Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Auxiliary-Controlled Regiodivergent NiH-Catalyzed *gem*-Difluoroallylation of Alkenyl Amines via Defluorinative Olefin Cross-Coupling

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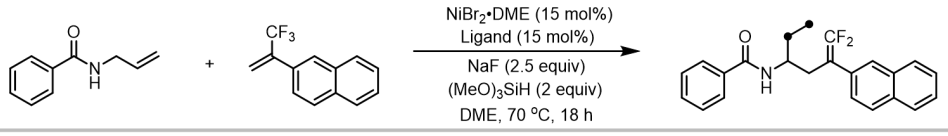
1. General remarks

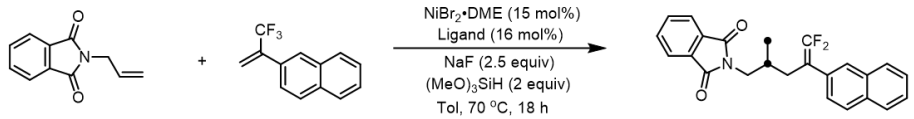
All the manipulations were performed in an argon-filled glovebox, unless mentioned otherwise. Anhydrous solvent was purchased from commercial sources and transferred under argon atmosphere. Alkene substrates and Trifluoromethyl alkenes were prepared according to previously reported procedures. $NiBr_2$•DME (CAS 28923-39-9) was purchased from Leyan. com. $(MeO)_3SiH$ (CAS 2487-90-3) was purchased from Meryer (Shanghai) Biochemical Technology Co., Ltd. and stored under nitrogen in glove box. Other reagents were purchased from Adamas-beta®, Energy Chemicals, Bidepharm and used directly without further purification unless otherwise specified. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded using Bruker 400 MHz NMR spectrometer. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were referenced to resonances of the residual protons in the deuterated solvents. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet and m = multiplet. GC-MS analysis was performed on Shimadzu GC-2010 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. Analytical HPLC/MS was performed with an Agilent 6520 Series HPLC; X-Ray Diffraction (XRD) was carried out on an Bruker D8 Venture Metaljet Photon II at Shiyanjia lab. Reactions carried out at elevated temperature were heated using oil bath.

2. Optimization of reaction condition

Table S1. Screening of ligands



4% yield	71% yield, >99:1 rr	58% yield, >99:1 rr	NR	NR
NR	NR	46% yield, >99:1 rr, **0% ee**	6% yield	8% yield
NR	NR	8% yield	NR	NR
NR	NR	n = 1, NR n = 4, NR n = 5, NR	R = H, NR R = Ph, NR R = ^{t}Bu, NR	30% yield, 95:5 rr, **0% ee**
NR	5% yield	9% yield	9% yield	30% yield, 95:5 rr, **0% ee**
27% yield, 95:5 rr, **0% ee**	1% yield	NR	NR	NR
R = OMe, 1% yield R = ^{t}Bu, 1% yield	n = 1, NR n = 4, NR	2% yield	NR	NR



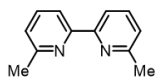
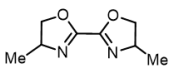
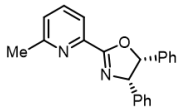
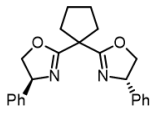
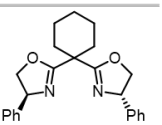
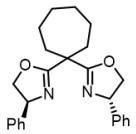
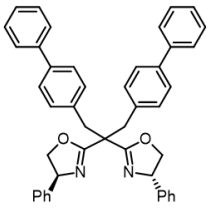
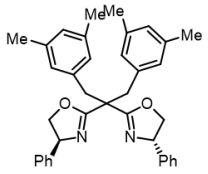
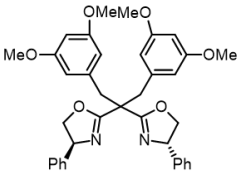
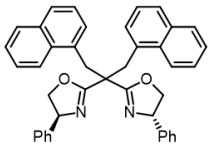
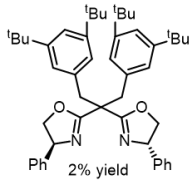
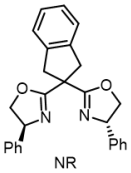
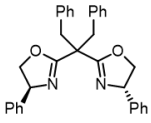
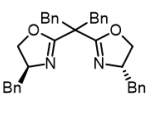
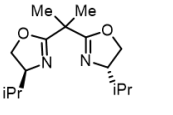
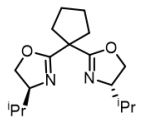
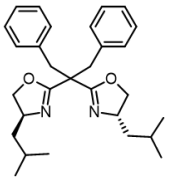
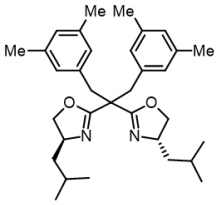
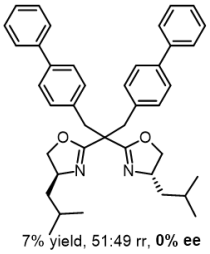
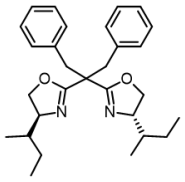
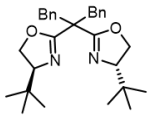
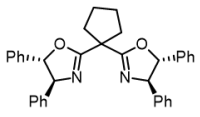
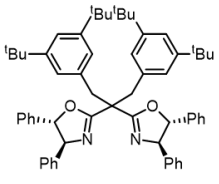
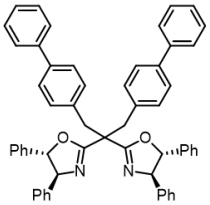
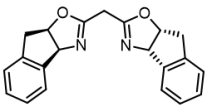
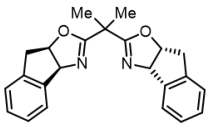
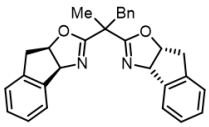
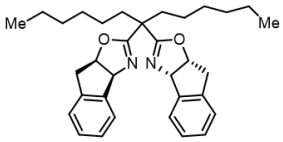
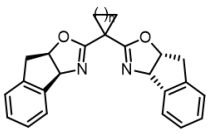
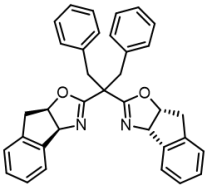
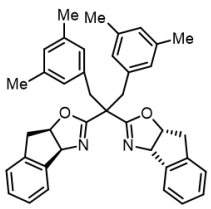
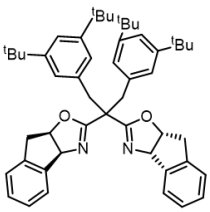
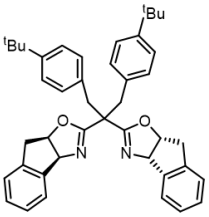
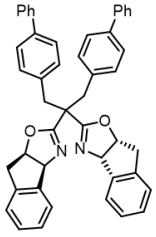
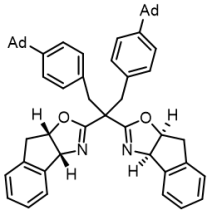
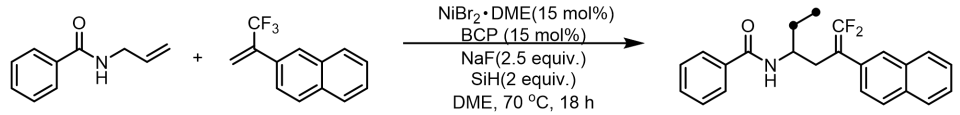
				
31% yield, 66:34 rr	NR	5% yield, 53:47 rr, **0% ee**	NR	18% yield, 94:6 rr, **0% ee**
				
NR	6% yield, 52:48 rr, **0% ee**	10% yield, 73:27 rr, **0% ee**	4% yield	4% yield
				
2% yield	NR	5% yield, 77:23 rr, **0% ee**	19% yield, 95:5 rr, **0% ee**	20% yield, 90:10 rr, **0% ee**
				
29% yield, 92:8 rr, **0% ee**	39% yield, 94:6 rr, **0% ee**	20% yield, 84:16 rr, **0% ee**	7% yield, 51:49 rr, **0% ee**	37% yield, 95:5 rr, **0% ee**
				
2% yield	8% yield, 35:65 rr, **0% ee**	11% yield, 50:50 rr, **0% ee**	7% yield, 28:72 rr, **0% ee**	28% yield, 69:31 rr, **0% ee**
				
28% yield, 91:9 rr, **0% ee**	16% yield, 91:9 rr, **0% ee**	11% yield, 95:5 rr, **0% ee**	n = 1, 13% yield, 60:40 rr, **0% ee** n = 2, 28% yield, 90:10 rr, **0% ee** n = 3, 13% yield, 97:3 rr, **0% ee** n = 4, 16% yield, 76:24 rr, **0% ee**	5% yield, 86:14 rr, **0% ee**
				
13% yield, 88:12 rr, **0% ee**	25% yield, 94:6 rr, **0% ee**	12% yield, 92:8 rr, **0% ee**	3% yield	NR

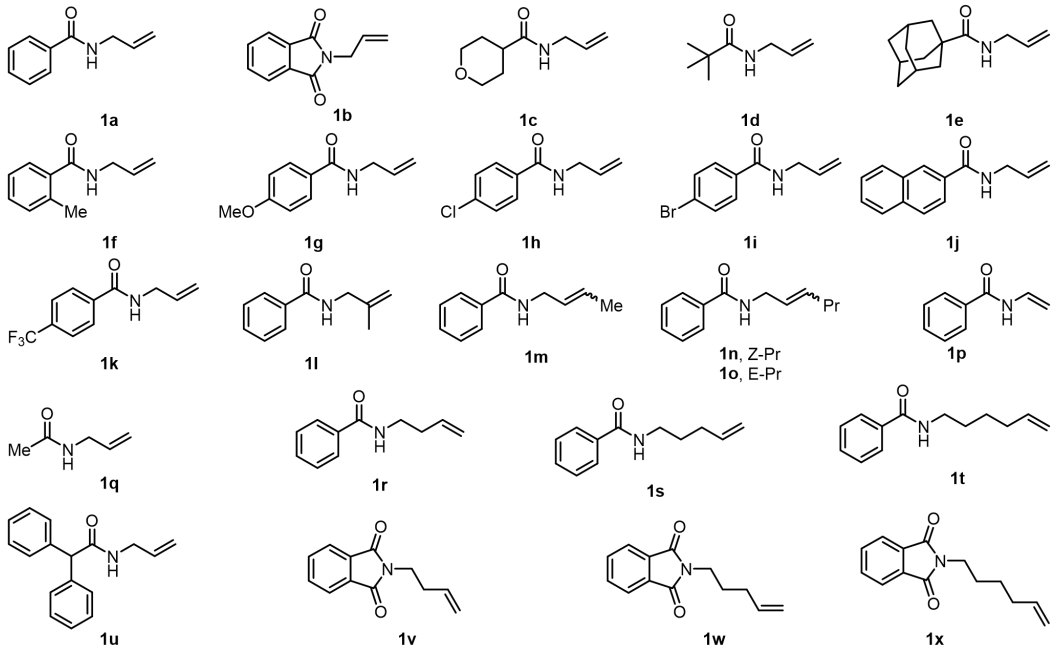
Table S2. Screening of silane



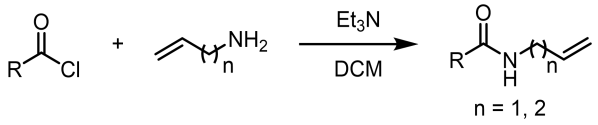
entry	SiH	yield(%)	rr(%)
1	$(MeO)_3SiH$	93	>99:1
2	$(EtO)_3SiH$	90	95:5
3	PMHS	74	97:3
4	$Me(MeO)_2SiH$	69	87:13
5	Ph_2SiH_2	30	94:6
6	PhSiH	29	88:12
7	$MePh_2SiH$	0	

3. Alkene substrate synthesis

Table S3 Benzamide-containing alkene substrates **1a-1q.**



General Procedure for Amide Coupling (GP1):

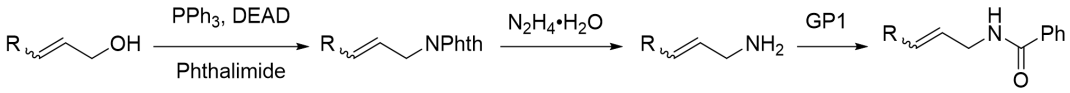


Compound **1a-1k, 1q-1t** were synthesized from acyl chloride and alkenyl amines.

Allylamine derivatives (20 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (20 mL), triethylamine (42 mmol, 2.1 equiv) was added and the mixture was stirred for 10 min, benzoyl chloride derivatives (20 mmol, 1.0 equiv) dissolve in CH_2Cl_2 (20 mL) was added dropewise over 15 min and the mixture was stirred for different reaction times at room temperature under Ar atmosphere. Then,

the aqueous layer was extracted with NaOH solution (1 M, 30 mL) was added and stirred was stirred for 5 min, extracted with CH_2Cl_2 (3 × 50 mL), dried over sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by using column chromatography (ethyl acetate:petroleum ether = 1:8) to provide the desired product.

General Procedure for Amide Coupling (GP2):



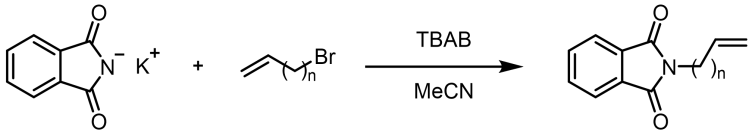
Compound **1m-1o** were synthesized from enols.

To a mixture of triphenylphosphine (25 mmol, 1.0 equiv), phthalimide (25 mmol, 1.0 equiv) and the corresponding allyl alcohol (25 mmol, 1.0 equiv) in THF (30 mL) was slowly added diethyl azodicarboxylate (DEAD) (25 mmol, 1.0 equiv) at 0 °C. The mixture was stirred at room temperature for 3 h. After the completion of the reaction, the reaction mixture was diluted with n-hexane and filtered. The filtrate was dried over Na_2SO_4 and concentrated in vacuo to give the crude product, which was used without further purification.

To the solution of phthalimide product in ethanol (100 mL) was added hydrazine monohydrate (25 mmol) at 50 ºC. The mixture was stirred for 6 h and quenched with 6 M HCl (20 mL). The precipitates formed were removed by filtration, and the resultant filtrate was dried over Na_2SO_4 and concentrated in vacuo to give an unsaturated amine hydrochloride. Aqueous NaOH (6.0 M, 10 mL) was added to the amine salt, and the resulting solution was extracted with CH_2Cl_2 (25 mL × 3). The combined organic extracts were then washed again with brine (10 mL), dried over Na_2SO_4, and filtered. The amine solution was used without further purification.

To the solution of amine (25 mmol, 1.0 equiv) was successively added benzoyl chloride (30 mmol, 1.2 equiv). The resultant mixture was stirred at room temperature overnight. Water was added and the mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (ethyl acetate:petroleum ether = 1:8) to give the desired product.

General Procedure for Amide Coupling (GP3):

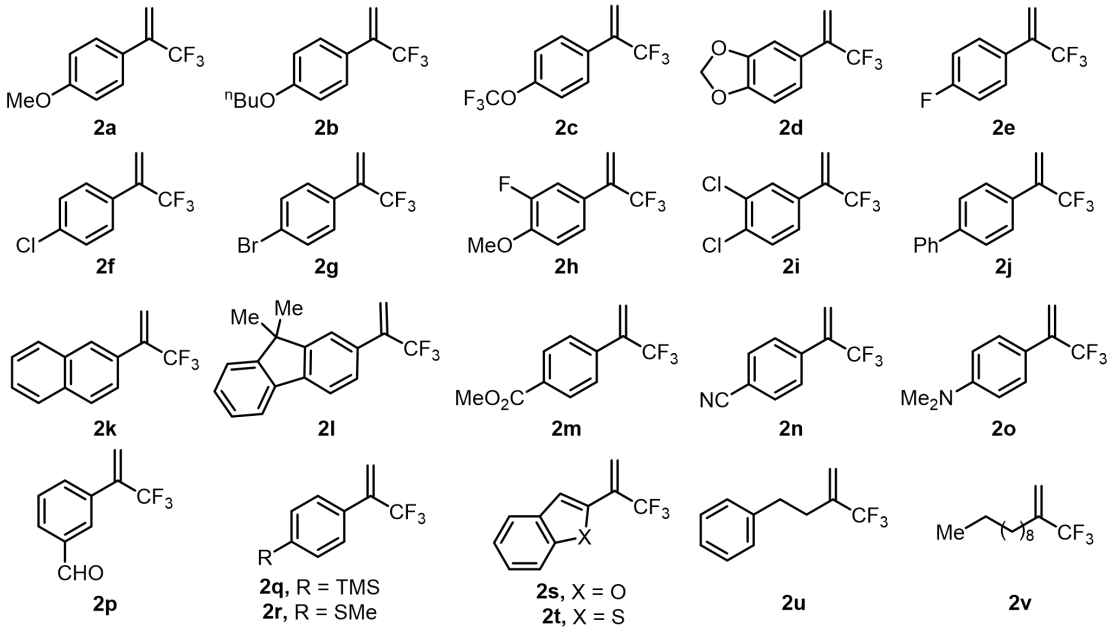


Potassium phthalimide (20 mmol, 1.0 equiv) and tetrabutylammonium bromide (TBAB) (20 mmol, 1.0 equiv) were added to MeCN (100 mL). To this solution alkenyl bromide (20 mmol, 1.0 equiv) was added dropwise. The reaction was heated to 50 °C and stirred for 12 h. The MeCN was removed in vacuo and the remaining yellow liquid was dissolved in DCM. The solution was washed with water (25 mL × 3) and brine (25 mL × 3). The organics were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give an off-white solid. The crude material was purified by silica gel flash chromatography (ethyl acetate:petroleum ether = 1:12) to give the desired product.

Synthesis of compound **1a-1o, 1r-1s, 1v** were according the literature[1], and the characterization data are consistent with the literature reported data. The NMR spectras of alkene substrates **1a**[1], **1b**[2], **1d**[3], **1f**[4], **1g**[5], **1h**[5], **1i**[4] ,**1j**[4], **1k**[4], **1l**[5], **1m**[6], **1n**[6], **1o**[6], **1p**[7], **1q**[5], **1r**[8], **1s**[9], **1u**[10], **1v**[11], **1w**[12], **1x**[13] matches those previously described in literature.

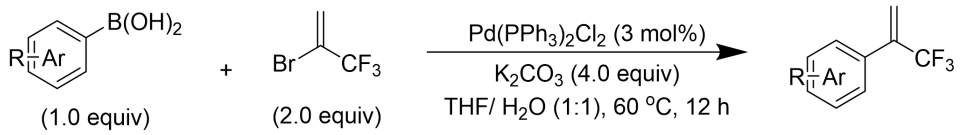
4. Procedures for the synthesis of trifluoromethyl alkenes

Table S4 Trifluoromethyl alkenes



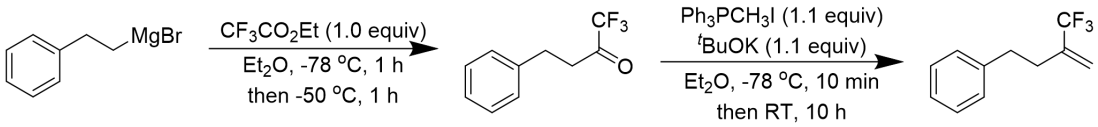
General Procedure for trifluoromethyl alkenes(GP3):

Synthetic procedure for 2a-2t.



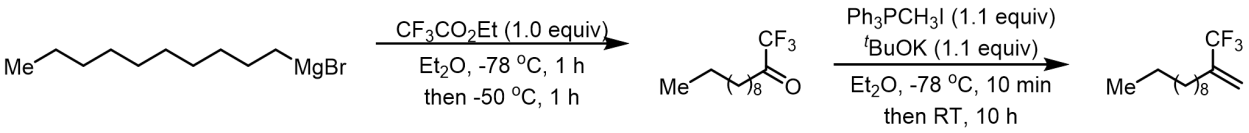
According to the reported procedure,[14] to a 100 mL schlenk tube equipped a magnetic stir bar, boronic acid (10.0 mmol, 1.0 equiv), and $Pd(PPh_3)_2Cl_2$ (126.4 mg, 3 mol%) were added. The vessel was evacuated and filled with argon (three times), and then THF (40 mL) and aqueous K_2CO_3 (2.0 M, 20 mL, 4.0 equiv) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (2.08 mL, 20 mmol, 2.0 equiv), the reaction mixture was stirred at 60 °C overnight under an argon atmosphere. The resultant mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/EtOAc) to give the desired trifluoromethyl.

Synthetic procedure for 2u



According to the reported procedure,[15] To a diethyl ether solution (100 mL) of ethyl trifluoroacetate (50.0 mmol, 1.0 equiv) was added phenethylmagnesium bromide (1.0 M in Et_2O, 50.0 mL, 50.0 mmol), prepared from phenethyl bromide (50.0 mmol, 1.0 equiv) and magnesium turning (55 mmol, 1.1 equiv), at –78 °C over 30 min. After stirring for 30 min at the same temperature, the mixture was warmed to –50 °C over 1 h, and saturated aqueous NH_4Cl was added. Organic materials were extracted three times with Et_2O. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by distillation under reduced pressure to give the aldehydes compound as a colorless liquid. To a diethyl ether solution (64 mL) of Ph_3PCH_3I (1.1 equiv) was added t-BuOK (1.1 equiv) at room temperature. The reaction mixture was stirred for 30 min at room temperature and then cooled to –78 °C. To the mixture was added slowly a diethyl ether solution (16 mL) of 1,1,1-trifluoro-4-phenylbutan-2-one (3.23 g, 16.0 mmol, 1.0 equiv) at –78 °C over 10 min. The mixture was then warmed to room temperature over 10 h, and aqueous HCl (1.0 M) was added. Organic materials were extracted three times with Et_2O. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) and further distillation under reduced pressure to give **2u** as a colorless liquid.

Synthetic procedure for 2v



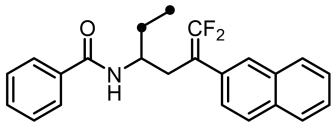
According to the reported procedure,[15] To a diethyl ether solution (100 mL) of ethyl trifluoroacetate (50.0 mmol, 1.0 equiv) was added decylmagnesium bromide (1.0 M in Et_2O, 50.0 mL, 50.0 mmol), prepared from 1-bromodecane (50.0 mmol, 1.0 equiv) and magnesium turning (55 mmol, 1.1 equiv), at –78 °C over 30 min. After stirring for 30 min at the same temperature, the mixture was warmed to –50 °C over 1 h, and saturated aqueous NH_4Cl was added. Organic materials were extracted three times with Et_2O. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by distillation under reduced pressure to give the aldehydes

compound as a colorless liquid. To a diethyl ether solution (70 mL) of Ph_3PCH_3I (1.1 equiv) was added t-BuOK (1.1 equiv) at room temperature. The reaction mixture was stirred for 30 min at room temperature and then cooled to –78 °C. To the mixture was added slowly a diethyl ether solution (16 mL) of 1,1,1-trifluorododecan-2-one (16.0 mmol, 1.0 equiv) at –78 °C over 10 min. The mixture was then warmed to room temperature over 10 h, and aqueous HCl (1.0 M) was added. Organic materials were extracted three times with Et_2O. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) and further distillation under reduced pressure to give **2v** as a colorless liquid.

5. Procedure for the Ni-catalyzed α-selective hydrodifluoroallylation

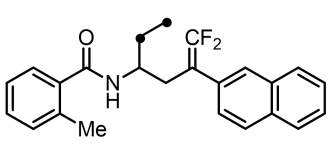
In an argon-filled glovebox, $NiBr_2$•DME (0.03 mmol, 15 mol%), bathocuproine (0.03 mmol, 15 mol%), NaF (0.5 mmol, 2.5 eq), alkene substrate (0.2 mmol, 1.0 eq), appropriate trifluoromethyl alkenes (0.6 mmol, 3.0 eq), $(MeO)_3SiH$ (0.4 mmol, 2.0 equiv), DME (1 mL) were added to a 10 mL schlenk flask. The reaction mixture was stirred at 70 °C for 18 h. After the reaction time, the vessel was allowed to silica gel column chromatography. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent. The conditions for flash chromatography and data for characterization of the products are listed below.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide **(3a)**



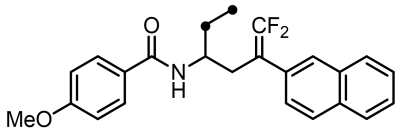
The title compound was isolated as a white solid (68.1 mg, 93% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81–7.76 (m, 3H), 7.49–7.43 (m, 3H), 7.36–7.31 (m, 1H), 7.28–7.25 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 5.67 (d, *J* = 8.7 Hz, 1H), 4.24–4.15 (m, 1H), 2.82–2.80 (dd, *J* = 5.2, 2.8 Hz, 2H), 1.72–1.63 (m, 1H), 1.58–1.49 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 154.6 (dd, *J* = 291.3, 287.9 Hz), 134.4, 133.3, 132.5, 131.1, 131.1, 128.5, 128.2, 128.0, 127.6, 127.5 (t, *J* = 3.1 Hz), 126.5, 126.4, 126.3, 126.0 (t, *J* = 2.9 Hz), 89.9 (dd, *J* = 21.1, 15.1 Hz), 50.5, 32.7, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.75 (d, *J* = 40.1 Hz, 1F), -89.97 (d, *J* = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{22}F_2NO^+$ $[M+H]^+$: 366.1664, found: 366.1670.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)-2-methylbenzamide **(3b)**



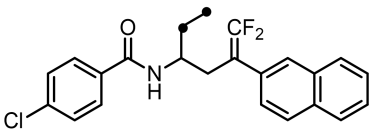
The title compound was isolated as a yellow oil (58.5 mg, 77% yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.80 (m, 4H), 7.52–7.45 (m, 3H), 7.23–7.19 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.1 Hz, 1H), 5.36 (d, *J* = 9.1 Hz, 1H), 4.20–4.12 (m, 1H), 2.85–2.72 (m, 2H), 2.38 (s, 3H), 1.73–1.66 (m, 1H), 1.54–1.48 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 136.5, 135.9, 133.3, 132.6, 130.8, 129.6, 128.4, 128.0, 127.6, 127.5, 127.5, 126.3, 126.2, 126.1, 126.0 (t, *J* = 2.9 Hz), 125.5, 90.1 (dd, *J* = 16.6, 12.0 Hz), 50.1, 33.3, 27.5, 19.6, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.78 (d, *J* = 40.5 Hz, 1F), -89.93 (d, *J* = 40.6 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{24}F_2NO^+$ $[M+H]^+$: 380.1820, found: 380.1828.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)-4-methoxybenzamide **(3c)**



The title compound was isolated as a white solid (66.6 mg, 84% yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.76 (m, 4H), 7.49–7.43 (m, 3H), 7.24–7.17 (m, 2H), 6.65–6.57 (m, 2H), 5.56 (d, *J* = 8.8 Hz, 1H), 4.23–4.14 (m, 1H), 3.75 (s, 3H), 2.80 (dd, *J* = 5.4, 2.4 Hz, 2H), 1.70–1.62 (m, 1H), 1.58–1.48 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.8, 154.5 (dd, *J* = 291.5, 287.7 Hz), 133.3, 132.5, 131.2 (dd, *J* = 3.9, 2.7 Hz), 131.2, 128.5, 128.2, 128.0, 127.5, 127.4 (t, *J* = 3.1 Hz), 126.6, 126.3 (d, *J* = 16.1 Hz), 126.0 (t, *J* = 2.9 Hz), 113.3, 89.9 (dd, *J* = 21.4, 14.8 Hz), 55.3, 50.4, 32.7, 27.3, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, *J* = 40.2 Hz, 1F), -90.04 (d, *J* = 40.2 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{24}F_2NO^+$ $[M+H]^+$: 396.1770, found: 396.1778.

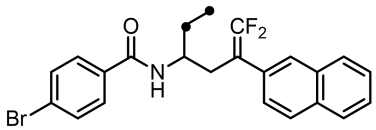
4-chloro-N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide **(3d)**



The title compound was isolated as a white solid (58.4 mg, 73% yield, 95:5 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.74 (m, 4H), 7.52–7.45 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.14–7.09 (m, 2H), 7.08–7.00 (m, 2H), 5.56 (d, *J* = 8.8 Hz, 1H), 4.22–4.14 (m, 1H), 2.88–2.81 (m, 1H), 2.81–2.73 (m, 1H), 1.70–1.66 (m, 1H), 1.59–1.50 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 154.5 (dd, *J* = 291.6, 287.9 Hz), 137.3, 133.3, 132.6, 132.5, 131.2 (dd, *J* = 4.0, 2.7 Hz), 128.6, 128.3, 127.9, 127.8, 127.5, 127.4 (t, *J* = 3.0 Hz), 126.5, 126.4, 125.9 (t, *J* = 2.8 Hz), 89.8 (dd, *J* = 21.4, 15.0 Hz), 50.8, 32.6, 27.3, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.63 (d, *J* = 39.6 Hz, 1F), -89.91 (d,

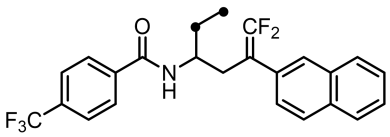
J = 39.7 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{21}ClF_2NO^+$ $[M+H]^+$: 400.1274, found: 400.1282.

4-bromo-N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide **(3e)**



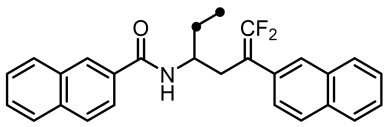
The title compound was isolated as a yellow oil (60.4 mg, 68% yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.74 (m, 4H), 7.52–7.47 (m, 2H), 7.43 (d, J = 8.5 Hz, 1H), 7.25–7.18 (m, 2H), 7.04 (d, J = 8.5 Hz, 2H), 5.50 (d, J = 8.7 Hz, 1H), 4.23–4.15 (m, 1H), 2.89–2.82 (m, 1H), 2.81–2.74 (m, 1H), 1.71–1.65 (m, 1H), 1.57–1.51 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 154.5 (dd, J = 291.5, 287.9 Hz), 133.3, 133.0, 132.5, 131.3, 131.2 (dd, J = 3.8, 2.5 Hz), 128.6, 128.0, 127.8, 127.5, 127.4 (t, J = 3.0 Hz), 126.5, 126.3, 125.9 (t, J = 2.9 Hz), 125.7, 89.7 (dd, J = 21.2, 15.2 Hz), 50.8, 32.6, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.65 (d, J = 39.7 Hz, 1F), -89.90 (d, J = 39.7 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{20}F_2NO^+$ $[M+H]^+$: 444.0769, found: 444.0769.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)-4-(trifluoromethyl)benzamide **(3f)**



The title compound was isolated as a white solid (61.4 mg, 71% yield, 88:12 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.71 (m, 4H), 7.50–7.40 (m, 3H), 7.31 (d, J = 8.3 Hz, 2H), 7.27–7.24 (m, 2H), 5.58 (d, J = 8.7 Hz, 1H), 4.26–4.17 (m, 1H), 2.93–2.84 (m, 1H), 2.82–2.75 (m, 1H), 1.73–1.67 (m, 1H), 1.61–1.53 (m, 1H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 154.5 (dd, J = 291.7, 288.1 Hz), 137.3, 133.3, 132.8 (d, J = 32.7 Hz), 132.5, 131.2 (dd, J = 4.0, 2.6 Hz), 128.6, 127.8, 127.5, 127.4 (t, J = 3.0 Hz), 126.8, 126.6, 126.4, 125.8, 125.1 (q, J = 3.7 Hz), 122.2, 89.7 (dd, J = 21.4, 15.1 Hz), 51.0, 32.5, 27.3, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.06(s, 3), -89.58 (d, J = 39.5 Hz, 1F), -89.85 (d, J = 39.5 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{21}F_5NO^+$ $[M+H]^+$: 434.1538, found: 434.1544.

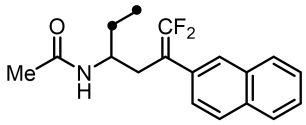
N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)-2-naphthamide **(3g)**



The title compound was isolated as a white solid (59.9 mg, 72% yield, 95:5 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–8.18 (m, 1H), 7.90 (s, 1H), 7.86–7.76 (m, 5H), 7.54–7.47 (m, 5H), 7.14–7.07 (m, 1H), 6.98 (dd, J =

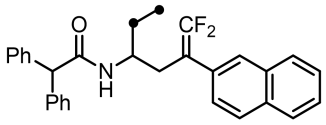
7.0, 0.9 Hz, 1H), 5.61 (d, *J* = 9.0 Hz, 1H), 4.34–4.26 (m, 1H), 2.90–2.80 (m, 2H), 1.77–1.70 (m, 1H), 1.60–1.52 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 154.6 (dd, *J* = 291.4, 287.9 Hz), 134.5, 133.6, 133.3, 132.6, 130.9 (dd, *J* = 3.5, 2.7 Hz), 130.3, 130.0, 128.5, 128.1, 128.0, 127.6, 127.5, 127.0, 126.4, 126.3, 126.3, 126.1 (t, *J* = 3.0 Hz), 125.3, 124.4, 124.3, 90.1 (dd, *J* = 20.9, 15.0 Hz), 50.4, 33.2, 27.6, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.58 (d, *J* = 40.2 Hz, 1F), -89.82 (d, *J* = 40.2 Hz, 1F). HRMS (ESI) m/z calculated for $C_{27}H_{24}F_2NO^+$ $[M+H]^+$: 416.1820, found: 416.1827.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)acetamide **(3h)**



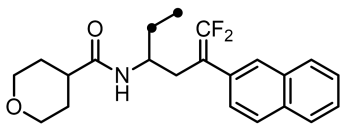
The title compound was isolated as a yellow oil (49.3 mg, 81% yield, 91:9 rr) after chromatography on silica with ethyl acetate/hexane (1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.78 (m, 4H), 7.52–7.39 (m, 3H), 5.03 (d, *J* = 8.6 Hz, 1H), 4.06–3.87 (m, 1H), 2.75–2.60 (m, 2H), 1.72 (s, 3H), 1.61–1.52 (m, 1H), 1.42–1.33 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 154.5 (t, *J* = 289.5 Hz), 133.28, 132.5, 130.9, 128.2, 128.0, 127.6, 127.4 (t, *J* = 3.1 Hz), 126.3, 126.2, 126.0 (t, *J* = 3.0 Hz), 89.9 (t, *J* = 18.0 Hz), 49.9, 32.8, 27.1, 23.2, 10.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.04 (s, 2F). HRMS (ESI) m/z calculated for $C_{18}H_{20}F_2NO^+$ $[M+H]^+$: 304.1507, found: 304.1513.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)-2,2-diphenylacetamide **(3i)**



The title compound was isolated as a white solid (62.0 mg, 68% yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.76 (m, 3H), 7.70 (s, 1H), 7.51–7.45 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.28–7.18 (m, 6H), 7.16–7.07 (m, 4H), 5.24 (d, *J* = 8.6 Hz, 1H), 4.71 (s, 1H), 4.03–3.92 (m, 1H), 2.66–2.54 (m, 2H), 1.57–1.47 (m, 1H), 1.37–1.29 (m, 1H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 154.4 (t, *J* = 289.6 Hz), 139.4 (d, *J* = 5.3 Hz), 133.3, 132.6, 130.6, 128.9, 128.8, 128.7 (d, *J* = 2.4 Hz), 128.3, 128.1, 127.6, 127.4 (t, *J* = 3.2 Hz), 127.2, 126.3 (d, *J* = 4.2 Hz), 126.0 (t, *J* = 3.0 Hz), 89.9 (t, *J* = 17.8 Hz), 59.4, 49.9, 32.6, 27.2, 10.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.73 (s, 2F). HRMS (ESI) m/z calculated for $C_{30}H_{28}F_2NO^+$ $[M+H]^+$: 456.2133, found: 456.2142.

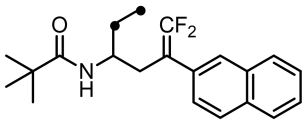
N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)tetrahydro-2H-pyran-4-carboxamide **(3j)**



The title compound was isolated as a white solid (55.4 mg, 74% yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* =

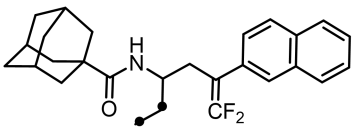
16.2, 8.6 Hz, 1H), 7.61–7.33 (m, 1H), 4.99 (d, *J* = 8.1 Hz, 1H), 3.97 (d, *J* = 6.2 Hz, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 3.16 (t, *J* = 11.3 Hz, 1H), 2.68 (s, 1H), 1.93 (t, *J* = 11.4 Hz, 1H), 1.66–1.45 (m, 1H), 1.48–1.34 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 154.5 (dd, *J* = 291.5, 287.4 Hz), 133.2, 132.5, 131.1 (dd, *J* = 4.0, 2.9 Hz), 128.3, 127.9, 127.5, 127.4 (d, *J* = 3.1 Hz), 126.5, 126.3, 126.0 (t, *J* = 2.9 Hz), 89.9 (dd, *J* = 21.5, 14.7 Hz), 67.1 (d, *J* = 9.9 Hz), 49.8, 42.2, 32.8, 29.0, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.82 (d, *J* = 40.3 Hz, 1F), -90.11 (d, *J* = 40.4 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{26}F_2NO^+$ $[M+H]^+$: 374.1926, found: 374.1930.

N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)pivalamide **(3k)**



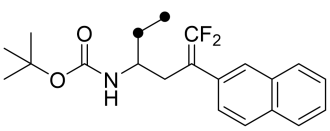
The title compound was isolated as a white solid (57.5 mg, 83% yield, 98:2 rr) after chromatography on silica with ethyl acetate/hexane (1:10). δ 7.88–7.77 (m, 4H), 7.53–7.41 (m, 3H), 5.23 (d, *J* = 8.4 Hz, 1H), 4.01–3.91 (m, 1H), 2.73–2.60 (m, 2H), 1.63–1.53 (m, 1H), 1.47–1.37 (m, 1H), 1.00 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 154.5 (dd, *J* = 291.4, 287.2 Hz), 133.3, 132.5, 131.0 (dd, *J* = 4.2, 2.9 Hz), 128.3, 127.9, 127.5, 127.4 (t, *J* = 3.2 Hz), 126.3, 126.2, 126.1 (t, *J* = 3.0 Hz), 90.0 (dd, *J* = 21.5, 14.4 Hz), 49.5, 38.5, 33.0, 27.4, 27.3, 10.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.97 (d, *J* = 41.0 Hz, 1F), -90.33 (d, *J* = 41.0 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{26}F_2NO^+$ $[M+H]^+$: 346.1977, found: 346.1985.

(3r,5r,7r)-N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)adamantane-1-carboxamide **(3l)**



The title compound was isolated as a white solid (65.3 mg, 77% yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.78 (m, 4H), 7.51–7.40 (m, 3H), 5.08 (d, *J* = 8.6 Hz, 1H), 4.04–3.93 (m, 1H), 2.73–2.60 (m, 2H), 1.80 (s, 3H), 1.57 (d, *J* = 10.7 Hz, 4H), 1.53 (s, 1H), 1.51–1.48 (m, 2H), 1.43 (d, *J* = 12.2 Hz, 7H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 154.5 (dd, *J* = 291.3, 287.4 Hz), 133.4, 132.6, 131.3 (dd, *J* = 4.3, 2.9 Hz), 128.4, 127.9, 127.5, 127.5, 126.4, 126.3, 126.1 (t, *J* = 2.9 Hz), 89.9 (dd, *J* = 21.7, 14.5 Hz), 49.4 (t, *J* = 2.6 Hz), 40.3, 38.8, 36.3, 32.7, 28.0, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.64 (d, *J* = 39.6 Hz, 1F), -89.90 (d, *J* = 39.8 Hz, 1F). HRMS (ESI) m/z calculated for $C_{27}H_{32}F_2NO^+$ $[M+H]^+$: 424.2446, found: 424.2451.

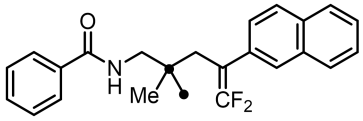
tert-butyl 2-((6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)amino)-2-oxoacetate **(3m)**



The title compound was isolated as a yellow oil (43.5 mg, 60%

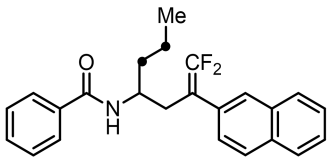
yield, >99:1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.70 (m, 4H), 7.43–7.34 (m, 3H), 4.12 (d, *J* = 8.9 Hz, 1H), 3.67–3.38 (m, 1H), 2.65–2.48 (m, 2H), 1.57–1.38 (m, 3H), 1.29 (s, 9H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.47, 154.38 (d, *J* = 1.5 Hz), 153.60, 150.72, 132.31, 131.58, 130.03 (d, *J* = 2.8 Hz), 127.07 (d, *J* = 18.1 Hz), 126.57, 126.51 (t, *J* = 3.0 Hz), 125.21, 125.13, 89.12 (t, *J* = 18.0 Hz), 79.25–77.10 (m), 50.01, 32.51, 27.28, 26.61, 9.16; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.30 (s, 2F). HRMS (ESI) m/z calculated for $C_{22}H_{26}F_2NO_3^+$ $[M+H]^+$: 362.1926, found: 362.1930.

N-(5,5-difluoro-2,2-dimethyl-4-(naphthalen-2-yl)pent-4-en-1-yl)benzamide **(3n)**



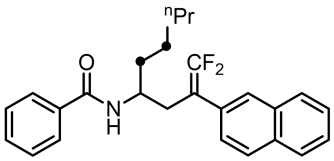
The title compound was isolated as a yellow oil (37.3 mg, 49% yield, 60:40 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.74 (m, 4H), 7.46–7.40 (m, 3H), 7.38–7.32 (m, 3H), 7.24–7.18 (m, 2H), 5.66 (t, *J* = 5.5 Hz, 1H), 3.13 (d, *J* = 6.6 Hz, 2H), 2.51–2.42 (m, 2H), 0.85 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 154.7 (dd, *J* = 291.4, 288.3 Hz), 134.5, 133.3, 132.7 (dd, *J* = 4.7, 2.5 Hz), 132.5, 131.3, 128.6, 128.4, 127.9, 127.7, 127.4–127.1 (m), 126.6, 126.6, 126.4, 126.2 (t, *J* = 2.5 Hz), 90.2 (dd, *J* = 21.9, 13.9 Hz), 48.5, 37.8, 37.4 (t, *J* = 2.4 Hz), 25.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.39 (d, *J* = 39.0 Hz, 1F), -90.61 (d, *J* = 39.0 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{24}F_2NO^+$ $[M+H]^+$: 380.1820, found: 380.1819.

N-(1,1-difluoro-2-(naphthalen-2-yl)hept-1-en-4-yl)benzamide **(3o)**



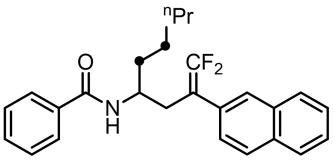
The title compound was isolated as a yellow solid (55.5 mg, 73% yield, 89:11 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81–7.77 (m, 3H), 7.49–7.43 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (dd, *J* = 6.2, 2.1 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 5.62 (d, *J* = 8.7 Hz, 1H), 4.31–4.26 (m, 1H), 2.86–2.76 (m, 2H), 1.68–1.55 (m, 2H), 1.41–1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.6 (dd, *J* = 291.3, 287.8 Hz), 134.3, 133.3, 132.5, 131.2 (dd, *J* = 5.1, 2.6 Hz), 131.1, 128.5, 128.2, 127.9, 127.5, 127.5 (t, *J* = 3.1 Hz), 126.4, 126.4, 126.3, 126.0 (t, *J* = 2.9 Hz), 89.9 (dd, *J* = 21.0, 15.2 Hz), 48.9, 36.6, 33.1, 19.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, *J* = 40.1 Hz, 1F), -89.99 (d, *J* = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{24}F_2NO^+$ $[M+H]^+$: 380.1820, found: 380.1820.

N-(1,1-difluoro-2-(naphthalen-2-yl)non-1-en-4-yl)benzamide **(3p)**



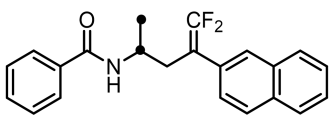
The title compound was isolated as a white solid (45.7 mg, 56% yield, 94:6 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81–7.77 (m, 3H), 7.49–7.44 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 3.6 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 2H), 5.60 (d, *J* = 8.8 Hz, 1H), 4.32–4.25 (m, 1H), 2.81 (dd, *J* = 5.4, 2.1 Hz, 2H), 1.69–1.61 (m, 1H), 1.53–1.45 (m, 1H), 1.37–1.32 (m, 2H), 1.27–1.23 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 159.1–149.2 (m), 134.4, 133.3, 132.5, 131.2–131.1 (m), 131.1, 128.5, 128.2, 127.9, 127.5, 127.5 (t, *J* = 3.0 Hz), 126.4, 126.4, 126.2, 126.0 (t, *J* = 2.7 Hz), 89.9 (dd, *J* = 21.1, 15.3 Hz), 49.1, 34.4, 33.1, 31.6, 25.5, 22.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, *J* = 40.1 Hz, 1F), -90.00 (d, *J* = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{26}H_{28}F_2NO^+$ $[M+H]^+$: 408.2133, found: 408.2141

N-(1,1-difluoro-2-(naphthalen-2-yl)non-1-en-4-yl)benzamide **(3q)**



The title compound was isolated as a white solid (53.1 mg, 65% yield, 98: 2 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81–7.77 (m, 3H), 7.49–7.44 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 6.7 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 2H), 5.63 (d, *J* = 8.8 Hz, 1H), 4.31–4.23 (m, 1H), 2.81 (dd, *J* = 5.2, 2.2 Hz, 2H), 1.65–1.60 (m, 1H), 1.55–1.45 (m, 1H), 1.38–1.31 (m, 2H), 1.28–1.21 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 154.6 (dd, *J* = 291.4, 288.1 Hz), 134.4, 133.3, 132.5, 131.2 (dd, *J* = 3.6, 2.3 Hz), 131.1, 128.5, 128.2, 127.9, 127.5, 127.5 (t, *J* = 3.1 Hz), 126.4, 126.4, 126.2, 126.0 (t, *J* = 2.9 Hz), 89.9 (dd, *J* = 21.0, 15.2 Hz), 49.1, 34.4, 33.1, 31.6, 25.5, 22.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, *J* = 40.1 Hz, 1F), -90.00 (d, *J* = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{26}H_{28}F_2NO^+$ $[M+H]^+$: 408.2133, found: 408.2138.

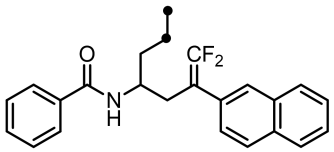
N-(5,5-difluoro-4-(naphthalen-2-yl)pent-4-en-2-yl)benzamide **(3r)**



The title compound was isolated as a white solid (66.9 mg, 95% yield, 99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.81 (dd, *J* = 9.0, 3.9 Hz, 3H), 7.52–7.46 (m, 3H), 7.38–7.29 (m, 3H), 7.20–7.10 (m, 2H), 5.87 (d, *J* = 8.0 Hz, 1H), 4.41–4.28 (m, 1H), 2.91–2.82 (m, 1H), 2.81–2.72 (m, 1H), 1.26 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.7 (dd, *J* = 291.8, 287.8 Hz), 134.3, 133.3, 132.6, 131.2, 130.9

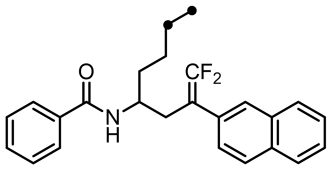
(dd, J = 3.9, 3.0 Hz), 128.6, 128.2, 128.0, 127.6, 127.5 (t, J = 3.2 Hz), 126.5, 126.4, 126.3, 125.9 (t, J = 2.9 Hz), 89.8 (dd, J = 21.4, 14.7 Hz), 45.0, 34.4, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.60 (d, J = 39.7 Hz, 1F), -89.89 (d, J = 39.6 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{20}F_2NO^+$ $[M+H]^+$: 352.1507, found: 352.1514.

N-(1,1-difluoro-2-(naphthalen-2-yl)hept-1-en-4-yl)benzamide **(3s)**



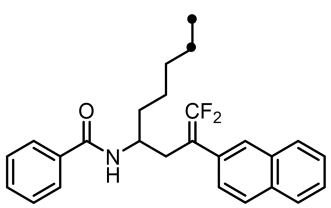
The title compound was isolated as a white solid (47.1 mg, 62% yield, 63: 37 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81–7.75 (m, 3H), 7.49–7.44 (m, 3H), 7.33 (t, J = 7.4 Hz, 1H), 7.27–7.24 (m, 2H), 7.13 (t, J = 7.7 Hz, 2H), 5.63 (d, J = 8.8 Hz, 1H), 4.33–4.23 (m, 1H), 2.87–2.75 (m, 2H), 1.67–1.56 (m, 1H), 1.55–1.46 (m, 1H), 1.42–1.32 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.6 (dd, J = 291.5, 287.8 Hz), 134.3, 133.3, 132.5, 131.2 (dd, J = 6.0, 3.5 Hz), 131.1, 128.5, 128.2, 127.9, 127.6, 127.5 (t, J = 3.1 Hz), 126.4, 126.4, 126.3, 126.0 (t, J = 2.9 Hz), 89.9 (dd, J = 21.1, 15.1 Hz), 48.9, 36.6, 33.1, 19.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, J = 40.1 Hz, 1F), -89.99 (d, J = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{24}F_2NO^+$ $[M+H]^+$: 380.1820, found: 380.1818.

N-(1,1-difluoro-2-(naphthalen-2-yl)oct-1-en-4-yl)benzamide **(3t)**



The title compound was isolated as a white solid (26.0 mg, 33% yield, 60: 40 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82–7.75 (m, 3H), 7.51–7.44 (m, 3H), 7.34 (t, J = 7.4 Hz, 1H), 7.27–7.25 (m, 2H), 7.14 (t, J = 7.8 Hz, 2H), 5.61 (d, J = 8.7 Hz, 1H), 4.31–4.23 (m, 1H), 2.87–2.75 (m, 2H), 1.67–1.62 (m, 1H), 1.53–1.44 (m, 1H), 1.36–1.27 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 154.5 (dd, J = 291.3, 287.6 Hz), 134.4, 133.3, 132.5, 131.2, 131.1, 128.5, 128.2, 127.9, 127.6, 127.4 (t, J = 3.0 Hz), 126.4, 126.4, 126.3, 126.0 (t, J = 2.9 Hz), 89.9 (dd, J = 21.2, 15.0 Hz), 49.1, 34.1, 33.1, 28.0, 22.5, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, J = 40.1 Hz, 1F), -90.00 (d, J = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{25}H_{26}F_2NO^+$ $[M+H]^+$: 394.1977, found: 394.1983.

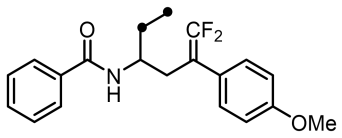
N-(1,1-difluoro-2-(naphthalen-2-yl)non-1-en-4-yl)benzamide **(3u)**



The title compound was isolated as a white solid (28.6 mg, 35% yield, 85: 15 rr) after chromatography on silica with ethyl acetate/hexane

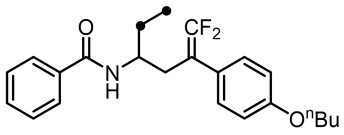
(1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82–7.75 (m, 3H), 7.50–7.44 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27–7.24 (m, 2H), 7.14 (t, *J* = 7.7 Hz, 2H), 5.60 (d, *J* = 8.8 Hz, 1H), 4.31–4.23 (m, 1H), 2.87–2.77 (m, 2H), 1.69–1.60 (m, 1H), 1.54–1.46 (m, 1H), 1.40–1.31 (m, 2H), 1.28–1.23 (m, 4H), 0.86–0.80 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 151.3 (dd, *J* = 357.6, 350.6 Hz), 134.4, 133.3, 132.5, 131.1, 128.5, 128.2, 127.9, 127.5, 127.5 (t, *J* = 3.0 Hz), 126.4, 126.4, 126.2, 126.1–125.9 (m), 89.9 (dd, *J* = 21.1, 15.2 Hz), 49.1, 34.4, 33.1, 31.6, 25.6, 22.5, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (d, *J* = 40.1 Hz, 1F), -90.00 (d, *J* = 40.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{26}H_{28}F_2NO^+$ $[M+H]^+$: 408.2133, found: 408.2139.

N-(6,6-difluoro-5-(4-methoxyphenyl)hex-5-en-3-yl)benzamide **(3aa)**



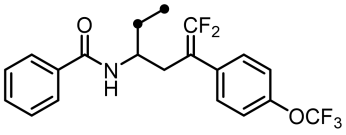
The title compound was isolated as a white solid (55.4 mg, 80% yield, 97: 3 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.90 (d, *J* = 8.5 Hz, 1H), 4.16–4.06 (m, 1H), 3.74 (s, 3H), 2.68–2.57 (m, 2H), 1.68–1.59 (m, 1H), 1.54–1.45 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 158.9, 154.2 (dd, *J* = 289.8, 286.7 Hz), 134.6, 131.2, 129.5 (t, *J* = 3.0 Hz), 128.3, 126.7, 125.6 (dd, *J* = 3.5, 2.2 Hz), 114.2, 89.3 (dd, *J* = 20.9, 15.4 Hz), 55.1, 50.3, 32.8, 27.2, 10.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.30 (d, *J* = 3.4 Hz, 1F), -91.44 (d, *J* = 43.8 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{22}F_2NO_2^+$ $[M+H]^+$: 346.1613, found: 346.1619.

N-(5-(4-butoxyphenyl)-6,6-difluorohex-5-en-3-yl)benzamide **(3ab)**



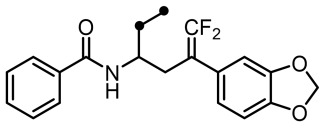
The title compound was isolated as a white solid (69.9 mg, 90% yield, 99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 3H), 7.36– 7.32 (m, 2H), 7.27–7.24 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.71 (d, *J* = 8.6 Hz, 1H), 4.18– 4.09 (m, 1H), 3.97– 3.86 (m, 2H), 2.67– 2.65 (m, 2H), 1.79– 1.72 (m, 3H), 1.54– 1.45 (m, 3H), 1.00–0.96 (m, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.5, 154.2 (dd, *J* = 289.9, 286.5 Hz), 134.6, 131.2, 129.4 (t, *J* = 3.0 Hz), 128.3, 126.6, 125.3 (dd, *J* = 3.7, 2.5 Hz), 114.6 (d, *J* = 24.0 Hz), 89.2 (dd, *J* = 21.1, 15.3 Hz), 67.6, 50.3, 32.7, 31.3, 27.3, 19.2, 13.8, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.27 (d, *J* = 43.9 Hz, 1F), -91.51 (d, *J* = 43.9 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{28}F_2NO_2^+$ $[M+H]^+$: 388.2083, found: 388.2090.

N-(6,6-difluoro-5-(4-(trifluoromethoxy)phenyl)hex-5-en-3-yl)benzamide **(3ac)**



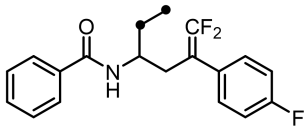
The title compound was isolated as a white solid (73.6 mg, 92% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.50–7.45 (m, 1H), 7.42–7.35 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.70 (d, *J* = 8.7 Hz, 1H), 4.17–4.08 (m, 1H), 2.73–2.63 (m, 2H), 1.71–1.64 (m, 1H), 1.55–1.46 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 154.5 (dd, *J* = 291.0, 288.6 Hz), 148.4, 134.5, 132.1 (d, *J* = 1.6 Hz), 131.4, 129.8 (t, *J* = 3.2 Hz), 128.5, 126.5, 120.4 (q, *J* = 257.5 Hz), 120.4 (d, *J* = 257.5 Hz), 89.1 (dd, *J* = 20.4, 16.3 Hz), 50.2 (t, *J* = 2.7 Hz), 33.0, 27.4, 10.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.80 (s, 3F), -89.55 (d, *J* = 2.2 Hz, 2F). HRMS (ESI) m/z calculated for $C_{20}H_{19}F_2NO_2^+$ $[M+H]^+$: 400.1330, found: 400.1335.

N-(5-(benzo[d][1,3]dioxol-5-yl)-6,6-difluorohex-5-en-3-yl)benzamide **(3ad)**



The title compound was isolated as a white solid (56.2 mg, 78% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 2H), 7.48–7.44 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 6.83–6.74 (m, 3H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.87 (d, *J* = 1.4 Hz, 1H), 5.74 (d, *J* = 8.7 Hz, 1H), 4.17–4.08 (m, 1H), 2.66–2.59 (m, 2H), 1.71–1.60 (m, 1H), 1.55–1.46 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 154.3 (dd, *J* = 290.4, 286.6 Hz), 147.9, 147.0, 134.6, 131.3, 128.4, 127.1 (dd, *J* = 4.4, 2.8 Hz), 126.6, 121.9 (t, *J* = 3.0 Hz), 108.9 (t, *J* = 3.2 Hz), 108.5, 101.1, 89.6 (dd, *J* = 22.0, 14.9 Hz), 50.2, 33.0, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.25 (d, *J* = 28.6 Hz, 1F), -87.11 (d, *J* = 28.6 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{20}F_2NO_3^+$ $[M+H]^+$: 360.1406, found: 360.1412.

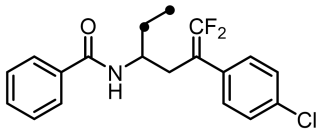
N-(6,6-difluoro-5-(4-fluorophenyl)hex-5-en-3-yl)benzamide **(3ae)**



The title compound was isolated as a white solid (50.1 mg, 75% yield, 98: 2 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41–7.29 (m, 4H), 7.08–6.98 (m, 2H), 5.70 (d, *J* = 8.7 Hz, 1H), 4.16–4.06 (m, 1H), 2.70–2.55 (m, 2H), 1.69–1.63 (m, 1H), 1.55–1.46 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 162.0 (d, *J* = 247.2 Hz), 154.3 (d, *J* = 4.5 Hz), 134.5, 131.4, 130.1 (dt, *J* = 8.0, 3.1 Hz), 129.3 (d, *J* = 3.0 Hz), 128.5, 126.6, 115.7 (d, *J* = 21.6 Hz), 89.1 (dd, *J* = 21.8, 15.1 Hz), 50.1, 33.1, 27.4, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.34 (d, *J* = 41.7 Hz, 1F),

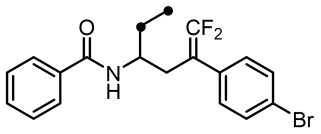
-90.61 (d, *J* = 41.7 Hz, 1F), -110.91–-116.07 (m, 1F). HRMS (ESI) m/z calculated for $C_{19}H_{19}F_3NO^+$ $[M+H]^+$: 334.1413, found: 334.1415.

N-(5-(4-chlorophenyl)-6,6-difluorohex-5-en-3-yl)benzamide (3af)



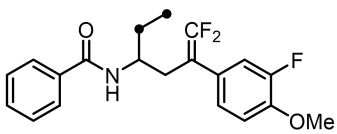
The title compound was isolated as a white solid (58.8 mg, 84% yield, 97: 3 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.45 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 4H), 5.67 (d, *J* = 8.6 Hz, 1H), 4.17–4.05 (m, 1H), 2.70–2.60 (m, 2H), 1.68–1.62 (m, 1H), 1.54–1.46 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 154.3 (dd, *J* = 291.7, 287.6 Hz), 134.5, 133.5, 131.9 (dd, *J* = 4.0, 2.7 Hz), 131.4, 129.7 (t, *J* = 3.1 Hz), 128.9, 128.5, 126.5, 89.1 (dd, *J* = 21.8, 14.9 Hz), 50.2, 32.9, 27.4, 10.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.54 (d, *J* = 39.9 Hz, 1F), -89.74 (d, *J* = 39.8 Hz, 1F). HRMS (ESI) m/z calculated for $C_{19}H_{19}ClF_2NO^+$ $[M+H]^+$: 350.1118, found: 350.1123.

***N-(5-(4-bromophenyl)-6,6-difluorohex-5-en-3-yl)benzamide* (3ag)**



The title compound was isolated as a white solid (63.0 mg, 80% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.42 (m, 5H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 2H), 5.67 (d, *J* = 8.6 Hz, 1H), 4.15–4.04 (m, 1H), 2.73–2.61 (m, 2H), 1.68–1.63 (m, 1H), 1.55–1.45 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 154.3 (dd, *J* = 291.6, 288.1 Hz), 134.4, 132.5 (dd, *J* = 3.7, 2.3 Hz), 131.9, 131.4, 130.0 (t, *J* = 3.1 Hz), 128.5, 126.5, 121.6, 89.2 (dd, *J* = 21.4, 15.2 Hz), 50.2, 32.8, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.43 (d, *J* = 39.5 Hz, 1F), -89.60 (d, *J* = 39.5 Hz, 1F). HRMS (ESI) m/z calculated for $C_{19}H_{19}BrF_2NO^+$ $[M+H]^+$: 394.0613, found: 394.0620.

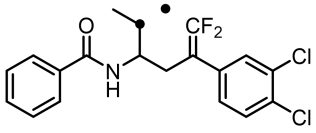
***N-(6,6-difluoro-5-(3-fluoro-4-methoxyphenyl)hex-5-en-3-yl)benzamide* (3ah)**



The title compound was isolated as a white solid (51.7 mg, 71% yield, 90: 10 rr) after chromatography on silica with ethyl acetate/hexane (1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.49–7.45 (m, 1H), 7.40–7.36 (m, 2H), 7.12–7.08 (m, 2H), 6.92–6.86 (m, 1H), 5.72 (d, *J* = 8.7 Hz, 1H), 4.16–4.07 (m, 1H), 3.84 (s, 3H), 2.66–2.62 (m, 2H), 1.70–1.63 (m, 1H), 1.54–1.45 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 154.4 (dd, *J* = 291.5, 286.9 Hz), 146.9 (d, *J* = 10.7 Hz), 134.6, 131.3, 128.4, 126.6, 124.3 (q, *J* = 3.2 Hz), 116.0 (dt, *J* = 19.4, 3.4 Hz), 113.5 (d, *J* = 2.3 Hz), 88.8 (dd, *J* = 22.3, 14.4 Hz), 56.2, 50.2, 32.8, 27.3, 10.2;

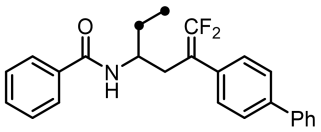
^{19}F NMR (376 MHz, $CDCl_3$) δ -89.94 (d, *J* = 41.4 Hz, 1F), -90.28 (dt, *J* = 41.7, 2.4 Hz, 1F), -130.78–-139.64 (m, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{21}F_3NO_2^+$ $[M+H]^+$: 364.1519, found: 364.1524.

N-(5-(3,4-dichlorophenyl)-6,6-difluorohex-5-en-3-yl)benzamide **(3ai)**



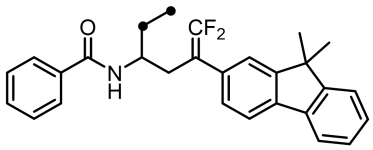
The title compound was isolated as a white solid (62.2 mg, 81% yield, 97: 3 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 2H), 7.50–7.45 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 3H), 7.27–7.19 (m, 1H), 5.74 (d, *J* = 8.7 Hz, 1H), 4.24–3.86 (m, 1H), 2.87–2.50 (m, 2H), 1.74–1.60 (m, 1H), 1.50 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 154.5 (dd, *J* = 293.0, 288.4 Hz), 134.3, 133.6 (dd, *J* = 4.4, 3.1 Hz), 132.8, 131.6, 131.5, 130.6, 130.1 (t, *J* = 3.4 Hz), 128.5, 127.7 (t, *J* = 3.2 Hz), 126.5, 88.6 (dd, *J* = 22.8, 14.3 Hz), 50.2, 32.9, 27.4, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.22 (d, *J* = 37.1 Hz, 1F), -88.50 (d, *J* = 37.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{19}H_{18}Cl_2F_2NO^+$ $[M+H]^+$: 384.0728, found: 384.0735.

N-(5-([1,1'-biphenyl]-4-yl)-6,6-difluorohex-5-en-3-yl)benzamide **(3aj)**



The title compound was isolated as a yellow solid (65.1 mg, 83% yield, 92: 8 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 8.3 Hz, 4H), 7.46–7.42 (t, *J* = 6.4 Hz, 6H), 7.40–7.33 (m, 2H), 7.28 (dd, *J* = 14.0, 6.5 Hz, 2H), 5.69 (d, *J* = 8.6 Hz, 1H), 4.25–4.13 (m, 1H), 2.83–2.67 (m, 2H), 1.74–1.64 (m, 1H), 1.59–1.49 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 157.3, 154.4 (d, *J* = 4.2 Hz), 151.5, 140.4, 134.6, 132.6, 131.2, 128.8, 128.7 (t, *J* = 3.1 Hz), 128.4, 127.4, 127.0, 126.6, 89.5 (dd, *J* = 18.5, 17.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.83 (s, 2F). HRMS (ESI) m/z calculated for $C_{25}H_{24}F_2NO^+$ $[M+H]^+$: 392.1820, found: 392.1826.

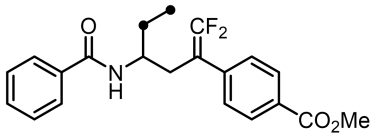
N-(5-(9,9-dimethyl-9H-fluoren-2-yl)-6,6-difluorohex-5-en-3-yl)benzamide **(3ak)**



The title compound was isolated as a white solid (72.6 mg, 84% yield, 98: 2 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.68 (m, 2H), 7.41–7.38 (m, 2H), 7.35–7.26 (m, 6H), 7.13 (t, *J* = 7.7 Hz, 2H), 5.69 (d, *J* = 8.8 Hz, 1H), 4.26–4.16 (m, 1H), 2.78–2.76 (m, 2H), 1.68–1.63 (m, 1H), 1.59–1.51 (m, 1H), 1.45 (s, 3H), 1.29 (s, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.4 (dd, *J* = 290.7,

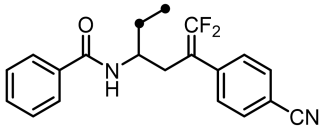
287.9 Hz), 138.9, 138.5, 134.4, 132.7 (dd, J = 3.1, 2.1 Hz), 131.2, 128.3, 127.5, 127.2 (t, J = 2.9 Hz), 127.0, 126.5, 122.6, 122.5, 120.3, 120.0, 90.1 (dd, J = 20.6, 15.4 Hz), 50.6, 46.9, 32.7, 27.3, 27.2, 26.7, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.50 (d, J = 42.7 Hz, 1F), -91.11 (d, J = 42.8 Hz, 1F). HRMS (ESI) m/z calculated for $C_{28}H_{28}F_2NO^+$ $[M+H]^+$: 432.2133, found: 432.2133.

N-(5-(4-cyanophenyl)-6,6-difluorohex-5-en-3-yl)benzamide **(3al)**



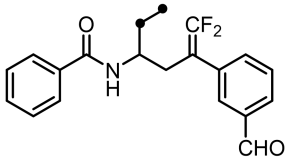
The title compound was isolated as a white solid (68.1 mg, 81% yield, 95: 5 rr) after chromatography on silica with ethyl acetate/hexane (1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.52–7.47 (m, 3H), 7.40 (t, J = 7.6 Hz, 2H), 5.76 (d, J = 8.6 Hz, 1H), 4.12–4.03 (m, 1H), 2.75–2.66 (m, 2H), 1.70–1.64 (m, 1H), 1.55–1.47 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 154.7 (dd, J = 294.3, 289.4 Hz), 138.4 (dd, J = 4.2, 3.4 Hz), 134.3, 132.3, 131.6, 129.0 (t, J = 3.4 Hz), 128.5, 126.5, 118.5, 111.1, 89.5 (dd, J = 22.4, 13.8 Hz), 50.1, 32.8, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.11 (d, J = 34.2 Hz, 1F), -87.33 (d, J = 34.3 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{19}F_2N_2O^+$ $[M+H]^+$: 374.1562, found: 374.1568.

methyl 4-(4-benzamido-1,1-difluorohex-1-en-2-yl)benzoate **(3am)**



The title compound was isolated as a white solid (60.6 mg, 79% yield, 95: 5 rr) after chromatography on silica with ethyl acetate/hexane (1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.96 (m, 2H), 7.51–7.49 (m, 2H), 7.46–7.42 (m, 3H), 7.37–7.33 (m, 2H), 5.68 (d, J = 8.7 Hz, 1H), 4.16–4.07 (m, 1H), 3.91 (s, 3H), 2.74–2.71 (m, 2H), 1.69–1.65 (m, 1H), 1.54–1.45 (m, 1H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.5, 154.5 (dd, J = 292.1, 289.9 Hz), 138.3, 134.5, 131.3, 129.9, 129.1, 128.4, 128.2 (t, J = 3.2 Hz), 126.5, 89.7 (dd, J = 19.9, 16.2 Hz), 52.0, 50.3, 32.7, 27.3, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.30(s, 2F). HRMS (ESI) m/z calculated for $C_{21}H_{22}F_2NO_3^+$ $[M+H]^+$: 341.1562, found: 341.1568.

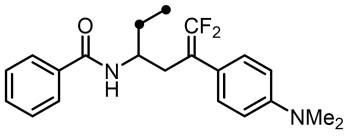
N-(6,6-difluoro-5-(3-formylphenyl)hex-5-en-3-yl)benzamide (**3an)**



The title compound was isolated as a yellow oil (60.6 mg, 88% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.86 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.58–7.52 (m, 2H), 7.50–7.41 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 5.90 (d, J = 8.8 Hz, 1H), 4.26–3.93 (m, 1H), 2.73–2.70 (m, 2H),

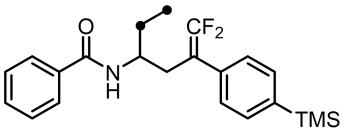
1.73–1.60 (m, 1H), 1.57–1.44 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 167.2, 154.6 (dd, J = 292.1, 288.6 Hz), 136.6, 134.6 (dd, J = 3.8, 2.3 Hz), 134.4 (t, J = 3.0 Hz), 131.4, 129.5 (t, J = 3.2 Hz), 129.4, 128.6, 128.4, 126.6, 89.3 (dd, J = 21.5, 15.0 Hz), 50.2, 33.0, 27.4, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.92 (d, J = 38.3 Hz, 1F), -89.08 (d, J = 38.4 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{20}F_2NO_2^+$ $[M+H]^+$: 344.1457, found: 344.1463.

N-(5-(4-(dimethylamino)phenyl)-6,6-difluorohex-5-en-3-yl)benzamide **(3ao)**



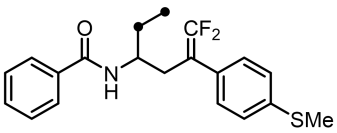
The title compound was isolated as a red solid (61.8 mg, 86% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 3H), 7.26–7.20 (m, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 5.69 (d, J = 8.7 Hz, 1H), 4.13–4.03 (m, 1H), 2.86 (s, 6H), 2.66–2.50 (m, 2H), 1.63–1.50 (m, 1H), 1.48–1.40 (m, 1H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.1 (dd, J = 288.8, 286.8 Hz), 149.7, 134.6, 131.1, 129.0 (t, J = 3.0 Hz), 128.3 (d, J = 14.2 Hz), 126.7, 120.9, 112.6, 89.2 (dd, J = 20.0, 16.1 Hz), 50.4, 40.4, 32.3, 27.1, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.95 (d, J = 45.7 Hz, 1F), -92.10 (d, J = 45.7 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{25}F_2N_2O^+$ $[M+H]^+$: 359.1929, found: 359.1936.

N-(6,6-difluoro-5-(4-(trimethylsilyl)phenyl)hex-5-en-3-yl)benzamide **(3ap)**



The title compound was isolated as a white solid (68.3 mg, 88% yield, 99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.21 (m, 5H), 7.16–7.09 (m, 4H), 5.52 (d, J = 8.7 Hz, 1H), 4.00–3.90 (m, 1H), 2.58–2.44 (m, 2H), 1.51–41 (m, 1H), 1.36–1.25 (m, 1H), 0.73 (t, J = 7.4 Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 155.5 (dd, J = 291.0, 288.1 Hz), 141.0, 135.7, 135.0 (dd, J = 2.5, 1.7 Hz), 134.8, 132.3, 129.5, 128.6 (t, J = 3.0 Hz), 127.7, 91.0 (dd, J = 20.0, 15.6 Hz), 51.5, 33.6, 28.4, 11.4, 0.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.94 (d, J = 40.9 Hz, 1F), -90.10 (d, J = 40.9 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{28}F_2NOSi^+$ $[M+H]^+$: 388.1903, found: 388.1912.

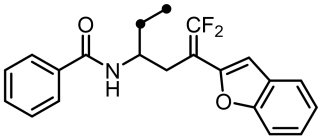
N-(6,6-difluoro-5-(4-(methylthio)phenyl)hex-5-en-3-yl)benzamide **(3aq)**



The title compound was isolated as a white solid (58.7 mg, 81% yield, 97: 3 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 3H), 7.40–7.33 (m, 2H), 7.30–7.26 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.67 (d, J = 8.7 Hz, 1H),

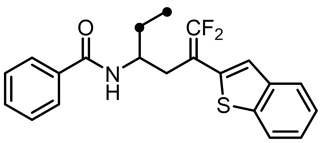
4.18–4.08 (m, 1H), 2.75–2.63 (m, 2H), 2.44 (s, 3H), 1.67–1.62 (m, 1H), 1.55–1.45 (m, 1H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 154.3 (dd, J = 290.9, 287.6 Hz), 138.1, 134.5, 131.3, 130.1 (dd, J = 3.4, 2.4 Hz), 128.7 (t, J = 3.2 Hz), 128.4, 126.6, 126.6, 89.3 (dd, J = 21.0, 15.2 Hz), 50.3, 32.6, 27.3, 15.5, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.08 (d, J = 41.2 Hz, 1F), -90.25 (d, J = 41.2 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{22}F_2NOS^+$ $[M+H]^+$: 362.1385, found: 362.1390.

N-(5-(benzofuran-2-yl)-6,6-difluorohex-5-en-3-yl)benzamide **(3ar)**



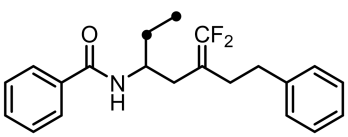
The title compound was isolated as a white solid (55.6 mg, 78% yield, 93: 7 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 3H), 7.41 (t, J = 8.2 Hz, 2H), 7.30–7.25 (m, 3H), 7.23–7.20 (m, 1H), 6.85 (s, 1H), 5.99 (d, J = 8.4 Hz, 1H), 4.37–4.29 (m, 1H), 2.82–2.72 (m, 2H), 1.80–1.72 (m, 1H), 1.68–1.60 (m, 1H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 155.3 (dd, J = 300.8, 289.1 Hz), 154.2, 149.3 (t, J = 6.5 Hz), 134.5, 131.3, 128.7, 128.4, 126.6, 124.2, 123.1, 120.9, 110.9, 105.0 (dd, J = 8.8, 5.4 Hz), 83.9 (dd, J = 28.2, 12.0 Hz), 50.9, 29.8, 27.5, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -79.21 (d, J = 23.1 Hz, 1F), -85.71 (d, J = 23.0 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{20}F_2NO_2^+$ $[M+H]^+$: 356.1457, found: 356.1464.

N-(5-(benzo[b]thiophen-2-yl)-6,6-difluorohex-5-en-3-yl)benzamide **(3as)**



The title compound was isolated as a yellow solid (57.3 mg, 77% yield, 93: 7 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.69 (m, 2H), 7.57–7.51 (m, 2H), 7.46 (s, 1H), 7.42–7.38 (m, 1H), 7.33–7.22 (m, 4H), 5.96 (d, J = 8.6 Hz, 1H), 4.38–4.28 (m, 1H), 2.86–2.76 (m, 1H), 2.76–2.68 (m, 1H), 1.77–1.70 (m, 1H), 1.61–1.52 (m, 1H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 154.8 (dd, J = 297.9, 289.3 Hz), 139.6, 139.3 (dd, J = 5.0, 1.2 Hz), 135.7 (dd, J = 6.9, 4.1 Hz), 134.5, 131.3, 128.4, 126.6, 124.5, 124.5, 123.6, 122.9 (dd, J = 5.6, 4.7 Hz), 121.8, 86.4 (dd, J = 26.2, 13.1 Hz), 50.6, 33.0, 27.1, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.93 (d, J = 40.4 Hz, 1F), -90.08 (d, J = 40.4 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{20}F_2NOS^+$ $[M+H]^+$: 372.1228, found: 372.1234.

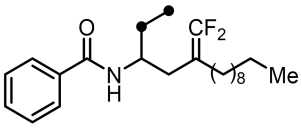
N-(5-(difluoromethylene)-7-phenylheptan-3-yl)benzamide **(3at)**



The title compound was isolated as a yellow oil (24.8 mg, 36% yield, >99: 1 rr) after chromatography on silica with ethyl

acetate/hexane (1:8).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 2H), 7.45–7.41 (m, 1H), 7.39–7.33 (m, 2H), 7.22–7.19 (m, 2H), 7.17–7.08 (m, 3H), 5.71 (d, *J* = 8.7 Hz, 1H), 4.19–4.10 (m, 1H), 2.68 (t, *J* = 7.9 Hz, 2H), 2.38–2.27 (m, 2H), 2.20–2.14 (m, 1H), 2.11–2.04 (m, 1H), 1.64–1.57 (m, 1H), 1.47–1.39 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 153.4 (dd, *J* = 285.7, 283.4 Hz), 140.0, 133.8, 130.4, 127.6, 127.3, 125.7, 125.0, 85.2 (dd, *J* = 17.8, 16.7 Hz), 48.2 (t, *J* = 2.7 Hz), 32.8 (t, *J* = 2.5 Hz), 30.7 (d, *J* = 2.5 Hz), 26.9, 26.8, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.40 (d, *J* = 53.7 Hz, 1F), -94.69 (d, *J* = 53.6 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{24}F_2NO^+$ $[M+H]^+$: 344.1820, found: 344.1820.

N-(5-(difluoromethylene)hexadecan-3-yl)benzamide **(3au)**

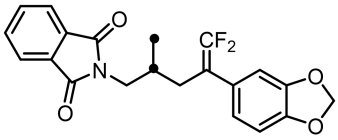


The title compound was isolated as a yellow oil (21.3 mg, 28% yield, >99: 1 rr) after chromatography on silica with ethyl acetate/hexane (1:8).^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71–7.63 (m, 2H), 7.45–7.40 (m, 1H), 7.40–7.33 (m, 2H), 5.72 (d, *J* = 9.1 Hz, 1H), 4.18–4.07 (m, 1H), 2.22–2.06 (m, 2H), 2.03–1.91 (m, 2H), 1.65–1.58 (m, 1H), 1.48–1.40 (m, 1H), 1.38–1.29 (m, 2H), 1.25–1.17 (m, 14H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 153.3 (dd, *J* = 278.6, 276.3 Hz), 133.8, 130.4, 127.6, 125.7, 85.7 (dd, *J* = 18.3, 15.9 Hz), 48.3, 30.9, 30.4 (d, *J* = 2.5 Hz), 28.7, 28.6 (d, *J* = 1.7 Hz), 28.4, 28.3, 28.1, 27.0, 26.4 (t, *J* = 2.3 Hz), 24.9 (d, *J* = 1.7 Hz), 21.7, 13.1 (d, *J* = 3.8 Hz), 9.3 (d, *J* = 3.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.46 (d, *J* = 56.0 Hz, 1F), -95.35 (d, *J* = 56.0 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{36}F_2NO^+$ $[M+H]^+$: 380.2759, found: 380.2765.

6. Procedure for olefin cross-coupling

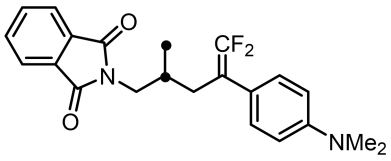
In an argon-filled glovebox, $NiCl_2$•DME (0.02 mmol, 10 mol%), bathocuproine (0.02 mmol, 10 mol%), NaF (0.5 mmol, 2.5 eq), alkene substrate (0.2 mmol, 1.0 eq), appropriate trifluoromethyl alkenes (0.4 mmol, 2.0 eq), $(MeO)_3SiH$ (0.4 mmol, 2.0 equiv), Tol/DMSO (0.92 mL / 0.08 mL) were added to a 10 mL schlenk flask. The reaction mixture was stirred at 80 °C for 18 h. After the reaction time, the vessel was allowed to silica gel column chromatography. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent. The conditions for flash chromatography and data for characterization of the products are listed below.

2-(4-(benzo[d][1,3]dioxol-5-yl)-5,5-difluoro-2-methylpent-4-en-1-yl)isoindoline-1,3-dione **(4a)**



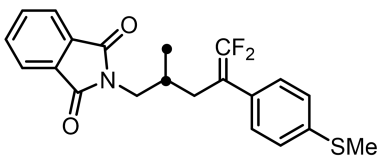
The title compound was isolated as a yellow oil (64.1 mg, 83% yield, 92: 8 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.63 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.70–6.63 (m, 3H), 5.86 (s, 2H), 3.53 (dd, *J* = 13.6, 6.3 Hz, 1H), 3.43 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.37–2.29 (m, 1H), 2.22–2.11 (m, 1H), 1.99–1.88 (m, 1H), 0.81 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 152.9 (dd, *J* = 289.4, 286.8 Hz), 146.7, 145.8, 132.9, 130.9, 125.8 (dd, *J* = 4.1, 2.5 Hz), 122.2, 120.8 (t, *J* = 3.0 Hz), 107.7 (t, *J* = 3.2 Hz), 107.3, 100.1, 89.4 (dd, *J* = 21.7, 14.6 Hz), 42.6, 32.1, 30.1, 16.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.08 (dd, *J* = 43.8, 2.1 Hz, 1F), -91.35 (d, *J* = 43.8 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{18}F_2NO_4^+$ $[M+H]^+$: 386.1198, found: 386.1196.

2-(4-(4-(dimethylamino)phenyl)-5,5-difluoro-2-methylpent-4-en-1-yl)isoindoline-1,3-dione **(4b)**



The title compound was isolated as a yellow solid (51.6 mg, 67% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.62 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.55 (dd, *J* = 13.5, 6.2 Hz, 1H), 3.44 (dd, *J* = 13.5, 8.1 Hz, 1H), 2.86 (s, 6H), 2.40–2.33 (m, 1H), 2.23–2.15 (m, 1H), 2.03–1.94 (m, 1H), 0.81 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 153.8 (dd, *J* = 288.7, 286.0 Hz), 149.5, 133.9, 132.0, 128.8 (t, *J* = 3.2 Hz), 123.2, 120.7 (t, *J* = 2.9 Hz), 112.2, 90.2 (dd, *J* = 20.5, 14.7 Hz), 43.8, 40.4, 32.7, 31.3 (t, *J* = 2.4 Hz), 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.34 (d, *J* = 46.9 Hz, 1F), -92.54 (dd, *J* = 46.9 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{23}F_2N_2O_2^+$ $[M+H]^+$: 385.1722, found: 385.1717.

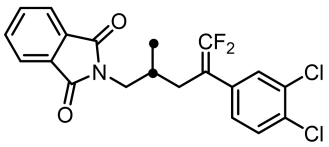
2-(5,5-difluoro-2-methyl-4-(4-(methylthio)phenyl)pent-4-en-1-yl)isoindoline-1,3-dione **(4c)**



The title compound was isolated as a colourless oil (60.5 mg, 78% yield, 92: 8 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.19 (s, 4H), 3.61 (dd, *J* = 13.5, 6.3 Hz, 1H), 3.51 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.47 (s, 4H), 2.33–2.25 (m, 1H), 2.06–1.97 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 154.0 (dd, *J* = 290.4, 287.5 Hz), 137.7, 133.9, 131.9, 129.9–129.8 (m), 128.6 (t, *J* = 3.2 Hz), 126.4, 123.2, 90.2 (dd, *J* = 21.3, 14.3 Hz), 43.7, 32.6, 31.3 (t, *J* = 2.3 Hz), 17.3, 15.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.40 (d, *J* = 42.1 Hz, 1F), -

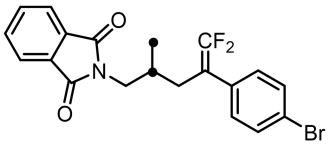
90.63 (d, J = 42.2 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{20}F_2NOS^+$ $[M+H]^+$: 388.1177, found: 388.1168.

2-(4-(3,4-dichlorophenyl)-5,5-difluoro-2-methylpent-4-en-1-yl)isoindoline-1,3-dione **(4d)**



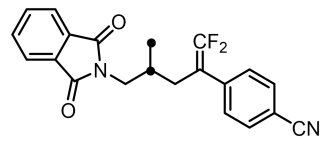
The title compound was isolated as a white solid (67.2 mg, 82% yield, 90: 10 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 5.4, 3.1 Hz, 2H), 7.64 (dd, J = 5.4, 3.1 Hz, 2H), 7.31–7.25 (m, 2H), 7.06–7.03 (m, 1H), 3.53 (dd, J = 13.6, 6.5 Hz, 1H), 3.43 (dd, J = 13.6, 7.7 Hz, 1H), 2.39–2.33 (m, 1H), 2.25–2.16 (m, 1H), 1.97–1.86 (m, 1H), 0.82 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 153.1 (dd, J = 291.9, 288.9 Hz), 133.0, 132.3 (dd, J = 4.1, 2.7 Hz), 131.6, 130.8, 130.5, 129.4, 129.0 (t, J = 3.4 Hz), 126.5 (t, J = 3.3 Hz), 122.2, 88.4 (dd, J = 22.5, 14.1 Hz), 42.5, 31.5, 30.2 (t, J = 2.3 Hz), 16.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.51 (d, J = 38.0 Hz, 1F), -88.70 (d, J = 37.9 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{16}Cl_2F_2NO_2^+$ $[M+H]^+$: 410.0521, found: 410.0510.

2-(4-(4-bromophenyl)-5,5-difluoro-2-methylpent-4-en-1-yl)isoindoline-1,3-dione **(4e)**



The title compound was isolated as a white solid (69.7 mg, 83% yield, 90: 10 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 5.4, 3.1 Hz, 2H), 7.71 (dd, J = 5.7, 2.9 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 3.60 (dd, J = 13.6, 6.3 Hz, 1H), 3.51 (dd, J = 13.6, 8.0 Hz, 1H), 2.48–2.42 (m, 1H), 2.34–2.25 (m, 1H), 2.05–1.95 (m, 1H), 0.89 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 153.9 (dd, J = 291.1, 287.9 Hz), 134.0, 132.2 (dd, J = 4.2, 2.9 Hz), 131.9, 131.7, 129.9 (t, J = 3.1 Hz), 123.2, 121.4, 90.0 (dd, J = 22.0, 14.1 Hz), 43.6, 32.6, 31.3, 17.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.68 (d, J = 40.4 Hz, 1F), -89.96 (dd, J = 40.1, 2.9 Hz, 1F). HRMS (ESI) m/z calculated for $C_{20}H_{17}F_2BrNO_2^+$ $[M+H]^+$: 420.0405, found: 420.0400.

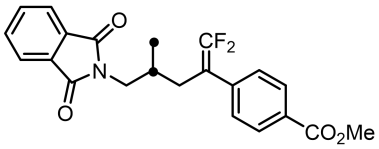
4-(5-(1,3-dioxoisoindolin-2-yl)-1,1-difluoro-4-methylpent-1-en-2-yl)benzonitrile **(4f)**



The title compound was isolated as a colourless oil (53.6 mg, 73% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 5.4, 3.1 Hz, 2H), 7.65 (dd, J = 5.5, 3.0 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 3.53 (dd, J = 13.6, 6.3 Hz, 1H), 3.44 (dd, J = 13.6, 7.9 Hz, 1H), 2.47–2.40 (m, 1H), 2.32–2.21 (m, 1H), 1.95–1.86 (m, 1H), 0.82 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 154.3

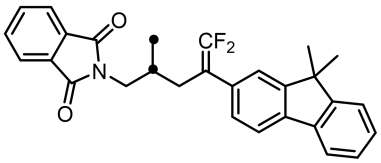
(dd, J = 293.7, 289.6 Hz), 138.3 (dd, J = 4.6, 3.7 Hz), 134.1, 132.3, 131.8, 128.9 (t, J = 3.4 Hz), 123.3, 118.5, 111.1, 90.2 (dd, J = 23.0, 12.9 Hz), 43.5, 32.3, 31.3 (t, J = 2.3 Hz), 17.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.14 (d, J = 35.0 Hz, 1F), -87.80 (d, J = 35.2 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{17}F_2N_2O_2^+$ $[M+H]^+$: 367.1253, found: 367.1258.

methyl 4-(5-(1,3-dioxoisoindolin-2-yl)-1,1-difluoro-4-methylpent-1-en-2-yl)benzoate **(4g)**



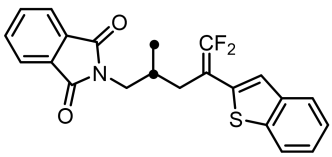
The title compound was isolated as a white solid (60.0 mg, 75% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.74 (dd, J = 5.4, 3.1 Hz, 2H), 7.63 (dd, J = 5.4, 3.0 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 3.83 (s, 3H), 3.53 (dd, J = 13.6, 6.5 Hz, 1H), 3.43 (dd, J = 13.6, 7.8 Hz, 1H), 2.47–2.41 (m, 1H), 2.33–2.20 (m, 1H), 1.98–1.87 (m, 1H), 0.81 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.6, 153.2 (dd, J = 292.6, 288.5 Hz), 137.1 (dd, J = 4.3, 3.4 Hz), 132.9, 130.8, 128.7, 128.0, 127.1 (t, J = 3.3 Hz), 122.2, 89.5 (dd, J = 22.2, 13.4 Hz), 51.0, 42.6, 31.4, 30.3 (t, J = 2.3 Hz), 16.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.41 (d, J = 37.5 Hz, 1F), -88.80 (d, J = 37.4 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{20}F_2NO_4^+$ $[M+H]^+$: 400.1355, found: 400.1345.

