Supplementary Information

for

Expedient Deaminative Phosphorylation and Sulfonylation of Benzylic Tertiary Amines Enabled by Difluorocarbene

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1. Supplementary methods

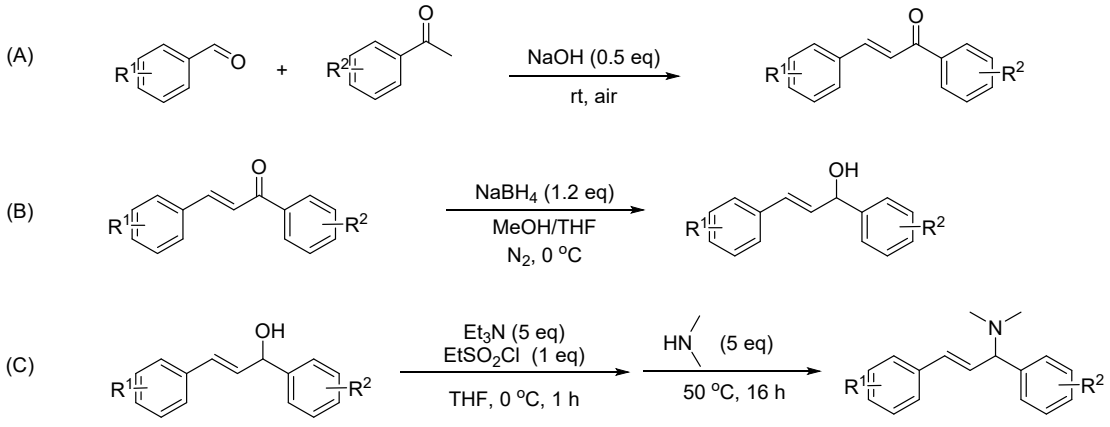
1.1 General information

All chemicals were purchased from Leyan.com ($BrCF_2COOK$, $BrCF_2COONa$), Energy chemical company ($BrCF_2COOEt$, $BrCF_2PO(OEt)_2$, $ClCF_2COONa$), Adamas Reagent, Bide Pharmatech Ltd ($TMSCF_2Br$,), and Shang Fluoro Company ($ClCF_2H$). Unless otherwise stated, all experiments were conducted in a sealed tube under N_2 atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C (CPD), 202 MHz ^{31}P，470 MHz ^{19}F) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR) as an internal reference. Coupling constants (*J*) were reported in Hertz (Hz).

1.2 General process

General process 1：Preparation of allylic amines 1



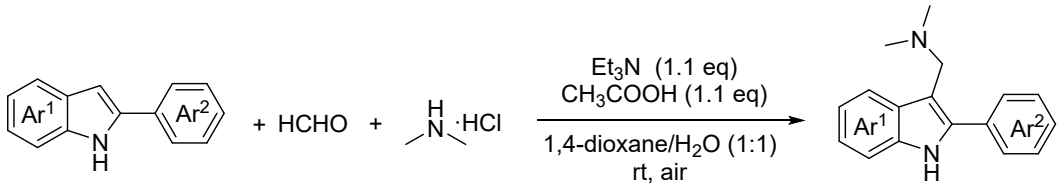
General process 1A:[1] NaOH (75 mg, 0.5 equiv) was added under stirring to a solution of Acetophenone (3 mmol, 1 equiv) and Benzaldehyde (3 mmol, 1 equiv) in ethanol (2 mL). The mixture was stirred for 24 h at room temperature. After, the

reaction mixture was neutralized with HCl 5% until pH ≈ 7 and extracted with ethyl acetate (3 × 30 mL). Then, the organic layer was dried, concentrated, and purified by flash column chromatography (silica gel, petroleum ether: EtOAc =30:1, v/v) to give the desiredproducts

General process 1B[2]**:** Under argon atmosphere, $NaBH_4$ (1.2 equiv.) was amed to a stirred solution of chalcone (1.0 equiv) in dry THF and methanol at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour, and the reaction was quenched with water. Then, water (20 mL) was amed and the mixture was extracted with EtOAc (3 × 30 mL). Then, the organic layer was dried, concentrated, and purified by flash column chromatography (silica gel, petroleum ether: EtOAc =10:1, v/v) to give the desired products.

General process 1C[2]**:** To a solution of the alcohol (1 equiv) and triethylamine (5 equiv) was amed Ethanesulfonyl chlorid (1 equiv) at 0 ºC. The reaction was stirred for 1h at room temperature and then, a solution of dimethylamine (2 M in THF, 5 equiv) was amed to the mixture. The temperature was raised to 50 ºC and the reaction mixture was stirred for 16 h. Then, the organic layer was dried, concentrated, and purified by flash column chromatography (silica gel, petroleum ether: EtOAc =3:1, v/v) to give the desired products.

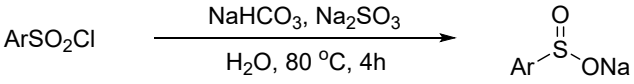
General process 2[3]**: Preparation of 1H-indol-3-yl methaneamines 1**



A three-necked round bottom flask equipped with a magnetic stirring bar and a dropping funnel was charged with a mixture of formaldehyde (37 wt% in water, 1.1 equiv), water (15 mL), Et_3N (1.1 equiv), dimethylamine hydrochloride (1.1 equiv), indole (10 mmol, 1.1 equiv) and glacial acetic acid (1.5 equiv) in dioxane (15 mL). The mixture was stirred for 24 h at room temperature. The mixture was extracted with EtOAc (3 × 30 mL). Then, the organic layer was dried, concentrated, and purified by

flash column chromatography (silica gel, petroleum ether: EtOAc =1:1, v/v) to give the desired products.

General process 3: For synthesis of diarylmethyl alkynes 2[4]



Sodium sulfite (20.0 mmol, 2.0 equiv), sodium bicarbonate (20.0 mmol, 2.0 equiv) and the corresponding aryl sulfonyl chloride (10.0 mmol, 1.0 equiv) were dissolved in distilled water (10.0 mL). The reaction mixture was stirred for 4 h at 80 °C using oil bath. After cooling down to room temperature, water was removed in vacuo. Ethanol (25 mL) was then added to this white residue and the resulting heterogeneous solution was filtered. The filtrate was concentrated under reduced pressure and the desired sodium sulfinates were obtained as white crystalline powders in 82-96% yields.

General process 4: For synthesis of diarylmethylenes 4 and 5

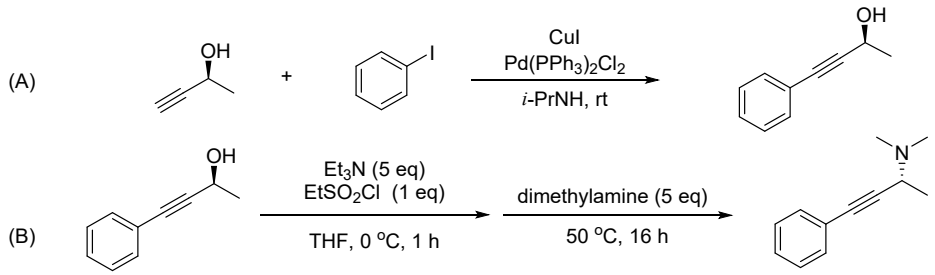
1a 2 3a 4 or 5

In air, amines (0.20 mmol), $BrCF_2COOK$ (3.0 eq, 0.6 mmol) CH_3COOLi (3.0 eq, 0.6 mmol (**Only when $Ph_2P(O)H$ is used as a nucleophilic reagent, the base is required))** and nucleophile (1.0 eq, 0.2 mmol) were amed to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). CH_3CN (2 mL) was added by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 ºC for 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: ethyl acetate =5:1~1:1, v/v) to give the desired products.

General process 5: Gram-scale synthesis of 4a

In air, propargyl amines **1a** or allylic amines **5a** (1.0 eq, 5.0 mmol), $BrCF_2COOK$ (3.0eq, 15.0 mmol), CH_3COOLi (3.0 eq, 15.0 mmol) and diphenylphosphine oxide (1.0 eq, 5.0 mmol) were amed to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). CH_3CN (15 mL) was added by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 ºC for 24 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: ethyl acetate = 3:1, v/v) to give the desired products.

General process 6: For synthesis of *N, N*-dimethyl-4-phenylbut-3-yn-2-amine

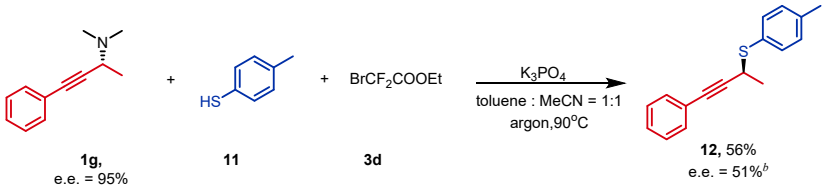


General process 6A: To an oven-dried round bottom flask was added the corresponding aryl iodine (1.2 equiv), $Pd(PPh_3)_2Cl_2$ (0.04 equiv) and copper(I) iodine (0.08 equiv). The flask was connected to an argon-vacuum line, evacuated and backfilled with argon (Three times). Diisopropylamine (2.8 mL/mmol alcohol) was added and the reaction mixture was stirred at 0 ºC for 5 min. 3-Butyn-2-ol (1 equiv) was added dropwise at 0 ºC and the reaction mixture was stirred for 16 h at room temperature. Silica gel was added to the mixture and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using the appropriate mixture of solvents.

General process 6B: Solution of phenylacetylene (10 mmol, 1.1 equiv) in anhydrous THF (10 mL) was cooled to −78 °C, 2.5 M solution of *n*-butyllithium in THF (4.8 mL, 12 mmol; 1.2 equiv) was amed dropwise, and solution was stirred with cooling under an argon atmosphere for 1 h. Then, solution of corresponding aldehyde (10 mmol, 1.0 equiv) in anhydrous THF (5 mL) was amed dropwise and solution was warmed to room temperature for 1 h. Then, water (20 mL) was amed and the mixture

was extracted with EtOAc (3 × 30 mL). Then, the organic layer was dried, concentrated, and purified by flash column chromatography (silica gel, petroleum ether: EtOAc =10:1, v/v) to give the desired products.

General process 7: For synthesis of (S)-(4-phenylbut-3-yn-2-yl)(p-tolyl)sulfane



1g, e.e. = 95% **11** **3d** **12,** 56% e.e. = 51%[b]

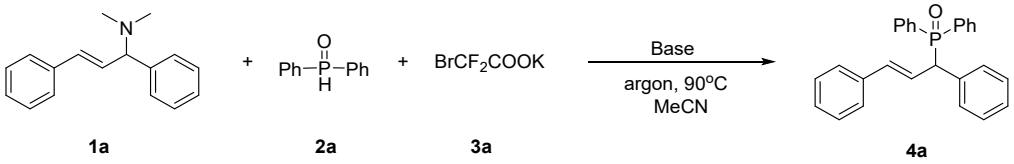
In air, amines (0.20 mmol), $BrCF_2COOEt$ (3.0 eq, 0.6 mmol), K_3PO_4 (3.0 eq, 0.6 mmol and p-Toluenethiol (1.5 eq, 0.3 mmol) were amed to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). CH_3CN (2 mL) was added by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at 90 ºC for 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: Dichloromethane =100:1, v/v) to give the desired products.

2. Supplementary discussion

2.1 Optimization studies

1.1.1 The condition screening for the diarylmethyl alkynes synthesis

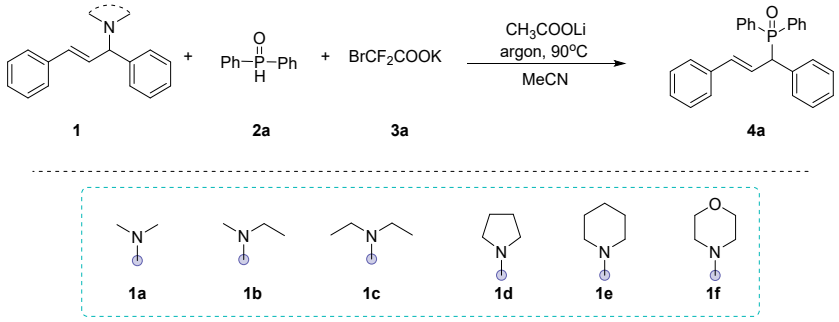
Supplementary Table 1. The effects of base



Entries	Base	Yield (%)[a]
1	Li_2CO_3	51
2	Na_2CO_3	42
3	K_2CO_3	35
4	Rb_2CO_3	37
5	CS_2CO_3	27
6	K_3PO_4	30
7	Na_2HPO_4	41
8	K_3PO_4	30
9	Na_3PO_4	34
10	LiOH	40
11	LiF	42
12	KHF_2	39
13	KF	58
14	CSF	45
15	HCOOLi	53
16	HCOONa	42
17	CH_3COOLi	61
18	CH_3COONa	51
19	CH_3COOCs	19
20	CH_3OLi	Trace
21	KO^t-Bu	Trace
22	K_2S	Trace
23	NaOTf	Trace
24	$NaBO_3 \cdot 4H_2O$	Trace

Reaction condition: **1a** (1.0 equiv., 0.2 mmol), **2a** (1.5 equiv., 0.2 mmol), $BrCF_2COOK$ (3.0 eq, 0.6 mmol) base (3 equiv.), CH_3CN (2 mL) at 90 °C for 12 h under argon; [a] isolated yields.

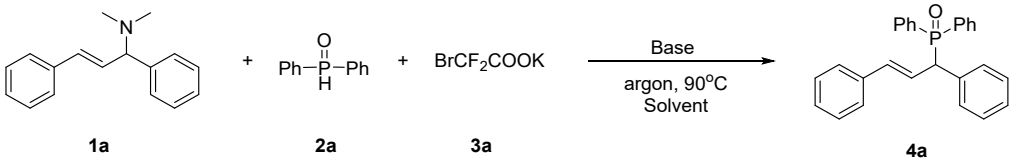
Supplementary Table 2. The effects of leaving group



Entries	**1**	Yield (%)[a]
1	**1a**	61
2	**1b**	59
3	**1c**	47
4	**1d**	29
5	**1e**	31
6	**1f**	38

Reaction condition: 1 (1.0 equiv., 0.2 mmol), 2a (1.5 equiv., 0.3 mmol), $BrCF_2COOK$ (3.0 eq, 0.6 mmol) CH_3COOLi (3 equiv.0.6mmol), CH_3CN (2 mL) at 90 °C for 12 h under argon; [a] isolated yields.

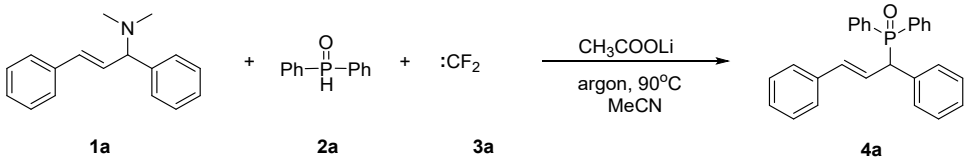
Supplementary Table 3. The effects of solvent



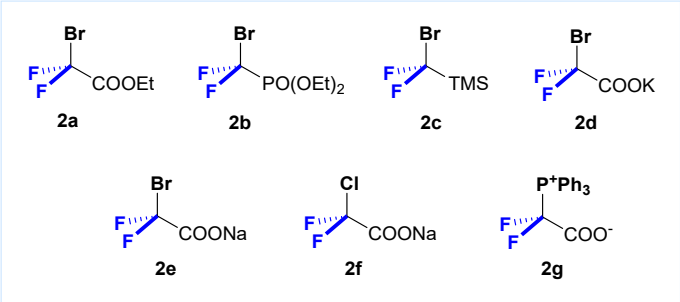
Entries	solvent	Yield (%)[a]
1	CH_3CN	61
2	Toluene	NR
3	DME	Trace
4	1,4-dioxane	Trace
5	DMF	ND
6	DMSO	ND
7	CH_3CN/ Toluene (1:1)	43%

Reaction condition: 1a (1.0 equiv., 0.2 mmol), 2a (1.5 equiv., 0.3 mmol), $BrCF_2COOK$ (3.0 eq, 0.6 mmol) CH_3COOLi (3 equiv.0.6mmol), solvent (2 mL) at 90 °C for 12 h under argon; [a] isolated yields.

