A Facile Access to Aliphatic Trifluoromethyl Ketones via Photocatalyzed Cross-Coupling of Bromotrifluoroacetone and Alkenes

Satoshi Mizuta,[a]* Tomoko Yamaguchi,[a] Masaharu Iwasaki,[b,c,d,e] and Takeshi Ishikawa[f]*

[a] Center for Bioinformatics and Molecular Medicine, Graduate School of Biomedical Sciences, Nagasaki University, 1-14 Bunkyo, Nagasaki, 852-8521, Japan

[b] Laboratory of Emerging Viral Diseases, International Research Center for Infectious Diseases, Research Institute for Microbial Diseases, Osaka University, 3-1 Yamadaoka, Suita, Osaka 565-0871, Japan

[c] Center for Infectious Disease Education and Research, Osaka University, 2-8 Yamadaoka, Suita, Osaka 565-0871, Japan

[d] Center for Advanced Modalities and Drug Delivery System, Osaka University, 2-8 Yamadaoka, Suita, Osaka 565-0871, Japan

[e] RNA Frontier Science Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University, Suita, Osaka, Japan

[f] Department of Chemistry, Biotechnology, and Chemical Engineering, Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

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1. General Information

All nuclear magnetic resonance (NMR) spectra were recorded on a Varian 500PS spectrometer, or on JEOL JMN-ECZ400R. ^{1}H, ^{13}C and ^{19}F NMR spectra were reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak using tetramethylsilane (^{1}H and ^{13}C) as an internal standard. Chemical shifts (δ) are quoted in parts per million (ppm), and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations were used to describe multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sext. = sextet, sept. = septet, br = broad, m = multiplet. The NMR spectra were processed using ACD/SpecManager. High-resolution mass spectra (HRMS, *m*/*z*) were obtained on a JEOL JMS-700N for fast atom bombardment (FAB) using m-nitrobenzyl alcohol as a matrix or electron ionization (EI). All the reactions were performed in an apparatus with magnetic stirring under an inert atmosphere. Flash column chromatography was performed using Fuji Silysia Chemical Ltd. Silica Gel C60 (50–200 μm) using an eluent system, as described in the next section, i.e., Experimental Procedures. Thin-layer chromatography was performed using TLC Silica Gel 60 F_{254} aluminum sheets (Merck) and Silica Gel F_{254} glass plates (Merck). Photochemical reactions were carried with
SynLED Parallel Photoreactor (Merck), emitting 12 W of blue light at 470 nm. The LEDs were cooled by built-in fans to maintain an ambient temperature.

Materials. Unless otherwise stated, all starting materials and reagents were obtained from commercial suppliers and were used without further purification. Chemicals were purchased from Aldrich, Nacalai Tesque, Tokyo Chemical Industry, and Wako Pure Chemical Industries and used as received. All solvents were purchased from Wako Pure Chemical Industries.

2. Reaction Condition Optimization

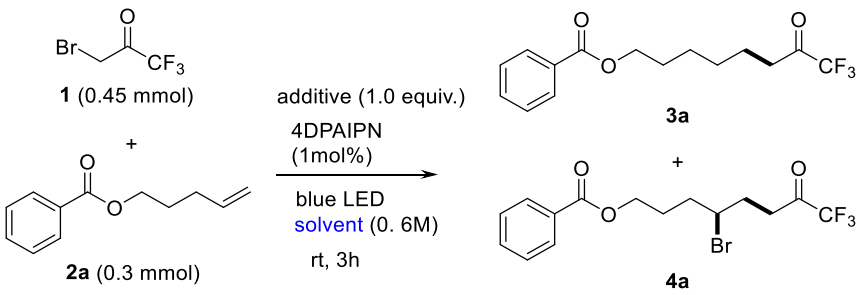
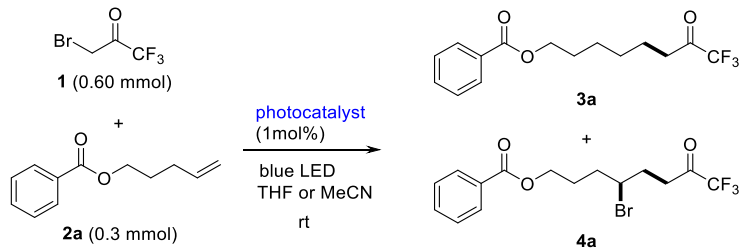


Table S1. Screening of reaction solvents and investigation of quenchers

entry	solvent	additive	yield % [a]	
			3a	**4a**
1	1,4-dioxane	—	33	11
2	1,4-dioxane	K_2CO_3	8	12
3	1,4-dioxane	1-adamantanethiol	22	5
4	1,4-dioxane	Hantzshe ester	3	24
5	1,4-dioxane	Et_3N	0	0
6	tBuOMe	—	22	6
7	MeOH	—	0	0
8	THF	—	48	5
9	THF	H_2O	26	2
10	THF	CF_3CH_2OH	49	7
11	THF	HCO_2Na	4	72
12	MeCN	—	0	63

[a] Yields determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

Table S2. Screening of photocatalyst

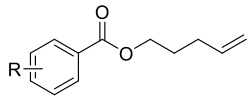


entry	photocatalyst	solvent	time (h)	yield % [a]	
				3a	**4a**
1	4DPAIPN	THF	3	60	13
2	3DPA2FBN	THF	3	77	12
3	3DPA2FBN	THF (0.1 M)	3	33	6
4	4CzIPN	THF	3	73	12
5	$Ir[dFCF_3)ppy]_2(drppy)PF_6$	THF	3	39	13
6	4DPAIPN	MeCN	8	0	75
7	3DPA2FBN	MeCN	8	4	49
8	4CzIPN	MeCN	8	13	57
9	$Ir[dFCF_3)ppy]_2(drppy)PF_6$	MeCN	8	5	70

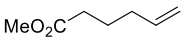
[a] Yields determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

3. Experimental Procedures and Characterization Data.

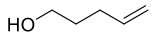
Table S3. Substrate Scope



2a, R=H
2b, R=2-M
2c, R=4-F
2d, R=4-Br
2e, R=4-OMe



2f



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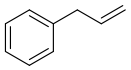
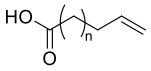


2h



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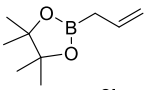
2j, n=2
2k,n=3



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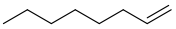

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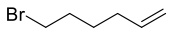
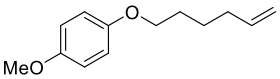
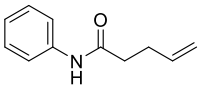


2n



2o



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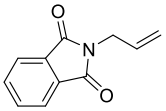
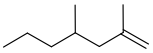
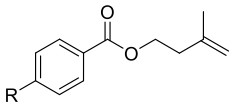


2q

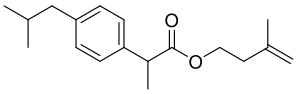


2r



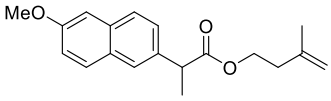
2s, R = H
2z, R = OMe

2t



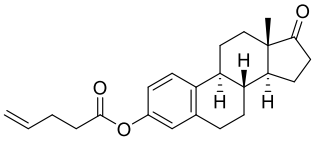
from ibuprofen

2u



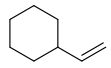
from naproxen

2v

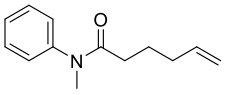


from estrone

2w

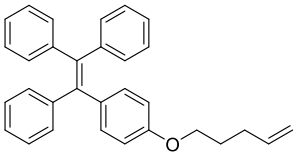


2x



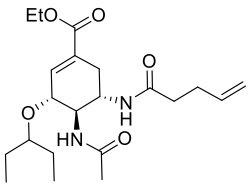
2y

2aa



from TPE

2ab

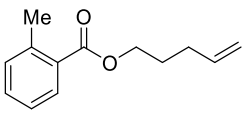


2ac

Substrates; **2f**−**2n**, **2r**, **2t**, **2x**, and **2aa**, were purchased and used directly without further purification. Substrates; **2a**,[1] **2c**,[1] **2d**,[2] **2e**,[3] **2o**,[4] **2p**,[5] **2q**,[6] **2s**,[7] **2u**,[8] **2v**,[8] **2y**,[9] and **2z**,[2] were prepared according to previous reports.

Substrates; **2b**, **2ab**, and **2ac**, were prepared as follows:

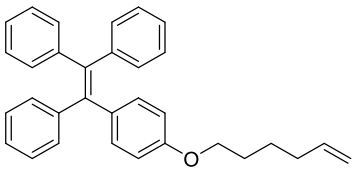
3-1. Synthesis of alkene substrates (2b, 2ab and 2ac)



Synthesis of pent-4-en-1-yl 2-methylbenzoate (2b)

To a solution of 4-penten-1-ol (861 mg, 10 mmol) in CH_2Cl_2 (24 mL) was added 2-methylbenzoyl chloride (1.55 mL, 1.2 equiv.), Et_3N (2.08 mL, 1.5 equiv.) at 0 °C. The mixture was stirred at room temperature for 12 h before quenching with sat. $NaHCO_3$ aqueous solution. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography and eluted with hexane−AcOEt (95:5). This afforded the title compound as a colorless oil (1.49 g, 73% yield).

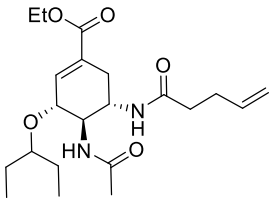
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 2.5, 8.3 Hz, 1H), 7.40 (dt, *J* = 1.2, 7.4 Hz, 1H), 7.26−7.25 (m, 2H), 5.90−5.82 (m, 1H), 5.11−5.06 (m, 1H), 5.04−5.01 (m, 1H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.61 (s, 3H), 2.26−2.21 (m, 2H), 1.91−1.85 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.7, 140.0, 137.5, 131.8, 131.6, 130.5, 129.8, 125.7, 115.4, 64.1, 30.2, 27.9, 21.8; HRMS (FAB) *m/z* Calcd for $C_{13}H_{17}O_2$ $[M+H]^+$ 205.1229 found 205.1230.



Synthesis of (2-(4-(hex-5-en-1-yloxy)phenyl)ethene-1,1,2-triyl)tribenzene (2ab)

A 100 mL round bottom flask with a magnetic stirring bar was charged with 4-(1,2,2-triphenylvinyl)phenol (500 mg, 1.43 mmol), 6-bromo-1-hexene (650 μL, 3.4 equiv.), K_3PO_4 (592 mg, 3.0 equiv.), and Acetone (15 mL). The resulting mixture was stirred at 50 °C for 70 h. For the precipitate removal, the mixture was filtered through a Celite pad and washed with AcOEt. The filtrate was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as a white solid (324 mg, 53% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16−7.00 (m, 15H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 6.9 Hz, 2H), 5.88−5.79 (m, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 10.3 Hz, 1H), 3.91−3.89 (m, 2H), 2.12 (q, *J* = 6.4 Hz, 2H), 1.77 (quint., *J* = 6.4 Hz, 2H), 1.58−1.53 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.6, 144.0, 143.9, 140.5, 139.9, 138.5, 135.9, 132.5, 131.4, 131.3, 131.3, 127.7, 127.6, 126.3, 126.2, 114.7, 113.5, 67.5, 33.4, 28.7, 25.3; HRMS (FAB) *m/z* Calcd for $C_{32}H_{30}O$ $[M]^+$ 430.2296 found 430.2297.



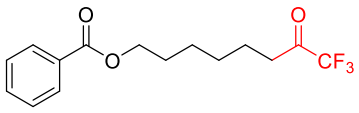
Synthesis of ethyl (3R,4R,5S)-4-acetamido-5-(pent-4-enamido)-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate (2ac)

To a solution of oseltamivir phosphate (410 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added 4-pentenoyl chloride (178 μL, 1.5 equiv.), Et_3N (415 μL, 3.0 equiv.) at 0 °C. The mixture was stirred at room temperature for 12 h before quenching with sat. $NaHCO_3$ aqueous solution. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography and eluted with AcOEt. This afforded the title compound as a white solid (363 mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78−6.77 (m, 2H), 6.42 (br. s, 1H), 5.81-5.74 (m, 1H), 5.81−5.74 (m, 1H), 5.04 (dt, *J* = 1.5, 17.1 Hz, 1H), 4.99 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.22−4.17 (m, 2H), 4.14−4.05 (m, 3H), 3.38 (quint., *J* = 5.6 Hz, 1H), 2.74 (dd, *J* = 4.7, 17.6 Hz, 1H), 2.36−2.24 (m, 6H), 1.99 (s, 3H), 1.54−1.47 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.94−0.85 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 172.9, 171.6, 165.8, 173.3, 136.6, 129.2, 115.6, 82.1, 75.4, 61.0, 54.0, 48.5, 35.7, 30.5, 29.5, 26.2, 25.7, 23.3, 14.2, 9.52, 9.20; HRMS (FAB) *m/z* Calcd for $C_{21}H_{35}N_2O_5$ $[M+H]^+$ 395.2546 found 395.2546.

3-2. General procedure (GP) for the synthesis of trifluoromethyl ketones with bromotrifluoroacetone

A 4 mL vial with a magnetic stirring bar was charged with photocatalyst (1 mol%). Alkene (1.0 equiv.), and solvent (0.6 M) was added. Finally, bromotrifluoroacetone (2.0 equiv.) was introduced to the reaction mixture. The resulting mixture was stirred at room temperature under 12 W blue LED irradiation (470 nm) for indicated times. The reaction mixture was evaporated in vacuo, and the residue was purified by column chromatography on SiO_2 gel, isolating the aliphatic trifluoromethyl ketone derivatives containing occasionally <20% hydrate.

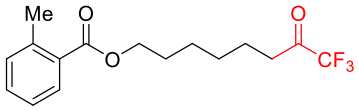


Synthesis of 8,8,8-trifluoro-7-oxooctyl benzoate (3a): The GP was followed with pent-4-en-1-yl benzoate (57.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (65.3 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.03 (m, 2H), 7.57 (tt, *J* = 1.4, 5.5 Hz, 1H), 7.47−7.43 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.74 (t, *J* = 7.1 Hz, 2H), 1.81−1.71 (m, 4H), 1.51−1.40 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5 (q, *J* = 34.5 Hz), 166.6, 132.9, 130.3, 129.5, 128.3, 115.5 (q, *J* =

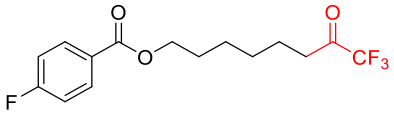
291.1 Hz), 64.7, 36.2, 28.4, 28.4, 25.7, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{18}F_3O_3$ $[M+H]^+$ 303.1208 found 303.1208.

Scale up reaction: The GP was followed with pent-4-en-1-yl benzoate (456 mg, 2.4 mmol), bromotrifluoroacetone (552 µL, 4.8 mmol), 3DPA2FBN (15.3 mg, 1 mol%) and THF (4.0 mL). The reaction was irradiated with blue LEDs for 20 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as brown oil (479 mg, 66% yield).



Synthesis of 8,8,8-trifluoro-7-oxooctyl 2-methylbenzoate (3b): The GP was followed with pent-4-en-1-yl 2-methylbenzoate (61.3 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (50.3 mg, 53% yield).

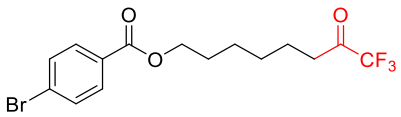
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 1.6, 8.3 Hz, 1H), 7.40 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.26−7.23 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.80−1.70 (m, 4H), 1.51−1.42 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5 (q, *J* = 34.5 Hz), 167.7, 140.0, 131.9, 131.7, 130.4, 129.7, 125.7, 115.5 (q, *J* = 291.3 Hz), 64.5, 36.2, 28.4, 28.3, 25.8, 22.2, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{16}H_{20}F_3O_3$ $[M+H]^+$ 317.1365 found 317.1365.



Synthesis of 8,8,8-trifluoro-7-oxooctyl 4-fluorobenzoate (3c): The GP was followed with pent-4-en-1-yl 4-fluorobenzoate (62.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (59.6 mg, 62% yield).

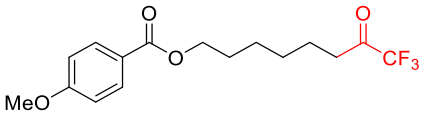
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 6.9, 8.9 Hz, 2H), 7.11 (t, *J* = 8.9 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 6.8 Hz, 2H), 1.80−1.79 (m, 4H), 1.48−1.42 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.4 (q, *J* = 35.5 Hz), 165.7 (d, *J* = 252 Hz), 165.7, 132.0 (d, *J* = 9.6 Hz), 126.5 (d, *J* = 2.9 Hz), 115.5 (q, *J* = 290.4 Hz), 115.4 (d, *J* = 22.0 Hz), 64.9, 36.2, 28.4, 28.3, 25.7, 22.2; ^{19}F

NMR (376 MHz, $CDCl_3$): −79.3 (s, 3F), −105.8 (m, 1F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{17}F_4O_3$ $[M+H]^+$ 321.1114 found 321.1113.



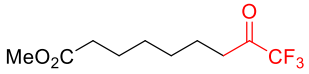
Synthesis of 8,8,8-trifluoro-7-oxooctyl 4-bromobenzoate (3d): The GP was followed with pent-4-en-1-yl 4-bromobenzoate (80.7 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as a yellow solid (57.8 mg, 51% yield).

^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 1.80−1.70 (m, 4H), 1.48−1.40 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.4 (q, *J* = 34.5 Hz), 165.9, 131.7, 131.0, 129.2, 128.0, 115.5 (q, *J* = 291.3 Hz), 65.0, 36.2, 28.3, 28.3, 25.7, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{17}BrF_3O_3$ $[M+H]^+$ 381.1013 found 381.1012.



Synthesis of 8,8,8-trifluoro-7-oxooctyl 4-methoxybenzoate (3e): The GP was followed with pent-4-en-1-yl 4-methoxybenzoate (66.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded the title compound as a yellow solid (48.3 mg, 48% yield).

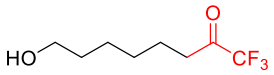
^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.29 (t, *J* = 6.2 Hz, 2H), 3.86 (s, 3H), 2.73 (t, *J* = 7.1 Hz, 2H), 1.81−1.78 (m, 4H), 1.52−1.38 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.6 (d. *J* = 34.5 Hz), 166.6, 163.4, 131.6, 122.8, 115.6 (q, *J* = 290.4 Hz), 113.7, 64.6, 55.5, 36.3, 35.3, 28.6, 28.5, 25.8, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F), −83.8 (hydrate); HRMS (FAB) *m/z* Calcd for $C_{15}H_{17}F_3O_4$ $[M]^+$ 318.1079 found 318.1081.



Synthesis of methyl 9,9,9-trifluoro-8-oxononanoate (3f): The GP was followed with methyl hex-5-enoate (38.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was

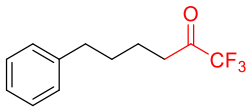
purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded the title compound as colorless oil (58.1 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 3H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.70−1.64 (m, 4H), 1.37−1.34 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5 (q, *J* = 34.5 Hz), 174.1, 115.5 (q, *J* = 290.4 Hz), 51.5, 36.2, 33.9, 28.6, 28.3, 24.6, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F), −85.7 (hydrate); HRMS (FAB) *m/z* Calcd for $C_{10}H_{16}F_3O_3$ $[M+H]^+$ 241.1052 found 241.1050.



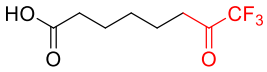
Synthesis of 1,1,1-trifluoro-8-hydroxyoctan-2-one (3g): The GP was followed with pent-4-en-1-ol (43.1 mg, 0.50 mmol), bromotrifluoroacetone (103 µL, 1.00 mmol), 3DPA2FBN (3.2 mg, 1 mol%) and THF (850 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded the title compound as brown oil (43.6 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (t, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 7.1 Hz, 2H), 1.72−1.55 (m, 4H), 1.42−1.36 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.6 (q, *J* = 34.5 Hz), 115.5 (q, *J* = 290.4 Hz), 62.7, 36.2, 32.4, 28.5, 25.4, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_8H_{14}F_3O_2$ $[M+H]^+$ 199.0946 found 199.0946.



Synthesis of 1,1,1-trifluoro-6-phenylhexan-2-one (3h): The GP was followed with allylbenzene (35.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (3:1). This afforded the title compound yellow oil (31.1 mg, 45% yield).

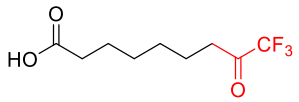
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.1 Hz, 2H), 7.23−7.17 (m, 3H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 1.76−1.60 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.4 (q, *J* = 34.5 Hz), 141.6, 128.4, 128.3, 125.9, 115.5 (q, *J* = 290.4 Hz), 36.2, 35.3, 30.4, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{12}H_{13}F_3O$ $[M]^+$ 230.0918 found 230.0918.



Synthesis of 8,8,8-trifluoro-7-oxooctanoic acid (3i): The GP was followed with pent-4-enoic acid (50.1 mg, 0.50 mmol), bromotrifluoroacetone (103 µL, 1.00 mmol), 3DPA2FBN (3.2 mg, 1 mol%)

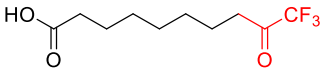
and THF (850 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as a yellow solid (42.0 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (t, *J* = 7.1 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.75−1.64 (m, 4H), 1.45−1.39 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 191.3 (q, *J* = 34.5 Hz), 179.4, 115.5 (q, *J* = 290.4 Hz), 36.0, 33.6, 28.0, 24.1, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_8H_{12}F_3O_2$ $[M+H]^+$ 213.0739 found 213.073.



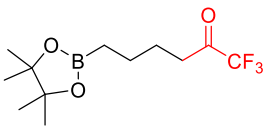
Synthesis of 9,9,9-trifluoro-8-oxononanoic acid (3j): The GP was followed with hex-5-enoic acid (34.2 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as yellow oil (26.0 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.70 (t, *J* = 7.1 Hz, 2H), 2.35 (t, *J* = 7.3 Hz, 2H), 1.71−1.59 (m, 4H), 1.40−1.31 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 191.5 (q, *J* = 34.5 Hz), 179.6, 115.5 (q, *J* = 290.4 Hz), 36.2, 33.8, 28.5, 28.3, 24.3, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_9H_{14}F_3O$ $[M+H]^+$ 227.0895 found 227.0895.



Synthesis of 10,10,10-trifluoro-9-oxodecanoic acid (3k): The GP was followed with hept-6-enoic acid (64.1 mg, 0.50 mmol), bromotrifluoroacetone (103 μL, 1.00 mmol), 3DPA2FBN (3.2 mg, 1 mol%) and THF (850 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as yellow oil (58.8 mg, 49% yield).

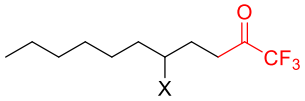
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (t, *J* = 7.3 Hz, 2H), 2.36 (d, *J* = 7.5 Hz, 2H), 1.70−1.62 (m, 2H), 1.41−1.30 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 190.6 (q, *J* = 34.5 Hz), 179.7, 115.5 (q, *J* = 290.4 Hz), 36.3, 33.9, 28.8, 28.7, 28.5, 24.5, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{10}H_{16}F_3O_2$ $[M+H]^+$ 241.1052 found 241.1052.



Synthesis of 1,1,1-trifluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (3l): The GP was followed with 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50.4 mg, 0.30 mmol),

bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:3). This afforded the title compound as yellow oil (38.0 mg, 45% yield).

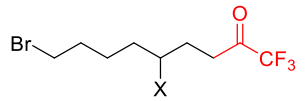
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (t, *J* = 7.1 Hz, 2H), 1.72−1.65 (m, 2H), 1.51−1.43 (m, 2H), 1.25 (s, 12 H), 0.81 (t, *J* = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.6 (q, *J* = 34.5 Hz), 115.6 (q, *J* = 290.4 Hz), 83.1 ,36.2, 24.8, 24.2, 23.2, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); ^{11}B NMR (101 MHz, $CDCl_3$): 32.7 (s, 1B); HRMS (EI) *m/z* Calcd for $C_{12}H_{20}F_3O_3B$ $[M]^+$ 280.1458 found 280.1457.



(X: H/Br = 3.5/1)

Synthesis of 1,1,1-trifluoroundecan-2-one (3m) and 5-bromo-1,1,1-trifluoroundecan-2-one (4m): The GP was followed with oct-1-ene (33.7 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:4). This afforded the title compounds (36.2 mg, 50% yield; **3m**/**4m** = 3.5/1). The ratio of **3m** to **4m** was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$, **3m**): δ 2.72 (t, *J* = 7.1 Hz, 2H), 1.72−1.64 (m, 2H), 1.35−1.22 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, **3m**): δ 191.7 (q, *J* = 34.5 Hz), 115.5 (q, *J* = 290.4 Hz), 36.4, 31.8, 29.3, 29.2, 28.7, 22.6, 22.3, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 2/3F, **4m**), −79.2 (s, 7/3F, **3m**), −85.8 (hydrated **3m**); HRMS (EI) *m/z* Calcd for $C_{11}H_{18}F_3O$ $[M-H]^+$ 223.1310 found 223.1309.

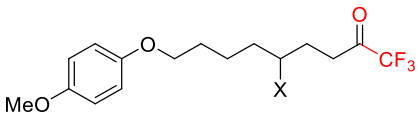


(X: H/Br = 4.2/1)

Synthesis of 9-bromo-1,1,1-trifluorononan-2-one (3n) and 5,9-dibromo-1,1,1-trifluorononan-2-one (4n): The GP was followed with 6-bromohex-1-ene (48.9 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:4). This afforded the title compounds (43.5 mg, 50% yield; **3n**/**4n** = 4.2/1). The ratio of **3n** to **4n** was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$, **3n**): δ 3.41 (t, *J* = 6.9 Hz, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 1.90−1.83 (m, 2H), 1.73−1.65 (m, 2H), 1.49−1.42 (m, 2H), 1.37−1.33 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, **3n**): 191.5 (q, *J* = 34.5 Hz), 115.5 (q, *J* = 290.4 Hz), 36.2, 33.8, 32.6, 28.5, 28.3, 27.8, 22.2; ^{19}F

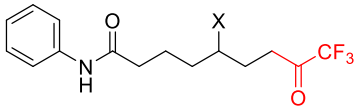
NMR (376 MHz, $CDCl_3$): −79.1 (s, 3/5F, **4n**), −79.2 (s, 12/5F, **3n**); HRMS (EI) *m/z* Calcd for $C_9H_{13}BrF_3O$ $[M-H]^+$ 273.0102 found 273.0101.



(X: H/Br = 2.8/1)

Synthesis of 1,1,1-trifluoro-9-(4-methoxyphenoxy)nonan-2-one (3o) and 5-bromo-1,1,1-trifluoro-9-(4-methoxyphenoxy)nonan-2-one (4o): The GP was followed with 1-(hex-5-en-1-yloxy)-4-methoxybenzene (61.9 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:4). This afforded the title compounds (77.3 mg, 76% yield; **3o**/**4o** = 2.8/1). The ratio of **3o** to **4o** was determined by ^{19}F NMR analysis.

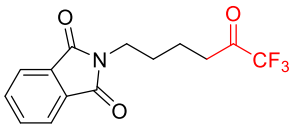
^1H NMR (400 MHz, $CDCl_3$, **3o**): δ 6.84−6.83 (m, 4H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.73 (t, *J* = 3.1 Hz, 2H), 1.81−1.68 (m, 6H), 1.41−1.35 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, **3o**): 191.5 (q, *J* = 34.5 Hz), 153.6, 153.2, 115.5 (q, *J* = 290.4 Hz), 115.4, 114.1, 68.4, 55.7, 36.3, 29.2, 28.9, 28.6, 25.8, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 4/5F, **4o**), −79.2 (s, 11/5F, **3o**); HRMS (EI) *m/z* Calcd for $C_{16}H_{21}F_3O_3$ $[M+H]^+$ 318.1443 found 318.1443.



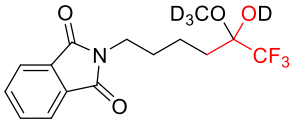
(X: H/Br = 1/1)

Synthesis of 9,9,9-trifluoro-8-oxo-*N*-phenylnonanamide (3p) and 5-bromo-9,9,9-trifluoro-8-oxo-*N*-phenylnonanamide (4p): The GP was followed with *N*-phenylhex-5-enamide (56.8 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4CzIPN (2.4 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:4). This afforded the title compounds (60.2 mg, 59% yield; **3p**/**4p** = 1/1). The ratio of **3p** to **4p** was determined by ^{19}F NMR analysis.

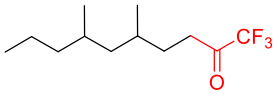
^1H NMR (400 MHz, $CDCl_3$, **3p**): δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (br.,s 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 6.9 Hz, 1H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 1.76−1.64 (m, 4H), 1.43−1.32 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, **3p**): 191.6 (q, *J* = 34.5 Hz), 170.6, 137.8, 129.0, 124.3, 119.8, 115.5 (q, *J* = 290.4 Hz), 36.2, 28.7, 28.4, 23.4, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$): −79.0 (s, 3/2F, **4p**), −79.2 (s, 3/2F, **3p**), −85.7 (hydrated **3p**) ; HRMS (FAB) *m/z* Calcd for $C_{15}H_{19}F_3NO_2$ $[M+H]^+$ 302.1368 found 302.1368.



Synthesis of 2-(6,6,6-trifluoro-5-oxohexyl)isoindoline-1,3-dione (3q): The GP was followed with 2-allylisoindoline-1,3-dione (56.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4CzIPN (2.4 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (57.6 mg, 64% yield). NMR spectra showed the hemiacetal form of **3q** with CD_3OD.

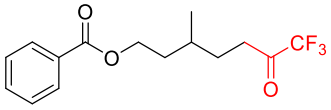


^{1}H NMR (400 MHz, CD_3OD): δ 7.84−7.82 (m, 2H), 7.79−7.77 (m, 2H), 3.66 (t, *J* = 7.1 Hz, 2H), 1.82−1.78 (m, 2H), 1.71−1.63, 1.50−1.42 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CD_3OD): δ 170.0, 13.3, 133.4, 125.3 (q, *J* = 290.5 Hz), 124.2, 97.3 (q, *J* = 29.7), 38.7, 34.5, 29.8, 20.9; ^{19}F NMR (376 MHz, CD_3OD): −82.4 (s, 3F); HRMS (EI) *m/z* Calcd for $C_{14}H_{12}F_3NO_3$ $[M]^+$ 299.0769 found 299.0769.



Synthesis of 1 1,1,1-trifluoro-5,7-dimethyldecan-2-one (3r): The GP was followed with 2,4-dimethylhept-1-ene (63.1 mg, 0.50 mmol), bromotrifluoroacetone (103 µL, 1.00 mmol), 3DPA2FBN (3.2 mg, 1 mol%) and THF (850 µL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:4). This afforded the title compound as yellow oil (59.6 mg, 50% yield, dr = 1:1).

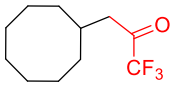
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75−2.69 (m, 2H), 1.74−0.92 (m, 12H), 0.94−0.81 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.9 (m), 115.6 (q, *J* = 291.3 Hz), 44.6, 44.3, 40.1, 39.0, 34.1, 34.0, 30.0, 29.7, 29.5, 29.3, 29.0, 20.1, 19.9, 19.7, 19.3, 19.0, 14.4, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (EI) *m/z* Calcd for $C_{12}H_{21}F_3O$ $[M]^+$ 238.1545 found 38.1544.



Synthesis of 7,7,7-trifluoro-3-methyl-6-oxoheptyl benzoate (3s): The GP was followed with 3-methylbut-3-en-1-yl benzoate (57.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 µL). The reaction was irradiated with blue LEDs for 3

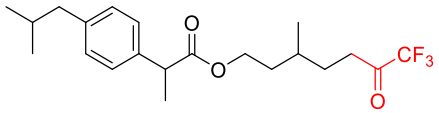
h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (65.0 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 1.4, 8.4 Hz, 2H), 7.57 (tt, *J* = 1.4, 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.42−4.40 (m, 2H), 2.80−2.75 (m, 2H), 1.86−1.55 (m, 5H), 1.01 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5 (q, *J* = 34.5 Hz), 166.6, 132.9, 130.2, 129.5, 128.4, 115.5 (q, *J* = 290.4 Hz), 62.9, 35.2, 34.0, 29.3, 29.1, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{18}F_3O_3$ $[M+H]^+$ 303.1208 found 303.1208.



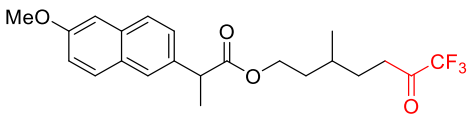
Synthesis of 3-cyclooctyl-1,1,1-trifluoropropan-2-one (3t): The GP was followed with *cis*-cyclooctene (33.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (28.6 mg, 43% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.61 (d, *J* = 2.5 Hz, 2H), 2.28−2.18 (m, 1H), 1.74−1.34 (m, 14H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.3 (q, *J* = 34.5 Hz), 115.5 (q, *J* = 290.4, Hz), 44.7, 32.3, 32.2, 26.9, 26.1, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$): −79.4 (s, 3F); HRMS (EI) *m/z* Calcd for $C_{11}H_{17}F_3O$ $[M]^+$ 222.1231 found 222.1228.



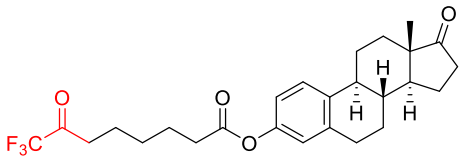
Synthesis of 7,7,7-trifluoro-3-methyl-6-oxoheptyl 2-(4-isobutylphenyl)propanoate (3u): The GP was followed with 3-methylbut-3-en-1-yl 2-(4-isobutylphenyl)propanoate (82.3 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as brown oil (105.2 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 4.33−4.29 (m, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 2.99−2.95 (m, 2H), 2.44 (d, *J* = 7.3 Hz, 2H), 2.20−2.03 (m, 5H), 1.84 (sept., *J* = 6.6 Hz, 1H), 1.63 (d, *J* = 3.9 Hz, 3H), 1.45 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.4 (q, *J* = 35.5 Hz), 174.5, 170.7, 137.4, 129.4, 127.1, 115.5 (q, *J* = 290.4 Hz), 67.0, 62.1, 45.1, 45.0, 43.5, 37.5, 33.6, 31.2, 31.1, 30.2, 22.3, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$): −78.9 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{21}H_{28}F_3O_3$ $[M-H]^+$ 385.1991 found 385.1988.



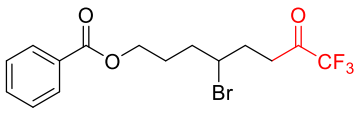
Synthesis of 7,7,7-trifluoro-3-methyl-6-oxoheptyl 2-(6-methoxynaphthalen-2-yl)propanoate (3v): The GP was followed with 3-methylbut-3-en-1-yl 2-(6-methoxynaphthalen-2-yl)propanoate (89.4 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded the title compound as brown oil (81.1 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.7 Hz, 2H), 7.66 (s, 1H), 7.38 (dd, *J* = 1.8, 8.5 Hz, 1H), 7.15 (dd, *J* = 2.5, 8.9 Hz, 1H), 7.11 (d, *J* = 2.5 Hz), 4.31 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 3.84 (q, *J* = 7.1 Hz, 1H), 2.94−2.88 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.4 (m), 174.4, 135.3, 133.7, 129.2, 128.8, 127.2, 126.9, 126.0, 119.1, 115.5 (q, *J* = 290.4 Hz), 105.5, 67.0, 62.2, 55.2, 45.4, 43.5, 37.4, 37.3, 33.5, 33.5, 31.1, 31.0, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$): −78.9 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{22}H_{23}F_3O_4$ $[M-2H]^+$ 408.1548 found 408.1546.



Synthesis of (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 8,8,8-trifluoro-7-oxooctanoate (3w): The GP was followed with (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl pent-4-enoate (110 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4CzIPN (2.4 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 22 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded the title compound as a brown solid (50.2 mg, 36% yield).

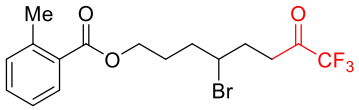
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 2.7, 8.4 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 2.93−2.90 (m, 2H), 2.77 (t, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.55−2.49 (m, 1H), 2.43−2.39 (m, 1H), 2.33−2.25 (m, 1H), 2.20−1.96 (m, 4H), 1.83−1.74 (m, 4H), 1.67−1.43 (m, 8H), 0.91 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 220.8, 191.4 (q, *J* = 34.5 Hz), 172.2, 148.5, 138.0, 137.4, 126.4, 121.5, 118.7, 115.5 (q, *J* = 290.4 Hz), 50.4, 47.9, 44.1, 38.0, 36.1, 35.8, 34.0, 31.5, 29.4, 28.1, 26.3, 25.7, 24.4, 22.0, 21.6, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{27}H_{32}F_3O_4$ $[M+H]^+$ 465.2253 found 465.2241.



Synthesis of 4-bromo-8,8,8-trifluoro-7-oxooctyl benzoate (4a): The GP was followed with pent-4-en-1-yl benzoate (57.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (82.6 mg, 72% yield).

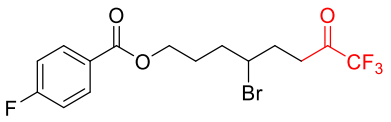
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.03 (m, 2H), 7.60−7.56 (m, 1H), 7.48−7.44 (m, 2H), 4.41−4.34 (m, 2H), 4.12−4.07 (m, 1H), 3.11−2.95 (m, 2H), 2.31−2.27 (m, 1H), 2.15−1.93 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7 (q, *J* = 35.5 Hz), 166.5, 133.0, 130.0, 129.5, 128.4, 115.4 (q, *J* = 290.4 Hz), 63.9, 55.0, 35.9, 34.7, 31.5, 27.0; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{17}BrF_3O_3$ $[M+H]^+$ 381.0313 found 381.0313.

Scale up reaction: The GP was followed with pent-4-en-1-yl benzoate (456 mg, 2.4 mmol), bromotrifluoroacetone (552 μL, 4.8 mmol), 4DPAIPN (19.1 mg, 1 mol%) and MeCN (4.0 mL). The reaction was irradiated with blue LEDs for 12 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as brown oil (781 mg, 85% yield).



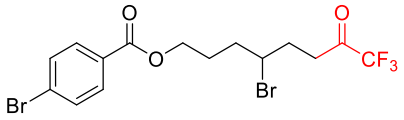
Synthesis of 4-bromo-8,8,8-trifluoro-7-oxooctyl 2-methylbenzoate (4b): The GP was followed with pent-4-en-1-yl 2-methylbenzoate (61.3 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (85.7 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 6.6 Hz, 1H), 7.42 (dt, *J* = 1.4, 7.6 Hz, 1H), 7.28−7.24 (m, 2H), 4.38−4.30 (m, 2H), 4.11−4.06 (m, 1H), 3.11−2.94 (m, 2H), 2.61 (s, 3H), 2.31−2.25 (m, 1H), 2.14−1.92 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7 (q, *J* = 35.5 Hz), 167.5, 140.2, 132.1, 131.7, 130.5, 129.4, 125.7, 115.4 (q, *J* = 290.4 Hz), 64.0, 55.0, 36.0, 34.7, 31.5, 26.9, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{16}H_{19}BrF_3O_3$ $[M+H]^+$ 395.0470 found 395.0470.



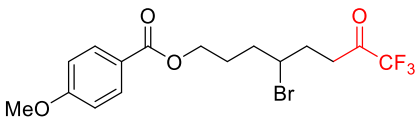
Synthesis of 4-bromo-8,8,8-trifluoro-7-oxooctyl 4-fluorobenzoate (4c): The GP was followed with pent-4-en-1-yl 4-fluorobenzoate (62.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as a yellow solid (85.0 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 5.5, 8.9 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 4.41−4.32 (m, 2H), 4.11−4.07 (m, 1H), 3.11−2.95 (m, 2H), 2.31−2.28 (m, 1H), 2.14−1.93 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7 (q, *J* = 35.5 Hz), 167.1, 165.0 (d, *J* = 103.5 Hz), 132.1 (d, *J* = 9.6 Hz), 126.3, 115.6 (d, *J* = 22.0 Hz), 115.4 (q, *J* = 290.4 Hz), 64.1, 54.9, 35.9, 34.7, 31.5, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): −79.0 (s, 3F), −105.3 (m, 1F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{16}BrF_4O_3$ $[M+H]^+$ 399.0219 found 399.0219



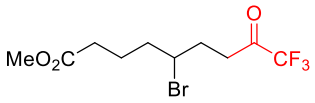
Synthesis of 4-bromo-8,8,8-trifluoro-7-oxooctyl 4-bromobenzoate (4d): The GP was followed with pent-4-en-1-yl 4-bromobenzoate (80.7 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as a yellow solid (114.5 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 4.41−4.33 (m, 2H), 4.11−4.06 (m, 1H), 3.11−2.95(m, 2H), 2.32−2.24 (m, 1H), 2.17−1.90 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.6 (q, *J* = 35.5 Hz), 165.8, 131.7, 131.1, 128.9, 128.2, 115.4 (d, *J* = 290.4 Hz), 64.2, 54.9, 35.8, 34.7, 31.5, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{15}Br_2F_3O_3$ $[M]^+$ 457.9340 found 357.9340



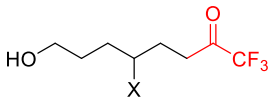
Synthesis of 4-bromo-8,8,8-trifluoro-7-oxooctyl 4-methoxybenzoate (4e): The GP was followed with pent-4-en-1-yl 4-methoxybenzoate (66.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as a yellow solid (100.3 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.38−4.29 (m, 2H), 4.13−4.05 (m, 1H), 3.87 (s, 3H), 3.11−2.94 (m, 2H), 2.32−2.27 (m, 1H), 2.15−1.89 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7 (q, *J* = 35.5 Hz), 166.3, 163.4, 131.6, 122.5, 115.4 (q, *J* = 290.4 Hz), 113.6, 63.6, 55.4, 55.1, 35.9, 34.7, 31.5, 27.0; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{16}H_{19}BrF_3O_4$ $[M+H]^+$ 411.0419 found 411.0419.



Synthesis of 4 methyl 5-bromo-9,9,9-trifluoro-8-oxononanoate (4f): The GP was followed with methyl hex-5-enoate (38.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (62.7 mg, 66% yield).

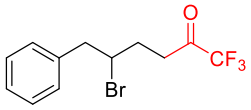
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.11−3.99 (m, 1H), 3.69 (s, 3H), 3.09−2.93 (m, 2H), 2.37 (t, *J* = 6.9 Hz, 2H), 2.99−2.22 (m, 1H), 2.14−1.77 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7 (q, *J* = 35.5 Hz), 173.5, 115.4 (q, *J* = 290.4 Hz), 54.9, 51.6, 38.4, 34.7, 33.0, 31.3, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F), −85.6 (hydrate); HRMS (FAB) *m/z* Calcd for $C_{10}H_{15}BrF_3O_3$ $[M+H]^+$ 319.0157 found 319.0157.



(X: H/Br = 1/4)

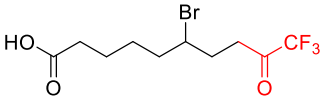
Synthesis of 1,1,1-trifluoro-8-hydroxyoctan-2-one (3g) and 5-bromo-1,1,1-trifluoro-8-hydroxyoctan-2-one (4g): The GP was followed with pent-4-en-1-ol (43.1 mg, 0.50 mmol), bromotrifluoroacetone (103 µL, 1.00 mmol), 4DPAIPN (4.0 mg, 1 mol%) and MeCN (850 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compounds (86.9 mg, 65% yield; **3g**/**4g** = 1/4). The ratio of **4g** to **3g** was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$, **4g**): δ 5.13 (br.s, 1H), 4.10−4.04 (m, 1H), 3.74 (t, *J* = 6.2 Hz, 2H), 3.10−2.94 (m, 2H), 2.29−2.25 (m, 1H), 2.14−1.67 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, **4g**): δ 190.7 (q, *J* = 35.5 Hz), 115.4 (q, *J* = 290.4 Hz), 62.1, 55.5, 35.5, 34.7, 31.5, 30.1; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 12/5F, **4g**), −79.2 (s, 3/5F, **3g**); HRMS (EI) *m/z* Calcd for $C_8H_{13}BrF_3O_2$ $[M+H]^+$ 277.0051 found 277.0043.



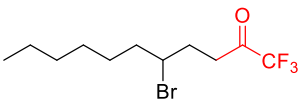
Synthesis of 5-bromo-1,1,1-trifluoro-6-phenylhexan-2-one (4h): The GP was followed with allylbenzene (35.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (63.0 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.33 (m, 2H), 7.33−7.29 (m, 1H), 7.24−7.22 m, 2H), 4.27−4.21 (m, 1H), 3.29 (dd, *J* = 7.4, 14.2 Hz, 1H), 3.18 (dd, *J* = 7.1, 14.2 Hz, 1H), 3.08 (ddd, *J* = 4.9, 8.3, 19.6 Hz, 1H), 2.95 (ddd, *J* = 4.9, 8.4, 19.6 Hz, 1H), 2.32−2.26 (m, 1H), 2.10−2.02 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.6 (q, *J* = 35.5 Hz), 137.6, 129.1, 128.6, 127.1, 115.4 (q, *J* = 290.4 Hz), 54.9, 45.8, 34.8, 30.4; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{12}H_{12}BrF_3O$ $[M]^+$ 308.0024 found 308.0022.



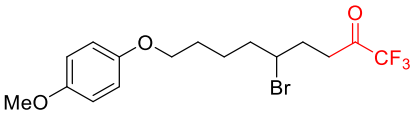
Synthesis of 6-bromo-10,10,10-trifluoro-9-oxodecanoic acid (4k): The GP was followed with hept-6-enoic acid (38.5 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as yellow oil (56.4 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.06−3.99 (m, 1H), 3.09−2.93 (m, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.30−2.21 (m, 1H), 2.13−2.03 (m, 1H), 1.92−1.85 (m, 2H), 1.71−1.62 (m, 3H), 1.56−1.50 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7 (q, *J* = 35.5 Hz), 179.4, 115.5 (q, *J* = 290.4 Hz), 55.3, 38.9, 34.7, 33.7, 31.4, 27.0, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{10}H_{15}BrF_3O_3$ $[M+H]^+$ 319.0157 found 319.0157.



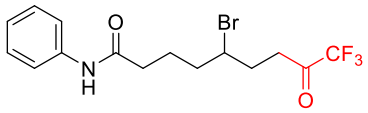
Synthesis of 5-bromo-1,1,1-trifluoroundecan-2-one (4m): The GP was followed with oct-1-ene (33.7 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as yellow oil (57.8 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05−4.01 (m, 1H), 3.09−2.93 (m, 2H), 2.29−2.21 (m, 1H), 2.13−2.03 (m, 1H), 1.92−1.78 (m, 2H), 1.58−1.51 (m, 1H), 1.46−1.39 (m, 1H), 1.35−1.26 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.8 (q, *J* = 35.5 Hz), 115.5 (q, *J* = 290.4 Hz), 56.1, 39.3, 34.8, 31.6, 31.4, 28.6, 27.5, 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{11}H_{18}BrF_3O$ $[M]^+$ 302.0493 found 302.0486.



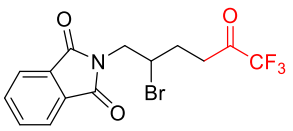
Synthesis of 5-bromo-1,1,1-trifluoro-9-(4-methoxyphenoxy)nonan-2-one (4o): The GP was followed with 1-(hex-5-en-1-yloxy)-4-methoxybenzene (61.9 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as yellow oil (74.7 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85−6.83 (m, 4H), 4.11−4.02 (m, 1H), 3.94 (t, *J* = 6.1 Hz, 2H), 3.78 (s, 3H), 3.09−2.95 (m, 2H), 2.32−2.23 (m, 1H), 2.20−2.03 (m, 1H), 1.98−1.91 (m, 2H), 1.82−1.74 (m, 3H), 1.66−1.60 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.8 (d, *J* =35.5 Hz), 153.7, 153.0, 115.4 (q, *J* = 290.4 Hz), 115.4, 114.6, 68.1, 55.7, 55.6, 39.0, 34.8, 31.4, 28.6, 24.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F); HRMS (EI) *m/z* Calcd for $C_{16}H_{20}BrF_3O_3$ $[M]^+$ 396.0548 found 396.0548.



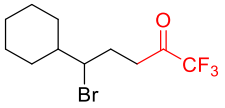
Synthesis of 5-bromo-9,9,9-trifluoro-8-oxo-*N*-phenylnonanamide (4o): The GP was followed with *N*-phenylhex-5-enamide (56.8 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as a brown solid (97.5 mg, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (br.s, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 4.11−3.96 (m, 1H) 3.09−2.90 (m, 2H), 2.47−2.39 (m, 2H), 2.31−2.15 (m, 1H), 2.15−1.78 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.7 (q, *J* = 35.5 Hz), 171.0, 137.6, 129.0, 124.5, 120.6, 115.4 (q, *J* = 290.4 Hz), 55.2, 38.4, 36.3, 34.7, 31.3, 23.5; ^{19}F NMR (376 MHz, $CDCl_3$): −79.0 (s, 3F,); HRMS (FAB) *m/z* Calcd for $C_{15}H_{17}BrF_3NO_2$ $[M]^+$ 379.0395 found 379.0395.



Synthesis of 2-(2-bromo-6,6,6-trifluoro-5-oxohexyl)isoindoline-1,3-dione (4q): The GP was followed with 2-allylisoindoline-1,3-dione (56.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (22.7 mg, 20% yield).

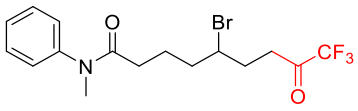
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91−7.87 (m, 2H), 7.79−7.75 (m, 2H), 4.44−4.37 (m, 1H), 4.15 (dd, *J* = 7.8, 14.2 Hz, 1H), 3.99 (dd, *J* = 7.1, 14.4 Hz, 1H), 3.14 (ddd, *J* = 5.0, 8.9, 19.7 Hz, 1H), 2.99 (ddd, *J* = 6.4, 8.7, 19.7 Hz, 1H), 2.37−2.29 (m, 1H), 2.15−2.05 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.3 (q, *J* = 35.5 Hz), 167.8, 134.4, 131.6, 123.7, 115.4 (q, *J* = 290.4 Hz), 49.4, 44.0, 34.3, 28.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.0 (s, 3F,); HRMS (FAB) *m/z* Calcd for $C_{14}H_{12}BrF_3NO_3$ $[M]^+$ 377.9953 found 377.9945.



Synthesis of 5-bromo-5-cyclohexyl-1,1,1-trifluoropentan-2-one (4y): The GP was followed with vinylcyclohexane (32.4 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (47.5 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96−3.92 (m, 1H), 3.07 (ddd, *J* = 5.3, 8.5, 19.7 Hz, 1H), 2.95 (ddd, *J* = 6.6,

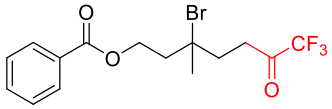
7.8, 19.4 Hz, 1H), 2.27−2.07 (m, 2H), 1.88−1.55 (m, 6H), 1.32−1.14 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.9 (q, *J* = 35.5 Hz), 115.5 (q, *J* = 290.4 Hz), 63.1, 44.8, 35.3, 30.6, 29.5, 28.6, 26.1, 26.0, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F,); HRMS (EI) *m/z* Calcd for $C_{11}H_{16}F_3O$ $[M-Br]^+$ 221.1153 found 211.1155.



Synthesis of 5-bromo-9,9,9-trifluoro-*N*-methyl-8-oxo-*N*-phenylnonanamide (4z): The GP was followed with *N-methyl-N-phenylhex-5-enamide* (56.8 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 μL). The reaction was irradiated with

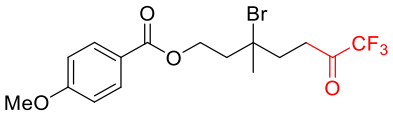
blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as yellow oil (78.6 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 3.99−3.91 (m, 1H), 3.28 (s, 3H), 3.06−2.89 (m, 2H), 2.25−2.17 (m, 1H), 2.15−1.99 (s, 3H), 1.84−1.71 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.7 (q, *J* = 35.5 Hz), 172.4, 143.9, 129.9, 127.9, 127.3, 115.4 (q, *J* = 290.4 Hz), 55.3, 38.5, 37.4, 34.7, 33.1, 31.2, 23.4; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F,); HRMS (FAB) *m/z* Calcd for $C_{16}H_{20}BrF_3NO_2$ $[M+H]^+$ 394.0630 found 394.0628.



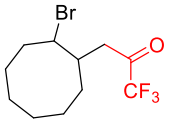
Synthesis of 3-bromo-7,7,7-trifluoro-3-methyl-6-oxoheptyl benzoate (4s): The GP was followed with 3-methylbut-3-en-1-yl benzoate (57.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as yellow oil (95.0 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 1.4, 8.2 Hz, 2H), 7.58 (tt, *J* = 1.2, 6.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.59 (d, *J* = 6.6 Hz, 2H), 3.10−3.06 (m, 1H), 2.44−2.28 (m, 3H), 2.25−2.17 (m, 1H), 1.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.5 (q, *J* = 34.5 Hz), 166.4, 133.2, 129.8, 129.5, 128.4, 115.5 (q, *J* = 290.4 Hz), 66.7, 62.3, 43.8, 37.7, 33.6, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$): −78.9 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{18}BrF_3O_3$ $[M+H]^+$ 381.0313 found 381.0313.



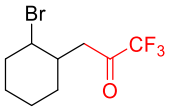
Synthesis of 3-bromo-7,7,7-trifluoro-3-methyl-6-oxoheptyl 4-methoxybenzoate (4z): The GP was followed with 3-methylbut-3-en-1-yl 4-methoxybenzoate (66.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (4:1). This afforded the title compound as a brown solid (80.0 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.54 (dt, *J* = 1.2, 6.6 Hz, 2H), 3.87 (s, 3H), 3.09−3.05 (m, 2H), 2.43−2.16 (m, 4H), 1.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.5 (q, *J* = 35.5 Hz), 166.1, 163.5, 131.6, 122.2, 115.5 (q, *J* = 290.4 Hz), 113.7, 66.9, 62.0, 55.4, 43.8, 37.7, 33.6, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$): −78.9 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{16}H_{19}BrF_3O_4$ $[M+H]^+$ 411.0419 found 411.0418.



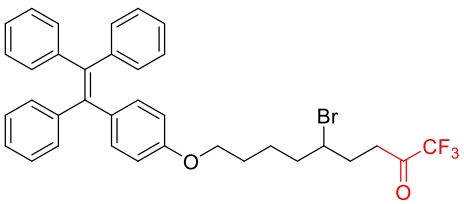
Synthesis of 3-(2-bromocyclooctyl)-1,1,1-trifluoropropan-2-one (4t): The GP was followed with *cis*-cyclooctene (33.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN (500 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (8:1). This afforded the title compound as colorless oil (39.8 mg, 44% yield, dr = 1:1.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.60−4.59 (m, 2/5H), 4.18−4.14 (m, 3/5H), 3.36−2.53(m, 2H), 2.46−1.39 (m, 13H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.7 (q, *J* = 34.5 Hz), 115.4 (q, *J* = 291.3 Hz), 62.2, 61.6, 44.5, 40.9, 33.3, 32.6, 32.2, 31.0, 28.1, 26.8, 26.0, 25.8, 25.2, 25.0, 24.4; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (EI) *m/z* Calcd for $C_{11}H_{15}BrF_3O$ $[M-H]^+$ 299.0258 found 299.0258.



Synthesis of 3-(2-bromocyclohexyl)-1,1,1-trifluoropropan-2-one (4aa): The GP was followed with cyclohexene (41.1 mg, 0.30 mmol), bromotrifluoroacetone (103 µL, 1.00 mmol), 4DPAIPN (4.0 mg, 1 mol%) and MeCN (850 µL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (8:1). This afforded the title compound as colorless oil (61.0 mg, 45% yield, dr = 1:1).

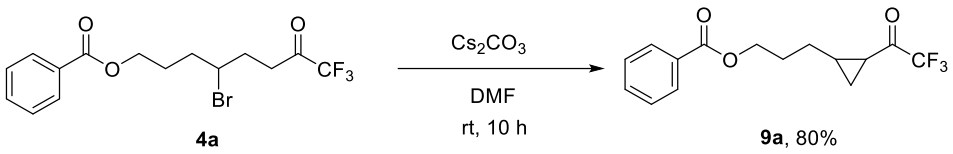
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.60−4.57 (m, 1/2H), 3.87 (dt, *J* = 4.1, 11.4 Hz, 1/2H), 3.32 (dd, *J* = 3.0, 18.8 Hz, 1/2H), 2.93 (dd, *J* = 6.6, 19.4 Hz, 1/2H), 2.73−2.62 (m, 1H), 2.44−1.10 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.4 (q, *J* = 34.5 Hz), 115.4 (q, *J* = 290.4 Hz), 59.6, 57.6, 42.4, 42.1, 41.6, 38.5, 36.8, 34.7, 32.5, 27.4, 27.0, 25.1, 25.0, 20.5; ^{19}F NMR (376 MHz, $CDCl_3$): −79.3 (s, 3/2F), −79.4 (s, 3/2F). The mass spectrum of product was not obtained due to the thermal decomposition



Synthesis of 5-bromo-1,1,1-trifluoro-9-(4-(1,2,2-triphenylvinyl)phenoxy)nonan-2-one (4ab): The GP was followed with (2-(4-(hex-5-en-1-yloxy)phenyl)ethene-1,1,2-triyl)tribenzene (129.1 mg, 0.30 mmol), bromotrifluoroacetone (62.0 µL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%) and MeCN

(500 μL). The reaction was irradiated with blue LEDs for 20 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (115.8 mg, 56% yield).

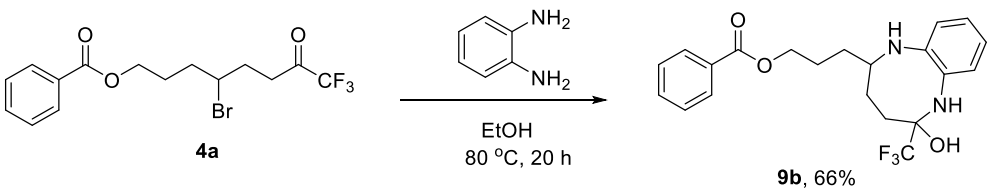
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14−7.00 (m, 15H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 4.07−4.01 (m, 1H), 3.90 (t, *J* = 6.1 Hz, 2H), 3.08−2.94 (m, 2H), 2.29−2.24 (m, 1H), 2.15−2.06 (m, 1H), 1.96−1.86 (m, 2H), 1.81−1.68 (m, 3H), 1.65, 1.53 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.8 (q, *J* = 34.5 Hz), 157.4, 144.0, 143.9, 140.5, 140.0 136.1, 132.5, 131.4, 131.3, 127.7, 127.6, 126.3, 126.2, 115.5 (q, *J* = 290.4 Hz), 114.0, 67.2, 55.6, 39.0, 34.8, 31.4, 28.6, 24.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.0 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{35}H_{32}BrF_3O_2$ $[M]^+$ 620.1538 found 620.1537.



Synthesis of ethyl 3-(2-(2,2,2-trifluoroacetyl)cyclopropyl)propyl benzoate (9a)

To a solution of 4-bromo-8,8,8-trifluoro-7-oxooctyl benzoate (**4a**) (30.0 mg, 0.08 mmol) in DMF (500 μL) was added Cs_2CO_3 (30.9 mg, 1.2 equiv.). The mixture was stirred at room temperature for 10 h before quenching with H_2O. The crude mixture was extracted with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography and eluted with hexane−AcOEt (2:1), affording the title compound as colorless oil (18.9 mg, 80% yield, dr = 1:1).

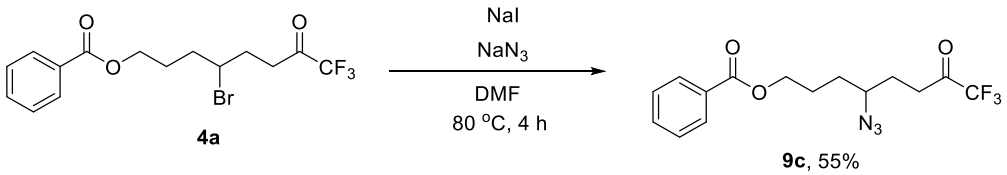
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05−8.03 (m, 2H), 7.59−7.55 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.36 (t, *J* = 6.4 Hz, 1H), 4.33 (t, *J* = 6.2 Hz, 1H), 2.45−2.42 (m, 1/2H), 2.12−2.05 (m, 1/2H), 1.94−1.70 (m, 3H), 1.65−1.55 (m, 2H), 1.44−1.36 (m, 3/2H), 1.20−1.16 (m, 1/2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.9 (q, *J* = 35.5 Hz), 189.8 (q, *J* = 34.5 Hz), 166.6, 166.5, 133.0, 132.9, 130.2, 130.1, 129.5, 129.5, 128.4, 128.3, 115.8 (q, *J* = 289.4 Hz), 115.7 (q, *J* = 290.4 Hz), 64.1, 29.7, 29.6, 29.0, 28.4, 28.1, 23.6, 22.5, 21.3, 20.8, 17.7; ^{19}F NMR (376 MHz, $CDCl_3$): −78.6 (s, 3/2F), −78.6 (s, 3/2F); HRMS (FAB) *m/z* Calcd for $C_{15}H_{16}F_3O_3$ $[M+H]^+$ 301.1052 found 301.1052.



Synthesis of 3-(5-hydroxy-5-(trifluoromethyl)-1,2,3,4,5,6-hexahydrobenzo[b][1,4]diazocin-2-yl)propyl benzoate (9b)

To a solution of 4-bromo-8,8,8-trifluoro-7-oxooctyl benzoate (**4a**) (57.0 mg, 0.15 mmol) in EtOH (2.0 mL) was added 1,2-phenylenediamine (32.4 mg, 2.0 equiv.). The mixture was stirred at 80 °C for 20 h before quenching with H_2O. The crude mixture was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography and eluted with hexane−AcOEt (1:1), affording the title compound as brown oil (40.7 mg, 66% yield, dr = 1:1).

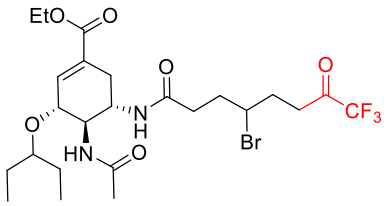
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 1.4, 8.2 Hz, 1H), 8.01 (dd, *J* = 1.2, 8.3 Hz, 1H), 7.60−7.56 (m, 2H), 7.49−7.44 (m, 2H), 6.83−6.68 (m, 3H), 6.63 (d, *J* = 7.3 Hz, 1H), 4.45−4.41 (m, 1H), 4.35−4.25 (m, 1H), 3.79−3.69 (m, 1/2H), 3.48−3.41 (m, 1/2H), 2.61−2.55 (m, 1/2H), 2.47−2.41 (m, 1/2H), 2.28−2.22 (m, 1/2H), 2.18−1.91 (m, 7/2H), 1.83−1.65 (m, 5/2H), 1.39−1.27 (m, 1/2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.6, 166.5, 142.7, 142.7, 140.3, 137.5, 133.0, 132.9, 130.3, 130.1, 129.5, 128.3, 125.0 (q, *J* = 285.6 Hz), 124.7 (q, *J* = 282.7 Hz), 122.5, 122.4, 120.5, 120.0, 115.7, 112.6, 109.1, 109.0, 90.2 (q, *J* = 30.7 Hz), 89.4 (q, *J* = 29.7 Hz), 69.6, 64.8, 64.5, 64.2, 33.9, 33.0, 32.6, 30.7, 30.0, 26.5, 26.3, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$): −84.7 (s, 3/2F), −85.7 (s, 3/2F); HRMS (FAB) *m/z* Calcd for $C_{21}H_{23}F_3N_2O_3$ $[M]^+$ 408.1611 found 408.1659.



Synthesis of 4-azido-8,8,8-trifluoro-7-oxooctyl benzoate (9c)

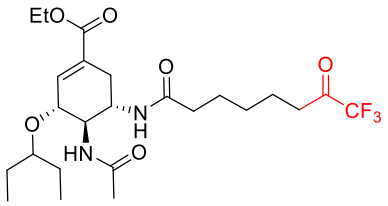
To a solution of 4-bromo-8,8,8-trifluoro-7-oxooctyl benzoate (**4a**) (38.1 mg, 0.10 mmol) in DMF (1.0 mL) was added NaI (3.0 mg, 20 mol%), and NaN_3 (13.0 mg, 2.0 equiv.). The mixture was stirred at 80 °C for 4 h before quenching with H_2O. The crude mixture was extracted with AcOEt, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography and eluted with hexane−AcOEt (2:1), affording the title compound as yellow oil (18.8 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.02 (m, 2H), 7.60−7.56 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 4.40−4.38 (m, 2H), 3.52−3.28 (m, 1H), 2.97−2.83 (m, 2H), 2.05−1.74 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.8 (q, *J* = 35.5 Hz), 166.5, 133.0, 130.0, 129.5, 128.4,115.4 (q, *J* = 290.4 Hz), 64.1, 61.0, 32.8, 31.0, 27.0, 25.3; ^{19}F NMR (376 MHz, $CDCl_3$): −79.1 (s, 3F), −85.9 (hydrate); HRMS (FAB) *m/z* Calcd for $C_{15}H_{27}F_3N_3O_3$ $[M+H]^+$ 344.1222 found 344.1222.



