One Pot Synthesis of Trifluoromethylketone-Containing Heterocycles via Tandem Photocatalytic Halo-alkylation of Olefin and Intramolecular Cyclization

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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, 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 F254 aluminum sheets (Merck) and Silica Gel F254 glass plates (Merck). Photochemical reactions were carried out 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 noted, all starting materials and reagents were obtained from commercial suppliers and were used without further purification. All chemicals were purchased from Merck, Nacalai Tesque, Tokyo Chemical Industry, and Wako Pure Chemical Industries and used as received. All solvents were purchased from Wako Pure Chemical Industries. Photocatalyst, 2,4,5,6-tetrakis(diphenylamino)isophthalonitrile (4DPAIPN), was purchased from Combi-Blocks.

2. Reaction Condition Optimization of 5a

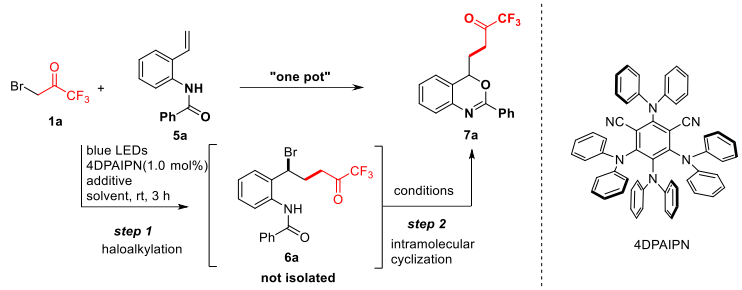


Table S1

	Haloalkylation (*step 1*)			intramolecular cyclization (*step 2*)	
Entry	additive	Solvent	**6a** Yield (%)[b]	Conditions	**7a** Yield (%)[c]
1	–	CH_3CN	54	Add Al_2O_3, then evaporate, rt, 24 h, no stirring	4
2	–	acetone	55	Add silica gel, then evaporate, rt, 24 h, no stirring	11
3	–	$CHCl_3$	49	K_2CO_3 (5.0 equiv), rt, 12 h	29
4	–	CH_2Cl_2	58	K_2CO_3 (5.0 equiv), rt, 12 h	48
5	$Zn(OAc)_2$ (0.2 equiv)	CH_2Cl_2	70	K_2CO_3 (5.0 equiv), rt, 12 h	66
6[d]	$Zn(OAc)_2$ (0.2 equiv)	CH_2Cl_2	40	–	–

[a] Reaction conditions [*Step 1*]: **1a** (0.4 mmol), **2a** (0.2 mmol), photocatalyst (1 mol%), solvent (500 μL), blue LED, room temperature (rt), 3h; [*Step 2*] indicated reaction conditions. [b] Yields determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard. [c] Isolated yield. [d] Reaction time: 1 h.

3. Two-dimensional thin-layer chromatography

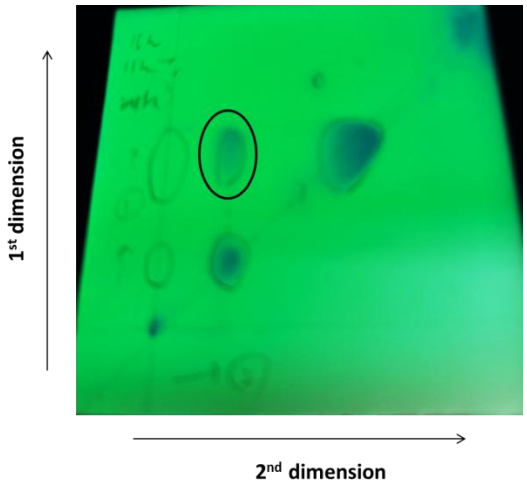


Figure S1. Image of Two-dimensional thin layer chromatography under UV irradiation. 2D TLC of the crude reaction mixture after the photocatalyzed difunctionalization of **2a** with **1a**. Eluting with AcOEt/n-hexane 1 :1 as the first dimension and left for 16 h. Then, eluting with AcOEt/n-hexane 1 :1 as the second dimension.

4. ^{1}H and ^{19}F NMR spectrum of the reaction 1a with CD_3OD

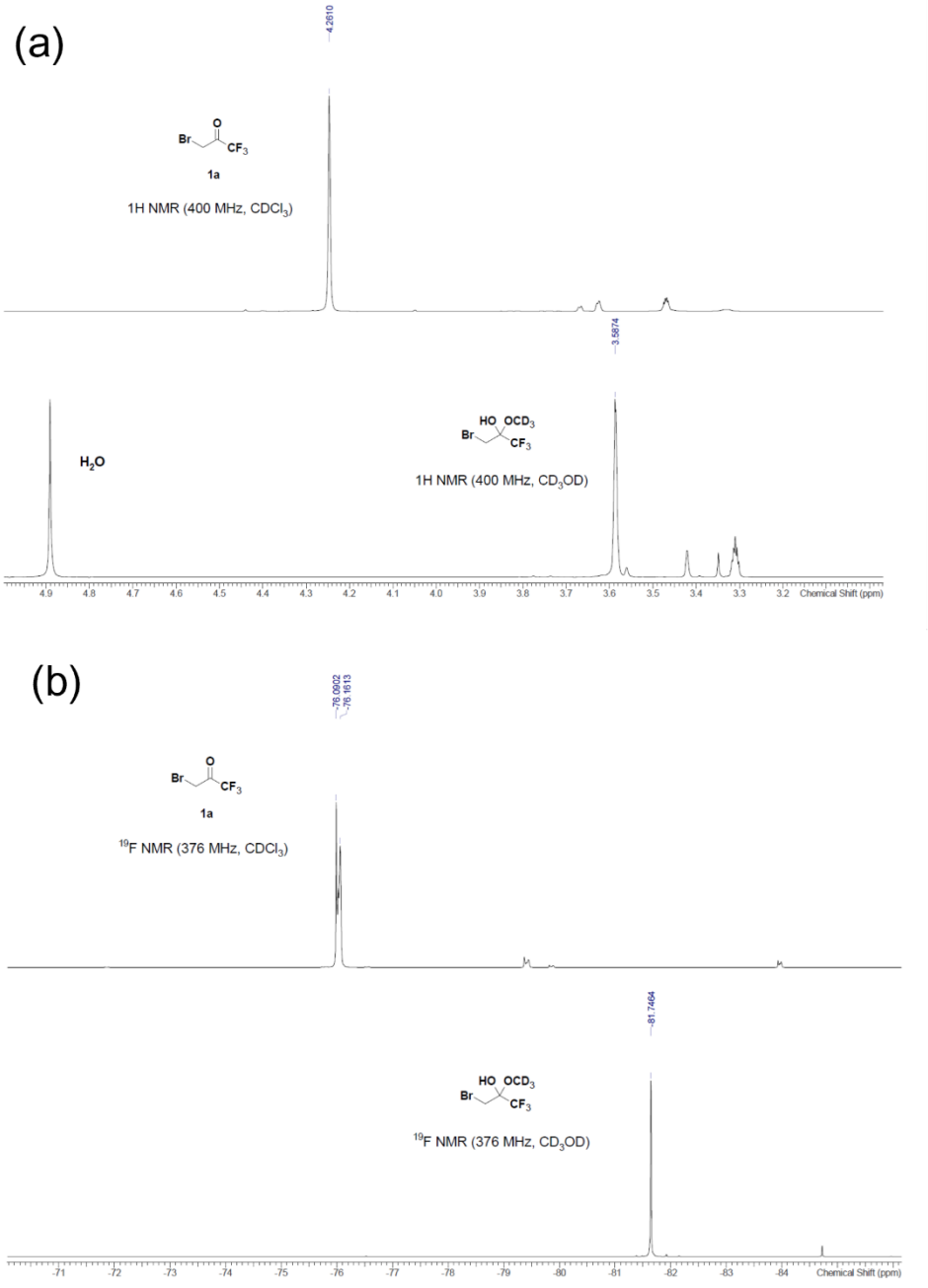
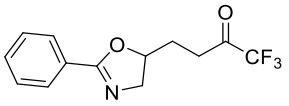


Figure S2. (a) ^{1}H NMR spectra of bromo trifluoromethylketone 1a in $CDCl_3$ and CD_3OD. (b) ^{19}F NMR spectra of bromo trifluoromethylketone 1a in $CDCl_3$ and CD_3OD.

5. Experimental procedures and characterization data

5-1. General procedure 1 (GP1) for the one-pot synthesis of trifluoromethyl ketone containing oxazolines

A 4 mL vial with a magnetic stirring bar was charged with N-allylbenzamide (0.3 mmol, 1.0 equiv.). 4DPAIPN (1 mol%), $Zn(OAc)_2$ (0.2 equiv.) and CH_2Cl_2 (500 μL, 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 3 h. To the reaction mixture, Al2O3 (1.0 g) was added, and then the mixture was evaporated and left for 1 day. The residue was filtered through a glass filter and washed with AcOEt/MeOH (9:1). The residue was purified by column chromatography on SiO_2 gel, isolating the trifluoromethyl ketone containing oxazolines.

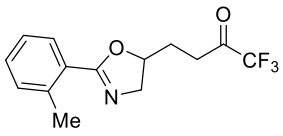


Synthesis of 1,1,1-trifluoro-4-(2-phenyl-4,5-dihydrooxazol-5-yl)butan-2-one (4a)

The GP1 was followed with N-allylbenzamide (48.4 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a brown oil (52.9 mg, 65% yield; Ketone/Hydrate = 15/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 7.1 Hz, 2H), 7.52–7.48 (m, 1H), 7.43 (t, *J* = 7.1 Hz, 2H), 4.79 –4.76 (m, 1H), 4.20 (dd, *J* = 9.6, 14.9 Hz, 1H), 3.71 (dd, *J* = 7.1, 14.9 Hz, 1H), 3.00–2.95 (m, 2H), 2.12–2.03 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.2 (q, *J* = 35.5 Hz), 163.8, 131.6, 128.4, 128.1, 127.3, 115.5(q, *J* = 290.4 Hz), 78.1, 59.8, 32.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 14/5F), –85.6 (s, 1/5F hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{12}F_3NO_2$ $[M]^+$ 271.0820, found 271.0820.

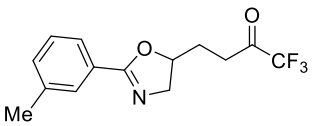
Scale up reaction: The GP1 was followed with N-allylbenzamide (322 mg, 2.0 mmol), bromotrifluoroacetone (460 μL, 4.0 mmol), 4DPAIPN (16 mg, 1 mol%), $Zn(OAc)_2$ (73 mg, 0.4 mmol), and CH_2Cl_2 (3.0 mL). The reaction was irradiated with blue LED for 3 h. To the reaction mixture, Al2O3 (5.0 g) was added, and then the mixture was evaporated and left for 1 day. The residue was filtered through a glass filter and washed with AcOEt/MeOH (9:1). The residue was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as brown oil (353 mg, 65% yield).



Synthesis of 1,1,1-trifluoro-4-(2-(o-tolyl)-4,5-dihydrooxazol-5-yl)butan-2-one (4b)

The GP1 was followed with N-allyl-2-methylbenzamide (52.6 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow oil (35.9 mg, 42% yield; Ketone/Hydrate = >20/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

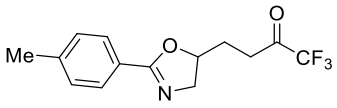
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.0 Hz, 1H), 7.38–7.34 8m, 1H), 7.26–7.24 (m, 2H), 4.73–4.70 (m, 1H), 4,23 (dd, *J* = 9.8, 14.9 Hz, 1H), 3.74 (dd, *J* = 7.1, 14.9 Hz, 1H), 2.98–2.95 (m, 2H), 2.58 (s, 3H), 2,13–2.02 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 164.0, 138.7, 131.3, 130.7, 129.7, 125.6, 126.8, 125.6, 115.5 (q, *J* = 290.4 Hz), 77.1, 60.4, 32.5, 28.2, 21.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.1 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{14}F_3NO_2$ $[M]^+$ 285.0977, found 285.0977.



Synthesis of 1,1,1-trifluoro-4-(2-(m-tolyl)-4,5-dihydrooxazol-5-yl)butan-2-one (4c)

The GP1 was followed with N-allyl-3-methylbenzamide (52.6 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (41.9 mg, 49% yield; Ketone/Hydrate = >20/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

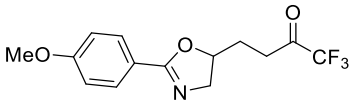
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (s, 1H), 7.72–7.69 (m, 1H), 7.30 (dd, *J* = 1.1, 5.3 Hz, 2H), 4.80–4.74 (m, 1H), 4.19 (dd, *J* = 9.6, 14.6 Hz, 1H), 3.69 (dd, *J* = 7.1, 14.6 Hz, 1H), 2.99–2.94 (m, 2H), 2.39 (s, 3H), 2.09–2.05 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.8 (q, *J* = 35.6 Hz), 138.2, 132.3, 128.7, 128.3, 127.2, 125.2, 115.5 (q, *J* = 290.4 Hz), 78.0, 59.8, 32.4, 28.1, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{14}F_3NO_2$ $[M]^+$ 285.0977, found 285.0977.



Synthesis of 1,1,1-trifluoro-4-(2-(p-tolyl)-4,5-dihydrooxazol-5-yl)butan-2-one (4d)

The GP1 was followed with N-allyl-4-methylbenzamide (52.6 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (44.0 mg, 51% yield; Ketone/Hydrate = 8/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

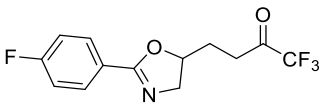
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.17 (dd, *J* = 9.6, 14.6 Hz, 1H), 3.68 (dd, *J* = 7.1, 14.8 Hz, 1H), 3.02–2.89 (m, 2H), 2.40 (s, 3H), 2.14–1.97 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 163.7, 141.9, 129.1, 128.0, 124.6, 115.5 (q, *J* = 290.4 Hz), 77.9, 59.9, 32.4, 28.1, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 8/3F), –85.6 (s, 1/3F hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{14}F_3NO_2$ $[M]^+$ 285.0977, found 285.0977.



Synthesis of 1,1,1-trifluoro-4-(2-(4-methoxyphenyl)-4,5-dihydrooxazol-5-yl)butan-2-one (4e)

The GP1 was followed with N-allyl-4-methoxybenzamide (57.4 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:2). This afforded the title compound as a yellow solid (50.6 mg, 56% yield, Rf = 0.38).

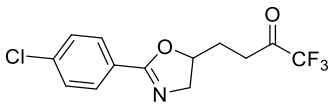
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 2H), 4.75–4.72 (m, 1H), 4.17 (dd, *J* = 9.6, 14.6 Hz, 1H), 3.86 (s, 3H), 3.67 (dd, *J* = 7.1, 14.6 Hz, 1H), 3.03–2.89 (m, 2H), 2.10–1.99 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 163.4, 162.2, 129.8, 119.9, 115.5 (q, *J* = 290.4 Hz), 113.7, 77.9, 59.9, 55.4, 32.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{14}F_3NO_3$ $[M]^+$ 301.0926, found 301.0926.



Synthesis of 1,1,1-trifluoro-4-(2-(4-fluorophenyl)-4,5-dihydrooxazol-5-yl)butan-2-one (4f)

The GP1 was followed with N-allyl-4-fluorobenzamide (53.8 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (39.9 mg, 46% yield, Rf = 0.2).

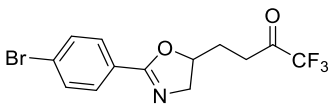
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93–7.89 (m, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 4.78–4.75 (m, 1H), 4.18 (dd, *J* = 9.6, 14.7 Hz, 1H), 3.79 (dd, *J* = 7.3, 14.9 Hz, 1H), 3.03–2.89 (m, 2H), 2.14–2.03 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 164.7 (d, *J* = 250.1 Hz), 162.8, 130.4 (d, *J* = 8.6 Hz), 123.6 (d, *J* = 2.9 Hz), 115.6 (d, *J* = 22.0 Hz), 115.5 (q, *J* = 290.4 Hz), 78.3, 56.0, 32.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F), –107.7 (m, 1F); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{11}F_4NO_2$ $[M]^+$ 289.0726, found 289.0727.



Synthesis of 4-(2-(4-chlorophenyl)-4,5-dihydrooxazol-5-yl)-1,1,1-trifluorobutan-2-one (4g)

The GP1 was followed with N-allyl-4-chlorobenzamide (53.8 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a white solid (44.0 mg, 48% yield; Ketone/Hydrate = 19/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

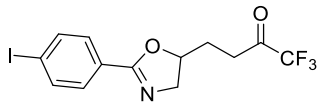
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.81–4.75 (m, 1H), 4.19 (dd, *J* = 9.6, 14.9 Hz, 1H), 3.70 (dd, *J* = 7.1, 14.9 Hz, 1H), 3.03–2.88 (m, 2H), 2.15–2.01 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 162.8, 137.7, 129.4, 128.7, 125.9, 115.5 (q, *J* = 290.4 Hz), 78.3, 60.1, 32.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 57/20F), –85.8 (s, 3/20F, hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{11}ClF_3NO_2$ $[M]^+$ 305.0430, found 305.0429.



Synthesis of 4-(2-(4-bromophenyl)-4,5-dihydrooxazol-5-yl)-1,1,1-trifluorobutan-2-one (4h)

The GP1 was followed with N-allyl-4-bromobenzamide (53.8 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (50.6 mg, 56% yield; Ketone/Hydrate = >20/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

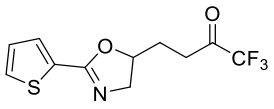
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 4.80–4.74 (m, 1H), 4.18 (dd, *J* = 9.6, 14.8 Hz, 1H), 3.70 (dd, *J* = 7.1, 14.8 Hz, 1H), 3.03–2.88 (m, 2H), 2.12–1.99 8m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 162.9, 131.7, 129.6, 126.3, 126.2, 115.5 (q, *J* = 290.4 Hz), 78.3, 60.1, 32.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{11}BrF_3NO_2$ $[M]^+$ 348.9925, found 348.9925.



Synthesis of 4-(2-(4-iodophenyl)-4,5-dihydrooxazol-5-yl)-1,1,1-trifluorobutan-2-one (4i)

The GP1 was followed with N-allyl-4-iodobenzamide (57.4 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (33.1 mg, 54% yield; Rf = 0.2).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 4.82–4.72 (m, 1H), 4.18 (dd, *J* = 9.5, 14.7 Hz, 1H), 3.69 (dd, *J* = 7.1, 14.9 Hz, 1H), 3.02–2.89 (m, 2H), 2.11–1.96 (m, 2H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 36.0 Hz), 163.0, 137.6, 129.6, 137.6, 129.6, 126.9, 115.5 (q, *J* = 288.9 Hz), 98.5, 78.3, 60.4, 32.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{12}F_3NO_2I$ $[M+H]^+$ 397.9865, found 397.9865.

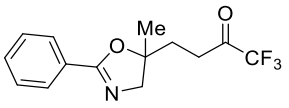


Synthesis of 1,1,1-trifluoro-4-(2-(thiophen-2-yl)-4,5-dihydrooxazol-5-yl)butan-2-one (4k)

The GP1 was followed with N-allylthiophene-2-carboxamide (50.2 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the

intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (35.8 mg, 43% yield; Ketone/Hydrate = 16/1, Rf = 0.25). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 3.6 Hz, 1H), 7.47 (d, *J* = 4.8 Hz, 1H), 7.10−7.07 (m, 1H), 4.81−4.73 (m, 1H), 4.17 (dd, *J* = 9.6, 14.6 Hz, 1H), 3.58 (dd, *J* = 7.1, 14.6 Hz, 1H), 3.03−2.88 (m, 2H), 2.14−1.98 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 159.5, 130.5, 130.1, 129.9, 127.6, 115.5 (q, *J* = 290.4 Hz), 78.7, 59.9, 32.3, 28.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 14/5F), –85.6 (s, 1/5F hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{11}H_{11}F_3NO_2S$ $[M+H]^+$ 278.0463, found 278.0462.



Synthesis of 1,1,1-trifluoro-4-(5-methyl-2-phenyl-4,5-dihydrooxazol-5-yl)butan-2-one (4m)

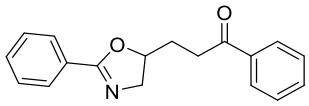
The GP1 was followed with N-(2-methylallyl)benzamide (52.6 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow solid (17.1 mg, 20% yield; Ketone/Hydrate = >20/1. Rf = 0.18). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 7.1 Hz, 2H), 7.57–7.41 (m, 3H), 3.84 (s, 2H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.19–2.05 (m, 2H), 1.51 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 163.4, 131.7, 128.6, 128.4, 128.1, 127.3, 115.5 (q, *J* = 290.4 Hz), 84.7, 65.2, 32.5, 31.2, 25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –78.9 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{14}F_3NO_2$ $[M+H]^+$ 286.1055, found 286.1055.

4-1. General procedure 2 (GP2) for the one-pot synthesis of phenyl ketone containing oxazolines

A 4 mL vial with a magnetic stirring bar was charged with N-allylbenzamide (0.3 mmol, 1.0 equiv.). 4DPAIPN (1 mol%), $Zn(OAc)_2$ (0.2 equiv.), and acetone (500 μL, 0.6 M) were added. Finally, phenacyl bromide (1.2 equiv.) or 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 9 h. To the reaction mixture, K_2CO_3 (5.0 equiv.) was added, and then stirred for 1day. The reaction mixture was filtered and purified by column chromatography on SiO_2 gel, affording the

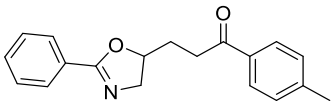
phenyl ketone containing oxazolines.



Synthesis of 1-phenyl-3-(2-phenyl-4,5-dihydrooxazol-5-yl)propan-1-one (4n)

The GP2 was followed with N-allylbenzamide (48.4 mg, 0.30 mmol), phenacyl bromide (71.7 mg, 0.36 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and acetone (500 μL). The reaction was irradiated with blue LED for 9 h. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a brown oil (42.7 mg, 51% yield, Rf = 0.4).

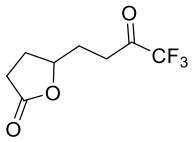
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 7.1 Hz, 2H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 3H), 7.41 (t, *J* = 7.8 Hz, 2H), 4.88–4.83 (m, 1H), 4.20 (dd, *J* = 9.8, 14.7 Hz, 1H), 3.75 (dd, *J* = 7.1, 14.4 Hz, 1H), 3.21 (t, *J* = 7.6 Hz, 2H), 2.20–2.10 (m, 2H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 199.0, 163.8, 136.7, 133.2, 131.3, 128.6, 128.3, 128.1, 128.0, 127.8, 79.1, 60.1, 34.1, 29.8; **HRMS** (FAB) *m/z* Calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1338, found 280.1338.



Synthesis of 3-(2-phenyl-4,5-dihydrooxazol-5-yl)-1-(p-tolyl)propan-1-one (4o)

The GP2 was followed with N-allylbenzamide (48.4 mg, 0.30 mmol), 2-bromo-1-(p-tolyl)ethan-1-one (76.7 mg, 0.36 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and acetone (500 μL). The reaction was irradiated with blue LED for 9 h. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (5:1). This afforded the title compound as a yellow solid (44.0 mg, 50% yield, Rf = 0.4).

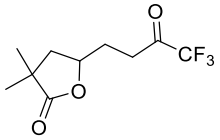
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 7.41 (t, *J* = 7.6 Hz, 2H), 7.28–7.27 (m, 2H), 4.88–4.83 (m, 1H), 4.19 (dd, *J* = 9.6, 14.7 Hz, 1H), 3.74 (dd, *J* = 7.3, 14.7 Hz, 1H), 3.18 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 2.23–2.08 (m, 2H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 198.7, 163.8, 144.0, 134.3, 131.3, 129.3, 128.3, 128.2, 128.1, 127.8, 79.1, 60.1, 33.9, 29.9, 21.6; **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.1494, found 294.1494.



Synthesis of 5-(4,4,4-trifluoro-3-oxobutyl)dihydrofuran-2(3H)-one (4p)

The GP1 was followed with pent-4-enoic acid (30.0 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with hexane−AcOEt (2:1). This afforded the title compound as a yellow solid (33.6 mg, 53% yield; Ketone/Hydrate = 15/1, Rf = 0.12). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

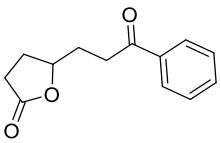
^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.55–4.49 (m, 1H), 3.04–2.88 (m, 2H), 2.59–2.56 (m, 2H), 2.43–2.39 (m, 1H), 2.14–2.07 (m, 1H), 2.00–1.85 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 176.4, 115.3 (q, *J* = 290.4 Hz), 78.8, 32.6, 28.6, 28.2, 27.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.1 (s, 14/5F), –85.3 (s, 1/5F hydrate); **HRMS** (FAB) *m/z* Calcd for $C_8H_{10}F_3O_3$ $[M+H]^+$ 211.0582, found 211.0582.



Synthesis of 3,3-dimethyl-5-(4,4,4-trifluoro-3-oxobutyl)dihydrofuran-2(3H)-one (4q)

The GP1 was followed with 2,2-dimethylpent-4-enoic acid (38.4 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with Al_2O_3 (1.0 g), the crude was purified by column chromatography and eluted with AcOEt. This afforded the title compound as a brown solid (22.6 mg, 31% yield; Ketone/Hydrate = 3/1, Rf = 0.12). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

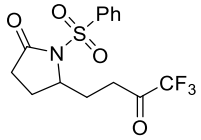
^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.49–4.46 (m, 1H), 3.01–2.95 (m, 2H), 2.25–1.92 (m, 3H), 1.80–1.74 (m, 1H), 1.29 (s, 3H), 1.27 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 181.3, 115.4 (q, *J* = 290.4 Hz), 75.1, 43.4, 40.5, 32.7, 28.4, 25.0, 24.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.1 (s, 9/4F), –85.9 (s, 3/4F, hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{10}H_{14}F_3O_3$ $[M+H]^+$ 239.0895, found 239.0895.



Synthesis of 5-(3-oxo-3-phenylpropyl)dihydrofuran-2(3H)-one (4r)

The GP2 was followed with pent-4-enoic acid (30.0 mg, 0.30 mmol), phenacyl bromide (71.7 mg, 0.36 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and acetone (500 μL). The reaction was irradiated with blue LED for 9 h. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol), the crude product was purified by column chromatography, eluted with hexane−AcOEt (1:1). This afforded the title compound as a brown solid (30.1 mg, 46% yield, Rf = 0.38).

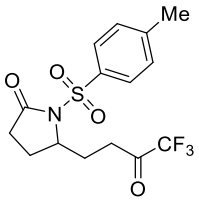
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 4.64–4.60 (m, 1H), 3.23–3.19 (m, 2H), 2.60–2.56 (m, 2H), 2.45–2.39 (m, 1H), 2.25–2.20 (m, 1H), 2.04–1.90 (m, 2H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 198.9, 177.0, 136.6, 133.3, 128.7, 128.0, 80.1, 34.4, 29.9, 28.8, 28.2; **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{15}O_3$ $[M+H]^+$ 219.1021, found 219.1021.



Synthesis of 1-(phenylsulfonyl)-5-(4,4,4-trifluoro-3-oxobutyl)pyrrolidin-2-one (4s)

The GP2 was followed with N-(phenylsulfonyl)pent-4-enamide (47.9 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h, and then evaporated to remove the solvent. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol) in acetone (1.0 mL), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a yellow oil (27.9 mg, 40% yield; Ketone/Hydrate = 6/1, Rf = 0.3). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 4.54–4.45 (m, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.64–2.54 (m, 1H), 2.42–2.17 (m, 3H), 2.14–2.05 (m, 1H), 1.91–1.78 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.2 (q, *J* = 35.5 Hz), 173.3, 138.4, 134.2, 129.0, 128.2,115.4 (q, *J* = 290.4 Hz), 58.9, 32.5, 30.4, 27.5, 24.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –78.8 (s, 13/5F), –86.0 (s, 2/5F , hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{15}F_3NO_4S$ $[M+H]^+$ 350.0674, found 350.0674.



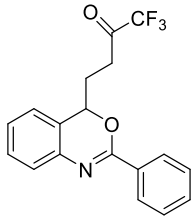
Synthesis of 1-tosyl-5-(4,4,4-trifluoro-3-oxobutyl)pyrrolidin-2-one (4t)

The GP2 was followed with N-tosylpent-4-enamide (50.7 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h, and then evaporated to remove the solvent. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol) in acetone (1.0 mL), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a colourless oil (29.1 mg, 40% yield; Ketone/Hydrate = >20/1, Rf = 0.45). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.49–4.44 (m, 1H), 2.85 (t, *J* = 7.3 Hz, 2H), 2.61–2.52 (m, 1H), 2.44 (s, 3H), 2.40–2.34 (m, 1H), 2.33–2.21 (m, 2H), 2.12–2.05 (m, 1H), 1.83–1.80 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.3 (q, *J* = 35.5 Hz), 173.2, 145.4, 135.4, 129.6, 128.3, 115.4 (q, *J* = 290.4 Hz), 58.8, 32.4, 30.4, 27.5, 24.5, 21.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –78.9 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{15}H_{17}F_3NO_4S$ $[M]^+$ 364.0830, found 364.0830.

5-2. General procedure 3 (GP3) for the one-pot synthesis of trifluoromethyl ketone containing benzoxazines

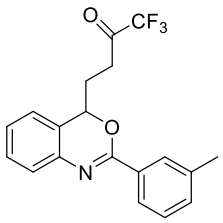
A 4 mL vial with a magnetic stirring bar was charged with N-(2-vinylphenyl)benzamide (0.2 mmol, 1.0 equiv.). 4DPAIPN (1 mol%), $Zn(OAc)_2$ (0.2 equiv.), and acetone (500 μL, 0.4 M) were added. Finally, bromotrifluoroacetone (2.0 equiv.) or phenacyl bromide (1.2 equiv.) was introduced to the reaction mixture. The resulting mixture was stirred at room temperature under 12 W blue LED irradiation (470 nm) for 3 or 9 h. To the reaction mixture, K_2CO_3 (5.0 equiv.) was added, and then stirred for 1day. The reaction mixture was filtered and purified by column chromatography on SiO_2 gel, affording the phenyl ketone containing benzoxazines.



Synthesis of 1,1,1-trifluoro-4-(2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7a)

The GP3 was followed with N-(2-vinylphenyl)benzamide (44.7 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude product was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a pale brown solid (44.0 mg, 66% yield; Ketone/Hydrate = 4/1, Rf = 0.3). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

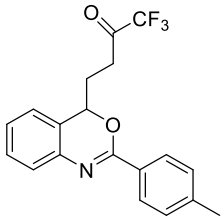
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13−8.11 (m, 2H), 7.72−7.45 (m, 3H), 7.36−7.32 (m, 2H), 7.26−7.22 (m, 1H), 7.05 (d, *J* = 7.1 Hz, 1H), 5.55 (t, *J* = 6.2 Hz, 1H), 3.07−2.92 (m, 2H), 2.34 (q, *J* = 6.8 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.3 (q, *J* = 35.5 Hz), 156.1, 138.9, 132.2, 129.3, 128.4, 127.7, 126.8, 125.2, 124.4, 123.6, 115.4 (q, *J* = 290.4 Hz), 74.6, 31.4, 28.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 12/5F), –85.7 (s, 3/5F , hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{18}H_{15}F_3NO_2$ $[M+H]^+$ 334.1055, found 334.1055.



Synthesis of 1,1,1-trifluoro-4-(2-(m-tolyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7b)

The GP3 was followed with 3-methyl-N-(2-vinylphenyl)benzamide (47.5 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown oil (45.6 mg, 66% yield, Rf = 0.3).

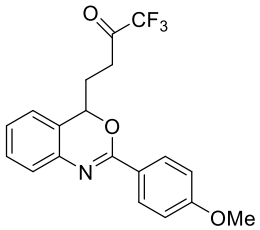
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (s, 1H), 7.82 (d, *J* = 6.6 Hz, 1H), 7.31−7.26 (m, 3H), 7.20−7.22 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 5.48 (t, *J* = 6.0 Hz, 1H), 2.98−2.85 (m, 2H), 2.36 (s, 3H), 2.35−2.31 (m, 2H), 2.27 (q, *J* = 7.1 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 34.5 Hz), 156.5, 138.9, 138.2, 132.5, 132.0, 129.3, 128.4, 128.3, 126.8, 125.2, 124.9, 124.4, 123.6, 115.5 (q, *J* = 290.4 Hz), 74.6, 31.4, 28.4, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{17}F_3NO_2$ $[M+H]^+$ 348.1211, found 348.1211.



Synthesis of 1,1,1-trifluoro-4-(2-(p-tolyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7c)

The GP3 was followed with 4-methyl-N-(2-vinylphenyl)benzamide (47.5 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude product was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown solid (58.3 mg, 84% yield, Rf = 0.3).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 8.4 Hz, 2H), 7.35−7.33 8m, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.24−7.20 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 5.53 (t, *J* = 6.2 Hz, 1H), 3.06−2.90 (m, 2H), 2.43 (s, 3H), 2.33 (q, *J* = 6.6 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.8 (q, *J* = 35.5 Hz), 156.5, 142.3, 139.2, 130.3,129.4, 129.2, 127.9, 126.7, 125.2, 124.6, 123.6, 115.6 (q, *J* = 290.4 Hz), 74.7, 31.6, 28.5, 21.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{17}F_3NO_2$ $[M+H]^+$ 348.1211, found 348.1211.

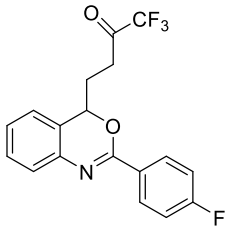


Synthesis of 1,1,1-trifluoro-4-(2-(4-methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7d)

The GP3 was followed with 4-methoxy-N-(2-vinylphenyl)benzamide (60.4 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (1:1). This afforded the title compound as a brown oil (30.1 mg, 41% yield, Rf = 0.25).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 9.1 Hz, 2H), 7.36−7.30 (m, 2H), 7.21 (dt, *J* = 1.8, 7.3 Hz, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 5.51 (t, *J* = 7.0 Hz, 1H), 3.88 (s, 3H), 3.06−2.91 (m, 2H), 2.33 (q, *J* = 6.6 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 162.5, 156.2, 139.2, 129.6, 129.3, 126.4, 124.9, 124.5, 124.3, 123.5, 115.5 (q, *J* = 290.4 Hz),

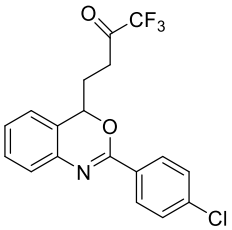
113.7, 74.5, 55.4, 31.5, 28.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{17}F_3NO_3$ $[M+H]^+$ 364.1161, found 364.1161.



Synthesis of 1,1,1-trifluoro-4-(2-(4-fluorophenyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7e)

The GP3 was followed with 4-fluoro-N-(2-vinylphenyl)benzamide (48.3 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown oil (38.3 mg, 55% yield; Ketone/Hydrate = 6/1, Rf = 0.55). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26−8.23 (m, 2H), 7.50−7.45 (m, 2H), 7.36 (dt, *J* = 1.6, 7.3 Hz, 1H), 7.27 (t, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 5.68 (t, *J* = 6.2 Hz, 1H), 3.20−3.04 (m, 2H), 2.47 8 (q, *J* = 6.6 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 165.0 (d, *J* = 251.1 Hz), 155.2, 138.8, 130.0 (d, *J* = 8.6 Hz), 129.4, 128.3 (d, *J* = 2.9 Hz9, 126.9, 125.2, 124.2, 123.6, 115.5 (d, *J* = 22.0 Hz), 115.4 (q, *J* = 290.5 Hz), 74.8, 31.4, 28.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 18/7F), –85.6 (s, 3/7F), –107.7 (m, 1F); **HRMS** (FAB) *m/z* Calcd for $C_{18}H_{14}F_4NO_2$ $[M+H]^+$ 352.0961, found 352.0969.

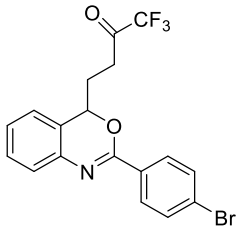


Synthesis of 1,1,1-trifluoro-4-(2-(4-chlorophenyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7f)

The GP3 was followed with 4-chloro-N-(2-vinylphenyl)benzamide (51.5 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown solid (40.3 mg, 55% yield; Ketone/Hydrate = 10/1, Rf = 0.4). The ratio of ketone and hydrate was

determined by ^{19}F NMR analysis.

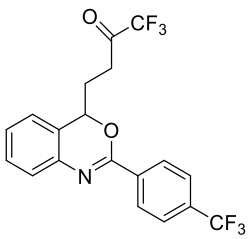
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 7.37−7.30 (m, 2H), 7.26−7.22 8m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 5.55 (t, *J* = 6.2 Hz, 1H), 3.06−2.88 (m, 2H), 2.34 (q, *J* = 6.9 Hz); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 155.2, 138.7, 137.8, 130.6, 129.4, 129.0, 128.7, 127.1, 125.3, 124.2, 123.6, 115.4 (q, *J* = 290.4 Hz), 74.8, 31.4, 28.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 27/10F), –84.1 (s, 3/10F); **HRMS** (FAB) *m/z* Calcd for $C_{18}H_{14}ClF_3NO_2$ $[M+H]^+$ 368.0665, found 368.0665.



Synthesis of 1,1,1-trifluoro-4-(2-(4-bromophenyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7g)

The GP3 was followed with 4-bromo-N-(2-vinylphenyl)benzamide (60.4 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown solid (40.7 mg, 50% yield; Ketone/Hydrate = 20/1, Rf = 0.55). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

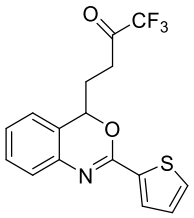
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.38−7.30 (m, 2H), 7.24 (dt, *J* = 1.6, 7.3 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.55 (t, *J* = 6.2 Hz, 1H), 3.04−2.90 (m, 2H), 2.34 (q, *J* = 6.6 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 155.3, 138.7, 131.6, 131.6, 129.4, 129.2, 127.1, 126.4, 125.3, 124.3, 123.6, 115.4 (q, *J* = 290.4 Hz), 74.8, 31.3, 28.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{18}H_{14}BrF_3NO_2$ $[M+H]^+$ 412.0154, found 412.0152.



Synthesis of 1,1,1-trifluoro-4-(2-(4-trifluoromethylphenyl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7h)

The GP3 was followed with 4-trifluoromethyl-N-(2-vinylphenyl)benzamide (58.3 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown solid (44.6 mg, 55% yield; Ketone/Hydrate = 3/1, Rf = 0.55). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

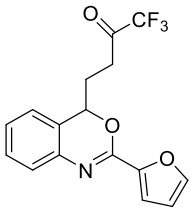
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.39−7.33 (m, 2H), 7.28−7.25 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 5.59 (t, *J* = 6.0 Hz, 1H), 3.05−2.91 (m, 2H), 2.36 (q, *J* = 6.8 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 154.6, 138.5, 135.6, 133.1 (q, *J* = 32.6 Hz), 129.5, 128.0, 127.5, 125.6, 125.3 (q, *J* = 3.8 Hz), 124.3, 123.8 (q, *J* = 271.1 Hz), 123.6, 115.4 (q, *J* = 290.4 Hz), 75.0, 31.4, 28.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –62.8 (s, 9/4F), –62.8 (s, 3/4F, hydrate), –79.0 (s, 9/4F), –84.2 (s, 3/4F, hydrate) ; **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{14}F_6NO_2$ $[M+H]^+$ 402.0929, found 402.0929.



Synthesis of 1,1,1-trifluoro-4-(2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7j)

The GP3 was followed with N-(2-vinylphenyl)thiophene-2-carboxamide (45.9 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol) and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown oil (34.4 mg, 51% yield; Ketone/Hydrate = 10/1, Rf = 0.3). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

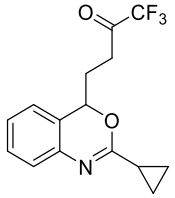
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (dd, *J* = 1.0, 3.6 Hz, 1H), 7.51 (dd, *J* = 1.1, 5.0 Hz, 1H), 7.37−7.28 (m, 2H), 7.21 (dt, *J* = 1.6, 7.4 Hz, 1H), 7.13 (dd, *J* = 3.7, 5.0 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.50 (dd, *J* = 5.2, 7.6 Hz, 1H), 3.09−2.93 (m, 2H), 2.35−2.29 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.7 (q, *J* = 35.5 Hz), 152.7, 138.8, 136.5, 130.5, 129.8, 129.3, 127.9, 126.6, 125.0, 124.4, 123.6, 115.5 (q, *J* = 290.4 Hz), 74.9, 31.4, 28.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 30/11F), –85.7 (s, 3/11F, hydrate); **HRMS** (FAB) *m/z* Calcd for $C_{16}H_{13}F_3NO_2S$ $[M+H]^+$ 340.0618, found 340.0619.



Synthesis of 1,1,1-trifluoro-4-(2-(furan-2-yl)-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7k)

The GP3 was followed with N-(2-vinylphenyl)furan-2-carboxamide (42.6 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude product was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a brown oil (29.1 mg, 45% yield, Rf = 0.35).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62−7.62 (m, 1H), 7.38−7.32 (m, 2H), 7.22 (dt, *J* = 1.2, 7.1 Hz, 1H), 7.05−7.02 (m, 2H), 6.55 (dd, *J* = 1.8, 3.7 Hz, 1H), 5.49 (dd, *J* = 4.6, 7.8 Hz, 1H), 3.08−2.91 (m, 2H), 2.37−2.29 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 149.0, 146.2, 145.8, 138.3, 129.4, 126.9, 125.4, 124.5, 123.6, 115.5 (q, *J* = 290.4 Hz), 114.7, 111.9, 74.7, 31.3, 28.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: −79.0 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{16}H_{14}F_3NO_3$ $[M+H]^+$ 325.0942, found 325.0941.

