Supplementary Information

Divergent Dehydroxyfluorination and Carbonation of Alcohols with Trifluoromethyl Trifluoromethanesulfonate

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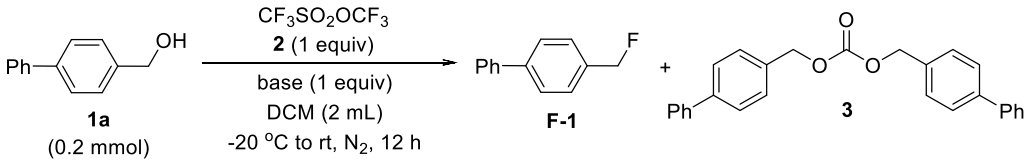
1. General information.

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, the NMR spectra were recorded in $CDCl_3$ or CD_3CN on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm) for ^1H NMR and $PhOCF_3$ (-58.0 ppm) or $PhCF_3$ (-63.0 ppm) for ^{19}F NMR. The HPLC experiments were conducted on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of products were determined by using the corresponding pure compounds as the external standards, respectively. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points of the solid products were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. $CF_3SO_3CF_3$ was prepared according to the literature.[1] Solvents were dried before use according to the literature.[2] Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

2. Screening the optimal reaction conditions for dehydroxyfluorination of 4-biphenylmethanol (1a) with $CF_3SO_2OCF_3$ (2).

Table S1. Dehydroxyfluorination of **1a** with **2** in the presence of different bases.

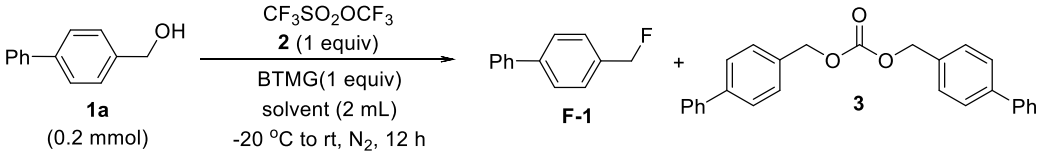


Entry [a]	Base	Yield (**F-1**, %)	Yield (**3**, %)
1	Et_3N	14	50
2 [b]	Et_3N	trace	40
3	propan-2-amine	0	0
4	DBU	10	40
5	DABCO	0	57
6	2,6-di-*tert*-butylpyridine	0	35
7	2,4-lutidine	< 1	38
8	DMF	< 1	0
9	MTBD	15	20

10	DMAP	trace	69
11 [b]	DMAP	1	61
12 [c]	DMAP	trace	72
13 [d]	DMAP	trace	37
14 [c,d]	DMAP	1	70
15	$^{i}Pr_2NEt$	25	27
16	DMAc	0	0
17	pyridine	0	60
18	**BTMG**	**61**	**22**
19	none	0	0

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), base (0.2 mmol), CH_2Cl_2 (2 mL), -20 °C to r.t., N_2, 12 h. Yields were determined by HPLC (λ = 249 nm, water/methanol = 10/90 (v/v)) using **F-1** (t_R = 5.26 min) and **3** (t_R = 11.96 min) as external standards. Abbreviations: DBU = 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepine, DABCO = 1,4-diazabicyclo[2.2.2]octane, DMF = *N*,*N*-dimethylformamide, MTBD = 1-methyl-1,3,4,6,7,8-hexahydro-*2H*-pyrimido[1,2-*a*]pyrimidine, DMAP = 4-dimethylaminopyridine, $^{i}Pr_2NEt$ = *N*-ethyl-*N*-isopropylpropan-2-amine, DMAc = *N*,*N*-dimethylacetamide, BTMG = 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine. [b] -20 °C to 40 °C. [c] 24 h. [d] -20 °C to 80 °C.

Table S2. Dehydroxyfluorination of **1a** with **2** in different solvents.

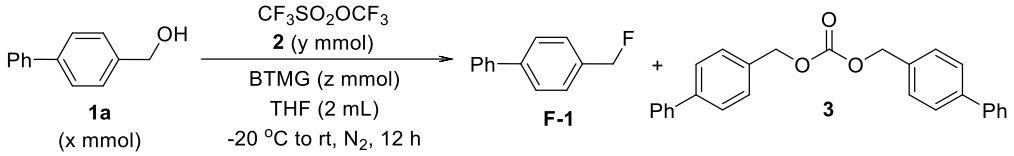


Entry [a]	Solvent	Yield (**F-1**, %)	Yield (**3**, %)
1	DMF	4	27
2	**THF**	**65**	**19**
3	MeCN	29	18
4	toluene	30	10
5	DME	14	10

6	DMSO	trace	7
7	PhCl	52	23
8	1,4-dioxane	59	21
9	*n*-hexane	23	0
10	DMAc	0	27
11	DCM	61	22

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), BTMG (0.2 mmol), solvent (2 mL), -20 °C to r.t., N_2, 12 h. Yields were determined by HPLC (λ = 249 nm, water/methanol = 10/90 (v/v)) using **F-1** (t_R = 5.26 min) and **3** (t_R = 11.96 min) as external standards.

Table S3. Dehydroxyfluorination of **1a** with **2**/BTMG in different reactant ratios.

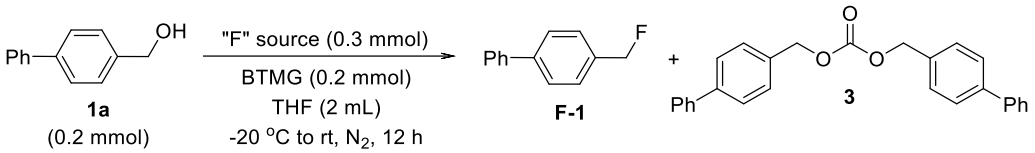


Entry [a]	x : y : z	Yield (**F-1**, %)	Yield (**3**, %)
1	1 : 0.5 : 1	47	27
2	1 : 0.5 : 1.5	48	22
3	1 : 0.5 : 2	28	17
4	1 : 1 : 1	65	19
5	1 : 1 : 1.5	56	30
6	1 : 1 : 2	58	36
7	1 : 1 : 2.5	57	29
8	1 : 1 : 3	64	22
9	1 : 1.5 : 0.2	3	trace
10	1 : 1.5 : 0.5	13	10
11	**1 : 1.5 : 1**	**71 (67)**	**18**
12 [b]	1 : 1.5 : 1	40	18
13 [c]	1 : 1.5 : 1	45	15
14	1 : 1.5 : 1.5	61	30

[a] Reaction conditions: **1a** (0.2 mmol), **2** (y mmol), BTMG (z mmol), THF (2 mL), -20

°C to r.t., N_2, 12 h. Yields were determined by HPLC (λ = 249 nm, water/methanol = 10/90 (v/v)) using **F-1** (t_R = 5.26 min) and **3** (t_R = 11.96 min) as external standards. Isolated yield is depicted in the parenthesis. [b] -20 °C to 80 °C. [c] Under air.

Table S4. Comparing the dehydroxyfluorination of **1a** with $CF_3SO_2OCF_3$ (**2**) to those with other "F" sources.

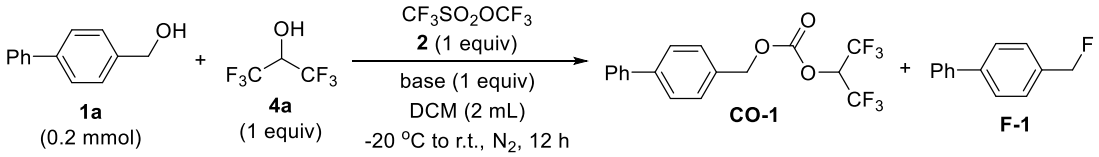


Entry [a]	"F" source	Yield (**F-1**, %)	Yield (**3**, %)
1	**$CF_3SO_2OCF_3$**	**71 (67)**	**18**
2	$CsOCF_3$	28	34
3	$AgOCF_3$	26	39
4	4-Me-$C_6H_4SO_2OCF_3$	14	46
5	$CF_3CF_2CF_2CF_2SO_2F$	40	0

[a] Reaction conditions: **1a** (0.2 mmol), "F" source (0.3 mmol), BTMG (0.2 mmol), THF (2 mL), -20 °C to r.t., N_2, 12 h. Yields were determined by HPLC (λ = 249 nm, water /methanol = 10/90 (v/v)) using **F-1** (t_R = 5.26 min) and **3** (t_R = 11.96 min) as external standards. Isolated yield is depicted in the parenthesis.

3. Screening the optimal reaction conditions for asymmetric carbonation of 4-biphenylmethanol (1a) and 1,1,1,3,3,3-hexafluoro-2-propanol (4a) with $CF_3SO_2OCF_3$ (2).

Table S5. Carbonation of **1a** and **4a** with **2** in the presence of different bases.

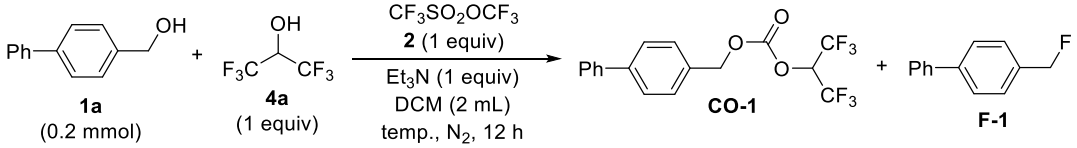


Entry [a]	Base	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	DMAP	63	0
2 [b]	DMAP	54	7
3 [c]	DMAP	70	8
4 [b, c]	DMAP	50	5
5 [d]	DMAP	85	trace

6	DABCO	60	trace
7	**Et_3N**	**80**	**4**
8	BTMG	60	trace
9	1-methyl-1*H*-imidazole	72	3
10	pyridine	47	1
11	CsF	4	24
12	DBU	trace	0
13	none	0	0

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (0.2 mmol), base (0.2 mmol), DCM (2 mL), -20 °C to r.t., N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards. Abbreviations: DMAP = 4-dimethylaminopyridine, DABCO = 1,4-diazabicyclo[2.2.2]octane, BTMG = 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine, DBU = 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepine. [b] -20 °C to 80 °C. [c] 24 h. [d] -20 °C to 40 °C.

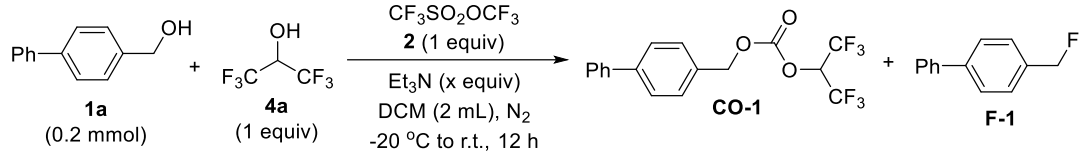
Table S6. Carbonation of **1a** and **4a** with **2**/Et_3N at different temperatures.



Entry [a]	Temp.	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	-20 °C to r.t.	80	4
2	**-20 °C to 40 °C**	**95 (87)**	**trace**
3	-20 °C to 60 °C	75	11
4	-20 °C to 80 °C	71	5
5	-20 °C to 100 °C	54	trace

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (0.2 mmol), Et_3N (0.2 mmol), DCM (2 mL), N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards. Isolated yield is depicted in the parenthesis.

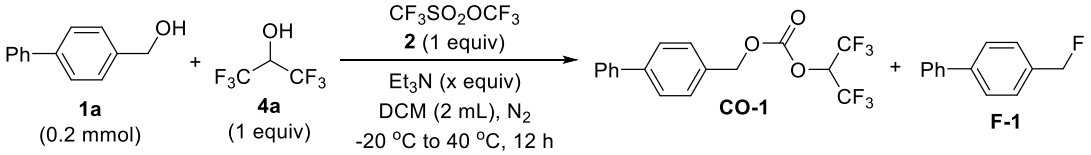
Table S7. Carbonation of **1a** and **4a** with different equivalents of Et_3N at -20 °C to room temperature.



Entry [a]	x (equiv)	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	0.5	51	10
2	1	80	4
3	1.5	86	4
4	2	86	3
5	2.5	87	4
6	3	89	2

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (1 equiv), Et_3N (x equiv), DCM (2 mL), -20 °C to r.t., N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards.

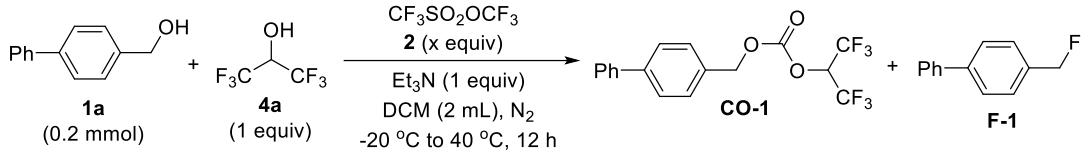
Table S8. Carbonation of **1a** and **4a** with different equivalents of Et_3N at -20 °C to 40 °C.



Entry [a]	x (equiv)	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	0.5	70	9
2	**1**	**95 (87)**	**trace**
3	1.5	87	4
4	2	87	5
5	2.5	89	3
6	3	90	2

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (1 equiv), Et_3N (x equiv), DCM (2 mL), -20 °C to 40 °C, N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards. Isolated yield is depicted in the parenthesis.

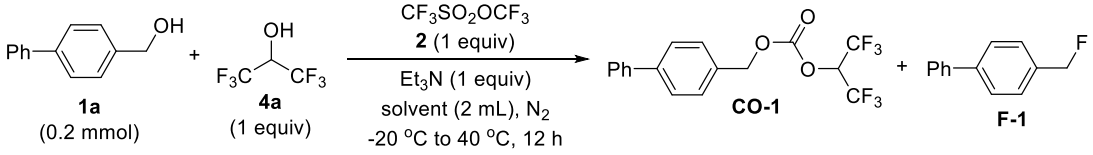
Table S9. Carbonation of **1a** and **4a** with different equivalents of $CF_3SO_2OCF_3$.



Entry [a]	x (equiv)	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	**1**	**95 (87)**	**trace**
2	0.8	73	8
3	0.6	57	6
4	0.4	40	10
5	0.2	19	2
6	0.1	10	trace

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (x equiv), Et_3N (0.2 mmol), DCM (2 mL), -20 °C to 40 °C, N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards. Isolated yield is depicted in the parenthesis.

Table S10. Carbonation of **1a** and **4a** with **2**/Et_3N in different solvents.

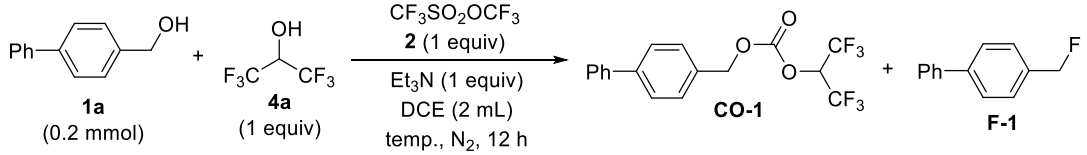


Entry [a]	Solvent	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	DCE	94	trace
2	**DCM**	**95 (87)**	**trace**
3 [b]	DCM	91	trace
4	THF	67	4
5	toluene	77	2
6	CH_3CN	36	trace
7	1,4-dioxane	81	15
8	DMSO	trace	0
9	DMF	trace	0

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (0.2 mmol), Et_3N (0.2 mmol),

solvent (2 mL), -20 °C to 40 °C, N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards. Isolated yield is depicted in the parenthesis. [b] Under air.

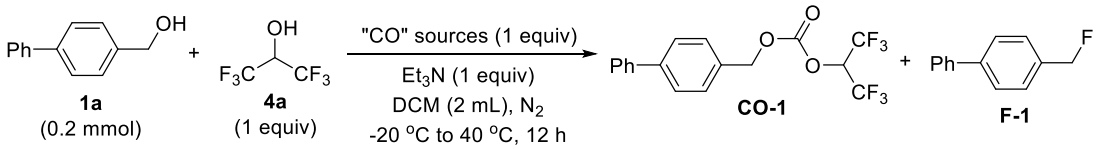
Table S11. Carbonation of **1a** and **4a** with **2**/Et_3N in DCE at different temperatures.



Entry [a]	Temp. (°C)	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	r.t.	70	2
2	**40**	**94**	**trace**
3	60	75	7
4	80	62	13
5	100	59	8

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), **2** (0.2 mmol), Et_3N (0.2 mmol), DCE (2 mL), N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards.

Table S12. Comparing the carbonation of **1a** and **4a** with $CF_3SO_2OCF_3$ (**2**) to those with other "CO" sources.



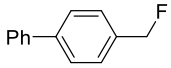
Entry [a]	"CO" source	Yield (**CO-1**, %)	Yield (**F-1**, %)
1	**$CF_3SO_2OCF_3$**	**95 (87)**	**trace**
2	$Cl_3COCO_2CCl_3$	50, 38 [b]	0, 0 [b]
3	CDI	37	0
4	$CsOCF_3$	92	trace
5	$AgOCF_3$	89	trace
6	4-Me-$C_6H_4SO_2OCF_3$	80	trace
7	CF_3SO_2Na	0	0

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), "CO" source (0.2 mmol), Et_3N (0.2 mmol), DCM (2 mL), -20 °C to 40 °C, N_2, 12 h. Yields were determined by HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) using **F-1** (t_R = 5.26 min) and **CO-1** (t_R = 6.56 min) as external standards. Isolated yield is depicted in the parenthesis. [b] $Cl_3COCO_2CCl_3$ (1/3 equiv) was used.

4. General procedure for dehydroxyfluorination of alcohols (1) with 2.

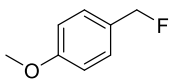
Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with alcohol (**1**, 0.2 mmol), BTMG (34.3 mg, 0.2 mmol, 1 equiv), and THF (1.5 mL) with vigorous stirring and cooled to -20 °C. A solution of $CF_3SO_2OCF_3$ (65.4 mg, 0.3 mmol, 1.5 equiv) in THF (0.5 mL) was quickly introduced. The mixture was reacted at room temperature for 12 h and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the dehydroxyfluorinated product.

4-(Fluoromethyl)-1,1'-biphenyl (**F-1**)[3]



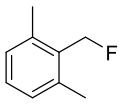
White solid, 24.9 mg, 67% yield. Petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.60 (m, 4H), 7.47-7.44 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 5.44 (d, *J* = 47.9 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -206.2 (t, *J* = 48.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8 (d, *J* = 3.2 Hz), 140.6, 135.2 (d, *J* =17.0 Hz), 128.8, 128.1 (d, *J* = 5.7 Hz), 127.6, 127.4 (d, *J* = 1.3 Hz), 127.2, 84.4 (d, *J* = 166.0 Hz).

1-(Fluoromethyl)-4-methoxybenzene (**F-2**)[4]



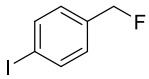
Due to the low boiling point of the product, the yield (41%) was determined by ^{19}F NMR analysis of the reaction mixture using PhF (0.2 mmol) as an internal standard. ^{19}F NMR (471 MHz) δ -199.9 (t, *J* = 48.6 Hz, 1F).

2-(Fluoromethyl)-1,3-dimethylbenzene (**F-3**)[5]



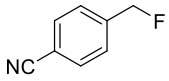
Due to the low boiling point of the product, the yield (40%) was determined by ^{19}F NMR analysis of the reaction mixture using PhF (0.2 mmol) as an internal standard. ^{19}F NMR (471 MHz) δ -209.1 (t, *J* = 49.5 Hz, 1F).

1-(Fluoromethyl)-4-iodobenzene (**F-4**)[6]



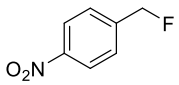
White solid, 29.3 mg, 62% yield. Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.32 (d, *J* = 47.4 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -208.9 (t, *J* = 48.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8 (d, *J* = 0.5 Hz), 135.8 (d, *J* = 17.5 Hz), 129.1 (d, *J* = 6.0 Hz), 94.5 (d, *J* = 3.8 Hz), 83.4 (d, *J* = 167.5 Hz).

4-(Fluoromethyl)benzonitrile (**F-5**)[7]



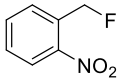
Yellow oil, 8.6 mg, 32% yield or 9.5 mg, 35% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 5.45 (d, *J* = 46.9 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -215.1 (t, *J* = 47.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5 (d, *J* = 17.7 Hz), 132.4, 127.9 (d, *J* = 7.0 Hz), 118.5, 112.4, (d, *J* = 2.3 Hz), 83.1 (d, *J* = 170.1 Hz).

1-(Fluoromethyl)-4-nitrobenzene (**F-6**)[6]



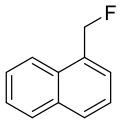
Yellow solid, 12.4 mg, 40% yield or 14.9 mg, 48% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 5.51 (d, *J* = 46.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -215.7 (t, *J* = 47.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 143.4 (d, *J* = 17.6 Hz), 127.0 (d, *J* = 7.2 Hz), 123.9, 82.9 (d, *J* = 170.8 Hz).

1-(Fluoromethyl)-2-nitrobenzene (**F-7**)[8]



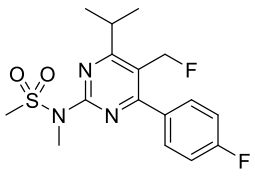
Yellow solid, 13.0 mg, 42% yield or 15.5 mg, 50% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.82-7.73 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 5.87 (d, *J* = 47.9 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -219.1 (t, *J* = 48.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 134.4, 134.3 (d, *J* = 19.2 Hz), 128.5 (d, *J* = 1.0 Hz), 126.9 (d, *J* = 17.6 Hz), 124.9, 81.3 (d, *J* = 172.9 Hz).

1-(Fluoromethyl)naphthalene (**F-8**)[9]



White solid, 17.9 mg, 56% yield. Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.92-7.89 (m, 2H), 7.59 (tm, *J* = 7.5 Hz, 1H), 7.56-7.53 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 5.87 (d, *J* = 48.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -206.2 (t, *J* = 48.9 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 131.8 (d, *J* = 15.4 Hz), 131.4 (d, *J* = 1.9 Hz), 129.9 (d, *J* = 3.3 Hz), 128.7, 126.8 (d, *J* = 8.4 Hz), 126.7 (d, *J* = 0.8 Hz), 126.1, 125.2 (d, *J* = 1.8 Hz), 123.6, 83.3 (d, *J* = 165.7 Hz).

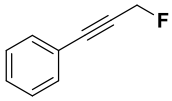
N-(5-(fluoromethyl)-4-(4-fluorophenyl)-6-isopropylpyrimidin-2-yl)-*N*-methylmethane sulfonamide (**F-9**)[10]



White solid, 35.6 mg, 50% yield. Petroleum ether / EtOAc = 5 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.20 (t, *J* = 8.7 Hz, 2H), 5.36 (d, *J* = 48.8 Hz, 2H), 3.60 (s, 3H), 3.52 (s, 3H), 3.49 (m, 1H), 1.36 (d, *J* = 6.7 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.5 (m, 1F), -195.4 (t, *J* = 48.8 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 167.3 (d, *J* = 3.9 Hz), 164.0 (d, *J* = 251.5

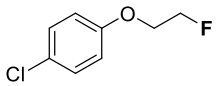
Hz), 158.7, 133.4 (d, *J* = 3.6 Hz), 131.7 (dd, *J* = 8.6, 2.6 Hz), 116.7 (d, *J* = 17.7 Hz), 115.6 (d, *J* = 21.8 Hz), 77.6 (d, *J* = 165.7 Hz), 42.5, 33.1, 31.8, 22.1.

(3-Fluoroprop-1-yn-1-yl)benzene (**F-10**)[10]



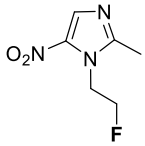
Colorless oil, 7.2 mg, 27% yield or 8.0 mg, 30% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.38-7.32 (m, 3H), 5.19 (d, *J* = 47.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -213.5 (t, *J* = 47.7 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.9 (d, *J* = 3.1 Hz), 129.1, 128.4, 121.8 (d, *J* = 4.3 Hz), 89.5 (d, *J* = 11.9 Hz), 82.6 (d, *J* = 21.7 Hz), 71.2 (d, *J* = 165.3 Hz).

1-Chloro-4-(2-fluoroethoxy)benzene (**F-11**)[11]



Colorless oil, 10.5 mg, 30% yield or 17.5 mg, 50% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive) or 25.9 mg, 74% yield (using 0.5 equivalent of Me_4NF (9.3 mg, 0.1 mmol) as an additive). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.78 (dt, *J* = 47.4, 4.0 Hz, 2H), 4.22 (dt, *J* = 27.7, 4.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -223.9 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 129.4, 126.3, 116.0, 81.8 (d, *J* = 170.6 Hz), 67.5 (d, *J* = 20.5 Hz).

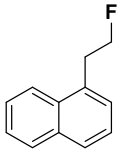
1-(2-Fluoroethyl)-2-methyl-5-nitro-*1H*-imidazole (**F-12**)[12]



Colorless oil, 17.3 mg, 50% yield. Petroleum ether / EtOAc = 4 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 4.77 (dt, *J* = 47.2, 4.1 Hz, 2H), 4.63 (dt, *J* = 26.0, 4.2 Hz, 2H), 2.51 (s, 3H). ^{19}F NMR (471 MHz,

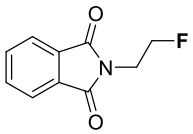
$CDCl_3$) δ -224.0 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 138.3 (brs), 133.3, 82.2 (d, *J* = 171.9 Hz), 46.8 (d, *J* = 20.0 Hz), 14.4 (d, *J* = 3.4 Hz).

1-(2-Fluoroethyl)naphthalene (**F-13**)[13]



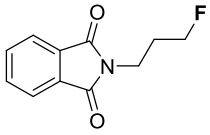
Colorless oil, 18.1 mg, 52% yield. Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.57-7.50 (m, 2H), 7.46-7.41 (m, 2H), 4.79 (dt, *J* = 47.1, 6.9 Hz, 2H), 3.53 (dt, *J* = 20.3, 6.9 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -213.4 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 132.8 (d, *J* = 7.5 Hz), 132.1, 128.9, 127.6, 127.2, 126.2, 125.7, 125.6, 123.4, 83.5 (d, *J* = 169.2 Hz), 33.9 (d, *J* = 20.8 Hz).

2-(2-Fluoroethyl)isoindoline-1,3-dione (**F-14**)[14]



White solid, 25.1 mg, 65% yield. Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.74-7.73 (m, 2H), 4.65 (dt, *J* = 46.9, 5.2 Hz, 2H), 4.02 (dt, *J* = 23.9, 5.3 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -224.7 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 134.1, 132.0, 123.4, 80.4 (d, *J* = 172.3 Hz), 38.2 (d, *J* = 22.0 Hz).

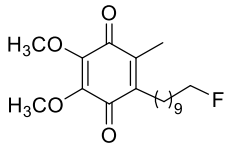
2-(3-Fluoropropyl)isoindoline-1,3-dione (**F-15**)[14]



White solid, 16.6 mg, 40% yield or 21.5 mg, 52% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.73-7.70 (m, 2H), 4.52 (dt, *J* = 47.0, 5.8 Hz, 2H), 3.84 (t, *J* = 6.9 Hz, 2H), 2.09 (dm, *J* = 26.2 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -220.8 (m, 1F). ^{13}C NMR (126 MHz,

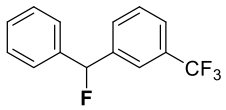
$CDCl_3$) δ 168.3, 134.0, 132.1, 123.3, 81.7 (d, *J* = 166.0 Hz), 34.6 (d, *J* = 5.3 Hz), 29.5 (d, *J* = 19.9 Hz).

2-(10-Fluorodecyl)-5,6-dimethoxy-3-methylcyclohexa-2,5-diene-1,4-dione (**F-16**)[13]



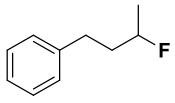
Orange solid, 28.6 mg, 42% yield or 30.6 mg, 45% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (dt, *J* = 47.4, 6.3 Hz, 2H), 3.98 (s, 3H), 3.98 (s, 3H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.00 (s, 3H), 1.72-1.64 (m, 2H), 1.39-1.28 (m, 14H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -218.0 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 184.1, 144.3, 144.3, 143.1, 138.7, 84.2 (d, *J* = 164.3 Hz), 61.1, 30.4 (d, *J* = 19.3 Hz), 29.8, 29.4, 29.4, 29.3, 29.2, 28.7, 26.4, 25.1 (d, *J* = 5.5 Hz), 11.9.

1-(Fluoro(phenyl)methyl)-3-(trifluoromethyl)benzene (**F-17**)[15]



Colorless oil, 16.3 mg, 32% yield or 17.8 mg, 35% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.53-7.48 (m, 2H), 7.42-7.37 (m, 3H), 7.34 (d, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 47.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.7 (s, 3F), -167.7 (d, *J* = 47.3 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9 (d, *J* = 22.7 Hz), 138.9 (d, *J* = 20.9 Hz), 131.0 (q, *J* = 32.5 Hz), 129.7 (d, *J* = 6.3 Hz), 129.0, 128.9 (d, *J* = 1.8 Hz), 128.8, 126.8 (d, *J* = 6.0 Hz), 125.2 (m), 124.0 (q, J = 273.2 Hz), 123.2 (m), 93.8 (d, *J* = 174.5 Hz).

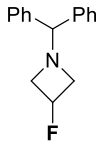
(3-Fluorobutyl)benzene (**F-18**)[6]



Colorless oil, 15.2 mg, 50% yield. Petroleum ether / EtOAc = 80 : 1 (v/v) as eluents

for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.21-7.18 (m, 3H), 4.67 (dm, *J* = 48.9, 1H), 2.76 (m, 2H), 2.02-1.75 (m, 2H), 1.35 (dd, *J* = 23.9, 6.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -174.2 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 128.4, 126.0, 90.1 (d, *J* = 164.8 Hz), 38.7 (d, *J* = 20.8 Hz), 31.4 (d, *J* = 4.8 Hz), 21.0 (d, *J* = 22.7 Hz).

1-Benzhydryl-3-fluoroazetidine (**F-19**)[11]

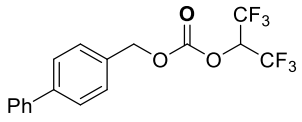


White solid, 19.3 mg, 40% yield or 24.1 mg, 50% yield (using 0.1 equivalent of Me_4NF (1.9 mg, 0.02 mmol) as an additive) or 31.3 mg, 65% yield (using 0.5 equivalent of Me_4NF (9.3 mg, 0.1 mmol) as an additive). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.22 (t, *J* = 7.4 Hz, 2H), 5.17 (dm, J = 57.5 Hz, 1H), 4.42 (s, 1H), 3.57 (m, 2H), 3.16 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -178.6 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 127.5, 126.3, 126.3, 80.9 (d, *J* = 204.2 Hz), 77.3, 59.7 (d, *J* = 20.5 Hz).

5. General procedure for asymmetric carbonation of two different alcohols (1 and 4) with 2.

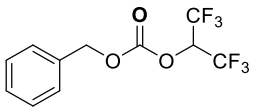
Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with two different alcohols (0.2 mmol each), Et_3N (20.2 mg, 0.2 mmol, 1 equiv), and CH_2Cl_2 (1 mL) with vigorous stirring. A solution of $CF_3SO_2OCF_3$ (43.6 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was quickly introduced. The mixture was reacted at 40 ^{o}C or 80 ^{o}C for 12 h or 24 h and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the carbonated product.

[1,1'-Biphenyl]-4-ylmethyl (1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-1**)



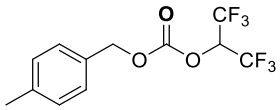
White solid, 65.8 mg, 87% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 68.5-69.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.48-7.45 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 1H), 5.59 (m, 1H), 5.34 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 142.2, 140.4, 132.5, 129.0, 128.9, 127.7, 127.6, 127.2, 120.2 (q, *J* = 285.5 Hz), 71.8, 70.4 (m). IR (KBr): 3064, 3034, 2973, 1774, 1490, 1461, 1389, 1364, 1308, 1266, 1244, 1198, 1132, 1110, 1020, 972, 909, 847, 821, 761, 732, 693 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{13}F_6O_3]^+$ ([M + H]$^+$): 379.0763; found: 379.0764.

Benzyl (1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-2**)



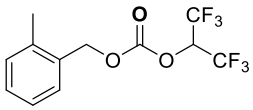
Colorless oil, 37.5 mg, 62% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 5H), 5.59 (m, 1H), 5.30 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.3 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 133.6, 129.2, 128.8, 128.5, 120.2 (q, *J* = 283.0 Hz), 72.0, 70.4 (m). IR (KBr): 3068, 3039, 2972, 1778, 1458, 1385, 1362, 1302, 1251, 1201, 1140, 1112, 1019, 935, 909, 781, 751, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_9F_6O_3]^+$ ([M + H]$^+$): 303.0450; found: 303.0457.

1,1,1,3,3,3-Hexafluoropropan-2-yl (4-methylbenzyl) carbonate (**CO-3**)



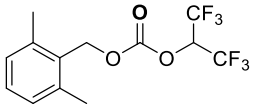
Colorless oil, 19.0 mg, 30% yield (at 40 °C for 12 h) or 43.6 mg, 69% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.58 (m, 1H), 5.26 (s, 2H), 2.38 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 6.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 139.2, 130.6, 129.5, 128.7, 120.2 (q, *J* = 284.5 Hz), 72.1, 70.3 (m), 21.3. IR (KBr): 3032, 2964, 2928, 2856, 1778, 1519, 1457, 1384, 1363, 1302, 1265, 1202, 1140, 1112, 1021, 927, 907, 807, 782, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{11}F_6O_3]^+$ ([M + H]$^+$): 317.0607; found: 317.0613.

1,1,1,3,3,3-Hexafluoropropan-2-yl (2-methylbenzyl) carbonate (**CO-4**)



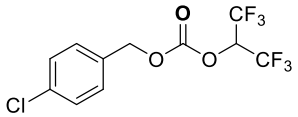
White solid, 32.3 mg, 51% yield (at 40 °C for 12 h) or 38.6 mg, 61% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 50.1-51.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25-7.22 (m, 2H), 5.59 (m, 1H), 5.34 (s, 2H), 2.39 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 6.5 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 137.3, 131.7, 130.7, 129.7, 129.5, 126.2, 120.2 (q, *J* = 283.0 Hz), 70.5, 70.4 (m), 18.8. IR (KBr): 2994, 2962, 2925, 2854, 1773, 1497, 1468, 1395, 1370, 1299, 1262, 1201, 1134, 1110, 1016, 927, 908, 886, 802, 756, 741, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{10}F_6NaO_3]^+$ ([M + Na]$^+$): 339.0426; found: 339.0423.

2,6-Dimethylbenzyl (1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-5**)



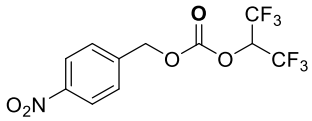
White solid, 23.1 mg, 35% yield (at 40 °C for 12 h) or 31.0 mg, 47% yield (at 80 °C for 24 h, DCE) or 31.7 mg, 48% yield (at 80 °C for 12 h) or 39.6 mg, 60% yield (at 40 °C for 12 h using 2 equivalents of Et_3N as the base). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 92.5-94.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 2H), 5.59 (m, 1H), 5.44 (s, 2H), 2.41 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 138.6, 129.9, 129.6, 128.5, 120.2 (q, *J* = 284.7 Hz), 70.7 (m), 67.0, 19.5. IR (KBr): 3032, 2996, 2958, 2921, 2860, 1769, 1599, 1475, 1396, 1384, 1297, 1261, 1224, 1199, 1135, 1112, 1011, 977, 921, 887, 840, 776, 759, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{13}F_6O_3]^+$ ([M + H]$^+$): 331.0763; found: 331.0764.

4-Chlorobenzyl (1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-6**)



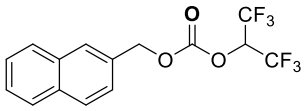
White solid, 44.4 mg, 66% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 65.8-67.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.57 (m, 1H), 5.26 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.6 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 135.3, 132.1, 129.9, 129.1, 120.2 (q, *J* = 283.0 Hz), 71.1, 70.4 (m). IR (KBr): 2989, 2966, 1778, 1601, 1496, 1469, 1411, 1388, 1368, 1298, 1248, 1202, 1137, 1107, 1092, 1015, 959, 938, 904, 886, 842, 820, 779, 724, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_8ClF_6O_3]^+$ ($[M + H]^+$): 337.0061; found: 337.0060.

1,1,1,3,3,3-Hexafluoropropan-2-yl (4-nitrobenzyl) carbonate (**CO-7**)



Colorless oil, 35.4 mg, 51% yield (at 40 °C for 12 h) or 48.6 mg, 70% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 5.57 (m, 1H), 5.39 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 148.3, 140.6, 128.6, 124.1, 120.1 (q, *J* = 283.0 Hz), 70.6 (m), 70.1. IR (KBr): 3087, 2976, 2865, 1780, 1610, 1528, 1458, 1384, 1352, 1301, 1250, 1201, 1142, 1112, 1026, 980, 943, 906, 874, 850, 807, 779, 739, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_7F_6NNaO_5]^+$ ($[M + Na]^+$): 370.0121; found: 370.0126.

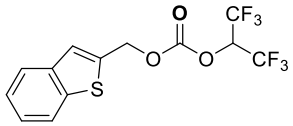
1,1,1,3,3,3-Hexafluoropropan-2-yl (naphthalen-2-ylmethyl) carbonate (**CO-8**)



White solid, 54.9 mg, 78% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 76.8-78.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.83 (m, 4H), 7.55-7.53 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 5.62 (m, 1H), 5.47 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.7 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 133.5, 133.1, 131.0, 128.8, 128.1, 128.0, 127.8, 126.8, 126.6, 125.5, 120.2 (q, *J* = 282.6 Hz), 72.2, 70.4 (m). IR (KBr): 3077, 2993, 2967, 2924, 2853, 2786, 1769, 1603, 1514, 1466, 1396, 1371, 1298, 1265, 1205, 1112, 1015, 990, 938, 902, 858, 817, 780, 750, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for

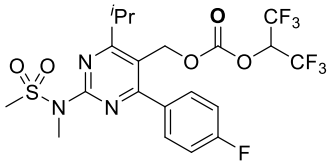
$[C_{15}H_{10}F_6NaO_3]^+$ ([M + Na]$^+$): 375.0426; found: 375.0436.

Benzo[*b*]thiophen-2-ylmethyl (1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-9**)



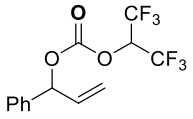
White solid, 21.5 mg, 30% yield (at 40 ºC for 12 h) or 41.6 mg, 58% yield (at 80 ºC for 24 h) or 41.6 mg, 58% yield (at 40 ºC for 12 h using 2 equivalents of Et_3N as the base). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. M.p.: 65.5-66.6 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 1H), 7.80 (m, 1H), 7.41 (s, 1H), 7.39-7.36 (m, 2H), 5.59 (m, 1H), 5.53 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.4 (d, *J* = 6.7 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 140.8, 138.9, 135.8, 126.0, 125.3, 124.7, 124.2, 122.5, 120.1 (q, *J* = 282.6 Hz), 70.5 (m), 66.8. IR (KBr): 3068, 2996, 2964, 2925, 2854, 1769, 1460, 1436, 1397, 1381, 1296, 1259, 1203, 1111, 1010, 974, 928, 909, 884, 836, 803, 779, 751, 722, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_8F_6NaO_3S]^+$ ([M + Na]$^+$): 380.9991; found: 380.9999.

(4-(4-Fluorophenyl)-6-isopropyl-2-(*N*-methylmethylsulfonamido)pyrimidin-5-yl)meth yl (1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-10**)



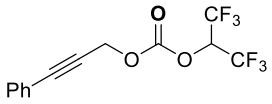
White solid, 78.8 mg, 72% yield (at 40 ºC for 12 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. M.p.: 114.0-115.2 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 5.60 (m, 1H), 5.29 (s, 2H), 3.58 (s, 3H), 3.51 (s, 3H), 3.27 (m, 1H), 1.34 (d, *J* = 6.7 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 6.8 Hz, 6F), -110.3 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 167.9, 163.9 (d, *J* = 251.7 Hz), 158.8, 152.4, 133.4 (d, *J* = 3.4 Hz), 131.1 (d, *J* = 8.6 Hz), 120.1 (q, *J* = 282.6 Hz), 115.8 (d, *J* = 21.7 Hz), 114.9, 70.5 (m), 65.5, 42.5, 33.1, 32.1, 22.0. IR (KBr): 3084, 3015, 2985, 2935, 2878, 1775, 1607, 1557, 1511, 1475, 1440, 1393, 1365, 1332, 1287, 1201, 1160, 1140, 1111, 1066, 1021, 967, 948, 847, 816, 777, 757, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{21}F_7N_3O_5S]^+$ ([M + H]$^+$): 548.1085; found: 548.1088.

1,1,1,3,3,3-Hexafluoropropan-2-yl (1-phenylallyl) carbonate (**CO-11**)



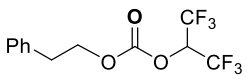
White solid, 31.5 mg, 48% yield (at 40 °C for 12 h) or 21.7 mg, 33% yield (at 40 °C for 12 h using 2 equivalents of Et_3N as the base). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 37.7-39.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.60 (m, 1H), 4.94 (d, *J* = 6.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 136.6, 135.6, 128.7, 128.7, 126.9, 120.6, 120.2 (q, *J* = 283.0 Hz), 70.9, 70.3 (m). IR (KBr): 3085, 3072, 3025, 2978, 2921, 2856, 1774, 1656, 1497, 1451, 1387, 1366, 1298, 1246, 1199, 1130, 1111, 1019, 968, 908, 831, 780, 742, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{10}F_6NaO_3]^+$ ([M + Na]$^+$): 351.0426; found: 351.0433.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3-phenylprop-2-yn-1-yl) carbonate (**CO-12**)



Colorless oil, 44.4 mg, 68% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 2H), 7.39-7.32 (m, 3H), 5.60 (m, 1H), 5.11 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 130.9, 128.2, 127.4, 120.5, 119.1 (q, *J* = 283.5 Hz), 87.7, 79.5, 69.5 (m), 57.5. IR (KBr): 2974, 2925, 2848, 2228, 1781, 1492, 1444, 1384, 1363, 1302, 1250, 1202, 1141, 1113, 1038, 994, 929, 906, 757, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_9F_6O_3]^+$ ([M + H]$^+$): 327.0450; found: 327.0450.

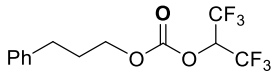
1,1,1,3,3,3-Hexafluoropropan-2-yl phenethyl carbonate (**CO-13**)



Colorless oil, 39.2 mg, 62% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 2H), 5.55 (m, 1H), 4.50

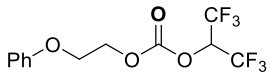
(t, *J* = 7.1 Hz, 2H), 3.06 (t, *J* = 7.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.6 (d, *J* = 5.5 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 136.3, 128.9, 128.7, 127.0, 120.2 (q, *J* = 283.3 Hz), 70.7, 70.3 (m), 34.9. IR (KBr): 3070, 3034, 2974, 2929, 2844, 1778, 1499, 1456, 1387, 1364, 1305, 1261, 1202, 1143, 1112, 1010, 949, 908, 782, 749, 700 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{11}F_6O_3]^+$ ([M + H]$^+$): 317.0607; found: 317.0619.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3-phenylpropyl) carbonate (**CO-14**)



Colorless oil, 39.6 mg, 60% yield (at 40 ºC for 12 h) or 48.2 mg, 73% yield (at 80 ºC for 24 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 6.8 Hz, 2H), 7.24-7.18 (m, 3H), 5.57 (m, 1H), 4.30 (t, *J* = 6.3 Hz, 2H), 2.74 (t, *J* = 6.8 Hz, 2H), 2.07 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.3 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 140.4, 128.6, 128.4, 126.3, 120.3 (q, *J* = 282.3 Hz), 70.2 (m), 69.8, 31.6, 29.9. IR (KBr): 3031, 2966, 2925, 2856, 1779, 1498, 1456, 1386, 1364, 1304, 1263, 1202, 1143, 1112, 1018, 950, 908, 804, 748, 700 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{13}F_6O_3]^+$ ([M + H]$^+$): 331.0763; found: 331.0775.

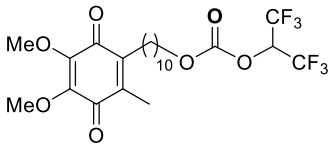
1,1,1,3,3,3-Hexafluoropropan-2-yl (2-phenoxyethyl) carbonate (**CO-15**)



Colorless oil, 49.8 mg, 75% yield (at 40 ºC for 12 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 5.61 (m, 1H), 4.65 (t, *J* = 4.6 Hz, 2H), 4.25 (t, *J* = 4.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.3 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 152.9, 129.6, 121.6, 120.2 (q, *J* = 282.3 Hz), 114.6, 70.5 (m), 68.4, 65.2. IR (KBr): 3031, 2966, 2938, 2856, 1779, 1498, 1456, 1387, 1364, 1304, 1263, 1202, 1143, 1112, 1018, 950, 908, 804, 748, 700 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{10}F_6NaO_4]^+$ ([M + Na]$^+$): 355.0375; found: 355.0379.

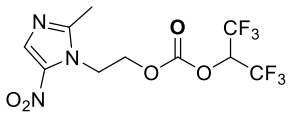
10-(4,5-Dimethoxy-2-methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)decyl

(1,1,1,3,3,3-hexafluoropropan-2-yl) carbonate (**CO-16**)



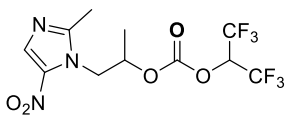
Yellow oil, 98.1 mg, 92% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 5 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (m, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.98 (s, 3H), 3.98 (s, 3H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.00 (s, 3H), 1.71 (m, 2H), 1.38-1.28 (m, 14H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.6 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 184.2, 152.9, 144.3, 144.3, 143.0, 138.7, 120.2 (q, *J* = 283.1 Hz), 70.8, 70.1 (m), 61.1, 29.8, 29.3, 29.3, 29.3, 29.0, 28.7, 28.3, 26.4, 25.4, 11.9. IR (KBr): 2931, 2857, 1779, 1652, 1613, 1456, 1386, 1363, 1301, 1263, 1200, 1143, 1111, 1069, 1012, 948, 907, 782, 746, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{23}H_{31}F_6O_7]^+$ ($[M + H]^+$): 533.1968; found: 533.1973.

1,1,1,3,3,3-Hexafluoropropan-2-yl (2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethyl) carbonate (**CO-17**)



White solid, 48.9 mg, 67% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 1 : 1 (v/v) as eluents for column chromatography. M.p.: 100.8-102.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 5.49 (m, 1H), 4.68-4.65 (m, 4H), 2.49 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.7 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 151.0, 138.4, 133.4, 120.0 (q, *J* = 283.0 Hz), 70.6 (m), 68.2, 45.0, 14.1. IR (KBr): 3126, 2974, 2924, 2848, 1776, 1524, 1483, 1462, 1433, 1369, 1310, 1268, 1201, 1155, 1109, 1039, 988, 949, 912, 888, 825, 770, 747, 688 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{10}H_{10}F_6N_3O_5]^+$ ($[M + H]^+$): 366.0519; found: 366.0529.

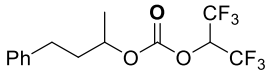
1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(2-methyl-5-nitro-1*H*-imidazol-1-yl)propan-2-yl) carbonate (**CO-18**)



Yellow solid, 53.1 mg, 70% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 1 : 1 (v/v) as eluents for column chromatography. M.p.: 58.7-61.0 °C. ^{1}H NMR (500 MHz,

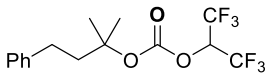
$CDCl_3$) δ 7.95 (s, 1H), 5.39 (m, 1H), 5.29 (m, 1H), 4.70 (dd, *J* = 14.8, 1.5 Hz, 1H), 4.24 (dd, *J* = 14.8, 9.5 Hz, 1H), 2.49 (s, 3H), 1.52 (d, *J* = 6.4 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.7 (dm, *J* = 31.5 Hz, 6F). ^{13}C NMR (126 MHz, CD_3CN) δ 151.8, 151.5, 139.0, 132.9, 120.4 (q, *J* = 283.0 Hz), 76.9, 69.8 (m), 49.6, 16.4, 13.5. IR (KBr): 3138, 2978, 2942, 1778, 1533, 1481, 1429, 1367, 1300, 1258, 1195, 1131, 1112, 1066, 1010, 926, 908, 888, 827, 777, 744, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{12}F_6N_3O_5]^+$ ($[M + H]^+$): 380.0676; found: 380.0683.

1,1,1,3,3,3-Hexafluoropropan-2-yl (4-phenylbutan-2-yl) carbonate (**CO-19**)



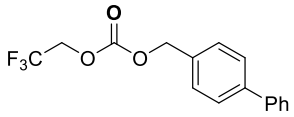
Colorless oil, 20.6 mg, 30% yield (at 40 ºC for 12 h) or 54.4 mg, 79% yield (at 80 ºC for 12 h). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 5.58 (m, 1H), 4.87 (m, 1H), 2.71 (m, 2H), 2.07 (m, 1H), 1.91 (m, 1H), 1.39 (d, *J* = 6.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.6 (d, *J* = 4.2 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 140.7, 128.6, 128.3, 126.2, 120.3 (q, *J* = 283.0 Hz), 78.2, 70.1 (m), 37.2, 31.4, 19.6. IR (KBr): 3030, 2984, 2933, 2868, 1773, 1497, 1456, 1386, 1365, 1302, 1265, 1230, 1201, 1126, 1112, 1047, 1006, 907, 782, 754, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_{15}F_6O_3]^+$ ($[M + H]^+$): 345.0920; found: 345.0917.

1,1,1,3,3,3-Hexafluoropropan-2-yl (2-methyl-4-phenylbutan-2-yl) carbonate (**CO-20**)



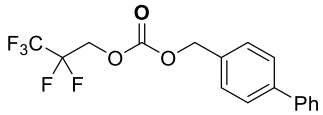
Colorless oil, 34.4 mg, 48% yield (at 40 ºC for 12 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.22-7.18 (m, 3H), 5.55 (m, 1H), 2.67 (m, 2H), 2.14 (m, 2H), 1.59 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5 (d, *J* = 5.8 Hz, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 141.3, 128.5, 128.3, 126.1, 120.4 (q, *J* = 283.3 Hz), 87.8, 69.5 (m), 42.1, 30.2, 25.6. IR (KBr): 3030, 2969, 2929, 2868, 1772, 1497, 1456, 1387, 1361, 1305, 1265, 1230, 1198, 1111, 1003, 908, 893, 802, 744, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{17}F_6O_3]^+$ ($[M + H]^+$): 359.1076; found: 359.1079.

[1,1'-Biphenyl]-4-ylmethyl (2,2,2-trifluoroethyl) carbonate (**CO-21**)



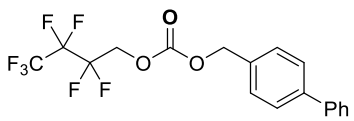
White solid, 32.9 mg, 53% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. M.p.: 53.4-54.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.49-7.45 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.28 (s, 2H), 4.54 (q, *J* = 8.2 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.2 (t, *J* = 8.8 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 140.9, 139.5, 132.3, 128.0, 127.8, 126.6, 126.4, 126.1, 121.5 (q, *J* = 277.6 Hz), 69.5, 62.5 (q, *J* = 37.0 Hz). IR (KBr): 3084, 3035, 2985, 2954, 2897, 1755, 1568, 1491, 1449, 1421, 1386, 1321, 1297, 1256, 1195, 1175, 1159, 1134, 975, 839, 826, 788, 761, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{13}F_3NaO_3]^+$ ($[M + Na]^+$): 333.0709; found: 333.0717.

[1,1'-Biphenyl]-4-ylmethyl (2,2,3,3,3-pentafluoropropyl) carbonate (**CO-22**)



White solid, 34.6 mg, 48% yield (at 40 °C for 12 h) or 38.9 mg, 54% yield (at 80 °C for 12 h). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. M.p.: 42.0-43.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.48-7.45 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.28 (s, 2H), 4.62 (t, *J* = 12.6 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -83.8 (s, 3F), -123.9 (t, *J* = 13.4 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 142.0, 140.5, 133.3, 129.0, 128.9, 127.6, 127.5, 127.2, 118.4 (m), 111.7 (m), 70.7, 62.4 (t, *J* = 27.8 Hz). IR (KBr): 3034, 2987, 2897, 1761, 1568, 1491, 1465, 1446, 1412, 1387, 1357, 1315, 1282, 1238, 1205, 1171, 1123, 1106, 1046, 969, 845, 826, 803, 786, 761, 731, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{13}F_5NaO_3]^+$ ($[M + Na]^+$): 383.0677; found: 383.0688.

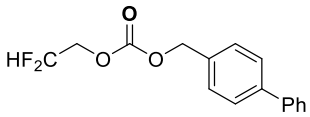
[1,1'-Biphenyl]-4-ylmethyl (2,2,3,3,4,4,4-heptafluorobutyl) carbonate (**CO-23**)



White solid, 33.6 mg, 41% yield (at 40 °C for 12 h) or 36.9 mg, 45% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column

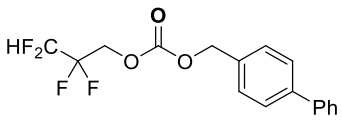
chromatography. M.p.: 42.2-43.9 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.48-7.44 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.28 (s, 2H), 4.66 (t, *J* = 13.2 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.8 (t, *J* = 9.9 Hz, 3F), -121.0 (m, 2F), -127.7 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 141.9, 140.5, 133.3, 129.0, 128.9, 127.6, 127.5, 127.2, 117.6 (m), 113.6 (m), 108.9 (m), 70.7, 62.6 (t, *J* = 27.2 Hz). IR (KBr): 3035, 2988, 2964, 2925, 2897, 2852, 1767, 1489, 1448, 1409, 1383, 1347, 1258, 1185, 1145, 1124, 1031, 963, 940, 904, 853, 792, 769, 739, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{14}F_7O_3]^+$ ($[M + H]^+$): 411.0826; found: 411.0827.

[1,1'-Biphenyl]-4-ylmethyl (2,2-difluoroethyl) carbonate (**CO-24**)



White solid, 33.3 mg, 57% yield (at 40 ºC for 12 h) or 34.5 mg, 59% yield (at 80 ºC for 12 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 52.6-54.0 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.49-7.45 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.99 (tt, *J* = 54.9, 4.0 Hz, 1H), 5.26 (s, 2H), 4.36 (td, *J* = 13.3, 4.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -126.0 (dt, *J* = 54.8, 13.3 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 141.8, 140.5, 133.6, 129.0, 128.9, 127.6, 127.5, 127.2, 112.4 (t, *J* = 214.5 Hz), 70.2, 65.6 (t, *J* = 30.4 Hz). IR (KBr): 3085, 3034, 2970, 2905, 2852, 1759, 1567, 1489, 1469, 1427, 1409, 1386, 1332, 1263, 1105, 1071, 1006, 931, 890, 850, 829, 784, 765, 738, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{14}F_2NaO_3]^+$ ($[M + Na]^+$): 315.0803; found: 315.0814.

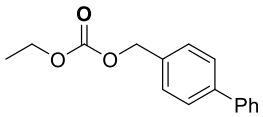
[1,1'-Biphenyl]-4-ylmethyl (2,2,3,3-tetrafluoropropyl) carbonate (**CO-25**)



White solid, 27.4 mg, 40% yield (at 40 ºC for 12 h) or 28.1 mg, 41% yield (at 80 ºC for 24 h) or 26.7 mg, 39% yield (at 40 ºC for 12 h using 2 equivalents of Et_3N as the base). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 56.0-57.7 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.48-7.44 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H), 5.91 (tt, *J* = 53.1, 3.8 Hz, 1H), 5.27 (s, 2H), 4.55 (t, *J* = 12.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -124.4 (m, 2F), -138.0 (d, *J* = 53.6 Hz,

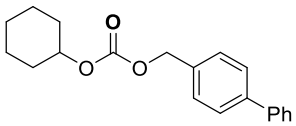
2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 141.9, 140.5, 133.3, 129.0, 128.9, 127.6, 127.5, 127.2, 115.7 (m), 109.1 (m), 70.5, 63.0 (t, *J* = 29.9 Hz). IR (KBr): 3034, 2973, 2925, 2855, 1752, 1568, 1490, 1457, 1409, 1379, 1267, 1201, 1134, 1112, 1099, 1011, 967, 915, 835, 786, 766, 734, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{14}F_4NaO_3]^+$ ($[M + Na]^+$): 365.0771; found: 365.0776.

[1,1'-Biphenyl]-4-ylmethyl ethyl carbonate (**CO-26**)



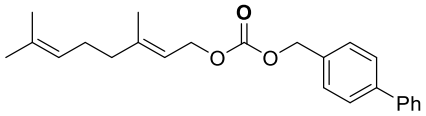
White solid, 17.9 mg, 35% yield (at 40 °C for 12 h) or 23.1 mg, 45% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. M.p.: 39.0-39.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.48-7.44 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 5.21 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 141.5, 140.7, 134.4, 128.8, 127.5, 127.4, 127.2, 69.2, 64.2, 14.3. IR (KBr): 3027, 2984, 2921, 2897, 2848, 1738, 1488, 1465, 1450, 1400, 1384, 1367, 1275, 1174, 1105, 1077, 996, 966, 946, 875, 853, 827, 793, 765, 743, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}O_3]^+$ ($[M + H]^+$): 257.1172; found: 257.1178.

[1,1'-Biphenyl]-4-ylmethyl cyclohexyl carbonate (**CO-27**)



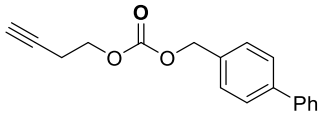
White solid, 21.1 mg, 34% yield (at 40 °C for 12 h) or 32.3 mg, 52% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 10 : 1 (v/v) as eluents for column chromatography. M.p.: 55.7-56.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.48-7.44 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 5.20 (s, 2H), 4.66 (m, 1H), 1.95 (m, 2H), 1.77 (m, 2H), 1.59-1.28 (m, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 154.5, 140.9, 140.4, 135.3, 128.9, 128.7, 127.6, 127.1, 127.0, 76.6, 68.5, 31.2, 25.0, 23.3. IR (KBr): 3075, 3030, 2949, 2919, 2855, 2845, 1737, 1485, 1461, 1390, 1256, 1094, 1072, 1033, 1009, 931, 847, 815, 791, 764, 742, 695 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{23}O_3]^+$ ($[M + H]^+$): 311.1642; found: 311.1652.