2-(4-(9,9-dimethyl-9H-fluoren-2-yl)-5,5-difluoro-2-methylpent-4-en-1-yl)isoindoline-1,3-dione **(4h)**



The title compound was isolated as a yellow solid (75.1 mg, 82% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 5.4, 3.1 Hz, 2H), 7.63–7.58 (m, 3H), 7.56 (d, J = 7.8 Hz, 1H), 7.33 (dd, J = 5.7, 2.7 Hz, 1H), 7.27–7.21 (m, 3H), 7.19–7.16 (m, 1H), 3.57 (dd, J = 13.5, 6.6 Hz, 1H), 3.45 (dd, J = 13.6, 7.7 Hz, 1H), 2.51–2.42 (m, 1H), 2.32–2.21 (m, 1H), 2.05–1.95 (m, 1H), 1.36 (d, J = 4.7 Hz, 6H), 0.84 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 153.0 (dd, J = 289.9, 287.6 Hz), 152.8, 152.7, 137.6, 137.4, 132.9, 131.2–131.1 (m), 130.9, 126.2, 126.1 (t, J = 3.2 Hz), 125.9, 122.2, 121.5, 121.3 (t, J = 3.1 Hz), 119.0, 118.9, 90.0 (dd, J = 20.1, 15.1 Hz), 45.7, 42.7, 31.9, 30.4 (t, J = 2.3 Hz), 26.0, 16.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.45 (d, J = 42.6 Hz, 1F), -90.59 (d, J = 42.5 Hz, 1F). HRMS (ESI) m/z calculated for $C_{29}H_{26}F_2NO_2^+$ $[M+H]^+$: 458.1926, found: 458.1913.

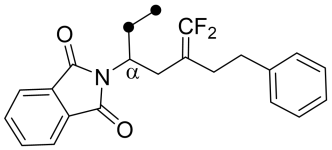
2-(4-(benzo[b]thiophen-2-yl)-5,5-difluoro-2-methylpent-4-en-1-yl)isoindoline-1,3-dione **(4i)**



The title compound was isolated as a white solid (63.7 mg, 80%

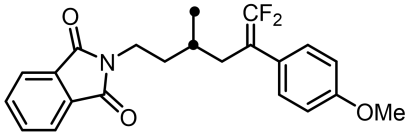
yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.0 Hz, 3H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.24–7.17 (m, 2H), 7.12 (s, 1H), 3.62 (dd, *J* = 13.5, 6.4 Hz, 1H), 3.53 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.50–2.44 (m, 1H), 2.34–2.23 (m, 2H), 0.90 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 153.5 (dd, *J* = 297.3, 289.6 Hz), 138.4, 138.1 (dd, *J* = 4.7, 1.3 Hz), 134.7 (dd, *J* = 7.0, 4.1 Hz), 132.9, 130.9, 123.3, 123.3, 122.3, 122.2, 121.2 (t, *J* = 5.4 Hz), 120.8, 86.1 (dd, *J* = 26.3, 12.5 Hz), 42.7, 31.7, 30.9 (t, *J* = 2.3 Hz), 16.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.72 (d, *J* = 29.1 Hz, 1F), -87.13 (d, *J* = 29.1 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{18}F_2NO_2S^+$ $[M+H]^+$: 398.1021, found: 398.1020.

2-(5-(difluoromethylene)-7-phenylheptan-3-yl)isoindoline-1,3-dione **(4j)**



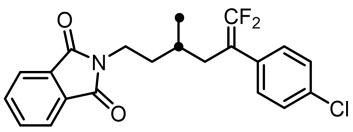
The title compound was isolated as a yellow oil (29.6 mg, 40% yield, 80: 20 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 2H), 7.65–7.59 (m, 2H), 7.22–7.17 (m, 2H), 7.14–7.07 (m, 3H), 4.20–4.12 (m, 1H), 2.80–2.71 (m, 1H), 2.62 (t, *J* = 7.9 Hz, 2H), 2.27–2.17 (m, 3H), 2.12–2.02 (m, 1H), 1.74–1.64 (m, 1H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 153.4 (t, *J* = 286.1 Hz), 139.9, 132.9, 130.7, 127.4, 127.3, 125.1, 122.2, 85.0 (dd, *J* = 18.2, 16.6 Hz), 50.5, 32.8, 28.2 (d, *J* = 2.5 Hz), 26.8 (d, *J* = 2.0 Hz), 24.1, 10.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.56 (d, *J* = 50.2 Hz, 1F), -93.61 (d, *J* = 50.2 Hz, 1F) HRMS (ESI) m/z calculated for $C_{22}H_{22}F_2NO_2^+$ $[M+H]^+$: 370.1613, found: 370.1617.

2-(6,6-difluoro-5-(4-methoxyphenyl)-3-methylhex-5-en-1-yl)isoindoline-1,3-dione **(4k)**



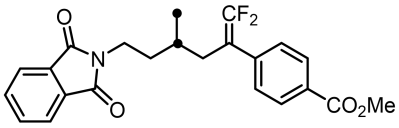
The title compound was isolated as a yellow oil (56.4 mg, 73% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.76 (dd, 2H), 3.73 (s, 3H), 3.68–3.60 (m, 2H), 2.42–2.36 (m, 1H), 2.28–2.21 (m, 1H), 1.79–1.70 (m, 1H), 1.50–1.40 (m, 2H), 0.97 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 158.5, 153.9 (t, *J* = 287.3 Hz), 133.7, 132.1, 129.3 (t, *J* = 3.0 Hz), 125.4 (d, *J* = 1.0 Hz), 123.1, 113.8, 90.4 (dd, *J* = 18.3, 17.2 Hz), 55.1, 35.9, 34.7, 34.6, 28.5 (t, *J* = 2.3 Hz), 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.29 (s, 2F). HRMS (ESI) m/z calculated for $C_{22}H_{21}F_2NO_3^+$ $[M+H]^+$: 386.1562, found: 386.1568.

2-(5-(4-chlorophenyl)-6,6-difluoro-3-methylhex-5-en-1-yl)isoindoline-1,3-dione **(4l)**



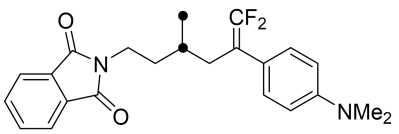
The title compound was isolated as a yellow oil (67.1 mg, 86% yield, 92: 8 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.16 (s, 4H), 3.70–3.61 (m, 2H), 2.43–2.37 (m, 1H), 2.30–2.22 (m, 1H), 1.77–1.70 (m, 1H), 1.48–1.35 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 154.0 (dd, *J* = 290.0, 287.7 Hz), 133.9, 132.9, 131.9, 131.7 (dd, *J* = 3.2, 1.5 Hz), 129.5 (t, *J* = 3.1 Hz), 128.5, 123.1, 90.3 (dd, *J* = 20.8, 14.9 Hz), 35.8, 34.5, 34.4, 28.4, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.48 (d, *J* = 41.8 Hz, 1F), -90.63 (d, *J* = 42.0 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{18}ClF_2NO_2^+$ $[M+H]^+$: 390.1067, found: 390.1067.

methyl 4-(6-(1,3-dioxoisoindolin-2-yl)-1,1-difluoro-4-methylhex-1-en-2-yl)benzoate **(4m)**



The title compound was isolated as a yellow oil (65.4 mg, 79% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.80–7.76 (m, 2H), 7.70–7.65 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 3.69–3.60 (m, 2H), 2.49–2.43 (m, 1H), 2.37–2.27 (m, 1H), 1.78–1.72 (m, 1H), 1.49–1.37 (m, 2H), 0.98 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 166.4, 154.2 (dd, *J* = 292.1, 288.0 Hz), 138.1 (dd, *J* = 4.1, 3.2 Hz), 133.8, 131.9, 129.5, 128.7, 128.1 (t, *J* = 3.2 Hz), 123.1, 90.8 (dd, *J* = 22.0, 13.1 Hz), 52.0, 35.7, 34.4, 34.2, 28.5 (t, *J* = 2.0 Hz), 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.05 (d, *J* = 38.6 Hz, 1F), -89.30 (d, *J* = 38.6 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{21}F_2NO_4^+$ $[M+H]^+$: 414.1511, found: 414.1511.

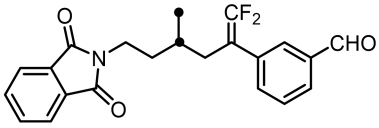
2-(5-(4-(dimethylamino)phenyl)-6,6-difluoro-3-methylhex-5-en-1-yl)isoindoline-1,3-dione **(4n)**



The title compound was isolated as a yellow oil (55.1 mg, 69% yield, 91: 9 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.71–3.63 (m, 2H), 2.89 (s, 6H), 2.41–2.34 (m, 1H), 2.27–2.19 (m,

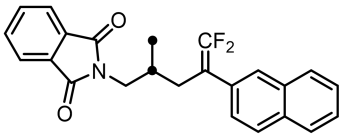
1H), 1.79–1.72 (m, 1H), 1.51–1.39 (m, 2H), 0.96 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 153.8 (t, *J* = 286.9 Hz), 149.4, 133.7, 132.1, 128.9 (t, *J* = 3.1 Hz), 123.0, 120.8, 112.1, 90.5 (dd, *J* = 17.9, 17.0 Hz), 40.3, 36.0, 34.7, 34.6, 28.7 (t, *J* = 2.3 Hz), 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.01 (s, 2F). HRMS (ESI) m/z calculated for $C_{23}H_{24}F_2N_2O_2^+$ $[M+H]^+$: 399.1879, found: 399.1876.

***3-(6-(1,3-dioxoisoindolin-2-yl)-1,1-difluoro-4-methylhex-1-en-2-yl)benzaldehyde* (4o)**



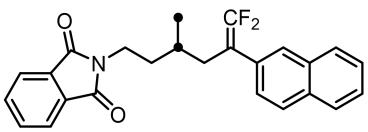
The title compound was isolated as a yellow oil (65.3 mg, 85% yield, 92: 8 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.80–7.76 (m, 3H), 7.72–7.68 (m, 2H), 7.68–7.64 (m, 1H), 7.54–7.51 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 3.70–3.59 (m, 2H), 2.54–2.48 (m, 1H), 2.38–2.30 (m, 1H), 1.78–1.72 (m, 1H), 1.53–1.38 (m, 2H), 0.98 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 168.2, 154.2 (dd, *J* = 291.2, 287.7 Hz), 136.5, 134.4 (dd, *J* = 4.6, 2.9 Hz), 134.2 (t, *J* = 3.0 Hz), 133.8, 131.9, 129.9 (t, *J* = 3.1 Hz), 129.1, 128.0, 123.1, 90.3 (dd, *J* = 22.5, 13.2 Hz), 35.7, 34.6, 34.3, 28.5 (t, *J* = 2.2 Hz), 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.72 (d, *J* = 40.3 Hz, 1F), -90.15 (d, *J* = 40.4 Hz, 1F). HRMS (ESI) m/z calculated for $C_{22}H_{20}F_2NO_3^+$ $[M+H]^+$: 384.1406, found: 384.1410.

***2-(5,5-difluoro-2-methyl-4-(naphthalen-2-yl)pent-4-en-1-yl)isoindoline-1,3-dione* (4p)**



The title compound was isolated as a white solid (67.4 mg, 86% yield, 93: 7 rr) after chromatography on silica with ethyl acetate/hexane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 6H), 7.51 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.33–7.27 (m, 3H), 3.53 (dd, *J* = 13.5, 6.4 Hz, 1H), 3.40 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.51–2.44 (m, 1H), 2.33–2.25 (m, 1H), 2.01–1.91 (m, 1H), 0.80 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 154.3 (dd, *J* = 290.9, 287.4 Hz), 133.9, 133.2, 132.5, 131.9, 130.7 (dd, *J* = 4.0, 3.2 Hz), 128.2, 127.9, 127.6, 127.4 (t, *J* = 3.2 Hz), 126.2, 126.1, 126.0 (t, *J* = 3.0 Hz), 123.1, 90.9 (dd, *J* = 21.6, 13.8 Hz), 43.7, 32.9, 31.5 (t, *J* = 2.3 Hz), 17.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.96 (d, *J* = 41.4 Hz, 1F), -90.40 (d, *J* = 41.5 Hz, 1F). HRMS (ESI) m/z calculated for $C_{24}H_{19}F_2NO_2$ $[M+H]^+$: 392.1457, found: 392.1460.

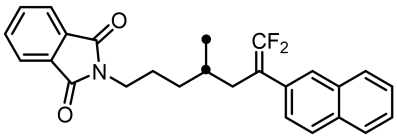
***2-(6,6-difluoro-3-methyl-5-(naphthalen-2-yl)hex-5-en-1-yl)isoindoline-1,3-dione* (4q)**



The title compound was isolated as a yellow oil (71.5 mg, 88%

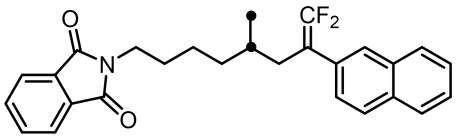
yield, 92: 8 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.75 (m, 1H), 7.72–7.66 (m, 5H), 7.59 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.45–7.40 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 3.69–3.59 (m, 2H), 2.57–2.51 (m, 1H), 2.42–2.31 (m, 1H), 1.84–1.75 (m, 1H), 1.52–1.43 (m, 2H), 0.99 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 154.2 (dd, *J* = 290.3, 286.9 Hz), 133.7, 133.1, 132.3, 131.9, 130.7 (dd, *J* = 3.9, 2.6 Hz), 127.9, 127.5, 127.4, 127.4, 126.1, 126.1–126.0 (m), 126.0, 123.0, 91.2 (dd, *J* = 21.4, 13.8 Hz), 35.8, 34.6, 28.6 (t, *J* = 2.1 Hz), 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.76 (d, *J* = 42.5 Hz, 1F), -91.00 (d, *J* = 42.7 Hz, 1F). HRMS (ESI) m/z calculated for $C_{25}H_{21}F_2NO_2$ $[M+H]^+$: 406.1613, found: 406.1617.

2-(7,7-difluoro-4-methyl-6-(naphthalen-2-yl)hept-6-en-1-yl)isoindoline-1,3-dione **(4r)**



The title compound was isolated as a yellow oil (69.7 mg, 83% yield, 83: 17 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 5H), 7.66 (s, 1H), 7.60 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.40–7.36 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 3.52 (t, *J* = 7.3 Hz, 2H), 2.46–2.39 (m, 1H), 2.28–2.14 (m, 1H), 1.65–1.58 (m, 1H), 1.53–1.46 (m, 1H), 1.44–1.37 (m, 1H), 1.33–1.27 (m, 1H), 1.17–1.08 (m, 1H), 0.78 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 153.1 (dd, *J* = 290.5, 286.6 Hz), 132.8, 132.2, 131.3, 131.0, 130.1 (dd, *J* = 4.4, 3.1 Hz), 127.0, 126.9, 126.5, 126.3 (t, *J* = 3.2 Hz), 125.1, 125.0, 125.0, 122.1, 90.4 (dd, *J* = 21.9, 12.9 Hz), 37.0, 33.7, 32.5, 29.8 (t, *J* = 2.2 Hz), 24.9, 17.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.80 (d, *J* = 42.9 Hz, 1F), -91.33 (d, *J* = 42.9 Hz, 1F). HRMS (ESI) m/z calculated for $C_{26}H_{23}F_2NO_2^+$ $[M+H]^+$: 420.1770, found: 420.1774.

2-(8,8-difluoro-5-methyl-7-(naphthalen-2-yl)oct-7-en-1-yl)isoindoline-1,3-dione **(4s)**



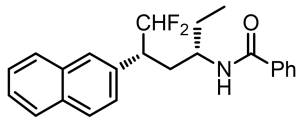
The title compound was isolated as a yellow oil (38.2 mg, 44% yield, 90: 10 rr) after chromatography on silica with ethyl acetate/hexane (1:10). This product was isolated as a 1:1 mixture of diastereomers. The reported dr was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 5H), 7.67 (s, 1H), 7.63–7.60 (m, 2H), 7.40–7.32 (m, 3H), 3.55 (t, *J* = 7.3 Hz, 2H), 2.42–2.36 (m, 1H), 2.27–2.17 (m, 1H), 1.54–1.47 (m, 2H), 1.34–1.14 (m, 5H), 0.77 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 153.1 (dd, *J* = 290.4, 286.5

Hz), 132.7, 132.2, 131.3, 131.0, 130.2 (dd, J = 4.4, 3.0 Hz), 126.9, 126.8, 126.5, 126.3 (t, J = 3.2 Hz), 125.1, 125.1, 124.9, 122.1, 90.5 (dd, J = 21.9, 12.9 Hz), 36.8, 34.9, 33.9, 29.9, 27.7, 23.1, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.97 (d, J = 43.2 Hz, 1F), -91.46 (d, J = 43.2 Hz, 1F). HRMS (ESI) m/z calculated for $C_{27}H_{26}F_2NO_2^+$ $[M+H]^+$: 434.1926, found: 434.1926.

7. Synthetic transformations

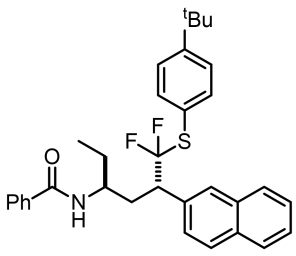
N-(6,6-difluoro-5-(naphthalen-2-yl)hexan-3-yl)benzamide **(5a)**

The synthesis of **5a** was conducted according to a reported procedure.[16] The title compound was



isolated as a colourless oil (61.9 mg, 84% yield) after chromatography on silica with ethyl acetate/hexane (1:8). To a schlenk tube equipped with a magnetic stir bar were added **3a** (73 mg, 0.2 mmol), MeOH (2 mL) and 10% Pd/C (5.6 mg), then replacement of hydrogen (balloon). The resulting solution was stirred at 25 ºC for 12 h. After the solution of the crude product was concentrated in vacuum, brine (10 mL) was added and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried by anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The solvent was removed under reduced pressure to give the crude. After that, the title compound was purified by column chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.63 (m, 4H), 7.39–7.30 (m, 3H), 7.25 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.5 Hz, 2H), 7.06 (t, J = 7.6 Hz, 2H), 5.89 (m, 1H), 5.50 (d, J = 8.8 Hz, 1H), 4.17–4.08 (m, 1H), 3.33–3.21 (m, 1H), 2.30–2.20 (m, 1H), 2.11–2.01 (m, 1H), 1.71–1.59 (m, 1H), 1.50–1.41 (m, 1H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 133.4 (dd, J = 4.9, 2.9 Hz), 133.1, 132.4, 131.7, 130.1, 127.6, 127.1, 126.9, 126.7, 126.5, 125.4, 125.2, 125.2, 125.0, 116.5 (t, J = 245.2 Hz), 49.2, 46.8 (t, J = 19.8 Hz), 32.2 (dd, J = 4.3, 3.0 Hz), 27.1, 9.0； ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.12 (ddd, J = 276.4, 56.6, 15.2 Hz, 1F), -122.94 (ddd, J = 276.4, 56.6, 17.0 Hz, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{24}F_2NO^+$ $[M+H]^+$: 368.1820, found: 368.1823.

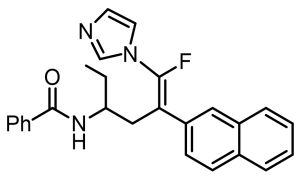
N-(6-((4-(tert-butyl)phenyl)thio)-6,6-difluoro-5-(naphthalen-2-yl)hexan-3-yl)benzamide **(5b)**



The synthesis of **5b** was conducted according to a reported procedure.[17] The title compound was isolated as a colourless oil (91.5 mg, 86% yield) after chromatography on silica with ethyl acetate/hexane (1:8). To a 10 mL schlenk tube was charged with *gem*-difluoroalkene **3a** (0.2 mmol,

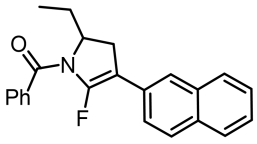
1.0 equiv), 4-*tert*-butylthiophenol (0.24 mmol, 1.2 equiv.), and dry DCE (40 μL). The reaction mixture was placed in a preheated metal block and stirred at 80 ºC for 2 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.74 (m, 4H), 7.45–7.39 (m, 5H), 7.36–7.30 (m, 3H), 7.25–7.18 (m, 4H), 5.64 (d, *J* = 9.3 Hz, 1H), 3.96–3.83 (m, 1H), 3.67–3.48 (m, 1H), 2.40–2.16 (m, 2H), 1.51–1.44 (m, 2H), 1.20 (s, 9H), 0.78 (t, *J* = 7.4 Hz, 3H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 153.0, 136.5 (d, *J* = 6.0 Hz), 136.0, 134.6, 134.0 (d, *J* = 4.4 Hz), 133.3, 133.1, 131.3, 129.3, 128.6, 128.4, 128.1, 127.7, 126.8, 126.7, 126.3 (d, *J* = 2.6 Hz), 126.0, 123.1, 51.3 (t, *J* = 22.3 Hz), 48.9, 35.1, 34.7, 31.2, 28.4, 10.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.06 (dd, *J* = 202.7, 11.1 Hz, 1F), -77.53 (dd, *J* = 202.7, 17.3 Hz, 1F). HRMS (ESI) m/z calculated for $C_{33}H_{36}F_2NOS^+$ $[M+H]^+$: 532.2480, found: 532.2485.

(E)-N-(6-fluoro-6-(1H-imidazol-1-yl)-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide **(5c)**



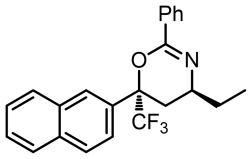
The synthesis of **5c** was conducted according to a reported procedure.[18] The title compound was isolated as a colourless oil (87% yield) after chromatography on silica with ethyl acetate/hexane (1:8). A solution of imidazole (0.25 mmol, 1.0 equiv.) in DMF (0.5 mL) was added dropwise to a mixture of *gem*-difluoroalkene **3a** (0.3 mmol, 1.2 equiv.) and K_3PO_4 (0.5 mmol, 2 equiv.) in DMF (0.5 mL) via syring and then stirred at room temperature for 12 h (monitored by TLC). After completion of the reaction, the mixture was quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried by anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The solvent was removed under reduced pressure to give the crude. After that, the title compound was purified by column chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.64 (m, 4H), 7.48–7.36 (m, 5H), 7.28–7.20 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 6.79 (s, 1H), 5.80 (d, *J* = 9.1 Hz, 1H), 4.35–4.24 (m, 1H), 3.03–2.92 (m, 2H), 1.77–1.68 (m, 1H), 1.64–1.54 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 145.2, 142.6, 137.2, 134.3, 133.2, 132.7, 132.6, 131.3, 129.6, 129.0, 128.4, 128.0, 127.6, 127.3 (d, *J* = 3.5 Hz), 126.6 (d, *J* = 3.3 Hz), 126.5, 125.5 (d, *J* = 2.7 Hz), 118.7 (d, *J* = 1.8 Hz), 112.3 (d, *J* = 24.0 Hz), 50.2 (d, *J* = 2.6 Hz), 36.0, 28.2, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.75 (s, 1F). HRMS (ESI) m/z calculated for $C_{26}H_{25}FN_3O^+$ $[M+H]^+$: 414.1976, found: 414.1980.

***(S)-(2-ethyl-5-fluoro-4-(naphthalen-2-yl)-2,3-dihydro-1H-pyrrol-1-yl)(phenyl)methanone* (5d)**



The synthesis of **5d** was conducted according to a reported procedure.[19] The title compound was isolated as a white solid (93% yield) after chromatography on silica with ethyl acetate/hexane (1:8). To a solution of *gem*-difluoroalkene **3a** (0.2 mmol, 1.0 equiv.) in dry DMF (2 mL), NaH (12 mg, 0.3 mmol, 60% dispersion in mineral oil) was added at 0 °C. Then the reaction mixture was stirred for 5 hours at room temperature. The reaction was quenched with water and extracted with EtOAc (10 mL x 3), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 8.0 Hz, 3H), 7.65 (s, 1H), 7.61–7.55 (m, 3H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 6.1 Hz, 4H), 4.76–4.65 (m, 1H), 3.32–3.19 (m, 1H), 2.76–2.65 (m, 1H), 2.12–2.02 (m, 1H), 1.96–1.86 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, *J* = 3.0 Hz), 147.1, 144.3, 135.2 (d, *J* = 3.4 Hz), 132.4, 130.8 (d, *J* = 1.3 Hz), 129.6, 129.0 (d, *J* = 6.4 Hz), 127.0, 126.9, 126.7, 126.6–126.5 (m), 125.3, 124.7, 122.9, 122.8 (d, *J* = 2.5 Hz), 93.9 (d, *J* = 6.0 Hz), 56.5, 29.0 (d, *J* = 4.6 Hz), 25.4, 7.3, -0.4–-5.7 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.52 (s, 1F). HRMS (ESI) m/z calculated for $C_{23}H_{21}FNO^+$ $[M+H]^+$: 346.1602, found: 346.1606.

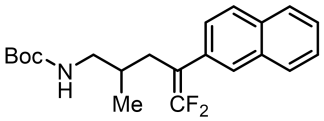
***((5S)-5-ethyl-2-(naphthalen-2-yl)-2-(trifluoromethyl)pyrrolidin-1-yl)(phenyl)methanone* (5e)**



The synthesis of **5e** was conducted according to a reported procedure.[20] The title compound was isolated as a colourless oil (80% yield) after chromatography on silica with ethyl acetate/hexane (1:8). Selectfluor (0.3 mmol, 1.5 equiv.), and *gem*-difluoroalkene **3a** (0.2 mmol, 1 equiv.) were added in turn to an oven-dried 10 mL schlenk tube equipped with a stir bar under a nitrogen atmosphere. The reactants were dissolved in dry CH_3CN (0.8 mL), followed by the addition of dry MeOH (1 mmol, 5 equiv.). The reaction mixture was stirred at 40 ºC for 12 h. The reaction mixture was diluted with ethyl acetate (20.0 mL) and transferred to a flask. The solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 8.02 (s, 1H), 7.86–7.75 (m, 3H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.45–7.37 (m, 5H), 3.64–3.57 (m, 1H), 2.83 (dd, *J* = 14.5, 5.0 Hz, 1H), 1.85–1.77 (m, 1H), 1.56–1.42 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 133.9, 132.3, 132.2, 131.7, 129.7, 127.4, 127.3, 127.2, 126.5, 126.3, 125.8, 125.5, 124.0, 121.6 (d, *J* = 0.9 Hz), 109.2

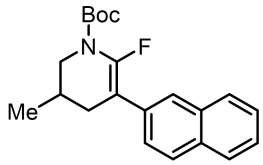
(dd, J = 26.5, 19.7 Hz), 77.0 (q, J = 29.3 Hz), 49.3, 31.3, 29.1, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.33 (s, 3F). HRMS (ESI) m/z calculated for $C_{24}H_{23}F_3NO^+$ $[M+H]^+$: 398.1726, found: 398.1730.

tert-butyl (5,5-difluoro-2-methyl-4-(naphthalen-2-yl)pent-4-en-1-yl)carbamate **(5f)**



To the solution of **5f** in ethanol (10 mL) was added hydrazine monohydrate (5.5 mmol) at 50 ºC. The mixture was stirred for 6 h and quenched with 6 M HCl (2 mL). The precipitates formed were removed by filtration, and the resultant filtrate was dried over Na_2SO_4 and concentrated in vacuo to give an unsaturated amine hydrochloride. Aqueous NaOH (6.0 M, 1 mL) was added to the amine salt, and the resulting solution was extracted with CH_2Cl_2 (25 mL × 3). The combined organic extracts were then washed again with brine (5 mL), dried over Na_2SO_4, and filtered. The amine solution was used without further purification. To a stirring solution of di-*tert*-butyldicarbonate (1.2 equiv) in CH_2Cl_2 (3 mL) was added the amine and triethylamine in CH_2Cl_2 (5 mL) and the reaction was stirred overnight. Water was added and the mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Hexane/EtOAc) to give the desired product. The title compound was isolated as a colourless oil (80% yield) after chromatography on silica with ethyl acetate/hexane (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.79 (m, 3H), 7.76 (s, 1H), 7.50–7.45 (m, 2H), 7.42 (d, J = 8.5 Hz, 1H), 4.50 (s, 1H), 3.14–3.03 (m, 1H), 3.03–2.92 (m, 1H), 2.58–2.51 (m, 1H), 2.38–2.27 (m, 1H), 1.68–1.57 (m, 1H), 1.41 (s, 9H), 0.89 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2–155.9 (m), 154.2 (dd, J = 290.7, 287.0 Hz), 133.2, 132.5, 131.1–130.7 (m), 128.1, 127.9, 127.6, 127.4 (t, J = 3.1 Hz), 126.3, 126.2, 126.0 (t, J = 2.5 Hz), 91.0 (dd, J = 21.6, 13.7 Hz), 79.1, 45.9, 32.3, 32.3, 28.4, 17.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.46 (d, J = 42.3 Hz, 1F), -90.78 (d, J = 42.3 Hz, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{26}F_2NO_2^+$ $[M+H]^+$: 362.1926, found: 362.1930.

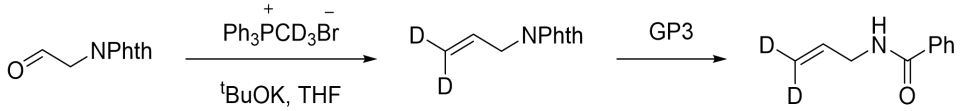
tert-butyl (R)-6-fluoro-3-methyl-5-(naphthalen-2-yl)-3,4-dihydropyridine-1(2H)-carboxylate **(5g)**



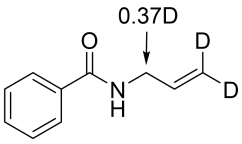
The synthesis of **5g** was conducted according to a reported procedure. [19] The title compound was isolated as a white solid (90% yield) after chromatography on silica with ethyl acetate/hexane (1:8). To a solution of

gem-difluoroalkene **5f** (0.2 mmol, 1 equiv.) in dry DMF (2 mL), NaH (12 mg, 0.3 mmol, 60% dispersion in mineral oil) was added at 0 °C. Then the reaction mixture was stirred for 5 hours at room temperature. The reaction was quenched with water and extracted with EtOAc (10 mL x 3), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.67 (m, 4H), 7.57–7.52 (m, 1H), 7.41–7.32 (m, 2H), 3.96–3.87 (m, 1H), 3.07–2.98 (m, 1H), 2.70–2.61 (m, 1H), 2.18–2.07 (m, 1H), 2.05–1.96 (m, 1H), 1.45 (s, 9H), 1.02 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2 (d, J = 6.1 Hz), 146.6, 144.0, 132.9 (d, J = 3.5 Hz), 132.2, 131.1, 126.9, 126.4 (d, J = 3.2 Hz), 125.2 (d, J = 6.6 Hz), 125.1 (d, J = 4.2 Hz), 124.9, 124.7, 99.8 (d, J = 14.3 Hz), 80.9, 50.1, 33.7 (d, J = 2.0 Hz), 28.4 (d, J = 1.4 Hz), 27.1, 17.2 (d, J = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.84 (s, 1F). HRMS (ESI) m/z calculated for $C_{21}H_{25}FNO_2^+$ $[M+H]^+$: 342.1864, found: 342.1868.

8. Isotopic labelling experiment



N-(allyl-3,3-d2)benzamide **(1a-D)**



Procedure for synthesis **1a-D** was according the report literature.[21] The title compound was isolated as a yellow oil after chromatography on silica with ethyl acetate/petroleum ether (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H), 7.56–7.48 (m, 1H), 7.47–7.41 (m, 2H), 6.19 (s, 0.93H), 5.99–5.91 (m, 1H), 5.48–5.05 (m, 0.59H), 4.10 (t, J = 5.7 Hz, 1.63H).

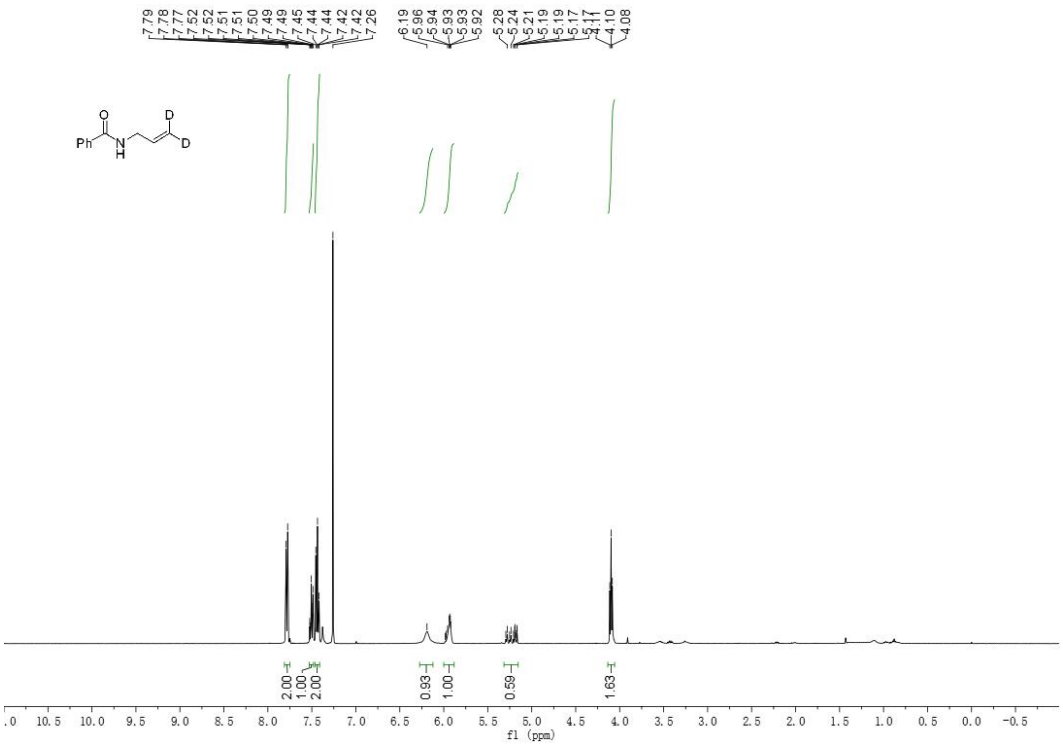
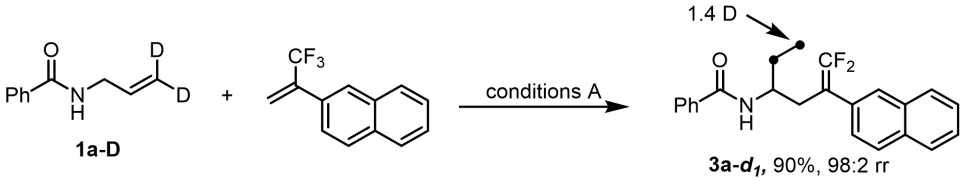
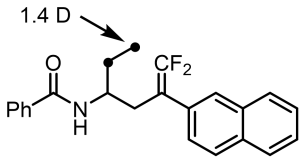


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1a-D**



In an argon-filled glovebox, $NiBr_2$•DME (0.03 mmol, 15 mol%), bathocuproine (0.03 mmol, 15 mol%), NaF (0.5 mmol, 2.5 equiv), alkene substrate (0.2 mmol, 1.0 equiv), appropriate trifluoromethyl alkenes (0.6 mmol, 3.0 equiv), $(MeO)_3SiH$ (0.4 mmol, 2.0 equiv), DME (1 mL) were added to a 10 mL schlenk flask. The reaction mixture was stirred at 70 °C for 18 h. After the reaction time, the vessel was allowed to silica gel column chromatography. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent.

***N-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide* (3a-*d*$_1$)**



The title compound was isolated as a yellow oil (90% yield, 98:2 rr) after chromatography on silica with ethyl acetate/petroleum ether (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.75–7.68 (m, 3H), 7.40 (t, J = 8.4 Hz, 3H), 7.27 (t, J = 7.3 Hz, 1H), 7.19 (d, J = 6.8 Hz, 2H), 7.07 (t, J = 7.6 Hz, 2H), 5.56

(d, *J* = 8.1 Hz, 1H), 4.16–4.10 (m, 0.63H), 2.75 (d, *J* = 5.2 Hz, 2H), 1.65–1.57 (m, 1H), 1.51–1.42 (m, 1H), 0.90–0.82 (m, 1.6H).

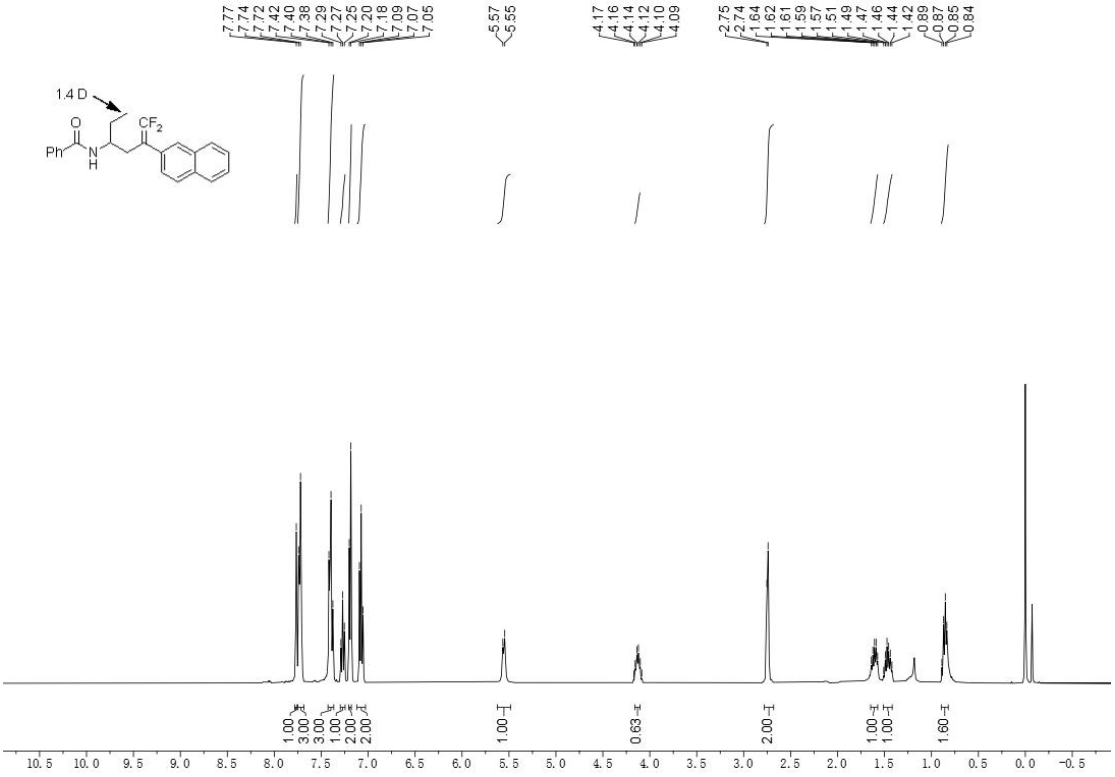
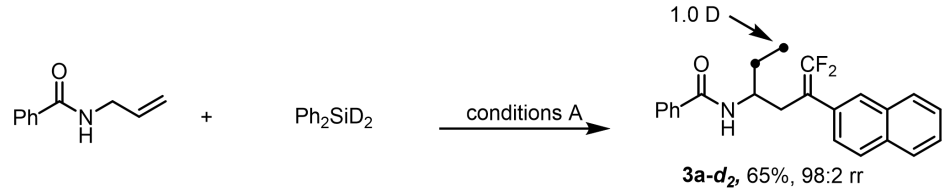
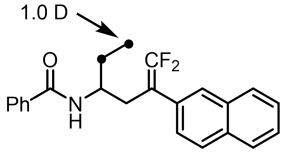


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3a-*d*$_1$**



3a-*d*$_2$, 65%, 98:2 rr

***N*-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide (3a-*d*$_2$)**



The title compound was isolated as a yellow oil (65% yield, 98:2 rr) after chromatography on silica with ethyl acetate/petroleum ether (1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.75–7.71 (m, 3H), 7.43–7.38 (m, 3H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.20–7.18 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 5.54 (d, *J* = 8.8 Hz, 1H), 4.18–4.10 (m, 1H), 2.75 (d, *J* = 5.7 Hz, 2H), 1.67–1.60 (m, 1H), 1.50–1.43 (m, 1H), 0.90–0.84 (m, 2H).

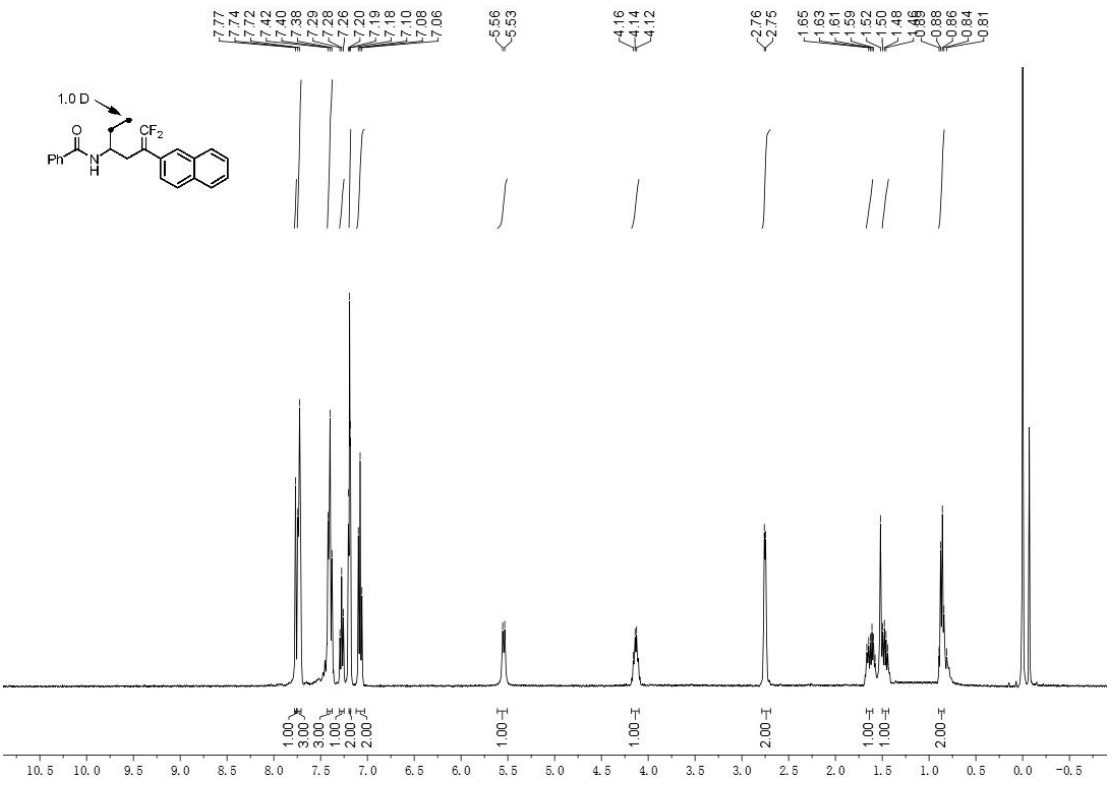
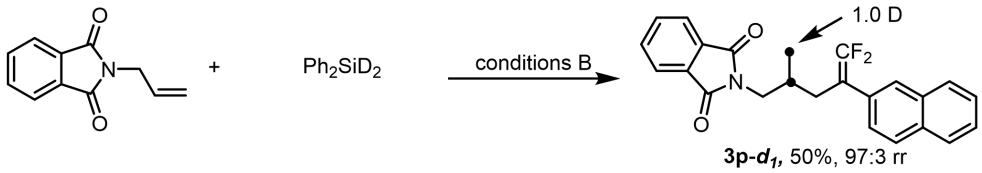
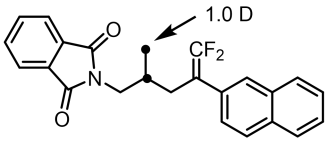


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3a-*d*$_2$**



***N*-(6,6-difluoro-5-(naphthalen-2-yl)hex-5-en-3-yl)benzamide (4p-*d*$_1$)**



The title compound was isolated as a yellow oil (50% yield, 97:3 rr) after chromatography on silica with ethyl acetate/petroleum ether (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.69 (m, 4H), 7.69–7.58 (m, 4H), 7.42–7.36 (m, 2H), 7.33 (d, *J* = 8.6 Hz, 1H), 3.58 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.46 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.56–2.49 (m, 1H), 2.37–2.30 (m, 1H), 2.04–1.95 (m, 1H), 0.84 (d, *J* = 7.0 Hz, 2H).

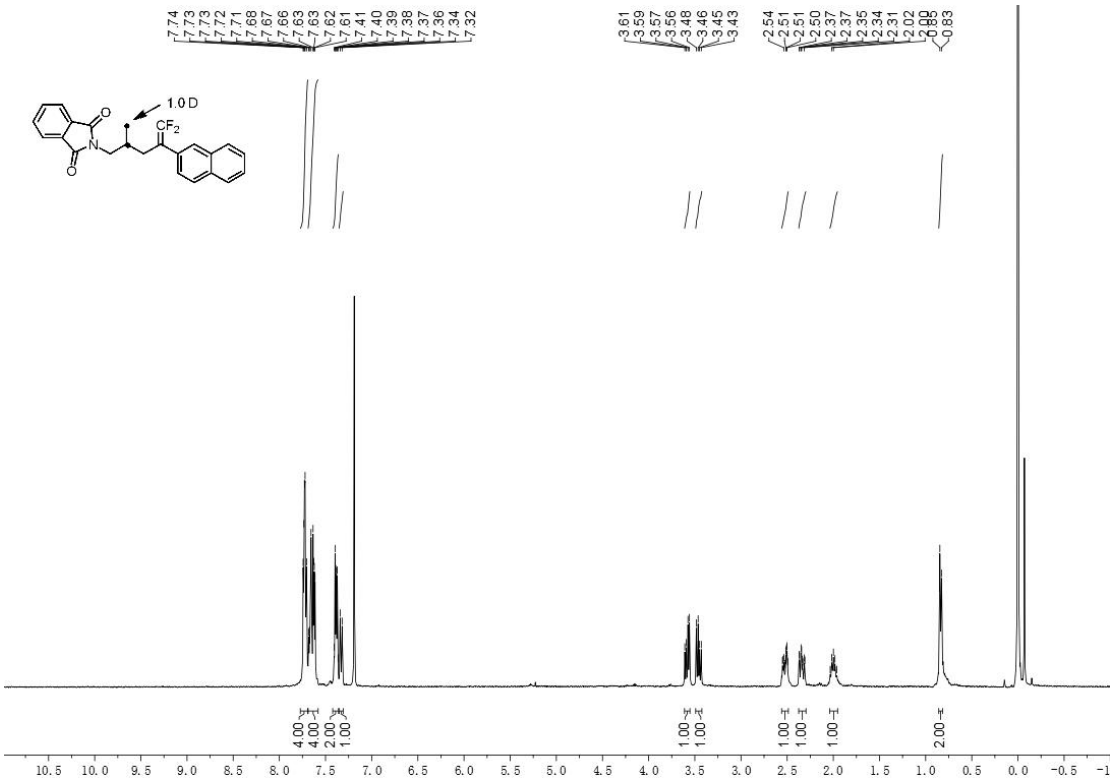


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4p-*d*$_1$**

9. X-ray crystallographic data

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **5a** in a mixture of petroleum ether and ethyl acetate at room temperature. X-Ray structural analysis of single crystal **5a** was obtained to confirm the absolute configuration. The X-ray data of **5a** is deposited in the Cambridge Crystallographic Data Centre with a number of **CCDC 2265601**.

Crystal Data for $C_{23}H_{23}F_2NO$ (M =367.42 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 20.5335(14) Å, b = 9.8096(6) Å, c = 9.9263(6) Å, β = 90.145(6)°, V = 1999.4(2) Å^3, Z = 4, T = 293(2) K, μ(CuKα) = 0.711 mm^{-1}, *Dcalc* = 1.221 g/cm^3, 15300 reflections measured (4.304° ≤ 2Θ ≤ 134.128°), 3559 unique (R_{int} = 0.0391, R_{sigma} = 0.0281) which were used in all calculations. The final R_1 was 0.1165 (I > 2σ(I)) and wR_2 was 0.3255 (all data).

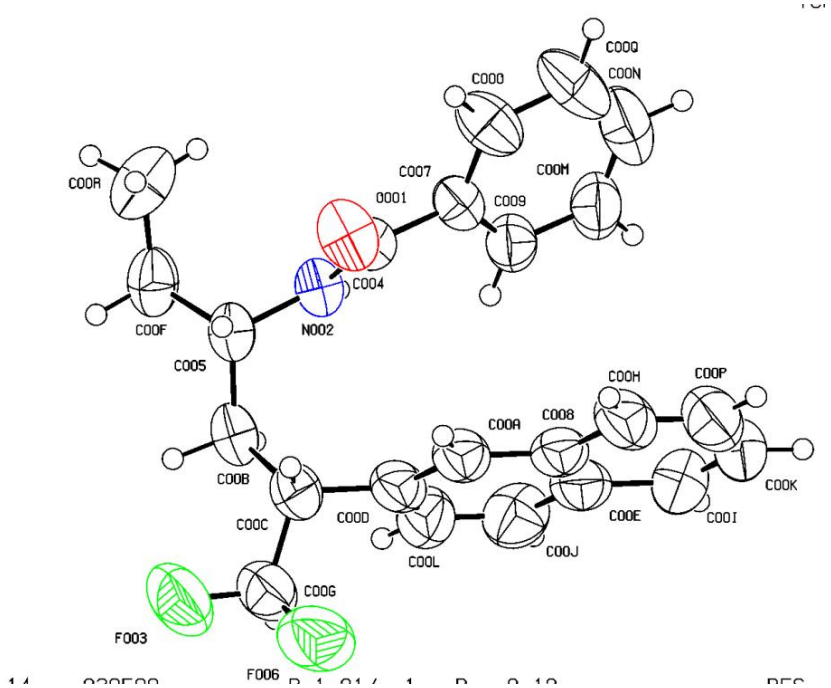


Figure S5. X-ray structure of compound **5a** (CCDC **2265601**)

Table S5. Crystal data and structure refinement for 5a.

Identification code	**5a**
Empirical formula	$C_{23}H_{23}F_2NO$
Formula weight	367.42
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.5335(14)
b/Å	9.8096(6)
c/Å	9.9263(6)
α/°	90
β/°	90.145(6)
γ/°	90
Volume/Å^3	1999.4(2)
Z	4
ρ_{calc}g/cm^3	1.221
μ/mm^{-1}	0.711
F(000)	776.0
Crystal size/mm^3	0.28 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.304 to 134.128
Index ranges	$-24 \le h \le 24$, $-11 \le k \le 11$, $-8 \le l \le 11$
Reflections collected	15300

Independent reflections	3559 [R_{int} = 0.0391, R_{sigma} = 0.0281]
Data/restraints/parameters	3559/0/246
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.1165, wR_2 = 0.3155
Final R indexes [all data]	R_1 = 0.1325, wR_2 = 0.3255
Largest diff. peak/hole / e $Å^{-3}$	0.45/-0.24

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **5b** in a mixture of petroleum ether and ethyl acetate at room temperature. X-Ray structural analysis of single crystal **5b** was obtained to confirm the absolute configuration. The X-ray data of **5b** is deposited in the Cambridge Crystallographic Data Centre with a number of **CCDC 2265605**.

Crystal Data for $C_{33}H_{35}F_2NOS$ (M =531.68 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), a = 10.0610(5) Å, b = 19.1206(9) Å, c = 14.7518(8) Å, V = 2837.8(2) $Å^3$, Z = 4, T = 193.00 K, μ(GaKα) = 0.865 mm^{-1}, *Dcalc* = 1.244 g/cm^3, 41287 reflections measured (6.584° ≤ 2Θ ≤ 121.15°), 6391 unique (R_{int} = 0.0868, R_{sigma} = 0.0597) which were used in all calculations. The final R_1 was 0.0460 (I > 2σ(I)) and wR_2 was 0.1118 (all data).

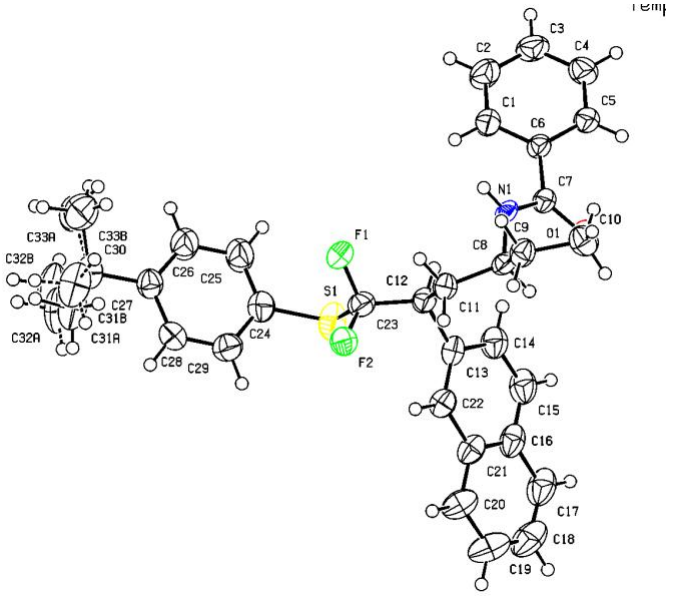


Figure S6. X-ray structure of compound **5b** (CCDC **2265605**)

Table S6 Crystal data and structure refinement for 5b.

Identification code	**5b**
Empirical formula	$C_{33}H_{35}F_2NOS$
Formula weight	531.68
Temperature/K	193.00

Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	10.0610(5)
b/Å	19.1206(9)
c/Å	14.7518(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2837.8(2)
Z	4
ρ_{calc}g/cm^3	1.244
μ/mm^{-1}	0.865
F(000)	1128.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.584 to 121.15
Index ranges	-12 ≤ h ≤ 12, -24 ≤ k ≤ 21, -18 ≤ l ≤ 18
Reflections collected	41287
Independent reflections	6391 [R_{int} = 0.0868, R_{sigma} = 0.0597]
Data/restraints/parameters	6391/112/384
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.0908
Final R indexes [all data]	R_1 = 0.0983, wR_2 = 0.1118
Largest diff. peak/hole / e Å^{-3}	0.17/-0.24
Flack parameter	0.45(4)

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **5e** in a mixture of petroleum ether and ethyl acetate at room temperature. X-Ray structural analysis of single crystal **5e** was obtained to confirm the absolute configuration. The X-ray data of **5e** is deposited in the Cambridge Crystallographic Data Centre with a number of **CCDC 2253478**.

Crystal Data for $C_{23}H_{20}F_3NO$ (*M* =383.40 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.6001(6) Å, *b* = 12.1058(5) Å, *c* = 14.3702(8) Å, *α* = 99.463(4)°, *β* = 103.907(4)°, *γ* = 103.592(4)°, *V* = 1851.06(16) Å^3, *Z* = 4, *T* = 120.01(10) K, μ(CuKα) = 0.876 mm^{-1}, *Dcalc* = 1.376 g/cm^3, 12544 reflections measured (6.518° ≤ 2Θ ≤ 134.126°), 6601 unique (R_{int} = 0.0271, R_{sigma} = 0.0354) which were used in all calculations. The final R_1 was 0.0465 (I > 2σ(I)) and wR_2 was 0.1278 (all data).

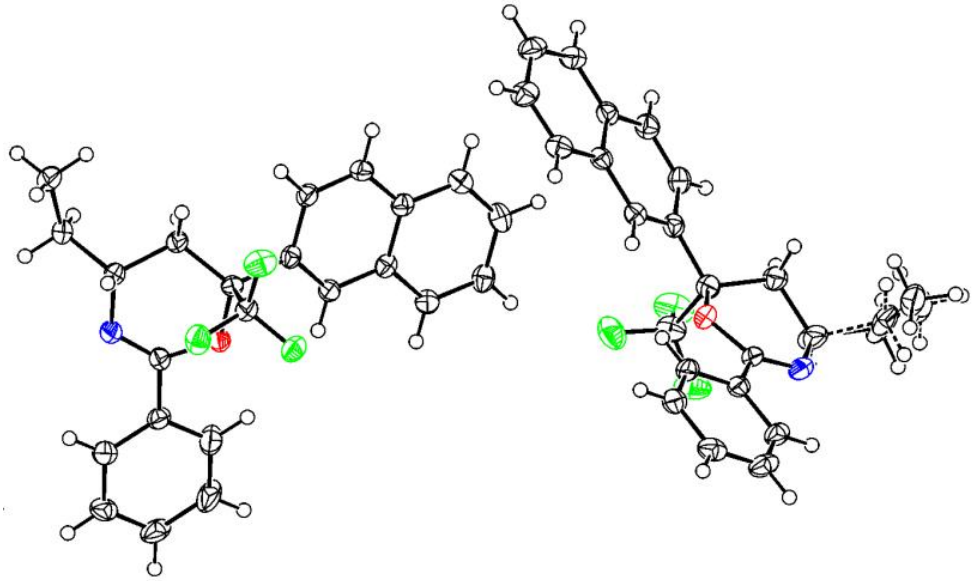


Figure S7. X-ray structure of compound **5e** (CCDC **2253478**)

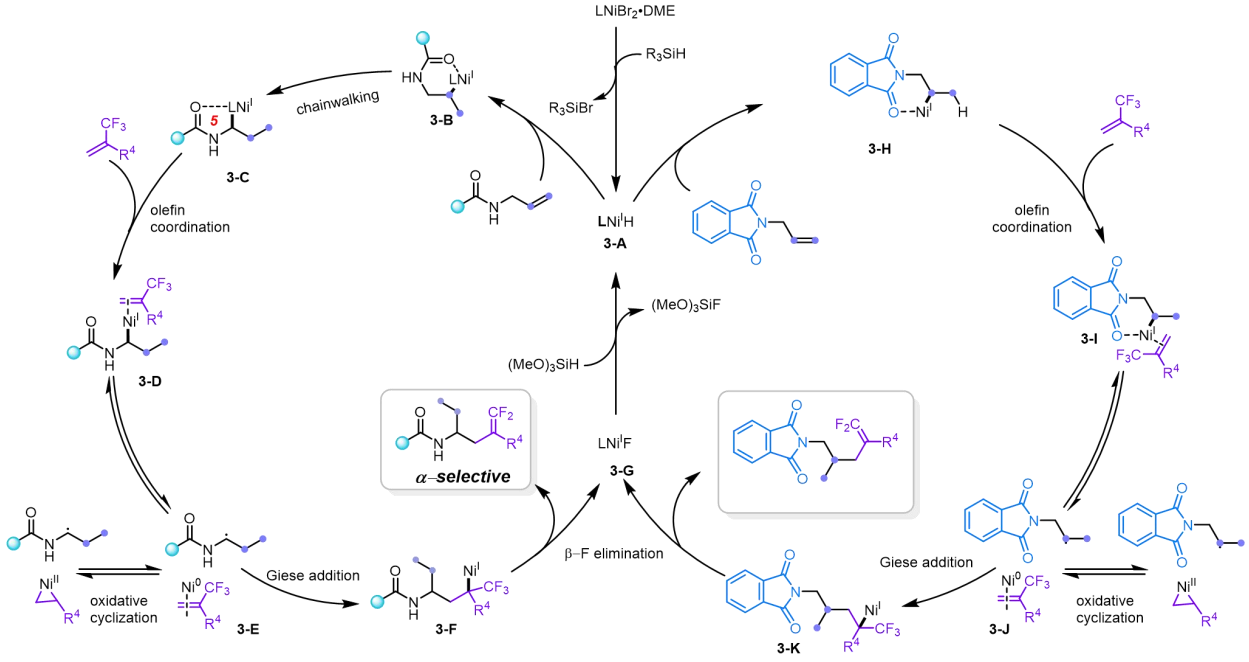
Table S7 Crystal data and structure refinement for 5e.

Identification code	**5e**
Empirical formula	$C_{23}H_{20}F_3NO$
Formula weight	383.40
Temperature/K	120.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.6001(6)
b/Å	12.1058(5)
c/Å	14.3702(8)
α/°	99.463(4)
β/°	103.907(4)
γ/°	103.592(4)
Volume/Å^3	1851.06(16)
Z	4
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	0.876
F(000)	800.0
Crystal size/mm^3	0.25 × 0.24 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.518 to 134.126
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 14, -15 ≤ l ≤ 17
Reflections collected	12544
Independent reflections	6601 [R_{int} = 0.0271, R_{sigma} = 0.0354]

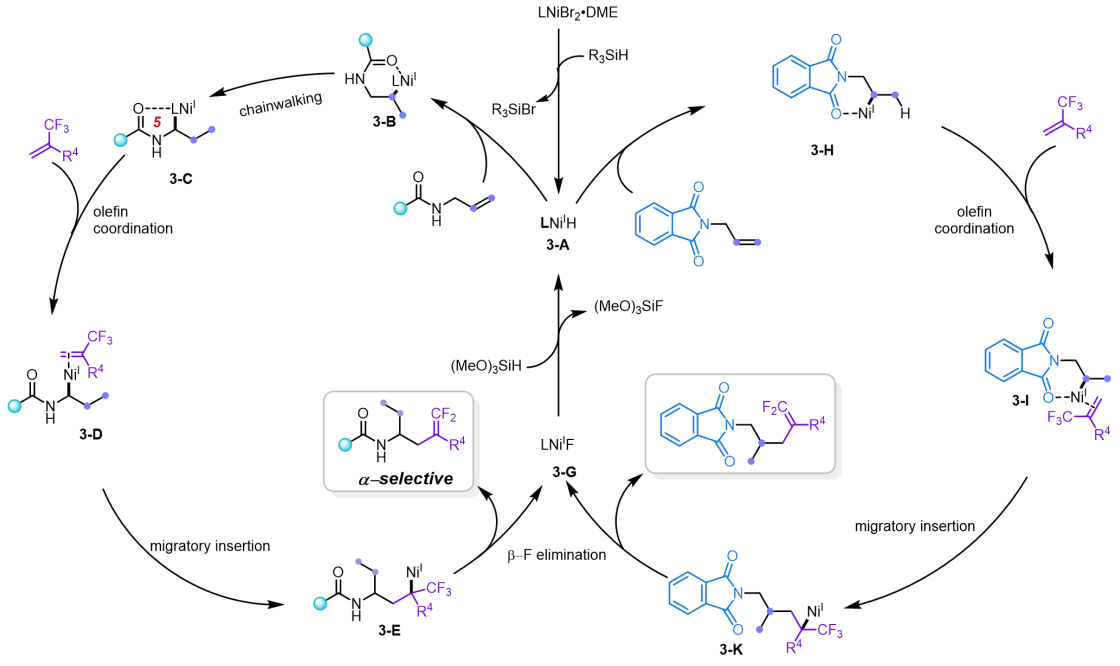
Data/restraints/parameters	6601/4/515
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	$R_1 = 0.0465$, $wR_2 = 0.1179$
Final R indexes [all data]	$R_1 = 0.0573$, $wR_2 = 0.1278$
Largest diff. peak/hole / e $Å^{-3}$	0.67/-0.36

