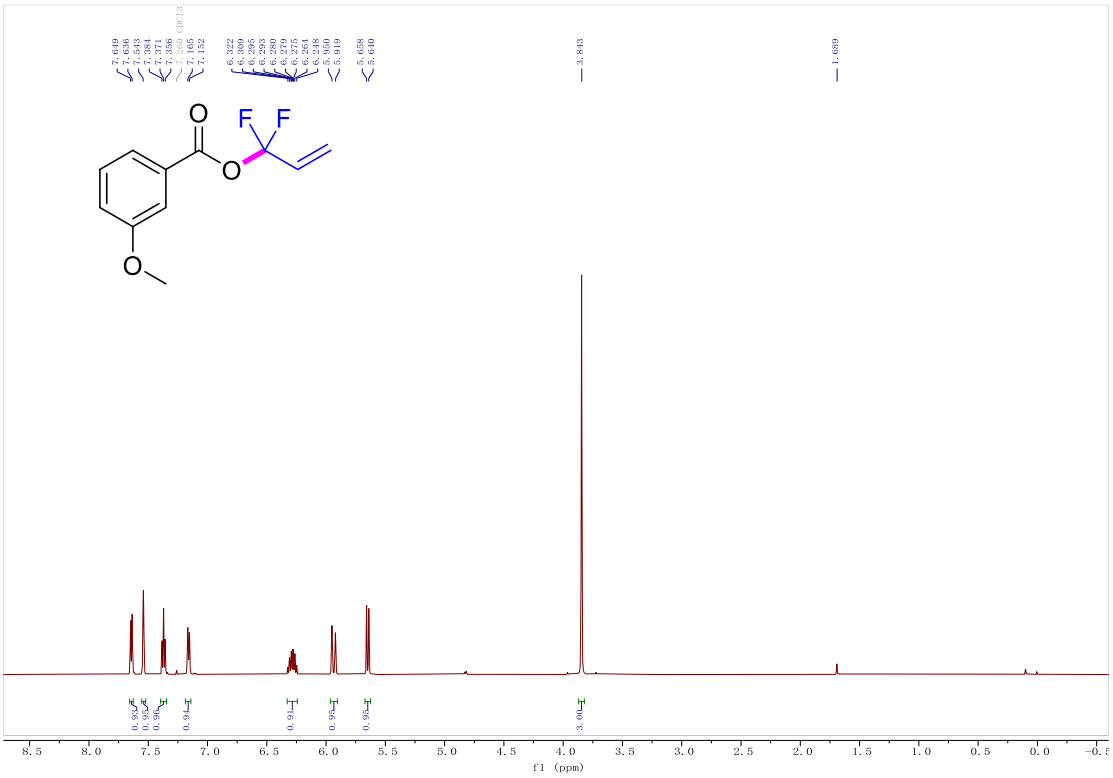


Figure S133. Compound 7f ^{13}C NMR (150 MHz, $CDCl_3$)

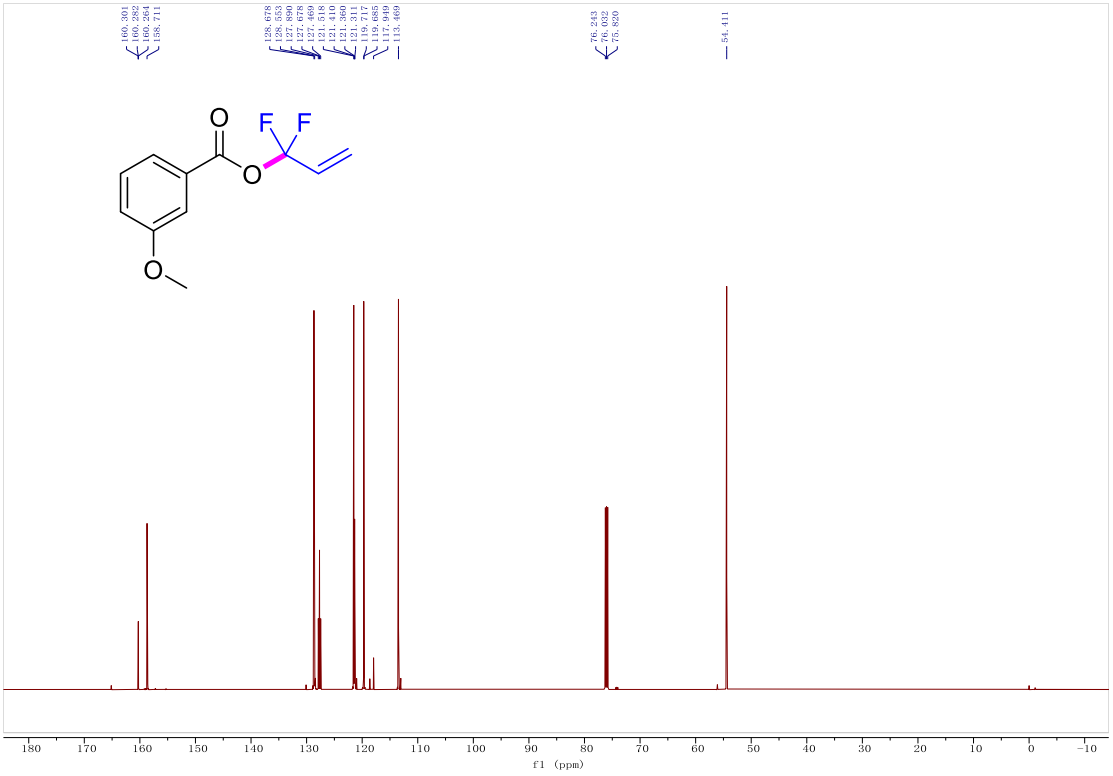


Figure S134. Compound 7f ^{19}F NMR (565 MHz, $CDCl_3$)

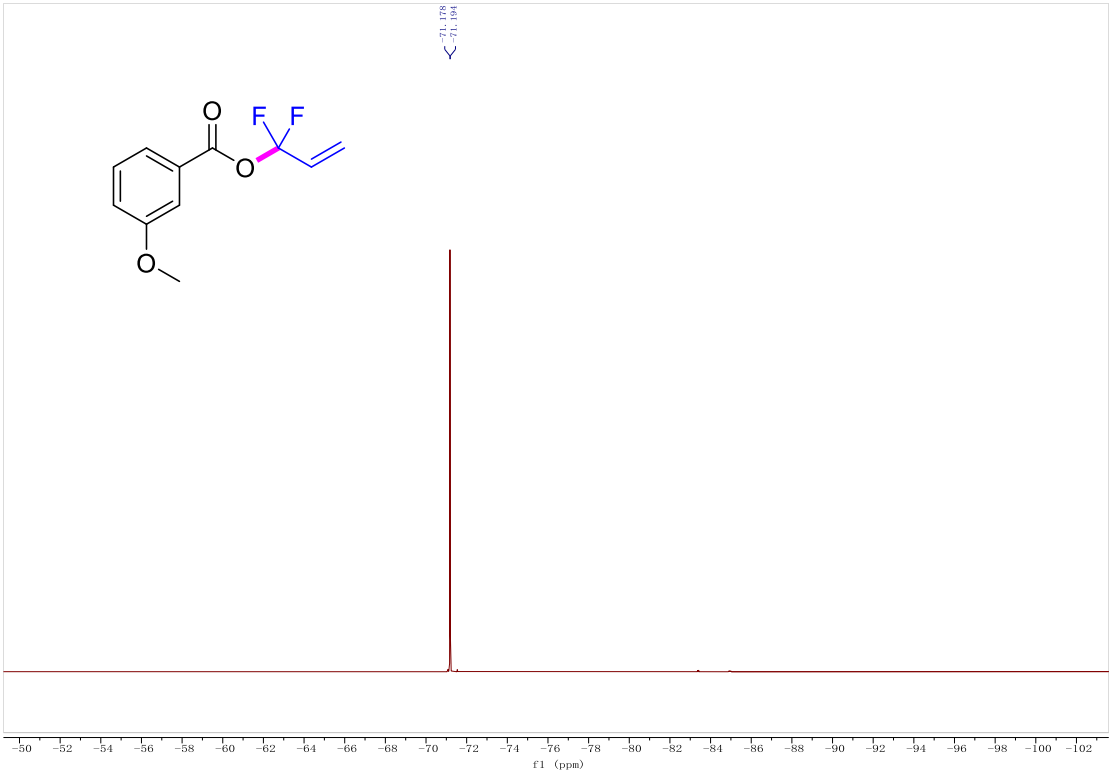


Figure S135. Compound 7g ^{1}H NMR (600 MHz, $CDCl_3$)

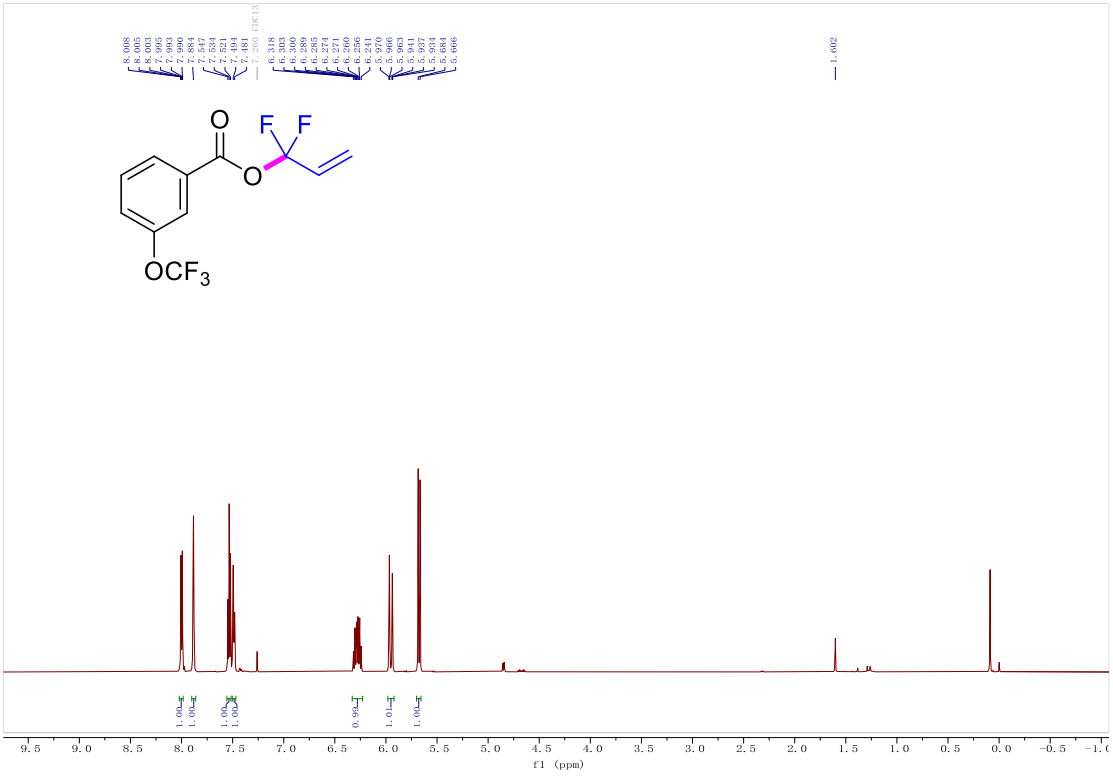


Figure S136. Compound 7g ^{13}C NMR (150 MHz, $CDCl_3$)

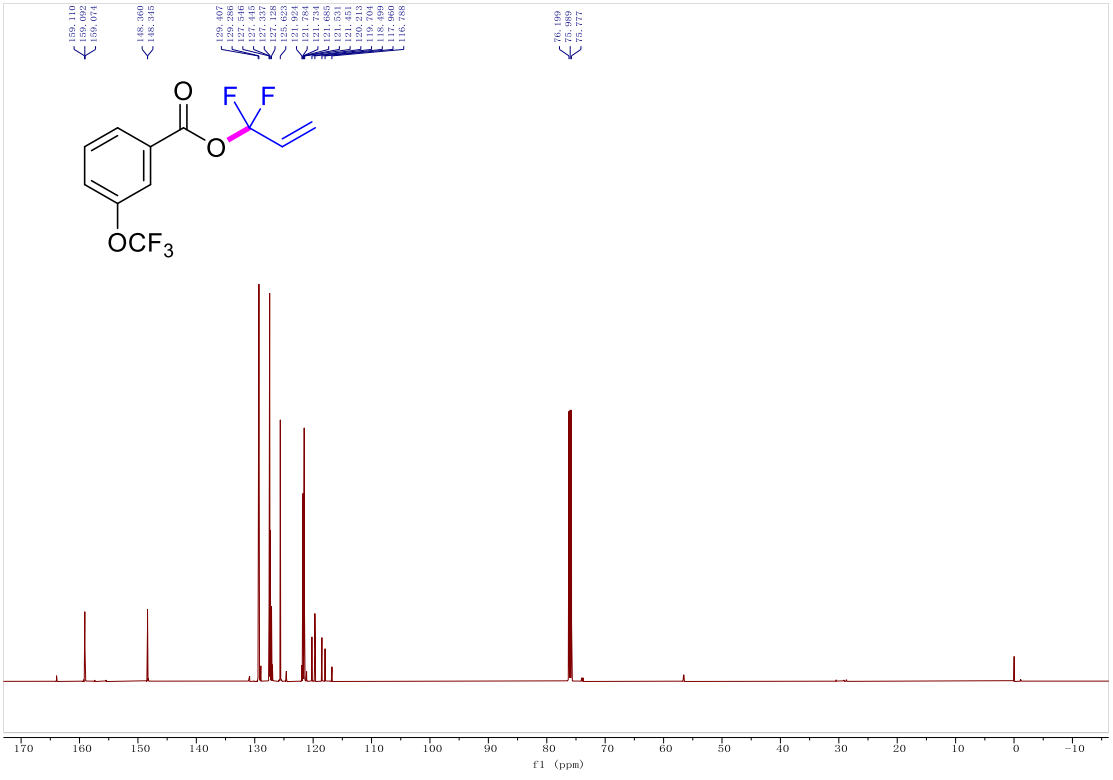


Figure S137. Compound 7g **^{19}F NMR (565 MHz, $CDCl_3$)**

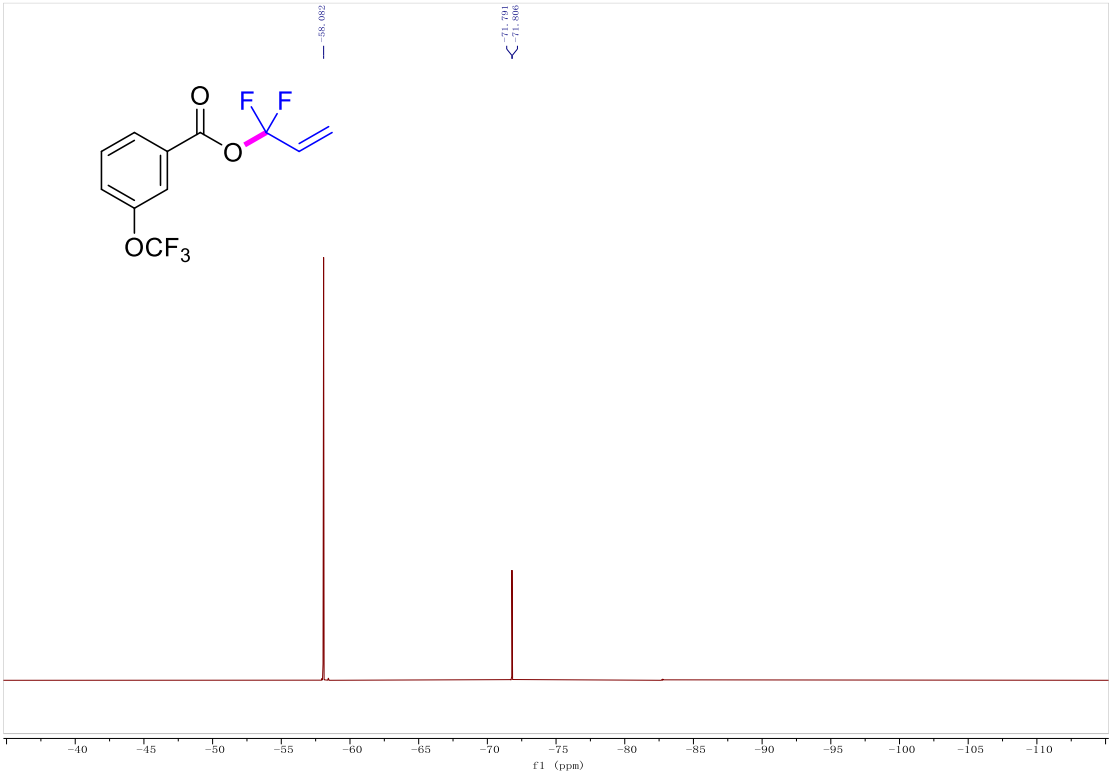


Figure S138. Compound 7h **^{1}H NMR (600 MHz, $CDCl_3$)**

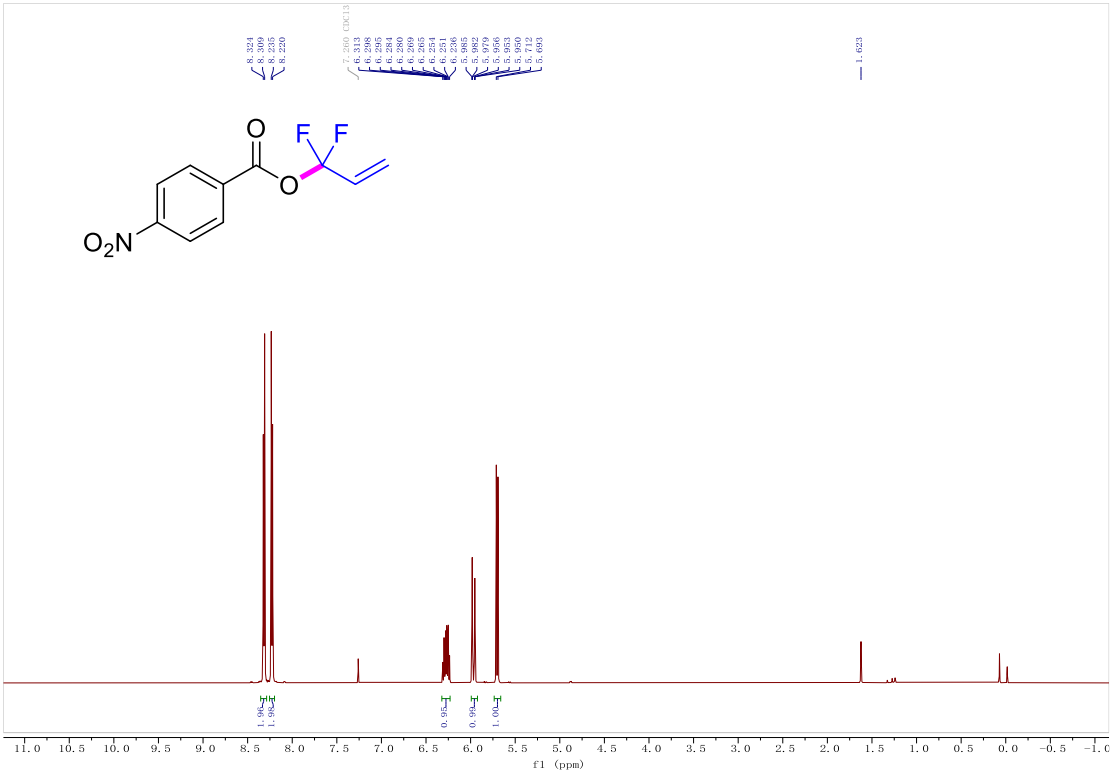


Figure S139. Compound 7h ^{13}C NMR (150 MHz, $CDCl_3$)