Supplementary Table 4. The effects of halodifluorinated reagents



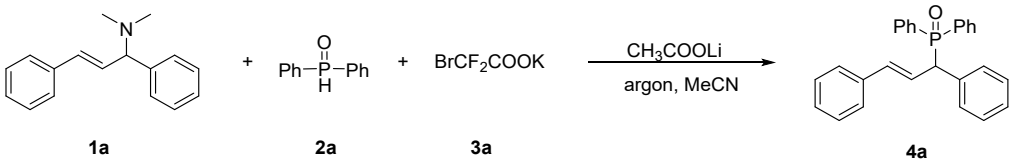
1a 2a 3a 4a



Entries	Base	Yield (%)[a]
1	**2a**	32
2	**2b**	47
3	**2c**	ND
4	**2d**	61
5	**2e**	45
6	**2f**	53
7	**2g**	ND

Reaction condition: 1a (1.0 equiv., 0.2 mmol), 2a (1.5 equiv., 0.3 mmol), halodifluorinated reagents (3.0 eq, 0.6 mmol) CH_3COOLi (3 equiv.0.6mmol), MeCN (2 mL) at 90 °C for 12 h under argon; [a] isolated yields. ND = not detected.

Supplementary Table 5. The effects of temperature, equivalent of $BrCF_2COOK$ and CH_3COOLi.

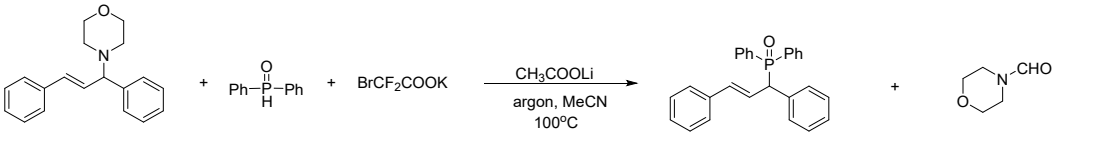


1a 2a 3a 4a

Entries	CH_3COOLi	T °C	$BrCF_2COOK$	Yield (%)[a]
1	3eq	80	3eq	55
2	3eq	90	3eq	61
3	3eq	100	3eq	86
4	3eq	110	3eq	71
5	2eq	100	3eq	77
6	1eq	100	3eq	64
7	0eq	100	3eq	46
8	3eq	100	2eq	75
9	3eq	100	1eq	57

Reaction condition: **1a** (1.0 equiv., 0.2 mmol), **2a** (1.5 equiv., 0.3 mmol), $BrCF_2COOK$ (1-3 equiv.) CH_3COOLi (0-3 equiv.), CH_3CN (2 mL) at 80 ~ 110 °C for 12 h under argon; [a] isolated yields.

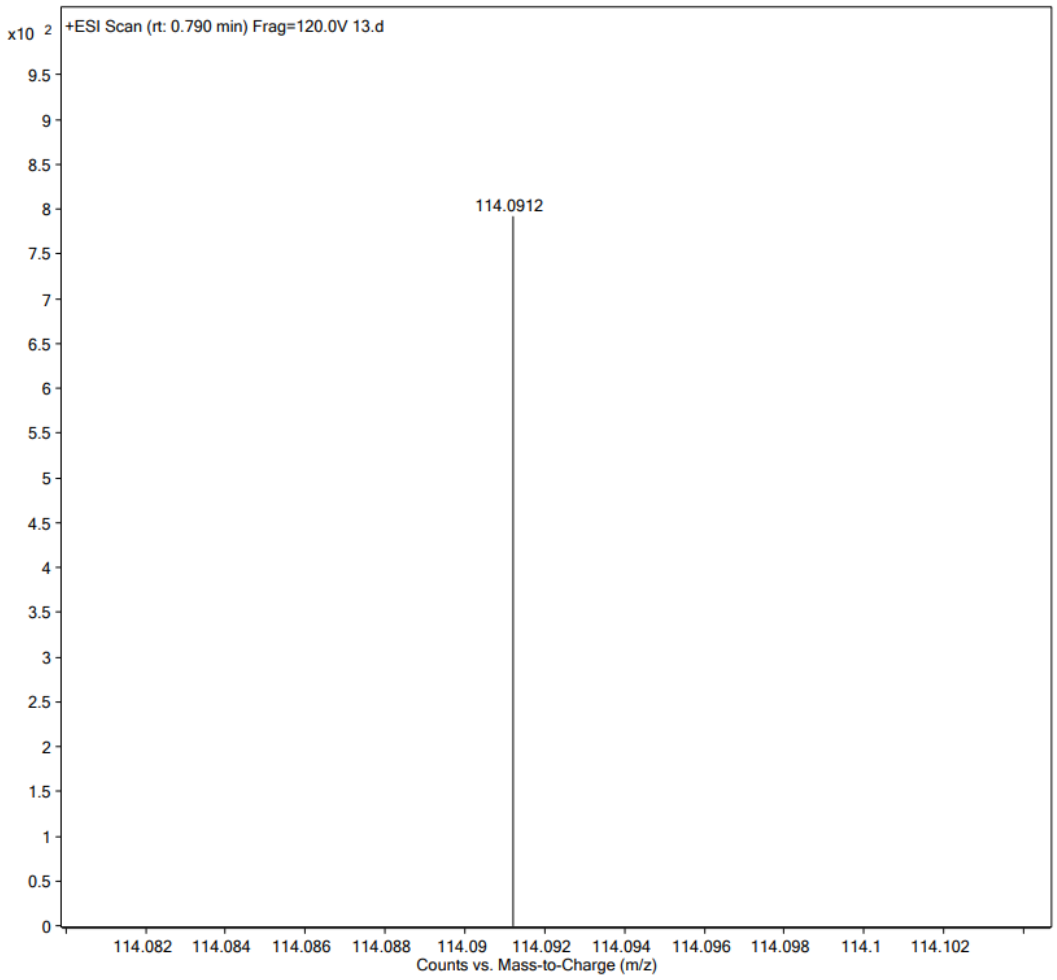
Experiments with leaving group monitoring



1f 2a 3a 4a

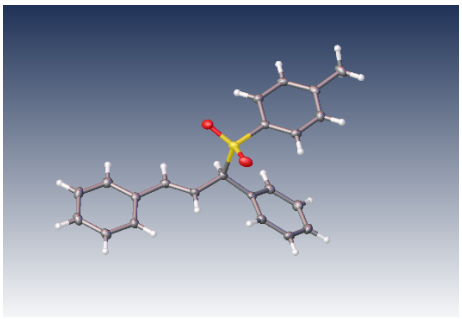
5o, detected by GC-MS and HRMS: $[M+H]^+$
Calcd: 114.0913
Found: 114.0912

In air, 1f (0.2 mmol), $BrCF_2COOK$ (3.0 eq, 0.6 mmol) CH_3COOLi (3.0 eq, 0.6 mmol and 2a (1.5 eq, 0.3 mmol) were amed to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). CH_3CN (2 mL) was added by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: ethyl acetate =1:1, v/v) to give the desired products.


+ESI Scan (rt: 0.790 min) Frag=120.0V 13.d
x10 2
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
114.0912
114.082
114.084
114.086
114.088
114.09
114.092
114.094
114.096
114.098
114.1
114.102
Counts vs. Mass-to-Charge (m/z)

2.2 Crystal data

Crystallographic data for compound **4m** (CCDC-2305694) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0019 A Wavelength=1.54178

Cell: a=18.1661(7) b=5.6830(2) c=17.2863(7)
alpha=90 beta=97.593(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1768.95(12)	1768.95(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C22 H20 O2 S	C22 H20 O2 S
Sum formula	C22 H20 O2 S	C22 H20 O2 S
Mr	348.44	348.44
Dx,g cm-3	1.308	1.308
Z	4	4
Mu (mm-1)	1.712	1.711
F000	736.0	736.0
F000'	739.25	
h,k,lmax	21,6,20	21,6,20
Nref	3221	3191
Tmin,Tmax	0.512,0.531	0.562,0.753
Tmin'	0.464	

Correction method= # Reported T Limits: Tmin=0.562 Tmax=0.753
AbsCorr = MULTI-SCAN

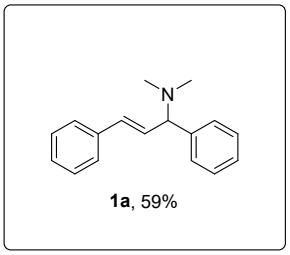
Data completeness= 0.991 Theta(max)= 68.191

R(reflections)= 0.0357(3132) wR2(reflections)= 0.0900(3191)

S = 1.078 Npar= 227

2.3 Characterization data for products

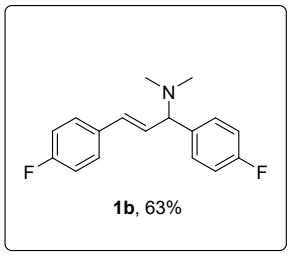
(E)-N,N-dimethyl-1,3-diphenylprop-2-en-1-amine(1a)



Following the **general procedure 1** on 20 mmol scale, yellow oil, yield: 59% (2.8g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 7.44 (m, 2H), 7.44 – 7.36 (m, 4H), 7.36 – 7.29 (m, 3H), 7.29 – 7.22 (m, 1H), 6.62 (d, J = 15.8 Hz, 1H), 6.44 (dd, J = 15.8, 8.8 Hz, 1H), 3.76 (d, J = 8.7 Hz, 1H), 2.31 (s, 6H).

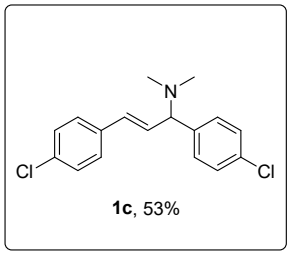
(E)-1,3-bis(4-fluorophenyl)-N,N-dimethylprop-2-en-1-amine(1b)



Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 63% (1.7 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.34 (ddd, J = 18.1, 8.7, 5.5 Hz, 4H), 7.01 (dt, J = 24.0, 8.7 Hz, 4H), 6.51 (d, J = 15.8 Hz, 1H), 6.24 (dd, J = 15.8, 8.7 Hz, 1H), 3.69 (d, J = 8.7 Hz, 1H), 2.26 (s, 6H).

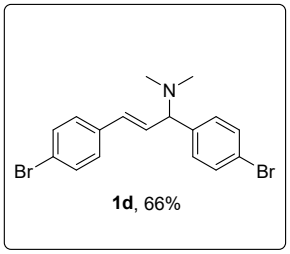
(E)-1,3-bis(4-chlorophenyl)-N,N-dimethylprop-2-en-1-amine(1c)



Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 53% (1.6 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.39 – 7.32 (m, 4H), 7.32 – 7.25 (m, 4H), 6.54 (d, J = 15.8 Hz, 1H), 6.31 (dd, J = 15.8, 8.7 Hz, 1H), 3.72 (d, J = 8.7 Hz, 1H), 2.26 (s, 6H).

(E)-1,3-bis(4-bromophenyl)-N,N-dimethylprop-2-en-1-amine(1d)

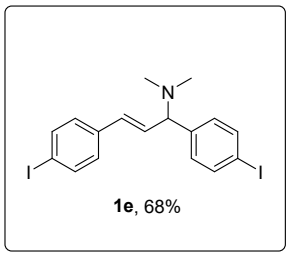


1d, 66%

Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 66% (2.6 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.26 (m, 2H), 7.26 – 7.18 (m, 2H), 6.52 (d, J = 15.8 Hz, 1H), 6.31 (dd, J = 15.8, 8.7 Hz, 1H), 3.70 (d, J = 8.7 Hz, 1H), 2.25 (s, 6H).

(E)-1,3-bis(4-iodophenyl)-N,N-dimethylprop-2-en-1-amine(1e)

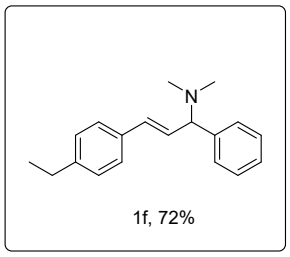


1e, 68%

Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 68% (3.3 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.69 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.31 (dd, J = 15.8, 8.7 Hz, 1H), 3.67 (d, J = 8.7 Hz, 1H), 2.24 (s, 6H).

(E)-3-(4-ethylphenyl)-N,N-dimethyl-1-phenylprop-2-en-1-amine(1f)

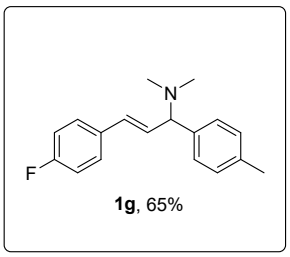


1f, 72%

Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 72% (1.9 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 7.44 (m, 1H), 7.44 – 7.39 (m, 1H), 7.39 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 7.24 (dd, J = 7.8, 3.1 Hz, 1H), 7.20 – 7.17 (m, 1H), 6.61 (dd, J = 15.8, 4.4 Hz, 1H), 6.42 (ddd, J = 25.6, 15.8, 8.7 Hz, 1H), 3.75 (dd, J = 8.8, 6.5 Hz, 1H), 2.68 (dq, J = 12.6, 7.6 Hz, 2H), 2.31 (d, J = 0.8 Hz, 6H), 1.28 (dt, J = 11.3, 7.6 Hz, 3H).

(E)-3-(4-fluorophenyl)-N,N-dimethyl-1-(p-tolyl)prop-2-en-1-amine(1g)

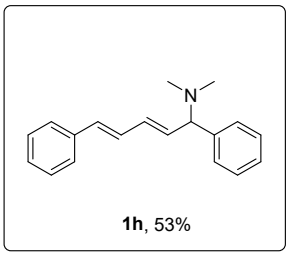


1g, 65%

Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 65% (1.7 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.11 – 6.99 (m, 2H), 6.58 (d, J = 15.7 Hz, 1H), 6.33 (dd, J = 15.7, 8.8 Hz, 1H), 3.75 (d, J = 8.8 Hz, 1H), 2.39 (d, J = 8.3 Hz, 3H), 2.30 (d, J = 5.6 Hz, 6H).

(2E,4E)-N,N-dimethyl-1,5-diphenylpenta-2,4-dien-1-amine(1h)

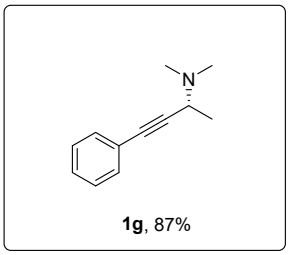


1h, 53%

Following the **general procedure 1** on 10 mmol scale, yellow oil, yield: 53% (1.4 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 – 7.34 (m, 6H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.21 (m, 1H), 6.79 (ddd, J = 15.7, 10.5, 0.8 Hz, 1H), 6.54 (d, J = 15.7 Hz, 1H), 6.40 (dd, J = 15.1, 10.5 Hz, 1H), 6.01 (dd, J = 15.1, 8.9 Hz, 1H), 3.66 (d, J = 8.8 Hz, 1H), 2.27 (s, 6H).

N,N-dimethyl-4-phenylbut-3-yn-2-amine (1g)



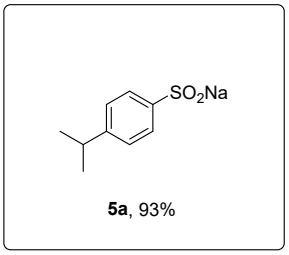
1g, 87%

Following the **general procedure 7** on 0.2 mmol scale, yellow oil, yield: 87% (1.5 g), R_f = 0.3 (silica gel, PE: EA = 5:1, v/v), column chromatography (silica gel, PE: EA = 10:1, v/v).

HPLC analysis: The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 90:10, 0.5 mL/min, λ = 254 nm, τ_R (major) = 7.4 min and τ_R(minor) = 7.9 min.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.41 (m, 2H), 7.29 (dt, J = 4.6, 2.8 Hz, 3H), 3.70 (q, J = 7.0 Hz, 1H), 2.33 (s, 6H), 1.41 (d, J = 7.1 Hz, 3H).