10. Proposed catalytic cycle

Scheme S1. Radical pathway



Scheme S2. Migratory insertion pathway



11. Supplementary references

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12. NMR spectra

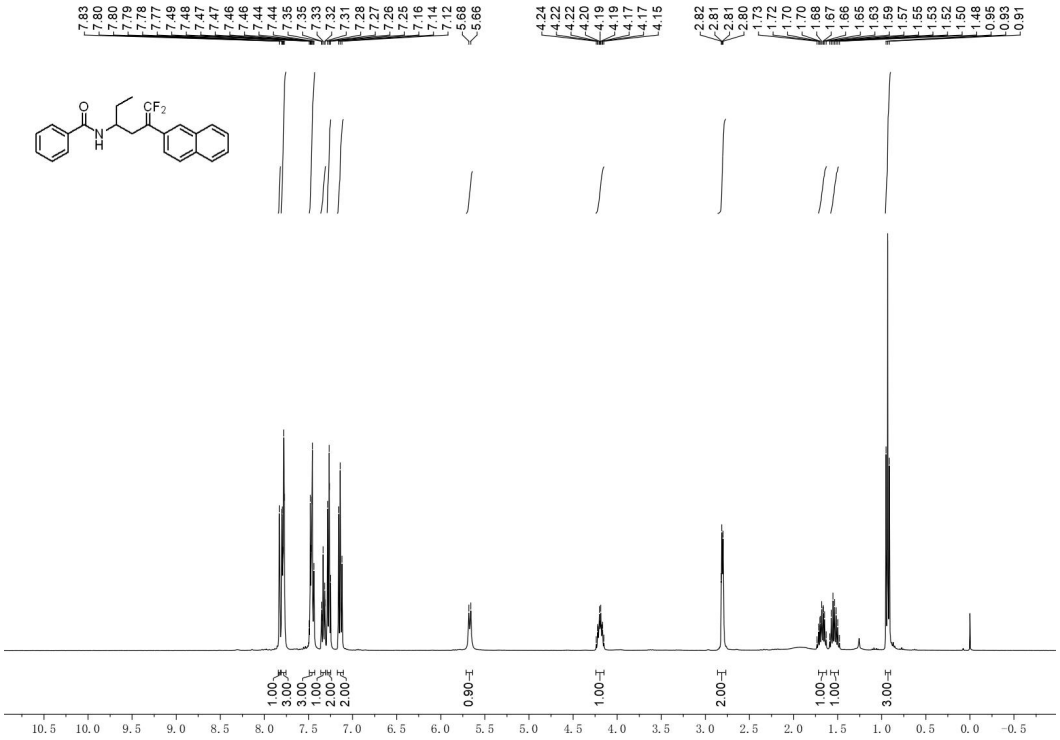

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3a**

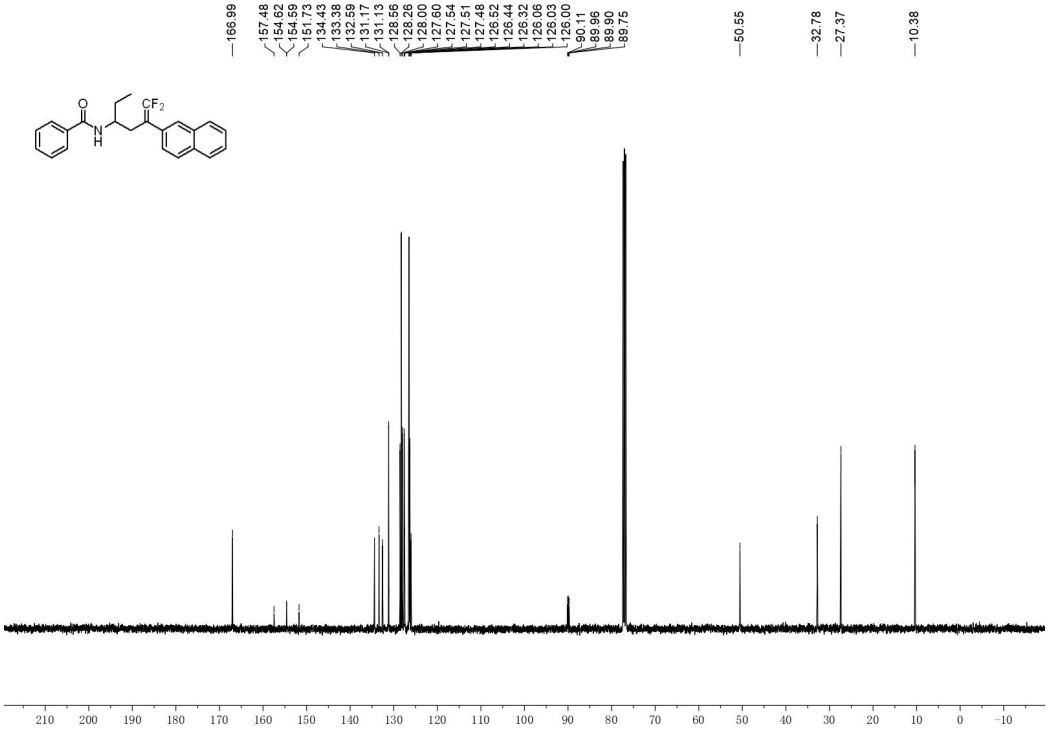

Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3a**

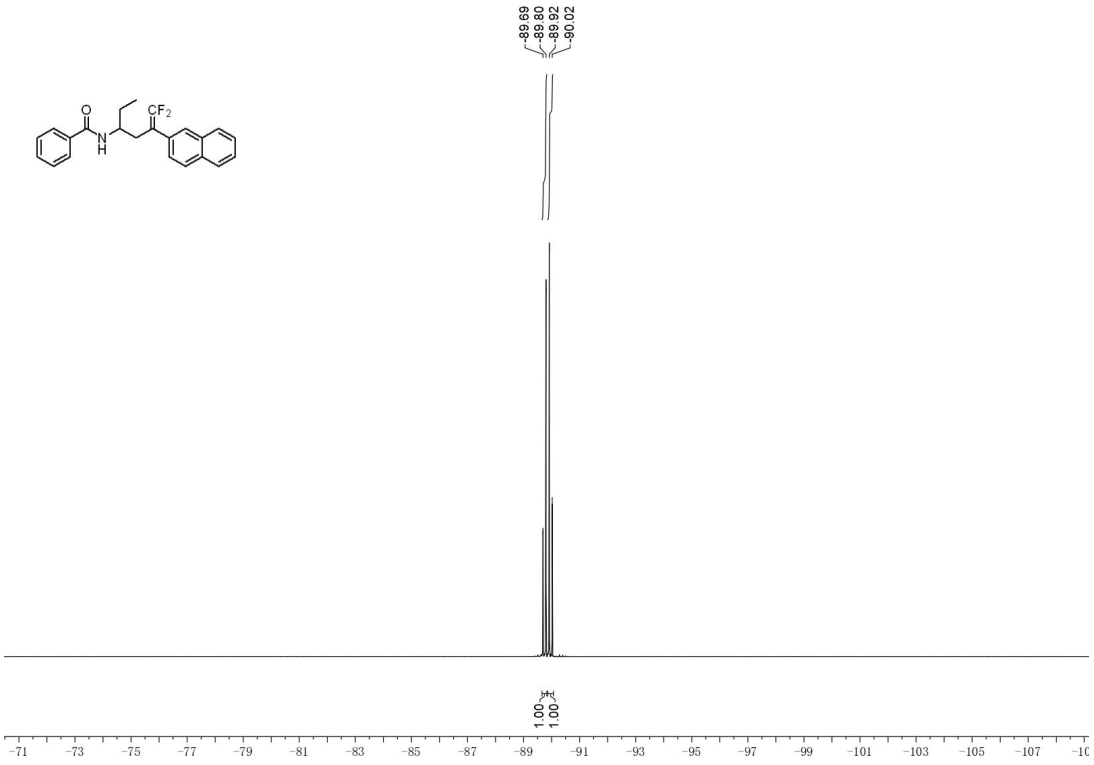

Figure S10. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3a**

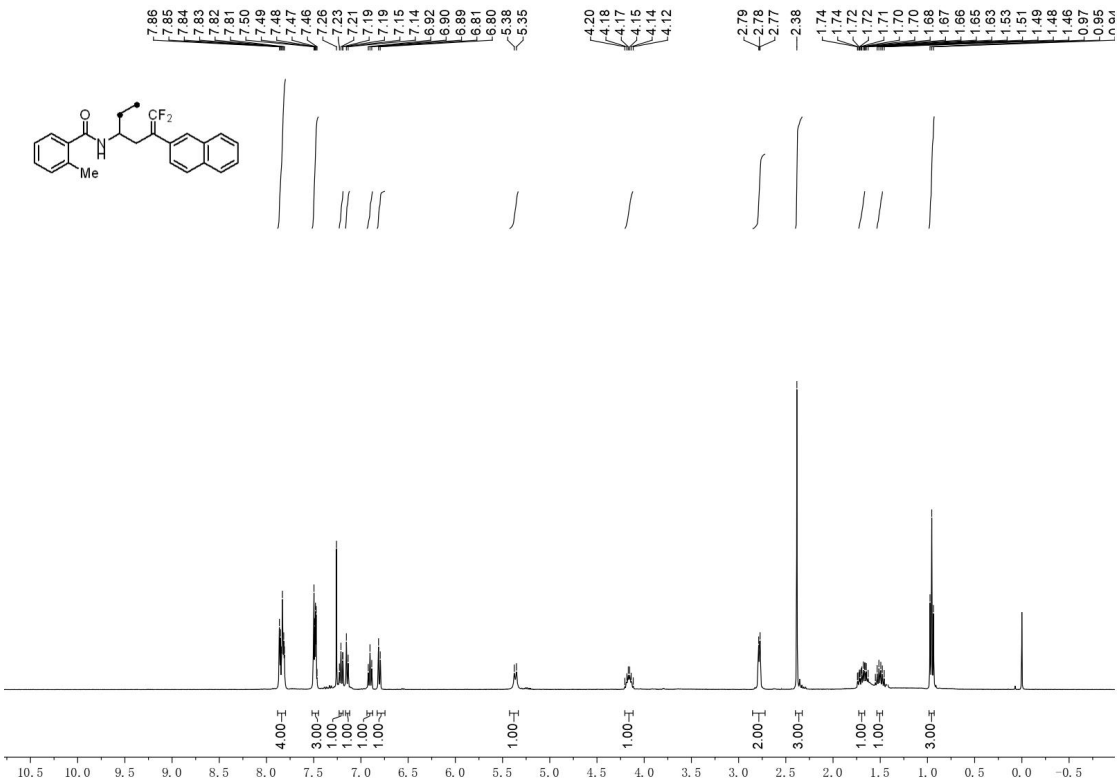

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3b**

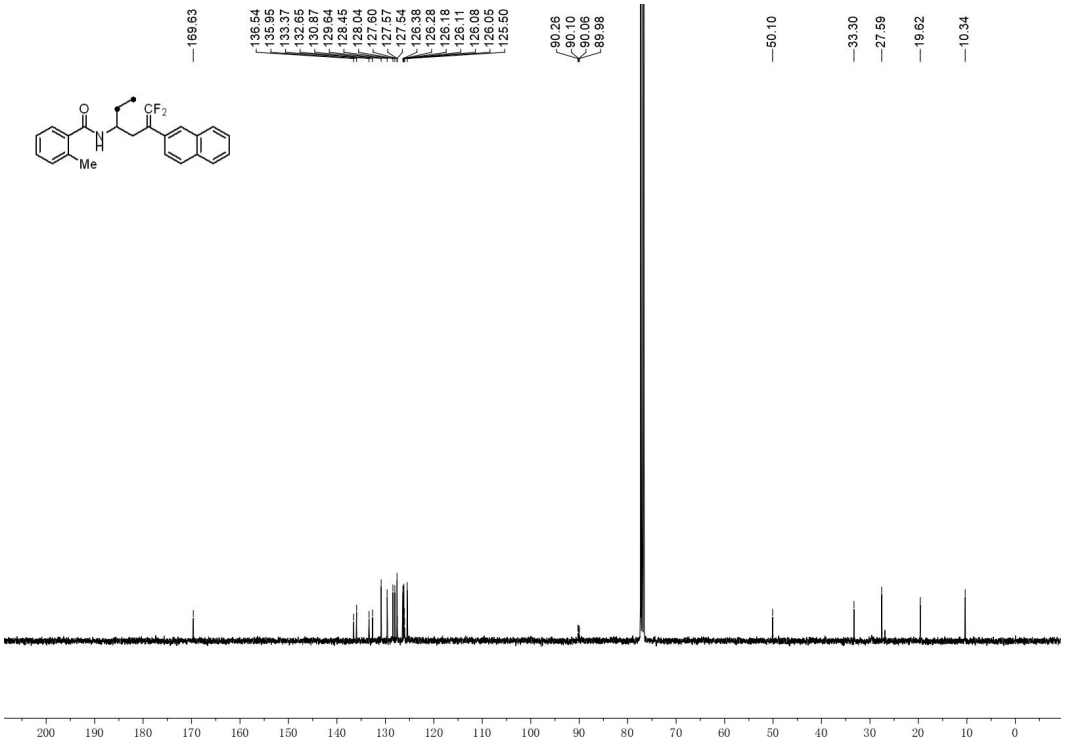

Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3b**

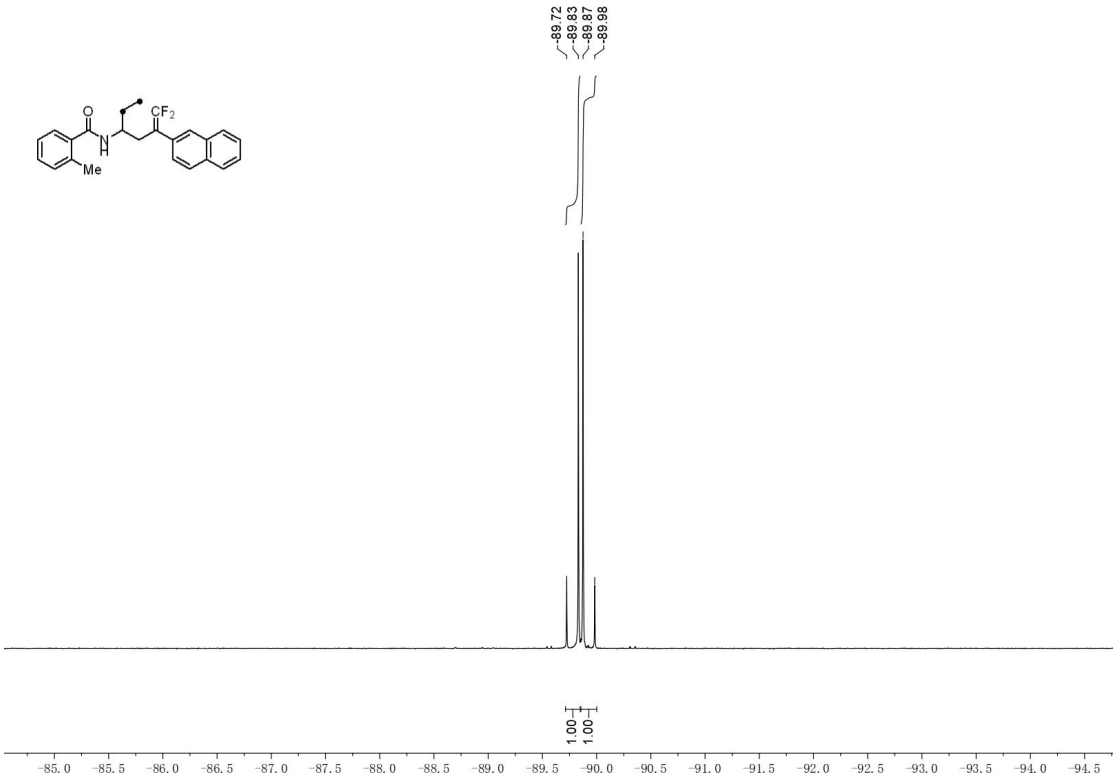

Figure S13. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3b**

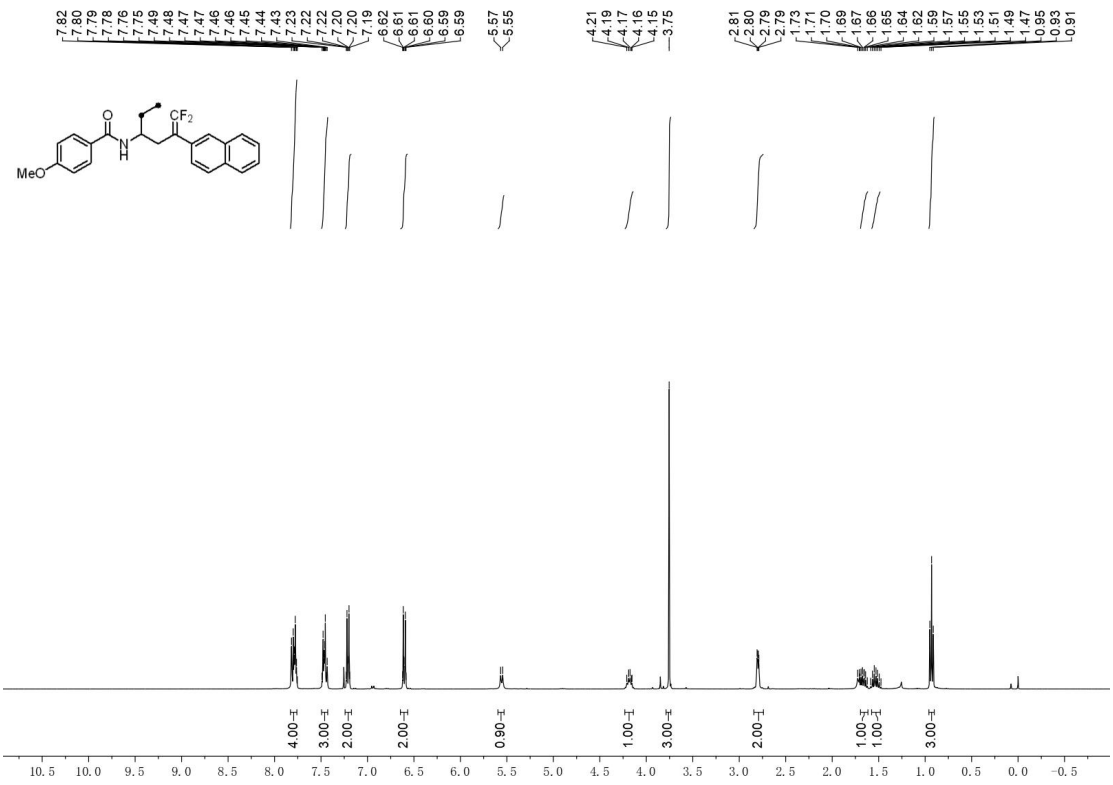

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3c**

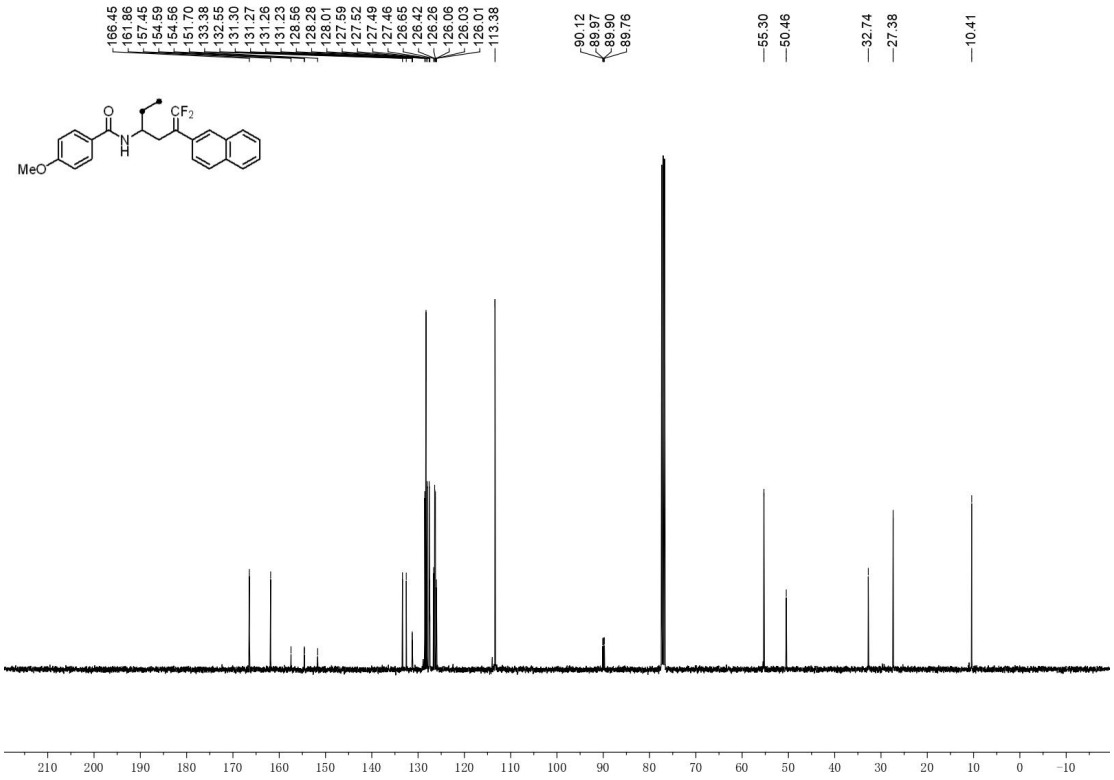

Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3c**

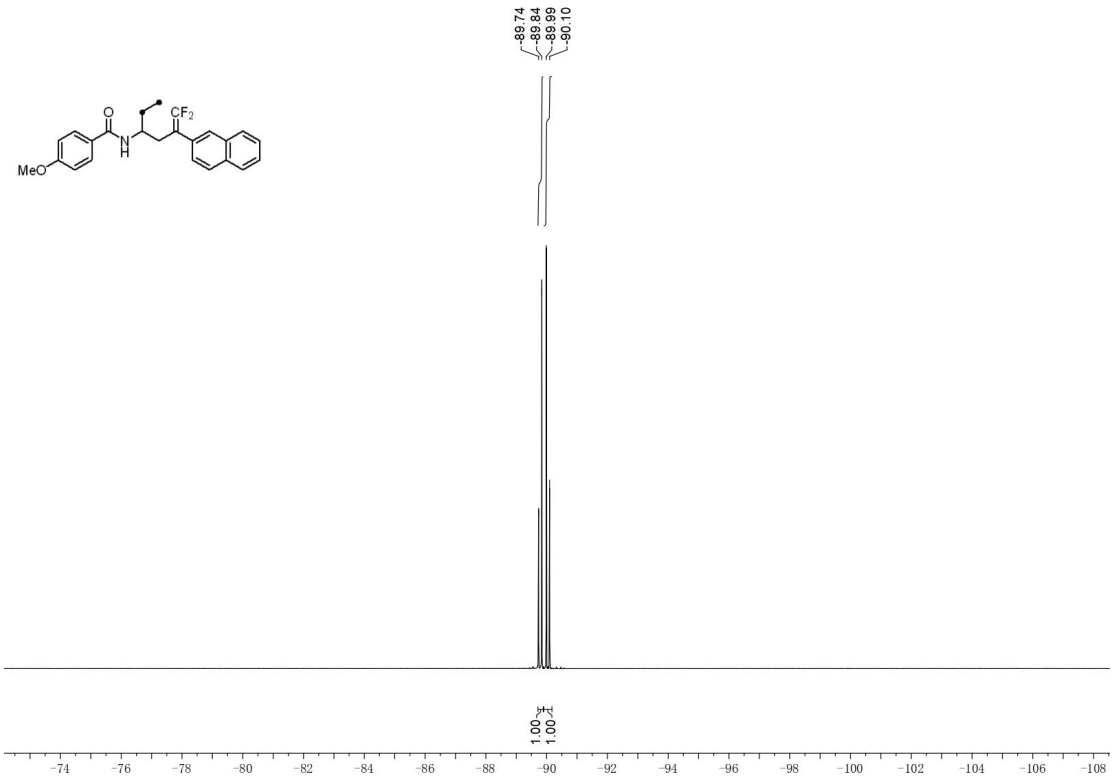

Figure S16. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3c**

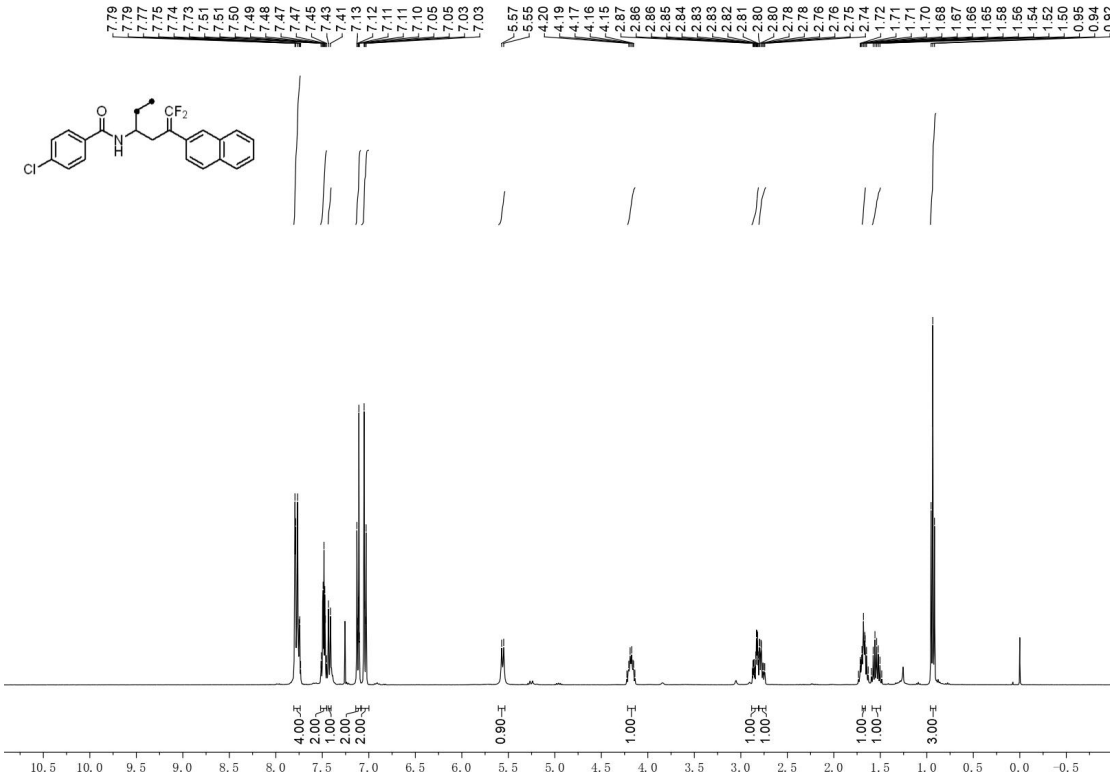

Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3d**

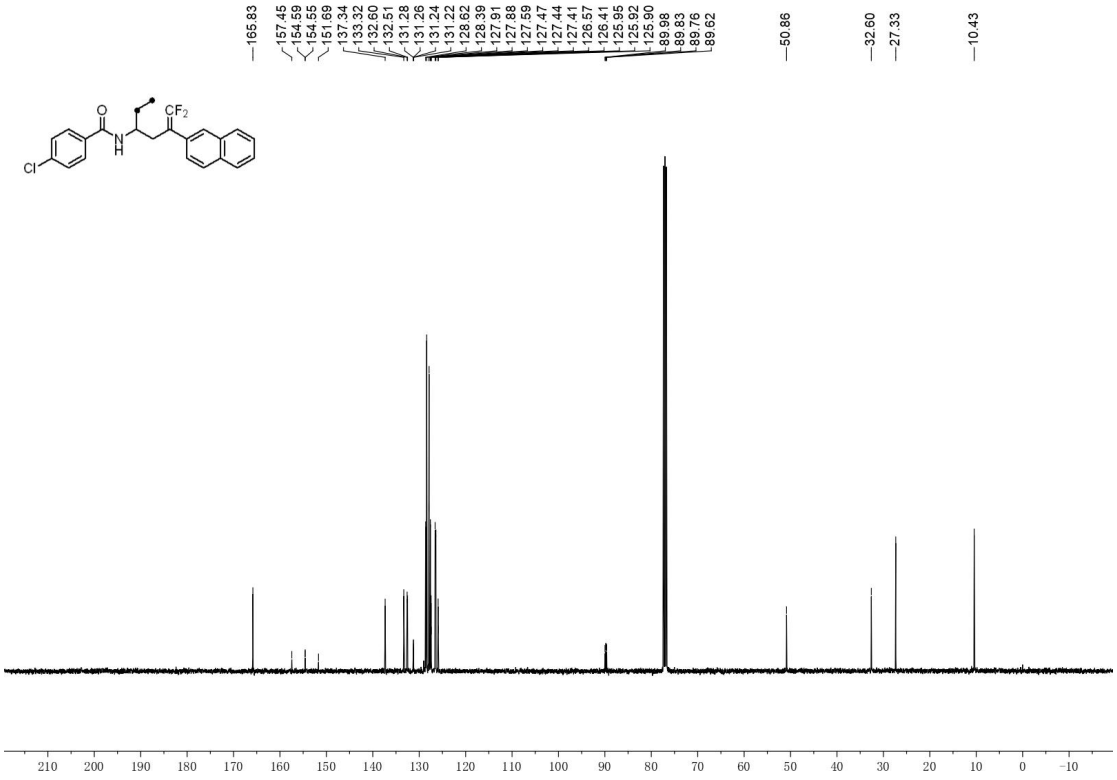

Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3d**

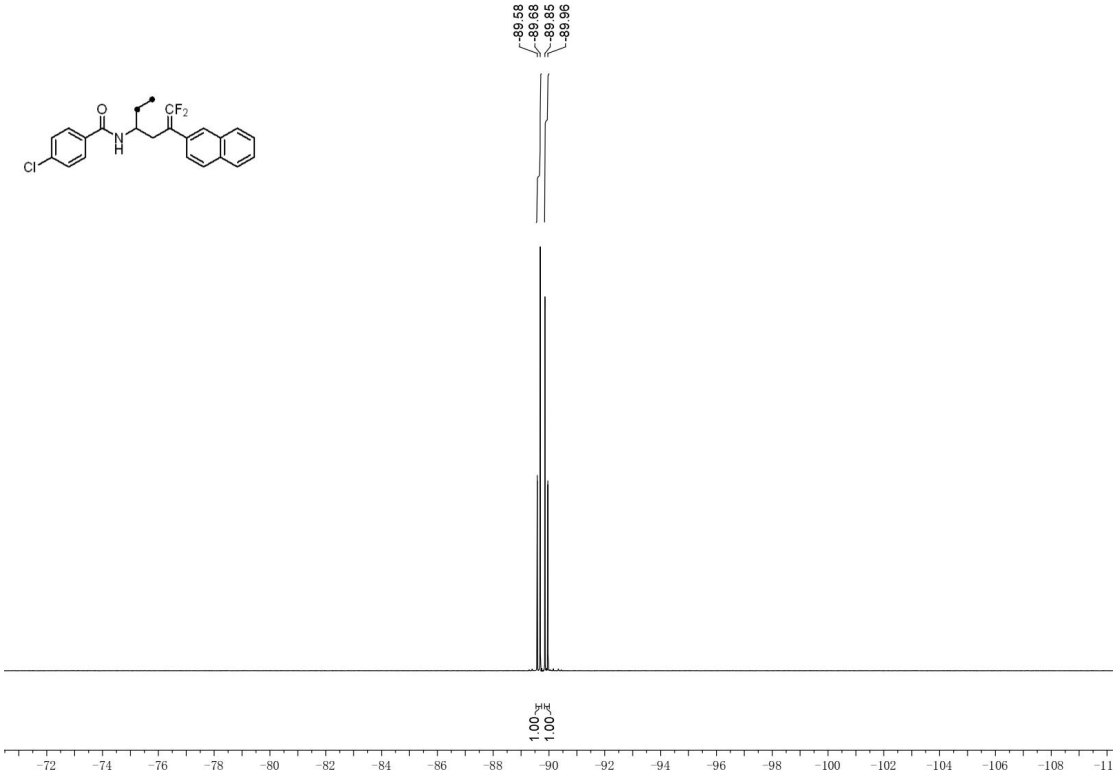

Figure S19. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3d**

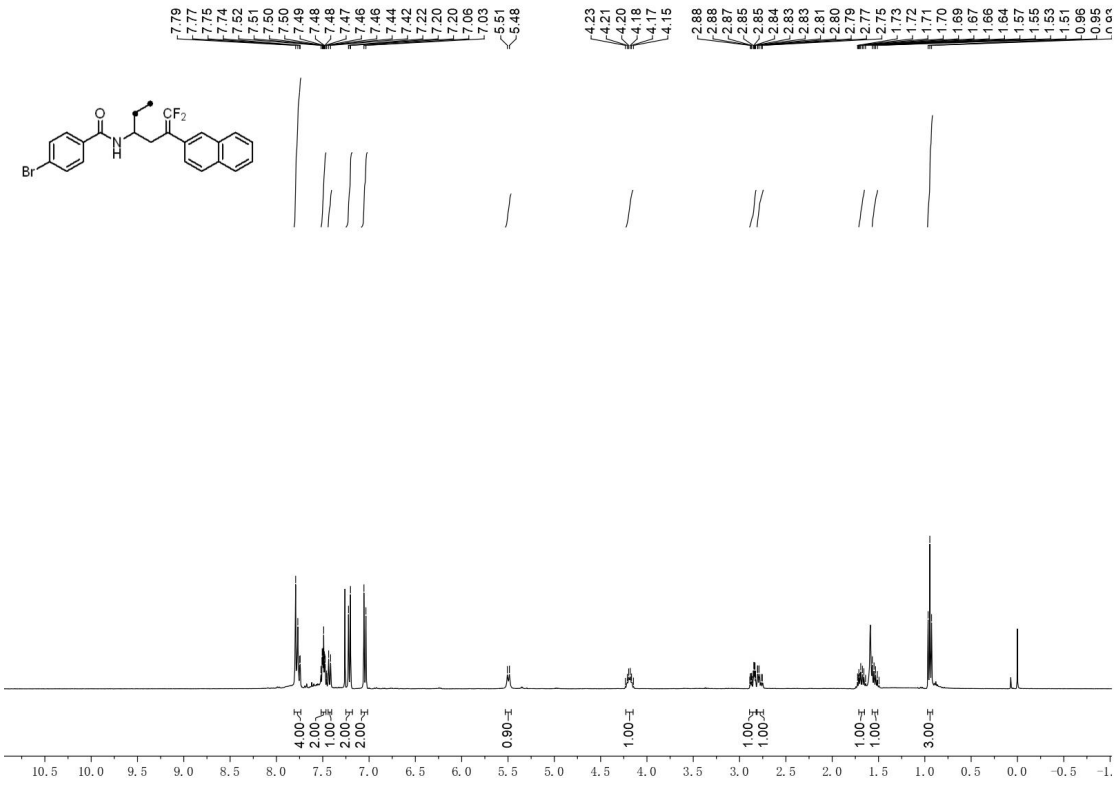

Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3e**

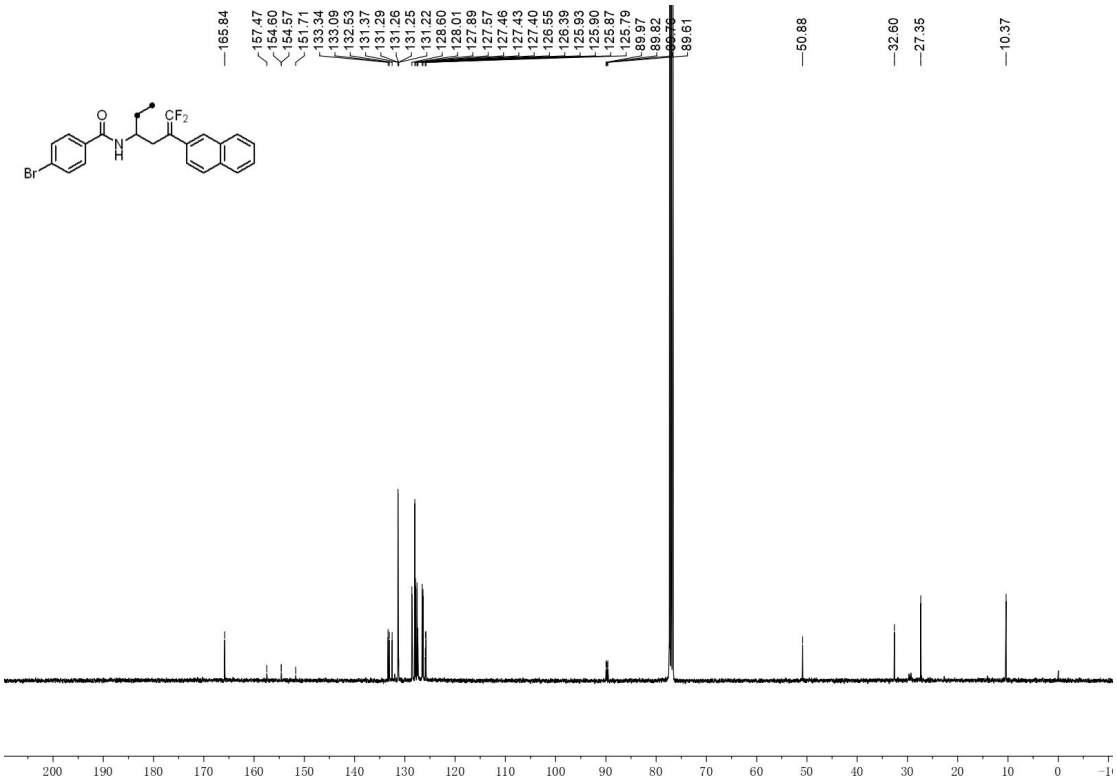

Figure S21. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3e**

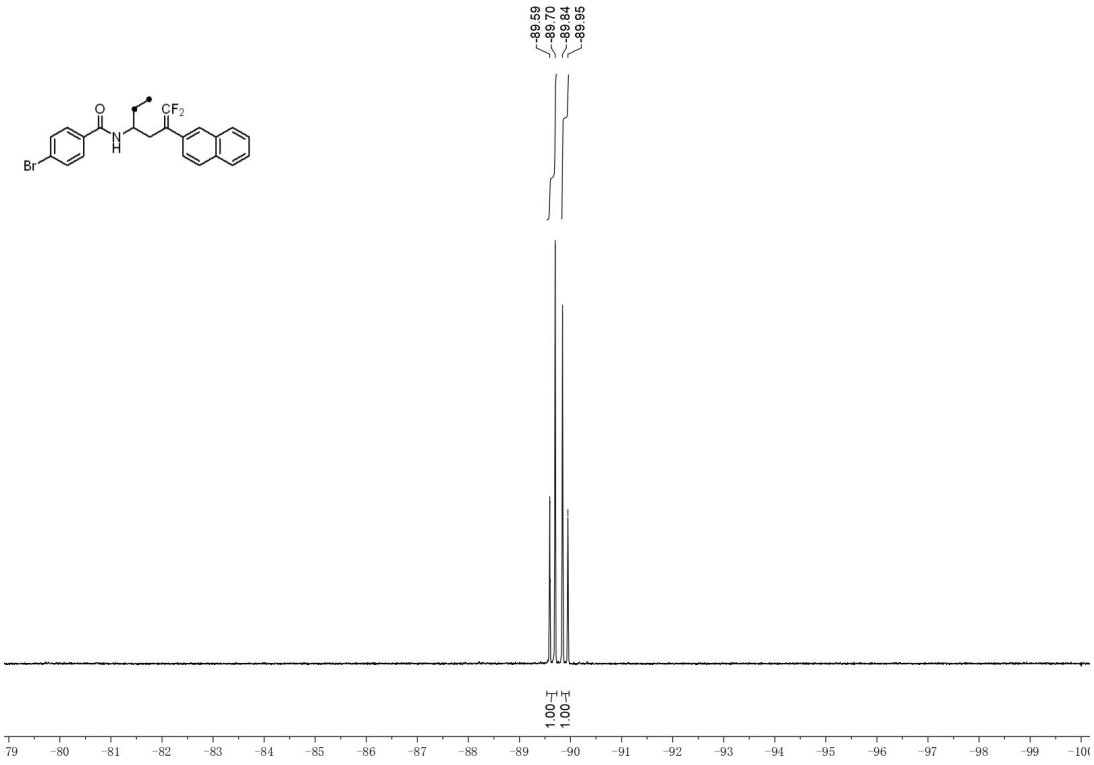

Figure S22. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3e**

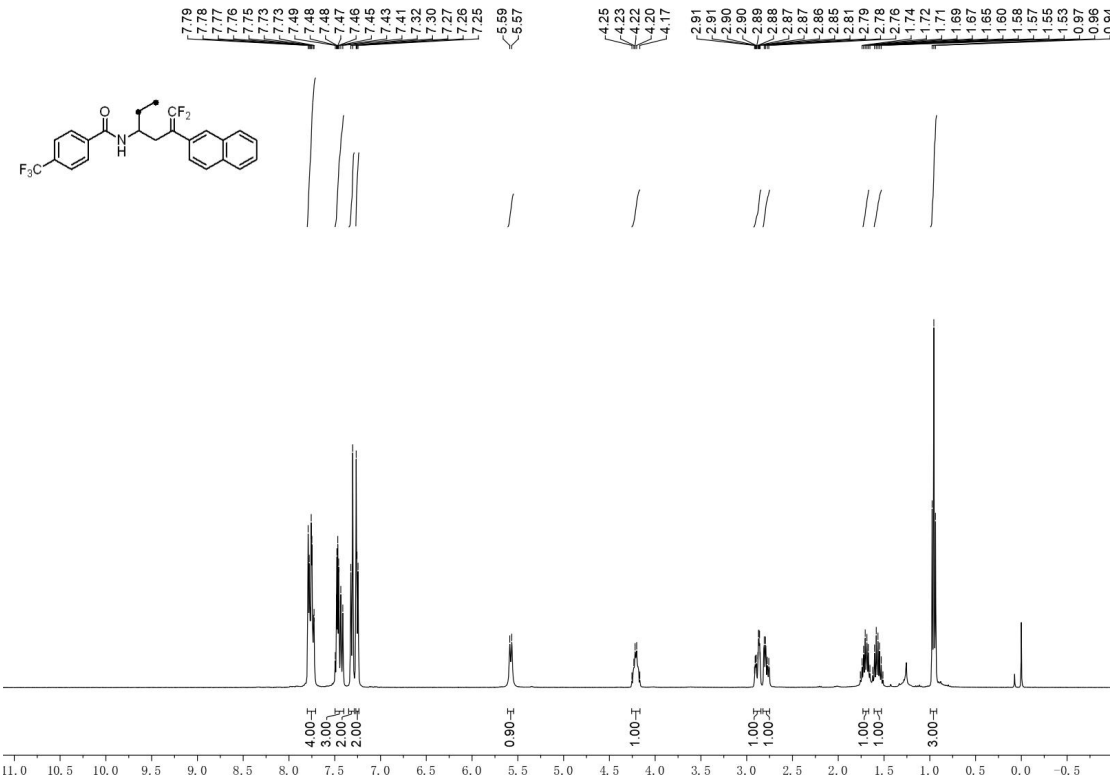

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3f**

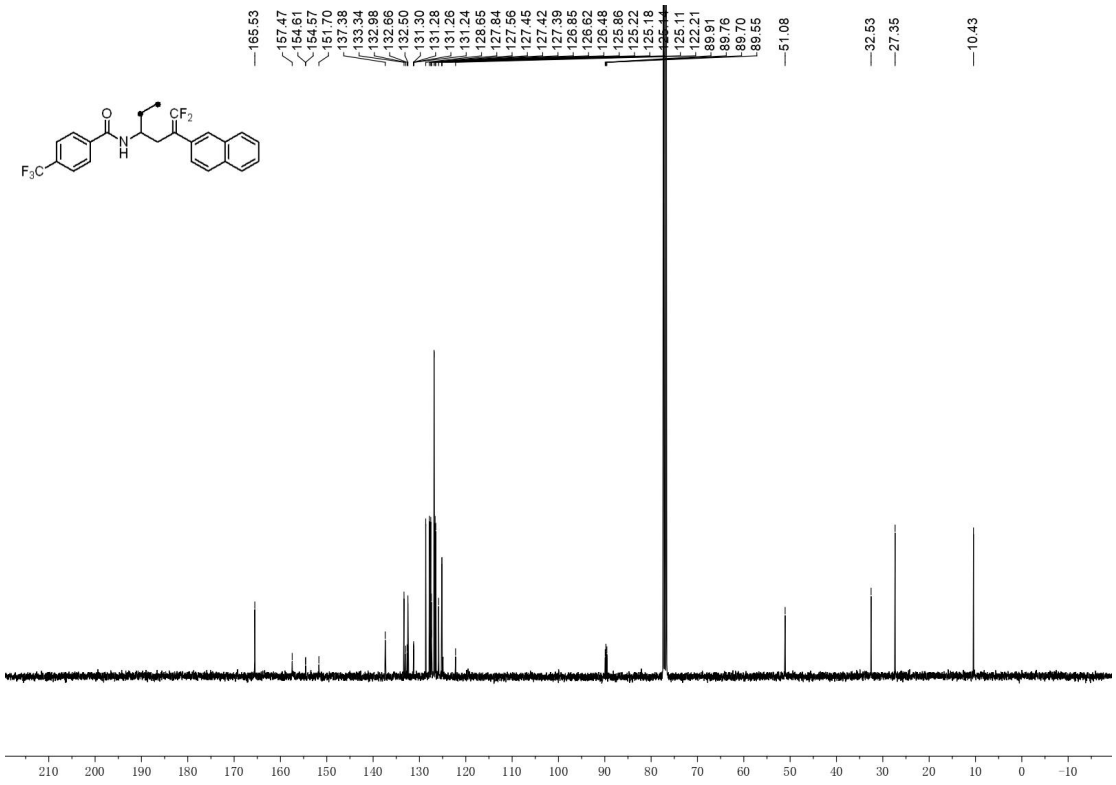

Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3f**

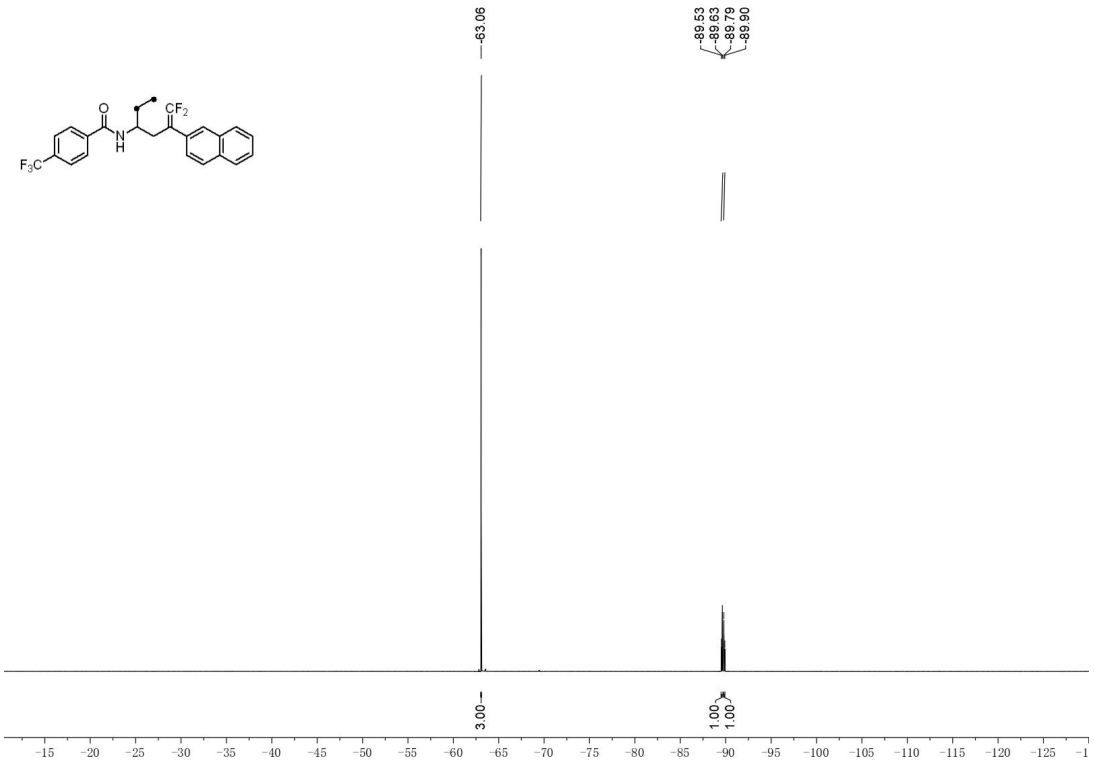

Figure S25. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3f**

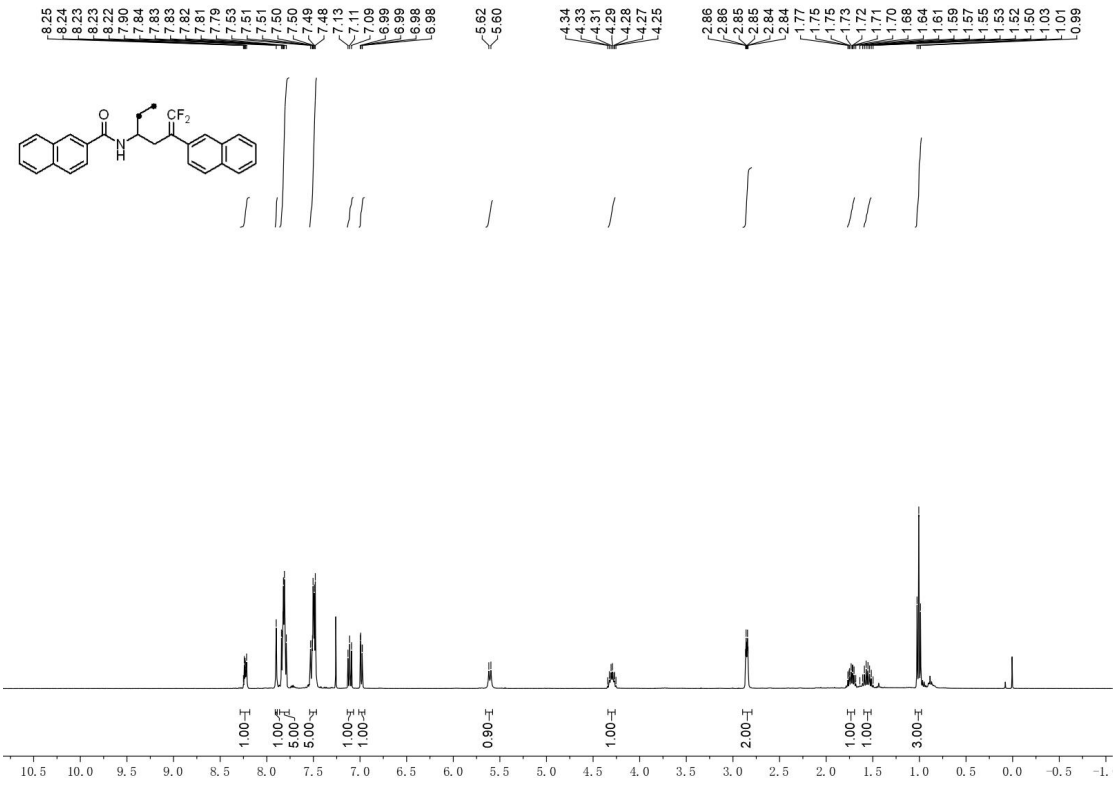

Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3g**

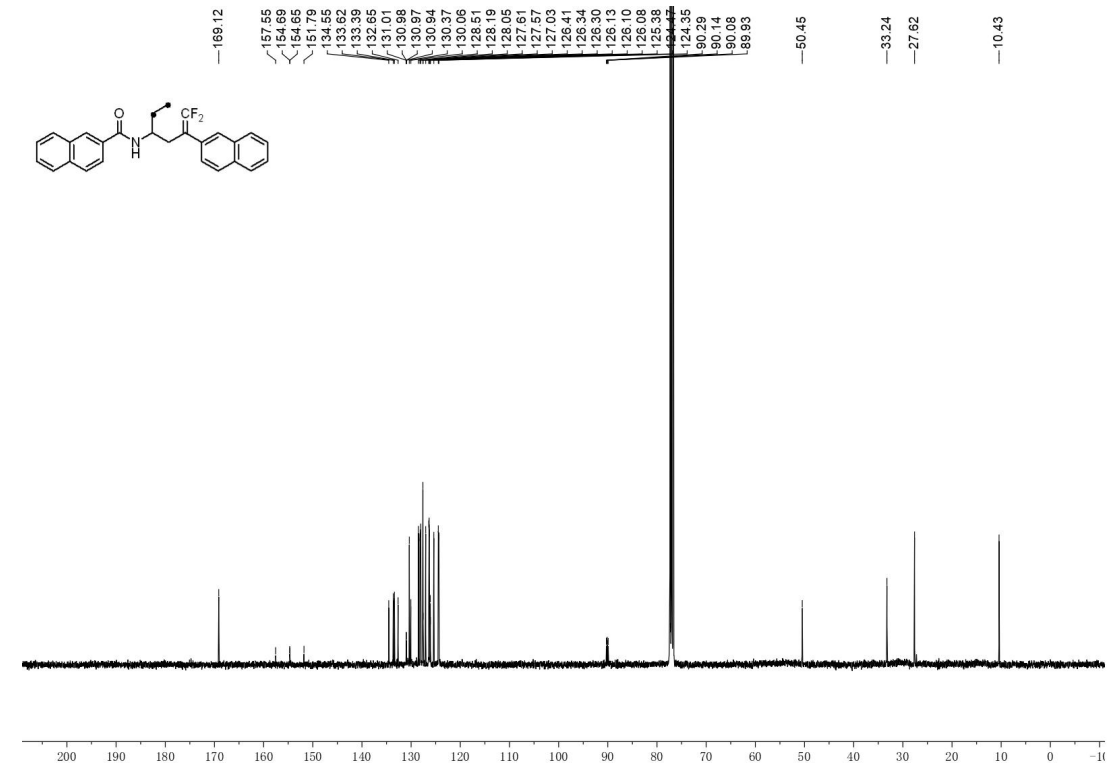

Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3g**

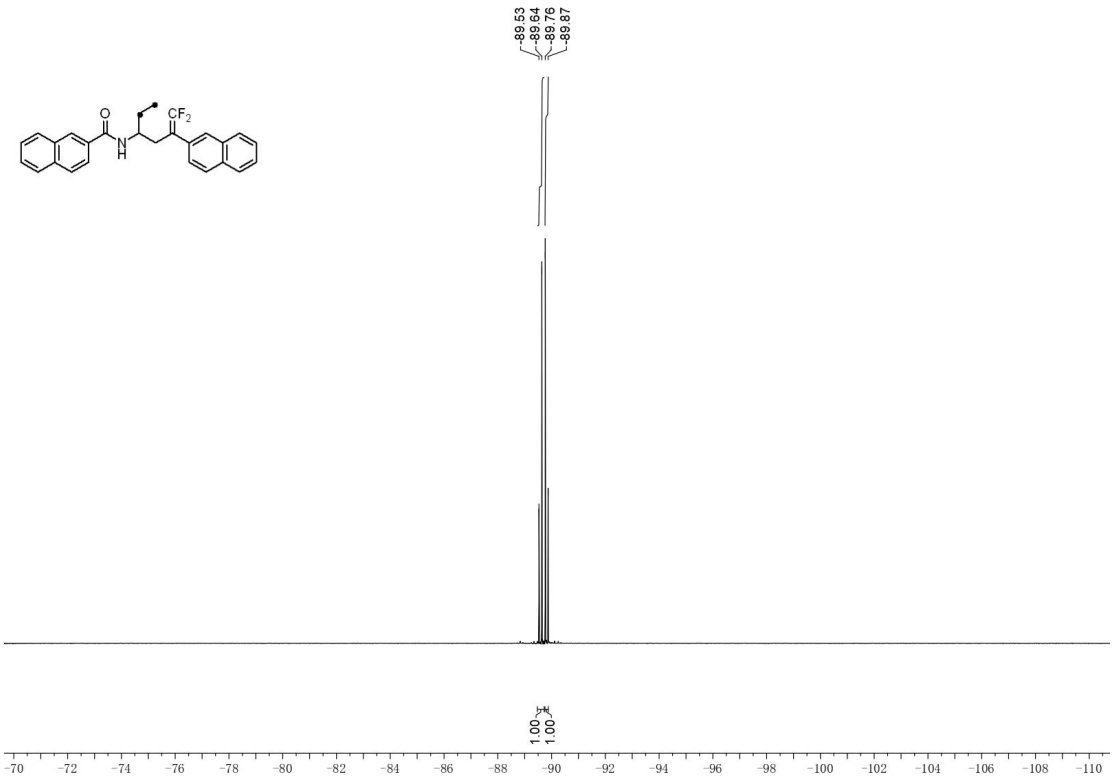

Figure S28. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3g**

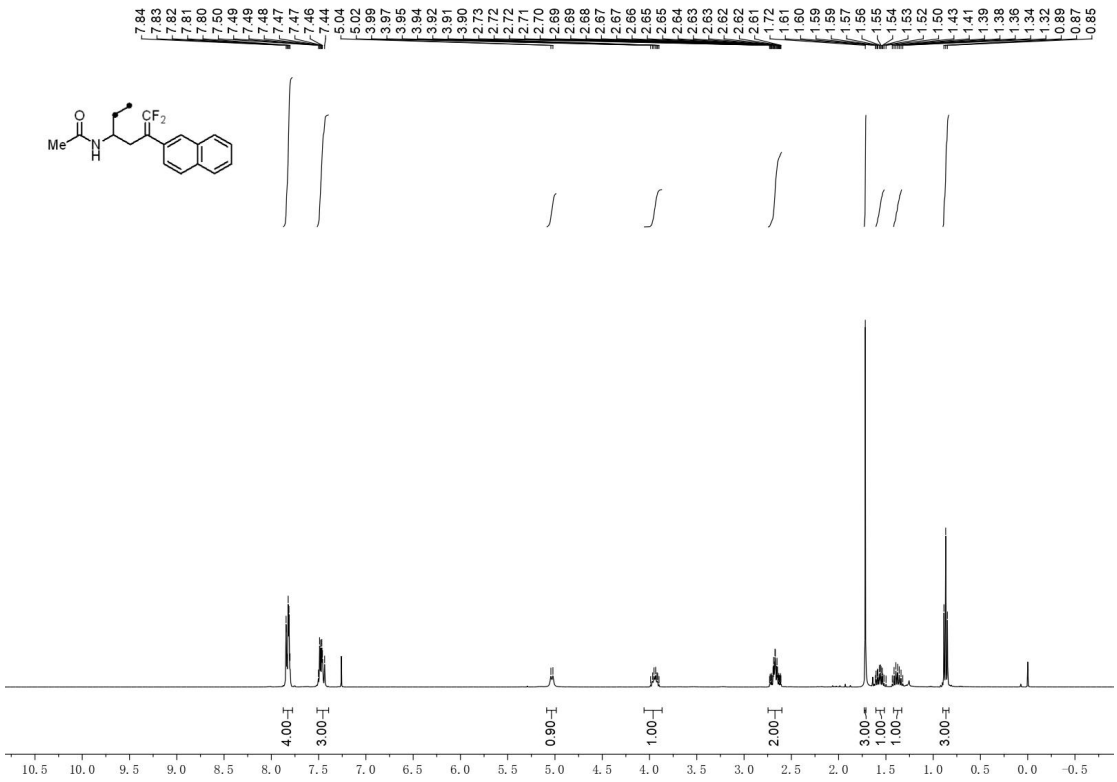

Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3h**

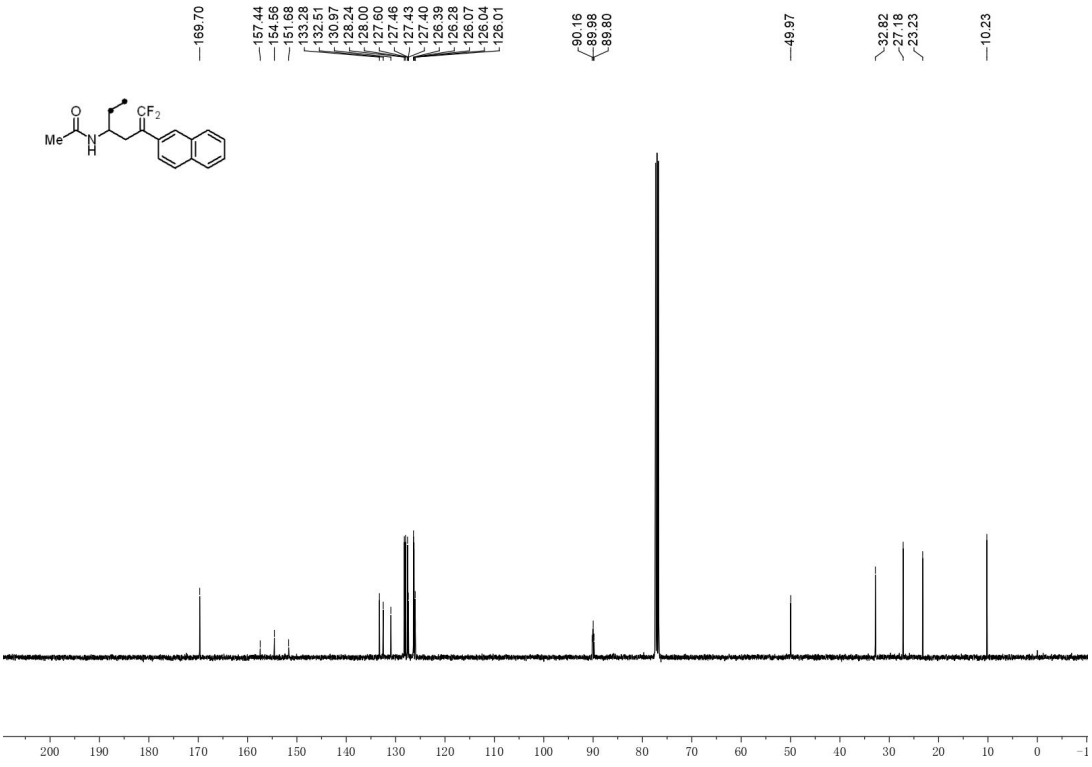

Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3h**

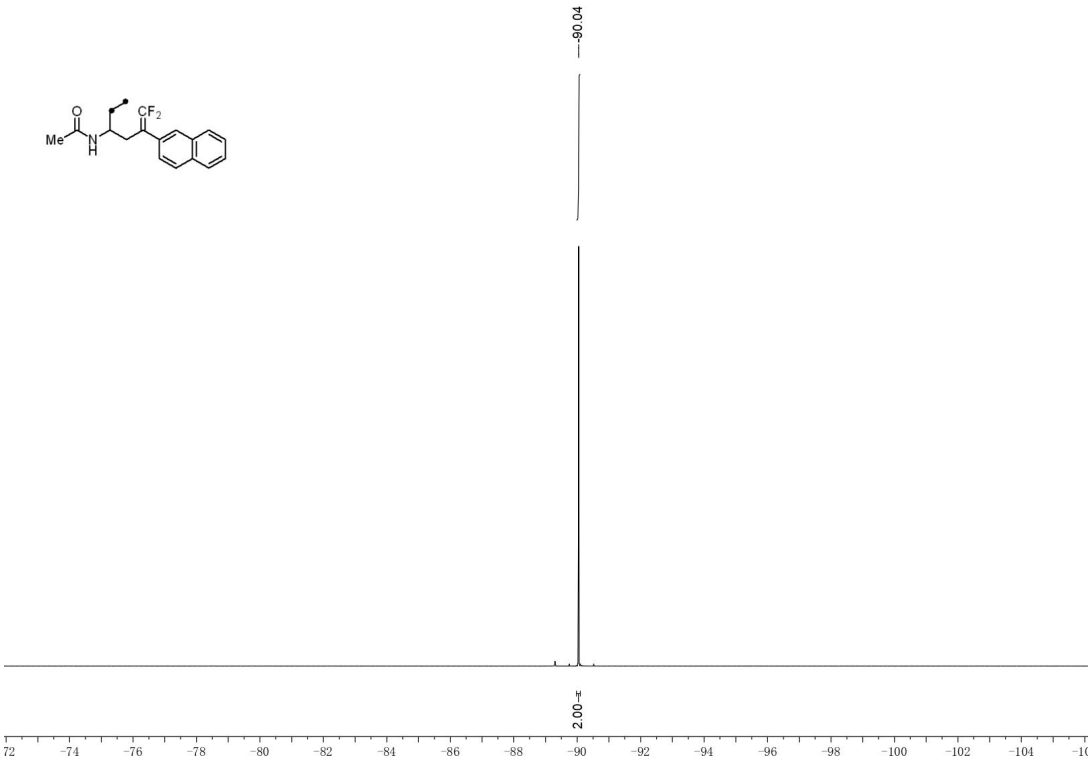

Figure S31. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3h**

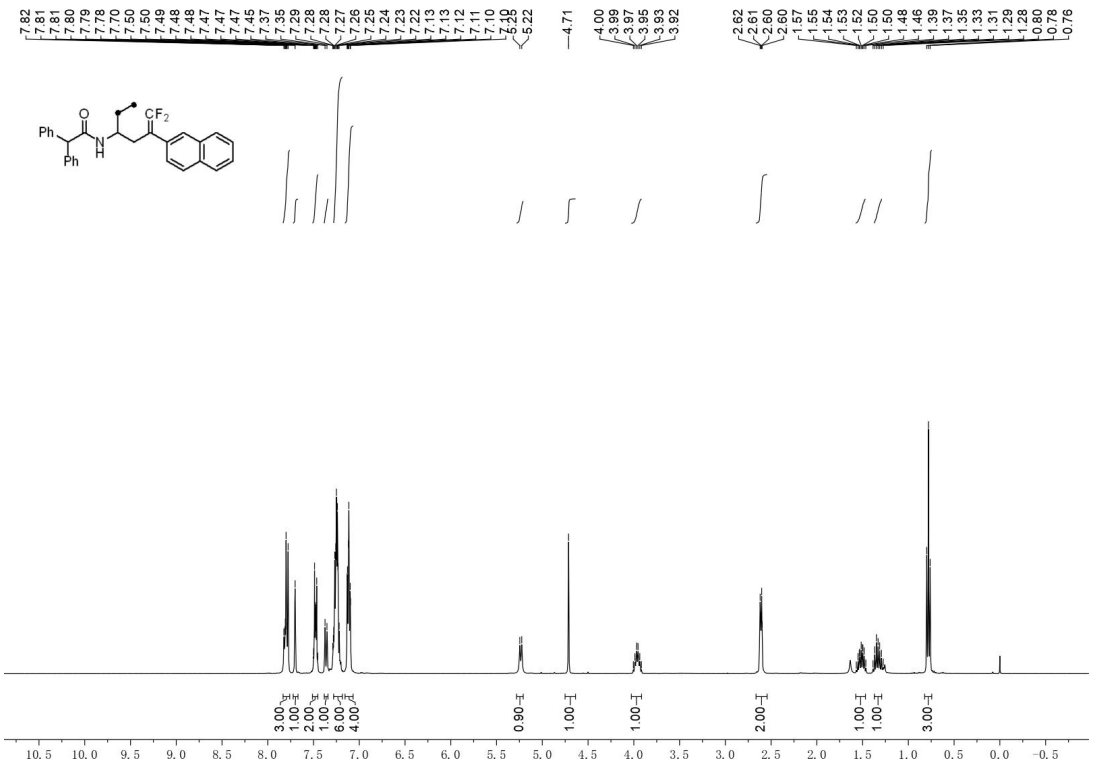

Figure 32. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3i**

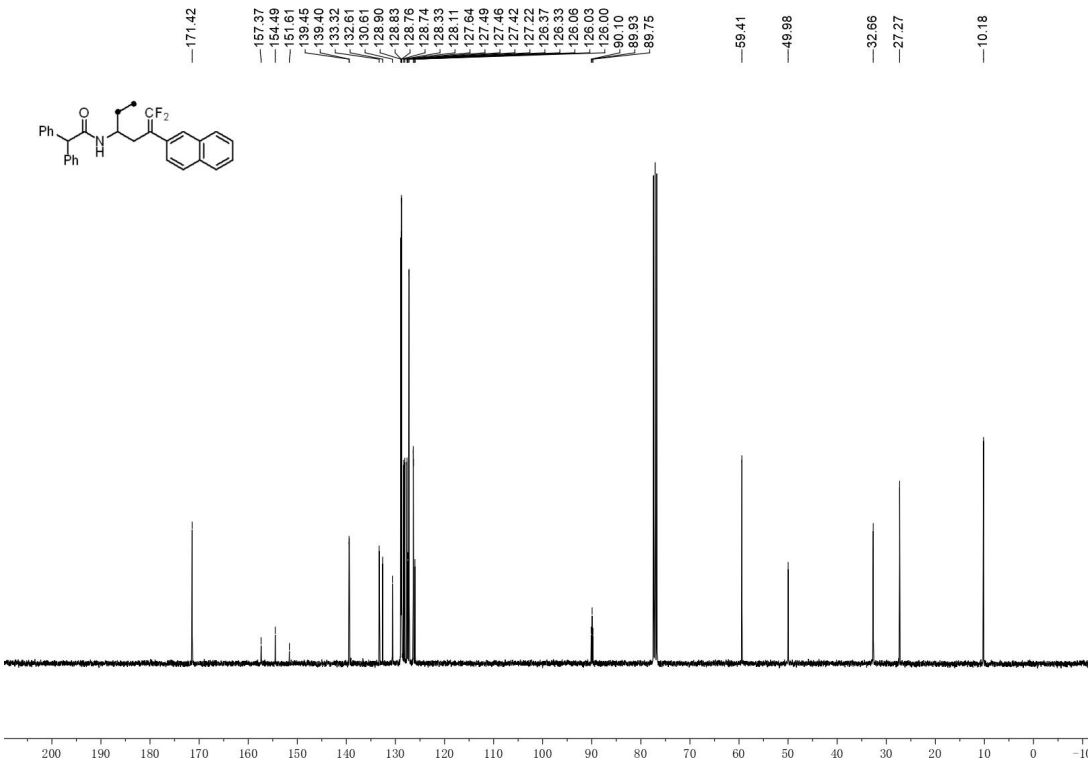

Figure S33. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3i**

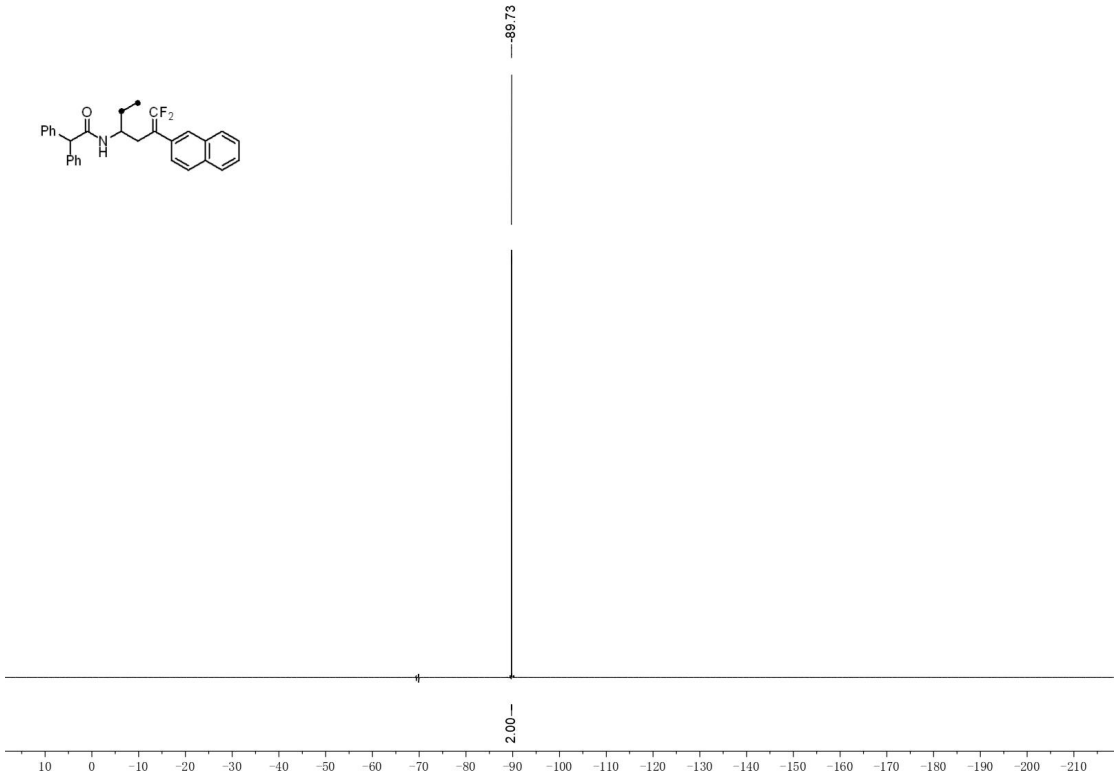

Figure S34. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3i**

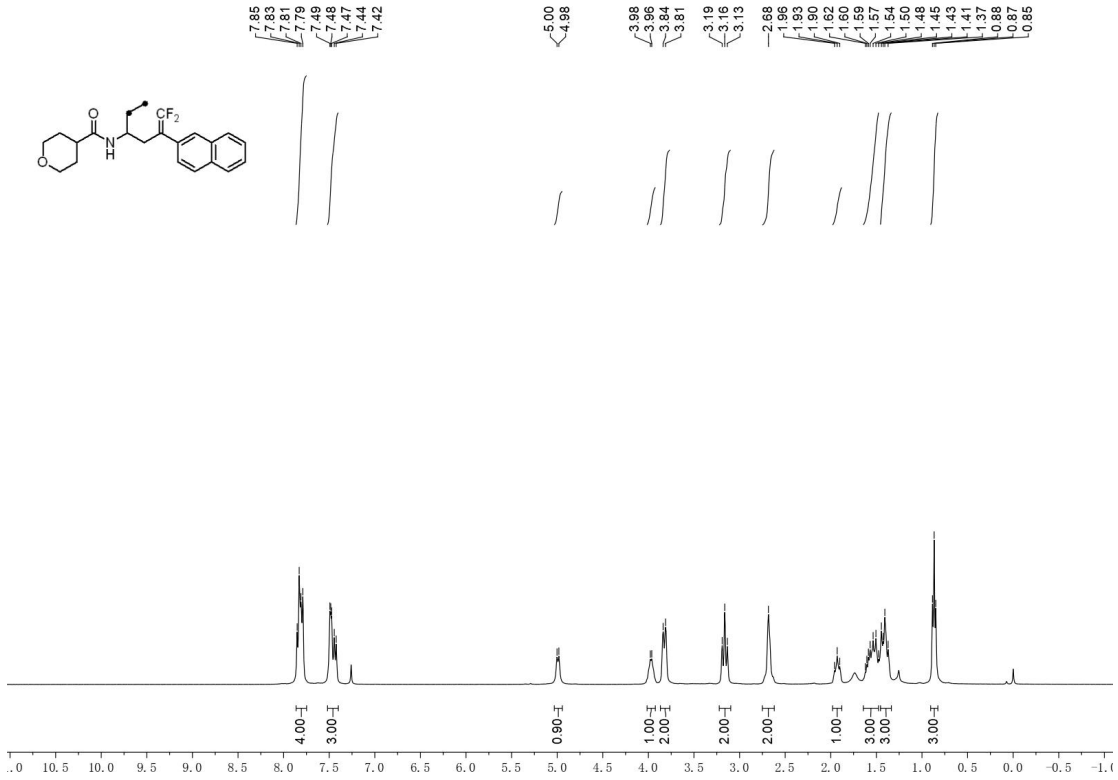

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3j**

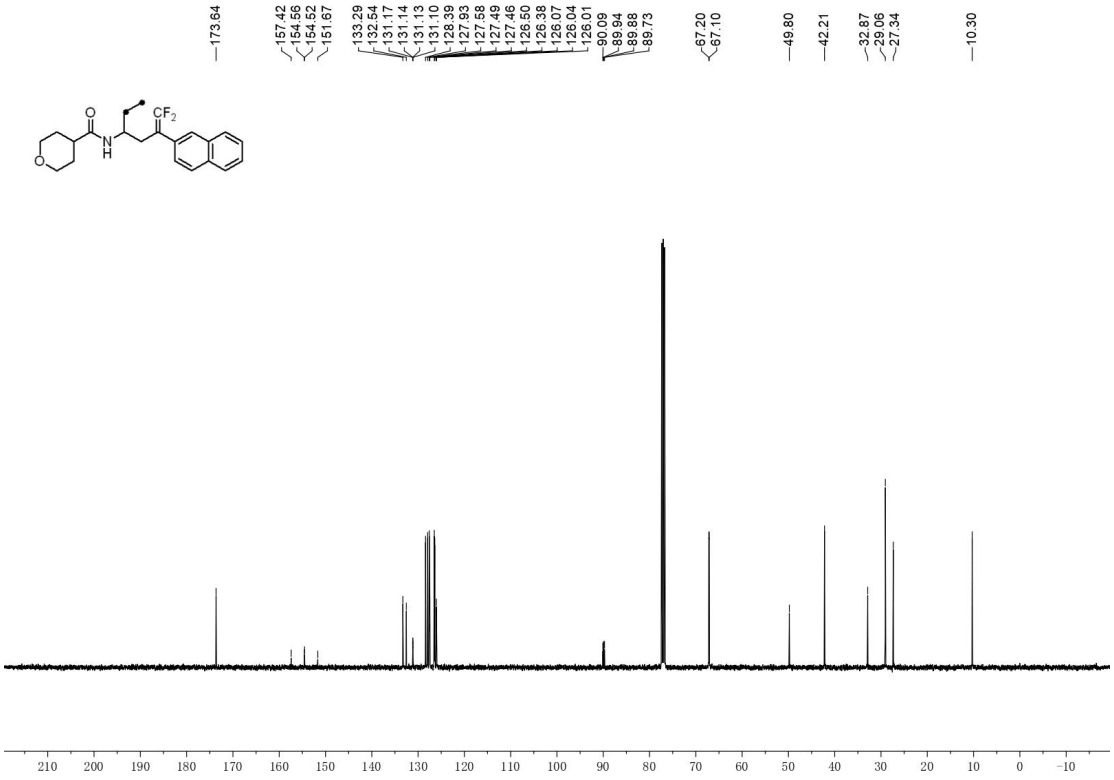

Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3j**

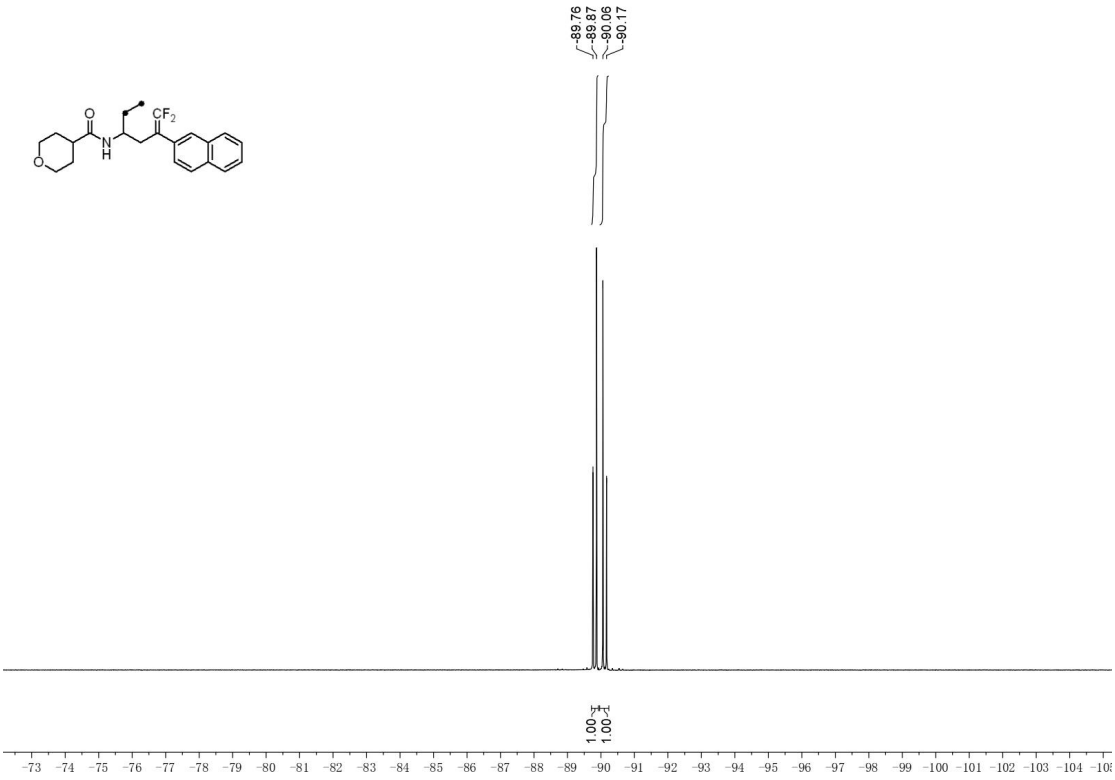

Figure S37. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3j**

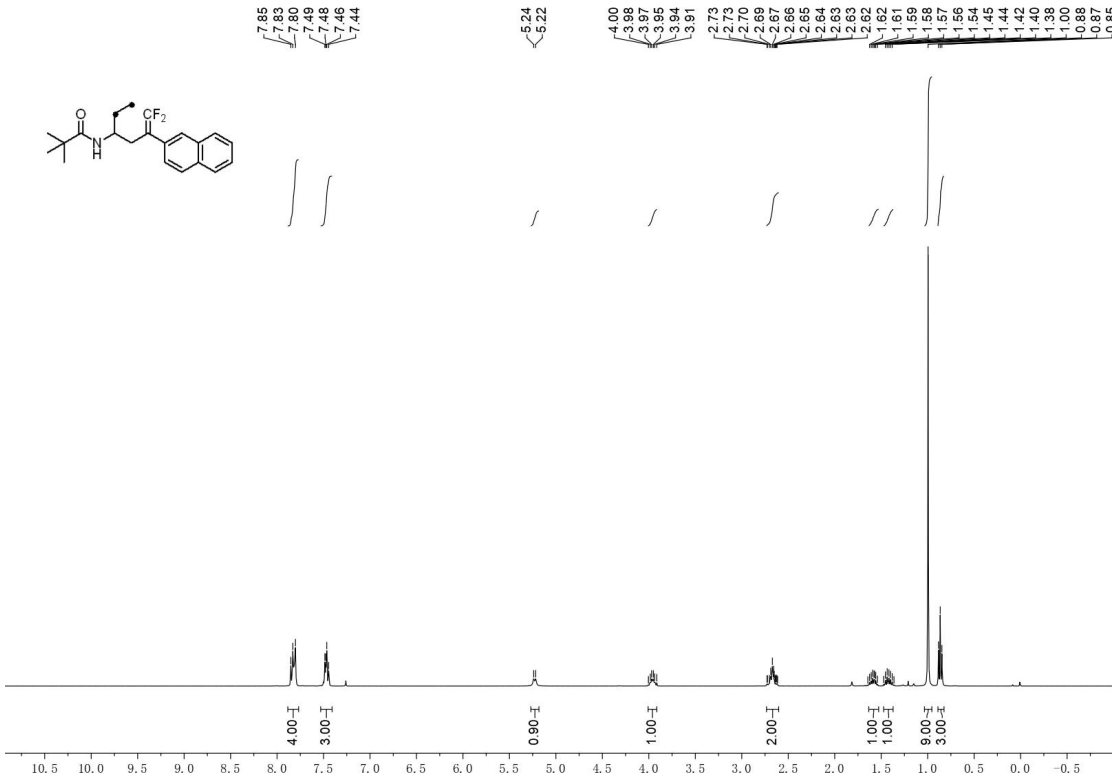

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3k**

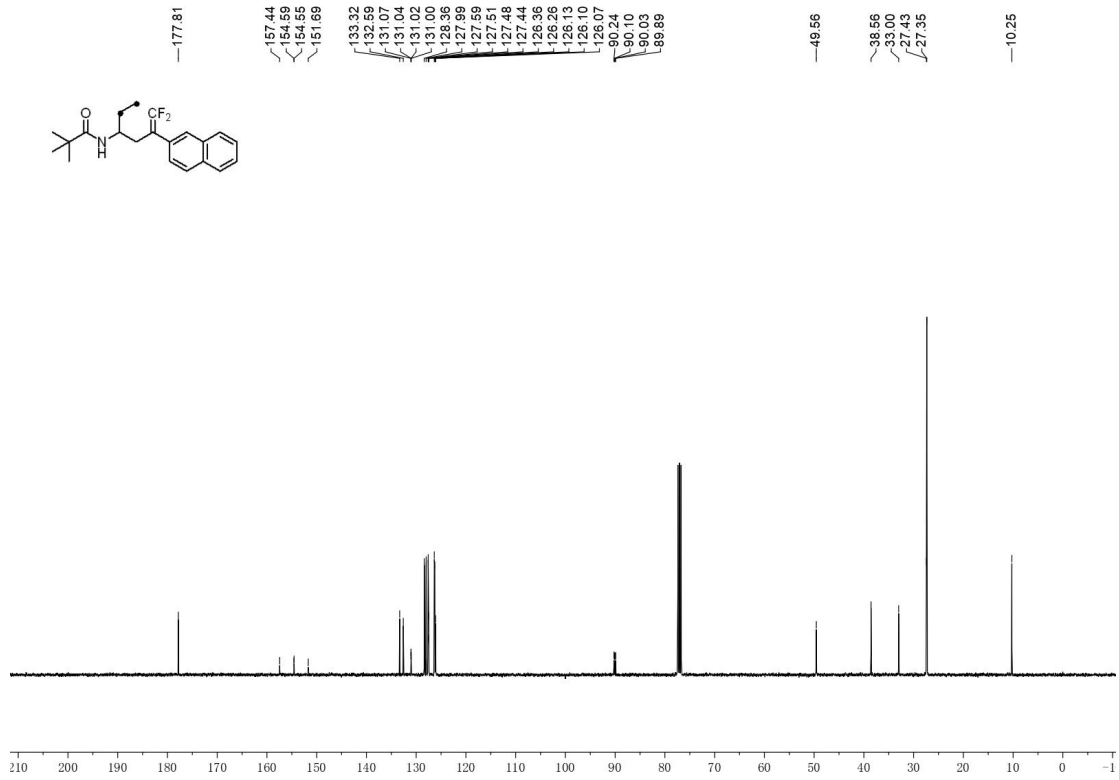

Figure S39. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3k**

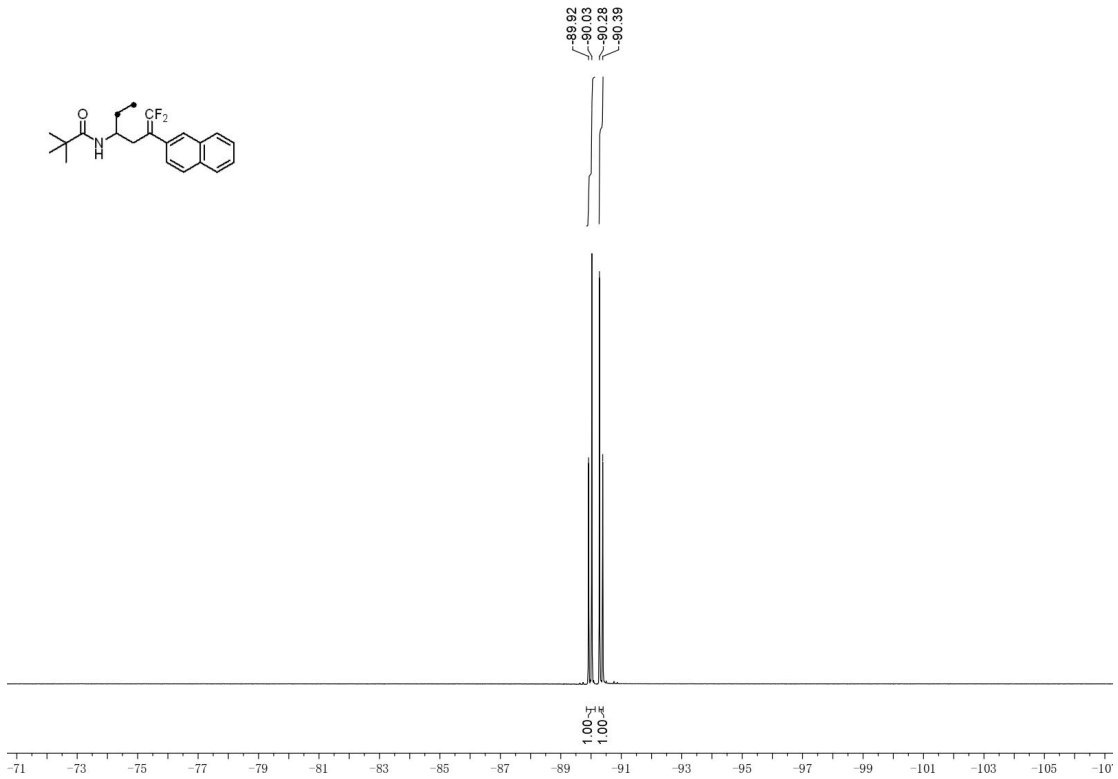

Figure S40. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3k**

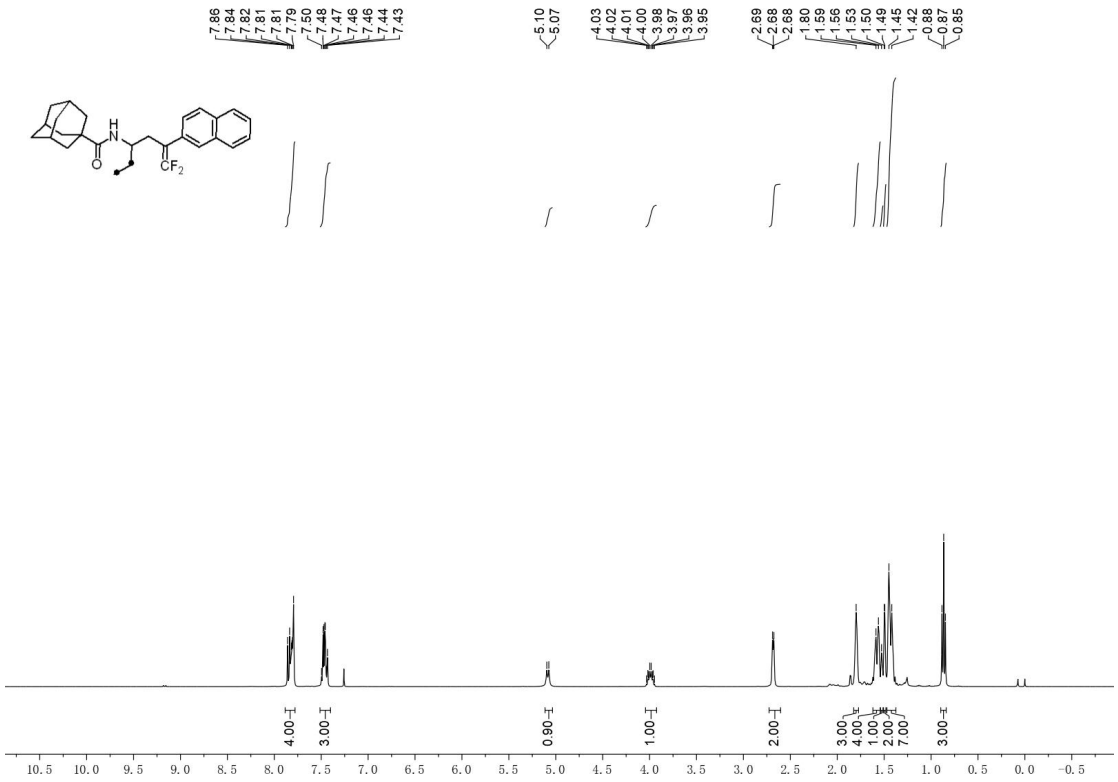

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3l**