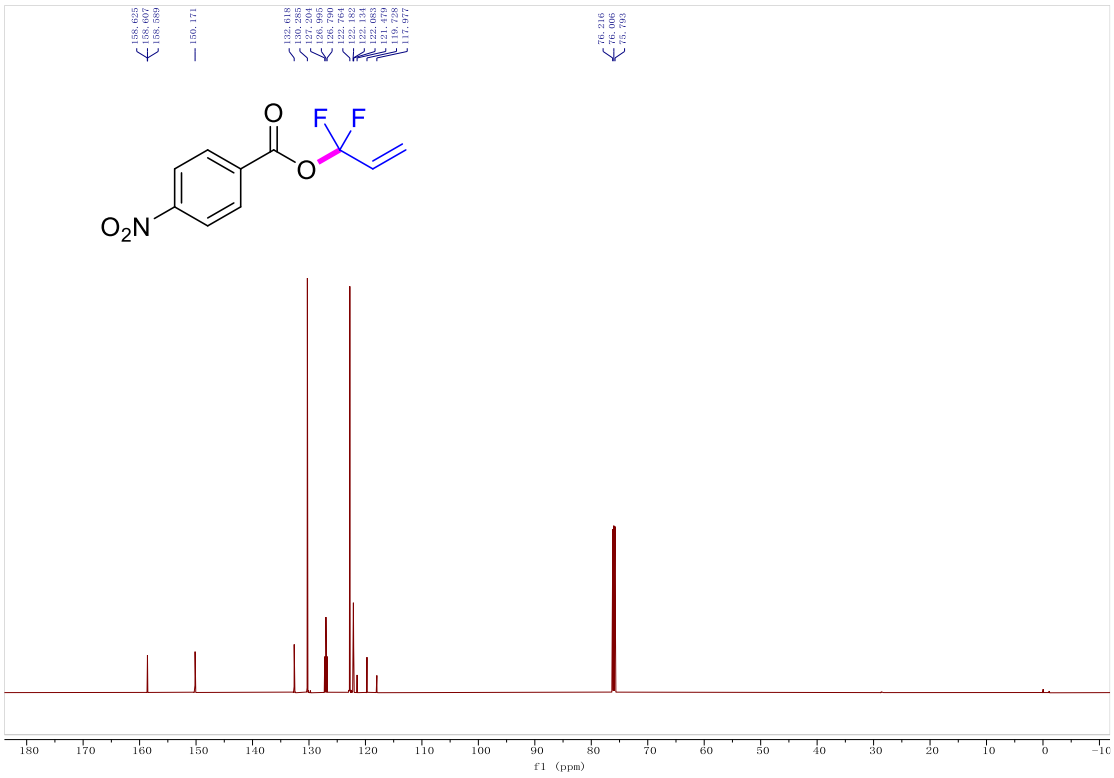


Figure S140. Compound 7i ^{1}H NMR (600 MHz, $CDCl_3$)

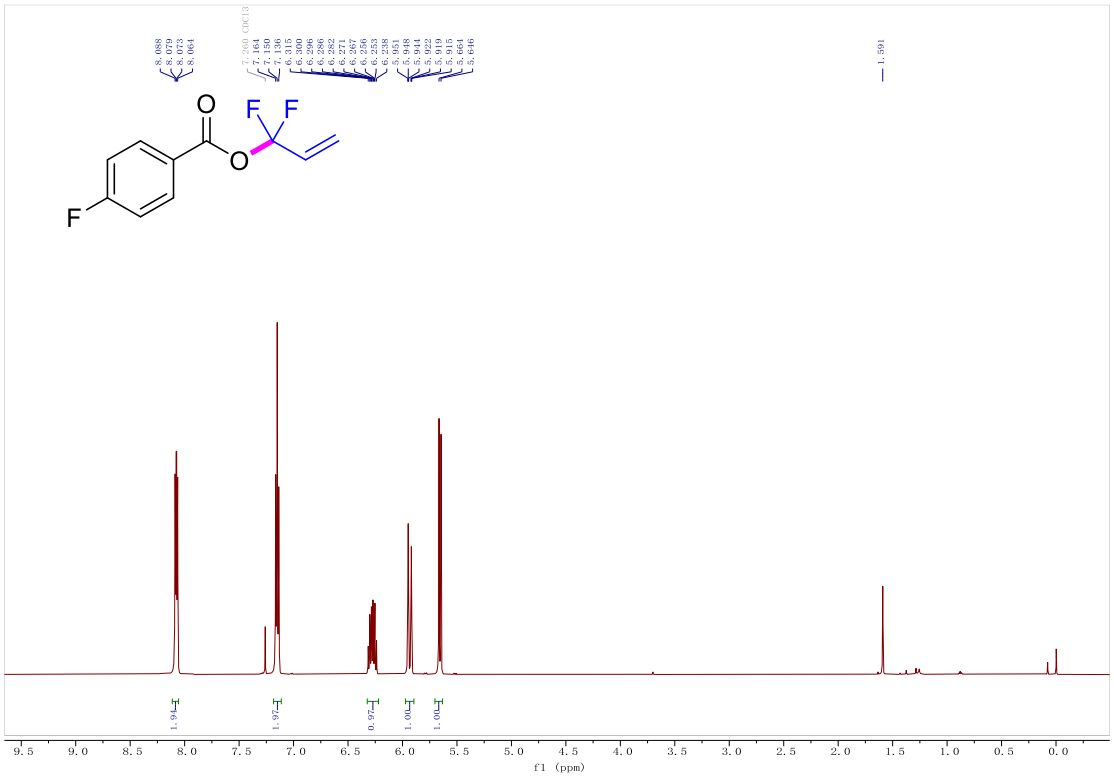


Figure S141. Compound 7i ^{13}C NMR (150 MHz, $CDCl_3$)

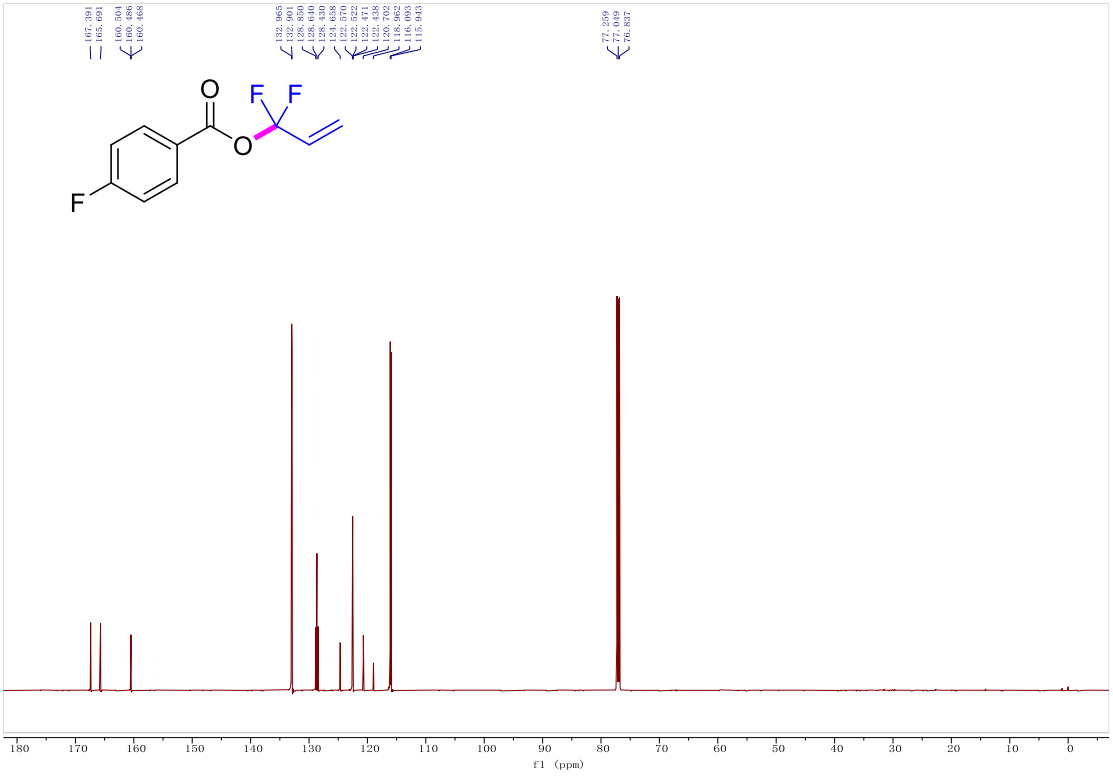


Figure S142. Compound 7i ^{19}F NMR (565 MHz, $CDCl_3$)

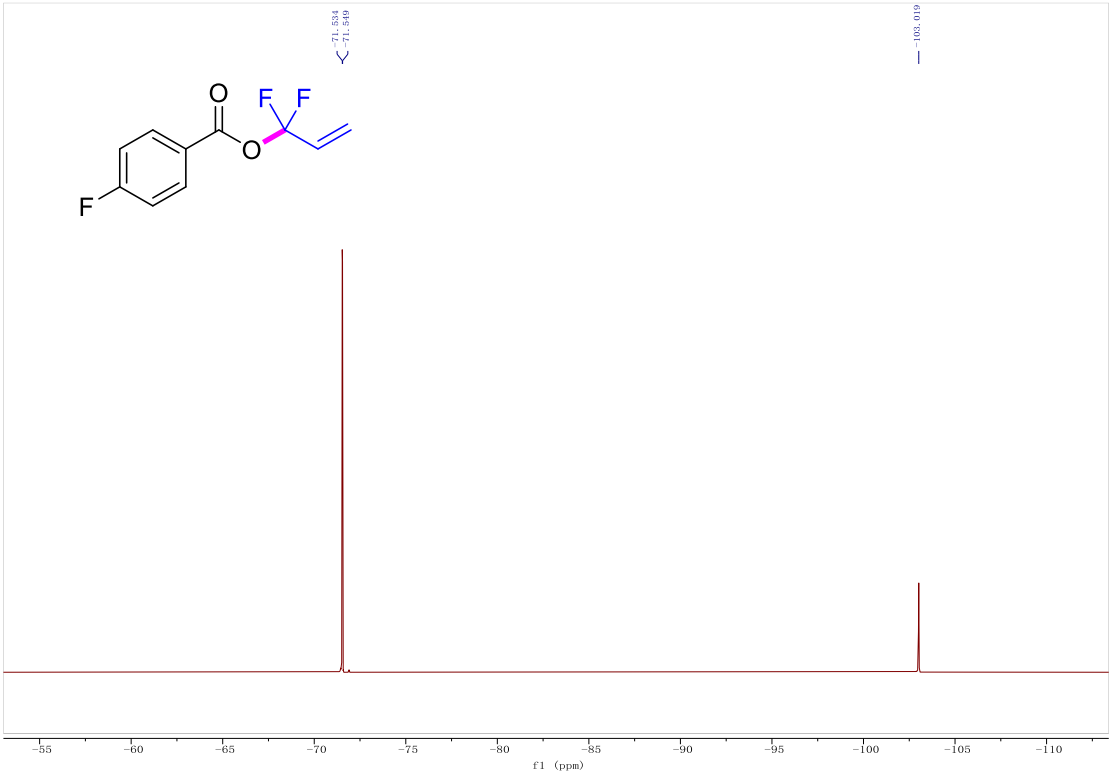


Figure S143. Compound 7j **^{1}H NMR (600 MHz, $CDCl_3$)**

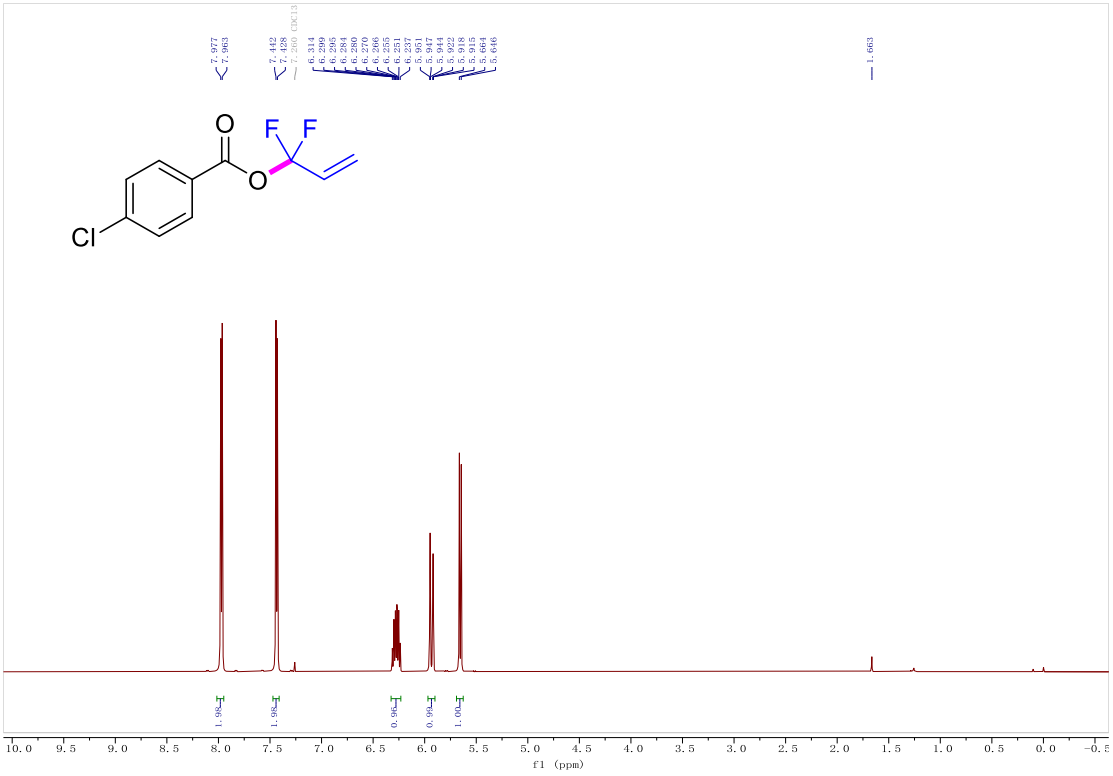


Figure S144. Compound 7j **^{13}C NMR (150 MHz, $CDCl_3$)**

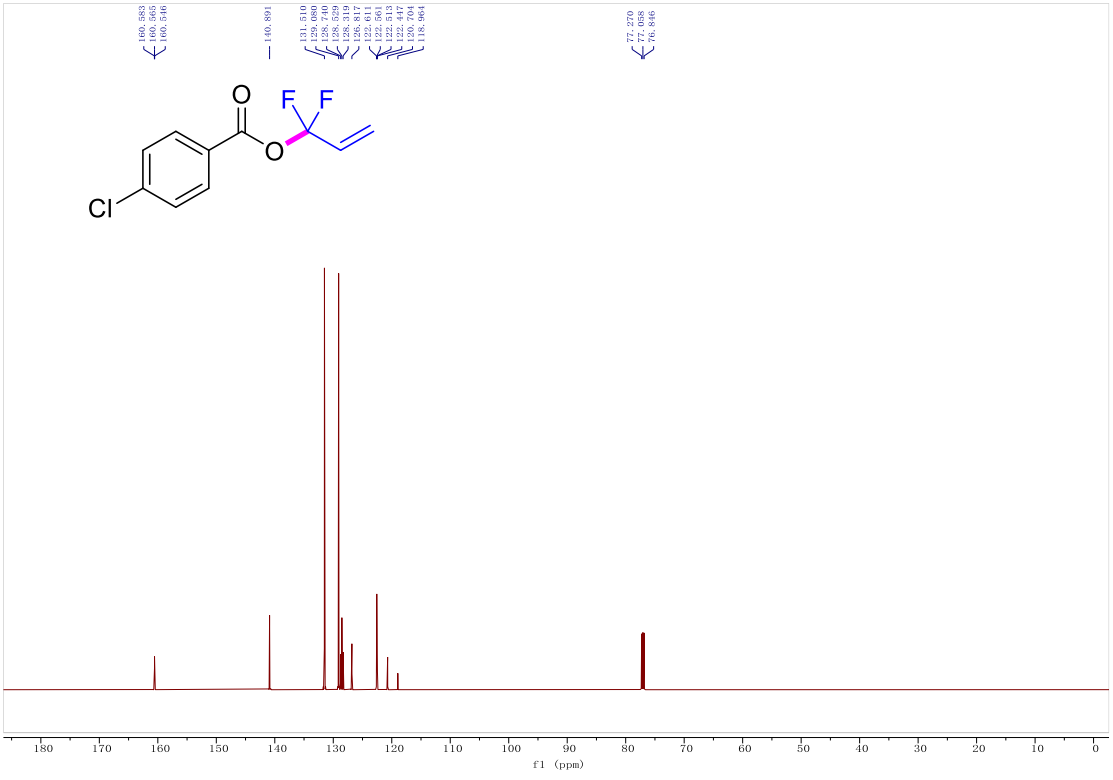


Figure S145. Compound 7k ^{1}H NMR (600 MHz, $CDCl_3$)

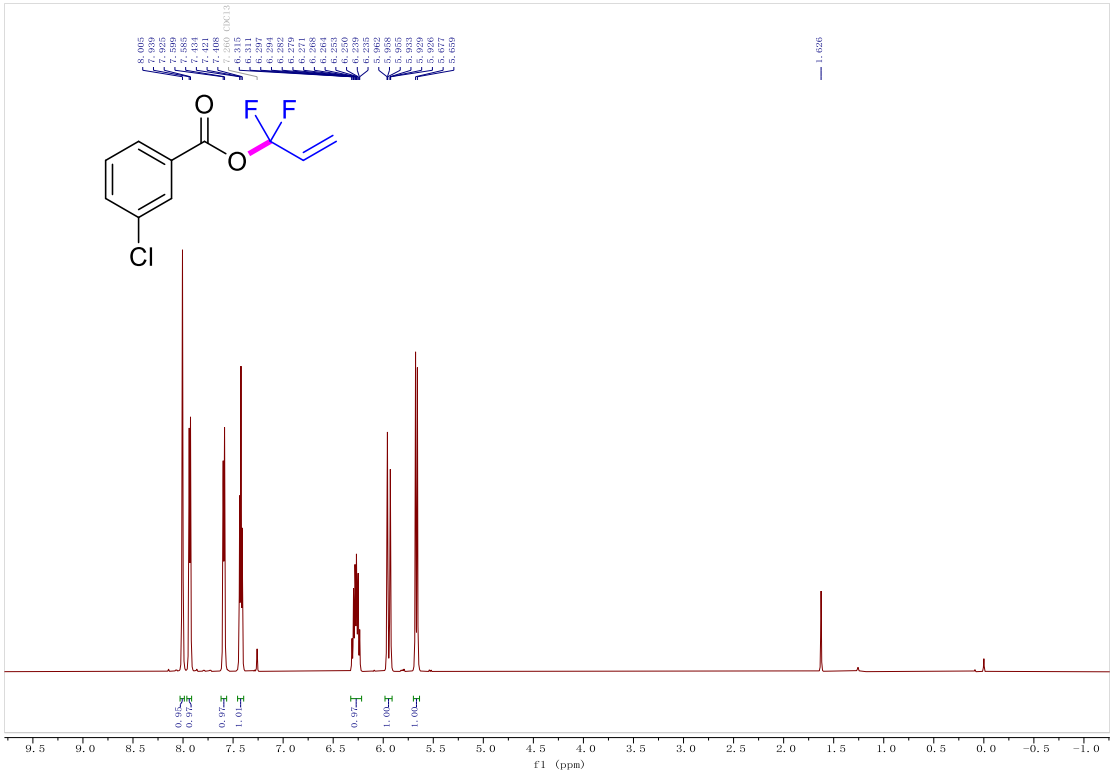


Figure S146. Compound 7k ^{13}C NMR (150 MHz, $CDCl_3$)

