Silver-Catalysed Intermolecular Benzylic-Selective C–H Amidation via Nitrene Transfer

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Supplementary Information

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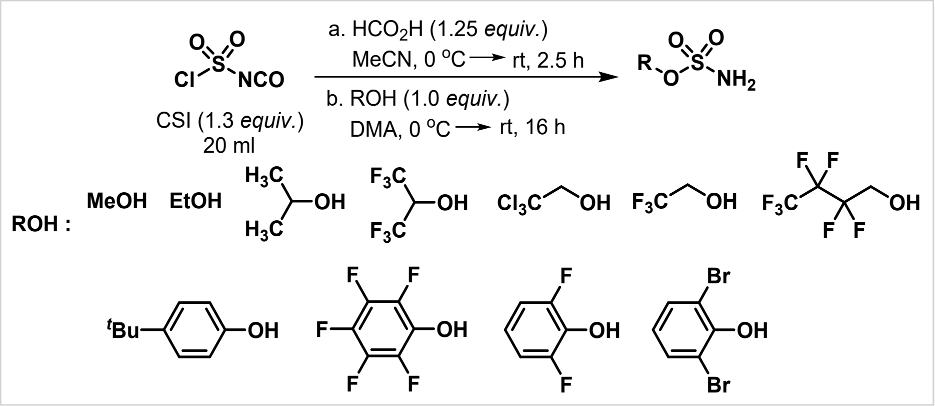
1. General information.

All glassware was either oven-dried overnight at 130 °C or flame-dried using a Bunsen burner. All glassware was then allowed to cool to room temperature in a desiccator filled with DrieriteTM as a desiccant or under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from Sigma-Aldrich, Oakwood Products, Alfa Aesar, Tokyo Chemical Industry, Combi-Blocks, Acros Organics or Cayman Chemicals and directly used without further purification. All the solvents were purified using accepted procedures from the sixth edition of "Purification of Laboratory Chemicals".[1] Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{24} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh). Product purification was typically carried out by preparative TLC, or by column chromatography using a gradient method employing mixtures of hexanes and diethyl ether (Et_2O). The stain was used to visualize reaction products using phosphomolybdic acid (PMA). ^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker Avance-400 (400 and 100 MHz) and Bruker Avance-500 (500 and 125 MHz) spectrometers. ^{19}F NMR spectra were obtained using Bruker Avance–400 (377 MHz). ^{1}H chemical shifts were reported using tetramethylsilane (TMS) ($CDCl_3$ referenced at δ 0.00) or protiated solvent peaks ($CDCl_3$ referenced at δ 7.26) as an internal standard. ^{13}C chemical shifts were reported using absolute referencing (TMS in $CDCl_3$, ϕ= 1%, □ = 25.145020). Accurate mass measurements were acquired at the University of Wisconsin-Madison using a micro mass LCT (electrospray ionization, time-of-flight analyzer, or electron impact methods).

2. Synthesis of starting materials.

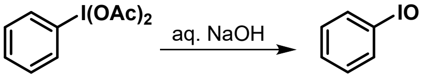
2.1. Synthesis of sulfonamide derivatives.[2]

Formic acid (2.26 mL, 219 mmol) was added at 0 °C dropwise over a period of 5 min to a vigorously stirring solution of chlorosulfonyl isocyanate (CSI, 20.1 mL, 228 mmol) in MeCN (20 mL) in a 250 mL round bottle flask (caution: strong evolution of CO and CO_2 gas upon addition). The solution was stirred at 0 °C for an additional 10 min and then allowed to warm to rt. After stirring at rt for 2.5 h, the reaction mixture was cooled to 0 °C and a solution of the corresponding alcohol (175 mmol) in DMA (20 mL) was slowly added dropwise over 20 min *via* syringe pump. The reaction mixture was stirred at 0 °C for 10 min and then at rt for 16 h. The reaction was carefully quenched with the slow addition of H_2O (50 mL) and transferred to a separatory funnel with additional H_2O (50 mL). The aqueous layer was extracted with Et_2O (3 × 75 mL) and the combined organic extracts were washed with H_2O (4 × 75 mL), saturated aqueous NaCl (75 mL), and 10% LiCl (2 × 25 mL) (to aid in DMA removal), dried over Na_2SO_4, and concentrated under reduced pressure to provide the corresponding sulfonamide as a colorless oil that solidified under vacuum. The resulting solid was broken up into a white powder that was determined to be pure by ^1H NMR and used in sulfamoylation reactions without further purification. Spectral data are consistent with previous reports.[3]

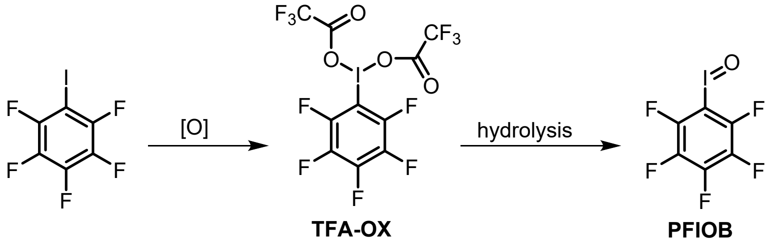


2.2. Synthesis of hypervalent iodine oxidant: PhIO, TFA-OX and PFIOB

PhIO:



The desired compound was prepared based on the literature procedure.[4] Finely ground iodosobenzene diacetate (32.2 g., 0.10 mole) was placed in a 250-mL beaker, and 150 mL of 3 N sodium hydroxide was added over a 5 min period with vigorous stirring. The lumps of solid form were triturated with a stirring rod or spatula for 15 min, and the reaction mixture was allowed to stand for an additional 45 min to complete the reaction. A portion of 100 mL of water was added, the mixture was stirred vigorously, and the crude, solid iodosobenzene was collected on a Büchner funnel. The wet solid was returned to the beaker and triturated in 200 mL of water. The solid was again collected on the Büchner funnel, washed with 200 mL of water, and dried by maintaining suction. Final purification was effected by triturating the dried solid in 75 mL of chloroform in a beaker. The iodosobenzene is separated by filtration and air-dried to furnish 19.8 g (90%) of the product.



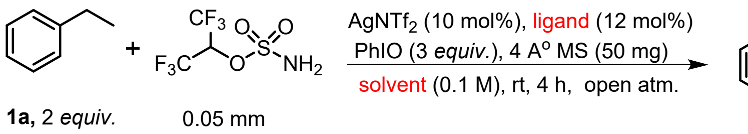
TFA-Ox was prepared according to a variant of the protocol described by Zhdankin and coworkers.[5] PFIOB was prepared according to a variant of the protocol described by Goldberg and co-workers.[6] To a solution of iodopentafluorobenzene (8.82 g, 30.0 mmol) in trifluoroacetic acid (90 mL) and $CHCl_3$ (30 mL) was added Oxone® (27.7 g, 45.0 mmol) under air. After stirring at room temperature for 4 h, the reaction mixture was concentrated under reduced pressure, diluted in $CHCl_3$ and the insoluble inorganic salts were removed by filtration. Liberal washing of the salts with $CHCl_3$ and concentration of the filtrate under reduced pressure afforded the crude TFA-Ox. To obtain the purified TFA-Ox, the crude TFA-Ox was washed with plenty of ice-cold hexane on a filter and dried under high vacuum to afford the desired product as a white solid (~7.0 g, 45%). The spectroscopic data matched the literature report.[7]

To obtain pentafluoroiodosobenzene (PFIOB), the TFA-Ox (4.36 g, 8.39 mmol) was suspended in saturated aqueous $NaHCO_3$ solution (75 mL) and stirred overnight under air. The remaining solids were isolated by filtration, washed with ice-cold H_2O (20 mL), ice-cold $CHCl_3$ (20 mL), ice-cold Et_2O (20 mL) and dried under high vacuum to afford the desired product as a white solid (~1.85 g, 71%). The spectral data is in agreement with that reported in the literature.[6]

3. Optimization of reaction conditions.

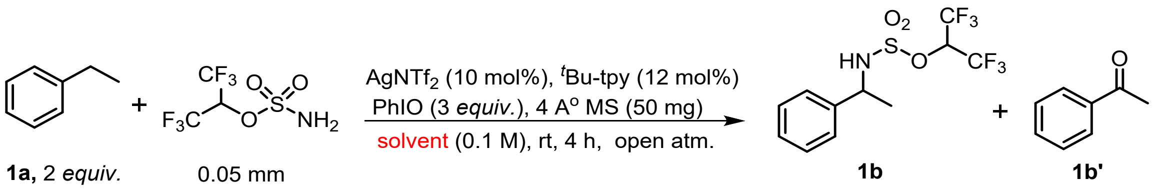
3.1. Optimization for the benzylic amidation reaction.

Table S1: Initial reaction development for benzylic amidation reaction.



Entry	Solvent	Condition	Yields	
			1b	1b′
1	DCE	^{t}Bu-tpy	40%	12%
2	DCE	4,7-di Ph Phen	33%	30%
3	**TFE**	**^{t}Bu-tpy**	**45%**	**11%**
4	TFE	4,7-di Ph Phen	18%	2%
5	HFIP	^{t}Bu-tpy	16%	3%
6	HFIP	4,7-di Ph Phen	17%	10%
7	NFTBA	^{t}Bu-tpy	35%	4%
8	NFTBA	4,7-di Ph Phen	24%	25%
9	PhNO$_2$	^{t}Bu-tpy	36%	2%
10	PhNO$_2$	4,7-di Ph Phen	-	-
11	*o*-DCB	^{t}Bu-tpy	-	-
12	*o*-DCB	4,7-di Ph Phen	no rxn	no rxn

Table S2: Solvent optimization for benzylic amidation reaction.



Entry	Solvent	Yields	
		1b	1b′
11	PhCF$_3$	30%	19%
12	1,1,1-trichloroethane	31%	27%
14	1,1,2,2-*tetra* chloro ethane	22%	34%
15	EtOH	0%	4%
16	DMA	0%	2%
17	MeO^{t}Bu	0%	2%
18	PhOMe	6%	3%
19	CCl$_4$	9%	7%

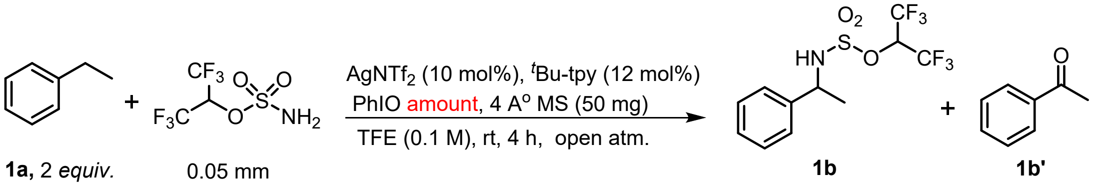
Entry	**Solvent**	**Yields**	
		1b	**1b′**
1	MeCN	20%	5%
2	MeOH	9%	4%
3	EtOAc	22%	12%
4	MeCOMe	20%	28%
5	DMF	0%	3%
6	DME	0%	3%
7	1,4- dioxane	0%	2%
8	THF	0%	2%
9	*p*-xylene	0%	4%
10	Hexane	22%	4%

20	$MeNO_2$	24%	7%

Entry	**Solvent**	**Yields**	
		1b	**1b′**
21	*i*-PrOH	0%	0%
22	PhH	36%	28%
23	*m*-xylene	0%	3%
24	Ph_2O	11%	9%
25	*n*-BuOH	23%	7%
26	1,3-dibromo propane	18%	18%
27	PhMe	0%	7%
28	*tetra*-hydropyran	0%	0%
29	*o*-xylene	-%	100%
30	2-Methyl THF	0%	0%
31	Dibromo methane	25%	-%
32	TFA	0%	4%

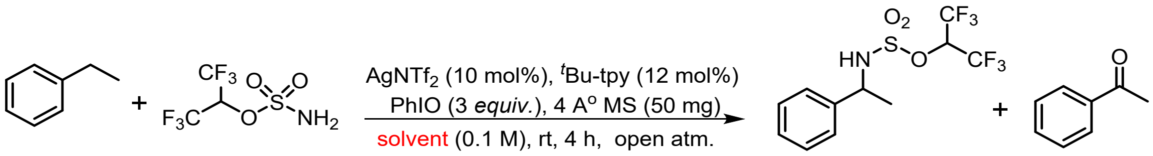
Entry	**Solvent**	**Yields**	
		1b	**1b′**
33	PivCN	10%	6%
34	Ethyl trifluoro acetate	10%	6%
35	DMSO	0%	0%
36	*t*-BuOAc	27%	15%
37	PhCN	34%	11%
38	Me_2CO_3	24%	19%
39	2-Methyl, 3-butanol	0%	5%
40	*tert*-Amyl methyl ether	9%	9%
41	$CHCl_3$	15%	19%
42	PhEt	39%	133%
43	AcOH	0%	2%
44	**TFE**	**45%**	**11%**

Table S3: PhIO amount optimization for benzylic amidation reaction.



Entry	PhIO amount	Yields	
		1b	1b′
1	no amount	0%	<1%
2	0.5 *equiv.*	15%	7%
3	1.0 *equiv.*	26%	1%
4	1.2 *equiv.*	33%	1%
5	1.5 *equiv.*	20%	0%
6	2.0 *equiv.*	41%	5%
7	2.5 *equiv.*	17%	1%
8	**3.0 *equiv.***	**45%**	**11%**
9	3.5 *equiv.*	36%	4%
10	4.0 *equiv.*	28%	3%
11	4.5 *equiv.*	45%	6%
12	5.0 *equiv.*	45%	4%

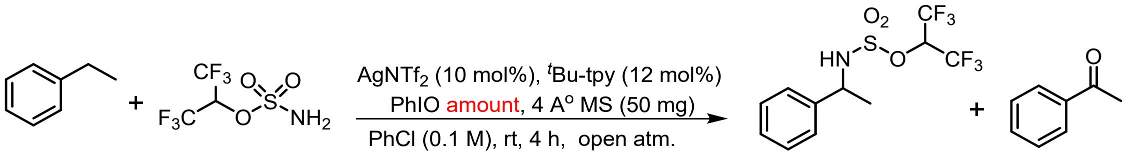
Table S4: Solvent optimization for benzylic amidation reaction.


AgNTf$_2$ (10 mol%), ^{t}Bu-tpy (12 mol%)
PhIO (3 *equiv.*), 4 A° MS (50 mg)
solvent (0.1 M), rt, 4 h, open atm.

1a, 2 *equiv.* 0.05 mm **1b** **1b'**

Entry	Solvent	Yields	
		1b	1b′
1	**PhCl**	**50%**	**16%**
2	Et$_2$O	0%	<1%
3	PhF	48%	33%
4	1,3 difluoro benzene	39%	29%
5	*t*-BuCN	20%	18%

Table S5: PhIO amount optimization (with PhCl solvent) for benzylic amidation reaction.


AgNTf$_2$ (10 mol%), ^{t}Bu-tpy (12 mol%)
PhIO amount, 4 A° MS (50 mg)
PhCl (0.1 M), rt, 4 h, open atm.

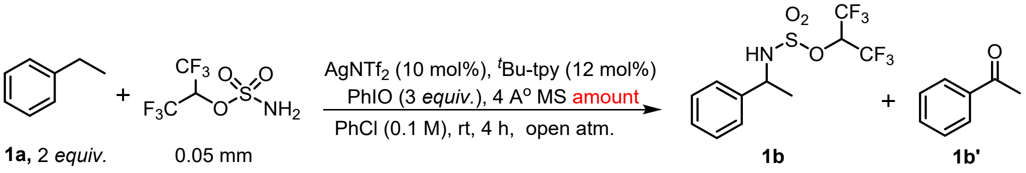
1a, 2 *equiv.* 0.05 mm **1b** **1b'**

Entry	PhIO amount	Yields	
		1b	1b′
1	no amount	0%	<1%
2	0.5 *equiv.*	37%	3%

3	1.0 *equiv.*	35%	14%
4	1.2 *equiv.*	45%	9%
5	1.5 *equiv.*	44%	20%
6	2.0 *equiv.*	41%	25%
7	2.5 *equiv.*	29%	2%
8	**3.0 *equiv.***	**50%**	**16%**
9	3.5 *equiv.*	20%	2%
10	4.0 *equiv.*	37%	19%
11	4.5 *equiv.*	30%	18%

Entry	**PhIO amount**	**Yields**	
		1b	**1b′**
12	5.0 *equiv.*	31%	19%
13	5.5 *equiv.*	33%	30%
14	6.0 *equiv.*	24%	27%
15	6.5 *equiv.*	22%	11%
16	7.0 *equiv.*	13%	14%
17	7.5 *equiv.*	27%	33%
18	8.0 *equiv.*	35%	21%
19	8.5 *equiv.*	32%	29%
20	9.0 *equiv.*	34%	24%
21	9.5 *equiv.*	32%	27%
22	10 *equiv.*	34%	24%

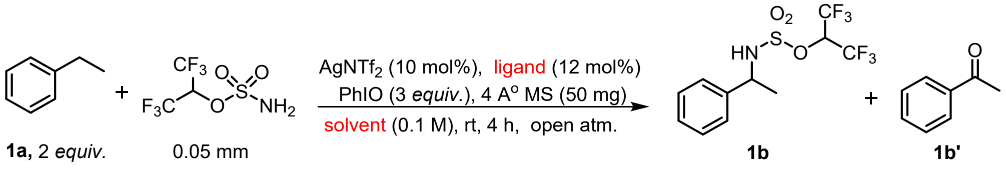
Table S6: Molecular sieve amount optimization for benzylic amidation reaction.



Entry	**MS amount**	**Yields**	
		1b	**1b′**
1	no amount	19%	21%
2	10 mg	7%	4%
3	20 mg	19%	6%
4	30 mg	36%	20%
5	40 mg	35%	4%
6	**50 mg**	**50%**	**16%**

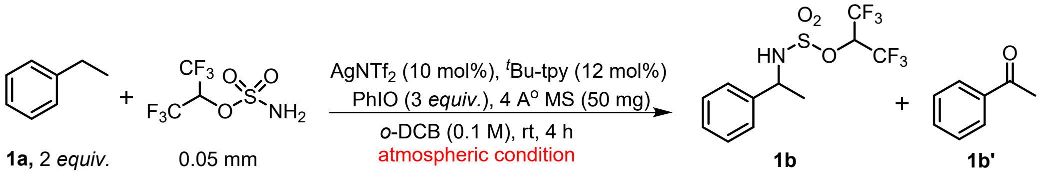
Entry	**Solvent**	**Yields**	
		1b	**1b′**
7	60 mg	39%	9%
8	70 mg	39%	23%
9	80 mg	25%	16%
10	90 mg	29%	10%
11	100 mg	40%	22%
12	200 mg	43%	11%

Table S7: Control experiments for benzylic amidation reaction.



Entry	Control experiments	Yields	
		1b	1b′
1	TFE- ^{t}Bu-tpy	37%	4%
2	HFIP-4,7 di Ph Phen	14%	11%
3	***o*-DCB- ^{t}Bu-tpy**	**64%**	**10%**

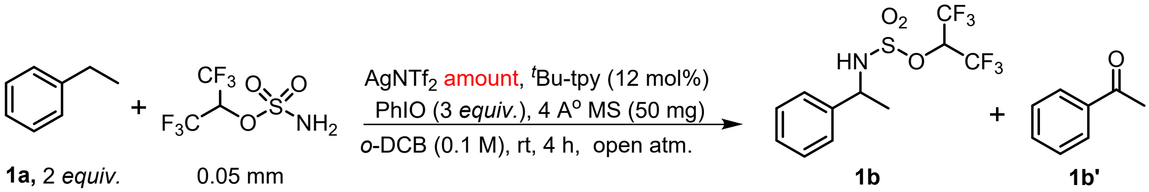
Table S8: Atmospheric condition optimization for benzylic amidation reaction.



Entry	Atmospheric variation	Yields	
		1b	1b′
1	**open atm.**	**64%**	**10%**
2	open atm. (no cap)	25%	2%
3	O_2 atm.	50%	3%

Entry	Atmospheric variation	Yields	
		1b	1b′
4	N_2 atm.	50%	6%
5	N_2 atm. (glove box)	50%	2%

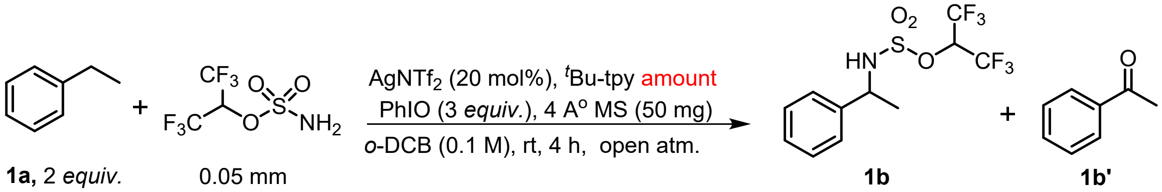
Table S9: AgNTf$_2$ amount optimization for benzylic amidation reaction.



Entry	AgNTf$_2$ amount	Yields	
		1b	1b′
1	no cat.	0%	2%
2	5 mol%	41%	11%
3	10 mol%	57%	13%
4	12 mol%	64%	10%
5	15 mol%	70%	7%

Entry	AgNTf$_2$ amount	Yields	
		1b	1b′
6	**20 mol%**	**73%**	**7%**
7	25 mol%	76%	14%
8	30 mol%	73%	33%
9	35 mol%	28%	1%

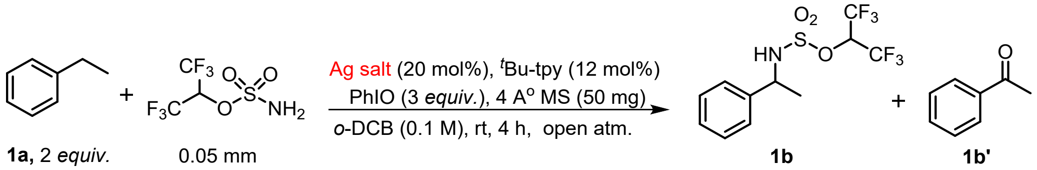
Table S10: TPY2 ligand amount optimization for benzylic amidation reaction.



Entry	Ag cat.: Ligand	Yields	
		1b	**1b′**
1	1:0.5	64%	10%
2	**1:0.6**	**73%**	**7%**
3	1:0.75	54%	4%
4	1:1	54%	2%

Entry	Ag cat.: Ligand	Yields	
		1b	**1b′**
5	1:1.2	61%	10%
5	1:1.5	71%	20%
7	1:2	43%	7%
6	1:3	26%	14%

Table S11: Ag salt variation optimization for benzylic amidation reaction.

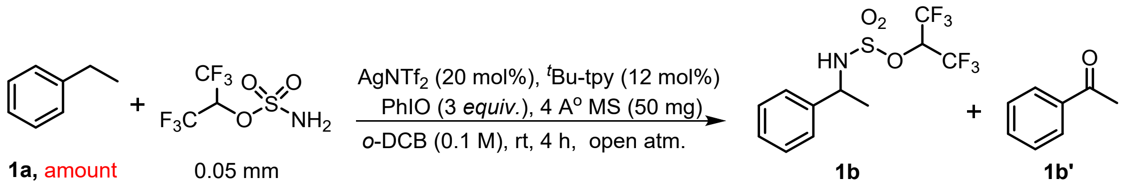


Entry	Ag salts	Yields	
		1b	**1b′**
1	**$AgNTf_2$**	**73%**	**7%**
2	$AgNO_3$	27%	9%
3	$AgBF_4$	29%	12%
4	AgTFA	29%	3%
5	AgOTs	20%	3%
6	$AgSbF_6$	45%	2%
7	AgOTf	36%	20%
8	AgOAc	25%	4%

9	Ag(MeCN)$_4$BF$_4$	17%	10%
10	AgPF$_6$	42%	7%

Entry	Ag salts	Yields	
		1b	1b′
11	AgI	6%	2%
12	AgCl	0%	2%
13	AgF	28%	5%
14	AgBr	0%	0%
15	AgO	19%	3%
16	Ag$_2$O	20%	14%
17	Ag-picolinate	19%	7%
18	Ag$_2$CO$_3$	9%	2%
19	Ag$_2$SO$_4$	0%	0%

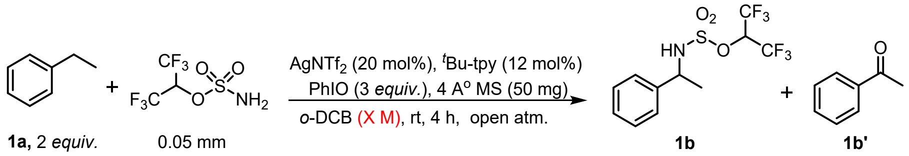
Table S12: Arene amount optimization for benzylic amidation reaction.



Entry	Arene amount	Yields	
		1b	1b′
1	1 *equiv.*	39%	22%
1-1	1.15 *equiv.*	36%	13%
2	1.5 *equiv.*	59%	26%
3	**2 *equiv.***	**73%**	**7%**

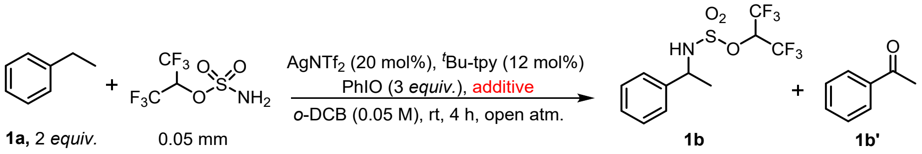
Entry	Arene amount	Yields	
		1b	1b′
4	2.5 *equiv.*	32%	8%
5	3 *equiv.*	73%	26%
6	4 *equiv.*	29%	6%
7	5 *equiv.*	85%	28%

Table S13: Solvent concentration optimization for benzylic amidation reaction.



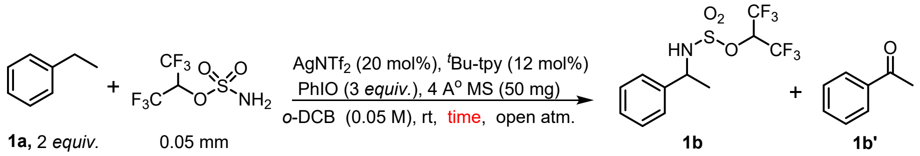
Entry	Solvent amount	Yields	
		1b	**1b′**
1	0.5 M (100 µl)	53%	30%
2	0.25 M (200 µl)	45%	27%
3	0.2 M (250 µl)	55%	23%
3	0.1 M (500 µl)	73%	10%
4	**0.05 M (1000 µl)**	**85%**	**10%**
5	0.0375 M (1500 µl)	73%	14%
6	0.025 M (2000 µl)	25%	<1%

Table S14: MS/MgO optimization for benzylic amidation reaction.



Entry	Additive	Yields	
		1b	**1b′**
1	3 A° MS (50 mg)	63%	4%
2	**4 A° MS (50 mg)**	**85%**	**10%**
3	5 A° MS (50 mg)	45%	2%
4	MgO (2.3 *equiv.*)	8%	<1%
5	MgO (2.6 *equiv.*)	38%	12%

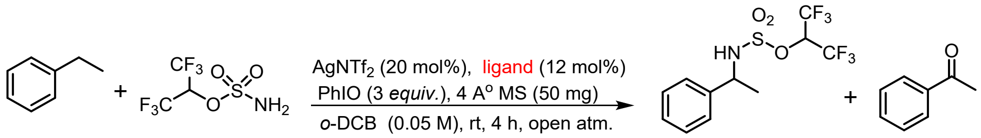
Table S15: Time optimization for benzylic amidation reaction.



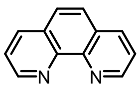
Entry	Time	Yields	
		1b	**1b′**
1	0.5 h	58%	6%
2	1.0 h	67%	9%
3	1.5 h	54%	5%
4	2.0 h	29%	<1%
5	2.5 h	27%	4%
6	3.0 h	56%	8%
7	3.5 h	58%	8%
9	4.5 h	59%	5%
10	5.0 h	72%	5%
11	6.0 h	39%	1%
12	7.0 h	46%	1%
13	8.0 h	60%	8%
14	9.0 h	57%	3%
15	10.0 h	63%	4%

8	**4 h**	**85%**	**10%**				

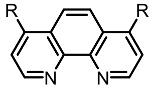
Table S16: Ligand optimization for benzylic amidation reaction.



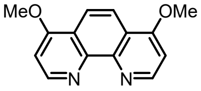
1a, 2 *equiv.* 0.05 mm **1b** **1b'**



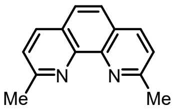
L1, 0% [0%]



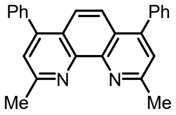
L2, R = Ph, 0% [0%]
L3, R = Me, 3% [<1%]



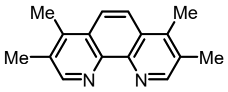
L4, 2% [<1%]



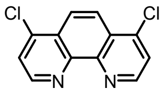
L5, 0% [35%]



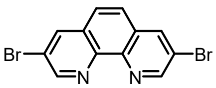
L6, 0% [<1%]



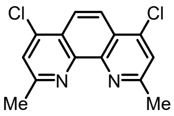
L7, 3% [20%]



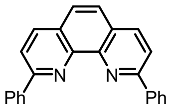
L8, 0% [0%]



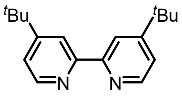
L9, 0% [<1%]



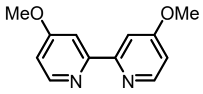
L10, 0% [11%]



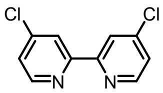
L11, 0% [0%]



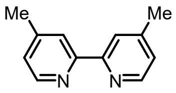
L12, 3% [<1%]



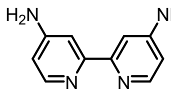
L13, 1% [<1%]



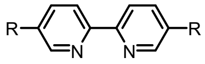
L14, 0% [1%]



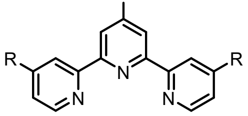
L15, 2% [<1%]



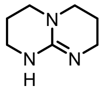
L16, 0% [0%]



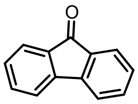
L17, R = H, 3% [1%]
L18, R = Me, 2% [0%]



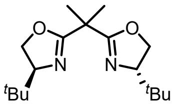
L19, R = H, 63% [0%]
L20, R = ^{t}Bu, 85% [10%]



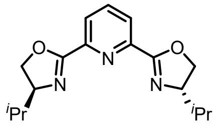
L21, 0% [0%]



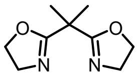
L22, 0% [0%]



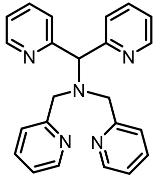
L23, 0% [0%]



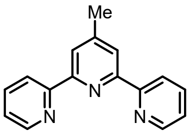
L24, 0% [1%]



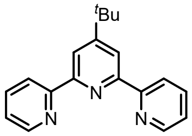
L25, 0% [0%]



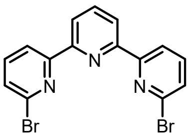
L26, 5% [<1%]



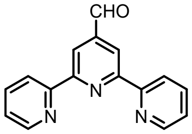
L27, R = Me, 56% [15%]
L28, R = Br, 27% [6%]



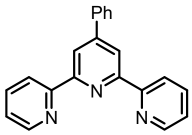
L29, 55% [6%]



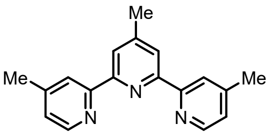
L30, n.r. [3%]



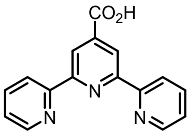
L31, 10% [n.r.]



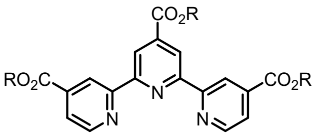
L32, 56% [10%]



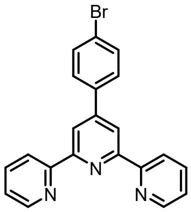
L33, 22% [5%]



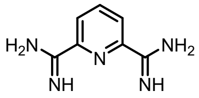
L34, 22% [3%]



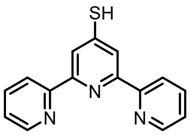
L35, R = H, 5% [1%]
L36, R = Me, 34% [5%]



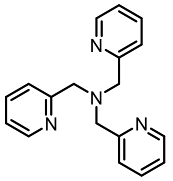
L37, 1% [5%]



L38, 11% [5%]



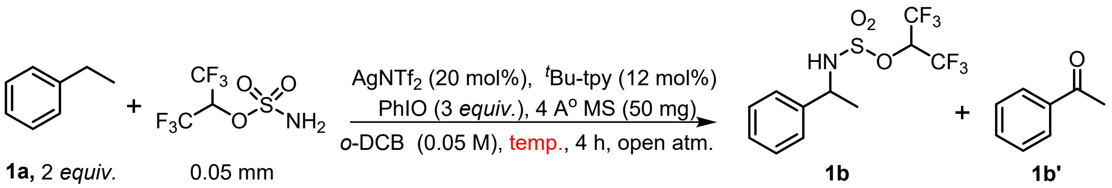
L39, 6% [3%]



L40, 13% [23%]

[Manuscript **L', L1, L2, L3, L4, L5 are here L12, L20, L17, L8, L38, L25** respectively]

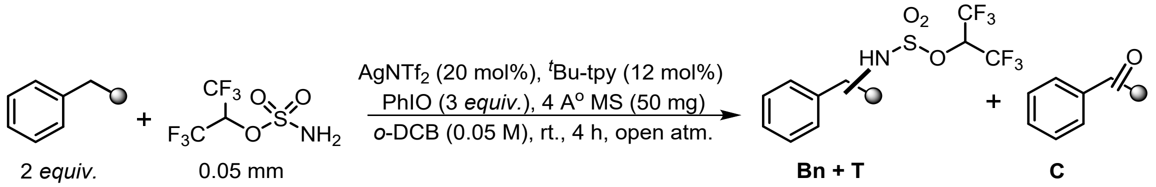
Table S17: Temperature optimization for benzylic amidation reaction.

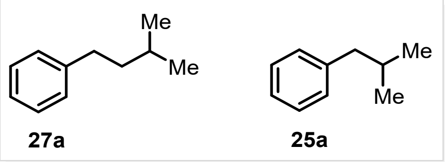


Entry	Temperature	Yields	
		1b	1b′
1	**rt**	**85%**	**10%**
2	0-5 ºC	29%	<1%
3	50 ºC	18%	0%

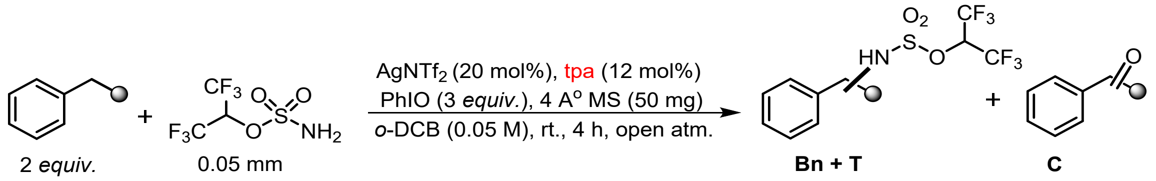
3.2. Optimization of unbiased systems for benzylic amidation.

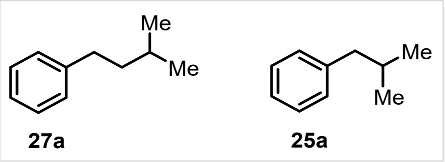
Table S18: Initial reaction developments of unbiased systems for benzylic amidation reaction.



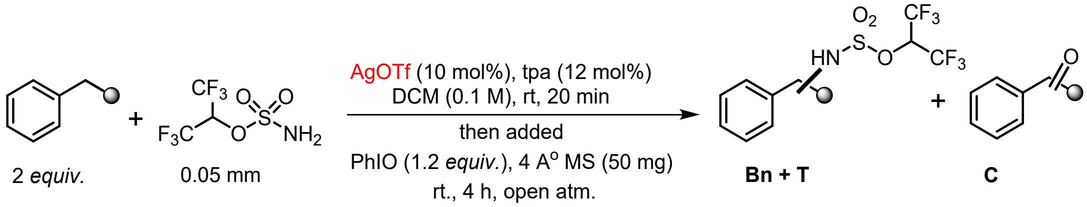


Entry	Bn yield	T yield	Bn: T	C
27a	37%	-	-	3%
25a	-	10%	-	-

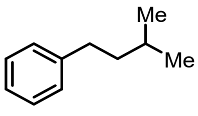




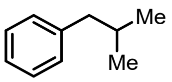
Entry	Bn yield	T yield	Bn: T	C
27a	10%	-	-	1%
25a	-	4%	-	-



Entry	Bn yield	T yield	Bn: T	C
27a	3%	-	-	1%
25a	-	-	-	-

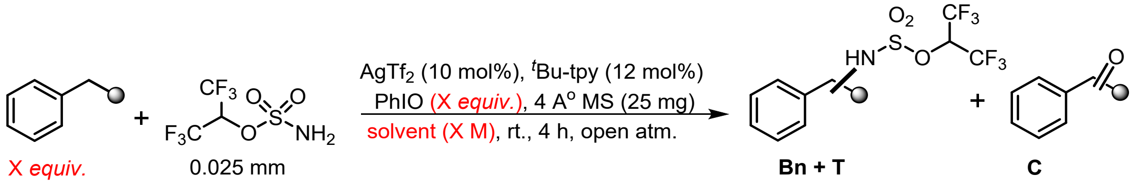


27a

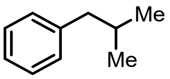


25a

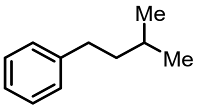
Table S19: Temperature optimization of unbiased systems for benzylic amidation reaction.



Arene (5 *equiv.*), amine (0.025 mm), $AgTf_2$ (10 mol%), TPY2 (12 mol%), PhIO (1.2 *equiv.*), 4 Aº MS (25 mg), TFE (0.05 M), rt, open atm, 4 h.



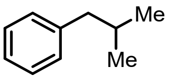
25a



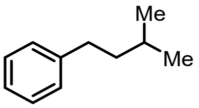
27a

Entry	**yield**	**Bn: T**	**C**
25a	36%	5:1	4%
27a	26%	1.6:1	-

Arene (5 *equiv.*), amine (0.025 mm), $AgTf_2$ (10 mol%), TPY2 (12 mol%), PhIO (2 *equiv.*), 4 Aº MS (25 mg), TFE (0.1 M), rt, open atm, 4 h.



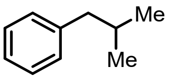
25a



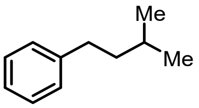
27a

Entry	**yield**	**Bn: T**	**C**
25a	**40%**	**5.7:1**	**4%**
27a	**42%**	**2:1**	**4%**

Arene (3 *equiv.*), amine (0.025 mm), $AgTf_2$ (10 mol%), TPY2 (12 mol%), PhIO (2 *equiv.*), 4 Aº MS (25 mg), TFE (0.1 M), rt, open atm, 4 h.



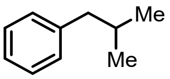
25a



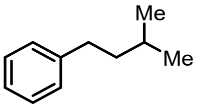
27a

Entry	**yield**	**Bn: T**	**C**
25a	39%	6.8:1	4%
27a	36%	2.6:1	3%

Arene (1.2 *equiv.*), amine (0.025 mm), $AgTf_2$ (10 mol%), TPY2 (12 mol%), PhIO (3 *equiv.*), 4 Aº MS (25 mg), TFE (0.1 M), rt, open atm, 4 h.



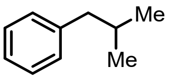
25a



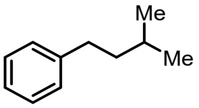
27a

Entry	**yield**	**Bn: T**	**C**
25a	**43%**	**2.3:1**	**5%**
27a	23%	1.9:1	2%

Arene (1.2 *equiv.*), amine (0.025 mm), $AgTf_2$ (10 mol%), TPY2 (12 mol%), PhIO (2 *equiv.*), 4 Aº MS (25 mg), TFE (0.1 M), rt, open atm, 4 h.



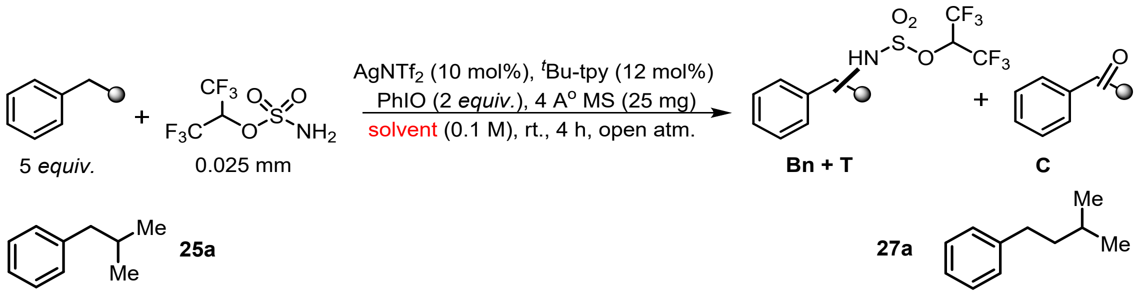
25a



27a

Entry	**yield**	**Bn: T**	**C**
25a	21%	2:1	3%
27a	-	-	-

Table S20: Solvent optimization of unbiased systems for benzylic amidation reaction.

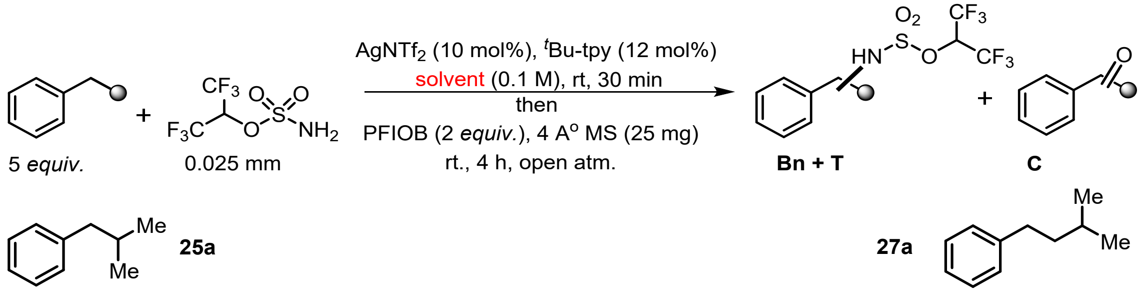


Solvent	Yields	Bn: T	C
PhCl	48%	2.4:1	13%
$PhCF_3$	32%	2.2:1	9%
PhH	28%	3:1	7%
***o*-DCB**	**62%**	**3.2:1**	**12%**
PhCN	15%	2:1	19%
TFE*	56%	2.1:1	6%

Solvent	Yields	Bn: T	C
PhCl	26%	1.6:1	20%
$PhCF_3$	26%	1.6:1	20%
PhH	26%	1.6:1	20%
o-DCB	26%	1.6:1	20%
PhCN	26%	1.6:1	20%
TFE*	**57%**	**4.7:1**	**2%**

[* indicates the preparation of Ag/L complex first (rt, 30 min) followed by addition of other reagents]

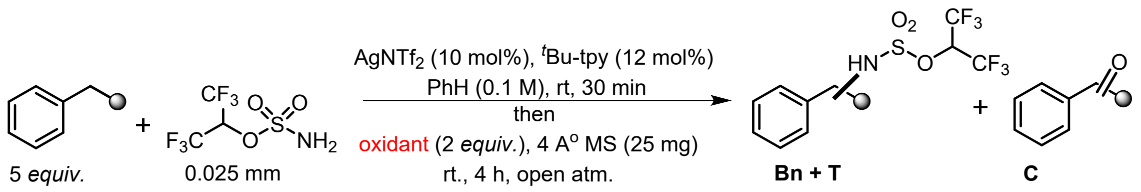
Table S21: Solvent optimization of unbiased systems for benzylic amidation reaction [precatalyst formation followed by reaction set up].

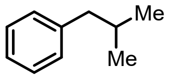


Solvent	Yields	Bn: T	C
TFE	43%	2.1:1	2%
PhCl	70%	4.5:1	11%
PhH	**71%**	**4.6:1**	**15%**
o-DCB	68%	4.3:1	6%

Solvent	Yields	Bn: T	C
TFE	49%	9:1	4%
PhCl	76%	5:1	17%
PhH	**83%**	**4.3:1**	**21%**
o-DCB	74%	4:1	9%

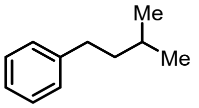
Table S22: Oxidant optimization of unbiased systems for benzylic amidation reaction.





25a

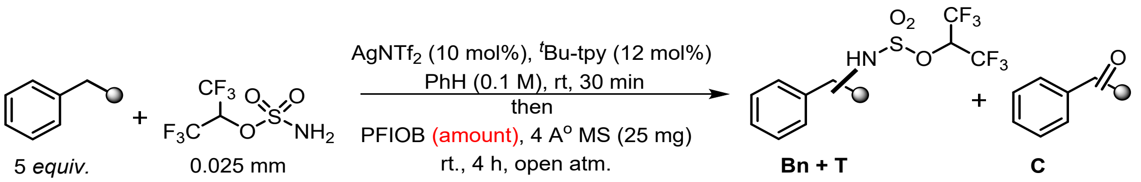
27a

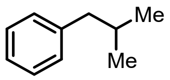


Oxidant	Yields	Bn: T	C
$PhI(OAc)_2$	44%	5.:1	8%
$C_6F_5(OCOCF_3)_2$	41%	3.8:1	8%
PFIOB	**71%**	**4.6:1**	**15%**

Oxidant	Yields	Bn: T	C
$PhI(OAc)_2$	45%	4.8:1	8%
$C_6F_5(OCOCF_3)_2$	55%	3.9:1	18%
PFIOB	**83%**	**4.3:1**	**21%**

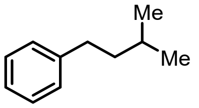
Table S23: PFIOB amount optimization of unbiased systems for benzylic amidation reaction.





25a

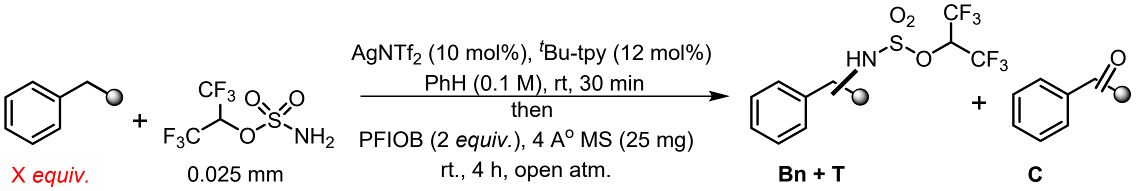
27a

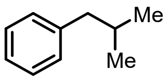


Amount	Yields	Bn: T	C
no amount	no rxn	-	-
0.5 *equiv.*	32%	2.5:1	4%
1.0 *equiv.*	messy	nmr	-
1.5 *equiv.*	48%	3.8:1	5%
2.0 *equiv.*	**71%**	**4.6:1**	**15%**
2.5 *equiv.*	48%	4.1:1	7%
3.0 *equiv.*	72%	4.2:1	23%
3.5 *equiv.*	72%	4.1:1	16%
4.0 *equiv.*	73%	4:1	30%
4.5 *equiv.*	64%	4.2:1	24%
5.0 *equiv.*	65%	2.3:1	8%

Amount	Yields	Bn: T	C
no amount	no rxn	-	-
0.5 *equiv.*	30%	3.1:1	6%
1.0 *equiv.*	45%	5.7:1	6%
1.5 *equiv.*	53%	6.8:1	16%
2.0 *equiv.*	**83%**	**4.3:1**	**21%**
2.5 *equiv.*	59%	6.2:1	20%
3.0 *equiv.*	69%	7.5:1	23%
3.5 *equiv.*	71%	6.5:1	23%
4.0 *equiv.*	72%	6:1	22%
4.5 *equiv.*	59%	6.1:1	7%
5.0 *equiv.*	messy	nmr	-

Table S24: Arene amount optimization of unbiased systems for benzylic amidation reaction.





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Amount	Yields	Bn: T	C
1.2 *equiv.*	33%	4.8:1	5%
2.0 *equiv.*	35%	3.6:1	4%
3.0 *equiv.*	51%	4.1:1	16%
5.0 *equiv.*	**71%**	**4.6:1**	**15%**

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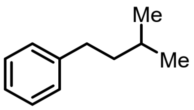
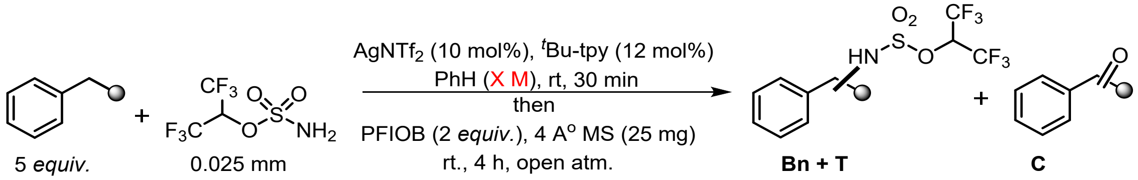
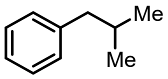


Amount	Yields	Bn: T	C
1.2 *equiv.*	34%	6.7:1	4%
2.0 *equiv.*	50%	8.5:1	10%
3.0 *equiv.*	62%	7.0:1	18%
5.0 *equiv.*	**83%**	**4.3:1**	**21%**

Table S25: Solvent concentration optimization of unbiased systems for benzylic amidation reaction.





25a

Amount	Yields	Bn: T	C
0.25 M	76%	4.3:1	16%
0.125 M	67%	4.7:1	23%
0.1 M	**71%**	**4.6:1**	**15%**
0.05M	50%	3.8:1	12%
0.025 M	57%	3.8:1	11%
0.017 M	56%	3.8:1	18%

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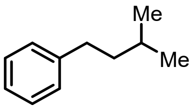
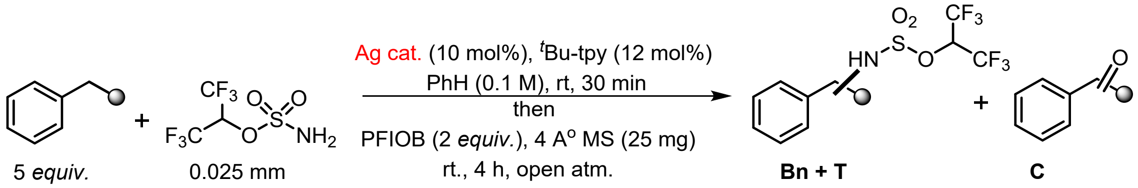
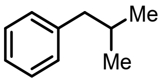


Amount	Yields	Bn: T	C
0.25 M	62%	7.7:1	14%
0.125 M	72%	8.4:1	20%
0.1 M	**83%**	**4.3:1**	**21%**
0.05M	61%	7.4:1	26%
0.025 M	57%	4.9:1	14%
0.017 M	47%	4.8:1	16%

Table S26: Ag cat. optimization of unbiased systems for benzylic amidation reaction.





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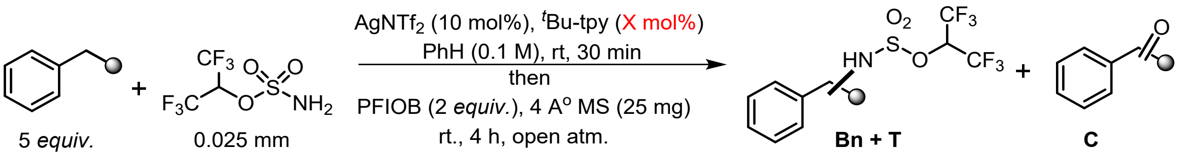
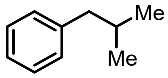
Ag cat.	Yields	Bn: T	C
AgNTf$_2$	**71%**	**4.6:1**	**15%**
AgOTf	51%	4.3:1	17%
AgSbF$_6$	52%	4.1:1	19%
AgPF$_6$	46%	3.8:1	10%

Table S27: Ligand **(**TPY2) amount optimization of unbiased systems for benzylic amidation reaction.





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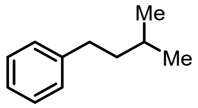
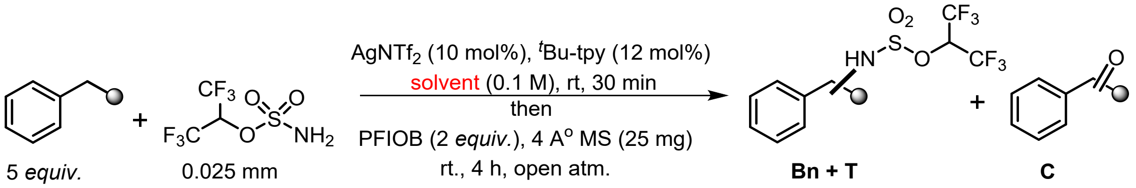
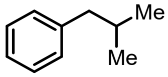


Amount	Yields	Bn: T	C
10 mol%	**71%**	**4.6:1**	**15%**
15 mol%	66%	4.6:1	11%
20 mol%	63%	4.4:1	20%
25 mol%	52%	3.9:1	6%
30 mol%	48%	3.5:1	8%
40 mol%	49%	3.7:1	12%

Amount	Yields	Bn: T	C
10 mol%	**83%**	**4.3:1**	**21%**
15 mol%	89%	>19:1	35%
20 mol%	33%	5.5:1	10%
25 mol%	59%	8.8:1	23%
30 mol%	55%	6.0:1	22%
40 mol%	48%	5.7:1	10%

Table S28: Solvent optimization of unbiased systems for benzylic amidation reaction.





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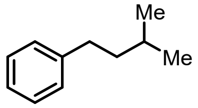
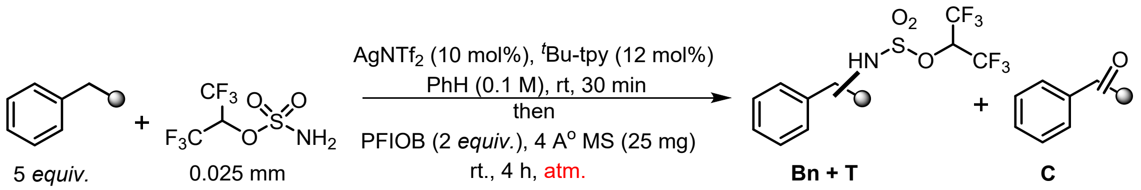
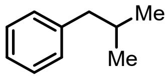


Solvent	Yields	Bn: T	C
PhH	**71%**	**4.6:1**	**15%**
DCM	44%	3.6:1	4%
$PhNO_2$	58%	3.2:1	17%
1,1,1 TCE	57%	3.8:1	11%
1,3 DFB	63%	4.8:1	6%
o-DCB	69%	6.6:1	6%

Solvent	Yields	Bn: T	C
PhH	**83%**	**4.3:1**	**21%**
DCM	53%	6.7:1	7%
$PhNO_2$	85%	9.9:1	14%
1,1,1 TCE	77%	6.0:1	10%
1,3 DFB	65%	6.2:1	14%

Table S29: Atmospheric condition optimization of unbiased systems for benzylic amidation reaction.





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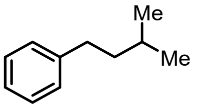
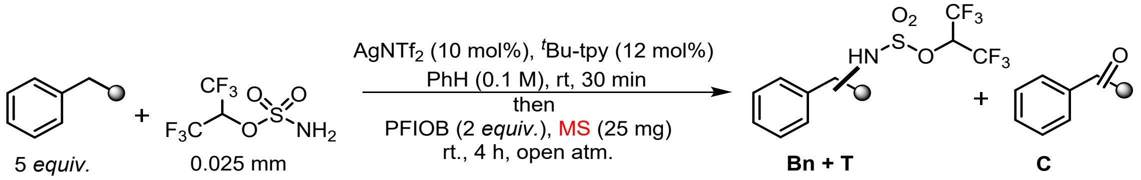
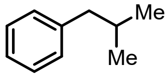


Atm.	Yields	Bn: T	C
O_2	53%	4.7:1	15%
N_2	56%	5.2:1	8%
open atm.	**71%**	**4.6:1**	**15%**

Atm.	Yields	Bn: T	C
O_2	65%	6.2:1	17%
N_2	67%	6.5:1	21%
open atm.	**83%**	**4.3:1**	**21%**

Table S30: Molecular sieve optimization of unbiased systems for benzylic amidation reaction.





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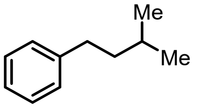
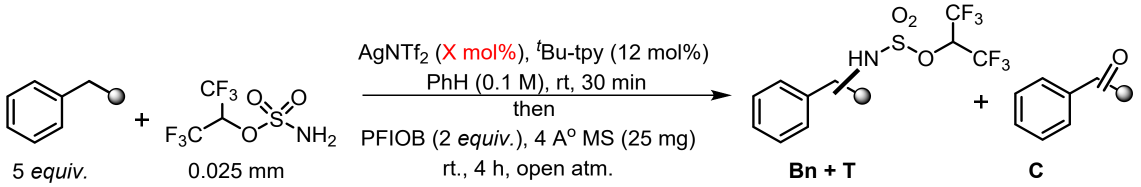
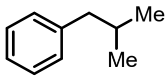


MS	Yields	Bn: T	C
3 A°	55%	4.5:1	15%
4 A°	**71%**	**4.6:1**	**15%**
5 A°	63%	4.2:1	18%

MS	Yields	Bn: T	C
3 A°	69%	5.4:1	17%
4 A°	**83%**	**4.3:1**	**21%**
5 A°	71%	7.0:1	21%

Table S31: AgNTf$_2$ optimization of unbiased systems for benzylic amidation reaction.





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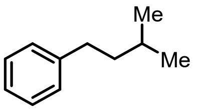
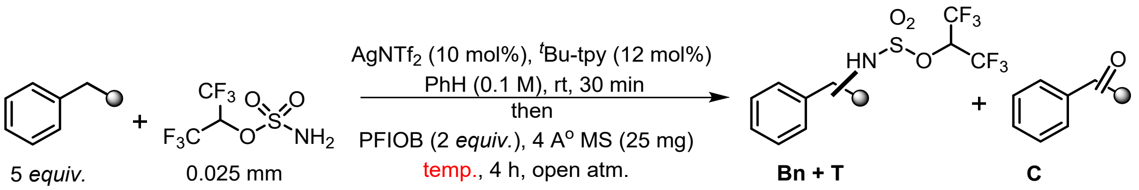
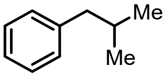


Ag amount	Yields	Bn: T	C
no cat.	33%	2.5:1	12%
10 mol%	**71%**	**4.6:1**	**15%**
15 mol%	68%	4.9:1	11%
20 mol%	52%	4.0:1	10%

Ag amount	Yields	Bn: T	C
no cat.	45%	5.9:1	14%
10 mol%	**83%**	**4.3:1**	**21%**
15 mol%	66%	5.2:1	18%
20 mol%	63%	6.2:1	15%

Table S32: Temperature optimization of unbiased systems for benzylic amidation reaction.





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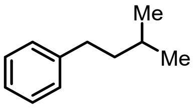
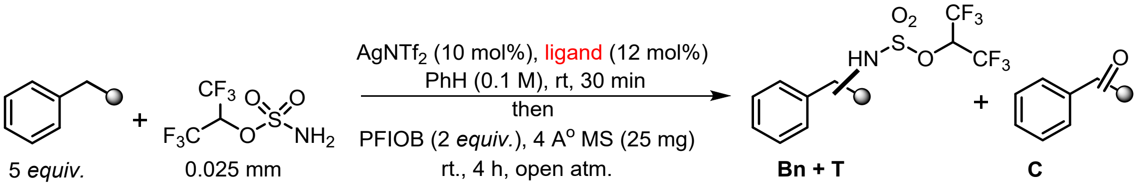
27a

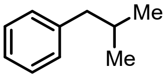


Temp.	Yields	Bn: T	C
0-5 °C	49%	4.0:1	10%
rt	**71%**	**4.6:1**	**15%**
50 °C	68%	4.2:1	11%

Temp.	Yields	Bn: T	C
0-5 °C	52%	>19:1	21%
rt	**83%**	**4.3:1**	**21%**
50 °C	73%	5.7:1	15%

Table S33: Ligand optimization of unbiased systems for benzylic amidation reaction.





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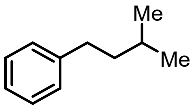
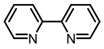
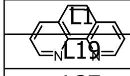


Ligand	Yields	Bn: T	C
L17	40%	4.1:1	15%
L1	25%	3.6:1	12%
L19	56%	4.8:1	10%
L27	56%	4.6:1	6%
L32	44%	4.4:1	7%
L29	63%	4.4:1	10%
L40	36%	3.8:1	15%
L41	8%	2.6:1	1%

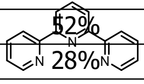
Ligand	Yields	Bn: T	C
L17	34%	4:1	8%
L1	52%	>19:1	10%
L19	28%	4.9:1	14%
L27	60%	7.3:1	10%
L32	79%	7.5:1	12%
L29	75%	8.5:1	10%
L40	39%	5.6:1	14%
L41	trace	-	trace



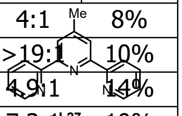
L17



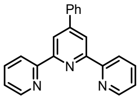
L1



L19



L27

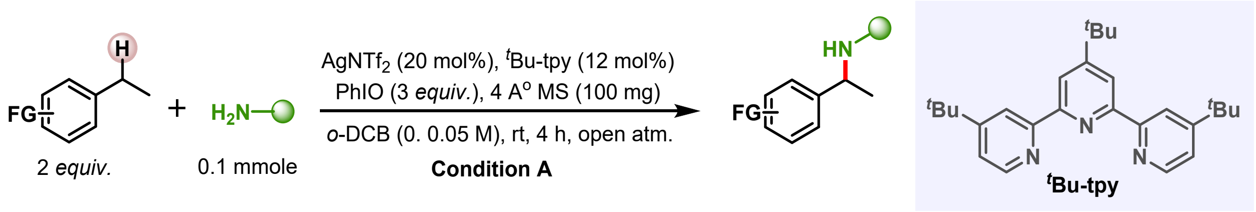


L32

4. Experiment details

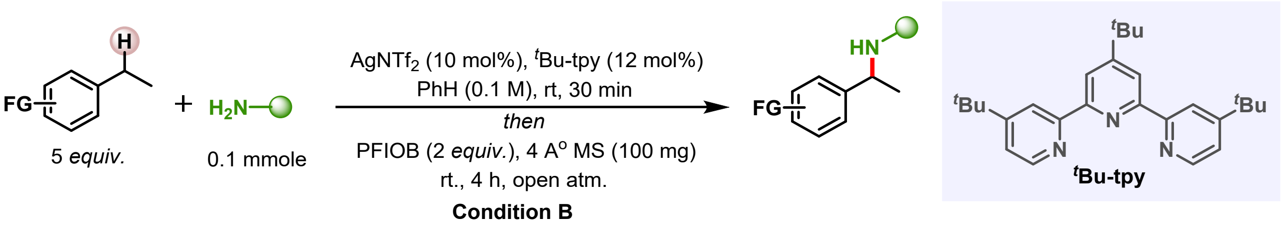
4.1. General procedure for substrate-controlled site-selective benzylic C-H amidation reaction

Condition A:



A pre-dried 4 ml sample vial was charged with a magnetic stir bar, silver bis(trifluoromethanesulfonyl)imide (7.76 mg, 20 mol%), 4,4,4-*tri*-*tert*-butyl-2,2:6,2-terpyridine (4.8 mg, 12 mol%), the nitrene precursor (0.1 mmol), iodosobenzene (66 mg, 3 *equiv.*), 4 Å molecular sieves (100 mg), and the corresponding arene (2 *equiv.*). The *ortho*-dichlorobenzene (*o*-DCB, 2 mL) was added to the vial and the mixture was stirred vigorously at rt for 4 h. The reaction mixture was filtered through a Celite pad and the filtrate concentrated under reduced pressure. The crude mixture was purified to furnish the corresponding products by column chromatography using silica (230-400 mesh size) and hexane/diethyl ether as the eluent. The yield and regioselectivity was determined from the crude NMR of the reaction mixture (0.025 mm reaction scale).

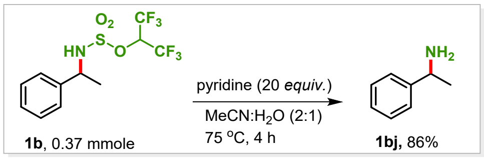
Condition B:



A pre-dried 4 ml sample vial was charged with a magnetic stir bar, silver bis(trifluoromethanesulfonyl)imide (3.8 mg, 10 mol%), 4,4,4-*tri*-*tert*-butyl-2,2:6,2-terpyridine (4.8 mg, 12 mol%), and benzene (PhH, 1 mL) and benzene as the solvent. The mixture was stirred vigorously at rt for 30 min to form the precatalyst. Another 4 mL sample vial was charged with the corresponding sulfonamide derivative (0.1 mmol), pentafluoroiodosobenzene (62 mg, 2 *equiv.*), 4 Å molecular sieves (100 mg), and the corresponding arene (5 *equiv.*). This was followed by addition of the precatalyst mixture and the reaction was stirred vigorously at rt for 4 h. The reaction mixture was filtered through a Celite pad and the filtrate concentrated under reduced pressure. The crude mixture was purified to furnish the products by column chromatography using silica (230-400 mesh size) and hexane/diethyl ether as the eluent. The yield and regioselectivity was determined from the crude NMR of the reaction mixture (0.025 mmol reaction scale).

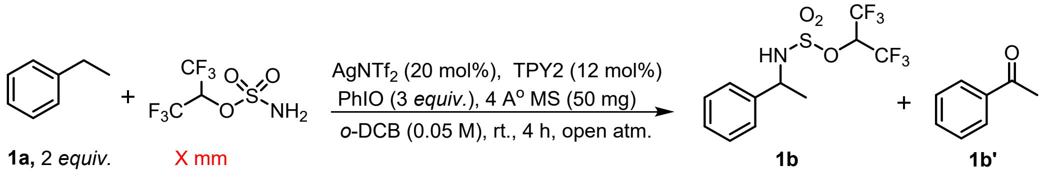
4.2. Post-synthetic functionalization [8]

Preparation of 1-phenylethyl amine (1bj):



A clean, oven–dried 10 ml round bottom flask equipped with a magnetic stir bar was charged with 1,1,1,3,3,3-hexafluoropropan-2-yl (1-phenylethyl)sulfamate (**1b**, 0.37 mmol), followed by the addition of acetonitrile-water (2:1, 8.7 mL) and pyridine (0.595 mL, 20.0 *equiv.*). The mixture was stirred at 75 °C for 4 h. Water was then added to the mixture, followed by 10 mL of EtOAc. The contents were transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted twice with EtOAc. The combined organic extracts were washed with HCl (1M) (3 x 5 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure; cycles of heptane addition/concentration were repeated until removal of the pyridine was achieved. The desired product was obtained in sufficient purity as a gummy liquid (38 mg, 86%).

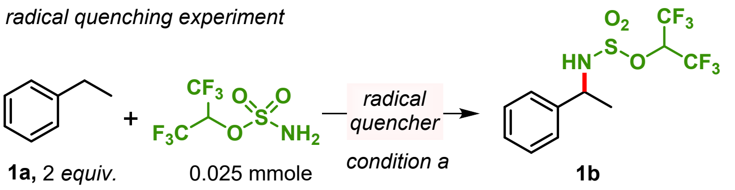
4.3. Scale-up of the Ag-catalyzed benzylic amidation.



Entry	Reaction scale (X mm)	Yields	
		1b	**1b’**
1	0.2 mmol	73%	10%
2	0.5 mmol	68%	12%
3	0.5 mmol (solvent 0.167 M)	52%	15%
4	0.5 g	82%	5%

4.4. Radical quenching experiment.

radical quenching experiment



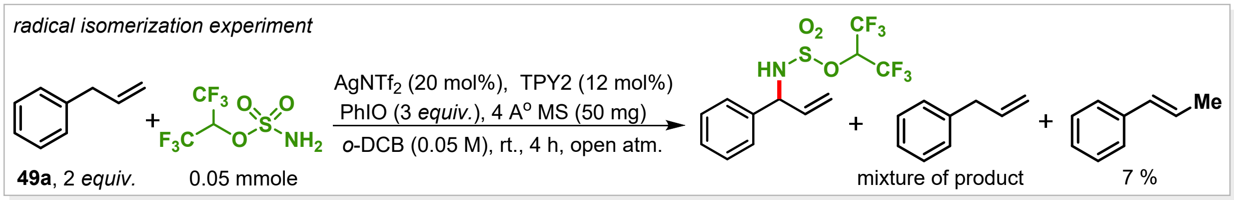
1a, 2 *equiv.*

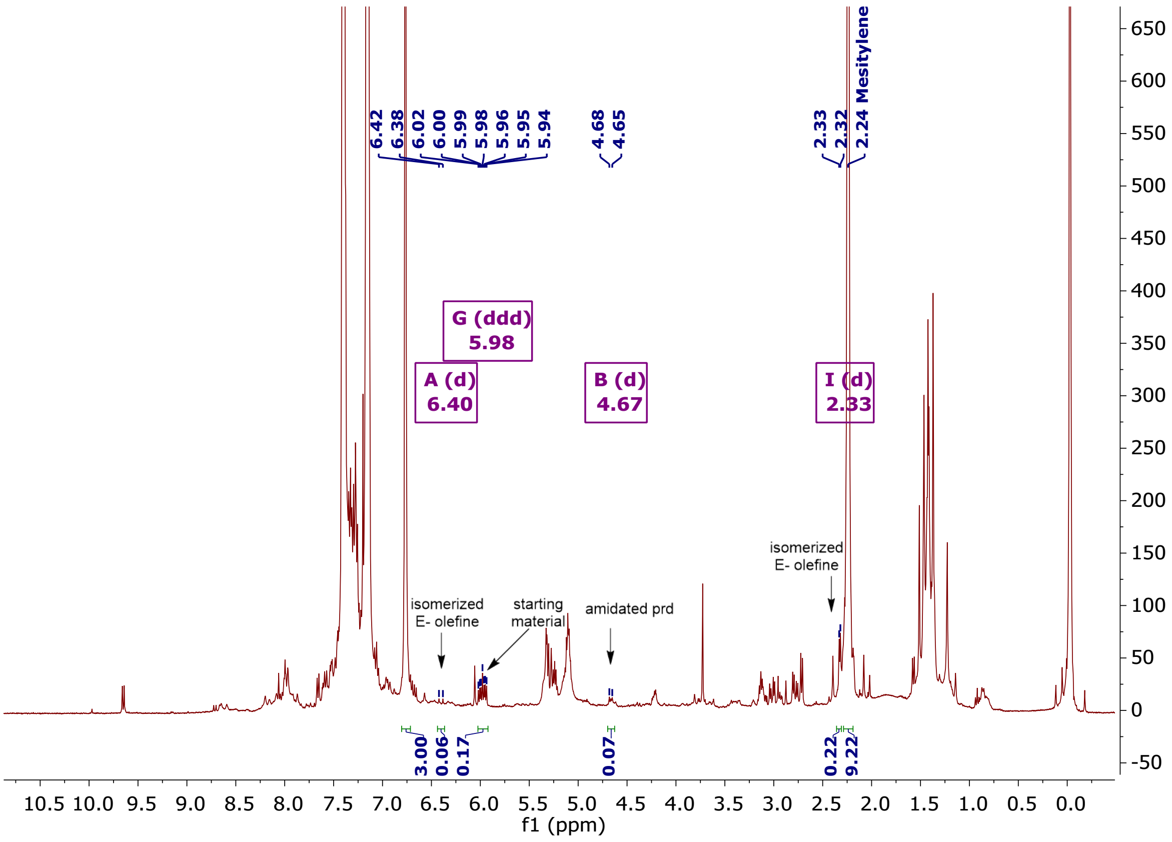
0.025 mmole

1b

radical quencher	desired product (1b) 2 *equiv.*	4 *equiv.*	6 *equiv.*
TEMPO	18%	12%	13%
BHT	4%	-	-
$P(OEt)_3$	-	-	-

4.5. Radical isomerization experiment.



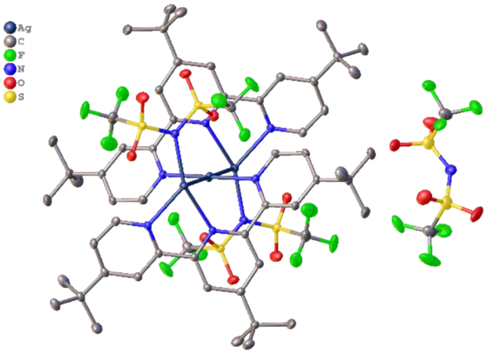


4.6. Details of the single-crystal X-ray diffraction experiments.

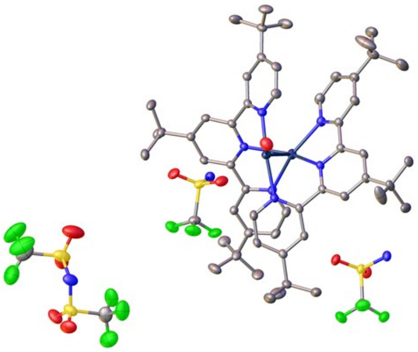
4.6.1. Preparation of the crystal structures.

Condition A (ML_1): $AgNTf_2$ (0.1 mm) + TPY (12 mol%) + *o*-DCB solvent (0.05 M) (Ag:L = 20:12).

Condition B (ML_2): $AgNTf_2$ (0.1 mm) + TPY (12 mol%) + PhH (0.1 M) solvent (Ag:L = 10:12).

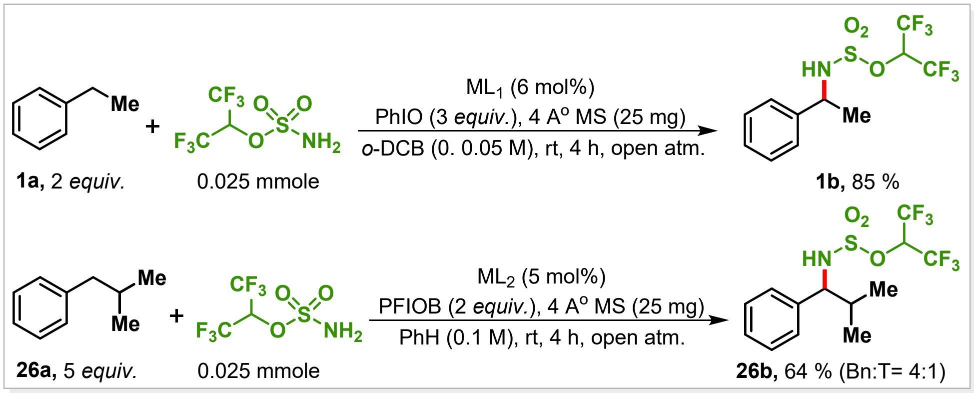


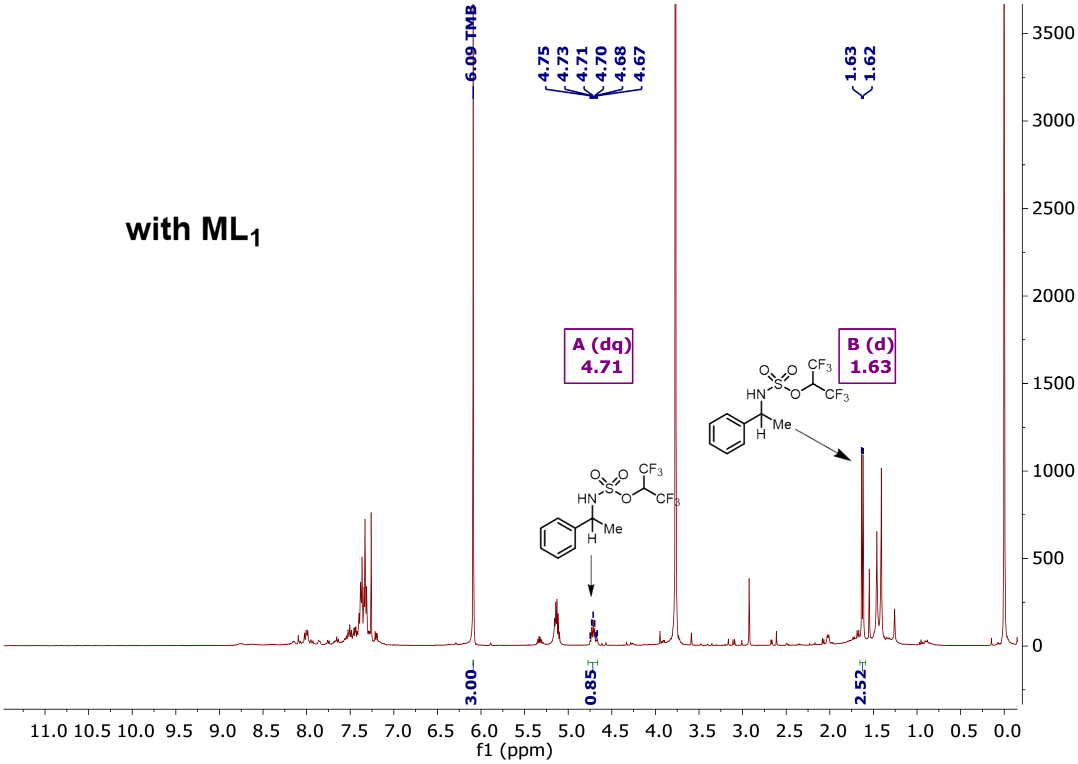
ML_1 (trinuclear species)

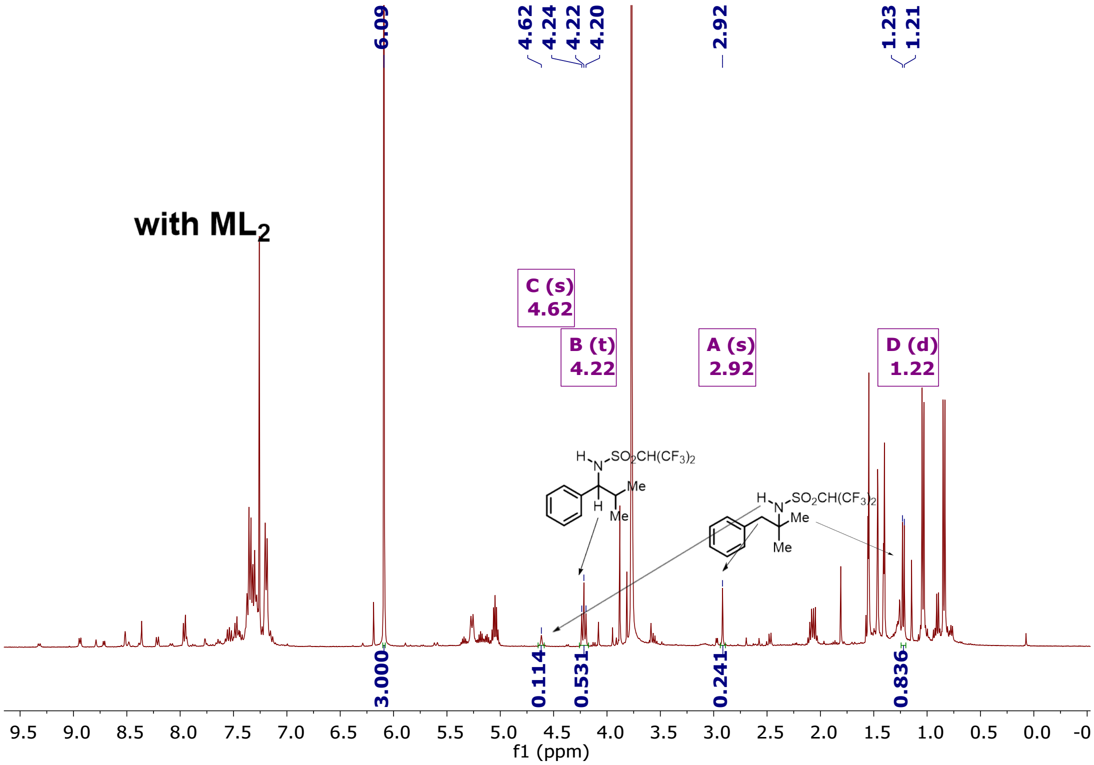


ML_2 (dinuclear species)

4.6.2. Experimental results with prepared crystals [ML_1 (Schomaker124), ML_2 (Schomaker125a)].




with ML_1
6.09 TMB
4.75
4.73
4.71
4.70
4.68
4.67
1.63
1.62
A (dq)
4.71
B (d)
1.63
HN
S
O
CF3
Me
H
3.00
0.85
2.52
3500
3000
2500
2000
1500
1000
500
0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


with ML_2
6.09
4.62
4.24
4.22
4.20
2.92
1.23
1.21
C (s)
4.62
B (t)
4.22
A (s)
2.92
D (d)
1.22
H
N
SO2CH(CF3)2
Me
H
3.000
0.114
0.531
0.241
0.836
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

Crystallographic Experimental Section.

Data Collection (ML_1)

A colorless crystal with approximate dimensions 0.08 x 0.07 x 0.07 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker D8 VENTURE Photon III four-circle diffractometer with Diamond II IμS Mo Kα (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.0 cm.[9]

The initial cell constants were obtained from a 180° ϕ scan conducted at a $2\theta = 30°$ angle with the exposure time of 1 second per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX6 program. The final cell constants were calculated from a set of 9909 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.74 Å. A total of 88983 data were harvested by collecting 13 sets of frames with 0.5–1.0º scans in ω and ϕ with an exposure time 1–15 sec per frame and 5.0 and 6.0 detector-to-crystal distances. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[10]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement.[11-16] A successful solution by intrinsic phasing provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The composition is one trinuclear Ag complex and one bistriflimide $[C_{58}H_{70}Ag_3F_{12}N_8O_8S_4][C_2F_6NO_4S_2]$. The Ag complex resides on a crystallographic inversion center. Atom Ag1 occupies the inversion center. The bistriflimide counterion is equally disordered over a crystallographic inversion center and only one half is symmetry-independent. Its disordered CF_3 group was refined with distance and atomic displacement parameter restraints. The final least-squares refinement of 547 parameters against 9865 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0338 and 0.0930, respectively. There were small (ca 1.4 e/Å^3) peaks in the final difference Fourier map near the Ag atoms; these are considered noise.

Summary

Crystal Data for $C_{60}H_{70}Ag_3F_{18}N_9O_{12}S_6$ (M =1967.22 g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 10.859(2) Å, b = 15.785(3) Å, c = 22.301(5) Å, β = 91.655(9)°, V = 3820.8(14) Å^3, Z = 2, T = 100.00 K, μ(Mo Kα) = 1.031 mm^{-1}, $Dcalc$ = 1.710 g/cm^3, 88983 reflections measured (4.126° ≤ 2Θ ≤ 57.442°), 9865 unique (R_{int} = 0.0359, R_{sigma} = 0.0191) which were used in all calculations. The final R_1 was 0.0338 (I > 2σ(I)) and wR_2 was 0.0930 (all data).

Acknowledgement

The purchase of the Bruker D8 VENTURE Photon III Diamond II IμS X-ray diffractometer was partially funded by a 2024 University of Wisconsin Research Core Revitalization Program Round 3 Award to the Department of Chemistry.

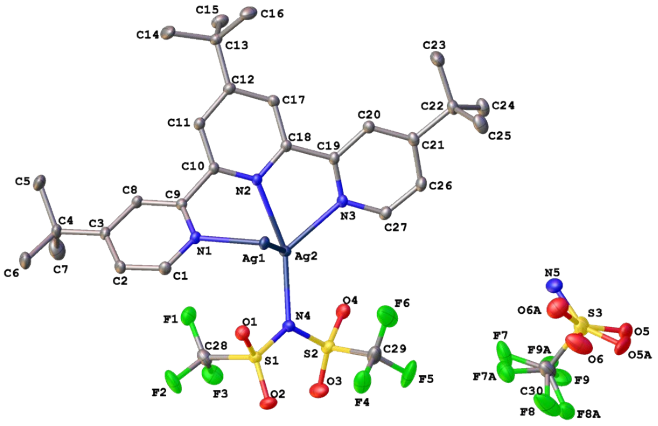


Figure S1. A molecular drawing of symmetry-independent part (half) of Schomaker124 (ML_1) shown with 50% probability ellipsoids. All H atoms are omitted. Both disorder positions of the bistriflimide are shown.

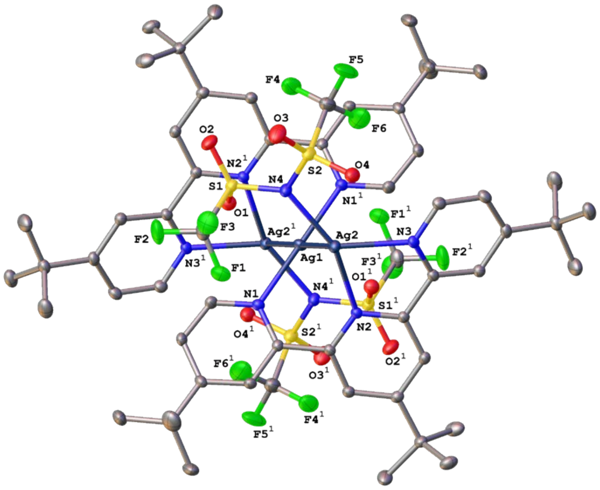


Figure S2. A molecular drawing of metal complex in Schomaker124 (ML_1) shown with 50% probability ellipsoids. All H atoms are omitted. Symmetry code (1) 1-x, 1-y, 1-z.

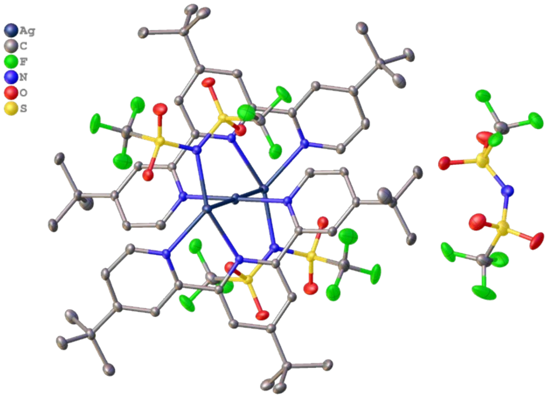


Figure S3. A molecular drawing of Schomaker124 (ML_1) shown with 50% probability ellipsoids. All H atoms and one half of the disordered atoms are omitted.

Table S34. Crystal data and structure refinement for Schomaker124 (ML_1).