Synthesis of ethyl (3R,4R,5S)-4-acetamido-5-(4-bromo-8,8,8-trifluoro-7-oxooctanamido)-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate (10): The GP was followed with ethyl (3R,4R,5S)-4-acetamido-5-(pent-4-enamido)-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate (78.9 mg, 0.20 mmol), bromotrifluoroacetone (46.2 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%) and MeCN/$CHCl_3$ (3:1, 400 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with AcOEt. This afforded the title compound as yellow oil (36.2 mg, 31% yield, dr = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (br.t, *J* = 8.2 Hz, 1H), 6.78 (s, 1H), 6.22 (br. s, 1H), 4.24−4.16 (m, 2H), 4.15−4.03 (m, 3H), 3.41−3.35 (m, 1H), 3.09−2.93 (m, 2H), 2.77−2.73 (m, 1H), 2.47−2.03 (m, 7H), 2.00 (s, 3/2H), 1.95 (s, 3/2H), 1.55−1.45 (m, 4H), 1.31−1.25 (m, 3H), 0.92−0.83 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 190.6 (q, *J* = 35.5 Hz), 172.1, 172.0, 171.6, 171.6, 165.9, 138.6, 137.1, 137.0, 129.3, 129.3, 127.1, 115.4 (q, *J* = 290.4 Hz), 82.1, 82.1, 75.3, 75.3, 61.1, 61.0, 54.5, 54.9, 53.9, 53.8, 48.3, 34.7, 34.7, 34.6, 34.5, 34.2, 34.0, 31.5, 30.3, 26.2, 25.7, 23.3, 23.3, 14.1, 9.49, 9.20; ^{19}F NMR (376 MHz, $CDCl_3$): −79.0 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{24}H_{37}BrF_3N_2O_6$ $[M+H]^+$ 585.1787 found 585.1786.

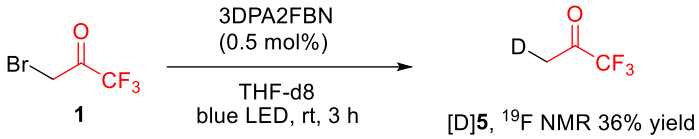


Synthesis of ethyl (3R,4R,5S)-4-acetamido-3-(pentan-3-yloxy)-5-(8,8,8-trifluoro-7-oxooctanamido)cyclohex-1-ene-1-carboxylate (11): To a solution of oseltamivir phosphate (41.0 mg, 0.10 mmol) and 8,8,8-trifluoro-7-oxooctanoic acid (**3i**) (21.2 mg, 0.10 mmol) in DMF (1.5 mL) was added TBTU (46.4 mg, 0.15 mmol), and iPr_2NEt (52.4 μL, 0.30 mmol). The mixture was stirred at room temperature for 2 d. The reaction mixture was evaporated in vacuo. The residue was purified by column chromatography on SiO_2 gel, affording the title compound as yellow oil (31.4 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 1H), 6.73 (d, *J* = 6.8 Hz, 1H), 6.27 (d, *J* = 6.8 Hz, 1H), 4.22−4.17 (m, 2H), 4.14−4.02 (m, 3H), 3.40−3.35 (m, 1H), 2.81−2.71 (m, 3H), 2.33−2.27 (m, 1H), 2.19−2.12 (m, 2H), 1.97 (s, 3H), 1.70−1.60 (m, 4H), 1.54−1.46 (m, 4H), 1.38−1.33 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.92−0.86 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 191.4 (q, *J* = 34.5 Hz), 173.2, 171.5, 165.9, 137.2, 129.2, 115.5 (q, *J* = 290.4 Hz), 82.1, 75.4, 61.0, 53.9, 48.4, 36.2, 36.0, 36.0, 30.5, 28.2, 26.2, 25.7, 25.2, 23.2, 22.0, 14.1, 9.49, 9.18; ^{19}F NMR (376 MHz, $CDCl_3$): −79.2 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{24}H_{38}F_3N_2O_6$ $[M+H]^+$ 506.2682 found 506.2681.

4. Control experiments

4-1. Deuteration of bromotrifluoroacetone (1) with THF-d8 as solvent



A 4 mL vial with a magnetic stirring bar was charged with 3DPA2FBN (1.9 mg, 1 mol%), and THF-d8 (500 μL) Bromotrifluoroacetone (**1**) (31.0 μL, 0.30 mmol) was added to the solution. The resulting mixture was stirred at room temperature under blue LED irradiation (470 nm) for 3 h. The reaction mixture is analyzed by ^{1}H, and ^{13}C NMR (Figure S1). Yield of [D]**5** is 36%, which is determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard (Figure S2).

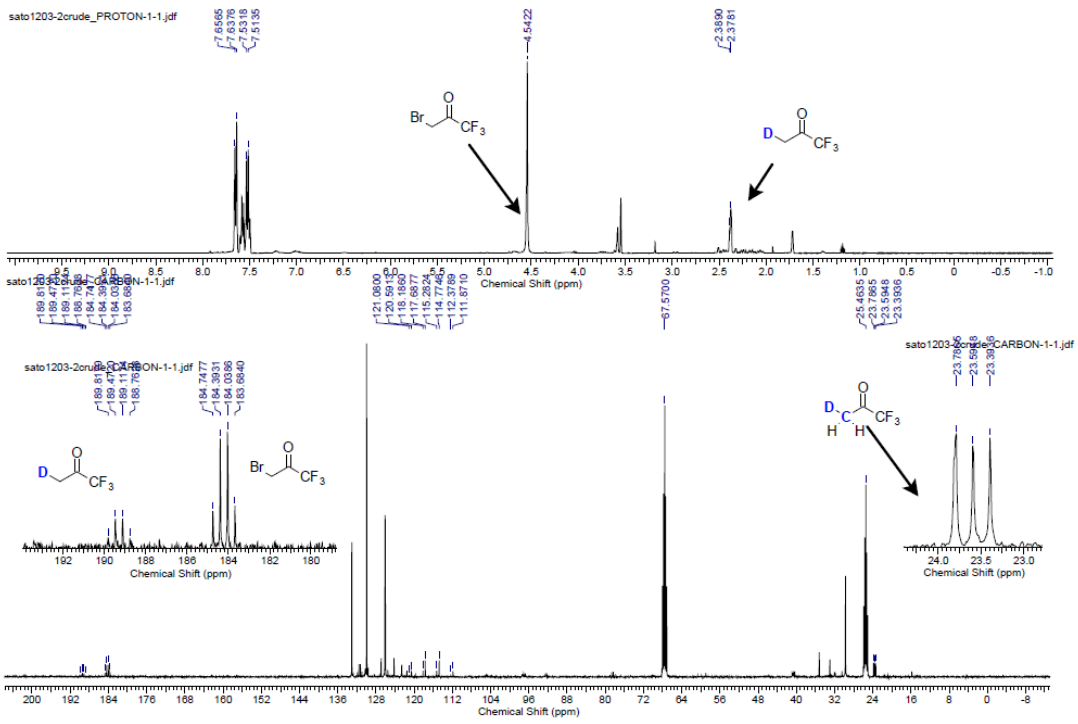


Figure S1. ^{1}H and ^{13}C NMR spectrum of the reaction mixture of the reaction (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, THF-d8).

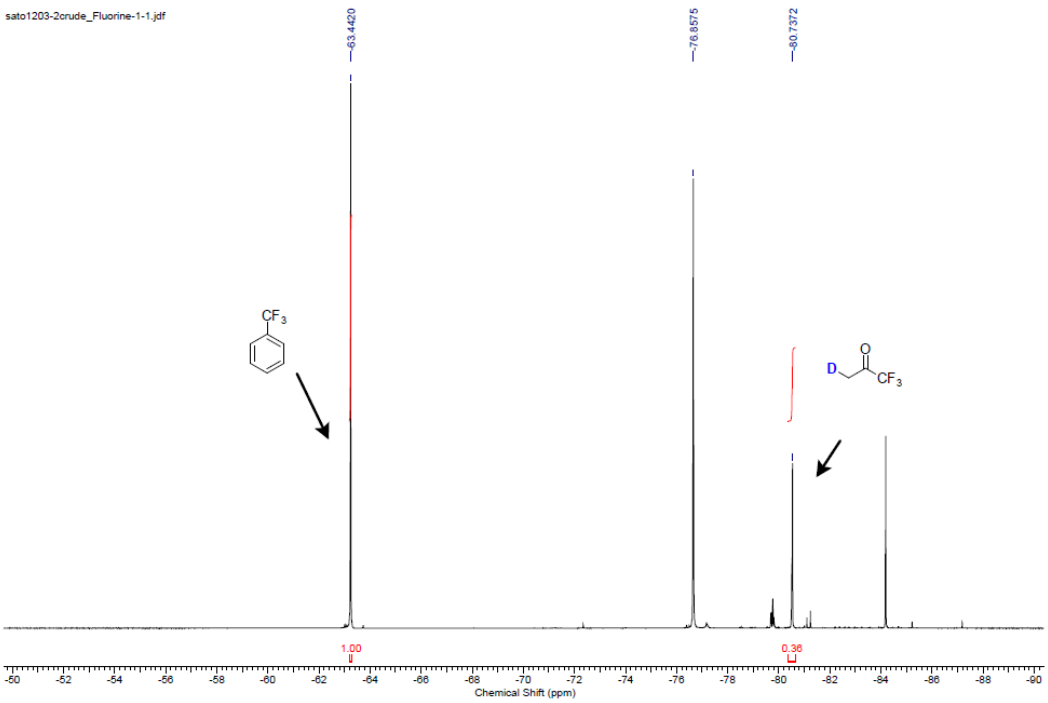
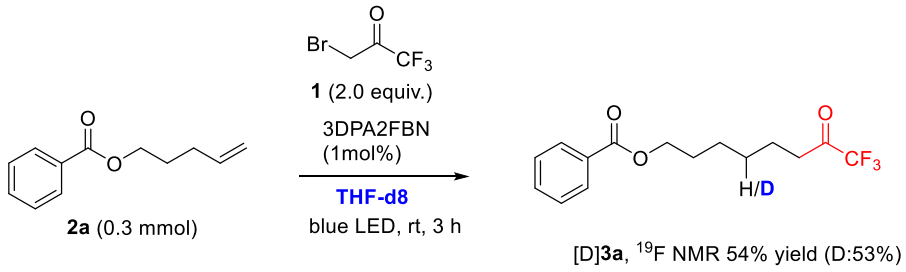


Figure S2. ^{19}F NMR spectra of the crude mixture involving [D]**5** (376 MHz, THF-d8).

4-2. Kinetic isotope effect



A 4 mL vial with a magnetic stirring bar was charged with 3DPA2FBN (1.9 mg, 1 mol%). pent-4-en-1-yl benzoate (57.1 mg, 0.30 mmol), and THF-d8 (500 μL) was added. Finally, bromotrifluoroacetone (62.0 μL, 0.60 mmol) was introduced to the reaction mixture. The resulting mixture was stirred at room temperature under blue LED irradiation (470 nm) for 3 h. The reaction mixture was analyzed by ^{19}F NMR to determine yield of **3a** using benzotrifluoride as an internal standard (54% yield) as shown in Figure S3. The reaction mixture was evaporated in vacuo, and the residue was purified by column chromatography on SiO_2 gel, isolating **3a** (18.9 mg, 21% yield, D:53%). ^{1}H NMR spectrum should reflect a H/D ratio of hydrogens (Figure S4).

For [D]**3a**: HRMS (FAB) *m/z* Calcd for $C_{15}H_{16}DF_3O_3$ $[M]^+$ 303.1193 found 303.1193.

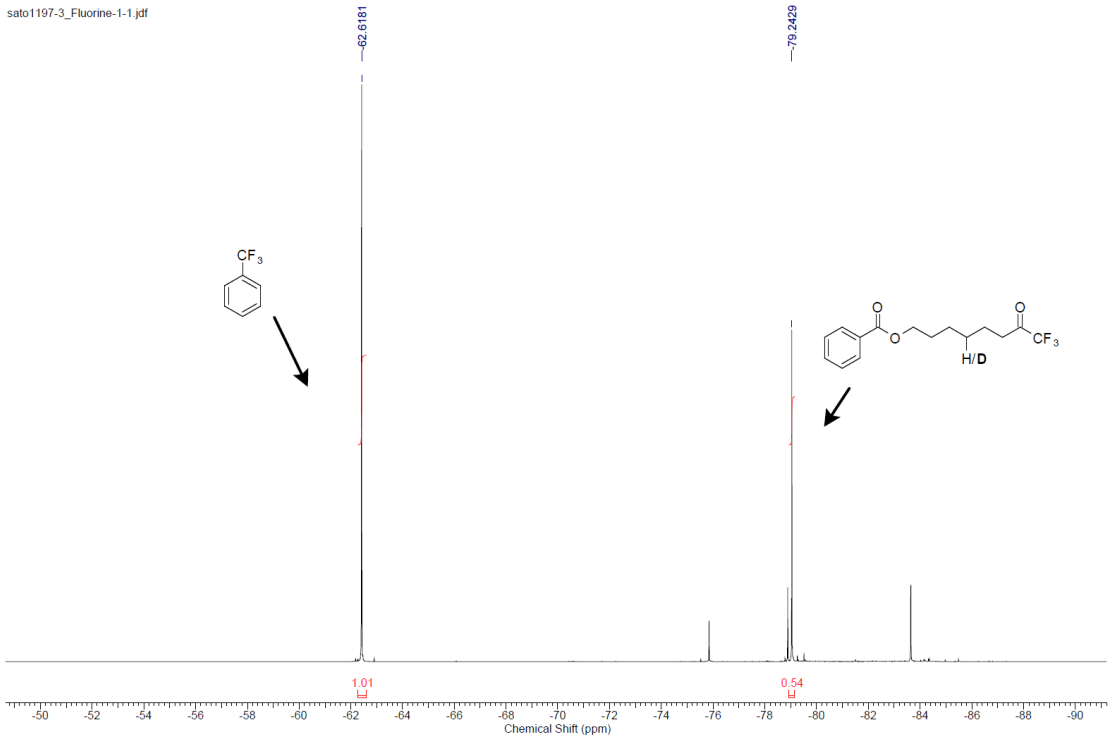


Figure S3. ^{19}F NMR spectra of the crude mixture of the reaction (376 MHz, THF-d8).

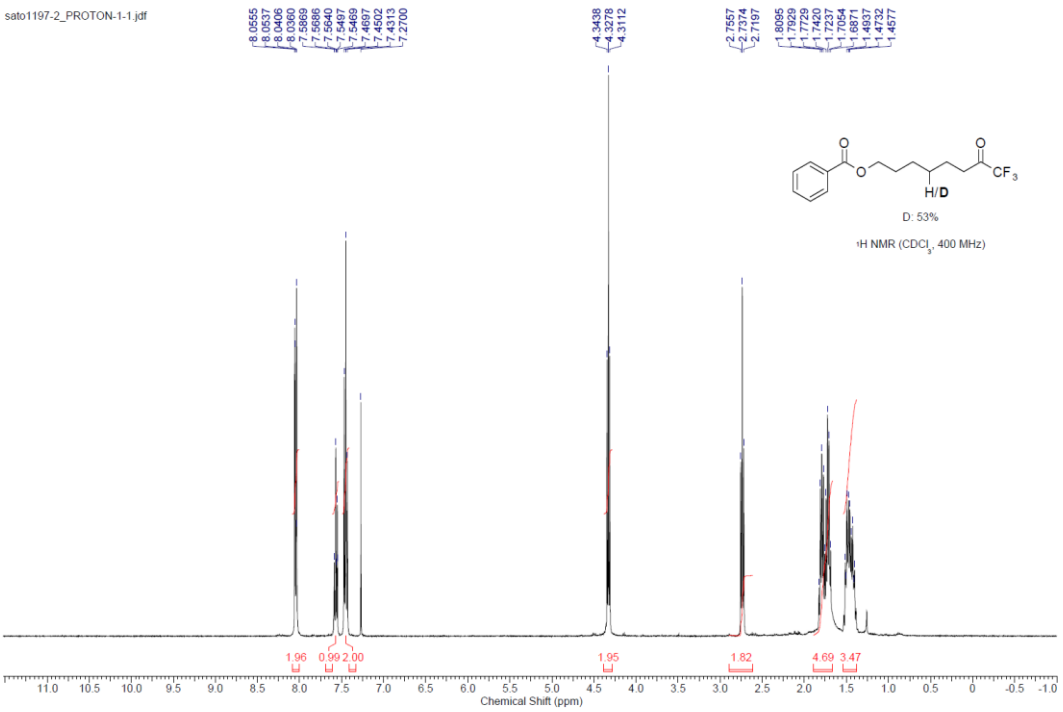


Figure S4. ^{1}H NMR spectra of [D]**3a** (D: 53%) (400 MHz, $CDCl_3$).

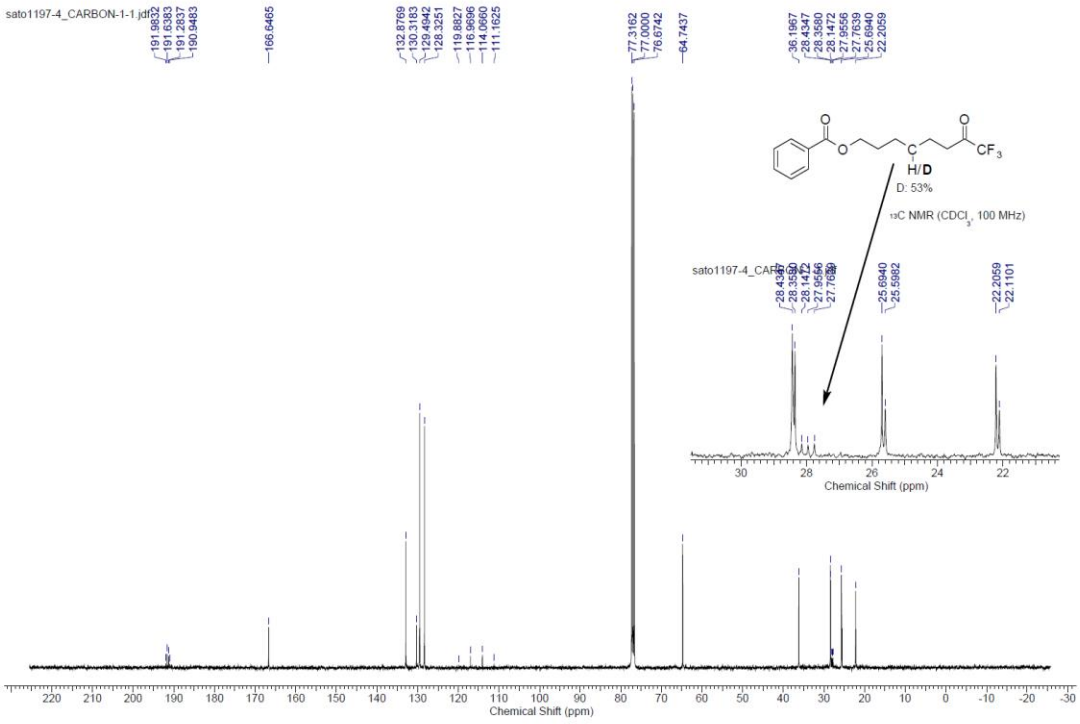


Figure S5. ^{13}C NMR spectra of [D]**3a** (D: 53%) (100 MHz, $CDCl_3$).

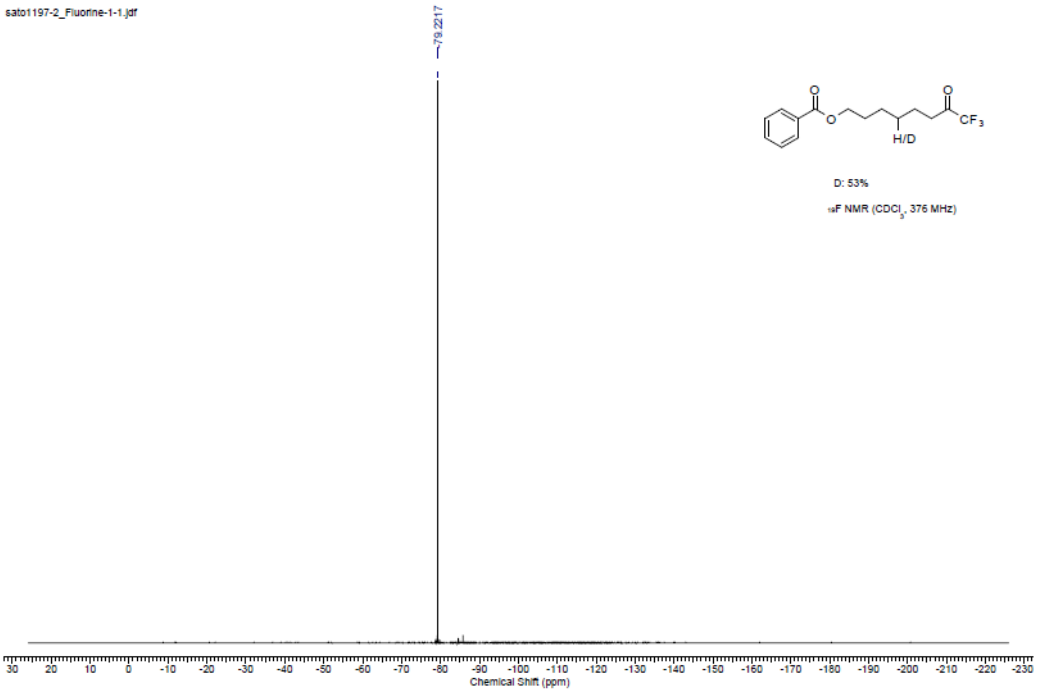
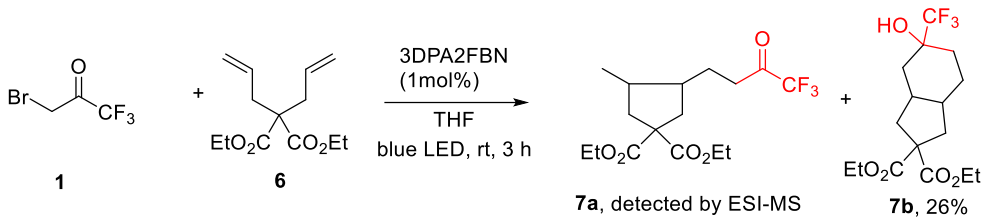


Figure S6. ^{19}F NMR spectra of [D]**3a** (D: 53%) (376 MHz, $CDCl_3$).

4-3. Cascade reactions of cross-coupling between diethyl 2,2-diallylmalonate (6) and 1/cyclization



Synthesis of diethyl 3-methyl-4-(4,4,4-trifluoro-3-oxobutyl)cyclopentane-1,1-dicarboxylate (7a) and diethyl 5-hydroxy-5-(trifluoromethyl)octahydro-2H-indene-2,2-dicarboxylate (7b): The GP was followed with diethyl 2,2-diallylmalonate (72.1 mg, 0.30 mmol)), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 3DPA2FBN (1.9 mg, 1 mol%) and THF (500 μL). The reaction was irradiated with blue LEDs for 3 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded **7a** with an impurity (7.2 mg, <7% yield), and analyzed by ^{1}H, and ^{19}F NMR, and ESI-MS (Figure S7 and S8). Moreover, isomers of **7b** were isolated in 26% yield (27.2 mg, dr = 1 : 5.7).

For a major isomer of **7b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20−4.15 (m, 4H), 2.59−2.52 (m, 1H), 2.42−2.34 (m, 2H), 2.31−2.24 (m, 1H), 2.19 (dd, *J* = 2.8, 14.2 Hz, 1H), 2.03−1.57 (m, 7H), 1.26−1.22 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 173.1, 172.9, 126.3(q, *J* = 283.6 Hz), 72.7 (q, *J* = 26.8 Hz), 61.4, 58.8, 39.3, 38.0, 37.8, 36.3, 29.4, 29.2, 22.1, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): −84.3 (s, 3F); HRMS (FAB) *m/z* Calcd for $C_{16}H_{24}F_3O_5$ $[M+H]^+$ 353.1576 found 353.1575.

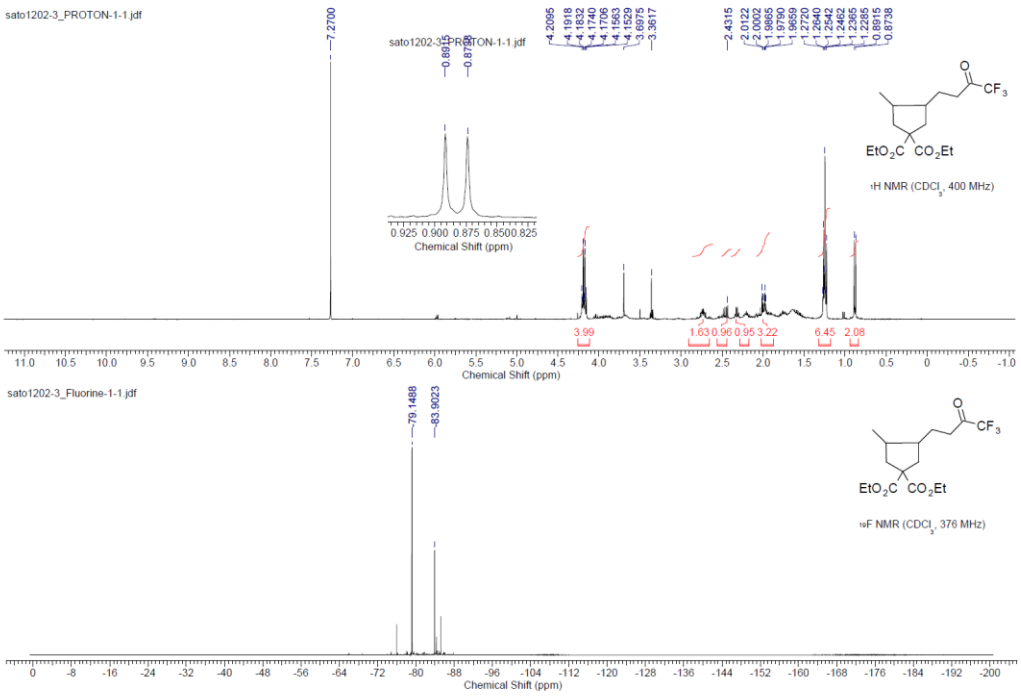


Figure S7. ^{1}H and ^{19}F NMR spectrum of **7a** with an impurity.

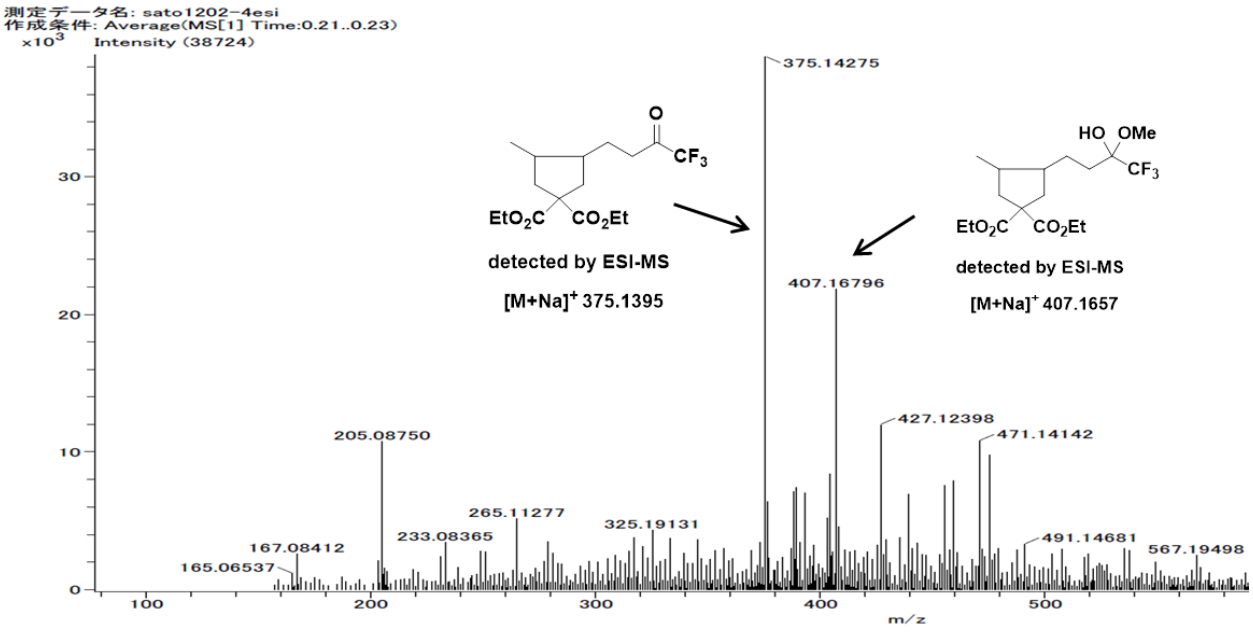
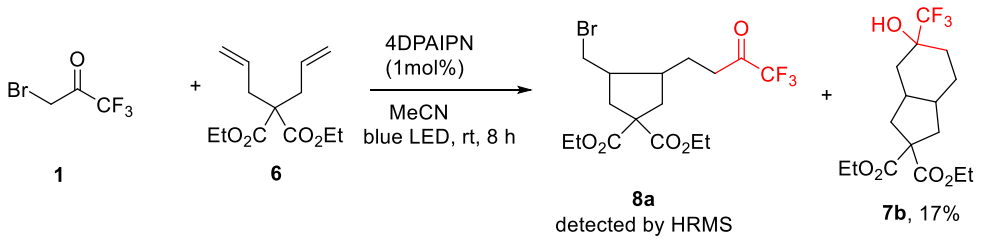


Figure S8. ES-MS spectra of **7a** with an impurity.



Synthesis of diethyl 3-(bromomethyl)-4-(4,4,4-trifluoro-3-oxobutyl)cyclopentane-1,1-dicarboxylate (8a) and diethyl 5-hydroxy-5-(trifluoromethyl)octahydro-2H-indene-2,2-dicarboxylate (7b)

The GP was followed with diethyl 2,2-diallylmalonate (72.1 mg, 0.30 mmol)), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (4.0 mg, 1 mol%) and MeCN (850 μL). The reaction was irradiated with blue LEDs for 8 h. The crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded **8a** with the impurity (9.0 mg, <7% yield), and analyzed by ^{1}H, and ^{19}F NMR (Figure S9) and HRMS. Moreover, isomers of **7b** were isolated in 17% yield (18.0 mg).

For **8a**: HRMS (FAB) *m/z* Calcd for $C_{16}H_{23}BrF_3O_5$ $[M+H]^+$ 431.0681 found 431.0681.

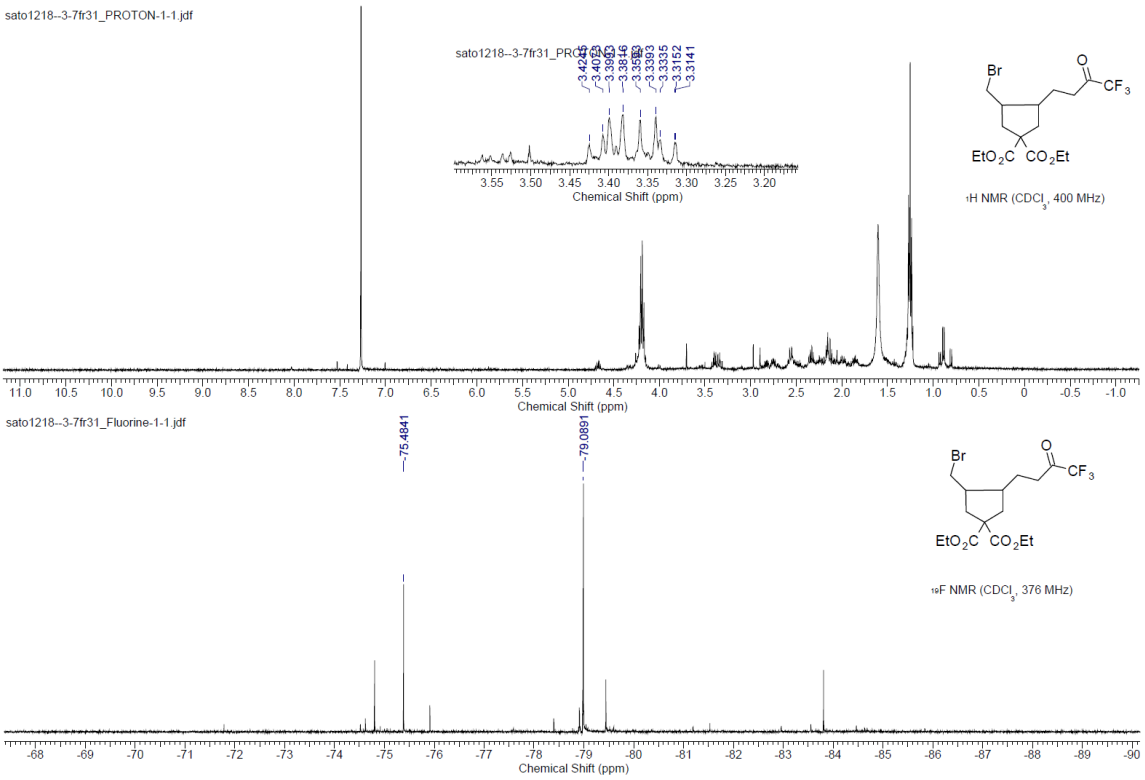


Figure S9. ^{1}H and ^{19}F NMR spectrum of **8a** with an impurity.

5. Cyclic Voltammetric Studies

Tetraethyl ammonium tetrafluoroborate (434 mg) as supporting electrolyte was dissolved in 20 mL anhydrous acetonitrile (0.1 M). The solvent was degassed with N_2 prior measurement. For each measurement 2.0 mL and the analyte were added to the cyclovoltammetric cell and experiments were purged with inert gas. Cyclic voltammetry measurements were performed with an ALS electrochemical analyzer (model 611E) equipped with platinum as the working electrode, Ag as the counter electrode, and $Ag/AgNO_3$ as the reference electrode. Scan rate was set to 0.1 V/s/.

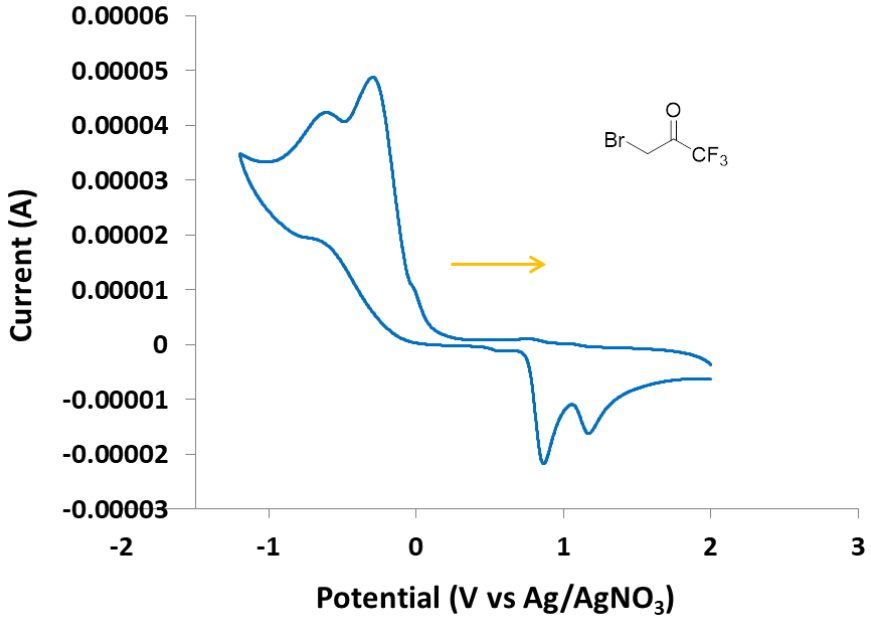


Figure S10. Cyclovoltammograms of bromotrifluoromethyl acetone (10 mM) in MeCN (0.1 M Et_4NBF_4). Measured in positive direction first.

$^{1}Ep^{red} = -0.30$ V Ag/$AgNO_3$

$^{2}Ep^{red} = -0.61$ V Ag/$AgNO_3$

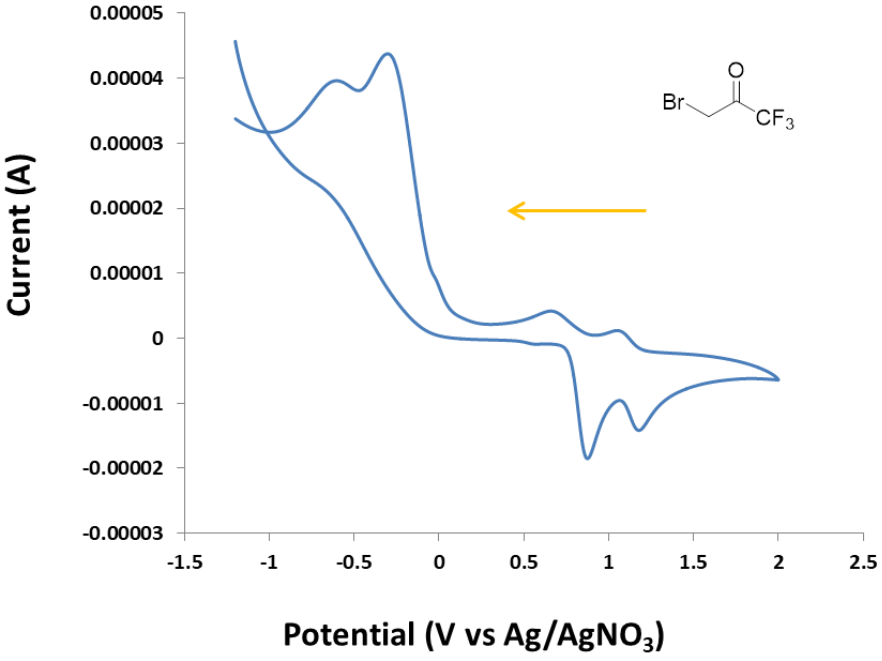


Figure S11. Cyclovoltammograms of bromotrifluoromethyl acetone (10 mM) in MeCN (0.1 M Et_4NBF_4). Measured in negative direction first.

$Ep^{ox} = 0.73$ V Ag/$AgNO_3$

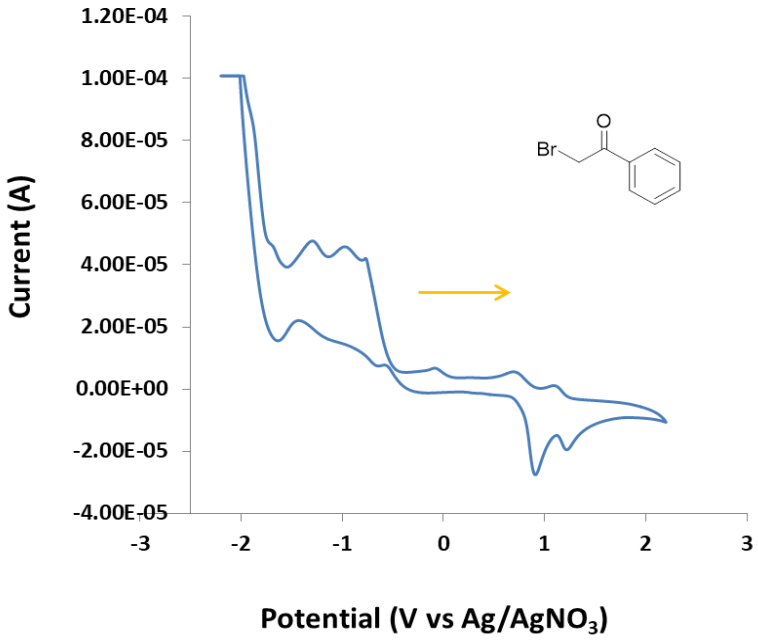


Figure S12. Cyclovoltammograms of phenacyl bromide (10 mM) in MeCN (0.1 M Et_4NBF_4). Measured in positive direction first.

$^{1}Ep^{red} = -0.95$ V Ag/$AgNO_3$

$^{2}Ep^{red} = -1.28$ V Ag/$AgNO_3$

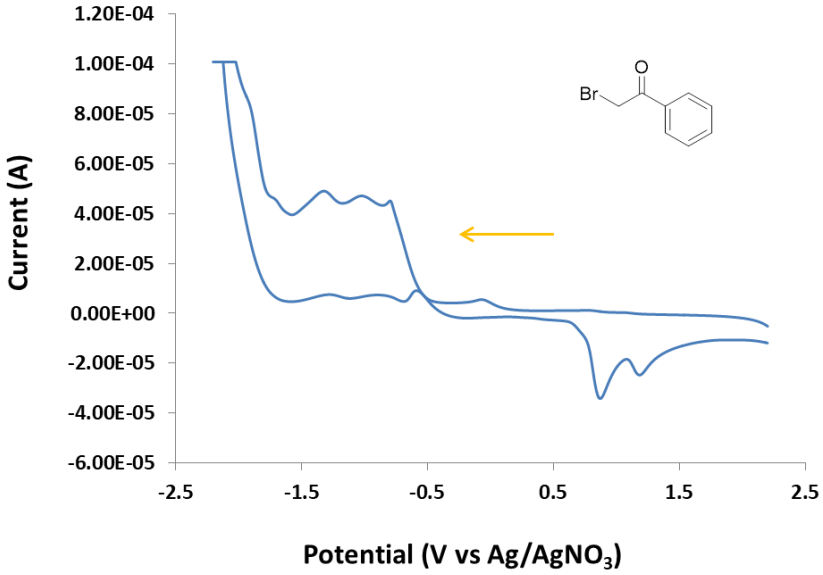


Figure S13. Cyclovoltammograms of phenacyl bromide (10 mM) in MeCN (0.1 M Et_4NBF_4). Measured in negative direction first.

$Ep^{ox} = 0.87$ V Ag/$AgNO_3$

6. Stern-Volmer Quenching Experiments

Stern-Volmer quenching experiments were carried out in a quartz cuvette (d = 10 mm) monitoring the emission intensity of solution of photocatalyst (20 μM) against concentrations of bromotrifluoroacetone (**1**) and alkene **2a**.

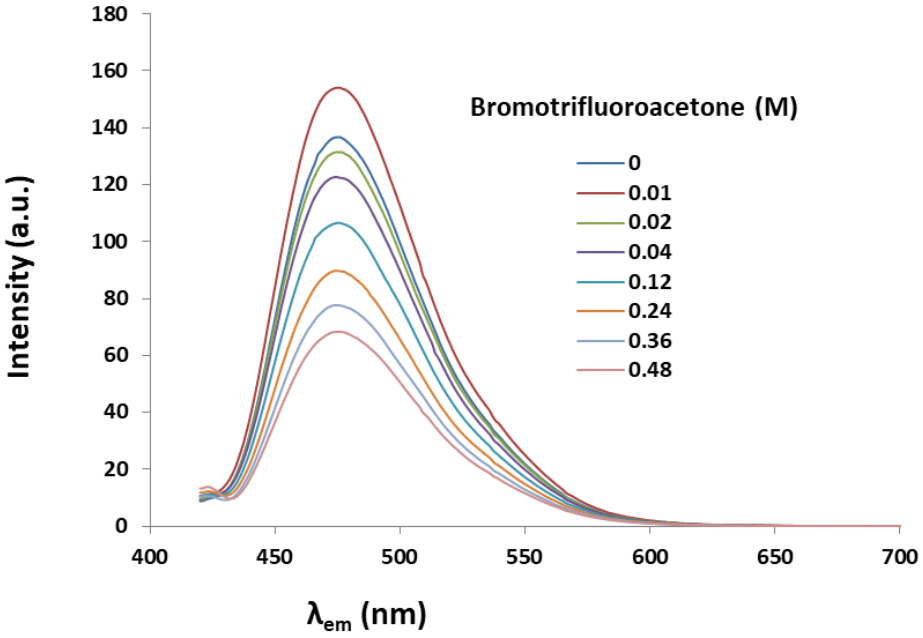


Figure S14. Emission quenching of 3DPA2FBN with bromotrifluoroacetone (**1**) in THF (λex = 420 nm, λem = 420-700 nm).

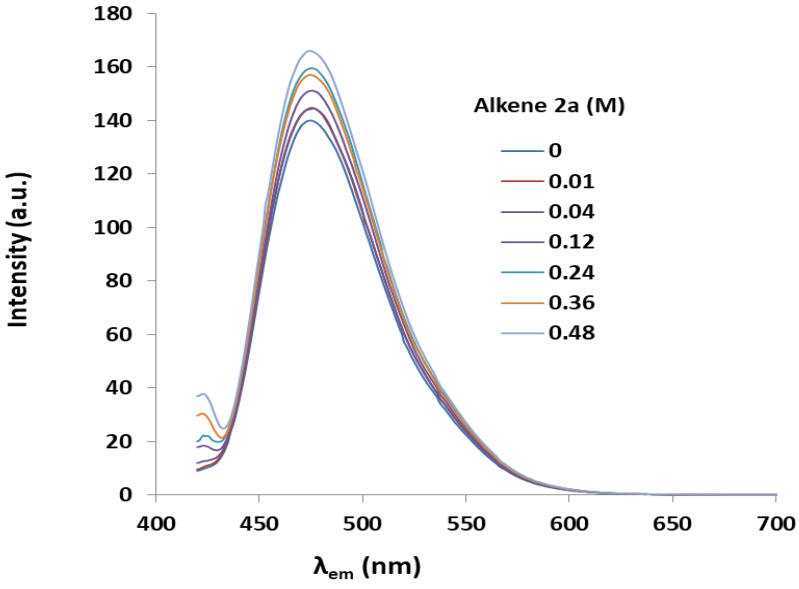


Figure S15. Emission quenching of 3DPA2FBN with alkene **2a** in THF (λex = 420 nm, λem = 420-700 nm).

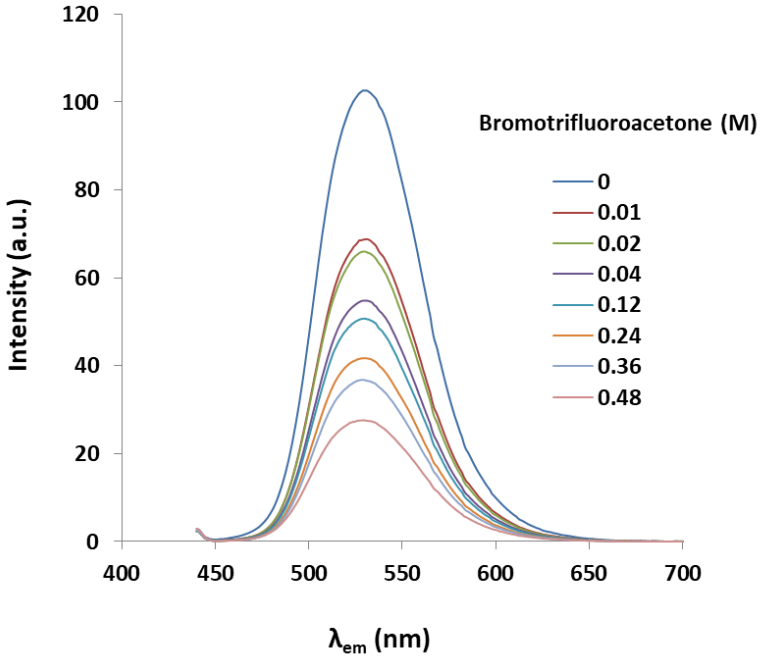


Figure S16. Emission quenching of 4DPAIPN with bromotrifluoroacetone (**1**) in MeCN (λex = 430 nm, λem = 440-700 nm).

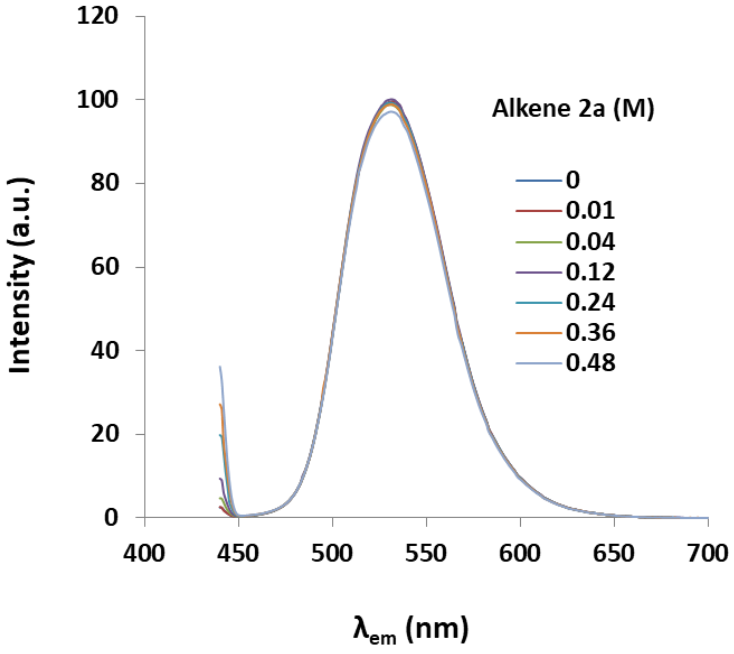


Figure S17. Emission quenching of 4DPAIPN with alkene **2a** in MeCN (λex = 430 nm, λem = 440-700 nm).

20 μM stock solution of photocatalyst was prepared. For the validation experimetns, the microplate used was a 96-well quartz microplate (Bio Medical Science Inc., BC-MGPL-96S). For each

measurement of solution (200 μL) and the conentrations of bromotrifluoroacetone (**1**) and alkene **2a** were added to the 96-well quartz microplate. Stern-Volmer measurements were performed with an plate reader (BioTek. Inc., Cytation3)

Plate data analysis

	Full Plate								
	Filter Set 1								
	Excitation: 420, Emission: 470								
	Optics: Top, Gain: 75								
	Light Source: Xenon Flash, Lamp Energy: High								
	Read Speed: Normal, Delay: 100 msec, Measurements/Data Point: 10								
	Read Height: 8.25 mm								
Results									
	Actual Temperature:	20.5							
		bromotrifluoroacetone 1				alkene 2a			
Q (mM)		1	2	3	4	5	6	7	8
0	A	53288	51977	51927	52656	51573	51534	49332	52605
20	B	53047	52525	54168	53670	53661	55924	53552	56732
40	C	52424	52064	54494	53752	54735	55363	54261	56439
120	D	53009	52477	53153	54750	56563	56545	55993	58675
240	E	50376	50209	50690	50669	56169	56978	58319	58535
360	F	47650	45827	45552	47281	56892	57464	59180	61360
480	G	44396	43806	42493	42205	59451	59197	60819	63339

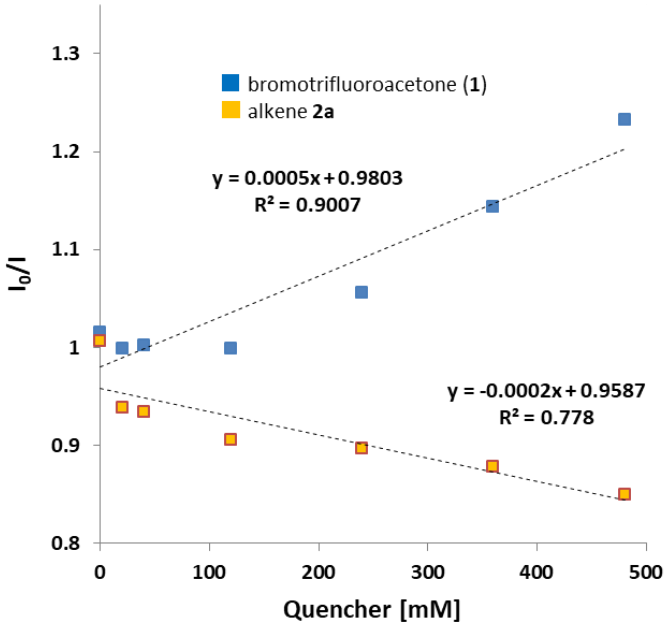


Figure S18. Fluorescence quenching of 20 μM 3DPA2FBN by bromotrifluoroacetone (**1**), and alkene **2a** with a Stern–Volmer plot (λex = 420 nm, λem = 470 nm).

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Plate data analysis

Plate Type	96 WELL PLATE									
Read	Fluorescence Endpoint									
	Full Plate									
	Filter Set 1									
	Excitation: 430, Emission: 530									
	Optics: Top, Gain: 75									
	Light Source: Xenon Flash, Lamp Energy: High									
	Read Speed: Normal, Delay: 100 msec, Measurements/Data Point: 10									
	Read Height: 9.5 mm									
Results										
	Actual Temperatur	19.6								
		bromotrifluoroacetone					alkene			
Q (mM)		1	2	3	4	Q (mM)	6	7	8	9
0	A	57988	58395	59322	56194	0	64152	63503	62050	64850
2	B	30706	37267	38227	34546	20	62977	63255	61529	63380
4	C	27568	30165	31442	30010	40	62306	61482	59672	63981
12	D	26735	28243	25016	27552	120	61144	60579	59761	60605
24	E	24323	26853	27940	26223	240	57436	58838	55478	57291
36	F	22047	23507	23535	23436	360	55654	55291	54152	56146
48	G	20926	23734	22498	21605	480	54962	53851	54588	54948

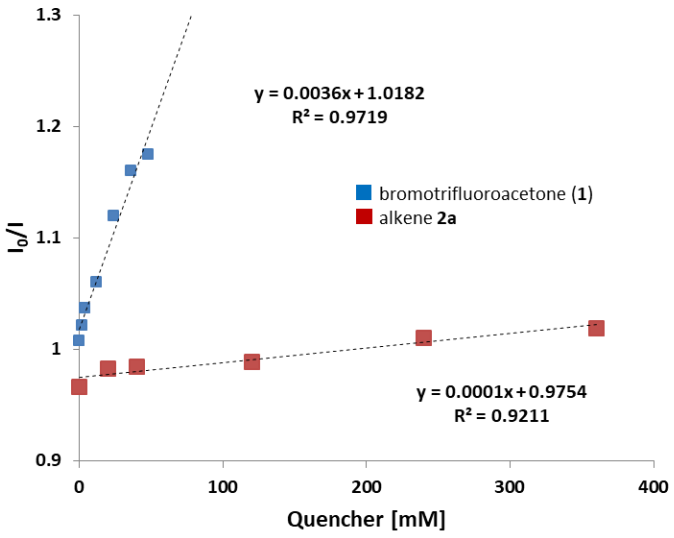


Figure S19. Fluorescence quenching of 20 μM 4DPAIPN by bromotrifluoroacetone (**1**), and alkene **2a**, with a Stern–Volmer plot (λex = 430 nm, λem = 530 nm).

7. Biological data of anti-influenza A virus activity of 2ac, 10, 11 and oseltamivir phosphate

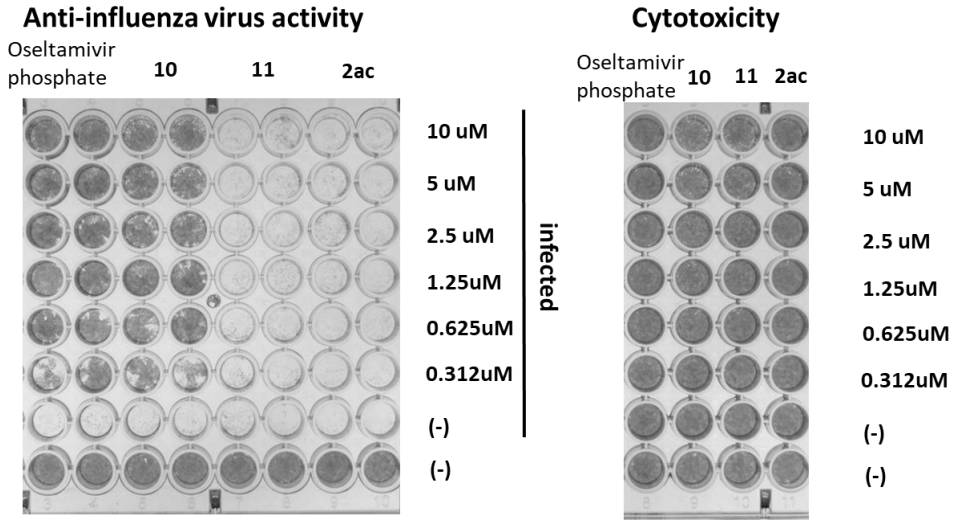
A virus (A/WSN/33) was propagated in MDCK cells at 37°C. Culture supernatants were harvested and stored at -80°C. Compounds **2ac**, and **10** were dissolved in DMSO to a stock concentration of 10 mM and stored at -20°C until use. MDCK cells (3×10^4 cells/well) were seeded in 96-well tissue culture plates and incubated for 24 h at 37°C. Compounds were serially diluted with MEM vitamin (MEM containing 1% of 100× MEM vitamin, Invitrogen, Carlsbad, CA). The cells were washed with FBS free MEM, and 100 µL of serially diluted compounds were added to the cells followed by addition of 100 µL of virus solution (1000 $TCID_{50}$ /mL in MEM vitamin). Oseltamivir phosphate was used as a positive control. Cells were incubated at 37°C for 48 h before fixing with 70% EtOH and staining with 0.5% crystal violet (CV), as previously described.[10] The plates were washed and air dried at RT.

A. Plata data analysis

	anti-influenza activity (A/WSN/33 (H1N1)							
	2ac		**10**		**11**		**Oseltamivir phosphate**	
con. (uM)	Exp: 1 viability (%)	Exp: 2 viability (%)	Exp: 1 viability (%)	Exp: 2 viability (%)	Exp: 1 viability (%)	Exp: 2 viability (%)	Exp: 1 viability (%)	Exp: 2 viability (%)
0	−1.4147	−1.56467	0.41	0.09	0.00919	−0.0007	−0.43	1.29
0.31	0.39405	−1.40678	39.34188	16.45036	0.01464	0.01049	48.33417	26.44468
0.63	0.41827	−1.5173	70.13614	62.2379	0.02319	0.01124	80.70606	57.34337
1.25	1.15308	0.51157	90.13744	62.97998	0.01889	0.01754	79.14763	66.4772
2.5	2.02516	−1.12258	75.71583	74.97158	0.00879	0.00434	99.13699	83.68701
5	0.49095	0.306303	81.1421	67.85083	0.00914	0.01299	93.78725	103.0599
10	1.18538	33788	78.7867928	81.93445	0.02464	0.03439	86.59259	100.5258
no drug	0.63336	0.65209	0.62089	0.62214	0.63019	0.66754	0.60599	0.62214
no virus/drug	107.967	102.9572	96.7265	98.03114	101.773	105.397	97.865	98.22849
EC50 (uM)	0	0	0.39658205	0.51930437	0	0	0.32384768	0.530075

	2ac		**10**		**11**		**Oseltamivir phosphate**	
EC50 (uM) ±	**ND**		**0.46±0.09**		**ND**		**0.43±0.15**	
CC50 (uM)	**>10**		**>10**		**>10**		**>10**	

B. Images of plates with CV assays



C. Anti-influenza virus activity of inhibitors 2ac, 10, 11 and oseltamivir phosphate were plotted.

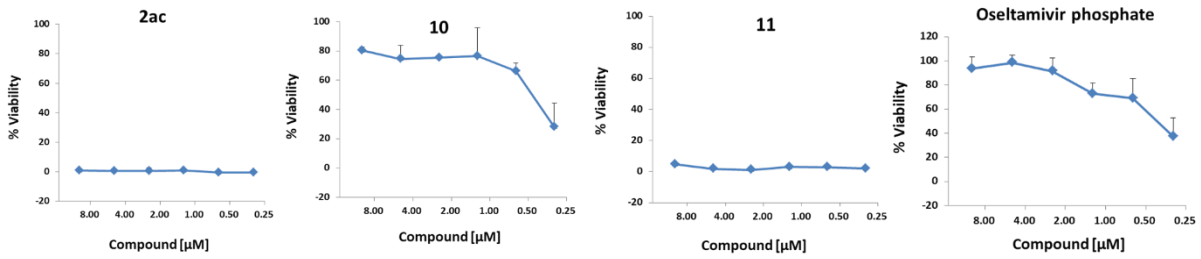


Figure S20. Influenza virus inhibitory activity and cytotoxicity of compounds **2ac**, **10**, **11** and oseltamivir phosphate. The potency was determined using CV assay by incubating MDCK cells infected with or without A/WSN/33 virus in the presence of varying concentrations of compounds **2ac**, **10** and **11**. At 48 h post-infection, the cells were fixed and stained with CV and relative OD values the cells were fixed and stained with CV and relative OD values (%) are expressed relative to the percentage of cells without infection. A: Plate data analysis. B: Images of plates with CV assays. C: Anti-influenza virus activity of inhibitors **2ac**, **10**, **11** and oseltamivir phosphate were plotted.

8. Docking studies

The three-dimensional structure of neuraminidase was extracted from an X-ray structure of the complex with an oseltamivir derivative (PDB-ID: 6HP0[11]). Missing hydrogen atoms were added to this structure, and the peptide chain was capped with -$COCH_3$ and -$NHCH_3$ at the N- and C-terminals, respectively, followed by a 100-step energy minimization using FF14SB force fields[12] with AmberTools22[13]. The resulting structure was used as a receptor in our docking simulation. The ligand structure was prepared by a quantum chemistry-based energy minimization at the B3LYP/6-31G(d, p) level of theory using Gaussian 16[14]. A cubic region of 30×30×30 Å, centered at the binding site of the oseltamivir derivative, was selected as the search region. AutoDock Vina[15] was used for our docking simulation, in which EXHAUSTIVENESS was set to 20 (Figure S21).

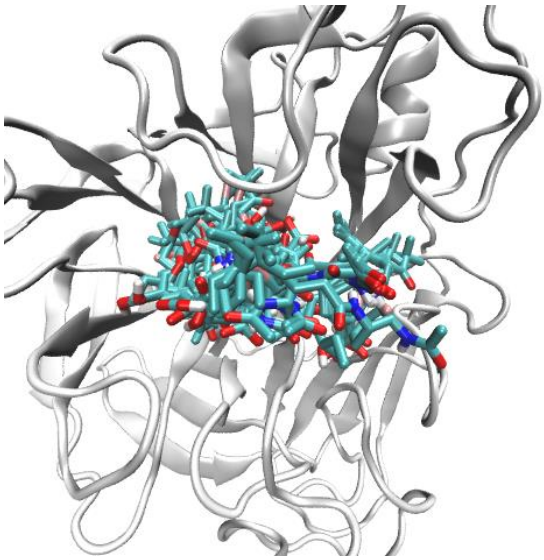
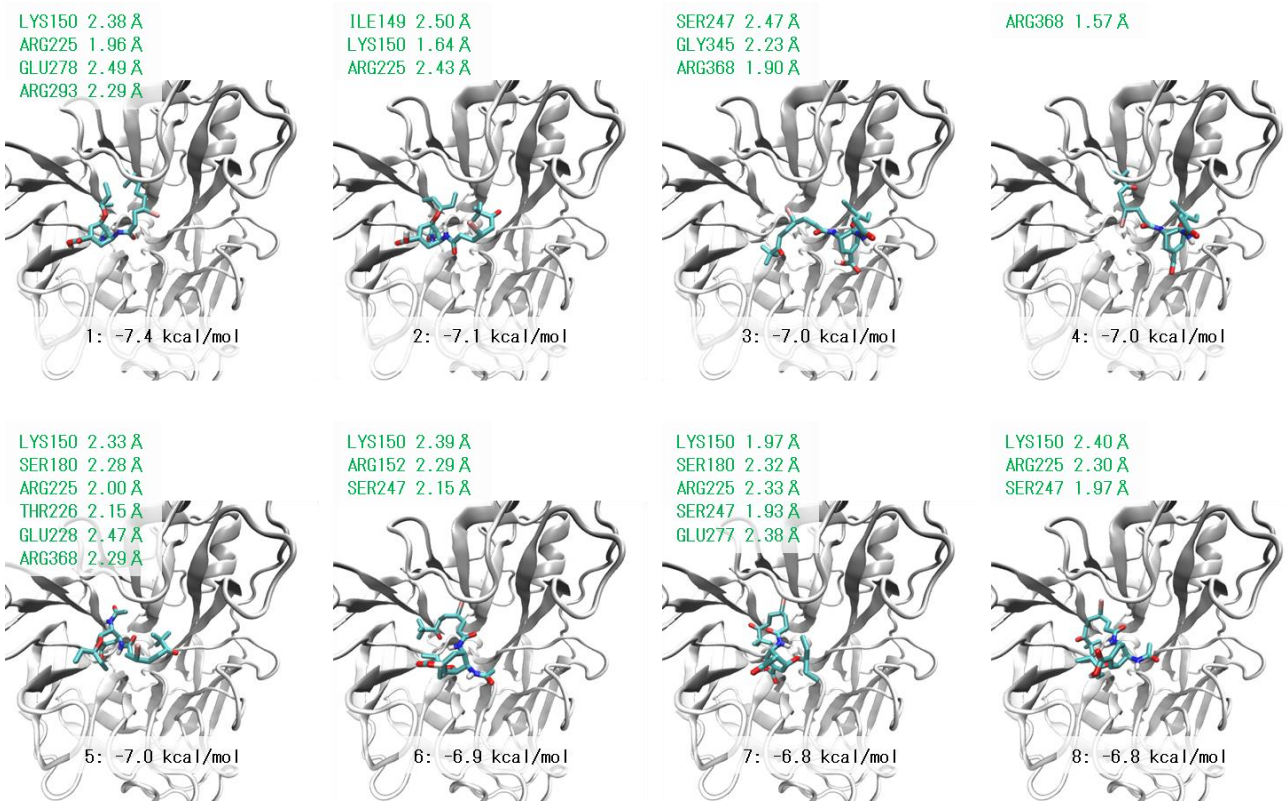


Figure S20. Docking simulation of neuraminidase influenza A virus with compound **10**.