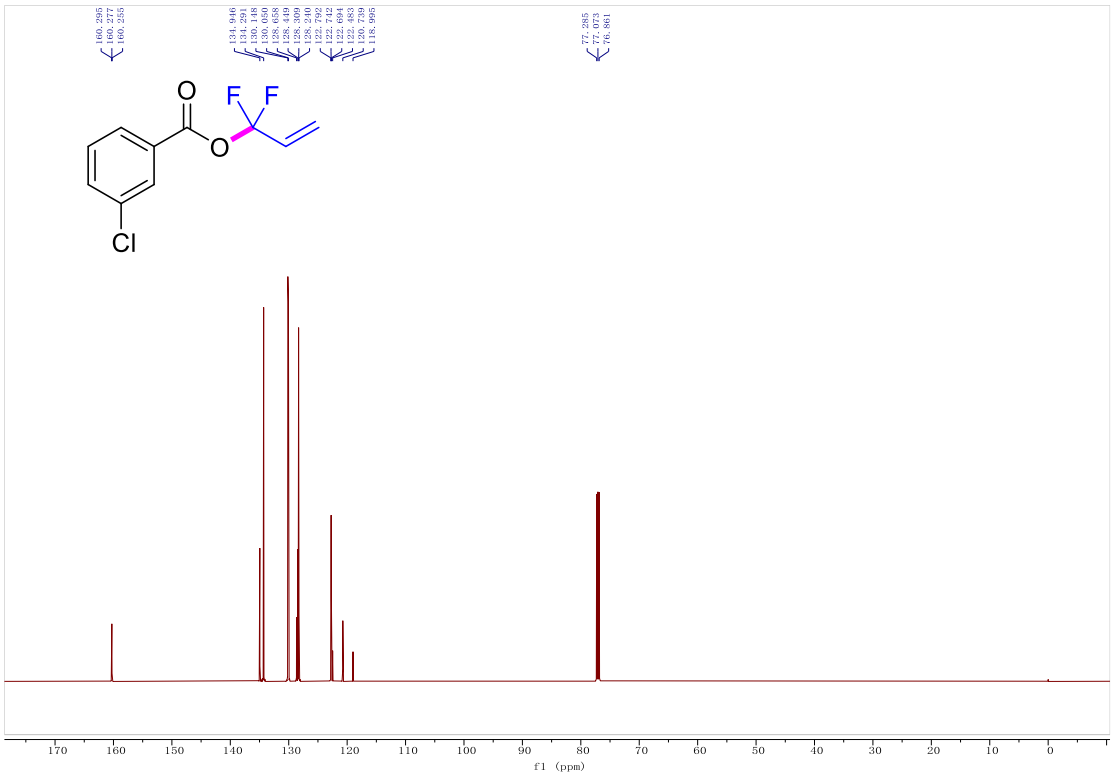


Figure S147. Compound 7l **^{1}H NMR (600 MHz, $CDCl_3$)**

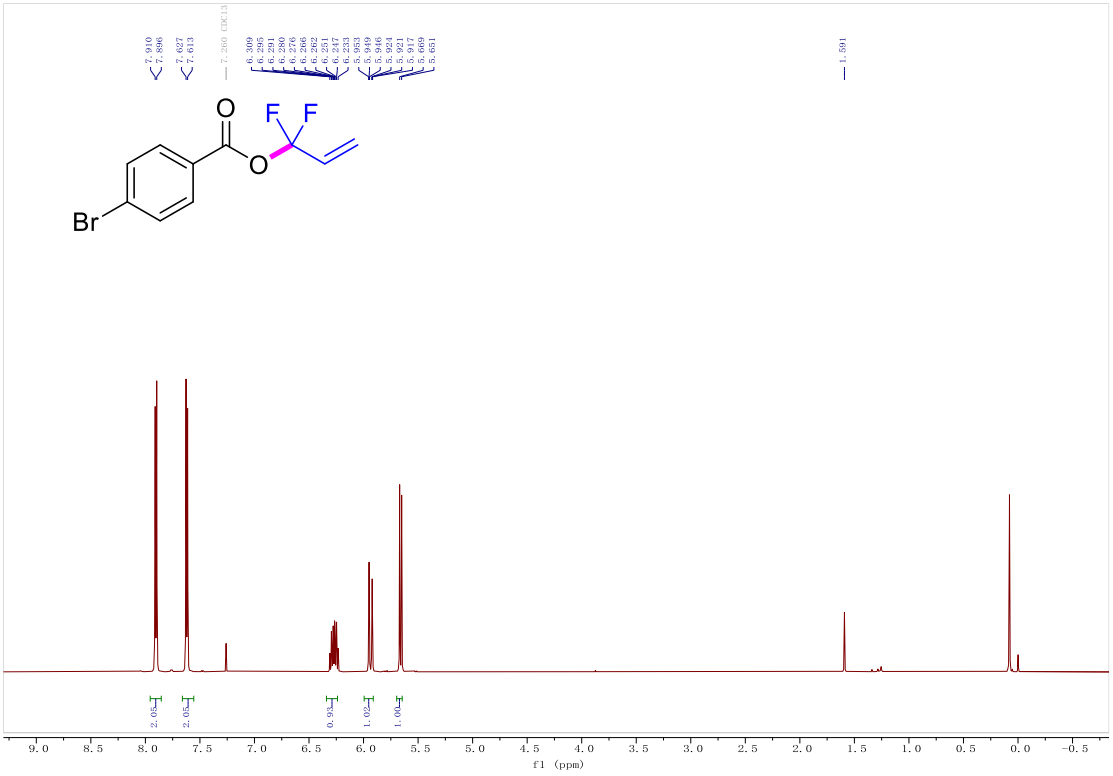


Figure S148. Compound 7l **^{13}C NMR (150 MHz, $CDCl_3$)**

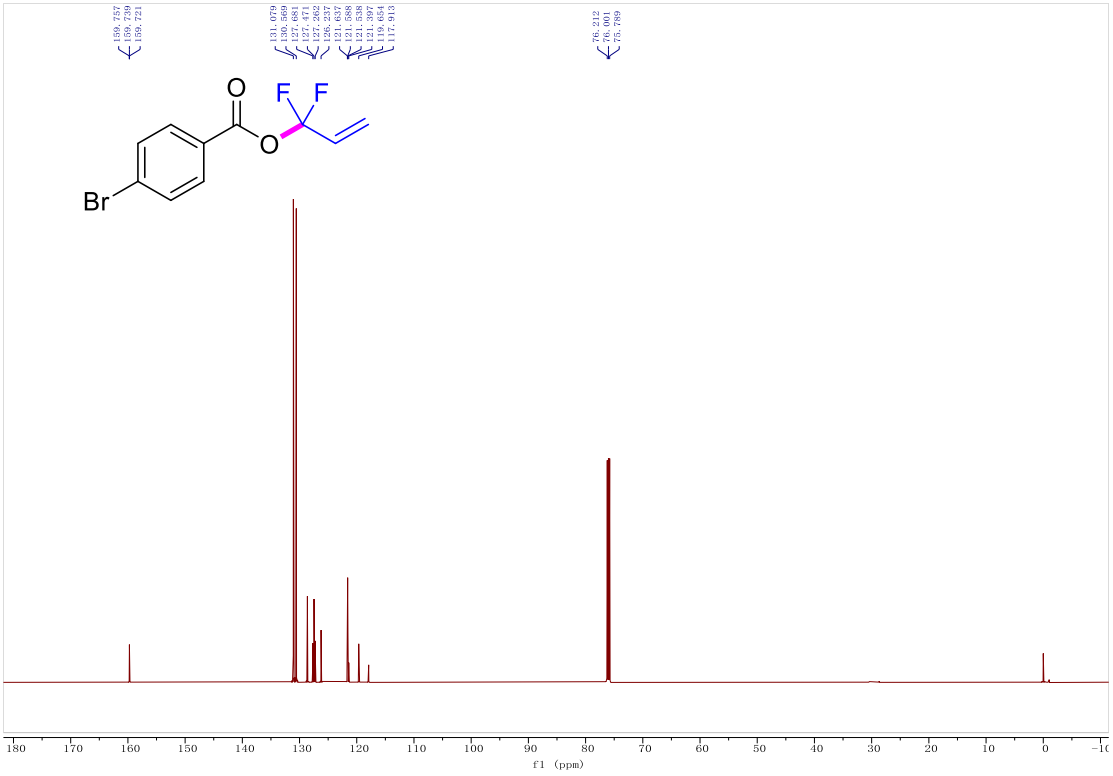


Figure S149. Compound 7l **^{19}F NMR (565 MHz, $CDCl_3$)**

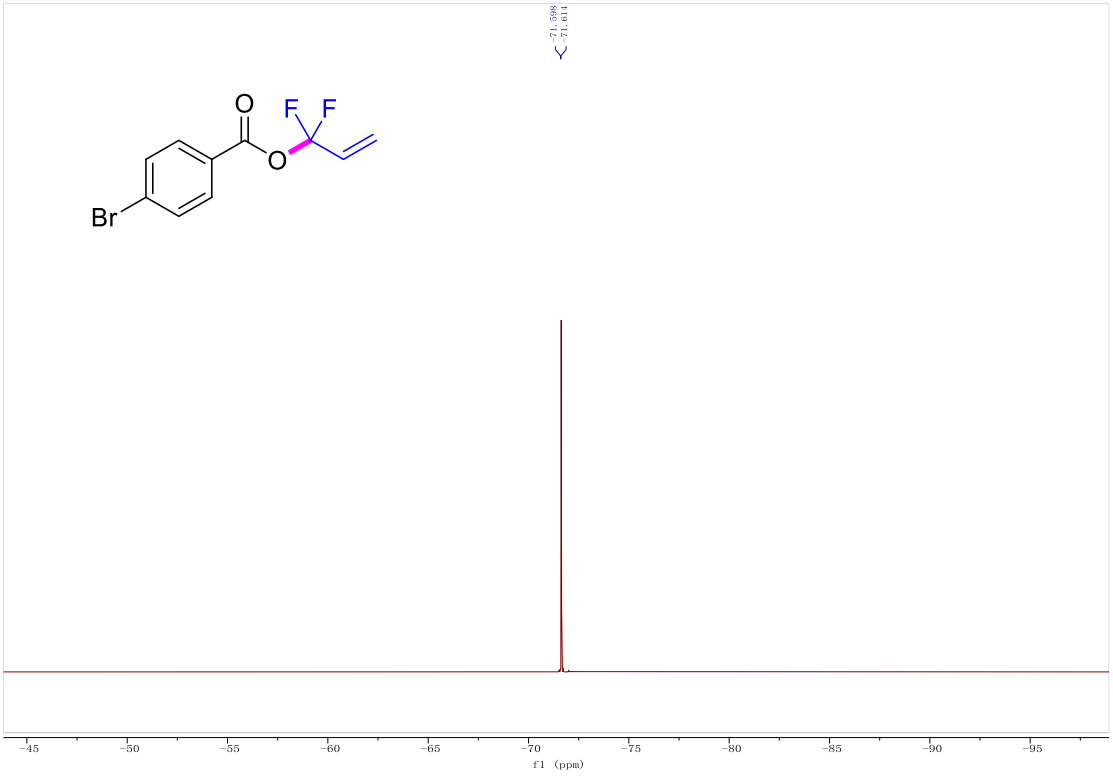


Figure S150. Compound 7m **^{1}H NMR (600 MHz, $CDCl_3$)**

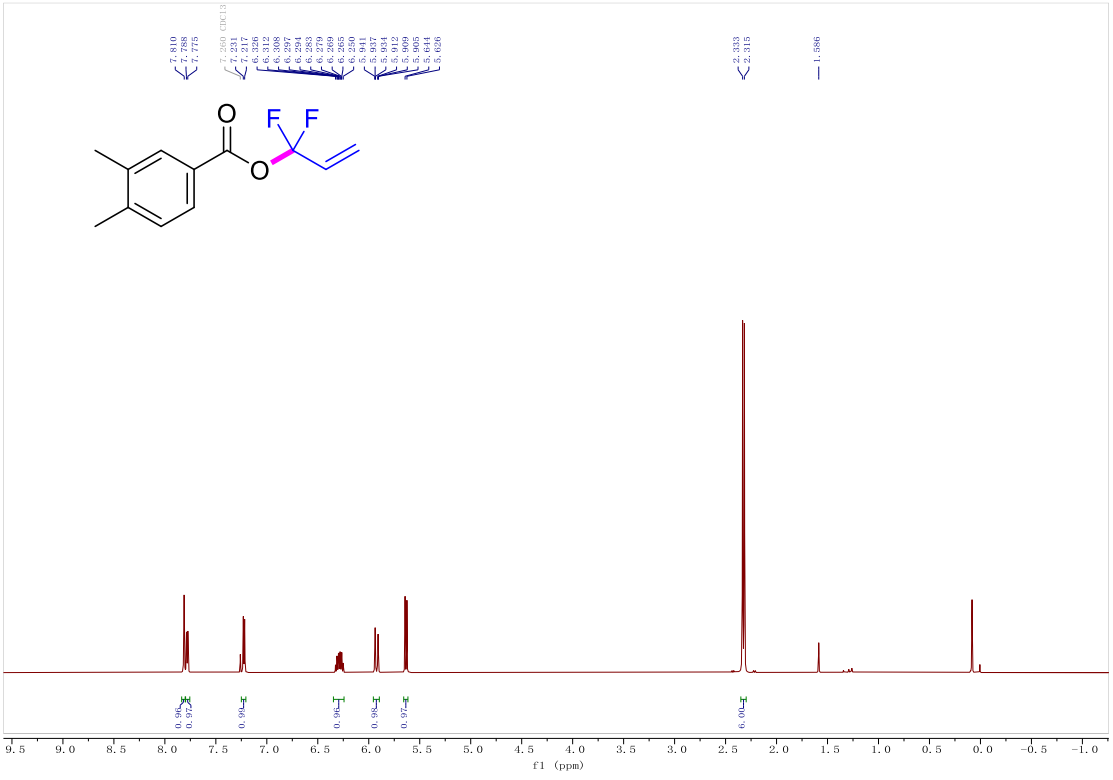


Figure S151. Compound 7m ^{13}C NMR (150 MHz, $CDCl_3$)

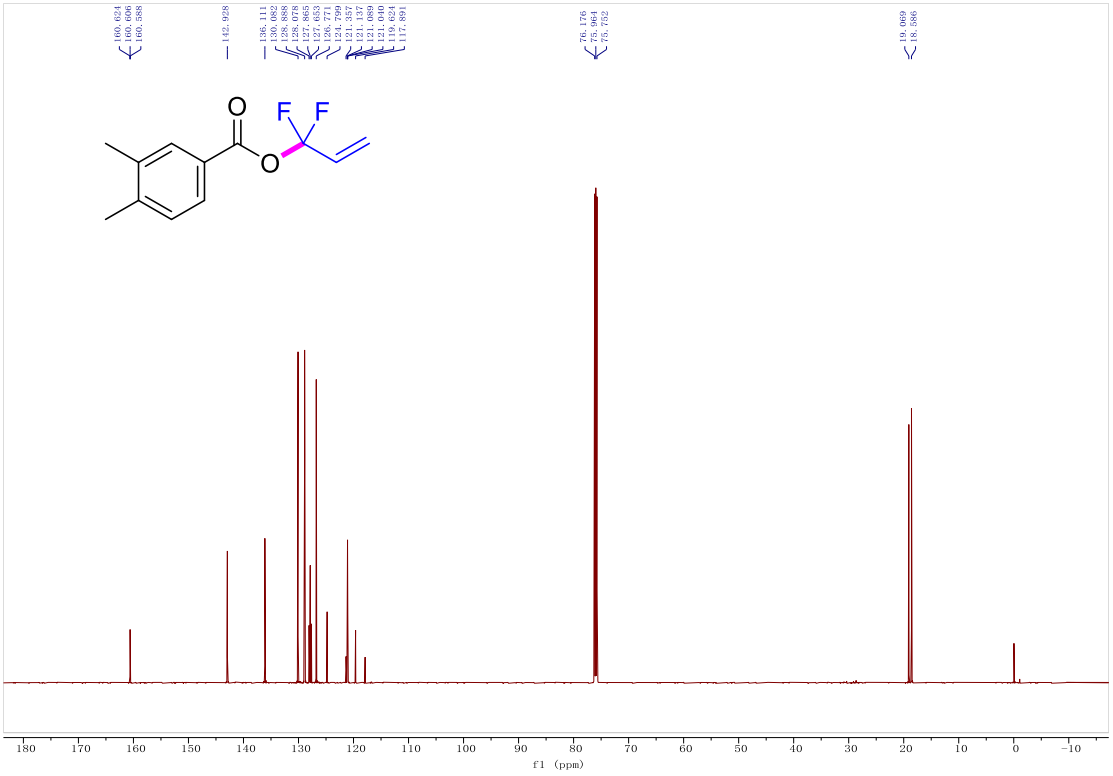


Figure S152. Compound 7m ^{19}F NMR (565 MHz, $CDCl_3$)

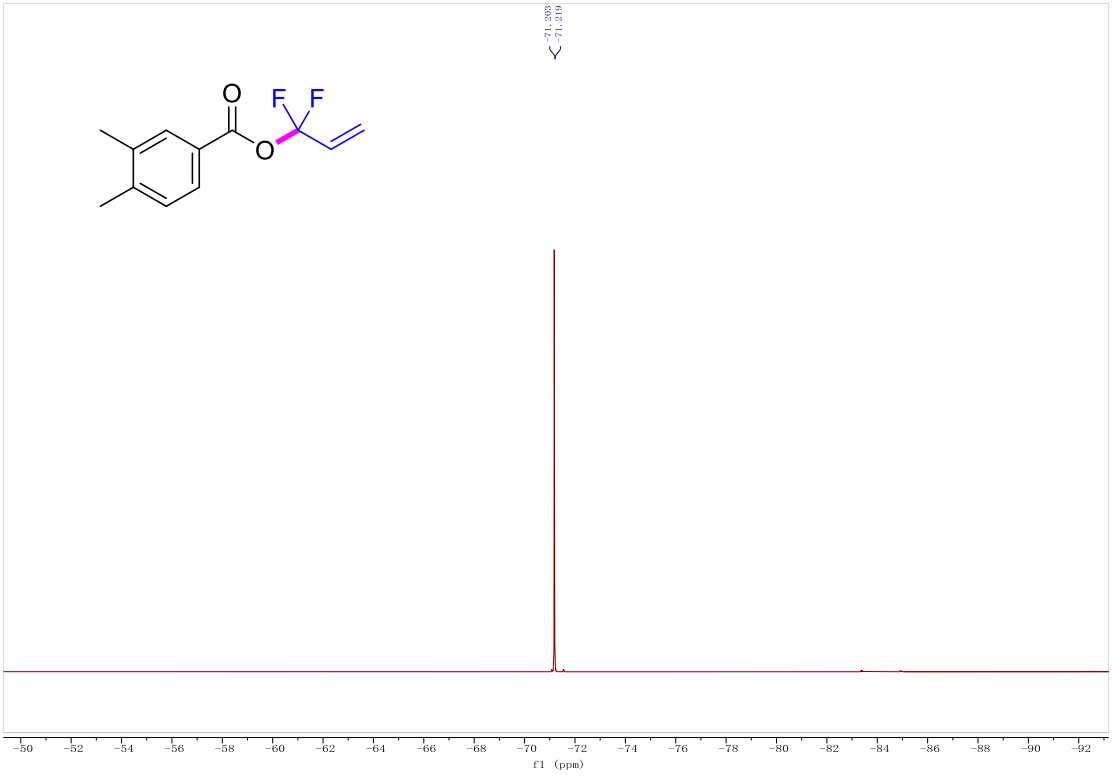


Figure S153. Compound 7n ^{1}H NMR (400 MHz, $CDCl_3$)

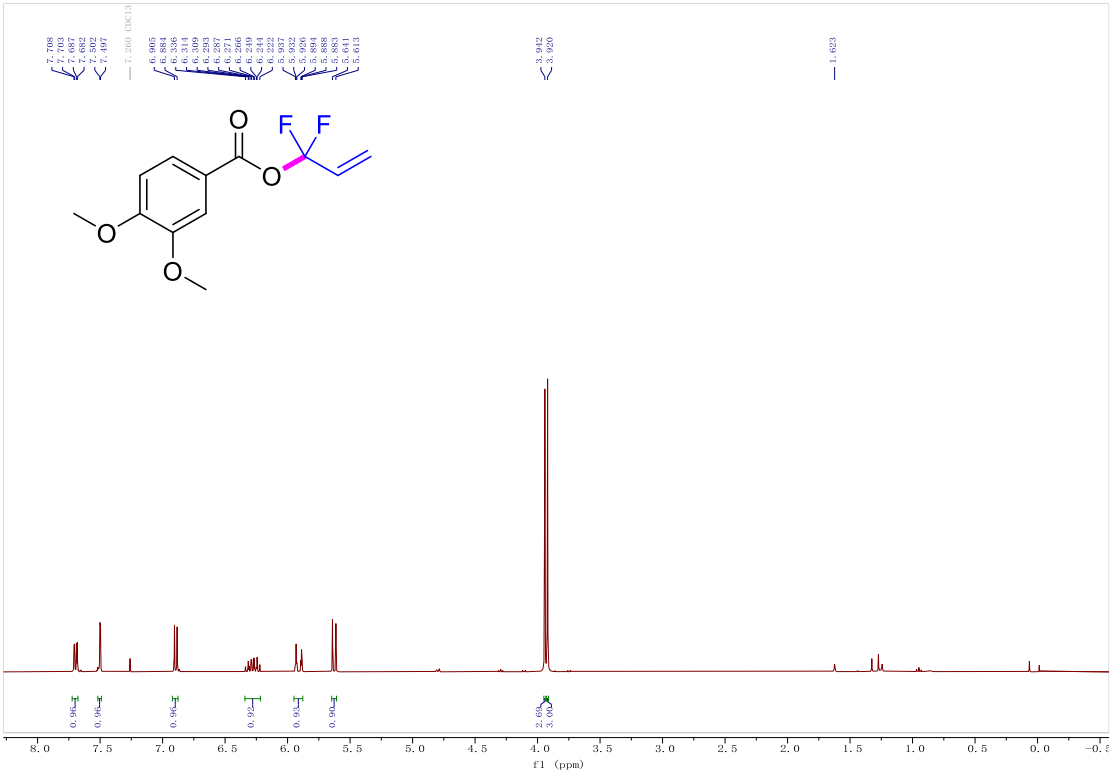


Figure S154. Compound 7n ^{13}C NMR (101 MHz, $CDCl_3$)