Identification code	Schomaker124
Empirical formula	$[C_{58}H_{70}Ag_3F_{12}N_8O_8S_4][C_2F_6NO_4S_2]$
Formula weight	1967.22
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.859(2)
b/Å	15.785(3)
c/Å	22.301(5)
α/°	90

β/°	91.655(9)
γ/°	90
Volume/Å^3	3820.8(14)
Z	2
ρ_{calc}g/cm^3	1.710
μ/mm^{-1}	1.031
F(000)	1976.0
Crystal size/mm^3	0.08 × 0.07 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.126 to 57.442
Index ranges	-14 ≤ h ≤ 14, -21 ≤ k ≤ 21, -30 ≤ l ≤ 30
Reflections collected	88983
Independent reflections	9865 [R_{int} = 0.0359, R_{sigma} = 0.0191]
Data/restraints/parameters	9865/145/547
Goodness-of-fit on F^2	1.133
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.0930
Largest diff. peak/hole / e Å^{-3}	1.42/-0.78

Table S35. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Schomaker124 (ML$_1$). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ag1	5000	5000	5000	15.61(6)
Ag2	2734.3(2)	5027.1(2)	4316.1(2)	16.02(5)
S1	4869.0(5)	5551.4(4)	3295.4(3)	16.84(11)
S2	2597.3(6)	6413.3(4)	3241.0(3)	20.74(12)
C29	3087(2)	7403.8(16)	3614.7(12)	32.8(7)
F4	4262.3(16)	7566.6(11)	3527.3(10)	41.2(5)
F5	2427.2(19)	8039.7(11)	3390.1(12)	56.1(7)
F6	2919(2)	7359.2(13)	4197.7(9)	53.2(6)
F1	4256.0(17)	3949.8(10)	3201.1(8)	31.2(4)
F2	5710.3(18)	4355.5(13)	2633.2(10)	42.8(5)
F3	3819.4(18)	4692.0(13)	2414.6(8)	37.3(4)

O1	5642.6(17)	5297.0(12)	3790.8(8)	20.8(4)
O2	5289.3(18)	6166.2(13)	2883.1(9)	26.8(4)
O3	2749.4(19)	6556.4(14)	2619.1(9)	31.6(5)
O4	1400.1(17)	6244.0(12)	3467.4(9)	25.0(4)
N1	5167.6(18)	3731.4(12)	4633.7(9)	15.0(4)
N2	2772.8(18)	4052.2(12)	5125.2(9)	13.3(4)
N3	1403.9(18)	5512.7(12)	5005.0(9)	14.6(4)
N4	3509.1(19)	5718.6(13)	3542.2(9)	18.1(4)
C1	6119(2)	3540.2(15)	4289.8(11)	16.8(4)
C2	6316(2)	2745.7(15)	4048.4(11)	17.7(5)
C3	5468(2)	2096.2(15)	4142.7(11)	16.5(4)
C4	5594(3)	1220.7(15)	3863.0(12)	22.3(5)
C5	5293(3)	534.7(18)	4321.0(16)	37.3(8)
C6	6901(3)	1066.1(18)	3643.4(15)	32.2(7)
C7	4677(3)	1179(2)	3325.6(15)	36.9(7)
C8	4465(2)	2303.4(14)	4492.4(11)	16.4(4)
C9	4346(2)	3110.5(14)	4737.7(10)	13.9(4)
C10	3348(2)	3293.8(14)	5158.3(10)	14.0(4)
C11	3083(2)	2692.1(14)	5591.4(11)	15.8(4)
C12	2193(2)	2852.8(15)	6013.8(11)	15.5(4)
C13	1835(2)	2222.9(15)	6494.8(11)	17.3(4)
C14	2673(3)	1444.8(18)	6509.1(14)	29.7(6)
C15	502(3)	1942.5(17)	6349.3(13)	24.7(5)
C16	1891(3)	2658.3(18)	7109.3(12)	26.0(6)
C17	1603(2)	3636.7(15)	5971.8(11)	15.4(4)
C18	1921(2)	4219.0(14)	5536.7(10)	13.3(4)
C19	1325(2)	5071.1(14)	5516.0(11)	14.2(4)
C20	730(2)	5396.8(15)	6014.8(11)	15.9(4)
C21	203(2)	6202.7(15)	5995.6(11)	16.2(4)
C22	-421(2)	6606.0(16)	6529.8(12)	19.5(5)
C23	-556(3)	5985.3(19)	7050.7(13)	30.5(6)
C24	-1705(2)	6925.5(18)	6332.5(13)	24.6(5)
C25	366(3)	7364.5(19)	6743.6(13)	27.6(6)
C26	305(2)	6651.7(15)	5458.4(11)	18.3(5)
C27	898(2)	6289.1(15)	4983.2(11)	17.1(4)
C28	4636(3)	4579.8(18)	2856.9(12)	24.9(5)
S3	814.5(7)	10606.6(5)	4784.7(3)	30.62(16)
C30	1015(2)	10298.8(15)	4000.4(12)	34.5(6)
F7	1326(4)	9467(2)	4001(2)	43.7(12

				)
F8	2002(4)	10700(3)	3818(2)	64.4(16)
F9	38(4)	10395(4)	3664(2)	49.4(15)
O5	-110(5)	11286(3)	4737(2)	36.2(11)
O6	2069(5)	10902(4)	4917(2)	49.2(14)
N5	547(5)	9798(3)	5071(2)	28.8(10)
F7A	1790(4)	9689(3)	3912(2)	41.5(11)
F8A	1356(4)	10972(2)	3663.5(18)	42.8(11)
F9A	-79(3)	10097(3)	3749(2)	32.5(10)
O5A	700(7)	11468(3)	4775(2)	50.1(15)
O6A	1774(5)	10223(3)	5171(2)	39.7(11)

Table S36. Anisotropic Displacement Parameters (Å^2×10^3) for Schomaker124 (ML$_1$). The Anisotropic displacement factor exponent takes the form: -$2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ag1	18.14(12)	10.18(11)	18.55(12)	-2.20(8)	1.05(9)	-0.09(8)
Ag2	17.39(9)	15.29(9)	15.60(9)	1.31(6)	4.08(6)	0.98(6)
S1	16.2(3)	16.3(3)	18.2(3)	1.7(2)	4.1(2)	-0.3(2)
S2	18.1(3)	17.8(3)	26.6(3)	5.8(2)	4.4(2)	2.6(2)
C29	29.0(15)	17.7(12)	52.2(19)	0.3(12)	13.3(13)	-0.3(11)
F4	25.8(9)	25.4(9)	72.9(14)	-4.7(9)	10.5(9)	-7.0(7)
F5	37.1(11)	16.5(9)	115(2)	8.0(10)	13.8(12)	6.6(8)
F6	69.9(15)	36.2(11)	54.7(13)	-	24.7(1	-

				20.3(10)	1)	20.5(10)
F1	37.5(10)	19.1(8)	37.0(9)	-4.2(7)	1.9(7)	-2.6(7)
F2	31.9(10)	45.9(11)	51.5(12)	-23.0(9)	18.5(9)	1.3(8)
F3	40.8(11)	46.8(11)	24.1(9)	-7.4(8)	-5.4(7)	-3.8(9)
O1	18.0(8)	20.4(8)	23.9(9)	0.7(7)	-0.4(7)	0.0(7)
O2	24.5(10)	26.1(10)	30.3(10)	11.1(8)	8.3(8)	-0.5(8)
O3	26.6(10)	37.9(12)	30.4(11)	14.5(9)	3.2(8)	7.3(9)
O4	20.2(9)	20.7(9)	34.4(11)	4.8(8)	6.1(8)	3.4(7)
N1	15.1(9)	11.7(9)	18.2(9)	-0.5(7)	2.0(7)	-0.4(7)
N2	13.1(9)	11.1(8)	15.9(9)	-0.7(7)	2.0(7)	0.2(7)
N3	11.1(9)	13.3(9)	19.5(9)	-0.4(7)	1.9(7)	1.1(7)
N4	16.7(10)	17.3(9)	20.6(10)	3.8(8)	5.8(8)	2.5(8)
C1	13.0(10)	14.5(10)	23.0(11)	-0.6(9)	3.4(8)	-1.8(8)
C2	14.7(11)	15.5(11)	23.4(12)	0.3(9)	6.7(9)	3.2(8)
C3	18.8(11)	11.7(10)	19.1(11)	0.4(8)	3.4(9)	3.5(8)
C4	26.1(13)	11.1(10)	30.2(13)	-2.3(9)	11.2(10)	0.9(9)
C5	49.7(19)	13.5(12)	50.3(19)	5.9(12)	25.7(15)	6.0(12)
C6	35.1(16)	17.2(12)	45.4(17)	-1.4(11)	19.1(13)	6.5(11)
C7	39.8(18)	31.1(15)	40.0(17)	-16.5(13)	3.7(14)	-3.3(13)
C8	16.3(11)	10.8(10)	22.4(11)	0.3(8)	4.5(9)	-0.9(8)
C9	12.9(10)	12.7(10)	16.2(10)	1.4(8)	2.3(8)	1.1(8)
C10	14.2(10)	11.0(9)	17.0(10)	-1.2(8)	2.3(8)	0.1(8)
C11	15.2(10)	11.9(10)	20.3(11)	0.3(8)	3.3(8)	0.0(8)
C12	15.2(10)	13.6(10)	17.7(11)	1.1(8)	1.6(8)	-1.7(8)
C13	19.4(11)	13.7(10)	19.2(11)	2.8(8)	5.2(9)	0.0(8)
C14	31.6(15)	22.8(13)	35.4(15)	13.3(11)	13.2(12)	10.7(11)
C15	24.3(13)	20.9(12)	29.1(13)	5.3(10)	2.5(10)	-6.5(10)
C16	38.2(15)	22.0(12)	17.8(12)	2.8(10)	1.6(10)	-5.3(11)
C17	13.9(10)	14.7(10)	17.9(11)	-0.9(8)	4.3(8)	-1.5(8)

C18	11.6(10)	11.9(9)	16.4(10)	-1.0(8)	1.4(8)	-0.9(8)
C19	11.5(10)	12.0(10)	19.1(11)	-0.9(8)	1.4(8)	0.6(8)
C20	14.2(10)	14.2(10)	19.5(11)	0.3(8)	3.2(8)	0.4(8)
C21	11.5(10)	16.7(10)	20.5(11)	-3.7(9)	2.4(8)	0.3(8)
C22	18.6(11)	16.8(11)	23.3(12)	-4.4(9)	4.7(9)	1.6(9)
C23	40.9(17)	26.3(14)	25.0(13)	-1.8(11)	13.1(12)	6.9(12)
C24	17.2(12)	23.8(12)	33.1(14)	-8.4(11)	4.2(10)	1.5(10)
C25	22.7(13)	28.3(14)	32.0(14)	-14.4(11)	3.3(11)	-3.6(11)
C26	16.9(11)	13.6(10)	24.5(12)	-0.9(9)	1.2(9)	3.4(8)
C27	14.3(10)	14.6(10)	22.4(11)	2.1(9)	0.7(8)	1.0(8)
C28	23.6(13)	28.4(13)	23.0(12)	-6.7(10)	4.1(10)	1.3(10)
S3	35.3(4)	23.2(3)	33.5(4)	-9.2(3)	2.6(3)	-2.4(3)
C30	35.7(14)	30.4(13)	38.2(16)	-9.7(12)	14.5(11)	-8.6(11)
F7	26(2)	43(2)	63(3)	-29(2)	9(2)	2.3(17)
F8	53(3)	71(3)	71(4)	-32(3)	40(3)	-38(3)
F9	56(2)	67(4)	25(2)	14(3)	6.7(18)	12(2)
O5	53(3)	16(2)	41(3)	-2.6(18)	19(2)	0(2)
O6	39(3)	71(4)	38(3)	-17(3)	9(2)	-25(3)
N5	29(3)	29(2)	28(2)	9(2)	6.3(19)	6(2)
F7A	37(2)	45(2)	43(2)	-7(2)	10(2)	9.7(19)
F8A	51(3)	28.2(18)	51(3)	-4.3(16)	28(2)	-6.1(17)
F9A	50(2)	29(2)	19(2)	6.7(16)	0.4(16)	1.6(16)
O5A	97(5)	13(2)	41(3)	0.9(19)	15(3)	0(3)
O6A	36(3)	38(2)	44(3)	3(2)	-7(2)	-6(2)

Table S37. Bond Lengths for Schomaker124 (ML$_1$).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag1	Ag2^1	2.8573(6)	C4	C7	1.537(4)
Ag1	Ag2	2.8573(5)	C8	C9	1.394(3)
Ag1	N1	2.172(2)	C9	C10	1.482(3)
Ag1	N1^1	2.172(2)	C10	C11	1.391(3)
Ag2	N2	2.371(2)	C11	C12	1.392(3)
Ag2	N3	2.272(2)	C12	C13	1.521(3)
Ag2	N4	2.227(2)	C12	C17	1.396(3)
S1	O1	1.4261(19)	C13	C14	1.529(3)
S1	O2	1.4212(19)	C13	C15	1.538(4)
S1	N4	1.613(2)	C13	C16	1.533(4)
S1	C28	1.832(3)	C17	C18	1.387(3)
S2	C29	1.843(3)	C18	C19	1.492(3)
S2	O3	1.419(2)	C19	C20	1.400(3)
S2	O4	1.433(2)	C20	C21	1.395(3)
S2	N4	1.611(2)	C21	C22	1.527(3)
C29	F4	1.322(3)	C21	C26	1.399(3)
C29	F5	1.323(3)	C22	C23	1.530(4)
C29	F6	1.320(3)	C22	C24	1.535(4)
F1	C28	1.329(3)	C22	C25	1.538(4)
F2	C28	1.330(3)	C26	C27	1.380(3)
F3	C28	1.319(3)	S3	C30	1.834(3)
N1	C1	1.339(3)	S3	O5	1.471(5)
N1	C9	1.350(3)	S3	O6	1.462(5)
N2	C10	1.351(3)	S3	N5	1.460(5)
N2	C18	1.348(3)	S3	N5^2	1.650(5)
N3	C19	1.341(3)	S3	O5A	1.366(5)
N3	C27	1.343(3)	S3	O6A	1.464(5)
C1	C2	1.384(3)	C30	F7	1.355(3)
C2	C3	1.397(3)	C30	F8	1.319(3)
C3	C4	1.524(3)	C30	F9	1.290(3)
C3	C8	1.397(3)	C30	F7A	1.298(3)
C4	C5	1.531(4)	C30	F8A	1.359(3)
C4	C6	1.533(4)	C30	F9A	1.338(3)

Table S38. Bond Angles for Schomaker124 (ML$_1$).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Ag2	Ag1	Ag2^1	180.0	C11	C12	C17	116.3(2)
N1^1	Ag1	Ag2	96.13(5)	C17	C12	C13	120.0(2)

Table S38. Bond Angles for Schomaker124 (ML$_1$).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Ag1	Ag2^1	96.13(5)	C12	C13	C14	112.0(2)
N1^1	Ag1	Ag2^1	83.87(5)	C12	C13	C15	107.3(2)
N1	Ag1	Ag2	83.87(5)	C12	C13	C16	109.4(2)
N1	Ag1	N1^1	180.0	C14	C13	C15	109.2(2)
N2	Ag2	Ag1	65.67(5)	C14	C13	C16	109.5(2)
N3	Ag2	Ag1	101.46(5)	C16	C13	C15	109.3(2)
N3	Ag2	N2	72.66(7)	C18	C17	C12	120.7(2)
N4	Ag2	Ag1	94.72(6)	N2	C18	C17	122.4(2)
N4	Ag2	N2	155.36(7)	N2	C18	C19	117.4(2)
N4	Ag2	N3	128.34(7)	C17	C18	C19	120.2(2)
O1	S1	N4	107.84(11)	N3	C19	C18	117.2(2)
O1	S1	C28	104.30(12)	N3	C19	C20	121.8(2)
O2	S1	O1	120.03(12)	C20	C19	C18	121.0(2)
O2	S1	N4	115.05(11)	C21	C20	C19	120.6(2)
O2	S1	C28	105.57(13)	C20	C21	C22	123.2(2)
N4	S1	C28	101.84(12)	C20	C21	C26	116.5(2)
O3	S2	C29	105.46(13)	C26	C21	C22	120.3(2)
O3	S2	O4	120.40(13)	C21	C22	C23	112.3(2)
O3	S2	N4	115.35(12)	C21	C22	C24	109.5(2)
O4	S2	C29	104.57(11)	C21	C22	C25	108.1(2)
O4	S2	N4	106.20(11)	C23	C22	C24	108.8(2)
N4	S2	C29	102.90(12)	C23	C22	C25	109.1(2)
F4	C29	S2	111.42(17)	C24	C22	C25	108.9(2)
F4	C29	F5	108.1(2)	C27	C26	C21	119.8(2)
F5	C29	S2	109.07(19)	N3	C27	C26	123.4(2)
F6	C29	S2	110.73(17)	F1	C28	S1	111.02(18)
F6	C29	F4	108.5(2)	F1	C28	F2	107.9(2)
F6	C29	F5	108.9(2)	F2	C28	S1	108.27(19)
C1	N1	Ag1	119.84(15)	F3	C28	S1	111.5(2)
C1	N1	C9	117.4(2)	F3	C28	F1	108.6(2)
C9	N1	Ag1	122.80(15)	F3	C28	F2	109.4(2)
C10	N2	Ag2	127.92(15)	O5	S3	C30	102.9(2)
C18	N2	Ag2	113.20(14)	O5	S3	N5^2	71.6(3)
C18	N2	C10	117.47(19)	O6	S3	C30	98.1(2)
C19	N3	Ag2	117.17(15)	O6	S3	O5	114.3(3)
C19	N3	C27	118.0(2)	O6	S3	N5^2	156.8(3)
C27	N3	Ag2	123.41(16)	N5^2	S3	C30	102.4(2)
S1	N4	Ag2	123.67(11)	N5	S3	C30	102.5(2)

Table S38. Bond Angles for Schomaker124 (ML$_1$).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
S2	N4	Ag2	114.53(11)	N5	S3	O5	121.7(3)
S2	N4	S1	121.80(13)	N5	S3	O6	112.8(3)
N1	C1	C2	123.9(2)	N5	S3	N5^2	52.1(3)
C1	C2	C3	119.8(2)	O5A	S3	C30	105.1(2)
C2	C3	C4	122.4(2)	O5A	S3	O6A	119.0(4)
C8	C3	C2	116.1(2)	O6A	S3	C30	110.5(2)
C8	C3	C4	121.4(2)	F7	C30	S3	107.0(3)
C3	C4	C5	110.2(2)	F8	C30	S3	106.6(3)
C3	C4	C6	111.7(2)	F8	C30	F7	105.1(3)
C3	C4	C7	107.1(2)	F9	C30	S3	113.9(3)
C5	C4	C6	108.6(2)	F9	C30	F7	108.4(3)
C5	C4	C7	110.1(3)	F9	C30	F8	115.2(4)
C6	C4	C7	109.2(2)	F7A	C30	S3	115.9(3)
C9	C8	C3	121.1(2)	F7A	C30	F8A	107.9(3)
N1	C9	C8	121.8(2)	F7A	C30	F9A	109.3(3)
N1	C9	C10	117.8(2)	F8A	C30	S3	111.2(2)
C8	C9	C10	120.3(2)	F9A	C30	S3	109.5(3)
N2	C10	C9	118.9(2)	F9A	C30	F8A	102.0(3)
N2	C10	C11	122.6(2)	S3	N5	S3^2	127.9(3)
C11	C10	C9	118.4(2)	S3^2	N5	O5^2	49.7(2)
C10	C11	C12	120.5(2)	S3	N5	O5^2	167.4(4)
C11	C12	C13	123.7(2)				

^{1}1-X,1-Y,1-Z; ^{2}-X,2-Y,1-Z

Table S39. Torsion Angles for Schomaker124 (ML$_1$).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Ag1	N1	C1	C2	178.53(19)	C9	C10	C11	C12	177.0(2)
Ag1	N1	C9	C8	179.29(17)	C10	N2	C18	C17	-1.8(3)
Ag1	N1	C9	C10	-4.9(3)	C10	N2	C18	C19	177.4(2)
Ag2	N2	C10	C9	18.4(3)	C10	C11	C12	C13	178.9(2)
Ag2	N2	C10	C11	-164.82(17)	C10	C11	C12	C17	0.1(3)
Ag2	N2	C18	C17	165.69(18)	C11	C12	C13	C14	7.2(3)
Ag2	N2	C18	C19	-15.1(2)	C11	C12	C13	C15	-112.7(3)
Ag2	N3	C19	C18	-11.7(3)	C11	C12	C13	C16	128.8(3)
Ag2	N3	C19	C20	167.20(17)	C11	C12	C17	C18	-1.3(3)
Ag2	N3	C27	C26	-165.89(18)	C12	C17	C18	N2	2.2(4)

Table S39. Torsion Angles for Schomaker124 (ML$_1$).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C29	S2	N4	Ag2	95.38(13)	C12	C17	C18	C19	-177.0(2)
C29	S2	N4	S1	-84.51(17)	C13	C12	C17	C18	179.9(2)
O1	S1	N4	Ag2	-30.76(17)	C17	C12	C13	C14	-174.1(2)
O1	S1	N4	S2	149.11(15)	C17	C12	C13	C15	66.1(3)
O1	S1	C28	F1	51.7(2)	C17	C12	C13	C16	-52.5(3)
O1	S1	C28	F2	-66.6(2)	C17	C18	C19	N3	-162.3(2)
O1	S1	C28	F3	172.94(19)	C17	C18	C19	C20	18.8(3)
O2	S1	N4	Ag2	-167.71(13)	C18	N2	C10	C9	-176.1(2)
O2	S1	N4	S2	12.2(2)	C18	N2	C10	C11	0.6(3)
O2	S1	C28	F1	179.05(18)	C18	C19	C20	C21	178.4(2)
O2	S1	C28	F2	60.8(2)	C19	N3	C27	C26	0.0(3)
O2	S1	C28	F3	-59.7(2)	C19	C20	C21	C22	-177.9(2)
O3	S2	C29	F4	-62.6(2)	C19	C20	C21	C26	0.1(3)
O3	S2	C29	F5	56.6(2)	C20	C21	C22	C23	-7.8(3)
O3	S2	C29	F6	176.53(19)	C20	C21	C22	C24	-128.8(2)
O3	S2	N4	Ag2	-150.34(13)	C20	C21	C22	C25	112.7(3)
O3	S2	N4	S1	29.8(2)	C20	C21	C26	C27	0.3(3)
O4	S2	C29	F4	169.45(18)	C21	C26	C27	N3	-0.4(4)
O4	S2	C29	F5	-71.3(2)	C22	C21	C26	C27	178.4(2)
O4	S2	C29	F6	48.6(2)	C26	C21	C22	C23	174.2(2)
O4	S2	N4	Ag2	-14.22(15)	C26	C21	C22	C24	53.3(3)
O4	S2	N4	S1	165.90(15)	C26	C21	C22	C25	-65.3(3)
N1	C1	C2	C3	2.3(4)	C27	N3	C19	C18	-178.5(2)
N1	C9	C10	N2	42.5(3)	C27	N3	C19	C20	0.4(3)
N1	C9	C10	C11	-134.4(2)	C28	S1	N4	Ag2	78.67(16)
N2	C10	C11	C12	0.2(4)	C28	S1	N4	S2	-101.46(17)
N2	C18	C19	N3	18.4(3)	C30	S3	N5	S3^{1}	-96.1(4)
N2	C18	C19	C20	-160.5(2)	C30	S3	N5	O5^{1}	-22.2(18)
N3	C19	C20	C21	-0.5(4)	O5	S3	C30	F7	-150.4(3)
N4	S1	C28	F1	-60.5(2)	O5	S3	C30	F8	97.5(4)
N4	S1	C28	F2	-178.7(2)	O5	S3	C30	F9	-30.7(4)
N4	S1	C28	F3	60.8(2)	O5	S3	N5	S3^{1}	17.8(6)
N4	S2	C29	F4	58.6(2)	O5	S3	N5	O5^{1}	91.7(17)
N4	S2	C29	F5	177.93(17)	O6	S3	C30	F7	92.3(3)
N4	S2	C29	F6	-62.2(2)	O6	S3	C30	F8	-19.8(4)
C1	N1	C9	C8	-0.8(3)	O6	S3	C30	F9	-148.0(4)
C1	N1	C9	C10	175.0(2)	O6	S3	N5	S3^{1}	159.4(4)
C1	C2	C3	C4	176.8(2)	O6	S3	N5	O5^{1}	-126.7(17)

Table S39. Torsion Angles for Schomaker124 (ML$_1$).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	C2	C3	C8	-1.0(4)	N5[1]	S3	C30	F7	-76.8(3)
C2	C3	C4	C5	138.0(3)	N5	S3	C30	F7	-23.3(3)
C2	C3	C4	C6	17.3(4)	N5[1]	S3	C30	F8	171.2(4)
C2	C3	C4	C7	-102.2(3)	N5	S3	C30	F8	-135.4(4)
C2	C3	C8	C9	-1.1(4)	N5	S3	C30	F9	96.4(4)
C3	C8	C9	N1	2.1(4)	N5[1]	S3	C30	F9	42.9(4)
C3	C8	C9	C10	-173.7(2)	N5[1]	S3	N5	S3[1]	-0.001(1)
C4	C3	C8	C9	-178.8(2)	N5[1]	S3	N5	O5[1]	73.9(17)
C8	C3	C4	C5	-44.4(3)	O5A	S3	C30	F7A	141.7(4)
C8	C3	C4	C6	-165.1(2)	O5A	S3	C30	F8A	17.9(4)
C8	C3	C4	C7	75.4(3)	O5A	S3	C30	F9A	-94.0(4)
C8	C9	C10	N2	-141.6(2)	O6A	S3	C30	F7A	12.2(4)
C8	C9	C10	C11	41.5(3)	O6A	S3	C30	F8A	-111.6(3)
C9	N1	C1	C2	-1.3(4)	O6A	S3	C30	F9A	136.5(3)

[1] -X,2-Y,1-Z

Table S40. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Schomaker124 (ML$_1$).

Atom	*x*	*y*	*z*	U(eq)
H1	6693.34	3975.78	4206.5	20
H2	7024.43	2641.99	3819.42	21
H5A	5849.96	588.34	4672.46	56
H5B	5395.33	-25.33	4139.44	56
H5C	4439.14	601.75	4444.38	56
H6A	7087.88	1480.18	3331.57	48
H6B	6954.62	492.47	3478.05	48
H6C	7493.84	1126.69	3980.18	48
H7A	4860.99	1632.05	3041.43	55
H7B	3836.97	1249.07	3466.43	55
H7C	4749.69	628.47	3126.18	55
H8	3854.51	1887.57	4564.32	20
H11	3512.35	2167.67	5599.08	19
H14A	2627.4	1161.46	6118.11	45
H14B	2404.95	1052.81	6820.2	45
H14C	3523.88	1621.31	6598.32	45
H15A	-44.05	2436.2	6357.99	37

Table S40. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Schomaker124 (ML_1).

Atom	***x***	***y***	***z***	**U(eq)**
H15B	245.58	1527.78	6647.84	37
H15C	457.24	1685.02	5949.41	37
H16A	2723.66	2878.58	7188.62	39
H16B	1686.65	2247.81	7420.79	39
H16C	1298.94	3126.74	7111.48	39
H17	975.95	3773.07	6244.18	19
H20	684.24	5065.95	6369.3	19
H23A	260.03	5786.42	7186.33	46
H23B	-1057.38	5500.8	6916.89	46
H23C	-958.67	6270.97	7382.49	46
H24A	-1626.12	7342.23	6010.06	37
H24B	-2101.34	7190.66	6674.17	37
H24C	-2206.15	6447.61	6187.14	37
H25A	1184.18	7164.83	6875.7	41
H25B	-33.51	7644.55	7078.62	41
H25C	448.18	7767.22	6412.74	41
H26	-34.06	7204.73	5420.72	22
H27	951.08	6604.76	4622.18	21

Table S41. Atomic Occupancy for Schomaker124 (ML_1).

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
F7	0.5	F8	0.5	F9	0.5
O5	0.5	O6	0.5	N5	0.5
F7A	0.5	F8A	0.5	F9A	0.5
O5A	0.5	O6A	0.5		

Data Collection

A colorless crystal with approximate dimensions 0.105 × 0.066 × 0.059 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker D8 VENTURE Photon III four-circle diffractometer with Diamond II IμS Mo Kα (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.0 cm.[9]

The initial cell constants were obtained from a 180° ϕ scan conducted at a 2θ = 30° angle with the exposure time of 1 second per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX6 program. The final cell constants were calculated from a set of 9638 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.78 Å. A total of 135287 data were harvested by collecting 17 sets of frames with 0.5º scans in ω and ϕ with an exposure time 1–30 secs per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[10]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.[11-16]

A successful solution by intrinsic phasing provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic atomic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic atomic displacement coefficients.

The overall molecular formula is $[Ag_2(C_{27}H_{35}N_3)_2(H_2O)_{0.669}][C_2F_6NO_4S_2]_2{\cdot}0.5CH_2Cl_2$. The asymmetric unit contains the full $[Ag_2(C_{27}H_{35}N_3)_2(H_2O)_{0.669}]^{2+}$ dication and two $[C_2F_6NO_4S_2]^-$ anions that share three crystallographic sites. The crystallographic site for the S1 $[C_2F_6NO_4S_2]^-$ anion is fully occupied. The S3 and S5 $[C_2F_6NO_4S_2]^-$ anions reside on crystallographic inversion centers, therefore, only half of the S3 and S5 $[C_2F_6NO_4S_2]^-$ anions are present in the asymmetric unit. In addition, the CH_2Cl_2 solvent molecule is disordered over an inversion center, therefore it is only half occupied in the asymmetric unit as well. The diffraction data is corrected for the disordered CH_2Cl_2 solvent molecule, as described below.

The C28 $C_{27}H_{35}N_3$ ligand of the $[Ag_2(C_{27}H_{35}N_3)_2(H_2O)_{0.669}]^{2+}$ dication contains one positionally disordered tertbutyl group. The C51 tertbutyl group is disordered over two positions with a dominant component occupation of 72.5(4) %. The major and minor components of this disorder are refined with restrained geometries and restrained anisotropic atomic displacement parameters. In addition, the aqua ligand of this cation is occupationally and positionally disordered. The major and minor components of the aqua ligand disorder are 35.1(7) % and 31.8(7) %, respectively. The O atoms of the disordered aqua ligand are refined with constrained anisotropic atomic displacement parameters.

There is positional disorder at all three crystallographic sites of the $[C_2F_6NO_4S_2]^-$ anion. The S1 bistriflimide is disordered over two positions with a dominant component occupation of 69.94(17) %. The S3 and S5 bistriflimides are equally disordered over crystallographic inversion centers. Atomic distance restraints and anisotropic atomic displacement parameter restraints are applied to the S1 and S5 bistriflimides.

There is a CH_2Cl_2 solvent molecule disordered over an inversion center in the asymmetric unit. This solvent molecule is likely disordered over multiple positions. A significant amount of time was invested in identifying and refining the disordered molecule. Bond length restraints and constraints were applied to model the molecule, but the resulting isotropic atomic displacement coefficients suggested the molecule was mobile. In addition, the refinement was computationally unstable. The OLEX2.Mask was used to correct the diffraction data for diffuse scattering effects and to identify the solvent molecules. OLEX2 calculated the upper limit of volume that can be occupied by the solvent to be 246 Å^3, or 7.0 % of the unit cell volume. The program calculated 44 electrons in the unit cell for the diffuse species. This approximately corresponds to 0.5 of a CH_2Cl_2 molecule (21 electrons) in the asymmetric unit. Please note that all derived results in the following tables are based on the known contents. No data are given for the diffusely scattering species.

The final least-squares refinement of 1167 parameters against 15442 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0316 and 0.0809, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{58.5}H_{72.338}Ag_2ClF_{12}N_8O_{8.669}S_4$ (M =1633.71 g/mol): triclinic, space group P 1 (no. 2), a = 10.7205(19) Å, b = 15.731(3) Å, c = 21.503(4) Å, α = 84.243(6)°, β = 83.807(7)°, γ = 77.184(7)°, V = 3504.5(11) Å^3, Z = 2, T = 100.00 K, μ(Mo Kα) = 0.805 mm^{-1}, *Dcalc* = 1.548 g/cm^3, 135287 reflections measured (3.822° ≤ 2Θ ≤ 54.214°), 15442 unique (R_{int} = 0.0367, R_{sigma} = 0.0197) which were used in all calculations. The final R_1 was 0.0316 (I > 2σ(I)) and wR_2 was 0.0809 (all data).

Acknowledgement

The purchase of the Bruker D8 VENTURE Photon III Diamond II IµS X-ray diffractometer was partially funded by a 2024 University of Wisconsin Research Core Revitalization Program Round 3 Award to the Department of Chemistry.

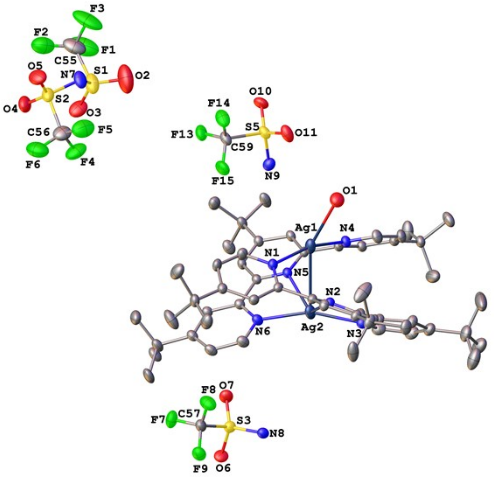


Figure S4. A molecular drawing of the asymmetric unit of Schomaker125a (ML_2) shown with 50% probability ellipsoids. All H atoms, the minor components of disorder, and C atom labels on the cation are omitted. The S3 and S5 bistriflimides reside around an inversion center, therefore only half of the molecules are present in the asymmetric unit and the N7 and N8 atoms are half occupied.

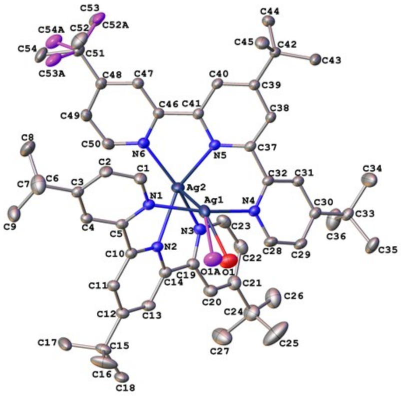


Figure S5. A molecular drawing of the $[Ag_2(C_{27}H_{35}N_3)_2(H_2O)_{0.669}]^{2+}$ dication in Schomaker125a (ML_2), highlighting the disordered C51 tertbutyl group and the occupationally and positionally disordered aqua ligand. The minor components of the disorder are highlighted in purple. All H atoms are omitted.

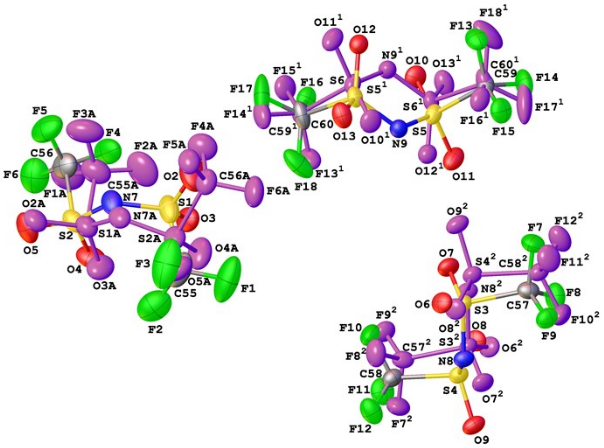


Figure S6. A molecular drawing of the three $[C_2F_6NO_4S_2]^-$ anions in Schomaker125a (ML_2). The S3 and S4 bistriflimide anions are disordered about an inversion center, so that each of the S3 and S4 disordered bistriflimide components are only half occupied. The minor component of the S1 bistriflimide and the symmetry-related disordered components of the S3 and S4 bistriflimides are drawn in purple. Symmetry code (1) 1-X, 1-Y, 1-Z; (2) -X, 1-Y, 2-Z.

Table S42. Crystal data and structure refinement for Schomaker125a (ML_2).

Identification code	Schomaker125a
Empirical formula	$[Ag_2(C_{27}H_{35}N_3)_2(H_2O)_{0.669}][C_2F_6NO_4S_2]_2\cdot 0.5CH_2Cl_2$
Formula weight	1633.71
Temperature/K	100.00
Crystal system	triclinic
Space group	1 *P*
a/Å	10.7205(19)
b/Å	15.731(3)
c/Å	21.503(4)
α/°	84.243(6)
β/°	83.807(7)
γ/°	77.184(7)
Volume/Å^3	3504.5(11)
Z	2
ρ_{calc}g/cm^3	1.548
μ/mm^{-1}	0.805
F(000)	1663.0
Crystal size/mm^3	0.105 × 0.066 × 0.059
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	3.822 to 54.214
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -27 ≤ l ≤ 27
Reflections collected	135287
Independent reflections	15442 [R_{int} = 0.0367, R_{sigma} = 0.0197]
Data/restraints/parameters	15442/1094/1167
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0316, wR_2 = 0.0772
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0809
Largest diff. peak/hole / e Å^{-3}	0.98/-1.53

Table S43. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML_2). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ag1	3854.5(2)	3320.2(2)	6783.2(2)	30.41(5)
Ag2	1857.6(2)	2698.6(2)	7610.0(2)	29.87(5)
O1	6249(7)	3338(6)	6461(4)	41.6(16)
O1A	6085(8)	3729(6)	6560(5)	41.6(16)
N1	3101.9(15)	4538.2(11)	7236.2(8)	21.6(3)
N2	3687.0(15)	3034.8(10)	8096.2(7)	19.7(3)
N3	2977.5(16)	1464.3(11)	8022.4(8)	23.8(3)
N4	4120.3(15)	2002.2(11)	6478.4(8)	21.7(3)
N5	1457.1(15)	2927.4(10)	6519.0(7)	19.3(3)
N6	270.5(15)	3856.9(11)	7487.9(8)	23.0(3)
C1	2492(2)	5246.6(14)	6901.2(10)	26.6(4)
C2	1953(2)	6028.3(13)	7155.1(10)	26.3(4)
C3	2016.4(18)	6114.5(13)	7790.2(9)	21.9(4)
C4	2625.8(18)	5372.3(12)	8138.3(9)	20.6(4)
C5	3158.0(17)	4602.7(12)	7850.2(9)	19.3(4)
C6	1438(2)	6980.8(13)	8075.8(10)	27.3(4)
C7	1953(3)	7717.2(15)	7675.2(13)	45.3(6)
C8	-17(2)	7159(2)	8075.8(16)	53.6(8)
C9	1813(3)	6975.8(15)	8740.5(11)	37.3(5)
C10	3848.3(17)	3820.9(12)	8224.4(9)	19.4(4)
C11	4617.6(18)	3922.1(13)	8678.6(9)	21.9(4)
C13	5068.8(19)	2385.3(13)	8898.1(9)	23.3(4)
C14	4277.3(18)	2327.5(12)	8436.8(9)	21.1(4)
C19	4037.7(18)	1464.4(13)	8311.3(9)	21.9(4)
C20	4853(2)	688.9(13)	8497.2(10)	26.4(4)
C21	4571(2)	-117.3(14)	8422.9(10)	29.1(4)

C22	3483(2)	-95.9(14)	8124.7(11)	31.4(5)
C23	2731(2)	693.2(15)	7926.1(10)	29.7(4)
C24	5448(3)	-958.8(15)	8660.5(13)	38.8(5)
C25	6734(3)	-1054(2)	8290(2)	77.1(12)
C26	4880(3)	-1756.4(16)	8602.6(13)	45.9(6)
C27	5572(3)	-916.8(17)	9365.0(15)	54.9(8)
C28	5186.0(19)	1394.6(14)	6602.8(10)	27.3(4)
C29	5370.2(19)	531.9(14)	6476.7(10)	26.9(4)
C30	4435.7(18)	245.5(13)	6201.6(9)	22.3(4)
C31	3331.5(18)	873.5(12)	6077.3(9)	21.3(4)
C32	3202.3(17)	1733.8(12)	6217.1(9)	20.0(4)
C33	4584.5(19)	-711.8(13)	6072.3(10)	24.8(4)
C34	3844(3)	-804.1(16)	5521.8(14)	45.7(7)
C35	5997(2)	-1144.4(15)	5922.5(13)	38.0(5)
C36	4058(3)	-1187.9(16)	6663.7(13)	46.0(7)
C37	2012.0(17)	2394.0(12)	6074.7(9)	18.9(4)
C38	1524.9(18)	2425.3(12)	5500.9(9)	20.6(4)
C39	413.2(18)	3035.0(12)	5366.2(9)	20.5(4)
C40	-176.5(18)	3571.4(12)	5841.5(9)	21.1(4)
C41	354.1(17)	3501.9(12)	6410.2(9)	19.0(4)
C42	-137.0(19)	3137.9(14)	4729.1(9)	24.6(4)
C43	649(2)	2471.9(16)	4287.0(10)	34.0(5)
C44	-1519(2)	3007.4(16)	4822.5(11)	31.6(5)
C45	-108(2)	4064.4(15)	4435.5(10)	32.1(5)
C46	-269.1(17)	4045.0(12)	6938.2(9)	19.9(4)
C47	-1368.0(18)	4701.8(13)	6877.0(9)	21.2(4)
C48	-1937.1(17)	5186.0(13)	7382.7(9)	23.2(4)
C49	-1319.4(19)	5008.9(14)	7932.1(10)	26.3(4)
C50	-238.6(19)	4347.0(14)	7963.0(10)	26.6(4)
C51	-3176.1(18)	5874.3(13)	7331.9(9)	30.3(5)
C52	-2959(3)	6599.9(19)	6857.2(16)	40.5(9)
C52A	-3724(7)	5998(5)	6696(2)	42(3)
C53	-4171(2)	5399(2)	7108.9(16)	34.9(8)
C53A	-2798(6)	6780(3)	7380(4)	39(2)
C54	-3743(3)	6183(2)	7969.6(13)	40.9(9)
C54A	-4185(6)	5798(5)	7867(3)	37(2)
C12	5274.8(18)	3186.9(12)	9020.9(9)	22.3(4)
C15	6146.6(18)	3294.0(12)	9512.3(9)	28.7(4)
C16	7070(3)	3869.2(19)	9220.8(14)	57.5(9)
C17	5304(2)	3723.5(16)	10063.9(11)	44.6(7)

C18	6948(2)	2415.1(13)	9749.5(10)	30.9(5)
S1	1104.0(9)	8539.0(6)	2775.9(7)	51.1(3)
S2	674.7(17)	10161.4(10)	3252.0(8)	37.6(3)
F1	732(3)	8231(3)	1638.9(17)	96.7(11)
F2	374(3)	9617(2)	1775.8(13)	76.2(8)
F3	2327(4)	8844(5)	1668(3)	99.4(17)
F4	-23(3)	9175.4(19)	4232.2(13)	60.9(7)
F5	1598(3)	9729(2)	4347.9(14)	68.2(8)
F6	-297(3)	10533(2)	4377.2(15)	70.7(8)
O2	2054(5)	7762(3)	2832(3)	93.3(15)
O3	-196(3)	8498.2(19)	2946.4(14)	50.4(7)
O4	-603(4)	10343(3)	3073.4(18)	50.7(10)
O5	1355(7)	10843(3)	3192(4)	53.1(15)
N7	1597(3)	9305(2)	3014(2)	41.0(7)
C55	1114(4)	8849(3)	1900(2)	62.9(9)
C56	487(5)	9883(3)	4102(2)	48.8(7)
S1A	866(4)	9980(3)	3050.6(18)	38.9(7)
S2A	1471.4(19)	8626.1(14)	2243.8(13)	39.9(6)
F1A	-218(8)	9998(6)	4198(4)	71.7(17)
F2A	42(6)	8770(5)	3792(4)	72.3(16)
F3A	1673(6)	9149(5)	4097(3)	68.8(16)
F4A	1955(6)	7421(5)	3174(3)	54.4(14)
F5A	3607(4)	7527(3)	2528(2)	39.5(11)
F6A	2162(5)	6946(4)	2233(3)	53.3(13)
O2A	1557(15)	10637(7)	3185(10)	41.4(19)
O3A	-376(9)	10247(8)	2816(5)	53(2)
O4A	159(6)	8533(5)	2314(4)	59.7(17)
O5A	2053(10)	8731(9)	1625(6)	53.4(19)
N7A	1835(7)	9271(6)	2694(4)	37.0(13)
C55A	576(9)	9440(8)	3839(4)	53.0(13)
C56A	2363(9)	7582(7)	2553(5)	39.9(12)
S3	-1059.4(11)	5264.7(8)	10029.6(5)	25.0(2)
S4	1434.4(11)	4315.9(8)	10189.0(5)	25.2(2)
F7	-1961(4)	6936(2)	9869.0(16)	43.5(8)
F8	5(3)	6606.3(19)	10090.0(17)	42.2(7)
F9	-1513(3)	6504.2(18)	10811.9(12)	35.2(6)
F10	543(4)	3371(2)	9464.6(17)	48.9(8)
F11	2498(3)	2867.8(19)	9677.4(15)	43.0(7)
F12	951(3)	2741.6(18)	10370.8(14)	43.3(7)
O6	-2295(6)	5105(5)	10296(4)	31.4(12)

O7	-755(3)	5283(2)	9366.9(14)	33.2(7)
O8	1939(6)	4782(5)	9659(4)	28.9(12)
O9	2186(3)	4056(2)	10712.8(14)	32.2(7)
N8	6(4)	4704(2)	10446.9(17)	25.8(7)
C57	-1117(7)	6386(4)	10212(4)	29.6(15)
C58	1344(7)	3275(5)	9909(3)	28.5(13)
S5	6012(4)	5376(2)	5099.2(13)	25.8(5)
S6	3926(4)	4569(2)	5107.2(11)	25.3(6)
F13	4363(4)	6841(4)	4830(3)	37.6(10)
F14	6123(7)	7003(5)	5124(3)	43.1(12)
F15	4730(4)	6615(2)	5806.3(18)	40.1(8)
F16	5607(3)	3578(2)	4350.2(17)	34.0(7)
F17	3836(8)	3146(6)	4629(4)	73(2)
F18	5313(6)	2987(4)	5274(3)	60.5(16)
O10	6246(3)	5356(2)	4429.5(19)	33.9(7)
O11	7084(4)	5197(3)	5470.7(18)	38.9(8)
O12	3485(3)	5095(2)	4553.1(16)	29.1(6)
O13	2991(3)	4344(2)	5580.3(16)	36.1(7)
N9	4991(4)	4856(2)	5431.3(17)	28.9(7)
C59	5253(6)	6509(5)	5222(3)	28.2(14)
C60	4734(7)	3492(5)	4821(3)	38.5(16)

Table S44. Anisotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ag1	37.99(9)	23.47(8)	28.26(9)	-7.41(6)	-11.31(7)	3.01(6)
Ag2	26.15(8)	33.65(9)	27.45(9)	-4.80(6)	-11.79(6)	4.20(6)
O1	29(2)	45(4)	50(3)	3(3)	-5(2)	-9(3)
O1A	29(2)	45(4)	50(3)	3(3)	-5(2)	-9(3)
N1	19.8(8)	21.6(8)	22.3(8)	-0.8(6)	-4.4(6)	-1.2(6)
N2	17.7(7)	20.5(8)	20.3(8)	0.5(6)	-3.5(6)	-2.9(6)
N3	21.6(8)	26.4(9)	24.5(8)	-1.3(7)	-4.1(7)	-6.7(7)
N4	17.8(7)	21.9(8)	24.5(8)	-3.2(6)	-3.2(6)	-1.1(6)
N5	16.5(7)	19.2(7)	21.5(8)	-1.4(6)	-2.2(6)	-2.3(6)
N6	19.0(8)	28.1(9)	21.3(8)	-4.3(7)	-2.7(6)	-2.2(6)
C1	27.9(10)	28.8(10)	21.0(10)	0.1(8)	-6.8(8)	-0.6(8)
C2	26.7(10)	24.0(10)	24.6(10)	2.9(8)	-7.6(8)	2.5(8)
C3	18.1(9)	22.3(9)	23.9(10)	-0.1(7)	-2.0(7)	-2.3(7)
C4	19.8(9)	23.4(9)	18.2(9)	-0.2(7)	-3.5(7)	-3.4(7)
C5	15.6(8)	21.9(9)	20.2(9)	1.6(7)	-3.2(7)	-4.3(7)

Table S44. Anisotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U$_{11}$**	**U$_{22}$**	**U$_{33}$**	**U$_{23}$**	**U$_{13}$**	**U$_{12}$**
C6	28.3(10)	22.1(10)	28.2(11)	-2.7(8)	-4.8(8)	3.3(8)
C7	68.8(18)	24.2(11)	40.1(14)	0.9(10)	-3.5(13)	-5.9(11)
C8	29.4(13)	56.8(17)	70(2)	-28.0(15)	-5.6(12)	10.5(12)
C9	50.4(14)	26.2(11)	32.0(12)	-5.9(9)	-6.9(10)	2.2(10)
C10	17.9(8)	19.7(9)	19.6(9)	0.6(7)	-1.2(7)	-3.0(7)
C11	20.9(9)	20.2(9)	25.2(10)	0.3(7)	-5.6(7)	-5.0(7)
C13	22.6(9)	21.0(9)	25.7(10)	4.6(7)	-7.3(8)	-4.0(7)
C14	19.4(9)	20.0(9)	23.7(9)	0.9(7)	-3.0(7)	-4.2(7)
C19	21.6(9)	22.5(9)	22.1(9)	0.9(7)	-3.7(7)	-6.1(7)
C20	27.4(10)	23.3(10)	29.0(11)	1.6(8)	-8.2(8)	-5.6(8)
C21	36.4(11)	22.1(10)	28.3(11)	0.4(8)	-3.4(9)	-5.7(8)
C22	39.0(12)	26.4(10)	32.5(11)	-2.6(9)	-4.0(9)	-14.4(9)
C23	29.8(11)	34.1(11)	29.4(11)	-3.0(9)	-4.6(9)	-14.3(9)
C24	46.8(14)	21.4(10)	46.7(14)	2.0(10)	-10.6(11)	-3.3(10)
C25	47.5(18)	37.4(16)	126(3)	19.7(18)	19.5(19)	10.4(13)
C26	68.1(18)	26.1(12)	42.5(14)	0.3(10)	-2.7(13)	-10.1(12)
C27	75(2)	29.2(13)	62.6(19)	4.3(12)	-33.7(16)	-6.6(13)
C28	17.9(9)	30.1(11)	33.4(11)	-5.0(9)	-7.9(8)	-0.4(8)
C29	18.9(9)	25.8(10)	32.6(11)	-2.3(8)	-5.9(8)	3.9(7)
C30	19.7(9)	21.8(9)	22.8(9)	-0.1(7)	0.3(7)	-0.7(7)
C31	17.9(9)	22.8(9)	22.3(9)	-2.0(7)	-3.5(7)	-1.7(7)
C32	15.6(8)	22.6(9)	19.7(9)	-0.2(7)	-2.1(7)	-0.5(7)
C33	22.2(9)	20.0(9)	29.5(10)	-1.8(8)	-1.0(8)	0.7(7)
C34	50.1(15)	25.6(11)	62.9(17)	-12.4(11)	-26.3(13)	2.9(10)
C35	27.5(11)	27.6(11)	55.4(15)	-11.6(10)	4.2(10)	1.8(9)
C36	56.8(16)	25.0(11)	49.9(16)	-0.7(10)	17.3(13)	-6.7(11)
C37	15.8(8)	17.4(8)	22.9(9)	-0.1(7)	-1.9(7)	-2.5(7)
C38	18.0(8)	19.6(9)	23.1(9)	-5.0(7)	-1.5(7)	-0.5(7)
C39	18.3(9)	21.5(9)	21.4(9)	-3.2(7)	-3.5(7)	-1.7(7)
C40	17.6(8)	19.7(9)	23.9(9)	-2.3(7)	-3.3(7)	1.2(7)
C41	16.6(8)	18.9(9)	21.0(9)	-1.7(7)	-0.6(7)	-3.0(7)
C42	20.2(9)	29.2(10)	22.2(10)	-6.5(8)	-5.3(7)	3.1(8)
C43	28.5(11)	42.6(13)	26.4(11)	-12.7(9)	-8.4(9)	9.6(9)
C44	23.3(10)	39.9(12)	32.2(11)	-12.4(9)	-8.1(8)	-1.2(9)
C45	32.7(11)	35.6(12)	25.0(11)	0.8(9)	-8.2(9)	0.4(9)
C46	17.6(8)	22.0(9)	20.6(9)	-3.1(7)	-2.5(7)	-4.4(7)
C47	19.2(9)	23.8(9)	20.6(9)	-2.9(7)	-2.6(7)	-3.7(7)

Table S44. Anisotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C48	17.9(9)	26.3(10)	24.9(10)	-5.7(8)	-0.4(7)	-3.1(7)
C49	21.5(9)	34.8(11)	22.5(10)	-9.2(8)	0.1(8)	-3.7(8)
C50	22.4(9)	36.4(11)	21.4(10)	-5.5(8)	-4.0(8)	-4.5(8)
C51	22.4(10)	38.3(12)	25.7(10)	-7.9(9)	-2.2(8)	5.7(9)
C52	36.5(18)	26.5(16)	51(2)	5.4(14)	2.2(15)	3.2(13)
C52A	29(4)	51(5)	38(4)	-18(4)	-15(3)	22(4)
C53	19.1(14)	40.9(18)	42.5(19)	-10.8(14)	-0.5(12)	0.7(12)
C53A	26(4)	43(4)	40(5)	0(4)	-3(3)	10(3)
C54	32.8(18)	42(2)	36.8(18)	-10.2(15)	1.1(14)	15.9(16)
C54A	24(4)	34(5)	47(5)	1(4)	-1(3)	0(3)
C12	22.5(9)	22.6(9)	22.4(9)	2.3(7)	-6.5(7)	-5.8(7)
C15	31.8(11)	26.0(10)	31.2(11)	3.5(8)	-17.4(9)	-8.2(8)
C16	57.1(17)	58.6(18)	71(2)	28.8(15)	-43.6(16)	-38.9(15)
C17	55.2(16)	36.0(13)	40.2(14)	-14.7(11)	-29.3(12)	12.6(11)
C18	31.0(11)	31.5(11)	30.0(11)	-1.8(9)	-16.1(9)	-0.2(9)
S1	34.1(5)	34.6(5)	88.5(9)	-8.7(5)	-15.2(5)	-9.5(4)
S2	27.0(6)	29.6(6)	54.0(9)	5.4(5)	-0.5(6)	-6.9(5)
F1	84(2)	137(2)	95(2)	-61(2)	24.0(17)	-72(2)
F2	65.8(16)	108.7(19)	57.0(16)	-6.7(14)	1.6(13)	-27.8(14)
F3	53.9(19)	135(3)	127(3)	-74(2)	45(2)	-54.2(18)
F4	65.8(16)	69.6(15)	58.0(15)	19.8(13)	-12.7(13)	-44.8(13)
F5	53.0(13)	101(2)	62.1(16)	5.6(16)	-16.9(12)	-40.3(14)
F6	65.4(16)	79.0(17)	71.4(18)	-13.8(15)	20.3(14)	-32.2(14)
O2	78(2)	50(2)	150(5)	-25(2)	-34(3)	8.3(19)
O3	48.0(14)	55.6(16)	57.6(17)	7.5(13)	-14.1(12)	-33.2(12)
O4	30.3(15)	50(2)	63(2)	10(2)	-6.0(15)	3.9(12)
O5	59(3)	37(2)	65(2)	-2(2)	13(2)	-24(3)
N7	21.1(13)	35.8(13)	67.2(19)	-5.2(16)	-9.6(14)	-5.4(11)
C55	40.7(19)	90(2)	69(2)	-29.0(17)	11.0(16)	-34.9(14)
C56	39.9(16)	58.8(18)	54.2(19)	4.4(14)	-3.2(13)	-28.5(14)
S1A	30.2(15)	33.8(16)	51.5(18)	2.6(11)	-5.7(13)	-5.3(12)
S2A	22.8(9)	40.0(10)	58.3(15)	-5.8(9)	-10.2(9)	-6.0(7)
F1A	58(3)	77(4)	69(3)	-2(3)	18(3)	-5(3)
F2A	59(3)	68(3)	87(4)	5(3)	25(3)	-26(3)
F3A	49(2)	89(4)	57(3)	23(3)	1(2)	-6(2)
F4A	39(3)	62(4)	57(3)	4(2)	7(2)	-12(3)
F5A	23.6(16)	39(2)	56(3)	-7(2)	-1.7(16)	-6.6(14)

Table S44. Anisotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
F6A	43(3)	46(2)	77(3)	-19(2)	-3(2)	-20(2)
O2A	34(4)	34(4)	52(5)	1(3)	-3(3)	-2(3)
O3A	33(3)	55(4)	65(5)	-13(4)	-12(3)	8(3)
O4A	27(2)	62(4)	95(5)	-24(3)	-10(2)	-10(2)
O5A	40(4)	70(5)	53(3)	-9(2)	-15(3)	-12(4)
N7A	23(3)	38(2)	51(3)	1(3)	-7(2)	-8(2)
C55A	41(2)	55(3)	57(3)	10(2)	6(2)	-7(2)
C56A	24.9(19)	45(3)	52(3)	-12(2)	0.0(19)	-10.2(18)
S3	25.4(6)	28.3(6)	22.1(5)	-2.0(5)	-5.3(5)	-6.1(4)
S4	23.8(5)	31.2(6)	20.3(5)	-2.9(5)	-0.9(4)	-5.0(4)
F7	49.5(19)	32.1(16)	45(2)	3.0(14)	-16.9(18)	2.1(14)
F8	33.1(15)	40.5(16)	56(2)	-12.4(14)	6.1(14)	-15.8(12)
F9	36.4(15)	39.3(15)	28.8(14)	-9.6(11)	-3.1(11)	-2.7(12)
F10	61(2)	36.8(16)	53(2)	-10.7(15)	-31.1(19)	-5.6(15)
F11	35.7(15)	41.3(16)	47.6(18)	-15.3(14)	12.0(13)	-1.3(12)
F12	50.9(17)	33.5(15)	42.5(16)	-2.3(12)	12.0(13)	-10.8(13)
O6	20(3)	39(3)	38(2)	1.9(18)	-3(2)	-15(2)
O7	39.3(19)	37.5(18)	21.6(15)	-6.0(13)	-4.5(14)	-3.5(14)
O8	20(3)	37(3)	31(2)	1.3(18)	7(2)	-13(2)
O9	27.3(15)	44.5(18)	24.4(15)	-6.9(13)	-4.8(12)	-3.4(13)
N8	23.0(18)	31.7(19)	20.7(17)	-0.9(14)	-1.3(15)	-2.8(14)
C57	25(3)	32(4)	28(3)	0(3)	-2(2)	2(3)
C58	25(3)	34(4)	26(4)	-6(3)	-4(2)	-2(3)
S5	19.8(7)	27.2(9)	30.9(14)	-11.3(12)	-1.7(12)	-2.4(6)
S6	23.9(7)	19.4(7)	32.2(16)	-7.7(11)	3.6(12)	-3.7(5)
F13	22.9(18)	34(2)	54(3)	0.2(18)	-8.1(19)	-1.5(14)
F14	28.8(18)	30.7(19)	74(3)	-10(2)	-2(2)	-13.3(14)
F15	41(2)	35.0(19)	41.2(19)	-15.9(14)	6.0(15)	0.0(14)
F16	25.0(16)	38.1(19)	39.0(18)	-17.3(13)	3.3(13)	-3.4(12)
F17	43(3)	50(4)	138(7)	-56(4)	13(4)	-21(3)
F18	69(4)	29(3)	66(3)	4.6(18)	21(2)	9(2)
O10	32.2(18)	40.0(19)	28(2)	-12.1(14)	8.1(14)	-5.6(15)
O11	27.8(17)	40(2)	48(2)	-18.2(16)	-11.0(15)	4.0(15)
O12	27.4(17)	28.4(17)	30.7(17)	-6.2(14)	-3.4(14)	-2.3(14)
O13	32.7(17)	31.0(16)	43.2(19)	-8.1(14)	12.7(14)	-9.5(14)
N9	34.8(18)	26.2(17)	26.7(17)	-1.8(14)	-5.4(14)	-7.5(14)
C59	19(3)	26(3)	40(3)	-10(2)	-1(2)	-3(2)

Table S44. Anisotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C60	36(4)	25(3)	55(3)	-11(2)	15(2)	-12(3)

Table S45. Bond Lengths for Schomaker125a (ML$_2$).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ag1	Ag2	2.9084(5)	C51	C52	1.494(3)
Ag1	O1	2.592(8)	C51	C52A	1.524(3)
Ag1	O1A	2.595(9)	C51	C53	1.568(3)
Ag1	N1	2.1887(17)	C51	C53A	1.581(3)
Ag1	N4	2.1862(17)	C51	C54	1.519(3)
Ag2	N2	2.4965(16)	C51	C54A	1.507(3)
Ag2	N3	2.2017(17)	C12	C15	1.529(2)
Ag2	N5	2.4079(16)	C15	C16	1.530(3)
Ag2	N6	2.2157(17)	C15	C17	1.529(3)
N1	C1	1.344(2)	C15	C18	1.528(2)
N1	C5	1.343(2)	S1	O2	1.411(4)
N2	C10	1.345(2)	S1	O3	1.416(3)
N2	C14	1.341(2)	S1	N7	1.568(4)
N3	C19	1.353(2)	S1	C55	1.897(5)
N3	C23	1.337(3)	S2	O4	1.422(4)
N4	C28	1.349(2)	S2	O5	1.413(5)
N4	C32	1.347(2)	S2	N7	1.578(4)
N5	C37	1.337(2)	S2	C56	1.837(5)
N5	C41	1.346(2)	F1	C55	1.328(4)
N6	C46	1.349(2)	F2	C55	1.311(5)
N6	C50	1.337(3)	F3	C55	1.339(5)
C1	C2	1.377(3)	F4	C56	1.339(5)
C2	C3	1.396(3)	F5	C56	1.319(5)
C3	C4	1.394(3)	F6	C56	1.316(7)
C3	C6	1.526(3)	S1A	O2A	1.465(12)
C4	C5	1.394(3)	S1A	O3A	1.435(10)
C5	C10	1.495(2)	S1A	N7A	1.548(9)
C6	C7	1.539(3)	S1A	C55A	1.846(8)
C6	C8	1.522(3)	S2A	O4A	1.437(6)
C6	C9	1.525(3)	S2A	O5A	1.418(13)
C10	C11	1.387(3)	S2A	N7A	1.604(9)
C11	C12	1.398(3)	S2A	C56A	1.810(11)
C13	C14	1.395(3)	F1A	C55A	1.324(13)

Table S45. Bond Lengths for Schomaker125a (ML_2).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C13	C12	1.383(3)	F2A	C55A	1.323(14)
C14	C19	1.492(3)	F3A	C55A	1.323(12)
C19	C20	1.384(3)	F4A	C56A	1.377(13)
C20	C21	1.395(3)	F5A	C56A	1.313(10)
C21	C22	1.383(3)	F6A	C56A	1.337(11)
C21	C24	1.520(3)	S3	O6	1.449(6)
C22	C23	1.377(3)	S3	O7	1.426(3)
C24	C25	1.502(4)	S3	N8	1.582(4)
C24	C26	1.532(3)	S3	C57	1.832(7)
C24	C27	1.544(4)	S4	O8	1.416(7)
C28	C29	1.378(3)	S4	O9	1.429(3)
C29	C30	1.392(3)	S4	N8	1.580(4)
C30	C31	1.395(3)	S4	C58	1.825(8)
C30	C33	1.529(3)	F7	C57	1.334(6)
C31	C32	1.389(3)	F8	C57	1.316(8)
C32	C37	1.494(2)	F9	C57	1.332(8)
C33	C34	1.530(3)	F10	C58	1.328(8)
C33	C35	1.530(3)	F11	C58	1.330(8)
C33	C36	1.529(3)	F12	C58	1.329(8)
C37	C38	1.383(3)	S5	O10	1.437(3)
C38	C39	1.391(3)	S5	O11	1.431(5)
C39	C40	1.398(3)	S5	N9	1.577(5)
C39	C42	1.529(3)	S5	C59	1.819(8)
C40	C41	1.388(3)	S6	O12	1.441(4)
C41	C46	1.498(3)	S6	O13	1.425(4)
C42	C43	1.532(3)	S6	N9	1.567(5)
C42	C44	1.530(3)	S6	C60	1.855(8)
C42	C45	1.534(3)	F13	C59	1.326(5)
C46	C47	1.392(3)	F14	C59	1.329(6)
C47	C48	1.397(3)	F15	C59	1.330(5)
C48	C49	1.390(3)	F16	C60	1.321(6)
C48	C51	1.523(2)	F17	C60	1.325(6)
C49	C50	1.378(3)	F18	C60	1.312(6)

Table S46. Bond Angles for Schomaker125a (ML_2).

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
O1	Ag1	Ag2	151.13(18)	C52	C51	C48	110.02(18)
O1A	Ag1	Ag2	152.5(2)	C52	C51	C53	109.8(2)

Table S46. Bond Angles for Schomaker125a (ML_2).

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
N1	Ag1	Ag2	83.53(5)	C52	C51	C54	113.5(2)
N1	Ag1	O1	104.3(2)	C52A	C51	C53A	102.7(3)
N1	Ag1	O1A	90.0(2)	C54	C51	C48	111.52(18)
N4	Ag1	Ag2	80.27(4)	C54	C51	C53	105.6(2)
N4	Ag1	O1	91.1(2)	C54A	C51	C48	113.9(3)
N4	Ag1	O1A	105.6(2)	C54A	C51	C52A	112.2(4)
N4	Ag1	N1	163.61(6)	C54A	C51	C53A	105.6(4)
N2	Ag2	Ag1	62.02(4)	C11	C12	C15	120.11(17)
N3	Ag2	Ag1	100.42(5)	C13	C12	C11	116.67(17)
N3	Ag2	N2	71.79(6)	C13	C12	C15	123.20(16)
N3	Ag2	N5	122.78(6)	C12	C15	C16	109.33(17)
N3	Ag2	N6	159.83(6)	C12	C15	C17	108.38(16)
N5	Ag2	Ag1	65.28(4)	C17	C15	C16	110.2(2)
N5	Ag2	N2	127.14(5)	C18	C15	C12	111.76(16)
N6	Ag2	Ag1	98.77(5)	C18	C15	C16	107.99(18)
N6	Ag2	N2	112.59(6)	C18	C15	C17	109.22(17)
N6	Ag2	N5	71.44(6)	O2	S1	O3	118.6(3)
C1	N1	Ag1	119.49(13)	O2	S1	N7	109.3(2)
C5	N1	Ag1	122.85(13)	O2	S1	C55	104.6(3)
C5	N1	C1	117.56(17)	O3	S1	N7	117.37(19)
C10	N2	Ag2	127.89(12)	O3	S1	C55	102.35(18)
C14	N2	Ag2	110.21(12)	N7	S1	C55	102.0(2)
C14	N2	C10	117.79(16)	O4	S2	N7	116.4(2)
C19	N3	Ag2	120.10(13)	O4	S2	C56	103.8(2)
C23	N3	Ag2	121.20(14)	O5	S2	O4	119.2(4)
C23	N3	C19	118.15(18)	O5	S2	N7	109.2(3)
C28	N4	Ag1	120.13(13)	O5	S2	C56	103.8(4)
C32	N4	Ag1	122.60(12)	N7	S2	C56	101.9(3)
C32	N4	C28	116.98(17)	S1	N7	S2	123.4(2)
C37	N5	Ag2	125.47(12)	F1	C55	S1	107.8(3)
C37	N5	C41	118.50(16)	F1	C55	F3	107.4(4)
C41	N5	Ag2	113.45(12)	F2	C55	S1	111.7(3)
C46	N6	Ag2	120.06(13)	F2	C55	F1	110.8(4)
C50	N6	Ag2	121.51(13)	F2	C55	F3	110.4(5)
C50	N6	C46	118.25(17)	F3	C55	S1	108.4(4)
N1	C1	C2	123.17(19)	F4	C56	S2	111.0(3)
C1	C2	C3	120.26(18)	F5	C56	S2	111.4(3)
C2	C3	C6	120.80(17)	F5	C56	F4	108.5(4)

Table S46. Bond Angles for Schomaker125a (ML_2).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	C3	C2	116.31(18)	F6	C56	S2	109.9(3)
C4	C3	C6	122.89(18)	F6	C56	F4	107.4(4)
C3	C4	C5	120.42(18)	F6	C56	F5	108.6(4)
N1	C5	C4	122.26(17)	O2A	S1A	N7A	107.7(7)
N1	C5	C10	117.87(17)	O2A	S1A	C55A	101.8(9)
C4	C5	C10	119.85(17)	O3A	S1A	O2A	120.1(8)
C3	C6	C7	108.96(18)	O3A	S1A	N7A	115.7(5)
C8	C6	C3	108.90(19)	O3A	S1A	C55A	105.1(6)
C8	C6	C7	109.5(2)	N7A	S1A	C55A	104.3(5)
C8	C6	C9	110.2(2)	O4A	S2A	N7A	116.3(4)
C9	C6	C3	111.86(17)	O4A	S2A	C56A	104.3(4)
C9	C6	C7	107.4(2)	O5A	S2A	O4A	117.5(6)
N2	C10	C5	116.99(16)	O5A	S2A	N7A	111.5(6)
N2	C10	C11	122.77(17)	O5A	S2A	C56A	103.8(6)
C11	C10	C5	120.23(17)	N7A	S2A	C56A	100.7(4)
C10	C11	C12	119.92(18)	S1A	N7A	S2A	125.5(5)
C12	C13	C14	120.59(17)	F1A	C55A	S1A	109.8(7)
N2	C14	C13	122.17(18)	F2A	C55A	S1A	109.3(8)
N2	C14	C19	117.21(17)	F2A	C55A	F1A	108.6(8)
C13	C14	C19	120.60(17)	F3A	C55A	S1A	110.2(6)
N3	C19	C14	117.66(17)	F3A	C55A	F1A	110.0(10)
N3	C19	C20	121.04(18)	F3A	C55A	F2A	108.9(9)
C20	C19	C14	121.28(17)	F4A	C56A	S2A	110.2(7)
C19	C20	C21	121.04(19)	F5A	C56A	S2A	114.1(7)
C20	C21	C24	120.0(2)	F5A	C56A	F4A	106.5(8)
C22	C21	C20	116.47(19)	F5A	C56A	F6A	108.0(8)
C22	C21	C24	123.5(2)	F6A	C56A	S2A	109.5(7)
C23	C22	C21	120.2(2)	F6A	C56A	F4A	108.3(8)
N3	C23	C22	123.0(2)	O6	S3	N8	108.1(4)
C21	C24	C26	111.4(2)	O6	S3	C57	103.5(4)
C21	C24	C27	108.6(2)	O7	S3	O6	119.7(4)
C25	C24	C21	109.0(2)	O7	S3	N8	116.4(2)
C25	C24	C26	109.8(2)	O7	S3	C57	103.9(3)
C25	C24	C27	111.0(3)	N8	S3	C57	103.0(3)
C26	C24	C27	107.0(2)	O8	S4	O9	118.6(3)
N4	C28	C29	123.52(19)	O8	S4	N8	116.5(3)
C28	C29	C30	120.22(18)	O8	S4	C58	104.8(4)
C29	C30	C31	116.15(18)	O9	S4	N8	108.14(19)

Table S46. Bond Angles for Schomaker125a (ML_2).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C29	C30	C33	121.86(17)	O9	S4	C58	103.2(3)
C31	C30	C33	121.93(18)	N8	S4	C58	103.5(3)
C32	C31	C30	120.86(18)	S4	N8	S3	124.3(2)
N4	C32	C31	122.27(17)	F7	C57	S3	109.0(5)
N4	C32	C37	118.05(17)	F8	C57	S3	112.4(5)
C31	C32	C37	119.68(17)	F8	C57	F7	108.3(5)
C30	C33	C34	111.76(17)	F8	C57	F9	108.2(6)
C30	C33	C35	111.11(17)	F9	C57	S3	111.6(4)
C35	C33	C34	108.2(2)	F9	C57	F7	107.0(5)
C36	C33	C30	107.77(18)	F10	C58	S4	112.7(5)
C36	C33	C34	109.1(2)	F10	C58	F11	108.0(5)
C36	C33	C35	108.85(19)	F10	C58	F12	107.1(6)
N5	C37	C32	117.59(16)	F11	C58	S4	110.2(5)
N5	C37	C38	122.90(17)	F12	C58	S4	111.6(4)
C38	C37	C32	119.50(17)	F12	C58	F11	106.9(6)
C37	C38	C39	119.84(17)	O10	S5	N9	116.4(3)
C38	C39	C40	116.63(17)	O10	S5	C59	104.7(3)
C38	C39	C42	122.55(17)	O11	S5	O10	118.9(3)
C40	C39	C42	120.81(16)	O11	S5	N9	107.8(3)
C41	C40	C39	120.73(17)	O11	S5	C59	103.8(3)
N5	C41	C40	121.33(17)	N9	S5	C59	103.1(3)
N5	C41	C46	116.30(16)	O12	S6	N9	116.6(3)
C40	C41	C46	122.37(16)	O12	S6	C60	104.5(3)
C39	C42	C43	111.75(16)	O13	S6	O12	118.3(3)
C39	C42	C44	109.39(17)	O13	S6	N9	108.6(3)
C39	C42	C45	107.83(17)	O13	S6	C60	102.5(3)
C43	C42	C45	109.10(18)	N9	S6	C60	104.0(3)
C44	C42	C43	108.64(18)	S6	N9	S5	126.1(3)
C44	C42	C45	110.13(17)	F13	C59	S5	112.5(5)
N6	C46	C41	116.75(16)	F13	C59	F14	106.6(6)
N6	C46	C47	120.90(17)	F13	C59	F15	108.6(5)
C47	C46	C41	122.34(17)	F14	C59	S5	110.0(6)
C46	C47	C48	120.82(18)	F14	C59	F15	106.0(6)
C47	C48	C51	121.35(17)	F15	C59	S5	112.8(5)
C49	C48	C47	116.87(17)	F16	C60	S6	111.1(5)
C49	C48	C51	121.78(17)	F16	C60	F17	109.5(6)
C50	C49	C48	119.33(19)	F17	C60	S6	107.2(6)
N6	C50	C49	123.66(19)	F18	C60	S6	110.0(6)

Table S46. Bond Angles for Schomaker125a (ML_2).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C48	C51	C52A	115.3(3)	F18	C60	F16	108.0(6)
C48	C51	C53	106.07(17)	F18	C60	F17	110.9(7)
C48	C51	C53A	105.6(3)				

Table S47. Torsion Angles for Schomaker125a (ML_2).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Ag1	N1	C1	C2	177.71(16)	C42	C39	C40	C41	-177.27(18)
Ag1	N1	C5	C4	-177.18(14)	C46	N6	C50	C49	3.0(3)
Ag1	N1	C5	C10	4.4(2)	C46	C47	C48	C49	3.1(3)
Ag1	N4	C28	C29	173.97(17)	C46	C47	C48	C51	-176.88(18)
Ag1	N4	C32	C31	-173.96(14)	C47	C48	C49	C50	-3.4(3)
Ag1	N4	C32	C37	6.2(2)	C47	C48	C51	C52	-64.2(3)
Ag2	N2	C10	C5	-23.8(2)	C47	C48	C51	C52A	-0.7(4)
Ag2	N2	C10	C11	156.47(14)	C47	C48	C51	C53	54.4(2)
Ag2	N2	C14	C13	-160.98(16)	C47	C48	C51	C53A	-113.4(4)
Ag2	N2	C14	C19	18.0(2)	C47	C48	C51	C54	168.9(2)
Ag2	N3	C19	C14	10.5(2)	C47	C48	C51	C54A	131.2(4)
Ag2	N3	C19	C20	-171.06(15)	C48	C49	C50	N6	0.4(3)
Ag2	N3	C23	C22	173.66(17)	C49	C48	C51	C52	115.8(2)
Ag2	N5	C37	C32	-16.7(2)	C49	C48	C51	C52A	179.3(4)
Ag2	N5	C37	C38	162.67(14)	C49	C48	C51	C53	-125.6(2)
Ag2	N5	C41	C40	-165.53(14)	C49	C48	C51	C53A	66.6(4)
Ag2	N5	C41	C46	13.5(2)	C49	C48	C51	C54	-11.1(3)
Ag2	N6	C46	C41	-6.8(2)	C49	C48	C51	C54A	-48.8(4)
Ag2	N6	C46	C47	171.87(14)	C50	N6	C46	C41	177.98(17)
Ag2	N6	C50	C49	-172.11(17)	C50	N6	C46	C47	-3.4(3)
N1	C1	C2	C3	-0.3(3)	C51	C48	C49	C50	176.54(19)
N1	C5	C10	N2	-39.6(2)	C12	C13	C14	N2	-0.1(3)
N1	C5	C10	C11	140.17(19)	C12	C13	C14	C19	-179.00(18)
N2	C10	C11	C12	0.6(3)	O2	S1	N7	S2	-157.2(4)
N2	C14	C19	N3	-20.2(3)	O2	S1	C55	F1	65.0(4)
N2	C14	C19	C20	161.40(19)	O2	S1	C55	F2	-172.9(3)
N3	C19	C20	C21	-3.5(3)	O2	S1	C55	F3	-51.0(5)
N4	C28	C29	C30	0.6(3)	O3	S1	N7	S2	-18.4(4)
N4	C32	C37	N5	-46.0(2)	O3	S1	C55	F1	-59.3(3)
N4	C32	C37	C38	134.64(19)	O3	S1	C55	F2	62.8(3)
N5	C37	C38	C39	0.3(3)	O3	S1	C55	F3	-175.3(4)
N5	C41	C46	N6	-5.5(3)	O4	S2	N7	S1	-18.2(4)

Table S47. Torsion Angles for Schomaker125a (ML_2).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N5	C41	C46	C47	175.89(18)	O4	S2	C56	F4	61.5(4)
N6	C46	C47	C48	0.3(3)	O4	S2	C56	F5	-177.5(4)
C1	N1	C5	C4	-0.8(3)	O4	S2	C56	F6	-57.1(4)
C1	N1	C5	C10	-179.27(17)	O5	S2	N7	S1	-156.7(5)
C1	C2	C3	C4	-1.0(3)	O5	S2	C56	F4	-173.2(4)
C1	C2	C3	C6	179.2(2)	O5	S2	C56	F5	-52.3(5)
C2	C3	C4	C5	1.4(3)	O5	S2	C56	F6	68.2(4)
C2	C3	C6	C7	-51.7(3)	N7	S1	C55	F1	178.9(3)
C2	C3	C6	C8	67.7(3)	N7	S1	C55	F2	-59.1(3)
C2	C3	C6	C9	-170.2(2)	N7	S1	C55	F3	62.9(4)
C3	C4	C5	N1	-0.5(3)	N7	S2	C56	F4	-59.8(4)
C3	C4	C5	C10	177.90(17)	N7	S2	C56	F5	61.2(4)
C4	C3	C6	C7	128.6(2)	N7	S2	C56	F6	-178.4(3)
C4	C3	C6	C8	-112.1(2)	C55	S1	N7	S2	92.5(3)
C4	C3	C6	C9	10.0(3)	C56	S2	N7	S1	93.9(3)
C4	C5	C10	N2	141.94(18)	O2A	S1A	N7A	S2A	-157.0(10)
C4	C5	C10	C11	-38.3(3)	O2A	S1A	C55A	F1A	66.1(11)
C5	N1	C1	C2	1.2(3)	O2A	S1A	C55A	F2A	-174.9(9)
C5	C10	C11	C12	-179.11(18)	O2A	S1A	C55A	F3A	-55.3(11)
C6	C3	C4	C5	-178.80(18)	O3A	S1A	N7A	S2A	-19.4(10)
C10	N2	C14	C13	-1.9(3)	O3A	S1A	C55A	F1A	-59.8(11)
C10	N2	C14	C19	177.04(17)	O3A	S1A	C55A	F2A	59.2(9)
C10	C11	C12	C13	-2.6(3)	O3A	S1A	C55A	F3A	178.8(9)
C10	C11	C12	C15	178.70(18)	O4A	S2A	N7A	S1A	-18.1(9)
C11	C12	C15	C16	-50.6(3)	O4A	S2A	C56A	F4A	-60.6(8)
C11	C12	C15	C17	69.5(2)	O4A	S2A	C56A	F5A	179.6(7)
C11	C12	C15	C18	-170.11(19)	O4A	S2A	C56A	F6A	58.4(7)
C13	C14	C19	N3	158.84(19)	O5A	S2A	N7A	S1A	120.2(8)
C13	C14	C19	C20	-19.6(3)	O5A	S2A	C56A	F4A	175.8(7)
C13	C12	C15	C16	130.7(2)	O5A	S2A	C56A	F5A	56.0(9)
C13	C12	C15	C17	-109.2(2)	O5A	S2A	C56A	F6A	-65.2(8)
C13	C12	C15	C18	11.2(3)	N7A	S1A	C55A	F1A	178.0(8)
C14	N2	C10	C5	-178.60(16)	N7A	S1A	C55A	F2A	-62.9(8)
C14	N2	C10	C11	1.6(3)	N7A	S1A	C55A	F3A	56.7(10)
C14	C13	C12	C11	2.3(3)	N7A	S2A	C56A	F4A	60.3(7)
C14	C13	C12	C15	-179.01(18)	N7A	S2A	C56A	F5A	-59.5(8)
C14	C19	C20	C21	174.94(19)	N7A	S2A	C56A	F6A	179.3(6)
C19	N3	C23	C22	2.1(3)	C55A	S1A	N7A	S2A	95.4(7)

Table S47. Torsion Angles for Schomaker125a (ML_2).

A	**B**	**C**	**D**	**Angle/˚**	**A**	**B**	**C**	**D**	**Angle/˚**
C19	C20	C21	C22	3.5(3)	C56A	S2A	N7A	S1A	-130.1(7)
C19	C20	C21	C24	-176.9(2)	O6	S3	N8	S4	149.3(4)
C20	C21	C22	C23	-0.9(3)	O6	S3	C57	F7	-69.6(6)
C20	C21	C24	C25	-65.4(3)	O6	S3	C57	F8	170.2(5)
C20	C21	C24	C26	173.2(2)	O6	S3	C57	F9	48.4(6)
C20	C21	C24	C27	55.6(3)	O7	S3	N8	S4	11.3(4)
C21	C22	C23	N3	-2.0(4)	O7	S3	C57	F7	56.1(5)
C22	C21	C24	C25	114.1(3)	O7	S3	C57	F8	-64.1(5)
C22	C21	C24	C26	-7.2(3)	O7	S3	C57	F9	174.1(4)
C22	C21	C24	C27	-124.8(3)	O8	S4	N8	S3	28.4(5)
C23	N3	C19	C14	-177.85(18)	O8	S4	C58	F10	-63.0(6)
C23	N3	C19	C20	0.6(3)	O8	S4	C58	F11	57.7(6)
C24	C21	C22	C23	179.6(2)	O8	S4	C58	F12	176.3(5)
C28	N4	C32	C31	-0.2(3)	O9	S4	N8	S3	165.0(3)
C28	N4	C32	C37	179.99(18)	O9	S4	C58	F10	172.2(4)
C28	C29	C30	C31	-0.9(3)	O9	S4	C58	F11	-67.1(5)
C28	C29	C30	C33	-178.11(19)	O9	S4	C58	F12	51.5(5)
C29	C30	C31	C32	0.8(3)	N8	S3	C57	F7	177.9(4)
C29	C30	C33	C34	-153.0(2)	N8	S3	C57	F8	57.8(5)
C29	C30	C33	C35	-32.0(3)	N8	S3	C57	F9	-64.1(5)
C29	C30	C33	C36	87.2(2)	N8	S4	C58	F10	59.5(5)
C30	C31	C32	N4	-0.3(3)	N8	S4	C58	F11	-179.8(5)
C30	C31	C32	C37	179.59(18)	N8	S4	C58	F12	-61.1(5)
C31	C30	C33	C34	30.0(3)	C57	S3	N8	S4	-101.6(4)
C31	C30	C33	C35	151.0(2)	C58	S4	N8	S3	-86.0(4)
C31	C30	C33	C36	-89.8(2)	O10	S5	N9	S6	-19.9(6)
C31	C32	C37	N5	134.14(19)	O10	S5	C59	F13	43.8(5)
C31	C32	C37	C38	-45.2(3)	O10	S5	C59	F14	-74.9(5)
C32	N4	C28	C29	0.0(3)	O10	S5	C59	F15	167.0(4)
C32	C37	C38	C39	179.65(17)	O11	S5	N9	S6	-156.5(3)
C33	C30	C31	C32	177.97(18)	O11	S5	C59	F13	169.2(4)
C37	N5	C41	C40	-2.7(3)	O11	S5	C59	F14	50.5(5)
C37	N5	C41	C46	176.34(16)	O11	S5	C59	F15	-67.5(5)
C37	C38	C39	C40	-2.1(3)	O12	S6	N9	S5	-26.9(6)
C37	C38	C39	C42	176.65(18)	O12	S6	C60	F16	52.8(6)
C38	C39	C40	C41	1.5(3)	O12	S6	C60	F17	-66.8(6)
C38	C39	C42	C43	2.4(3)	O12	S6	C60	F18	172.5(5)
C38	C39	C42	C44	122.7(2)	O13	S6	N9	S5	-163.7(3)

Table S47. Torsion Angles for Schomaker125a (ML_2).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C38	C39	C42	C45	-117.5(2)	O13	S6	C60	F16	176.9(5)
C39	C40	C41	N5	0.9(3)	O13	S6	C60	F17	57.2(6)
C39	C40	C41	C46	-178.07(18)	O13	S6	C60	F18	-63.5(6)
C40	C39	C42	C43	-178.94(19)	N9	S5	C59	F13	-78.5(5)
C40	C39	C42	C44	-58.6(2)	N9	S5	C59	F14	162.9(4)
C40	C39	C42	C45	61.2(2)	N9	S5	C59	F15	44.8(5)
C40	C41	C46	N6	173.58(18)	N9	S6	C60	F16	-70.0(5)
C40	C41	C46	C47	-5.1(3)	N9	S6	C60	F17	170.3(5)
C41	N5	C37	C32	-177.23(16)	N9	S6	C60	F18	49.6(5)
C41	N5	C37	C38	2.1(3)	C59	S5	N9	S6	94.1(4)
C41	C46	C47	C48	178.89(18)	C60	S6	N9	S5	87.6(5)

Table S48. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML_2).

Atom	***x***	***y***	***z***	**U(eq)**
H1A	6475.21	2885.35	6240.84	62
H1B	6791.58	3239.65	6746.47	62
H1AA	6774.49	3240.41	6609.55	62
H1AB	6257.77	3925.02	6135.66	62
H1	2430.88	5206.21	6468.14	32
H2	1535.62	6510.88	6897.19	32
H4	2678.9	5390.94	8574.68	25
H7A	2892.06	7589.67	7660.45	68
H7B	1602.41	8273.91	7861.46	68
H7C	1690.78	7756.93	7248.59	68
H8A	-246.73	7170.43	7645.68	80
H8B	-394.81	7724.53	8244.21	80
H8C	-345.81	6695.86	8337.67	80
H9A	1496.77	6513.03	9008.75	56
H9B	1432.13	7543.11	8905.9	56
H9C	2749.96	6867.93	8733.97	56
H11	4698.07	4490.32	8757.16	26
H13	5469.79	1869.27	9129.86	28
H20	5616.31	706.04	8678.22	32
H22	3253.5	-626.69	8056.68	38
H23	2003.92	689.58	7710.76	36
H25A	7309.94	-1589.38	8446.35	116
H25B	7100.56	-547.99	8335.38	116

Table S48. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML_2).