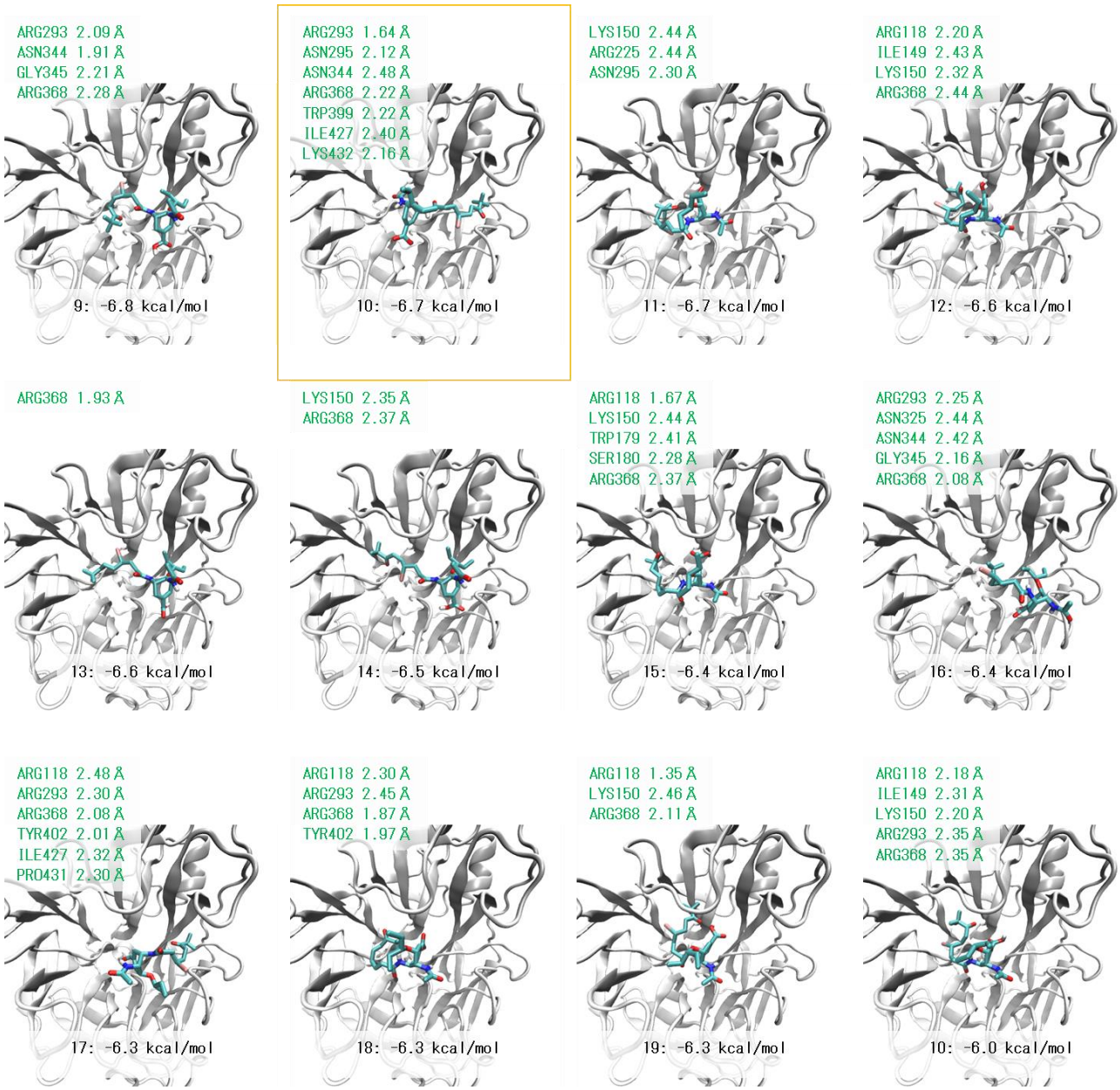


Figure S20. Docking structures of neuraminidase influenza A virus with 20 conformations of **10**.

Compound **10** sets to 20 conformations. These figures display the docking energy with neuraminidase and key amino acid residues within 2.5 Å from each **10** conformation. Among them, 10th conformer with -6.7 kcal/mol might be most reasonable because of interaction with various amino acid residues of neuraminidase; ARG293, ASN295, ASN344, ARG368, TRP399, ILE399, ILE427, and LYS432. We presume that a hydrogen bonding interaction between the acid moiety and Arg293 and a hydrophobic effect of the lipophilic trifluoromethyl group with a hydrophobic amino acid ILE427. In addition, an amino acid Lys432 may serve as a nucleophile to the TFMK moiety (Figure S21).

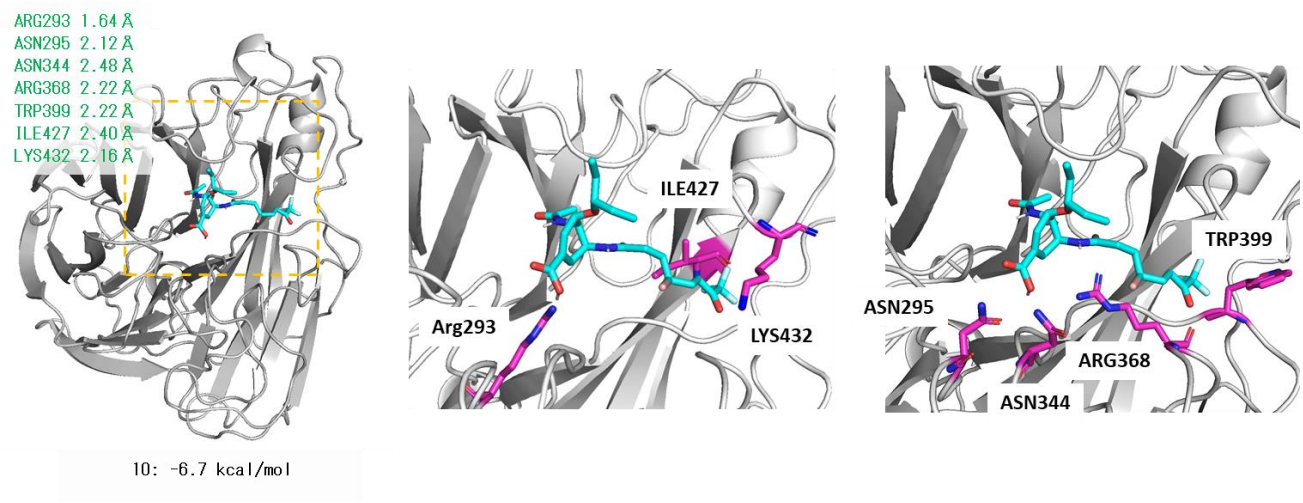


Figure S21. Docking structures of neuraminidase influenza A virus with 10th conformation of **10**.

9. References

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6. NMR spectra

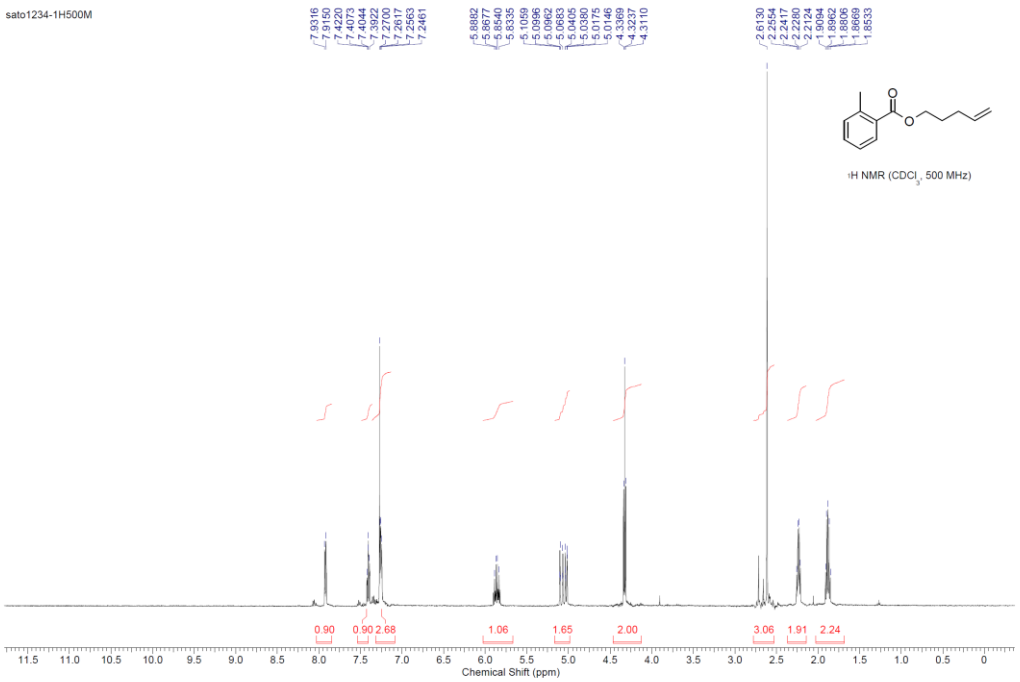

Figure S22. ^{1}H NMR of **2b** (500 MHz, $CDCl_3$)

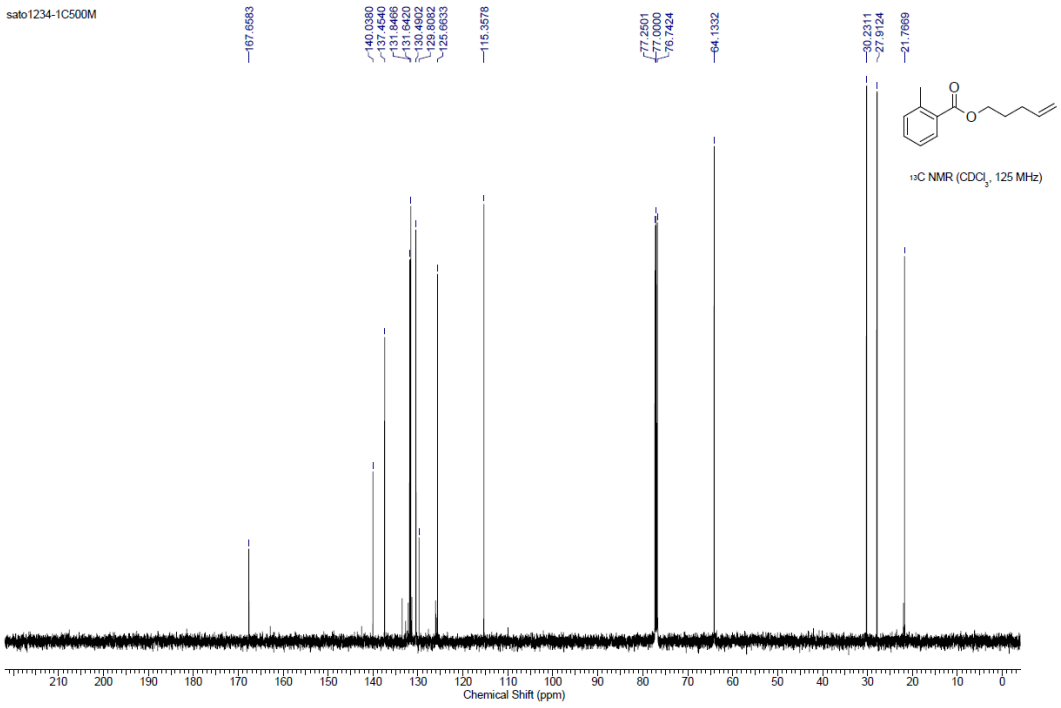

Figure S23. ^{13}C NMR of **2b** (125 MHz, $CDCl_3$)

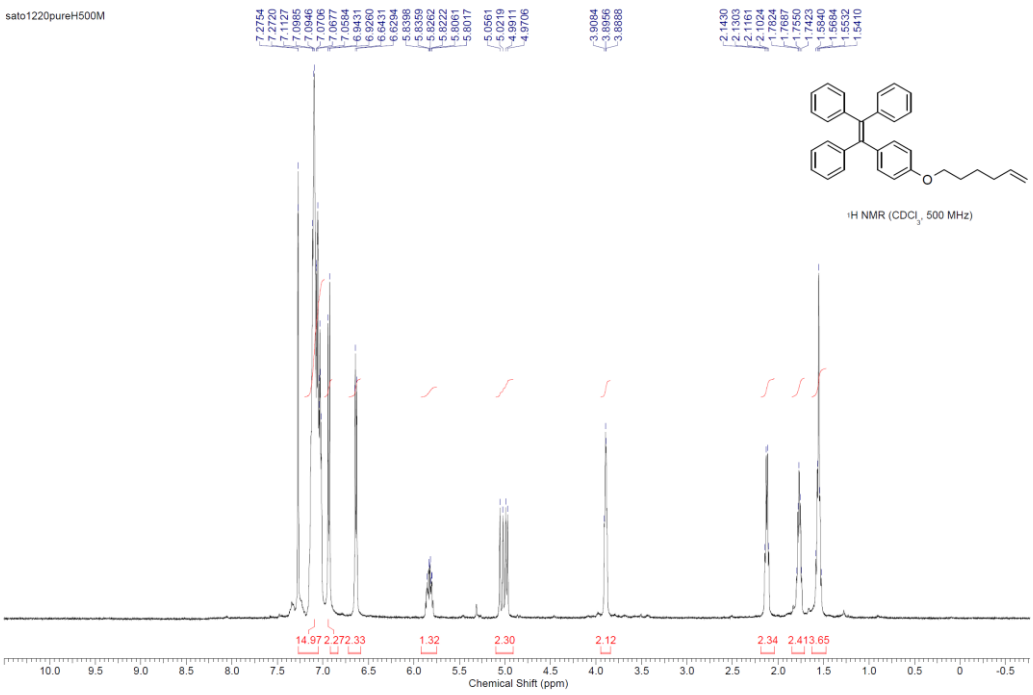

Figure S24. ^{1}H NMR of **2ab** (500 MHz, $CDCl_3$)

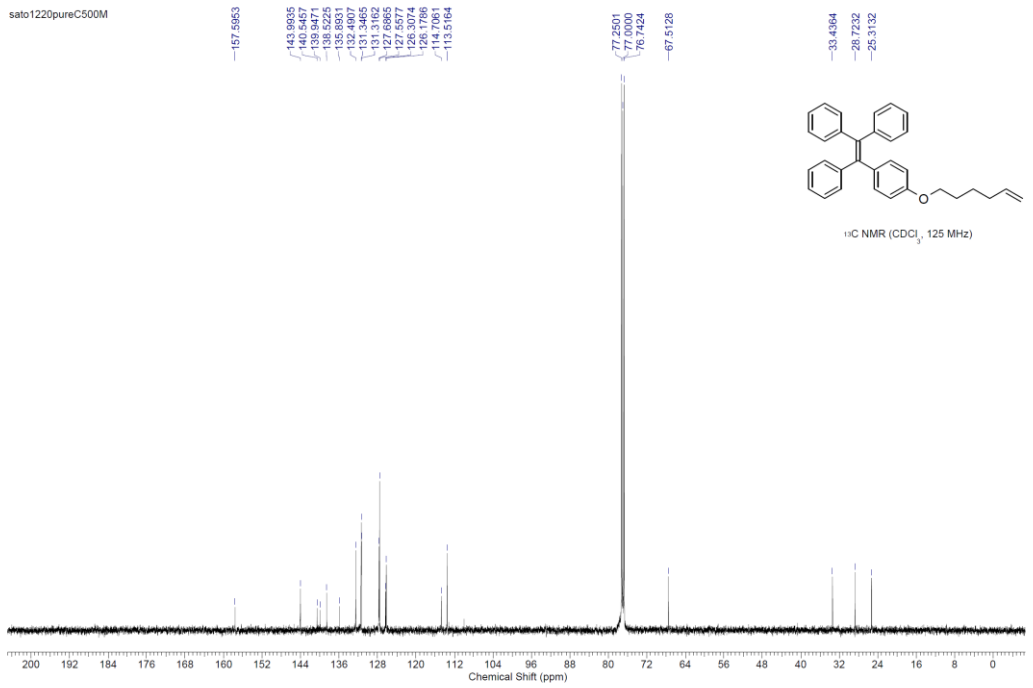

Figure S25. ^{13}C NMR of **2ab** (125 MHz, $CDCl_3$)

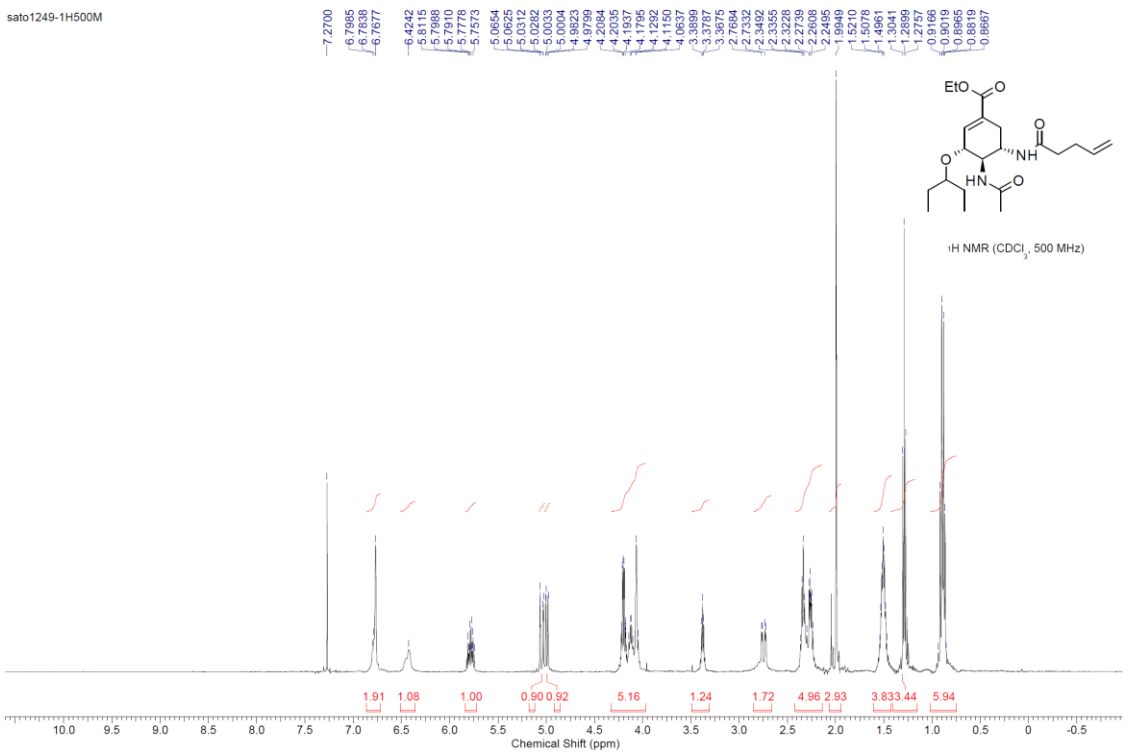

Figure S26. ^{1}H NMR of **2ac** (500 MHz, $CDCl_3$)

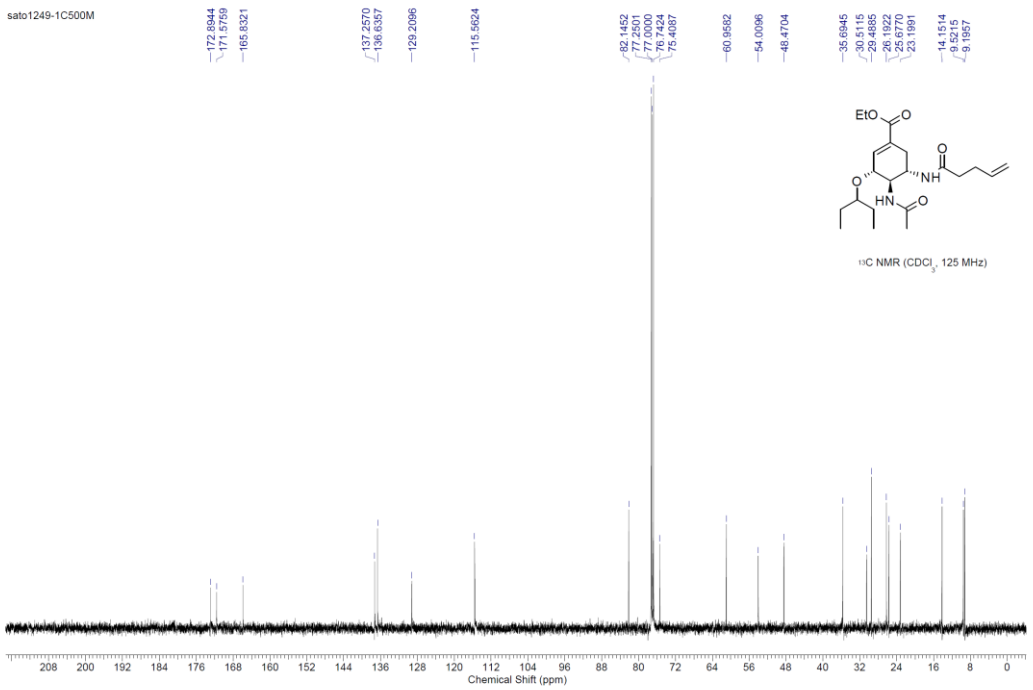

Figure S27. ^{13}C NMR of **2ac** (125 MHz, $CDCl_3$)

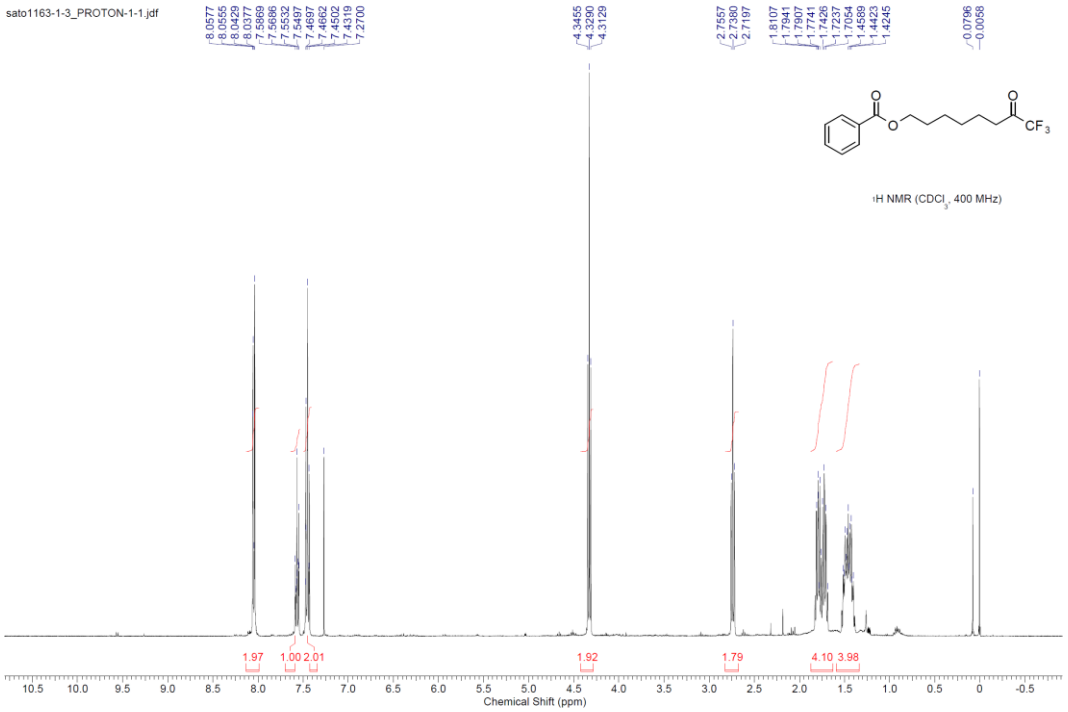

Figure S28. ^{1}H NMR of **3a** (400 MHz, $CDCl_3$)

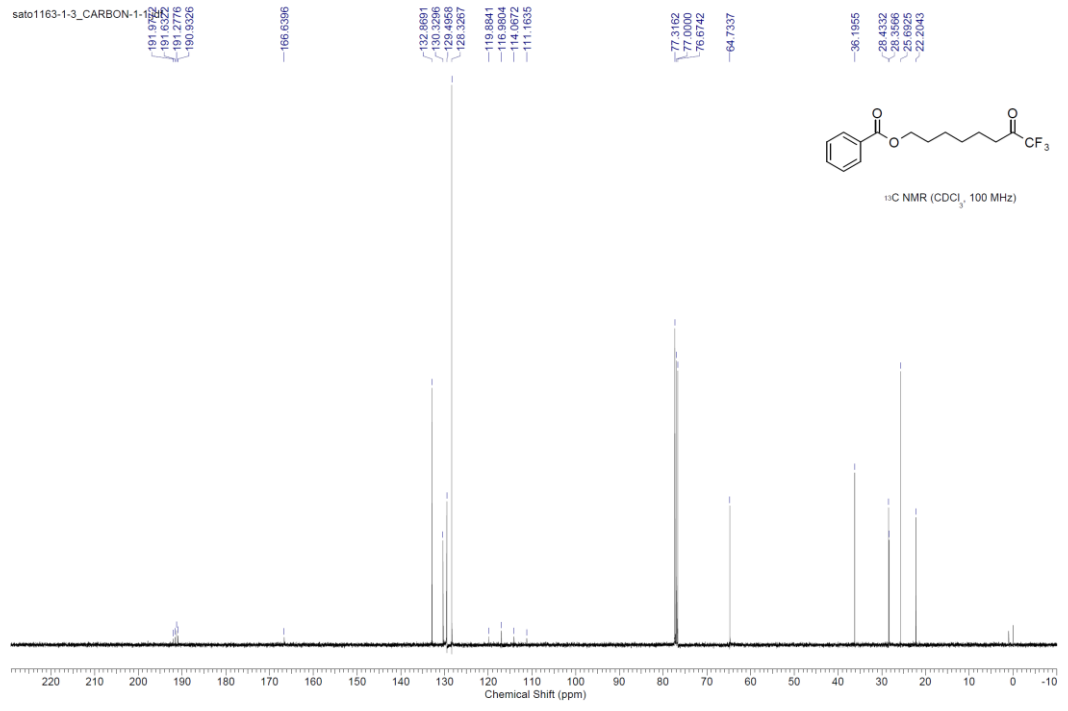

Figure S29. ^{13}C NMR of **3a** (100 MHz, $CDCl_3$)

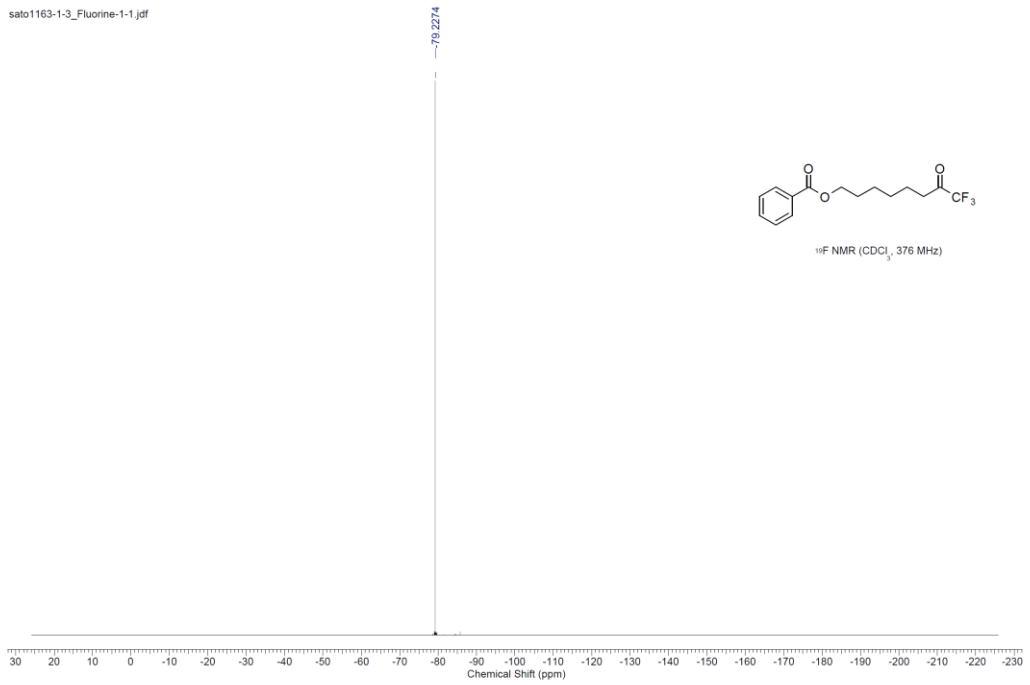

Figure S30. ^{19}F NMR of **3a** (376 MHz, $CDCl_3$)

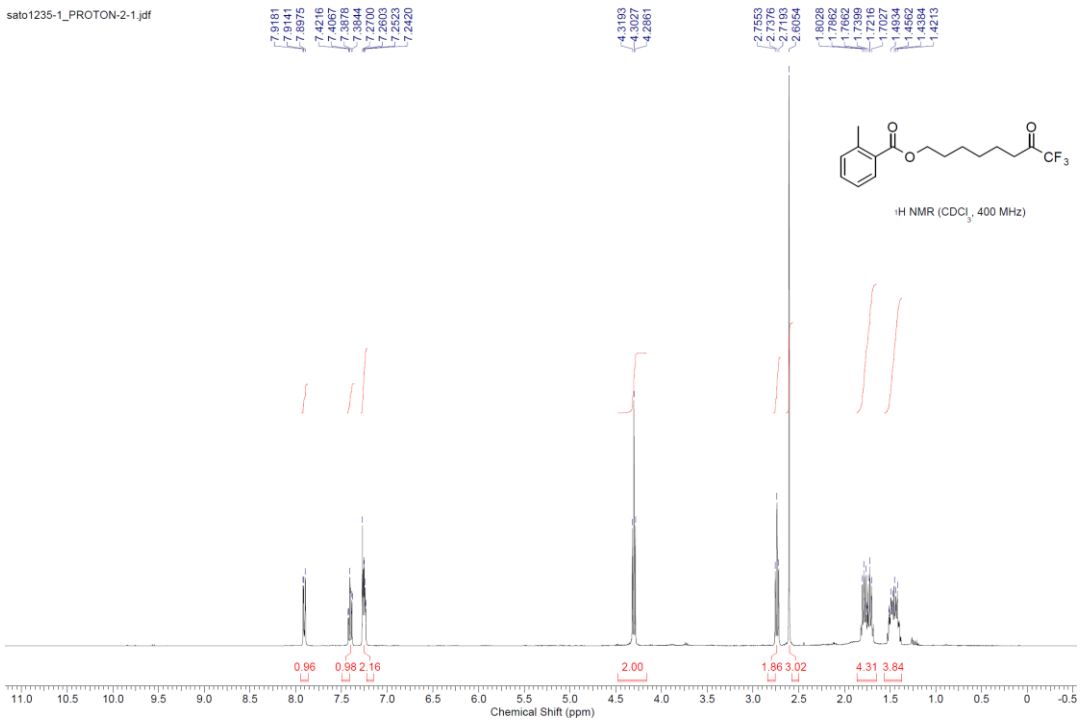

Figure S31. ^{1}H NMR of **3b** (400 MHz, $CDCl_3$)

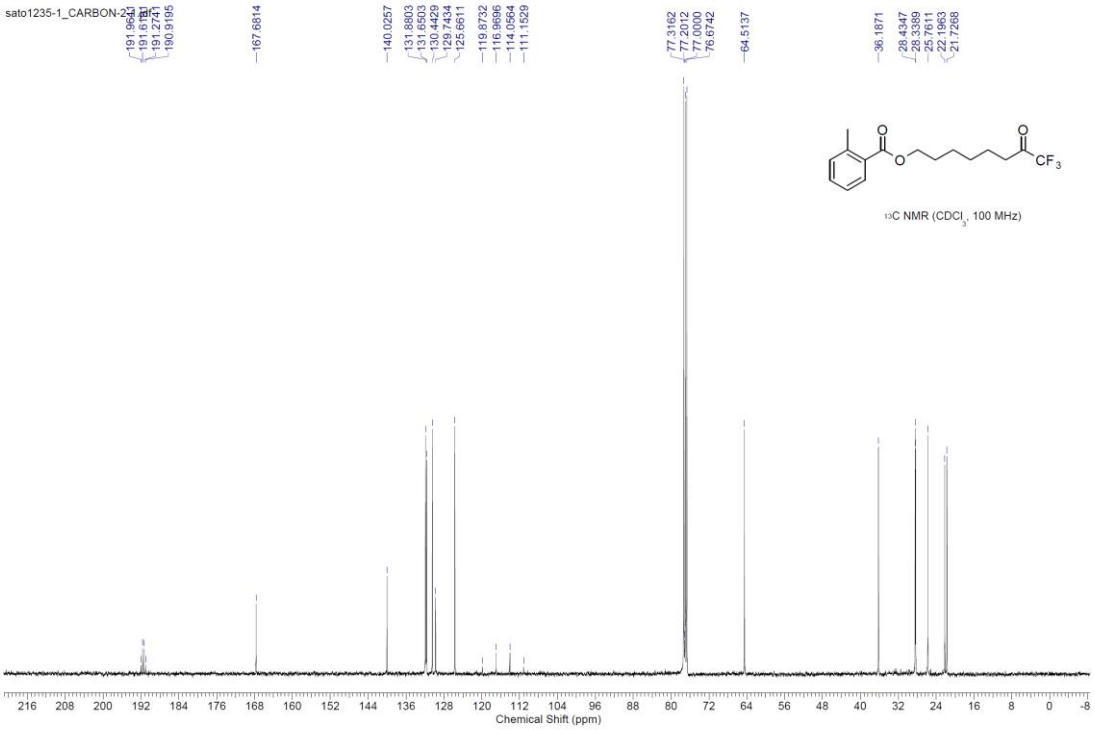

Figure S32. ^{13}C NMR of **3b** (100 MHz, $CDCl_3$)

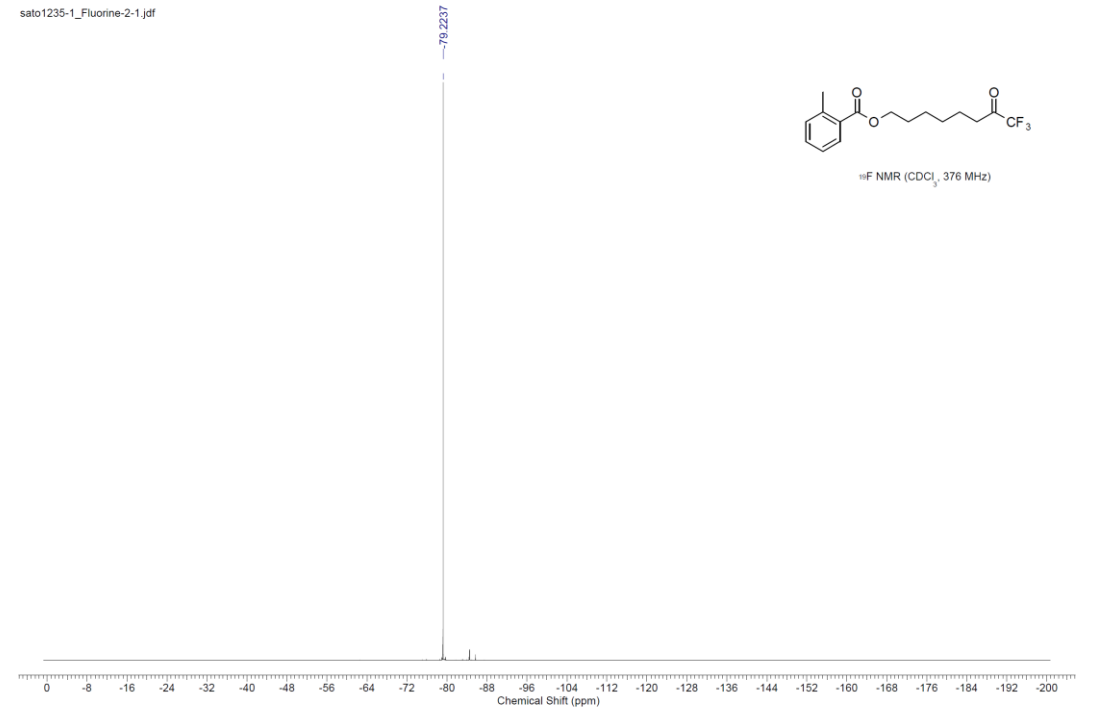

Figure S33. ^{19}F NMR of **3b** (376 MHz, $CDCl_3$)

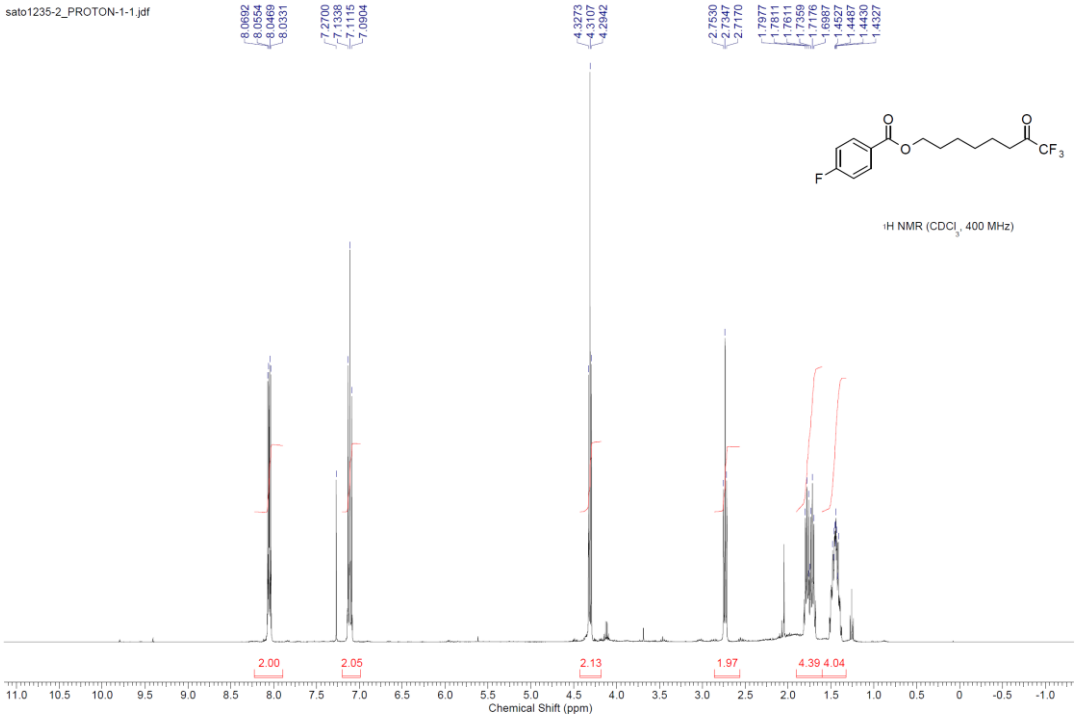

Figure S34. ^{1}H NMR of **3c** (400 MHz, $CDCl_3$)

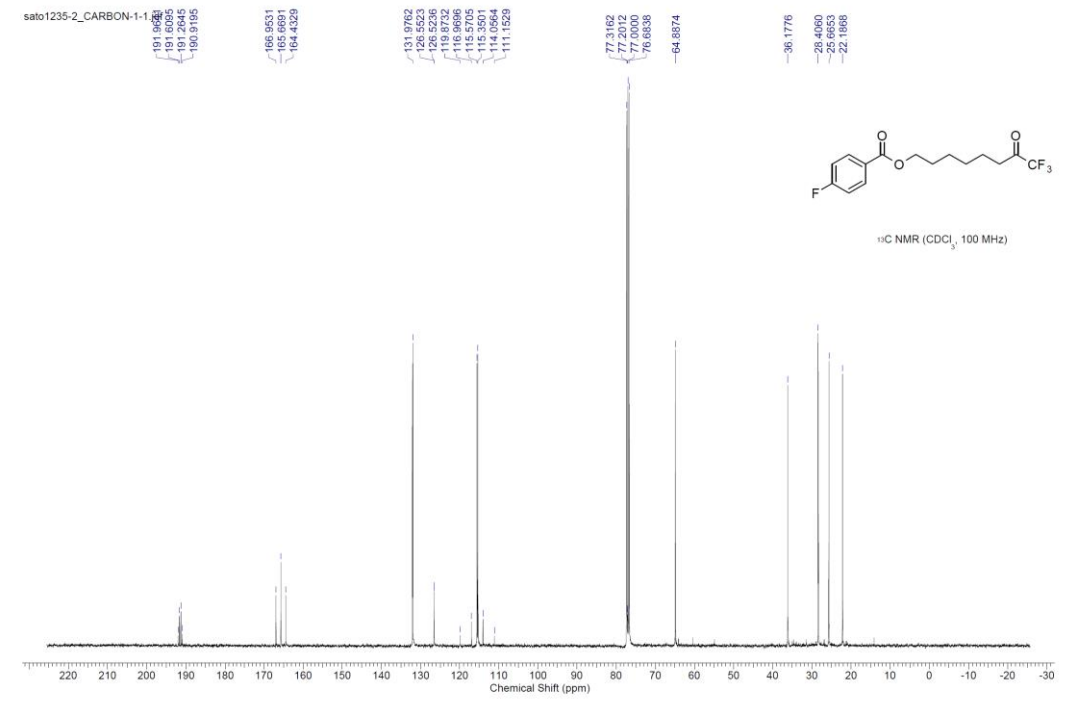

Figure S35. ^{13}C NMR of **3c** (100 MHz, $CDCl_3$)

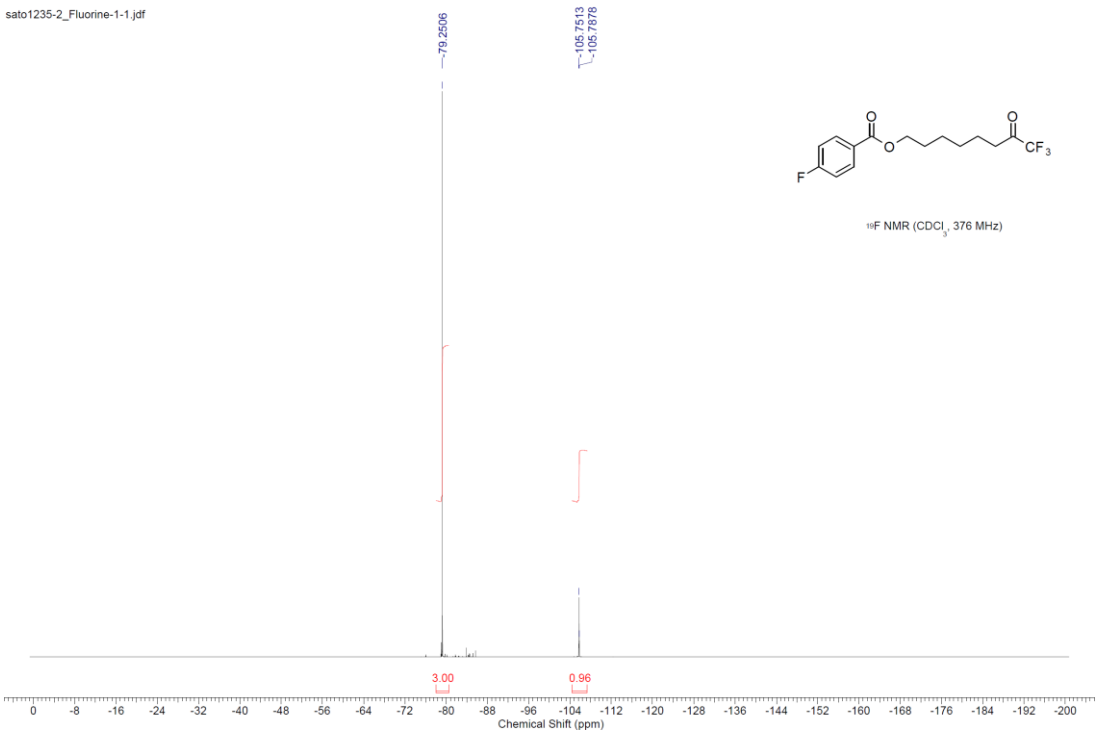

Figure S36. ^{19}F NMR of **3c** (376 MHz, $CDCl_3$)

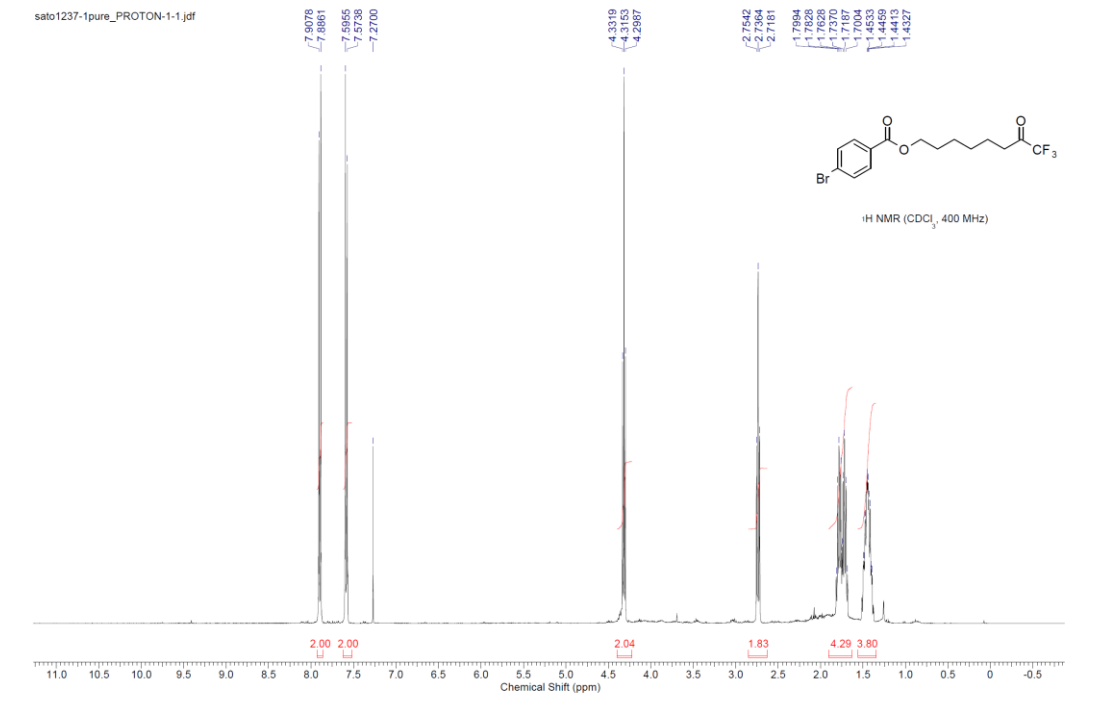

Figure S37. ^{1}H NMR of **3d** (400 MHz, $CDCl_3$)

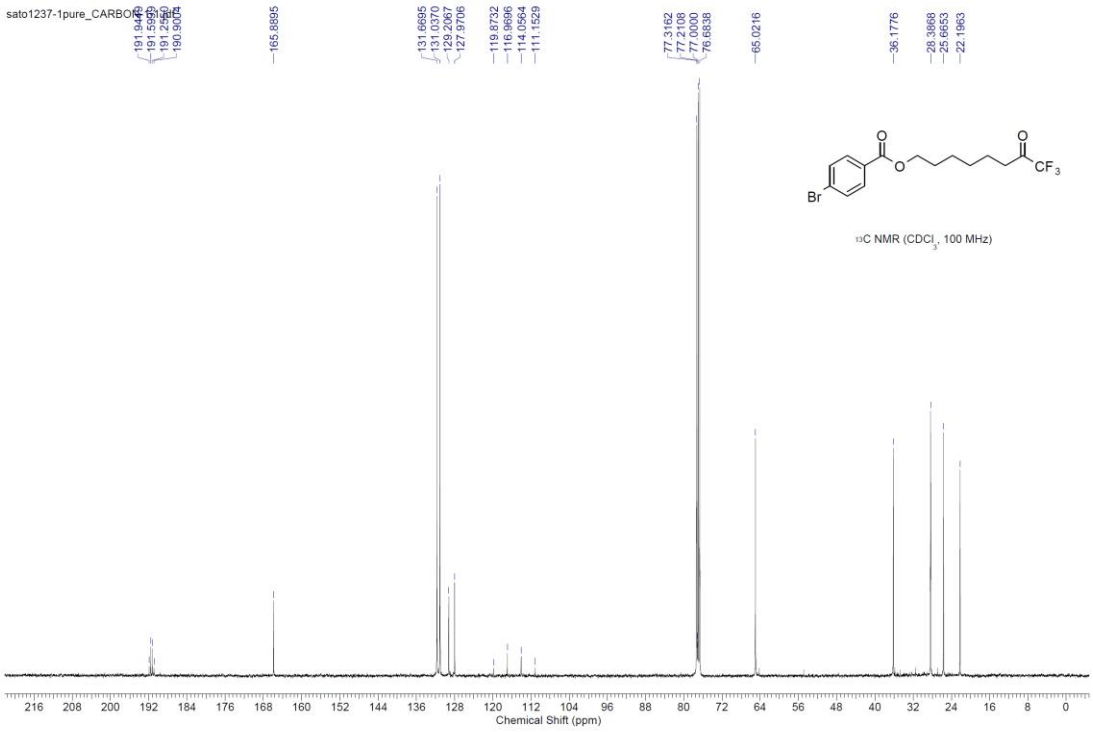

Figure S38. ^{13}C NMR of **3d** (100 MHz, $CDCl_3$)

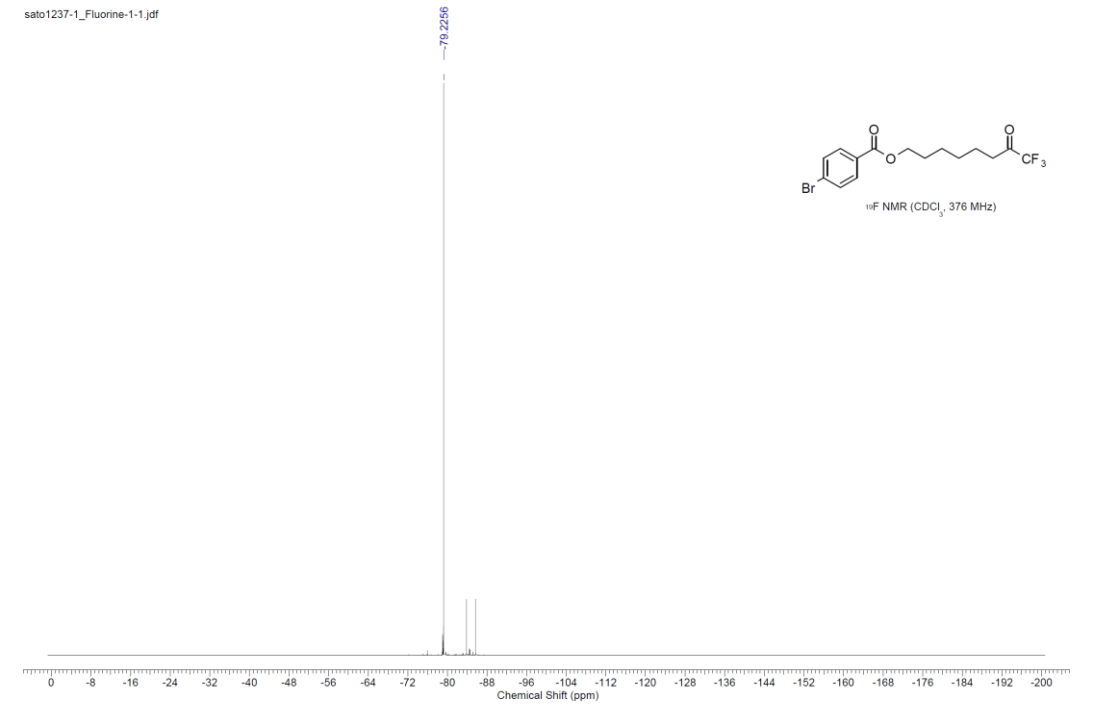

Figure S39. ^{19}F NMR of **3d** (376 MHz, $CDCl_3$)

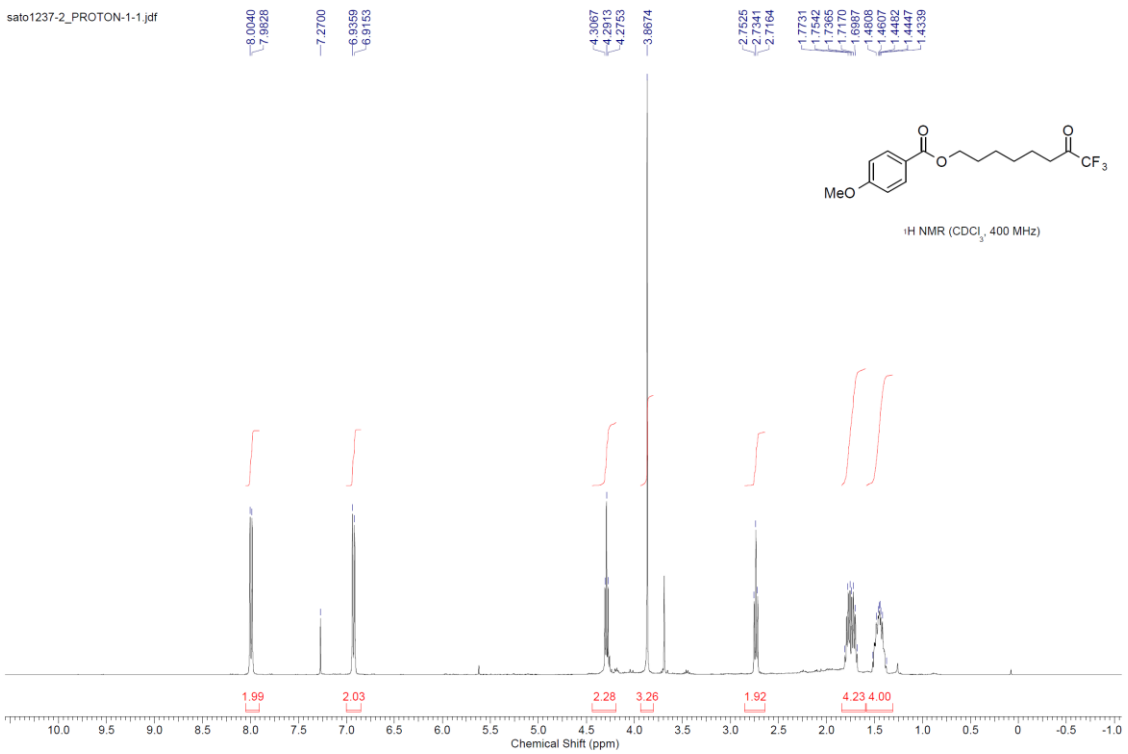

Figure S40. ^{1}H NMR of **3e** (400 MHz, $CDCl_3$)

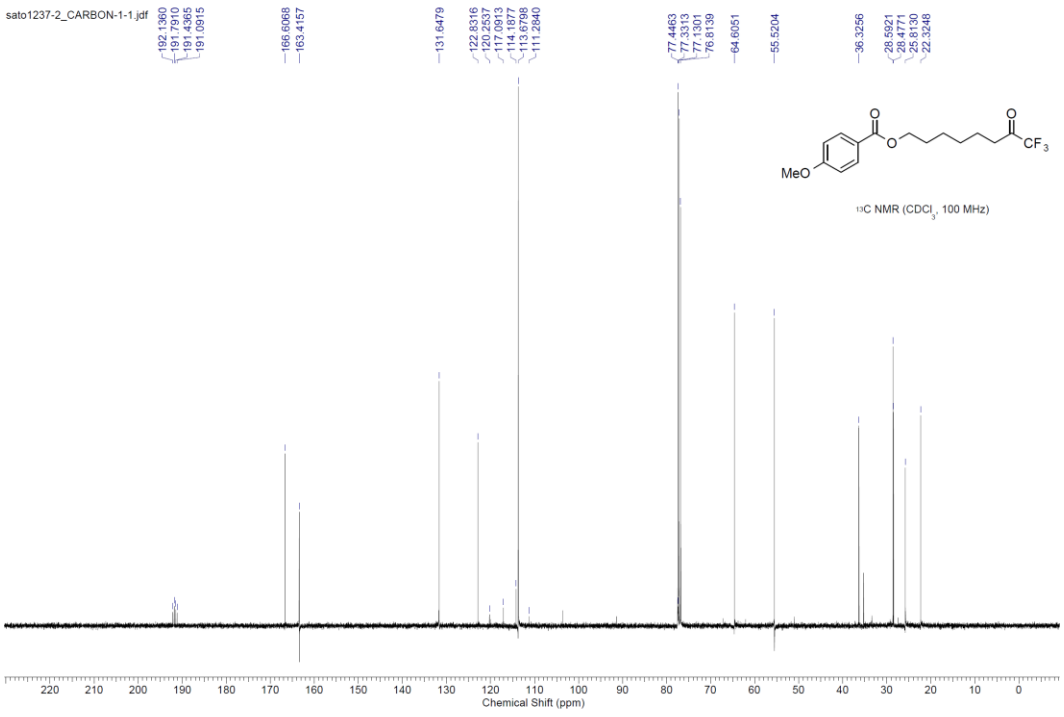

Figure S41. ^{13}C NMR of **3e** (100 MHz, $CDCl_3$)

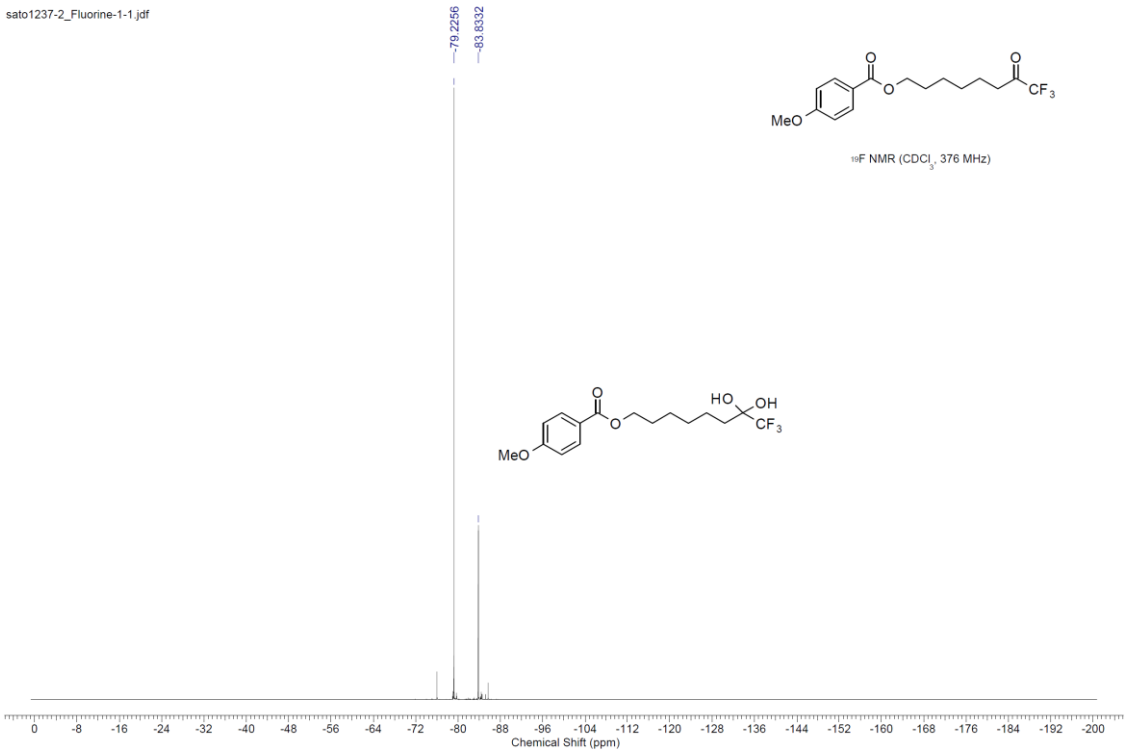

Figure S42. ^{19}F NMR of **3e** (376 MHz, $CDCl_3$)

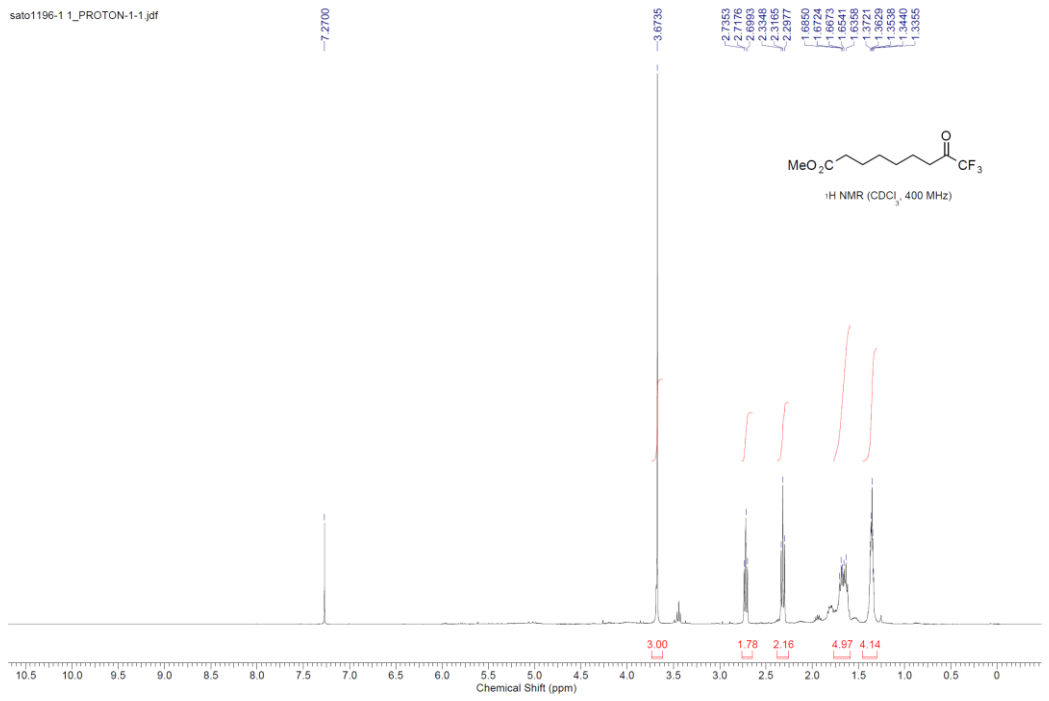

Figure S43. ^{1}H NMR of **3f** (400 MHz, $CDCl_3$)

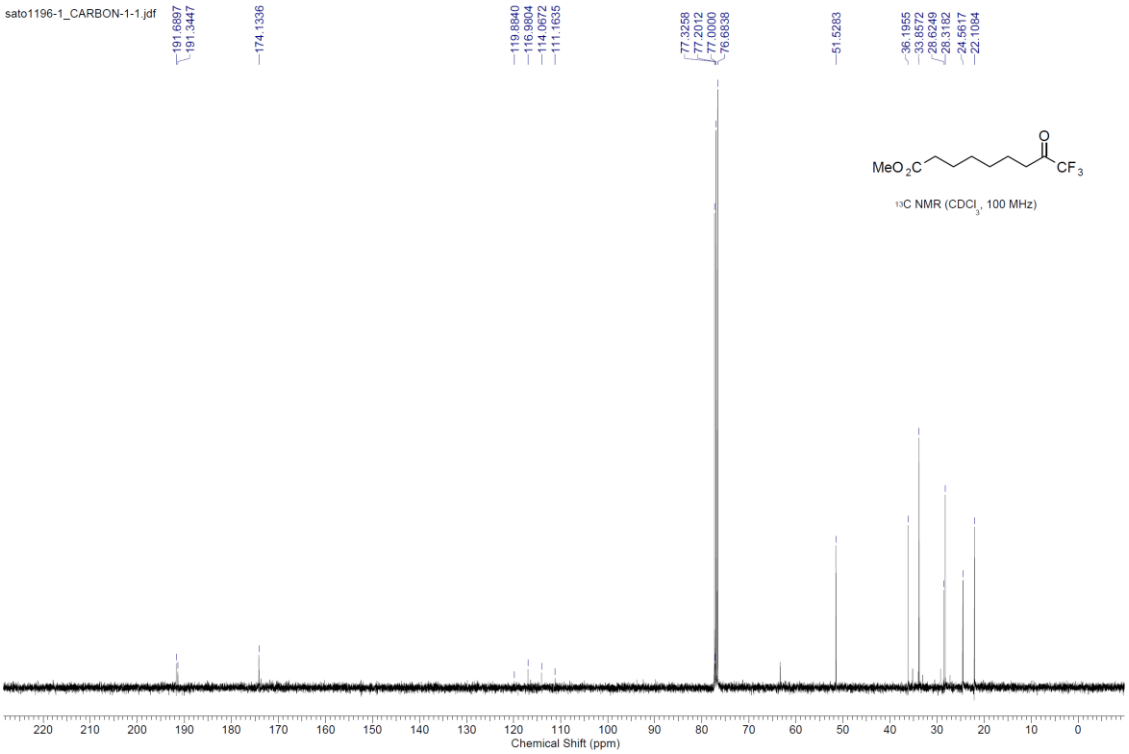

Figure S44. ^{13}C NMR of **3f** (100 MHz, $CDCl_3$)

