Supporting Information

Umpolung Difunctionalization of Carbonyls via Visible-light Photoredox Catalytic Radical-Carbanion Relay

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Contents

1. General information

All NMR spectra were recorded at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F), or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F) NMR spectrometer.[1] All chemical shifts are reported in δ - scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to the solvent residual peaks as the internal standard.[2] Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H - NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet. High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University, and are reported according to the IUPAC recommendations 2013. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q - TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. [35]. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40 - 63 μm, 230 - 440 mesh, Merck) on a Biotage® Isolera TM Spektra One device. All photocatalytic reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal - blue LEDs (λ = 455 nm (± 15 nm), 3.5 V, 700 mA). The sample was irradiated with a LED through the vial's plane bottom side and cooled from the side using custom-made aluminum cooling blocks connected to a thermostat (Figure S1). Gram-scale reactions were in a classic glass tube photochemical reactor setup irradiated from the outside (Figure S2). The glass tube with reaction mixture and LED cooling block were thermostated at 25 °C. CO_2 was bubbled continuously through the reaction mixture in the large-scale carboxylation reactions. UV–Vis and fluorescence measurements were performed with a Varian Cary 100 UV/Vis spectrophotometer and FluoroMax - 4 spectrofluorometer, respectively. Electrochemical studies were carried out under argon atmosphere. The measurements were performed in anhydrous solvent containing 0.1 M tetra-n-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc^{+}) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag quasi-reference electrode were employed. Commercially available starting materials and solvents were used without further purification.

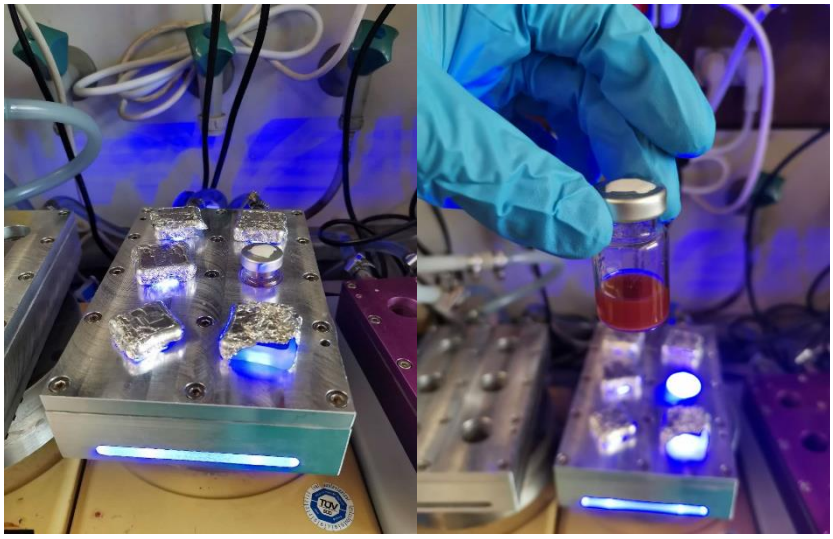


Figure S1. Photochemical set-up for regular-scale reactions

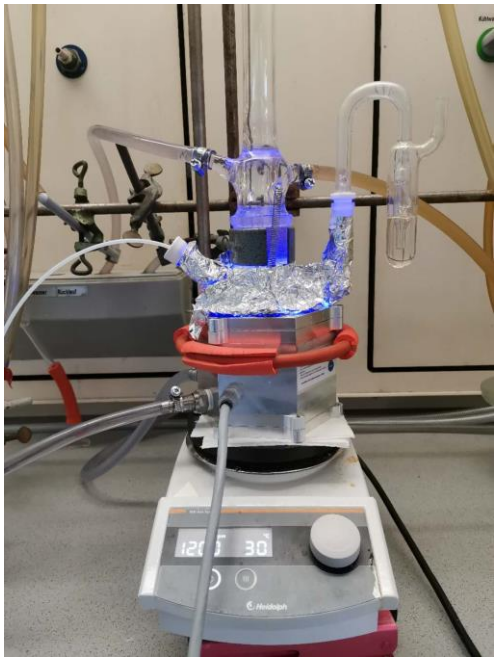
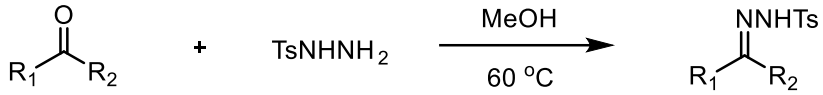


Figure S2. Photochemical set-up for large-scale reactions

2. Starting materials



N-tosylhydrazone was prepared according a reported procedure.[3] To a stirred solution of tosylhydrazide (10 mmol) in MeOH (10 mL) at 60 °C, aldehyde or ketone (1 equiv.) was added dropwise (or portionwise if solid). The reaction was completed within 0.5 h. After that, the solvent was removed directly under reduced pressure, and the crude mixture was either directly used or further purified by recrystallization.

3. Experimental procedures

General procedure A

To a 9 mL snap vial with magnetic stirring bar, tosylhydrazone (0.2 mmol), Cs_2CO_3 (0.6 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol) were added. The vial was evacuated and back filled with CO_2 for three times. A solution of thiol (0.3 mmol) in dry DMSO (2 mL) was added by syringe. Then the solution was bubbled with CO_2 for 3 minutes. After CO_2 (14 mL) was injected by syringe the vial was sealed with wax. The mixture was irradiated with a 455 nm LED at 25 °C. After 24 or 48 h, the mixture was quenched with 2N HCl and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: petroleum ether/EtOAc/HOAc=50/1/0.1% to 10/1/0.1%) to give the desired product.

General procedure B

To a 9 mL snap vial with magnetic stirring bar, tosylhydrazone (0.2 mmol), Cs_2CO_3 (0.3 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol) were added. The vial was evacuated and back filled with N_2 for three times. A solution of thiophenol (0.3 mmol) and carbonyl compound (0.8 mmol) in dry DMSO (2 mL) was added by syringe. The mixture was irradiated with a 455 nm LED at 25 °C. After 24 h, the mixture was quenched with H_2O and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: pentane/EtOAc =50/1 to 10/1) to give the desired product.

General procedure C

To a 9 mL snap vial with magnetic stirring bar, tosylhydrazone (0.2 mmol), Cs_2CO_3 (0.3 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.004 mmol) and CF_3SO_2Na (0.3 mmol) were added. The vial was evacuated and back filled with N_2 for three times, DMSO/acetone = 1/1 (1 mL) was added by syringe. The mixture was irradiated with a 455 nm LED at 25 °C. After the indicated time, the mixture was quenched with H_2O and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (eluent: pentane/EA) to give the desired product.

General procedure D-for "one-pot" thiocarboxylation of N-tosylhydrazone

To a 9 mL snap vial with magnetic stirring bar, carbonyl compound (0.2 mmol), tosylhydrazide (0.2 mmol) and MeOH (1 mL), the mixture was stirred at 60 ^{o}C for 30 minutes. After the solvent was removed under vacuum, [Ir(dFCF_3ppy)$_2$dtbbpy]PF_6 (0.002 mmol) and Cs_2CO_3 (0.6 mmol) were added. The vial was evacuated and back filled with CO_2 for three times. A solution of thiophenol (0.3 mmol) in dry DMSO (2 mL) was added by syringe. Then the solution was bubbled with CO_2 for 3 minutes. After CO_2 (14 mL) was injected by syringe the vial was sealed with wax. The mixture was irradiated with a 455 nm LED at 25 ^{o}C. After 24 or 48 h, the mixture was quenched with 2N HCl and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: petroleum ether/EtOAc/HOAc=50/1/0.1% to 10/1/0.1%) to give the desired product.

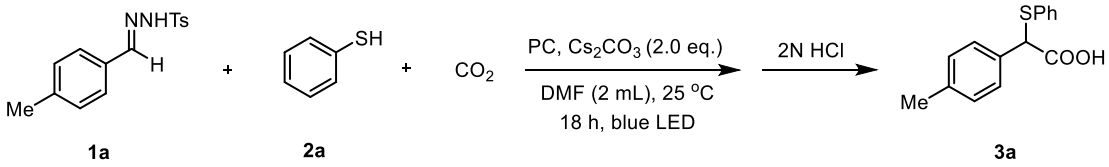
General procedure E-for "one-pot" 1,1-difluoroolefination of N-tosylhydrazone

To a 9 mL snap vial with magnetic stirring bar, carbonyl compound (0.2 mmol), tosylhydrazide (0.2 mmol) and MeOH (1 mL), the mixture was stirred at 60 ^{o}C for 30 minutes. After the solvent was removed under vacuum, [Ir(dFCF_3ppy)$_2$dtbbpy]PF_6 (0.004 mmol), Cs_2CO_3 (0.3 mmol) and CF_3SO_2Na (0.3 mmol) were added. The vial was evacuated and back filled with N_2 for three times, DMSO/acetone = 1/1 (1 mL) was added by syringe. The mixture was irradiated with a 455 nm LED at 25 ^{o}C. After the indicated time, the mixture was quenched with H_2O and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (eluent: pentane/EA) to give the desired product.

4. Optimization details for the reaction conditions

4.1 Optimization details for thiocarboxylation of tosylhydrazone 1a

Table S1. Screening of photocatalysts[a]

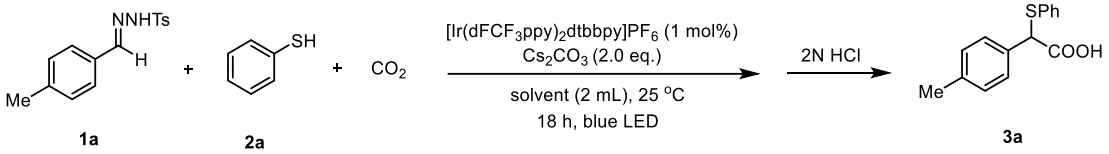


1a 2a 3a

Entry	PC (mol%)	CO_2	Yield (%)[b]
1	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	4 atm	**55**
2	$[Ir(dFCF_3ppy)_2bpy]PF_6$ (1 mol%)	4 atm	40
3	4CzIPN (2 mol%)	4 atm	0
4	Eosin Y (2 mol%)	4 atm	0
5	$[Ir(ppy)_2dtbbpy]PF_6$ (1 mol%)	4 atm	13
6	$Ru(bpy)_3Cl_2.6H_2O$ (1 mol%)	4 atm	34
7	-	4 atm	0

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), Cs_2CO_3 (0.4 mmol), photocatalyst and 4 atm of CO_2 in 2 mL DMF, irradiation with a blue LED at 25 °C for 24 hours. [b] Yields were determined by ^1H NMR analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Screening of solvents[a]



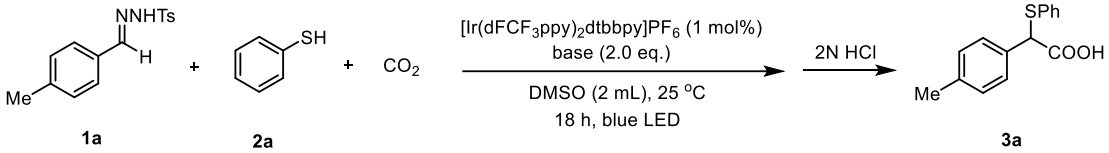
1a 2a 3a

Entry	Solvent	CO_2	Yield (%)[b]
1	DMF	4 atm	55
2	DMSO	4 atm	**68**
3	MeCN	4 atm	0
4	toluene	4 atm	0
5	THF	4 atm	0

6	$PhCF_3$	4 atm	0

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), Cs_2CO_3 (0.4 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%) and 4 atm of CO_2 in 2 mL solvent, irradiation with blue LED at 25 °C for 24 hours. [b] Yields were determined by ^1H NMR analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

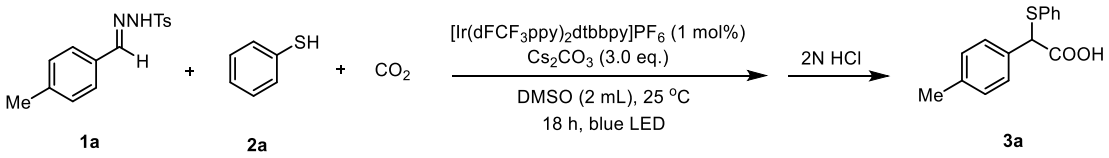
Table S3. Screening of bases[a]



Entry	Base	CO_2	Yield (%)[b]
1	Cs_2CO_3	4 atm.	68
2	K_2CO_3	4 atm.	39
3	Na_2CO_3	4 atm.	50
4	Li_2CO_3	4 atm.	10
5	$NaHCO_3$	4 atm.	16
6	K_3PO_4	4 atm.	53
7	CsOAc	4 atm.	55
8	KOAc	4 atm.	58
9	NaOAc	4 atm.	38
10	NaOH	4 atm.	47
11	DBU	4 atm.	44
12	Cs_2CO_3 (1.0 eq.)	4 atm.	57
13	Cs_2CO_3 (1.5 eq.)	4 atm.	66
14	Cs_2CO_3 (2.5 eq.)	4 atm.	71
15	Cs_2CO_3 (3.0 eq.)	4 atm.	**76**
16	-	4 atm.	**0**

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), base, $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%) and 4 atm of CO_2 in 2 mL DMSO, irradiation with blue LED at 25 °C for 24 hours. [b] Yields were determined by ^1H NMR analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

Table S4. Screening of substrate ratios and control experiments[a]

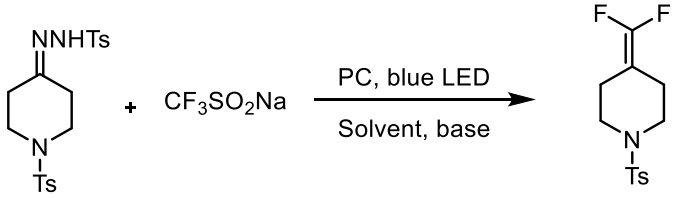


Entry	1a : 2a	CO_2	Yield (%)[b]
1[c]	1 : 2.0	4 atm.	21
2	1 : 2.0	4 atm.	76
3	1 : 1.5	4 atm.	**81**
4	1 : 1.0	4 atm.	62
5	1 : 2.5	4 atm.	72
6	1 : 3.0	4 atm.	48
7	1 : 1.5	2 atm.	65
8	1 : 1.5	balloon	70
9	1 : 1.5	3 atm.	**81**
10[d]	1 : 1.5	3 atm.	0
11[e]	1 : 1.5	3 atm.	0

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **7a** (0.2 mmol), **8** (0.4 mmol), base (0.6 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%) and 4 atm of CO_2 in 2 mL DMSO, irradiation with a blue LED at 25 °C for 24 hours. [b] Yields were determined by ^1H NMR analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard. [c] **2a** was replaced by 2.0 eq. of PhSSPh (diphenyl disulfide). [d] without light. [e] without photocatalyst.

4.2 Optimization details for *gem*-difluoroolefination of tosylhydrazone 7a

Table S5. Optimization of the reaction conditions[a]



7a **8** **9a**

Entry	Base (1.5 eq)	Photocatalyst	Solvent	Yield [%][b]
1	**Cs_2CO_3**	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	**59**
2	K_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	25
3	Na_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
4	NaOH	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
5	CH_3COOCs	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
6	K_3PO_4	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
7	KO^tBu	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
8	2,4,6-collidine	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
9	CsF	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
10	-	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d

[a]Unless otherwise noted, all the reactions were carried out with **7a** (0.2 mmol), **8** (0.3 mmol), base (0.3 mmol), $[IrdFCF_3(ppy)_2dtbbpy]PF_6$ (1 mol%, 0.002 mmol) in DMSO (1 mL), irradiation with a blue LED at 25 °C for 24 h. [b] ^{19}F NMR yield using 4,4'- difluorobenzophenone as an internal standard. n.d = not detected

Table S6. Photocatalyst screening

Entry	Base	Photocatalyst	Solvent	Yield[%][b]
1	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	59
2	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol%)	DMSO	61
3	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.5 mol%)	DMSO	44
4	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	41
5	Cs_2CO_3	$[IrdF(Me)(ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	trace
6	Cs_2CO_3	$[Ir(ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO	n.d
7	Cs_2CO_3	4CzIPN (5 mol%)	DMSO	18
8	Cs_2CO_3	EoSin Y (2 mol%)	DMSO	n.d
9	Cs_2CO_3	Rh-6G (10 mol%)	DMSO	n.d
10	Cs_2CO_3	Fukuzumi ClO_4^- (5 mol%)	DMSO	n.d
11	Cs_2CO_3	Carbon Nitride 20 mg	DMSO	n.d

[a] Unless otherwise noted, all the reactions were carried out with **7a** (0.2 mmol), **8** (0.3 mmol), base (0.3 mmol), photocatalyst (1 mol%, 0.002 mmol) in DMSO (1 mL), irradiation with a blue LED at 25 °C for 24 h. [b] ^{19}F NMR yield using 4,4'-difluorobenzophenone as an internal standard. n.d = not detected.

Table S7. Optimization of the reaction conditions[a]

Entry	Base	Photocatalyst	Solvent	Yield [%][b]
1	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMF	38
2	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMA	30
3	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	MeCN	trace
4	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DCE	n.d
5	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	THF	n.d

		(1 mol%)		
6	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	toluene	n.d
7	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	dioxane	n.d
8	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	MeOH	n.d
9	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	NMP	n.d
10	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/THF=4:1	52
11	Cs_2CO_3	$[IrdFCF_3(ppy)_2dtbpy]PF_6$ (1 mol%)	DMSO/1,4-dioxane=4:1	53
12	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/MeCN=4:1	62
13	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/EA=4:1	62
14	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/toluene=4:1	38
15	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/DME=4:1	46
16	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/H_2O=4:1	n.d
17	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/acetone=4:1	65
18	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/acetone=2:1	67
19	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/acetone=1:1	70
20	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/acetone=1:2	70
21	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/acetone=1:1 (0.6 mL in total)	65
22	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	DMSO/acetone=1:1 (1.5 mL in total)	70
23	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol%)	DMSO/acetone=1:1	**77 (73)**[c]
24	Cs_2CO_3	-	DMSO/acetone=1:1	n.d
25[d]	Cs_2CO_3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol%)	DMSO/acetone=1:1	n.d

[a] Unless otherwise noted, all the reactions were carried out with **7a** (0.2 mmol), **8** (0.3 mmol), Cs_2CO_3 (0.3 mmol), $[IrdFCF_3(ppy)_2dtbbpy]PF_6$ (1 mol%, 0.002 mmol) in solvent (1 mL),

irradiation with a blue LED at 25 ºC for 24 h. [b] ^{19}F NMR yield using 4,4'-difluorobenzophenone as an internal standard. n.d = not detected. [c] isolated yield. [d] in the dark.

5. Mechanistic studies

CV measurements

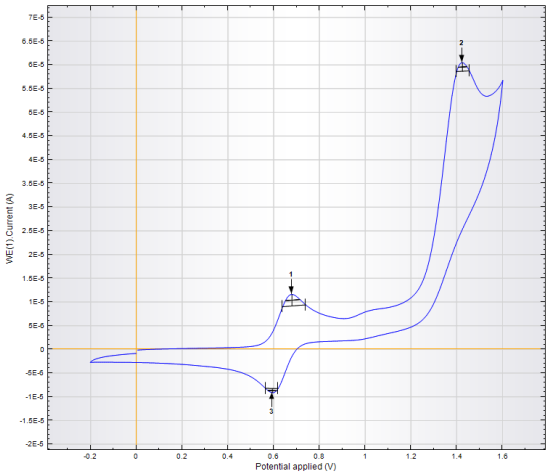
CV measurements were taken on a three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab by using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire as a reference electrode. The voltammograms were taken at room temperature in a degassed DMF or MeCN solution ([n-Bu_4NBF_4] = 0.1 M, [substrate] = 1 mM, ferrocene as the internal standard) under Argon atmosphere. The scan rate was 0.1 V/s. Potentials vs. SCE were reported according to $E_{SCE} = E_{Fc/Fc+} + 0.38$ V.

Index Peak position

1 0.67978

2 1.425

3 0.59418



E_{ox}(**1a**) = 1.17 V *vs.* SCE

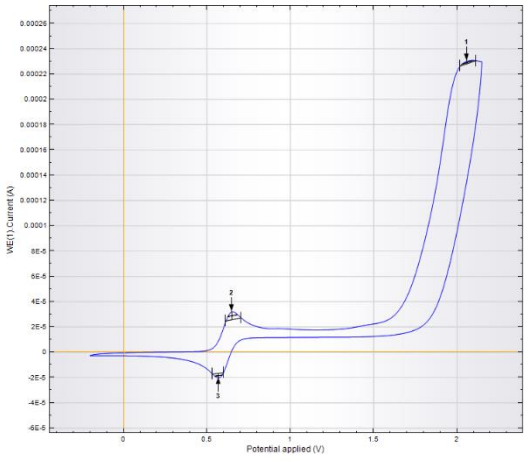
Figure S3. Cyclic voltammogram of N-tosylhydrazone **1a** in DMSO (with Ferrocene)

Index Peak position

1 2.0595

2 0.64957

3 0.569

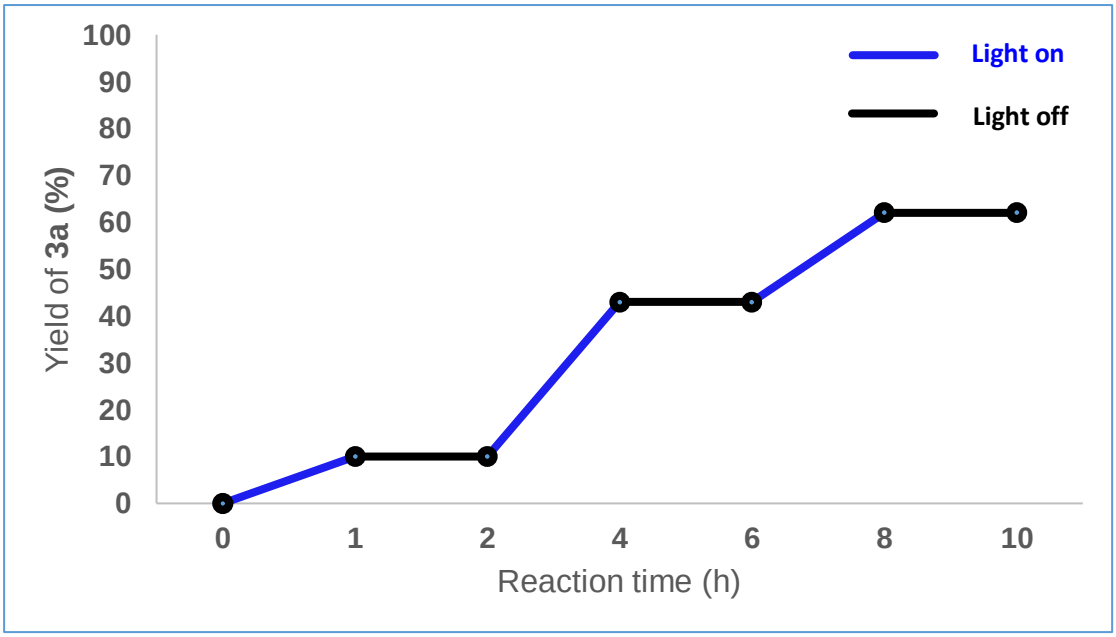


E_{ox}(**1a**) = 1.83 V *vs.* SCE

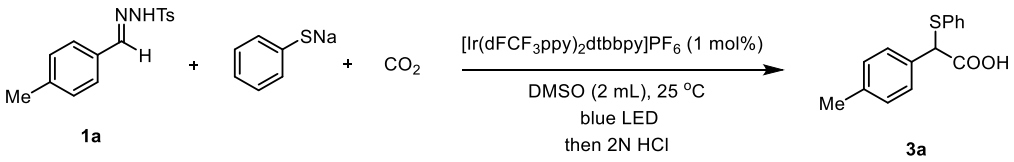
Figure S4. Cyclic voltammogram of N-tosylhydrazone **7a** in MeCN (with Ferrocene)

"On-off" Experiments

Tosylhydrazone **1a** (0.2 mmol, 57.6 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol, 2.2 mg) were added into a 9 mL snap vial equipped with a stirring bar. The vial was evacuated and back filled with CO_2 for three times. A solution of thiophenol **2a** (0.3 mmol) in dry DMSO (2 mL) was added by syringe. Then the solution was bubbled with CO_2 for 3 minutes. After CO_2 (14 mL) was injected by syringe the vial was sealed with wax. The reaction mixture was irradiated by a blue LED at 25 °C. Parallel reactions were carried out for various reaction times. The yield of carboxylic acid was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard after acidified with 2N HCl.



Determination of the reaction quantum yield



To a 9 mL snap vial, **1a** (0.2 mmol, 1.0 eq), sodium thiophenolate (0.3 mmol, 1.5 eq), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol, 1 mol%) were added. The vial was evacuated and back filled with CO_2 for three times, and then dry DMSO (6 mL) was added by syringe. After that, 2 mL solution was transferred from the vial into the cuvette by syringe, the solution in cuvette was bubbled with CO_2 for 5 minutes and equipped with a CO_2 balloon. The sample was placed in the quantum yield spectrometer and irradiated with a 455 nm LED for 300.76 s. After irrdadiation, the yield of the formed product was determined by ^1H NMR analysis of acidified crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard. The yield of **3a** was determined to be 28.5%.

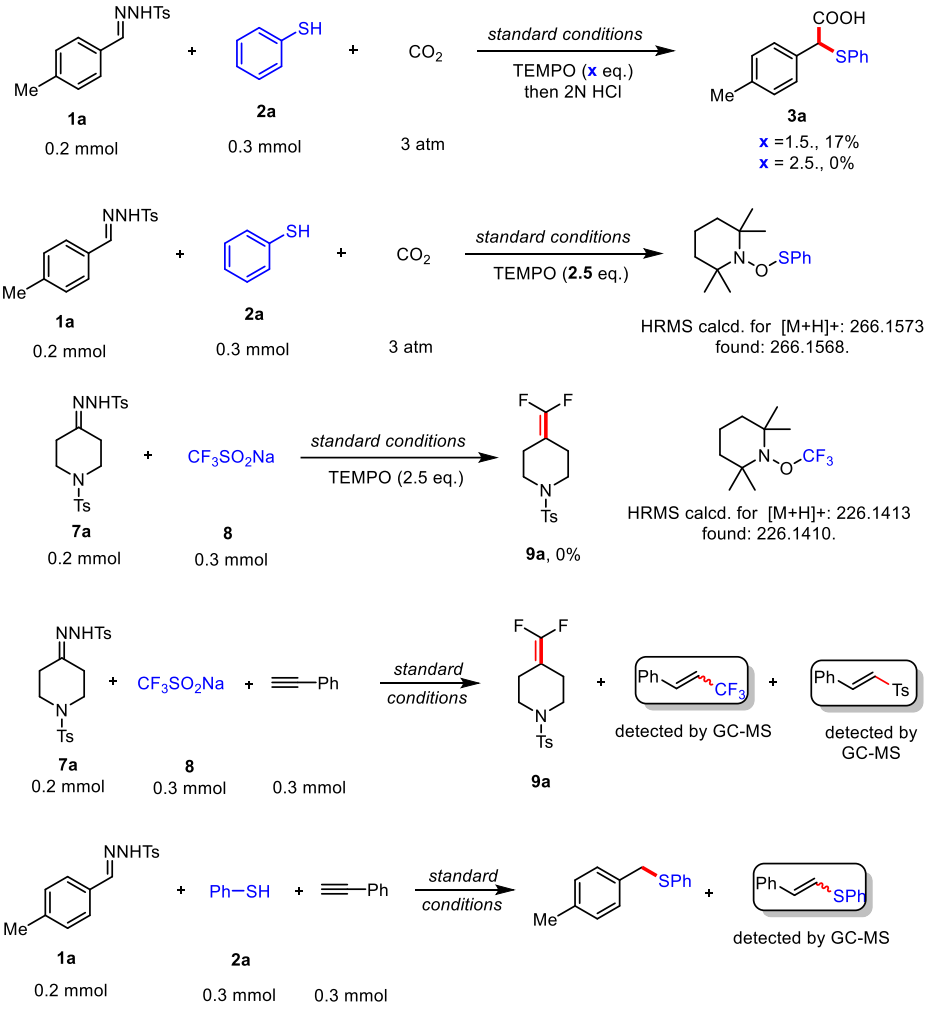
$$\Phi = \frac{\text{Number of product molecules}}{\text{Number of absorbed photons}} = \frac{\text{Nprod}}{\text{Nph,abs}} = \frac{\text{cprod} \cdot \text{V} \cdot \text{NA} \cdot \text{h} \cdot \text{c}}{\text{Pabs} \cdot \Delta\text{t} \cdot \lambda} = 2.1\%$$

c_{prod}: concentration of product **3a**; V: 2 mL; N_A: $6.02 \cdot 10^{23}$/mol; h: planck constant; c: speed of light; P_{abs}: absorbed optical power = 131.7 mW; Δt: illumination time = 300.76 s; λ: 455 nm.

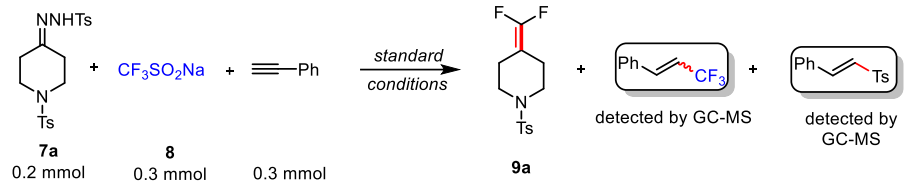
The quantum yield (Φ) was calculated to be 2.1%

Control experiments

(A) Radical inhibiting and trapping experiments



To further prove the existence of radicals (thiyl radicals, trifluoromethyl radical and tosyl radical) in the proposed catalytic cycle, we attempted to use trapping reagents including TEMPO and phenylacetylene under the standard conditions. First, products **3a** and **9a** were not formed when the radical scavenger TEMPO (2.5 eq.) was added to the thiocarboxylation and *gem*-difluoroolefination reaction respectively, TEMPO-SPh and TEMPO-CF_3 adducts were detected by HRMS. Moreover, hydrotrifluoromethylation and hydrothiolation products were detected by GC-MS when phenylacetylene was added. It is to be noted that the proposed tosyl radical could be trapped in the reaction of **7a** with **8** by the phenylacetylene to give hydrosulfonylation product.

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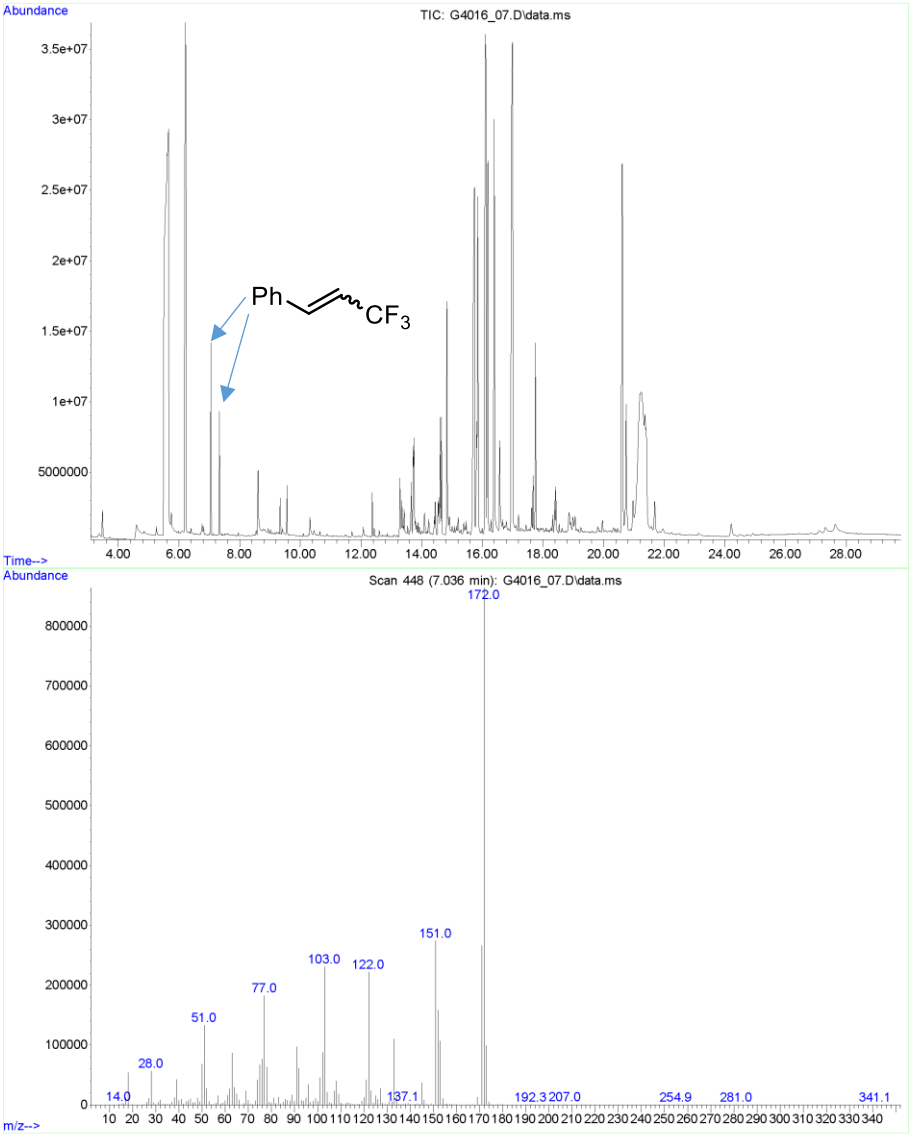
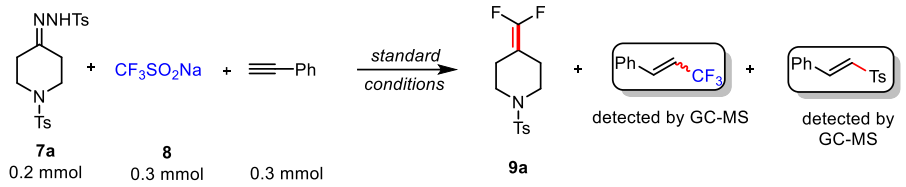


Figure S5. GC-MS report of hydrotrifluoromethylation product

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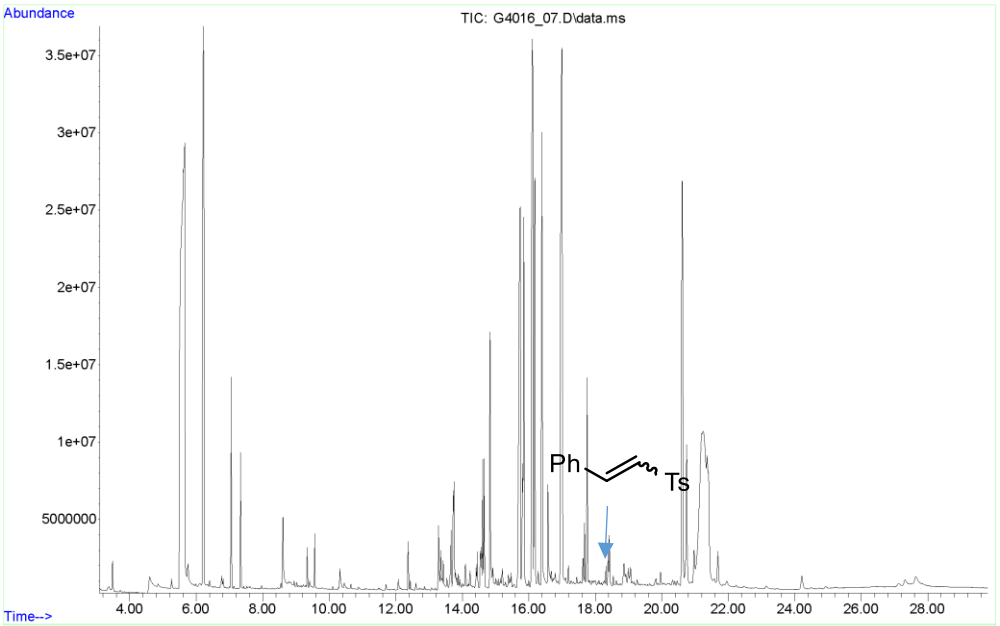


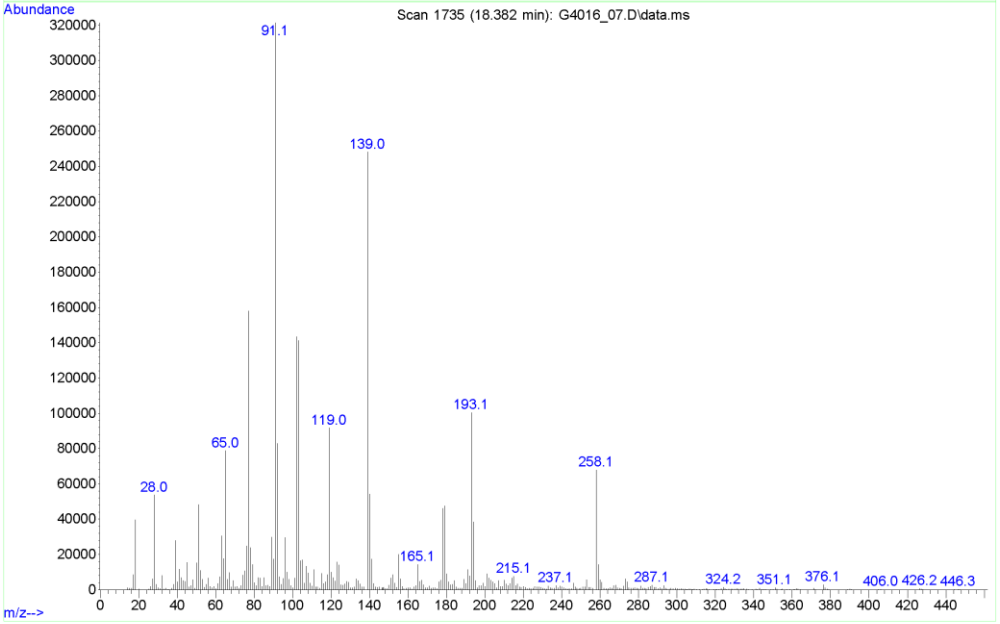
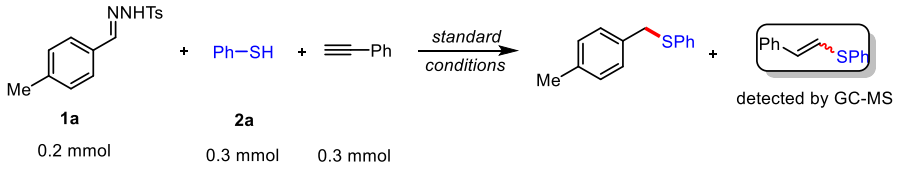


Figure S6. GC-MS report of hydrosulfonylation product

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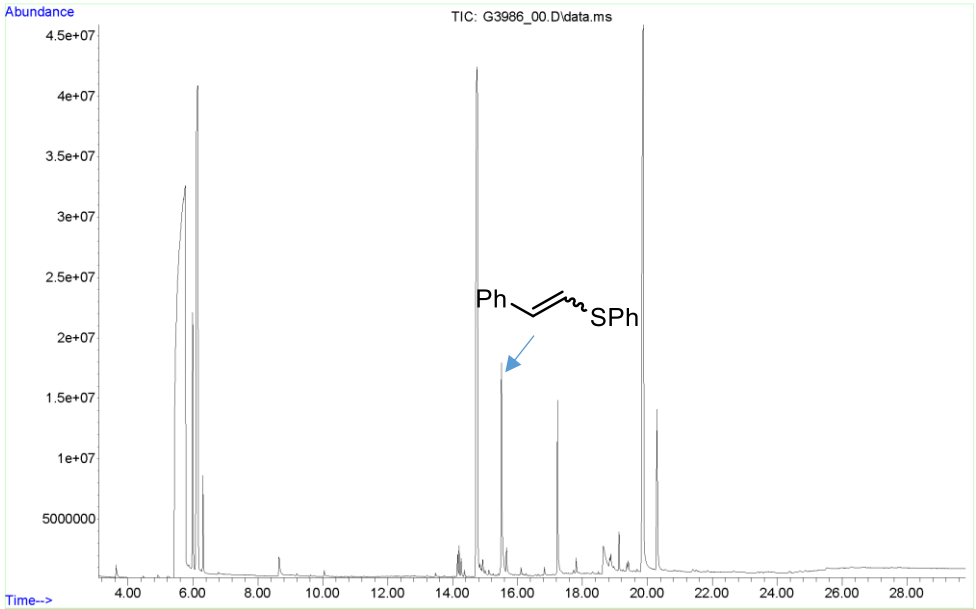


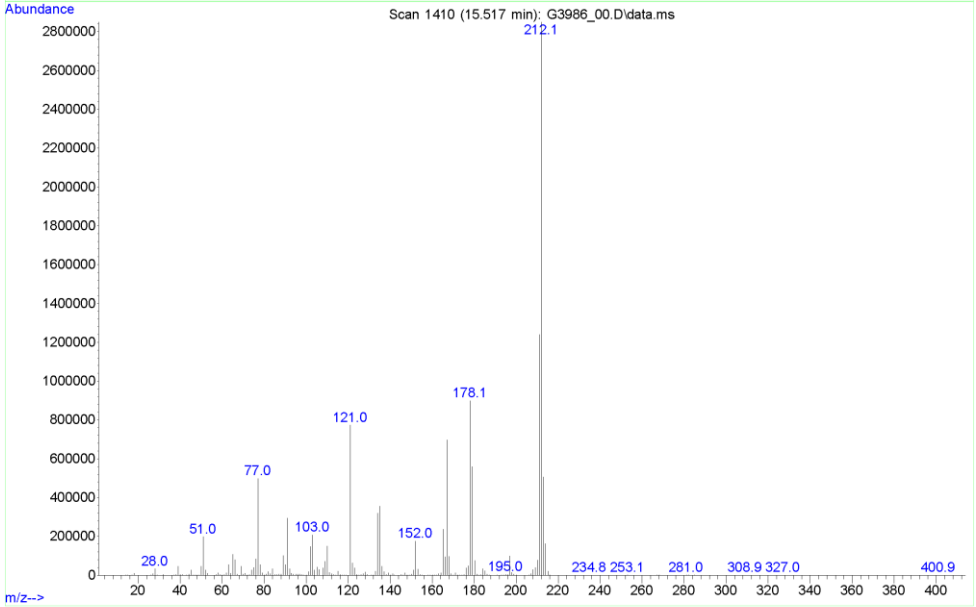
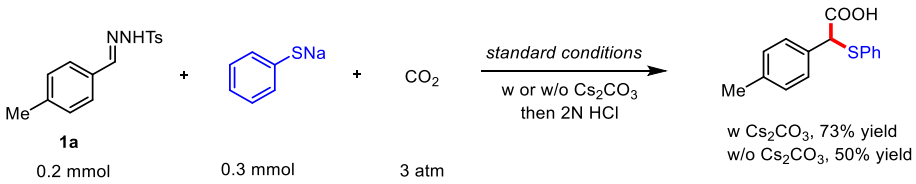
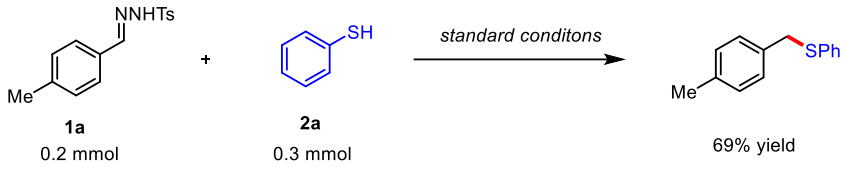


Figure S7. GC-MS report of hydrosulfonylation product

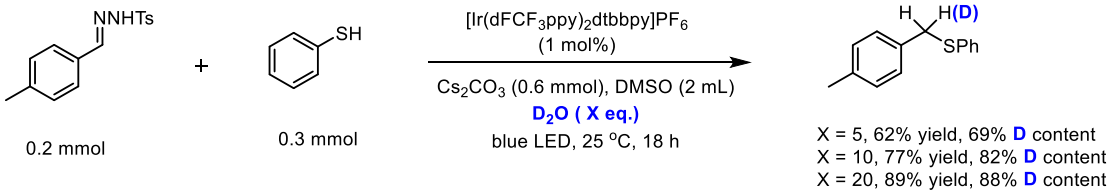
(B) Using sodium thiophenolate in place of thiophenol



(C) Control experiments in the absence of CO_2

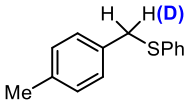


(D) Deuterium incorporation experiments

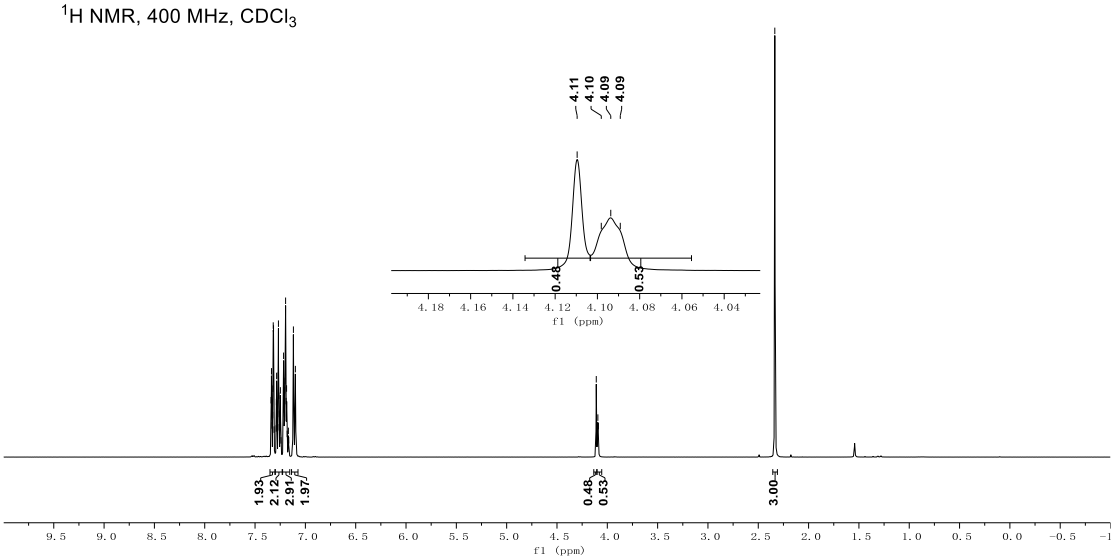


Tosylhydrazone **1a** (0.2 mmol, 57.6 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol, 2.2 mg) were added into a 9 mL snap vial equipped with a stirring bar. The vial was evacuated and back filled with N_2 for three times. Then PhSH (0.3 mmol), dry DMSO (2.0 mL) and D_2O (x eq.) were added sequentially by syringes. The reaction mixtures were irradiated with a blue LED at 25 °C for 24 h. The reaction mixture was quenched with H_2O and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to give the desired product. The recorded ^{1}H-NMR spectra are depicted below.

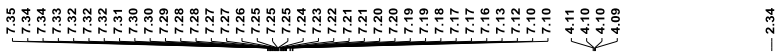
X = 5.0 eq.

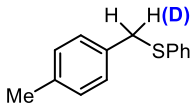


^{1}H NMR, 400 MHz, $CDCl_3$

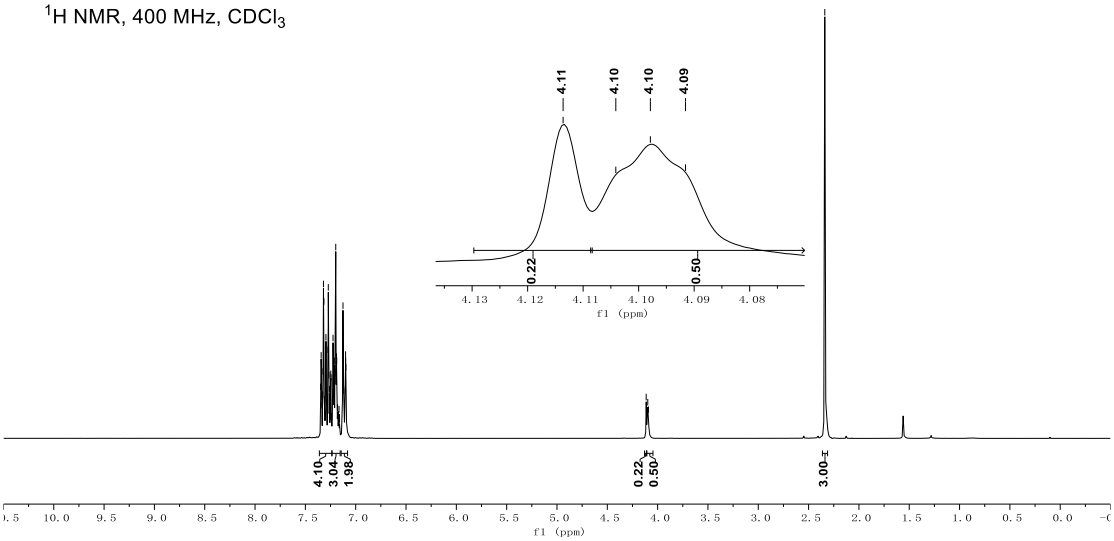


X = 10.0 eq.

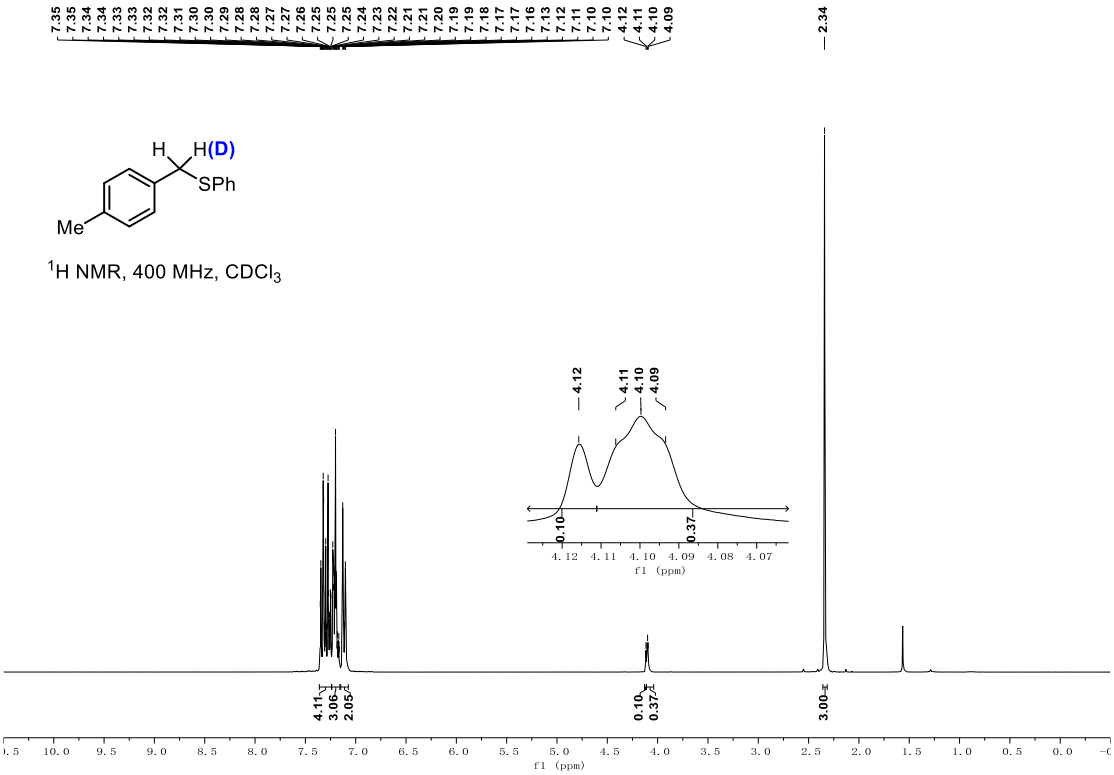




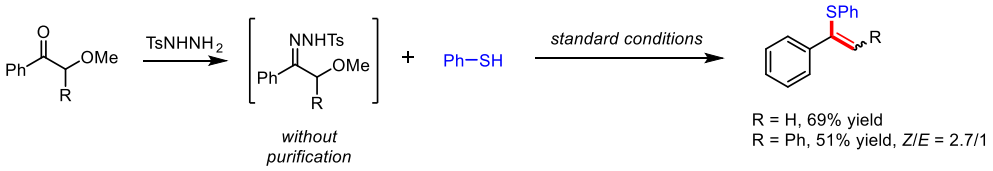
^{1}H NMR, 400 MHz, $CDCl_3$

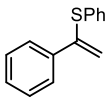


X = 20 eq.



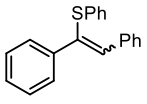
(E) E1cb elimination





phenyl(1-phenylvinyl)sulfane

The product was obtained as a colorless oil, 29.3 mg, yield = 69%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.32 – 7.28 (m, 2H), 7.22 – 7.11 (m, 4H), 7.16 – 7.11 (m, 2H), 5.57 (s, 1H), 5.21 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.43, 138.69, 133.75, 131.90, 129.01, 128.44, 128.26, 127.28, 127.12, 115.81. **HRMS** (EI) calcd for $C_{14}H_{12}S$ $[M]^+$:212.0654, found: 212.0653.



(Z) and (E)-(1,2-diphenylvinyl)(phenyl)sulfane

The product was obtained as a colorless oil, 29.4 mg, yield = 51% (Z/E = 2.7/1). **^{1}H NMR** (400 MHz, $CDCl_3$) (Z and E isomer) δ 7.75 (dd, *J* = 7.5, 1.7 Hz, 3H), 7.67 – 7.61 (m, 3H), 7.43 – 7.33 (m, 7H), 7.32 – 7.18 (m, 16H), 7.14 – 7.07 (m, 6H), 7.06 – 7.00 (m, 1H), 6.98 – 6.94 (m, 2H), 6.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) (Z and E isomer) δ 145.19, 144.59, 139.96, 138.15, 136.94, 134.73, 126.94, 125.75,

124.94, 124.72, 124.51, 123.82, 122.37, 121.91, 121.38, 120.96, 120.40, 119.63, 116.34, 111.60, 109.92, 109.45, 109.40. **HRMS** (EI) calcd for $C_{20}H_{16}S$ $[M]^+$: 288.0967, found: 288.0962.

Luminescence quenching experiments

Luminescence spectra of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1.0×10^{-5}M) was collected as a function of different quenchers in degassed DMSO with excitation at 420 nm and data of emission intensity at 480 nm was recorded.

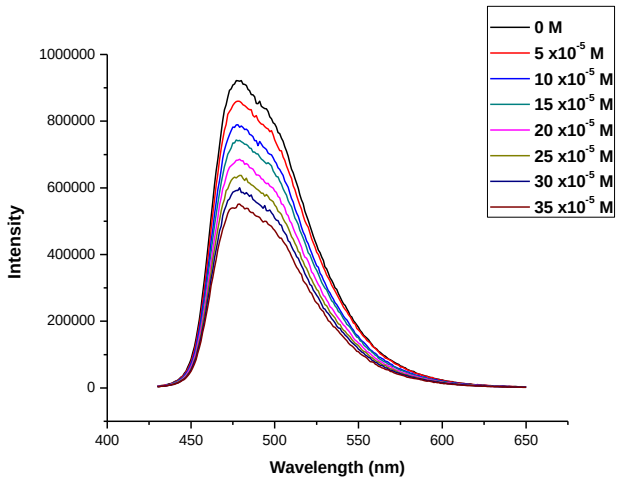


Figure S8. A solution of PhSNa in DMSO was added and its concentration was changed from 0 to 35×10^{-5} M

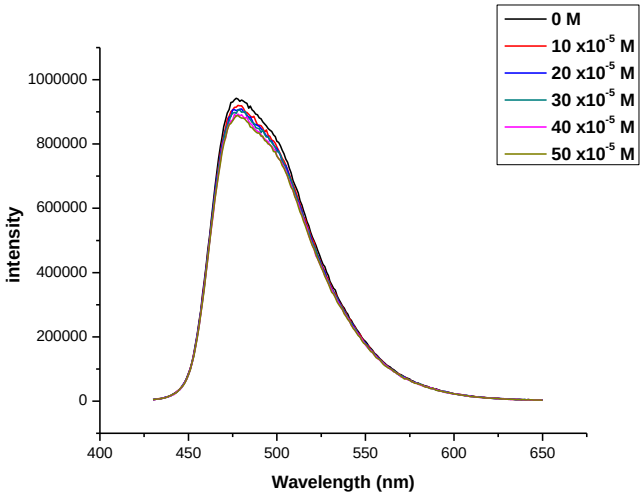


Figure S9. A solution of PhSH in DMSO was added and its concentration was changed from 0 to 50×10^{-5} M

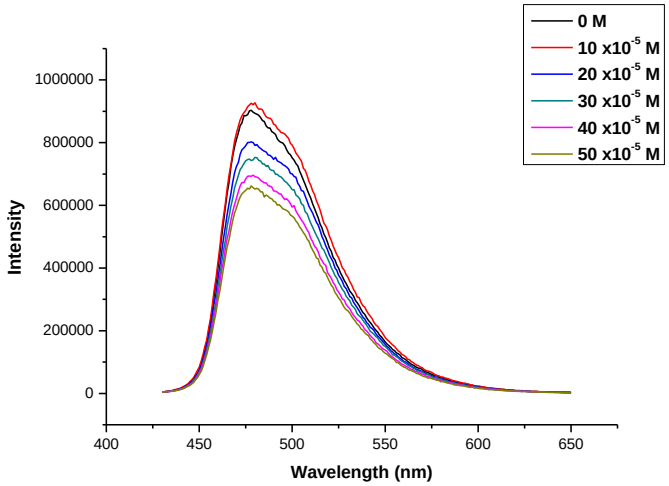


Figure S10. A solution of **1a** in DMSO was added and its concentration was changed from 0 to 50 × 10^{-5} M

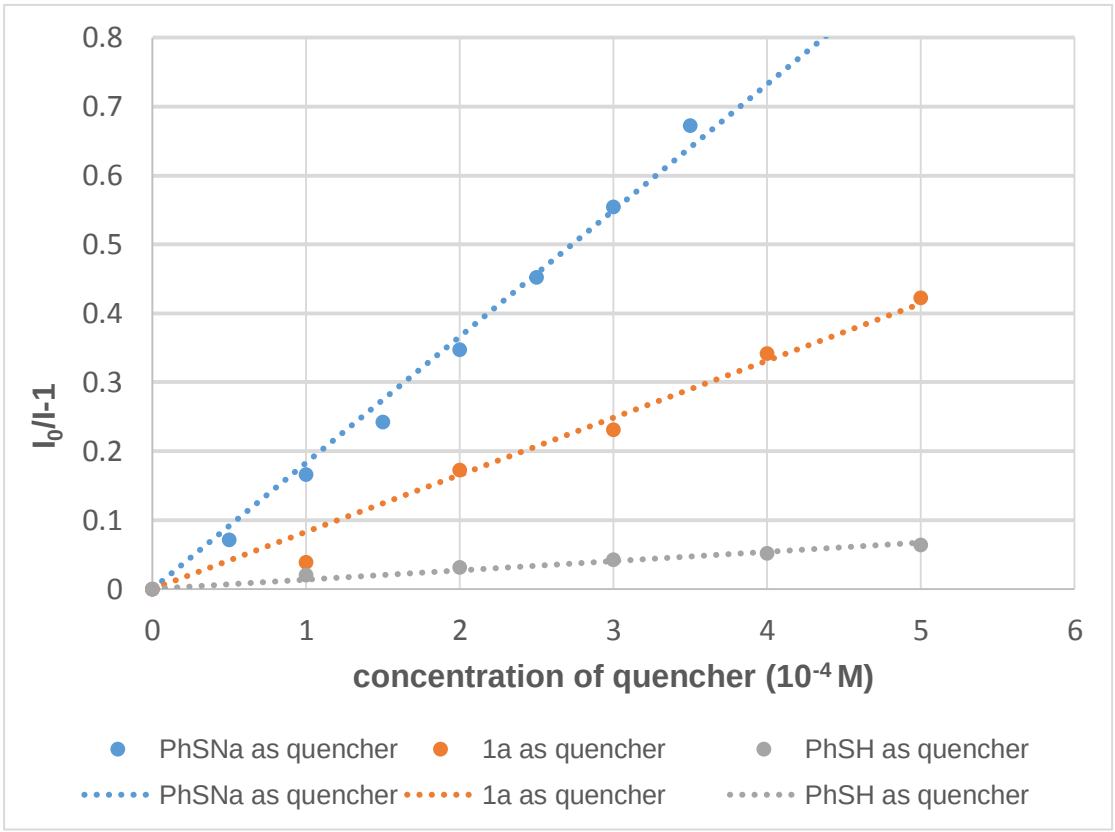


Figure S11. Stern-Volmer plot of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ by different components

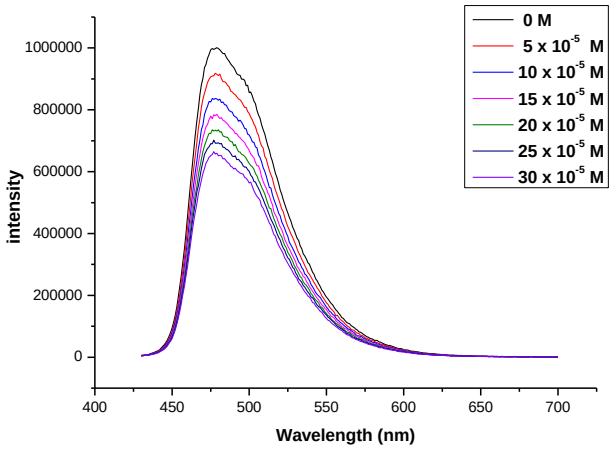


Figure S12. A solution of **8** (CF_3SO_2Na) in DMSO was added and its concentration was changed from 0 to 30 × 10^{-5} M

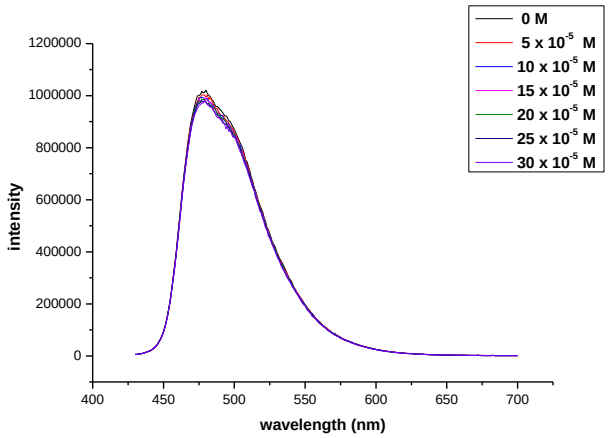


Figure S13. A solution of **7a** in DMSO was added and its concentration was changed from 0 to 30 × 10^{-5} M

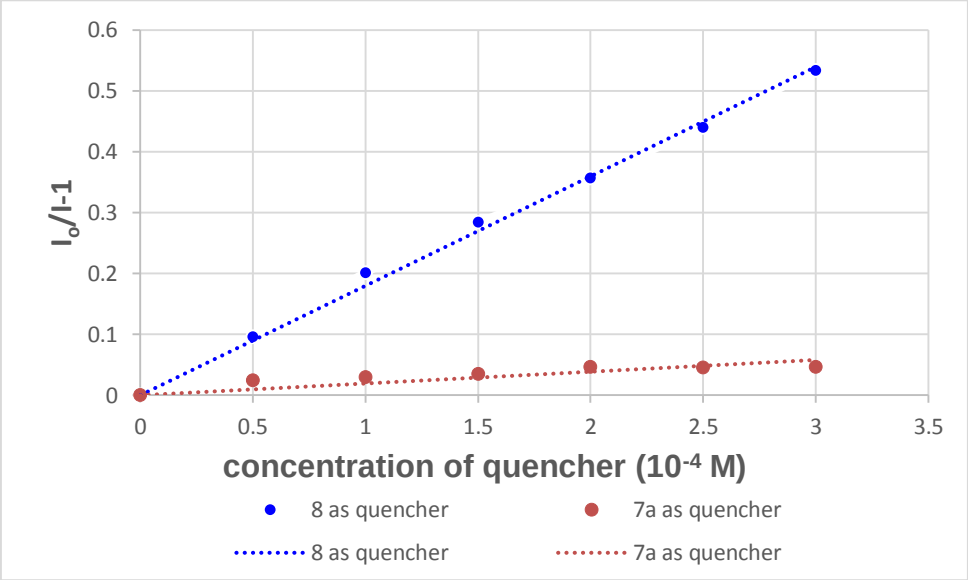
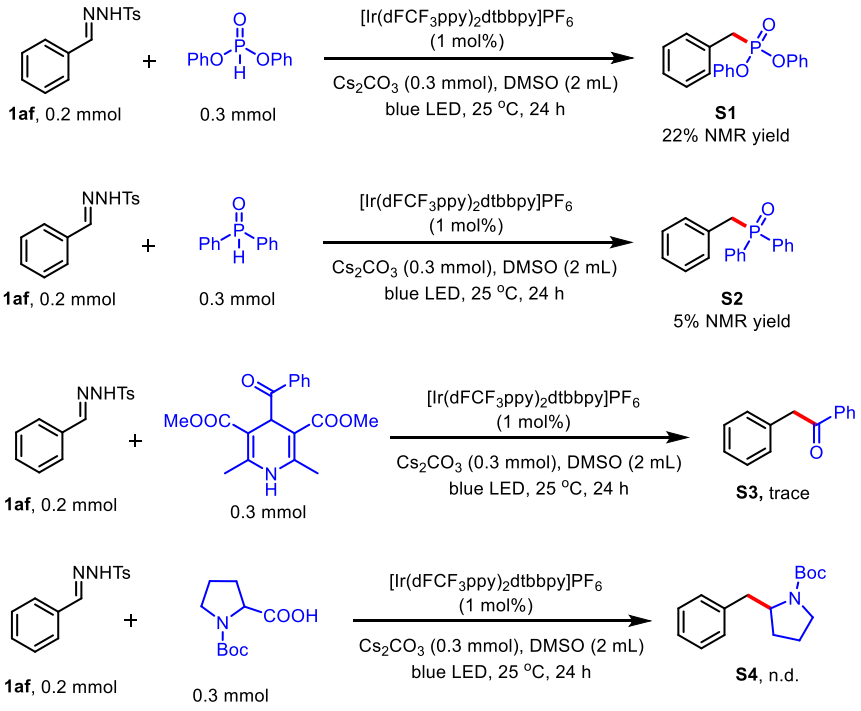
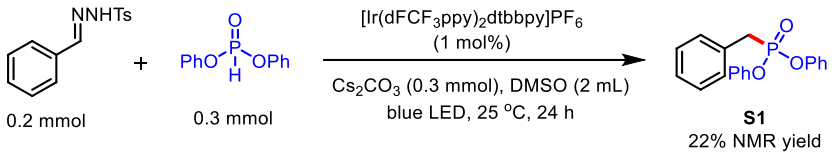


Figure S14. Stern-Volmer plot of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ by different components

Scheme S1. Testing other radical precusors in the photoredox catalytic Wolff-Kishner processes



In addition to CF_3SO_2Na and thiols, other radical precusors including phosphite, phosphine oxide, 1,4-dihydropyridine and carboxylic acid are tested in this photocatalytic radical-anion relay sequence. As summarized in **Scheme S1**, under the unoptimized reaction conditions phosphite, phosphine oxide and dihydropyridine could react with N-tosylhydrazone **1af** to give corresponding carbanions which are then trapped by the protons in the reaction mixture. These results demonstrated that this novel strategy could be further extended in the production and transformation of other functionalized carbanions. Further studies along this lines are currently underway in our laboratory.