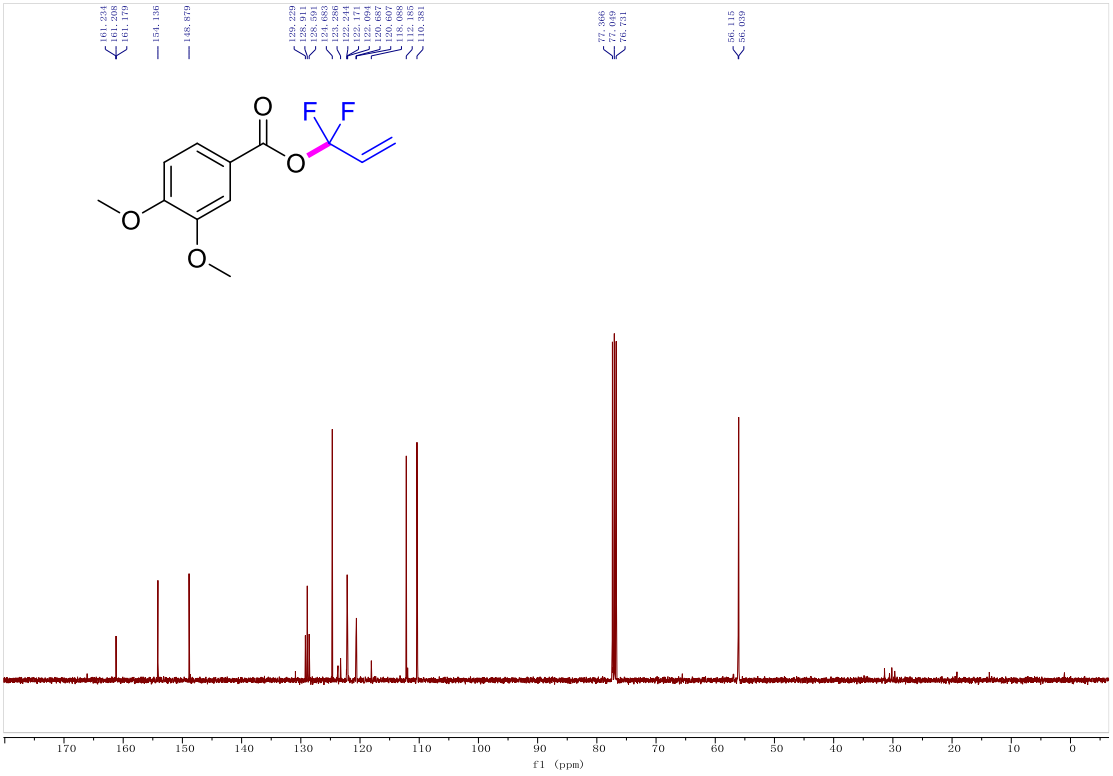


Figure S155. Compound 7o ^{1}H NMR (400 MHz, $CDCl_3$)

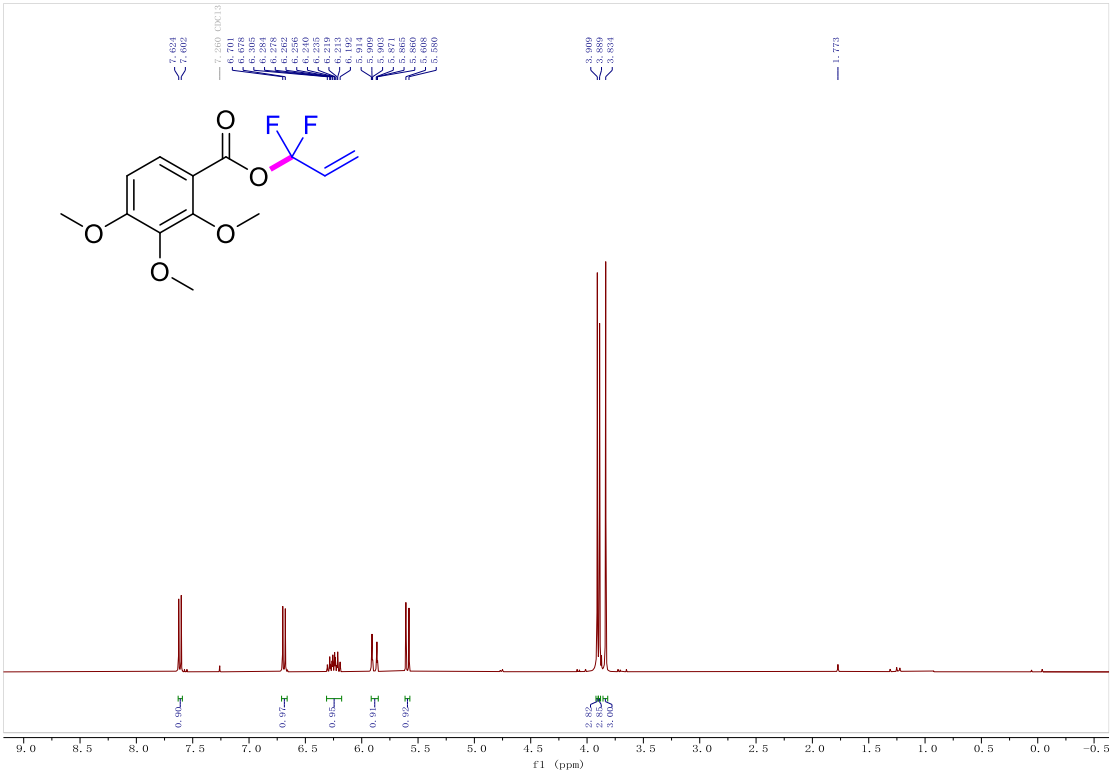


Figure S156. Compound 7o ^{13}C NMR (101 MHz, $CDCl_3$)

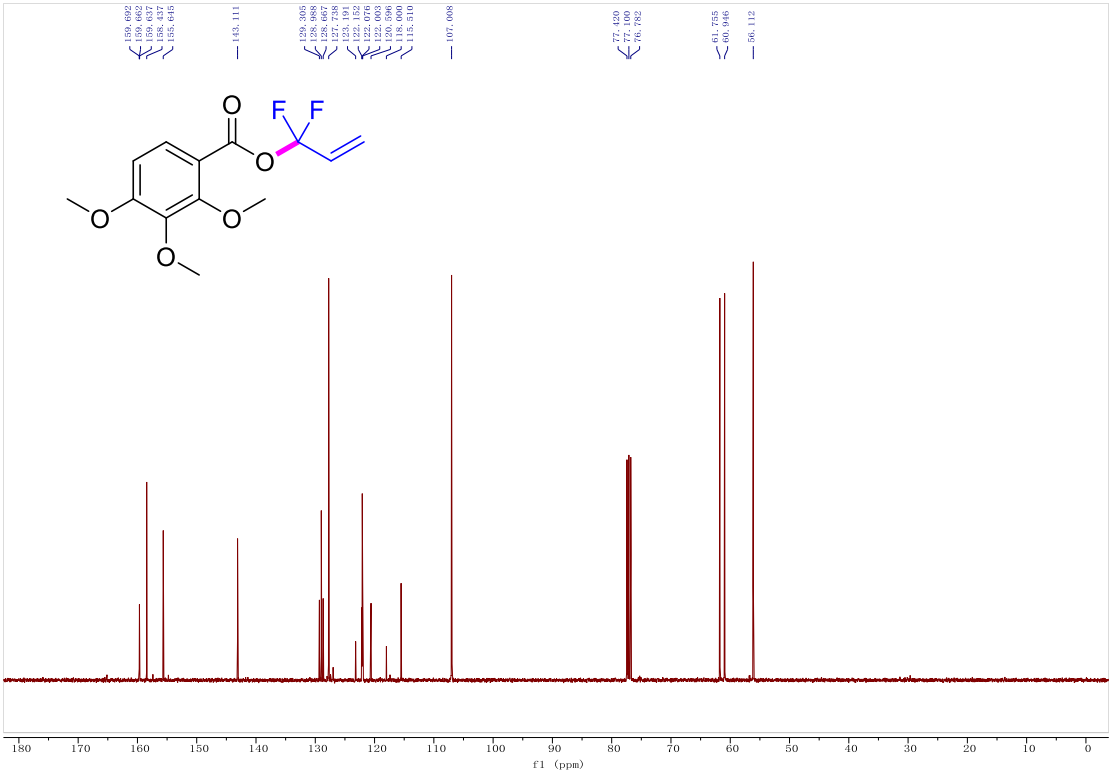


Figure S157. Compound 7p ^{1}H NMR (600 MHz, $CDCl_3$)

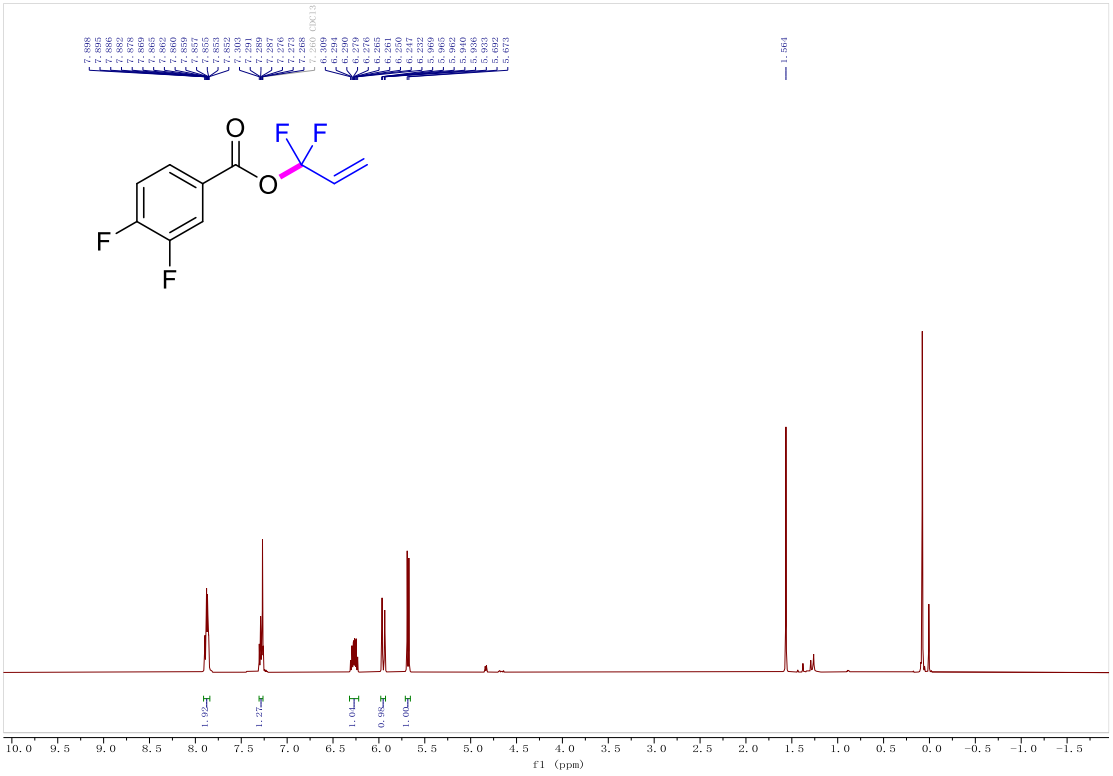


Figure S158. Compound 7p ^{13}C NMR (150 MHz, $CDCl_3$)

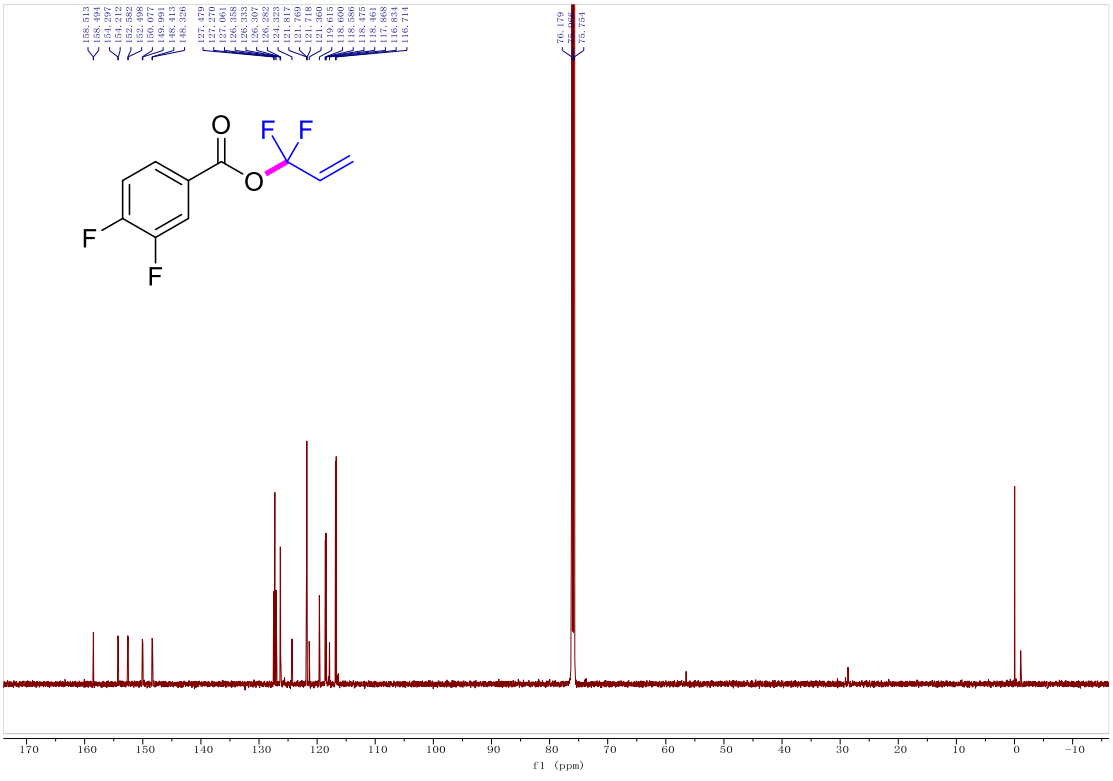


Figure S159. Compound 7p ^{19}F NMR (565 MHz, $CDCl_3$)

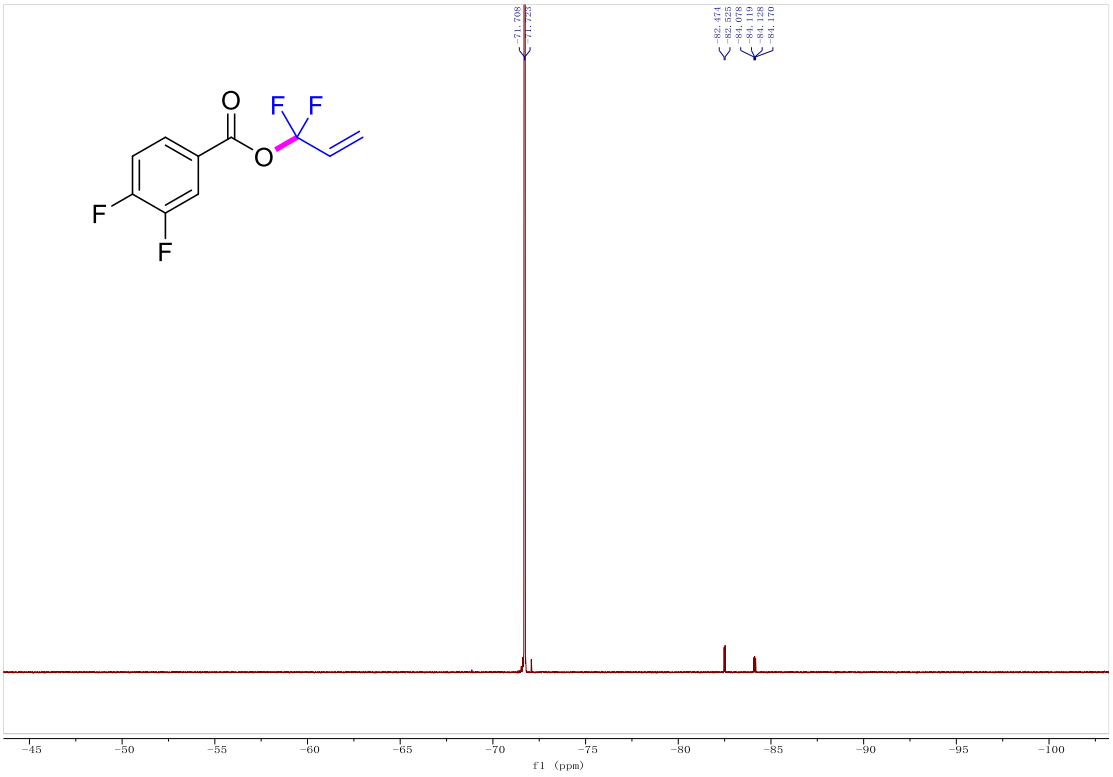


Figure S160. Compound 7q ^{1}H NMR (600 MHz, $CDCl_3$)

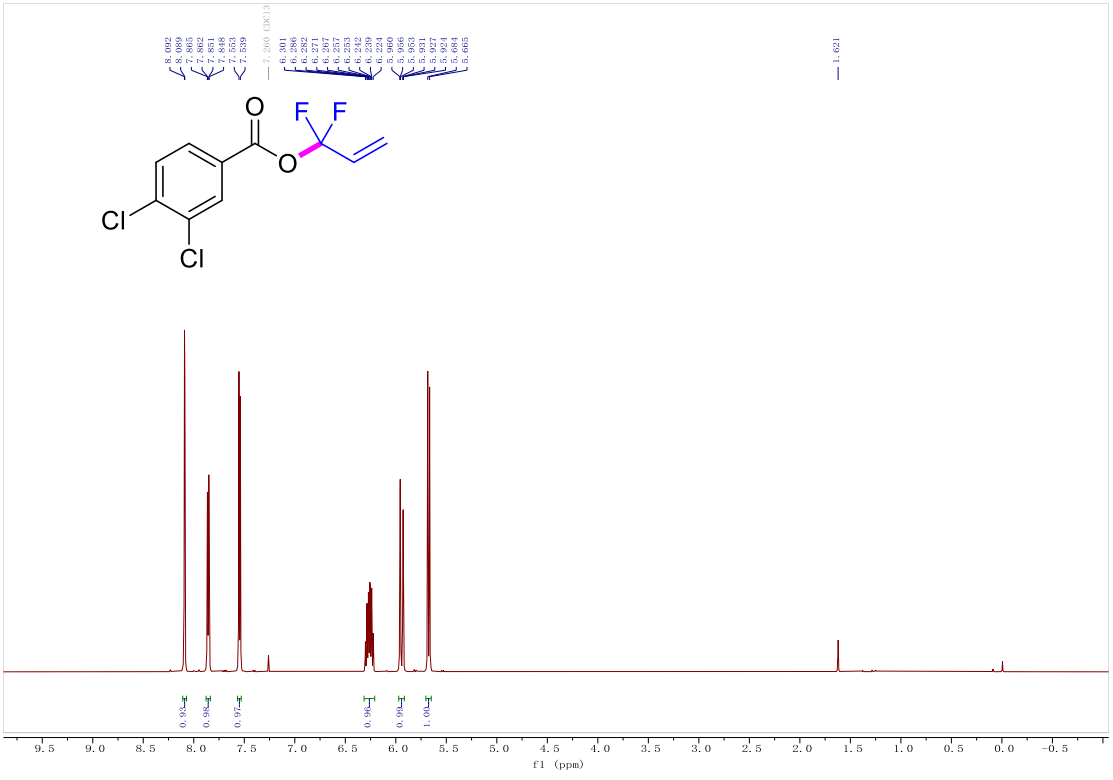


Figure S161. Compound 7q ^{13}C NMR (150 MHz, $CDCl_3$)