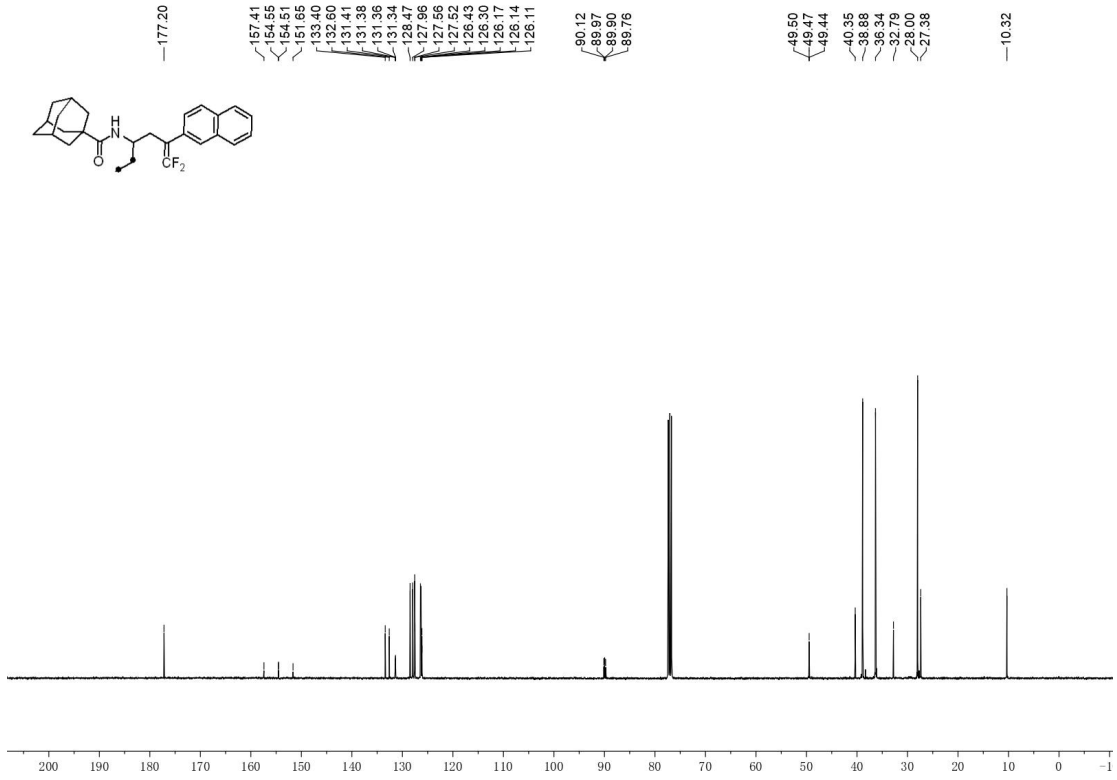

Figure S42. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3l**

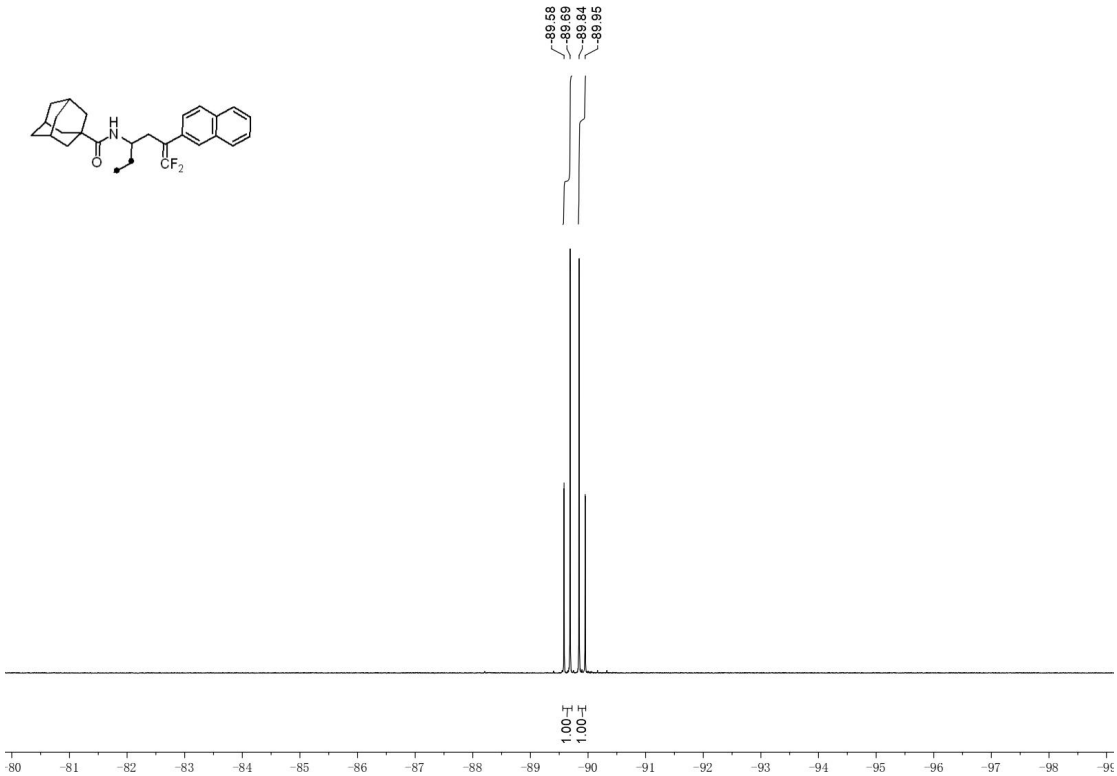

Figure 43. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3l**

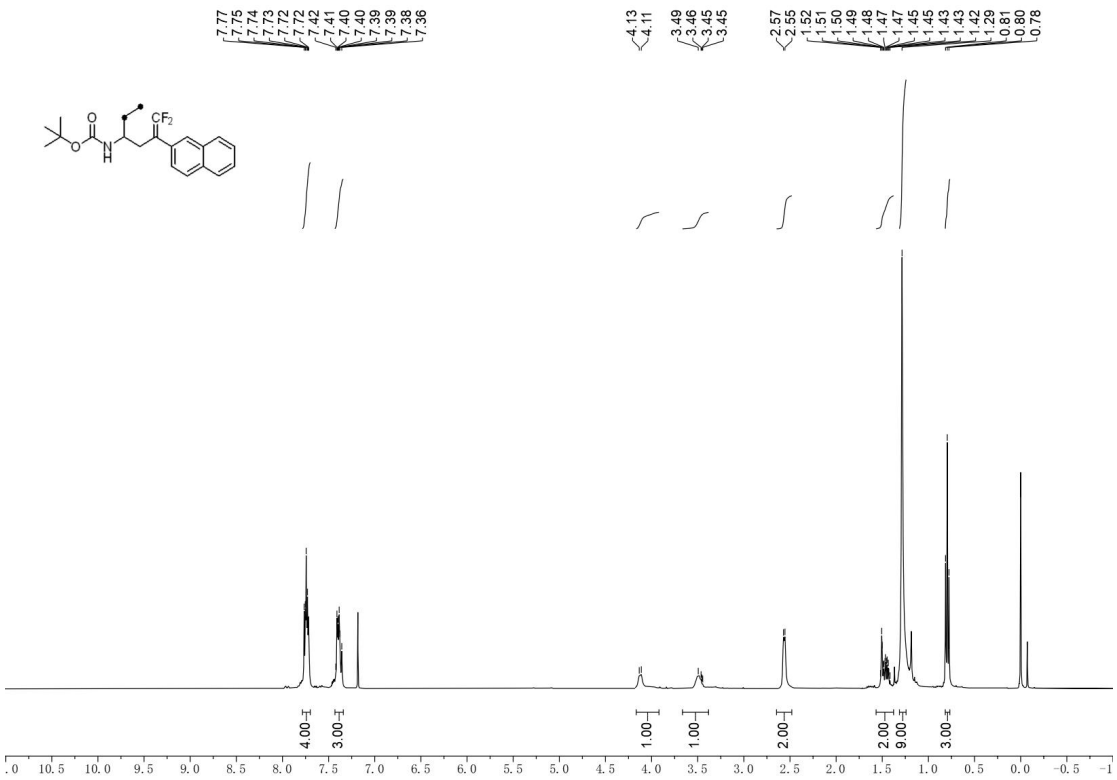

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3m**

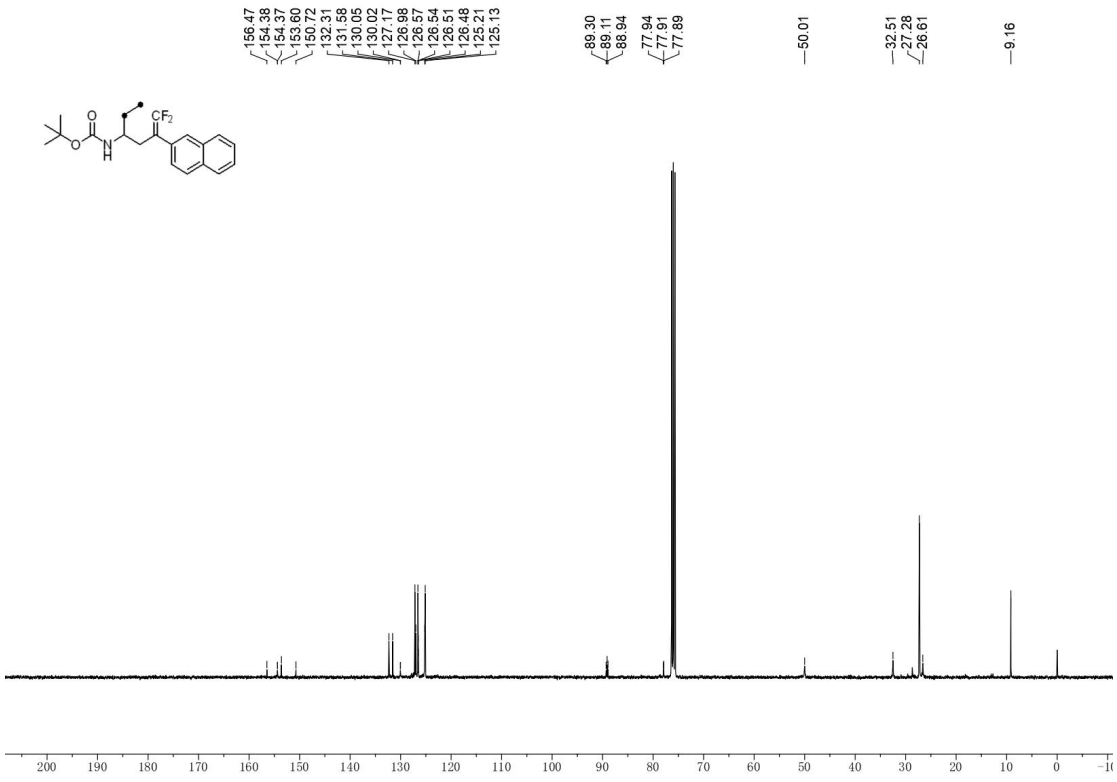

Figure S45. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3m**

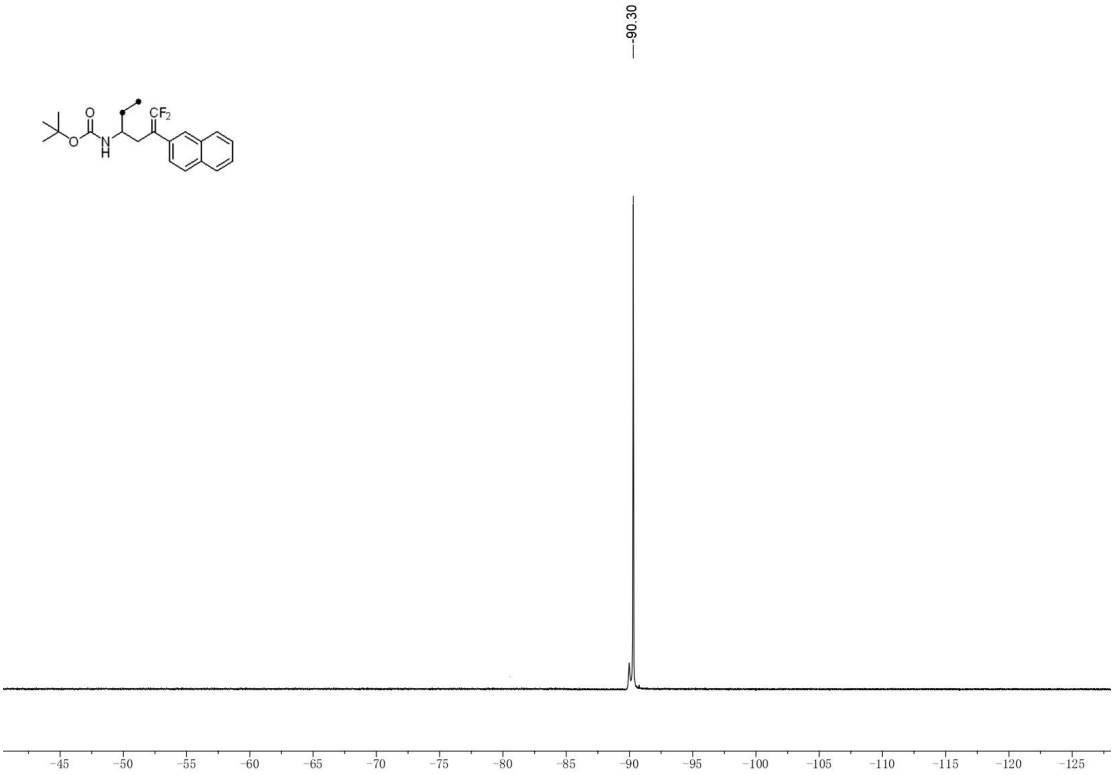

Figure S46. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3m**

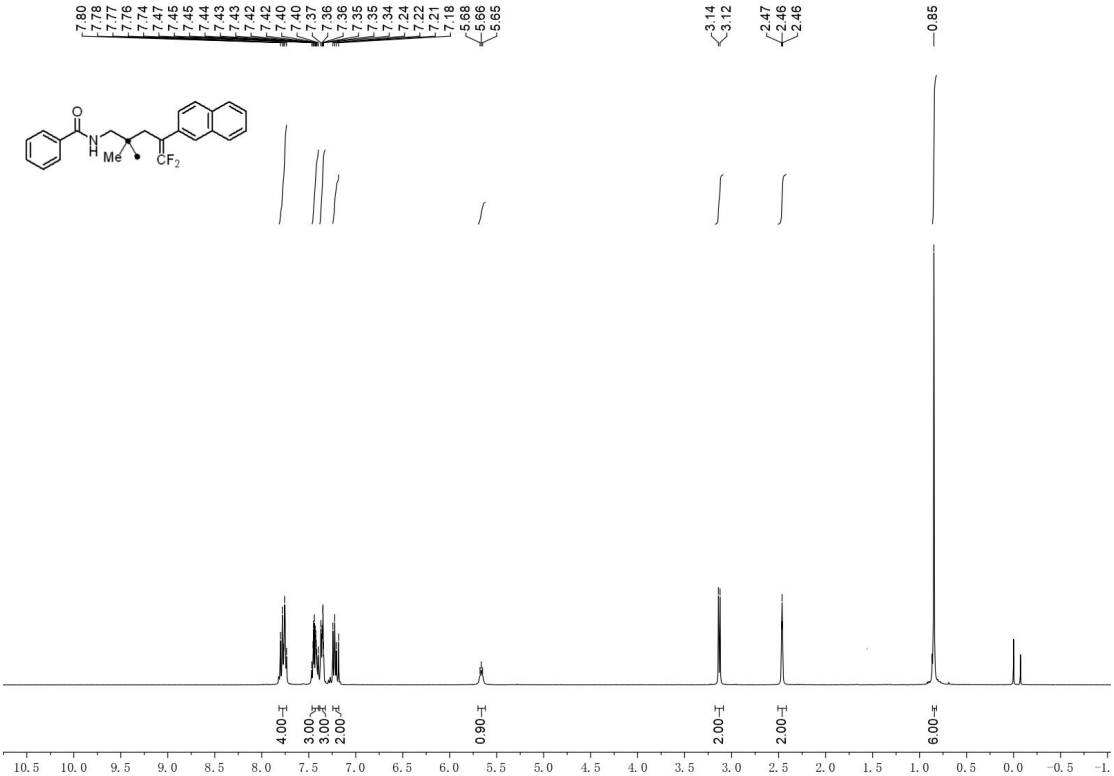

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3n**

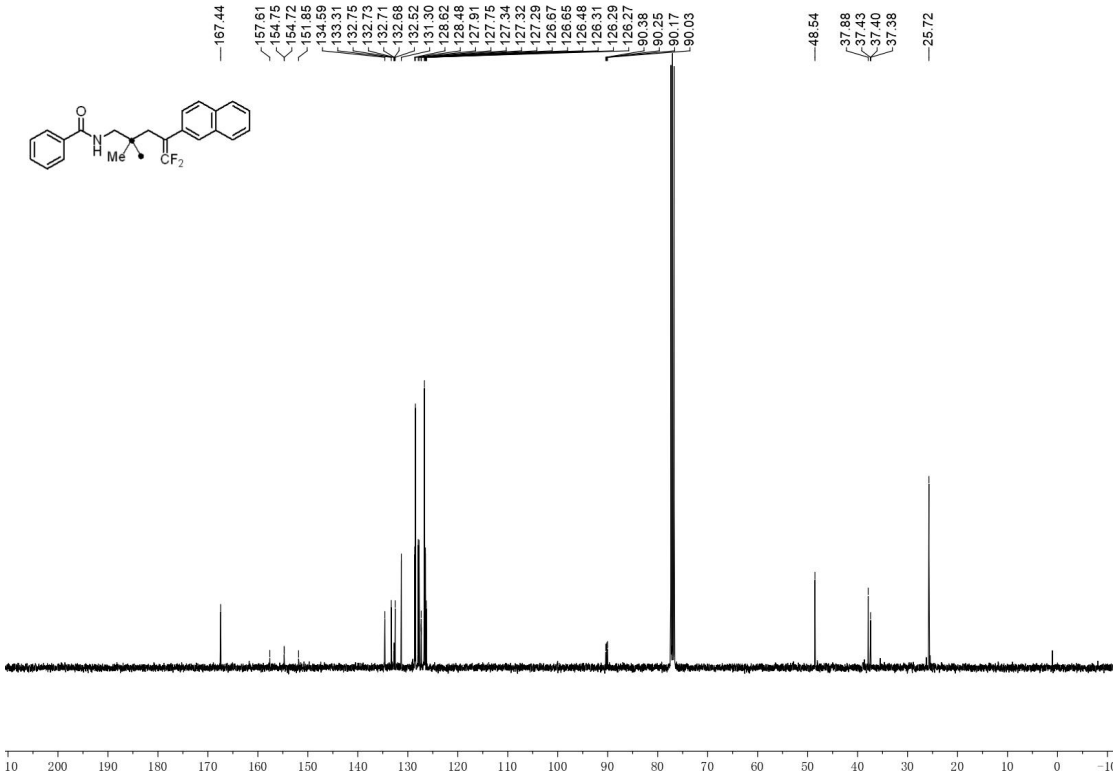

Figure S48. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3n**

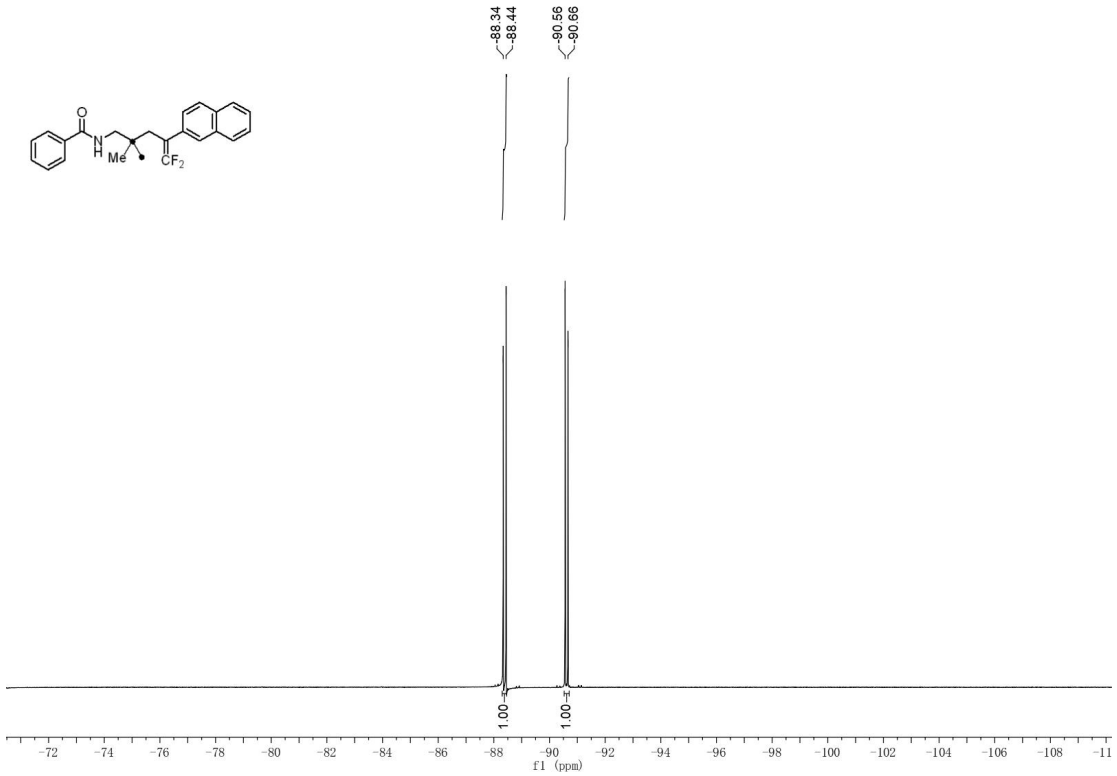

Figure S49. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3n**

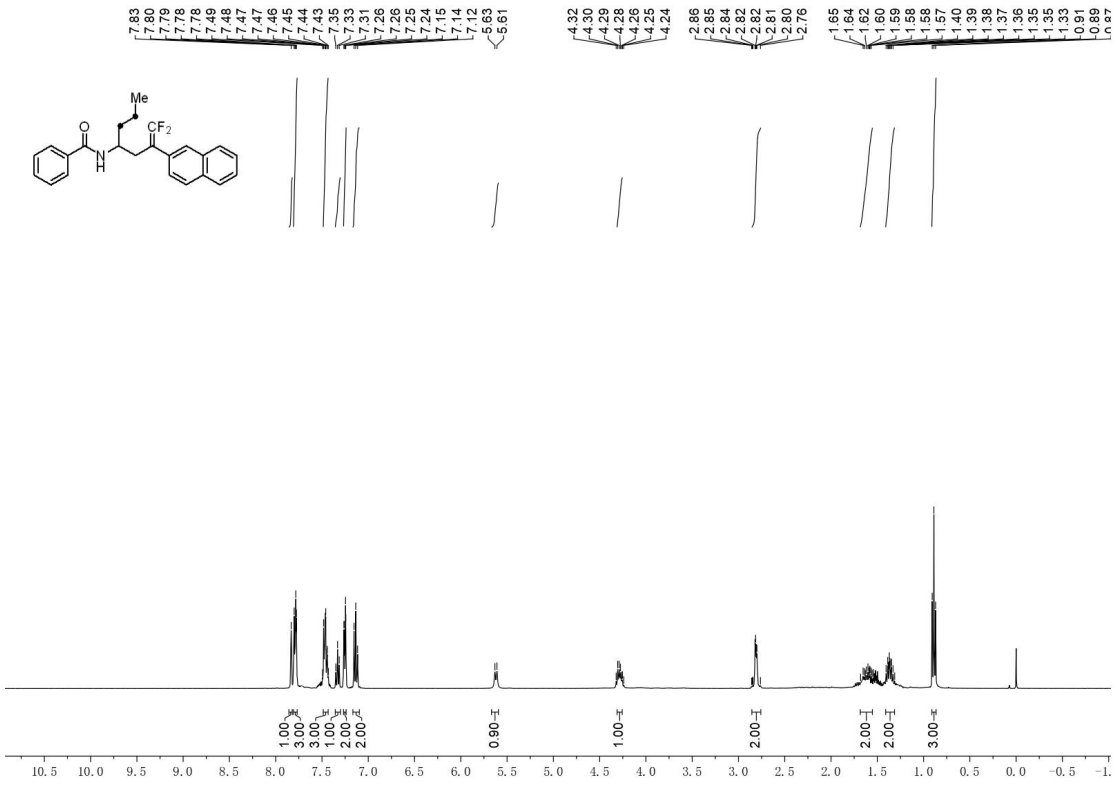

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3o**

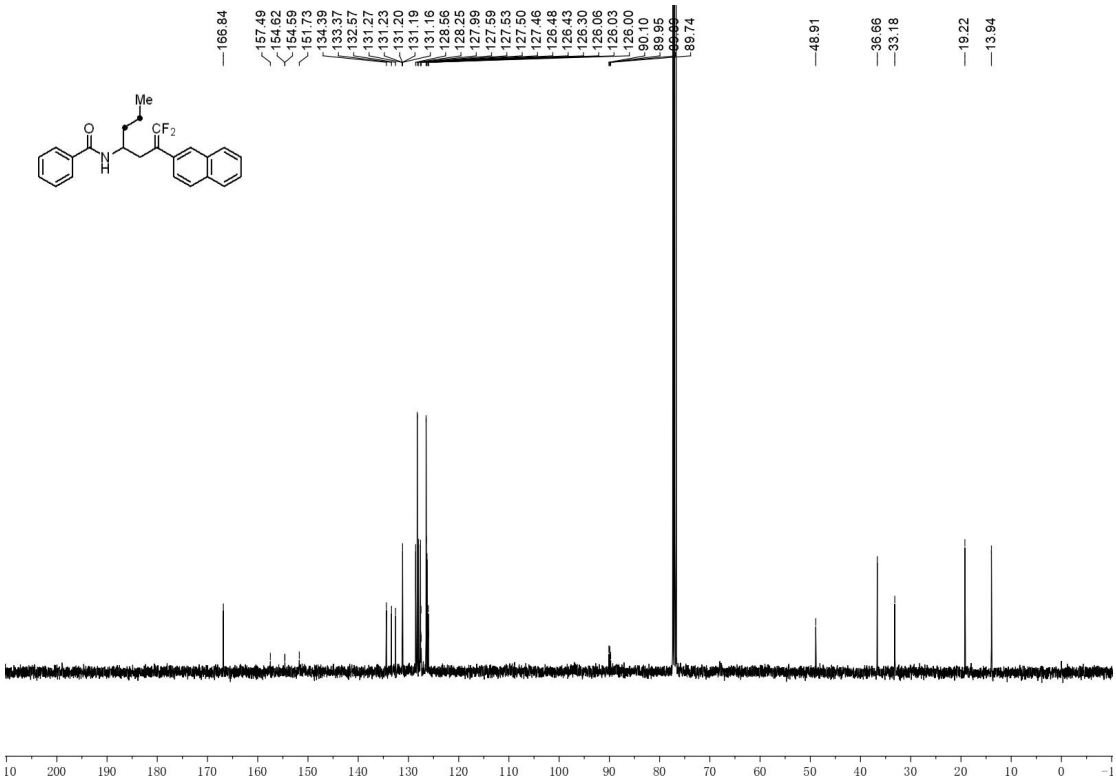

Figure S51. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3o**

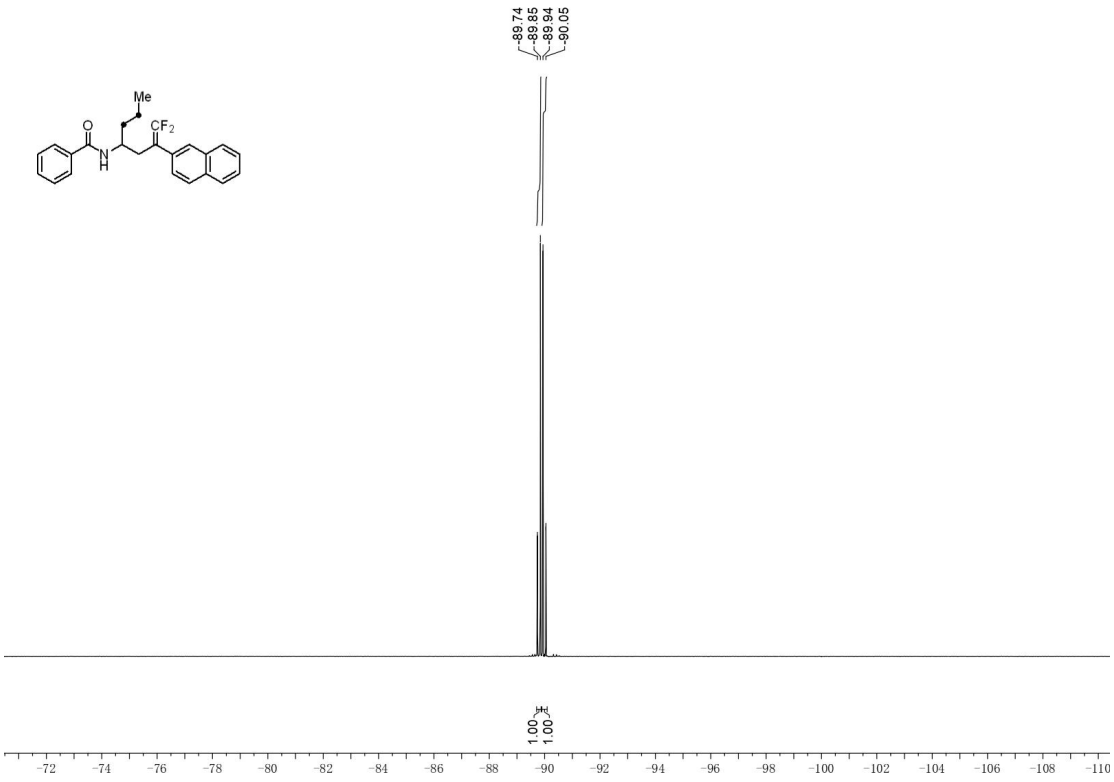

Figure S52. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3o**

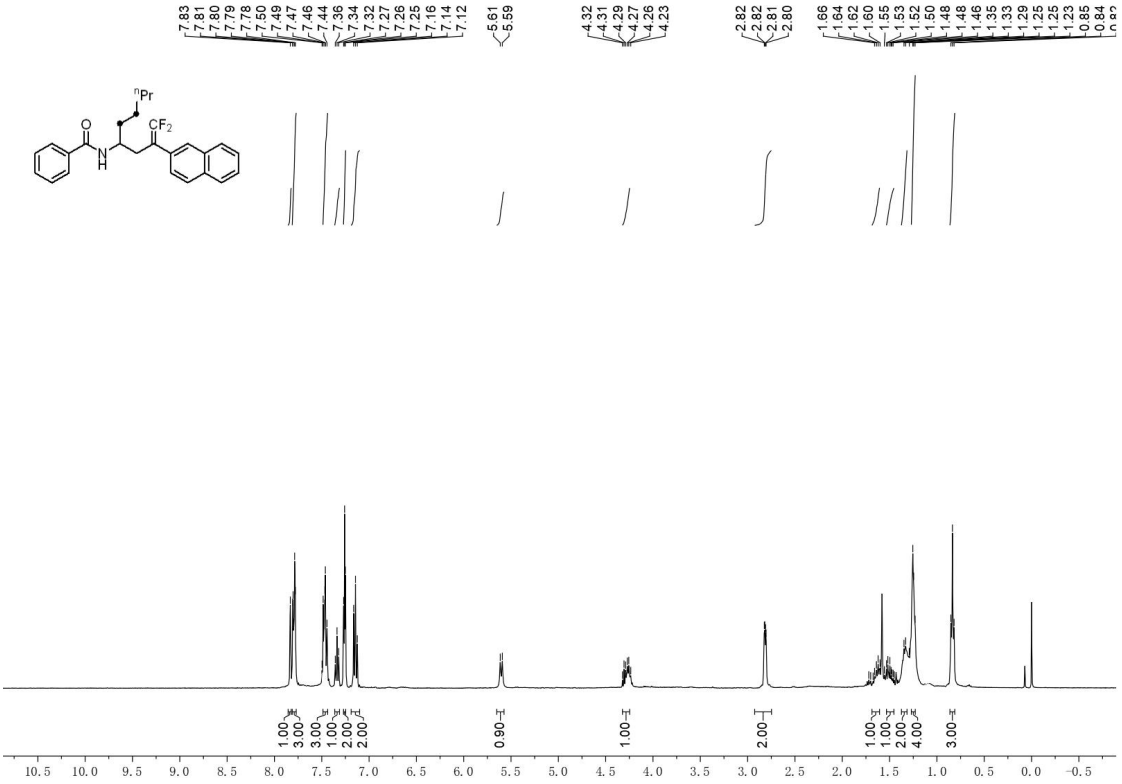

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3p**

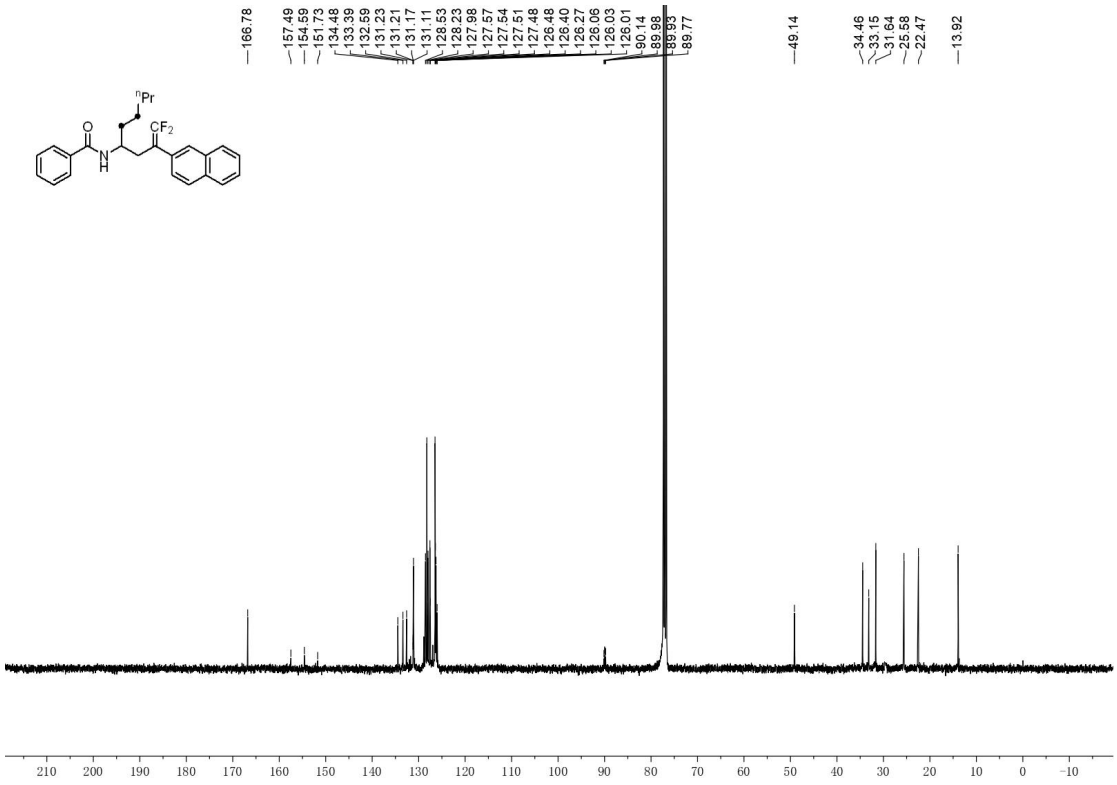

Figure S54. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3p**

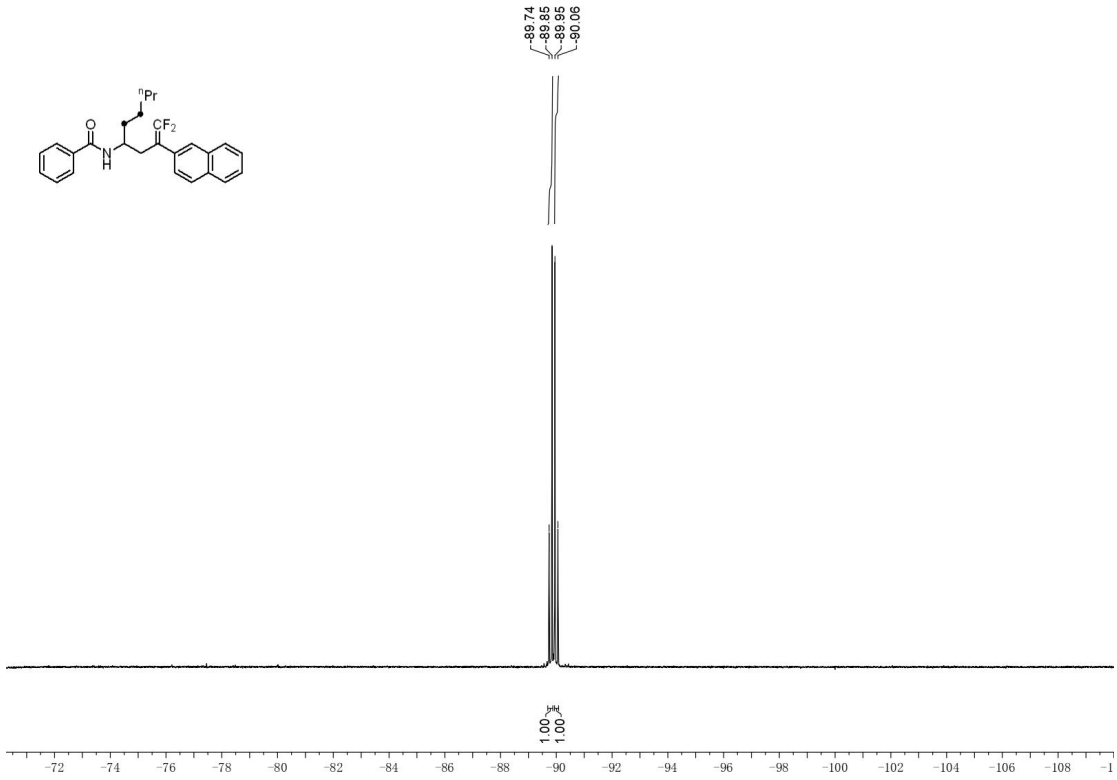

Figure S55. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3p**

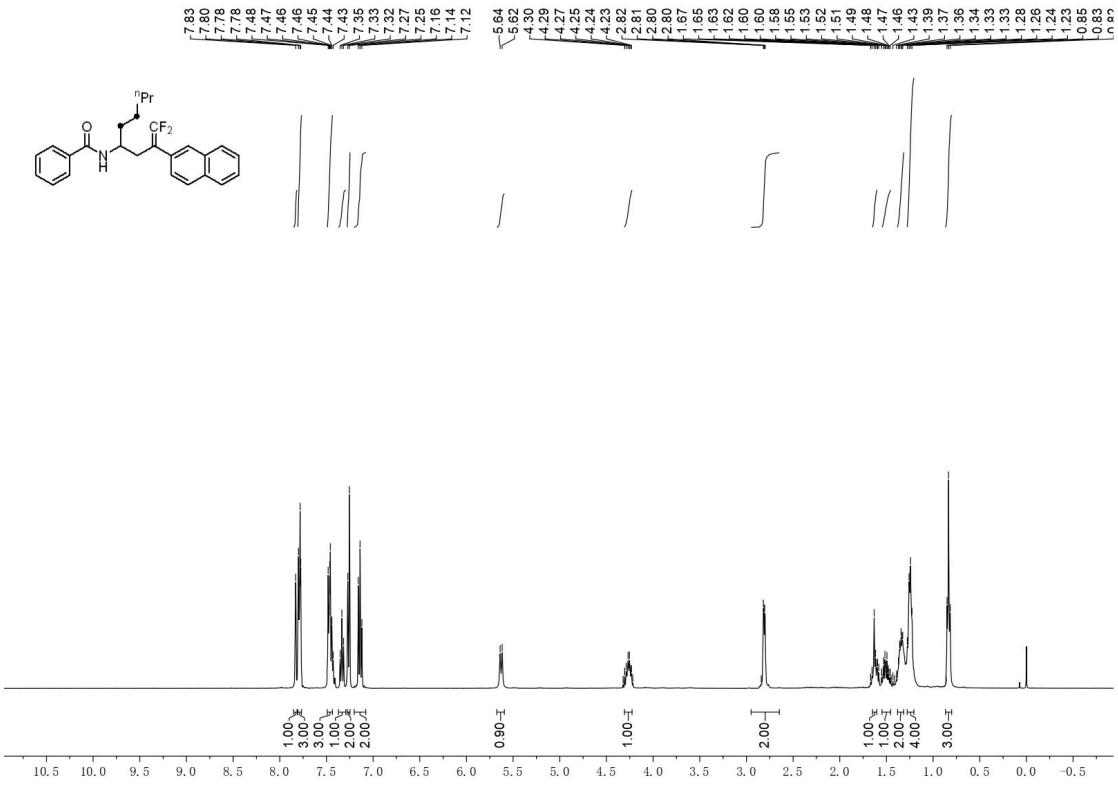

Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3q**

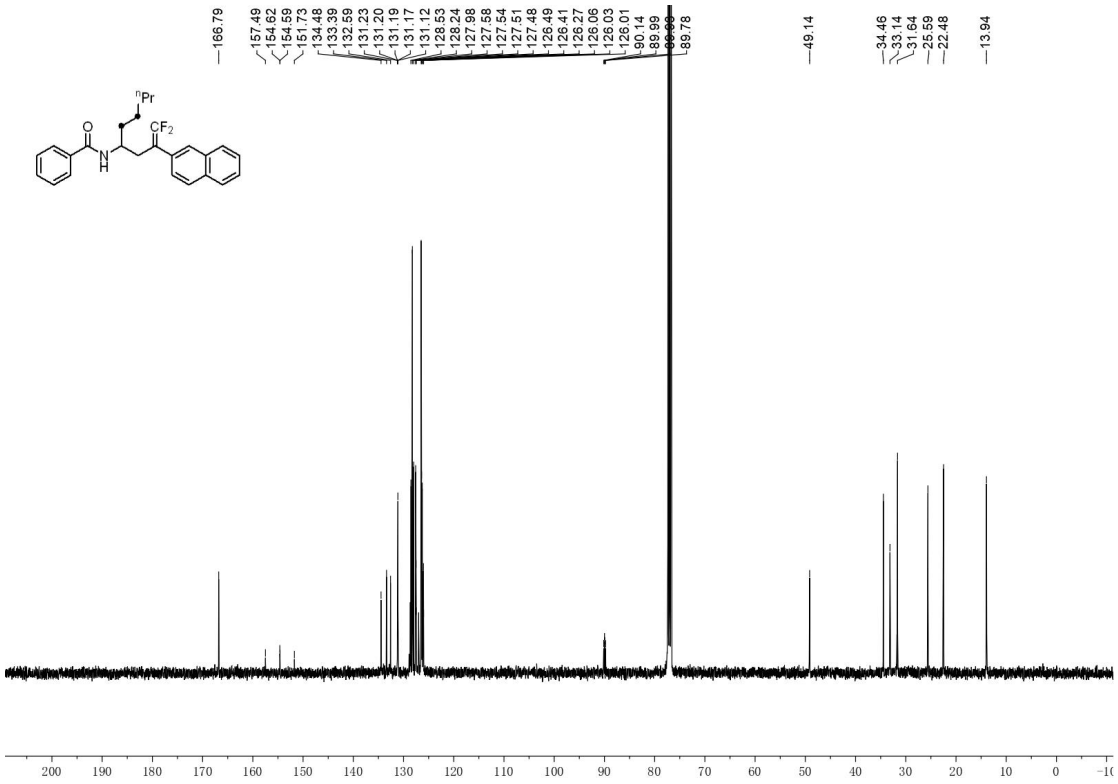

Figure S57. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3q**

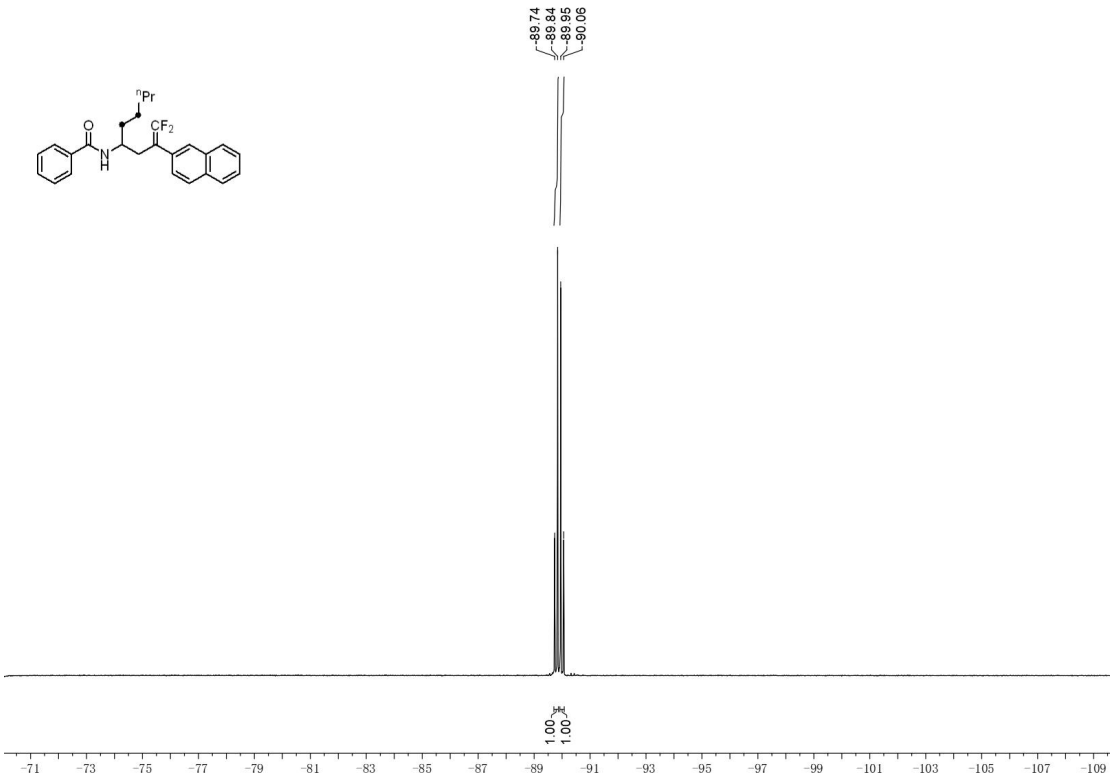

Figure S58. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3q**

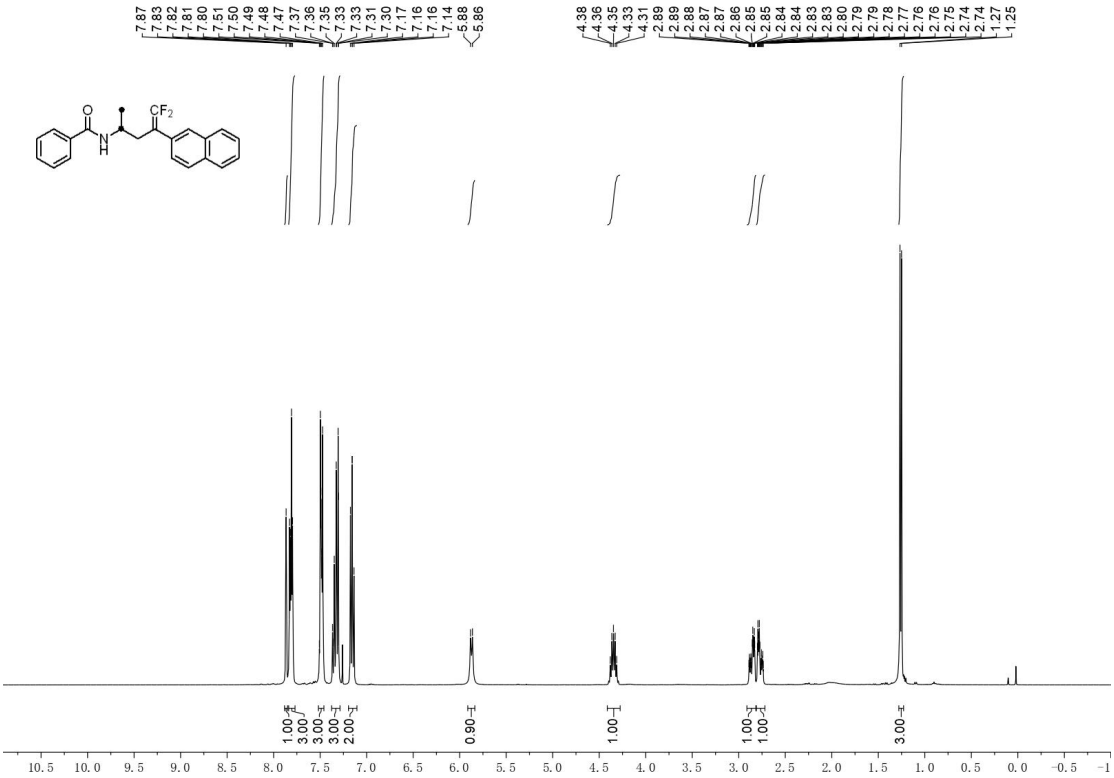

Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3r**

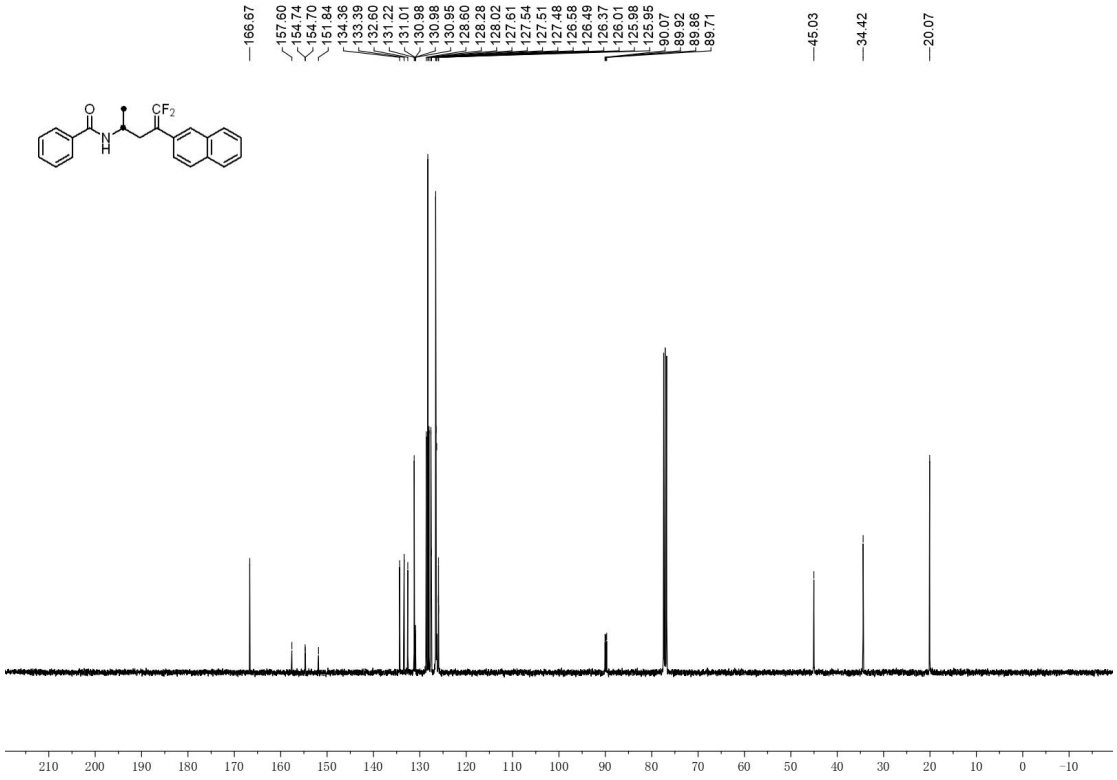

Figure S60. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3r**

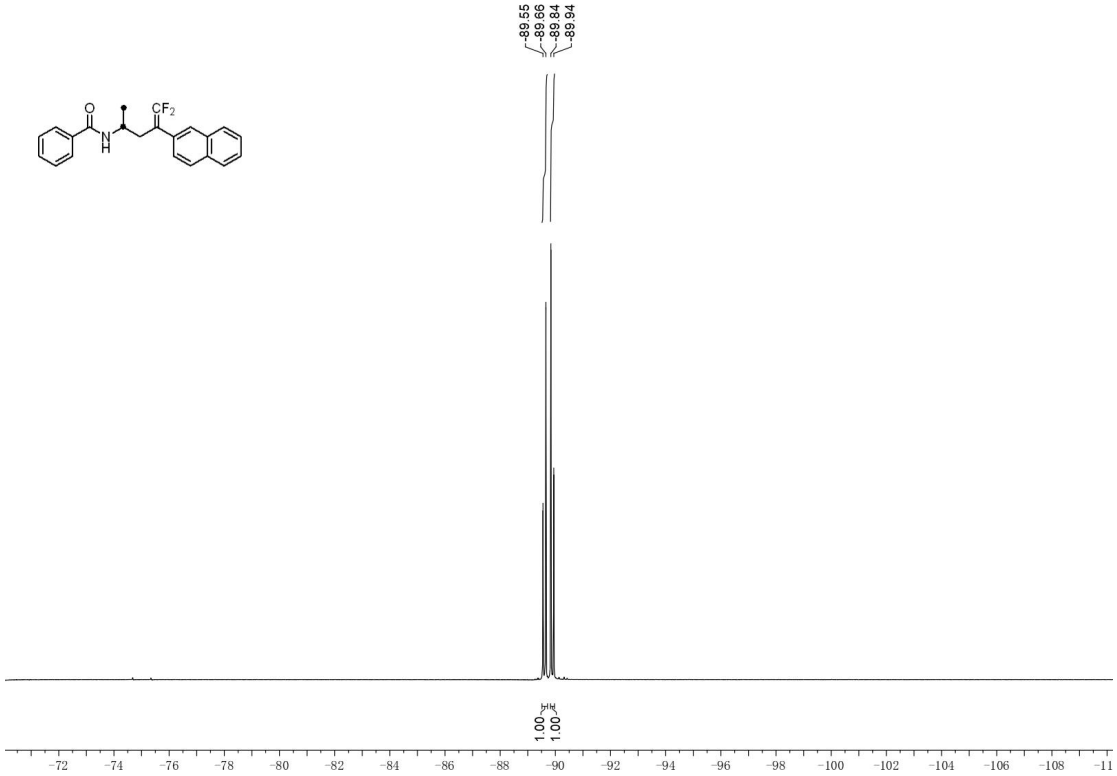

Figure S61. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3r**

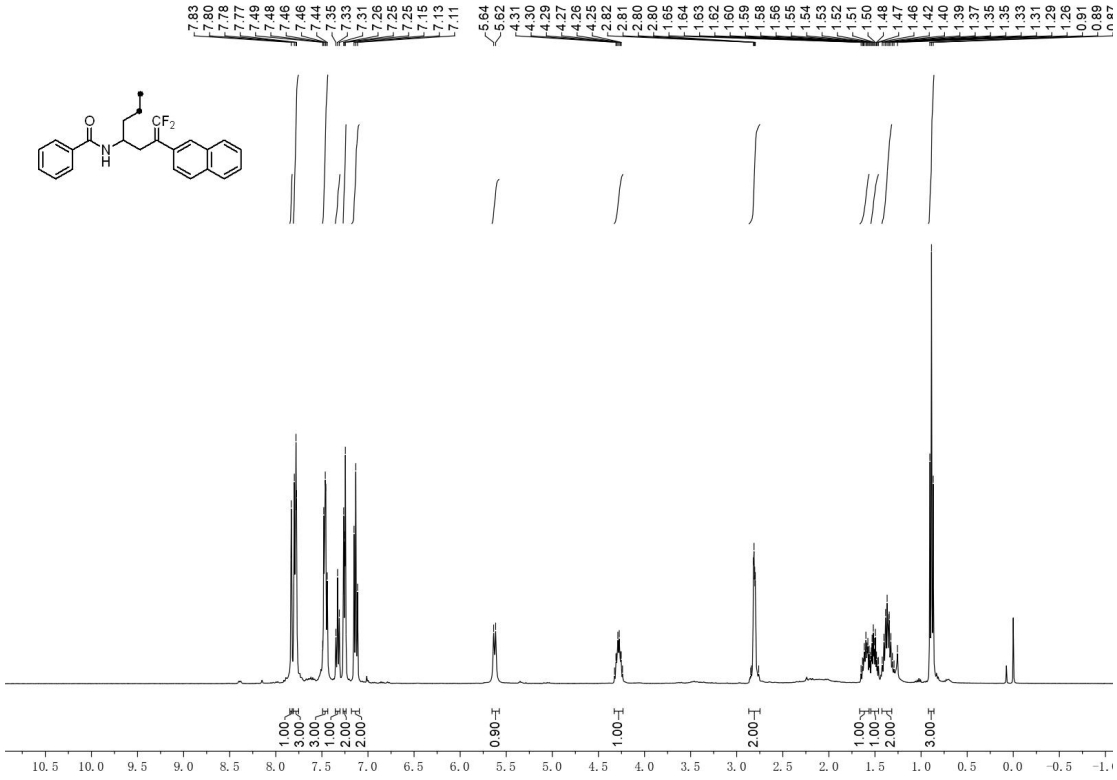

Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3s**

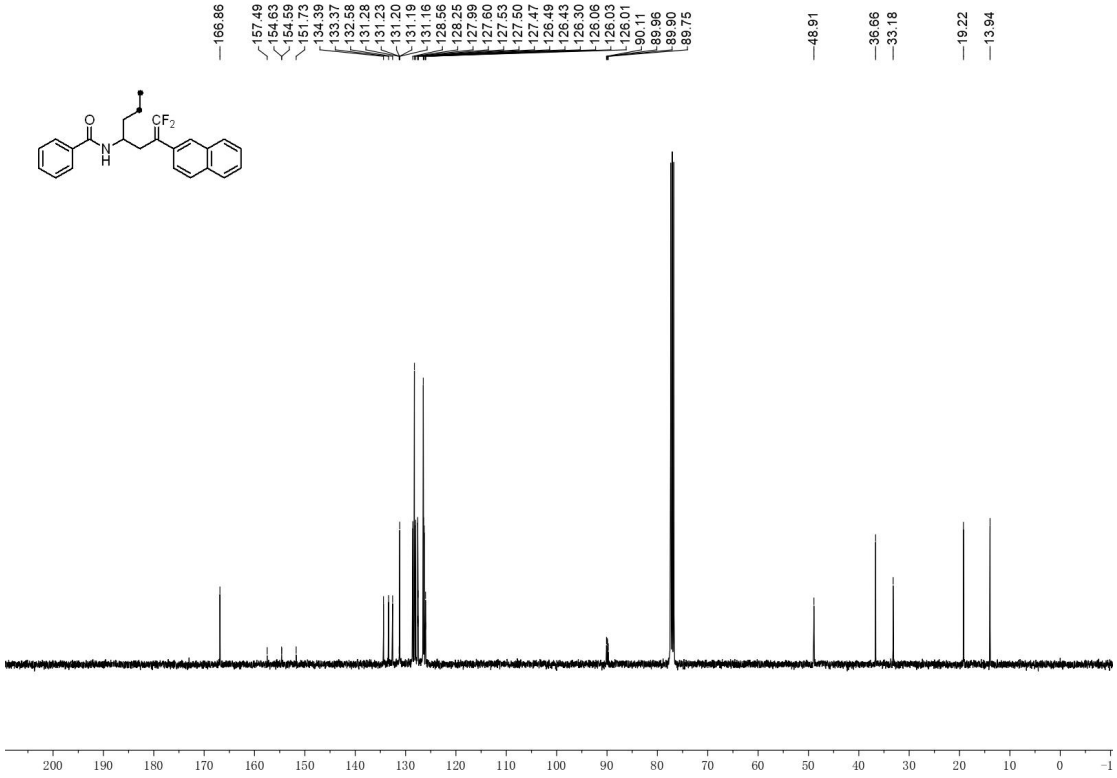

Figure S63. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3s**

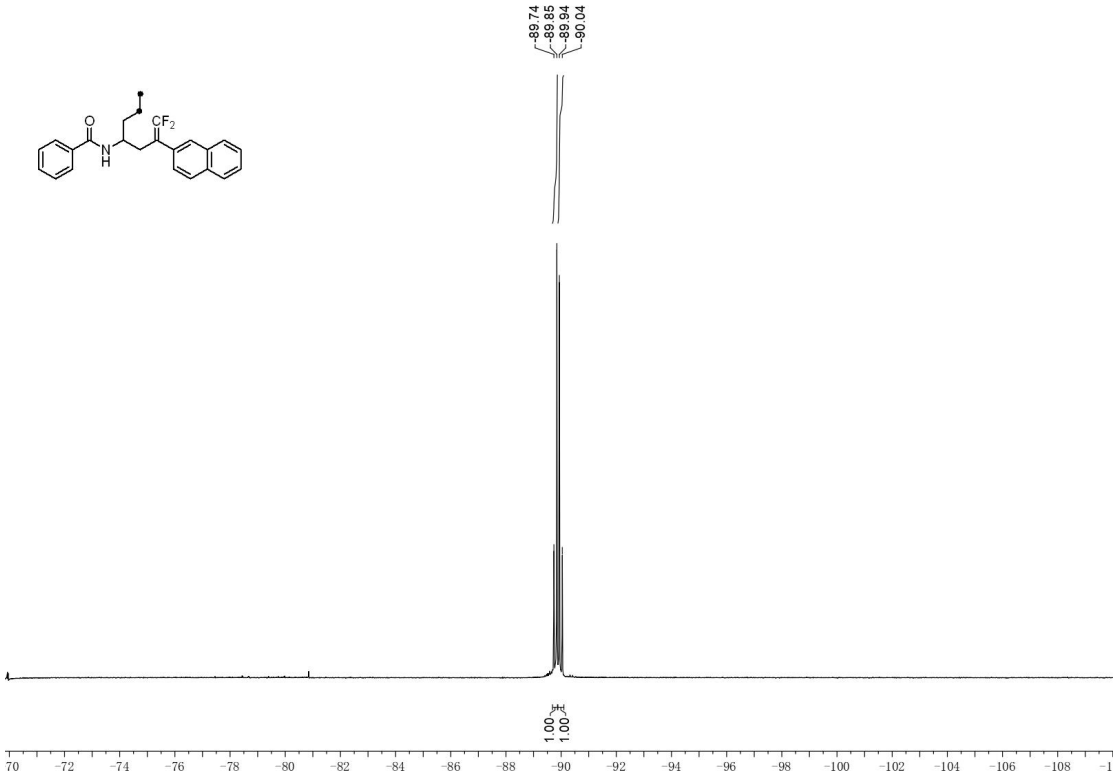

Figure S64. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3s**

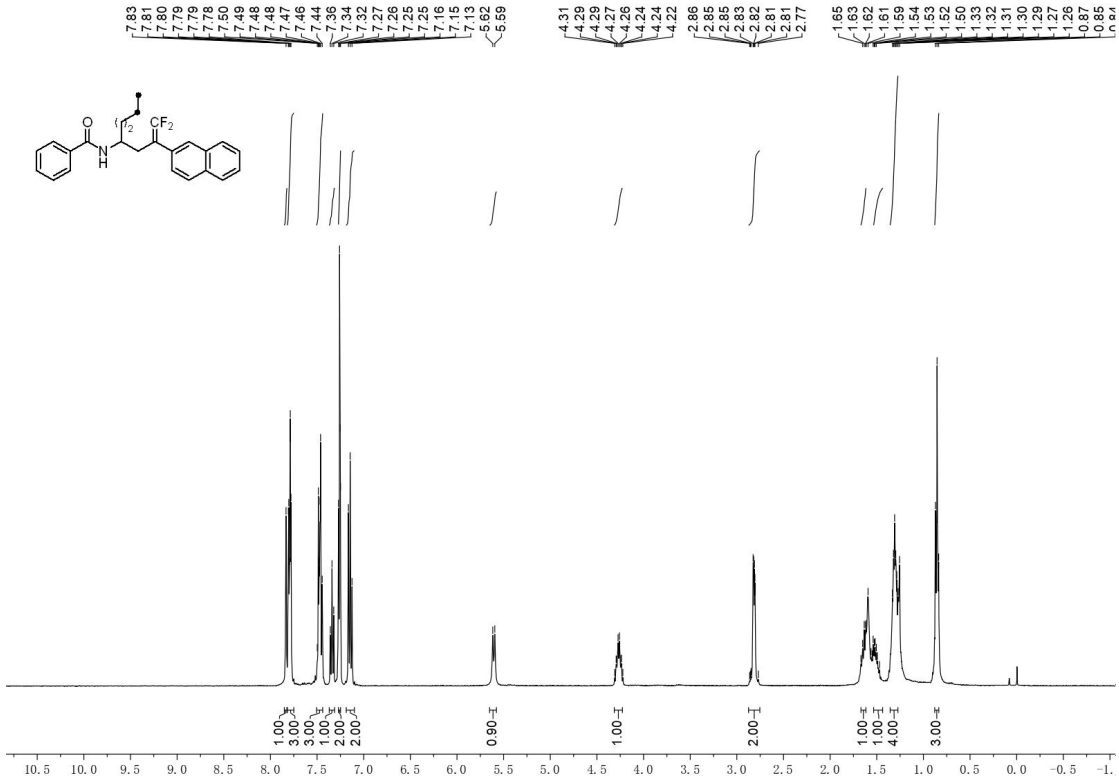

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3t**

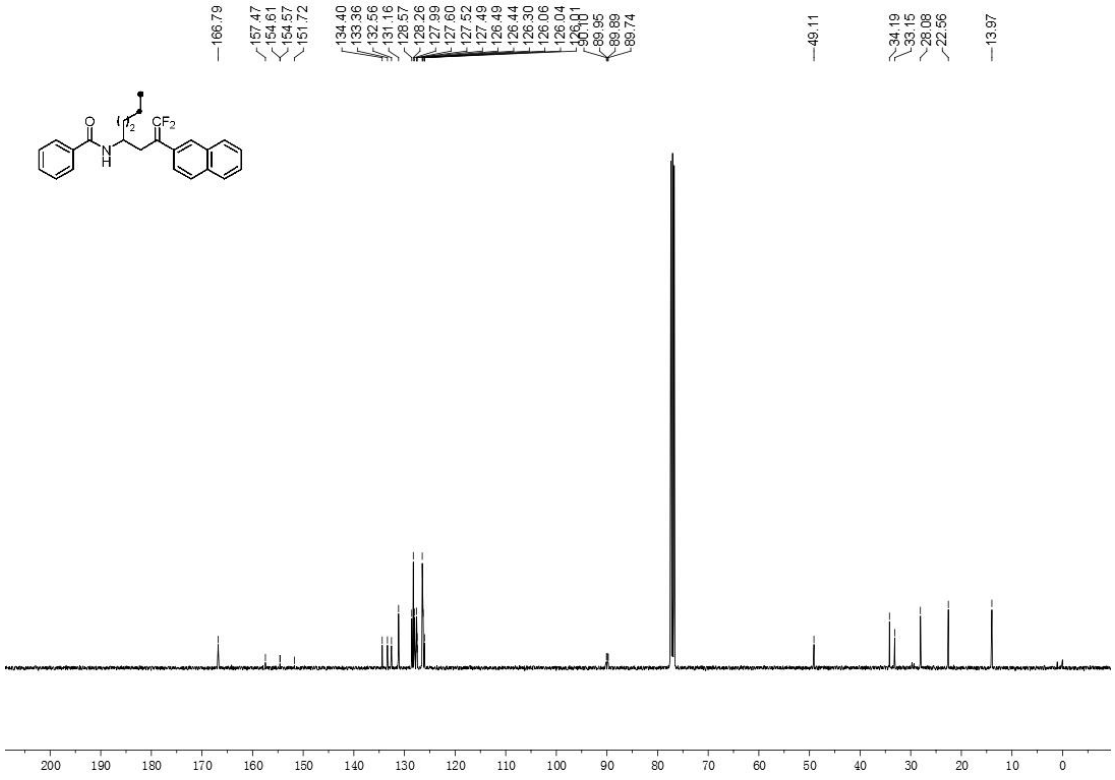

Figure S66. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3t**

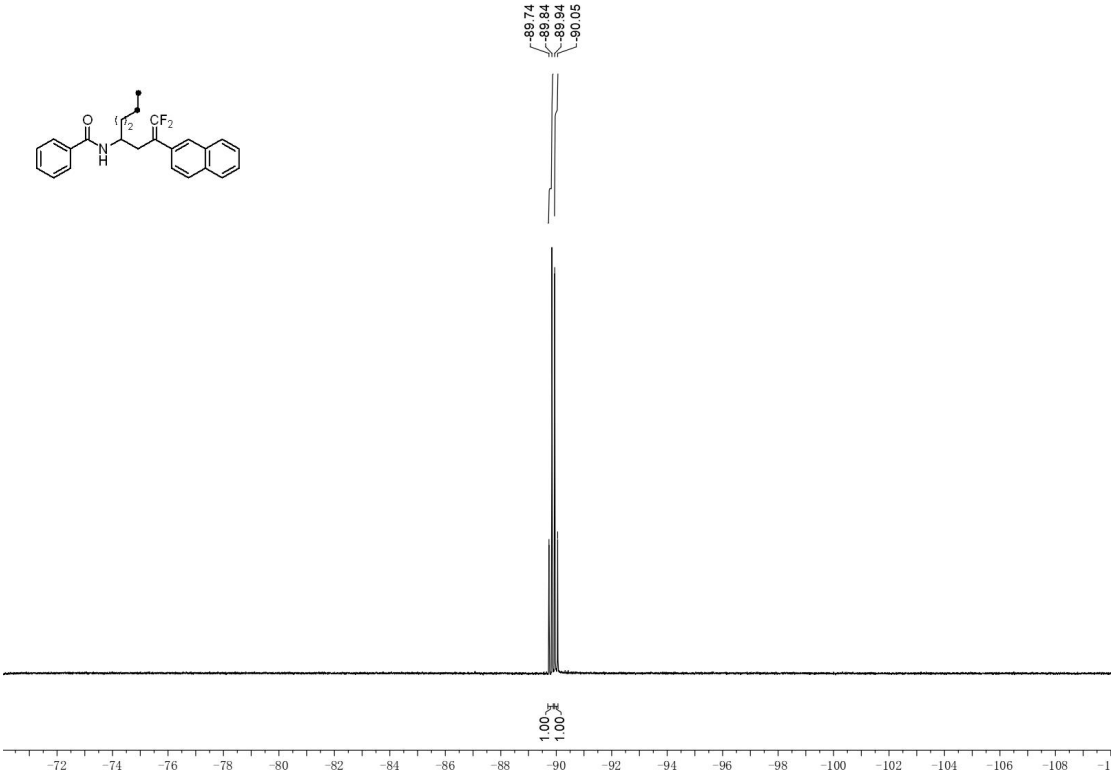

Figure S67. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3t**

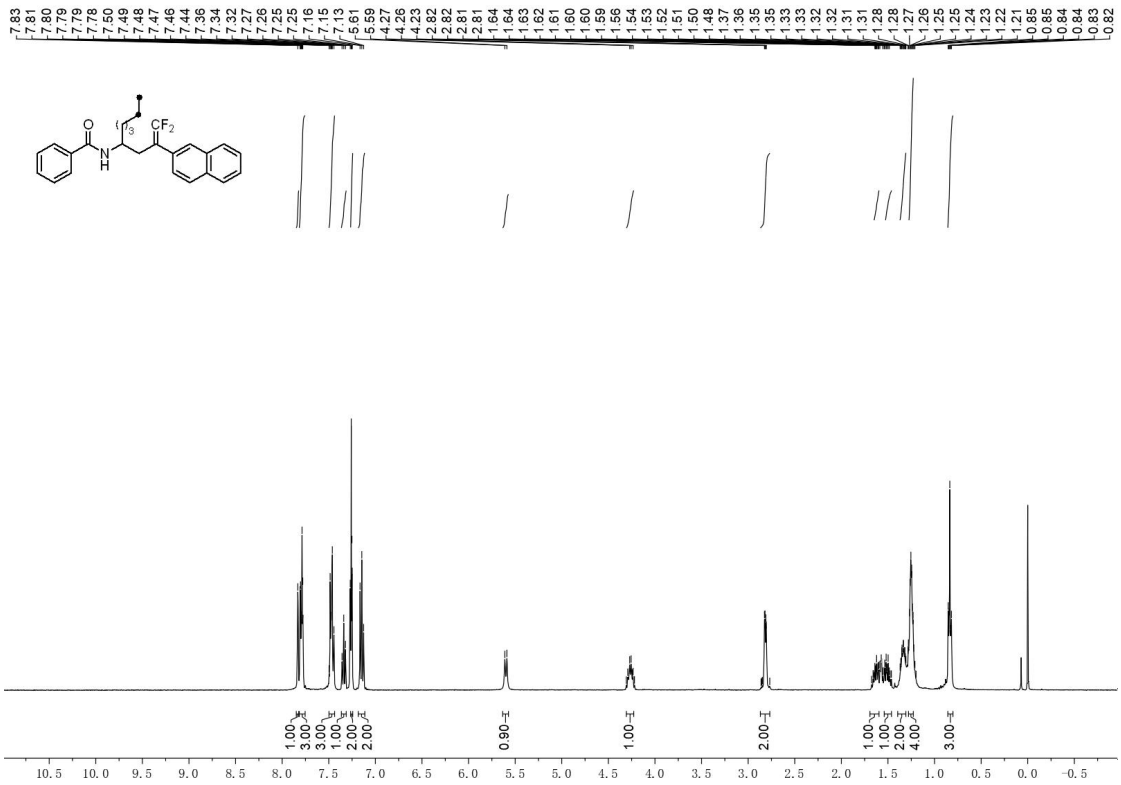

Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3u**

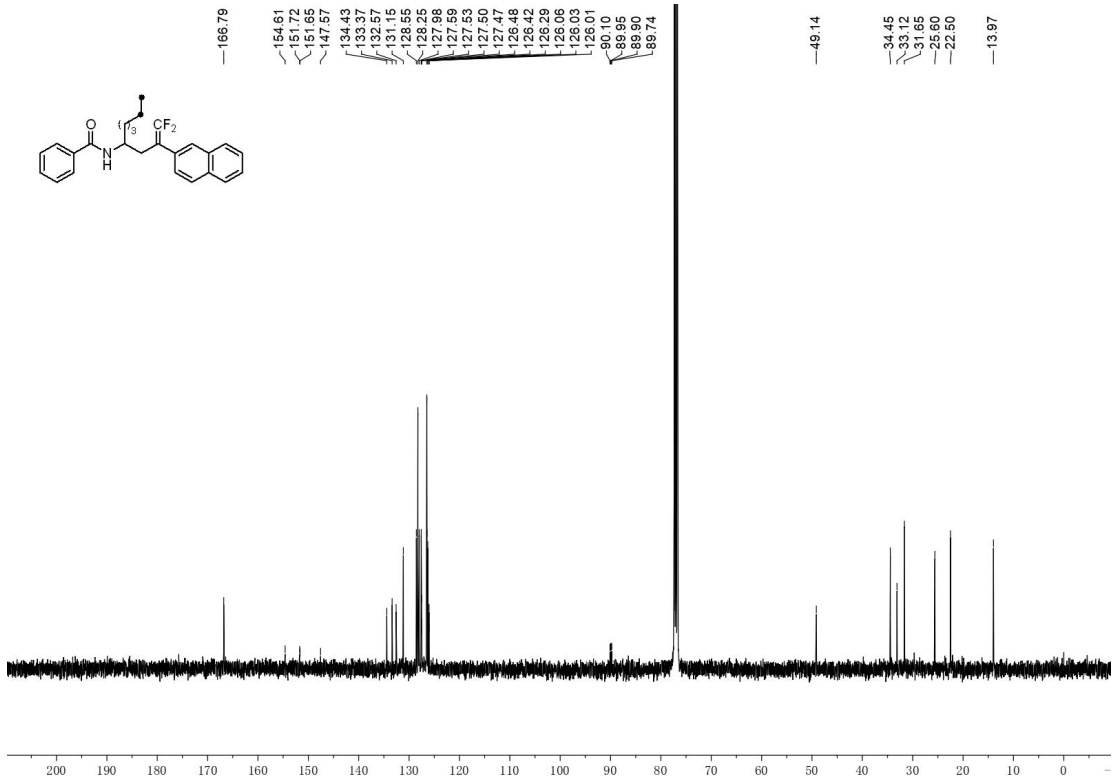

Figure S69. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3u**

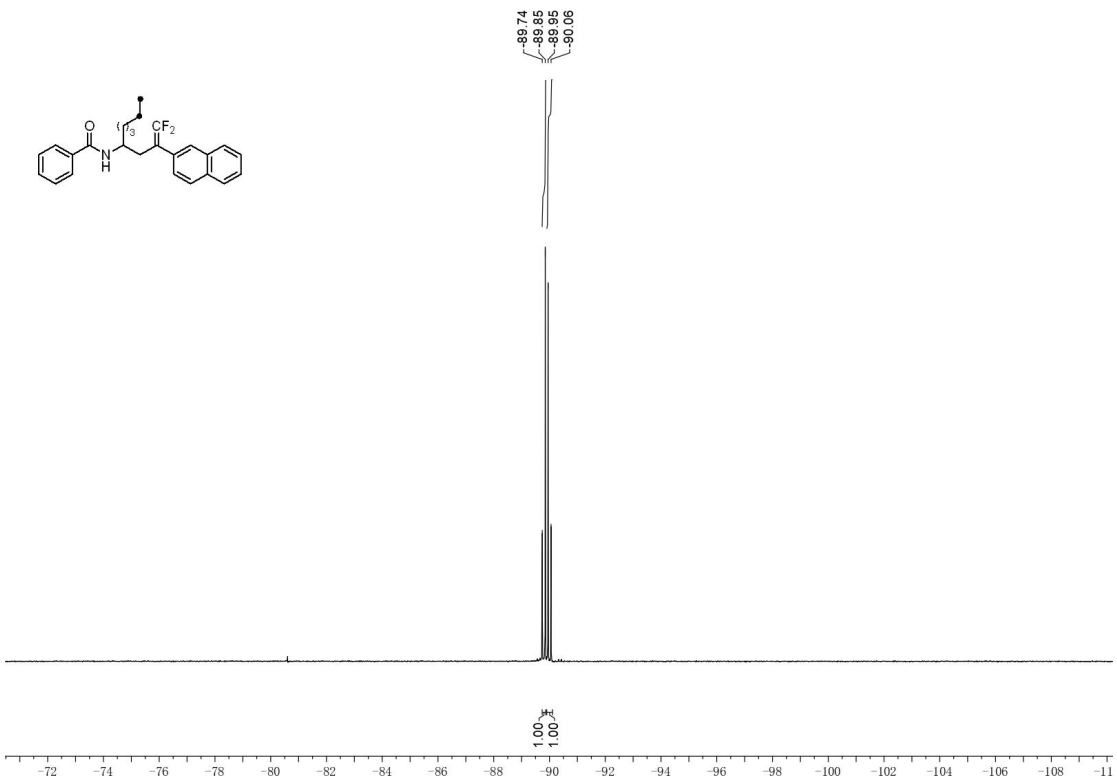

Figure S70. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3u**

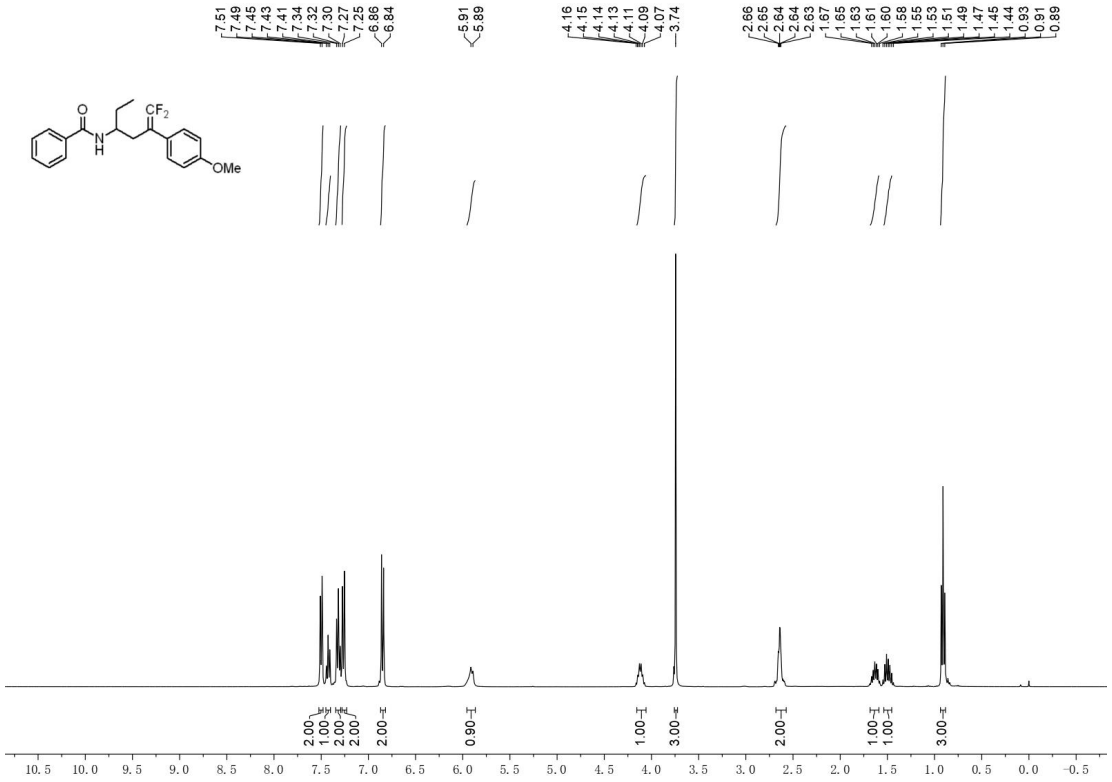

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**

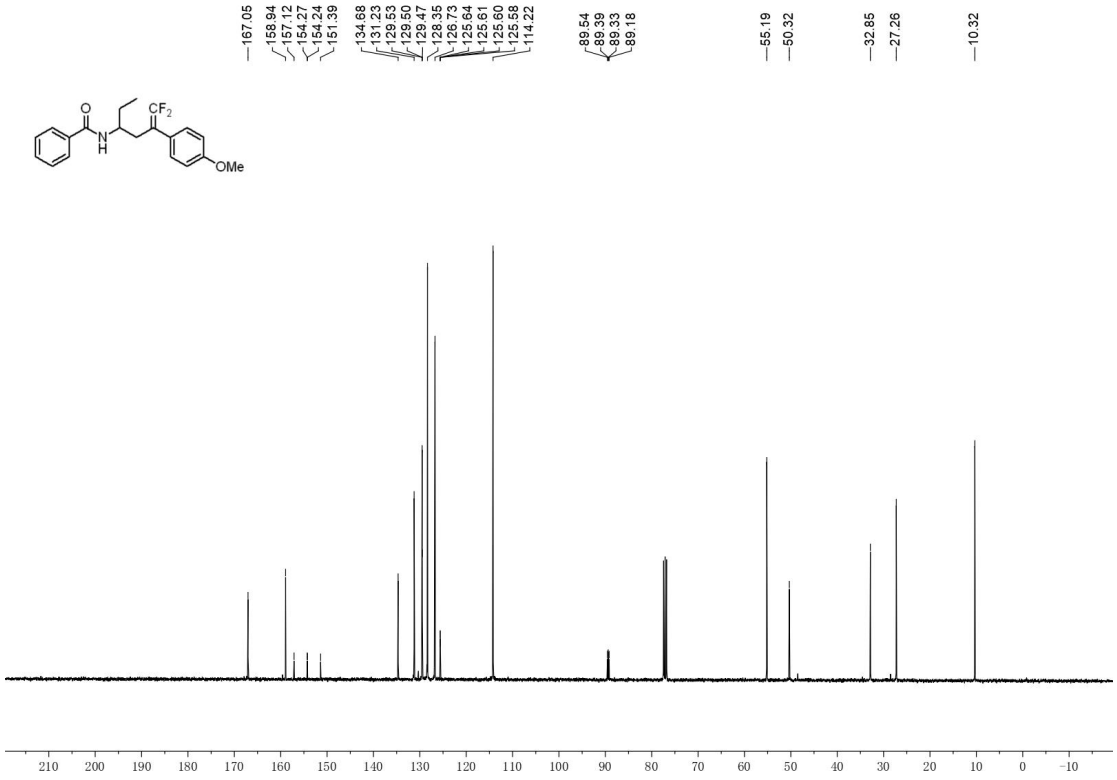

Figure S72. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aa**

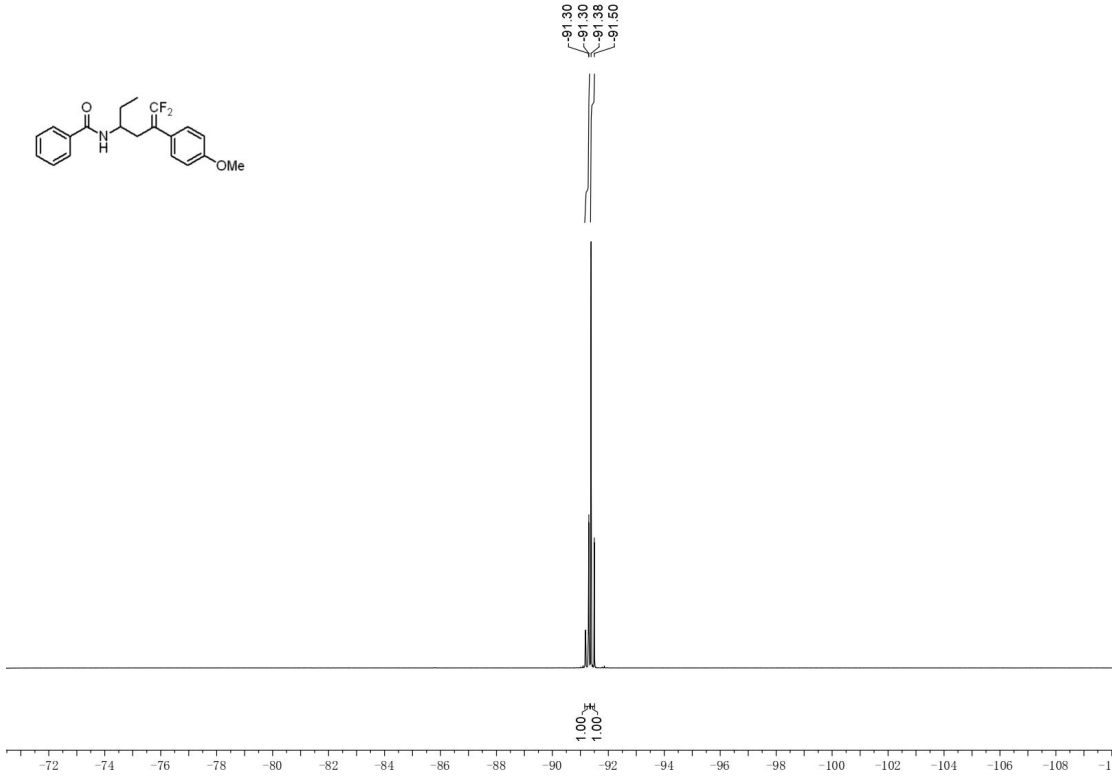

Figure S73. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3aa**

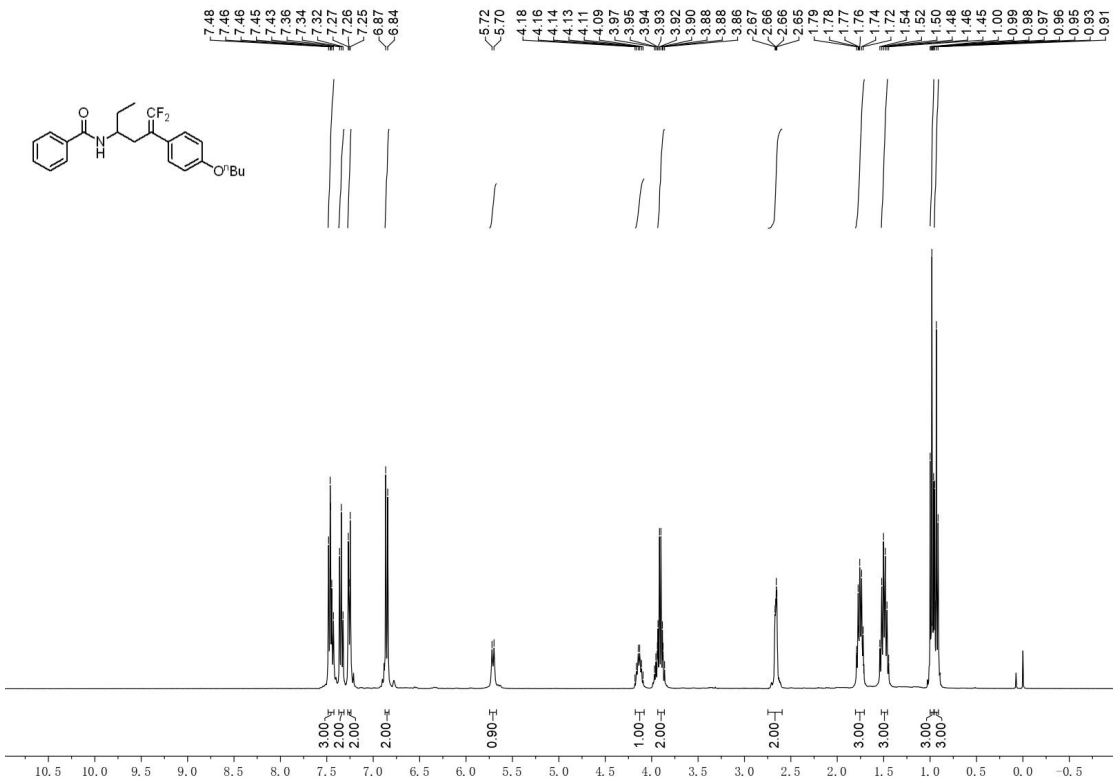

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ab**

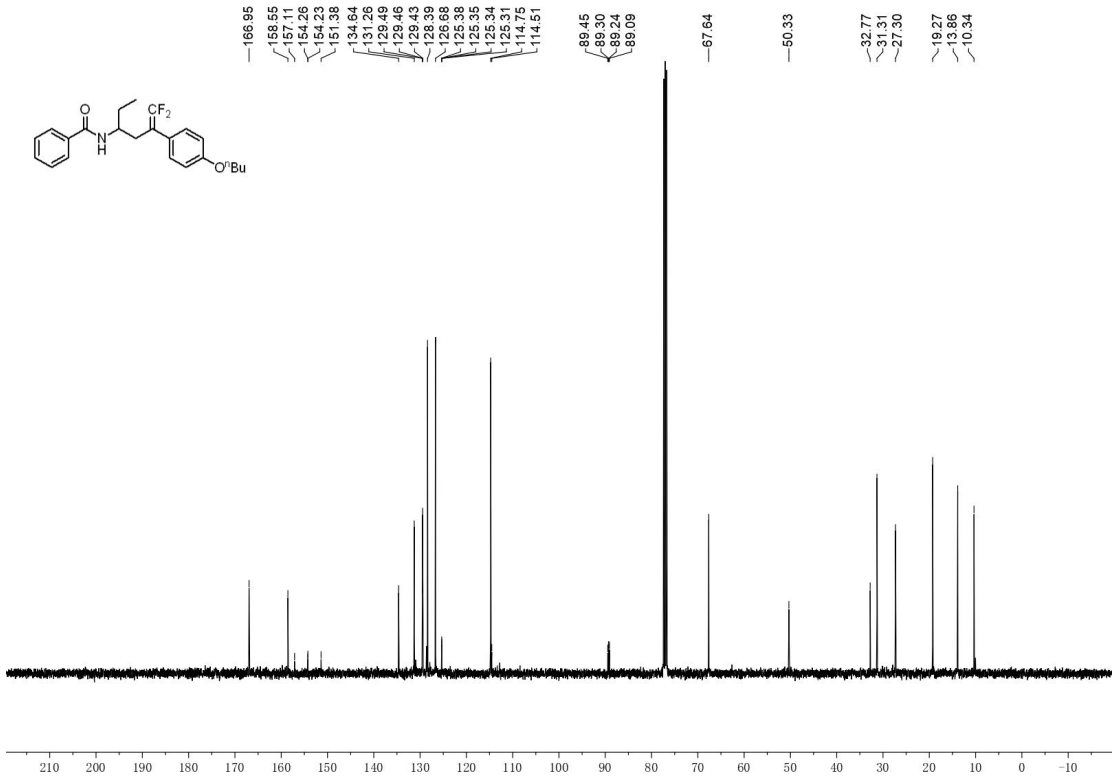

Figure S75. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ab**

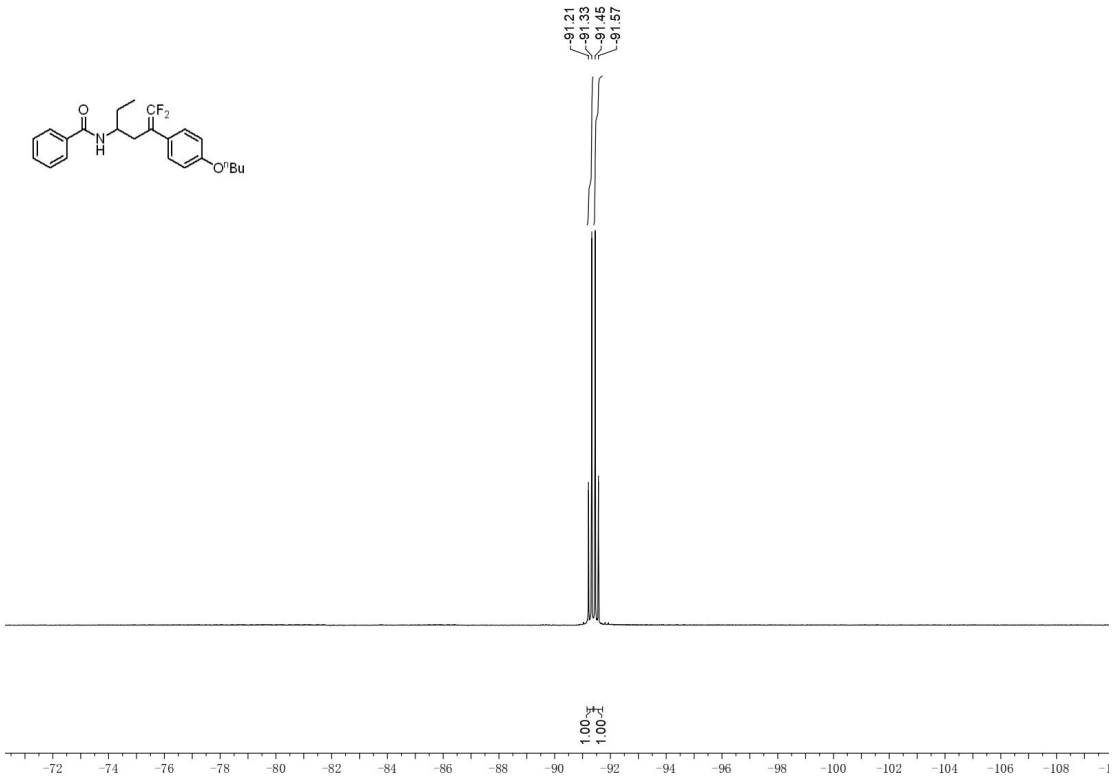

Figure S76. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ab**