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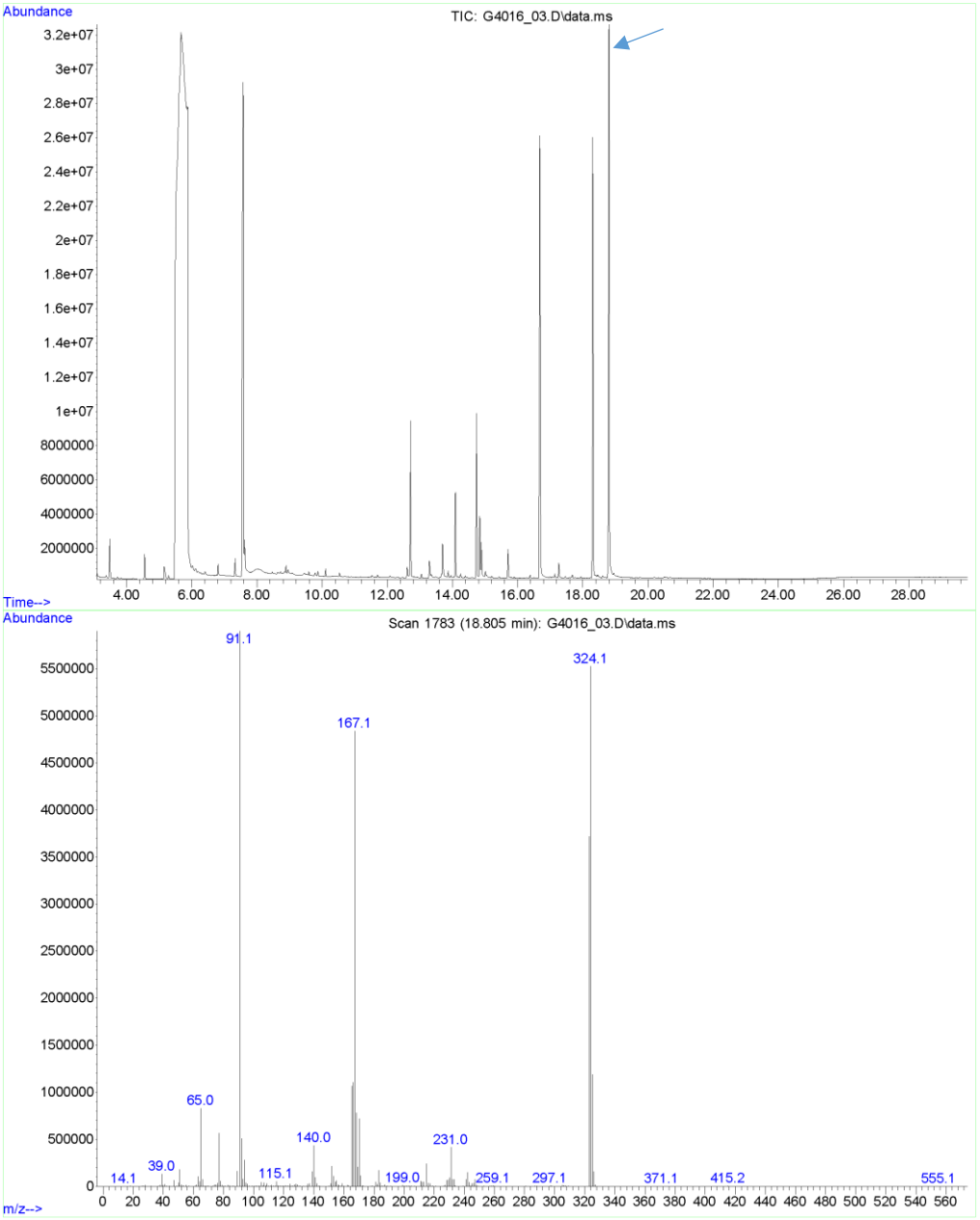


Figure S15. GC-MS report of product **S1**

Figure S16. Crude ^{1}H NMR spectrum of the reaction between **1af** and **diphenylphosphite**[4]

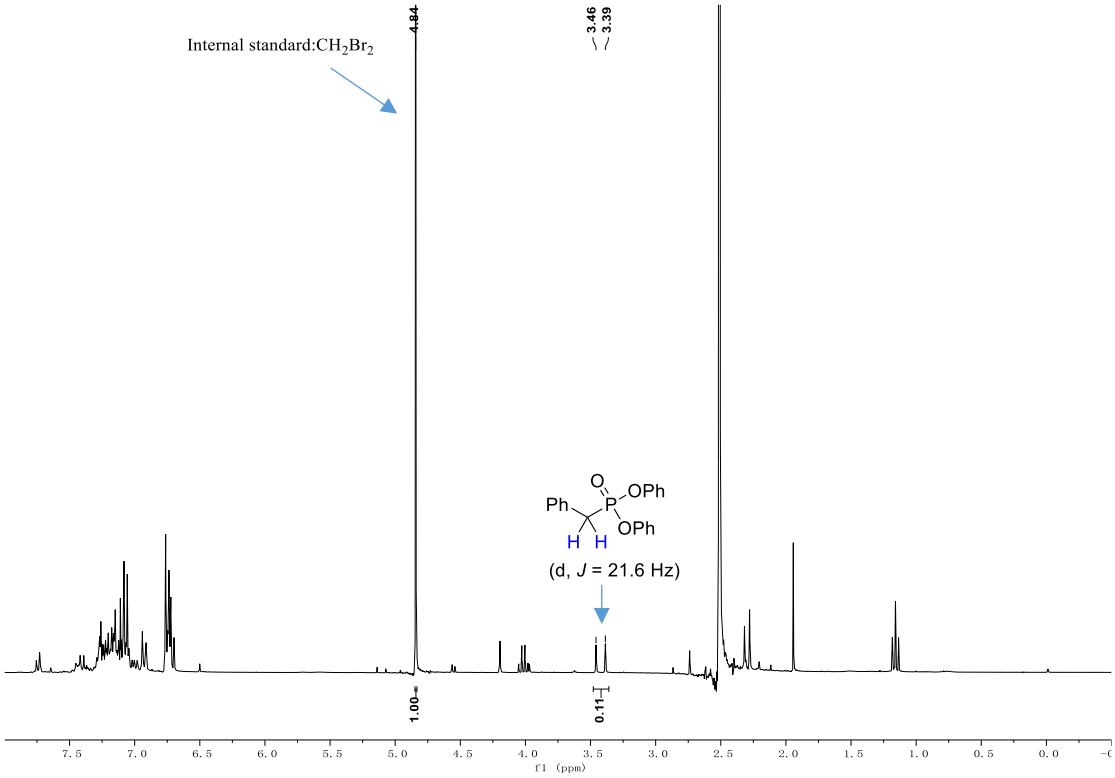
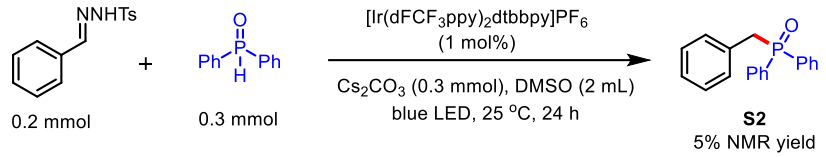


Figure S17. Crude ^{1}H NMR spectrum of the reaction between **1af** and diphenylphosphite[4]

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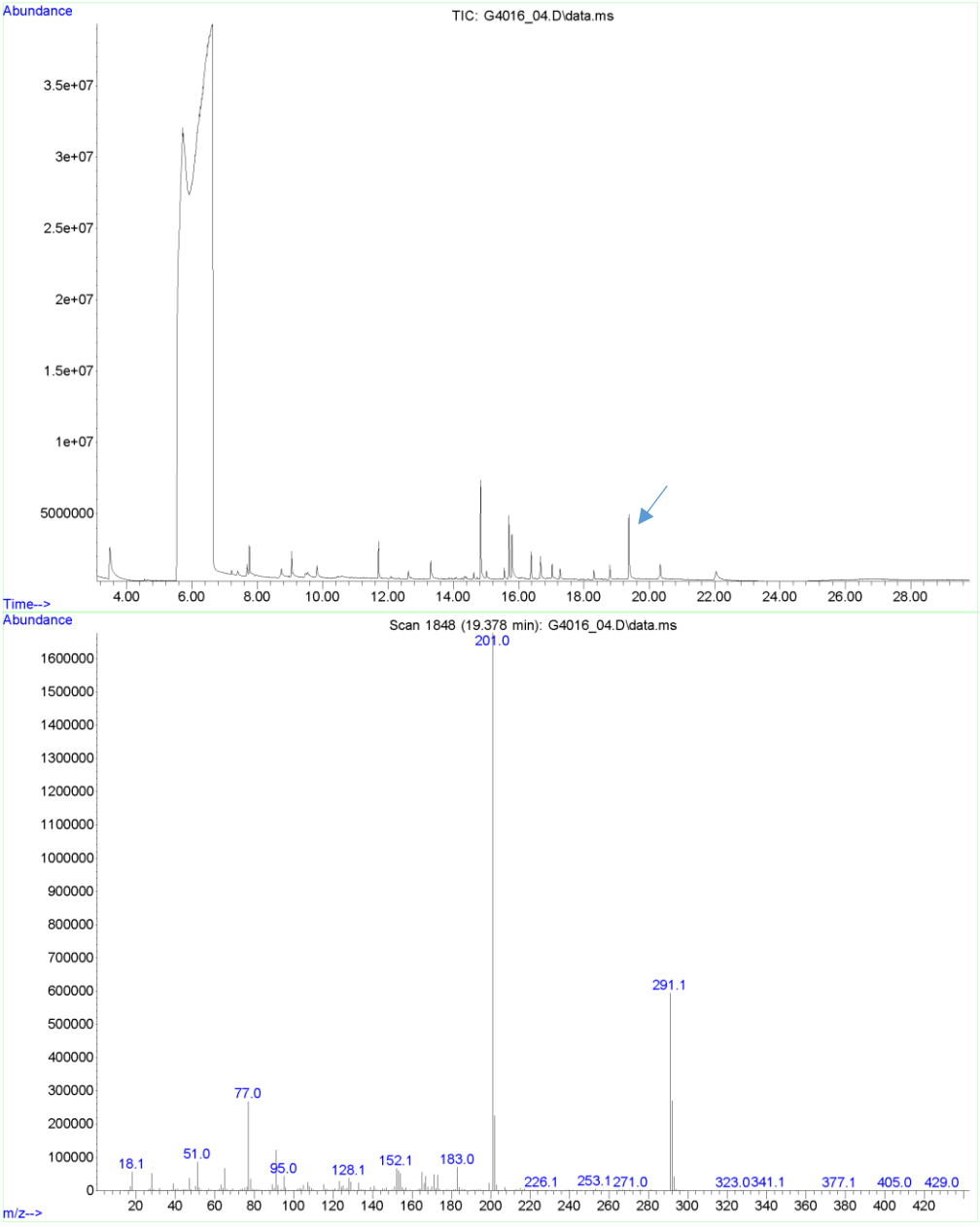


Figure S18. GC-MS report of product **S2**

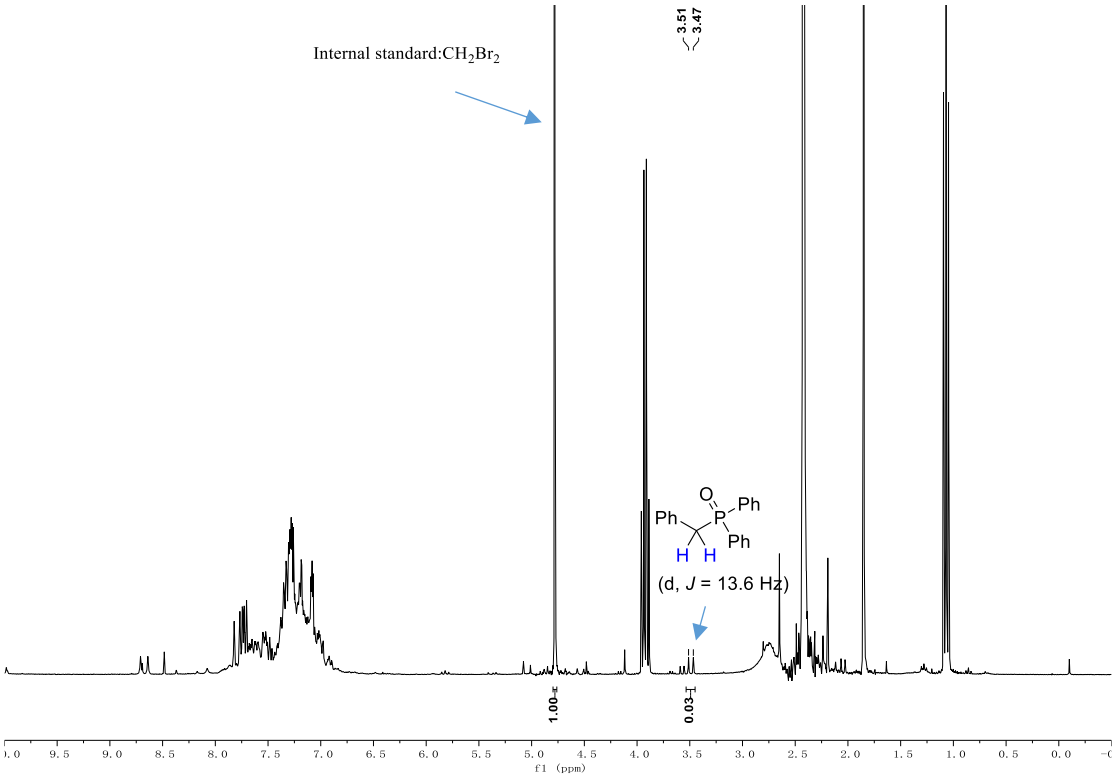
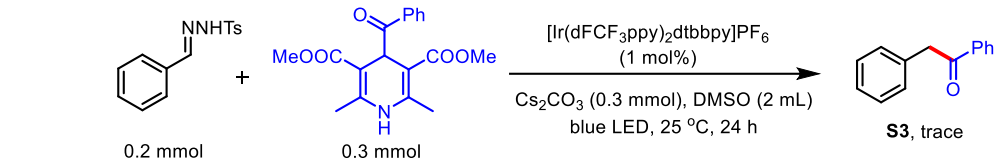


Figure S19. Crude ^{1}H NMR spectrum of the reaction between **1af** and **diphenylphosphine oxide**[5]

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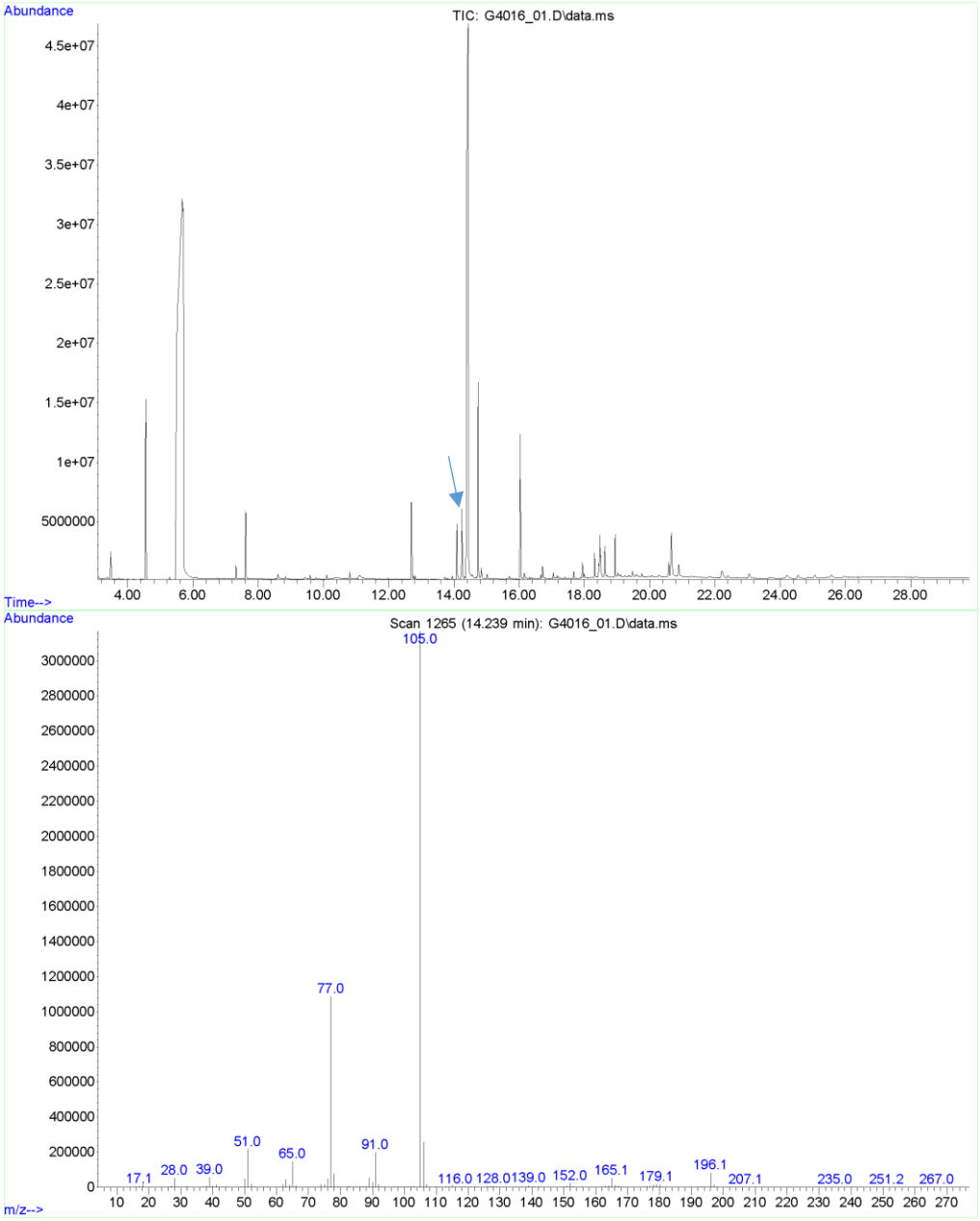
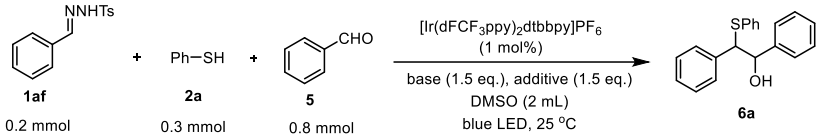


Figure S20. GC-MS report of product **S3**

Table S8. Diastereoselectivity of α-sulfenyl carbanion addition to benzaldehyde[a]

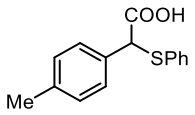


Entry	Base	Additive	Yield of 6a	*Syn:Anti*[b]
1	Cs_2CO_3	-	78%	44:56
2	Li_2CO_3	-	15%	44:56
3	$MgCO_3$	-	n.d.	-
4	Cs_2CO_3	$MgClO_4$	25%	43:57
5	Cs_2CO_3	LiCl	80%	51:49

[a]Reaction conditions: Unless otherwise noted, all reactions were carried out with **1af** (0.2 mmol), **2a** (0.3 mmol), **5** (0.8 mmol), base (0.3 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%) in 2 mL DMSO, irradiation with blue LED (455 nm) at 25 °C for 24 hours, NMR yields were shown. [b]Determined by ^1H NMR analysis.

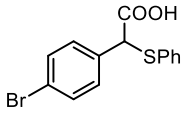
Regarding the diastereoselectivity of α-sulfenyl carbanion addition to benzaldehyde, we attempted to improve the syn/anti ratio by adding chelating bases or additives. We tested commonly used cheating metal cation including Li^+ and Mg^{2+} in this reaction. As demonstrated above, when Cs_2CO_3 was replaced by Li_2CO_3 or $MgCO_3$, the reaction efficiencies dropped dramatically whereas the diastereoselectivity remained unchanged. Adding $MgClO_4$ (1.5 eq) did not improve diastereoselectivity but decreased the yield significantly. Moreover, using LiCl as additive afforded the product in retained efficiency and poor diastereoselectivity.

6. Characterization of products



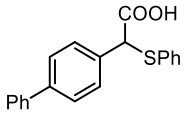
2-(phenylthio)-2-(p-tolyl)acetic acid (3a)

Following the general procedure A, the product was obtained as a white solid, 41.2 mg, 81% yield; mp 108.3-110.6 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.28 - 7.24 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.87 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.69 , 138.47 , 133.56 , 132.38 , 131.90 , 129.47 , 129.05 , 128.36 , 128.03 , 55.83 , 21.16 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 259.0787. Found: 259.0791.



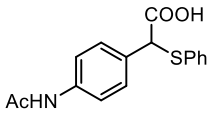
2-(4-bromophenyl)-2-(phenylthio)acetic acid (3b)

Following the general procedure A, the product was obtained as a white solid, 42.4 mg, 66% yield. mp 110.5-114.8 ºC.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.41 – 7.33 (m, 2H), 7.32 – 7.25 (m, 2H), 7.25 – 7.13 (m, 5H), 4.74 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.86 , 134.08 , 132.97 , 132.66 , 131.85 , 130.21 , 129.15 , 128.50 , 122.70 , 55.63 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 322.9736. Found: 322.9737.



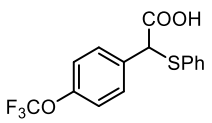
2-([1,1'-biphenyl]-4-yl)-2-(phenylthio)acetic acid (3c)

Following the general procedure A, the product was obtained as a white solid, 38.7 mg, 60% yield. mp 150.4-154.6 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.61 – 7.50 (m, 6H), 7.48 – 7.33 (m, 5H), 7.31 – 7.27 (m, 3H), 4.95 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.31 , 141.45 , 140.31 , 133.89 , 133.29 , 132.64 , 129.10 , 128.94 , 128.78 , 128.22 , 127.53 , 127.46 , 127.07 , 55.94. **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 338.1209. Found: 338.1214.



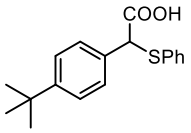
2-(4-acetamidophenyl)-2-(phenylthio)acetic acid (3d)

Following the general procedure A, the product was obtained as a white solid, 45.6 mg, 76% yield. mp 212.3-215.1 ºC.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 7.56 – 7.51 (m, 2H), 7.41 – 7.33 (m, 4H), 7.32 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 5.17 (s, 1H), 2.03 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.28 , 168.39 , 139.11 , 134.36 , 130.55 , 130.40 , 129.02 , 128.80 , 127.04 , 118.99 , 54.20 , 24.02 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 302.0845. Found: 302.0852.



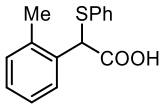
2-(phenylthio)-2-(4-(trifluoromethoxy)phenyl)acetic acid (3e)

Following the general procedure A, the product was obtained as a white solid, 43.2 mg, 66% yield. mp 78.9-83.2 °C.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.42 – 7.34 (m, 2H), 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 7.13 – 7.05 (m, 2H), 4.79 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.88 , 149.20 (q, *J* = 2.1 Hz), 133.68 , 133.08 , 132.59 , 130.11 , 129.16 , 128.57 , 121.06 , 55.43 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -58.32. **HRMS** (ESI) Calcd. for $[M+H]^+$: 329.0454. Found: 329.0456.



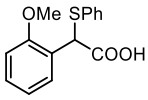
2-(4-(tert-butyl)phenyl)-2-(phenylthio)acetic acid (3f)

Following the general procedure, the product was obtained as a white solid, 43.3 mg, 72% yield. mp 105.7-110.8 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.35 – 7.25 (m, 6H), 7.20 – 7.14 (m, 3H), 4.79 (s, 1H), 1.22 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.42 , 151.63 , 133.74 , 132.27 , 131.71 , 129.05 , 128.14 , 127.99 , 125.75 , 55.76 , 34.59 , 31.24 . **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 318.1522. Found: 318.1529.



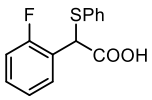
2-(phenylthio)-2-(o-tolyl)acetic acid (3g)

Following the general procedure A, the product was obtained as a yellow gel-like solid, 42.2 mg, 82% yield.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.50 – 7.44 (m, 1H), 7.31 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.14 – 7.05 (m, 3H), 5.05 (s, 1H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.41 , 136.24 , 133.63 , 133.34 , 132.58 , 130.61 , 129.06 , 128.39 , 128.25 , 128.13 , 126.60 , 52.67 , 19.50. **HRMS** (ESI) Calcd. for $[M+H]^+$: 259.0787. Found: 259.0787.



2-(phenylthio)-2-(o-tolyl)acetic acid (3h)

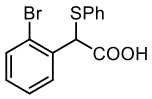
Following the general procedure A, the product was obtained as yellow gel-like solid, 36.9 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.40 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.21 – 7.14 (m, 4H), 6.86 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.30 (s, 1H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.22, 156.44, 134.04, 132.37, 129.59, 129.41, 128.89, 127.80, 123.85, 120.86, 110.86, 55.69, 49.53. **HRMS** (ESI) Calcd. for $[M+H]^+$: 275.0739. Found: 275.0736.



2-(2-fluorophenyl)-2-(phenylthio)acetic acid (3i)

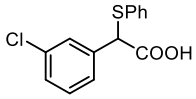
Following the general procedure A, the product was obtained as yellow gel-like solid, 30.2 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.48 (td, *J* = 7.6, 1.8 Hz, 1H), 7.35 – 7.30 (m, 2H),

7.23 – 7.14 (m, 4H), 7.04 (td, *J* = 7.6, 1.3 Hz, 1H), 6.95 (ddd, *J* = 9.7, 8.2, 1.2 Hz, 1H), 5.17 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.87, 161.15, 158.68 ,133.10, 132.78, 130.09 (d, *J* = 8.4 Hz), 130.01 (d, *J* = 2.6 Hz), 129.08, 128.46, 124.42 (d, *J* = 3.6 Hz), 122.66 (d, *J* = 13.9 Hz), 115.43 (d, *J* = 21.8 Hz), 48.39 (d, *J* = 3.2 Hz).**HRMS** (ESI) Calcd. for $[M+H]^+$: 263.0538. Found: 263.0537.



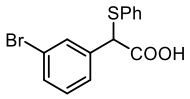
2-(2-bromophenyl)-2-(phenylthio)acetic acid (3j)

Following the general procedure A, the product was obtained as yellow gel-like solid, 40.4 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.24 – 7.18 (m, 4H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H), 5.40 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.98, 134.84, 133.03, 132.95, 132.84, 130.26, 129.80, 129.09, 128.42, 127.85, 124.49, 54.92. **HRMS** (ESI) Calcd. for $[M+H]^+$: 322.9737. Found: 322.9736.



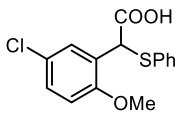
2-(3-chlorophenyl)-2-(phenylthio)acetic acid (3k)

Following the general procedure A, the product was obtained as a yellow gel-like solid, 35.6 mg, 64% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.45 (t, *J* = 1.8 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.33 – 7.23 (m, 6H), 4.82 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.78, 136.93, 134.53, 133.01, 132.62, 129.90, 129.16, 128.72, 128.69, 128.54, 126.77, 55.74. **HRMS** (ESI) Calcd. for $[M-H]^-$: 277.0092. Found: 277.0096.



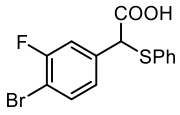
2-(3-bromophenyl)-2-(phenylthio)acetic acid (3l)

Following the general procedure A, the product was obtained as a white solid, 40.3 mg, 63% yield, mp 92.8 - 93.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 3H), 7.32 – 7.26 (m, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.27 (s, 1H), 4.82 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.09, 137.26, 133.05, 132.66, 131.64, 131.59, 130.18, 129.17, 128.57, 127.24, 122.65, 55.67. **HRMS** (ESI) Calcd. for $[M+H]^+$: 322.9735. Found: 322.9736.



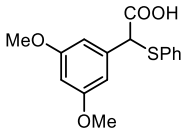
2-(5-chloro-2-methoxyphenyl)-2-(phenylthio)acetic acid (3m)

Following the general procedure A, the product was obtained as a white solid, 35.2 mg, 57% yield. mp 136.3-140.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.31 – 7.26 (m, 3H), 7.23 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.30 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.96 , 155.06 , 133.29 , 132.79 , 129.39 , 129.24 , 128.99 , 128.21 , 125.75 , 125.54 , 111.96 , 55.99 , 49.05 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 309.0347. Found: 309.0353.



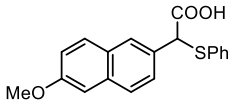
2-(4-bromo-3-fluorophenyl)-2-(phenylthio)acetic acid (3n)

Following the general procedure A, the product was obtained as a white solid, 29.4 mg, 43% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.53 – 7.46 (m, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.23 (m, 4H), 7.09 – 7.04 (m, 1H), 4.80 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.40 , 158.94 (d, *J* = 248.4 Hz), 136.72 (d, *J* = 6.8 Hz), 133.59 , 133.16 , 132.24 , 129.23 , 128.74 , 125.44 (d, *J* = 3.5 Hz), 116.76 (d, *J* = 23.7 Hz), 109.30 (d, *J* = 21.0 Hz), 55.43. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -106.44. **HRMS** (ESI) Calcd. for $[M+H]^+$: 340.9642. Found: 340.9644.



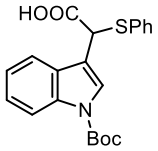
2-(3,5-dimethoxyphenyl)-2-(phenylthio)acetic acid (3o)

Following the general procedure A, the product was obtained as a white solid, 35.1 mg, 58% yield. mp 115.3-119.9 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.33 – 7.27 (m, 2H), 7.19 – 7.16 (m, 3H), 6.51 (d, *J* = 2.3 Hz, 2H), 6.32 (t, *J* = 2.3 Hz, 1H), 4.71 (s, 1H), 3.67 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.89, 160.86, 136.97, 133.37, 132.52, 129.08, 128.16, 106.54, 100.76, 56.35, 55.40. **HRMS** (ESI) Calcd. for $[M+H]^+$: 305.0842. Found: 305.0846.



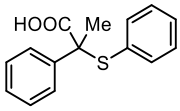
2-(6-methoxynaphthalen-2-yl)-2-(phenylthio)acetic acid (3p)

Following the general procedure A, the product was obtained as a white solid, 41.2 mg, 64% yield. mp 162.8-168.4 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.78 – 7.64 (m, 3H), 7.57 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.26 – 7.20 (m, 3H), 7.17 – 7.08 (m, 2H), 5.02 (s, 1H), 3.92 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.17 , 158.12 , 134.38 , 133.37 , 132.62 , 129.86 , 129.53 , 129.05 , 128.53 , 128.14 , 127.63 , 127.48 , 126.46 , 119.25 , 105.57 , 56.36 , 55.31 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 325.0893. Found: 325.0901.



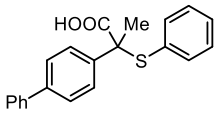
2-(1-(tert-butoxycarbonyl)-1H-indol-3-yl)-2-(phenylthio)acetic acid (3q)

Following the general procedure A, the product was obtained as a yellowish oil, 40.6 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.64 (s, 1H), 7.46 – 7.40 (m, 2H), 7.38 – 7.27 (m, 5H), 5.12 (s, 1H), 1.65 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.96 , 149.34 , 135.46 , 133.26 , 133.14 , 129.03 , 128.48 , 128.43 , 125.42 , 124.90 , 122.84 , 119.40 , 115.39 , 113.75 , 84.06 , 47.68 , 28.14 . **HRMS** (ESI) Calcd. for $[M-H]^-$: 382.1119. Found: 382.1119.



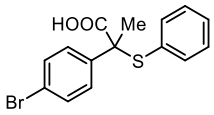
2-phenyl-2-(phenylthio)propanoic acid (3r)

Following the general procedure A, the product was obtained as a white solid, 31.2 mg, 62% yield. mp 96.4-98.9 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.39 -7.27 (m, 7H), 7.25 – 7.20 (m, 1H), 1.82 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.40 , 139.85 , 136.69 , 130.86 , 129.47 , 128.69 , 128.36 , 127.92 , 127.10 , 59.57 , 25.20 . **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 276.1053. Found: 276.1055.



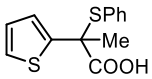
2-([1,1'-biphenyl]-4-yl)-2-(phenylthio)propanoic acid (3s)

Following the general procedure A, the product was obtained as a white solid, 52.9 mg, 79% yield. mp 138.4-142.3 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.56 – 7.46 (m, 6H), 7.39 – 7.21 (m, 6H), 7.19 – 7.11 (m, 2H), 1.77 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.57 , 140.68 , 140.28 , 138.80 , 136.75 , 130.91 , 129.48 , 128.78 , 128.69 , 127.62 , 127.48 , 127.04 , 126.95 , 59.21 , 25.00 . **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 352.1366. Found: 352.1373.



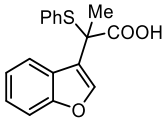
2-(4-bromophenyl)-2-(phenylthio)propanoic acid (3t)

Following the general procedure A, the product was obtained as a white solid, 38.3 mg, 57% yield. mp 111.7-114.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.41 – 7.31 (m, 4H), 7.27 (ddt, *J* = 10.0, 7.3, 1.6 Hz, 3H), 7.20 – 7.14 (m, 2H), 1.71 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.09 , 139.00 , 136.74 , 131.37 , 130.55 , 129.64 , 129.07 , 128.76 , 122.05 , 58.87 , 24.89 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 336.9892. Found:336.9889.



2-(phenylthio)-2-(thiophen-2-yl)propanoic acid (3u)

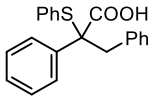
Following the general procedure A, the product was obtained as a white solid, 30.7 mg, 58% yield, mp 68.5 -69.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.32 – 7.26 (m, 3H), 7.14 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.7 Hz, 1H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.91, 143.40, 136.69, 130.90, 129.81, 128.74, 126.95, 126.55, 126.12, 56.04, 25.72. **HRMS** (ESI) Calcd. for $[M-H]^-$: 263.0206. Found: 263.0213.



2-(benzofuran-3-yl)-2-(phenylthio)propanoic acid (3v)

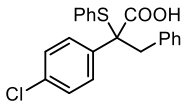
Following the general procedure A, the product was obtained as a white solid, 30.6 mg, 51% yield, mp 131.5 - 133.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 8.5 Hz, 2H), 7.38 – 7.29 (m, 4H),

7.22 (dtd, *J* = 8.4, 4.1, 2.1 Hz, 3H), 6.64 (d, *J* = 0.9 Hz, 1H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.74, 154.75, 154.11, 137.13, 130.00, 129.87, 128.69, 127.80, 124.71, 122.95, 121.17, 111.31, 106.15, 55.09, 23.03. **HRMS** (ESI) Calcd. for $[M+H]^+$: 299.0736. Found: 299.0737.



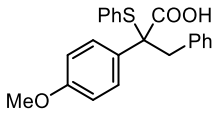
2,3-diphenyl-2-(phenylthio)propanoic acid (3w)

Following the general procedure A, the product was obtained as a oily solid, 42.1 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.26 – 7.15 (m, 6H), 7.14 – 7.00 (m, 5H), 6.83 (dt, *J* = 6.8, 1.5 Hz, 2H), 3.40 (dd, *J* = 93.5, 13.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.41, 137.97, 136.21, 135.65, 130.92, 130.90, 129.37, 128.72, 128.51, 127.85, 127.66, 127.62, 126.76, 65.49, 44.50. **HRMS** (EI) Calcd. for $[M-H]^-$: 333.0955. Found: 333.0962.



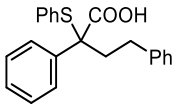
2-(4-chlorophenyl)-3-phenyl-2-(phenylthio)propanoic acid (3x)

Following the general procedure A, the product was obtained as a oily solid, 44.2 mg, 60% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.31 – 7.23 (m, 2H), 7.23 – 6.98 (m, 10H), 6.84 – 6.76 (m, 2H), 3.36 (dd, *J* = 92.5, 13.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.28 , 136.48 , 136.12 , 135.27 , 133.51 , 130.83 , 130.63 , 130.17 , 129.58 , 128.82 , 127.89 , 127.80 , 126.96 , 64.87 , 44.67 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 369.0711. Found: 369.0708.



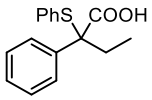
2-(4-methoxyphenyl)-3-phenyl-2-(phenylthio)propanoic acid (3y)

Following the general procedure A, the product was obtained as a oily solid, 44.8 mg, 62% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.10 (m, 8H), 6.97 – 6.86 (m, 2H), 6.84 – 6.75 (m, 2H), 3.81 (s, 3H), 3.46 (dd, *J* = 69.9, 13.5 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.88 , 158.78 , 136.13 , 135.78 , 131.07 , 130.93 , 129.97 , 129.78 , 129.29 , 128.69 , 127.61 , 126.68 , 113.14 , 64.91 , 55.26 , 44.50 . **HRMS** (ESI) Calcd. for $[M+Na]^+$: 387.1025. Found: 387.1027.



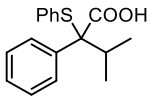
2,4-diphenyl-2-(phenylthio)butanoic acid (3z)

Following the general procedure A, the product was obtained as a oily solid, 51.9 mg, 75% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.14 (m, 8H), 7.13 – 7.00 (m, 5H), 2.67 (dtd, *J* = 50.4, 13.1, 4.7 Hz, 2H), 2.29 (dddd, *J* = 33.5, 13.9, 12.1, 4.7 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.66 , 141.31 , 139.04 , 136.48 , 130.30 , 129.47 , 128.67 , 128.40 , 128.37 , 128.31 , 127.82 , 127.52 , 126.00 , 64.53 , 38.12 , 31.29 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 349.1257. Found: 349.1259.



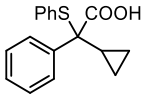
3-methyl-2-phenyl-2-(phenylthio)butanoic acid (3aa)

Following the general procedure A, the product was obtained as a yellow gel-like solid, 34.8 mg, 64% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.26 (d, *J* = 5.8 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.18 – 7.07 (m, 4H), 2.16 – 1.91 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.13, 139.04, 136.59, 130.43, 129.34, 128.58, 128.14, 127.62, 127.59, 65.55, 29.12, 9.27. **HRMS** (ESI) Calcd. for $[M-H]^-$: 271.0798. Found: 271.0801.



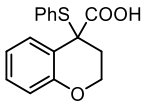
3-methyl-2-phenyl-2-(phenylthio)butanoic acid (3ab)

Following the general procedure A, the product was obtained as a white solid, mp 130.1-131.2 °C, 33.2 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.35 (d, *J* = 1.2 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.28 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.23 – 7.17 (m, 2H), 2.60 (p, *J* = 6.7 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.90, 135.99, 135.10, 131.26, 129.74, 129.25, 128.61, 127.42, 127.23, 70.22, 33.74, 19.36, 18.01. **HRMS** (ESI) Calcd. for $[M-H]^-$: 285.0955. Found: 285.0958.



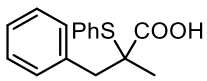
2-cyclopropyl-2-phenyl-2-(phenylthio)acetic acid (3ac)

Following the general procedure A, the product was obtained as a yellow gel-like solid, 45.1 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 3H), 7.21 – 7.11 (m, 3H), 1.45 (ddd, *J* = 14.0, 8.4, 5.5 Hz, 1H), 0.51 (qq, *J* = 8.8, 4.4 Hz, 2H), 0.31 (dq, *J* = 10.5, 5.3, 4.8 Hz, 1H), 0.19 (dq, *J* = 8.6, 4.6, 4.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.20, 136.67, 136.48, 130.92, 129.31, 129.06, 128.56, 127.83, 127.70, 66.06, 17.87, 4.25, 2.33. **HRMS** (ESI) Calcd. for $[M-H]^-$: 283.0798. Found: 283.0803.



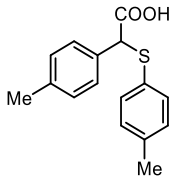
4-(phenylthio)chromane-4-carboxylic acid (3ad)

Following the general procedure A, the product was obtained as a white solid, mp 130.2 -131.4 °C, 24.3 mg, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.11 (m, 3H), 6.91 – 6.84 (m, 1H), 6.76 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.32 (ddd, *J* = 11.4, 6.5, 3.2 Hz, 1H), 4.02 (ddd, *J* = 11.5, 8.9, 2.5 Hz, 1H), 2.47 (ddd, *J* = 14.4, 6.5, 2.5 Hz, 1H), 2.12 (ddd, *J* = 14.4, 8.9, 3.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.23, 154.57, 136.66, 130.83, 130.49, 129.91, 129.84, 129.00, 120.52, 119.27, 117.37, 63.48, 53.80, 31.74. **HRMS** (ESI) Calcd. for $[M+Na]^+$: 309.0556. Found: 309.0556.



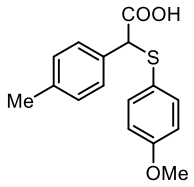
2-methyl-3-phenyl-2-(phenylthio)propanoic acid (3ae)

Following the slightly modified procedure A (reaction was conducted at 0 °C in 2 mL DMF, reaction time: 48 h) , the product was obtained as a white solid, 26.5 mg, 49% yield. mp 101.5-105.3 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 6H), 7.26 – 7.14 (m, 4H), 6.50 (s, 1H), 2.21 – 2.00 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.09 , 139.03 , 136.59 , 130.43 , 129.35 , 128.58 , 128.14 , 127.63 , 127.59 , 65.55 , 29.14 , 9.27 . **HRMS** (ESI) Calcd. for $[M-H]^-$: 271.0798. Found: 271.0799.



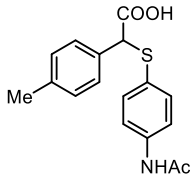
2-(p-tolyl)-2-(p-tolylthio)acetic acid (4a)

Following the general procedure A, the product was obtained as a white solid, 40.6 mg, 75% yield. mp 124.7-128.8 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.35 – 7.26 (m, 4H), 7.17 – 7.11 (m, 2H), 7.10 – 7.03 (m, 2H), 4.79 (s, 1H), 2.34 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.40 , 138.44 , 138.36 , 133.12 , 132.03 , 129.83 , 129.74 , 129.41 , 128.38 , 56.35 , 21.16 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 273.0944. Found: 273.0951.



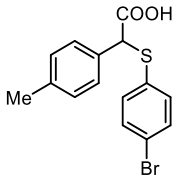
2-((4-methoxyphenyl)thio)-2-(p-tolyl)acetic acid (4b)

Following the general procedure A, the product was obtained as a white solid, 29.7 mg, 55% yield. mp 136.9-141.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.83 – 6.75 (m, 2H), 4.71 (s, 1H), 3.78 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.34 , 160.22 , 138.27 , 136.03 , 132.12 , 129.35 , 128.43 , 123.53 , 114.58 , 57.04 , 55.28 , 21.15 . **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 306.1158. Found: 306.1165.



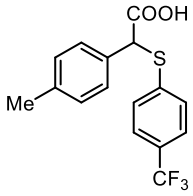
2-((4-acetamidophenyl)thio)-2-(p-tolyl)acetic acid (4c)

Following the general procedure A, the product was obtained as a yellowish solid, 31.3 mg, 50% yield. mp 208.9-220.4 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 9.98 (s, 1H), 7.51 – 7.45 (m, 2H), 7.32 – 7.25 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.01 (s, 1H), 2.26 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.32 , 168.37 , 138.92 , 137.23 , 133.43 , 132.57 , 129.00 , 128.26 , 126.97 , 119.29 , 55.40, 24.01 , 20.69 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 316.1002. Found: 316.1009.



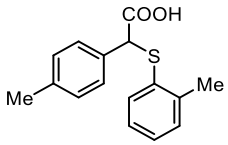
2-((4-bromophenyl)thio)-2-(p-tolyl)acetic acid (4d)

Following the general procedure A, the product was obtained as a white solid, 41.5 mg, 62% yield. mp 118.5-122.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.45 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 4.83 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.00 , 138.68 , 134.09 , 132.49 , 132.14 , 131.49 , 129.55 , 128.36 , 122.50 , 55.80 , 21.17 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 336.9892. Found: 336.9890.



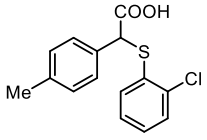
2-(p-tolyl)-2-((4-(trifluoromethyl)phenyl)thio)acetic acid (4e)

Following the general procedure A, the product was obtained as a white solid, 43.1 mg, 66% yield. mp 109.1-119.8 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.54 – 7.46 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.21 – 7.12 (m, 2H), 4.97 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.05, 139.02 (d, *J* = 1.2 Hz), 138.96, 131.10, 130.50, 129.69, 128.32, 125.84 (q, *J* = 3.8 Hz), 54.74, 21.15. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -63.14. **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 344.0927. Found: 344.0931.



2-(p-tolyl)-2-(o-tolylthio)acetic acid (4f)

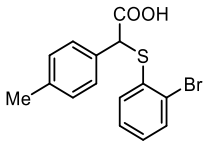
Following the general procedure A, the product was obtained as a white solid, 38.7 mg, 71% yield. mp 91.3-93.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.37 – 7.34 (m, 3H), 7.21 – 7.13 (m, 4H), 7.10 (ddd, *J* = 8.7, 5.1, 2.5 Hz, 1H), 4.80 (s, 1H), 2.39 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.62 , 140.17 , 138.44 , 132.90 , 132.59 , 131.93 , 130.42 , 129.43 , 128.35 , 128.06 , 126.60 , 55.04 , 21.15 , 20.54 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 273.0944. Found: 273.0948.



2-((2-chlorophenyl)thio)-2-(p-tolyl)acetic acid (4g)

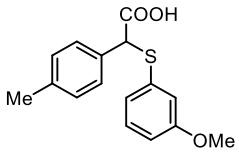
Following the general procedure A, the product was obtained as a white solid, 49.7 mg, 85% yield . mp 107.4-109.9 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.42-7.35 (m, 4H), 7.23 – 7.10 (m, 4H), 5.03 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.08 , 138.65 , 136.13 , 132.88 , 132.76 , 131.21 , 129.92 , 129.53 , 128.87 , 128.38 , 127.28 , 53.87 , 21.15 **HRMS** (ESI) Calcd. for $[M+H]^+$:

293.0398. Found: 293.0395.



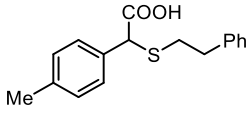
2-((2-bromophenyl)thio)-2-(p-tolyl)acetic acid (4h)

Following the general procedure A, the product was obtained as a white solid, 55.1 mg, 82% yield. mp 91.9-93.8 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.58 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.35 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H), 5.02 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.89 , 138.70 , 134.92 , 133.26 , 132.50 , 131.11 , 129.56 , 128.86 , 128.42 , 127.94 , 126.47 , 54.22 , 21.16 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 336.9892. Found: 336.9895.



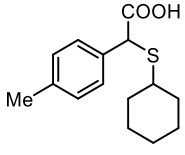
2-((3-methoxyphenyl)thio)-2-(p-tolyl)acetic acid (4i)

Following the general procedure A, the product was obtained as a white solid, 44.3 mg, 77% yield. mp 96.1-99.4 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.12 (m, 3H), 6.98 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.90 (t, *J* = 2.0 Hz, 1H), 6.80 (ddd, *J* = 8.3, 2.5, 1.0 Hz, 1H), 4.89 (s, 1H), 3.72 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.53 , 159.67 , 138.48 , 134.80 , 131.88 , 129.83 , 129.47 , 128.37 , 124.15 , 116.87 , 114.19 , 55.69 , 55.19 , 21.12 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 289.0893. Found: 289.0897.



2-(phenethylthio)-2-(p-tolyl)acetic acid (4j)

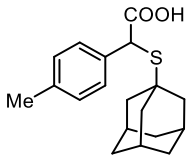
Following the general procedure A, the product was obtained as a yellowish oil, 23.1 mg, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.04 (m, 4H), 4.43 (s, 1H), 2.81 – 2.64 (m, 4H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.72 , 139.95 , 138.29 , 132.18 , 129.42 , 128.50 , 128.48 , 128.39 , 126.44 , 51.70 , 35.68 , 33.45 , 21.13 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 287.1100. Found: 287.1107.



2-(cyclohexylthio)-2-(p-tolyl)acetic acid (4k)

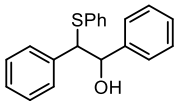
Following the general procedure A, the product was obtained as a white solid, 22.8 mg, 43% yield. mp 62.9-64.6 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 1H), 2.74 (tt, *J* = 10.4, 3.7 Hz, 1H), 2.33 (s, 3H), 2.00 – 1.91 (m, 2H), 1.79 – 1.68 (m, 2H), 1.63 – 1.54

(m, 1H), 1.40 – 1.19 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.21 , 138.10 , 132.86 , 129.38 , 128.29 , 50.17 , 44.25 , 33.19 , 33.09 , 25.79 , 25.76 , 25.68 , 21.12 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 265.1257. Found: 265.1262.



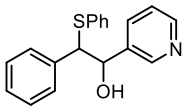
2-((adamantan-1-yl)thio)-2-(p-tolyl)acetic acid (4l)

Following the general procedure A, the product was obtained as a white solid, 21.6 mg, 34% yield. mp 173.3-175.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.37 – 7.31 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.62 (s, 1H), 2.32 (s, 3H), 2.04 (q, *J* = 3.2 Hz, 3H), 1.93 – 1.85 (m, 6H), 1.73 – 1.60 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.34, 137.78, 134.01, 129.36, 128.14, 47.28, 46.77, 43.28, 36.05, 29.66, 21.07. **HRMS** (ESI) Calcd. for $[M+H]^+$: 317.1570. Found: 317.1576.



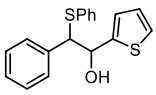
1,2-diphenyl-2-(phenylthio)ethan-1-ol (6a)

Following the general procedure B, the product was obtained as a colorless oil, 47.0 mg, 78% yield; *syn*: *anti* = 44: 56; **^{1}H NMR of (*syn*)- and (*anti*)-6a** (300 MHz, $CDCl_3$) δ 7.23 – 7.01 (m, 26H), 6.97 – 6.89 (m, 2H), 4.95 (d, *J* = 5.8 Hz, 1H, *anti*), 4.85 (d, *J* = 8.6 Hz, 1H, *syn*), 4.36 (d, *J* = 5.8 Hz, 1H, *anti*), 4.27 (d, *J* = 8.6 Hz, 1H, *syn*), 3.24 (s, 1H, *syn*), 2.52 (s, 1H, *anti*). **^{13}C NMR of (*syn*)- and (*anti*)-6a** (75 MHz, $CDCl_3$) δ 140.47, 140.31, 139.13, 137.50, 134.27, 134.06, 132.32, 132.21, 129.09, 128.83, 128.50, 128.15, 128.07, 127.96, 127.93, 127.80, 127.73, 127.60, 127.38, 127.30, 127.21, 126.83, 126.62, 76.80 , 75.77, 63.87, 61.34. **HRMS** (ESI) Calcd. for $[M+H]^+$: 307.1151. Found: 307.1161.



2-phenyl-2-(phenylthio)-1-(pyridin-3-yl)ethan-1-ol (6b)

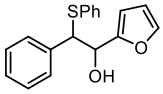
Following the general procedure B, the product was obtained as a sticky oil, 46.7 mg, 76% yield; *syn*: *anti* = 44: 56; **^{1}H NMR of (*syn*)- and (*anti*)-6b** (300 MHz, $CDCl_3$) δ 8.23 – 8.10 (m, 4H), 7.41 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.33 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.21 – 7.12 (m, 9H), 7.12 – 7.02 (m, 8H), 7.02 – 6.89 (m, 4H), 4.96 (d, *J* = 5.8 Hz, 1H), 4.87 (d, *J* = 8.0 Hz, 1H), 4.29 (d, *J* = 5.8 Hz, 2H), 4.25 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR of (*syn*)- and (*anti*)-6b** (75 MHz, $CDCl_3$) δ 148.38, 148.32, 148.06, 147.90, 138.47, 137.23, 136.84, 136.71, 134.72, 134.61, 134.06, 133.82, 132.23, 132.09, 129.05, 128.88, 128.82, 128.50, 128.21, 127.70, 127.50, 127.38, 127.35, 122.95, 122.90, 74.46, 73.52, 63.14, 61.14. **HRMS** (EI) Calcd. for $C_{19}H_{17}NOS$ $[M]^+$: 307.1019. Found: 307.1018.



2-phenyl-2-(phenylthio)-1-(thiophen-2-yl)ethan-1-ol (6c)

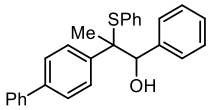
Following the general procedure B, the product was obtained as a sticky oil, 38 mg, 61% yield; *syn*: *anti*

= 53:47. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 10H), 7.26 – 7.22 (m, 5H), 7.22 – 7.17 (m, 6H), 7.16 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.95 – 6.86 (m, 2H), 6.78 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.63 (dt, *J* = 3.6, 0.9 Hz, 1H), 5.33 (d, *J* = 6.1 Hz, 1H), 5.25 (d, *J* = 8.5 Hz, 1H), 4.50 (d, *J* = 6.1 Hz, 1H), 4.38 (d, *J* = 8.5 Hz, 1H), 3.50 (s, 1H), 2.76 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.15, 143.85, 139.00, 137.66, 134.07, 133.45, 132.83, 132.35, 129.02, 128.86, 128.41, 128.32, 128.16, 127.77, 127.67, 127.42, 126.24, 126.21, 125.32, 125.26, 125.03, 124.78, 72.82, 72.38, 63.73, 61.74. **HRMS** (ESI) Calcd. for $[M+H]^+$:313.0715. Found: 313.0710.



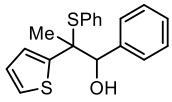
1-(furan-2-yl)-2-phenyl-2-(phenylthio)ethan-1-ol (6d)

Following the general procedure B, the product was obtained as a sticky oil, 41.6 mg, 70% yield; *syn*: *anti* = 48:52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 11H), 7.19 – 7.11 (m, 9H), 7.11 – 7.05 (m, 2H), 6.23 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.16 – 6.11 (m, 2H), 6.07 – 6.04 (m, 1H), 5.03 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.95 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.61 (d, *J* = 6.7 Hz, 1H), 4.58 (d, *J* = 8.2 Hz, 1H), 3.21 (d, *J* = 3.8 Hz, 1H), 2.48 (d, *J* = 4.7 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.09, 152.56, 141.91, 138.94, 137.90, 134.04, 133.39, 132.80, 132.34, 128.81, 128.78, 128.66, 128.37, 128.14, 128.12, 127.70, 127.58, 127.37, 127.33, 110.23, 110.10, 108.23, 108.16, 77.32, 77.00, 76.68, 70.36, 70.24, 60.35, 58.71. **HRMS** (ESI) Calcd. for $[M+H]^+$: 297.0944. Found: 297.0937.



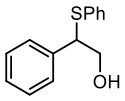
2-([1,1'-biphenyl]-4-yl)-1-phenyl-2-(phenylthio)propan-1-ol (6e)

Following the general procedure B, the product was obtained as a colorless oil, 41.4 mg, 52% yield; *syn*:*anti* = 46:54. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 5H), 7.44 (s, 5H), 7.39 – 7.29 (m, 9H), 7.29 – 7.21 (m, 6H), 7.20 – 7.14 (m, 3H), 7.14 – 7.04 (m, 8H), 7.04 – 6.95 (m, 4H), 6.88 (ddt, *J* = 13.9, 7.0, 1.5 Hz, 4H), 5.19 (s, 1H), 4.78 (s, 1H), 3.23 (s, 1H), 3.14 (s, 1H), 1.47 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.51, 140.41, 140.28, 139.83, 139.49, 139.36, 138.54, 138.50, 136.89, 136.29, 131.30, 130.90, 129.06, 128.94, 128.80, 128.75, 128.68, 128.63, 128.53, 128.34, 127.83, 127.73, 127.35, 127.33, 127.31, 127.19, 126.94, 126.83, 126.19, 126.08, 79.54, 78.66, 62.60, 60.30, 22.89, 18.78. **HRMS** (ESI) Calcd. for $[M+Na]^+$: 419.1440. Found: 419.1441.



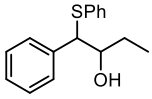
phenyl-2-(phenylthio)-2-(thiophen-2-yl)propan-1-ol (6f)

Following the general procedure B, the product was obtained as a colorless oil, 48.9 mg, 75% yield; *syn*:*anti* = 46:54. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.45 – 7.38 (m, 1H), 7.37 – 7.29 (m, 7H), 7.27 – 7.14 (m, 9H), 7.14 – 7.08 (m, 2H), 7.03 – 6.97 (m, 2H), 6.94 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.87 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.80 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.49 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.15 (s, 1H), 4.77 (s, 1H), 3.73 – 3.23 (m, 2H), 1.56 (s, 3H), 1.53 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.27, 144.28, 138.41, 138.05, 136.93, 136.48, 130.83, 130.59, 129.41, 129.11, 128.77, 128.58, 128.04, 127.93, 127.67, 127.55, 127.41, 127.28, 126.80, 126.15, 126.10, 125.96, 125.63, 124.68, 79.16, 78.97, 60.84, 59.18, 24.67, 20.61. **HRMS** (ESI) Calcd. for $[M+Na]^+$: 349.0691. Found: 349.0697.



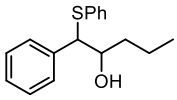
2-phenyl-2-(phenylthio)ethan-1-ol (6g)

Following the modified general procedure B, paraformaldehyde (4.0 eq., 0.8 mmol) and DMSO (4 mL) were used, the product was obtained as a colorless oil, 22.1 mg, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 6H), 7.21 – 7.14 (m, 4H), 4.24 (t, *J* = 6.9 Hz, 1H), 3.89 – 3.79 (m, 2H), 1.79 (s, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.88 , 133.68 , 132.55 , 128.92 , 128.71 , 128.05 , 127.79 , 127.56 , 65.24 , 56.07 . **HRMS** (ESI) Calcd. for $[M+H]^+$: 231.0838. Found: 231.0840.



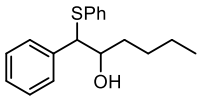
1-phenyl-1-(phenylthio)butan-2-ol (6h)

Following the general procedure B, the product was obtained as a colorless oil, 21.3 mg, 41% yield; *syn*:*anti* = 53:47; **^{1}H NMR of (*syn*)- and (*anti*)-6c** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.30 (m, 3H), 7.30 – 7.23 (m, 8H), 7.23 – 7.15 (m, 8H), 4.25 (d, *J* = 5.0 Hz, 1H, *anti*), 4.08 (d, *J* = 8.3 Hz, 1H, *syn*), 3.83 - 3.88 (m, 2H), 1.63 – 1.49 (m, 2H, *anti*), 1.45 – 1.28 (m, 3H, *syn*), 0.95 (td, *J* = 7.4, 5.9 Hz, 7H, mix). **^{13}C NMR of (*syn*)- and (*anti*)-6c** (101 MHz, $CDCl_3$) δ 140.05, 138.29, 134.46, 133.99, 132.66, 132.09, 128.99, 128.91, 128.81, 128.43, 128.20, 127.58, 127.45, 127.36, 127.28, 74.77, 74.47, 62.21, 59.89, 27.12, 27.05, 10.28, 9.97. **HRMS** (ESI) Calcd. for $[M+H]^+$: 259.1151. Found: 259.1153.



phenyl-1-(phenylthio)pentan-2-ol (6i)

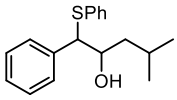
Following the modified general procedure B, the product was obtained as a colorless oil, 23.4 mg, 43% yield; *syn*:*anti* = 55:45; **^{1}H NMR of (*syn*)- and (*anti*)-6d** (400 MHz, $CDCl_3$) δ 7.34 – 7.07 (m, 22H), 4.16 (d, *J* = 4.9 Hz, 1H, *anti*), 4.00 (d, *J* = 8.1 Hz, 1H, *syn*), 3.84 (td, *J* = 7.8, 3.1 Hz, 2H), 2.03 (d, *J* = 49.7 Hz, 2H), 1.51 – 1.20 (m, 9H), 0.77 (dt, *J* = 12.9, 6.5 Hz, 7H). **^{1}H NMR of (*syn*)- and (*anti*)-6c** (101 MHz, $CDCl_3$) δ 140.03, 138.29, 134.48, 134.05, 132.60, 132.05, 129.00, 128.90, 128.81, 128.44, 128.42, 128.22, 127.56, 127.41, 127.35, 127.26, 73.31, 72.85, 62.53, 60.23, 36.28, 36.26, 19.16, 18.96, 13.93, 13.90. **HRMS** (ESI) Calcd. for $[M+H]^+$: 273.1308. Found: 273.1310.



phenyl-1-(phenylthio)hexan-2-ol (6j)

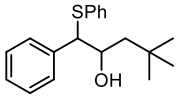
Following the general procedure B, the product was obtained as a colorless oil, 24.4 mg, 43% yield; *syn*:*anti* = 54:46; **^{1}H NMR of (*syn*)- and (*anti*)-6e** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H, mix, 7.28 – 7.22 (m, 3H), 7.21- 7.14 (m, 9H), 7.14 – 7.06 (m, 7H), 4.16 (d, *J* = 5.0 Hz, 1H, *anti*), 4.00 (d, *J* = 8.1 Hz, 1H, *syn*), 3.83 (dtt, *J* = 7.6, 4.0, 2.2 Hz, 2H), 2.62 (s, 1H, *anti*), 2.00 (s, 1H, *syn*), 1.53 – 1.05 (m, 16H), 0.76 (dt, *J* = 11.5, 7.1 Hz, 7H). **^{13}C NMR of (*syn*)- and (*anti*)-6e** (101 MHz, $CDCl_3$) δ 140.05, 138.29, 134.49, 134.04, 132.61, 132.05, 128.99, 128.90, 128.80, 128.43, 128.21, 127.56, 127.41, 127.35, 127.26,

73.52, 73.11, 62.49, 60.19, 33.87, 33.83, 28.10, 27.89, 22.57, 22.51, 13.98, 13.95. **HRMS** (ESI) Calcd. for $[M+H]^+$: 287.1464. Found: 287.1467.



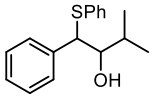
4-methyl-1-phenyl-1-(phenylthio)pentan-2-ol (6k)

Following the general procedure B, the product was obtained as a colorless oil, 20.6 mg, 36% yield; *syn*:*anti* = 52:48; **^{1}H NMR of (*syn*)- and (*anti*)-6f** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 3H), 7.21 -7.17 (m, 7H), 7.16 – 7.06 (m, 9H), 4.14 (d, *J* = 4.8 Hz, 1H, *anti*), 3.98 (d, *J* = 8.0 Hz, 1H, *syn*), 3.96 – 3.87 (m, 2H), 2.03 (s, 2H), 1.81 -1.67 (m, 2H), 1.33 – 1.01 (m, 6H), 0.77 (dt, *J* = 10.8, 6.6 Hz, 13H). **^{13}C NMR of (*syn*)- and (*anti*)-6f** (101 MHz, $CDCl_3$) δ 140.01, 138.26, 134.53, 134.11, 132.59, 131.97, 129.03, 128.89, 128.82, 128.45, 128.42, 128.23, 127.56, 127.41, 127.35, 127.23, 71.71, 71.19, 62.95, 60.61, 43.33, 43.26, 24.81, 24.78, 23.68, 23.47, 21.76, 21.36. **HRMS** (ESI) Calcd. for $[M+H]^+$: 287.1464. Found: 287.1466.



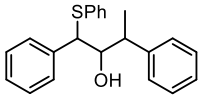
4,4-dimethyl-1-phenyl-1-(phenylthio)pentan-2-ol (6l)

Following the general procedure B, the product was obtained as a colorless oil, 22.1 mg, 37% yield; *syn*:*anti* = 64:36; **^{1}H NMR of (*syn*)- and (*anti*)-6g** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.37 (ddd, *J* = 6.8, 3.9, 1.9 Hz, 3H), 7.35 – 7.20 (m, 14H), 4.24 (d, *J* = 5.0 Hz, 1H, *syn*), 4.11 (tt, *J* = 4.3, 2.4 Hz, 3H), 2.12 (s, 2H, mix), 1.60 (dd, *J* = 14.6, 1.6 Hz, 1H), 1.46 – 1.37 (m, 2H), 0.94 (s, 9H), 0.93 (s, 9H).**^{13}C NMR of (*syn*)- and (*anti*)-6g** (101 MHz, $CDCl_3$) δ 140.07, 138.35, 134.64, 134.26, 132.45, 131.74, 129.06, 128.89, 128.81, 128.42, 128.36, 127.53, 127.35, 127.33, 127.14, 77.32, 77.00, 76.68, 71.42, 70.85, 63.55, 61.70, 47.72, 47.52, 30.34, 29.98, 29.95. **HRMS** (ESI) Calcd. for $[M+H]^+$: 301.1621. Found: 301.1624.



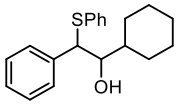
3-methyl-1-phenyl-1-(phenylthio)butan-2-ol (6m)

Following the general procedure B, the product was obtained as a colorless oil, 17.8 mg, 33% yield; *syn*:*anti* = 51:49; **^{1}H NMR of (*syn*)- and (*anti*)-6h** (300 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.28 (m, 4H), 7.28 – 7.19 (m, 14H), 7.18 – 7.10 (m, 3H), 4.32 (d, *J* = 5.5 Hz, 1H, *anti*), 4.16 (d, *J* = 8.8 Hz, 1H, *syn*), 3.76 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.61 (dd, *J* = 6.7, 5.5 Hz, 1H), 1.89 – 1.72 (m, *J* = 6.7 Hz, 1H), 1.62 (pd, *J* = 6.8, 3.5 Hz, 1H), 1.02 – 0.84 (m, 14H). **^{13}C NMR of (*syn*)- and (*anti*)-6h** (75 MHz, $CDCl_3$) δ 140.26, 138.38, 134.12, 133.81, 132.92, 132.49, 129.14, 128.91, 128.77, 128.46, 128.42, 128.06, 127.57, 127.50, 127.45, 127.29, 60.70, 57.65, 30.51, 29.76, 20.56, 19.53, 17.52, 14.82. **HRMS** (ESI) Calcd. for $[M+H]^+$: 273.1308. Found: 273.1309.



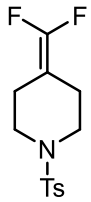
1,3-diphenyl-1-(phenylthio)butan-2-ol (6n)

Following the general procedure B, the product was obtained as a colorless oil, 19.2 mg, 29% yield; *syn*:*anti* = 53:47; **^{1}H NMR of (*syn*)- and (*anti*)-6i** (400 MHz, $CDCl_3$) δ 7.24 – 7.05 (m, 26H), 6.94 – 6.89 (m, 2H), 4.08 – 4.00 (m, 2H), 3.99 – 3.93 (m, 2H), 2.91 – 2.80 (m, 1H, *syn*), 2.72 – 2.63 (m, 1H, *anti*), 2.47 (s, 1H), 2.34 (s, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR of (*syn*)- and (*anti*)-6i** (101 MHz, $CDCl_3$) δ 144.69, 144.10, 140.66, 137.33, 134.08, 134.01, 132.52, 132.09, 129.56, 128.93, 128.71, 128.58, 128.50, 128.44, 128.23, 128.02, 127.80, 127.71, 127.68, 127.37, 127.23, 126.58, 126.49, 78.81, 76.11, 59.53, 56.42, 42.91, 42.22, 18.48, 14.94. **HRMS** (ESI) Calcd. for $[M+H]^+$: 335.1464. Found: 335.1463.



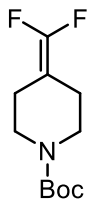
cyclohexyl-2-phenyl-2-(phenylthio)ethan-1-ol (6o)

Following the general procedure B, the product was obtained as a colorless oil, 16.5 mg, 26% yield; *syn*:*anti* = 54:46; **^{1}H NMR of (*syn*)- and (*anti*)-6i** (300 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 (d, *J* = 2.2 Hz, 2H), 7.26 – 7.15 (m, 14H), 4.36 (d, *J* = 5.4 Hz, 1H, *anti*), 4.26 (d, *J* = 8.0 Hz, 1H, *syn*), 3.72 – 3.63 (m, 2H), 2.65 (s, 1H), 2.17 (s, 1H), 1.96 – 1.51 (m, 14H), 1.50 – 1.29 (m, 4H), 1.23 – 0.92 (m, 11H). **^{13}C NMR of (*syn*)- and (*anti*)-6i** (75 MHz, $CDCl_3$) δ 140.40, 138.40, 134.28, 134.14, 132.50, 132.34, 129.13, 128.90, 128.75, 128.48, 128.43, 128.09, 127.53, 127.37, 127.29, 127.27, 77.75, 76.85, 39.94, 39.73, 30.56, 29.66, 27.74, 26.35, 26.31, 25.98, 25.91, 25.82, 25.76. **HRMS** (ESI) Calcd. for $[M+H]^+$: 313.1621. Found: 313.1624.



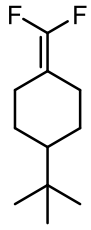
4-(difluoromethylene)-1-tosylpiperidine (9a)

Following the general procedure C, the product was obtained as a white solid, 42 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 5.7 Hz, 4H), 2.42 (s, 3H), 2.30 – 2.23 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.23 (t, J = 283.0 Hz), 143.67 , 133.14 , 129.67 , 127.56 , 83.64 (t, J = 20.7 Hz), 46.20 (t, J = 2.1 Hz), 23.62 (t, J = 1.9 Hz), 21.47 .**^{19}F NMR** (377 MHz, $CDCl_3$) δ -96.51.**HRMS** (ESI) Calcd. for $C_{13}H_{16}F_2NO_2S$ $[M+H]^+$: 288.0864, found: 288.0866.