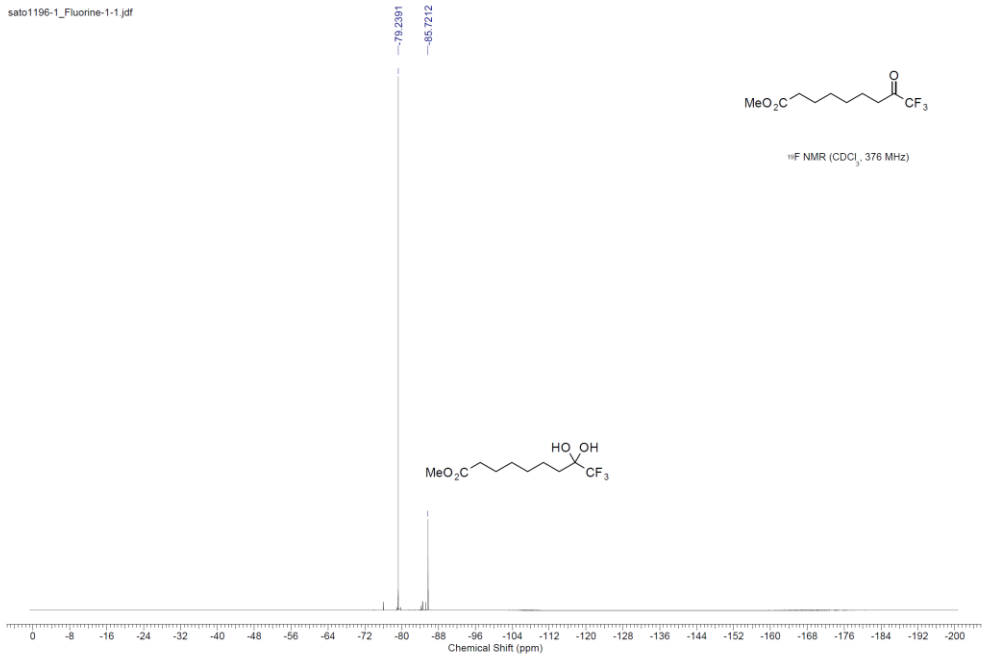

Figure S45. ^{19}F NMR of **3f** (376 MHz, $CDCl_3$)

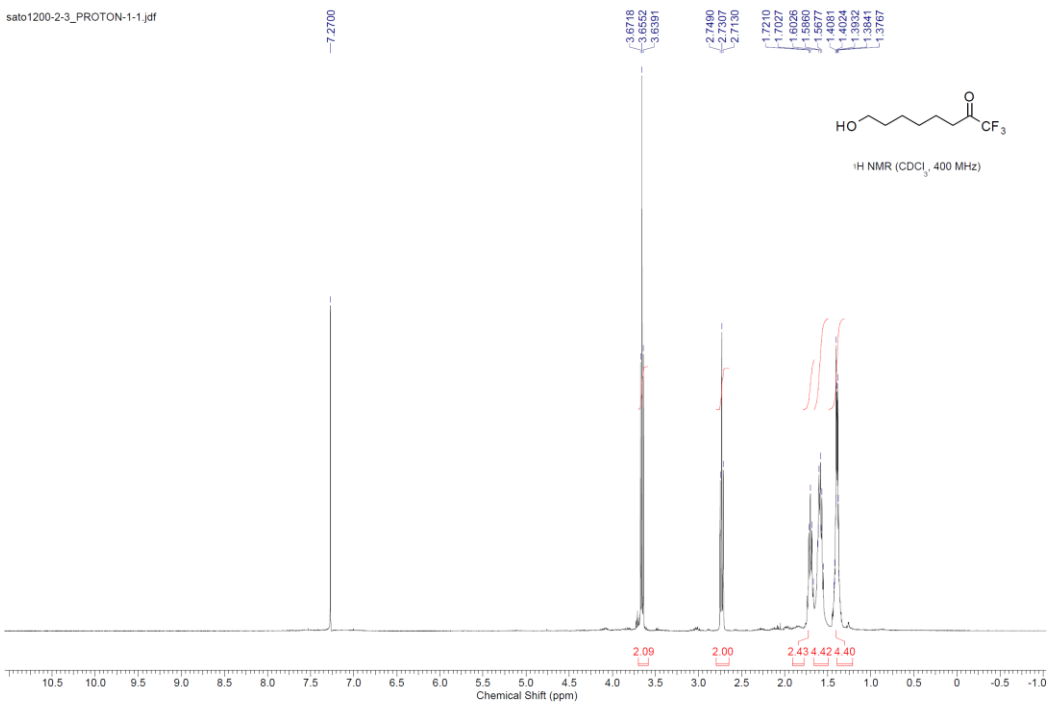

Figure S46. ^{1}H NMR of **3g** (400 MHz, $CDCl_3$)

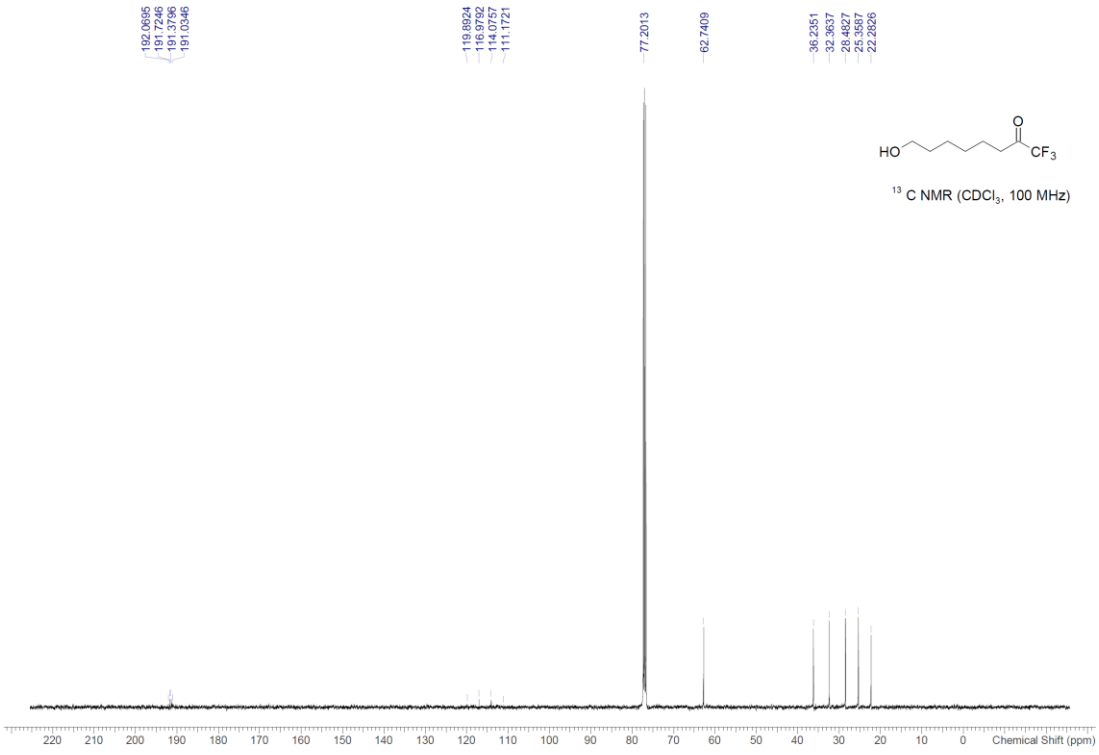

Figure S47. ^{13}C NMR of **3g** (100 MHz, $CDCl_3$)

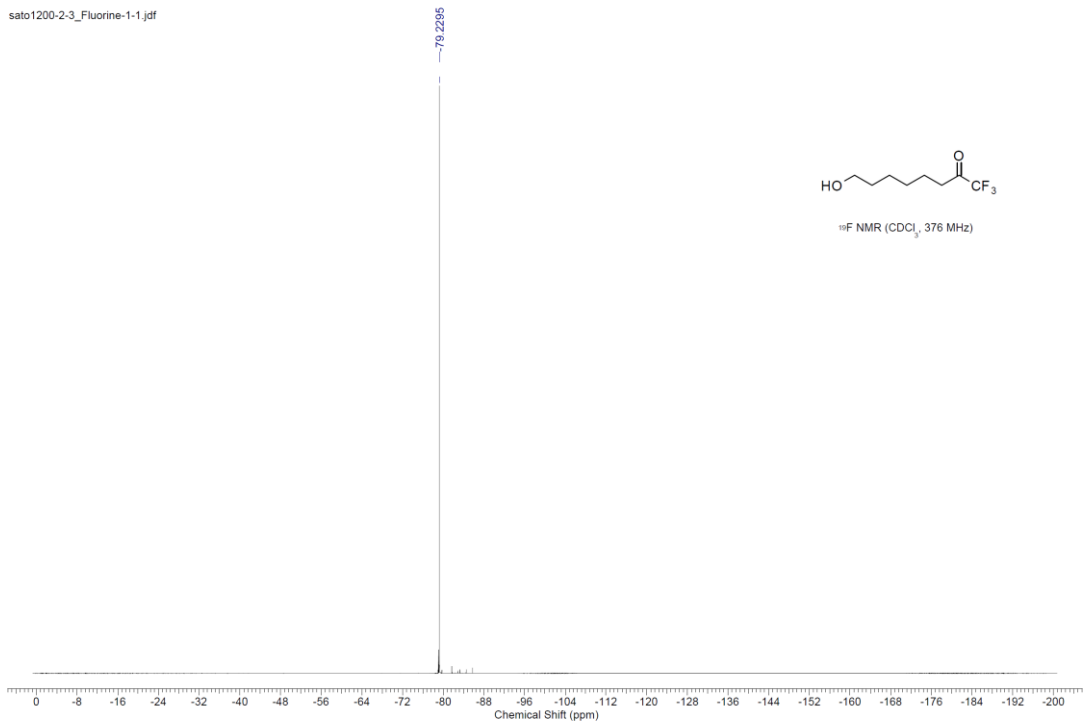

Figure S48. ^{19}F NMR of **3g** (376 MHz, $CDCl_3$)

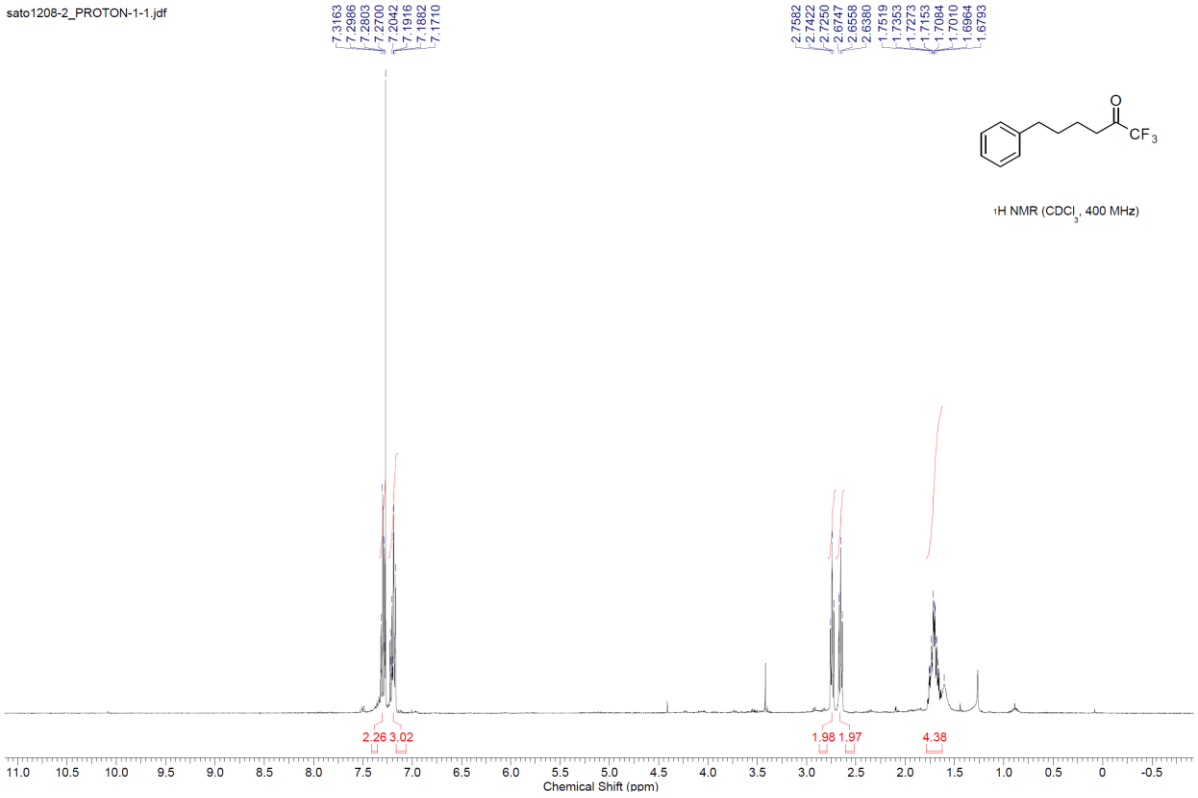

Figure S49. ^{1}H NMR of **3h** (400 MHz, $CDCl_3$)

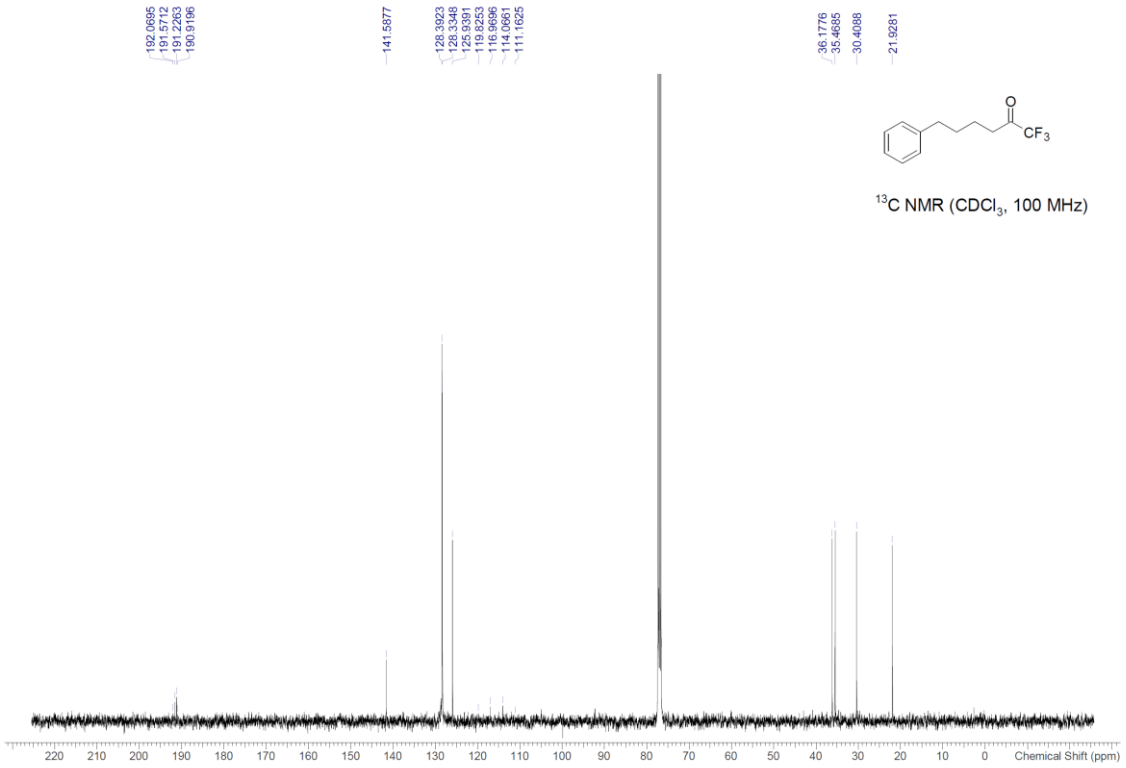

Figure S50. ^{13}C NMR of **3h** (100 MHz, $CDCl_3$)

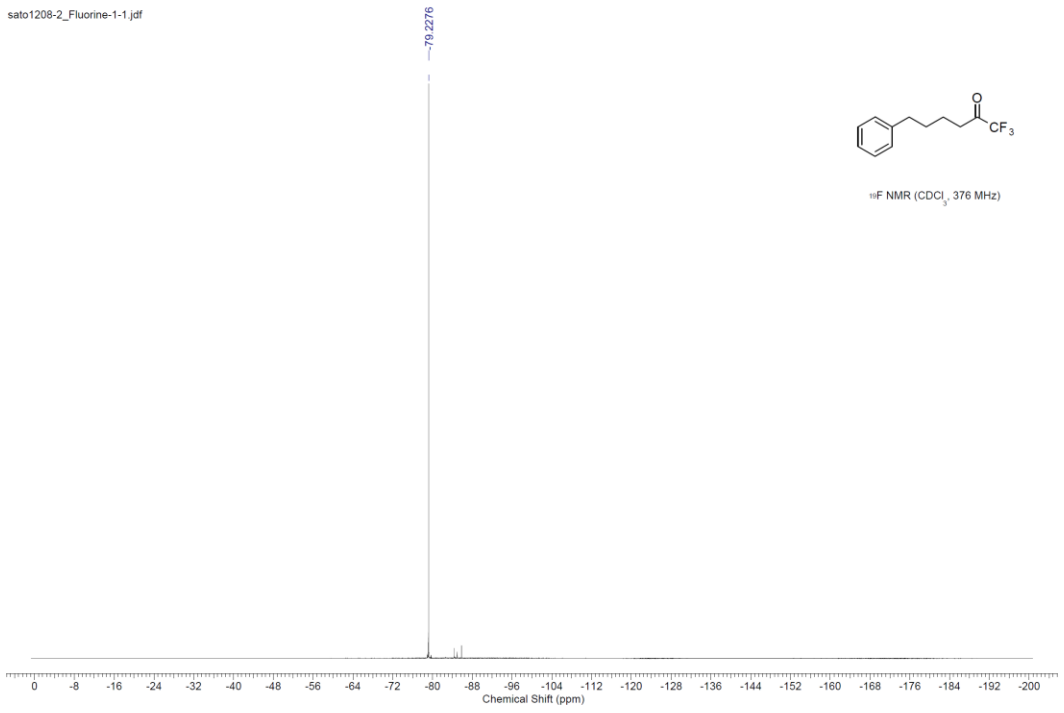

Figure S51. ^{19}F NMR of **3h** (376 MHz, $CDCl_3$)

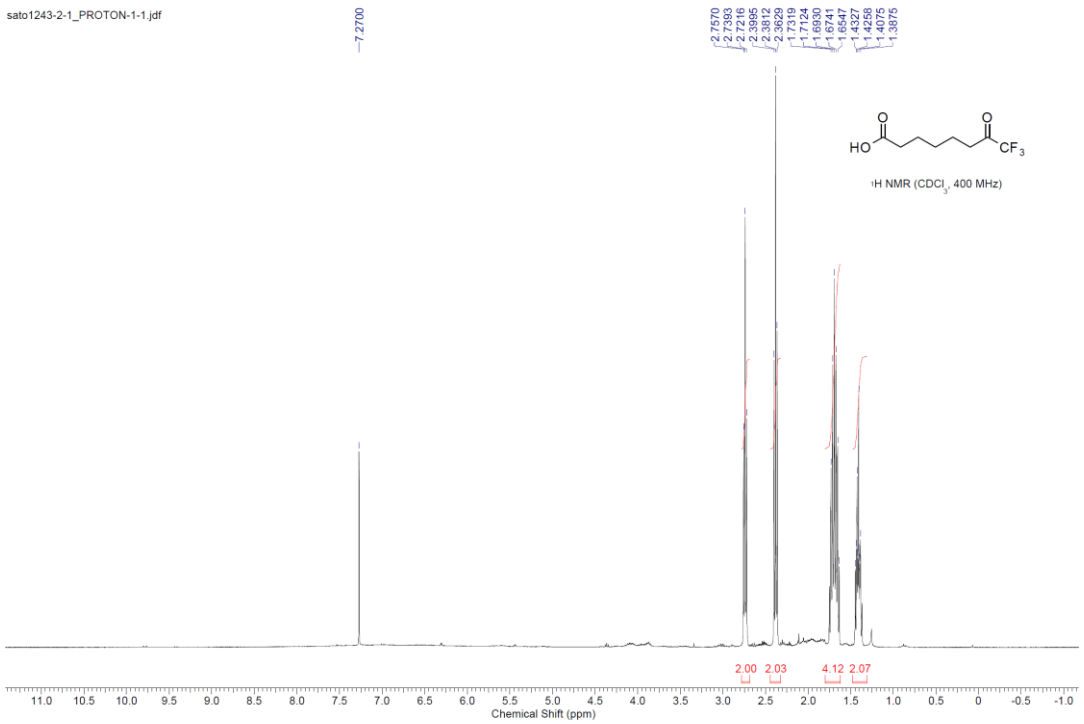

Figure S52. ^{1}H NMR of **3i** (400 MHz, $CDCl_3$)

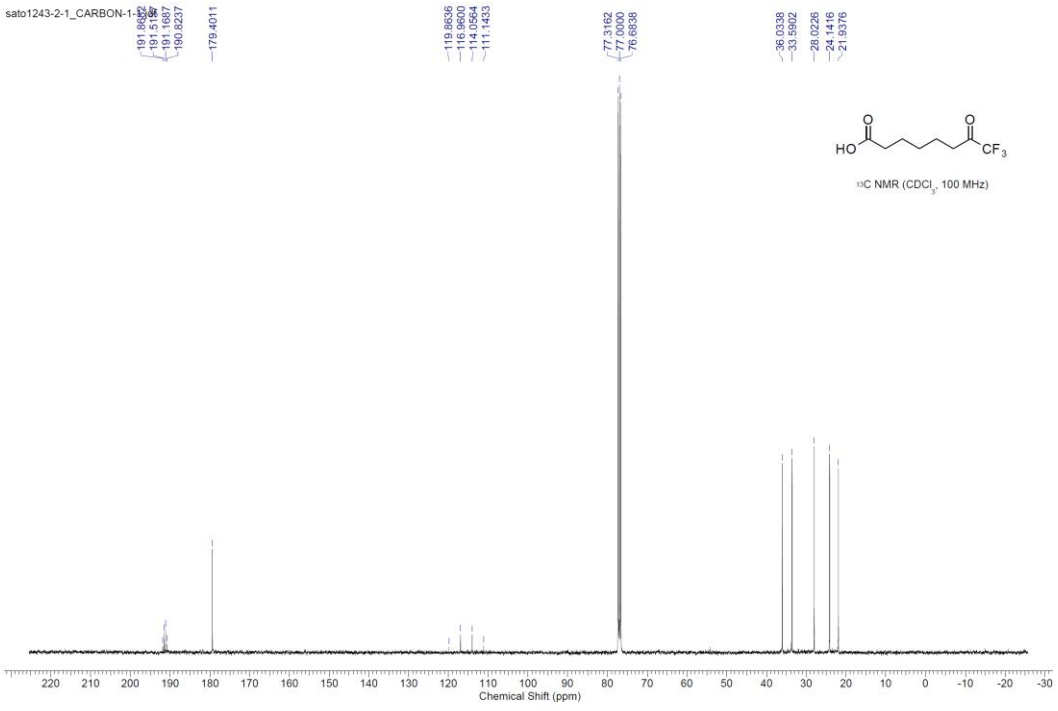

Figure S53. ^{13}C NMR of **3i** (100 MHz, $CDCl_3$)

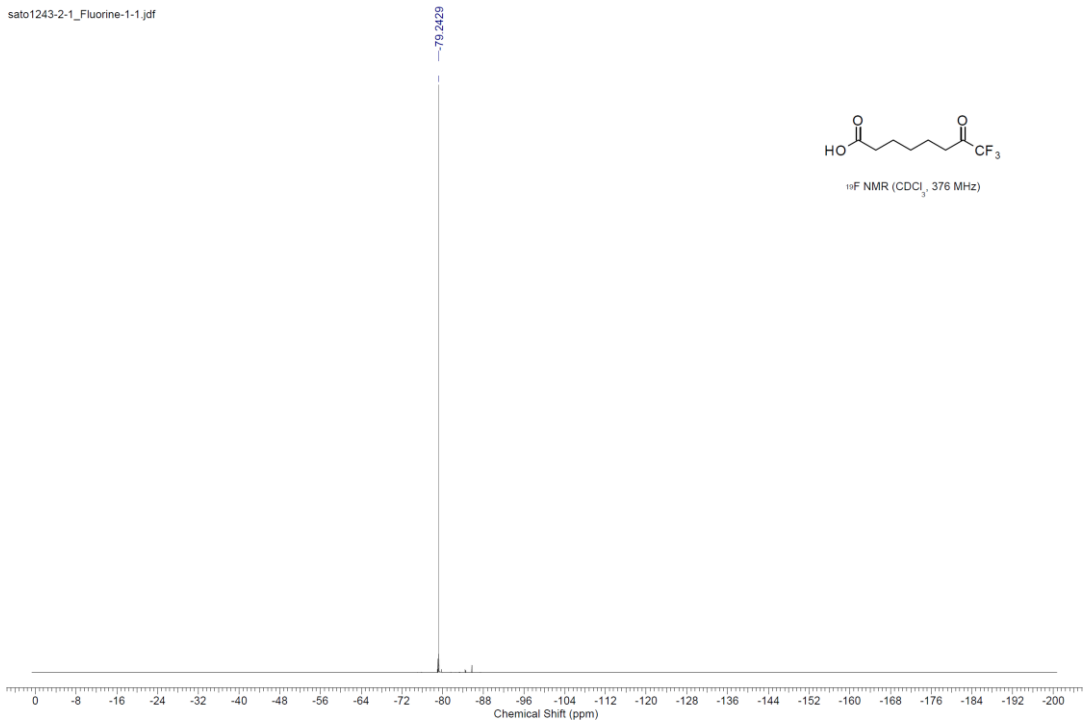

Figure S54. ^{19}F NMR of **3i** (376 MHz, $CDCl_3$)

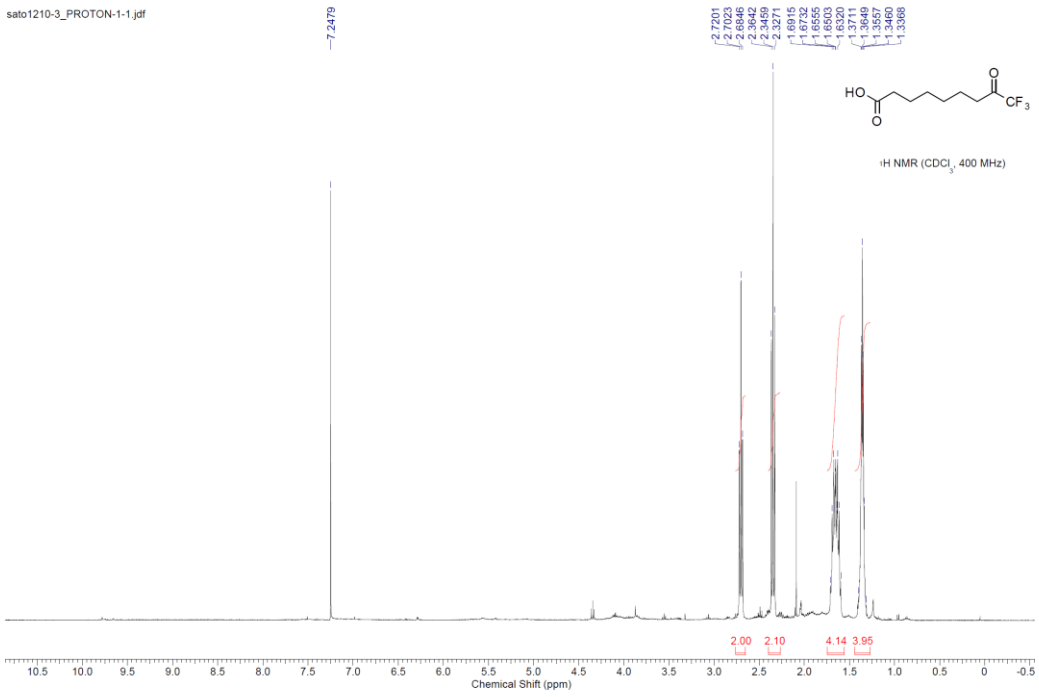

Figure S55. ^{1}H NMR of **3j** (400 MHz, $CDCl_3$)

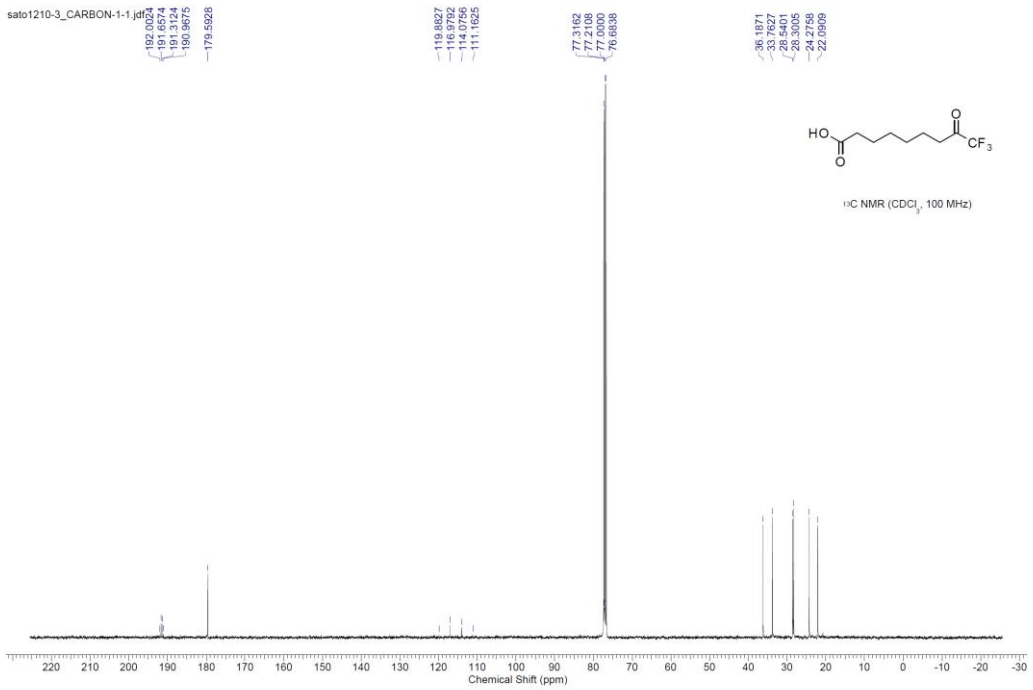

Figure S56. ^{13}C NMR of **3j** (100 MHz, $CDCl_3$)

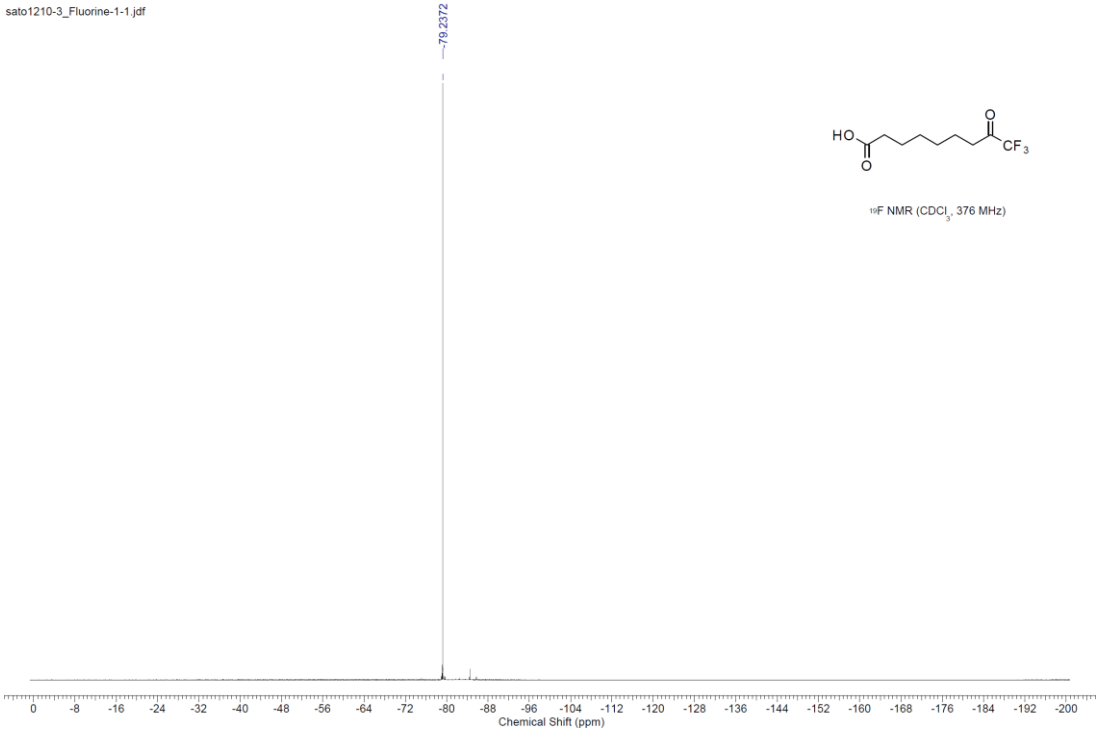

Figure S57. ^{19}F NMR of **3j** (376 MHz, $CDCl_3$)

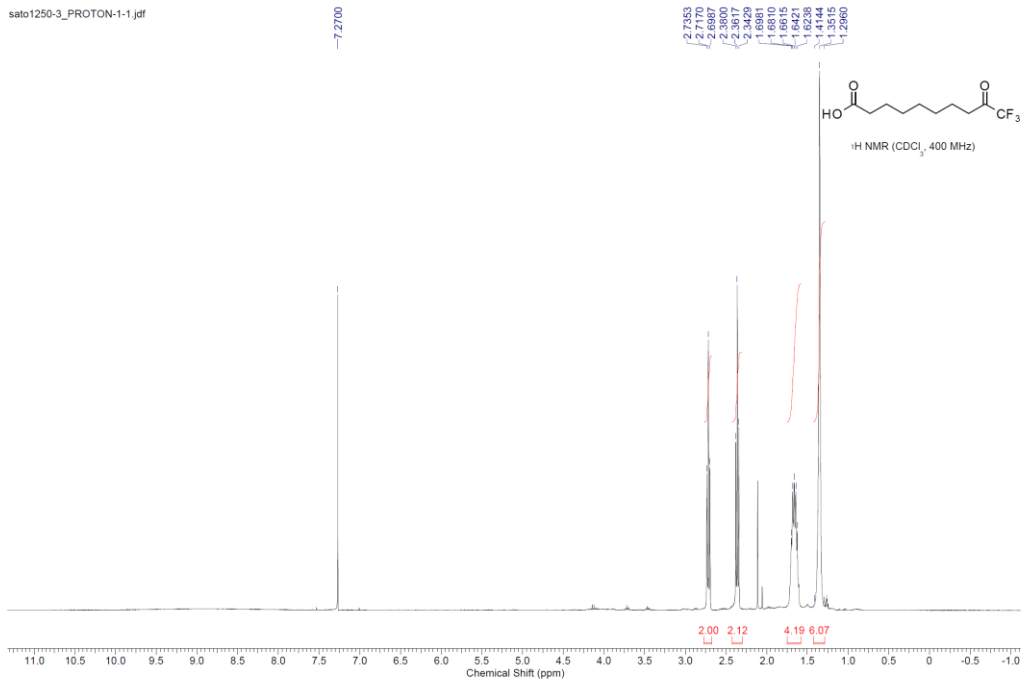

Figure S58. ^{1}H NMR of **3k** (400 MHz, $CDCl_3$)

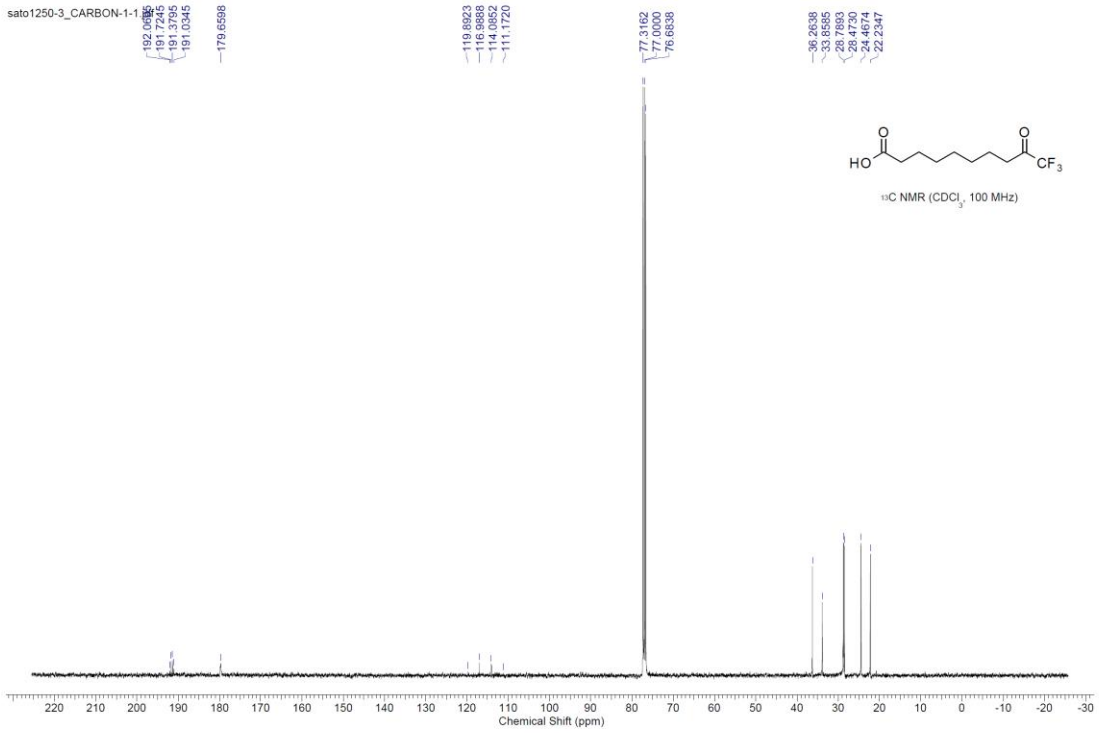

Figure S59. ^{13}C NMR of **3k** (100 MHz, $CDCl_3$)

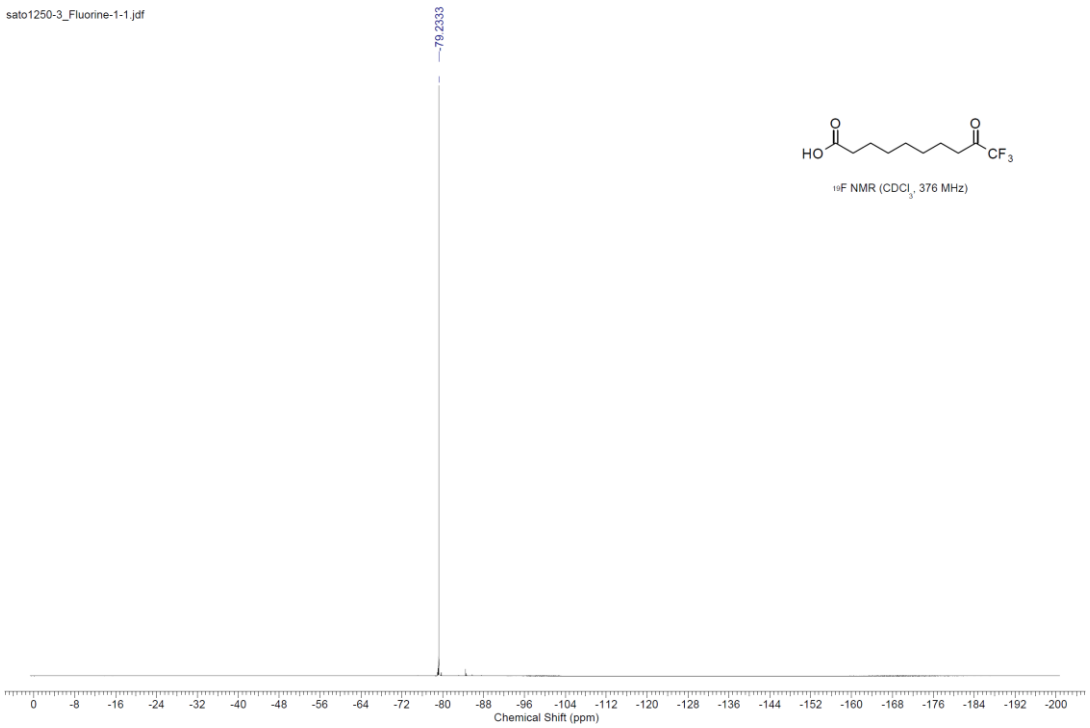

Figure S60. ^{19}F NMR of **3k** (376 MHz, $CDCl_3$)

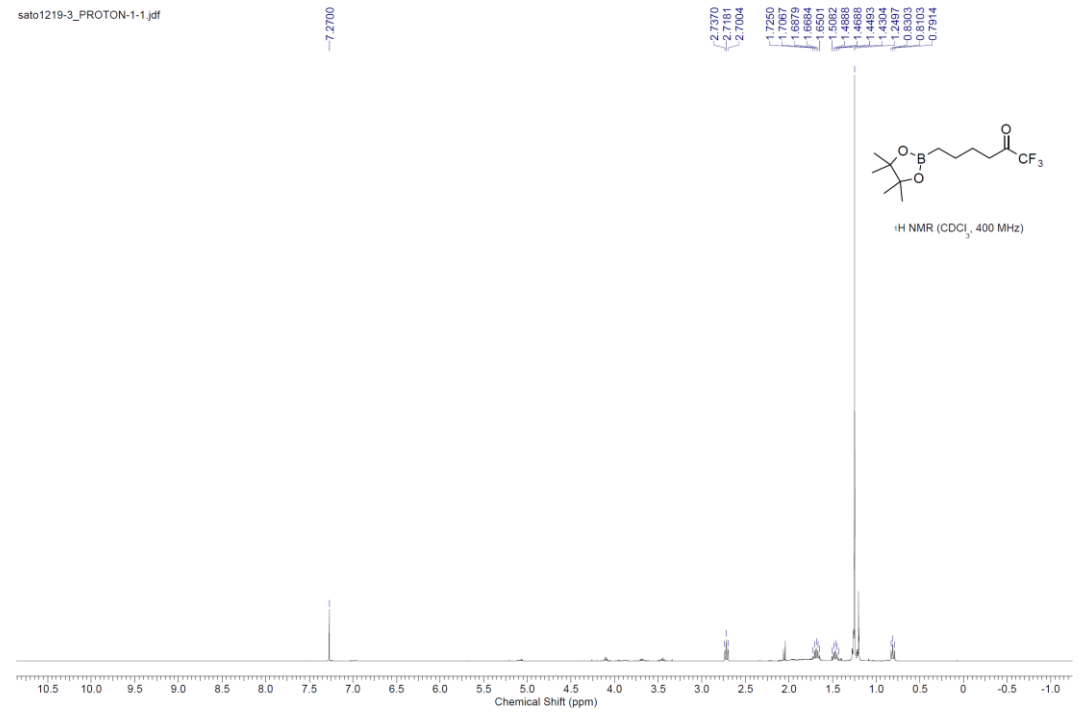

Figure S61. ^{1}H NMR of **3l** (400 MHz, $CDCl_3$)

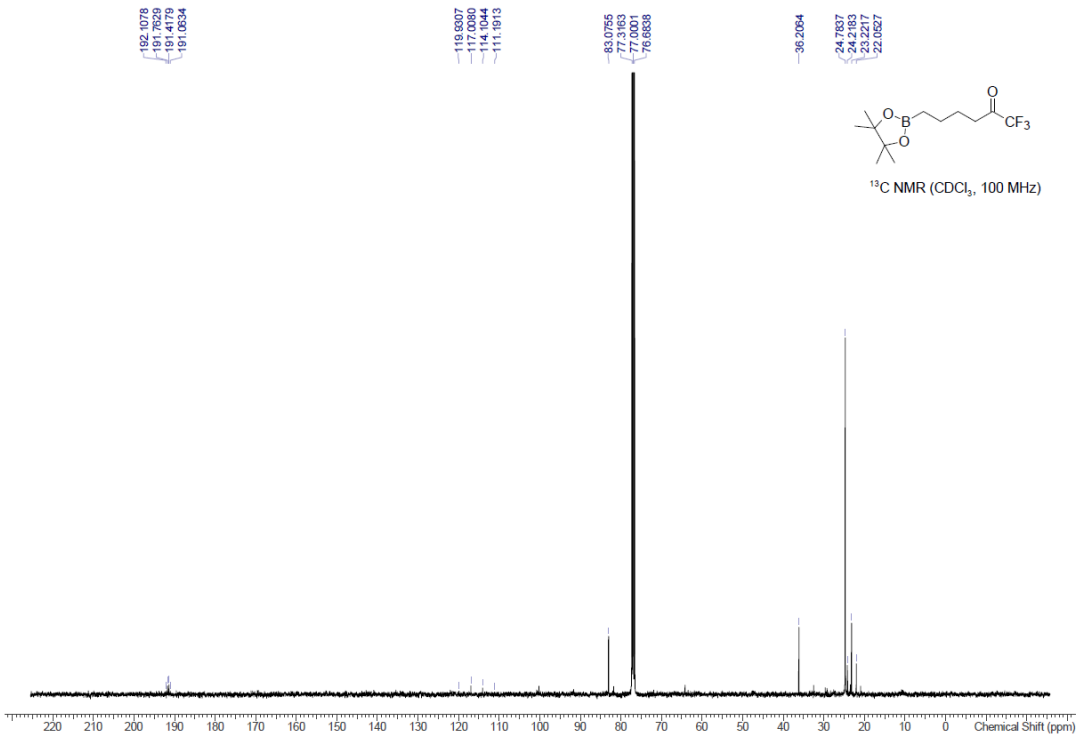

Figure S62. ^{13}C NMR of **3l** (100 MHz, $CDCl_3$)

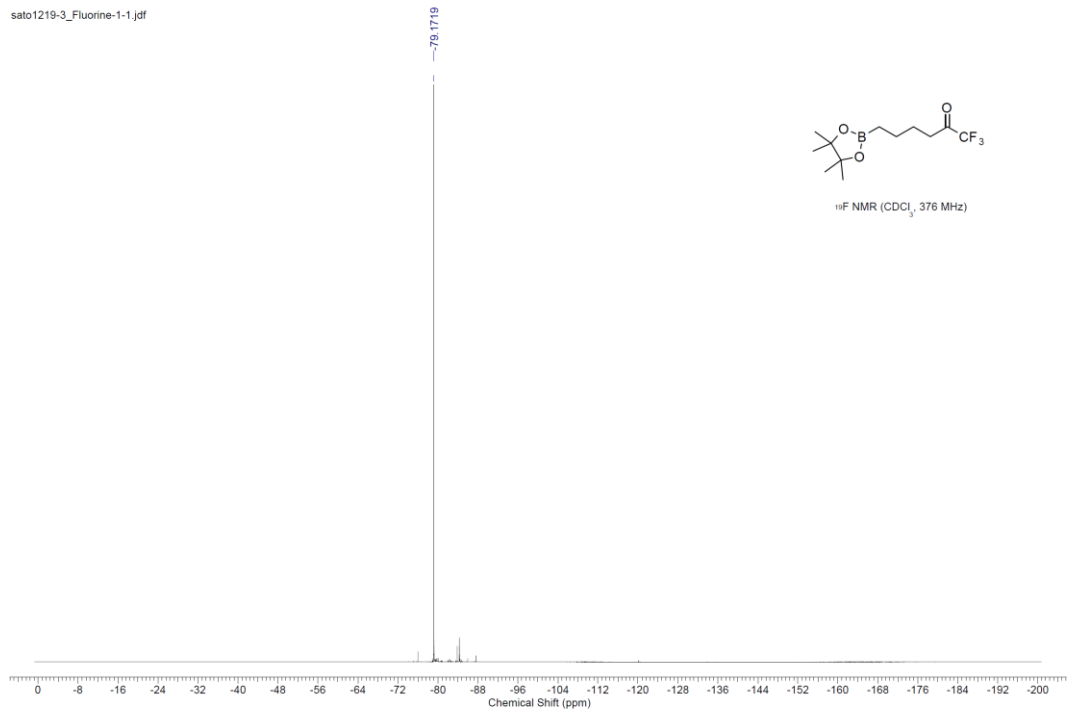

Figure S63. ^{19}F NMR of **3l** (376 MHz, $CDCl_3$)

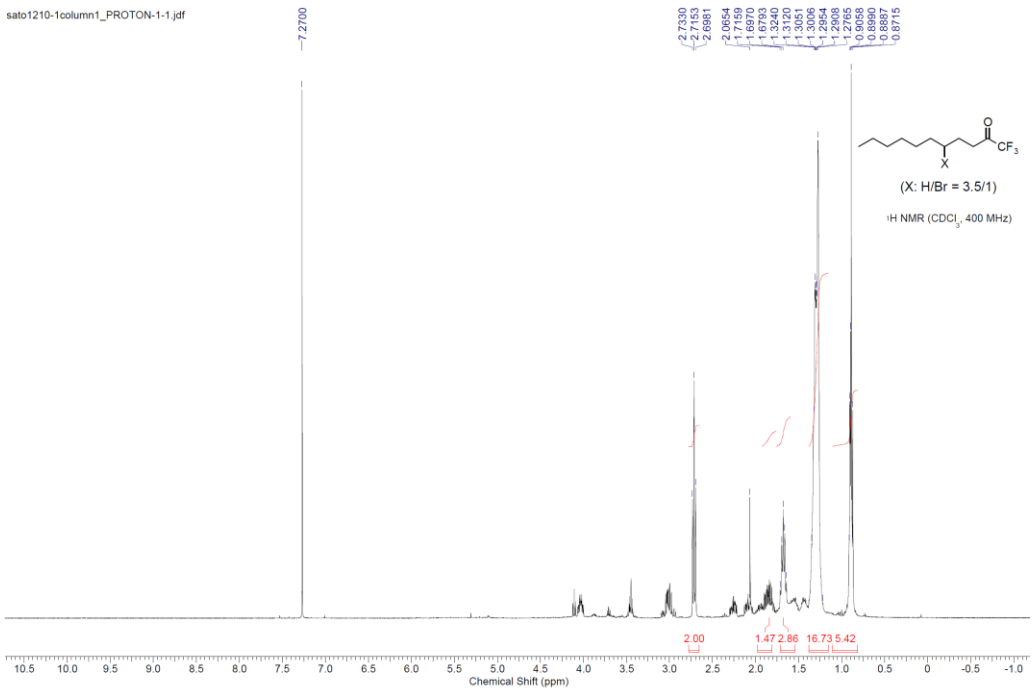

Figure S64. ^{1}H NMR of **3m/4m** (400 MHz, $CDCl_3$)

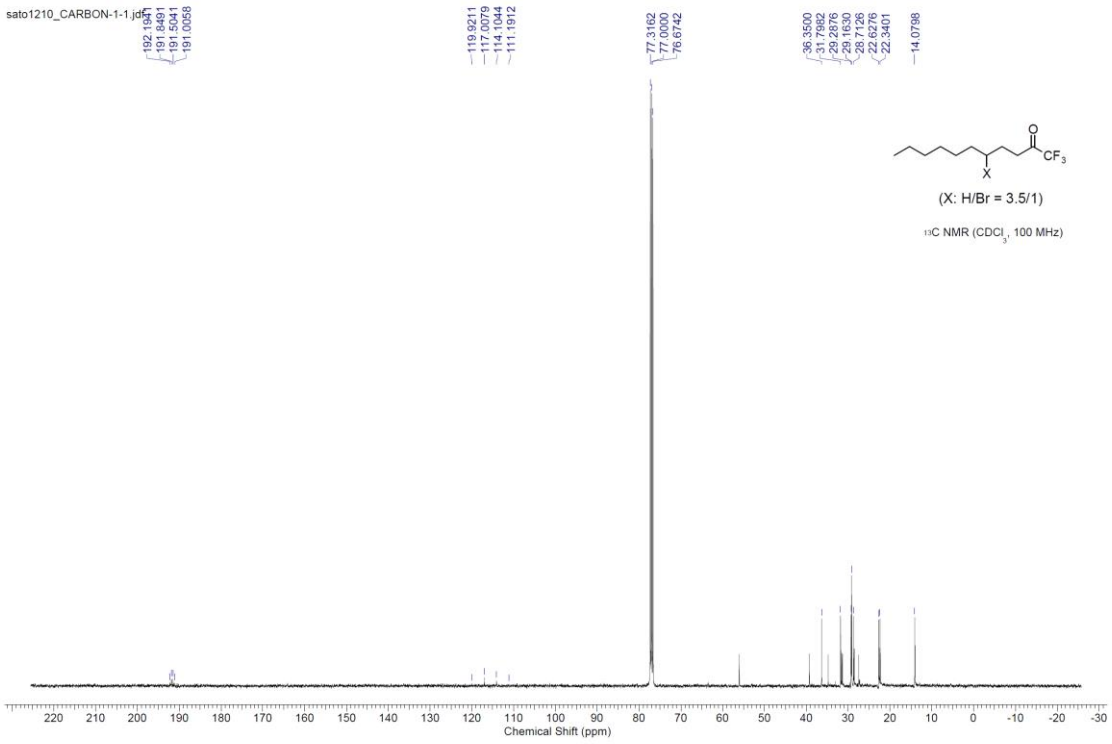

Figure S65. ^{13}C NMR of **3m/4m** (100 MHz, $CDCl_3$)

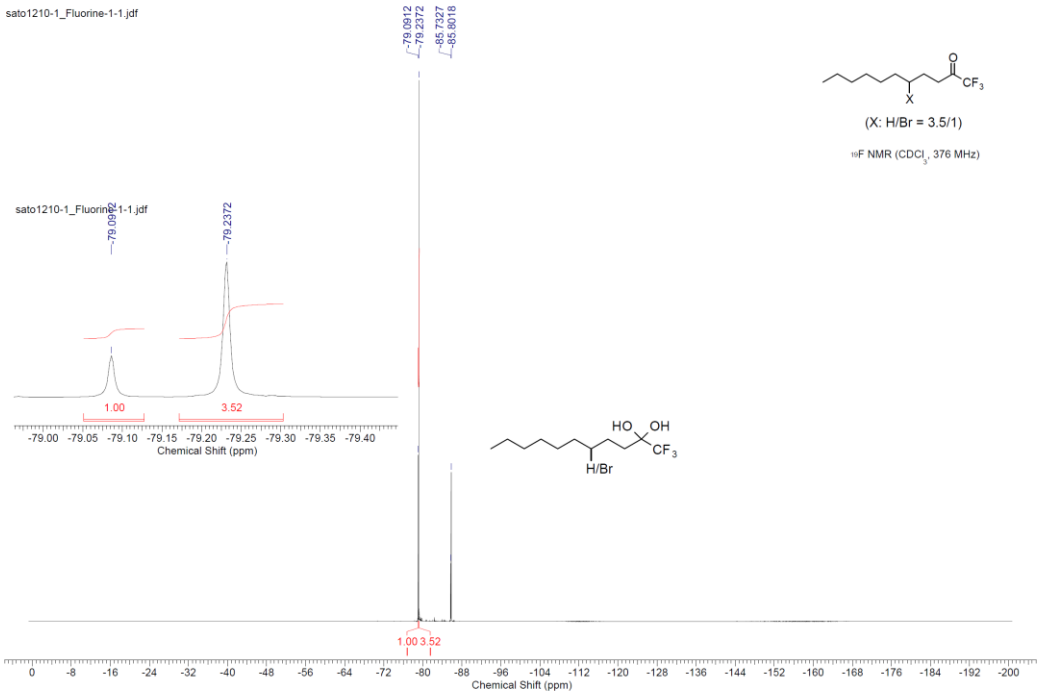

Figure S66. ^{19}F NMR of **3m/4m** (376 MHz, $CDCl_3$)

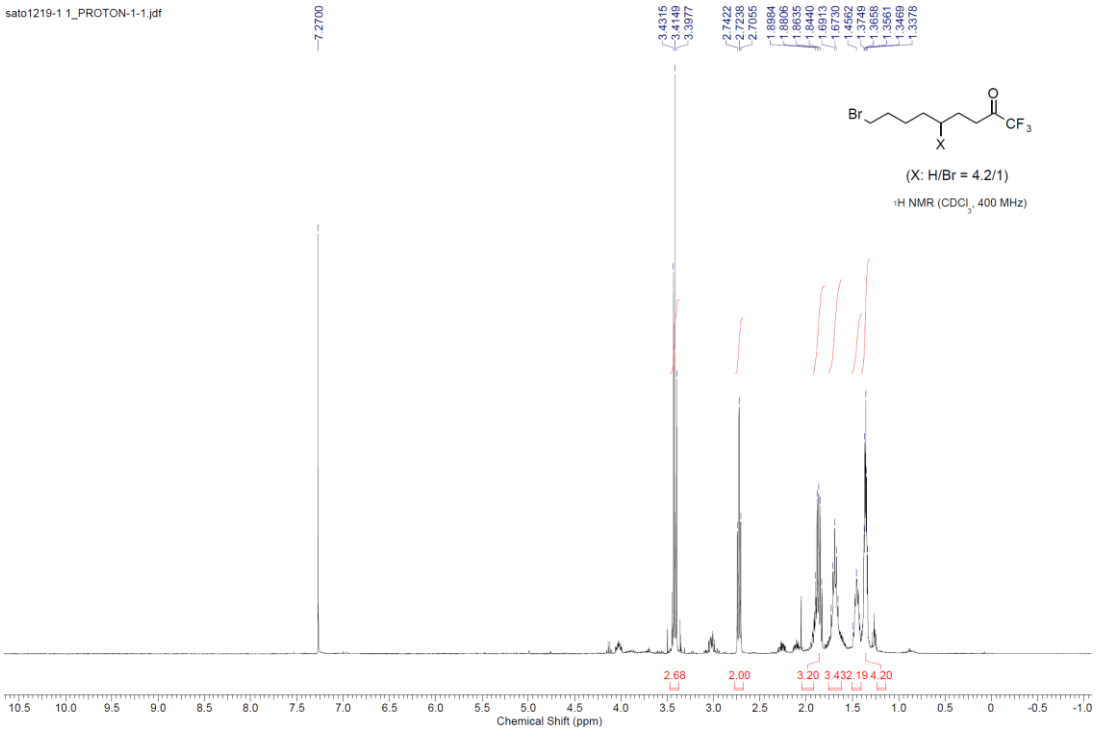

Figure S67. ^{1}H NMR of **3n/4n** (400 MHz, $CDCl_3$)

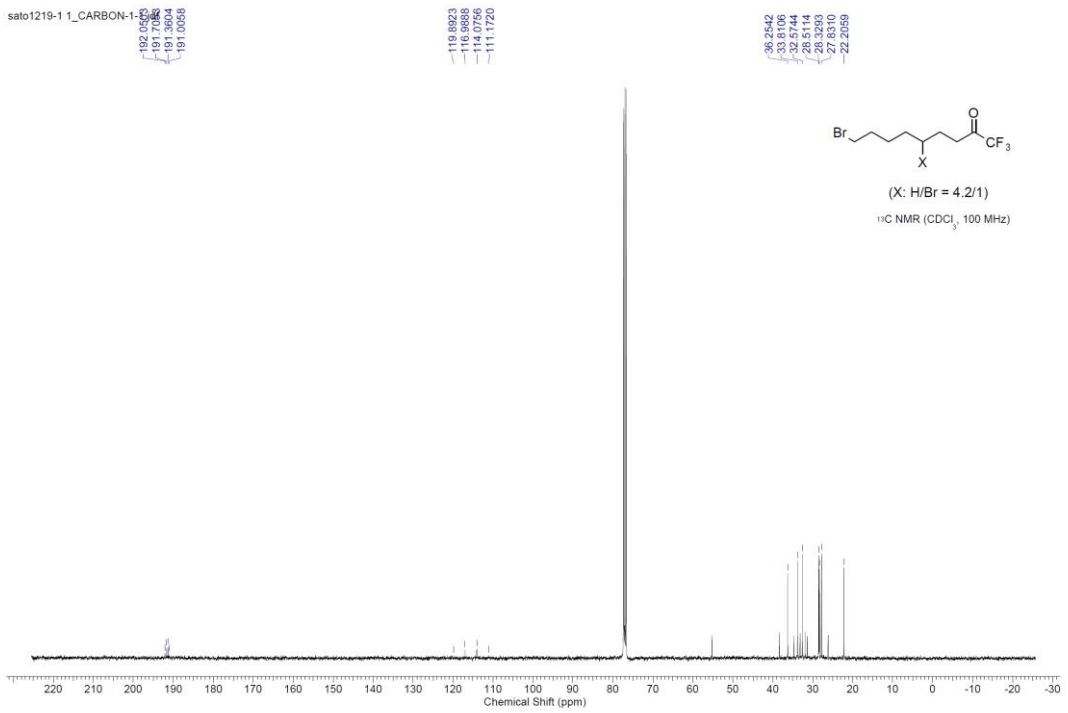

Figure S68. ^{13}C NMR of **3n/4n** (100 MHz, $CDCl_3$)

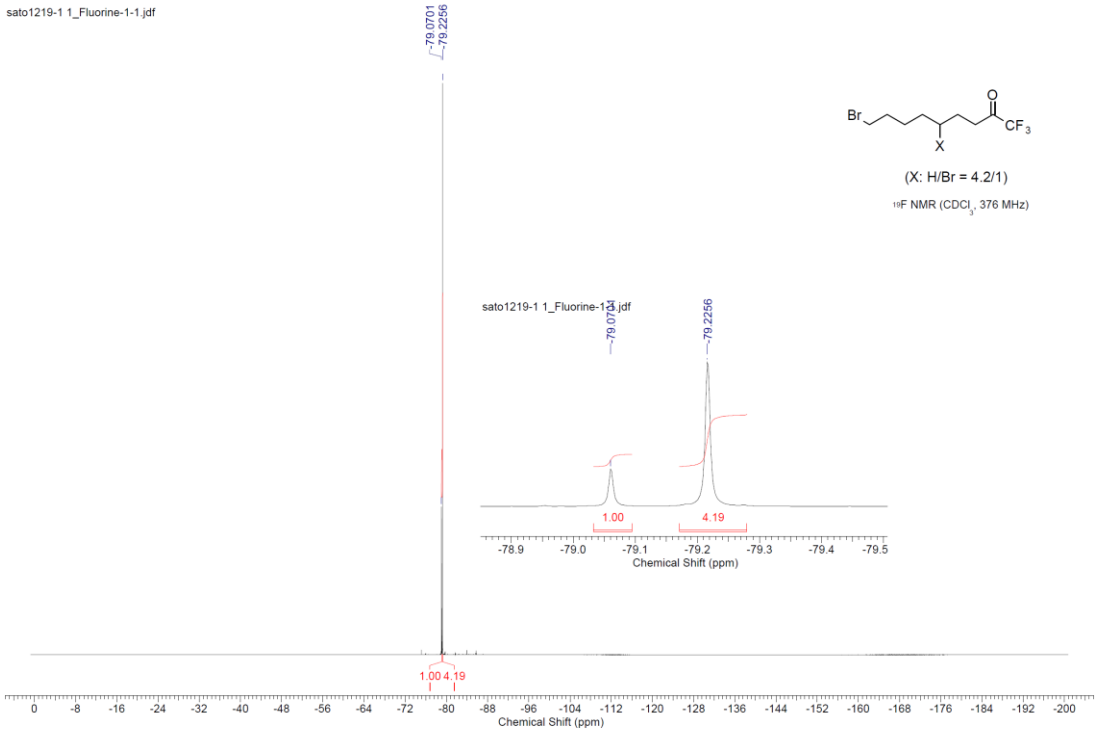

Figure S69. ^{19}F NMR of **3n/4n** (376 MHz, $CDCl_3$)

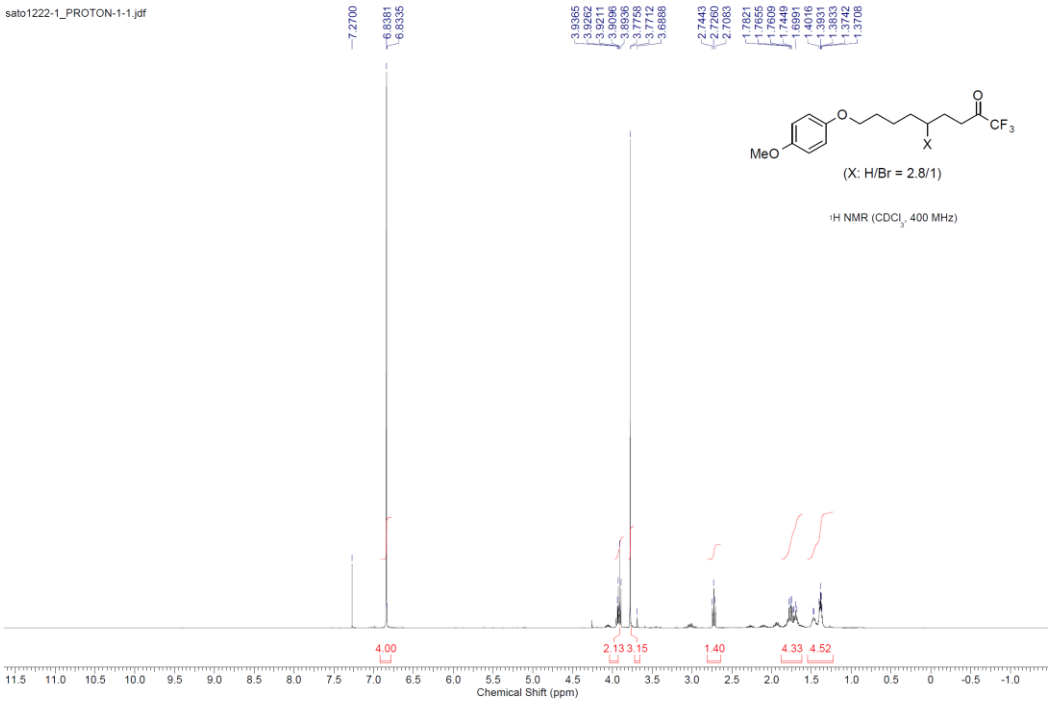

Figure S70. ^{1}H NMR of **3o/4o** (400 MHz, $CDCl_3$)