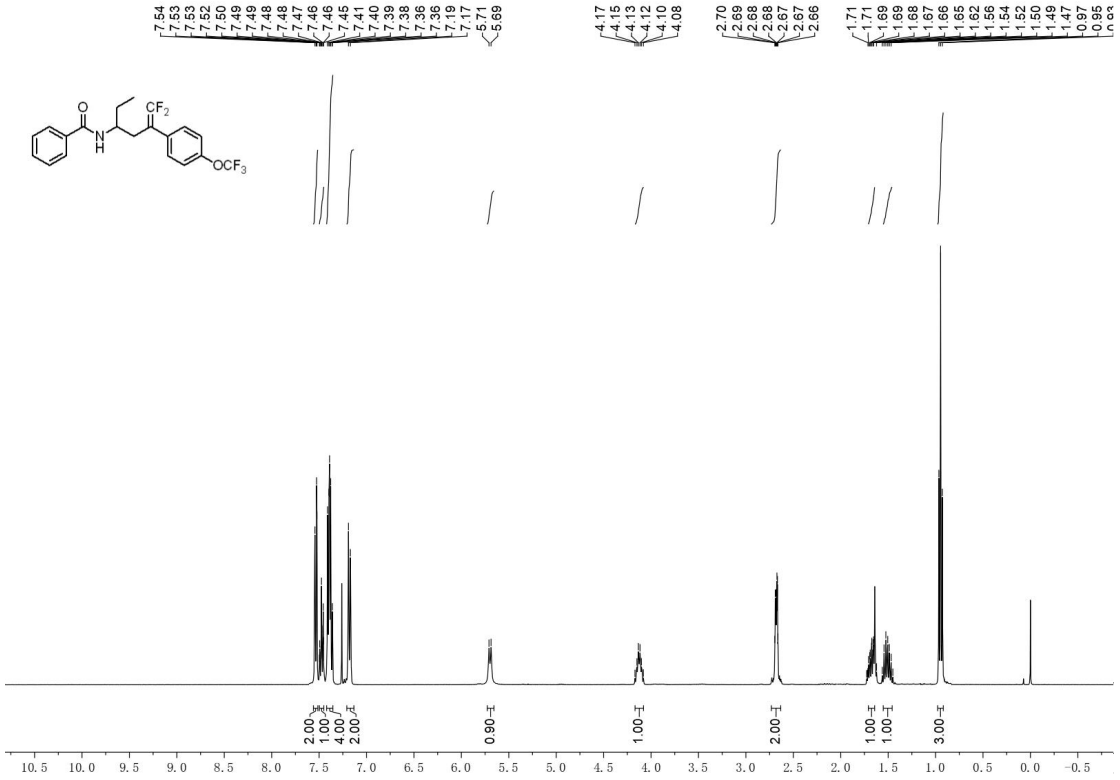

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ac**

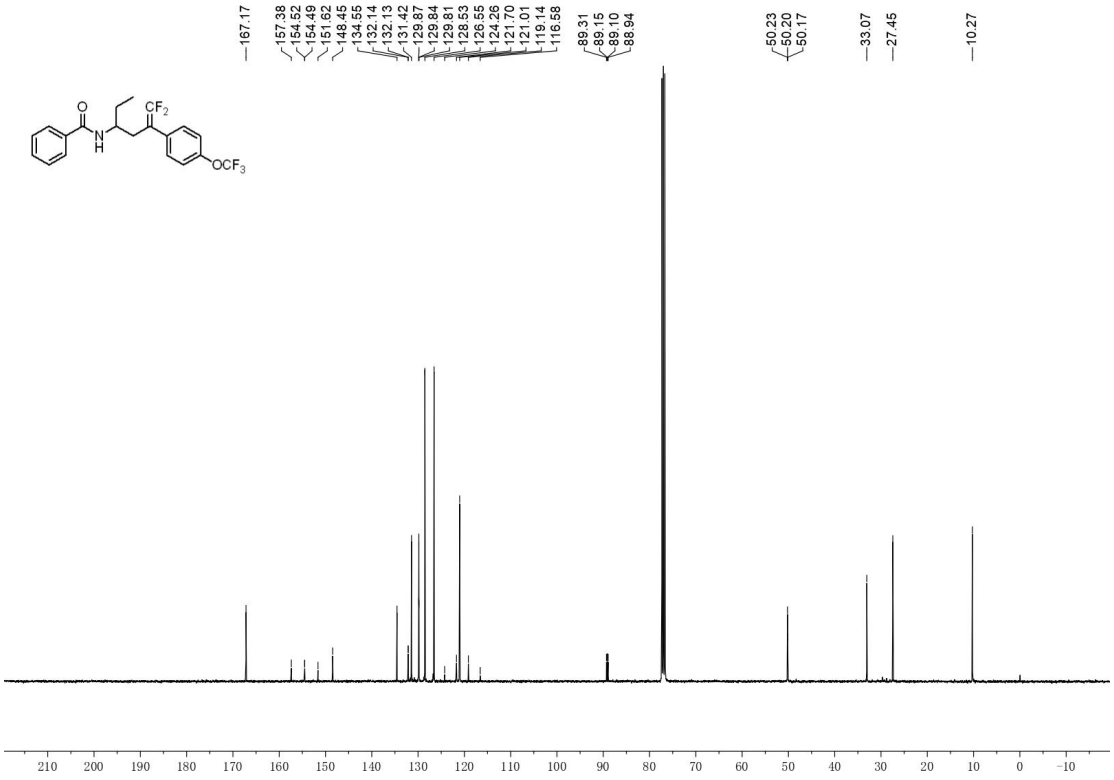

Figure S78. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ac**

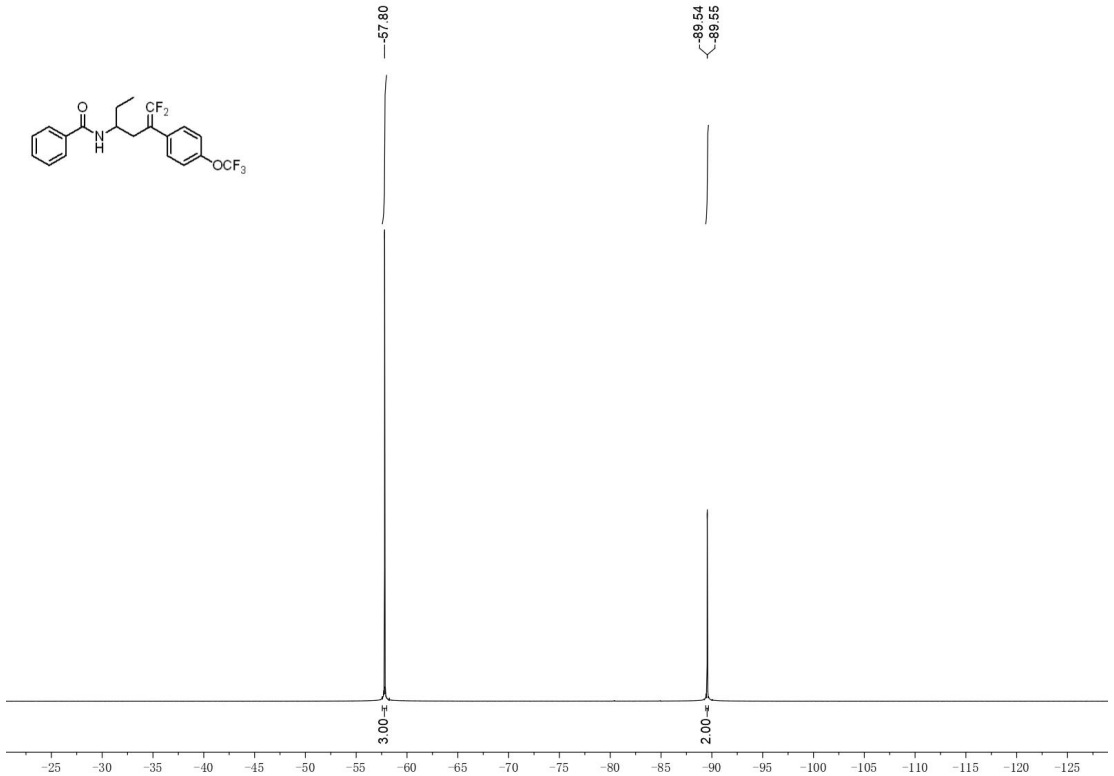

Figure S79. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ac**

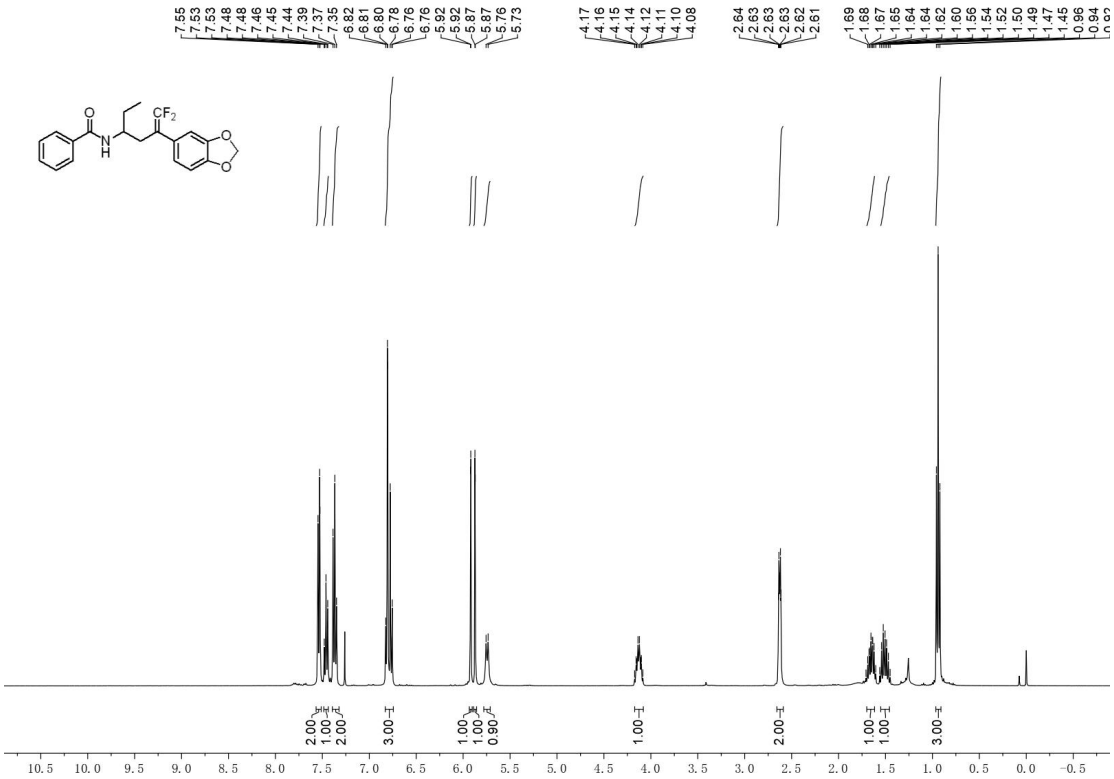

Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ad**

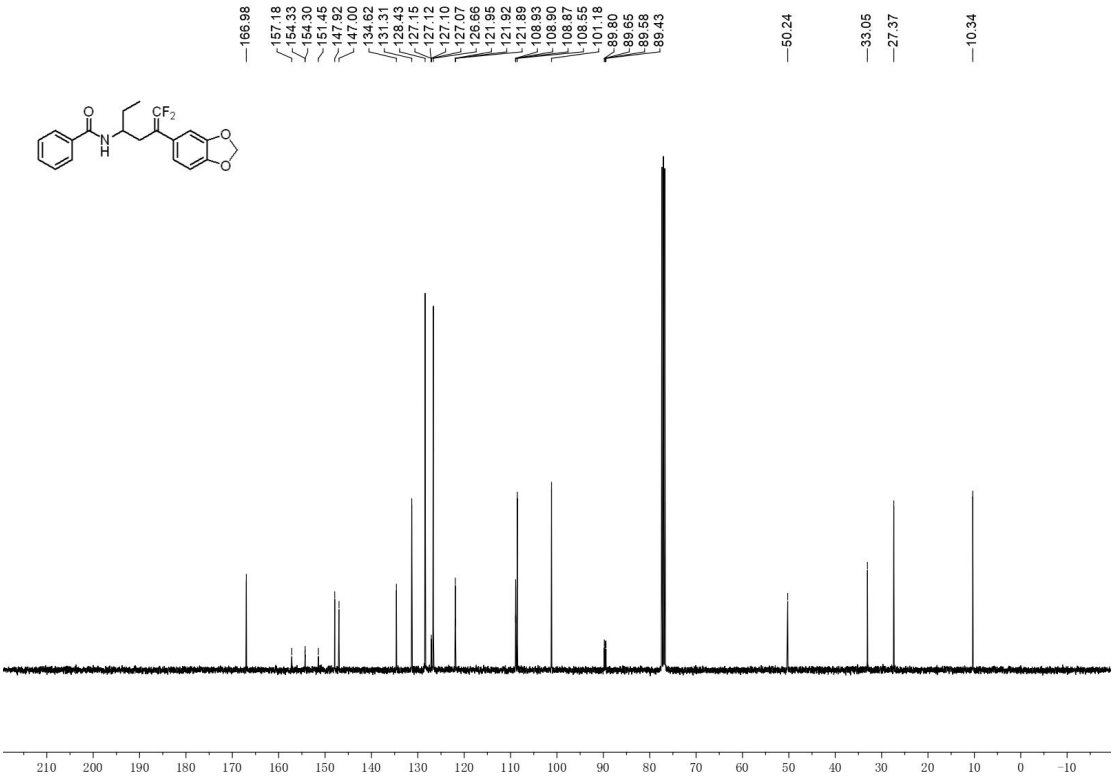

Figure S81. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ad**

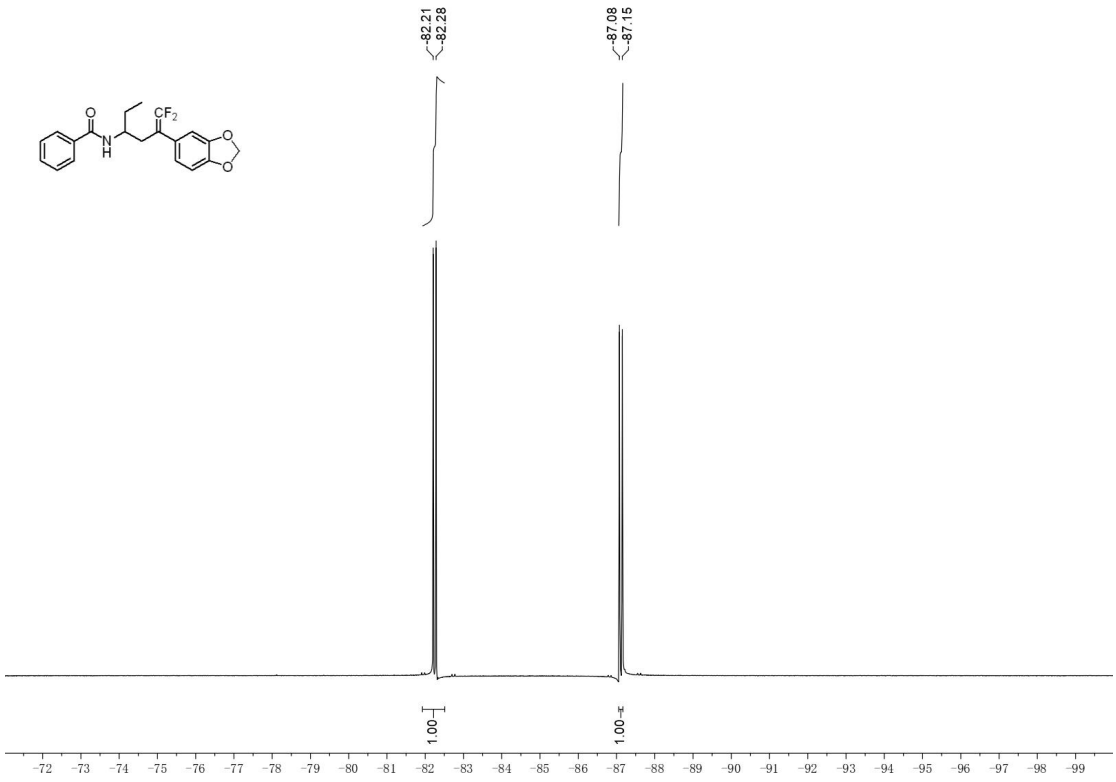

Figure S82. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ad**

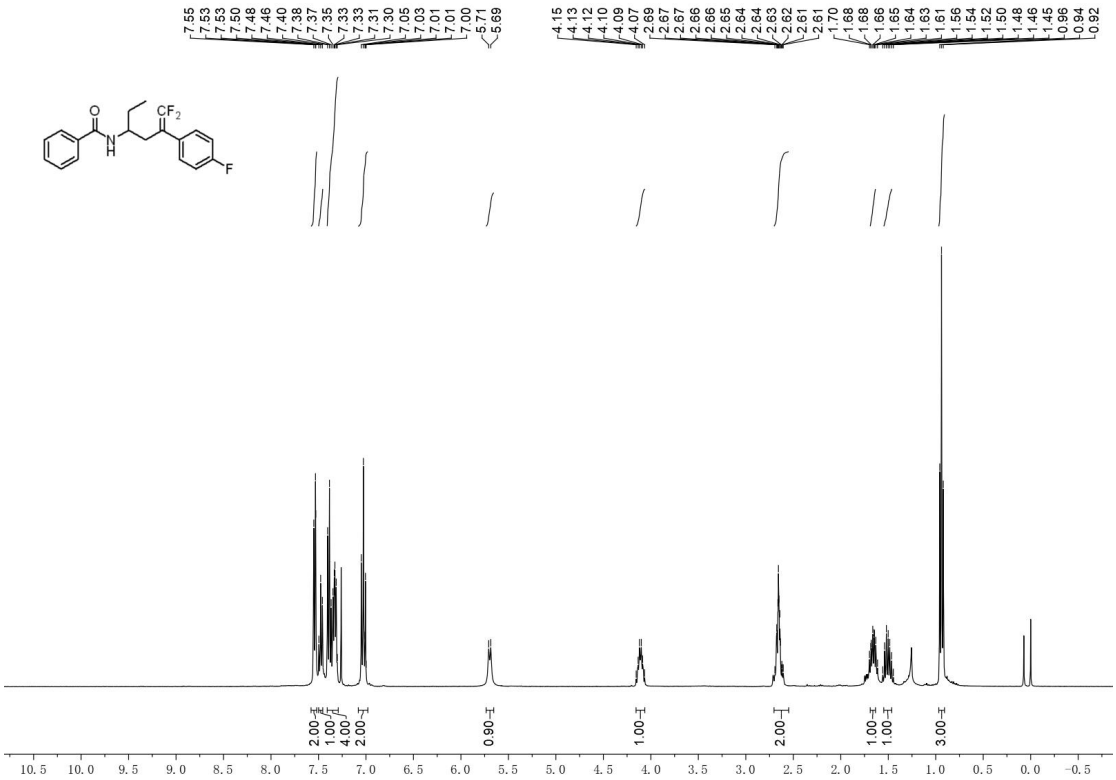

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ae**

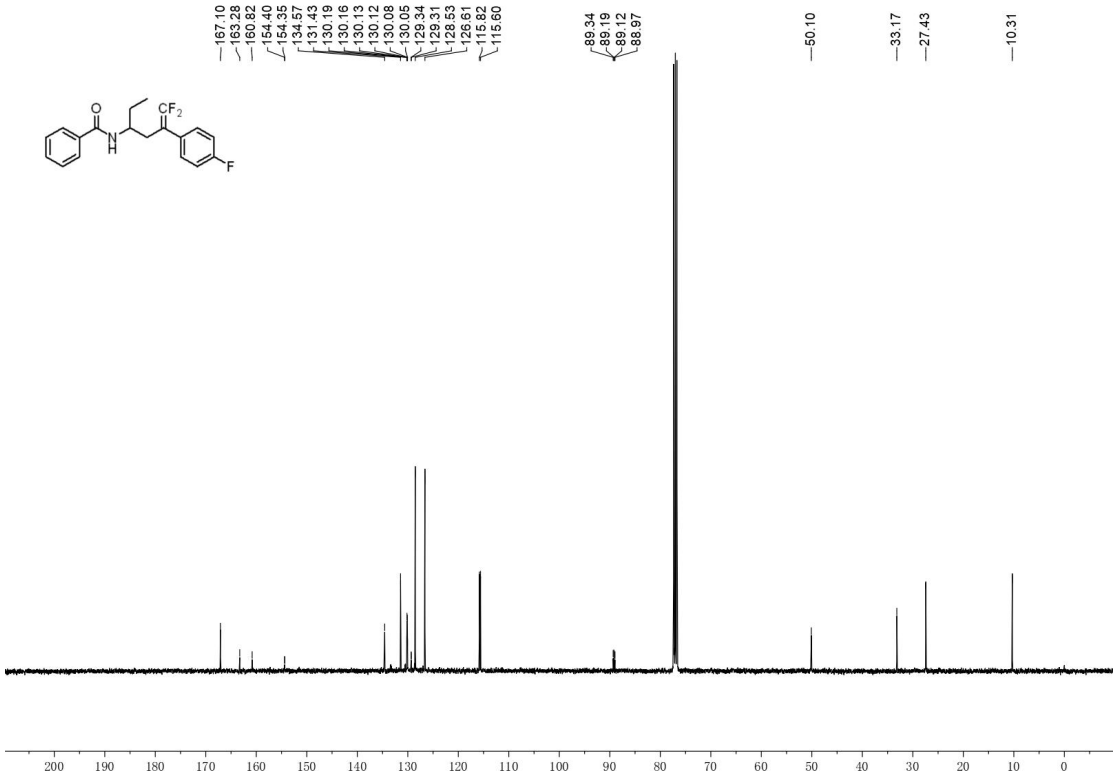

Figure S84. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ae**

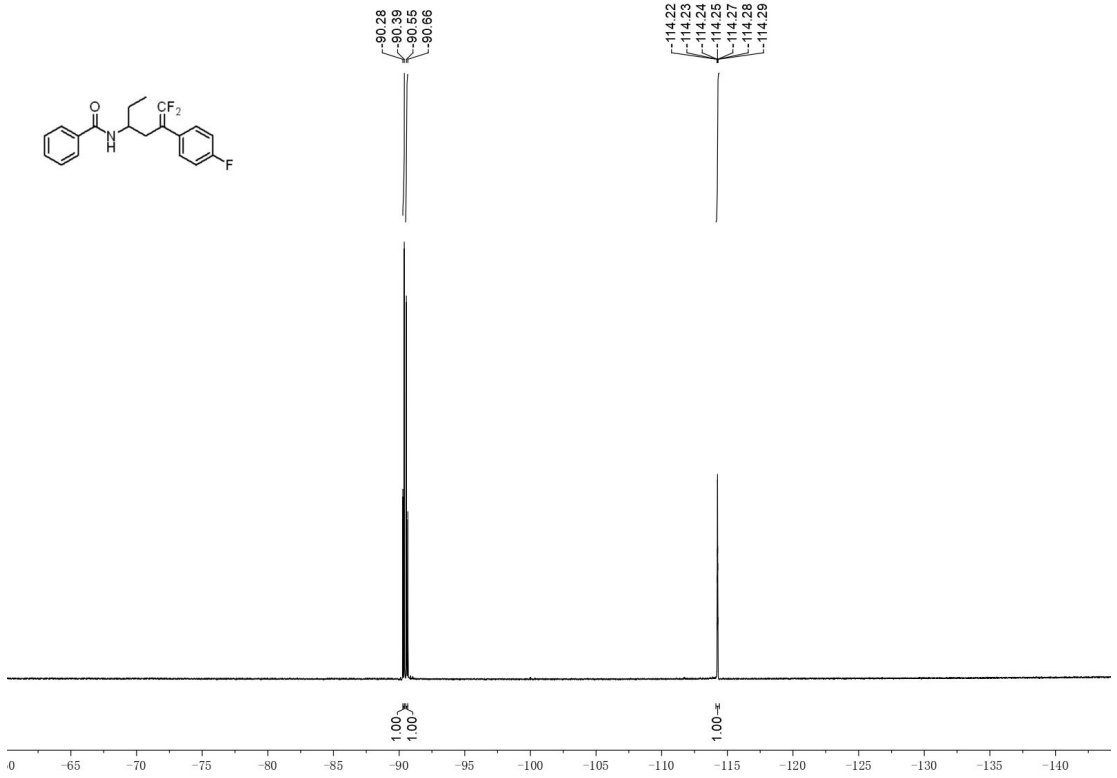

Figure S85. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ae**

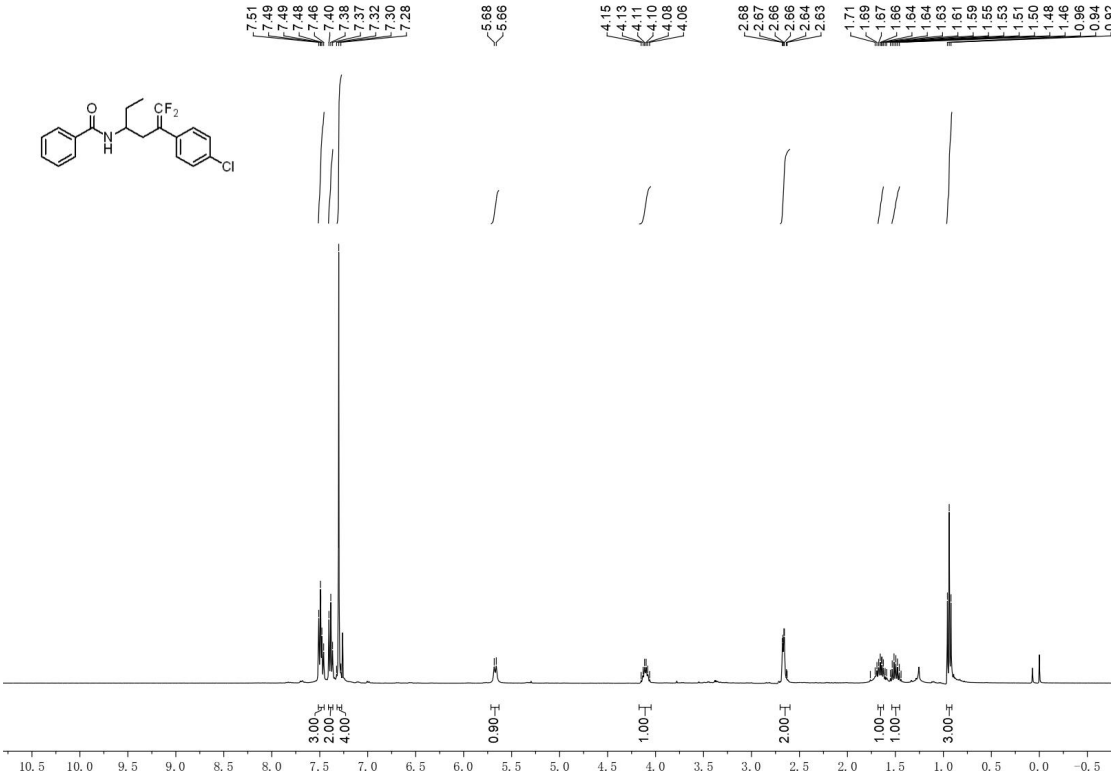

Figure S86. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3af**

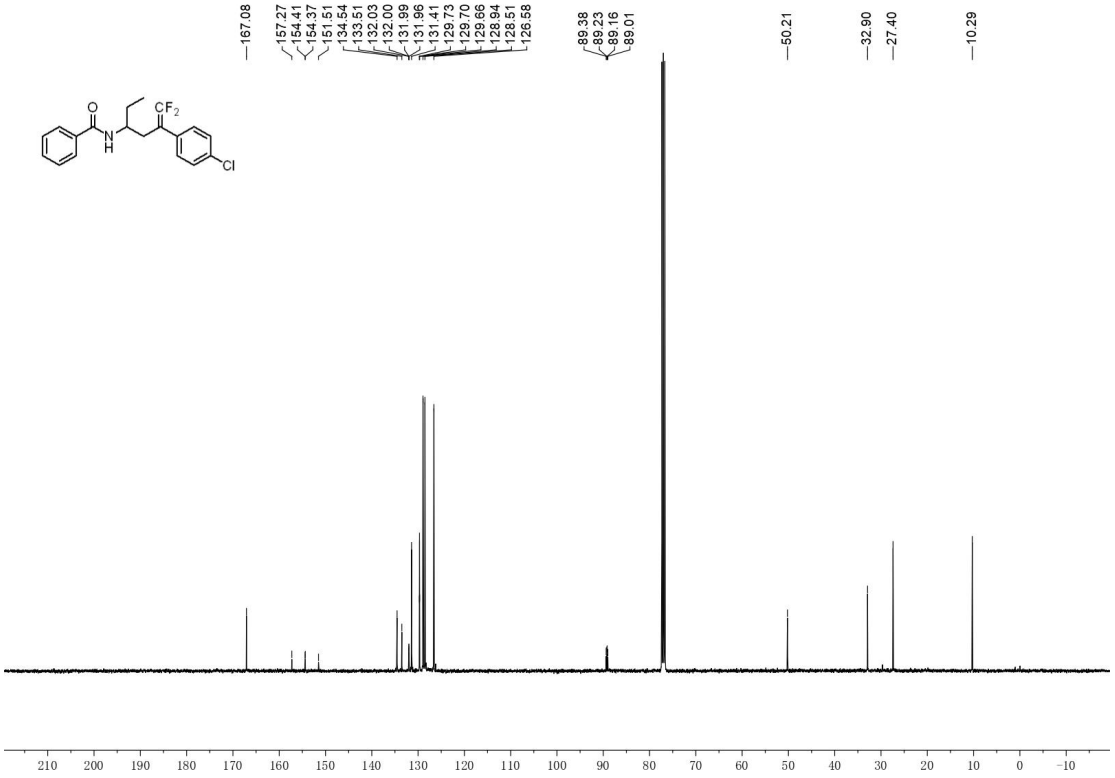

Figure S87. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3af**

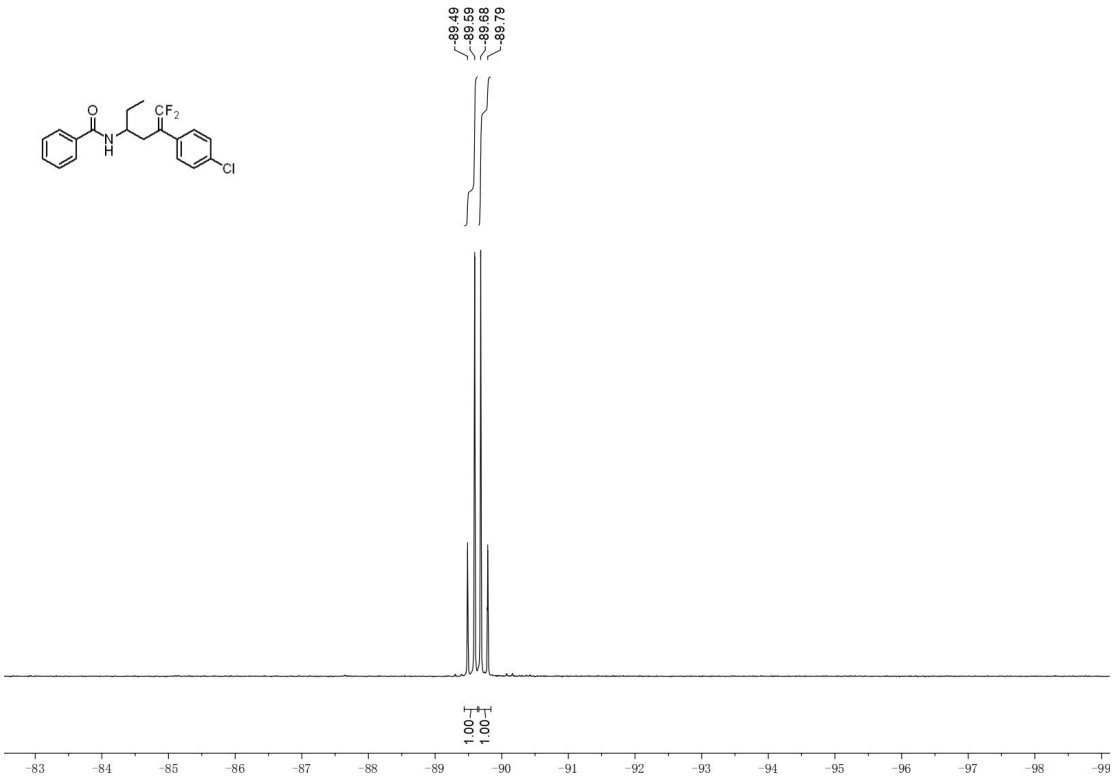

Figure S88. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3af**

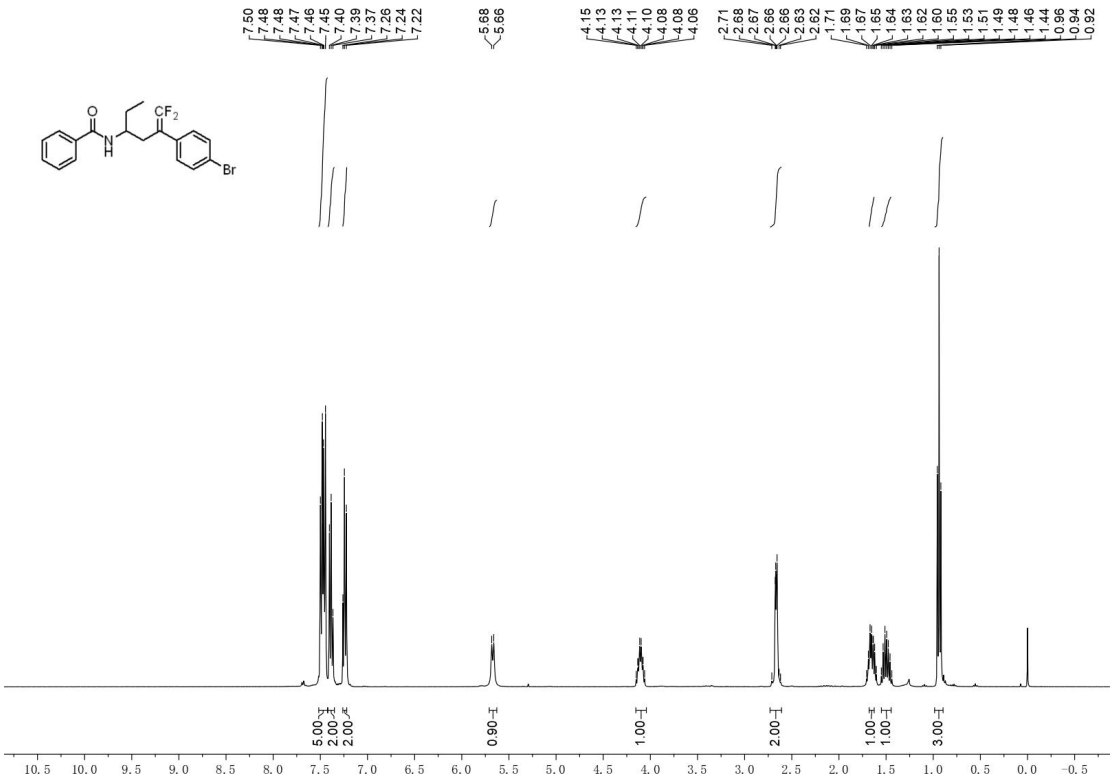

Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ag**

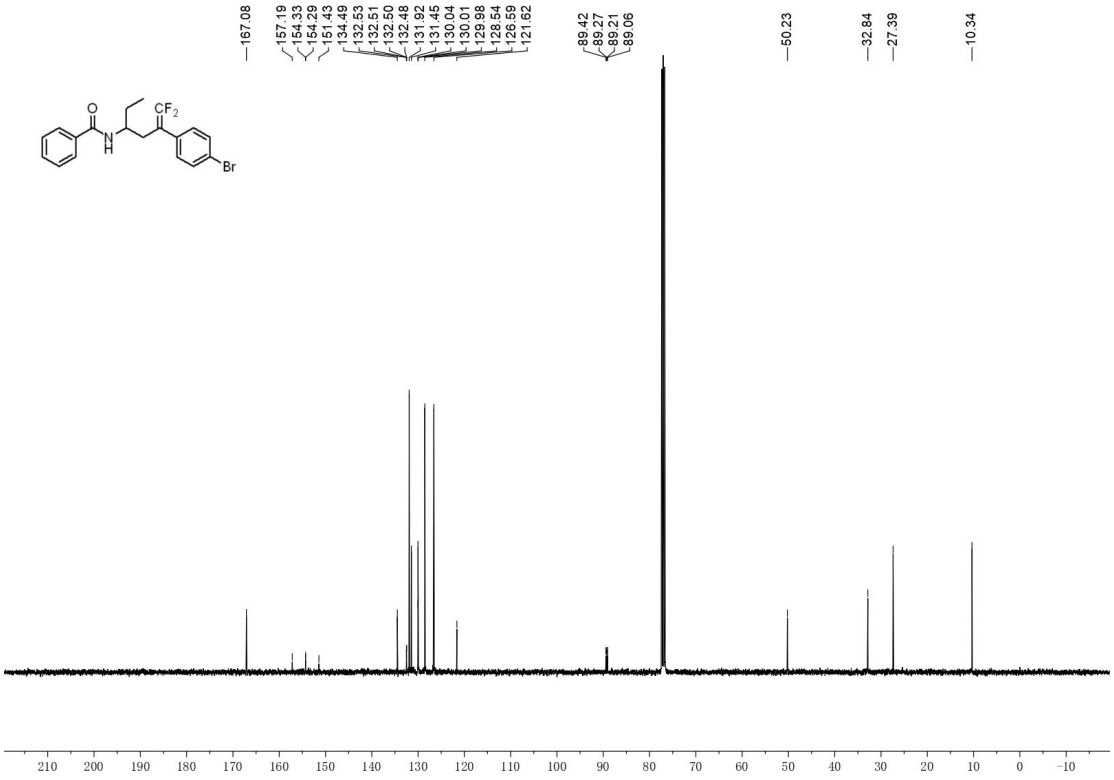

Figure S90. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ag**

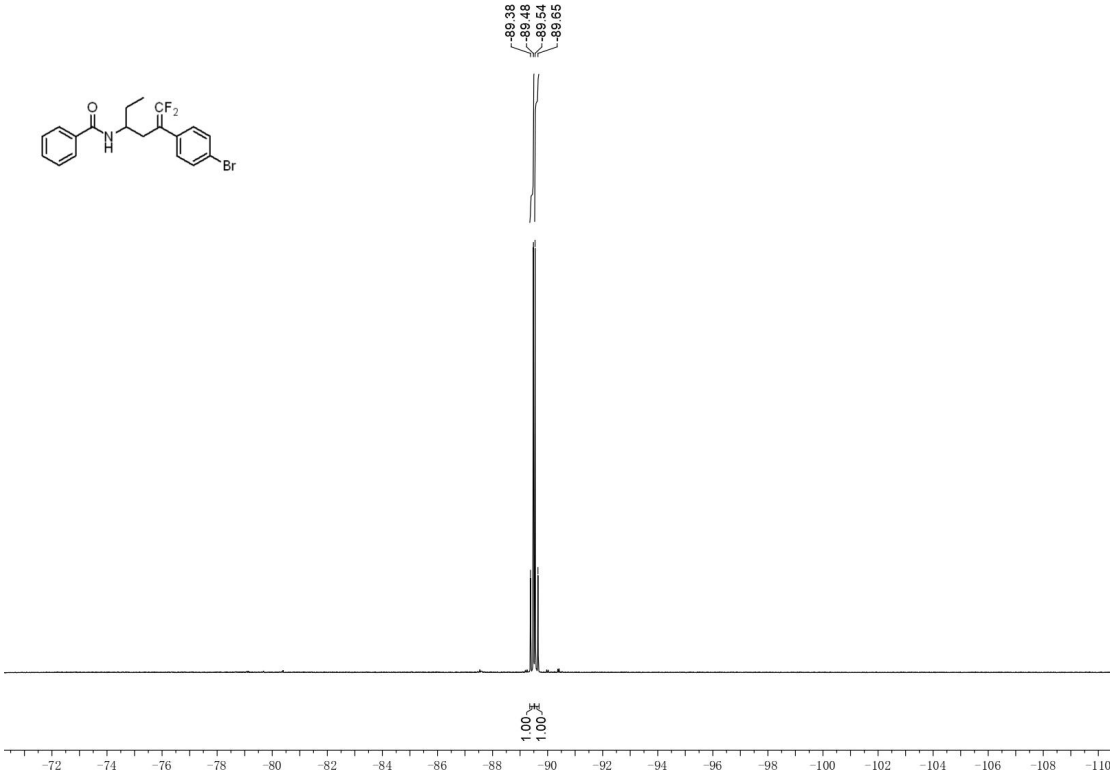

Figure S91. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ag**

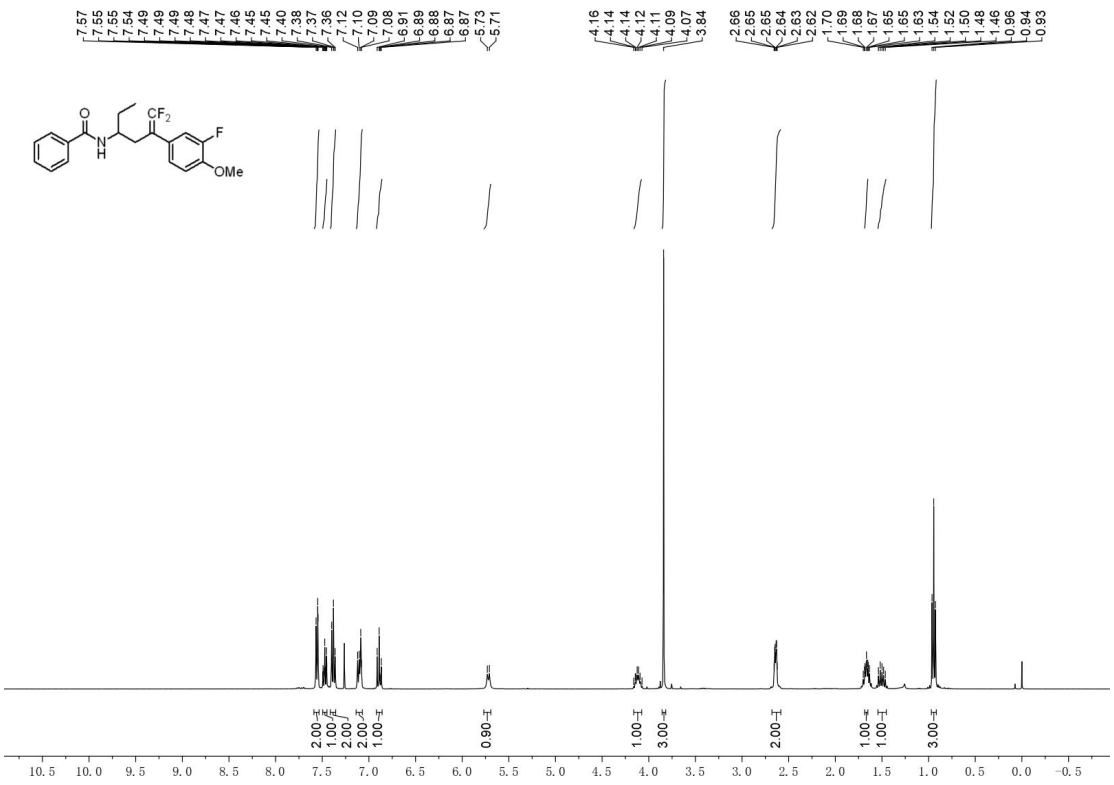

Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah**

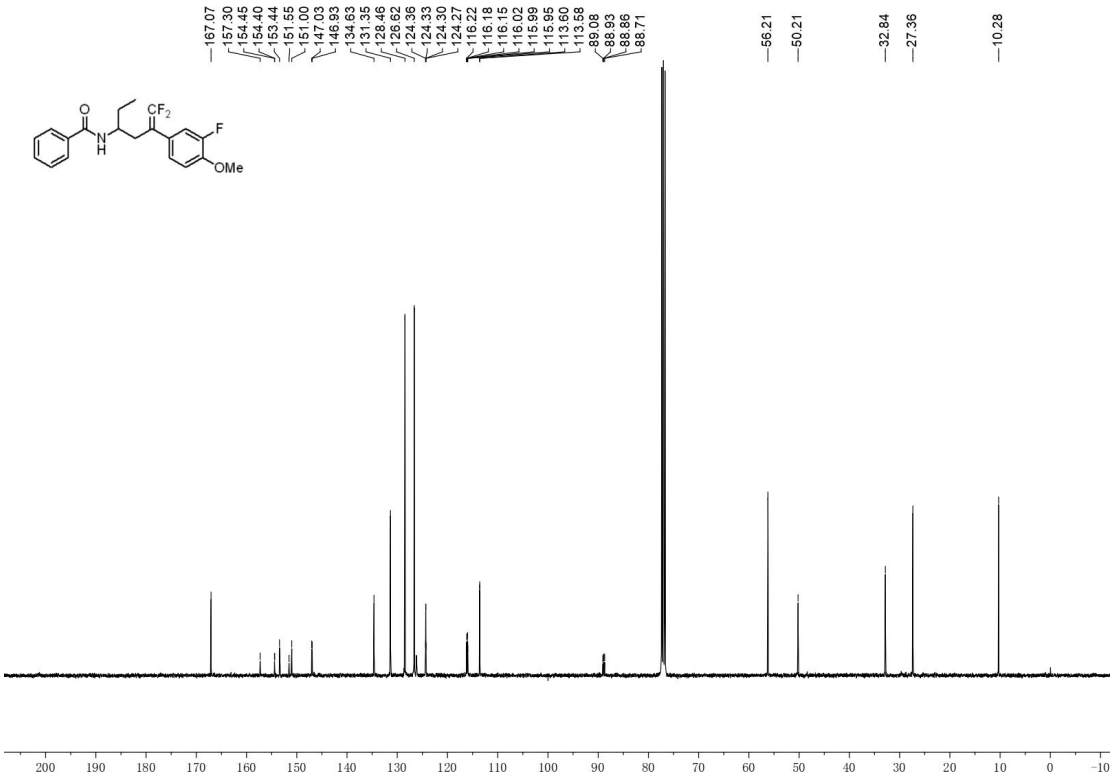

Figure S93. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ah**

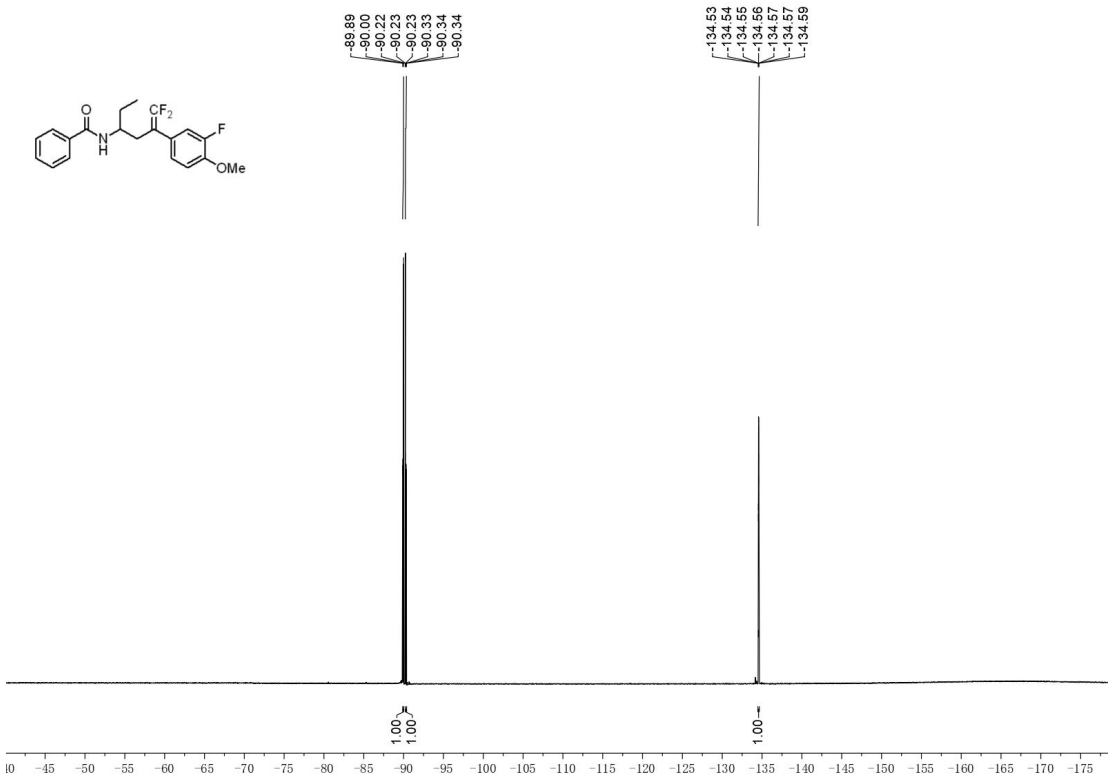

Figure S94. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ah**

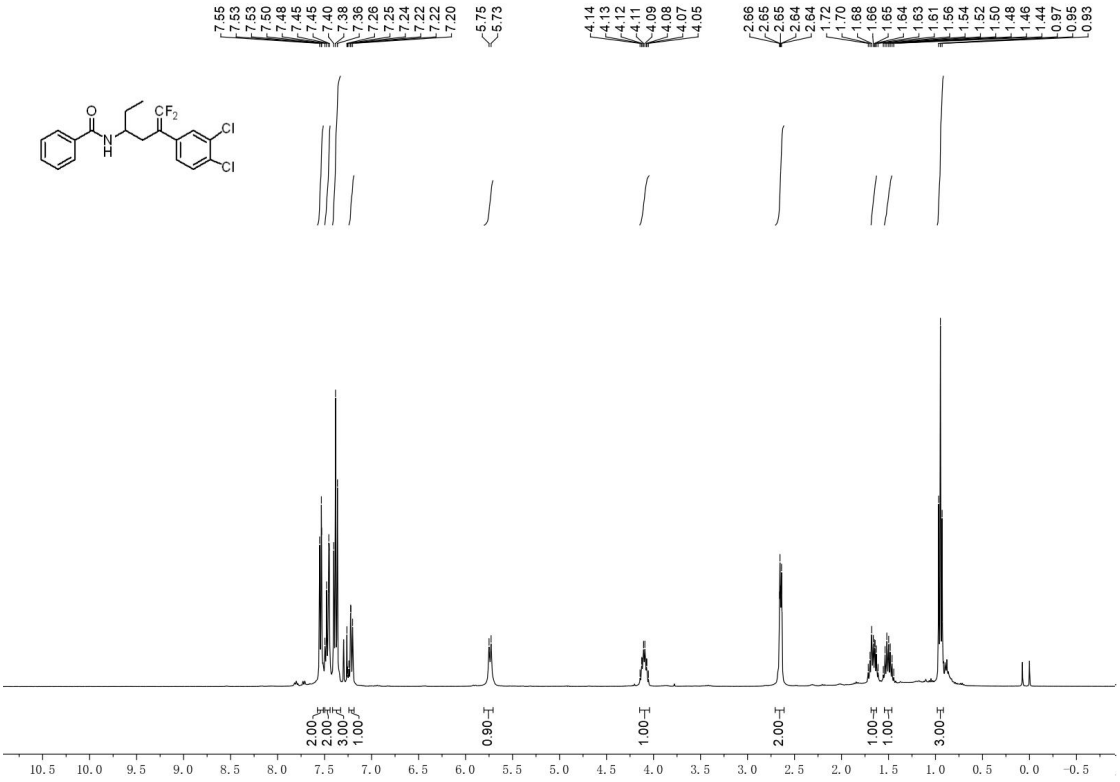

Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ai**

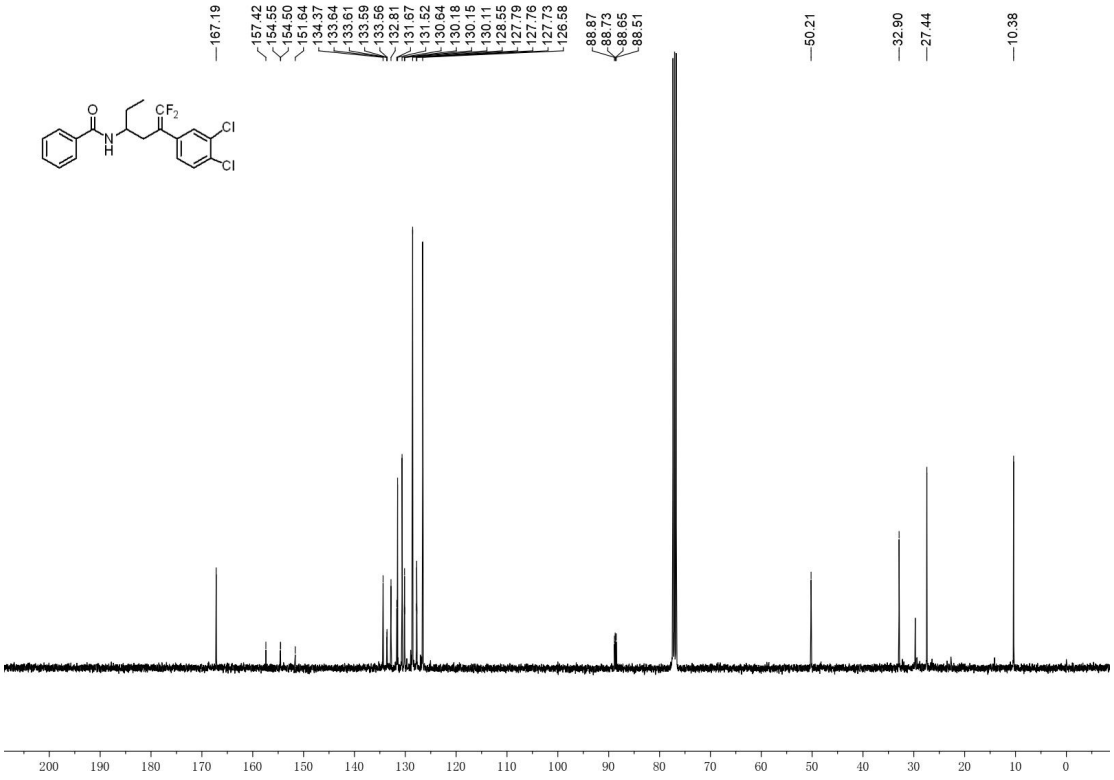

Figure S96. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ai**

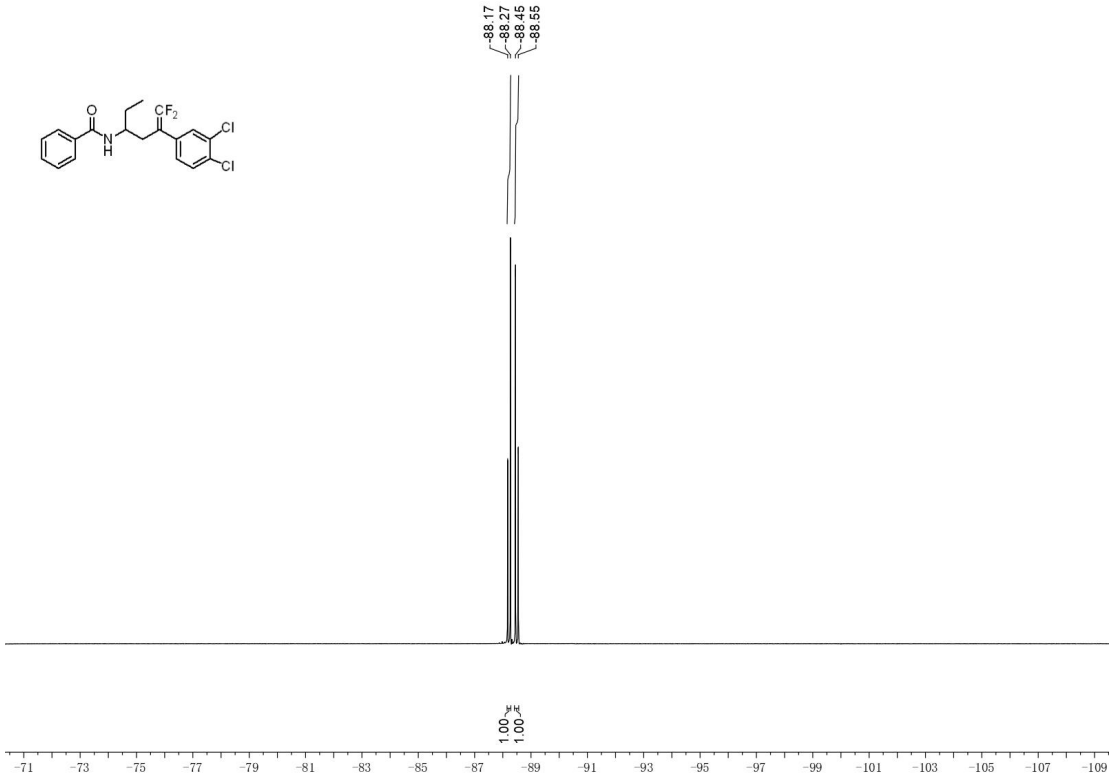

Figure S97. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ai**

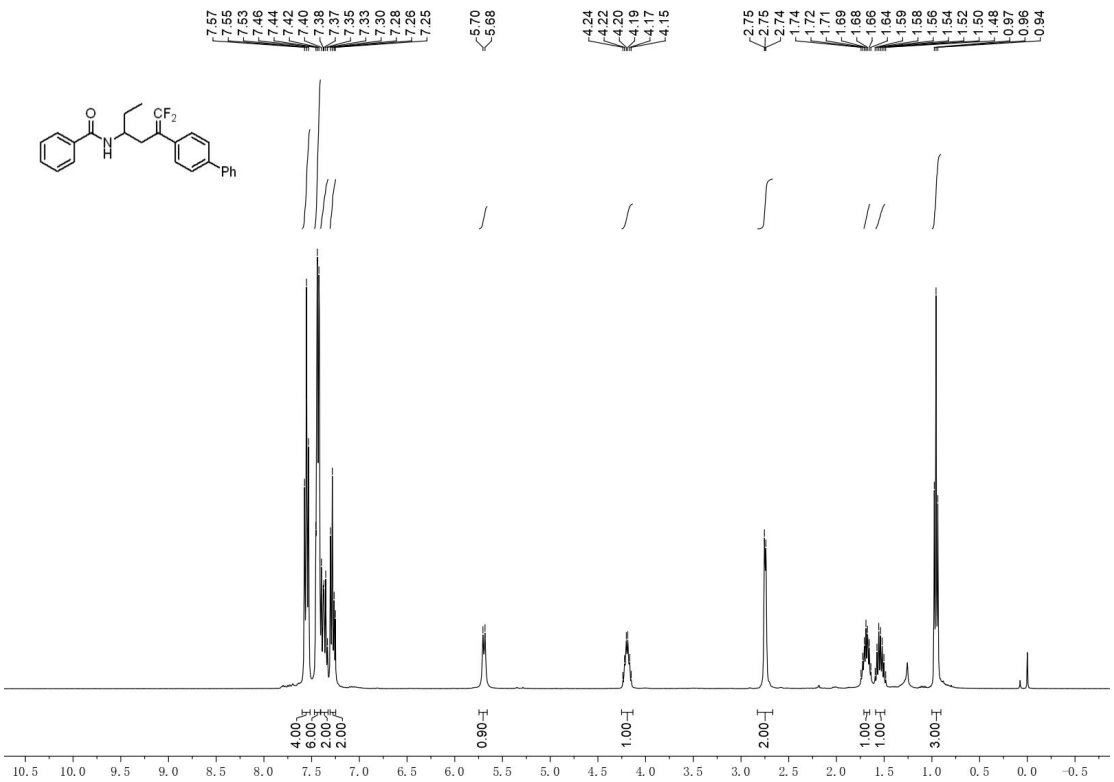

Figure S98. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aj**

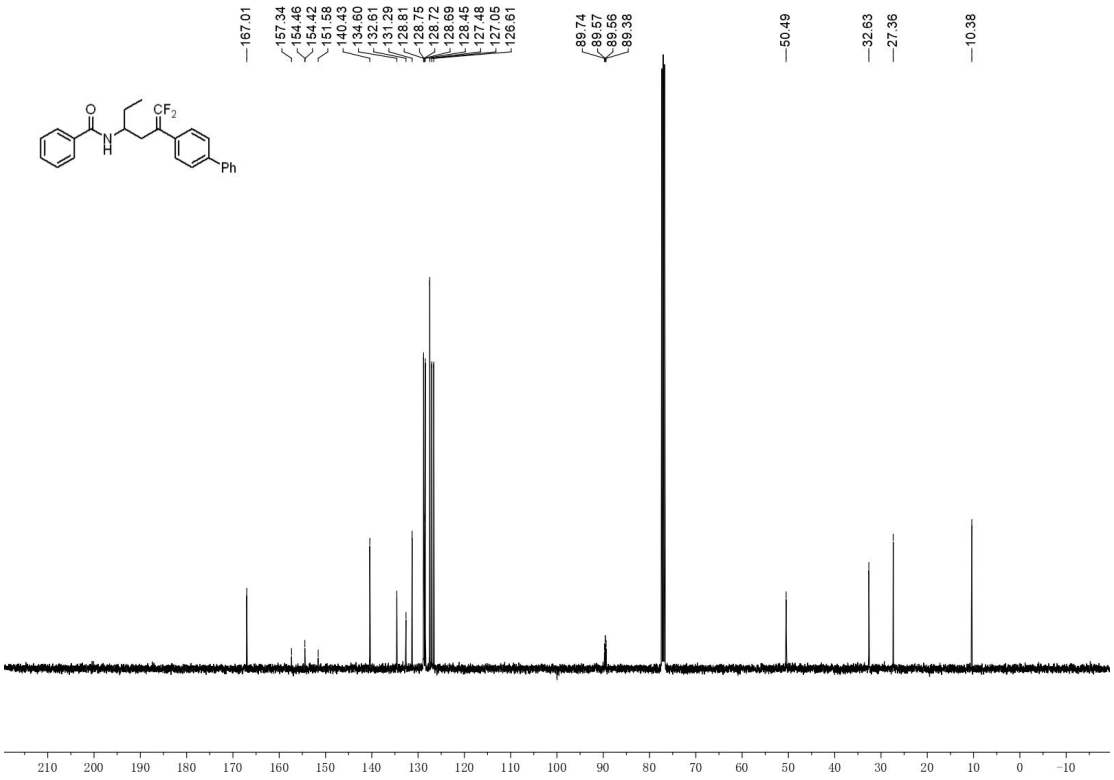

Figure S99. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aj**

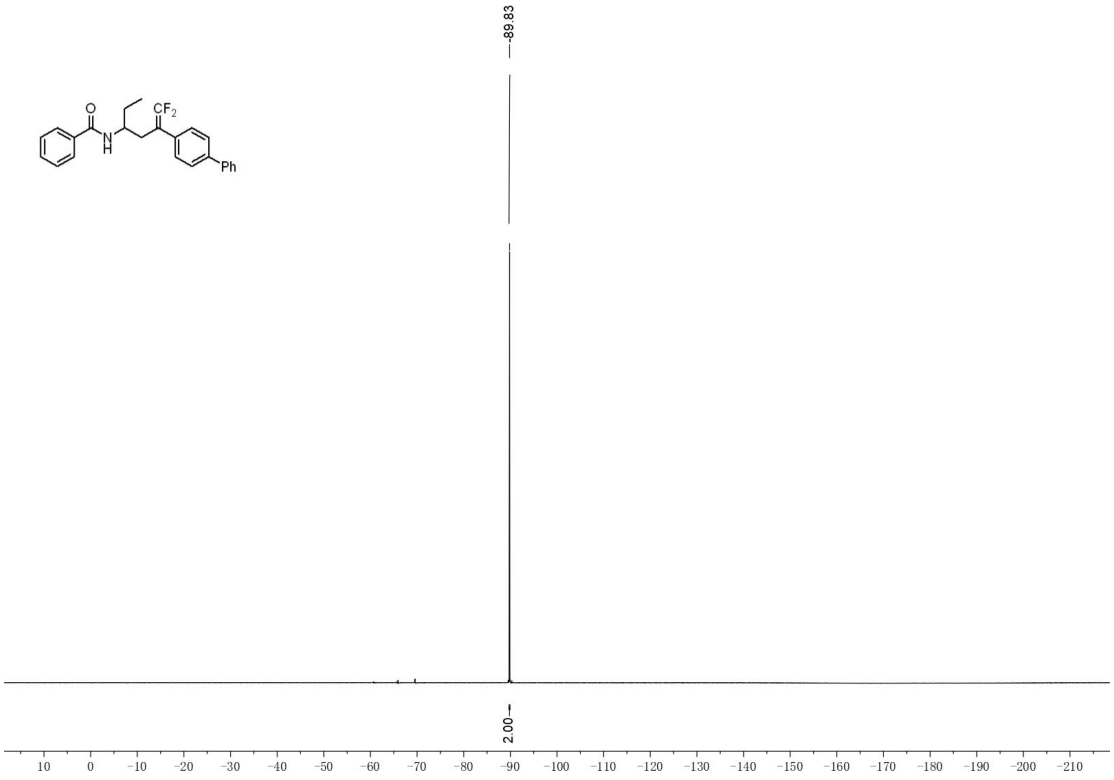

Figure S100. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3aj**

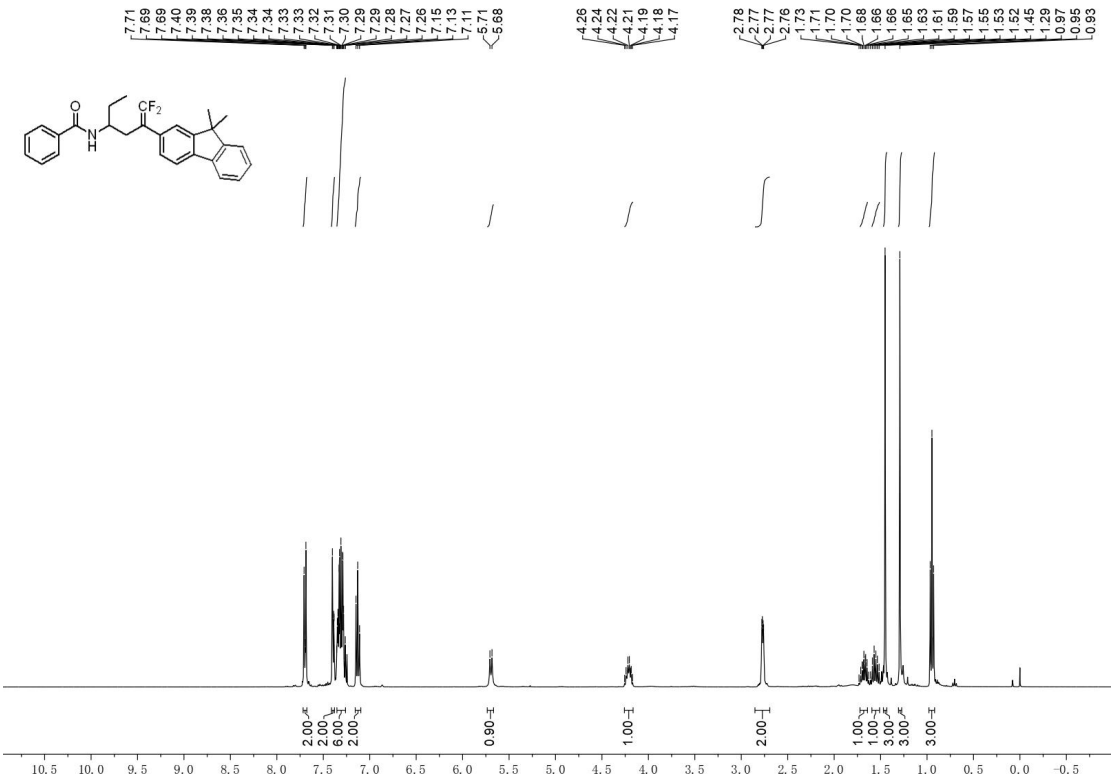

Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ak**

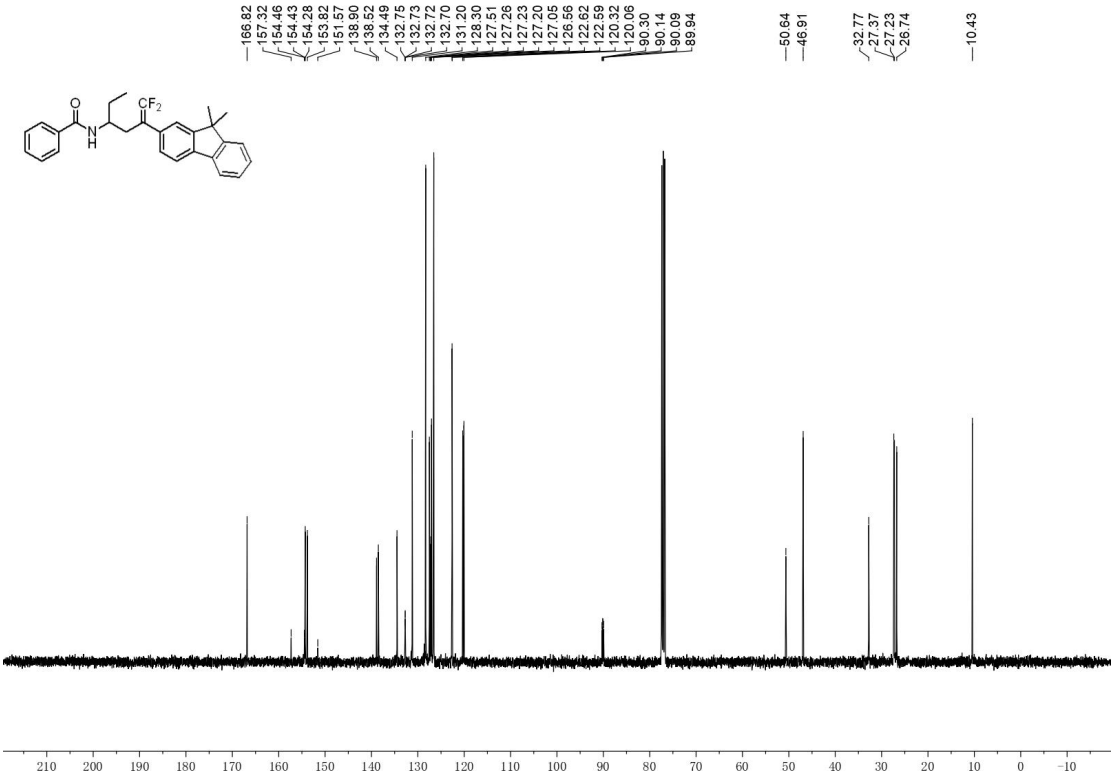

Figure S102. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ak**

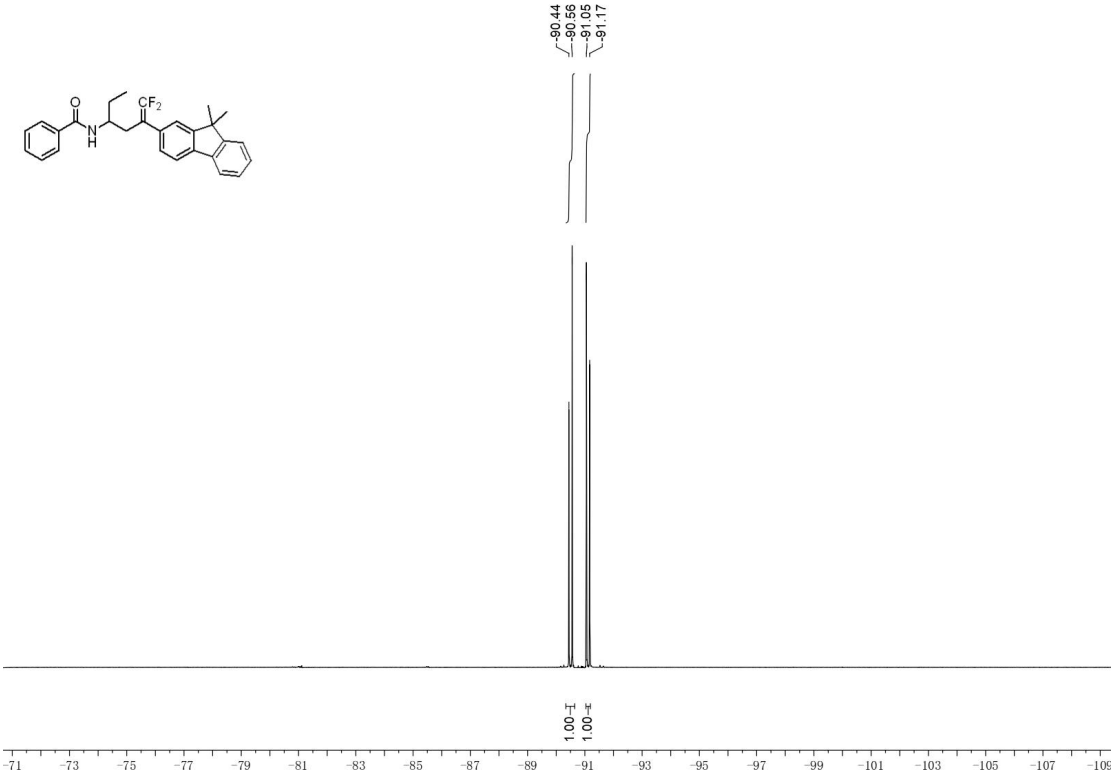

Figure S103. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ak**

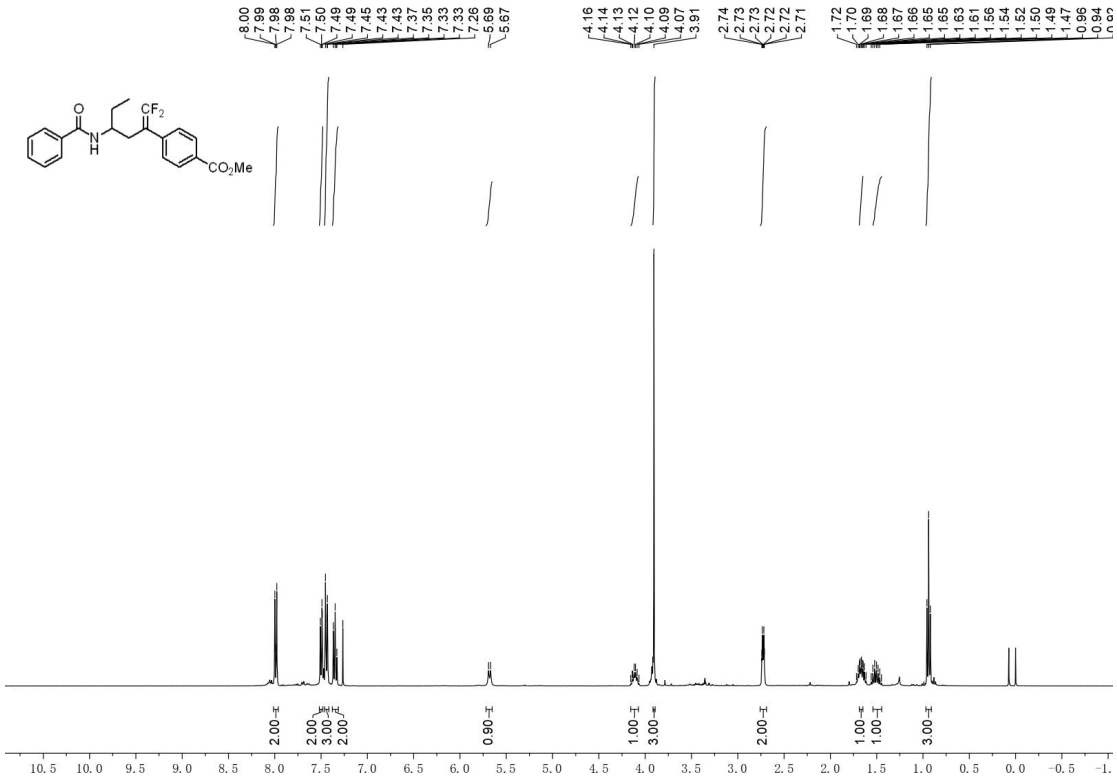

Figure S104. ^{1}H NMR and ^{13}C NMR spectra of **3al**

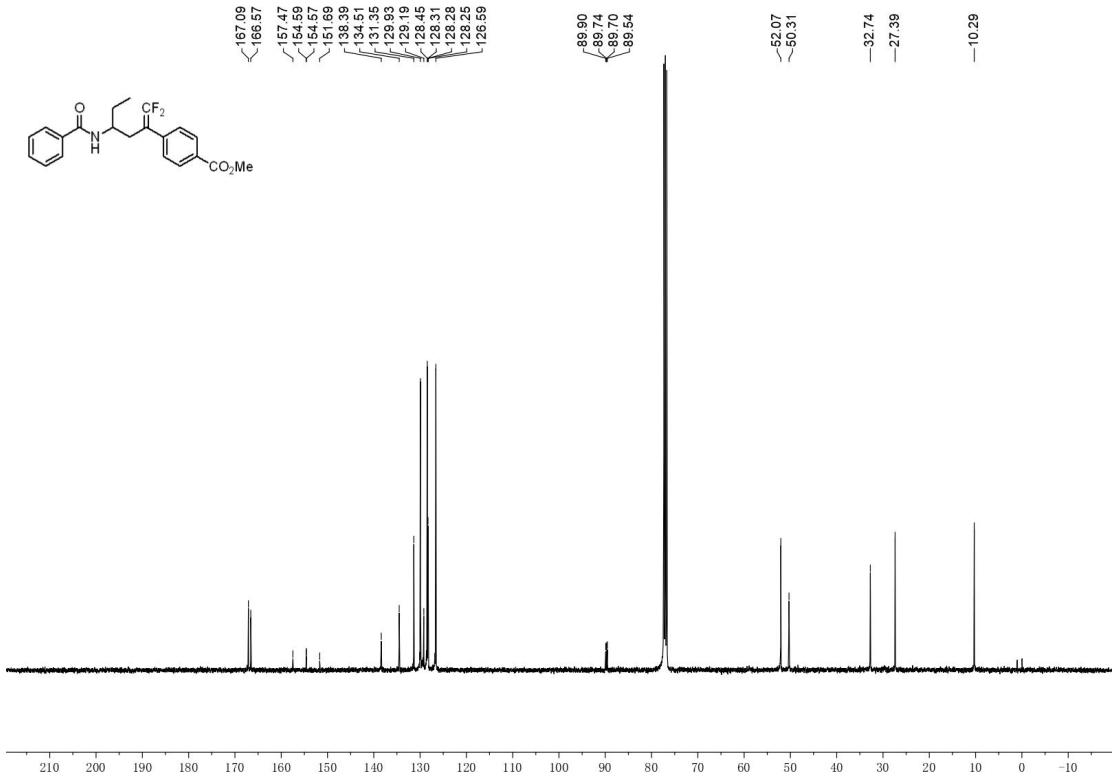

Figure S105. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3al**

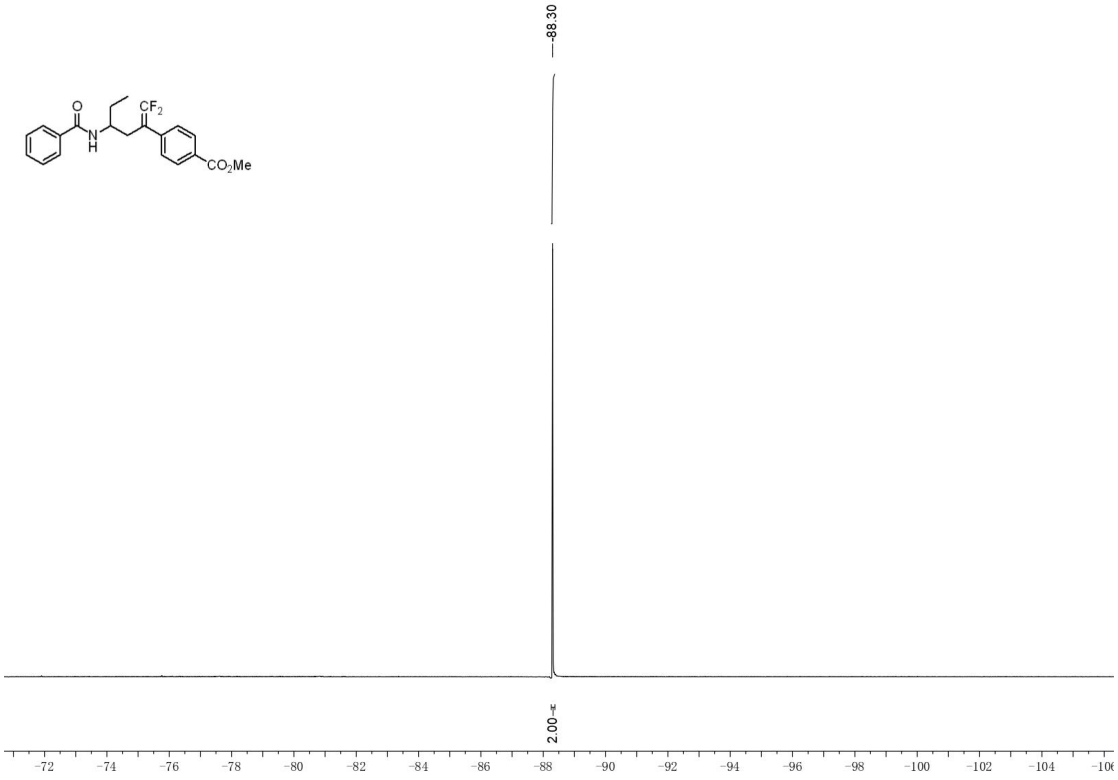

Figure S106. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3al**

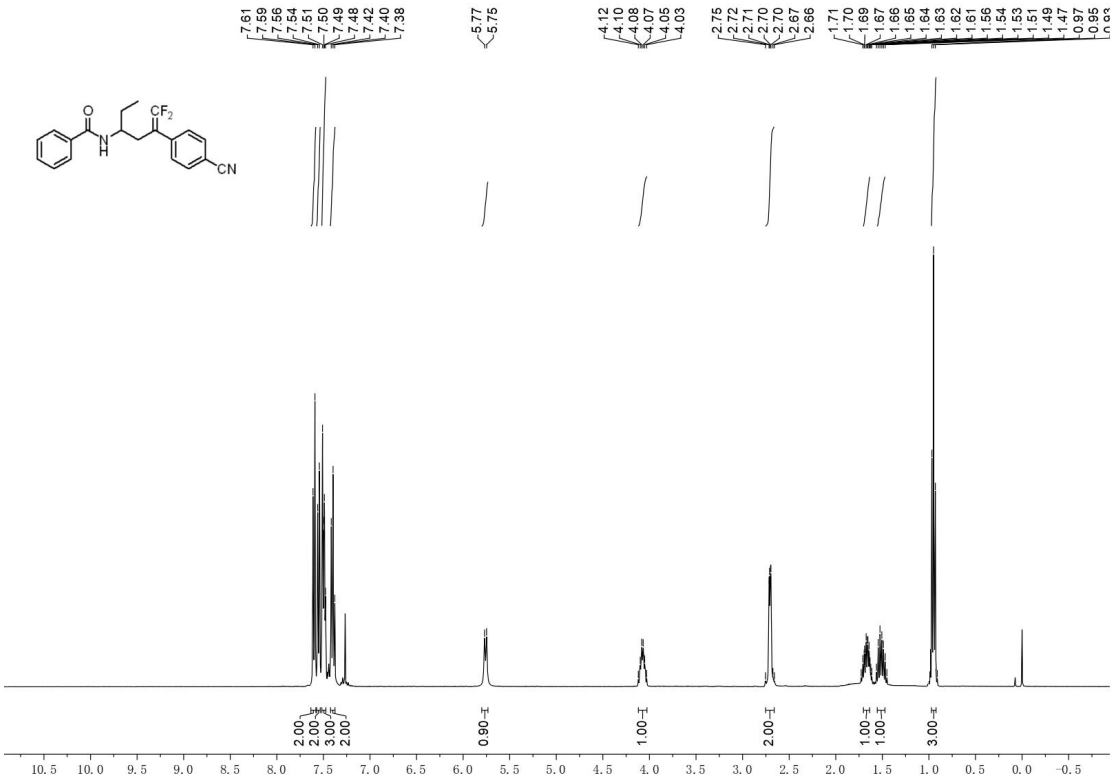

Figure S107. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3am**

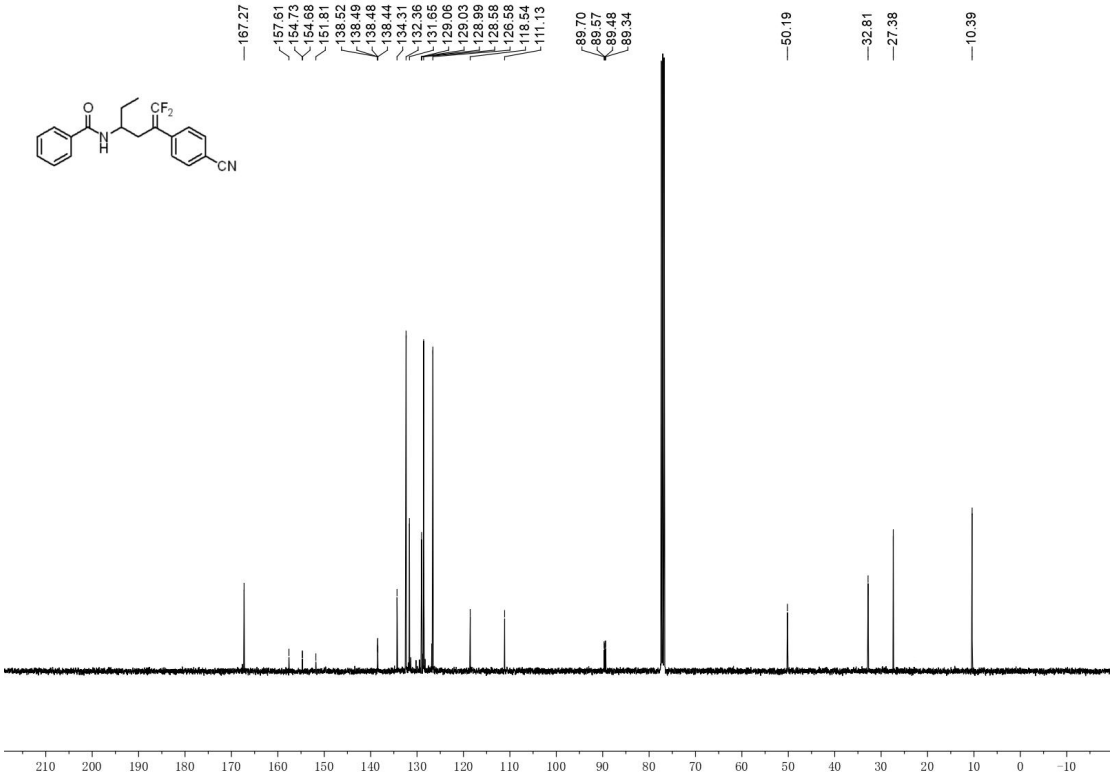

Figure S108. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3am**

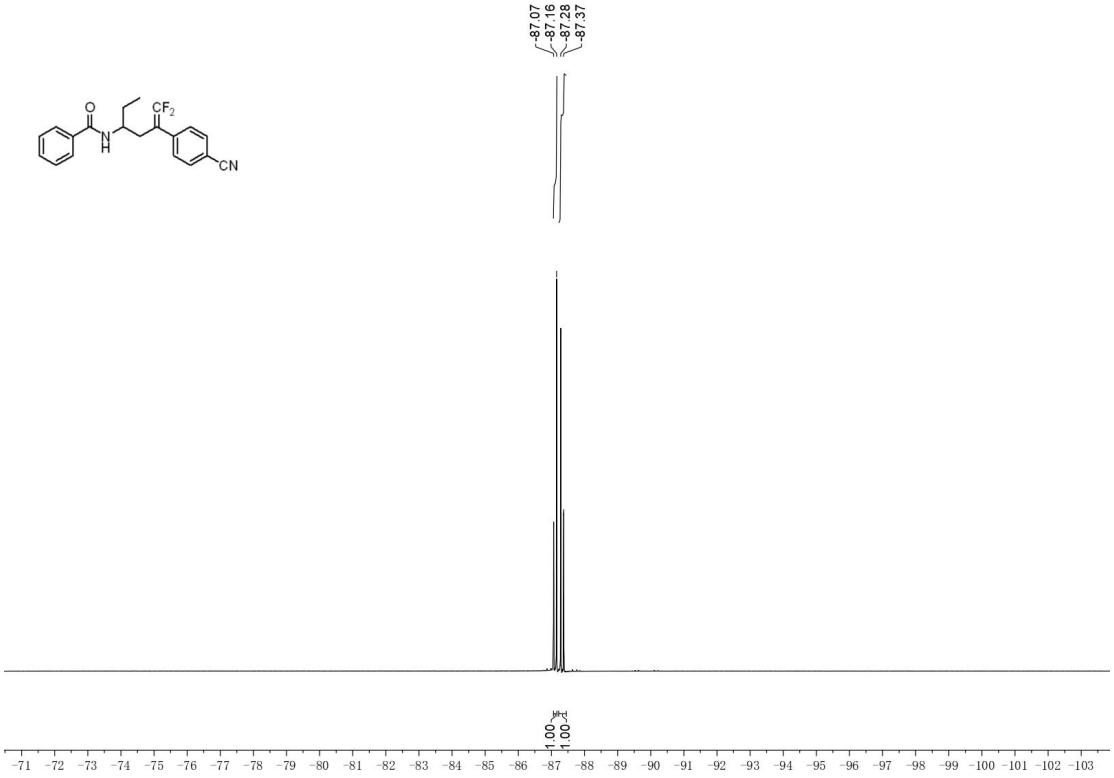

Figure S109. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3am**

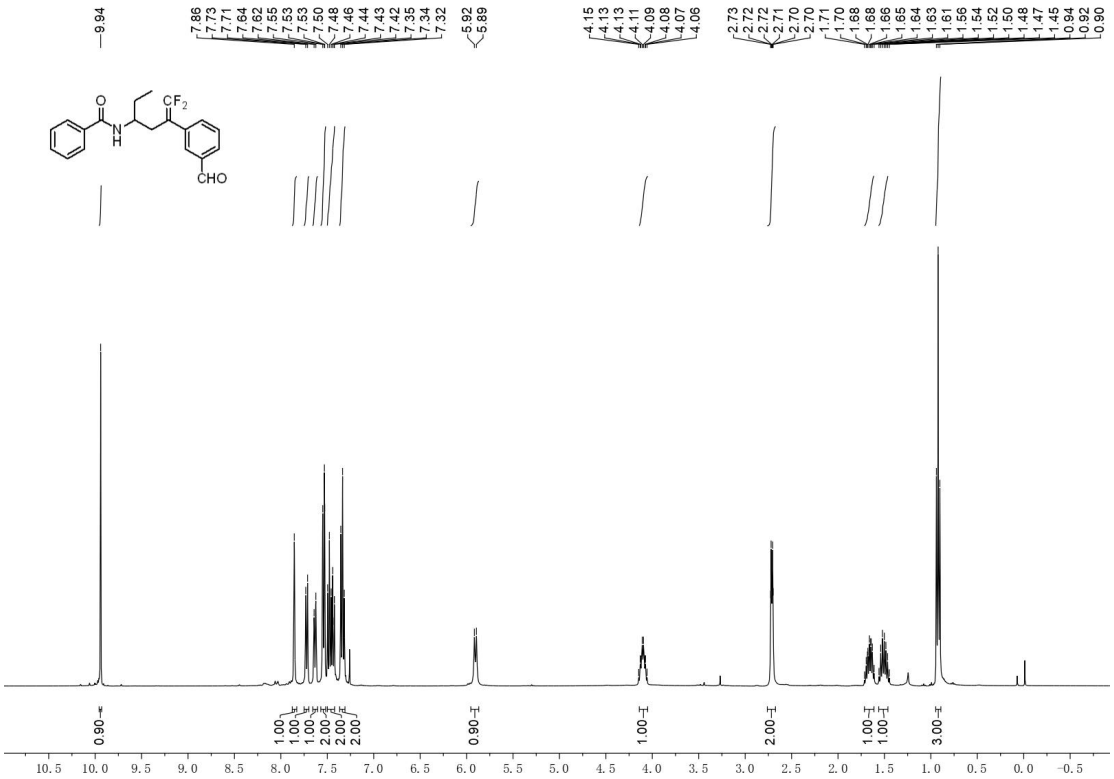

Figure S110. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3an**

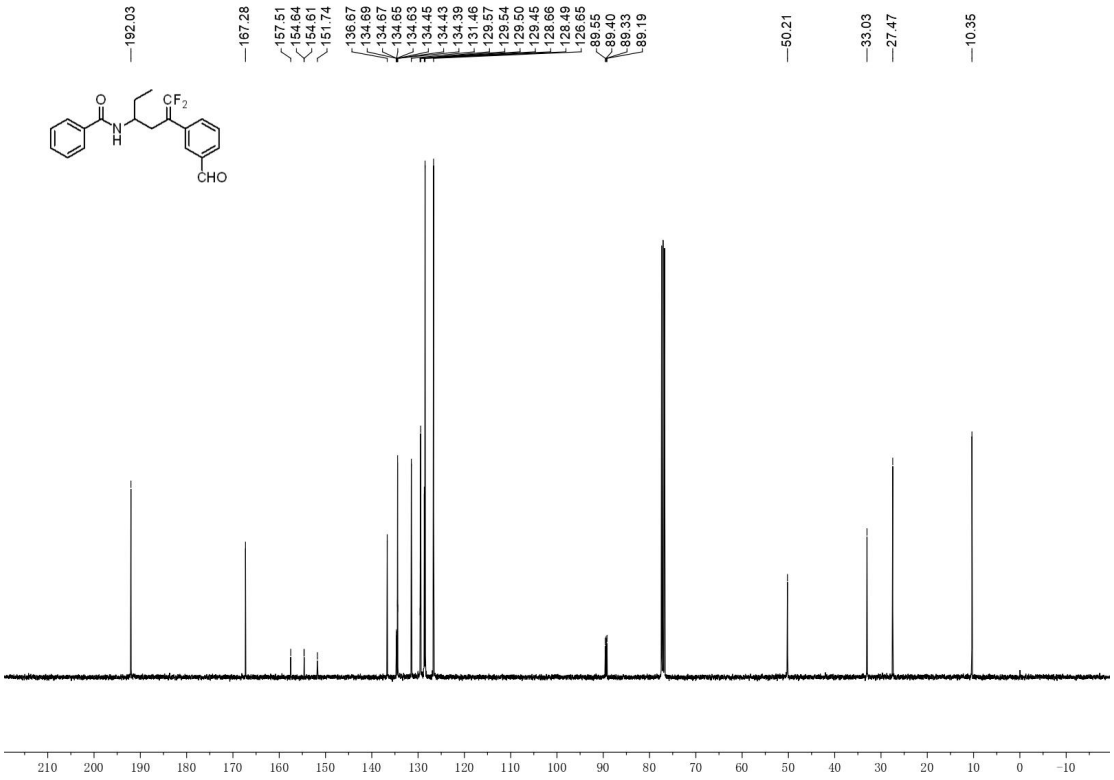