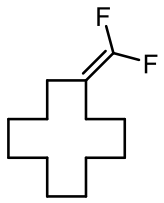
tert-butyl 4-(difluoromethylene)piperidine-1-carboxylate (9b)

Following the general procedure C, the product was obtained as a colorless oil, 23.7 mg, 51% yield.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.44 – 3.35 (m, 4H), 2.16 – 2.12 (m, 4H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.60 , 151.41 (t, *J* = 281.9 Hz), 84.97 (t, *J* = 20.2 Hz), 79.76 , 43.83 , 28.39 , 23.95 . **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.37. **HRMS** (ESI) calcd for $C_{11}H_{18}F_2NO_2$ $[M+H]^+$: 234.1300, found: 234.1299.



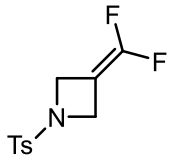
1-(tert-butyl)-4-(difluoromethylene)cyclohexane (9c)

Following the general procedure C, the product was obtained as a colorless oil, 14.8 mg, 39% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.54 – 2.45 (m, 2H), 1.88 – 1.80 (m, 2H), 1.77 – 1.64 (m, 2H), 1.10 – 0.94 (m, 3H), 0.85 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.42 (t, *J* = 280.0 Hz), 88.00 (t, *J* = 18.6 Hz), 47.81 , 32.47 , 27.51 , 27.22 (t, *J* = 1.9 Hz), 24.61 (t, *J* = 1.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.99. **HRMS** (EI) calcd for $C_{13}H_{22}F_2$ $[M]^+$: 188.1377, found: 188.1367.



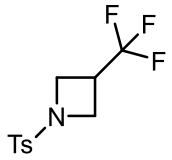
(difluoromethylene)cyclododecane (9d)

Following the general procedure C, the product was obtained as a colorless oil, 17.1 mg, 40% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.02 (tt, *J* = 7.0, 2.4 Hz, 4H), 1.48 (p, *J* = 6.7, 6.3 Hz, 4H), 1.38 – 1.31 (m, 14H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.64, (t, *J* = 281.25 Hz), 87.05 (t, *J* = 16.0 Hz), 25.12 (t, *J* = 1.5 Hz), 24.34 , 24.17 (t, *J* = 1.5Hz), 23.38 , 23.05 .**^{19}F NMR** (282 MHz, $CDCl_3$) δ -94.71. **HRMS** (EI) calcd for $C_{13}H_{22}F_2$ $[M]^+$: 216.1684, found: 216.1688.



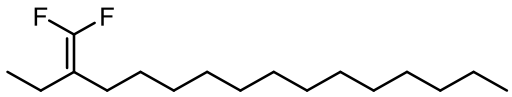
3-(difluoromethylene)-1-tosylazetidine (9e)

Following the general procedure C, the product was obtained as a white solid,19.8 mg, 38% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 2H), 7.43 – 7.34 (m, 2H), 4.38 (t, *J* = 3.8 Hz, 4H), 2.46 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.19 (t, *J* = 284.6 Hz), 144.69 , 131.34 , 130.04 , 128.41 , 78.24 (t, *J* = 30.1 Hz), 53.06 (t, *J* = 2.8 Hz), 21.66. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -91.60. **HRMS** (ESI) calcd for $[M+H]^+$: 260.0551, found: 260.0558.



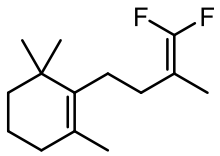
tosyl-3-(trifluoromethyl)azetidine (9e')

Following the general procedure C, the product was obtained as a white solid (by product), 14.8 mg, 21% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.97 (t, *J* = 8.8 Hz, 2H), 3.81 (dd, *J* = 8.8, 6.4 Hz, 2H), 3.10 (ht, *J* = 8.5, 6.4 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.60 , 131.04 , 129.92 , 128.27 , 125.26 (q, *J* = 275.5 Hz), 49.61 (q, *J* = 3.8 Hz), 31.10 (q, *J* = 32.9 Hz), 21.59 .**^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.79. **HRMS** (ESI) calcd for $[M+H]^+$: 280.0614, found: 280.0617.



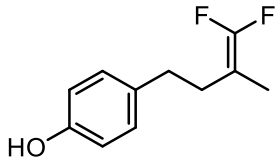
3-(difluoromethylene)hexadecane (9f)

Following the general procedure C, the product was obtained as a colorless oil, 33.9 mg, 62% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.03 – 1.92 (m, 4H), 1.43 – 1.33 (m, 2H), 1.26 (s, 20H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.92 – 0.84 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.95 (t, J = 282.5 Hz), 90.33 (t, J = 16.4 Hz), 31.95 , 29.71 , 29.68 , 29.62 , 29.44 , 29.39 , 29.20 , 27.45 (t, J = 2.6 Hz), 26.01 – 25.19 (m), 22.71 , 19.28 (t, *J* = 2.0 Hz), 14.12 , 12.43 (t, *J* = 2.7 Hz).**^{19}F NMR** (282 MHz, $CDCl_3$) δ -97.45 (d, *J* = 59.2 Hz, 1F), δ -97.69 (d, *J* = 59.2 Hz, 1F), **HRMS** (EI) calcd for $C_{17}H_{32}F_2$ $[M]^+$: 274.2467, found: 274.2461.



2-(4,4-difluoro-3-methylbut-3-en-1-yl)-1,3,3-trimethylcyclohex-1-ene (9g)

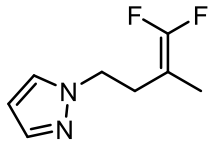
Following the general procedure C, the product was obtained as a colorless oil, 20.0 mg, 44% yield.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.09 – 2.03 (m, 2H), 2.03 – 1.95 (m, 2H), 1.95 – 1.88 (m, 2H), 1.61 (q, *J* = 3.4 Hz, 6H), 1.59 – 1.54 (m, 2H), 1.45 – 1.39 (m, 2H), 1.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.72 (dd, *J* = 282.8, 280.7 Hz), 136.31 , 127.72 , 85.25 (dd, *J* = 20.4, 16.9 Hz), 39.78 , 34.94 , 32.75 , 28.99 (d, *J* = 2.1 Hz), 28.52 , 26.76 (dd, *J* = 2.6, 2.3 Hz), 22.35 , 19.65 , 19.50 , 14.06 , 11.92 (t, *J* = 2.1 Hz).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -97.41 (d, *J* = 59.5 Hz, 1F), -98.25 (d, *J* = 59.3 Hz, 1F). **HRMS** (EI) calcd for $C_{14}H_{22}F_2$ $[M]^+$: 228.1684, found: 228.1683.



4-(4,4-difluoro-3-methylbut-3-en-1-yl)phenol (9h)

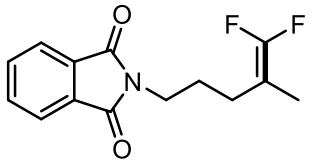
Following the general procedure C, the product was obtained as a colorless oil, 20.6 mg, 52% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.11 – 6.99 (m, 2H), 6.82 – 6.70 (m, 2H), 4.78 (s, 1H), 2.63 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.23 (ddt, *J* = 7.5, 6.5, 2.1 Hz, 2H), 1.57 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ

153.69, 152.96 (t, *J* = 281.2 Hz), 150.16, 133.50, 129.41, 115.18, 84.12 (dd, *J* = 19.5, 18.2 Hz) 32.67 (t, *J* = 2.0 Hz) , 30.38 (d, *J* = 2.4 Hz), 11.95 (t, *J* = 2.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.81 (d, *J* = 57.6 Hz, 1F), -97.10 (d, *J* = 57.6 Hz, 1F).



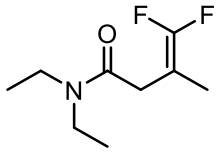
1-(4,4-difluoro-3-methylbut-3-en-1-yl)-1H-pyrazole (9i)

Following the general procedure C, the product was obtained as a colorless oil, 15.5 mg, 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 1H), 7.35 (dd, *J* = 2.3, 0.6 Hz, 1H), 6.24 (t, *J* = 2.1 Hz, 1H), 4.20 (t, *J* = 7.1 Hz, 2H), 2.52 (tt, *J* = 7.1, 2.1 Hz, 2H), 1.51 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.44 (t, *J* = 284.8 Hz), 139.37, 128.90, 105.52, 81.77 (t, *J* = 19.7 Hz), 49.83 (t, *J* = 3.2 Hz), 29.72 (d, *J* = 2.7 Hz), 11.90 (t, *J* = 1.9 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -94.76 (d, *J* = 53.2 Hz), -95.25 (d, *J* = 53.2 Hz). **HRMS** (EI) Calcd. for $C_8H_9F_2N_2$ $[M]^+$: 171.0728. Found: 171.0731.



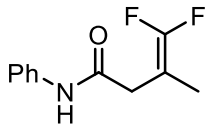
2-(5,5-difluoro-4-methylpent-4-en-1-yl)isoindoline-1,3-dione (9j)

Following the general procedure C, the product was obtained as a white solid, 44.2 mg, 83% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.75 – 7.65 (m, 2H), 3.68 – 3.60 (m, 2H), 2.03 (tt, *J* = 8.1, 2.2 Hz, 2H), 1.77 (tt, *J* = 9.3, 6.5 Hz, 2H), 1.56 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.24 , 152.74 (t, *J* = 282.1 Hz), 133.88 , 132.01 , 123.15 , 83.61 (t, *J* = 19.0 Hz), 37.39 , 25.86 (t, *J* = 2.6 Hz), 25.57 (t, *J* = 1.8 Hz), 11.54 (t, *J* = 1.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -96.39 (d, *J* = 57.2 Hz, 1F) , -96.41 (d, *J* = 57.2 Hz, 1F) .**HRMS** (EI) calcd for $C_{14}H_{13}NO_2F_2$ $[M]^+$: 265.0909, found: 265.0905.



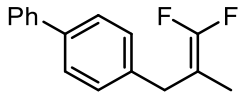
N,N-diethyl-4,4-difluoro-3-methylbut-3-enamide (9k)

Following the general procedure C, the product was obtained as a colorless oil, 16.1 mg, 42% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.32 (m, 3.39-3.25, 4H), 2.99 (t, *J* = 2.0 Hz, 2H), 1.64 (t, *J* = 3.2 Hz, 3H), 1.13 (dt, *J* = 19.9, 7.1 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.41 (t, *J* = 3.0 Hz), 153.27 (t, *J* = 280.7 Hz), 81.33 (dd, *J* = 22.1, 19.0 Hz), 41.98 , 40.27 , 33.17 (d, *J* = 2.8 Hz), 14.15 , 12.93 , 12.31 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -95.76 (d, *J* = 54.5 Hz, 1F), -96.06 (d, *J* = 54.5 Hz, 1F). **HRMS** (ESI) calcd for $C_9H_{16}F_2NO$ $[M+H]^+$: 192.1194, found: 192.1196.



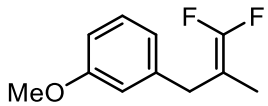
4,4-difluoro-3-methyl-N-phenylbut-3-enamide (9l)

Following the general procedure C, the product was obtained as a white solid, 18.3 mg, 43% yield.; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 3H), 7.36 – 7.27 (m, 2H), 7.17 – 7.08 (m, 1H), 3.05 (t, *J* = 2.0 Hz, 2H), 1.71 (t, *J* = 3.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.54 (t, *J* = 3.0 Hz), 154.07 (t, *J* = 282.7 Hz), 137.43 , 128.98 , 124.61 , 120.02 , 80.79 (t, *J* = 20.6 Hz), 37.22 , 12.43 .**^{19}F NMR** (282 MHz, $CDCl_3$) δ -93.82. **HRMS** (ESI) calcd for $C_{11}H_{12}F_2NO$ $[M+H]^+$: 212.0881, found: 212.0885.



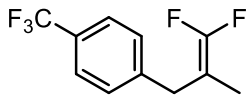
4-(3,3-difluoro-2-methylallyl)-1,1'-biphenyl (9m)

Following the general procedure C, the product was obtained as a colorless oil, 31.8 mg, 65% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 4H), 7.50 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.30 – 7.24 (m, 2H), 3.35 (t, *J* = 2.1 Hz, 2H), 1.56 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.1 (dd, *J* = 280.5 Hz, 279.8 Hz), 140.86 , 139.43 , 137.62 (t, *J* = 2.7 Hz), 128.96 , 128.73 , 127.21 , 127.15 , 126.99 , 84.61 (t, *J* = 19.0 Hz), 34.14 (q, *J* = 1.6 Hz), 11.84 (t, *J* = 1.6 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -96.97 (d, *J* = 56.2 Hz, 1F), -97.23 (d, *J* = 56.2 Hz, 1F). **HRMS** (EI) calcd for $C_{16}H_{14}F_2$ $[M]^+$: 244.1058, found: 244.1054.



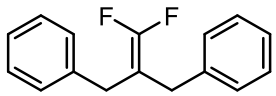
1-(3,3-difluoro-2-methylallyl)-3-methoxybenzene (9n)

Following the general procedure C, the product was obtained as a colorless oil, 21.8 mg, 55% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.3, 7.4 Hz, 1H), 6.82 – 6.71 (m, 3H), 3.81 (s, 3H), 3.27 (t, *J* = 2.1 Hz, 2H), 1.51 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.72 , 153.27 (dd, 280.5 Hz, 279.8 Hz), 140.15 (t, *J* = 2.6 Hz), 129.42 , 120.96 , 114.36 , 111.57 , 84.57 (t, *J* = 19.0 Hz), 55.13 , 34.50 (t, *J* = 2.0 Hz), 11.78 (t, *J* = 1.7 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -97.11 (d, *J* = 56.4 Hz, 1F), -97.36 (d, *J* = 56.4 Hz, 1F).**HRMS** (EI) calcd for $C_{11}H_{12}OF_2$ $[M]^+$: 198.0851, found: 198.0852.



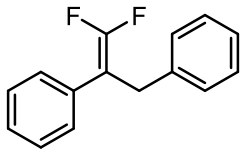
1-(3,3-difluoro-2-methylallyl)-4-(trifluoromethyl)benzene (9o)

Following the general procedure C, the product was obtained as a colorless oil, 17 mg, 36% yield. Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 2.0 Hz, 2H), 1.46 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.47 (dd, 283.8 Hz, 283.7 Hz), 142.67 , 129.10 , 128.84 , 125.45 (q, *J* = 3.8 Hz), 122.87 , 84.03 (t, *J* = 19.4 Hz), 34.39 (t, *J* = 1.9 Hz), 11.75 (d, *J* = 1.9 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.98 (s, 3H), -96.37 (d, *J* = 56.6 Hz, 1F), -96.59 (d, *J* = 56.6 Hz, 1F). **HRMS** (EI) calcd for $C_{11}H_9F_5$ $[M]^+$: 236.0624, found: 236.0623.



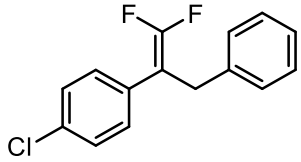
(2-(difluoromethylene)propane-1,3-diyl)dibenzene (9p)

Following the general procedure C, the product was obtained as a colorless oil, 14.6 mg, 30% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.26 – 7.20 (m, 2H), 7.17 – 7.11 (m, 4H), 3.21 (d, *J* = 2.1 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.22 (t, *J* = 284.6 Hz), 138.30 (t, *J* = 2.6 Hz), 128.76 , 128.50 , 126.49 , 88.97 (t, *J* = 17.4 Hz), 31.54 (t, *J* = 1.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.59. **HRMS** (EI) calcd for $C_{16}H_{14}F_2$ $[M]^+$: 244.1058, found: 244.1051.



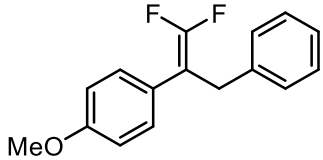
(3,3-difluoroprop-2-ene-1,2-diyl)dibenzene (9q)

Following the general procedure C, the product was obtained as a colorless oil, 26.3 mg, 57% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.27 – 7.22 (m, 3H), 7.22 – 7.14 (m, 3H), 3.75 (t, *J* = 2.3 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.38 (dd, *J* = 291.8, 287.4 Hz), 138.43 (t, *J* = 2.7 Hz), 133.48 (t, *J* = 3.8 Hz), 128.45 , 128.33 , 128.24 (t, *J* = 3.4 Hz), 127.25 , 126.37 , 91.66 (dd, *J* = 21.4, 13.6 Hz), 33.89 (d, *J* = 1.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -90.87 (d, *J* = 40.1 Hz, 1F), -91.43 (d, *J* = 40.0 Hz, 1F). **HRMS** (EI) calcd for $C_{15}H_{12}F_2$ $[M]^+$: 230.0902, found: 230.0904.



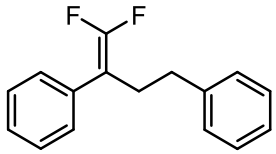
chloro-4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzene (9r)

Following the general procedure C, the product was obtained as a colorless oil, 26.9 mg, 51% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.23 - 7.20 (m, 2H), 7.19 – 7.12 (m, 3H), 3.72 (t, *J* = 2.3 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.35 (dd, *J* = 292.2, 288.1 Hz), 138.00 (t, *J* = 2.6 Hz), 133.10 , 131.89 (t, *J* = 3.7 Hz), 129.56 (t, *J* = 3.6 Hz), 128.56 (d, *J* = 1.7 Hz), 128.21 , 126.54 , 90.96 (dd, *J* = 22.0, 13.6 Hz), 33.75 .**^{19}F NMR** (282 MHz, $CDCl_3$) δ -90.21 (d, *J* = 38.7 Hz, 1F), -90.63 (d, *J* = 38.8 Hz, 1F). **HRMS** (EI) calcd for $C_{15}H_{11}F_2Cl$ $[M]^+$: 254.0512, found: 254.0506.



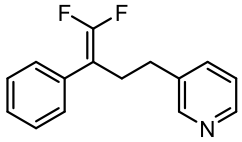
1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-methoxybenzene (9s)

Following the general procedure C, the product was obtained as a colorless oil, 29.2 mg, 56% yield. **^{1}H NMR**δ 7.18 – 7.12 (m, 2H), 7.12 – 7.05 (m, 5H), 6.76 – 6.70 (m, 2H), 3.68 (s, 3H), 3.62 (t, *J* = 2.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.62 , 154.23 (dd, *J* = 290.6, 286.8 Hz), 138.56 (t, *J* = 2.6 Hz), 129.38 (t, *J* = 3.5 Hz), 128.43 , 128.27 , 126.33 , 113.79 , 91.13 (dd, *J* = 21.3, 13.9 Hz), 55.15 , 33.99 (d, *J* = 2.5 Hz).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.01 (d, *J* = 42.9 Hz, 1F), -92.41 (d, *J* = 42.9 Hz, 1F). **HRMS** (EI) calcd for $C_{16}H_{14}OF_2Cl$ $[M]^+$: 260.1007, found: 260.1003.



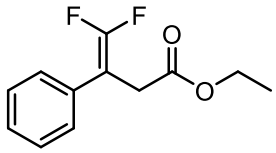
(4,4-difluorobut-3-ene-1,3-diyl)dibenzene (9t)

Following the general procedure C, the product was obtained as a colorless oil, 21.1 mg, 43% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 7H), 7.25 – 7.07 (m, 3H), 2.78 – 2.59 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.72 (dd, *J* = 290.8, 287.0 Hz), 141.00 , 133.46 (dd, *J* = 4.5, 3.2 Hz), 128.48 , 128.36 (d, *J* = 3.2 Hz), 128.28 (t, *J* = 3.2 Hz), 127.30 , 126.07 , 91.81 (dd, *J* = 21.6, 13.3 Hz), 34.01 (t, *J* = 2.6 Hz), 29.67 (d, *J* = 1.6 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -91.58 (d, *J* = 42.5 Hz, 1F), -92.02 (d, *J* = 42.5 Hz, 1F). **HRMS** (EI) calcd for $C_{16}H_{14}F_2$ $[M]^+$: 244.1058, found: 244.1056.



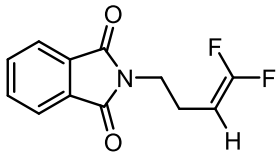
3-(4,4-difluoro-3-phenylbut-3-en-1-yl)pyridine (9u)

Following the general procedure C, the product was obtained as a colorless oil, 23.5 mg, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.33 (d, *J* = 2.2 Hz, 1H), 7.42 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 7.20 – 7.14 (m, 1H), 2.73 – 2.59 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.76 (dd, *J* = 291.2, 287.5 Hz), 149.58, 147.35, 136.24, 136.11, 132.92 (dd, *J* = 14.3, 11.3 Hz), 128.61, 128.23 (t, *J* = 3.2 Hz), 127.51, 123.36, 91.23 (dd, *J* = 21.3, 14.2 Hz), 30.97 (t, *J* = 2.7 Hz), 29.12 (d, *J* = 1.7 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -91.24 (d, *J* = 41.5 Hz), -91.53 (d, *J* = 41.5 Hz). **HRMS** (EI) Calcd. for $C_{15}H_{13}F_2N$ $[M]^+$: 245.1009. Found: 245.1008.



ethyl 4,4-difluoro-3-phenylbut-3-enoate (9v)

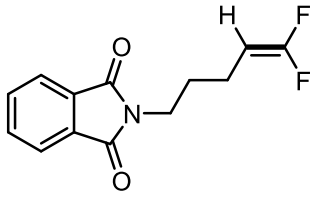
Following the general procedure C, the product was obtained as a colorless oil, 17.6 mg, 39% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.40 (dd, *J* = 2.5, 2.0 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.13 (dd, *J* = 3.0 Hz, 2.6 Hz), 154.78 (dd, *J* = 292.4, 289.0 Hz), 133.02 (t, *J* = 3.8 Hz), 128.48 , 127.83 (t, *J* = 3.5 Hz), 127.52 , 87.16 (dd, *J* = 21.5, 17.7 Hz), 61.09 , 33.88 (d, *J* = 2.6 Hz), 14.05 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -88.41 (d, *J* = 35.3 Hz, 1F), -89.69 (d, *J* = 35.3 Hz, 1F). **HRMS** (EI) calcd for $C_{12}H_{12}F_2O_2$ $[M]^+$: 226.0805, found:226.0808.



2-(4,4-difluorobut-3-en-1-yl)isoindoline-1,3-dione (9w)

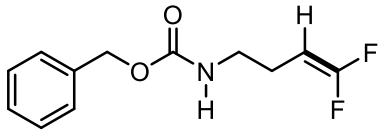
Following the general procedure C, the product was obtained as a white solid, 15.9 mg, 34% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 2H), 7.76 – 7.67 (m, 2H), 4.18 (dtd, *J* = 24.9, 7.9, 2.1 Hz,

1H), 3.73 (td, *J* = 7.0, 0.8 Hz, 2H), 2.44 – 2.32 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.31 , 156.36 (dd, *J* = 287.6, 285.4 Hz), 133.93 , 132.04 , 123.21 , 76.92 (d, *J* = 2.1 Hz), 37.18 , 28.25 (t, *J* = 2.4 Hz), 19.71 (d, *J* = 4.6 Hz).**^{19}F NMR** (282 MHz, $CDCl_3$) δ -87 .00 (d, *J* = 42.6 Hz, 1F), -90.05 (d, *J* = 42.6 Hz, 1F). **HRMS** (EI) calcd for $C_{12}H_9NF_2O_2$ $[M]^+$:237.0596, found: 237.0597.



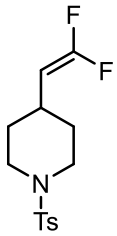
2-(5,5-difluoropent-4-en-1-yl)isoindoline-1,3-dione (9x)

Following the general procedure C, the product was obtained as a white solid, 15.8 mg, 31% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.20 (dtd, *J* = 25.2, 7.8, 2.4 Hz, 1H), 3.73 – 3.66 (m, 2H), 2.04 (qt, *J* = 7.8, 1.9 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.31, 159.21, 156.37, 156.35, 153.52, 133.93, 132.04, 123.21, 77.32, 77.14, 77.00, 76.93, 76.91, 76.68, 37.18, 28.27, 28.25, 28.23, 19.73, 19.69. **^{19}F NMR** (282 MHz, $CDCl_3$) ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.91 (d, *J* = 46.4 Hz), -91.13 (d, *J* = 46.4 Hz). **HRMS** (EI) calcd for $C_{13}H_{11}NO_2F_2$ $[M]^+$:251.0752, found: 251.0748.



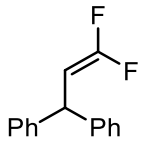
benzyl (4,4-difluorobut-3-en-1-yl)carbamate (9y)

Following the general procedure C, the product was obtained as a white solid, 18.5 mg, 38% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.10 (s, 2H), 4.87 (s, 1H), 4.15 (dtd, *J* = 25.1, 7.9, 2.2 Hz, 1H), 3.24 (q, *J* = 6.6 Hz, 2H), 2.28 – 2.11 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, Chloroform-*d*) δ 156.31 , 156.94 (dd, 285.0 Hz, 284.3 Hz), 136.40 , 128.51 , 128.13 , 128.07 , 74.95 (dd, 21.0 Hz, 20.3 Hz), 66.73 , 40.43 , 23.18 (d, *J* = 4.3 Hz).**^{19}F NMR** (282 MHz, $CDCl_3$) δ -87.37 (d, *J* = 44.0 Hz, 1F), -90.39 (d, *J* = 44.1 Hz, 1F). **HRMS** (ESI) calcd for $[M+H]^+$:242.0987, found: 242.0988.



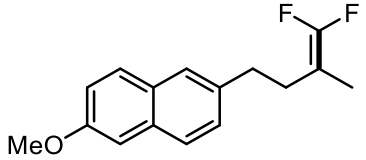
4-(2,2-difluorovinyl)-1-tosylpiperidine (9z)

Following the general procedure C, the product was obtained as a colorless oil, 29.5 mg, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.02 (ddd, *J* = 25.4, 9.3, 2.7 Hz, 1H), 3.71 (dt, *J* = 11.6, 3.5 Hz, 2H), 2.43 (s, 3H), 2.30 (td, *J* = 11.9, 2.7 Hz, 2H), 2.18 – 2.00 (m, 1H), 1.78 – 1.68 (m, 2H), 1.54 – 1.42 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.87 (t, *J* = 288.8 Hz), 143.51 , 132.93 , 129.59 , 127.65 , 81.77 (dd, *J* = 20.8, 19.7 Hz), 45.85 , 31.46 (t, *J* = 2.3 Hz), 29.86 (d, *J* = 4.5 Hz), 21.47 .**^{19}F NMR** (377 MHz, $CDCl_3$) δ -89.08 (d, *J* = 46.0 Hz, 1F), -89.82 (d, *J* = 45.9 Hz, 1F). **HRMS** (ESI) calcd for $[M+H]^+$: 302.1021, found: 302.1026.



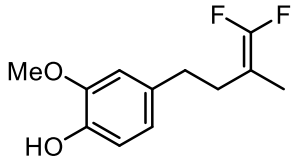
(3,3-difluoroprop-2-ene-1,1-diyl)dibenzene (9aa)

Following the general procedure C, the product was obtained as a white solid, 40 mg, 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 4H), 7.17 – 7.06 (m, 6H), 4.83 – 4.77 (m, 1H), 4.69 (ddd, *J* = 23.8, 10.5, 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.96 (dd, *J* = 288.7, 287.4 Hz), 143.09 (t, *J* = 2.1 Hz), 128.60 , 127.89 , 126.69 , 82.00 (dd, *J* = 22.3, 19.1 Hz), 44.52 (d, *J* = 4.9 Hz).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -88.70 (d, *J* = 42.7 Hz, 1F), -90.43 (d, *J* = 42.8 Hz, 1F). **HRMS** (EI) calcd. for $C_{15}H_{11}F_2$ $[M]^+$:229.0823, found: 229.0826.



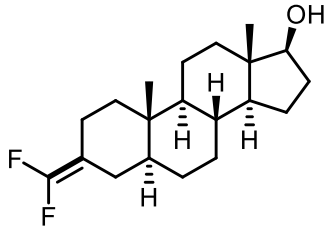
2-(4,4-difluoro-3-methylbut-3-en-1-yl)-6-methoxynaphthalene (9ab)

Following the general procedure C, the product was obtained as a colorless oil, 24.3 mg, 46% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.56 (dt, *J* = 1.4, 0.8 Hz, 1H), 7.31 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.17 – 7.11 (m, 2H), 3.92 (s, 3H), 2.84 (dd, *J* = 9.2, 6.7 Hz, 2H), 2.36 (ddt, *J* = 7.7, 6.4, 2.2 Hz, 2H), 1.62 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.20 , 152.95 (dd, *J* = 280.5 Hz, 279.8 Hz), 136.39 , 133.05 , 129.03 , 128.90 , 127.54 , 126.79 , 126.26 , 118.72 , 105.59 , 84.22 (dd, *J* = 18.8 Hz, 18.0 Hz), 55.25 , 33.57 (t, *J* = 2.6 Hz), 30.18 (d, *J* = 2.3 Hz), 12.02 (t, *J* = 2.1 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -96.62 (d, *J* = 57.4 Hz, 1F), -96.97 (d, *J* = 57.4 Hz, 1F). **HRMS** (EI) calcd for $C_{16}H_{16}F_2O$ $[M]^+$: 262.1164, found: 262.1164.



4-(4,4-difluoro-3-methylbut-3-en-1-yl)-2-methoxyphenol (9ac)

Following the general procedure C, the product was obtained as a colorless oil, 26.5 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.5 Hz, 1H), 6.70 – 6.65 (m, 2H), 5.50 (s, 1H), 3.88 (s, 3H), 2.64 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.25 (tt, *J* = 8.0, 2.1 Hz, 2H), 1.58 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.95 (dd, *J* = 282.3, 281.4 Hz), 146.36 , 143.83 , 133.14 , 120.91 , 114.20 , 110.79 , 84.18 (dd, *J* = 19.4, 18.3 Hz), 55.86 , 33.22 (t, *J* = 2.7 Hz), 30.35 (d, *J* = 2.2 Hz), 11.94 .**^{19}F NMR** (377 MHz, $CDCl_3$) δ -96.79 (d, *J* = 57.8 Hz, 1F), -97.11 (d, *J* = 57.7 Hz, 1F). **HRMS** (EI) calcd for $C_{12}H_{14}F_2O_2$ $[M]^+$: 228.0956, found: 228.0956.



3-(difluoromethylene)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol (9ad)

Following the general procedure C, the product was obtained as a white solid, 27.2 mg, 48% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.62 (dd, *J* = 9.0, 8.0 Hz, 1H), 2.34 – 2.20 (m, 1H), 2.04 (dtd, *J* = 13.2, 9.2, 5.7 Hz, 2H), 1.90 (tddd, *J* = 14.7, 6.2, 3.4, 1.4 Hz, 1H), 1.83 – 1.61 (m, 4H), 1.61 – 1.51 (m, 2H), 1.48 – 1.29 (m, 4H), 1.29 – 0.83 (m, 8H), 0.84 (d, *J* = 0.7 Hz, 3H), 0.73 (d, *J* = 0.7 Hz, 3H), 0.65 (ddd, *J* = 12.3, 10.4, 4.2 Hz, 1H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.62 (t, *J* = 280.3 Hz), 87.60 (t, *J* = 18.5 Hz), 81.90 , 54.22 , 50.95 , 46.22 (t, *J* = 1.8 Hz), 42.91 , 37.92 (t, *J* = 1.5 Hz), 36.67 , 36.09 , 35.43 , 31.35 , 30.47 , 28.43 , 26.62 (d, *J* = 1.8 Hz), 23.34 , 20.54 , 19.86 (t, *J* = 2.3 Hz), 11.38 , 11.12 .**^{19}F NMR** (282 MHz, $CDCl_3$) δ -99.52 (d, *J* = 63.3 Hz, 1F), -99.92 (d, *J* = 63.2 Hz, 1F). **HRMS** (EI) calcd for $C_{20}H_{30}F_2O$ $[M]^+$: 324.2259, found: 324.2258.

7. References

1. Harris, R.; Becker, E.; De Menezes, S. C.; Goodfellow, R.; Granger, P.; Int, C., Union Pure Applied. *Magn. Reson. Chem.* **2002,** *40*, 489-505.

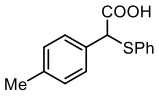
2. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A., NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem.* **1997,** *62*, 7512-7515.

3. Zhang, B.-H.; Lei, L.-S.; Liu, S.-Z.; Mou, X.-Q.; Liu, W.-T.; Wang, S.-H.; Wang, J.; Bao, W.; Zhang, K., Zinc-promoted cyclization of tosylhydrazones and 2-(dimethylamino)malononitrile: an efficient strategy for the synthesis of substituted 1-tosyl-1H-pyrazoles. *Chem. Commun.* **2017,** *53*, 8545-8548.

4. Gavara, L.; Petit, C.; Montchamp, J.-L., DBU-promoted alkylation of alkyl phosphinates and H-phosphonates. *Tetrahedron Lett.* **2012**, *53*, 5000-5003.

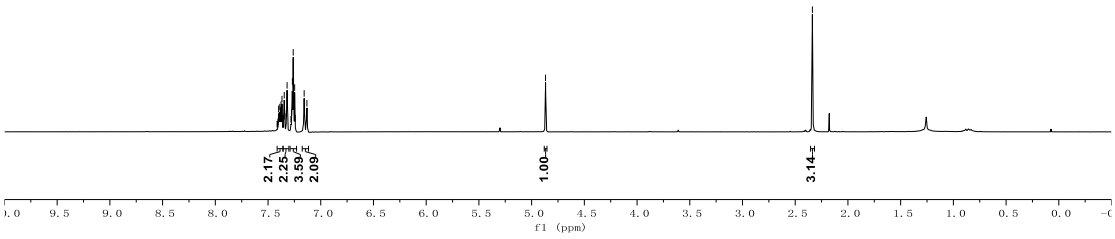
5. Stepen, A. J.; Bursch, M.; Grimme, S.; Stephan, D. W.; Paradies, J., Electrophilic Phosphonium Cation-Mediated Phosphane Oxide Reduction Using Oxalyl Chloride and Hydrogen. *Angew. Chem. Int. Ed.* **2018**, *57*, 15253-15256.

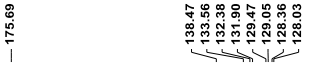
8. Copies of NMR spectra

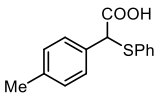


3a

^{1}H NMR, 300 MHz, $CDCl_3$

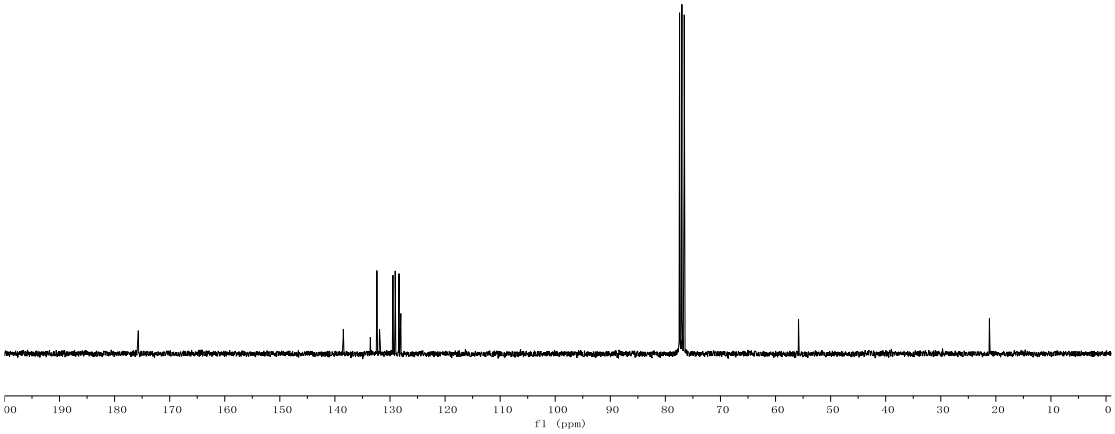


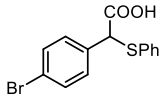




3a

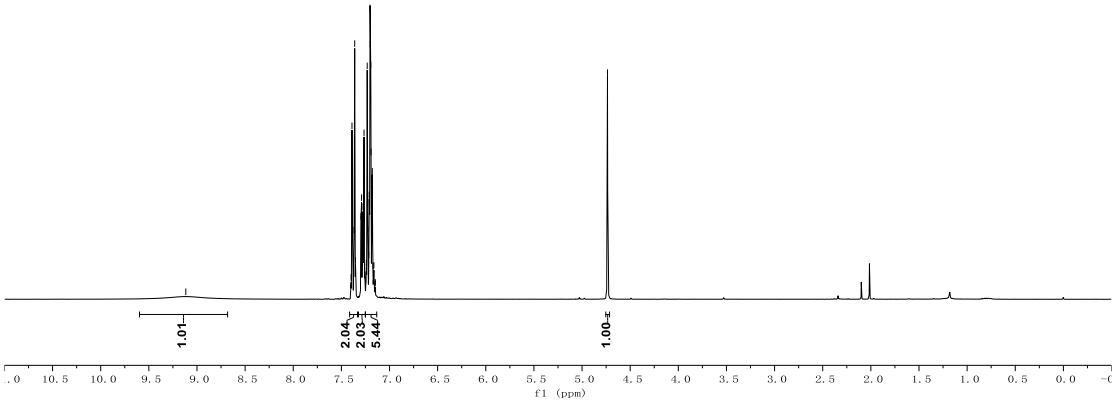
^{13}C NMR, 75 MHz, $CDCl_3$

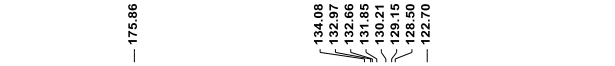


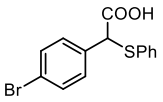


3b

^{1}H NMR, 300 MHz, $CDCl_3$

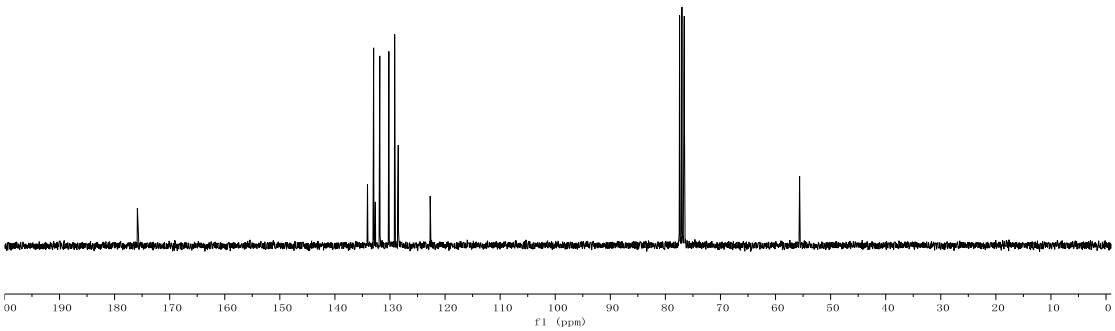


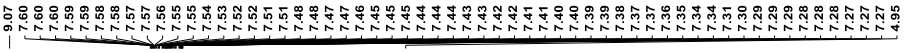


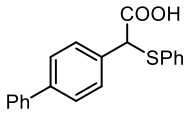


3b

^{13}C NMR, 75 MHz, $CDCl_3$

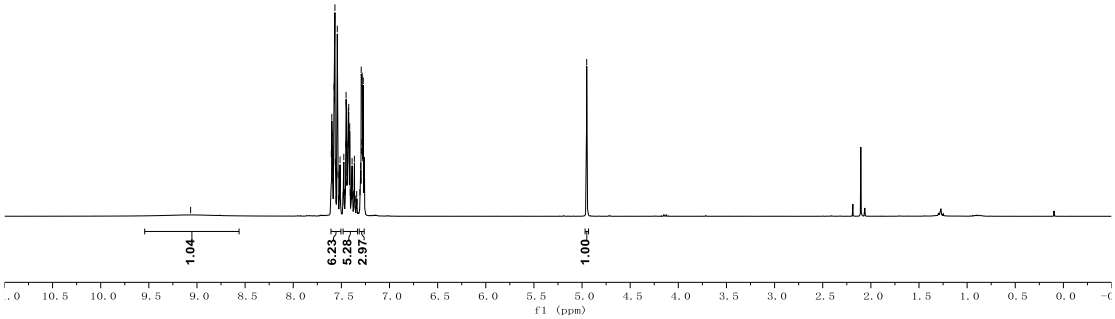


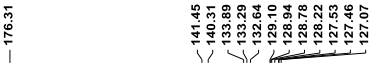


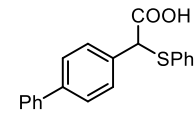


3c

^{1}H NMR, 300 MHz, $CDCl_3$

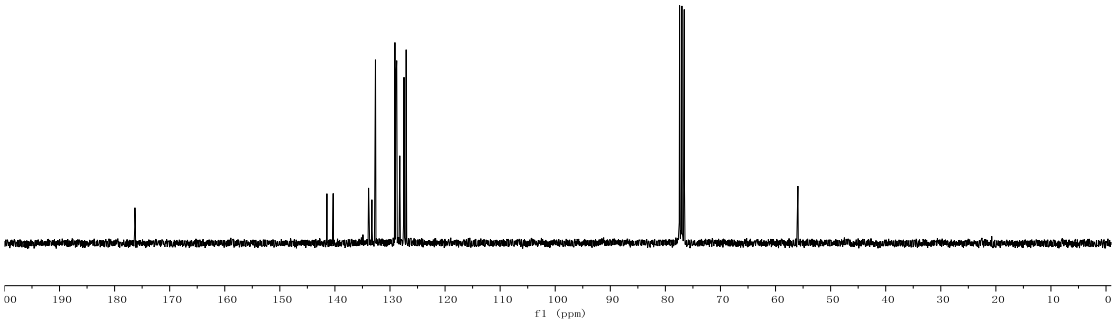


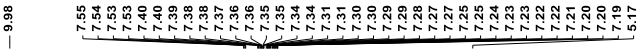


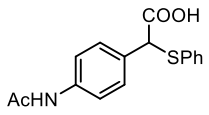


3c

^{13}C NMR, 75 MHz, $CDCl_3$

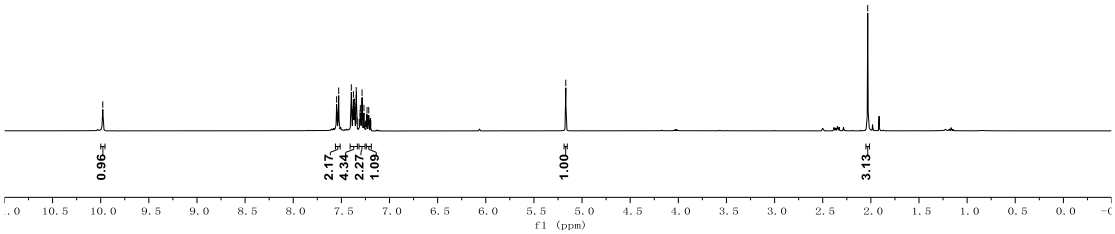


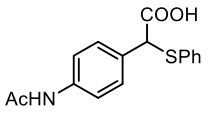




3d

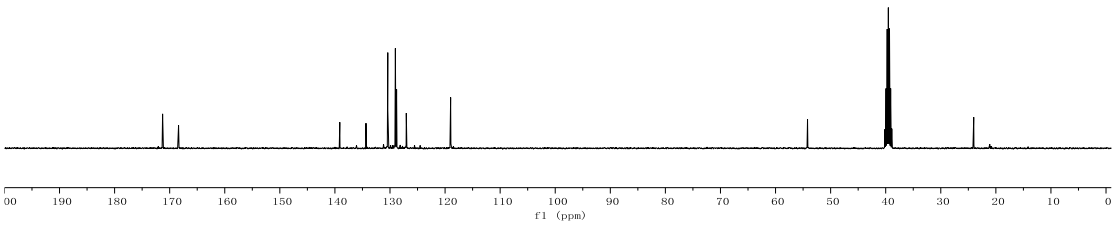
^{1}H NMR, 400 MHz, DMSO-d_6

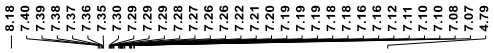


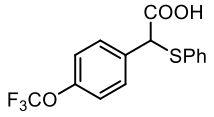


3d

^{13}C NMR, 100 MHz, DMSO-d_6

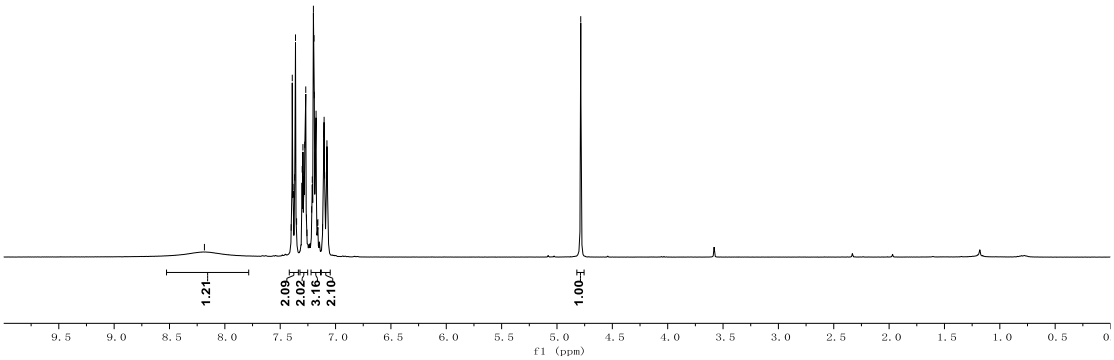


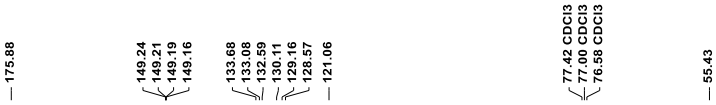


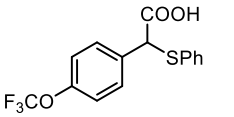


3e

^{1}H NMR, 300 MHz, $CDCl_3$

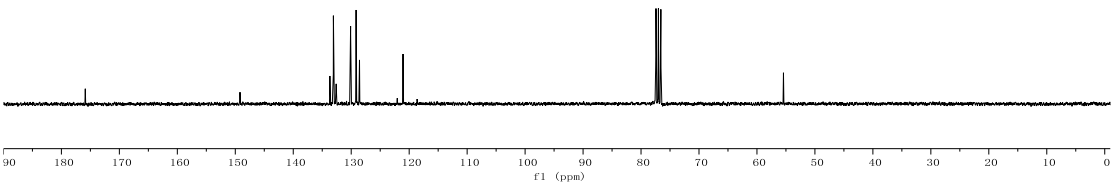


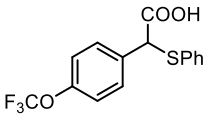




3e

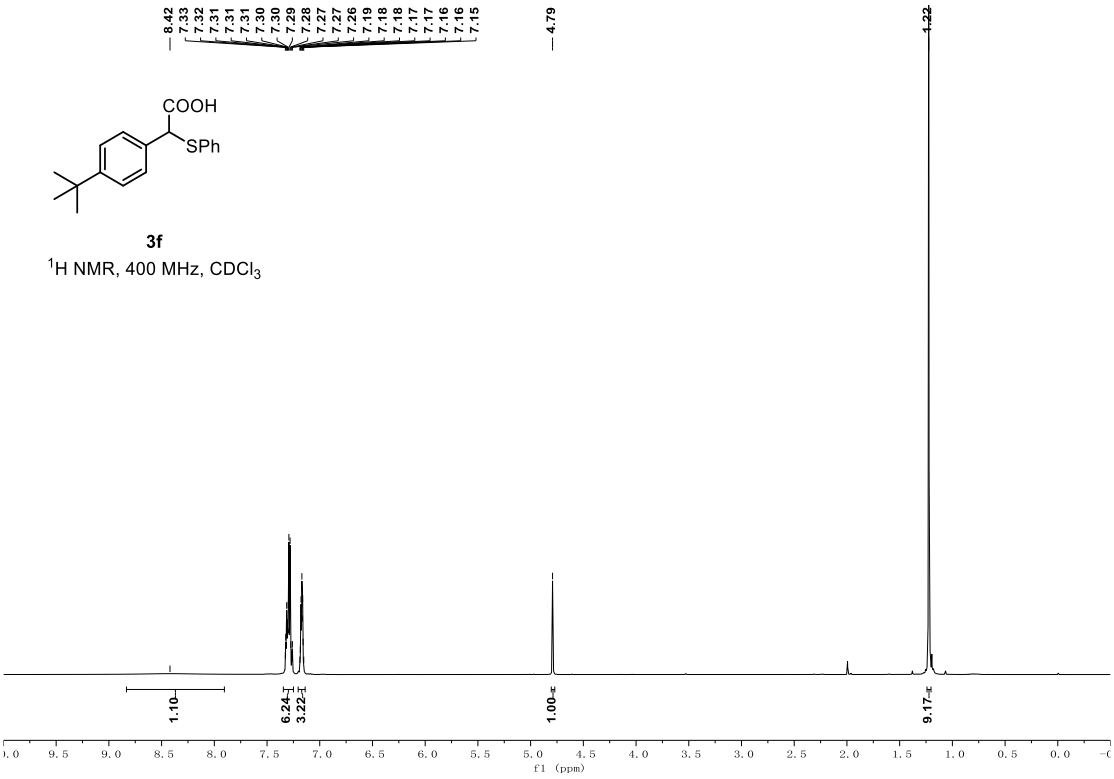
^{13}C NMR, 75 MHz, $CDCl_3$





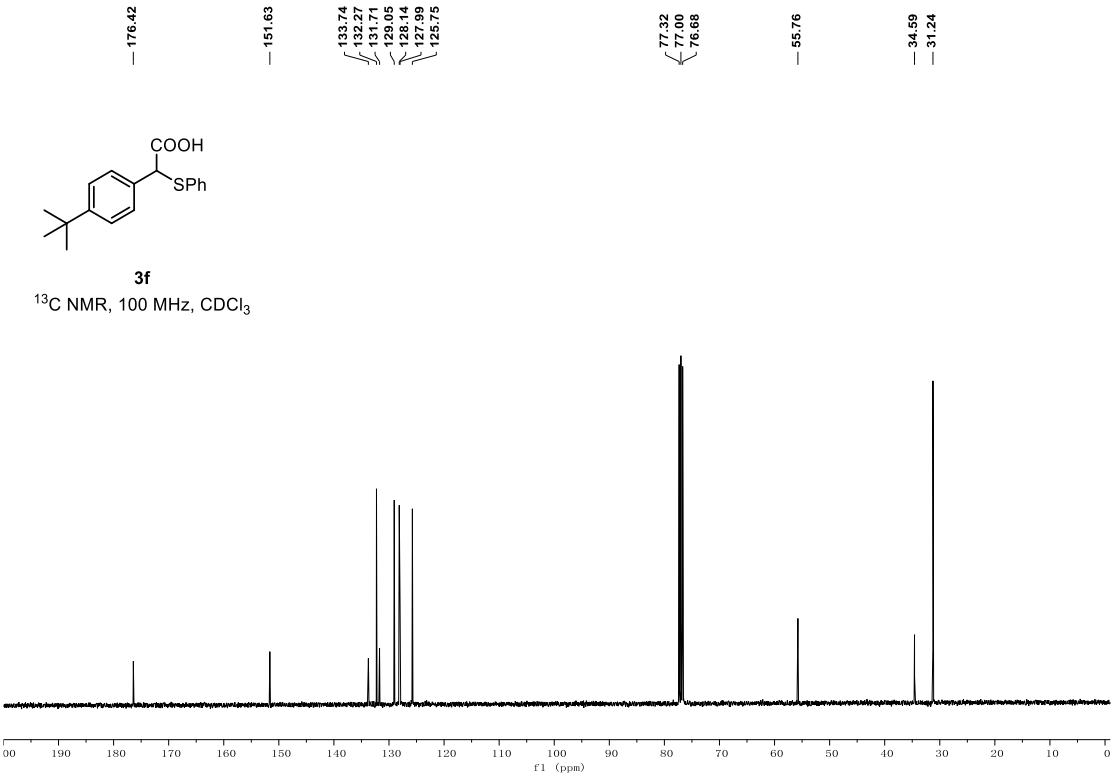
3e

^{19}F NMR, 282 MHz, $CDCl_3$



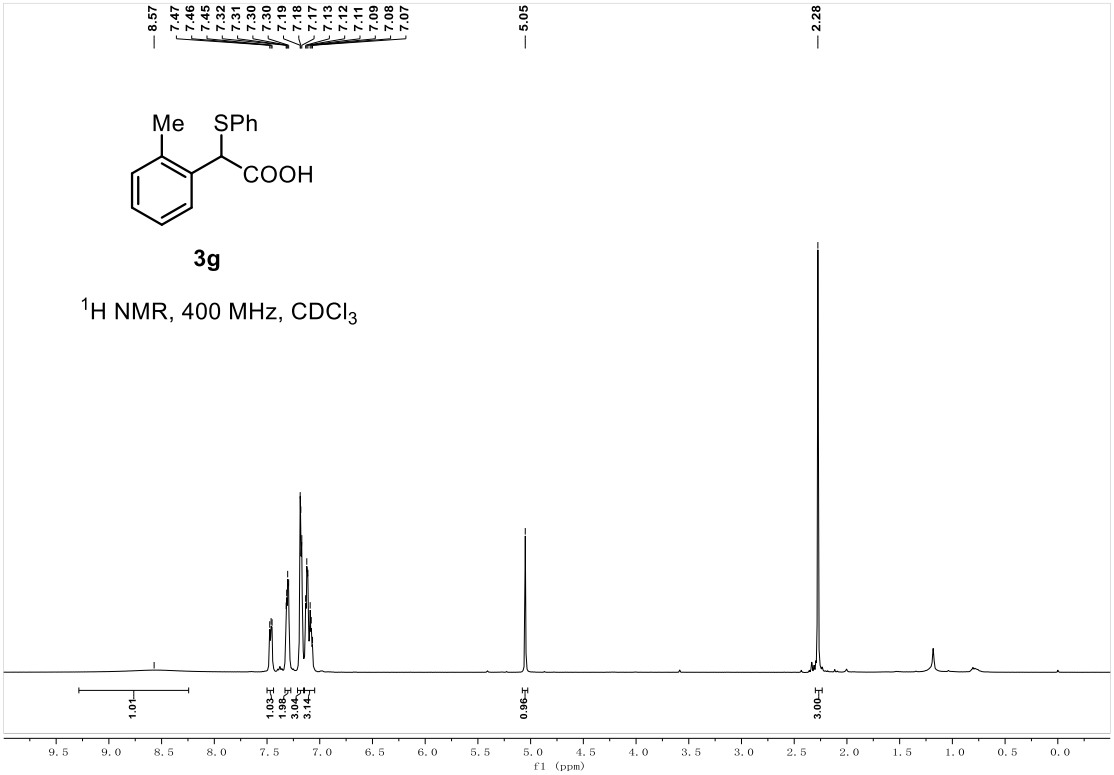
3f

^{1}H NMR, 400 MHz, $CDCl_3$



3f

^{13}C NMR, 100 MHz, $CDCl_3$



3g

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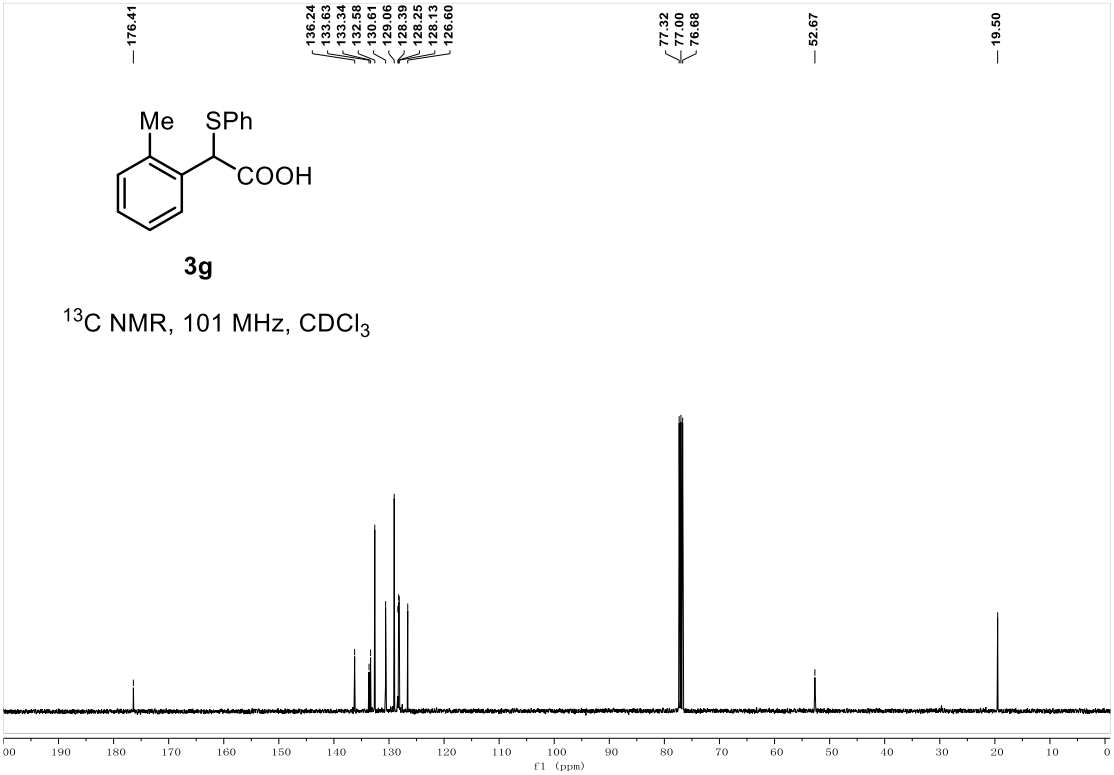
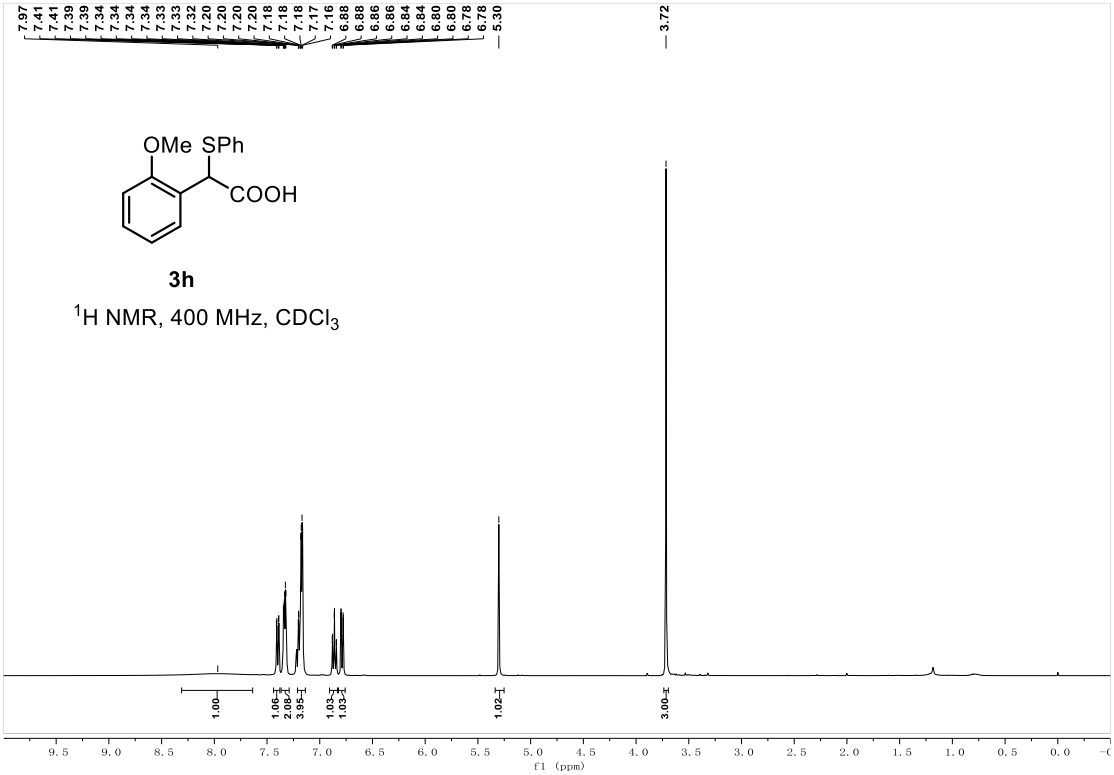


3g

^{13}C NMR, 101 MHz, $CDCl_3$



3h

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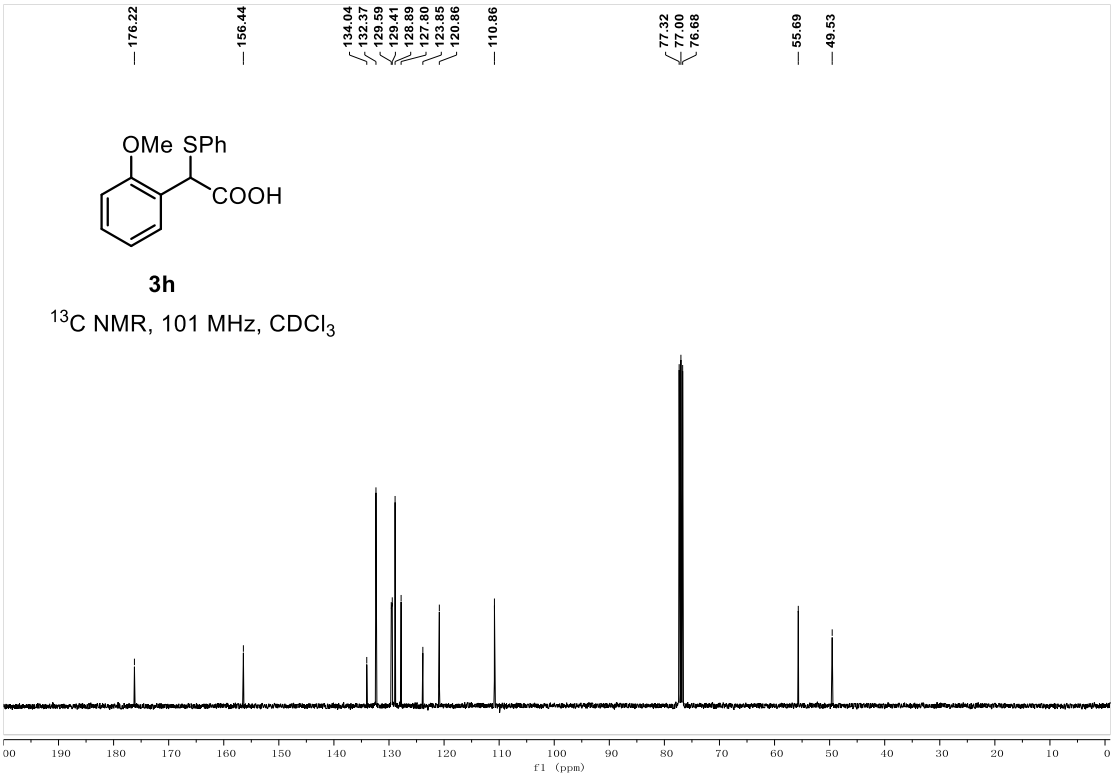

3h

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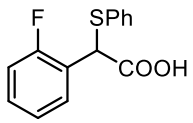
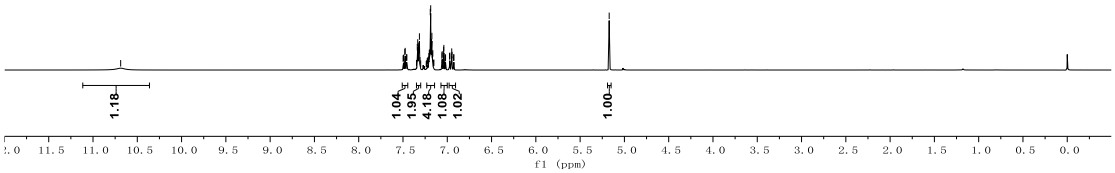
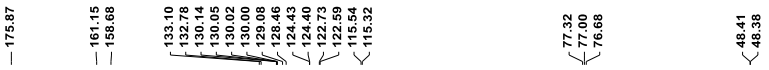
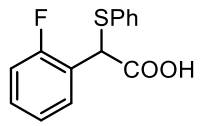