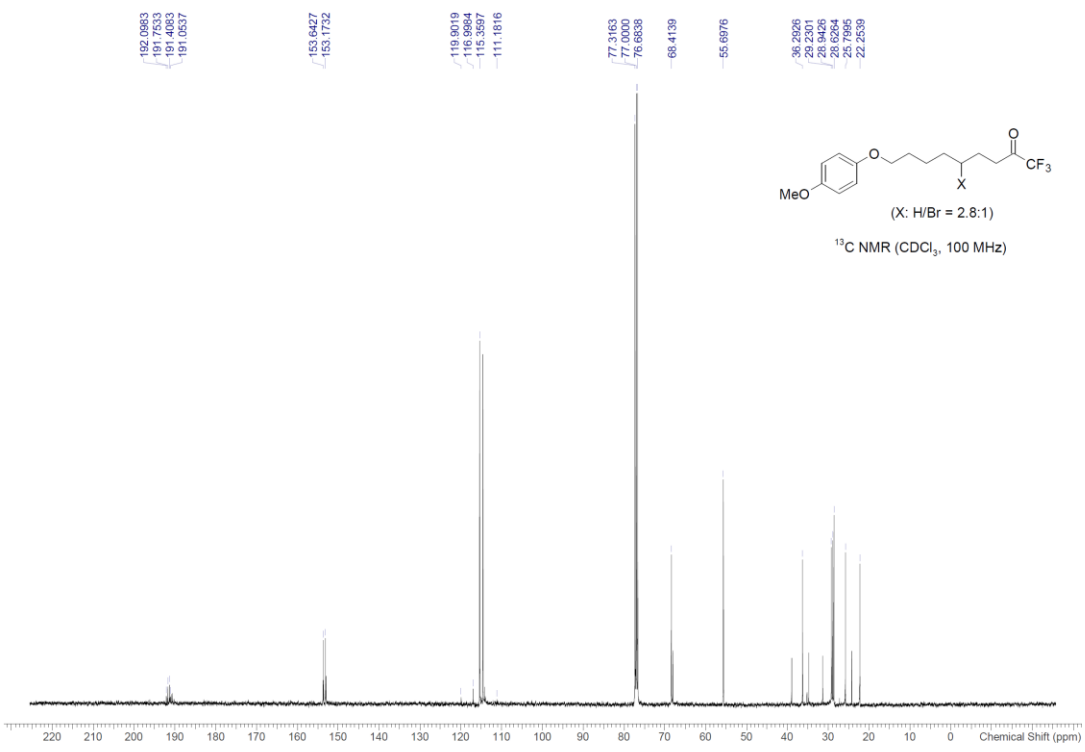

Figure S71. ^{13}C NMR of **3o/4o** (100 MHz, $CDCl_3$)

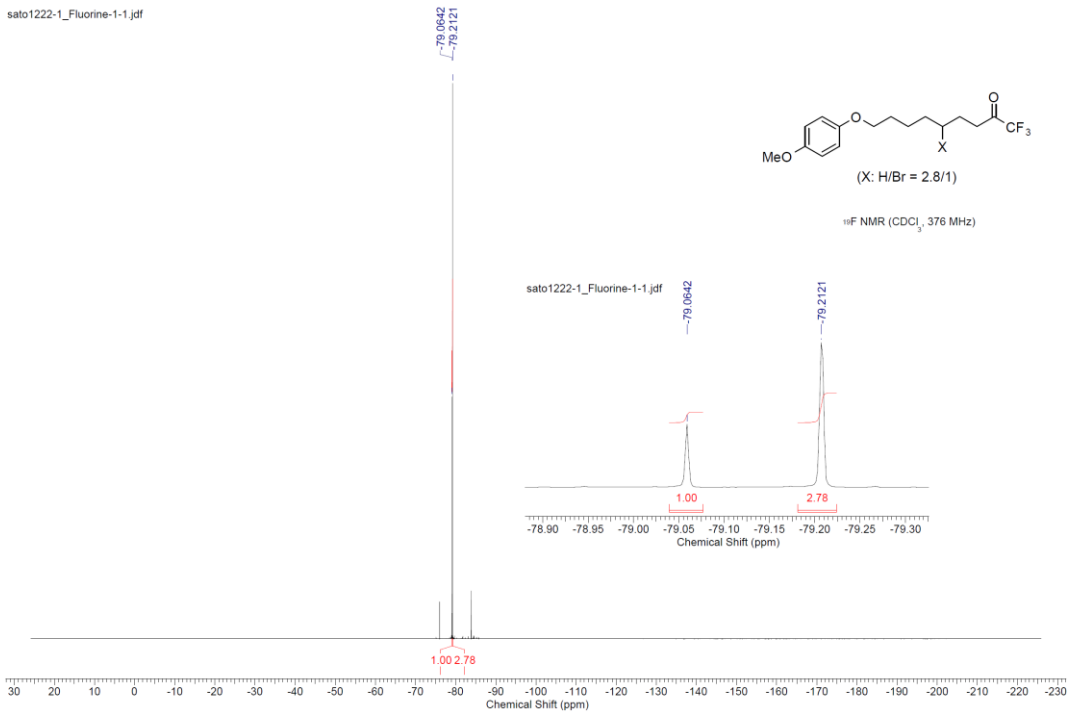

Figure S72. ^{19}F NMR of **3o/4o** (376 MHz, $CDCl_3$)

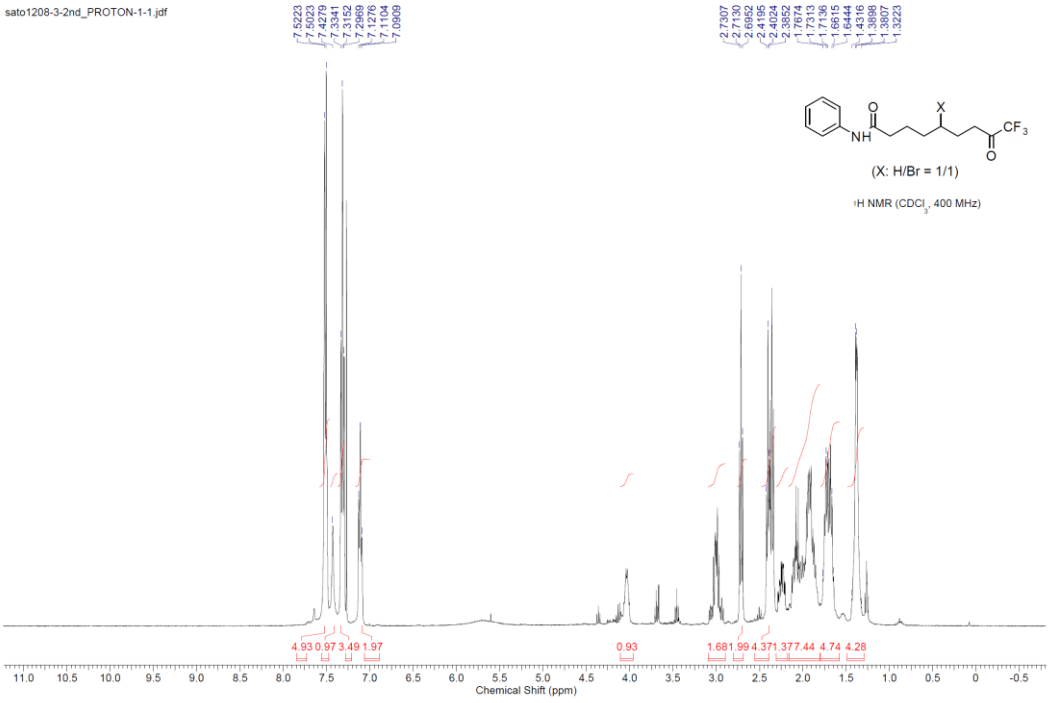

Figure S73. ^{1}H NMR of **3p/4p** (400 MHz, $CDCl_3$)

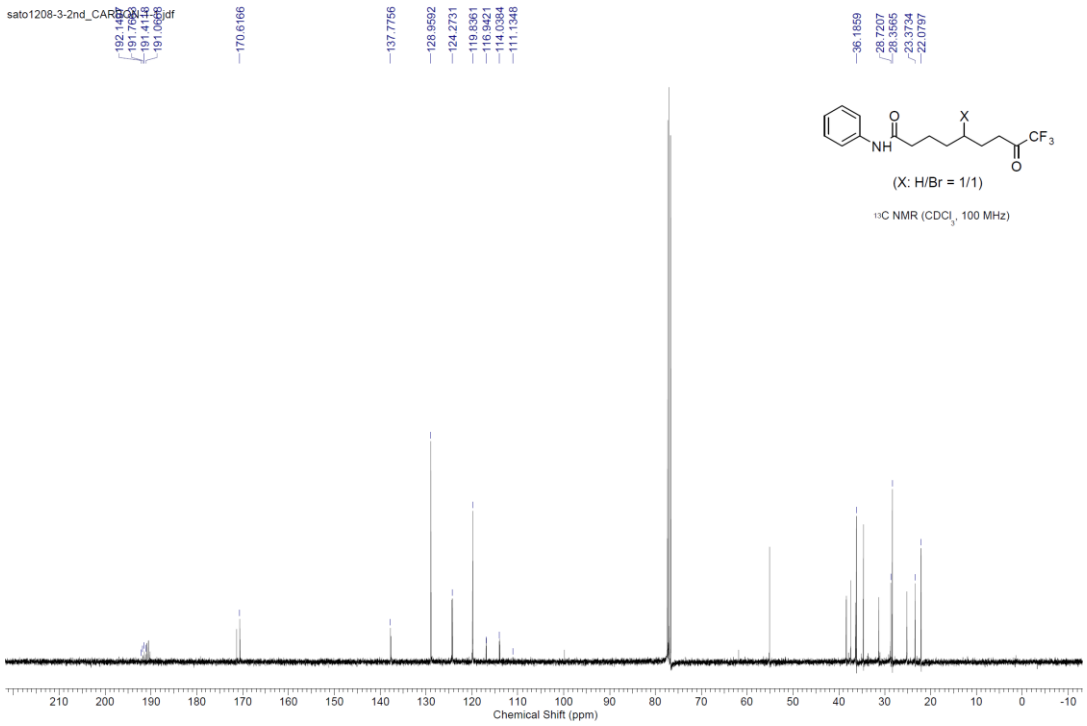

Figure S74. ^{13}C NMR of **3p/4p** (100 MHz, $CDCl_3$)

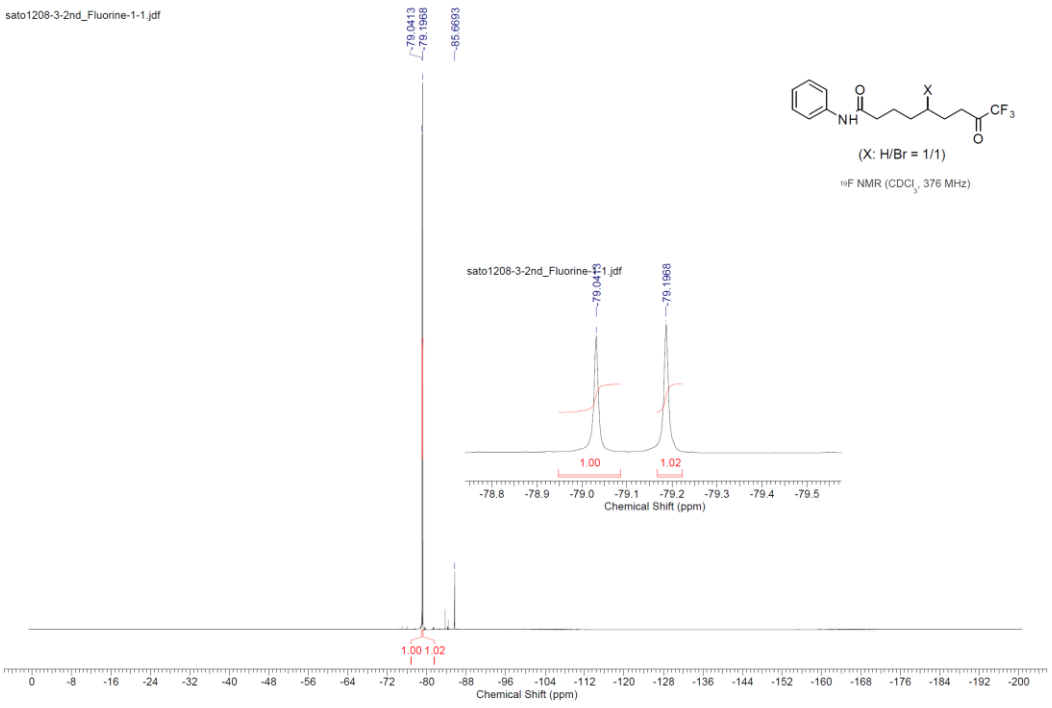

Figure S75. ^{19}F NMR of **3p/4p** (376 MHz, $CDCl_3$)

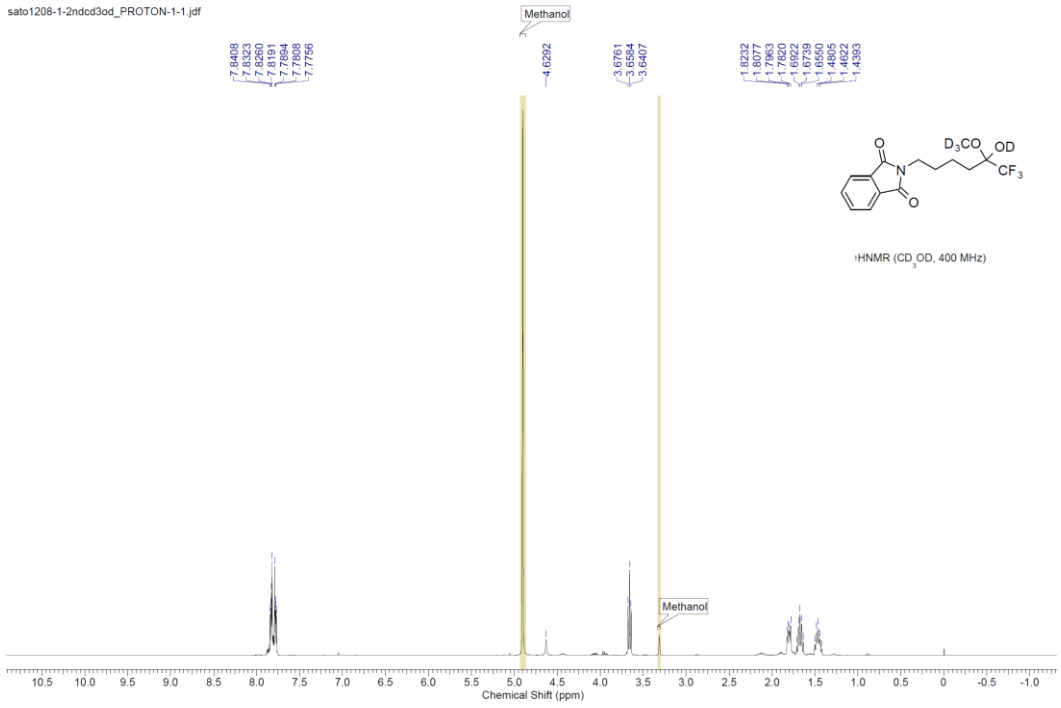

Figure S76. ^{1}H NMR of **3q** (400 MHz, CD_3OD)

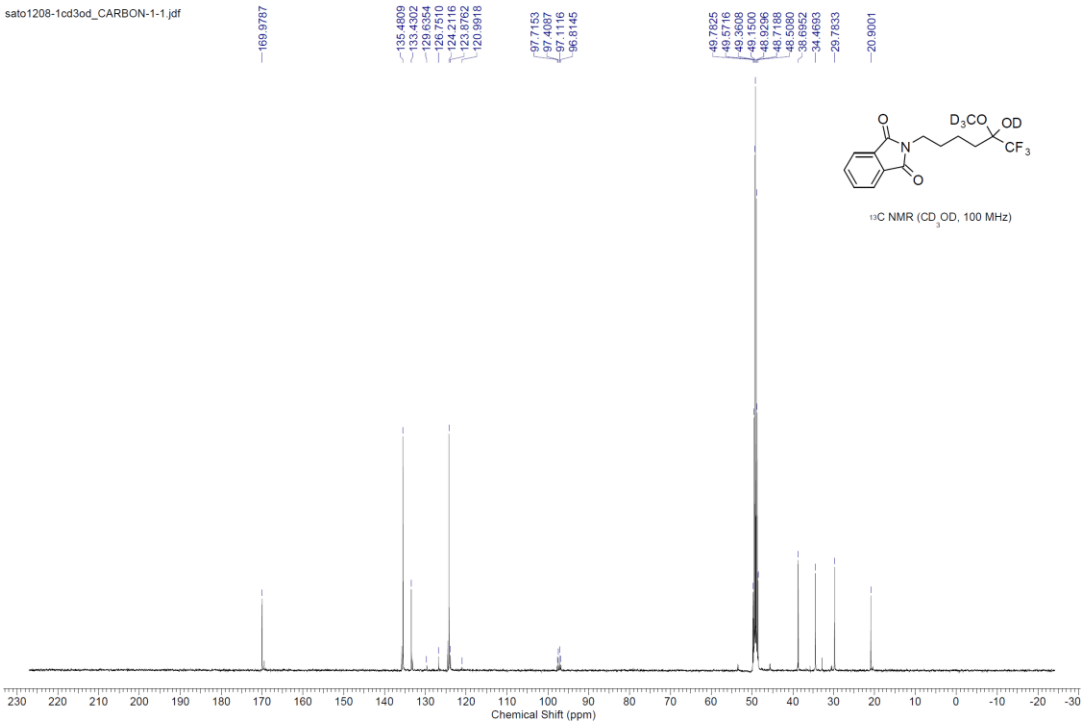

Figure S77. ^{13}C NMR of **3q** (100 MHz, CD_3OD)

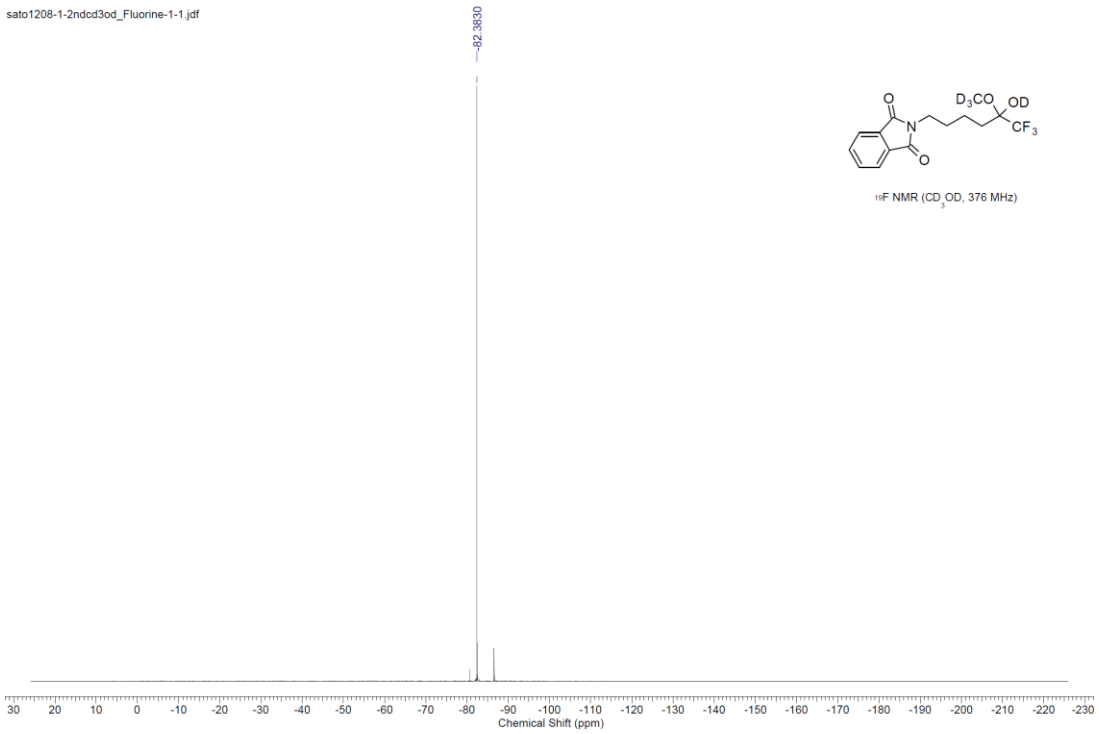

Figure S78. ^{19}F NMR of **3q** (376 MHz, CD_3OD)

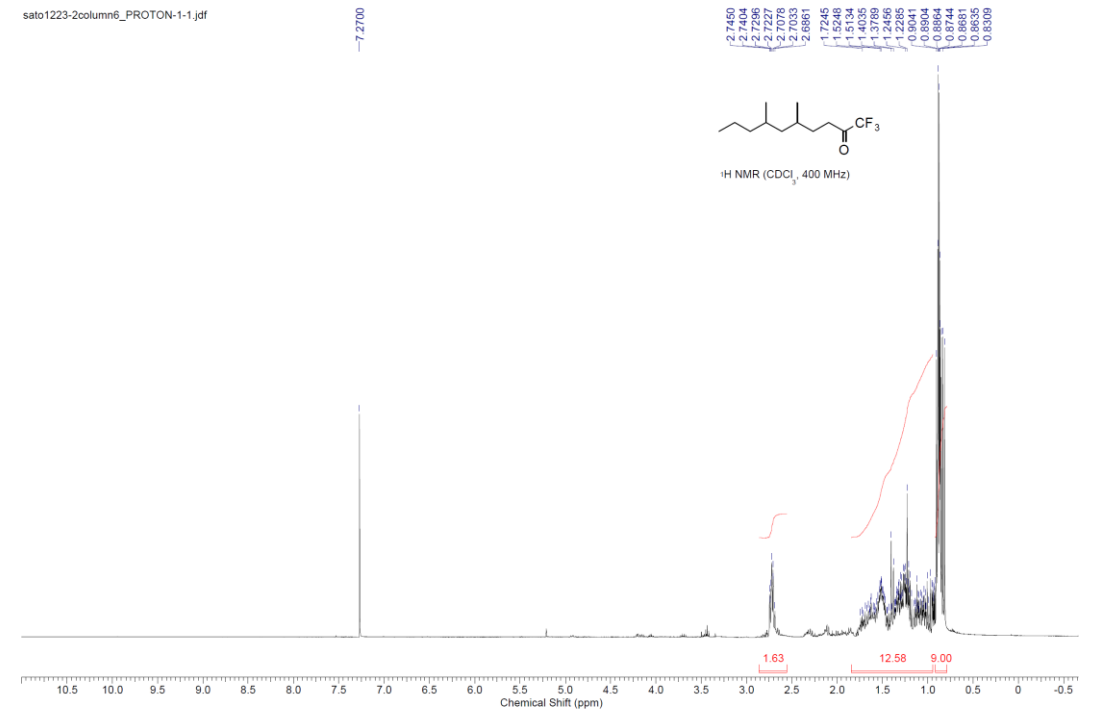

Figure S79. ^{1}H NMR of **3r** (400 MHz, $CDCl_3$)

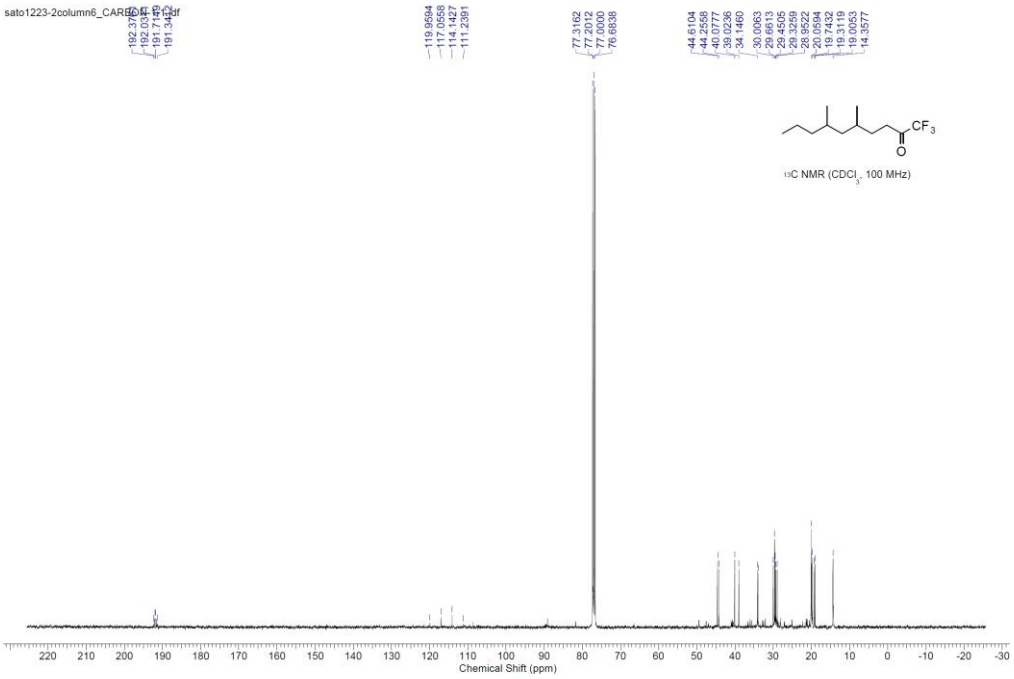

Figure S80. ^{13}C NMR of **3r** (100 MHz, $CDCl_3$)

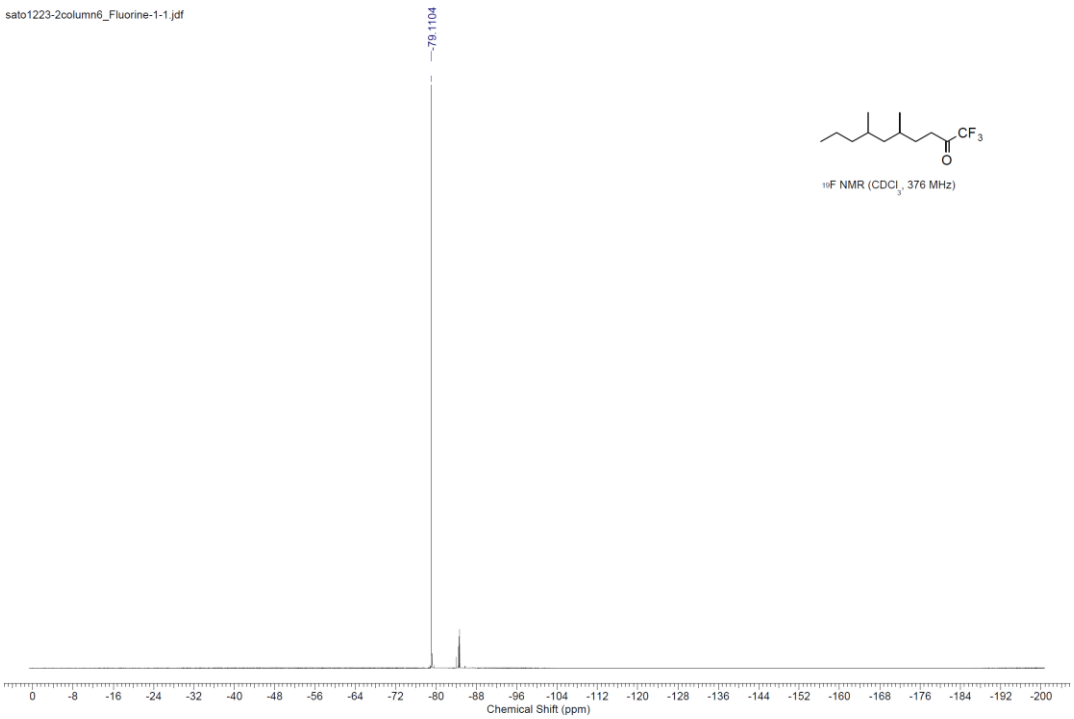

Figure S81. ^{19}F NMR of **3r** (376 MHz, $CDCl_3$)

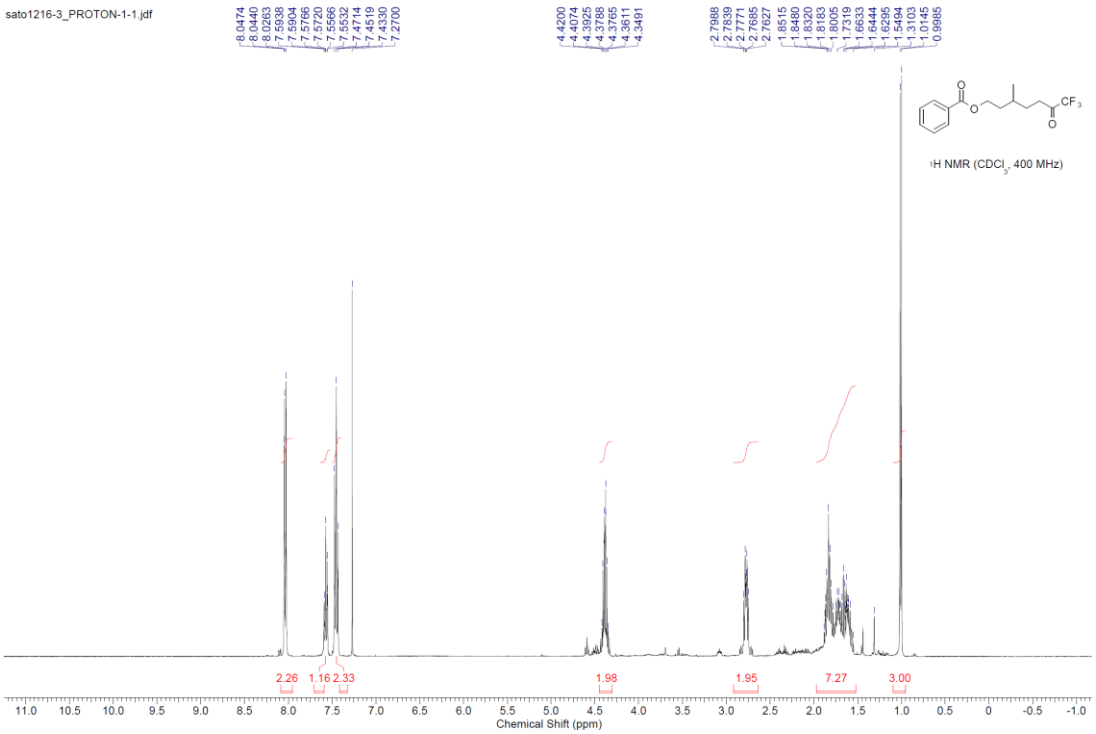

Figure S82. ^{1}H NMR of **3s** (400 MHz, $CDCl_3$)

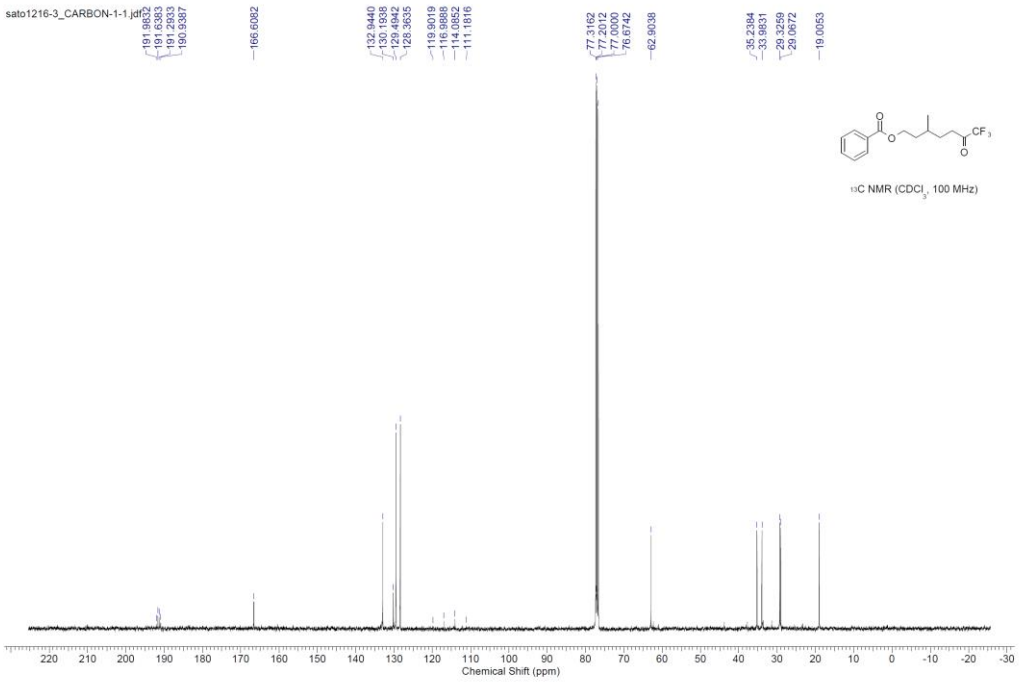

Figure S83. ^{13}C NMR of **3s** (100 MHz, $CDCl_3$)

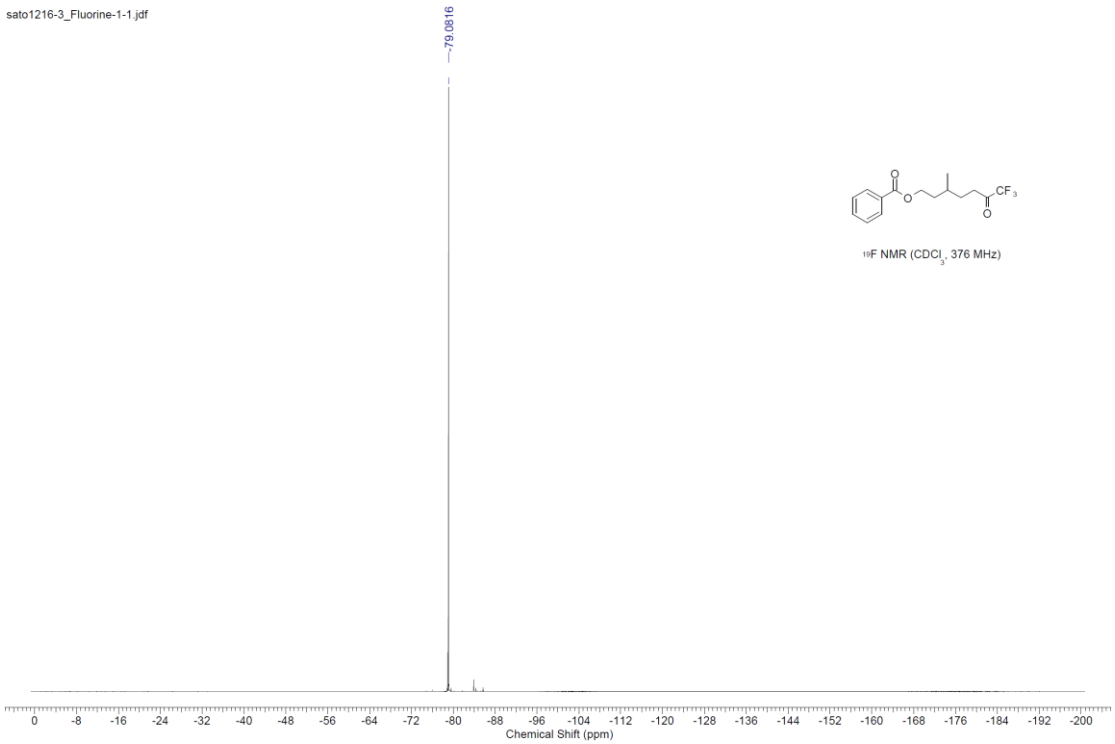

Figure S84. ^{19}F NMR of **3s** (376 MHz, $CDCl_3$)

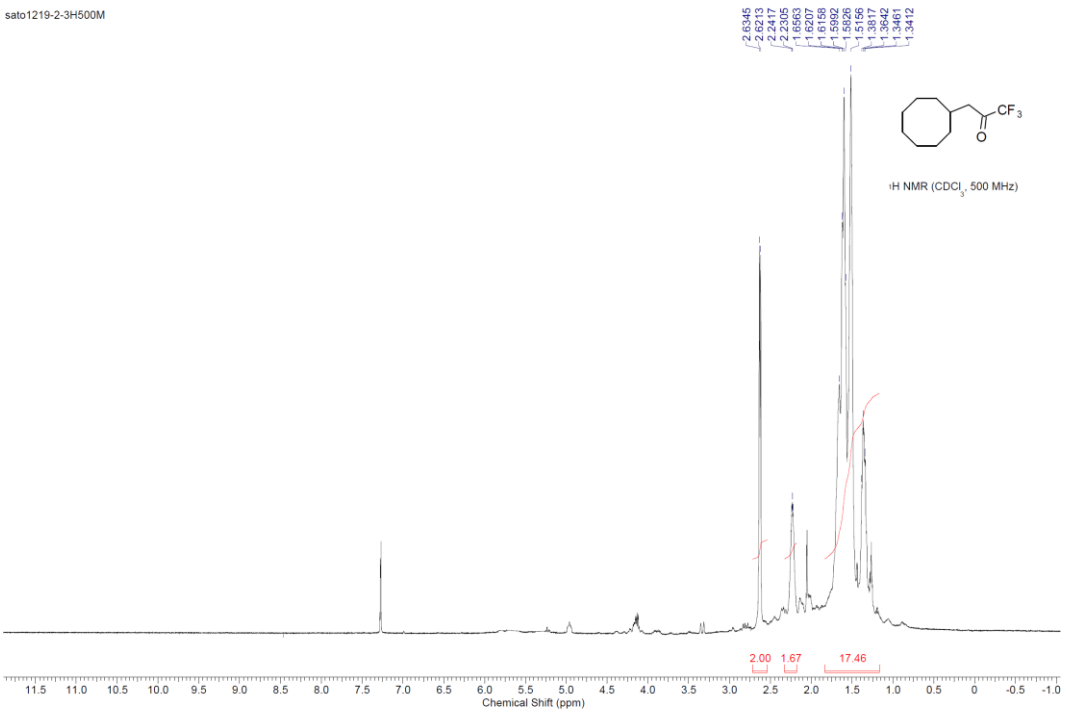

Figure S85. ^{1}H NMR of **3t** (500 MHz, $CDCl_3$)

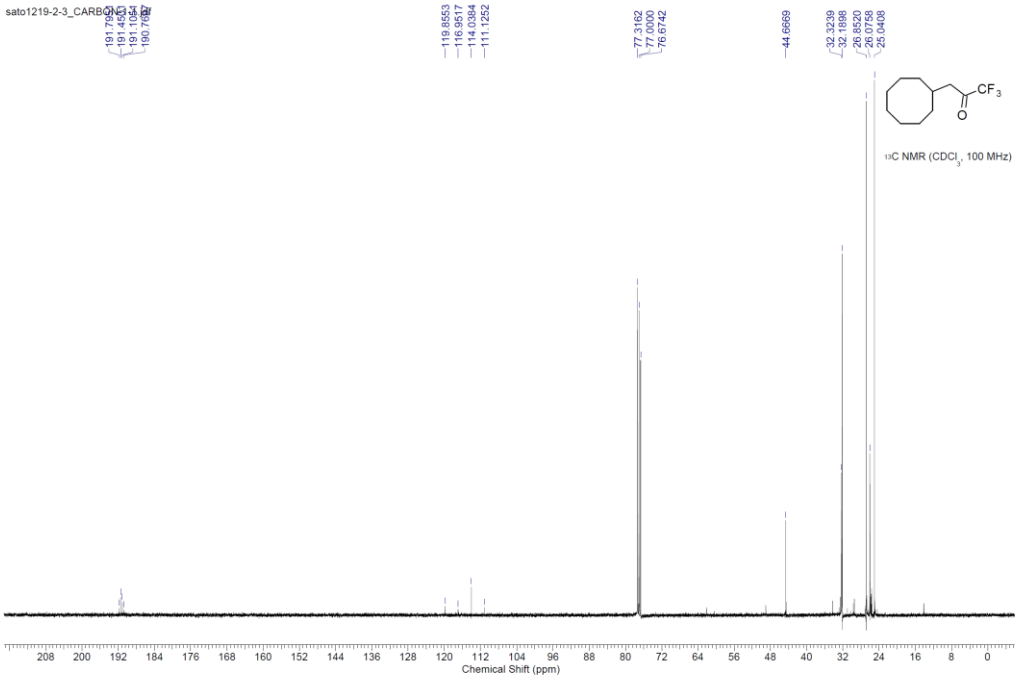

Figure S86. ^{13}C NMR of **3t** (100 MHz, $CDCl_3$)

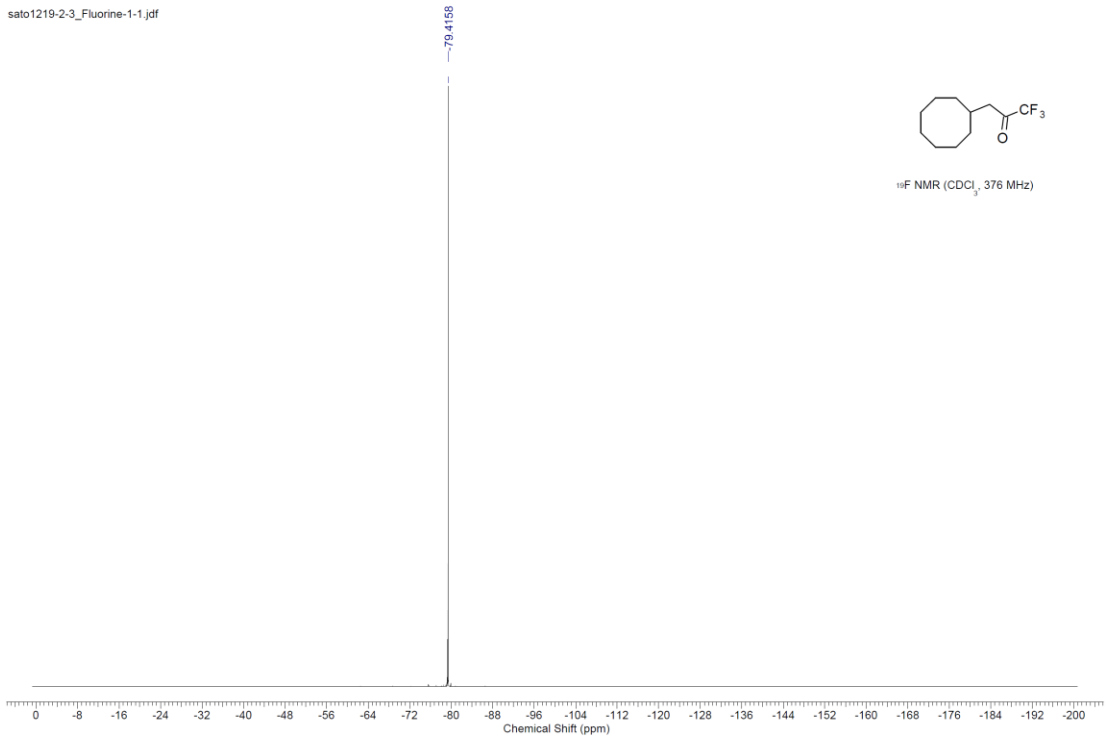

Figure S87. ^{19}F NMR of **3t** (376 MHz, $CDCl_3$)

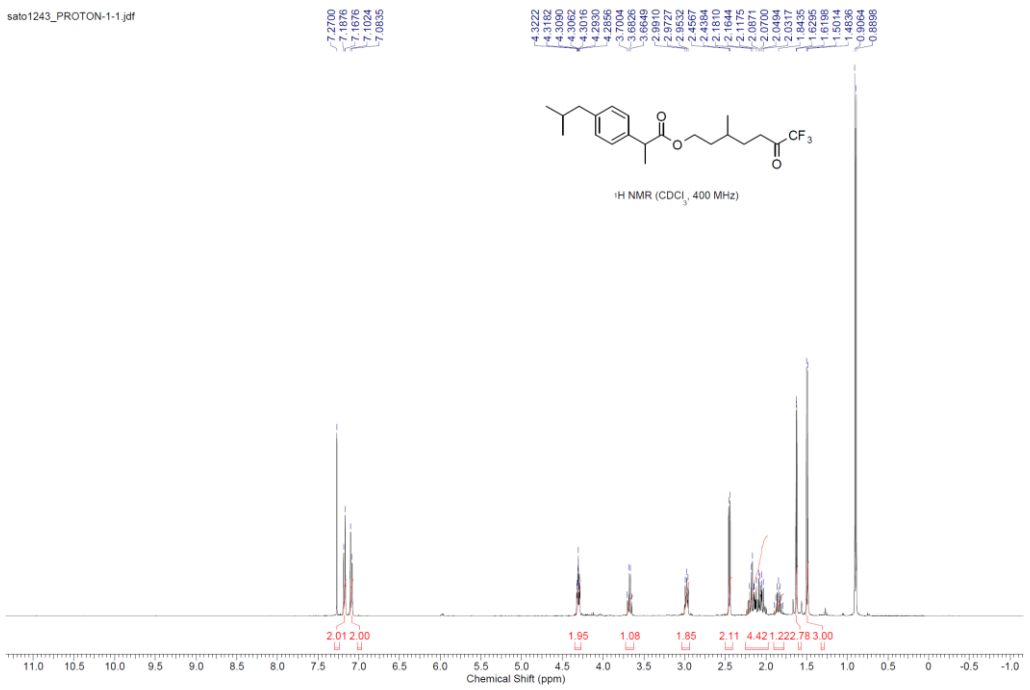

Figure S88. ^{1}H NMR of **3u** (400 MHz, $CDCl_3$)

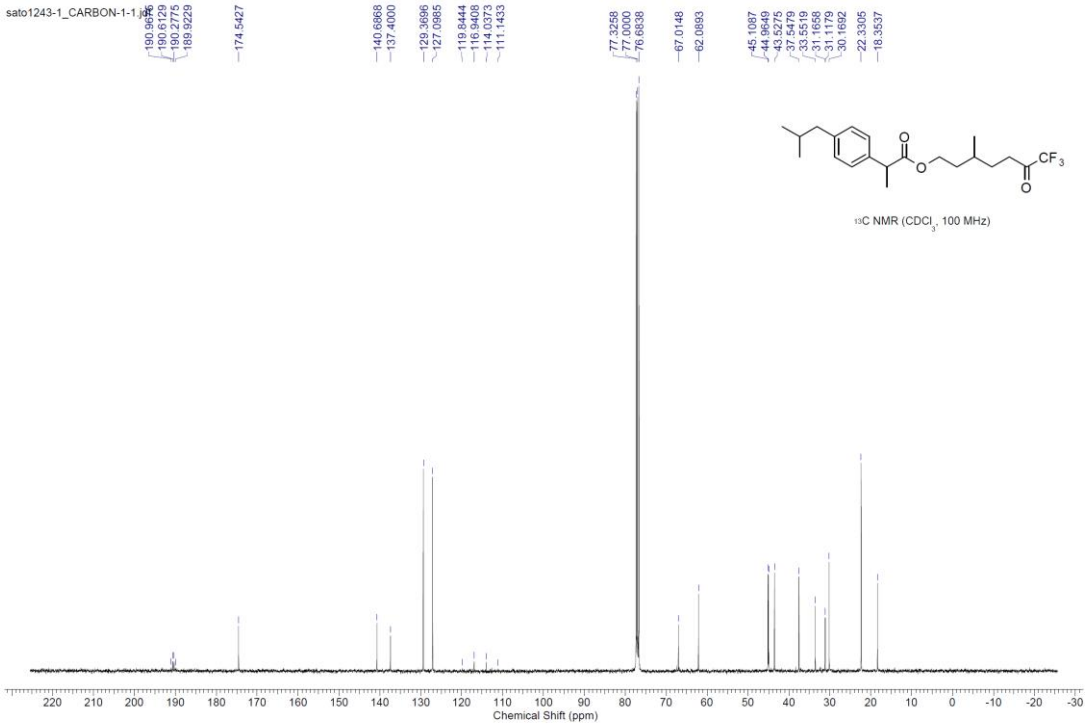

Figure S89. ^{13}C NMR of **3u** (100 MHz, $CDCl_3$)

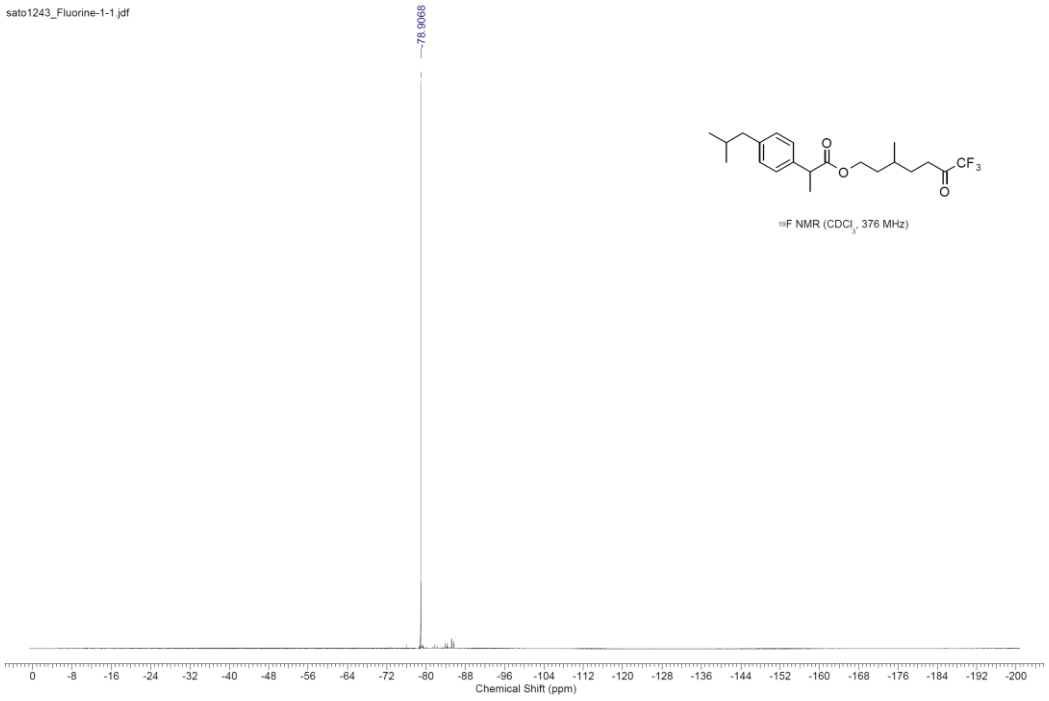

Figure S90. ^{19}F NMR of **3u** (376 MHz, $CDCl_3$)

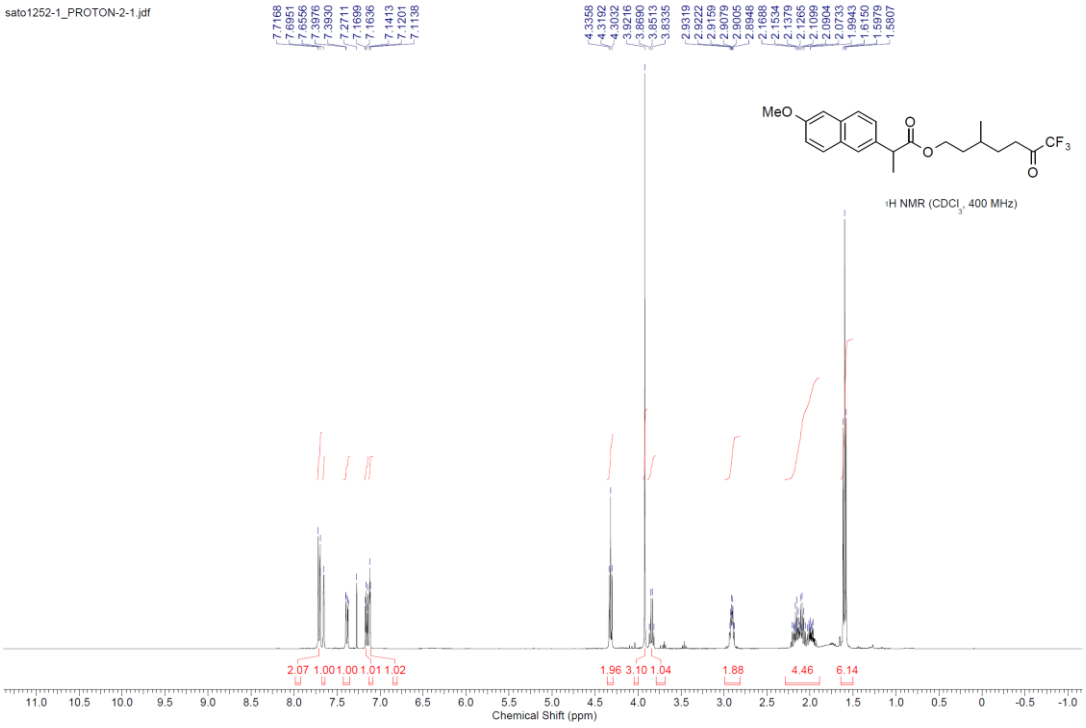

Figure S91. ^{1}H NMR of **3v** (400 MHz, $CDCl_3$)

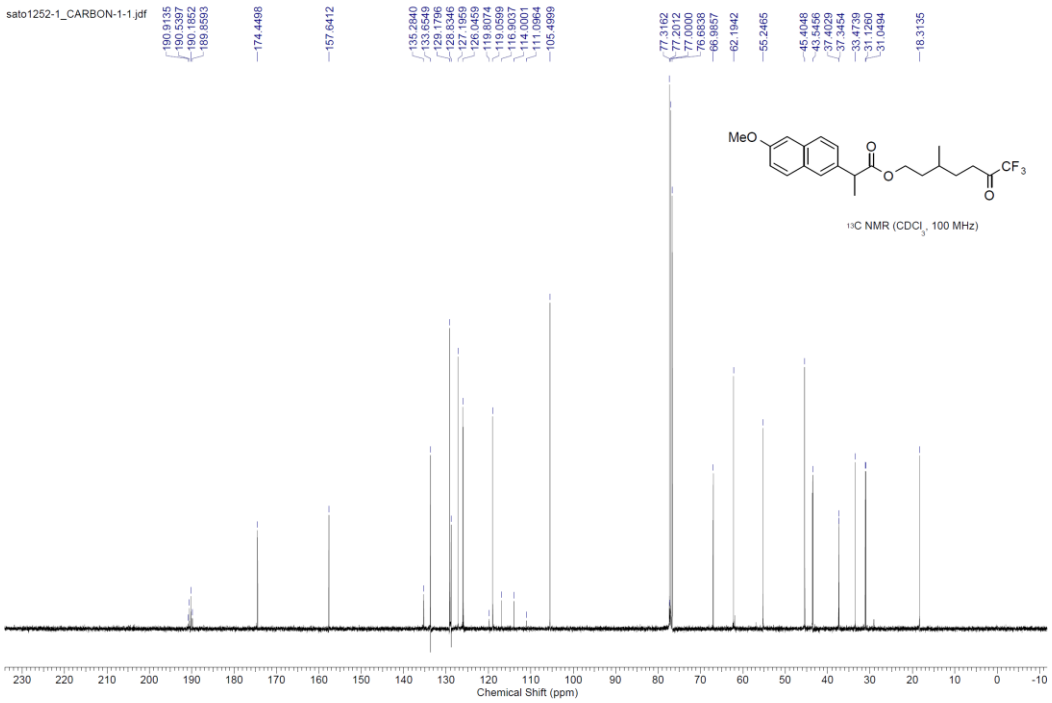

Figure S92. ^{13}C NMR of **3v** (100 MHz, $CDCl_3$)

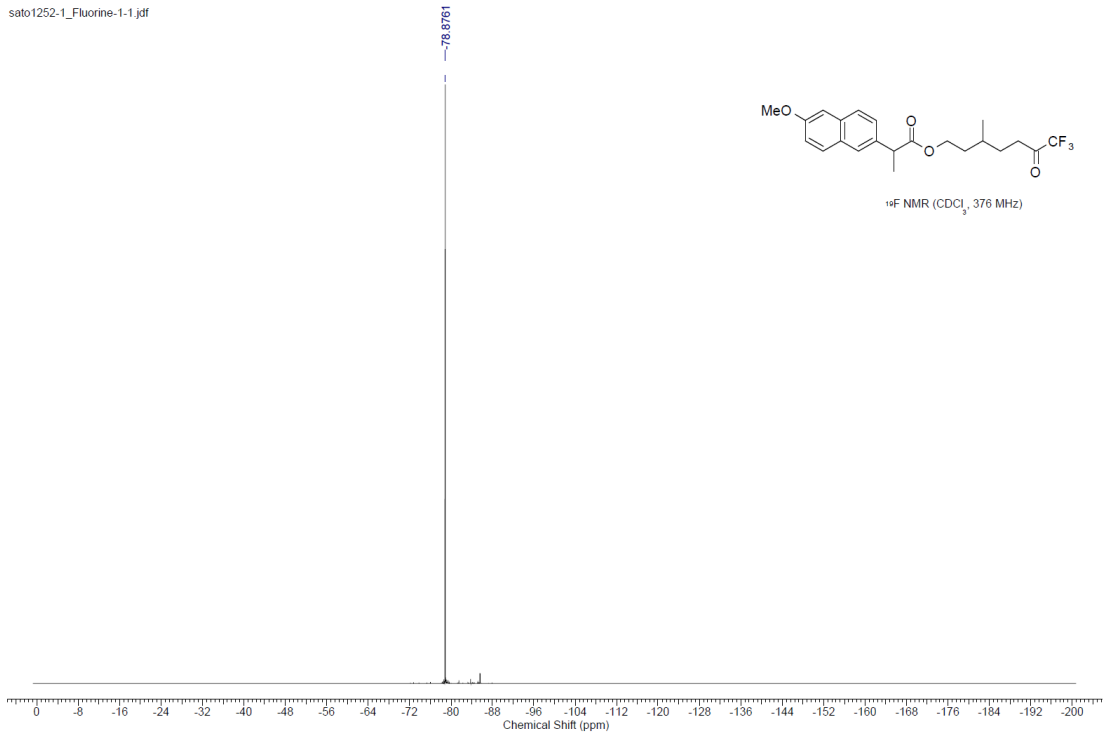

Figure S93. ^{19}F NMR of **3v** (376 MHz, $CDCl_3$)

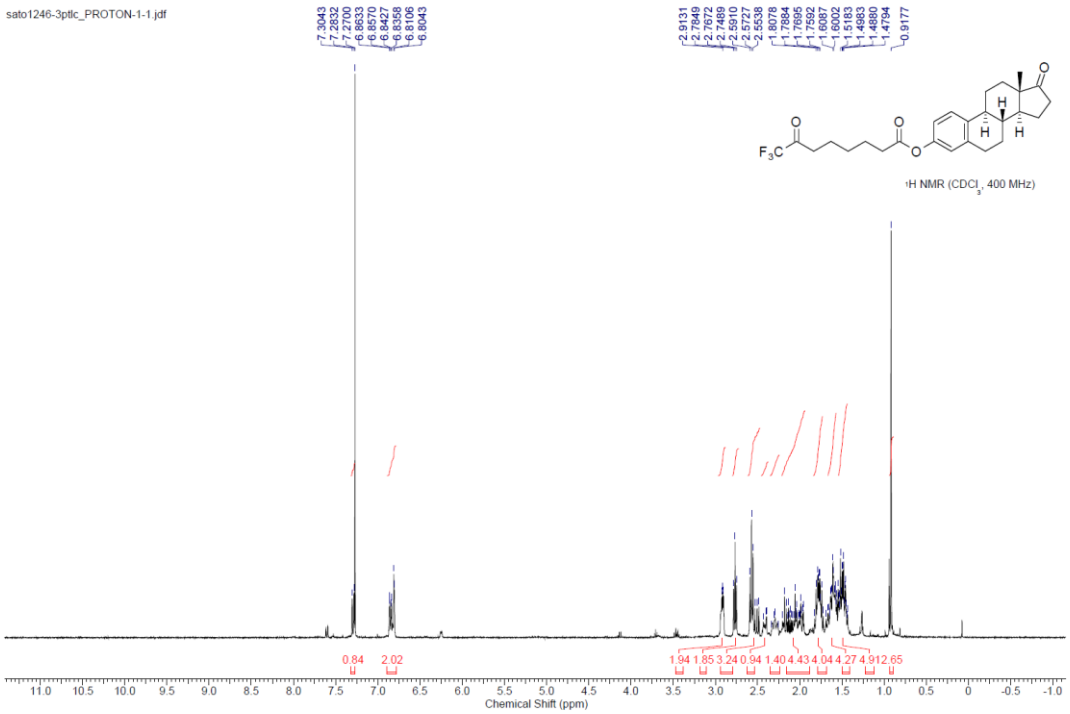

Figure S94. ^{1}H NMR of **3w** (400 MHz, $CDCl_3$)

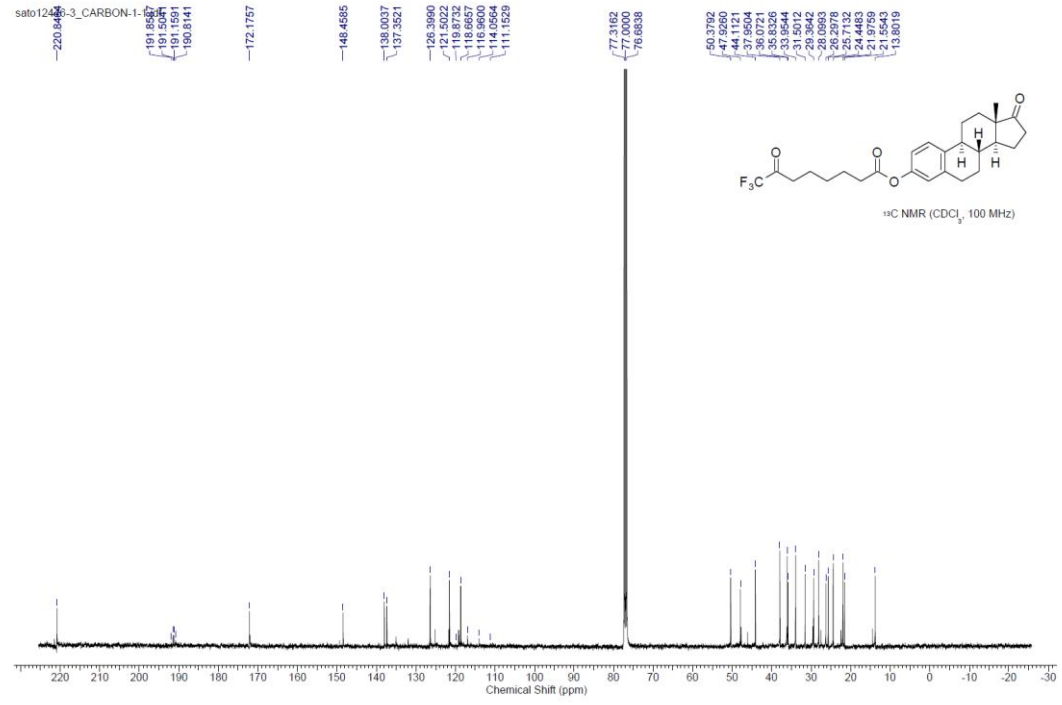

Figure S95. ^{13}C NMR of **3w** (100 MHz, $CDCl_3$)

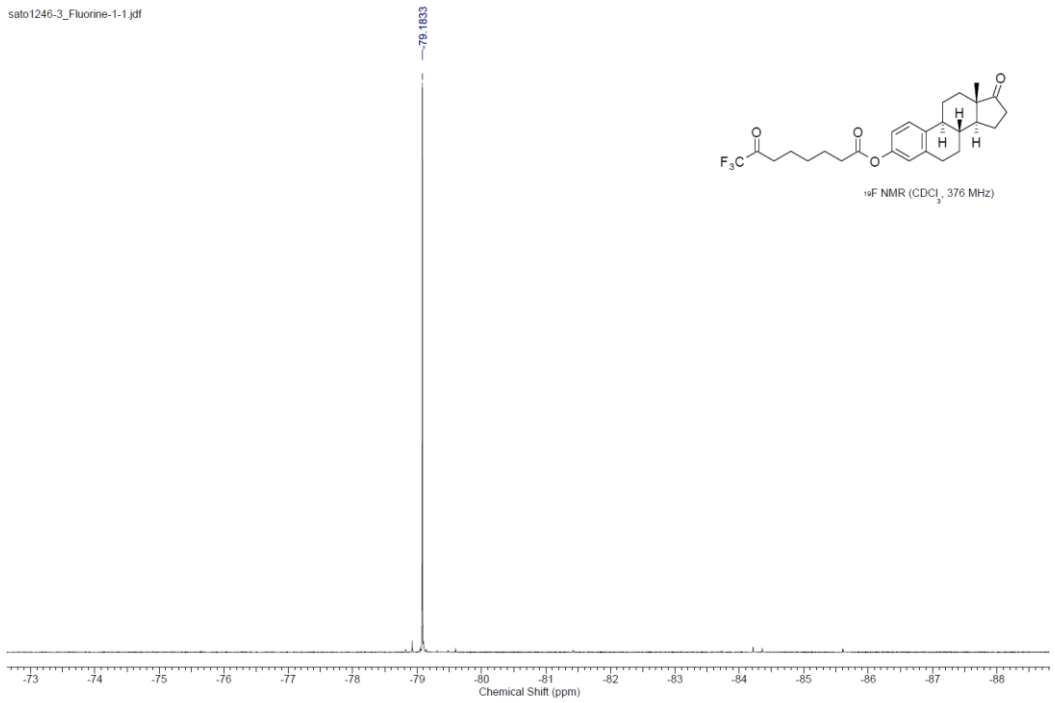

Figure S96. ^{19}F NMR of **3w** (376 MHz, $CDCl_3$)