Figure S111. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3an**

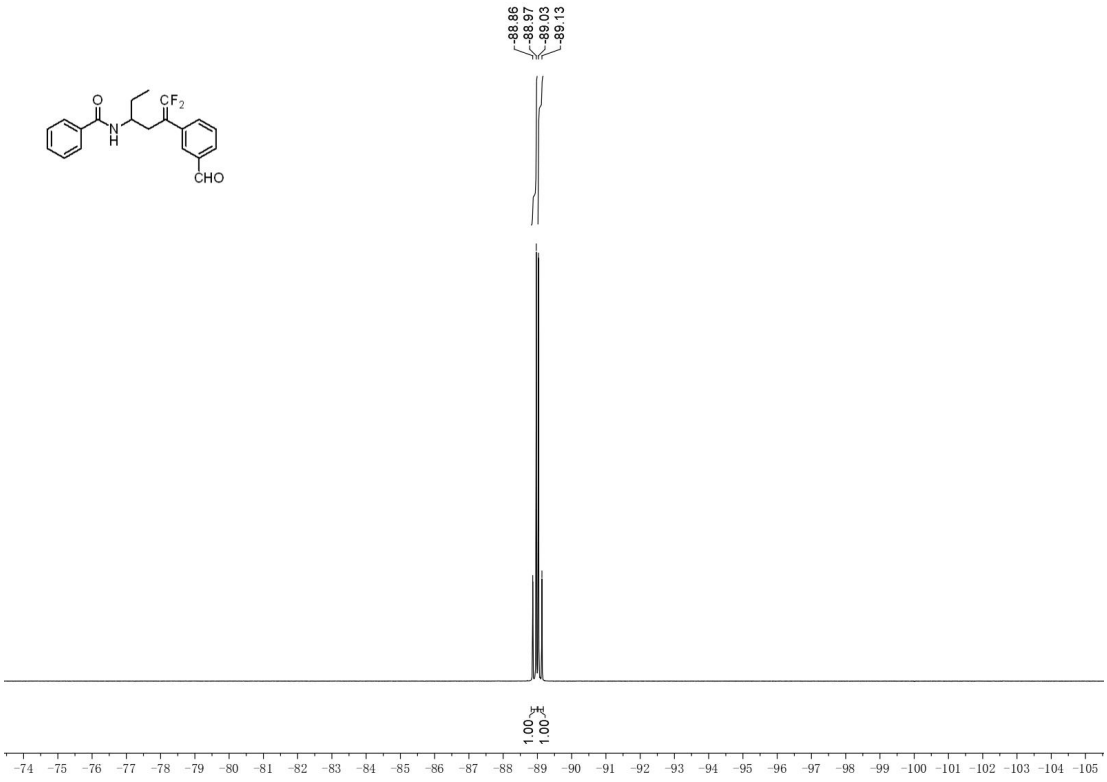

Figure S112. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3an**

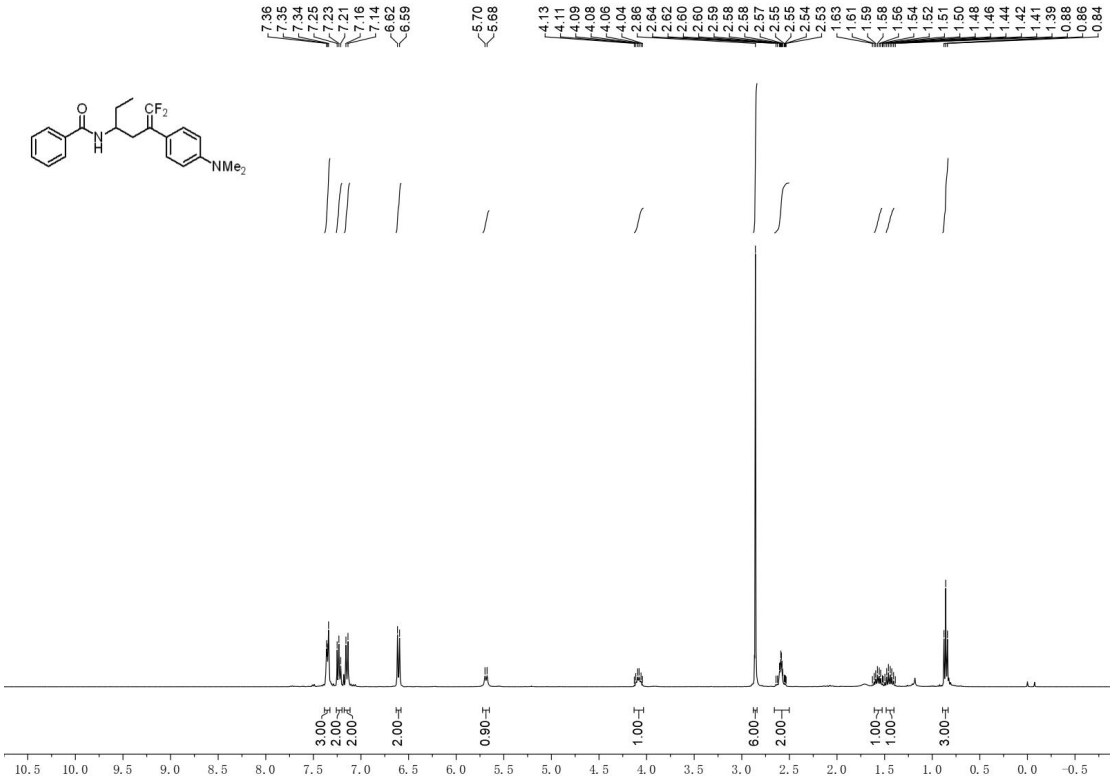

Figure S113. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ao**

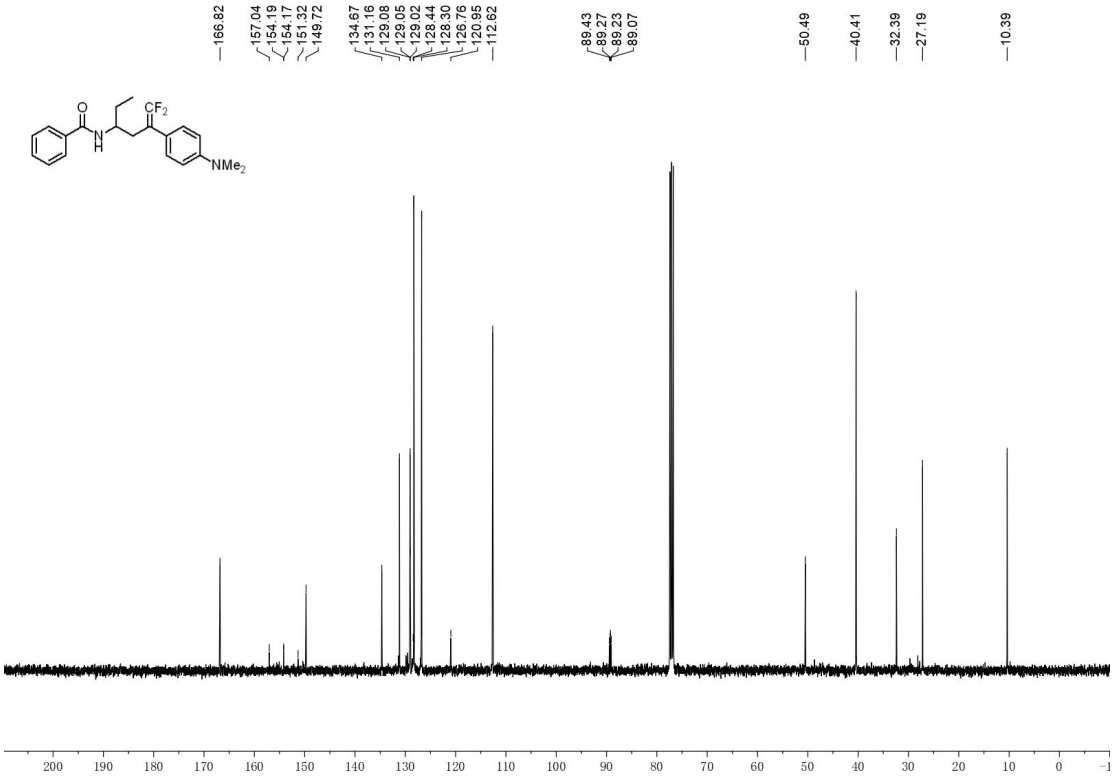

Figure S114. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ao**

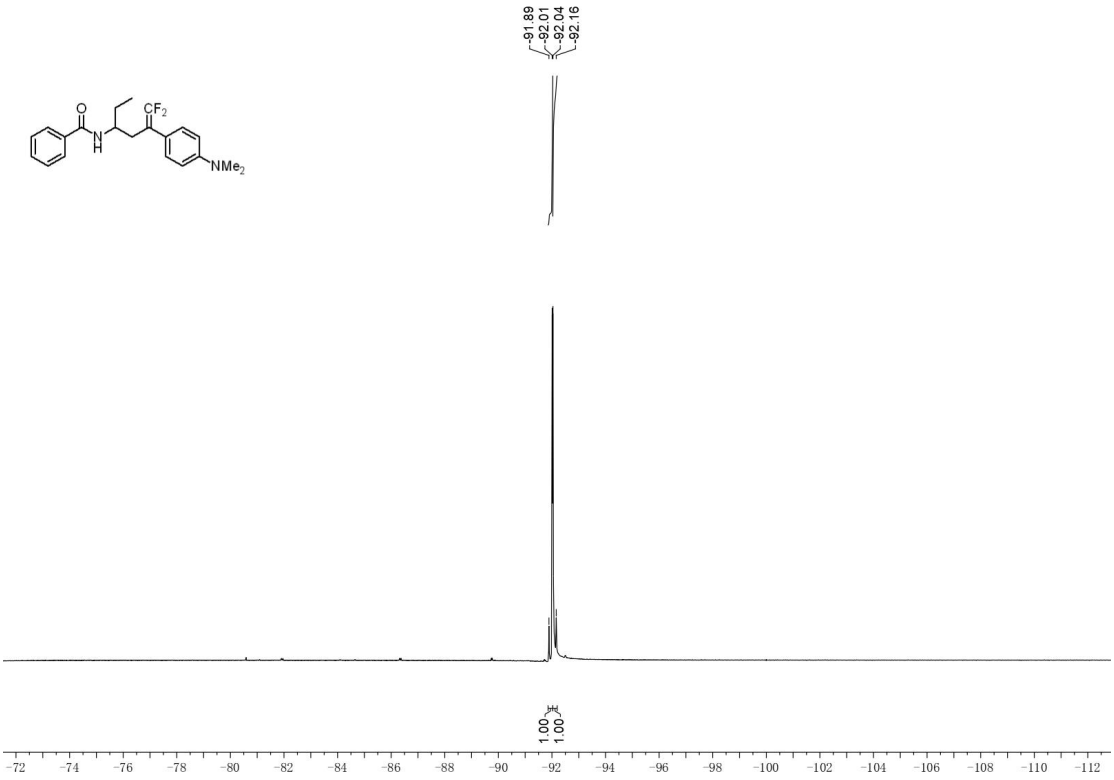

Figure S115. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ao**

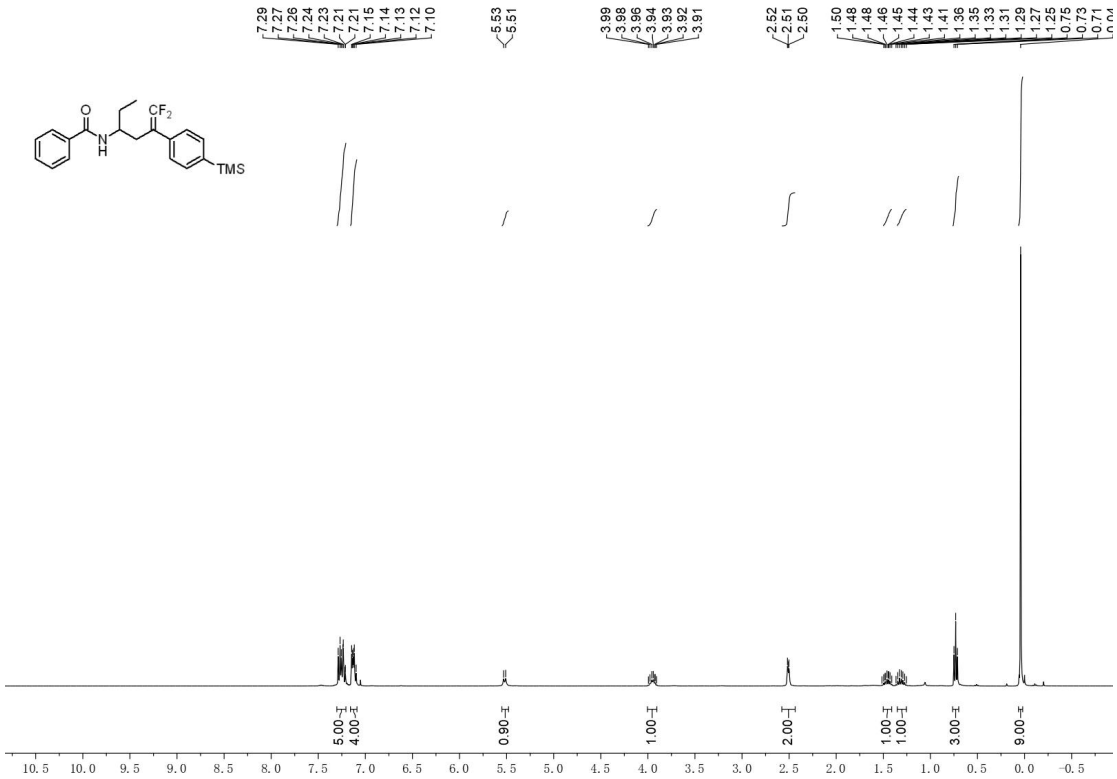

Figure S116. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ap**

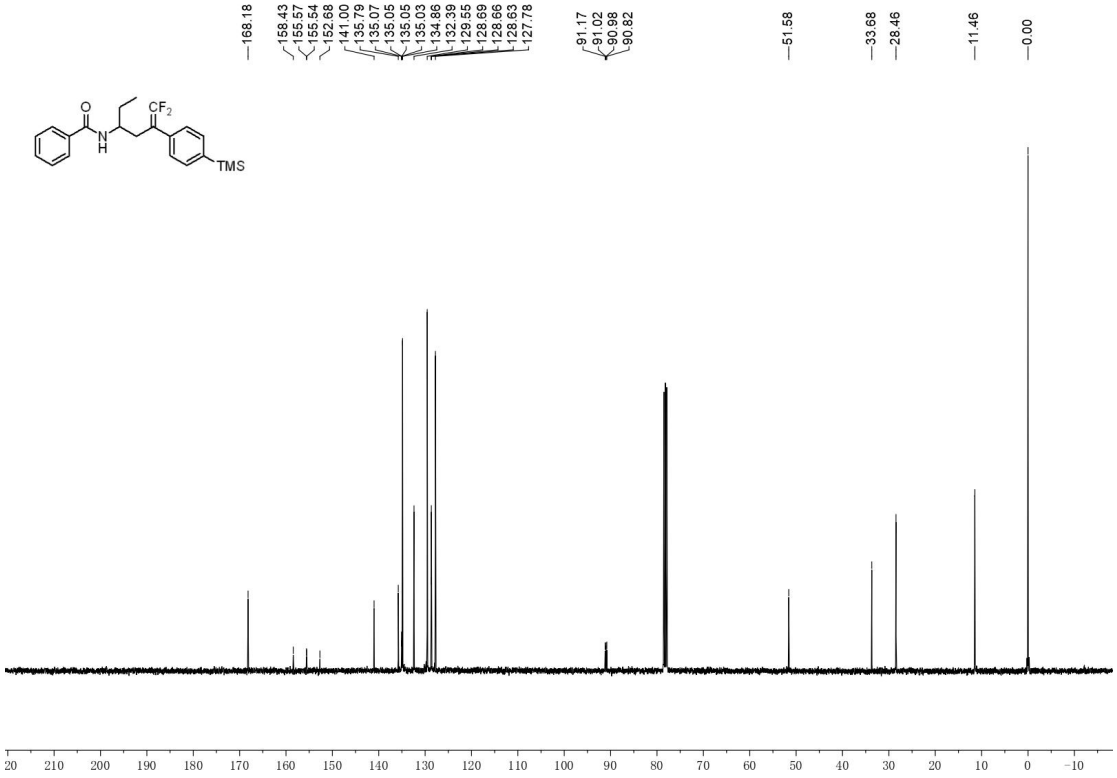

Figure S117. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ap**

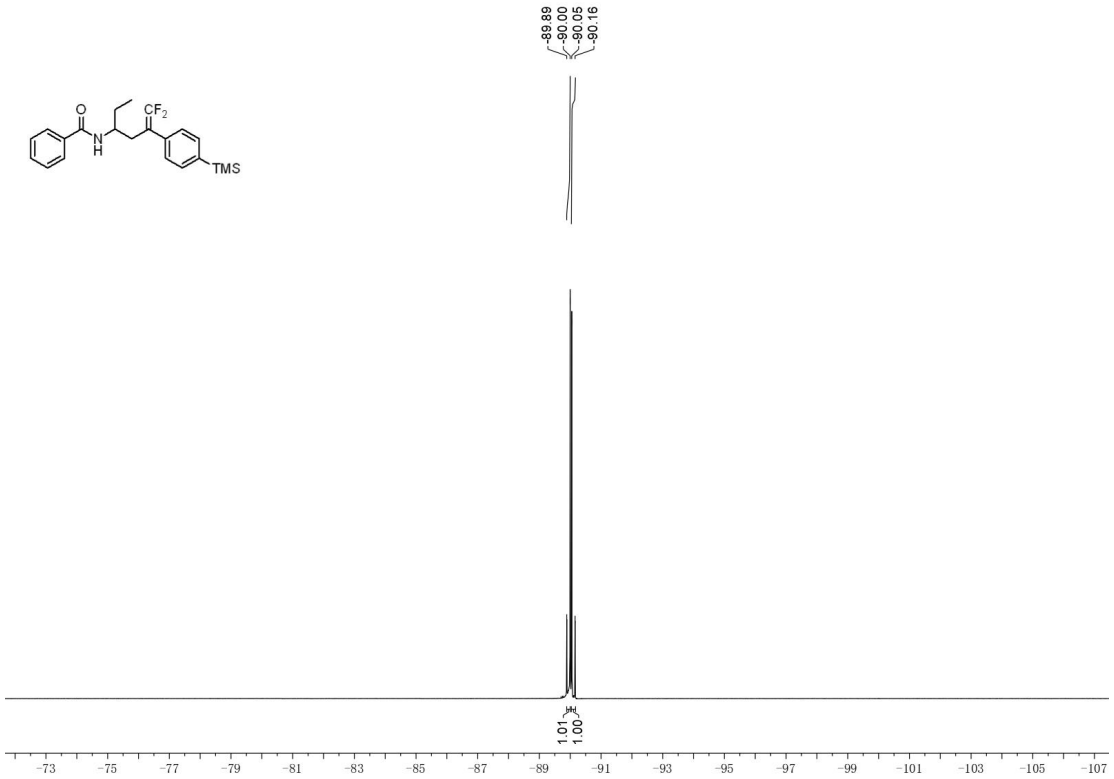

Figure S118. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ap**

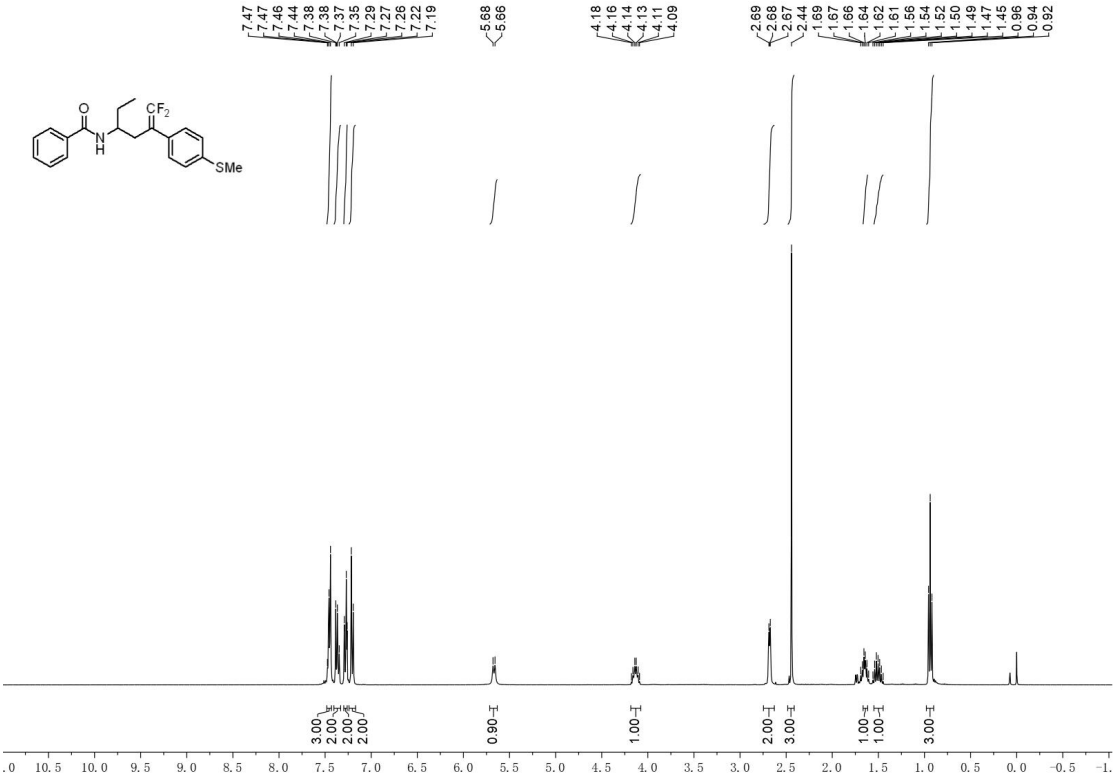

Figure S119. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aq**

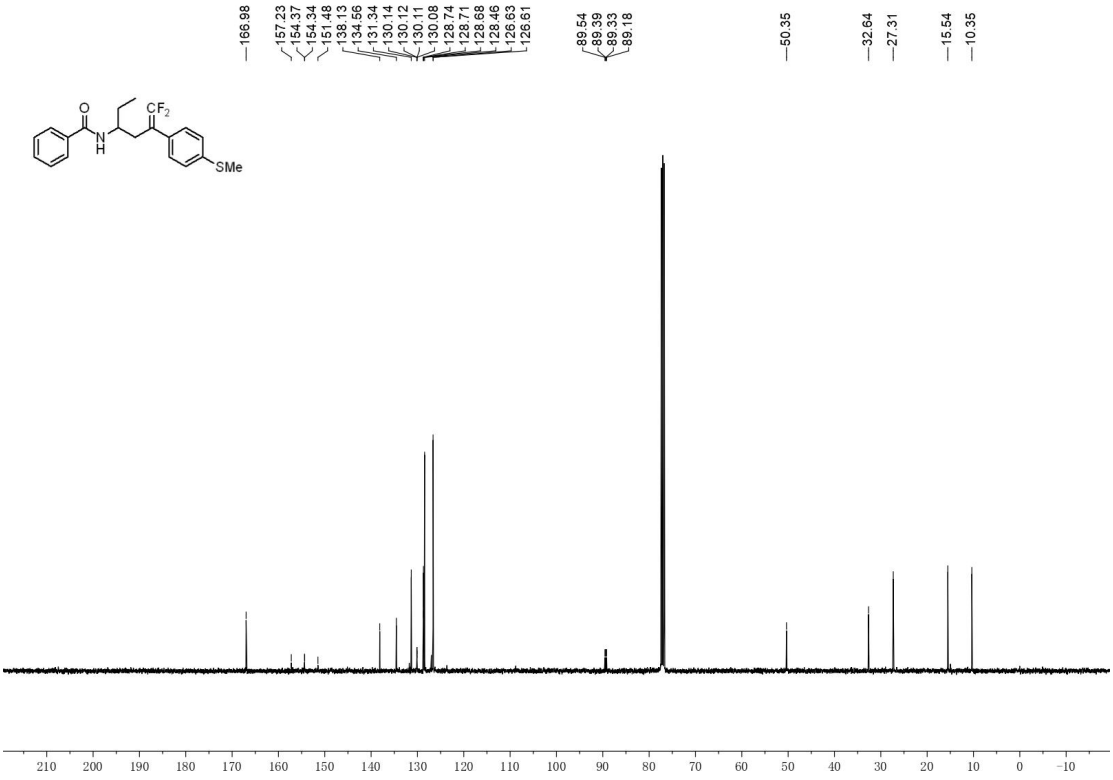

Figure S120. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aq**

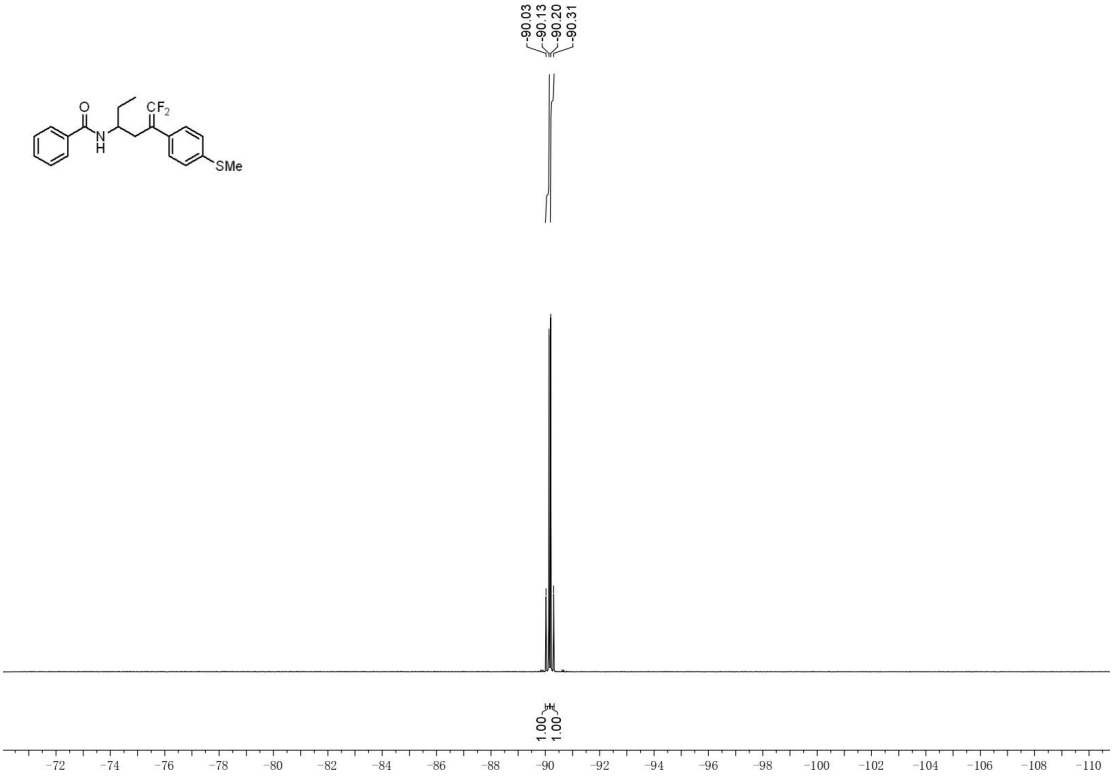

Figure S121. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3aq**

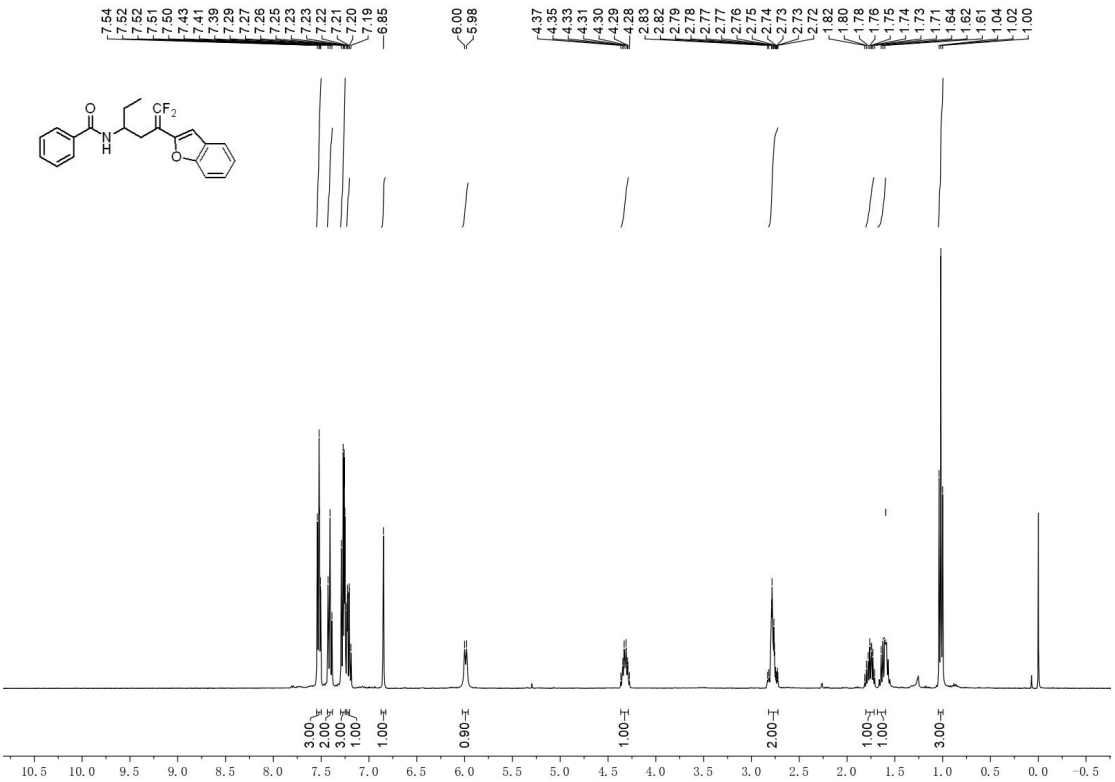

Figure S122. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ar**

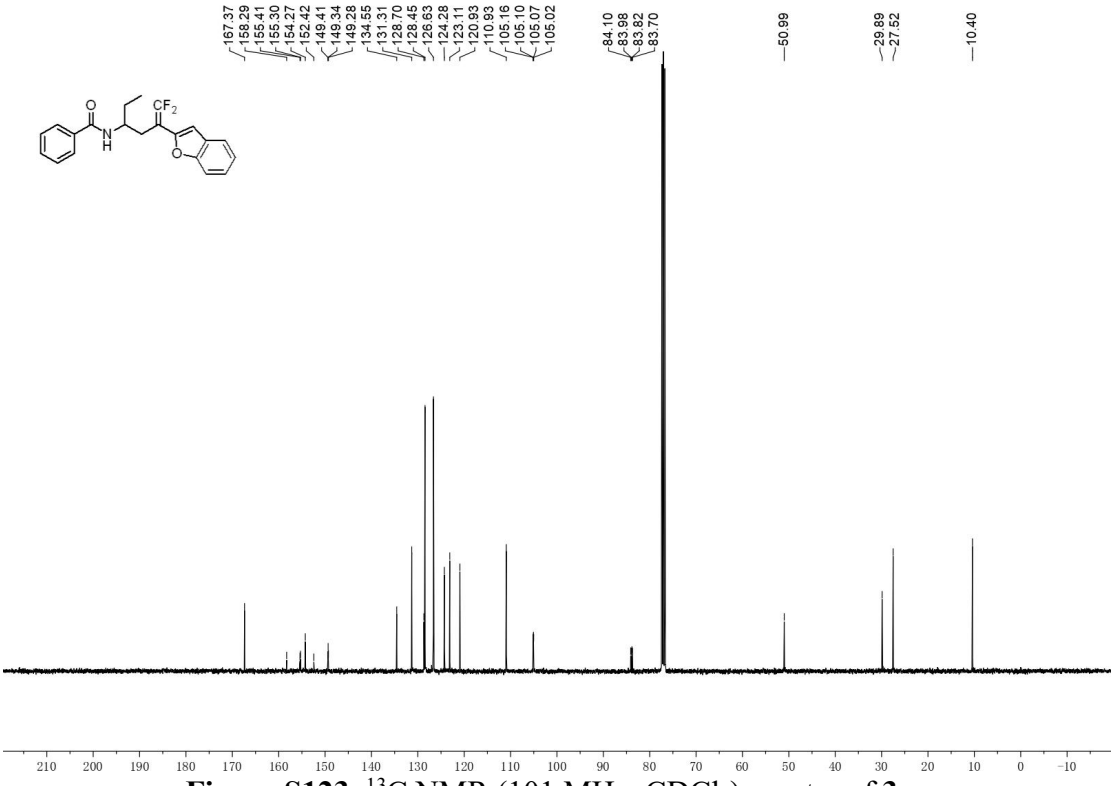

Figure S123. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ar**

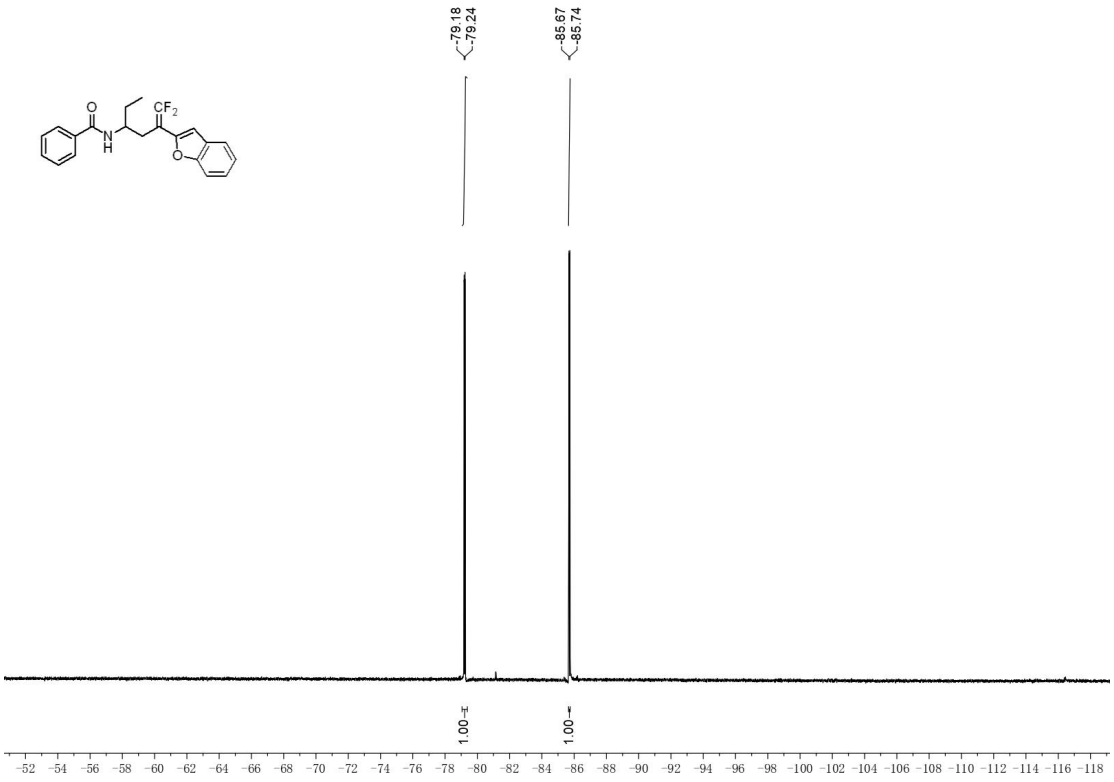

Figure S124. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ar**

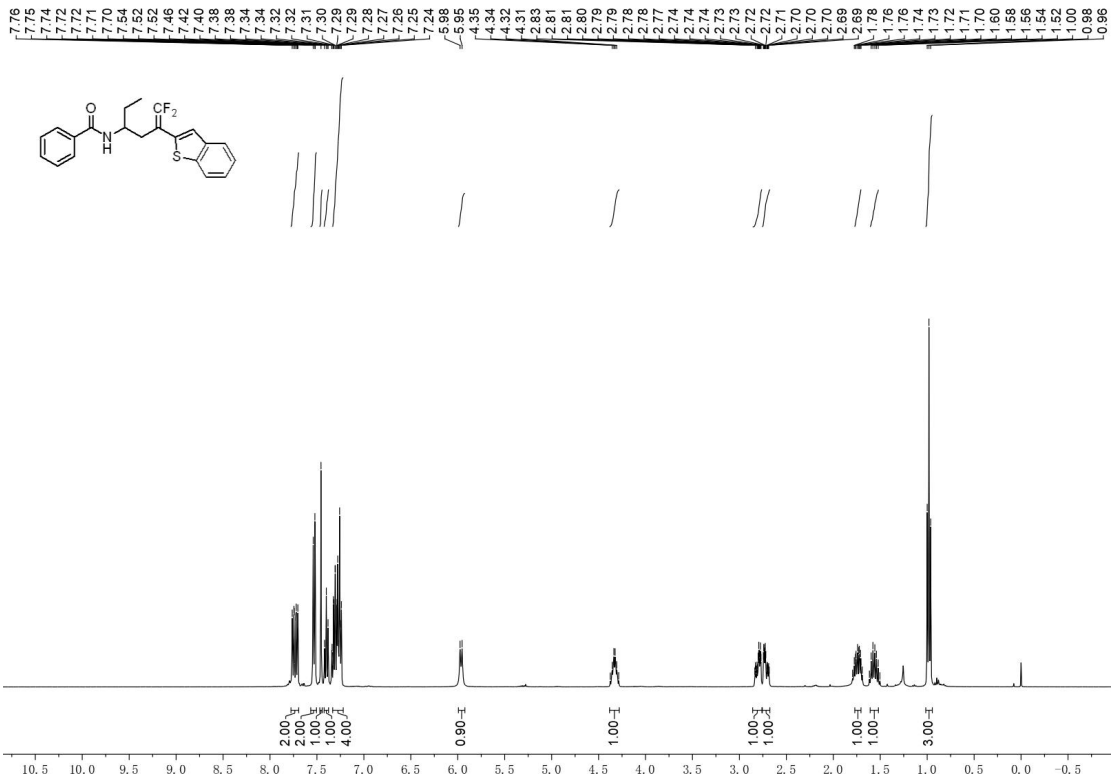

Figure S125. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3as**

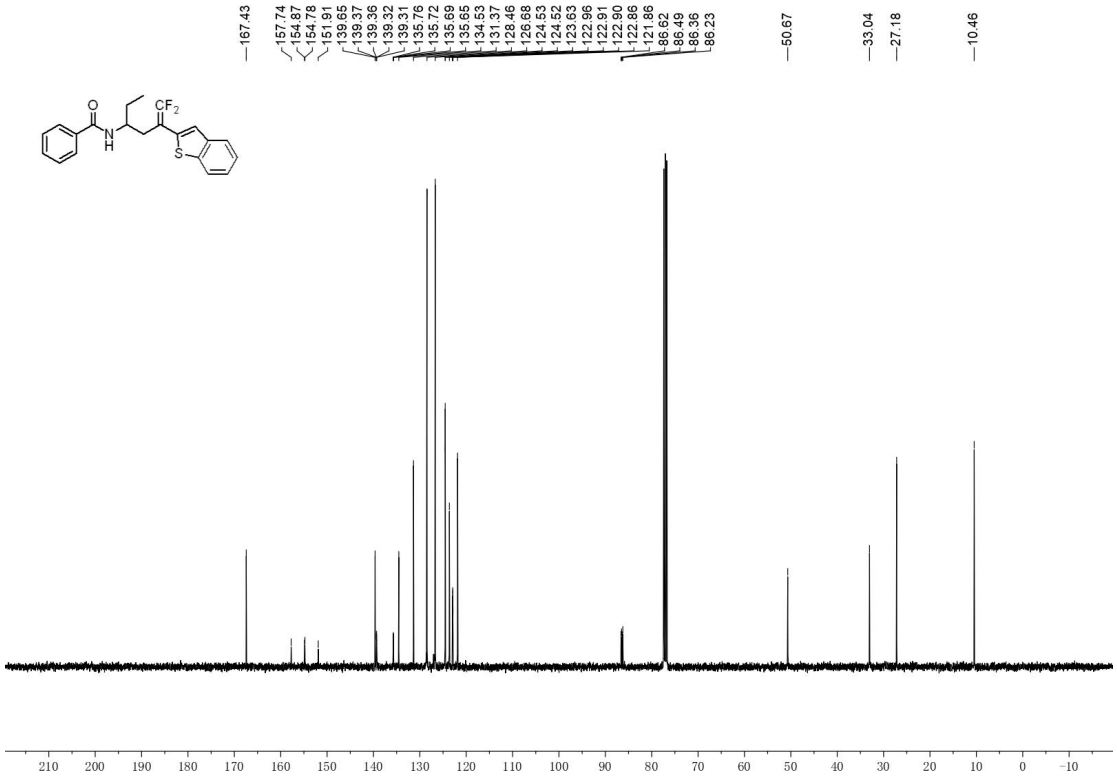

Figure S126. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3as**

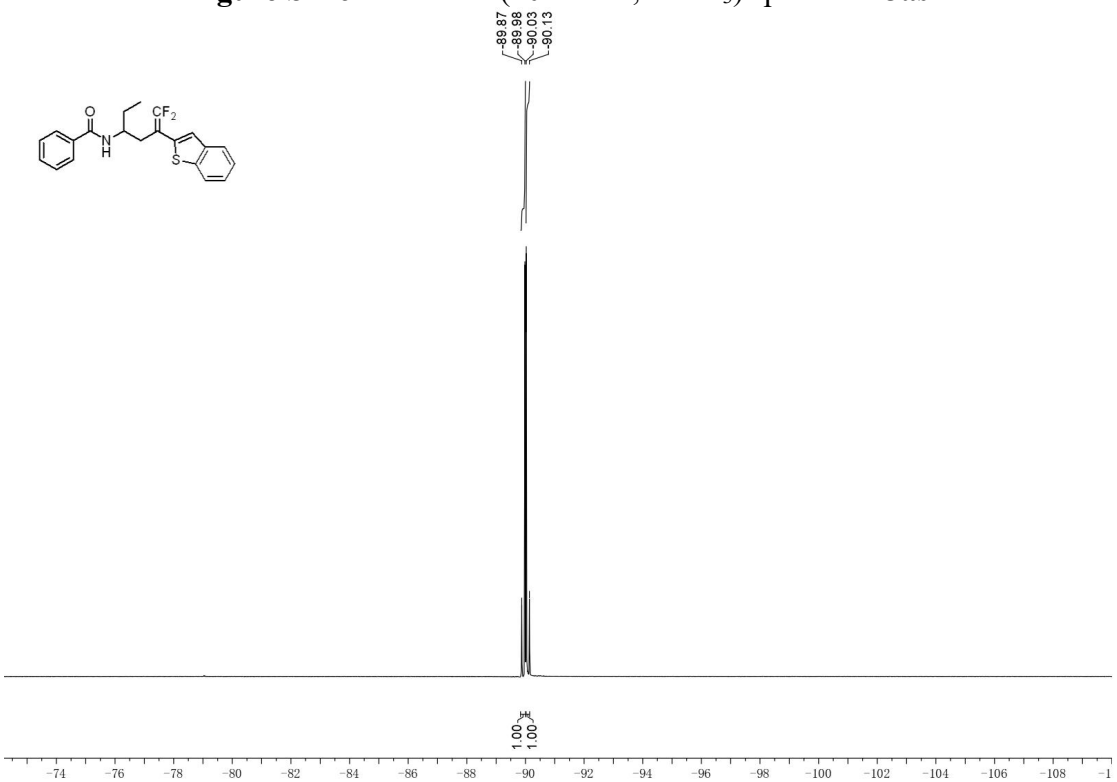

Figure S127. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3as**

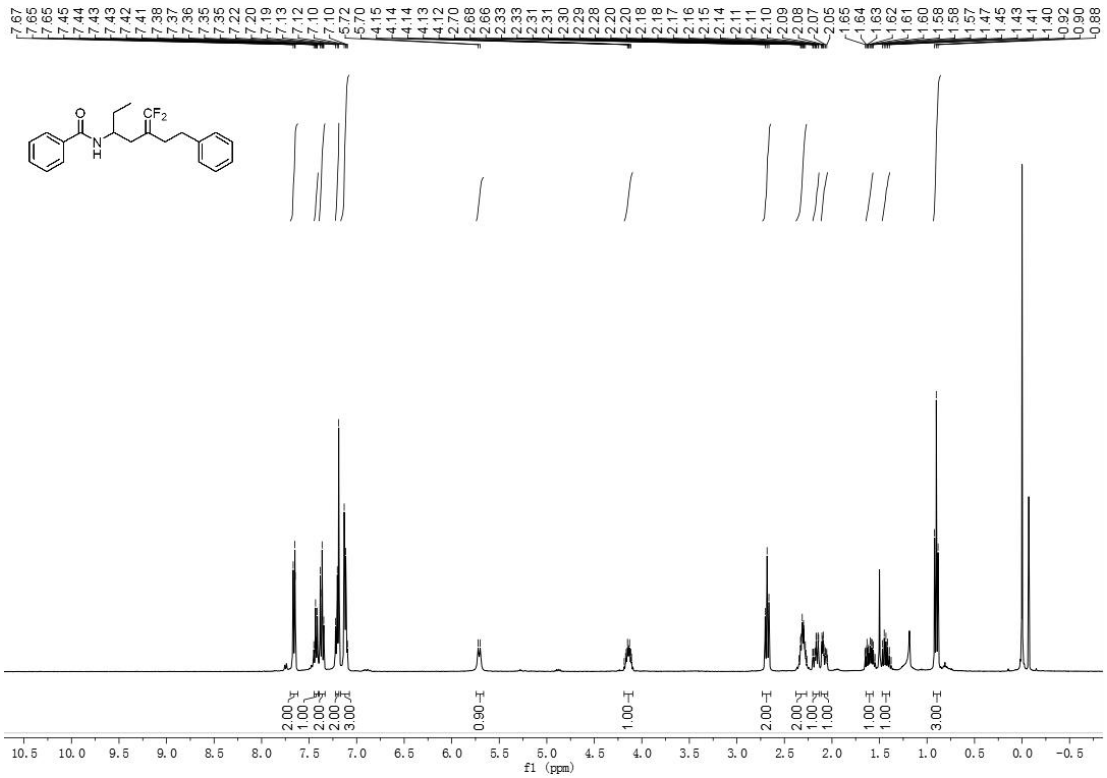

Figure S128. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3at**

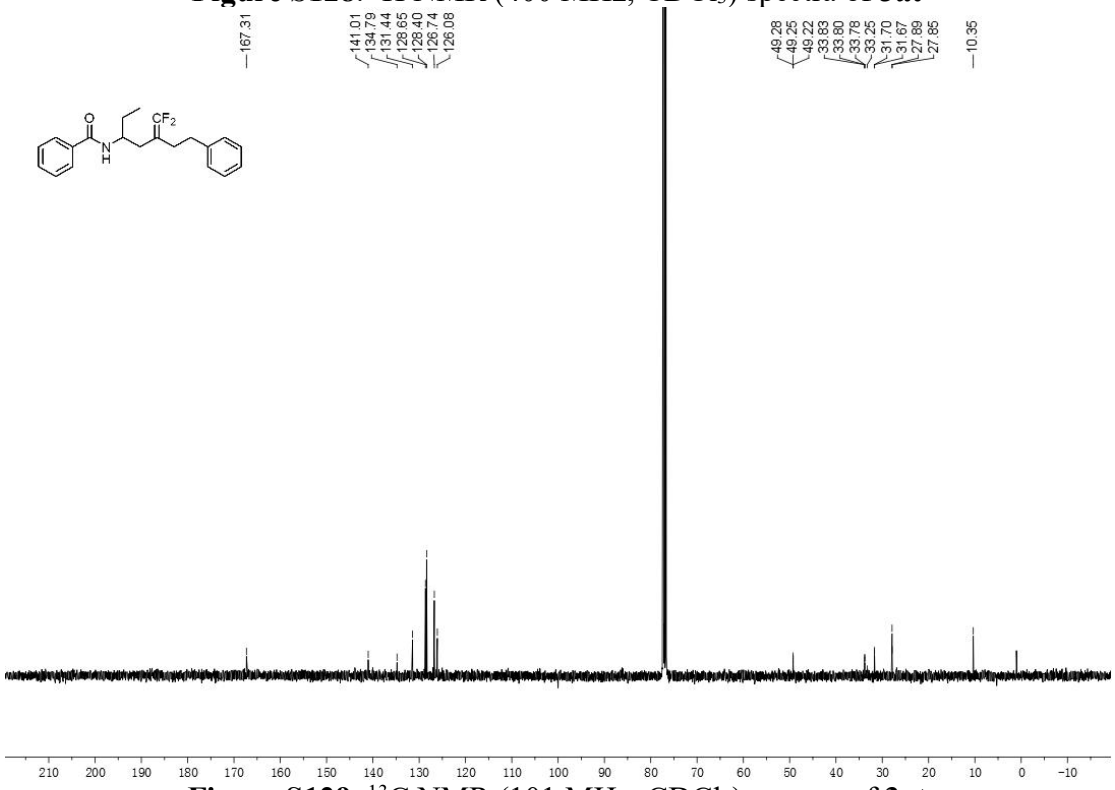

Figure S129. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3at**

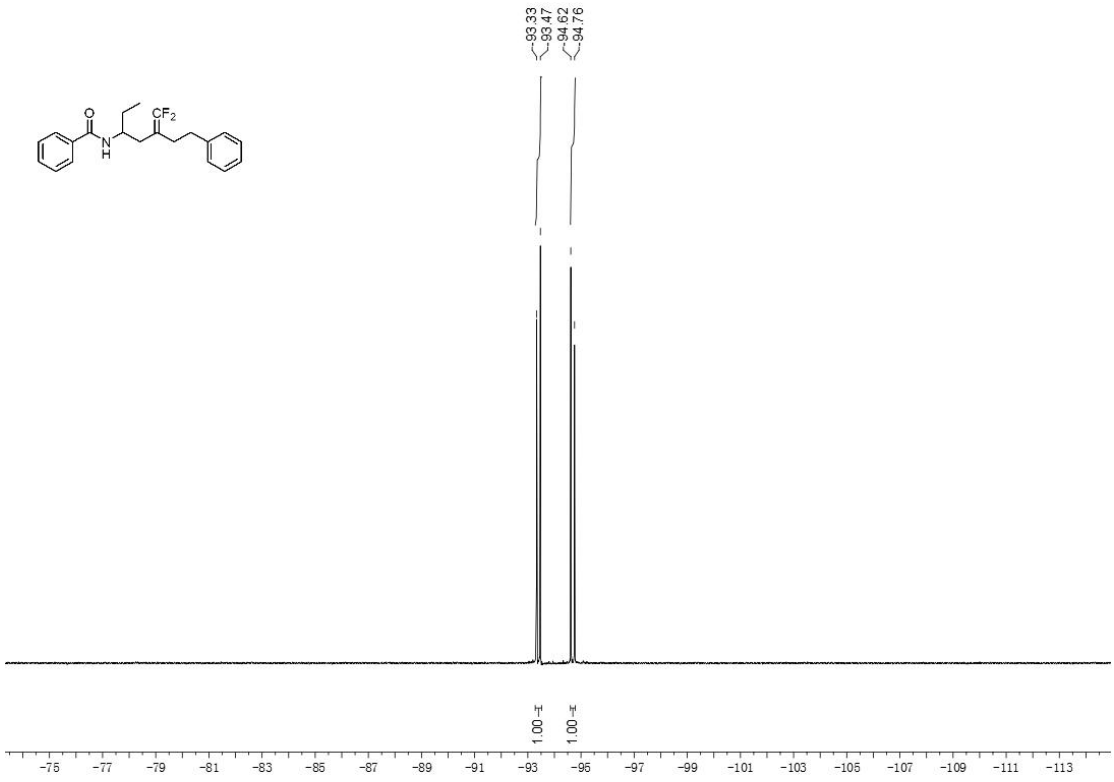

Figure S130. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3at**

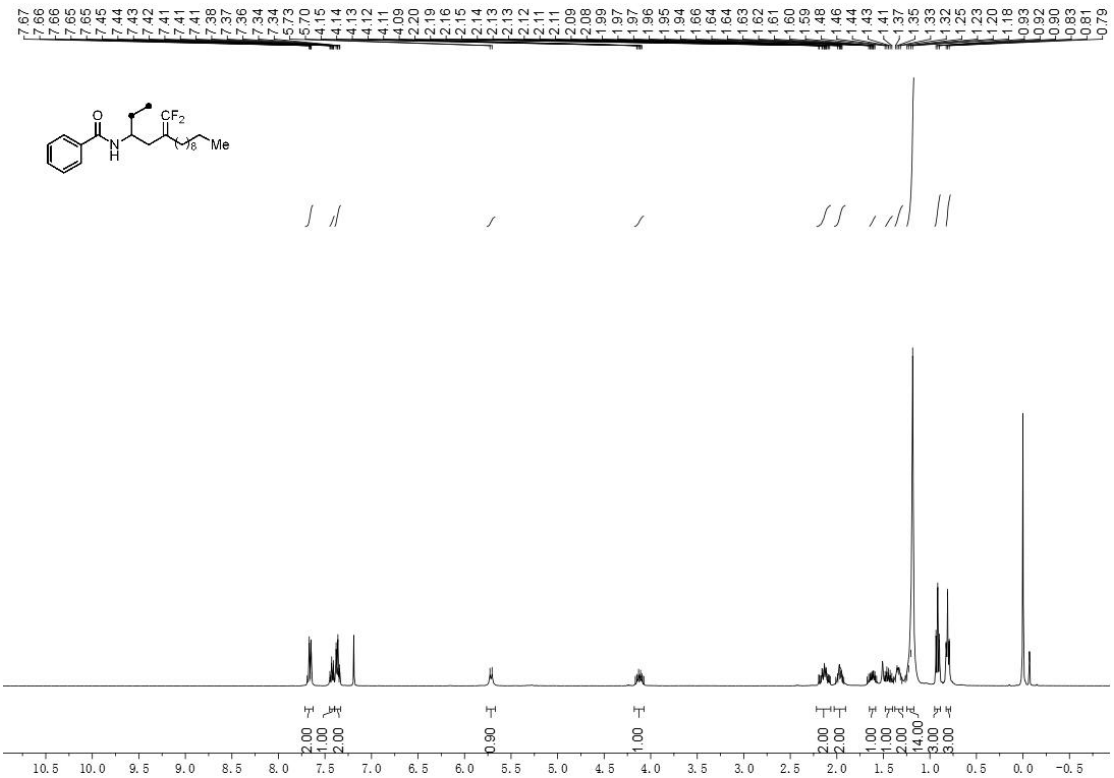

Figure S131. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3au**

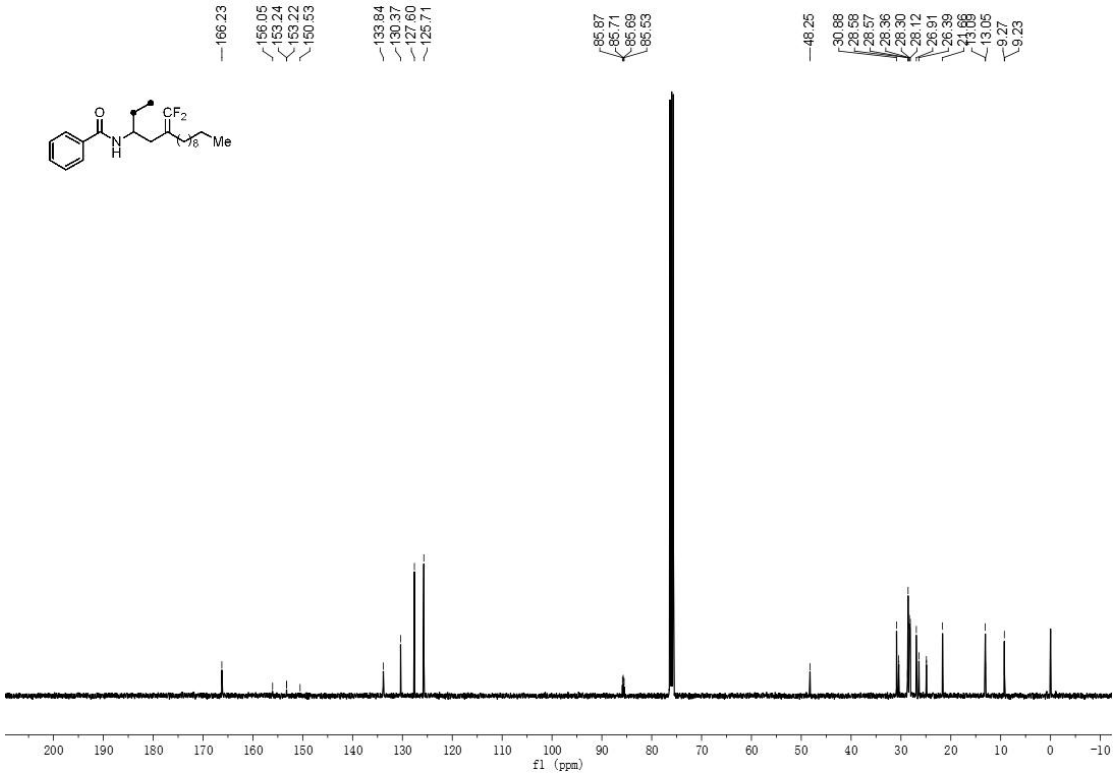

Figure S132. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3au**

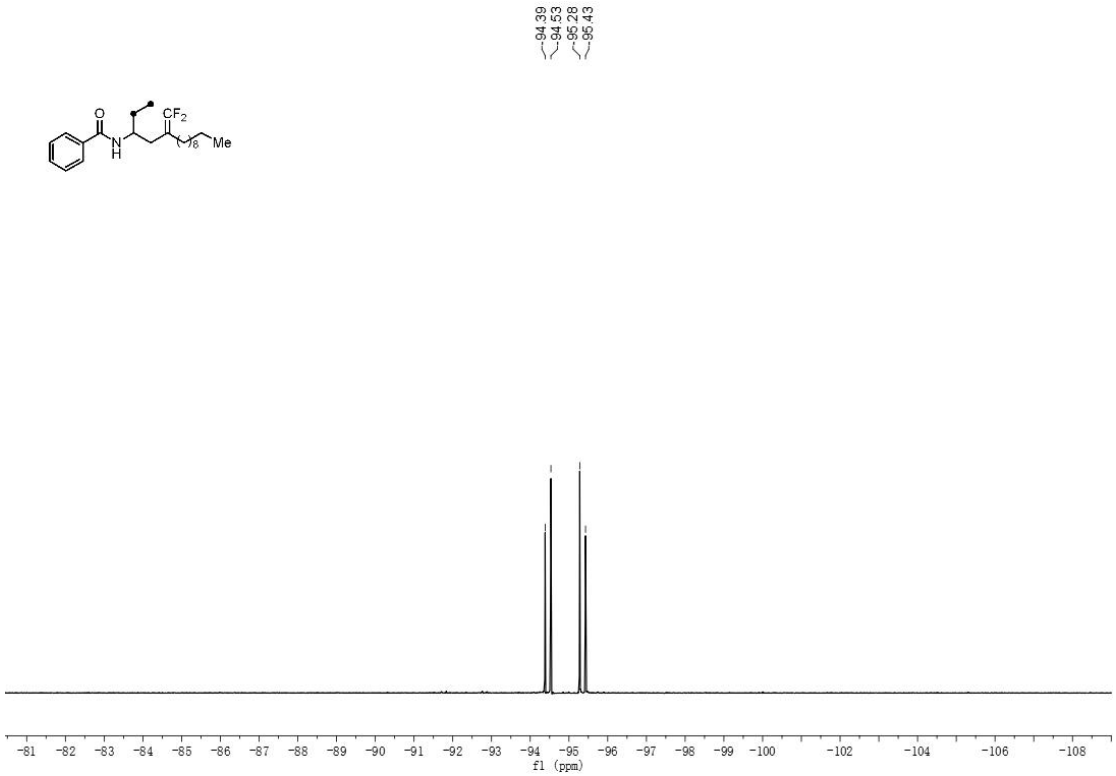

Figure S133. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3au**

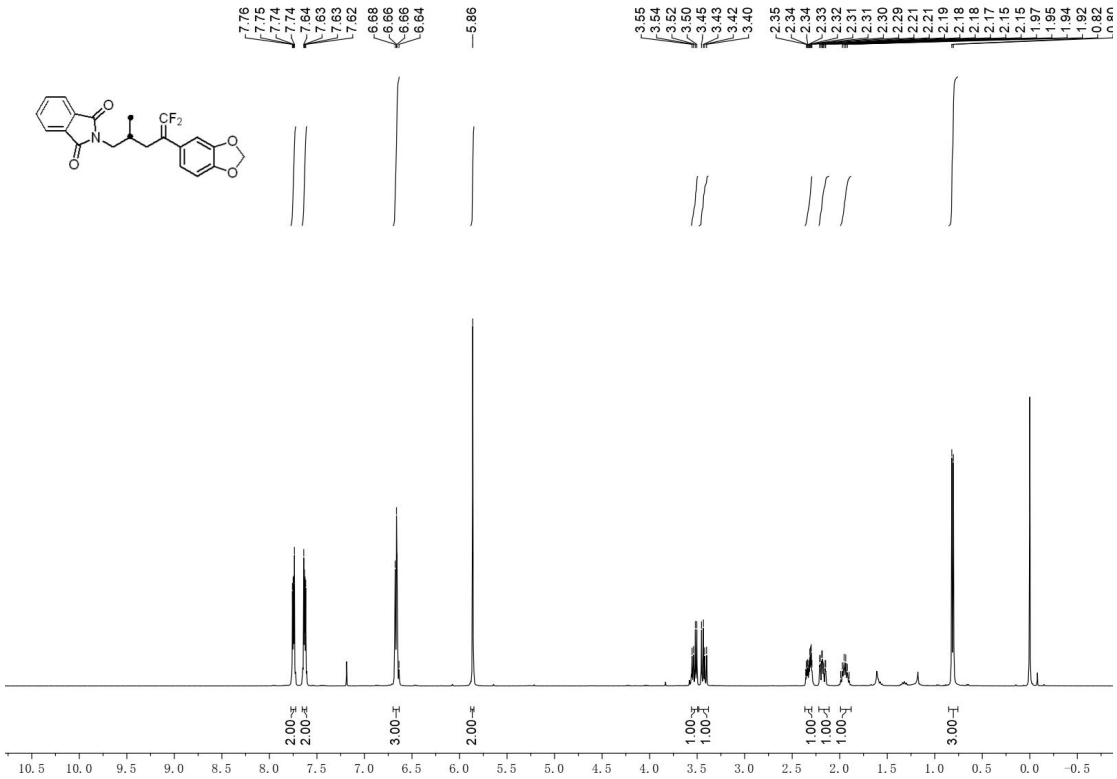

Figure S134. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4a**

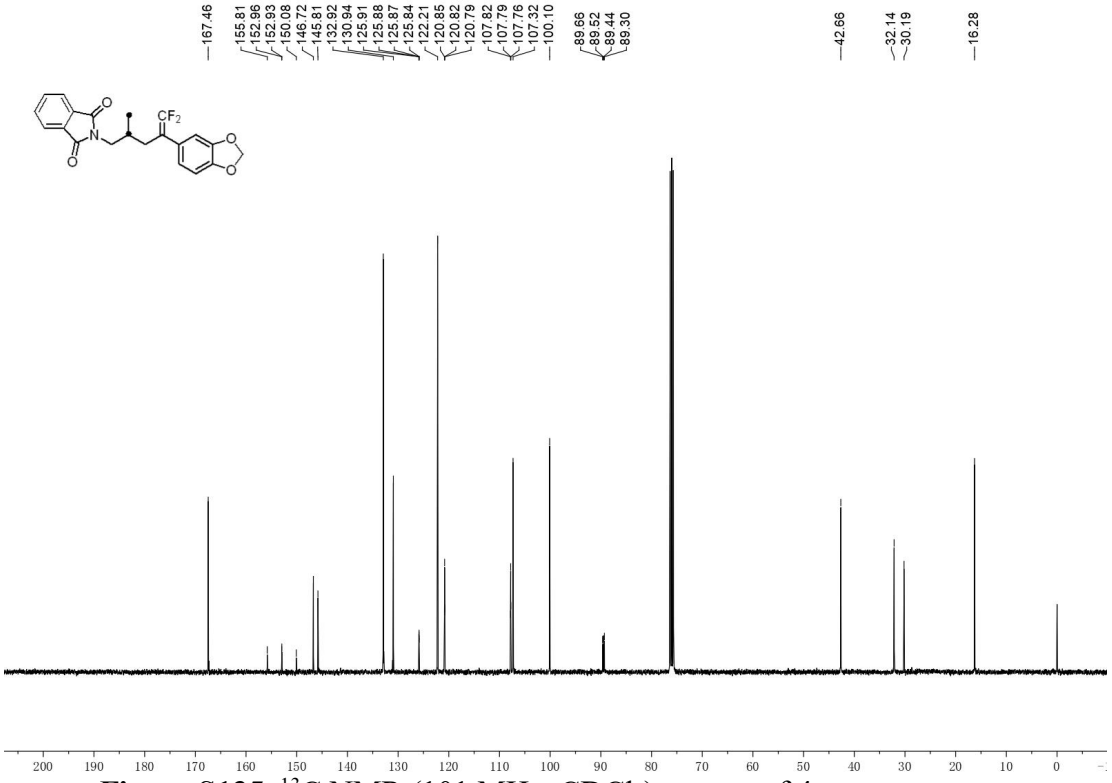

Figure S135. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4a**

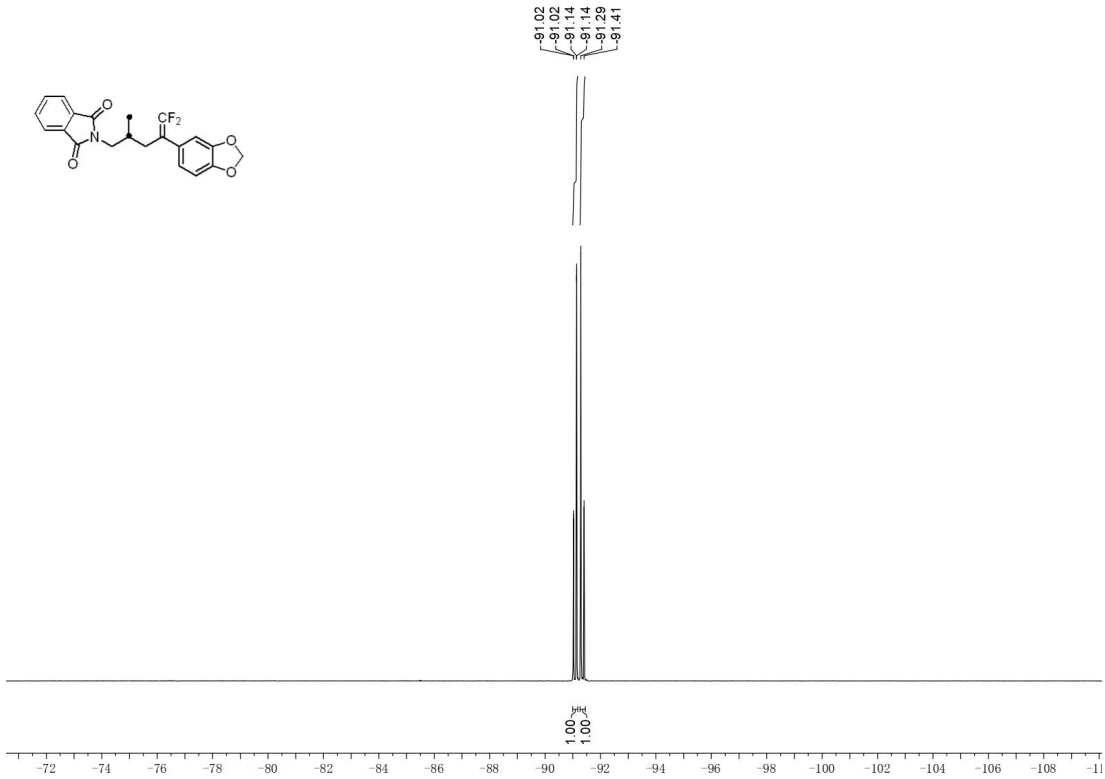

Figure S136. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4a**

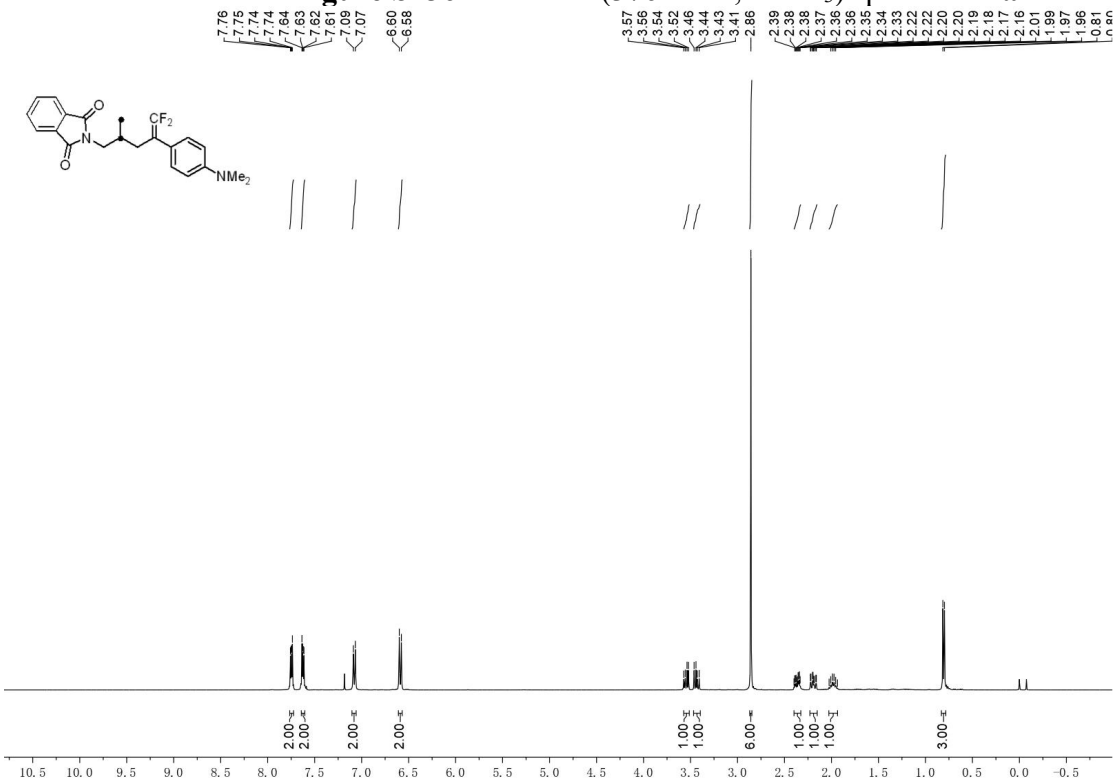

Figure S137. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4b**

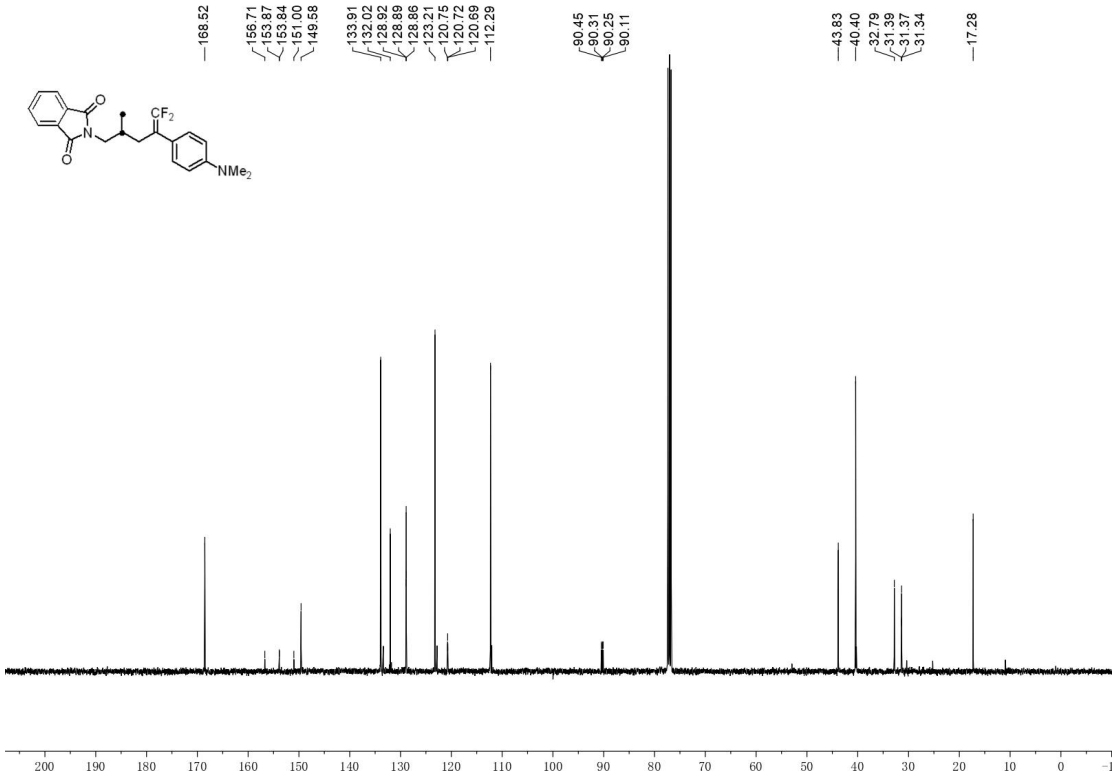

Figure S138. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4b**

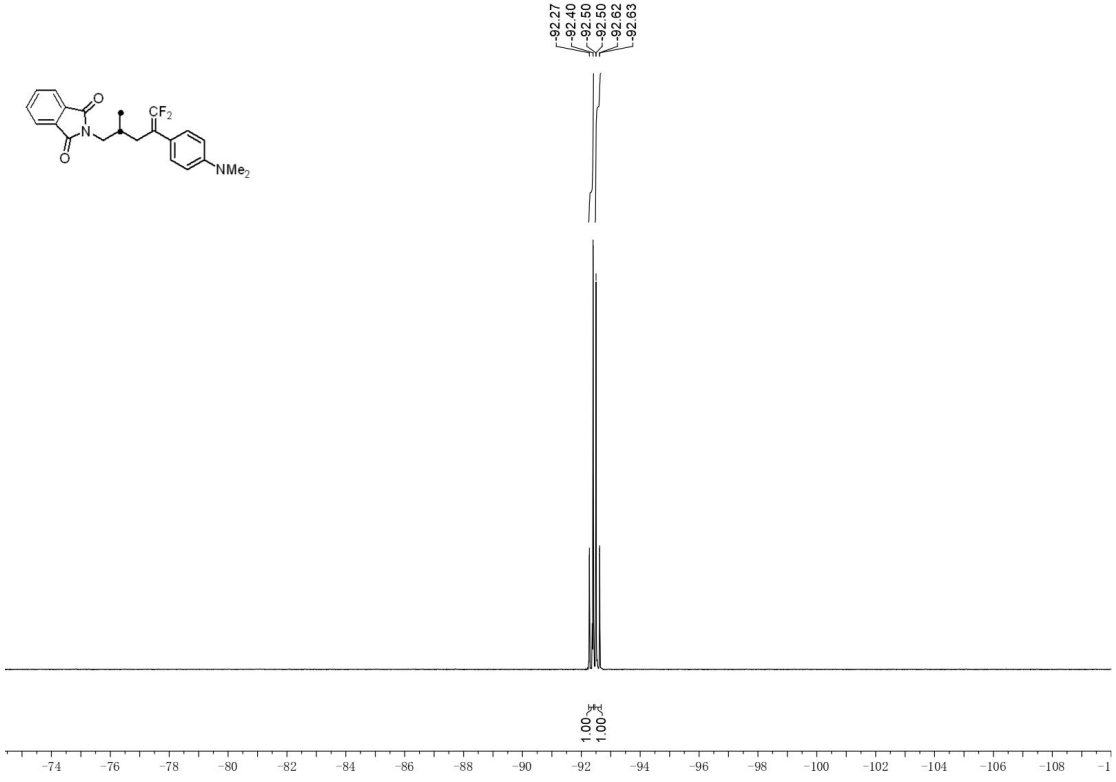

Figure S139. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4b**

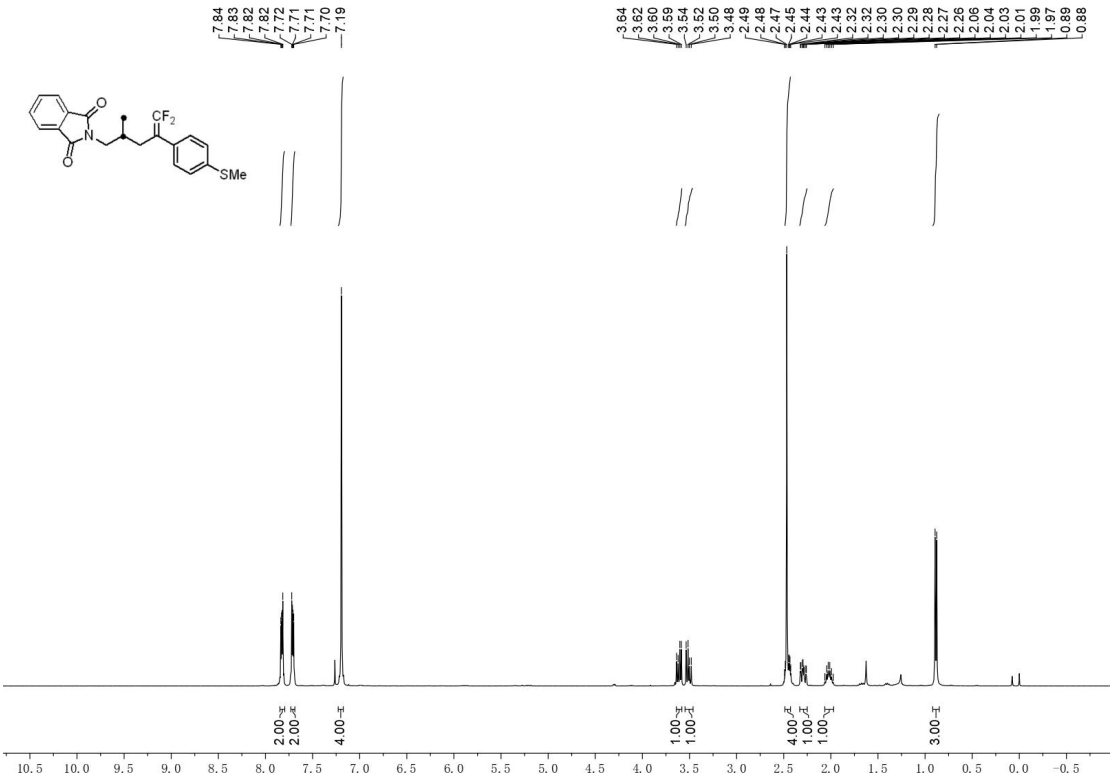

Figure S140. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4c**

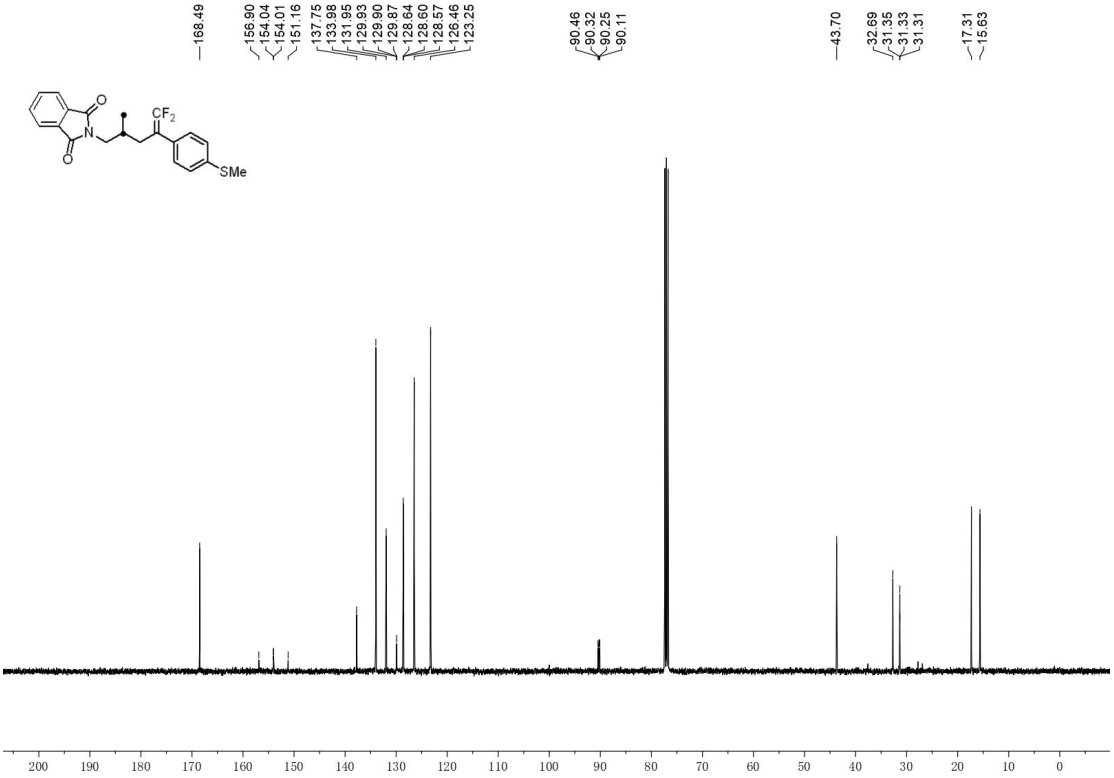

Figure S141. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4c**

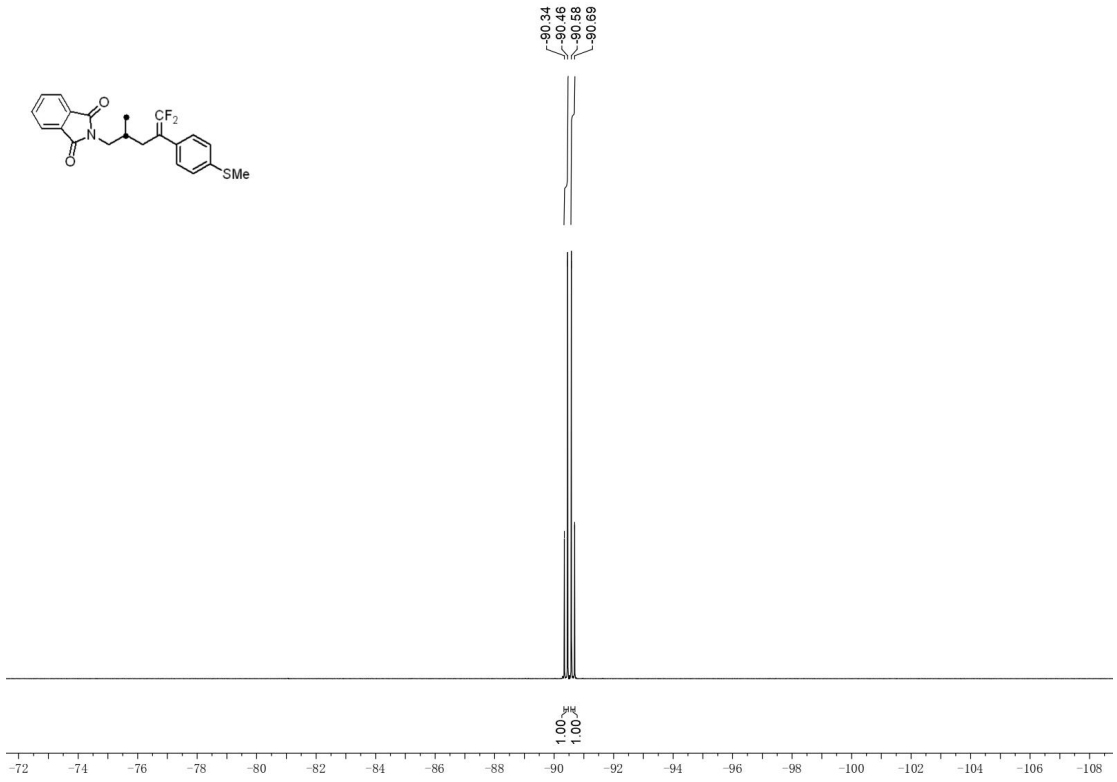

Figure S142. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4c**

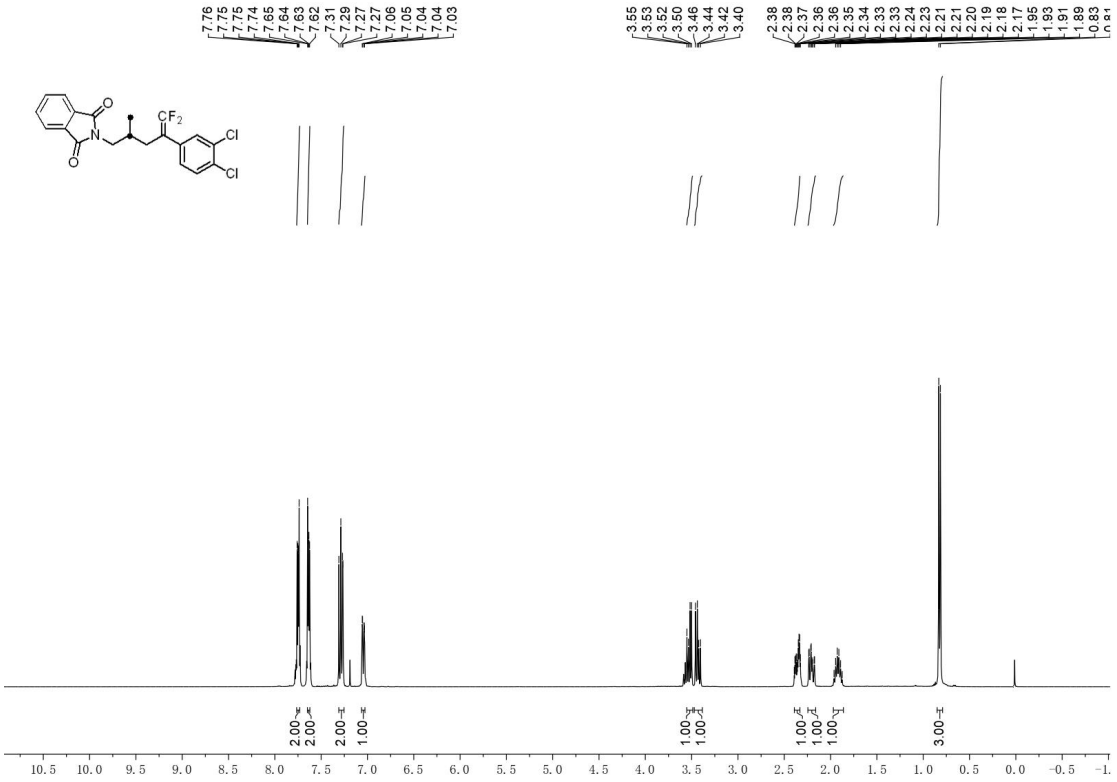

Figure S143. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4d**

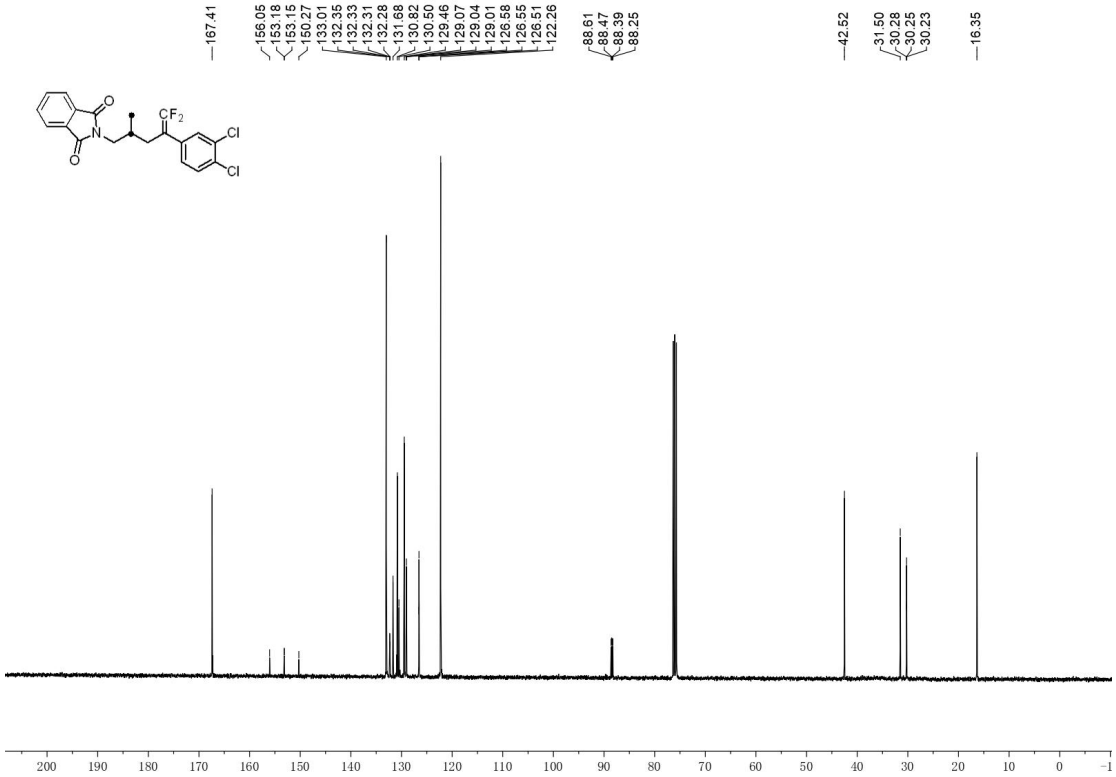

Figure S144. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4d**