(*E*)-[1,1'-Biphenyl]-4-ylmethyl (3,7-dimethylocta-2,6-dien-1-yl) carbonate (**CO-28**)



Colorless oil, 33.5 mg, 46% yield (at 40 °C for 12 h). Petroleum ether / EtOAc = 40 : 1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.48-7.43 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 5.40 (t, *J* = 7.0 Hz, 1H), 5.21 (s, 2H), 5.09 (t, *J* = 6.4 Hz, 1H), 4.70 (d, *J* = 7.1 Hz, 2H), 2.12-2.06 (m, 4H), 1.73 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 143.3, 141.5, 140.7, 134.4, 131.9, 128.8, 128.8, 127.5, 127.3, 127.2, 123.7, 117.7, 69.2, 64.9, 39.5, 26.3, 25.7, 17.7, 16.6. IR (KBr): 3056, 3031, 2964, 2927, 2856, 1741, 1670, 1488, 1449, 1386, 1339, 1256, 1115, 1076, 1008, 925, 851, 823, 790, 762, 697 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{24}H_{28}NaO_3]^+$ ([M + Na]$^+$): 387.1931; found: 387.1935.

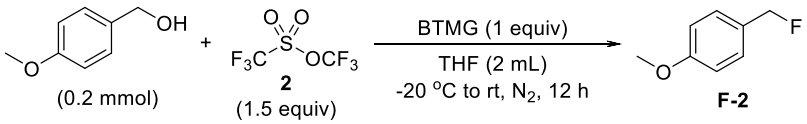
[1,1'-Biphenyl]-4-ylmethyl but-3-yn-1-yl carbonate (**CO-29**)



White solid, 19.6 mg, 35% yield (at 40 °C for 12 h) or 28.6 mg, 51% yield (at 80 °C for 24 h). Petroleum ether / EtOAc = 20 : 1 (v/v) as eluents for column chromatography. M.p.: 34.1-35.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.48-7.44 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 5.22 (s, 2H), 4.28 (t, *J* = 7.0 Hz, 2H), 2.60 (td, *J* = 6.8, 2.4 Hz, 2H), 2.02 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 141.6, 140.6, 134.1, 128.9, 128.8, 127.5, 127.4, 127.2, 79.4, 70.3, 69.5, 65.6, 19.1. IR (KBr): 3293, 3057, 3031, 2963, 2922, 2851, 1744, 1601, 1488, 1453, 1396, 1372, 1260, 1108, 1075, 1009, 968, 940, 851, 820, 790, 763, 643 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{17}O_3]^+$ ([M + H]$^+$): 281.1172; found: 281.1172.

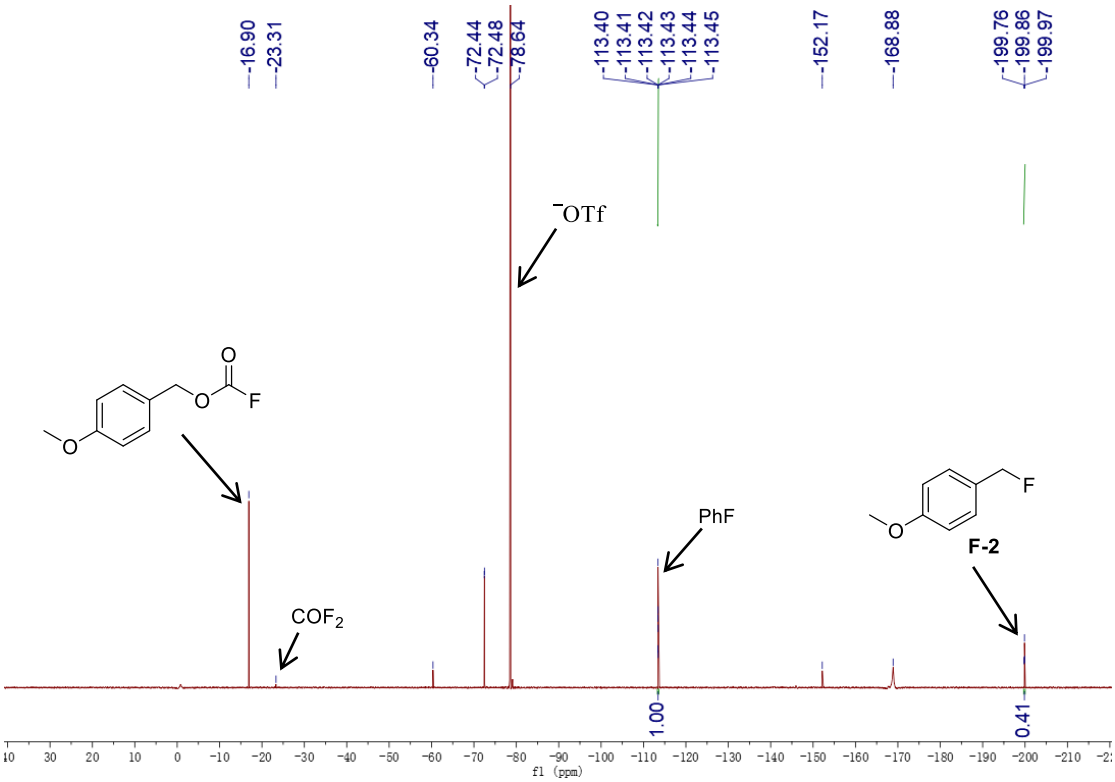
6. ^{19}F NMR and HPLC measurement for the mechanistic insights

6.1. ^{19}F NMR analysis of the reaction mixture of (4-methoxyphenyl)methanol, 2 and BTMG at room temperature for 12 hours.

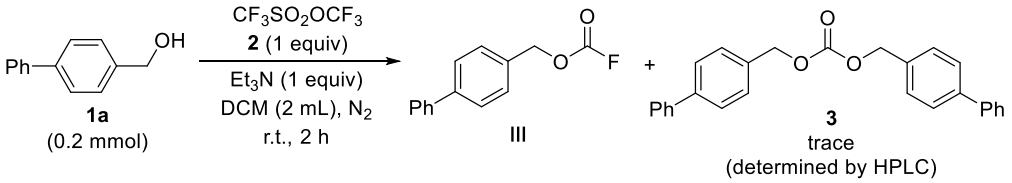


Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with (4-methoxyphenyl)methanol (0.2 mmol), BTMG (0.2 mmol, 1

equiv), and THF (1.5 mL) with vigorous stirring and cooled to -20 °C. A solution of $CF_3SO_2OCF_3$ (0.3 mmol, 1.5 equiv) in THF (0.5 mL) was quickly introduced. The mixture was reacted at room temperature for 12 h. PhF (0.2 mmol) was added as an internal standard. Then, the resulting mixture was measured by ^{19}F NMR (see the spectrum below). *Note*: The signals in the ^{19}F NMR spectrum were assigned according to the data reported in the literature.[16]

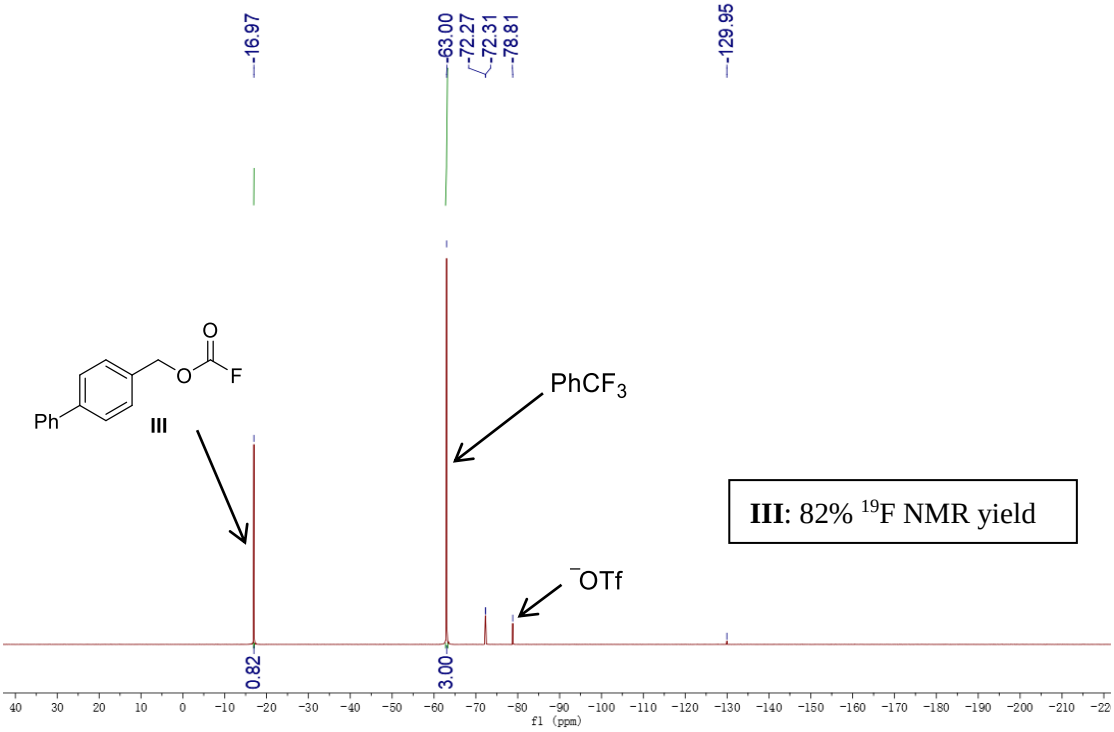


6.2. ^{19}F NMR and HPLC analysis of the reaction mixture of 1a, 2 and Et_3N without 4a at room temperature for 2 hours.

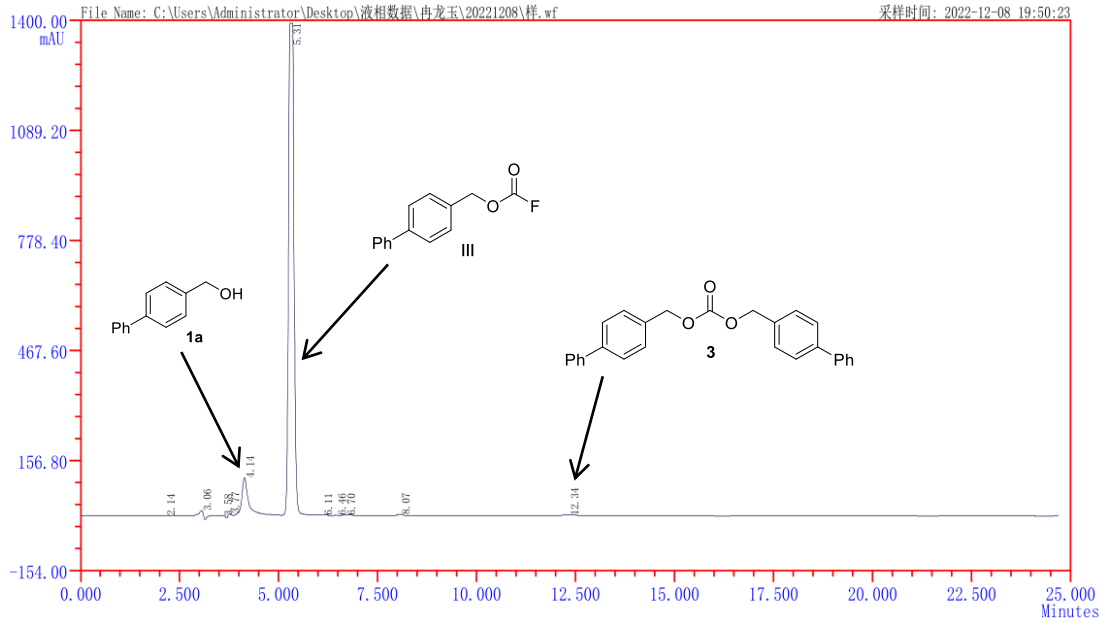


Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with **1a** (0.2 mmol), Et_3N (0.2 mmol, 1 equiv), and CH_2Cl_2 (1 mL) with vigorous stirring. A solution of $CF_3SO_2OCF_3$ (0.2 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was quickly introduced. The mixture was reacted at room temperature for 2 h. $PhCF_3$ (0.2 mmol) was added as an internal standard. Then, the resulting mixture was measured by ^{19}F NMR (see the spectrum below).

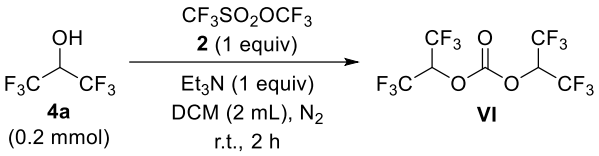
Note: The signals in the ^{19}F NMR spectrum were assigned according to the data reported in the literature.[16]



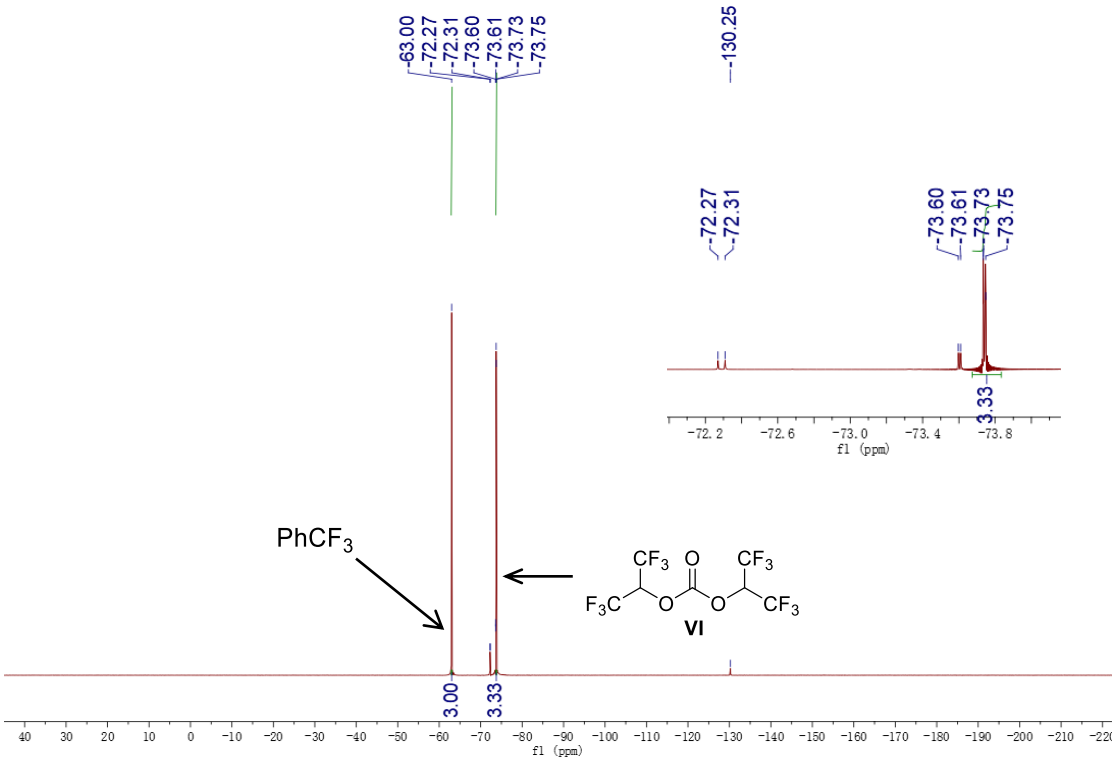
HPLC (λ = 243 nm, water/methanol (v/v) = 10:90)) analysis of the above reaction mixture before adding $PhCF_3$ (see the spectrum below).



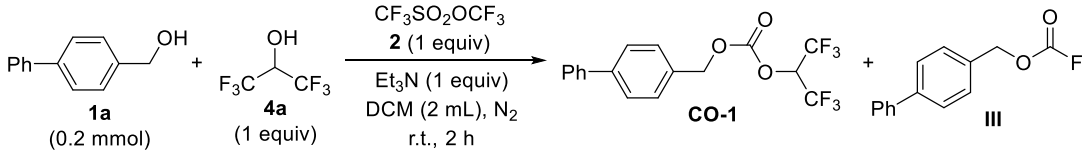
6.3. ^{19}F NMR analysis of the reaction mixture of 4a, 2 and Et_3N without 1a at room temperature for 2 hours.



Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with **4a** (0.2 mmol), Et_3N (0.2 mmol, 1 equiv), and CH_2Cl_2 (1 mL) with vigorous stirring. A solution of $CF_3SO_2OCF_3$ (0.2 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was quickly introduced. The mixture was reacted at room temperature for 2 h. $PhCF_3$ (0.2 mmol) was added as an internal standard. Then, the resulting mixture was measured by ^{19}F NMR (see the spectrum below). *Note*: The signals in the ^{19}F NMR spectrum were assigned according to the data reported in the literature.[16]

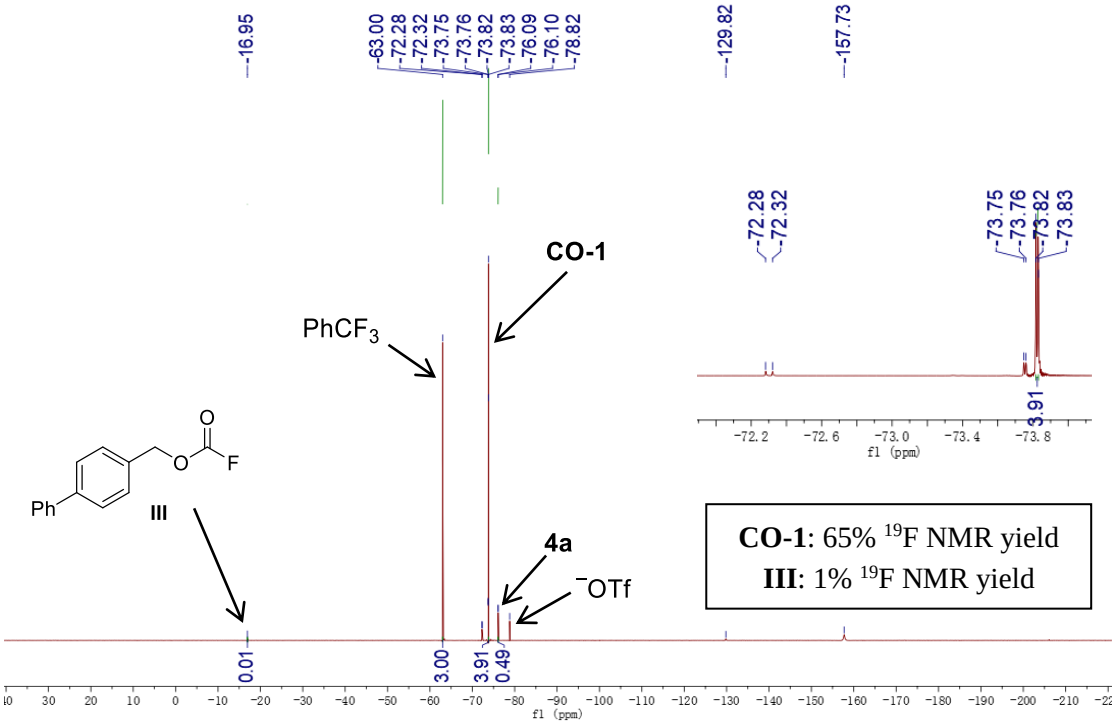


6.4. ^{19}F NMR and HPLC analysis of the reaction mixture of 1a, 4a, 2 and Et_3N at room temperature for 2 hours.

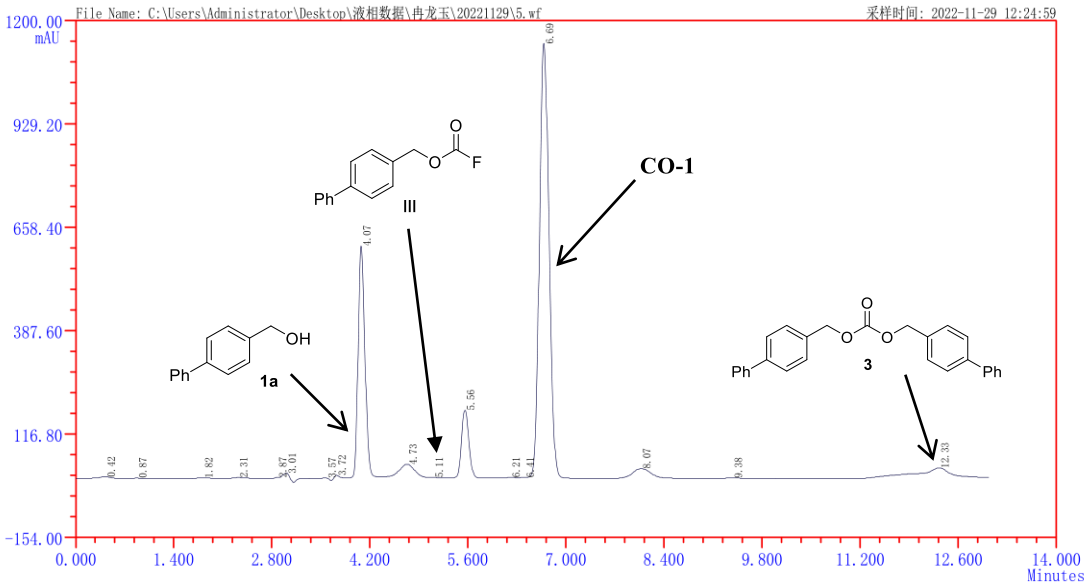


Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with **1a** (0.2 mmol), **4a** (0.2 mmol), Et_3N (0.2 mmol, 1 equiv), and

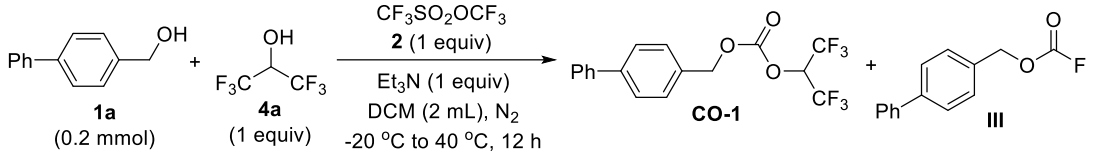
CH_2Cl_2 (1 mL) with vigorous stirring. A solution of $CF_3SO_2OCF_3$ (0.2 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was quickly introduced. The mixture was reacted at room temperature for 2 h. $PhCF_3$ (0.2 mmol) was added as an internal standard. Then, the resulting mixture was measured by ^{19}F NMR (see the spectrum below). *Note*: The signals in the ^{19}F NMR spectrum were assigned according to the data reported in the literature.[16]



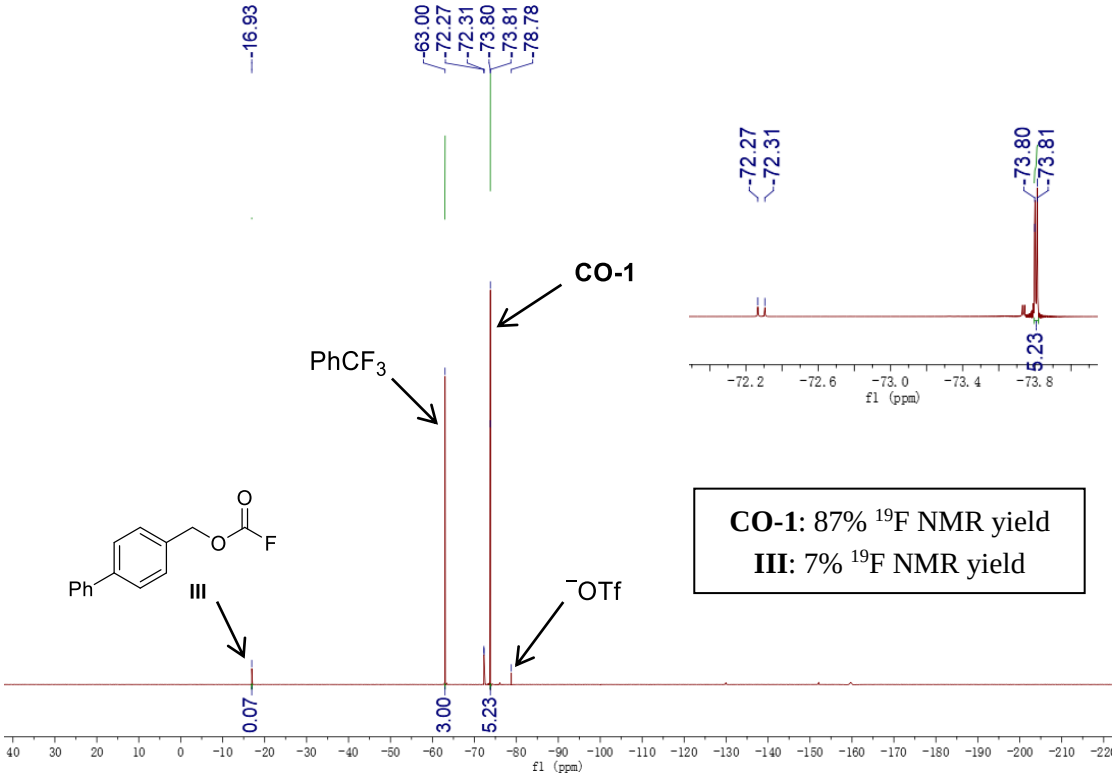
HPLC analysis of the above reaction mixture before adding $PhCF_3$ (λ = 243 nm, water/methanol (v/v) = 10:90))



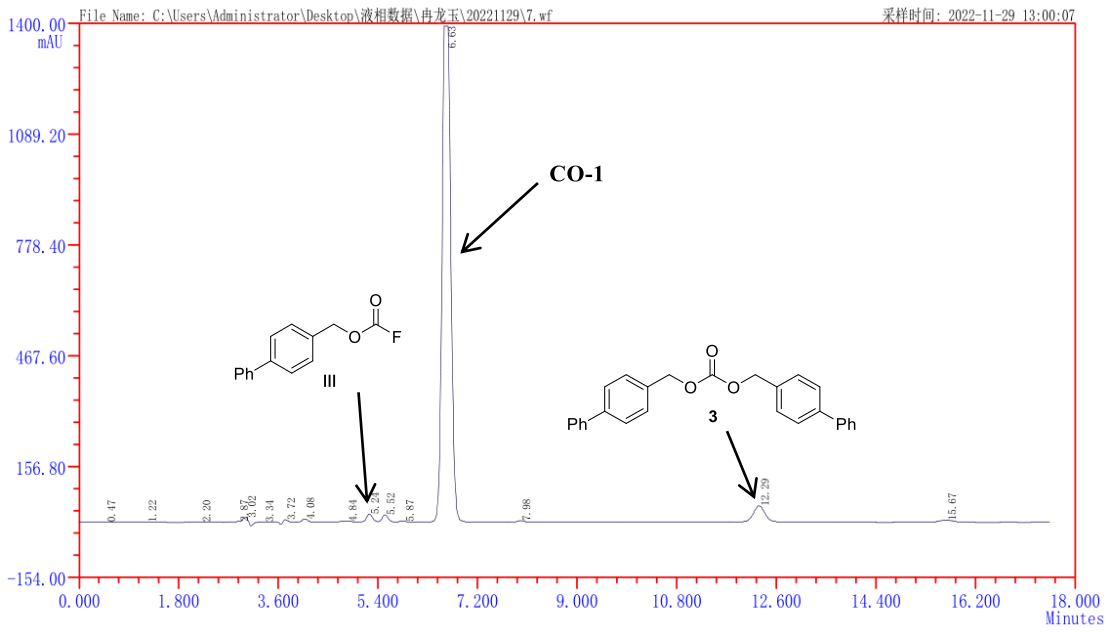
6.5. ^{19}F NMR and HPLC analysis of the reaction mixture of 1a, 4a, 2 and Et_3N at 40 °C for 12 hours.



Procedure: Under a nitrogen atmosphere, a sealed Schlenk tube (25 mL) was charged with **1a** (0.2 mmol), **4a** (0.2 mmol), Et_3N (0.2 mmol, 1 equiv), and CH_2Cl_2 (1 mL) with vigorous stirring. A solution of $CF_3SO_2OCF_3$ (0.2 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was quickly introduced. The mixture was reacted at 40 °C for 12 h. $PhCF_3$ (0.2 mmol) was added as an internal standard. Then, the resulting mixture was measured by ^{19}F NMR (see the spectrum below). *Note*: The signals in the ^{19}F NMR spectrum were assigned according to the data reported in the literature.[16]

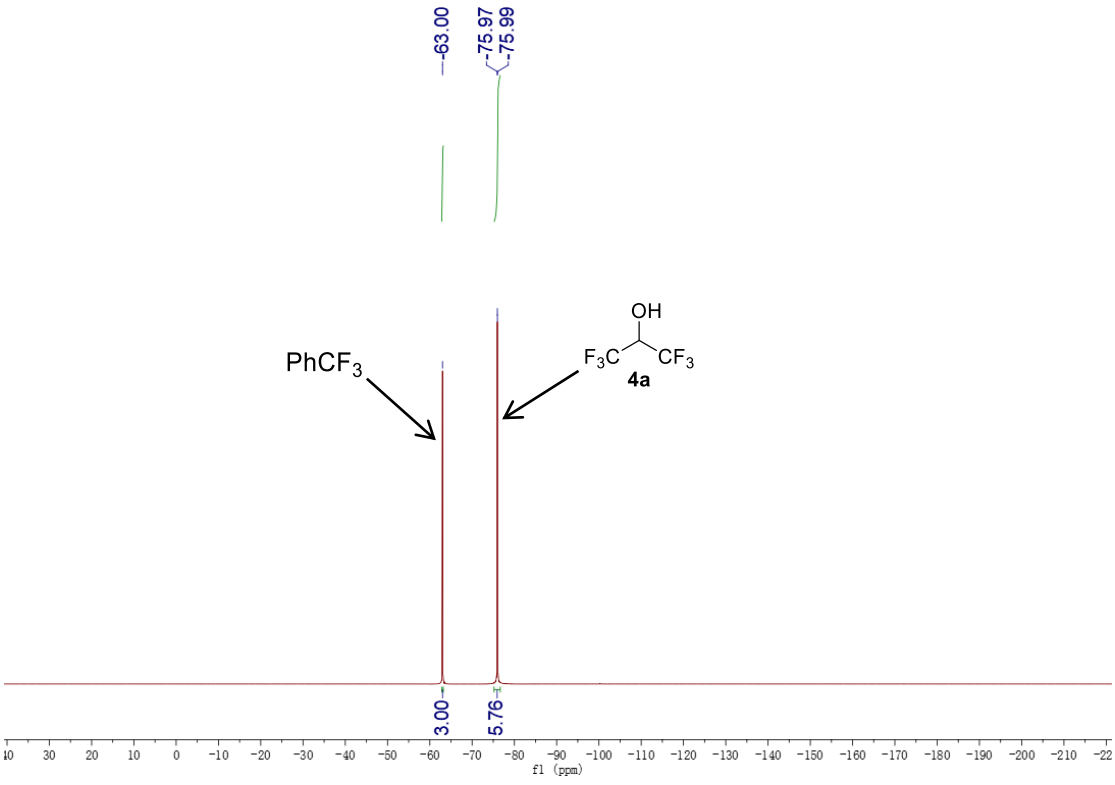


HPLC analysis of the above reaction mixture before adding $PhCF_3$ (λ = 243 nm, water/methanol (v/v) = 10:90))

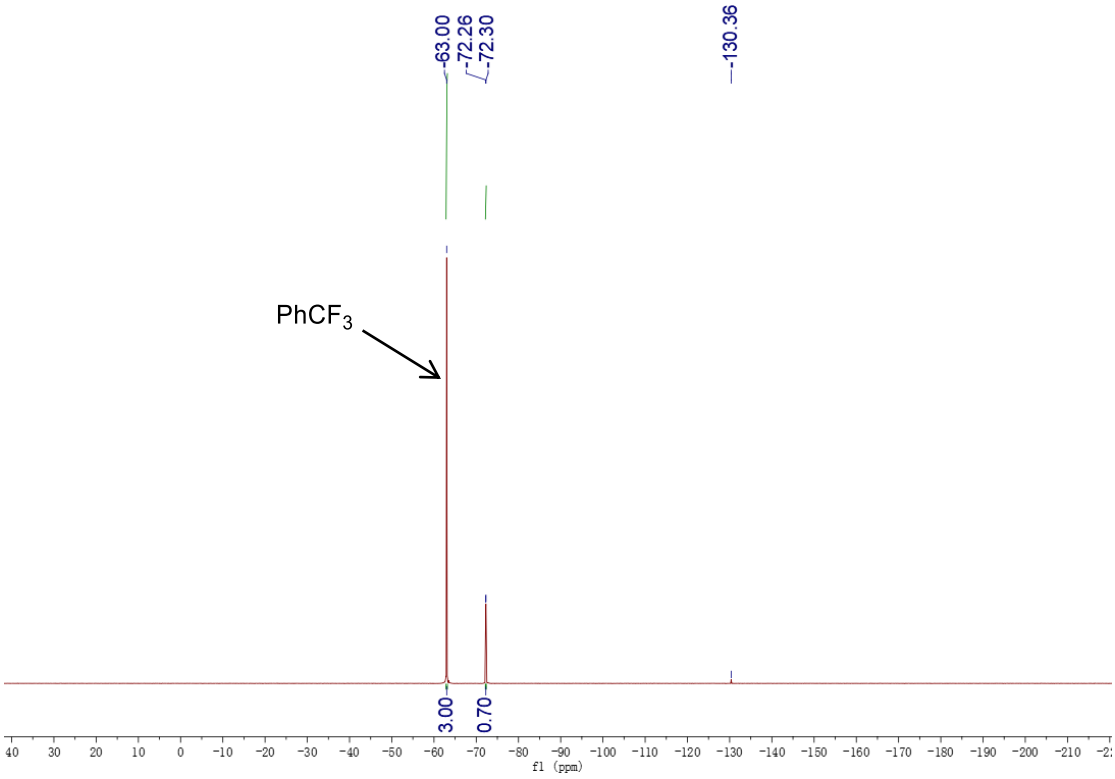


6.6. ^{19}F NMR spectrum of a solution of 4a (0.2 mmol) in CH_2Cl_2 (1 ml) that was maintained at room temperature for 2 hours using $PhCF_3$ (0.2 mmol) as an internal standard.

Note: The signals in the ^{19}F NMR spectrum were assigned according to the data reported in the literature.[16]



6.7. ^{19}F NMR spectrum of a solution of $CF_3SO_3CF_3$ (0.2 mmol) and Et_3N (0.2 mmol) in CH_2Cl_2 (1 mL) that was maintained at room temperature for 2 hours using $PhCF_3$ (0.2 mmol) as an internal standard.



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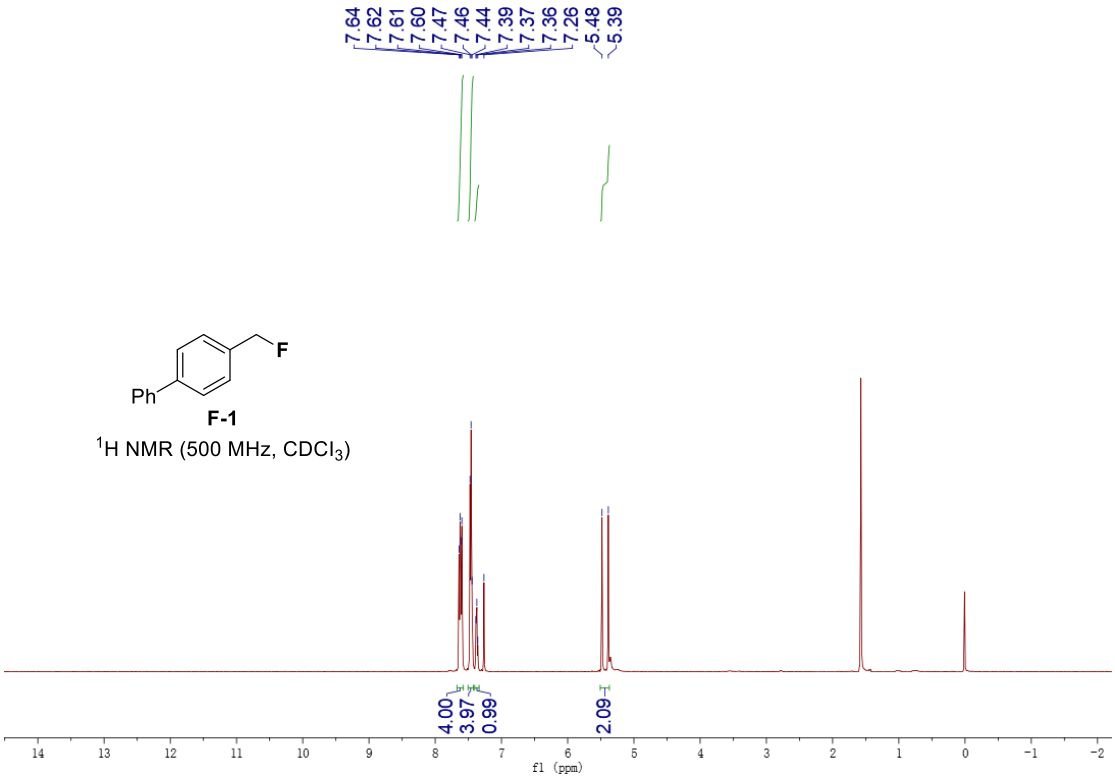
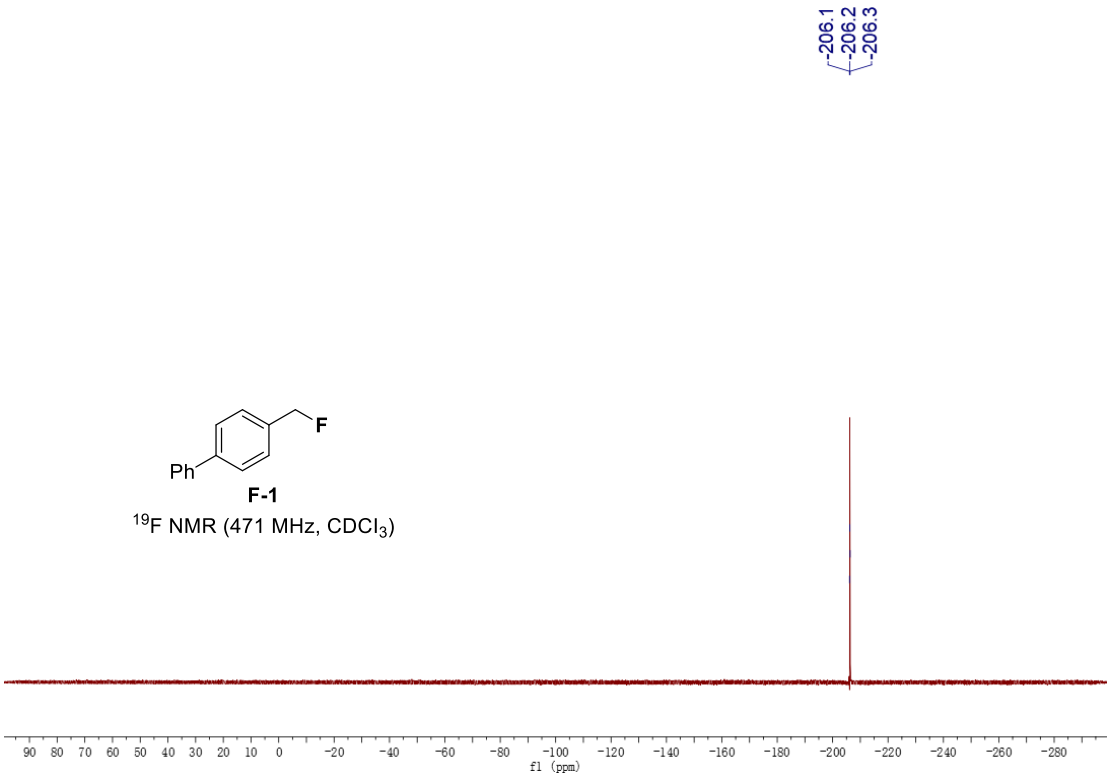
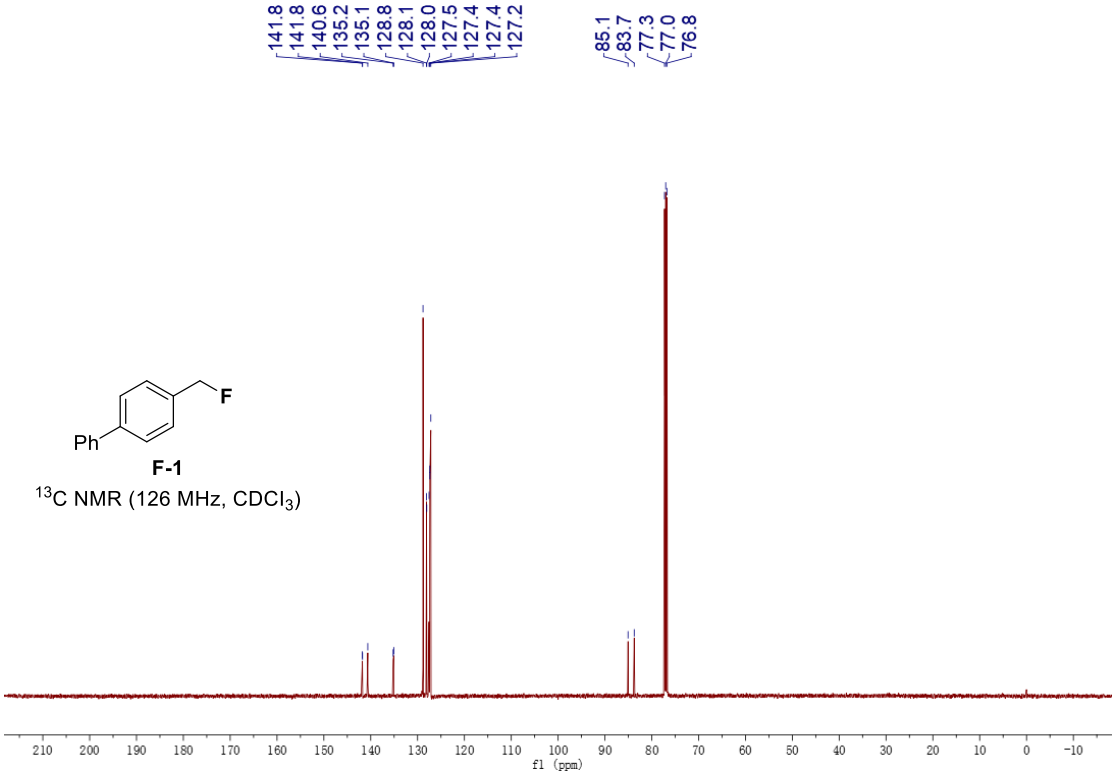
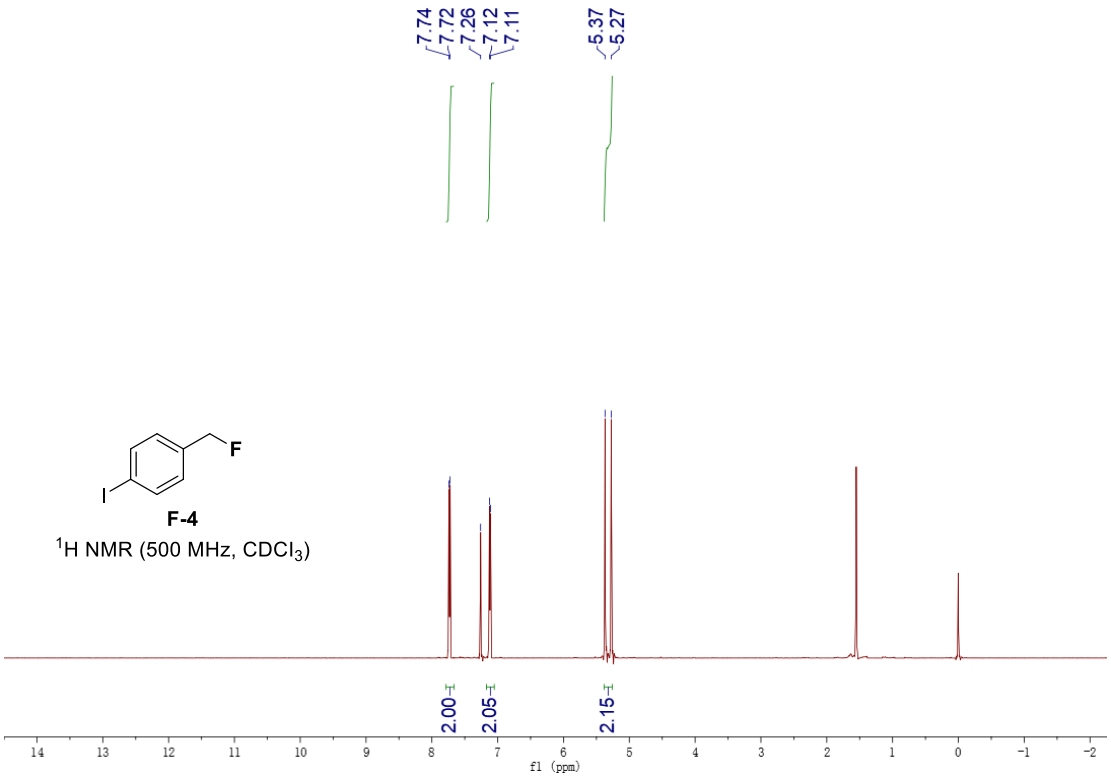
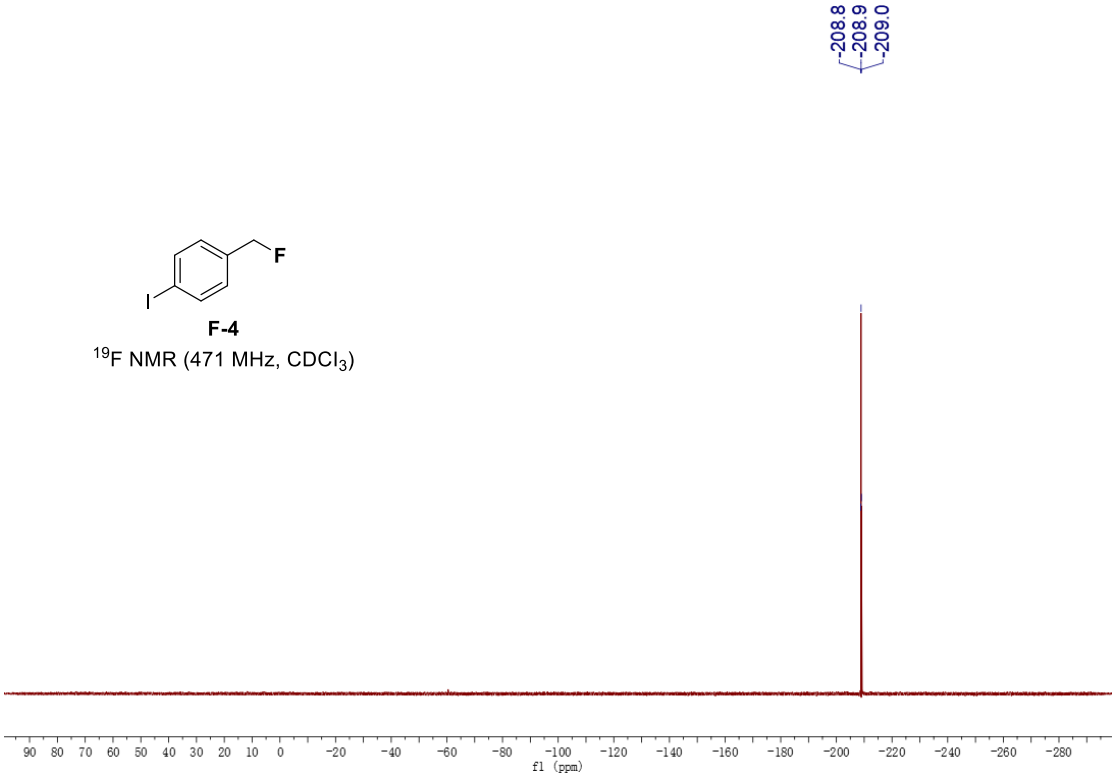
7. NMR spectra of the products.





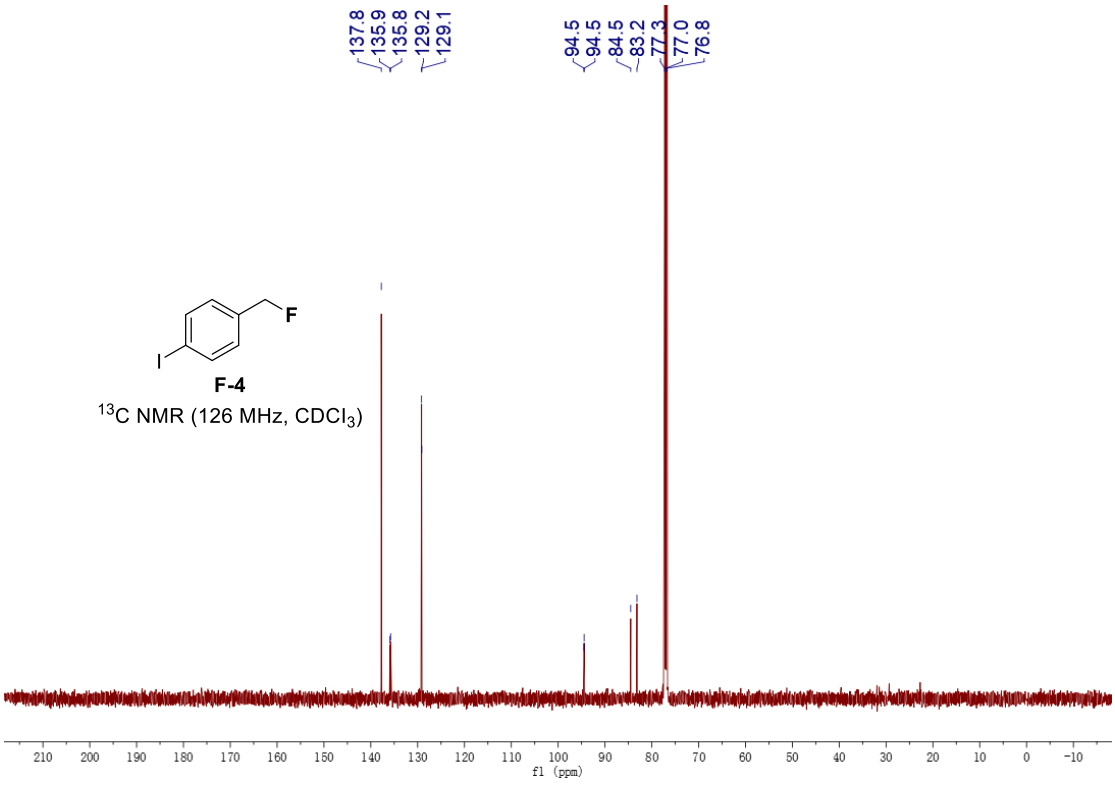

141.8
141.8
140.6
135.2
135.1
128.8
128.1
128.0
127.5
127.4
127.4
127.2
85.1
83.7
77.3
77.0
76.8
F
Ph
F-1
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.74
7.72
7.26
7.12
7.11
5.37
5.27
F
I
F-4
1H NMR (500 MHz, CDCl3)
2.00
2.05
2.15
f1 (ppm)



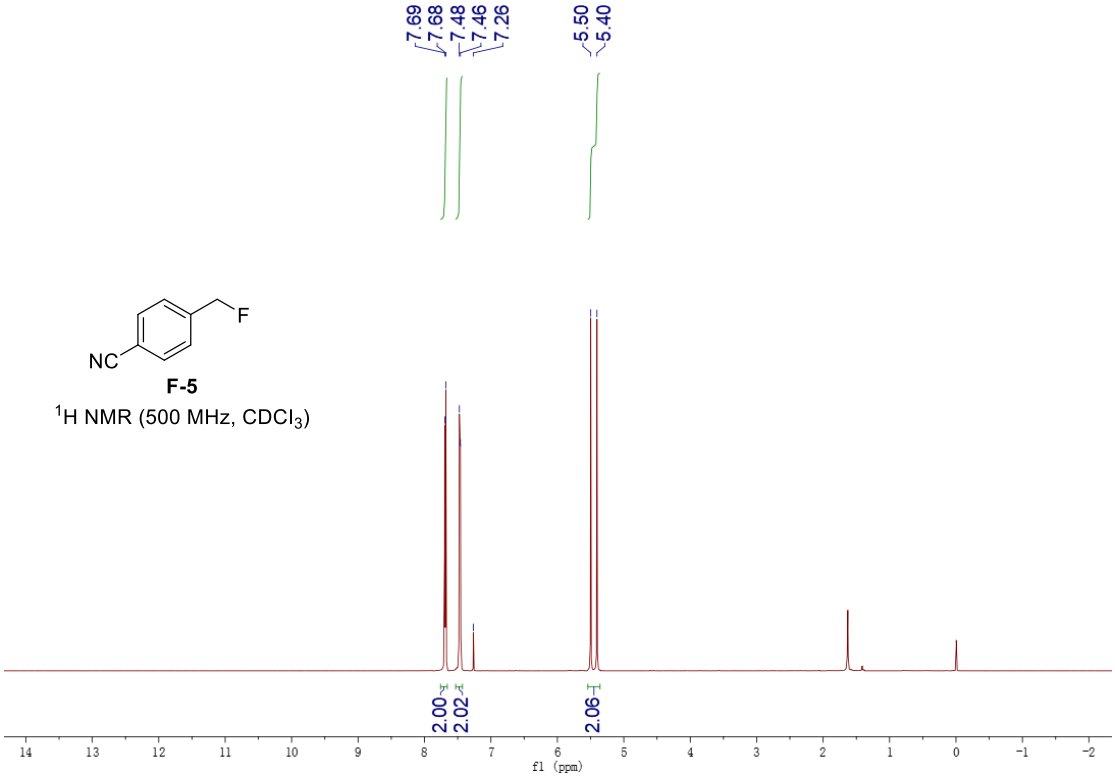
F-4

^{19}F NMR (471 MHz, $CDCl_3$)



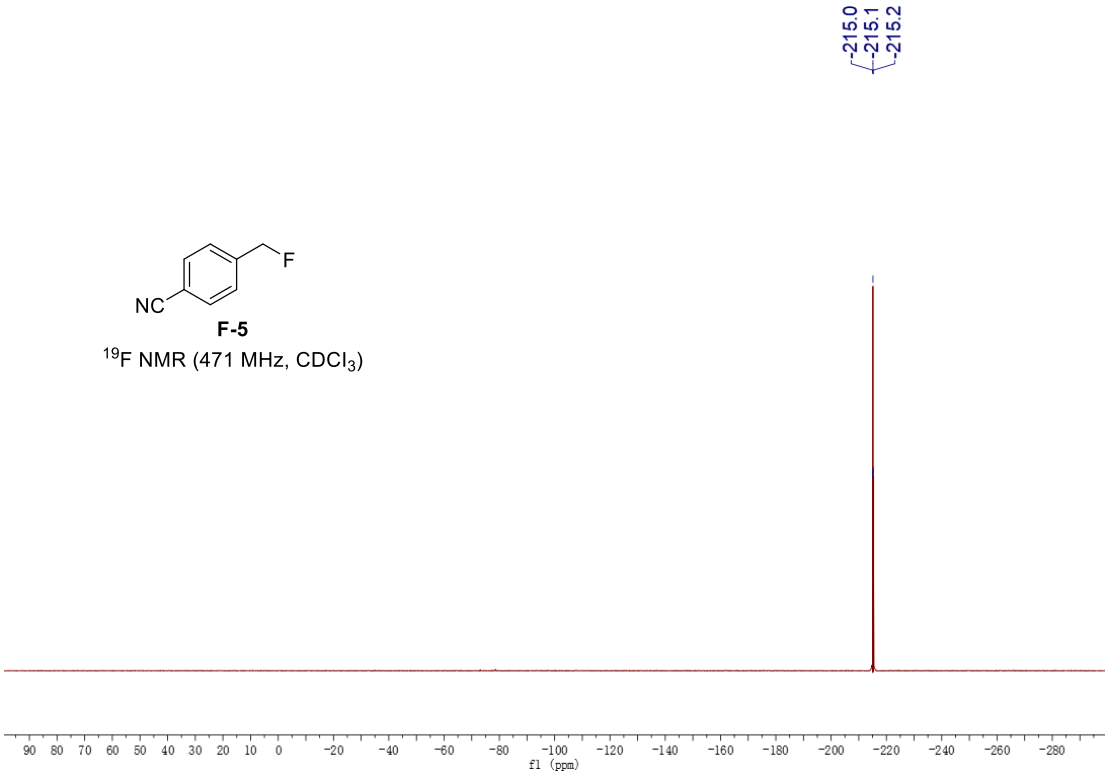
F-4

^{13}C NMR (126 MHz, $CDCl_3$)



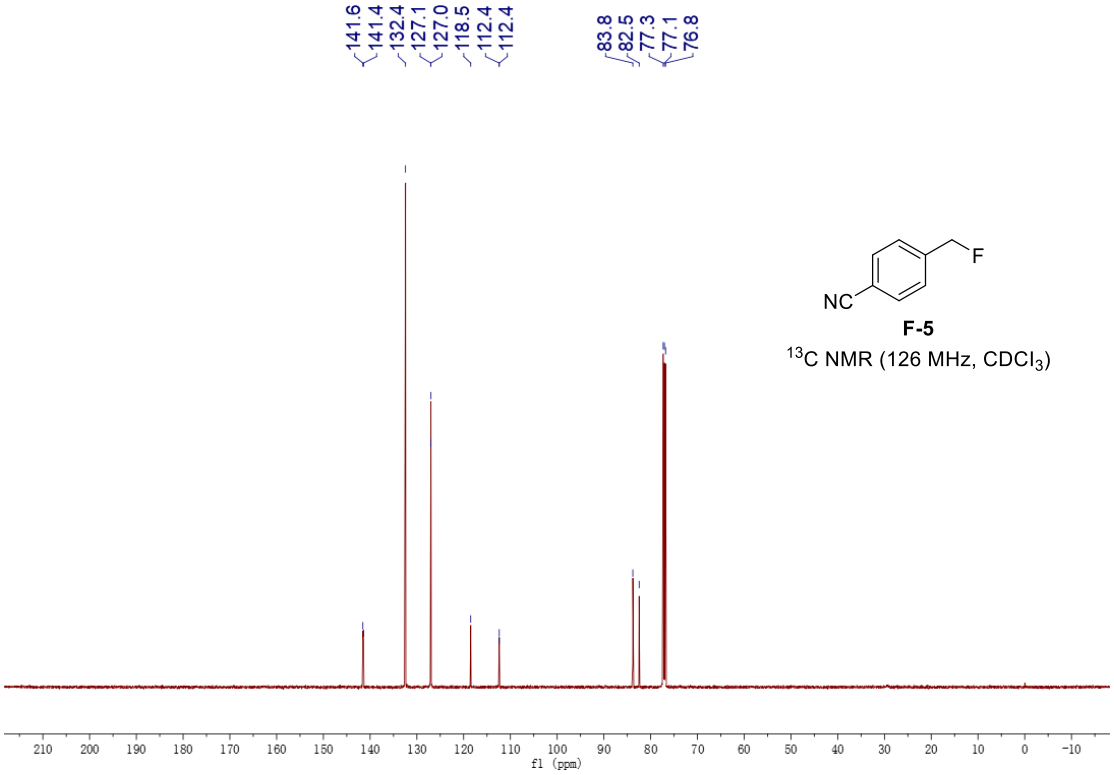
F-5

^{1}H NMR (500 MHz, $CDCl_3$)