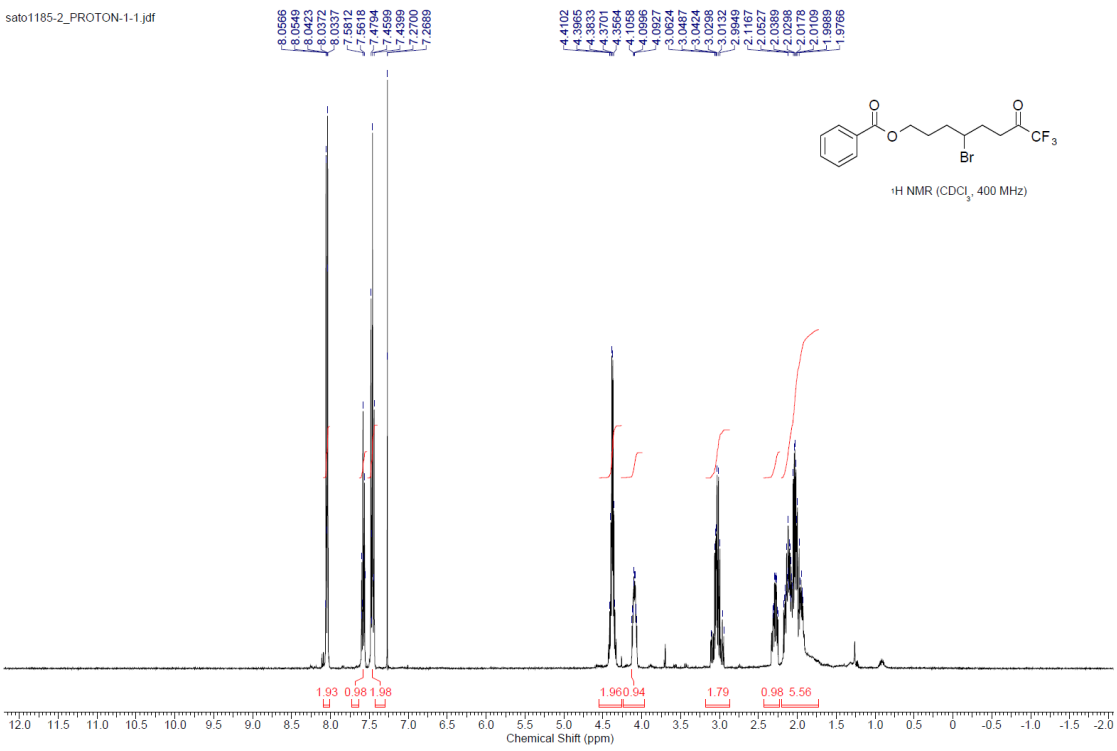

Figure S97. ^{1}H NMR of **4a** (400 MHz, $CDCl_3$)

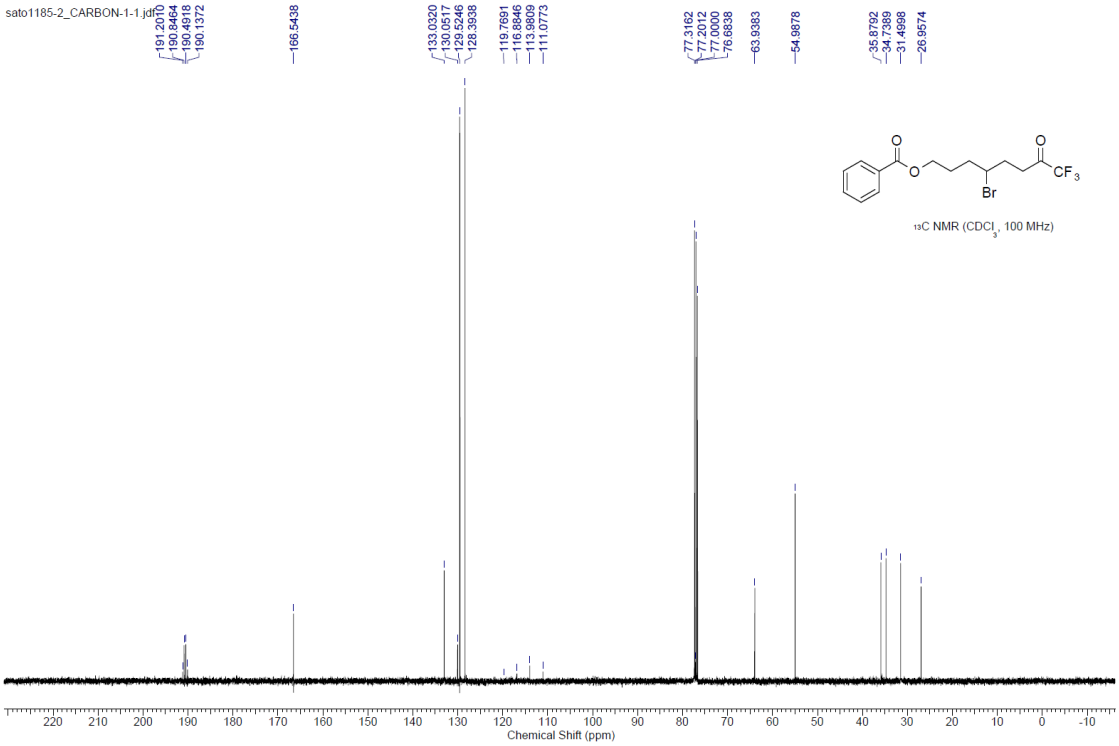

Figure S98. ^{13}C NMR of **4a** (100 MHz, $CDCl_3$)

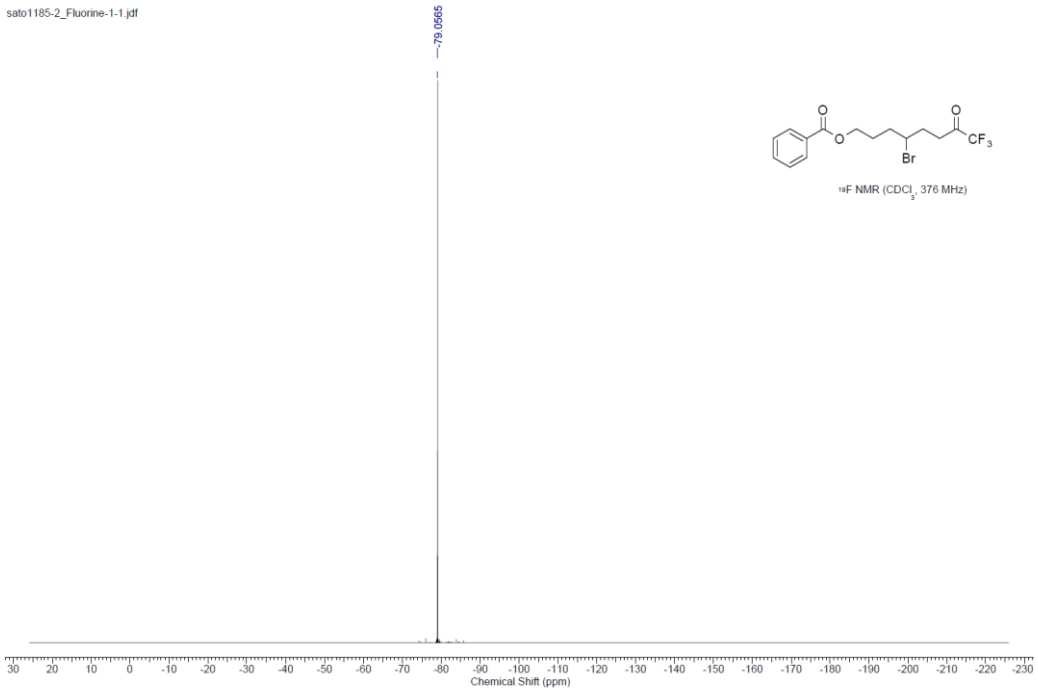

Figure S99. ^{19}F NMR of **4a** (376 MHz, $CDCl_3$)

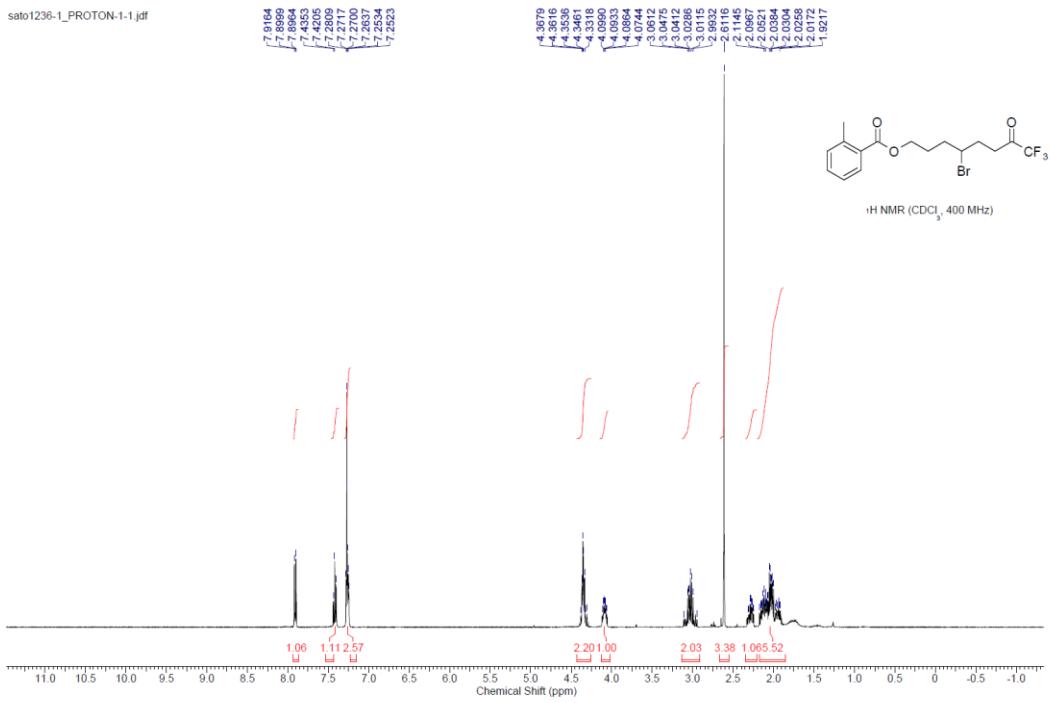

Figure S100. ^{1}H NMR of **4b** (400 MHz, $CDCl_3$)

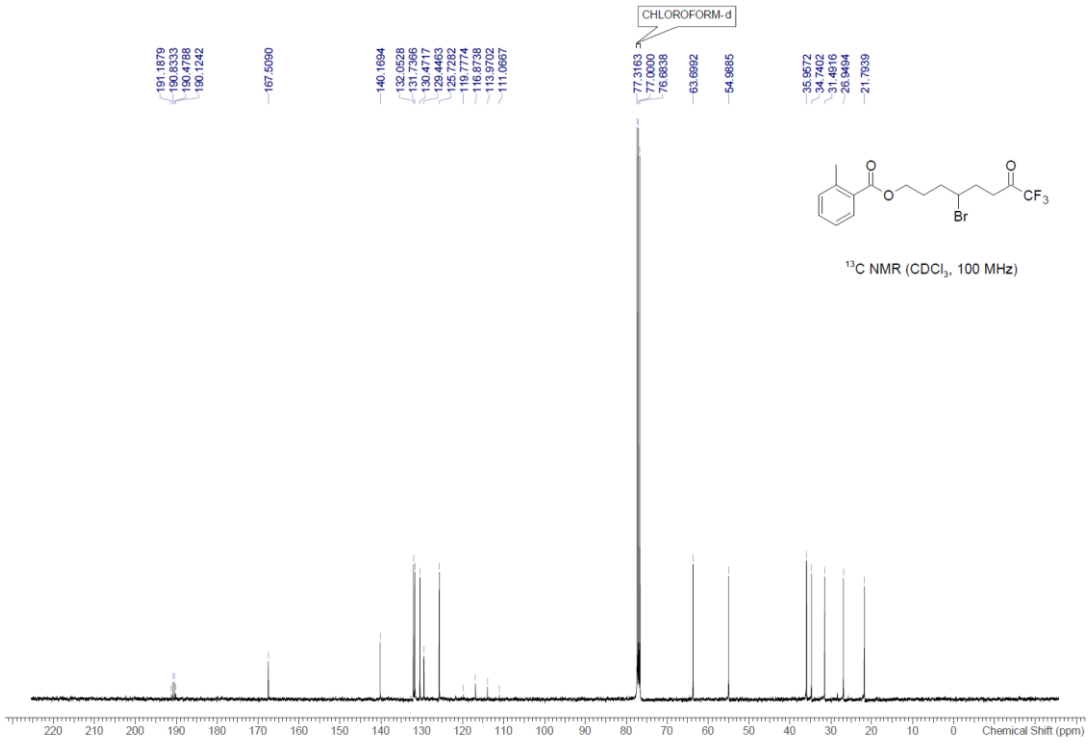

Figure S101. ^{13}C NMR of **4b** (100 MHz, $CDCl_3$)

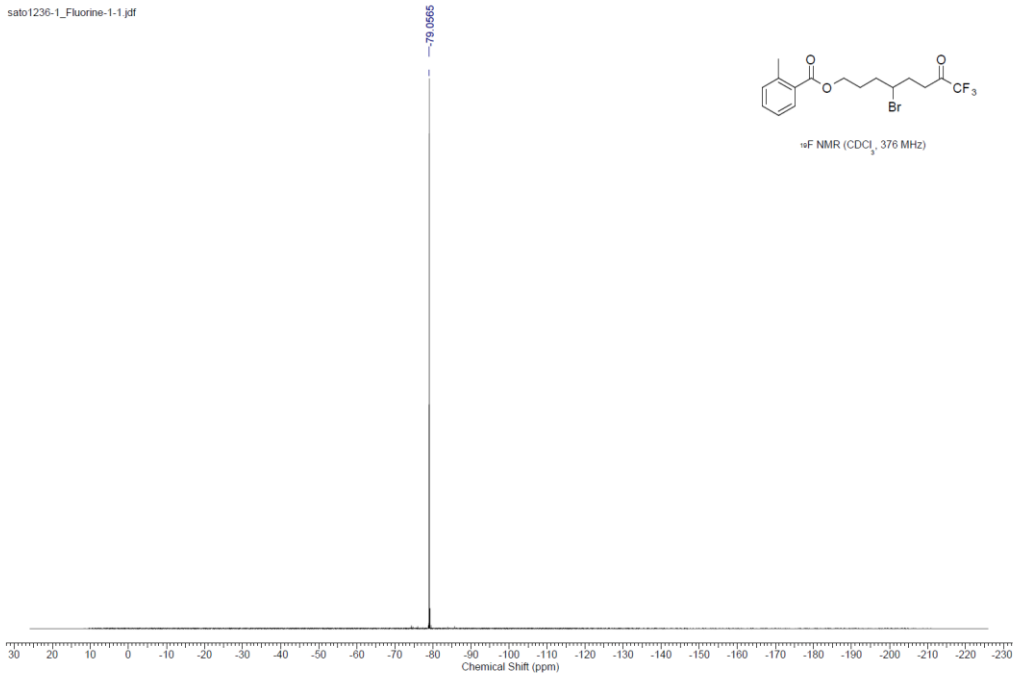

Figure S102. ^{19}F NMR of **4b** (376 MHz, $CDCl_3$)

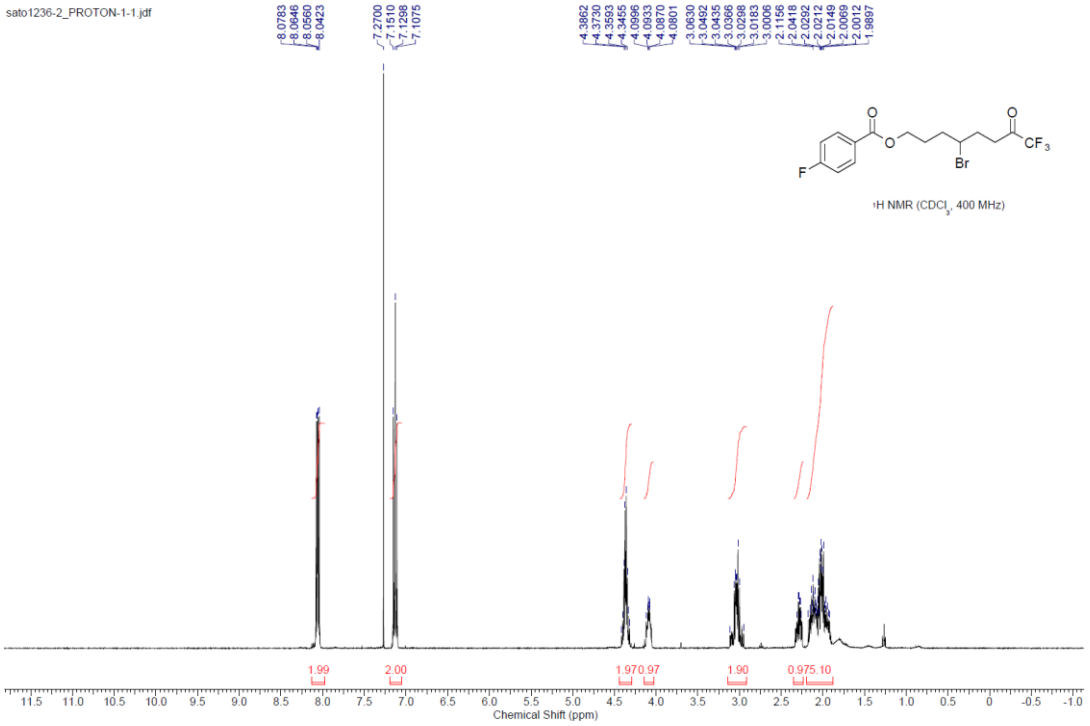

Figure S103. ^{1}H NMR of **4c** (400 MHz, $CDCl_3$)

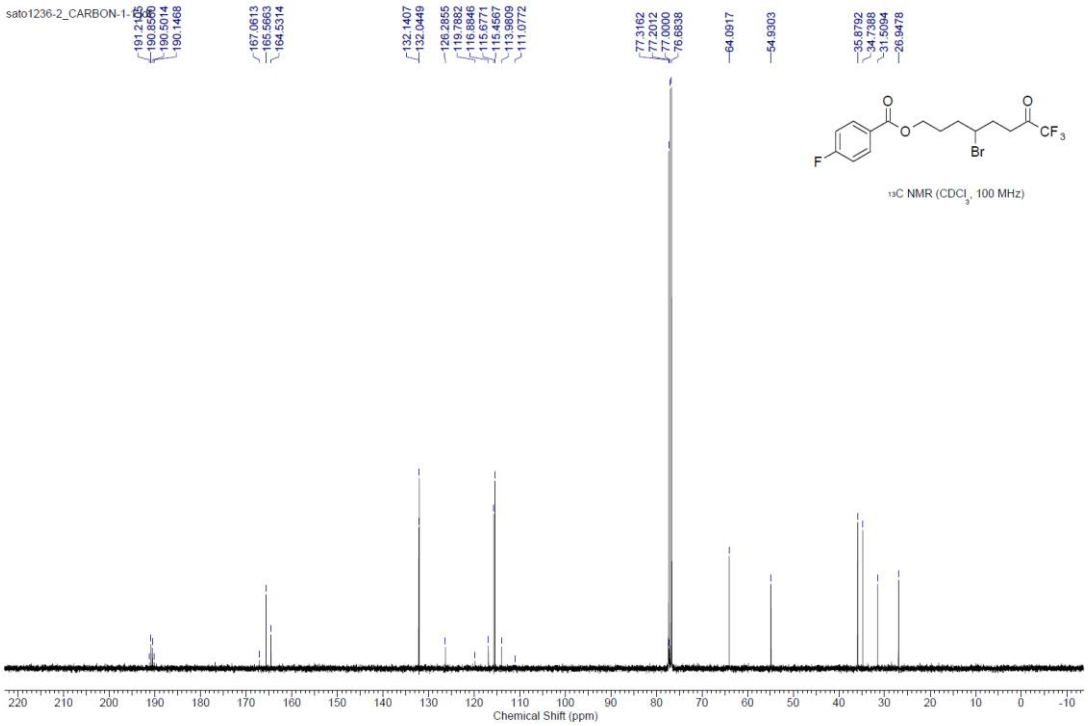

Figure S104. ^{13}C NMR of **4c** (100 MHz, $CDCl_3$)

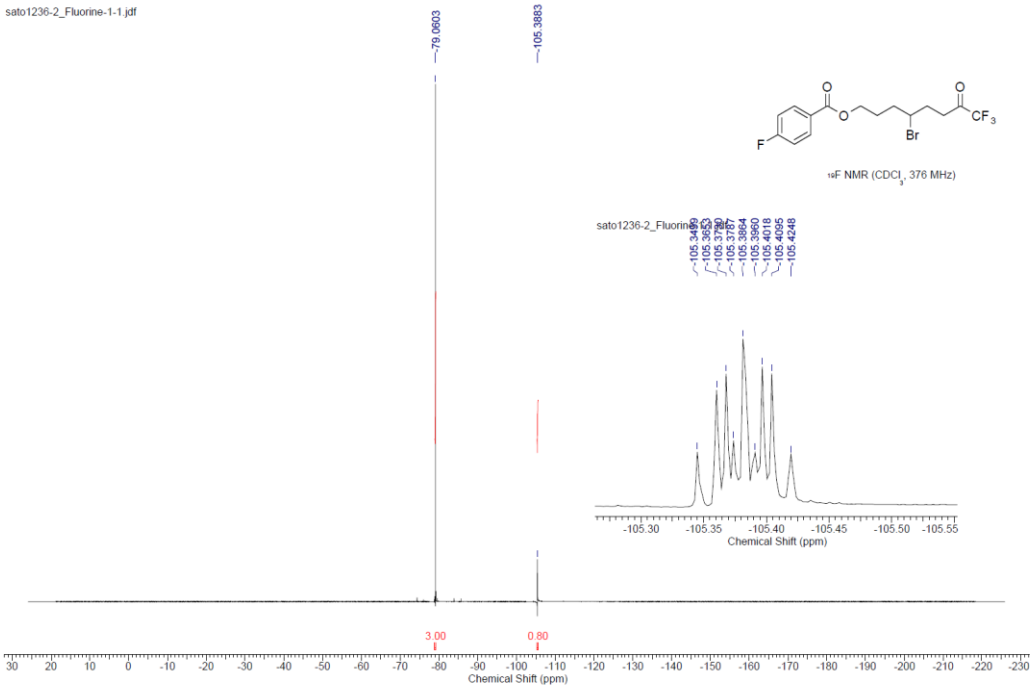

Figure S105. ^{19}F NMR of **4c** (376 MHz, $CDCl_3$)

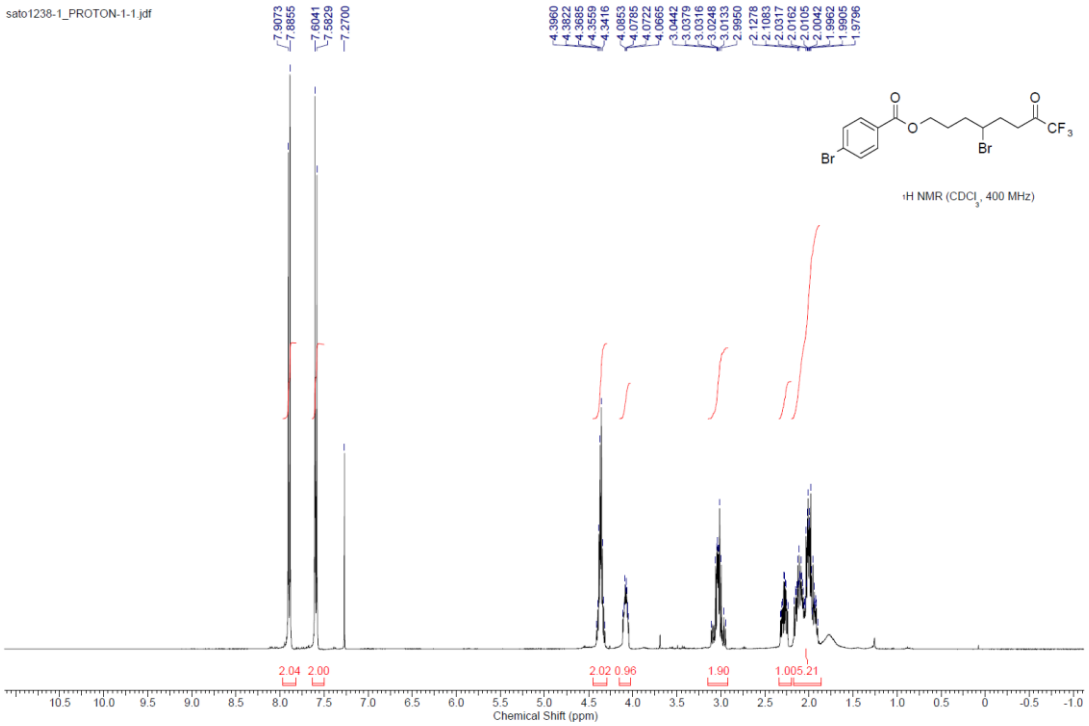

Figure S106. ^{1}H NMR of **4d** (400 MHz, $CDCl_3$)

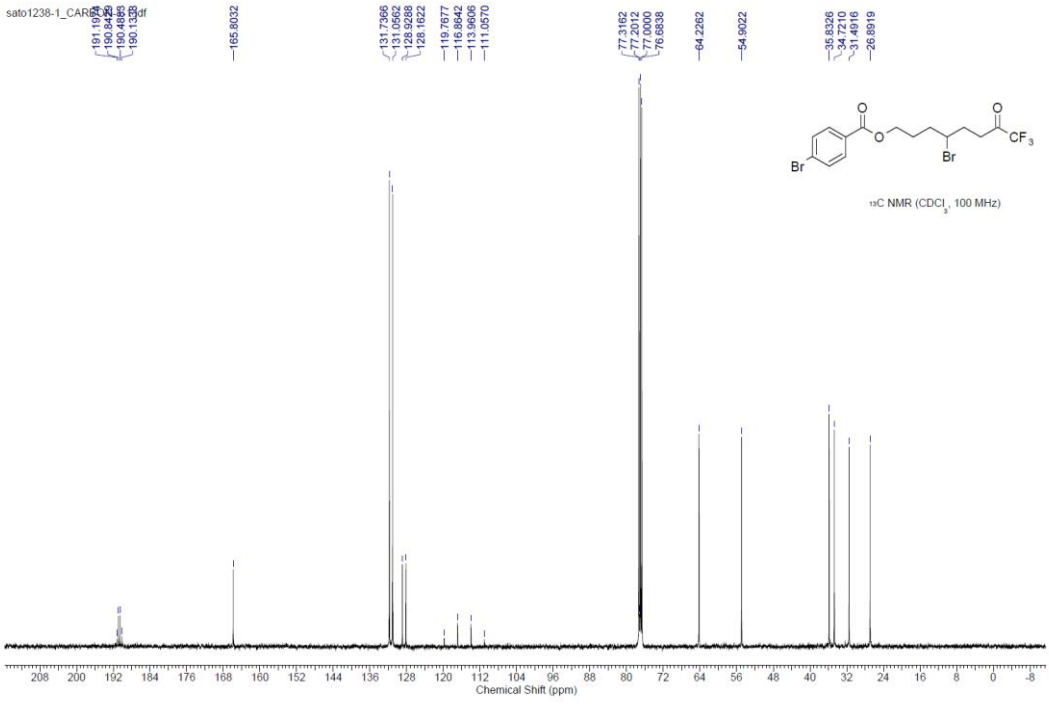

Figure S107. ^{13}C NMR of **4d** (100 MHz, $CDCl_3$)

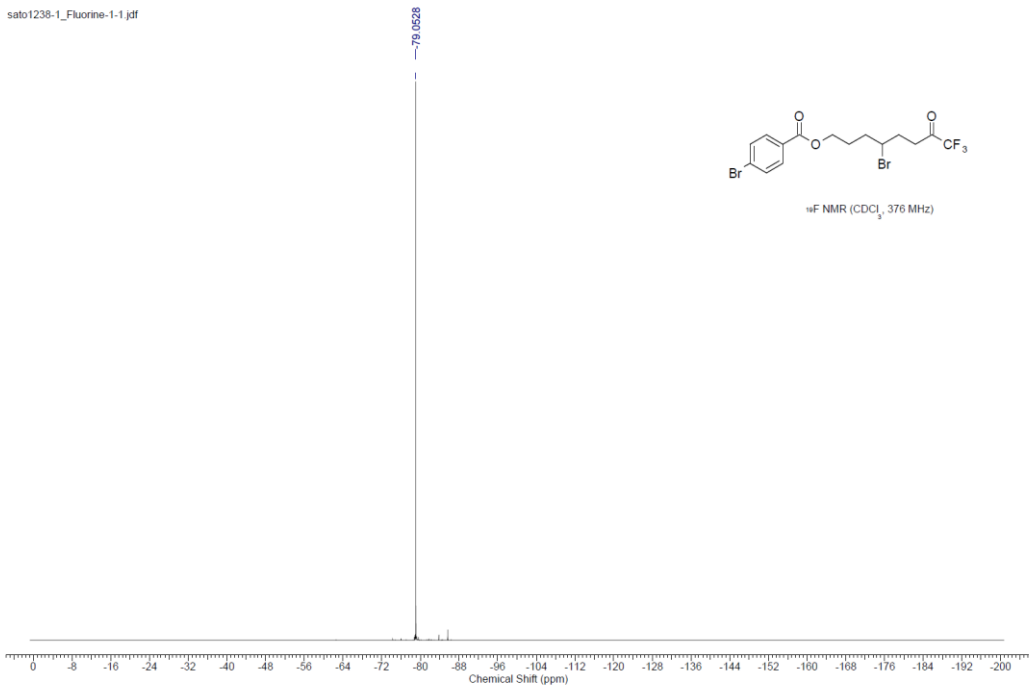

Figure S108. ^{19}F NMR of **4d** (376 MHz, $CDCl_3$)

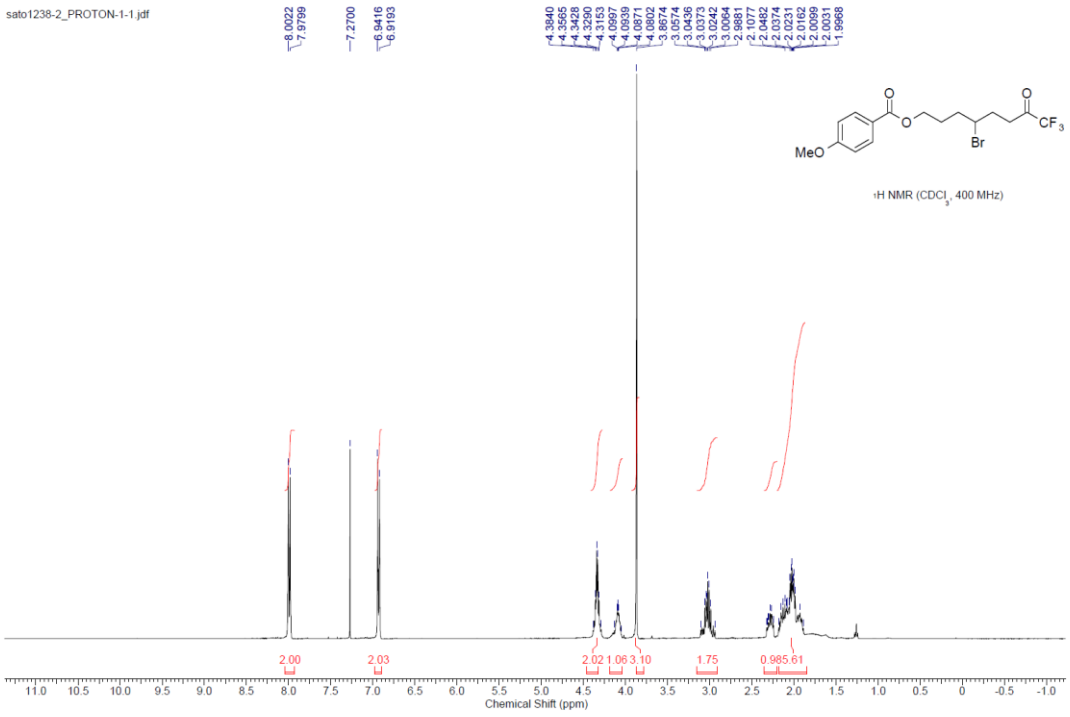

Figure S109. ^{1}H NMR of **4e** (400 MHz, $CDCl_3$)

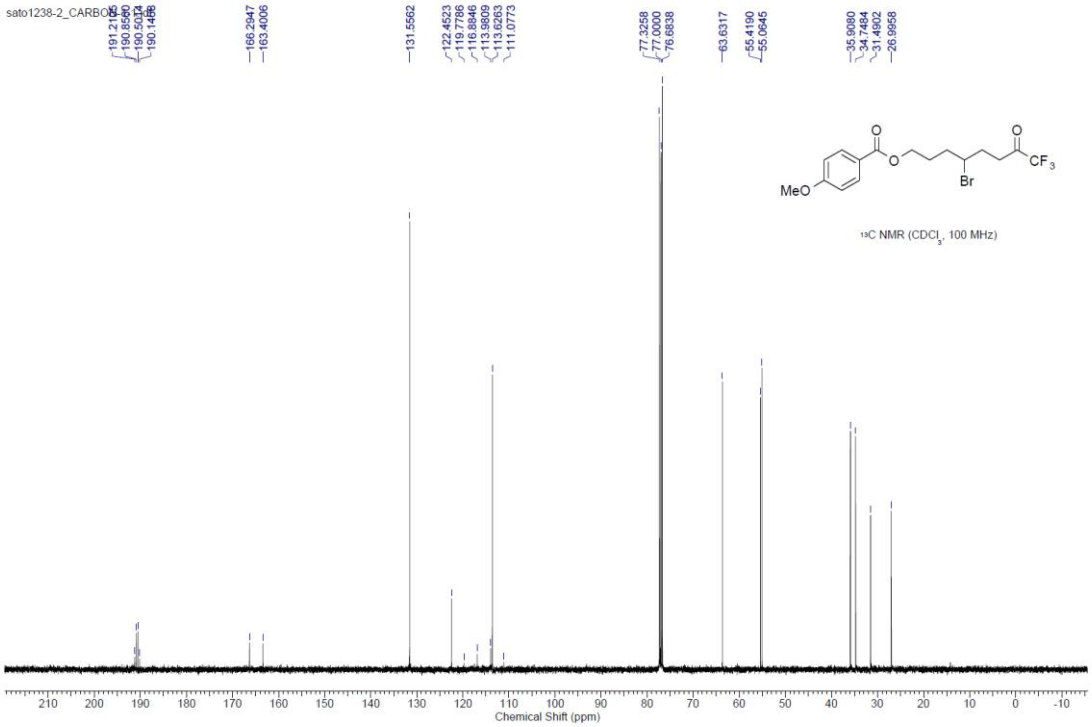

Figure S110. ^{13}C NMR of **4e** (100 MHz, $CDCl_3$)

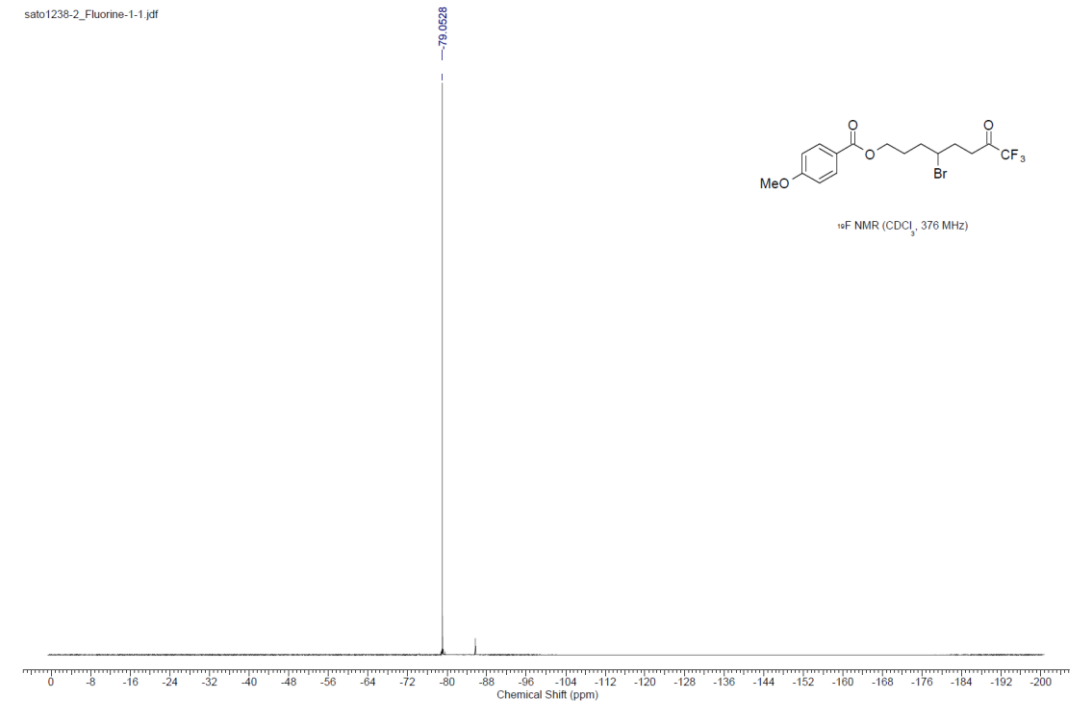

Figure S111. ^{19}F NMR of **4e** (376 MHz, $CDCl_3$)

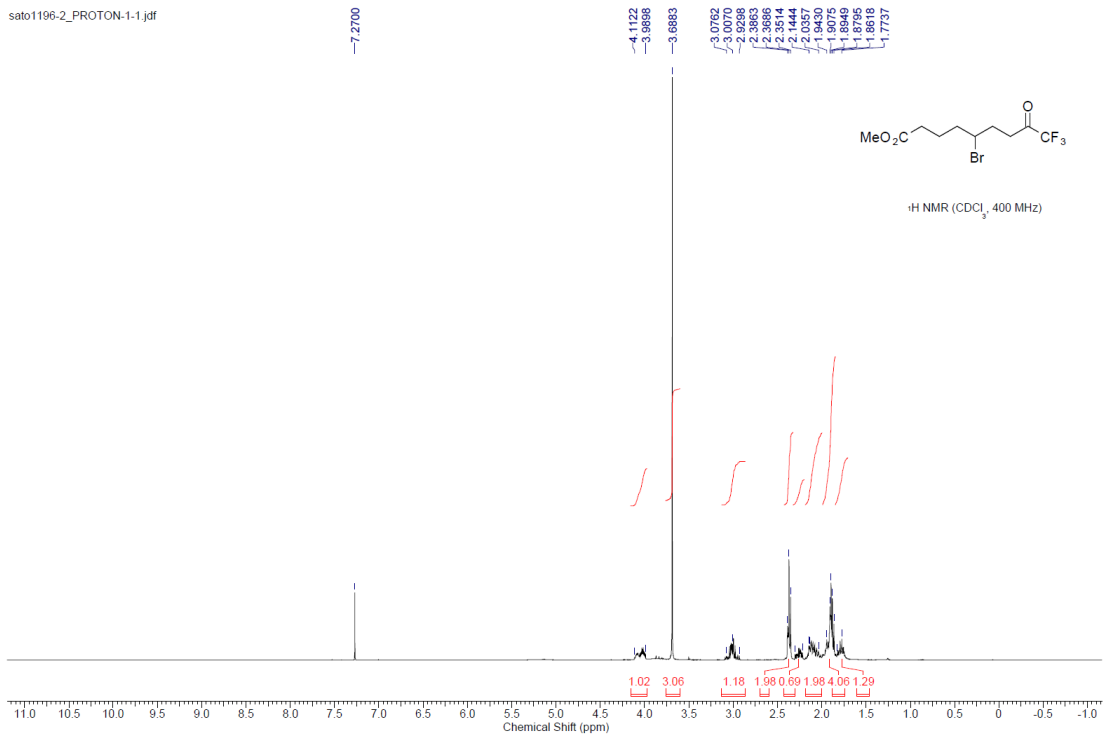

Figure S112. ^{1}H NMR of **4f** (400 MHz, $CDCl_3$)

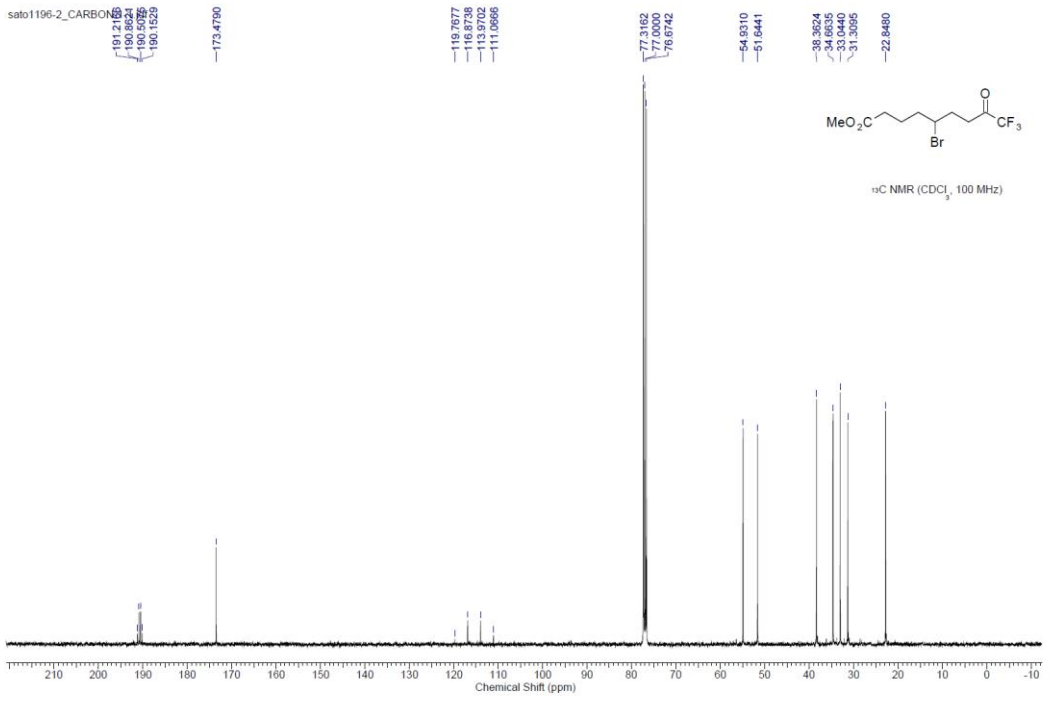

Figure S113. ^{13}C NMR of **4f** (100 MHz, $CDCl_3$)

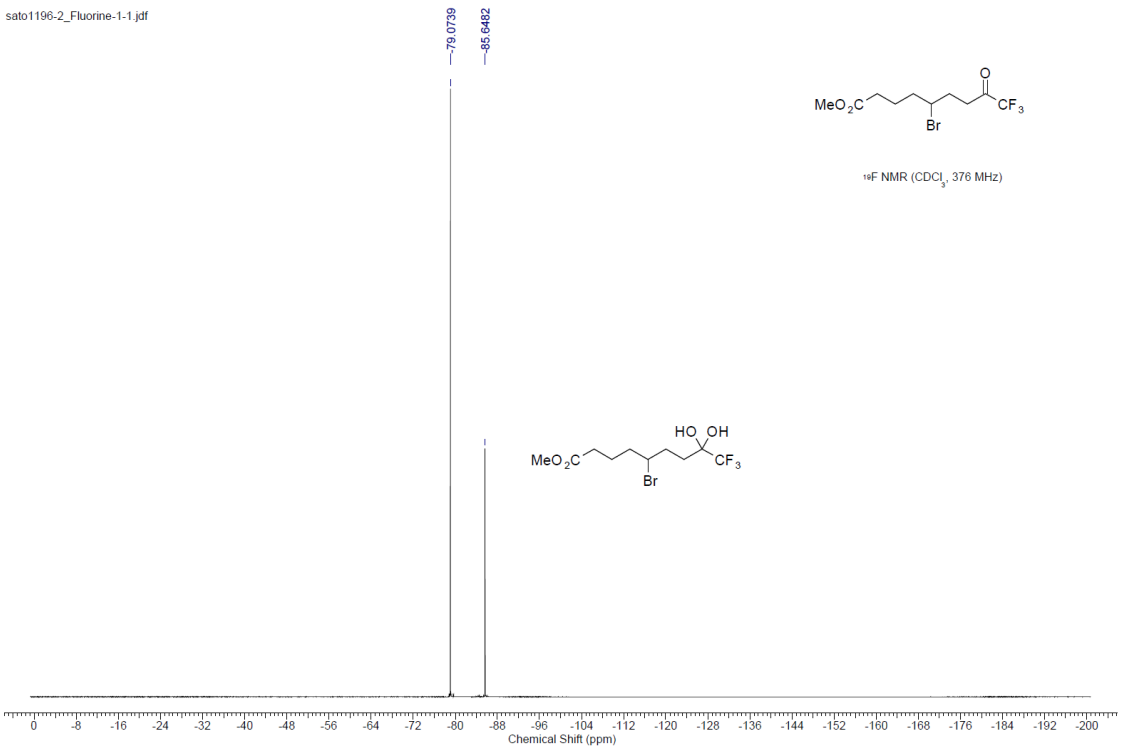

Figure S114. ^{19}F NMR of **4f** (376 MHz, $CDCl_3$)

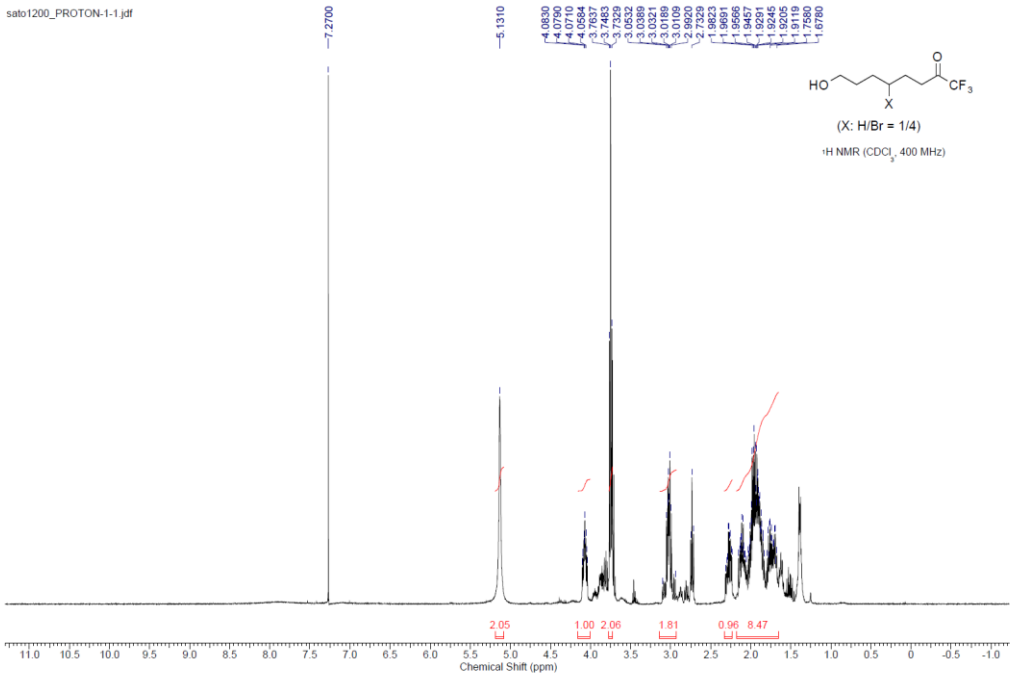

Figure S115. ^{1}H NMR of **3g/4g** (400 MHz, $CDCl_3$)

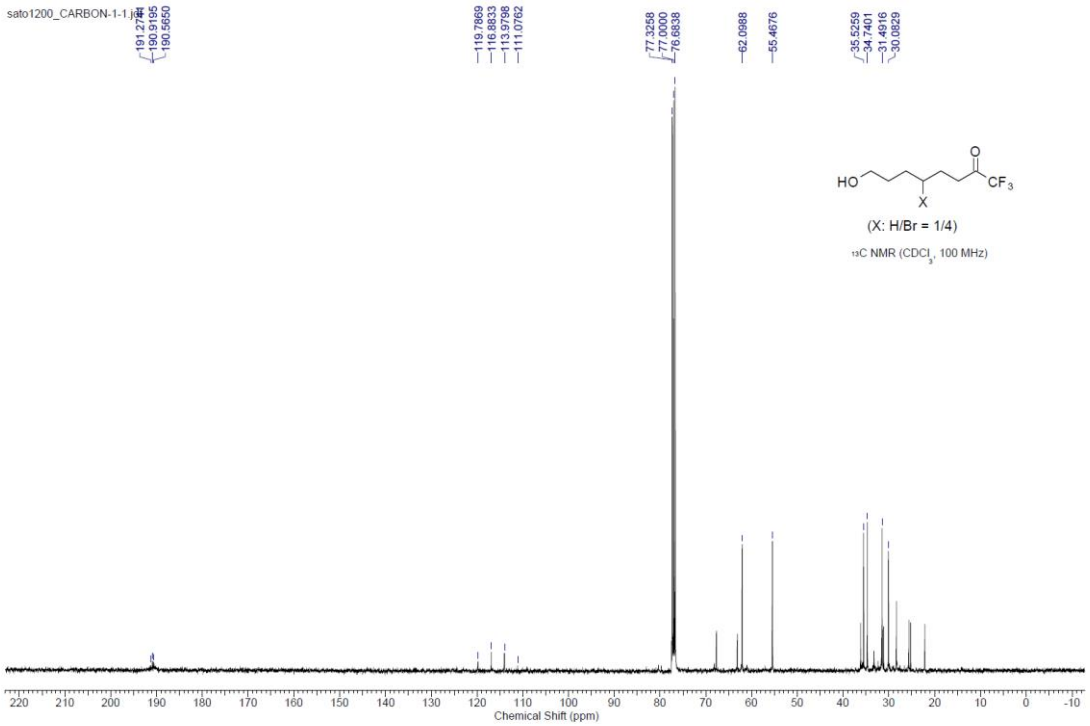

Figure S116. ^{13}C NMR of **3g/4g** (100 MHz, $CDCl_3$)

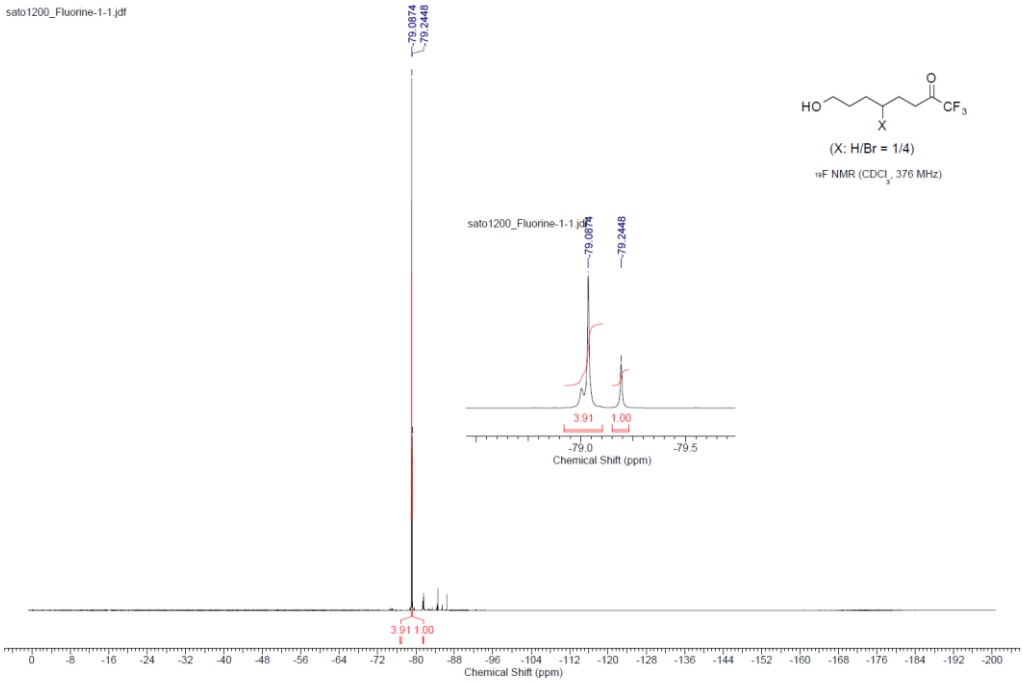

Figure S117. ^{19}F NMR of **3g/4g** (376 MHz, $CDCl_3$)

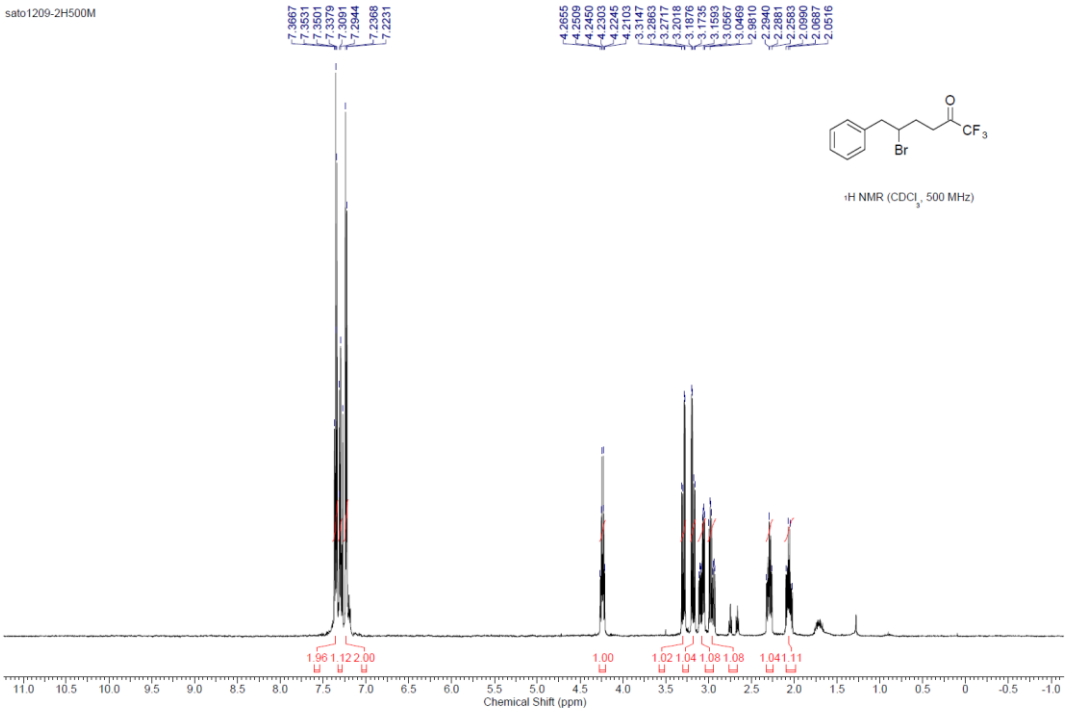

Figure S118. ^{1}H NMR of **4h** (500 MHz, $CDCl_3$)

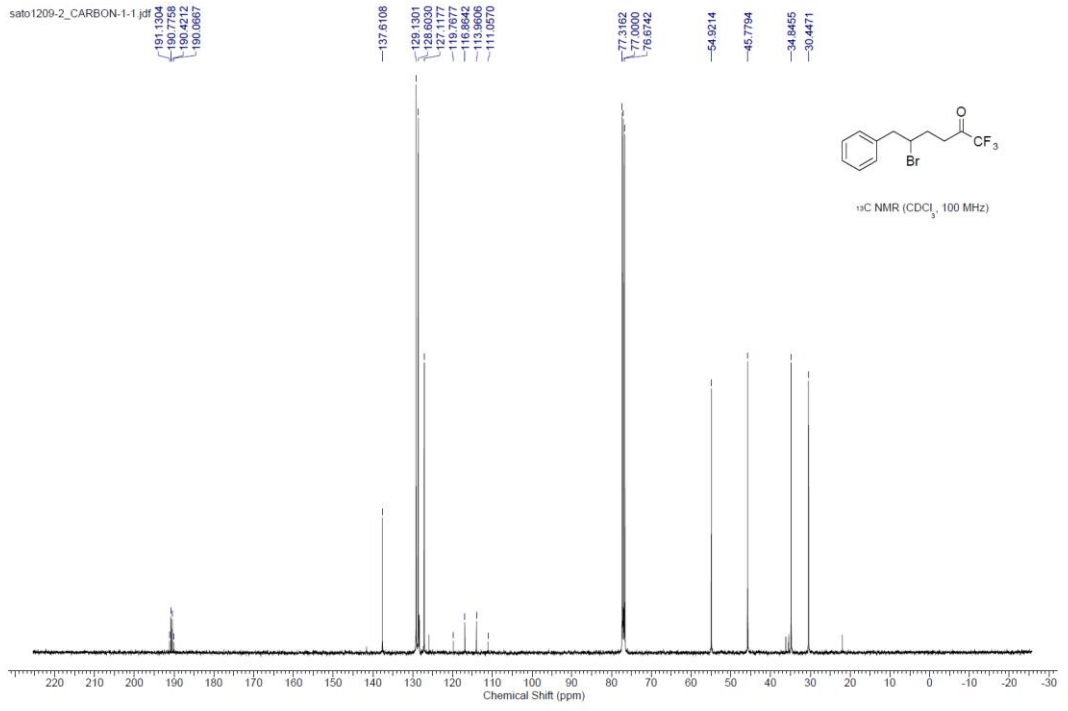

Figure S119. ^{13}C NMR of **4h** (100 MHz, $CDCl_3$)

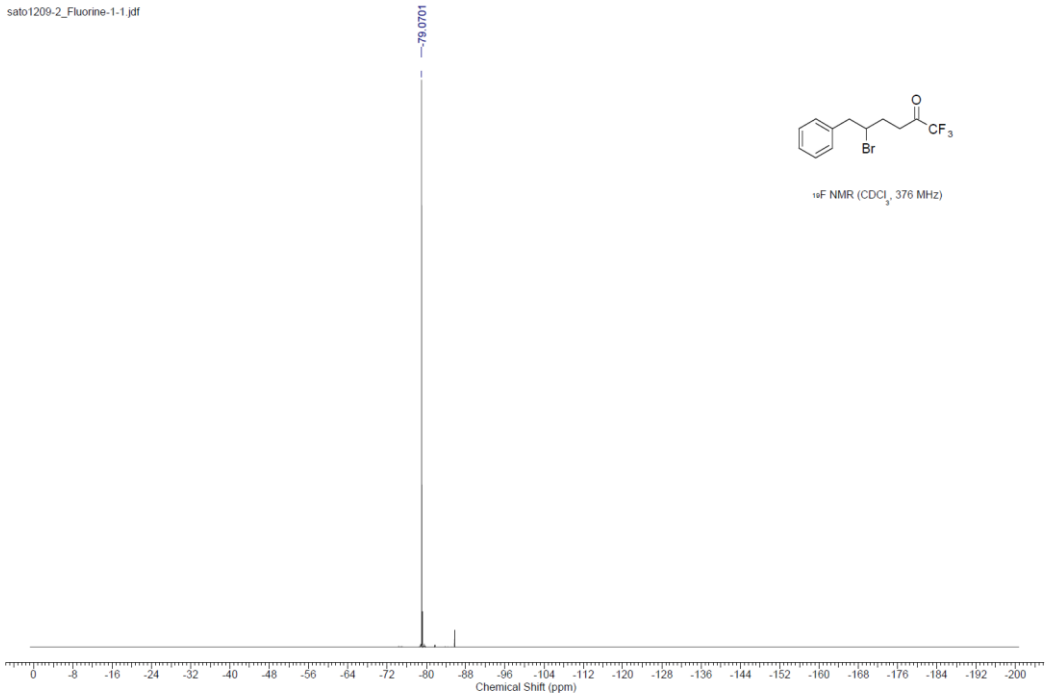

Figure S120. ^{19}F NMR of **4h** (376 MHz, $CDCl_3$)

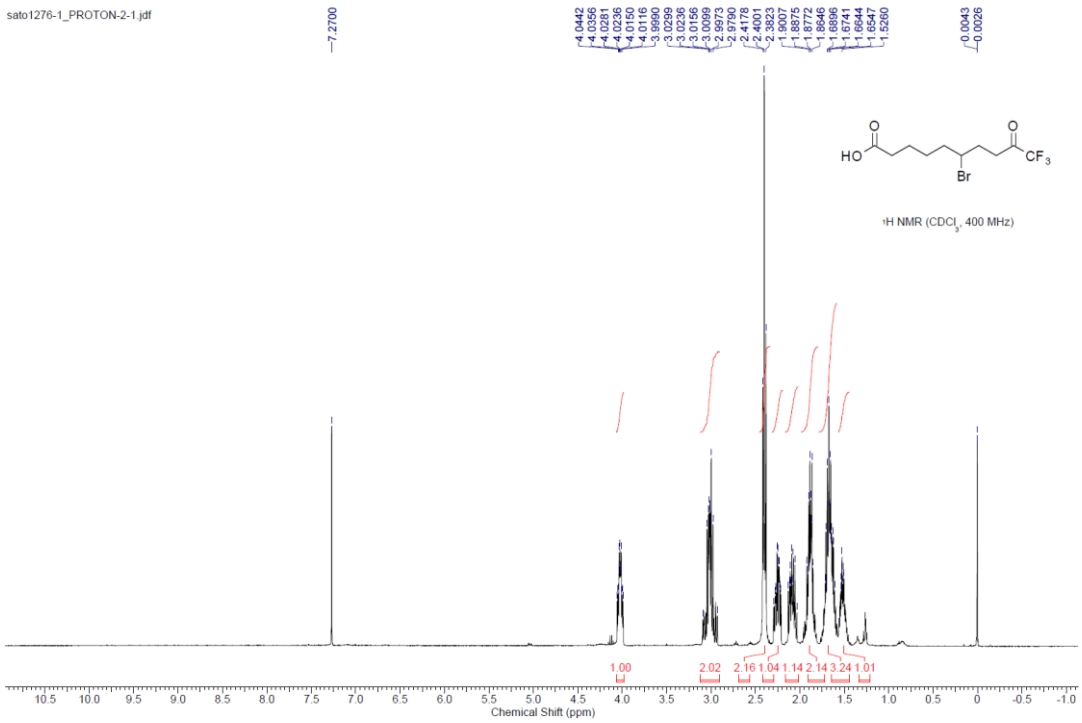

Figure S121. ^{1}H NMR of **4k** (400 MHz, $CDCl_3$)

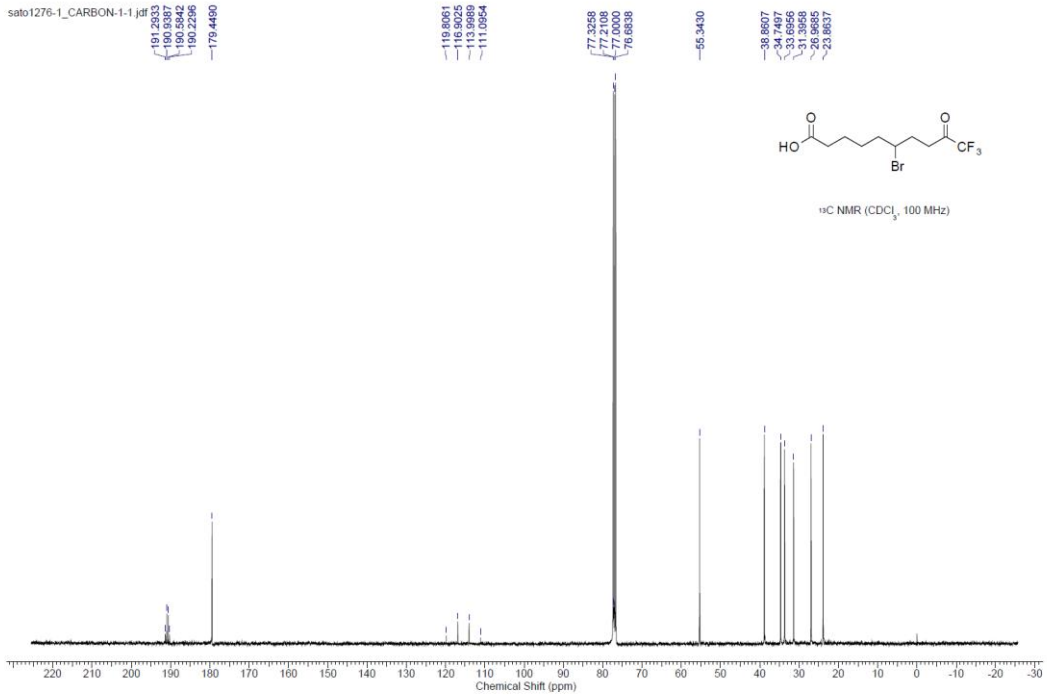

Figure S122. ^{13}C NMR of **4k** (100 MHz, $CDCl_3$)

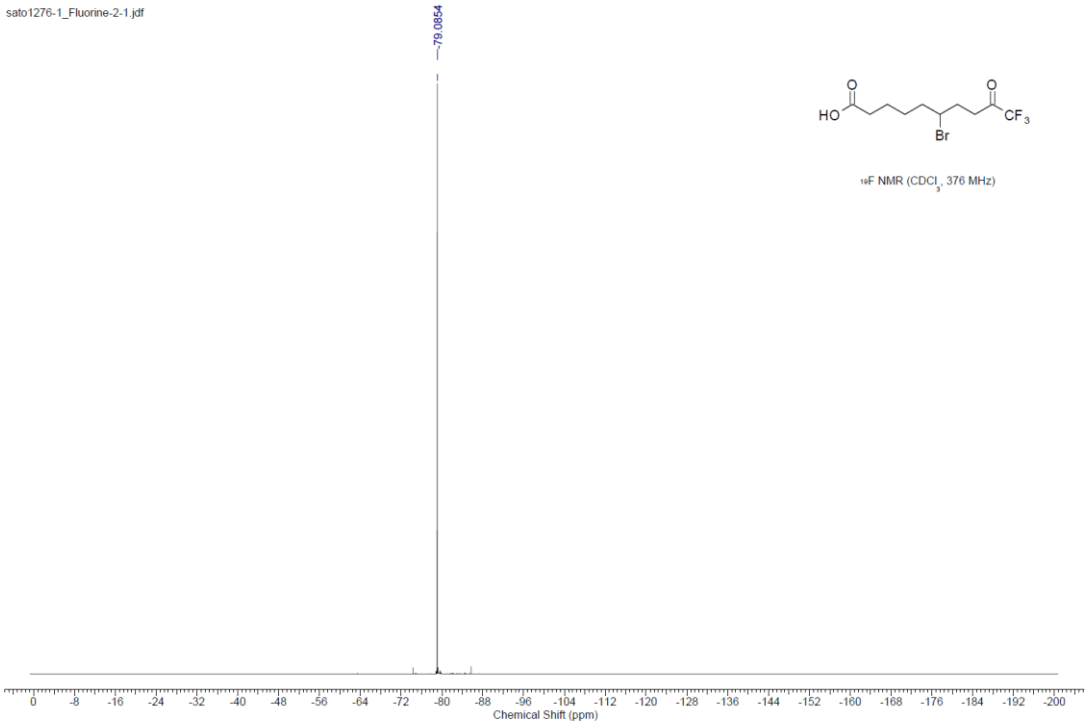

Figure S123. ^{19}F NMR of **4k** (376 MHz, $CDCl_3$)