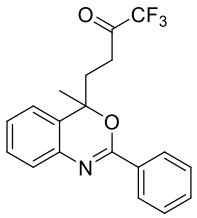


Synthesis of 4-(2-cyclopropyl-4H-benzo[d][1,3]oxazin-4-yl)-1,1,1-trifluorobutan-2-one (7l)

The GP3 was followed with N-(2-vinylphenyl)cyclopropanecarboxamide (37.4 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (4:1). This afforded the title compound as a brown oil (33.9 mg, 57% yield; Ketone/Hydrate = 17/1, Rf = 0.2). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (dt, *J* = 1.6, 7.8 Hz, 1H), 7.16−7.12 (m, 2H), 6.94 (dd, *J* = 1.0, 7.3 Hz, 1H), 5.29 (t, *J* = 5.9 Hz, 1H), 2.91−2.79 (m, 2H), 2.22 (q, *J* = 6.2 Hz, 2H), 1.73−1.67 (m, 1H), 1.08−1.03 (m, 1H), 1.00−0.96 (m, 1H), 0.91−0.88 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 163.1, 138.7, 129.3, 126.0, 124.0, 123.8, 123.4, 115.4 (q, *J* = 290.4 Hz),

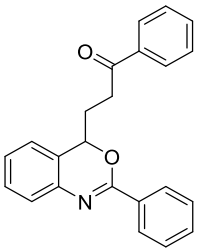
74.3, 31.4, 28.4, 14.4, 7.4, 7.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 17/6F), –85.1 (s, 1/6F); **HRMS** (FAB) *m/z* Calcd for $C_{15}H_{15}F_3NO_2$ $[M+H]^+$ 298.1055, found 298.1055.



Synthesis of 1,1,1-trifluoro-4-(4-methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)butan-2-one (7m)

The GP3 was followed with N-(2-(prop-1-en-2-yl)phenyl)benzamide (47.5 mg, 0.20 mmol), bromotrifluoroacetone (42.0 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the title compound as a pale yellow oil (16.7 mg, 24% yield; Ketone/Hydrate = 16/1, Rf = 0.3). The ratio of ketone and hydrate was determined by ^{19}F NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.2 Hz, 1H), 7.56−7.45 (m, 2H), 7.37−7.34 (m, 2H), 7.25−7.23 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.97−2.90 (m, 1H), 2.80−2.71 (m, 1H), 2.55−2.41 (m, 1H), 1.69 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.8 (q, *J* = 34.5 Hz), 156.1, 138.9, 132.4, 131.5, 129.1, 128.3, 127.9, 127.8, 127.0, 125.7, 122.3, 115.4 (q, *J* = 290.4 Hz), 79.8, 33.1,31.7, 28.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –79.0 (s, 14/5F), –84.8 (s, 1/5F) ; **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{17}F_3NO_2$ $[M+H]^+$ 348.1211, found 348.1212.

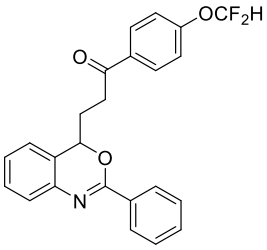


Synthesis of 1-phenyl-3-(2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)propan-1-one (7n)

The GP3 was followed with N-(2-vinylphenyl)benzamide (44.7 mg, 0.20 mmol), phenacyl bromide (47.8 mg, 0.24 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude product was purified by column chromatography and eluted with hexane−Acetone (4:1). This afforded the

title compound as a pale brown oil (47.8 mg, 70% yield, Rf = 0.8).

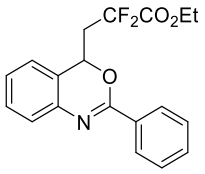
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 7.1 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.53−7,51 (m, 1H), 7.47−7.44 (m, 4H), 7.25−7.20 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 5.64 (dd, *J* = 4.9, 7.1 Hz, 1H), 3.32−3.25 (m, 1H), 3.21−3.16 (m, 1H), 2.47−2.37 (m, 2H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 199.0, 156.5, 139.1, 136.6, 133.2, 132.6, 131.4, 128.9. 128.6, 128.3, 128.0, 127.8, 126.6, 125.3, 125.0, 128.8, 75.6, 33.1, 30.3; **HRMS** (FAB) *m/z* Calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1494, found 342.1494.



Synthesis of 1-(4-(difluoromethoxy)phenyl)-3-(2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)propan-1-one (7o)

The GP3 was followed with N-(2-vinylphenyl)benzamide (44.7 mg, 0.20 mmol), 2-bromo-1-(4-(difluoromethoxy)phenyl)ethan-1-one (63.8 mg, 0.24 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude was purified by column chromatography and eluted with hexane−Acetone (4:1). This afforded the title compound as a white solid (61.0 mg, 75% yield, Rf = 0.75).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16−8.13 (m, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.51−7.49 (m, 1H), 7.47−7.43 (m, 2H), 7.34−7.33 (m, 2H), 7.24−7.20 (m, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 1H), 6.59 (t, *J* = 73.0 Hz, 1H), 5.65 (dd, *J* = 5.0, 7.1 Hz, 1H), 3.28−3.10 (m, 2H), 2.44−2.40 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 197.5, 156.4, 154.7, 139.1, 133.5, 132.5, 131.4, 130.2, 129.0, 128.3, 127.8, 126.6, 125.2, 125.1, 123.8, 118.7, 115.2 (t, *J* = 260.0 Hz), 75.5, 33.0, 30.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –81.7 (d, *J* = 72.9 Hz, 2F); **HRMS** (FAB) *m/z* Calcd for $C_{24}H_{20}F_2NO_3$ $[M+H]^+$ 408.1411, found 408.1410.



Synthesis of ethyl 2,2-difluoro-3-(2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)propanoate (7p)

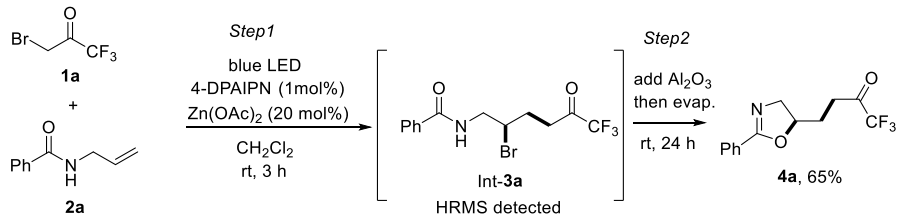
The GP3 was followed with N-(2-vinylphenyl)benzamide (44.7 mg, 0.20 mmol), ethyl

bromodifluoroacetate (51.3 μL, 0.40 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_3CN (500 μL). The reaction was irradiated with blue LED for 14 h. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the title compound as a white solid (22.8 mg, 33% yield, Rf = 0.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 8.0 Hz, 2H), 7.53−7.51 (m, 1H), 7.47−7.45 (m, 2H), −7.38−7.32 (m, 2H), 7.27−7.22 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 5.87 (dd, *J* = 2.8, 10.1 Hz, 1H), 4.22−4.16 (m, 1H), 4.10−4.02 (m, 1H), 3.00−2.91 (m, 1H), 2.60−2.48 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 163.4 (t, *J* = 31.7 Hz), 155.8, 138.8, 132.0, 131.6, 129.5, 128.2, 128.0, 126.9, 125.3, 123.6, 123.5, 114.3 (t, *J* = 248.2 Hz), 70.7, 63.1, 40.9 (t, *J* = 23.0 Hz), 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –102.4 (dt, *J* = 16.6, 268.6 Hz, 1F), –105.4 (dt, *J* = 16.6, 268.6 Hz, 1F); **HRMS** (FAB) *m/z* Calcd for $C_{19}H_{18}F_2NO_3$ $[M+H]^+$ 346.1254, found 346.1254.

6. Control experiments

6-1. High-resolution mass spectrometry



A 4 mL vial with a magnetic stirring bar was charged with N-allylbenzamide (48.4 mg, 0.30 mmol). 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (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 12 W blue LED irradiation (470 nm) for 3 h. The solution was removed by evaporation, and then Int-**3a** in the crude mixture was detected by HRMS mass spectrometry.

Int-3a: HRMS (FAB) *m/z* Calcd for $C_{13}H_{14}BrF_3NO_2$ $[M+H]^+$ 352.0160, found 352.0160.

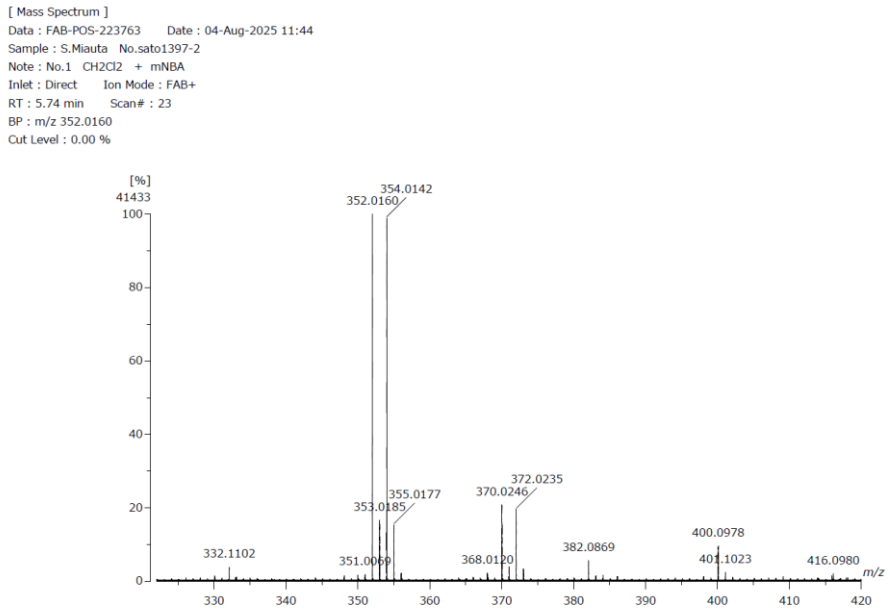
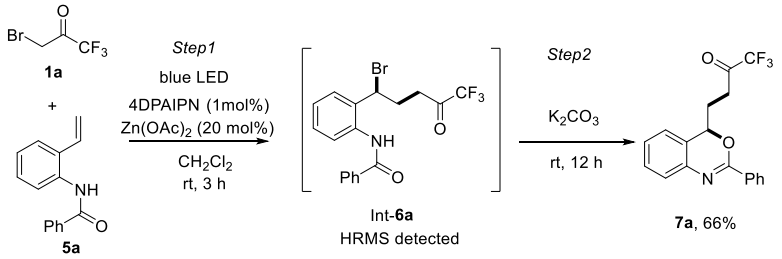


Figure S3. Mass spectrum of **Int-3a**



A 4 mL vial with a magnetic stirring bar was charged with N-(2-vinylphenyl)benzamide (44.7 mg, 0.20 mmol). 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (7.3 mg, 0.04 mmol), and CH_2Cl_2 (500 μL) was added. Finally, bromotrifluoroacetone (42.0 μL, 0.40 mmol) was introduced to the reaction mixture. The resulting mixture was stirred at room temperature under 12 W blue LED irradiation (470 nm) for 3 h. The solution was removed by evaporation, and then Int-**6a** in the crude mixture was detected by HRMS mass spectrometry.

Int-6a: HRMS (FAB) *m/z* Calcd for $C_{18}H_{16}BrF_3NO_2$ $[M]^+$ 413.0238, found 413.0241.

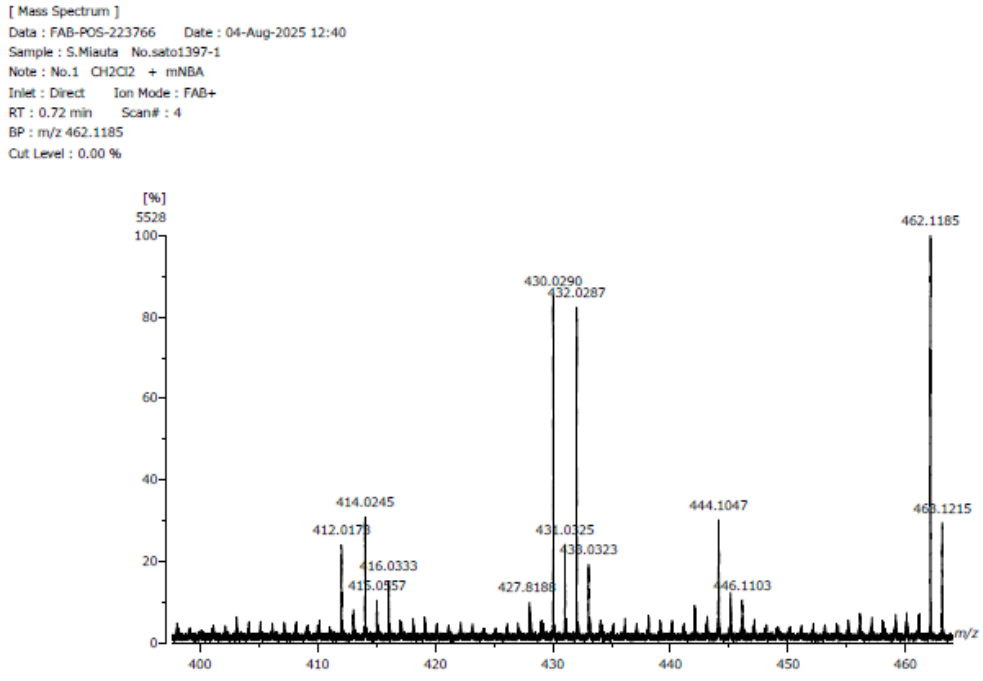


Figure S4. Mass spectrum of **Int-6a**

6-2. Stern-Volmer Quenching Experiments

A stock solution of photocatalyst (4DPAIPN: 20 μM) in MeCN was prepared. For the validation experiments, the microplate used was a 96-well quartz microplate (Bio Medical Science Inc., BC-MGPL-96S). For each measurement of solution (200 μL), the concentrations of bromotrifluoroacetone (**1a**), allylamide (**2a**), and *o*-vinylanilide (**5a)** were added to the 96-well quartz microplate. Stern-Volmer measurements were performed with a plate reader (BioTek. Inc., Cytation3)

Plate data analysis

Procedure Details													
Plate Type	96 WELL PLATE												
Read	Fluorescence Endpoint												
	Full Plate												
	Filter Set 1												
	Excitation: 430, Emission: 530												
	Optics: Top, Gain: 50												
	Light Source: Xenon Flash, Lamp Energy: High												
	Read Speed: Normal, Delay: 100 msec, Measurements/Data Point: 10												
	Read Height: 5.75 mm												
Results													
Actual Temperature:	13.4												
		bromotrifluoroacetone (1a)				allylamide (2a)				o-vinylanilide (5a)			
	Q (mM)	1	2	3	4	5	6	7	8	9	10	11	12
	0	2592	2735	2697	2727	2967	3062	3108	3256	3220	3360	3485	3519
	5	2258	2470	2450	2597	2977	3099	3191	3253	3128	3332	3322	3431
	10	2185	2251	2362	2533	3003	3117	3154	3161	3273	3326	3357	3431
	20	2020	2139	2201	2309	2934	3036	3201	3147	3242	3311	3356	3467
	40	1802	1825	1944	2011	2950	3018	3176	3075	3200	3258	3324	3434
	60	1642	1757	1804	1863	2855	3052	3016	3046	3110	3198	3198	3338
	80 or 120	1515	1640	1658	1713	2775	2866	2863	2995	2731	2771	2830	2923
		2245	2528	2613	2795	2857	2977	3040	3117	3246	3171	3234	3237

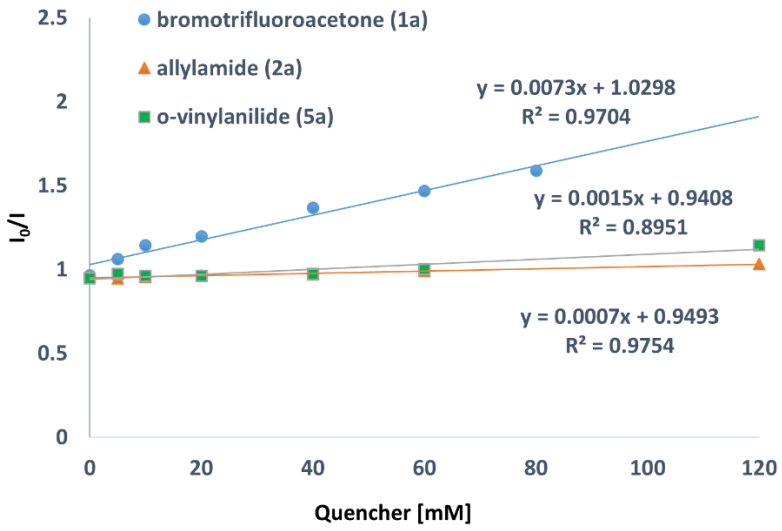
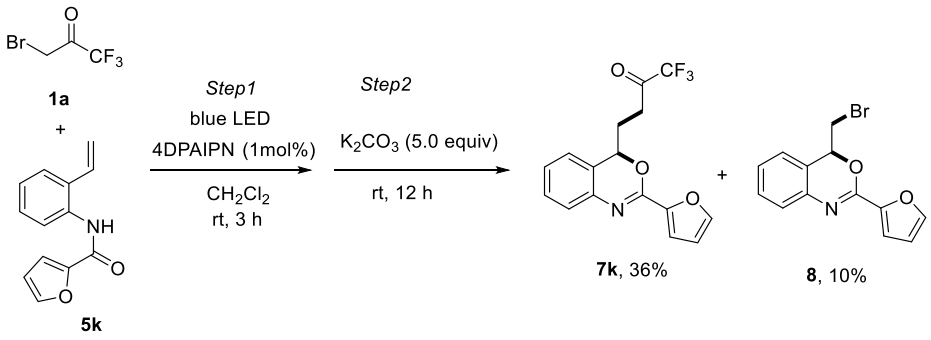


Figure S5. Fluorescence quenching of 20 μM 4DPAIPN by bromotrifluoroacetone (**1a**), allylamide (**2a**), and *o*-vinylanilide (**5a**) with a Stern–Volmer plot (λex = 430 nm, λem = 530 nm).

6-3. The reaction of 5k with 1a without $Zn(OAc)_2$

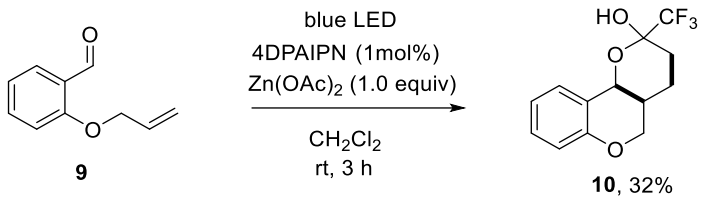


A 4 mL vial with a magnetic stirring bar was charged with N-(2-vinylphenyl)furan-2-carboxamide (42.6 mg, 0.20 mmol), 4DPAIPN (1.6 mg, 1 mol%), and CH_2Cl_2 (500 μL). Finally, bromotrifluoroacetone (42.0 μL, 0.40 mmol) was introduced to the reaction mixture. The resulting mixture was stirred at room temperature under 12 W blue LED irradiation (470 nm) for 3 h. After the intermolecular cyclization with K_2CO_3 (138 mg, 1.0 mmol), the crude product was purified by column chromatography and eluted with hexane−Acetone (2:1). This afforded the trifluoromethyl ketone derivative **7k** (23.3 mg, 36% yield) and the bromide derivative **8** (5.8 mg, 10% yield).

For **7k**: The ^{1}H NMR spectrum is consistent with above-reported data.

For **8**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.64−7.63 (m, 1H), 7.41−7.38 (m, 2H), 7.26−7.22 (m, 1H), 7.20−7.19 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.56 (dd, *J* = 1.8, 3.4 Hz, 1H), 5.60 (dd, *J* = 3.9, 8.2 Hz, 1H), 3.69−3.56 (m, 2H); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{11}BrNO_2$ $[M+H]^+$ 291.9973, found 291.9973.

7. Application examples

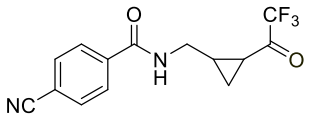


9 **10**, 32%

7-1. Synthesis of 2-(trifluoromethyl)-3,4,4a,10b-tetrahydro-2H,5H-pyrano[3,2-c]chromen-2-ol (10)

A 4 mL vial with a magnetic stirring bar was charged with 2-(allyloxy)benzaldehyde (48.7 mg, 0.30 mmol), 4DPAIPN (1.6 mg, 1 mol%), $Zn(OAc)_2$ (55.0 mg, 0.60 mmol) and CH_3CN (500 μL) was added. Finally, bromotrifluoroacetone (69.0 μL, 0.60 mmol) was introduced to the reaction mixture. The resulting mixture was stirred at room temperature under 12 W blue LED irradiation (470 nm) for 3 h. The crude was purified by column chromatography and eluted with hexane−Acetone (4:1). This afforded the title compound as a white solid (17.6 mg, 32% yield, dr = 5/1, Rf = 0.5).

For major isomers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6,80 (d, *J* = 8.2 Hz, 1H), 4.90 (d, *J* = 10.5 Hz, 1H), 4.25 (dd, *J* = 4,1, 11.2 Hz, 1H), 3.95 (t, *J* = 11.4 Hz, 1H), 2.93 (br.s, OH), 2.11–2.01 (m, 2H), 1.94–1.80 (m, 2H), 1.73–1.66 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 153.9, 128.9, 124.9, 122.0, 122.6 (q, *J* = 282.7 Hz), 120.4, 116.1, 69.3, 68.5, 35.2, 26.4, 20.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –87.2 (s, 5/2F, major isomer), –87.3 (s, 1/5F, minor isomers); **HRMS** (FAB) *m/z* Calcd for $C_{13}H_{13}F_3O_3$ $[M]^+$ 274.0817, found 274.0820.



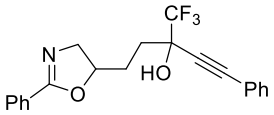
7-2. Synthesis of 4-cyano-N-((2-(2,2,2-trifluoroacetyl)cyclopropyl)methyl)benzamide (11)

The GP2 was followed with N-allyl-4-methylbenzamide (55.9 mg, 0.30 mmol), bromotrifluoroacetone (62.0 μL, 0.60 mmol), 4DPAIPN (2.4 mg, 1 mol%), $Zn(OAc)_2$ (11.0 mg, 0.06 mmol), and CH_2Cl_2 (500 μL). The reaction was irradiated with blue LED for 3 h. After the intermolecular cyclization with K_2CO_3 (207 mg, 1.5 mmol), the crude was purified by column chromatography and eluted with hexane−AcOEt (1:1). This afforded the trans isomer (36.4 mg, 41% yield, Rf = 0.25) as a yellow solid and the cis isomer as a yellow solid (17.8 mg, 10% yield, Rf = 0.13), respectively. For trans-**11,** the NOESY correlation between 1-H_a and 3-H_c could be observed. Whereas, the 1-H_a of cis-**11** has a NOESY correlation with 3-H_c.

For trans-**11**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 6.53

(br.s, N*H*), 3.81 (dt, *J* = 5.5, 14.6 Hz, 1H), 3.42–3.36 (m, 1H), 2.48 (q, *J* = 7.8 Hz, 1H), 2.36–2.26 (m, 1H), 1.56–1.48 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.6 (q, *J* = 35.5 Hz), 166.0, 137.9, 132.4, 127.6, 117.9, 116.0 (q, *J* = 290.4 Hz), 115.1, 37.4, 28.0, 20.7, 17.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –78.5 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{11}F_3N_2O_2$ $[M+H]^+$ 297.0851, found 297.0851.

For cys-**11**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 6.58–6.49 (m, 1H), 3.62–3.56 (m, 1H), 3.50–3.44 (m, 1H), 2.42–2.37 (m, 1H), 2.00–1.96 (m, 1H), 1.63–1.58 (m, 1H), 1.39–1.34 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 190.4 (q, *J* = 36.4 Hz), 166.0, 138.0, 132.5, 127.6, 117.9, 115.7 (q, *J* = 289.4 Hz), 115.3, 42.4, 28.2, 22.2, 18.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –78.6 (s, 3F); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{11}F_3N_2O_2$ $[M+H]^+$ 297.0851, found 297.0851.



7-3. Synthesis of 1-phenyl-5-(2-phenyl-4,5-dihydrooxazol-5-yl)-3-(trifluoromethyl)pent-1-yn-3-ol (12)

A 10 mL round bottle flask equipped with a magnetic stirring bar was charged with 1,1,1-trifluoro-4-(2-phenyl-4,5-dihydrooxazol-5-yl)butan-2-one (**4a**) (54.2 mg, 0.20 mmol), CuF_2 (2.0 mg, 10 mol%), 1,10-phenanthroline (3.6 mg, 10 mol%), and THF (2.0 mL). To the solution, K_2CO_3 (6.0 mg, 10 mol%) and phenylacetylene were added, and the mixture was stirred at 80 ºC for 15 h. The reaction mixture was extracted with AcOEt, washed 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 yellow oil (30.0 mg, 40% yield, dr = 1:1, Rf=0.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.41–7.27 (m, 7H), 4.86–4.76 (m, 1H), 4.21–4.14 (m, 1H), 3.73 (dd, *J* = 7.3, 14.4 Hz, 1H), 2.23–1.96 (m, 4H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 164.3,164.2, 131.9, 131.4, 129.3, 129.3, 128.4, 128.3, 128.3, 127.4, 127.4, 127.0, 126.8, 124.2 (q, *J* = 283.6 Hz), 121.0, 120.9, 87.5, 83.5, 83.4, 79.6, 79.5, 71.6 (q, *J* = 31.6 Hz), 71.6 (q, *J* = 31.6 Hz), 59.7, 59.6, 31.1, 31.0, 29.7, 29.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: –81.3 (s, 3/2F), –81.3 (s, 3/2F,); **HRMS** (FAB) *m/z* Calcd for $C_{21}H_{18}F_3NO_2$ $[M+H]^+$ 374.1368, found 374.1368.

8. NMR spectra

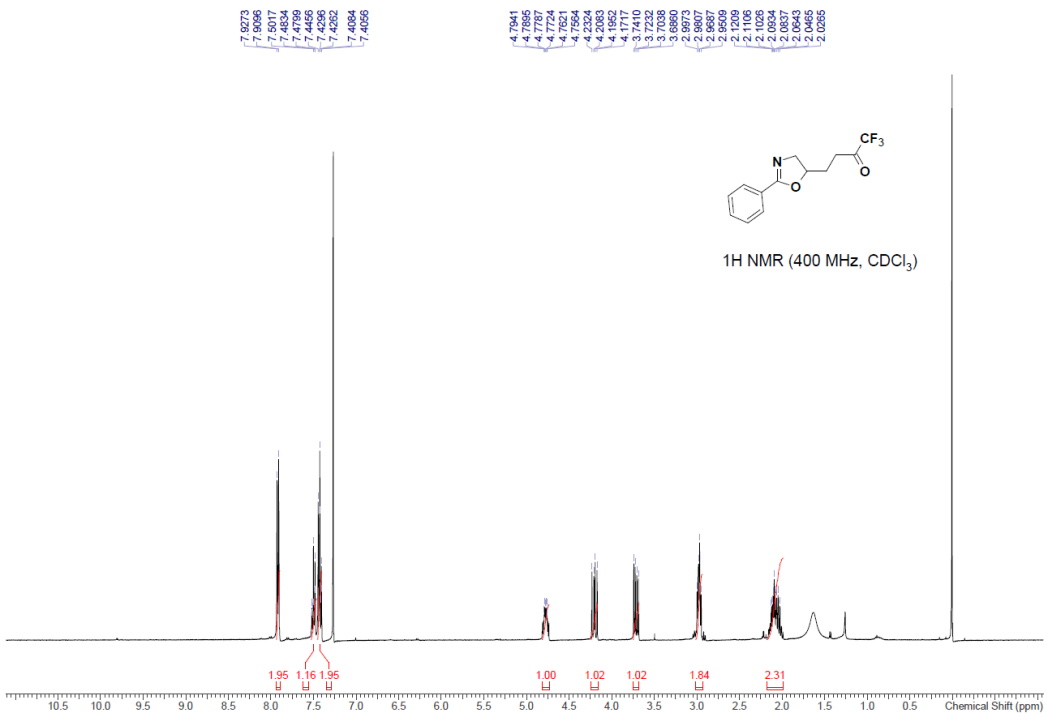


Figure S6. ^{1}H NMR of **4a** (400 MHz, $CDCl_3$)

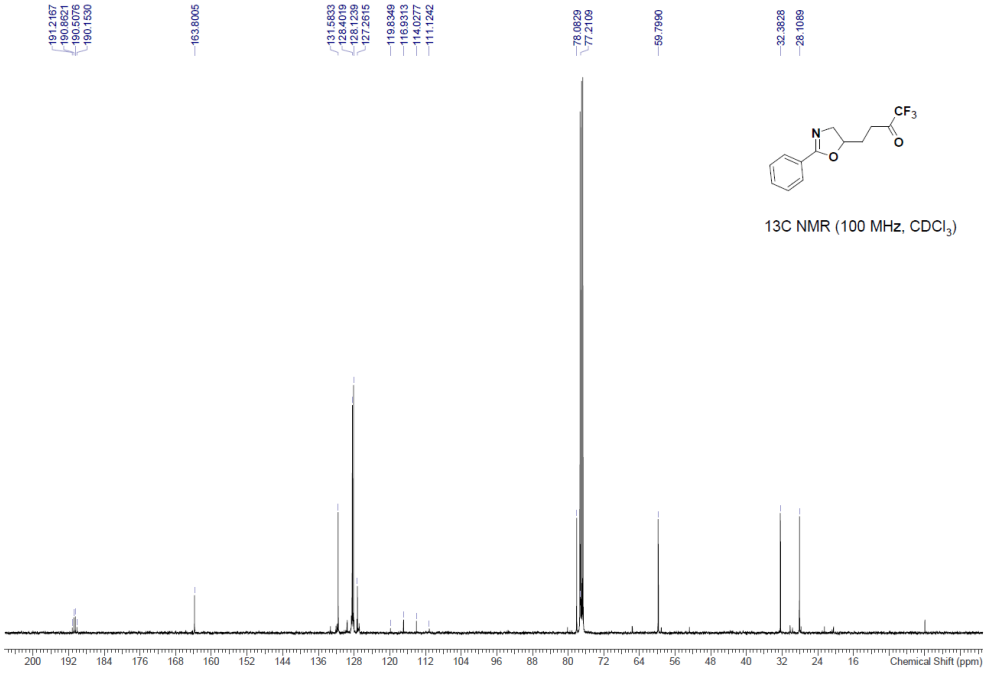


Figure S7. ^{13}C NMR of **4a** (100 MHz, $CDCl_3$)

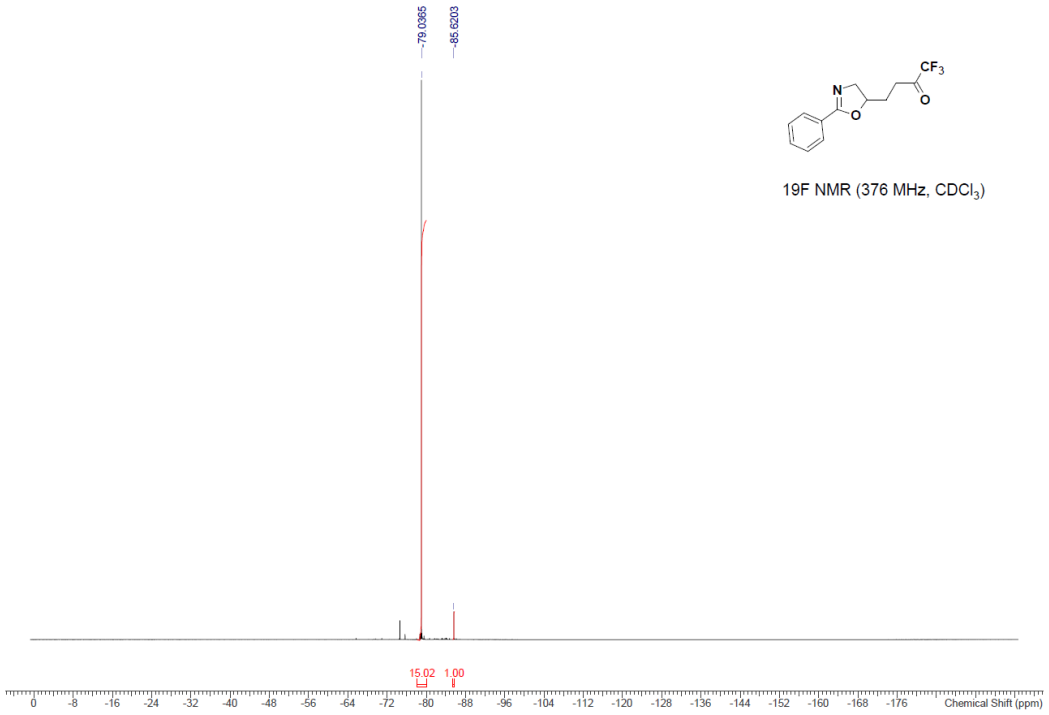


Figure S8. ^{19}F NMR of **4a** (376 MHz, $CDCl_3$)

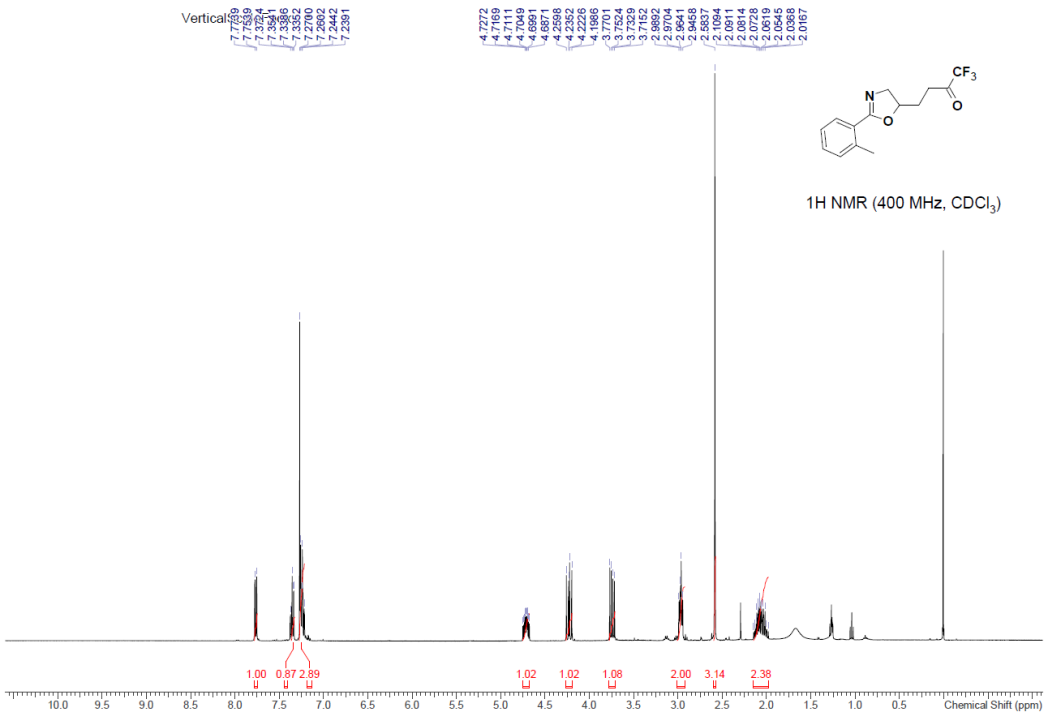


Figure S9. ^{1}H NMR of **4b** (500 MHz, $CDCl_3$)

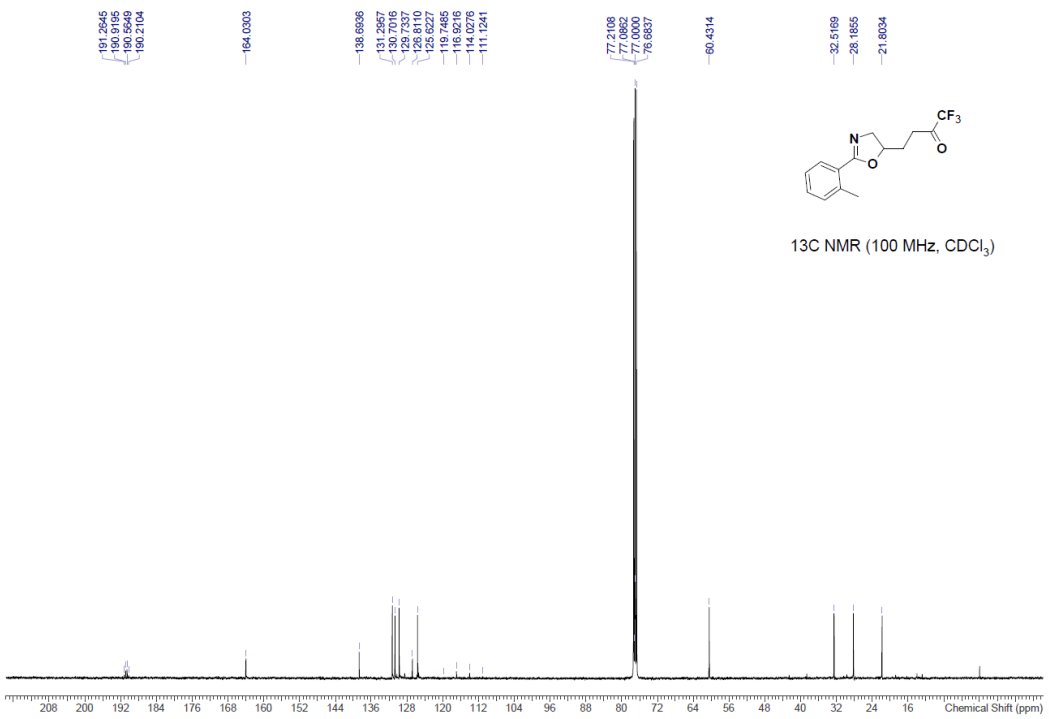


Figure S10. ^{13}C NMR of **4b** (125 MHz, $CDCl_3$)

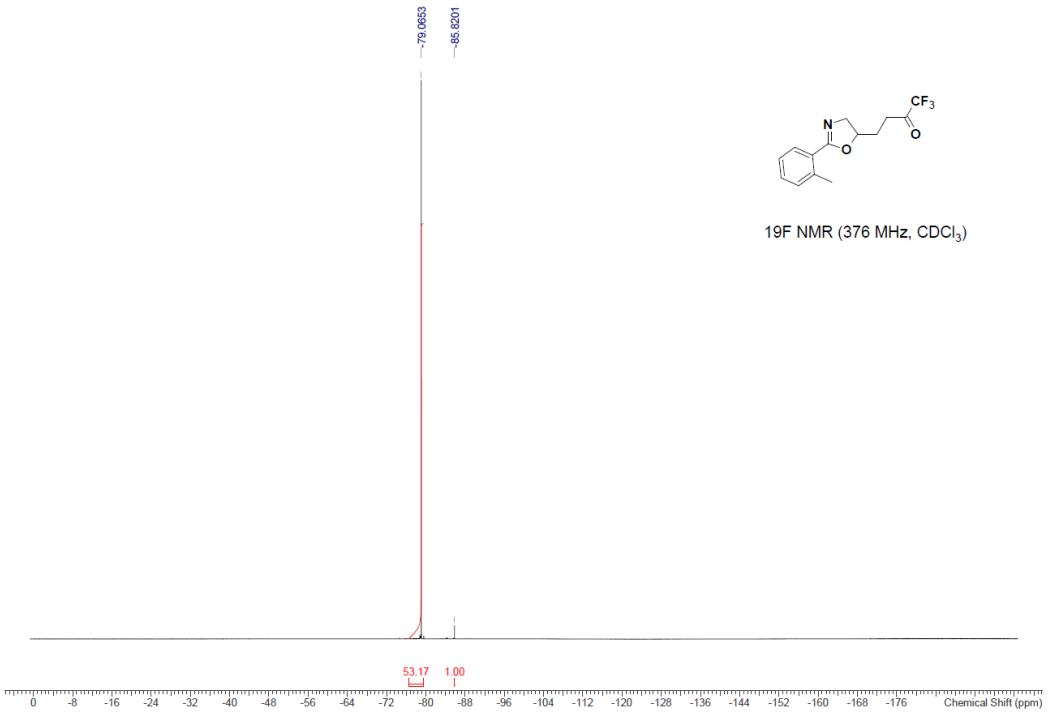


Figure S11. ^{19}F NMR of **4b** (376 MHz, $CDCl_3$)