3i

^{1}H NMR, 300 MHz, $CDCl_3$

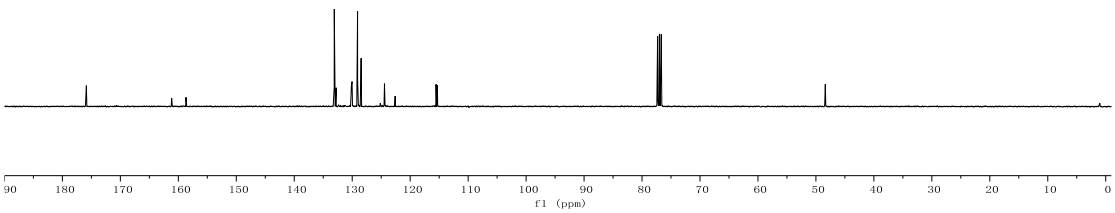


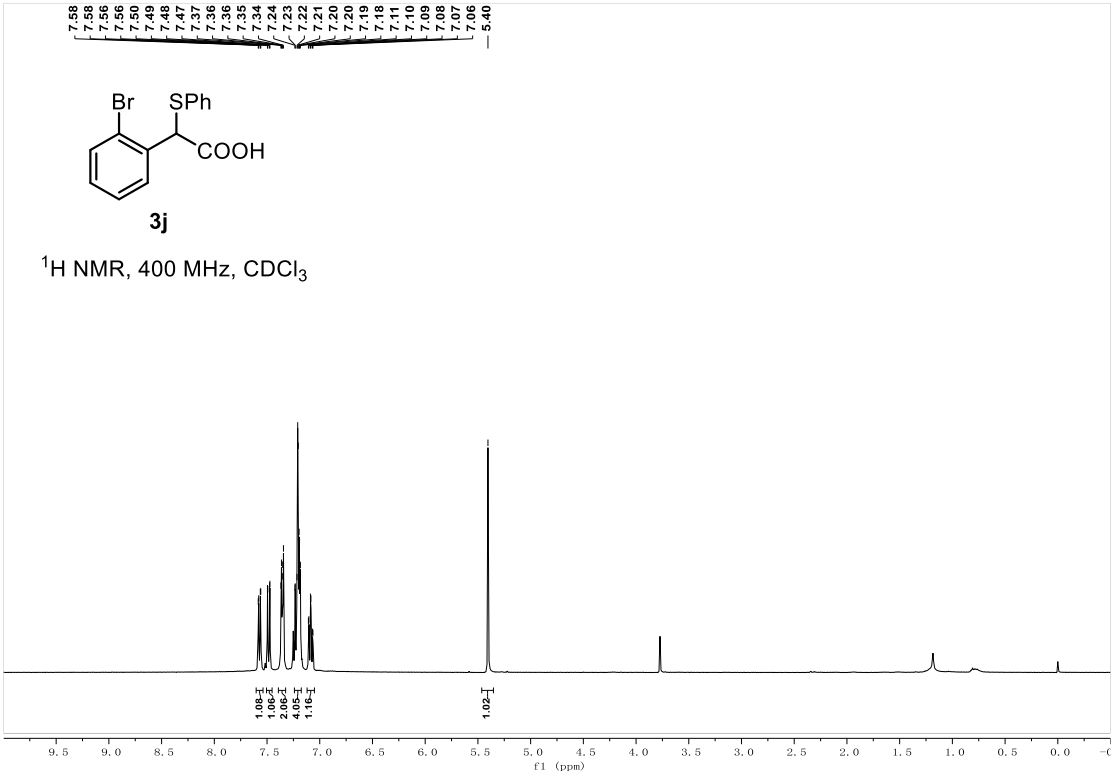




3i

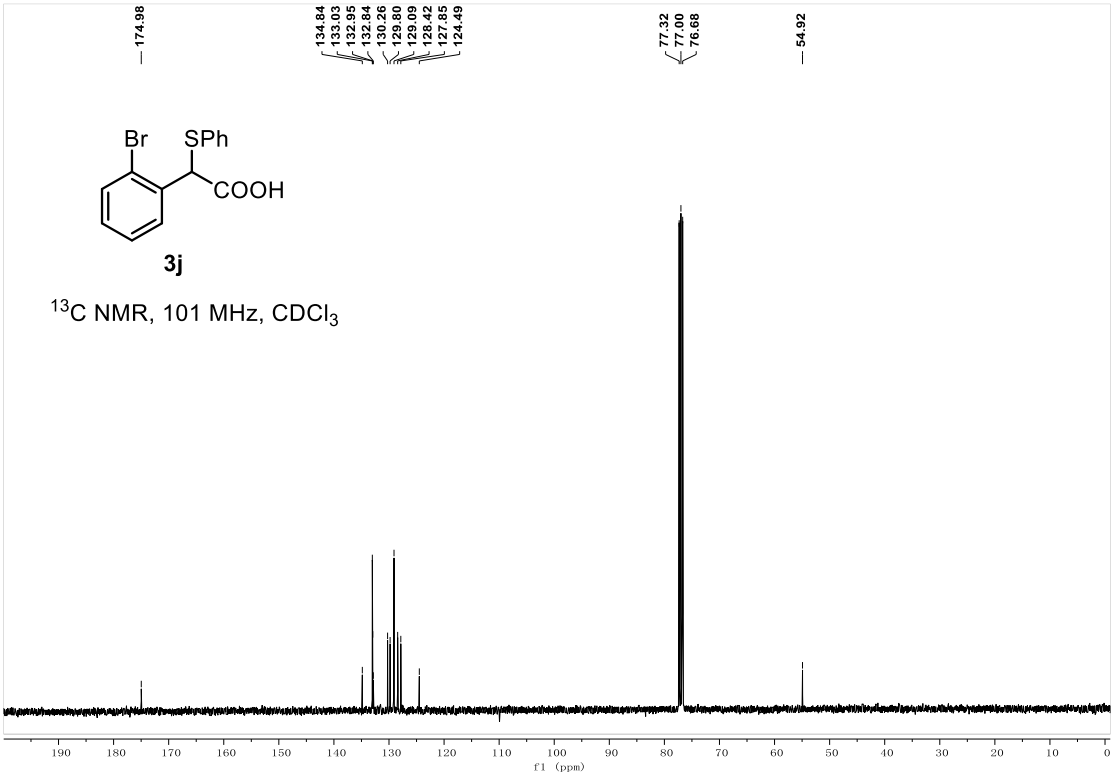
^{13}C NMR, 75 MHz, $CDCl_3$





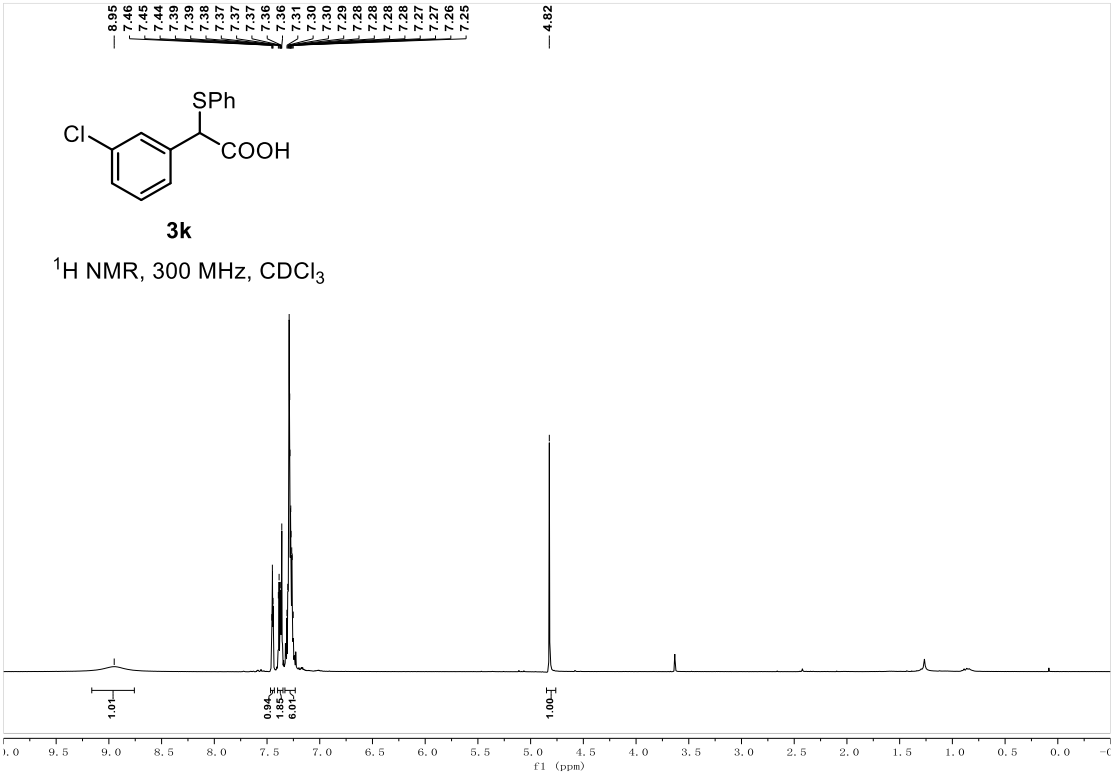
3j

^{1}H NMR, 400 MHz, $CDCl_3$



3j

^{13}C NMR, 101 MHz, $CDCl_3$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7.46
7.45
7.44
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.36
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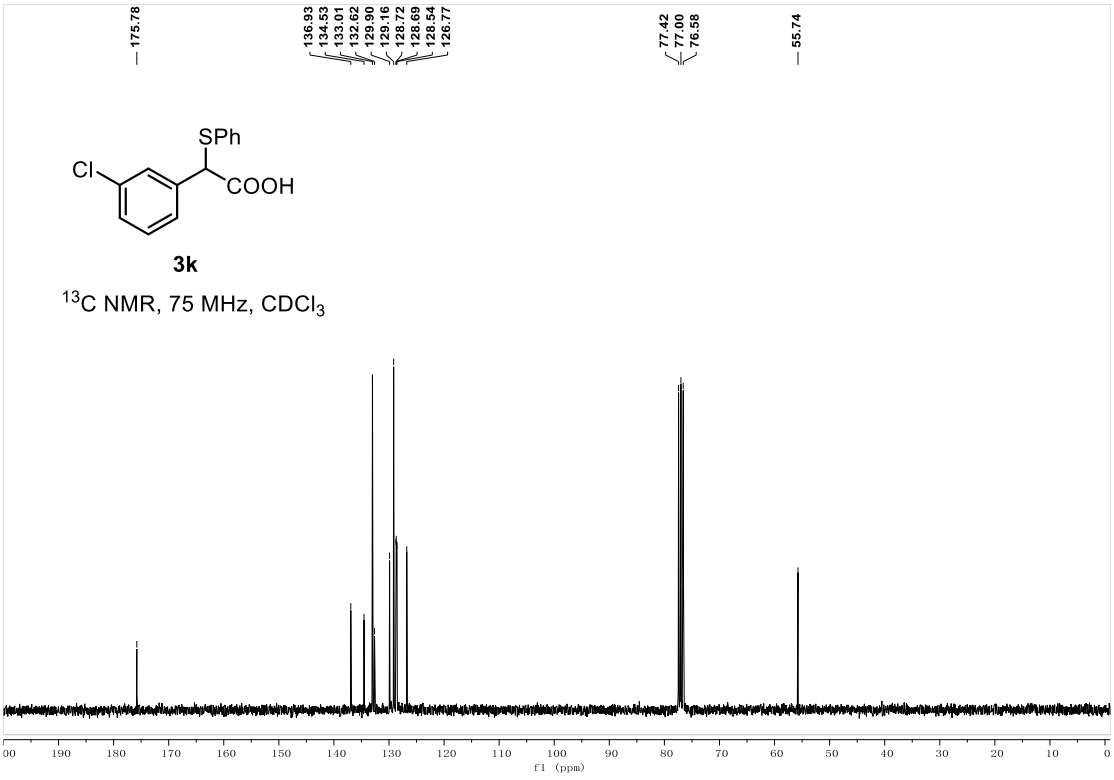
7.30
7.30
7.29
7.28
7.28
7.28
7.28
7.27
7.27
7.26
7.25
4.82
SPh
Cl
COOH
3k
1H NMR, 300 MHz, CDCl3
1.01
0.94
1.85
6.01
1.00
f1 (ppm)


175.78
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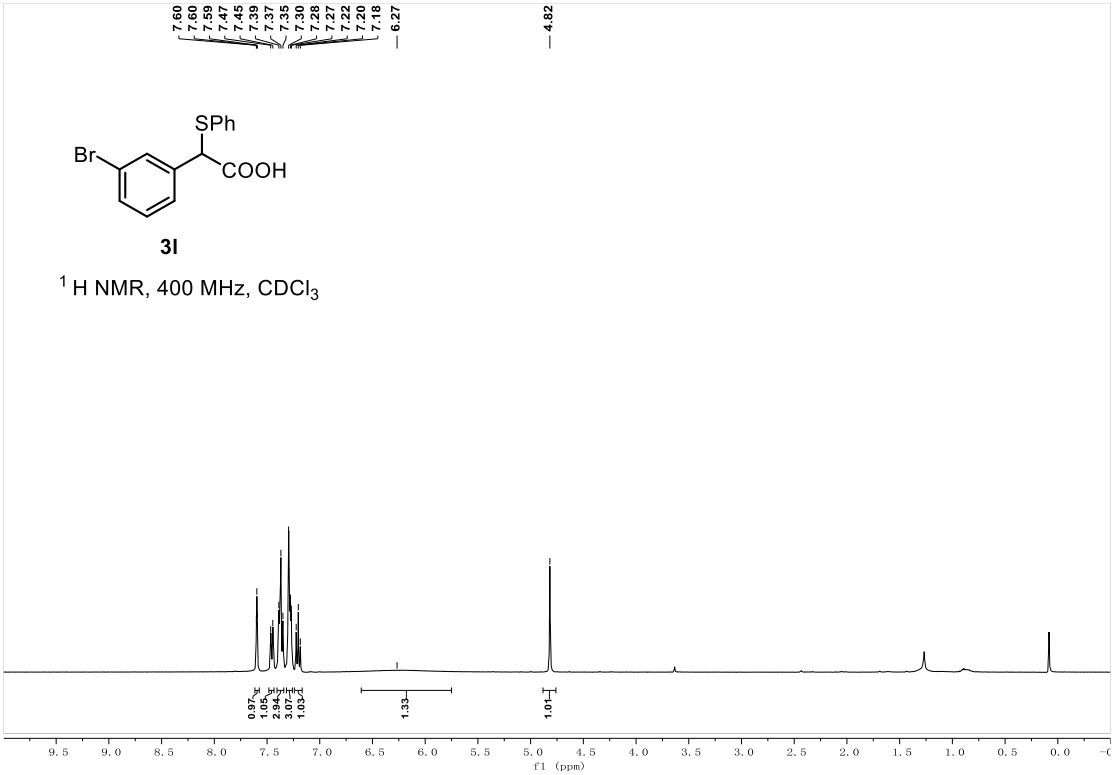
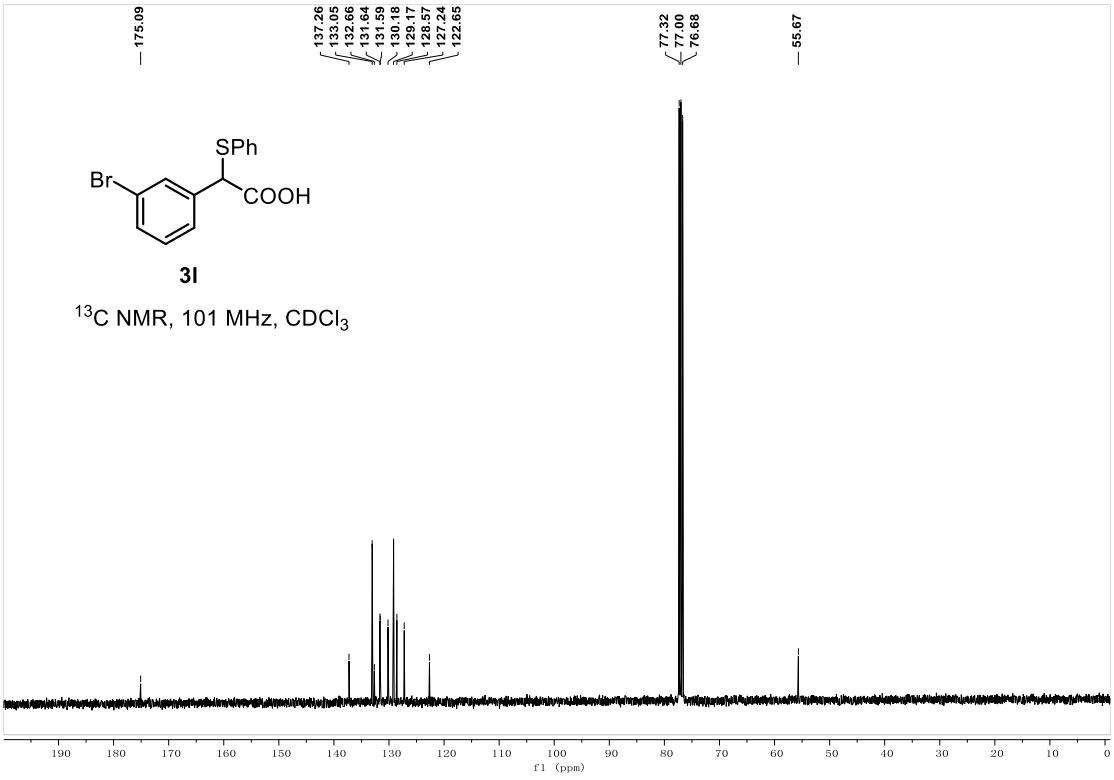
133.01
132.62
129.90
129.16
128.72
128.69
128.54
126.77
77.42
77.00
76.58
55.74
SPh
Cl
COOH
3k
13C NMR, 75 MHz, CDCl3
f1 (ppm)



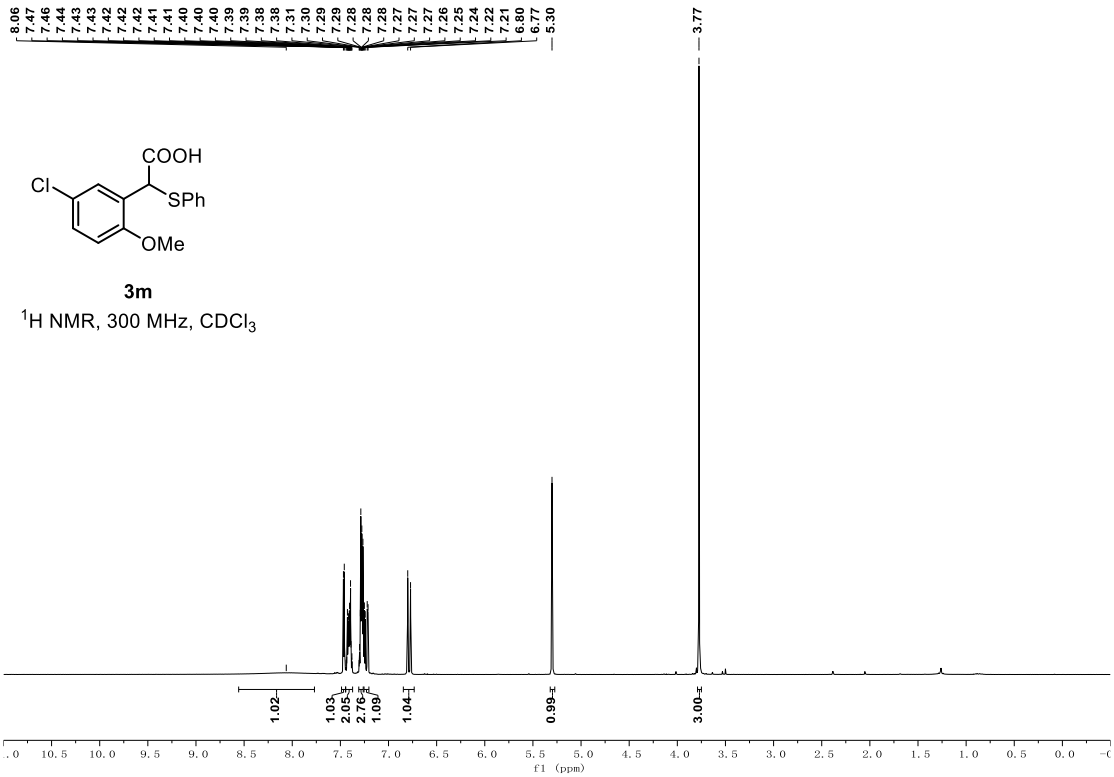
3l

^{1}H NMR, 400 MHz, $CDCl_3$



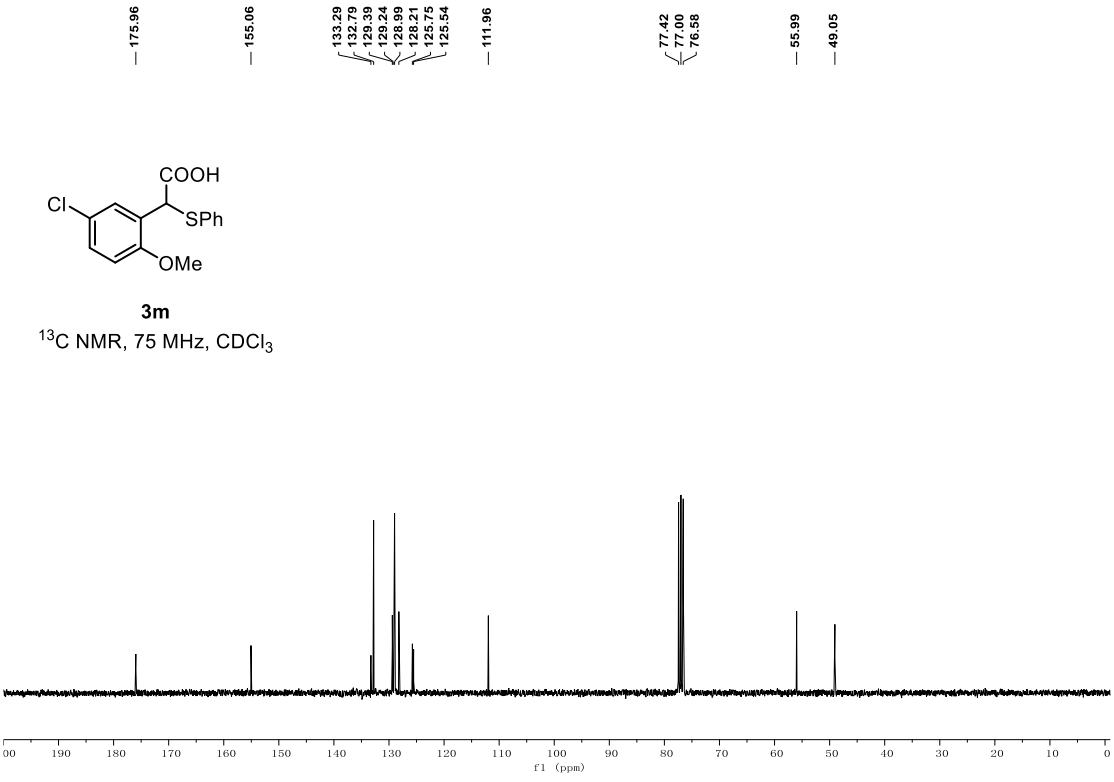
3l

^{13}C NMR, 101 MHz, $CDCl_3$



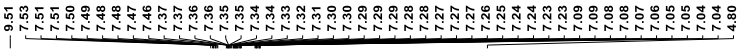
3m

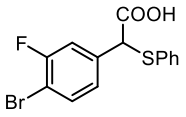
^{1}H NMR, 300 MHz, $CDCl_3$



3m

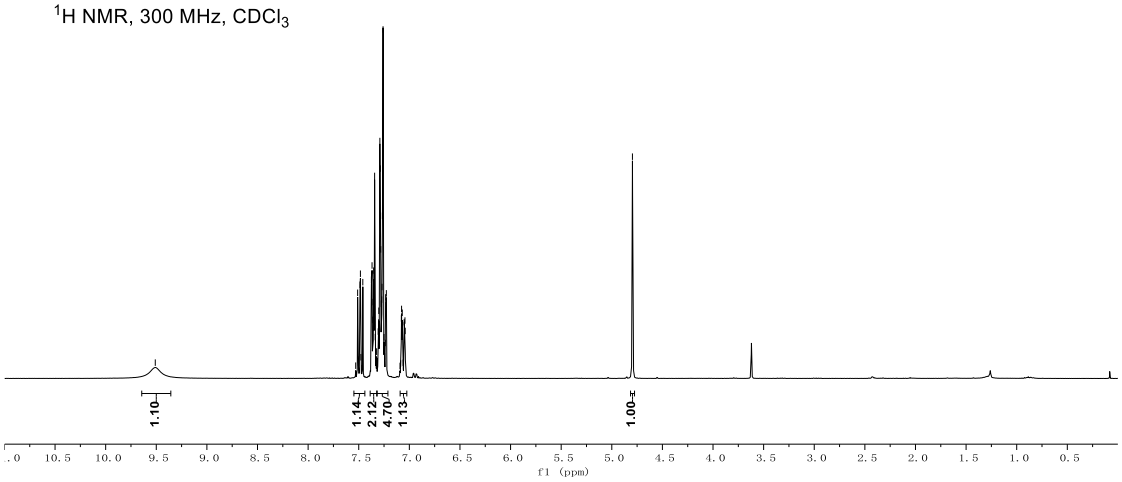
^{13}C NMR, 75 MHz, $CDCl_3$

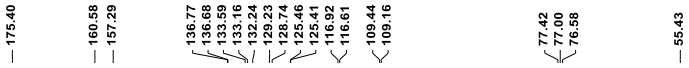


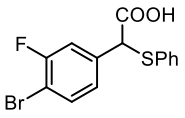


3n

^{1}H NMR, 300 MHz, $CDCl_3$

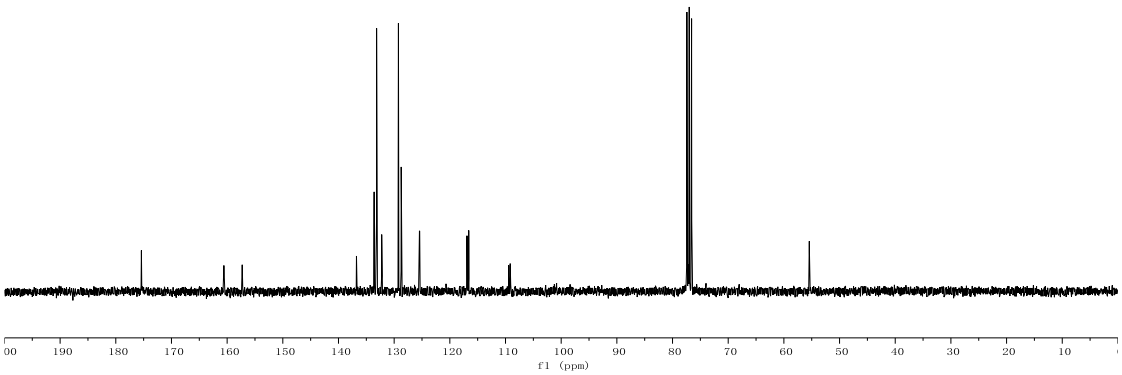


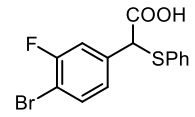




3n

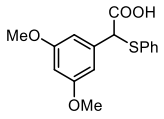
^{13}C NMR, 75 MHz, $CDCl_3$





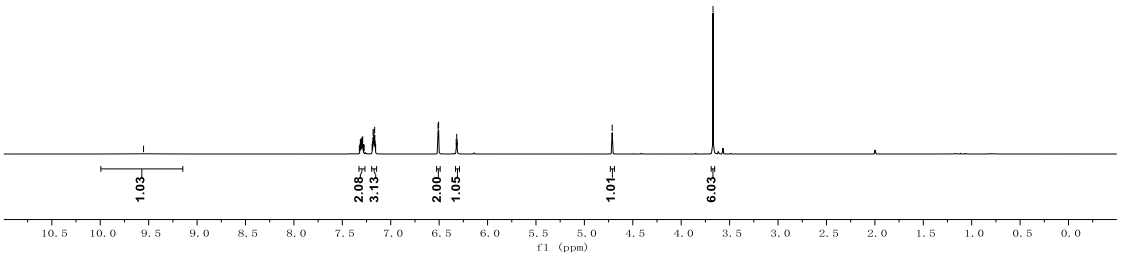
3n

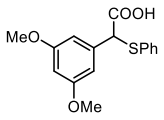
^{19}F NMR, 282 MHz, $CDCl_3$



3o

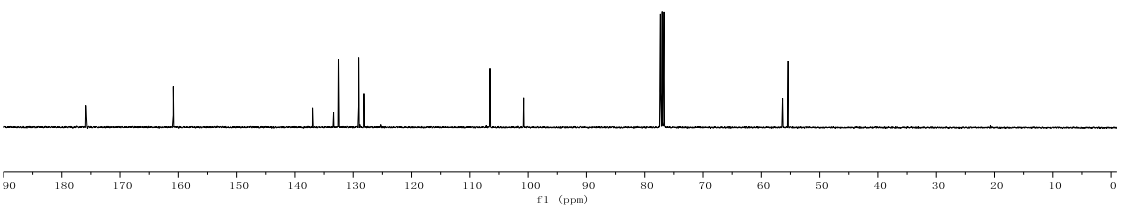
^{1}H NMR, 400 MHz, $CDCl_3$

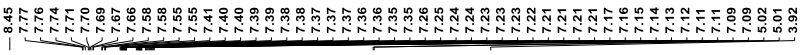


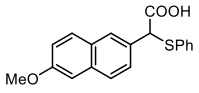


3o

^{13}C NMR, 101 MHz, $CDCl_3$

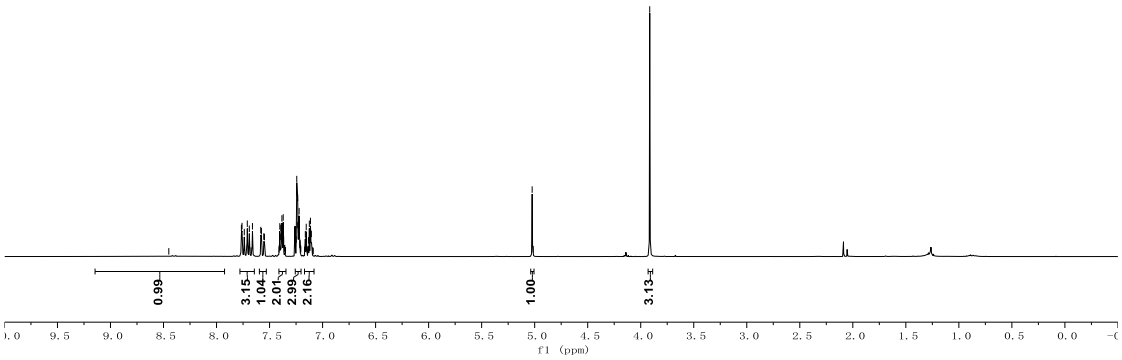


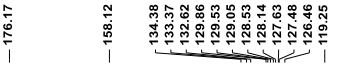


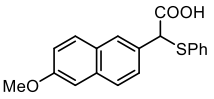


3p

^{1}H NMR, 300 MHz, $CDCl_3$

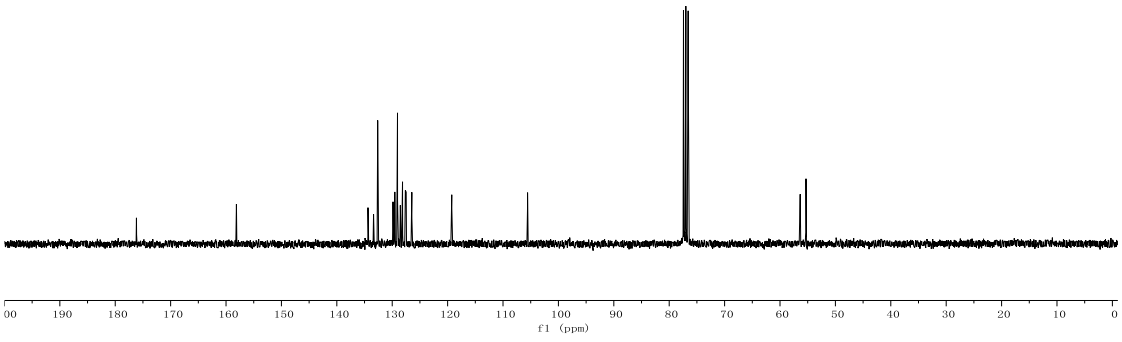


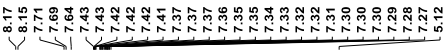


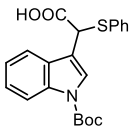


3p

^{13}C NMR, 75 MHz, $CDCl_3$

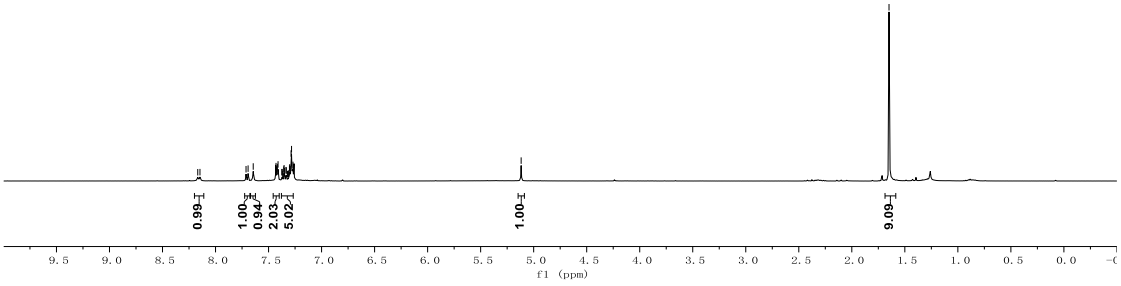


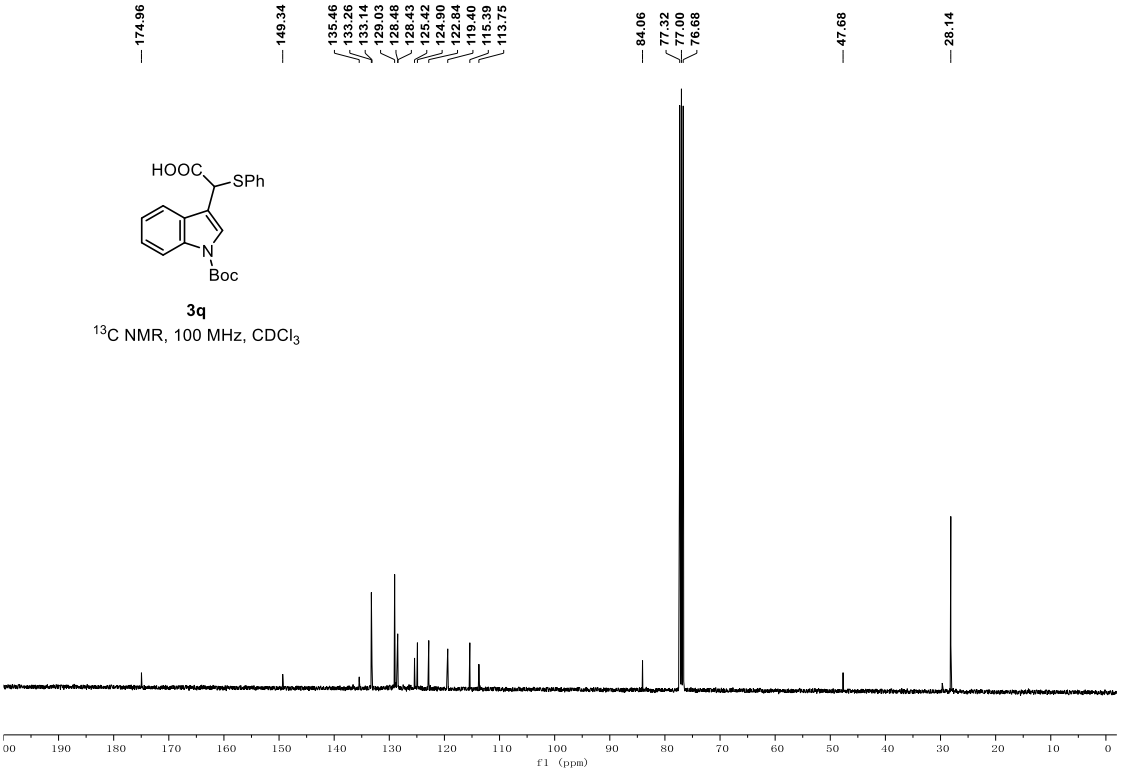




3q

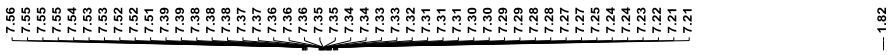
^{1}H NMR, 400 MHz, $CDCl_3$

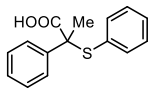




3q

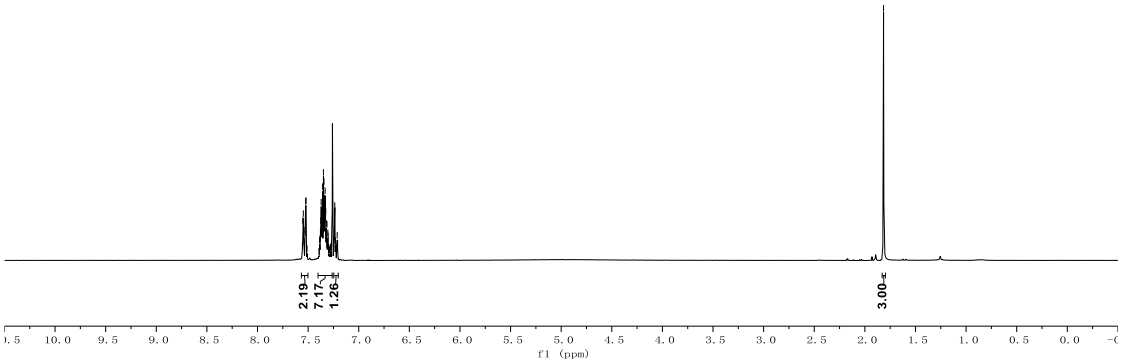
^{13}C NMR, 100 MHz, $CDCl_3$

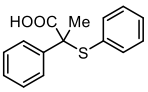




3r

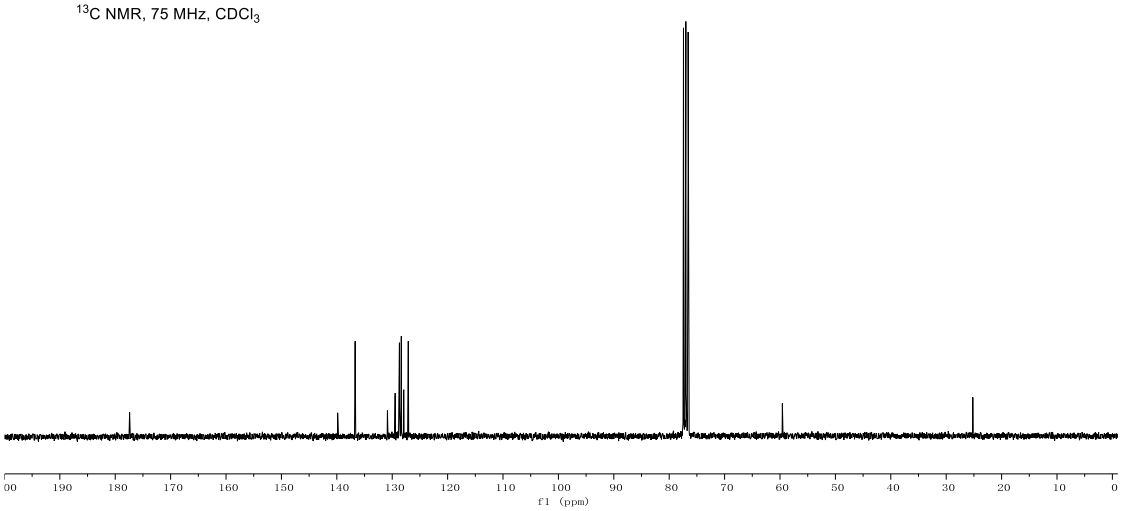
^{1}H NMR, 300 MHz, $CDCl_3$

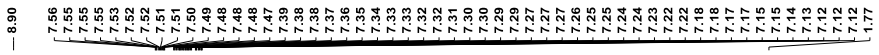


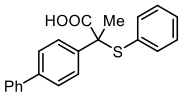


3r

^{13}C NMR, 75 MHz, $CDCl_3$

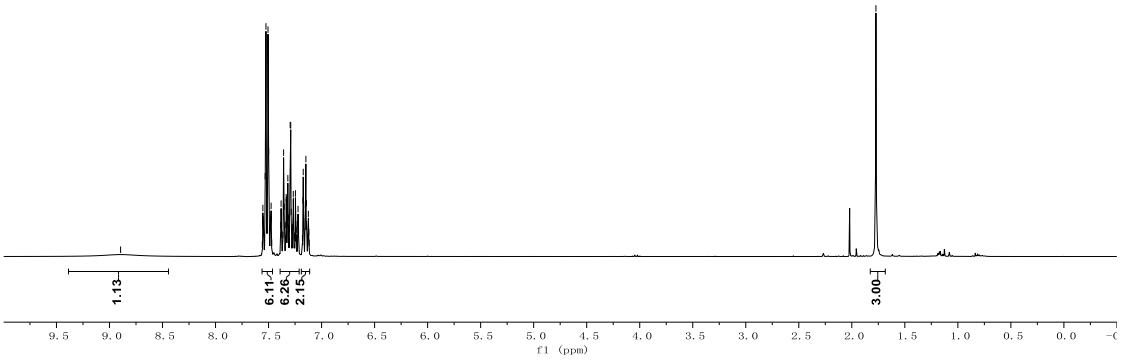


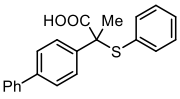




3s

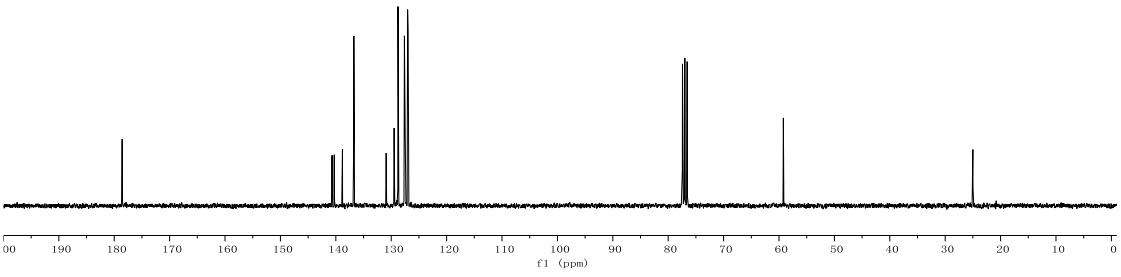
^{1}H NMR, 300 MHz, $CDCl_3$

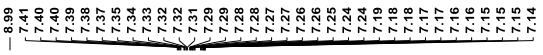


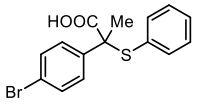


3s

^{13}C NMR, 75 MHz, $CDCl_3$

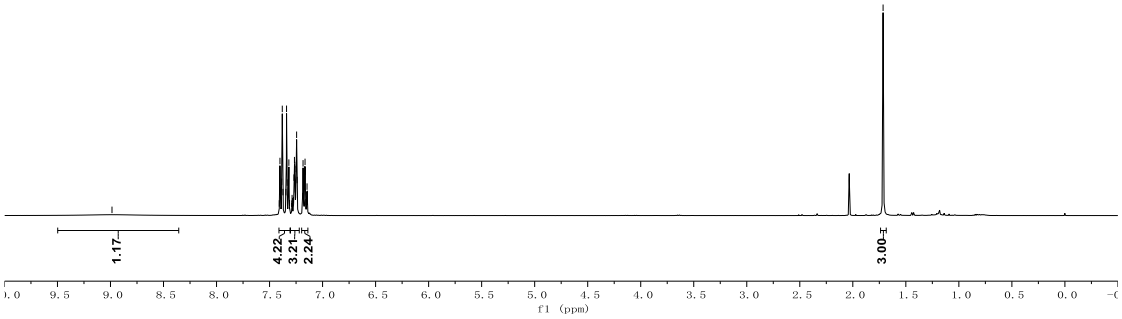


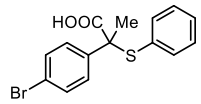




3t

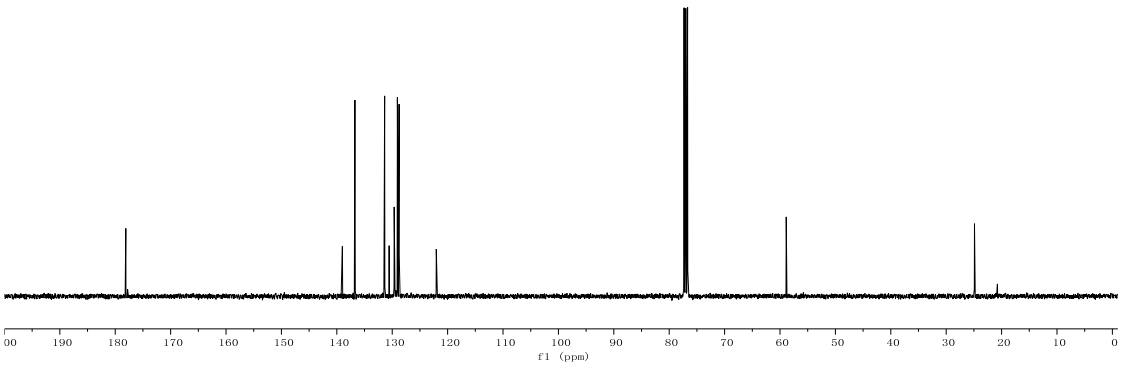
^{1}H NMR, 400 MHz, $CDCl_3$

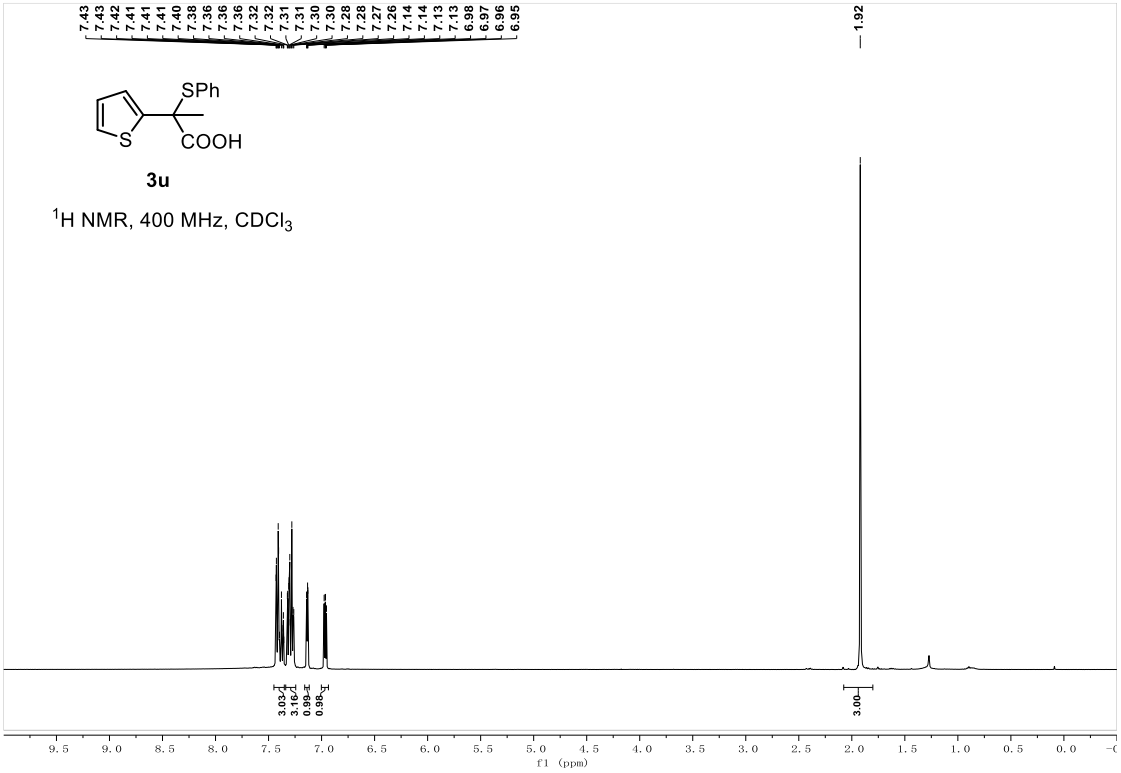




3t

^{13}C NMR, 101 MHz, $CDCl_3$

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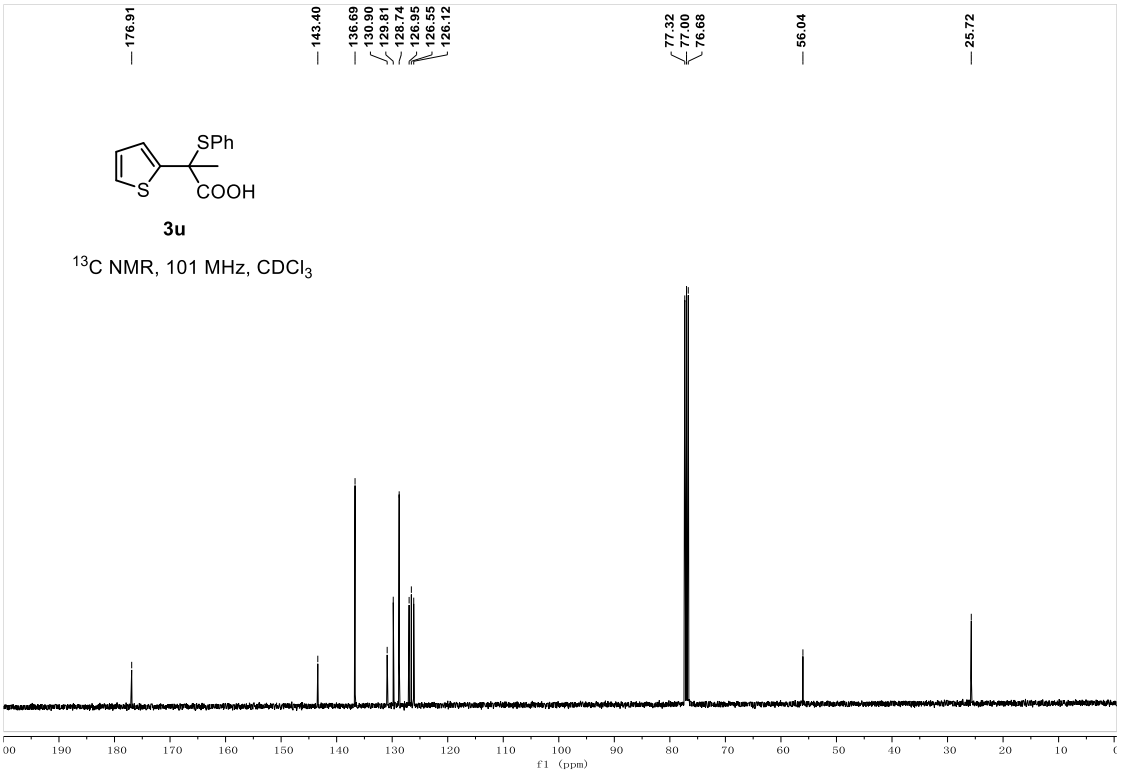
7.26
7.14
7.14
7.13
7.13
6.98
6.97
6.96
6.95
1.92
SPh
S
COOH
3u
1H NMR, 400 MHz, CDCl3
3.03
3.16
0.99
0.98
3.00
f1 (ppm)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76.68
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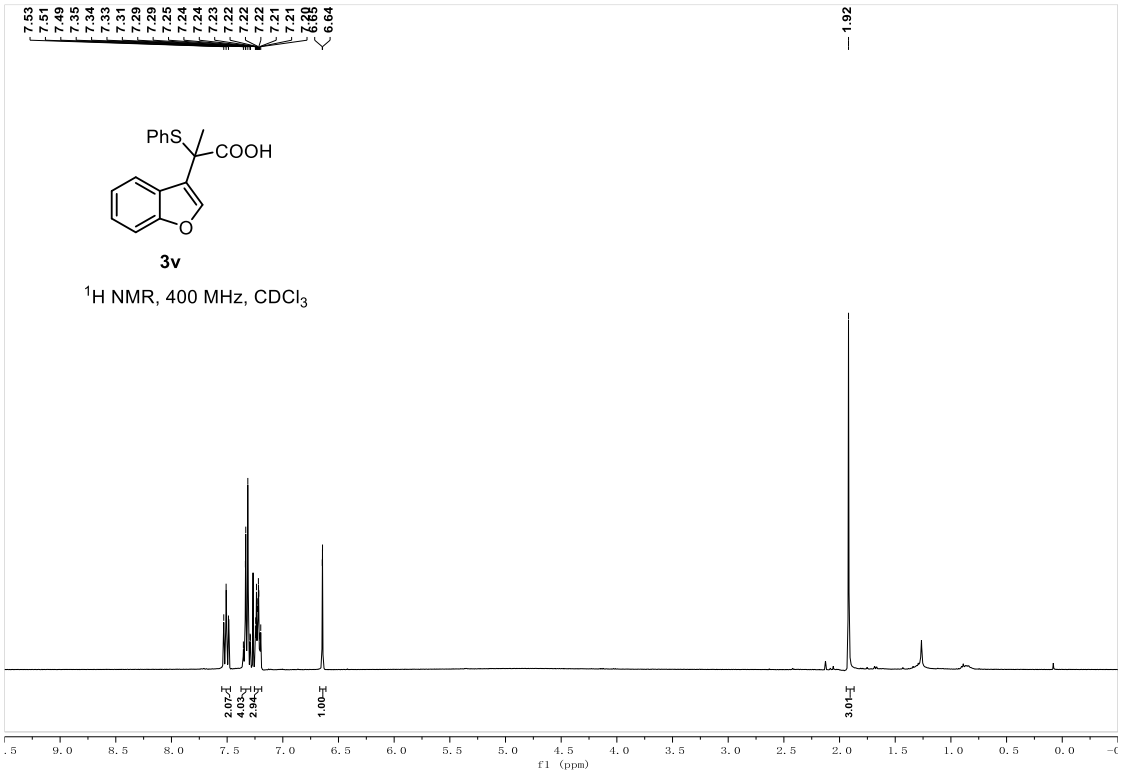
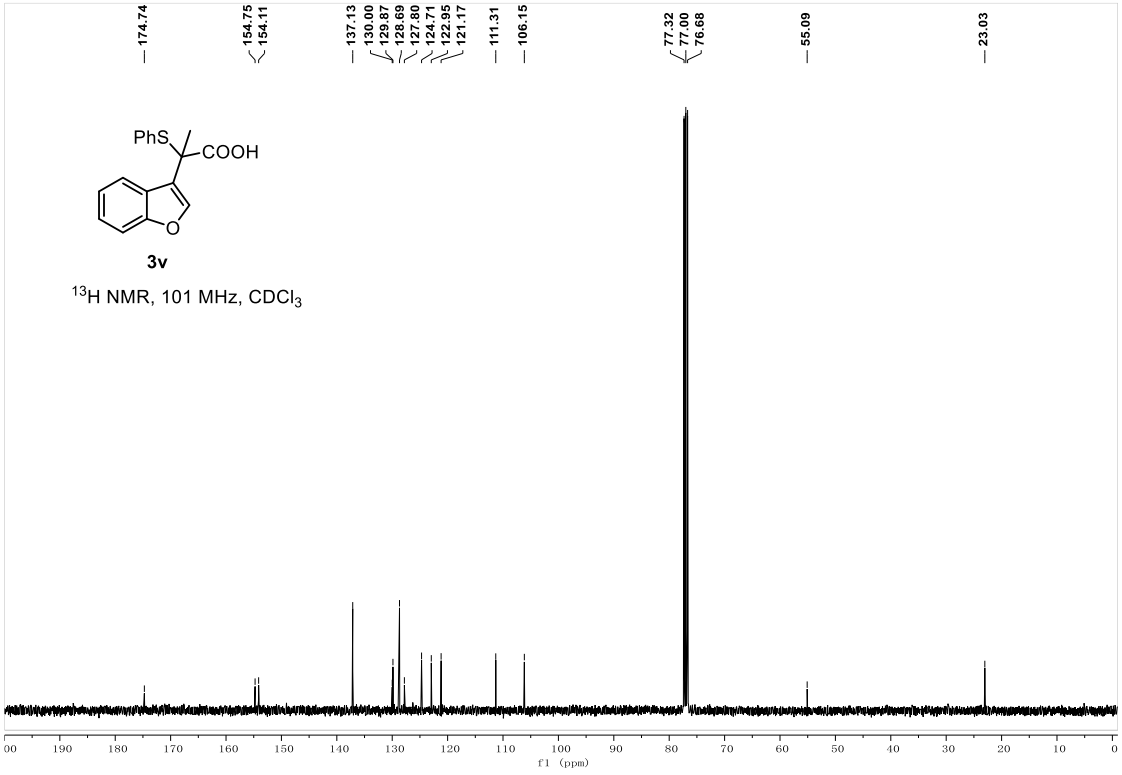
25.72
SPh
S
COOH
3u
13C NMR, 101 MHz, CDCl3
f1 (ppm)