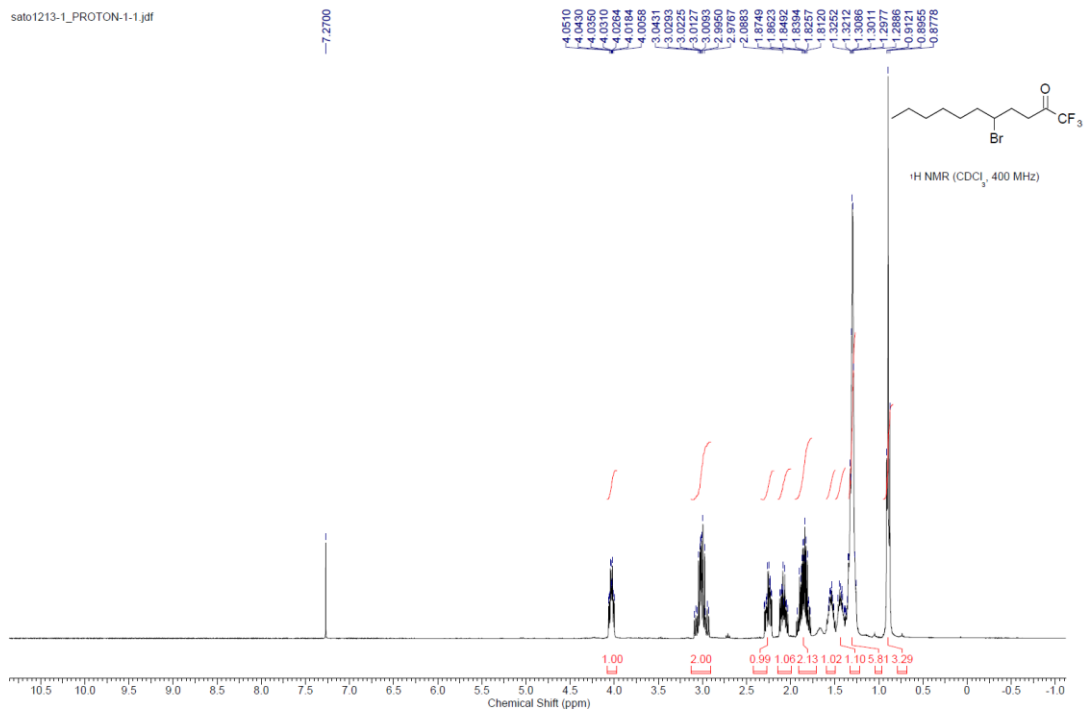

Figure S124. ^{1}H NMR of **4m** (400 MHz, $CDCl_3$)

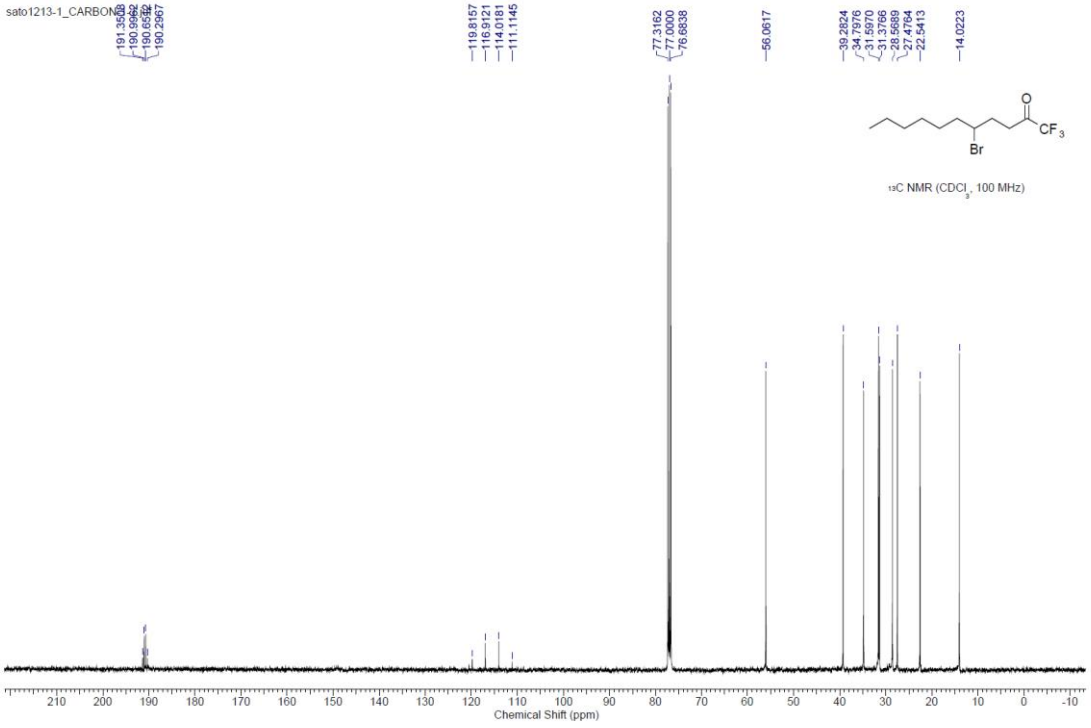

Figure S125. ^{13}C NMR of **4m** (100 MHz, $CDCl_3$)

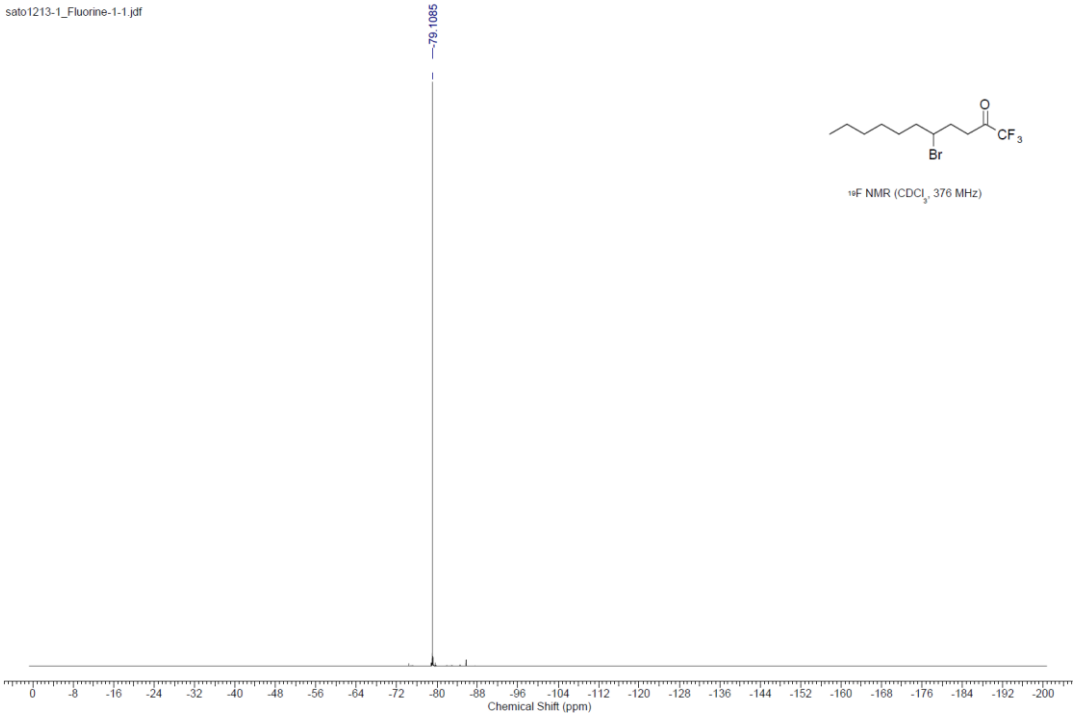

Figure S126. ^{19}F NMR of **4m** (376 MHz, $CDCl_3$)

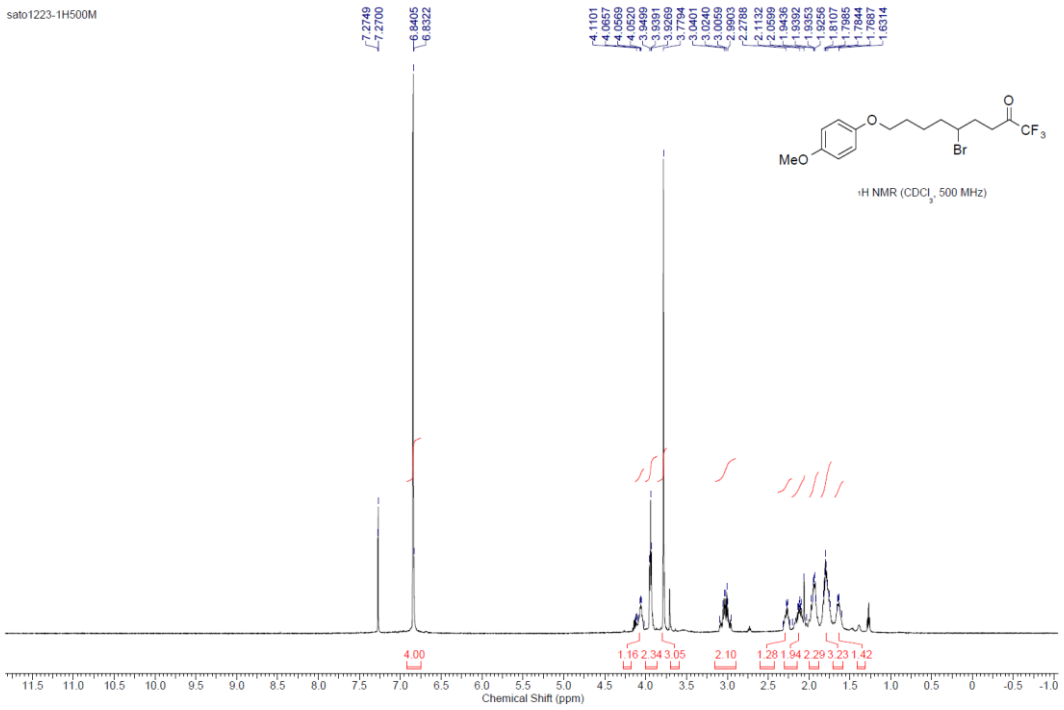

Figure S127. ^{1}H NMR of **4o** (400 MHz, $CDCl_3$)

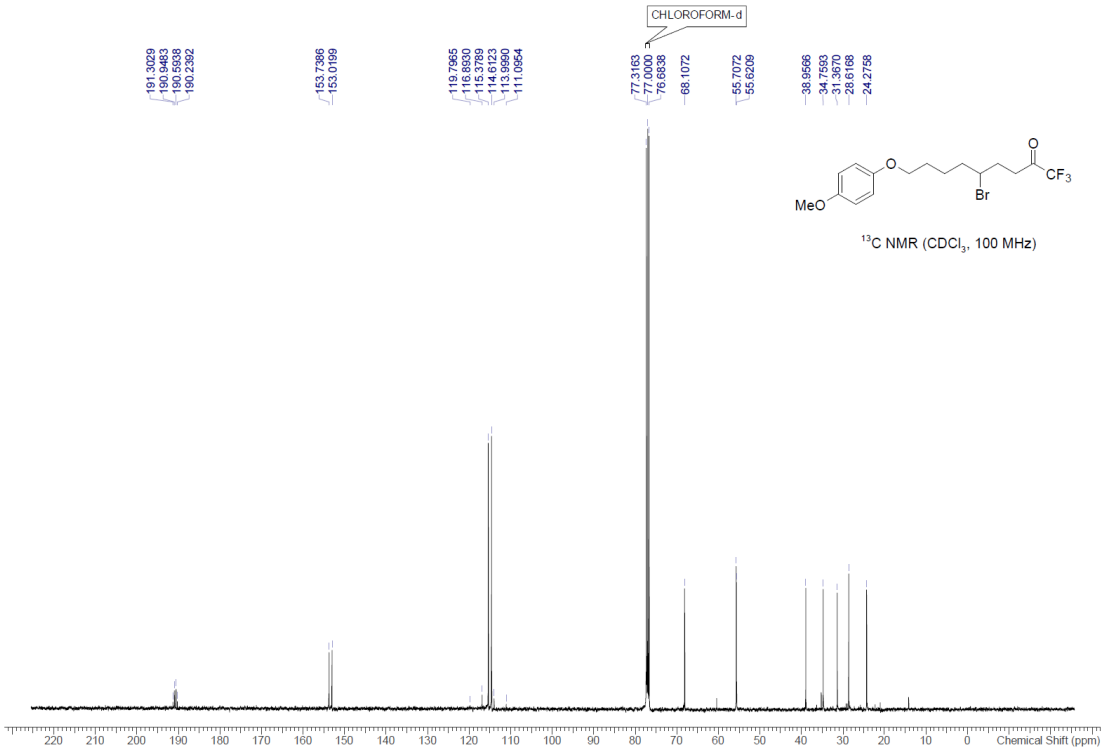

Figure S128. ^{13}C NMR of **4o** (100 MHz, $CDCl_3$)

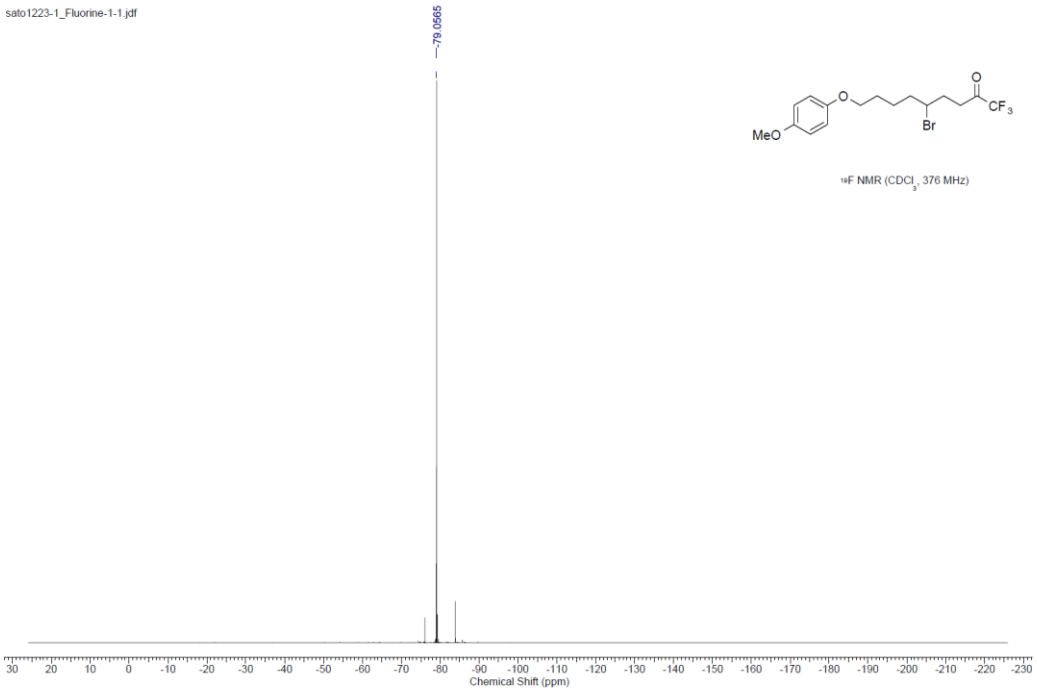

Figure S129. ^{19}F NMR of **4o** (376 MHz, $CDCl_3$)

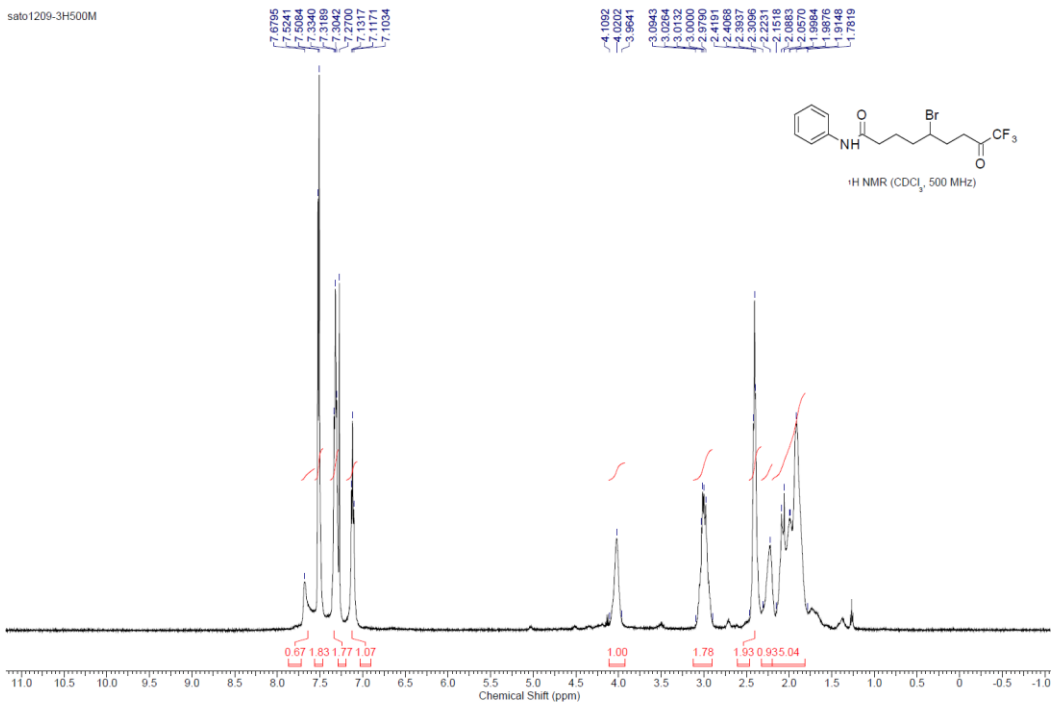

Figure S130. ^{1}H NMR of **4p** (500 MHz, $CDCl_3$)

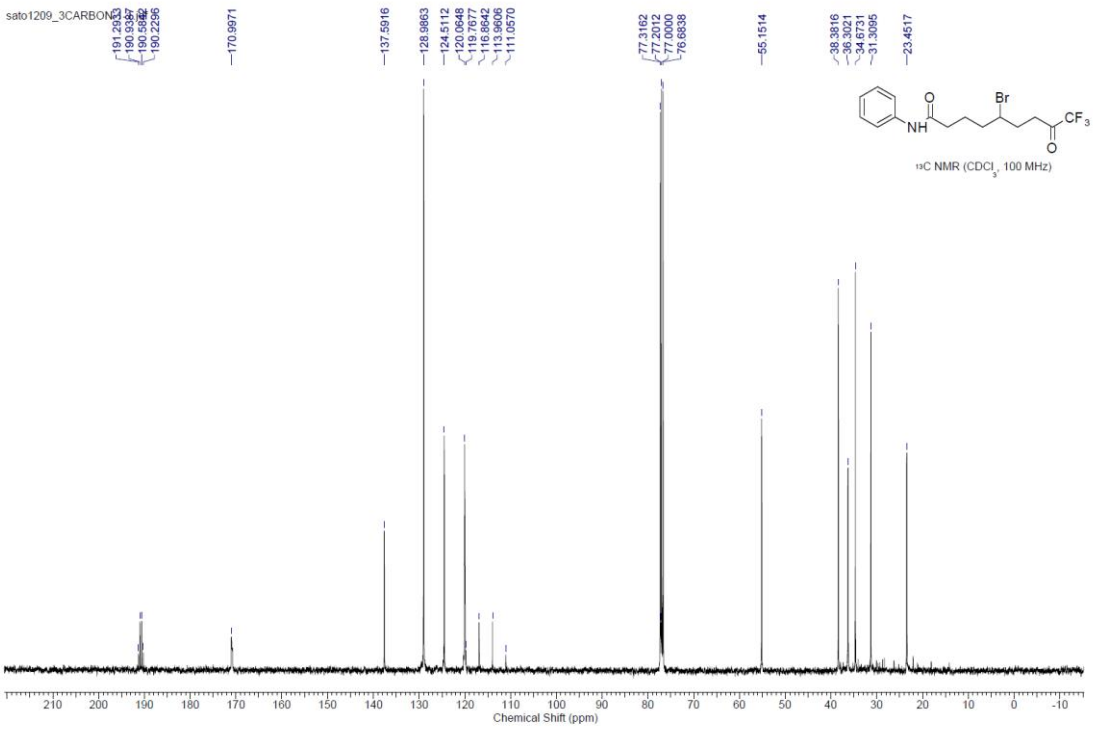

Figure S131. ^{13}C NMR of **4p** (100 MHz, $CDCl_3$)

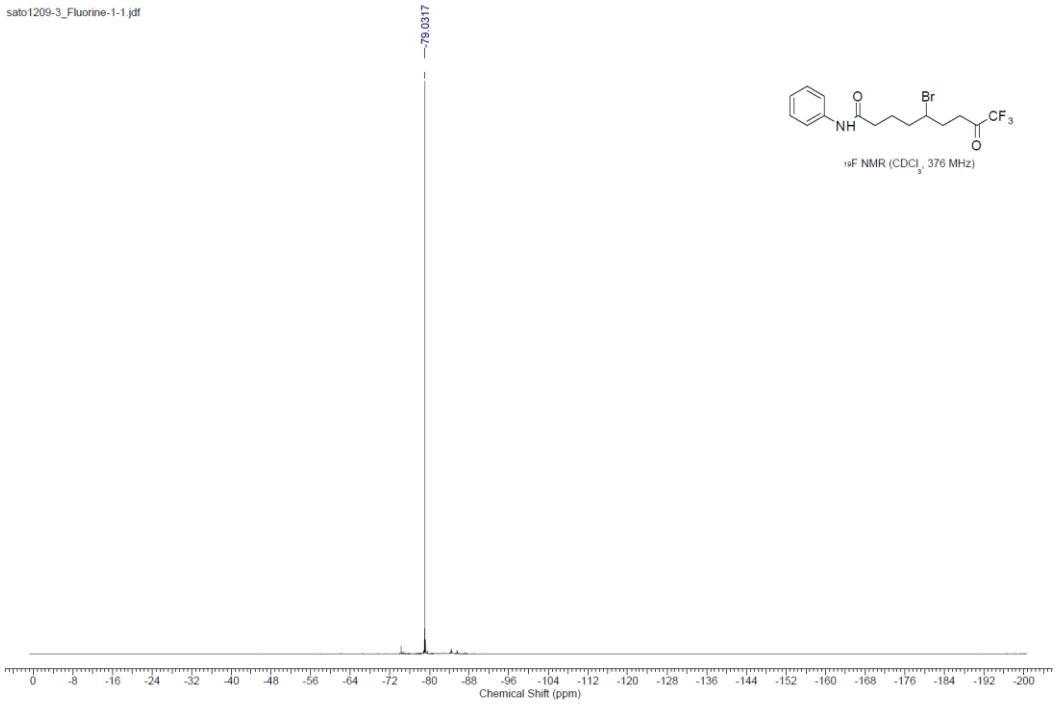

Figure S132. ^{19}F NMR of **4p** (376 MHz, $CDCl_3$)

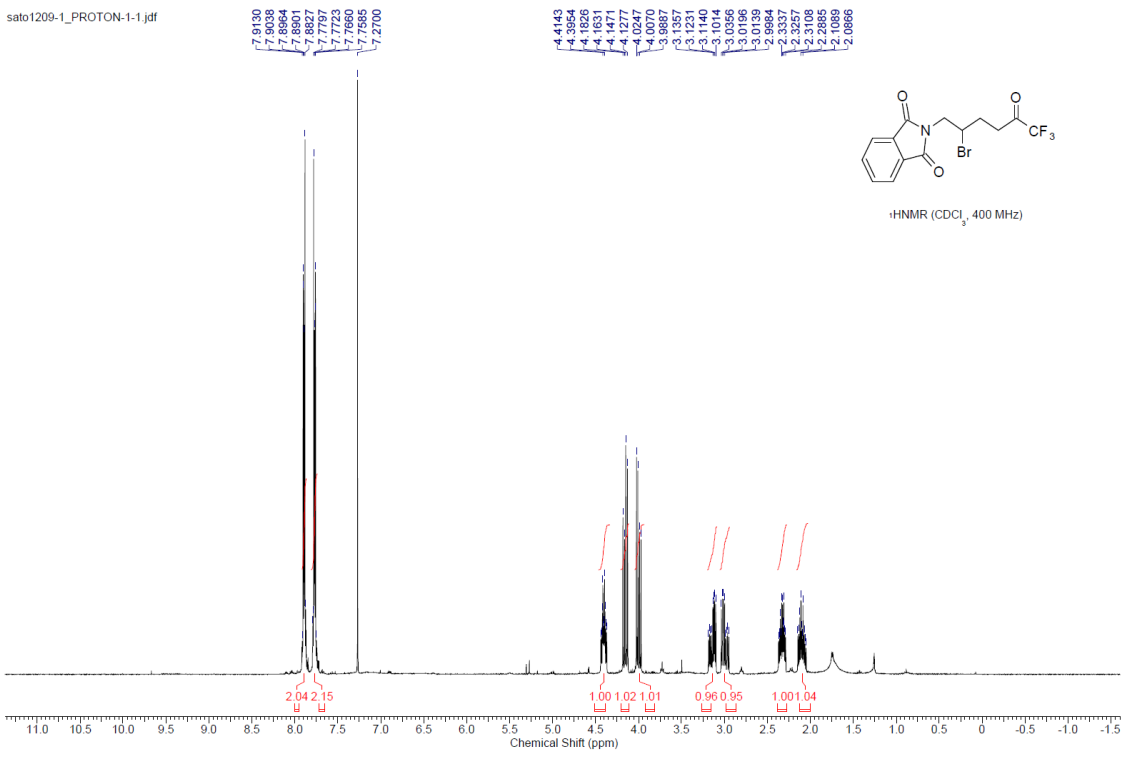

Figure S133. ^{1}H NMR of **4q** (400 MHz, $CDCl_3$)

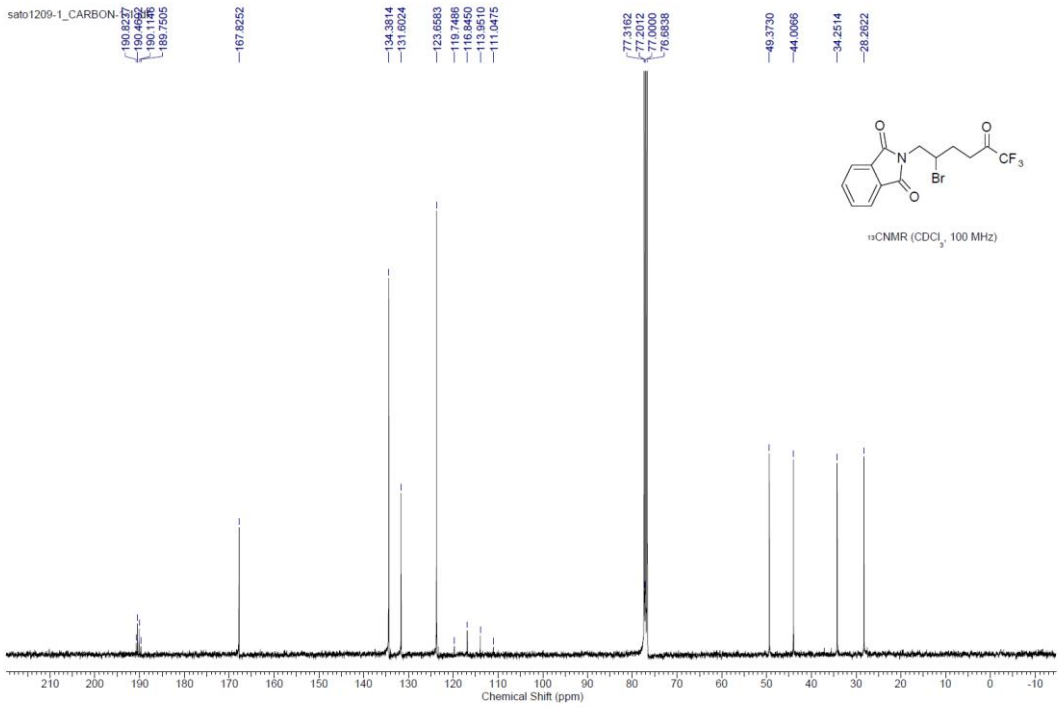

Figure S134. ^{13}C NMR of **4q** (100 MHz, $CDCl_3$)

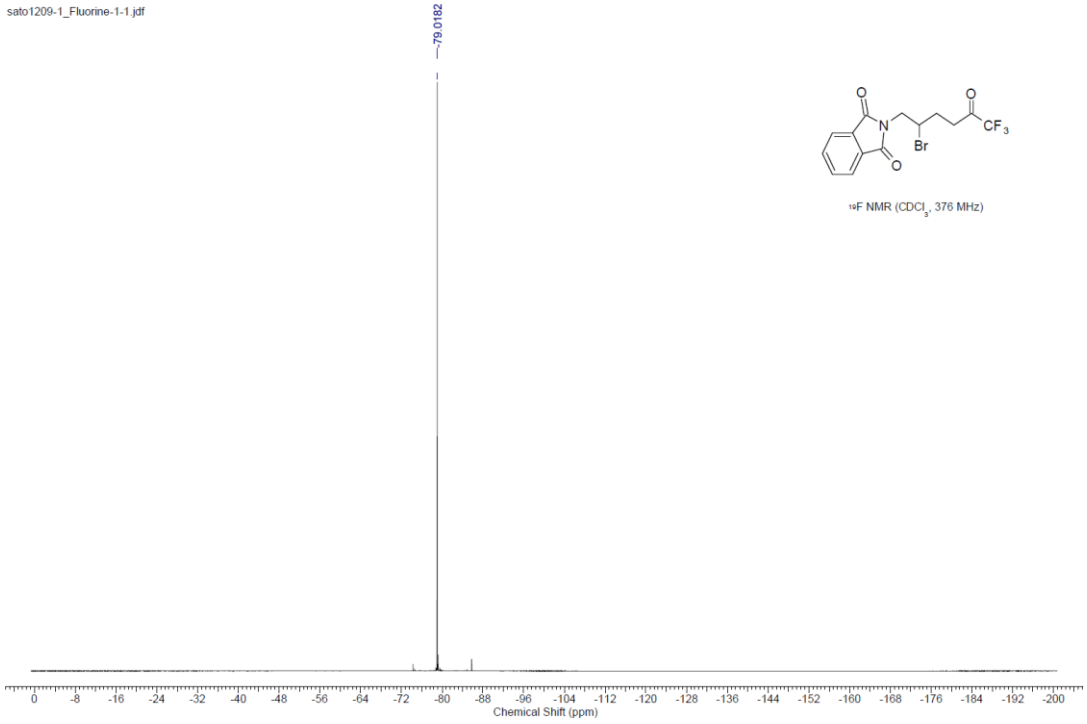

Figure S135. ^{19}F NMR of **4q** (376 MHz, $CDCl_3$)

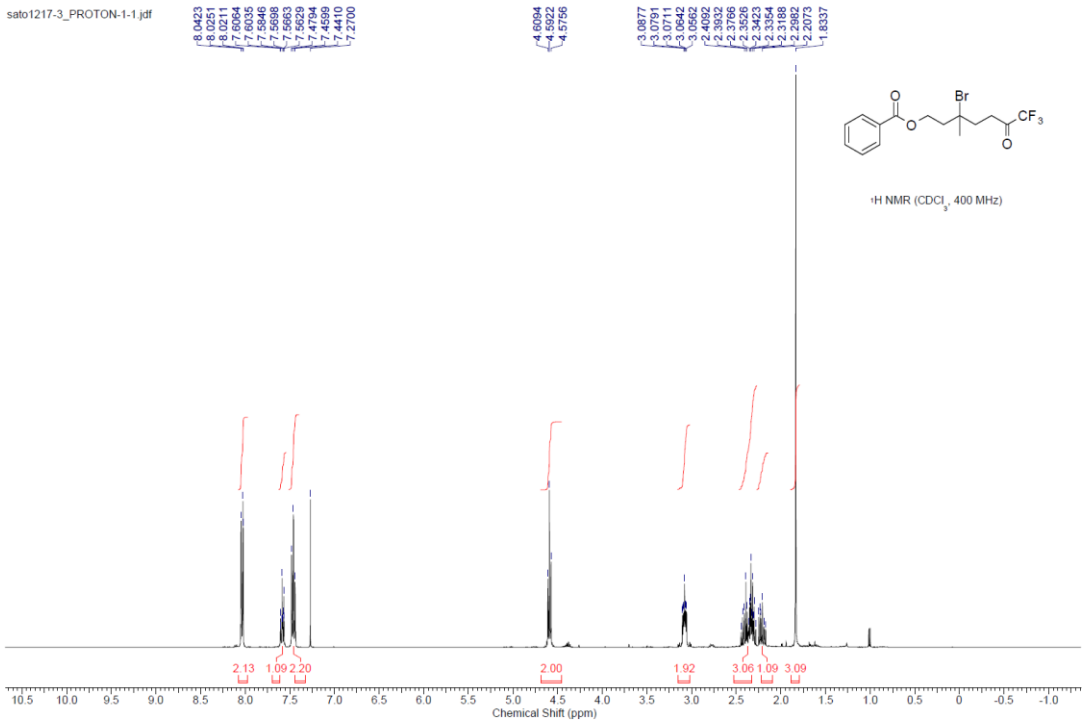

Figure S136. ^{1}H NMR of **4s** (400 MHz, $CDCl_3$)

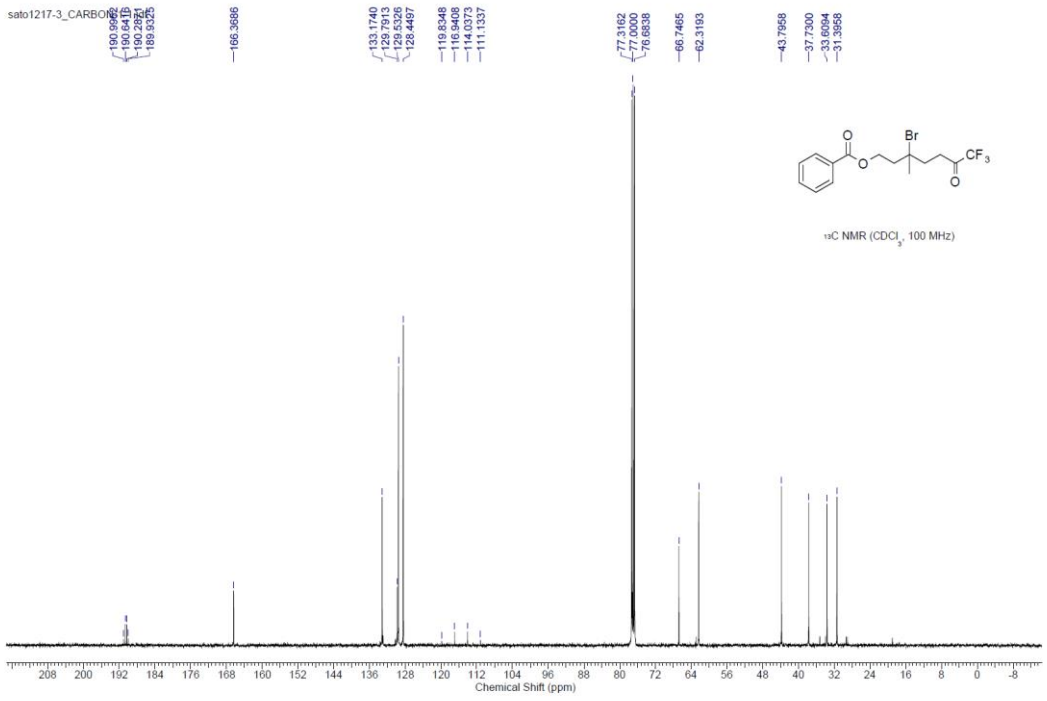

Figure S137. ^{13}C NMR of **4s** (100 MHz, $CDCl_3$)

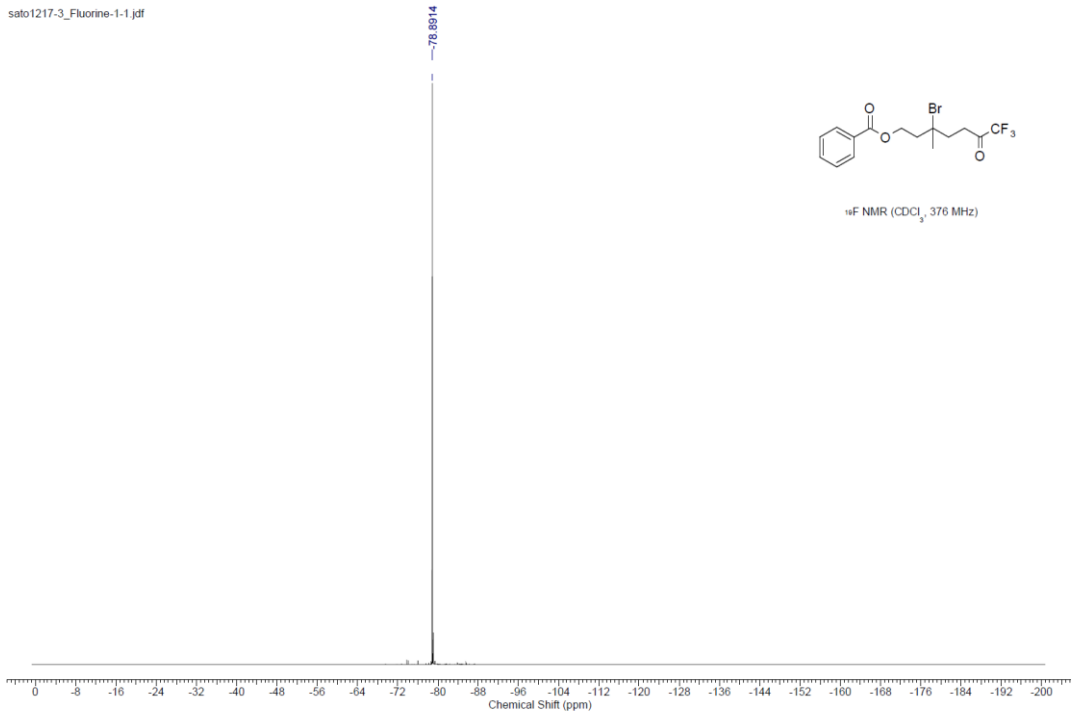

Figure S138. ^{19}F NMR of **4s** (376 MHz, $CDCl_3$)

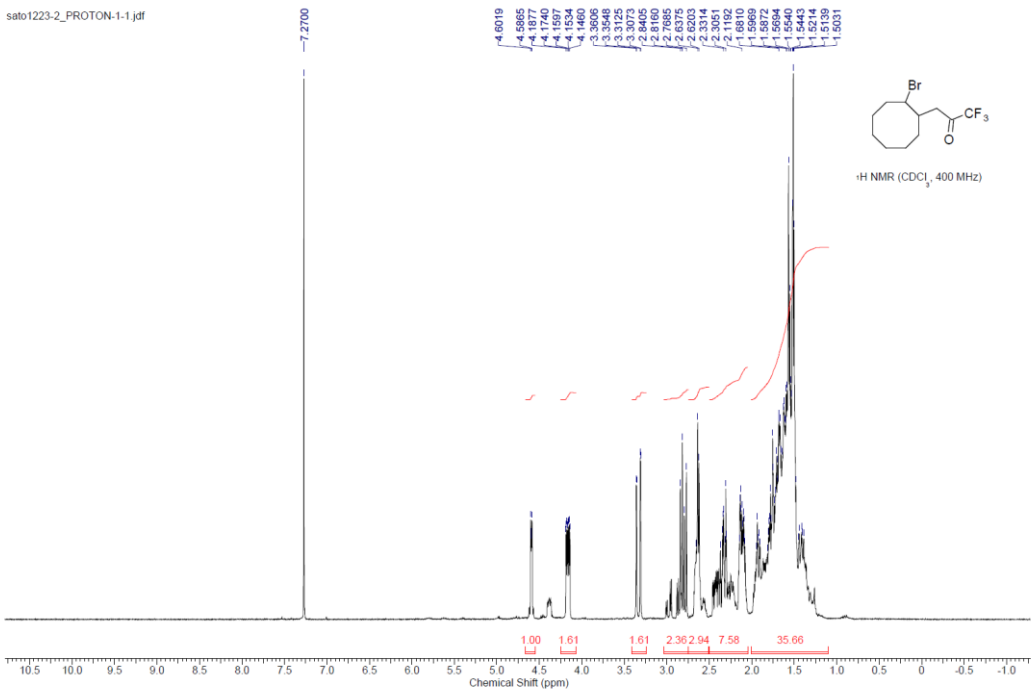

Figure S139. ^{1}H NMR of **4t** (400 MHz, $CDCl_3$)

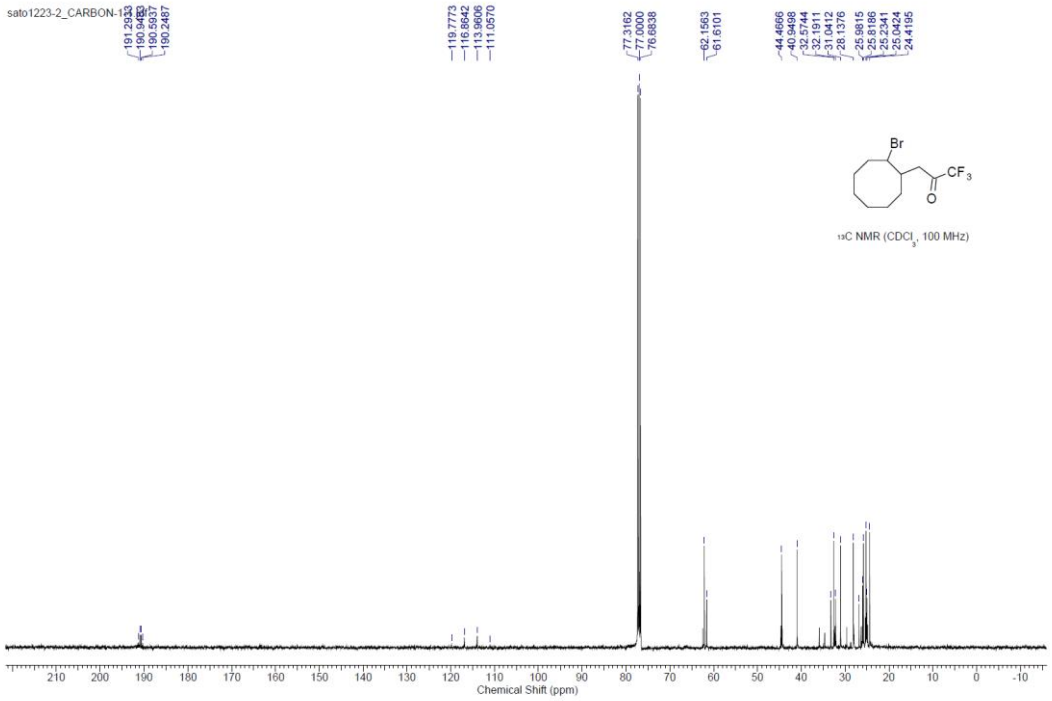

Figure S140. ^{13}C NMR of **4t** (100 MHz, $CDCl_3$)

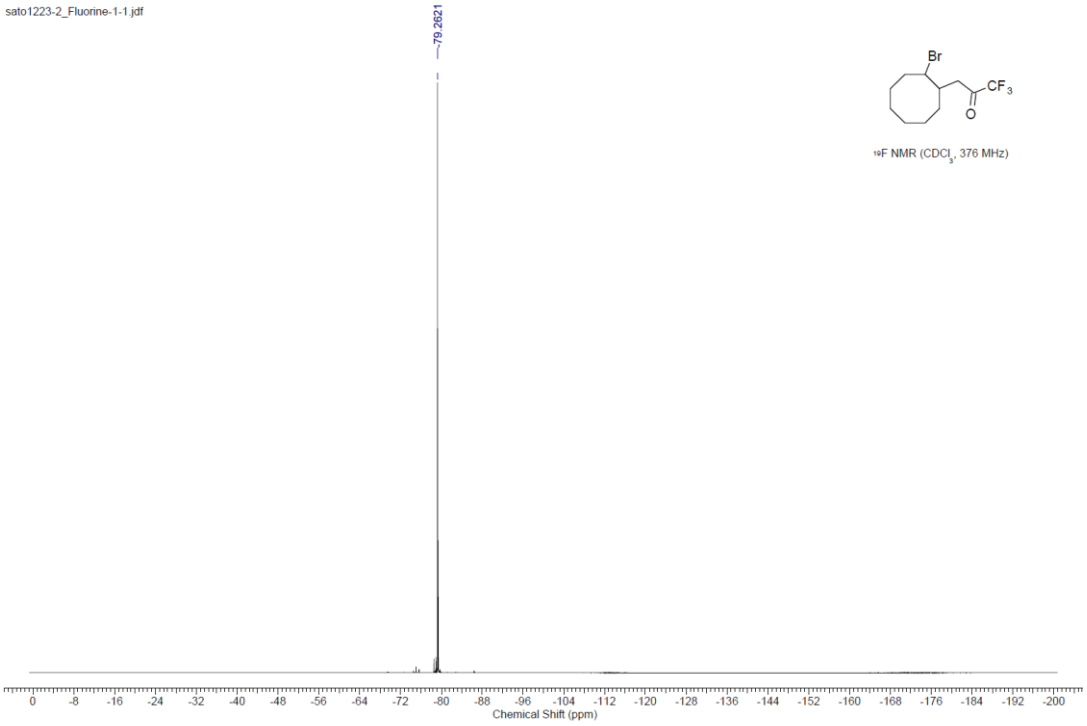

Figure S141. ^{19}F NMR of **4t** (376 MHz, $CDCl_3$)

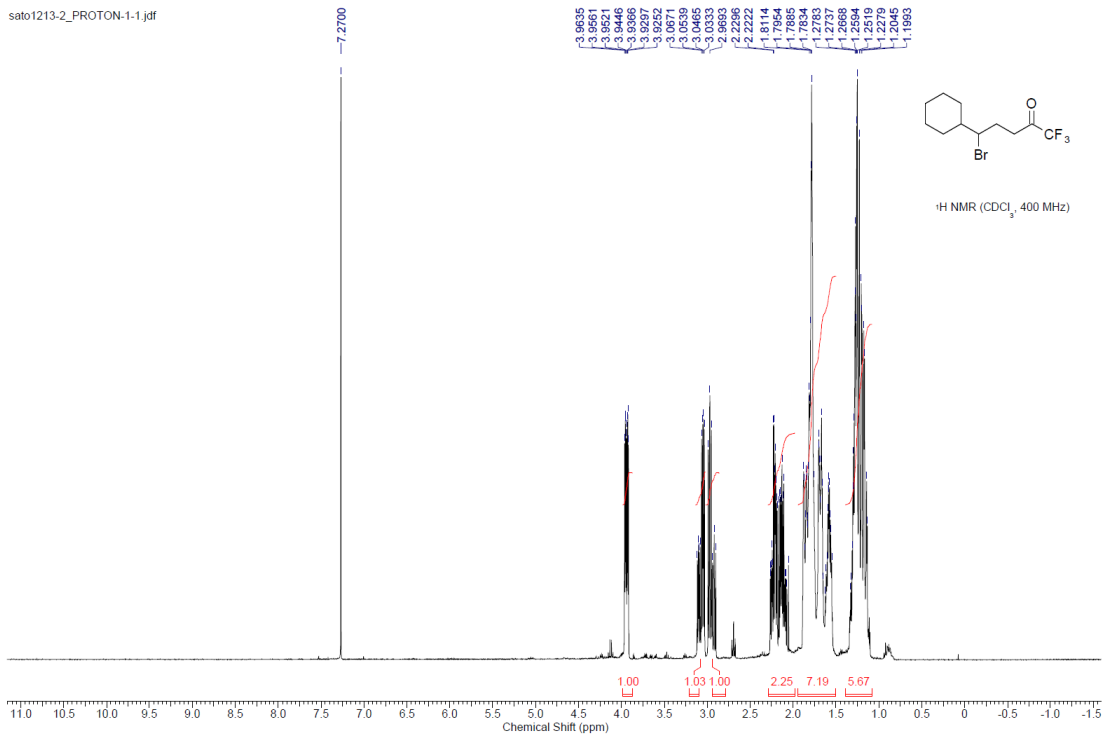

Figure S142. ^{1}H NMR of **4x** (400 MHz, $CDCl_3$)

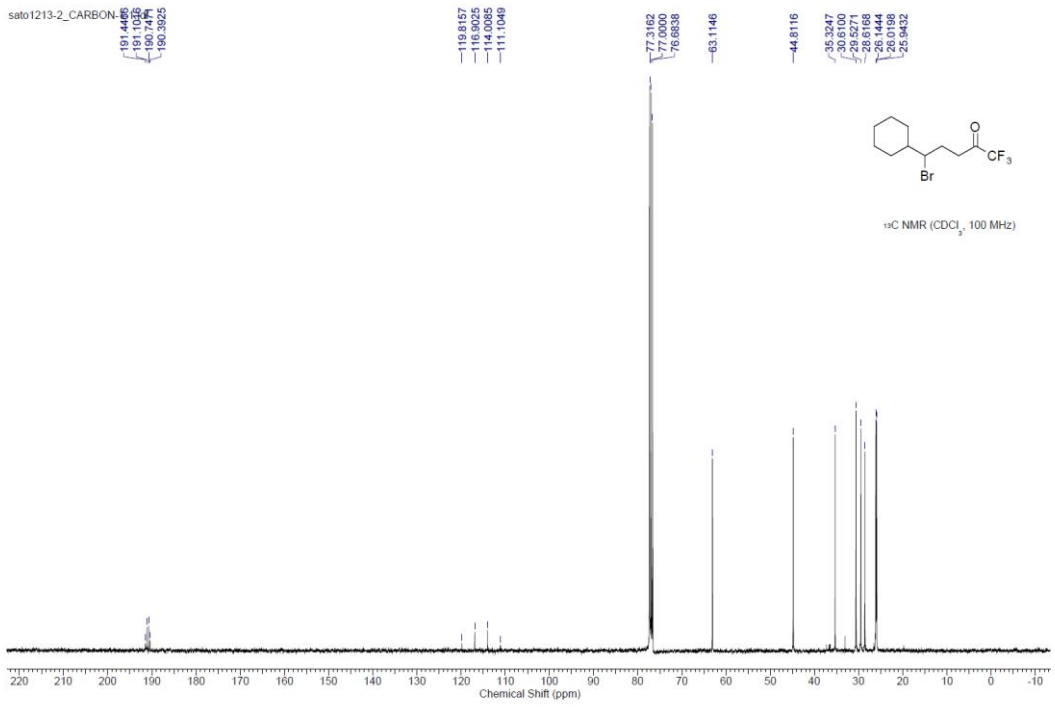

Figure S143. ^{13}C NMR of **4x** (100 MHz, $CDCl_3$)

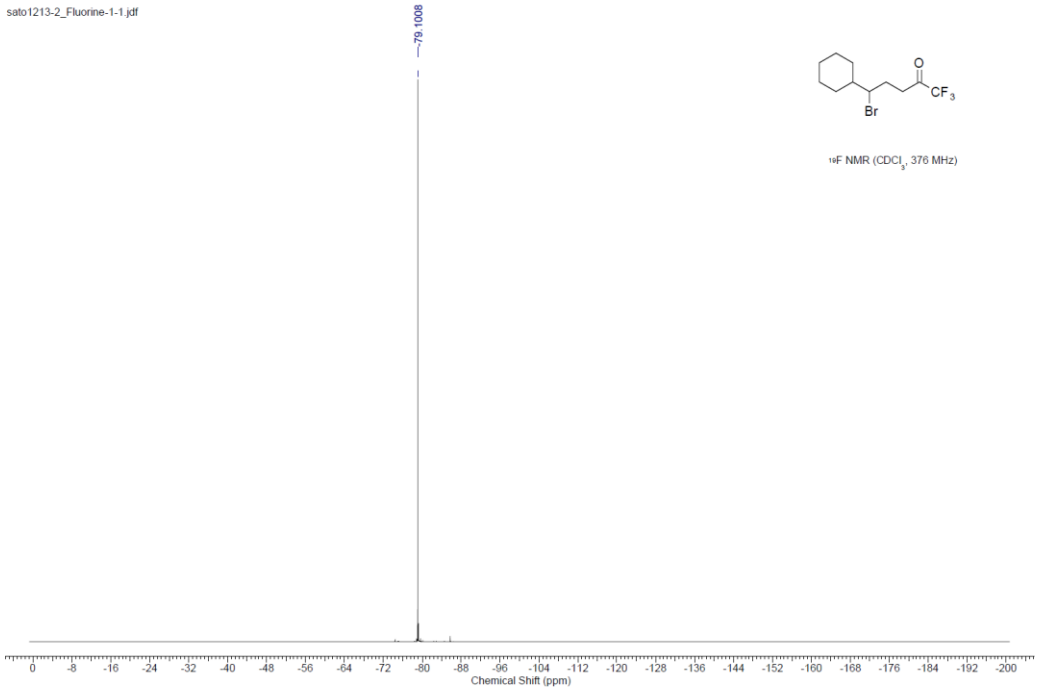

Figure S144. ^{19}F NMR of **4x** (376 MHz, $CDCl_3$)

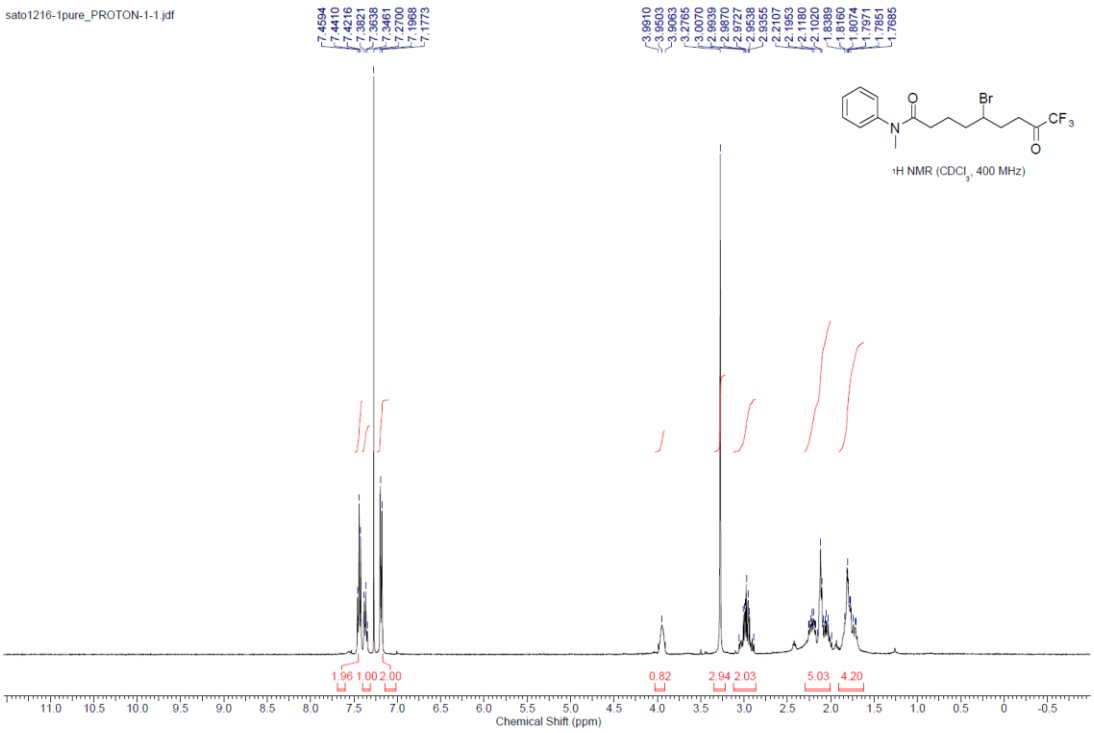

Figure S145. ^{1}H NMR of **4y** (400 MHz, $CDCl_3$)

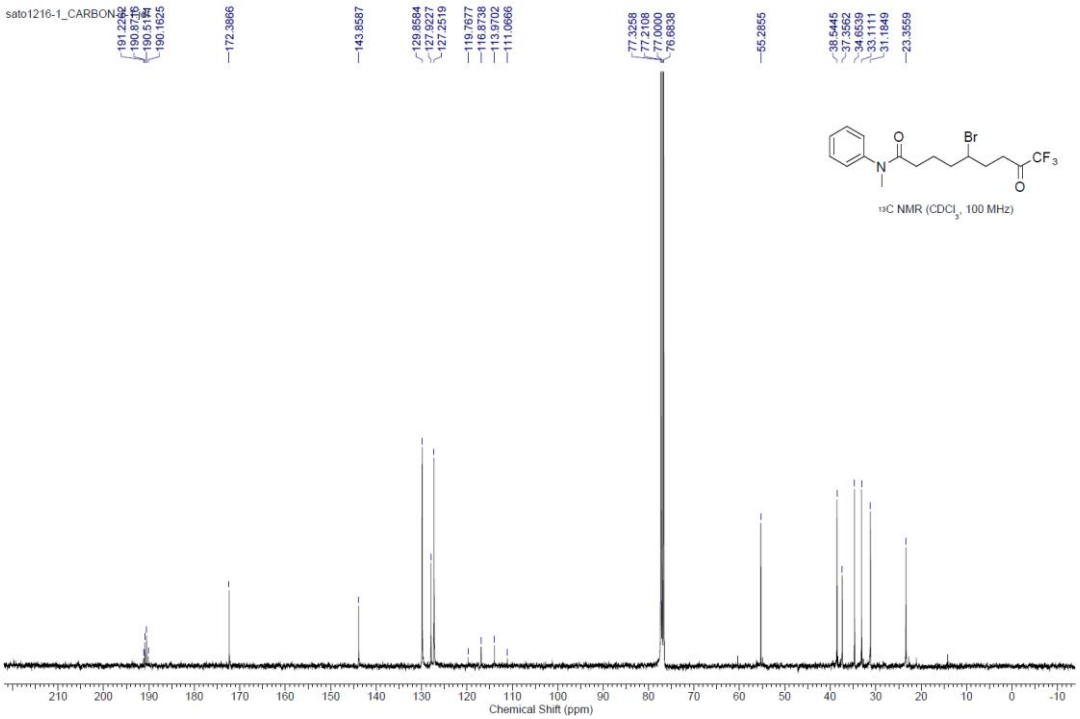

Figure S146. ^{13}C NMR of **4y** (100 MHz, $CDCl_3$)

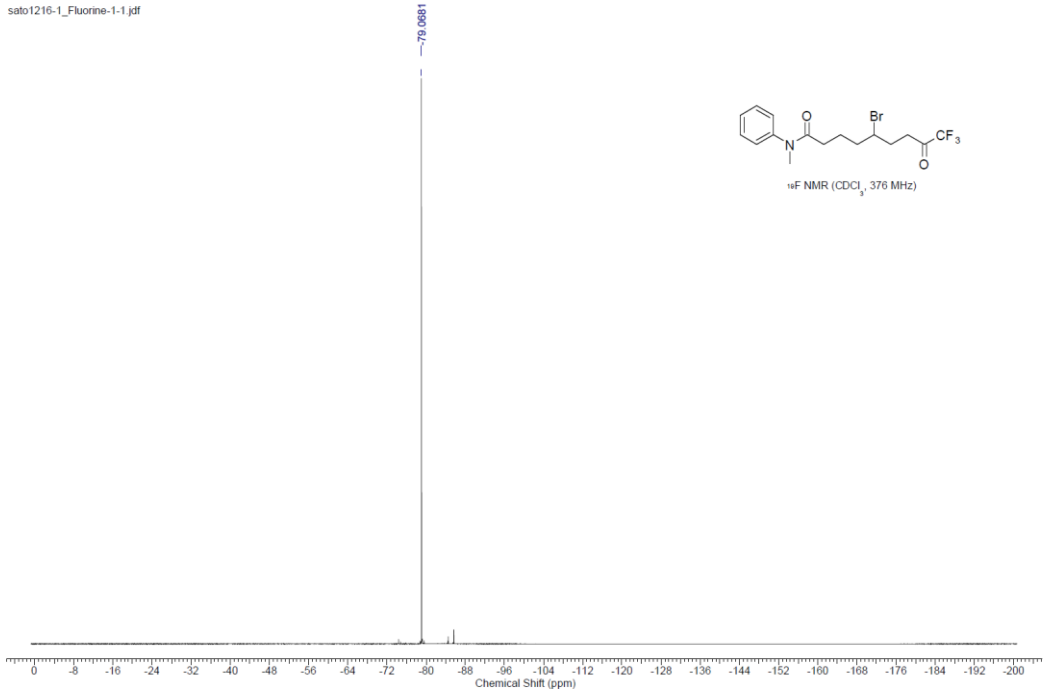

Figure S147. ^{19}F NMR of **4y** (376 MHz, $CDCl_3$)

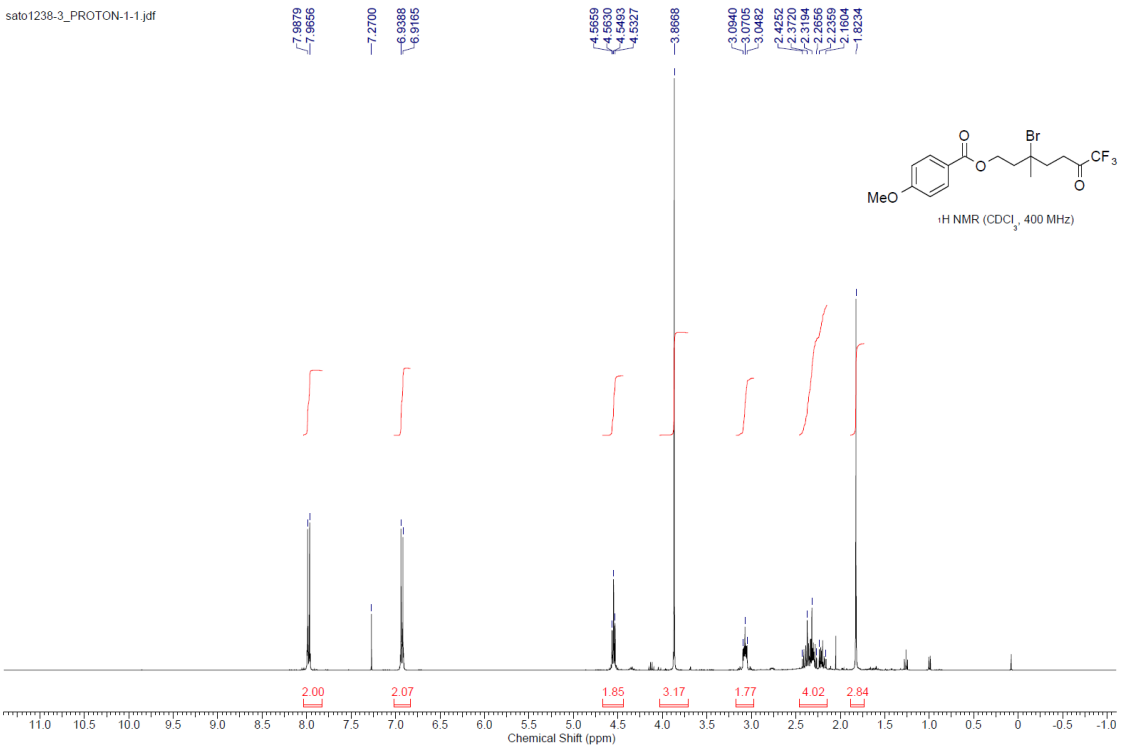

Figure S148. ^{1}H NMR of **4z** (400 MHz, $CDCl_3$)

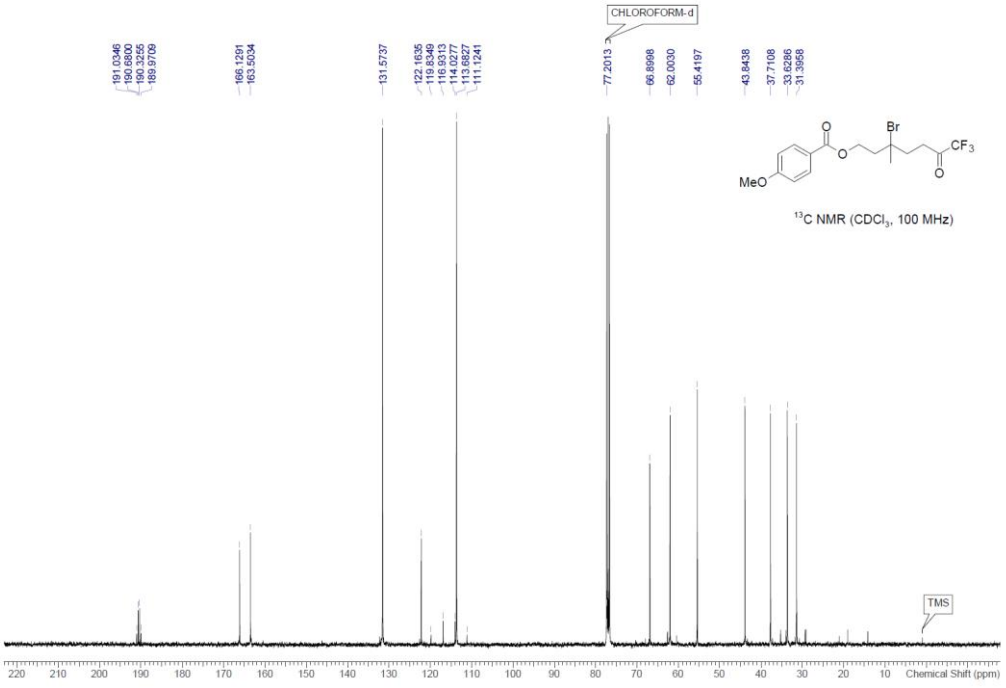

Figure S149. ^{13}C NMR of **4z** (100 MHz, $CDCl_3$)