Atom	***x***	***y***	***z***	**U(eq)**
H25C	6631.99	-1087.31	7846.14	116
H26A	5447.75	-2284.79	8774.34	69
H26B	4796.77	-1810.55	8159.63	69
H26C	4031.43	-1684.23	8836.82	69
H27A	4716.34	-815.17	9592.39	82
H27B	5989.91	-437.75	9418.98	82
H27C	6089.71	-1470.98	9530.74	82
H28	5844.61	1571.28	6787.18	33
H29	6137.51	131.05	6577.87	32
H31	2658.9	710.88	5894.74	26
H34A	4126	-458.64	5149.73	69
H34B	2922.47	-592.29	5629.01	69
H34C	4009.22	-1420.49	5434.16	69
H35A	6063.81	-1752.32	5832.89	57
H35B	6476.74	-1131.4	6283.06	57
H35C	6354.24	-826.44	5555.46	57
H36A	4108.18	-1798.86	6587.49	69
H36B	3161.02	-903.66	6771.3	69
H36C	4567.97	-1166.19	7011.41	69
H38	1948.49	2031.4	5199.46	25
H40	-949.07	3988.3	5774.58	25
H43A	659.66	1878.58	4478.83	51
H43B	1529.84	2561.82	4211.52	51
H43C	258.99	2549.17	3887.66	51
H44A	-2036.46	3437.25	5098.58	47
H44B	-1527.32	2415.98	5013.3	47
H44C	-1878.84	3085.46	4415.38	47
H45A	-695.03	4492.94	4689.68	48
H45B	-377.65	4128.75	4008.94	48
H45C	765.72	4163.2	4420.33	48
H47	-1735.33	4822.13	6486.46	25
H49	-1639.25	5340.91	8282.72	32
H50	167.3	4232.47	8343.14	32
H52A	-2605.43	6358.93	6456.78	61
H52B	-2353.76	6903.58	7003.32	61
H52C	-3777.16	7013.08	6800.22	61
H52D	-3058.87	6103.45	6365.44	63

Table S48. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Schomaker125a (ML_2).

Atom	***x***	***y***	***z***	**U(eq)**
H52E	-4453.32	6499.04	6691.02	63
H52F	-4011.34	5469.68	6622.21	63
H53A	-3870.61	5200.67	6690.42	52
H53B	-5005.77	5806.19	7092.87	52
H53C	-4256.6	4894.8	7404.1	52
H53D	-2561.03	6807.53	7803.87	59
H53E	-3531.18	7258.08	7291.59	59
H53F	-2068.37	6835.9	7074.1	59
H54A	-3829.7	5676.67	8262.58	61
H54B	-4589.5	6567.76	7928.89	61
H54C	-3174.47	6504.92	8128.64	61
H54D	-4425.47	5230.85	7876.86	55
H54E	-4943.36	6268.4	7809.8	55
H54F	-3841.92	5845.33	8264.04	55
H16A	7670.31	3903.98	9525.36	86
H16B	6579.78	4457.4	9104.82	86
H16C	7549.95	3614.84	8845.47	86
H17A	4757.9	4273.99	9910.65	67
H17B	5850.2	3841.78	10367.83	67
H17C	4762.62	3329.99	10266.77	67
H18A	7502.67	2509.76	10058.19	46
H18B	7479.41	2133.19	9396.23	46
H18C	6376.14	2038.68	9946.31	46

Table S49. Atomic Occupancy for Schomaker125a (ML_2).

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
O1	0.351(7)	H1A	0.351(7)	H1B	0.351(7)
O1A	0.318(7)	H1AA	0.318(7)	H1AB	0.318(7)
C52	0.725(4)	H52A	0.725(4)	H52B	0.725(4)
H52C	0.725(4)	C52A	0.275(4)	H52D	0.275(4)
H52E	0.275(4)	H52F	0.275(4)	C53	0.725(4)
H53A	0.725(4)	H53B	0.725(4)	H53C	0.725(4)
C53A	0.275(4)	H53D	0.275(4)	H53E	0.275(4)
H53F	0.275(4)	C54	0.725(4)	H54A	0.725(4)
H54B	0.725(4)	H54C	0.725(4)	C54A	0.275(4)
H54D	0.275(4)	H54E	0.275(4)	H54F	0.275(4)
S1	0.6994(17)	S2	0.6994(17)	F1	0.6994(17)

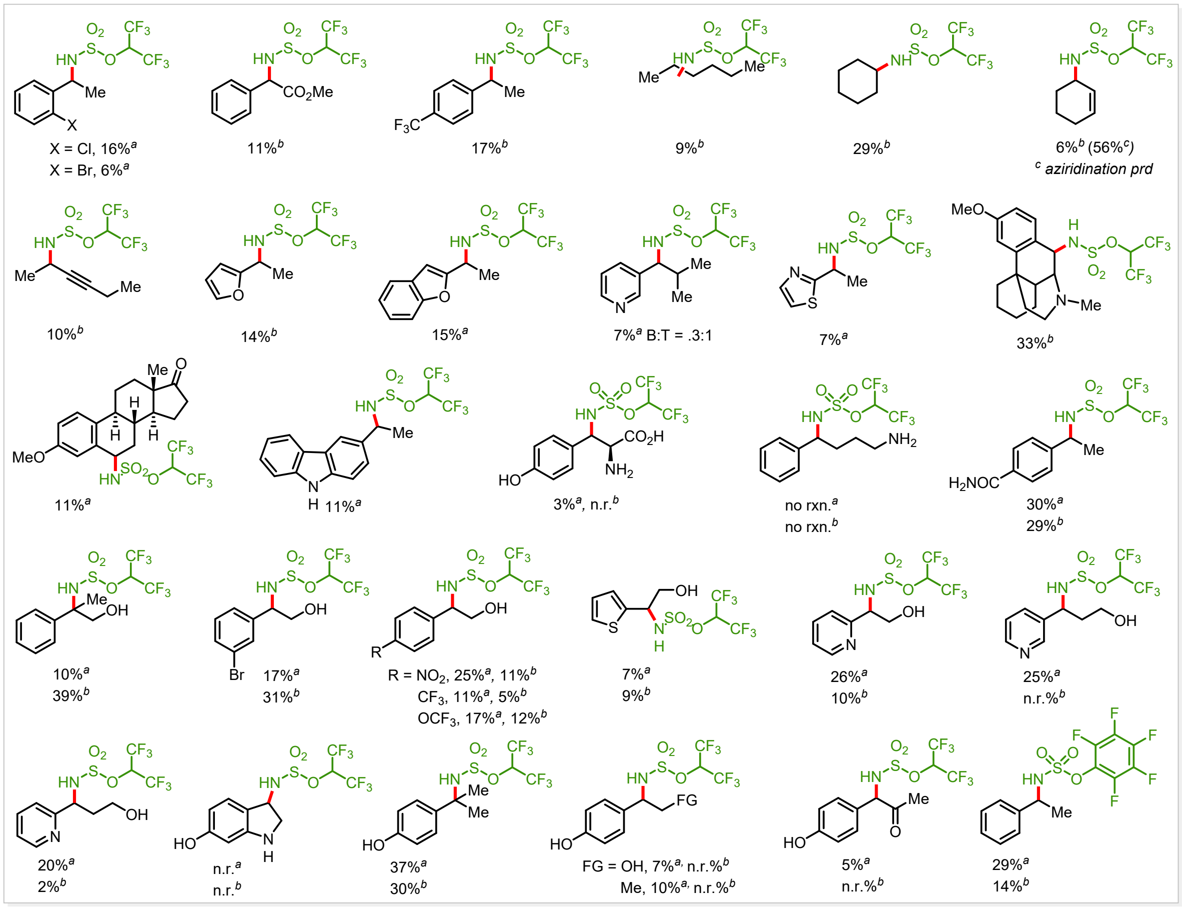
Table S49. Atomic Occupancy for Schomaker125a (ML_2).

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
F2	0.6994(17)	F3	0.6994(17)	F4	0.6994(17)
F5	0.6994(17)	F6	0.6994(17)	O2	0.6994(17)
O3	0.6994(17)	O4	0.6994(17)	O5	0.6994(17)
N7	0.6994(17)	C55	0.6994(17)	C56	0.6994(17)
S1A	0.3006(17)	S2A	0.3006(17)	F1A	0.3006(17)
F2A	0.3006(17)	F3A	0.3006(17)	F4A	0.3006(17)
F5A	0.3006(17)	F6A	0.3006(17)	O2A	0.3006(17)
O3A	0.3006(17)	O4A	0.3006(17)	O5A	0.3006(17)
N7A	0.3006(17)	C55A	0.3006(17)	C56A	0.3006(17)
S3	0.5	S4	0.5	F7	0.5
F8	0.5	F9	0.5	F10	0.5
F11	0.5	F12	0.5	O6	0.5
O7	0.5	O8	0.5	O9	0.5
N8	0.5	C57	0.5	C58	0.5
S5	0.5	S6	0.5	F13	0.5
F14	0.5	F15	0.5	F16	0.5
F17	0.5	F18	0.5	O10	0.5
O11	0.5	O12	0.5	O13	0.5
N9	0.5	C59	0.5	C60	0.5

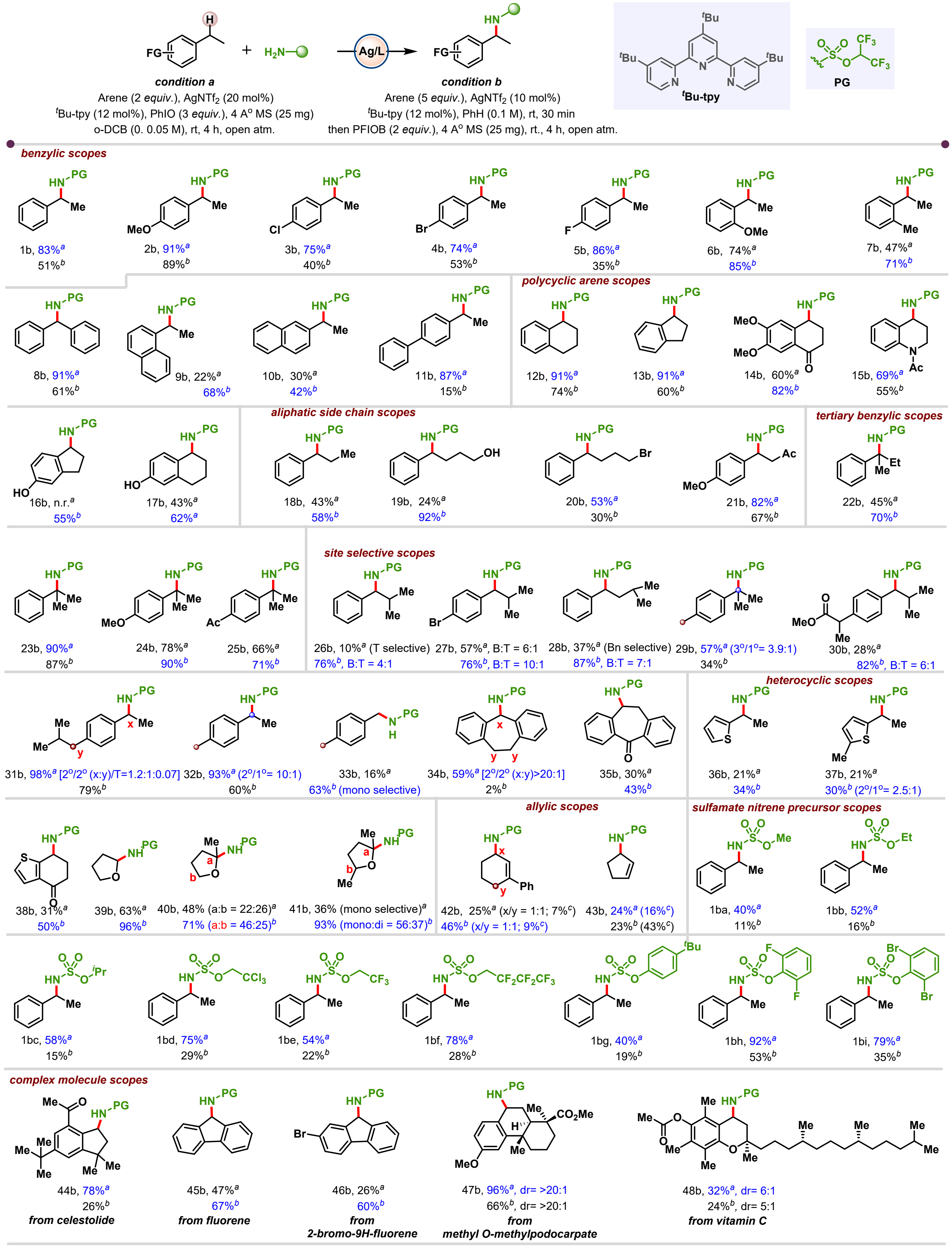
Table S50. Solvent masks information for Schomaker125a (ML_2).

Number	**X**	**Y**	**Z**	**Volume**	**Electron count**	**Content**
1	0.000	0.000	0.000	229.9	44.4	1 DCM
2	0.208	0.809	0.617	8.2	0.0	?
3	0.792	0.191	0.383	8.2	0.0	?

4.7. Unsuccessful scopes for substrate-controlled site-selective benzylic C-H amidation reaction.

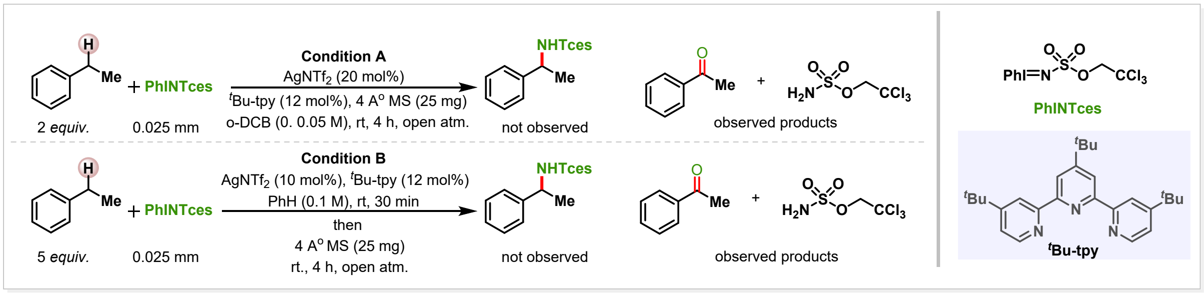

X = Cl, 16%^{a}
X = Br, 6%^{a}
11%^{b}
17%^{b}
9%^{b}
29%^{b}
6%^{b} (56%^{c})
^{c} aziridination prd
10%^{b}
14%^{b}
15%^{a}
7%^{a} B:T = .3:1
7%^{a}
33%^{b}
11%^{a}
11%^{a}
3%^{a}, n.r.^{b}
no rxn.^{a}
no rxn.^{b}
30%^{a}
29%^{b}
10%^{a}
39%^{b}
17%^{a}
31%^{b}
R = NO_2, 25%^{a}, 11%^{b}
CF_3, 11%^{a}, 5%^{b}
OCF_3, 17%^{a}, 12%^{b}
7%^{a}
9%^{b}
26%^{a}
10%^{b}
25%^{a}
n.r.%^{b}
20%^{a}
2%^{b}
n.r.^{a}
n.r.^{b}
37%^{a}
30%^{b}
FG = OH, 7%^{a}, n.r.%^{b}
Me, 10%^{a}, n.r.%^{b}
5%^{a}
n.r.%^{b}
29%^{a}
14%^{b}

4.8. Full scope for benzylic C-H amidations with condition A and condition B.

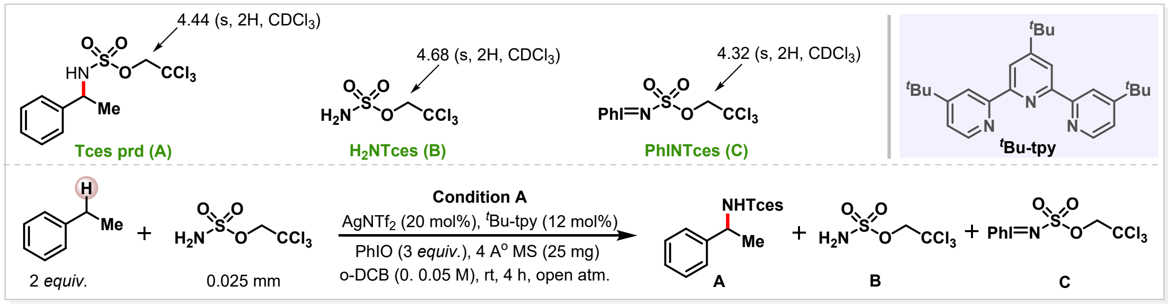


4.9. Control experiments to determine the role of the iminoiodinane.

We prepared the iminoiodane reagent PhIN(Tces) and evaluated it under our reaction conditions. Interestingly, the pre-oxidized nitrogen source did not perform well under the reaction conditions. Instead of the desired amidated product, the mixture consisted of remaining ethylbenzene, acetophenone and the Tces sulfamate. We hypothesize that the soluble oxidant is able to engage in a background reaction to form the acetophenone faster than it can be transferred to Ag to form the nitrene. In contrast, using the largely insoluble PhIO as the oxidant enables slow formation of the PhINTces and minimizes competing oxidation to the ketone.

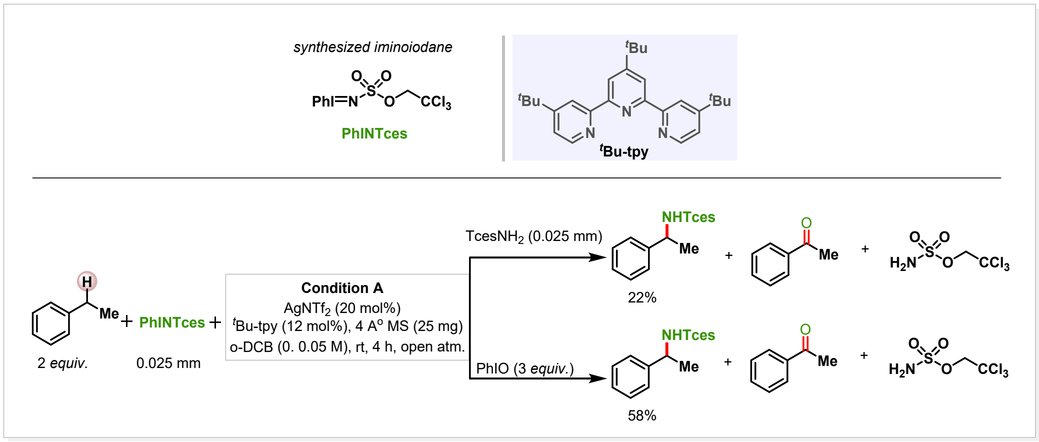


We also monitored the reaction mixture at different time intervals up to 4 h to detect the presence of iminoiodane **(C)** and any unreacted amine **(B)**, along with formation of the desired amidated product **(A)**. Sample aliquots were taken from the reaction mixture, quickly filtered, then analyzed immediately by NMR. A gradual increase in the amount of the amidated product over time was observed, but we were unable to detect the iminoiodane species in the crude NMR spectra. This may be due to a low concentration of the iminoiodinane in solution or decomposition during the filtration process. Unfortunately, we cannot monitor the reaction mixture directly by NMR, as it is heterogeneous in nature.

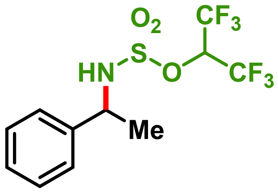


Time (min)	Tces prd. (A)	TcesNH$_2$ (B)	PhINTces (C)
10 min	31%	34%	-
20 min	46%	17%	-
30 min	49%	24%	-
40 min	40%	44%	-
50 min	49%	28%	-
60 min	42%	20%	-
75 min	52%	16%	-
90 min	53%	21%	-
105 min	54%	8%	-
120 min	52%	21%	-
150 min	58%	6%	-
180 min	67%	5%	-
210 min	68%	10%	-
240 min	70%	6%	-

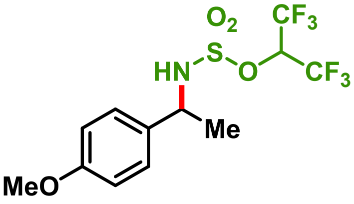
We also performed control experiments using PhINTces in the presence of either TcesNH$_2$, PhIO or PFIOB. A 58% yield of product was observed in the presence of oxidant (PhIO) under Condition A, while adding TcesNH$_2$ provided a 22% yield. This result suggests the presence of an oxidant is necessary to drive the formation of the desired product and may be due to potential decomposition or hydrolysis of iminoiodinane under the reaction conditions, despite the presence of molecular sieves. In the presence of excess oxidant, the active iminoiodinane species may be regenerated in situ, thereby driving the equilibrium toward the desired product formation; however, this is speculative at this point.



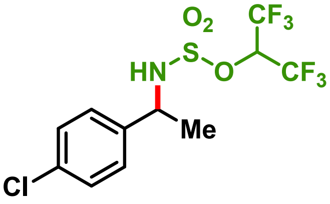
5. Characterization data.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-phenylethyl)sulfamate (1b):
The reaction was performed with condition A.
Physical appearance: white solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (85% from crude NMR) (29 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.27 (m, 5H), 5.12 (dq, *J* = 11.4, 5.7 Hz, 2H), 4.71 (p, *J* = 6.9 Hz, 1H), 1.63 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 140.8, 129.1, 128.5, 126.2, 120.19 (q, $J_{C\text{-}F}$ = 284.1), 73.0 (hept, *J* = 35.2 Hz), 55.5, 22.4. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{11}H_{10}F_6NO_3S$ 350.0286; Found, 350.0298.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(4-methoxyphenyl)ethyl)sulfamate (2b):
The reaction was performed with condition A.
Physical appearance: white solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (91% from crude NMR) (31 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 5.40 (p, *J* = 5.7 Hz, 1H), 5.28 (d, *J* = 6.5 Hz, 1H), 4.95 (p, *J* = 6.8 Hz, 1H), 4.08 (s, 3H), 1.88 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 158.7, 131.9, 126.6, 119.2 (q, $J_{C\text{-}F}$ = 284.4 Hz), 113.4, 71.9 (hept, *J* = 35.1 Hz), 54.4, 54.0, 21.2. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{12}F_6NO_4S$ 380.0391; Found, 380.0403.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(4-chlorophenyl)ethyl)sulfamate (3b):

The reaction was performed with condition A.

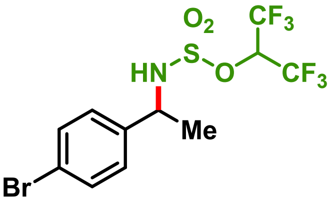
Physical appearance: white solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (75% from crude NMR) (25 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 5.15 – 4.90 (m, 2H), 4.60 (p, *J* = 6.9 Hz, 1H), 1.51 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.3, 134.4, 129.3, 127.6, 120.1 (q, $J_{C\text{-}F}$ = 282.6 Hz), 73.0 (hept, *J* = 35.2 Hz), 54.8, 22.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{11}H_9ClF_6NO_3S$ 383.9896; Found, 383.9910.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(4-bromophenyl)ethyl)sulfamate (4b):

The reaction was performed with condition A.

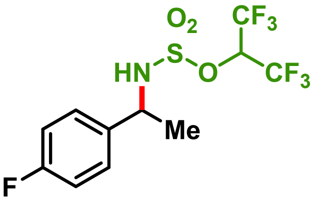
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (74% from crude NMR) (28 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.46 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 5.35 (d, *J* = 7.0 Hz, 1H), 5.13 (h, *J* = 5.7 Hz, 1H), 4.66 (q, *J* = 6.8 Hz, 1H), 1.57 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.9, 132.2, 127.9, 122.4, 120.1 (q, *J* = 284.7 Hz), 73.0 (hept, $J_{C\text{-}F}$ = 35.2 Hz), 54.9, 22.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{11}H_9BrF_6NO_3S$ 429.9396; Found, 429.9386.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(4-fluorophenyl)ethyl)sulfamate (5b):

The reaction was performed with condition A.

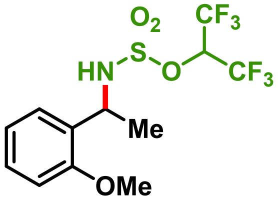
Physical appearance: colorless solid

Column material: 100-200 mesh silica

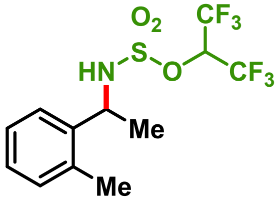
Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (86% from crude NMR) (28 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 5.25 (d, *J* = 6.9 Hz, 1H), 5.08 (q, *J* = 5.7 Hz, 1H), 4.64 (t, *J* = 6.9 Hz, 1H), 1.54 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.7 (d, J_{C-F} = 247.1 Hz), 136.7, 128.0 (d, J_{C-F} = 8.3 Hz), 120.1 (q, J_{C-F} = 280.8 Hz), 116.0 (d, J_{C-F} = 21.7 Hz), 73.0 (hept, *J* = 35.2 Hz), 54.8, 22.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2, -113.7. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{11}H_9F_7NO_3S$ 368.0197; Found, 368.0204.

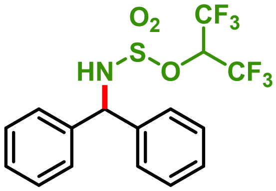


1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(2-methoxyphenyl)ethyl)sulfamate (6b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (85% from crude NMR) (30 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 7.9, 1.7 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.06 (d, *J* = 9.1 Hz, 1H), 5.11 (hept, *J* = 5.7 Hz, 1H), 4.73 (dq, *J* = 9.1, 7.0 Hz, 1H), 3.88 (s, 3H), 1.60 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.7, 129.5, 128.6, 128.3, 121.3, 120.2 (q, J_{C-F} = 289.8 Hz), 111.3, 72.8 (hept, *J* = 35.1 Hz), 55.4, 55.1, 21.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.4. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_{12}F_6NO_4S$ 380.0397; Found, 380.0404.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(*o*-tolyl)ethyl)sulfamate (7b):
The reaction was performed with condition B.
Physical appearance: white solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (71% from crude NMR) (24 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.18 (m, 1H), 7.18 – 7.06 (m, 3H), 5.10 (s, 1H), 5.04 (p, *J* = 5.7 Hz, 1H), 4.89 (p, *J* = 6.8 Hz, 1H), 2.30 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.0, 135.2, 131.1, 128.3, 126.9, 124.9, 120.2 (q, J_{C-F} = 282.5 Hz), 72.9

(hept, J = 35.1 Hz), 51.8, 22.1, 19.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.3. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{12}F_6NO_3S$ 364.0448; Found, 364.0455.



1,1,1,3,3,3-Hexafluoropropan-2-yl benzhydrylsulfamate (8b):

The reaction was performed with condition A.

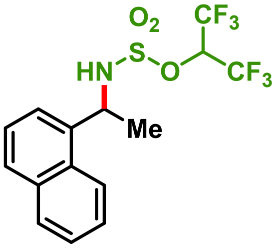
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (91% from crude NMR) (34 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (dp, J = 24.2, 7.6, 7.0 Hz, 10H), 5.99 – 5.59 (m, 2H), 5.16 (dp, J = 17.3, 5.6 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 139.4, 129.0, 128.4, 127.4, 120.1 (q, $J_{C\text{-}F}$ = 283.0 Hz), 73.0 (hept, J = 35.2 Hz), 62.8. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{16}H_{12}F_6NO_3S$ 412.0448; Found 412.0457.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(naphthalen-1-yl)ethyl)sulfamate (9b):

The reaction was performed with condition B.

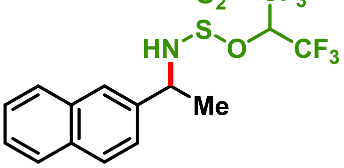
Physical appearance: colorless solid

Column material: 100-200 mesh silica

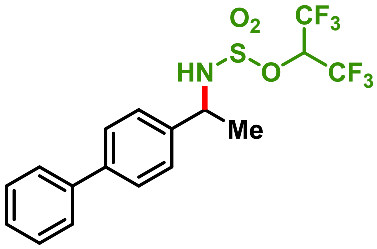
Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (68% from crude NMR) (23 mg, isolated yield)

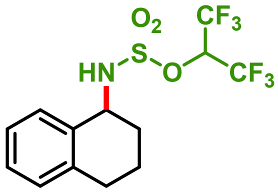
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.05 (m, 1H), 7.99 – 7.75 (m, 2H), 7.64 – 7.40 (m, 4H), 5.56 (t, J = 6.6 Hz, 1H), 5.25 (s, 1H), 5.18 (p, J = 5.7 Hz, 1H), 1.80 (d, J = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 136.1, 134.2, 130.3, 129.6, 129.2, 127.1, 126.3, 125.4, 123.3, 122.8, 120.2 (q, $J_{C\text{-}F}$ = 283.5 Hz), 73.0 (hept, J = 35.1 Hz), 51.6, 22.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{15}H_{12}F_6NO_3S$ 400.0448; Found, 400.0455.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(naphthalen-2-yl)ethyl)sulfamate (10b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (42% from crude NMR) (15 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 3H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.16 (hept, *J* = 5.7 Hz, 2H), 4.89 (q, *J* = 6.8 Hz, 1H), 1.71 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 138.0, 133.4, 133.3, 129.2, 128.2, 127.8, 126.8, 126.7, 125.3, 124.0, 120.2 (q, J_{C-F} = 282.6 Hz), 73.1 (hept, *J* = 35.2 Hz), 55.6, 22.4**.** **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{15}H_{12}F_6NO_3S$ 400.0448; Found, 400.0454.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-([1,1'-biphenyl]-4-yl)ethyl)sulfamate (11b):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (87% from crude NMR) (36 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 7.9 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (dd, *J* = 7.5, 4.8 Hz, 3H), 5.35 (d, *J* = 8.3 Hz, 1H), 5.17 (dq, *J* = 12.3, 6.6, 6.2 Hz, 1H), 4.78 (p, *J* = 6.9 Hz, 1H), 1.67 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.5, 140.5, 139.7, 129.0, 127.8, 127.7, 127.2, 126.7, 120.2 (q, J_{C-F} = 282.9 Hz), 73.0 (hept, *J* = 35.2 Hz), 55.2, 22.4. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.14. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{17}H_{14}F_6NO_3S$ 426.0604; Found, 426.0615.

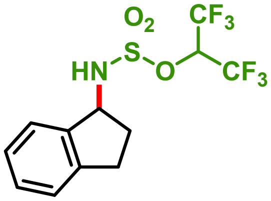


1,1,1,3,3,3-Hexafluoropropan-2-yl (1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate (12b):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (91% from crude NMR) (32 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 5.4, 3.8 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.99 (dd, *J* = 5.4, 3.7 Hz, 1H), 5.16 – 4.97 (m, 2H), 4.62 (dt, *J* = 7.8, 5.3 Hz, 1H), 2.68 (qt, *J* = 17.0, 6.4 Hz, 2H), 2.02 – 1.87 (m, 2H), 1.76 (qd, *J* = 5.4, 4.6, 2.6 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 137.8, 134.0, 129.6, 129.2, 128.4, 126.7, 120.4 (q, $J_{C\text{-}F}$ = 281.0 Hz), 73.1 (hept, *J* = 35.1 Hz), 54.1, 30.2, 28.9, 19.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{12}F_6NO_3S$ 376.0448; Found, 376.0455.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2,3-dihydro-1H-inden-1-yl)sulfamate (13b):

The reaction was performed with condition A.

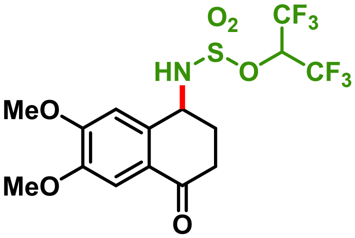
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (91% from crude NMR) (30 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.29 (m, 1H), 7.22 (d, *J* = 5.2 Hz, 3H), 5.14 (p, *J* = 5.7 Hz, 1H), 5.08 – 4.85 (m, 2H), 2.98 (ddd, *J* = 16.1, 8.7, 4.3 Hz, 1H), 2.83 (dt, *J* = 16.0, 7.8 Hz, 1H), 2.58 (dp, *J* = 17.7, 6.6, 5.4 Hz, 1H), 1.98 (dq, *J* = 13.3, 7.5 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 143.3, 140.4, 129.2, 127.3, 125.2, 124.4, 120.3 (q, $J_{C\text{-}F}$ = 281.0 Hz), 73.1 (hept, *J* = 35.1 Hz), 60.6, 34.0, 30.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{10}F_6NO_3S$ 362.0291; Found, 362.0299.



1,1,1,3,3,3-Hexafluoropropan-2-yl (6,7-dimethoxy-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate (14b):

The reaction was performed with condition B.

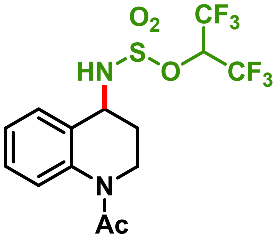
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (82% from crude NMR) (34 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 6.1 Hz, 1H), 7.00 – 6.89 (m, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 5.26 (p, *J* = 5.7 Hz, 1H), 4.76 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 2.67 (ddt, *J* = 13.8, 9.0, 4.3 Hz, 1H), 2.48 (ddt, *J* = 17.5, 10.9, 5.0 Hz, 1H), 2.41 – 2.13 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 196.0, 154.4, 149.6, 135.2, 125.4, 120.3 (q, J_{C-F} = 287.3 Hz), 109.7, 108.8, 73.1 (hept, *J* = 35.1 Hz), 56.2, 56.2, 53.2, 33.8, 30.4. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{16}F_6NO_6S$ 452.0603; Found, 452.9232.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-acetyl-1,2,3,4-tetrahydroquinolin-4-yl)sulfamate (15b):

The reaction was performed with condition A.

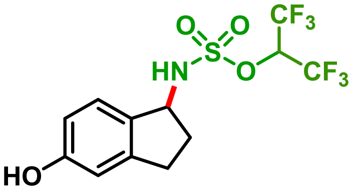
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (69% from crude NMR) (21 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.49 (m, 2H), 7.51 – 7.40 (m, 1H), 5.53 (p, *J* = 5.7 Hz, 1H), 4.99 (d, *J* = 5.1 Hz, 1H), 4.17 – 3.87 (m, 1H), 2.55 (s, 1H), 2.46 (s, 2H), 2.34 (s, 1H), 2.25 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 171.2, 170.6, 151.6, 135.9, 128.6, 125.6, 124.5, 120.3 (q, J_{C-F} = 283.5 Hz), 72.7 (hept, *J* = 34.9 Hz), 67.8, 51.6, 30.4, 22.7. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{14}H_{13}F_6N_2O_4S$ 419.0506; Found, 419.0514.



1,1,1,3,3,3-Hexafluoropropan-2-yl (5-hydroxy-2,3-dihydro-1H-inden-1-yl)sulfamate--methane (1/1) (16b):

The reaction was performed with condition B.

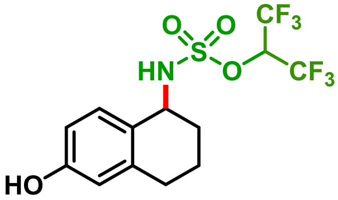
Physical appearance: yellowish gummy liquid.

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (90/10, v/v)

Yield: (55% from crude NMR) (The isolated product was a mixture of compounds, including the desired amidated product; therefore, we have reported only the yield of the crude reaction mixture).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 6.0 Hz, 2H), 5.20 (p, *J* = 5.7 Hz, 2H), 4.97 (t, *J* = 6.6 Hz, 1H), 3.63 (s, 1H), 2.96 – 2.72 (m, 2H), 2.58 (dtd, *J* = 12.8, 7.7, 5.0 Hz, 1H), 2.09 – 2.00 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 156.9, 145.5, 132.4, 125.5, 122.6 (q, *J* = 287.3 Hz), 114.7, 111.9, 73.1 (hept, *J* = 35.1 Hz), 60.1, 34.2, 30.1. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{10}F_6NO_4S$ 378.0235; Found, 378.0244.



1,1,1,3,3,3-Hexafluoropropan-2-yl (6-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)-sulfamate--methane (1/1) (17b):

The reaction was performed with condition B.

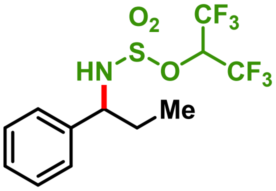
Physical appearance: yellowish gummy liquid.

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (90/10, v/v)

Yield: (62% from crude NMR) (The isolated product was a mixture of compounds, including the desired amidated product; therefore, we have reported only the yield of the crude reaction mixture).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.4 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.53 (d, *J* = 2.6 Hz, 1H), 5.22 (p, *J* = 5.7 Hz, 1H), 5.13 – 5.04 (m, 1H), 4.68 (s, 1H), 3.62 (s, 1H), 2.68 (dt, *J* = 14.6, 6.6 Hz, 2H), 2.08 – 1.99 (m, 2H), 1.81 (p, *J* = 6.4 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 155.8, 148.8, 139.5, 130.8, 120.1 (q, *J* = 273.4 Hz), 115.5, 114.4, 73.1 (hept, *J* = 35.3 Hz), 66.1, 53.7, 34.1, 30.6. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{12}F_6NO_4S$ 392.0391; Found, 392.0398.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-phenylpropyl)sulfamate (18b):

The reaction was performed with condition B.

Physical appearance: colorless solid

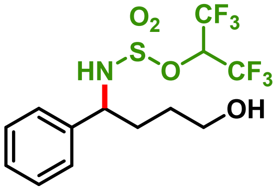
Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

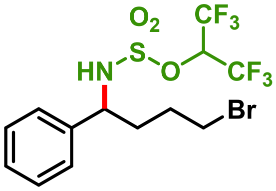
Yield: (58% from crude NMR) (19 mg, isolated yield)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 6.9 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.14 (m, 2H), 5.29 (td, *J* = 9.8, 8.9, 4.8 Hz, 1H), 5.00 (p, *J* = 5.7 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 1H), 1.87 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.83 – 1.70 (m, 1H), 0.80 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz,**

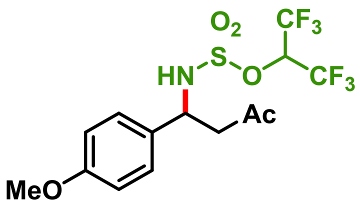
$CDCl_3$) δ 139.6, 129.0, 128.4, 126.6, 120.1 (q, J_{C-F} = 283.3 Hz), 72.9 (hept, J = 35.2 Hz), 61.7, 29.9, 10.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.3. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_{12}F_6NO_3S$ 364.0448; Found, 464.0454.



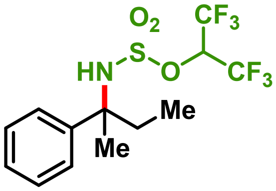
1,1,1,3,3,3-Hexafluoropropan-2-yl (4-hydroxy-1-phenylbutyl)sulfamate (19b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (70/30, v/v)
Yield: (92% from crude NMR) (24 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 – 8.52 (m, 1H), 7.65 – 7.57 (m, 3H), 7.57 – 7.52 (m, 2H), 5.36 (dt, J = 11.4, 5.7 Hz, 1H), 4.95 – 4.65 (m, 1H), 4.00 – 3.81 (m, 1H), 2.41 – 2.25 (m, 2H), 1.92 – 1.82 (m, 2H), 1.71 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.5, 149.0, 140.1, 128.9, 128.2, 126.6, 120.2 (q, J_{C-F} = 281.0 Hz), 72.7 (hept, J = 35.0 Hz), 62.3, 59.5, 30.6, 28.1. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.3. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{13}H_{14}F_6NO_4S$ 394.0553; Found, 394.0559.



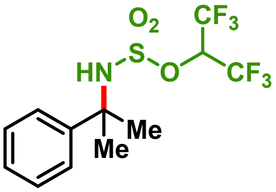
1,1,1,3,3,3-Hexafluoropropan-2-yl (4-bromo-1-phenylbutyl)sulfamate (20b):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (53% from crude NMR) (22 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dt, J = 11.8, 6.7 Hz, 3H), 7.25 – 7.19 (m, 2H), 5.36 (d, J = 8.8 Hz, 1H), 5.04 (p, J = 5.7 Hz, 1H), 4.45 (q, J = 7.5 Hz, 1H), 3.34 (t, J = 6.4 Hz, 2H), 2.16 – 1.93 (m, 2H), 1.88 (ddd, J = 15.7, 9.1, 5.4 Hz, 1H), 1.74 (ddt, J = 14.8, 10.4, 5.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.1, 129.3, 128.8, 126.5, 120.1 (q, J_{C-F} = 283.5 Hz), 72.9 (hept, J = 35.2 Hz), 59.6, 35.2, 32.7, 29.1. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{13}H_{13}BrF_6NO_3S$ 455.9709; Found, 455.9712.



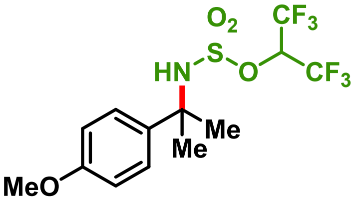
1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(4-methoxyphenyl)-3-oxobutyl)sulfamate (21b):
The reaction was performed with conditionAa.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (82% from crude NMR) (30 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.93 – 6.70 (m, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.14 (p, *J* = 5.7 Hz, 1H), 4.89 (q, *J* = 6.1 Hz, 1H), 3.78 (s, 3H), 3.09 (qd, *J* = 17.5, 5.7 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 207.3, 159.6, 130.9, 127.8, 120.1 (q, $J_{C\text{-}F}$ = 287.3 Hz), 114.3, 72.9 (hept, *J* = 35.1 Hz), 55.4, 55.1, 48.2, 30.8. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{14}H_{14}F_6NO_5S$ 422.0502; Found, 422.0511.



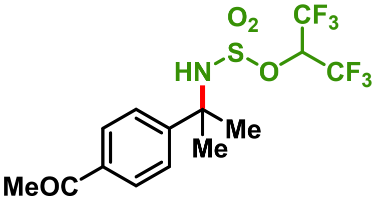
1,1,1,3,3,3-Hexafluoropropan-2-yl (2-phenylbutan-2-yl)sulfamate (22b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (70% from crude NMR) (25 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.34 (m, 4H), 7.31 (d, *J* = 7.0 Hz, 1H), 5.36 (d, *J* = 8.1 Hz, 1H), 5.22 – 5.05 (m, 1H), 2.02 (q, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 143.1, 128.7, 127.8, 125.9, 120.2 (q, $J_{C\text{-}F}$ = 287.3 Hz), 72.6 (hept, *J* = 35.1 Hz), 64.4, 35.8, 24.0, 8.5. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{14}F_6NO_3S$ 378.0604; Found, 378.0608.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2-phenylpropan-2-yl)sulfamate (23b):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (90% from crude NMR) (30 mg, isolated yield)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.45 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.29 (m, 1H), 5.26 (s, 1H), 5.13 (p, *J* = 5.7 Hz, 1H), 1.79 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 144.8, 128.8, 128.0, 125.2, 120.3 (q, $J_{C\text{-}F}$ = 284.8 Hz), 72.7 (hept, *J* = 35.1 Hz), 61.0, 28.9. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.0. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{12}F_6NO_3S$ 364.0448; Found, 364.0454.

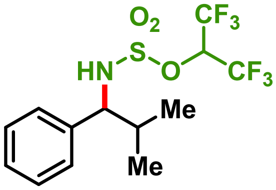


1,1,1,3,3,3-Hexafluoropropan-2-yl (2-(4-methoxyphenyl)propan-2-yl)sulfamate (24b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (90% from crude NMR) (33 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 6.93 – 6.86 (m, 2H), 5.21 – 5.01 (m, 2H), 3.81 (s, 3H), 1.78 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 159.3, 136.9, 126.6, 120.3 (q, $J_{C\text{-}F}$ = 284.76 Hz), 114.1, 72.7 (hept, *J* = 35.3 Hz), 60.8, 55.5, 29.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.0. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{14}F_6NO_4S$ 394.0553; Found, 394.0559.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2-(4-acetylphenyl)propan-2-yl)sulfamate (25b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (71% from crude NMR) (26 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 5.88 (s, 1H), 5.29 – 5.04 (m, 1H), 2.59 (s, 3H), 1.78 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 198.1, 150.2, 136.3, 128.8, 125.6, 120.2 (q, $J_{C\text{-}F}$ = 287.3 Hz), 72.7 (hept, *J* = 35.3 Hz), 60.6, 29.2, 26.7. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.0. **HRMS** (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{14}H_{19}F_6N_2O_4S$ 425.0964; Found, 425.0962.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2-methyl-1-phenylpropyl)sulfamate (26b):

The reaction was performed with condition B.

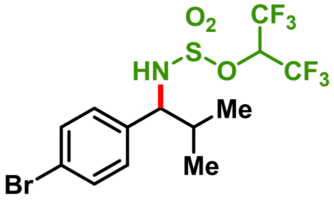
Physical appearance: colorless gummy liquid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: [76% (B:T = 4:1) from crude NMR] (24 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 3H), 7.21 (ddd, *J* = 7.9, 4.0, 1.5 Hz, 2H), 5.49 (s, 1H), 5.07 (p, *J* = 5.7 Hz, 1H), 4.23 (t, *J* = 8.0 Hz, 1H), 2.07 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 139.1, 130.8, 128.7, 128.7, 128.2, 127.0, 120.1 (q, $J_{C\text{-}F}$ = 281.0 Hz), 72.8 (hept, *J* = 35.2 Hz), 66.0, 34.2, 19.4, 18.8. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{13}H_{19}F_6N_2O_3S$ 397.1015; Found, 397.1017.



1,1,1,3,3,3-Hexafluoropropan-2-yl-(1-(4-bromophenyl)-2-methylpropyl)sulfamate (27b):

The reaction was performed with condition B.

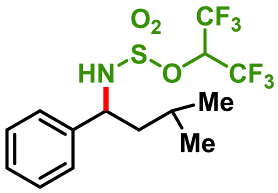
Physical appearance: colorless solid

Column material: 100-200 mesh silica

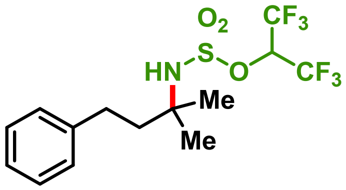
Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: [76% (B:T = 10:1) from crude NMR] (31 mg, isolated yield)

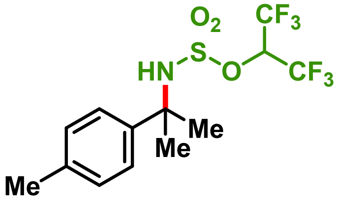
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.58 (s, 1H), 5.08 (p, *J* = 5.7 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 1H), 2.01 (h, *J* = 6.8 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 138.2, 131.9, 128.6, 122.1, 120.1 (q, $J_{C\text{-}F}$ = 283.5 Hz), 72.8 (hept, *J* = 35.2 Hz), 65.3, 34.1, 19.3, 18.7. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.3. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{13}BrF_6NO_3S$ 455.9709; Found, 455.9719.



1,1,1,3,3,3-Hexafluoropropan-2-yl (3-methyl-1-phenylbutyl)sulfamate (28b):
The reaction was performed with condition B.
Physical appearance: colorless gummy liquid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: [87% (B:T = 7:1) from crude NMR] (32 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.20 (m, 3H), 7.19 – 7.13 (m, 2H), 5.34 – 5.08 (m, 1H), 4.97 (hept, *J* = 5.7 Hz, 1H), 4.46 (q, *J* = 7.6 Hz, 1H), 1.78 – 1.53 (m, 2H), 1.42 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.84 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 140.1, 129.1, 128.5, 126.6, 120.1 (q, $J_{C\text{-}F}$ = 286.0 Hz), 72.8 (hept, *J* = 35.2 Hz), 58.6, 46.0, 24.8, 22.5, 22.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{14}H_{21}F_6N_2O_3S$ 411.1172; Found, 411.1173.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2-methyl-4-phenylbutan-2-yl)sulfamate:
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (10% from crude NMR) (4 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.18 (m, 2H), 7.18 – 7.10 (m, 3H), 5.08 (dt, *J* = 11.3, 5.7 Hz, 1H), 4.59 (s, 1H), 2.69 – 2.50 (m, 2H), 1.93 – 1.80 (m, 2H), 1.43 – 1.33 (m, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.2, 128.8, 128.4, 126.3, 120.3 (q, $J_{C\text{-}F}$ = 284.8 Hz), 72.8 (hept, *J* = 34.9 Hz), 59.4, 44.0, 30.5, 29.9, 27.3. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -72.9. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{14}H_{16}F_6NO_3S$ 392.0755; Found, 392.0766.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2-(*p*-tolyl)propan-2-yl)sulfamate (29b):

The reaction was performed with condition A.

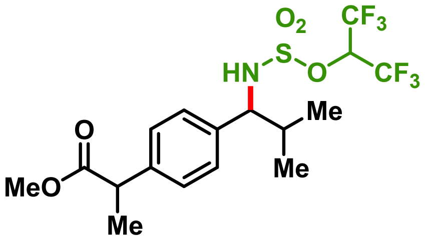
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: [57% (3°:1° = 3.9:1) from crude NMR] (20 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.13 (p, *J* = 5.7 Hz, 1H), 5.06 (s, 1H), 2.35 (s, 3H), 1.78 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.9, 137.8, 129.5, 125.1, 120.3 (q, $J_{C\text{-}F}$ = 284.8 Hz), 72.7 (hept, *J* = 35.1 Hz), 60.9, 28.9, 21.1. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -72.9. **HRMS** (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{13}H_{19}F_6N_2O_3S$ 397.1015; Found, 397.1019.



Methyl 2-(4-(1-((((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)sulfonyl)amino)-2-methylpropyl)phenyl)propanoate (30b):

The reaction was performed with condition B.

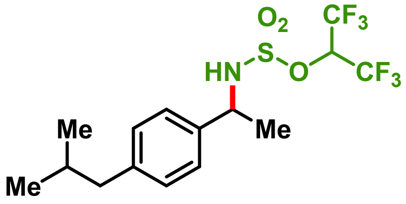
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (82%, (B:T = 6:1) from crude NMR) (37 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.77 (s, 1H), 5.06 (p, *J* = 5.7 Hz, 1H), 4.22 (t, *J* = 6.8 Hz, 1H), 3.75 (q, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 2.08 (h, *J* = 6.9 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 175.2, 140.4, 138.2, 127.8, 127.3, 120.1 (q, $J_{C\text{-}F}$ = 280.9 Hz), 72.6 (hept, *J* = 35.3 Hz), 65.8, 52.2, 45.2, 34.0, 30.5, 19.5, 19.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{17}H_{25}F_6N_2O_5S$ 483.1383; Found, 483.1383.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(4-isobutylphenyl)ethyl)sulfamate (31b):

The reaction was performed with condition A.

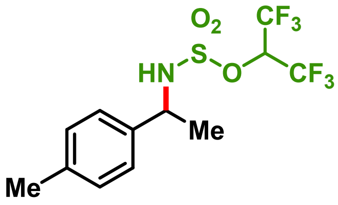
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: [98% (2°:2° = 1.2:1) from crude NMR] (36 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.12 (p, *J* = 5.7 Hz, 1H), 5.08 (s, 1H), 4.70 (p, *J* = 6.8 Hz, 2H), 2.48 (d, *J* = 7.2 Hz, 1H), 1.86 (dp, *J* = 13.6, 6.8 Hz, 3H), 1.62 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 2H), 0.90 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.3, 138.0, 129.8, 126.1, 120.2 (q, $J_{C\text{-}F}$ = 286.0 Hz), 73.0 (hept, *J* = 35.1 Hz), 55.4, 45.2, 30.3, 22.4, 22.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{15}H_{23}F_6N_2O_3S$ 425.1328; Found, 425.1328.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(*p*-tolyl)ethyl)sulfamate (32b):

The reaction was performed with condition A.

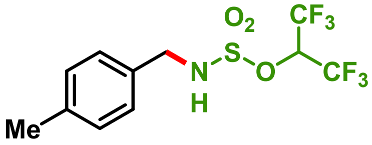
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: [93% (2°:1° = 10:1) from crude NMR] (31 mg, isolated yield)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 4H), 5.13 (hept, *J* = 5.7 Hz, 1H), 5.04 – 4.93 (m, 1H), 4.69 (p, *J* = 6.8 Hz, 1H), 2.36 (s, 3H), 1.61 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.4, 137.8, 129.8, 126.2, 120.2 (q, $J_{C\text{-}F}$ = 284.8 Hz), 73.0 (hept, *J* = 35.1 Hz), 55.3, 22.4, 21.2. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_{12}F_6NO_3S$ 364.0448; Found, 364.0454.



1,1,1,3,3,3-Hexafluoropropan-2-yl (4-methylbenzyl)sulfamate (33b):

The reaction was performed with condition B.

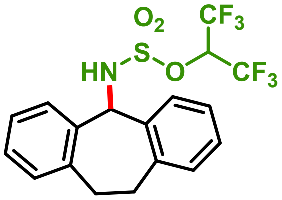
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (63% from crude NMR) (20 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.17 (m, 4H), 5.15 (p, *J* = 5.6 Hz, 1H), 4.99 (s, 1H), 4.32 (d, *J* = 5.6 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.8, 131.7, 129.9, 128.3, 120.2 (q, $J_{C\text{-}F}$ = 283.8 Hz), 73.1 (hept, *J* = 35.3 Hz), 48.2, 21.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{11}H_{10}F_6NO_3S$ 350.0291; Found, 350.0295.



1,1,1,3,3,3-Hexafluoropropan-2-yl-(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl) sulfamate (34b):

The reaction was performed with condition A.

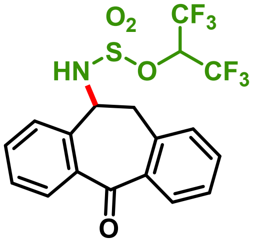
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (59% from crude NMR) (19 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.20 (dddd, *J* = 18.6, 6.4, 4.8, 1.9 Hz, 7H), 5.21 (p, *J* = 5.7 Hz, 1H), 5.10 (ddd, *J* = 9.2, 6.5, 2.9 Hz, 1H), 4.87 (d, *J* = 8.5 Hz, 1H), 4.31 (d, *J* = 15.4 Hz, 1H), 3.82 (d, *J* = 15.4 Hz, 1H), 3.59 (dd, *J* = 14.3, 3.1 Hz, 1H), 3.26 (dd, *J* = 14.3, 6.4 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 140.9, 137.7, 135.8, 134.4, 132.3, 130.6, 130.5, 128.6, 128.5, 127.8, 127.6, 127.5, 120.3 (q, $J_{C\text{-}F}$ = 283.0 Hz), 73.0 (hept, *J* = 35.1 Hz), 56.5, 41.2, 37.3. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.0. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{18}H_{14}F_6NO_3S$ 438.0604; Found, 438.0610.



1,1,1,3,3,3-Hexafluoropropan-2-yl-(5-oxo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-10-yl)sulfamate (35b):

The reaction was performed with condition B.

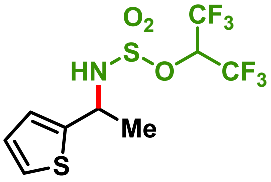
Physical appearance: colorless solid

Column material: 100-200 mesh silica

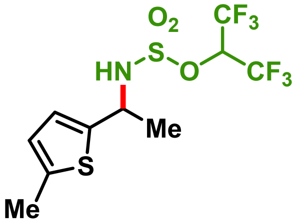
Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (43% from crude NMR) (19 mg, isolated yield)

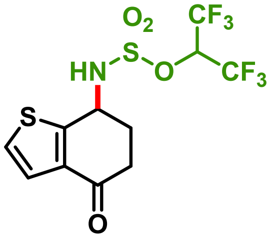
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.32 (m, 8H), 5.38 – 4.94 (m, 2H), 4.34 (s, 2H), 3.79 – 3.22 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 196.7, 139.3, 138.7, 137.0, 133.5, 133.1, 132.0, 131.2, 130.8, 130.4, 130.2, 129.2, 128.1, 119.5 (q, $J_{C\text{-}F}$ = 284.8 Hz), 74.1 (hept, *J* = 35.3 Hz), 57.7, 51.2. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{18}H_{12}F_6NO_4S$ 452.0397; Found, 452.0403.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(thiophen-2-yl)ethyl)sulfamate (36b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (34% from crude NMR) (10 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.05 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.15 (dq, *J* = 10.4, 5.2, 4.7 Hz, 2H), 4.99 (p, *J* = 7.0 Hz, 1H), 1.72 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 144.0, 127.2, 125.8, 125.5, 120.2 (q, $J_{C\text{-}F}$ = 284.8 Hz), 73.1 (hept, *J* = 35.2 Hz), 51.2, 22.9. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_9H_8F_6NO_3S_2$ 355.9855; Found, 355.9862.



1,1,1,3,3,3-Hexafluoropropan-2-yl (1-(5-methylthiophen-2-yl)ethyl)sulfamate (37b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (30% from crude NMR) (9 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (td, *J* = 7.8, 3.0 Hz, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 6.58 (d, *J* = 3.4 Hz, 1H), 5.25 – 4.91 (m, 1H), 4.86 (t, *J* = 7.0 Hz, 1H), 2.44 (s, 3H), 1.63 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 140.79, 131.24, 127.73, 124.04, 119.3 (q, $J_{C\text{-}F}$ = 284.8 Hz), 73.9 (hept, *J* = 35.3 Hz), 50.30, 21.71, 14.41. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{10}H_{10}F_6NO_3S_2$ 370.0012; Found, 370.0017.



1,1,1,3,3,3-Hexafluoropropan-2-yl-(4-oxo-4,5,6,7-tetrahydrobenzo[b]thiophen-7-yl)sulfamate (38b):

The reaction was performed with condition B.

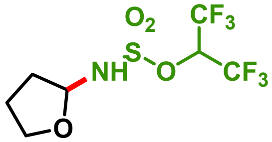
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (50% from crude NMR) (14 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 5.2 Hz, 1H), 7.22 (d, *J* = 5.3 Hz, 1H), 6.10 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.82 (ddd, *J* = 17.2, 9.8, 4.7 Hz, 1H), 2.61 – 2.51 (m, 1H), 2.45 (ddt, *J* = 14.1, 9.9, 4.3 Hz, 1H), 2.36 – 2.23 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.7, 151.3, 138.1, 126.7, 124.7, 120.2 (q, *J* = 284.5, 283.2 Hz), 72.9 (hept, *J* = 35.1 Hz), 66.0, 34.4, 30.1. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.2. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{11}H_8F_6NO_4S_2$ 395.9804; Found, 395.9812.

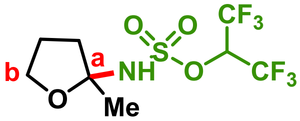


1,1,1,3,3,3-Hexafluoropropan-2-yl (tetrahydrofuran-2-yl)sulfamate (39b):

The reaction was performed with condition B.

Yield: 96% from crude NMR.

Isolation: We tried several times to isolate the desired product using 100–200 mesh silica, but the compound decomposes during column chromatography. We also tried adding triethylamine to the silica column and using neutral alumina instead, but the compound still decomposed. Thus, the yield has been reported based on the crude NMR.

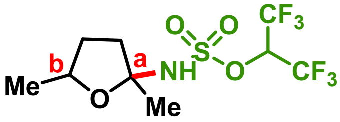


1,1,1,3,3,3-Hexafluoropropan-2-yl (2-methyltetrahydrofuran-2-yl)sulfamate (40b):

The reaction was performed with condition B.

Yield: (71%, a:b = 46:25 from crude NMR)

Isolation: Because the simple tetrahydrofuran derivative could not be isolated, here the yield is provided based on crude NMR analysis.

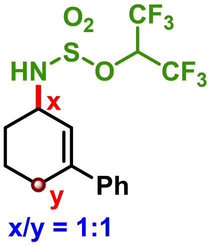


1,1,1,3,3,3-Hexafluoropropan-2-yl (2,5-dimethyltetrahydrofuran-2-yl)sulfamate (41b):

The reaction was performed with condition B.

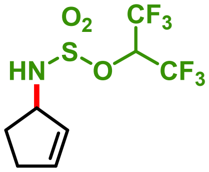
Yield: (93%, mono:di = 56:37 from crude NMR)

Isolation: Because the simple tetrahydrofuran derivative could not be isolated, here the yield is provided based on crude NMR analysis.



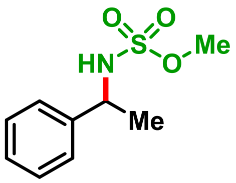
1,1,1,3,3,3-Hexafluoropropan-2-yl-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)sulfamate (42b):

The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: [46% (X/Y= 1:1) from crude NMR] (16 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.13 (m, 8H), 7.05 – 7.00 (m, 1H), 6.18 (t, *J* = 4.0 Hz, 1H), 5.89 (dd, *J* = 3.8, 1.9 Hz, 1H), 5.08 (dq, *J* = 11.4, 5.7 Hz, 2H), 4.98 (p, *J* = 5.7 Hz, 1H), 4.85 (s, 1H), 4.60 (s, 1H), 4.16 (t, *J* = 5.5 Hz, 1H), 2.38 – 2.24 (m, 2H), 2.14 (ddt, *J* = 12.9, 6.9, 3.9 Hz, 2H), 1.97 – 1.84 (m, 2H), 1.71 (ddt, *J* = 13.5, 6.7, 3.9 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.8, 140.7, 138.7, 135.1, 132.0, 128.7, 128.6, 128.1, 127.9, 126.1, 122.0, 120.3 (q, J_{C-F} = 283.5 Hz), 73.0 (hept, *J* = 34.0 Hz), 52.0, 51.6, 42.3, 35.2, 27.2, 25.7, 19.7, 16.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.13. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{15}H_{14}F_6NO_3S$ 402.0604; Found, 402.0609.
Note: The isolated product contains both the regioisomers in same amount.

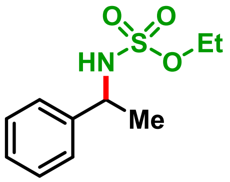


1,1,1,3,3,3-Hexafluoropropan-2-yl cyclopent-2-en-1-ylsulfamate (43b):

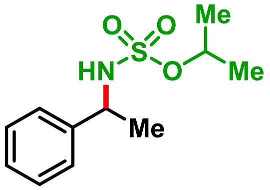
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (24% from crude NMR) (8 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.06 (dd, *J* = 5.5, 2.3 Hz, 1H), 5.74 (dt, *J* = 5.5, 2.3 Hz, 1H), 5.15 (p, *J* = 5.7 Hz, 1H), 4.61 (dt, *J* = 7.6, 3.4 Hz, 1H), 2.63 – 2.43 (m, 1H), 2.43 – 2.29 (m, 2H), 1.81 (dq, *J* = 13.2, 4.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.1, 129.2, 120.3 (q, J_{C-F} = 286.0 Hz), 73.0 (hept, *J* = 35.3 Hz), 61.8, 31.1, 31.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.20. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_8F_6NO_3S$ 312.0135; Found, 312.0143.



Methyl (S)-(1-phenylethyl)sulfamate (1ba):
The reaction was performed with condition A.
Physical appearance: white solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (40% from crude NMR) (8 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.27 (m, 5H), 5.00 (d, *J* = 7.1 Hz, 1H), 4.60 (p, *J* = 6.9 Hz, 1H), 3.61 (s, 3H), 1.57 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 142.1, 128.9, 128.2, 126.3, 56.4, 54.5, 23.1. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_9H_{12}NO_3S$ 214.0543; Found, 214.0538.

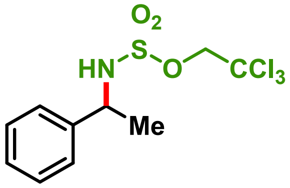


Ethyl (S)-(1-phenylethyl)sulfamate (1bb):
The reaction was performed with condition A.
Physical appearance: white solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (52% from crude NMR) (10 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 5.12 (s, 1H), 4.60 (p, *J* = 6.9 Hz, 1H), 4.03 (ddt, *J* = 9.5, 8.2, 6.5 Hz, 1H), 3.96 – 3.82 (m, 1H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 142.3, 128.9, 128.1, 126.4, 66.9, 54.4, 23.2, 14.4. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{10}H_{14}NO_3S$ 228.0700; Found, 228.0695.

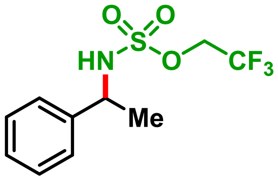


Isopropyl (S)-(1-phenylethyl)sulfamate (1bc):
The reaction was performed with condition A.
Physical appearance: yellowish solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (58% from crude NMR) (13 mg, isolated yield)

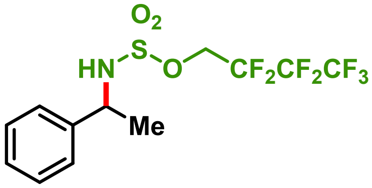
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 5H), 4.85 (s, 1H), 4.70 – 4.53 (m, 2H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 142.4, 128.9, 128.0, 126.4, 54.5, 23.5, 22.7, 22.6. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{11}H_{16}NO_3S$ 242.0856; Found, 242.0852.



2,2,2-Trichloroethyl (1-phenylethyl)sulfamate (1bd):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (75% from crude NMR) (22 mg, isolated yield)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 5.02 (d, *J* = 7.2 Hz, 1H), 4.73 (p, *J* = 6.9 Hz, 1H), 4.42 (d, *J* = 1.2 Hz, 2H), 1.63 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.6, 129.1, 128.4, 126.4, 93.4, 55.1, 23.0. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{10}H_{11}Cl_3NO_3S$ 329.9531; Found, 329.9538.



2,2,2-Trifluoroethyl (S)-(1-phenylethyl)sulfamate (1be):
The reaction was performed with condition A.
Physical appearance: white solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (54% from crude NMR) (14 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 5.20 (d, *J* = 7.1 Hz, 1H), 4.66 (p, *J* = 6.9 Hz, 1H), 4.15 (qq, *J* = 11.8, 8.0 Hz, 2H), 1.59 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.4, 129.1, 128.5, 126.3, 122.1 (q, *J* = 277.6 Hz), 65.1 (q, *J* = 37.8 Hz), 55.1, 22.8. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.9. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{10}H_{11}F_3NO_3S$ 282.0417; Found, 282.0415.



4,4,4,4,4,4,4-Heptafluoro-4l8-but-2-yn-1-yl (1-phenylethyl)sulfamate (1bf):

The reaction was performed with condition A.

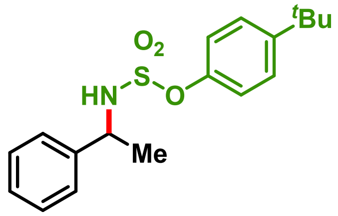
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (78% from crude NMR) (27 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 7.9, 6.5 Hz, 2H), 7.35 – 7.30 (m, 3H), 5.14 (s, 1H), 4.66 (p, *J* = 6.9 Hz, 1H), 4.33 – 4.16 (m, 1H), 1.59 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.4, 129.1, 128.5, 126.3, 121.0 (t, *J* = 33.3 Hz), 118.7 (t, *J* = 33.4 Hz), 116.4 (t, *J* = 33.4 Hz), 115.3 (t, *J* = 31.1 Hz), 114.1 (t, *J* = 33.5 Hz), 113.3 (t, *J* = 31.1 Hz), 111.2 (t, *J* = 31.5 Hz), 110.7 (q, *J* = 39.1 Hz), 108.5 (q, $J_{C\text{-}F}$ = 39.1 Hz), 64.2 (t, *J* = 27.2 Hz), 55.1, 22.8. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -80.9, -120.7, -127.5. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{11}F_7NO_3S$ 382.0353; Found, 382.0358.



4-(*tert*-Butyl)phenyl (1-phenylethyl)sulfamate (1bg):

The reaction was performed with condition A.

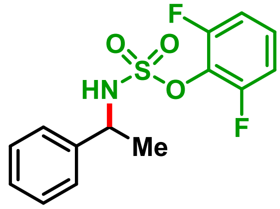
Physical appearance: colorless solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (40% from crude NMR) (11 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dtd, *J* = 13.2, 6.7, 1.8 Hz, 7H), 7.04 – 6.93 (m, 2H), 5.02 (d, *J* = 7.2 Hz, 1H), 4.76 (p, *J* = 6.9 Hz, 2H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.30 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 149.9, 147.9, 141.8, 129.0, 128.2, 126.7, 126.4, 121.3, 55.2, 34.7, 31.5, 23.2. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{18}H_{22}NO_3S$ 332.1320; Found, 332.1320.



2,6-Difluorophenyl (S)-(1-phenylethyl)sulfamate (1bh):

The reaction was performed with condition A.

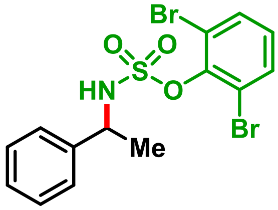
Physical appearance: white solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (92% from crude NMR) (23 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.40 (dddd, *J* = 12.5, 7.7, 6.3, 1.9 Hz, 4H), 7.35 – 7.29 (m, 1H), 6.98 (td, *J* = 8.1, 1.3 Hz, 1H), 5.26 (d, *J* = 25.9 Hz, 1H), 5.01 (p, *J* = 6.8 Hz, 1H), 1.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.8, 141.5, 133.2, 128.9, 128.6, 128.2, 126.5, 118.7, 55.8, 22.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -124.3. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{14}H_{12}F_2NO_3S$ 312.0511; Found, 312.0510.



2,6-Dibromophenyl (S)-(1-phenylethyl)sulfamate (1bi):

The reaction was performed with condition A.

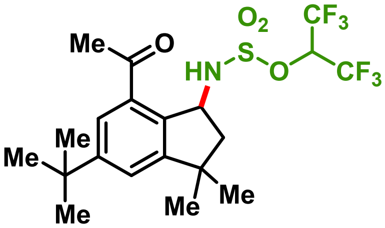
Physical appearance: white solid

Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

Yield: (79% from crude NMR) (29 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 4.3 Hz, 4H), 7.32 (q, *J* = 4.1 Hz, 1H), 7.19 (tt, *J* = 8.6, 5.9 Hz, 1H), 7.03 – 6.93 (m, 2H), 5.32 (d, *J* = 6.9 Hz, 1H), 4.87 (p, *J* = 6.8 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.1, 155.1, 141.6, 128.9, 128.2, 127.4, 126.3, 112.7, 55.5, 22.9. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{14}H_{12}Br_2NO_3S$ 431.8910; Found, 431.8909.



1,1,1,3,3,3-Hexafluoropropan-2-yl-(7-acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-yl)sulfamate (44b):

The reaction was performed with condition A.

Physical appearance: colorless solid

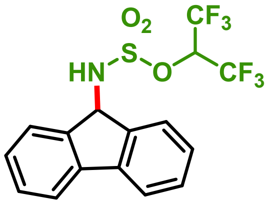
Column material: 100-200 mesh silica

Eluent: Hexane/diethyl ether (95/5, v/v)

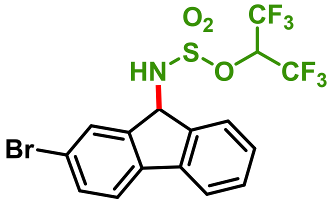
Yield: (78% from crude NMR) (36 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 6.70 (s, 1H), 5.27 (p, *J* = 5.7 Hz, 1H), 5.18 – 5.06 (m, 1H), 2.66 (s, 3H), 2.61 (dd, *J* = 14.1, 3.2 Hz, 1H), 2.20 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.39 (s, 6H), 1.38 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 202.6, 155.5, 153.7, 135.9, 134.9, 126.4, 124.6, 120.4 (q, J_{C-F} = 274.7 Hz), 72.7 (hept, *J* = 35.1 Hz), 58.7, 45.3, 43.2, 35.2, 31.5, 30.5, 29.6, 28.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -72.9.

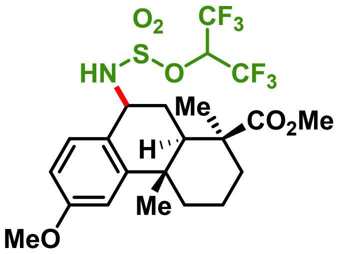
HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{20}H_{24}F_6NO_4S$ 488.1336; Found, 488.1341.



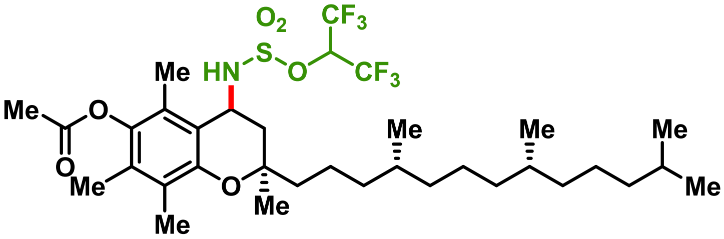
1,1,1,3,3,3-Hexafluoropropan-2-yl (9H-fluoren-9-yl)sulfamate (45b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (67% from crude NMR) (24 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (t, *J* = 7.1 Hz, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 5.53 (s, 1H), 5.30 (p, *J* = 5.7 Hz, 1H), 5.03 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.7, 140.3, 129.8, 128.4, 125.5, 120.3, 120.3 (q, J_{C-F} = 284.8 Hz), 73.4 (hept, *J* = 35.2 Hz), 59.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.0. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{16}H_{10}F_6NO_3S$ 410.0291; Found, 410.0297.



1,1,1,3,3,3-Hexafluoropropan-2-yl (2-bromo-9H-fluoren-9-yl)sulfamate (46b):
The reaction was performed with condition B.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (60% from crude NMR) (26 mg, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.64 (t, *J* = 6.8 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.41 (dt, *J* = 24.0, 7.5 Hz, 2H), 5.54 (s, 1H), 5.31 (p, *J* = 5.7 Hz, 1H), 5.16 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.7, 141.3, 139.4, 139.3, 133.0, 130.1, 129.0, 128.8, 125.5, 121.6, 121.4, 120.2 (q, J_{C-F} = 284.8 Hz), 119.1, 73.5 (hept, *J* = 35.3 Hz), 59.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -73.0. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{16}H_9BrF_6NO_3S$ 487.9396; Found, 487.9407.

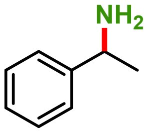


Methyl (9S)-9-((((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)sulfonyl)amino)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (47b):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (96% from crude NMR) (40 mg, *dr* >19:1, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.91 – 6.72 (m, 2H), 5.41 (dd, *J* = 7.0, 2.8 Hz, 1H), 5.24 (p, *J* = 5.7 Hz, 1H), 4.74 (d, *J* = 5.1 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 2.55 (d, *J* = 14.9 Hz, 1H), 2.33 – 2.11 (m, 3H), 1.96 (dtd, *J* = 24.1, 13.9, 11.7, 5.7 Hz, 1H), 1.75 – 1.56 (m, 1H), 1.40 – 1.29 (m, 1H), 1.26 (s, 3H), 1.09 (td, *J* = 11.6, 9.6, 4.1 Hz, 1H), 0.95 (s, 3H), 0.91 – 0.81 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 177.6, 160.2, 150.7, 131.5, 124.0, 120.3 (q, $J_{C\text{-}F}$ = 282.2 Hz), 112.7, 111.3, 72.9 (hept, *J* = 35.0 Hz), 55.4, 54.8, 51.5, 46.3, 43.7, 39.2, 38.7, 37.6, 28.2, 27.5, 22.2, 19.9. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -73.06. **HRMS** (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{22}H_{26}F_6NO_6S$ 546.1385; Found, 546.1389.



(2R)-4-((((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)sulfonyl)amino)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (48b):
The reaction was performed with condition A.
Physical appearance: colorless solid
Column material: 100-200 mesh silica
Eluent: Hexane/diethyl ether (95/5, v/v)
Yield: (32% from crude NMR) (15 mg, *dr* 6:1, isolated yield)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.28 – 5.16 (m, 1H), 5.14 – 4.97 (m, 1H), 4.82 (d, *J* = 4.8 Hz, 1H), 3.13 (qd, *J* = 7.3, 3.9 Hz, 2H), 2.34 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 1.82 (d, *J* = 6.7 Hz, 1H), 1.61 – 1.55 (m, 2H), 1.51 (dd, *J* = 13.2, 6.6 Hz, 2H), 1.32 (t, *J* = 7.3 Hz, 10H), 1.10 (ddt, *J* = 29.3, 7.5, 2.3 Hz, 6H), 0.87 (s, 3H), 0.86 (s, 9H), 0.83 (s, 3H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 171.4, 150.2, 140.6, 126.2, 124.8, 123.2, 121.6, 120.3 (q, $J_{C\text{-}F}$ = 283.5 Hz), 73.0 (hept, *J* = 35.3 Hz), 75.8, 75.6, 46.0, 39.5, 37.6, 37.5, 37.4, 37.4, 33.0, 32.8, 29.9, 28.1, 25.0, 24.6, 22.9, 22.8, 21.0, 20.6, 19.9, 19.7, 12.1, 8.7. **^{19}F NMR (377 MHz, CDCl$_3$)**

δ -73.1, -75.6. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{34}H_{52}F_6NO_6S$ 716.3425; Found, 716.3436.



1-Phenylethylamine (1bj):

The reaction was performed as described in the general procedure for post-synthetic functionalization.

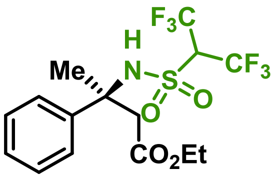
Physical appearance: colorless liquid

Column material: 100-200 mesh silica

Eluent: Hexane/ethyl acetate (40/60, v/v)

Yield: (86%, 38 mg, isolated yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 4.4 Hz, 4H), 7.16 (qq, *J* = 5.5, 3.0 Hz, 1H), 4.03 (q, *J* = 6.6 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 147.8, 128.5, 126.9, 125.7, 51.4, 25.7. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_{12}N$ 122.0964; Found, 122.0965.



Ethyl (S)-3-phenyl-3-((2,2,2-trifluoro-1-(trifluoromethyl)ethyl)sulfonamido)butanoate (50b):

The reaction was performed with condition B.

Physical appearance: colourless gummy liquid

Column material: 100-200 mesh silica

Eluent: Hexane/ethyl acetate (80/20, v/v)

Yield: (45%, 68% *ee*, 19 mg, isolated yield)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 5.20 (p, *J* = 5.7 Hz, 1H), 4.08 (qd, *J* = 7.1, 1.4 Hz, 2H), 3.07 – 2.79 (m, 2H), 1.87 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 171.5, 142.9, 128.8, 128.0, 125.1, 120.3 (q, $J_{C\text{-}F}$ = 284.8 Hz), 72.8 (hept, *J* = 35.3 Hz), 61.5, 61.4, 46.3, 26.3, 14.0. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -72.9. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{15}H_{16}F_6NO_3S$ 404.0761; Found, 404.0764.