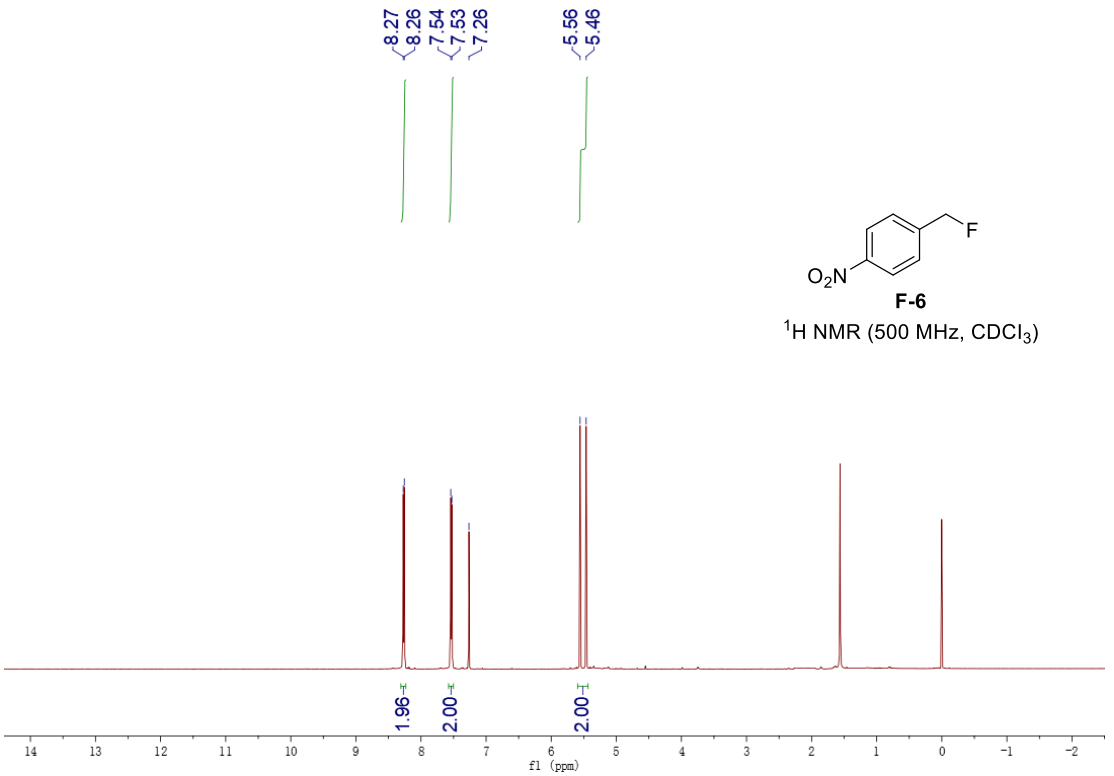
F-5

^{19}F NMR (471 MHz, $CDCl_3$)



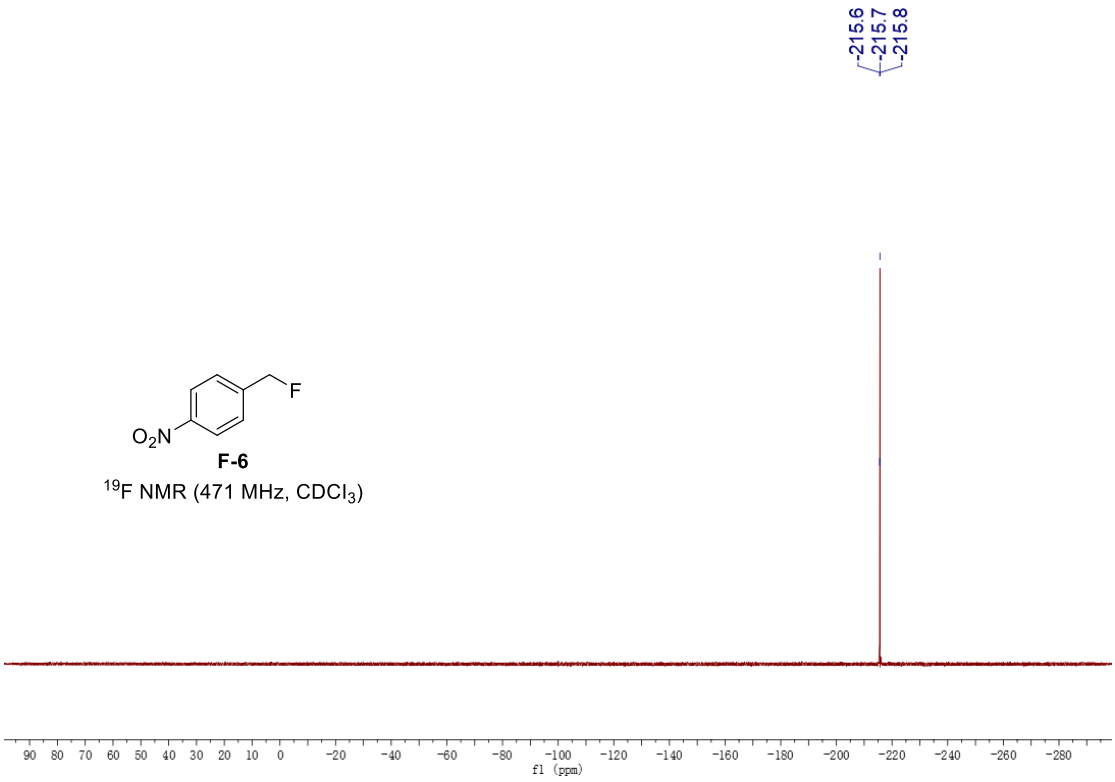
F-5

^{13}C NMR (126 MHz, $CDCl_3$)



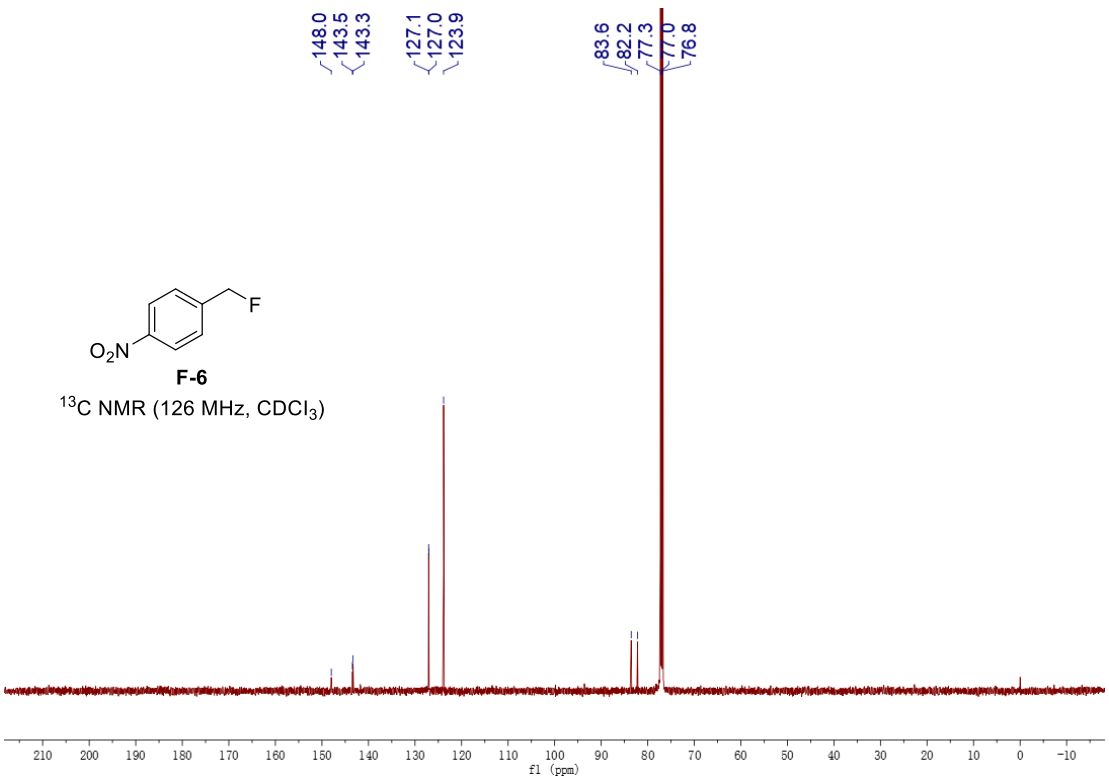
F-6

^{1}H NMR (500 MHz, $CDCl_3$)



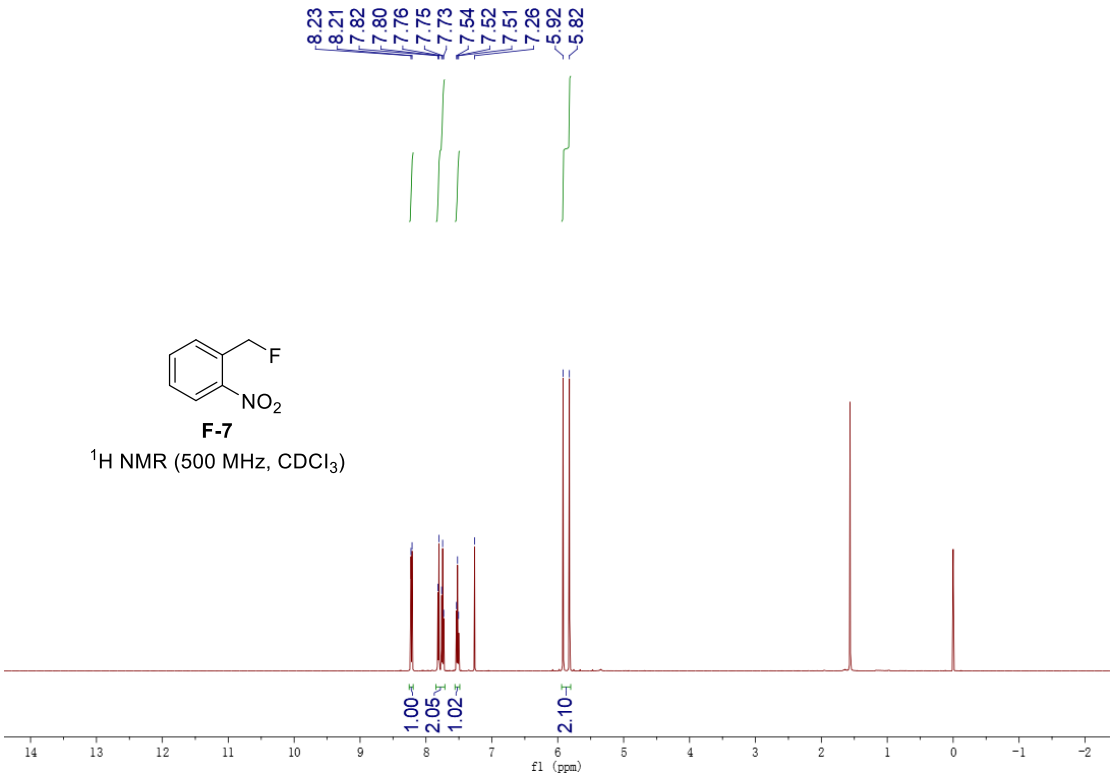
F-6

^{19}F NMR (471 MHz, $CDCl_3$)



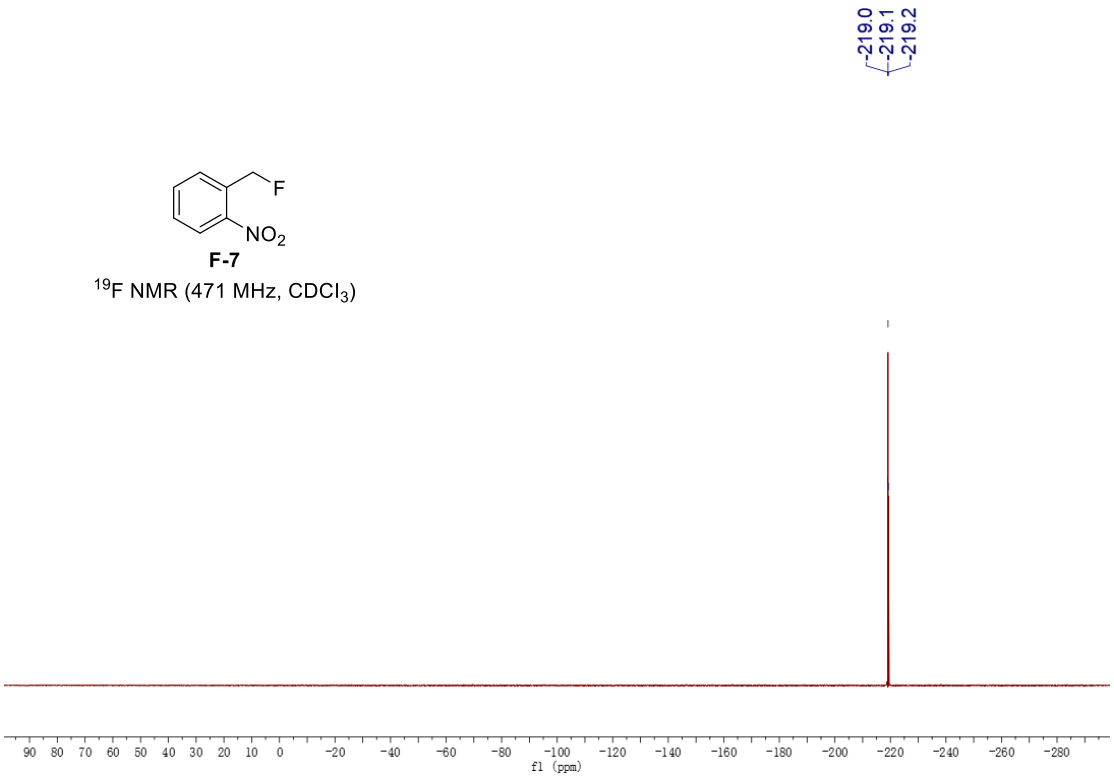
F-6

^{13}C NMR (126 MHz, $CDCl_3$)



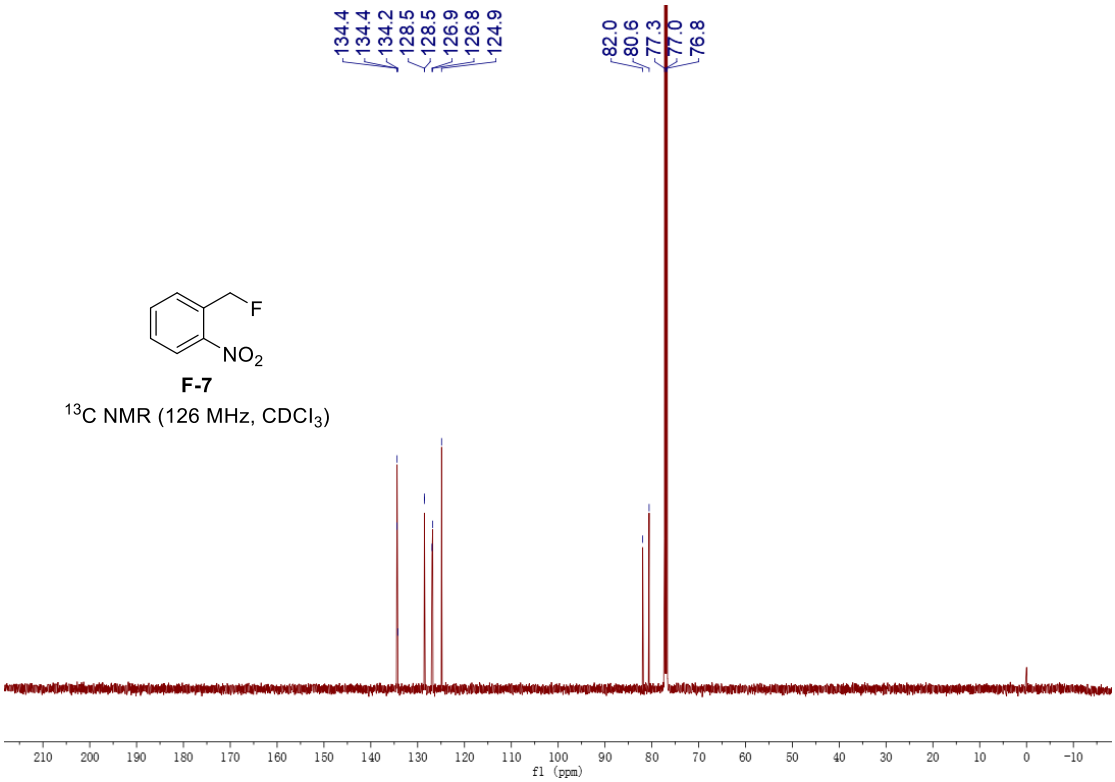
F-7

^{1}H NMR (500 MHz, $CDCl_3$)



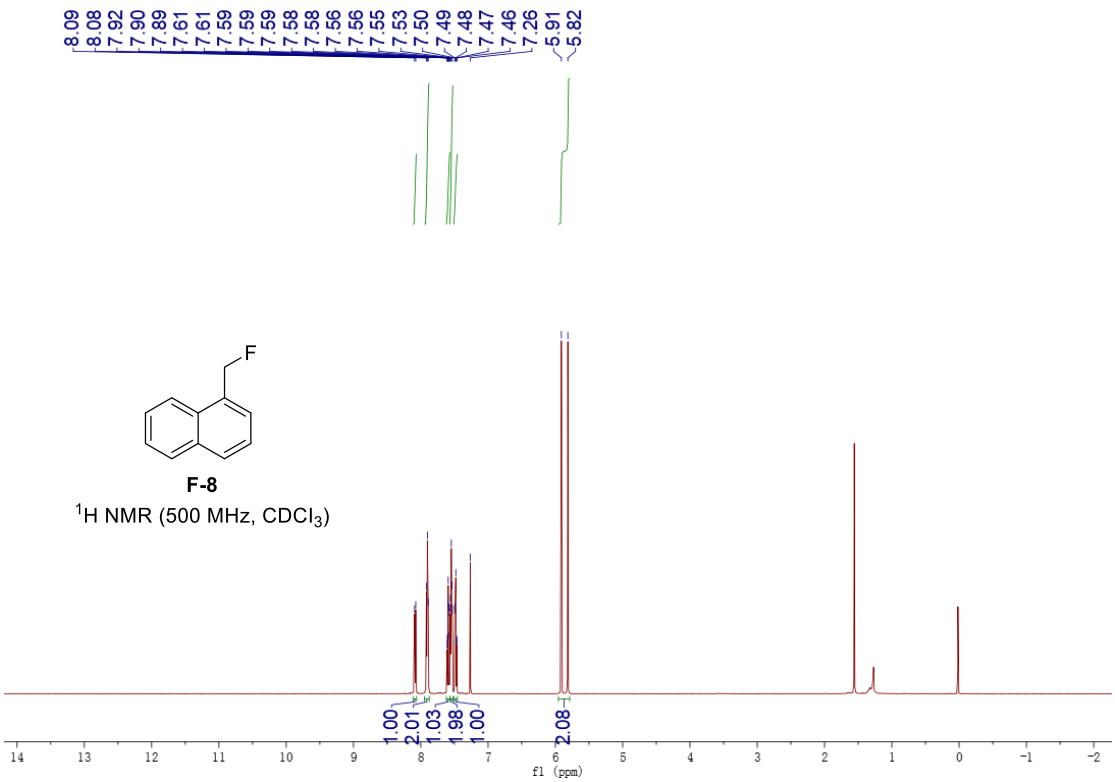
F-7

^{19}F NMR (471 MHz, $CDCl_3$)



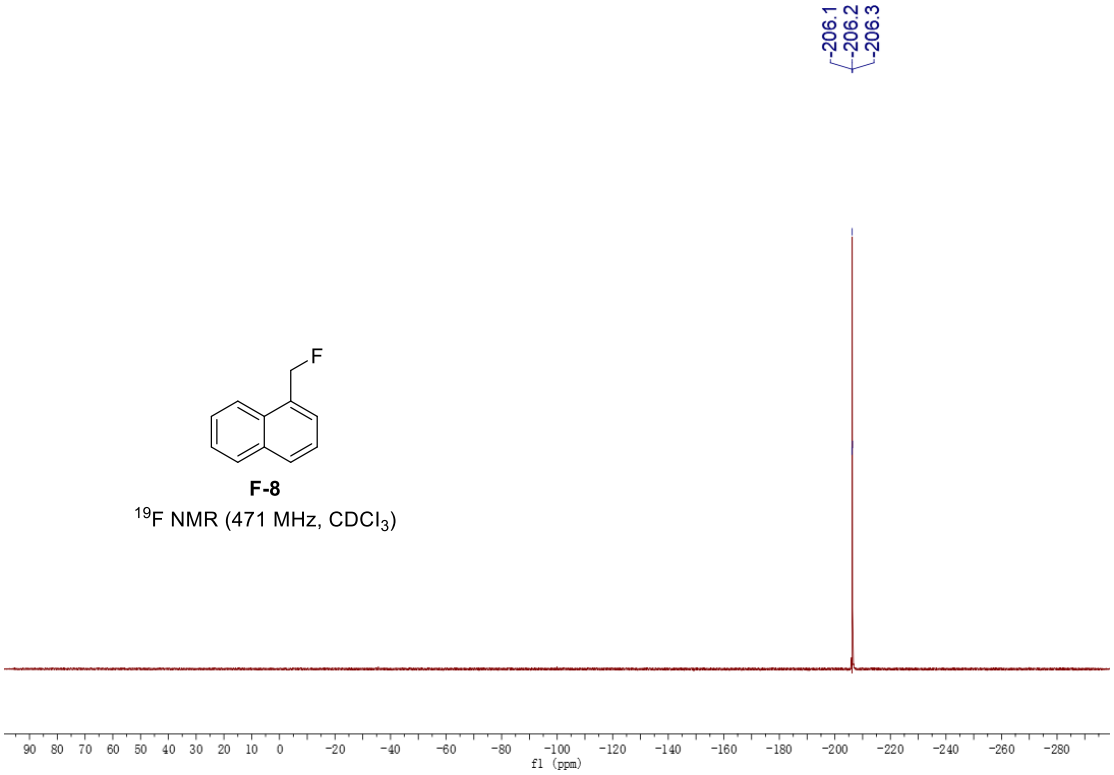
F-7

^{13}C NMR (126 MHz, $CDCl_3$)



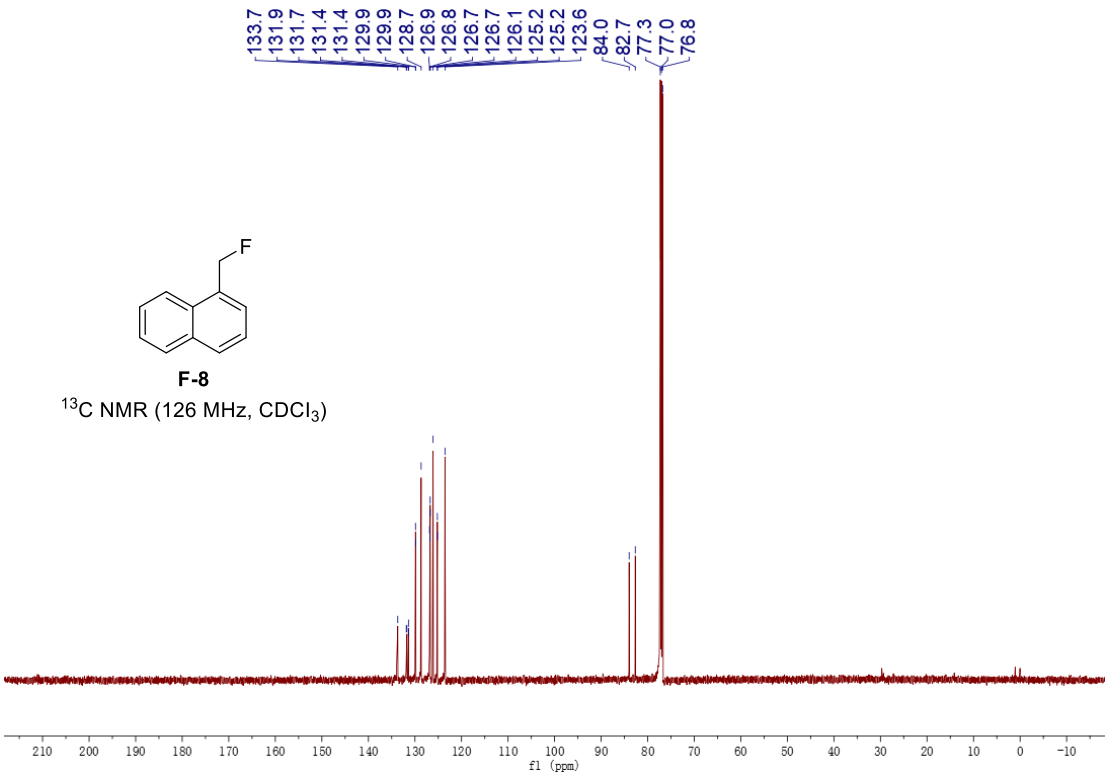
F-8

^{1}H NMR (500 MHz, $CDCl_3$)



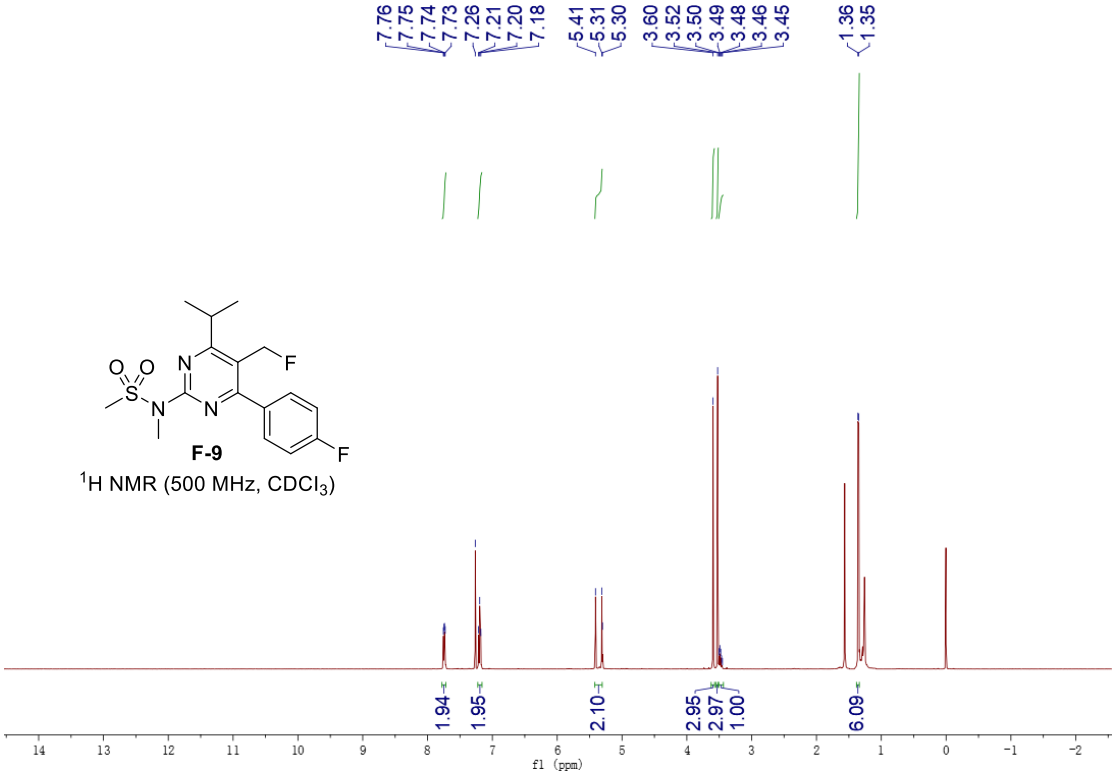
F-8

^{19}F NMR (471 MHz, $CDCl_3$)



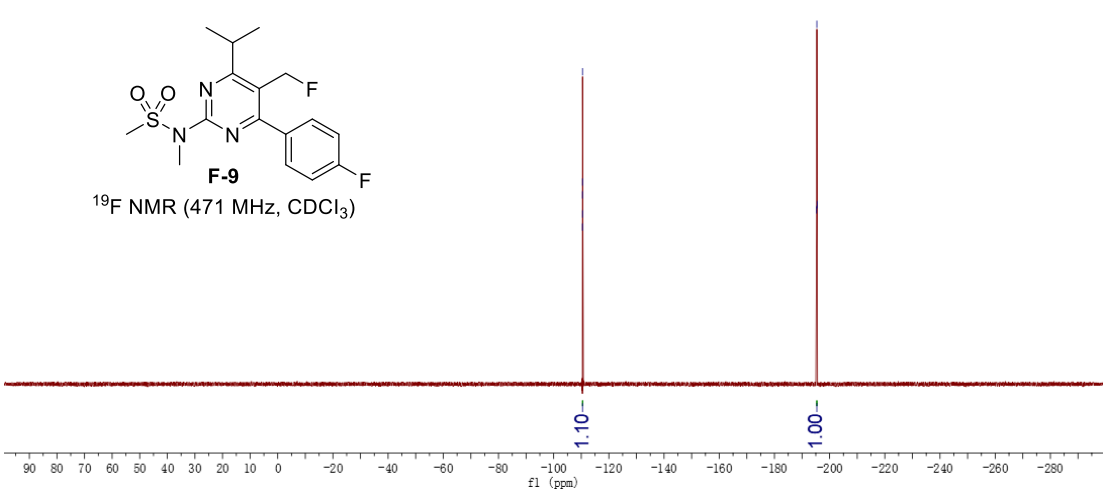
F-8

^{13}C NMR (126 MHz, $CDCl_3$)



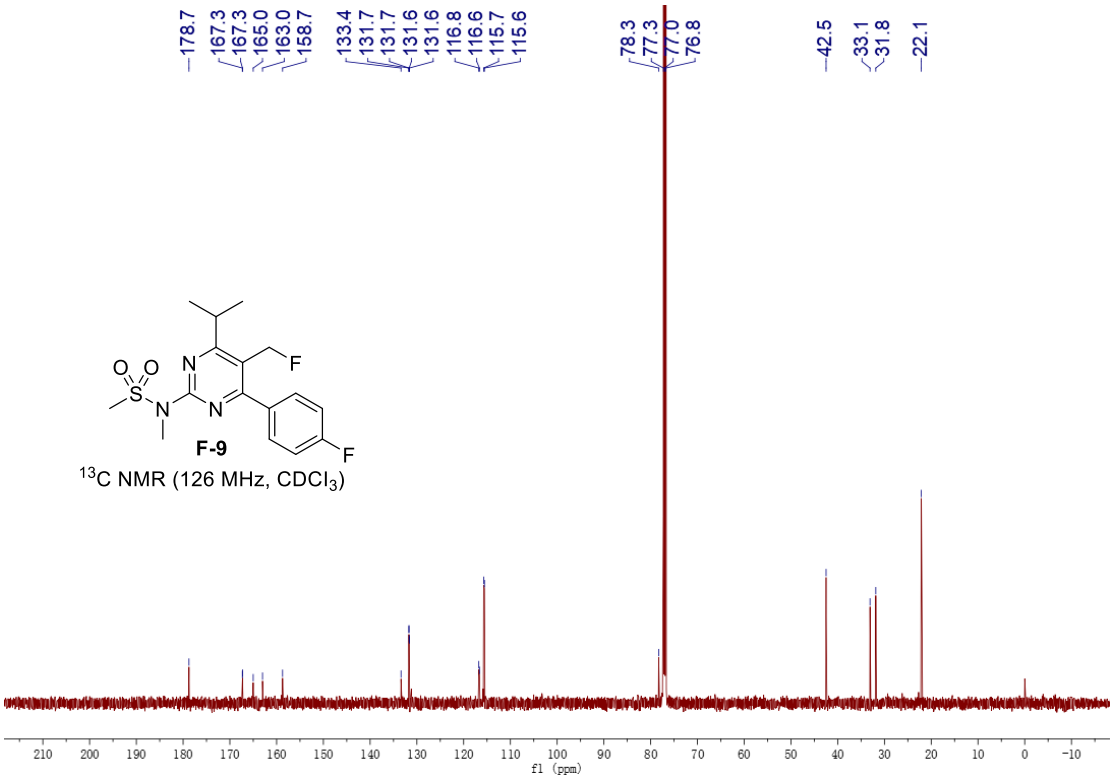
F-9

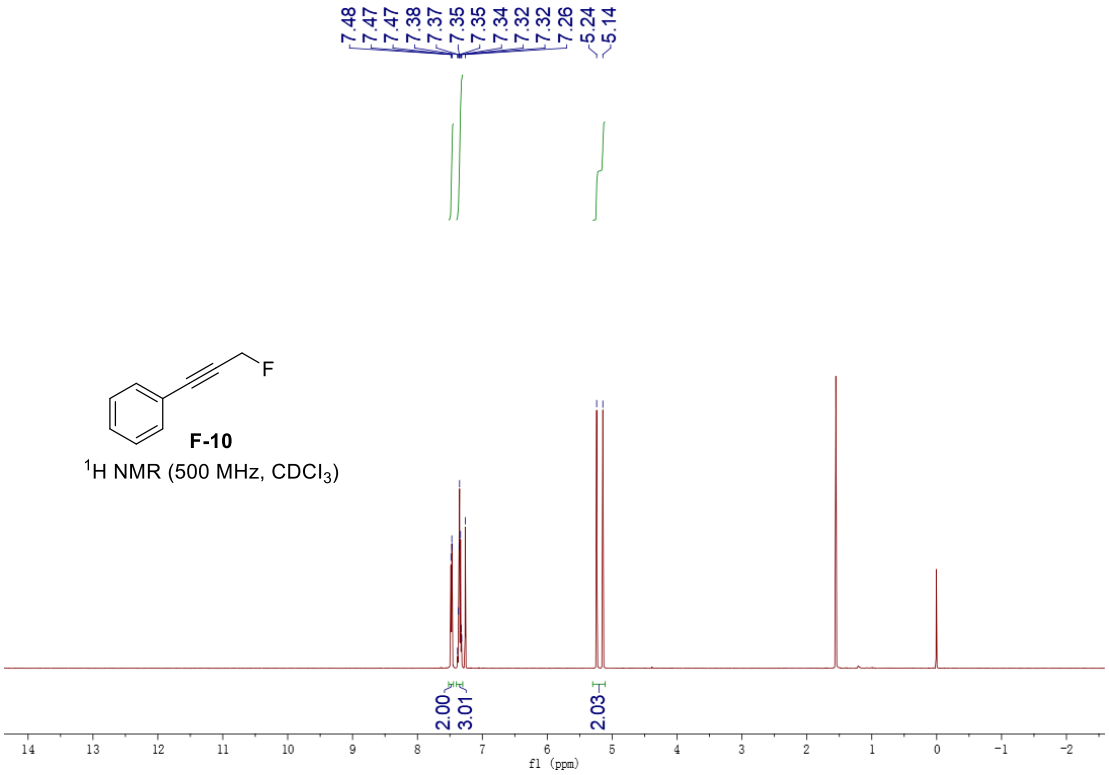
^{1}H NMR (500 MHz, $CDCl_3$)

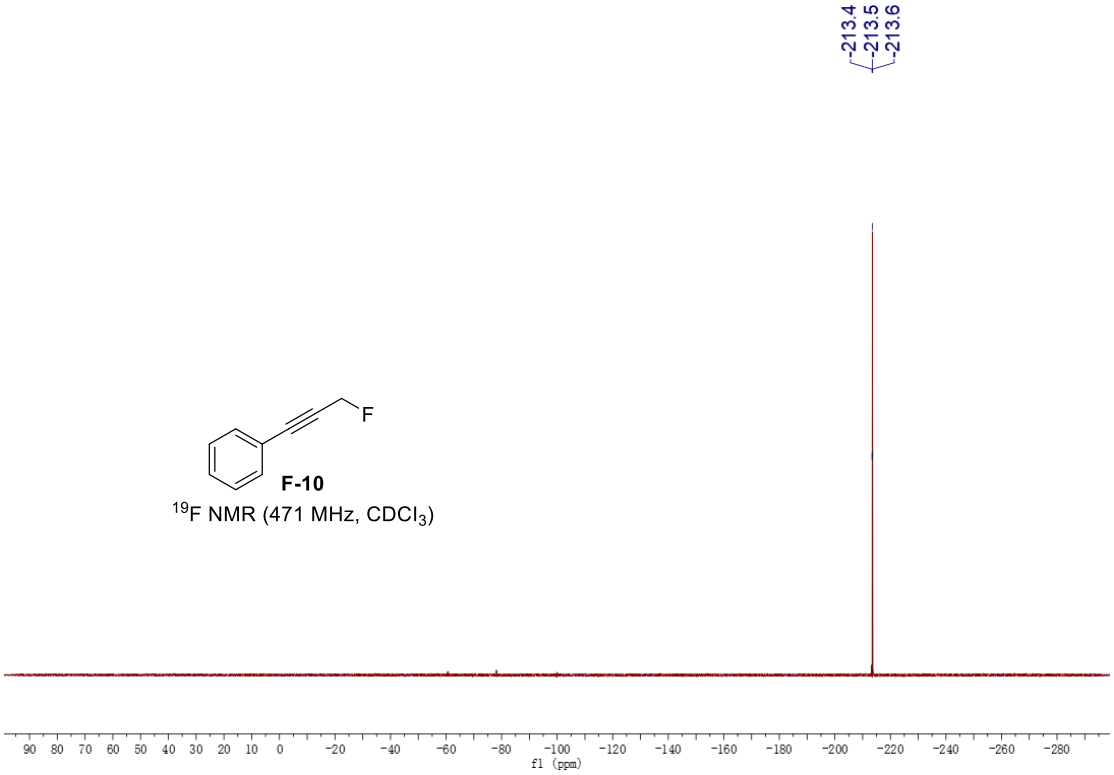


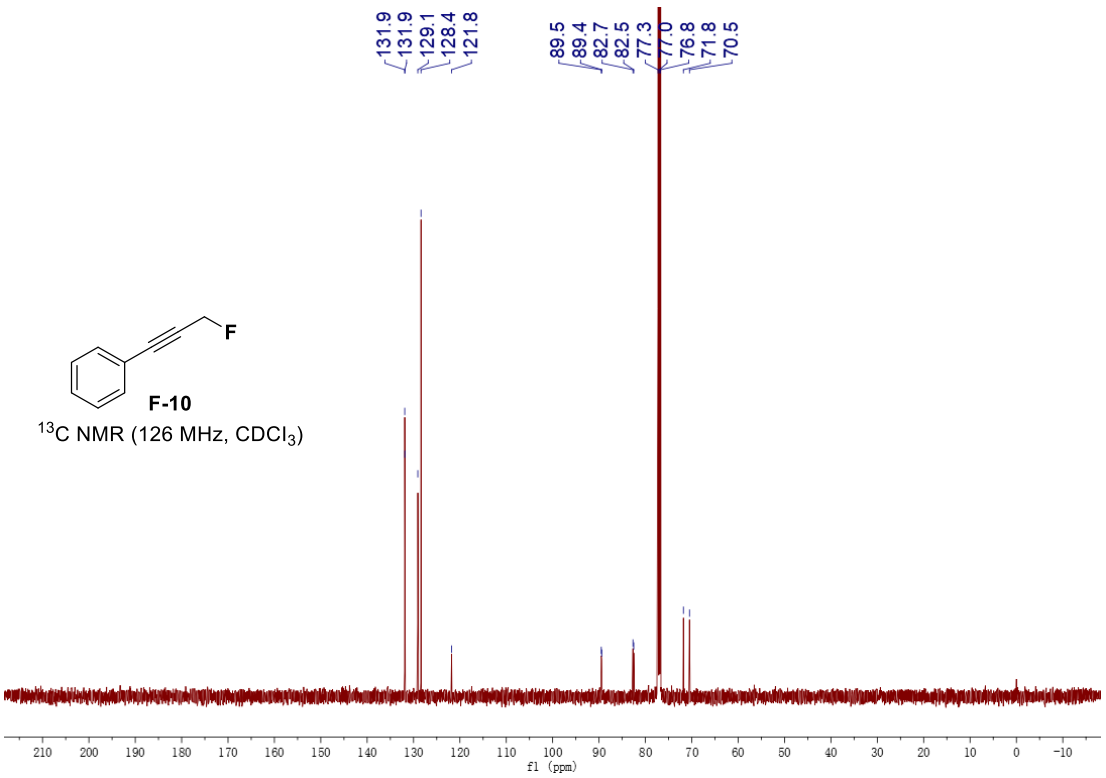
F-9

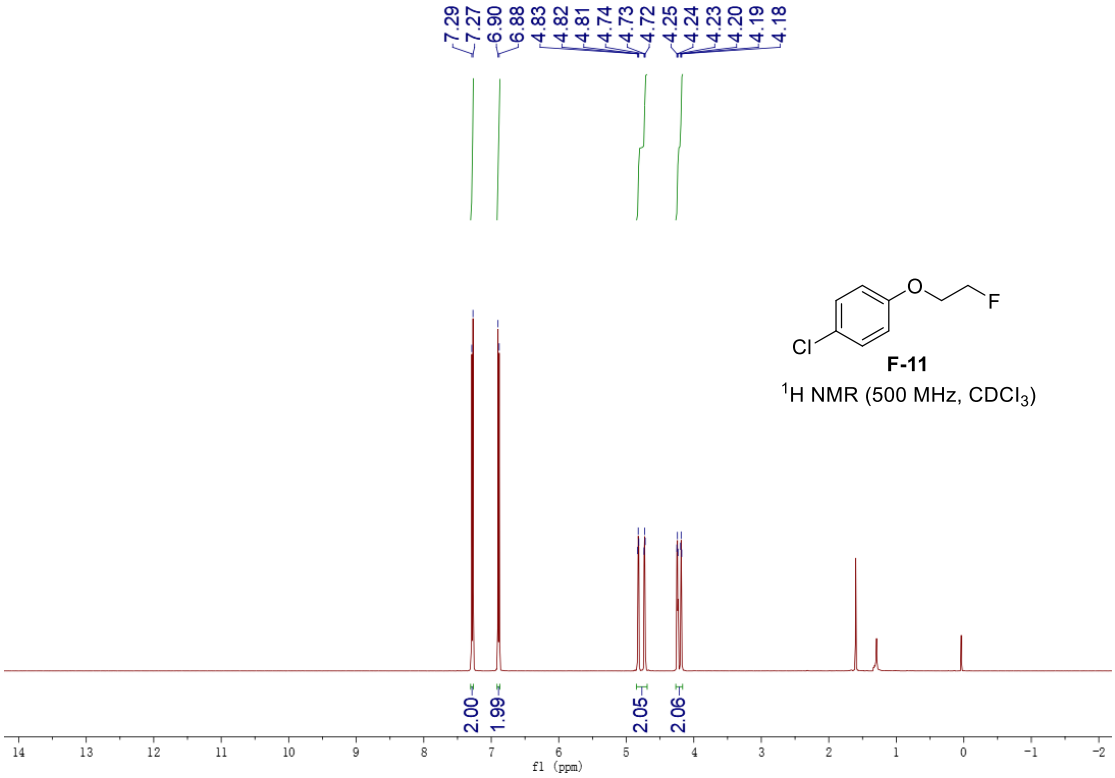
^{19}F NMR (471 MHz, $CDCl_3$)


178.7
167.3
167.3
165.0
163.0
158.7
133.4
131.7
131.7
131.6
131.6
116.8
116.6
115.7
115.6
78.3
77.3
77.0
76.8
42.5
33.1
31.8
22.1
F
F
F-9
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.48
7.47
7.47
7.38
7.37
7.35
7.35
7.34
7.32
7.32
7.26
5.24
5.14
F
F-10
1H NMR (500 MHz, CDCl3)
2.00
3.01
2.03
f1 (ppm)

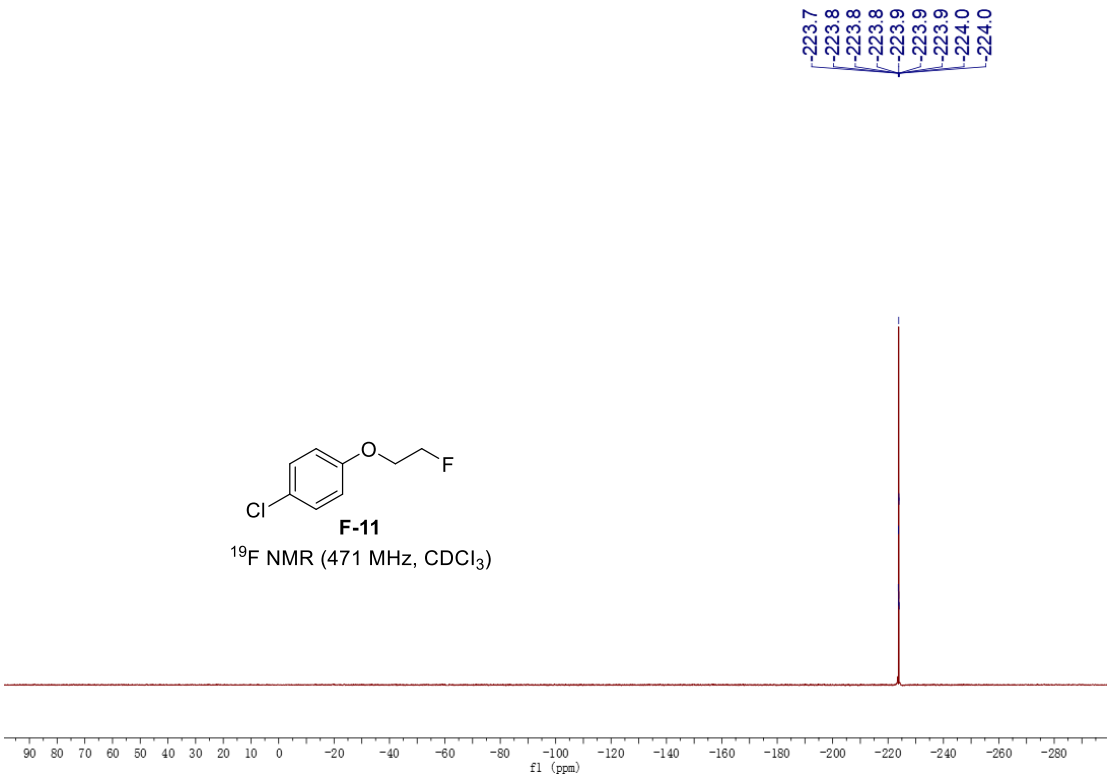

-213.4
-213.5
-213.6
F
F-10
19F NMR (471 MHz, CDCl3)
f1 (ppm)


131.9
131.9
129.1
128.4
121.8
89.5
89.4
82.7
82.5
77.3
77.0
76.8
71.8
70.5
F
F-10
13C NMR (126 MHz, CDCl3)
f1 (ppm)



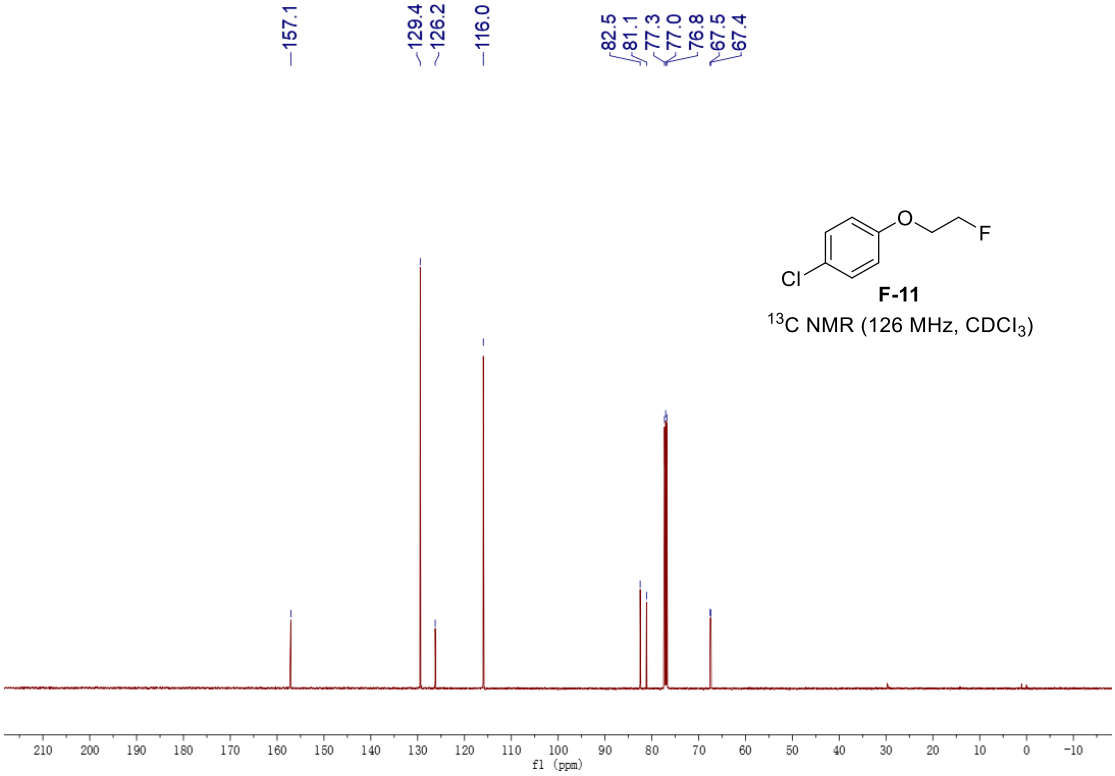
F-11

^{1}H NMR (500 MHz, $CDCl_3$)



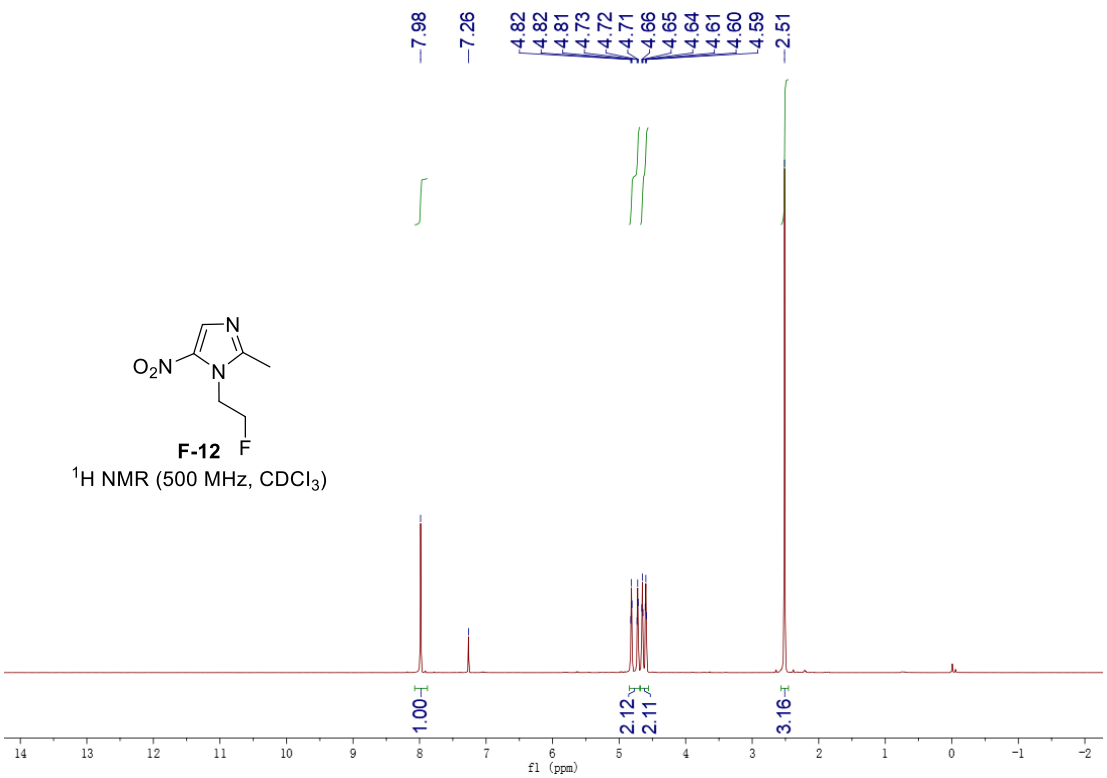
F-11

^{19}F NMR (471 MHz, $CDCl_3$)



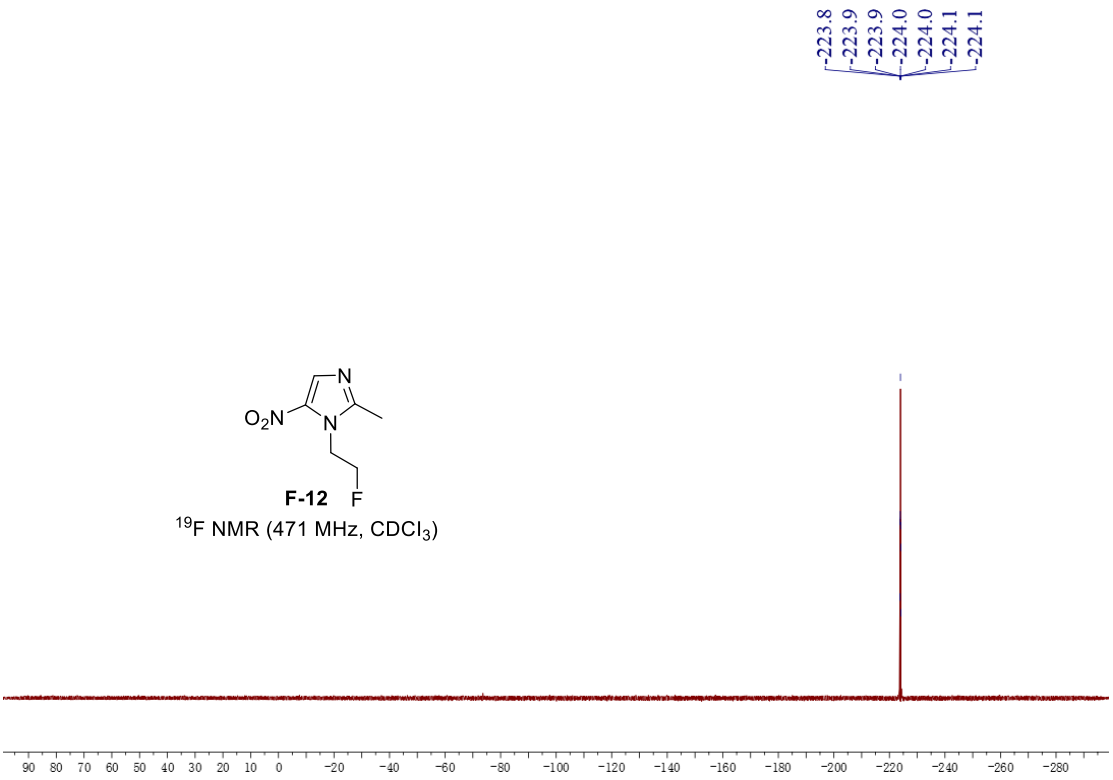
F-11

^{13}C NMR (126 MHz, $CDCl_3$)

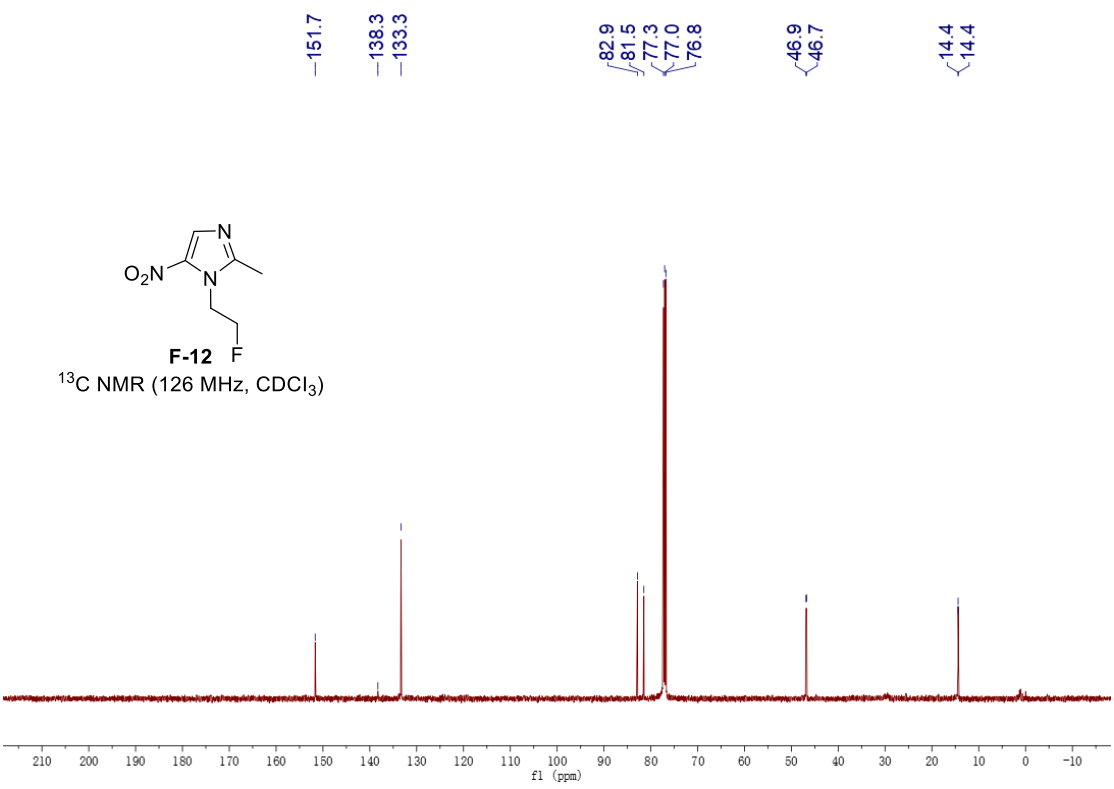


F-12

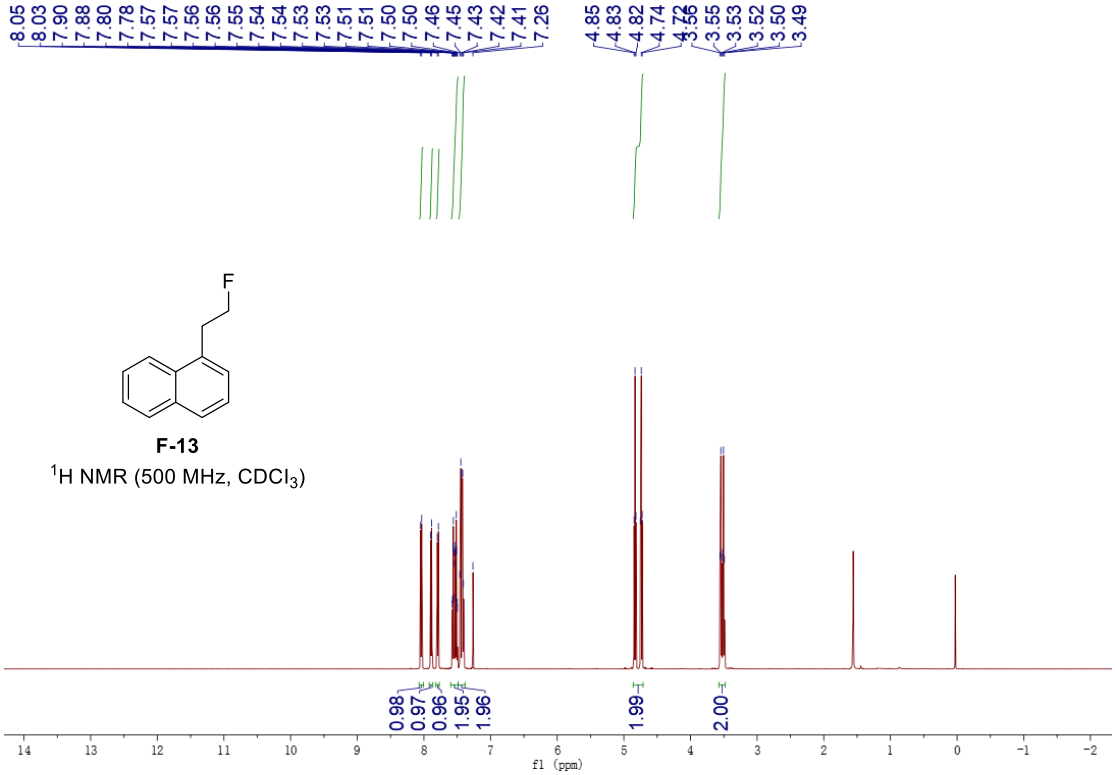
^{1}H NMR (500 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