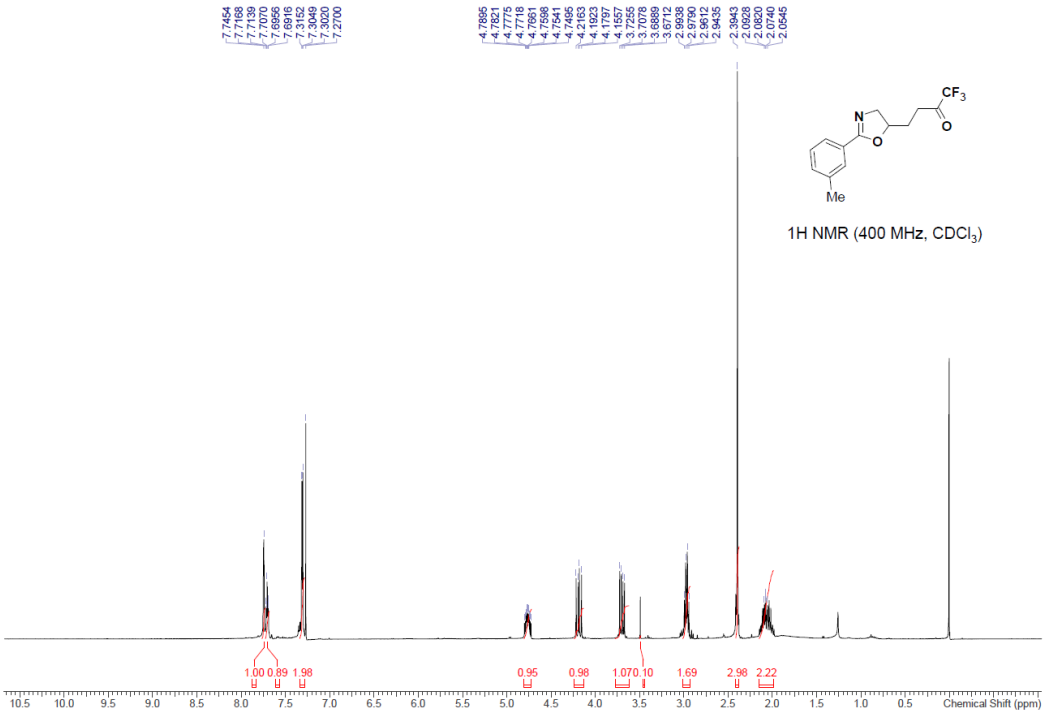


Figure S12. ^{1}H NMR of **4c** (400 MHz, $CDCl_3$)

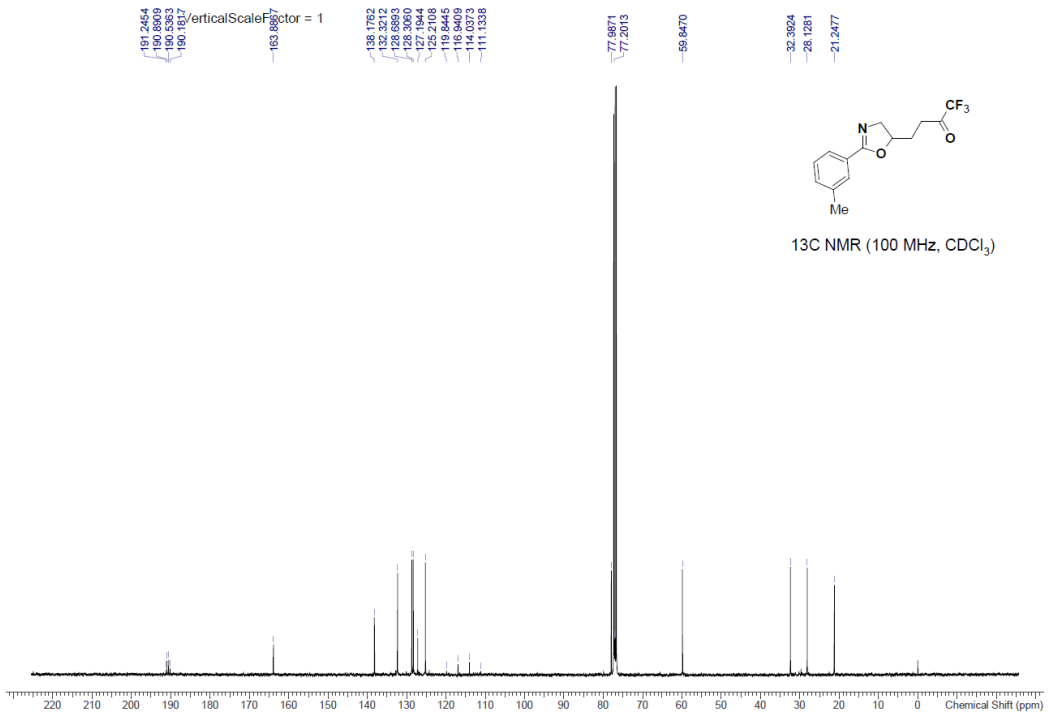


Figure S13. ^{13}C NMR of **4c** (100 MHz, $CDCl_3$)

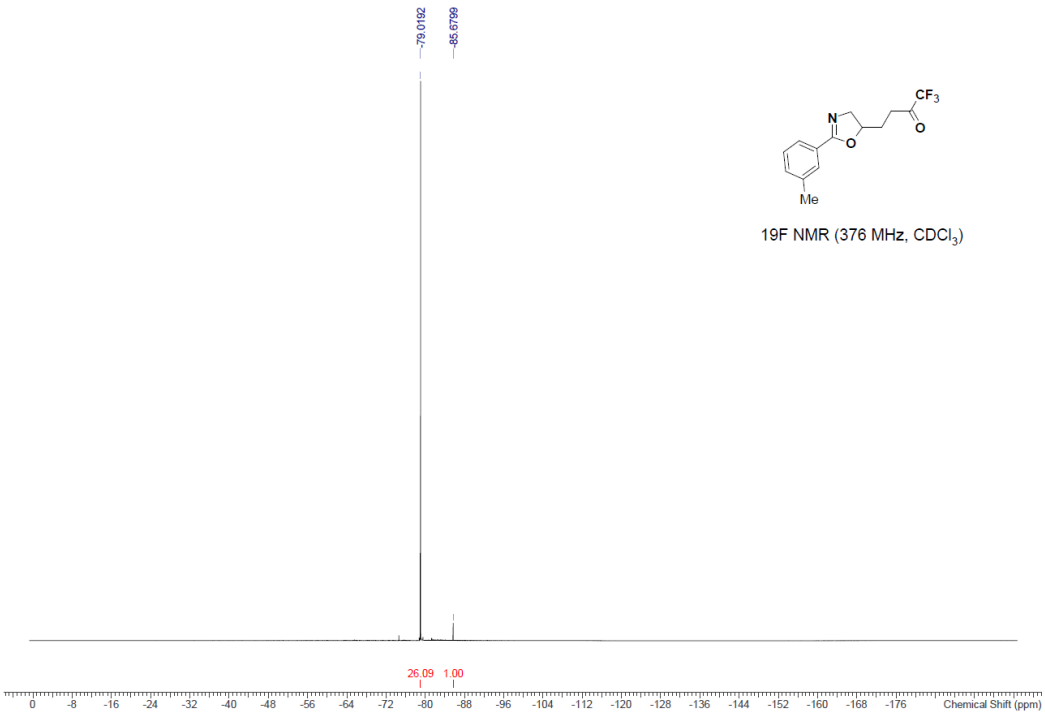


Figure S14. ^{19}F NMR of **4c** (376 MHz, $CDCl_3$)

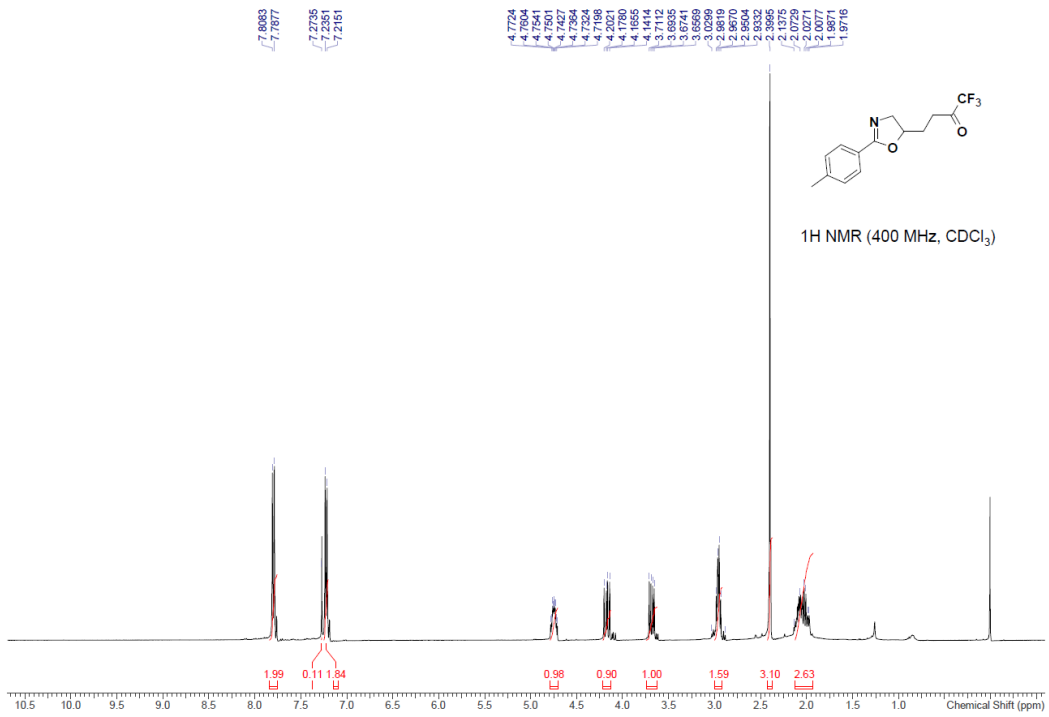


Figure S15. ^{1}H NMR of **4d** (400 MHz, $CDCl_3$)

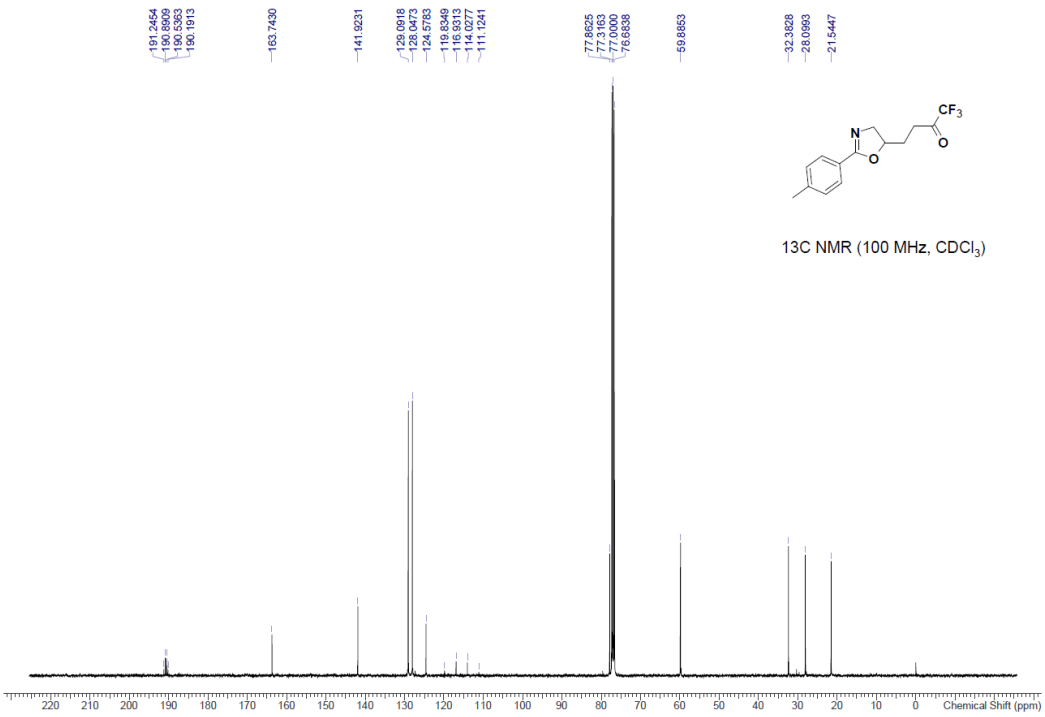


Figure S16. ^{13}C NMR of **4d** (100 MHz, $CDCl_3$)

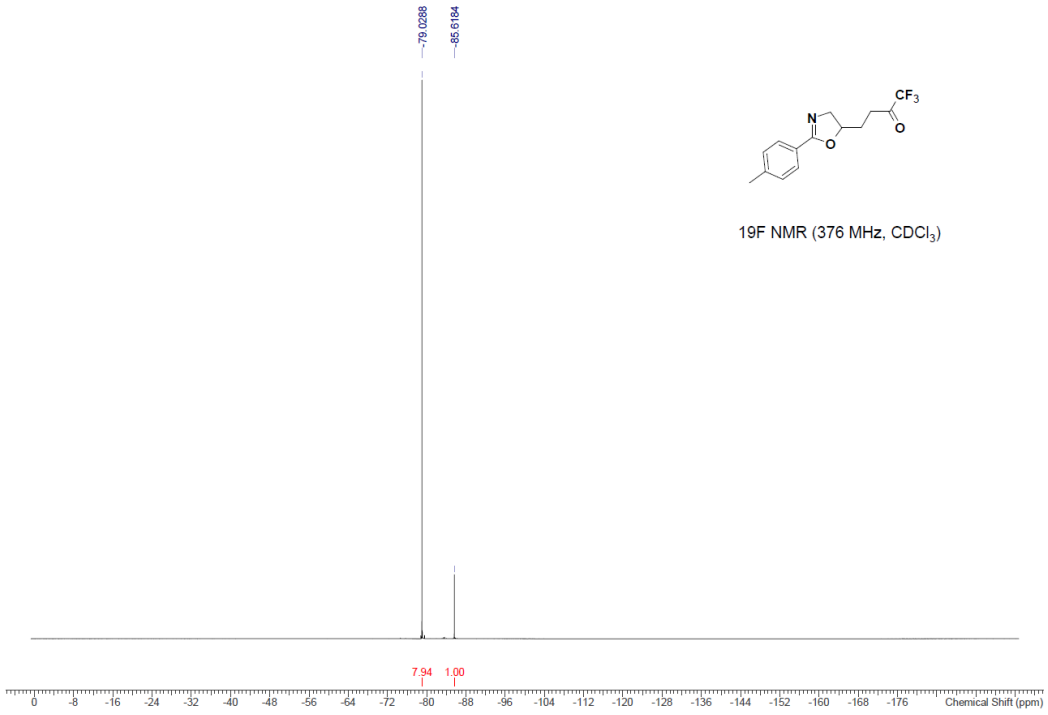


Figure S17. ^{19}F NMR of **4d** (376 MHz, $CDCl_3$)

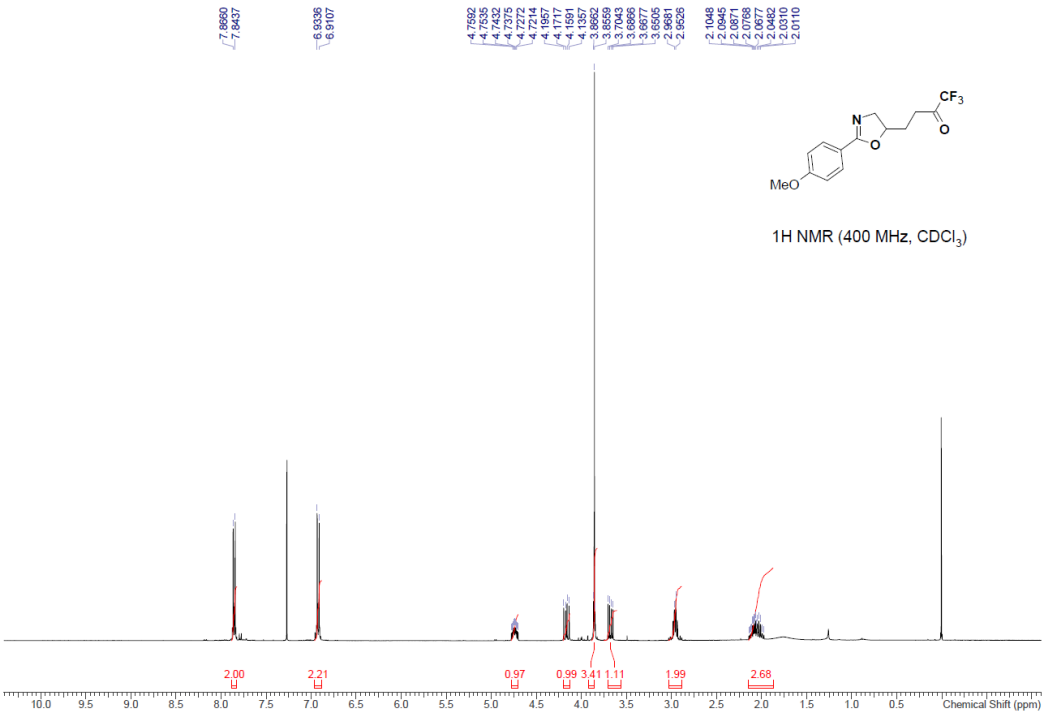


Figure S18. ^{1}H NMR of **4e** (400 MHz, $CDCl_3$)

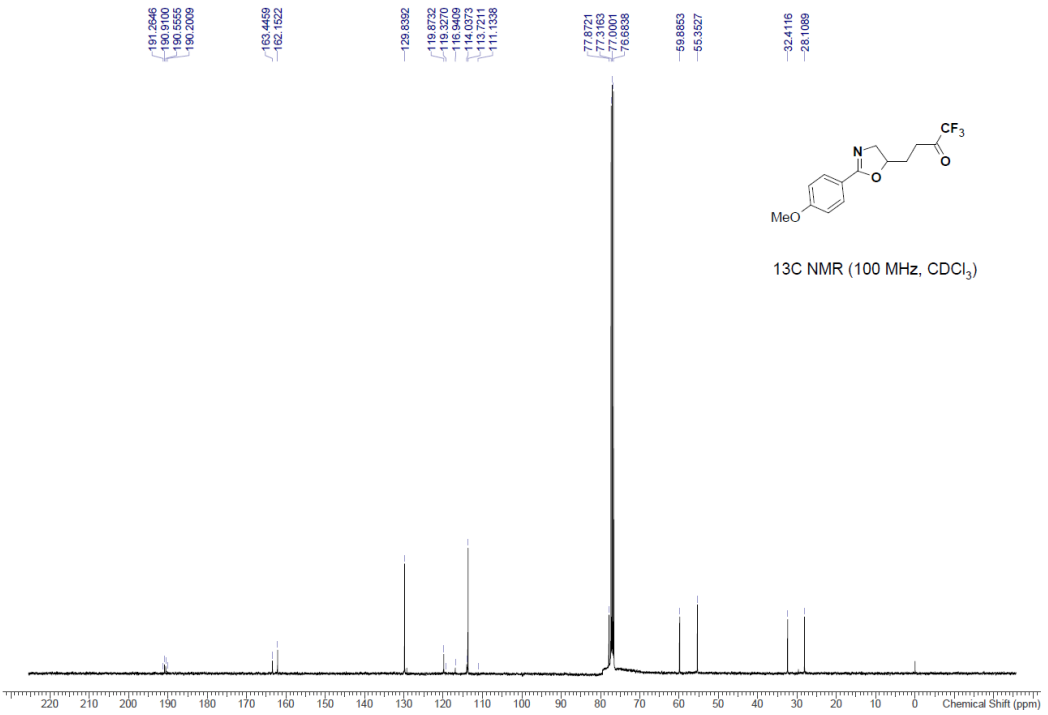


Figure S19. ^{13}C NMR of **4e** (100 MHz, $CDCl_3$)

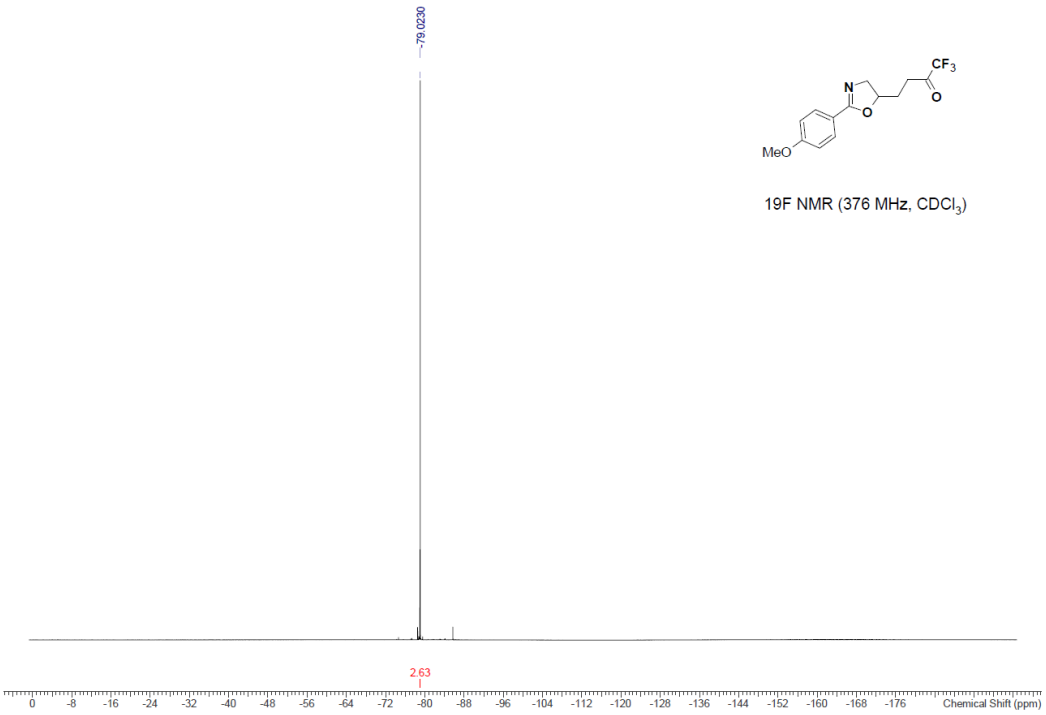


Figure S20. ^{19}F NMR of **4e** (376 MHz, $CDCl_3$)

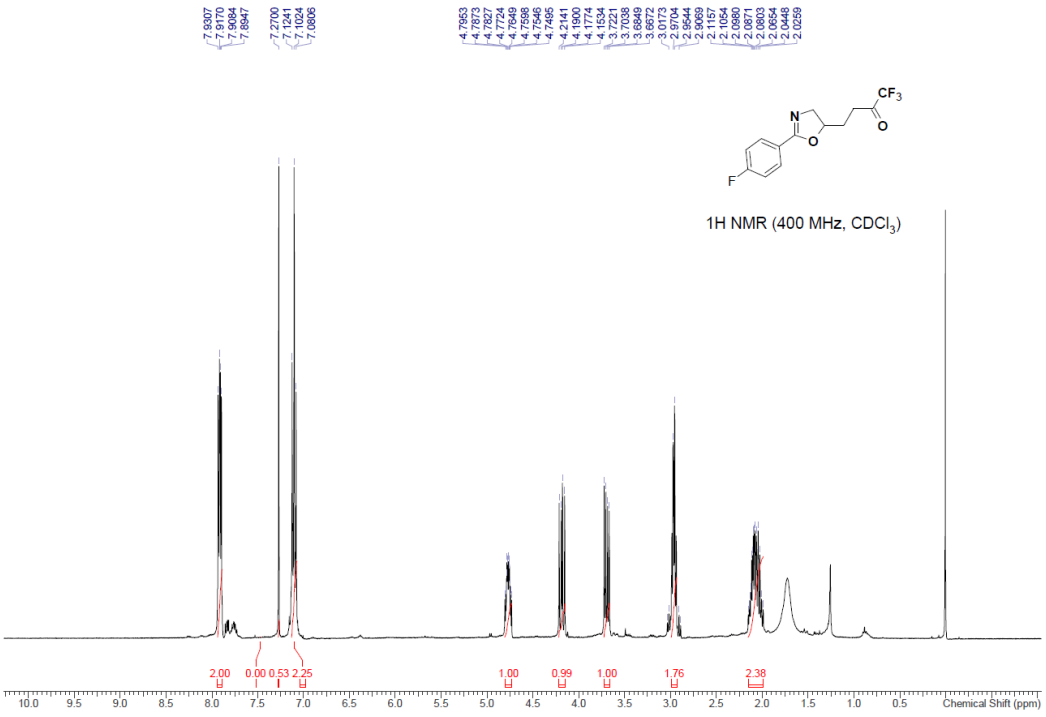


Figure S21. ^{1}H NMR of **4f** (400 MHz, $CDCl_3$)

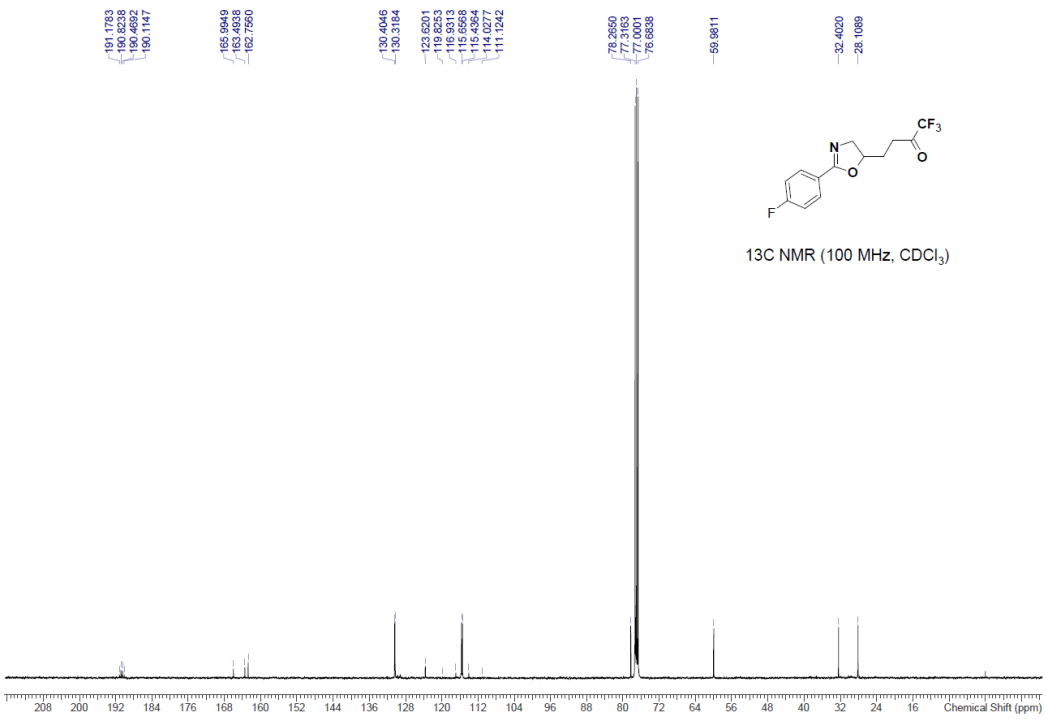


Figure S22. ^{13}C NMR of **4f** (100 MHz, $CDCl_3$)

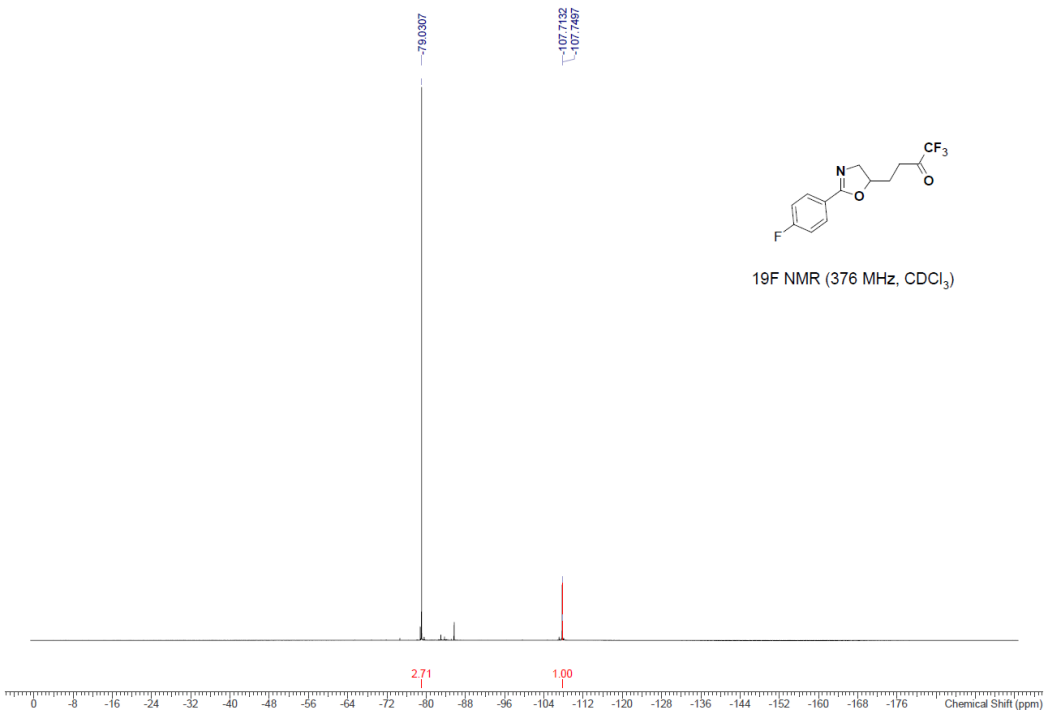


Figure S23. ^{19}F NMR of **4f** (376 MHz, $CDCl_3$)

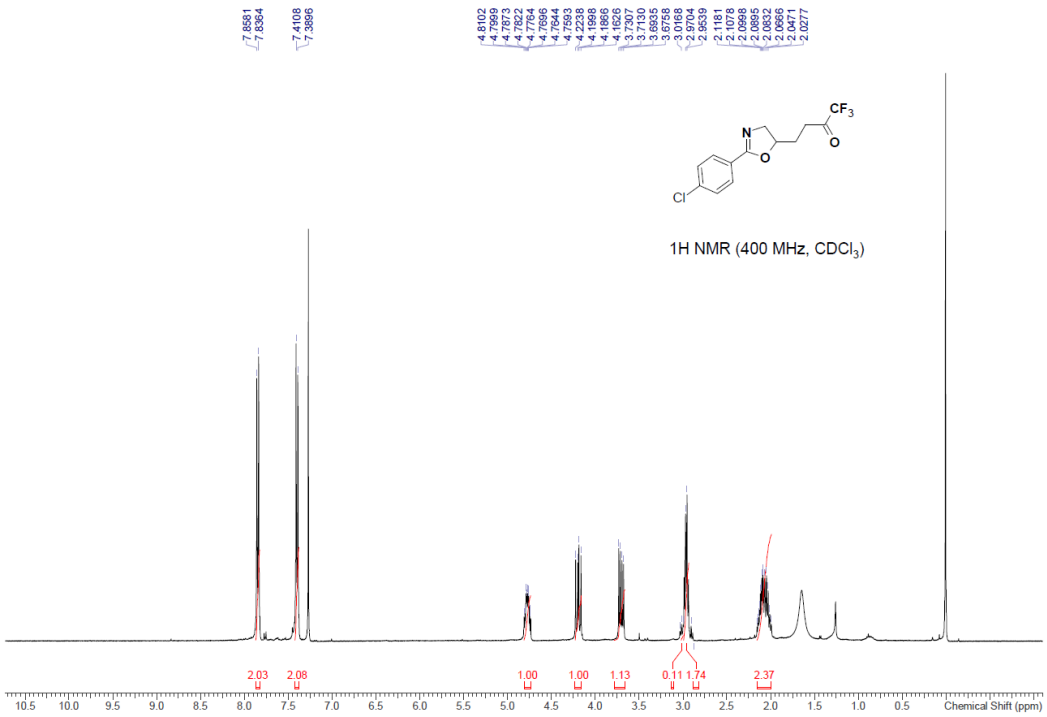


Figure S24. ^{1}H NMR of **4g** (400 MHz, $CDCl_3$)

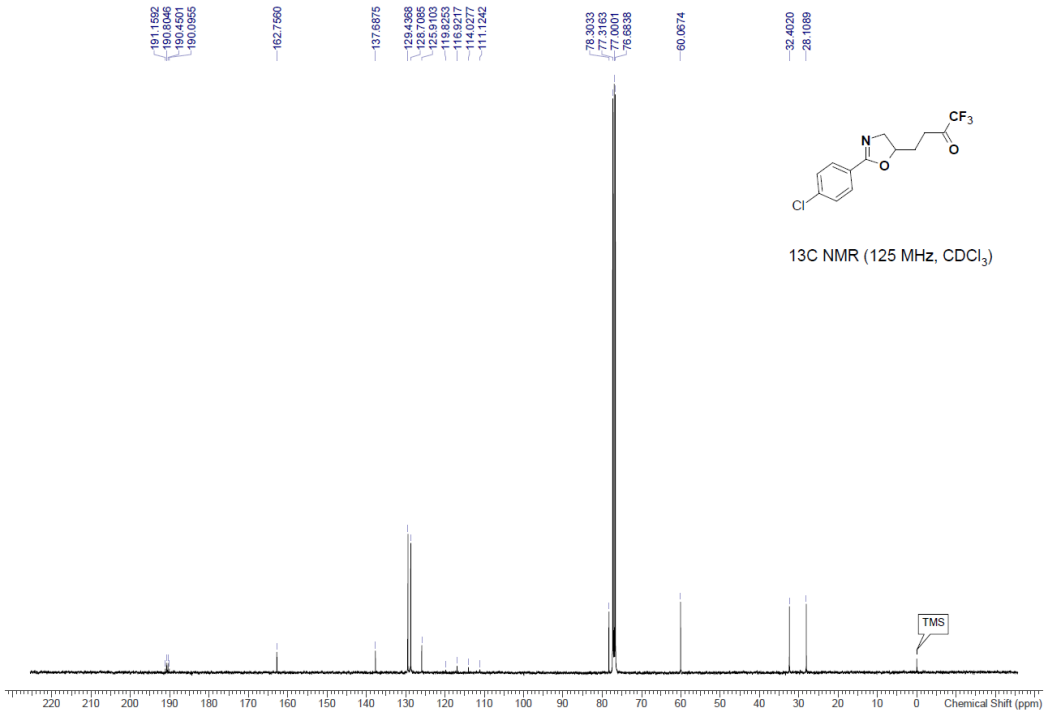


Figure S25. ^{13}C NMR of **4g** (100 MHz, $CDCl_3$)

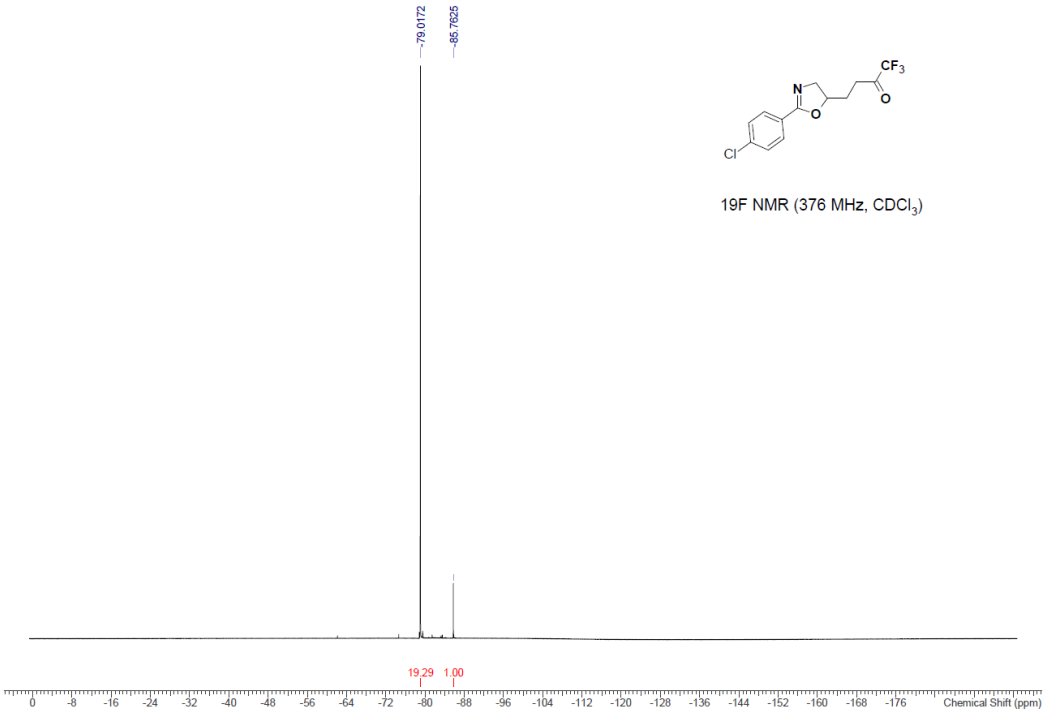


Figure S26. ^{19}F NMR of **4g** (376 MHz, $CDCl_3$)

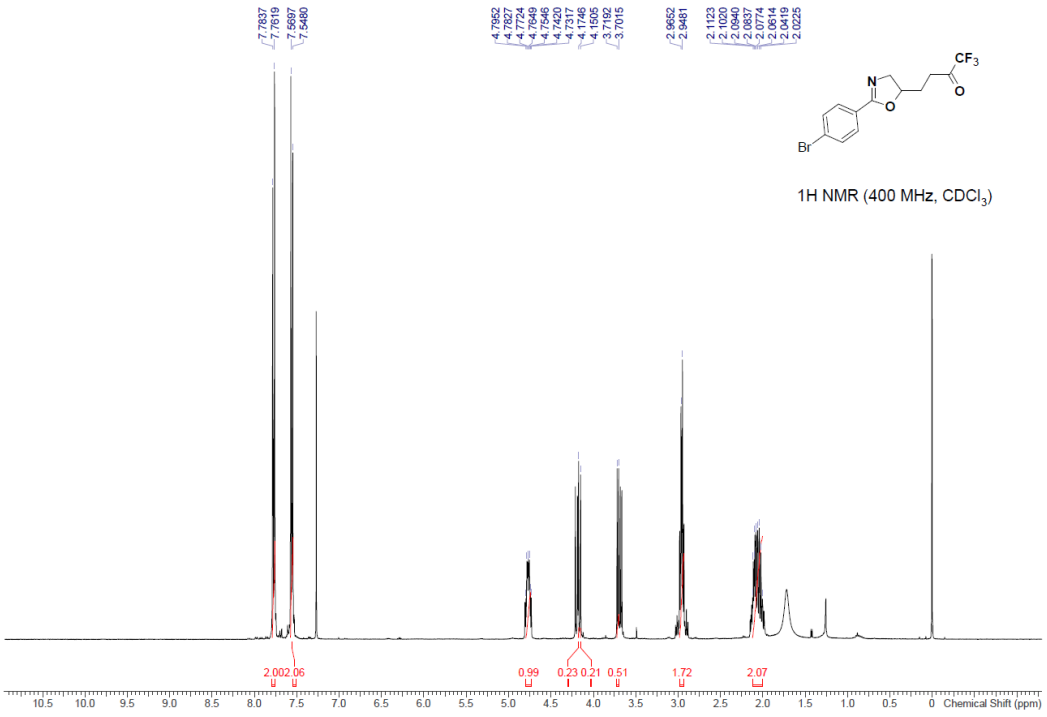


Figure S27. ^{1}H NMR of **4h** (400 MHz, $CDCl_3$)

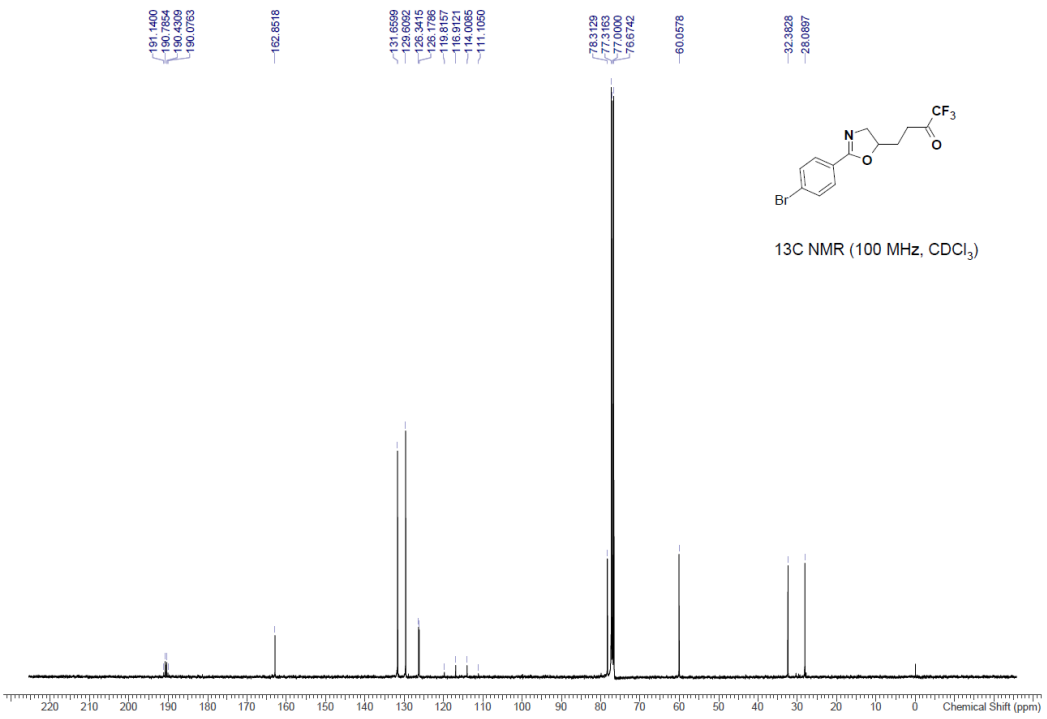


Figure S28. ^{13}C NMR of **4h** (100 MHz, $CDCl_3$)