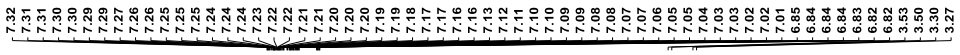
3v

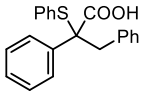
^{1}H NMR, 400 MHz, $CDCl_3$



3v

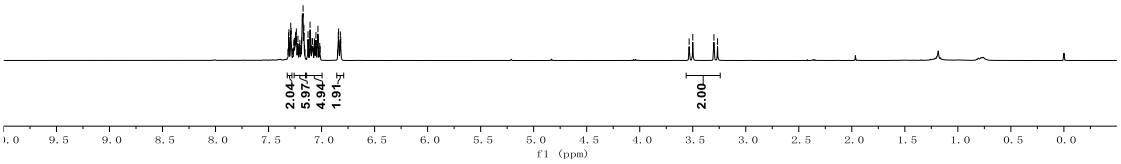
^{13}H NMR, 101 MHz, $CDCl_3$

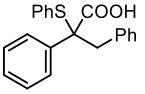




3w

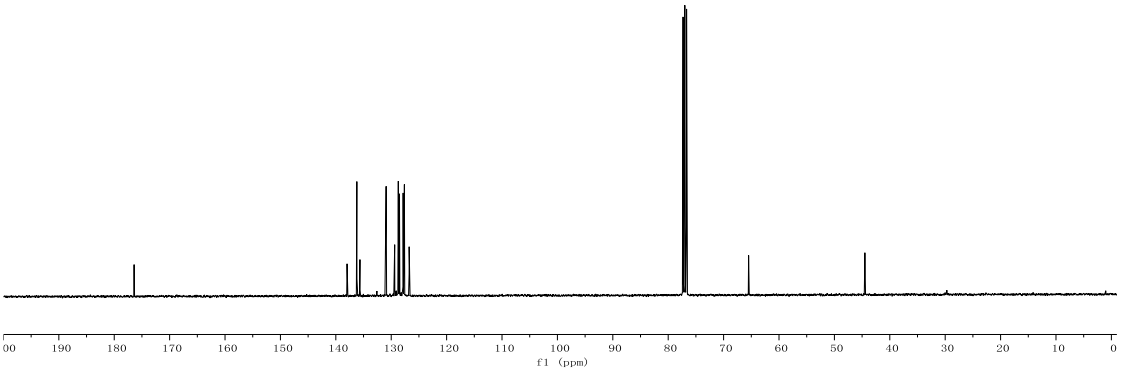
^{1}H NMR, 400 MHz, $CDCl_3$

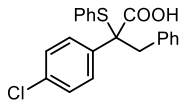




3w

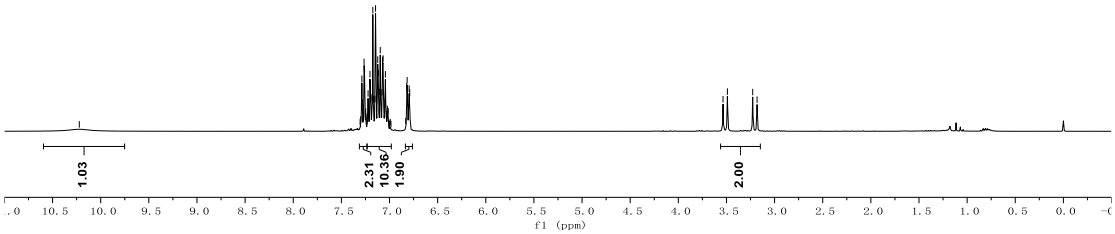
^{13}C NMR, 101 MHz, $CDCl_3$

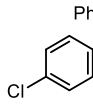




3x

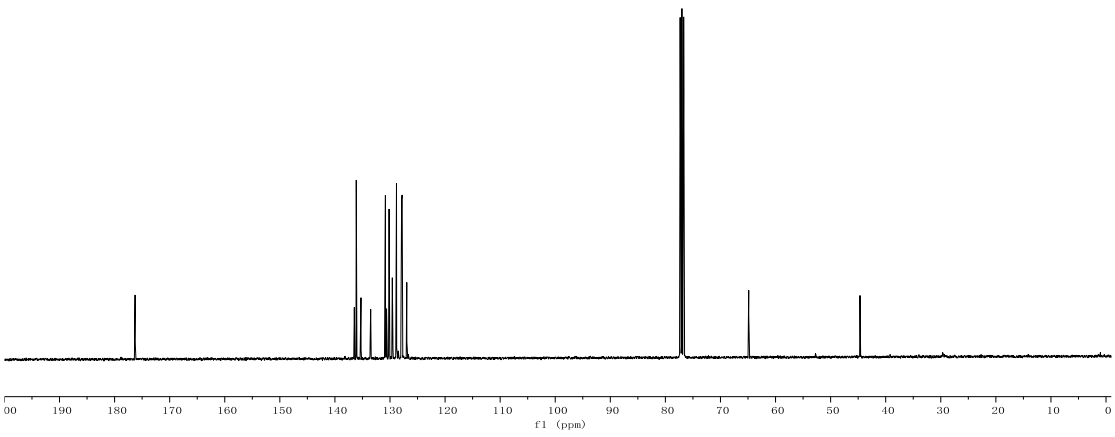
^{1}H NMR, 300 MHz, $CDCl_3$

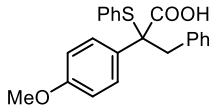




3x

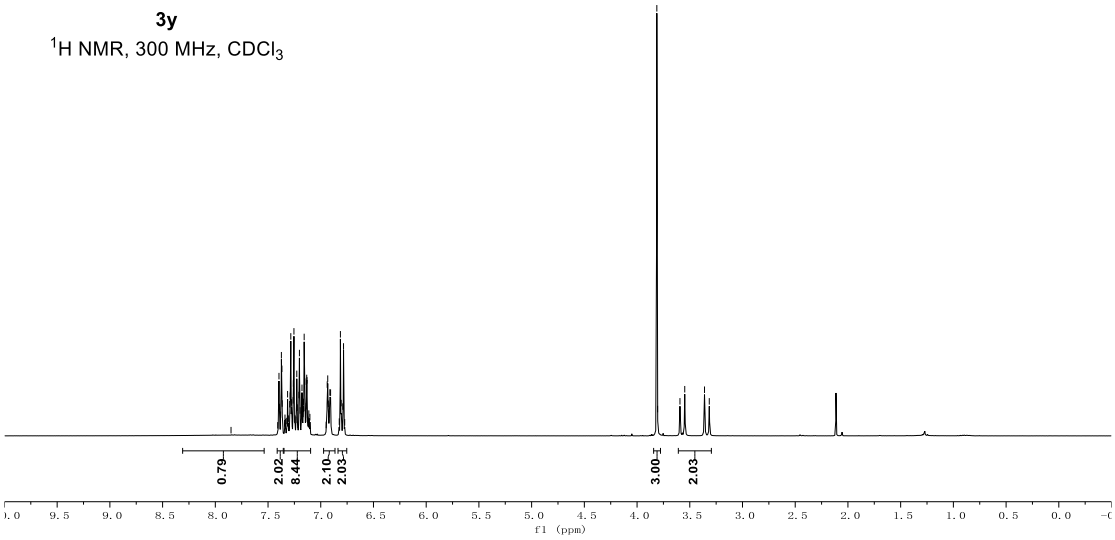
^{13}C NMR, 101 MHz, $CDCl_3$

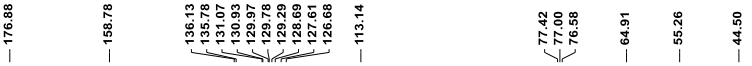


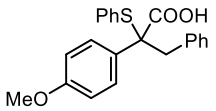


3y

^{1}H NMR, 300 MHz, $CDCl_3$

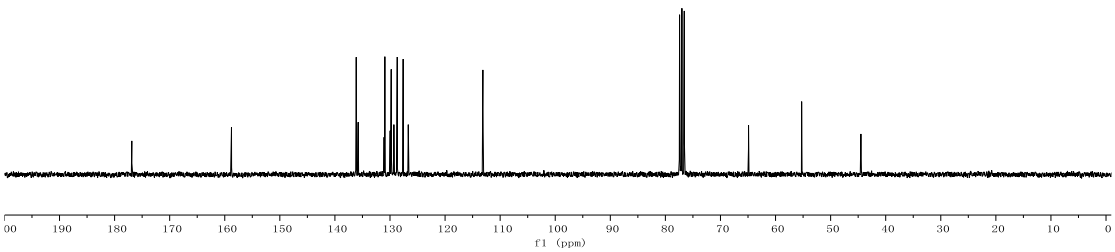


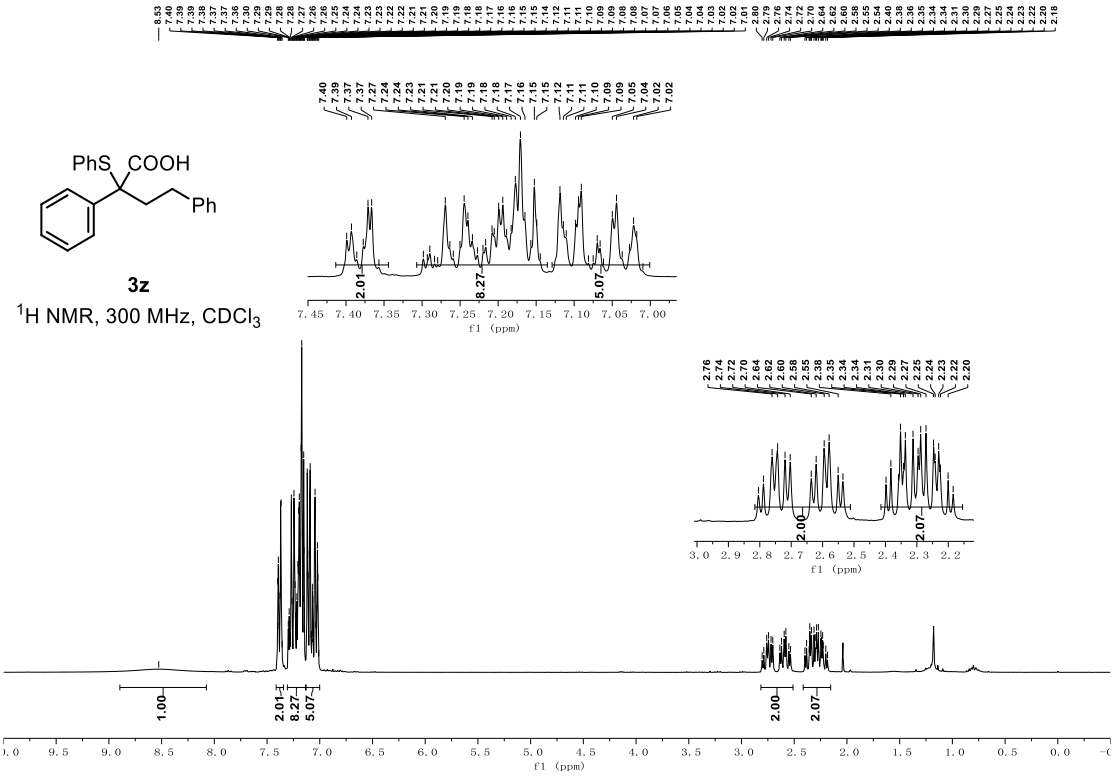




3y

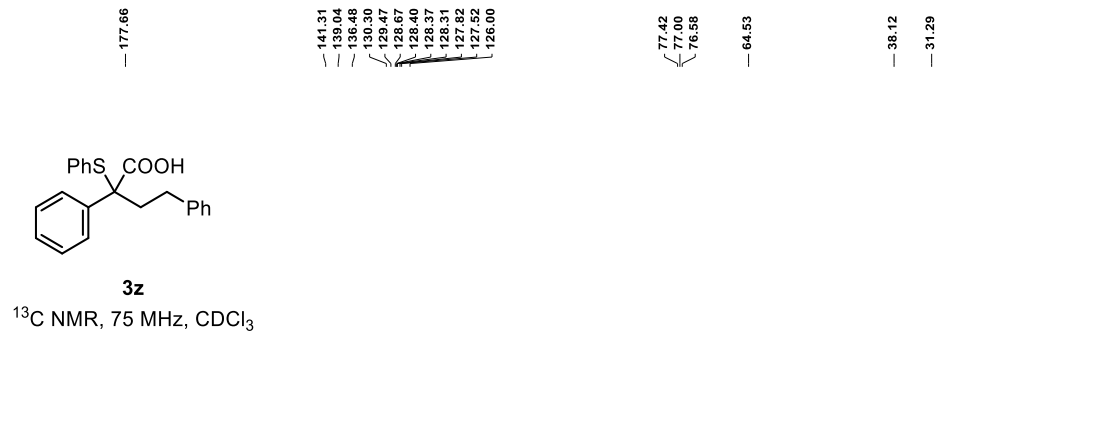
^{13}C NMR, 75 MHz, $CDCl_3$





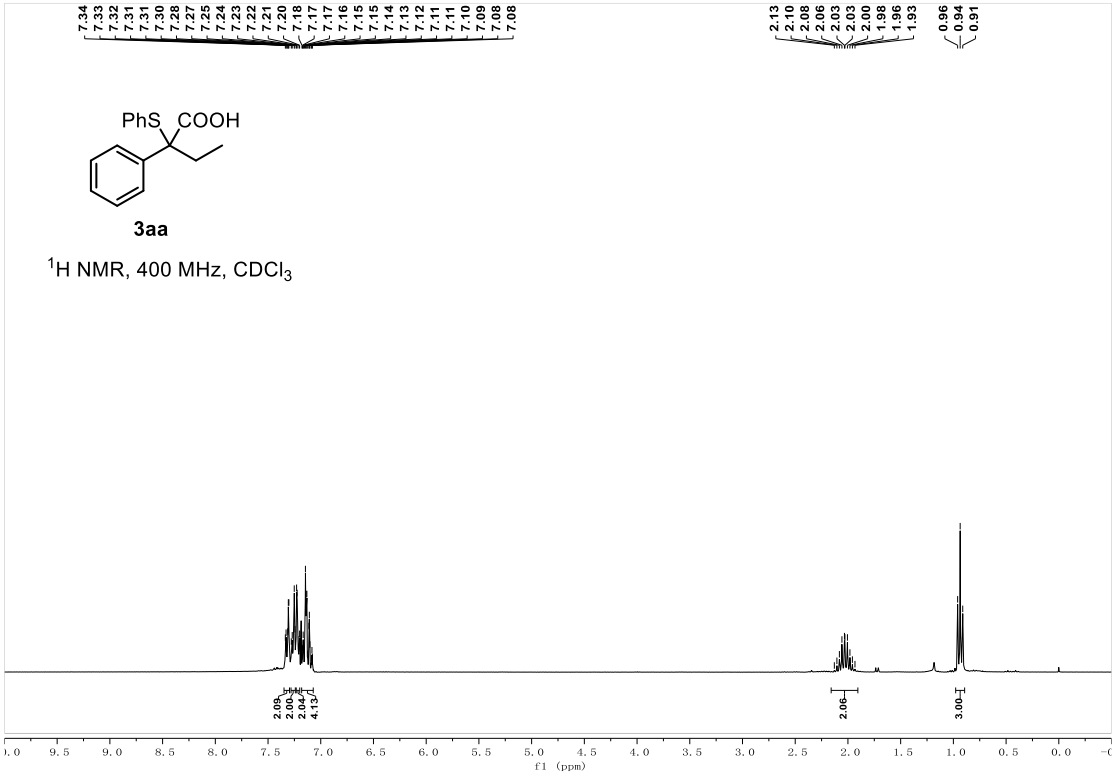
3z

^{1}H NMR, 300 MHz, $CDCl_3$



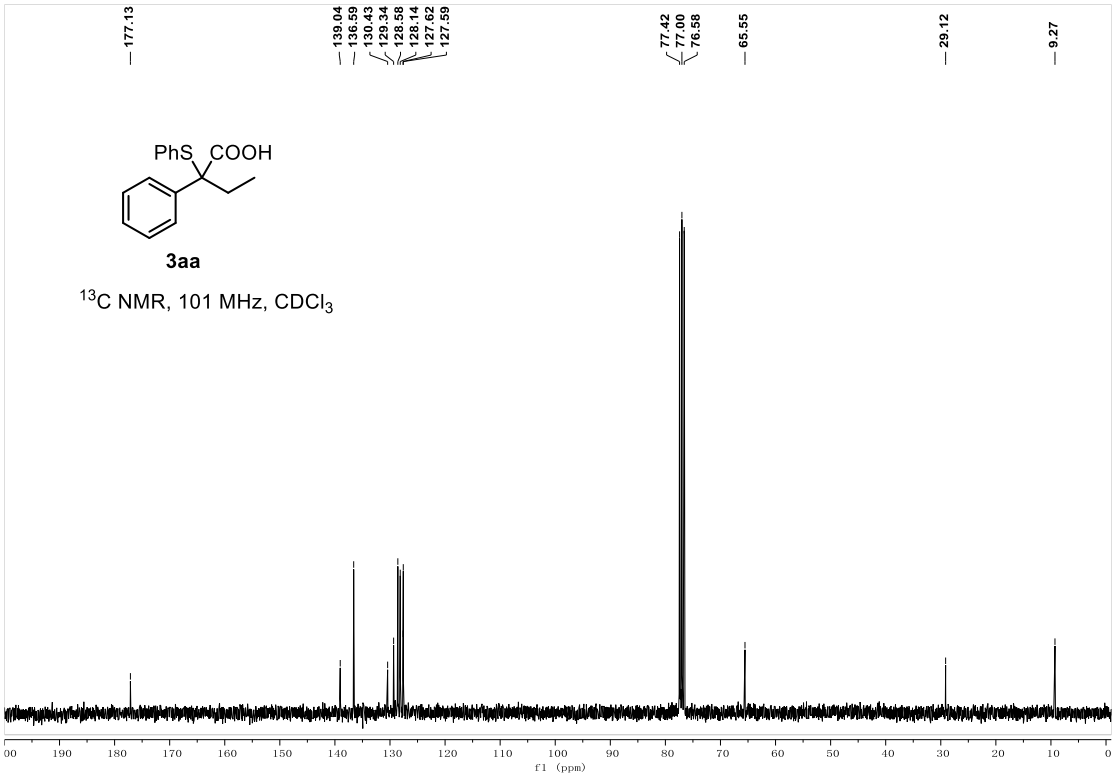
3z

^{13}C NMR, 75 MHz, $CDCl_3$



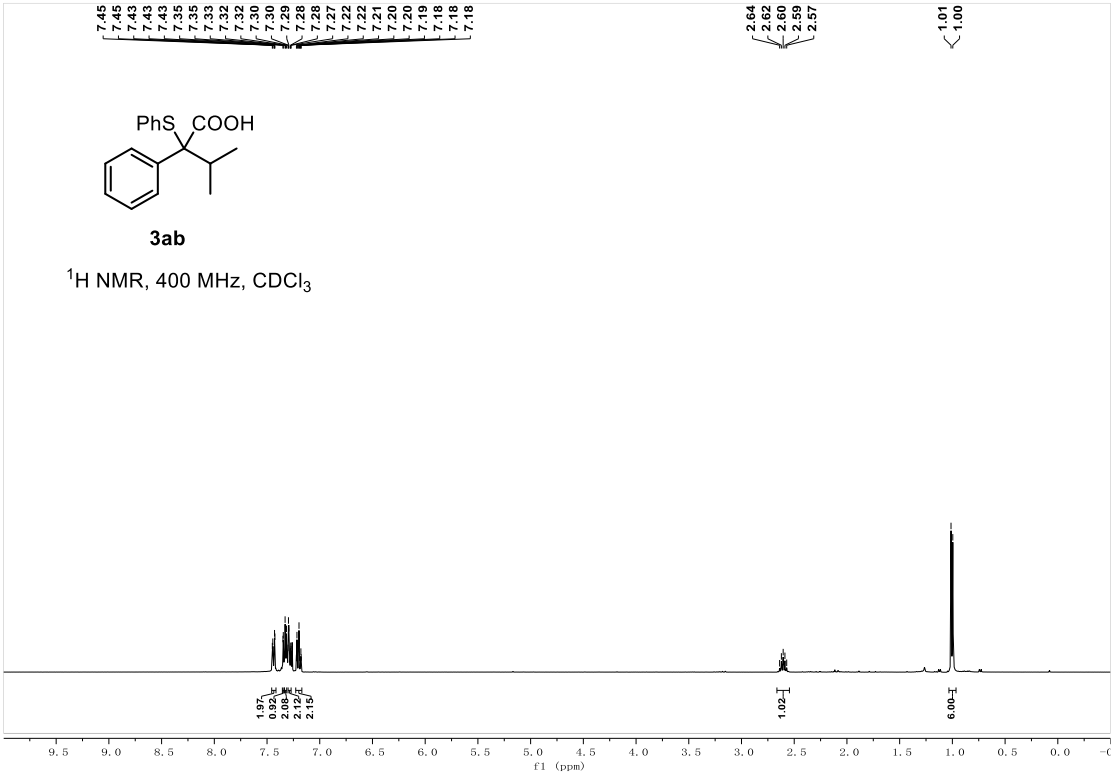
3aa

^{1}H NMR, 400 MHz, $CDCl_3$



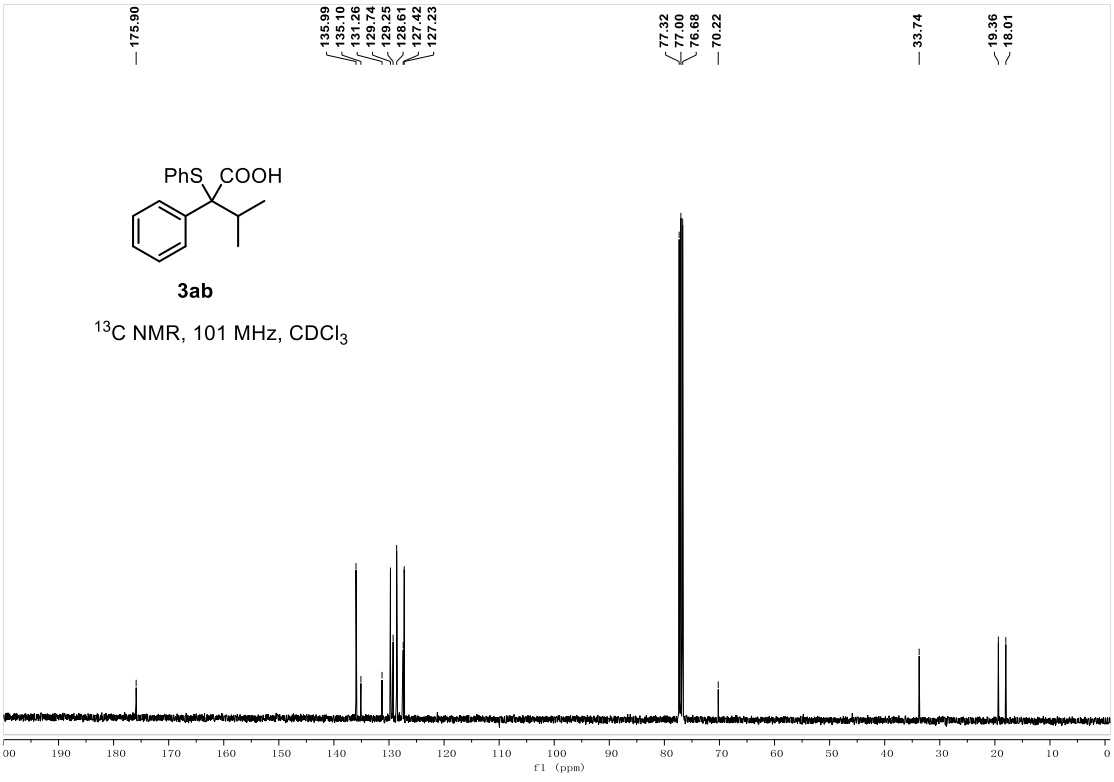
3aa

^{13}C NMR, 101 MHz, $CDCl_3$



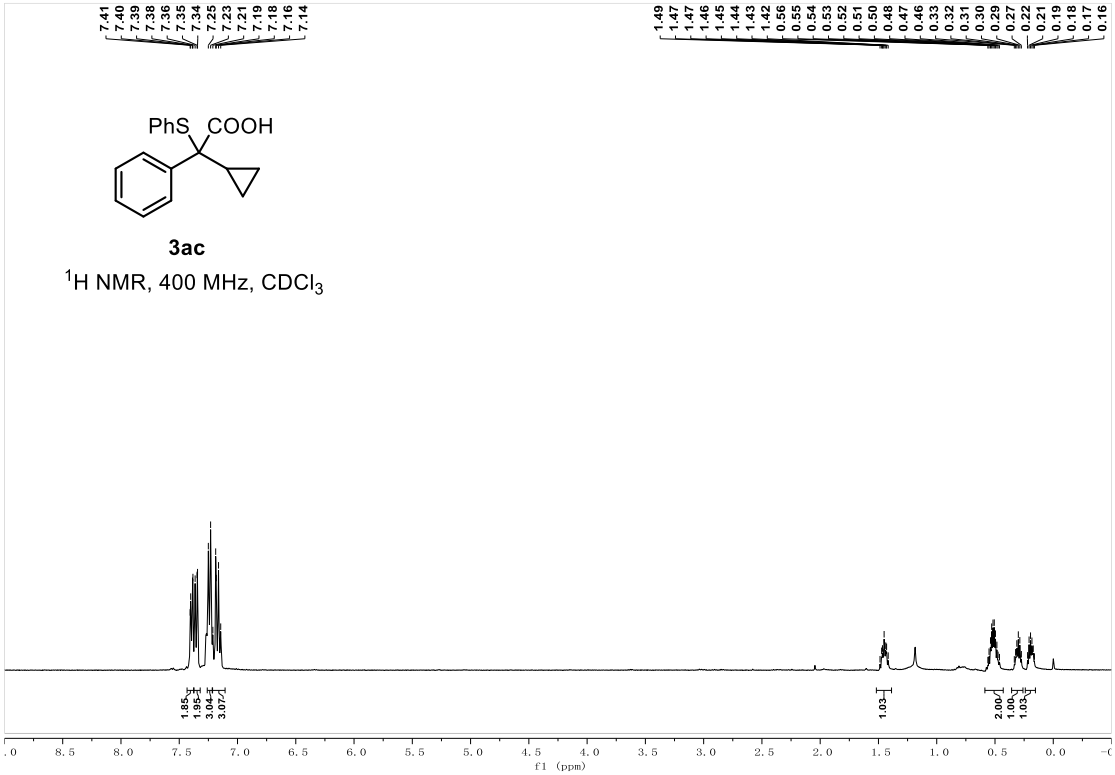
3ab

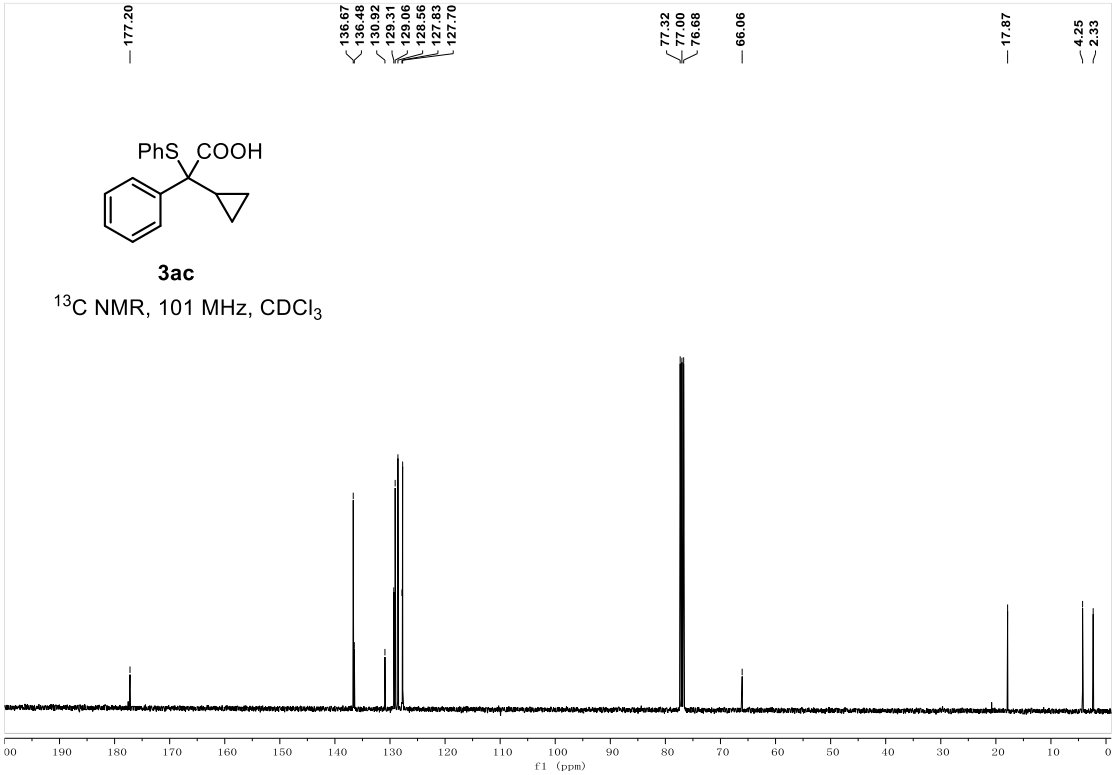
^{1}H NMR, 400 MHz, $CDCl_3$

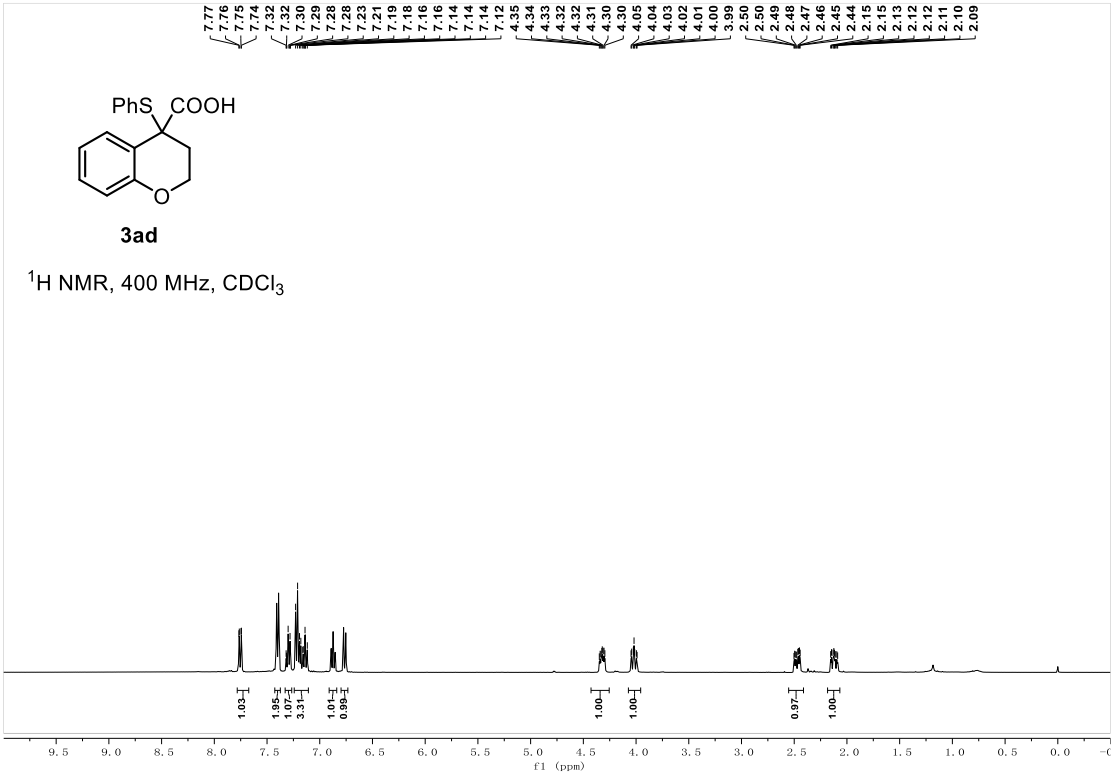


3ab

^{13}C NMR, 101 MHz, $CDCl_3$

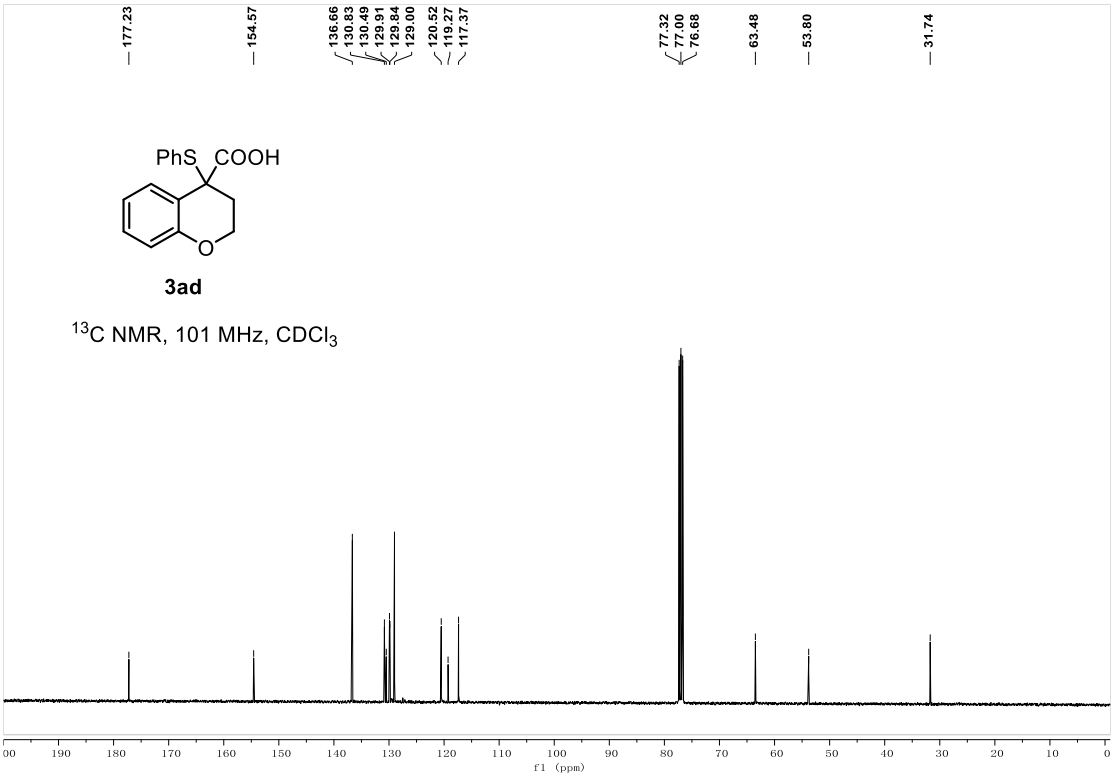

7.41
7.40
7.39
7.38
7.36
7.35
7.34
7.25
7.23
7.21
7.19
7.18
7.16
7.14
1.49
1.47
1.47
1.46
1.45
1.44
1.43
1.42
0.56
0.55
0.54
0.53
0.52
0.51
0.50
0.48
0.47
0.46
0.33
0.32
0.31
0.30
0.29
0.27
0.22
0.21
0.19
0.18
0.17
0.16
PhS COOH
3ac
1H NMR, 400 MHz, CDCl3
1.85
1.95
3.04
3.07
1.03
2.00
1.00
1.05
f1 (ppm)


177.20
136.67
136.48
130.92
129.31
129.06
128.56
127.83
127.70
77.32
77.00
76.68
66.06
17.87
4.25
2.33
PhS COOH
3ac
13C NMR, 101 MHz, CDCl3
f1 (ppm)