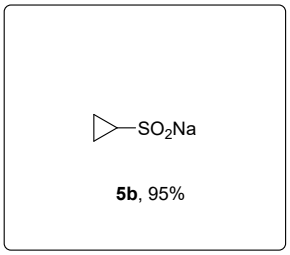
sodium 4-isopropylbenzenesulfinate(5a)



5a, 93%

Following the **general procedure 3** on 10 mmol scale, white solid, yield: 93% (1.9 g).
^{1}H NMR (500 MHz, DMSO-d6) δ 7.46 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 2.88 (hept, J = 6.9 Hz, 1H), 1.19 (d, J = 6.9 Hz, 6H).

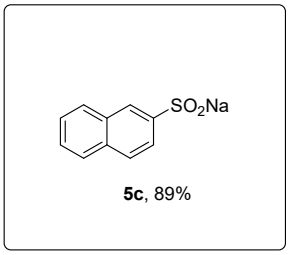
sodium cyclopropanesulfinate(5b)



5b, 95%

Following the **general procedure 3** on 10 mmol scale, white solid, yield: 95% (1.2 g).
^{1}H NMR (500 MHz, DMSO-d6) δ 1.58 (tt, J = 8.1, 5.0 Hz, 1H), 0.48 (dt, J = 5.6, 2.8 Hz, 2H), 0.37 – 0.19 (m, 2H).

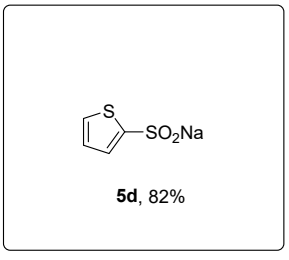
sodium naphthalene-2-sulfinate(5c)



5c, 89%

Following the **general procedure 3** on 10 mmol scale, white solid, yield: 89% (1.9 g).
^{1}H NMR (500 MHz, DMSO-d6) δ 7.99 – 7.82 (m, 4H), 7.70 (d, J = 1.5 Hz, 1H), 7.56 – 7.42 (m, 2H).

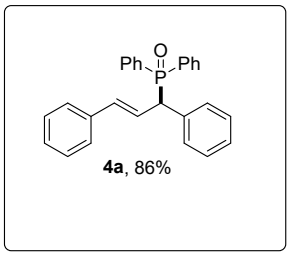
sodium thiophene-2-sulfinate(5d)



5d, 82%

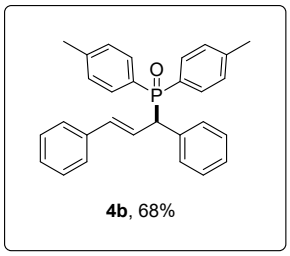
Following the **general procedure 3** on 10 mmol scale, white solid, yield: 82% (1.4 g).
^{1}H NMR (500 MHz, DMSO-d6) δ 7.39 (dd, J = 4.7, 1.5 Hz, 1H), 7.03 – 6.81 (m, 2H).

(E)-(1,3-diphenylallyl)diphenylphosphine oxide (4a)



Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 203-205 °C), yield: 86% (67.8 mg), R_f = 0.4 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.92 – 7.83 (m, 2H), 7.67 – 7.56 (m, 2H), 7.48 (ddd, J = 14.3, 7.3, 2.2 Hz, 3H), 7.42 – 7.34 (m, 3H), 7.30 (td, J = 7.6, 3.1 Hz, 2H), 7.25 – 7.20 (m, 6H), 7.20 – 7.13 (m, 2H), 6.61 (ddd, J = 16.0, 9.2, 7.1 Hz, 1H), 6.34 (dd, J = 15.7, 3.9 Hz, 1H), 4.40 (t, J = 9.4 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 136.7 (d, J = 2.4 Hz), 135.9 (d, J = 5.9 Hz), 134.4 (d, J = 11.4 Hz), 132.0 (d, J = 37.4 Hz), 131.8 (d, J = 2.8 Hz), 131.7 (d, J = 8.4 Hz), 131.6 (d, J = 2.9 Hz), 131.3 (d, J = 8.7 Hz), 131.1, 129.5 (d, J = 5.8 Hz), 128.6 (d, J = 1.7 Hz), 128.5, 128.4 (d, J = 1.7 Hz), 128.2 (d, J = 11.4 Hz), 127.6, 127.2 (d, J = 2.7 Hz), 126.4 (d, J = 1.4 Hz), 124.6 (d, J = 7.2 Hz), 52.4 (d, J = 65.0 Hz).
^{31}P NMR (202 MHz, CDCl3) δ 31.52.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{24}OP^+$ 395.1559.; Found: 395.1562

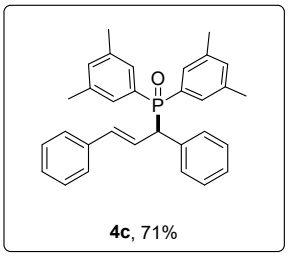
(E)-(1,3-diphenylallyl)di-p-tolylphosphine oxide (4b)



Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 210-211 °C), yield: 68% (57.4 mg), R_f = 0.4 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.76 – 7.66 (m, 2H), 7.44 (dd, J = 10.9, 8.1 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.20 (m, 8H), 7.20 – 7.14 (m, 2H), 7.10 (dd, J = 8.0, 2.8 Hz, 2H), 6.59 (ddd, J = 16.0, 9.1, 7.1 Hz, 1H), 6.33 (ddd, J = 15.8, 3.8, 0.9 Hz, 1H), 4.34 (t, J = 9.6 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 136.9 (d, J = 2.5 Hz), 136.2 (d, J = 5.9 Hz), 134.2 (d, J = 11.3 Hz), 131.7 (d, J = 8.7 Hz), 131.4 (d, J = 9.1 Hz), 129.5 (d, J = 5.8 Hz), 129.2 (d, J = 11.8 Hz), 128.9 (d, J = 12.1 Hz), 128.7, 128.5 (d, J = 1.8 Hz), 128.4, 128.3, 128.0, 127.5, 127.0 (d, J = 2.3 Hz), 126.4 (d, J = 1.5 Hz), 125.0 (d, J = 7.1 Hz), 52.5 (d, J = 65.3 Hz), 21.6 (d, J = 8.6 Hz).
^{31}P NMR (202 MHz, Chloroform-d) δ 31.85.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{28}OP^+$445.1692.; Found: 445.1686.

(E)-bis(3,5-dimethylphenyl)(1,3-diphenylallyl)phosphine oxide (4c)



4c, 71%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 210-212 °C), yield: 71% (63.9 mg), R_f = 0.4 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

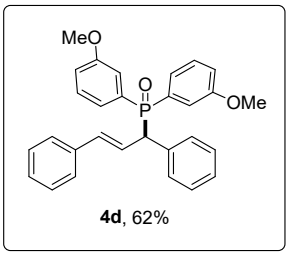
^{1}H NMR 1H NMR (500 MHz, Chloroform-d) δ 7.47 (dt, J = 11.2, 2.2 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.30 – 7.23 (m, 6H), 7.20 (dp, J = 6.0, 4.1, 2.9 Hz, 4H), 7.14 (s, 1H), 7.03 (s, 1H), 6.61 (dddt, J = 13.1, 8.8, 6.9, 2.0 Hz, 1H), 6.34 (dt, J = 15.8, 3.4 Hz, 1H), 4.38 (td, J = 9.6, 4.5 Hz, 1H), 2.34 (s, 6H), 2.22 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-d) δ 138.0 (d, J = 12.2 Hz), 137.7 (d, J = 12.1 Hz), 136.9 (d, J = 2.6 Hz), 136.3 (d, J = 5.9 Hz), 134.3 (d, J = 11.2 Hz), 133.5 (d, J = 2.8 Hz), 133.2 (d, J = 3.0 Hz), 131.7 (d, J = 32.6 Hz), 131.0 (d, J = 32.7 Hz), 129.6 (d, J = 5.7 Hz), 129.4 (d, J = 8.4 Hz), 129.0 (d, J = 8.7 Hz), 128.5 (d, J = 1.9 Hz), 128.4, 127.5, 127.0 (d, J = 2.3 Hz), 126.4 (d, J = 1.4 Hz), 125.0 (d, J = 7.2 Hz), 52.3 (d, J = 64.4 Hz), 21.3 (d, J = 14.6 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 32.23.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{32}OP^+$ 451.2185.; Found: 451.2182.

(E)-(1,3-diphenylallyl)bis(3-methoxyphenyl)phosphine oxide (4d)



4d, 62%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 164-165 °C), yield: 62% (56.3 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

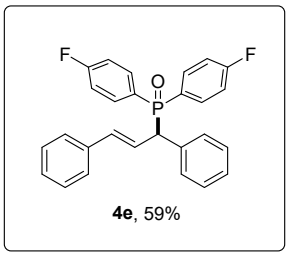
^{1}H NMR (500 MHz, Chloroform-d) δ 7.85 – 7.73 (m, 1H), 7.50 – 7.42 (m, 1H), 7.41 – 7.33 (m, 3H), 7.31 – 7.22 (m, 6H), 7.18 (ddd, J = 15.0, 7.7, 3.7 Hz, 5H), 7.04 (ddd, J = 11.8, 8.3, 5.2 Hz, 2H), 6.78 (dt, J = 15.8, 8.9 Hz, 1H), 6.50 (dd, J = 15.9, 3.1 Hz, 1H), 4.53 (t, J = 8.6 Hz, 1H), 2.37 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 143.1 (d, J = 7.2 Hz), 142.6 (d, J = 7.6 Hz), 137.0 (d, J = 5.5 Hz), 136.9, 134.22 (d, J = 11.5 Hz), 132.1 (d, J = 10.3 Hz), 131.9, 131.8, 131.7 – 131.5 (m), 131.3 (d, J = 2.5 Hz), 130.8 (d, J = 48.4 Hz), 129.6 (d, J = 5.5 Hz), 128.5, 127.6, 127.0 (d, J = 2.0 Hz), 126.4, 125.7 (d, J = 6.4 Hz), 125.2 (dd, J = 26.3, 11.9 Hz), 50.7 (d, J = 66.0 Hz), 21.2 (dd, J = 38.1, 3.7 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 35.16.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{28}O_3P^+$ 455.1771.; Found: 455.1769.

(E)-(1,3-diphenylallyl)bis(4-fluorophenyl)phosphine oxide (4e)



4e, 59%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 195-197 °C), yield: 59% (50.8 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.91 – 7.77 (m, 2H), 7.64 – 7.49 (m, 2H), 7.34 (dt, J = 8.0, 1.7 Hz, 2H), 7.31 – 7.15 (m, 10H), 7.03 (tt, J = 8.7, 2.2 Hz, 2H), 6.59 (ddd, J = 16.2, 9.2, 7.2 Hz, 1H), 6.36 (dd, J = 15.8, 3.9 Hz, 1H), 4.32 (t, J = 9.4 Hz, 1H).

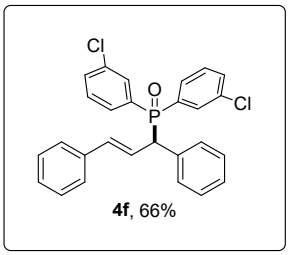
^{13}C NMR (126 MHz, Chloroform-d) δ 166.0 (d, J = 3.4 Hz), 165.8 (d, J = 3.4 Hz), 164.0 (d, J = 3.3 Hz), 163.8 (d, J = 3.2 Hz), 135.5 (d, J = 6.0 Hz), 134.7 (d, J = 11.6 Hz), 134.1 (t, J = 9.3 Hz), 133.9 – 133.6 (m), 129.4 (d, J = 5.7 Hz), 128.7 (d, J = 1.8 Hz), 128.5, 127.9, 127.6 (d, J = 3.4 Hz), 127.4 (d, J = 2.3 Hz), 127.1, 126.8 (d, J = 3.3 Hz), 126.4, 124.0 (d, J = 7.3 Hz), 115.9 (ddd, J = 37.0, 21.3, 12.6 Hz), 52.6 (d, J = 66.3 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 30.42.

^{19}F NMR (471 MHz, Chloroform-d) δ -106.48, -106.72.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{22}F_2OP^+$ 431.1371.; Found: 431.1374.

(E)-bis(3-chlorophenyl)(1,3-diphenylallyl)phosphine oxide (4f)



4f, 66%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 233-235 °C), yield: 66% (61.0 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

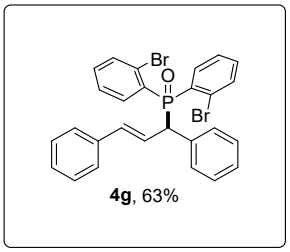
^{1}H NMR (500 MHz, Chloroform-d) δ 7.76 (dd, J = 10.4, 8.1 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.36 – 7.27 (m, 4H), 7.26 – 7.13 (m, 8H), 6.56 (ddd, J = 16.2, 9.2, 7.3 Hz, 1H), 6.37 (dd, J = 15.7, 3.8 Hz, 1H), 4.33 (t, J = 9.3 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 138.7 (d, J = 3.4 Hz), 138.4 (d, J = 3.4 Hz), 136.4 (d, J = 2.6 Hz), 135.3 (d, J = 6.1 Hz), 134.9 (d, J = 11.5 Hz), 133.4 (d, J = 10.5 Hz), 133.0 (d, J = 9.2 Hz), 132.6 (d, J = 9.5 Hz), 129.6 (d, J = 3.6 Hz), 129.4 (d, J = 5.9 Hz), 129.0 (d, J = 12.0 Hz), 128.8 (d, J = 1.8 Hz), 128.7 (d, J = 12.2 Hz), 128.6, 127.91, 127.5 (d, J = 2.4 Hz), 126.4 (d, J = 1.5 Hz), 123.8 (d, J = 7.3 Hz), 52.3 (d, J = 66.2 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 30.41.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{22}Cl_2OP^+$ 463.0780.; Found: 463.0783.

(E)-bis(2-bromophenyl)(1,3-diphenylallyl)phosphine oxide (4g)



4g, 63%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 241-243 °C), yield: 63% (69.3 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

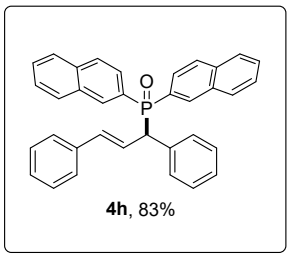
^{1}H NMR (500 MHz, Chloroform-d) δ 8.29 (ddd, J = 11.6, 7.7, 1.7 Hz, 1H), 7.91 – 7.81 (m, 1H), 7.60 – 7.49 (m, 3H), 7.46 – 7.37 (m, 2H), 7.34 – 7.28 (m, 3H), 7.28 – 7.22 (m, 2H), 7.22 – 7.09 (m, 6H), 6.82 (dt, J = 16.0, 9.2 Hz, 1H), 6.67 (dd, J = 15.9, 3.0 Hz, 1H), 5.17 (t, J = 8.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 137.0 (d, J = 7.0 Hz), 136.8 (d, J = 5.7 Hz), 136.7, 136.3 (d, J = 8.2 Hz), 134.7 – 134.3 (m), 133.6 (d, J = 7.8 Hz), 133.1 (dd, J = 30.9, 2.2 Hz), 132.1 (d, J = 43.7 Hz), 129.2 (d, J = 6.1 Hz), 128.7, 128.5, 127.8, 127.3 (d, J = 2.1 Hz), 126.8 (d, J = 10.6 Hz), 126.6, 126.5, 125.2 (d, J = 4.1 Hz), 123.8 (d, J = 5.6 Hz), 48.0 (d, J = 71.0 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 31.21.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{22}Br_2OP^+$ 550.9770.; Found: 550.9774.