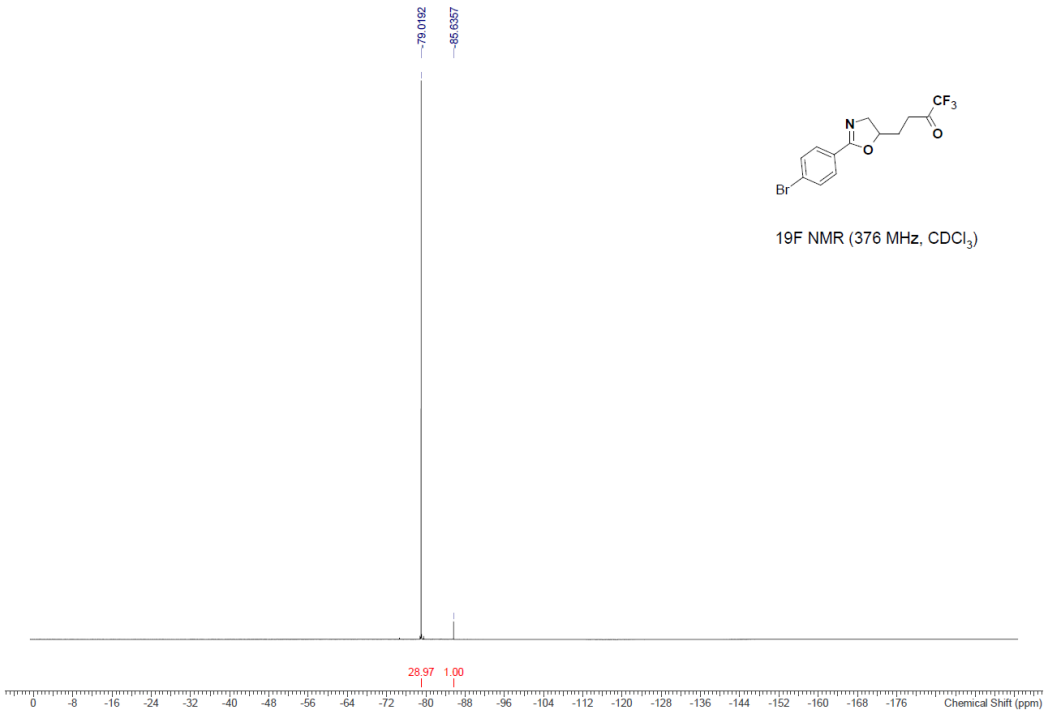


Figure S29. ^{19}F NMR of **4h** (376 MHz, $CDCl_3$)

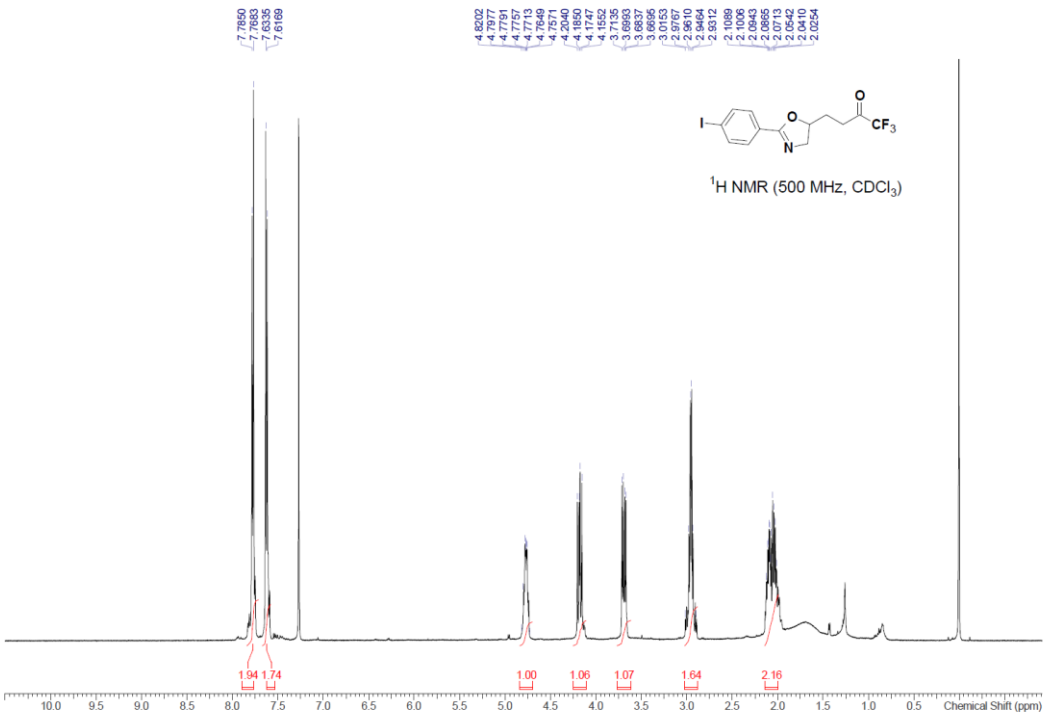


Figure S30. ^{1}H NMR of **4i** (500 MHz, $CDCl_3$)

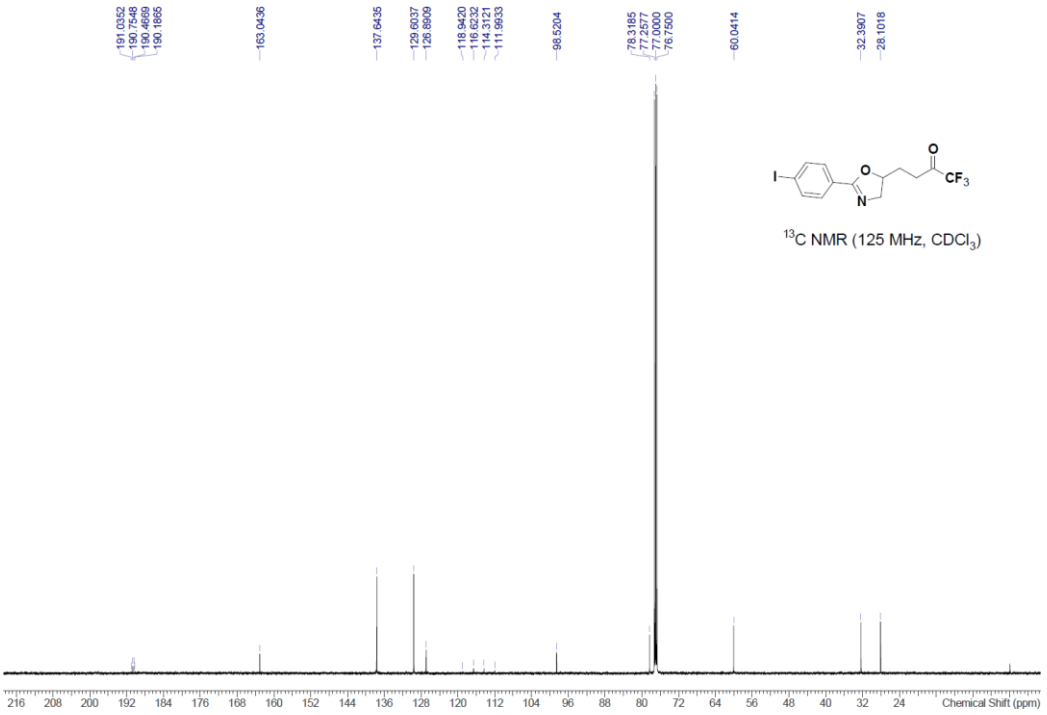


Figure S31. ^{13}C NMR of **4i** (125 MHz, $CDCl_3$)

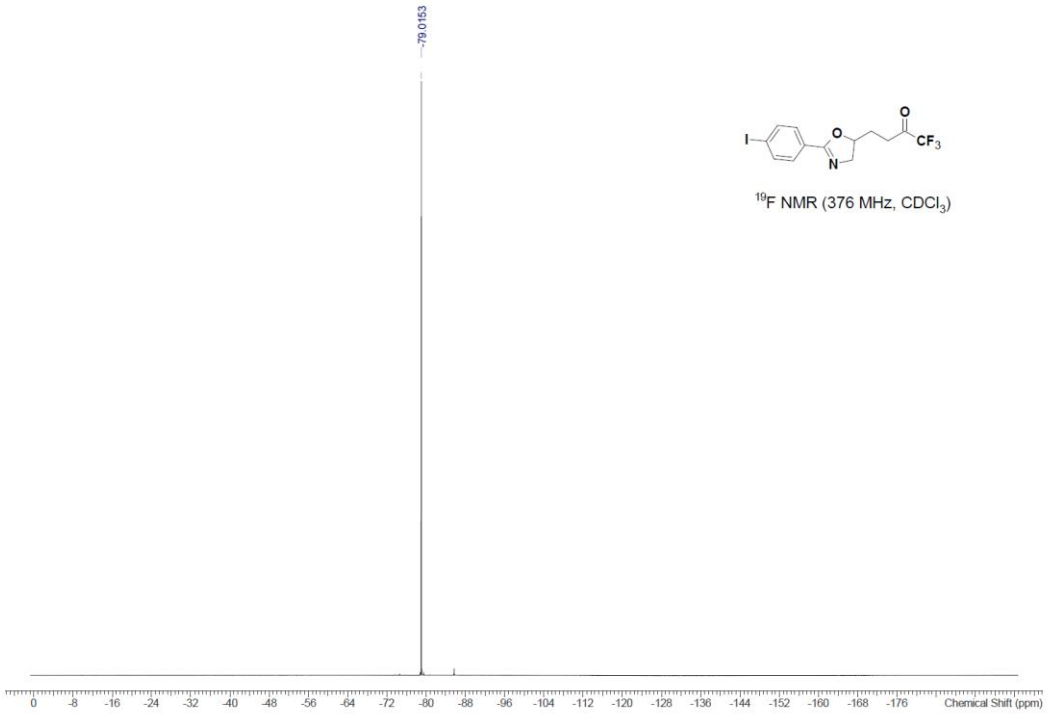


Figure S32 ^{19}F NMR of **4i** (376 MHz, $CDCl_3$)

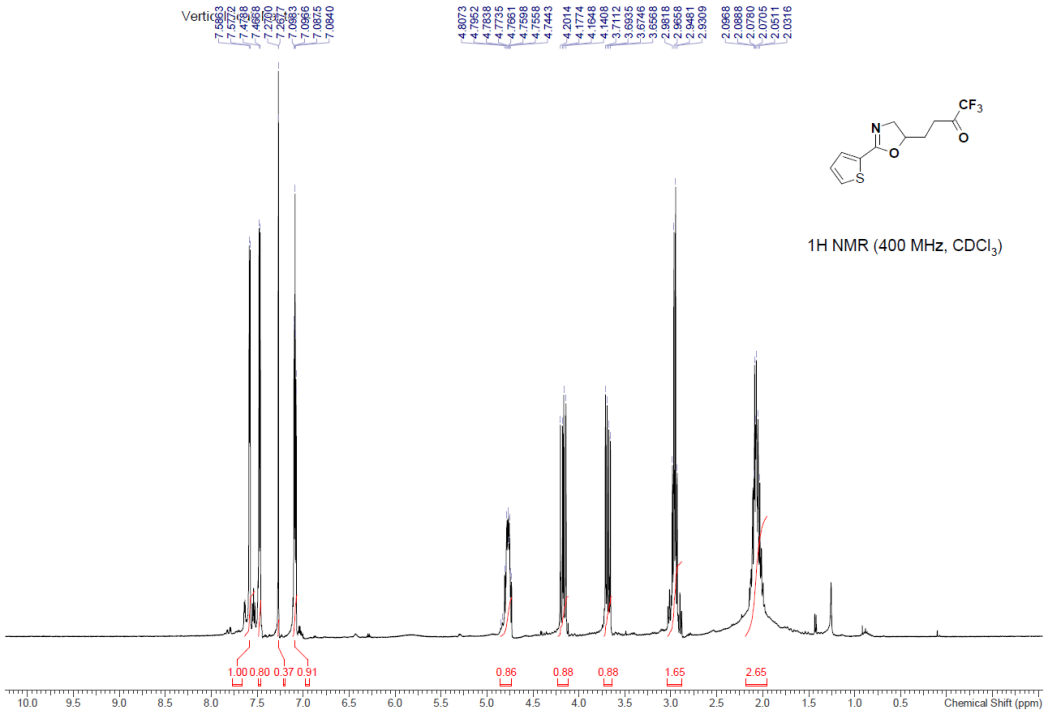


Figure S33. ^{1}H NMR of **4k** (400 MHz, $CDCl_3$)

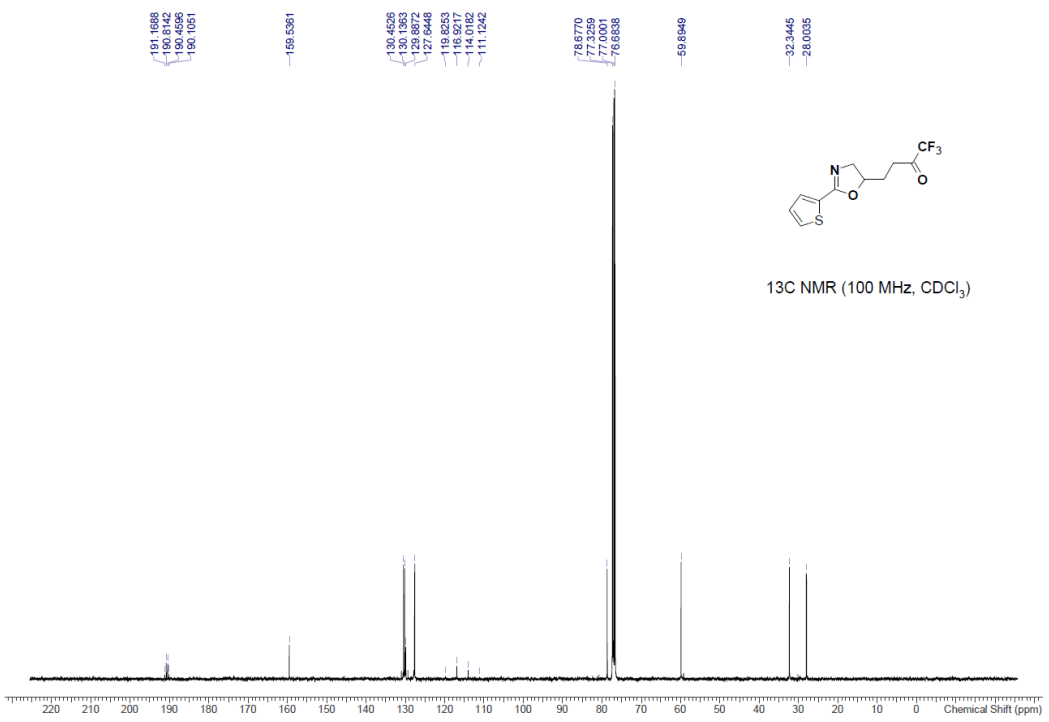


Figure S34. ^{13}C NMR of **4k** (100 MHz, $CDCl_3$)

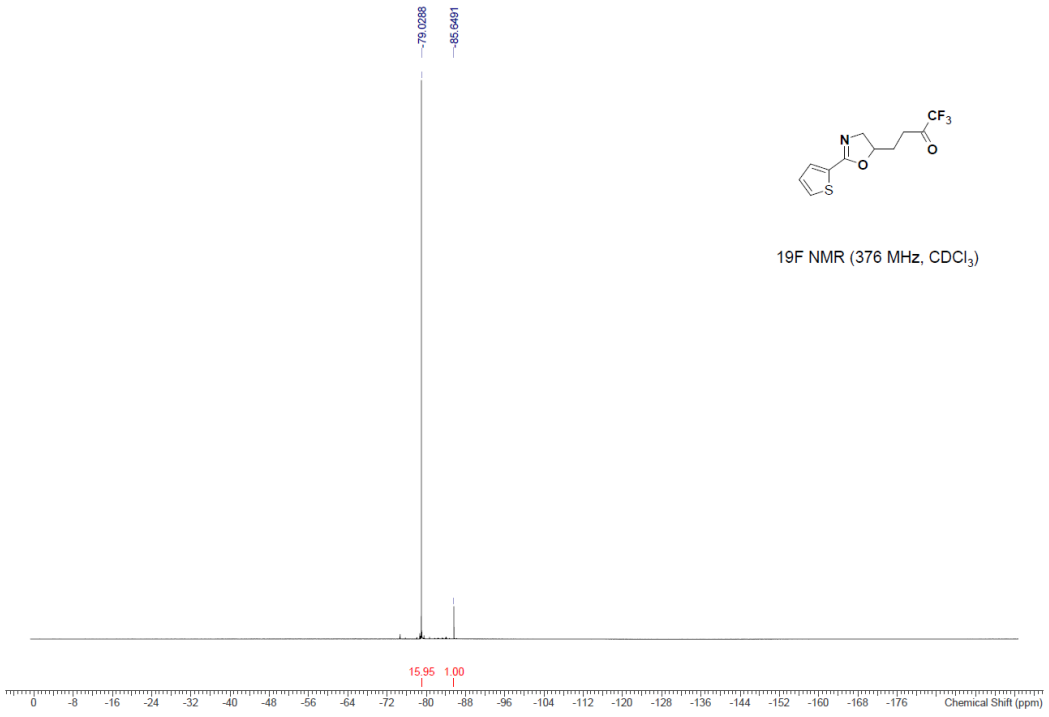


Figure S35. ^{19}F NMR of **4k** (376 MHz, $CDCl_3$)

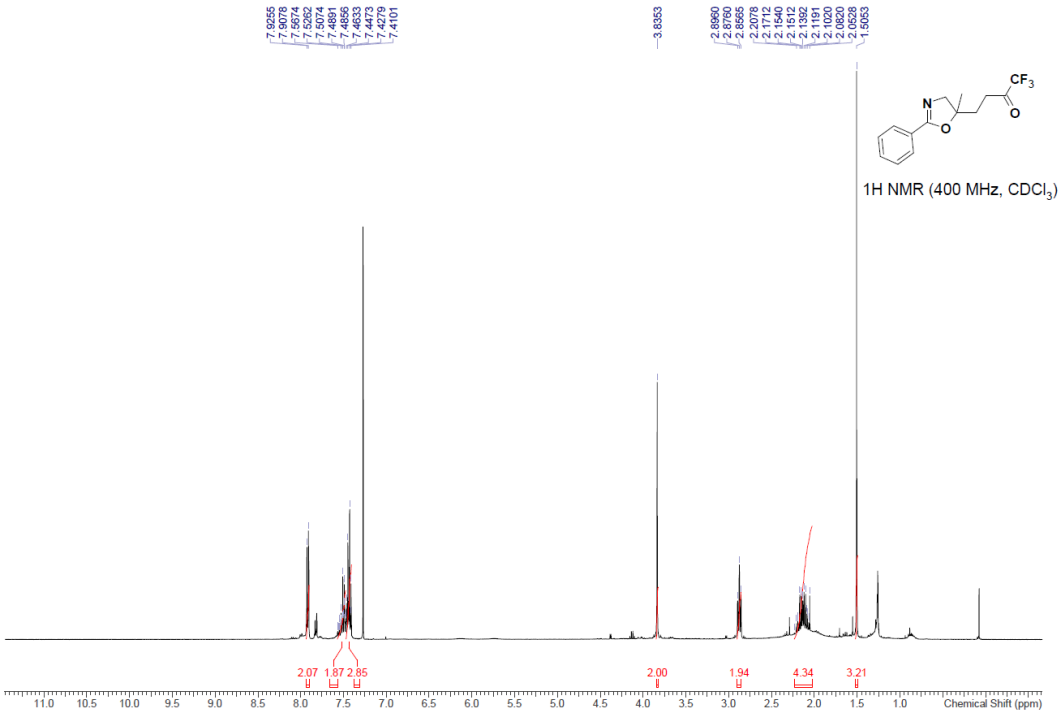


Figure S36. ^{1}H NMR of **4m** (400 MHz, $CDCl_3$)

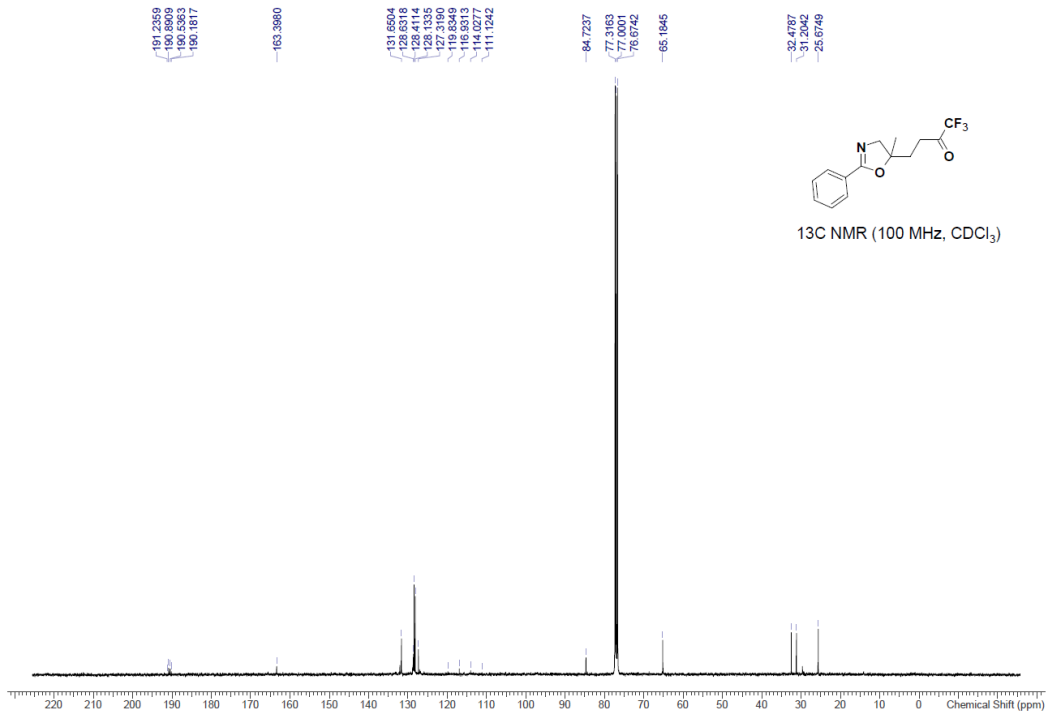


Figure S37. ^{13}C NMR of **4m** (100 MHz, $CDCl_3$)

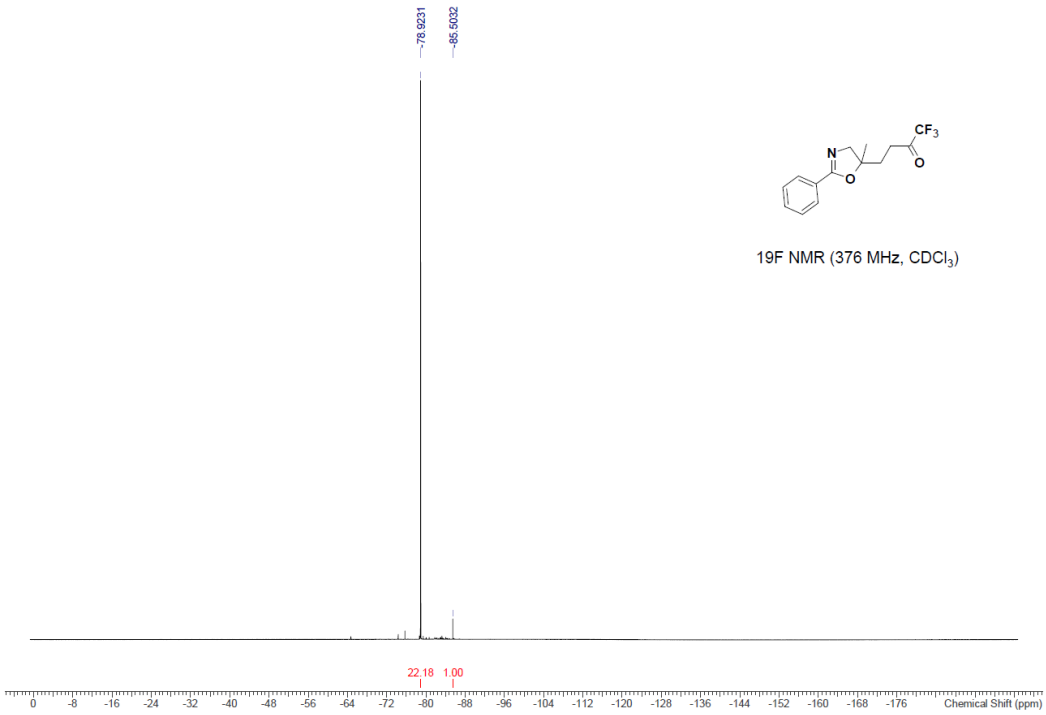


Figure S38. ^{19}F NMR of **4m** (376 MHz, $CDCl_3$)

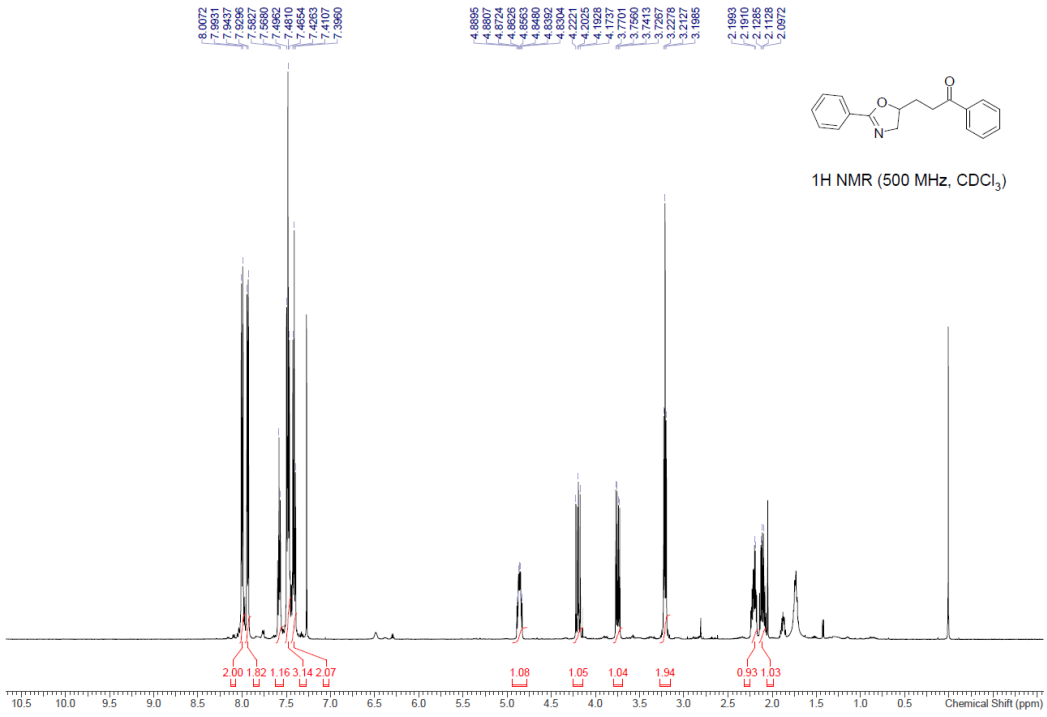


Figure S39. ^{1}H NMR of **4n** (500 MHz, $CDCl_3$)

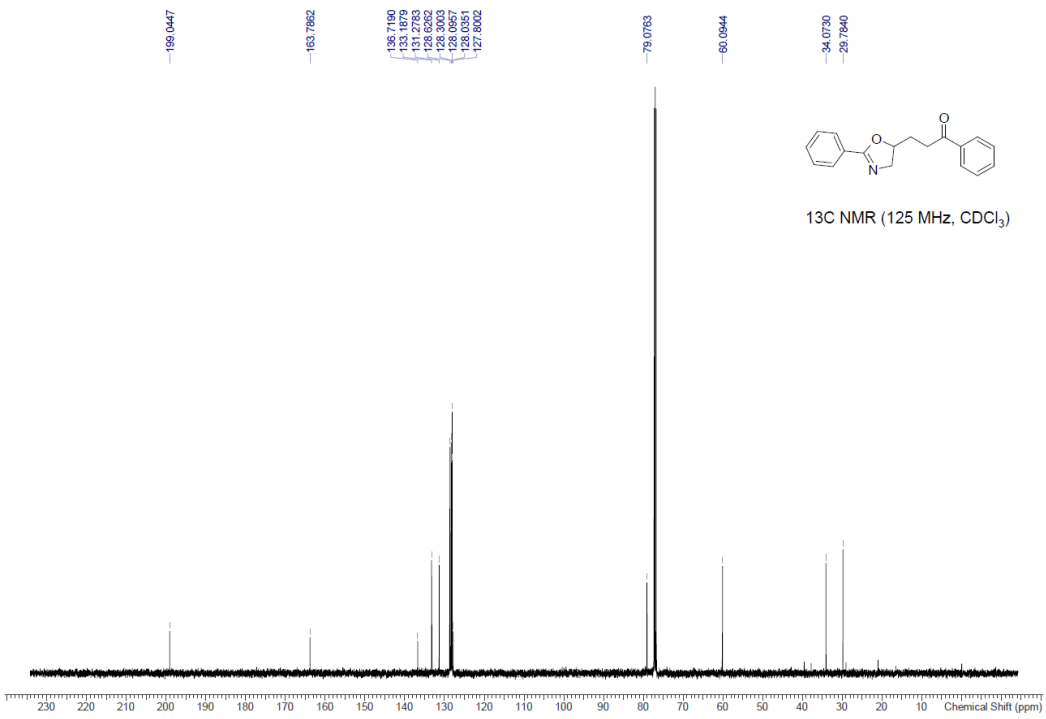


Figure S40. ^{13}C NMR of **4n** (125 MHz, $CDCl_3$)

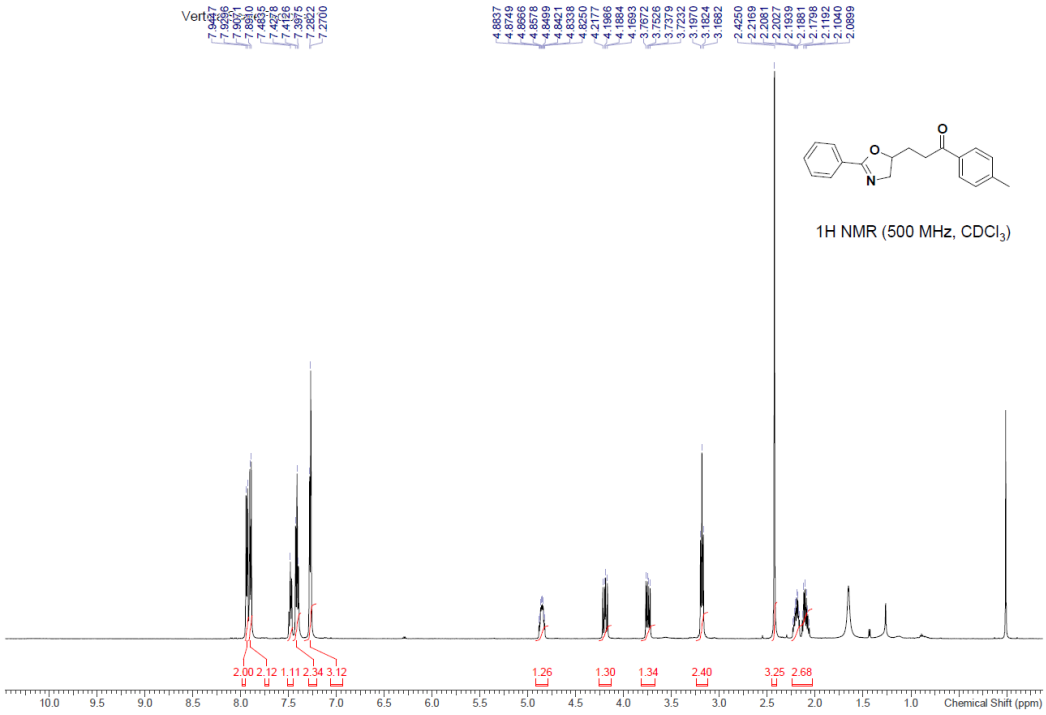


Figure S41. ^{1}H NMR of **4o** (500 MHz, $CDCl_3$)

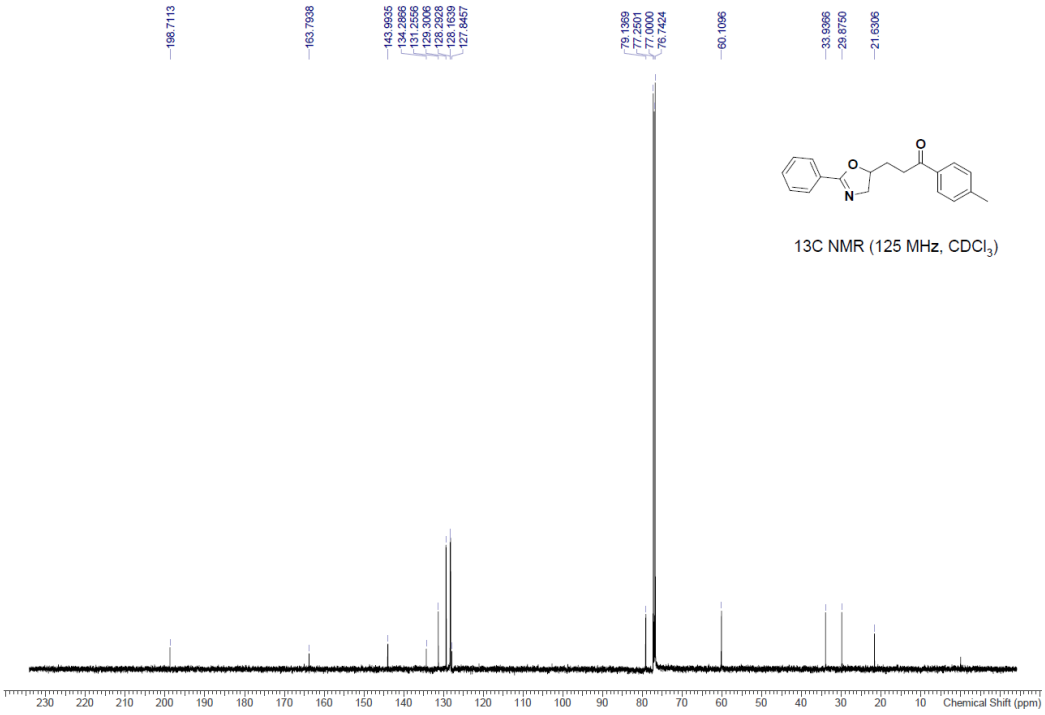


Figure S42. ^{13}C NMR of **4o** (125 MHz, $CDCl_3$)

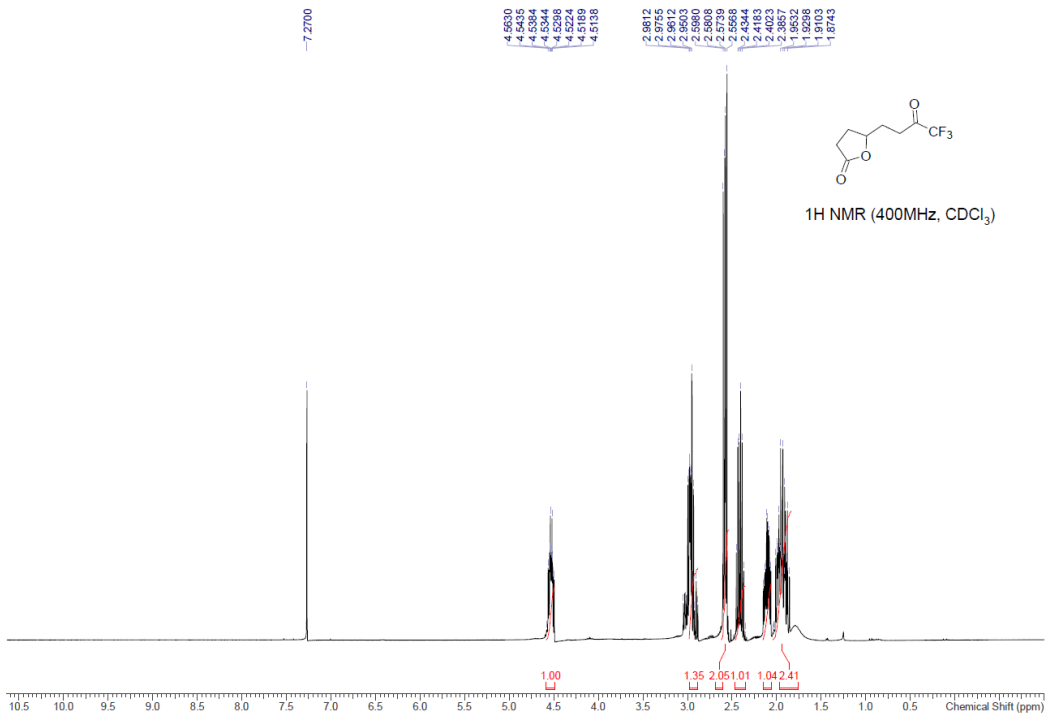


Figure S43. ^{1}H NMR of **4p** (400 MHz, $CDCl_3$)

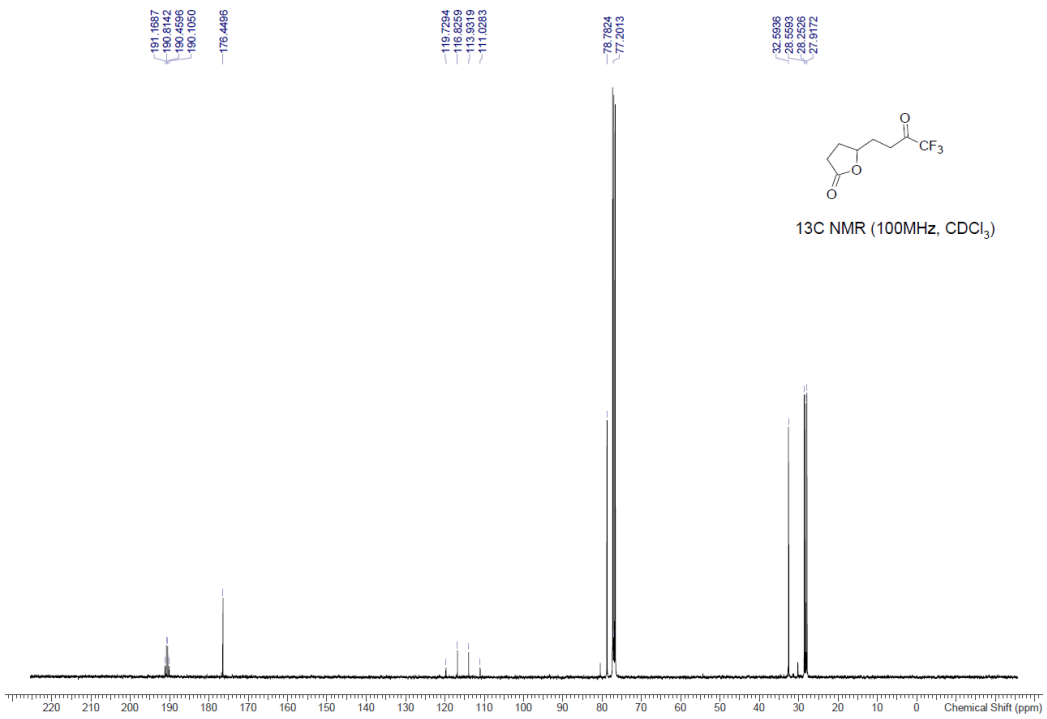


Figure S44. ^{13}C NMR of **4p** (100 MHz, $CDCl_3$)

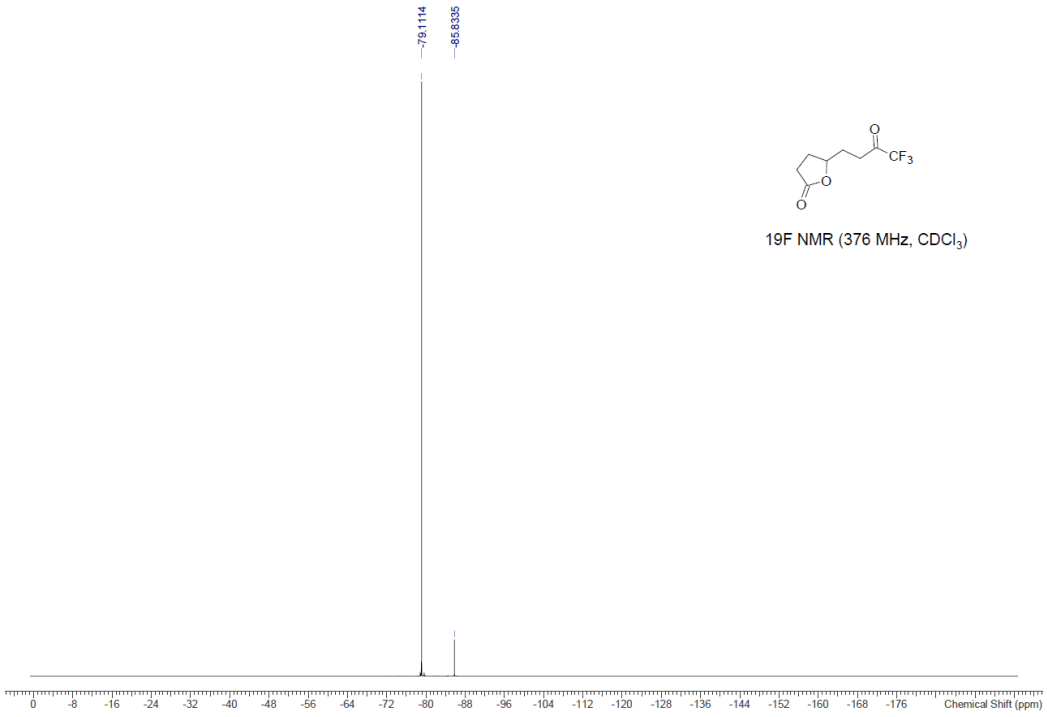


Figure S45. ^{19}F NMR of **4p** (376 MHz, $CDCl_3$)