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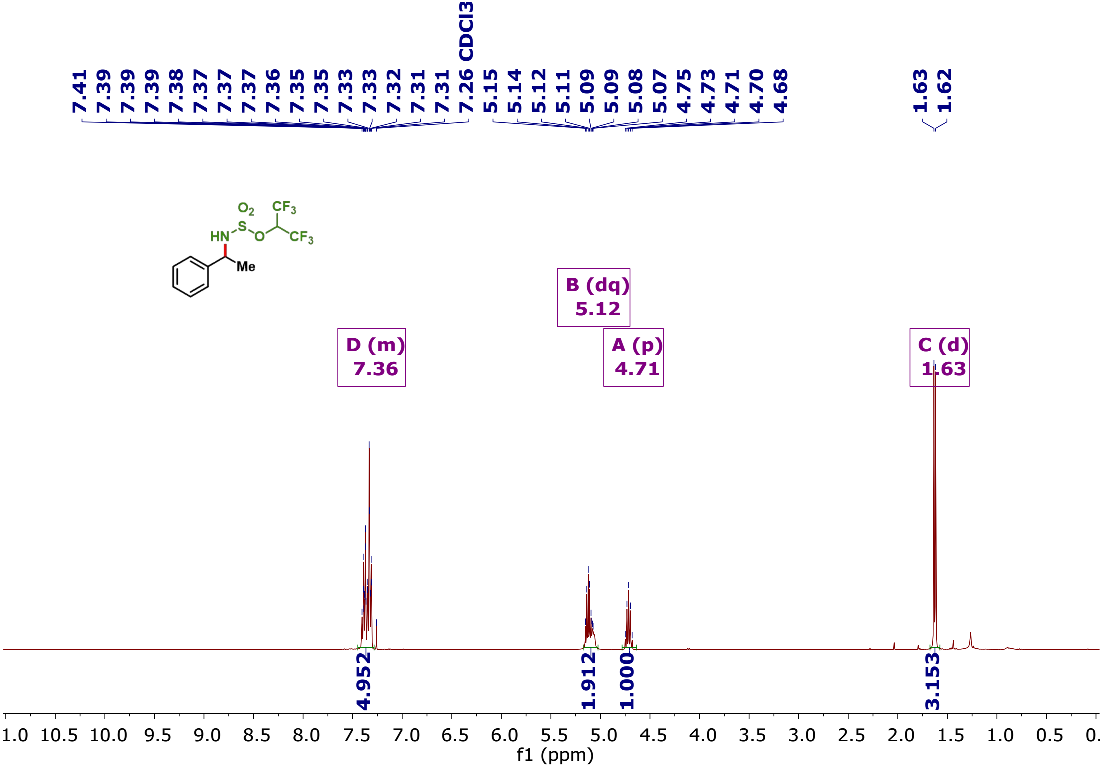
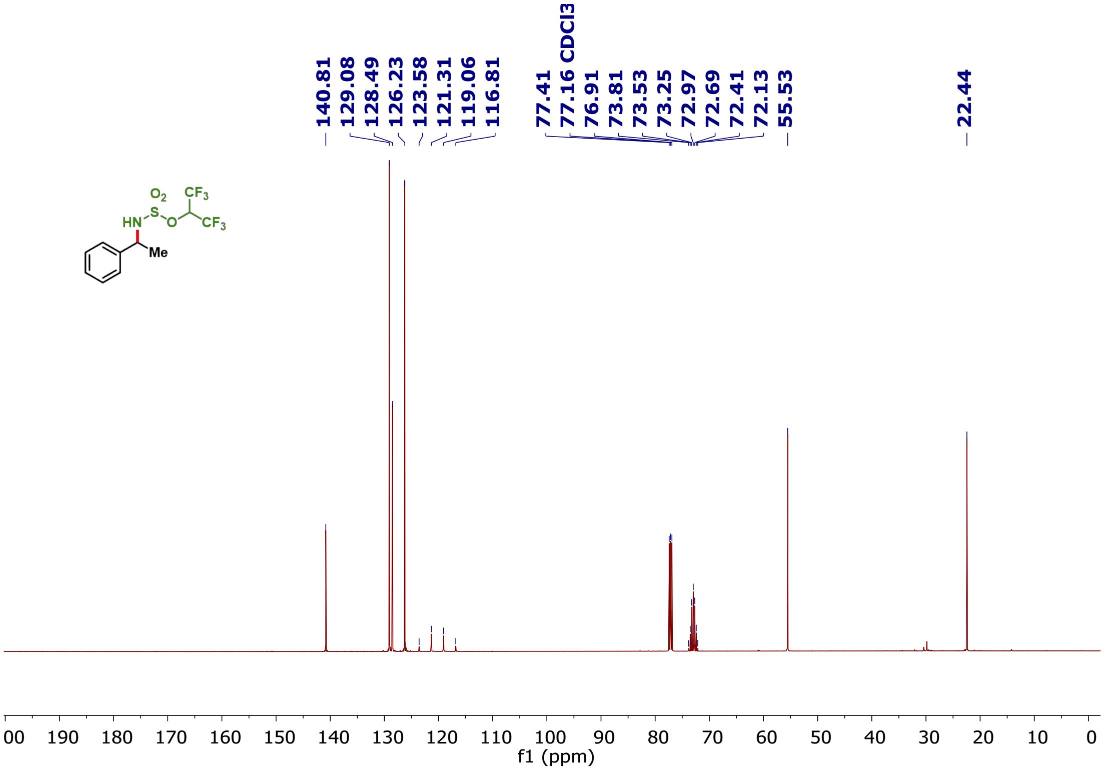
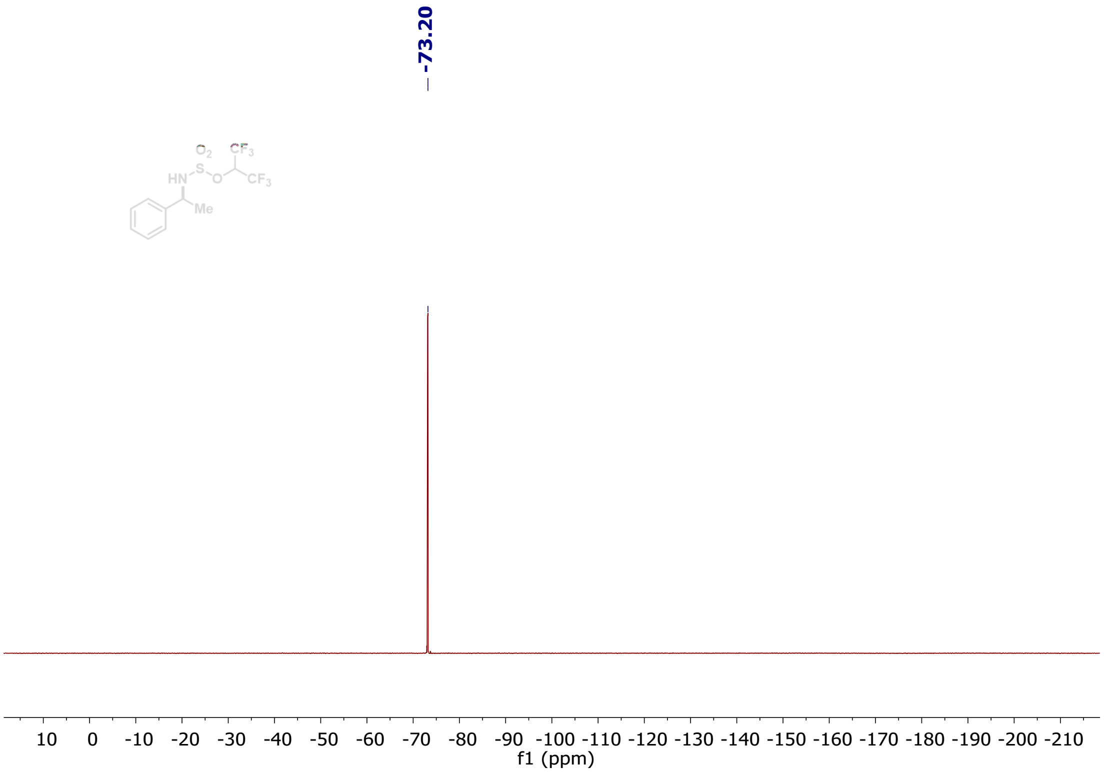
7. NMR spectra of the synthesized compounds.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 1b



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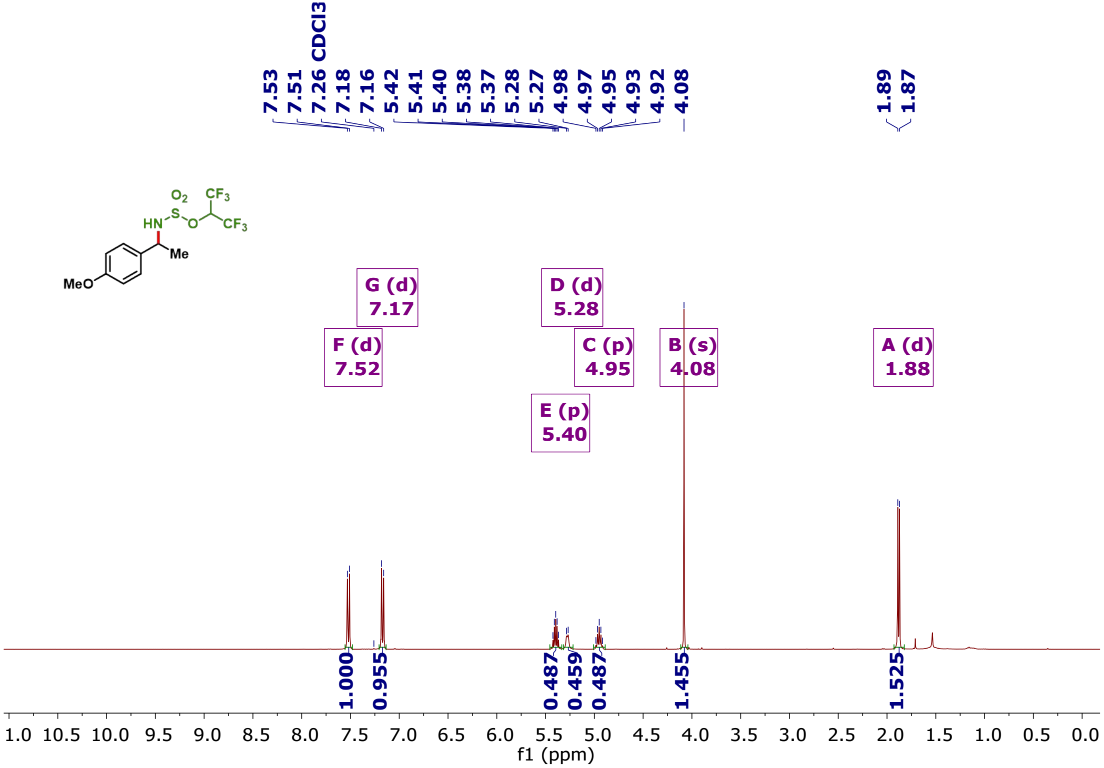
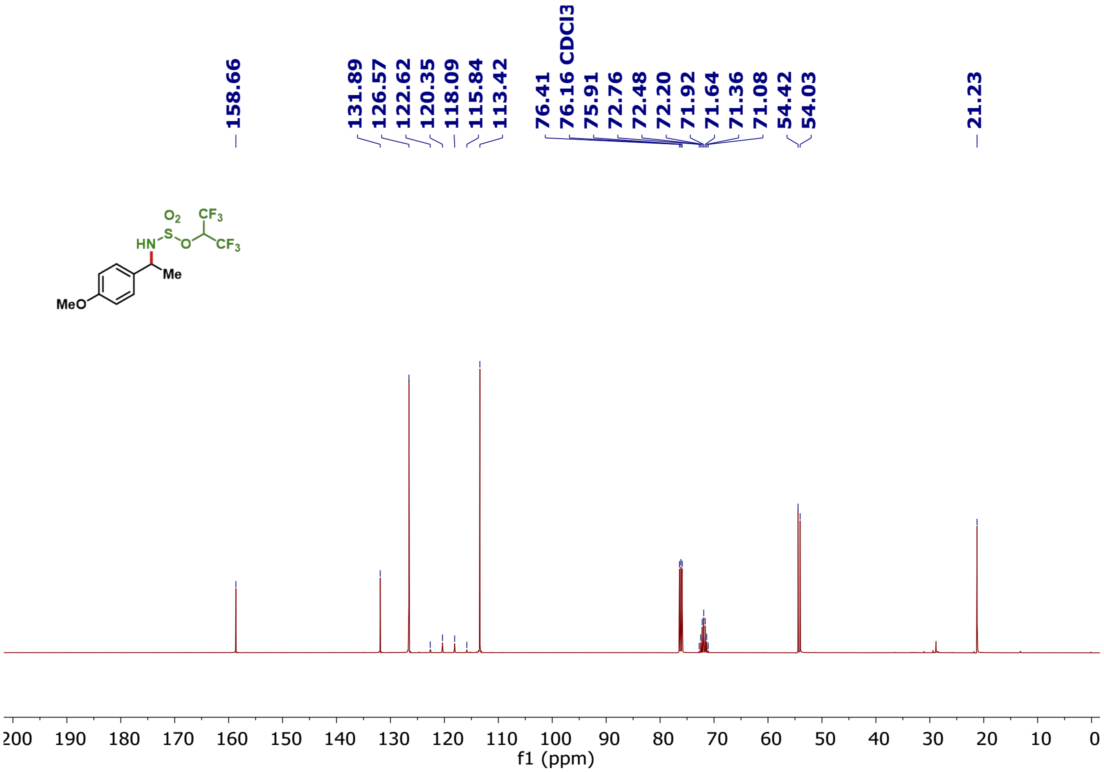
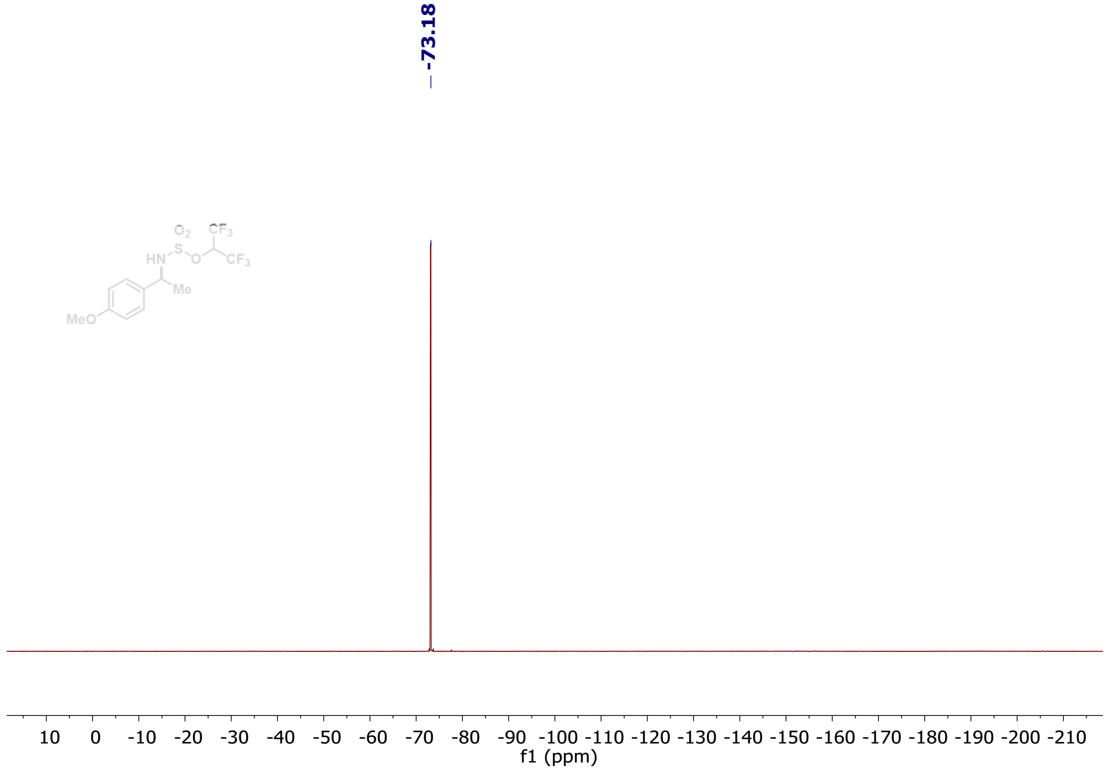
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 2b



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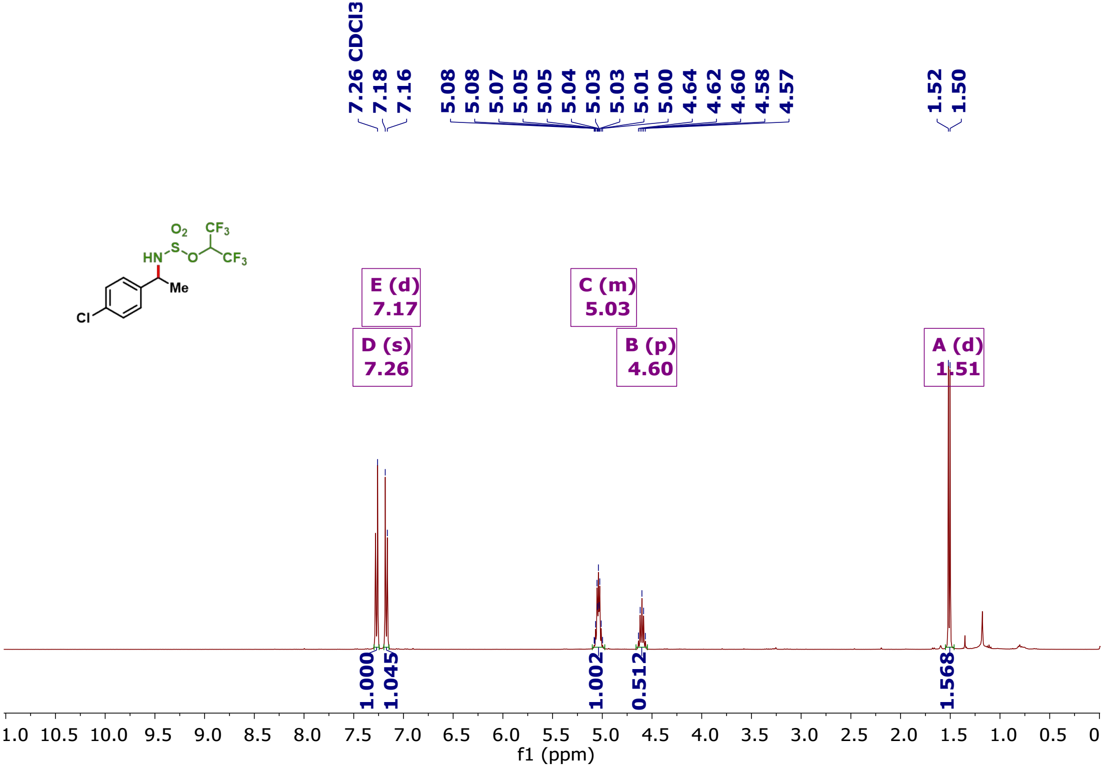
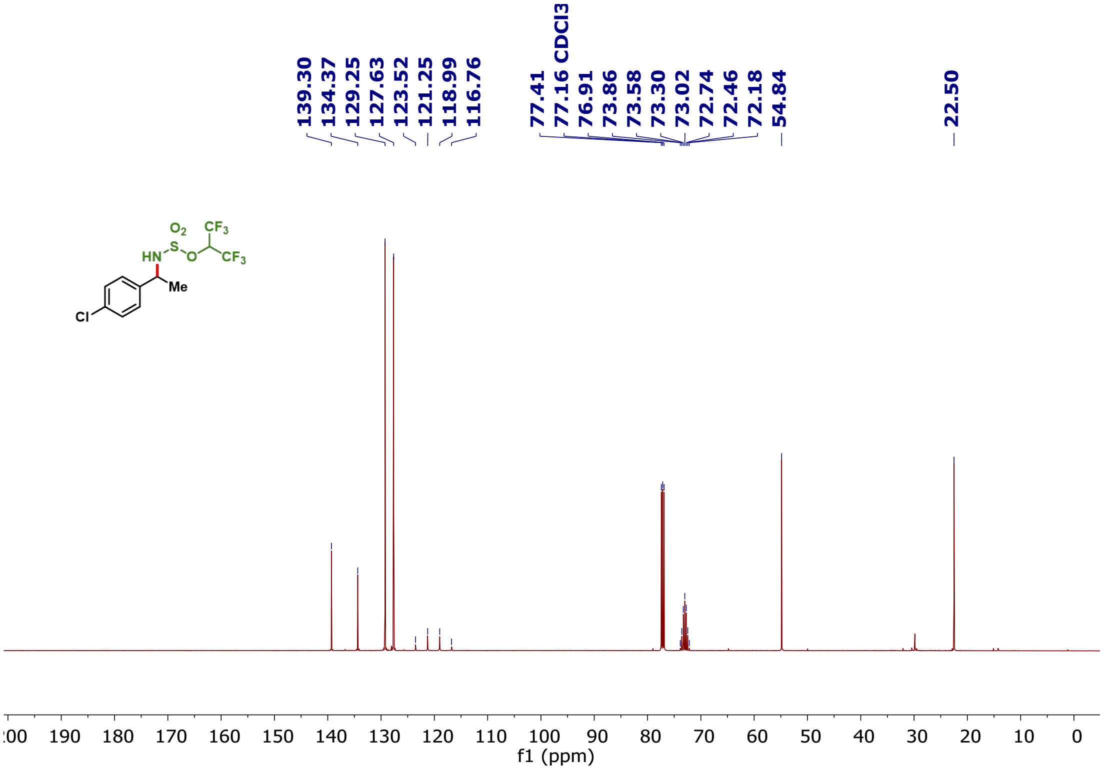
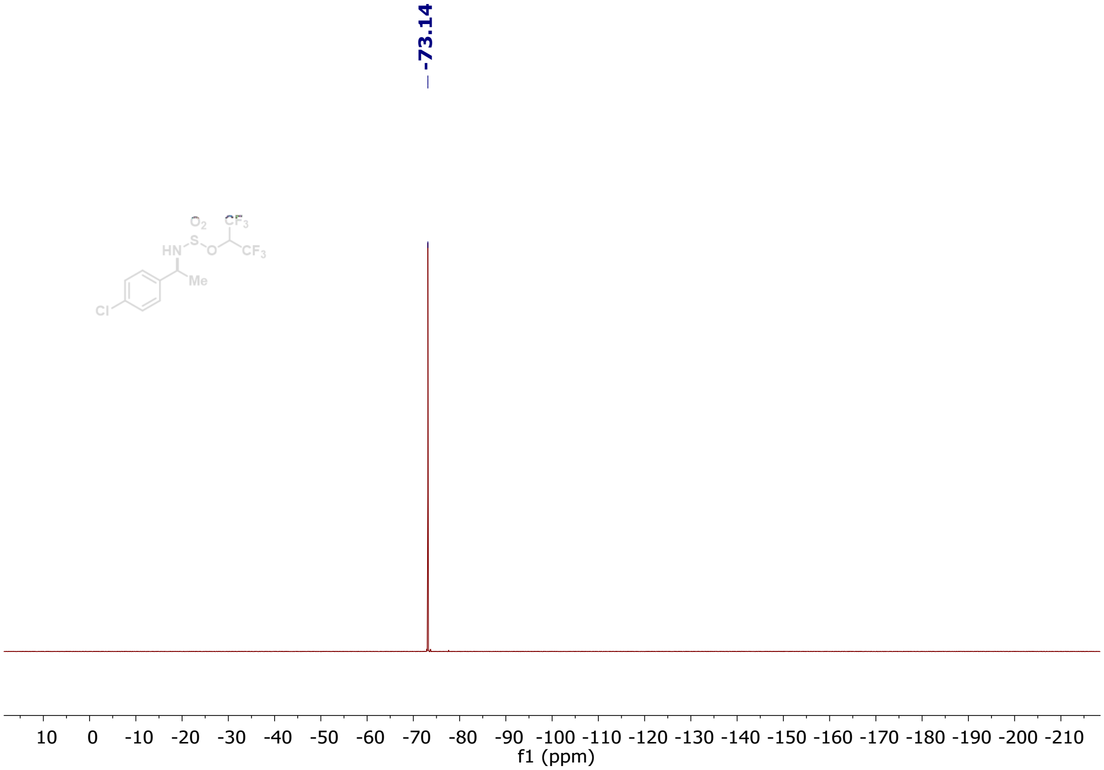
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 3b



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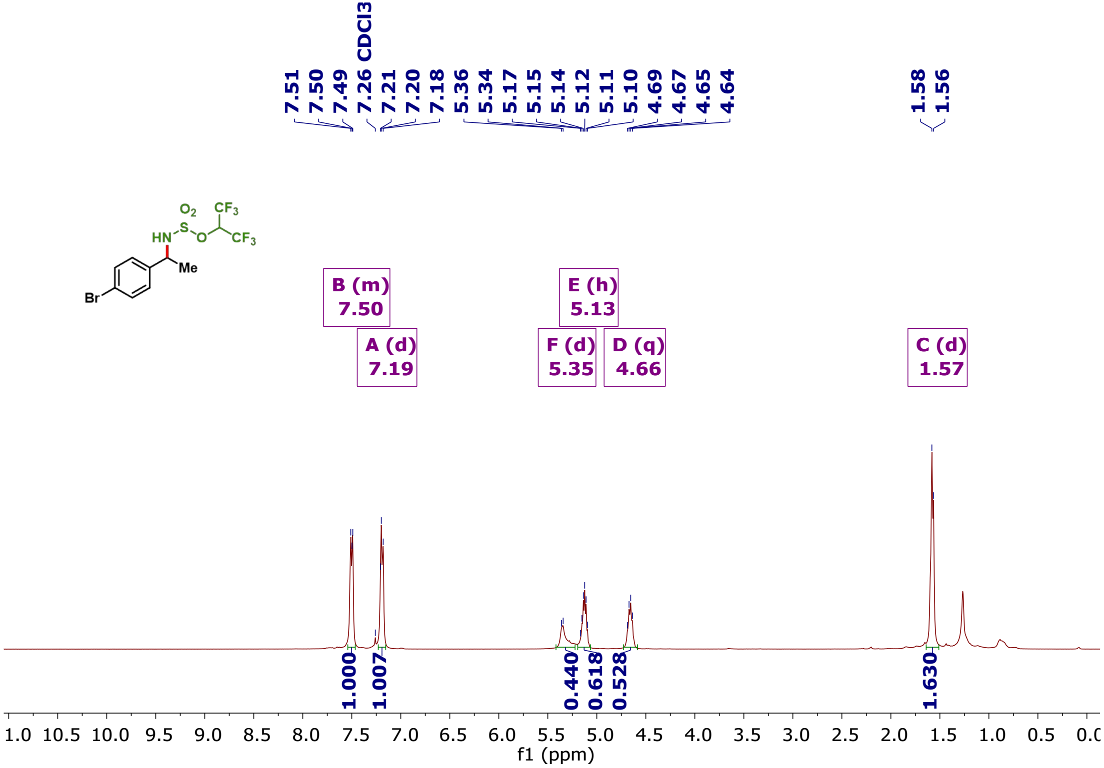
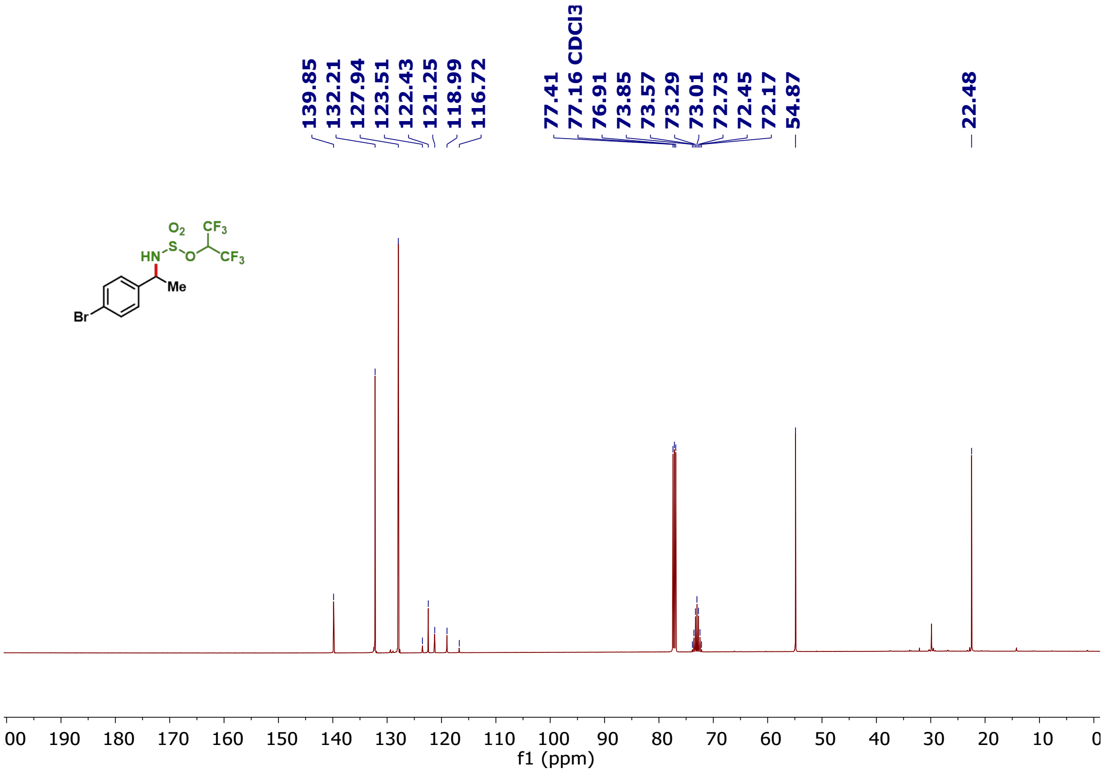
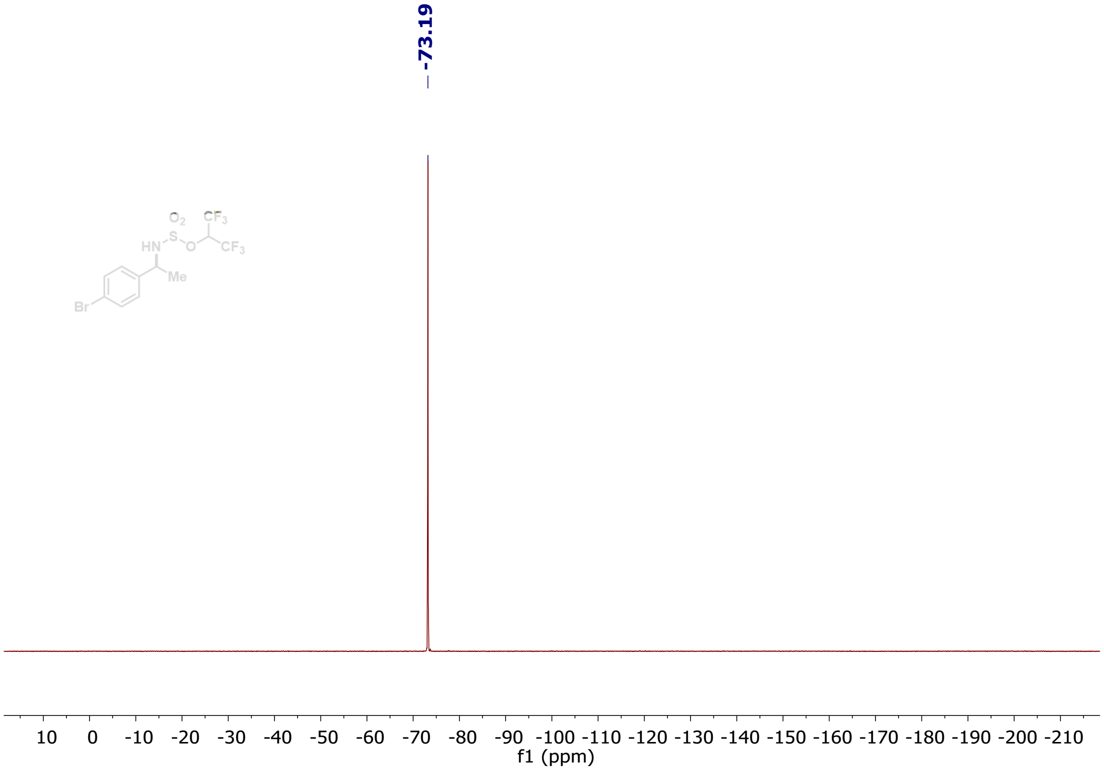
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 4b



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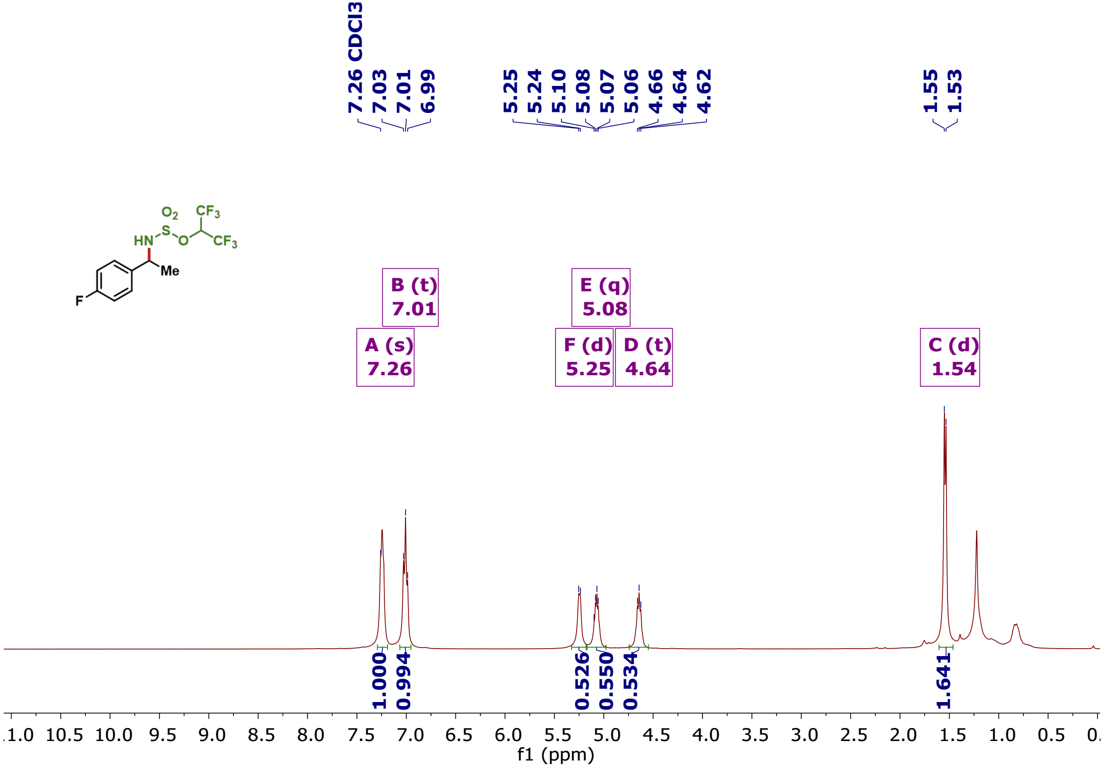
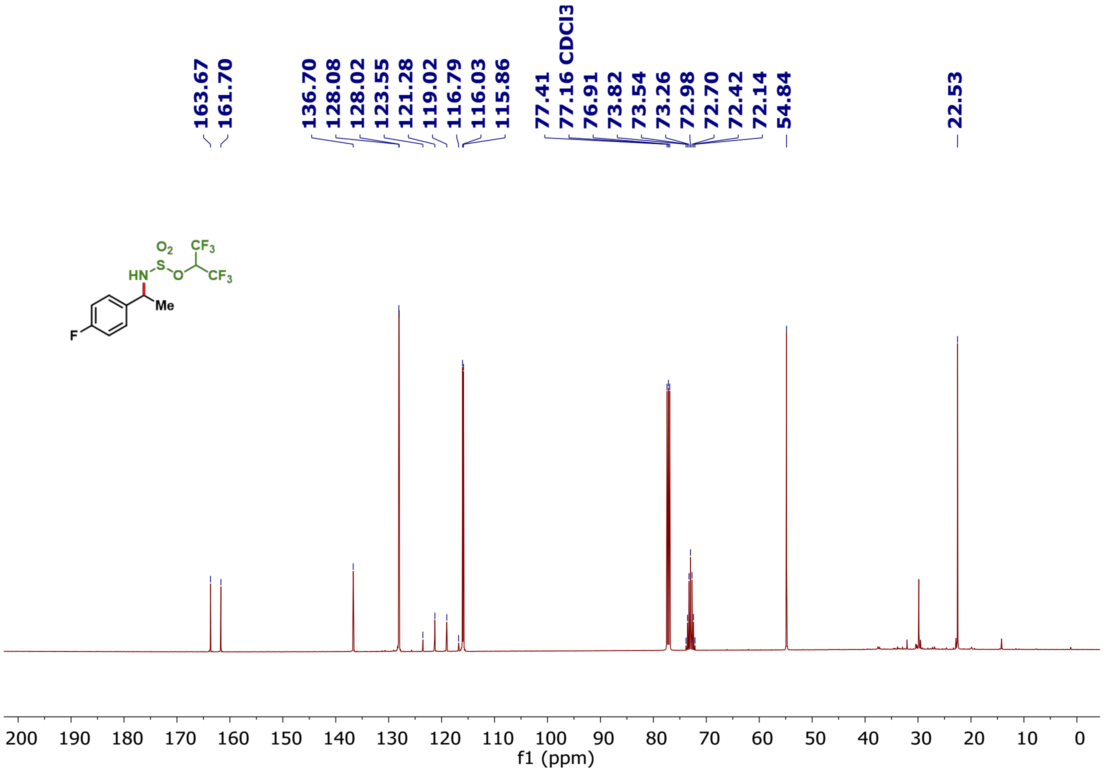
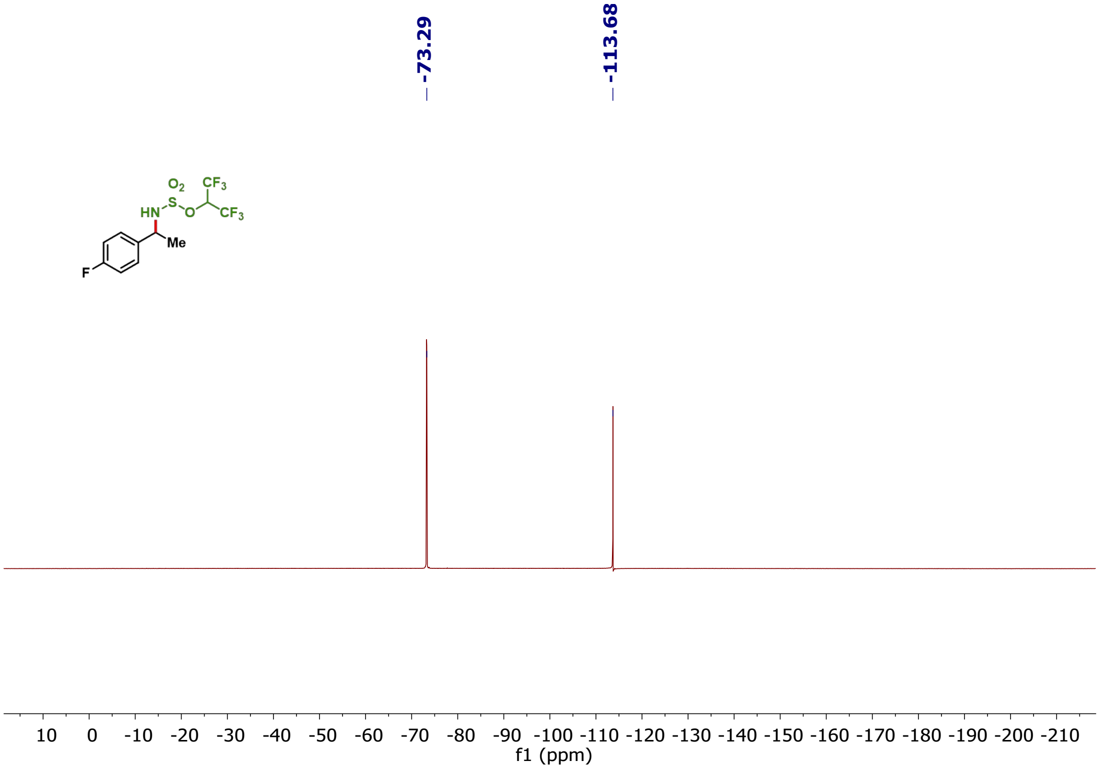
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 5b







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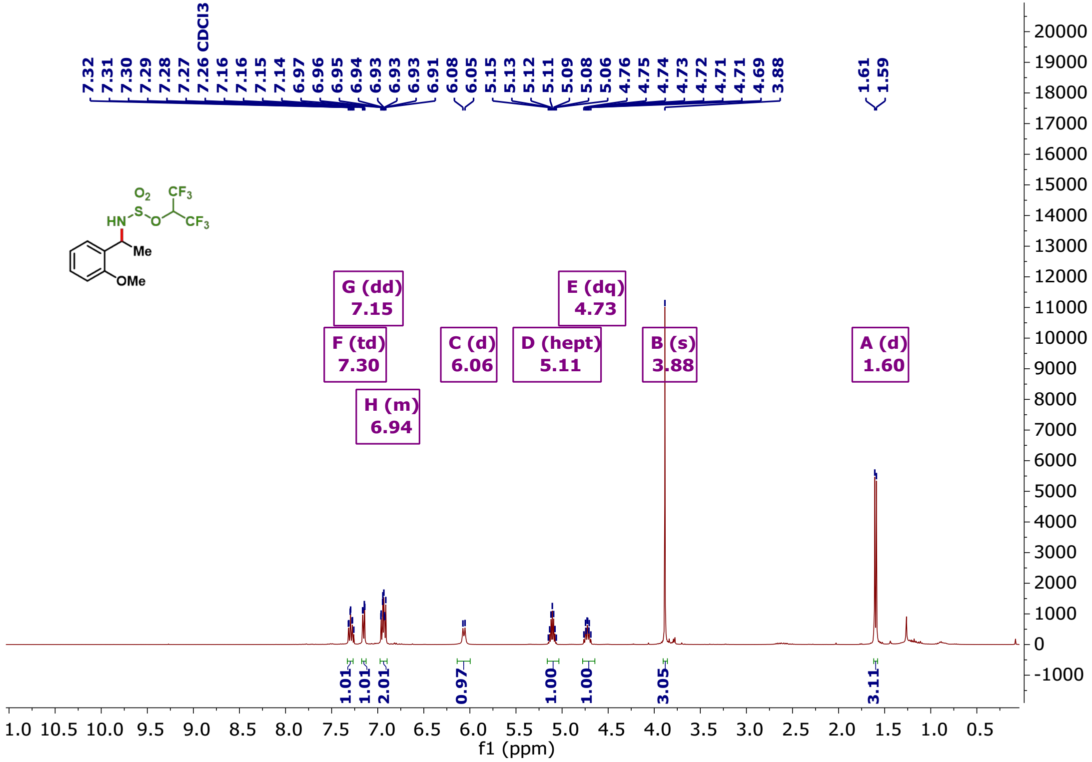
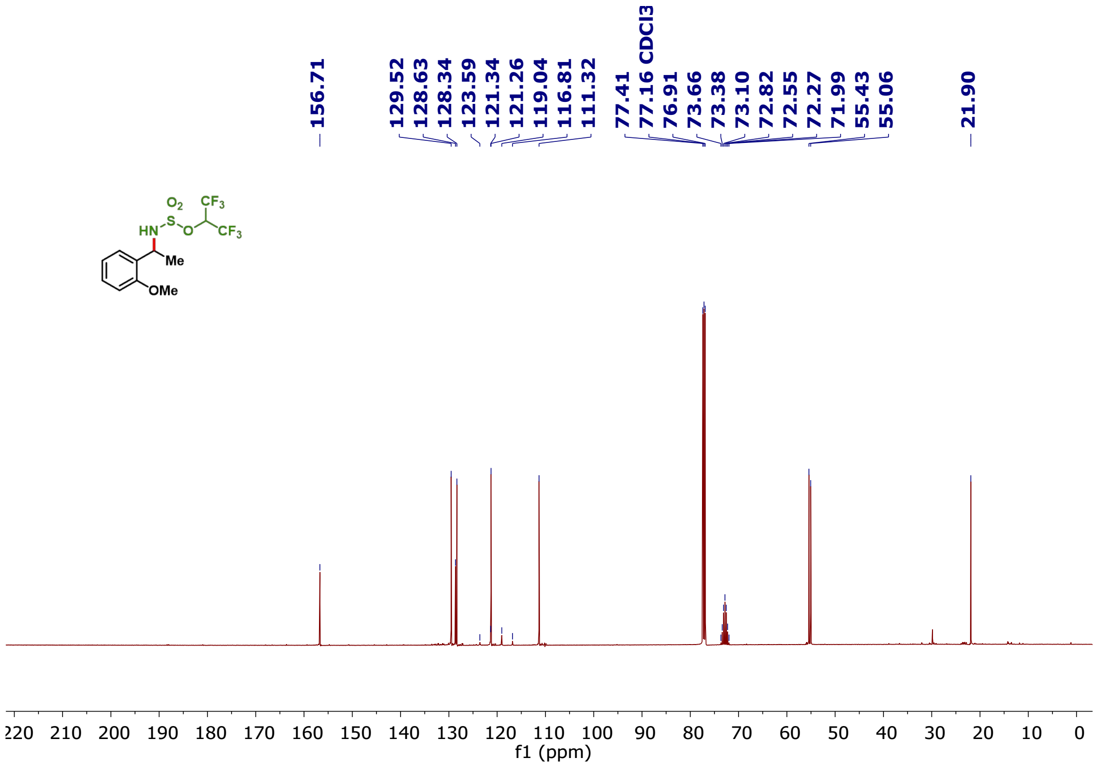
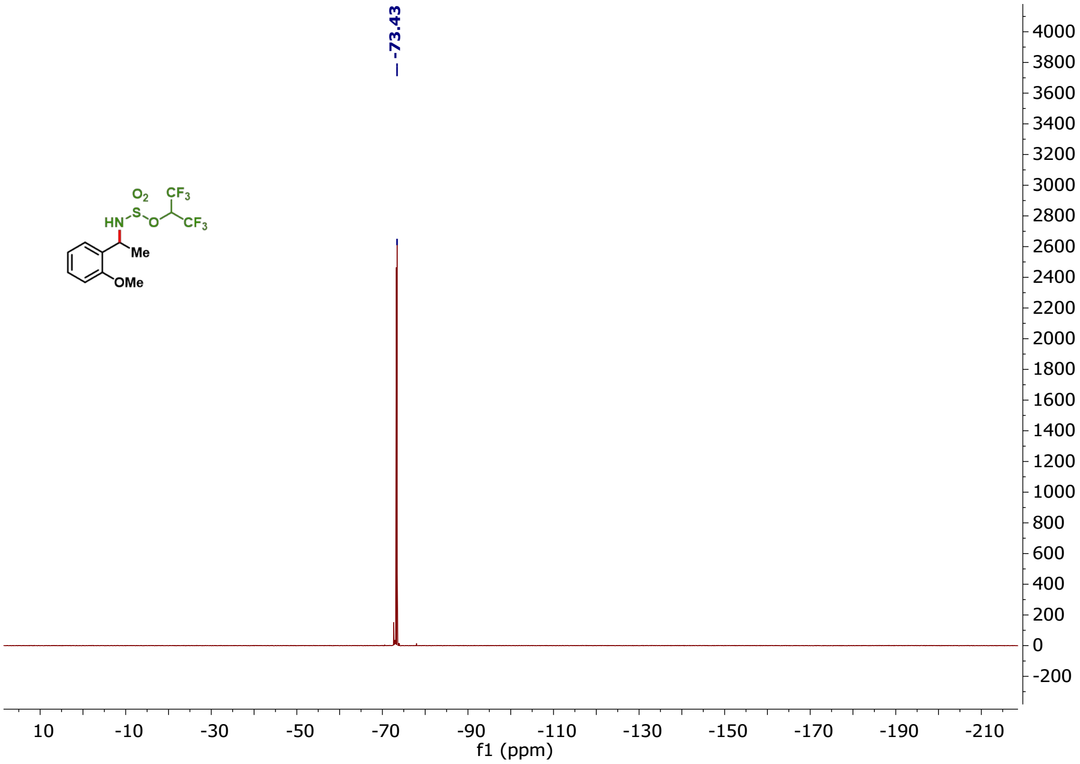
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 6b



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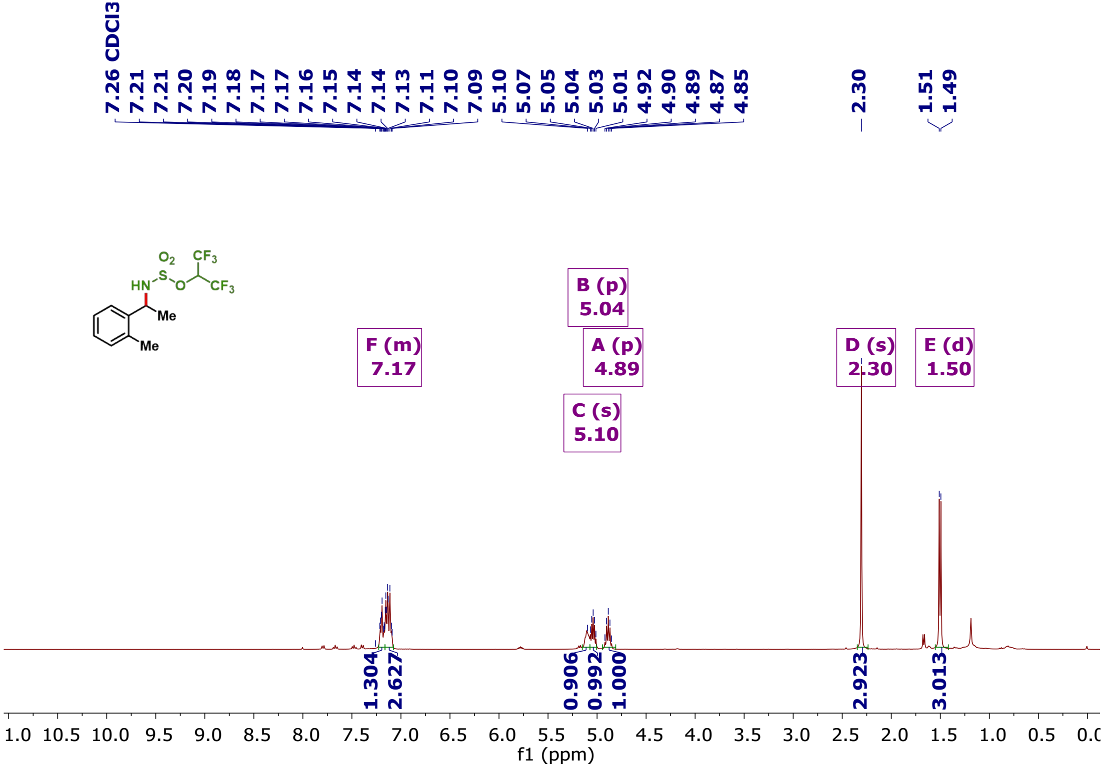
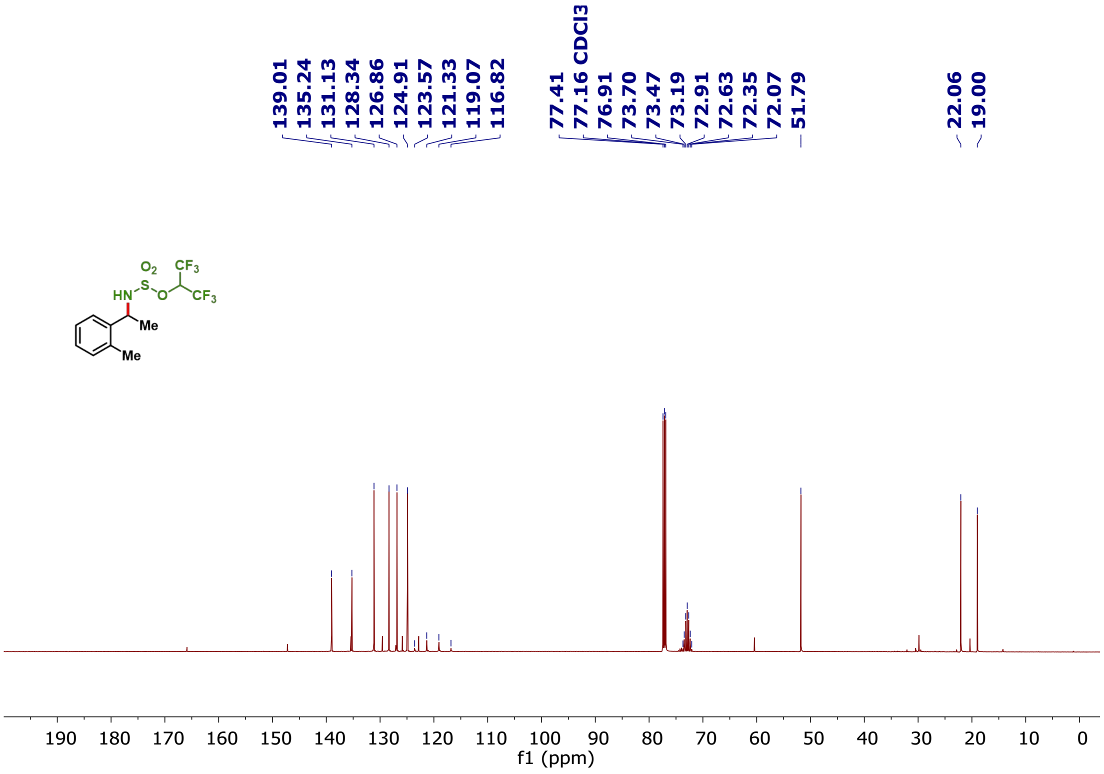
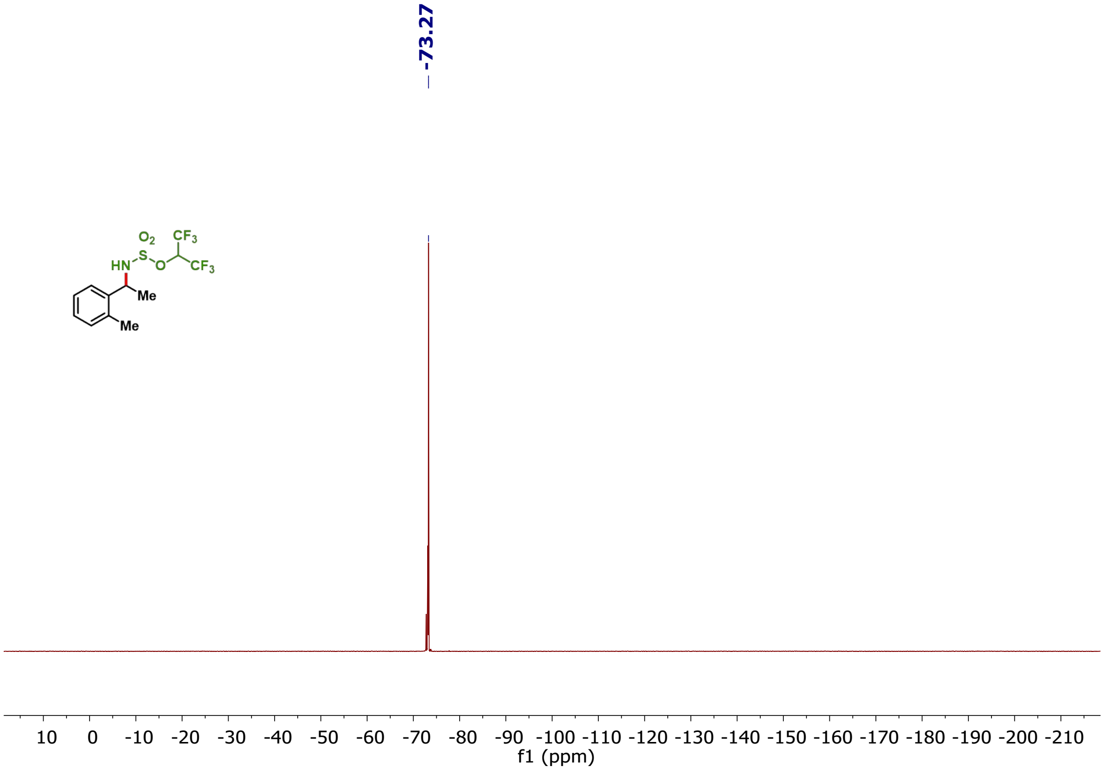
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 7b



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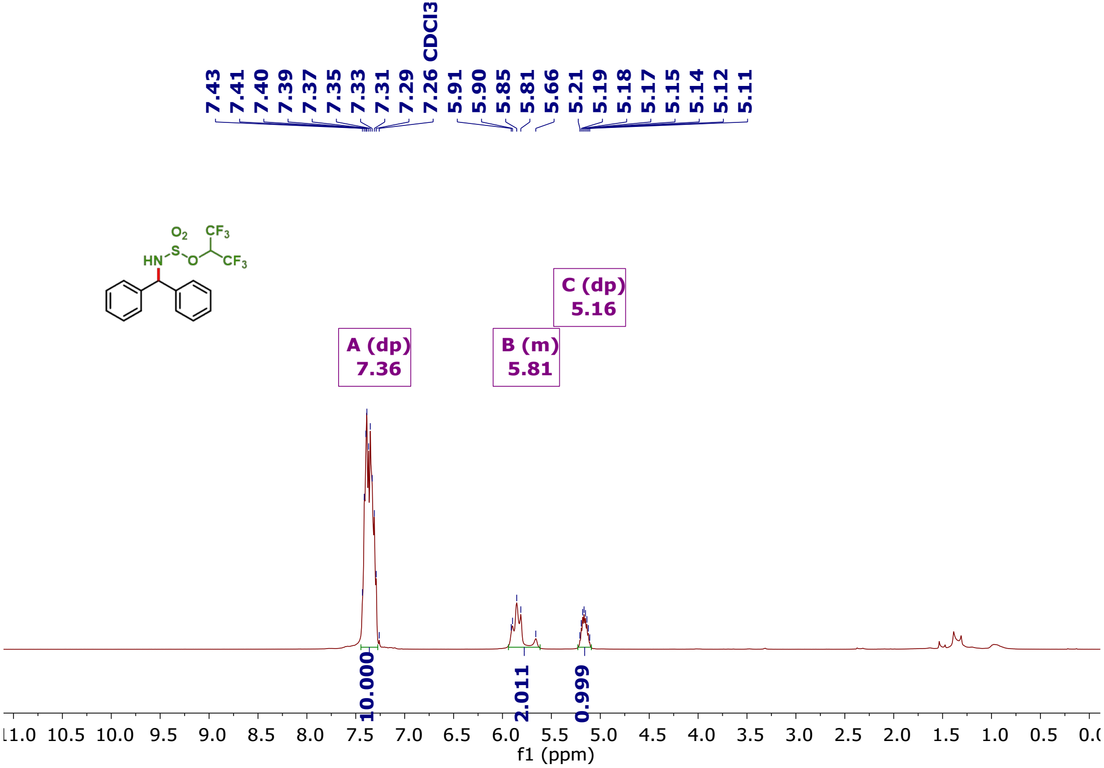
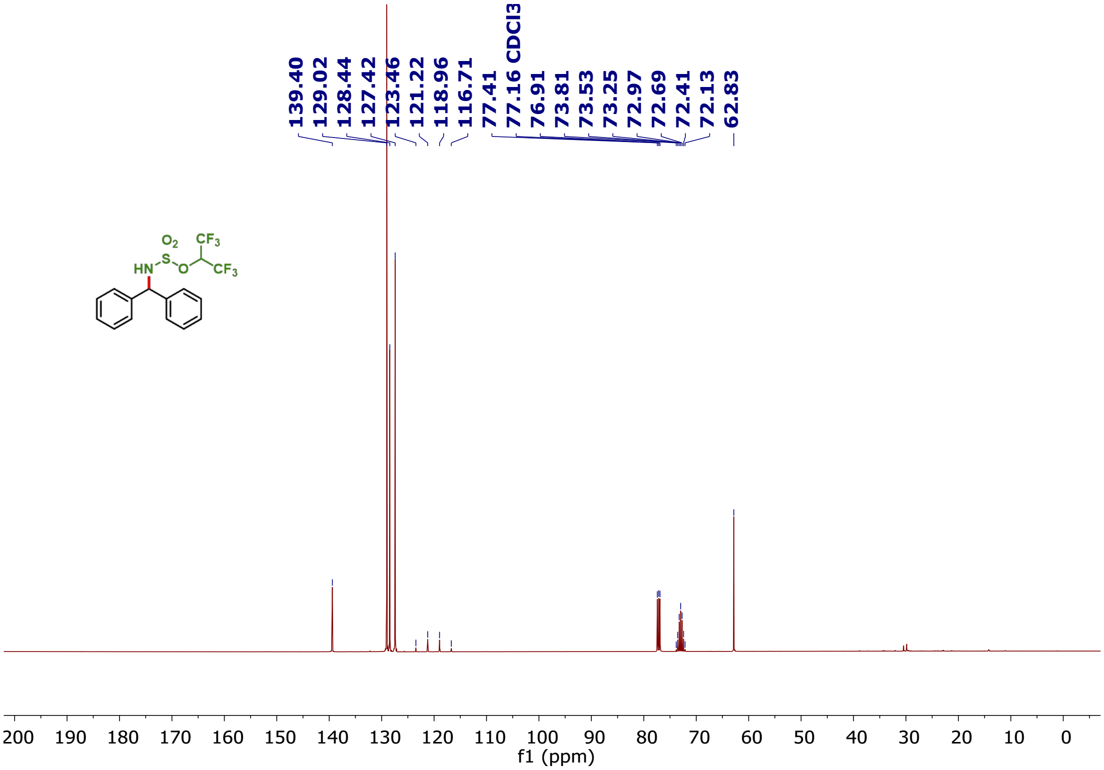
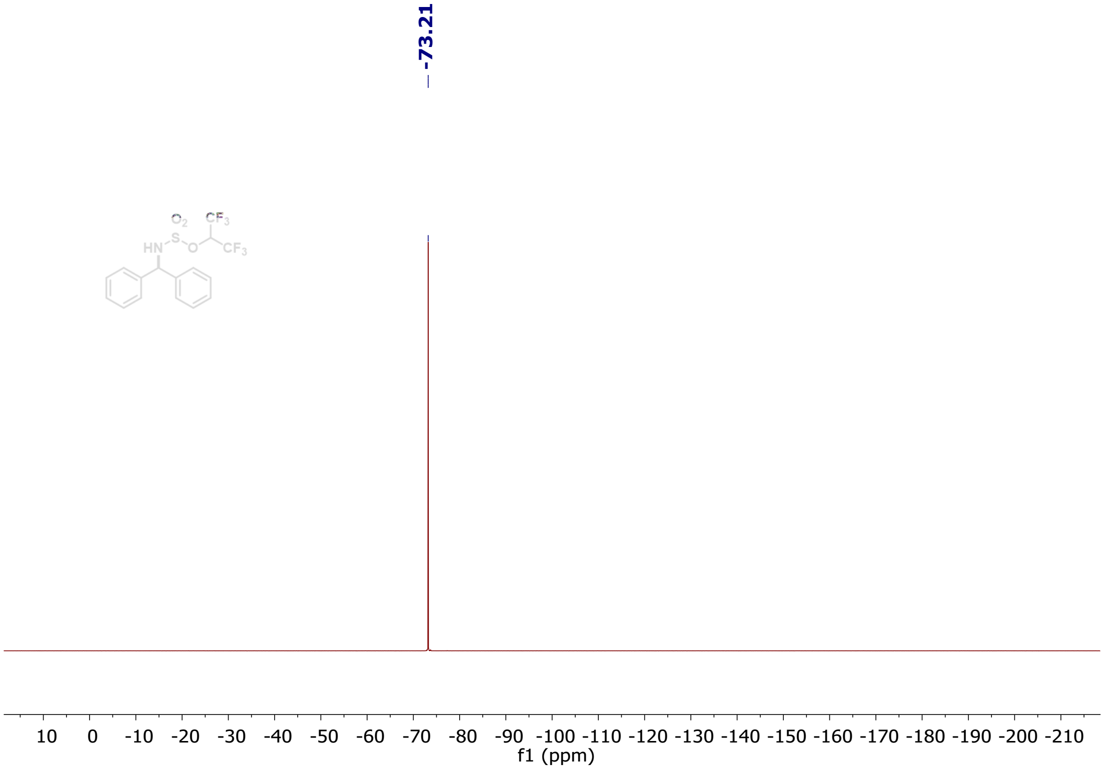
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 8b



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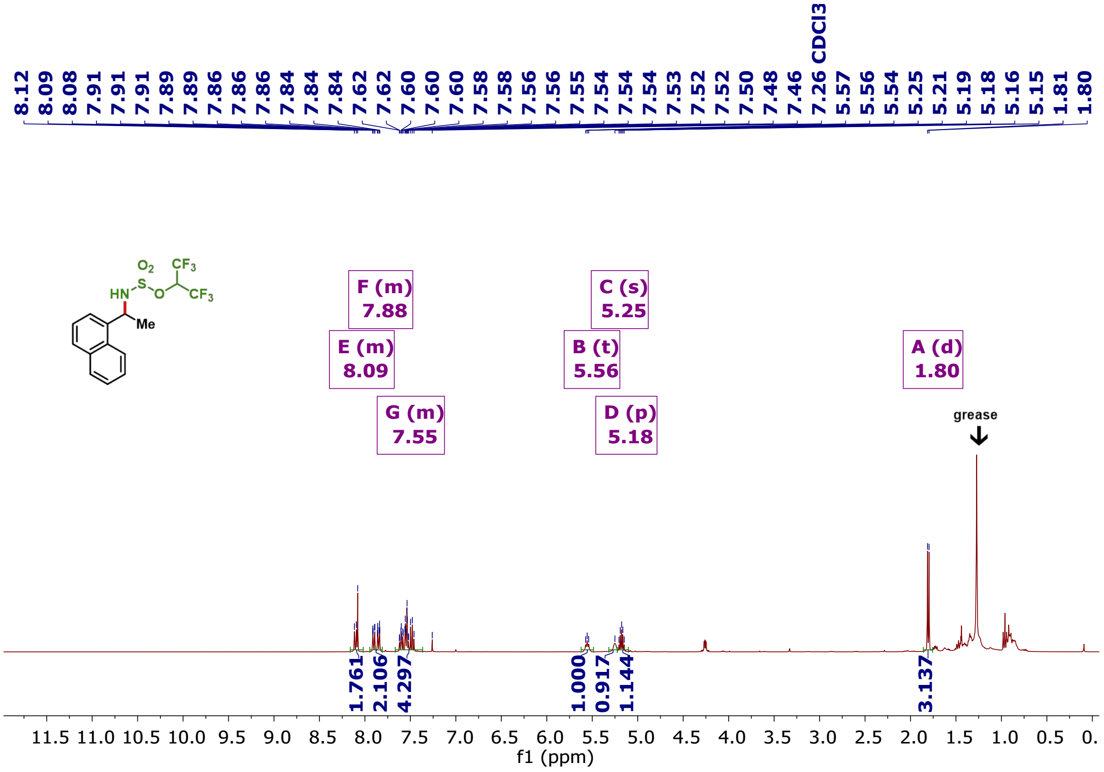
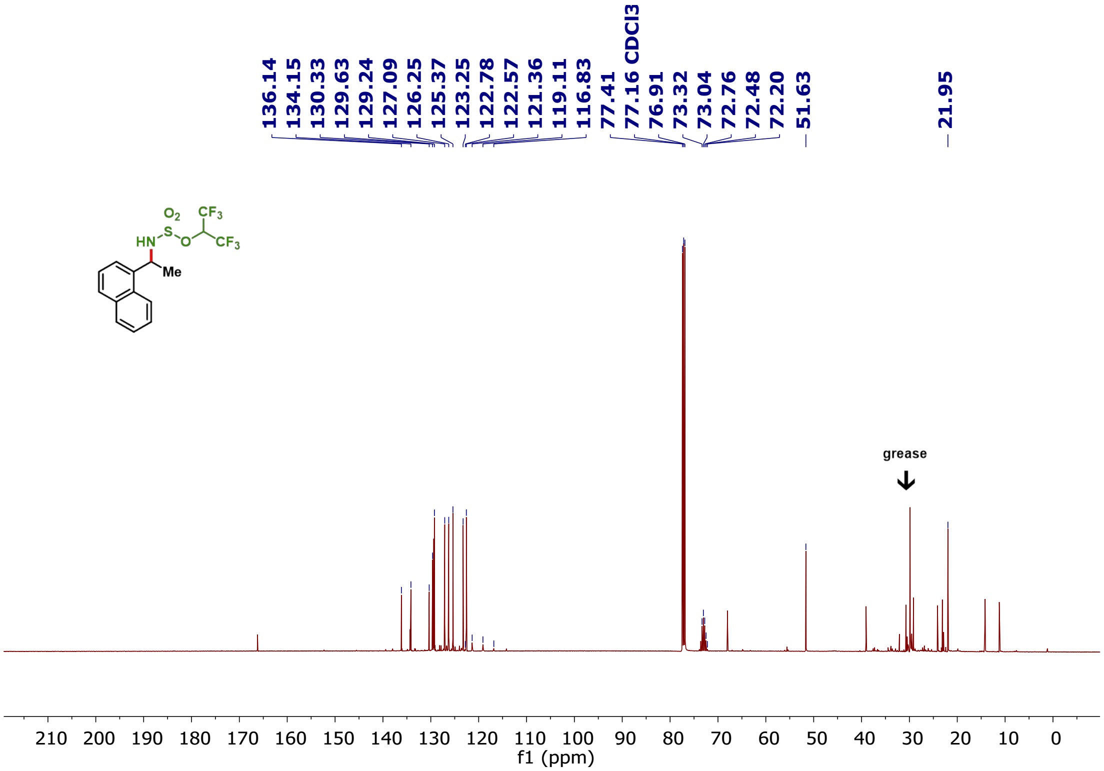
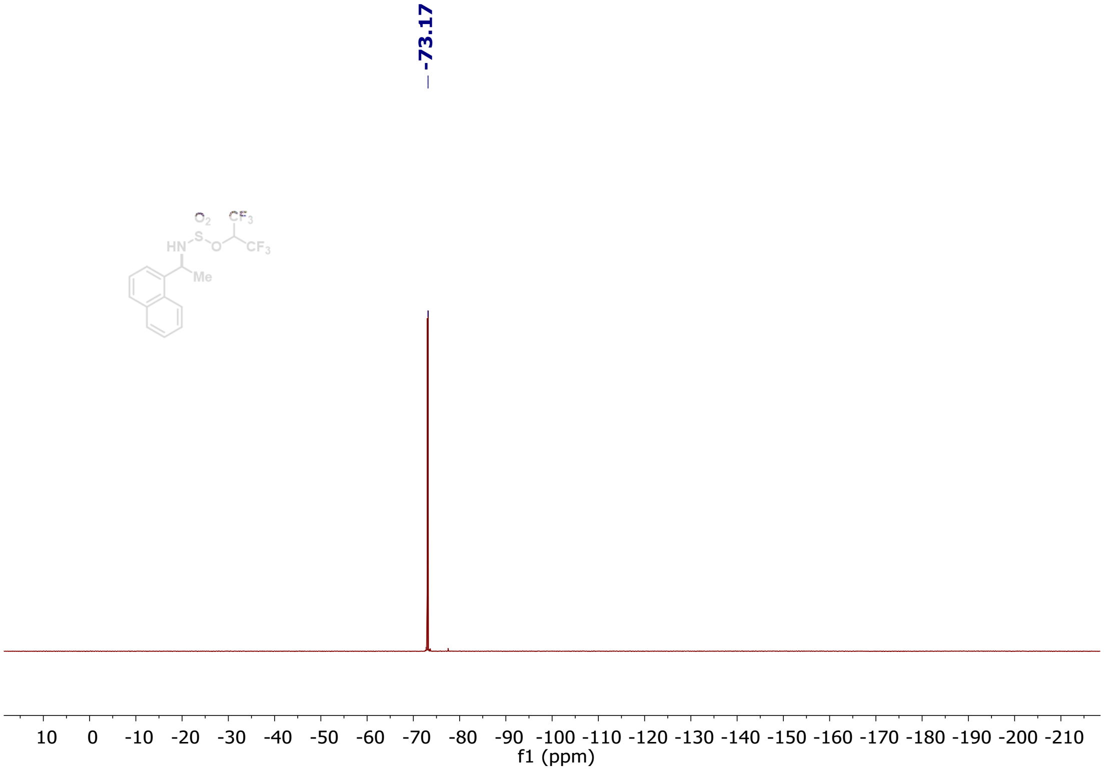
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 9b



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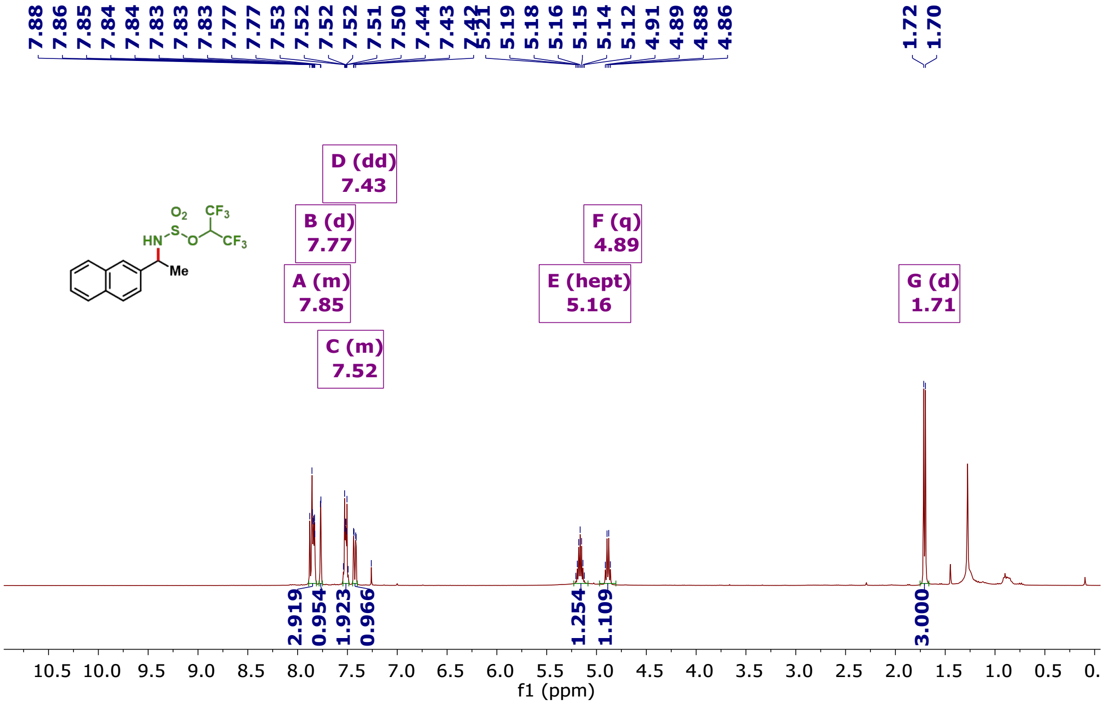
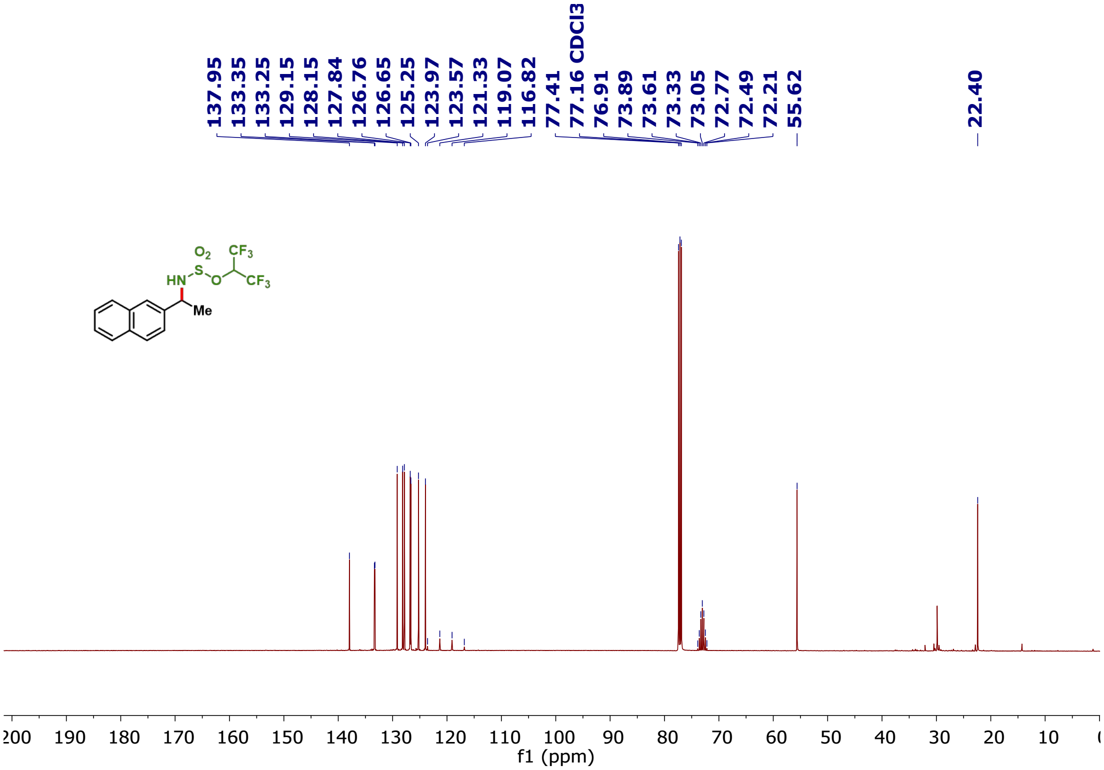
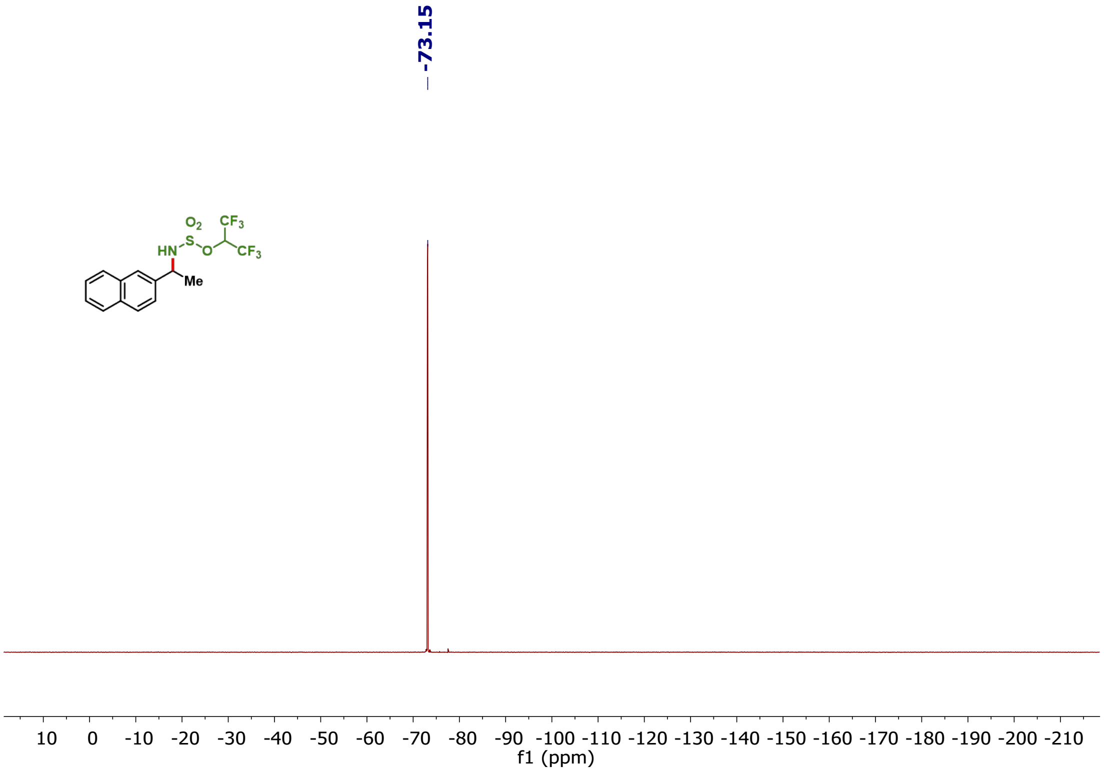
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 10b



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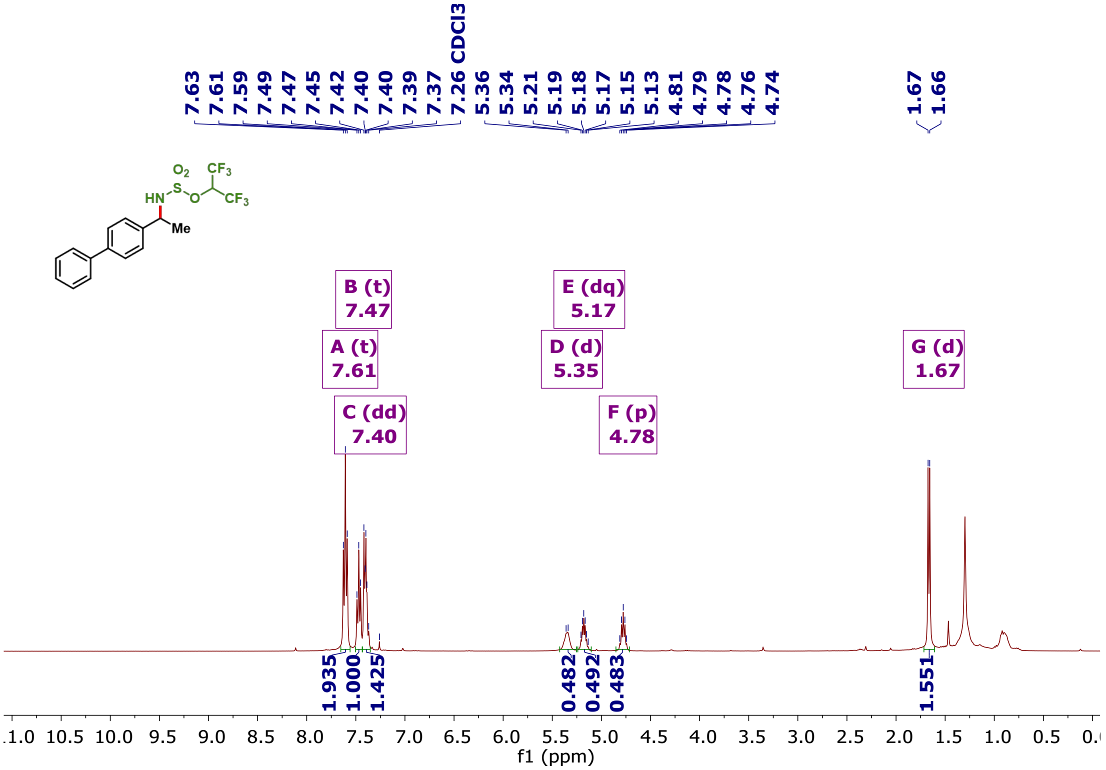
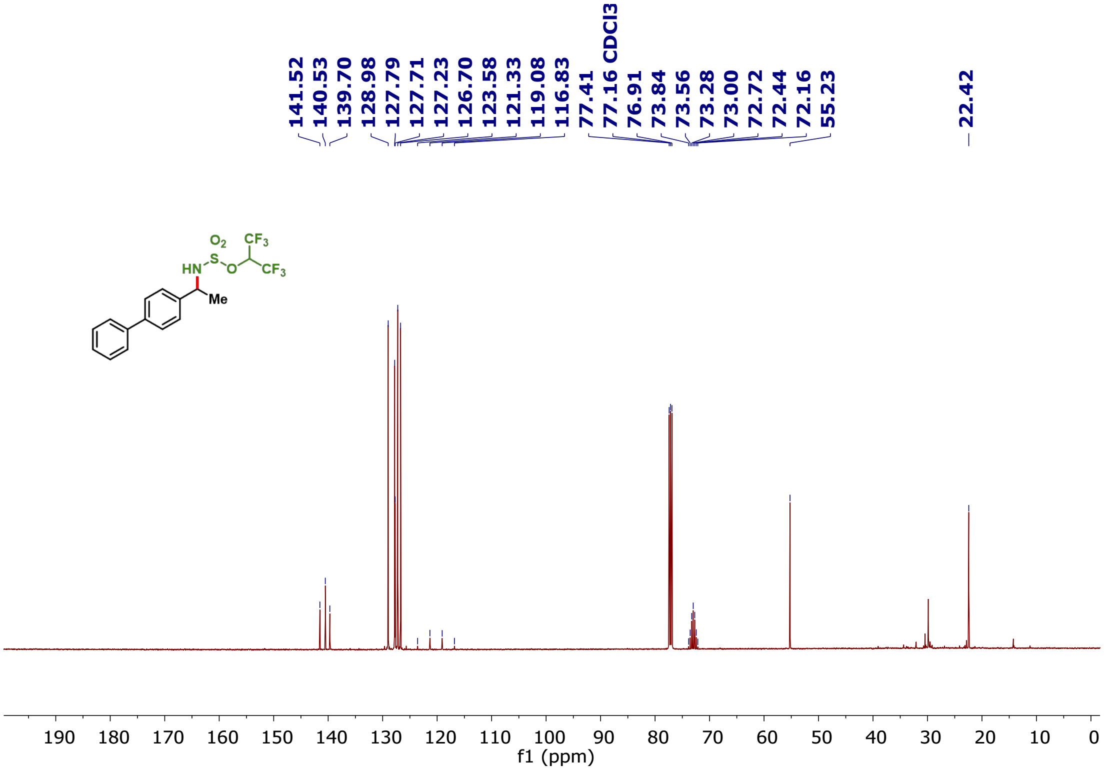
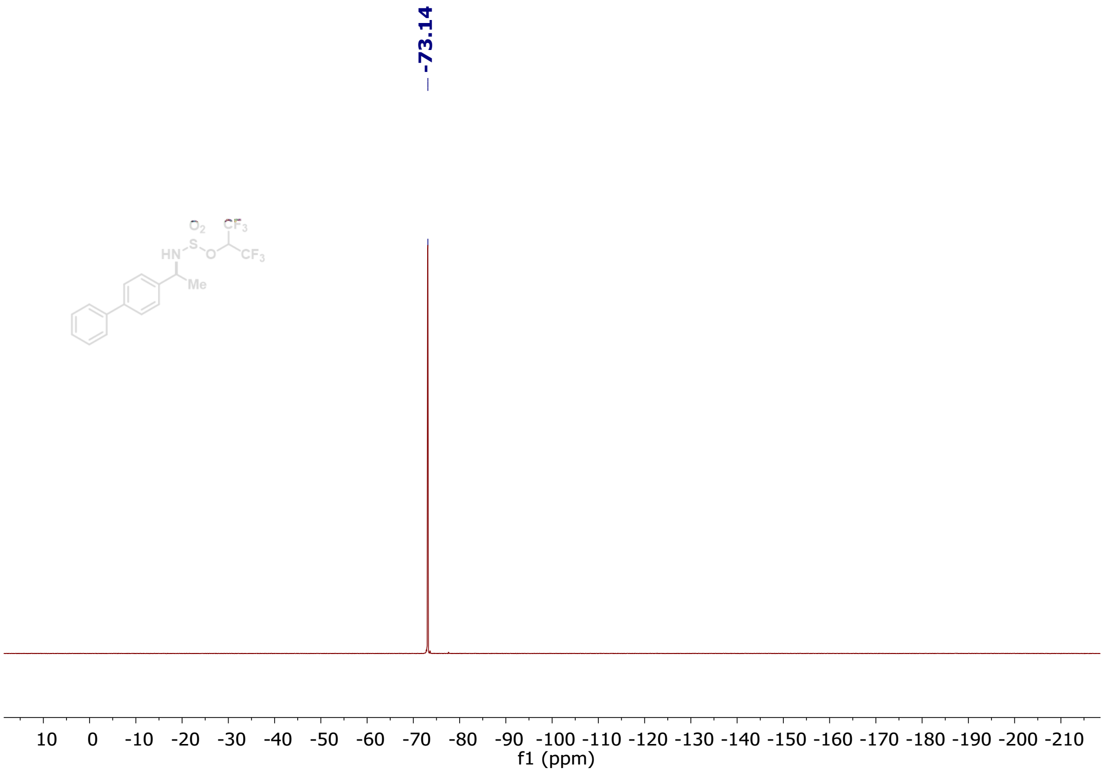
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 11b



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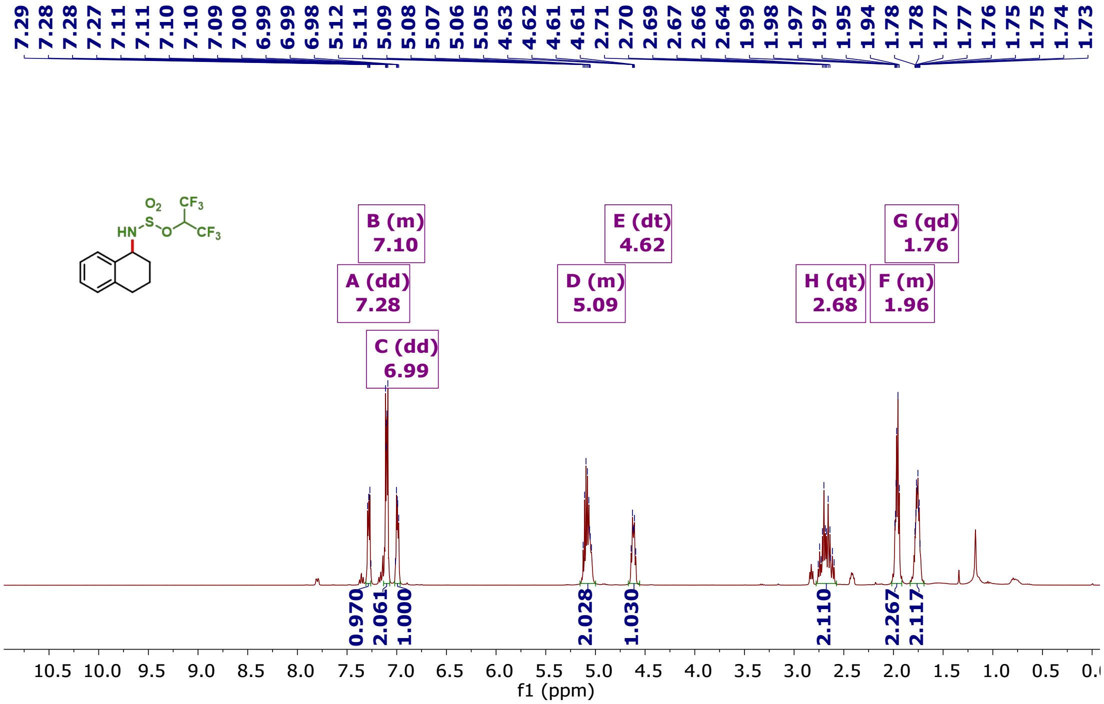
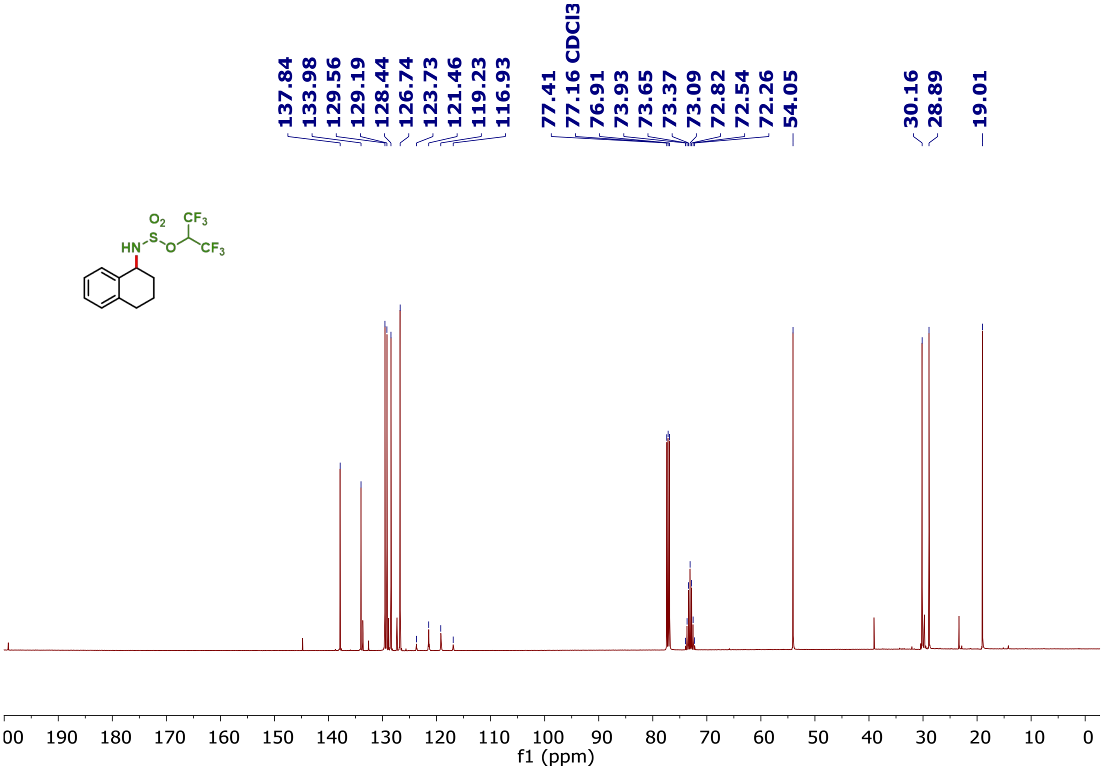
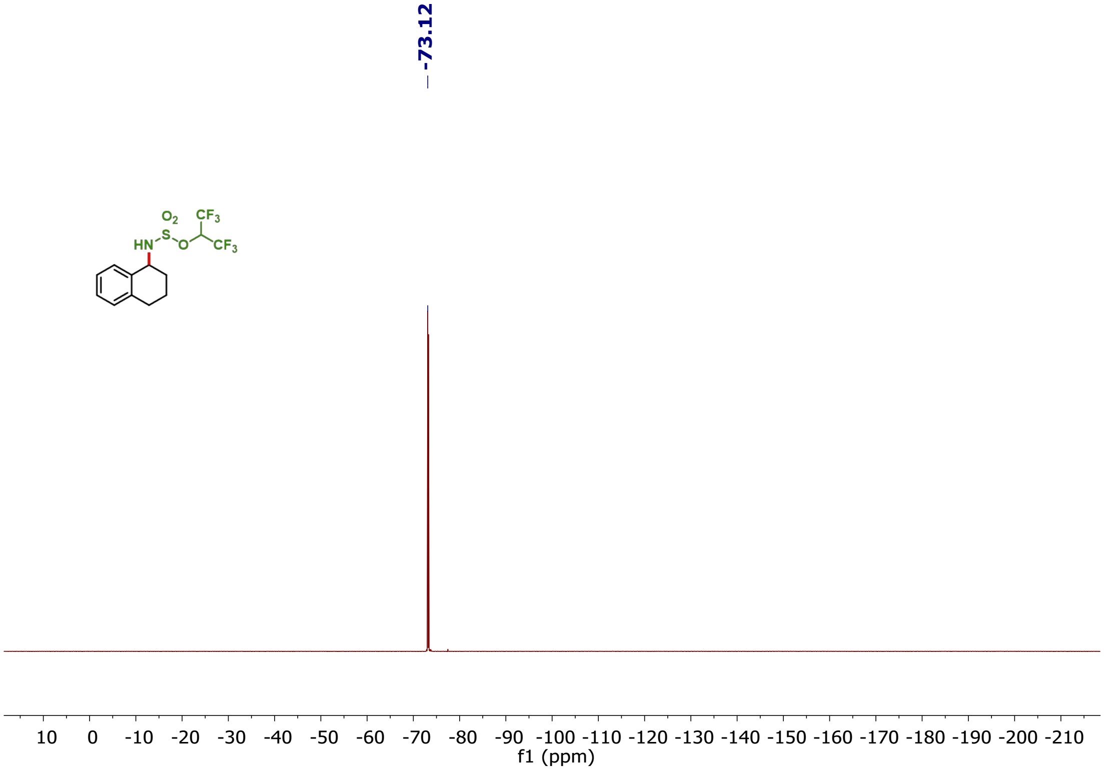
CF3
HN
S
O
CF3
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 12b