(E)-(1,3-diphenylallyl)di(naphthalen-2-yl)phosphine oxide (4h)



4h, 83%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 213-214 °C), yield: 83% (82.0 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

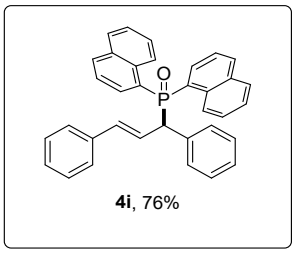
^{1}H NMR (500 MHz, Chloroform-d) δ 8.52 (dd, J = 12.8, 1.4 Hz, 1H), 8.21 (dd, J = 13.2, 1.5 Hz, 1H), 7.97 – 7.83 (m, 4H), 7.82 – 7.74 (m, 3H), 7.63 (td, J = 8.7, 1.6 Hz, 1H), 7.58 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.53 (td, J = 8.0, 1.4 Hz, 2H), 7.48 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.43 (dt, J = 8.0, 1.6 Hz, 2H), 7.25 – 7.12 (m, 8H), 6.68 (ddd, J = 16.0, 9.1, 7.2 Hz, 1H), 6.41 (dd, J = 15.8, 3.8 Hz, 1H), 4.61 (t, J = 9.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 136.6 (d, J = 2.3 Hz), 135.9 (d, J = 5.9 Hz), 134.7, 134.6, 134.5 (d, J = 2.2 Hz), 134.2 (d, J = 7.3 Hz), 133.7 (d, J = 7.8 Hz), 132.64, 132.55, 132.4, 132.3, 129.6 (d, J = 5.7 Hz), 129.4, 129.0 (d, J = 13.6 Hz), 128.7 (d, J = 1.6 Hz), 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3 (d, J = 2.2 Hz), 126.9, 126.8, 126.4, 126.1 (d, J = 9.8 Hz), 124.6 (d, J = 7.2 Hz), 52.3 (d, J = 65.3 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 31.68.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{35}H_{28}OP^+$ 495.1872.; Found: 495.1869.

(E)-(1,3-diphenylallyl)di(naphthalen-1-yl)phosphine oxide (4i)



Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 235-237 °C), yield: 76% (75.1 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

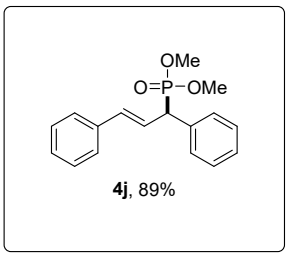
^{1}H NMR (500 MHz, Chloroform-d) δ 8.80 (d, J = 8.5 Hz, 1H), 8.62 (d, J = 8.6 Hz, 1H), 8.16 (dd, J = 14.3, 7.1 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.83 – 7.71 (m, 2H), 7.49 (td, J = 7.7, 2.6 Hz, 1H), 7.44 – 7.28 (m, 7H), 7.24 – 7.04 (m, 8H), 6.81 (dt, J = 15.6, 8.8 Hz, 1H), 6.41 (dd, J = 15.9, 3.3 Hz, 1H), 4.82 (t, J = 9.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 136.9 (d, J = 5.6 Hz), 136.8 (d, J = 1.8 Hz), 134.3, 134.23, 134.17, 134.0 (d, J = 3.3 Hz), 133.9 (d, J = 2.0 Hz), 133.6 (d, J = 9.1 Hz), 133.0 (d, J = 3.0 Hz), 132.8 (d, J = 3.0 Hz), 132.1 (d, J = 2.8 Hz), 132.0 (d, J = 2.8 Hz), 129.9 (d, J = 28.6 Hz), 129.6 (d, J = 5.9 Hz), 129.1 (d, J = 29.0 Hz), 128.8, 128.6, 128.5 (d, J = 1.7 Hz), 128.3, 127.6, 127.2, 127.1 (d, J = 4.6 Hz), 127.0, 126.6 (d, J = 4.4 Hz), 126.4, 126.2 (d, J = 22.5 Hz), 125.8 (d, J = 6.4 Hz), 124.4, 124.25, 124.2, 124.1, 52.0 (d, J = 66.9 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 36.10.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{35}H_{28}OP^+$ 495.1872.; Found: 495.1869.

dimethyl (E)-(1,3-diphenylallyl)phosphonate (4j)



Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 89% (53.8 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

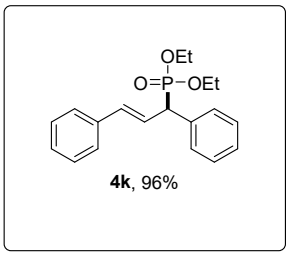
^{1}H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.34 (m, 4H), 7.32 – 7.27 (m, 3H), 7.24 (d, J = 7.7 Hz, 1H), 6.63 – 6.47 (m, 2H), 4.03 (dd, J = 24.8, 8.2 Hz, 1H), 3.73 (d, J = 10.7 Hz, 3H), 3.55 (d, J = 10.6 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 136.6 (d, J = 2.7 Hz), 135.6 (d, J = 7.5 Hz), 133.9 (d, J = 14.0 Hz), 129.0 (d, J = 7.1 Hz), 128.8 (d, J = 2.4 Hz), 128.6, 127.8, 127.5 (d, J = 2.8 Hz), 126.5 (d, J = 1.8 Hz), 124.2 (d, J = 9.6 Hz), 53.6 (d, J = 7.2 Hz), 49.5, 48.4.

^{31}P NMR (202 MHz, Chloroform-d) δ 27.14.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{20}O_3P^+$ 303.1145.; Found: 303.1143.

diethyl (E)-(1,3-diphenylallyl)phosphonate (4k)



Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 96% (63.4 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

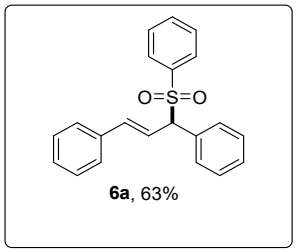
^{1}H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.40 – 7.33 (m, 4H), 7.33 – 7.26 (m, 3H), 7.25 – 7.19 (m, 1H), 6.63 – 6.47 (m, 2H), 4.14 – 4.04 (m, 2H), 4.03 – 3.93 (m, 2H), 3.81 (ddq, J = 10.2, 8.4, 7.1 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 136.8 (d, J = 2.9 Hz), 136.0 (d, J = 7.3 Hz), 133.7 (d, J = 13.9 Hz), 129.1 (d, J = 7.1 Hz), 128.7 (d, J = 2.2 Hz), 128.5, 127.69, 127.3 (d, J = 2.9 Hz), 126.5 (d, J = 1.9 Hz), 124.7 (d, J = 9.6 Hz), 62.7 (dd, J = 15.7, 7.1 Hz), 49.5 (d, J = 137.2 Hz), 16.4 (dd, J = 23.7, 5.8 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 24.83.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{24}O_3P^+$ 331.1458.; Found: 331.1456.

(E)-(3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6a)



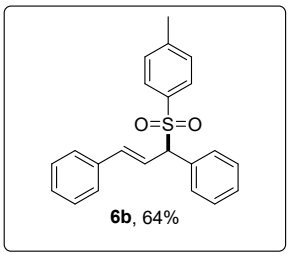
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 149-150 °C), yield: 63% (42.1 mg), R_f = 0.3 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.75 – 7.66 (m, 2H), 7.59 (td, J = 7.4, 1.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.41 – 7.27 (m, 10H), 6.66 – 6.50 (m, 2H), 4.88 (d, J = 8.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d)δ 138.2, 137.4, 135.9, 133.7, 132.3, 129.7, 129.3, 129.0, 128.74, 128.70, 128.66, 128.5, 126.7, 120.0, 75.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{19}O_2S^+$ 335.1100.; Found: 335.1099.

(E)-(3-tosylprop-1-ene-1,3-diyl)dibenzene (6b)



6b, 64%

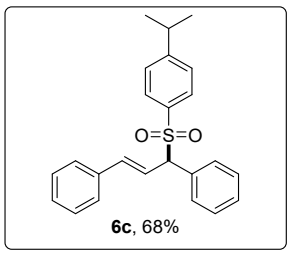
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 162-164 °C), yield: 64% (44.6 mg), R_f = 0.3 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.61 – 7.53 (m, 2H), 7.41 – 7.32 (m, 9H), 7.32 – 7.27 (m, 1H), 7.23 (d, J = 8.0 Hz, 2H), 6.67 – 6.52 (m, 2H), 4.86 (d, J = 8.3 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 144.6, 138.0, 136.0, 134.5, 132.5, 129.7, 129.4, 129.3, 128.9, 128.7, 128.6, 128.5, 126.8, 120.3, 75.4, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{21}O_2S^+$ 349.1257.; Found: 349.1254.

(E)-(3-((4-isopropylphenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6c)



6c, 68%

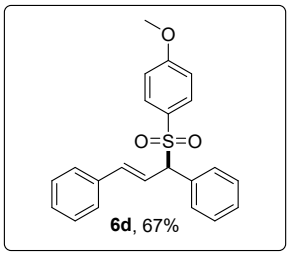
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 158-160 °C), yield: 68% (51.2 mg), R_f = 0.3 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 (d, J = 8.0 Hz, 2H), 7.37 – 7.29 (m, 9H), 7.26 (t, J = 8.0 Hz, 3H), 6.58 (dd, J = 15.7, 9.0 Hz, 1H), 6.49 (d, J = 15.7 Hz, 1H), 4.82 (d, J = 8.9 Hz, 1H), 2.94 (p, J = 6.9 Hz, 1H), 1.23 (d, J = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-d)δ 155.3, 138.0, 136.0, 134.7, 132.4, 129.7, 129.5, 128.9, 128.7, 128.6, 128.5, 126.8, 126.8, 120.3, 75.5, 34.2, 23.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{25}O_2S^+$ 377.1570.; Found: 377.1579.

(E)-(3-((4-methoxyphenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6d)



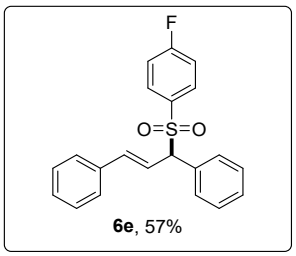
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 114-115 °C), yield: 67% (48.8 mg), R_f = 0.3 (silica gel, PE: EA = 1:3, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 (d, J = 8.9 Hz, 2H), 7.40 – 7.24 (m, 10H), 6.87 (d, J = 8.9 Hz, 2H), 6.68 – 6.48 (m, 2H), 4.83 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 163.7, 137.9, 136.0, 132.7, 131.5, 129.7, 128.9, 128.9, 128.69, 128.65, 128.5, 126.8, 120.4, 113.9, 75.6, 55.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{21}O_3S^+$ 365.1206.; Found: 387.1029.

(E)-(3-((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6e)



Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 115-117 °C), yield: 57% (40.1 mg), R_f = 0.3 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

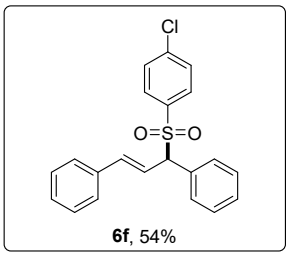
^{1}H NMR 1H NMR (500 MHz, Chloroform-d) δ 7.82 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.40 – 7.30 (m, 10H), 6.60 (d, J = 4.1 Hz, 2H), 4.89 (t, J = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d)δ 141.0, 138.9, 135.6, 131.7, 129.9, 129.7, 129.3, 128.9, 128.79, 128.75, 126.8, 125.8 (d, J = 3.8 Hz), 119.1, 75.6.

^{19}F NMR (471 MHz, Chloroform-d) δ -63.18.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{18}FO_2S^+$ 353.1006.; Found: 353.1002.

(E)-(3-((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6f)



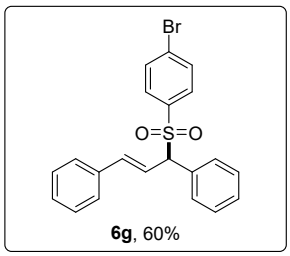
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 138-139 °C), yield: 54% (39.8 mg), R_f = 0.3 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 – 7.54 (m, 2H), 7.41 – 7.31 (m, 11H), 7.29 (d, J = 7.0 Hz, 1H), 6.62 – 6.53 (m, 2H), 4.84 (dd, J = 5.3, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 140.4, 138.6, 136.0, 135.7, 132.1, 130.8, 129.7, 129.1, 129.0, 128.9, 128.7, 126.82 119.5, 75.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{18}ClO_2S^+$ 369.0711.; Found: 369.0712

(E)-(3-((4-bromophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6g)



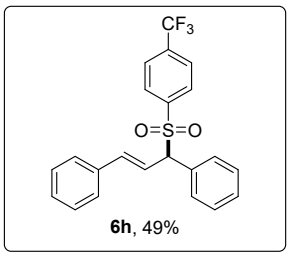
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp:153-155 °C), yield: 60% (49.4 mg), R_f = 0.3 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 – 7.47 (m, 4H), 7.43 – 7.28 (m, 10H), 6.66 – 6.53 (m, 2H), 4.85 (dd, J = 6.2, 2.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 138.6, 136.5, 135.7, 132.0, 132.0, 130.8, 129.7, 129.2, 129.1, 128.9, 128.7, 128.7, 126.8, 119.5, 75.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{18}BrO_2S^+$ 413.0205.; Found: 413.0207.

(E)-(3-((4-(trifluoromethyl)phenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6h)



6h, 49%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 118-120 °C), yield: 49% (39.4 mg), R_f = 0.3 (silica gel, PE: EA = 1:3, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

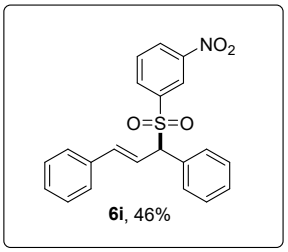
^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (dd, J = 58.3, 8.2 Hz, 4H), 7.35 (dt, J = 7.1, 5.4 Hz, 9H), 7.30 (d, J = 6.9 Hz, 1H), 6.63 – 6.52 (m, 2H), 4.92 – 4.82 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 141.1, 138.9, 135.6, 135.3 (d, J = 33.0 Hz), 131.7, 129.9, 129.7, 129.3, 128.9, 128.8, 128.7, 126.8, 125.8 (q, J = 3.6 Hz), 119.1, 75.6.

^{19}F NMR (471 MHz, Chloroform-d) δ -63.17.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}F_3O_2S^+$ 425.0974.; Found: 425.0792.

(E)-(3-((3-nitrophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6i)



6i, 46%

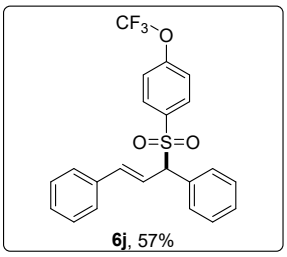
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 180-182 °C), yield: 46% (34.9 mg), R_f = 0.2 (silica gel, PE: EA = 1:3, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 8.50 (t, J = 2.0 Hz, 1H), 8.40 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 7.95 (dt, J = 7.9, 1.4 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.39 – 7.31 (m, 9H), 7.31 – 7.27 (m, 1H), 6.60 (d, J = 7.7 Hz, 2H), 4.90 (dd, J = 7.1, 1.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 148.0, 139.7, 139.3, 135.5, 134.8, 131.5, 130.0, 129.7, 129.5, 129.0, 128.9, 128.8, 128.1, 126.9, 124.5, 118.7, 75.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{18}NO_4S^+$ 380.0951.; Found: 380.0953.

(E)-(3-((4-(trifluoromethoxy)phenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6j)



6j, 57%

Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 134-136 °C), yield: 57% (47.7 mg), R_f = 0.4 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

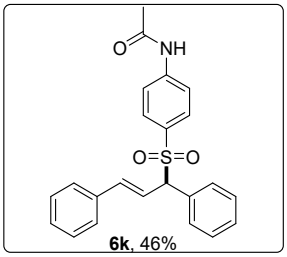
^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (dd, J = 8.6, 1.3 Hz, 2H), 7.38 – 7.31 (m, 9H), 7.31 – 7.27 (m, 1H), 7.23 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 6.4 Hz, 2H), 4.85 (dd, J = 6.8, 1.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d)δ 152.9, 138.7, 135.7, 132.0, 131.6, 129.7, 129.2, 128.9, 128.7 (d, J = 1.5 Hz), 128.6 (d, J = 7.3 Hz), 127.8, 126.8, 126.5 (d, J = 32.7 Hz), 120.4, 119.4, 75.6.

^{19}F NMR (471 MHz, Chloroform-d) δ -57.70.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{18}F_3O_3S^+$ 419.0923.; Found: 410.0922.