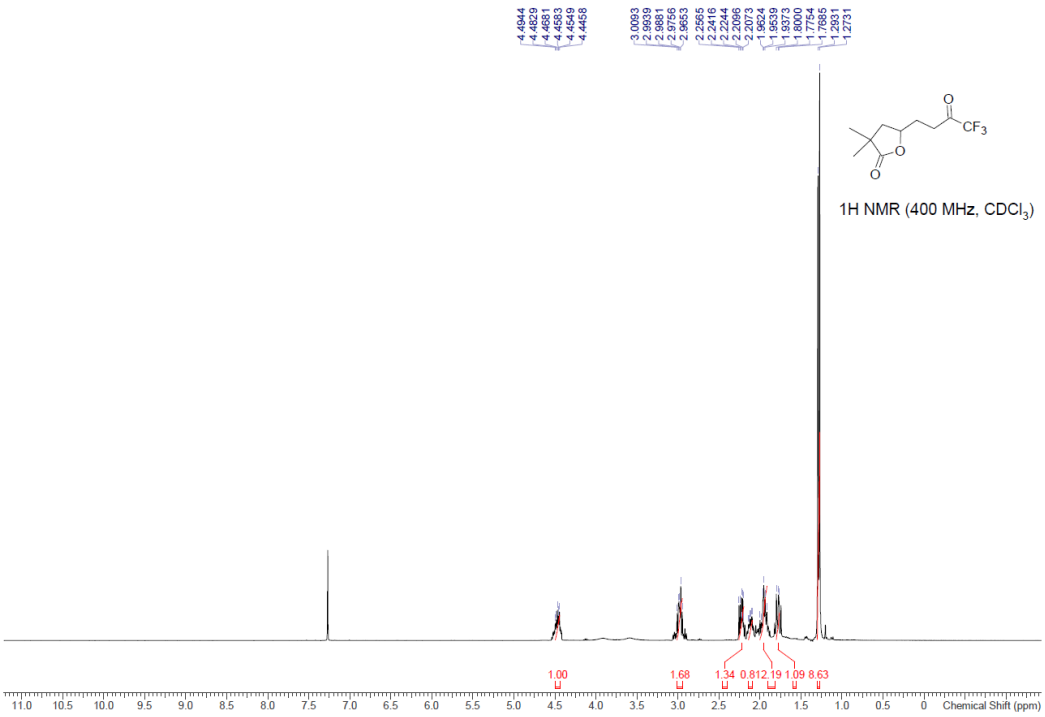


Figure S46. ^{1}H NMR of **4q** (400 MHz, $CDCl_3$)

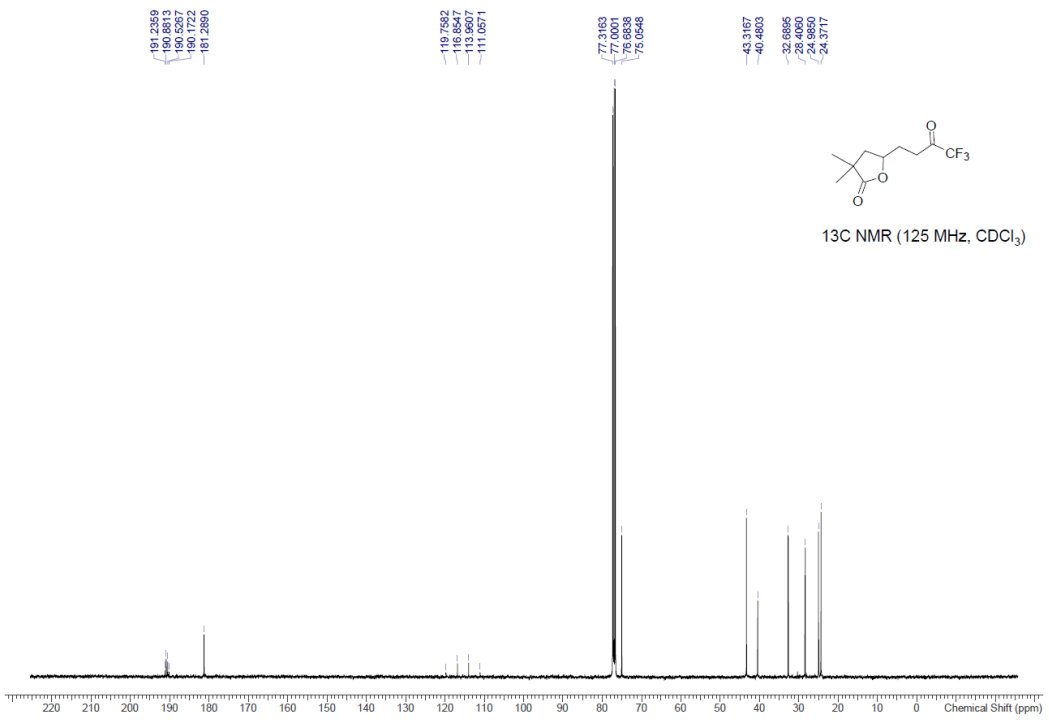


Figure S47. ^{13}C NMR of **4q** (100 MHz, $CDCl_3$)

Figure S48. ^{19}F NMR of **4q** (376 MHz, $CDCl_3$)

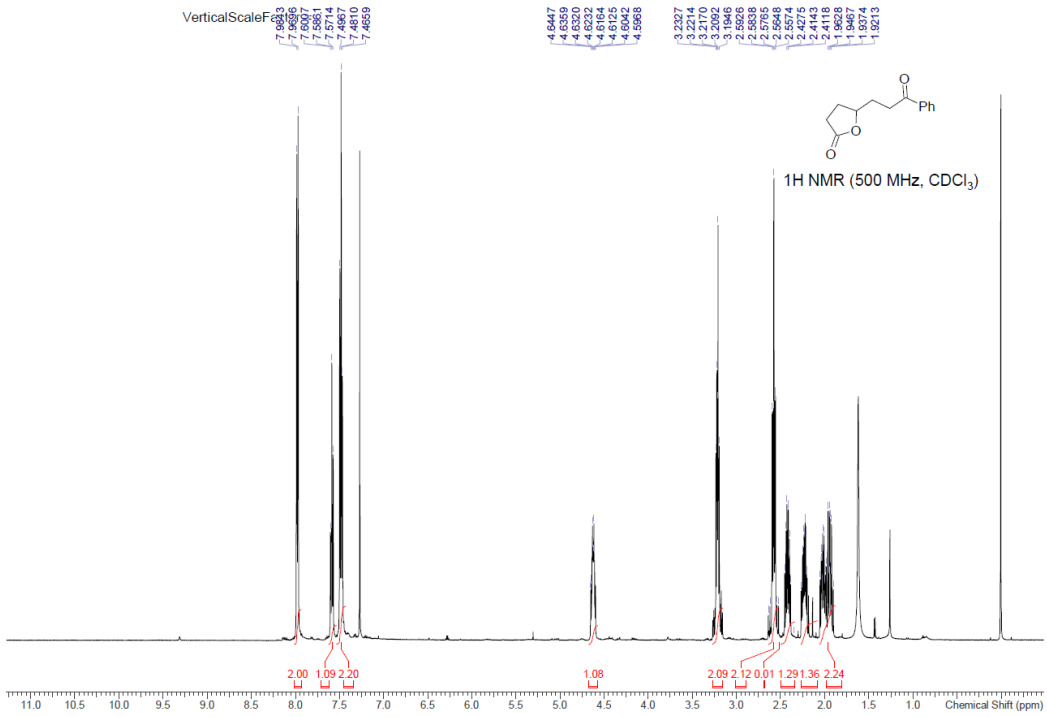


Figure S49. ^{1}H NMR of **4r** (500 MHz, $CDCl_3$)

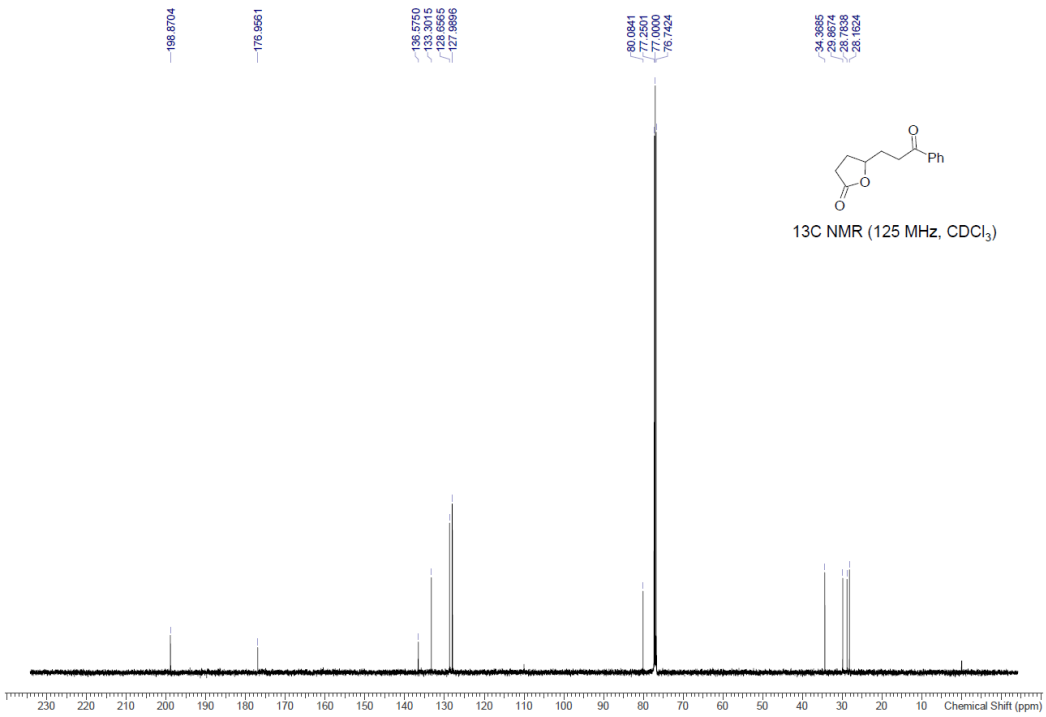


Figure S50. ^{13}C NMR of **4r** (125 MHz, $CDCl_3$)

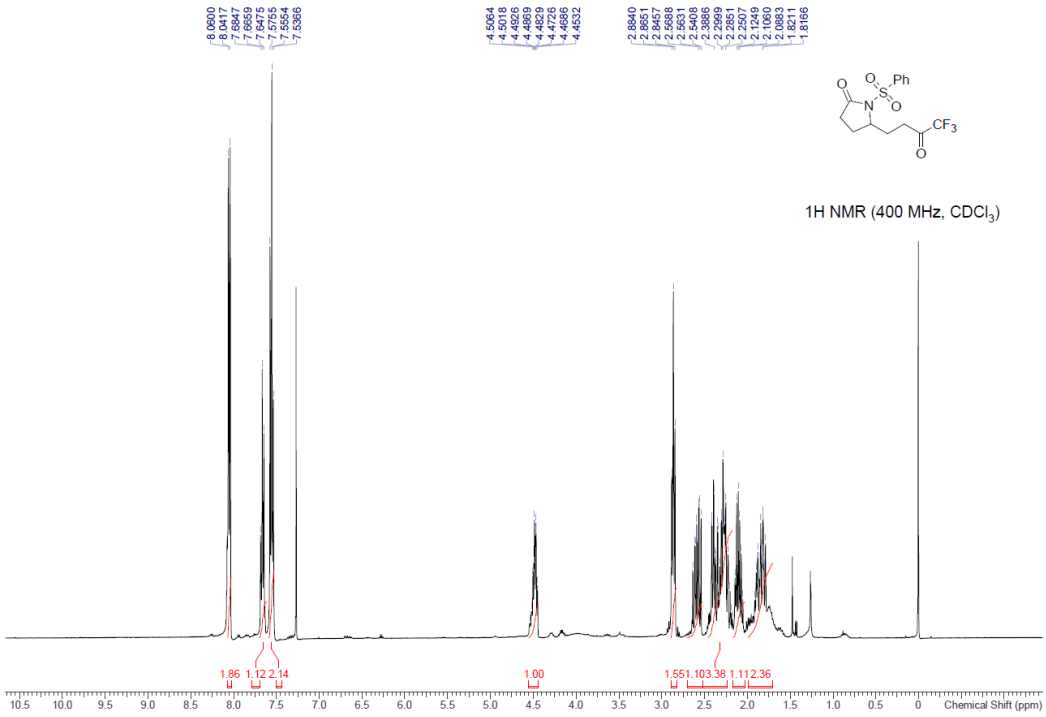


Figure S51. ^{1}H NMR of **4s** (400 MHz, $CDCl_3$)

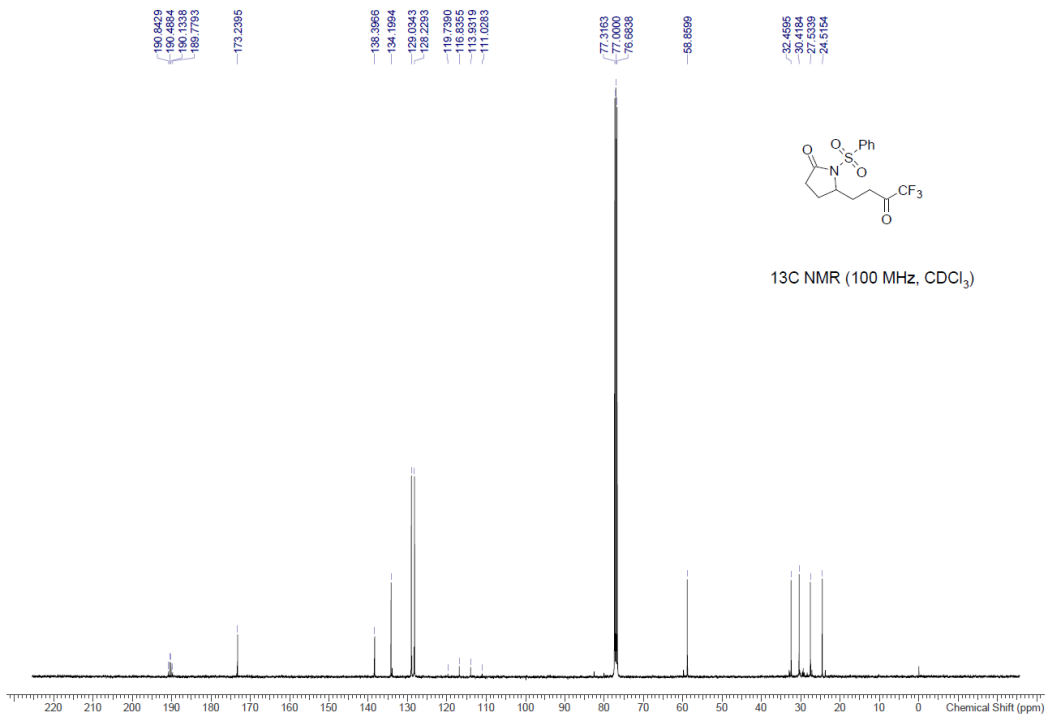


Figure S52. ^{13}C NMR of **4s** (100 MHz, $CDCl_3$)

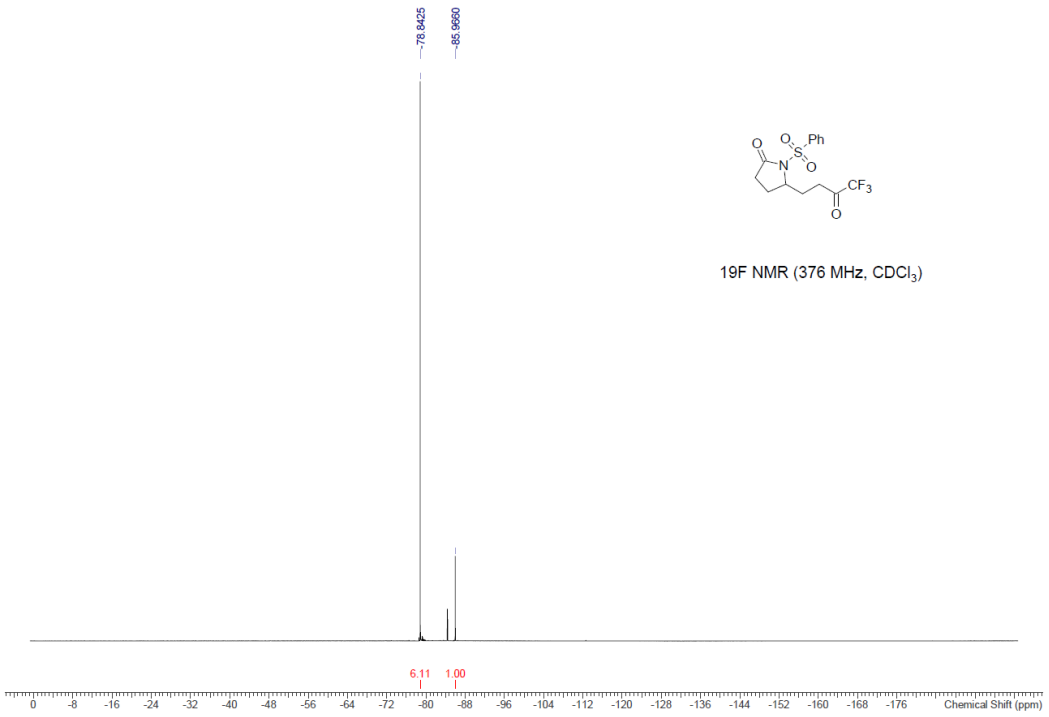


Figure S53. ^{19}F NMR of **4s** (376 MHz, $CDCl_3$)

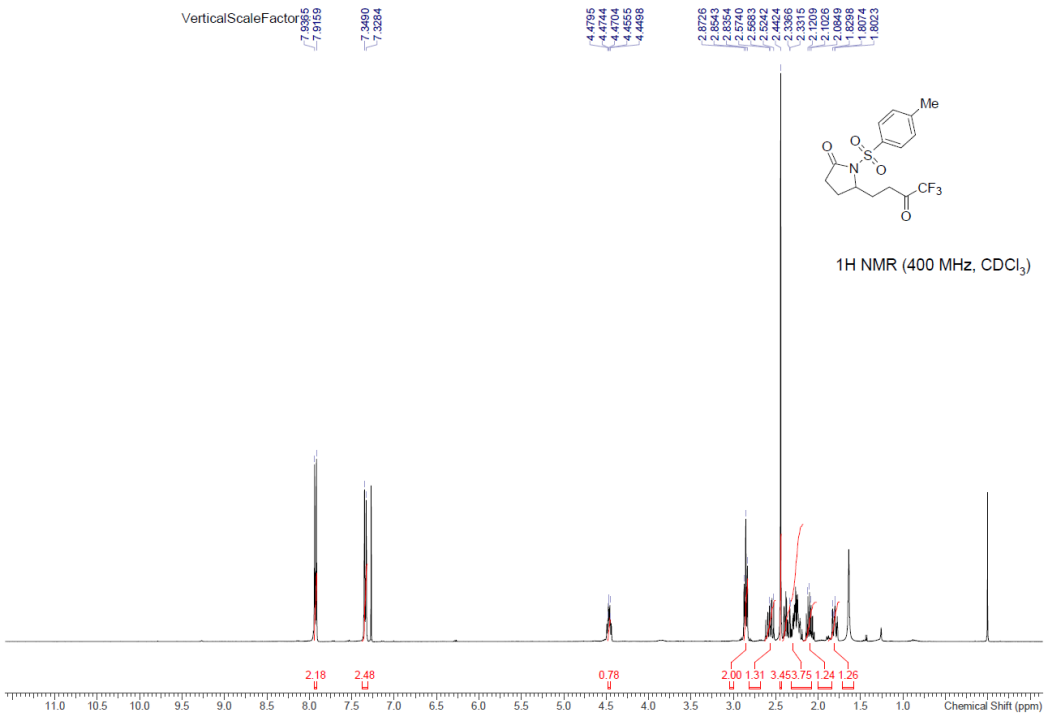


Figure S54. ^{1}H NMR of **4t** (400 MHz, $CDCl_3$)

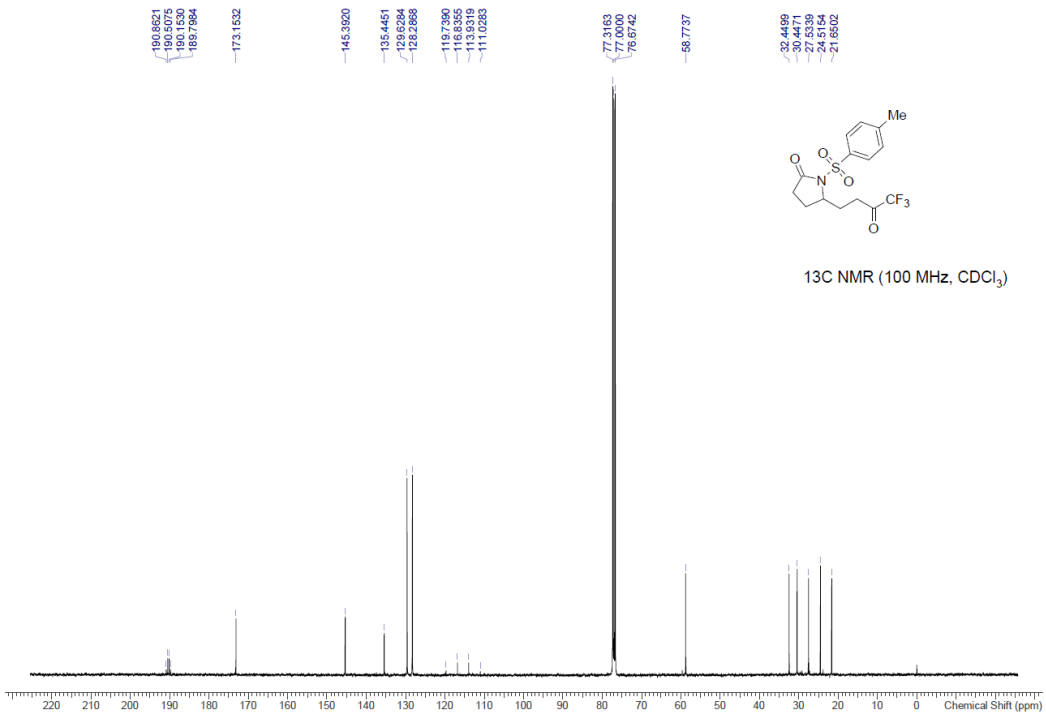


Figure S55. ^{13}C NMR of **4t** (100 MHz, $CDCl_3$)

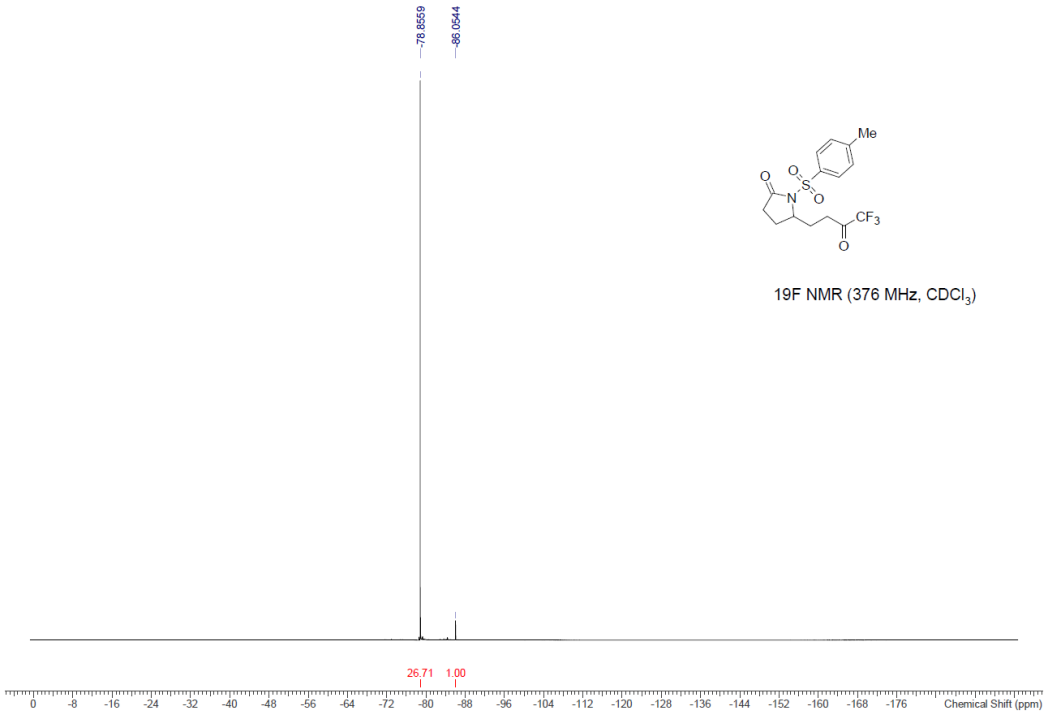


Figure S56. ^{19}F NMR of **4t** (376 MHz, $CDCl_3$)

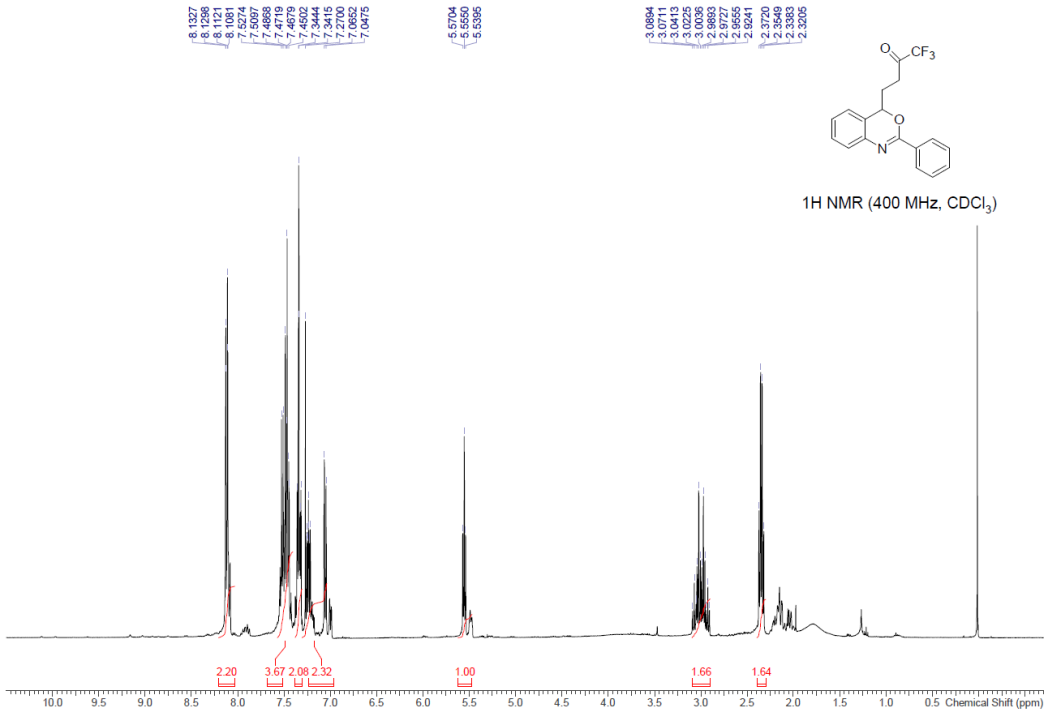


Figure S57. ^{1}H NMR of **7a** (400 MHz, $CDCl_3$)

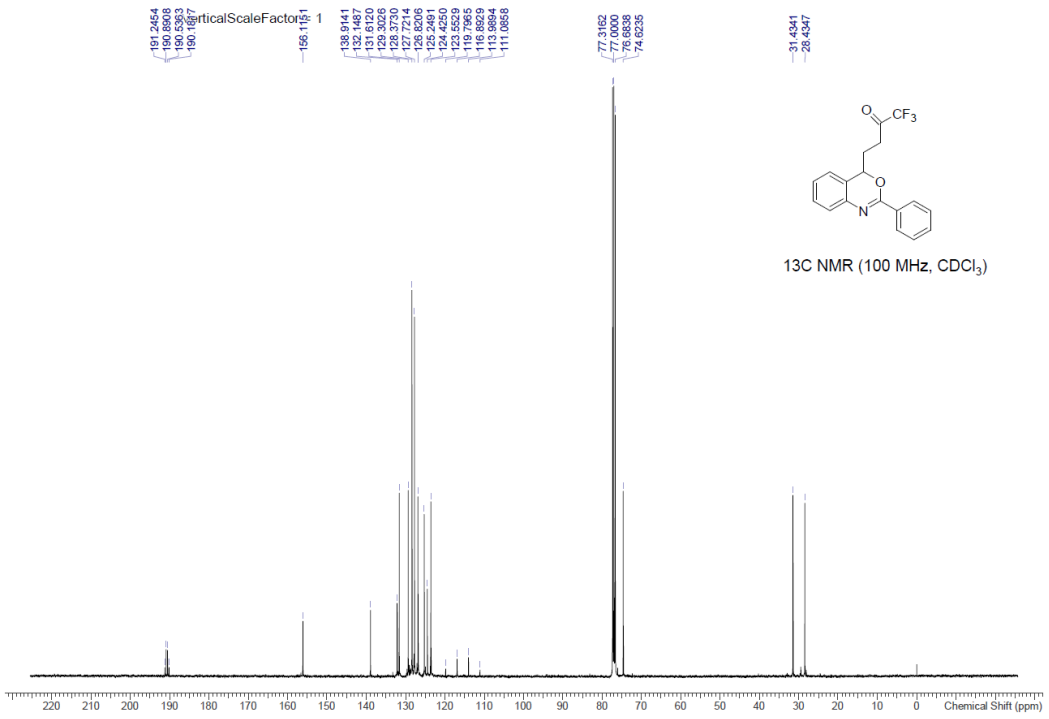


Figure S58. ^{13}C NMR of **7a** (100 MHz, $CDCl_3$)

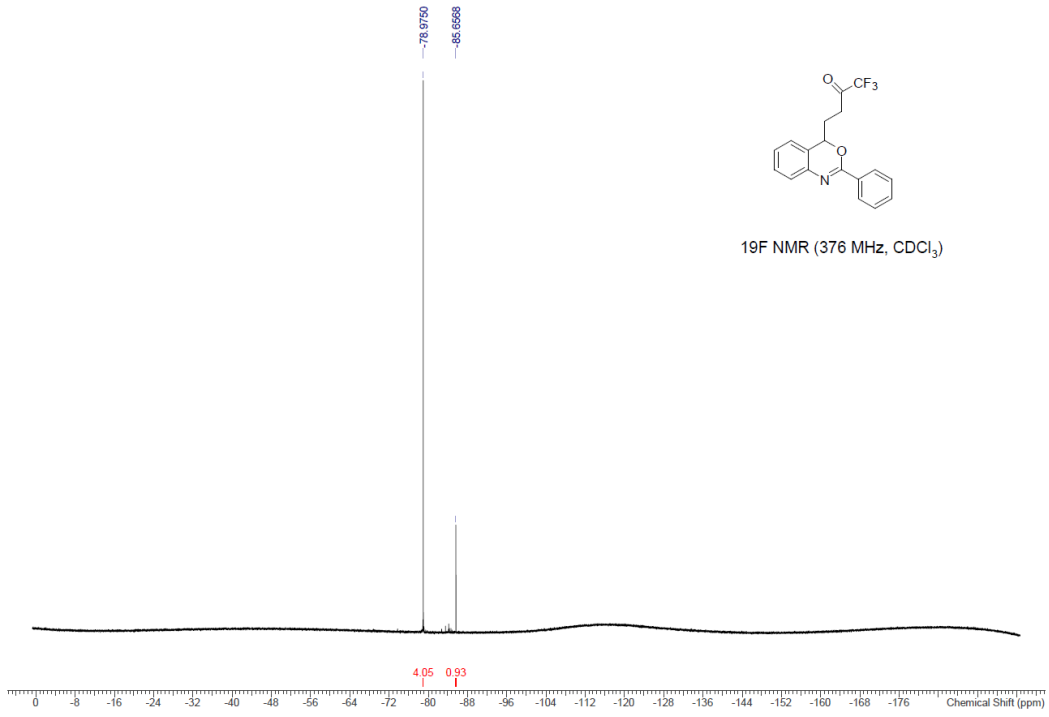


Figure S59. ^{19}F NMR of **7a** (376 MHz, $CDCl_3$)

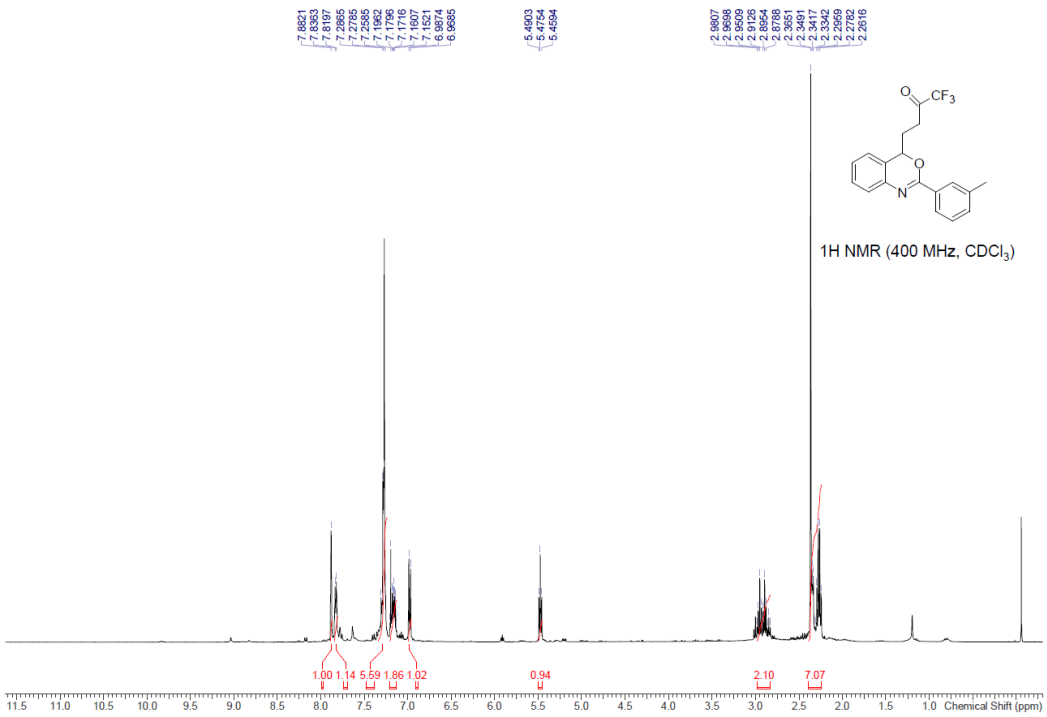


Figure S60. ^{1}H NMR of **7b** (400 MHz, $CDCl_3$)

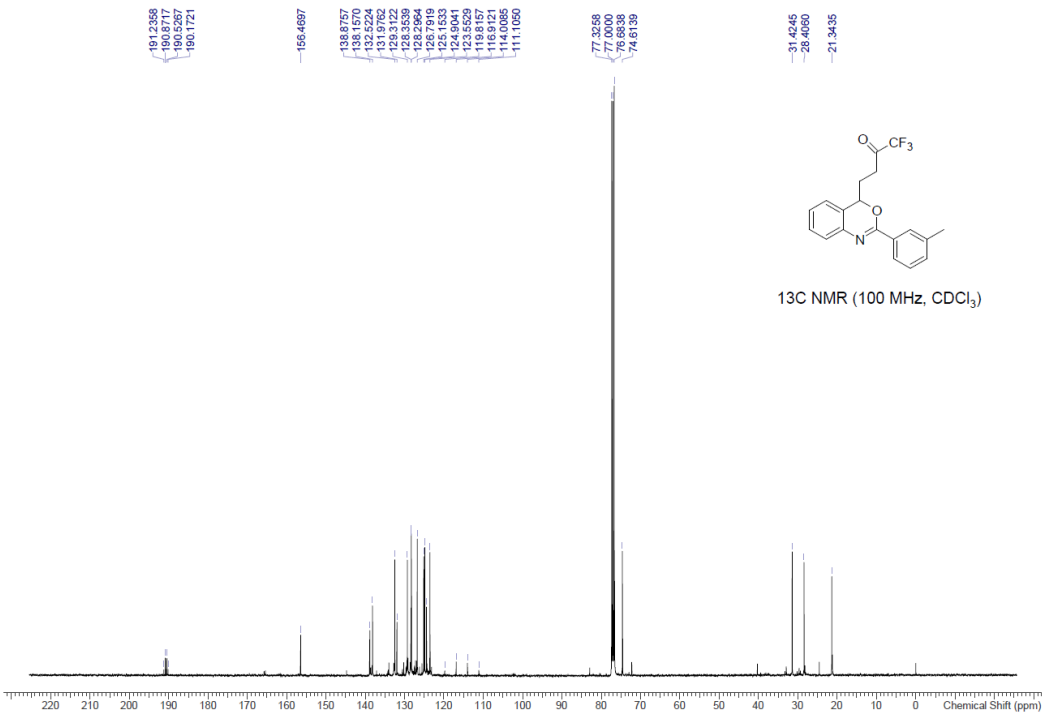


Figure S61. ^{13}C NMR of **7b** (100 MHz, $CDCl_3$)

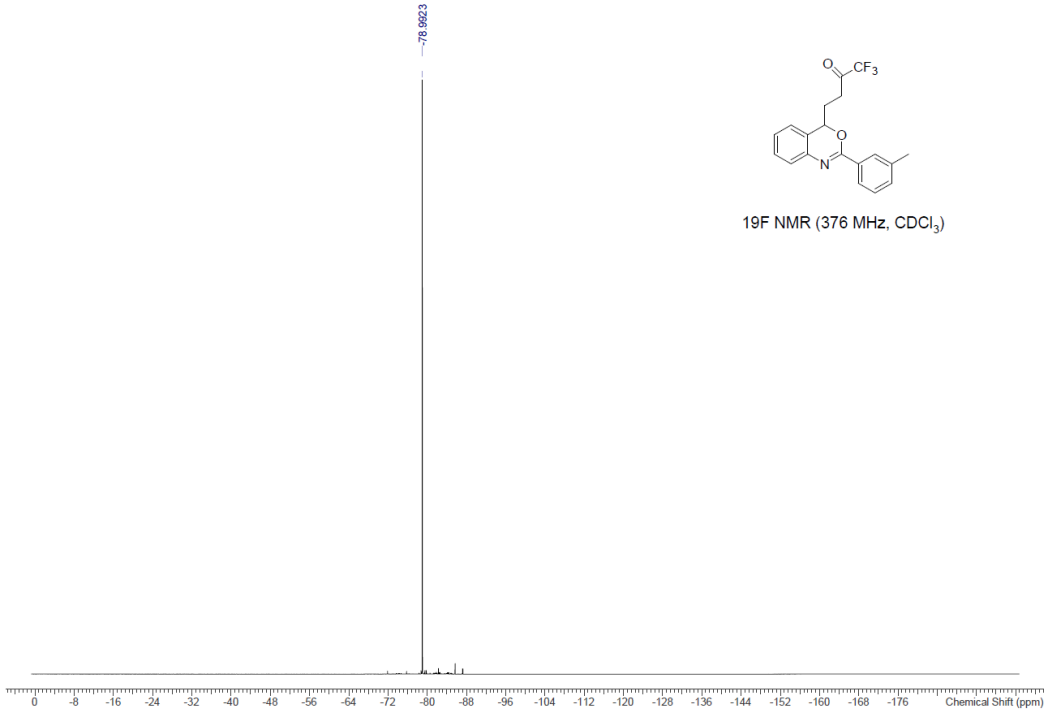


Figure S62. ^{19}F NMR of **7b** (376 MHz, $CDCl_3$)

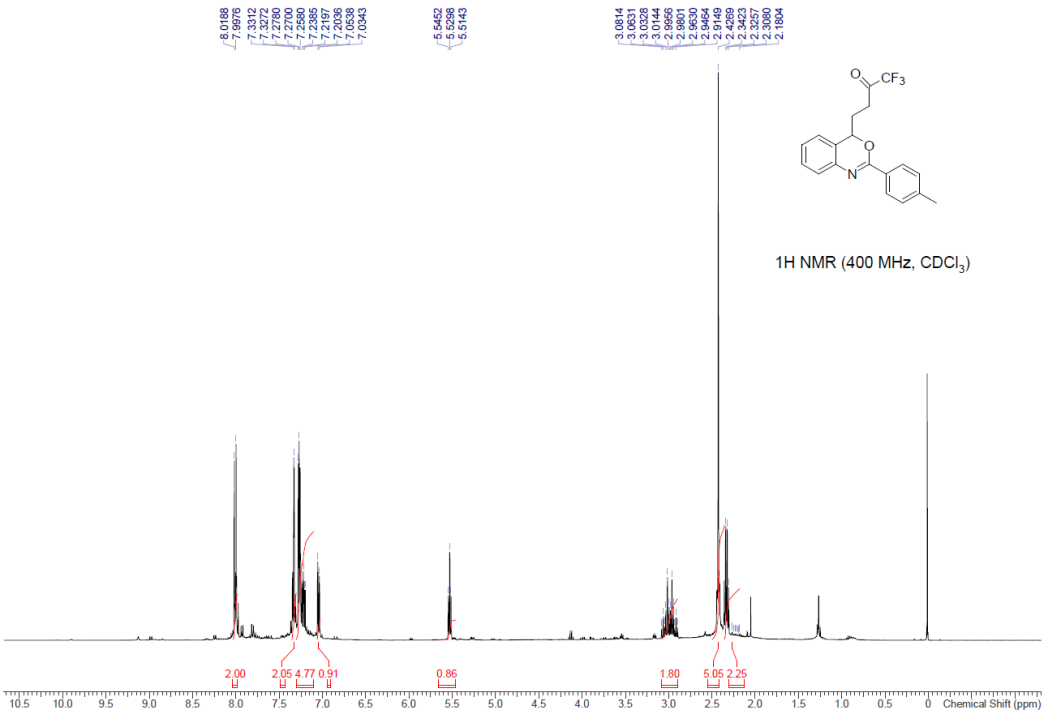


Figure S63. ^{1}H NMR of **7c** (400 MHz, $CDCl_3$)