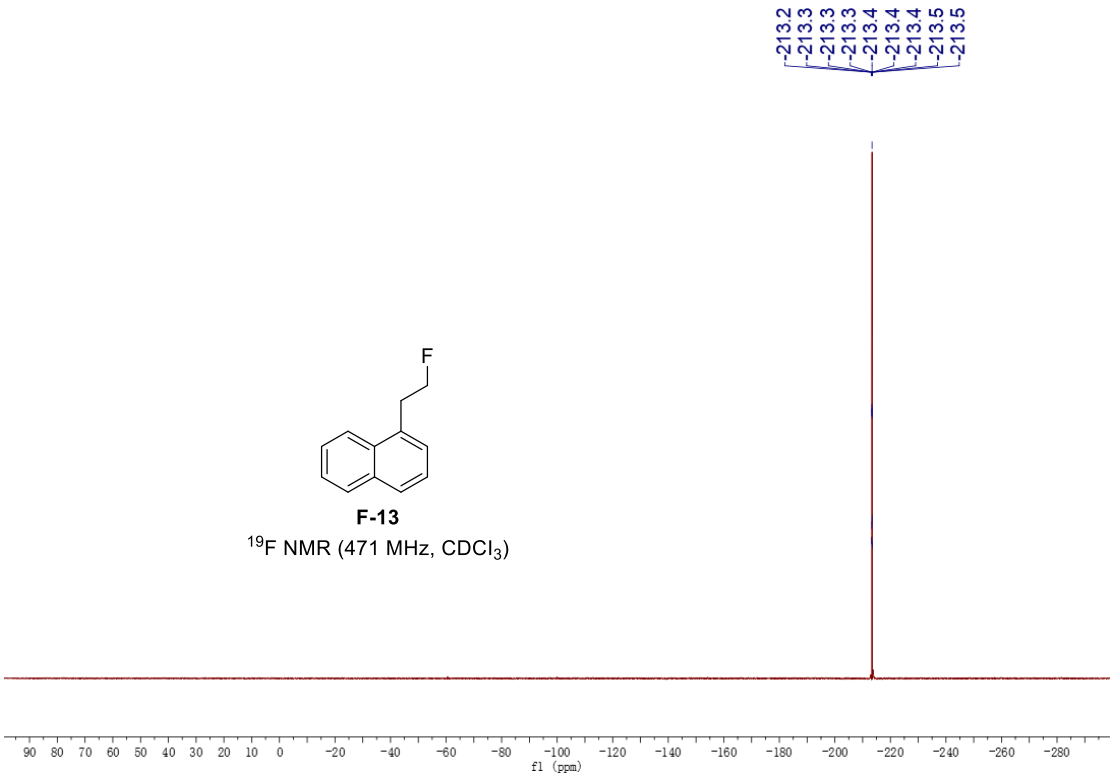


^{13}C NMR (126 MHz, $CDCl_3$)



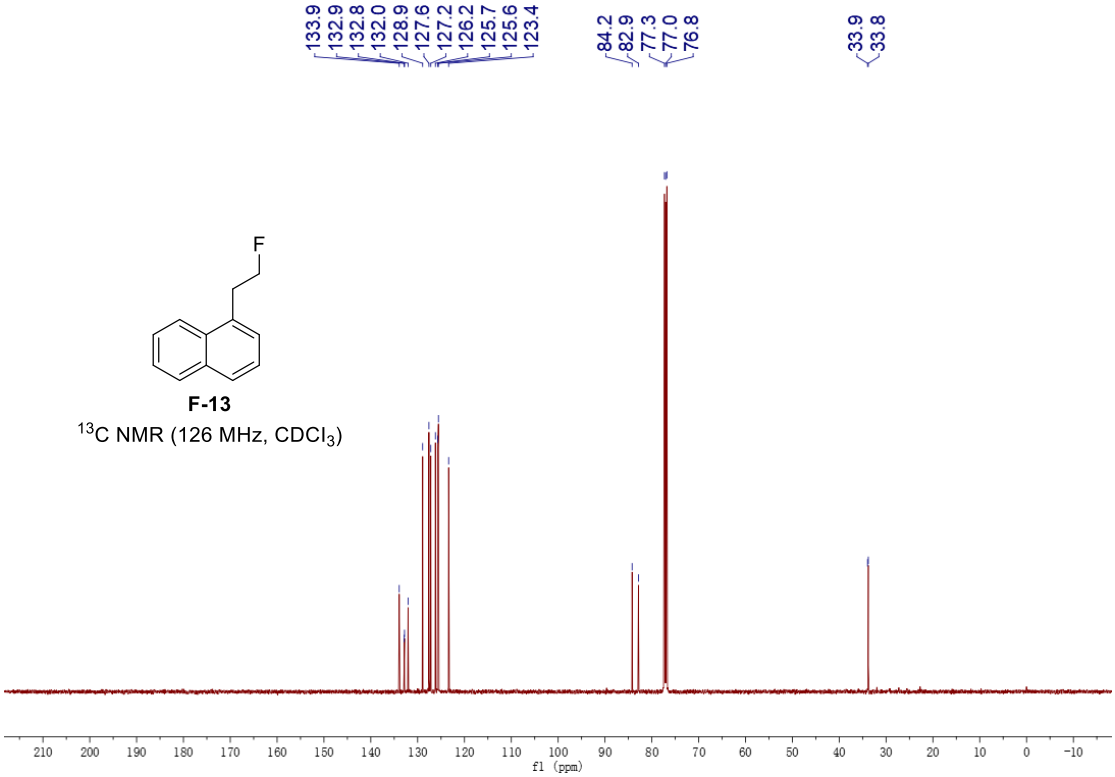
F-13

^{1}H NMR (500 MHz, $CDCl_3$)



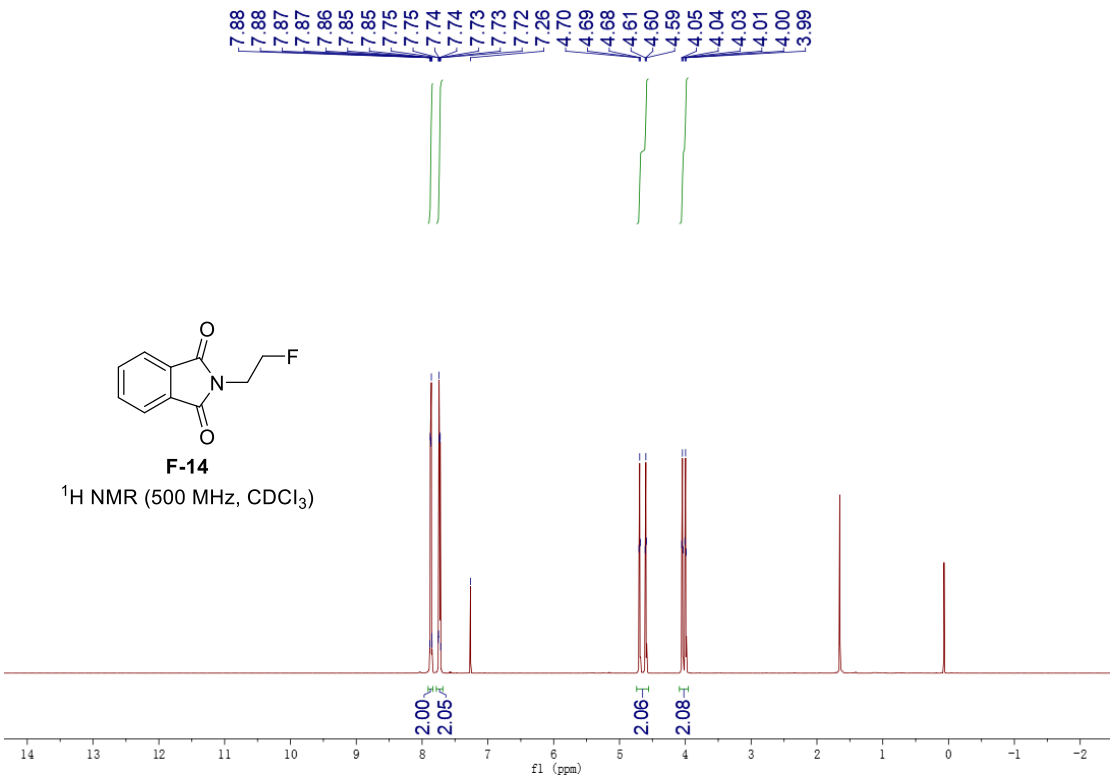
F-13

^{19}F NMR (471 MHz, $CDCl_3$)



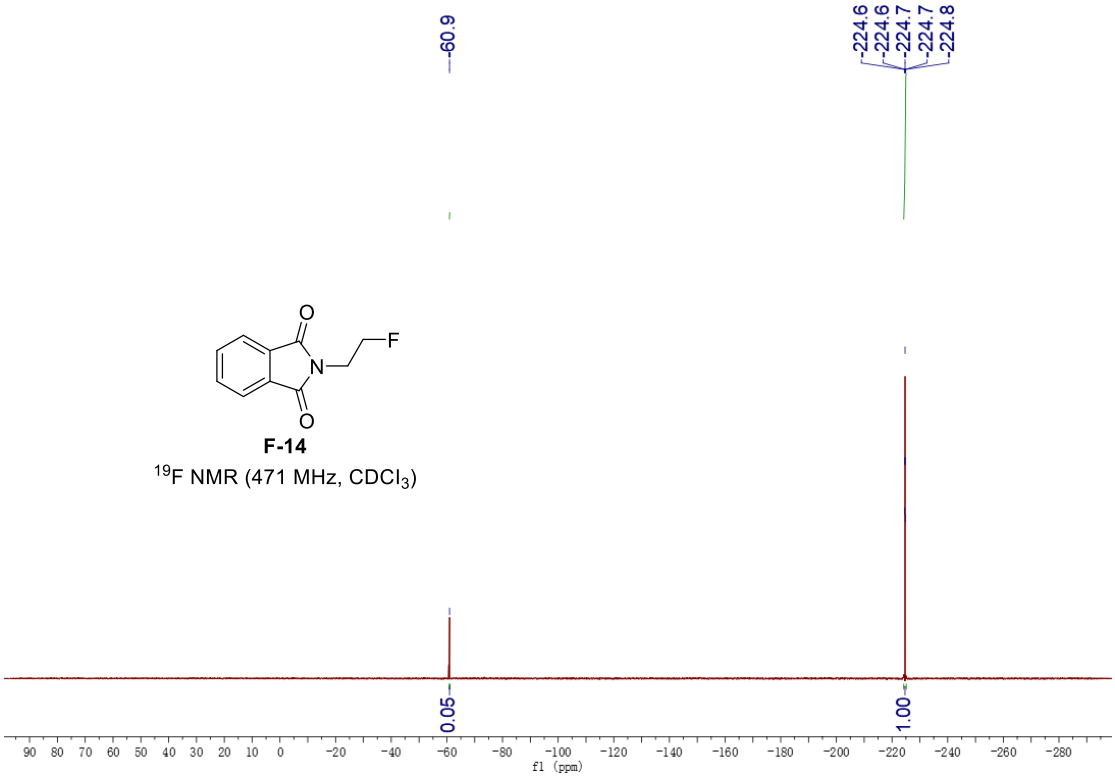
F-13

^{13}C NMR (126 MHz, $CDCl_3$)



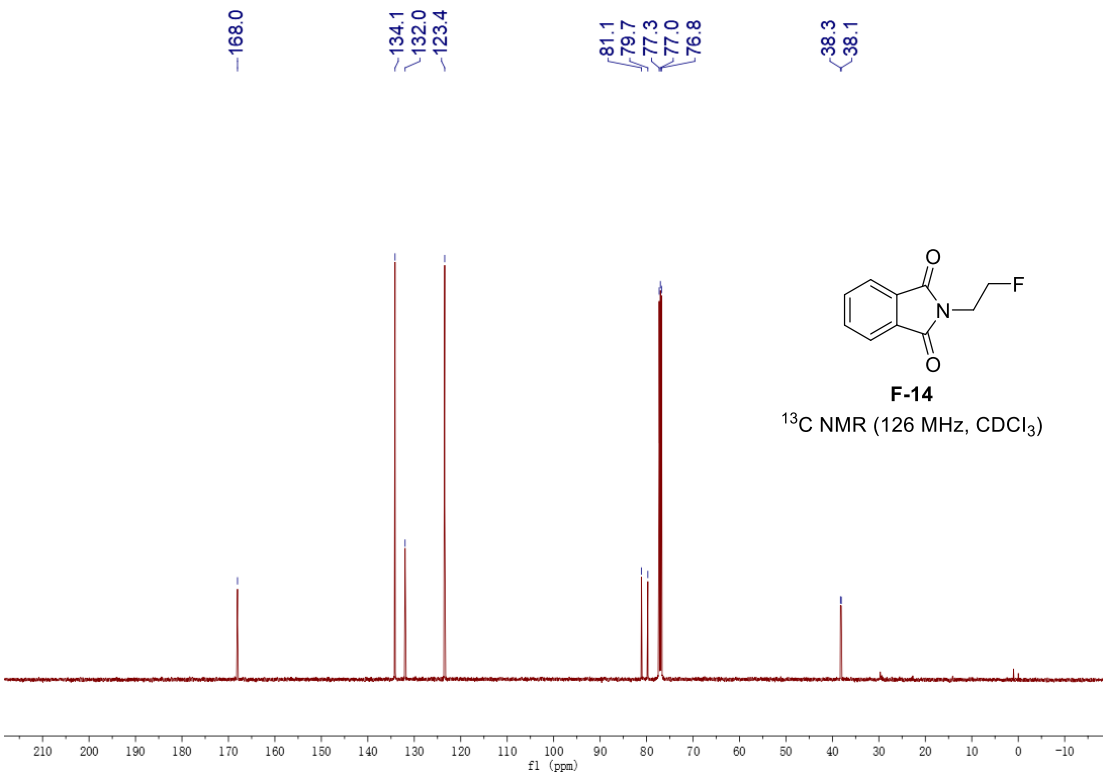
F-14

^{1}H NMR (500 MHz, $CDCl_3$)



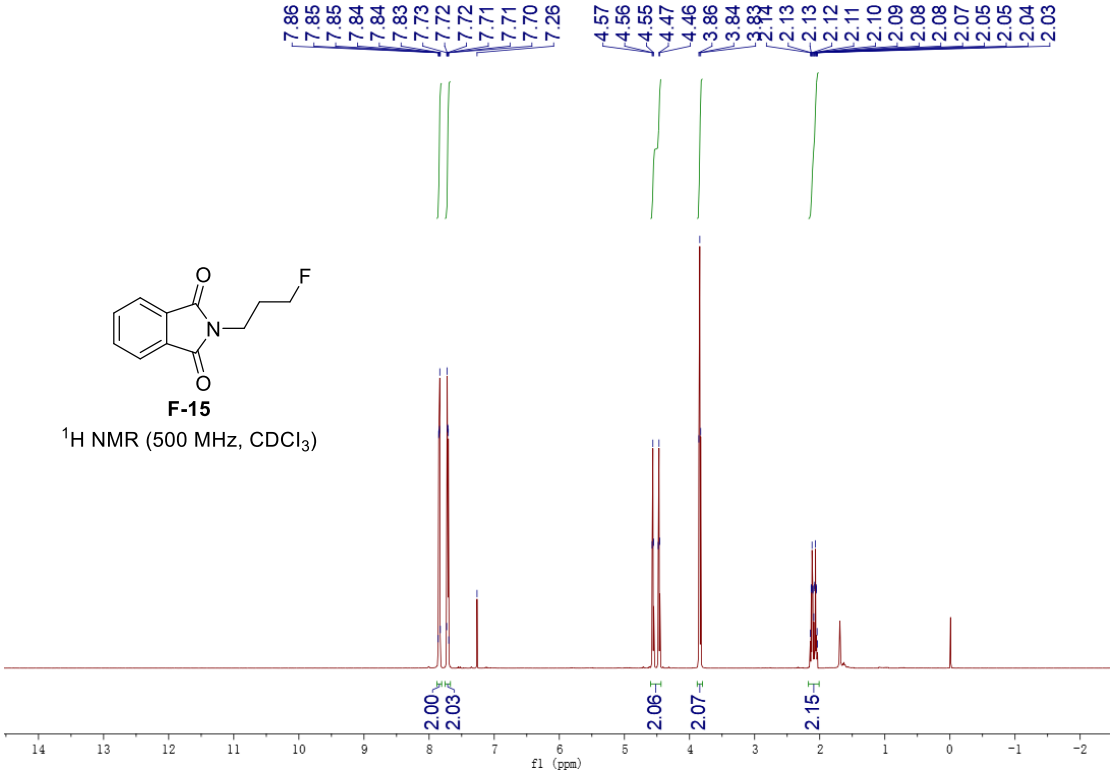
F-14

^{19}F NMR (471 MHz, $CDCl_3$)



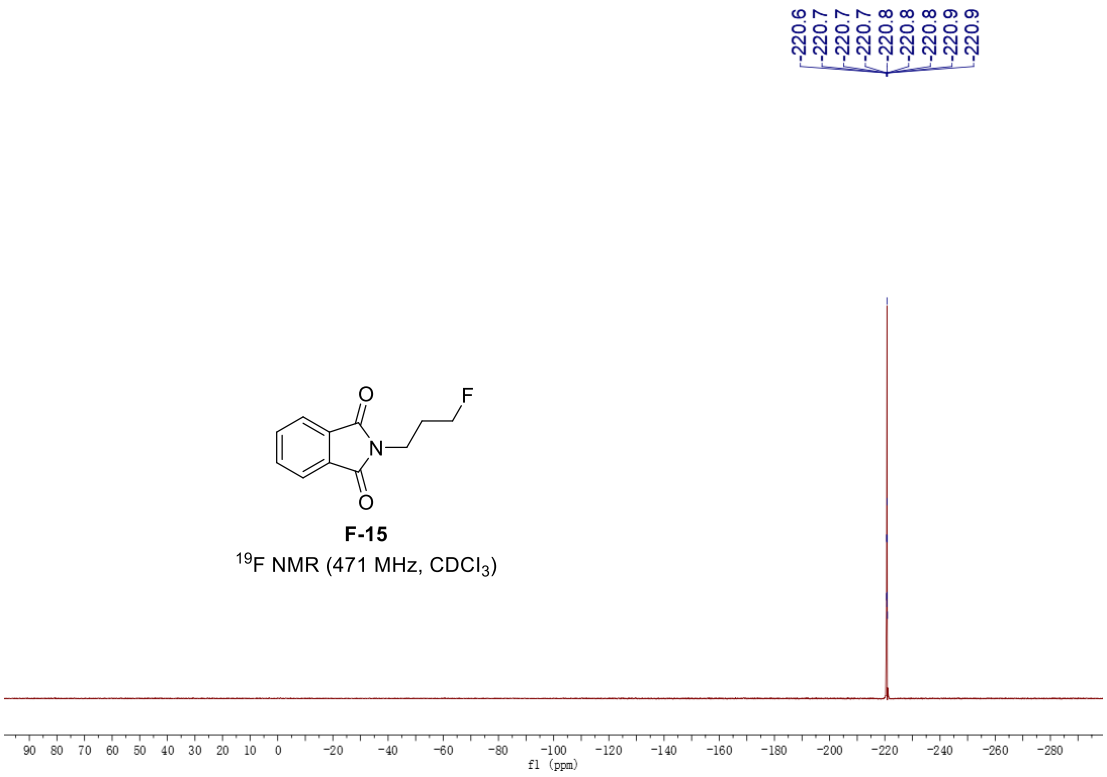
F-14

^{13}C NMR (126 MHz, $CDCl_3$)



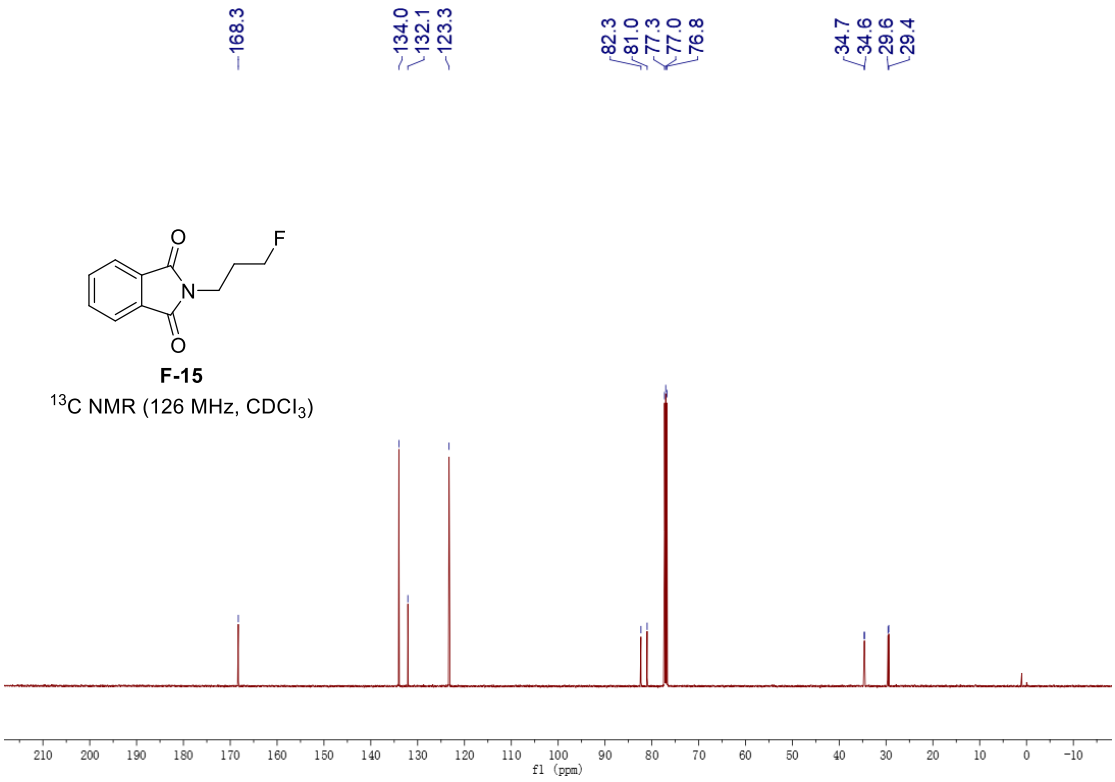
F-15

^{1}H NMR (500 MHz, $CDCl_3$)



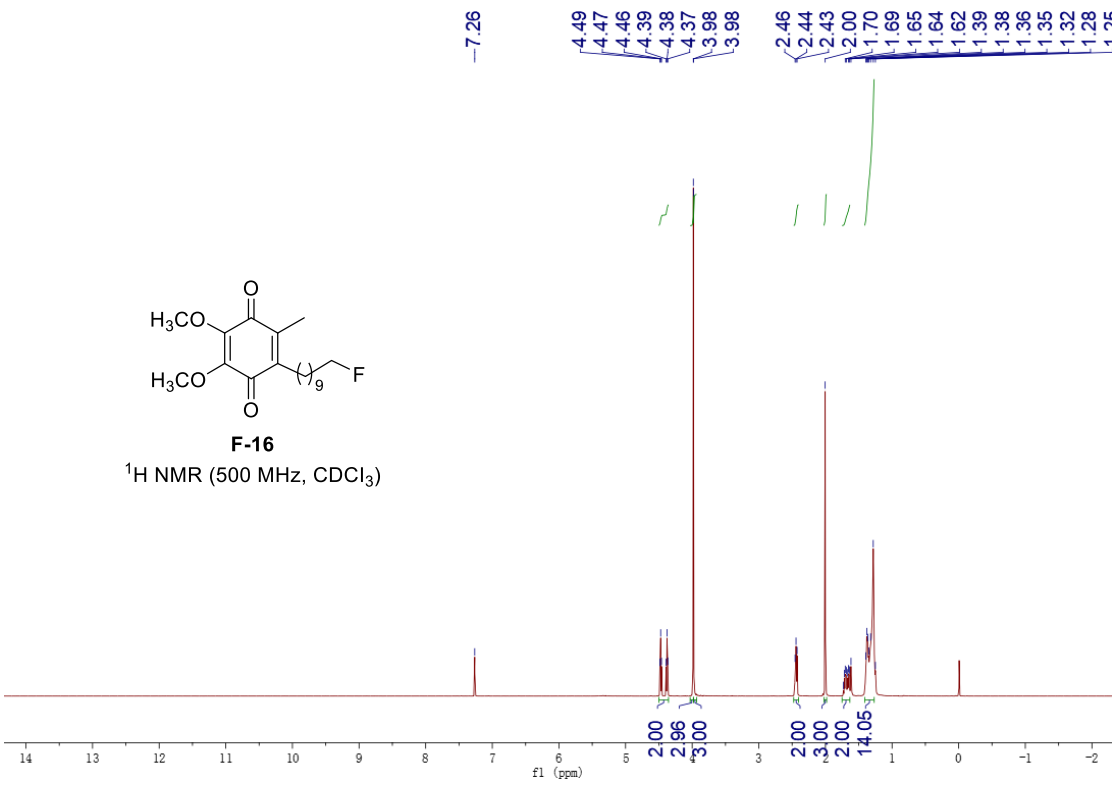
F-15

^{19}F NMR (471 MHz, $CDCl_3$)



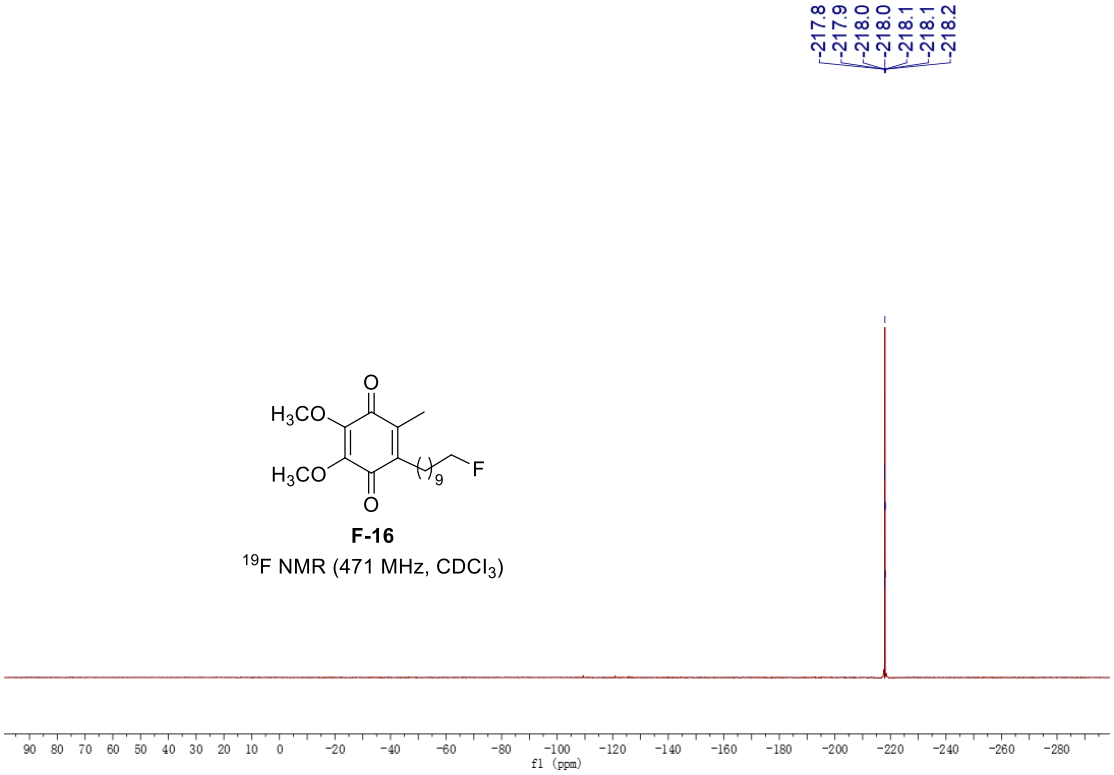
F-15

^{13}C NMR (126 MHz, $CDCl_3$)



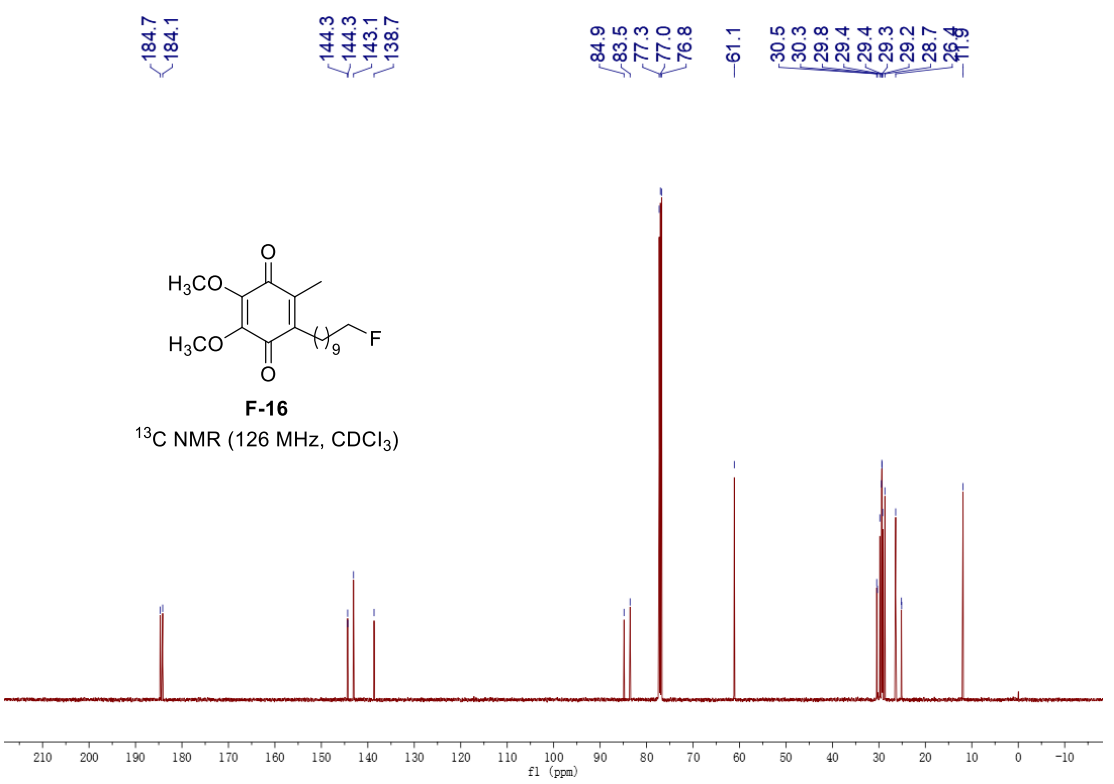
F-16

^{1}H NMR (500 MHz, $CDCl_3$)



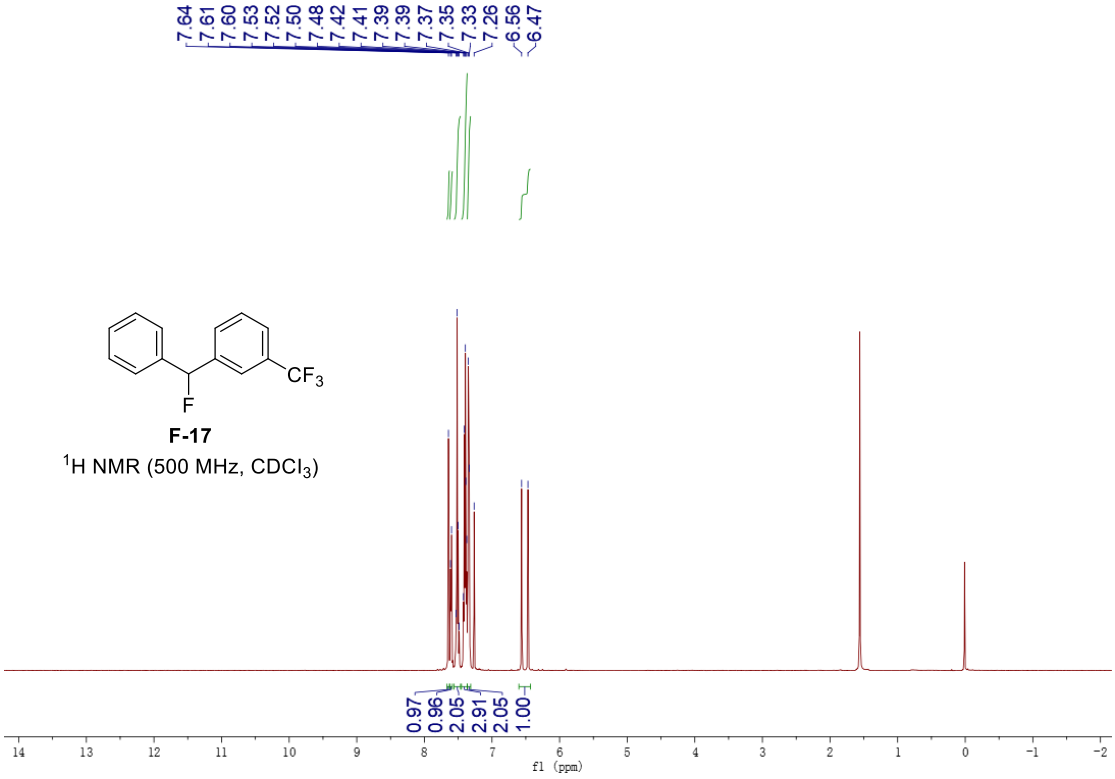
F-16

^{19}F NMR (471 MHz, $CDCl_3$)



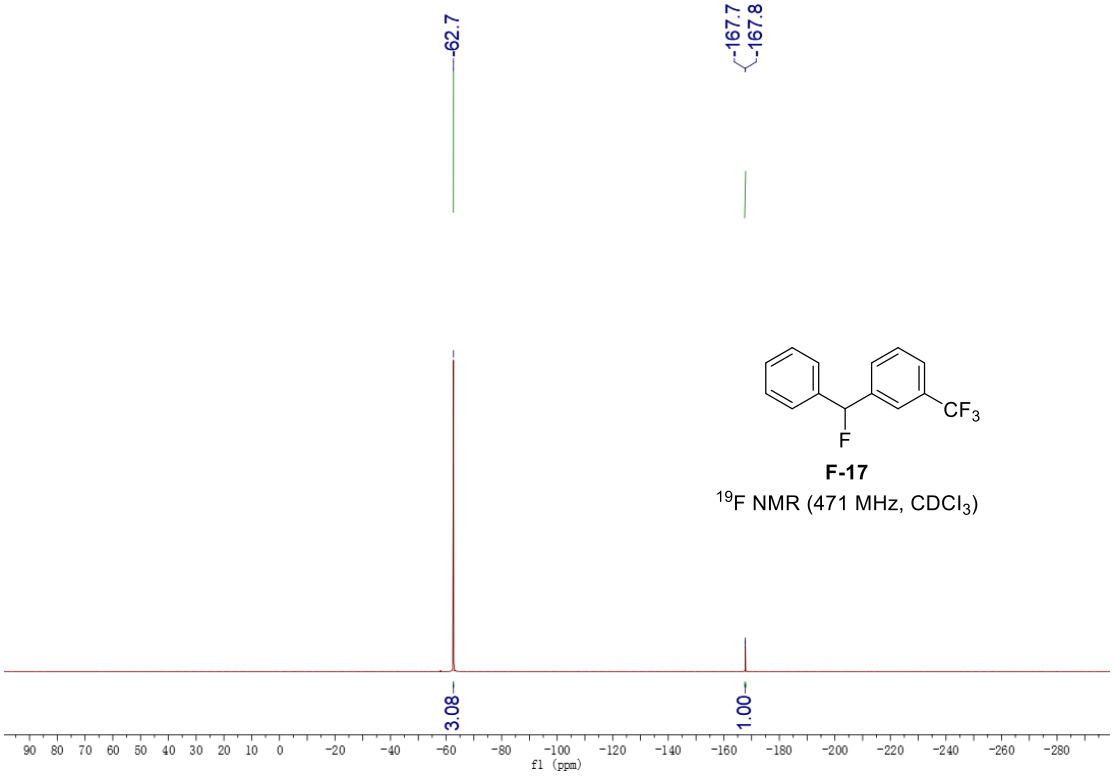
F-16

^{13}C NMR (126 MHz, $CDCl_3$)



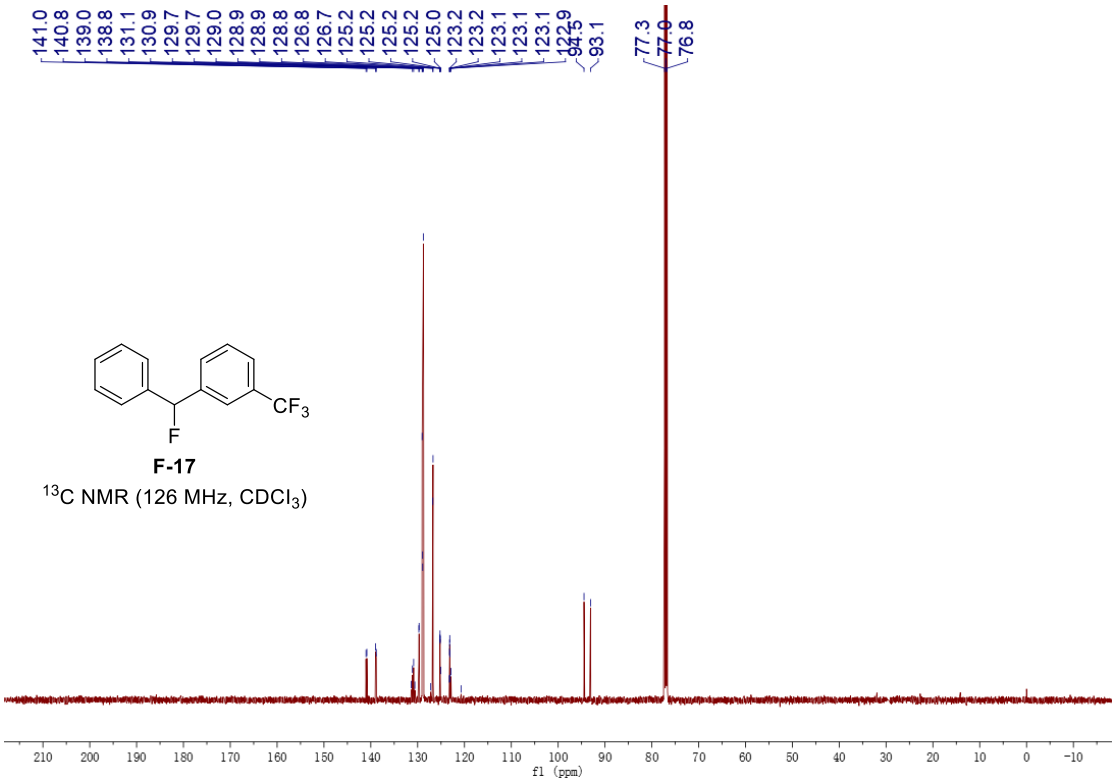
F-17

^{1}H NMR (500 MHz, $CDCl_3$)



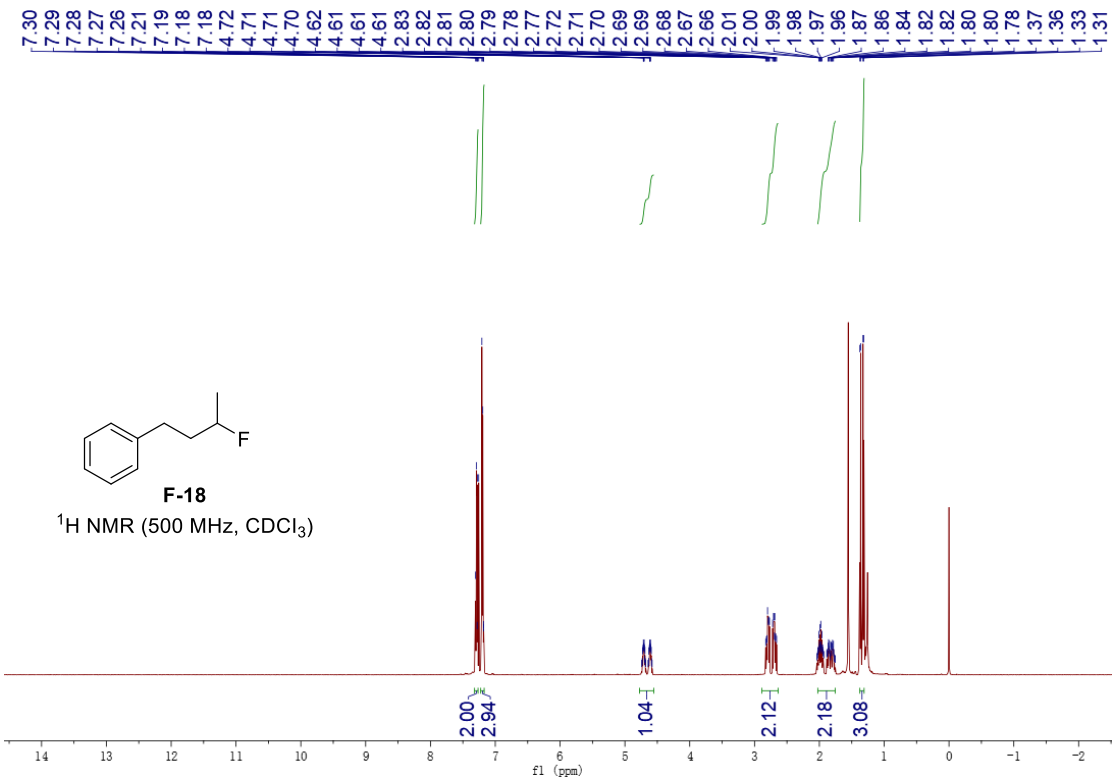
F-17

^{19}F NMR (471 MHz, $CDCl_3$)



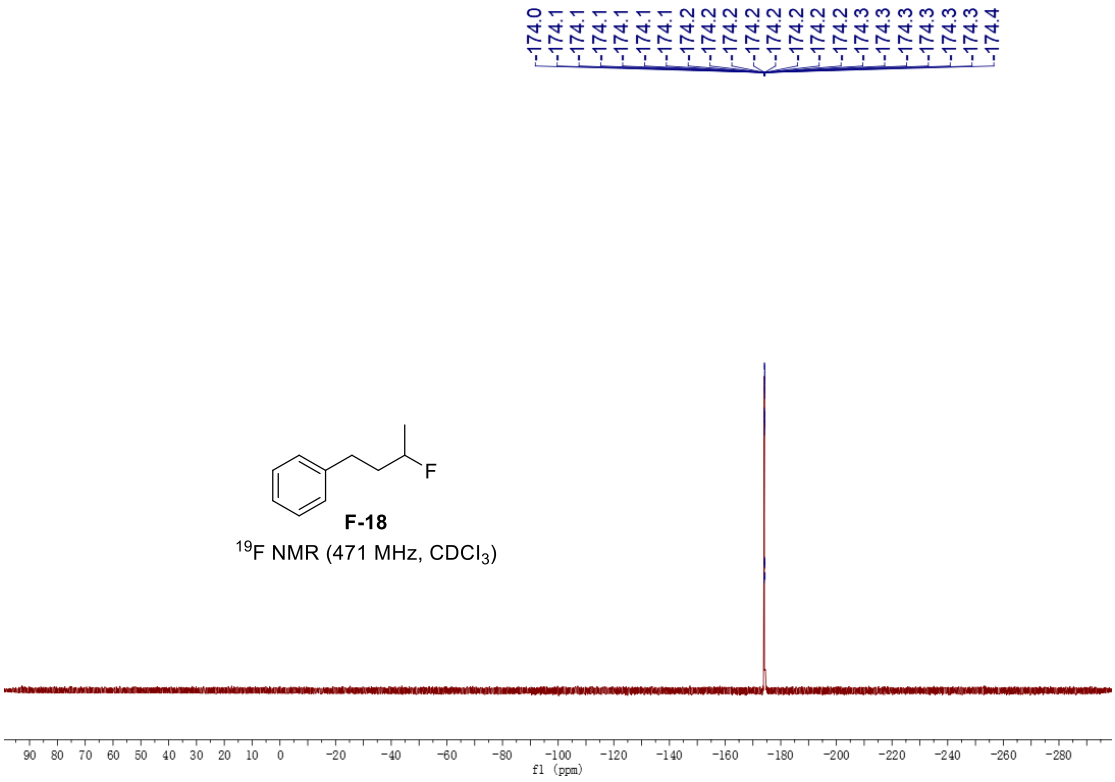
F-17

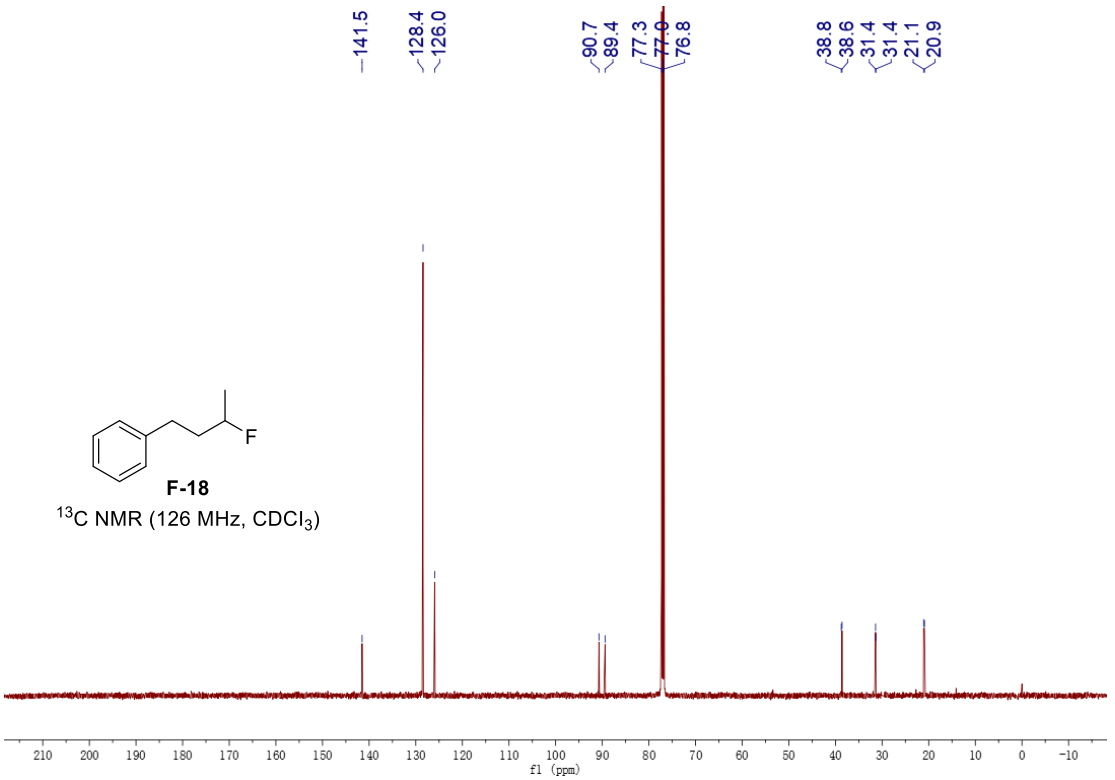
^{13}C NMR (126 MHz, $CDCl_3$)

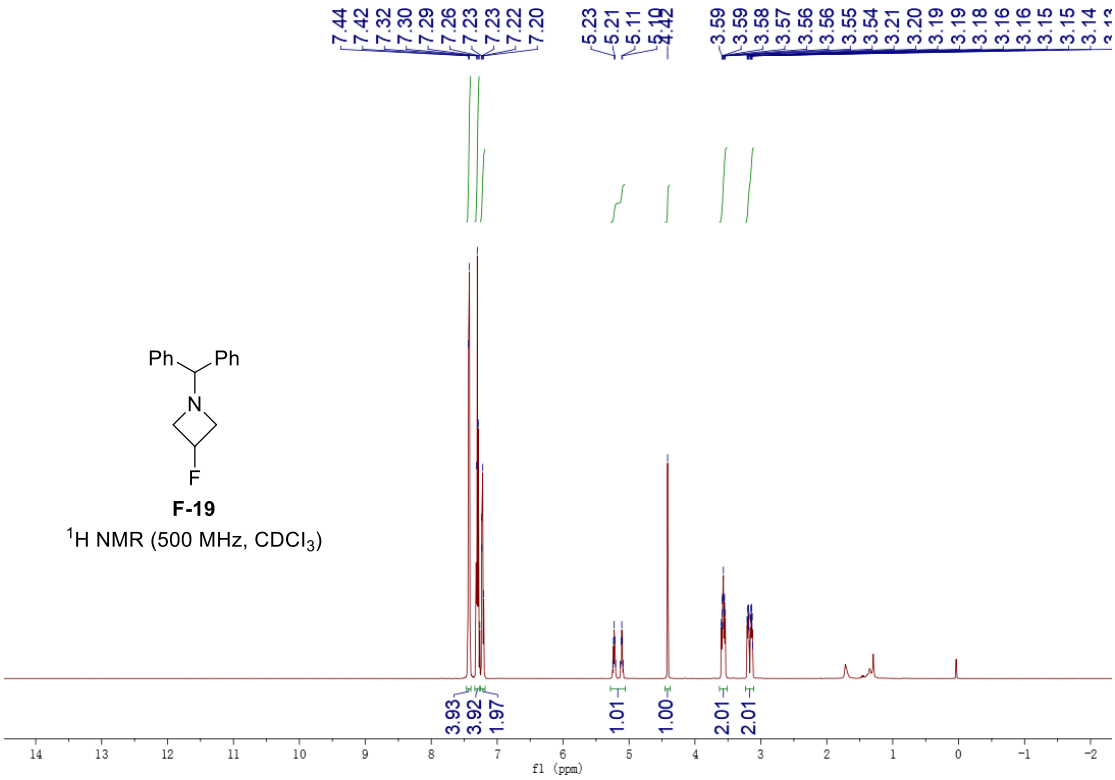


F-18

^{1}H NMR (500 MHz, $CDCl_3$)

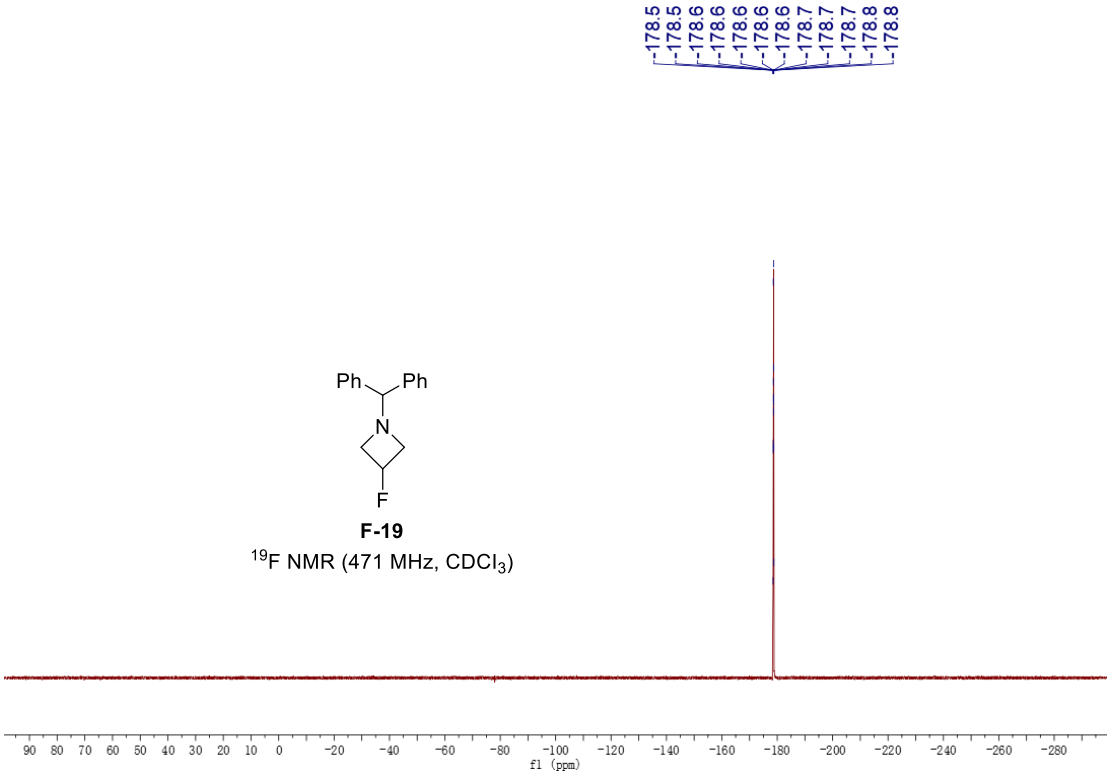

-174.0
-174.1
-174.1
-174.1
-174.1
-174.1
-174.1
-174.2
-174.2
-174.2
-174.2
-174.2
-174.2
-174.2
-174.2
-174.3
-174.3
-174.3
-174.3
-174.3
-174.4
F
F-18
19F NMR (471 MHz, CDCl3)
f1 (ppm)


141.5
128.4
126.0
90.7
89.4
77.3
77.0
76.8
38.8
38.6
31.4
31.4
21.1
20.9
F
F-18
13C NMR (126 MHz, CDCl3)
f1 (ppm)



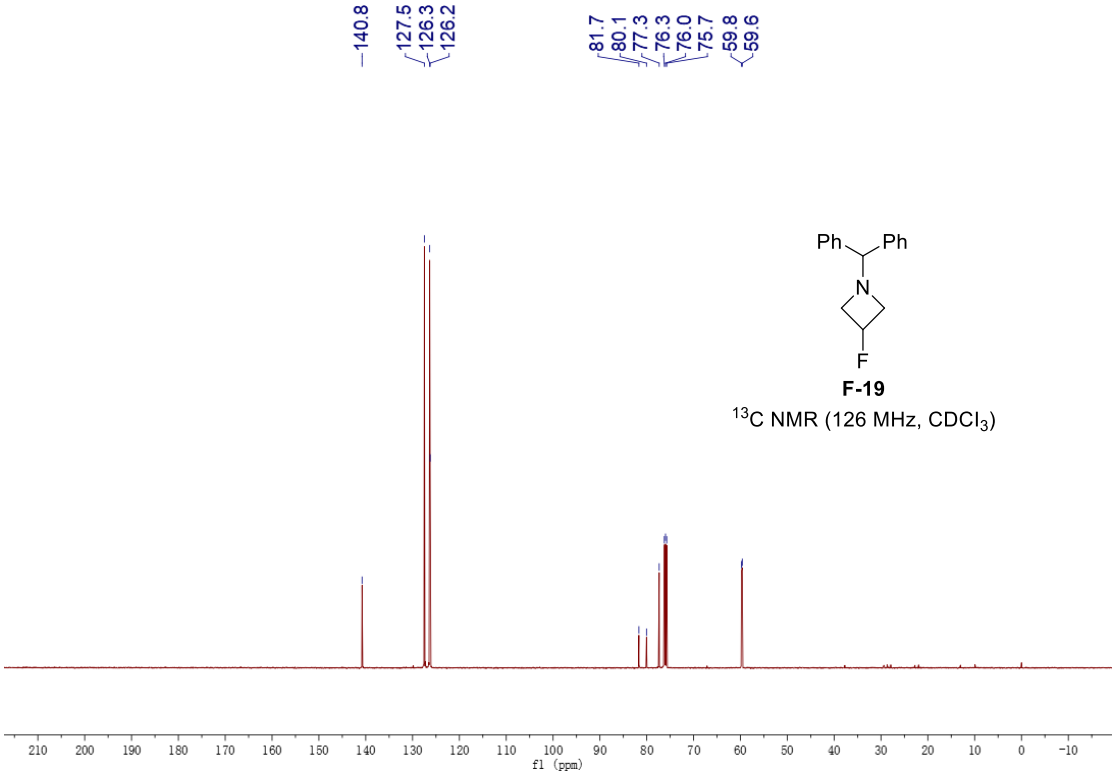
F-19

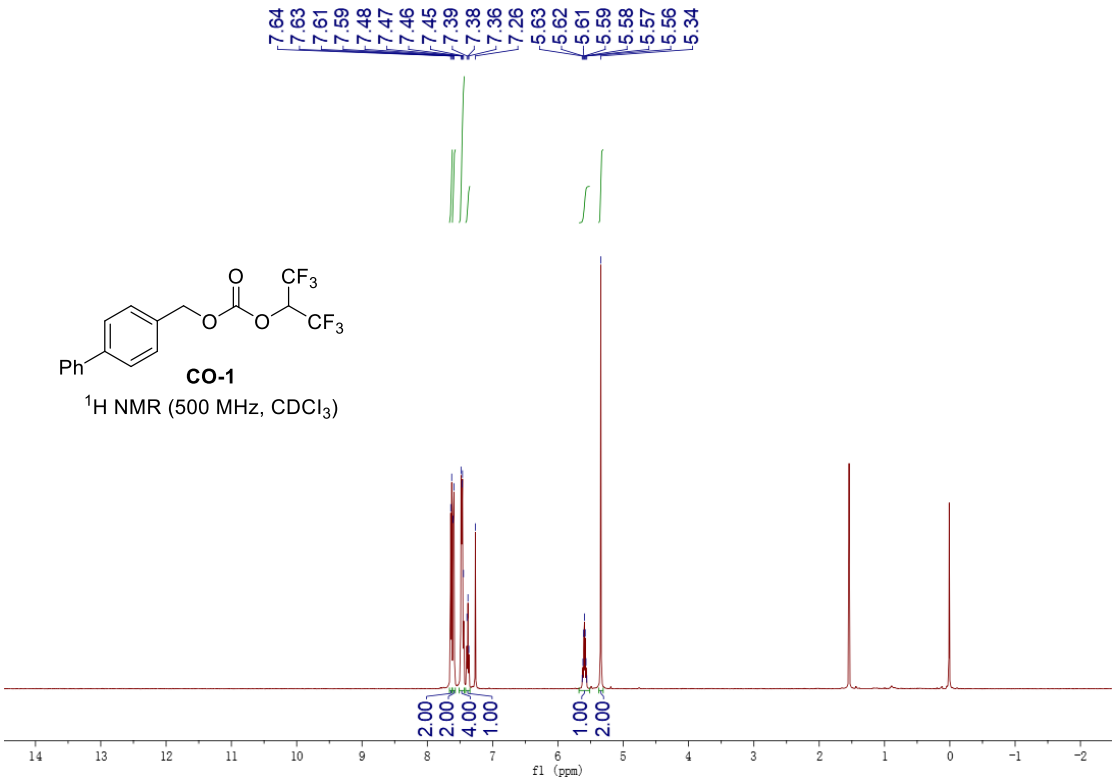
^{1}H NMR (500 MHz, $CDCl_3$)