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S
HN
O
CF_3
CF_3
10
0
-10
-20
-30
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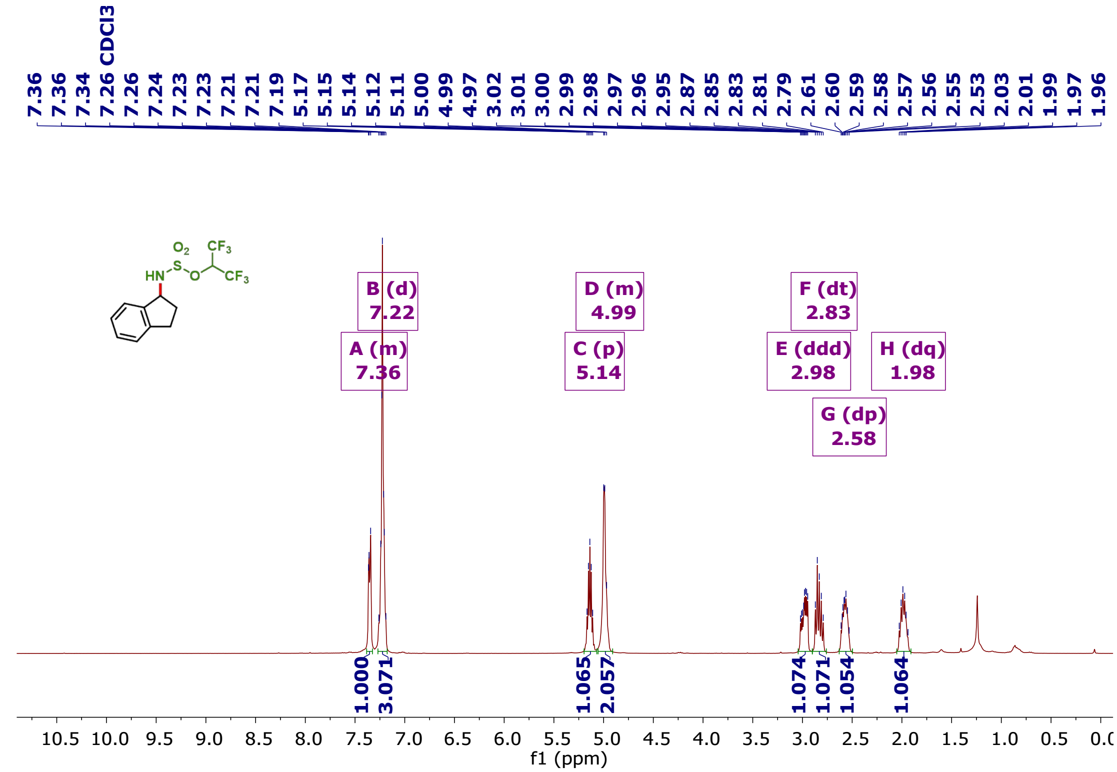
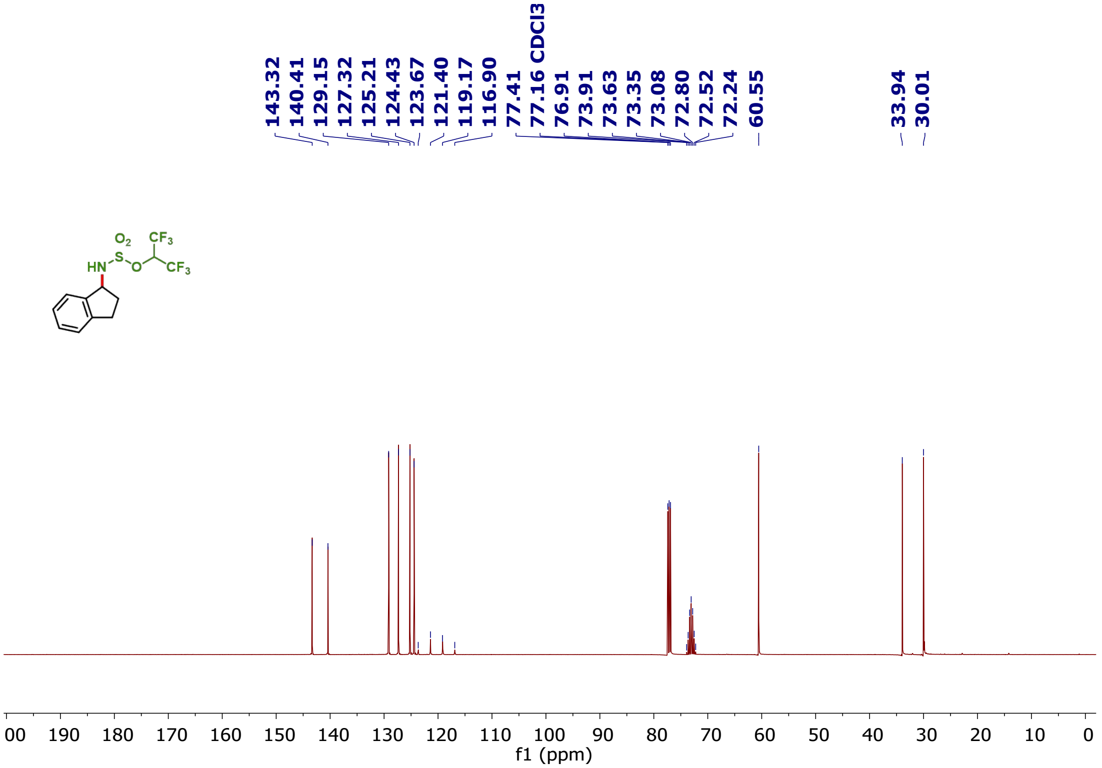
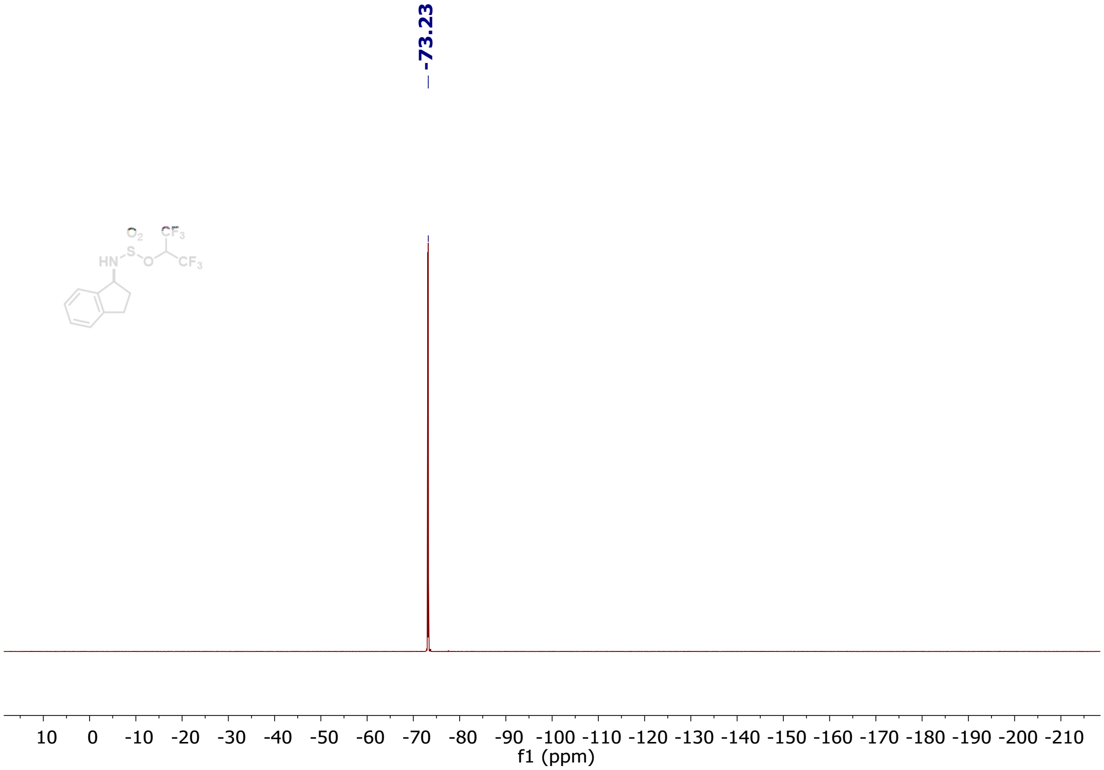
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 13b



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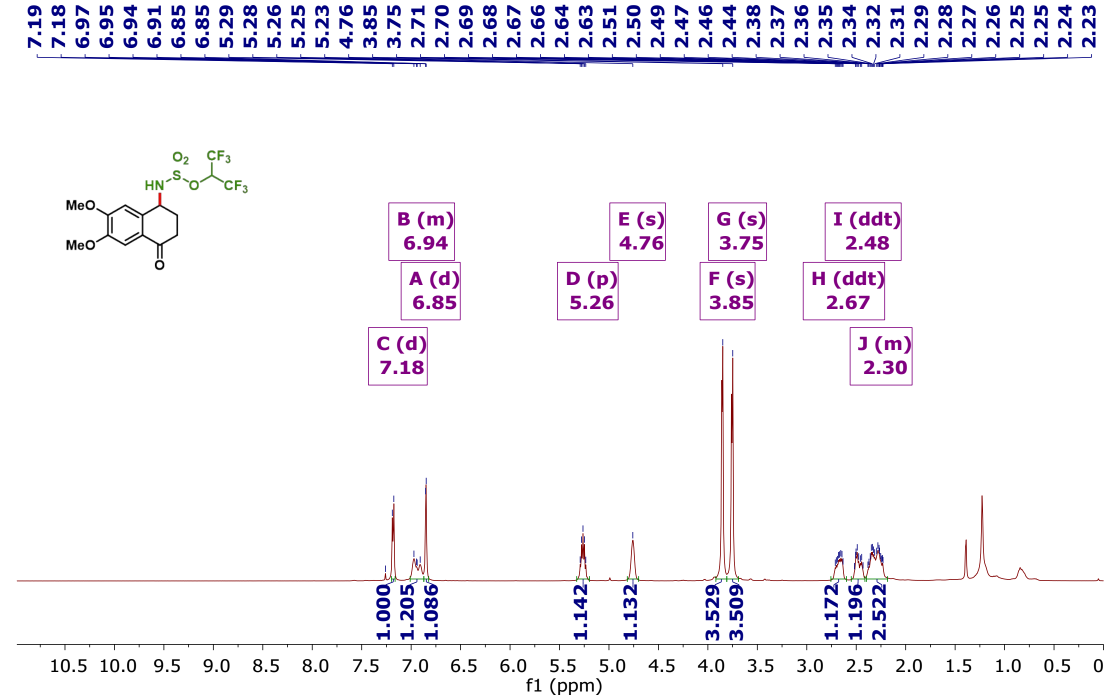
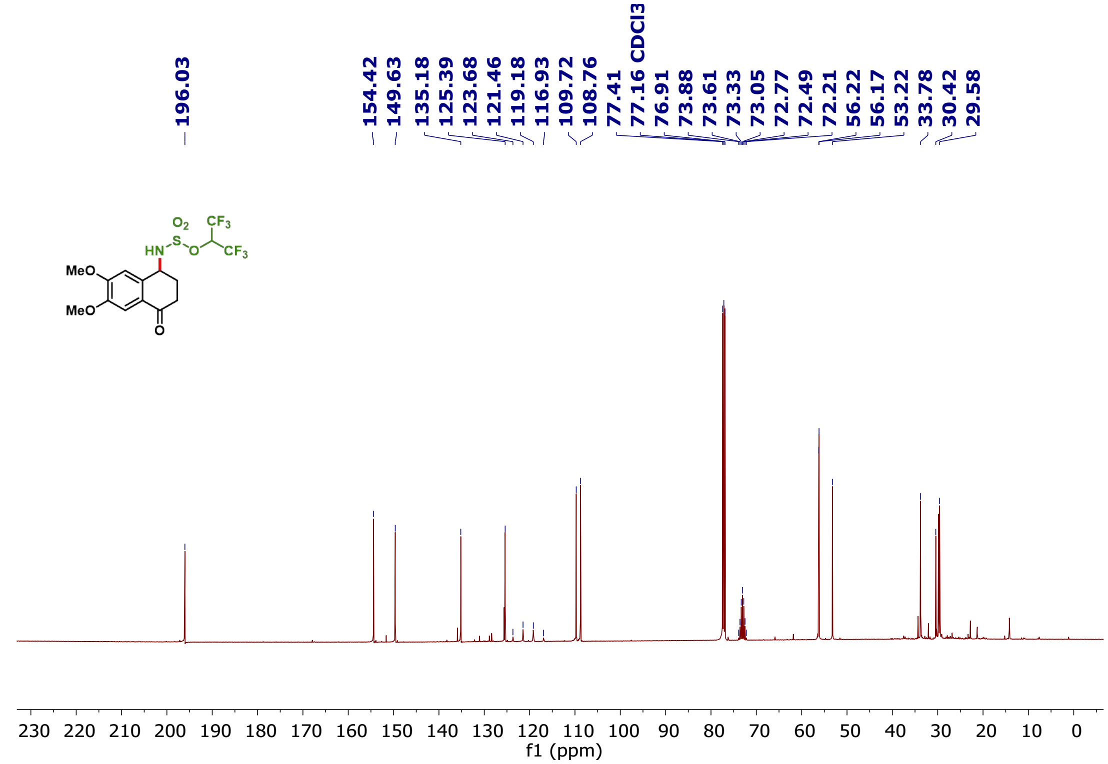
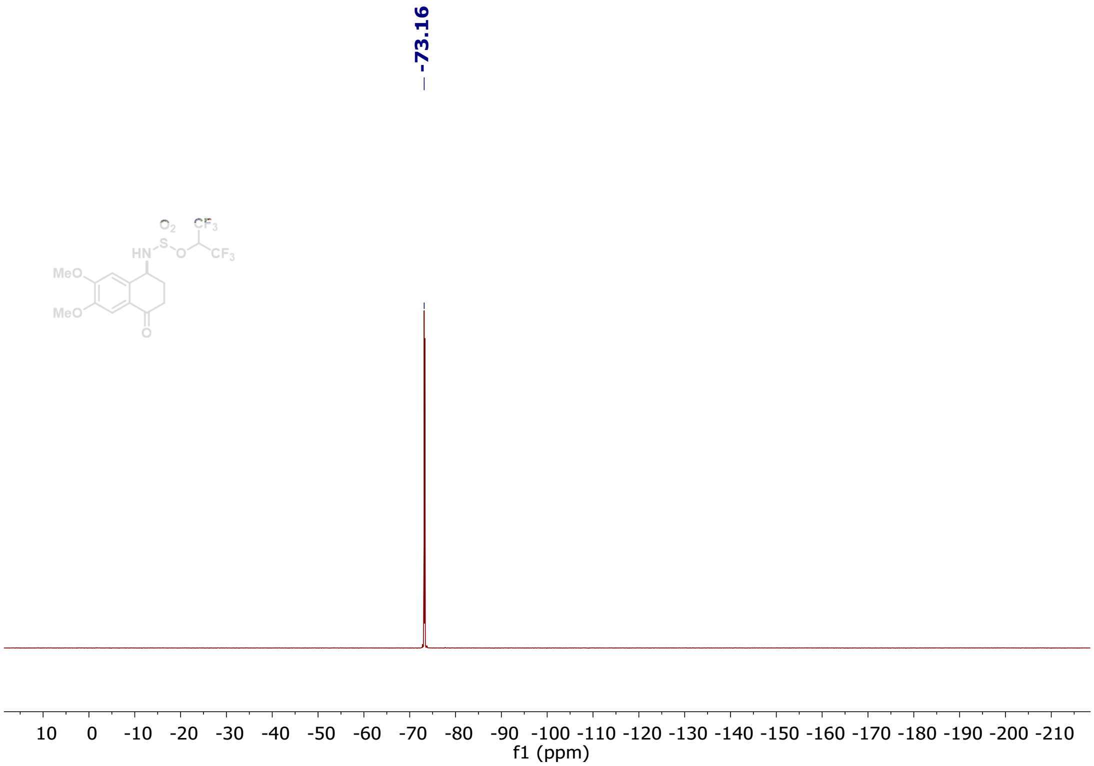
O2
CF3
HN
S
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 14b



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CF3
HN
S
O
CF3
MeO
MeO
O
10
0
-10
-20
-30
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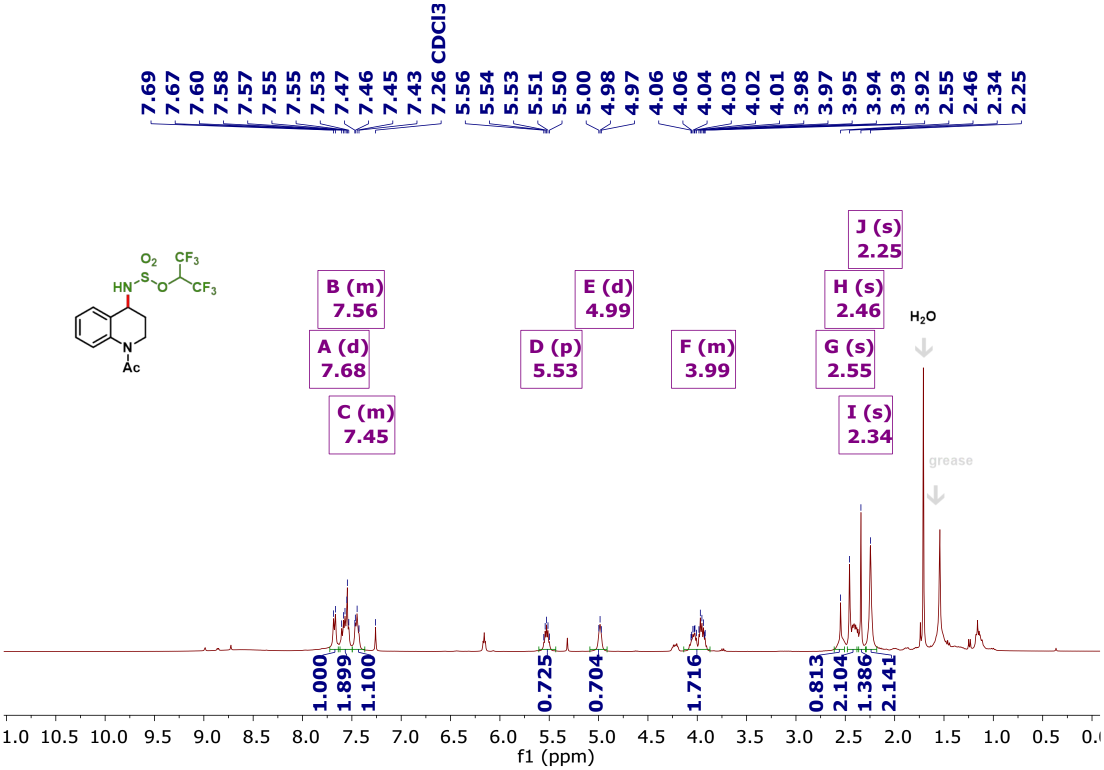
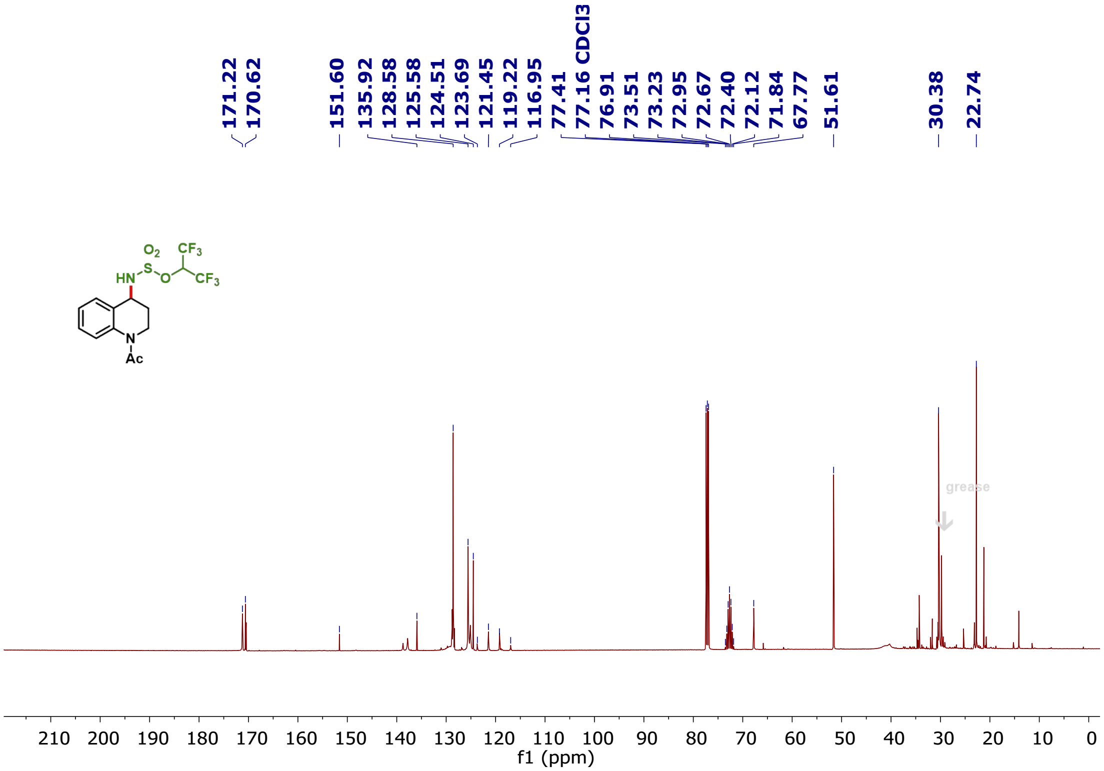
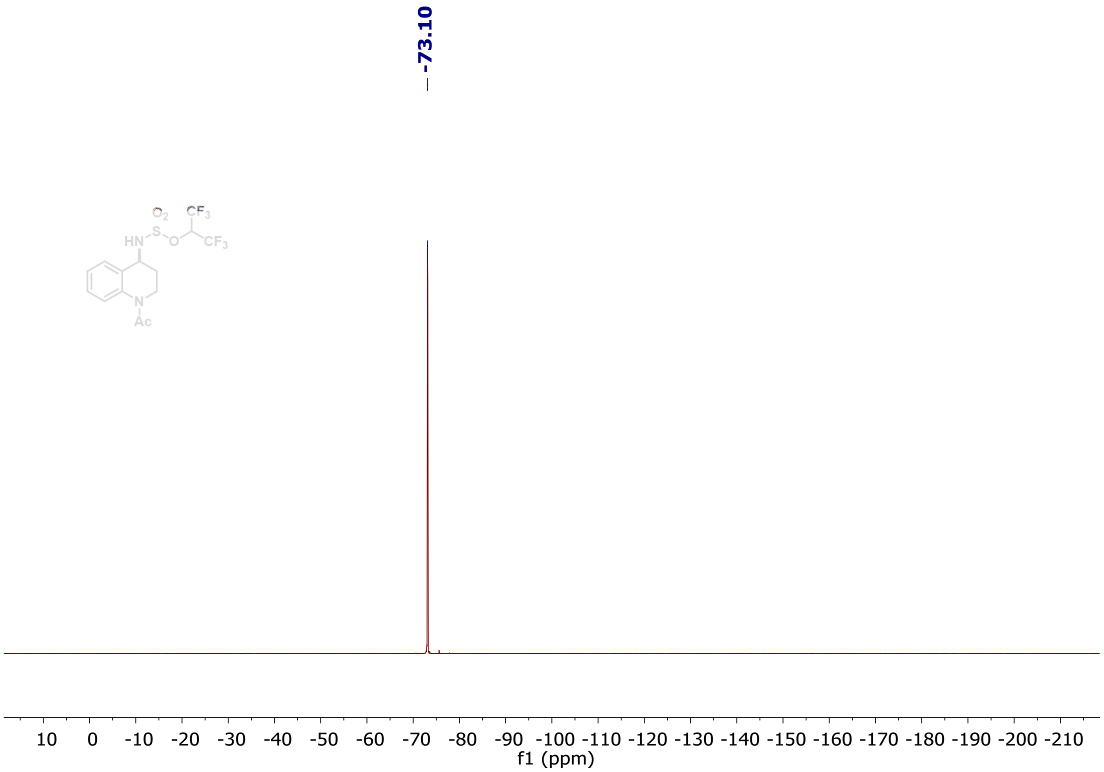
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 15b



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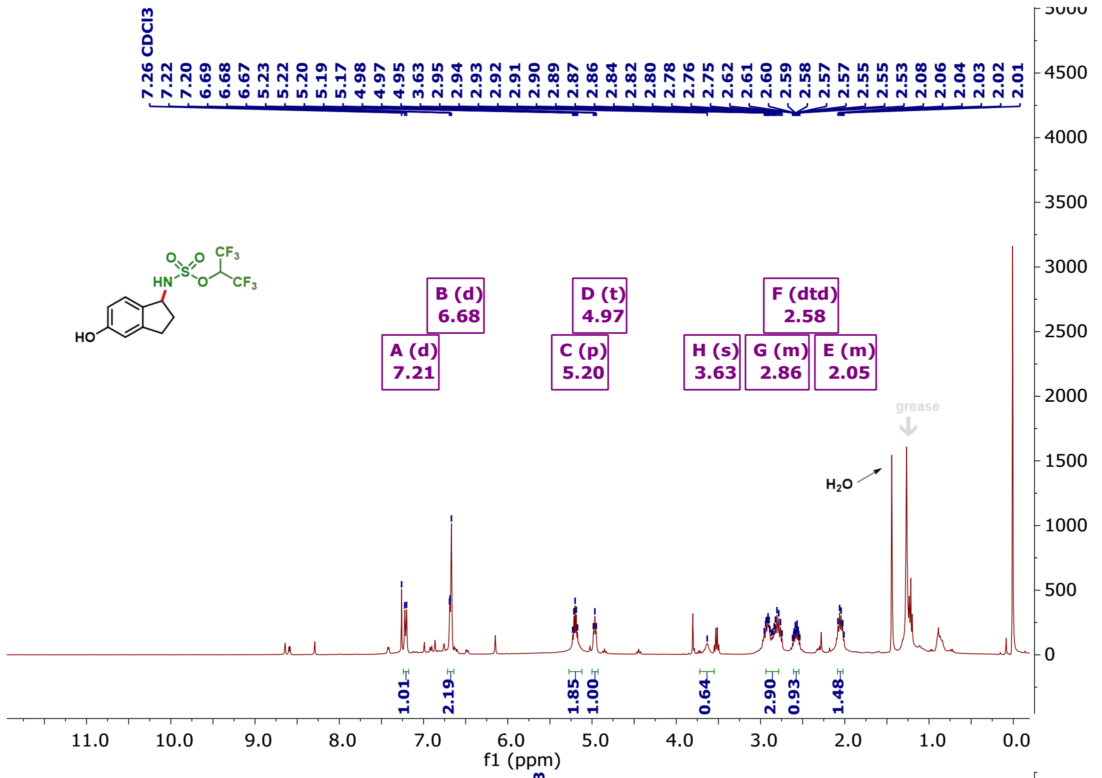
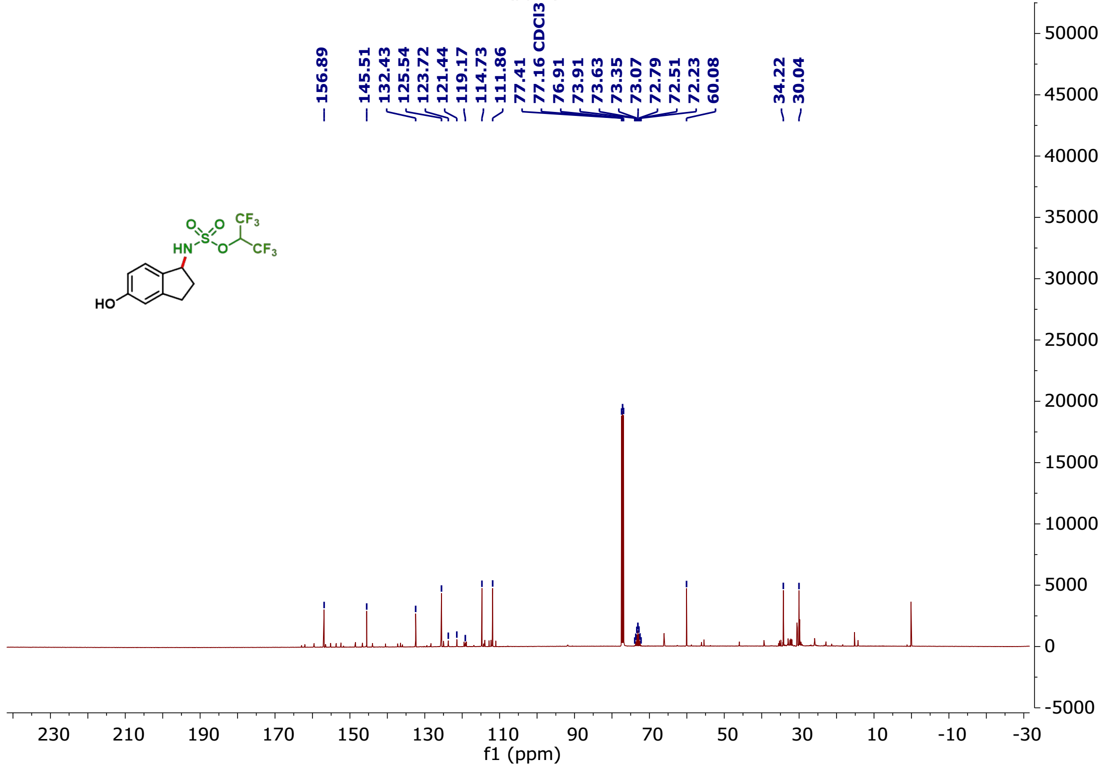
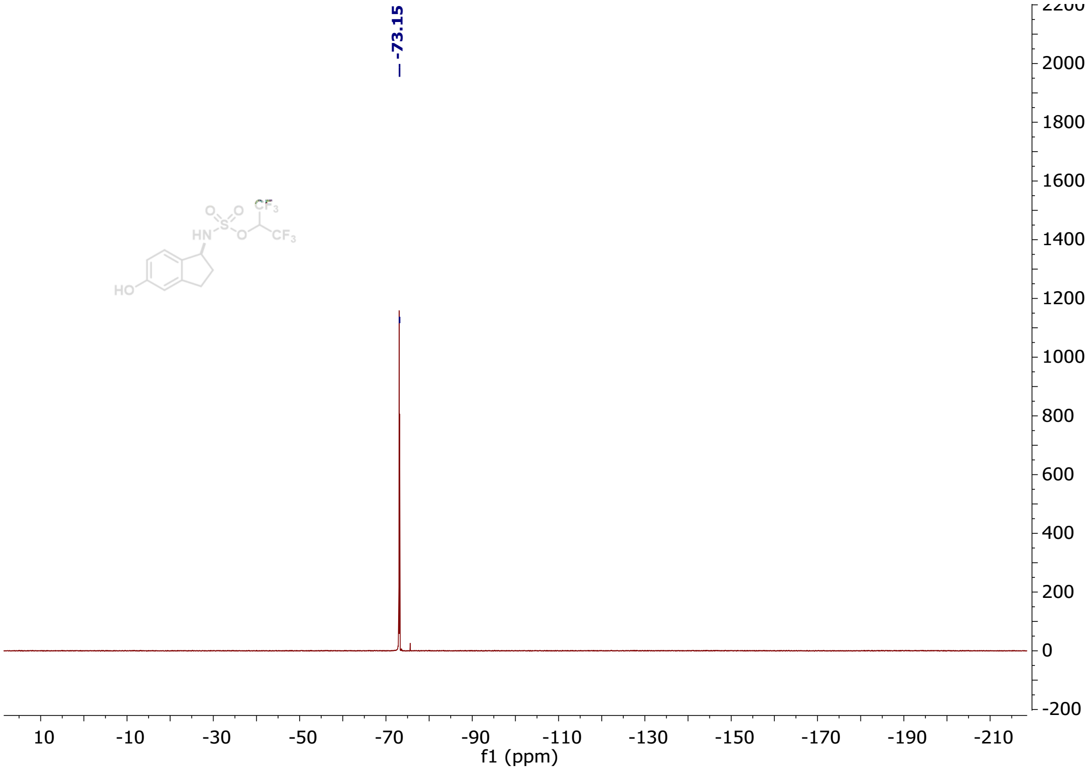
O2
CF3
HN
S
O
CF3
N
Ac
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

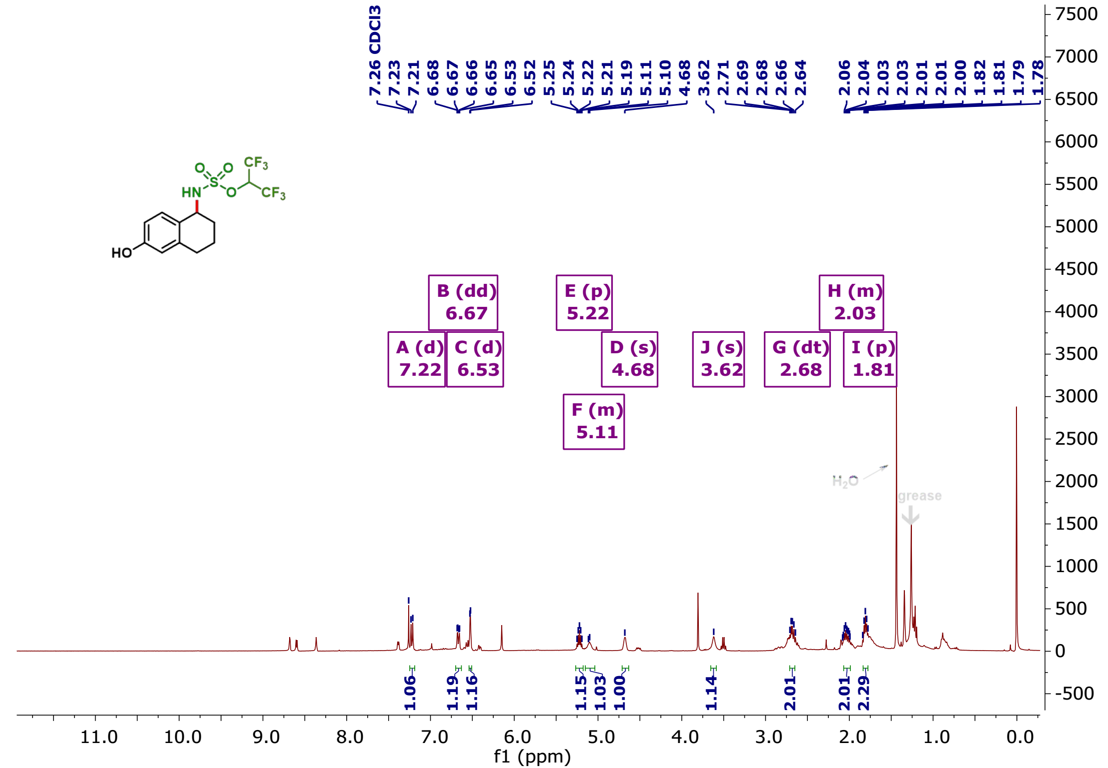
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 16b

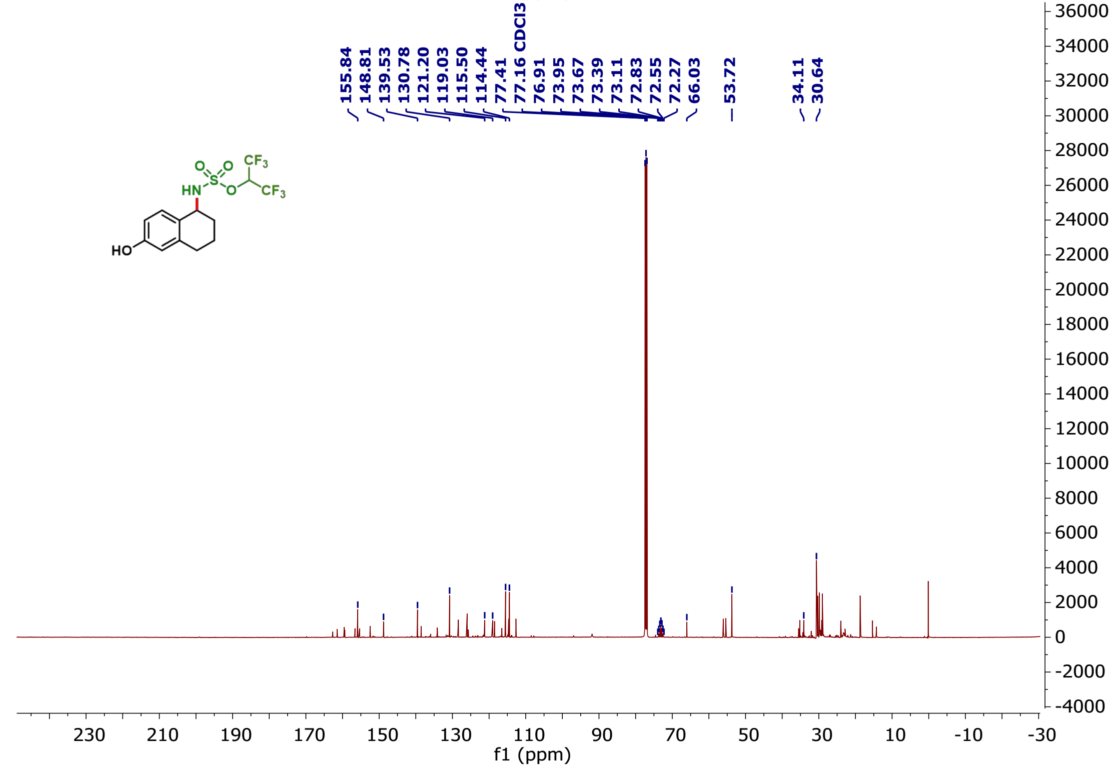


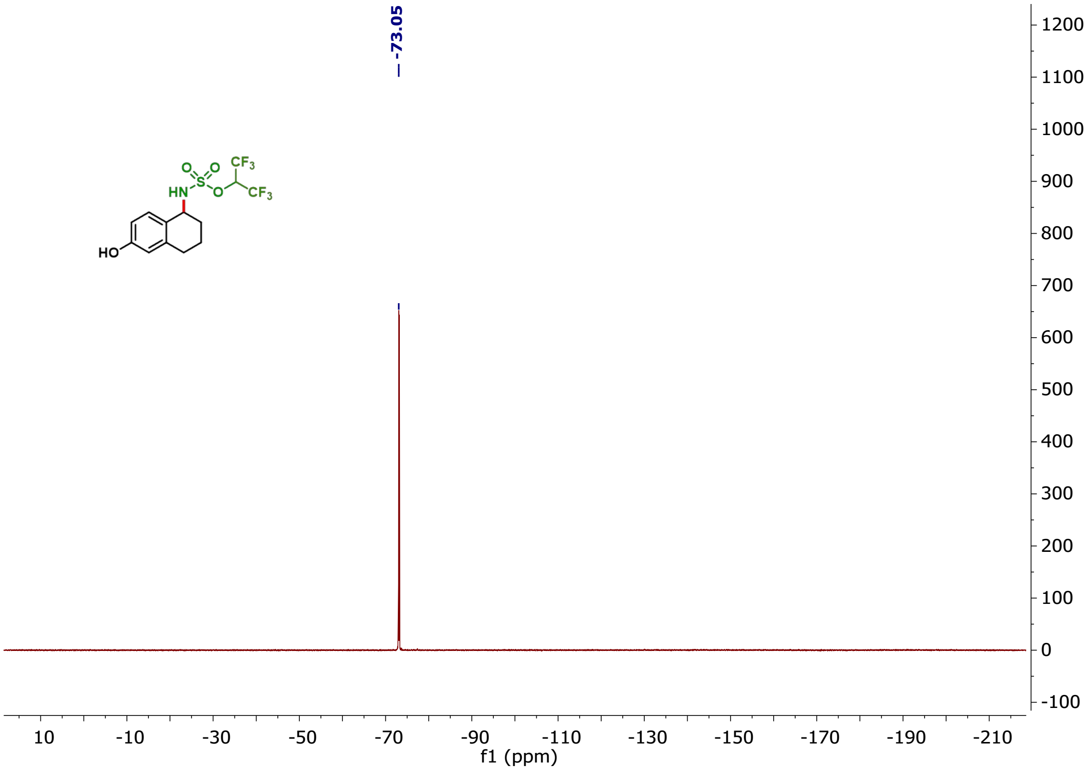



-73.15
HN
O
S
O
O
CF3
CF3
HO
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 17b



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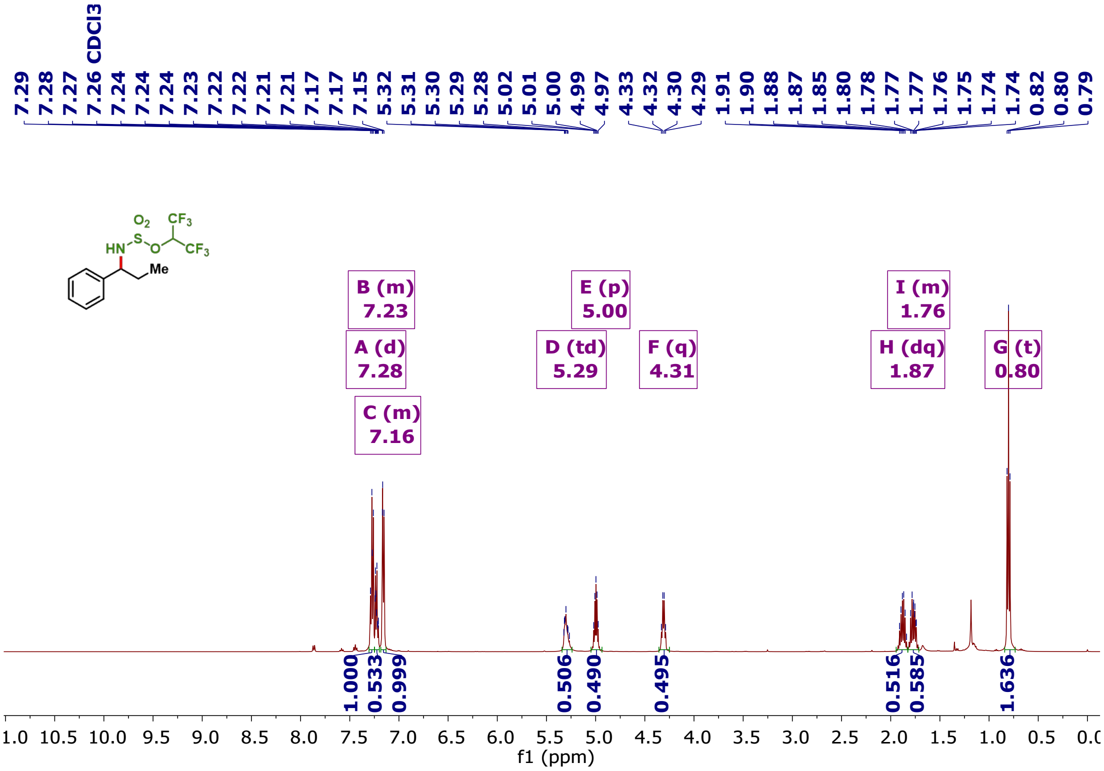
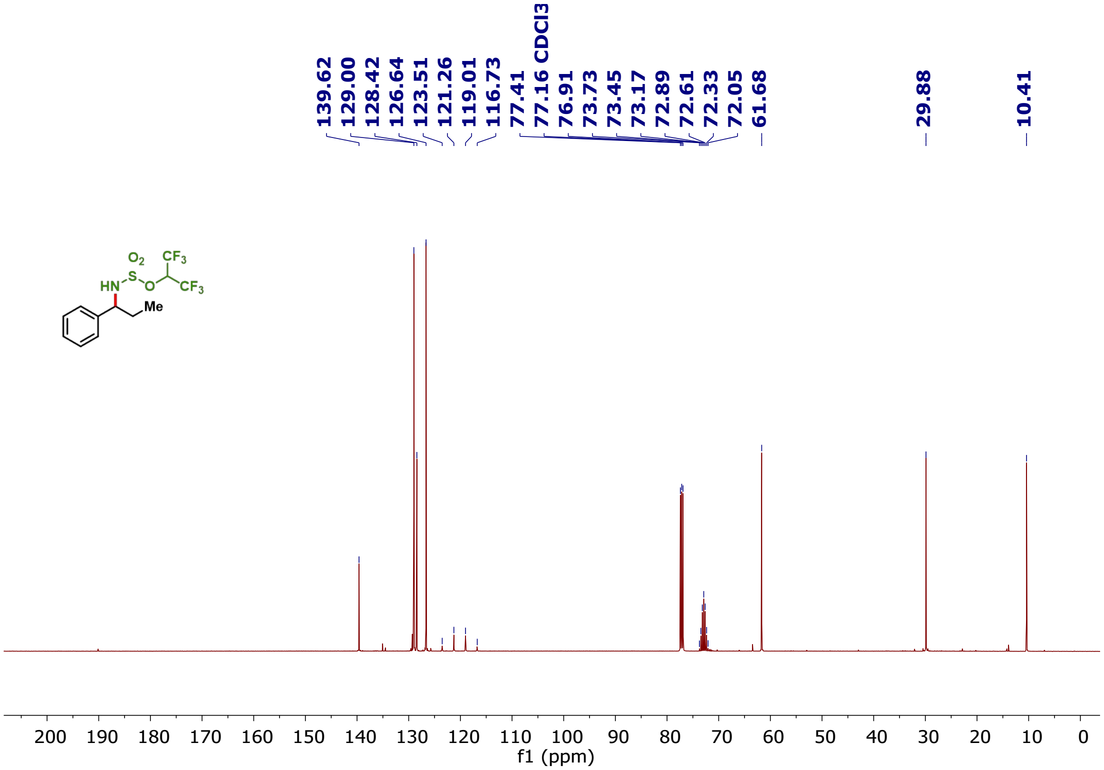
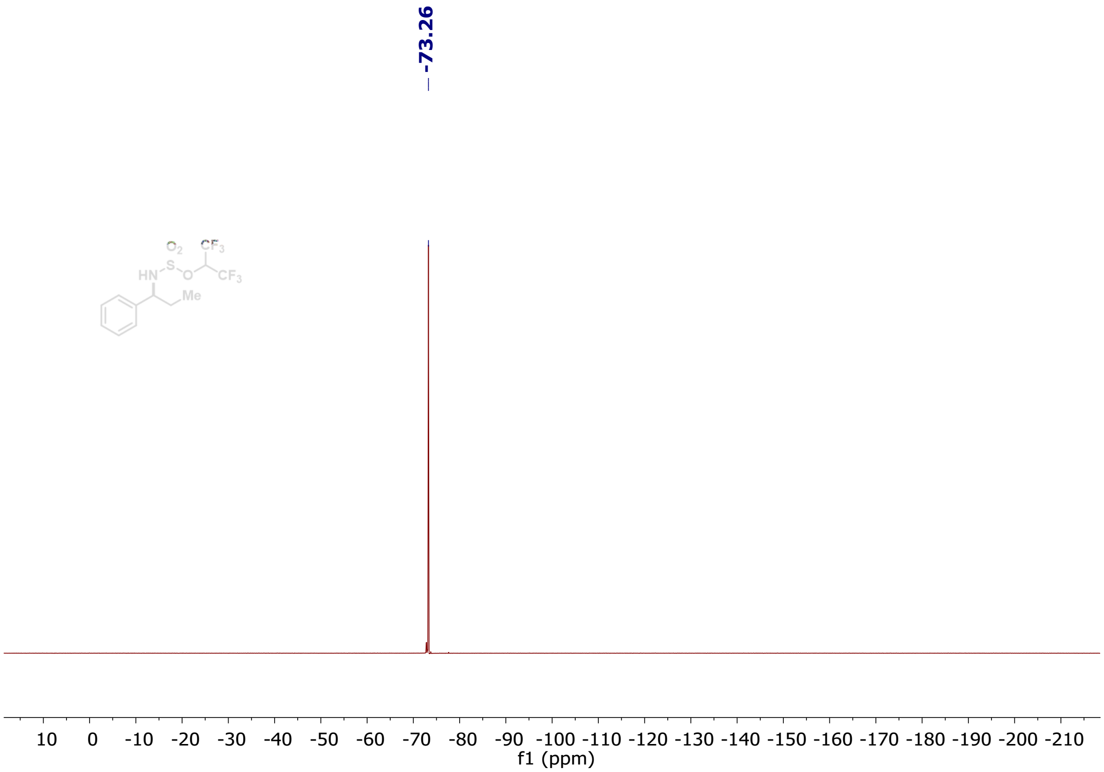
HO
HN
O
O
S
O
CF3
CF3
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 18b



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S
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CF3
Me
10
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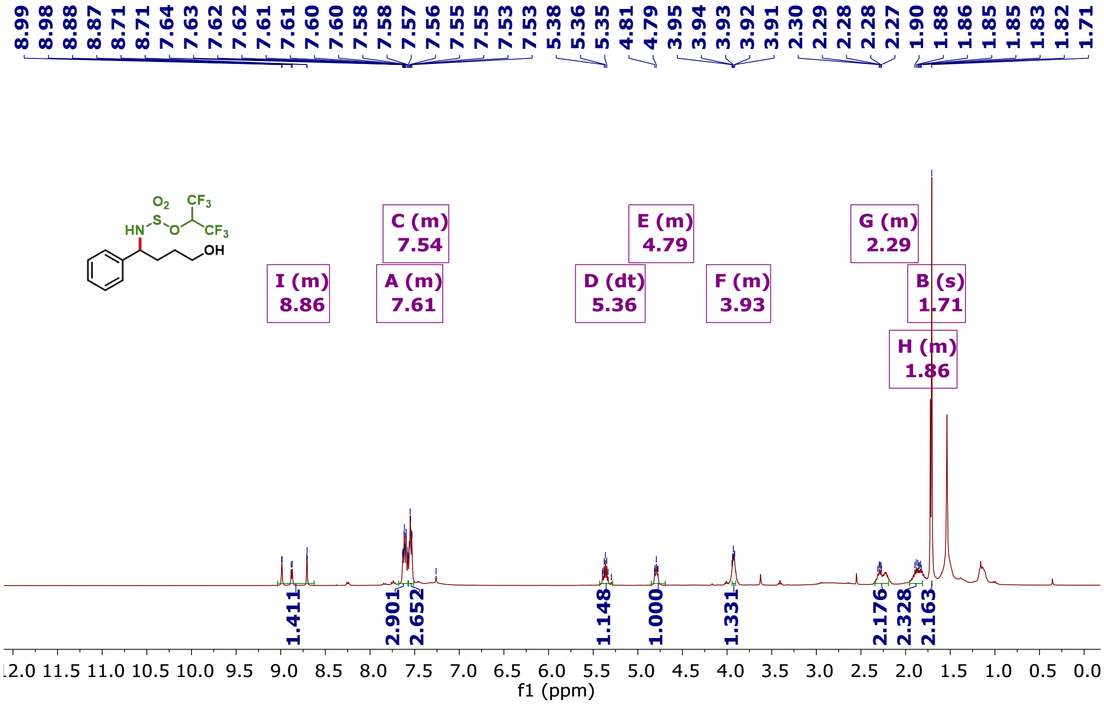
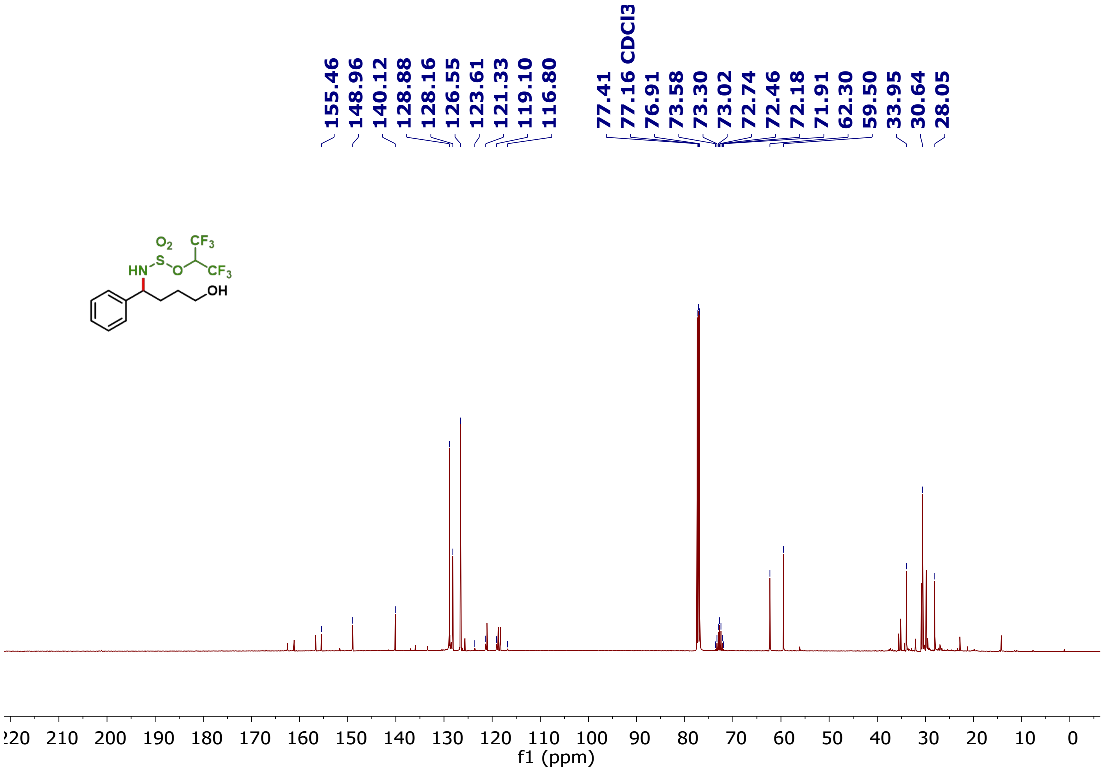
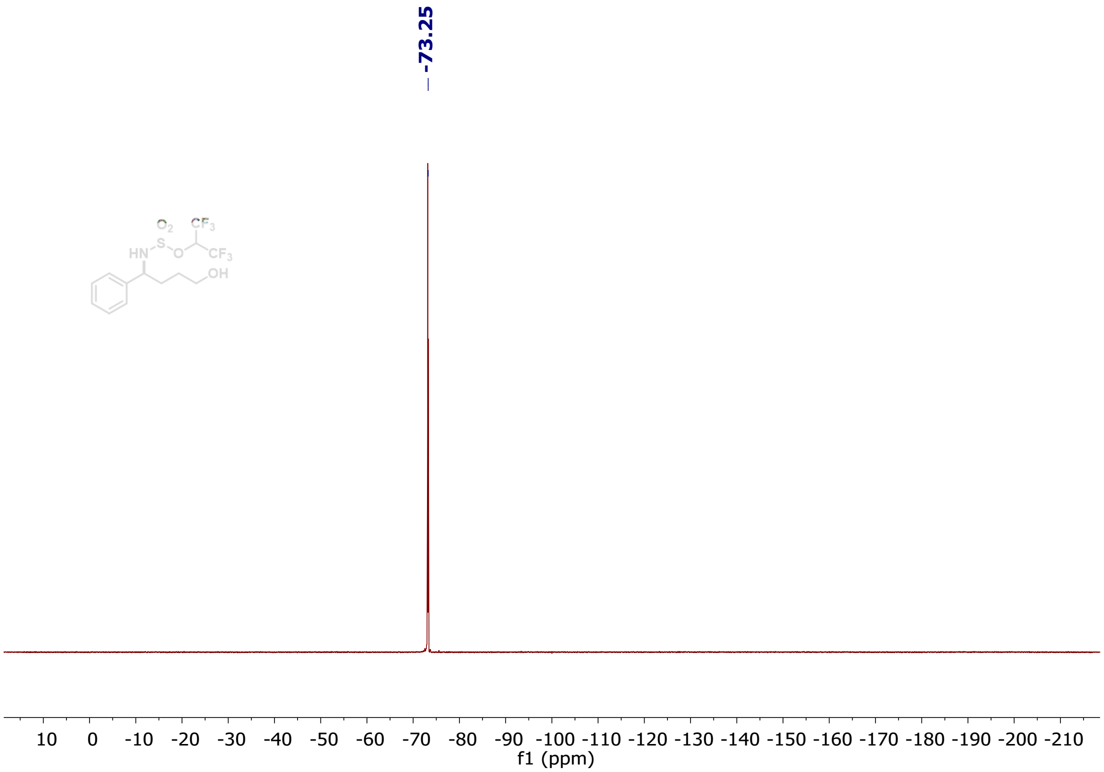
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

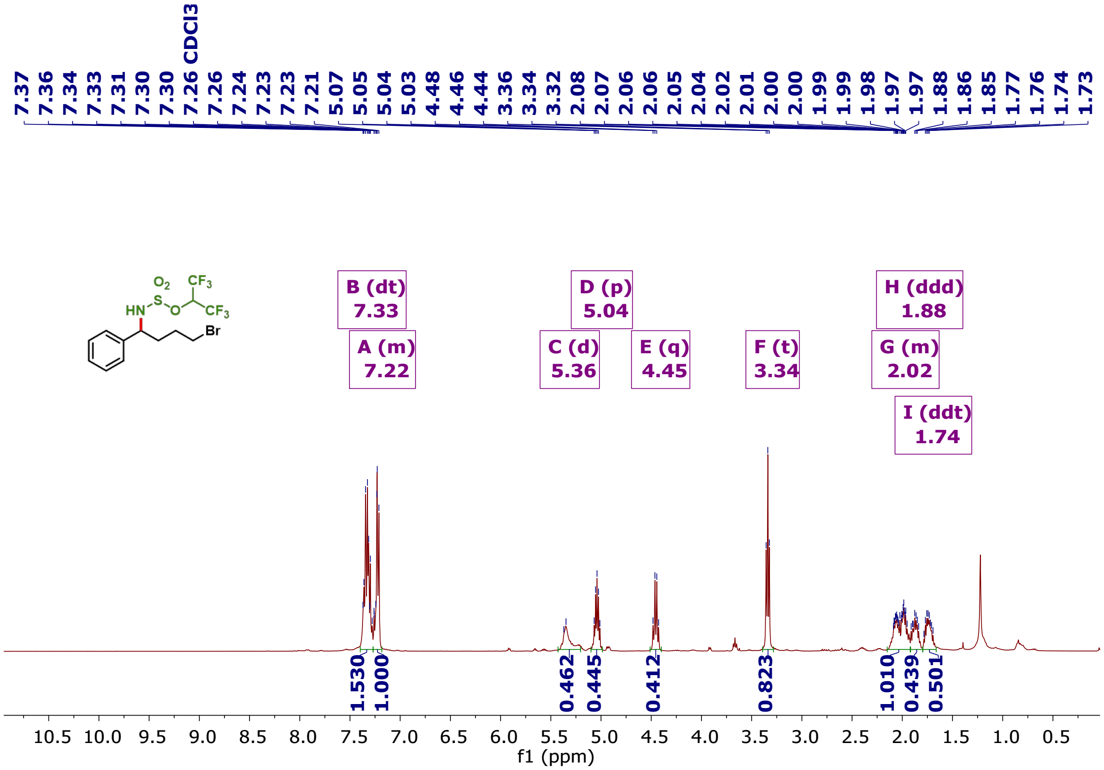
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 19b

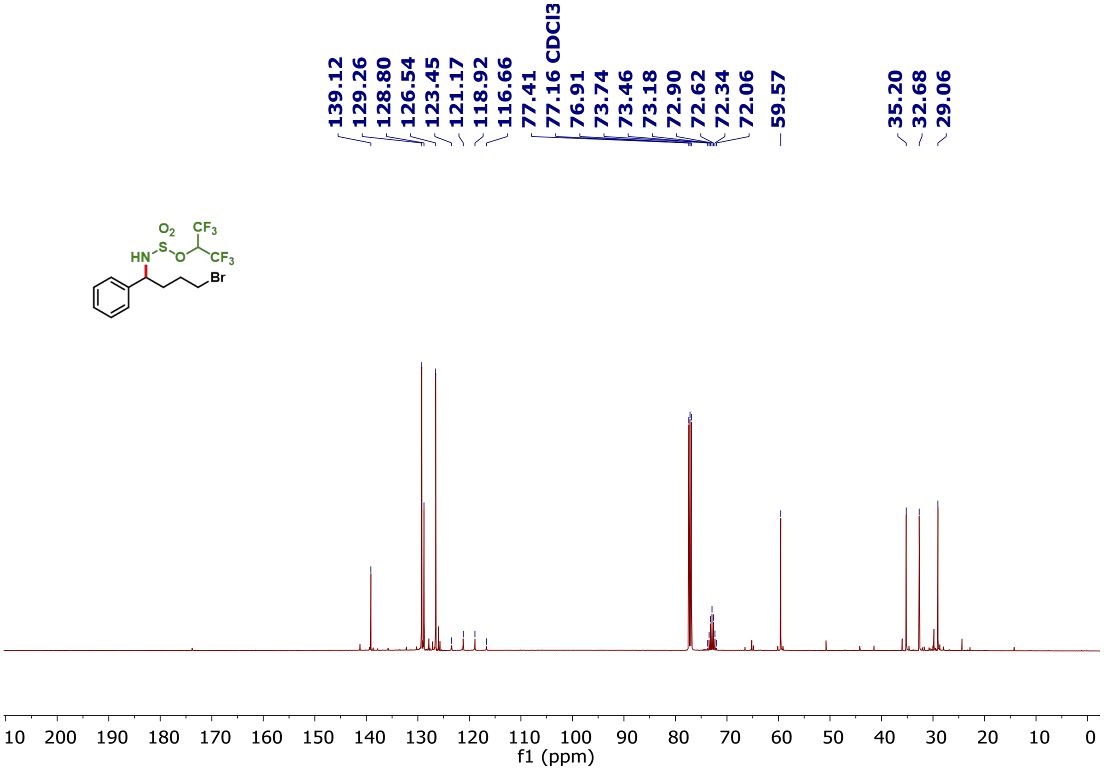


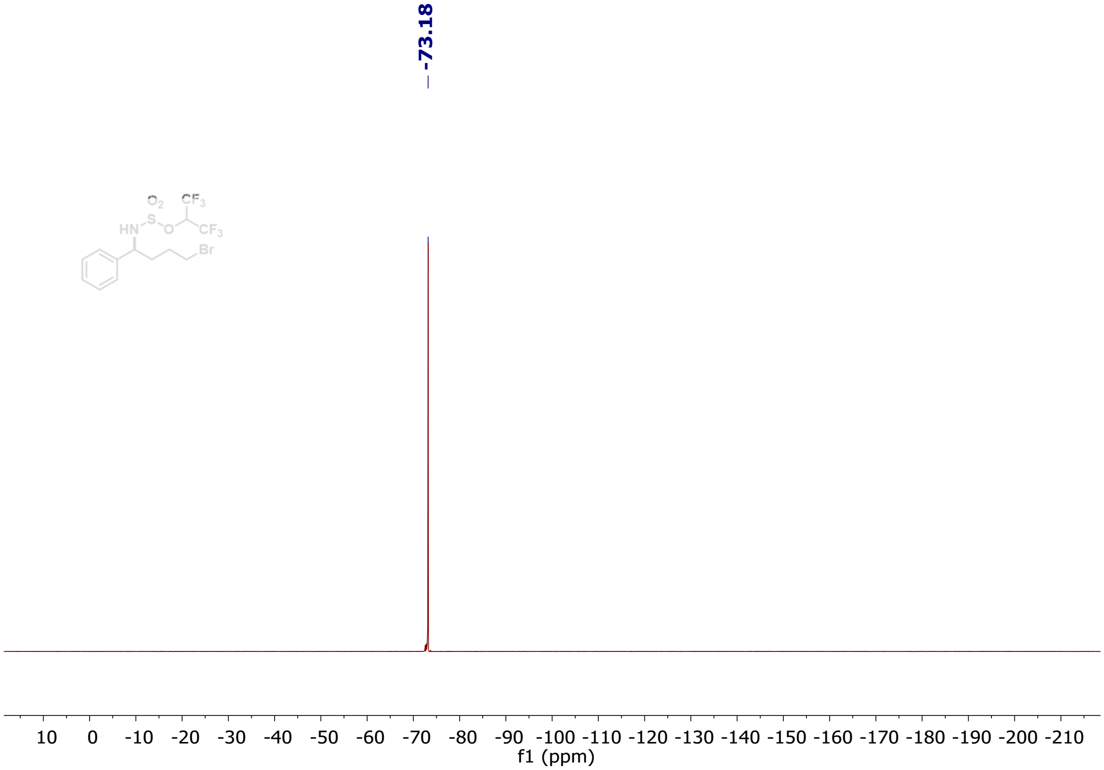



-73.25
O2
CF3
HN
S
O
CF3
OH
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 20b






-73.18
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HN
S
O
CF3
Br
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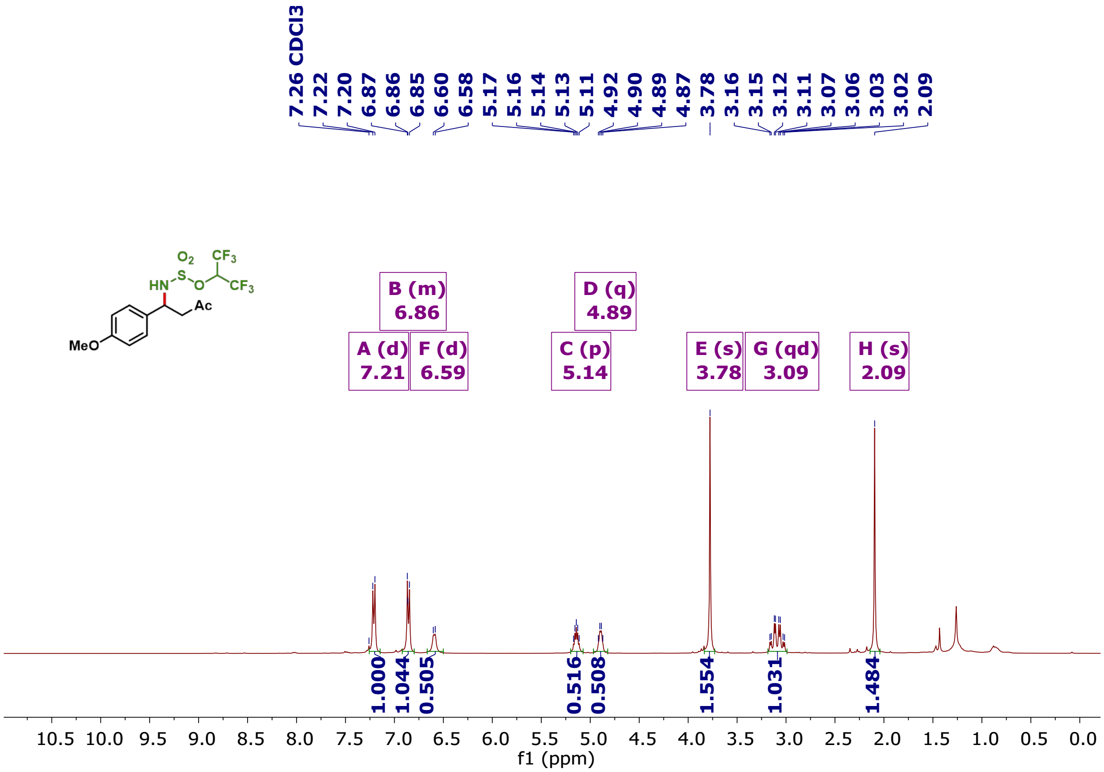
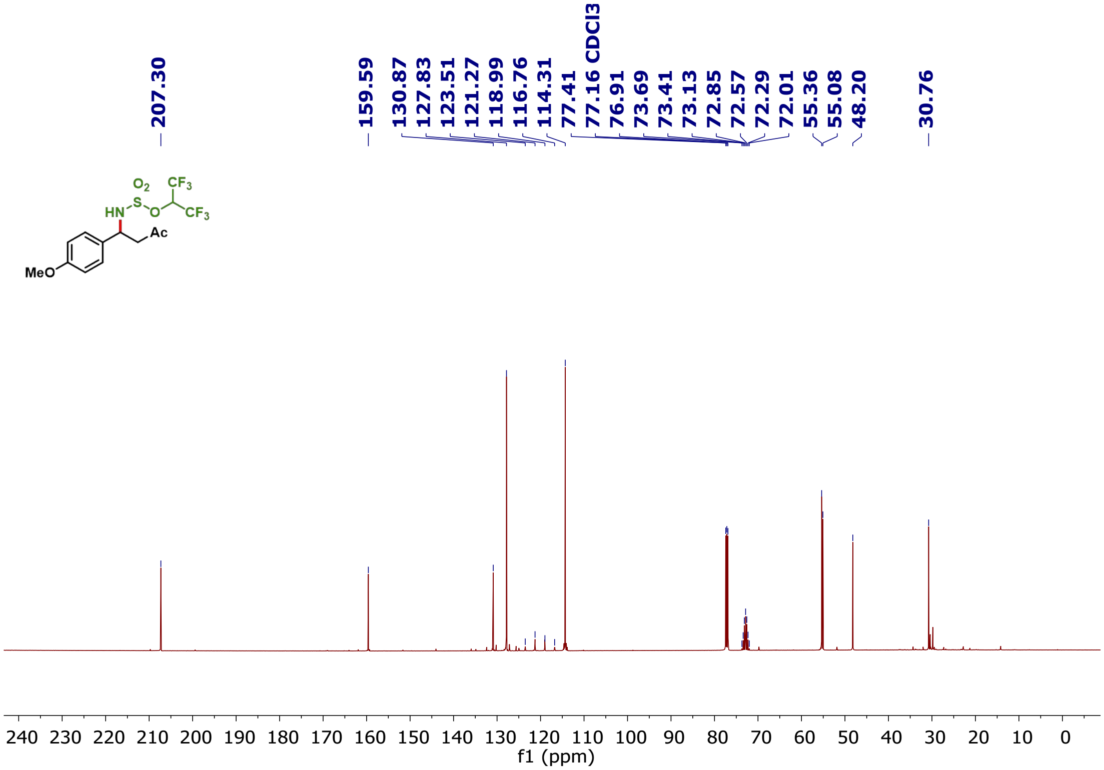
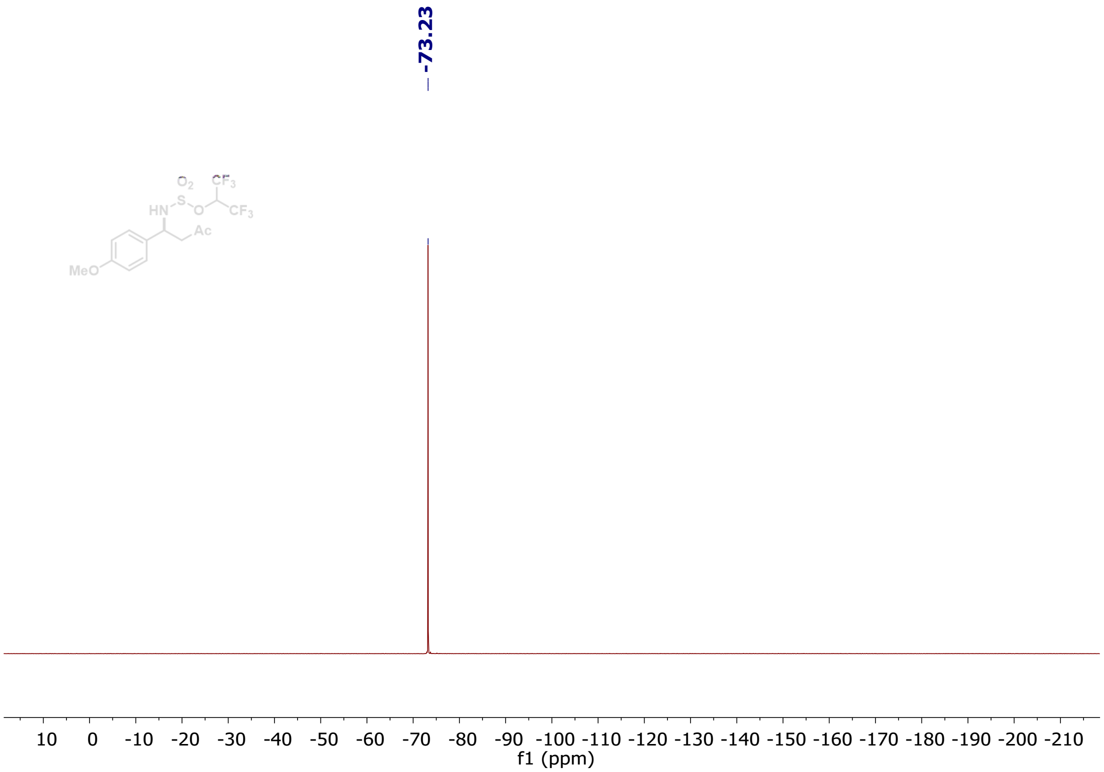
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

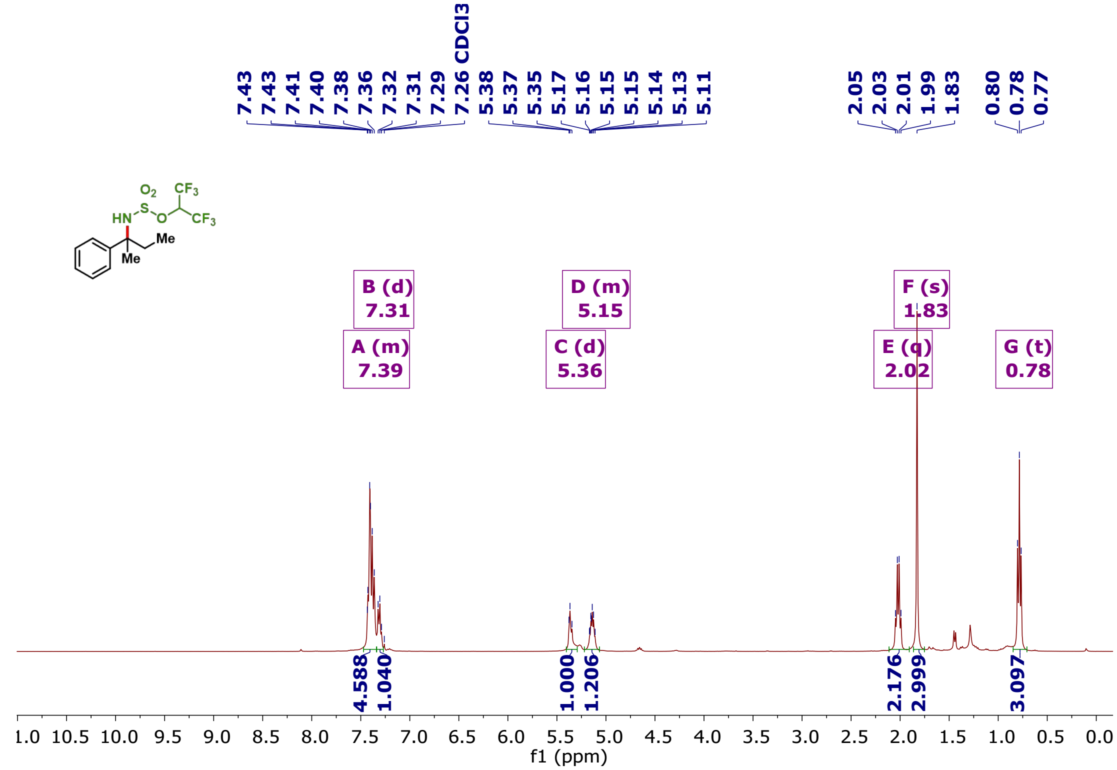
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 21b

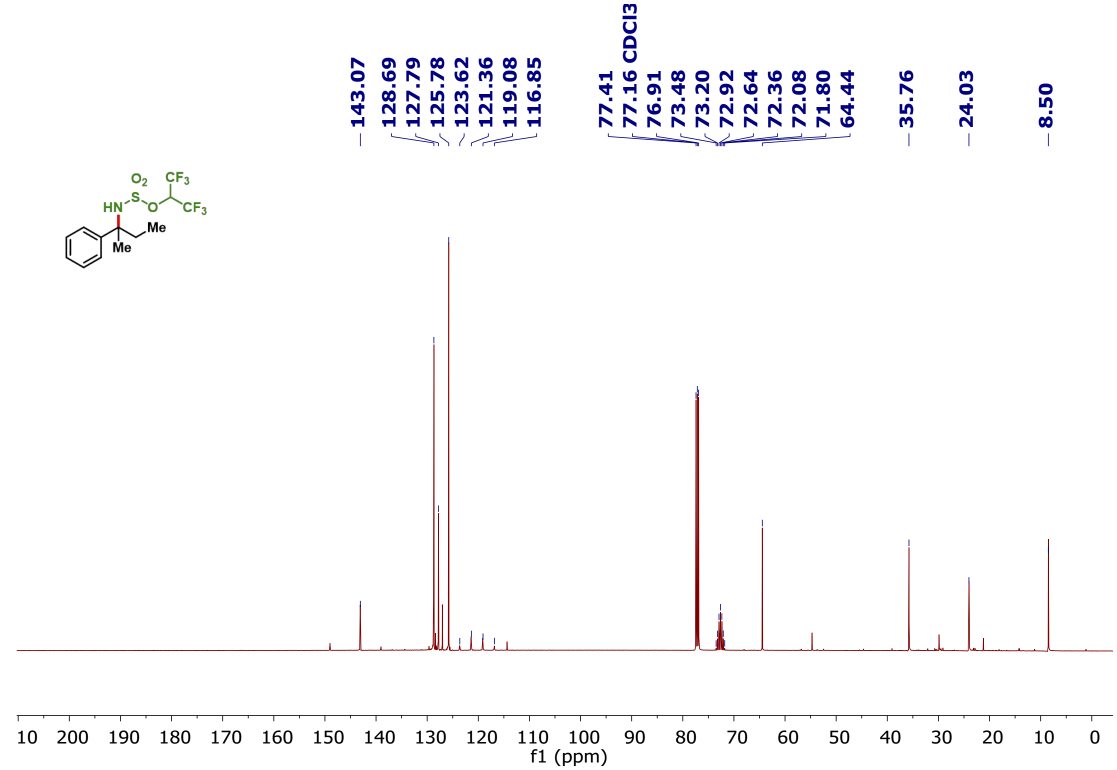


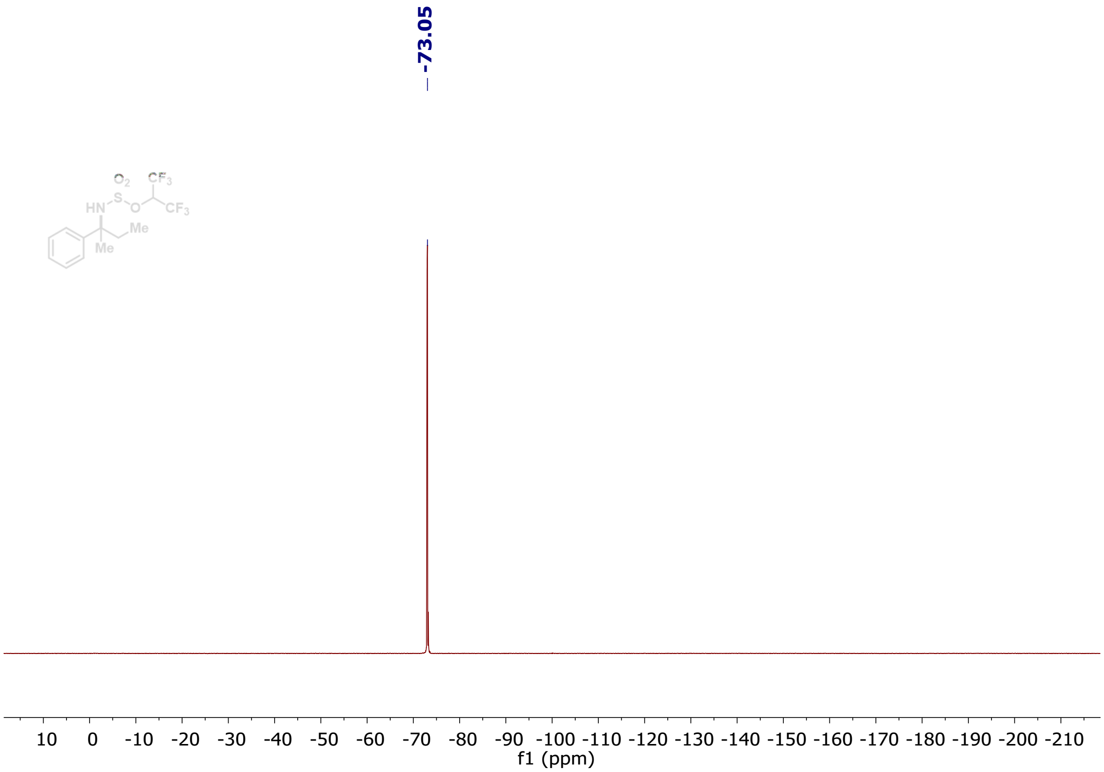



-73.23
O2
CF3
HN
S
O
CF3
Ac
MeO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

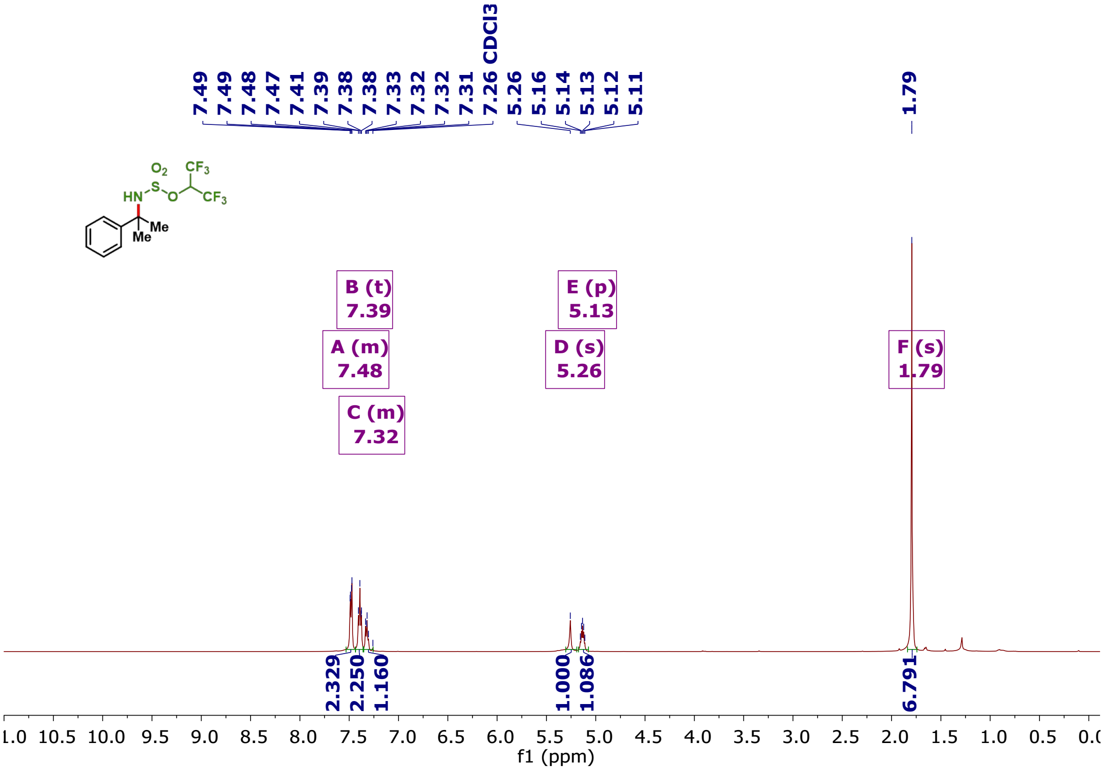
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 22b

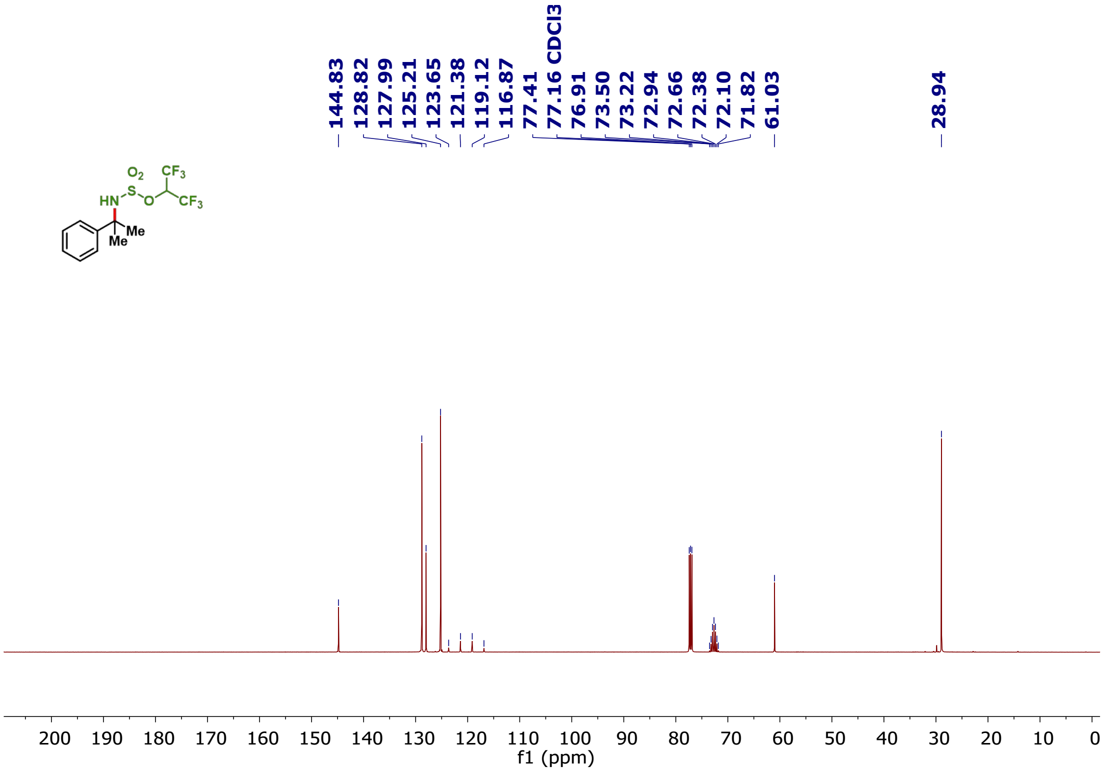


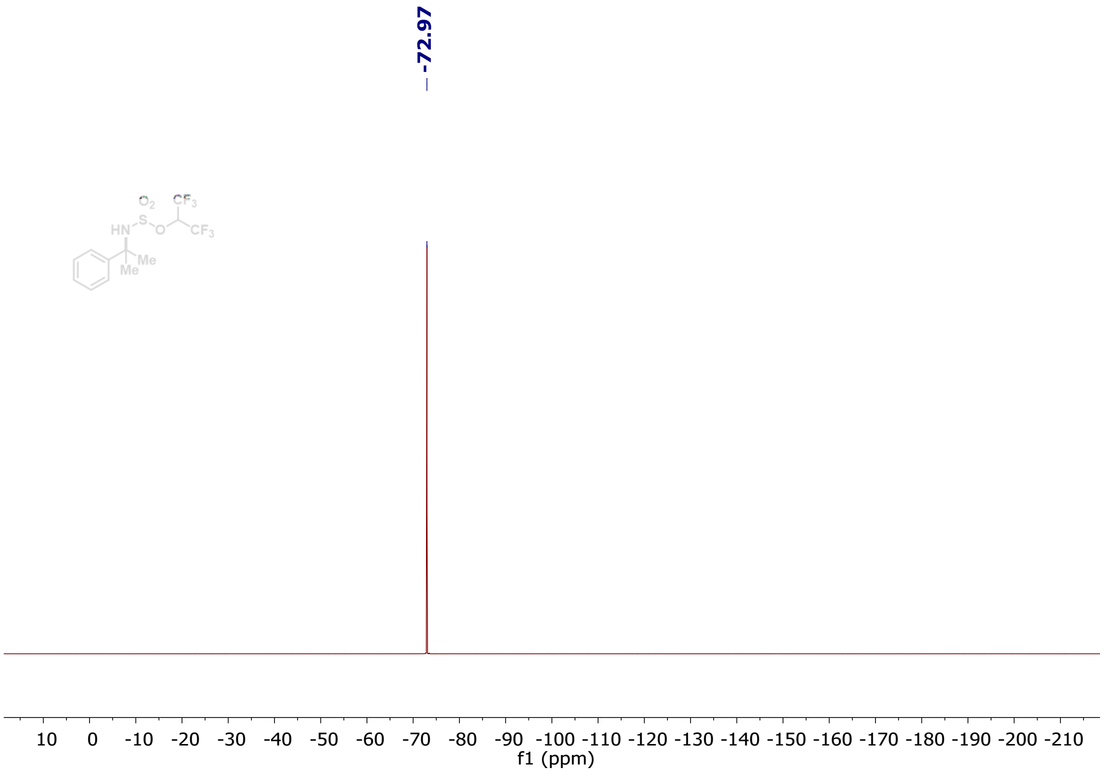



-73.05
O2
CF3
HN
S
O
CF3
Me
Me
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 23b