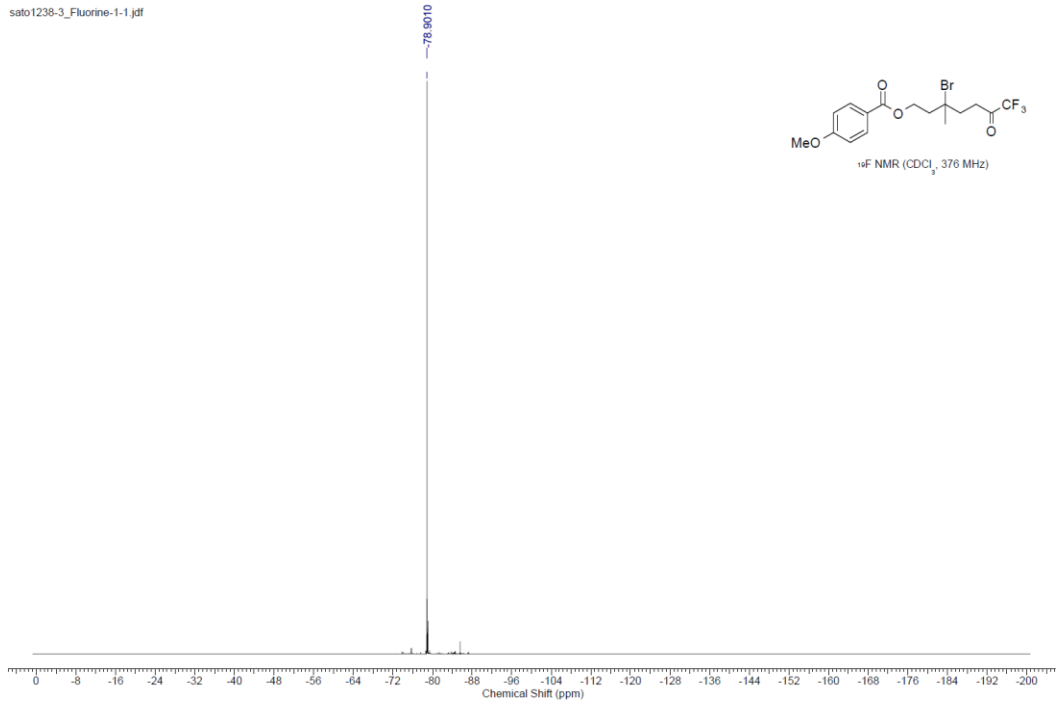

Figure S150. ^{19}F NMR of **4z** (376 MHz, $CDCl_3$)

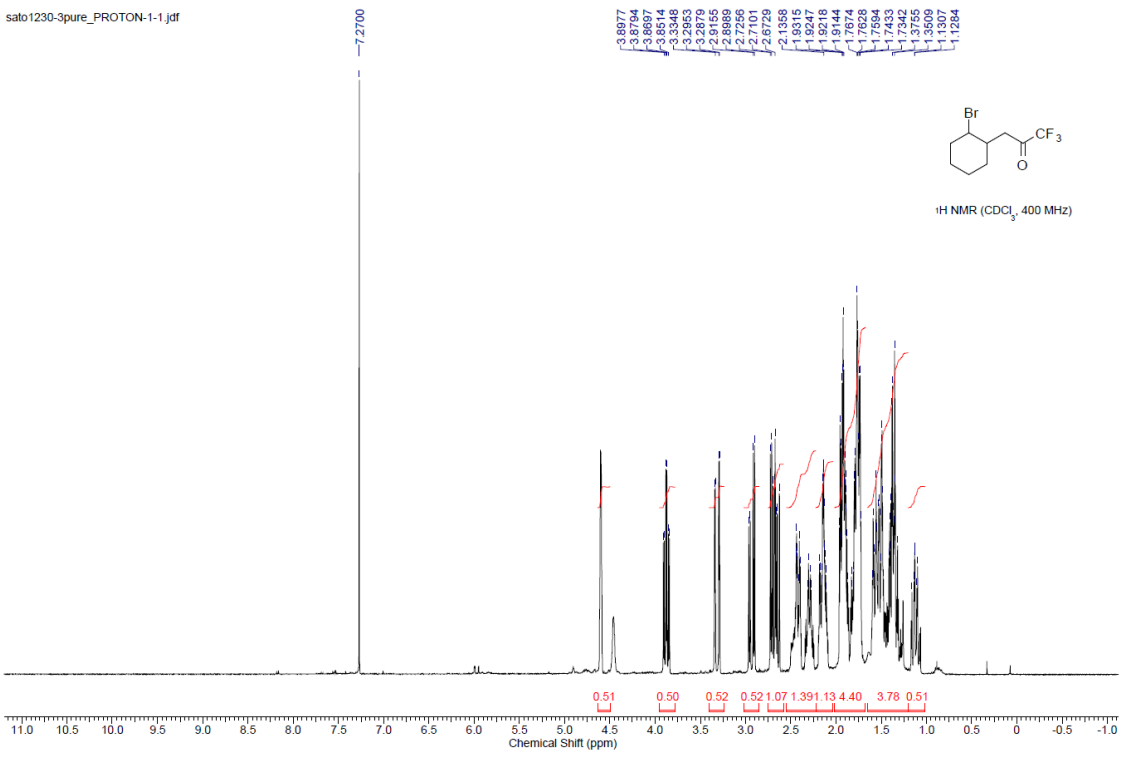

Figure S151. ^{1}H NMR of **4aa** (400 MHz, $CDCl_3$)

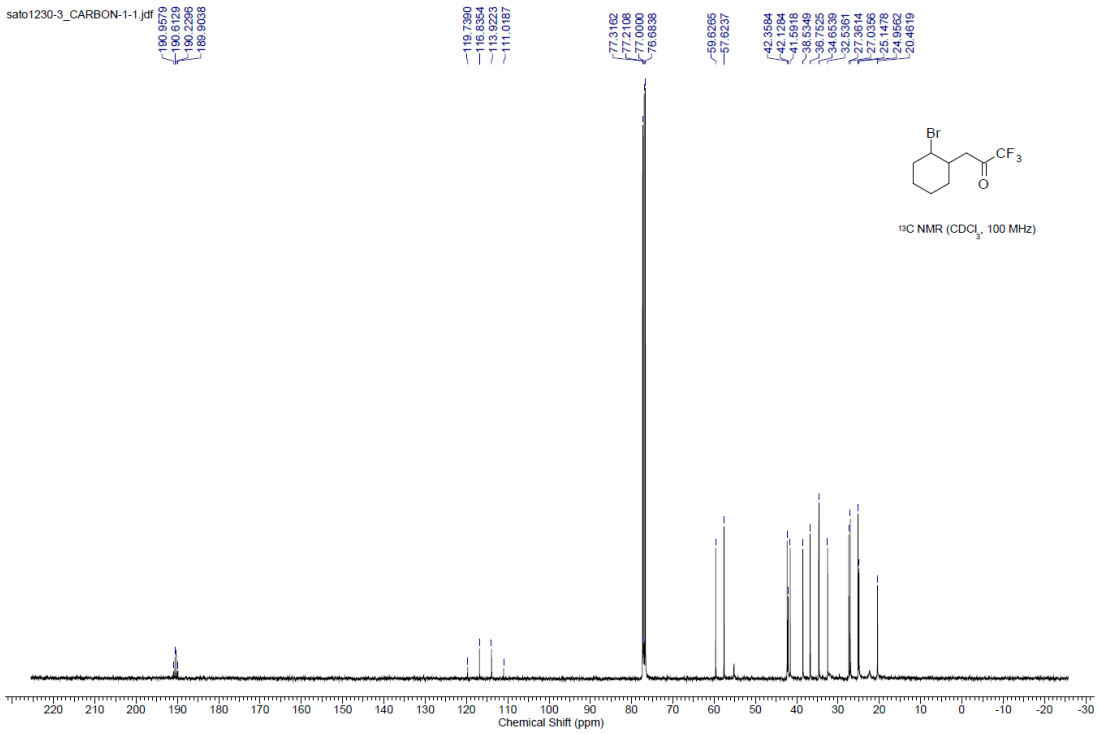

Figure S152. ^{13}C NMR of **4aa** (100 MHz, $CDCl_3$)

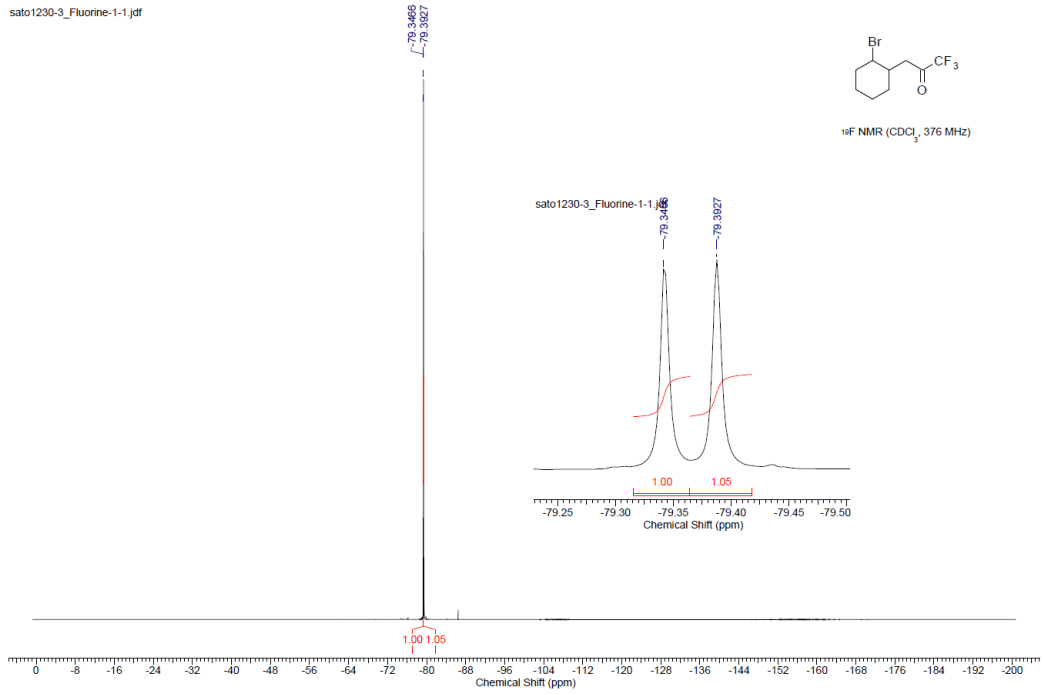

Figure S153. ^{19}F NMR of **4aa** (376 MHz, $CDCl_3$)

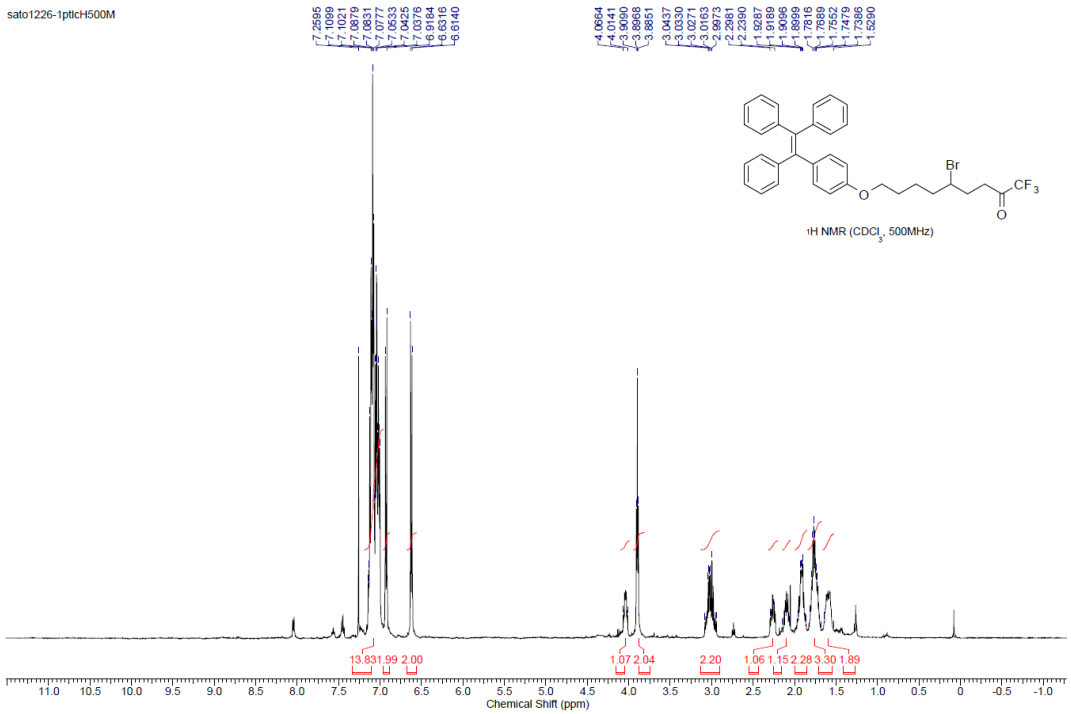

Figure S154. ^{1}H NMR of **4ab** (400 MHz, $CDCl_3$)

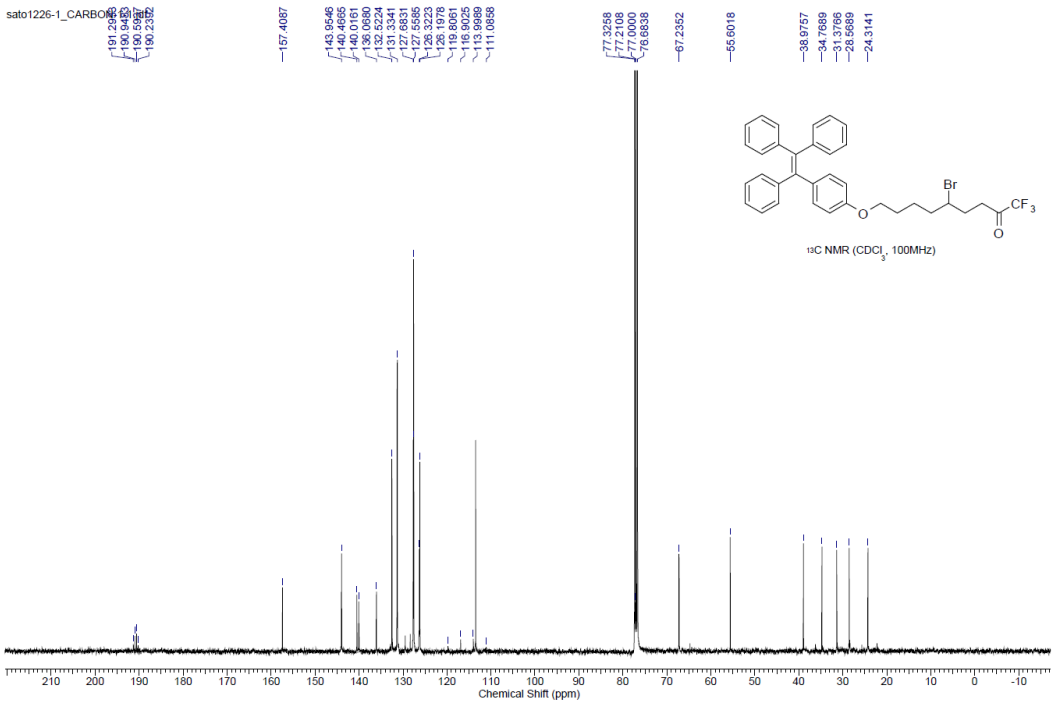

Figure S155. ^{13}C NMR of **4ab** (100 MHz, $CDCl_3$)

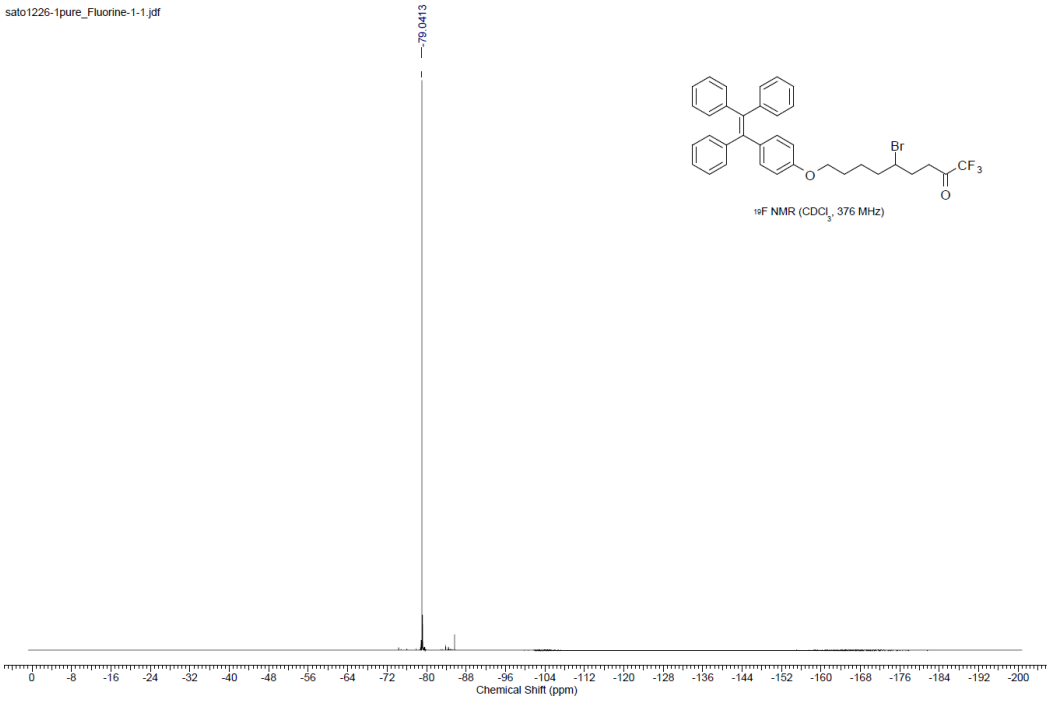

Figure S156. ^{19}F NMR of **4ab** (376 MHz, $CDCl_3$)

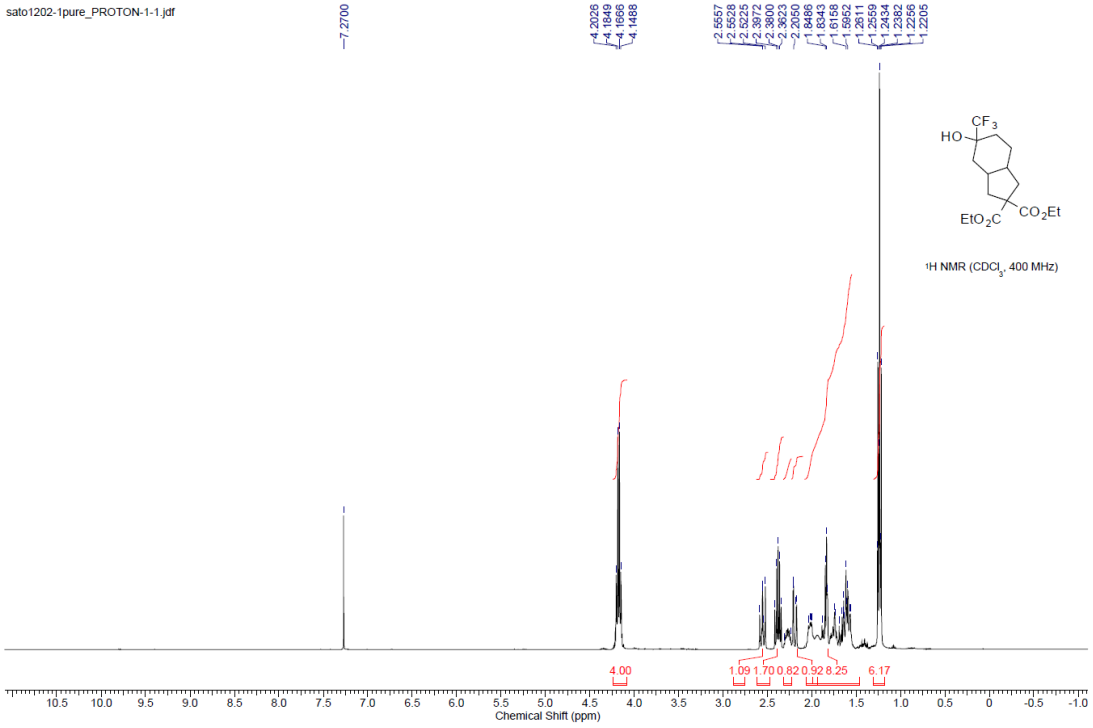

Figure S157. ^{1}H NMR of **7b** (400 MHz, $CDCl_3$)

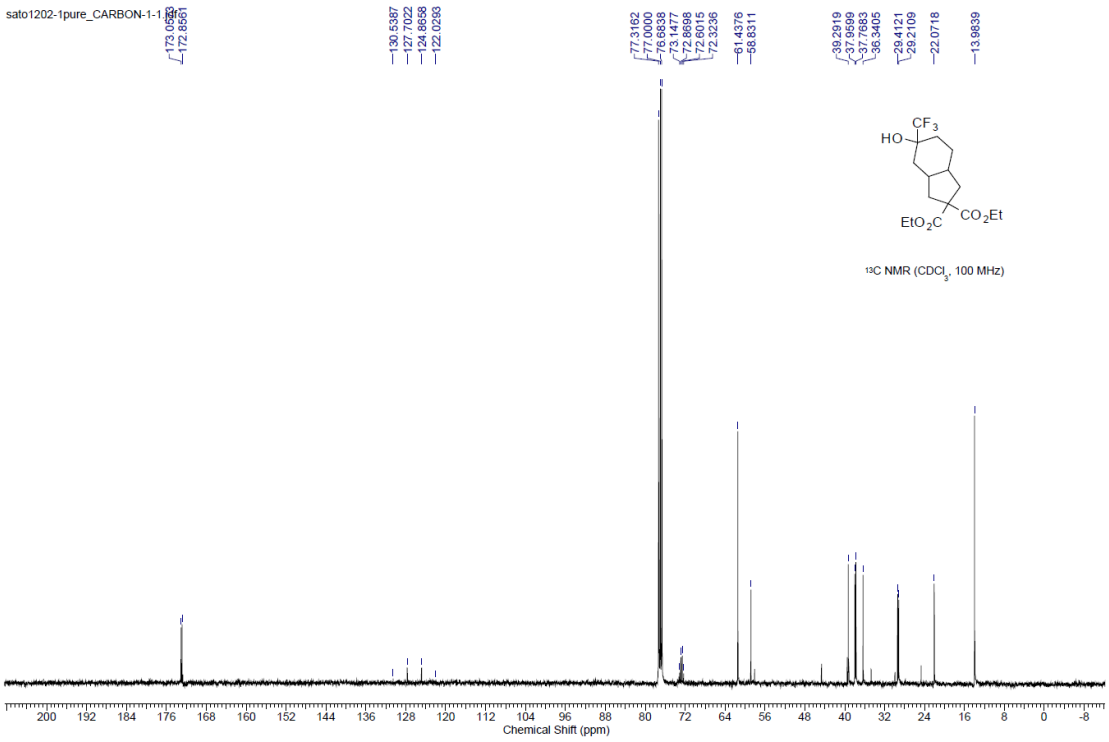

Figure S158. ^{13}C NMR of **7b** (100 MHz, $CDCl_3$)

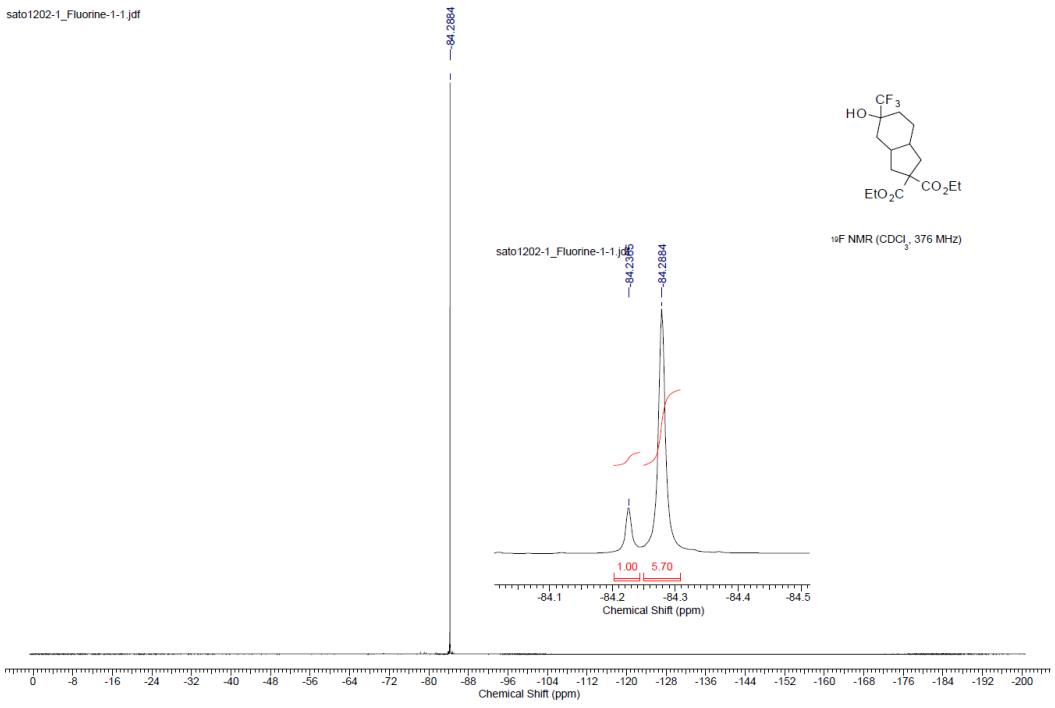

Figure S159. ^{19}F NMR of **7b** (376 MHz, $CDCl_3$)

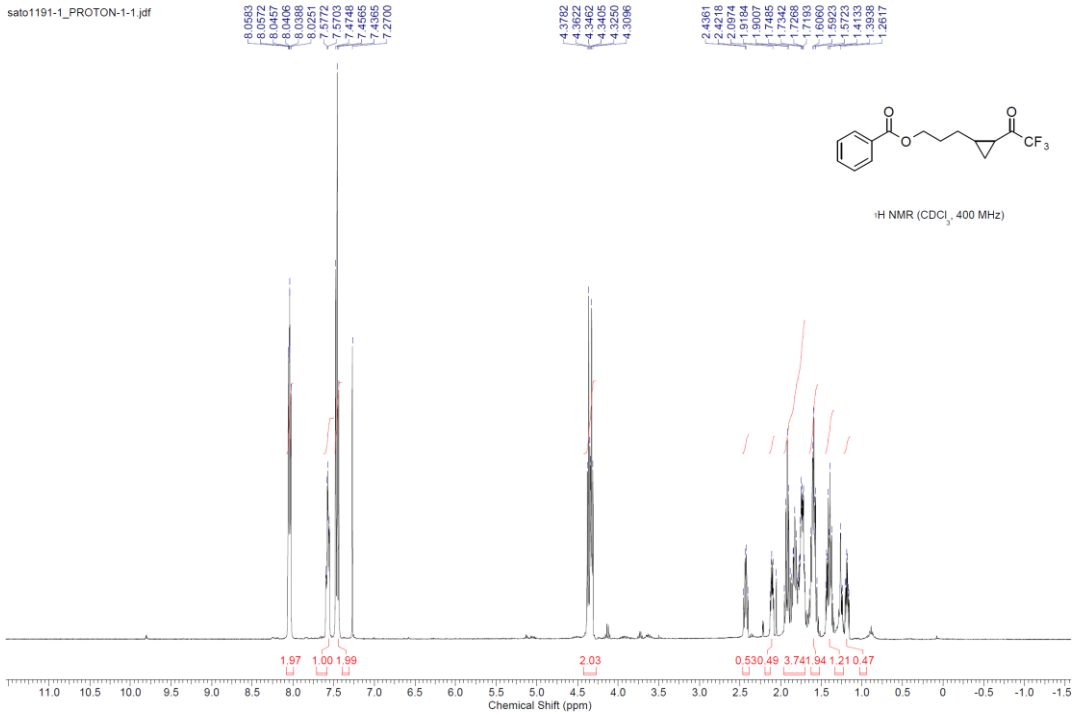

Figure S160. ^{1}H NMR of **9a** (400 MHz, $CDCl_3$)

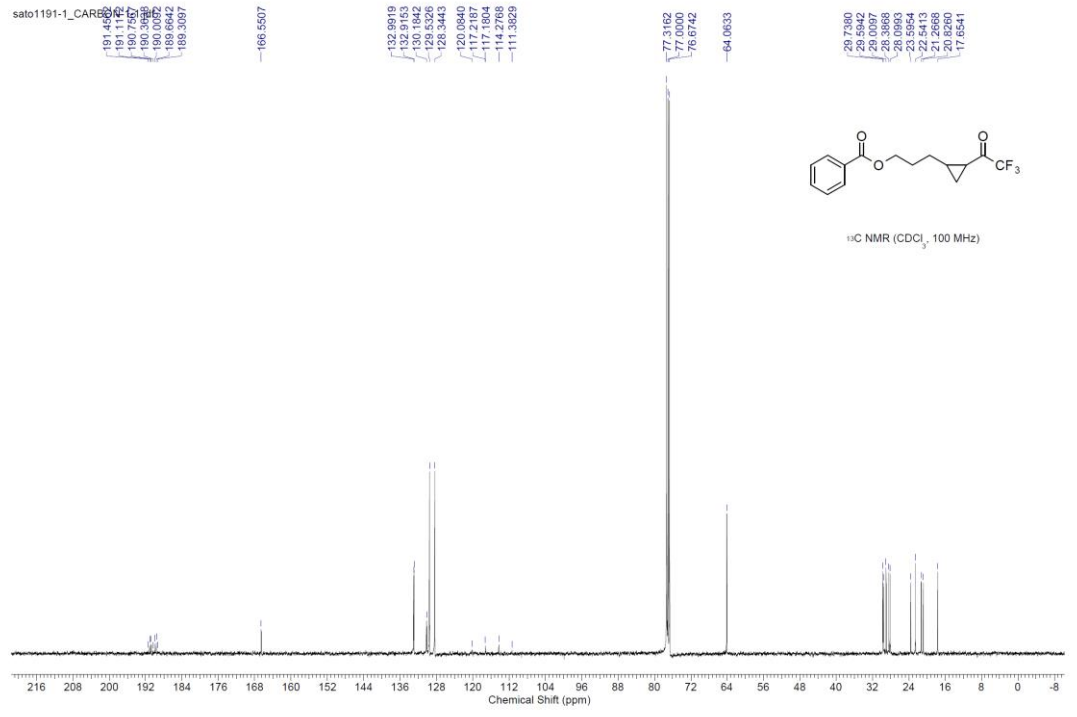

Figure S161. ^{13}C NMR of **9a** (100 MHz, $CDCl_3$)

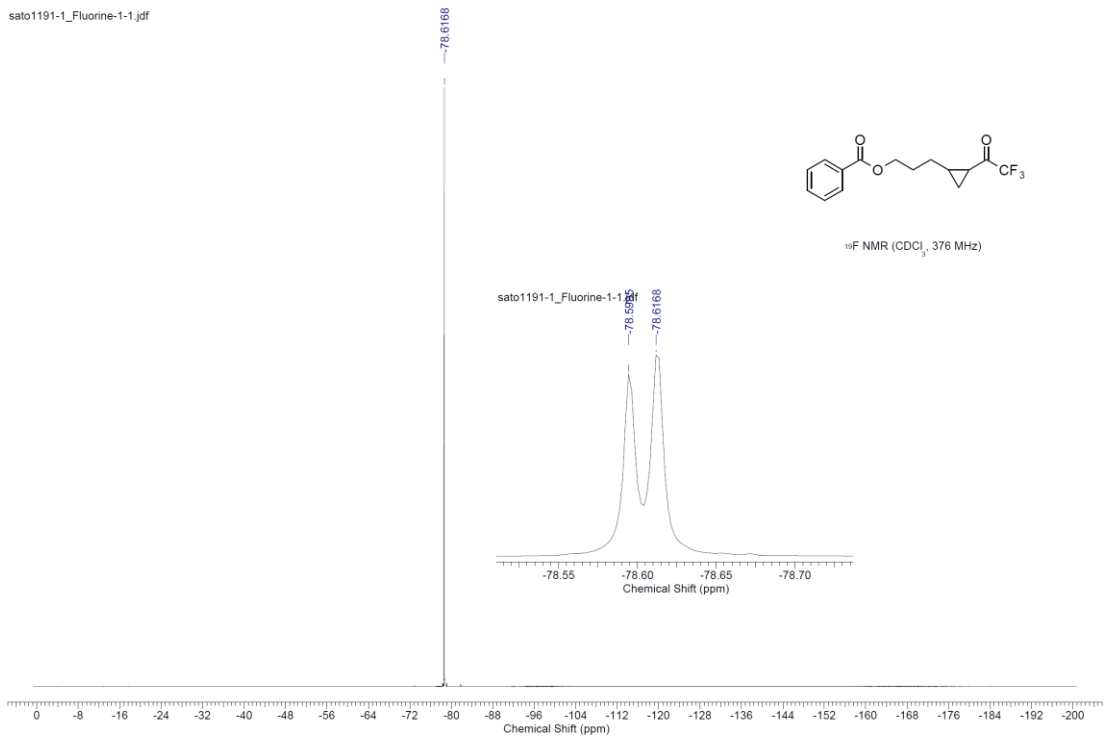

Figure S162. ^{19}F NMR of **9a** (376 MHz, $CDCl_3$)

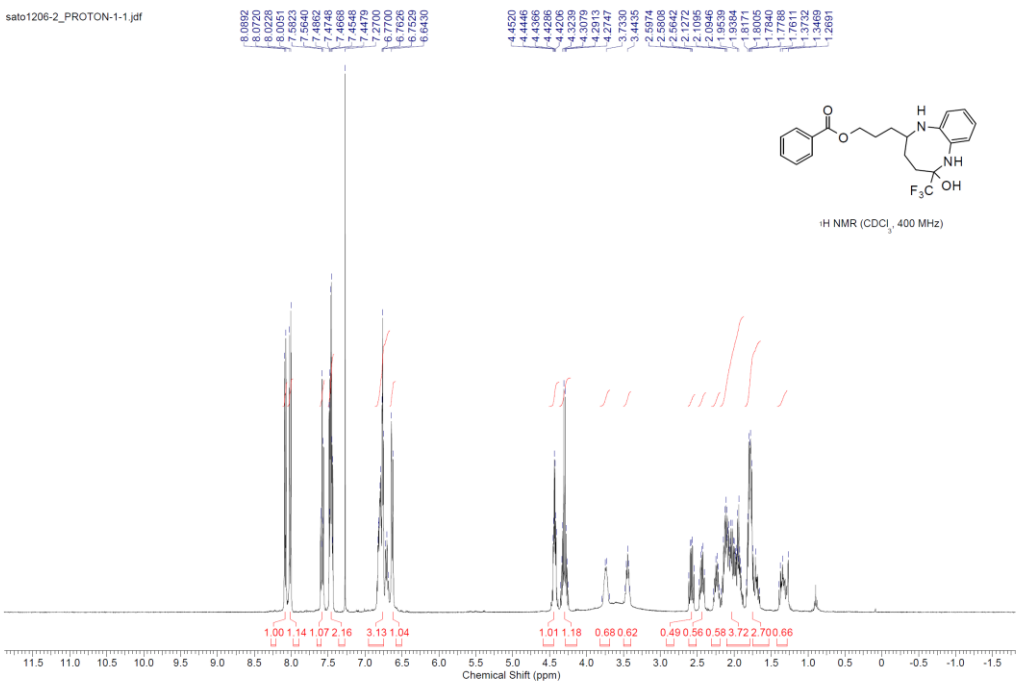

Figure S163. ^{1}H NMR of **9b** (400 MHz, $CDCl_3$)

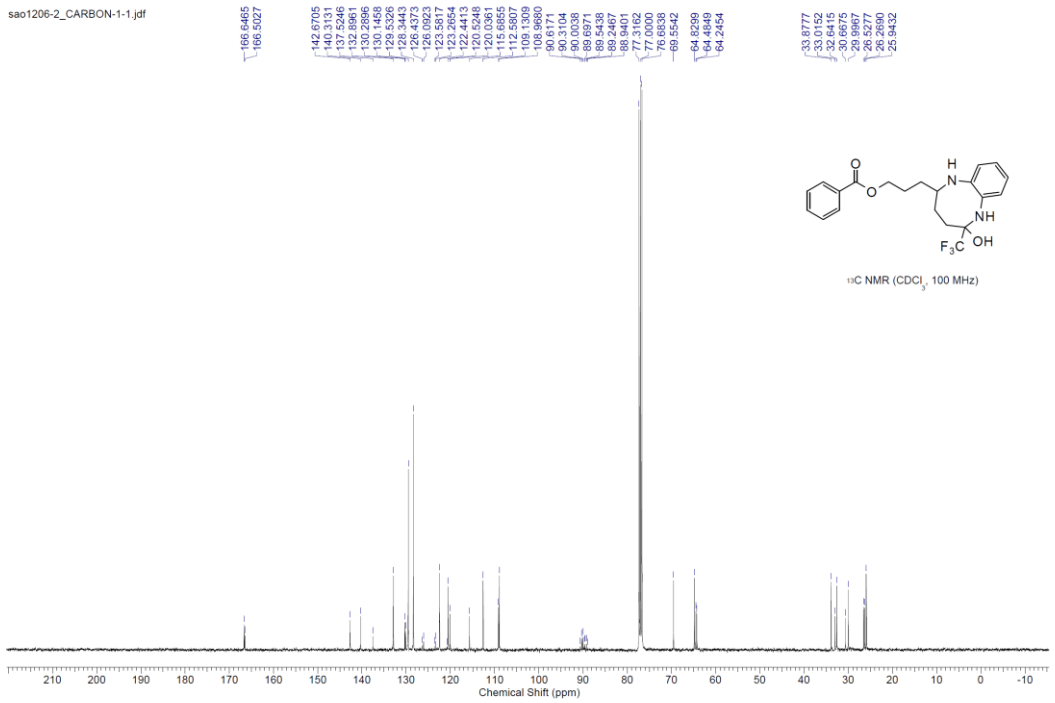

Figure S164. ^{13}C NMR of **9b** (100 MHz, $CDCl_3$)

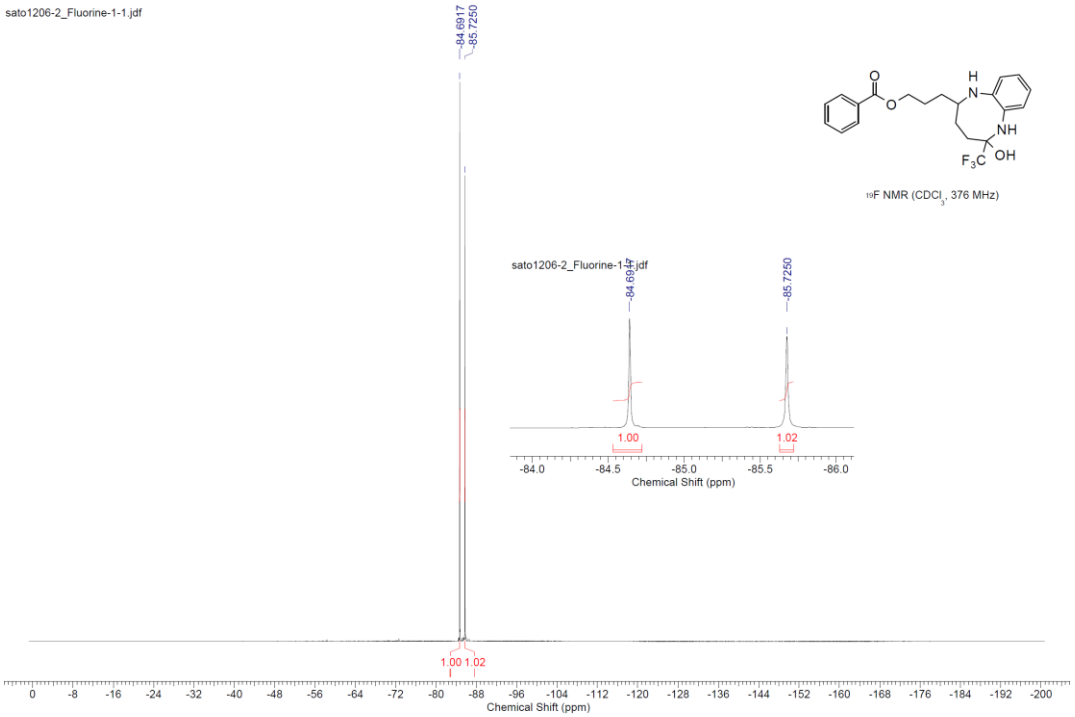

Figure S165. ^{19}F NMR of **9b** (376 MHz, $CDCl_3$)

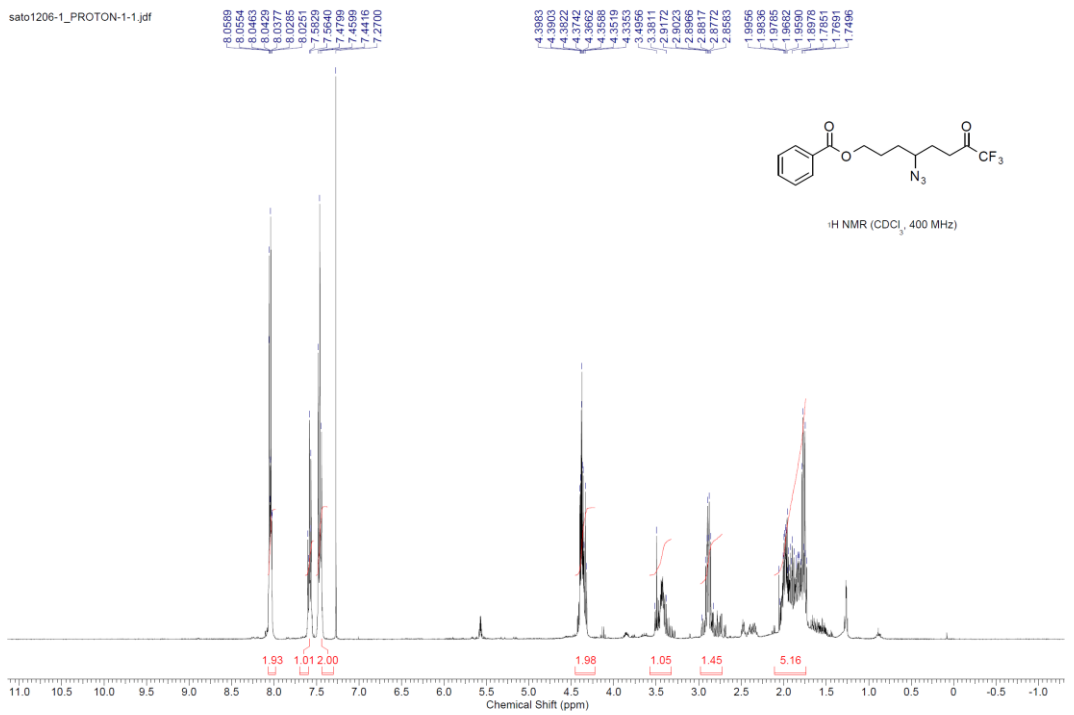

Figure S166. ^{1}H NMR of **9c** (400 MHz, $CDCl_3$)

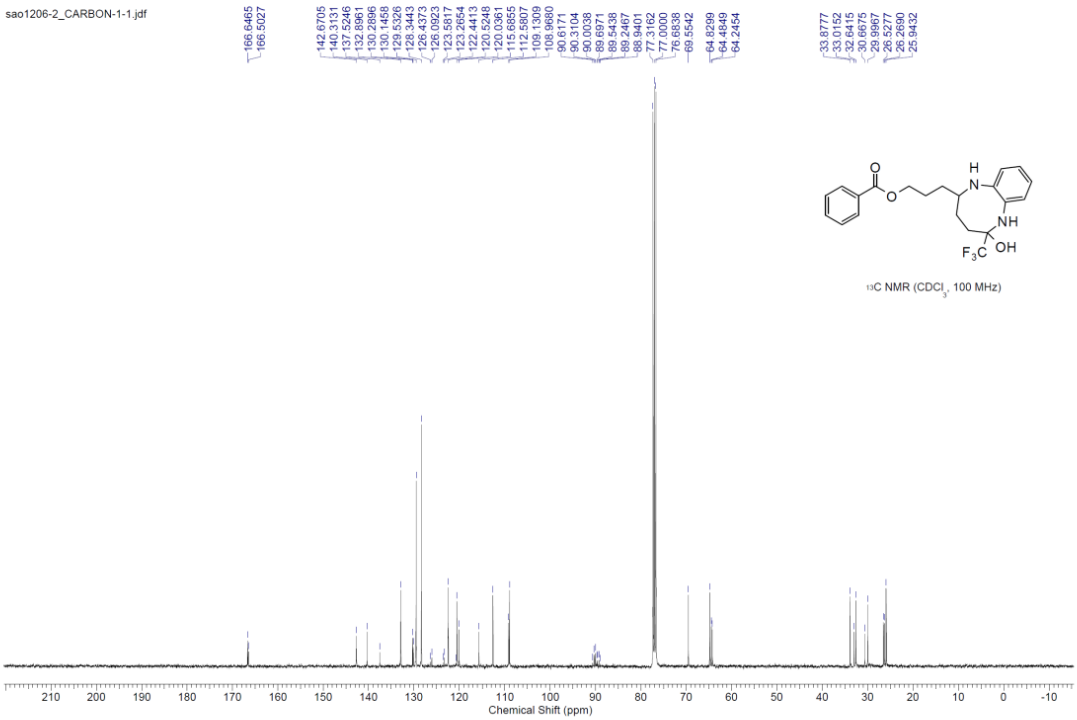

Figure S167. ^{13}C NMR of **9c** (100 MHz, $CDCl_3$)

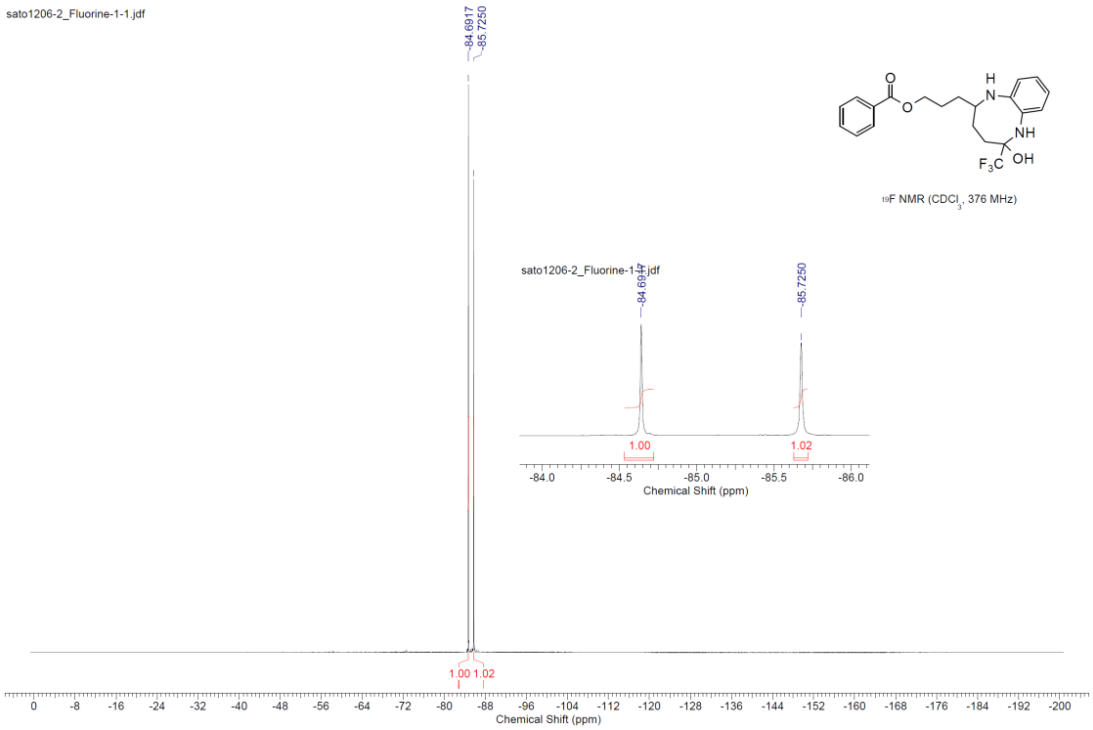

Figure S168. ^{19}F NMR of **9c** (376 MHz, $CDCl_3$)

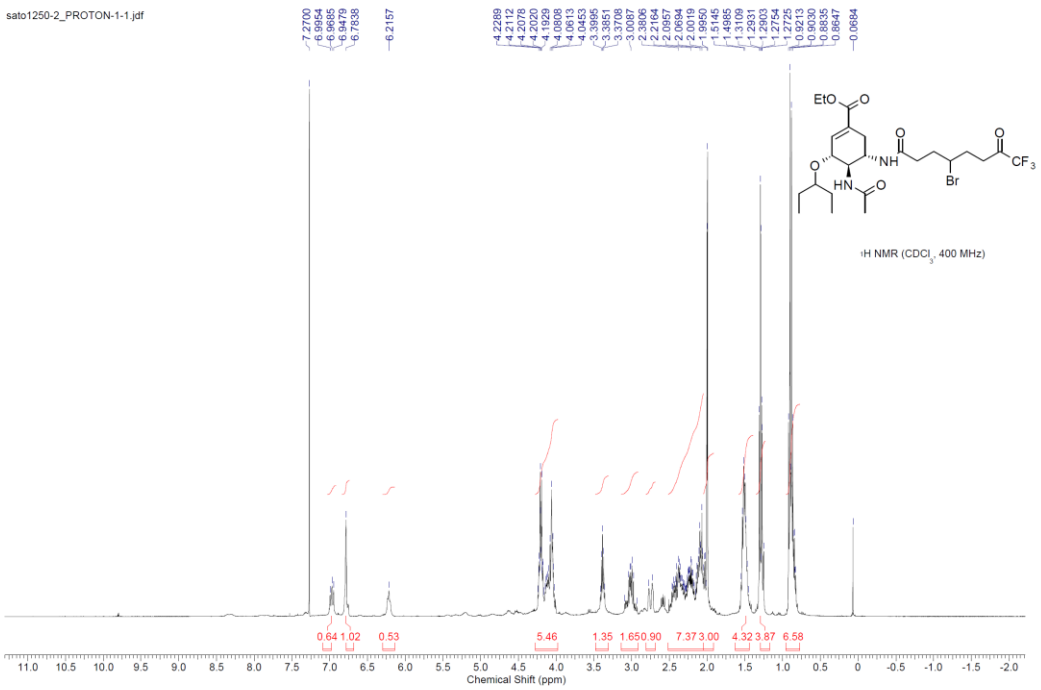

Figure S169. ^{1}H NMR of **10** (400 MHz, $CDCl_3$)

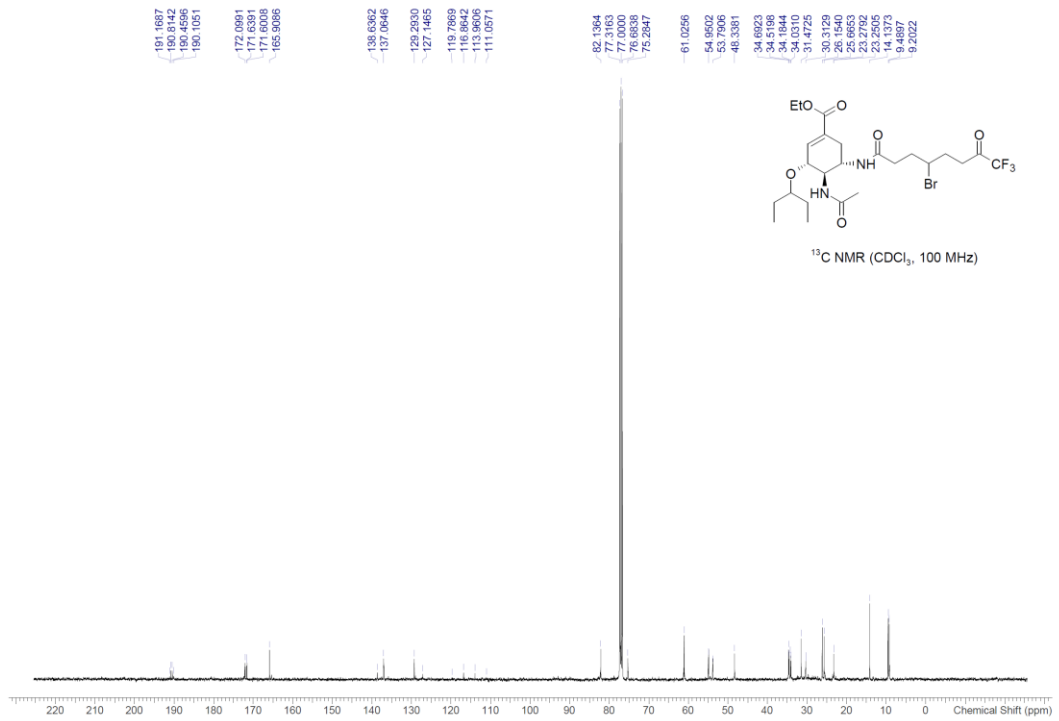

Figure S170. ^{13}C NMR of **10** (100 MHz, $CDCl_3$)

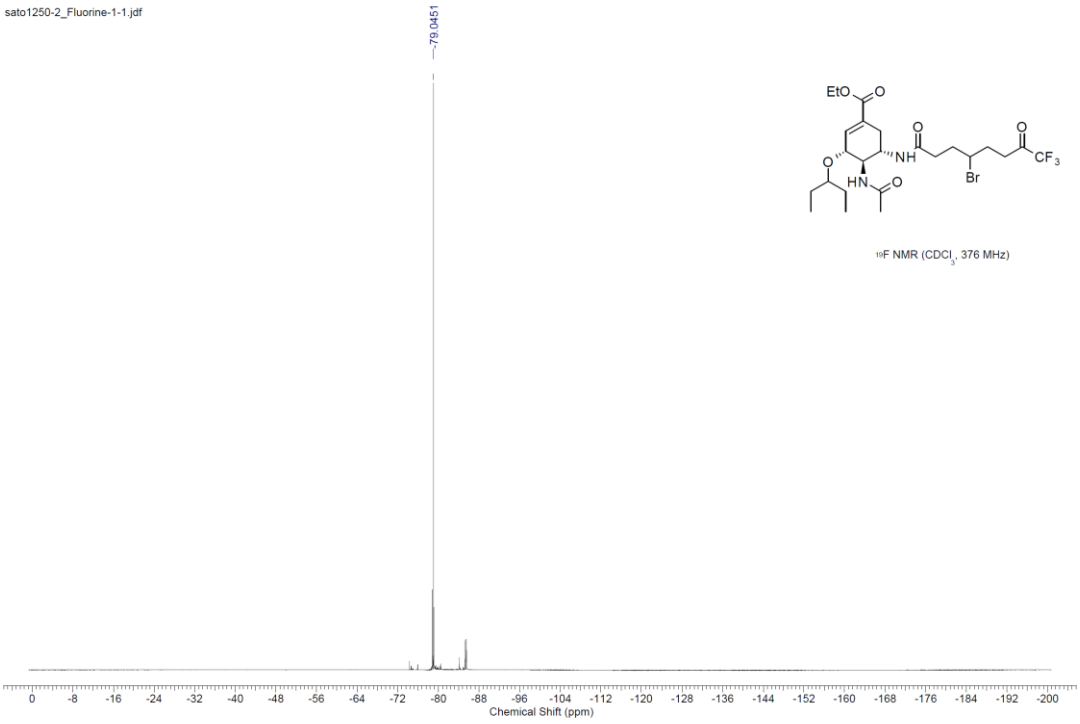

Figure S171. ^{19}F NMR of **10** (376 MHz, $CDCl_3$)

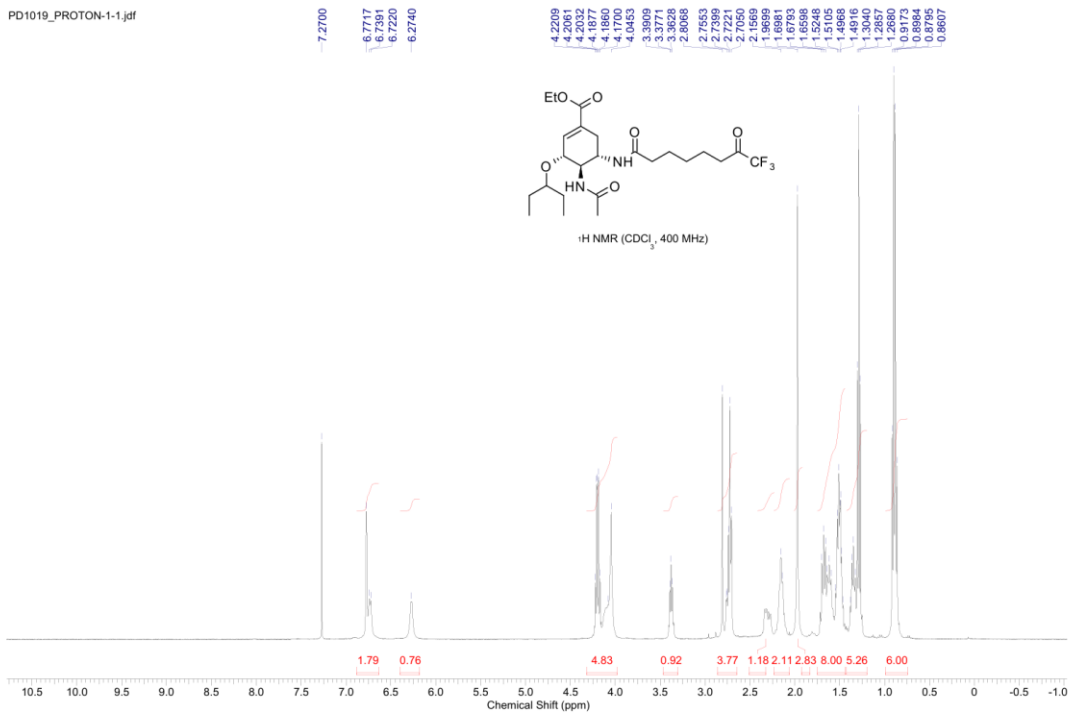

Figure S172. ^{1}H NMR of **11** (400 MHz, $CDCl_3$)

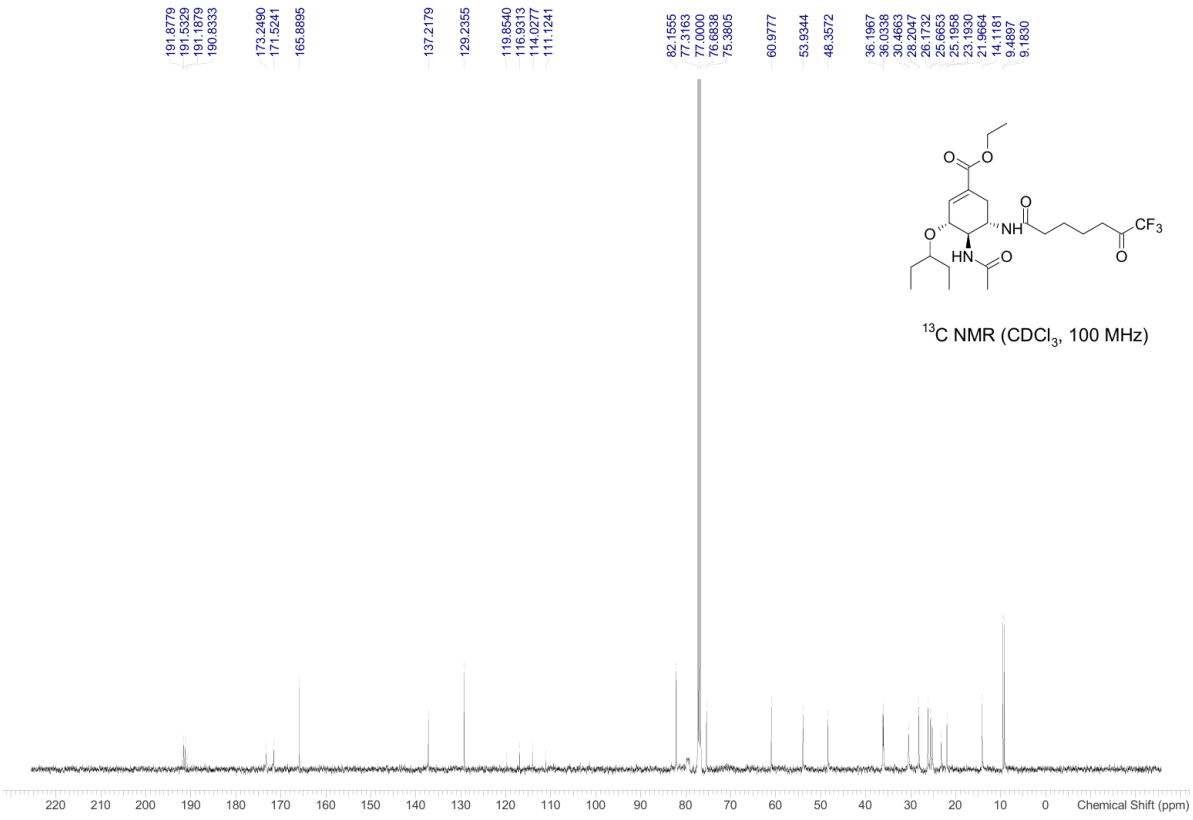

Figure S173. ^{13}C NMR of **11** (100 MHz, $CDCl_3$)

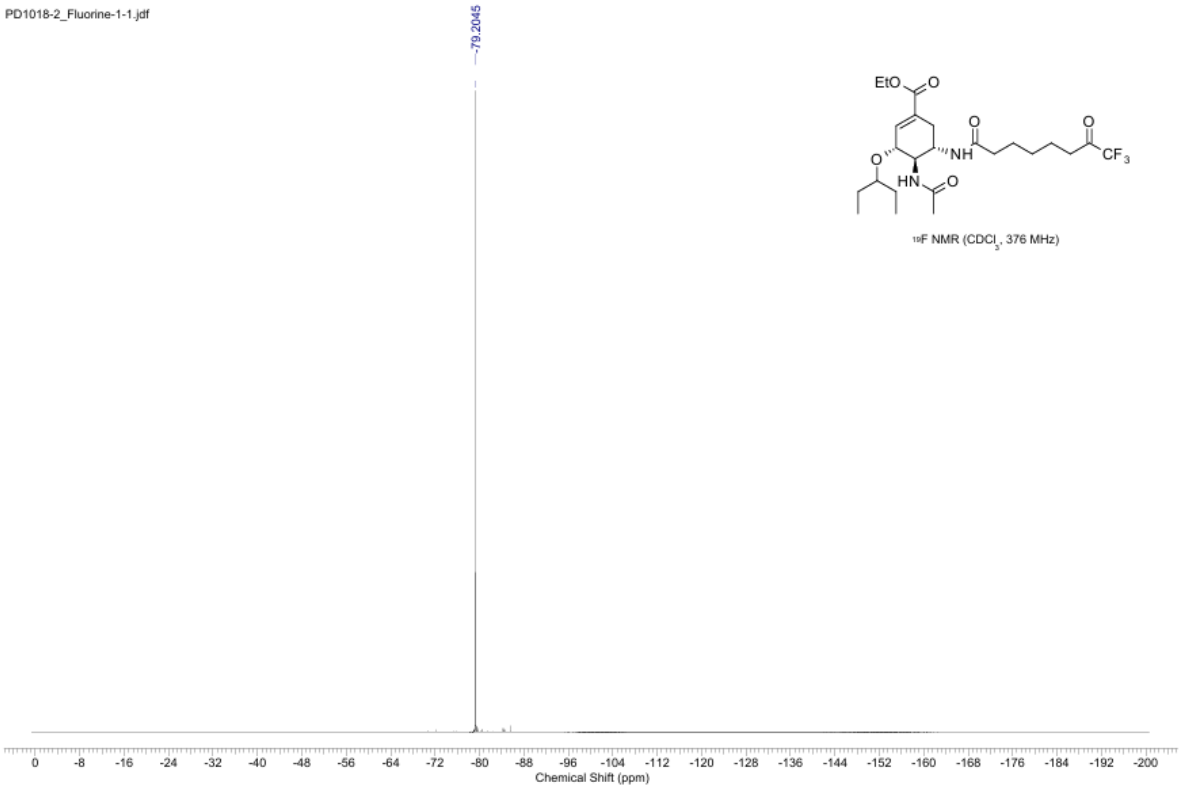

Figure S174. ^{19}F NMR of **11** (376 MHz, $CDCl_3$)