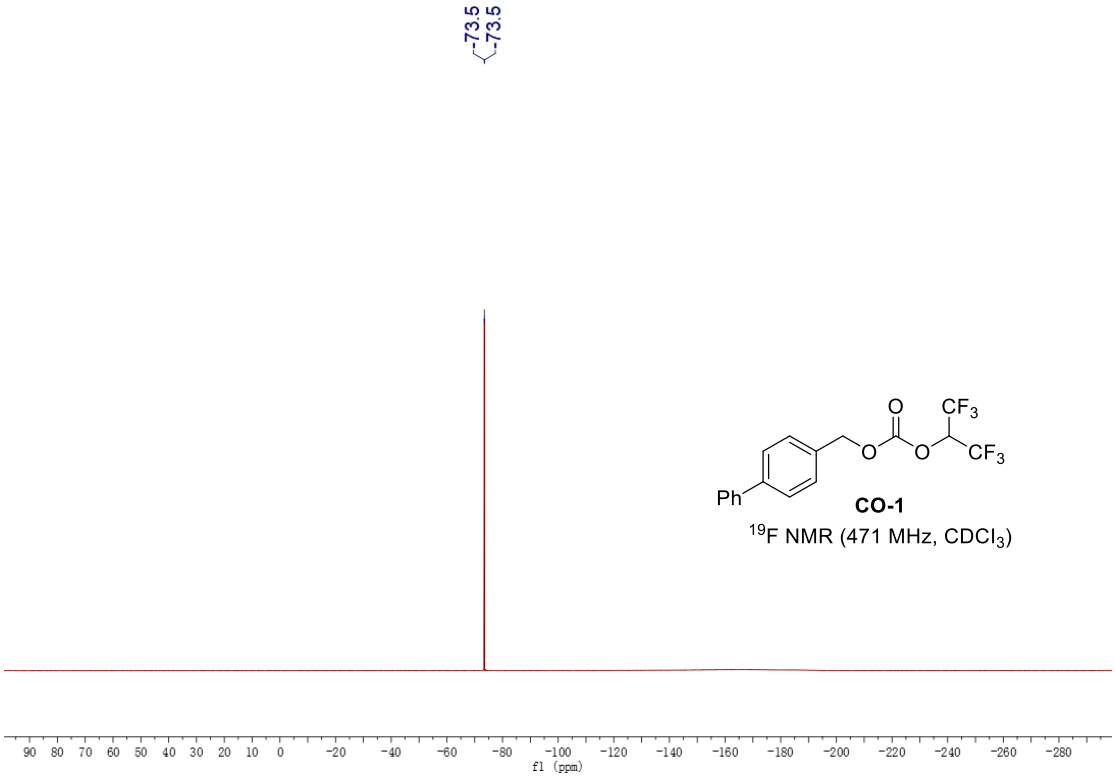


F-19

^{19}F NMR (471 MHz, $CDCl_3$)

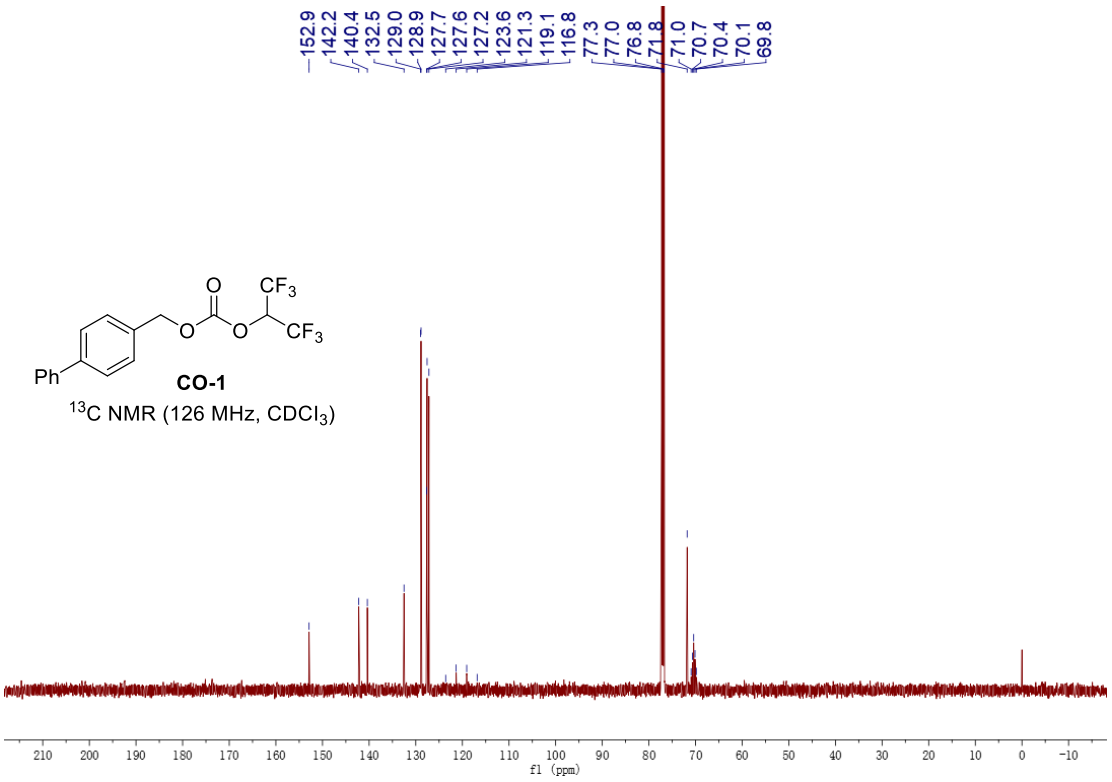

140.8
127.5
126.3
126.2
81.7
80.1
77.3
76.3
76.0
75.7
59.8
59.6
Ph
Ph
N
F
F-19
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.64
7.63
7.61
7.59
7.48
7.47
7.46
7.45
7.39
7.38
7.36
7.26
5.63
5.62
5.61
5.59
5.58
5.57
5.56
5.34
O
CF3
O
O
CF3
Ph
CO-1
1H NMR (500 MHz, CDCl3)
2.00
2.00
4.00
1.00
1.00
2.00
f1 (ppm)



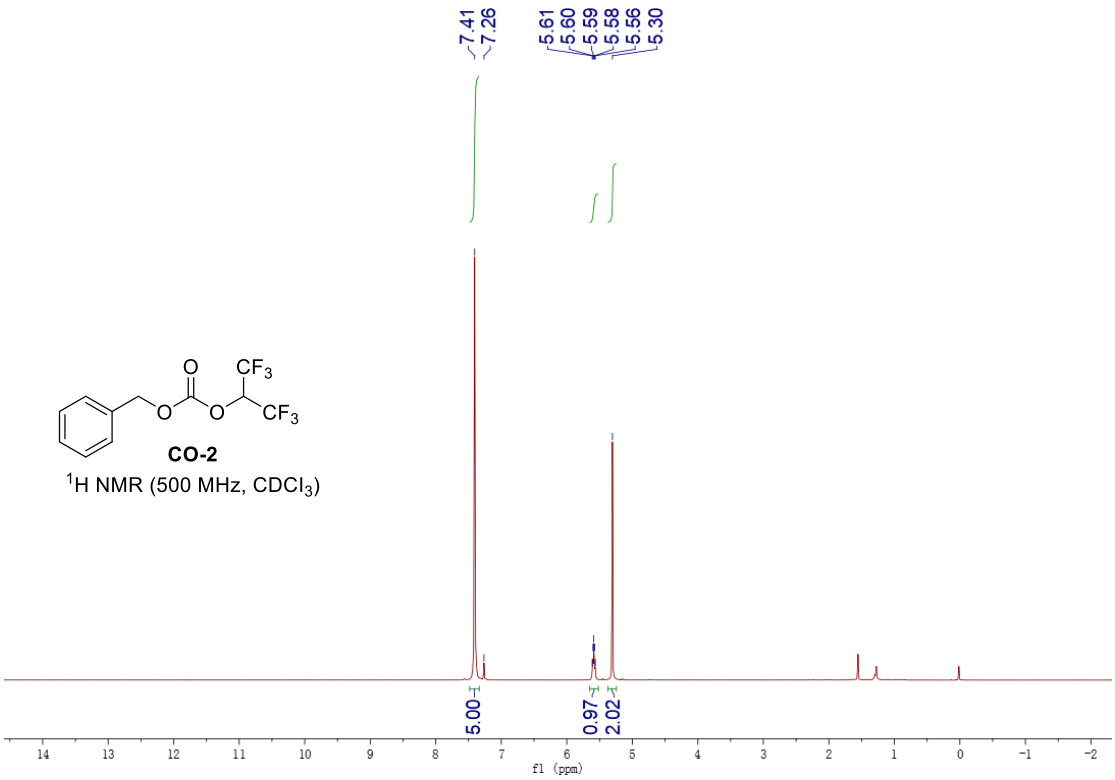
CO-1

^{19}F NMR (471 MHz, $CDCl_3$)



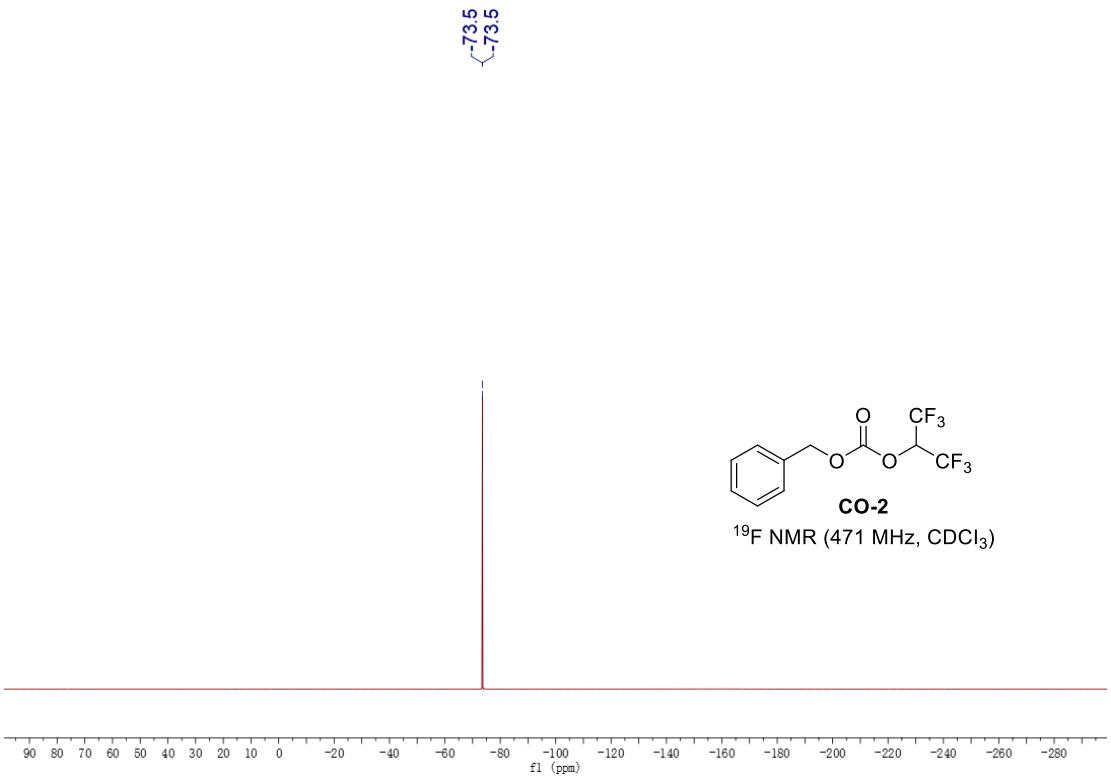
CO-1

^{13}C NMR (126 MHz, $CDCl_3$)



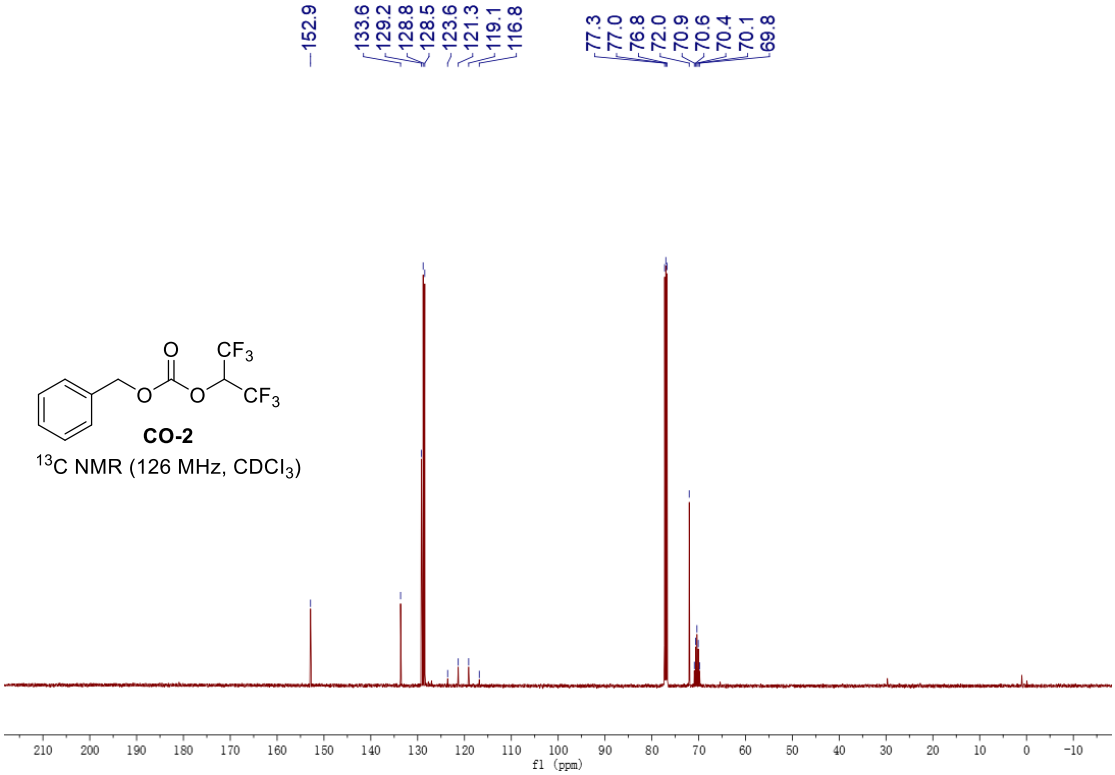
CO-2

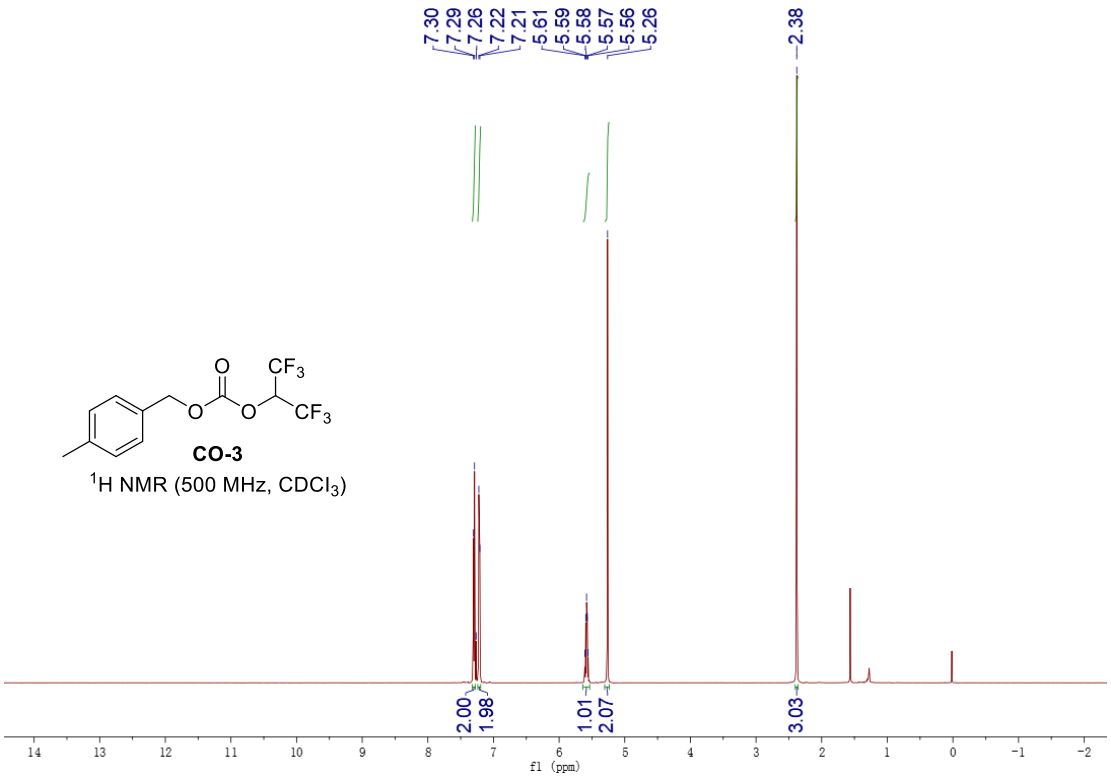
^{1}H NMR (500 MHz, $CDCl_3$)

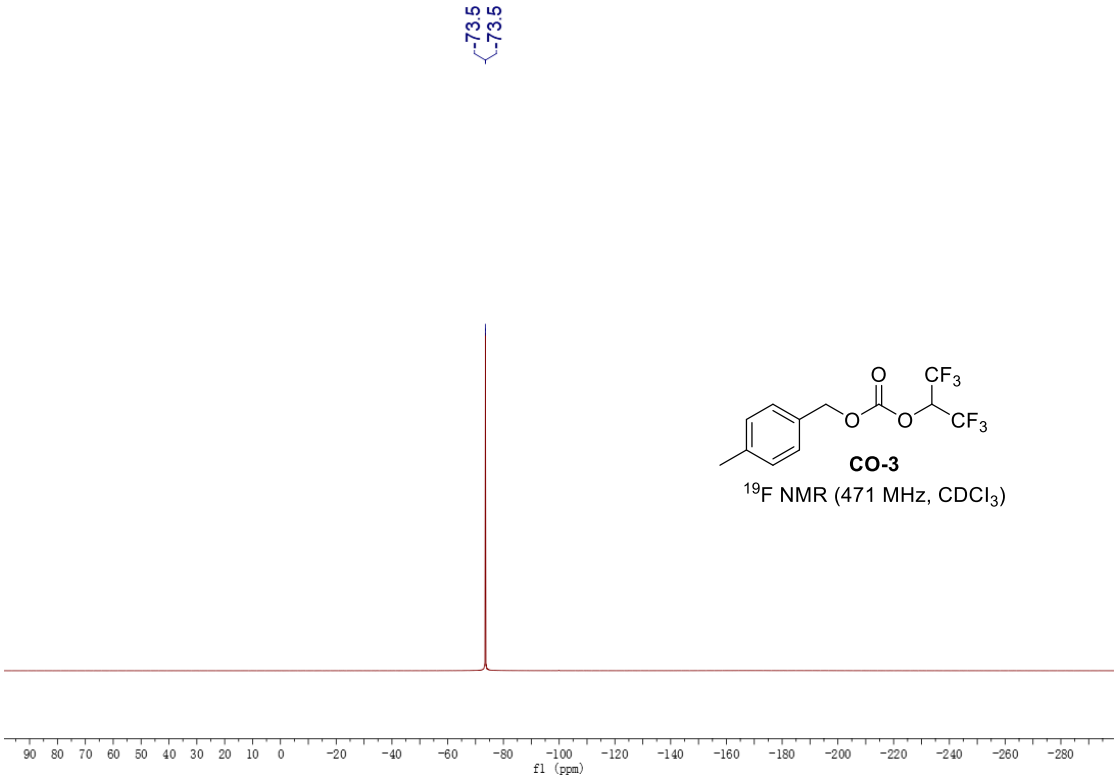


CO-2

^{19}F NMR (471 MHz, $CDCl_3$)

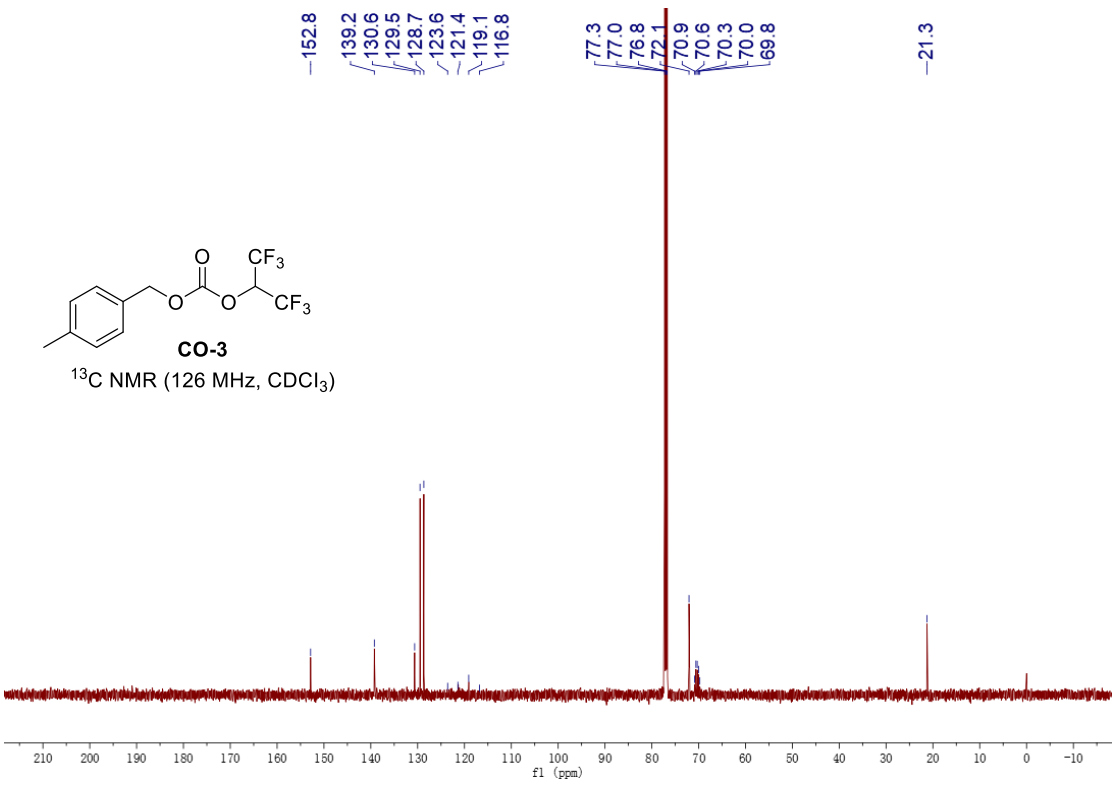

152.9
133.6
129.2
128.8
128.5
123.6
121.3
119.1
116.8
77.3
77.0
76.8
72.0
70.9
70.6
70.4
70.1
69.8
O
CF3
O
O
CF3
CO-2
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.30
7.29
7.26
7.22
7.21
5.61
5.59
5.58
5.57
5.56
5.26
2.38
O
CF3
O
O
CF3
CO-3
1H NMR (500 MHz, CDCl3)
2.00
1.98
1.01
2.07
3.03
f1 (ppm)



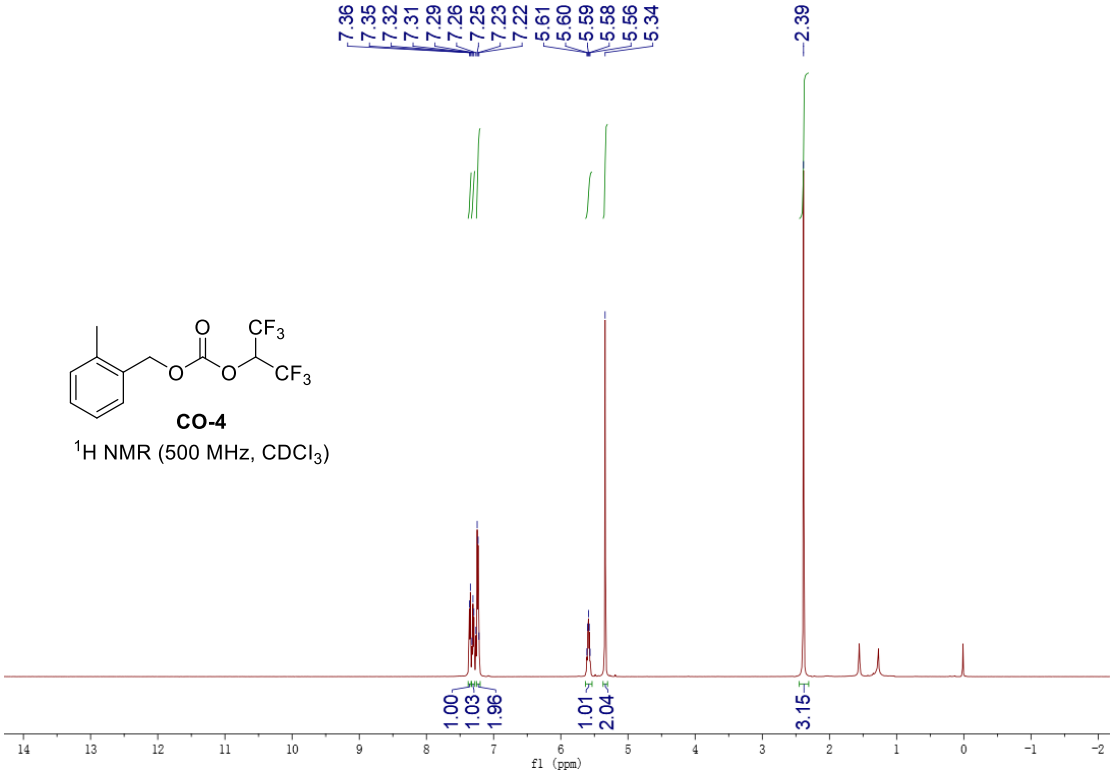
CO-3

^{19}F NMR (471 MHz, $CDCl_3$)



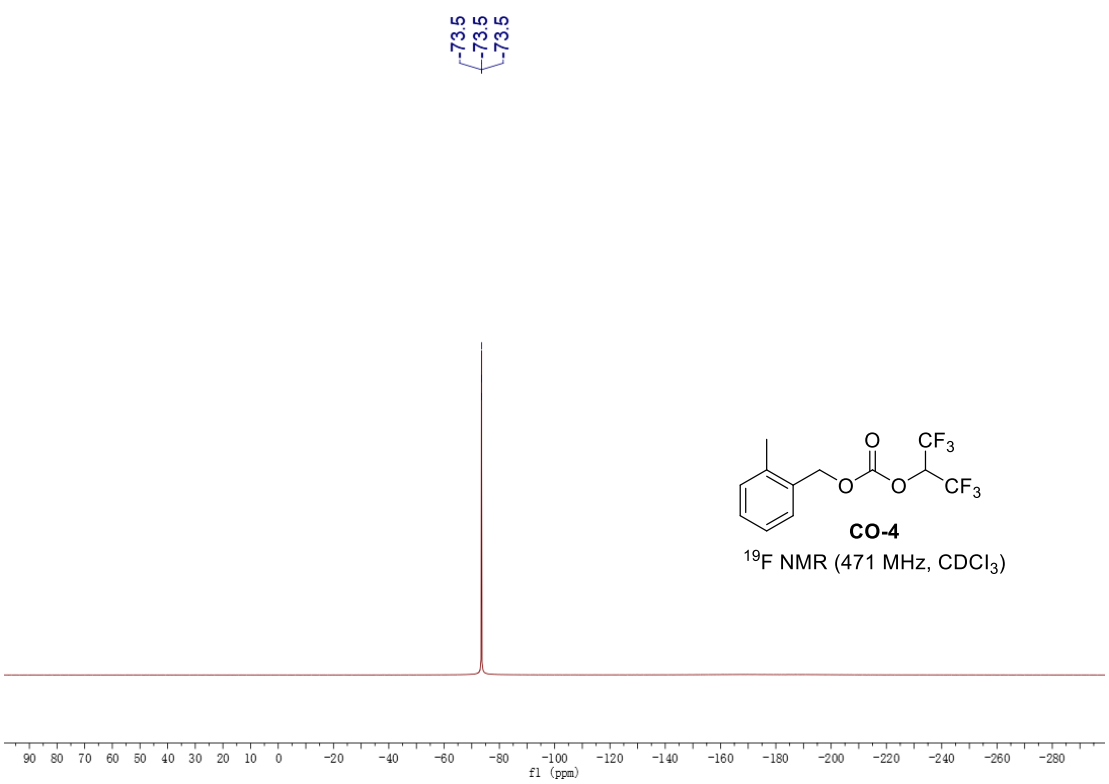
CO-3

^{13}C NMR (126 MHz, $CDCl_3$)



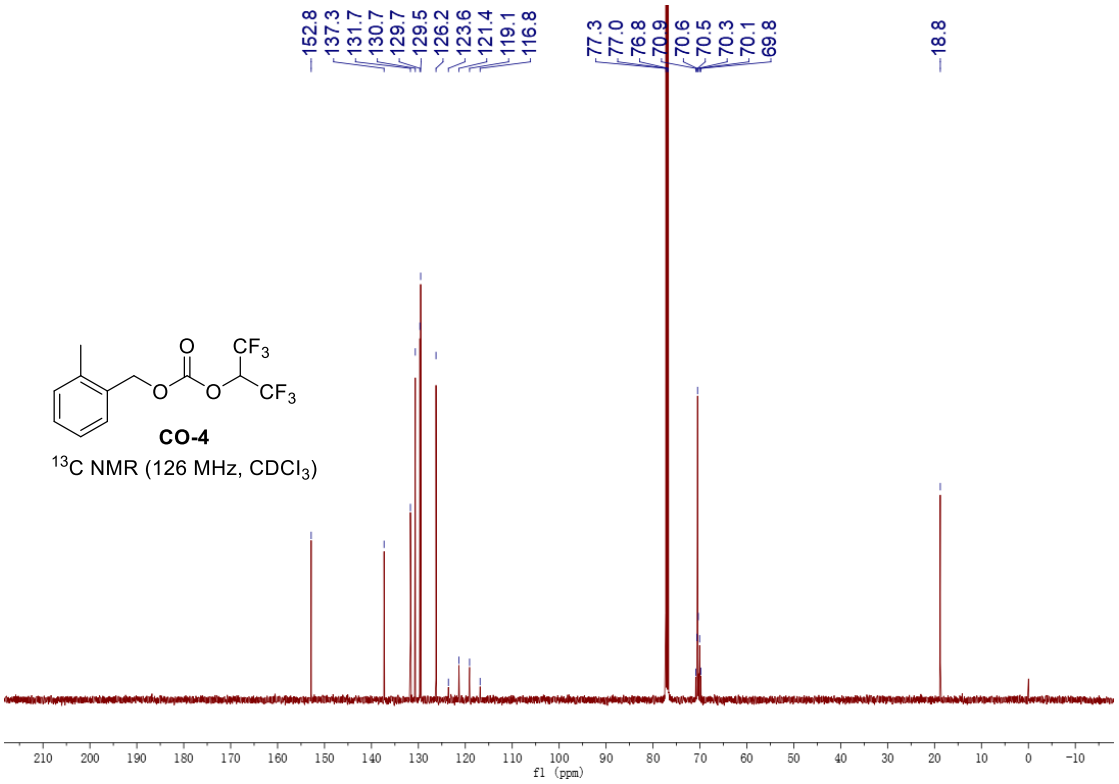
CO-4

^{1}H NMR (500 MHz, $CDCl_3$)



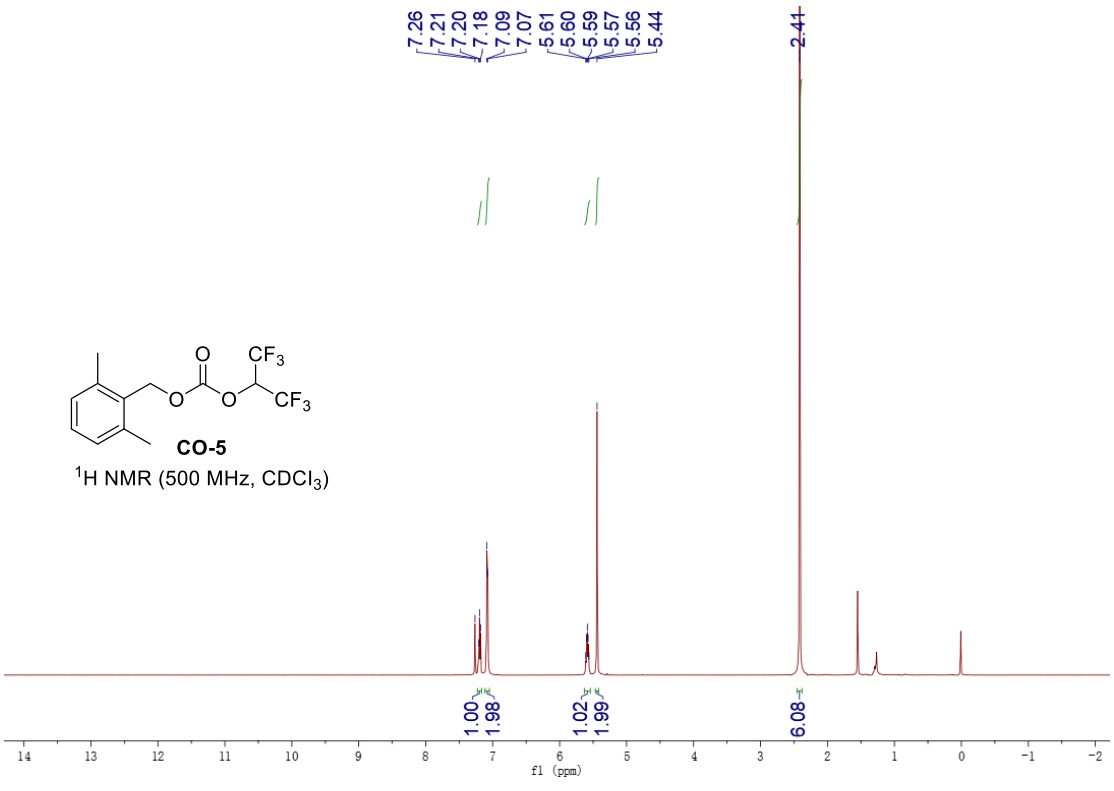
CO-4

^{19}F NMR (471 MHz, $CDCl_3$)



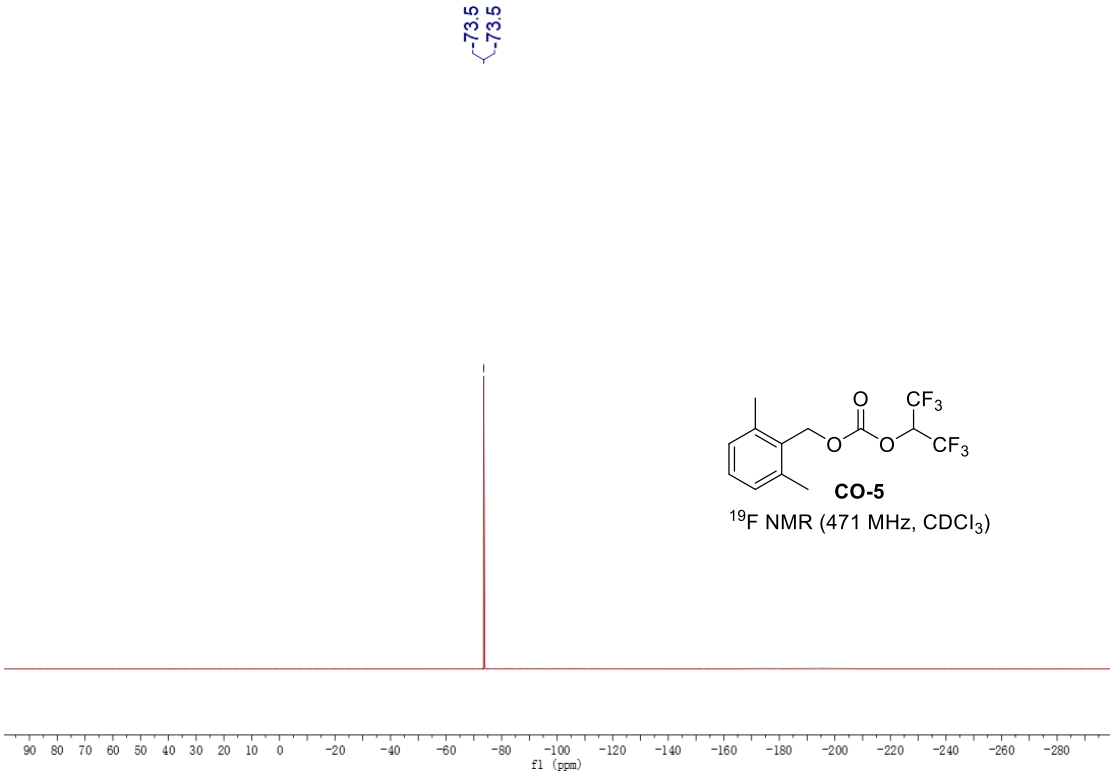
CO-4

^{13}C NMR (126 MHz, $CDCl_3$)



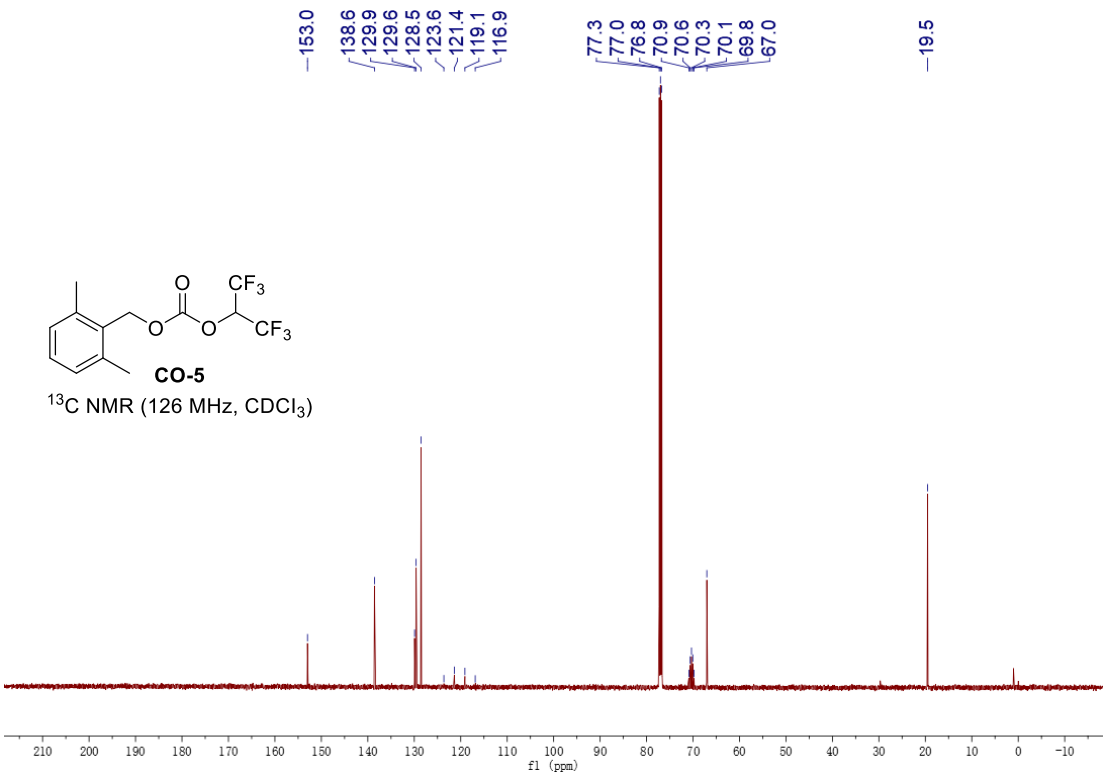
CO-5

^{1}H NMR (500 MHz, $CDCl_3$)



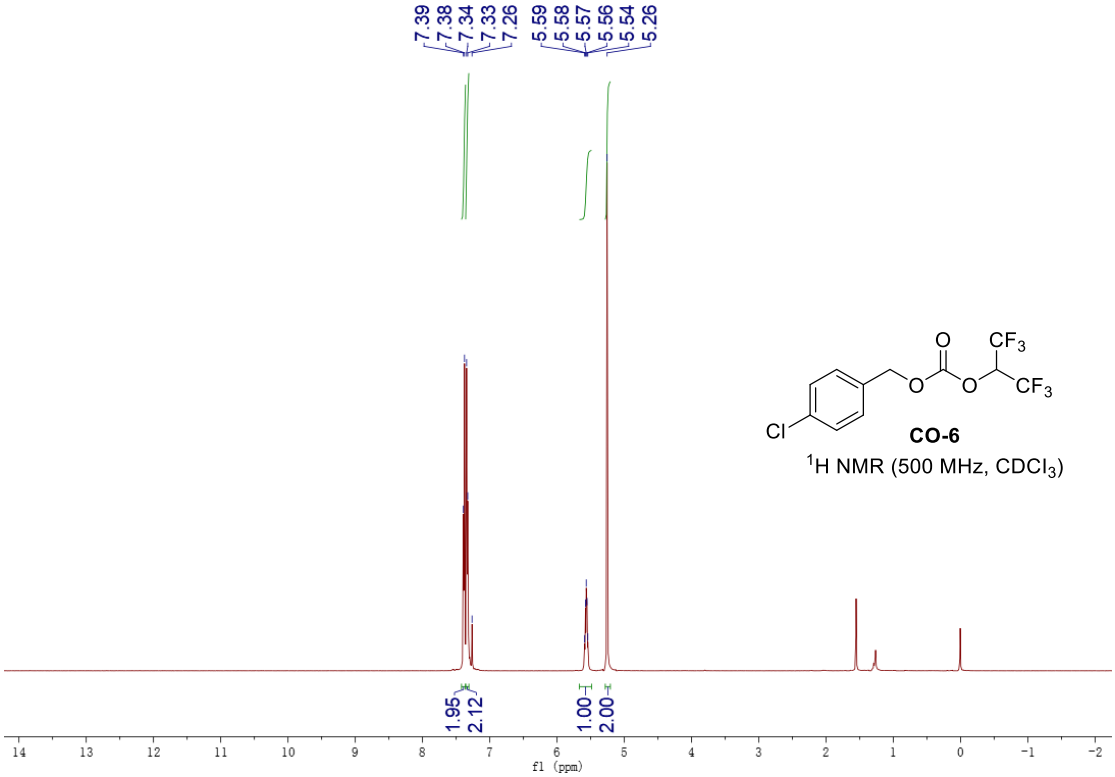
CO-5

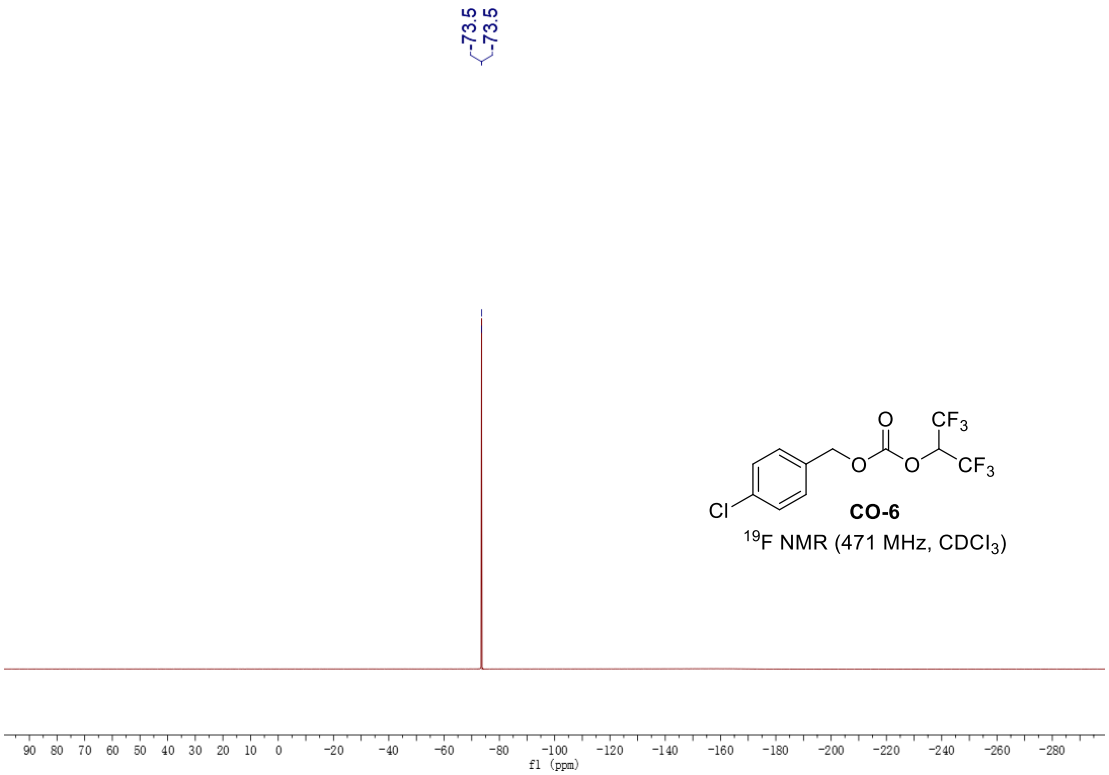
^{19}F NMR (471 MHz, $CDCl_3$)

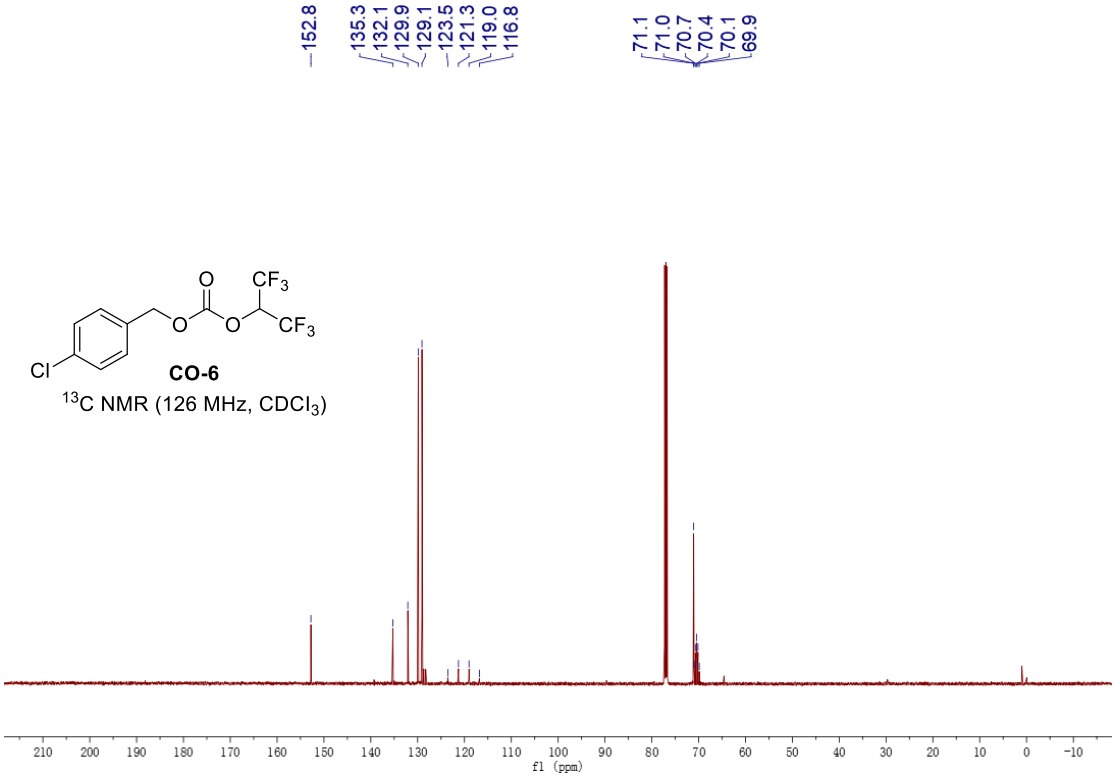


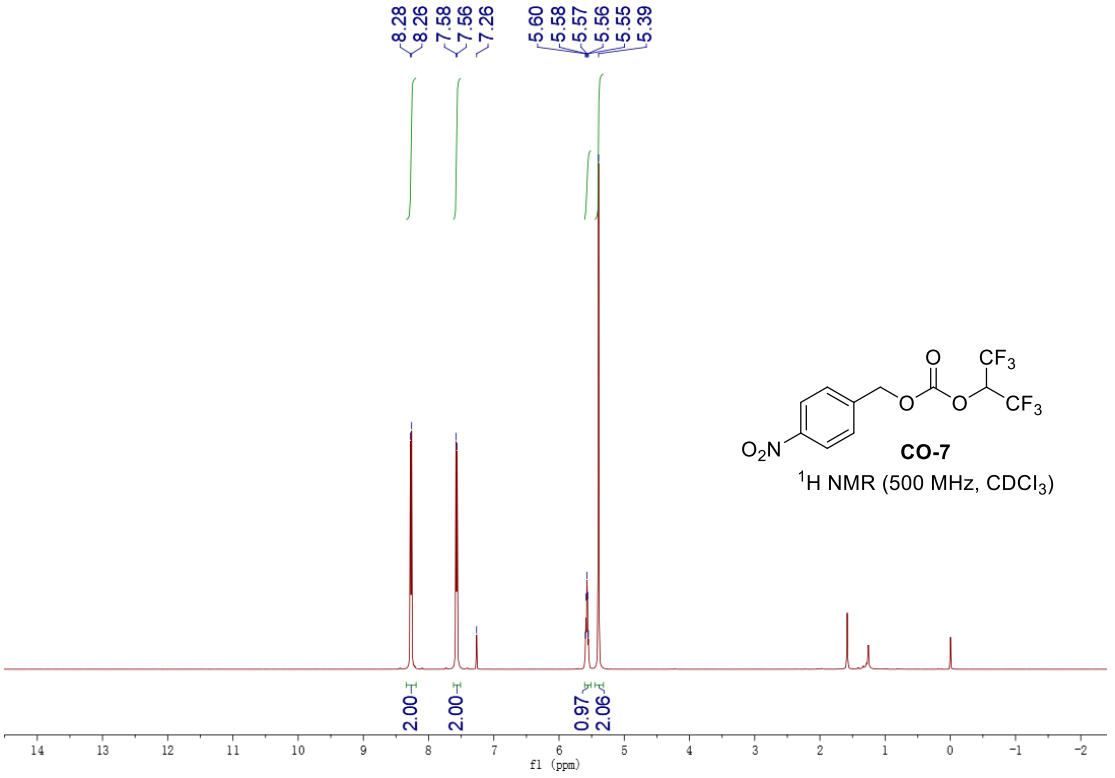
CO-5

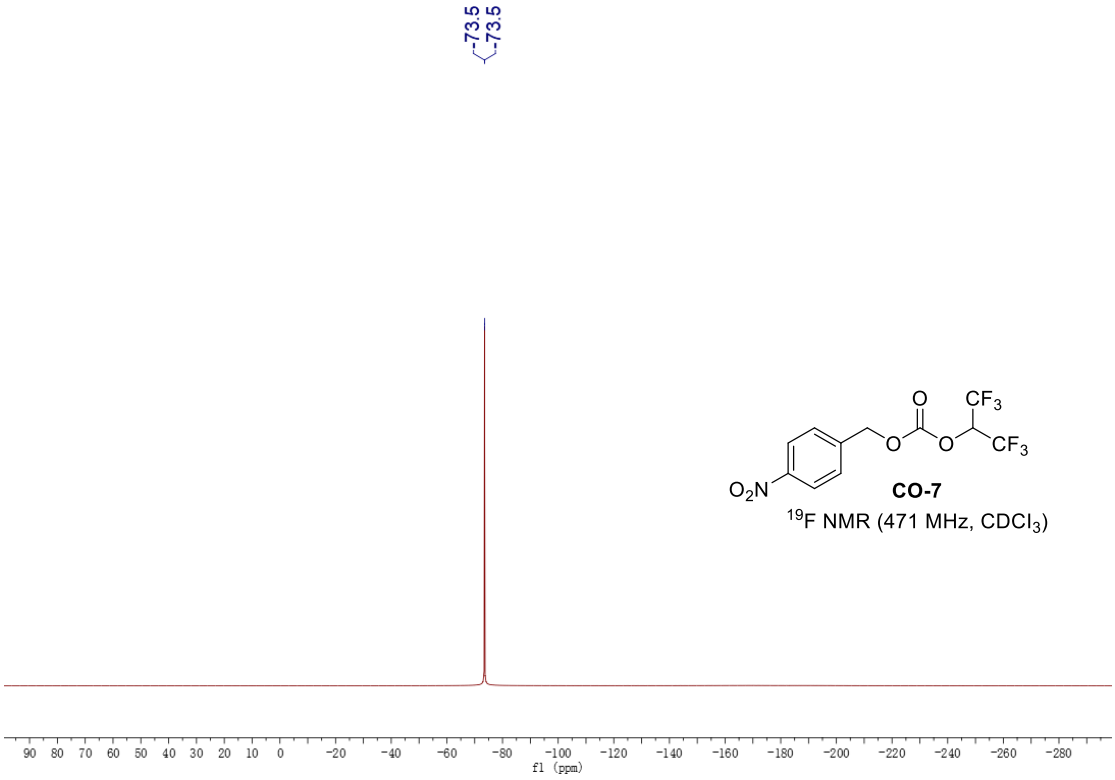
^{13}C NMR (126 MHz, $CDCl_3$)

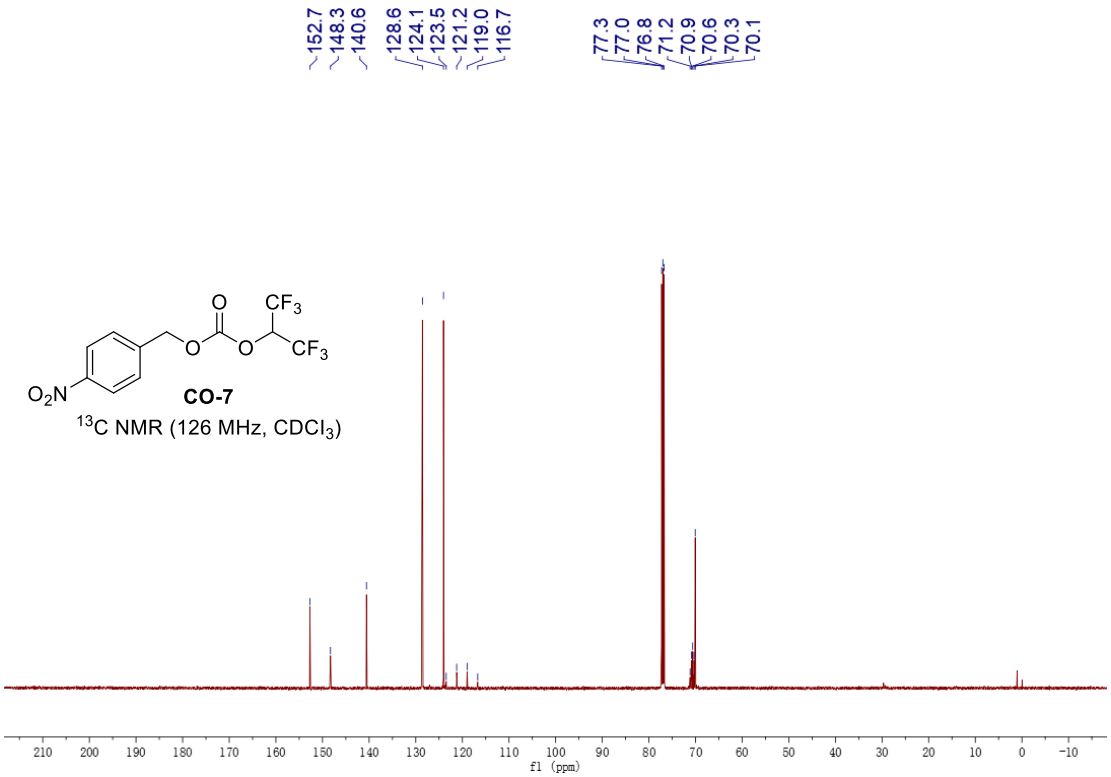

7.39
7.38
7.34
7.33
7.26
5.59
5.58
5.57
5.56
5.54
5.26
1.95
2.12
1.00
2.00
f1 (ppm)
O
CF3
O
O
CF3
Cl
CO-6
1H NMR (500 MHz, CDCl3)