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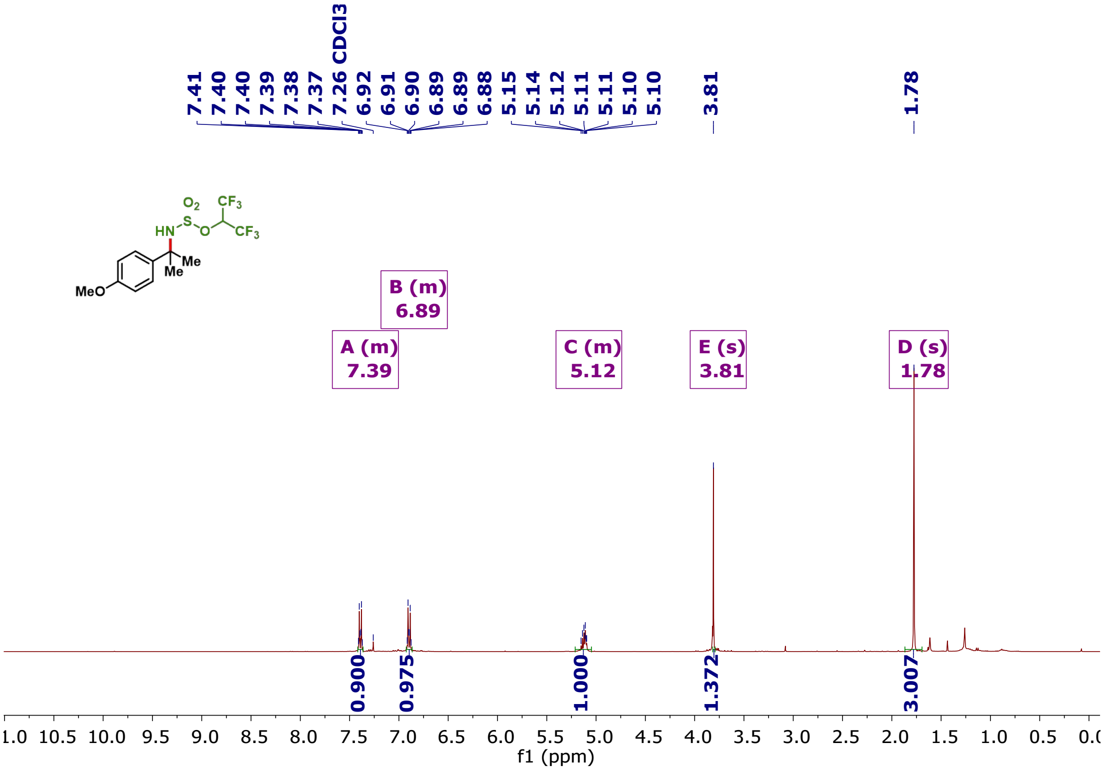
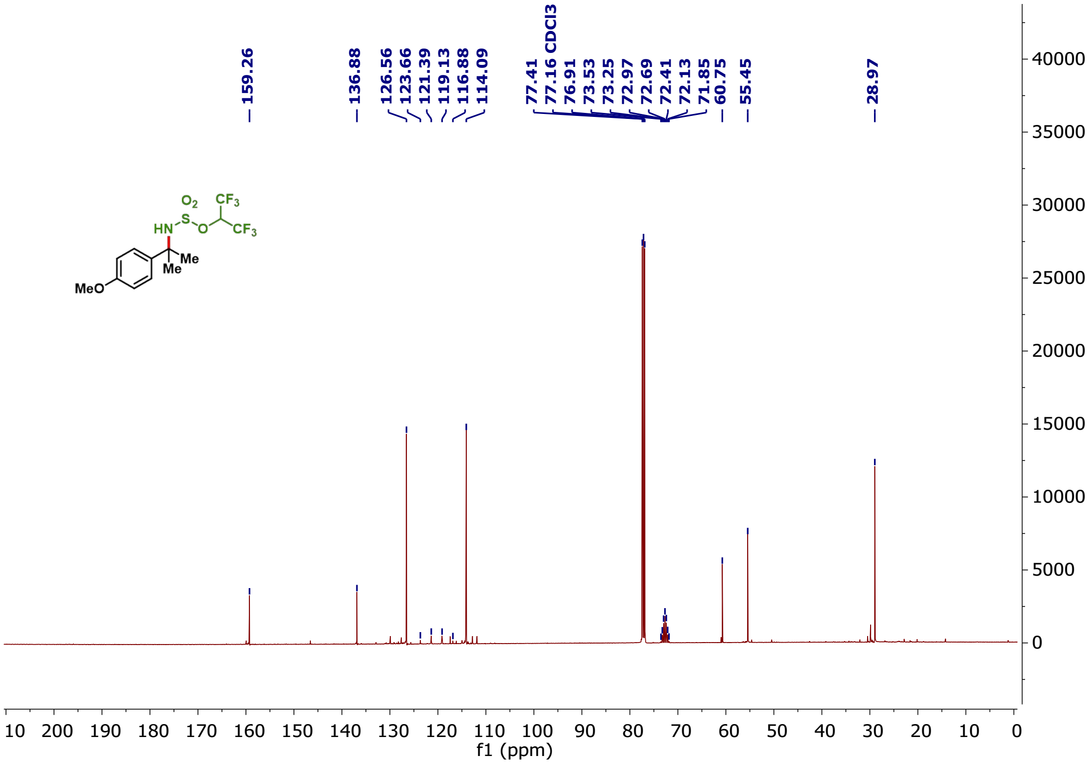
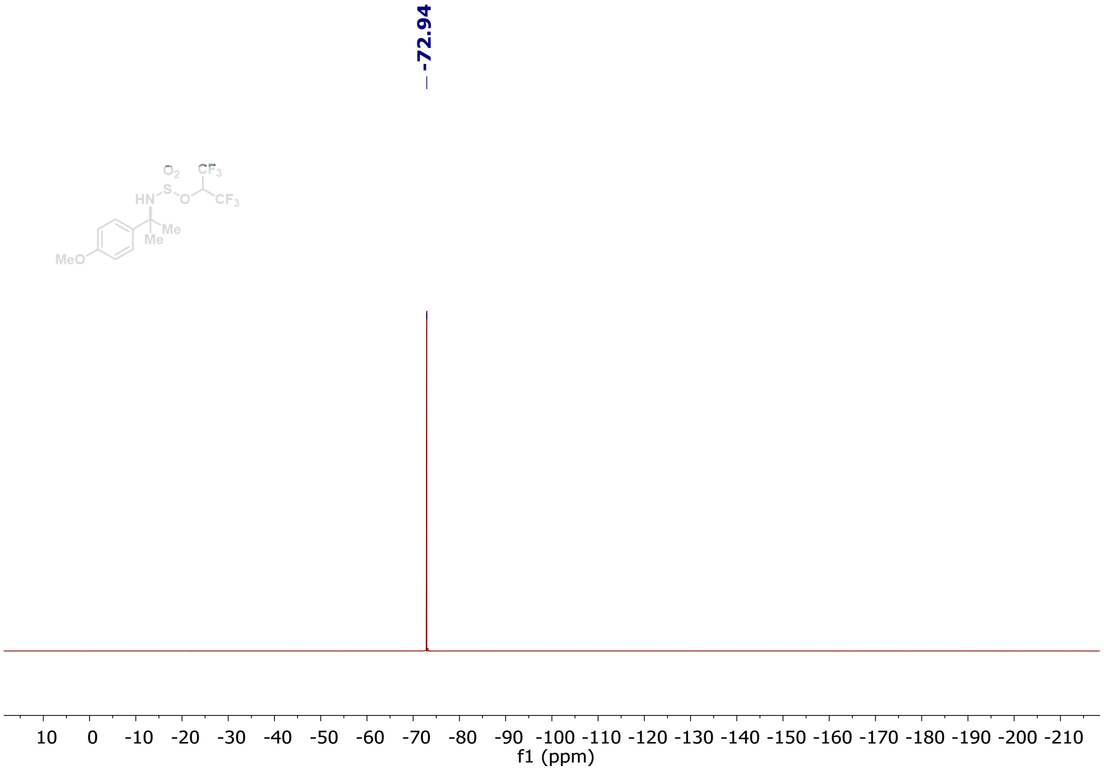
O2
S
HN
O
CF3
CF3
Me
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 24b



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CF3
Me
Me
MeO
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-10
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-80
-90
-100
-110
-120
-130
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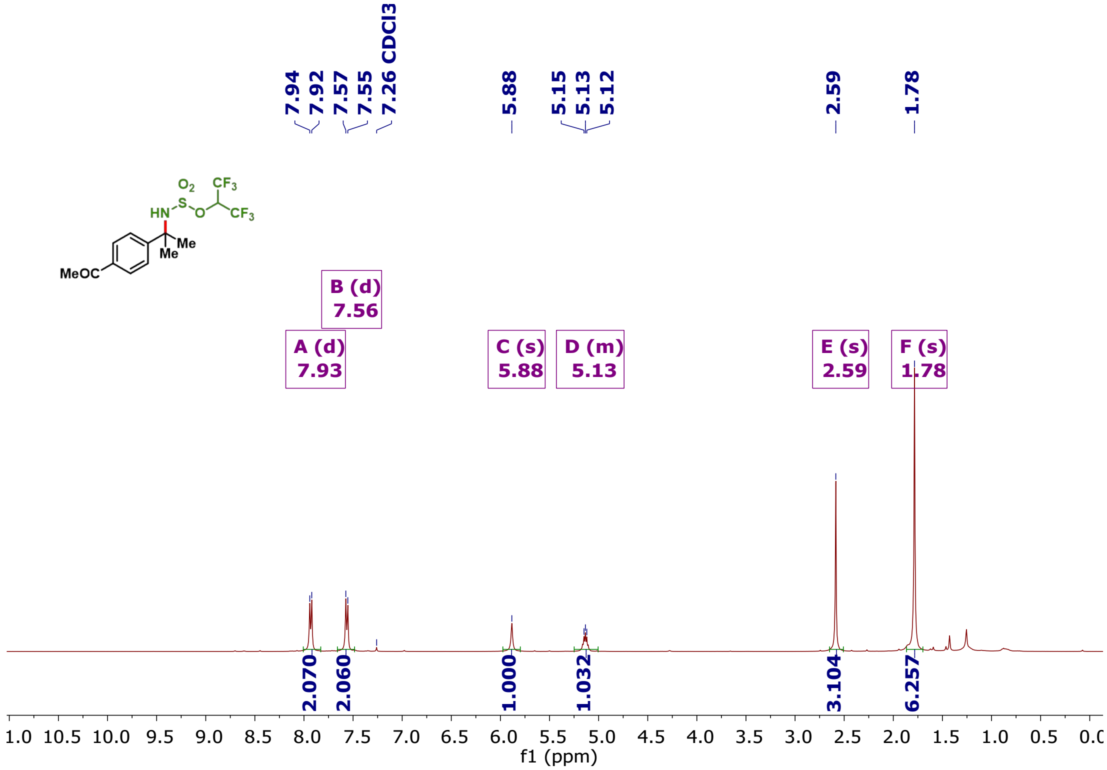
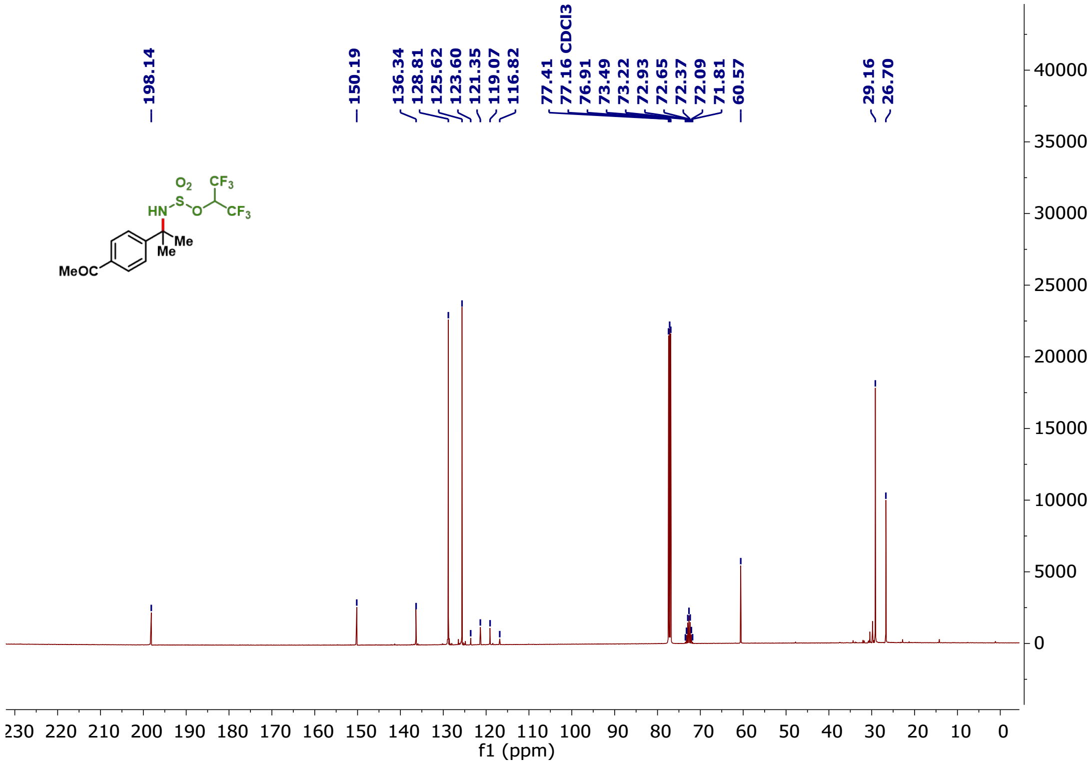
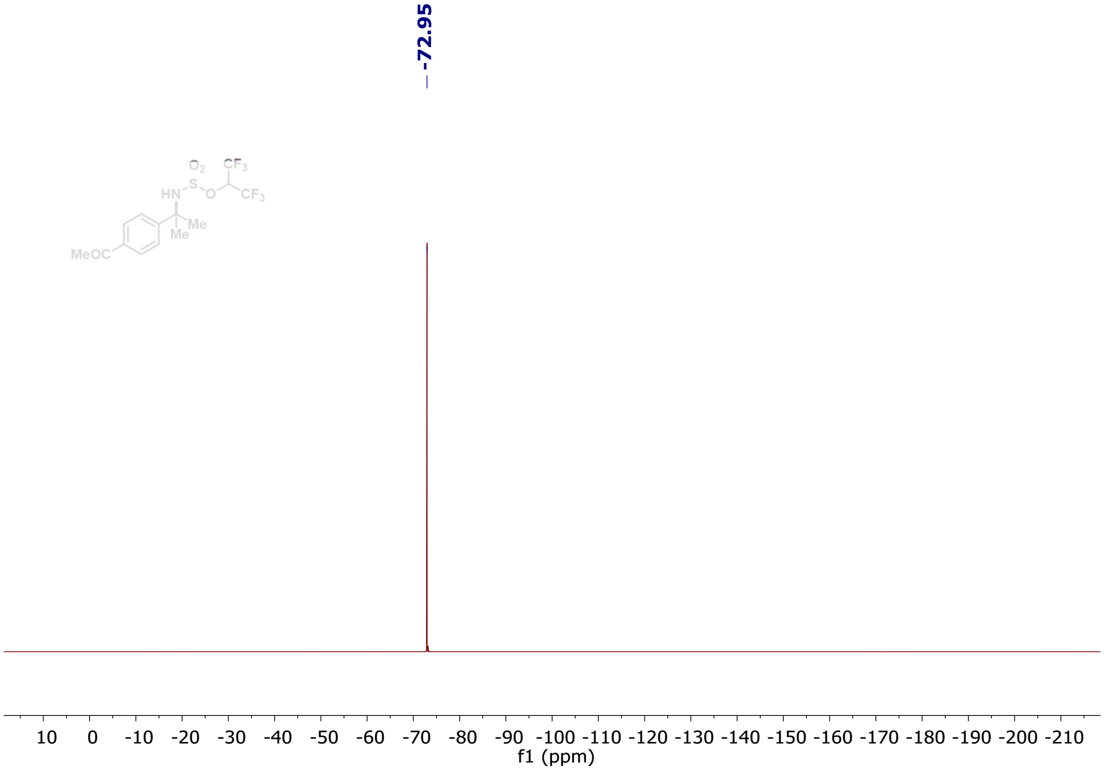
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 25b



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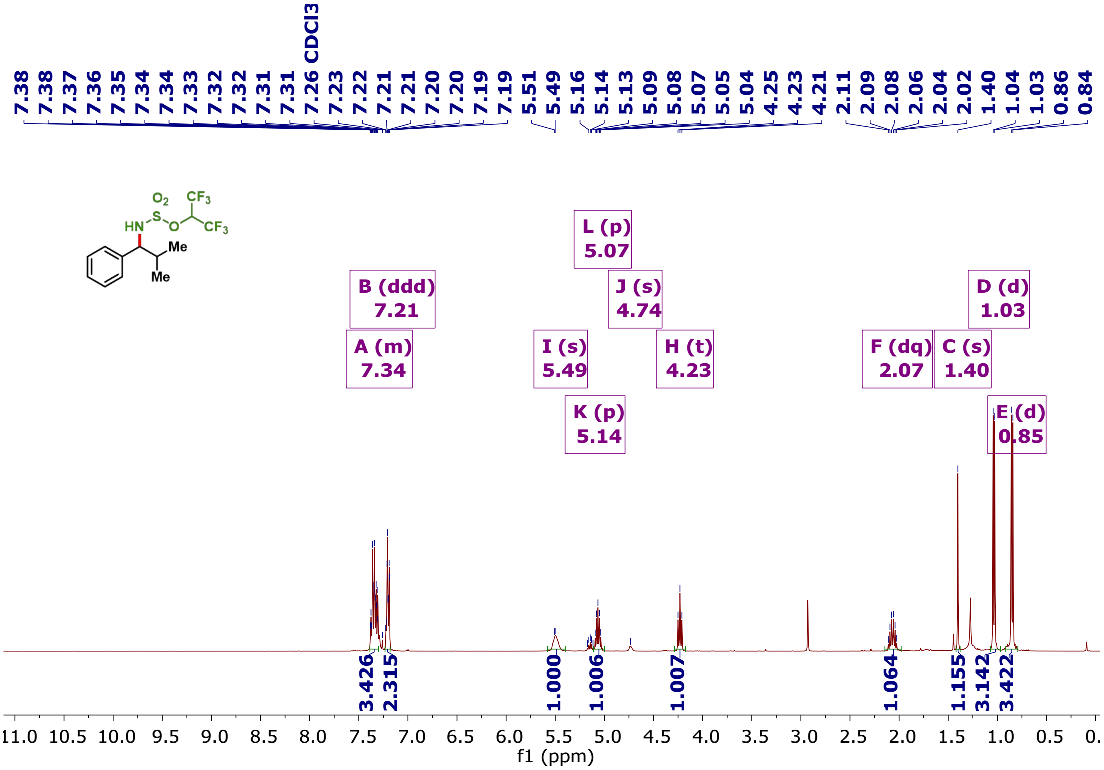
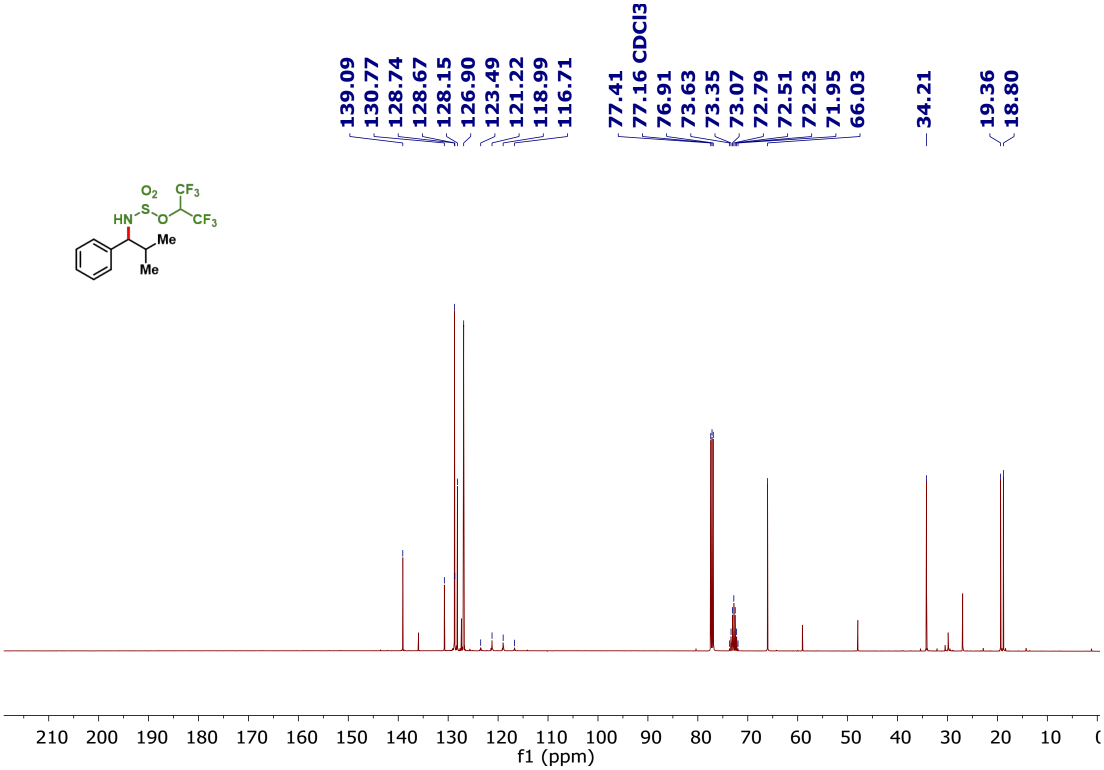
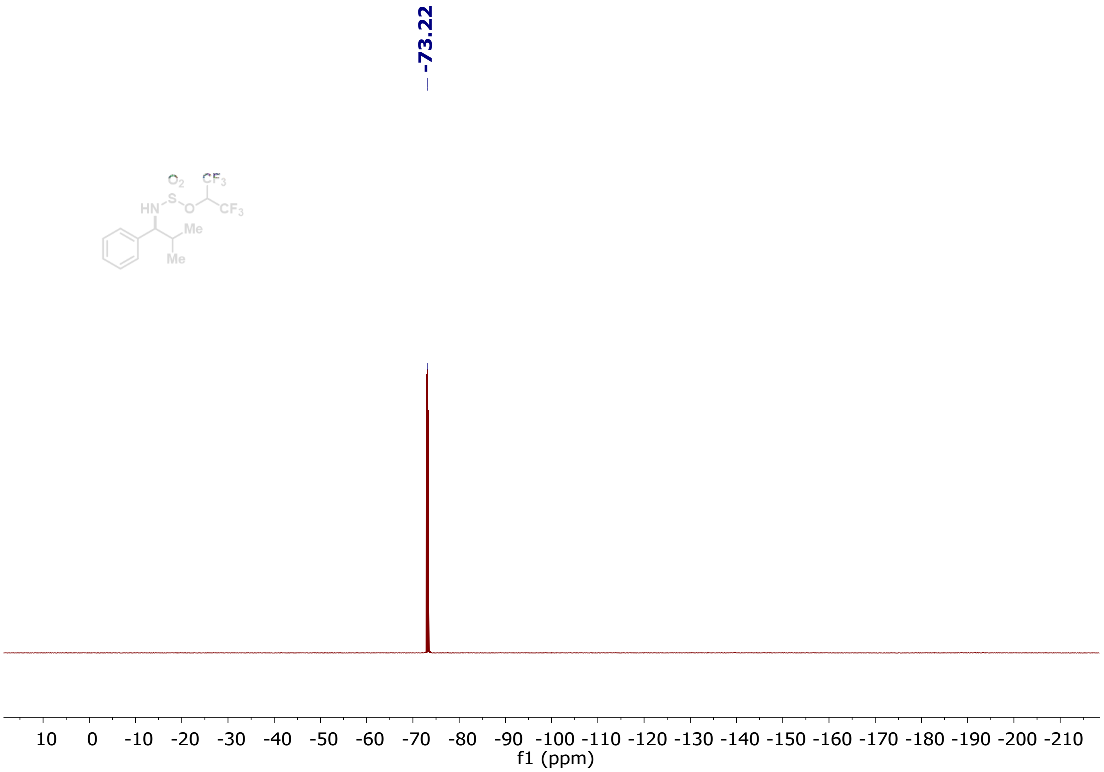
HN
S
O
CF3
Me
Me
MeOC
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 26b



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O2
CF3
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S
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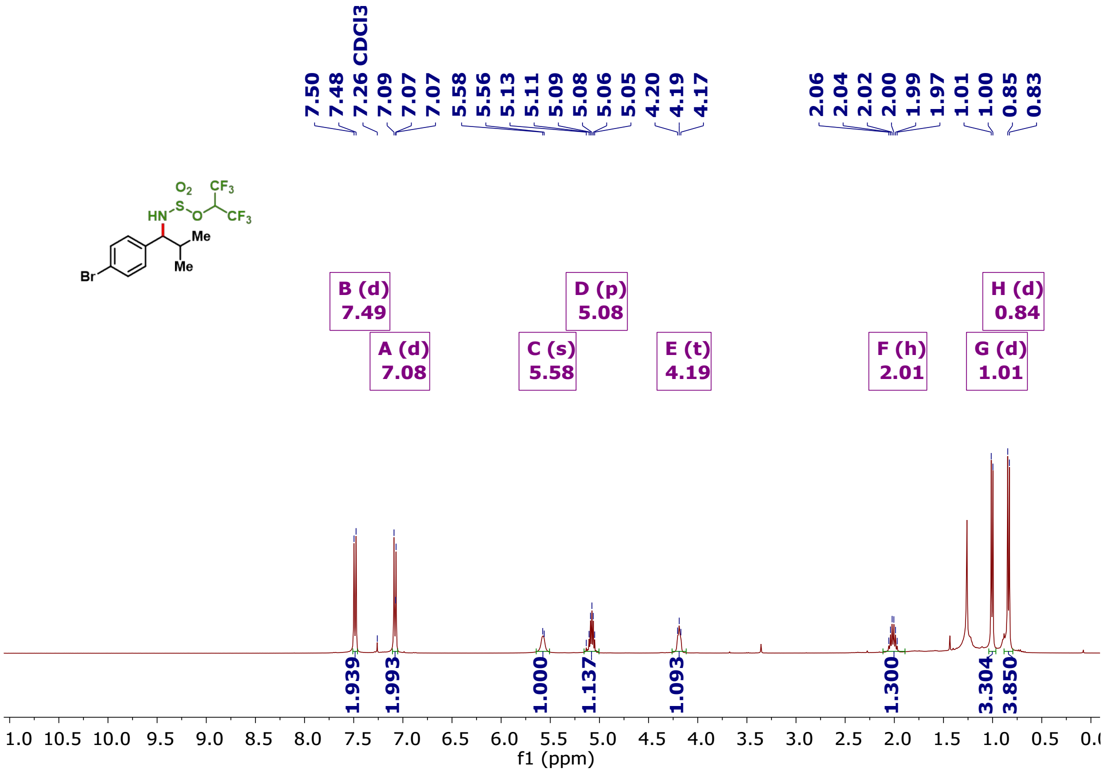
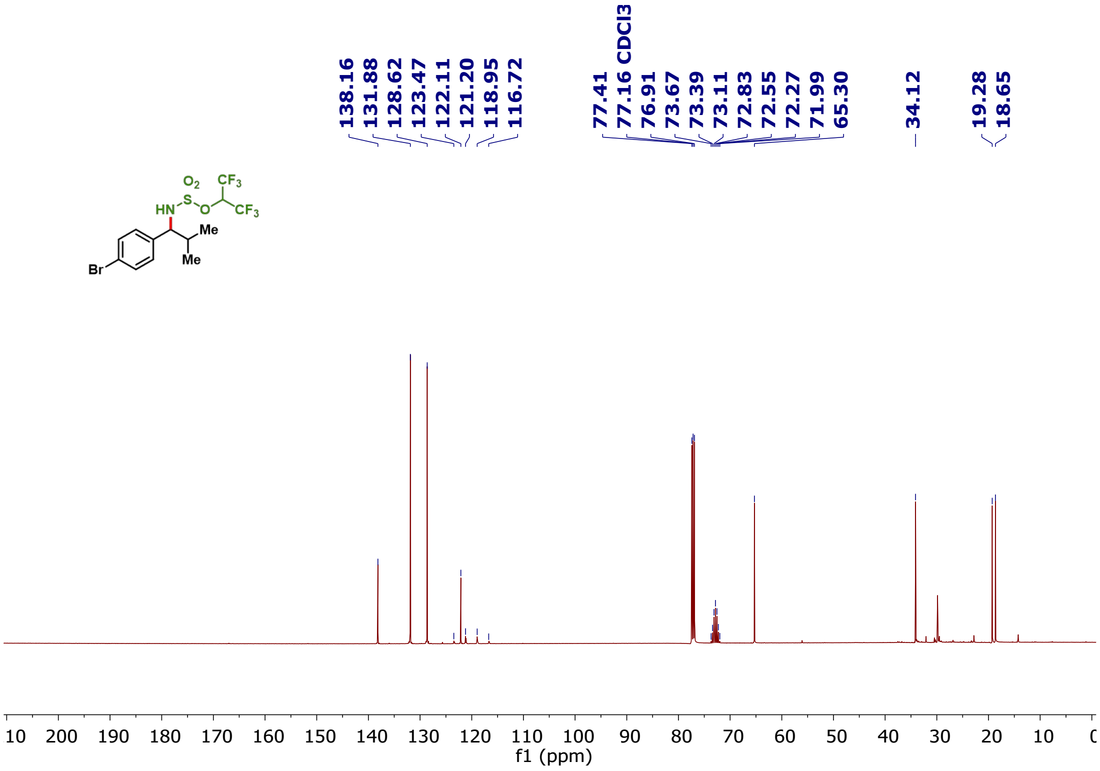
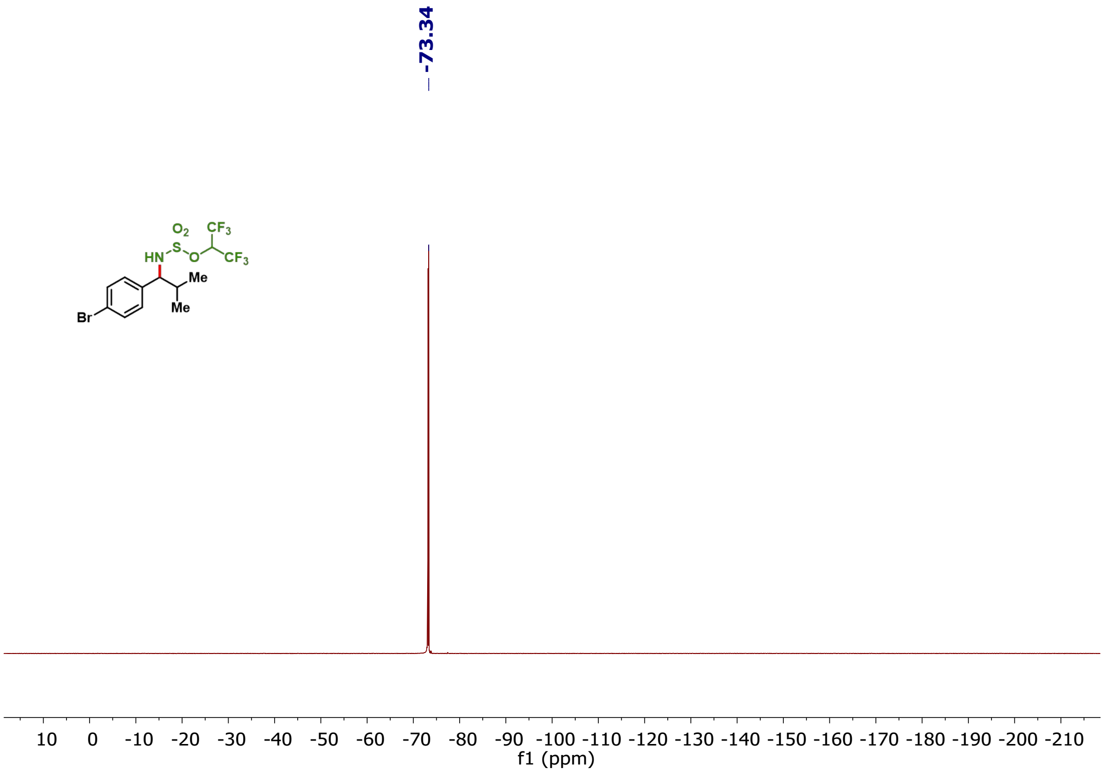
CF3
Me
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

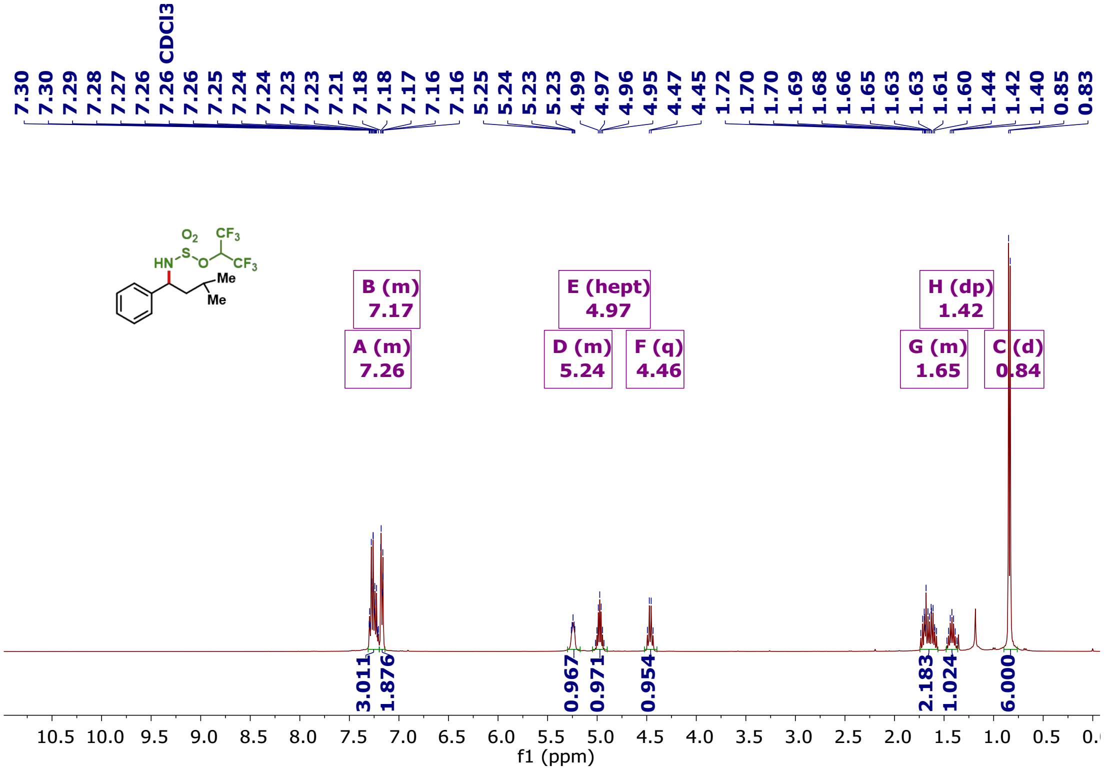
^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 27b

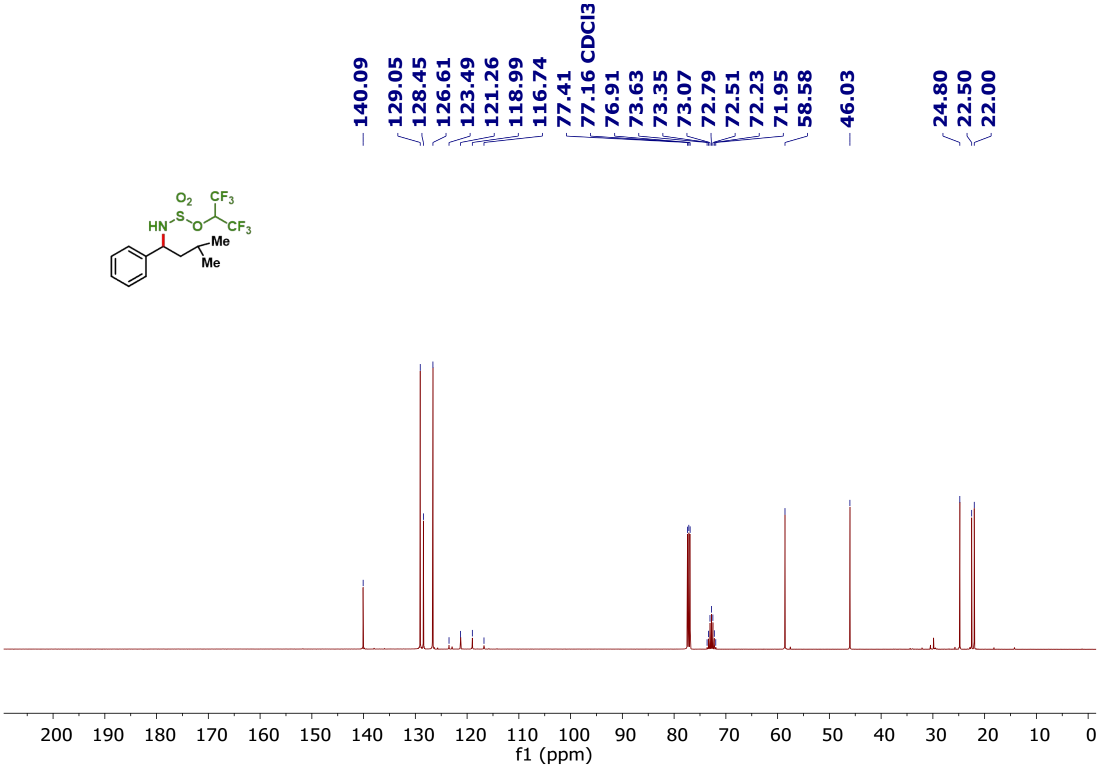


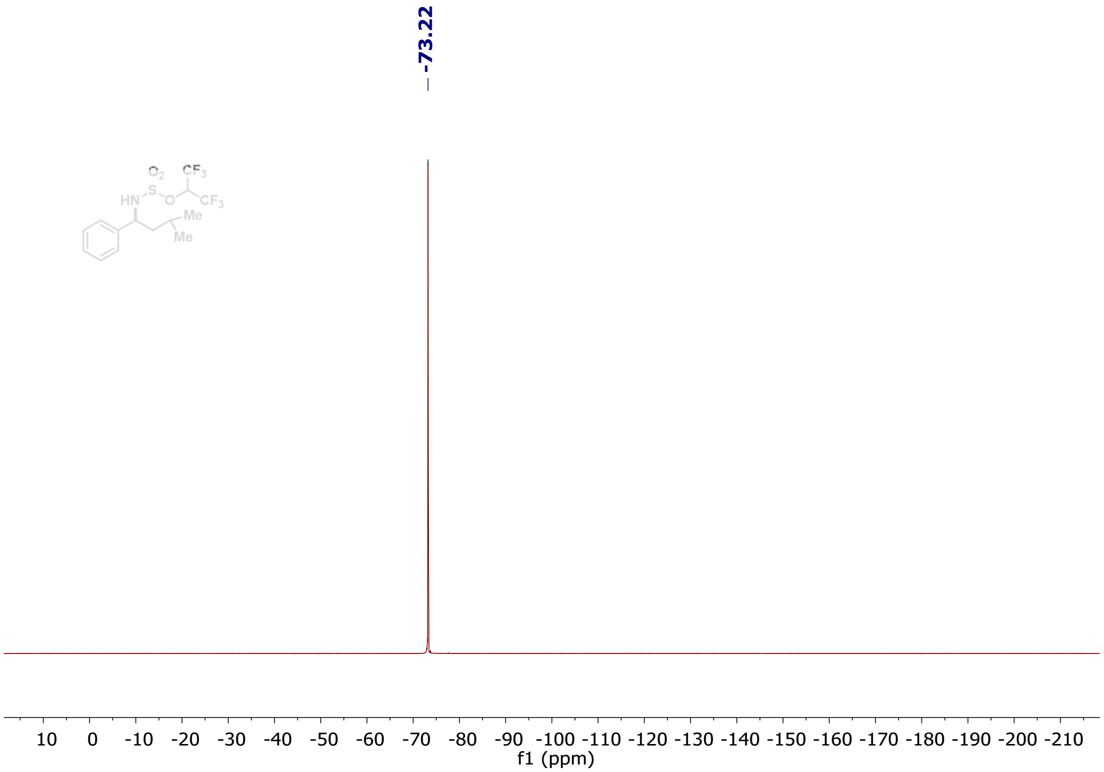



-73.34
HN
S
O2
O
CF3
CF3
Me
Me
Br
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

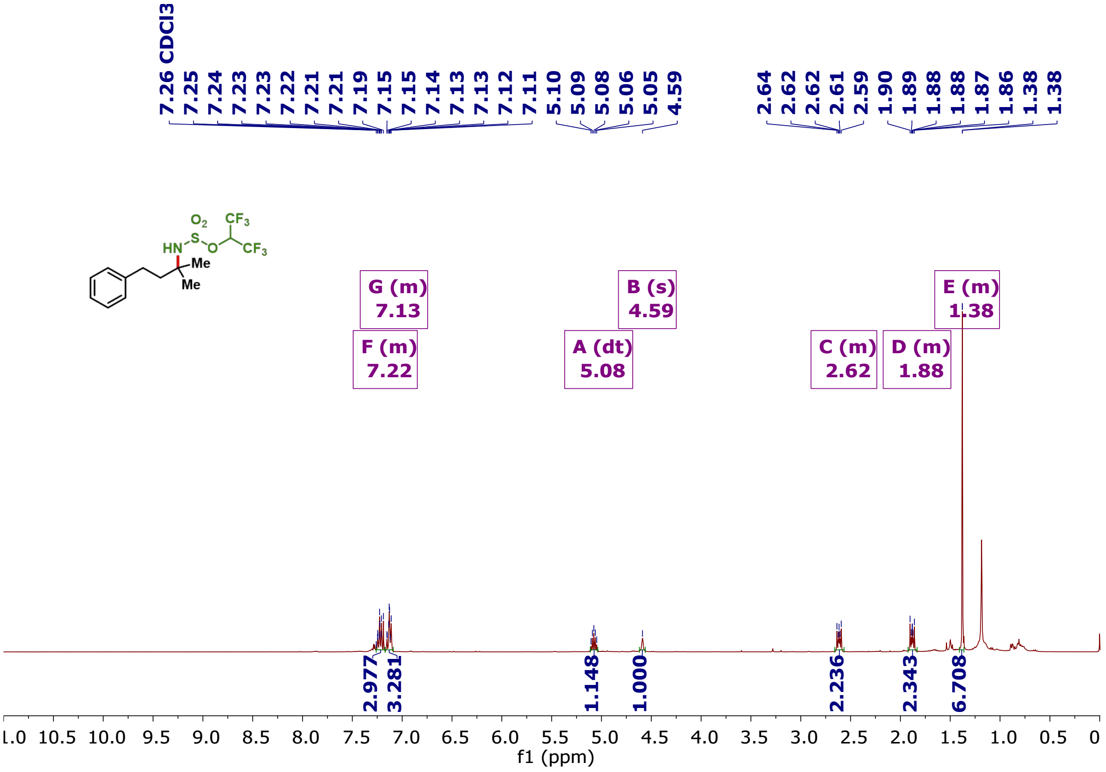
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 28b

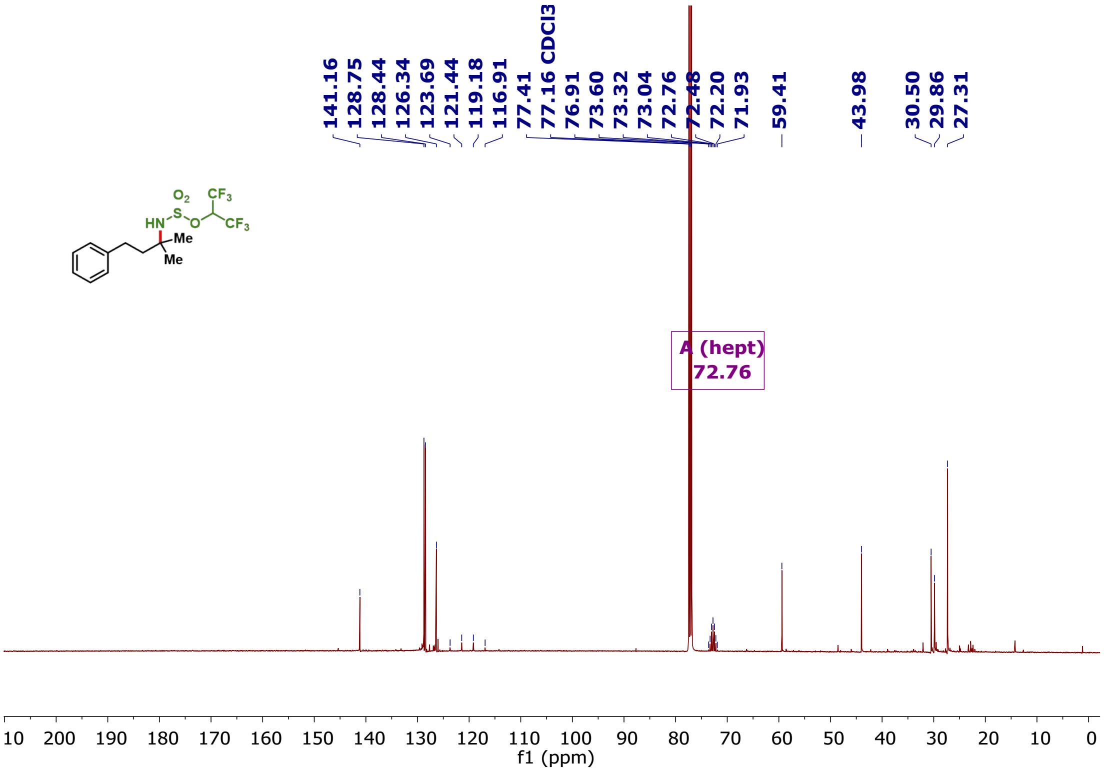


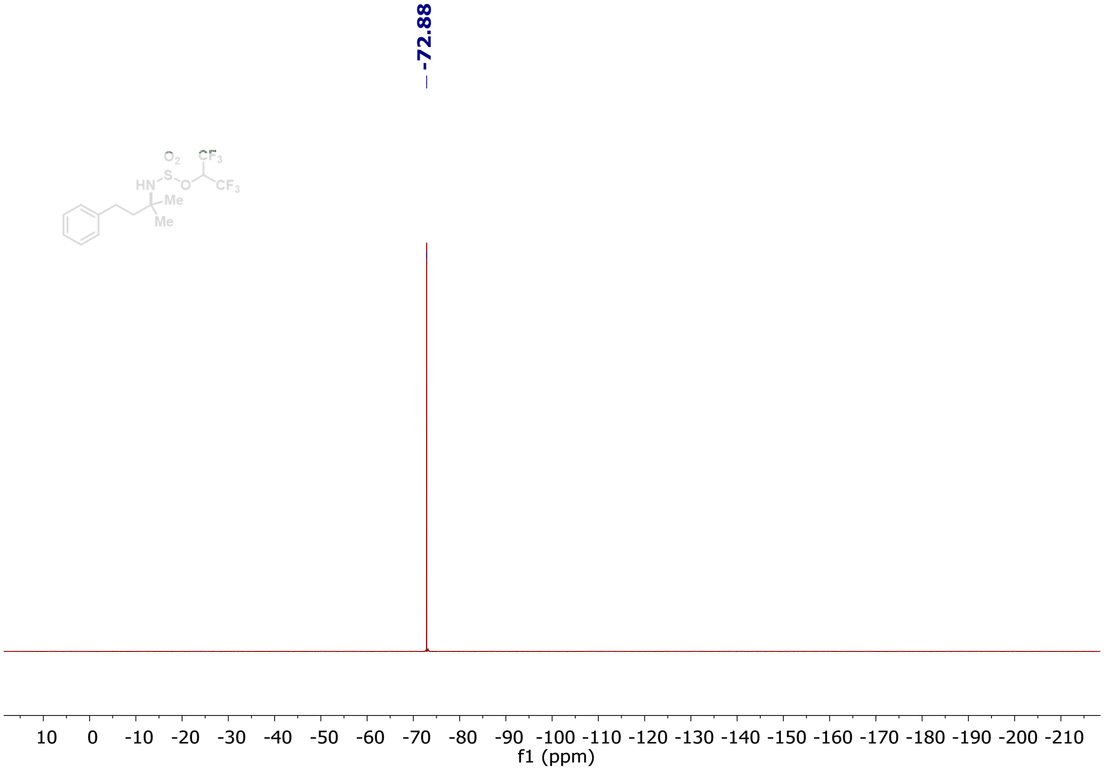



-73.22
O2
CF3
HN
S
O
CF3
Me
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 28b (other isomer)



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CF3
HN
S
O
CF3
Me
Me
10
0
-10
-20
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-40
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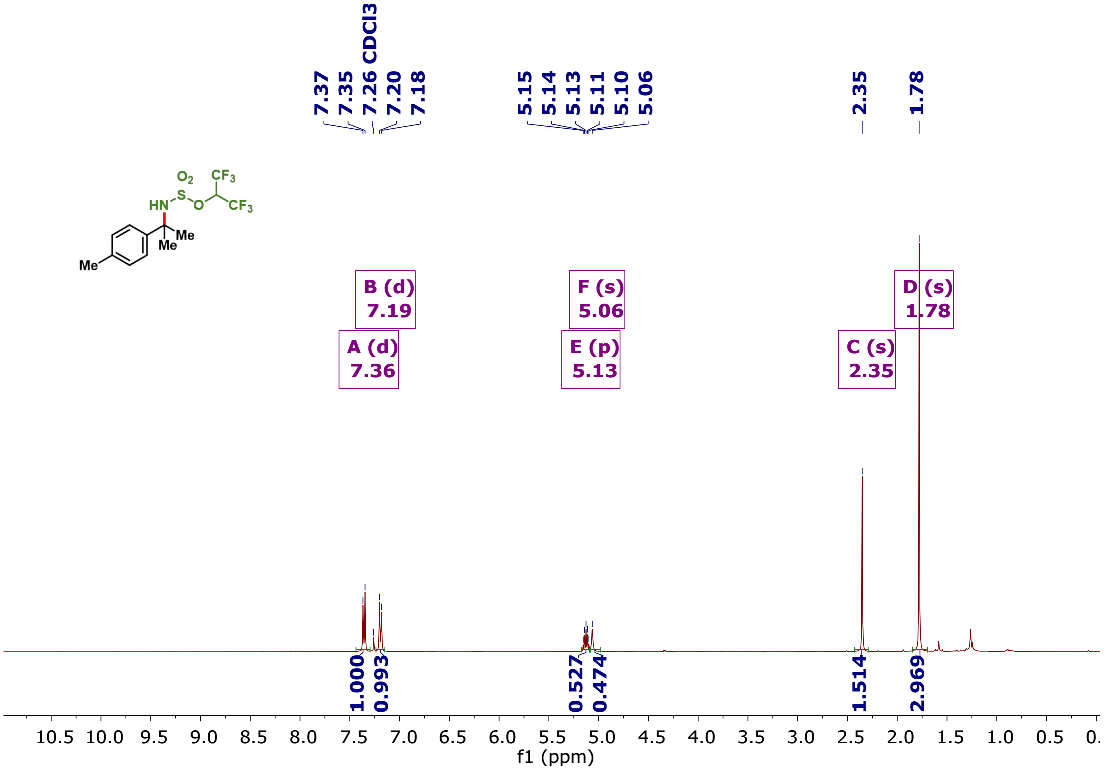
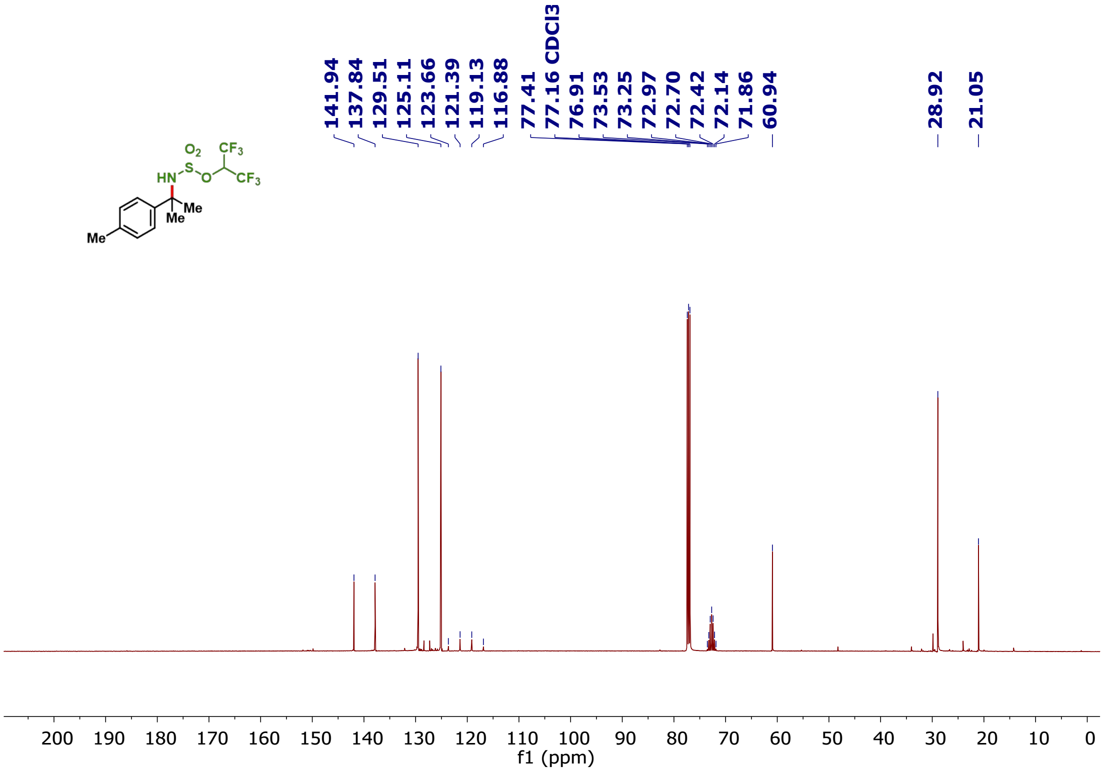
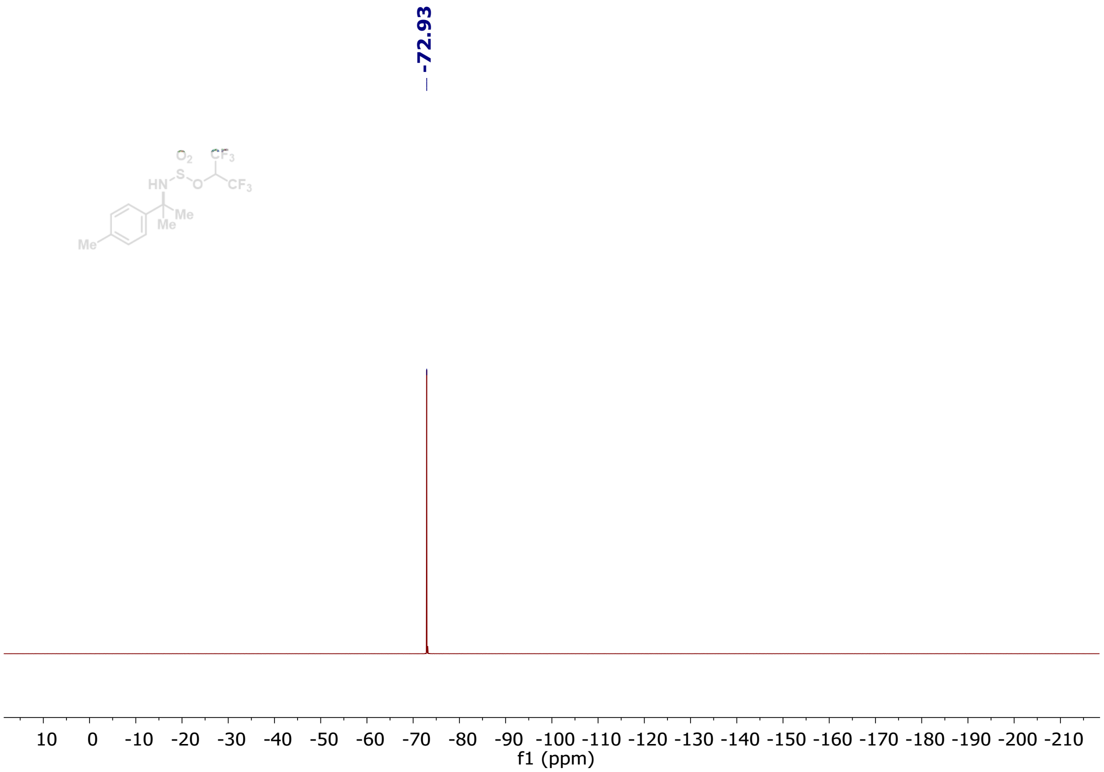
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 29b



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CF3
Me
Me
Me
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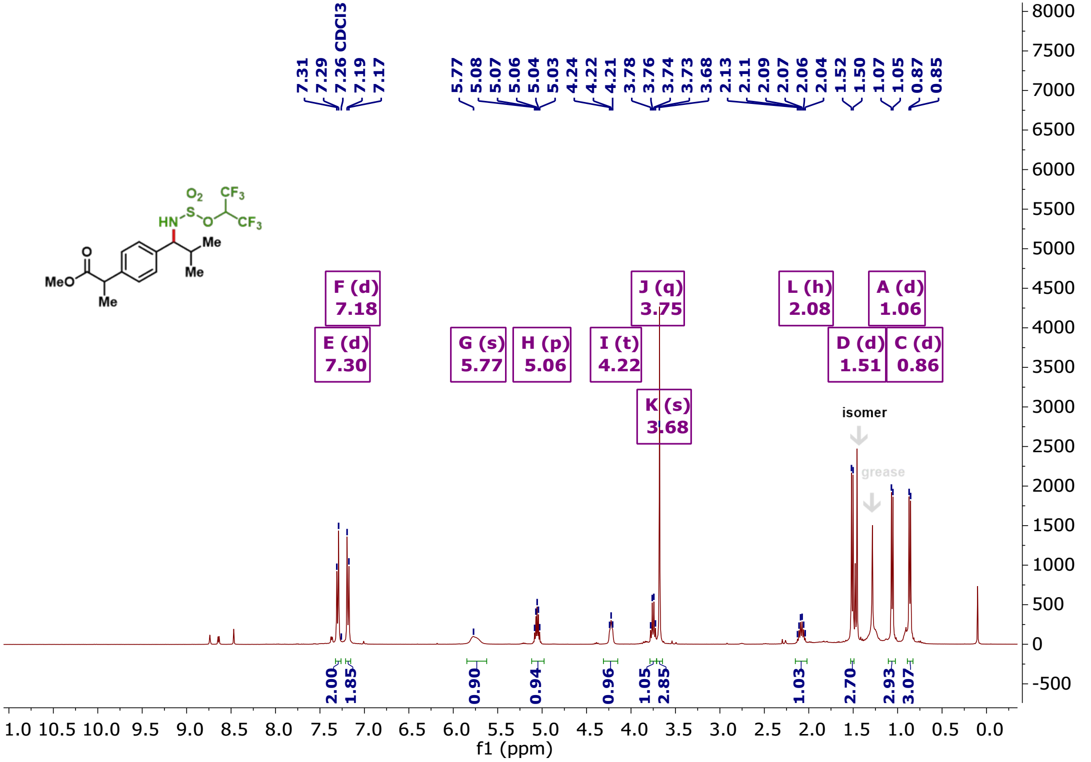
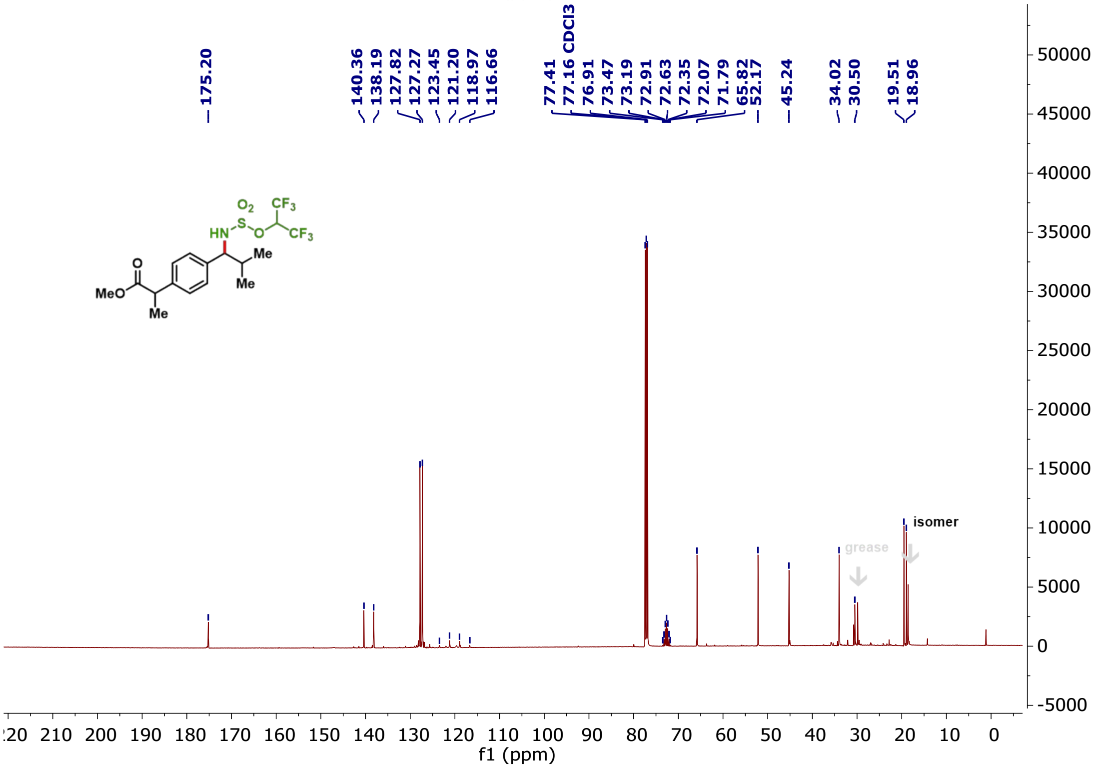
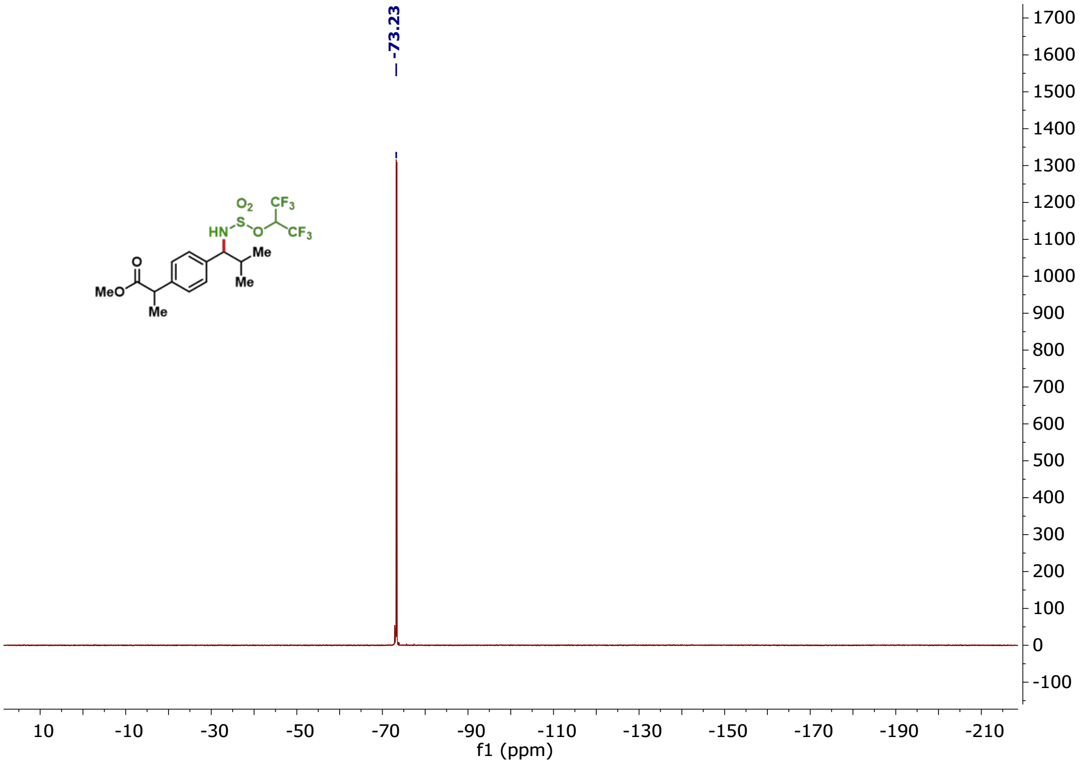
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 30b



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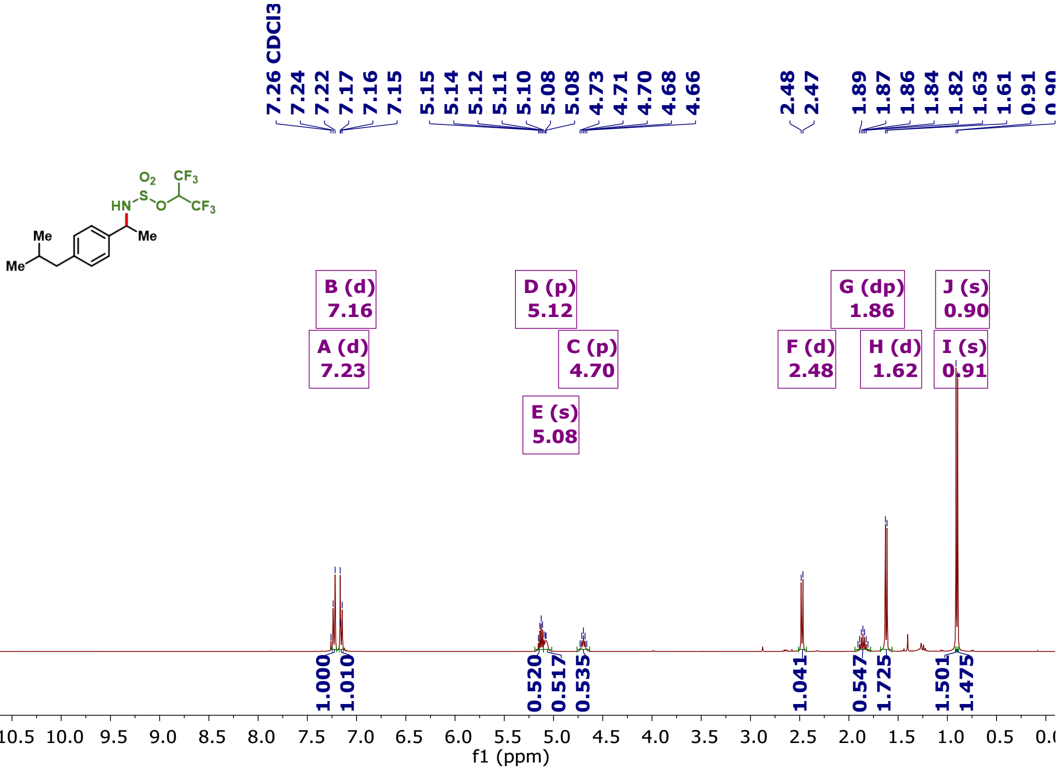
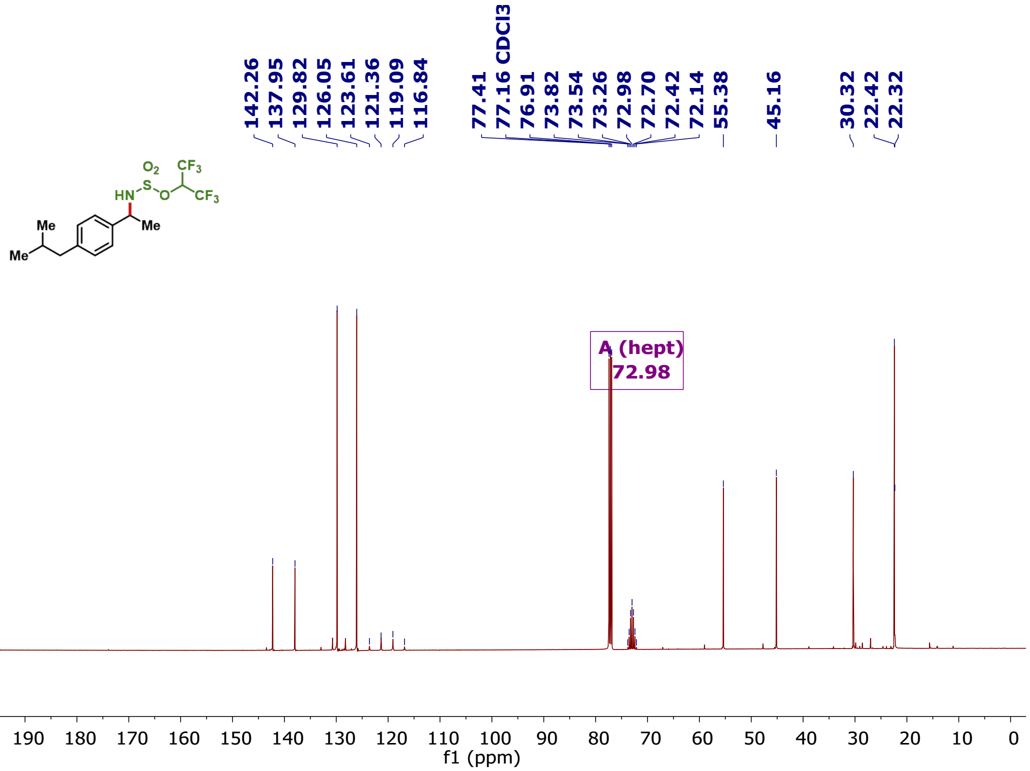
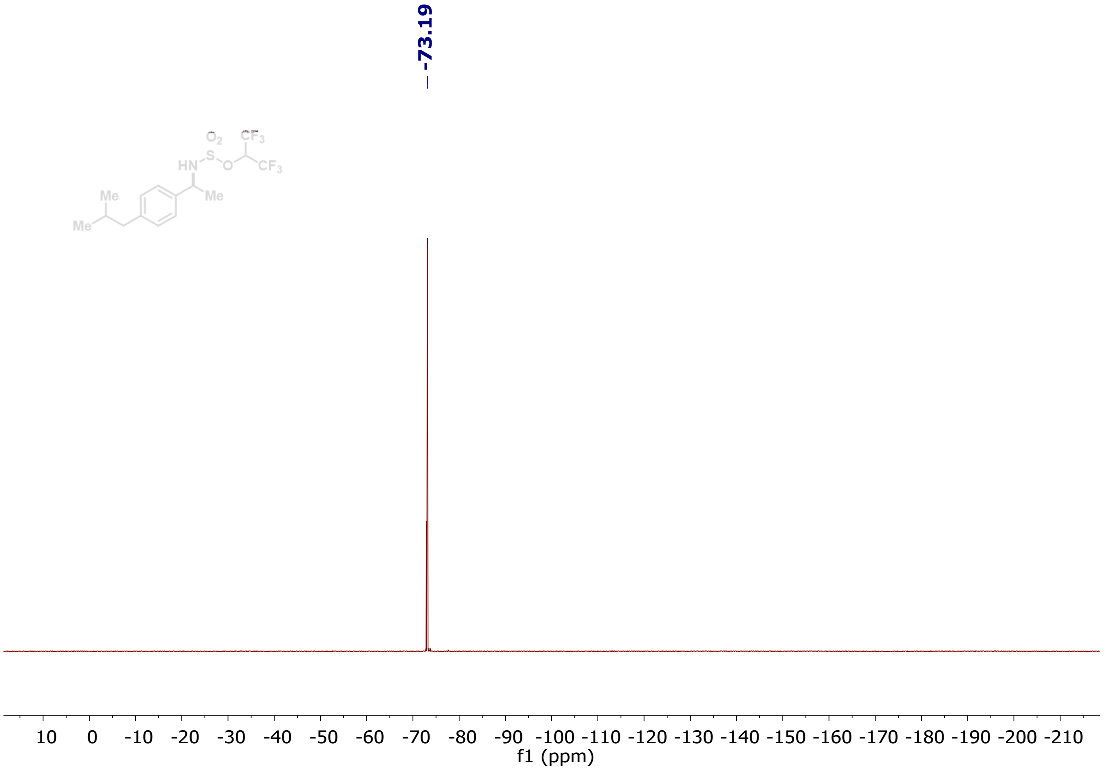
O2
CF3
HN
S
O
CF3
Me
O
MeO
Me
Me
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

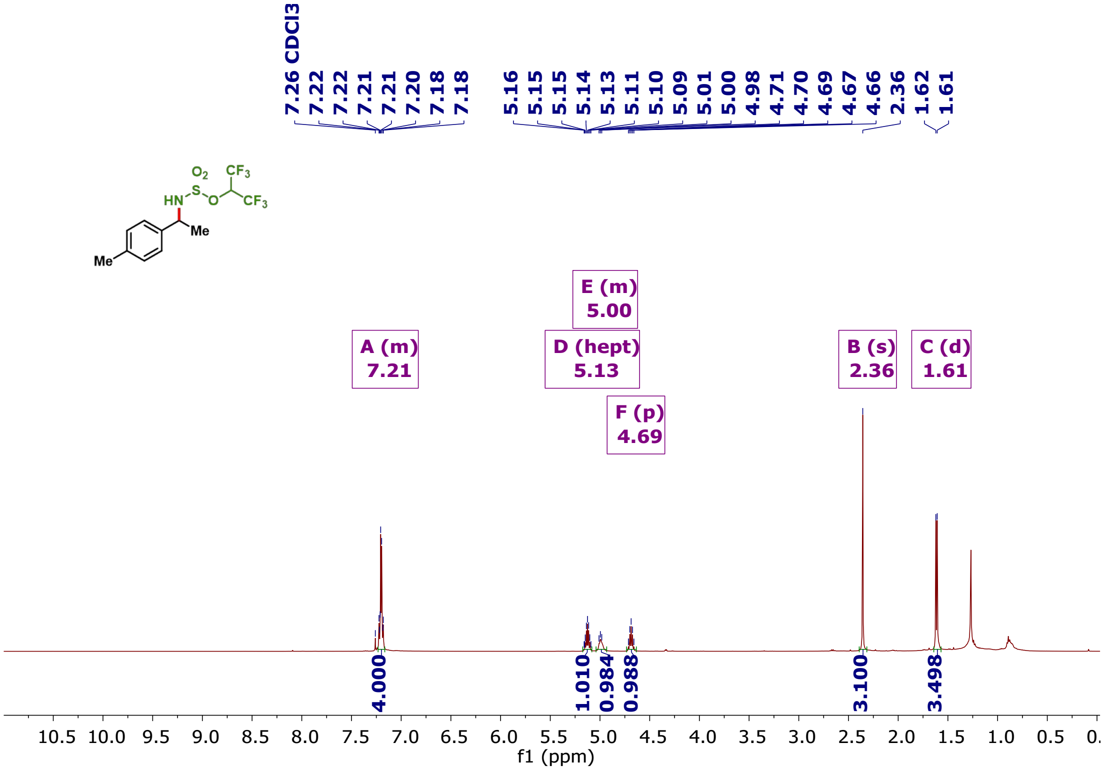
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 31b

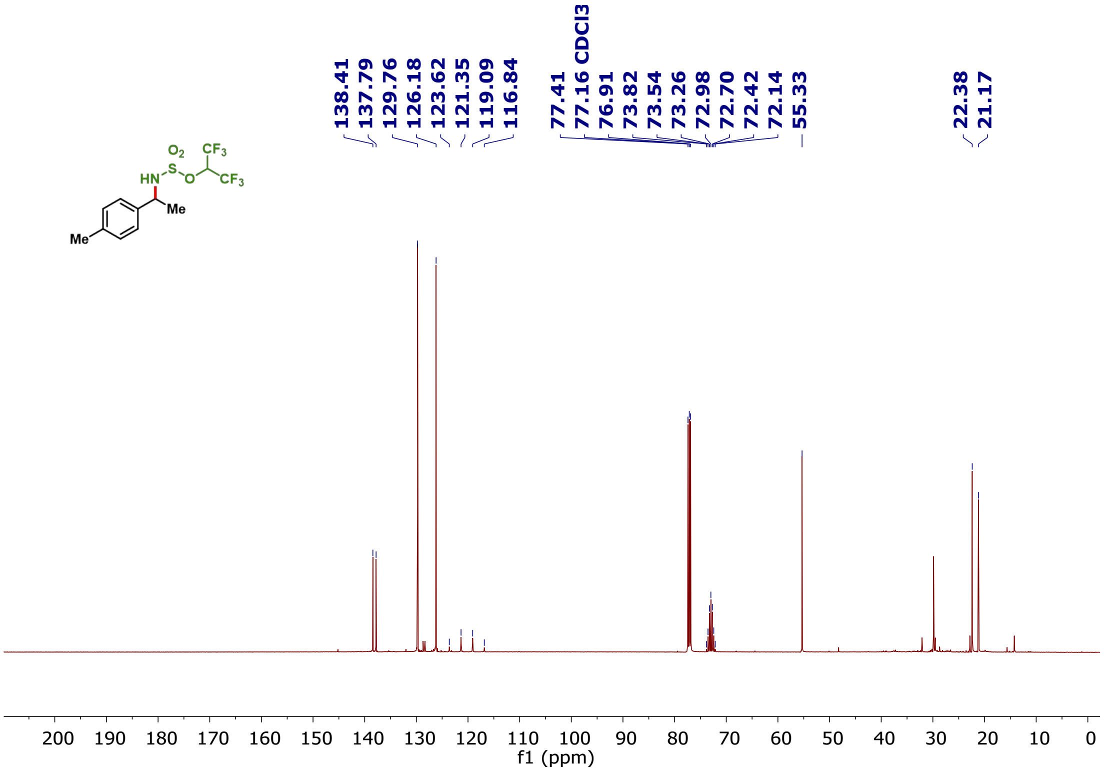


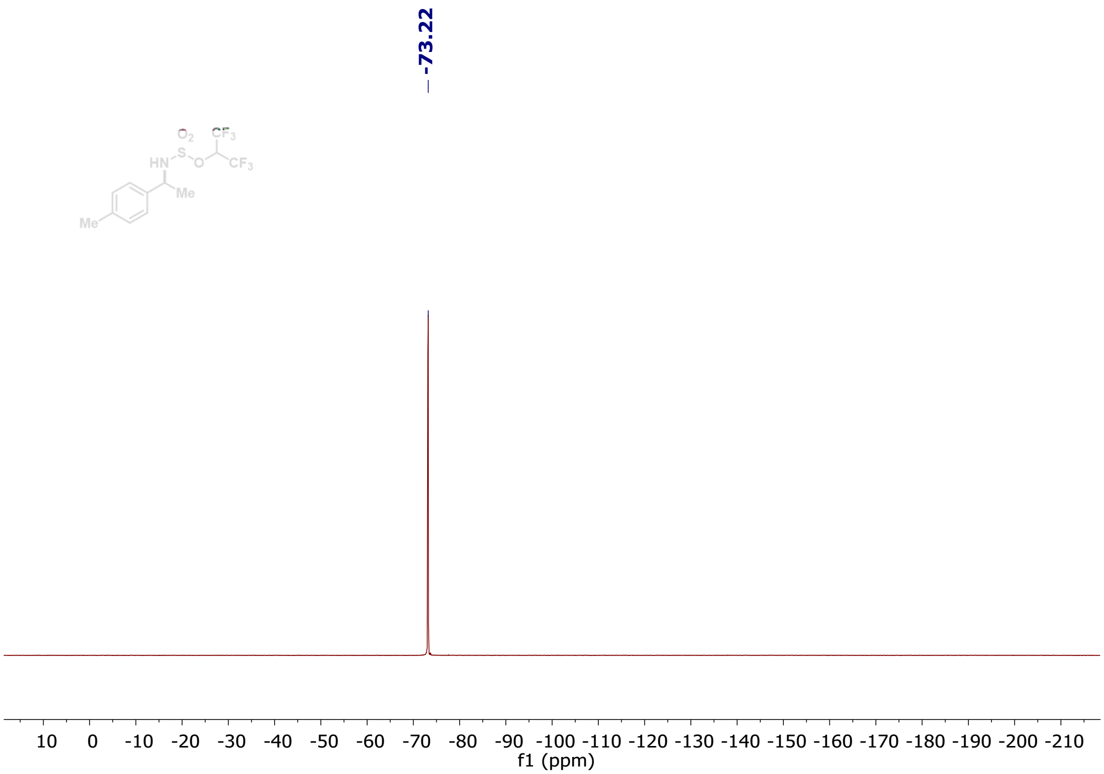



-73.19
O2
CF3
HN
S
O
CF3
Me
Me
Me
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

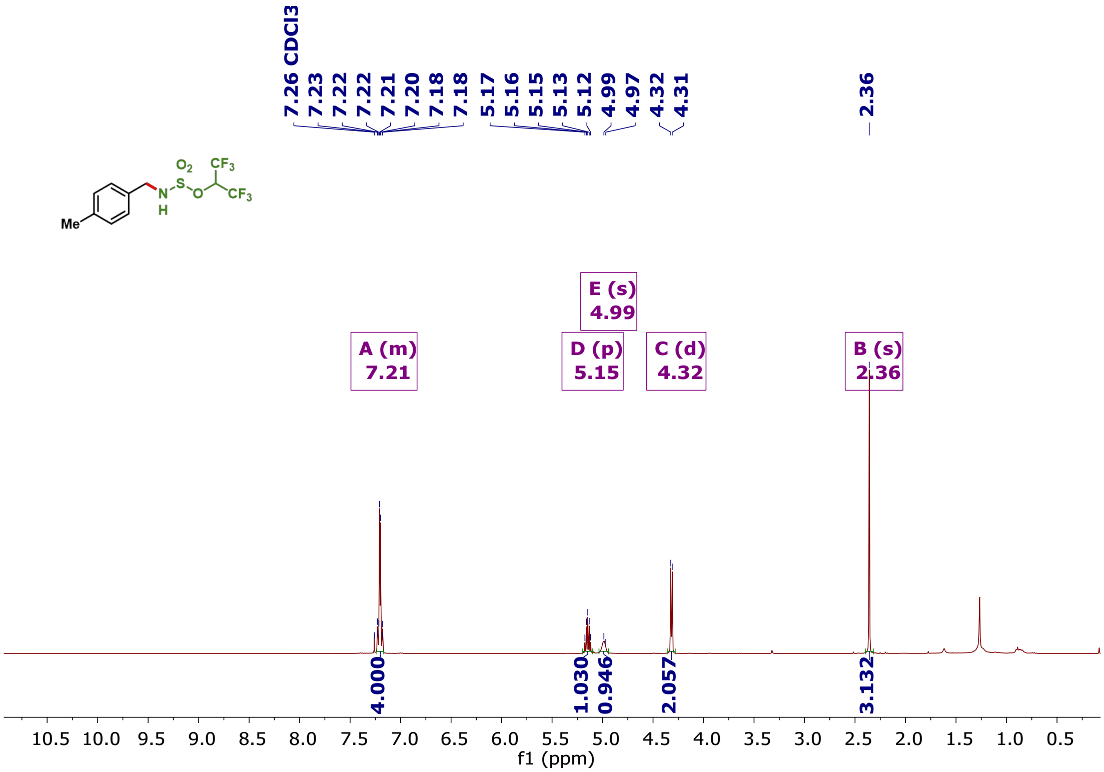
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 32b