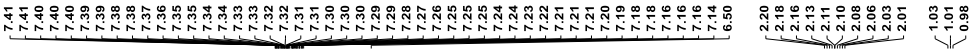
3ad

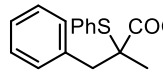
^{1}H NMR, 400 MHz, $CDCl_3$



3ad

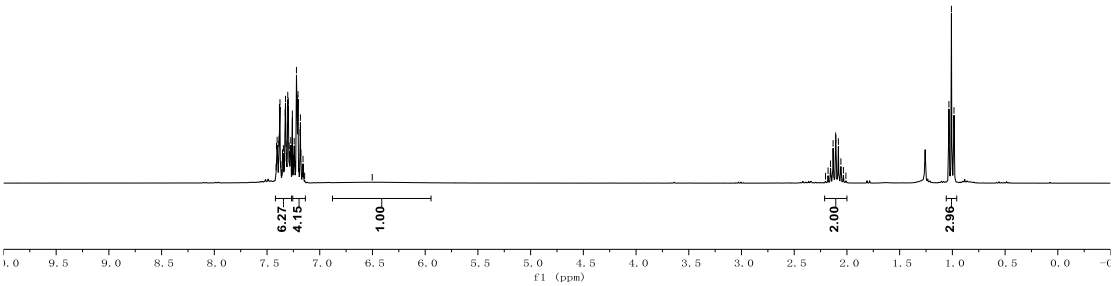
^{13}C NMR, 101 MHz, $CDCl_3$

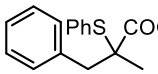




3ae

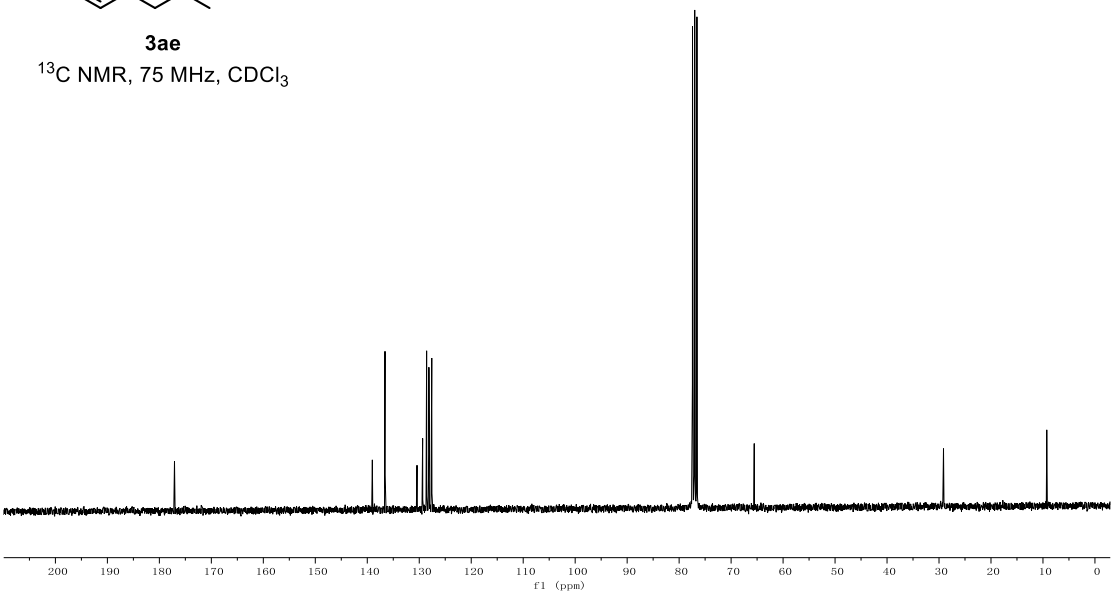
^{1}H NMR, 300 MHz, $CDCl_3$

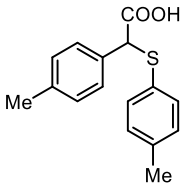




3ae

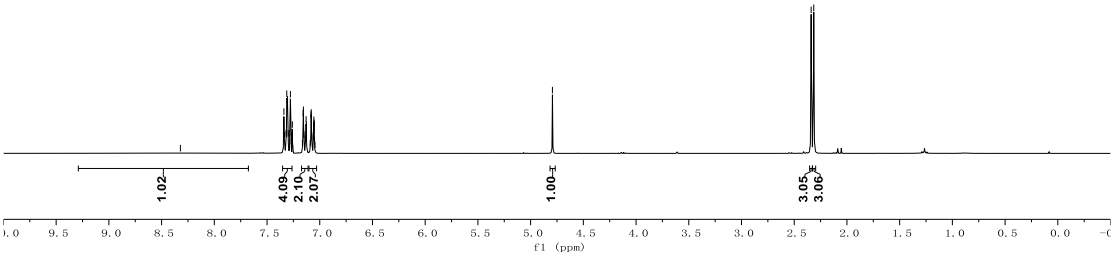
^{13}C NMR, 75 MHz, $CDCl_3$

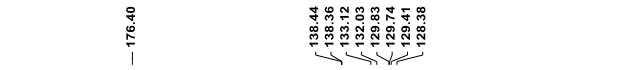


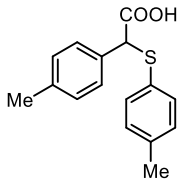


4a

^{1}H NMR, 300 MHz, $CDCl_3$

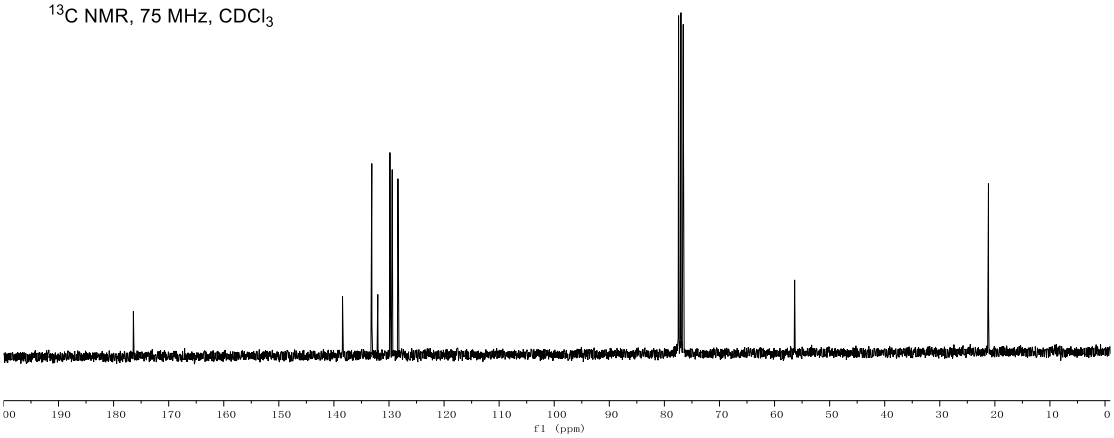


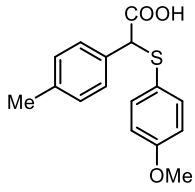




4a

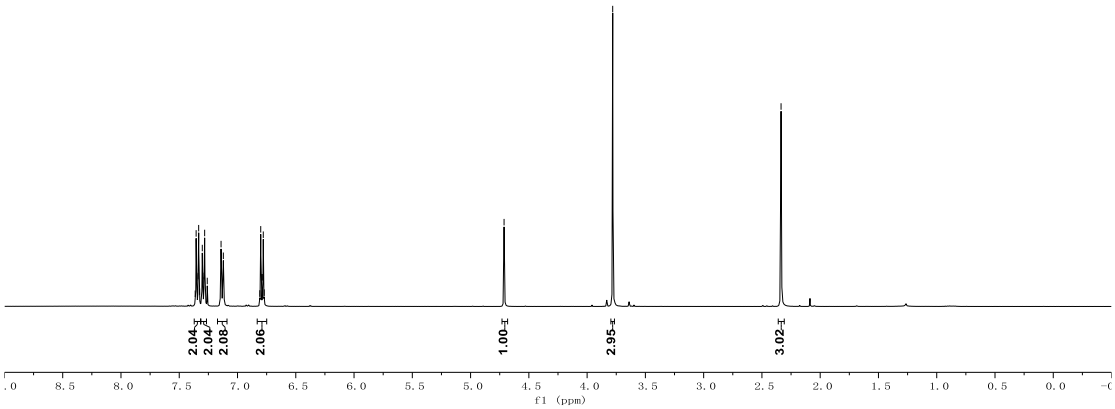
^{13}C NMR, 75 MHz, $CDCl_3$

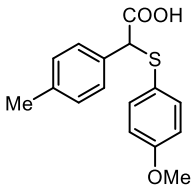




4b

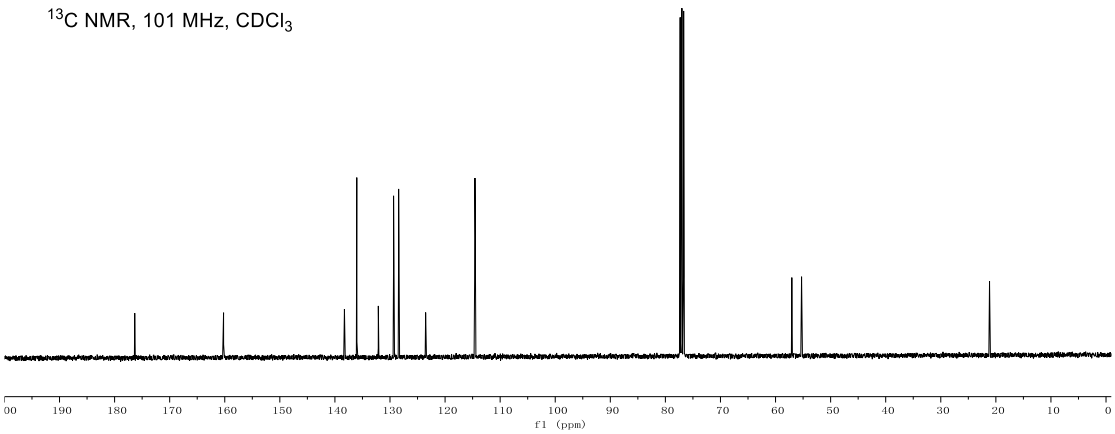
^{1}H NMR, 400 MHz, $CDCl_3$

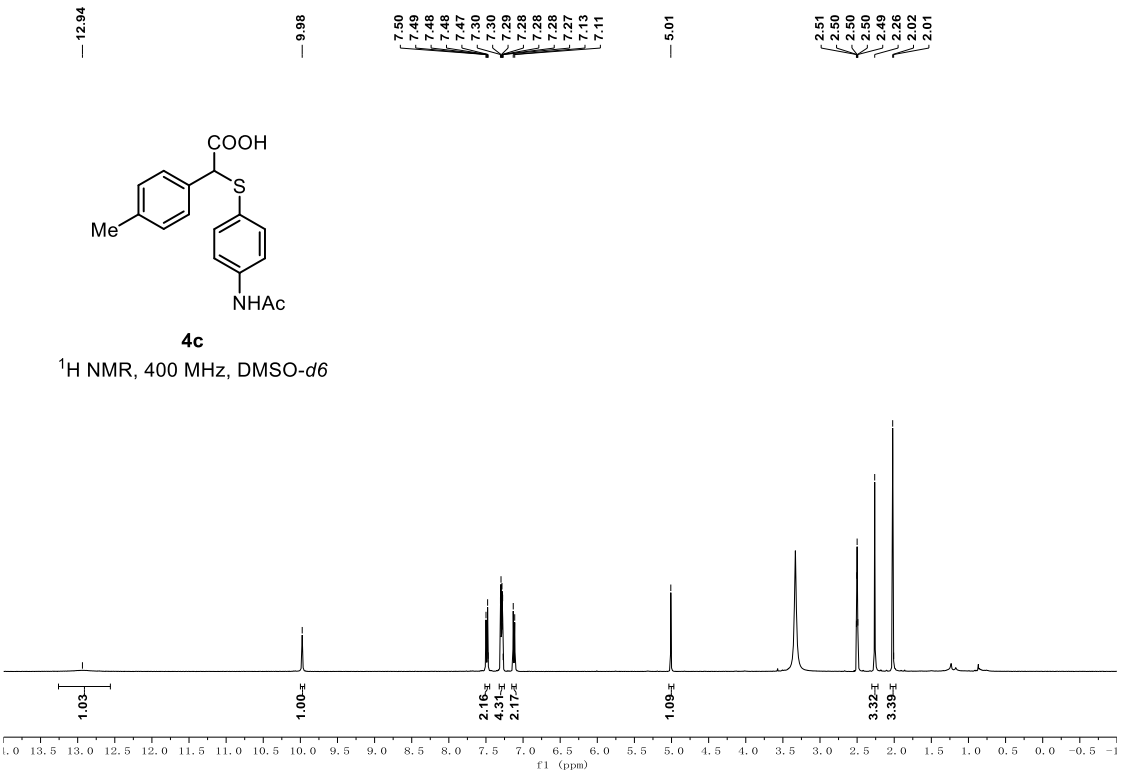




4b

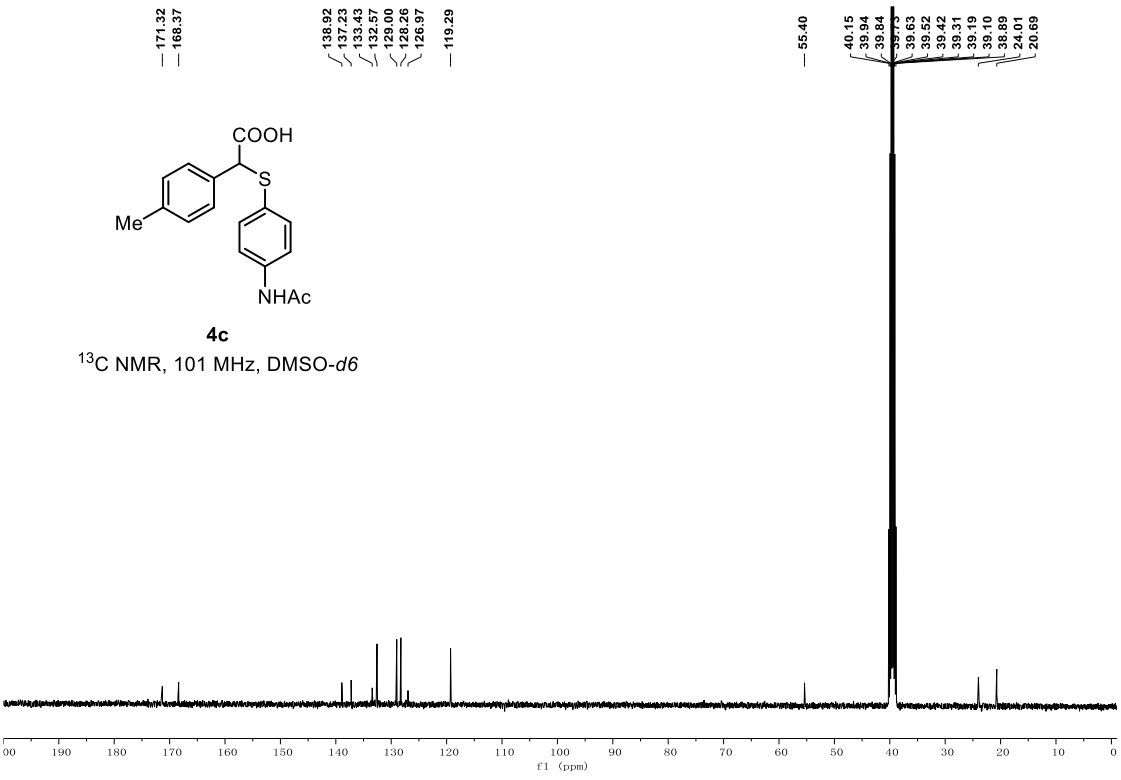
^{13}C NMR, 101 MHz, $CDCl_3$





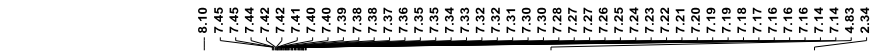
4c

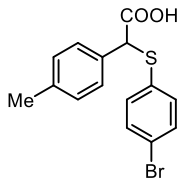
^{1}H NMR, 400 MHz, DMSO-*d6*



4c

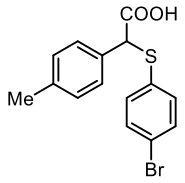
^{13}C NMR, 101 MHz, DMSO-*d6*





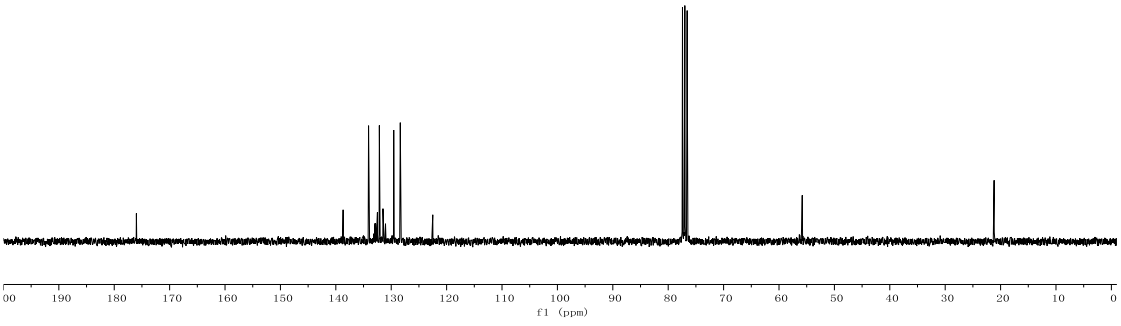
4d

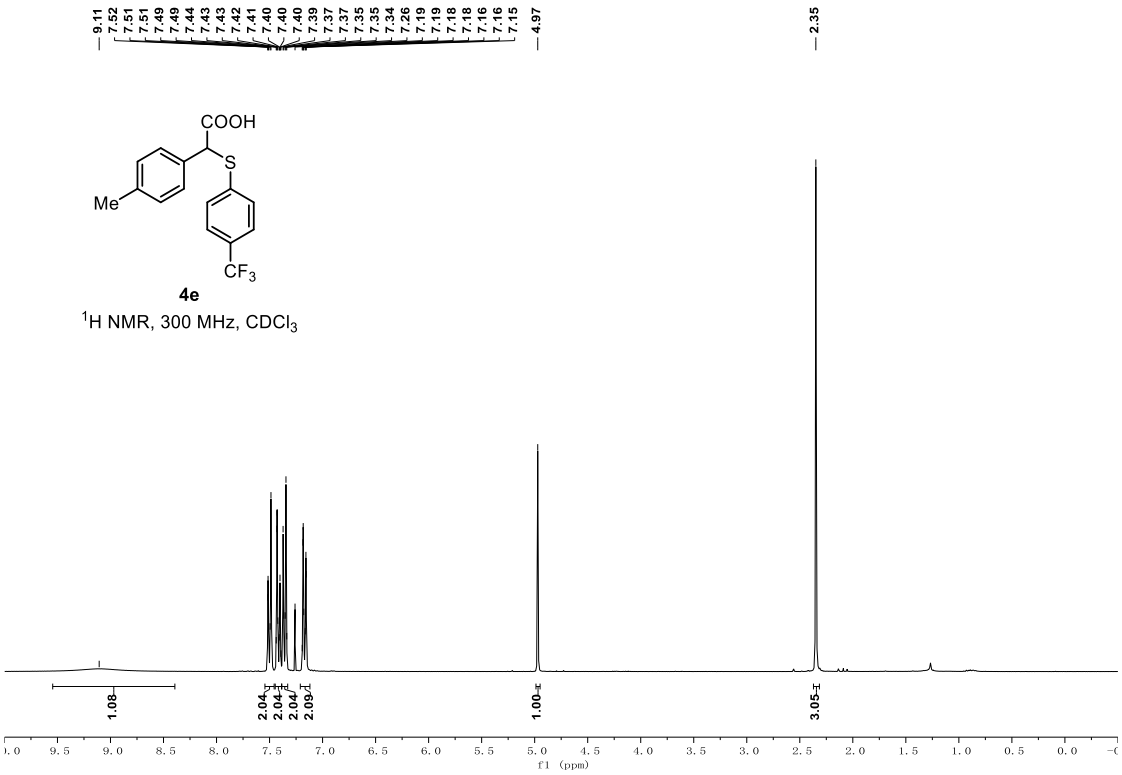
^{1}H NMR, 300 MHz, $CDCl_3$



4d

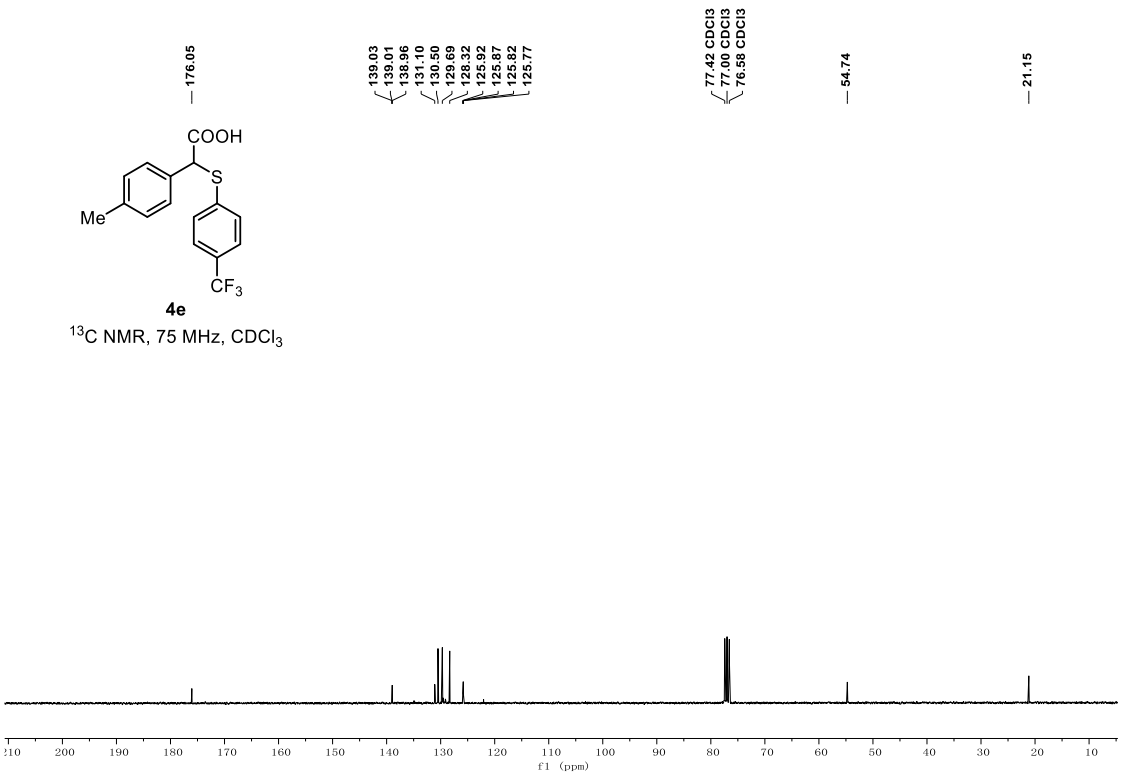
^{13}C NMR, 75 MHz, $CDCl_3$





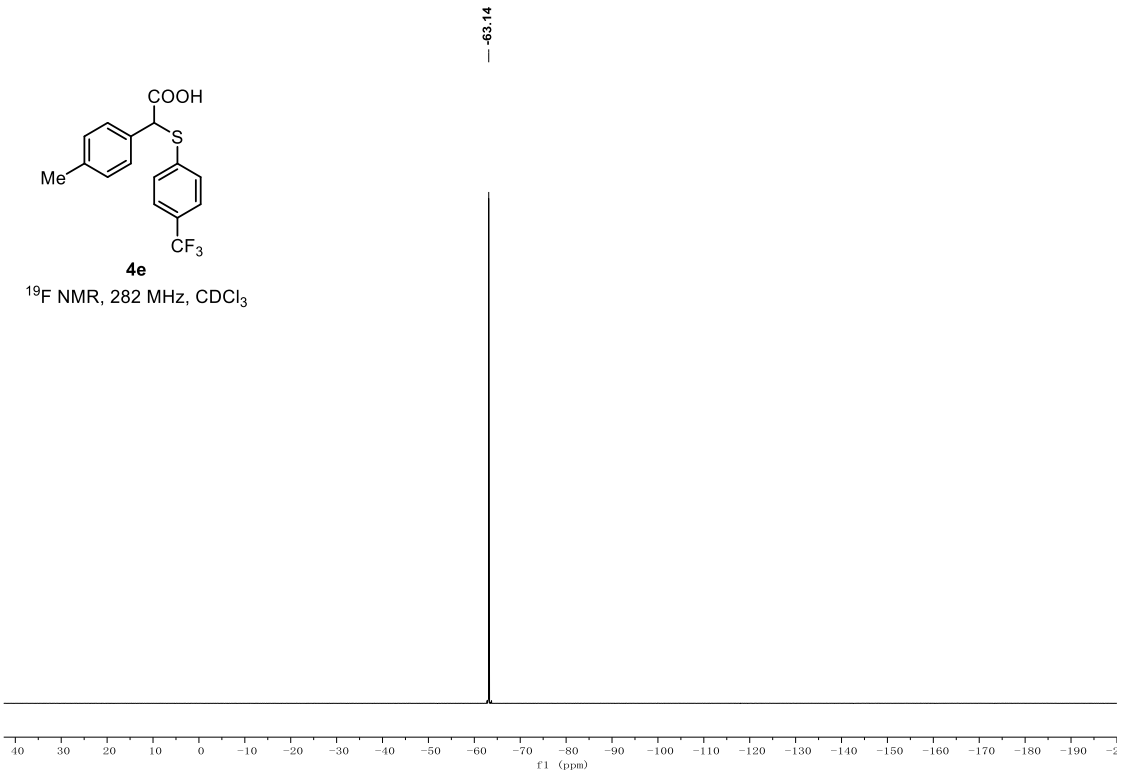
4e

^{1}H NMR, 300 MHz, $CDCl_3$



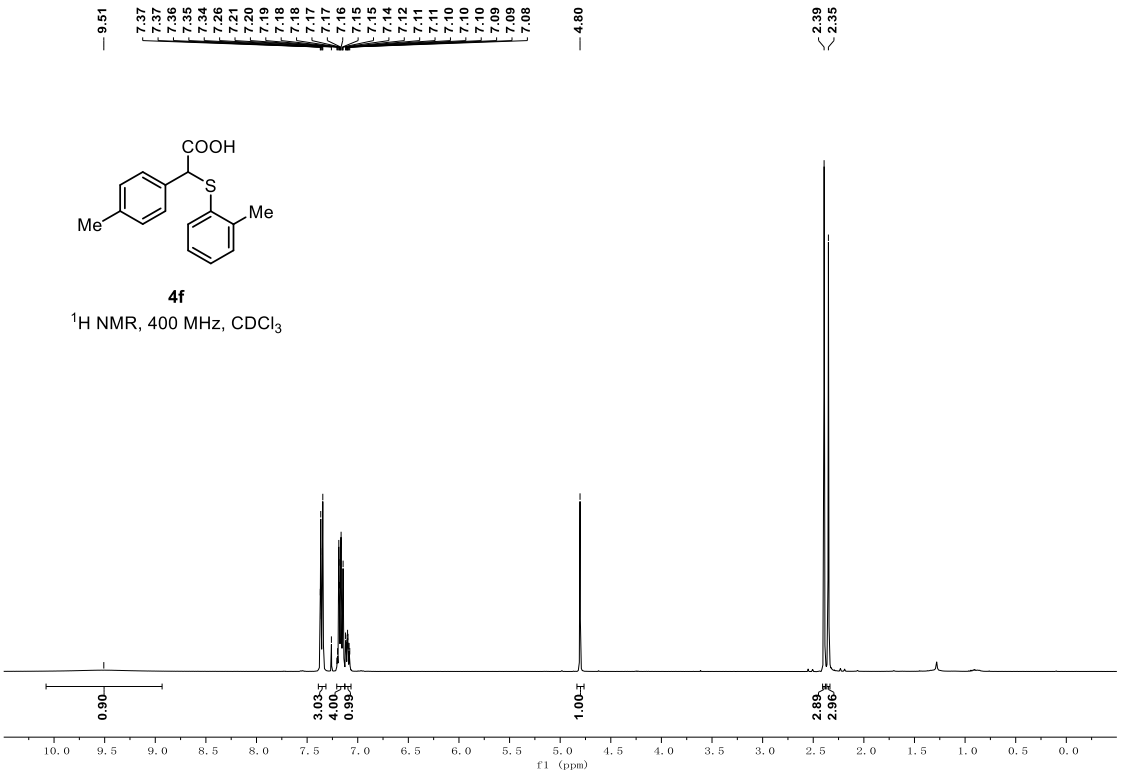
4e

^{13}C NMR, 75 MHz, $CDCl_3$



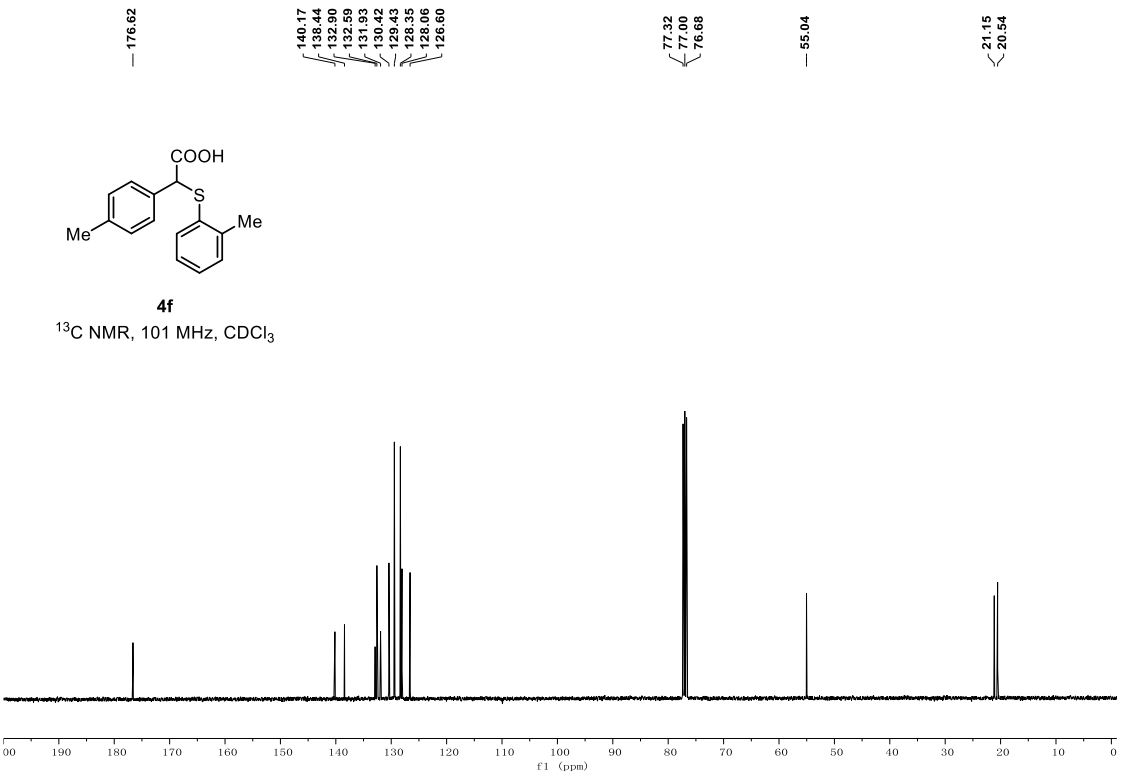
4e

^{19}F NMR, 282 MHz, $CDCl_3$



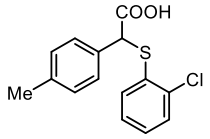
4f

^{1}H NMR, 400 MHz, $CDCl_3$



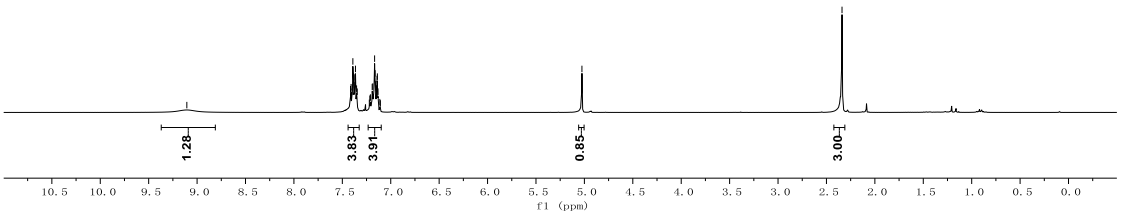
4f

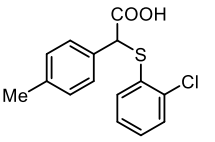
^{13}C NMR, 101 MHz, $CDCl_3$



4g

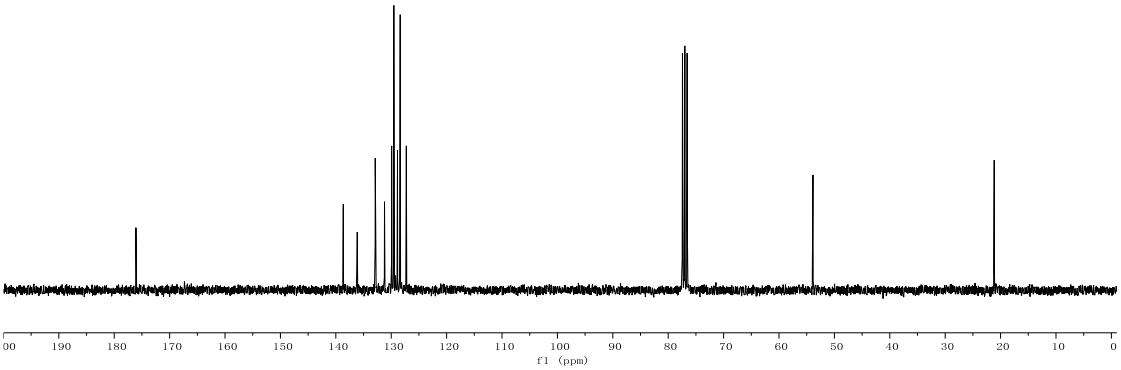
^{1}H NMR, 300 MHz, $CDCl_3$

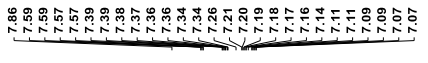


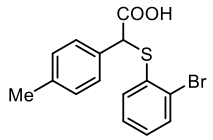


4g

^{13}C NMR, 75 MHz, $CDCl_3$

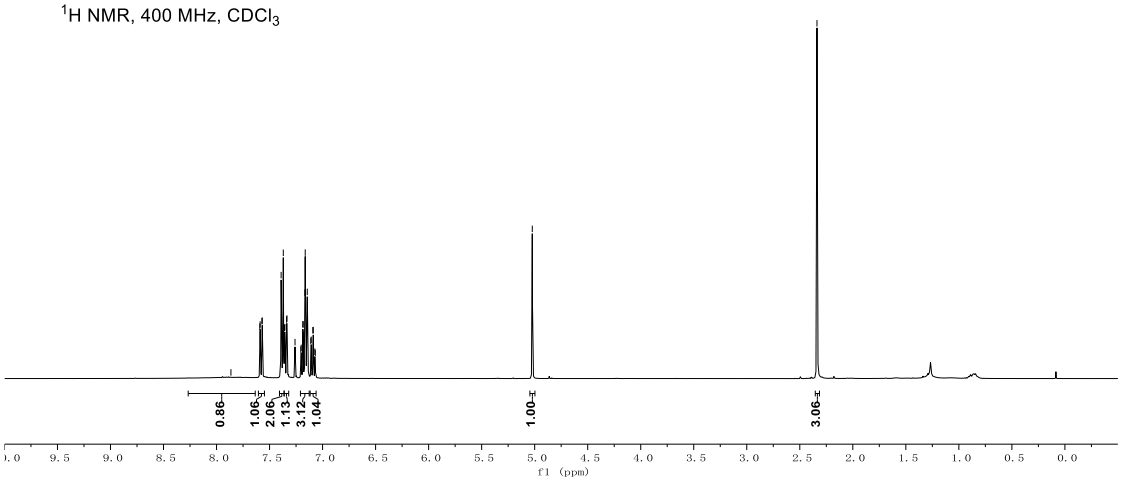


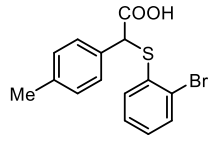




4h

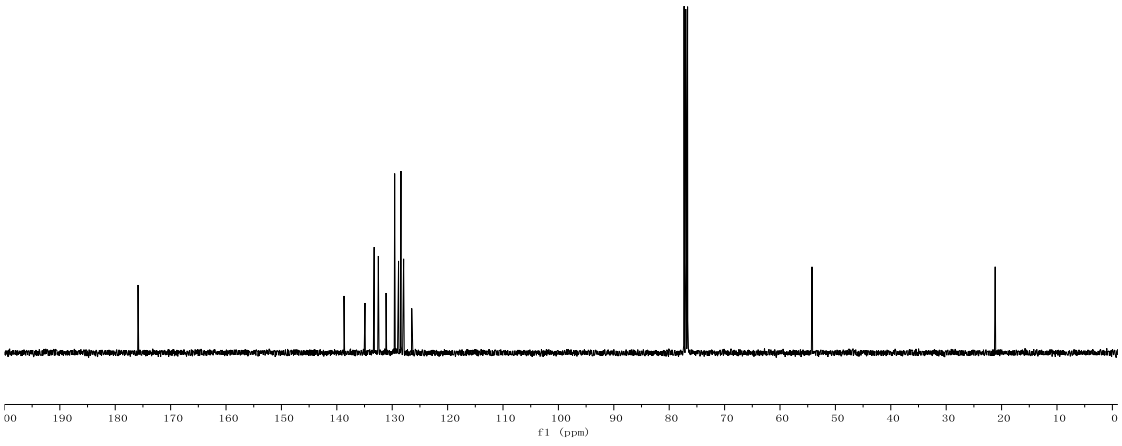
^{1}H NMR, 400 MHz, $CDCl_3$

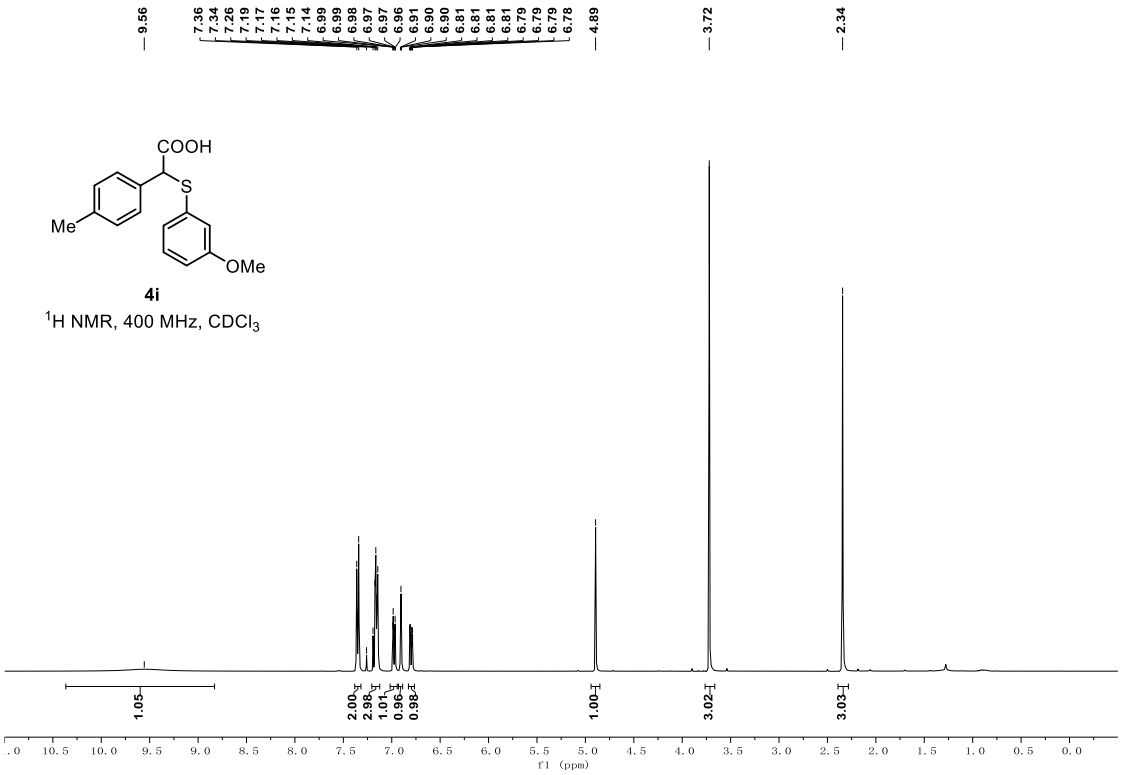




4h

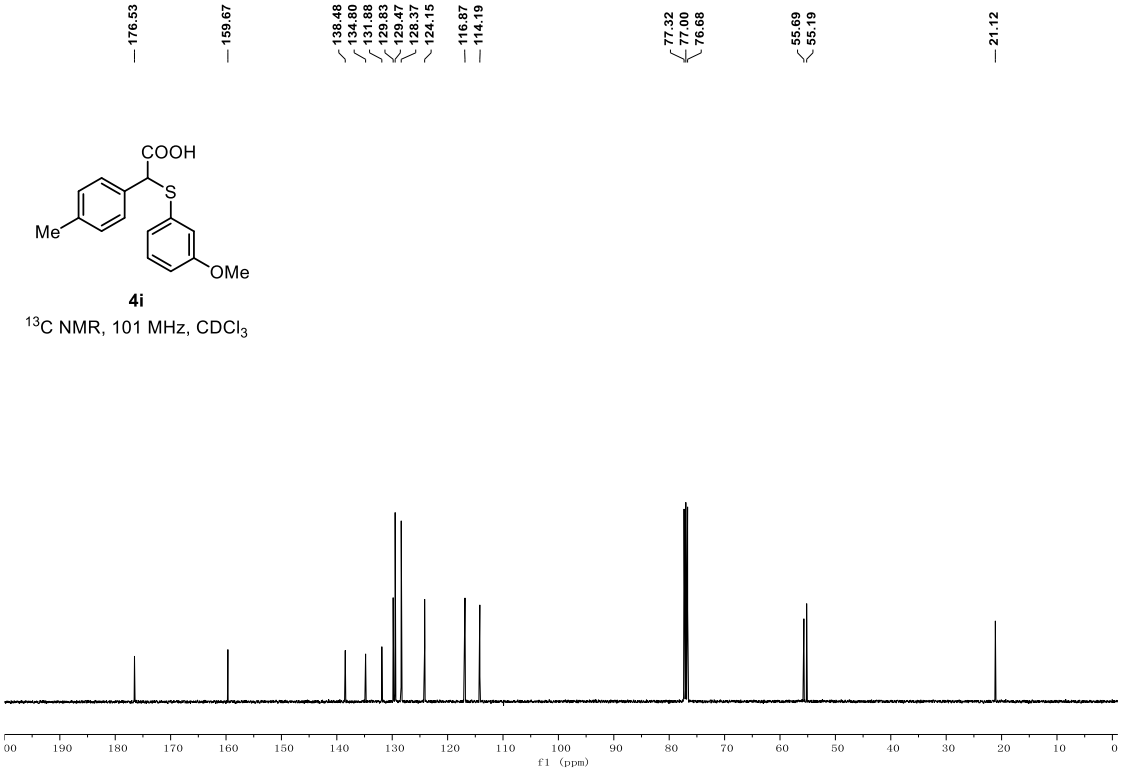
^{13}C NMR, 101 MHz, $CDCl_3$





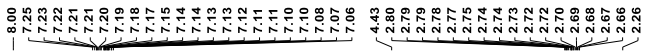
4i

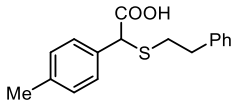
^{1}H NMR, 400 MHz, $CDCl_3$



4i

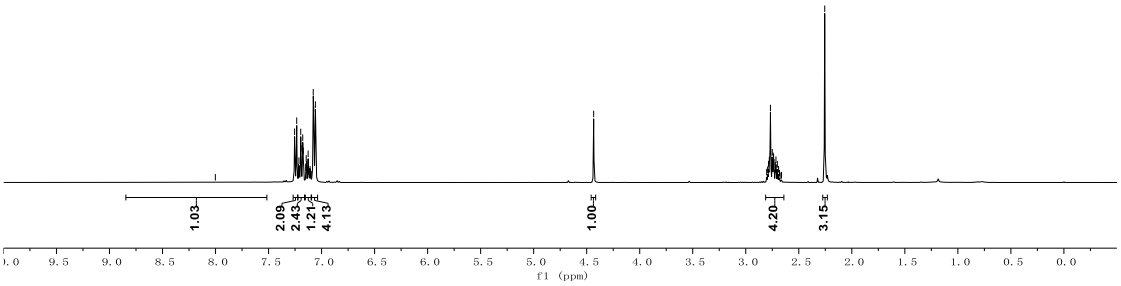
^{13}C NMR, 101 MHz, $CDCl_3$

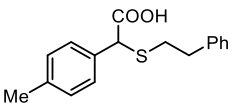




4j

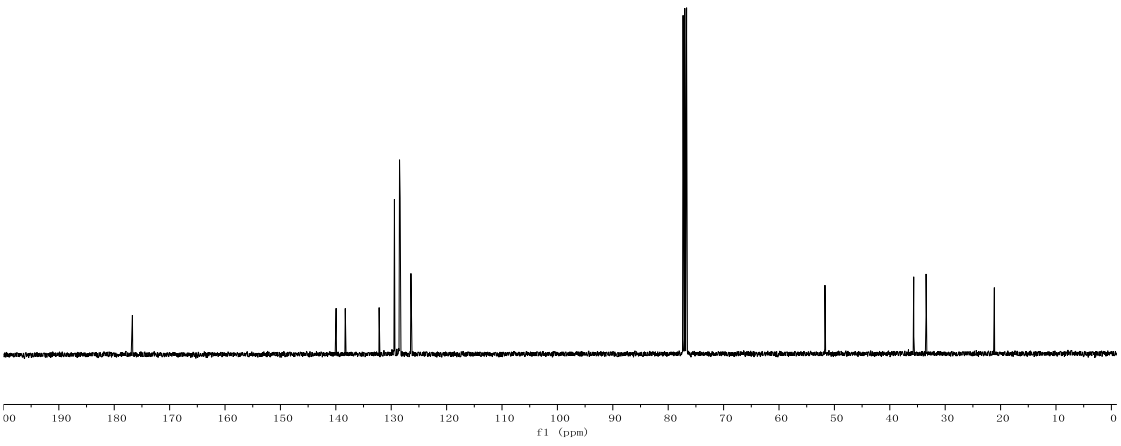
^{1}H NMR, 400 MHz, $CDCl_3$

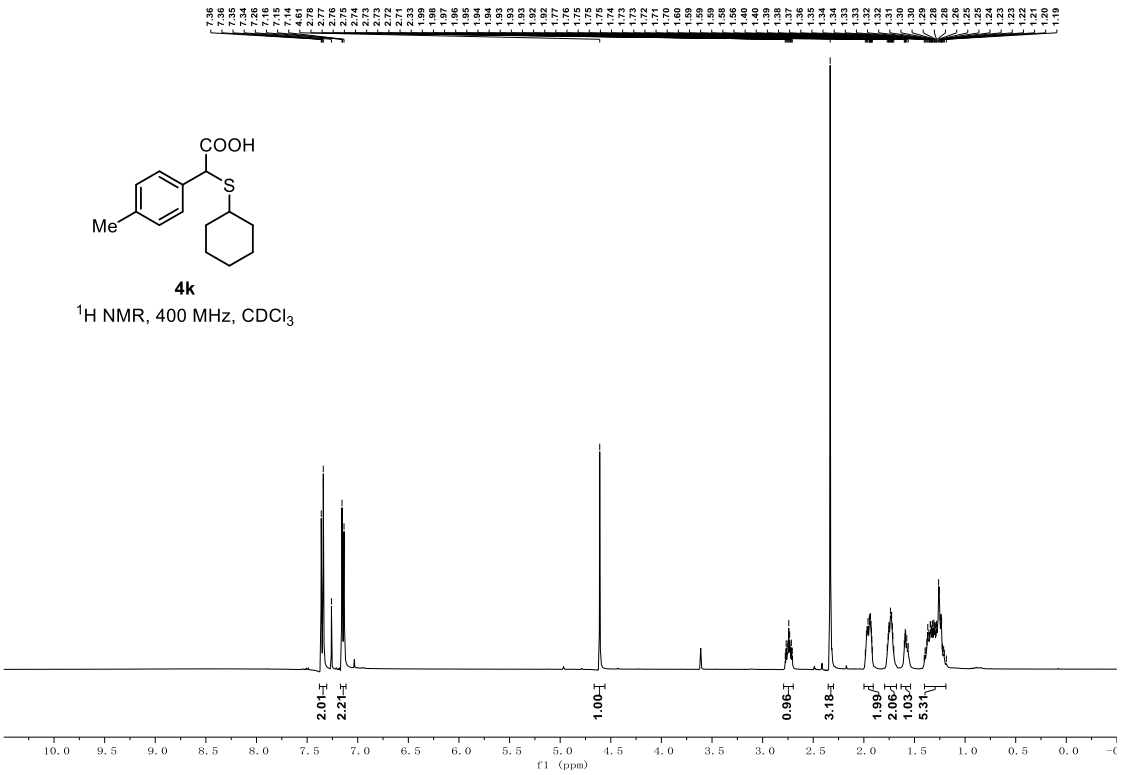




4j

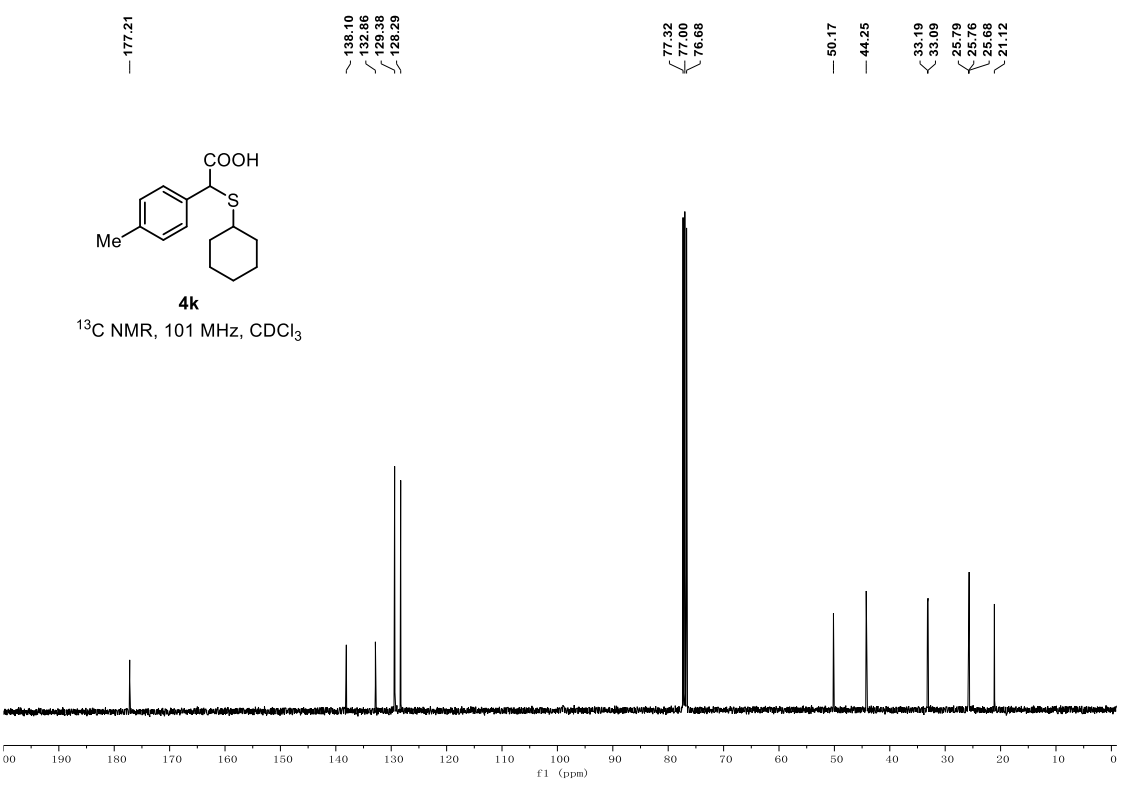
^{13}C NMR, 101 MHz, $CDCl_3$





4k

^{1}H NMR, 400 MHz, $CDCl_3$

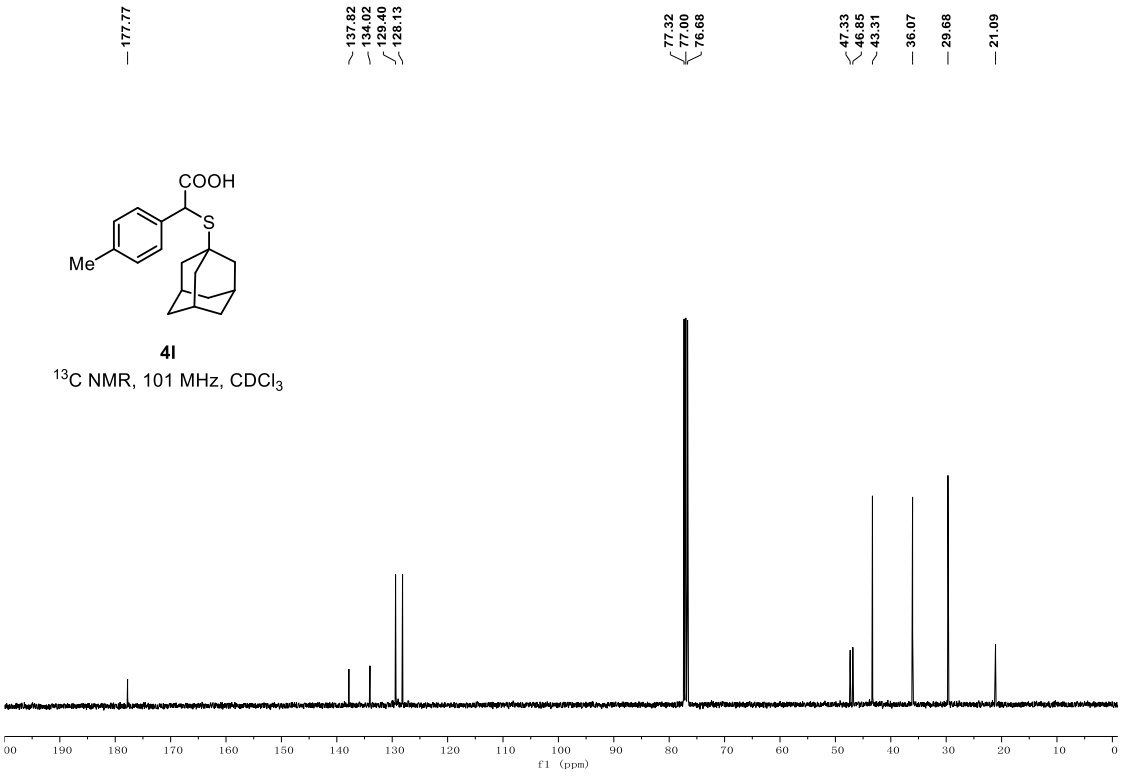


4k

^{13}C NMR, 101 MHz, $CDCl_3$

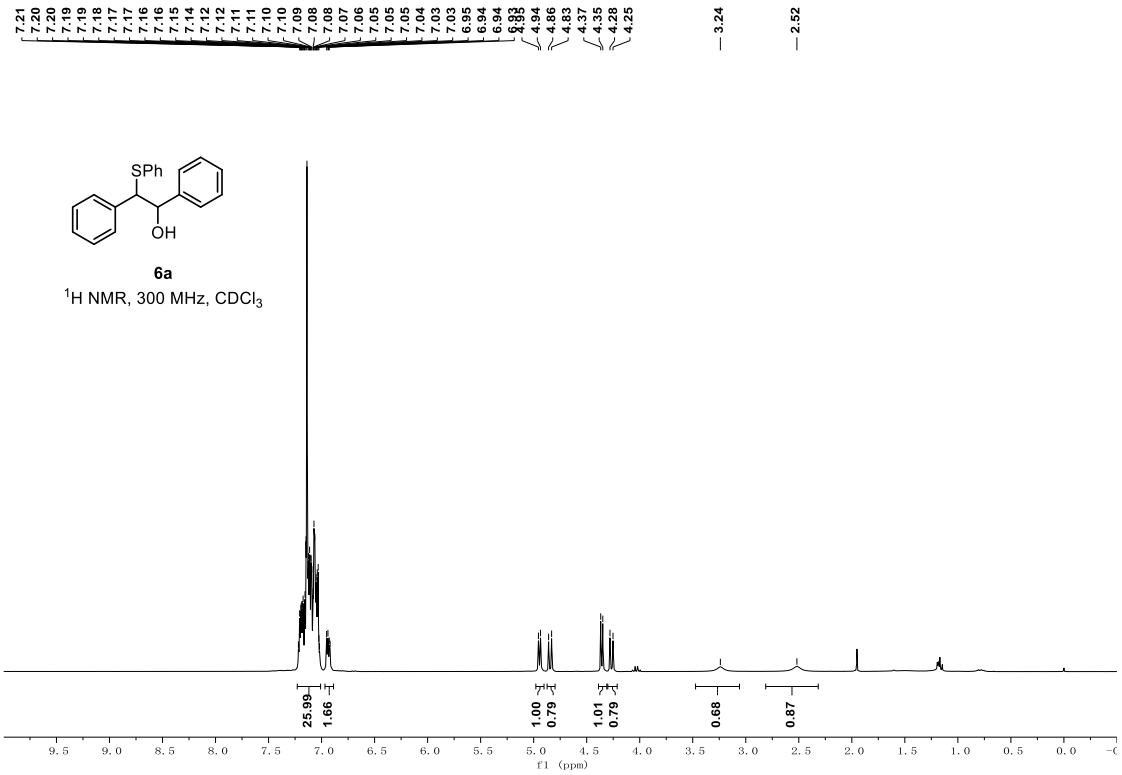
4l

^{1}H NMR, 400 MHz, $CDCl_3$



4l

^{13}C NMR, 101 MHz, $CDCl_3$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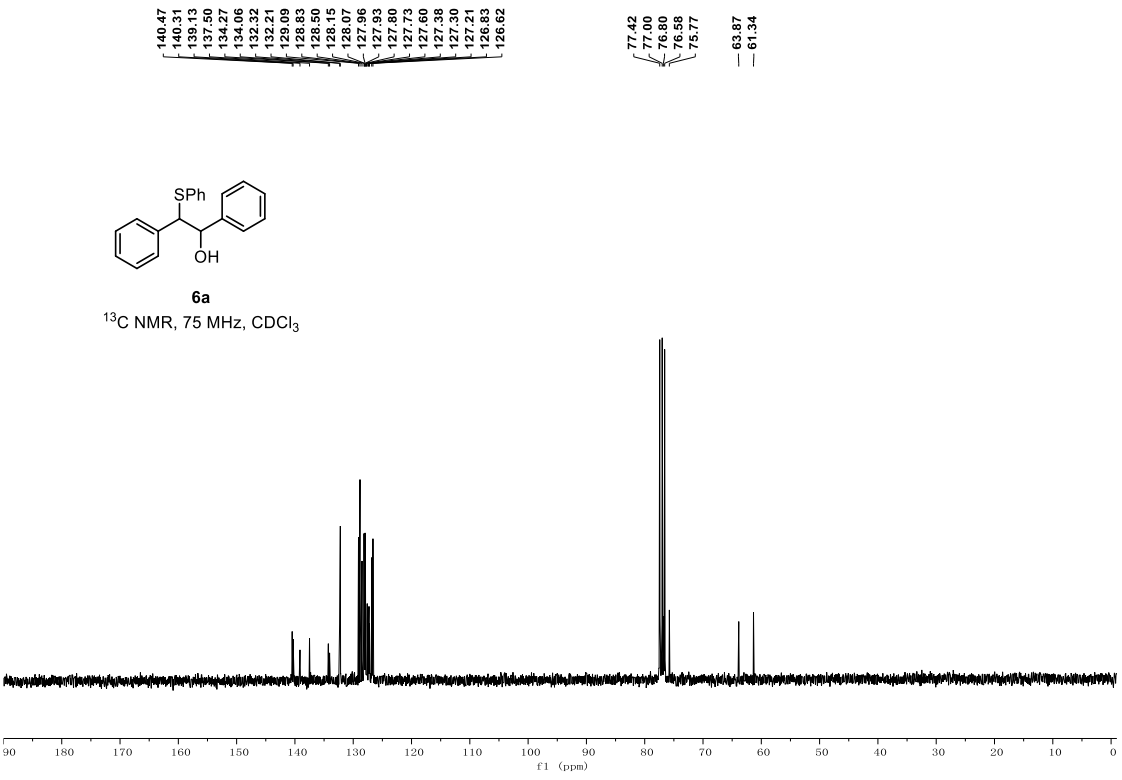
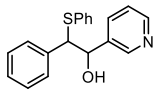
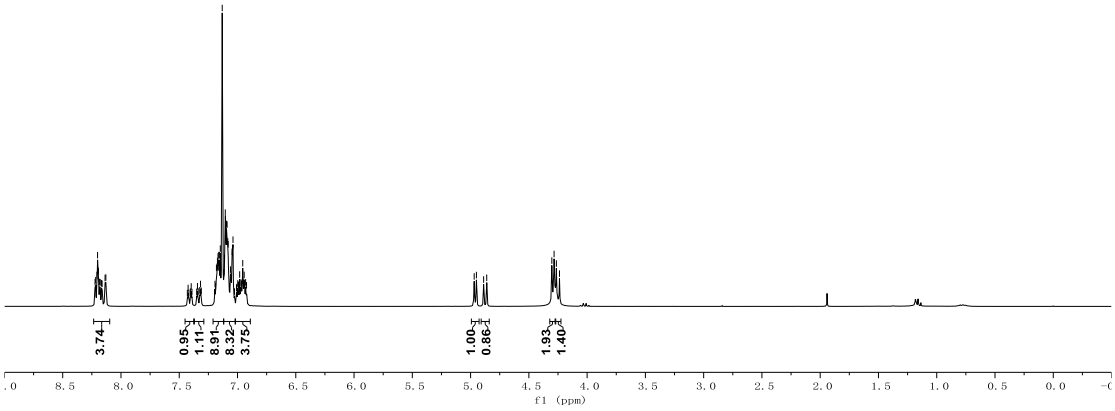
3.24
2.52
SPh
OH
6a
1H NMR, 300 MHz, CDCl3
25.99 1.66 1.00 0.79 1.01 0.79 0.68 0.87
f1 (ppm)

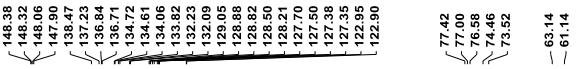

140.47 140.31 139.13 137.50 134.27 134.06 132.32 132.21 129.09 128.83 128.50 128.15 128.07 127.96 127.93 127.80 127.73 127.60 127.38 127.30 127.21 126.83 126.62
77.42 77.00 76.80 76.58 75.77
63.87
61.34
SPh
OH
6a
13C NMR, 75 MHz, CDCl3
f1 (ppm)