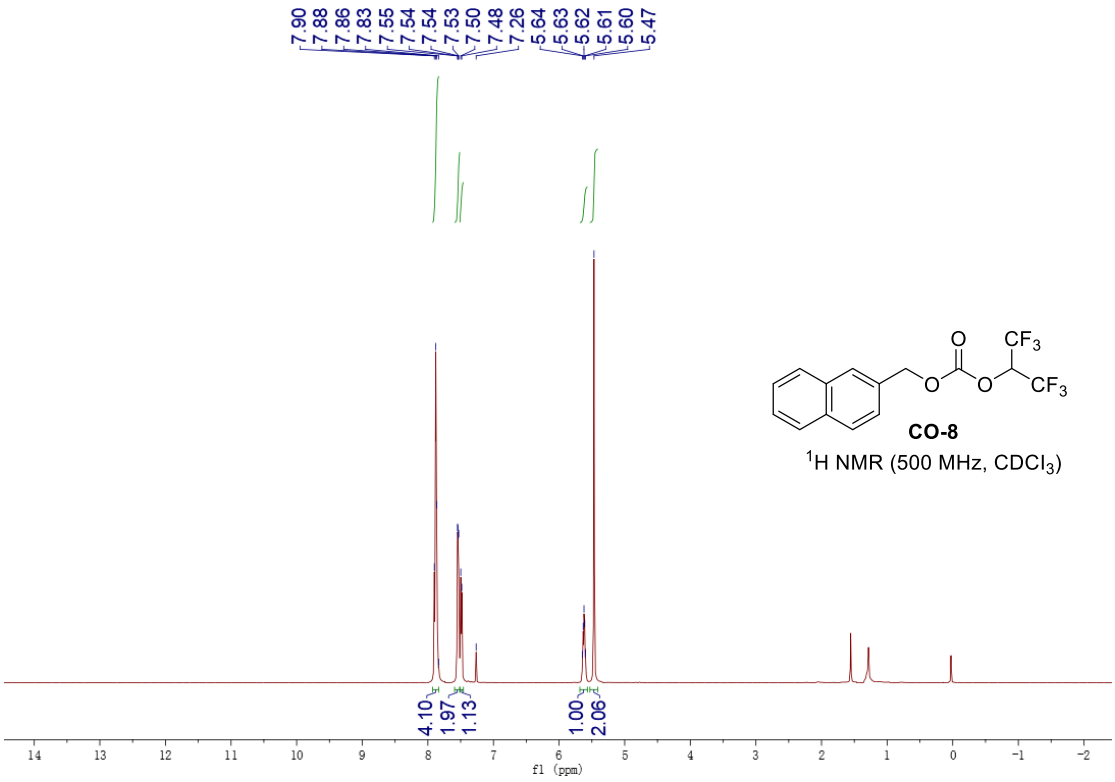

-73.5
-73.5
f1 (ppm)
O
CF3
O
O
CF3
Cl
CO-6
19F NMR (471 MHz, CDCl3)


152.8
135.3
132.1
129.9
129.1
123.5
121.3
119.0
116.8
71.1
71.0
70.7
70.4
70.1
69.9
O
CF3
O
O
CF3
Cl
CO-6
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.28
8.26
7.58
7.56
7.26
5.60
5.58
5.57
5.56
5.55
5.39
O
CF3
O
O
CF3
O2N
CO-7
1H NMR (500 MHz, CDCl3)
2.00
2.00
0.97
2.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

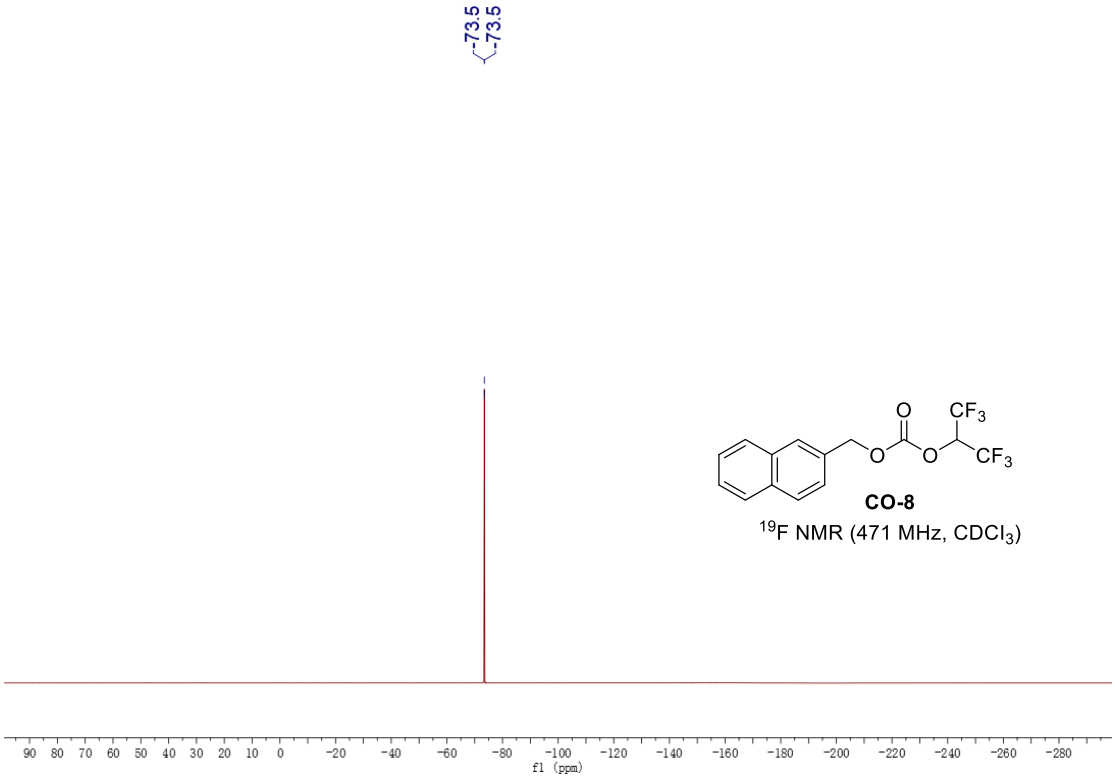

-73.5
-73.5
O
CF3
O
O
CF3
O2N
CO-7
19F NMR (471 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


152.7
148.3
140.6
128.6
124.1
123.5
121.2
119.0
116.7
77.3
77.0
76.8
71.2
70.9
70.6
70.3
70.1
O
CF3
O
O
CF3
O2N
CO-7
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



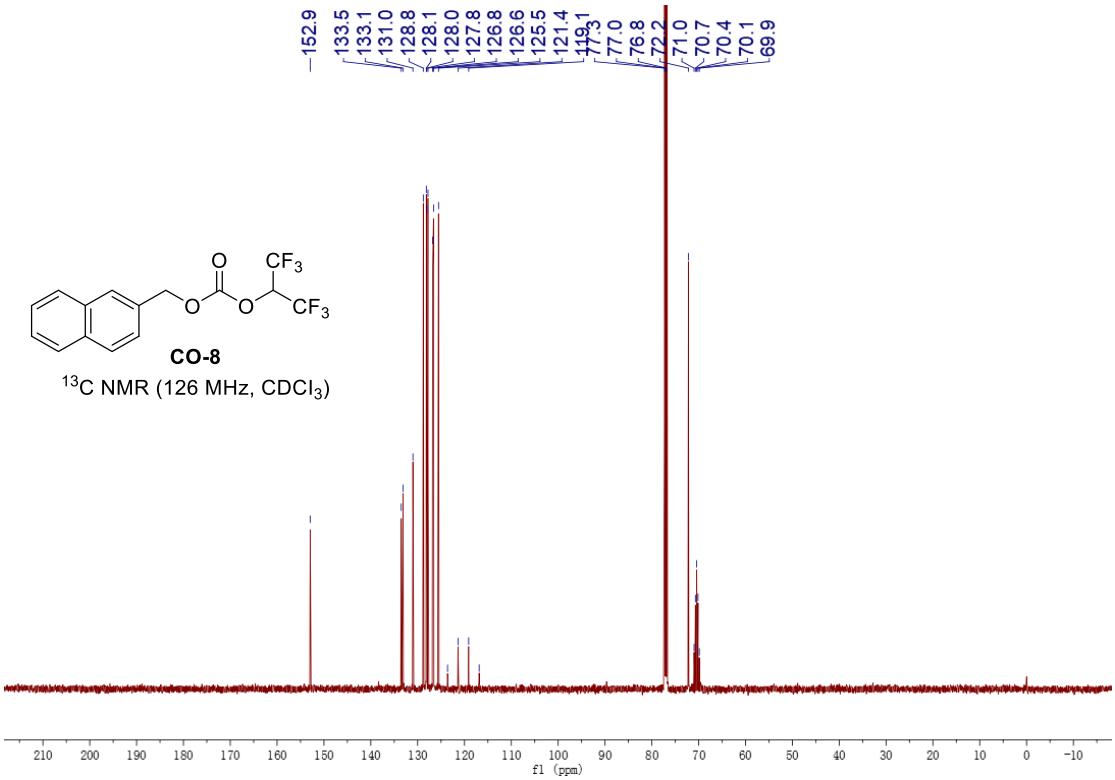
CO-8

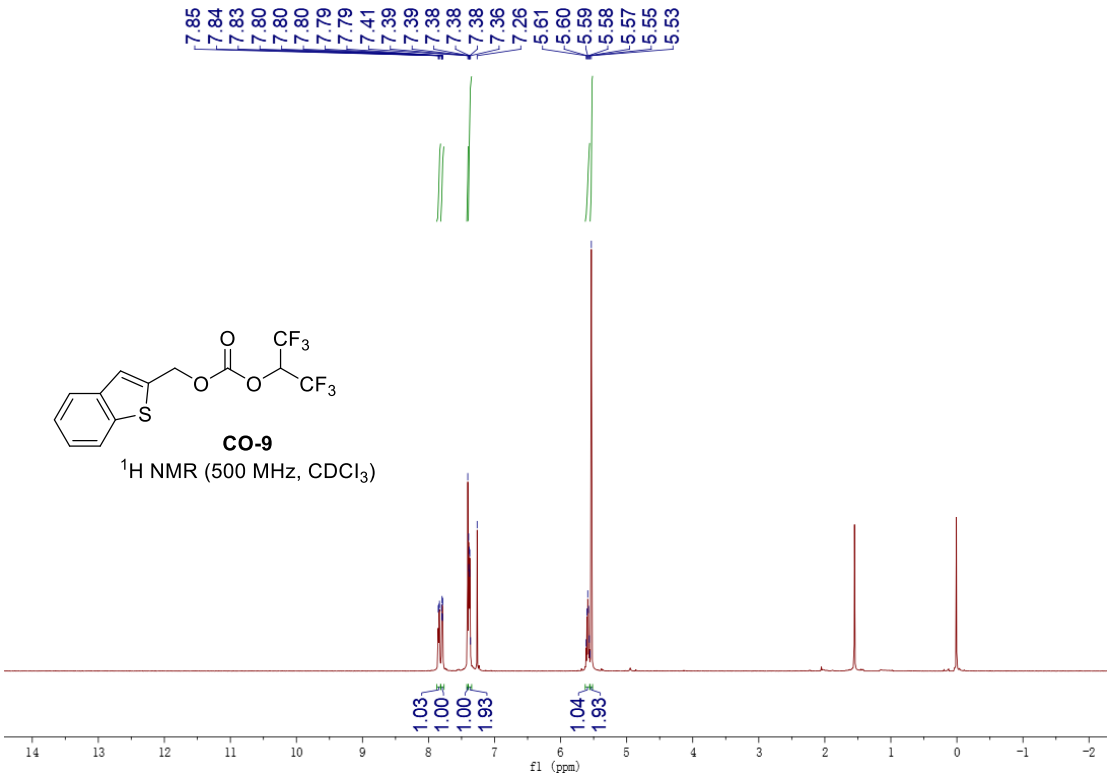
^{1}H NMR (500 MHz, $CDCl_3$)

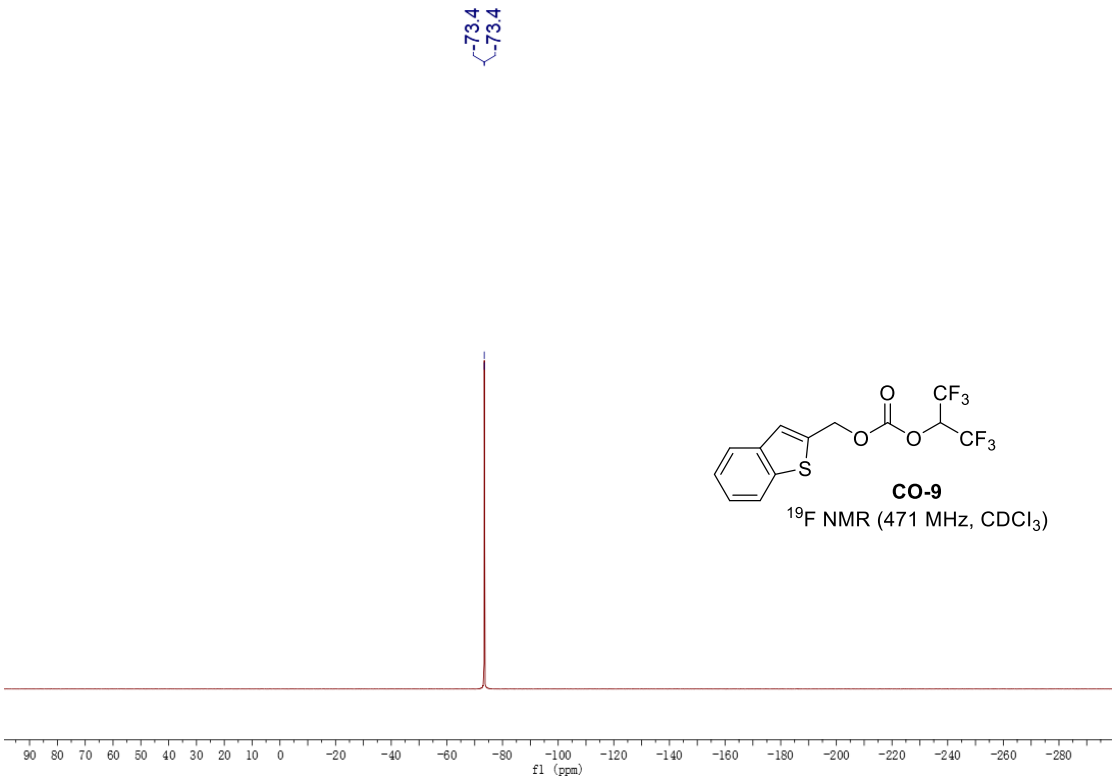


CO-8

^{19}F NMR (471 MHz, $CDCl_3$)

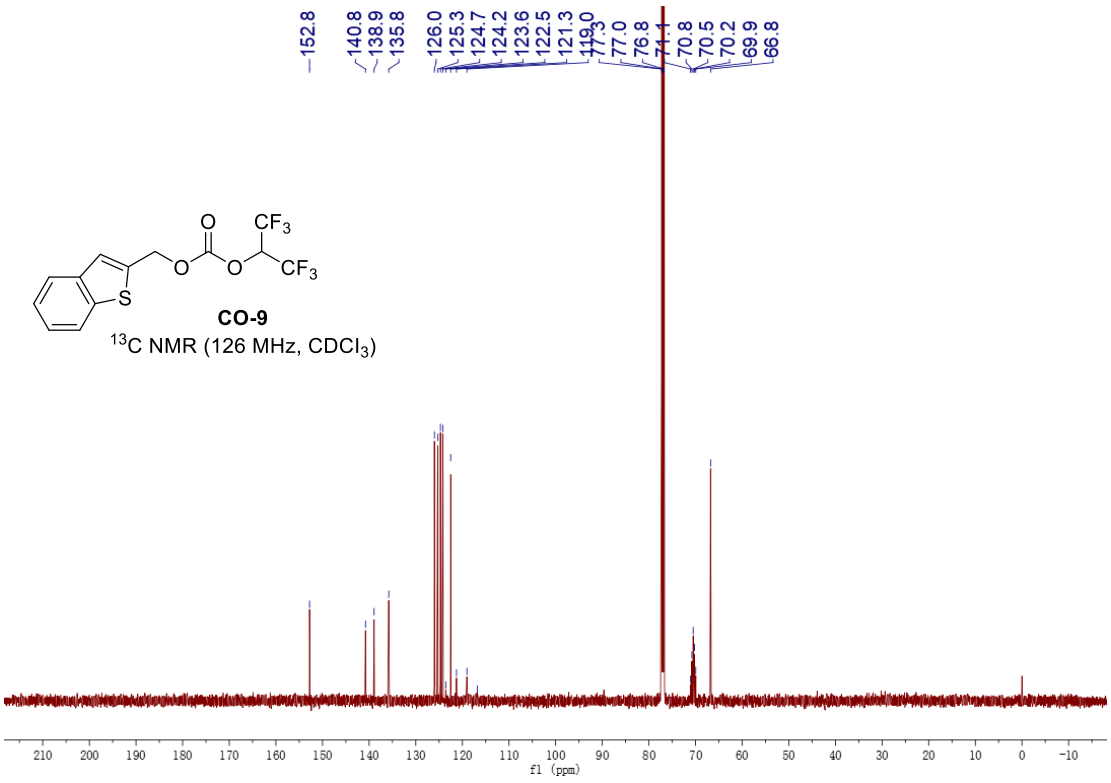

152.9
133.5
133.1
131.0
128.8
128.1
128.0
127.8
126.8
126.6
125.5
121.4
119.1
77.3
77.0
76.8
72.2
71.0
70.7
70.4
70.1
69.9
O
CF3
O
O
CF3
CO-8
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.85
7.84
7.83
7.80
7.80
7.80
7.79
7.79
7.41
7.39
7.39
7.38
7.38
7.38
7.36
7.26
5.61
5.60
5.59
5.58
5.57
5.55
5.53
O
CF3
O
O
CF3
S
CO-9
1H NMR (500 MHz, CDCl3)
1.03
1.00
1.00
1.93
1.04
1.93
f1 (ppm)



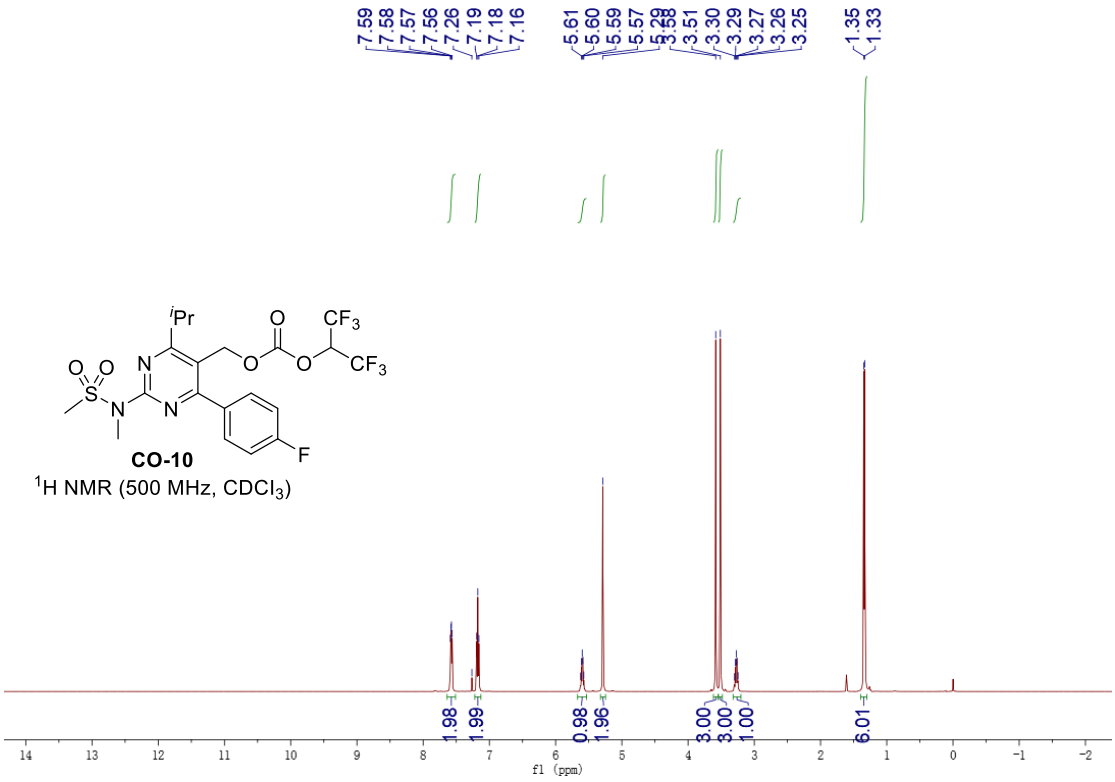
CO-9

^{19}F NMR (471 MHz, $CDCl_3$)



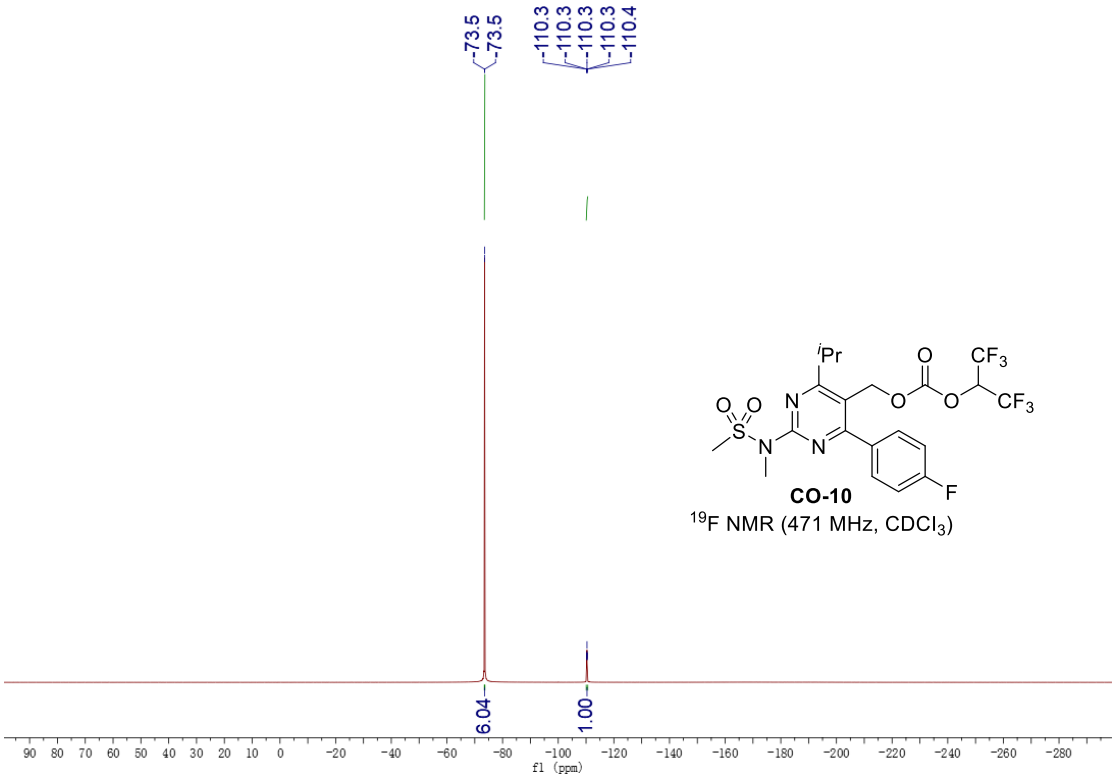
CO-9

^{13}C NMR (126 MHz, $CDCl_3$)



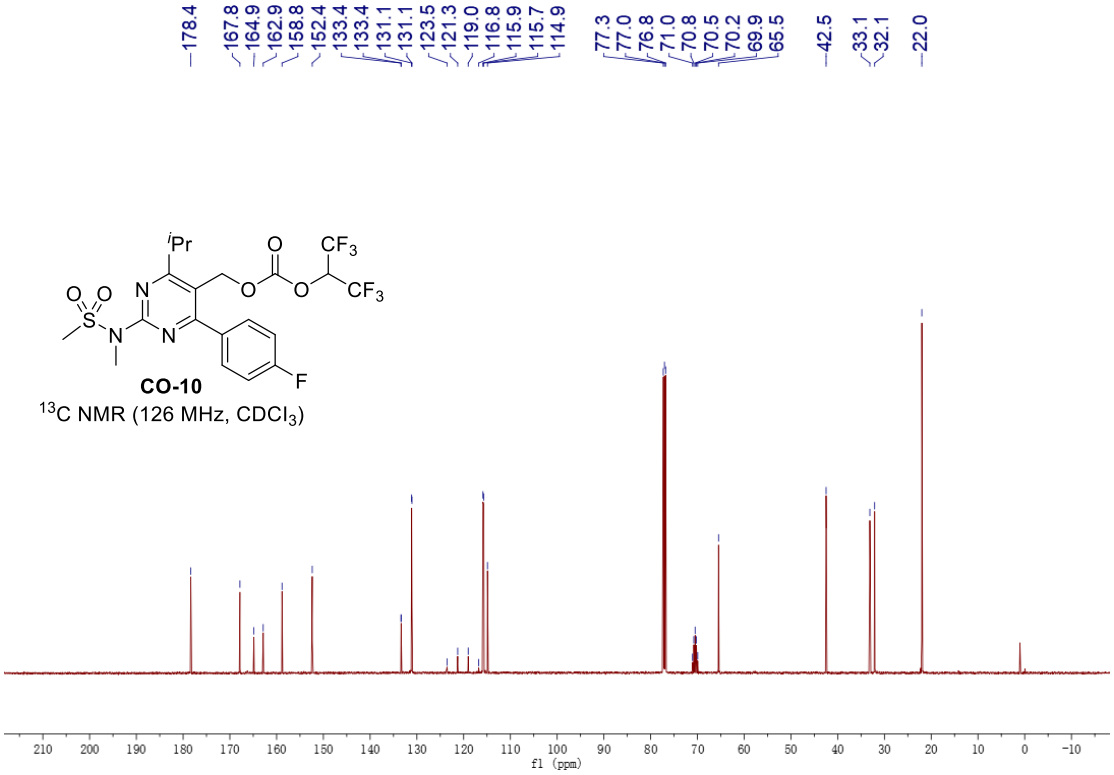
CO-10

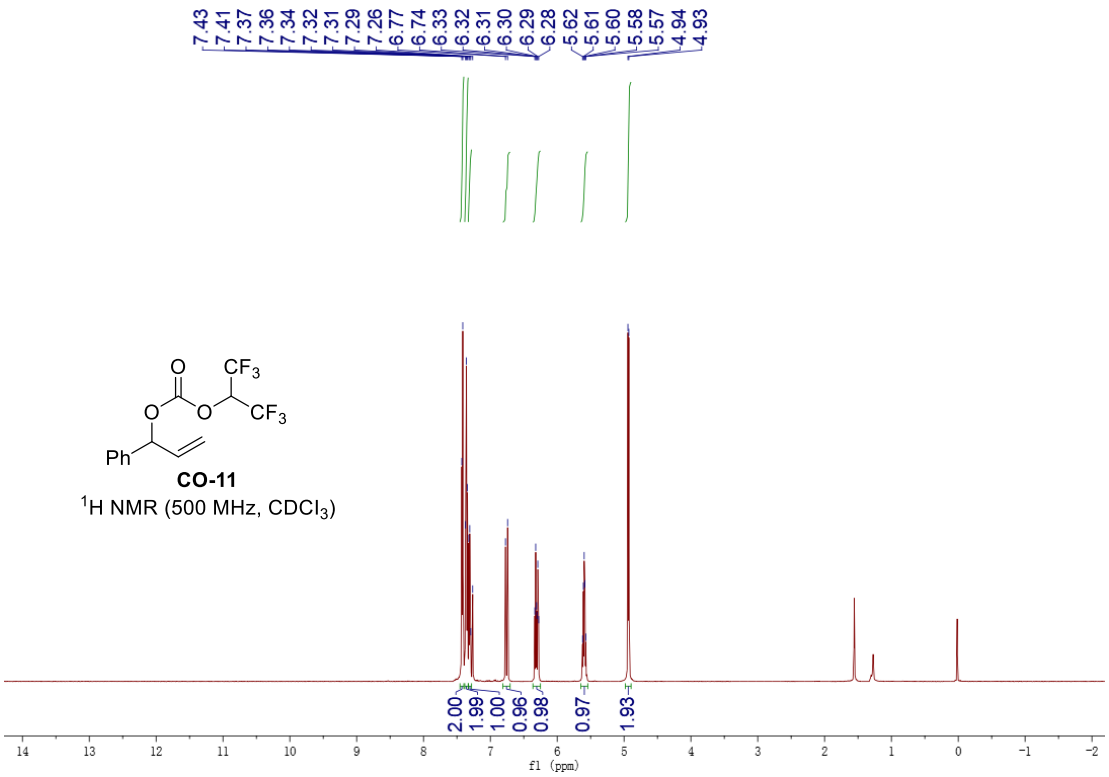
^{1}H NMR (500 MHz, $CDCl_3$)

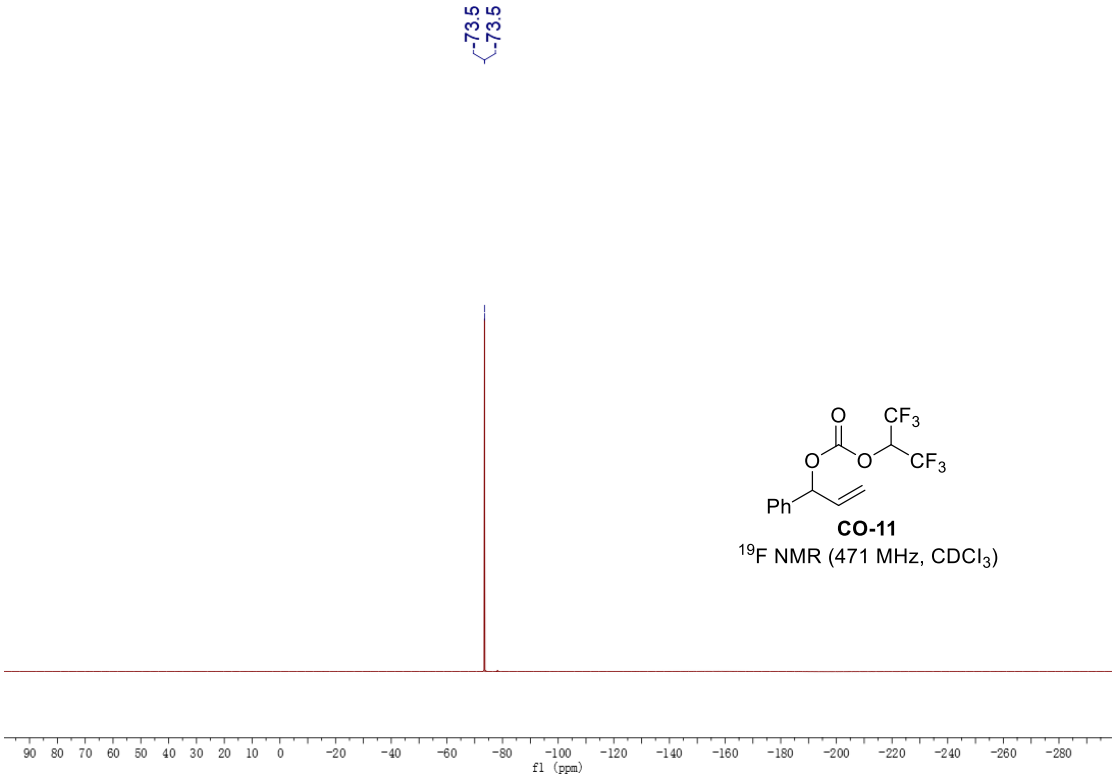


CO-10

^{19}F NMR (471 MHz, $CDCl_3$)

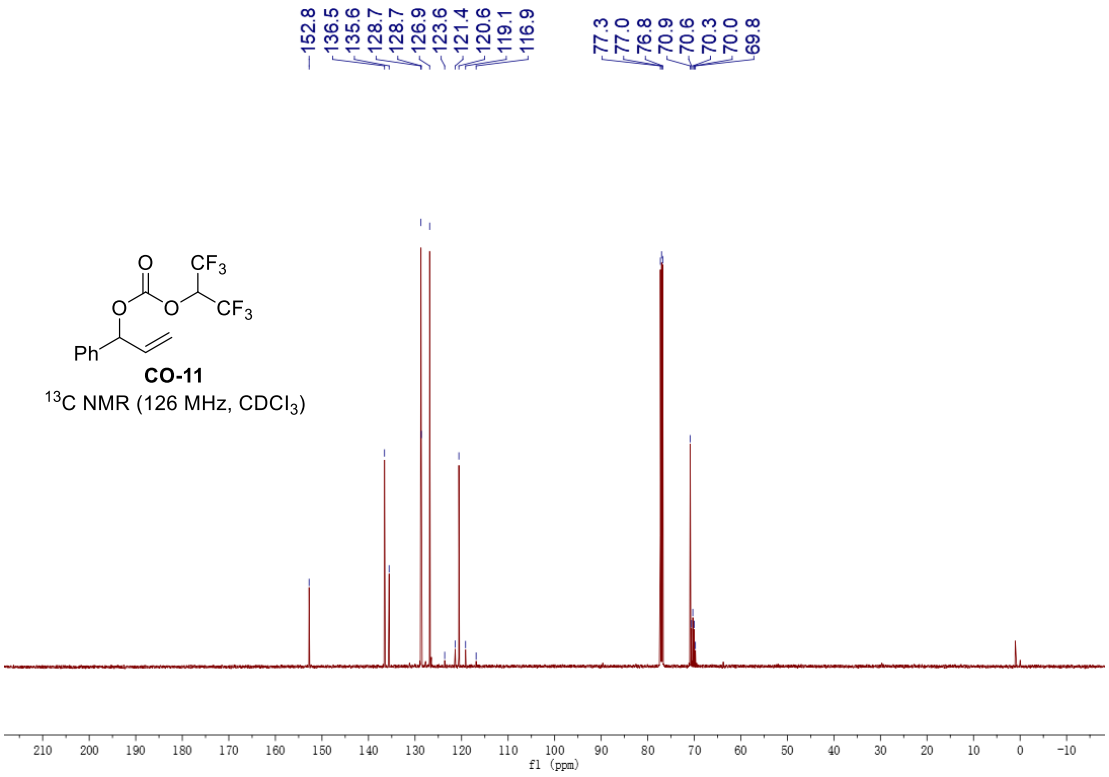

178.4
167.8
164.9
162.9
158.8
152.4
133.4
133.4
131.1
131.1
123.5
121.3
119.0
116.8
115.9
115.7
114.9
77.3
77.0
76.8
71.0
70.8
70.5
70.2
69.9
65.5
42.5
33.1
32.1
22.0
iPr
O
CF3
O
N
O
O
S
N
N
O
O
CF3
N
F
CO-10
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.43
7.41
7.37
7.36
7.34
7.32
7.31
7.29
7.26
6.77
6.74
6.33
6.32
6.31
6.30
6.29
6.28
5.62
5.61
5.60
5.58
5.57
4.94
4.93
O
CF3
O
O
CF3
Ph
CO-11
1H NMR (500 MHz, CDCl3)
2.00
1.99
1.00
0.96
0.98
0.97
1.93
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)



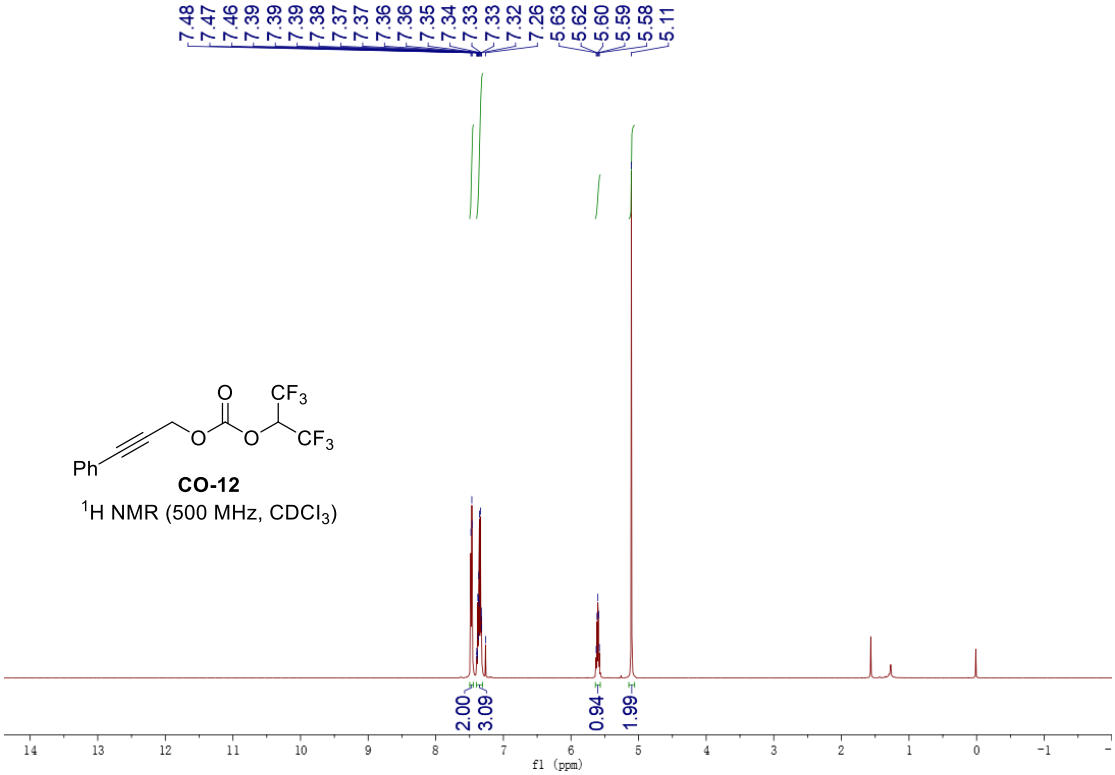
CO-11

^{19}F NMR (471 MHz, $CDCl_3$)



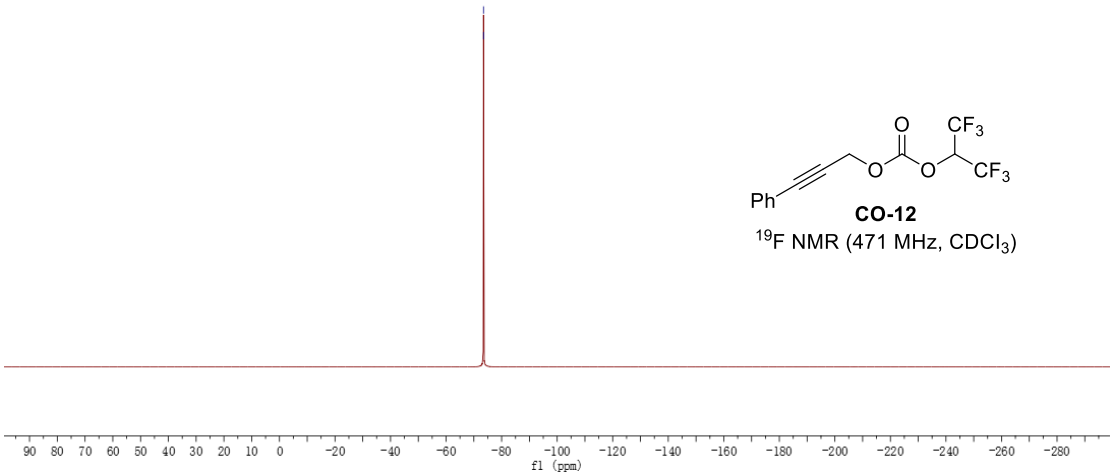
CO-11

^{13}C NMR (126 MHz, $CDCl_3$)



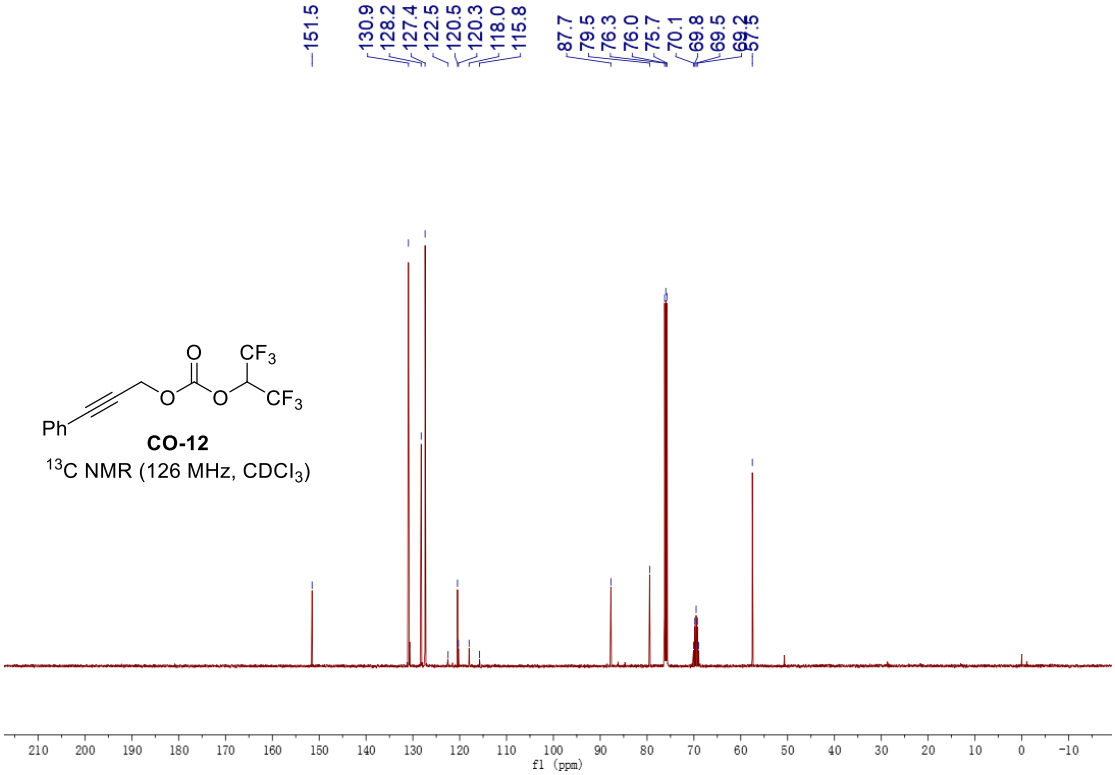
CO-12

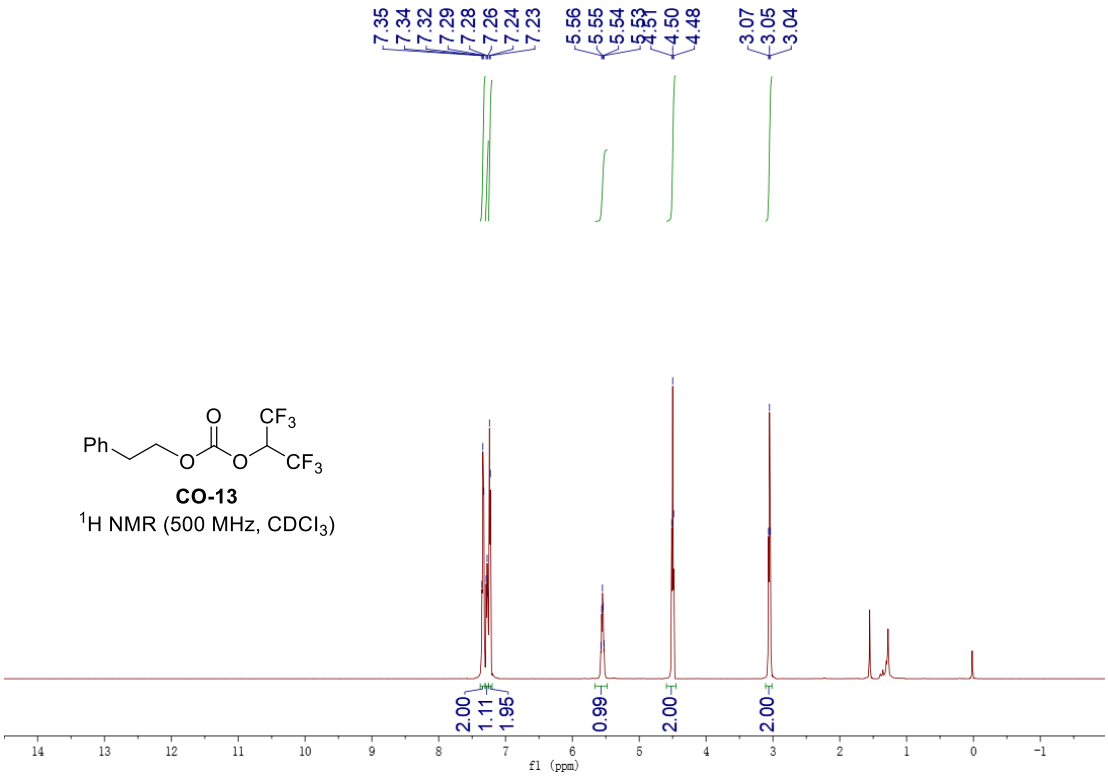
^{1}H NMR (500 MHz, $CDCl_3$)

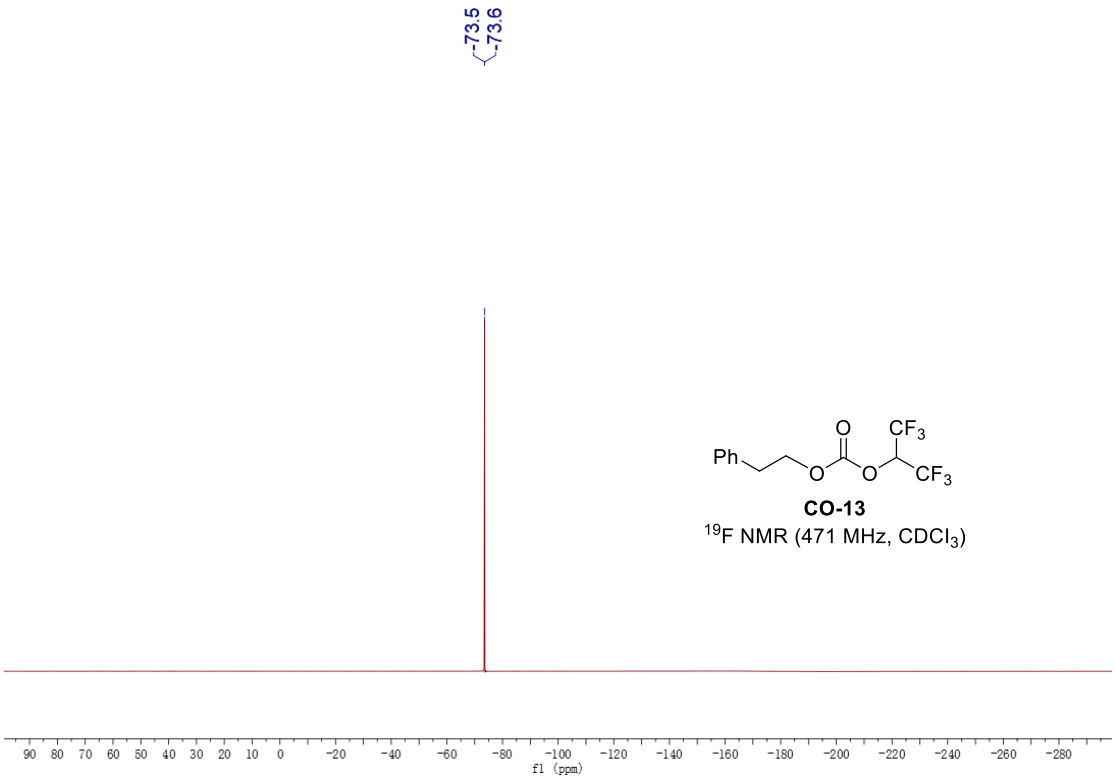


CO-12

^{19}F NMR (471 MHz, $CDCl_3$)

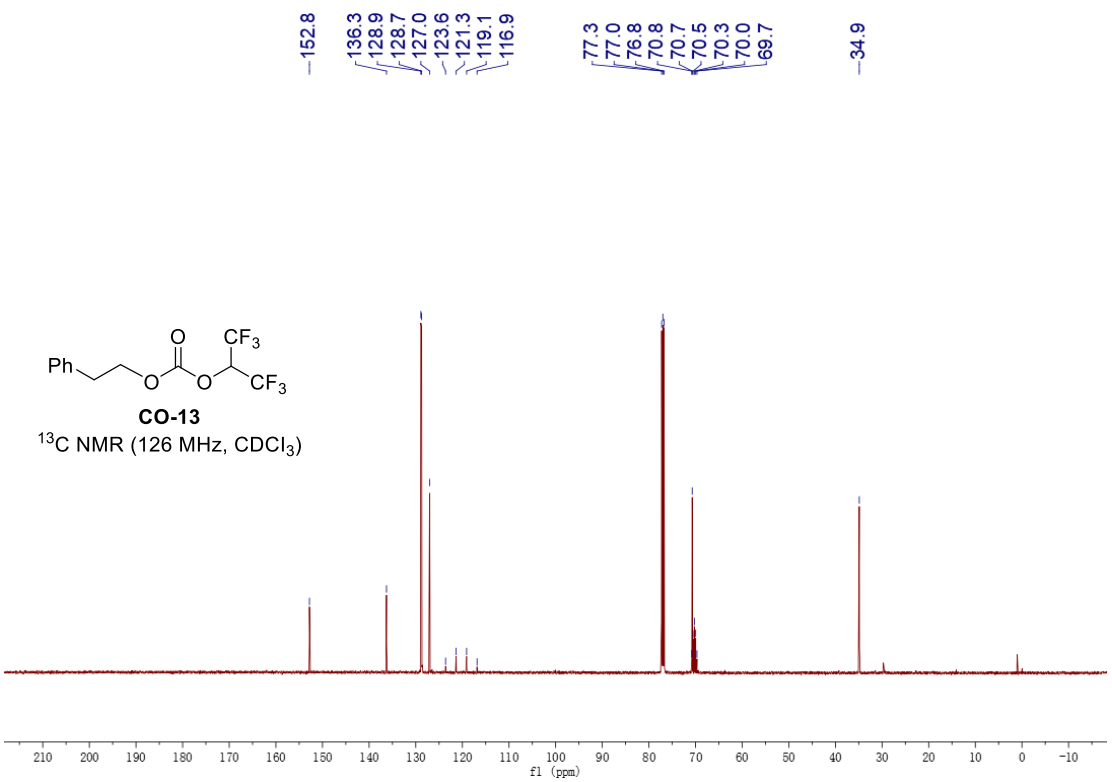

151.5
130.9
128.2
127.4
122.5
120.5
120.3
118.0
115.8
87.7
79.5
76.3
76.0
75.7
70.1
69.8
69.5
69.2
57.5
O
CF3
O
O
CF3
Ph
CO-12
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.35
7.34
7.32
7.29
7.28
7.26
7.24
7.23
5.56
5.55
5.54
5.53
5.51
4.50
4.48
3.07
3.05
3.04
Ph
O
CF3
O
O
CF3
CO-13
1H NMR (500 MHz, CDCl3)
2.00
1.11
1.95
0.99
2.00
2.00
f1 (ppm)



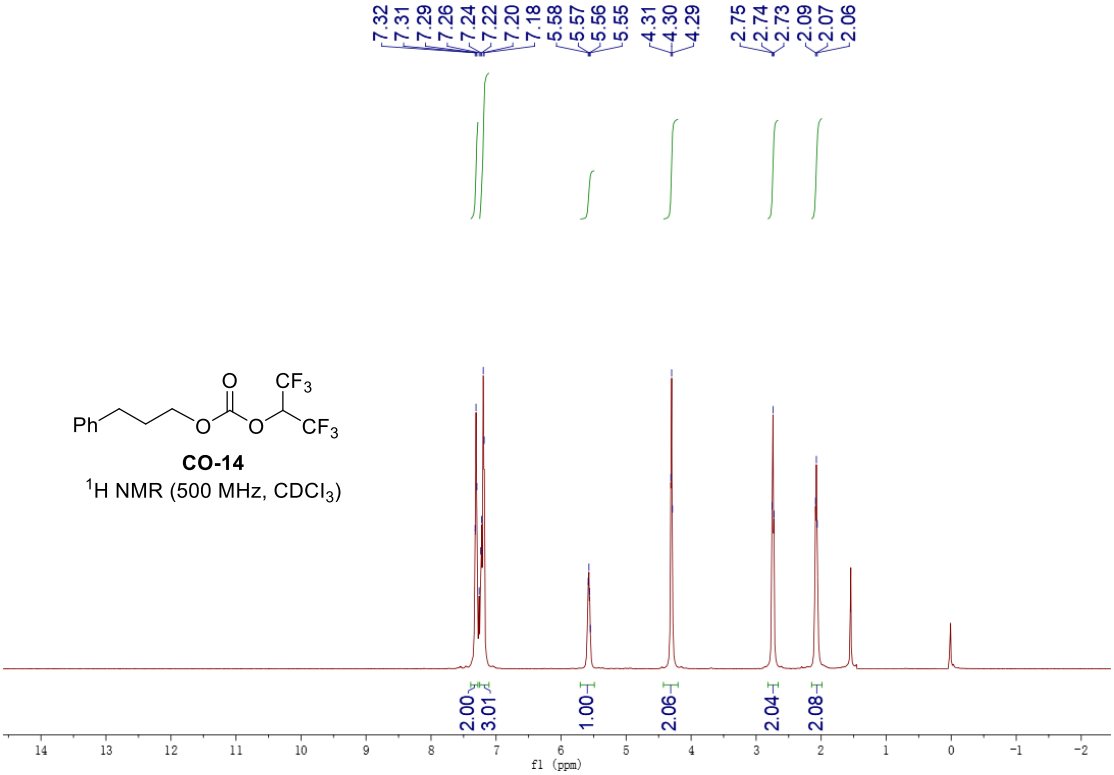
CO-13

^{19}F NMR (471 MHz, $CDCl_3$)



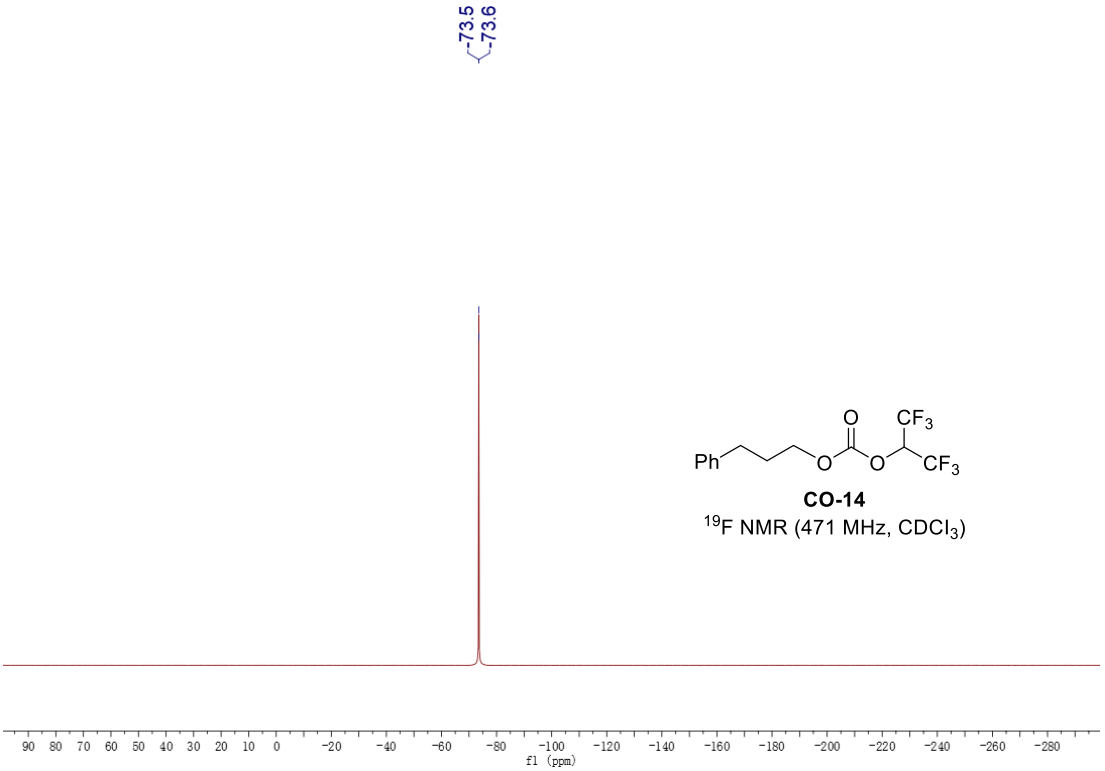
CO-13

^{13}C NMR (126 MHz, $CDCl_3$)



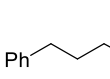
CO-14

^{1}H NMR (500 MHz, $CDCl_3$)



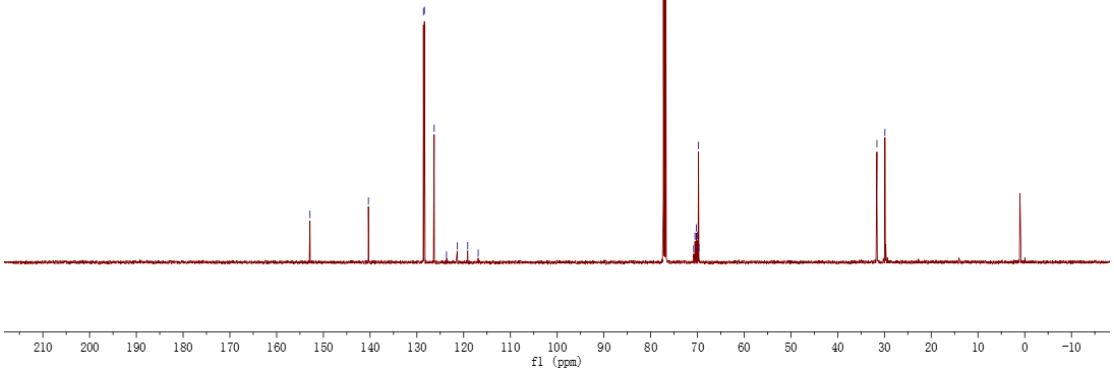
CO-14

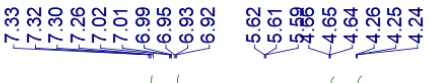
^{19}F NMR (471 MHz, $CDCl_3$)