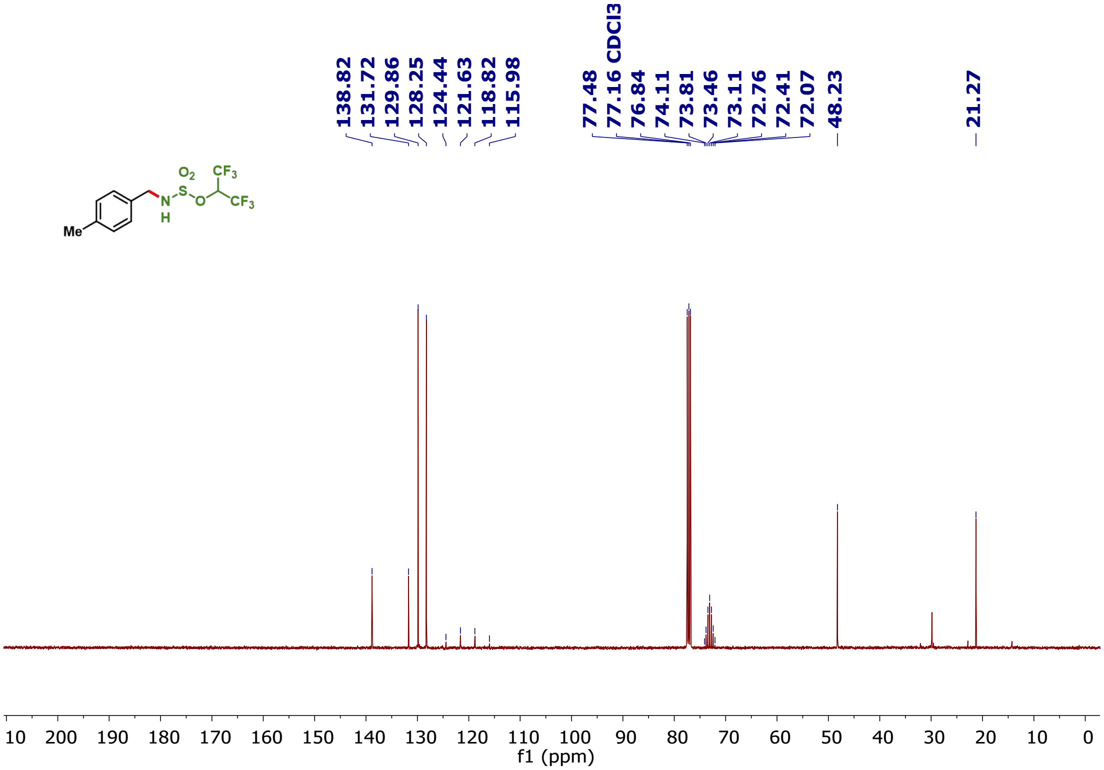


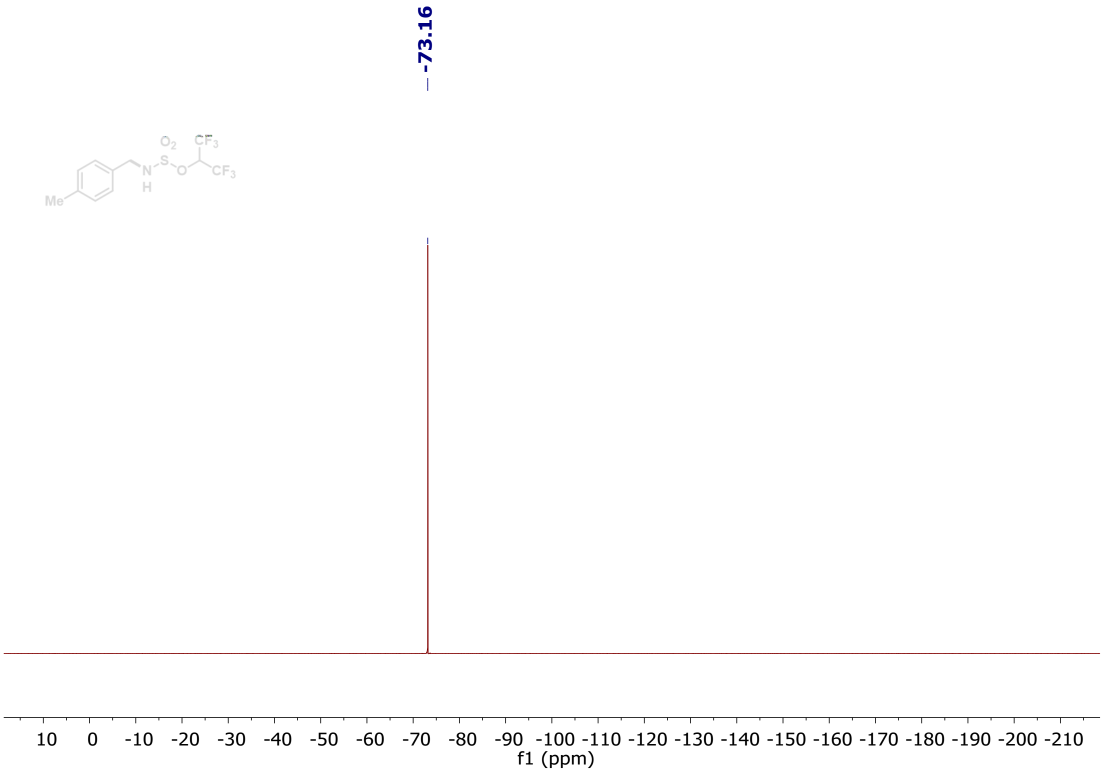



-73.22
O2
CF3
HN
S
O
CF3
Me
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

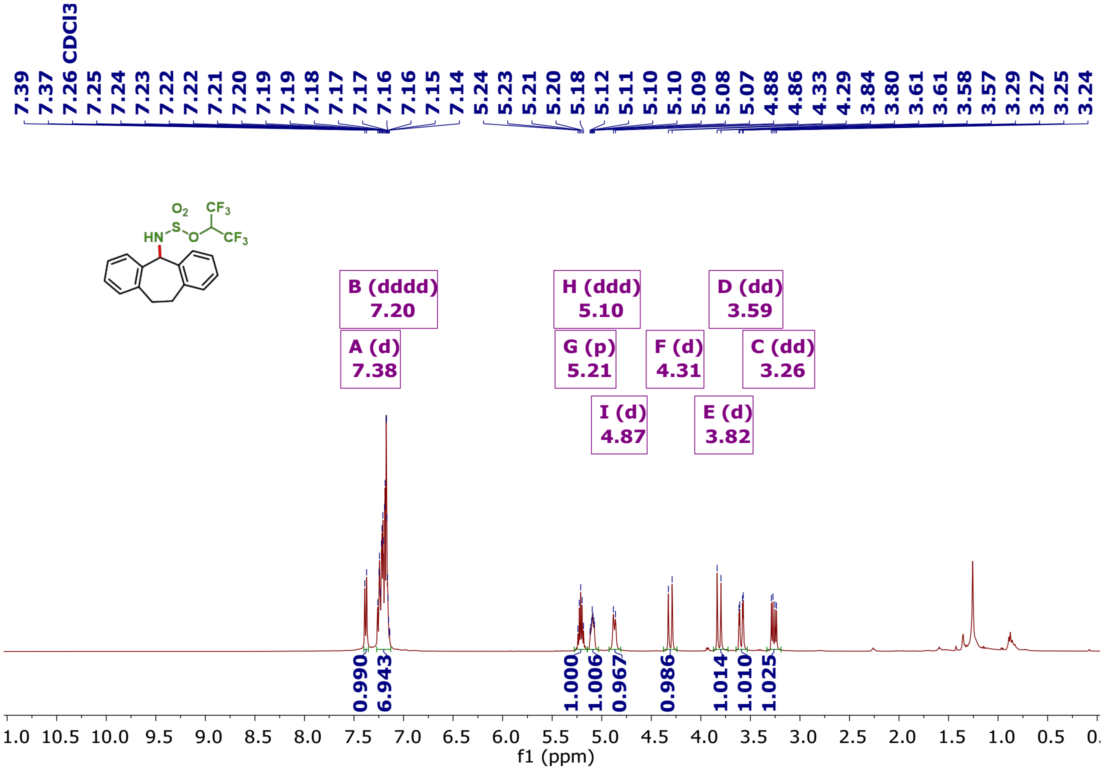
^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 33b

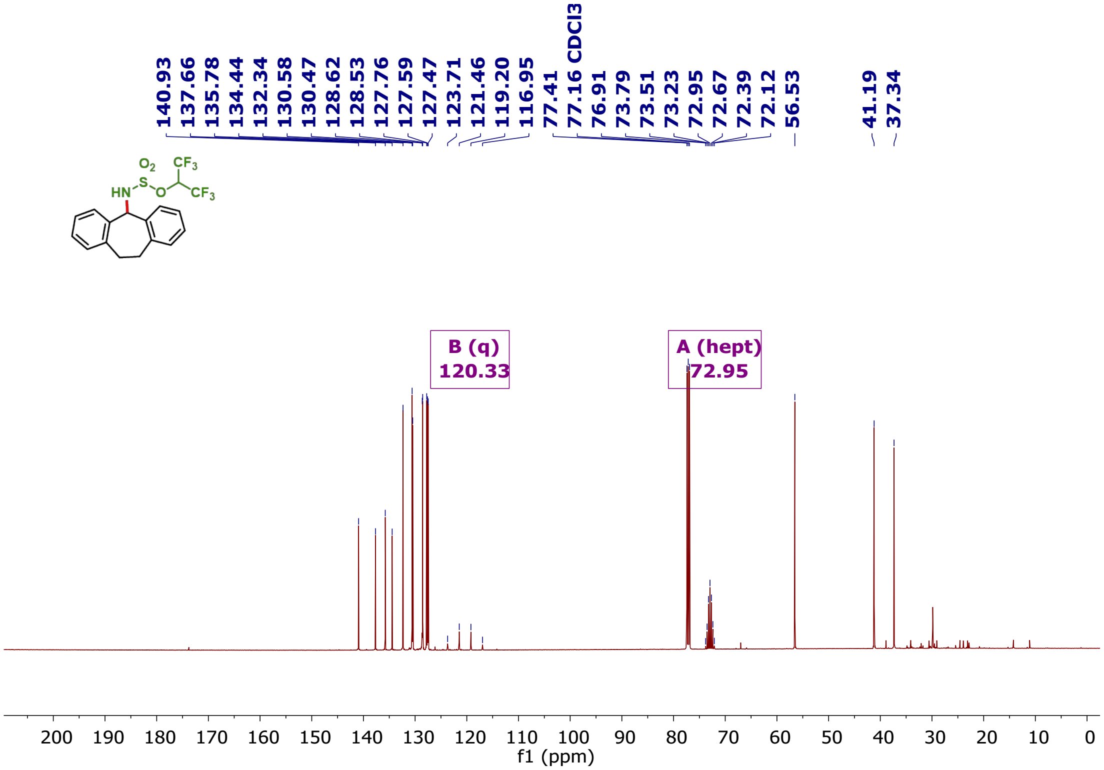


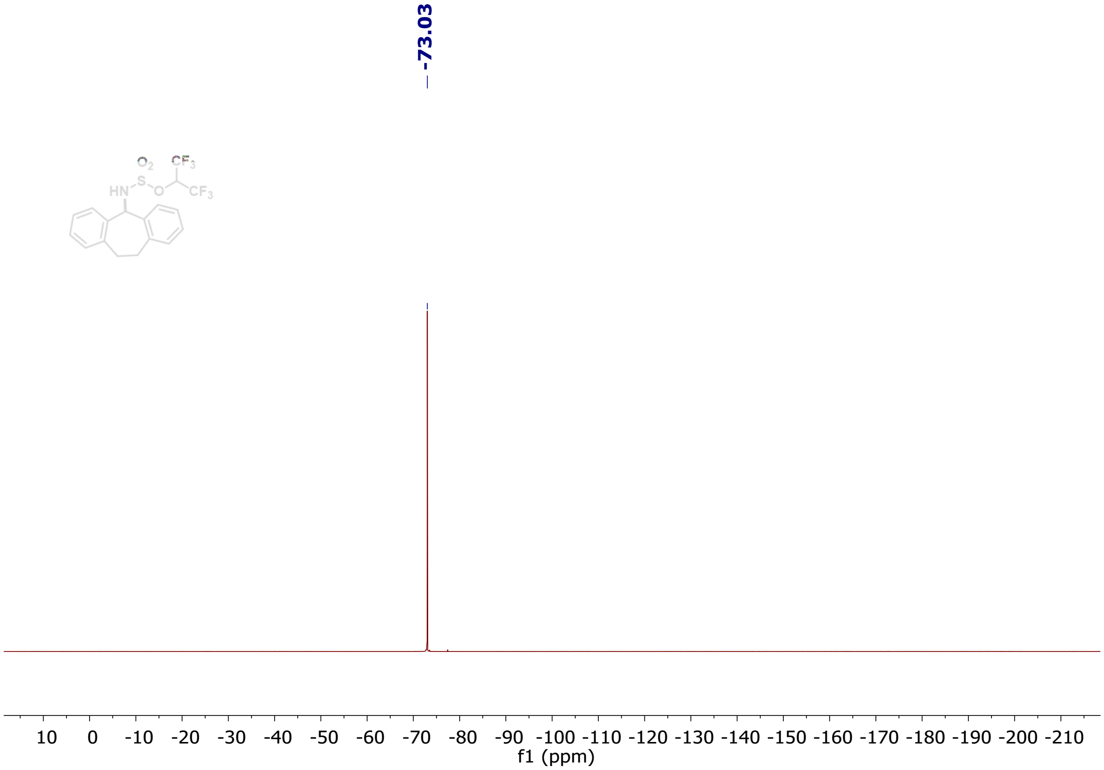



-73.16
Me
N
H
S
O2
O
CF3
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

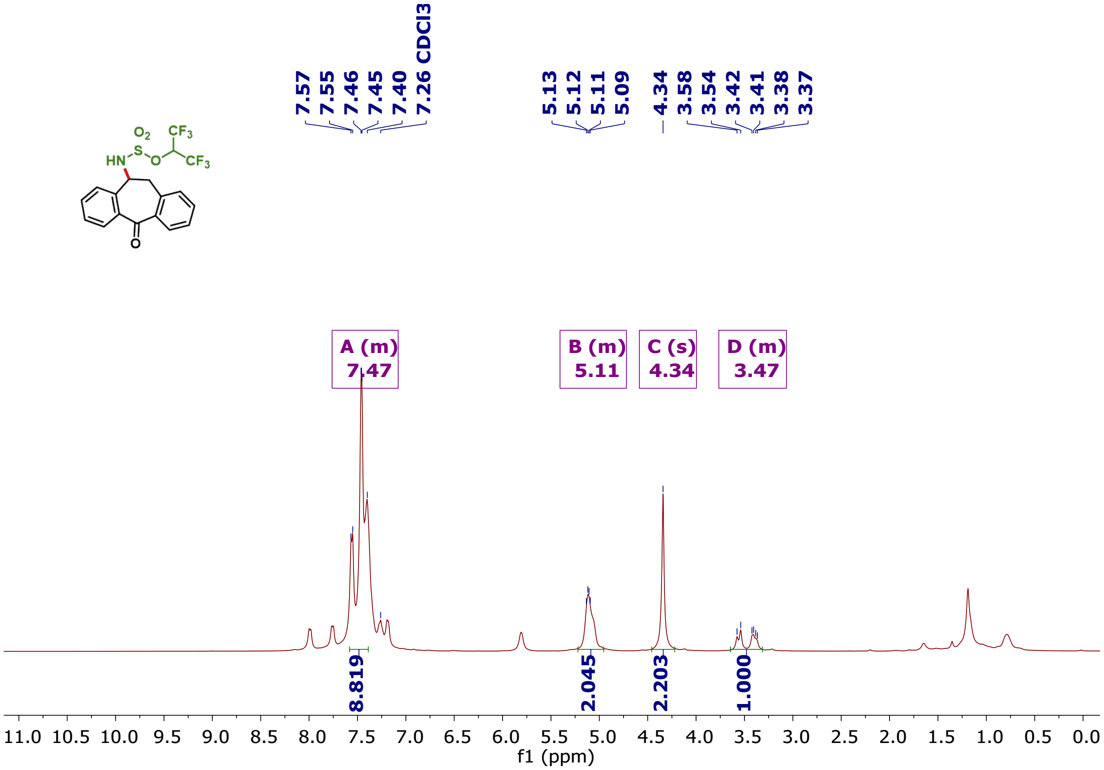
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 34b

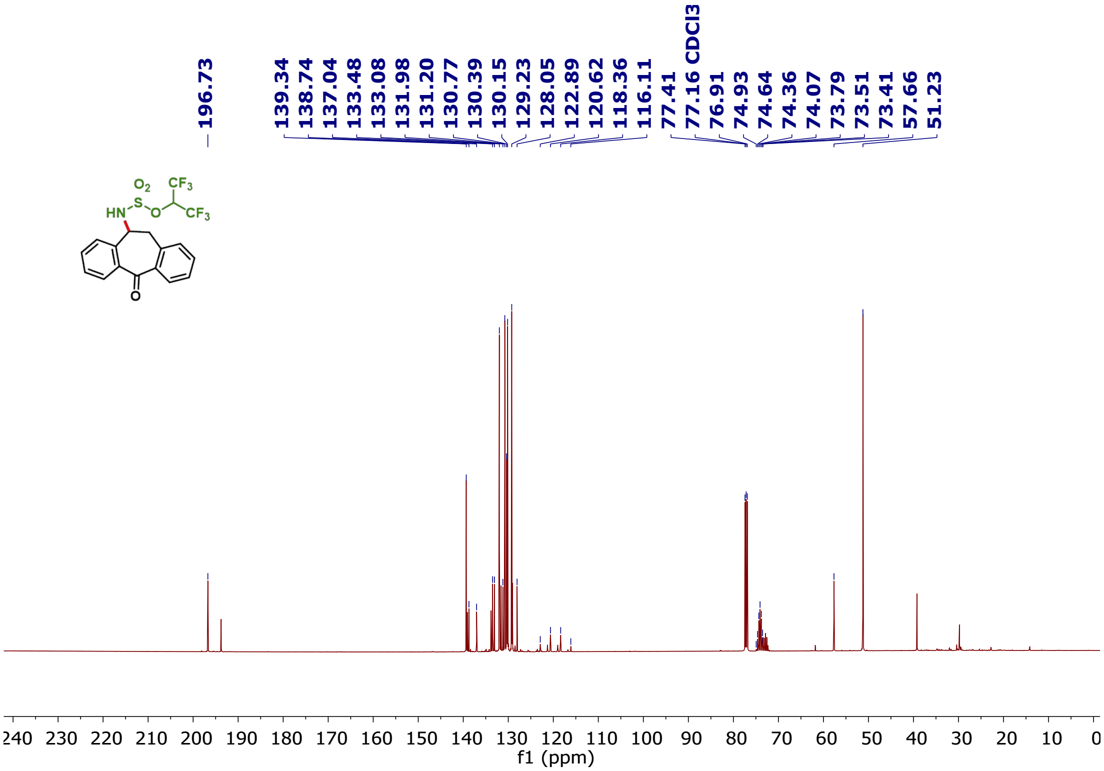


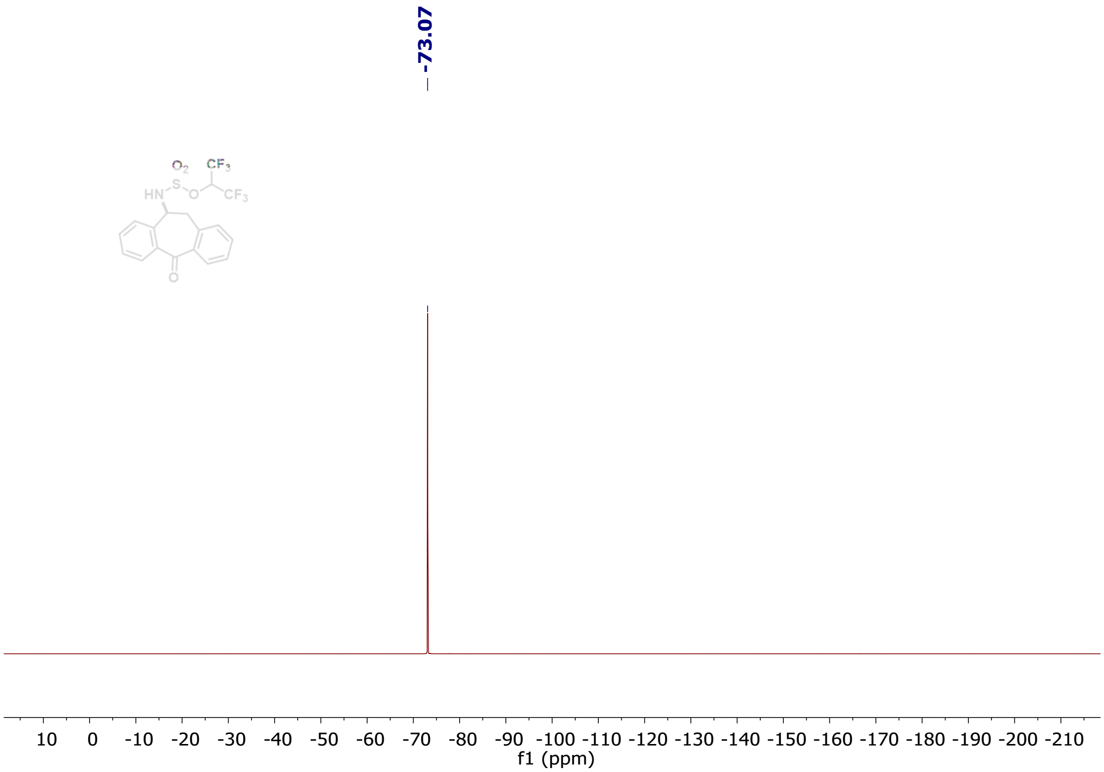



-73.03
O2
CF3
HN
S
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

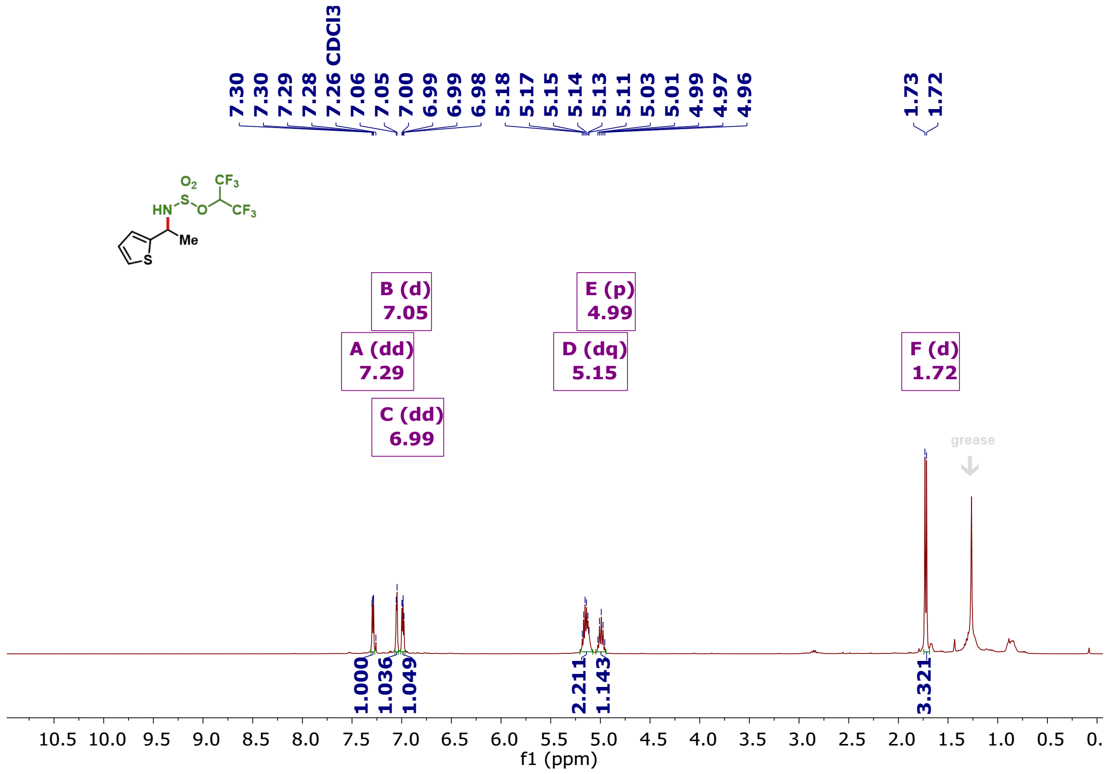
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 35b

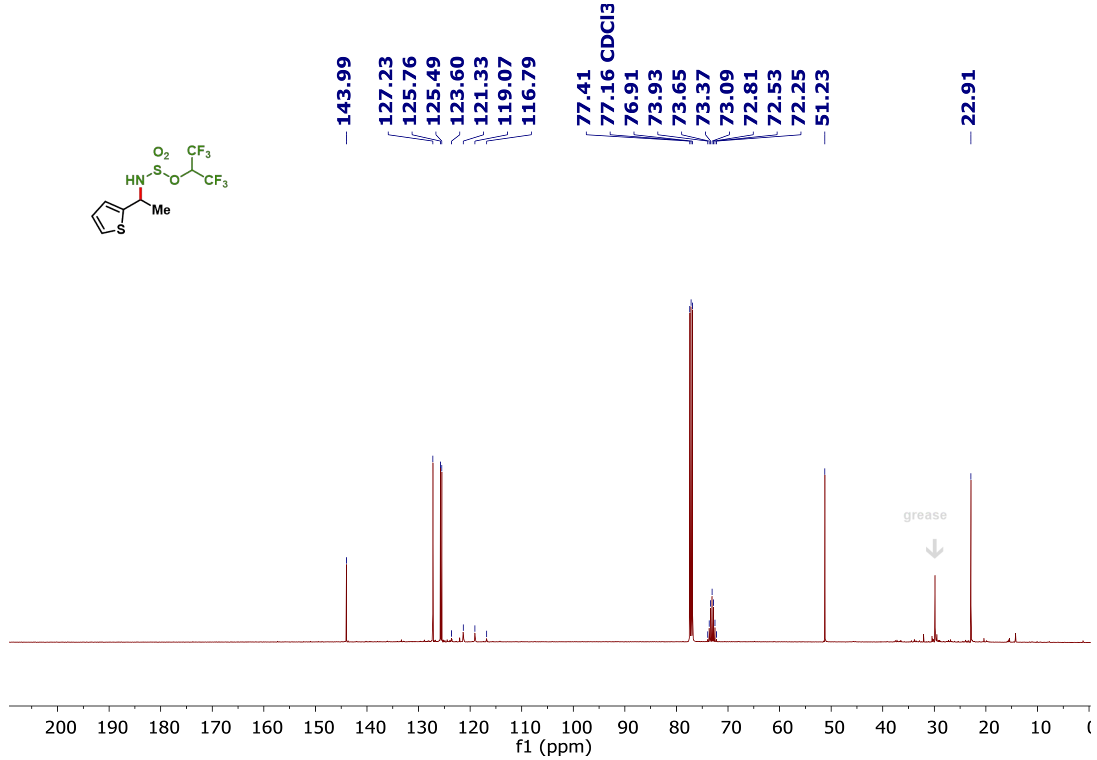


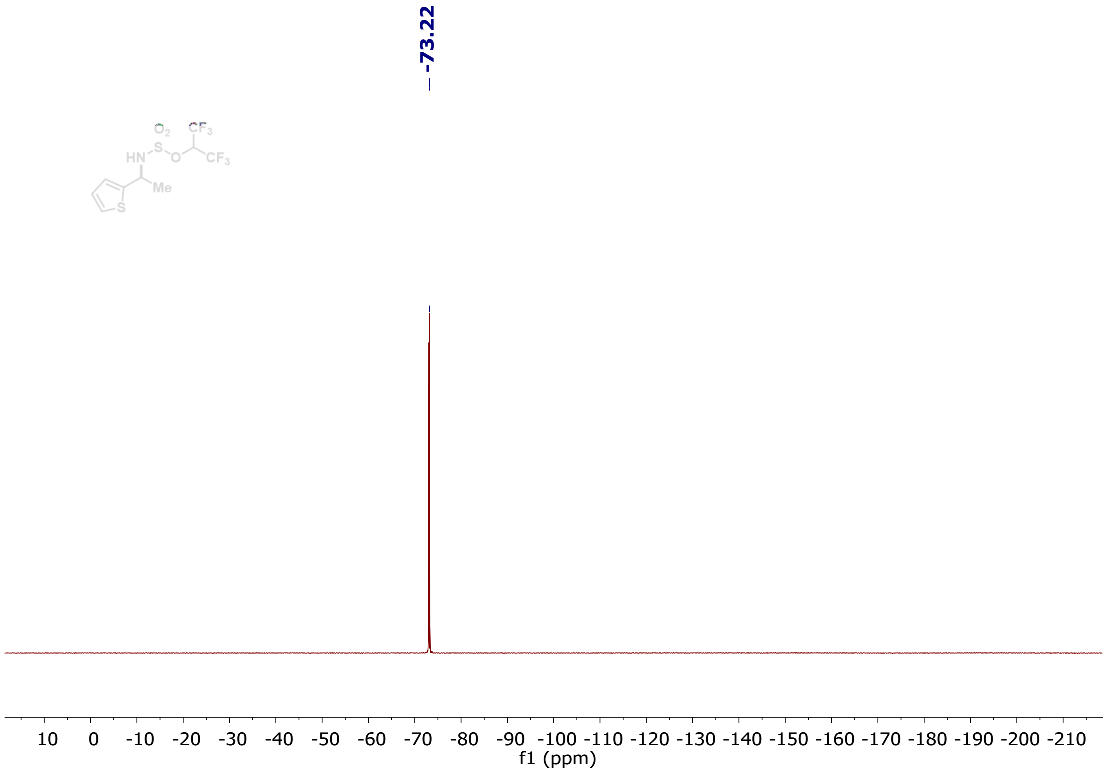



-73.07
O2
CF3
HN
S
O
CF3
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

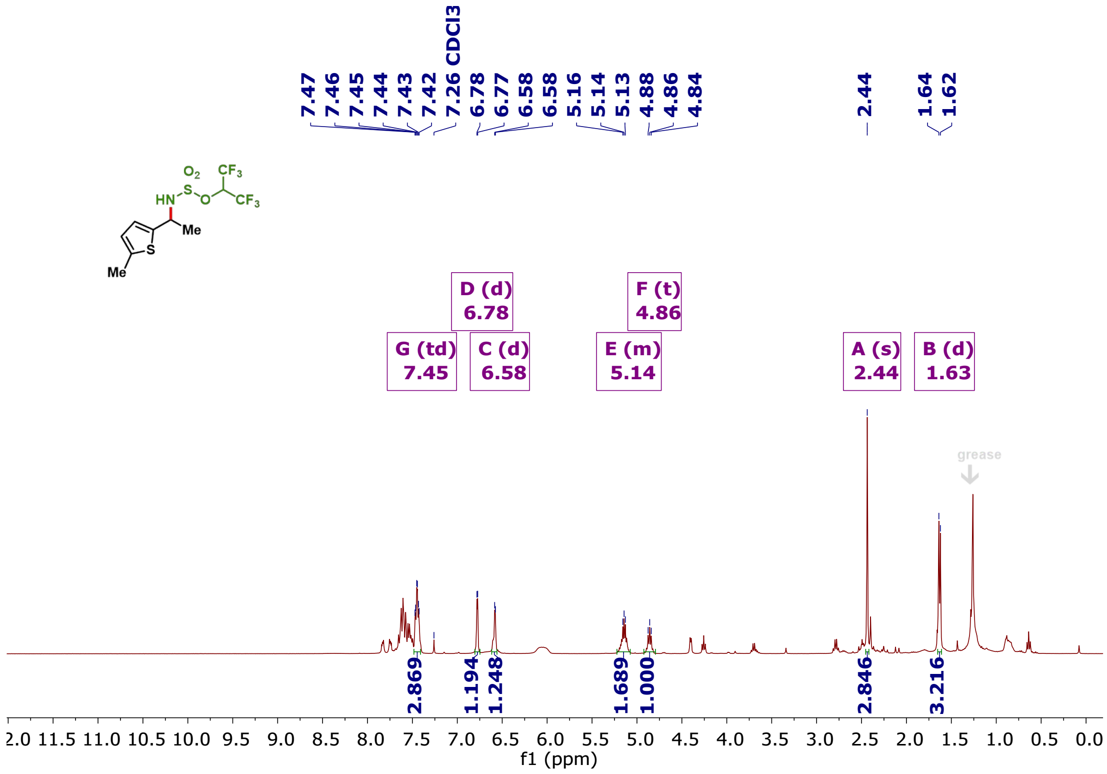
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 36b

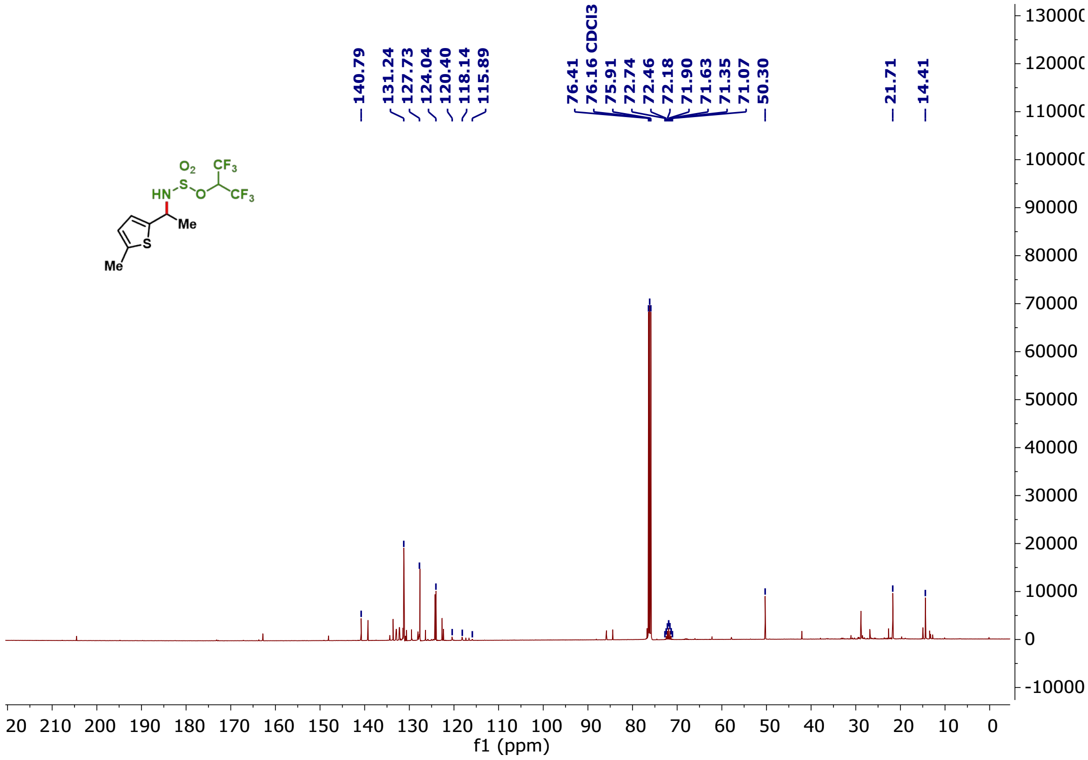


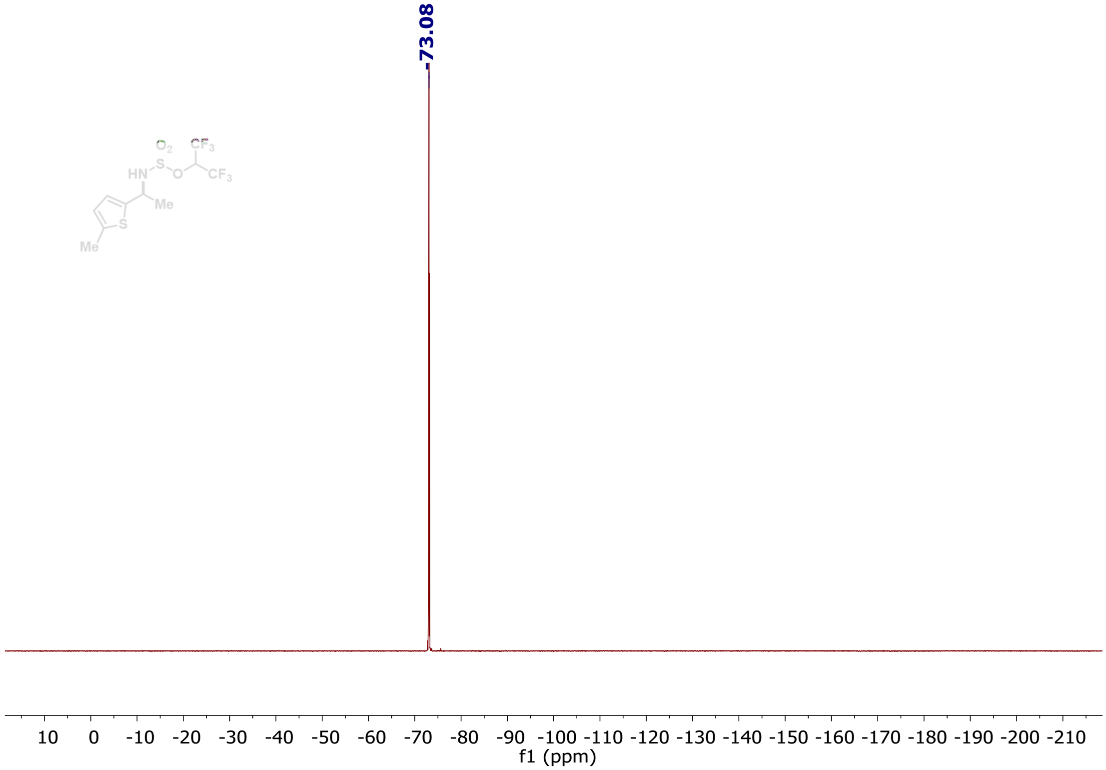



-73.22
O2
CF3
HN
S
O
CF3
Me
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

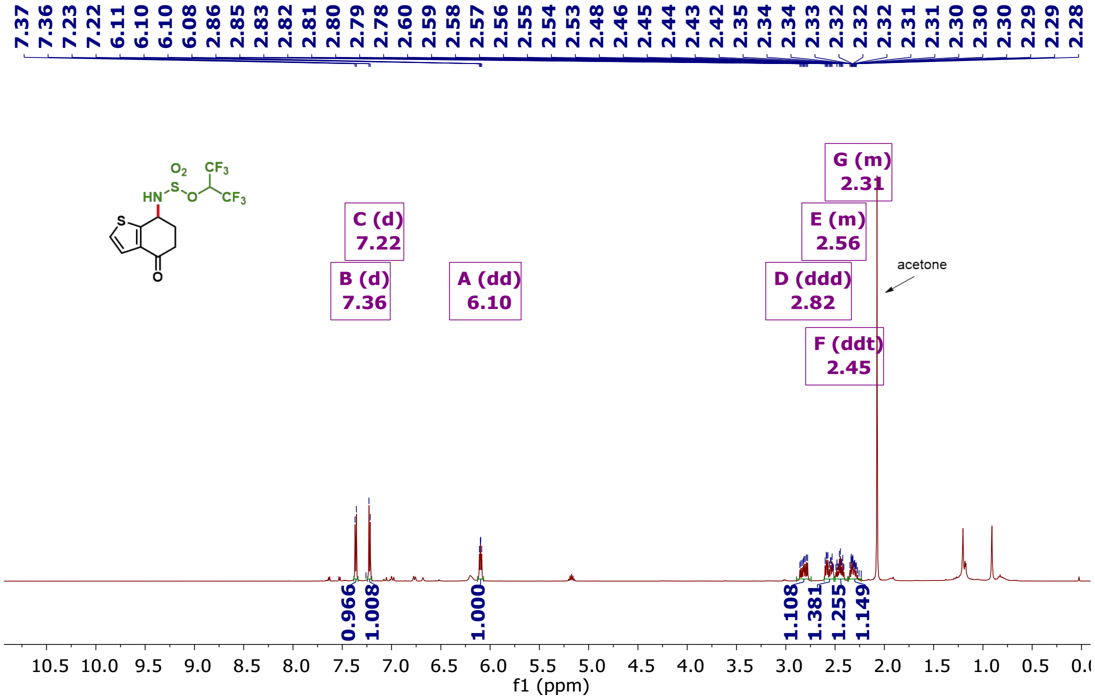
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 37b

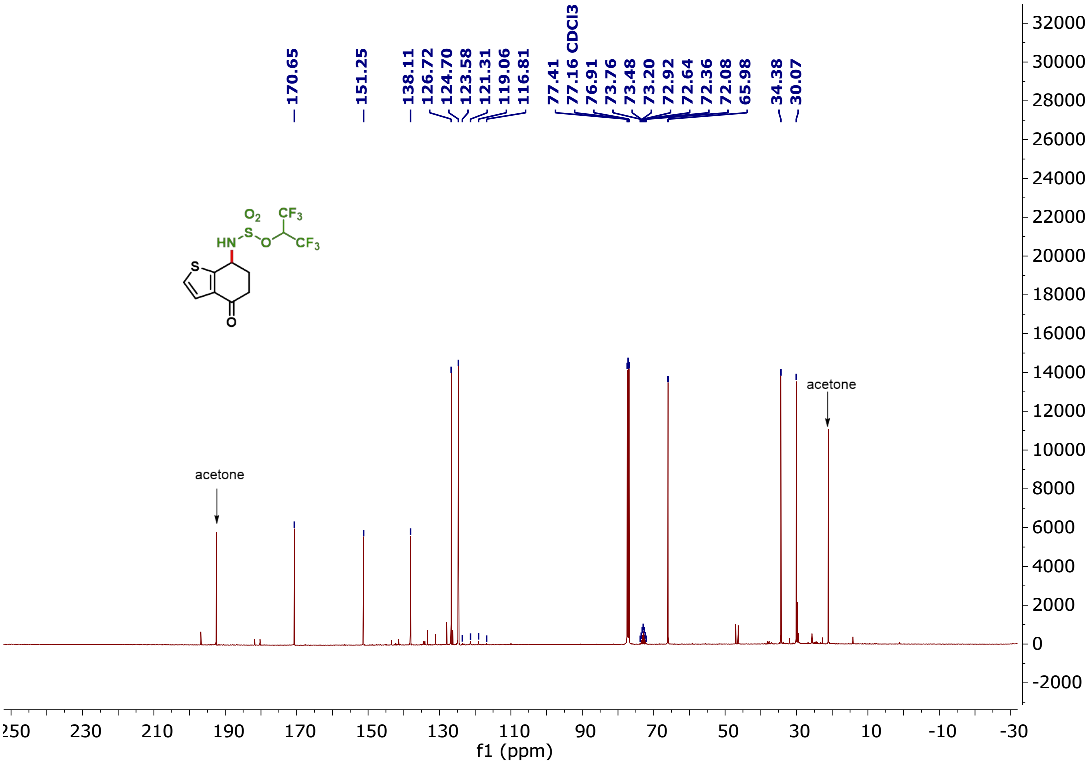


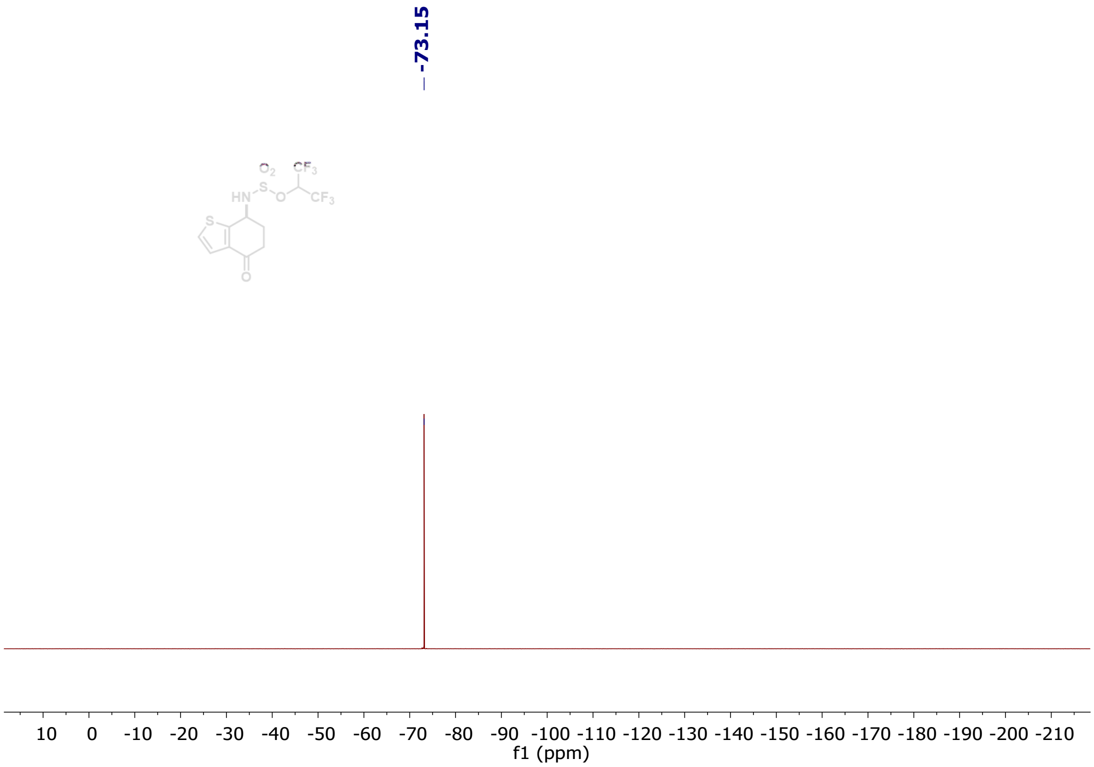



-73.08
O2
CF3
HN
S
O
CF3
Me
S
Me
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

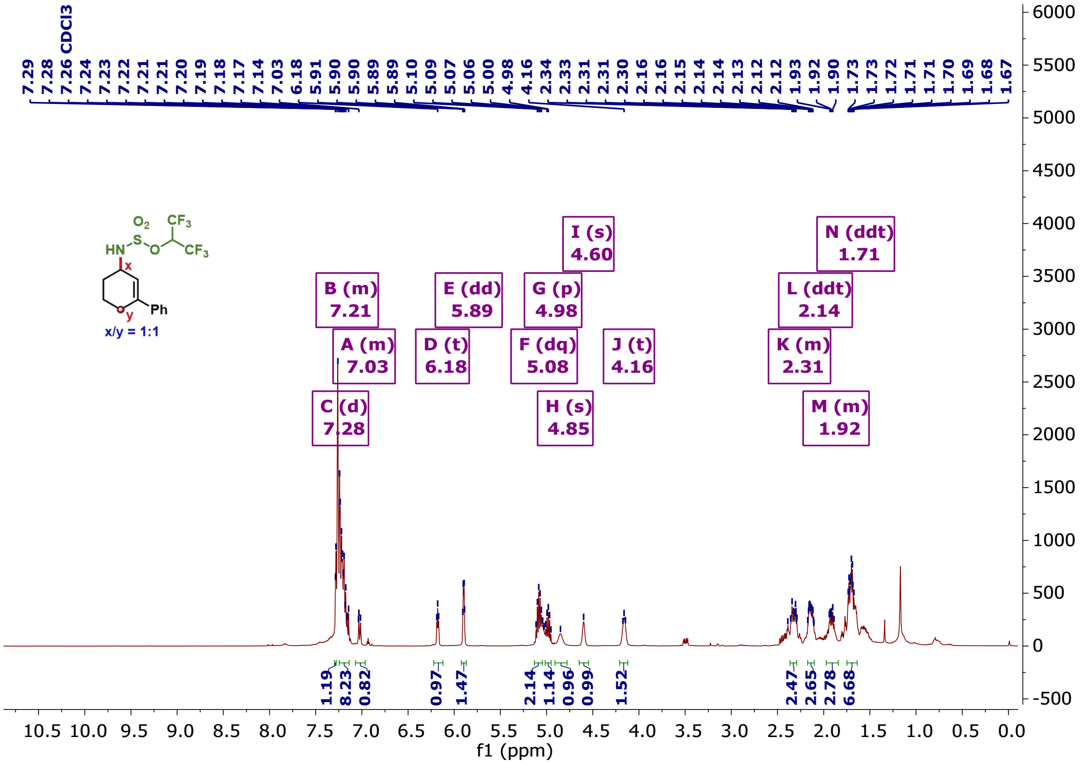
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 38b

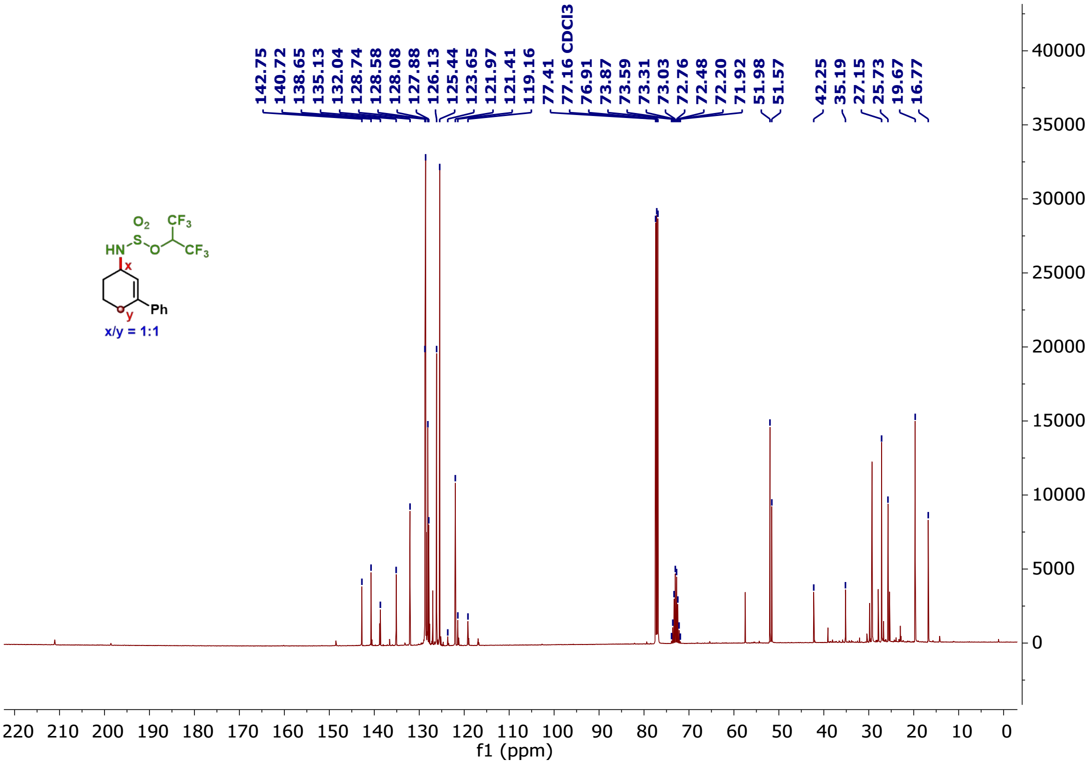


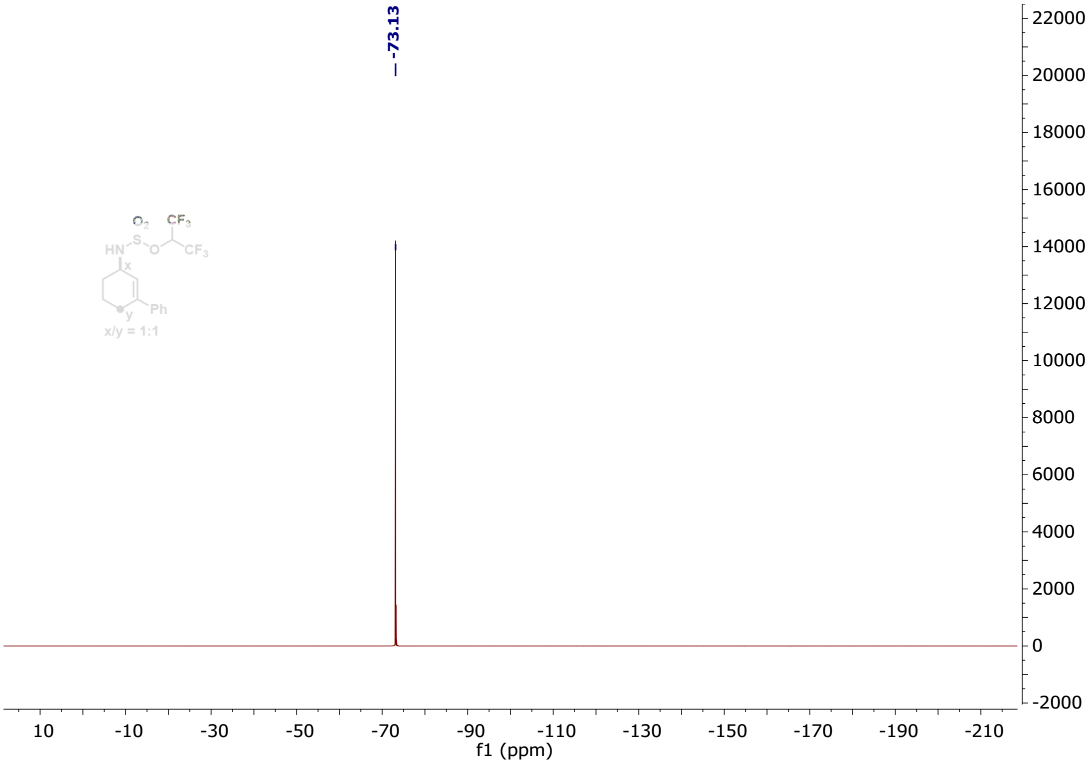



-73.15
O2
CF3
HN
S
O
CF3
S
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

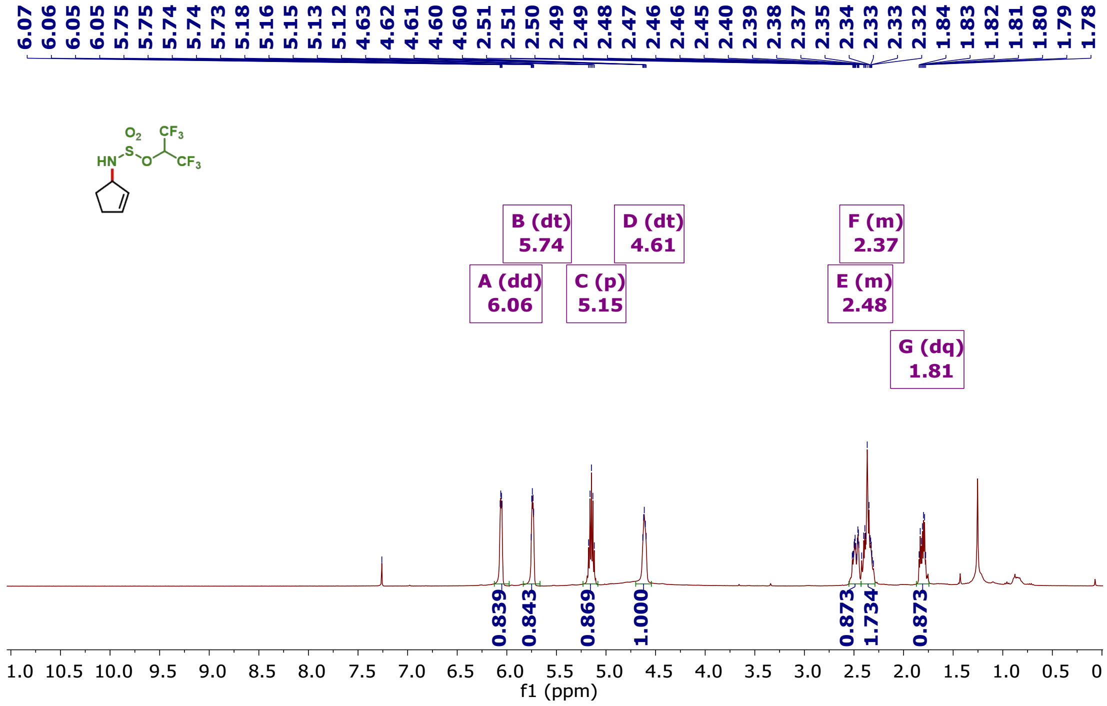
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 42b

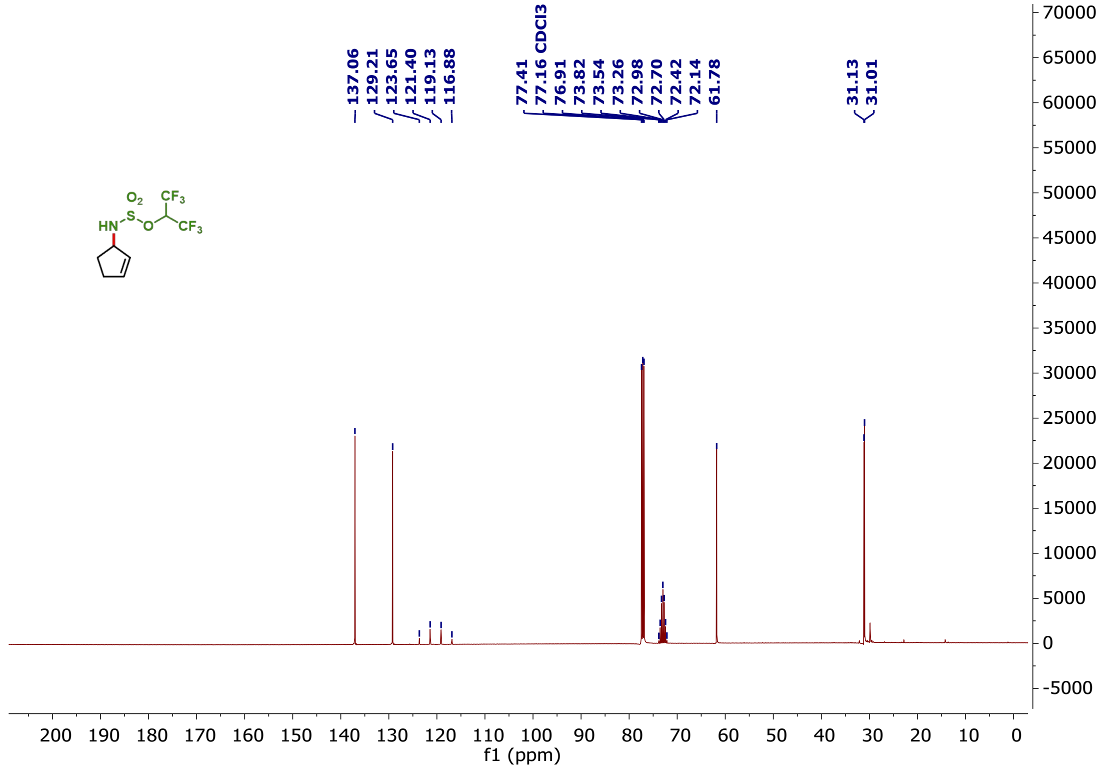


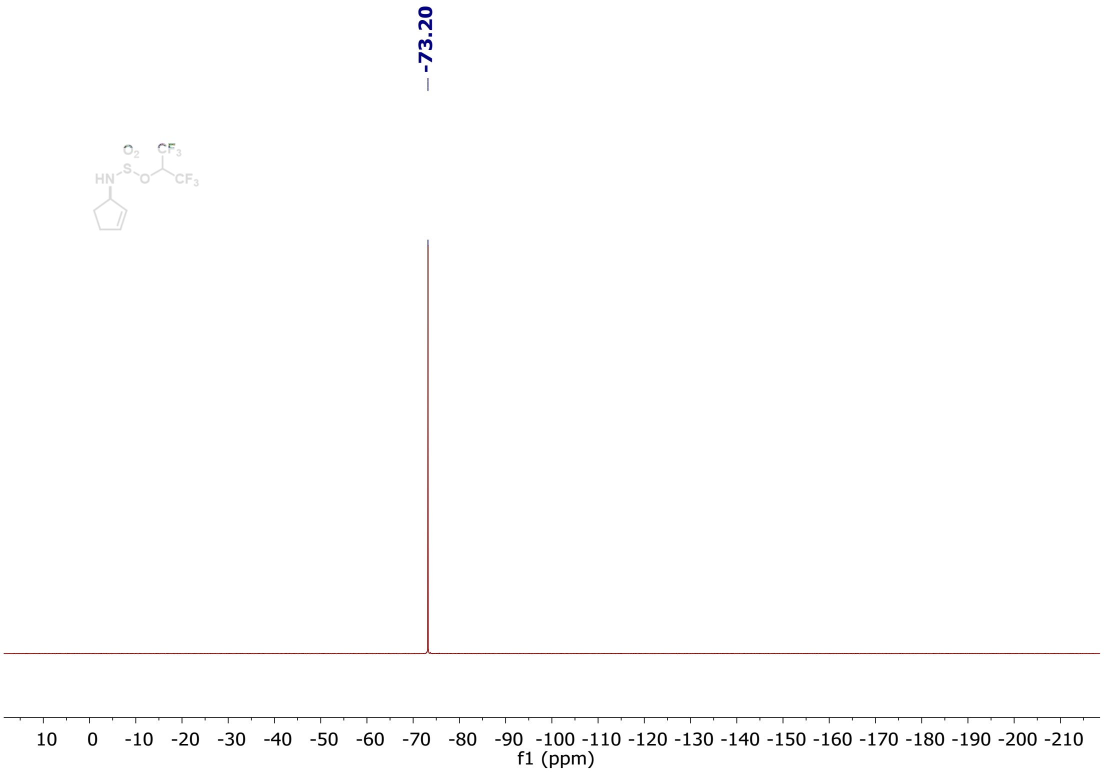



-73.13
O2
CF3
HN
S
O
CF3
x
y
Ph
x/y = 1:1
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

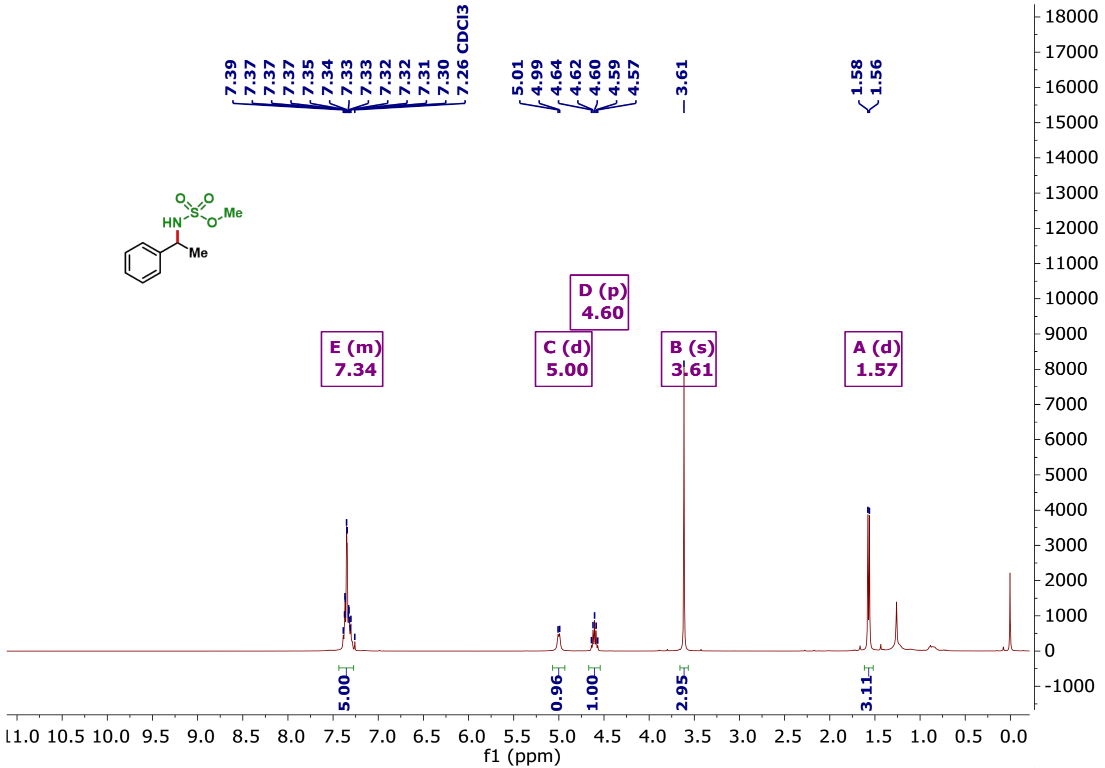
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 43b

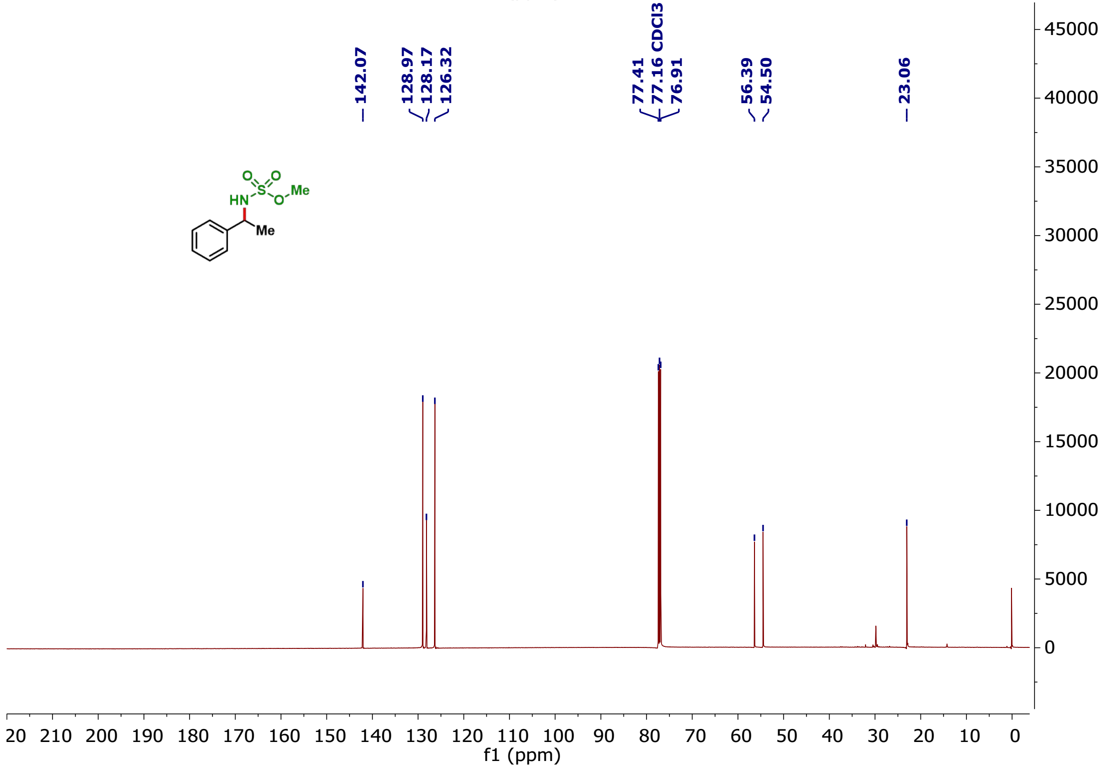




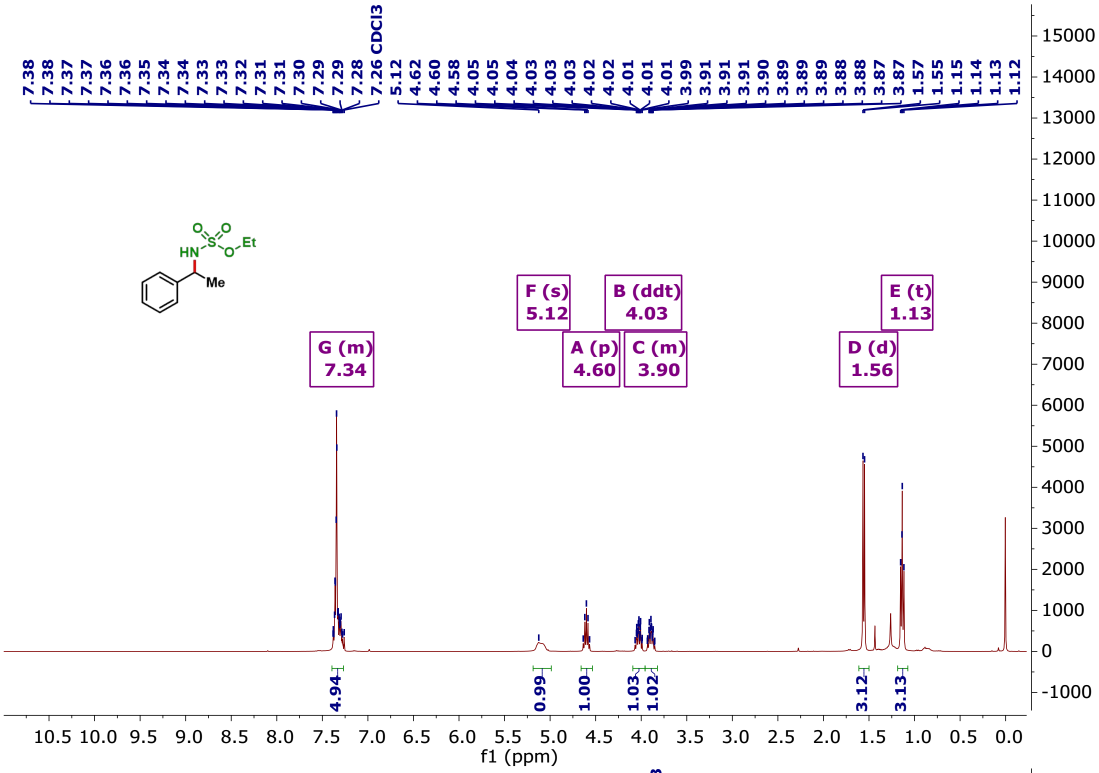

-73.20
O2
CF3
HN
S
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

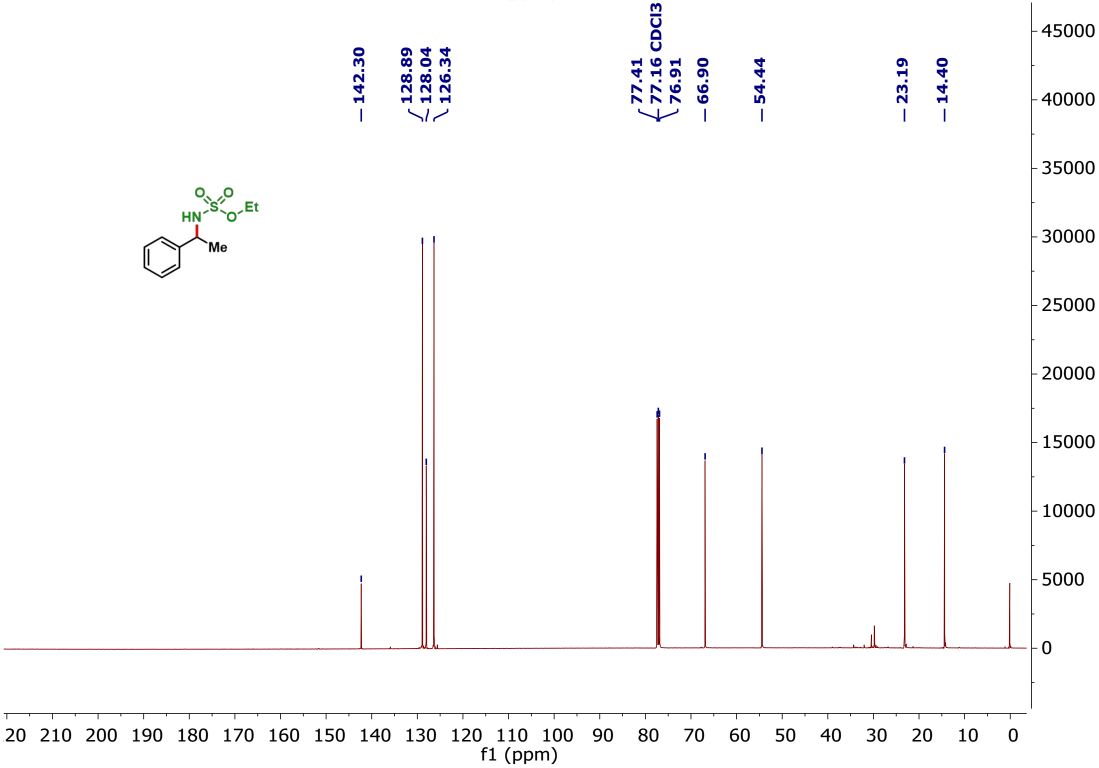
^{1}H NMR, ^{13}C NMR spectra for compound 1ba



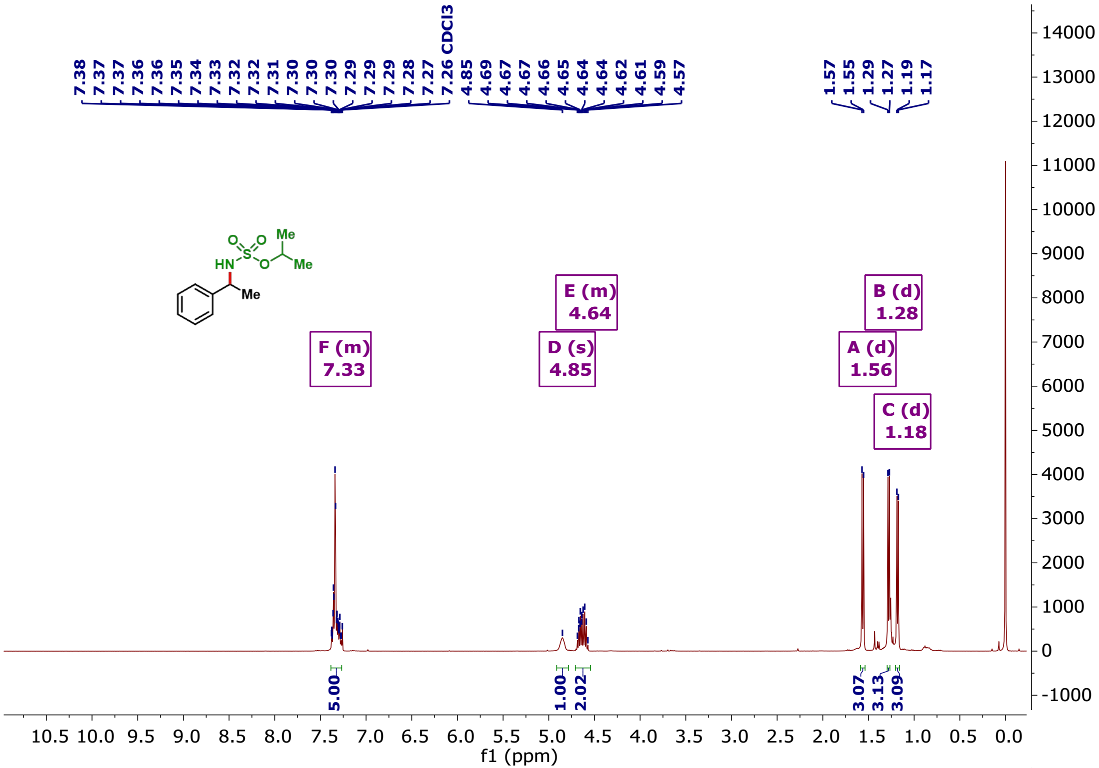


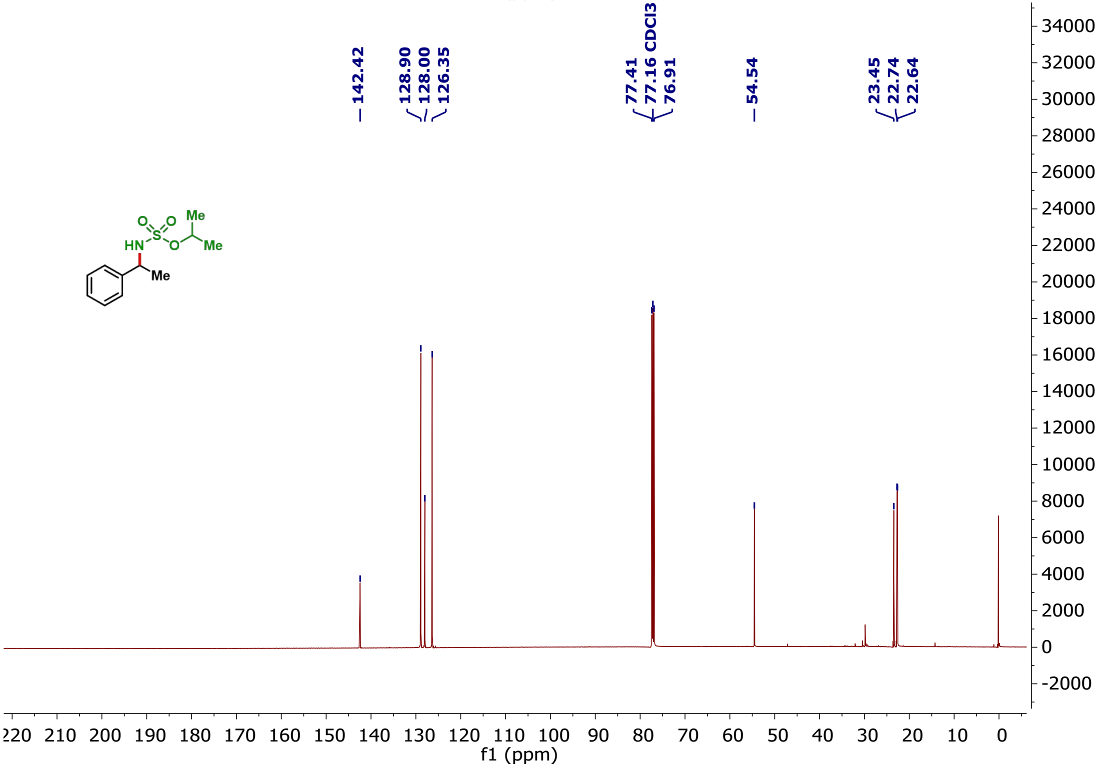
^{1}H NMR, ^{13}C NMR spectra for compound 1bb



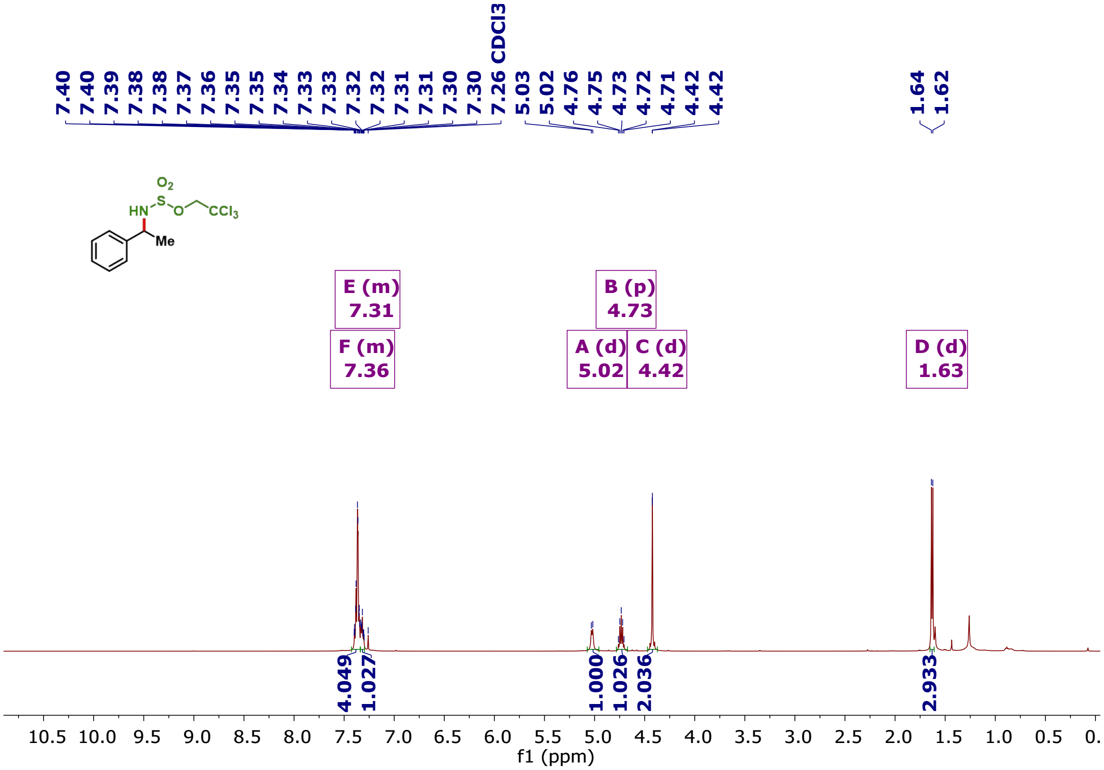


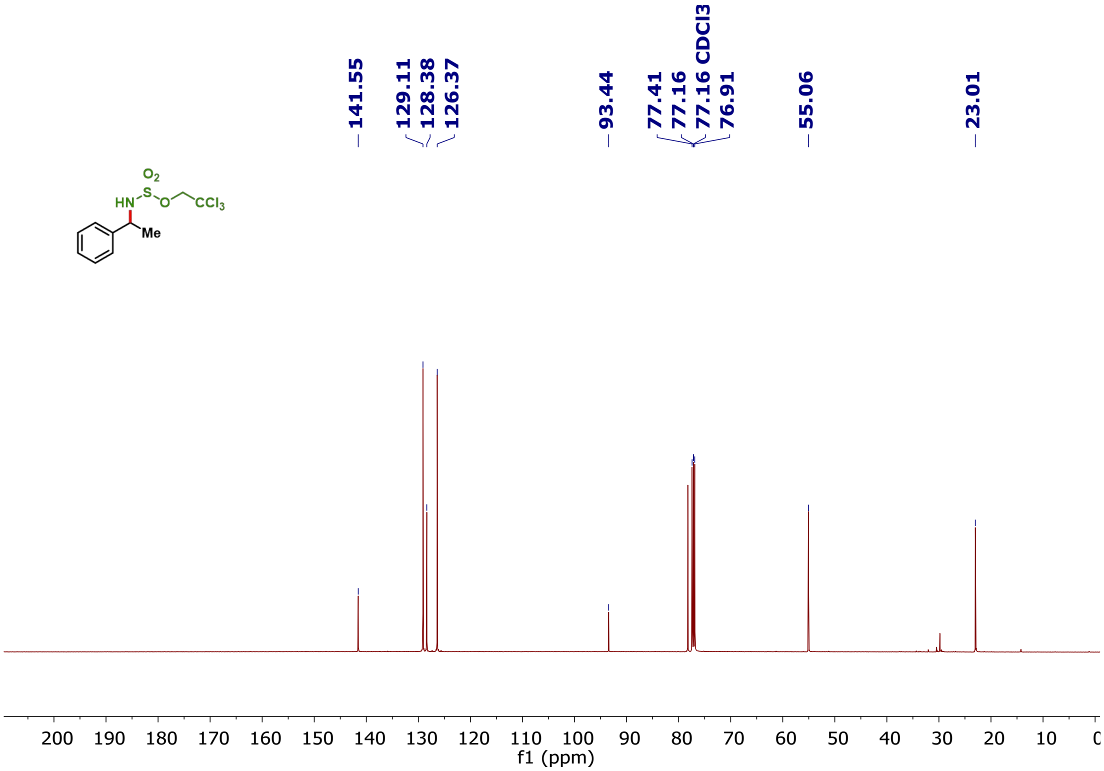
^{1}H NMR, ^{13}C NMR spectra for compound 1bc



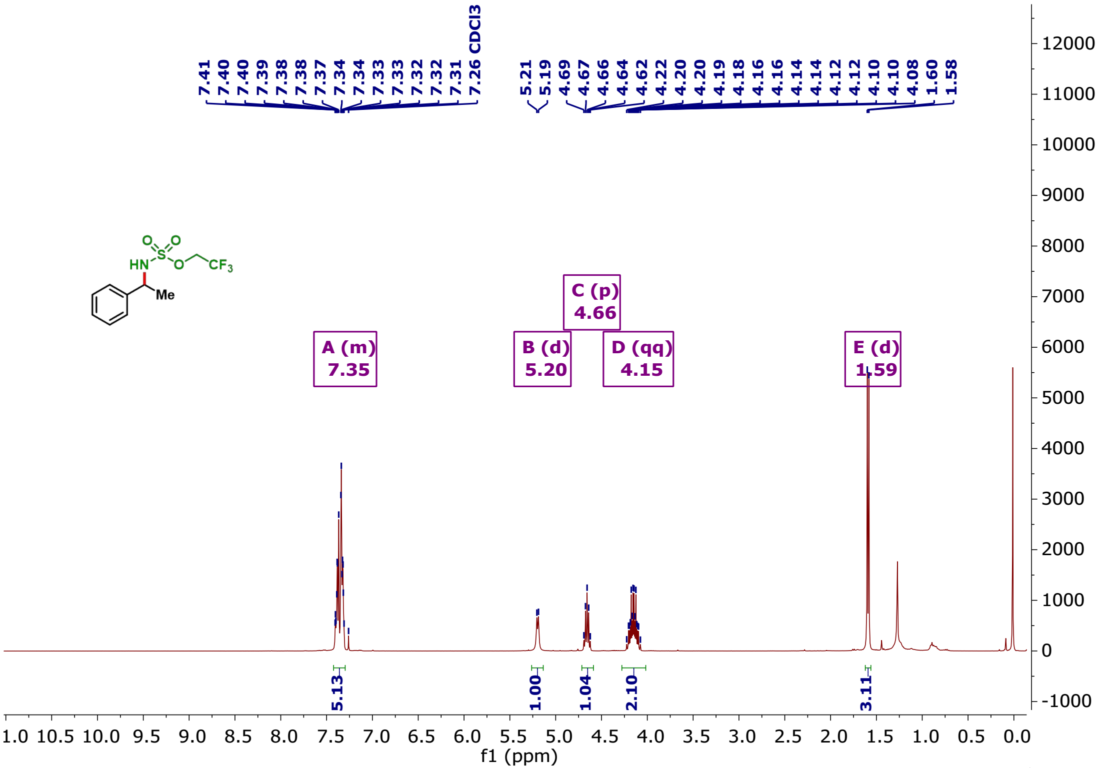


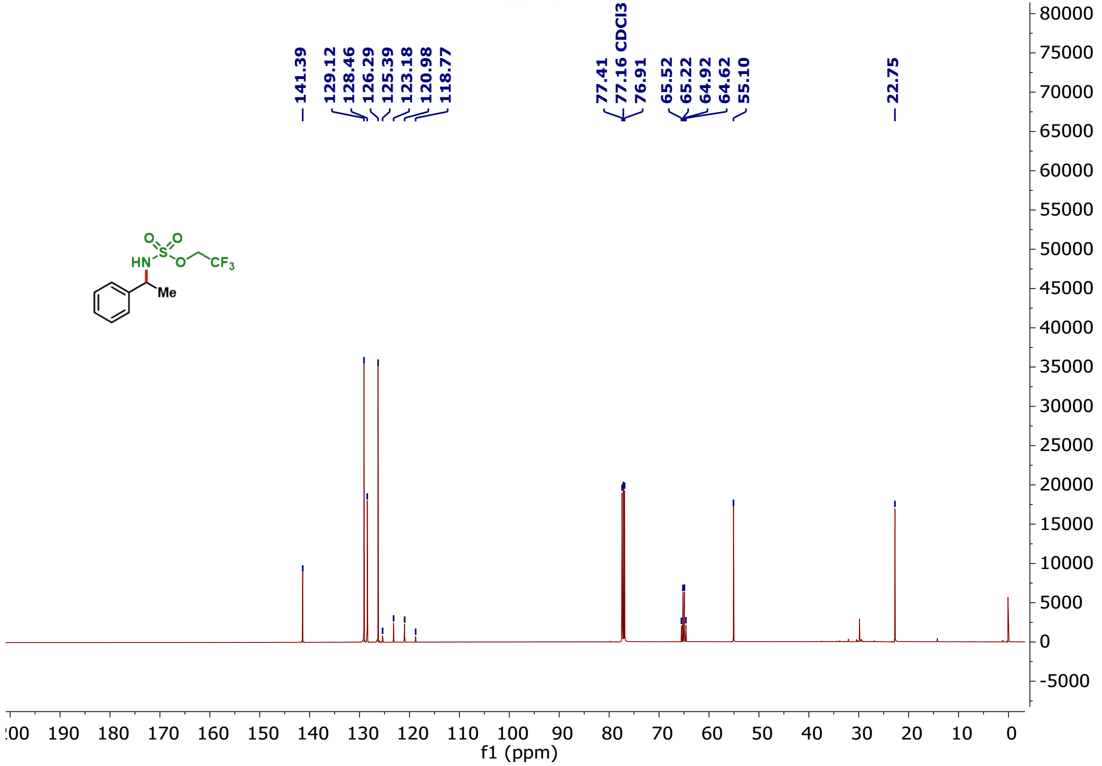
^1H NMR, ^{13}C NMR spectra for compound 1bd