(E)-N-(4-((1,3-diphenylallyl)sulfonyl)phenyl)acetamide (6k)



6k, 46%

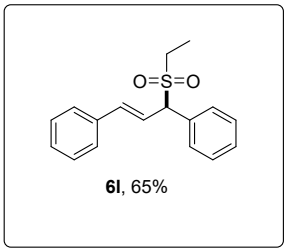
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 193-195 °C), yield: 46% (36.0 mg), R_f = 0.4 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, DMSO-d6) δ 10.35 (s, 1H), 7.80 – 7.52 (m, 4H), 7.50 – 7.22 (m, 10H), 6.68 (dd, J = 15.6, 9.6 Hz, 1H), 6.56 (d, J = 15.6 Hz, 1H), 5.38 (d, J = 9.6 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ 169.7, 144.4, 137.8, 136.2, 133.3, 131.2, 130.5, 130.3, 129.2, 129.0, 128.85, 127.1, 121.4, 118.5, 73.7, 24.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{22}NO_3S^+$ 392.1315.; Found: 392.1312.

(E)-(3-(ethylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6l)



6l, 65%

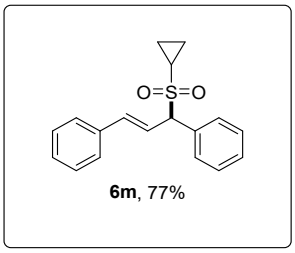
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 104-105 °C), yield: 65% (37.2 mg), R_f = 0.3 (silica gel, PE: EA = 1:3, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 – 7.53 (m, 2H), 7.43 (tdd, J = 8.6, 5.9, 4.2 Hz, 5H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 6.77 (d, J = 15.7 Hz, 1H), 6.65 (dd, J = 15.7, 9.1 Hz, 1H), 4.88 (d, J = 9.1 Hz, 1H), 2.94 (q, J = 7.5 Hz, 2H), 1.36 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 137.7, 135.7, 132.3, 129.5, 129.18, 129.16, 128.72, 128.68, 126.9, 120.4, 71.6, 45.2, 6.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{19}O_2S^+$ 287.1100.; Found: 287.1097.

(E)-(3-(cyclopropylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6m)



6m, 77%

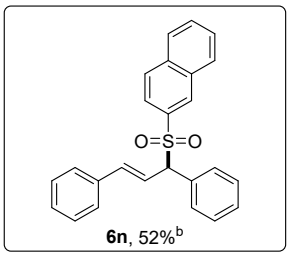
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 159-161 °C), yield: 77% (45.9 mg), R_f = 0.3 (silica gel, PE: EA = 1:3, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.60 – 7.54 (m, 2H), 7.47 – 7.37 (m, 5H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 6.80 (d, J = 15.7 Hz, 1H), 6.67 (dd, J = 15.7, 9.1 Hz, 1H), 4.89 (d, J = 9.1 Hz, 1H), 2.25 (tt, J = 8.1, 4.8 Hz, 1H), 1.29 – 1.11 (m, 2H), 1.02 – 0.85 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-d) δ 137.7, 135.9, 132.6, 129.7, 129.1, 129.0, 128.7, 128.6, 126.9, 120.4, 73.1, 28.1, 5.20, 5.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}O_2S^+$ 299.1100.; Found: 299.1106.

(E)-2-((1,3-diphenylallyl)sulfonyl)naphthalene (6n)



6n, 52%[b]

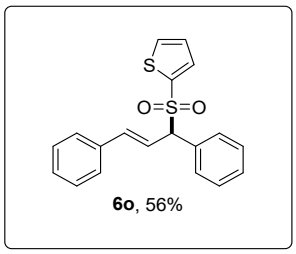
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 172-174 °C), yield: 52% (39.9 mg), R_f = 0.4 (silica gel, PE: EA = 1:5, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 8.28 (d, J = 1.8 Hz, 1H), 7.98 – 7.82 (m, 3H), 7.74 – 7.56 (m, 3H), 7.34 (dtdd, J = 19.8, 12.1, 8.2, 4.2 Hz, 10H), 6.67 (dd, J = 15.7, 8.9 Hz, 1H), 6.58 (d, J = 15.7 Hz, 1H), 4.97 (d, J = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d)δ 138.3, 135.9, 135.2, 134.4, 132.4, 131.9, 131.3, 129.8, 129.4, 129.3, 129.0, 128.7, 128.7, 128.6, 128.5, 127.9, 127.5, 126.8, 124.0, 120.0, 75.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{21}O_2S^+$ 385.1257.; Found: 385.1259.

(E)-2-((1,3-diphenylallyl)sulfonyl)thiophene (6o)



6o, 56%

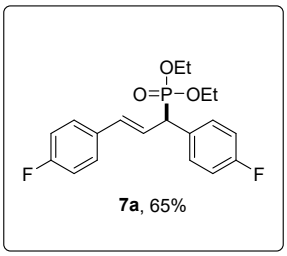
Following the **general procedure 4** on 0.2 mmol scale, White solid (mp: 195-197 °C), yield: 56% (38.1 mg), R_f = 0.3 (silica gel, PE: EA = 1:3, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 (dd, J = 4.9, 1.3 Hz, 1H), 7.44 – 7.31 (m, 10H), 7.31 – 7.26 (m, 1H), 7.03 (dd, J = 4.9, 3.8 Hz, 1H), 6.68 – 6.58 (m, 2H), 4.95 (dd, J = 5.7, 2.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 138.5, 138.1, 135.9, 135.4, 134.6, 132.4, 129.7, 129.1, 128.8, 128.7, 128.62, 127.56, 126.9, 119.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{17}O_2S_2^+$ 341.0664.; Found: 341.0665.

diethyl (E)-(1,3-bis(4-fluorophenyl)allyl)phosphonate (7a)



7a, 65%

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 65% (47.6 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (ddd, J = 8.9, 5.2, 2.3 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.07 – 7.01 (m, 2H), 7.01 – 6.95 (m, 2H), 6.51 (dd, J = 15.8, 4.3 Hz, 1H), 6.39 (dt, J = 16.0, 8.3 Hz, 1H), 4.16 – 4.03 (m, 2H), 4.03 – 3.89 (m, 2H), 3.83 (ddq, J = 10.1, 8.5, 7.1 Hz, 1H), 1.26 (t, J = 7.0 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H).

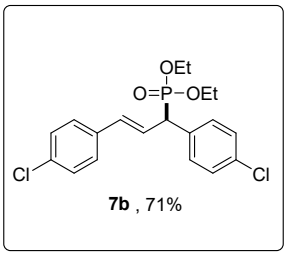
^{13}C NMR (126 MHz, Chloroform-d) δ 164.0 – 162.8 (m), 161.7 – 160.8 (m), 132.8 (t, J = 3.0 Hz), 132.6 (d, J = 13.7 Hz), 131.7 (dd, J = 7.3, 3.3 Hz), 130.6 (t, J = 7.5 Hz), 128.0 (dd, J = 8.2, 1.7 Hz), 124.1 (dd, J = 9.5, 2.3 Hz), 115.5 (d, J = 21.7 Hz), 62.8 (dd, J = 15.6, 7.2 Hz), 48.4 (d, J = 138.3 Hz), 16.4 (dd, J = 20.4, 5.9 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 24.48 (d, J = 4.6 Hz).

^{19}F NMR (471 MHz, Chloroform-d) δ -114.09 (d, J = 2.3 Hz), -115.15 (d, J = 4.4 Hz).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{22}F_2O_3P^+$ 367.1269.; Found: 367.1271.

diethyl (E)-(1,3-bis(4-chlorophenyl)allyl)phosphonate (7b)



7b , 71%

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 71% (52.5 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

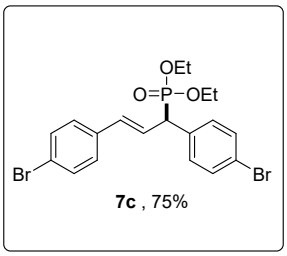
^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.30 (m, 4H), 7.30 – 7.23 (m, 4H), 6.52 – 6.39 (m, 2H), 4.13 – 4.03 (m, 2H), 4.03 – 3.89 (m, 2H), 3.89 – 3.80 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 135.0 (d, J = 1.8 Hz), 134.3 (d, J = 6.9 Hz), 133.5, 133.3 (d, J = 2.6 Hz), 132.8 (d, J = 13.4 Hz), 130.4 (d, J = 6.4 Hz), 128.9, 128.8, 127.7, 124.8 (d, J = 9.1 Hz), 62.9 (dd, J = 13.5, 6.6 Hz), 49.3, 48.2.

^{31}P NMR (202 MHz, Chloroform-d) δ 23.98.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{22}Cl_2O_3P^+$ 399.0678.; Found: 399.0679.

diethyl (E)-(1,3-bis(4-bromophenyl)allyl)phosphonate (7c)



7c , 75%

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 75% (72.9 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

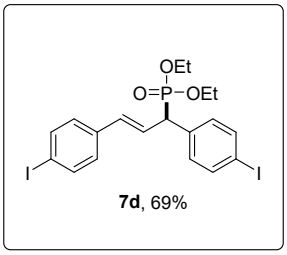
^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 (d, J = 8.2 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.32 (dd, J = 8.5, 2.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.53 – 6.38 (m, 2H), 4.14 – 4.03 (m, 2H), 4.03 – 3.89 (m, 2H), 3.85 (dddd, J = 10.0, 8.2, 7.0, 2.2 Hz, 1H), 1.26 (d, J = 5.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 135.4 (d, J = 2.5 Hz), 134.8 (d, J = 7.3 Hz), 132.9 (d, J = 13.6 Hz), 131.9. (d, J = 1.8 Hz), 131.7, 130.7 (d, J = 6.8 Hz), 128.0, 124.9 (d, J = 9.4 Hz), 121.7, 121.4 (d, J = 3.5 Hz), 62.9 (dd, J = 12.9, 7.0 Hz), 49.3, 48.2.

^{31}P NMR (202 MHz, Chloroform-d) δ 23.72.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{22}Br_2O_3P^+$ 508.9487.; Found: 508.9489.

diethyl (E)-(1,3-bis(4-iodophenyl)allyl)phosphonate (7d)



7d, 69%

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield:69% (80.3 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

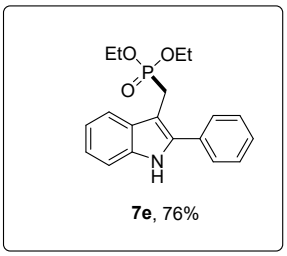
^{1}H NMR (500 MHz, Chloroform-d) δ 7.67 (d, J = 8.1 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.18 (dd, J = 8.5, 2.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.51 – 6.39 (m, 2H), 4.08 (dtd, J = 11.7, 7.2, 3.2 Hz, 2H), 4.03 – 3.80 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 137.8 (d, J = 2.2 Hz), 137.7, 136.0 (d, J = 2.8 Hz), 135.5 (d, J = 7.4 Hz), 133.0 (d, J = 13.7 Hz), 131.0 (d, J = 6.9 Hz), 128.2 (d, J = 1.9 Hz), 125.0 (d, J = 9.6 Hz), 93.2, 92.9 (d, J = 4.1 Hz), 62.9 (dd, J = 10.9, 7.2 Hz), 49.4, 48.3.

^{31}P NMR (202 MHz, Chloroform-d) δ 23.66.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{22}I_2O_3P^+$ 582.9390.; Found: 582.9385.

diethyl ((2-phenyl-1H-indol-3-yl)methyl)phosphonate (7e)



7e, 76%

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 76% (52.2 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

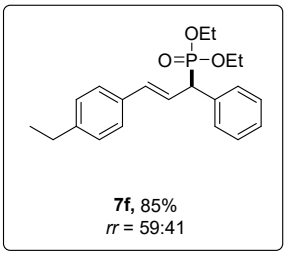
^{1}H NMR (500 MHz, Chloroform-d) δ 9.12 (s, 1H), 7.81 – 7.72 (m, 3H), 7.40 (dd, J = 8.3, 7.0 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.16 (dddd, J = 20.0, 8.1, 7.1, 1.2 Hz, 2H), 4.03 – 3.85 (m, 4H), 3.42 (d, J = 20.3 Hz, 2H), 1.17 (t, J = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-d) δ 136.5 (dd, J = 9.5, 4.6 Hz), 136.0 (d, J = 5.9 Hz), 132.7 (d, J = 3.3 Hz), 128.9 (d, J = 2.6 Hz), 128.8 (d, J = 2.5 Hz), 128.4, 127.8 (d, J = 3.1 Hz), 122.3 (d, J = 4.5 Hz), 120.0 (d, J = 3.2 Hz), 119.6 (d, J = 4.6 Hz), 111.1 (d, J = 7.7 Hz), 103.2 – 99.4 (m), 62.1 (d, J = 6.7 Hz), 23.7 (d, J = 145.2 Hz), 16.4 (d, J = 6.1 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 27.56.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}NO_3P^+$ 344.1410.; Found: 344.1409.

diethyl (E)-(3-(4-ethylphenyl)-1-phenylallyl)phosphonate (7f)



7f, 85%
rr = 59:41

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 85% (60.9 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

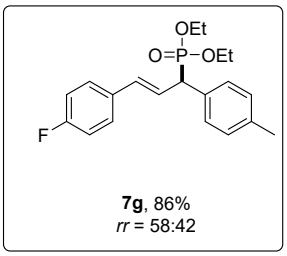
^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 – 7.46 (m, 1H), 7.43 – 7.35 (m, 3H), 7.32 (td, J = 8.0, 3.0 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.23 – 7.13 (m, 2H), 6.64 – 6.47 (m, 2H), 4.16 – 4.06 (m, 2H), 4.05 – 3.95 (m, 2H), 3.84 (ddt, J = 10.2, 8.4, 7.0 Hz, 1H), 2.66 (h, J = 7.6 Hz, 2H), 1.31 – 1.22 (m, 6H), 1.16 (td, J = 7.0, 5.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 143.9, 143.3 (d, J = 3.0 Hz), 136.9 (d, J = 2.7 Hz), 136.2 (d, J = 7.3 Hz), 134.3 (d, J = 2.8 Hz), 133.6 (dd, J = 13.8, 11.9 Hz), 133.1 (d, J = 7.4 Hz), 129.0 (dd, J = 13.8, 7.0 Hz), 128.7 (d, J = 2.3 Hz), 128.5, 128.2 (d, J = 2.3 Hz), 128.1, 127.6, 127.2 (d, J = 2.9 Hz), 126.4 (d, J = 1.9 Hz), 124.9 (d, J = 9.4 Hz), 123.6 (d, J = 9.6 Hz), 66.8 – 57.3 (m), 28.6 (d, J = 13.6 Hz), 16.5 (d, J = 5.9 Hz), 16.3 (d, J = 5.8 Hz), 15.5.

^{31}P NMR (202 MHz, Chloroform-d) δ 25.09, 24.97.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{28}O_3P^+$ 359.1771.; Found: 359.1775.

diethyl (E)-(3-(4-fluorophenyl)-1-(p-tolyl)allyl)phosphonate (7g)



7g, 86%
rr = 58:42

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 86% (62.3 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 7.27 (m, 4H), 7.16 (dd, J = 25.2, 7.9 Hz, 2H), 7.03 (dt, J = 32.3, 8.7 Hz, 2H), 6.54 (dt, J = 15.8, 4.2 Hz, 1H), 6.45 (dt, J = 15.9, 8.2 Hz, 1H), 4.17 – 4.05 (m, 2H), 4.05 – 3.91 (m, 2H), 3.85 (dddd, J = 17.2, 10.1, 8.2, 6.9 Hz, 1H), 2.42 – 2.28 (m, 3H), 1.28 (dt, J = 7.0, 3.6 Hz, 3H), 1.16 (td, J = 7.1, 3.1 Hz, 3H).