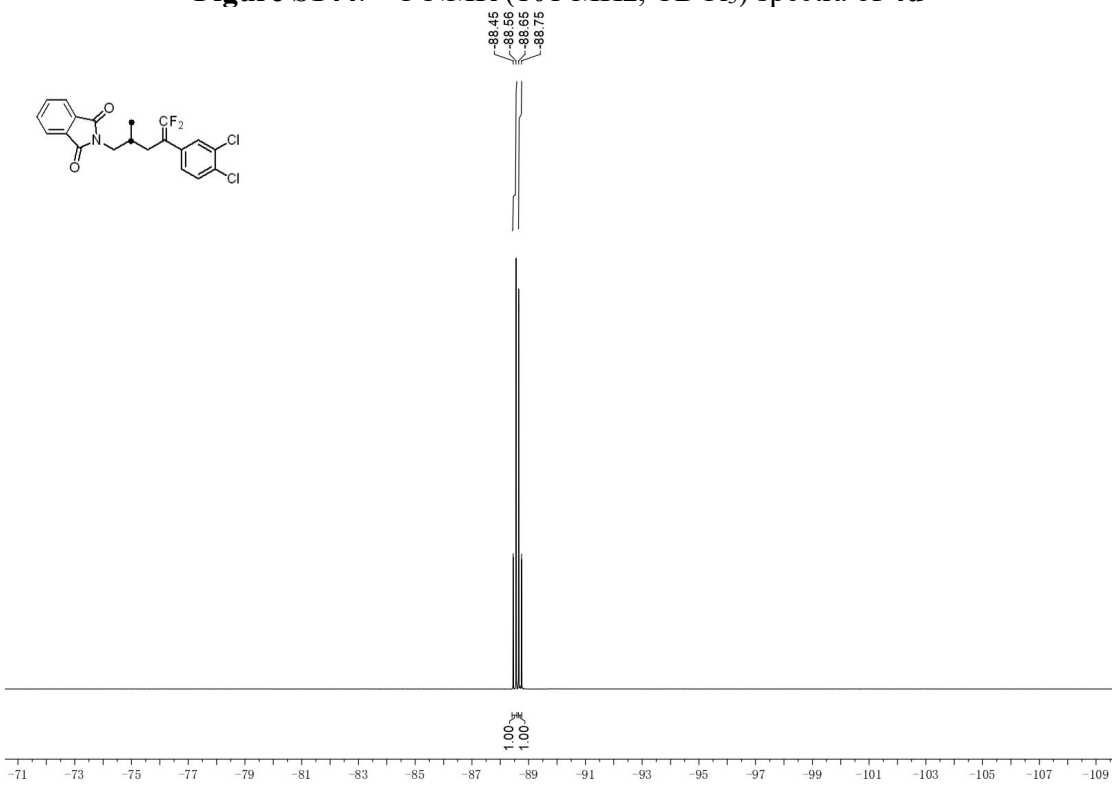

Figure S145. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4d**

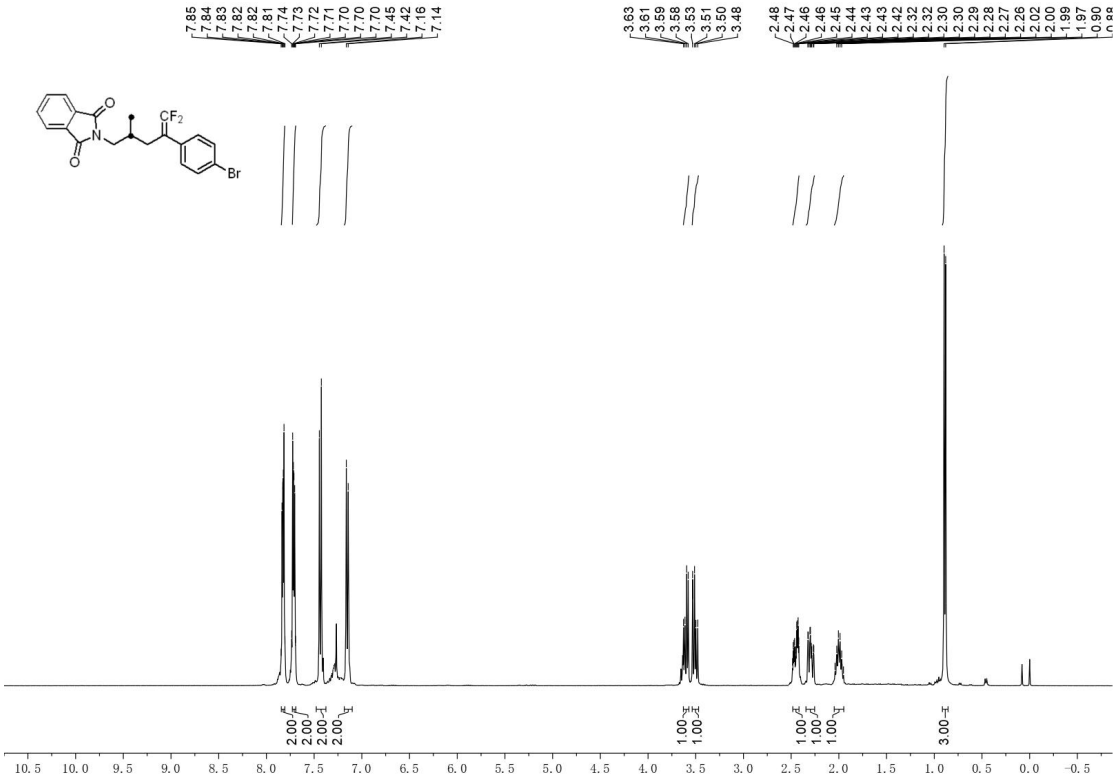

Figure S146. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4e**

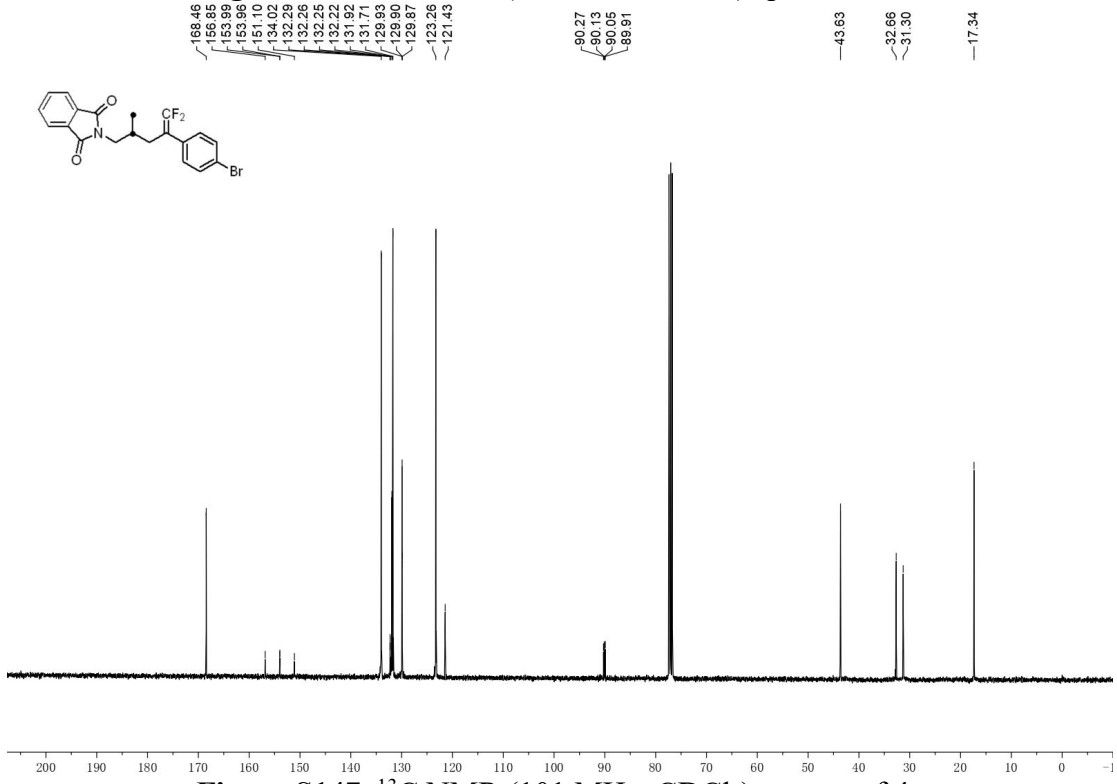

Figure S147. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4e**

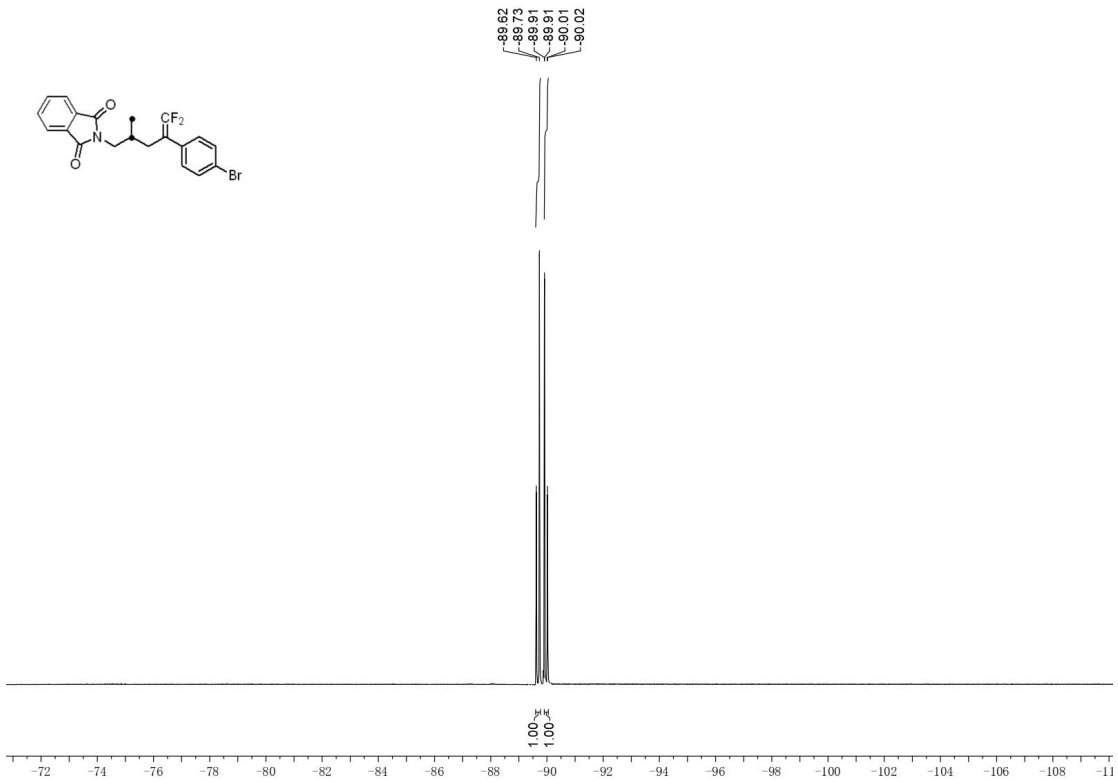

Figure S148. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4e**

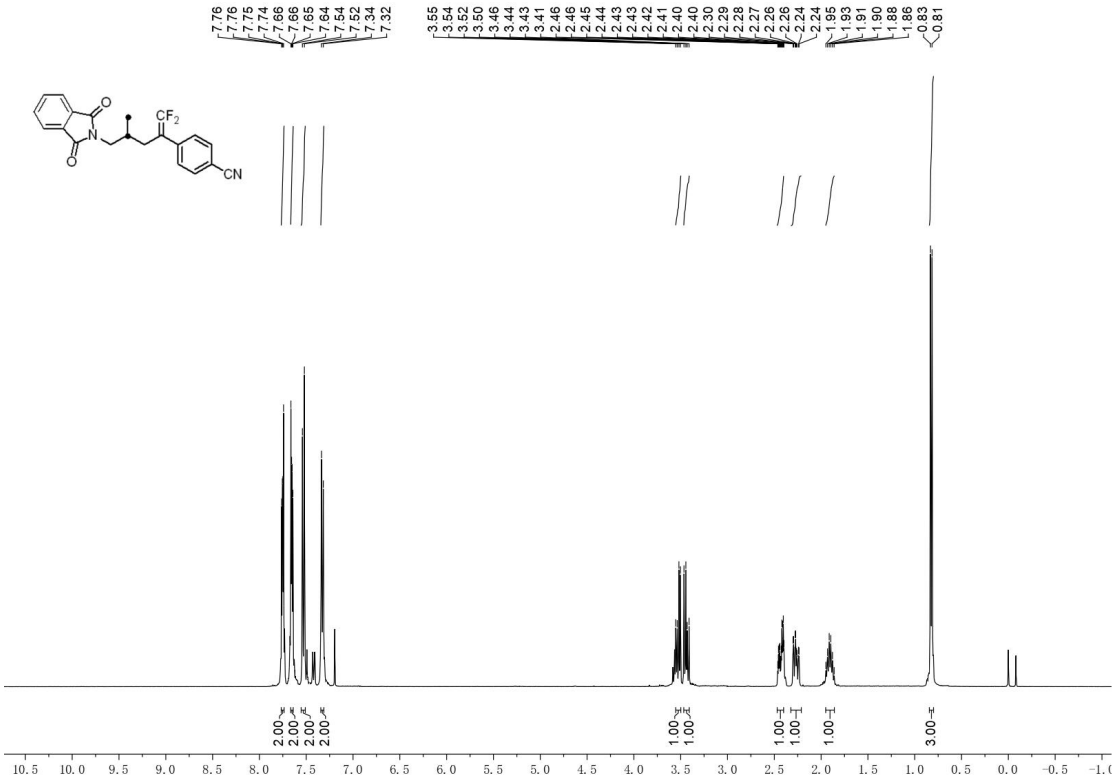

Figure S149. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4f**

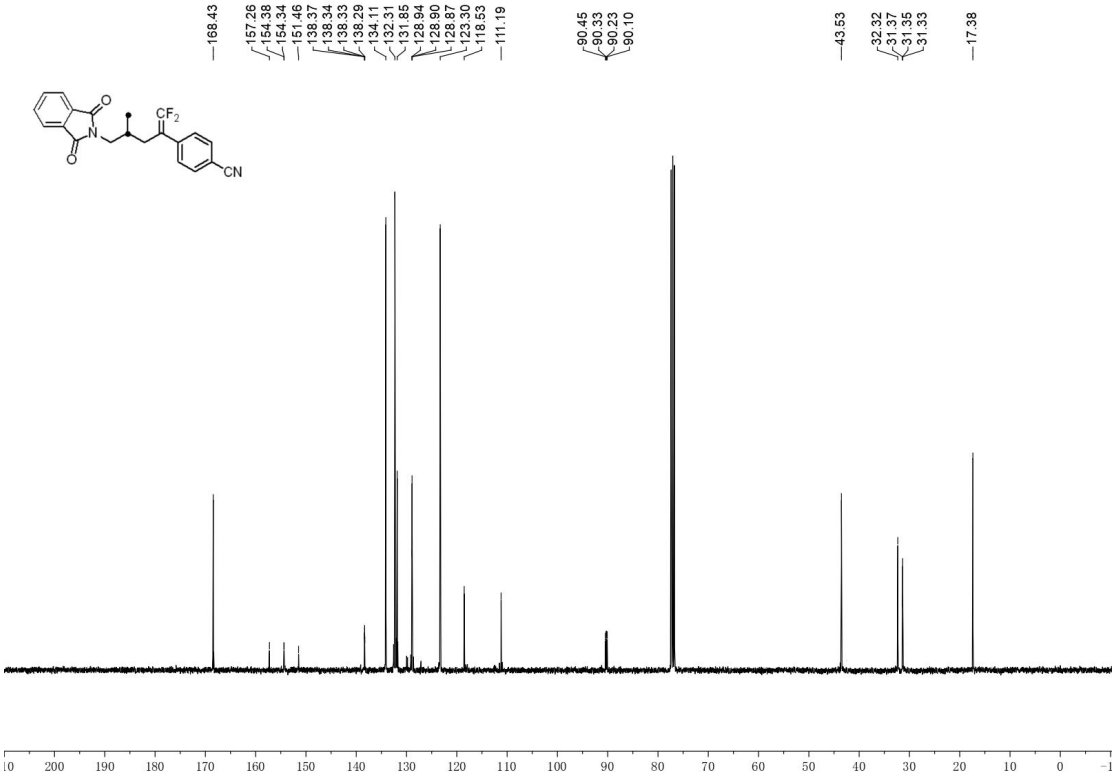

Figure S150. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4f**

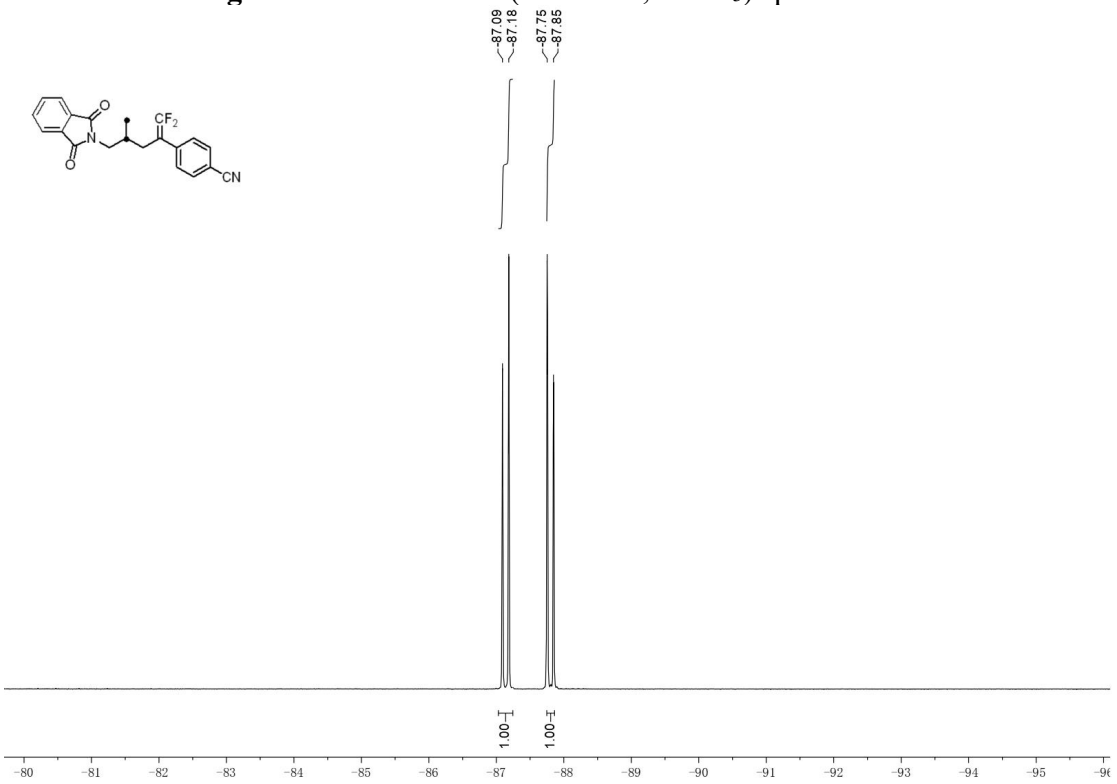

Figure S151. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4f**

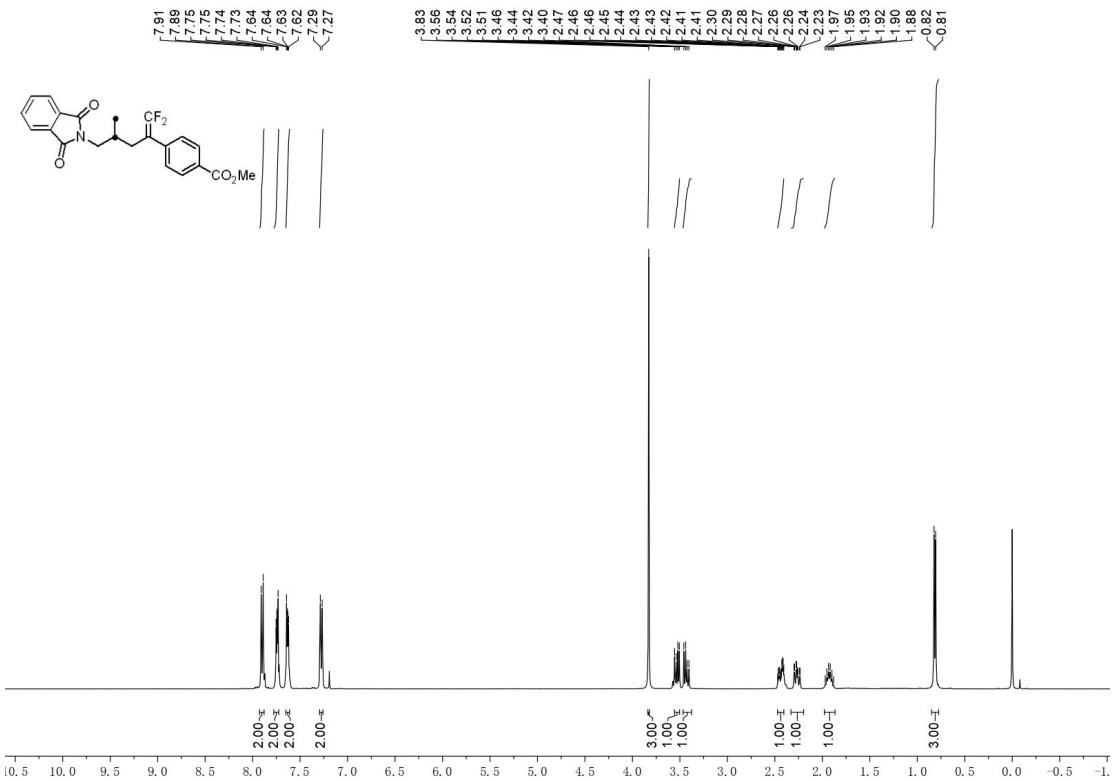

Figure S152. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4g**

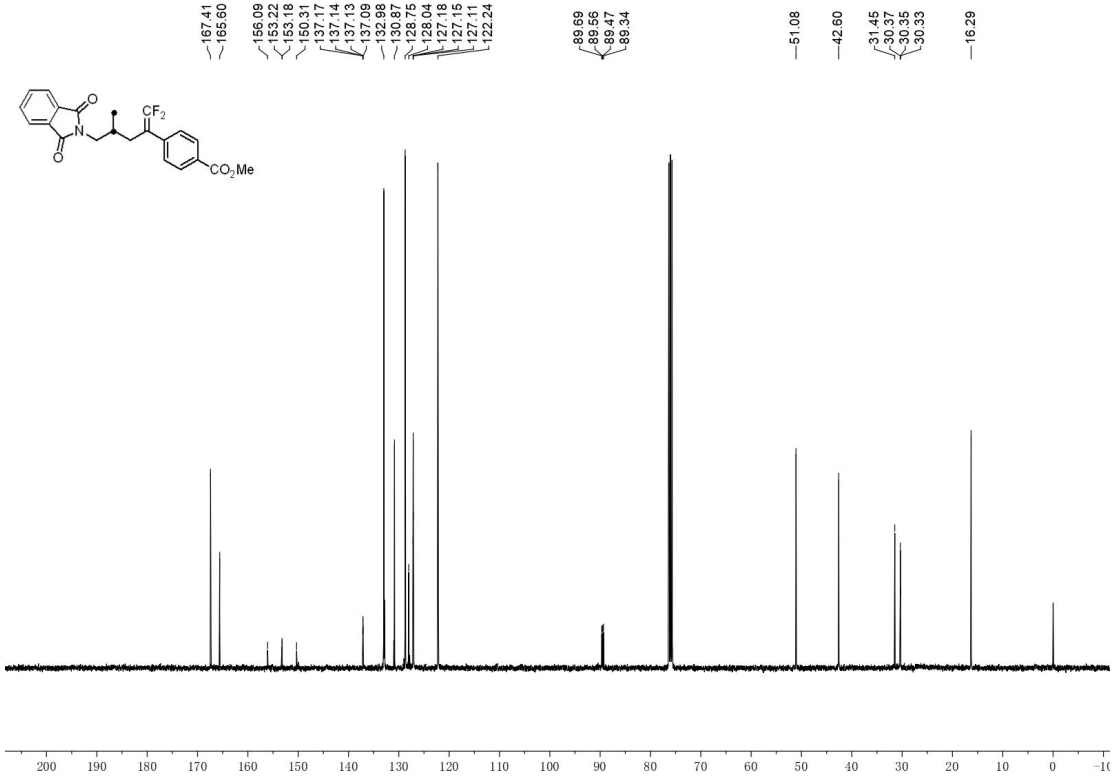

Figure S153. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4g**

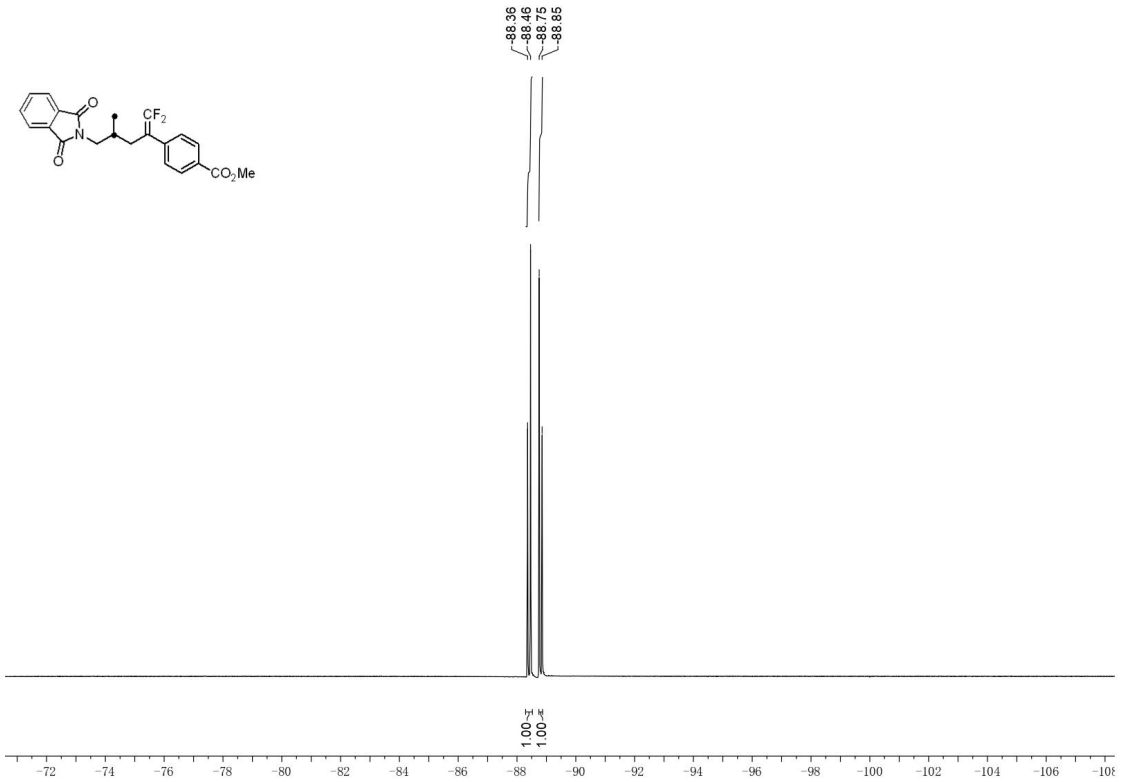

Figure S154. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4g**

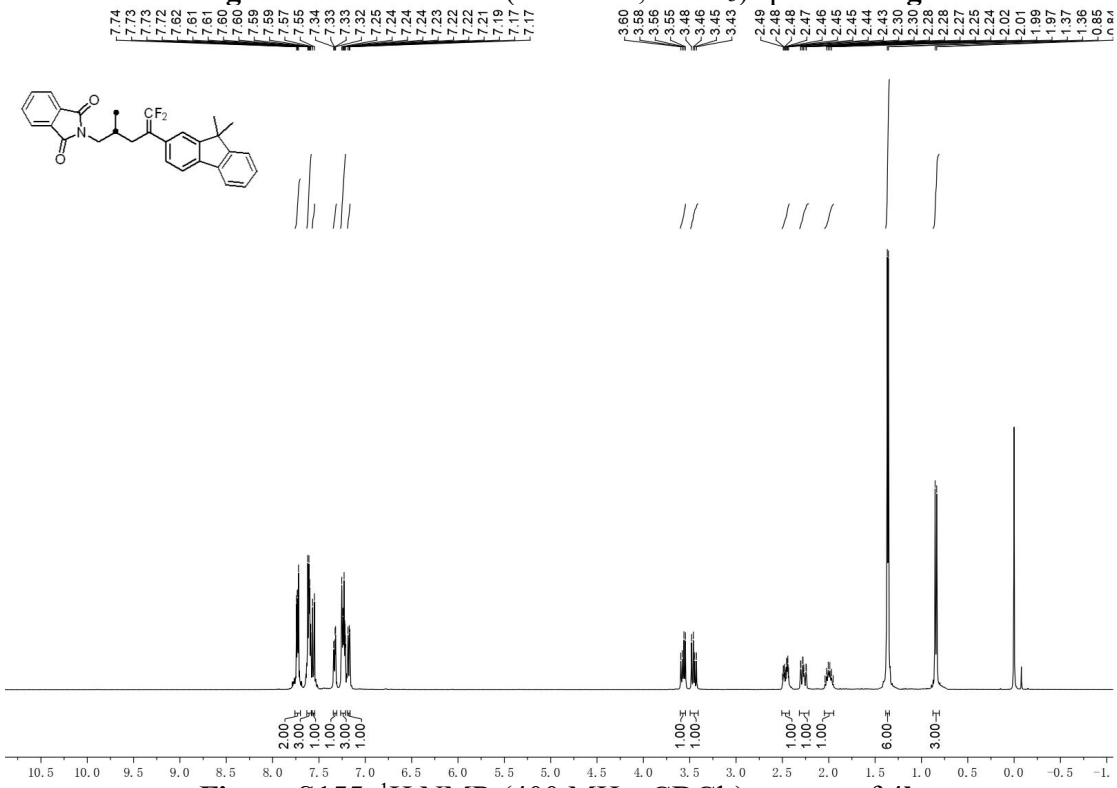

Figure S155. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4h**

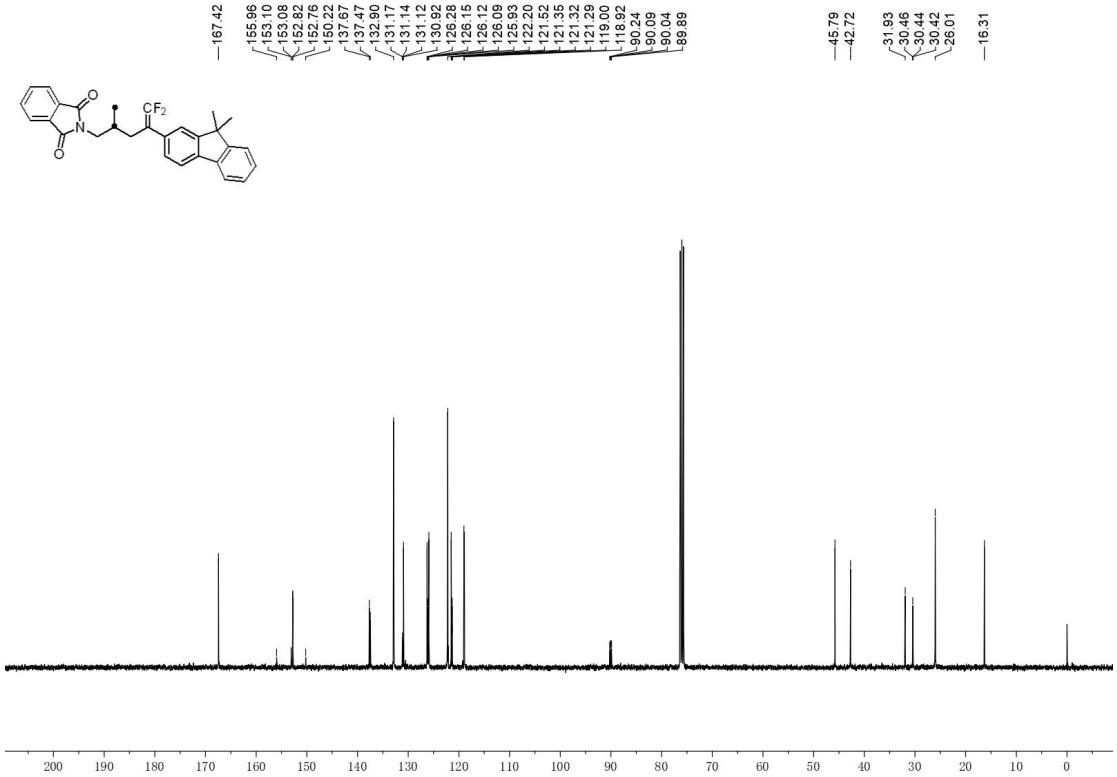

Figure S156. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4h**

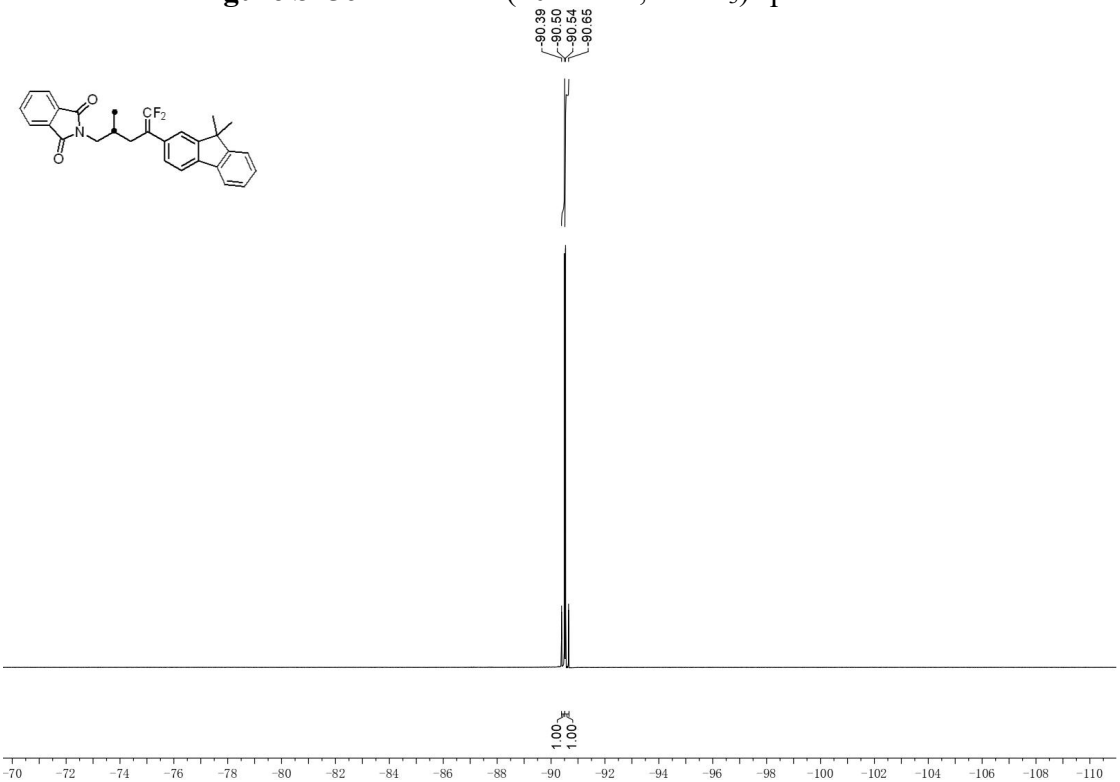

Figure S157. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4h**

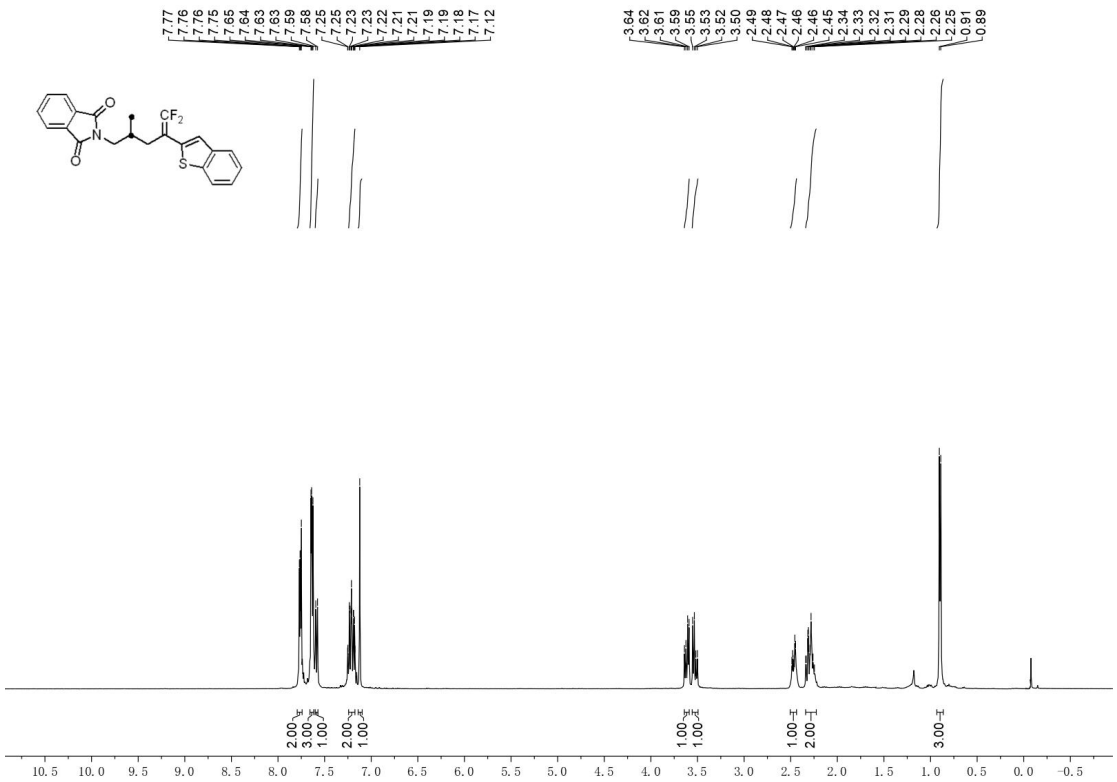

Figure S158. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4i**

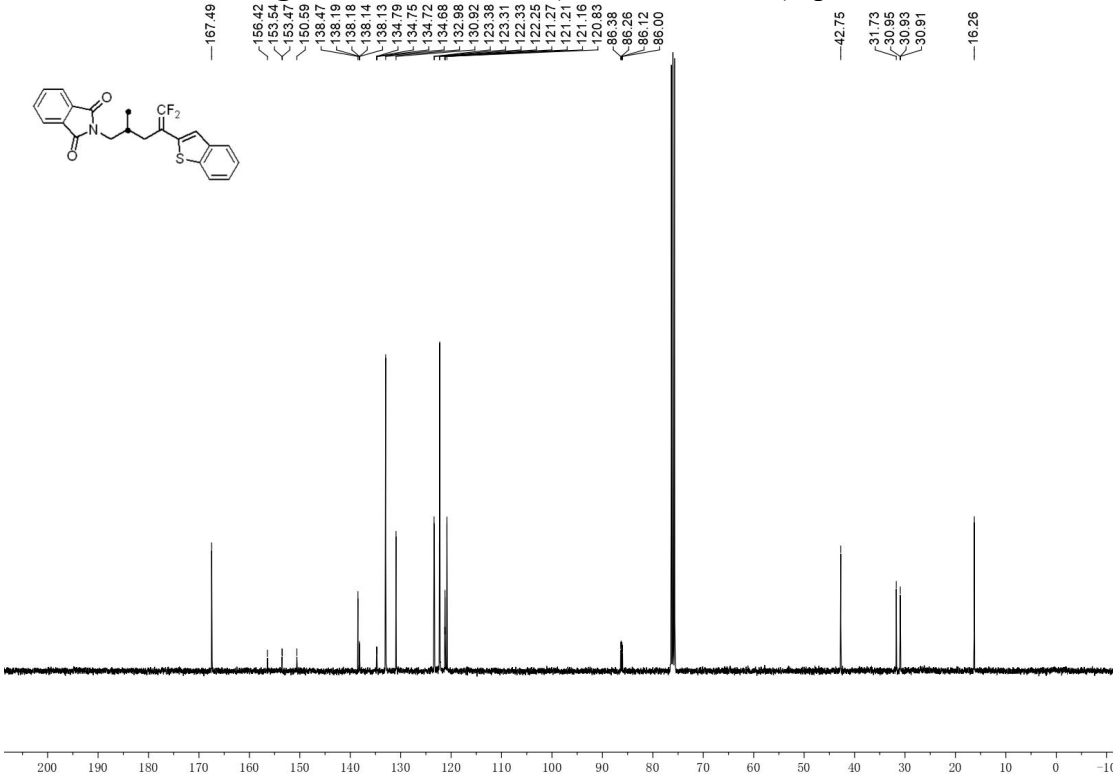

Figure S159. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4i**

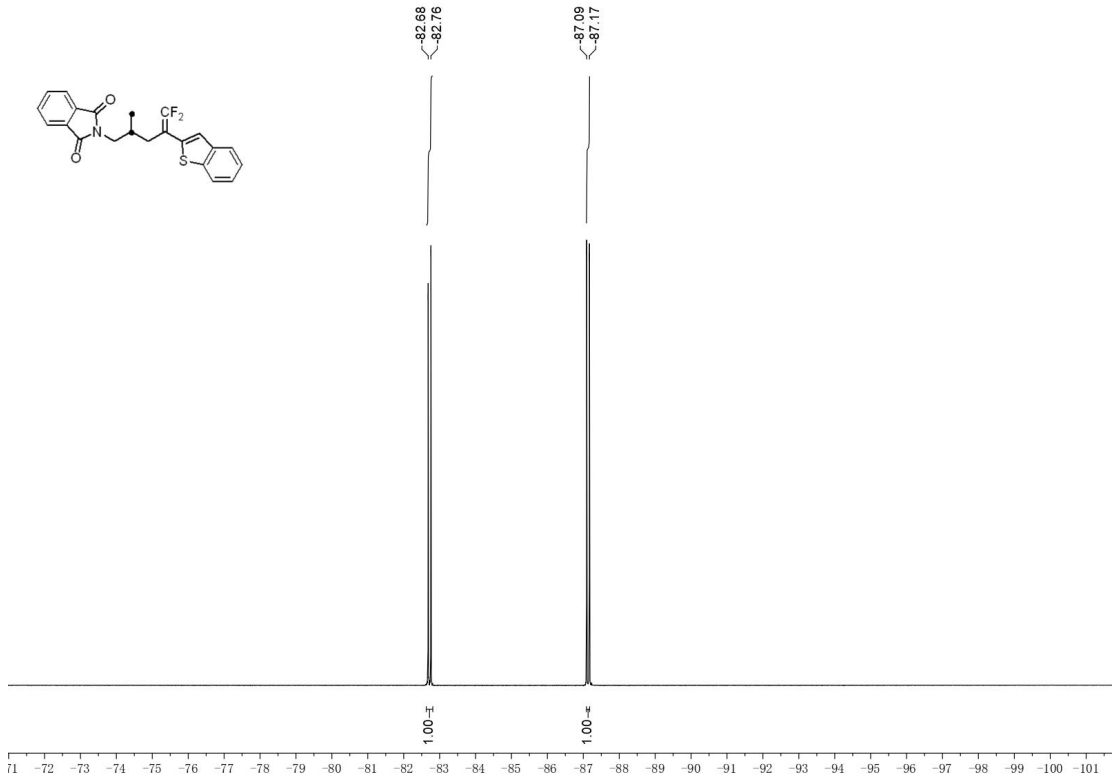

Figure S160. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4i**

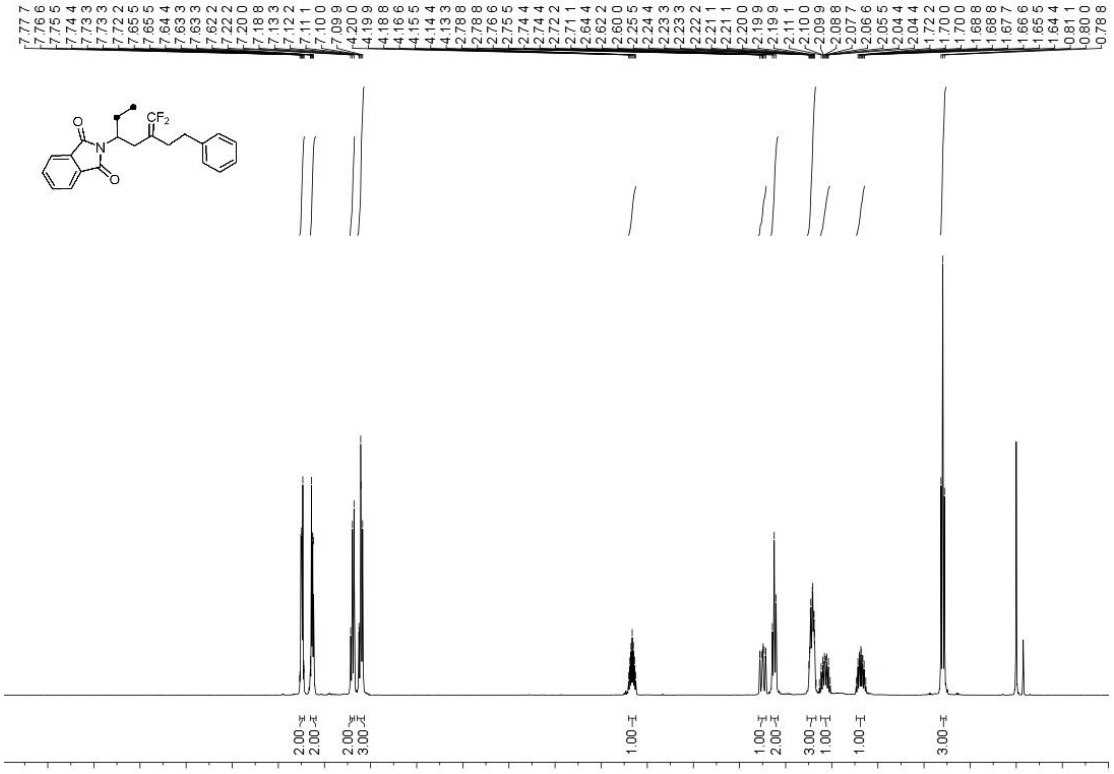

Figure S161. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4j**

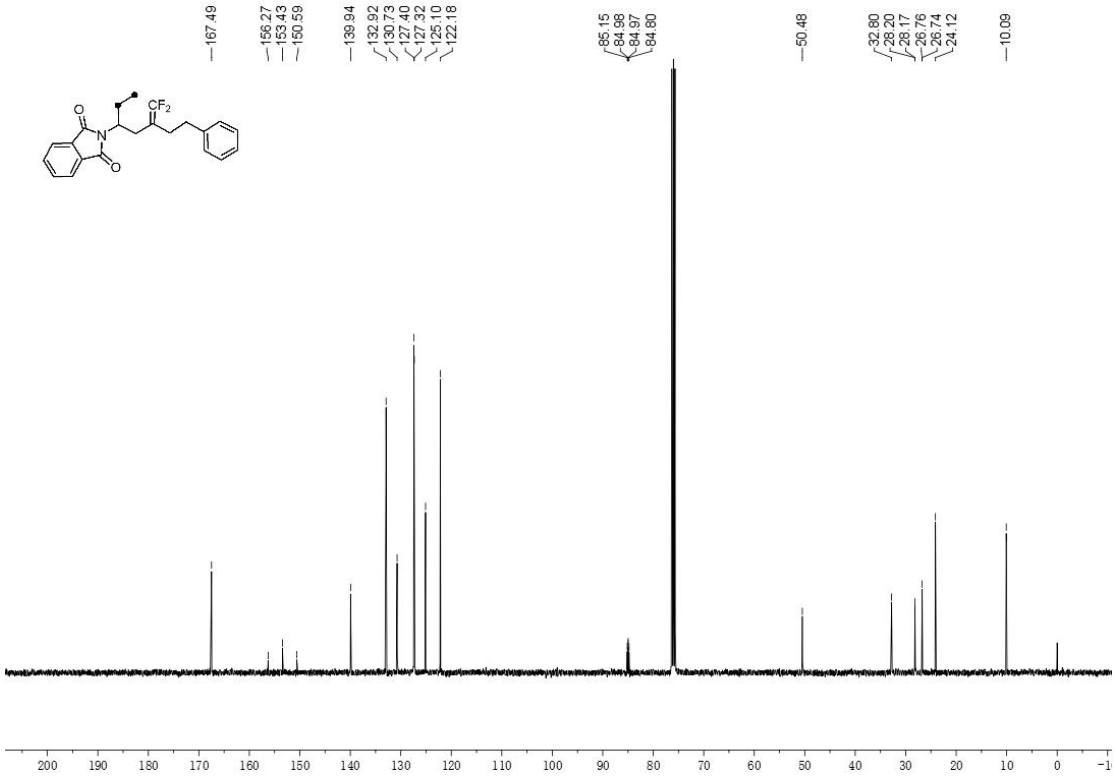

Figure S162. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4j**

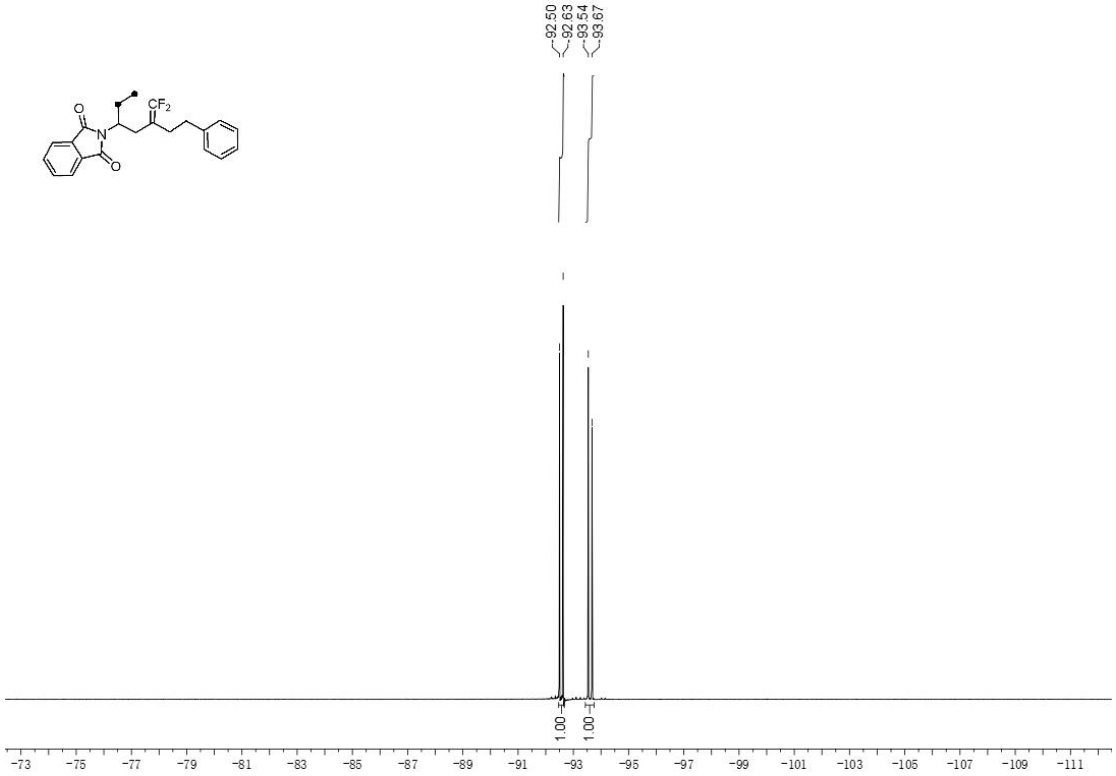

Figure S163. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4j**

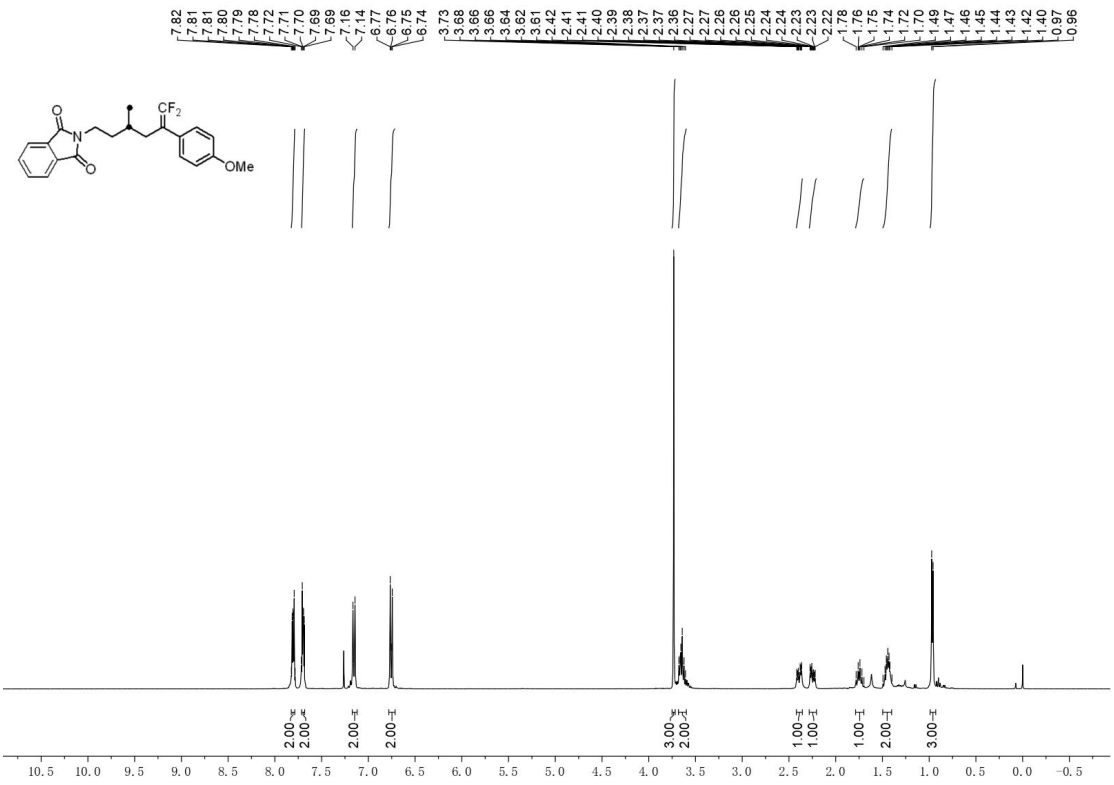

Figure S164. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4k**

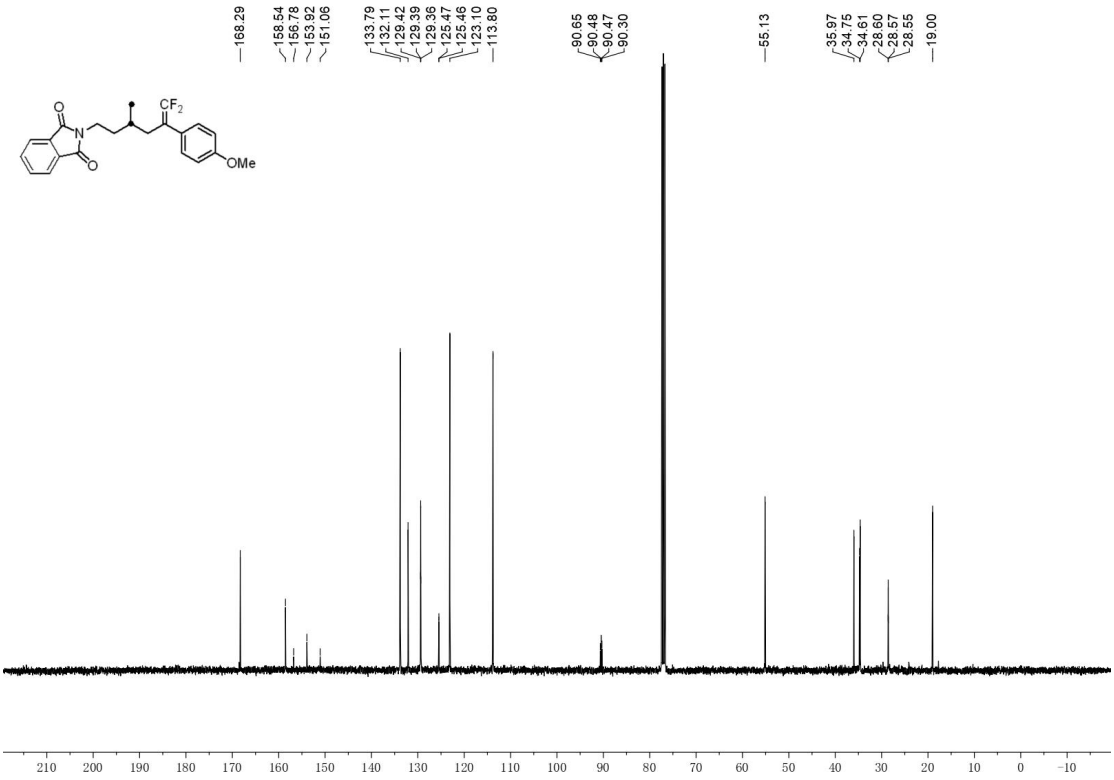

Figure S165. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4k**

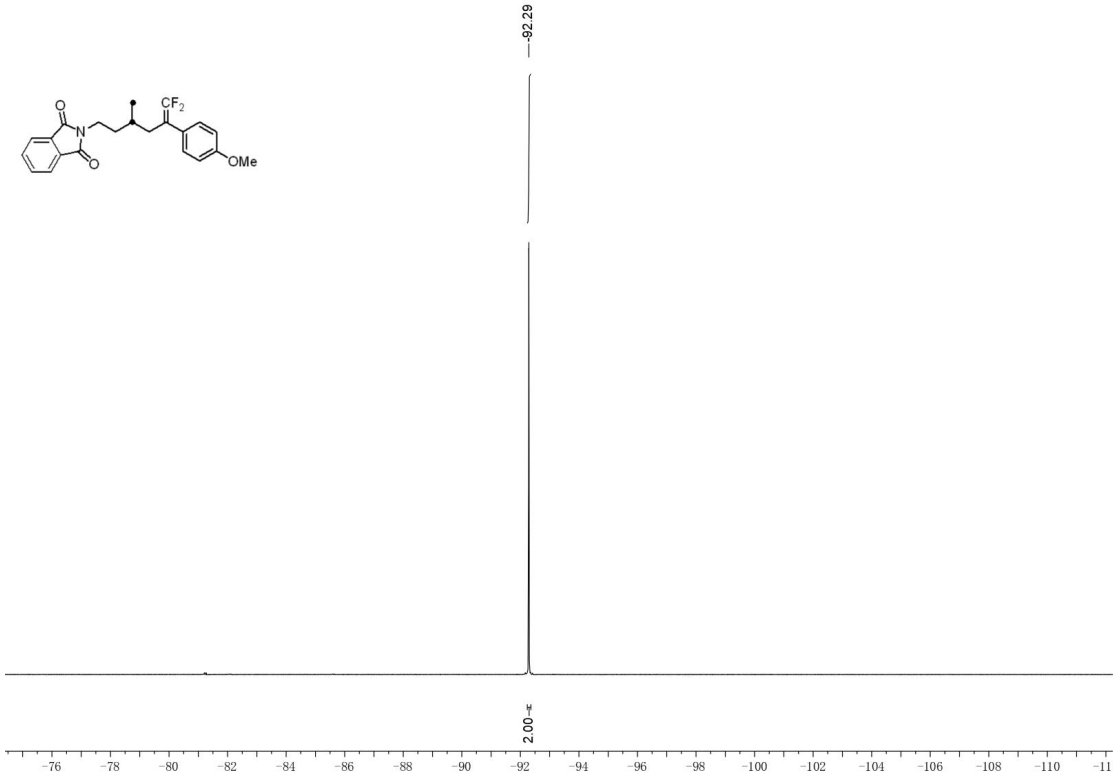

Figure S166. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4k**

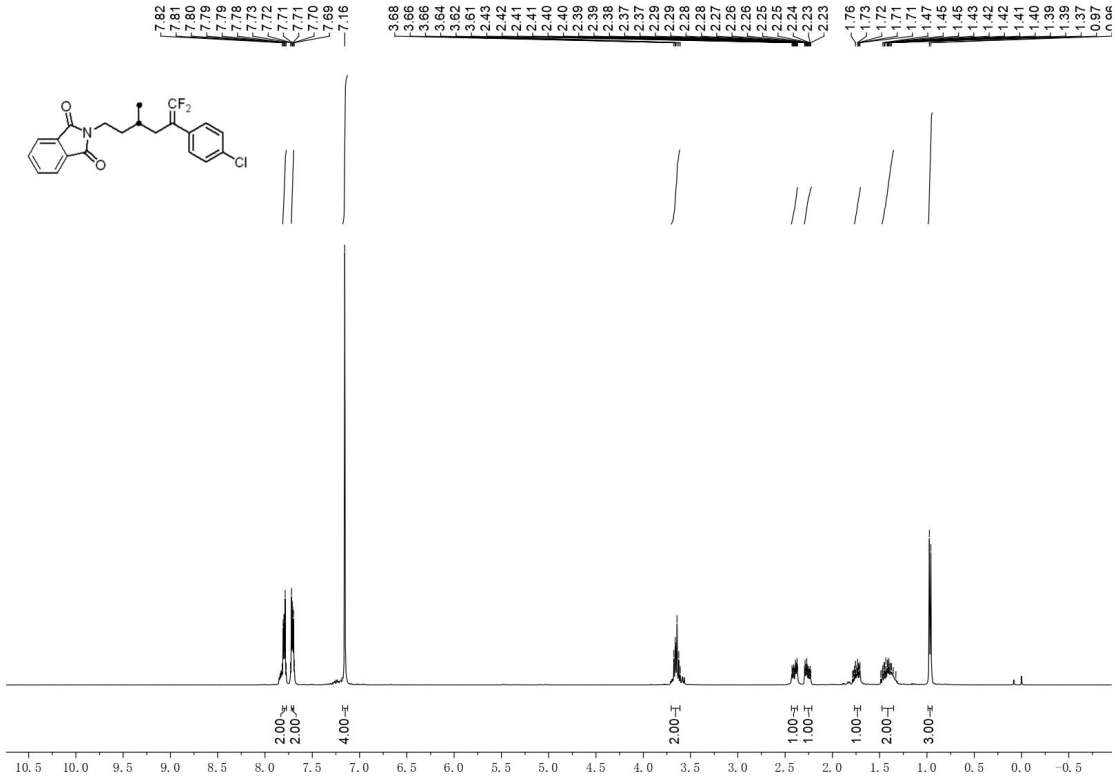

Figure S167. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4l**

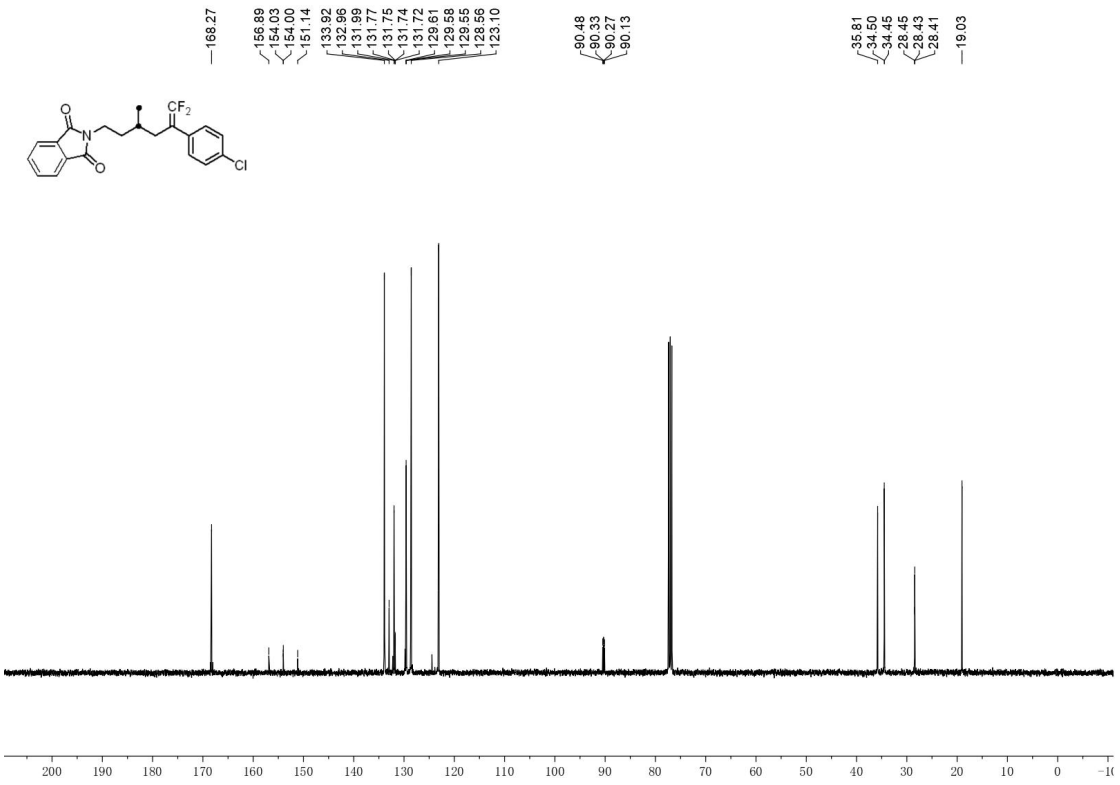

Figure S168. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4l**

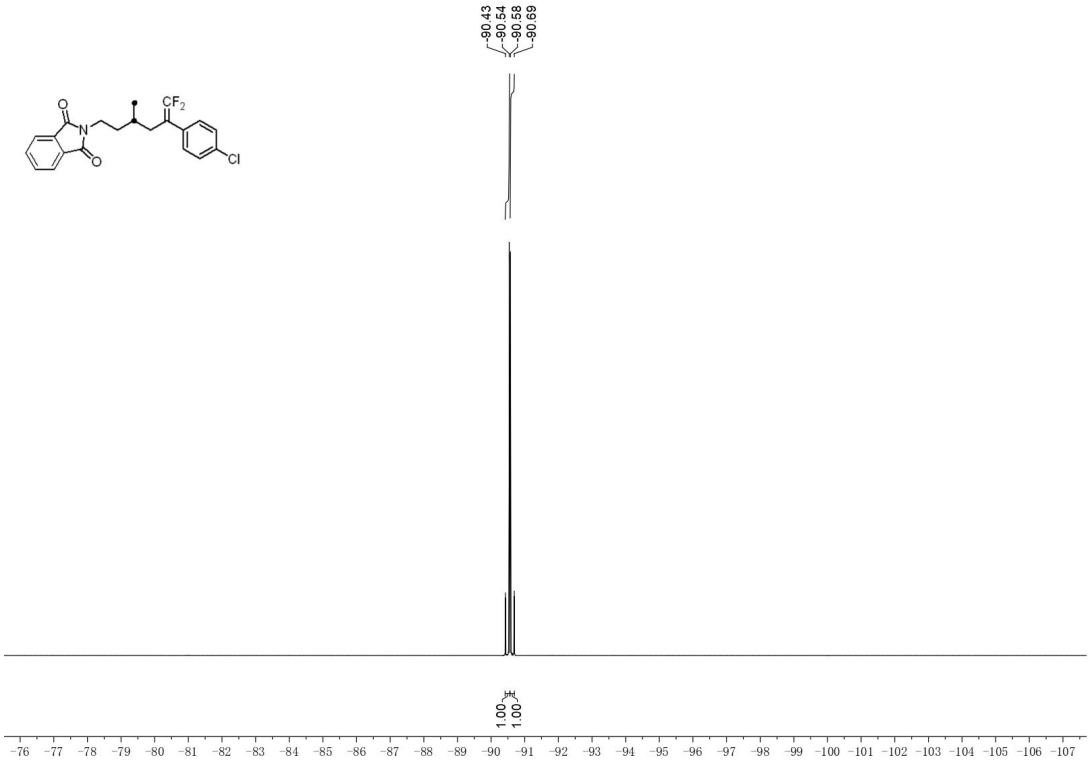

Figure S169. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4l**

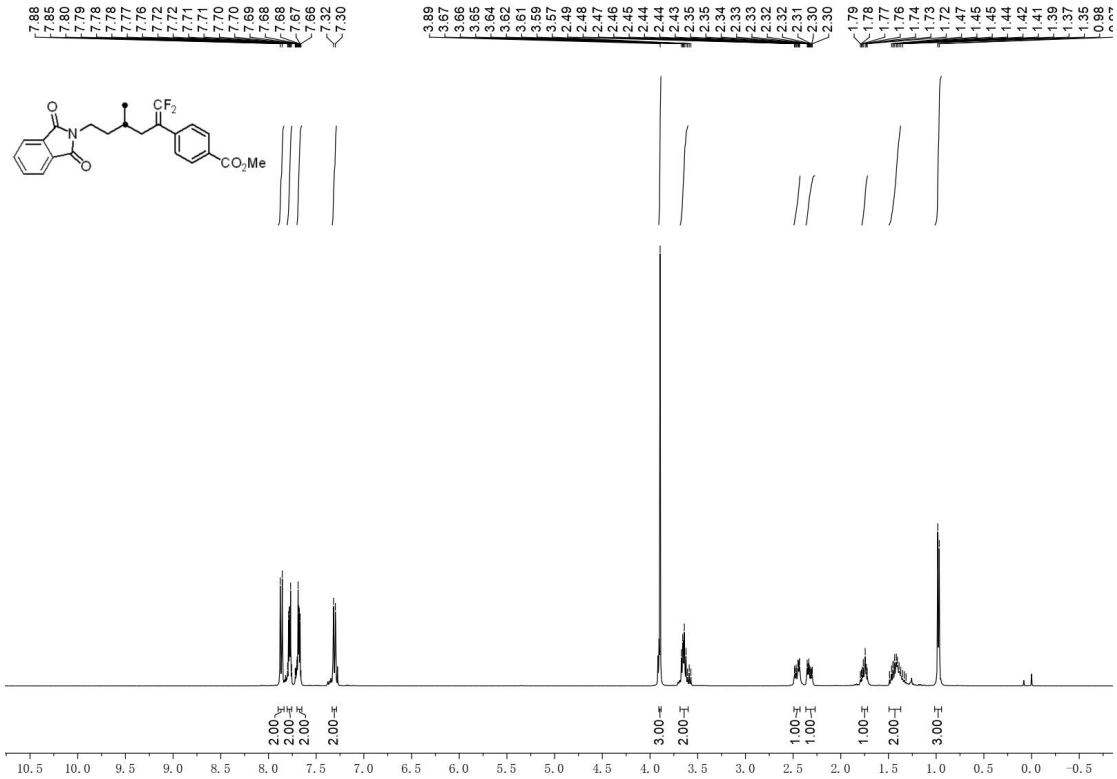

Figure S170. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4m**

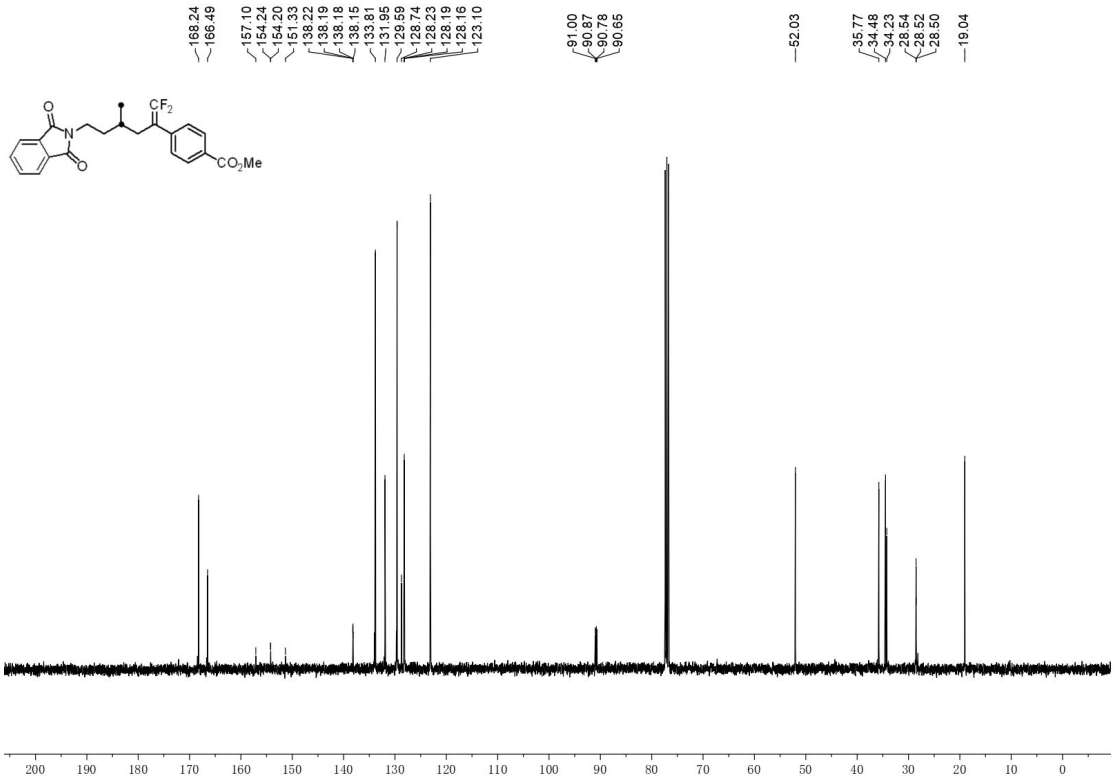

Figure S171. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4m**

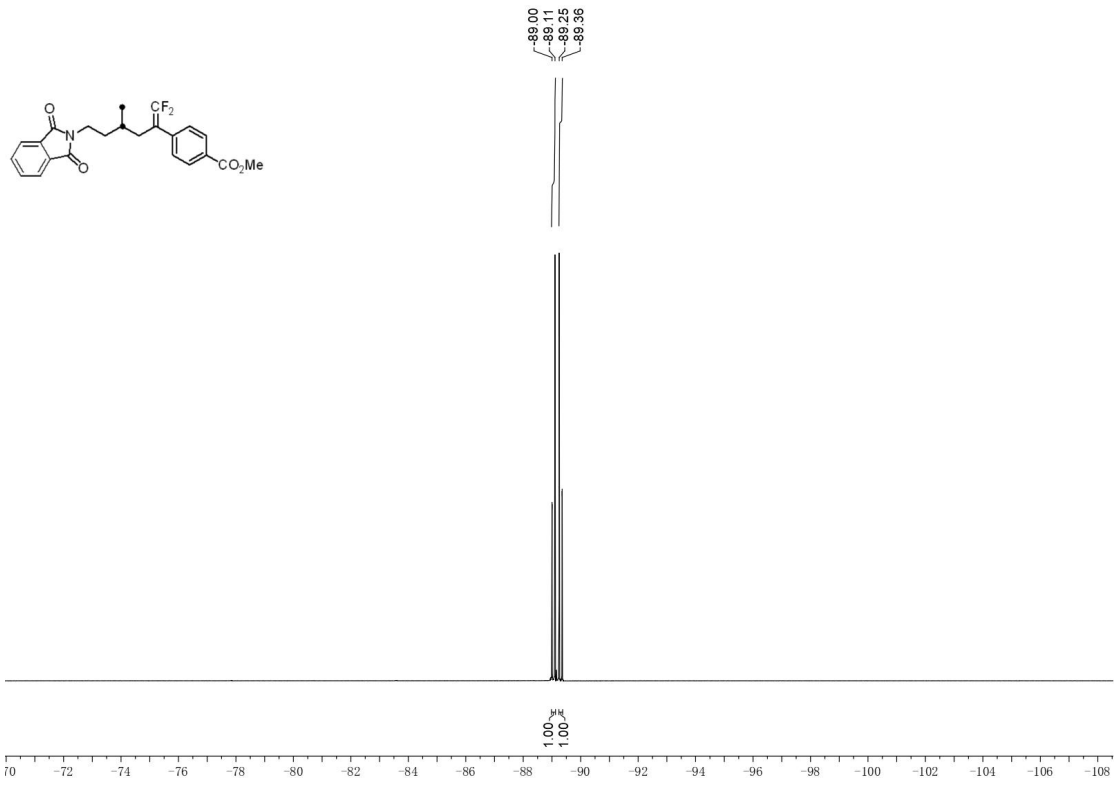

Figure S172. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4m**

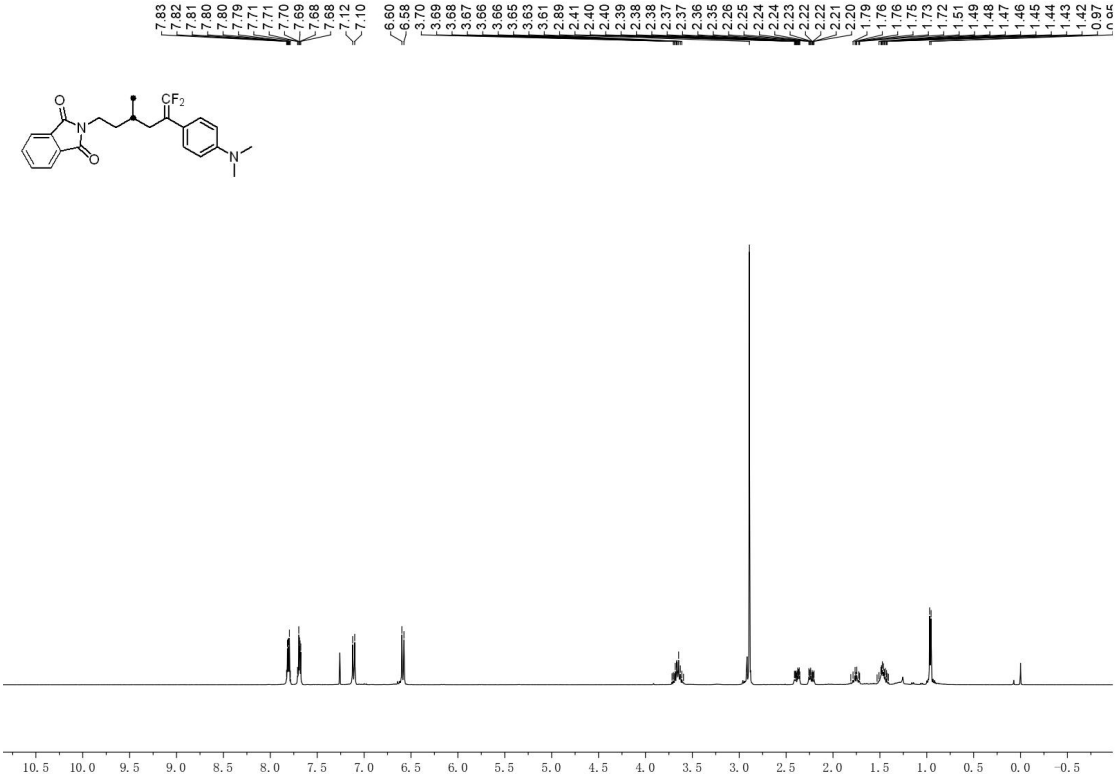

Figure S173. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4n**

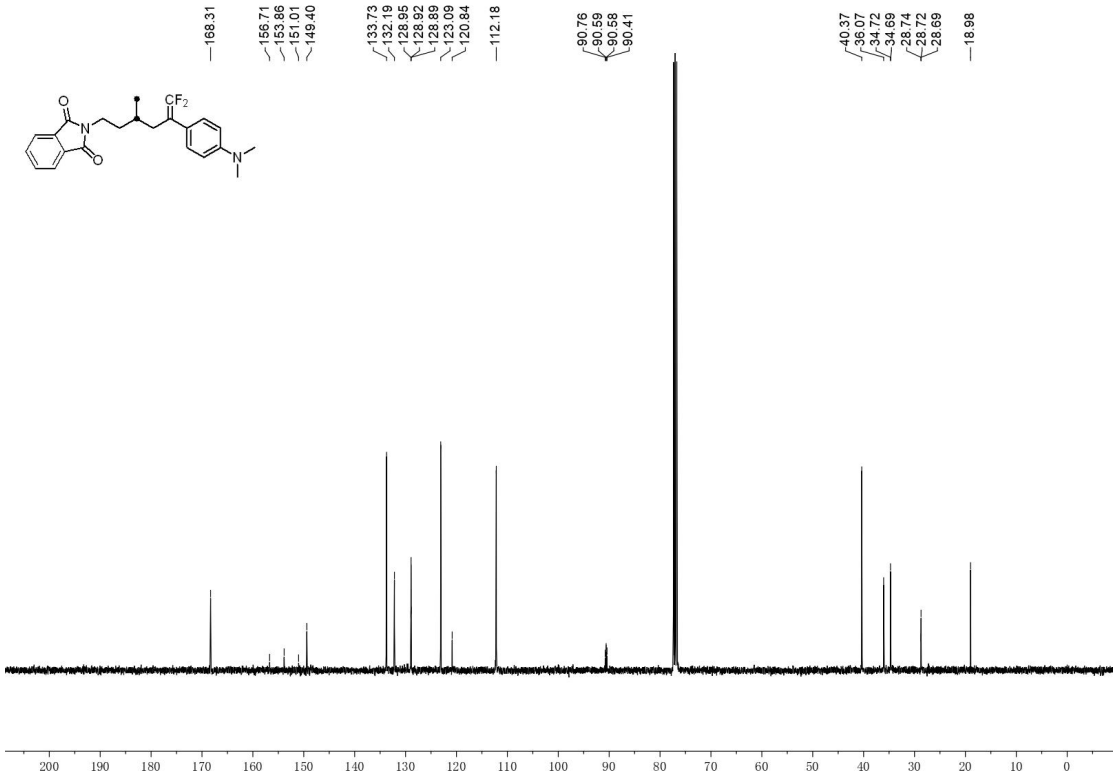

Figure S174. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4n**

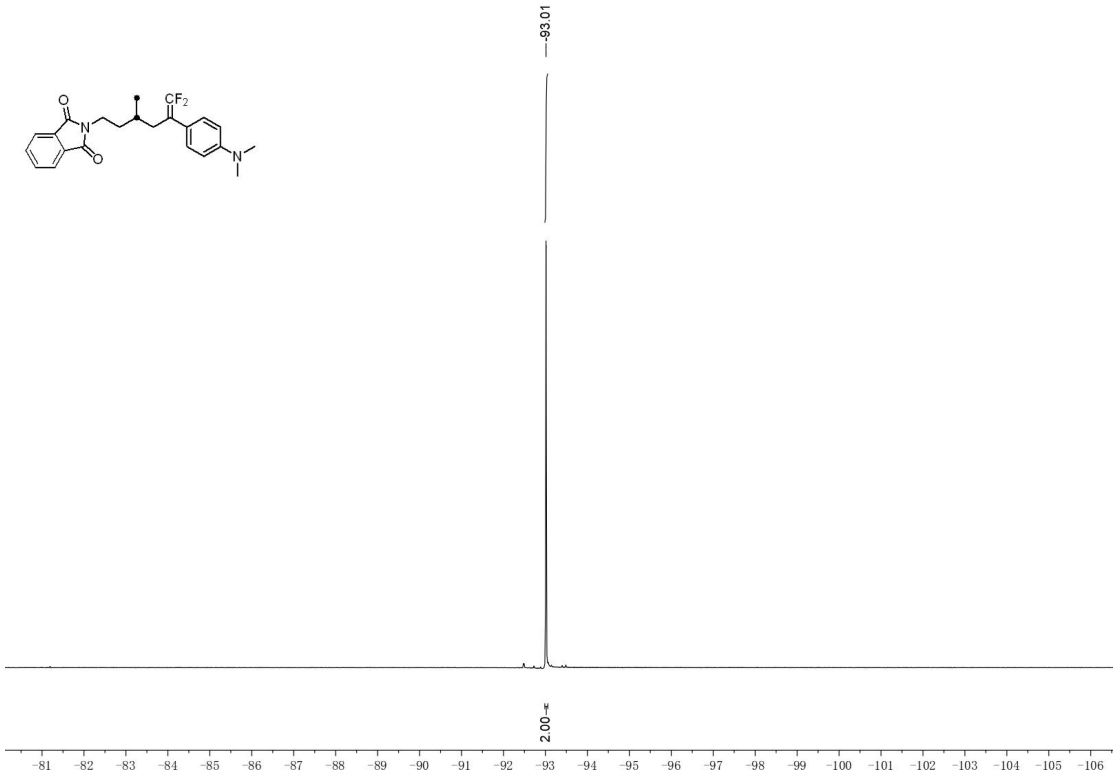

Figure S175. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4n**

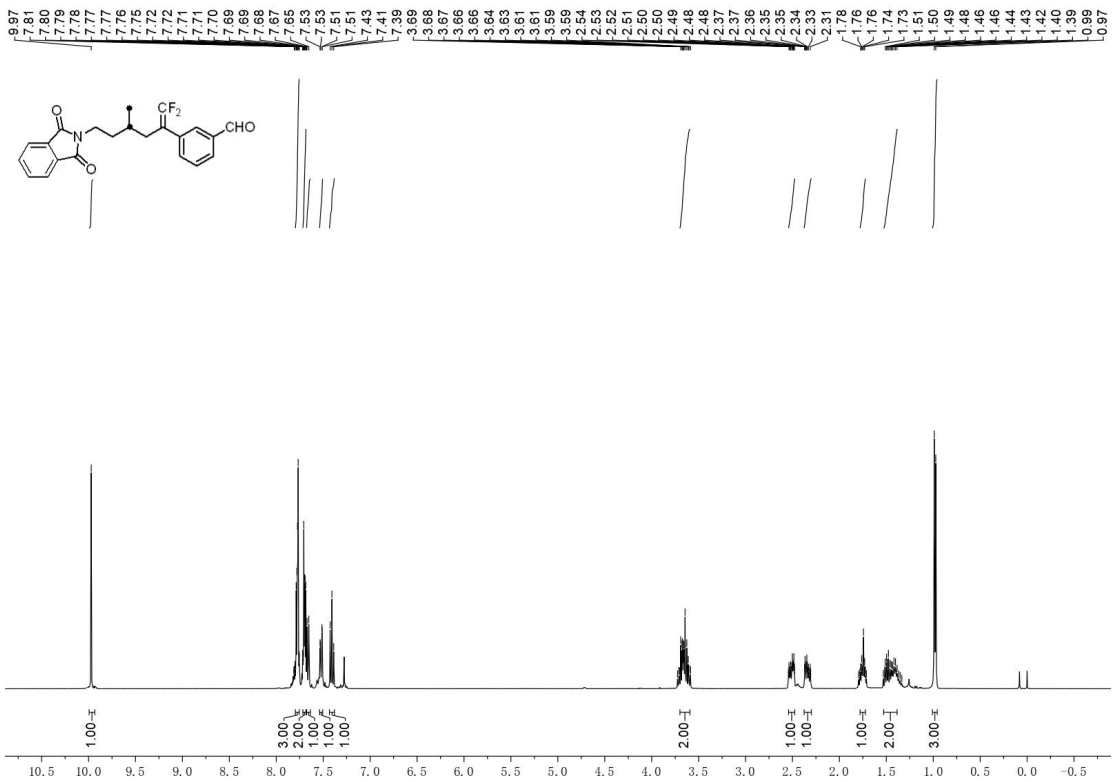

Figure S176. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4o**

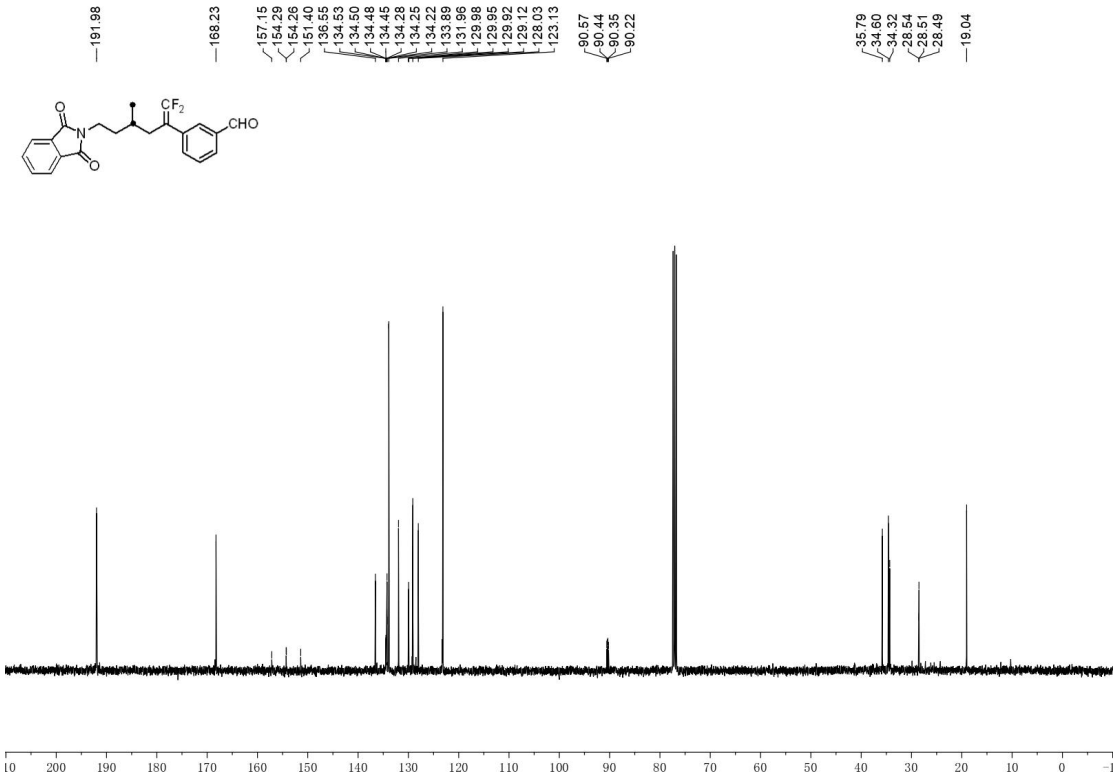

Figure S177. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4o**

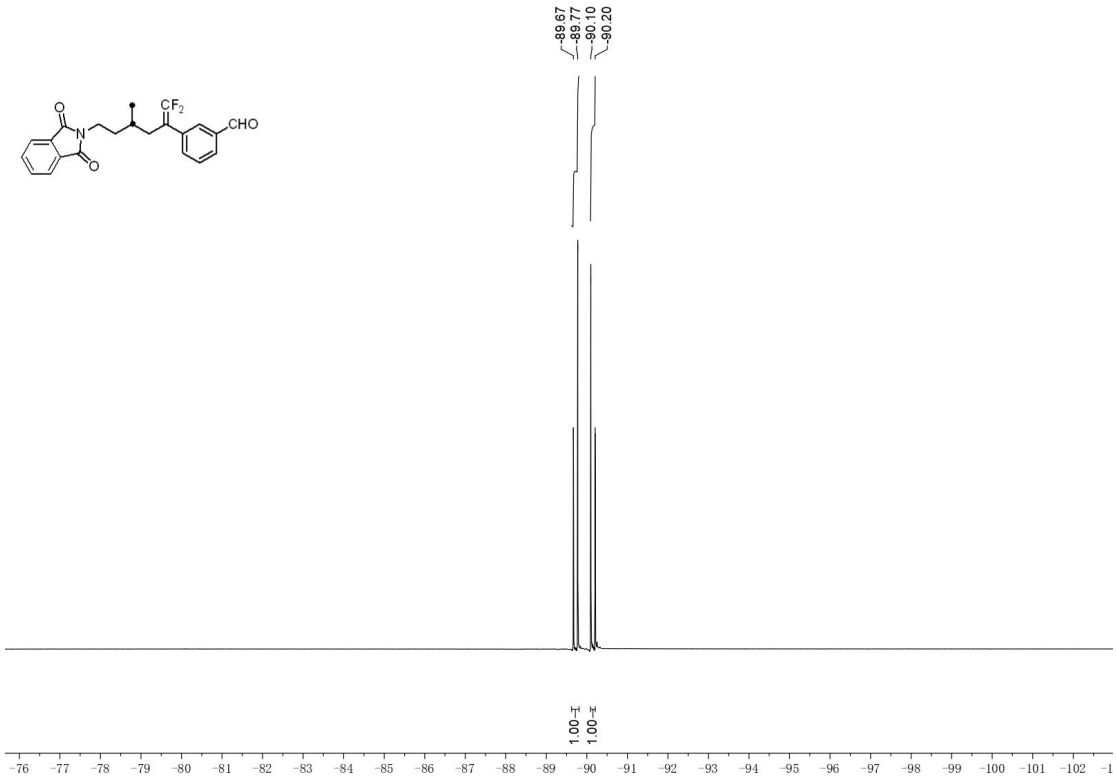