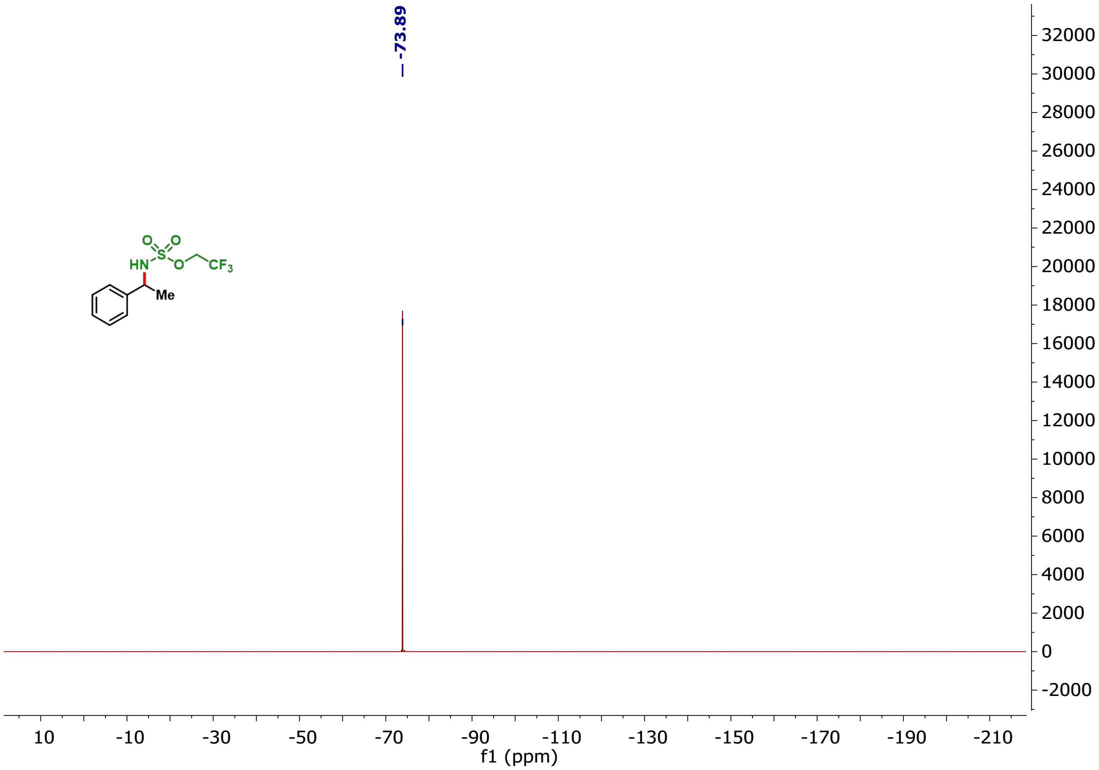




^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 1be

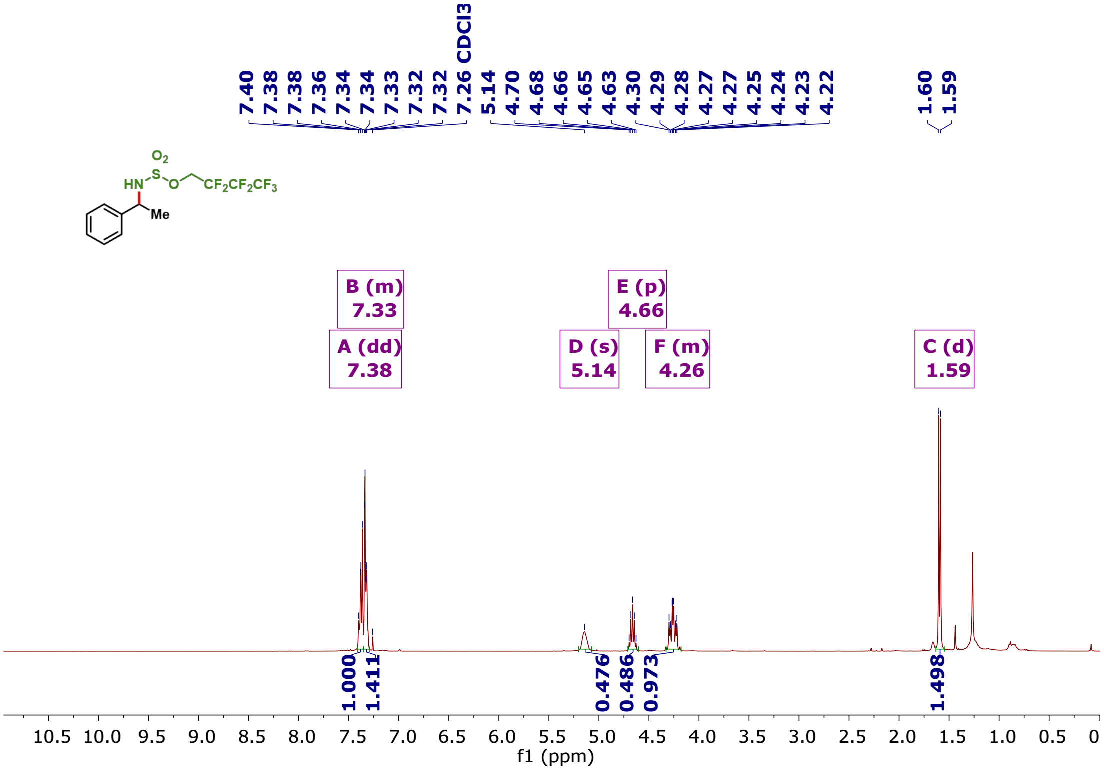


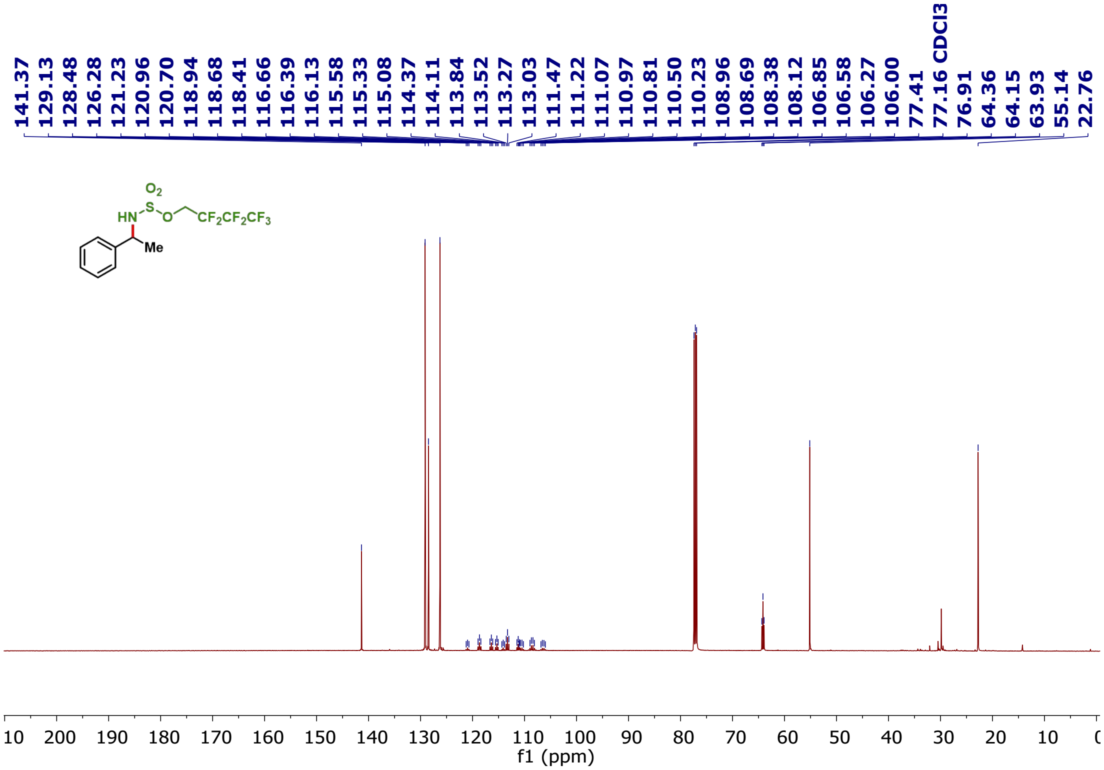


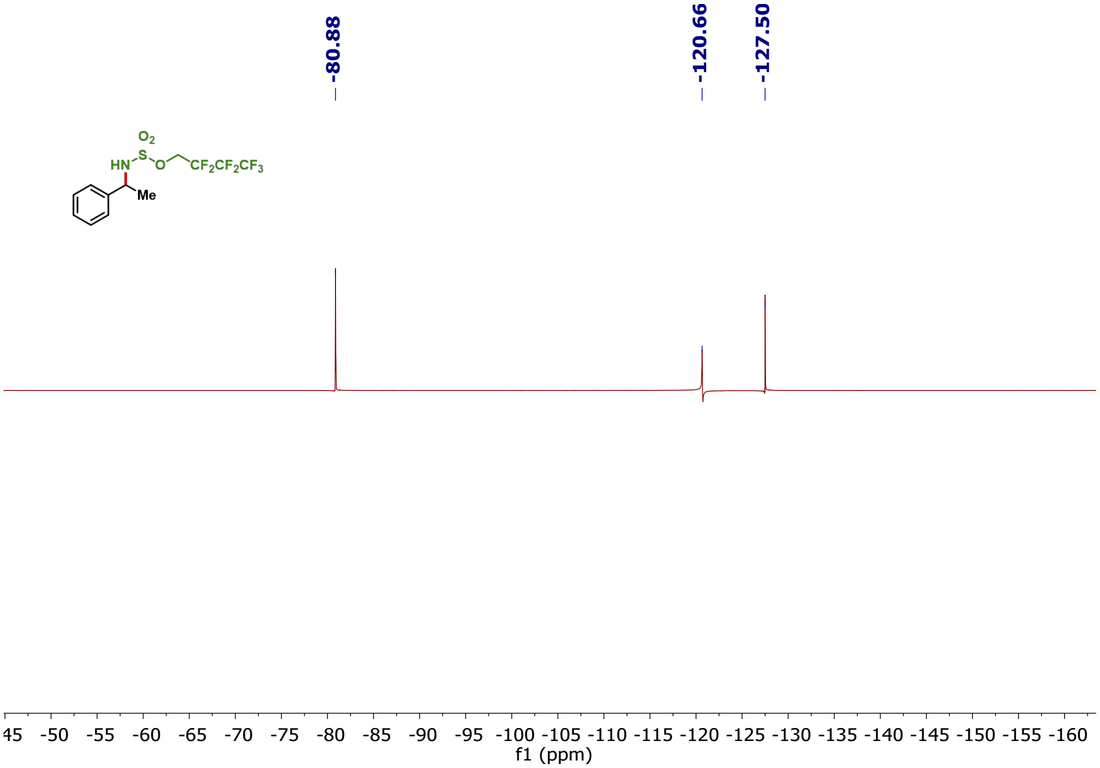


-73.89
O
O
HN
S
O
CF3
Me
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

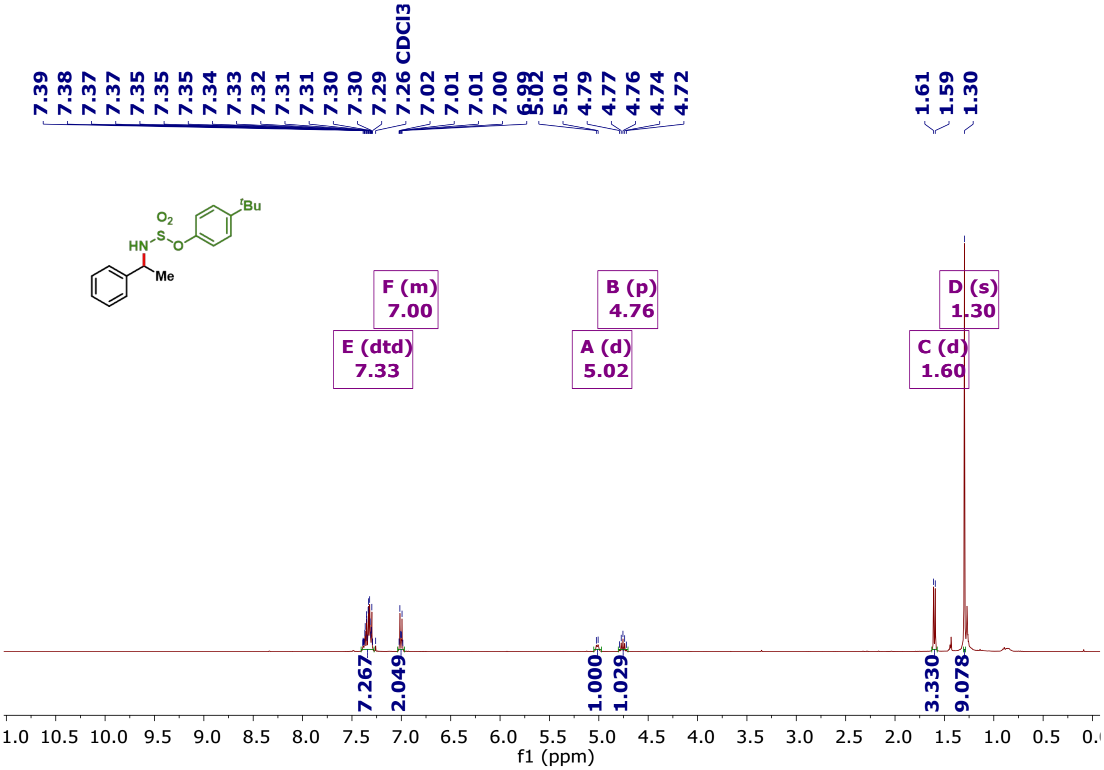
^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 1bf

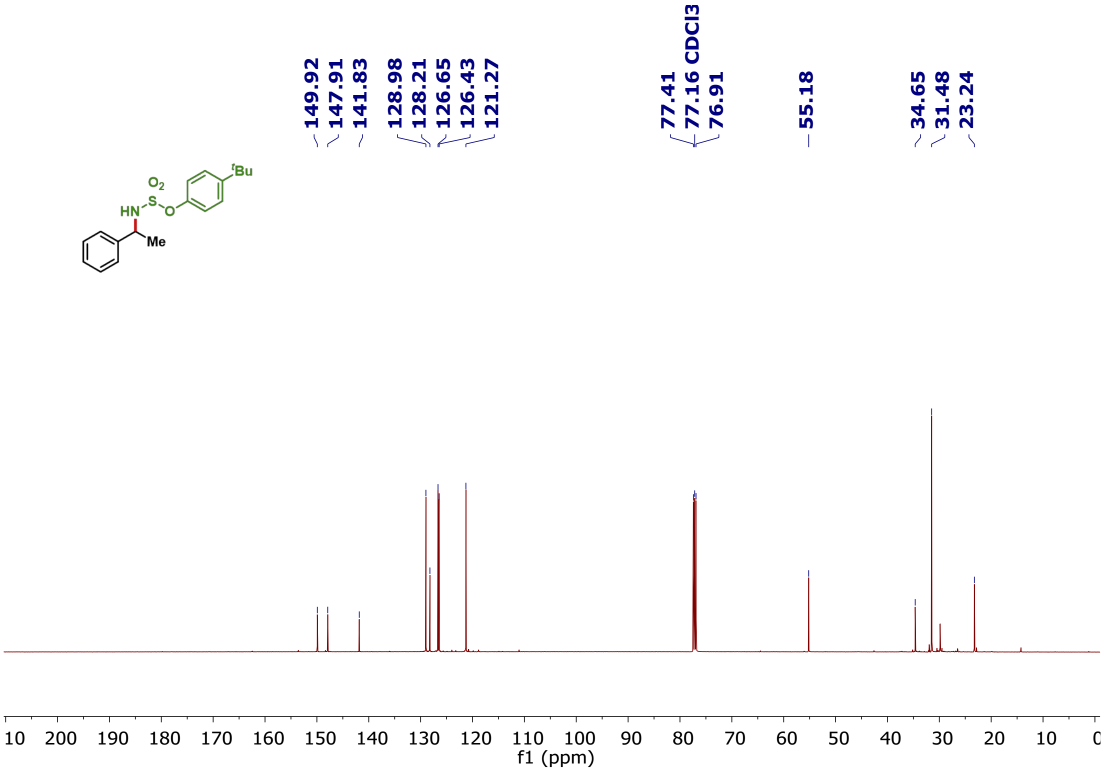




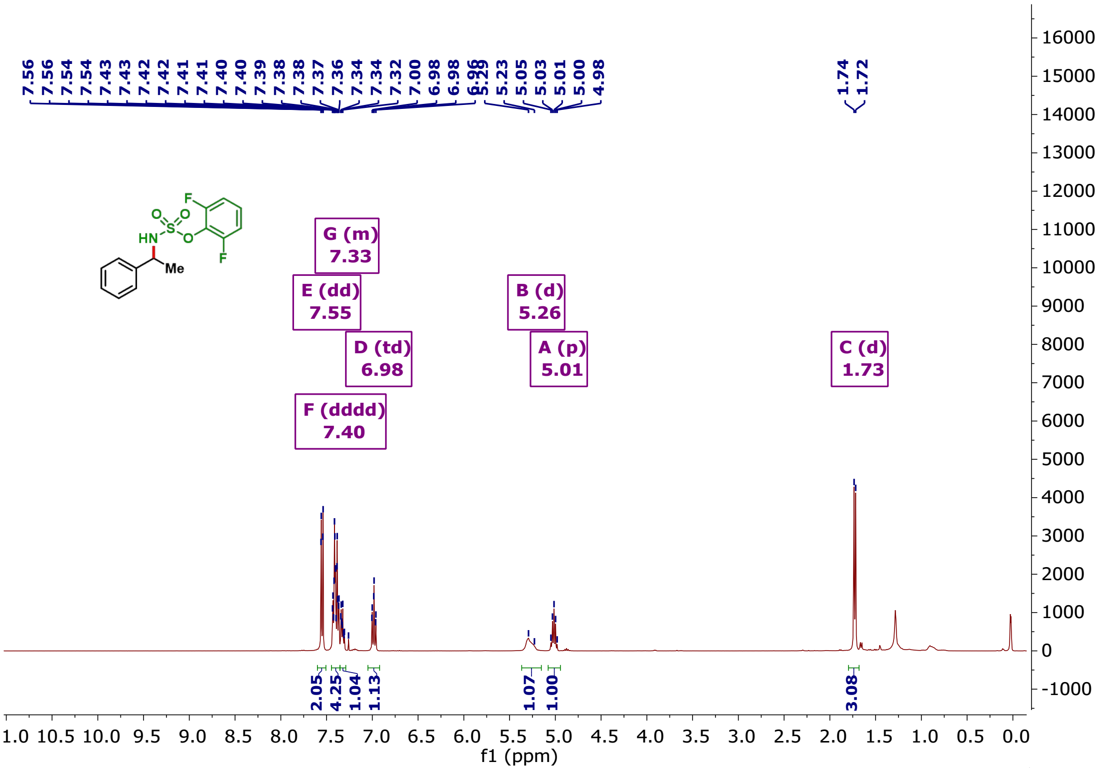

-80.88
-120.66
-127.50
O2
HN
S
O
CF2CF2CF3
Me
45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160
f1 (ppm)

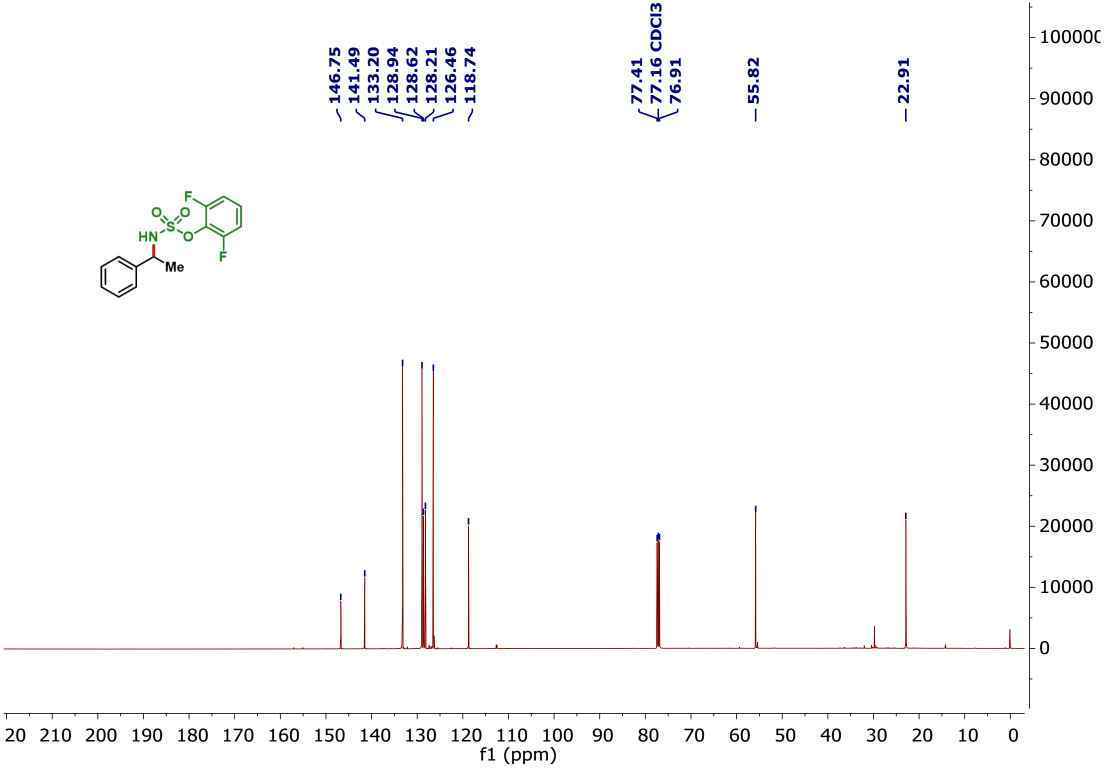
^{1}H NMR, ^{13}C NMR spectra for compound 1bg

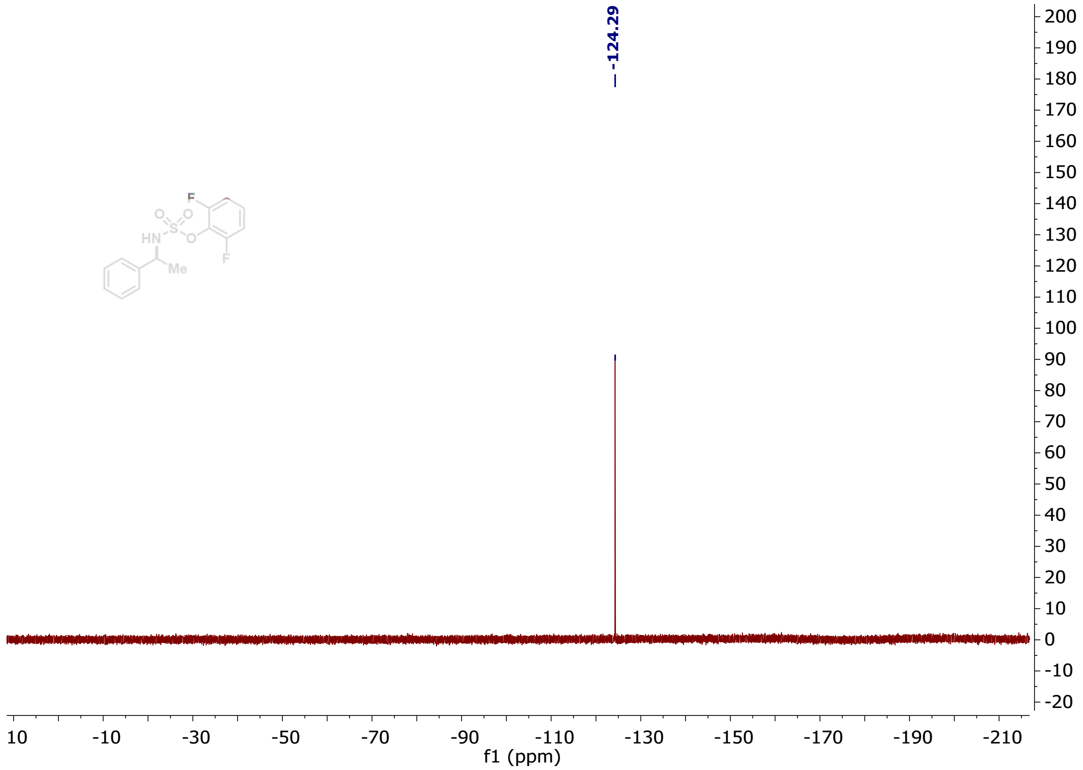




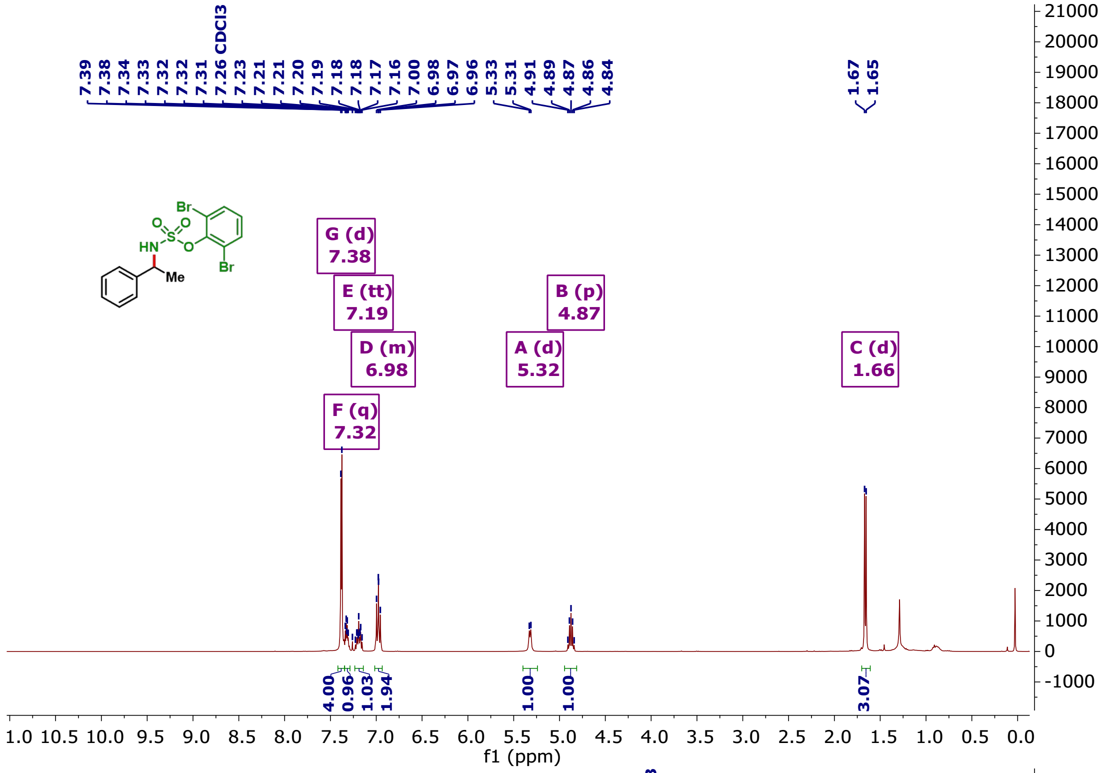
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 1bh

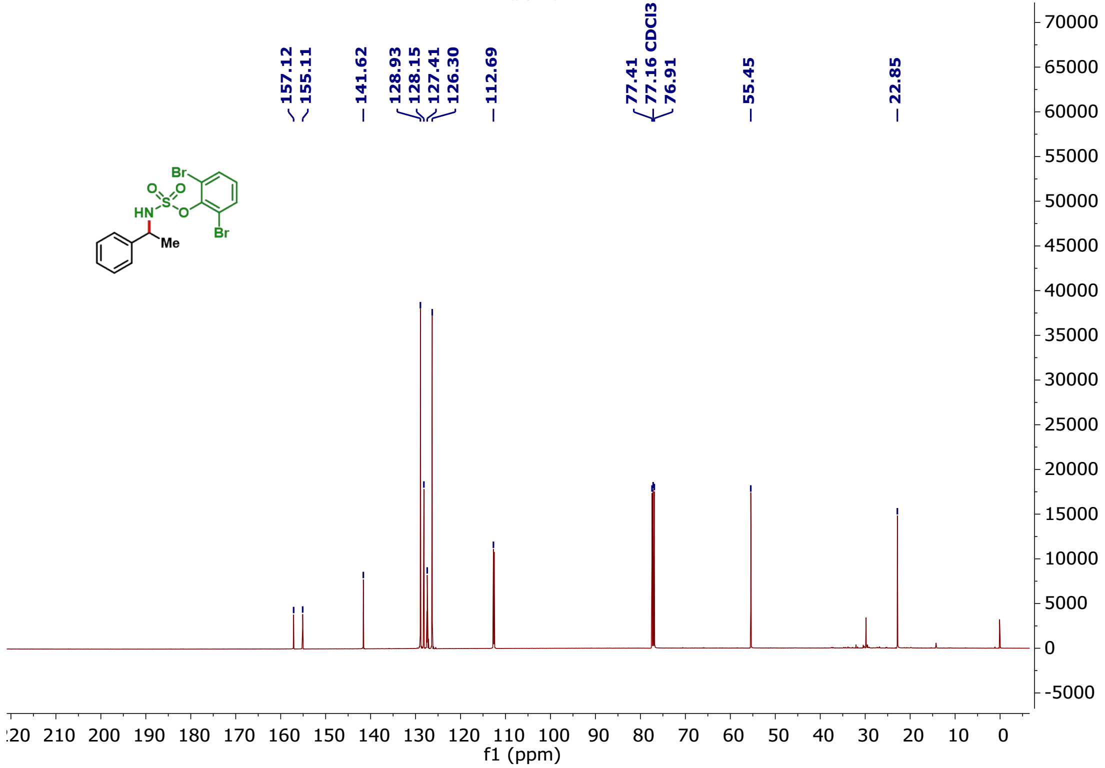




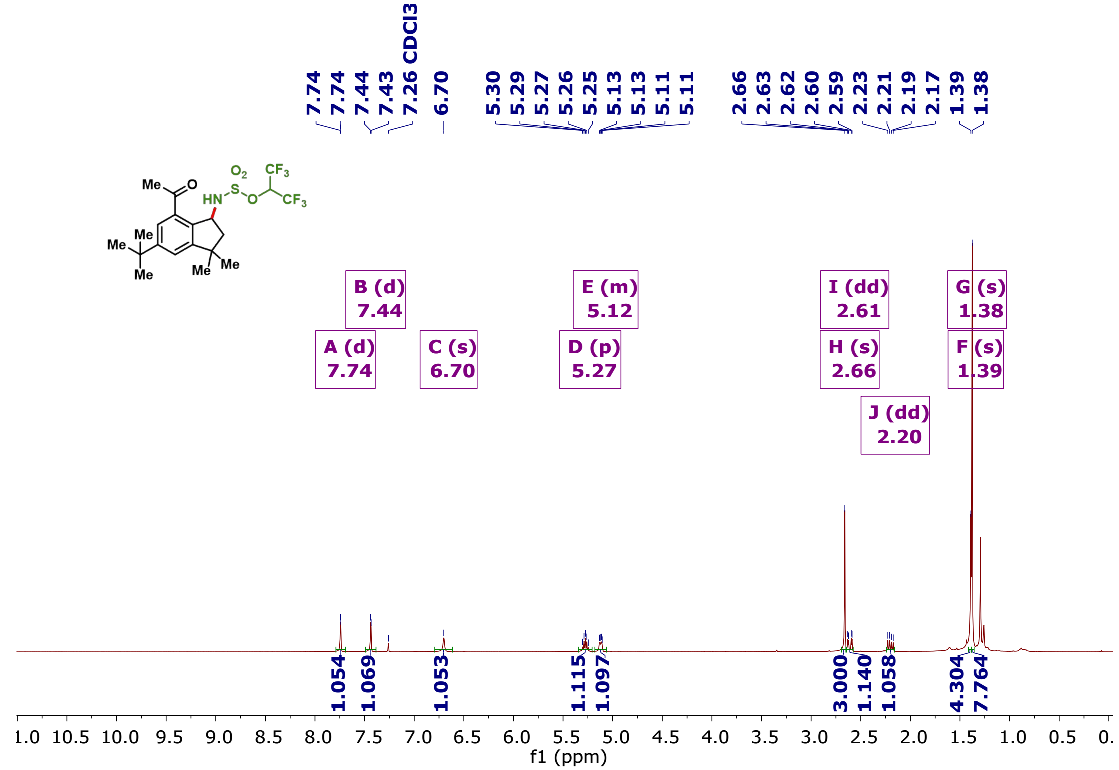

-124.29
F
O
O
HN
S
O
F
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

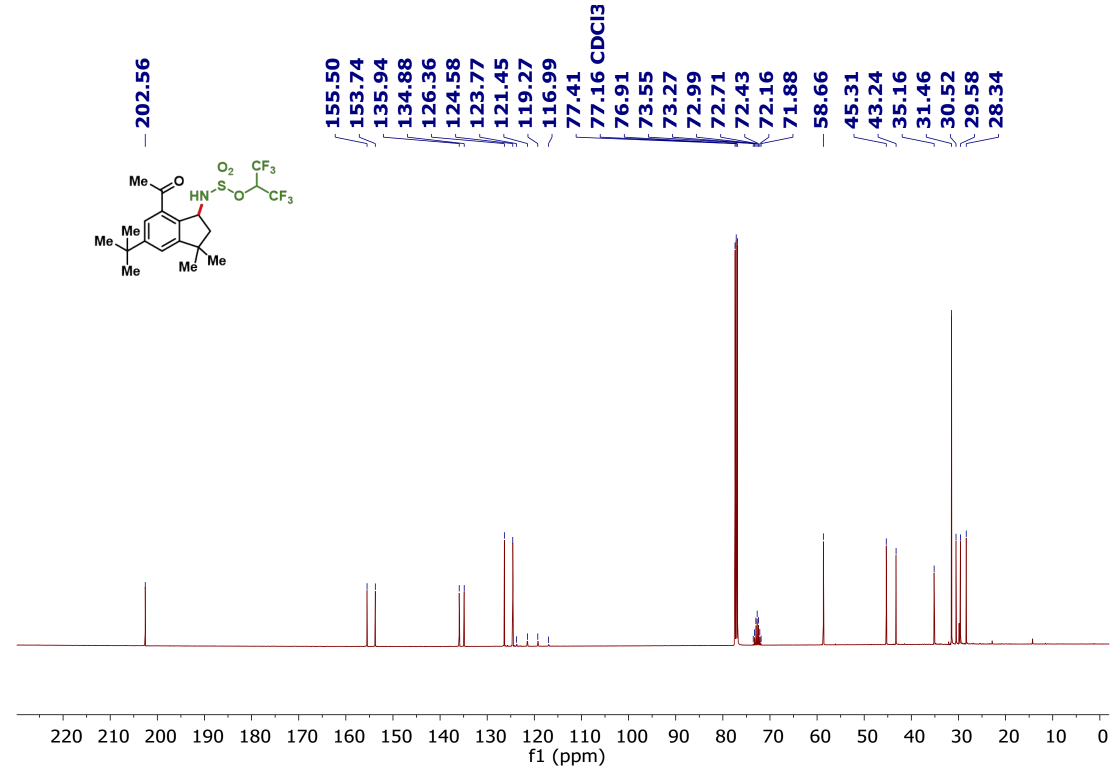
^{1}H NMR, ^{13}C NMR spectra for compound 1bi

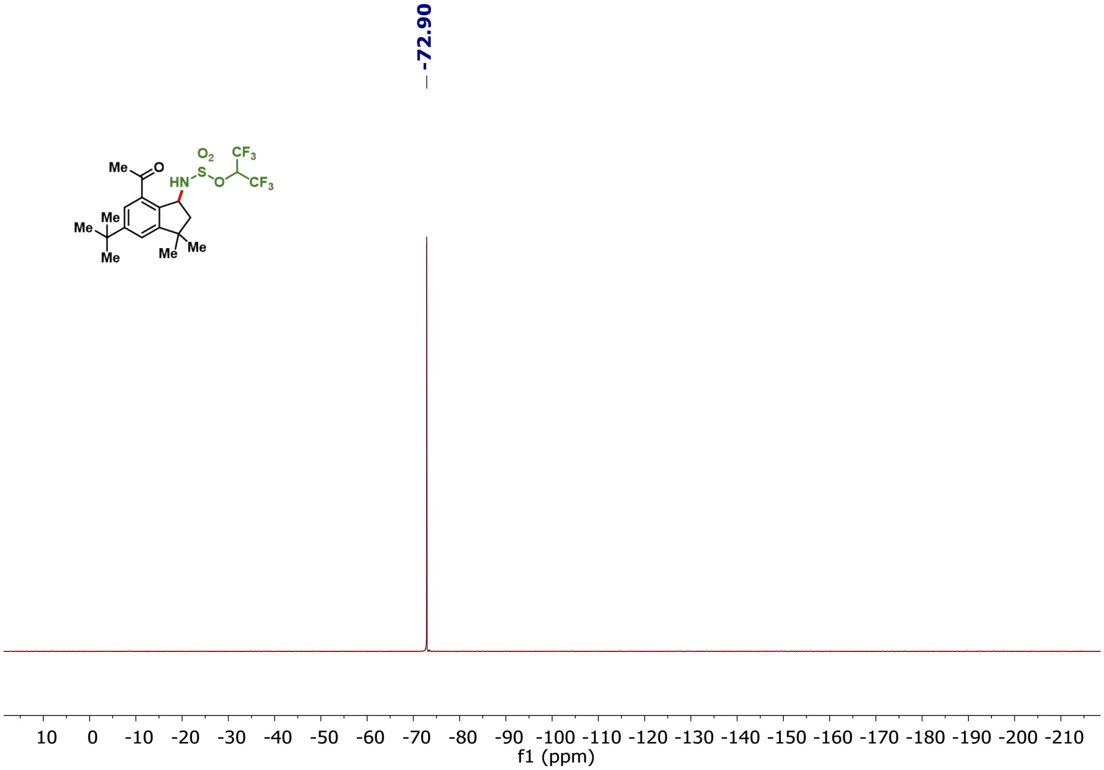




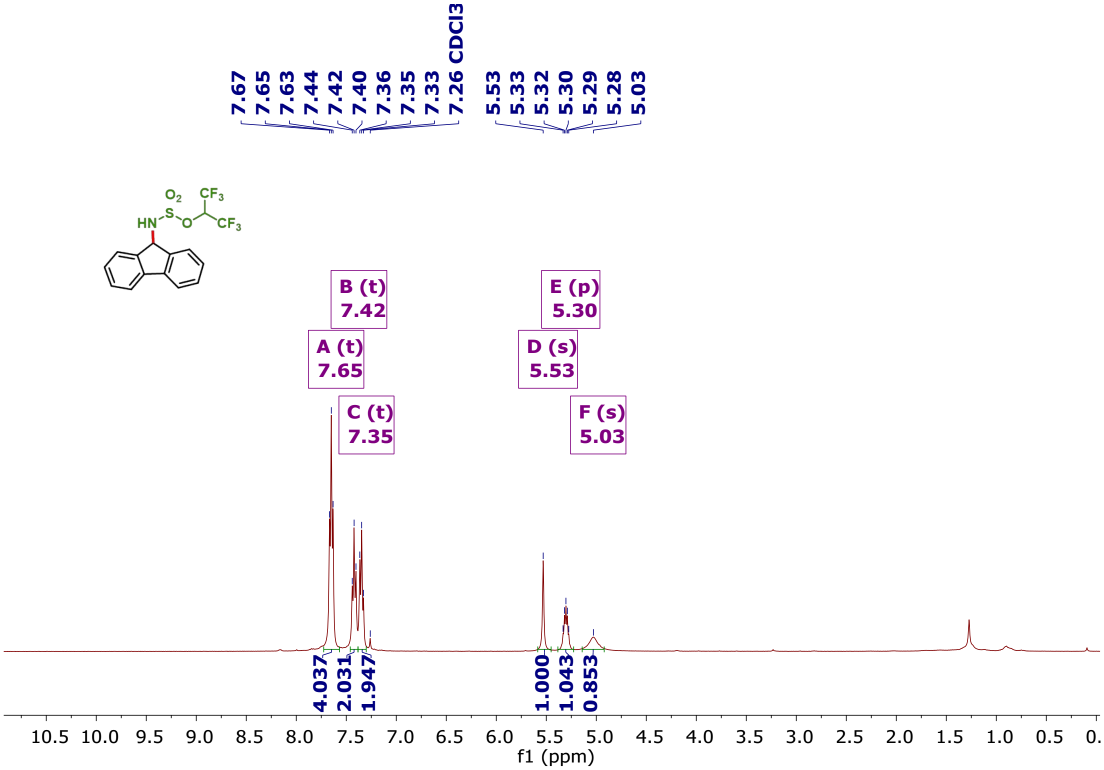
^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 44b

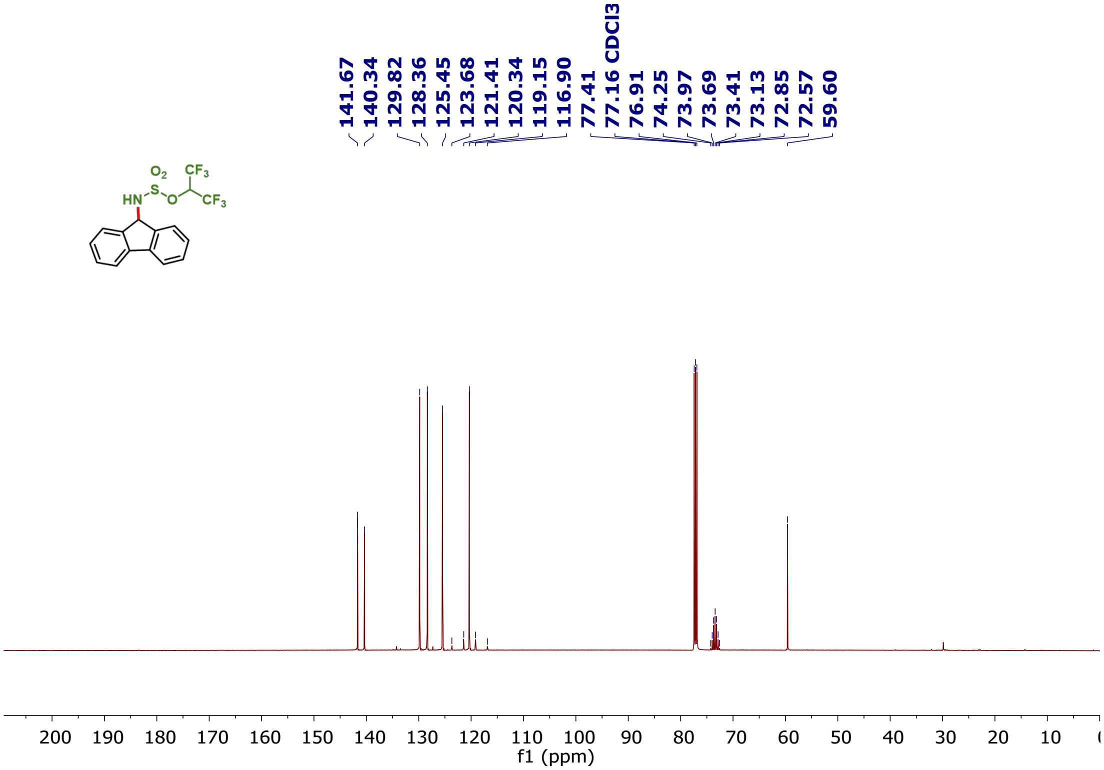


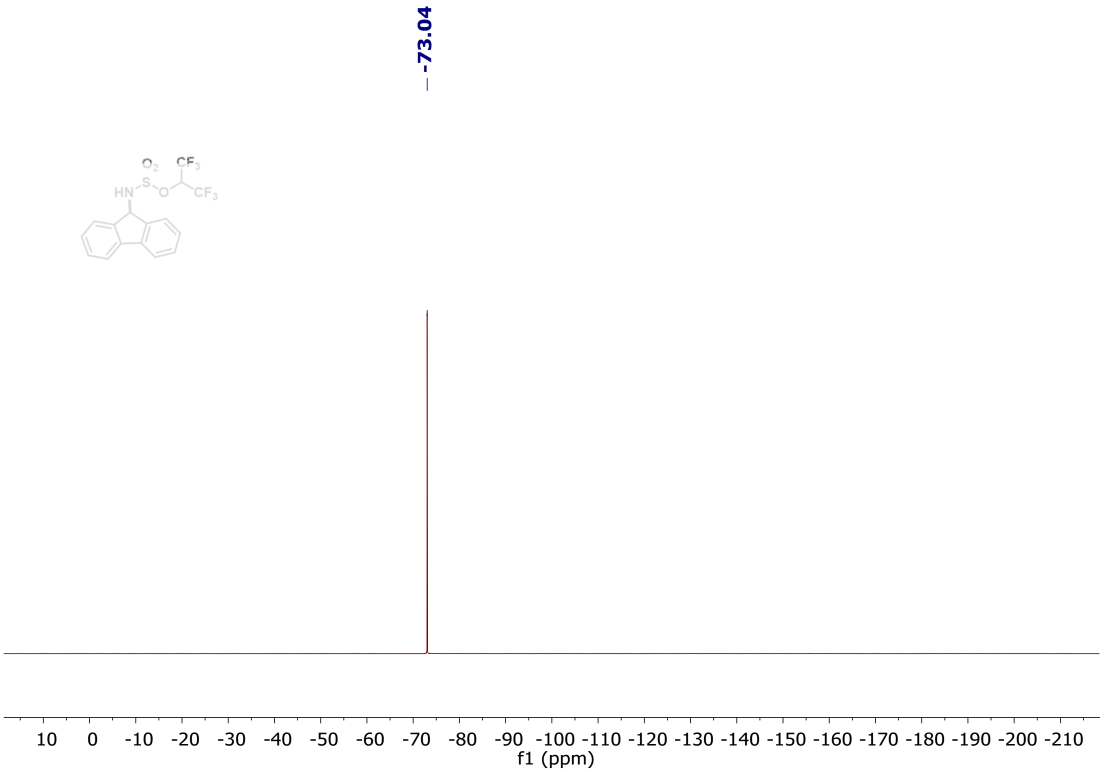



-72.90
Me
O
HN
S
O2
O
CF3
CF3
Me
Me
Me
Me
Me
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

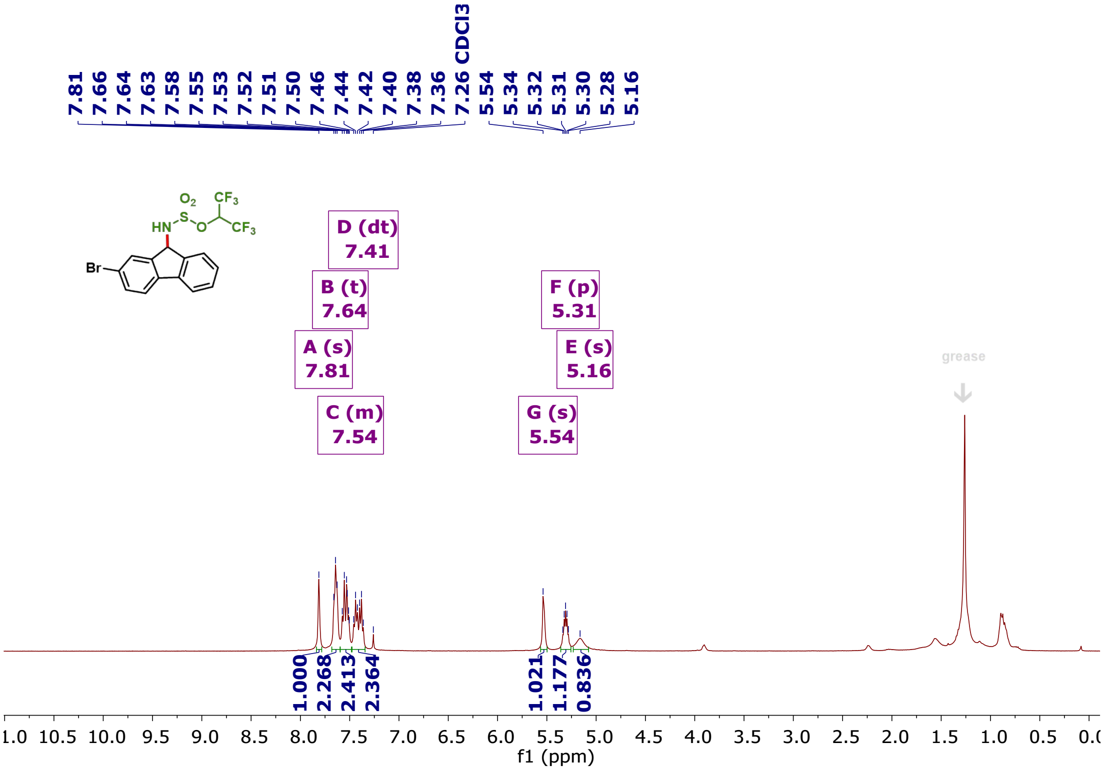
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 45b

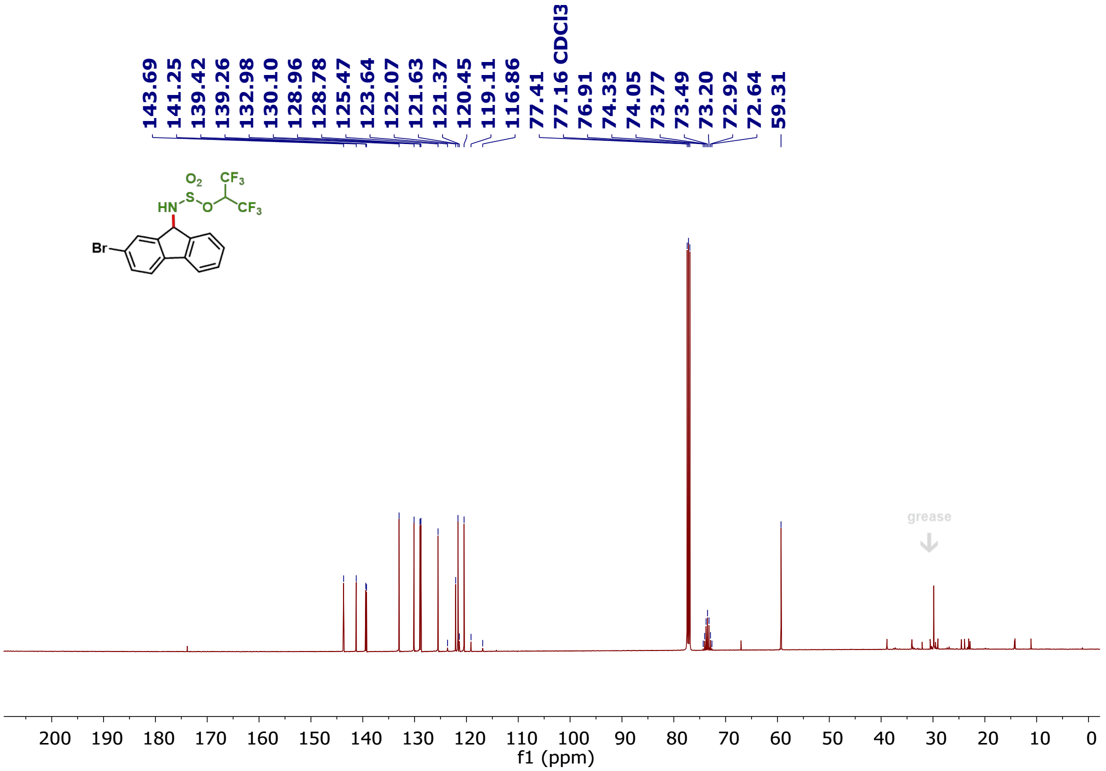


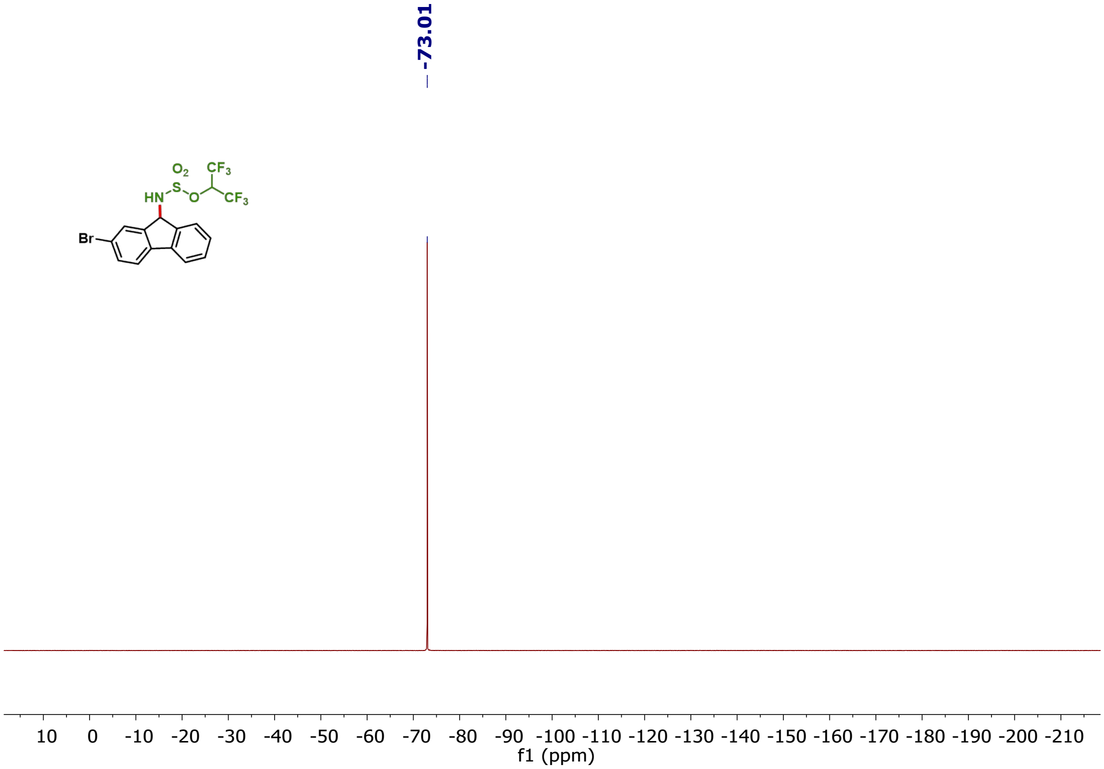



-73.04
O2 CF3
HN S O CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

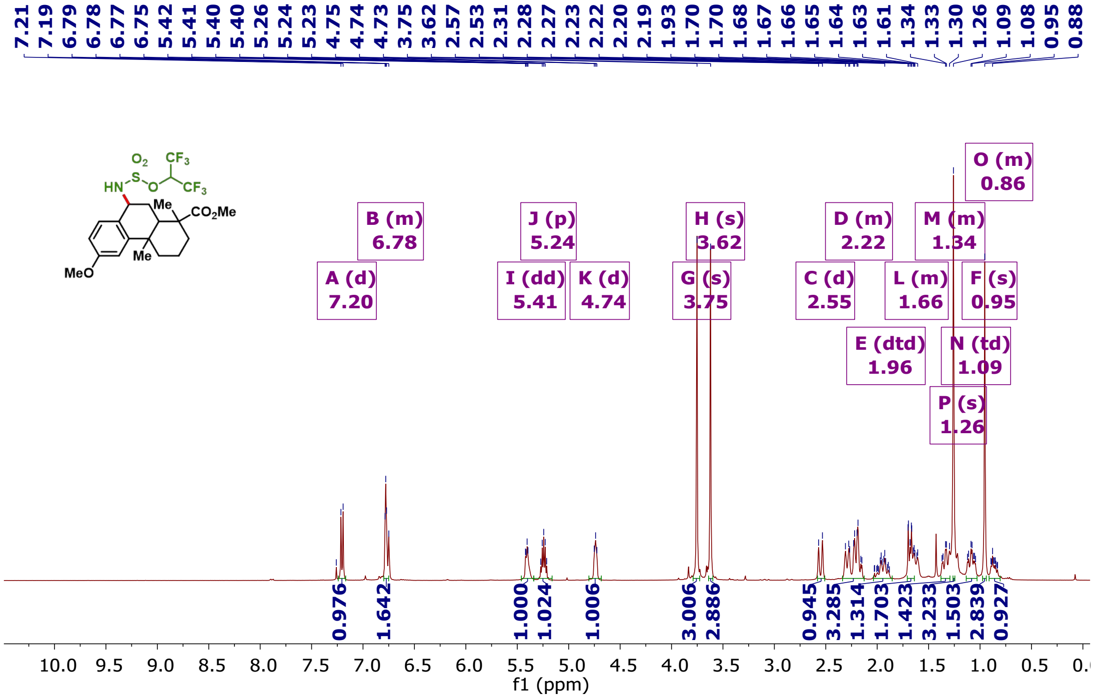
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 46b

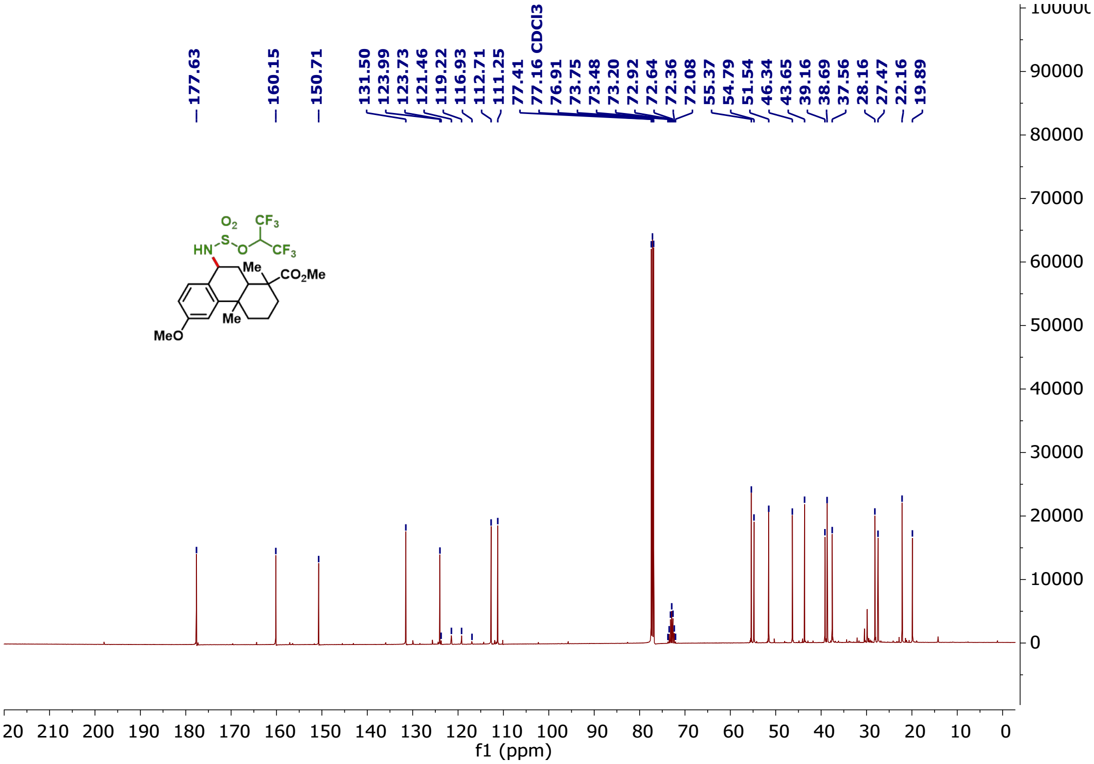


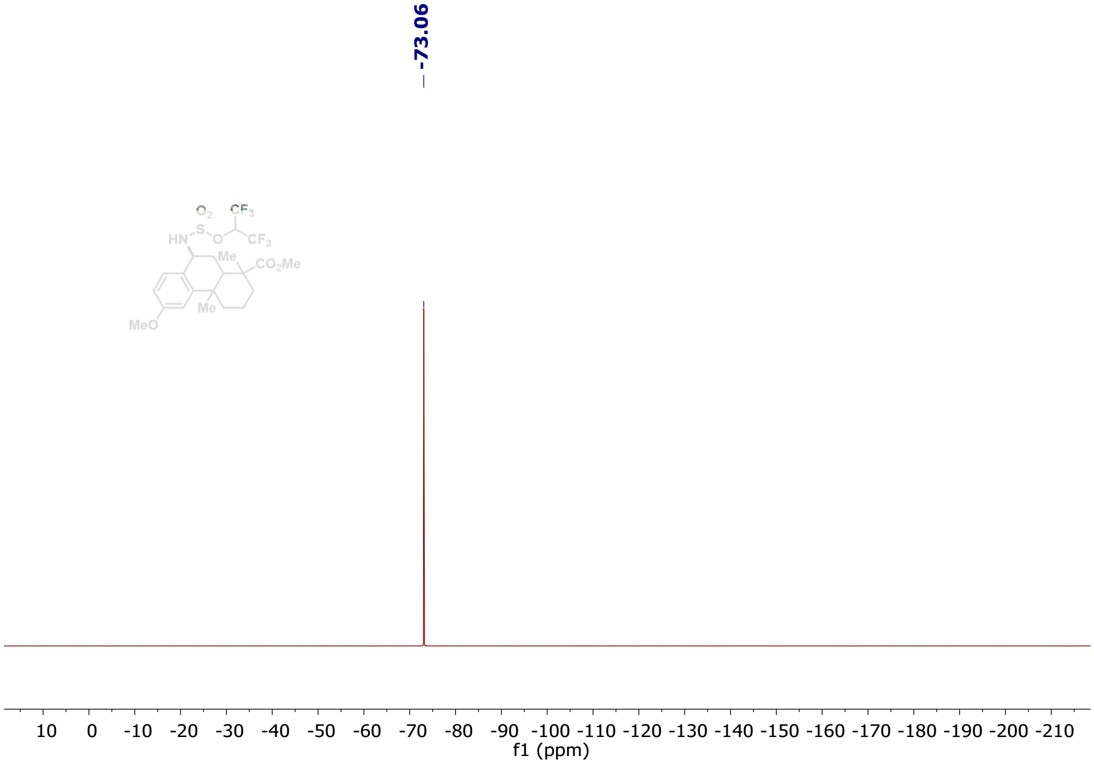



-73.01
Br
HN
S
O2
O
CF3
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

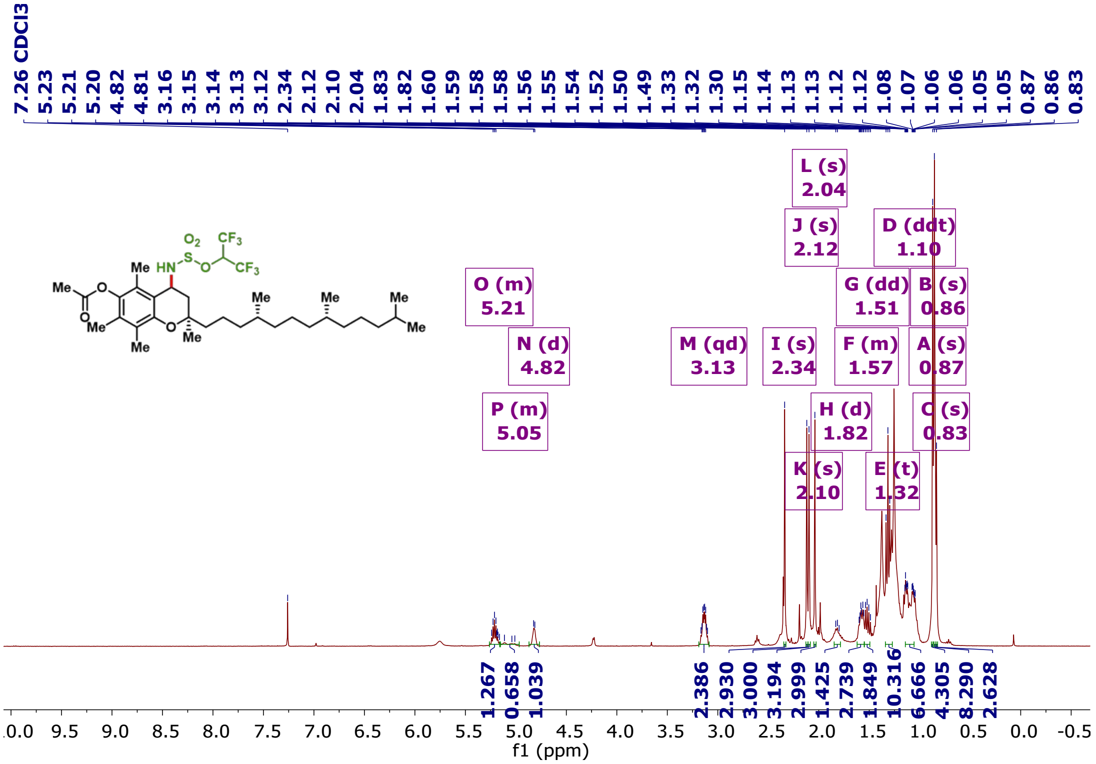
^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 47b

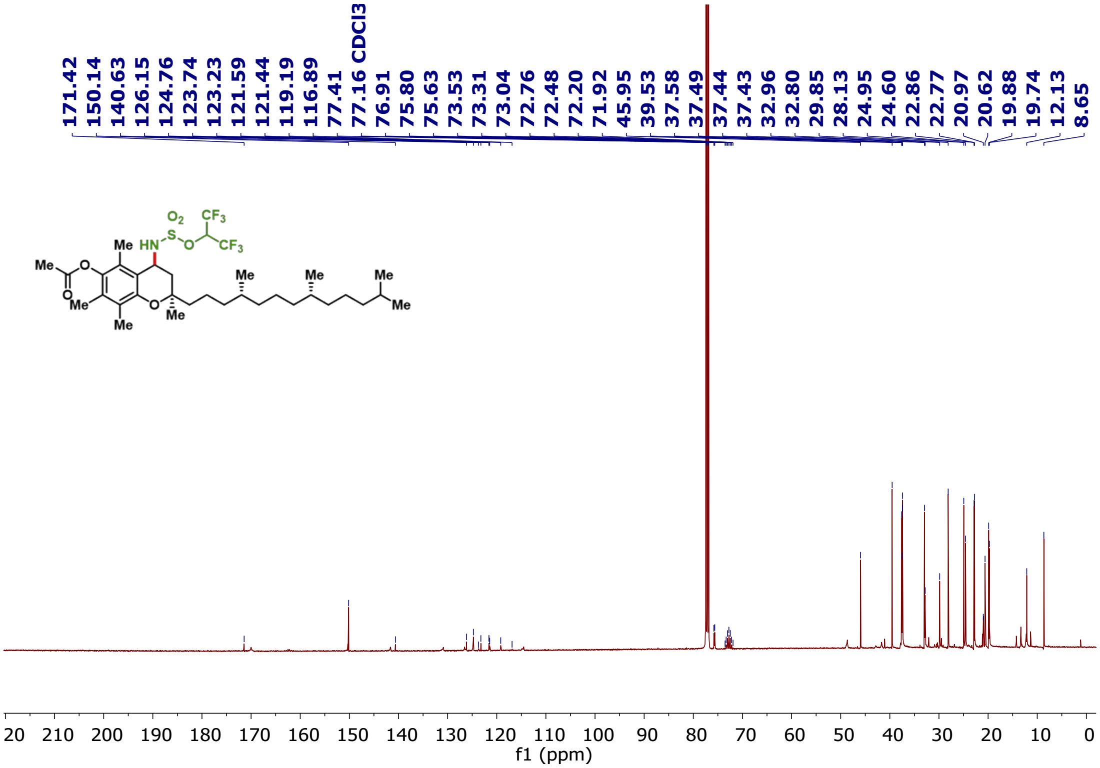


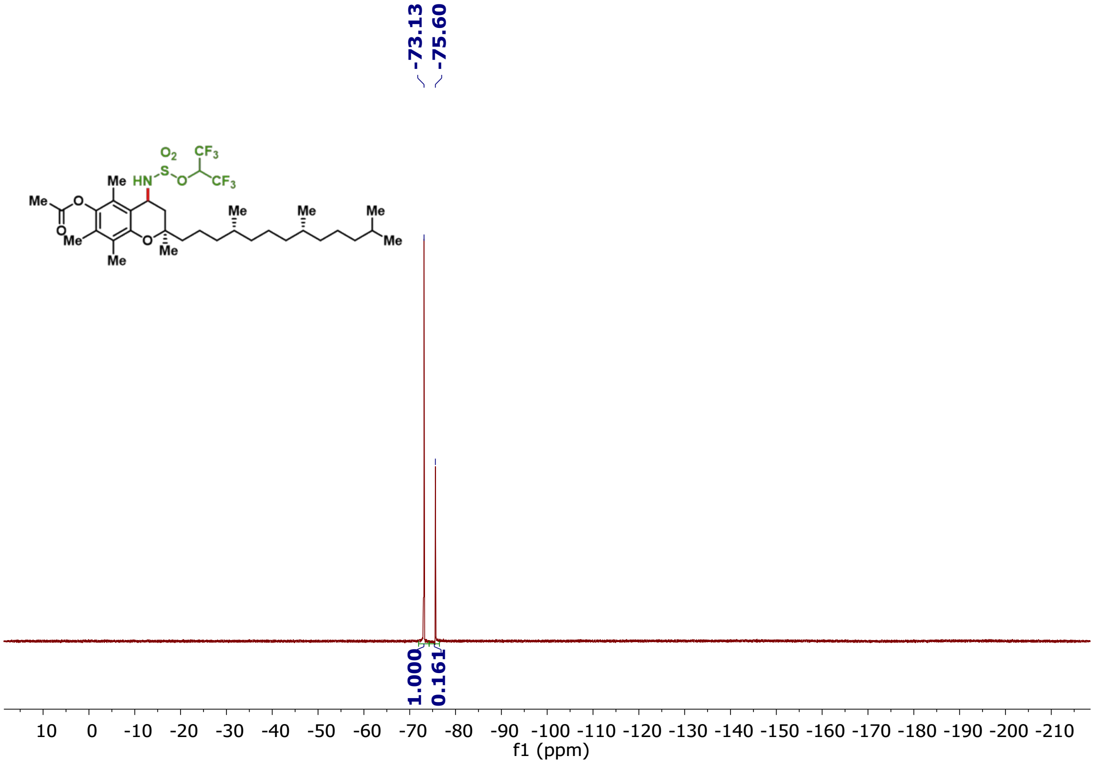



-73.06
O2
CF3
HN
S
O
CF3
Me
CO2Me
Me
MeO
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

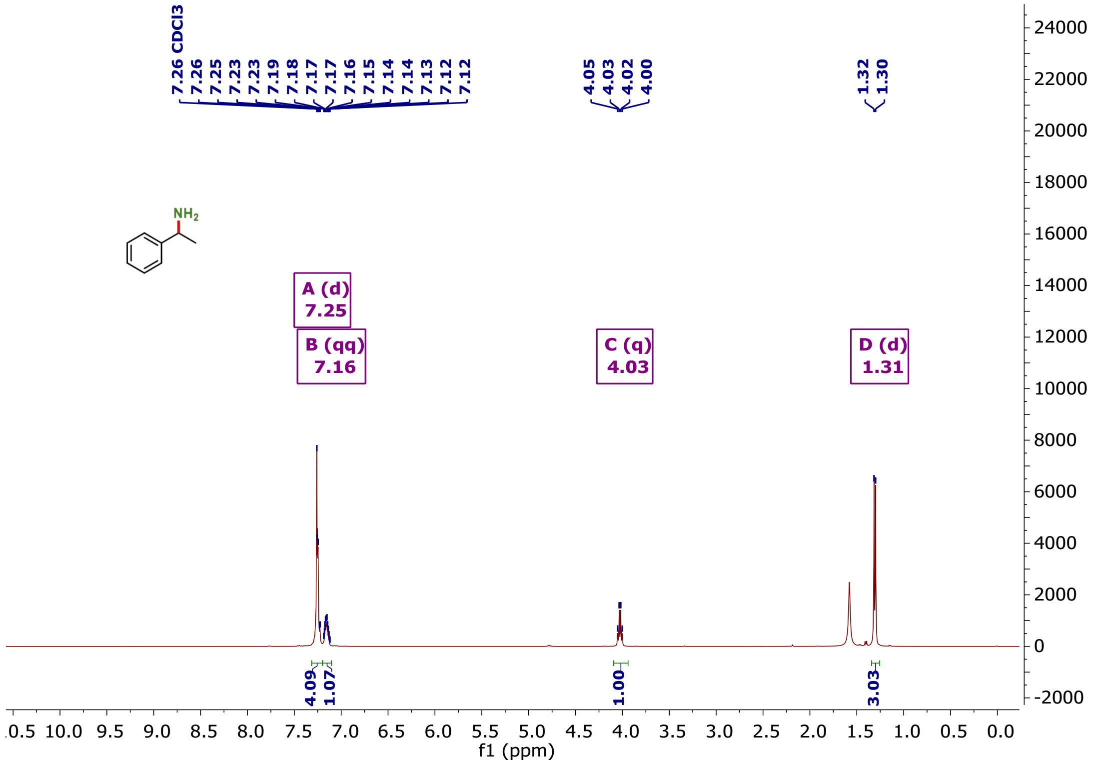
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 48b

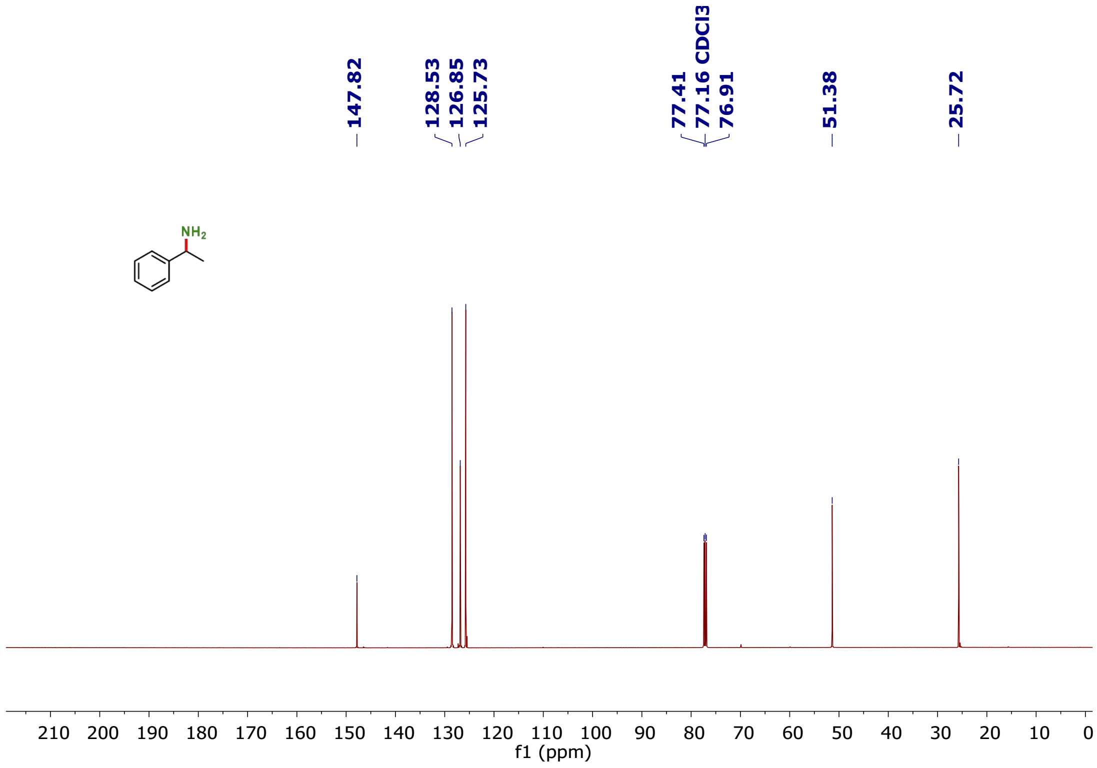




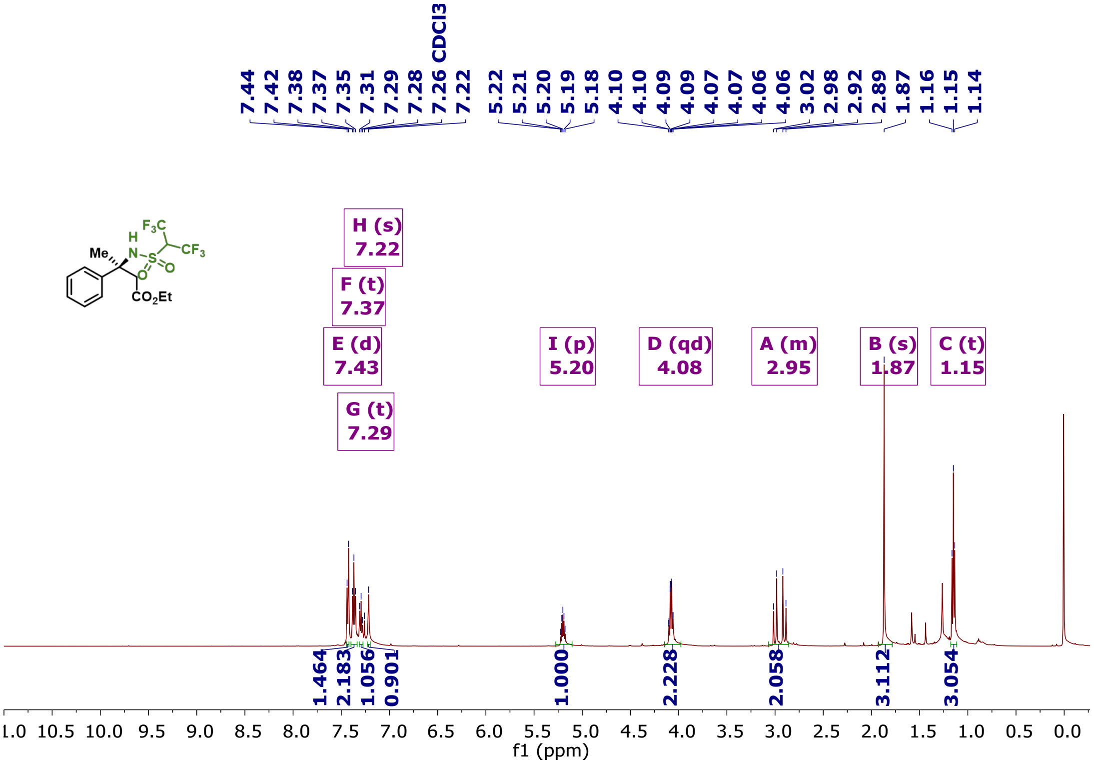

-73.13
-75.60
O2
CF3
HN
S
O
CF3
Me
Me
O
Me
O
Me
O
Me
Me
Me
Me
Me
1.000
0.161
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

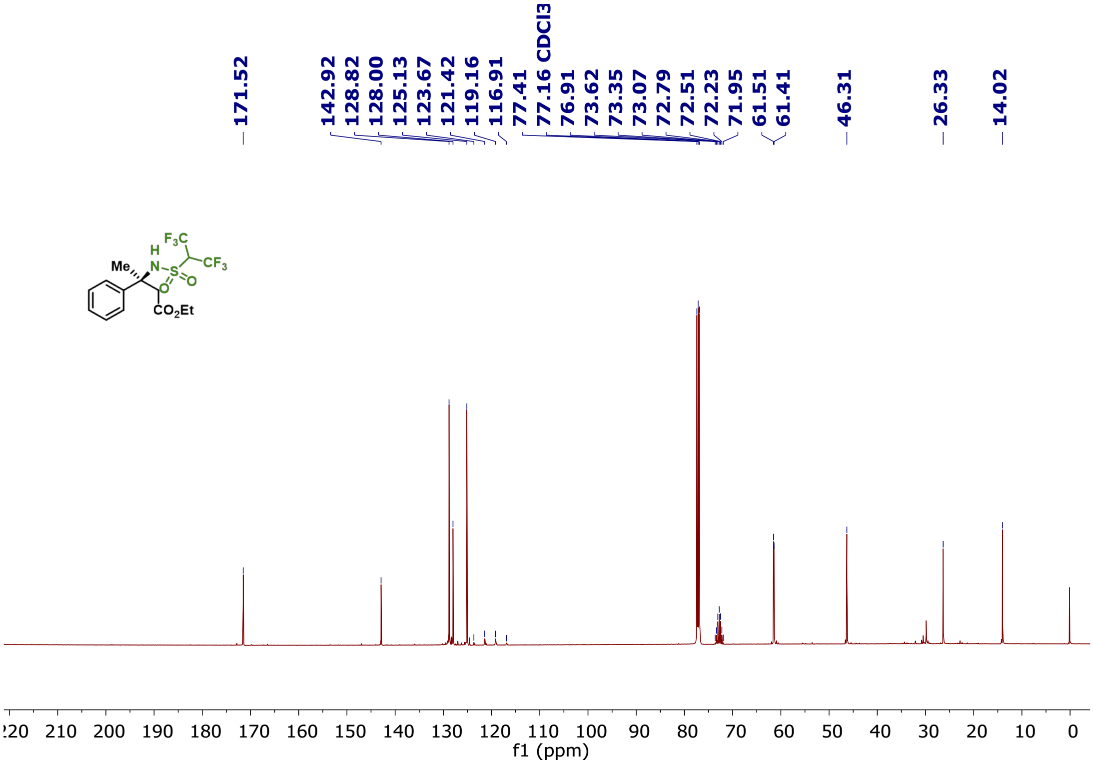
^1H NMR, ^{13}C NMR spectra for compound 1bj

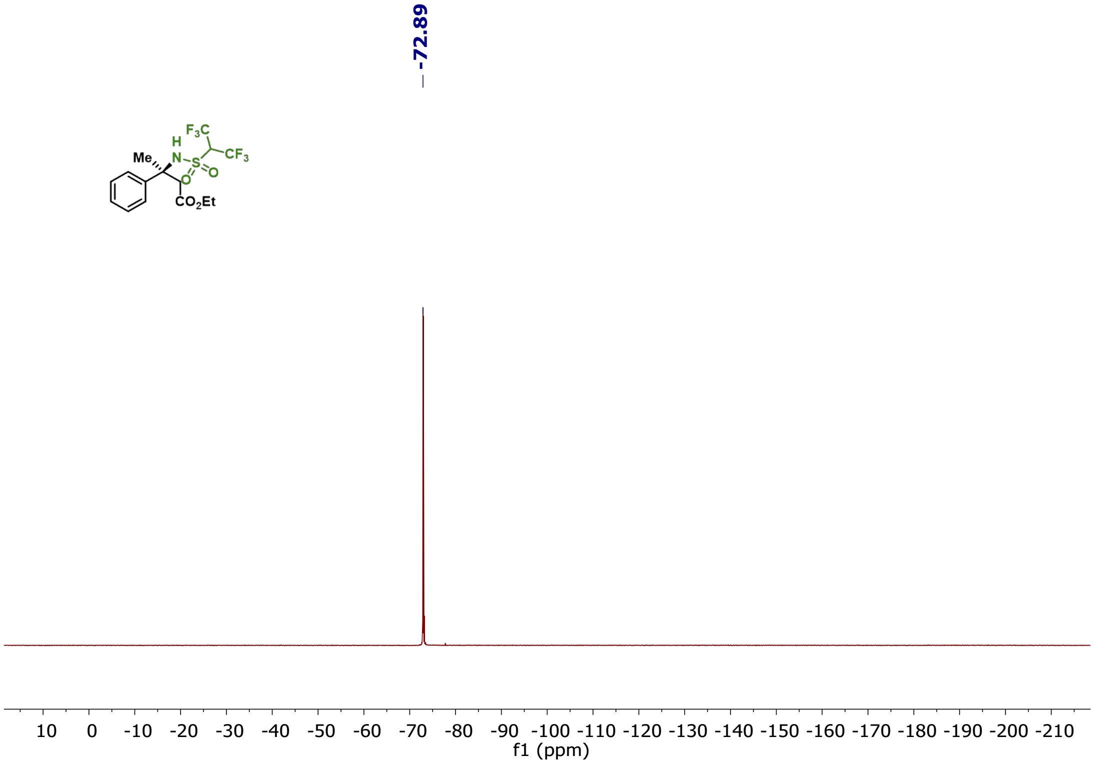




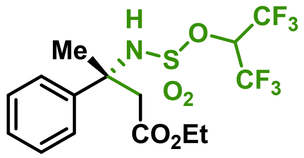
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for compound 50b





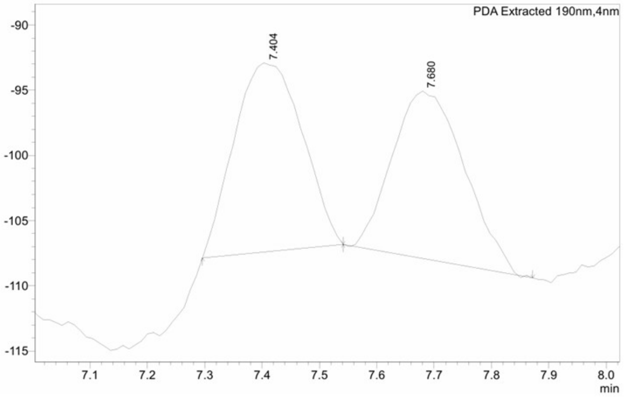


8. HPLC spectra of **50b**.



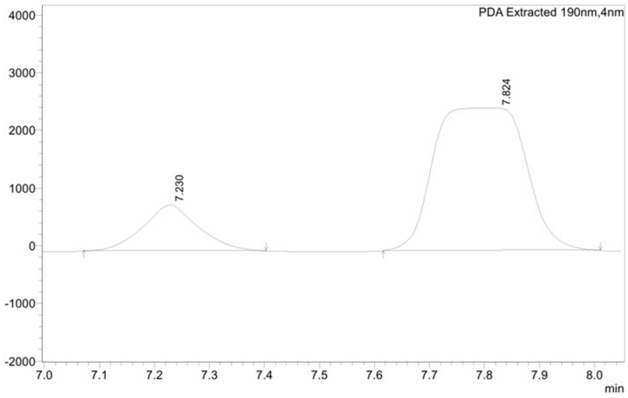
HPLC analysis for compound **50b** (CHIRALCEL® OJ-H, 5→20% ^{i}PrOH/hexane gradient over 30 min, 1.0 mL/min, 190 nm): t_R = 7.82 min (major), 7.23 min (minor); 68% *ee*

Racemic **50b**:



Peak	Retention Time	Area	Area %
1	7.404	120325	51.82
2	7.680	111902	48.19

Enantioenriched **50b**:



Peak	Retention Time	Area	Area %
1	7.230	5310149	15.84
2	7.824	28223260	84.16