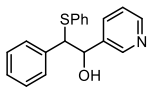


6b

^{1}H NMR, 300 MHz, $CDCl_3$

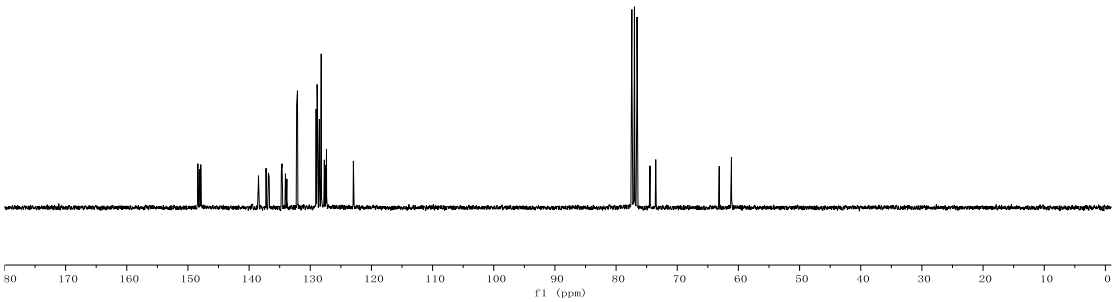


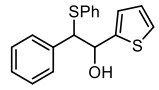




6b

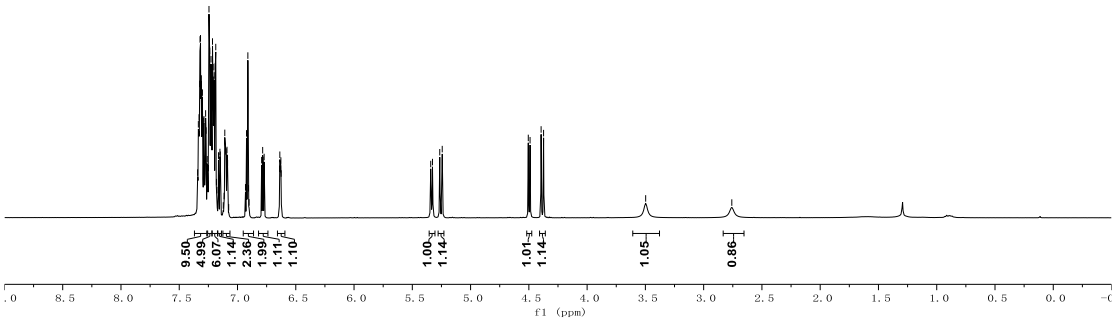
^{13}C NMR, 75 MHz, $CDCl_3$

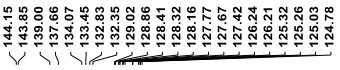


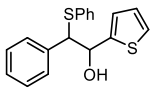


6c

^{1}H NMR, 400 MHz, $CDCl_3$

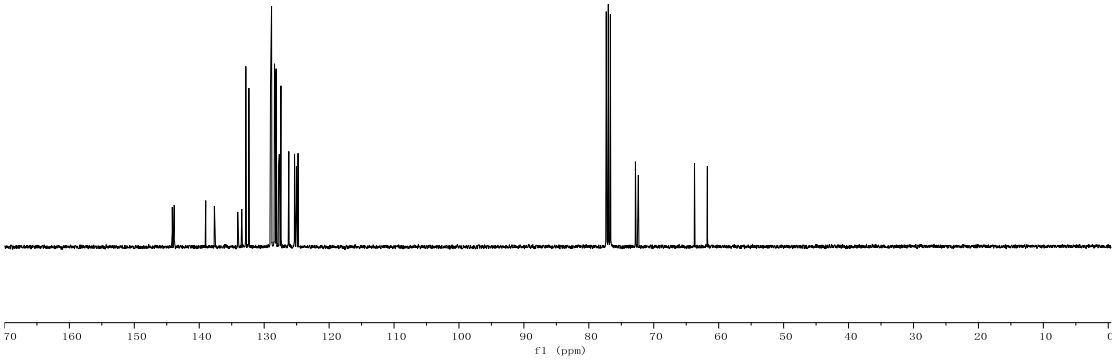


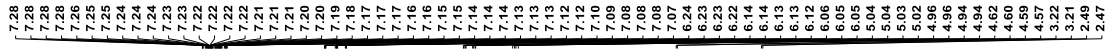


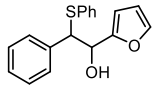


6c

^{13}C NMR, 101 MHz, $CDCl_3$

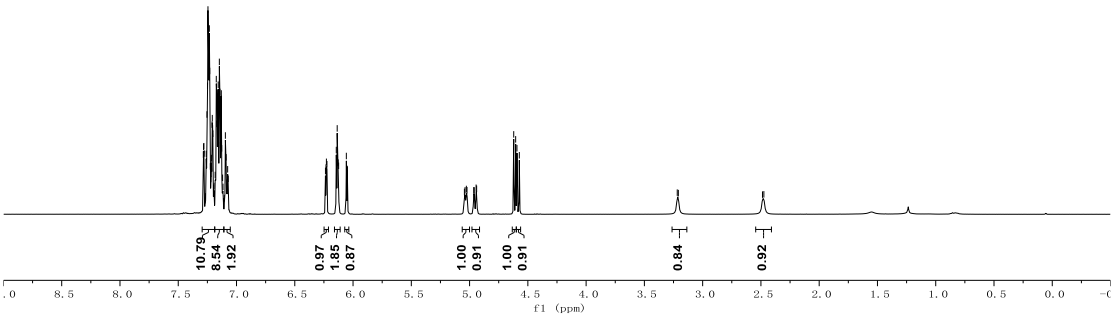


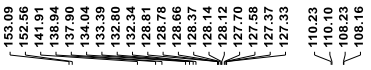


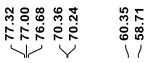


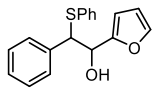
6d

^{1}H NMR, 400 MHz, $CDCl_3$



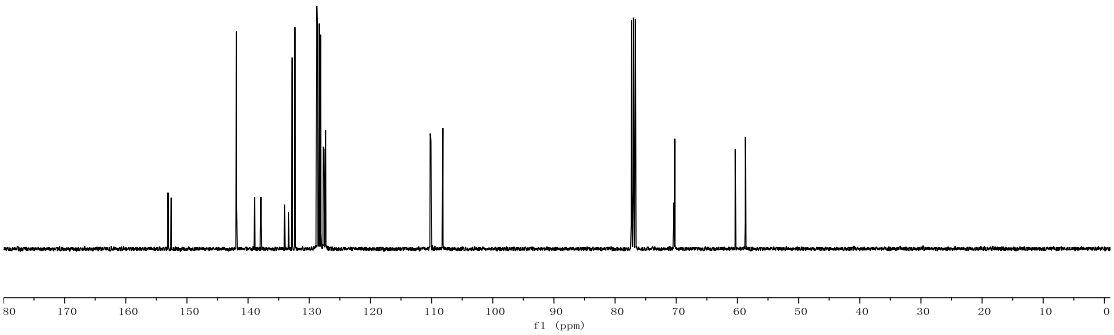


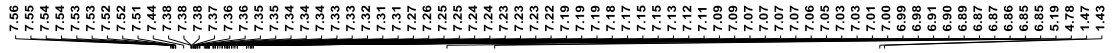


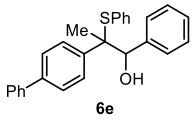


6d

^{13}C NMR, 101 MHz, $CDCl_3$

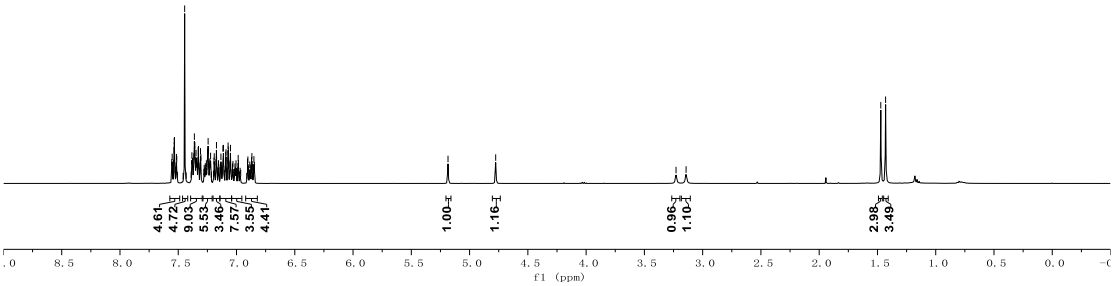


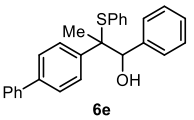




6e

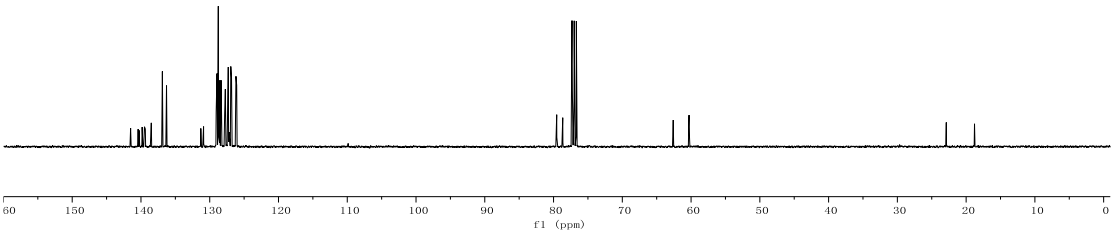
^{1}H NMR, 400 MHz, $CDCl_3$

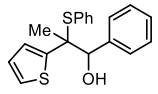




6e

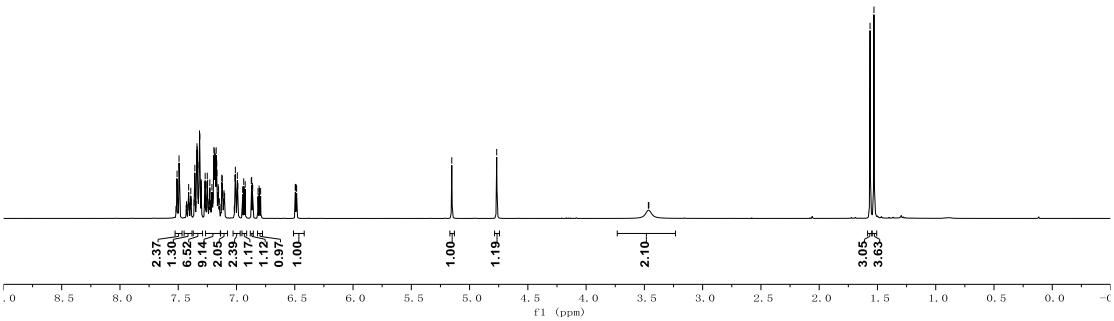
^{13}C NMR, 101 MHz, $CDCl_3$

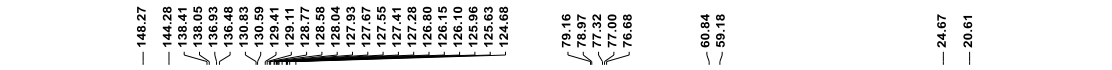


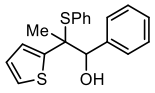


6f

^{1}H NMR, 400 MHz, $CDCl_3$

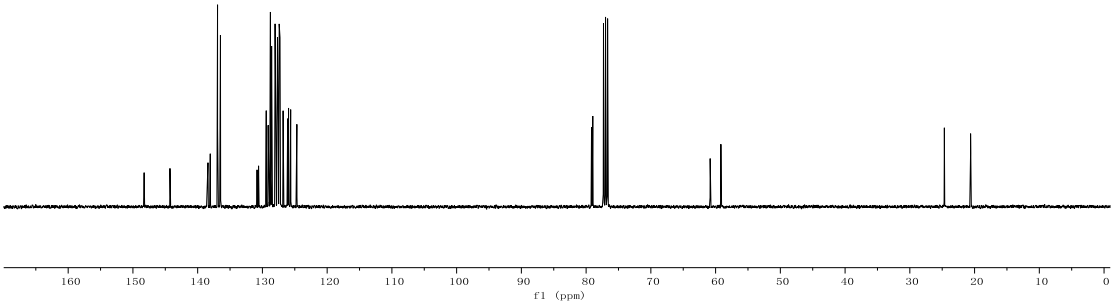


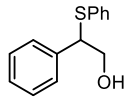




6f

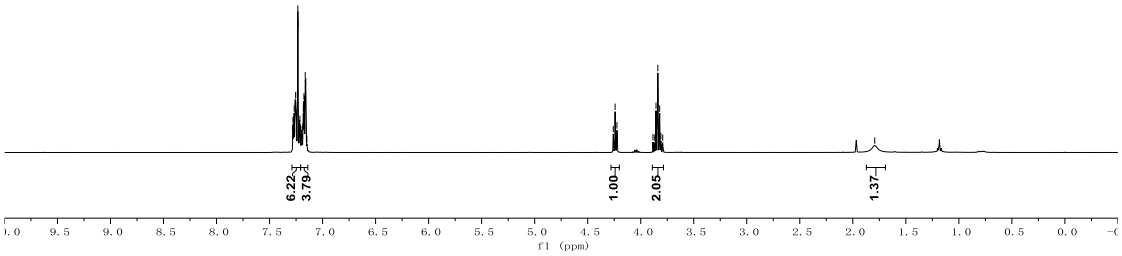
^{13}C NMR, 101 MHz, $CDCl_3$

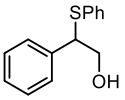




6g

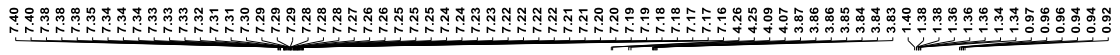
^{1}H NMR, 400 MHz, $CDCl_3$

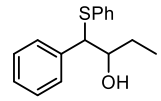




6g

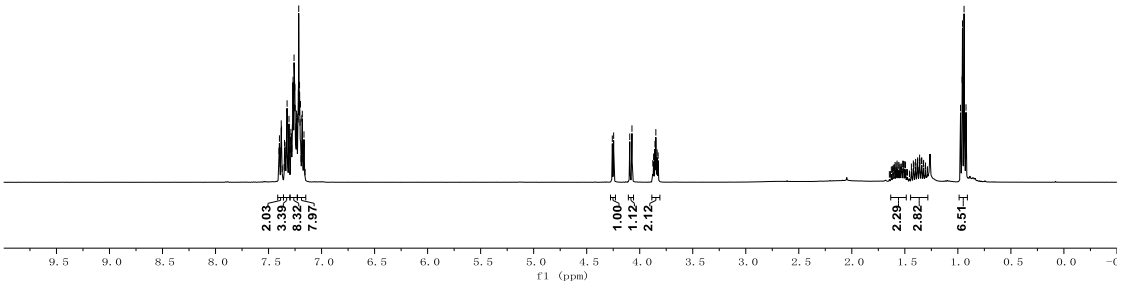
^{13}C NMR, 101 MHz, $CDCl_3$

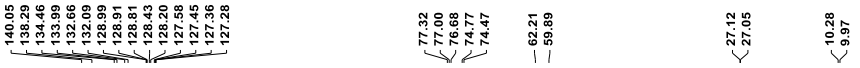


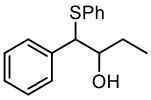


6h

^{1}H NMR, 400 MHz, $CDCl_3$

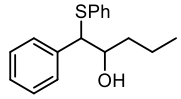






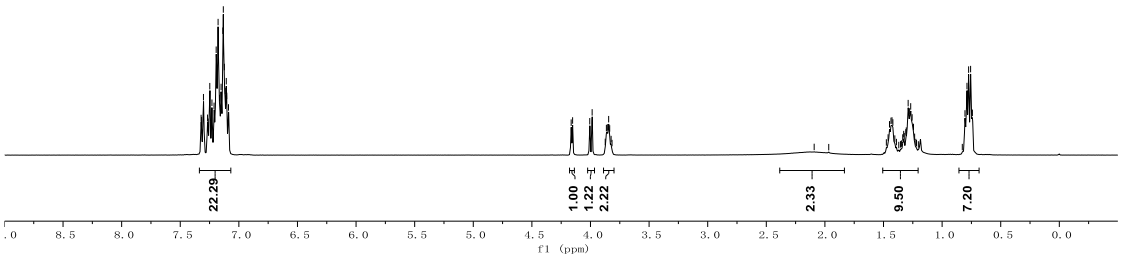
6h

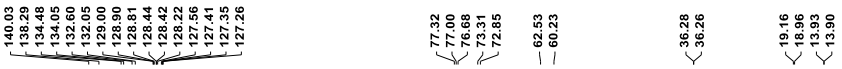
^{13}C NMR, 101 MHz, $CDCl_3$

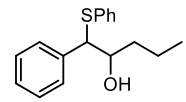


6i

^{1}H NMR, 400 MHz, $CDCl_3$

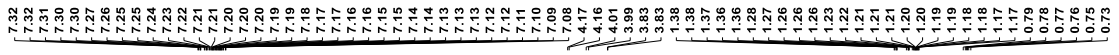


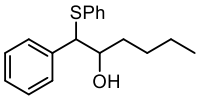




6i

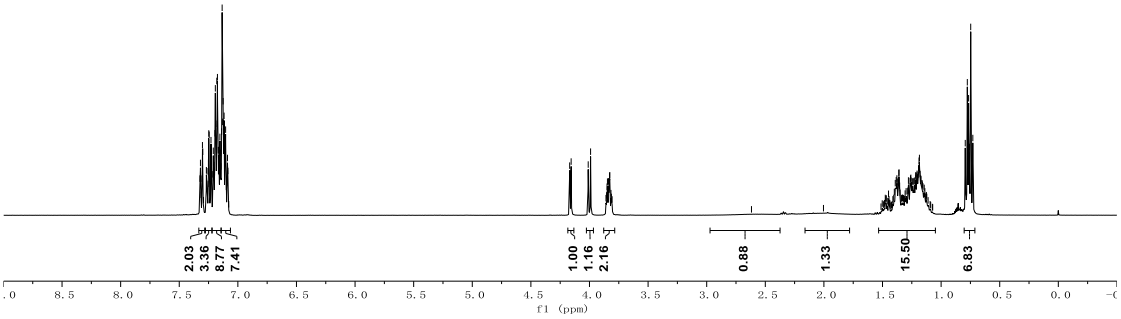
^{13}C NMR, 101 MHz, $CDCl_3$

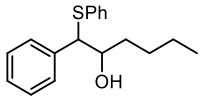




6j

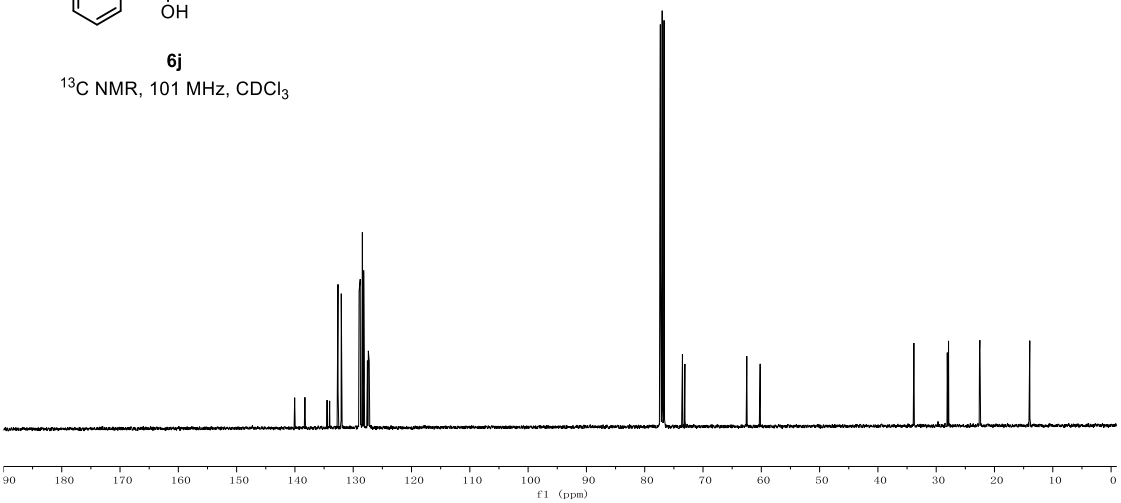
^{1}H NMR, 400 MHz, $CDCl_3$

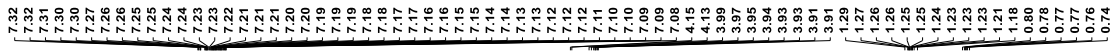


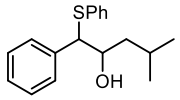


6j

^{13}C NMR, 101 MHz, $CDCl_3$

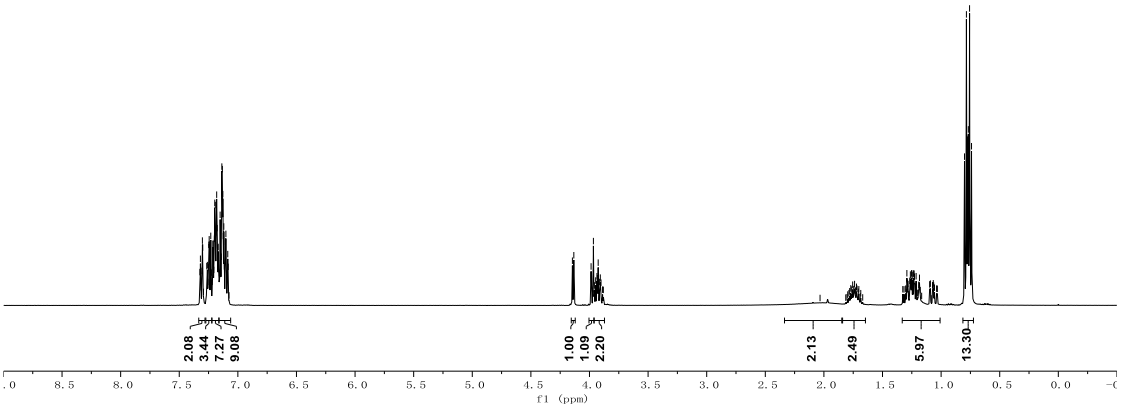


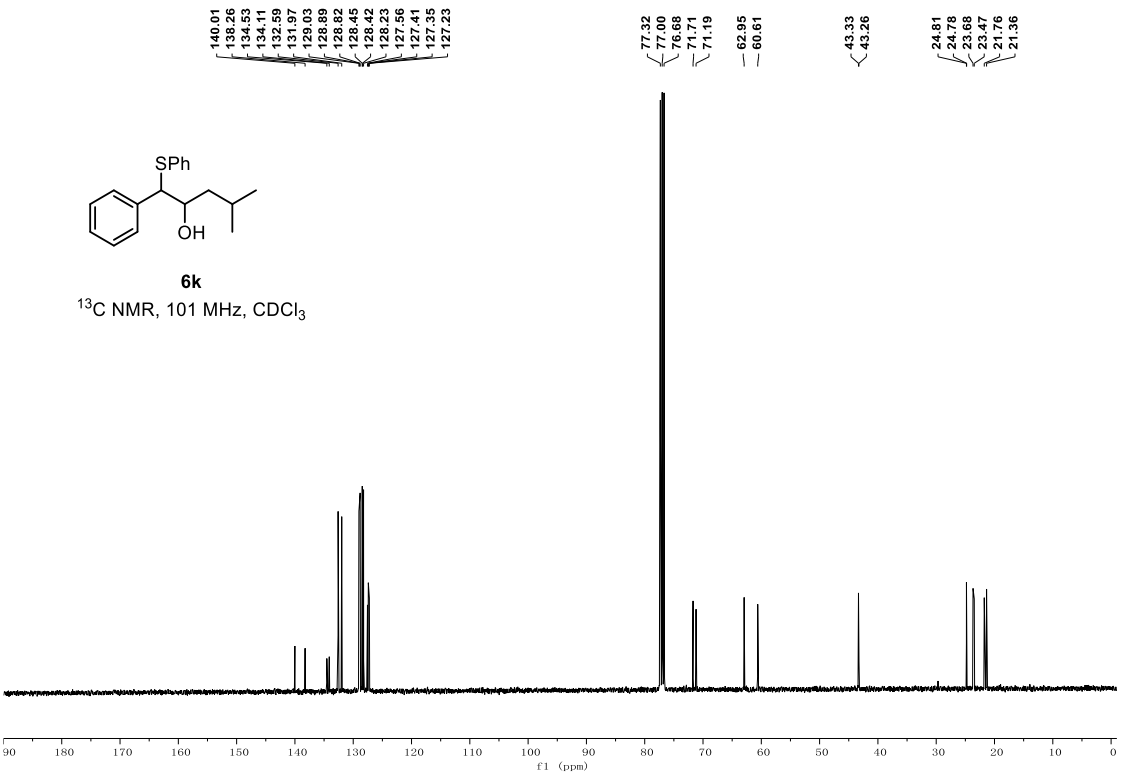




6k

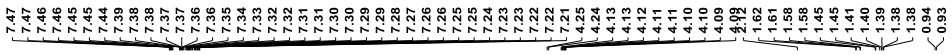
^{1}H NMR, 400 MHz, $CDCl_3$

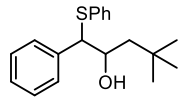




6k

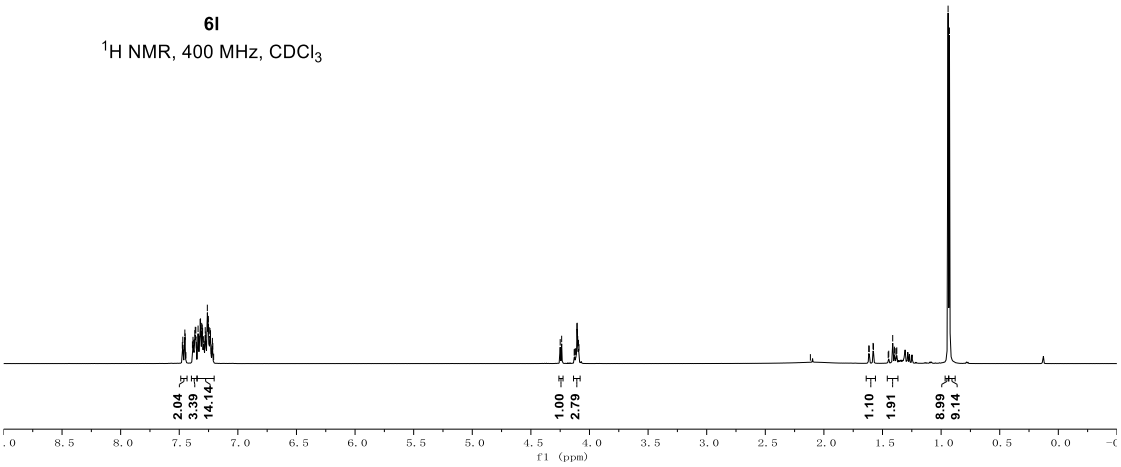
^{13}C NMR, 101 MHz, $CDCl_3$

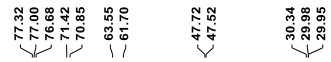


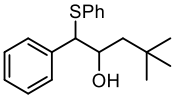


6l

^{1}H NMR, 400 MHz, $CDCl_3$

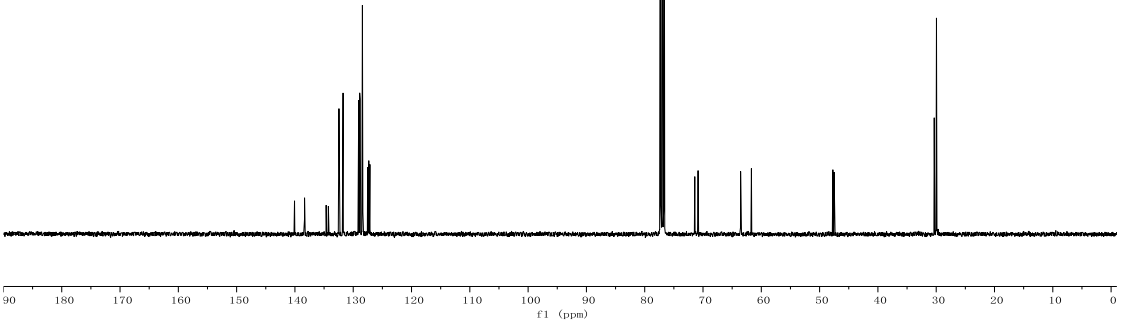


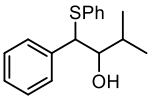




6l

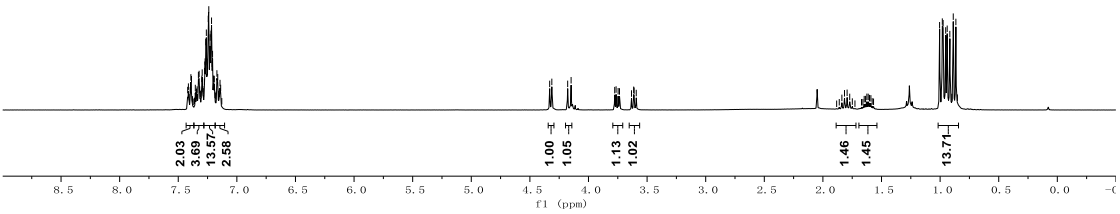
^{13}C NMR, 101 MHz, $CDCl_3$

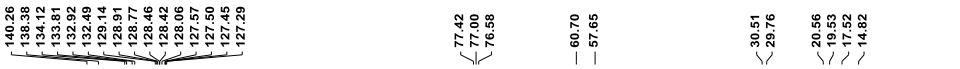


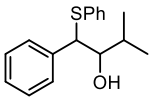


6m

^{1}H NMR, 300 MHz, $CDCl_3$

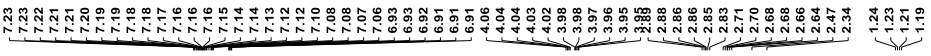


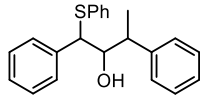




6m

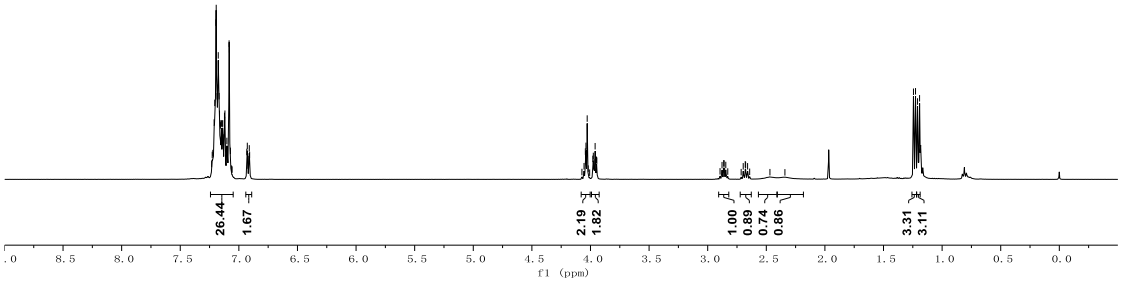
^{13}C NMR, 75 MHz, $CDCl_3$

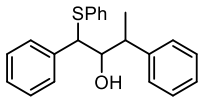




6n

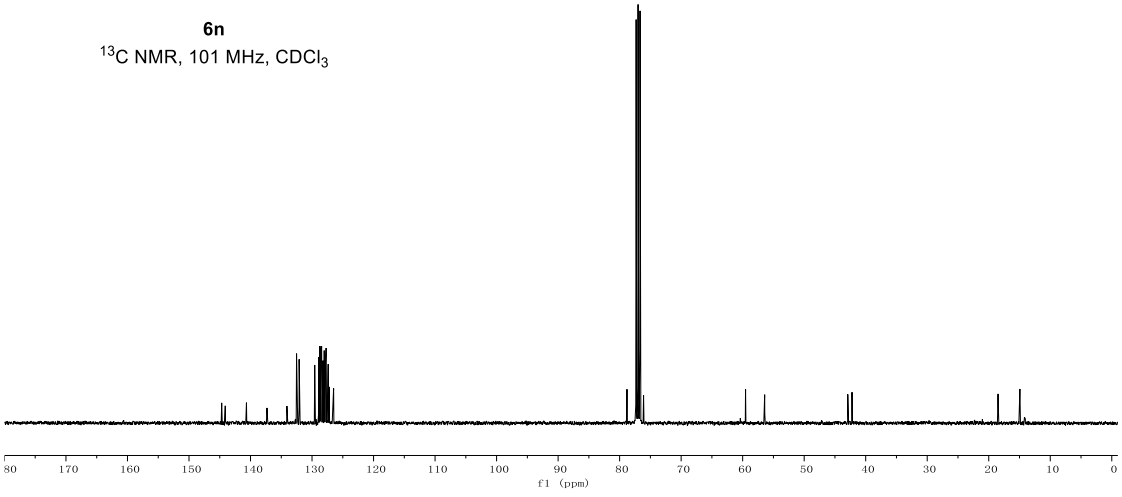
^{1}H NMR, 400 MHz, $CDCl_3$

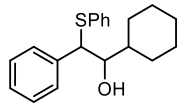




6n

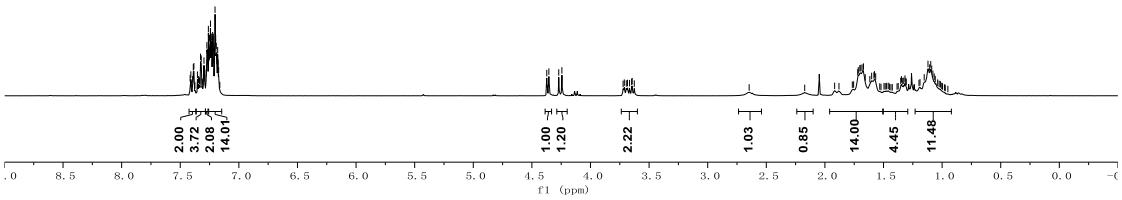
^{13}C NMR, 101 MHz, $CDCl_3$

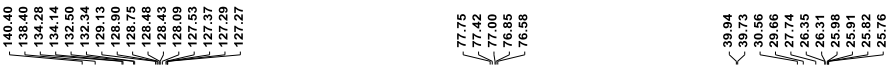


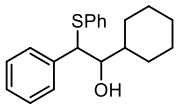


6o

^{1}H NMR, 300 MHz, $CDCl_3$

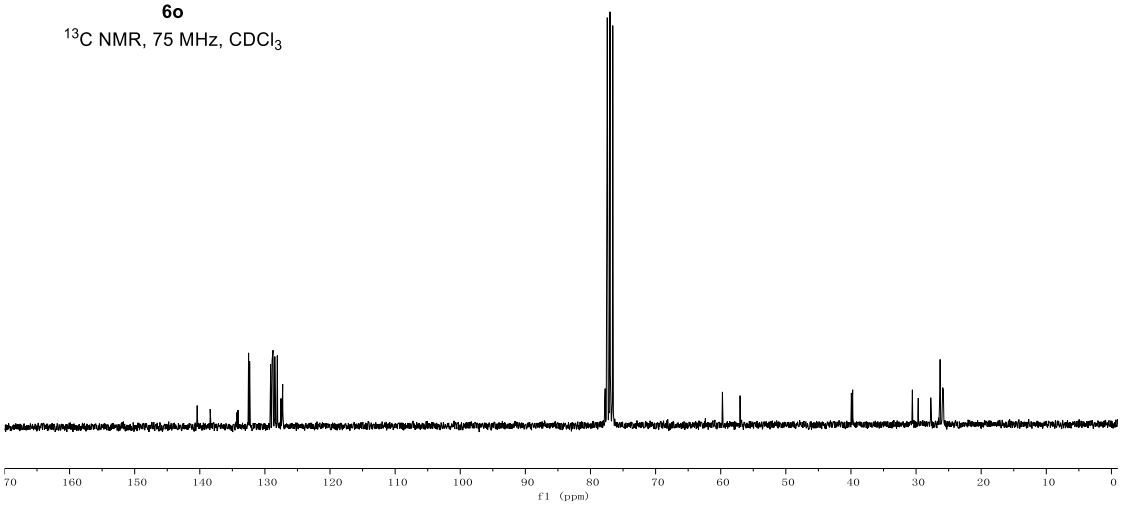


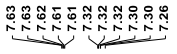


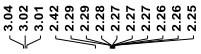


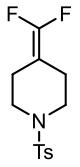
6o

^{13}C NMR, 75 MHz, $CDCl_3$



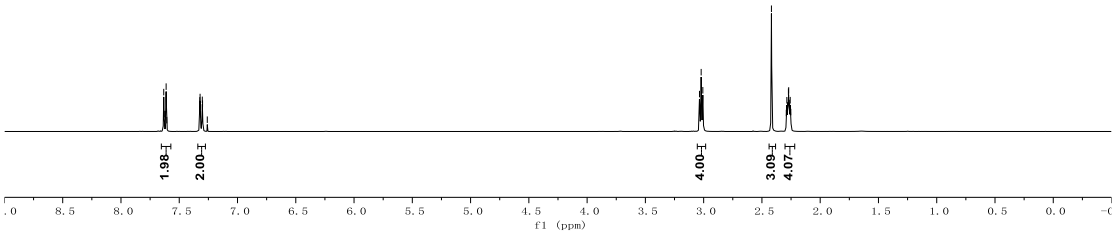


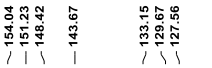


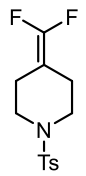


9a

^{1}H NMR, 400 MHz, $CDCl_3$

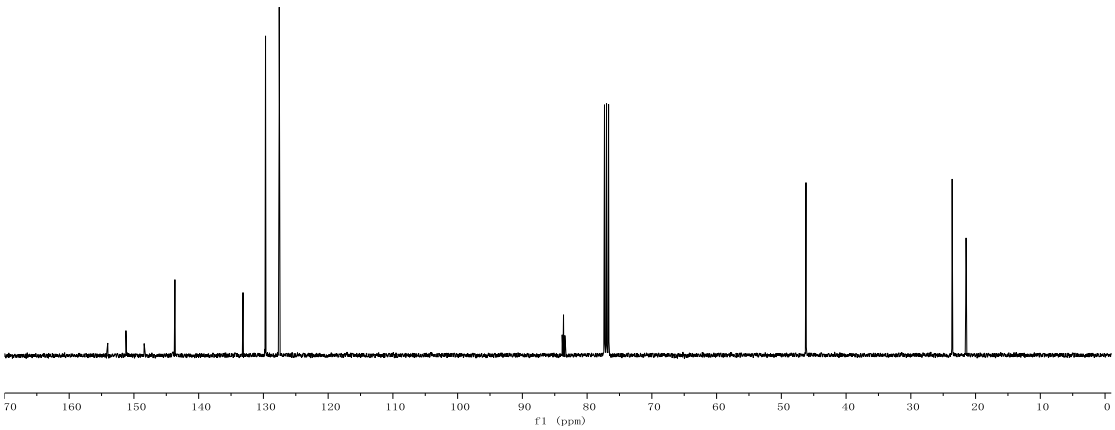


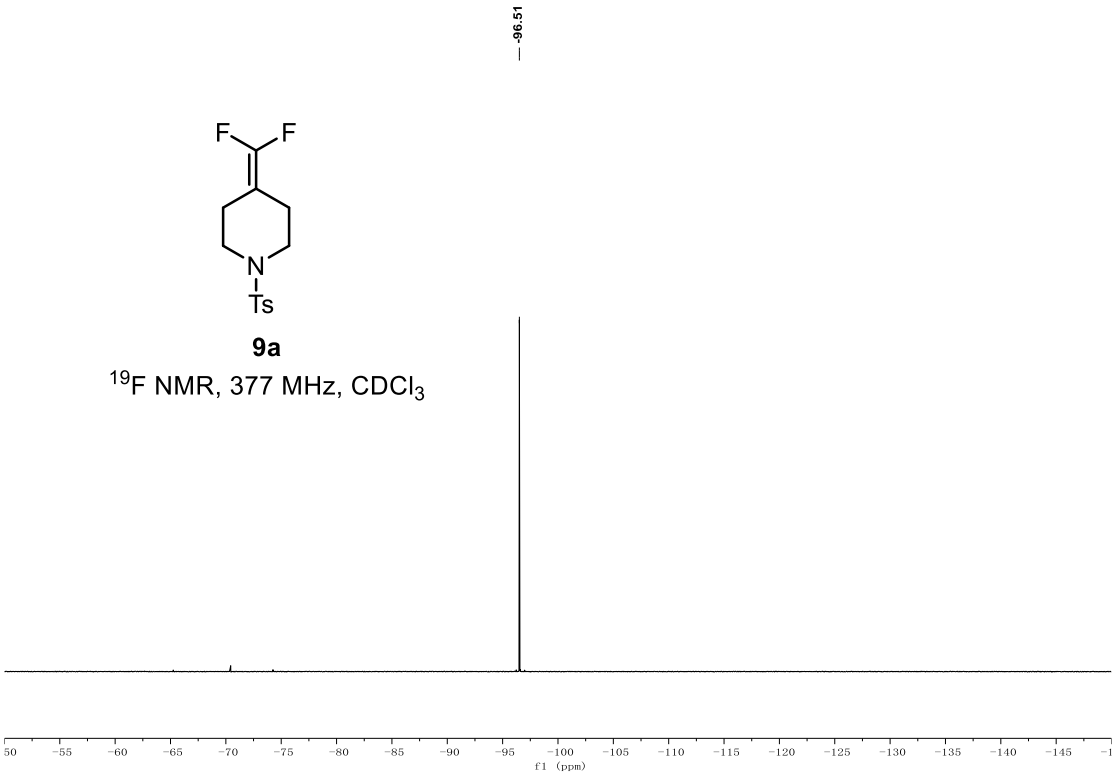




9a

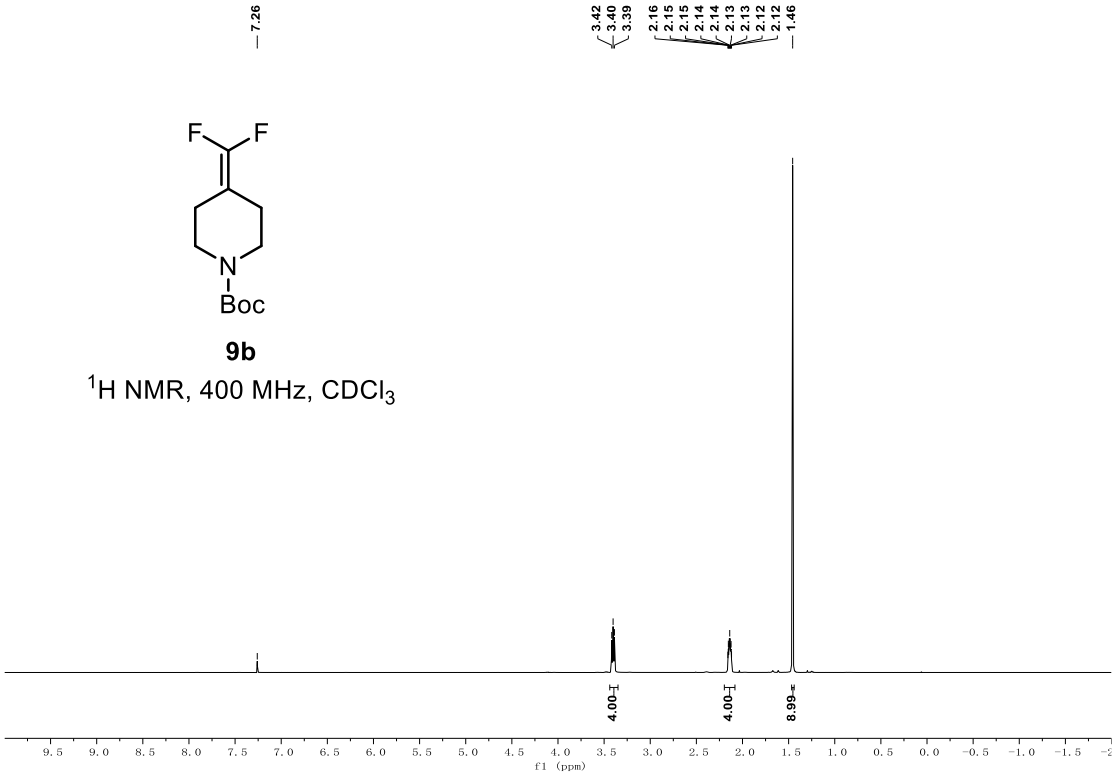
^{13}C NMR, 101 MHz, $CDCl_3$





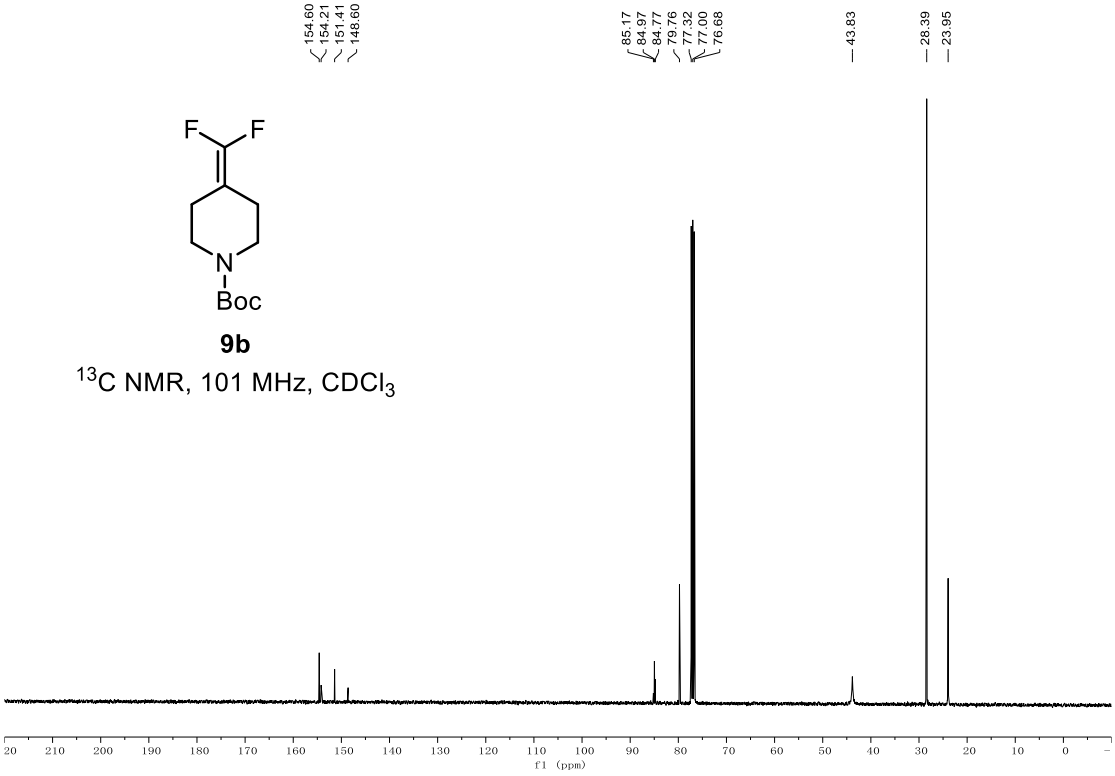
9a

^{19}F NMR, 377 MHz, $CDCl_3$



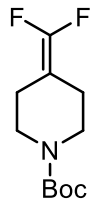
9b

^{1}H NMR, 400 MHz, $CDCl_3$



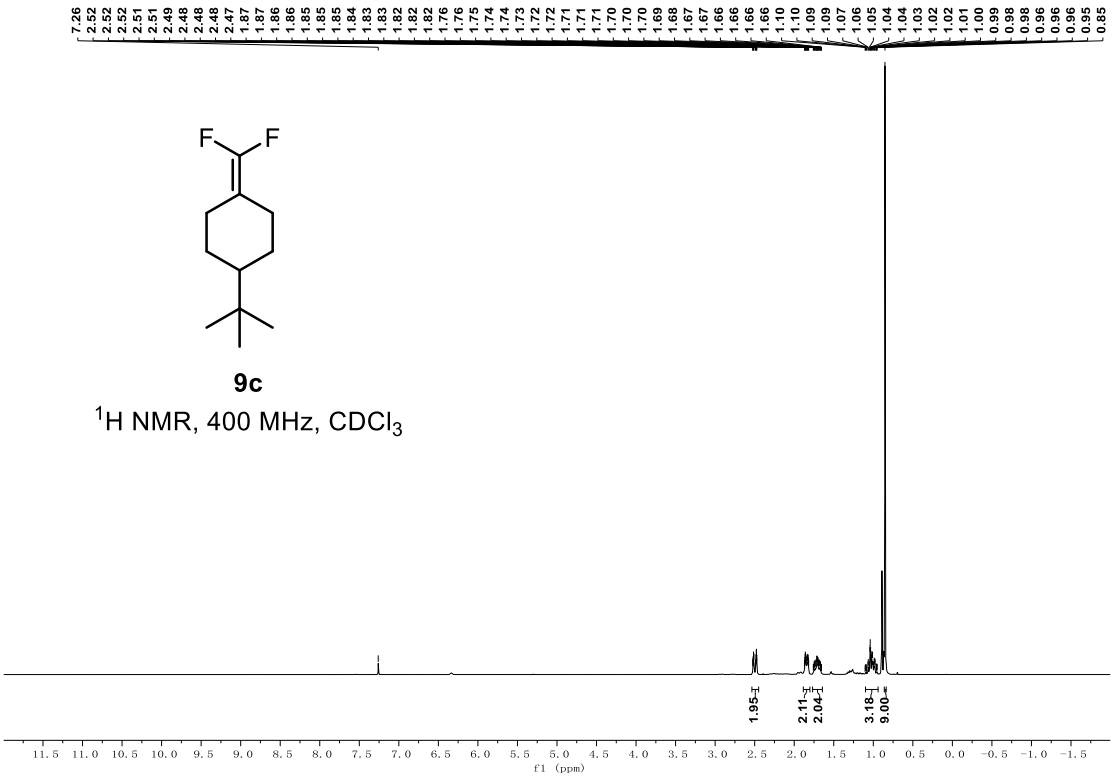
9b

^{13}C NMR, 101 MHz, $CDCl_3$



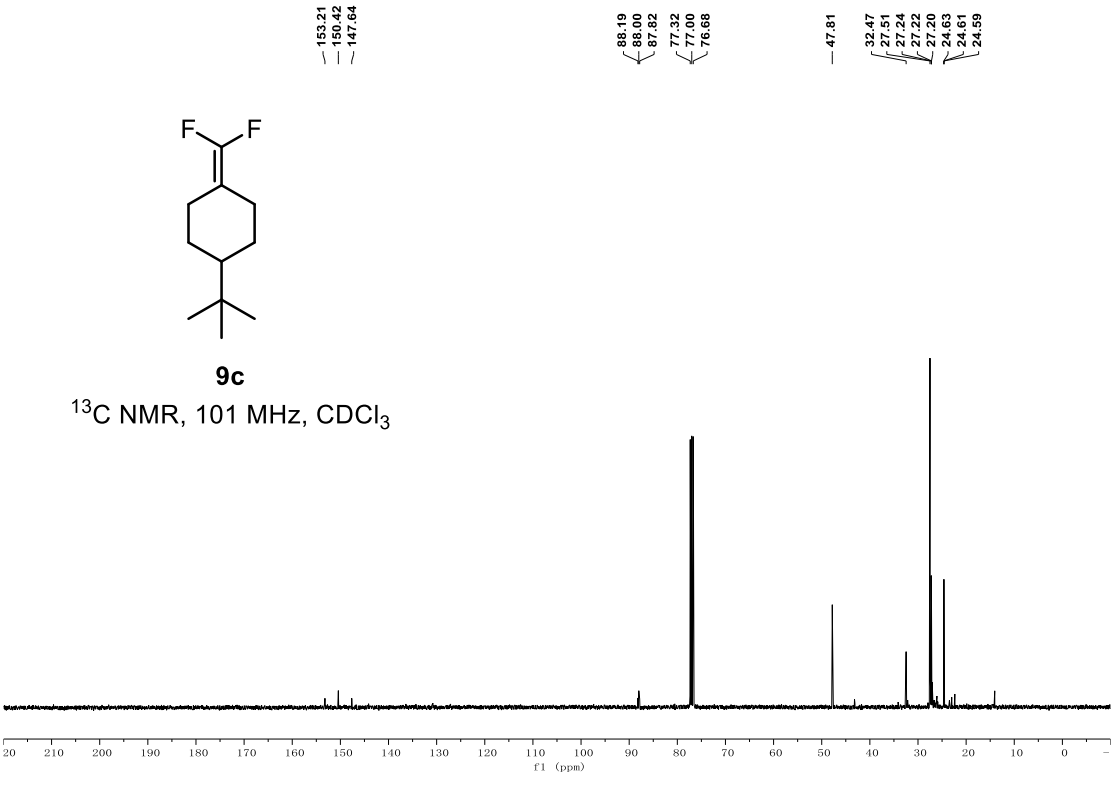
9b

^{19}F NMR, 377 MHz, $CDCl_3$



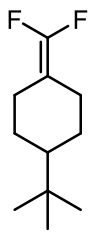
9c

^{1}H NMR, 400 MHz, $CDCl_3$



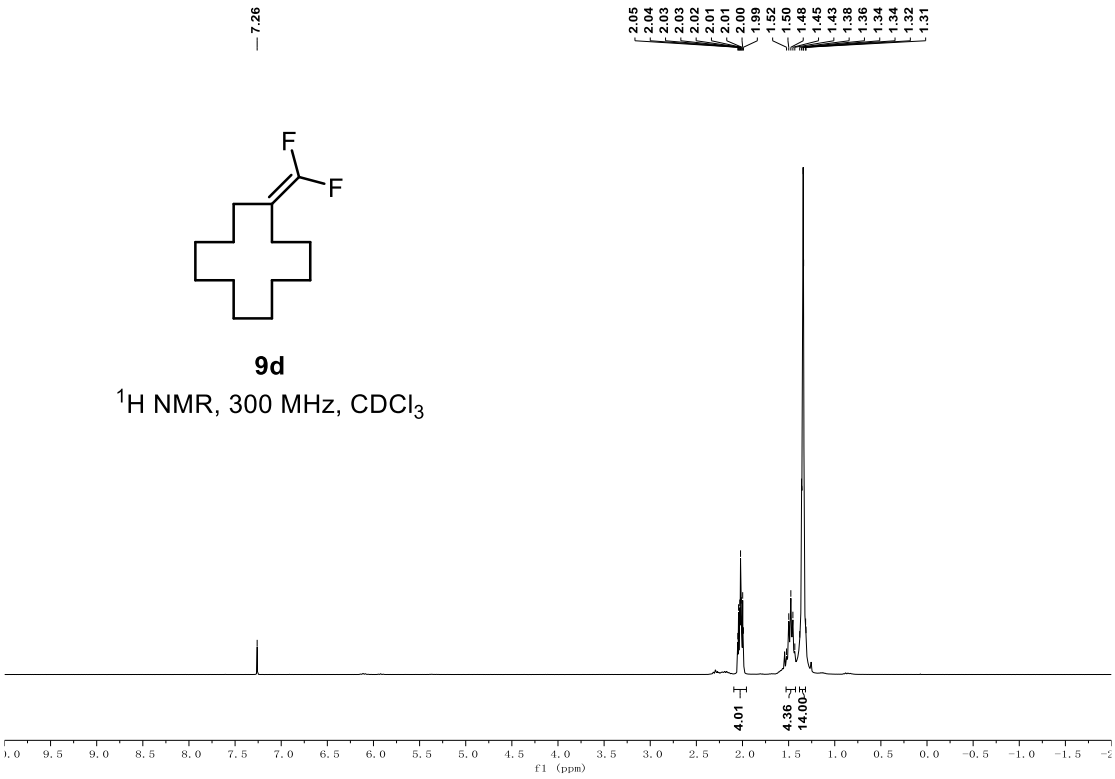
9c

^{13}C NMR, 101 MHz, $CDCl_3$



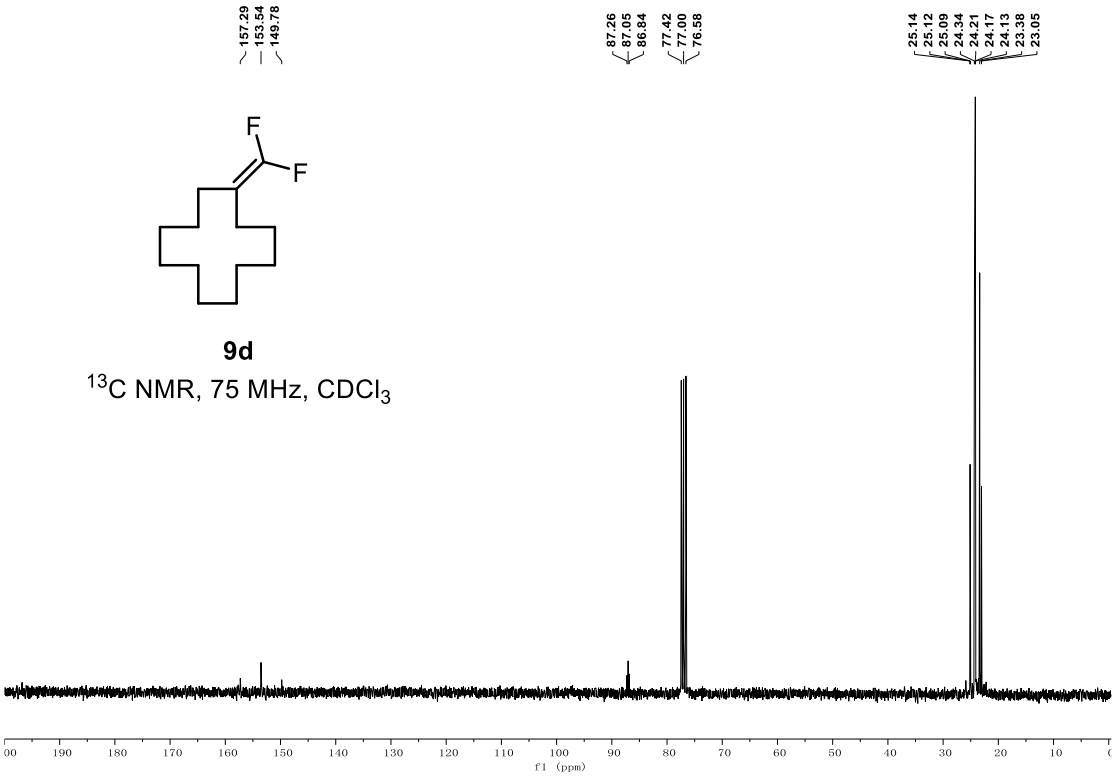
9c

^{19}F NMR, 377 MHz, $CDCl_3$



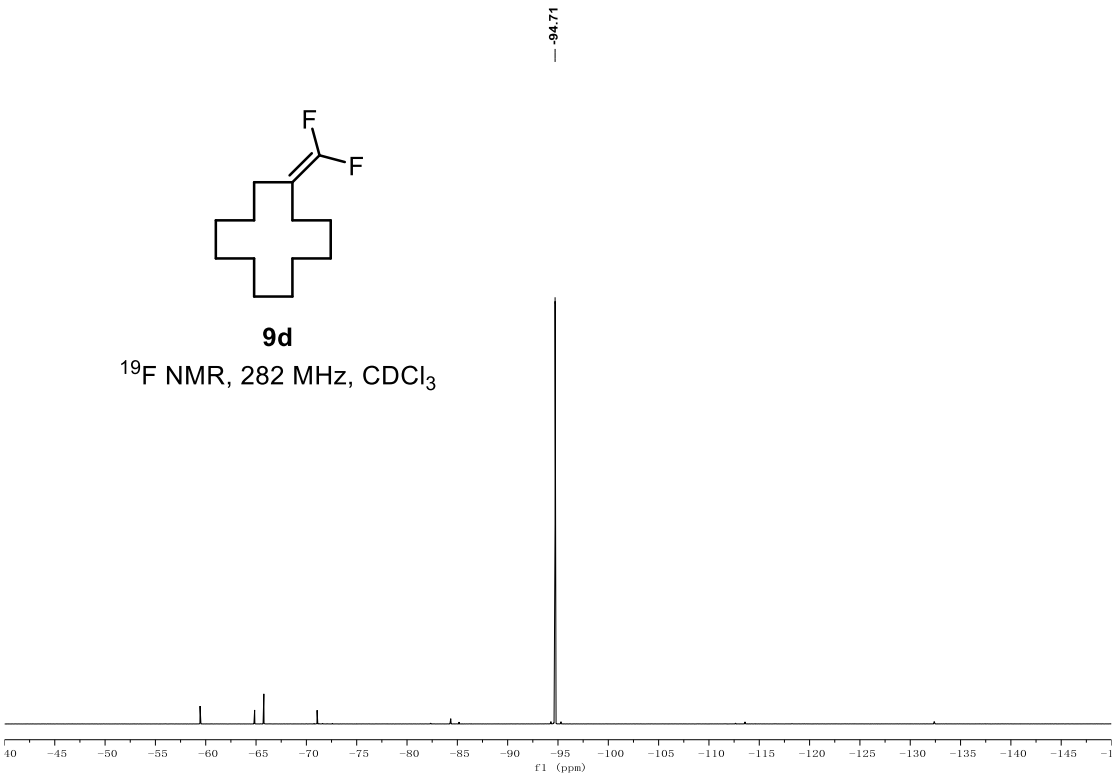
9d

^{1}H NMR, 300 MHz, $CDCl_3$



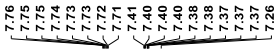
9d

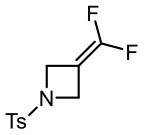
^{13}C NMR, 75 MHz, $CDCl_3$



9d

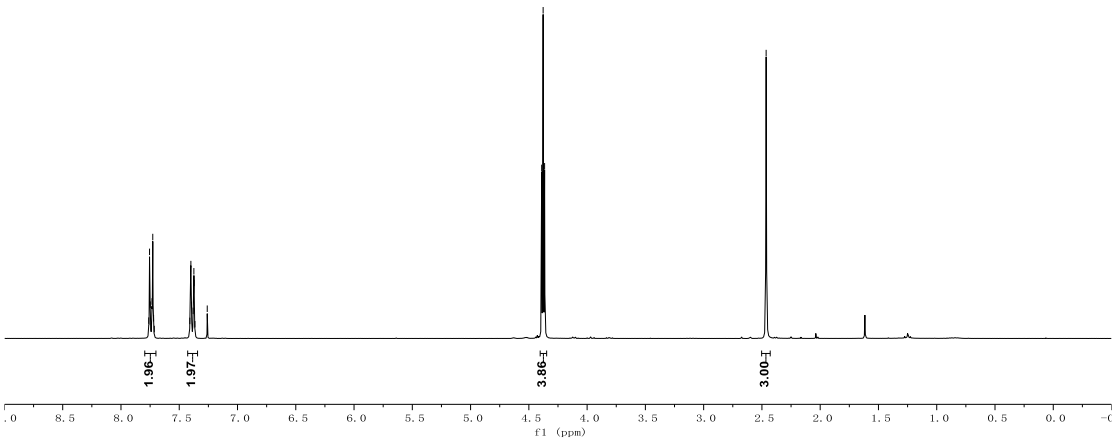
^{19}F NMR, 282 MHz, $CDCl_3$

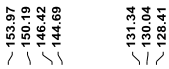


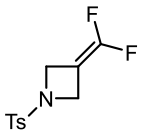


9e

^{1}H NMR, 300 MHz, $CDCl_3$

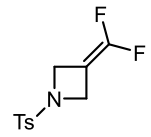






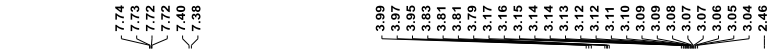
9e

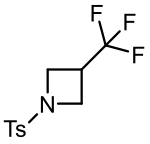
^{13}C NMR,75 MHz, $CDCl_3$



9e

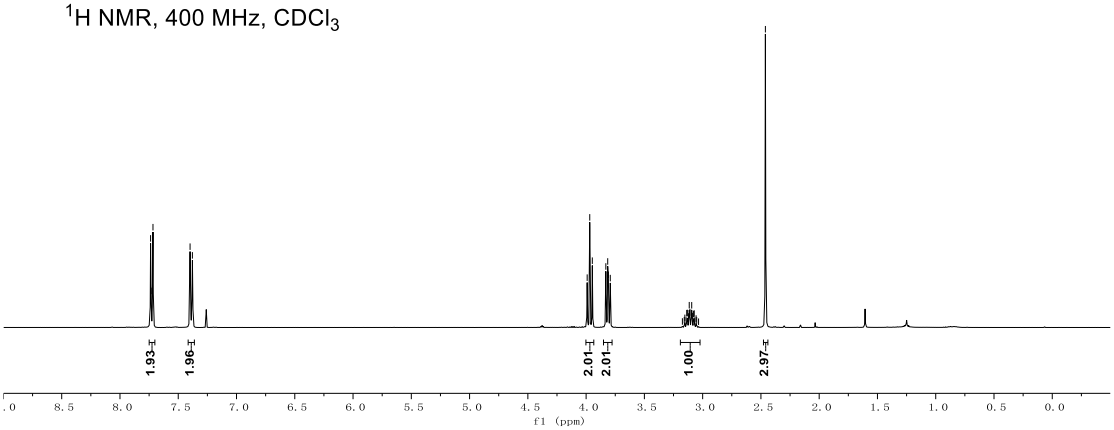
^{19}F NMR, 282 MHz, $CDCl_3$

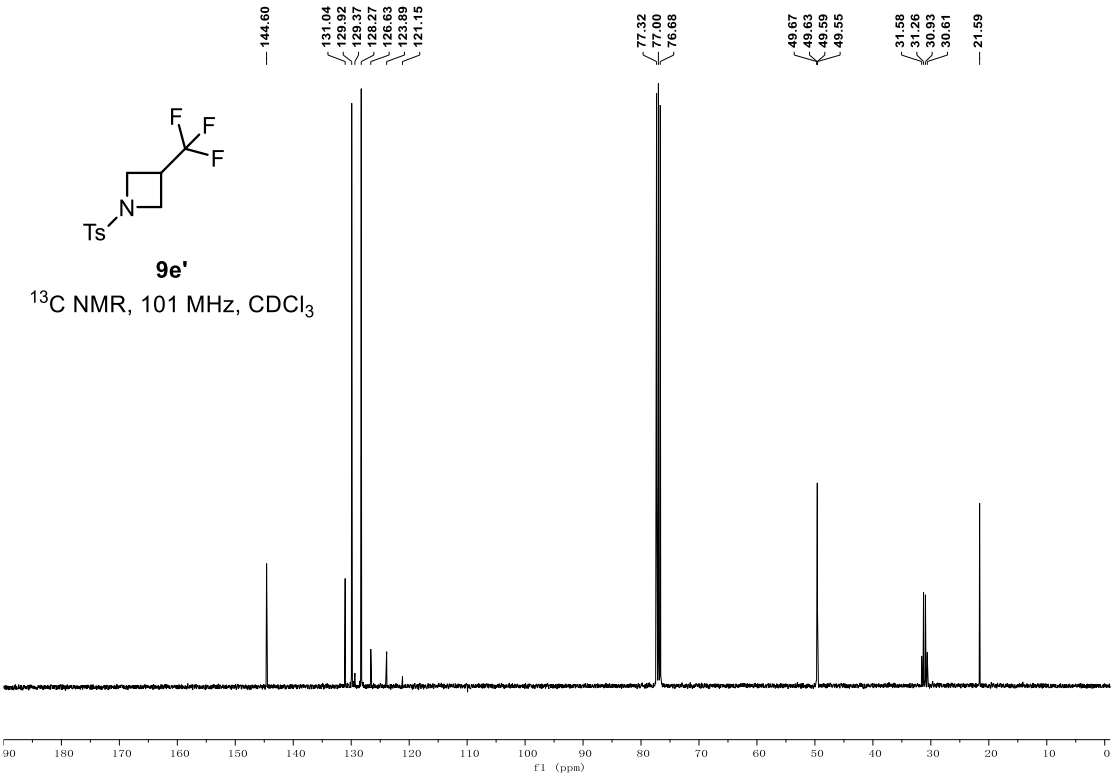




9e'

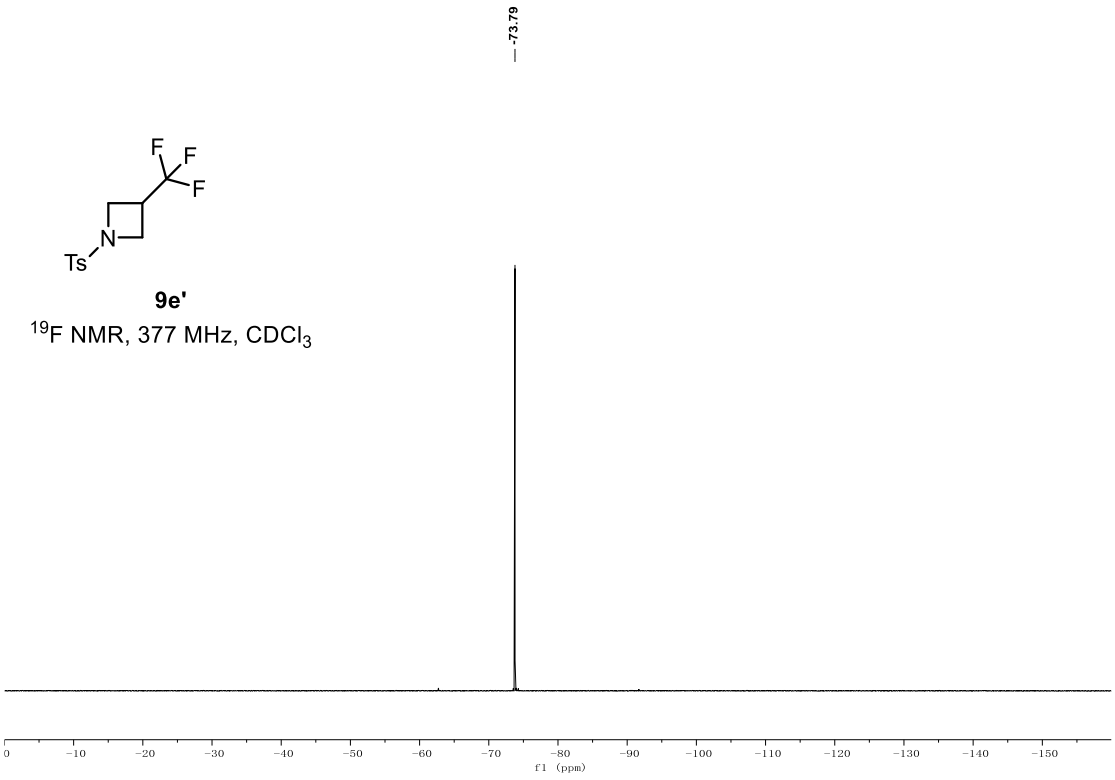
^{1}H NMR, 400 MHz, $CDCl_3$





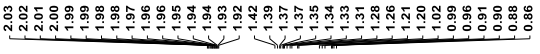
9e'

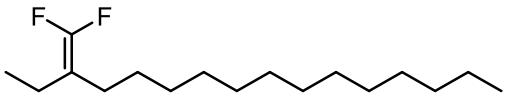
^{13}C NMR, 101 MHz, $CDCl_3$



9e'