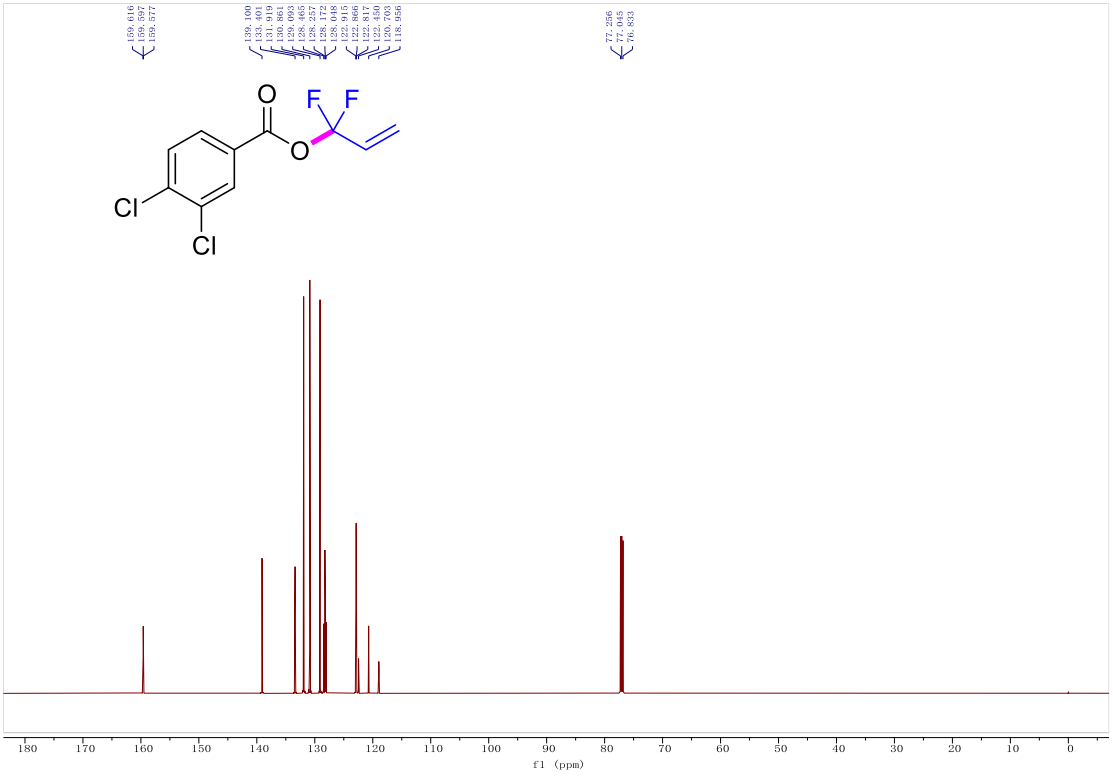


Figure S162. Compound 7q ^{19}F NMR (565 MHz, $CDCl_3$)

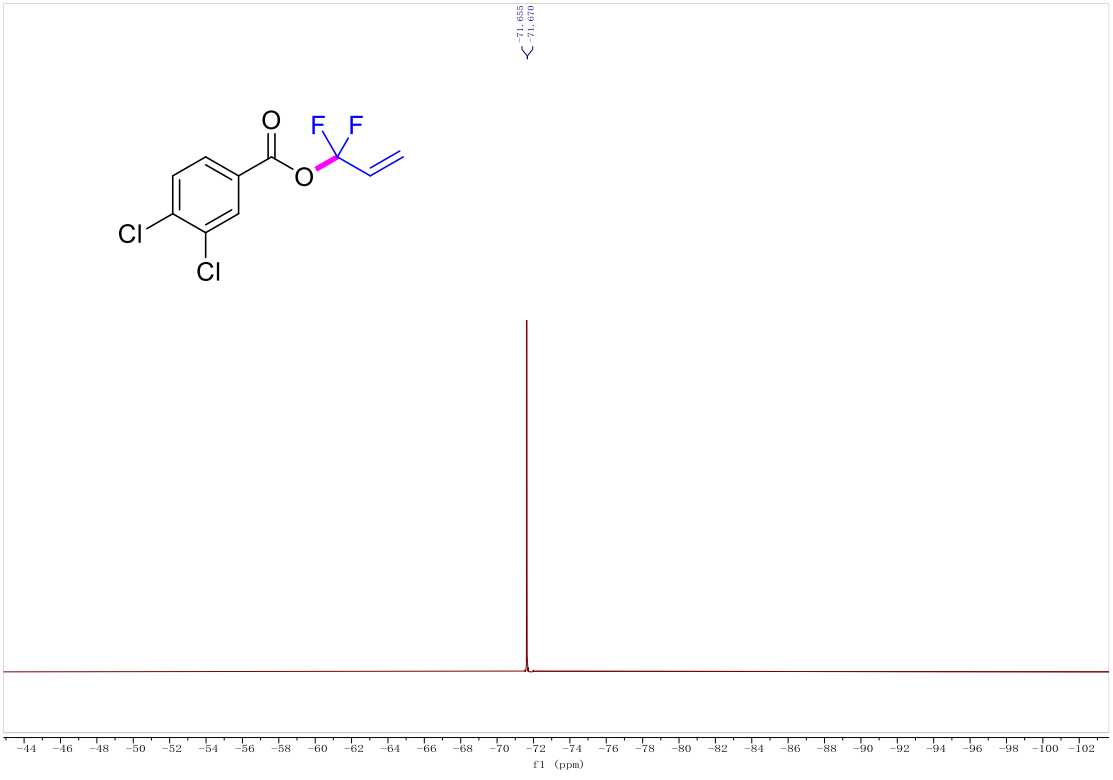


Figure S163. Compound 7r **^{1}H NMR (600 MHz, $CDCl_3$)**

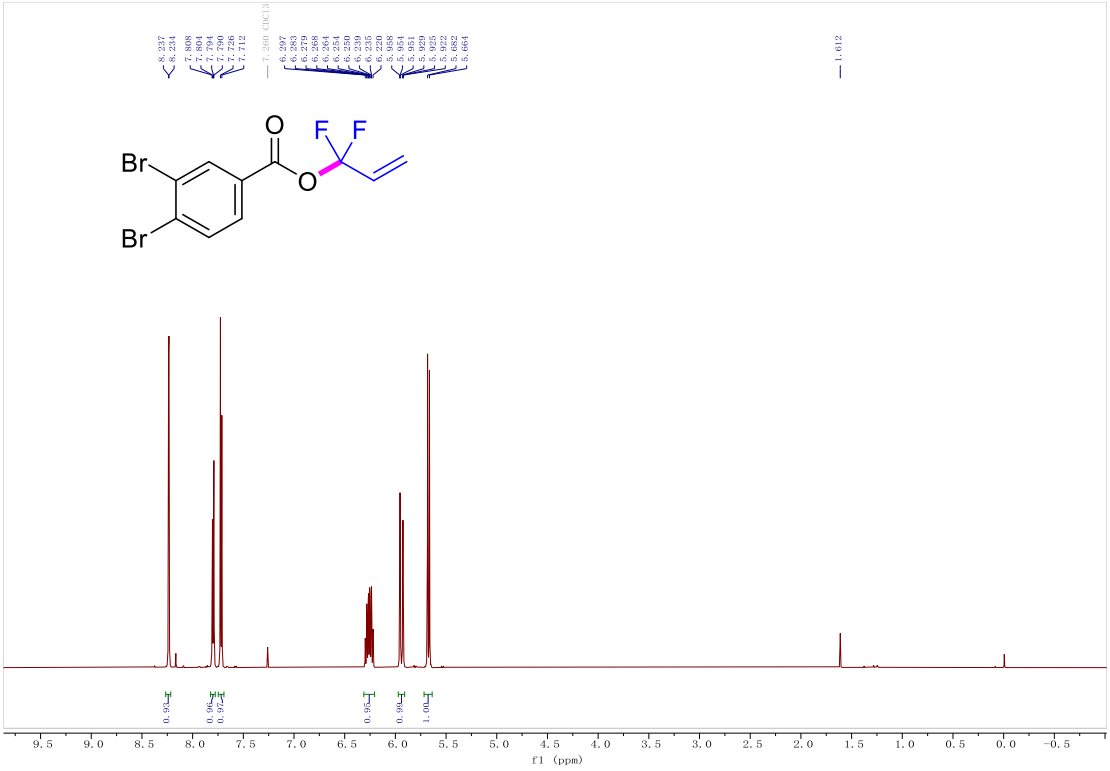


Figure S164. Compound 7r **^{13}C NMR (150 MHz, $CDCl_3$)**

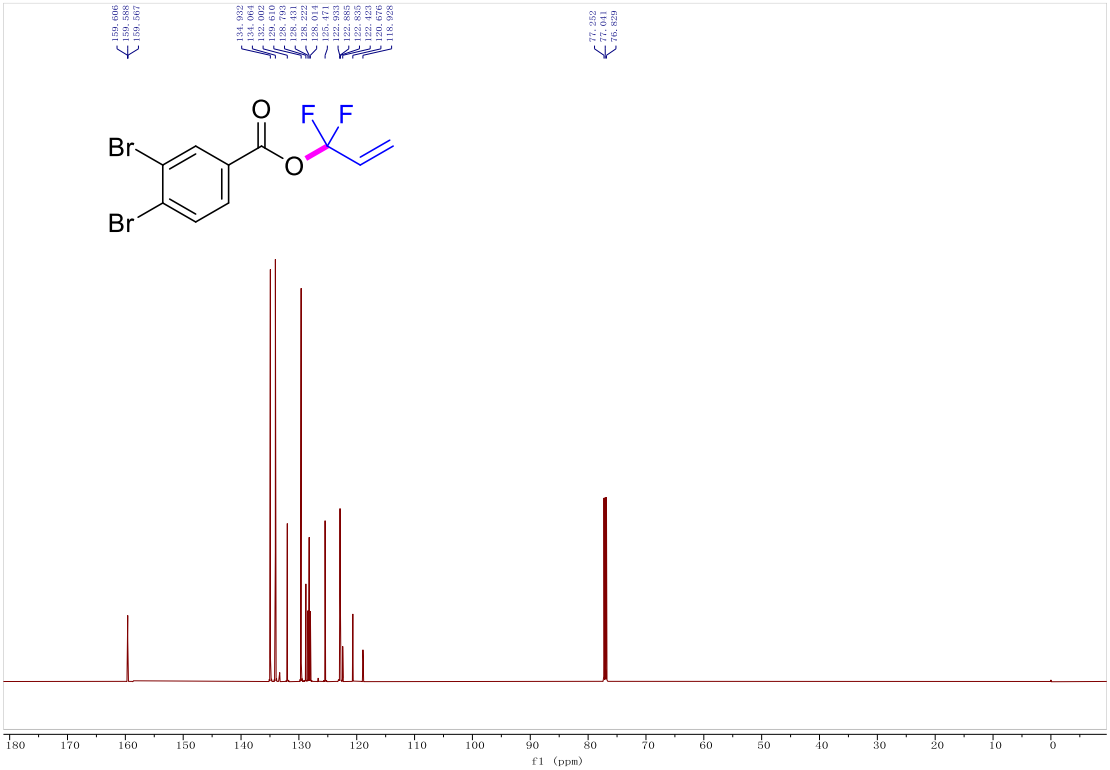


Figure S165. Compound 7r ^{19}F NMR (565 MHz, $CDCl_3$)

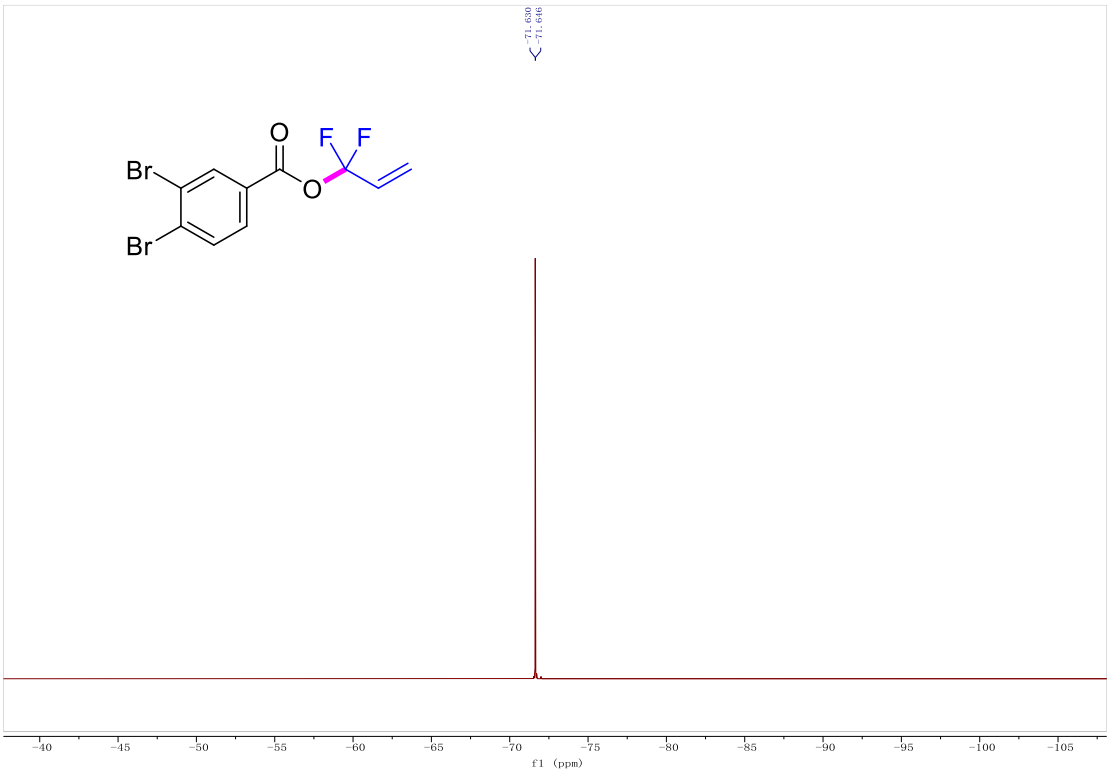


Figure S166. Compound 9a ^{1}H NMR (600 MHz, $CDCl_3$)

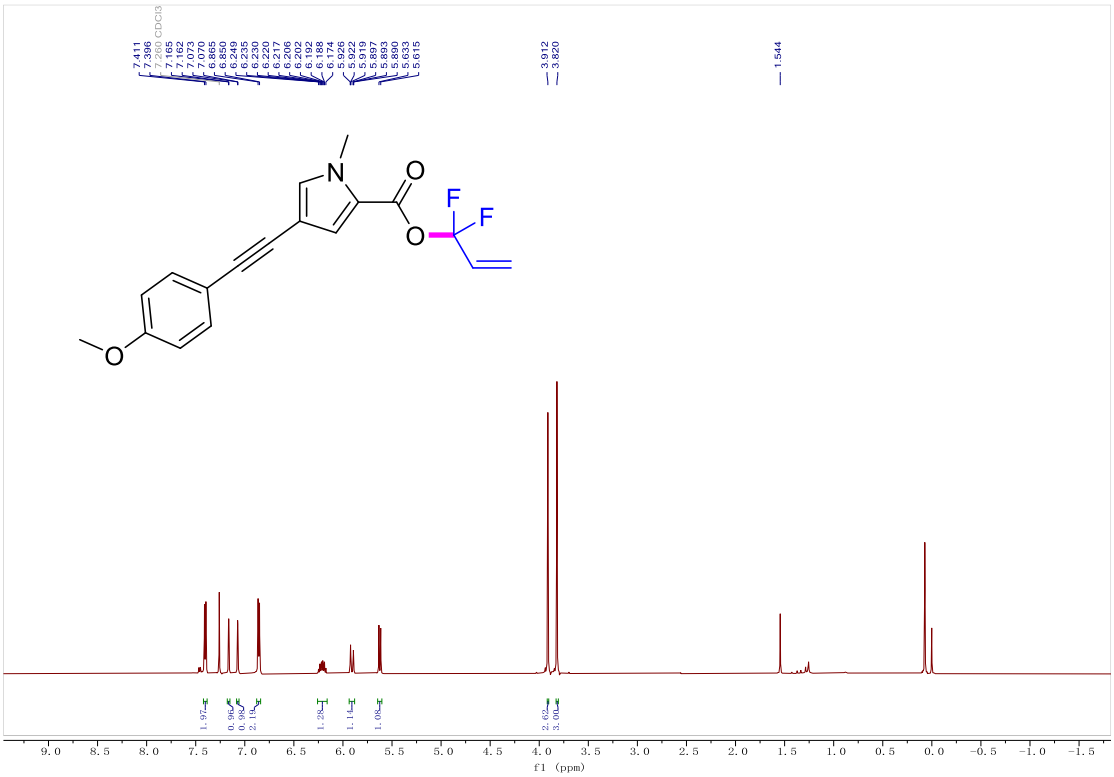


Figure S167. Compound 9a ^{13}C NMR (150 MHz, $CDCl_3$)

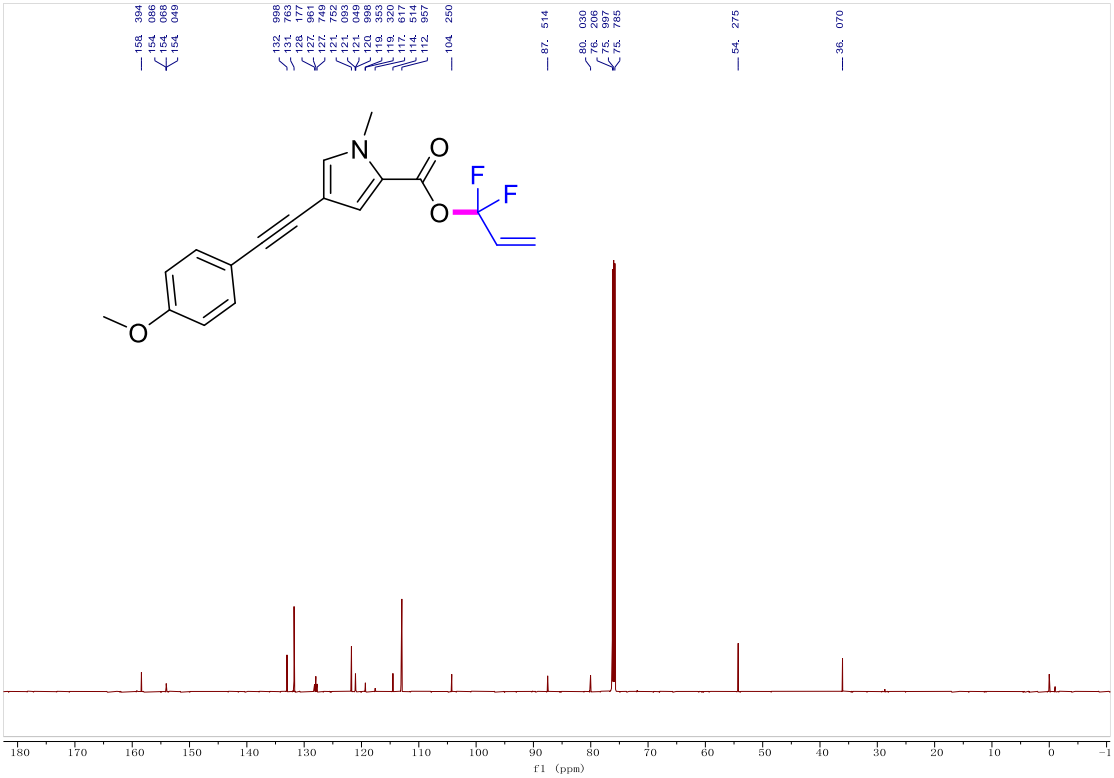


Figure S168. Compound 11a ^{1}H NMR (600 MHz, $CDCl_3$)