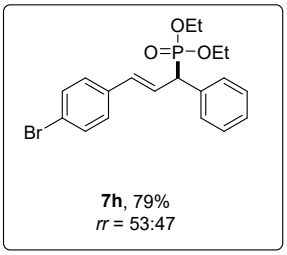
^{13}C NMR (126 MHz, Chloroform-d) δ 162.3 (d, J = 246.9 Hz), 137.7, 137.0 (d, J = 3.1 Hz), 133.8 (d, J = 3.3 Hz), 133.7, 133.0 (t, J = 3.0 Hz), 132.7 (d, J = 7.3 Hz), 132.3 (d, J = 13.8 Hz), 131.9 (dd, J = 7.5, 3.2 Hz), 130.6 (t, J = 7.5 Hz), 129.5 (d, J = 2.3 Hz), 129.3, 128.9 (d, J = 6.9 Hz), 127.9 (dd, J = 7.9, 1.8 Hz), 126.4 (d, J = 1.8 Hz), 124.7 (dd, J = 9.5, 2.3 Hz), 123.2 (d, J = 9.5 Hz), 115.5 (dd, J = 21.6, 15.6 Hz), 65.5 – 55.1 (m), 48.7 (dd, J = 137.8, 48.1 Hz), 21.2 (d, J = 13.3 Hz), 16.4 (dd, J = 20.9, 5.8 Hz).

^{19}F NMR (471 MHz, Chloroform-d) δ -114.38, -115.33 (d, J = 4.4 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 24.99, 24.72.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{25}FO_3P^+$ 363.1520.; Found: 363.1521.

diethyl (E)-(3-(4-bromophenyl)-1-phenylallyl)phosphonate (7h)



7h, 79%
rr = 53:47

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 79% (64.5 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

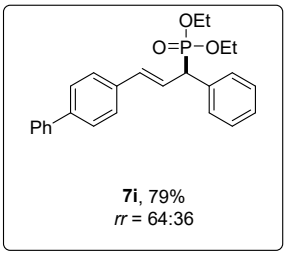
^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 – 7.39 (m, 3H), 7.39 – 7.27 (m, 4H), 7.25 – 7.07 (m, 2H), 6.63 – 6.38 (m, 2H), 4.15 – 4.04 (m, 2H), 4.04 – 3.90 (m, 2H), 3.90 – 3.74 (m, 1H), 1.26 (td, J = 7.1, 2.5 Hz, 3H), 1.14 (dt, J = 24.3, 7.0 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 137.8 (d, J = 2.2 Hz), 137.6, 136.5 (d, J = 2.6 Hz), 136.1 – 135.5 (m), 135.1 (d, J = 7.3 Hz), 134.1 (d, J = 13.8 Hz), 132.5 (t, J = 14.0 Hz), 131.8 (d, J = 2.2 Hz), 131.7, 131.0 (d, J = 6.8 Hz), 130.8 (d, J = 7.0 Hz), 129.1 (d, J = 6.8 Hz), 128.8 (d, J = 2.2 Hz), 128.6, 128.2 (d, J = 1.7 Hz), 128.0 (d, J = 1.7 Hz), 127.9, 127.4 (d, J = 2.8 Hz), 126.5 (d, J = 1.7 Hz), 125.6 (dd, J = 14.5, 9.5 Hz), 123.9 (d, J = 9.5 Hz), 122.2 – 120.1 (m), 64.8 – 58.8 (m), 49.1 (dd, J = 137.5, 81.1 Hz), 18.6 – 11.5 (m).

^{31}P NMR (202 MHz, Chloroform-d) δ 24.47 (d, J = 5.1 Hz), 24.05.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}BrO_3P^+$ 409.0563.; Found: 409.0566.

diethyl (E)-(3-([1,1'-biphenyl]-4-yl)-1-phenylallyl)phosphonate (7i)



7i, 79%
rr = 64:36

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 79% (64.2 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

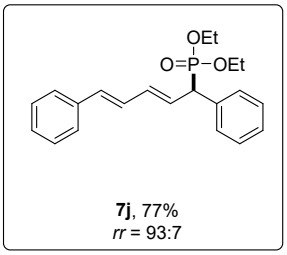
^{1}H NMR (500 MHz, Chloroform-d) δ 7.67 – 7.60 (m, 3H), 7.60 – 7.55 (m, 2H), 7.54 – 7.41 (m, 5H), 7.41 – 7.31 (m, 3H), 7.31 – 7.24 (m, 1H), 6.71 – 6.56 (m, 2H), 4.15 (dddd, J = 12.3, 10.2, 6.2, 2.6 Hz, 2H), 4.12 – 3.97 (m, 2H), 3.97 – 3.82 (m, 1H), 1.32 (td, J = 7.0, 2.9 Hz, 3H), 1.19 (dt, J = 14.1, 7.0 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 140.7 (d, J = 2.6 Hz), 140.5, 140.2 (d, J = 3.1 Hz), 136.8 (d, J = 2.7 Hz), 136.0 (d, J = 7.3 Hz), 135.8 (d, J = 2.8 Hz), 135.1 (d, J = 7.6 Hz), 133.9 (d, J = 13.8 Hz), 133.3 (d, J = 13.9 Hz), 129.5 (d, J = 7.0 Hz), 129.1 (d, J = 7.1 Hz), 128.8 (d, J = 2.3 Hz), 128.6, 127.8, 127.42 (d, J = 2.4 Hz), 127.37, 127.3, 127.1, 126.9 (d, J = 1.7 Hz), 126.5 (d, J = 1.8 Hz), 124.8 (d, J = 9.6 Hz), 124.5 (d, J = 9.5 Hz), 62.8 (t, J = 7.7 Hz), 49.3 (dd, J = 137.2, 52.8 Hz), 16.5 (dd, J = 21.3, 5.8 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 24.79 (d, J = 9.8 Hz).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{28}O_3P^+$ 407.1771.; Found: 407.1770.

diethyl ((2E,4E)-1,5-diphenylpenta-2,4-dien-1-yl)phosphonate (7j)



7j, 77%
rr = 93:7

Following the **general procedure 4** on 0.2 mmol scale, yellow oil, yield: 77% (54.8 mg), R_f = 0.3 (silica gel, PE: EA = 1:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v).

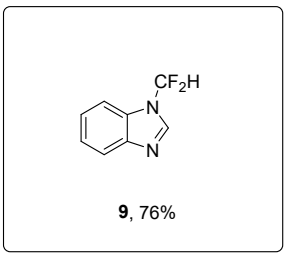
^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.26 (m, 3H), 7.24 – 7.19 (m, 1H), 6.80 (ddt, J = 15.6, 10.3, 1.0 Hz, 1H), 6.50 (dd, J = 15.7, 2.2 Hz, 1H), 6.43 – 6.31 (m, 1H), 6.15 (dt, J = 15.0, 8.7 Hz, 1H), 4.09 (dq, J = 8.0, 7.0 Hz, 2H), 4.01 – 3.87 (m, 2H), 3.86 – 3.74 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 137.1 (d, J = 1.7 Hz), 135.9 (d, J = 7.5 Hz), 134.1 (d, J = 14.0 Hz), 132.6 (d, J = 3.9 Hz), 129.1 (d, J = 6.9 Hz), 128.8, 128.7 (d, J = 2.6 Hz), 128.64, 128.59, 128.5, 128.4, 128.3 (d, J = 4.3 Hz), 128.2, 127.6, 127.3 (d, J = 2.9 Hz), 126.7 (d, J = 13.1 Hz), 126.4, 62.8 (dd, J = 26.0, 7.2 Hz), 62.0 (d, J = 5.4 Hz), 49.8, 48.8, 16.4 (dd, J = 24.4, 5.9 Hz).

^{31}P NMR (202 MHz, Chloroform-d) δ 24.71, 24.62, 18.70.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{26}O_3P^+$ 357.1614.; Found: 357.1609.

1-(difluoromethyl)-1H-benzo[d]imidazole



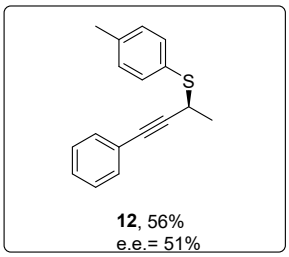
9, 76%

^{1}H NMR (500 MHz, Chloroform-d) δ 8.14 (s, 1H), 7.94 – 7.80 (m, 1H), 7.72 – 7.57 (m, 1H), 7.49 – 7.21 (m, 3H).

^{19}F NMR (471 MHz, Chloroform-d) δ -93.71.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{26}O_3P^+$ 169.0572.; Found: 169.0576.

N,N-dimethyl-4-phenylbut-3-yn-2-amine (12)



12, 56%
e.e.= 51%

Following the **general procedure 6** on 0.2 mmol scale, yellow oil, yield: 87% (28.2 mg), R_f = 0.7 (silica gel, PE: DCM = 10:1, v/v), column chromatography (silica gel, PE: DCM = 100:1, v/v).

HPLC analysis: The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel AD-H, hexane, 0.5 mL/min, λ = 254 nm, τ_R(major) = 19.8 min and τ_R(minor) = 21.5 min.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 (d, J = 7.7 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.28 (dd, J = 4.8, 2.1 Hz, 3H), 7.16 (d, J = 7.7 Hz, 2H), 4.06 (q, J = 7.0 Hz, 1H), 2.36 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H).

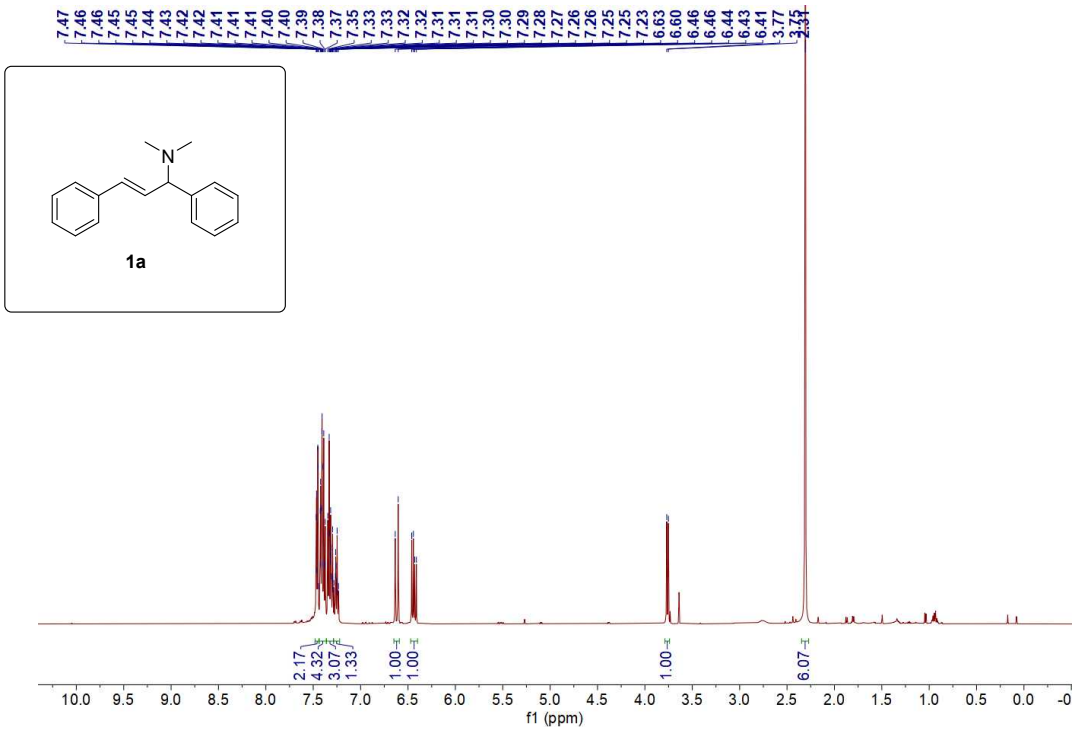
^{13}C NMR (126 MHz, Chloroform-d) δ 138.30, 134.25, 131.62, 129.88, 129.59, 128.20, 128.05, 123.15, 90.33, 83.68, 34.56, 21.86, 21.24.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}S^+$ 253.1045.; Found: 253.1048.

2.4 NMR spectroscopic data

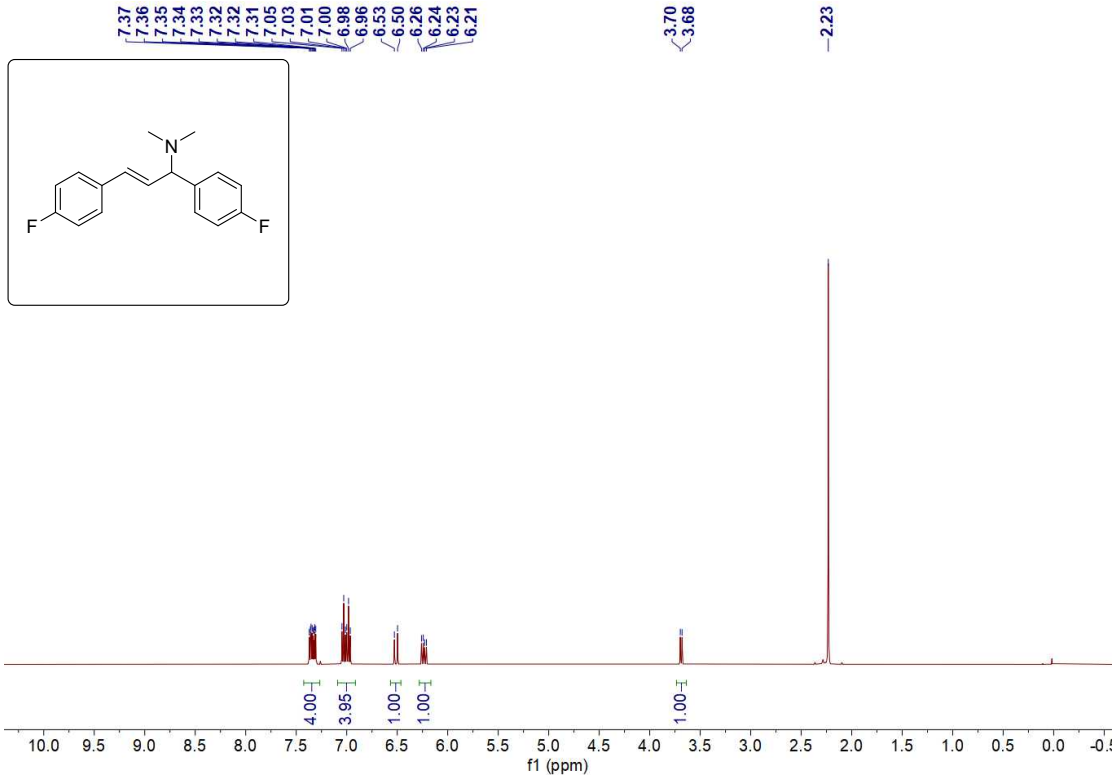
(E)-N,N-dimethyl-1,3-diphenylprop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



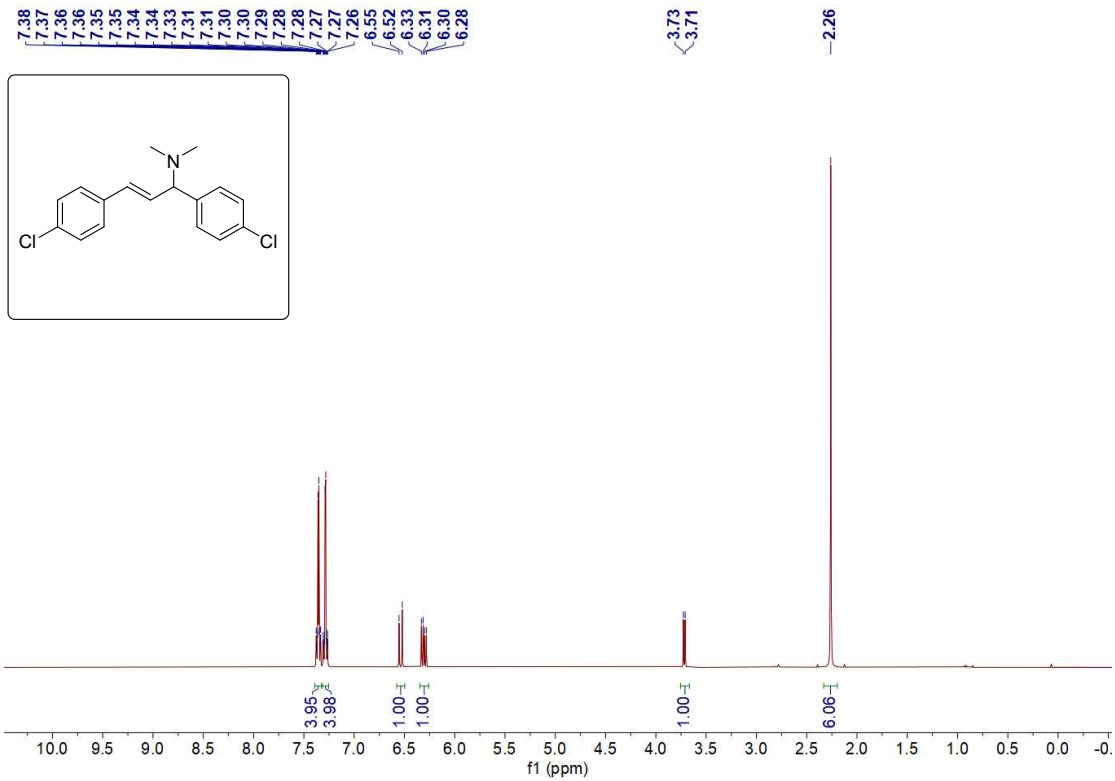
(E)-1,3-bis(4-fluorophenyl)-N,N-dimethylprop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