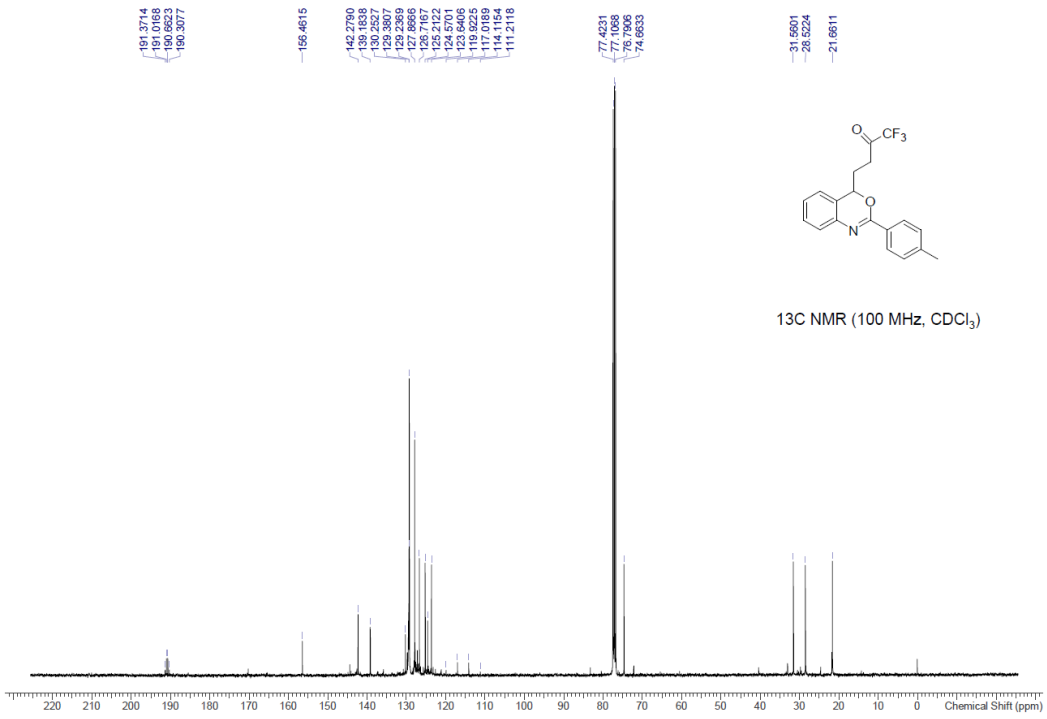


Figure S64. ^{13}C NMR of **7c** (100 MHz, $CDCl_3$)

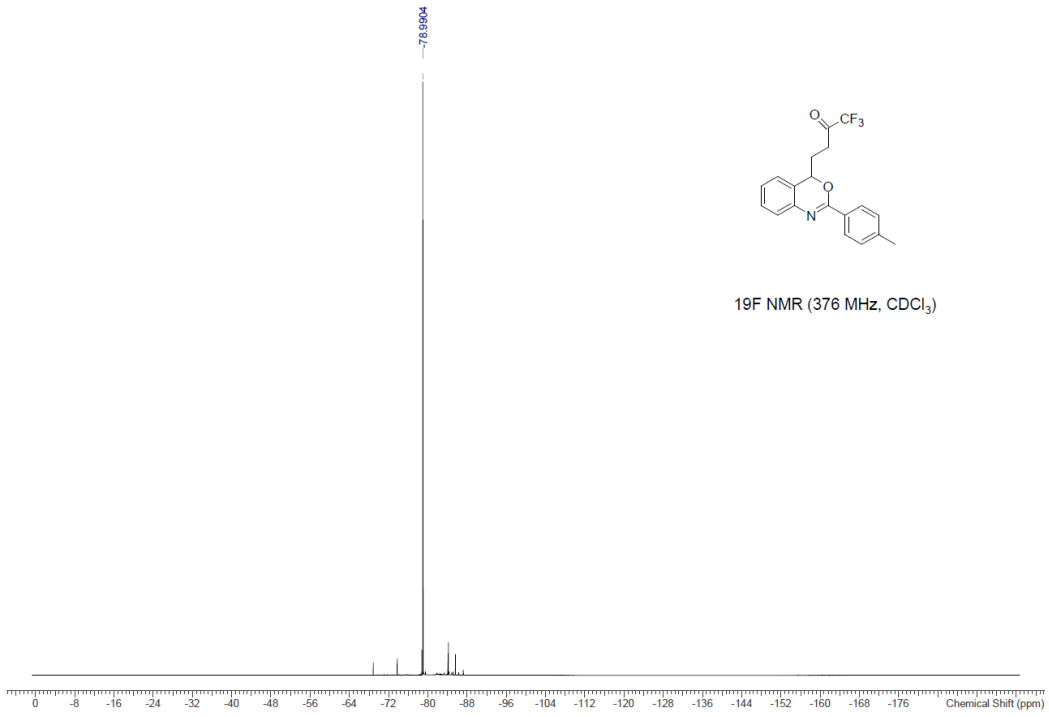


Figure S65. ^{19}F NMR of **7c** (376 MHz, $CDCl_3$)

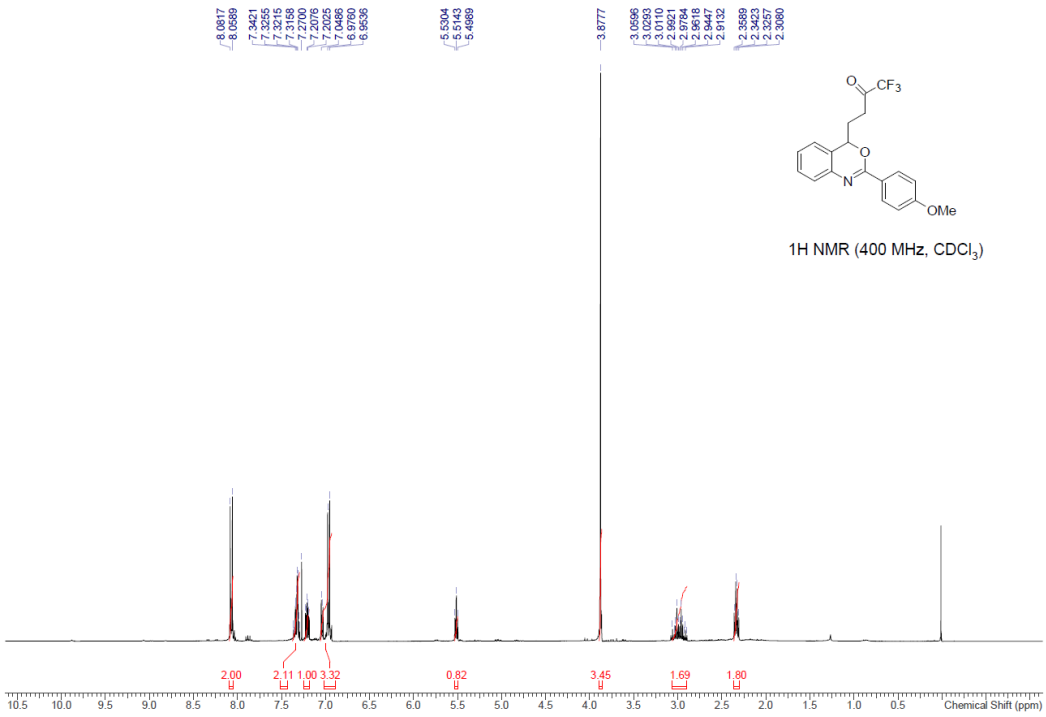


Figure S66. ^{1}H NMR of **7d** (500 MHz, $CDCl_3$)

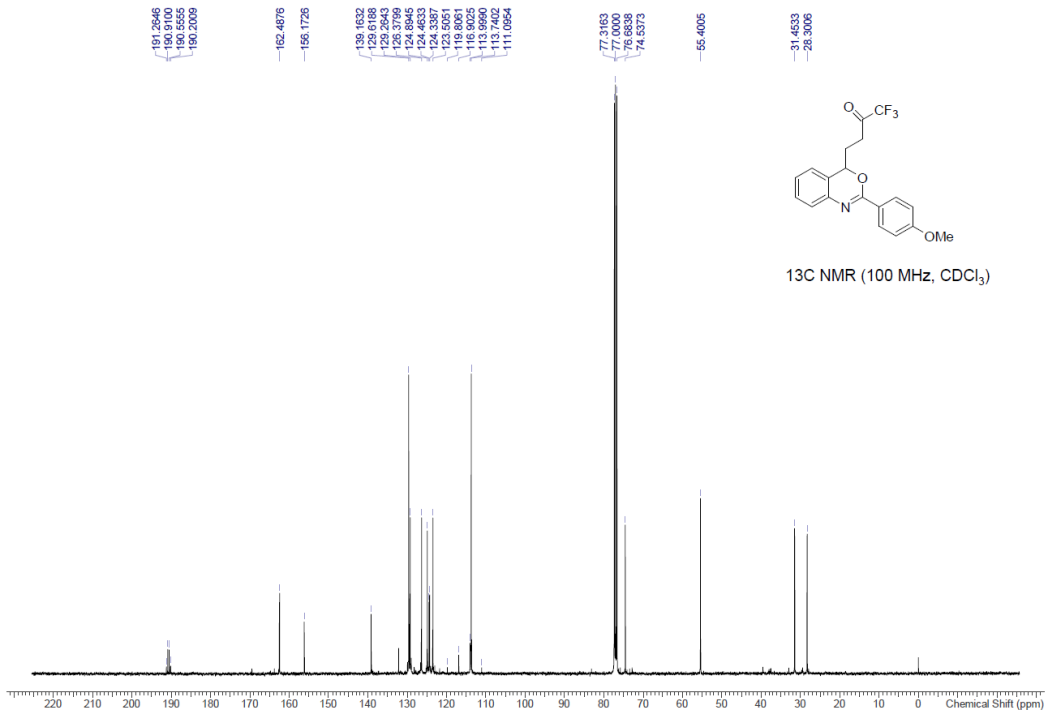


Figure S67. ^{13}C NMR of **7d** (125 MHz, $CDCl_3$)

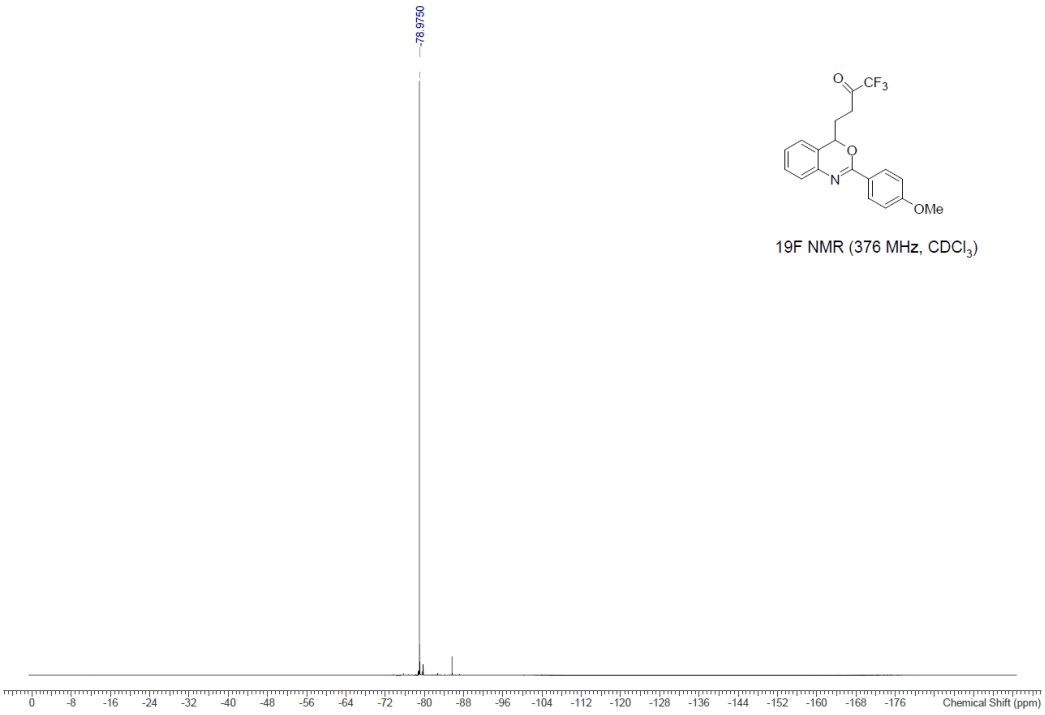


Figure S68. ^{19}F NMR of **7d** (376 MHz, $CDCl_3$)

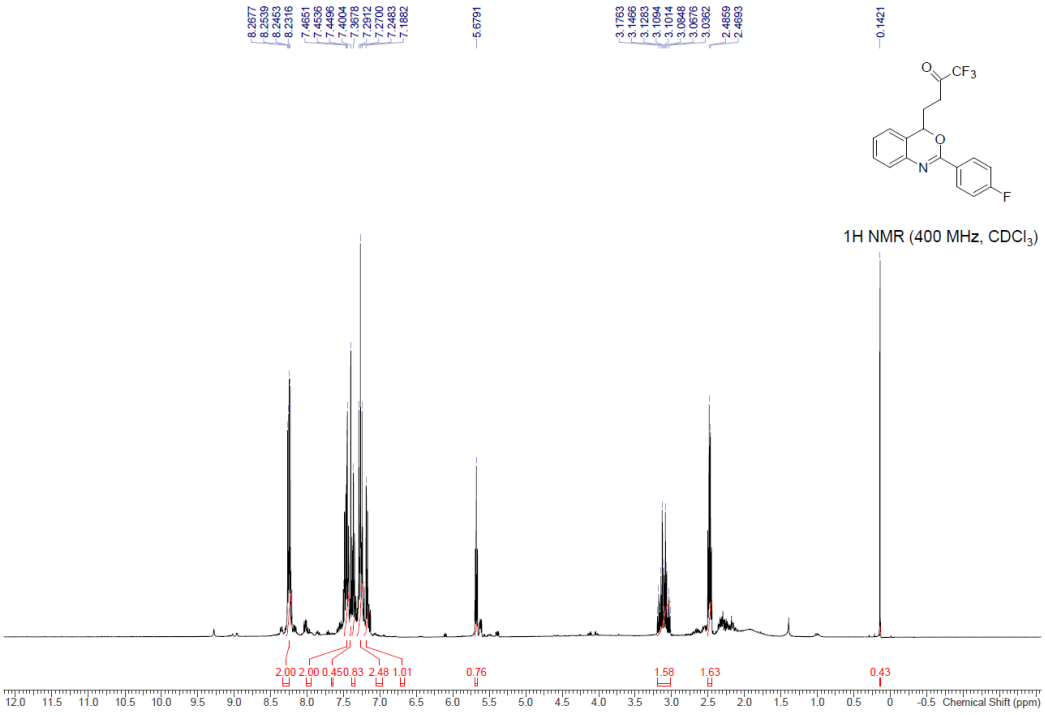


Figure S69. ^{1}H NMR of **7e** (400 MHz, $CDCl_3$)

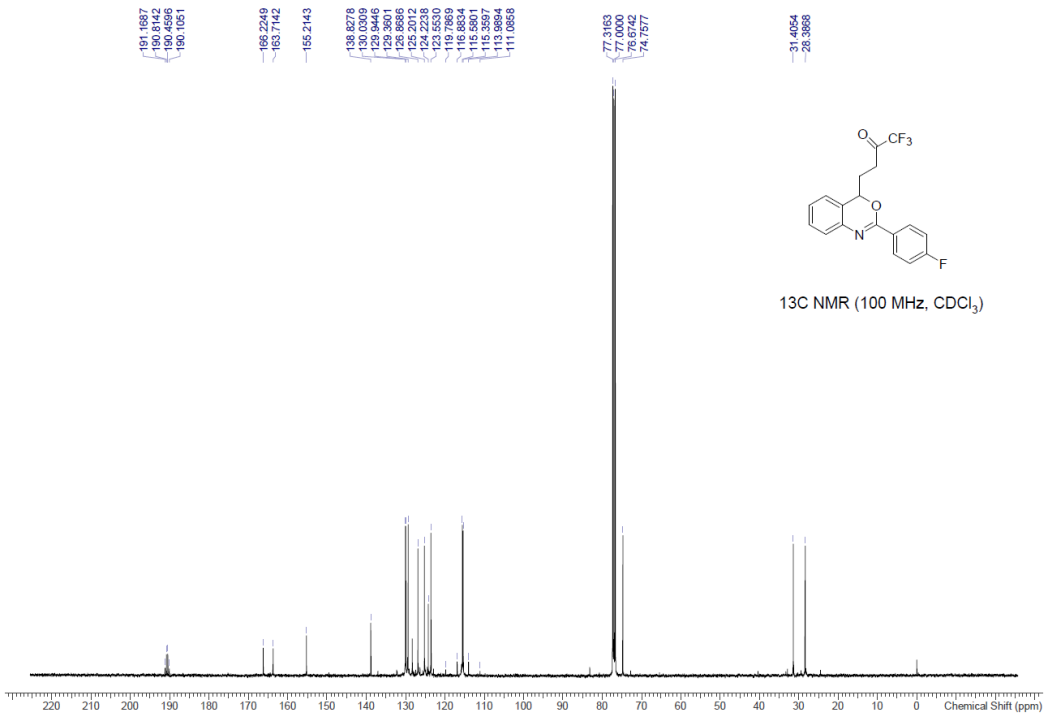


Figure S70. ^{13}C NMR of **7e** (100 MHz, $CDCl_3$)

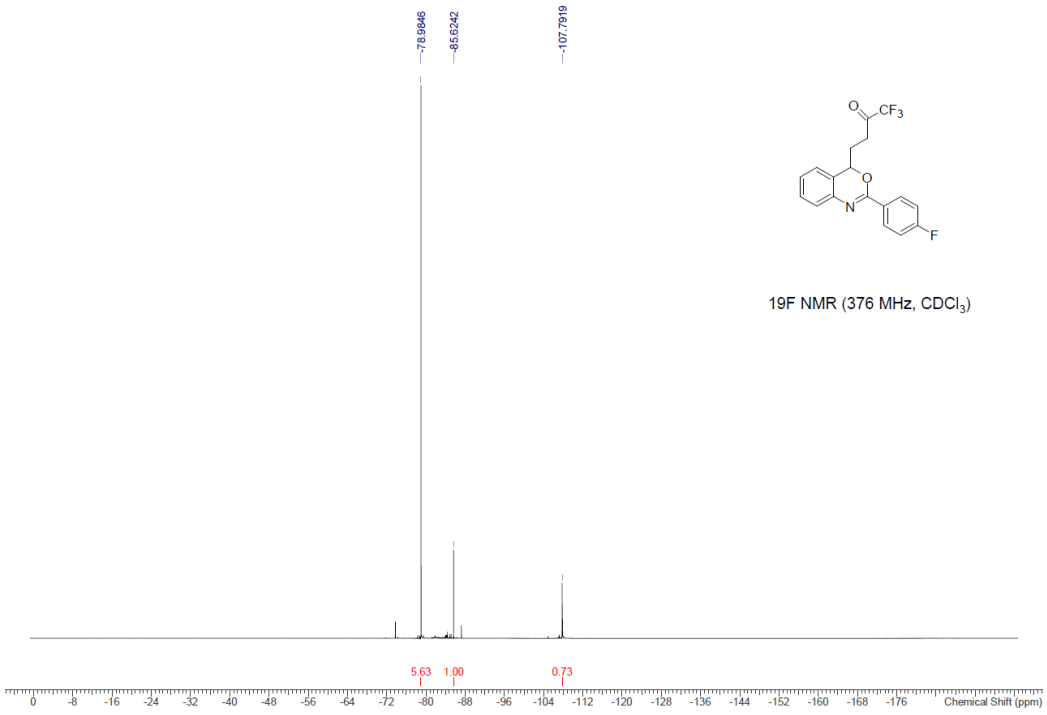


Figure S71. ^{19}F NMR of **7e** (376 MHz, $CDCl_3$)

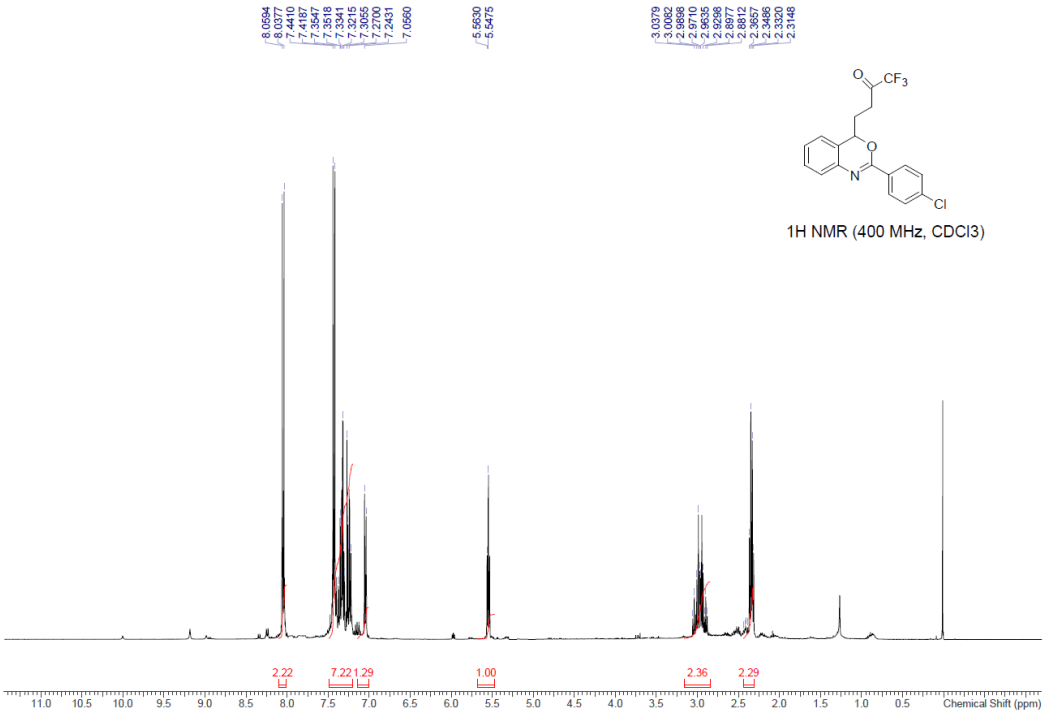


Figure S72. ^{1}H NMR of **7f** (400 MHz, $CDCl_3$)

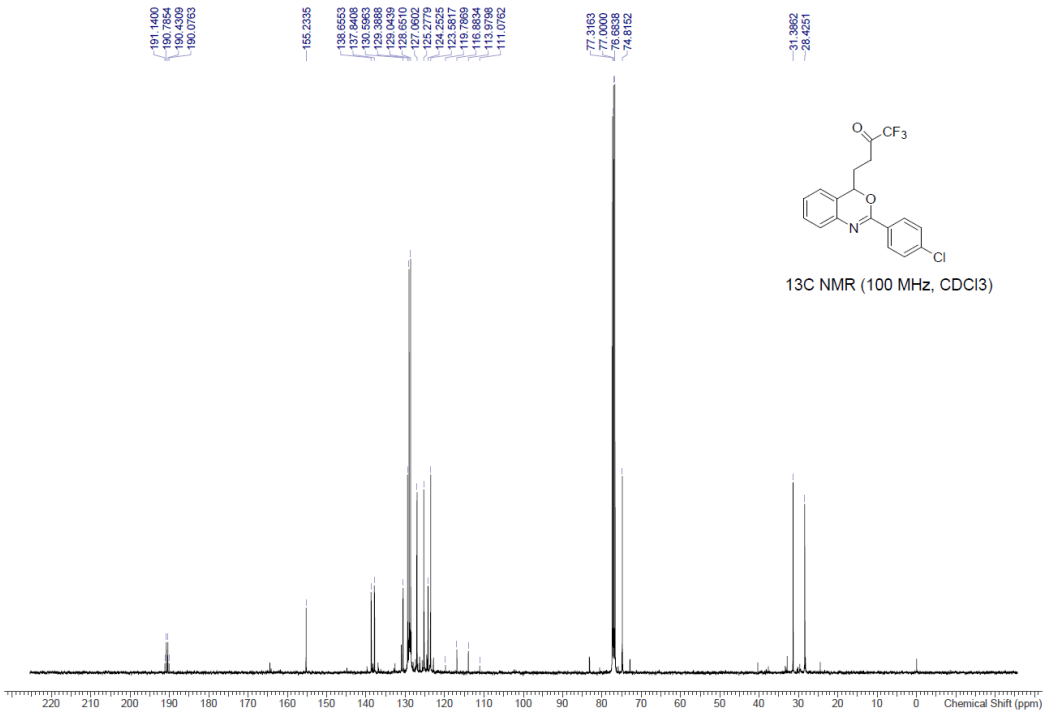


Figure S73. ^{13}C NMR of **7f** (100 MHz, $CDCl_3$)

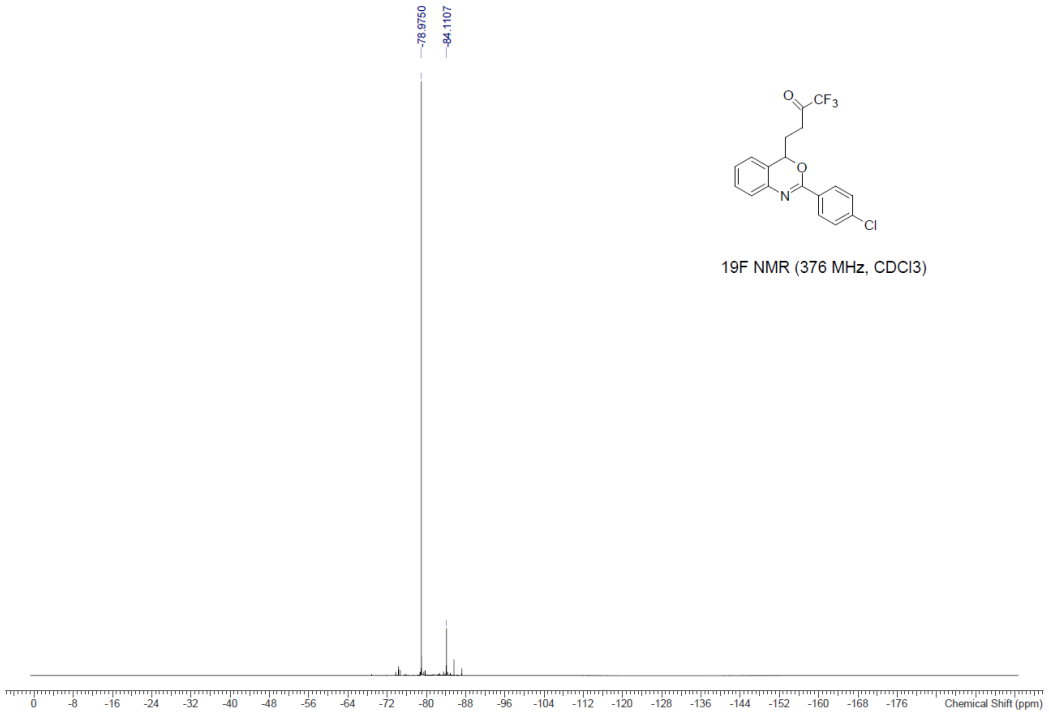


Figure S74. ^{19}F NMR of **7f** (376 MHz, $CDCl_3$)

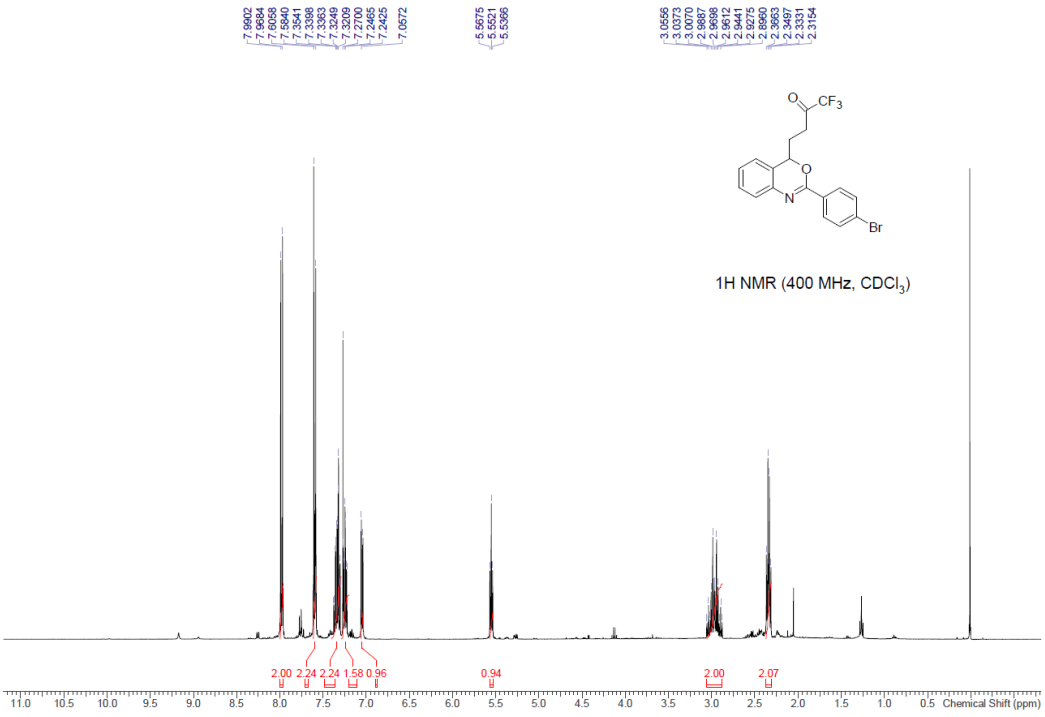


Figure S75. ^{1}H NMR of **7g** (400 MHz, $CDCl_3$)

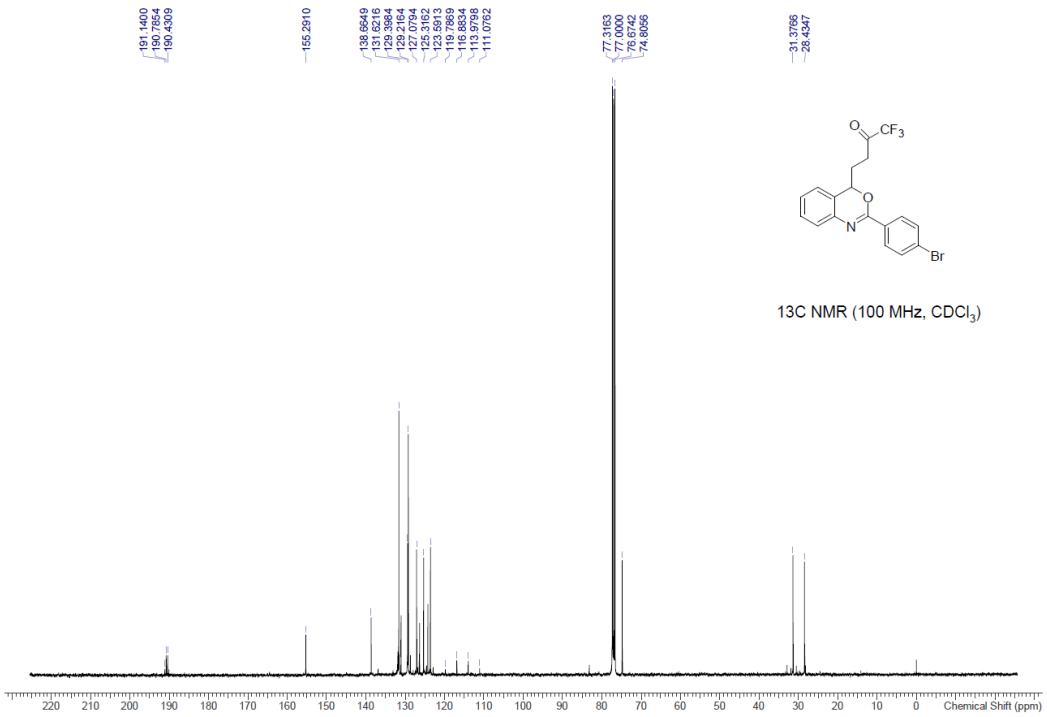


Figure S76. ^{13}C NMR of **7g** (100 MHz, $CDCl_3$)

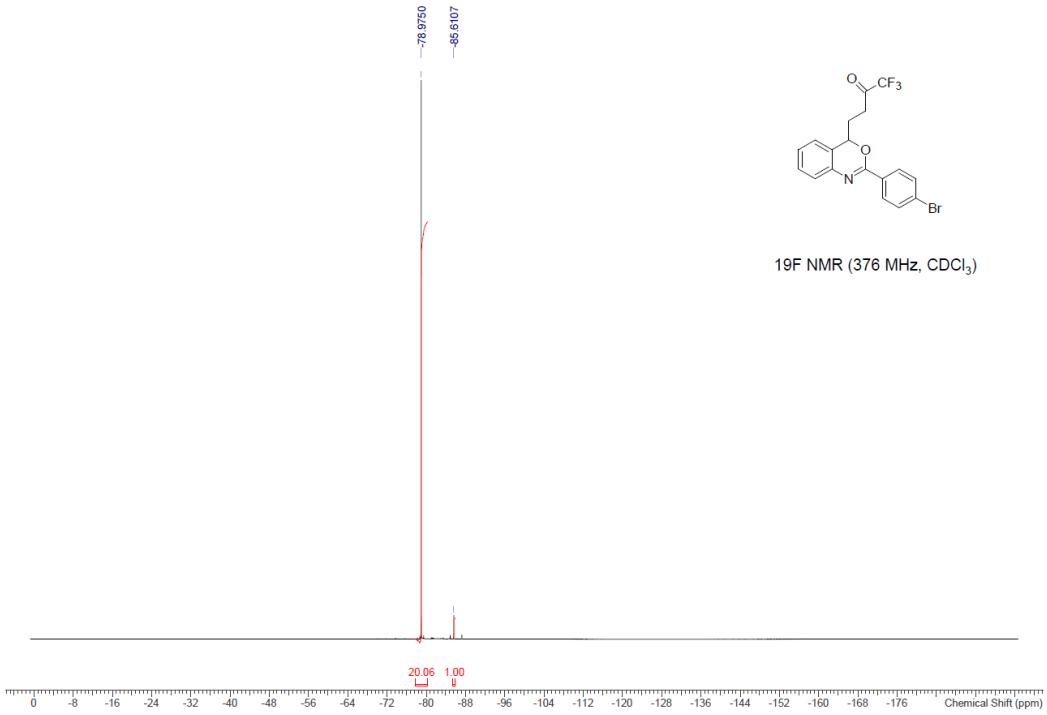


Figure S77. ^{19}F NMR of **7g** (376 MHz, $CDCl_3$)

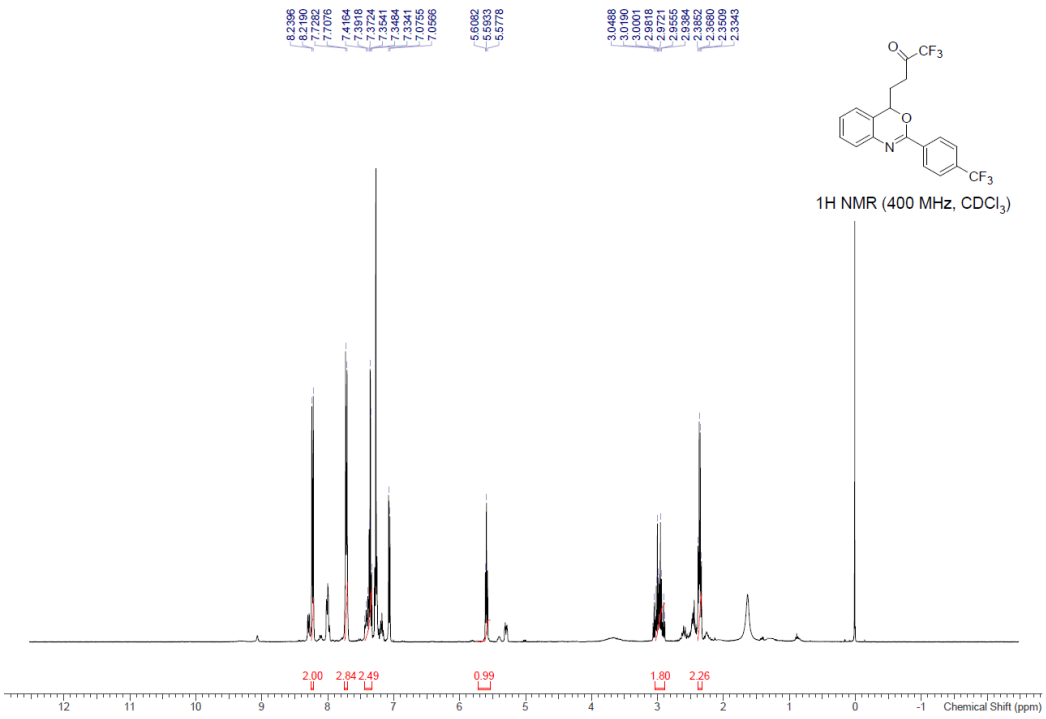


Figure S78.[1]H NMR of **7h** (400 MHz, $CDCl_3$)

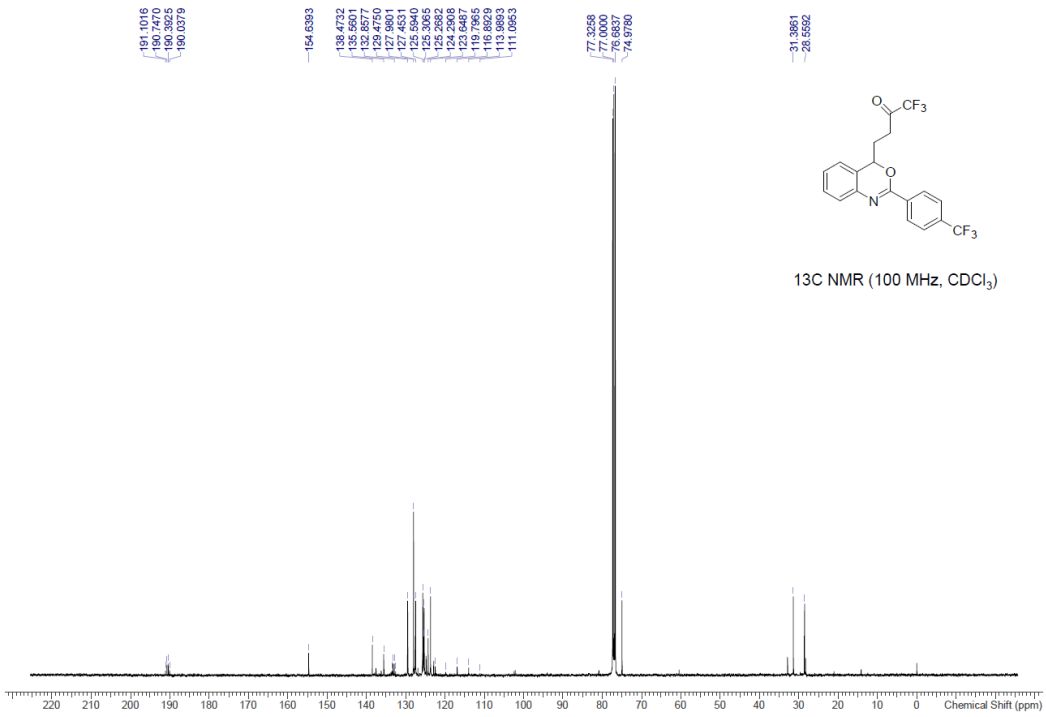


Figure S79. [13]C NMR of **7h** (100 MHz, $CDCl_3$)

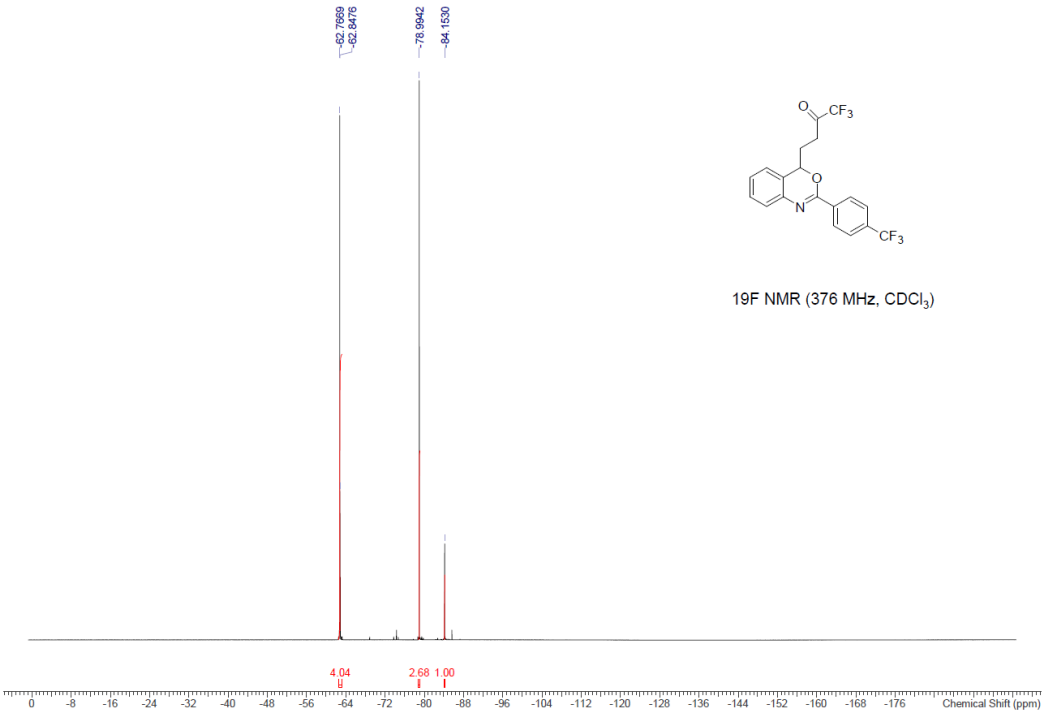


Figure S80. ^{19}F NMR of **7h** (376 MHz, $CDCl_3$)