Figure S178. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4o**

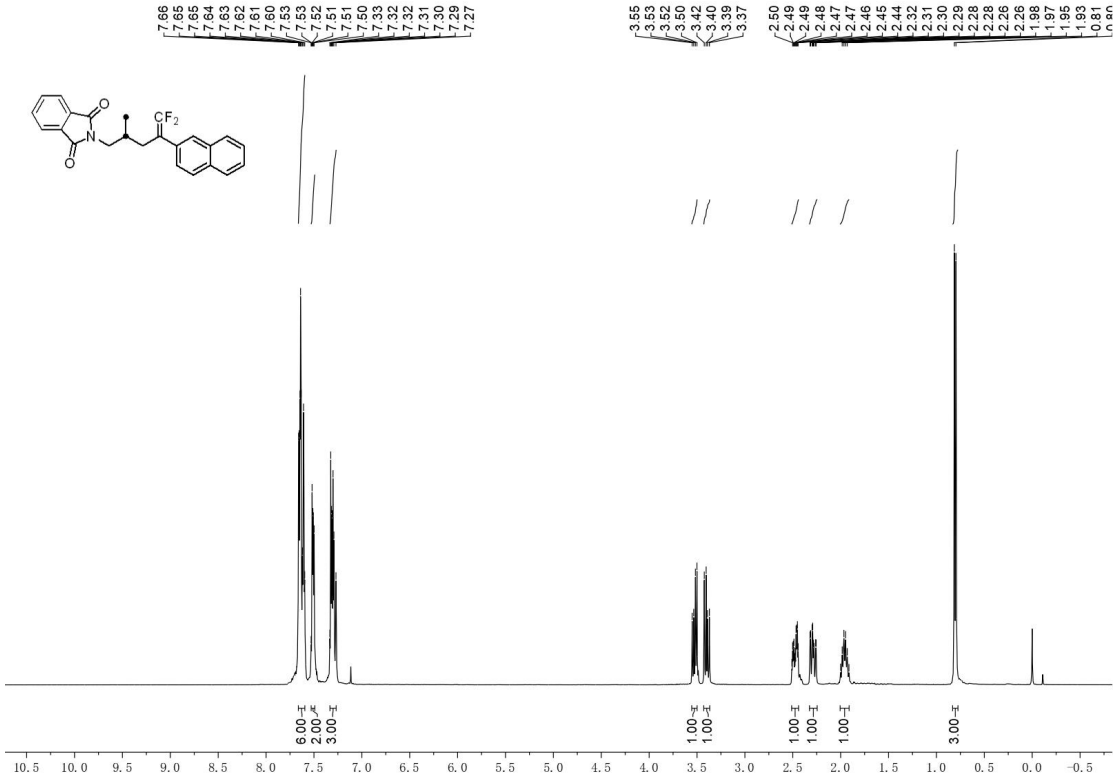

Figure S179. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4p**

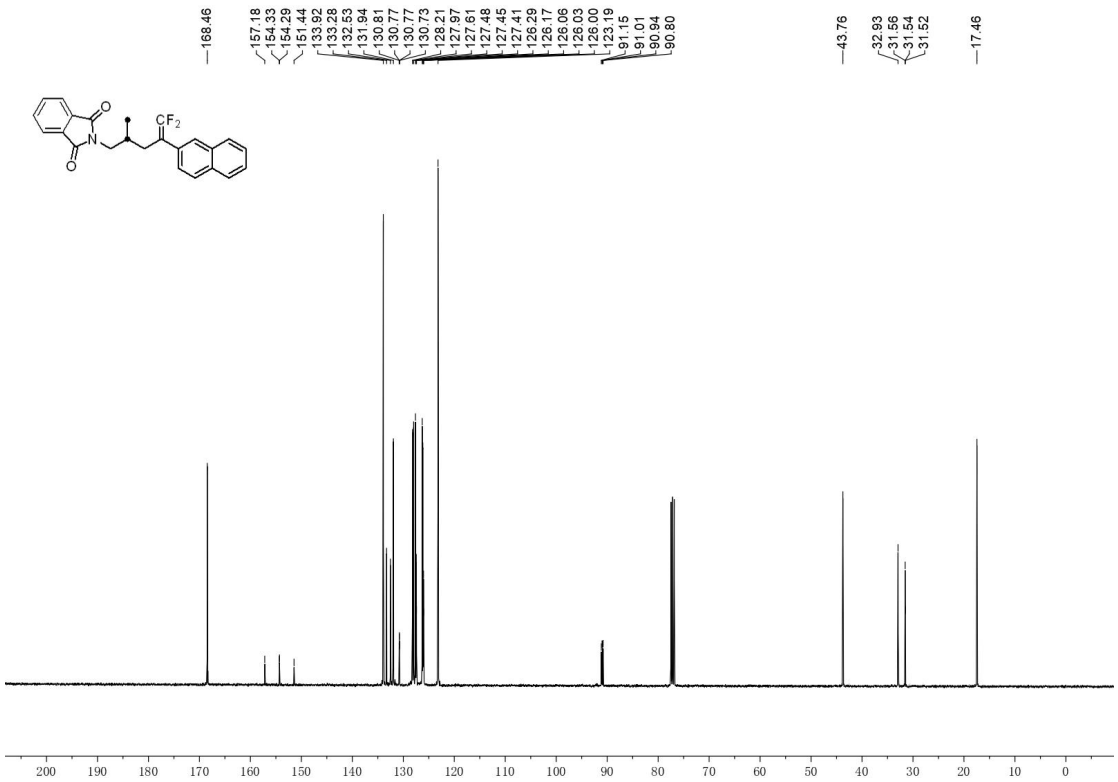

Figure S180. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4p**

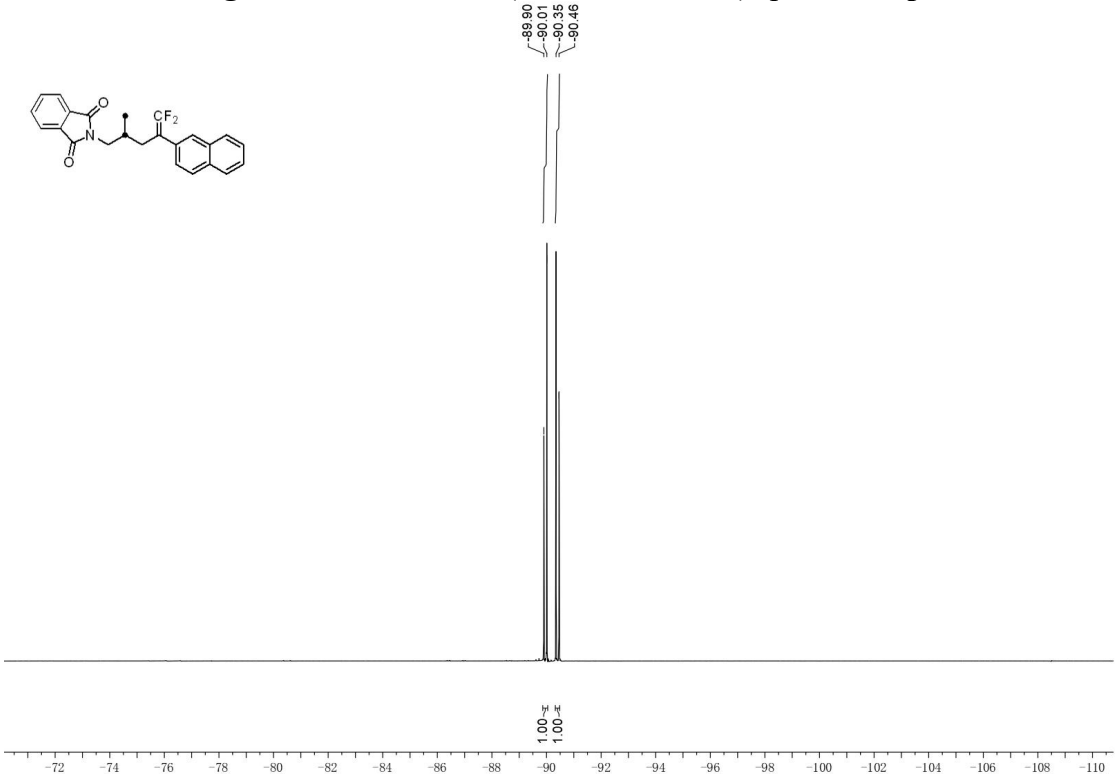

Figure S181. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4p**

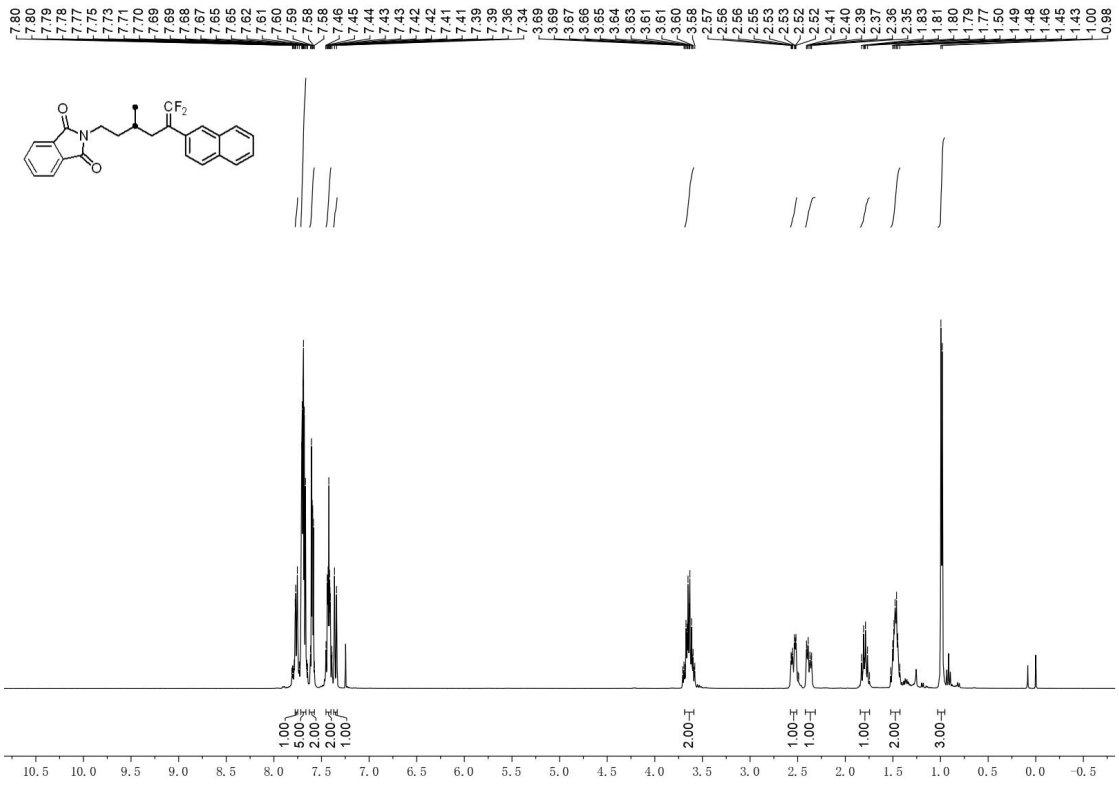

Figure S182. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4q**

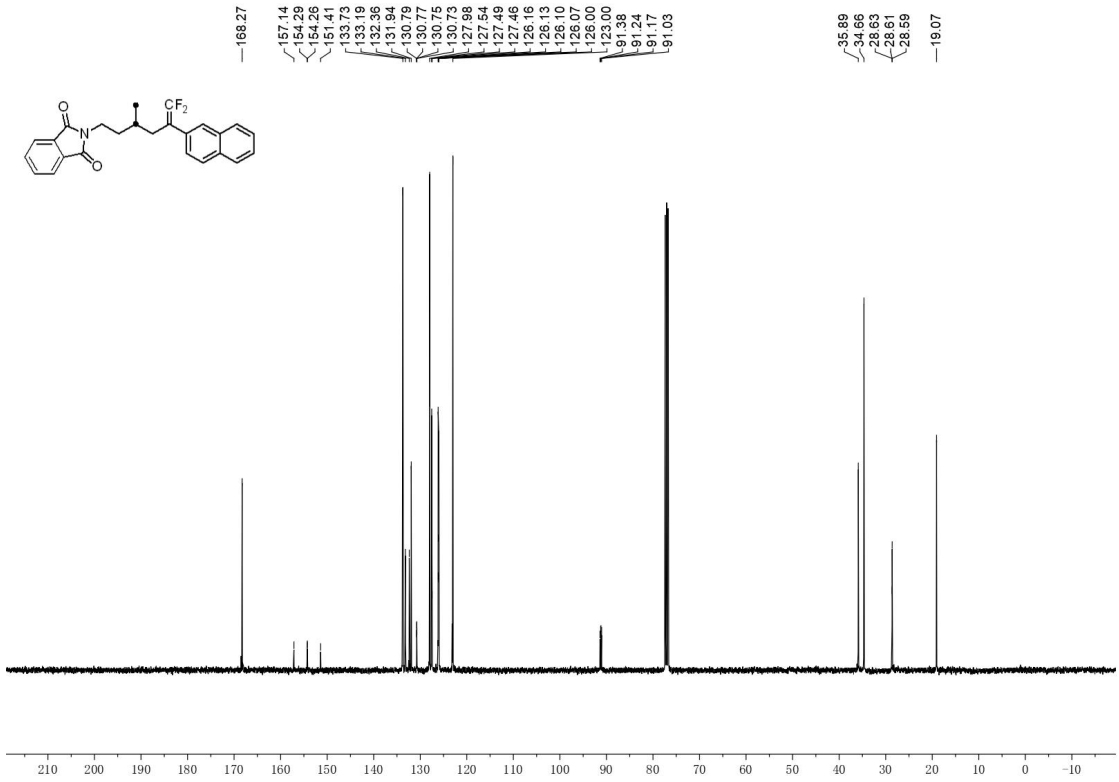

Figure S183. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4q**

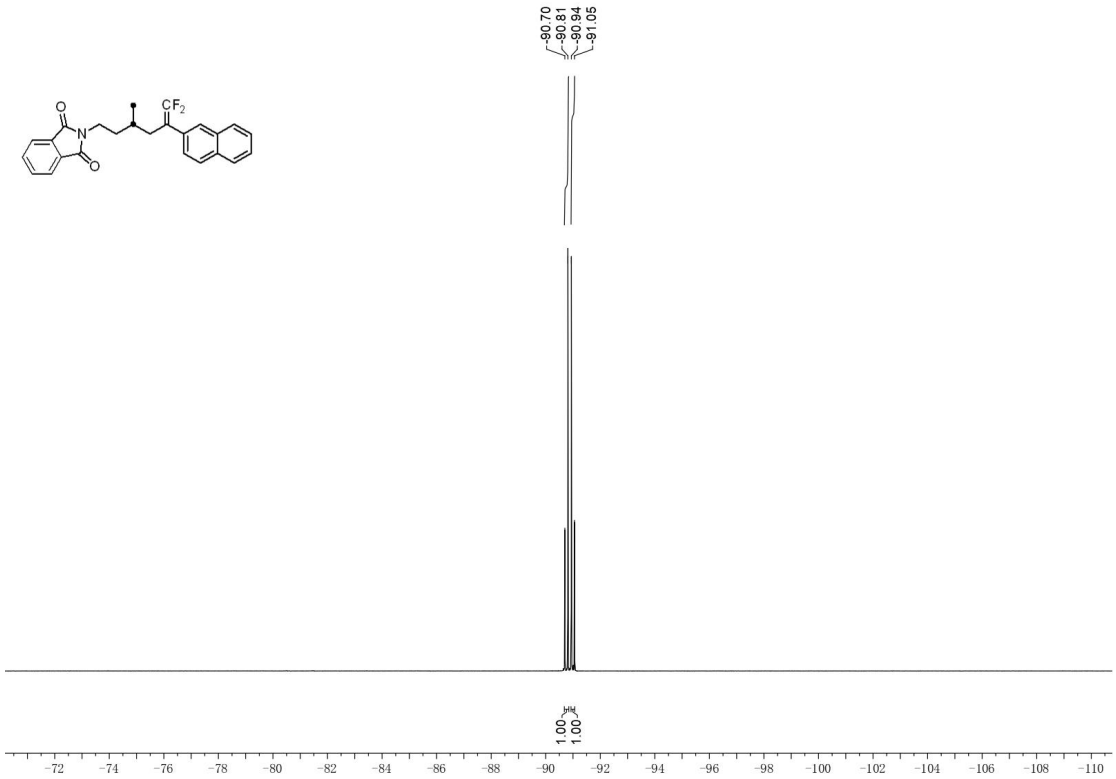

Figure S184. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4q**

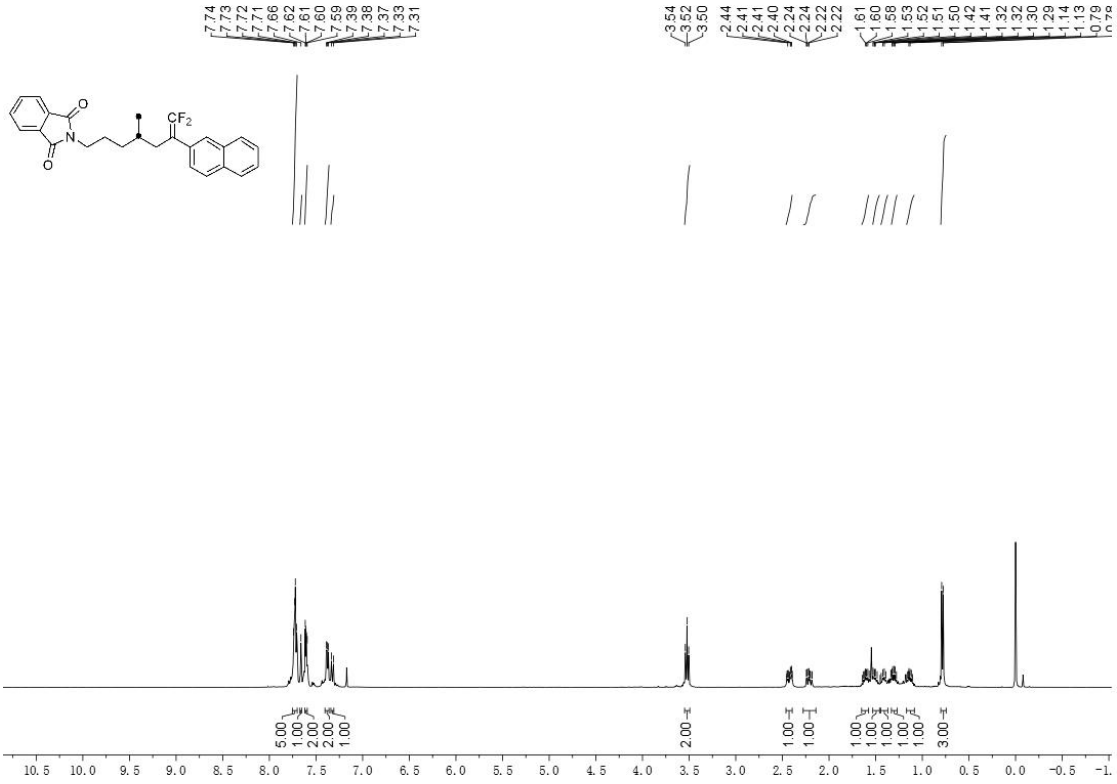

Figure S185. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4r**

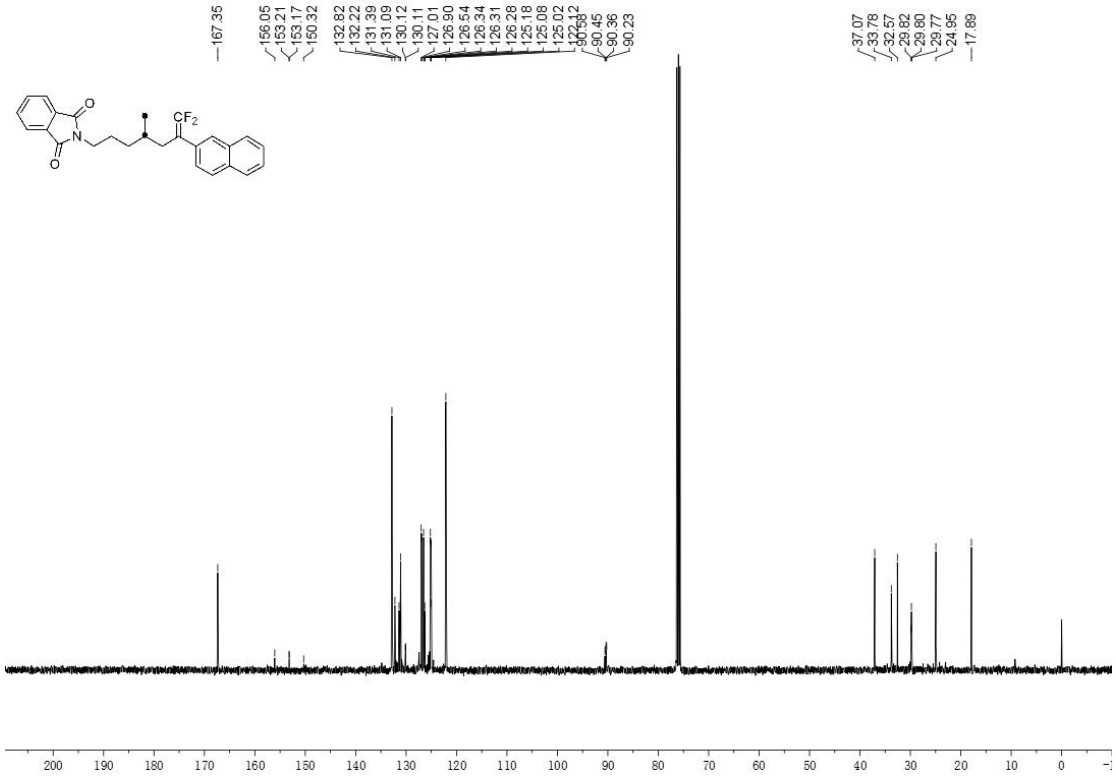

Figure S186. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4r**

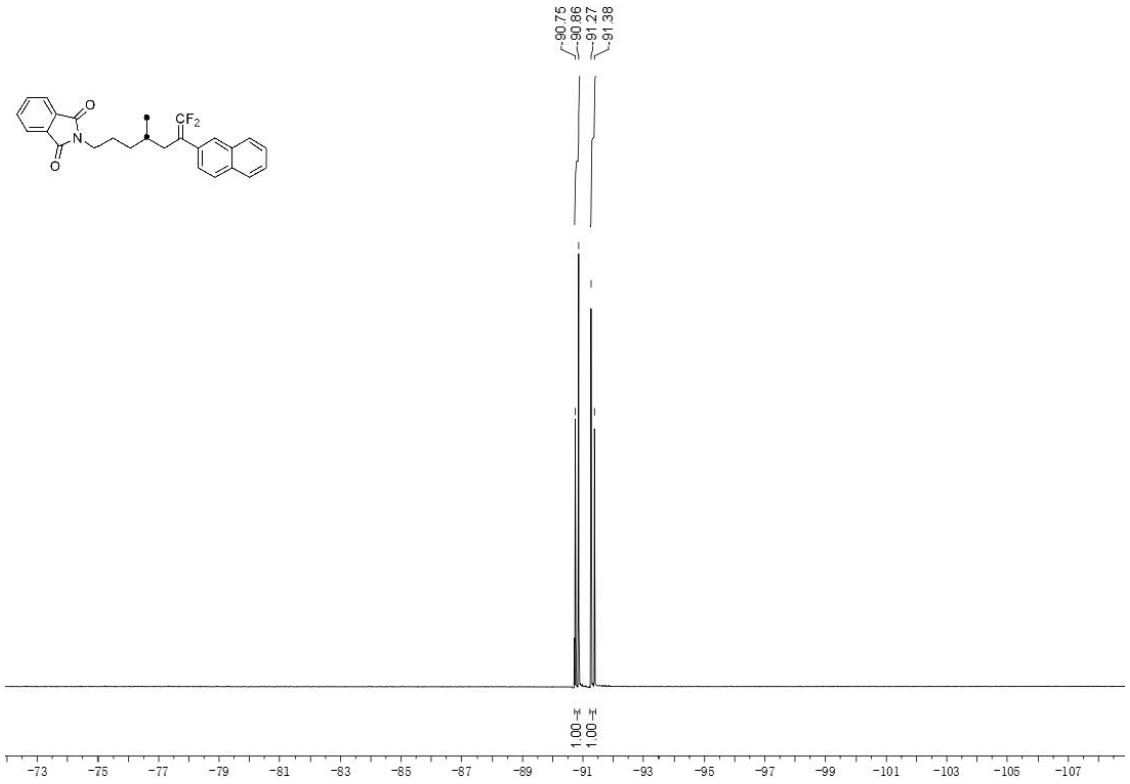

Figure S187. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4r**

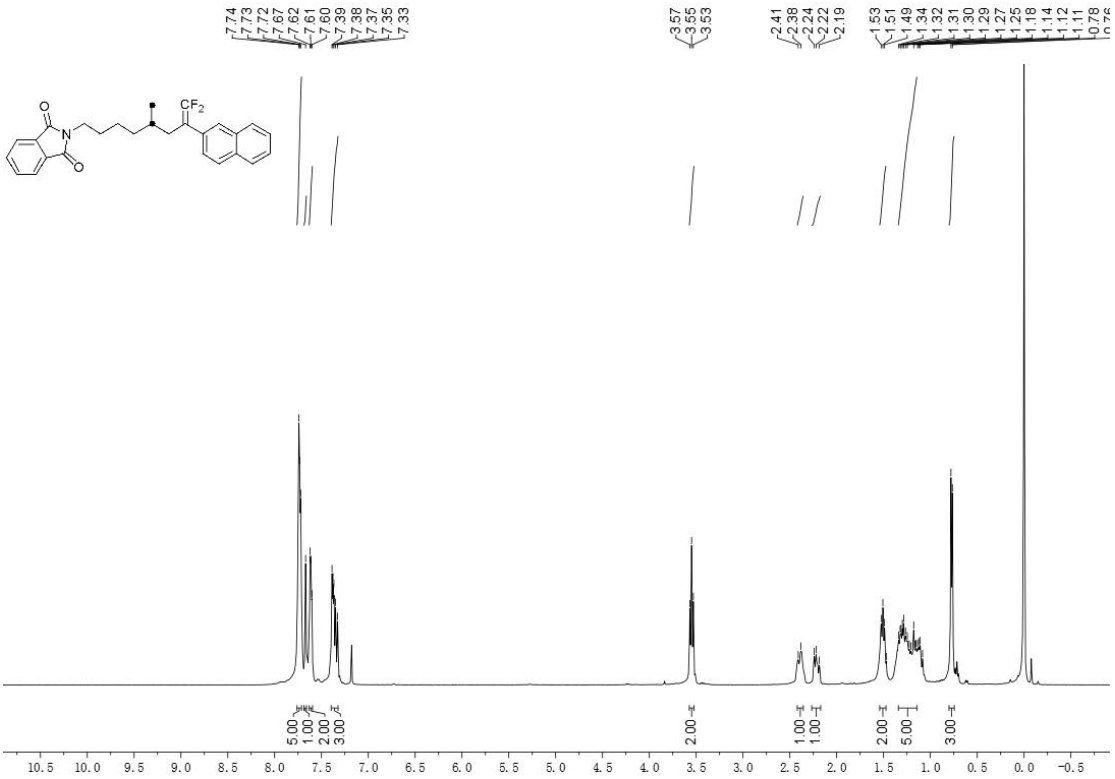

Figure S188. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4s**

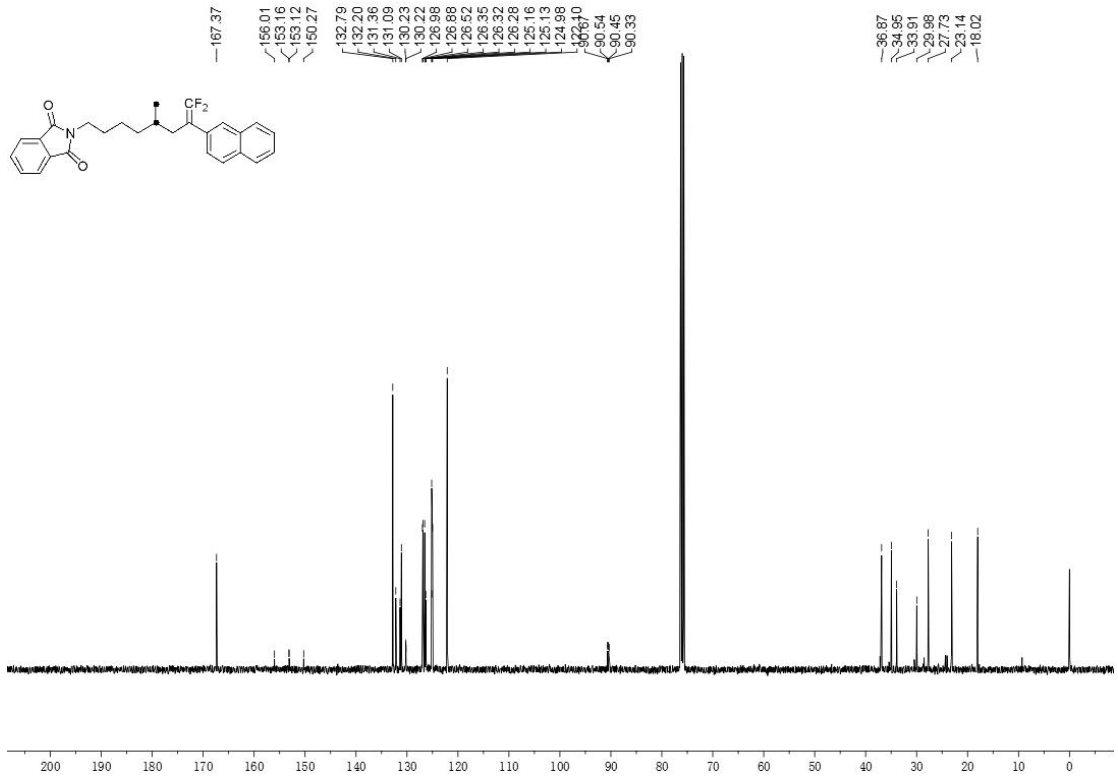

Figure S189. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4s**

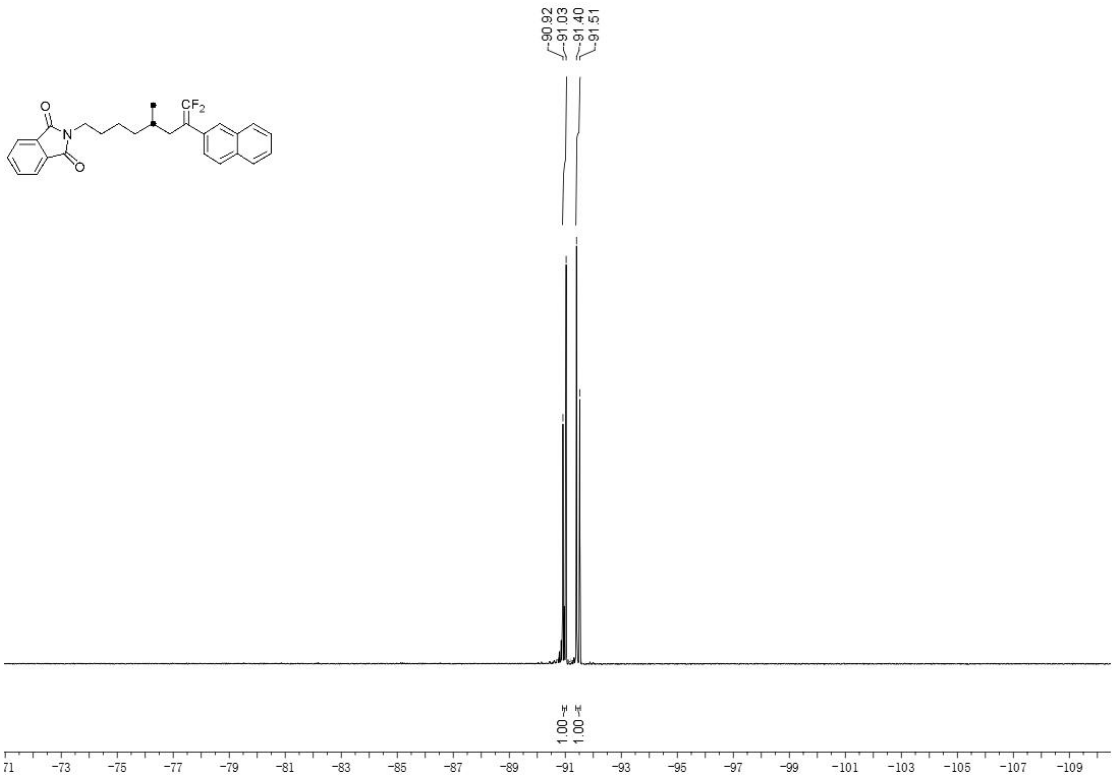

Figure S190. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **4s**

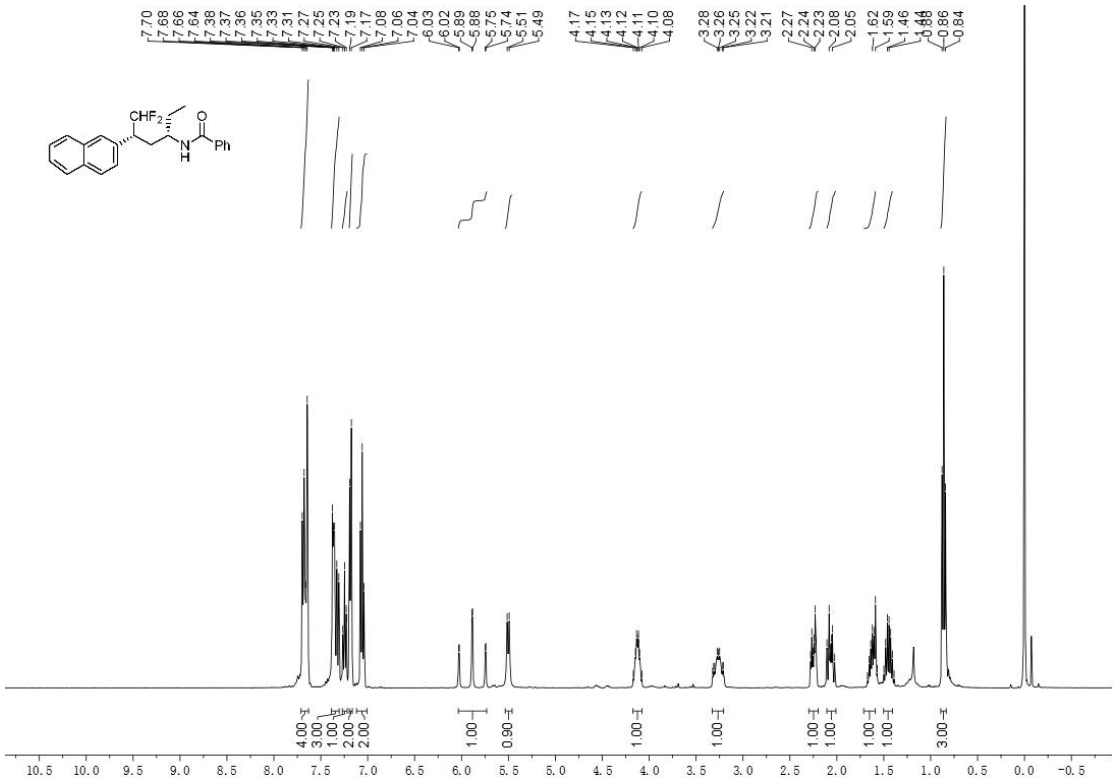

Figure S191. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5a**

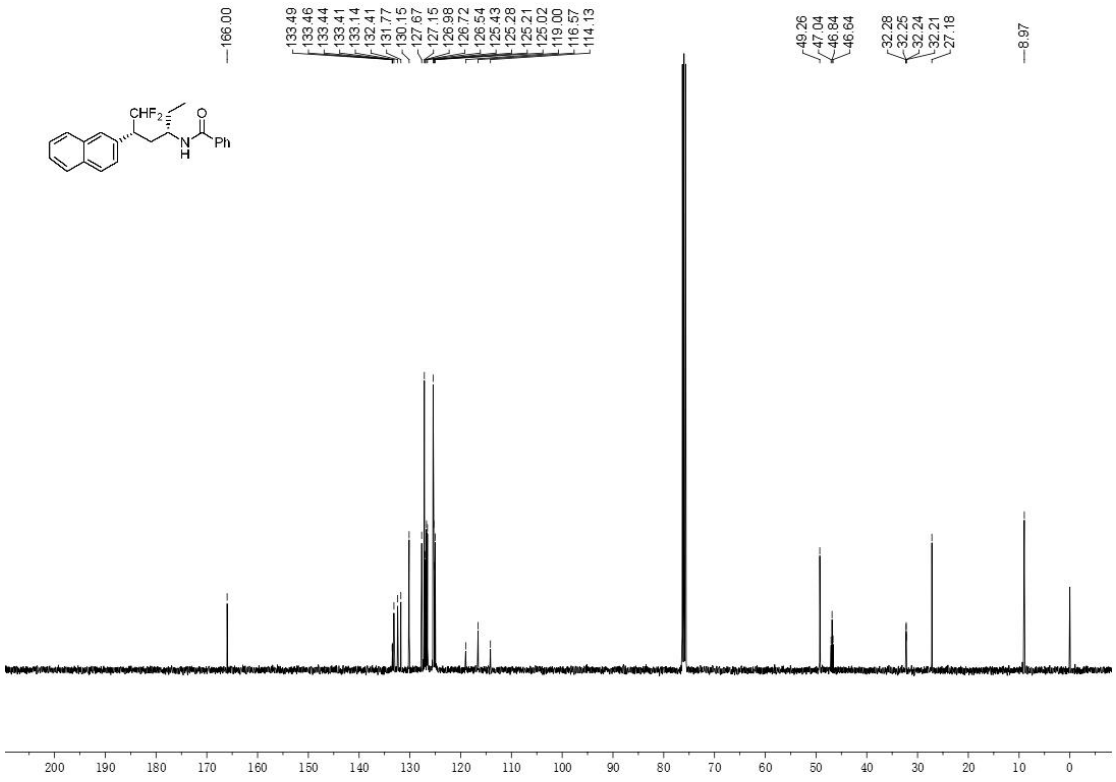

Figure S192. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5a**

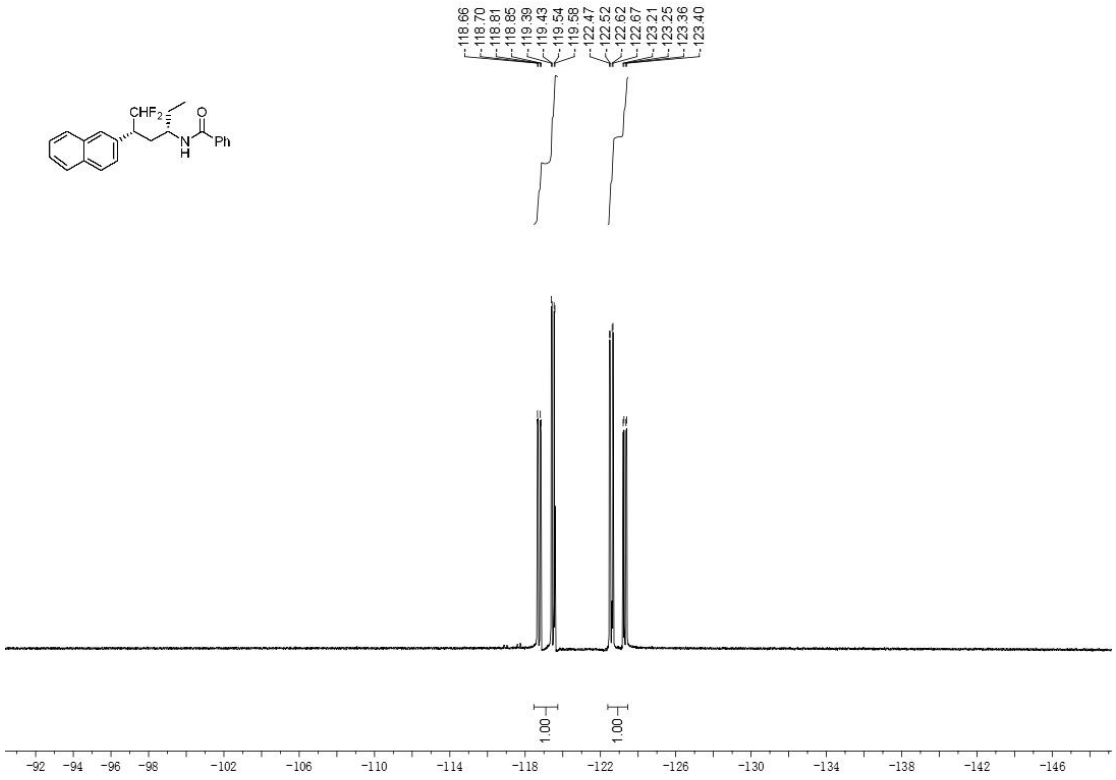

Figure S193. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5a**

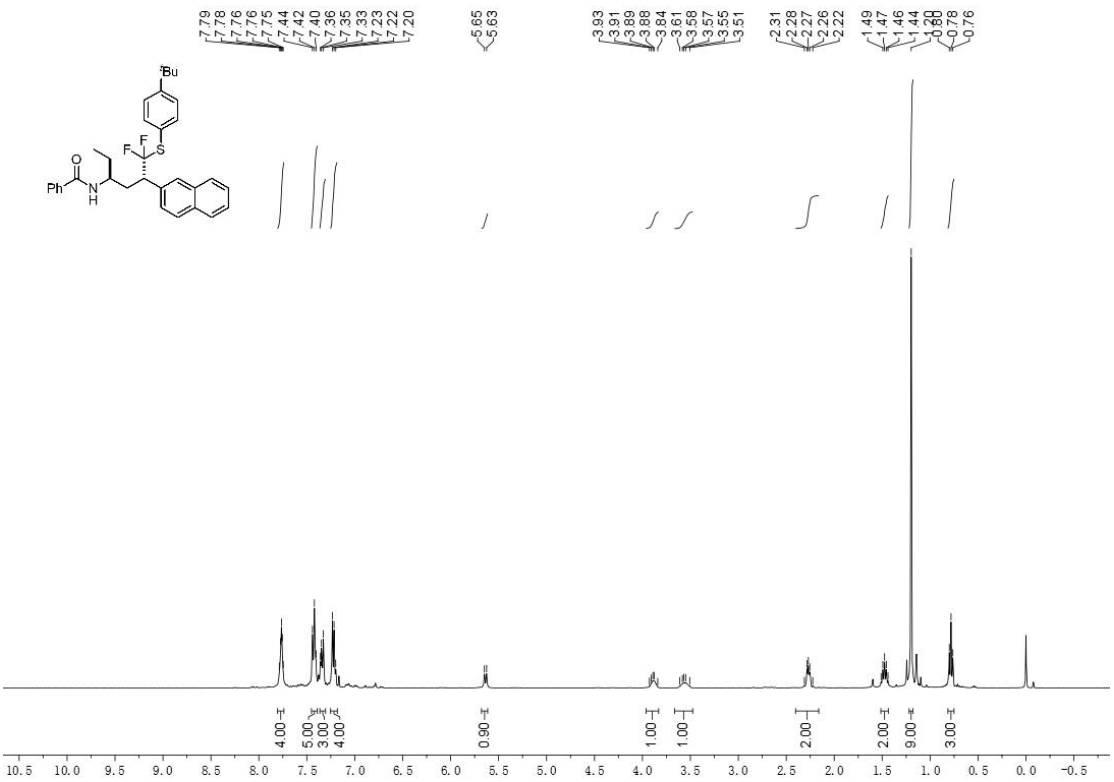

Figure S194. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5b**

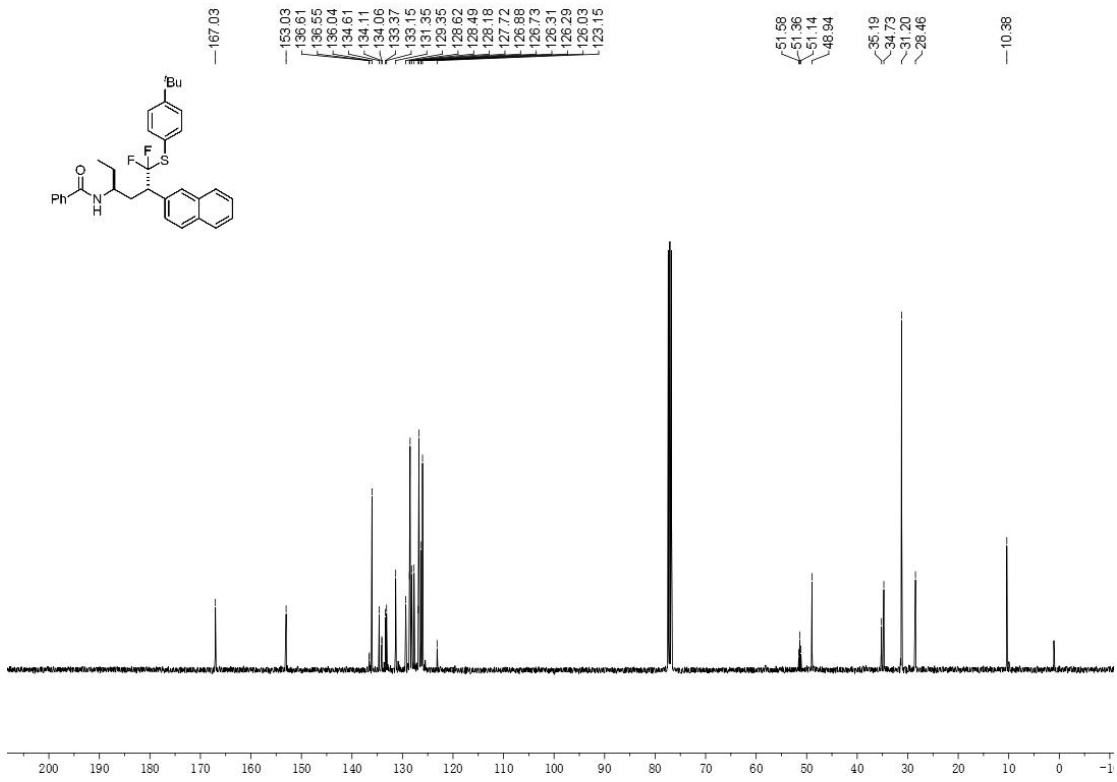

Figure S195. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5b**

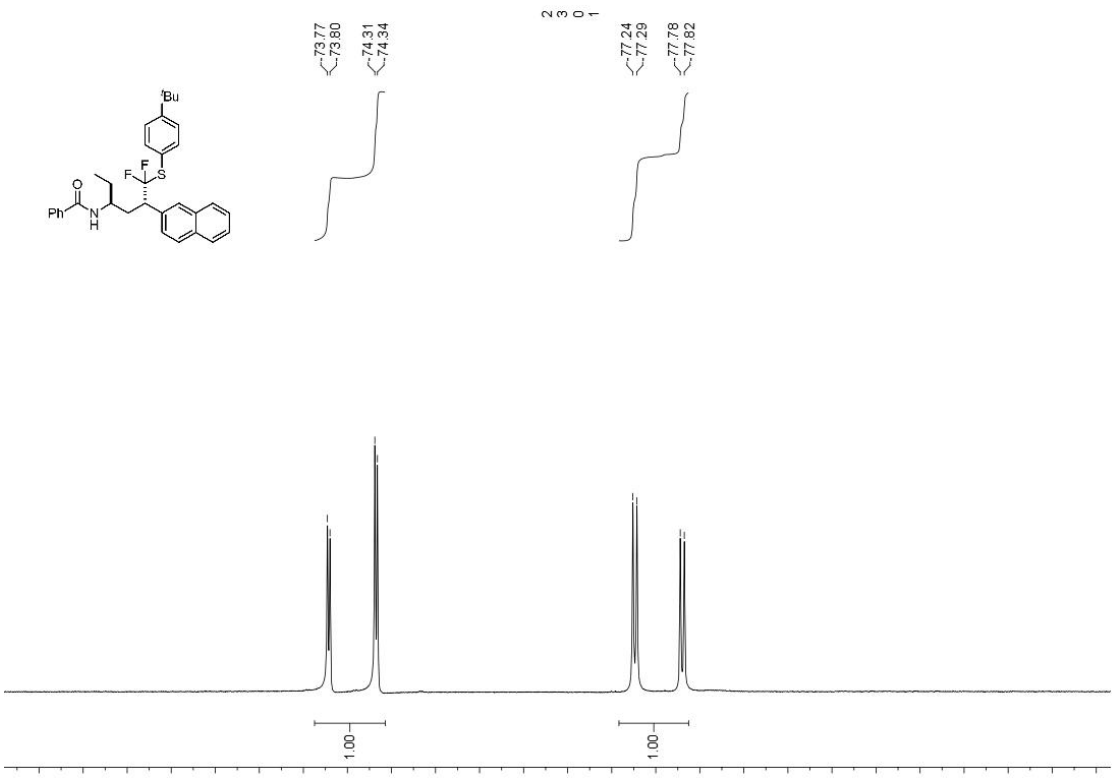

Figure S196. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5b**

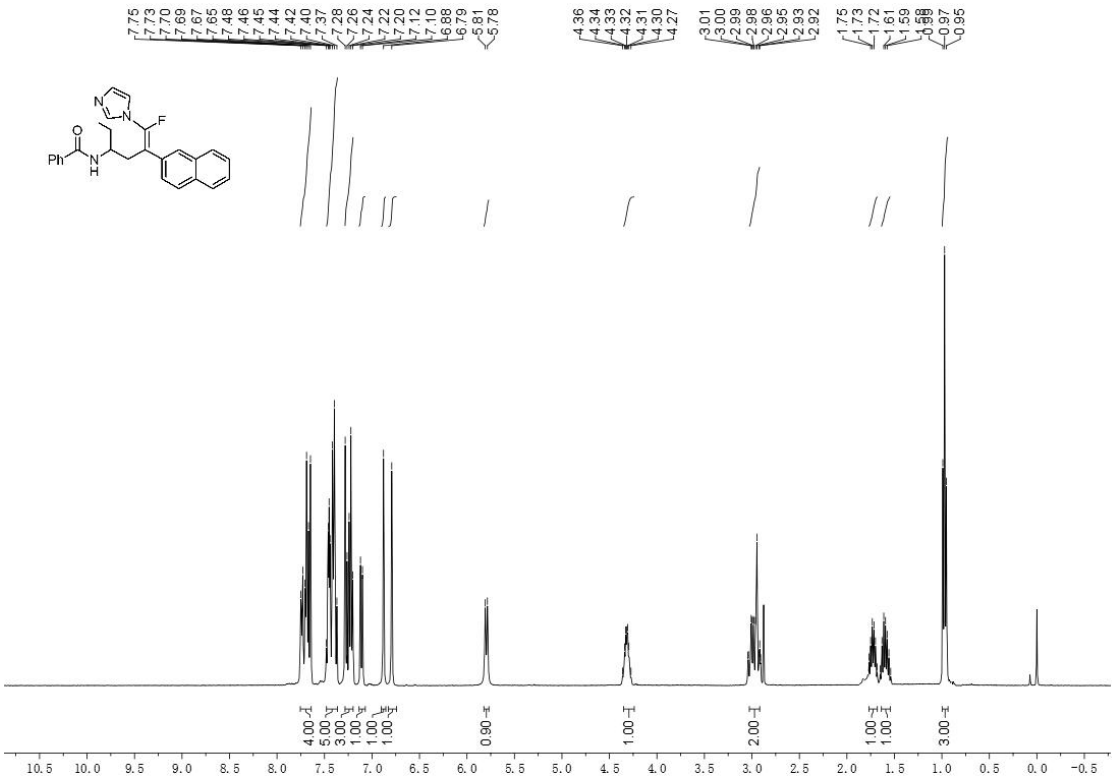

Figure S197. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5c**

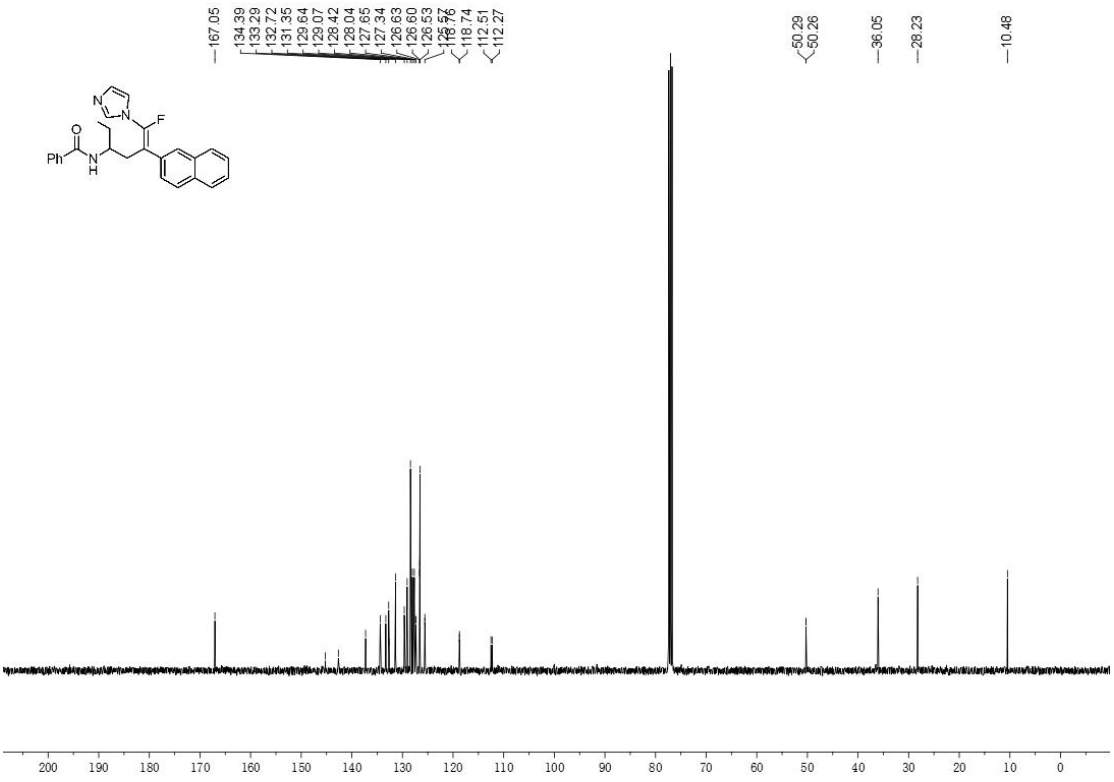

Figure S198. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5c**

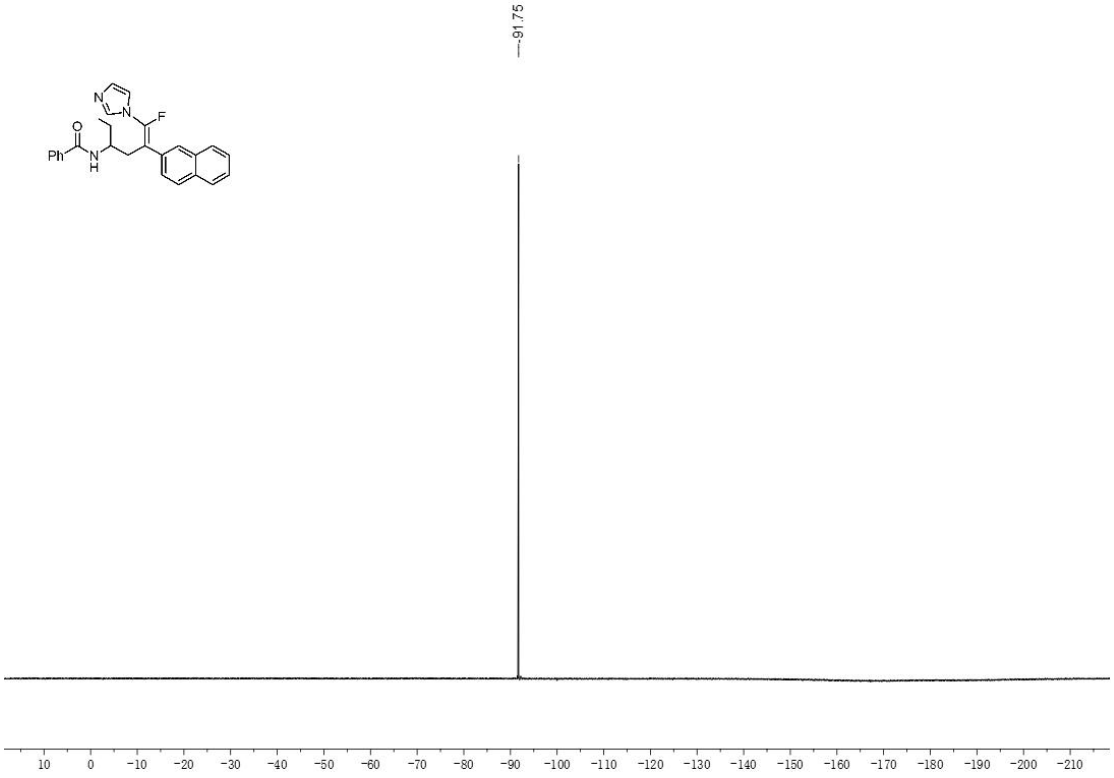

Figure S199. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5c**

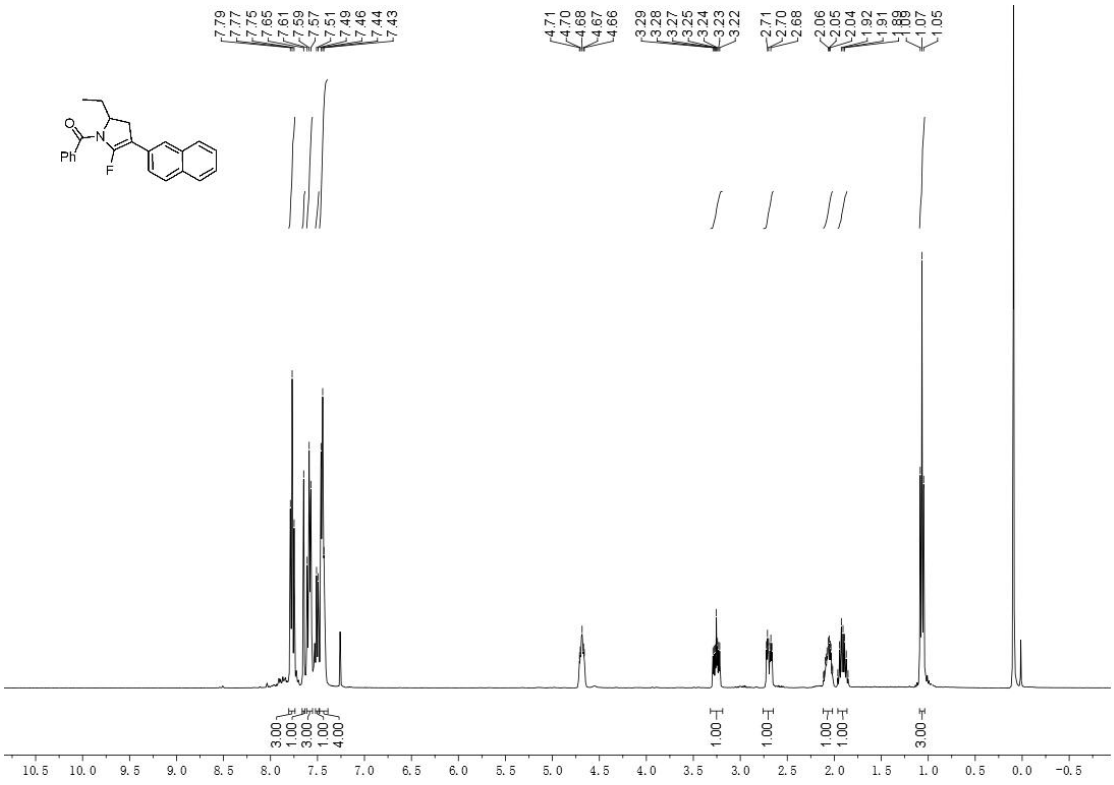

Figure S200. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5d**

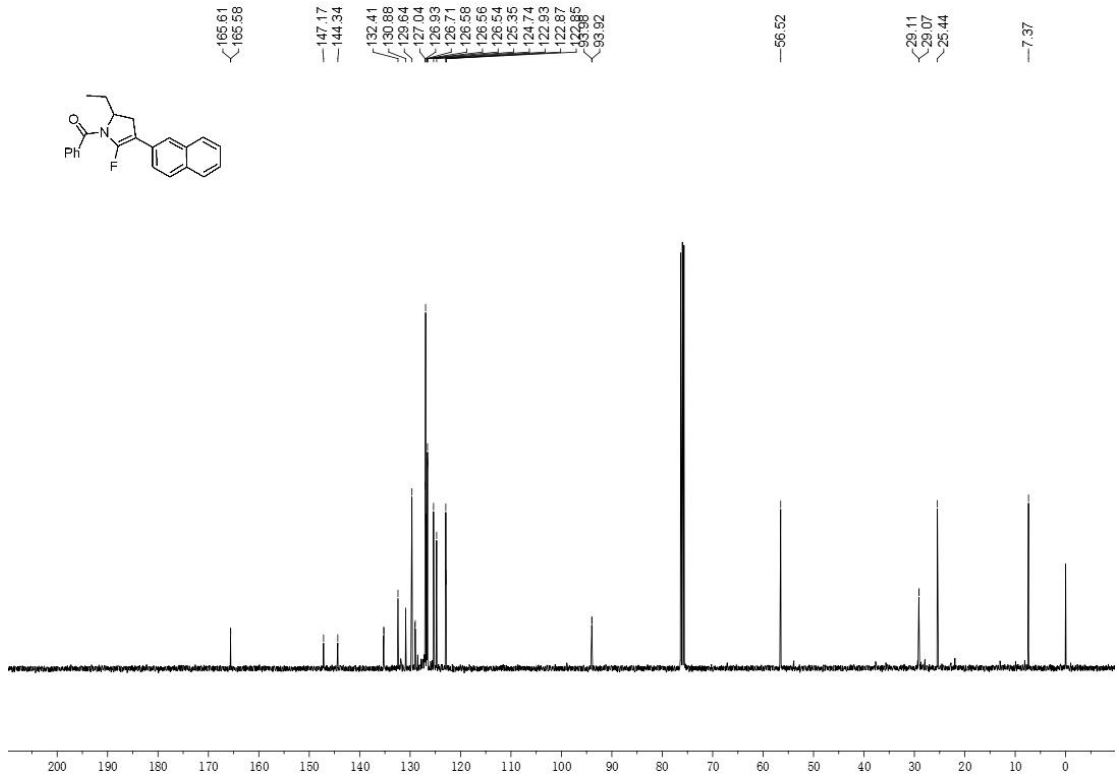

Figure S201. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5d**

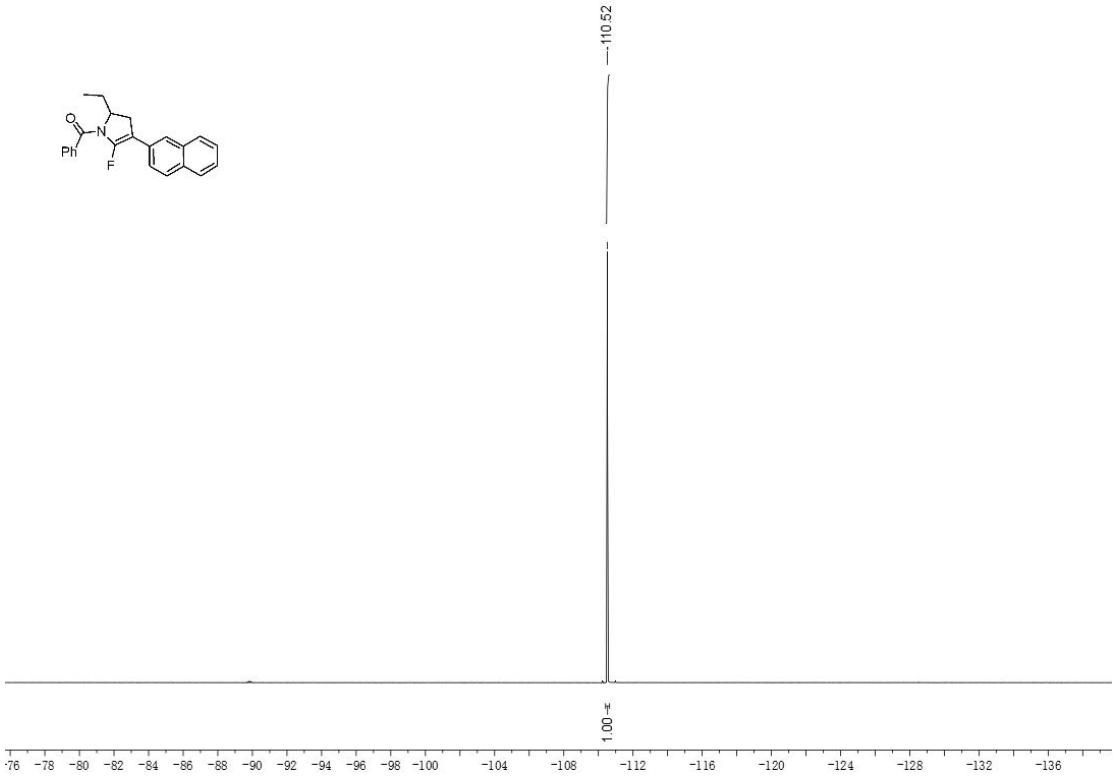

Figure S202. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5d**

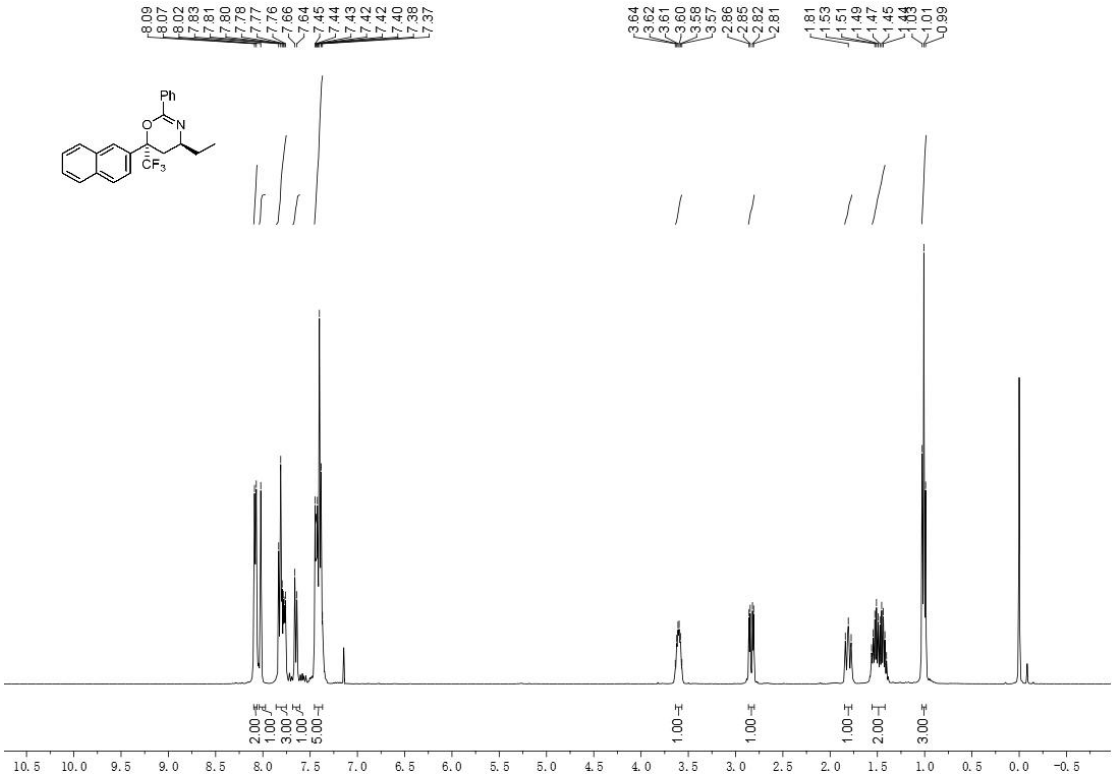

Figure S203. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5e**

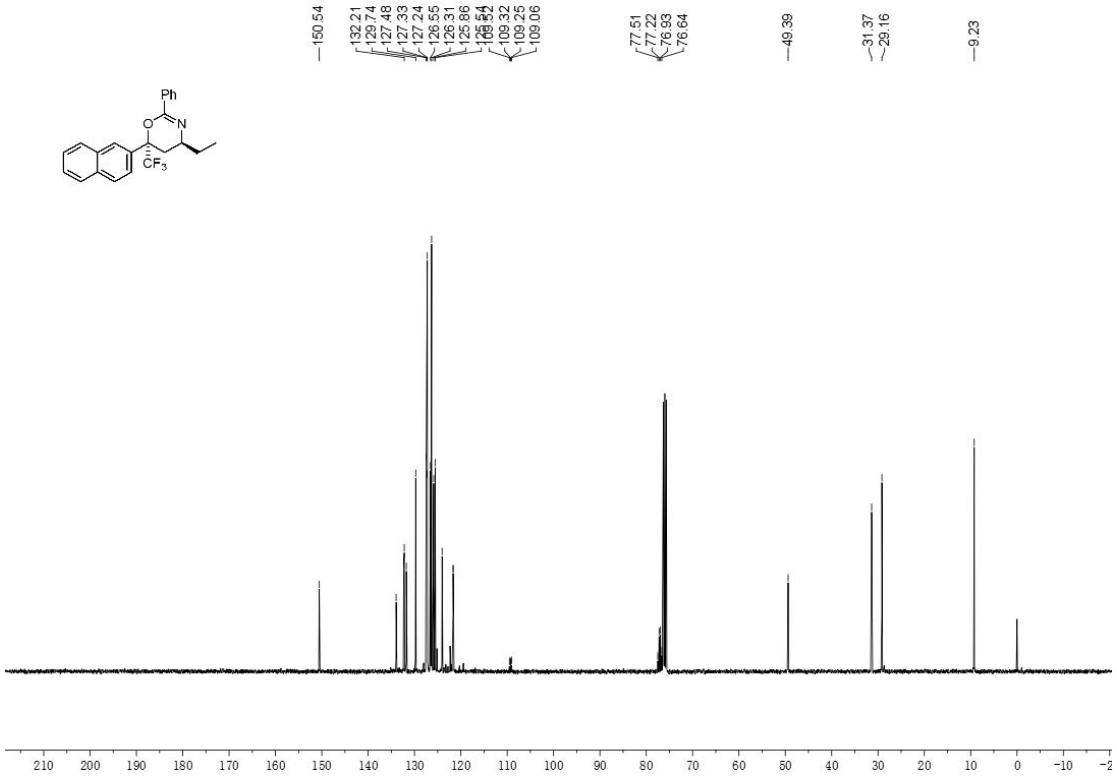

Figure S204. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5e**

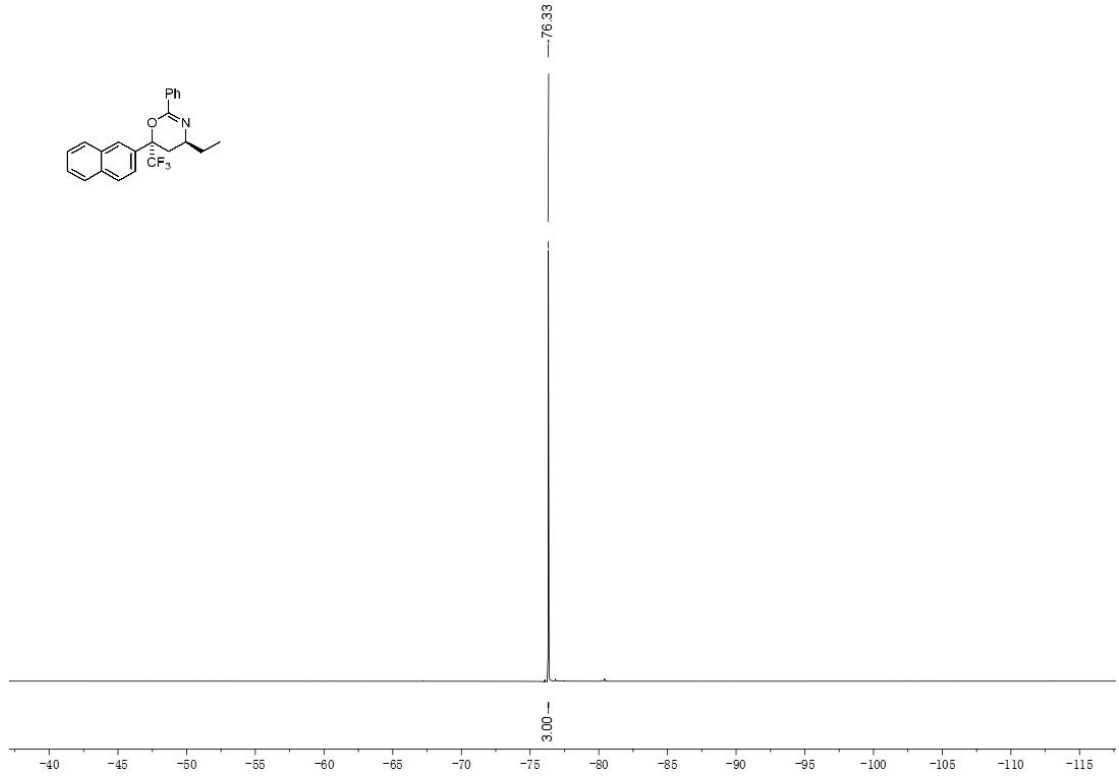

Figure S205. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5e**

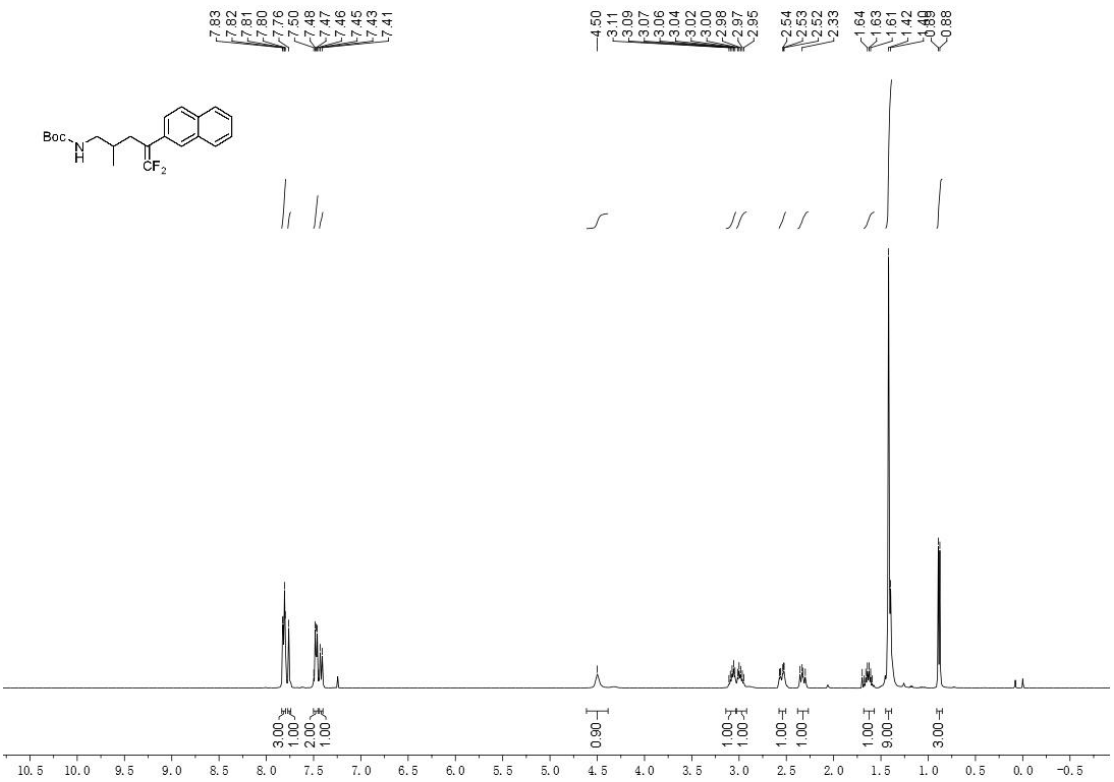

Figure S206. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5f**

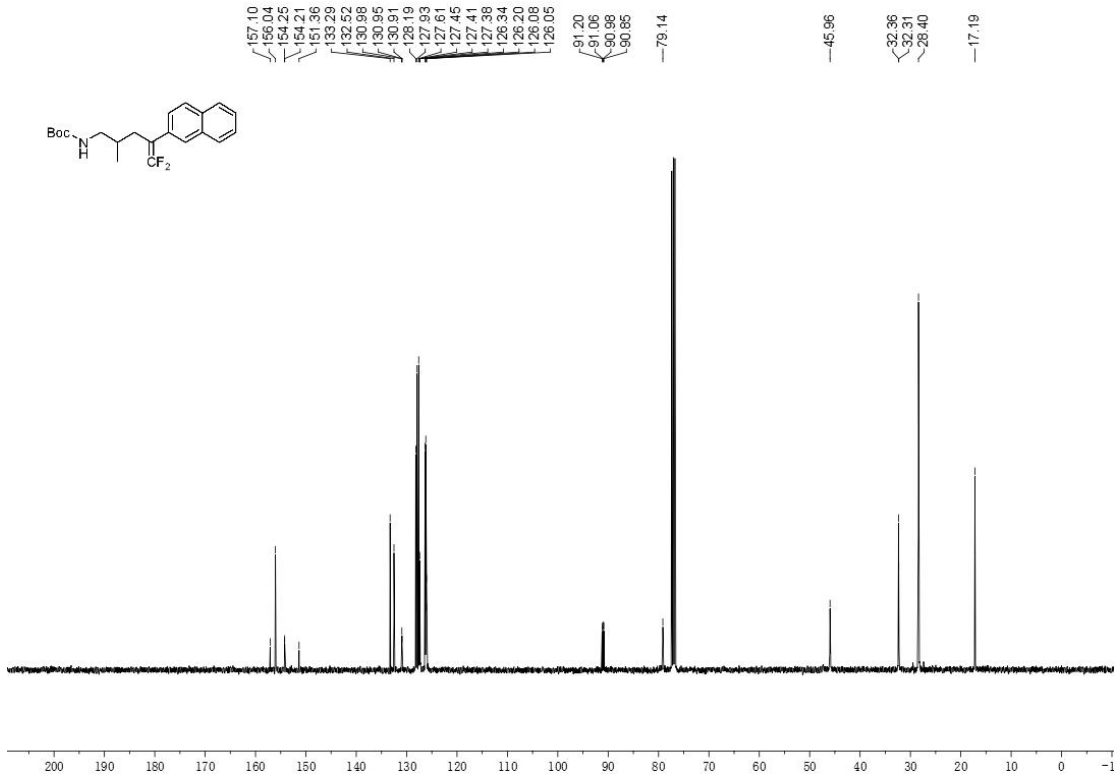

Figure S207. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5f**

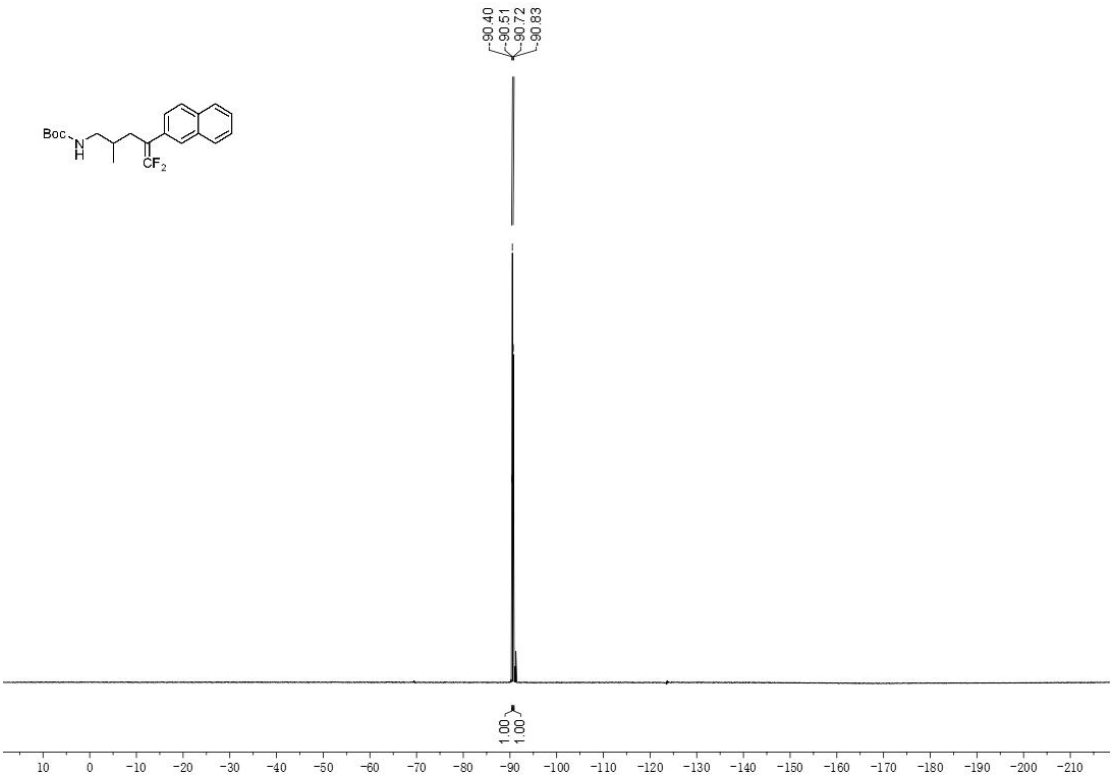

Figure S208. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5f**

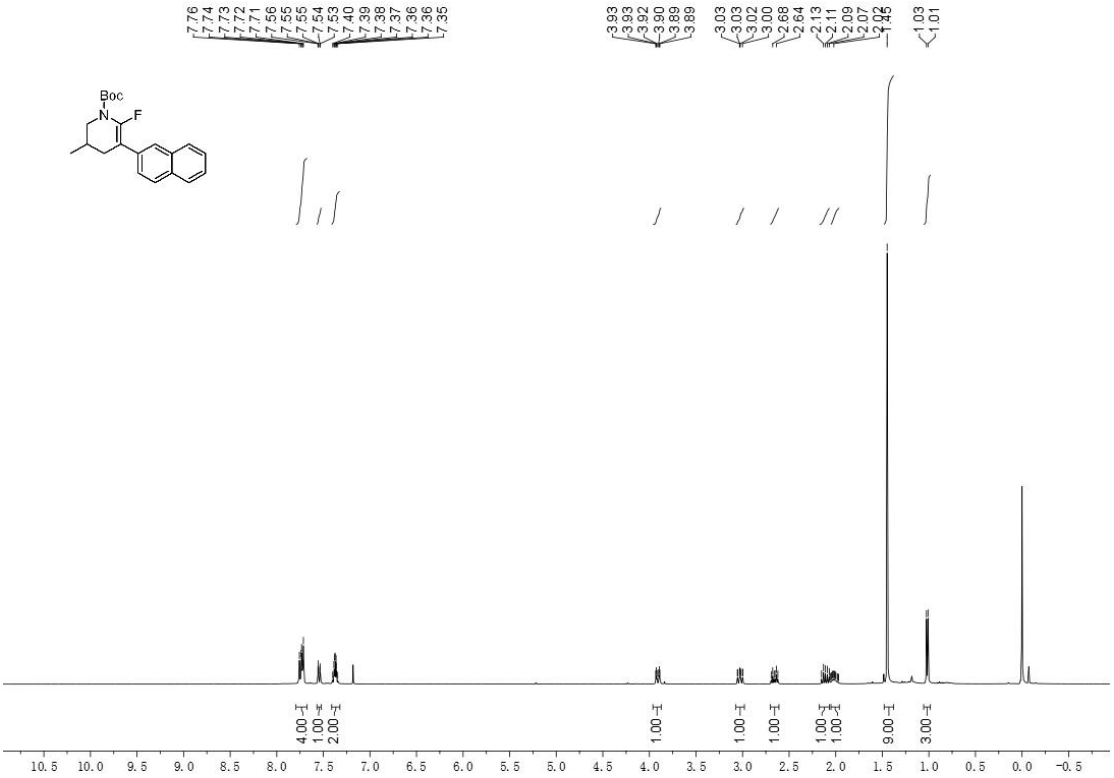

Figure S209. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5g**

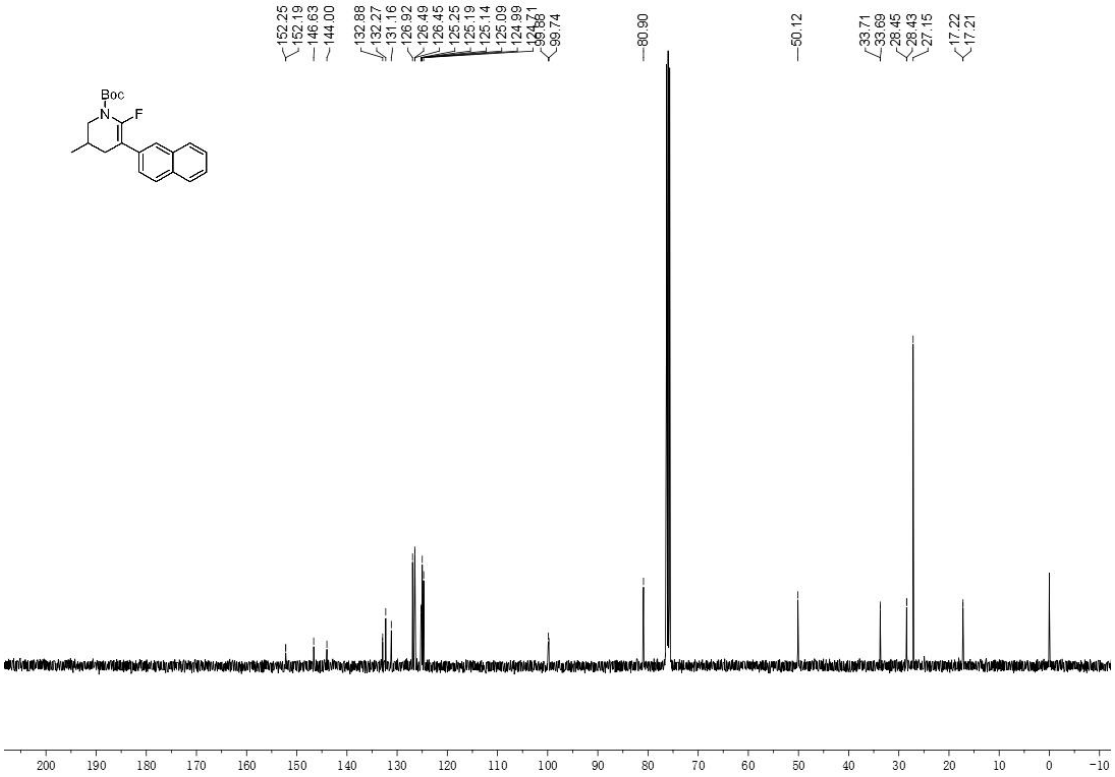

Figure S210. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5g**

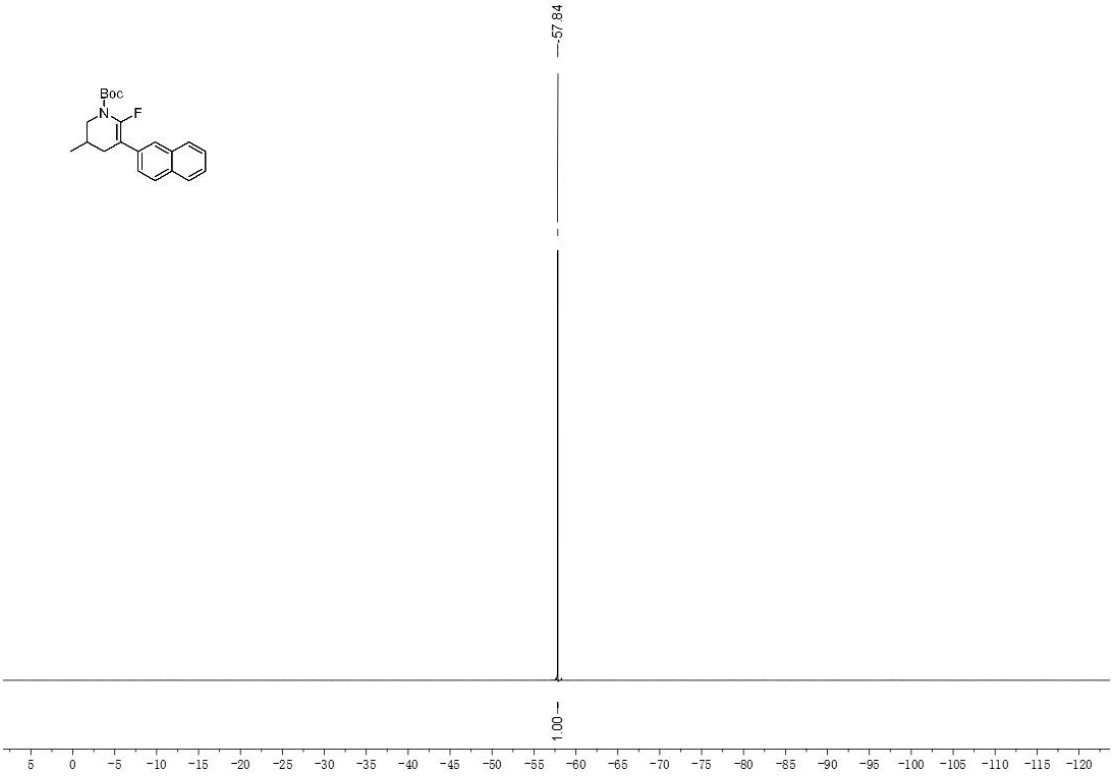

Figure S211. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5g**