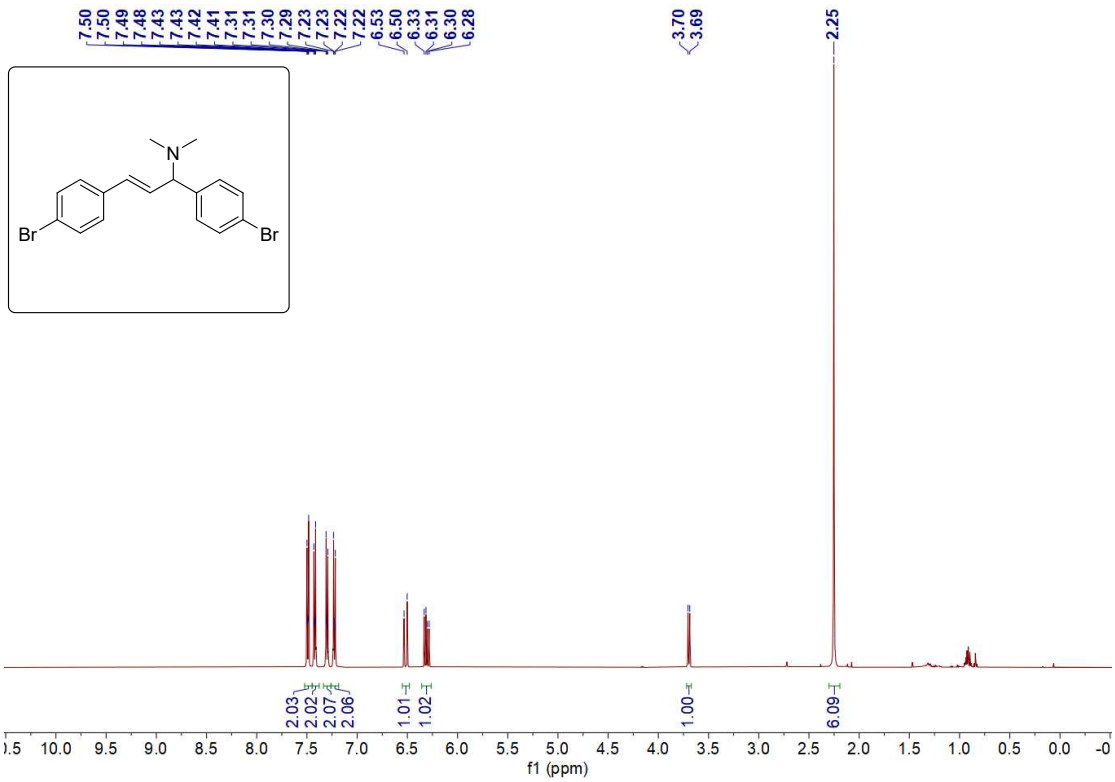
(E)-1,3-bis(4-chlorophenyl)-N,N-dimethylprop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



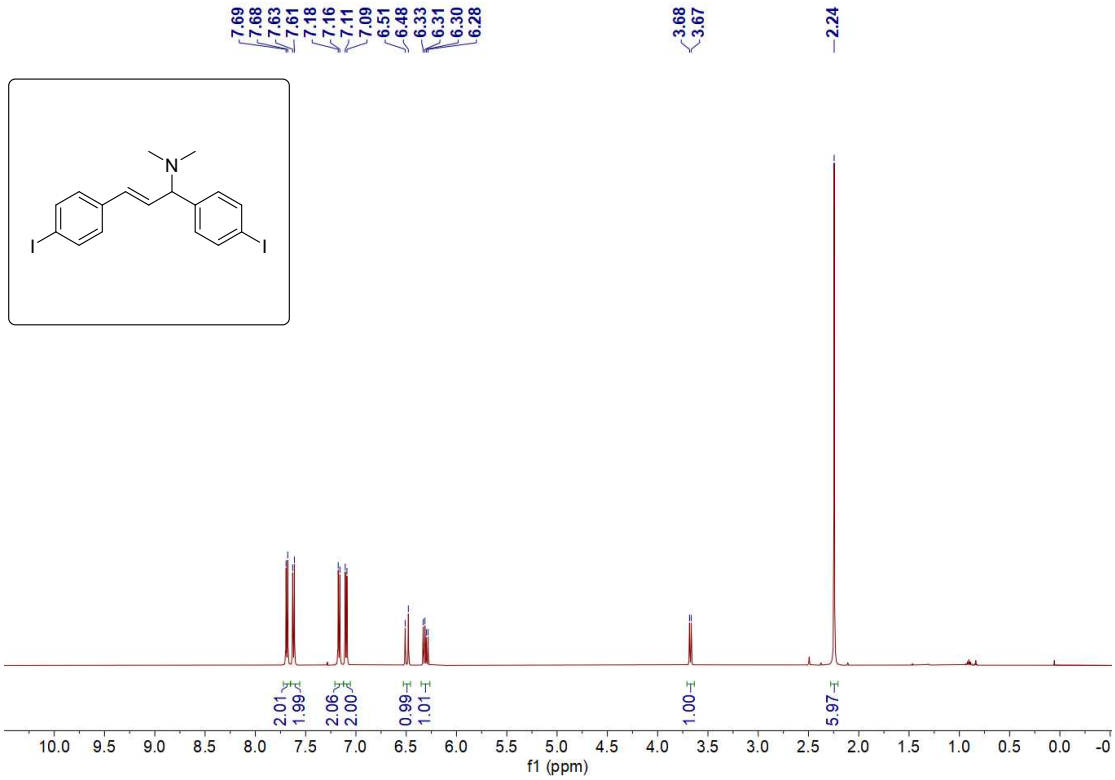
(E)-1,3-bis(4-bromophenyl)-N,N-dimethylprop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



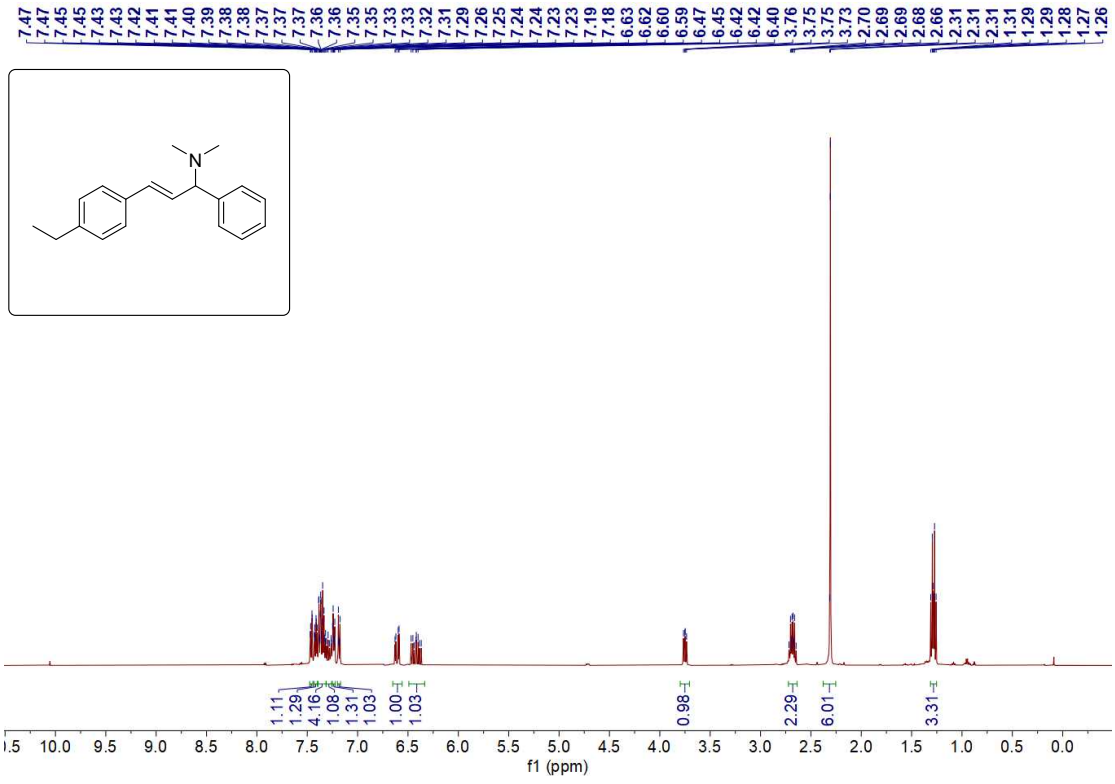
(E)-1,3-bis(4-iodophenyl)-N,N-dimethylprop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



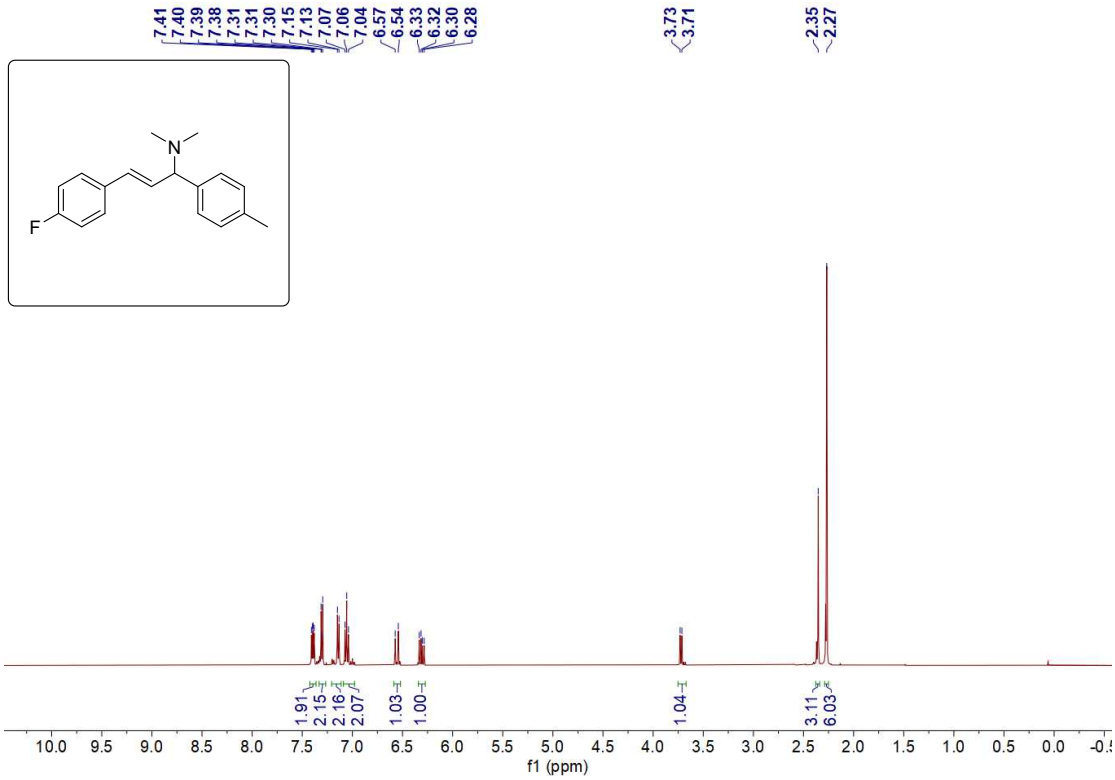
(E)-3-(4-ethylphenyl)-N,N-dimethyl-1-phenylprop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



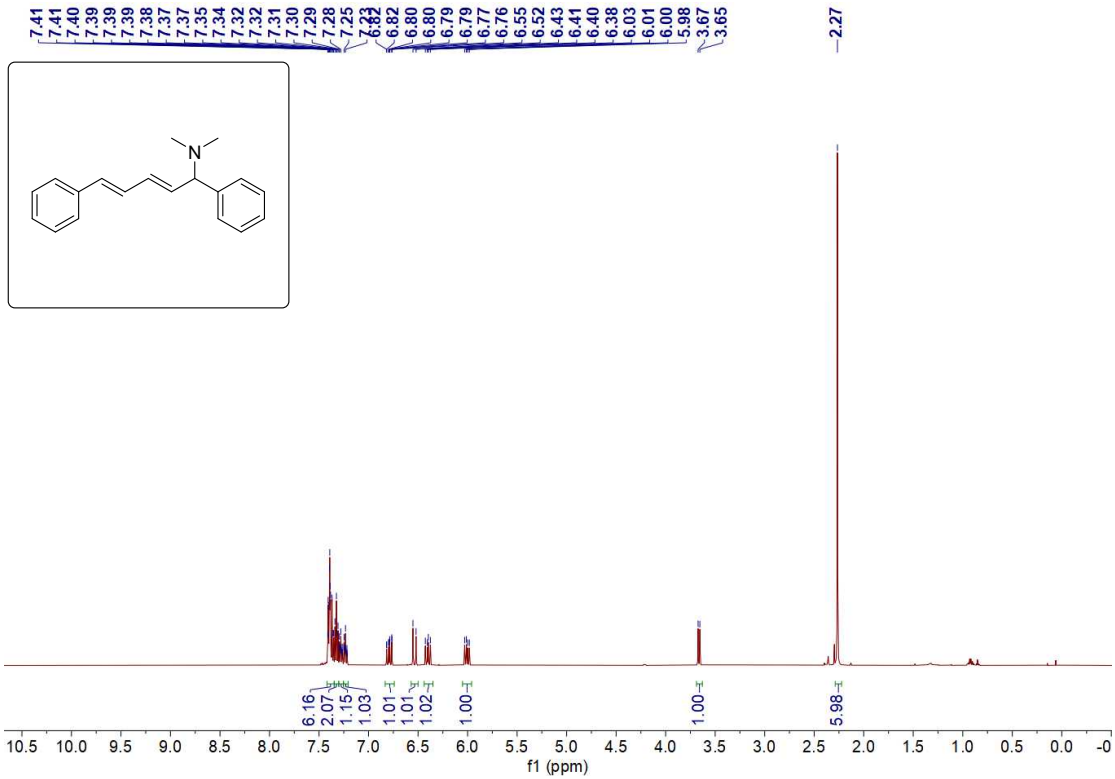
(E)-3-(4-fluorophenyl)-N,N-dimethyl-1-(p-tolyl)prop-2-en-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