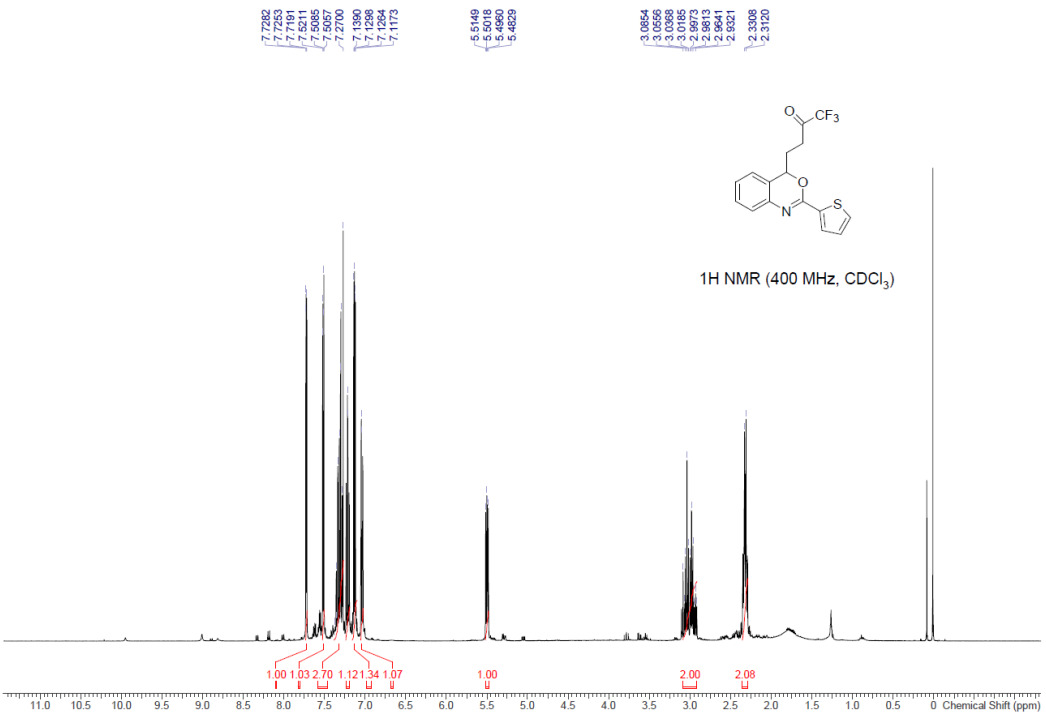


Figure S81. ^{1}H NMR of **7j** (400 MHz, $CDCl_3$)

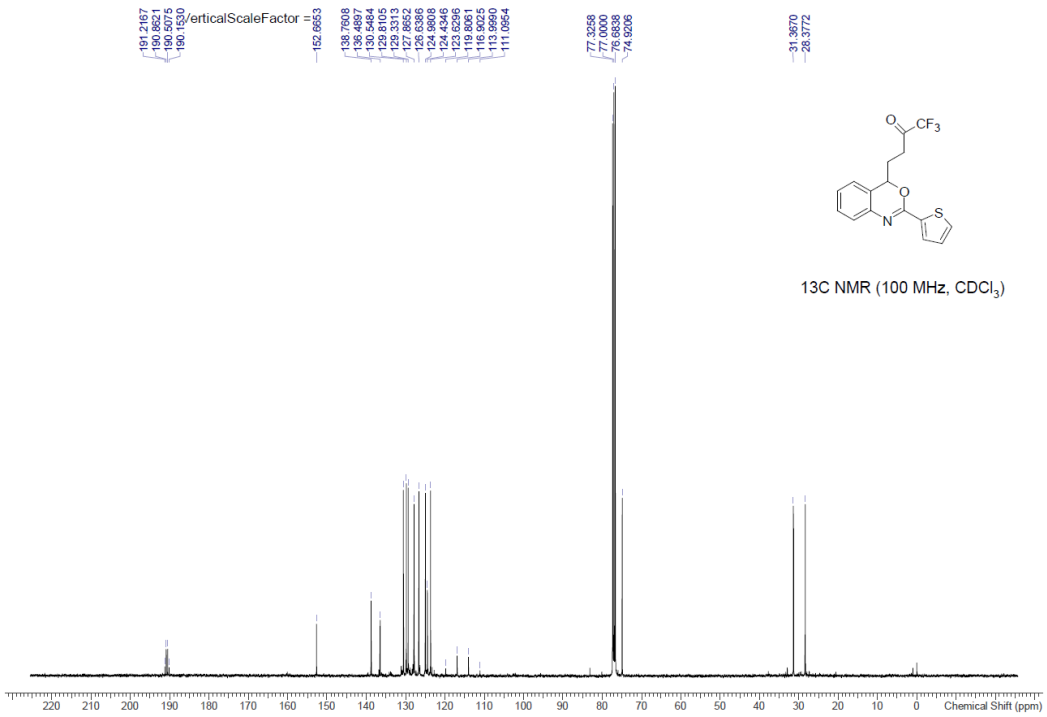


Figure S82. ^{13}C NMR of **7j** (100 MHz, $CDCl_3$)

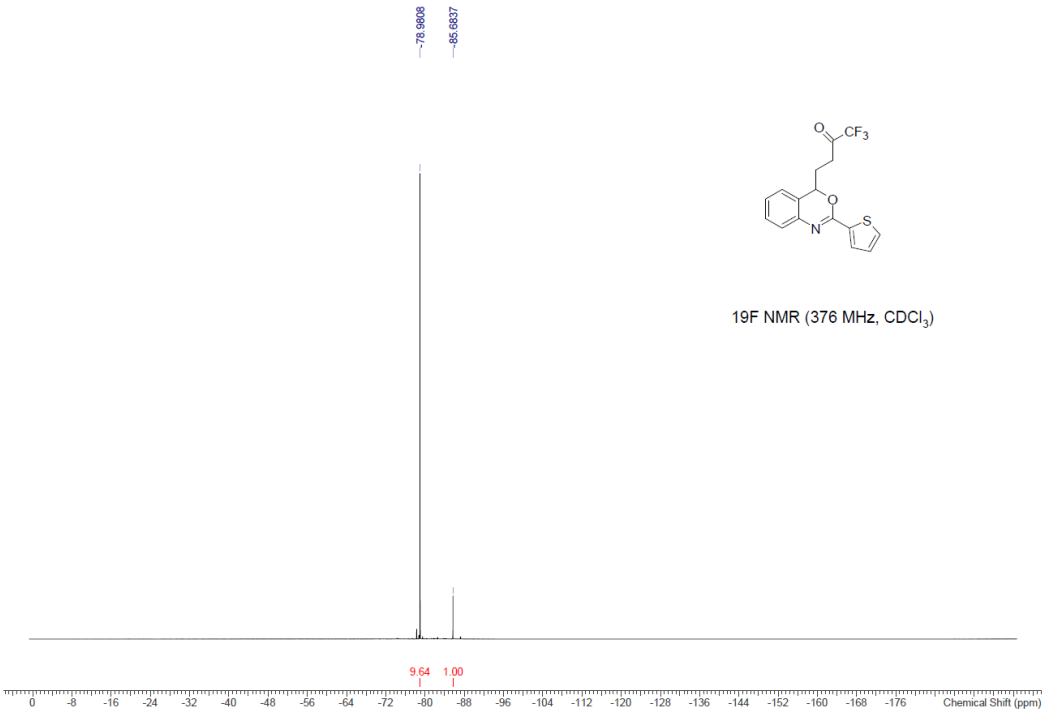


Figure S83. ^{19}F NMR of **7j** (376 MHz, $CDCl_3$)

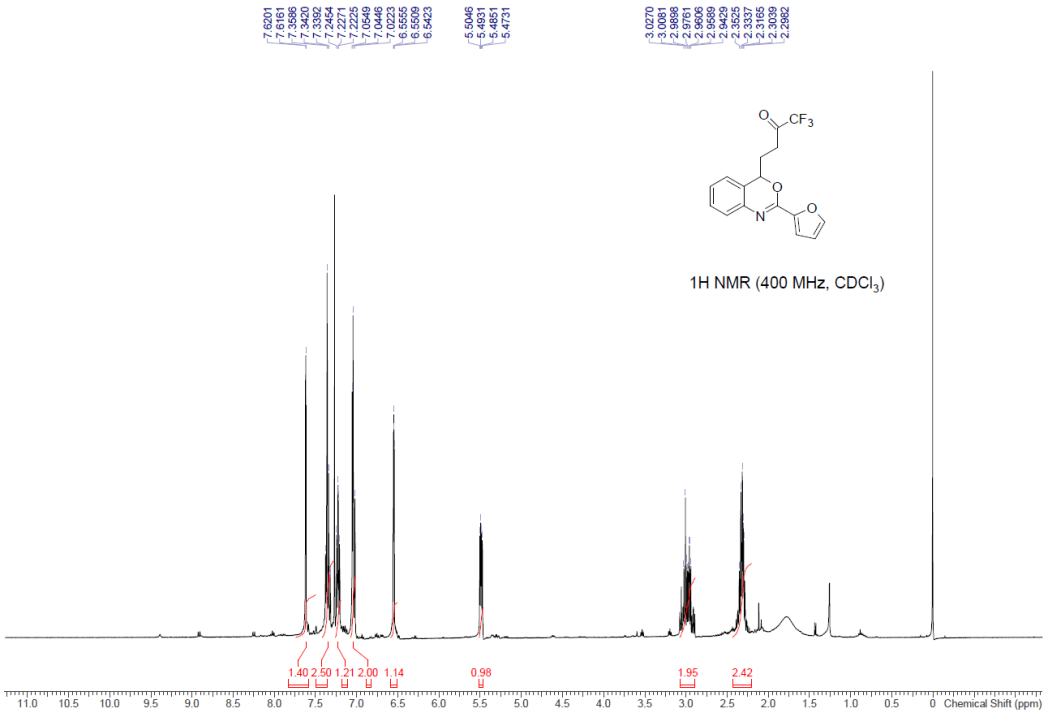


Figure S84. ^{1}H NMR of **7k** (400 MHz, $CDCl_3$)

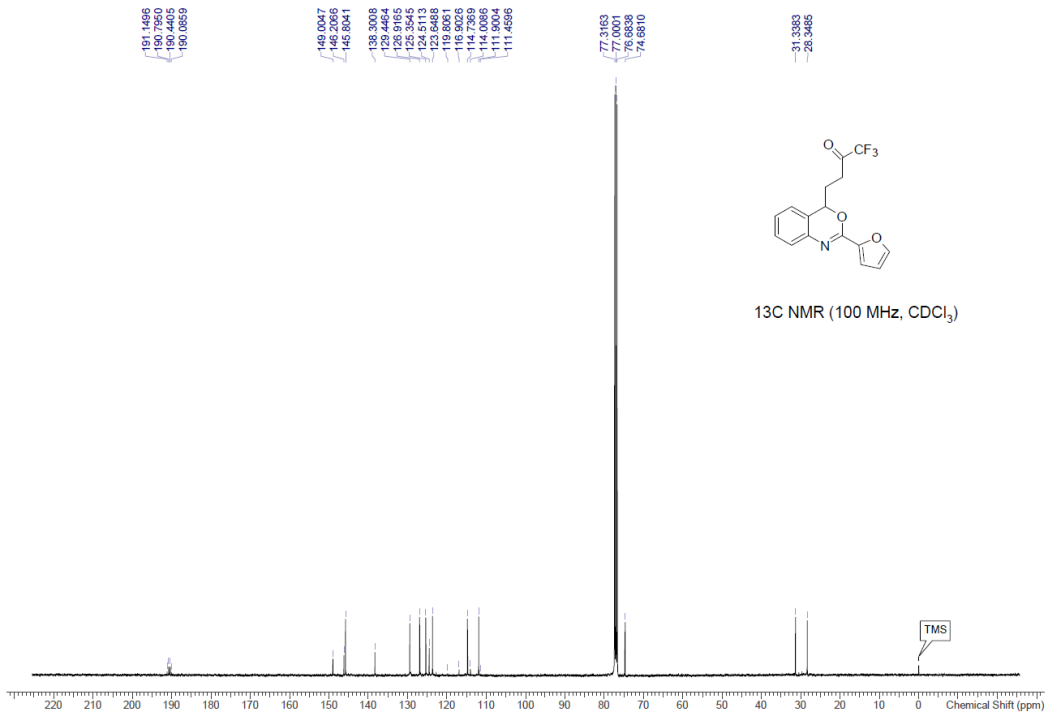


Figure S85. ^{13}C NMR of **7k** (100 MHz, $CDCl_3$)

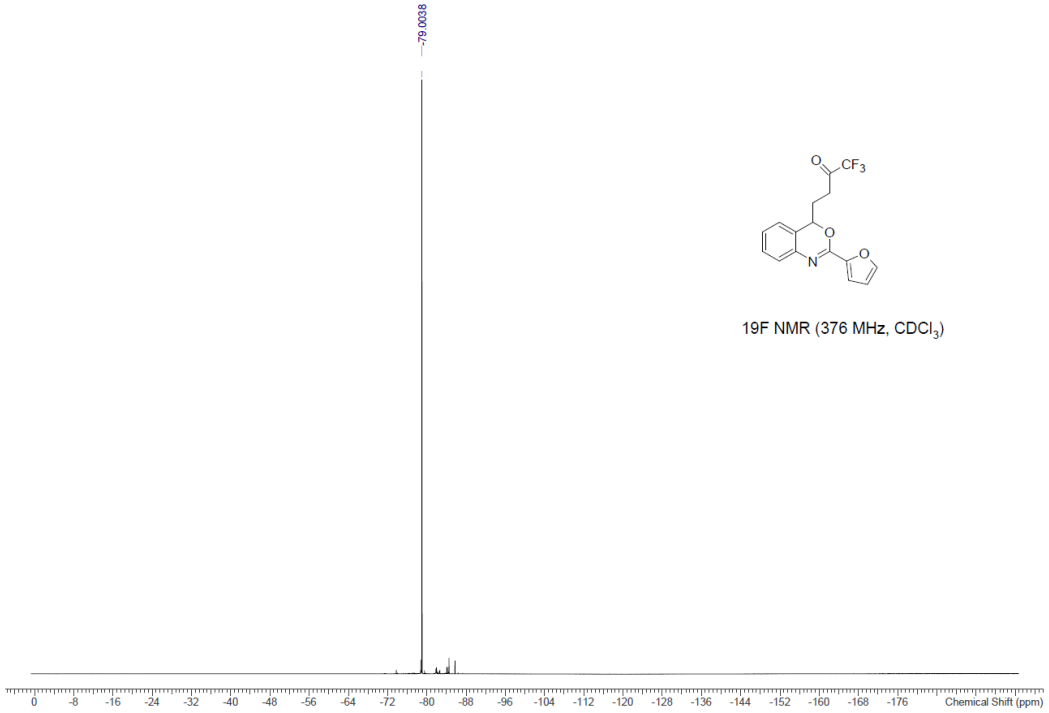


Figure S86. ^{19}F NMR of **7k** (376 MHz, $CDCl_3$)

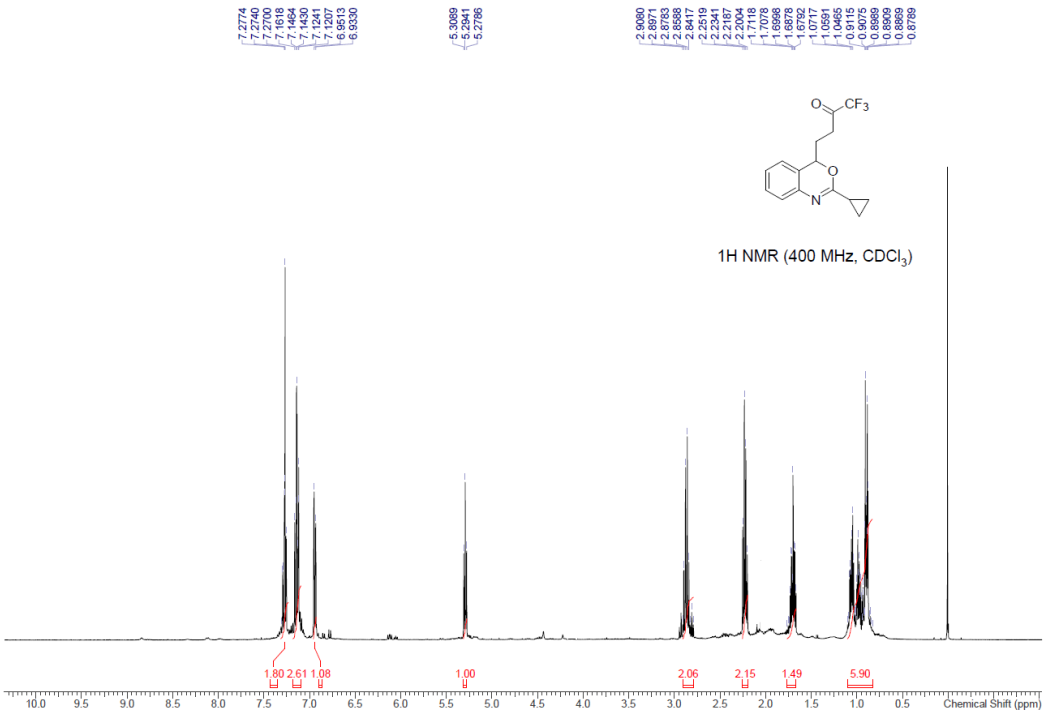


Figure S87. ^{1}H NMR of **7l** (400 MHz, $CDCl_3$)

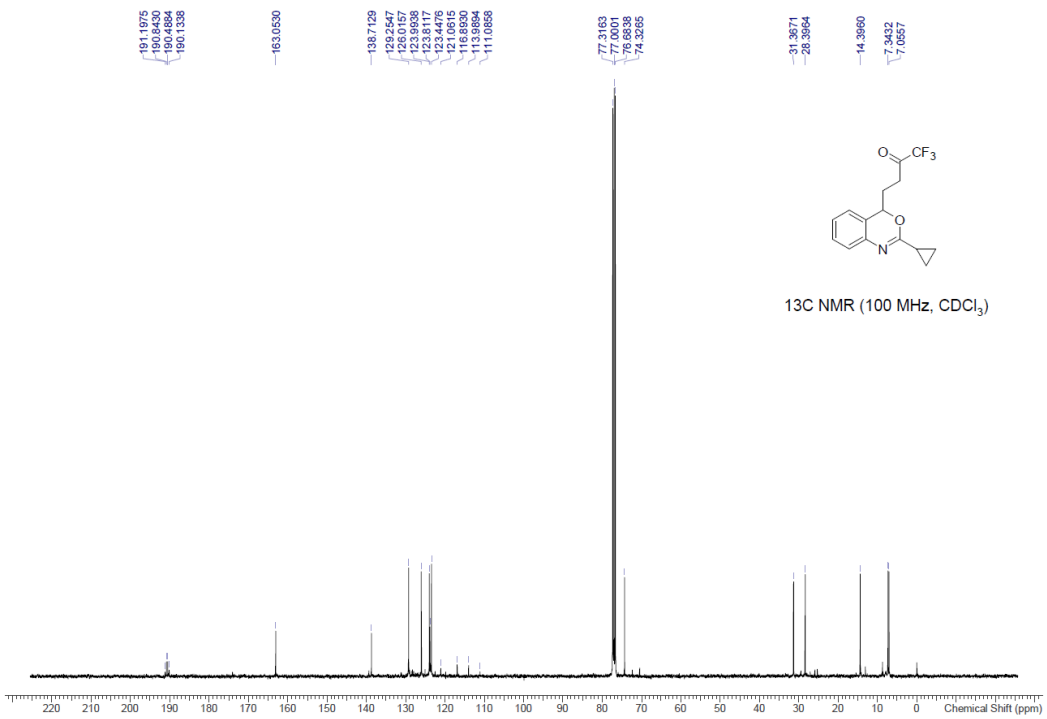


Figure S88. ^{13}C NMR of **7l** (100 MHz, $CDCl_3$)

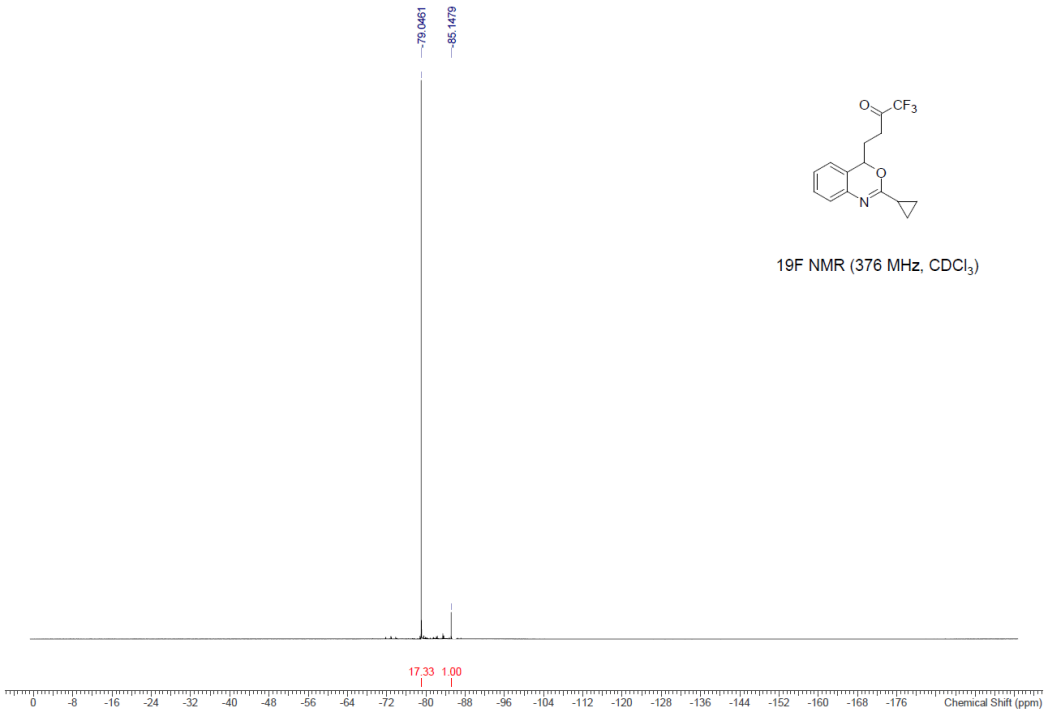


Figure S89. ^{19}F NMR of **7l** (376 MHz, $CDCl_3$)

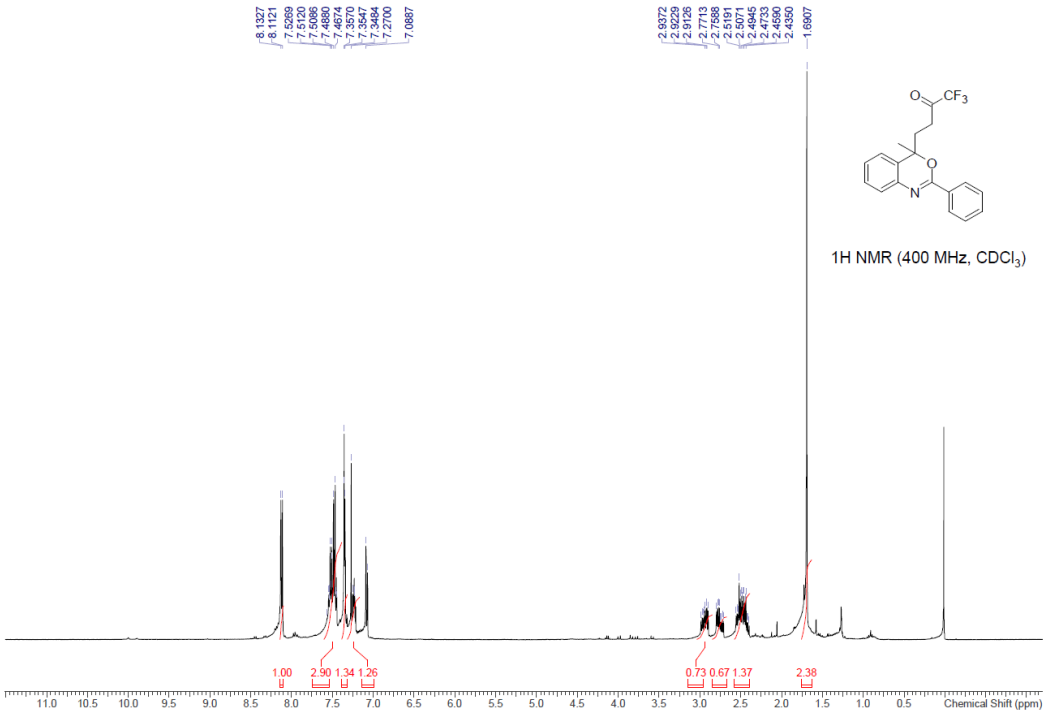


Figure S90. ^{1}H NMR of **7m** (400 MHz, $CDCl_3$)

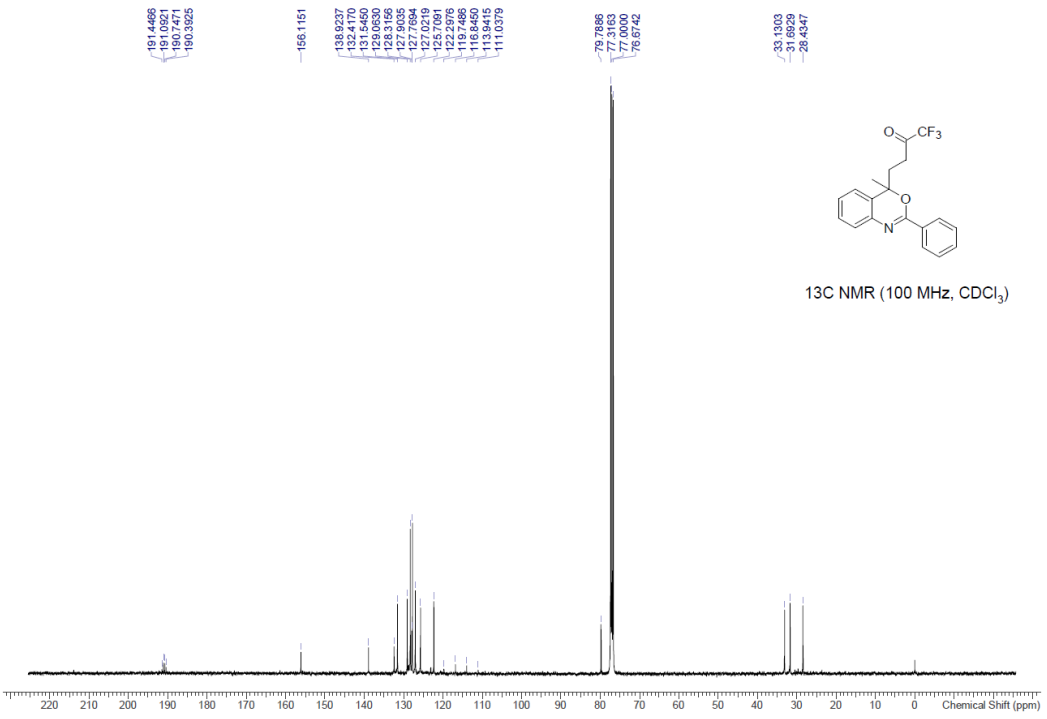


Figure S91. ^{13}C NMR of **7m** (100 MHz, $CDCl_3$)

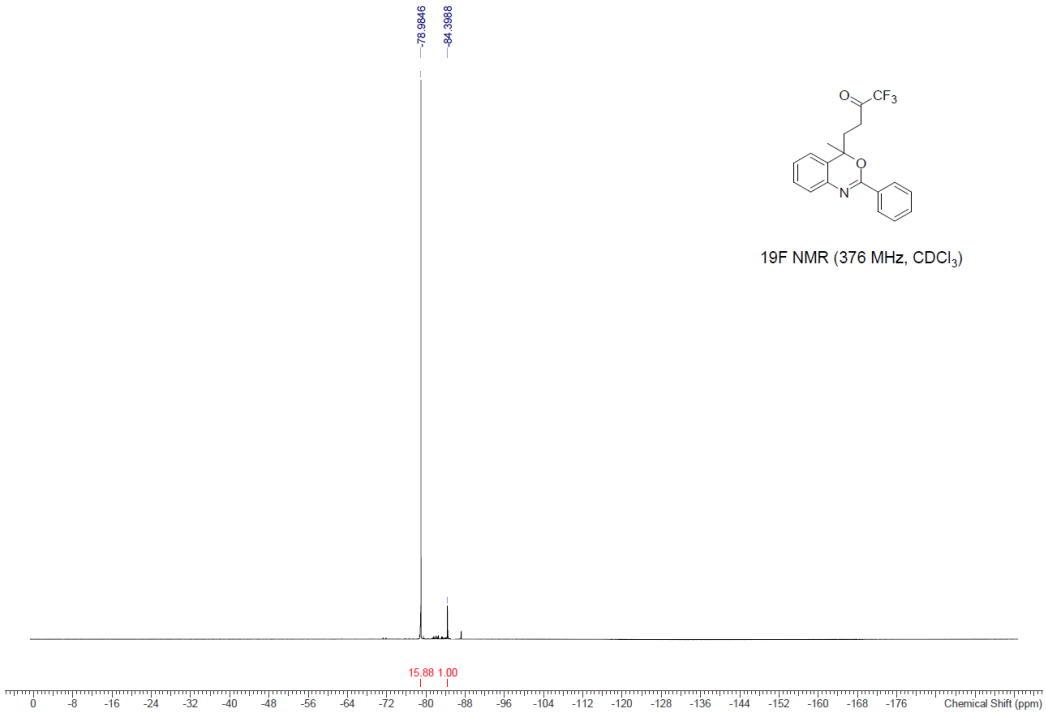


Figure S92. ^{19}F NMR of **7m** (376 MHz, $CDCl_3$)

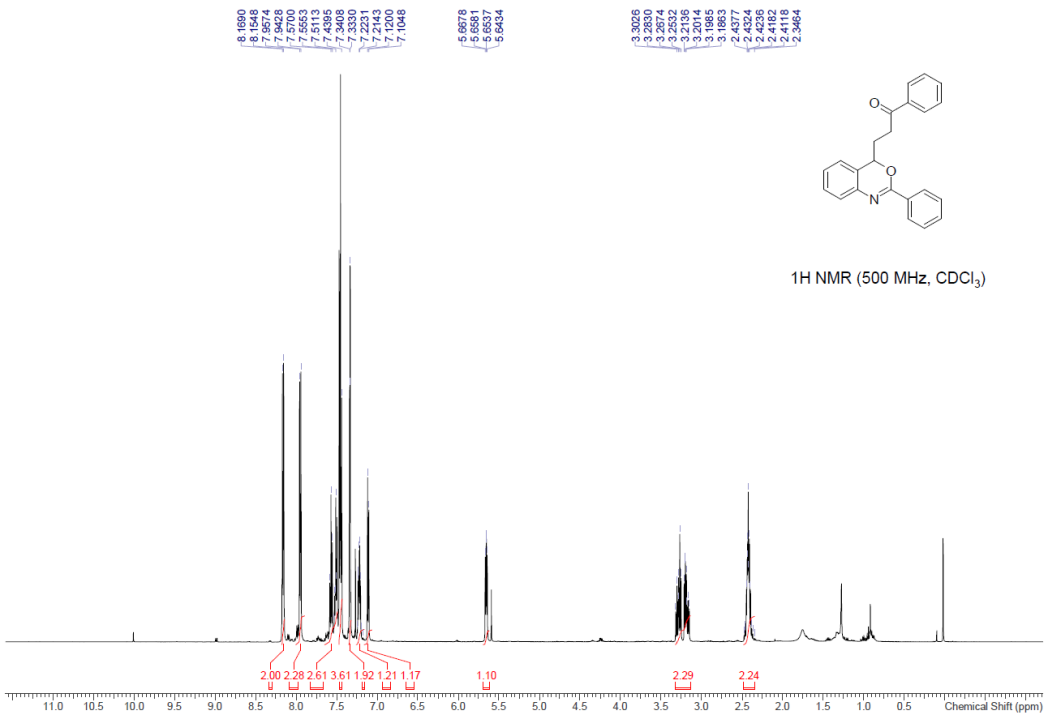


Figure S93. ^{1}H NMR of **7n** (500 MHz, $CDCl_3$)

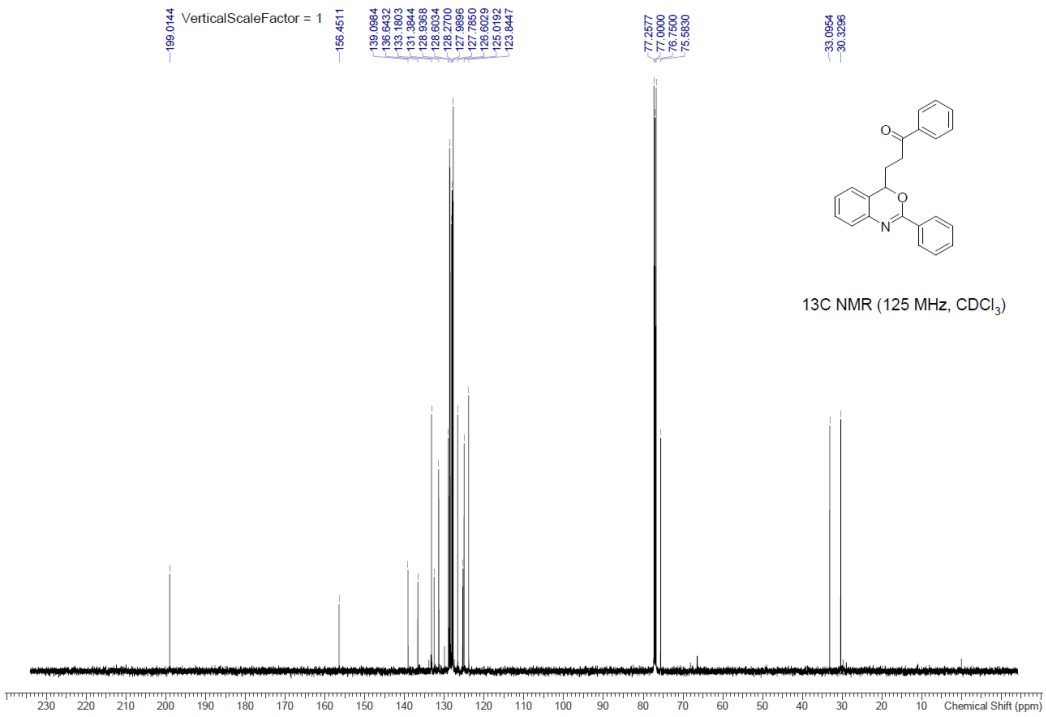


Figure S94. ^{13}C NMR of **7n** (125 MHz, $CDCl_3$)

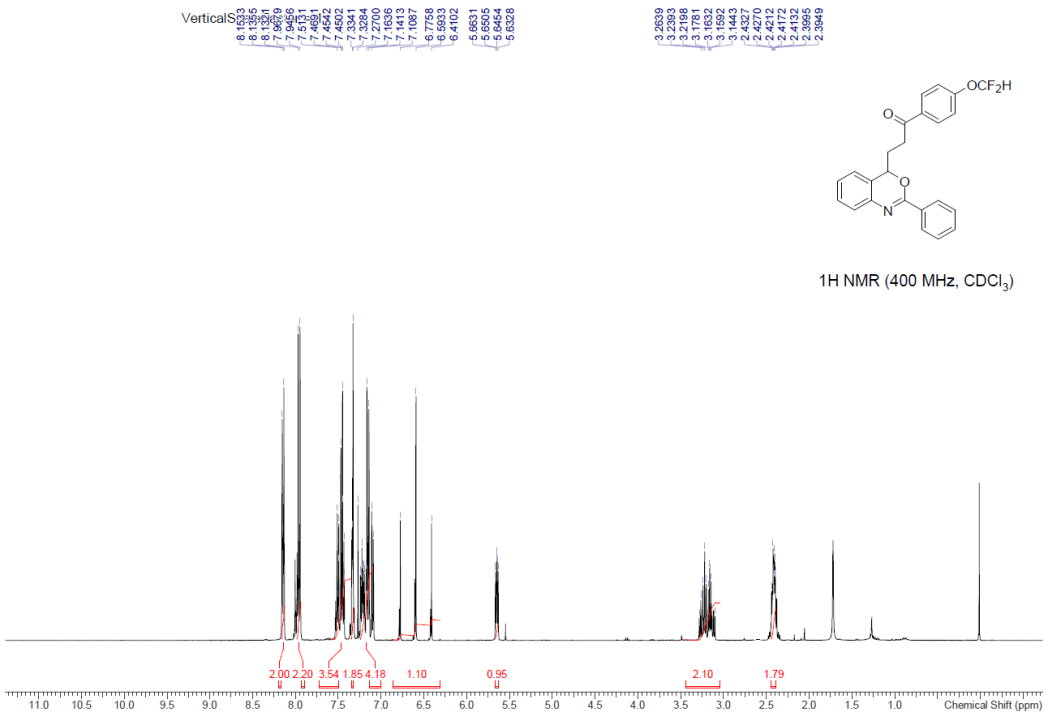


Figure S95. ^{1}H NMR of **7o** (400 MHz, $CDCl_3$)

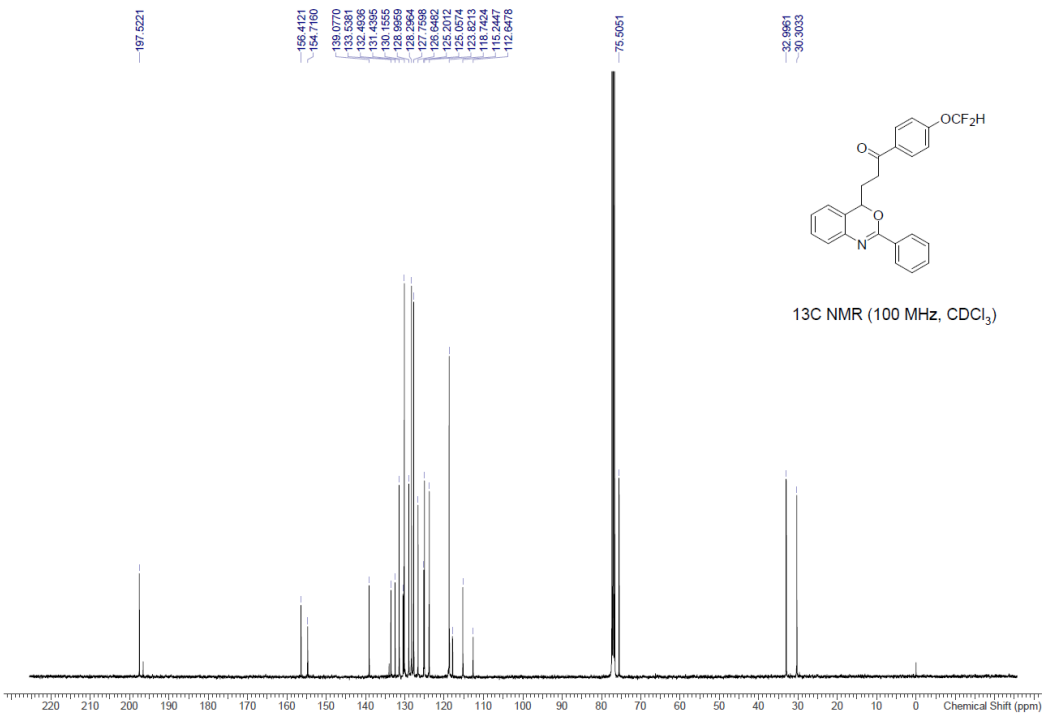


Figure S96. ^{13}C NMR of **70** (100 MHz, $CDCl_3$)

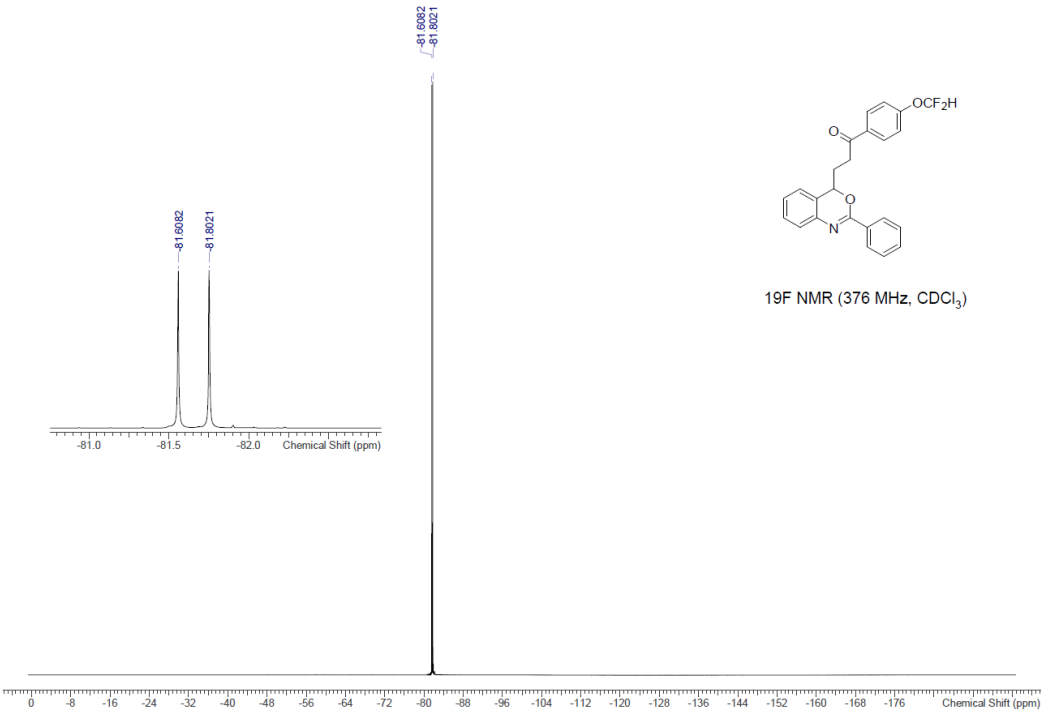


Figure S97. ^{19}F NMR of **7o** (376 MHz, $CDCl_3$)