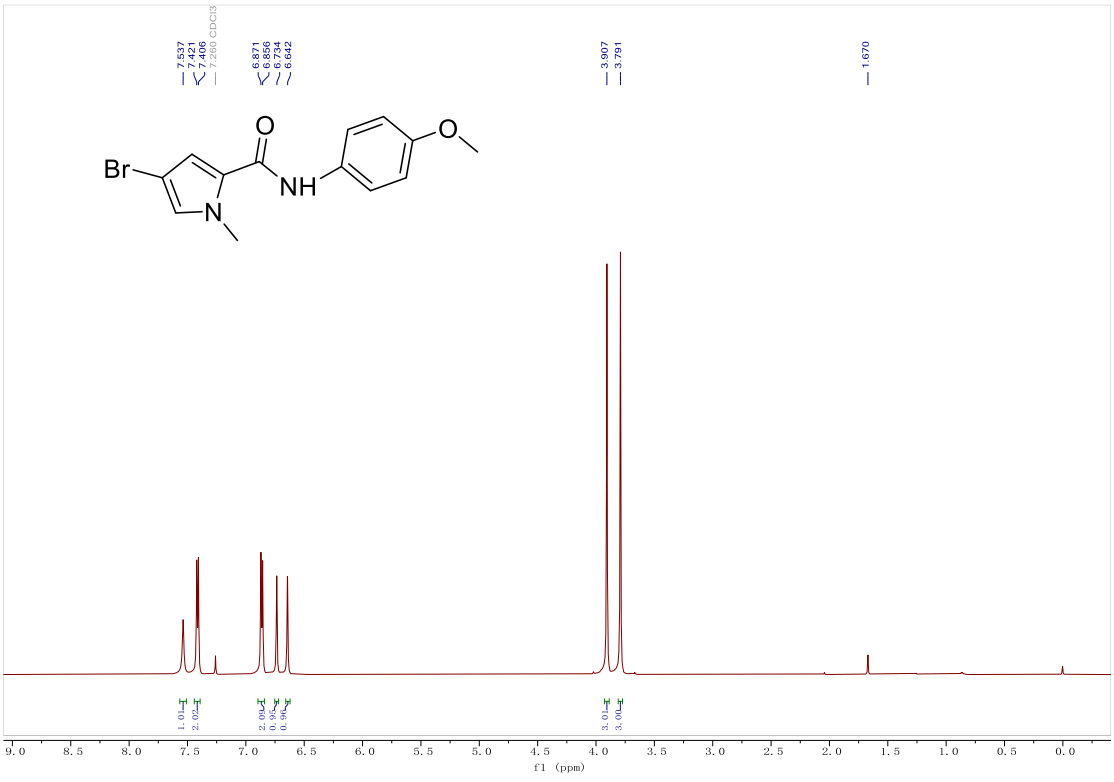


Figure S169. Compound 11a ^{13}C NMR (150 MHz, $CDCl_3$)

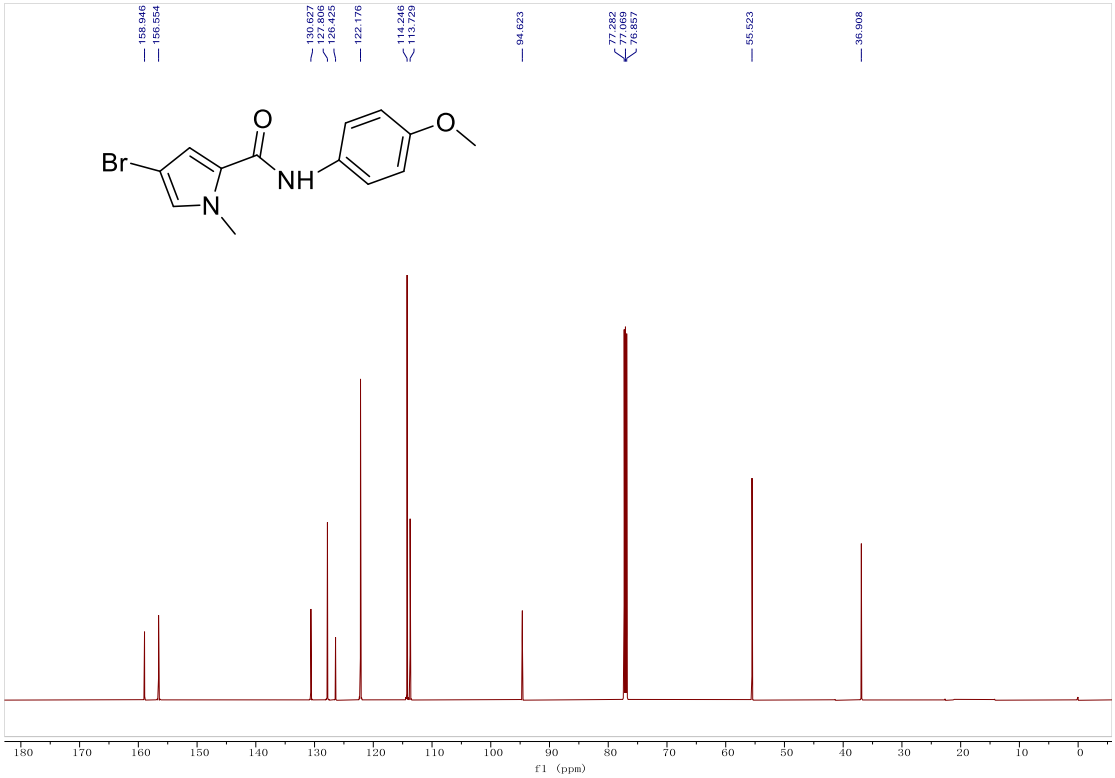


Figure S170. Compound 13a ^{1}H NMR (600 MHz, $CDCl_3$)

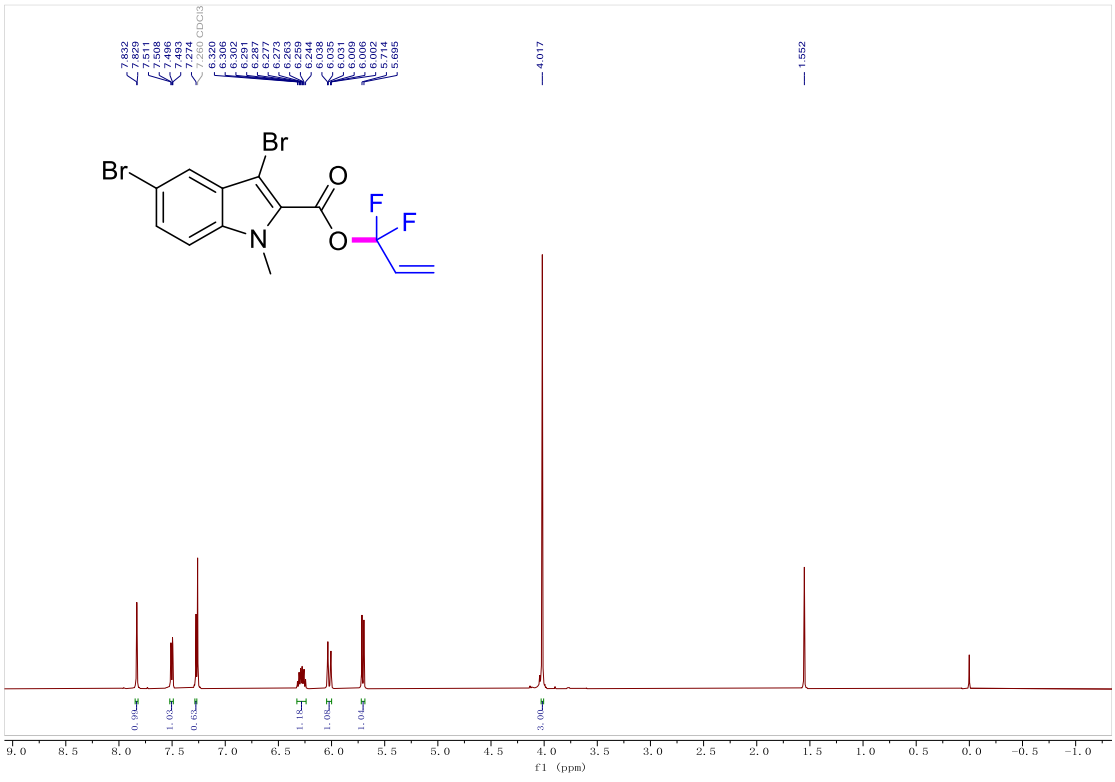
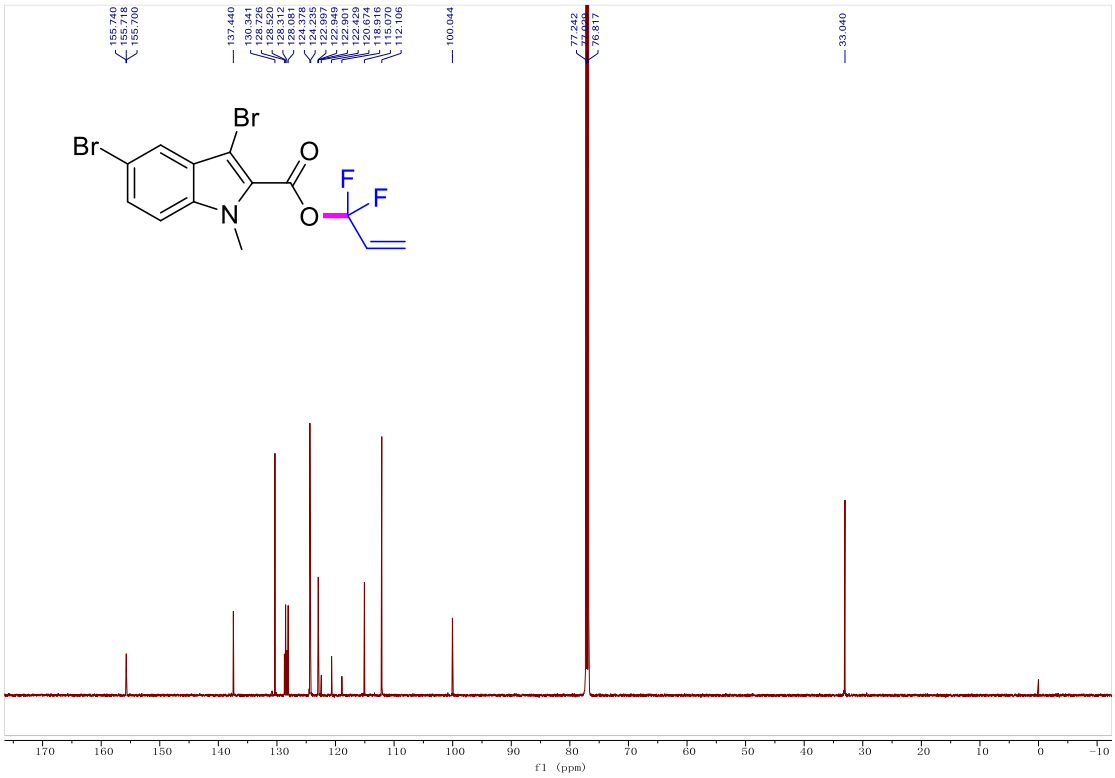


Figure S171. Compound 13a ^{13}C NMR (150 MHz, $CDCl_3$)

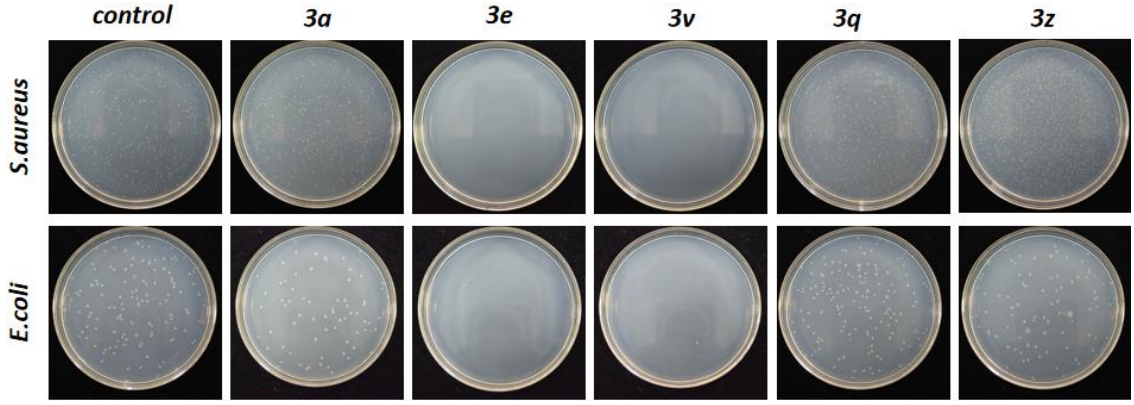


6. Antimicrobial performance testing experiment

To further evaluate the effectiveness of the above-mentioned synthesis method in constructing antibacterial active molecules, and to explore the potential functional value of the synthesized and the structure-activity rules. In this study, 5 target compounds (**3a, 3e, 3v, 3q, 3z**) were, and antibacterial activity experiments against *Staphylococcus aureus* and *Escherichia coli* were carried out (Table S7). The results showed **3e** and **3v** had significant antibacterial effects on Staphylococcus aureus and Escherichia coli, and the antibacterial rates reach more than 99%. Since the chlorine atom has moderate electronegativity, it can adjust the electron density of the indole ring through the induction effect, that the compound can be targeted to bind to the bacteria. We believe that if this kind of active antibacterial molecules need to be developed, the substituents with similar electroneativity and atomic radius to the chlorine atom can be introduced into its structure preferentially, and the introduction of substituents with too strong or too weak electronegativity be avoided.

Supplementary Table S7. Antimicrobial performance testing experiment

Entry	S.aureus			E.coli	
	dilution factor	bacterial solution concentration（CFU/mL）	antibacterial rate	bacterial solution concentration（CFU/mL）	antibacterial rate
control	10^4	3.13×10^7	/	1.07×10^7	/
3a	10^4	3.70×10^7	/	6.90×10^6	35.51%
3e	10^4	$<1.00\times10^5$	>99.68%	$<1.00\times10^5$	>99.07%
3v	10^4	1.00×10^5	99.68%	2.00×10^5	98.13%
3q	10^4	2.90×10^7	7.35%	1.67×10^7	/
3z	10^4	8.03×10^7	/	1.18×10^7	/



7. Crystal data 3e

Table 1 Crystal data and structure refinement for 3e.

Identification code	3e
Empirical formula	$C_{13}H_{10}ClF_2NO_2$
Formula weight	285.67
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.76030(10)
b/Å	13.7808(3)
c/Å	13.7988(4)
α/°	104.964(2)
β/°	95.599(2)
γ/°	90.149(2)
Volume/Å^3	1235.49(5)
Z	4
ρ_{calc}g/cm^3	1.536
μ/mm^{-1}	2.976
F(000)	584.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.098 to 146.448
Index ranges	-8 ≤ h ≤ 6, -17 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	15477
Independent reflections	4607 [R_{int} = 0.0263, R_{sigma} = 0.0202]
Data/restraints/parameters	4607/1/353
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0514, wR_2 = 0.1503
Final R indexes [all data]	R_1 = 0.0531, wR_2 = 0.1514
Largest diff. peak/hole / e Å^{-3}	0.77/-0.53

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3e. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	6826.8(11)	14443.2(5)	1535.9(5)	26.30(19)
F1	5460(3)	7723.7(13)	3007.4(14)	33.2(4)
F2	8661(3)	7704.6(13)	2958.6(14)	33.3(4)
O1	7345(3)	9452.7(15)	4150.3(15)	28.3(5)
O2	6936(3)	8898.5(14)	2436.4(14)	20.1(4)
N1	7276(3)	11498.1(16)	3925.5(17)	18.5(5)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3e. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	7186(4)	12297(2)	3496(2)	17.5(5)
C2	6960(4)	11915(2)	2439(2)	17.5(5)
C3	6828(4)	12581(2)	1814(2)	18.9(5)
C4	6941(4)	13592(2)	2281(2)	19.0(5)
C5	7168(4)	13975(2)	3335(2)	20.2(6)
C6	7289(4)	13335(2)	3957(2)	19.6(5)
C7	6907(4)	10854(2)	2231(2)	17.7(5)
C8	7097(4)	10622(2)	3144(2)	17.6(5)
C9	7151(4)	9636(2)	3344(2)	19.7(6)
C10	6932(4)	7902(2)	2460(2)	23.3(6)
C11	6646(5)	7217(2)	1428(2)	28.2(6)
C12	6436(5)	7510(2)	594(2)	29.7(7)
C13	7519(5)	11577(2)	5006(2)	25.1(6)
Cl2	1456.0(11)	8473.9(5)	720.1(6)	29.8(2)
F3	563(3)	15945.7(13)	3415.5(13)	28.4(4)
F4	3776(3)	15948.2(13)	3440.1(13)	28.3(4)
O3	2337(3)	14557.1(14)	4319.8(14)	23.4(4)
O4	2018(3)	14527.9(14)	2647.8(14)	19.9(4)
N2	2230(3)	12368.8(17)	3700.8(17)	18.1(5)
C14	1967(4)	9609(2)	2651(2)	21.7(6)
C15	1729(4)	9625(2)	1633(2)	21.4(6)
C16	1667(4)	10500(2)	1332(2)	20.9(6)
C17	1852(4)	11411(2)	2088(2)	18.1(5)
C18	2095(4)	11397(2)	3116(2)	18.3(5)
C19	2162(4)	10492(2)	3407(2)	20.8(6)
C20	1853(4)	12436(2)	2072(2)	18.2(5)
C21	2085(4)	12994(2)	3060(2)	18.1(5)
C22	2165(4)	14088(2)	3454(2)	19.2(5)
C23	2071(4)	15561(2)	2853(2)	21.3(6)
C24	1917(4)	15910(2)	1911(2)	25.7(6)
C25	1829(5)	15325(3)	1000(2)	31.3(7)
C38	2487(4)	12665(2)	4803(2)	22.6(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3e. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	31.3(4)	21.1(3)	29.9(4)	13.2(3)	1.4(3)	0.5(3)
F1	42.6(11)	25.7(9)	33.5(10)	9.6(7)	10.2(8)	-8.8(8)
F2	38.7(11)	25.0(9)	35.5(10)	9.8(7)	-5.6(8)	10.5(8)
O1	40.1(13)	21.7(10)	24.6(11)	9.8(8)	0.2(9)	0.1(9)
O2	22.2(10)	14.5(9)	23.7(10)	5.8(7)	0.4(8)	-0.2(8)
N1	19.7(12)	16.4(11)	19.6(11)	5.6(9)	0.9(9)	0.3(9)
C1	13.5(12)	17.3(13)	22.6(13)	6.7(10)	1.2(10)	0.6(10)
C2	13.5(12)	18.2(13)	20.9(13)	5.0(10)	1.6(10)	1.3(10)
C3	16.3(13)	19.9(13)	20.9(13)	6.4(10)	1.4(10)	1.0(11)
C4	14.0(13)	19.5(13)	25.8(14)	10.9(11)	0.4(10)	-0.5(10)
C5	17.7(13)	15.9(12)	26.2(14)	4.3(10)	1.9(11)	-1.1(10)
C6	18.1(13)	18.4(13)	21.3(13)	3.7(10)	1.0(10)	0.6(11)
C7	13.9(13)	17.5(12)	21.3(13)	5.1(10)	0.1(10)	1.1(10)
C8	13.7(13)	16.3(12)	21.6(13)	3.8(10)	-0.6(10)	-0.8(10)
C9	17.7(13)	19.7(13)	22.0(13)	6.4(10)	0.8(10)	0.2(11)
C10	22.8(15)	18.5(13)	30.4(15)	10.0(11)	1.6(11)	1.2(11)
C11	29.6(16)	17.8(14)	35.4(16)	4.2(12)	2.1(13)	0.6(12)
C12	30.2(17)	25.3(15)	30.6(16)	3.6(12)	-1.0(13)	-0.6(13)
C13	33.8(17)	22.2(14)	19.1(13)	6.3(11)	-0.1(11)	0.7(12)
Cl2	33.8(4)	19.2(3)	32.2(4)	-1.0(3)	3.5(3)	0.2(3)
F3	32.4(10)	23.9(8)	31.0(9)	8.8(7)	9.6(7)	9.2(7)
F4	30.8(10)	24.1(8)	28.8(9)	8.2(7)	-6.0(7)	-8.7(7)
O3	28.5(11)	19.1(9)	21.9(10)	5.0(8)	0.2(8)	1.1(8)
O4	21.3(10)	16.4(9)	21.9(9)	6.1(7)	-0.6(7)	-1.0(8)
N2	18.4(11)	17.5(11)	18.6(11)	5.7(9)	0.3(8)	0.3(9)
C14	16.2(13)	17.5(13)	32.1(15)	8.1(11)	1.9(11)	1.2(11)
C15	14.0(13)	19.3(13)	28.0(14)	1.5(11)	1.4(10)	-0.5(11)
C16	16.3(13)	22.7(14)	22.2(13)	3.7(11)	1.6(10)	0.2(11)
C17	12.3(12)	20.2(13)	22.0(13)	6.2(10)	0.6(10)	1.2(10)
C18	13.7(12)	18.2(13)	22.1(13)	4.0(10)	0.1(10)	-0.8(10)
C19	17.9(13)	21.9(13)	23.6(13)	8.1(11)	1.6(10)	1.8(11)
C20	15.1(13)	19.6(13)	20.3(13)	6.6(10)	-0.1(10)	0.9(10)
C21	14.2(13)	18.5(13)	22.5(13)	7.1(10)	0.9(10)	0.6(10)
C22	17.5(13)	19.9(13)	21.2(13)	7.2(10)	2.0(10)	0.8(11)
C23	20.4(14)	16.5(13)	26.0(14)	3.9(10)	1.6(11)	0.2(11)
C24	23.7(15)	24.0(14)	32.1(16)	12.8(12)	-0.2(12)	-0.6(12)
C25	33.8(17)	35.1(17)	28.2(16)	14.7(13)	1.3(13)	1.6(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3e. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C38	27.9(15)	21.3(13)	18.7(13)	6.8(10)	-1.7(11)	1.0(12)