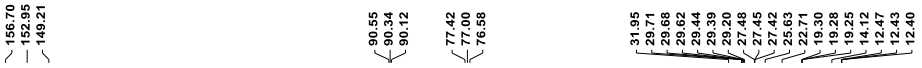
^{19}F NMR, 377 MHz, $CDCl_3$

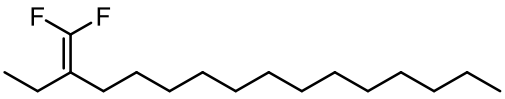




9f

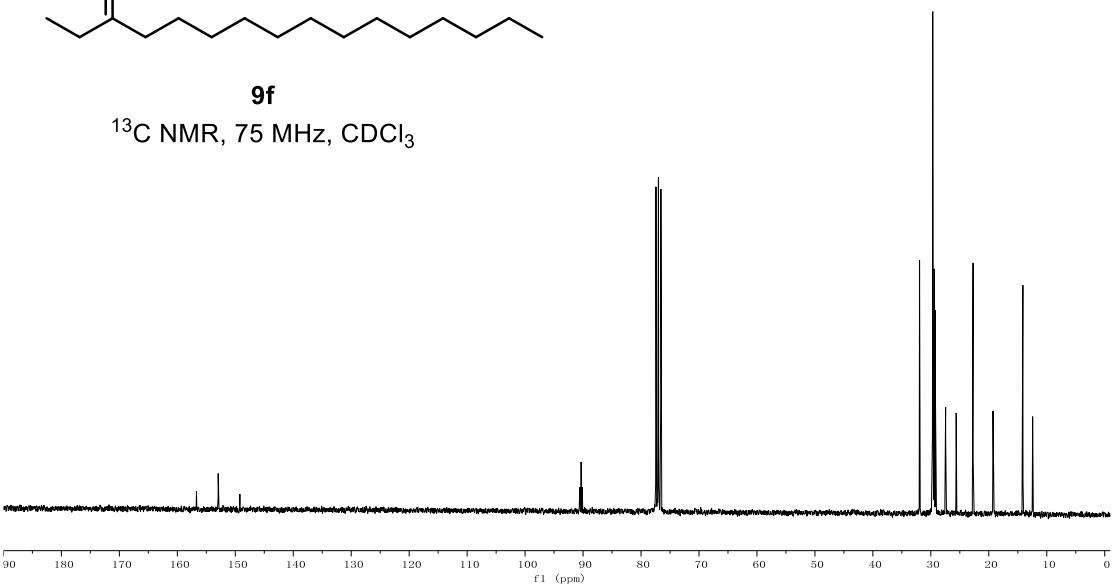
^{1}H NMR, 300 MHz, $CDCl_3$

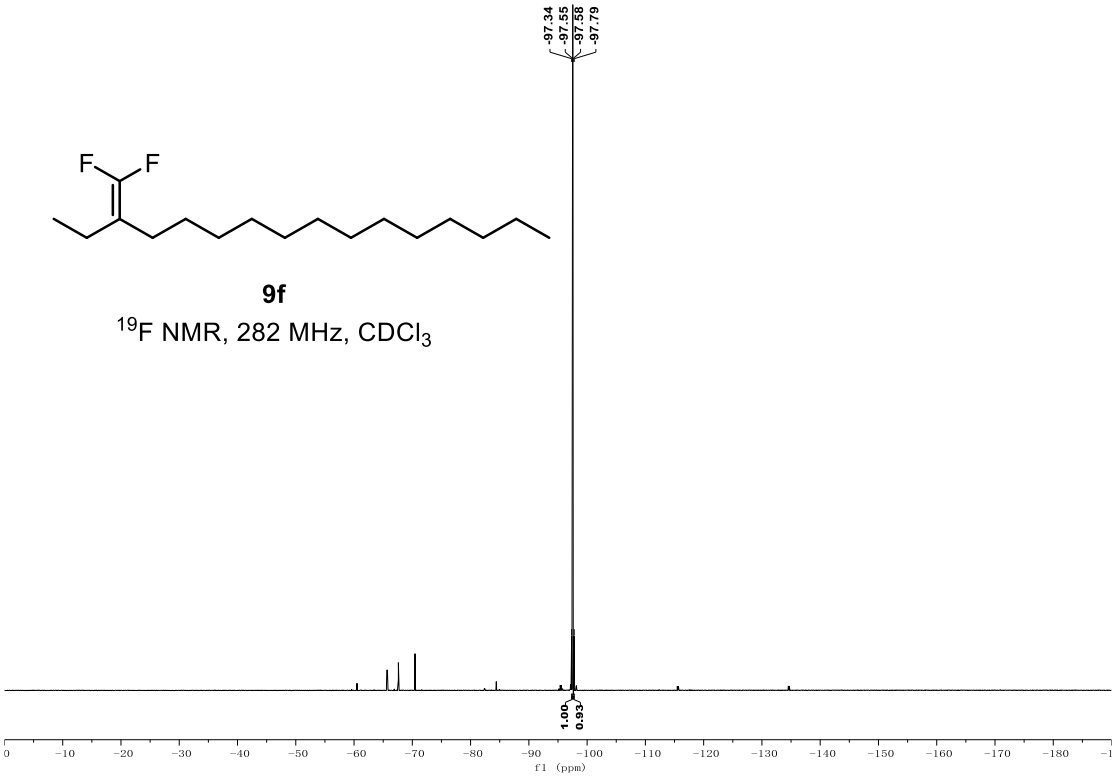




9f

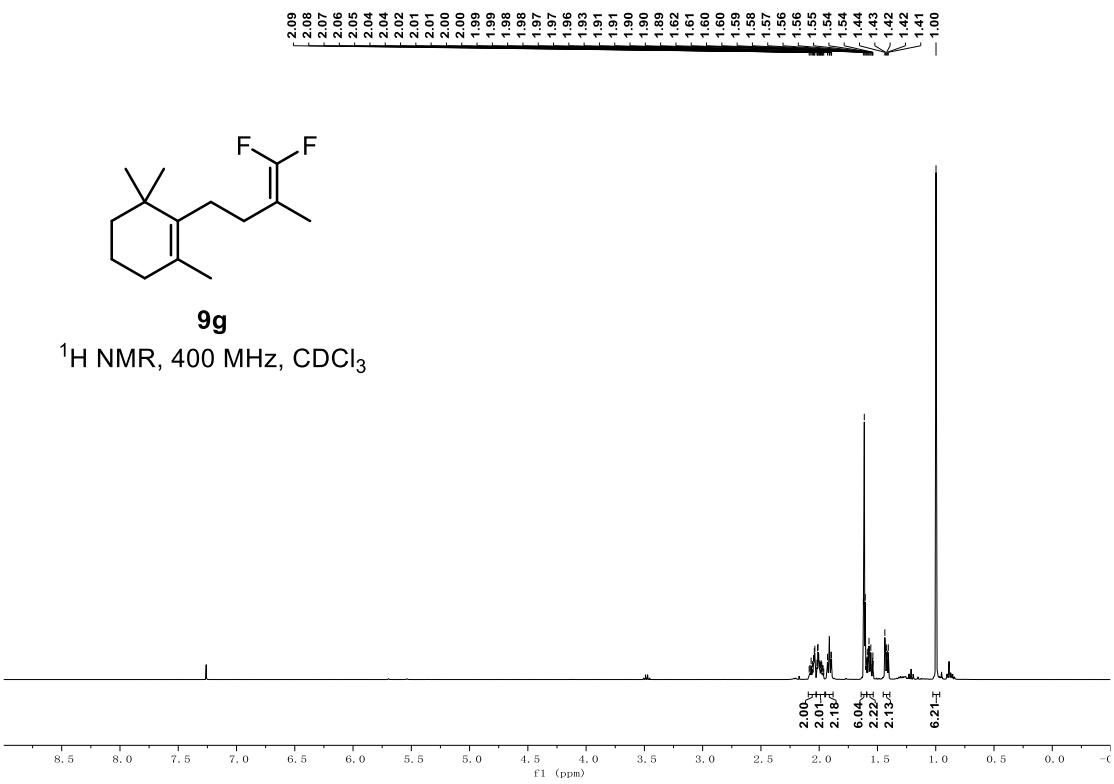
^{13}C NMR, 75 MHz, $CDCl_3$





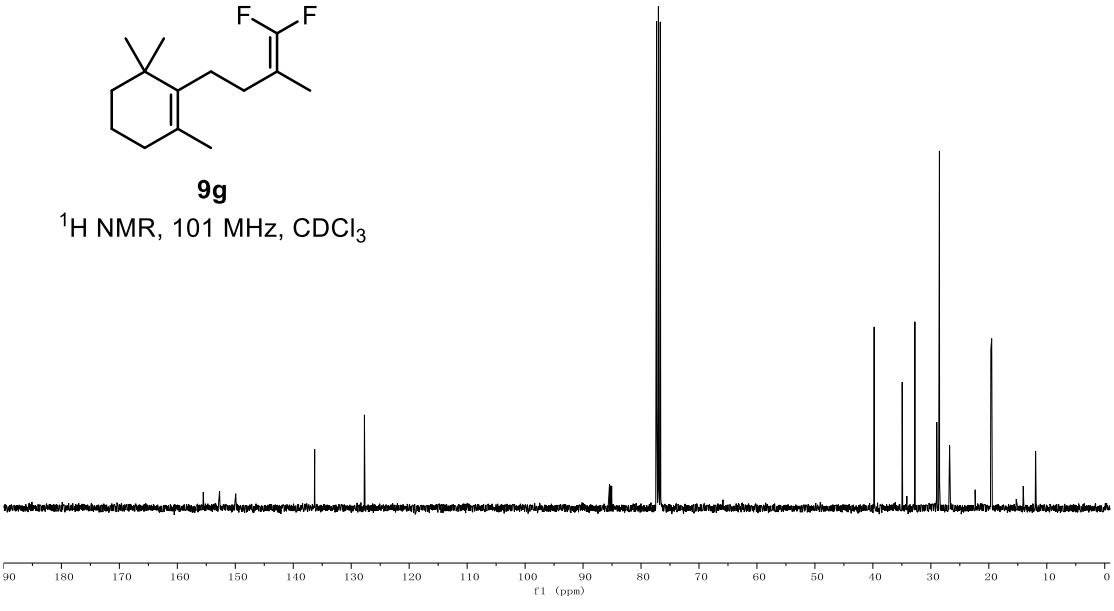
9f

^{19}F NMR, 282 MHz, $CDCl_3$



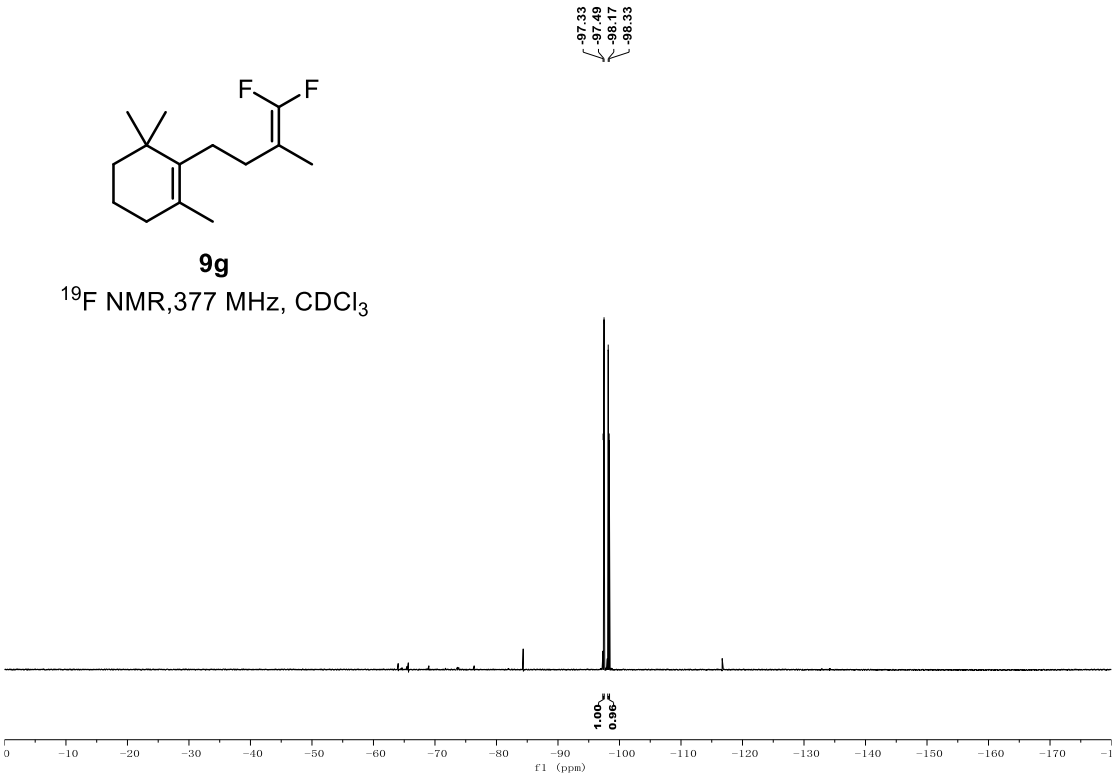
9g

^{1}H NMR, 400 MHz, $CDCl_3$



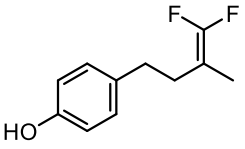
9g

^{1}H NMR, 101 MHz, $CDCl_3$



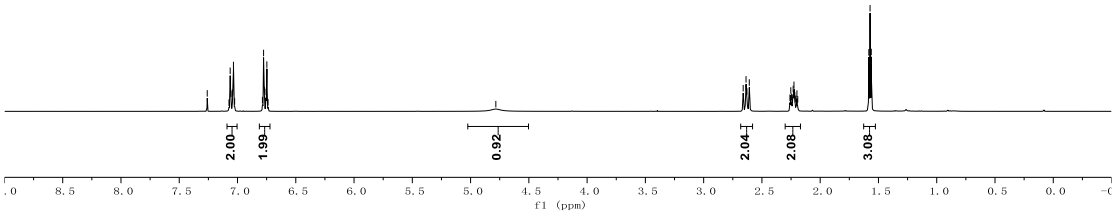
9g

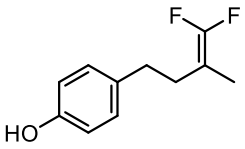
^{19}F NMR,377 MHz, $CDCl_3$



9h

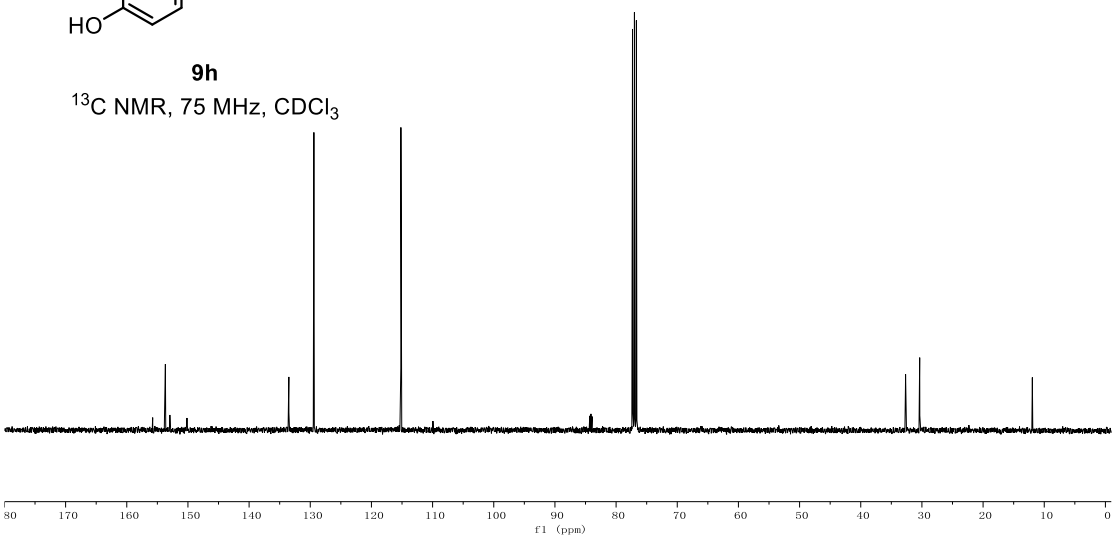
^{1}H NMR, 300 MHz, $CDCl_3$





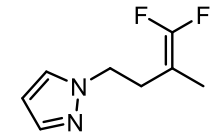
9h

^{13}C NMR, 75 MHz, $CDCl_3$



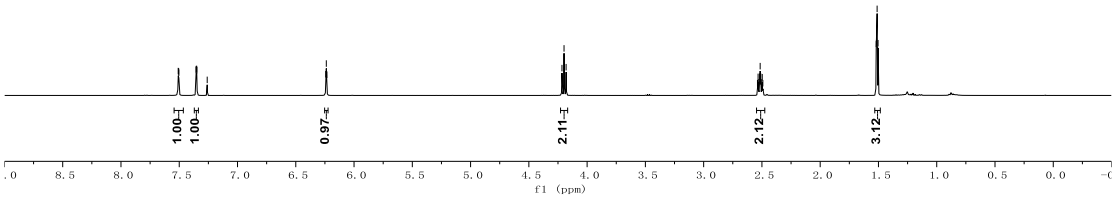
9h

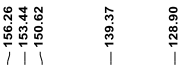
^{19}F NMR, 377 MHz, $CDCl_3$

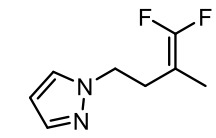


9i

^{1}H NMR, 400 MHz, $CDCl_3$

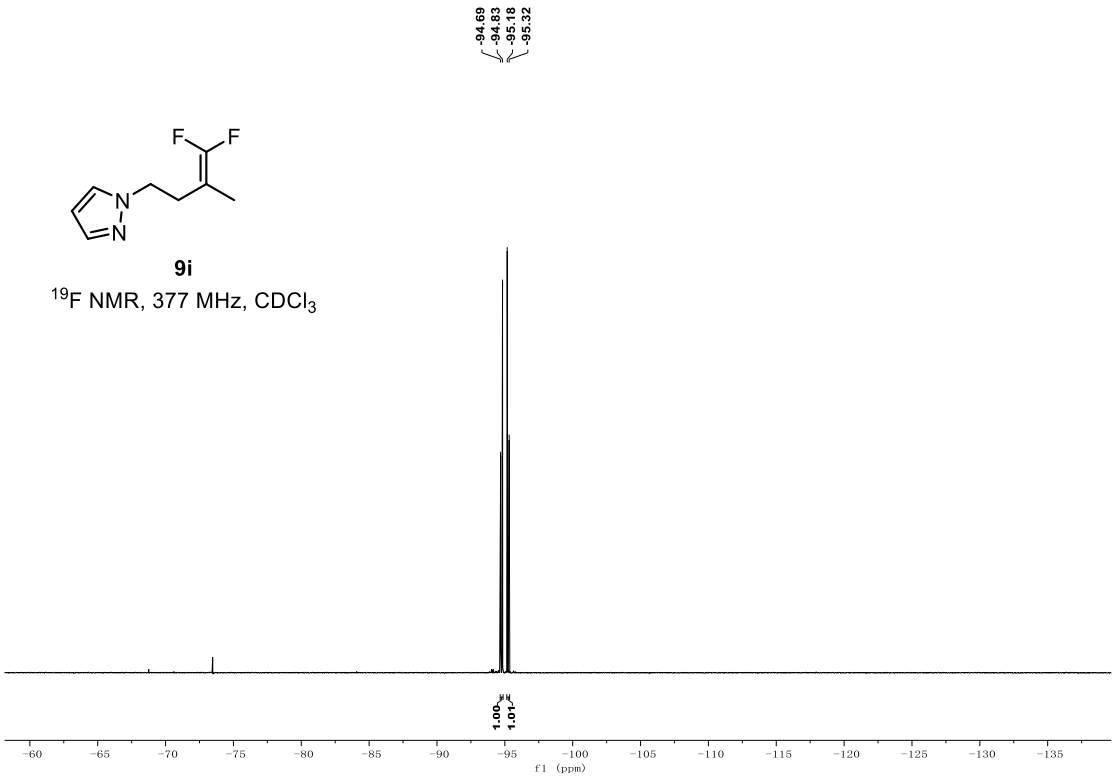






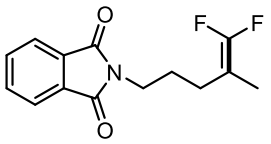
9i

^{13}C NMR, 101 MHz, $CDCl_3$



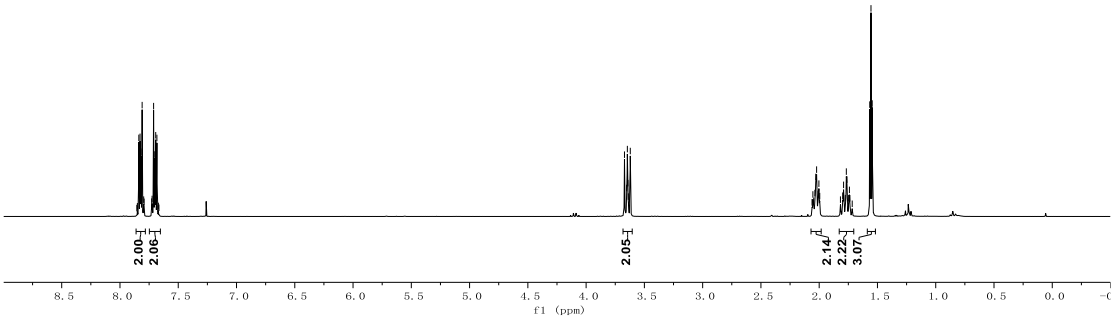
9i

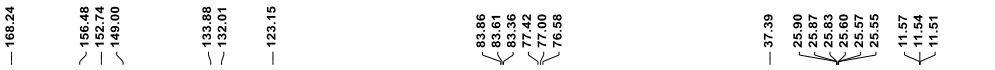
^{19}F NMR, 377 MHz, $CDCl_3$

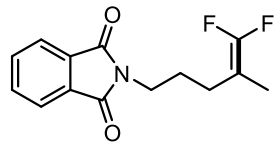


9j

^{1}H NMR, 300 MHz, $CDCl_3$

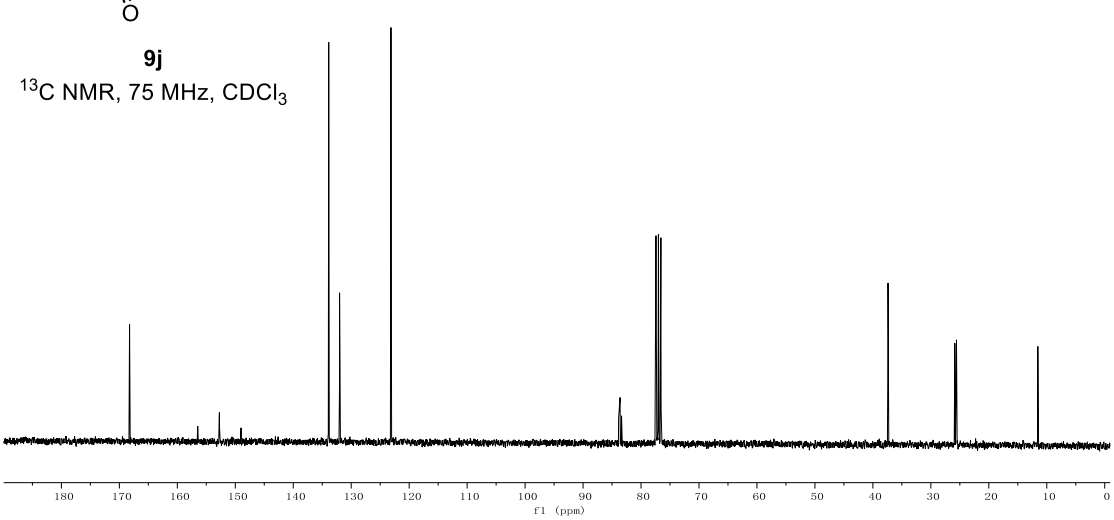


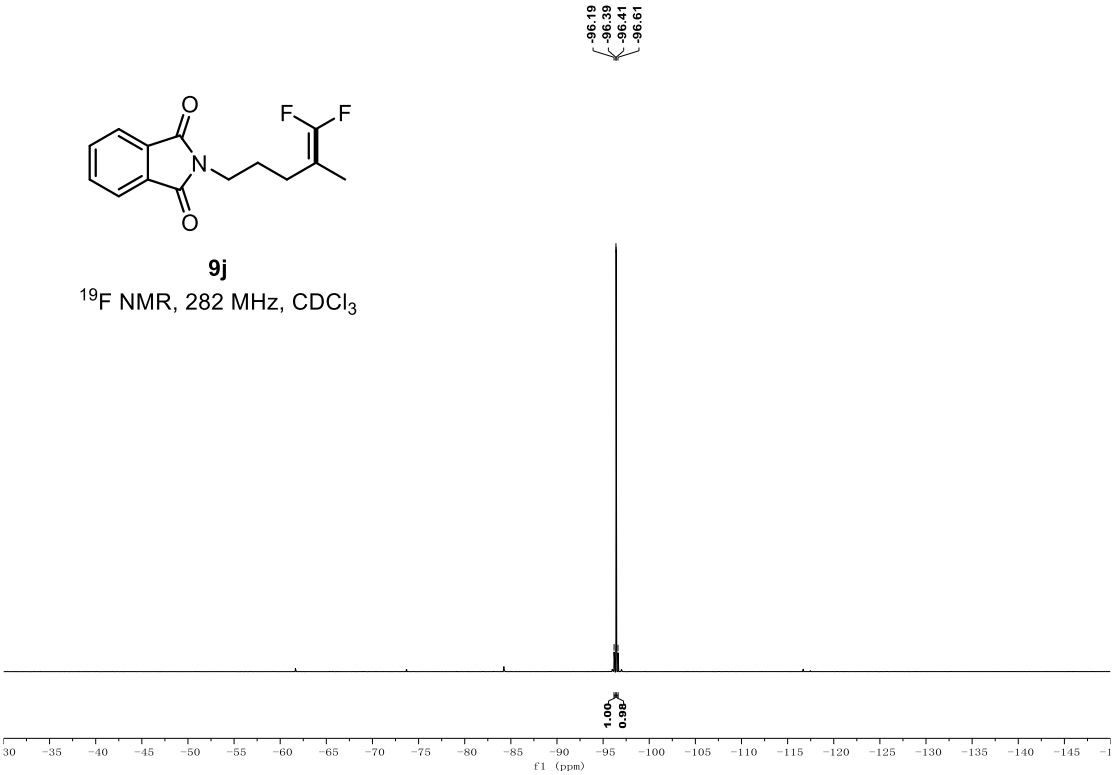




9j

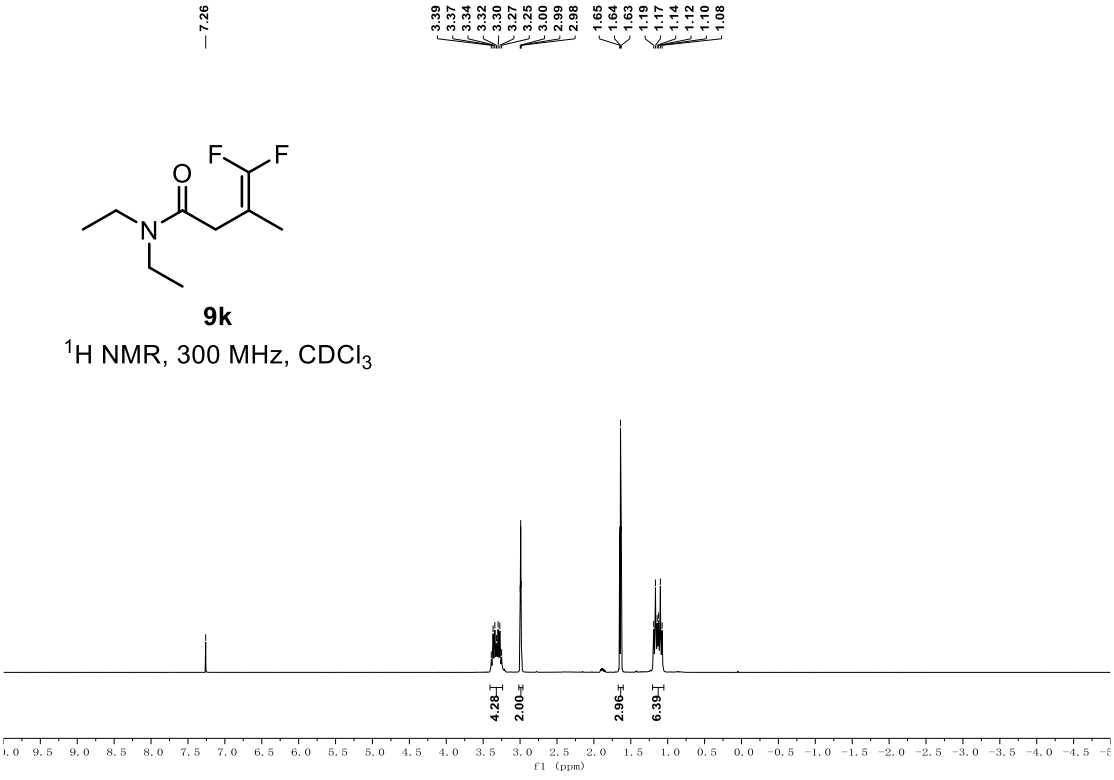
^{13}C NMR, 75 MHz, $CDCl_3$





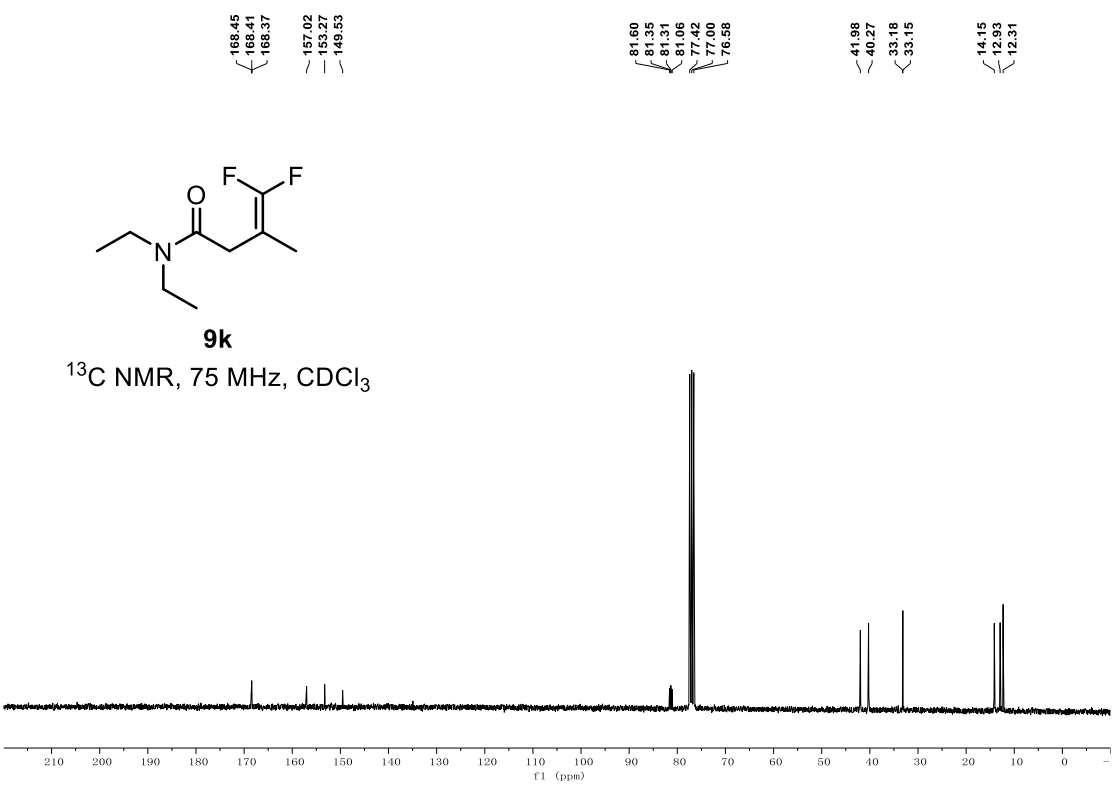
9j

^{19}F NMR, 282 MHz, $CDCl_3$



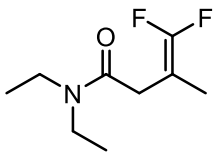
9k

^{1}H NMR, 300 MHz, $CDCl_3$



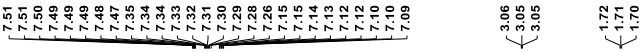
9k

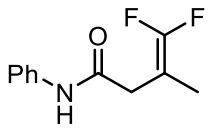
^{13}C NMR, 75 MHz, $CDCl_3$



9k

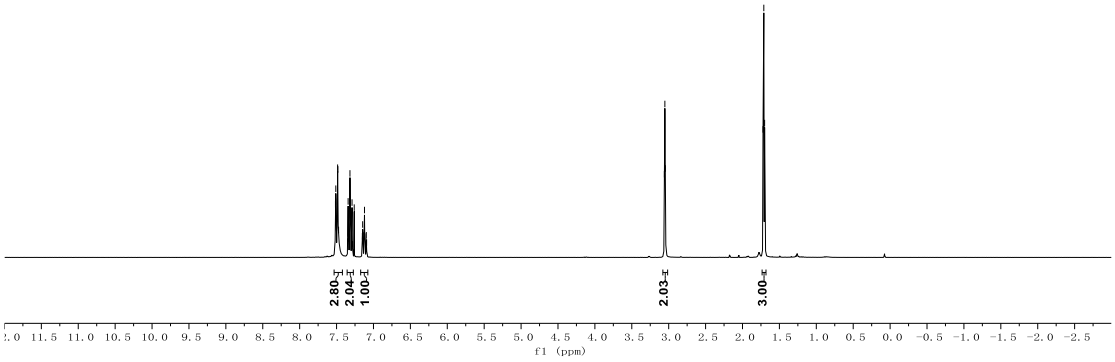
^{19}F NMR, 282 MHz, CDCl3

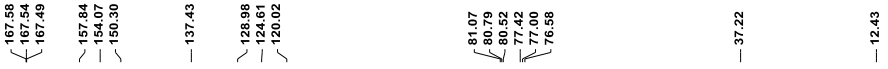


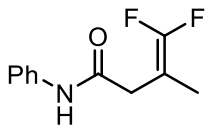


9l

^{1}H NMR, 300 MHz, $CDCl_3$

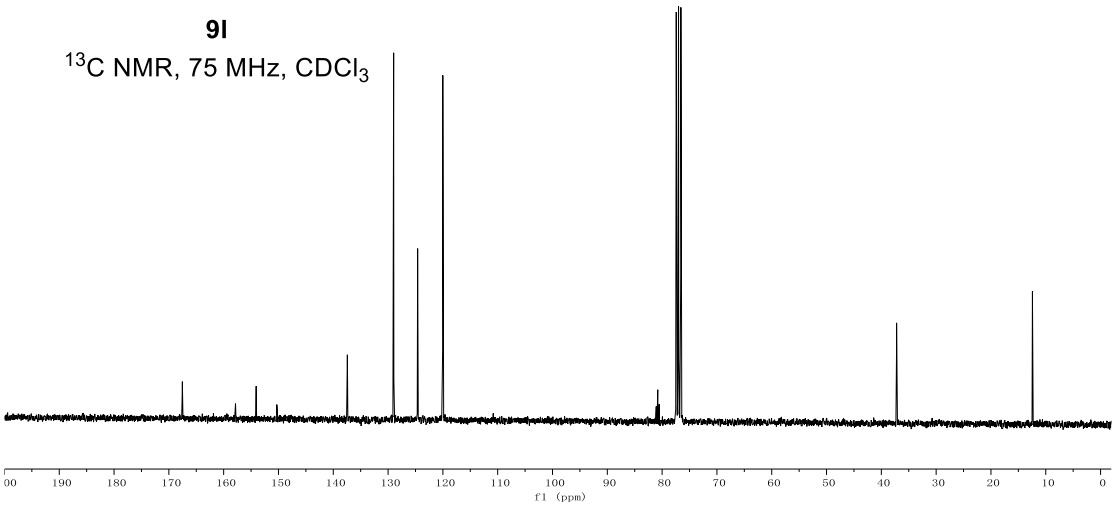


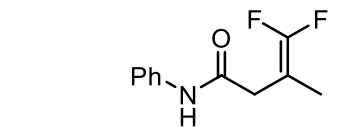




9l

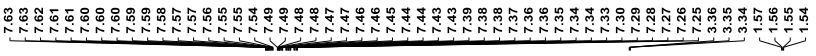
^{13}C NMR, 75 MHz, $CDCl_3$

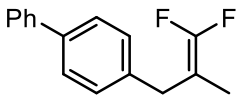




9l

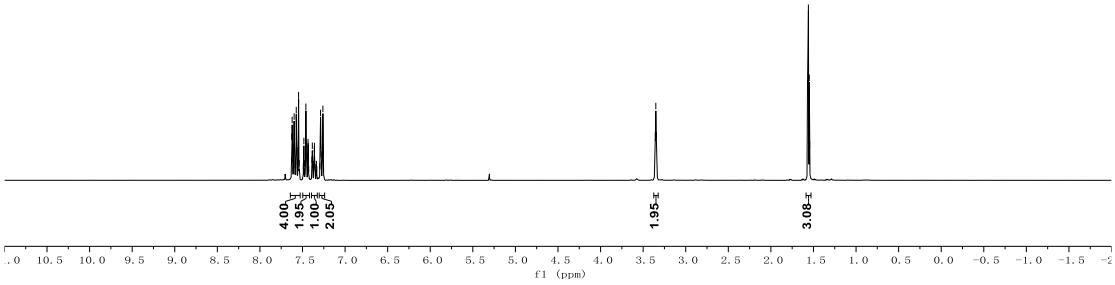
^{19}F NMR, 282 MHz, $CDCl_3$

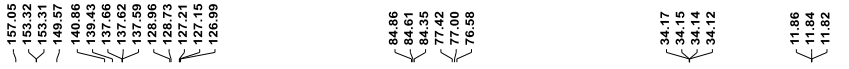


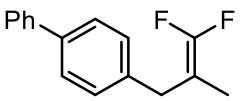


9m

^{1}H NMR, 300 MHz, $CDCl_3$

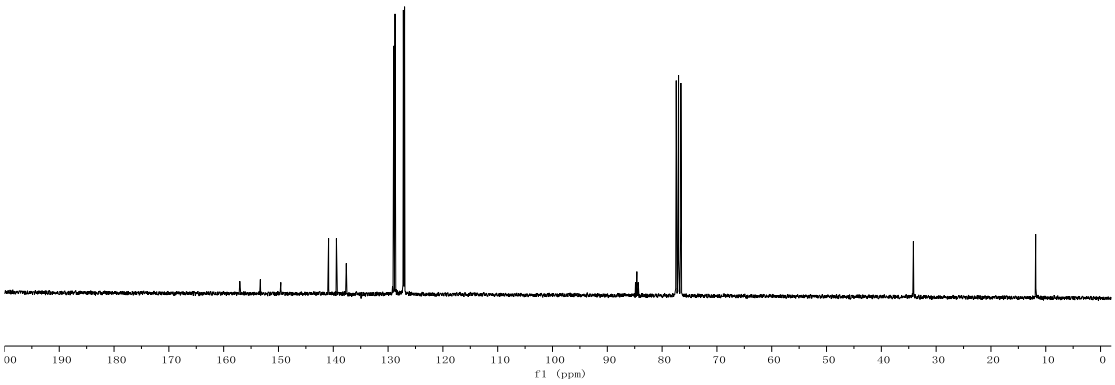


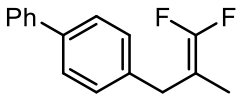




9m

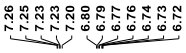
^{13}C NMR, 75 MHz, $CDCl_3$

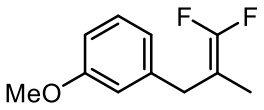




9m

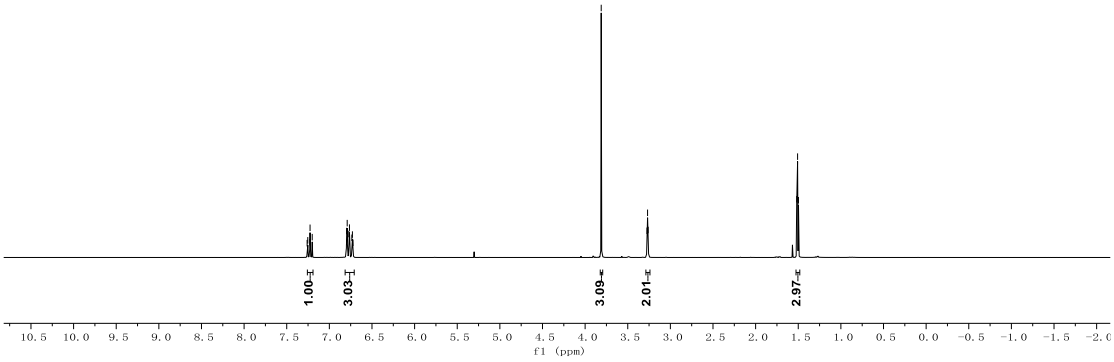
^{19}F NMR, 282 MHz, $CDCl_3$

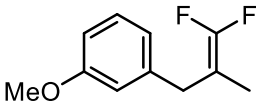




9n

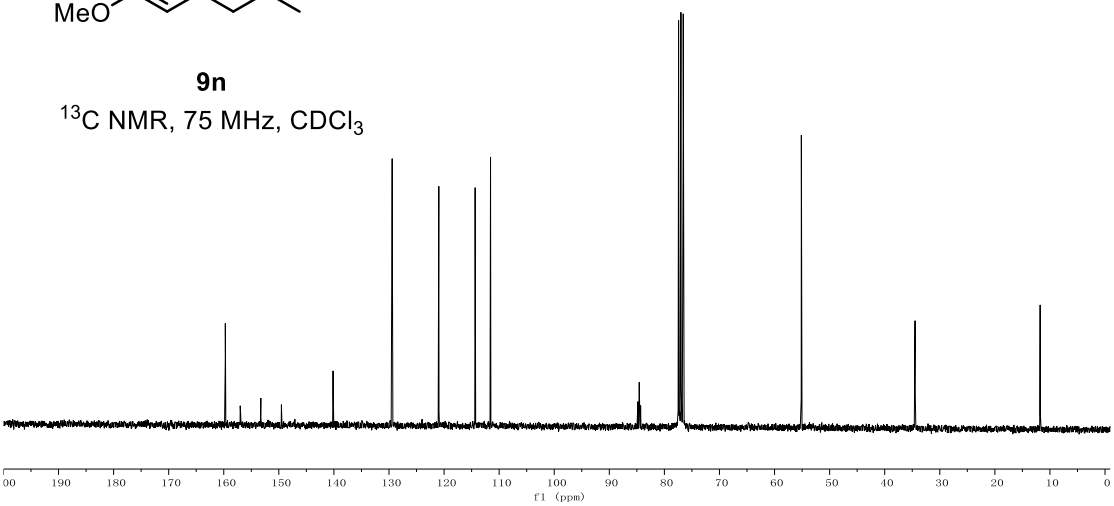
^{1}H NMR, 300 MHz, $CDCl_3$

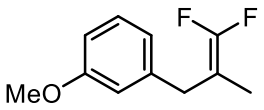




9n

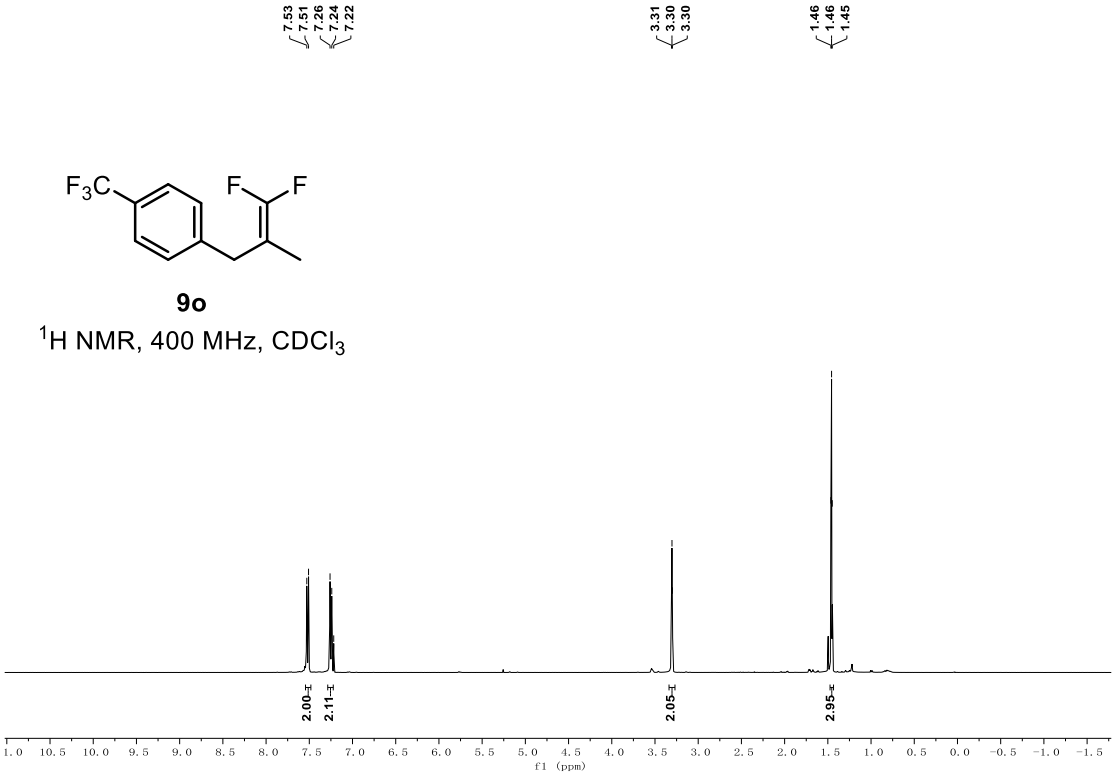
^{13}C NMR, 75 MHz, $CDCl_3$





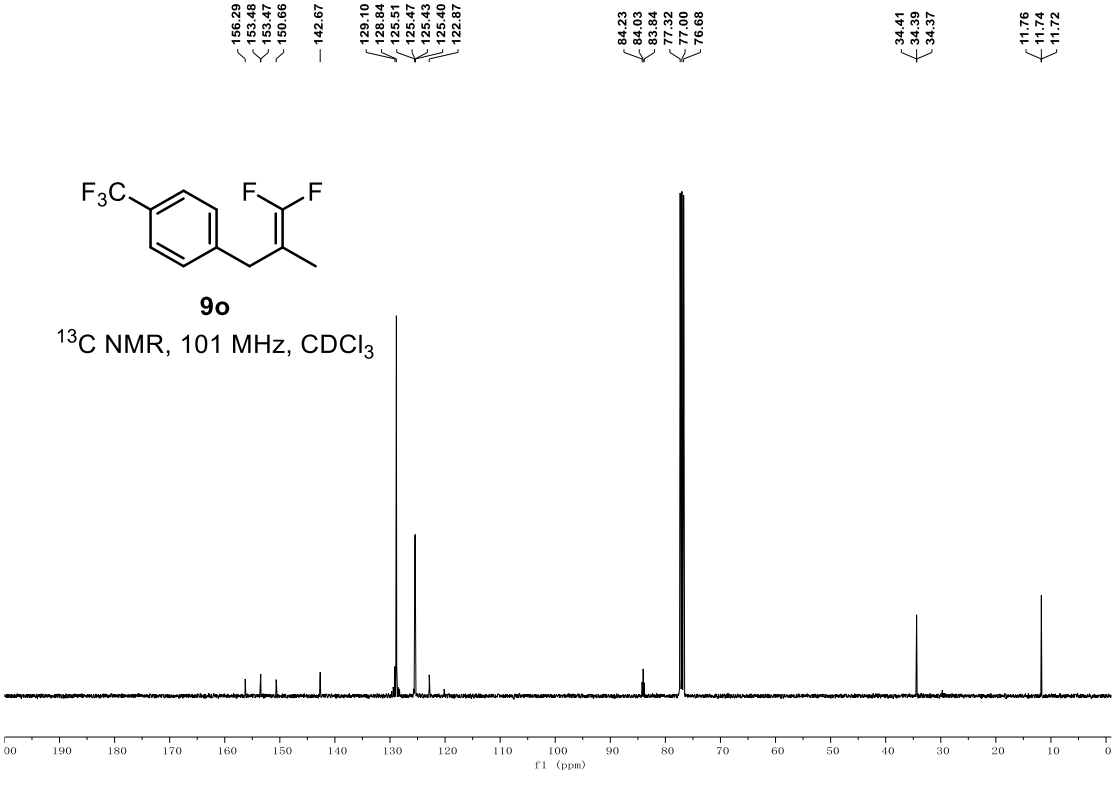
9n

^{19}F NMR, 282 MHz, $CDCl_3$



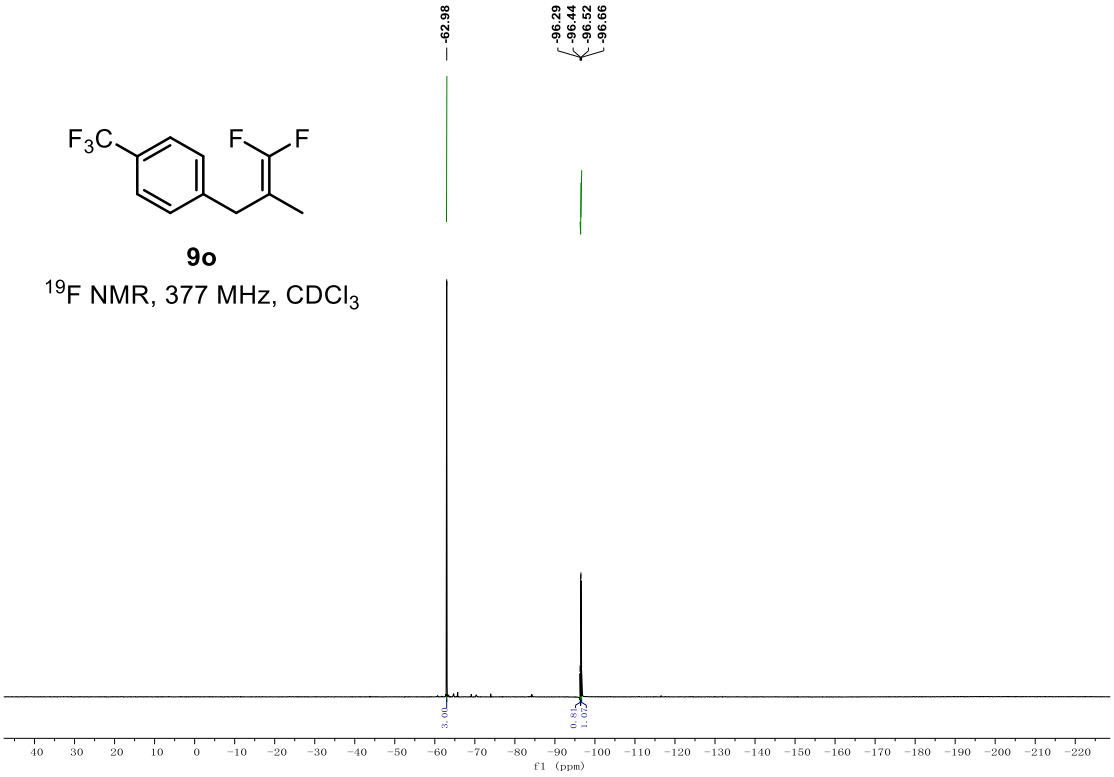
9o

^{1}H NMR, 400 MHz, $CDCl_3$



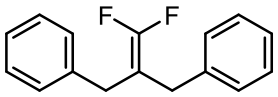
9o

^{13}C NMR, 101 MHz, $CDCl_3$



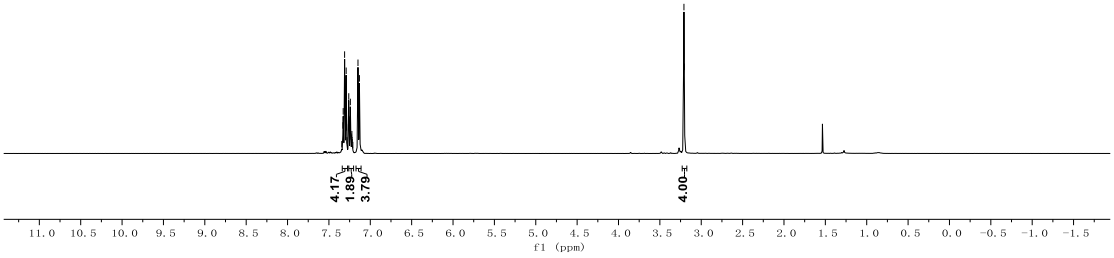
9o

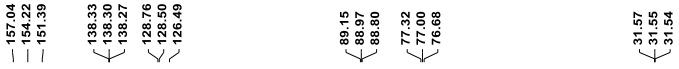
^{19}F NMR, 377 MHz, $CDCl_3$

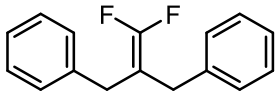


9p

^{1}H NMR, 400 MHz, $CDCl_3$

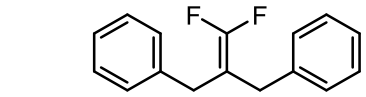






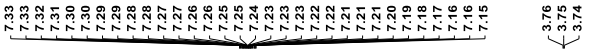
9p

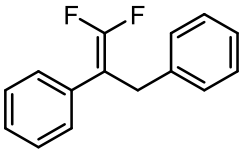
^{13}C NMR, 101 MHz, $CDCl_3$



9p

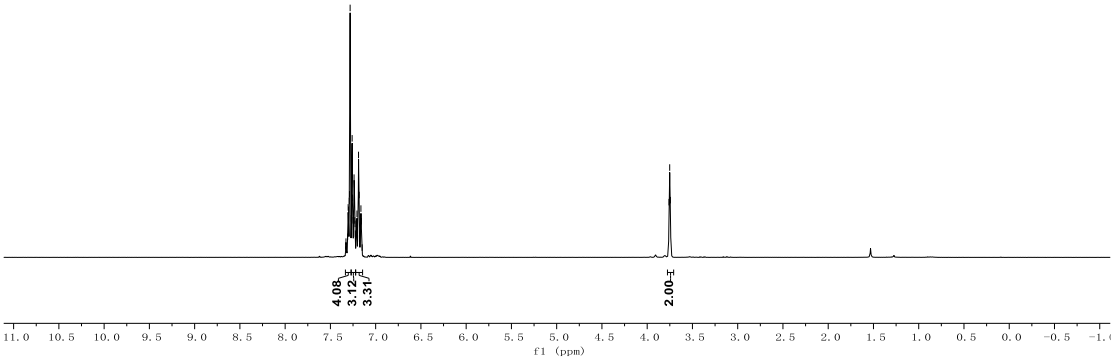
^{19}F NMR, 376 MHz, $CDCl_3$

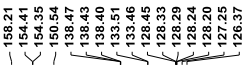


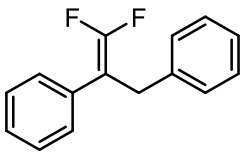


9q

^{1}H NMR, 300 MHz, $CDCl_3$

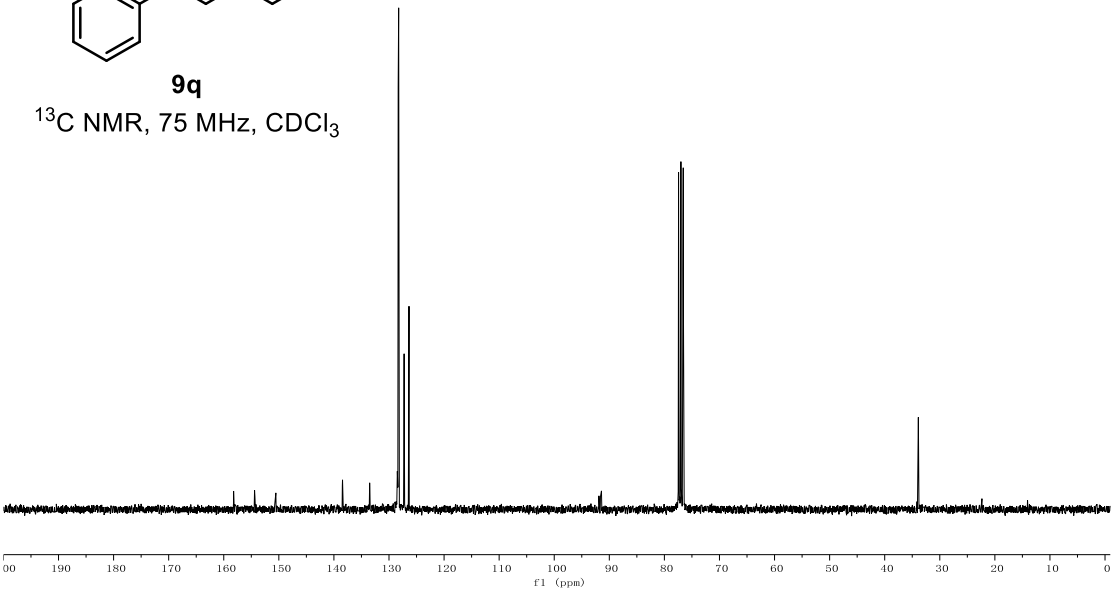


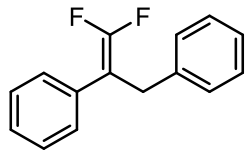




9q

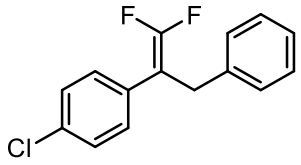
^{13}C NMR, 75 MHz, $CDCl_3$





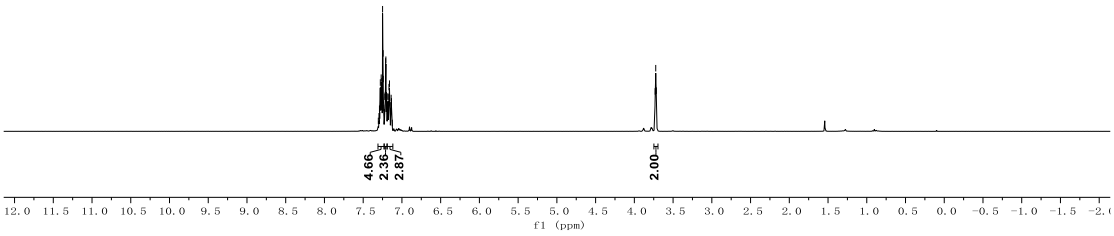
9q

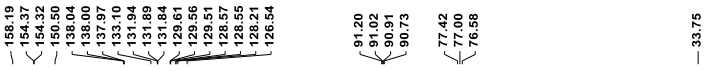
^{19}F NMR, 282 MHz, $CDCl_3$

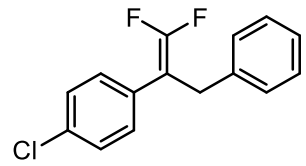


9r

^{1}H NMR, 300 MHz, $CDCl_3$

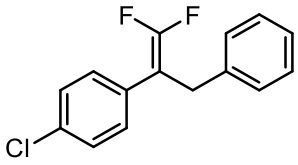






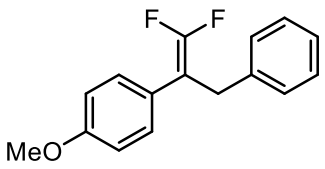
9r

^{13}C NMR, 75 MHz, $CDCl_3$



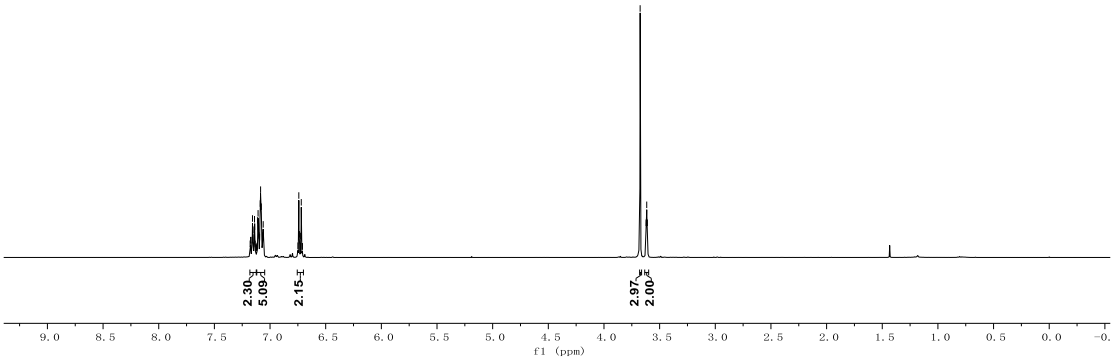
9r

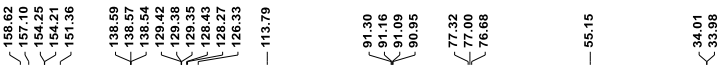
^{19}F NMR, 282 MHz, $CDCl_3$

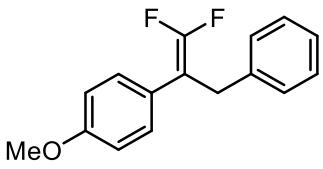


9s

^{1}H NMR, 400 MHz, $CDCl_3$

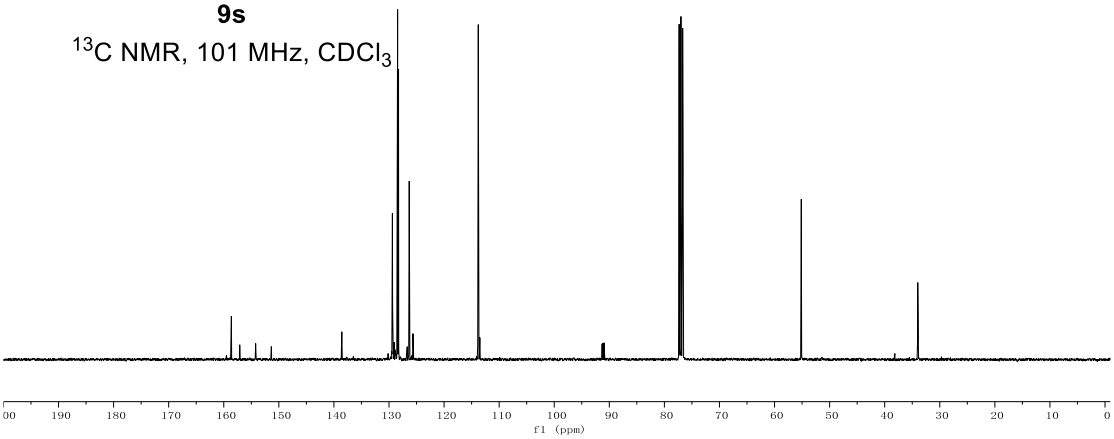


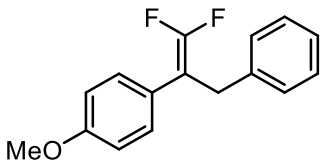




9s

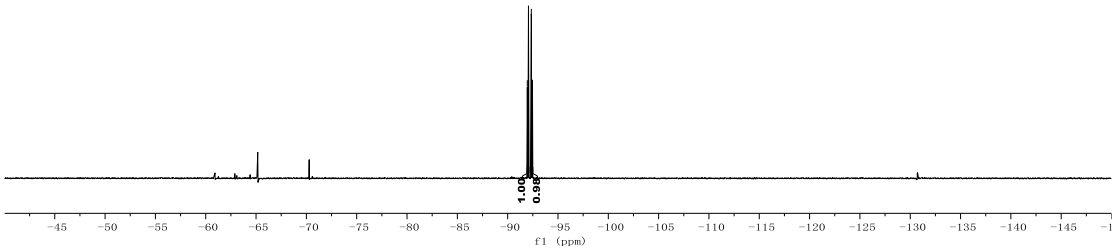
^{13}C NMR, 101 MHz, $CDCl_3$

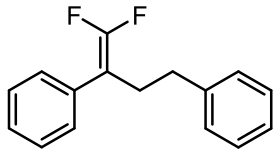




9s

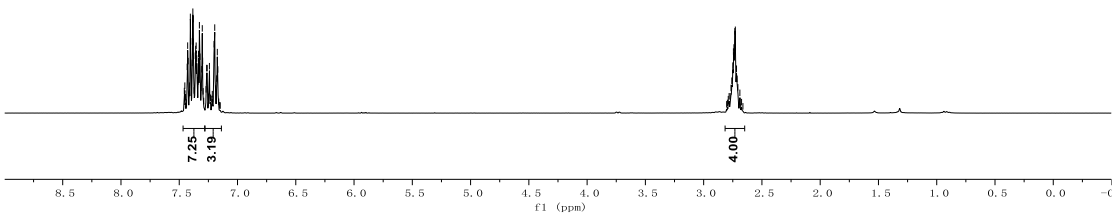
^{19}F NMR, 376 MHz, $CDCl_3$

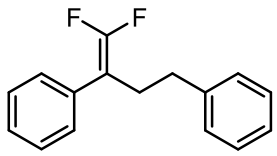




9t

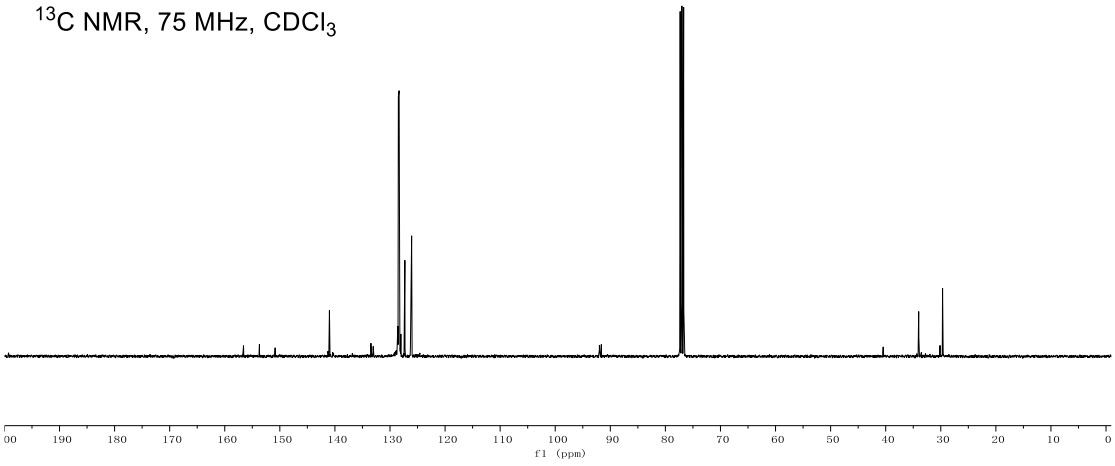
^{1}H NMR, 300 MHz, $CDCl_3$

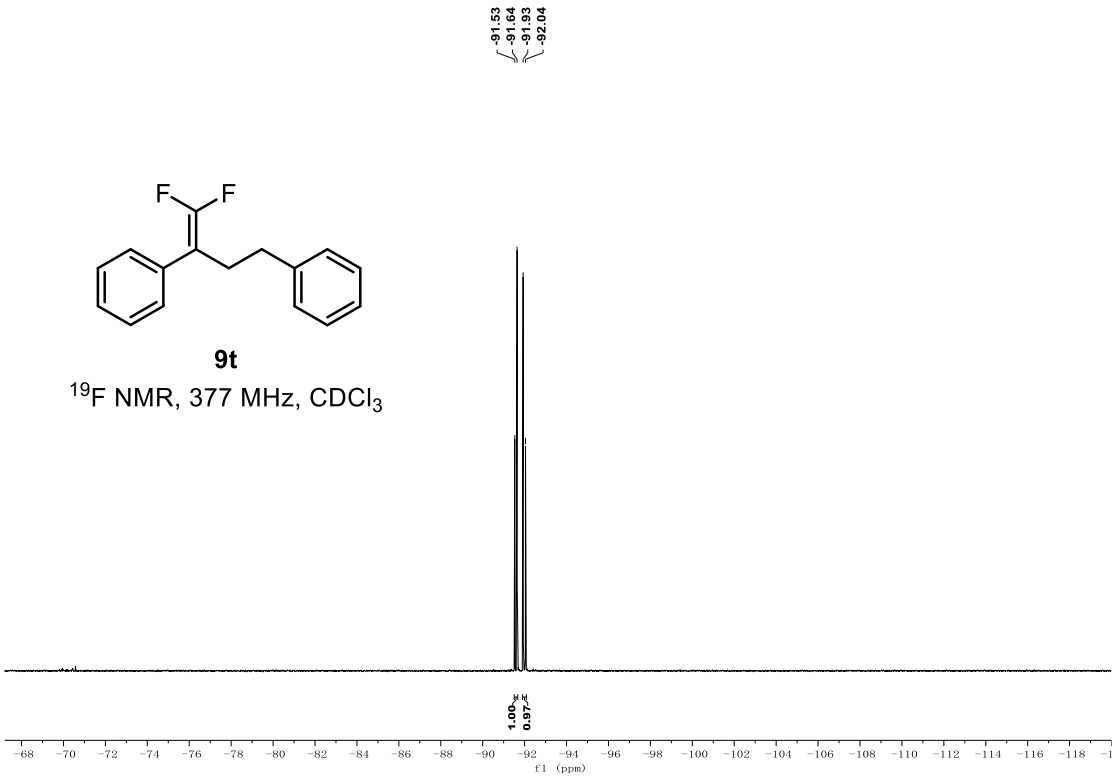




9t

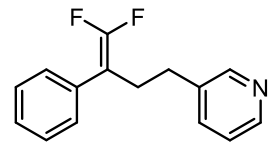
^{13}C NMR, 75 MHz, $CDCl_3$





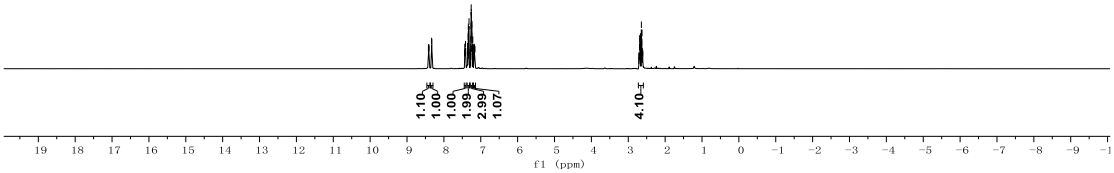
9t

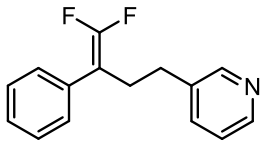
^{19}F NMR, 377 MHz, $CDCl_3$



9u

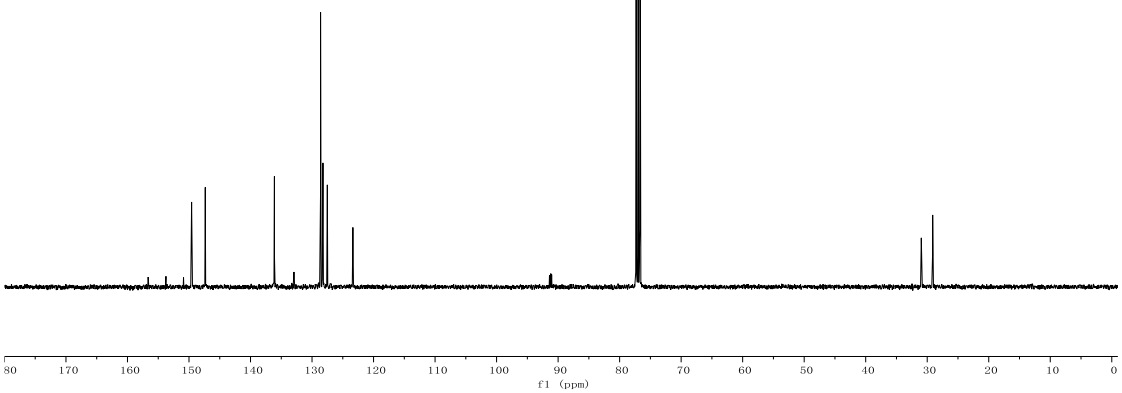
^{1}H NMR, 400 MHz, $CDCl_3$

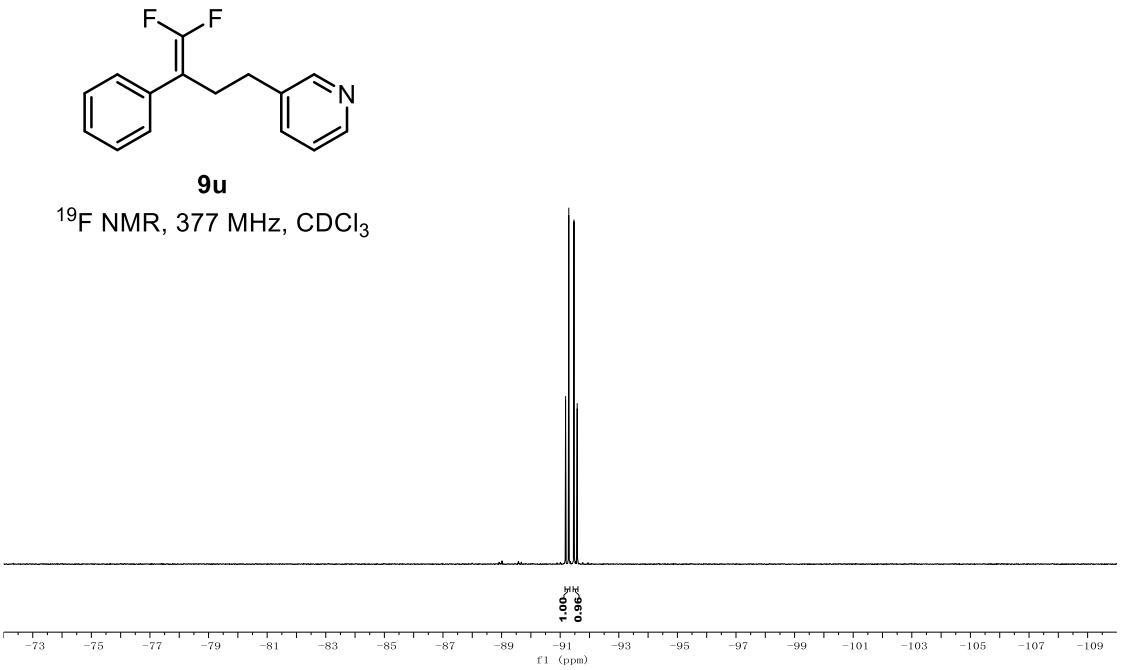




9u

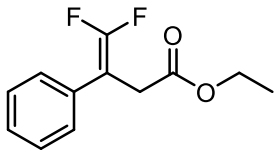
^{13}C NMR,101 MHz, $CDCl_3$





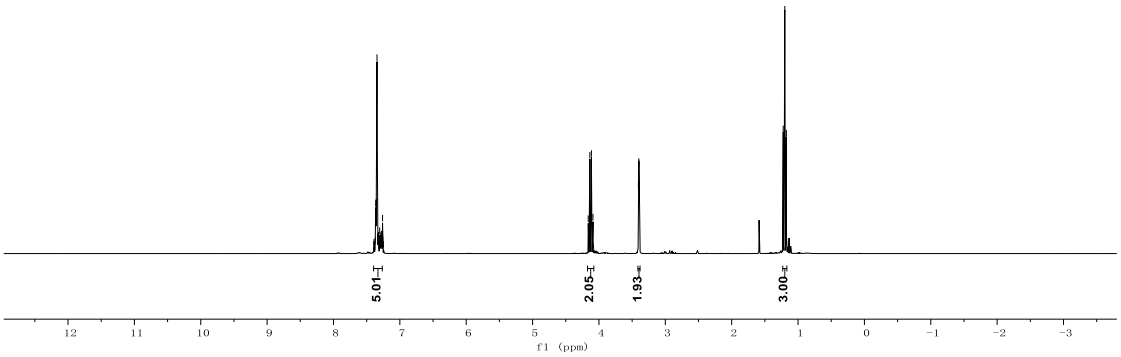
9u

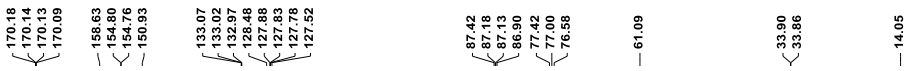
^{19}F NMR, 377 MHz, $CDCl_3$

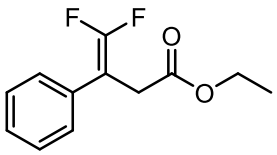


9v

^{1}H NMR, 300 MHz, $CDCl_3$

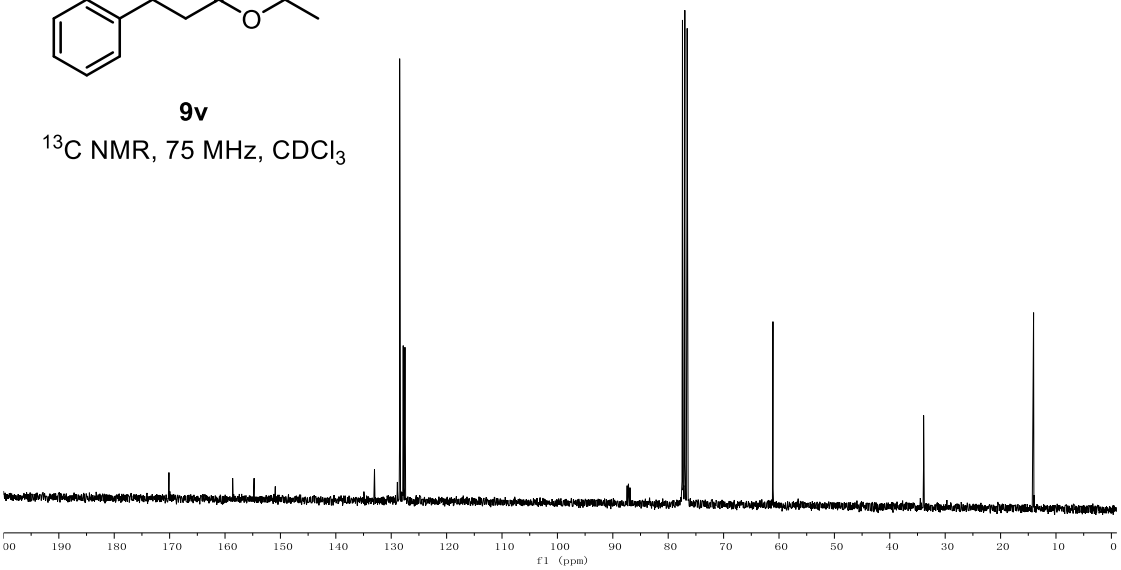


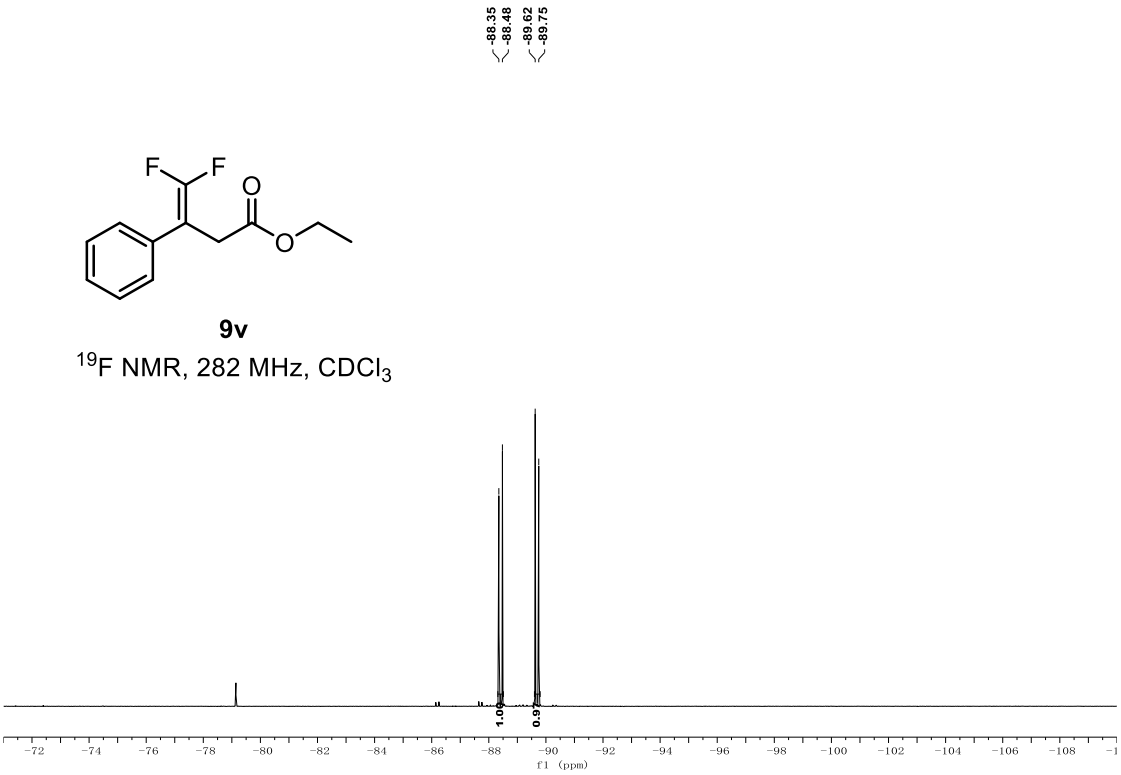




9v

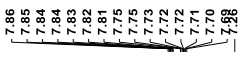
^{13}C NMR, 75 MHz, $CDCl_3$

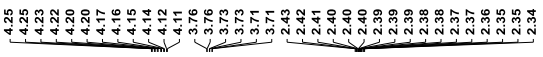


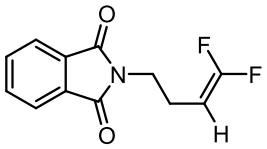


9v

^{19}F NMR, 282 MHz, $CDCl_3$

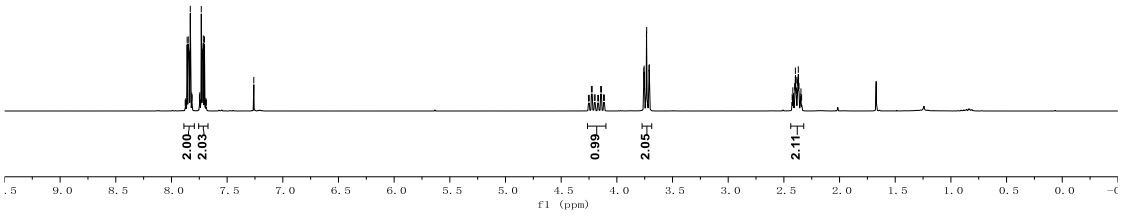


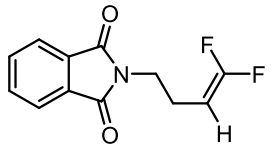




9w

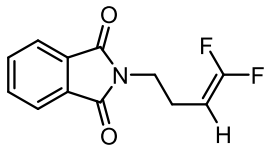
^{1}H NMR, 300 MHz, $CDCl_3$





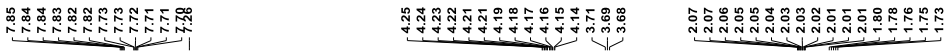
9w

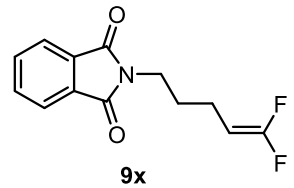
^{13}C NMR, 75 MHz, $CDCl_3$



9w

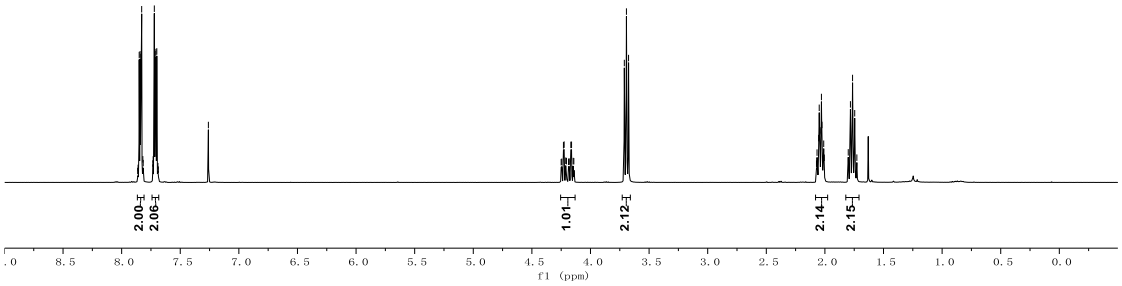
^{19}F NMR, 282 MHz, $CDCl_3$

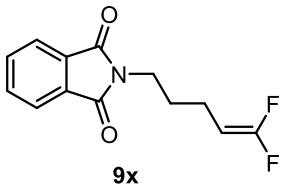




9x

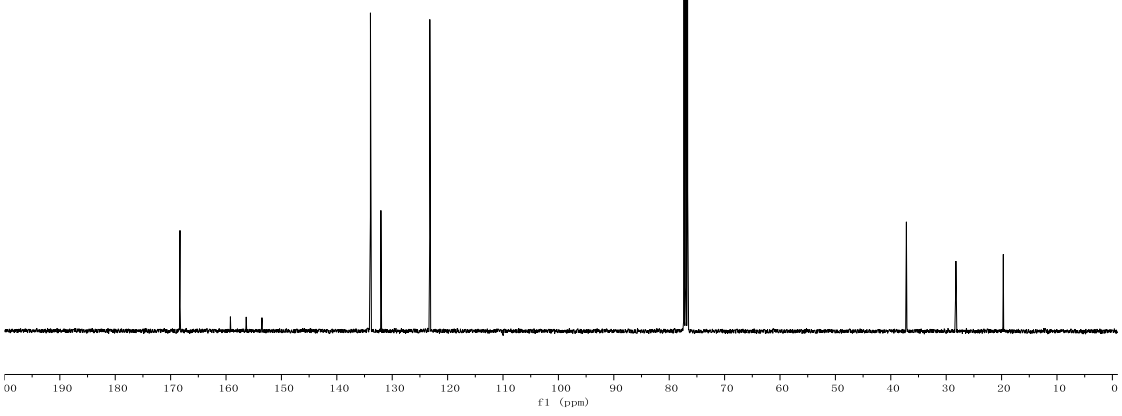
^{1}H NMR, 400 MHz, $CDCl_3$

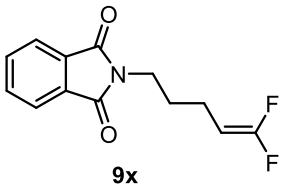




9x

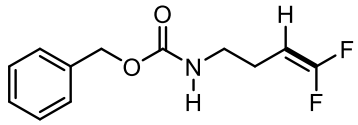
^{13}C NMR, 101 MHz, $CDCl_3$





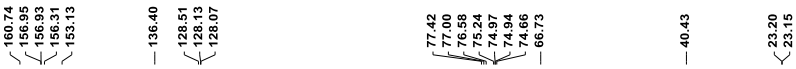
9x

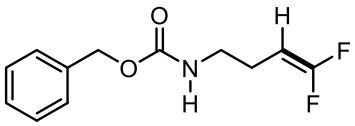
^{19}F NMR, 377 MHz, $CDCl_3$



9y

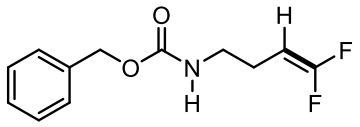
^{1}H NMR, 300 MHz, $CDCl_3$





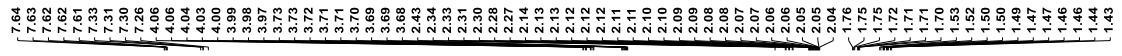
9y

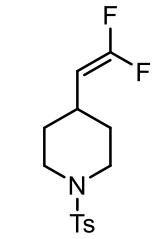
^{13}C NMR, 75 MHz, $CDCl_3$



9y

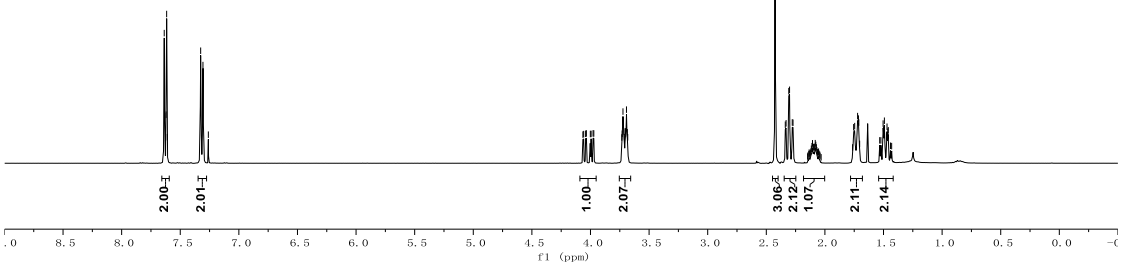
^{19}F NMR, 282 MHz, $CDCl_3$

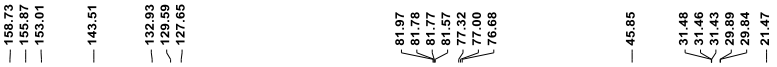


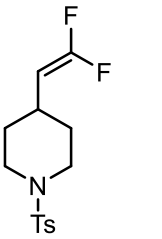


9z

^{1}H NMR, 400 MHz, $CDCl_3$

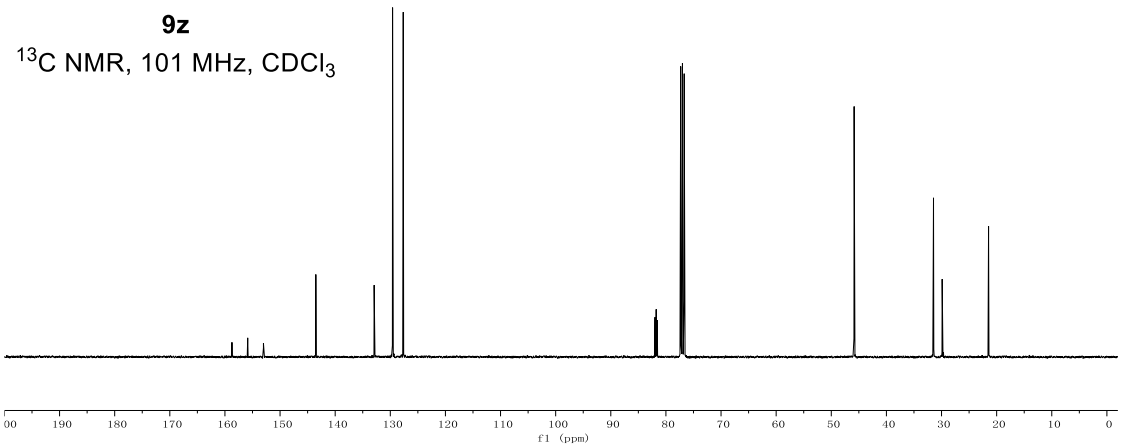


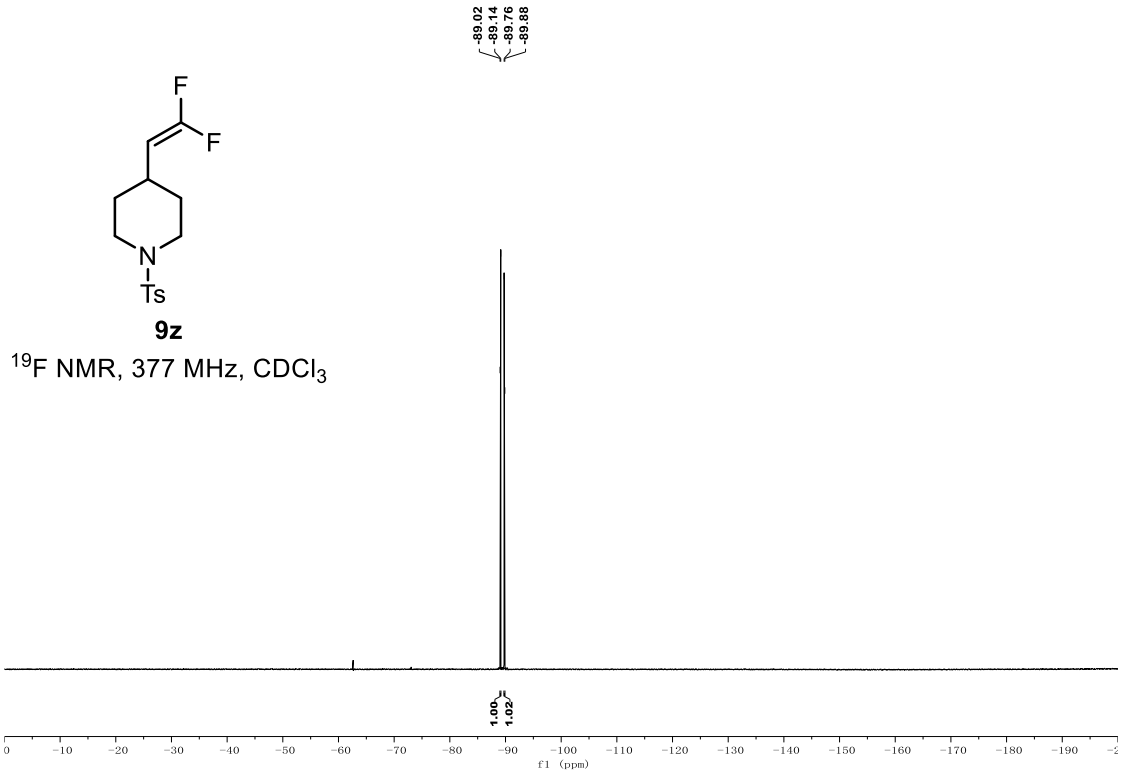




9z

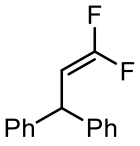
^{13}C NMR, 101 MHz, $CDCl_3$





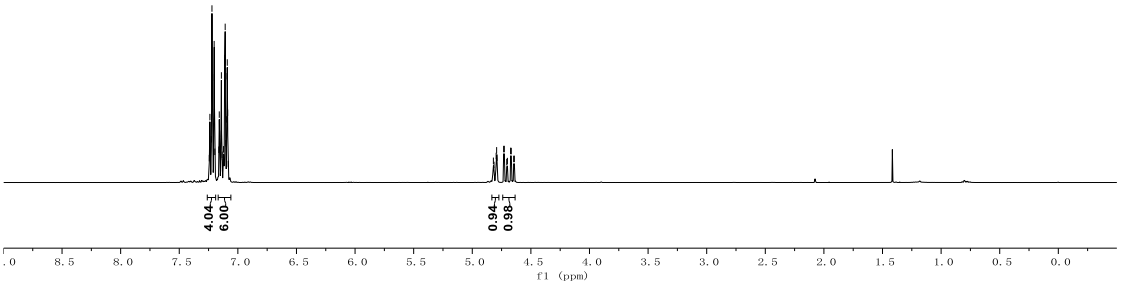
9z

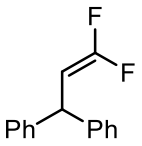
^{19}F NMR, 377 MHz, $CDCl_3$



9aa

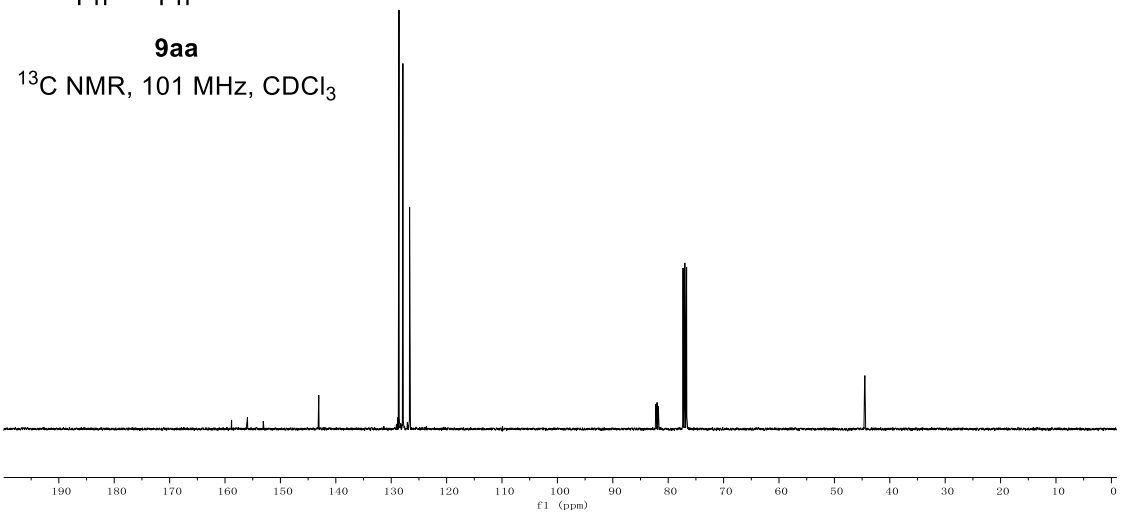
^{1}H NMR, 400 MHz, $CDCl_3$

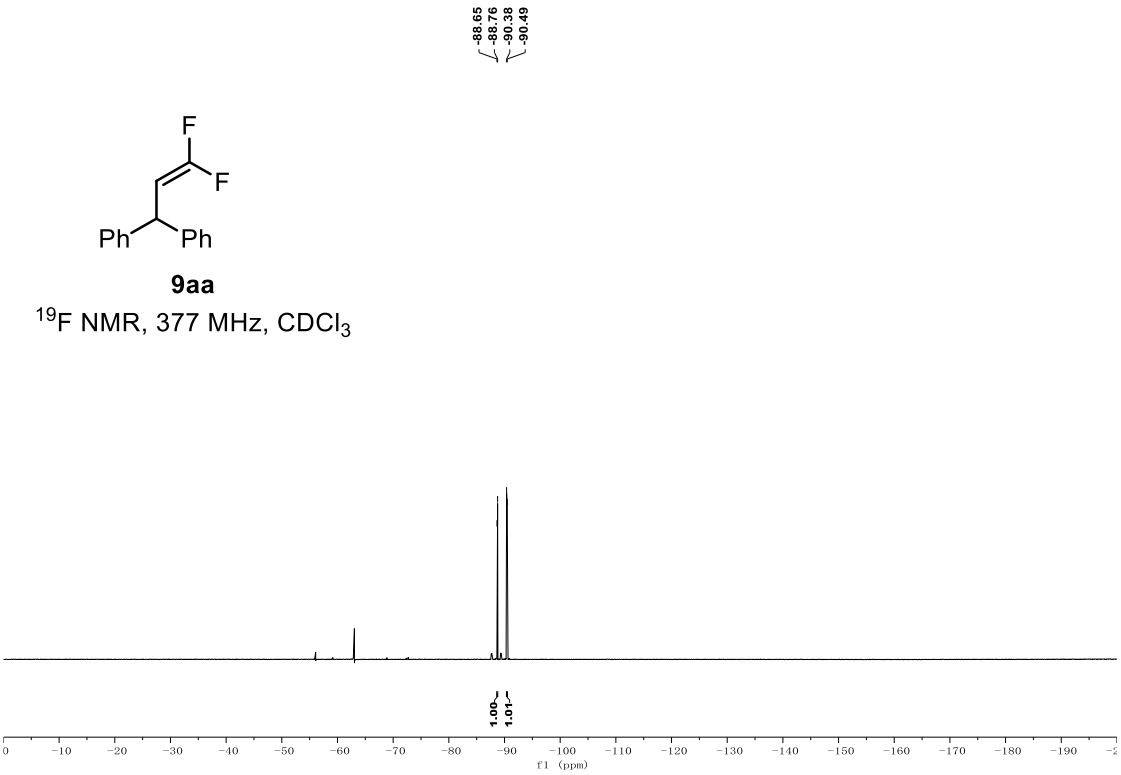




9aa

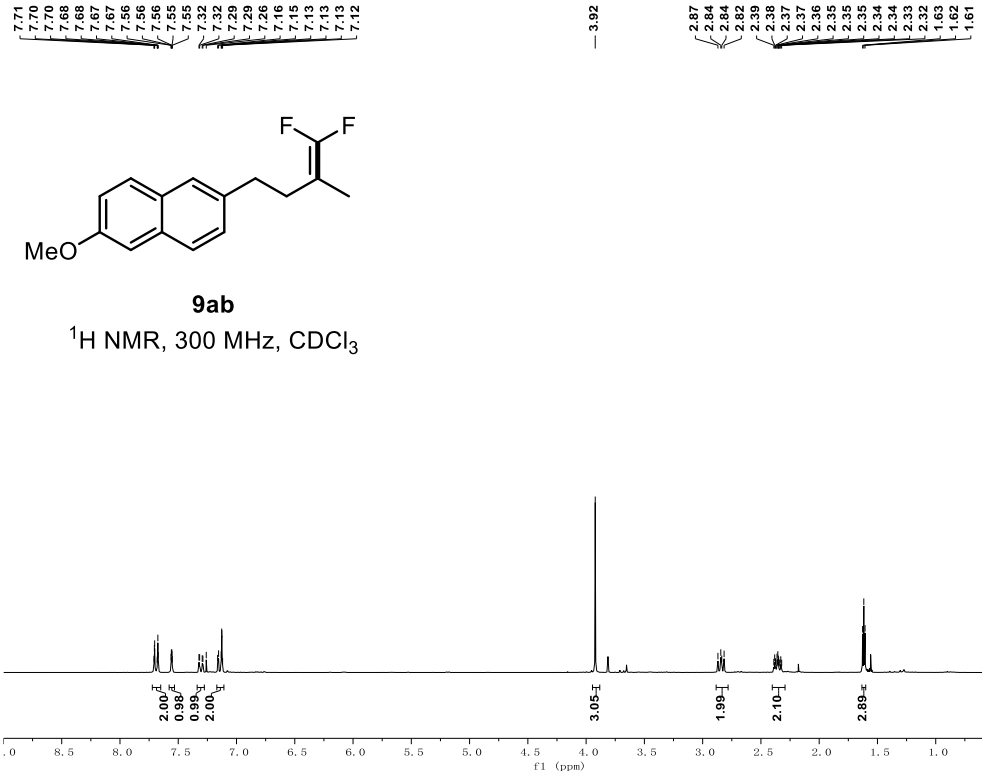
^{13}C NMR, 101 MHz, $CDCl_3$





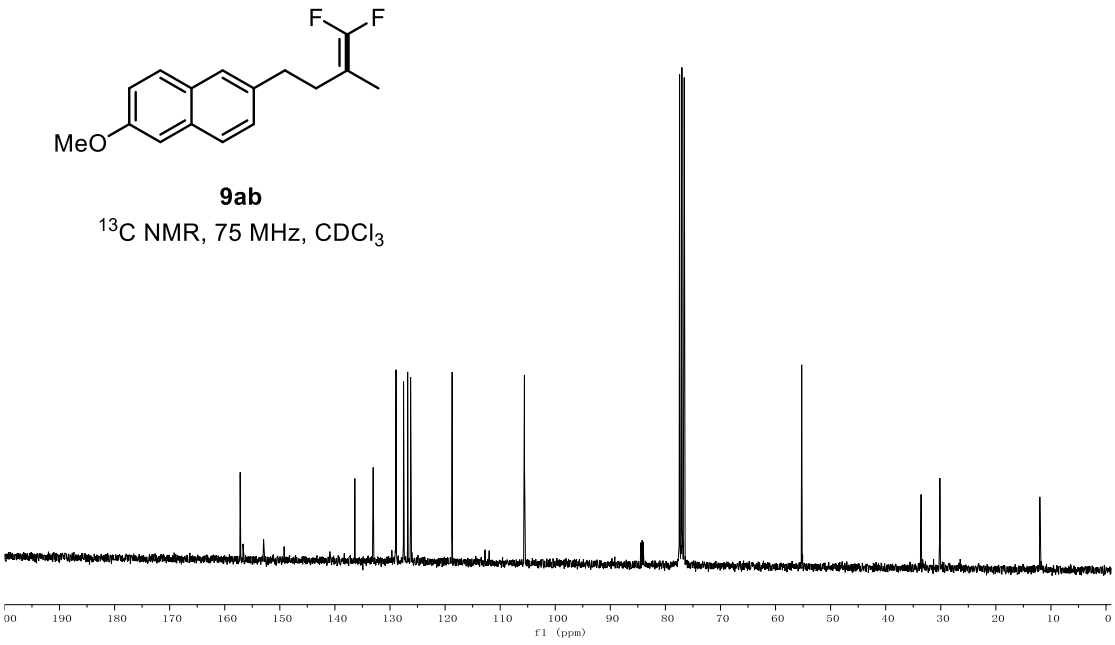
9aa

^{19}F NMR, 377 MHz, $CDCl_3$



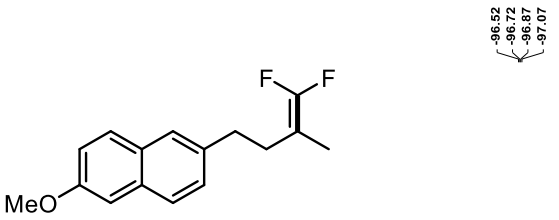
9ab

^{1}H NMR, 300 MHz, $CDCl_3$



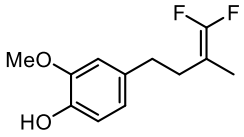
9ab

^{13}C NMR, 75 MHz, $CDCl_3$



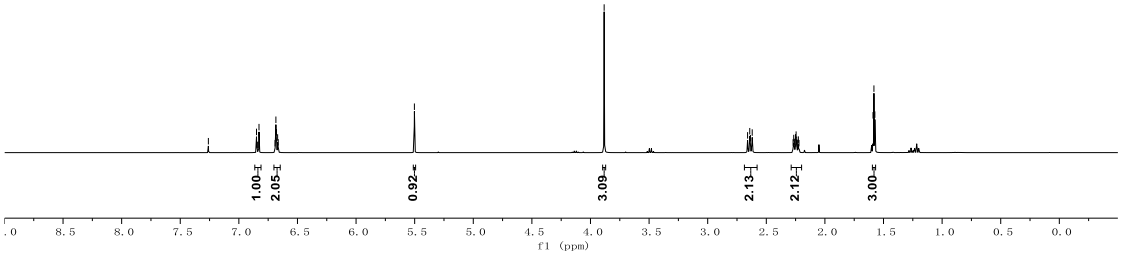
9ab

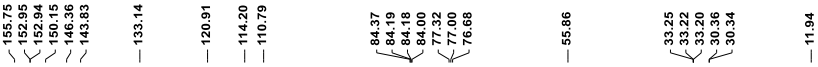
^{19}F NMR, 282 MHz, $CDCl_3$

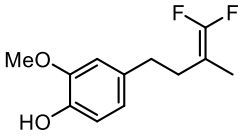


9ac

^{1}H NMR, 400 MHz, $CDCl_3$

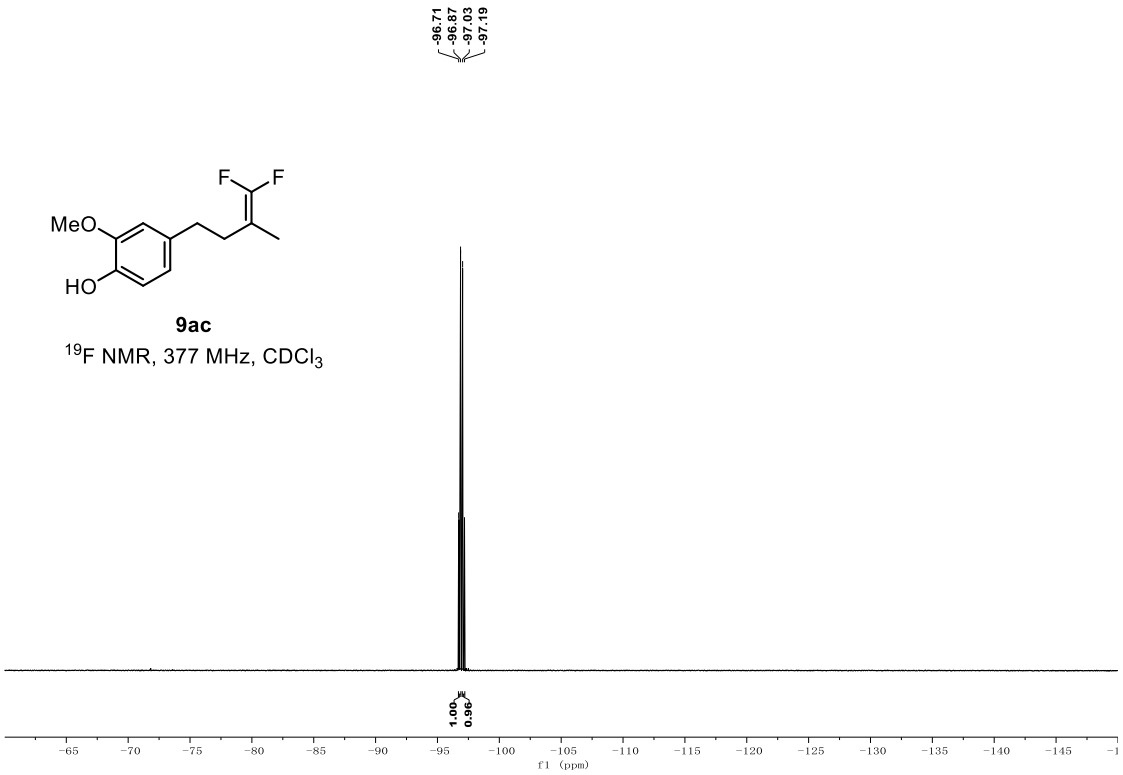






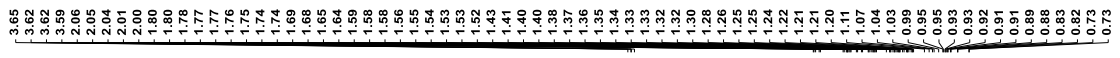
9ac

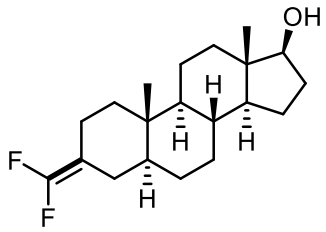
^{13}C NMR, 101 MHz, $CDCl_3$



9ac

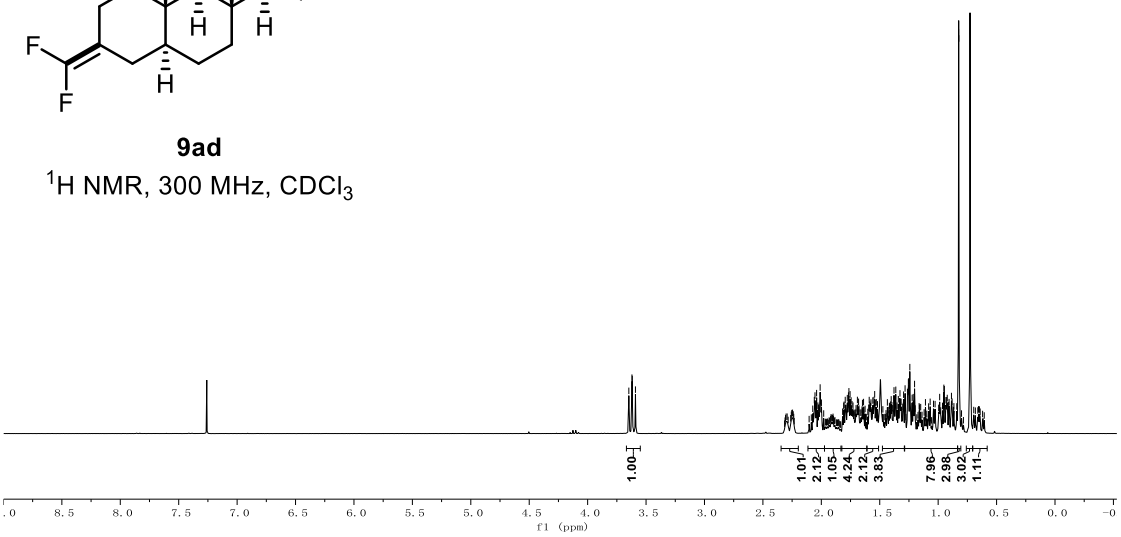
^{19}F NMR, 377 MHz, $CDCl_3$

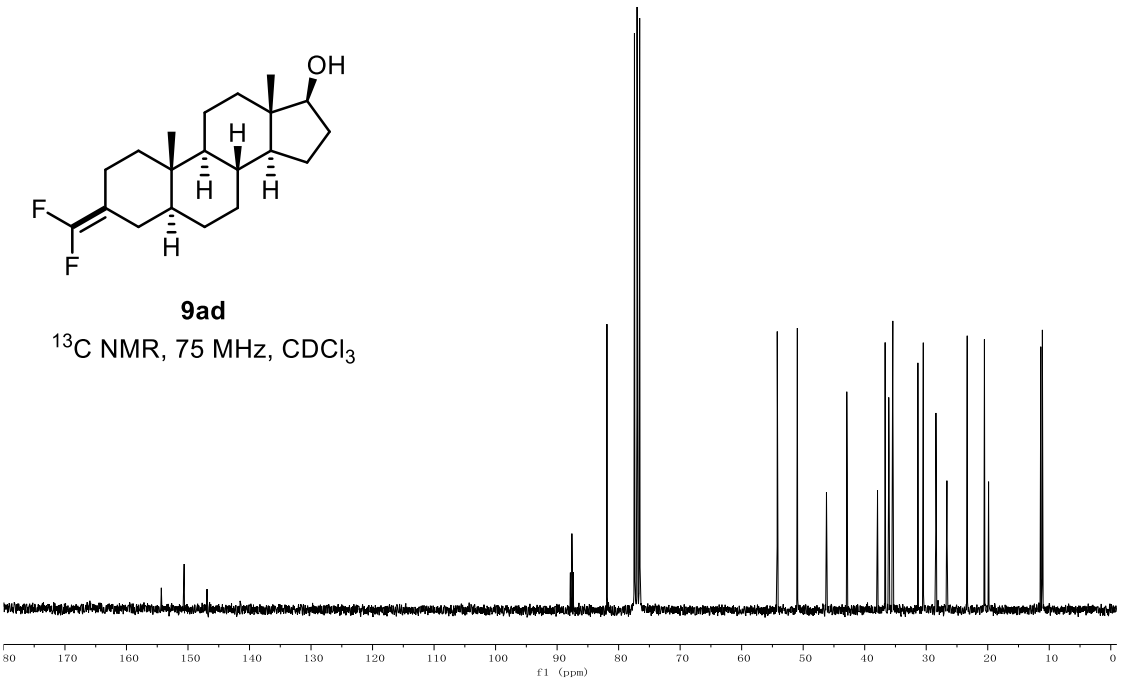




9ad

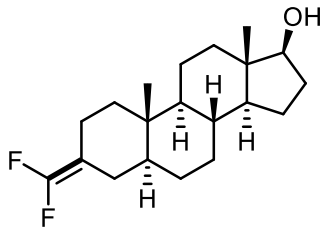
^{1}H NMR, 300 MHz, $CDCl_3$





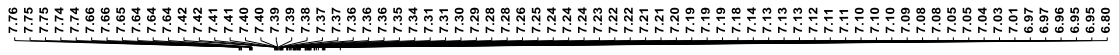
9ad

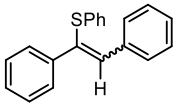
^{13}C NMR, 75 MHz, $CDCl_3$



9ad

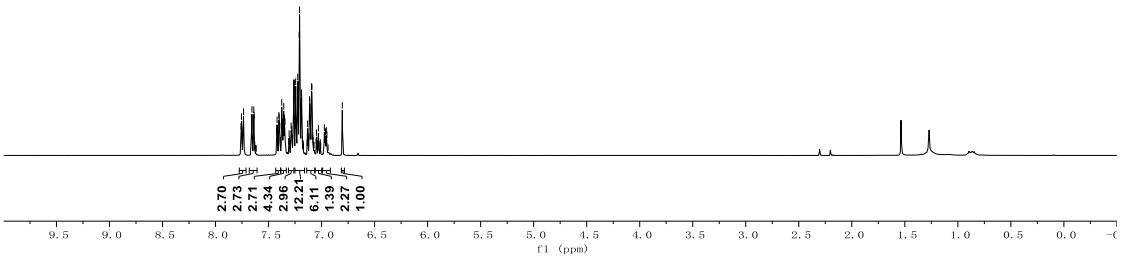
^{19}F NMR, 282 MHz, $CDCl_3$

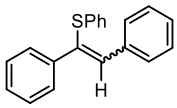




Z and E isomer

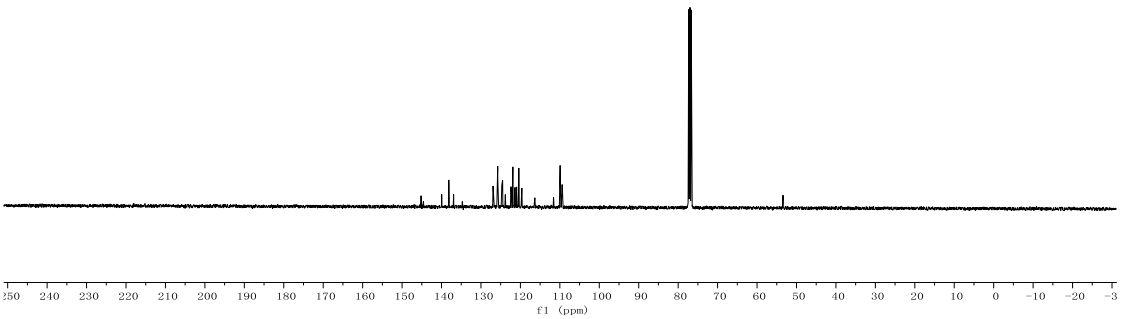
^{1}H NMR, 400 MHz, $CDCl_3$

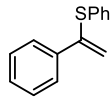




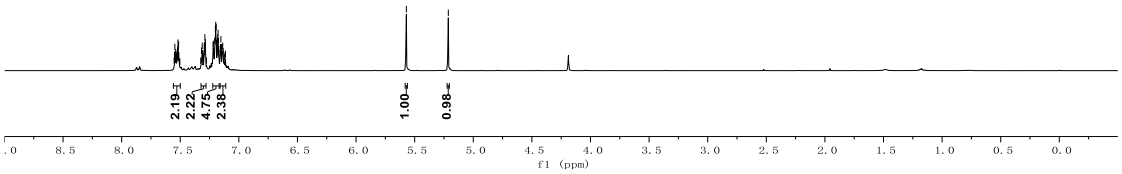
Z and E isomer

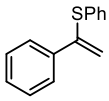
^{13}C NMR, 101 MHz, $CDCl_3$





^{1}H NMR, 300 MHz, $CDCl_3$





^{13}C NMR, 75 MHz, $CDCl_3$