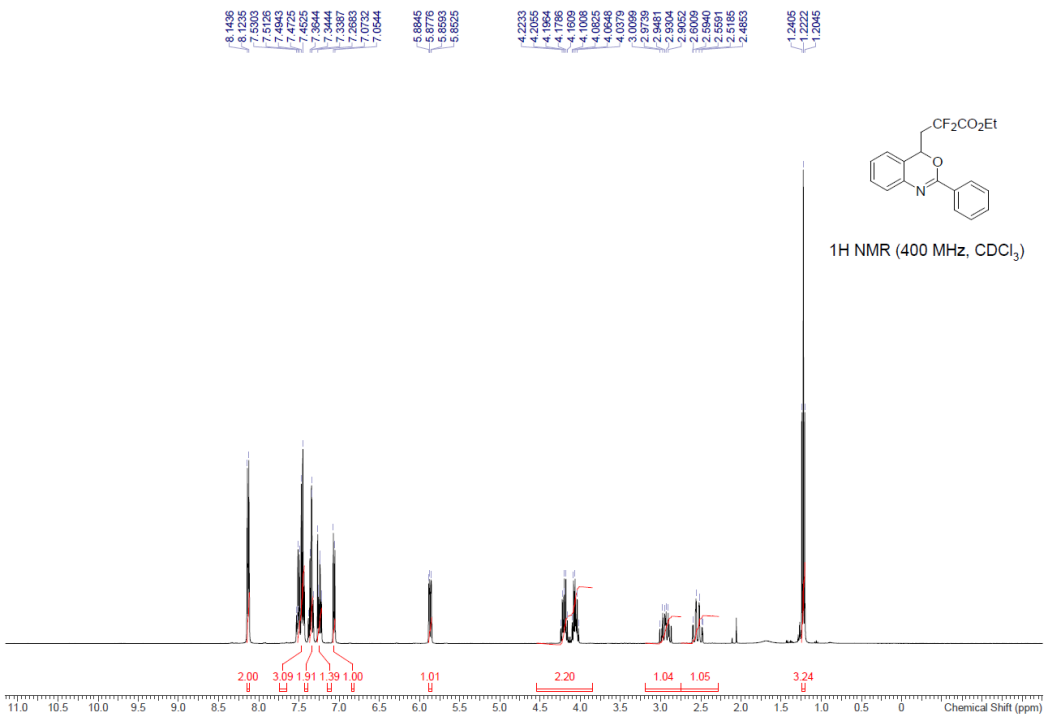


Figure S98. ^{1}H NMR of **7p** (400 MHz, $CDCl_3$)

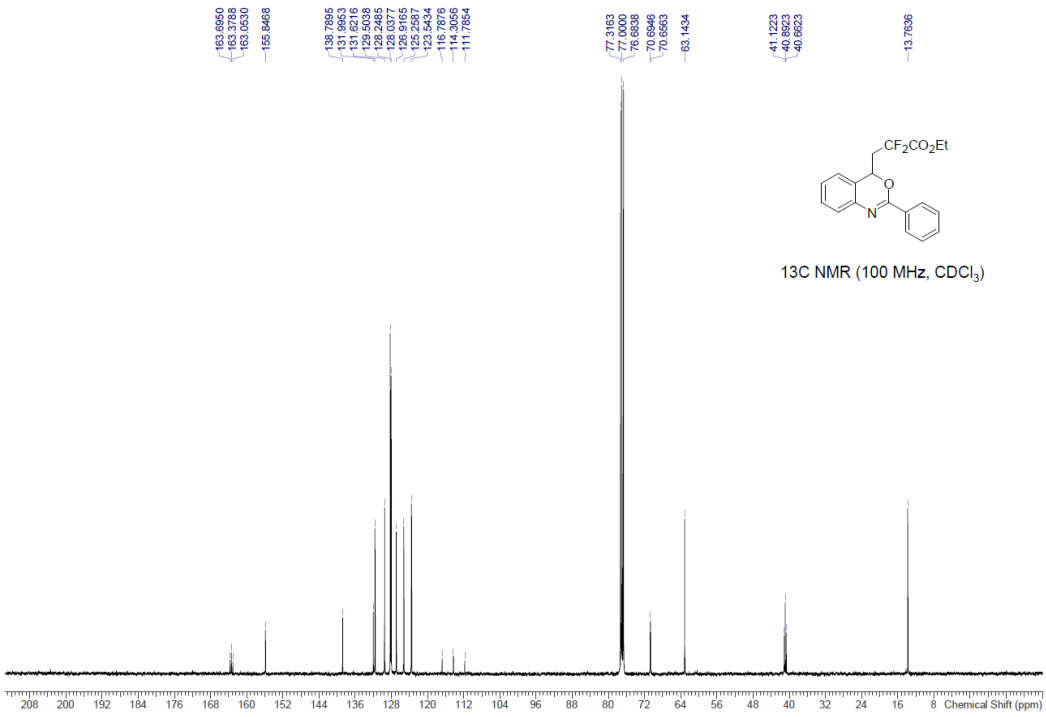


Figure S99. ^{13}C NMR of **7p** (100 MHz, $CDCl_3$)

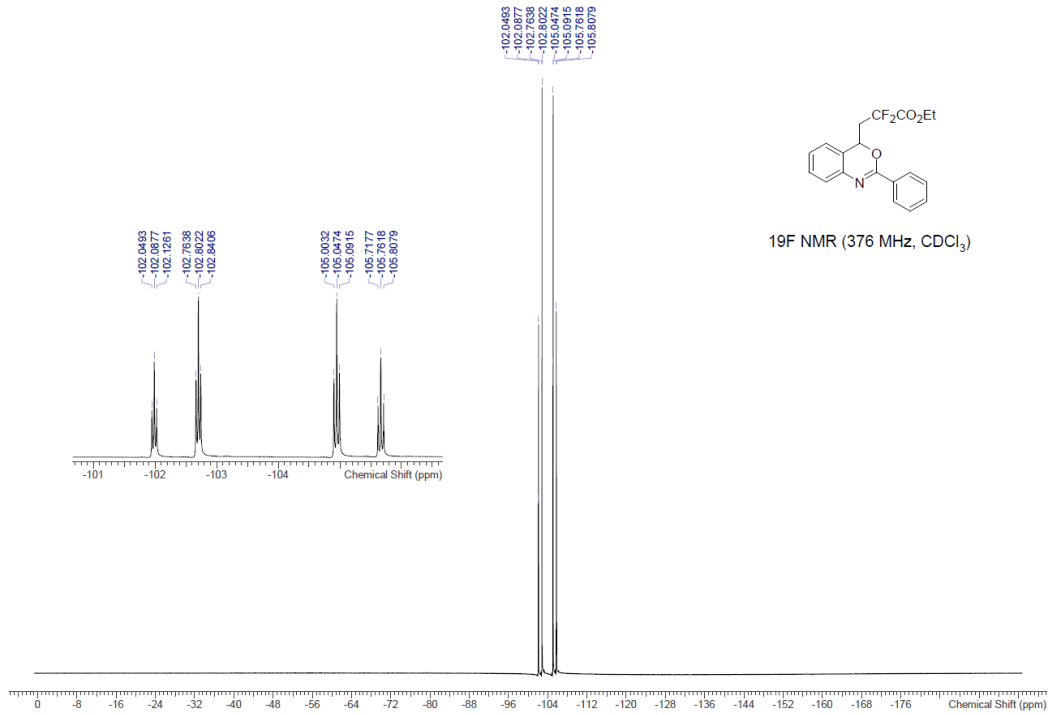


Figure S100. ^{19}F NMR of **7p** (376 MHz, $CDCl_3$)

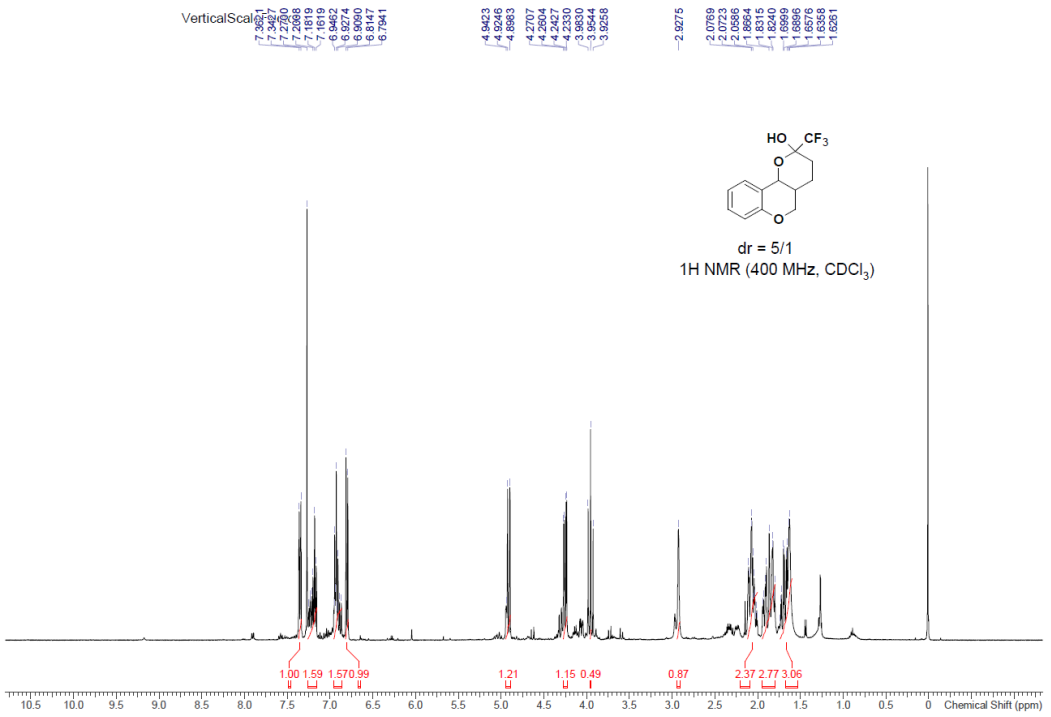


Figure S101. ^{1}H NMR of **10** (400 MHz, $CDCl_3$)

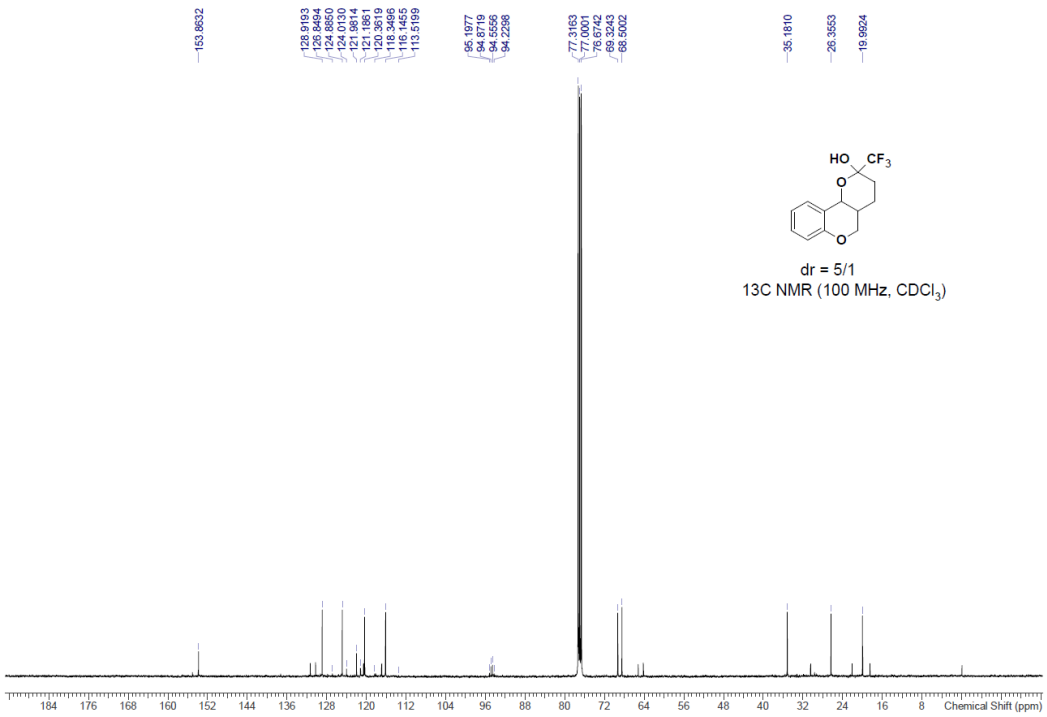


Figure S102. ^{13}C NMR of **10** (100 MHz, $CDCl_3$)

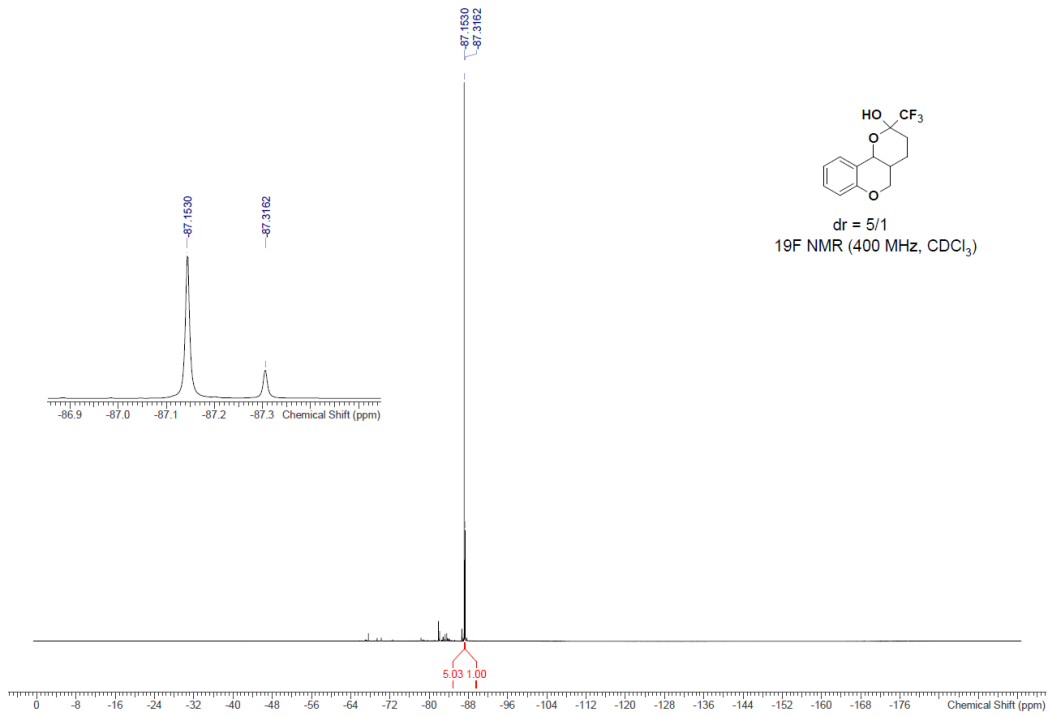


Figure S103. ^{19}F NMR of **10** (376 MHz, $CDCl_3$)

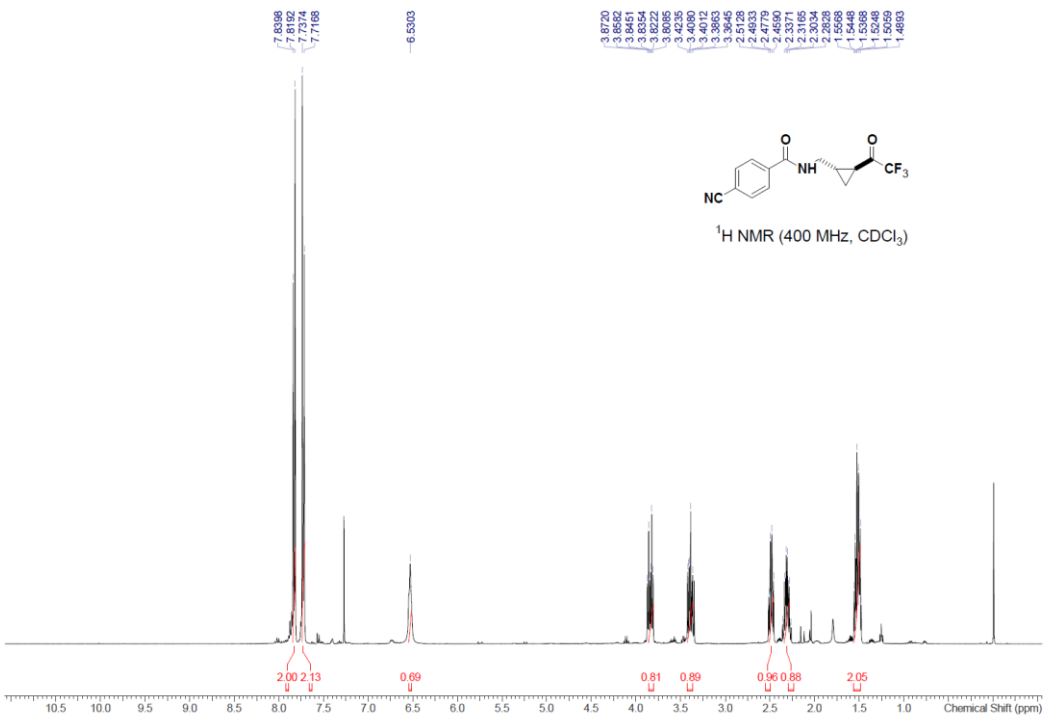


Figure S104. ^{1}H NMR of trans-**11** (400 MHz, $CDCl_3$)

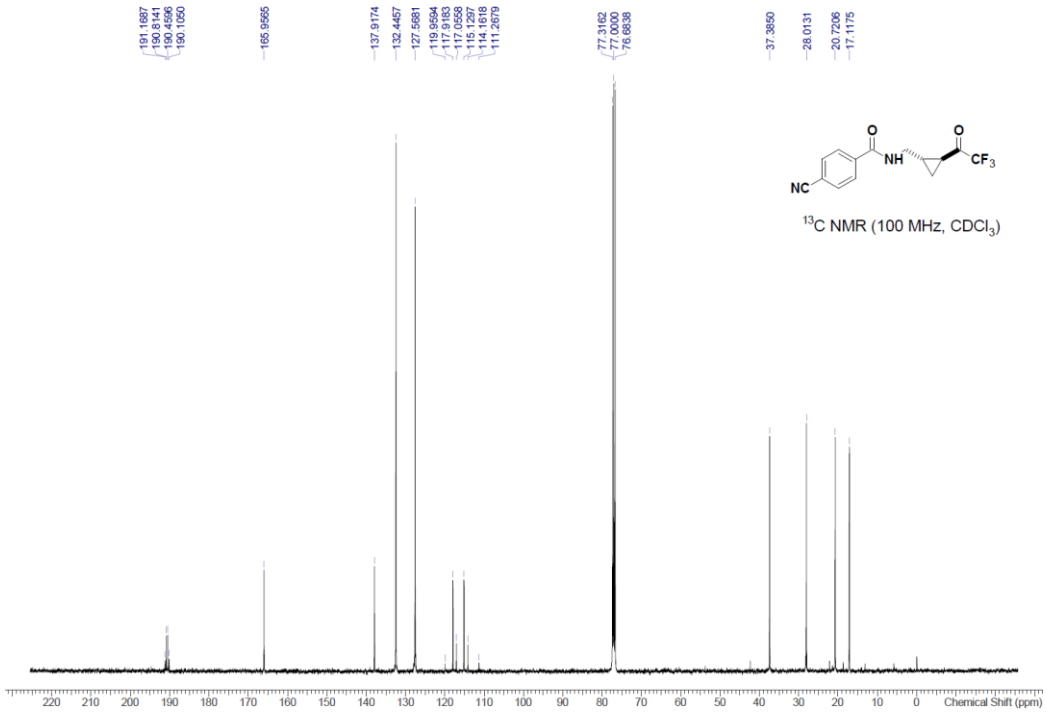


Figure S105. ^{13}C NMR of trans-**11** (100 MHz, $CDCl_3$)

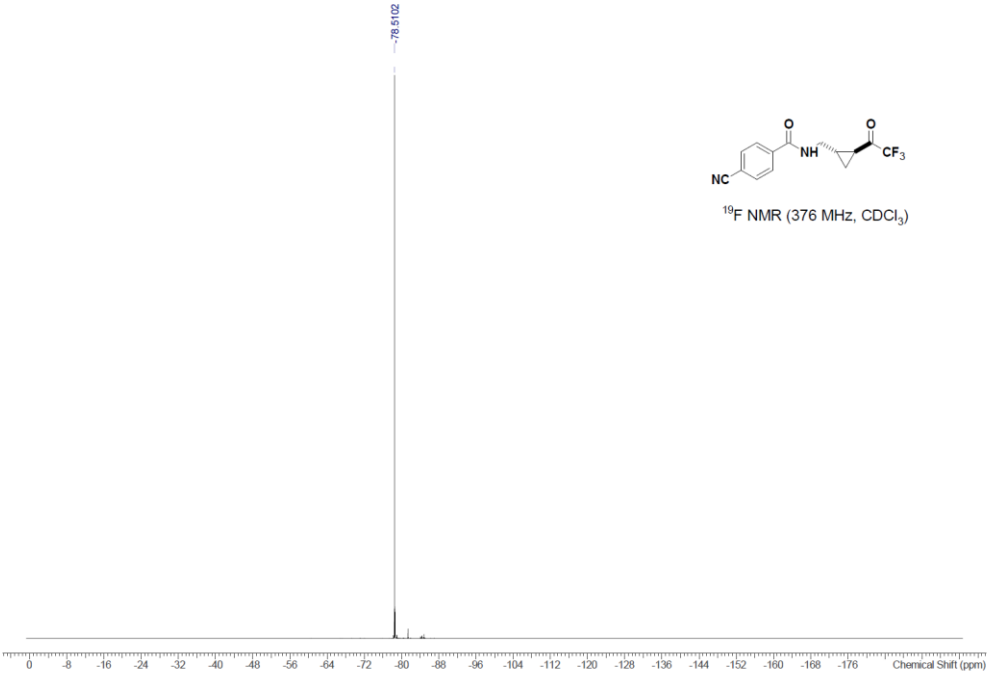


Figure S106. ^{19}F NMR of trans-**11** (376 MHz, $CDCl_3$)

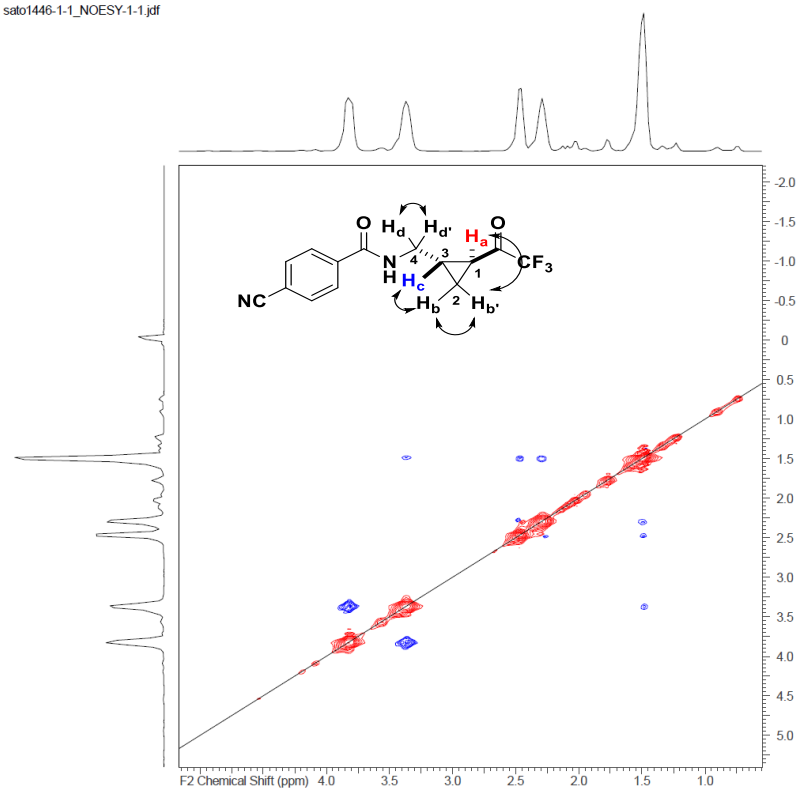


Figure S107. NOESY of trans-**11** (400 MHz, $CDCl_3$)

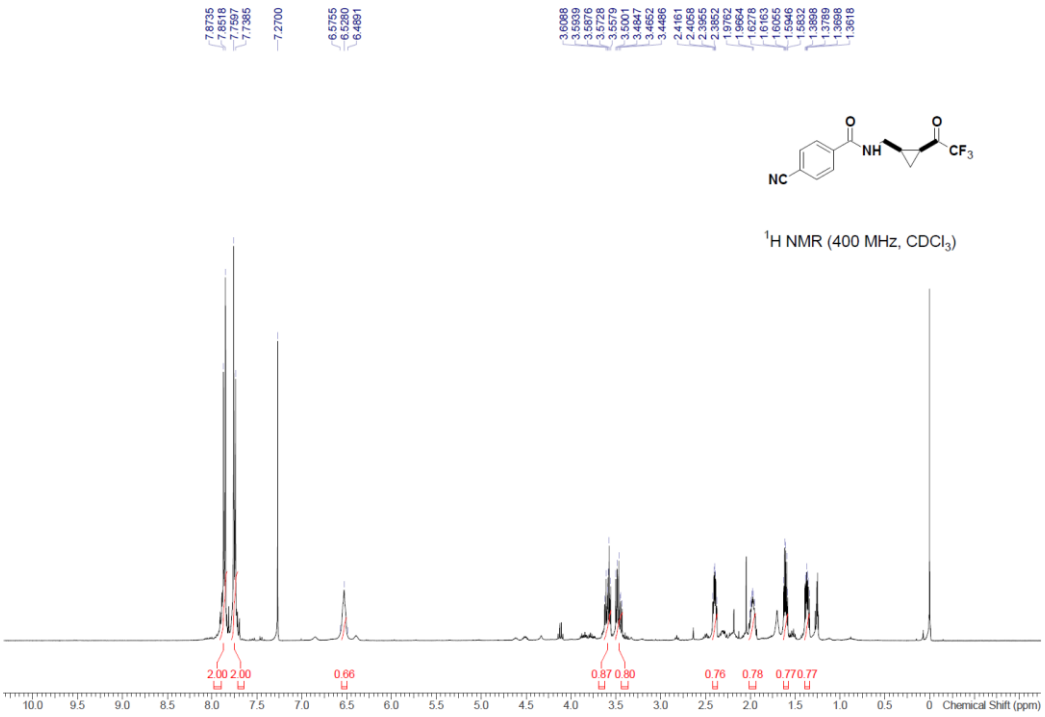


Figure S108. ^{1}H NMR of cis-**11** (400 MHz, $CDCl_3$)

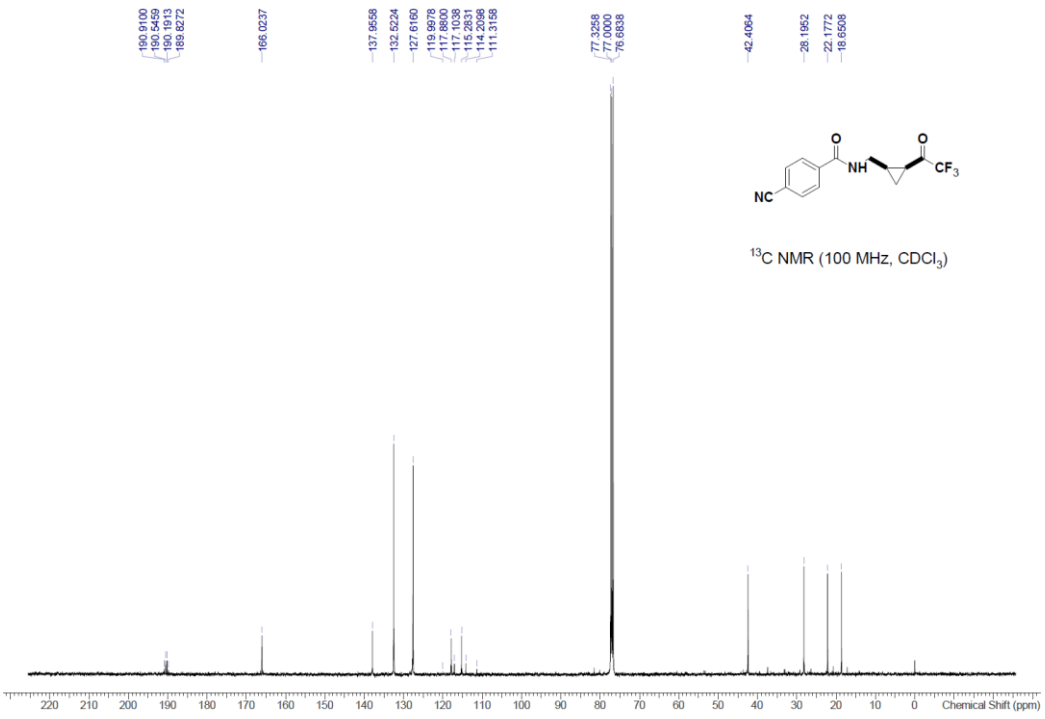


Figure S109. ^{13}C NMR of cis-**11** (100 MHz, $CDCl_3$)

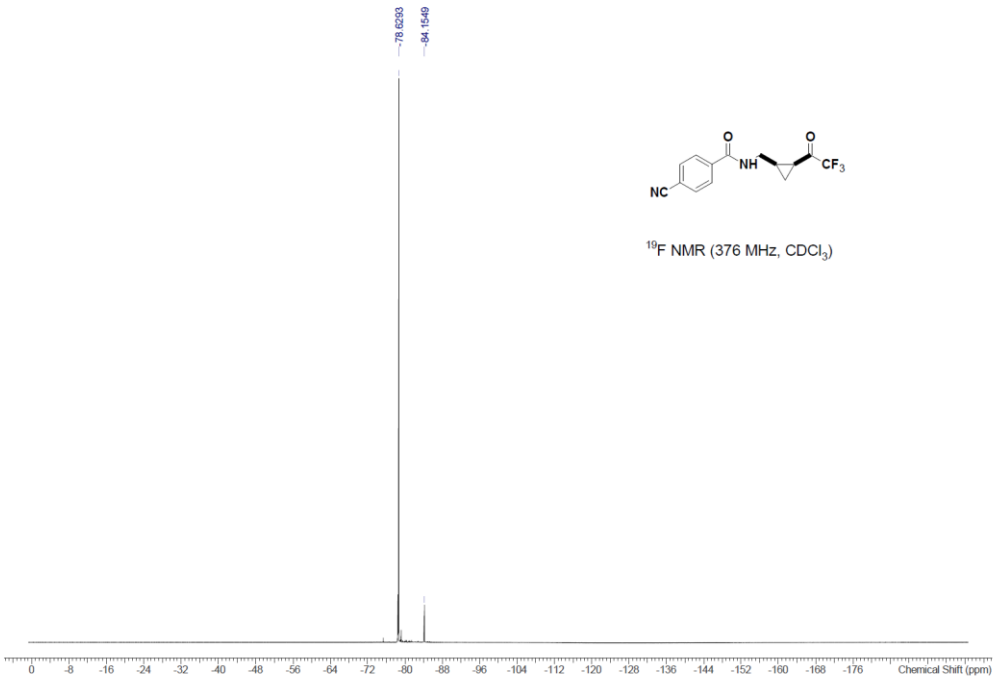


Figure S110. ^{19}F NMR of cis-**11** (376 MHz, $CDCl_3$)

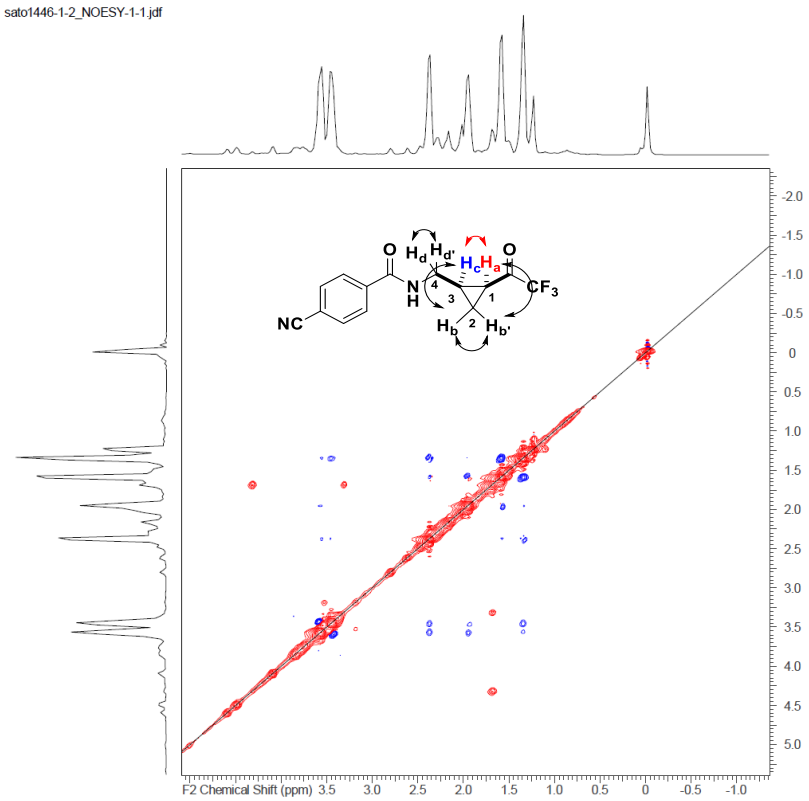


Figure S111. NOESY of cis-**11** (400 MHz, $CDCl_3$)

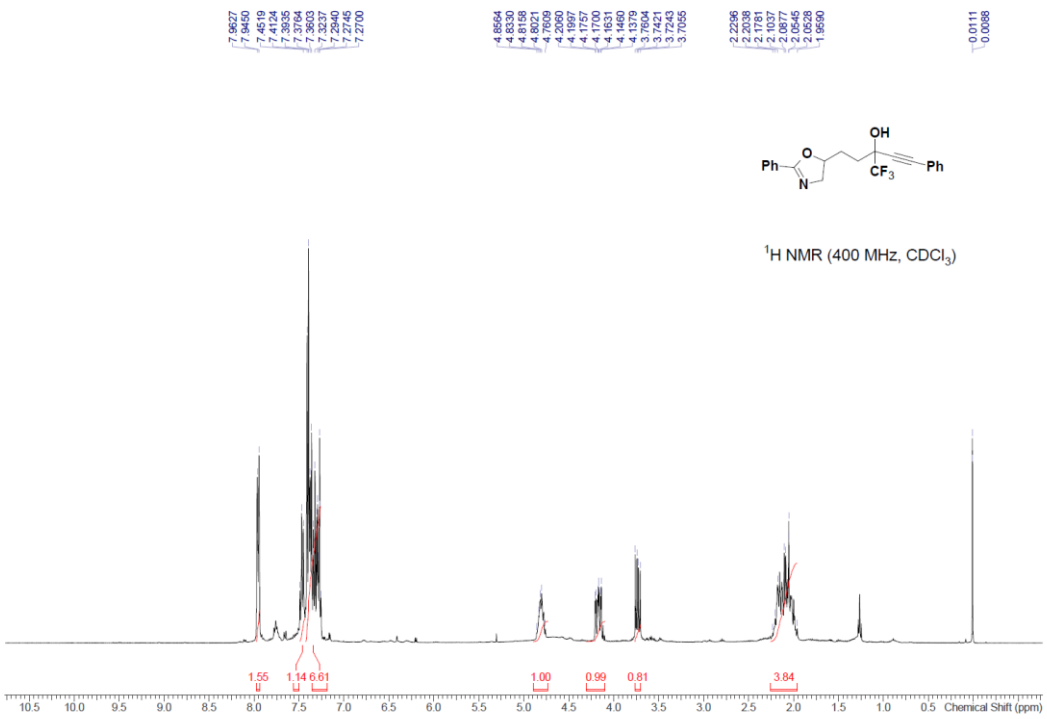


Figure S112. ^{1}H NMR of **12** (400 MHz, $CDCl_3$)

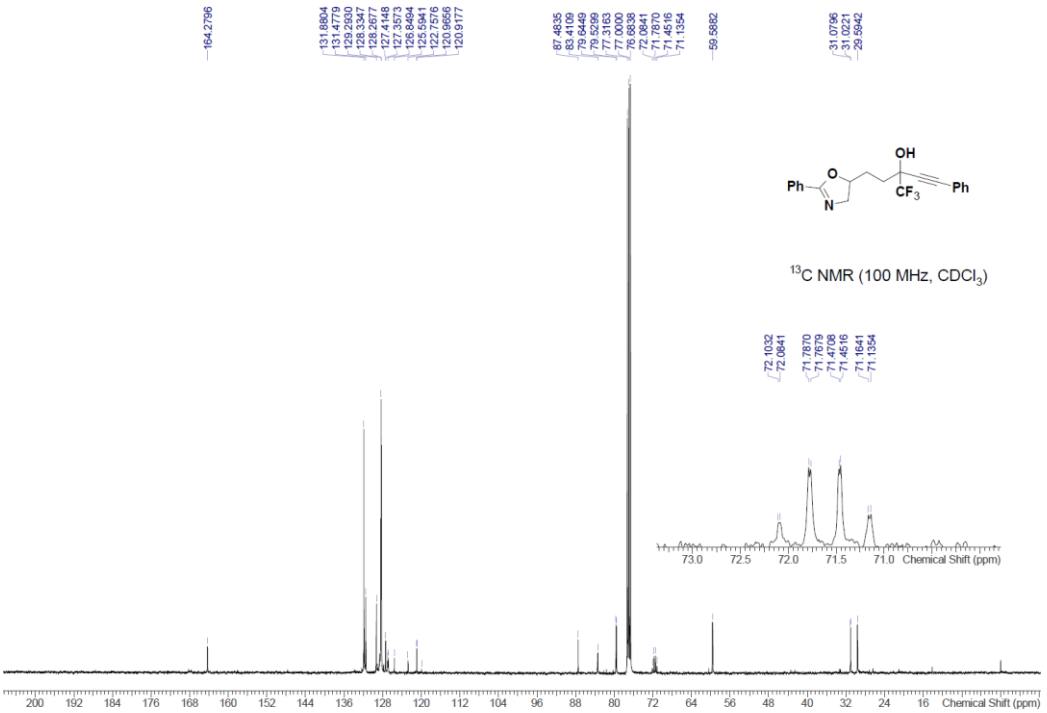


Figure S113. ^{13}C NMR of **12** (100 MHz, $CDCl_3$)

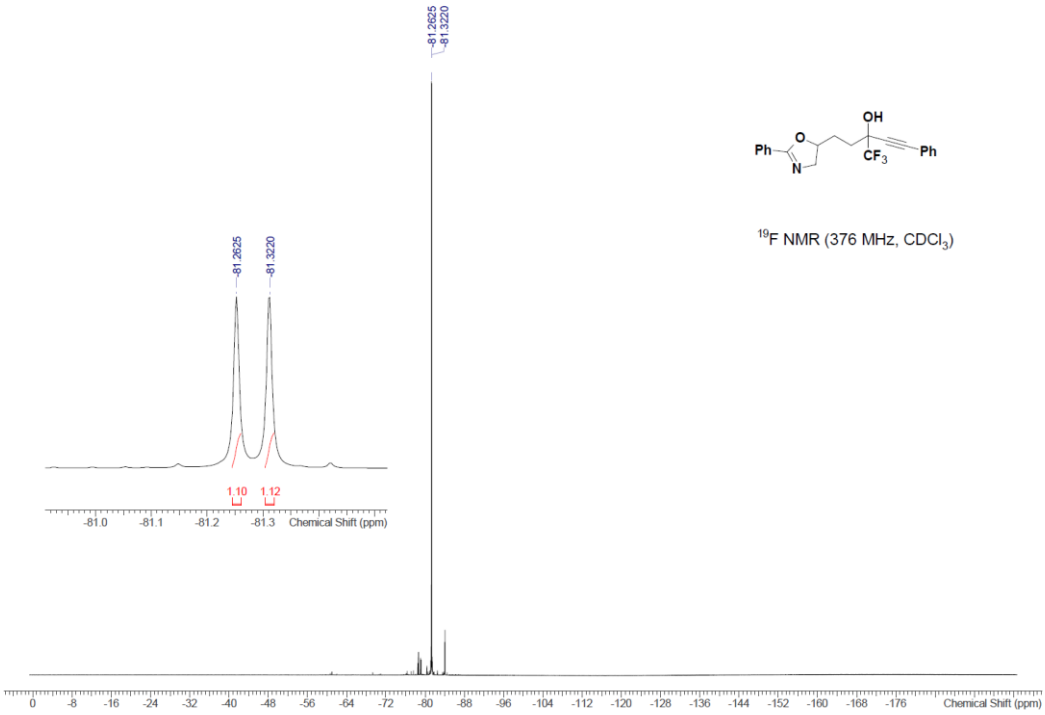


Figure S114. ^{19}F NMR of **12** (376 MHz, $CDCl_3$)