Table 4 Bond Lengths for 3e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C4	1.745(3)	Cl2	C15	1.749(3)
F1	C10	1.365(3)	F3	C23	1.366(3)
F2	C10	1.362(3)	F4	C23	1.364(3)
O1	C9	1.199(3)	O3	C22	1.197(3)
O2	C9	1.388(3)	O4	C22	1.393(3)
O2	C10	1.382(3)	O4	C23	1.377(3)
N1	C1	1.377(3)	N2	C18	1.371(3)
N1	C8	1.392(3)	N2	C21	1.383(3)
N1	C13	1.460(3)	N2	C38	1.461(3)
C1	C2	1.411(4)	C14	C15	1.405(4)
C1	C6	1.406(4)	C14	C19	1.379(4)
C2	C3	1.410(4)	C15	C16	1.372(4)
C2	C7	1.414(4)	C16	C17	1.407(4)
C3	C4	1.374(4)	C17	C18	1.417(4)
C4	C5	1.407(4)	C17	C20	1.418(4)
C5	C6	1.377(4)	C18	C19	1.405(4)
C7	C8	1.372(4)	C20	C21	1.374(4)
C8	C9	1.455(4)	C21	C22	1.463(4)
C10	C11	1.486(4)	C23	C24	1.493(4)
C11	C12	1.310(5)	C24	C25	1.303(4)

Table 5 Bond Angles for 3e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O2	C9	118.6(2)	C23	O4	C22	118.5(2)
C1	N1	C8	107.4(2)	C18	N2	C21	107.6(2)
C1	N1	C13	125.3(2)	C18	N2	C38	125.0(2)
C8	N1	C13	127.2(2)	C21	N2	C38	127.4(2)
N1	C1	C2	108.3(2)	C19	C14	C15	120.6(3)
N1	C1	C6	129.9(2)	C14	C15	Cl2	117.9(2)
C6	C1	C2	121.8(2)	C16	C15	Cl2	119.2(2)

Table 5 Bond Angles for 3e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	C2	C7	107.3(2)	C16	C15	C14	122.9(3)
C3	C2	C1	119.9(2)	C15	C16	C17	117.6(3)
C3	C2	C7	132.8(2)	C16	C17	C18	119.7(2)
C4	C3	C2	117.2(2)	C16	C17	C20	133.7(3)
C3	C4	Cl1	118.7(2)	C18	C17	C20	106.7(2)
C3	C4	C5	123.0(2)	N2	C18	C17	108.6(2)
C5	C4	Cl1	118.3(2)	N2	C18	C19	129.6(3)
C6	C5	C4	120.5(2)	C19	C18	C17	121.7(3)
C5	C6	C1	117.5(2)	C14	C19	C18	117.5(3)
C8	C7	C2	106.8(2)	C21	C20	C17	106.8(2)
N1	C8	C9	121.4(2)	N2	C21	C22	121.1(2)
C7	C8	N1	110.1(2)	C20	C21	N2	110.3(2)
C7	C8	C9	128.6(2)	C20	C21	C22	128.6(2)
O1	C9	O2	123.3(2)	O3	C22	O4	123.7(2)
O1	C9	C8	127.3(3)	O3	C22	C21	127.3(2)
O2	C9	C8	109.4(2)	O4	C22	C21	109.0(2)
F1	C10	O2	109.7(2)	F3	C23	O4	110.0(2)
F1	C10	C11	109.7(2)	F3	C23	C24	109.6(2)
F2	C10	F1	105.6(2)	F4	C23	F3	105.2(2)
F2	C10	O2	109.9(2)	F4	C23	O4	110.4(2)
F2	C10	C11	110.3(2)	F4	C23	C24	109.6(2)
O2	C10	C11	111.5(2)	O4	C23	C24	111.8(2)
C12	C11	C10	124.8(3)	C25	C24	C23	125.0(3)

Table 6 Torsion Angles for 3e.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C4	C5	C6	-179.2(2)	Cl2	C15	C16	C17	178.8(2)
F1	C10	C11	C12	122.1(3)	F3	C23	C24	C25	-125.0(3)
F2	C10	C11	C12	-122.0(3)	F4	C23	C24	C25	120.0(3)
O2	C10	C11	C12	0.4(4)	O4	C23	C24	C25	-2.8(4)
N1	C1	C2	C3	-180.0(2)	N2	C18	C19	C14	179.4(3)
N1	C1	C2	C7	0.2(3)	N2	C21	C22	O3	-0.7(4)
N1	C1	C6	C5	179.6(3)	N2	C21	C22	O4	179.0(2)
N1	C8	C9	O1	-0.1(4)	C14	C15	C16	C17	0.0(4)
N1	C8	C9	O2	179.8(2)	C15	C14	C19	C18	0.5(4)
C1	N1	C8	C7	0.3(3)	C15	C16	C17	C18	0.1(4)
C1	N1	C8	C9	179.5(2)	C15	C16	C17	C20	-179.8(3)

Table 6 Torsion Angles for 3e.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	0.4(4)	C16	C17	C18	N2	-179.7(2)
C1	C2	C7	C8	0.0(3)	C16	C17	C18	C19	0.1(4)
C2	C1	C6	C5	-0.2(4)	C16	C17	C20	C21	179.8(3)
C2	C3	C4	Cl1	178.91(19)	C17	C18	C19	C14	-0.4(4)
C2	C3	C4	C5	-0.3(4)	C17	C20	C21	N2	0.0(3)
C2	C7	C8	N1	-0.2(3)	C17	C20	C21	C22	-179.5(3)
C2	C7	C8	C9	-179.3(3)	C18	N2	C21	C20	0.2(3)
C3	C2	C7	C8	-179.8(3)	C18	N2	C21	C22	179.7(2)
C3	C4	C5	C6	-0.1(4)	C18	C17	C20	C21	-0.1(3)
C4	C5	C6	C1	0.3(4)	C19	C14	C15	Cl2	-179.1(2)
C6	C1	C2	C3	-0.1(4)	C19	C14	C15	C16	-0.3(4)
C6	C1	C2	C7	-179.9(2)	C20	C17	C18	N2	0.2(3)
C7	C2	C3	C4	-179.9(3)	C20	C17	C18	C19	-179.9(2)
C7	C8	C9	O1	178.9(3)	C20	C21	C22	O3	178.7(3)
C7	C8	C9	O2	-1.2(4)	C20	C21	C22	O4	-1.6(4)
C8	N1	C1	C2	-0.3(3)	C21	N2	C18	C17	-0.2(3)
C8	N1	C1	C6	179.8(3)	C21	N2	C18	C19	180.0(3)
C9	O2	C10	F1	57.1(3)	C22	O4	C23	F3	-58.5(3)
C9	O2	C10	F2	-58.5(3)	C22	O4	C23	F4	57.1(3)
C9	O2	C10	C11	178.8(2)	C22	O4	C23	C24	179.4(2)
C10	O2	C9	O1	0.4(4)	C23	O4	C22	O3	0.0(4)
C10	O2	C9	C8	-179.5(2)	C23	O4	C22	C21	-179.8(2)
C13	N1	C1	C2	179.6(2)	C38	N2	C18	C17	179.9(2)
C13	N1	C1	C6	-0.3(5)	C38	N2	C18	C19	0.1(5)
C13	N1	C8	C7	-179.6(3)	C38	N2	C21	C20	-180.0(2)
C13	N1	C8	C9	-0.4(4)	C38	N2	C21	C22	-0.5(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3e.

Atom	*x*	*y*	*z*	U(eq)
H3	6668.26	12340.9	1100.07	23
H5	7239.51	14680.97	3621.51	24
H6	7436.84	13585.54	4669.57	24
H7	6767.58	10391.47	1583.22	21
H11	6614.61	6514.27	1368.37	34
H12A	6270(50)	8250(15)	620(30)	31(9)
H12B	6330(50)	7010(30)	-70(30)	34(10)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3e.

Atom	*x*	*y*	*z*	U(eq)
H13A	8751.66	11258.22	5176.59	38
H13B	6387.03	11239.17	5187.64	38
H13C	7579.89	12287.28	5380.24	38
H14	1994.65	8982.94	2821.36	26
H16	1505.39	10490.79	637.72	25
H19	2333.81	10487.88	4097.32	25
H20	1719.19	12688.82	1491.11	22
H24	1881.11	16614.28	1982.2	31
H25A	1860.65	14616.56	898.17	38
H25B	1731.95	15605.82	437.51	38
H38A	1344.06	13050.32	5055.65	34
H38B	3706.04	13079.75	5035.36	34
H38C	2583.29	12062.43	5055.53	34

8. Crystal data 3x′

Table 1 Crystal data and structure refinement for 3x′.

Identification code	3x′
Empirical formula	$C_{15}H_{10}BrF_2NO_3$
Formula weight	370.15
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pccn
a/Å	28.9319(4)
b/Å	11.12268(15)
c/Å	8.86658(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2853.26(6)
Z	8
ρ_{calc}g/cm^3	1.723
μ/mm^{-1}	4.272
F(000)	1472.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.516 to 150.12
Index ranges	-36 ≤ h ≤ 33, -13 ≤ k ≤ 13, -10 ≤ l ≤ 11
Reflections collected	13221
Independent reflections	2847 [R_{int} = 0.0462, R_{sigma} = 0.0207]
Data/restraints/parameters	2847/1/199
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.1140
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.1145
Largest diff. peak/hole / e Å^{-3}	0.91/-0.80

Crystal structure determination of [3x′]

Crystal Data for $C_{15}H_{10}BrF_2NO_3$ (*M* =370.15 g/mol): orthorhombic, space group Pccn (no. 56), *a* = 28.9319(4) Å, *b* = 11.12268(15) Å, *c* = 8.86658(9) Å, *V* = 2853.26(6) Å^3, *Z* = 8, *T* = 100.00(10) K, μ(Cu Kα) = 4.272 mm^{-1}, *Dcalc* = 1.723 g/cm^3, 13221 reflections measured (8.516° ≤ 2Θ ≤ 150.12°), 2847 unique (R_{int} = 0.0462, R_{sigma} = 0.0207) which were used in all calculations. The final R_1 was 0.0382 (I > 2σ(I)) and wR_2 was 0.1145 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3x´. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	5646.4(2)	5400.3(2)	8153.0(3)	14.91(14)
F1	3026.9(6)	7019.3(15)	8555(2)	33.9(4)
F2	3509.2(6)	7361.3(17)	10372(2)	40.3(5)
O1	3851.6(6)	2159.1(15)	4801(2)	23.3(4)
O2	3266.2(6)	4555.0(15)	7630(2)	18.7(4)
O3	3697.1(5)	6030.2(15)	8718.9(19)	19.3(4)
N1	4125.7(6)	3799.4(17)	6045(2)	13.8(4)
C1	5323.1(8)	4349(2)	6858(2)	12.7(5)
C2	5556.8(8)	3551(2)	5951(3)	15.2(4)
C3	5310.2(8)	2796(2)	4968(3)	16.5(5)
C4	4832.3(8)	2786.5(19)	4907(2)	15.2(5)
C5	4600.2(7)	3579.9(19)	5871(2)	12.8(4)
C6	4837.5(9)	4379(2)	6833(2)	11.6(5)
C7	4501.9(8)	5077(2)	7607(2)	12.8(4)
C8	4075.8(9)	4719(2)	7119(3)	14.0(5)
C9	3631.2(8)	5046(2)	7799(3)	14.7(4)
C10	3784.8(8)	3193(2)	5154(3)	15.8(5)
C11	3388.1(8)	3911(2)	4607(3)	18.8(5)
C12	3049.7(9)	3370(3)	3860(3)	28.7(6)
C13	3317.0(8)	6470(2)	9528(3)	22.2(5)
C14	3075.4(9)	5599(2)	10531(3)	21.5(5)
C15	2627.0(10)	5633(3)	10746(3)	30.2(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3x´ The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	11.29(19)	17.7(2)	15.8(2)	-1.12(8)	-1.97(7)	-0.55(7)
F1	28.1(8)	32.5(9)	41.2(9)	13.0(8)	14.1(7)	14.0(7)
F2	31.6(9)	36.9(10)	52.3(10)	-27.3(8)	24.4(8)	-15.1(7)
O1	20.4(8)	18.3(9)	31.1(9)	-4.5(7)	-8.4(7)	-0.2(6)
O2	11.0(8)	25.2(10)	19.9(9)	1.6(6)	-1.4(7)	-0.7(6)
O3	12.9(7)	21.7(9)	23.4(9)	-6.0(7)	6.6(6)	-1.9(6)
N1	12.5(9)	13.9(9)	15.2(9)	-0.8(7)	-1.4(7)	-1.0(7)
C1	13.5(11)	11.6(10)	12.9(11)	2.4(8)	-2.4(8)	-0.6(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3x´ The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	13.2(9)	16.3(11)	16.0(10)	3.7(9)	1.3(8)	1.6(8)
C3	20.8(11)	13.9(11)	14.8(10)	1.3(8)	3.3(8)	4.3(8)
C4	19.6(11)	13.7(11)	12.2(9)	-0.7(8)	-1.3(8)	-0.4(8)
C5	13.9(10)	12.8(10)	11.6(9)	3.4(8)	-1.2(8)	-0.4(8)
C6	14.5(11)	11.3(10)	9.2(10)	0.8(7)	-0.8(7)	-1.3(9)
C7	14.2(11)	12.5(10)	11.7(10)	-1.0(8)	-0.1(8)	1.3(8)
C8	14.0(11)	15.6(11)	12.5(10)	1.6(8)	0.6(9)	-1.0(8)
C9	14.6(11)	15.7(11)	13.6(10)	2.0(10)	-0.2(9)	1.0(9)
C10	14.6(10)	16.9(11)	16.0(10)	-0.5(9)	-2.5(8)	-3.2(8)
C11	18.5(11)	19.8(11)	18.0(11)	-0.6(9)	-3.2(9)	2.2(9)
C12	21.1(12)	31.0(14)	34.0(15)	-5.5(12)	-9.6(11)	3.8(10)
C13	17.8(11)	21.0(12)	27.9(12)	-5.3(10)	7.1(10)	-1.2(9)
C14	15.4(11)	28.7(13)	20.3(12)	2.0(10)	2.2(9)	-1.9(9)
C15	18.3(12)	35.6(14)	36.8(15)	5.2(13)	7.9(11)	-2.7(11)

Table 4 Bond Lengths for 3x´.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.887(2)	C2	C3	1.405(3)
F1	C13	1.350(3)	C3	C4	1.384(3)
F2	C13	1.361(3)	C4	C5	1.400(3)
O1	C10	1.208(3)	C5	C6	1.410(3)
O2	C9	1.199(3)	C6	C7	1.420(3)
O3	C9	1.378(3)	C7	C8	1.366(3)
O3	C13	1.401(3)	C8	C9	1.467(3)
N1	C5	1.403(3)	C10	C11	1.480(3)
N1	C8	1.404(3)	C11	C12	1.327(4)
N1	C10	1.432(3)	C13	C14	1.489(4)
C1	C2	1.375(3)	C14	C15	1.312(4)
C1	C6	1.405(3)			

Table 5 Bond Angles for 3x´

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O3	C13	118.15(18)	N1	C8	C9	123.3(2)
C5	N1	C8	107.56(18)	C7	C8	N1	109.5(2)
C5	N1	C10	122.09(18)	C7	C8	C9	126.1(2)
C8	N1	C10	130.2(2)	O2	C9	O3	123.9(2)
C2	C1	Br1	120.80(18)	O2	C9	C8	127.4(2)
C2	C1	C6	119.9(2)	O3	C9	C8	108.63(19)
C6	C1	Br1	119.34(17)	O1	C10	N1	118.8(2)
C1	C2	C3	119.9(2)	O1	C10	C11	123.6(2)
C4	C3	C2	122.4(2)	N1	C10	C11	117.4(2)
C3	C4	C5	116.8(2)	C12	C11	C10	119.4(2)
N1	C5	C6	107.48(19)	F1	C13	F2	106.0(2)
C4	C5	N1	130.3(2)	F1	C13	O3	108.6(2)
C4	C5	C6	122.2(2)	F1	C13	C14	112.6(2)
C1	C6	C5	118.8(2)	F2	C13	O3	102.43(18)
C1	C6	C7	133.6(2)	F2	C13	C14	109.7(2)
C5	C6	C7	107.7(2)	O3	C13	C14	116.6(2)
C8	C7	C6	107.7(2)	C15	C14	C13	122.2(3)

Table 6 Torsion Angles for 3x´

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C1	C2	C3	-178.48(17)	C5	N1	C8	C9	-168.6(2)
Br1	C1	C6	C5	-179.35(16)	C5	N1	C10	O1	35.3(3)
Br1	C1	C6	C7	0.6(3)	C5	N1	C10	C11	-139.5(2)
F1	C13	C14	C15	-18.8(4)	C5	C6	C7	C8	-0.5(2)
F2	C13	C14	C15	98.9(3)	C6	C1	C2	C3	2.0(3)
O1	C10	C11	C12	9.7(4)	C6	C7	C8	N1	0.2(3)
O3	C13	C14	C15	-145.3(3)	C6	C7	C8	C9	168.7(2)
N1	C5	C6	C1	-179.37(19)	C7	C8	C9	O2	-161.9(2)
N1	C5	C6	C7	0.7(2)	C7	C8	C9	O3	17.1(3)
N1	C8	C9	O2	5.2(4)	C8	N1	C5	C4	-177.5(2)
N1	C8	C9	O3	-175.8(2)	C8	N1	C5	C6	-0.6(2)
N1	C10	C11	C12	-175.7(2)	C8	N1	C10	O1	-149.2(2)
C1	C2	C3	C4	-2.4(3)	C8	N1	C10	C11	36.0(3)
C1	C6	C7	C8	179.5(2)	C9	O3	C13	F1	-72.2(3)
C2	C1	C6	C5	0.2(3)	C9	O3	C13	F2	176.0(2)

Table 6 Torsion Angles for 3x´

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C1	C6	C7	-179.9(2)	C9	O3	C13	C14	56.2(3)
C2	C3	C4	C5	0.5(3)	C10	N1	C5	C4	-1.1(3)
C3	C4	C5	N1	178.3(2)	C10	N1	C5	C6	175.8(2)
C3	C4	C5	C6	1.8(3)	C10	N1	C8	C7	-175.8(2)
C4	C5	C6	C1	-2.1(3)	C10	N1	C8	C9	15.3(4)
C4	C5	C6	C7	177.9(2)	C13	O3	C9	O2	1.3(3)
C5	N1	C8	C7	0.3(2)	C13	O3	C9	C8	-177.8(2)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3x´

Atom	*x*	*y*	*z*	U(eq)
H2	5884.59	3511.16	5988.6	18
H3	5477.74	2272.11	4321.36	20
H4	4669.5	2266.81	4243.18	18
H7	4562.83	5683.84	8334.41	15
H11	3375.78	4752.4	4789.6	23
H12A	3063.5	2528.34	3680.19	34
H12B	2793.6	3822.95	3504.52	34
H14	3251.76	4999.88	11032.28	26
H15A	2445.45	6227	10253.41	36
H15B	2483.72	5064	11393.53	36

9. Crystal data 11a

Table 1 Crystal data and structure refinement for 11a.