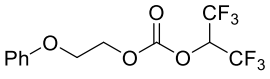


CO-14

^{13}C NMR (126 MHz, $CDCl_3$)

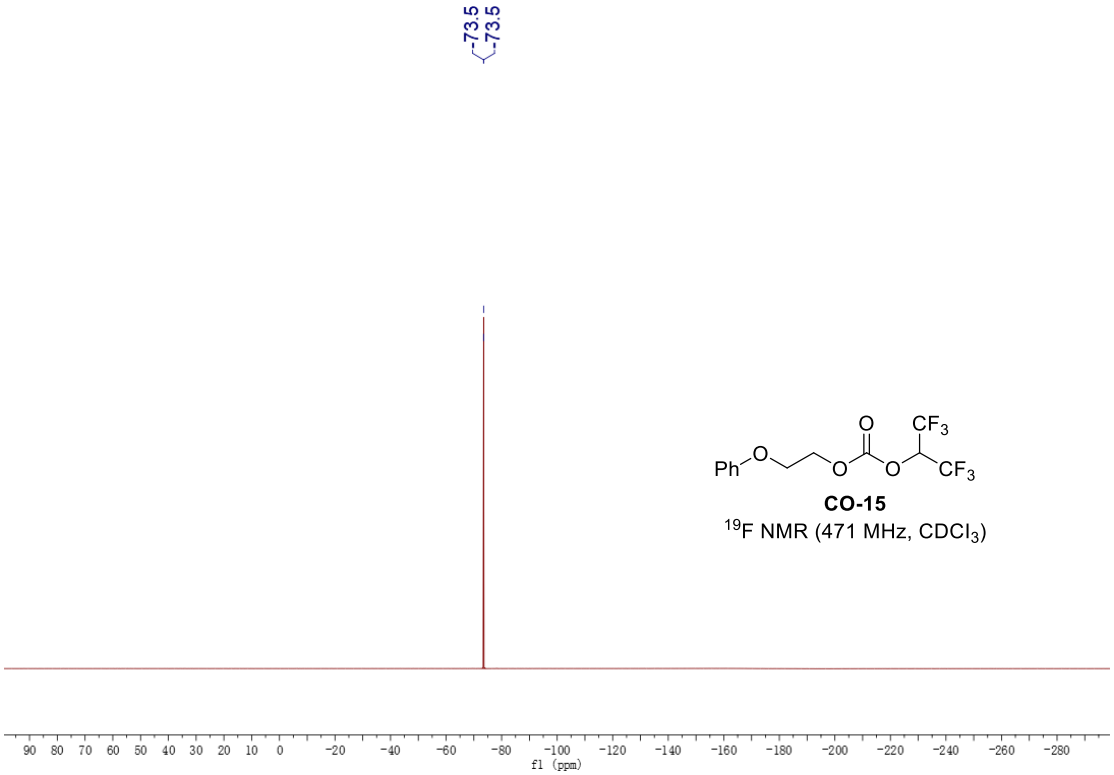






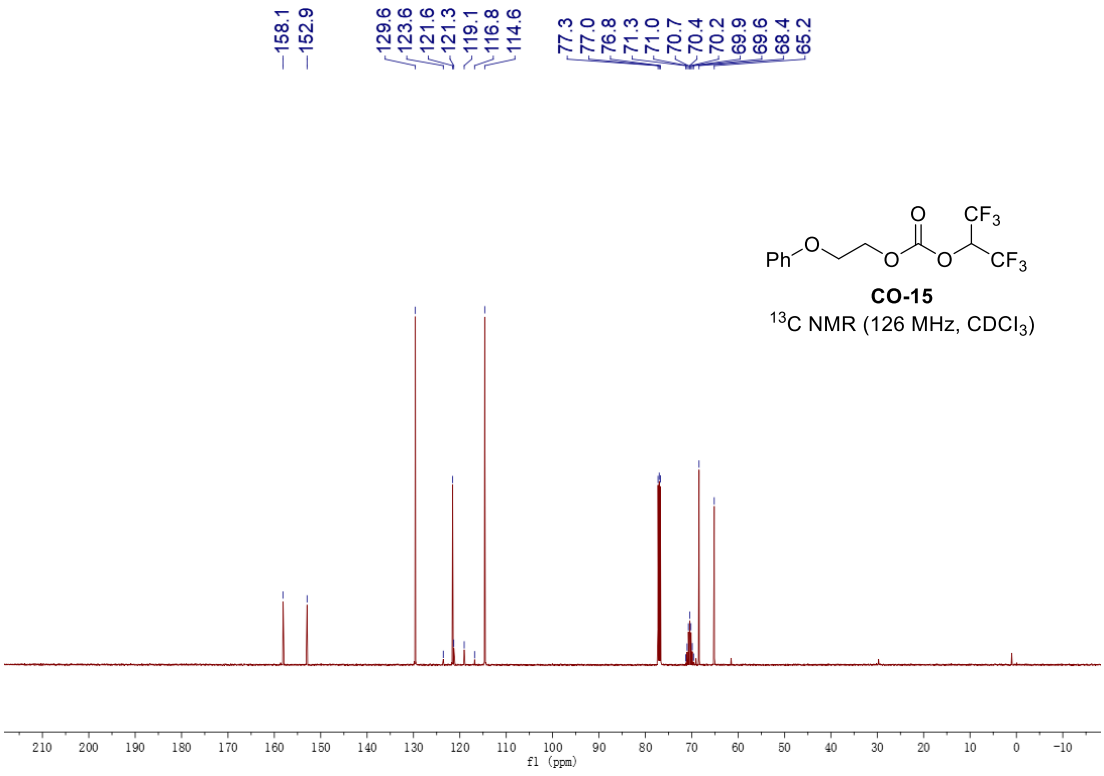
CO-15

^{1}H NMR (500 MHz, $CDCl_3$)



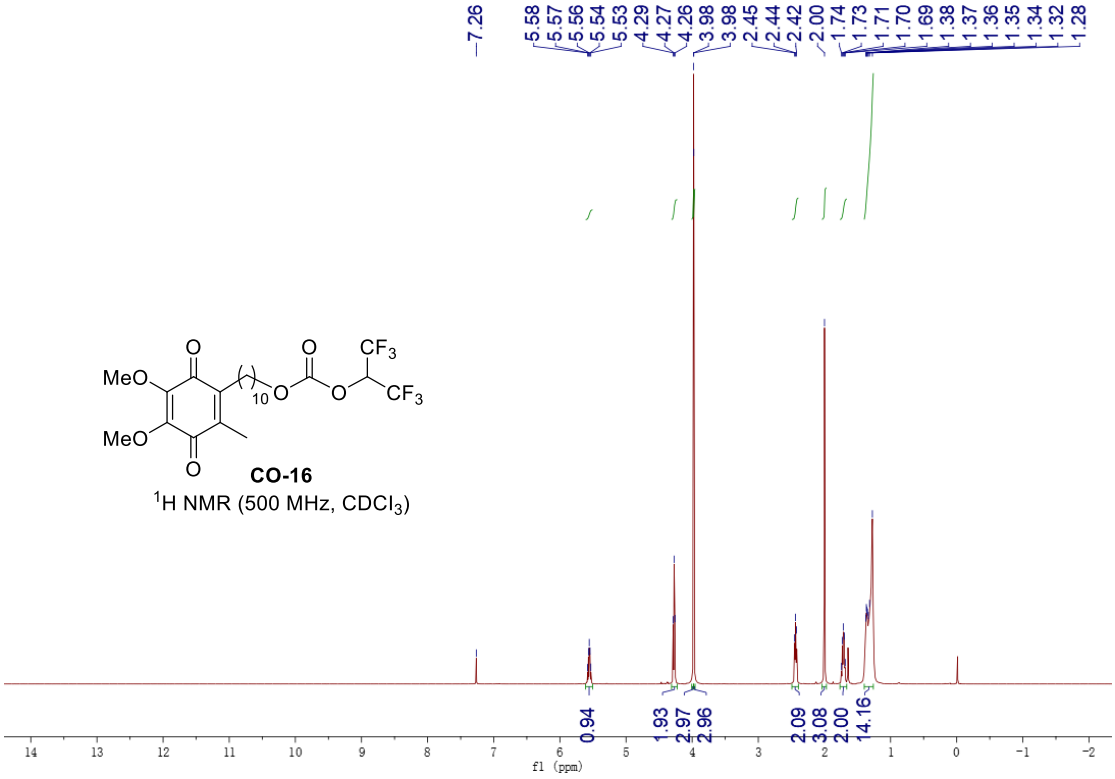
CO-15

^{19}F NMR (471 MHz, $CDCl_3$)



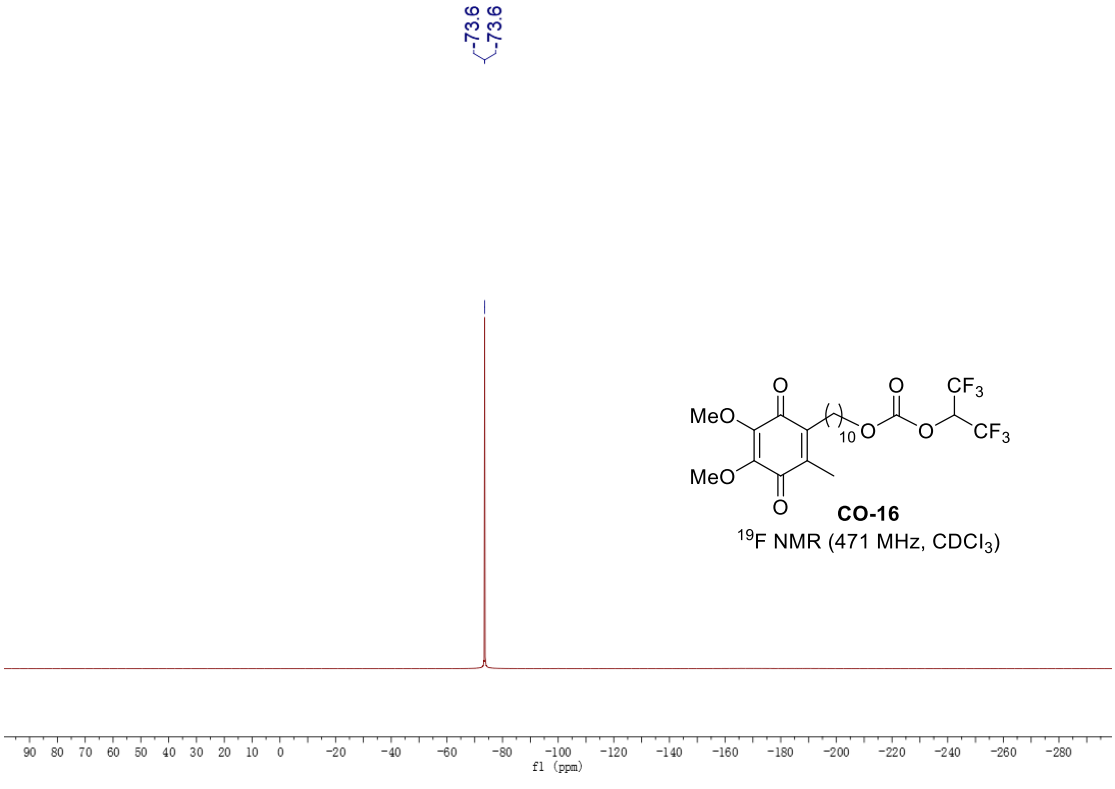
CO-15

^{13}C NMR (126 MHz, $CDCl_3$)



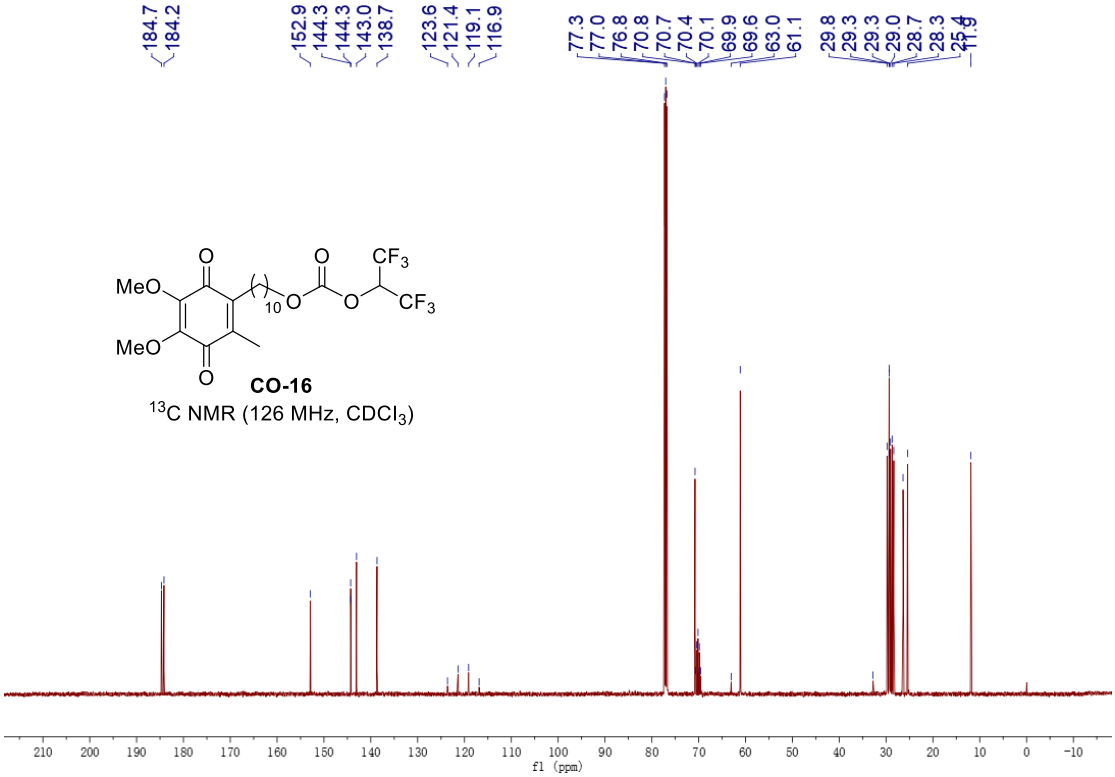
CO-16

^{1}H NMR (500 MHz, $CDCl_3$)



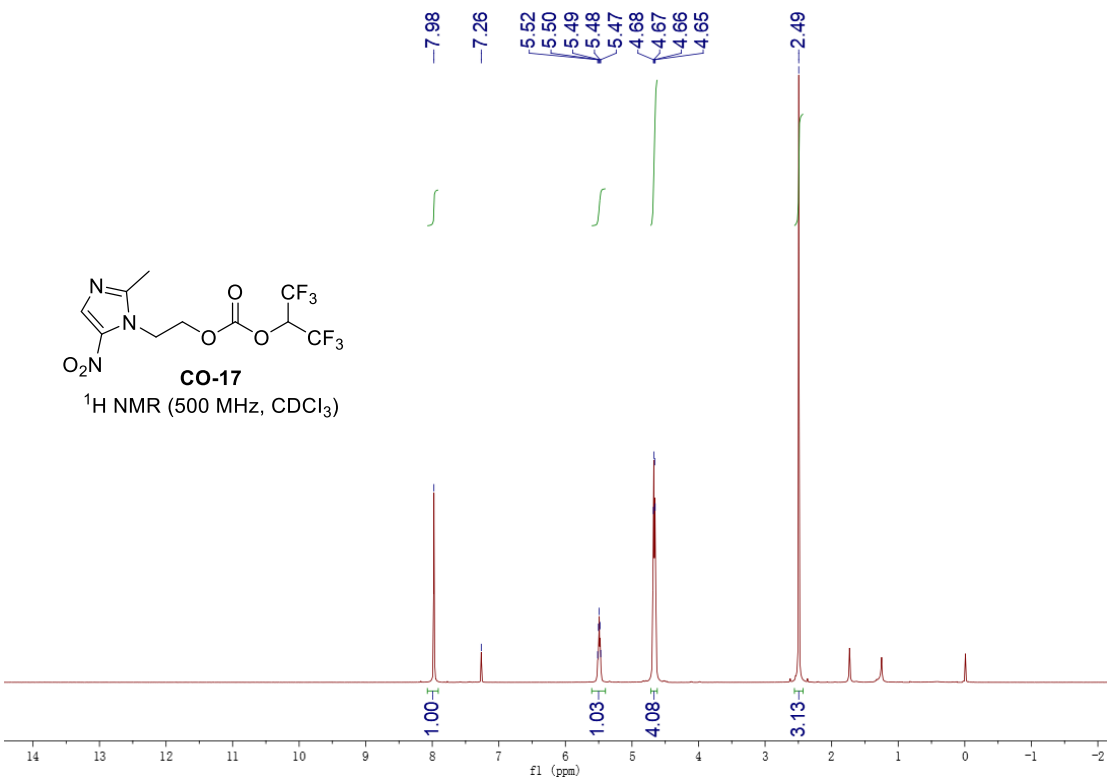
CO-16

^{19}F NMR (471 MHz, $CDCl_3$)



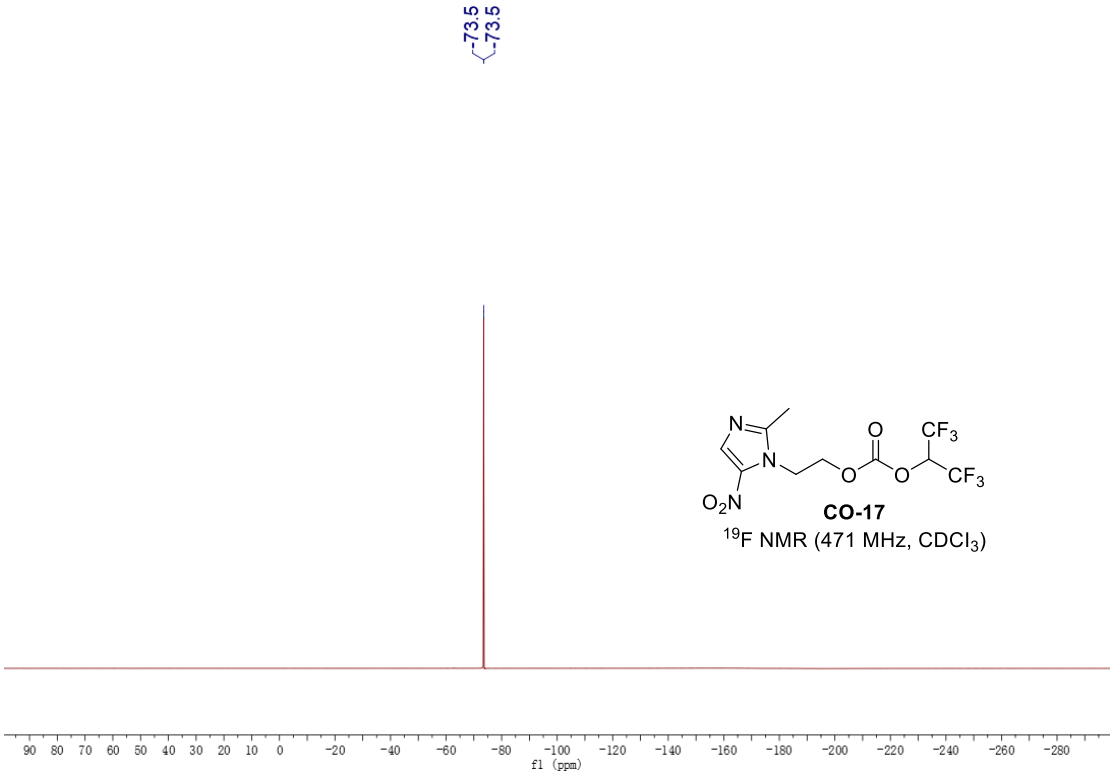
CO-16

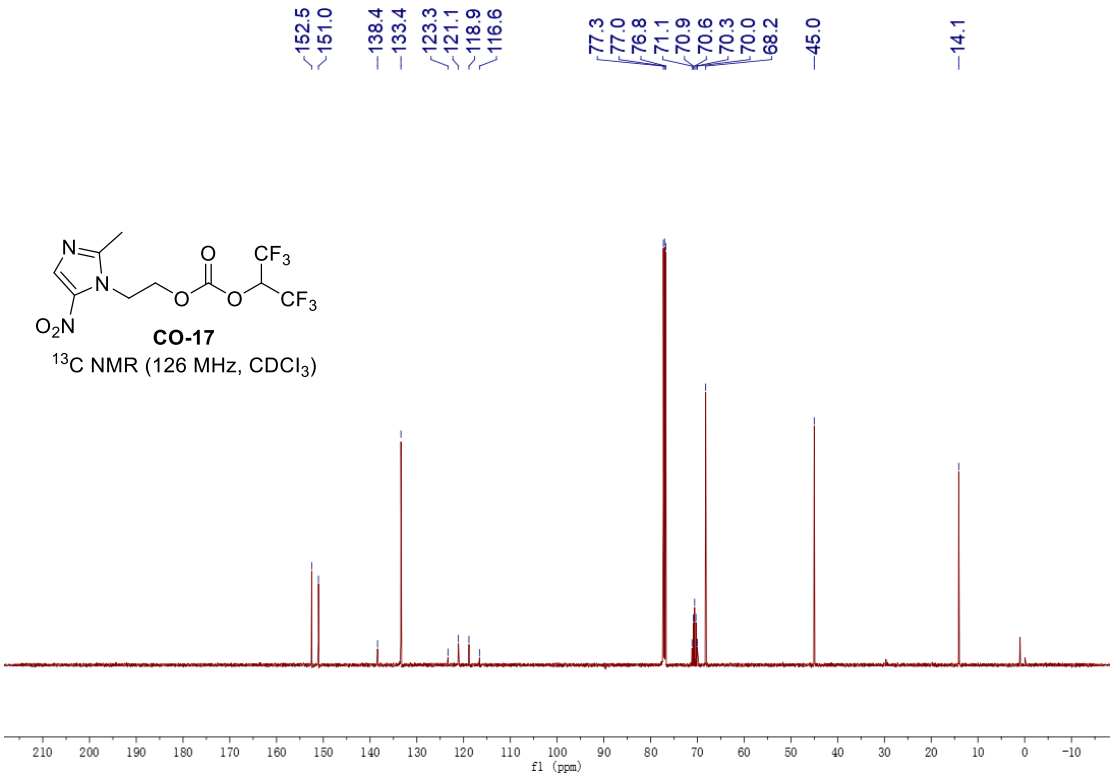
^{13}C NMR (126 MHz, $CDCl_3$)

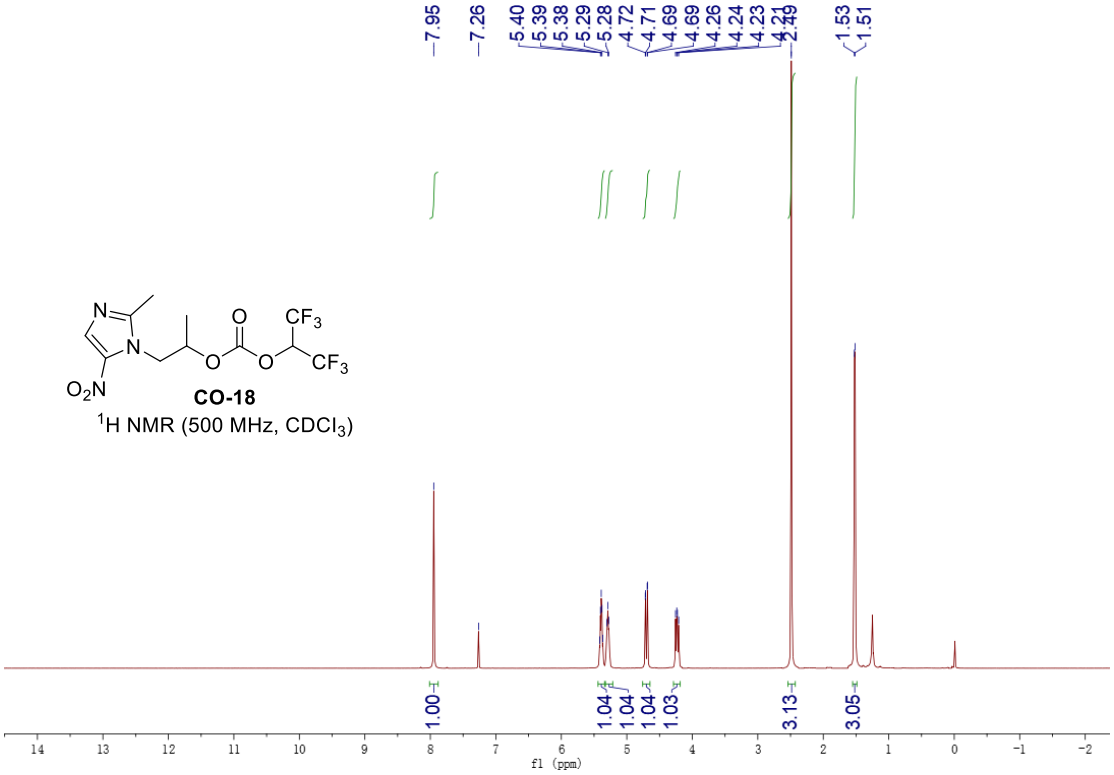


CO-17

^{1}H NMR (500 MHz, $CDCl_3$)

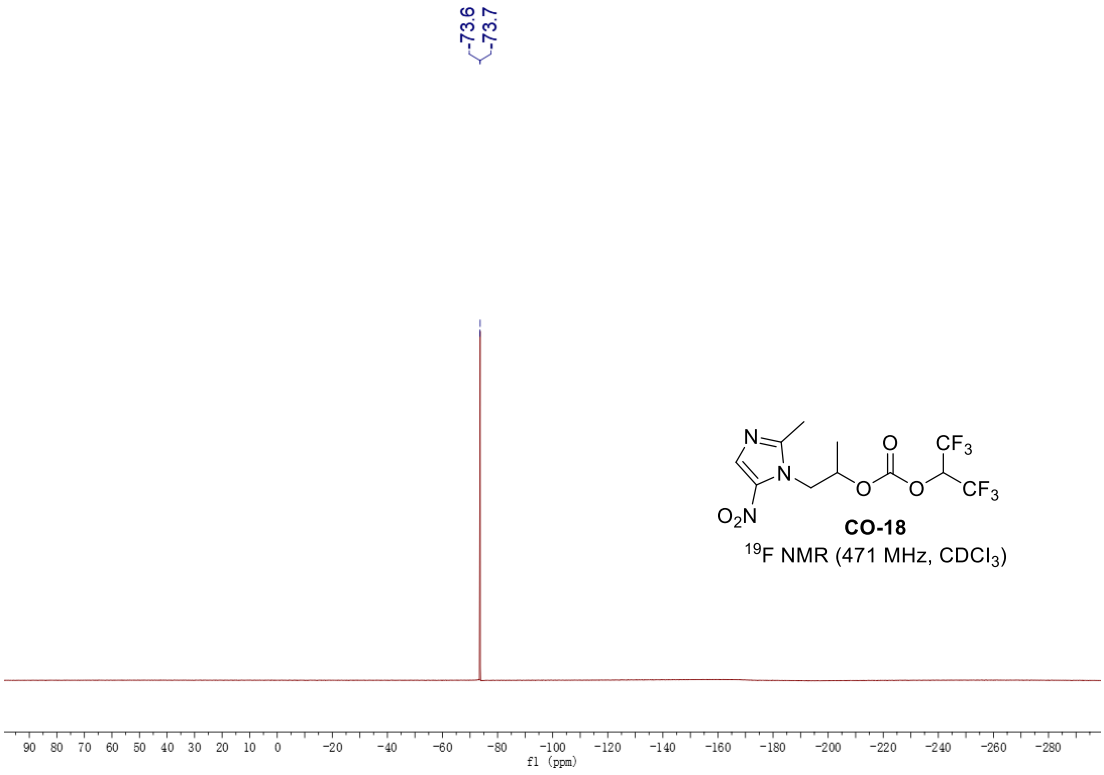

-73.5
-73.5
CO-17
^{19}F NMR (471 MHz, $CDCl_3$)
f1 (ppm)


152.5
151.0
138.4
133.4
123.3
121.1
118.9
116.6
77.3
77.0
76.8
71.1
70.9
70.6
70.3
70.0
68.2
45.0
14.1
CO-17
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)



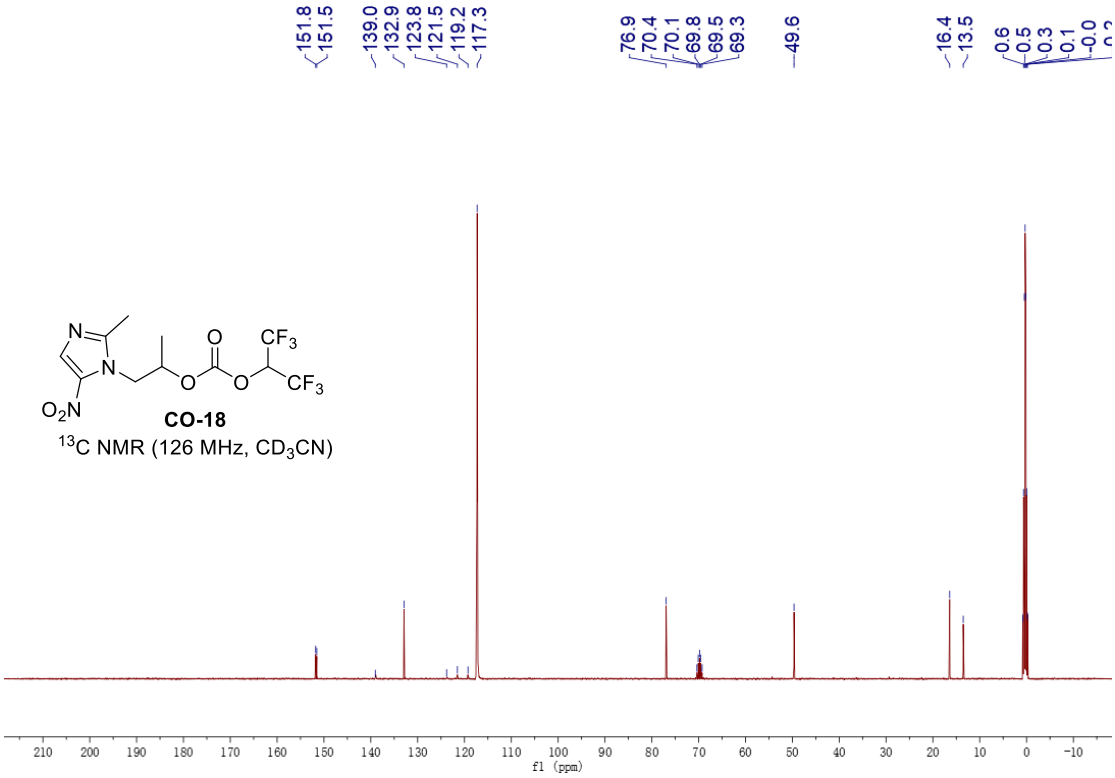
CO-18

^{1}H NMR (500 MHz, $CDCl_3$)



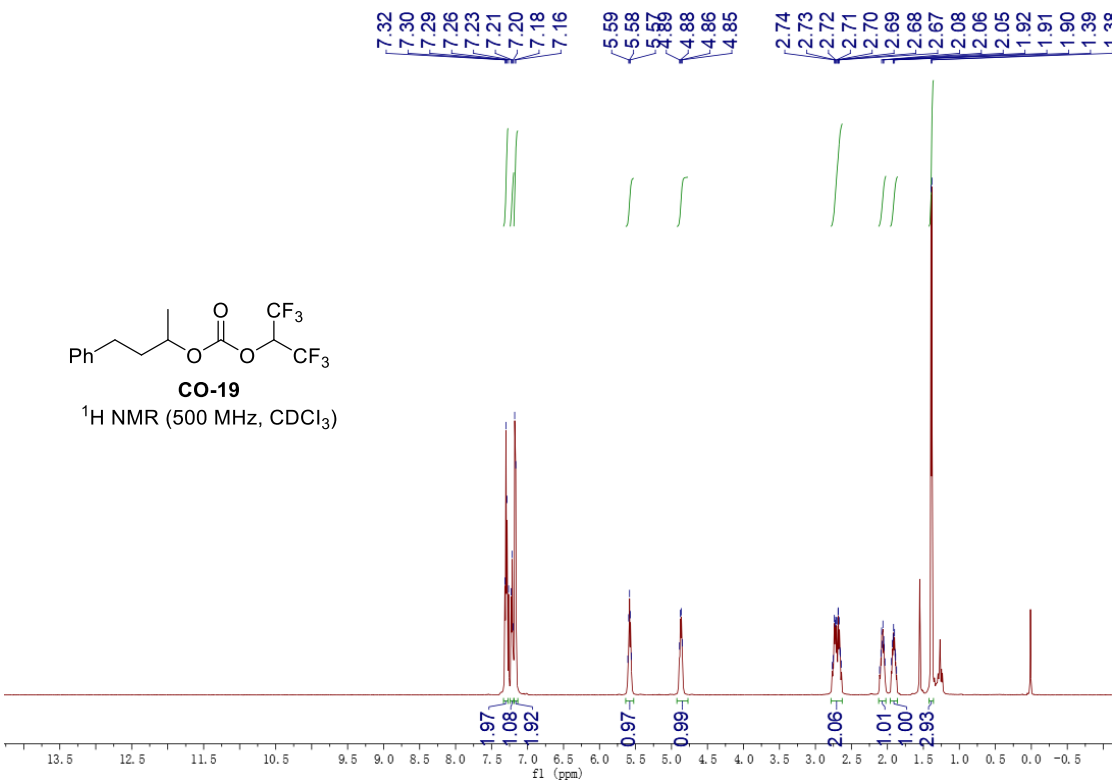
CO-18

^{19}F NMR (471 MHz, $CDCl_3$)



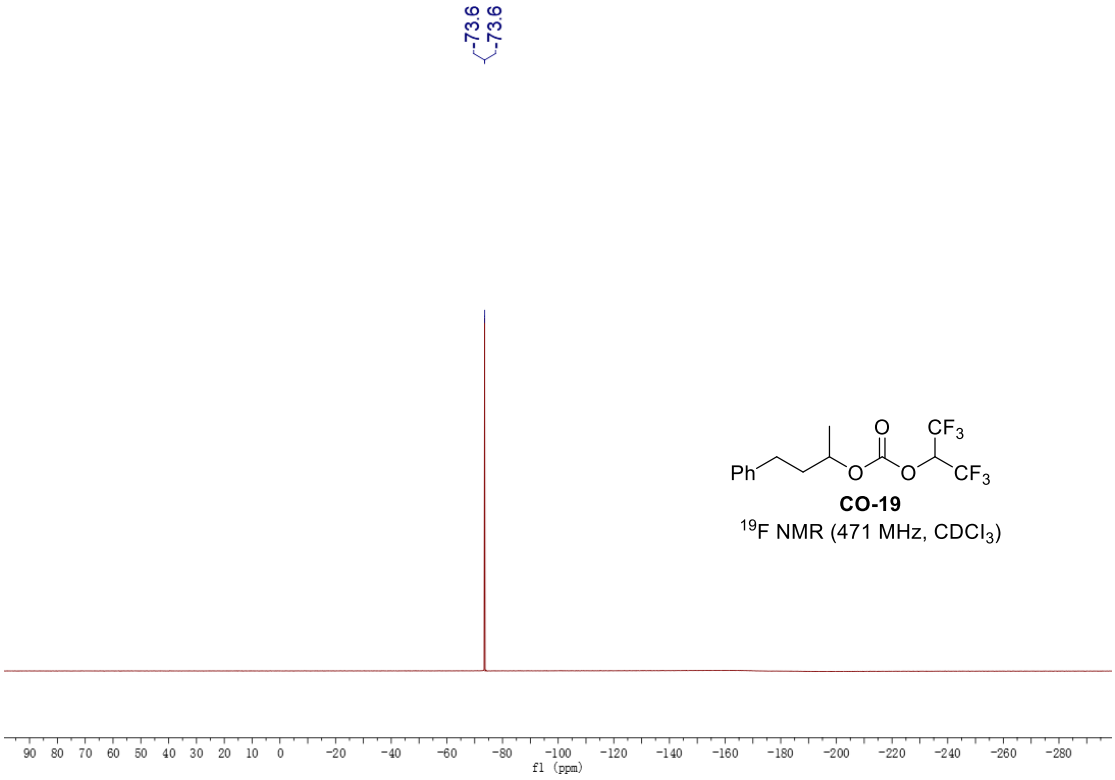
CO-18

^{13}C NMR (126 MHz, CD_3CN)



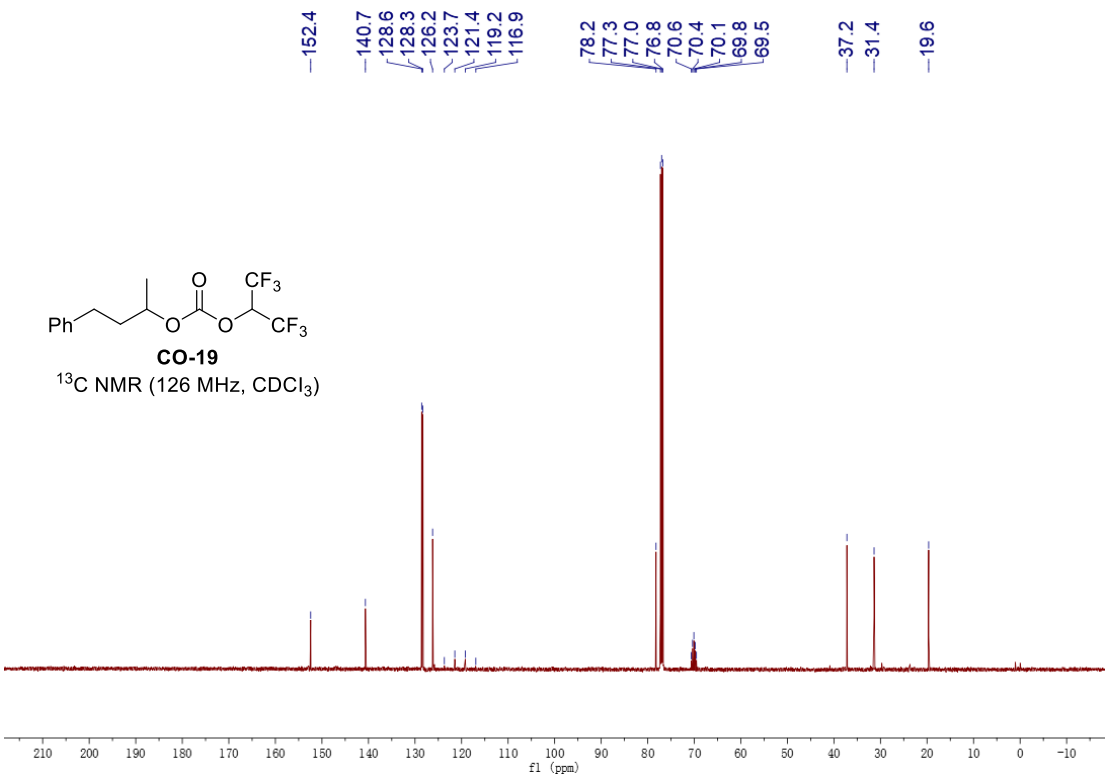
CO-19

^{1}H NMR (500 MHz, $CDCl_3$)



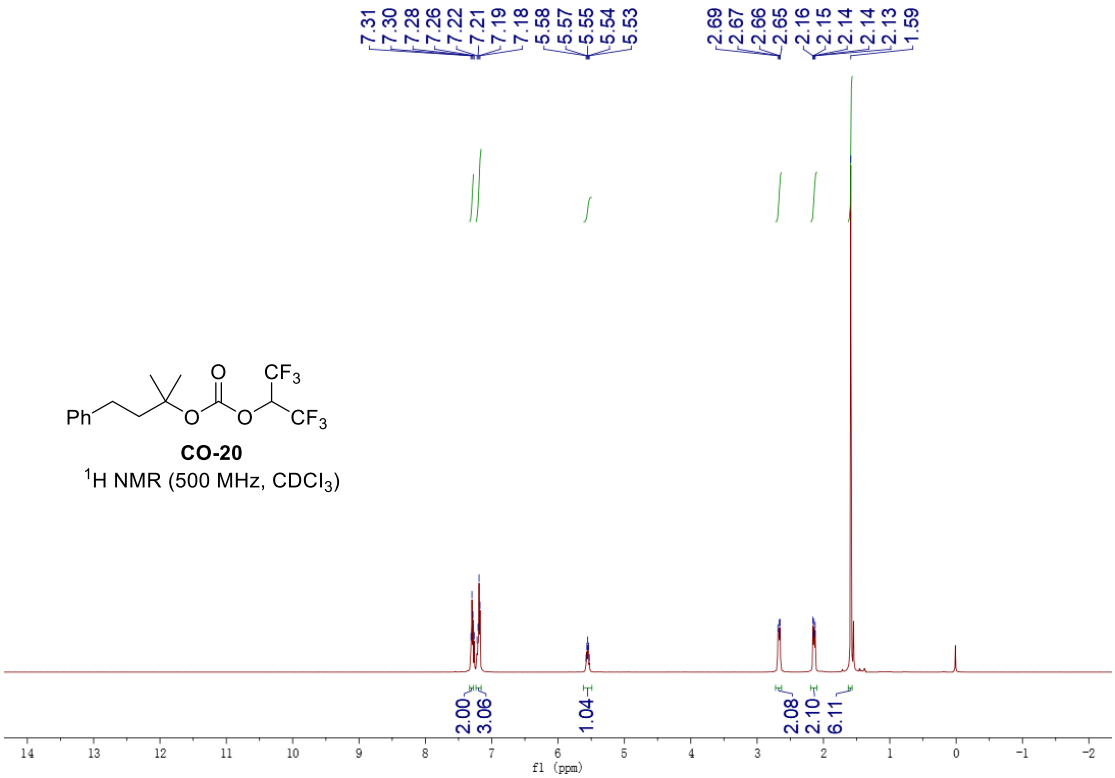
CO-19

^{19}F NMR (471 MHz, $CDCl_3$)



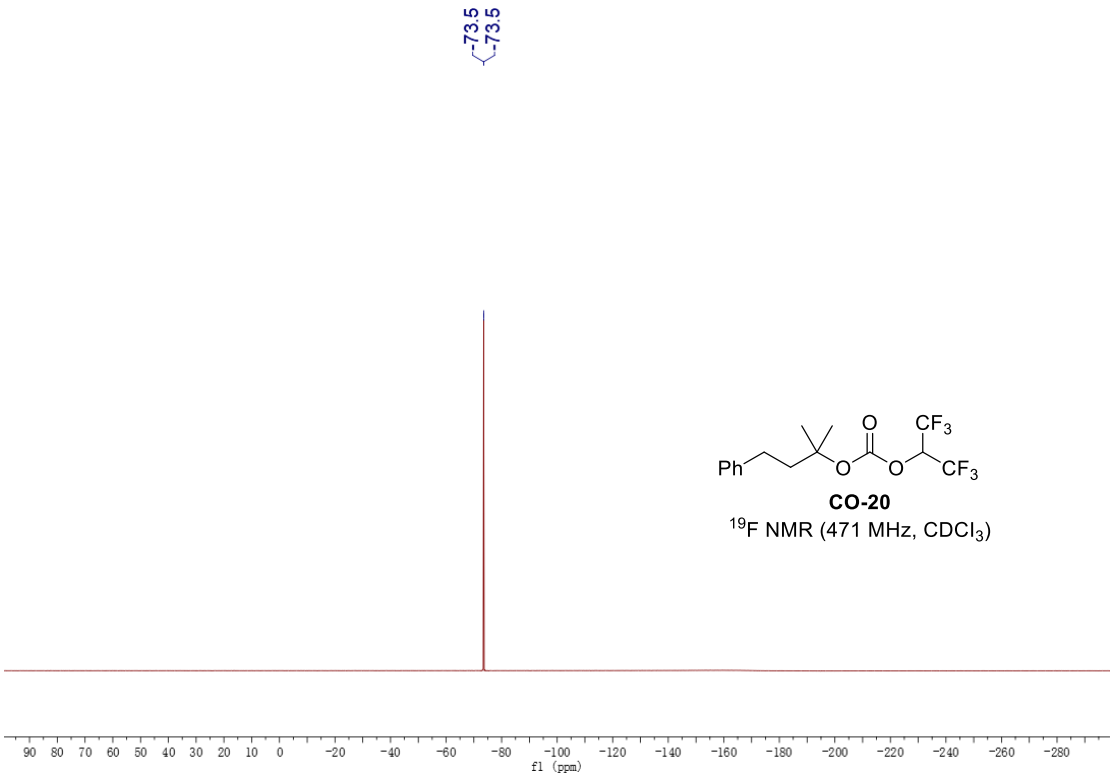
CO-19

^{13}C NMR (126 MHz, $CDCl_3$)



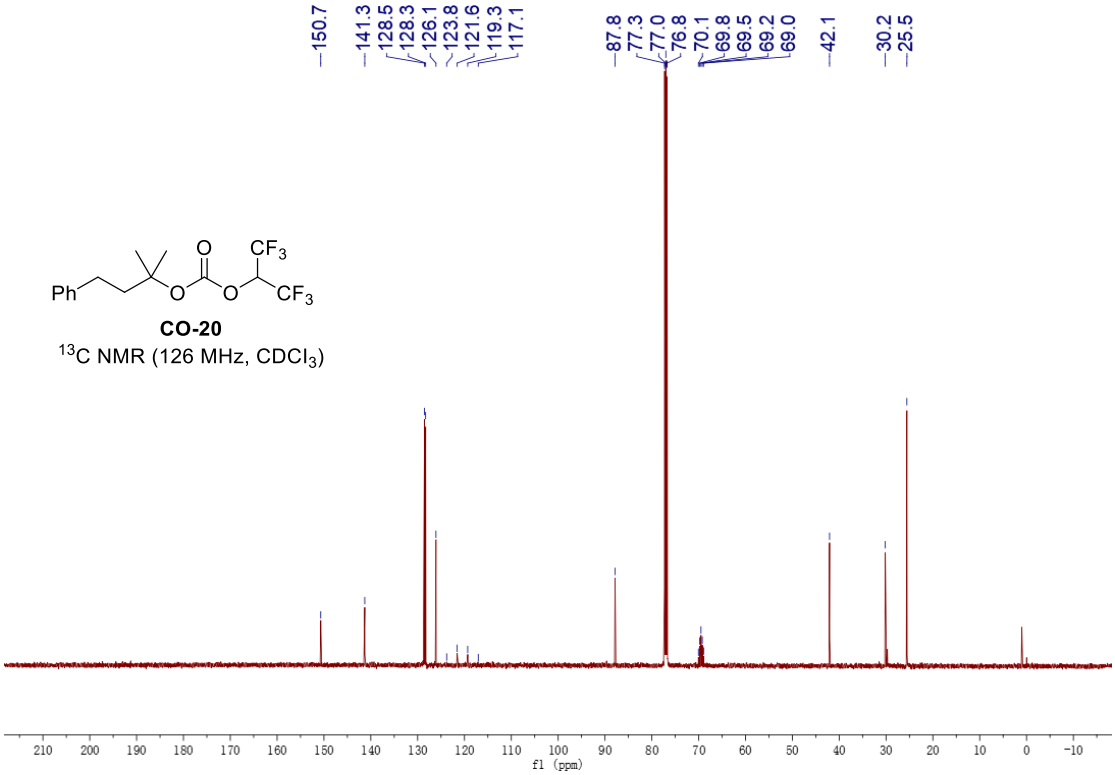
CO-20

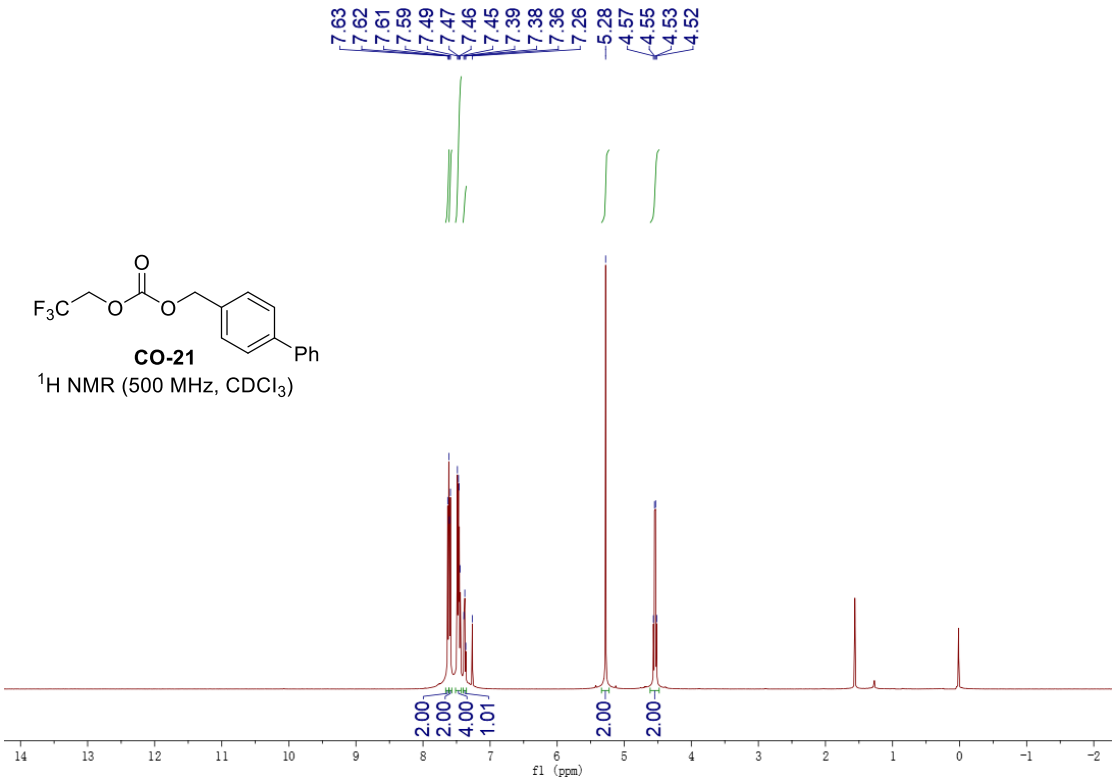
^{1}H NMR (500 MHz, $CDCl_3$)

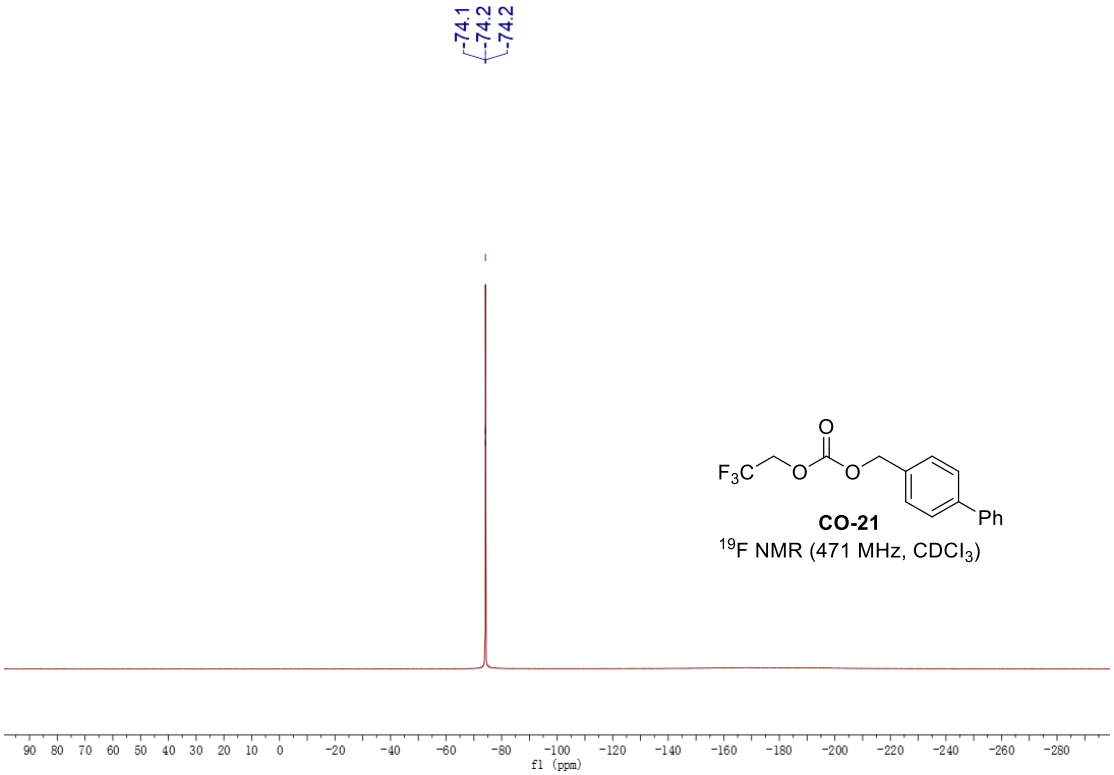


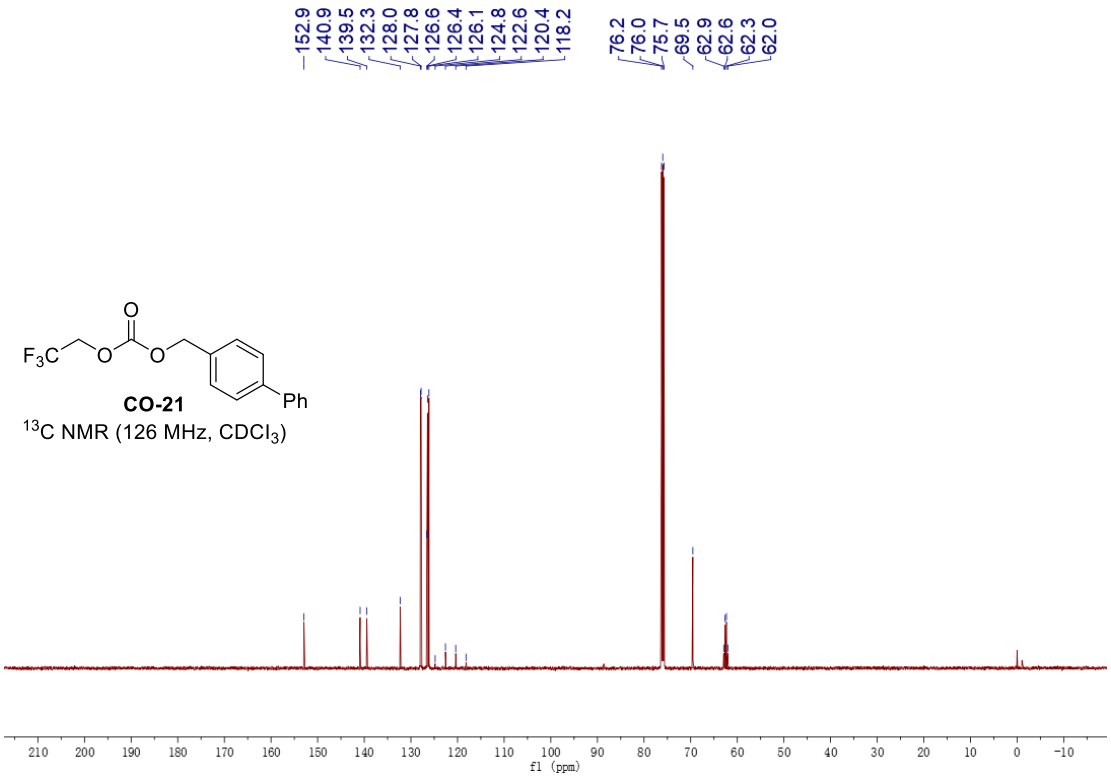
CO-20

^{19}F NMR (471 MHz, $CDCl_3$)


150.7
141.3
128.5
128.3
126.1
123.8
121.6
119.3
117.1
87.8
77.3
77.0
76.8
70.1
69.8
69.5
69.2
69.0
42.1
30.2
25.5
Ph
O
CF3
O
O
CF3
CO-20
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.63
7.62
7.61
7.59
7.49
7.47
7.46
7.45
7.39
7.38
7.36
7.26
5.28
4.57
4.55
4.53
4.52
F3C
O
O
O
Ph
CO-21
1H NMR (500 MHz, CDCl3)
2.00
2.00
4.00
1.01
2.00
2.00
f1 (ppm)