Identification code	11a
Empirical formula	$C_{13}H_{13}BrN_2O_2$
Formula weight	309.16
Temperature/K	298.24(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.15980(10)
b/Å	12.06170(10)
c/Å	20.9620(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1304.59(3)
Z	4
ρ_{calc}g/cm^3	1.574
μ/mm^{-1}	4.271
F(000)	624.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.436 to 146.952
Index ranges	$-6 \le h \le 4$, $-14 \le k \le 14$, $-24 \le l \le 25$
Reflections collected	9806
Independent reflections	2524 [R_{int} = 0.0172, R_{sigma} = 0.0113]
Data/restraints/parameters	2524/0/169
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0920
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0925
Largest diff. peak/hole / e Å^{-3}	0.71/-0.77
Flack parameter	-0.010(6)

Crystal structure determination of [11a]

Crystal Data for $C_{13}H_{13}BrN_2O_2$ (M =309.16 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 5.15980(10)Å, b = 12.06170(10) Å, c = 20.9620(3)Å, V = 1304.59(3)Å^3, Z = 4, T = 298.24(10)K, μ(Cu Kα)= 4.271 mm^{-1}, *Dcalc* = 1.574g/cm^3, 9806 reflections measured ($8.436 \le 2\Theta \le 146.952$), 2524 unique ($R_{int}$ = 0.0172, R_{sigma} = 0.0113) which were used in all calculations. The final R_1 was 0.0351 ($I > 2\sigma(I)$) and wR_2 was 0.0925 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 11a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br_1	4047.6(13)	2187.2(4)	3241.3(3)	73.1(2)
O_1	10679(5)	6621(2)	3407.1(13)	46.1(6)
O_2	7224(7)	10694(3)	5156.8(17)	63.8(9)
N_1	8988(7)	4608(3)	2726.3(15)	41.8(7)
N_2	6456(6)	6872(3)	3674.6(15)	38.7(7)
C_1	7674(7)	5169(3)	3199.8(18)	38.1(7)
C_2	5791(8)	4477(3)	3450.0(17)	42.1(8)
C_3	6045(8)	3469(3)	3113.6(18)	46.7(9)
C_4	7980(9)	3573(3)	2671.4(19)	48.3(9)
C_5	8425(7)	6278(3)	3426.0(16)	36.1(7)
C_6	6710(6)	7879(3)	4023.9(16)	34.1(7)
C_7	8714(7)	8021(3)	4459.3(17)	41.4(8)
C_8	8816(8)	8975(3)	4824.4(19)	45.9(9)
C_9	6943(8)	9785(3)	4764.1(19)	43.5(8)
C_{10}	4951(8)	9648(3)	4332.9(19)	45.4(9)
C_{11}	4846(7)	8684(3)	3965.1(19)	41.6(8)
C_{12}	5155(11)	11471(4)	5178(3)	71.0(14)
C_{13}	10966(10)	5055(4)	2290(2)	55.8(10)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br_1	92.2(4)	41.9(3)	85.3(4)	-5.6(2)	2.2(3)	-15.8(3)
O_1	32.2(11)	52.2(15)	54.0(14)	-8.0(12)	4.4(11)	-5.2(12)
O_2	70(2)	48.1(16)	74(2)	-22.3(15)	-17.1(18)	3.3(15)
N_1	41.1(16)	44.1(16)	40.4(14)	-3.8(12)	1.4(14)	5.6(15)
N_2	29.9(15)	39.1(16)	46.9(17)	-8.6(13)	2.0(13)	-4.7(12)
C_1	38.9(17)	36.9(17)	38.5(17)	-2.9(15)	-0.6(16)	2.8(14)
C_2	43.7(19)	42.4(19)	40.0(17)	-5.2(14)	-1.4(17)	-3.7(17)
C_3	53(2)	34.0(17)	53(2)	-4.0(15)	-11.6(19)	-0.7(18)
C_4	61(2)	39.0(19)	46(2)	-8.6(16)	-6.4(19)	13.2(19)
C_5	34.1(16)	39.7(18)	34.4(16)	-0.5(13)	1.5(14)	-0.8(14)
C_6	32.9(16)	34.1(16)	35.2(15)	-2.3(14)	4.7(13)	-4.3(14)
C_7	38.2(18)	44.4(19)	41.7(17)	-4.1(15)	-2.6(15)	4.1(16)
C_8	43(2)	50(2)	45.3(19)	-7.4(16)	-10.1(17)	-3.7(19)
C_9	47(2)	38.8(19)	45.0(19)	-5.9(15)	-3.5(16)	-6.7(16)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 11a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C_{10}	46(2)	37.7(19)	52(2)	-3.5(17)	-5.8(17)	2.7(16)
C_{11}	39.0(19)	40(2)	45.4(19)	-4.2(15)	-7.4(15)	-2.4(15)
C_{12}	77(3)	53(3)	83(3)	-26(2)	-1(3)	3(2)
C_{13}	53(2)	66(3)	48(2)	1.2(19)	13(2)	9(2)

Table 4 Bond Lengths for 11a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br_1	C_3	1.877(4)	C_1	C_5	1.471(5)
O_1	C_5	1.236(4)	C_2	C_3	1.411(5)
O_2	C_9	1.378(5)	C_3	C_4	1.368(6)
O_2	C_{12}	1.421(6)	C_6	C_7	1.390(5)
N_1	C_1	1.379(5)	C_6	C_{11}	1.372(5)
N_1	C_4	1.357(5)	C_7	C_8	1.383(5)
N_1	C_{13}	1.474(5)	C_8	C_9	1.380(6)
N_2	C_5	1.348(5)	C_9	C_{10}	1.379(6)
N_2	C_6	1.425(4)	C_{10}	C_{11}	1.396(5)
C_1	C_2	1.384(5)			

Table 5 Bond Angles for 11a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C_9	O_2	C_{12}	117.7(4)	O_1	C_5	N_2	122.9(3)
C_1	N_1	C_{13}	127.4(3)	O_1	C_5	C_1	122.8(3)
C_4	N_1	C_1	108.9(3)	N_2	C_5	C_1	114.2(3)
C_4	N_1	C_{13}	123.4(3)	C_7	C_6	N_2	120.7(3)
C_5	N_2	C_6	125.7(3)	C_{11}	C_6	N_2	119.5(3)
N_1	C_1	C_2	108.8(3)	C_{11}	C_6	C_7	119.6(3)
N_1	C_1	C_5	123.3(3)	C_8	C_7	C_6	119.6(4)
C_2	C_1	C_5	127.7(3)	C_9	C_8	C_7	120.8(4)
C_1	C_2	C_3	105.4(4)	O_2	C_9	C_8	115.8(4)
C_2	C_3	Br_1	125.9(3)	O_2	C_9	C_{10}	124.4(4)
C_4	C_3	Br_1	125.0(3)	C_{10}	C_9	C_8	119.8(3)
C_4	C_3	C_2	109.1(4)	C_9	C_{10}	C_{11}	119.4(4)
N_1	C_4	C_3	107.9(3)	C_6	C_{11}	C_{10}	120.8(3)

Table 6 Torsion Angles for 11a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br_1	C_3	C_4	N_1	-179.3(3)	C_5	N_2	C_6	C_{11}	145.5(4)
O_2	C_9	C_{10}	C_{11}	-179.2(4)	C_5	C_1	C_2	C_3	-173.1(4)
N_1	C_1	C_2	C_3	0.8(4)	C_6	N_2	C_5	O_1	-9.4(6)
N_1	C_1	C_5	O_1	-28.2(6)	C_6	N_2	C_5	C_1	168.6(3)
N_1	C_1	C_5	N_2	153.8(4)	C_6	C_7	C_8	C_9	0.4(6)
N_2	C_6	C_7	C_8	-175.6(4)	C_7	C_6	C_{11}	C_{10}	0.6(6)
N_2	C_6	C_{11}	C_{10}	175.7(4)	C_7	C_8	C_9	O_2	179.3(4)
C_1	N_1	C_4	C_3	-0.6(4)	C_7	C_8	C_9	C_{10}	-0.4(6)
C_1	C_2	C_3	Br_1	179.3(3)	C_8	C_9	C_{10}	C_{11}	0.5(6)
C_1	C_2	C_3	C_4	-1.2(5)	C_9	C_{10}	C_{11}	C_6	-0.6(6)
C_2	C_1	C_5	O_1	144.9(4)	C_{11}	C_6	C_7	C_8	-0.5(6)
C_2	C_1	C_5	N_2	-33.1(5)	C_{12}	O_2	C_9	C_8	-171.1(4)
C_2	C_3	C_4	N_1	1.1(5)	C_{12}	O_2	C_9	C_{10}	8.5(7)
C_4	N_1	C_1	C_2	-0.1(4)	C_{13}	N_1	C_1	C_2	173.5(4)
C_4	N_1	C_1	C_5	174.1(3)	C_{13}	N_1	C_1	C_5	-12.3(6)
C_5	N_2	C_6	C_7	-39.5(5)	C_{13}	N_1	C_4	C_3	-174.5(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 11a.

Atom	*x*	*y*	*z*	U(eq)
H_2	5060(90)	6660(40)	3610(20)	37(11)
H_{2A}	4609.05	4640.8	3771.42	50
H_4	8510.66	3030.91	2384.23	58
H_7	9979.39	7477.77	4504.84	50
H_8	10163.01	9071.84	5113.92	55
H_{10}	3688.28	10192.58	4287.44	54
H_{11}	3495.84	8585.92	3676.6	50
H_{12A}	5054.31	11857.38	4778.61	107
H_{12B}	5457.88	11992.76	5515.74	107
H_{12C}	3554.54	11087.06	5254.58	107
H_{13A}	10529.88	5804.75	2178.49	84
H_{13B}	11029.42	4610.54	1910.16	84
H_{13C}	12627.44	5042.88	2495.56	84

Experimental

Single crystals of $C_{13}H_{13}BrN_2O_2$ **[11a]** were obtained by slow evaporation of an ethyl acetate /hexane (1:1) solution. A suitable crystal was selected and silicone oil on a **ROD, Synergy Custom system, HyPix-Arc 150** diffractometer. The crystal was kept at 298.24(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXS [2] structure solution program using Direct Methods and refined with the SHELXL [3] refinement package using Least Squares minimisation.

10. Crystal data 13a

Table 1 Crystal data and structure refinement for 13a.

Identification code	13a
Empirical formula	$C_{13}H_9Br_2F_2NO_2$
Formula weight	409.03
Temperature/K	99.97(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.0558(4)
b/Å	15.0635(6)
c/Å	6.8043(3)
α/°	90
β/°	95.855(3)
γ/°	90
Volume/Å^3	1331.19(9)
Z	4
ρ_{calc}g/cm^3	2.041
μ/mm^{-1}	7.978
F(000)	792.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.99 to 145.672
Index ranges	$-15 \le h \le 15$, $-18 \le k \le 18$, $-5 \le l \le 7$
Reflections collected	2505
Independent reflections	2505 [R_{int} = 0.0371, R_{sigma} = 0.0226]
Data/restraints/parameters	2505/153/183
Goodness-of-fit on F^2	1.192
Final R indexes [I>=2σ (I)]	R_1 = 0.0919, wR_2 = 0.2816
Final R indexes [all data]	R_1 = 0.0932, wR_2 = 0.2823
Largest diff. peak/hole / e Å^{-3}	1.05/-1.04

Crystal structure determination of 13a

Crystal Data for $C_{13}H_9Br_2F_2NO_2$ (*M* =409.03 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.0558(4) Å, *b* = 15.0635(6) Å, *c* = 6.8043(3) Å, *β* = 95.855(3)°, *V* = 1331.19(9) Å^3, *Z* = 4, *T* = 99.97(10) K, μ(Cu Kα) = 7.978 mm^{-1}, *Dcalc* = 2.041 g/cm^3, 2505 reflections measured (8.99° ≤ 2Θ ≤ 145.672°), 2505 unique (R_{int} = 0.0371, R_{sigma} = 0.0226) which were used in all calculations. The final R_1 was 0.0919 (I > 2σ(I)) and wR_2 was 0.2823 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 13a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br_2	905.4(4)	6293.5(4)	6647.2(10)	17.76(16)
Br_1	1322.0(5)	10287.5(4)	6775.5(12)	23.99(17)
F_1	3183(3)	3740(3)	8795(7)	28.2(8)
F_2	3220(3)	3692(3)	5625(7)	29.5(8)
O_2	2582(3)	4905(3)	6974(8)	19.8(9)
O_1	4306(3)	5123(3)	7359(8)	25.8(10)
N_1	3942(4)	7007(3)	7260(8)	13.9(8)
C_2	1718(4)	8455(4)	6817(9)	13.9(10)
C_8	2227(4)	6779(4)	6913(9)	13.6(10)
C_1	2404(4)	7713(4)	6949(9)	14.8(9)
C_9	3461(4)	5421(4)	7168(10)	15.2(10)
C_6	3478(4)	7830(4)	7180(9)	12.8(9)
C_7	3176(5)	6366(4)	7100(11)	16.4(11)
C_3	2185(5)	9276(4)	6940(10)	18.2(10)
C_4	3248(5)	9402(4)	7127(10)	17.8(10)
C_5	3916(5)	8680(4)	7266(10)	17.5(11)
C_{10}	2642(5)	3994(4)	7038(11)	17.7(5)
C_{13}	5057(5)	6869(4)	7495(12)	20.4(13)
C_{11}	1584(5)	3608(4)	6817(11)	21.1(11)
C_{12}	1410(6)	2769(5)	6547(12)	31.0(17)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 13a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br_2	14.1(3)	16.1(3)	22.8(3)	-0.8(2)	0.8(3)	-1.1(2)
Br_1	28.6(3)	14.5(3)	28.8(4)	0.5(3)	2.7(3)	6.5(2)
F_1	27.6(16)	22.6(18)	32.1(12)	9.1(12)	-7.2(11)	-1.8(14)
F_2	27.5(14)	23.3(17)	39.2(13)	-9.4(12)	10.4(9)	-1.7(12)
O_2	16.9(11)	9.5(8)	33(2)	1.7(12)	1.3(15)	1.1(7)
O_1	18.3(8)	16.6(16)	42(3)	1.7(19)	1.5(11)	2.0(9)
N_1	14.6(8)	11.8(8)	15(2)	-1.2(12)	0.9(12)	-1.1(6)
C_2	16.9(14)	15.6(8)	8(3)	-1.1(13)	-5.3(16)	-1.4(7)
C_8	15.7(10)	15.4(9)	9(3)	-0.6(14)	-0.9(13)	-0.4(8)
C_1	17.8(8)	15.7(8)	10(3)	0.5(12)	-1.3(12)	-0.8(7)
C_9	17.4(7)	11.9(9)	16(3)	0.0(13)	1.4(10)	-0.2(6)
C_6	17.4(8)	12.3(7)	8(2)	-2.5(12)	-0.8(12)	-0.2(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 13a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C_7	15.6(9)	11.2(8)	22(3)	-0.8(13)	0.4(13)	-1.2(6)
C_3	21.2(9)	15.4(10)	18(3)	-1.5(16)	-0.1(14)	-2.7(8)
C_4	21.5(8)	14.7(13)	17(3)	1.2(16)	-0.5(13)	-3.3(8)
C_5	21.6(15)	14.2(8)	16(3)	-0.6(13)	-3.3(18)	-3.3(7)
C_{10}	18.0(9)	9.5(8)	25.2(10)	1.6(9)	0.0(7)	3.0(8)
C_{13}	14.5(9)	19(3)	27(3)	-3(3)	1.3(15)	-0.3(14)
C_{11}	20.7(11)	19.9(9)	22(3)	0.2(14)	1.0(17)	-2.6(9)
C_{12}	32(3)	20.8(9)	38(4)	-2.3(15)	-5(3)	-4.3(12)

Table 4 Bond Lengths for 13a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br_2	C_8	1.865(6)	C_2	C_3	1.377(8)
Br_1	C_3	1.892(6)	C_8	C_1	1.425(8)
F_1	C_{10}	1.379(8)	C_8	C_7	1.381(8)
F_2	C_{10}	1.360(8)	C_1	C_6	1.407(8)
O_2	C_9	1.381(7)	C_9	C_7	1.471(8)
O_2	C_{10}	1.375(7)	C_6	C_5	1.400(8)
O_1	C_9	1.186(7)	C_3	C_4	1.393(9)
N_1	C_6	1.378(7)	C_4	C_5	1.392(9)
N_1	C_7	1.386(7)	C_{10}	C_{11}	1.492(9)
N_1	C_{13}	1.463(8)	C_{11}	C_{12}	1.293(10)
C_2	C_1	1.430(8)			

Table 5 Bond Angles for 13a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C_{10}	O_2	C_9	121.0(5)	C_5	C_6	C_1	121.2(5)
C_6	N_1	C_7	108.2(5)	N_1	C_7	C_9	119.6(5)
C_6	N_1	C_{13}	124.1(5)	C_8	C_7	N_1	109.1(5)
C_7	N_1	C_{13}	127.6(5)	C_8	C_7	C_9	131.3(5)
C_3	C_2	C_1	115.3(5)	C_2	C_3	Br_1	117.5(4)
C_1	C_8	Br_2	122.4(4)	C_2	C_3	C_4	124.0(6)
C_7	C_8	Br_2	130.2(4)	C_4	C_3	Br_1	118.5(4)
C_7	C_8	C_1	107.5(5)	C_5	C_4	C_3	120.7(6)
C_8	C_1	C_2	132.2(5)	C_4	C_5	C_6	117.5(6)

Table 5 Bond Angles for 13a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C_6	C_1	C_2	121.3(5)	F_1	C_{10}	C_{11}	111.5(6)
C_6	C_1	C_8	106.5(5)	F_2	C_{10}	F_1	104.4(5)
O_2	C_9	C_7	109.7(5)	F_2	C_{10}	O_2	110.2(5)
O_1	C_9	O_2	123.5(5)	F_2	C_{10}	C_{11}	111.9(5)
O_1	C_9	C_7	126.8(6)	O_2	C_{10}	F_1	109.0(5)
N_1	C_6	C_1	108.7(5)	O_2	C_{10}	C_{11}	109.7(5)
N_1	C_6	C_5	130.1(5)	C_{12}	C_{11}	C_{10}	122.9(6)

Table 6 Torsion Angles for 13a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br_2	C_8	C_1	C_2	0.2(10)	C_1	C_8	C_7	C_9	179.6(7)
Br_2	C_8	C_1	C_6	179.6(5)	C_1	C_6	C_5	C_4	0.4(10)
Br_2	C_8	C_7	N_1	-179.9(5)	C_9	O_2	C_{10}	F_1	56.9(8)
Br_2	C_8	C_7	C_9	-0.6(12)	C_9	O_2	C_{10}	F_2	-57.1(8)
Br_1	C_3	C_4	C_5	179.6(5)	C_9	O_2	C_{10}	C_{11}	179.3(6)
F_1	C_{10}	C_{11}	C_{12}	-69.1(9)	C_6	N_1	C_7	C_8	0.2(8)
F_2	C_{10}	C_{11}	C_{12}	47.5(10)	C_6	N_1	C_7	C_9	-179.2(6)
O_2	C_9	C_7	N_1	-179.7(6)	C_7	N_1	C_6	C_1	-0.5(7)
O_2	C_9	C_7	C_8	1.0(11)	C_7	N_1	C_6	C_5	-179.6(7)
O_2	C_{10}	C_{11}	C_{12}	170.0(7)	C_7	C_8	C_1	C_2	-179.9(7)
O_1	C_9	C_7	N_1	0.3(11)	C_7	C_8	C_1	C_6	-0.5(7)
O_1	C_9	C_7	C_8	-179.0(8)	C_3	C_2	C_1	C_8	179.0(7)
N_1	C_6	C_5	C_4	179.3(6)	C_3	C_2	C_1	C_6	-0.3(9)
C_2	C_1	C_6	N_1	-179.9(6)	C_3	C_4	C_5	C_6	1.0(10)
C_2	C_1	C_6	C_5	-0.8(10)	C_{10}	O_2	C_9	O_1	1.5(10)
C_2	C_3	C_4	C_5	-2.1(11)	C_{10}	O_2	C_9	C_7	-178.4(6)
C_8	C_1	C_6	N_1	0.7(7)	C_{13}	N_1	C_6	C_1	-179.9(6)
C_8	C_1	C_6	C_5	179.8(6)	C_{13}	N_1	C_6	C_5	1.0(11)
C_1	C_2	C_3	Br_1	180.0(5)	C_{13}	N_1	C_7	C_8	179.6(6)
C_1	C_2	C_3	C_4	1.7(10)	C_{13}	N_1	C_7	C_9	0.1(11)
C_1	C_8	C_7	N_1	0.2(8)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 13a.

Atom	*x*	*y*	*z*	U(eq)
H_2	990.88	8387.15	6655.65	17
H_4	3519.27	9987.54	7158.77	21
H_5	4641.09	8759.88	7413.95	21
H_{13A}	5407.23	7444.18	7509.68	31
H_{13B}	5255.82	6511.42	6391.9	31
H_{13C}	5253.59	6557.4	8741.2	31
H_{11}	1013.57	3994.9	6876.69	25
H_{12A}	1968.58	2370.01	6481.8	37
H_{12B}	722.81	2552.44	6412.83	37

Experimental

Single crystals of $C_{13}H_9Br_2F_2NO_2$ **13a** were obtained by slow evaporation of an ethyl acetate /dichloromethane (2:1) solution. A suitable crystal was selected and silicone oil on a R**OD, Synergy Custom system, HyPix-Arc 150** diffractometer. The crystal was kept at 99.97(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXS [2] structure solution program using Direct Methods and refined with the SHELXL [3] refinement package using Least Squares minimisation.