-74.1
-74.2
-74.2
F3C
O
O
O
Ph
CO-21
19F NMR (471 MHz, CDCl3)
f1 (ppm)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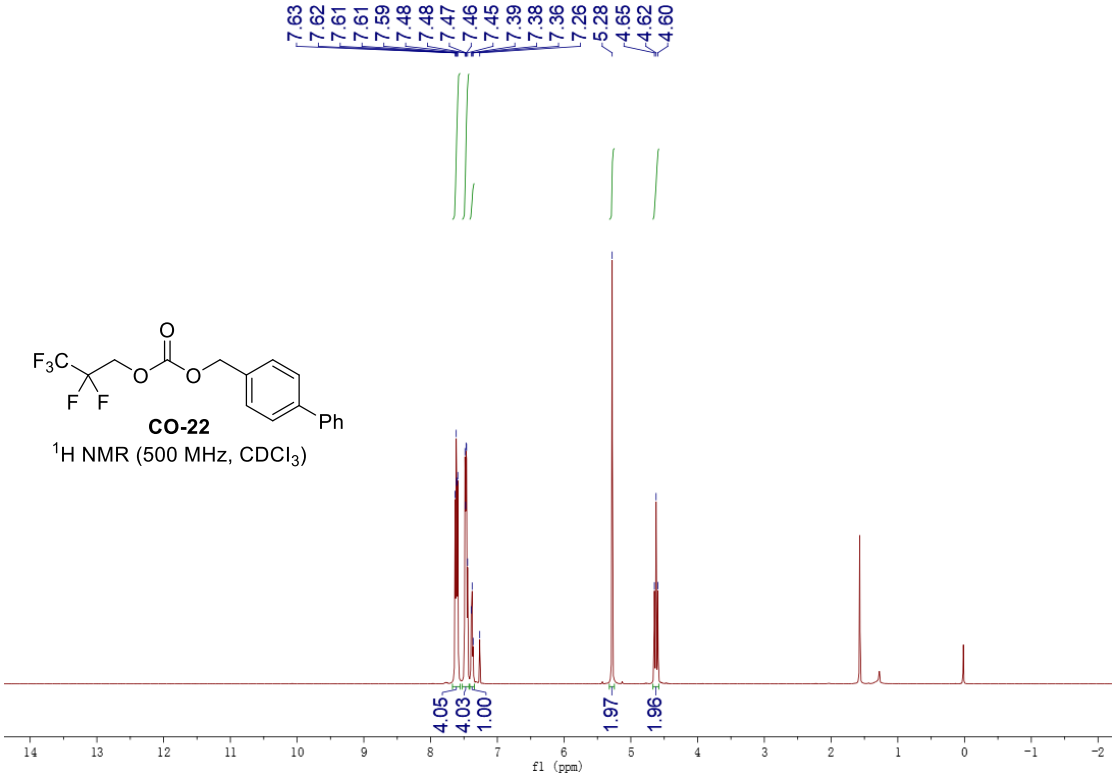
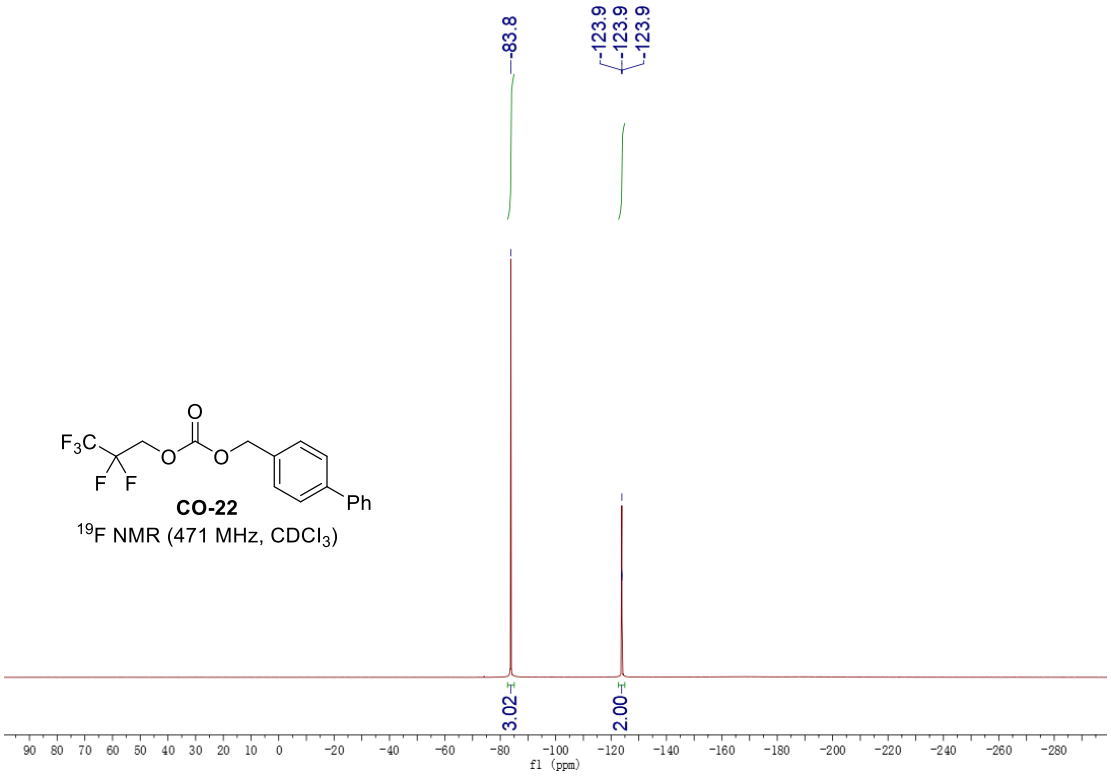
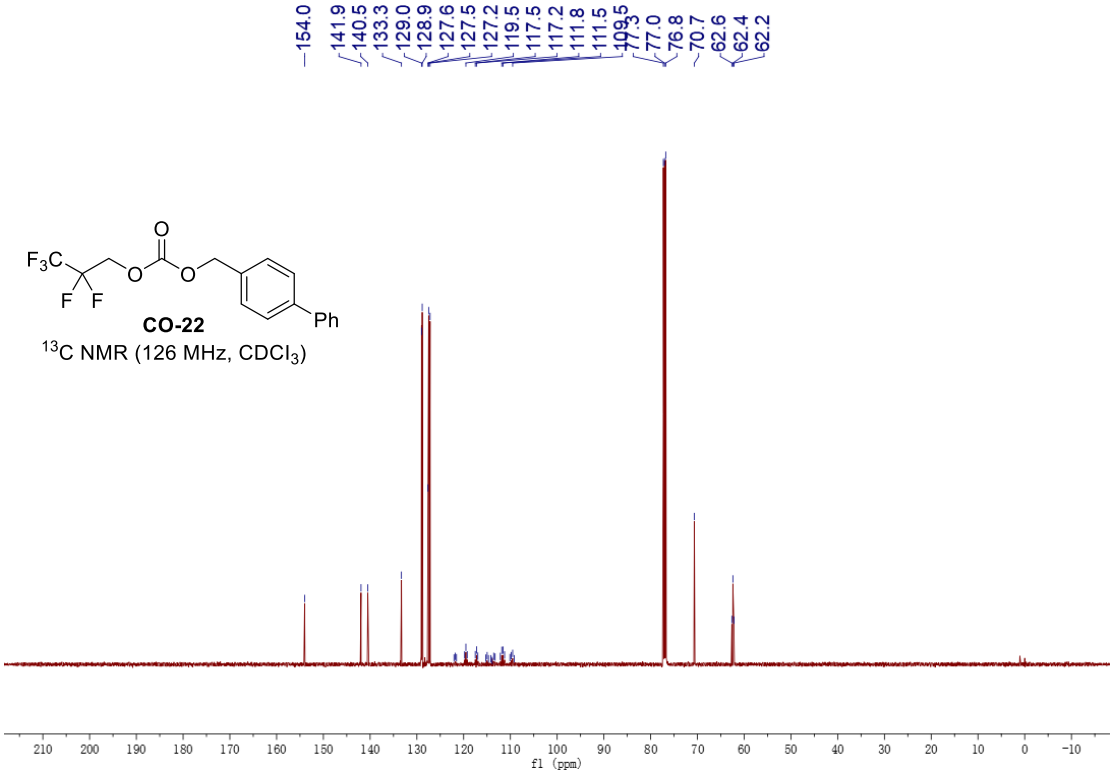
140.9
139.5
132.3
128.0
127.8
126.6
126.4
126.1
124.8
122.6
120.4
118.2
76.2
76.0
75.7
69.5
62.9
62.6
62.3
62.0
F3C
O
O
O
Ph
CO-21
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.63
7.62
7.61
7.61
7.59
7.48
7.48
7.47
7.46
7.45
7.39
7.38
7.36
7.26
5.28
4.65
4.62
4.60
F3C
F F
O
O
O
Ph
CO-22
1H NMR (500 MHz, CDCl3)
4.05
4.03
1.00
1.97
1.96
f1 (ppm)


-83.8
-123.9
-123.9
-123.9
F3C
F F
O
O
O
Ph
CO-22
19F NMR (471 MHz, CDCl3)
3.02
2.00
f1 (ppm)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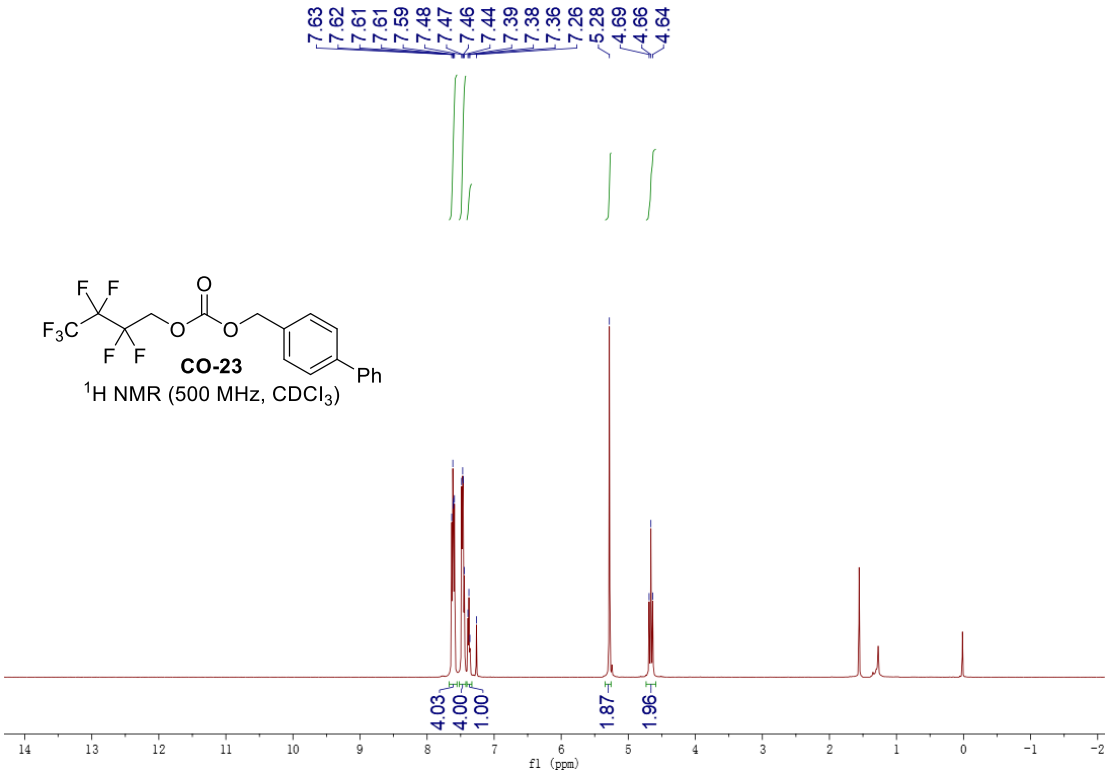
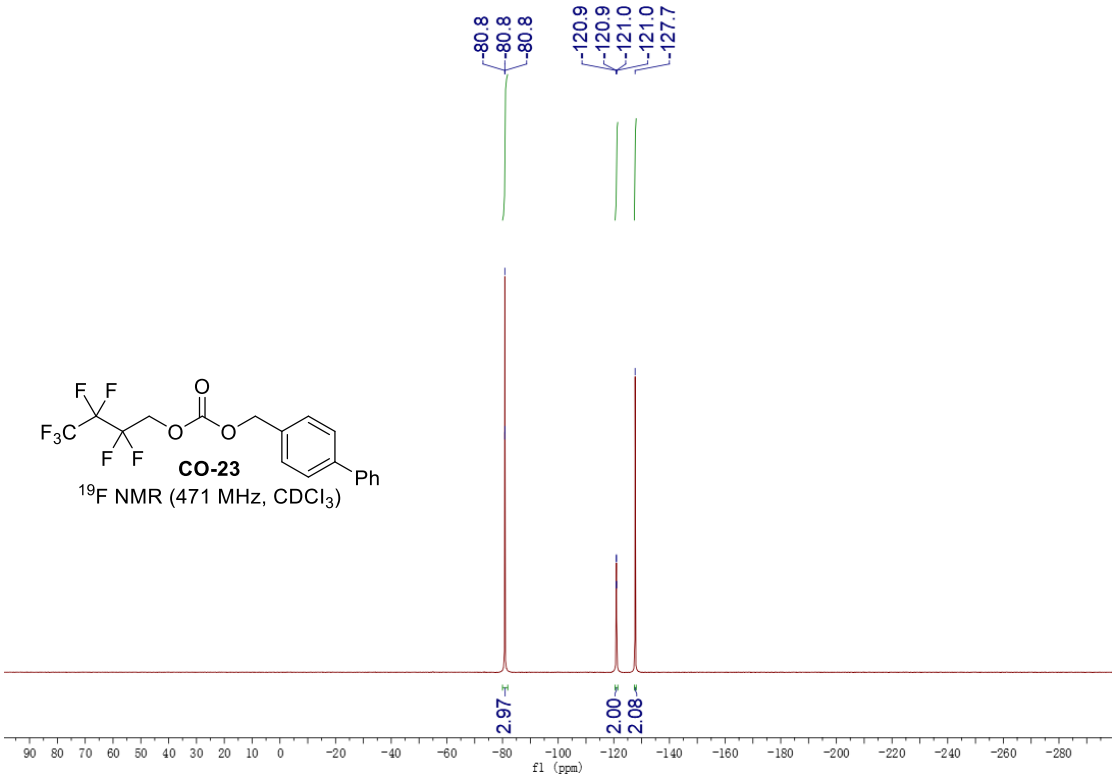
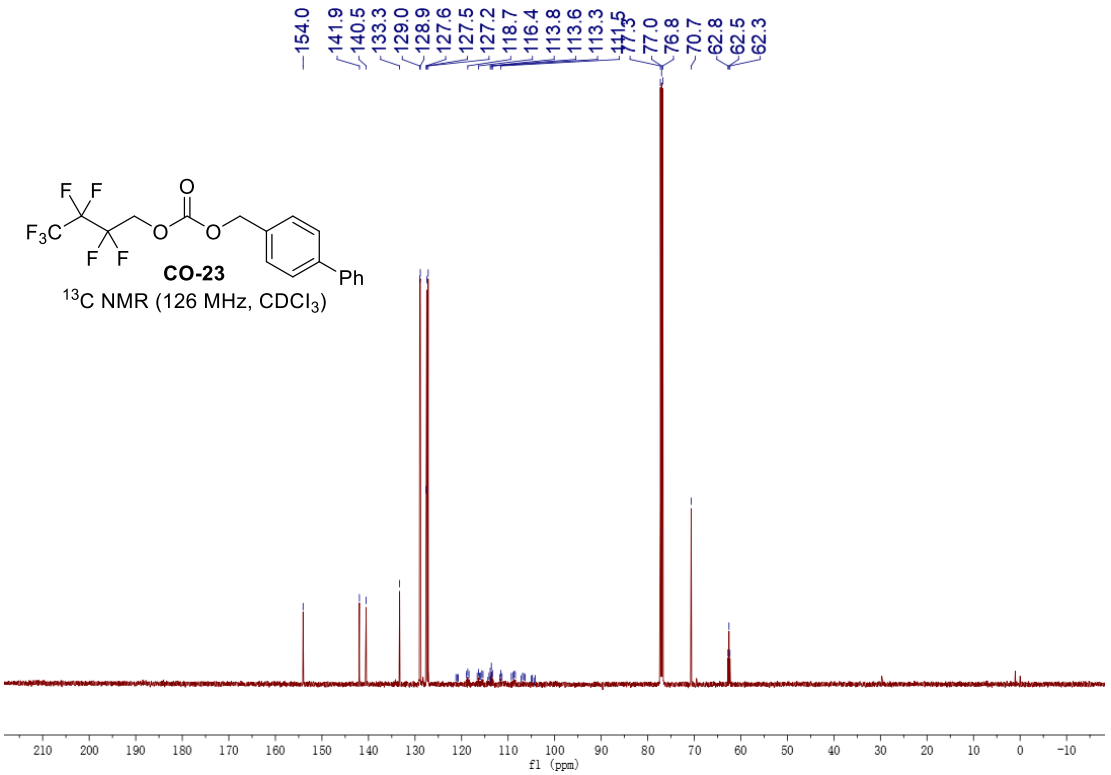
141.9
140.5
133.3
129.0
128.9
127.6
127.5
127.2
119.5
117.5
117.2
111.8
111.5
77.3
77.0
76.8
70.7
62.6
62.4
62.2
F3C
F F
O
O
O
Ph
CO-22
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.63
7.62
7.61
7.61
7.59
7.48
7.47
7.46
7.44
7.39
7.38
7.36
7.26
5.28
4.69
4.66
4.64
F F
F3C
F F
O
O
O
Ph
CO-23
1H NMR (500 MHz, CDCl3)
4.03
4.00
1.00
1.87
1.96
f1 (ppm)


-80.8
-80.8
-80.8
-120.9
-120.9
-121.0
-121.0
-127.7
F F
F3C
O
O
O
F F
CO-23
Ph
19F NMR (471 MHz, CDCl3)
2.97
2.00
2.08
f1 (ppm)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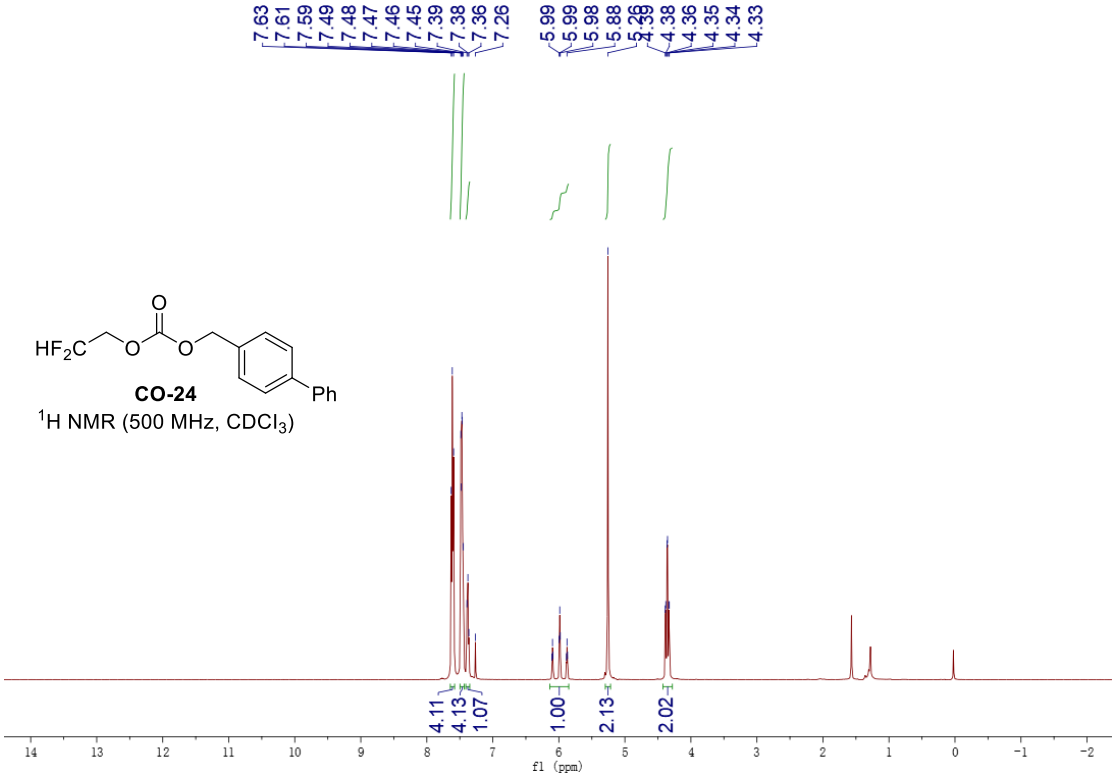
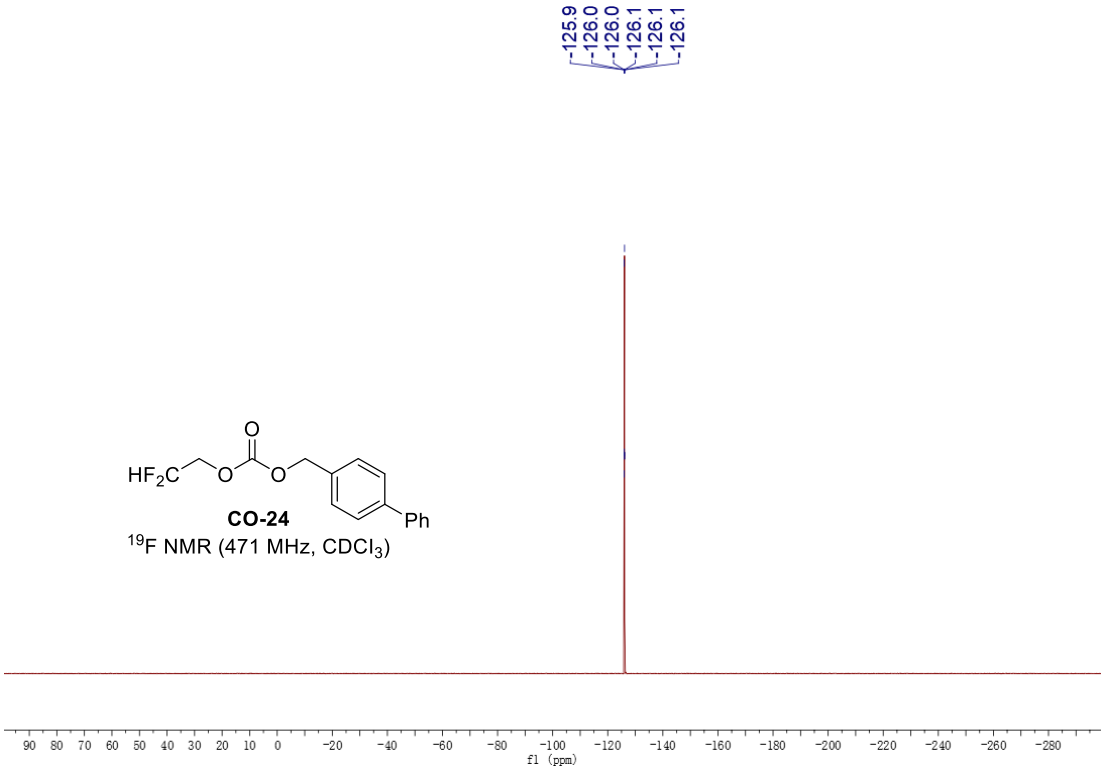
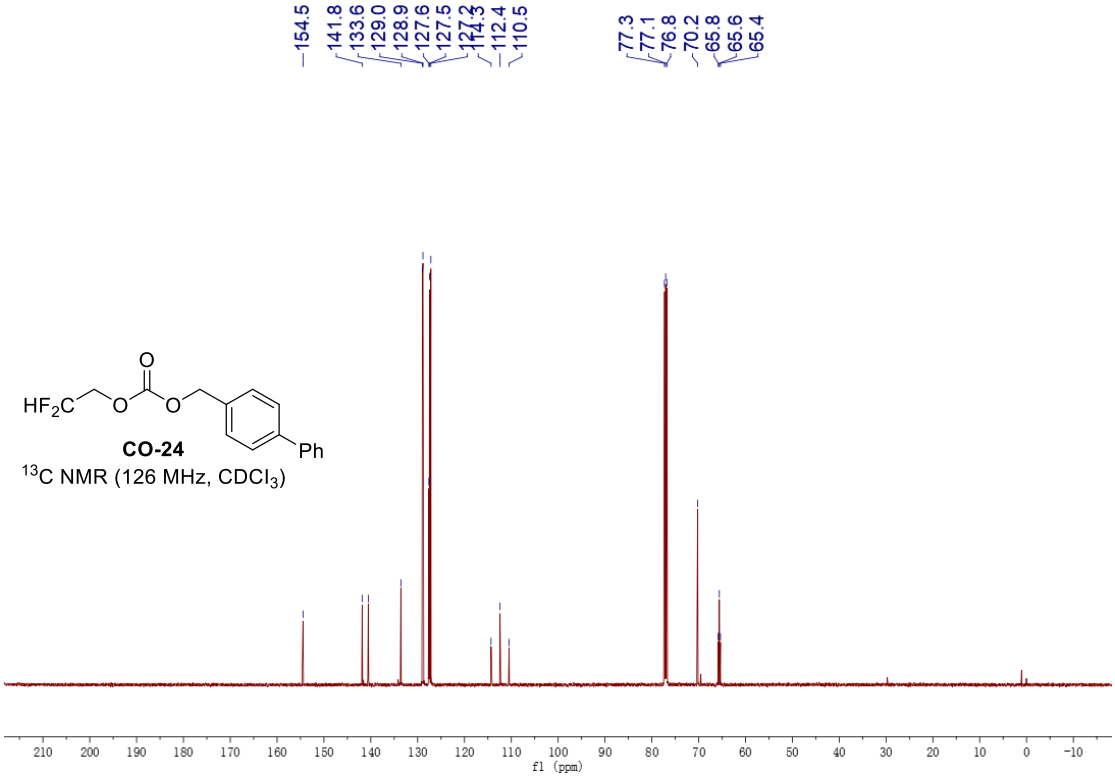
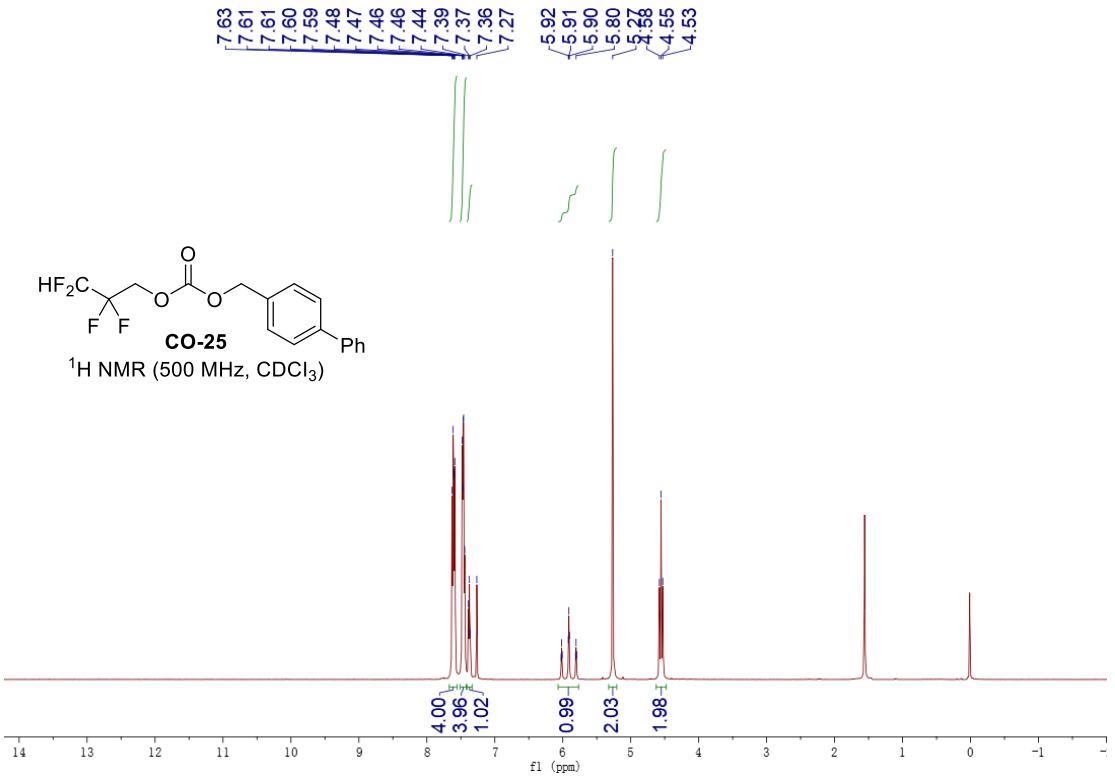
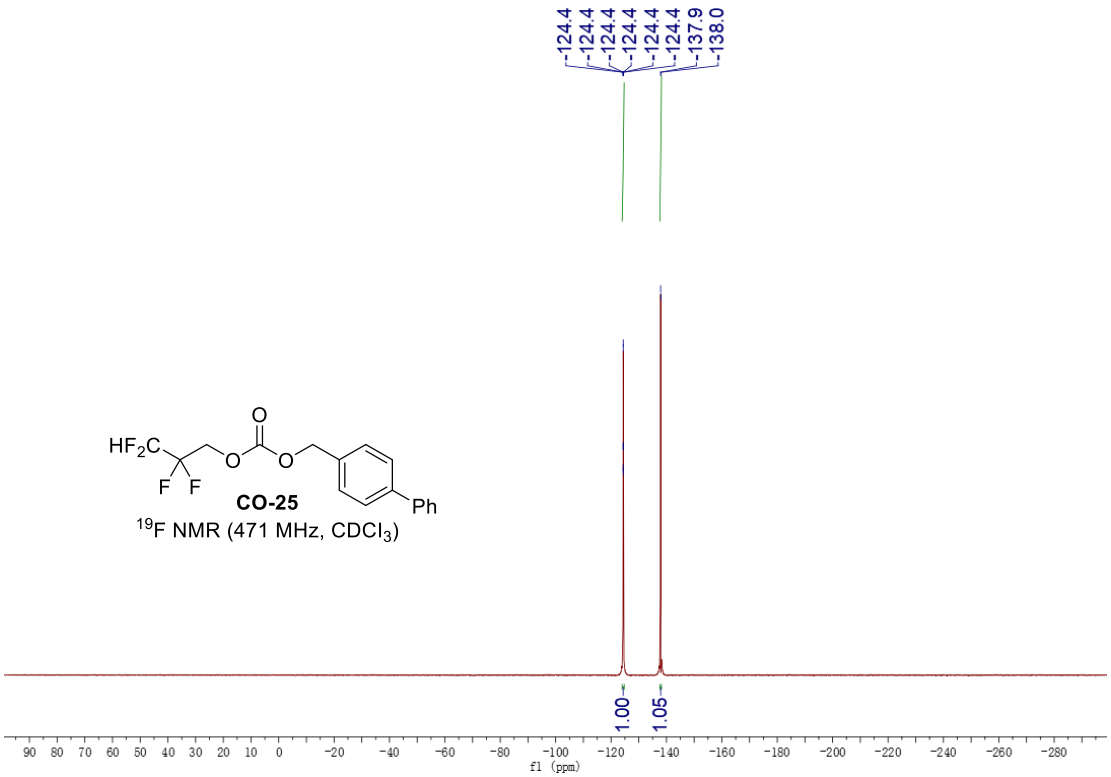
141.9
140.5
133.3
129.0
128.9
127.6
127.5
127.2
118.7
116.4
113.8
113.6
113.3
111.5
77.3
77.0
76.8
70.7
62.8
62.5
62.3
F F
F3C
O
O
O
F F
CO-23
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)

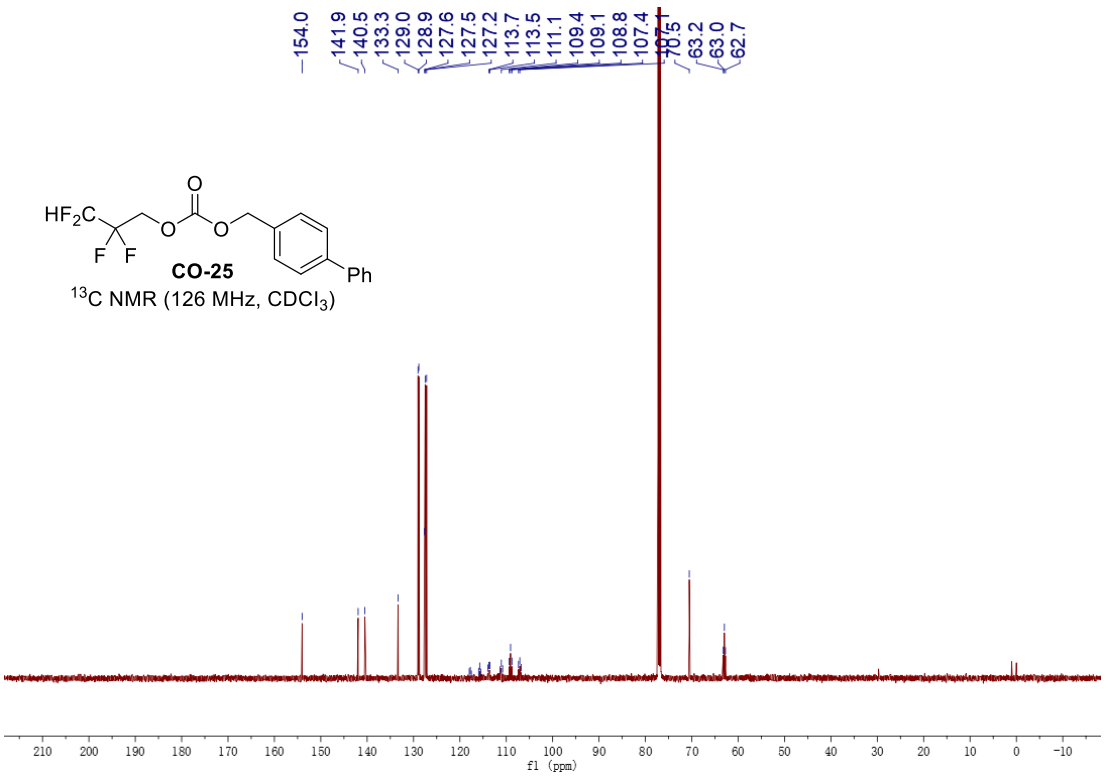

7.63
7.61
7.59
7.49
7.48
7.47
7.46
7.45
7.39
7.38
7.36
7.26
5.99
5.99
5.98
5.88
4.39
4.38
4.36
4.35
4.34
4.33
O
HF2C
O
O
Ph
CO-24
1H NMR (500 MHz, CDCl3)
4.11
4.13
1.07
1.00
2.13
2.02
f1 (ppm)

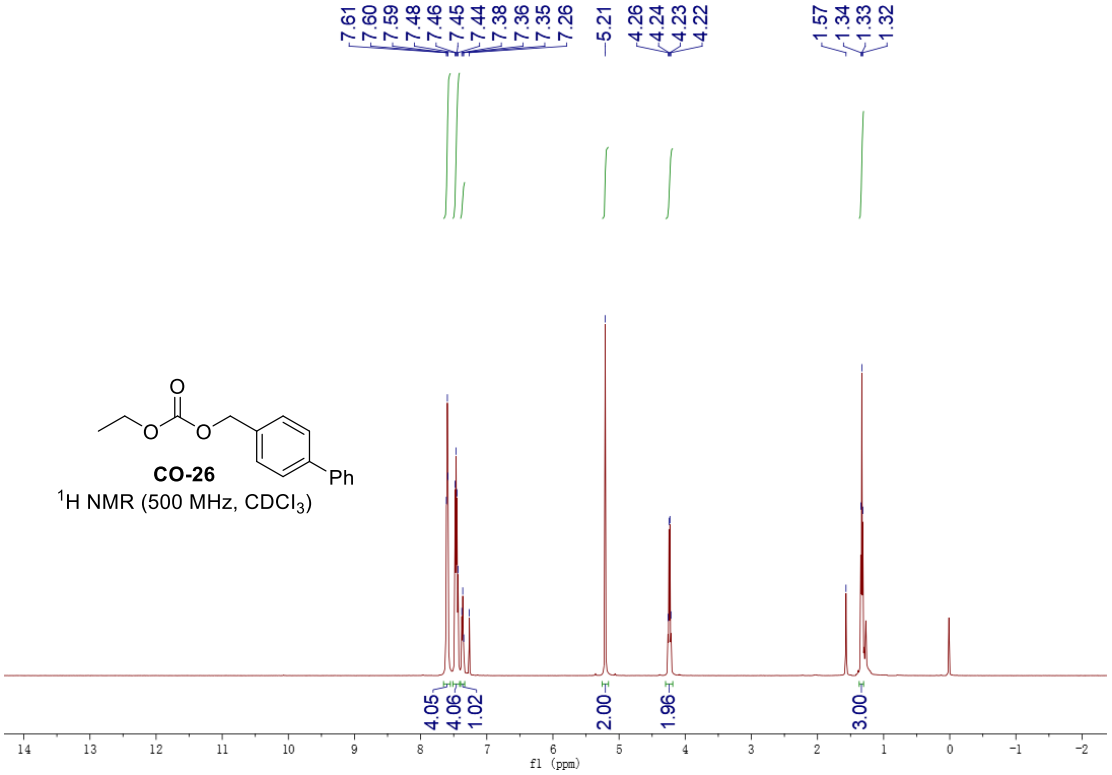

125.9
126.0
126.0
126.1
126.1
126.1
O
HF2C
O
O
Ph
CO-24
19F NMR (471 MHz, CDCl3)
f1 (ppm)

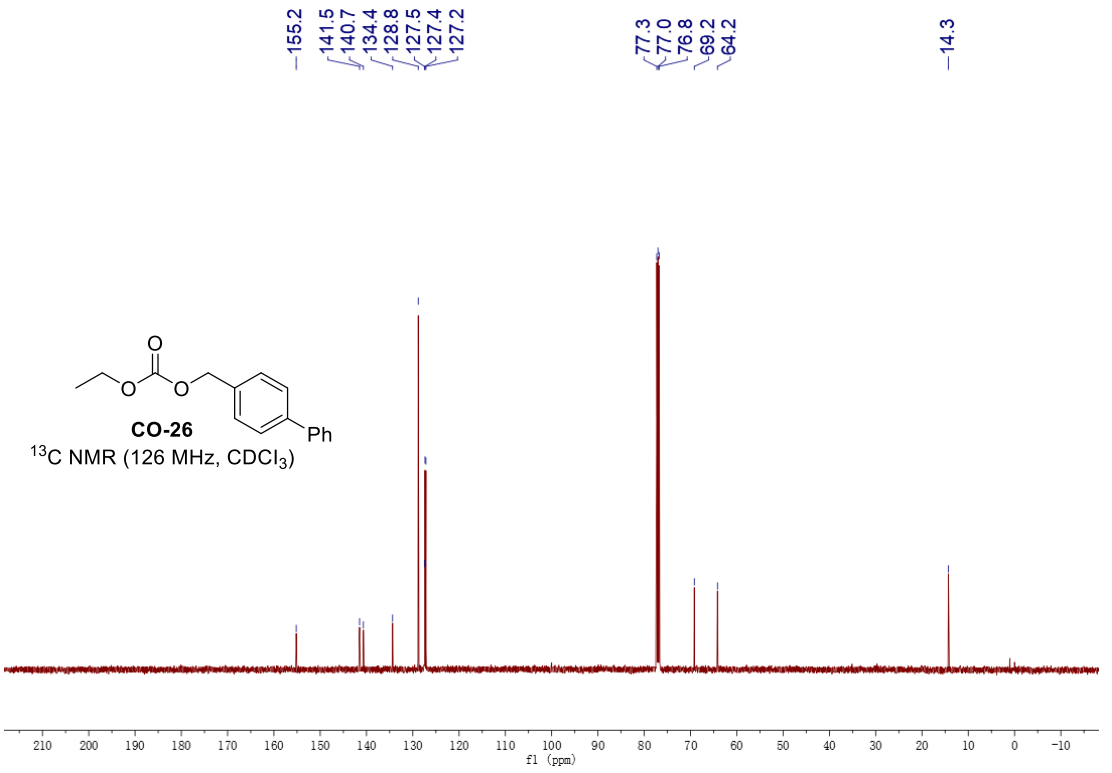

154.5
141.8
133.6
129.0
128.9
127.6
127.5
127.2
114.3
112.4
110.5
77.3
77.1
76.8
70.2
65.8
65.6
65.4
HF2C
O
O
O
Ph
CO-24
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.63
7.61
7.61
7.60
7.59
7.48
7.47
7.46
7.46
7.44
7.39
7.37
7.36
7.27
5.92
5.91
5.90
5.80
4.58
4.55
4.53
HF2C
F F
O
O
O
Ph
CO-25
1H NMR (500 MHz, CDCl3)
4.00
3.96
1.02
0.99
2.03
1.98
f1 (ppm)


-124.4
-124.4
-124.4
-124.4
-124.4
-124.4
-137.9
-138.0
O
HF2C
O
O
F F
CO-25
Ph
19F NMR (471 MHz, CDCl3)
1.00
1.05
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


154.0
141.9
140.5
133.3
129.0
128.9
127.6
127.5
127.2
113.7
113.5
111.1
109.4
109.1
108.8
107.4
107.1
70.5
63.2
63.0
62.7
O
HF2C
O
O
F F
CO-25
Ph
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.61
7.60
7.59
7.48
7.46
7.45
7.44
7.38
7.36
7.35
7.26
5.21
4.26
4.24
4.23
4.22
1.57
1.34
1.33
1.32
O
O
O
Ph
CO-26
1H NMR (500 MHz, CDCl3)
4.05
4.06
1.02
2.00
1.96
3.00
f1 (ppm)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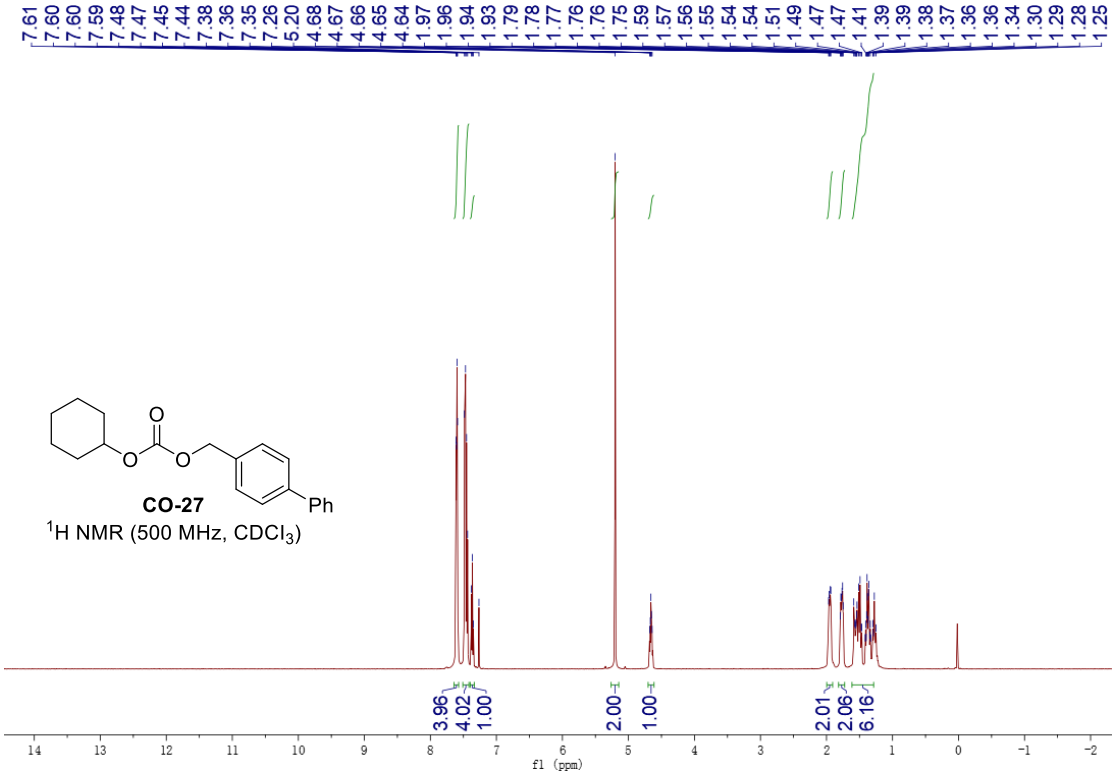
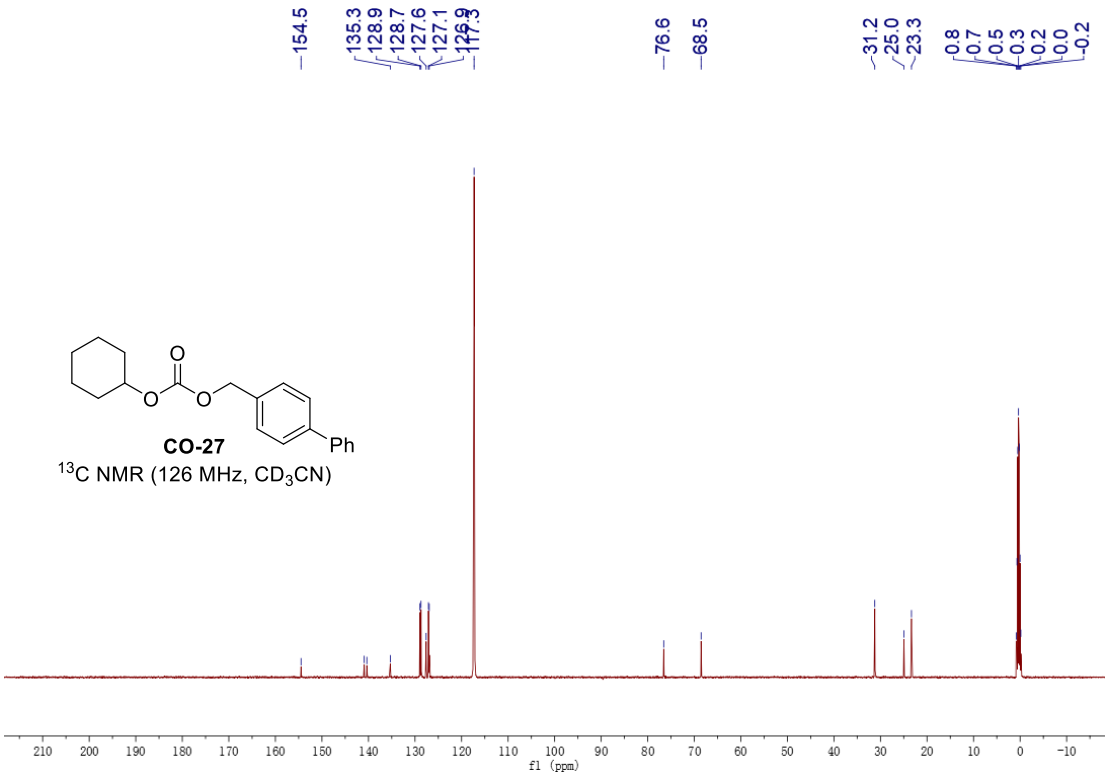
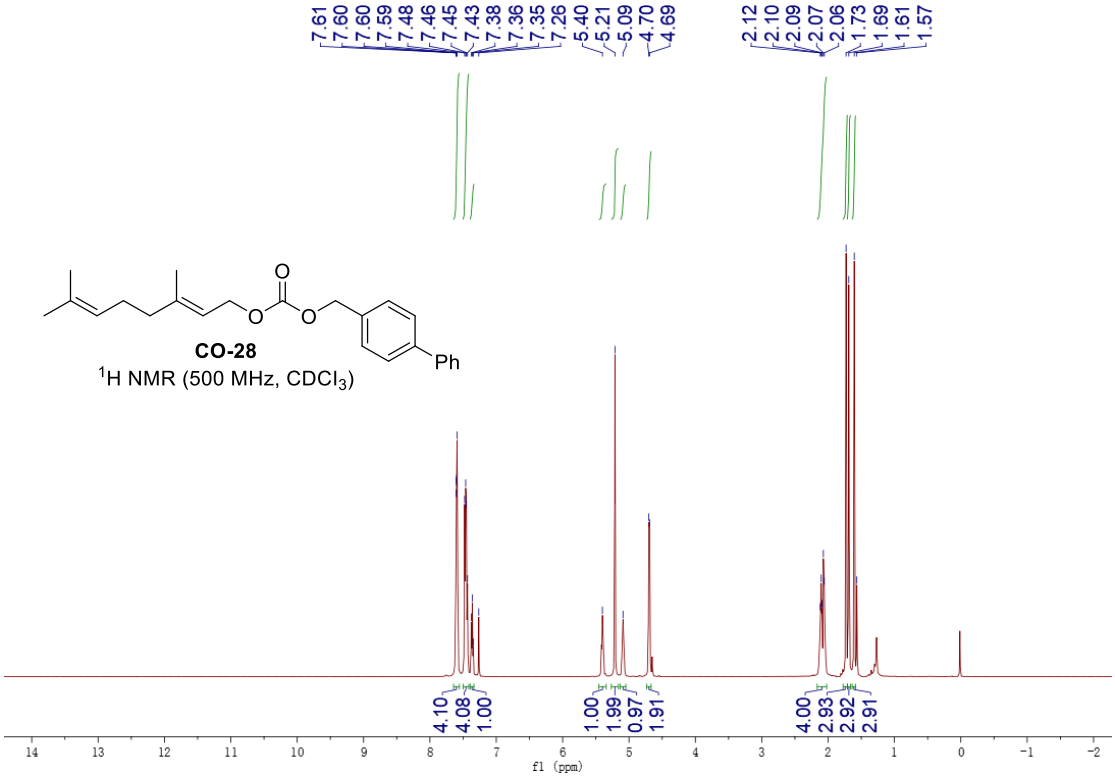
141.5
140.7
134.4
128.8
127.5
127.4
127.2
77.3
77.0
76.8
69.2
64.2
14.3
O
O
O
Ph
CO-26
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.61 7.60 7.60 7.59 7.48 7.47 7.45 7.44 7.38 7.36 7.35 7.26 5.20 4.68 4.67 4.66 4.65 4.64 1.97 1.96 1.94 1.93 1.79 1.78 1.77 1.76 1.76 1.75 1.59 1.57 1.56 1.55 1.54 1.54 1.51 1.49 1.47 1.47 1.41 1.39 1.39 1.38 1.37 1.36 1.36 1.34 1.30 1.29 1.28 1.25
O
O
O
Ph
CO-27
1H NMR (500 MHz, CDCl3)
3.96 4.02 1.00 2.00 1.00 2.01 2.06 6.16
f1 (ppm)


154.5 135.3 128.9 128.7 127.6 127.1 126.9 117.3 76.6 68.5 31.2 25.0 23.3 0.8 0.7 0.5 0.3 0.2 0.0 -0.2
O
O
O
Ph
CO-27
13C NMR (126 MHz, CD3CN)
f1 (ppm)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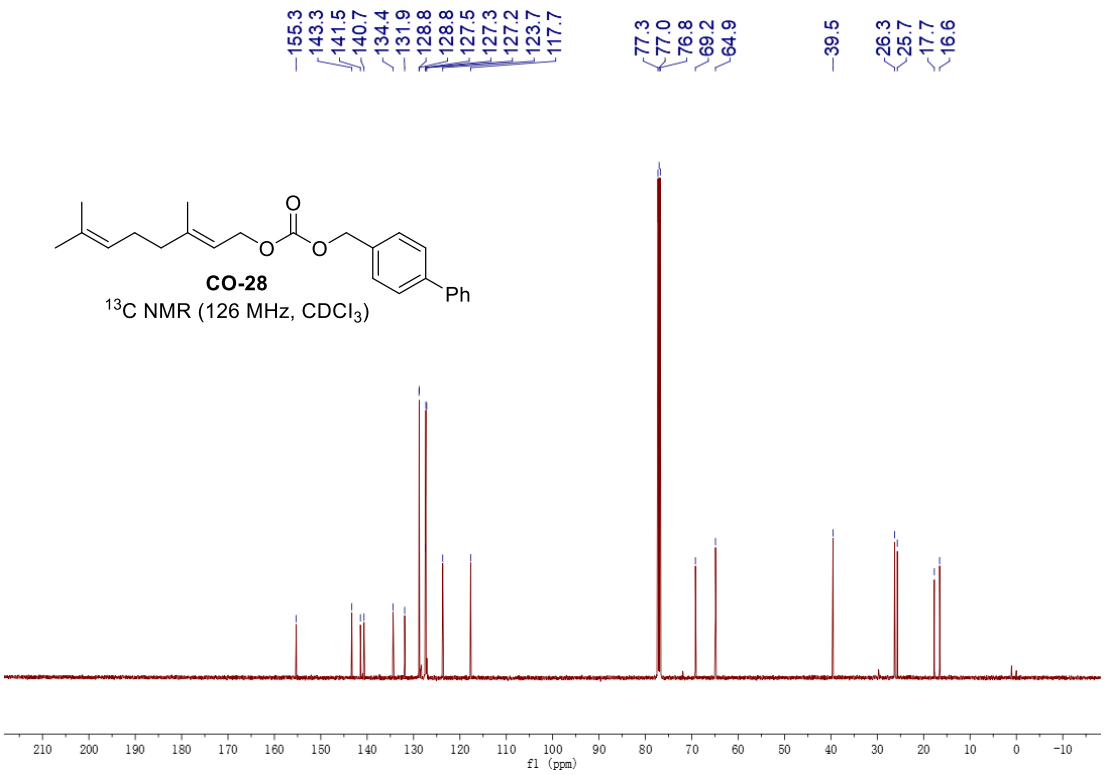
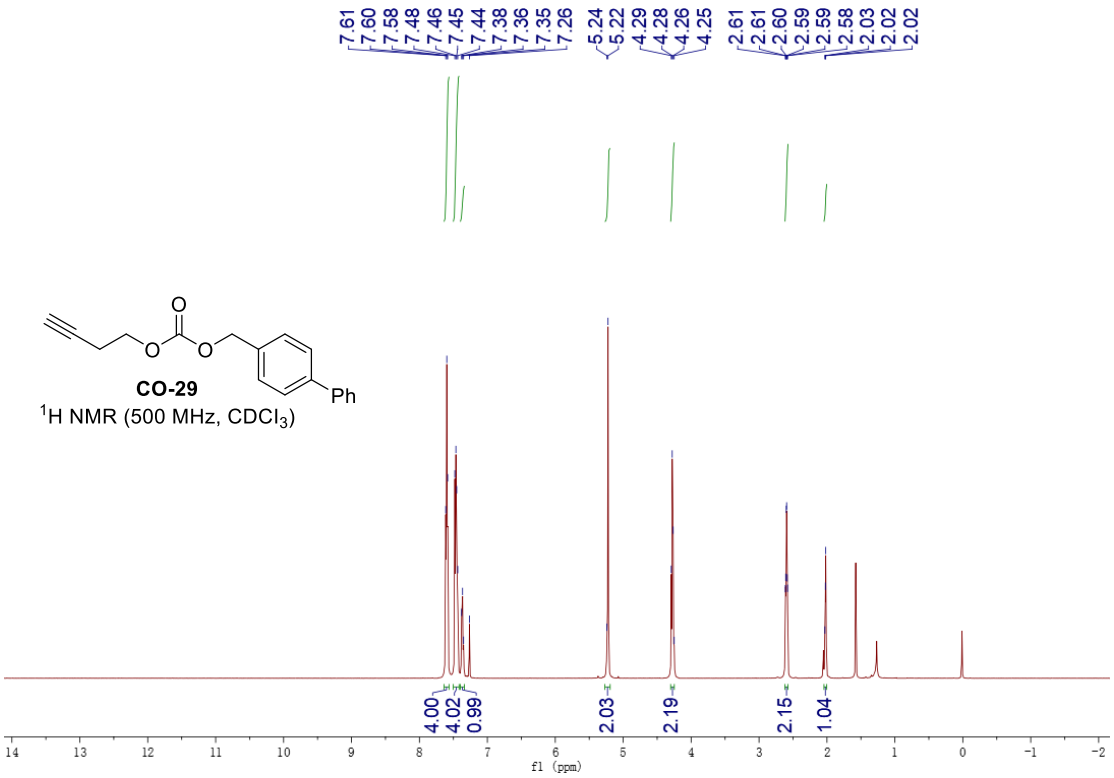
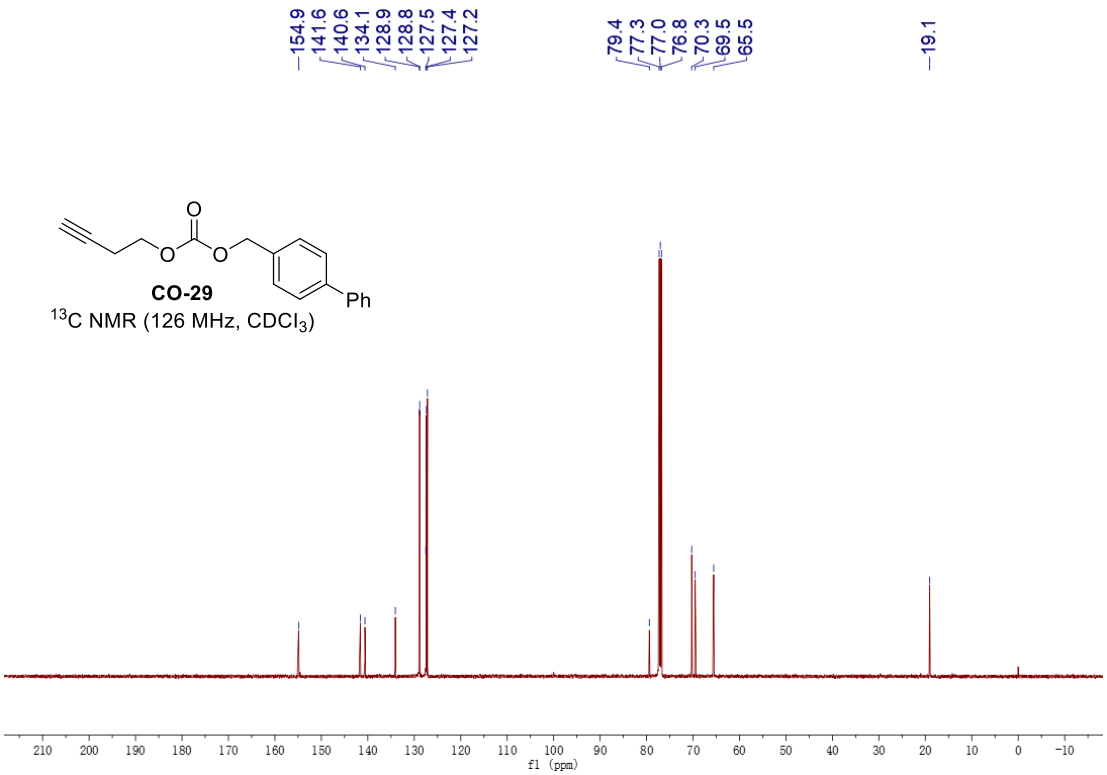
7.60
7.60
7.59
7.48
7.46
7.45
7.43
7.38
7.36
7.35
7.26
5.40
5.21
5.09
4.70
4.69
2.12
2.10
2.09
2.07
2.06
1.73
1.69
1.61
1.57
O
O
O
Ph
CO-28
1H NMR (500 MHz, CDCl3)
4.10
4.08
1.00
1.00
1.99
0.97
1.91
4.00
2.93
2.92
2.91
f1 (ppm)


155.3
143.3
141.5
140.7
134.4
131.9
128.8
128.8
127.5
127.3
127.2
123.7
117.7
77.3
77.0
76.8
69.2
64.9
39.5
26.3
25.7
17.7
16.6
O
O
O
Ph
CO-28
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.61
7.60
7.58
7.48
7.46
7.45
7.44
7.38
7.36
7.35
7.26
5.24
5.22
4.29
4.28
4.26
4.25
2.61
2.61
2.60
2.59
2.59
2.58
2.03
2.02
2.02
O
O
O
Ph
CO-29
1H NMR (500 MHz, CDCl3)
4.00
4.02
0.99
2.03
2.19
2.15
1.04
f1 (ppm)


154.9
141.6
140.6
134.1
128.9
128.8
127.5
127.4
127.2
79.4
77.3
77.0
76.8
70.3
69.5
65.5
19.1
O
O
O
Ph
CO-29
13C NMR (126 MHz, CDCl3)
f1 (ppm)