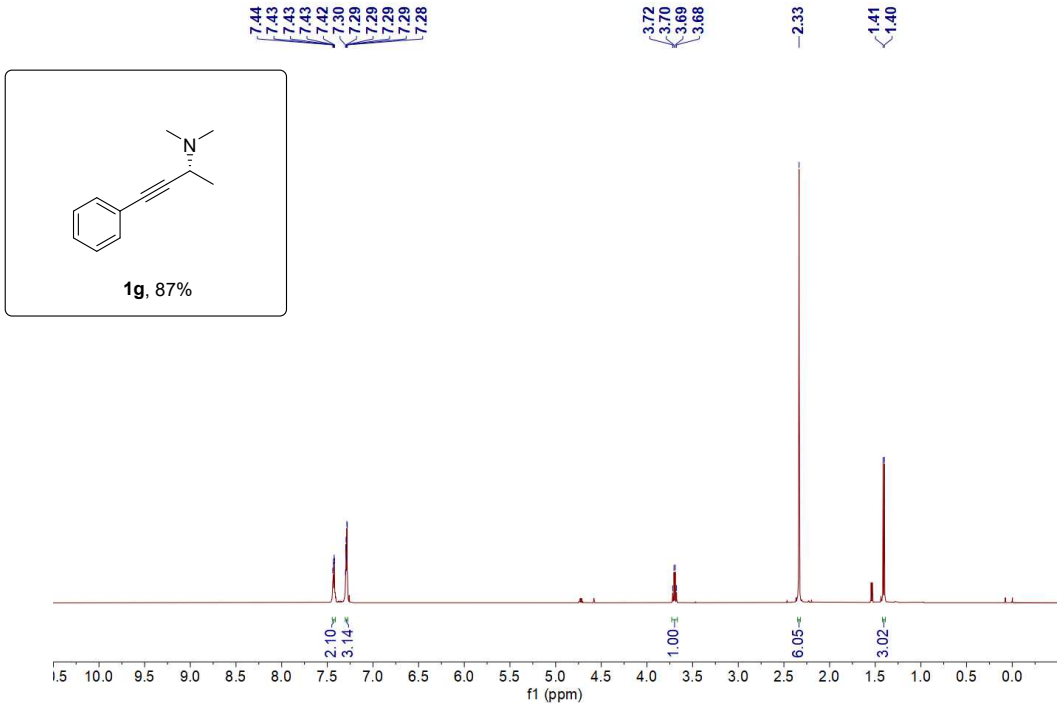
(2E,4E)-N,N-dimethyl-1,5-diphenylpenta-2,4-dien-1-amine

^{1}H NMR (500 MHz, Chloroform-d)



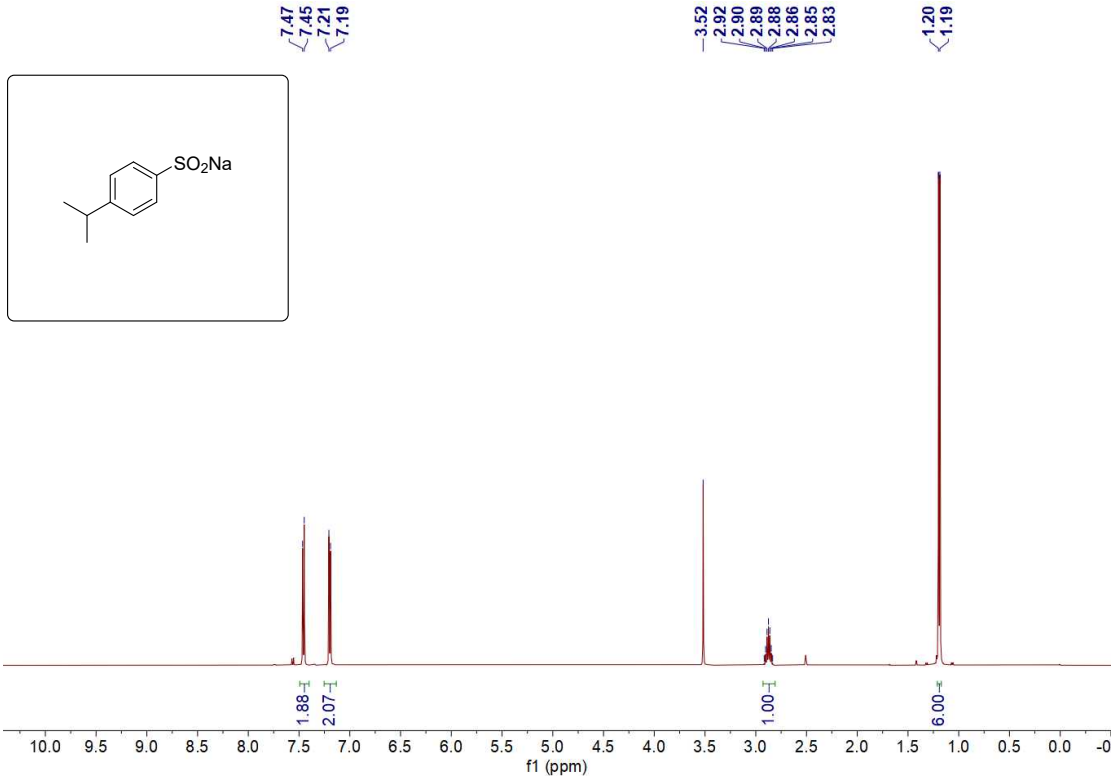
N,N-dimethyl-4-phenylbut-3-yn-2-amine (1g)

^{1}H NMR (500 MHz, Chloroform-d)



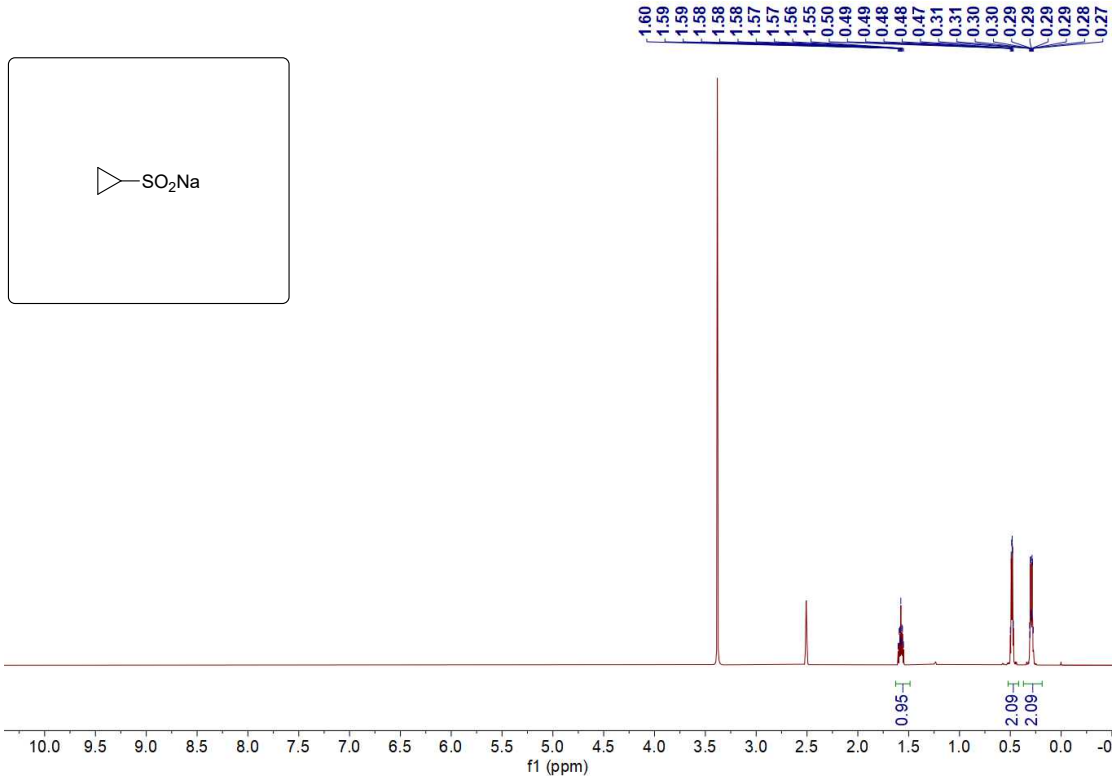
sodium 4-isopropylbenzenesulfinate

^{1}H NMR (500 MHz, DMSO-d6)



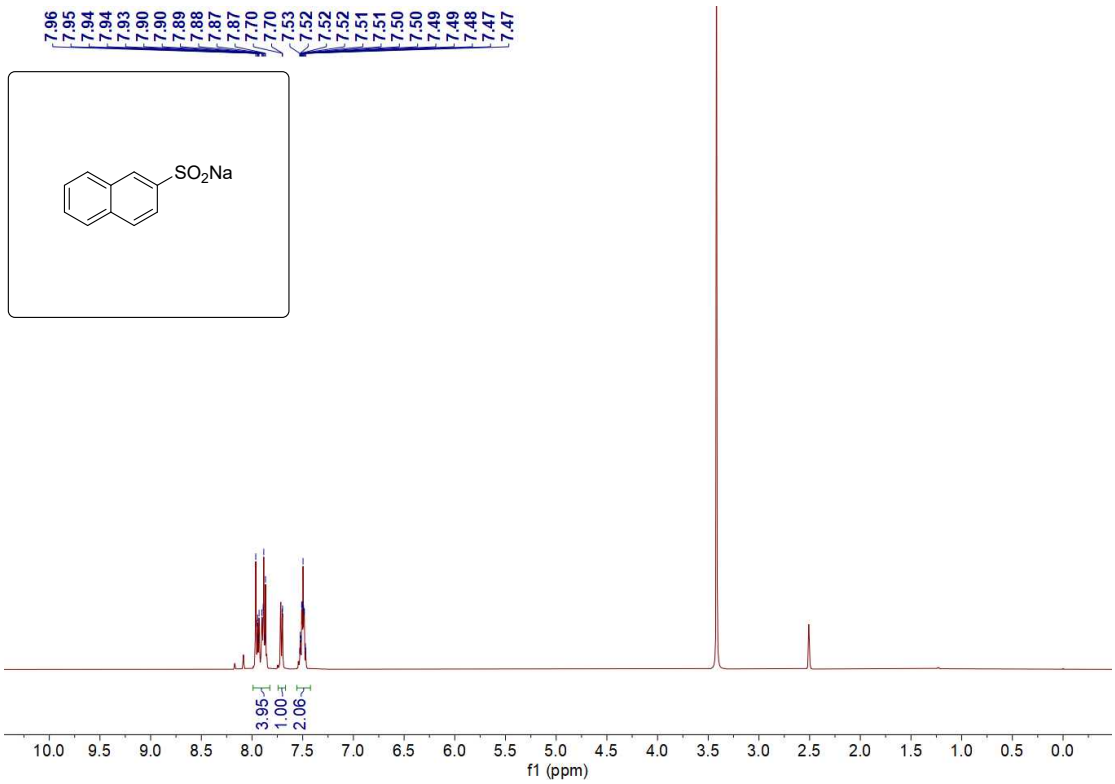
sodium cyclopropanesulfinate

^{1}H NMR (500 MHz, DMSO-d6)



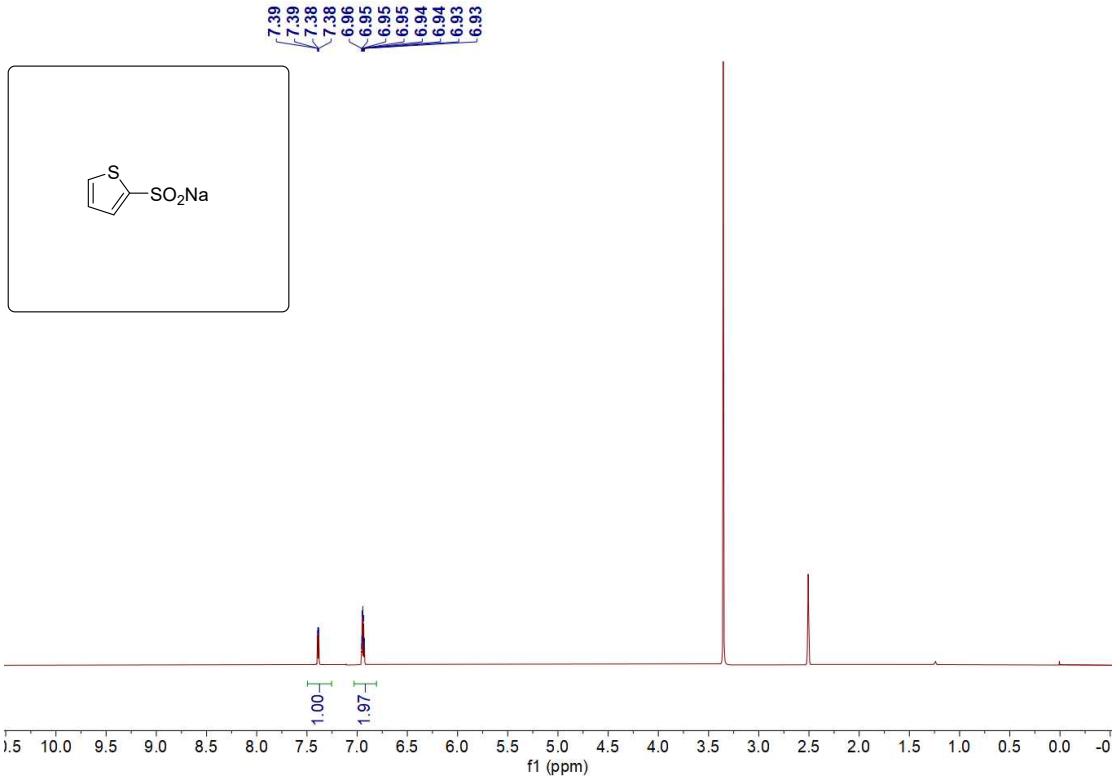
sodium naphthalene-2-sulfinate

^{1}H NMR (500 MHz, DMSO-d6)



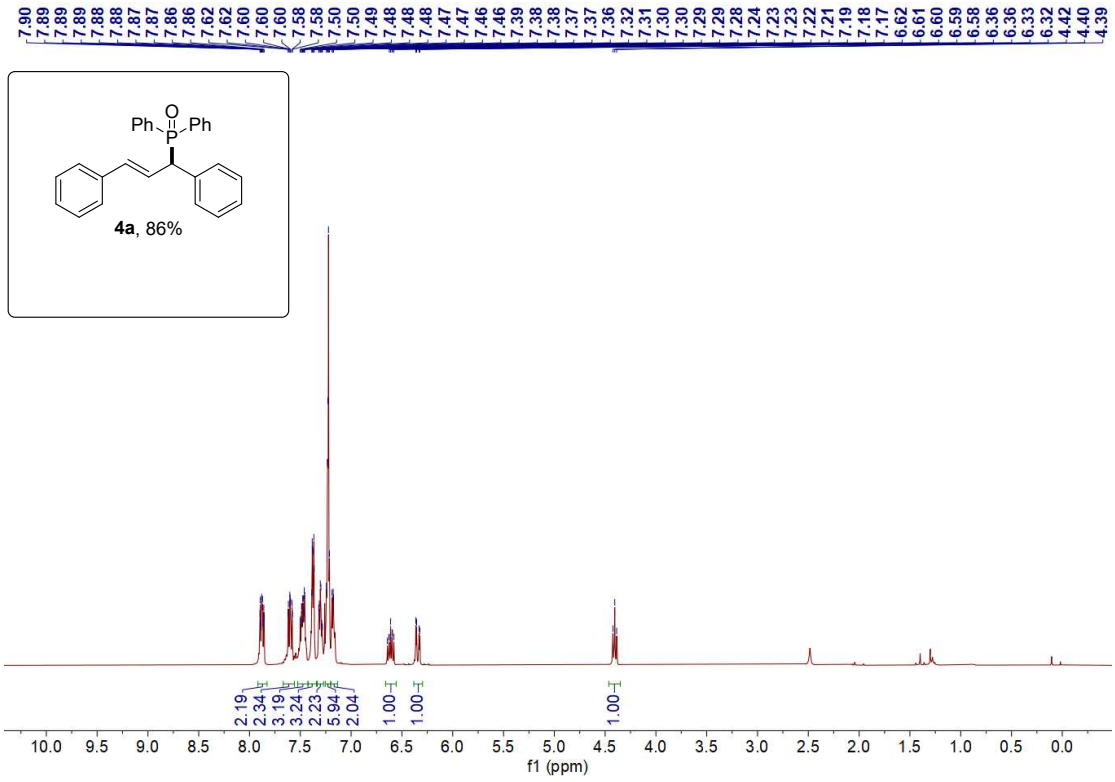
sodium thiophene-2-sulfinate

^{1}H NMR (500 MHz, DMSO-d6)

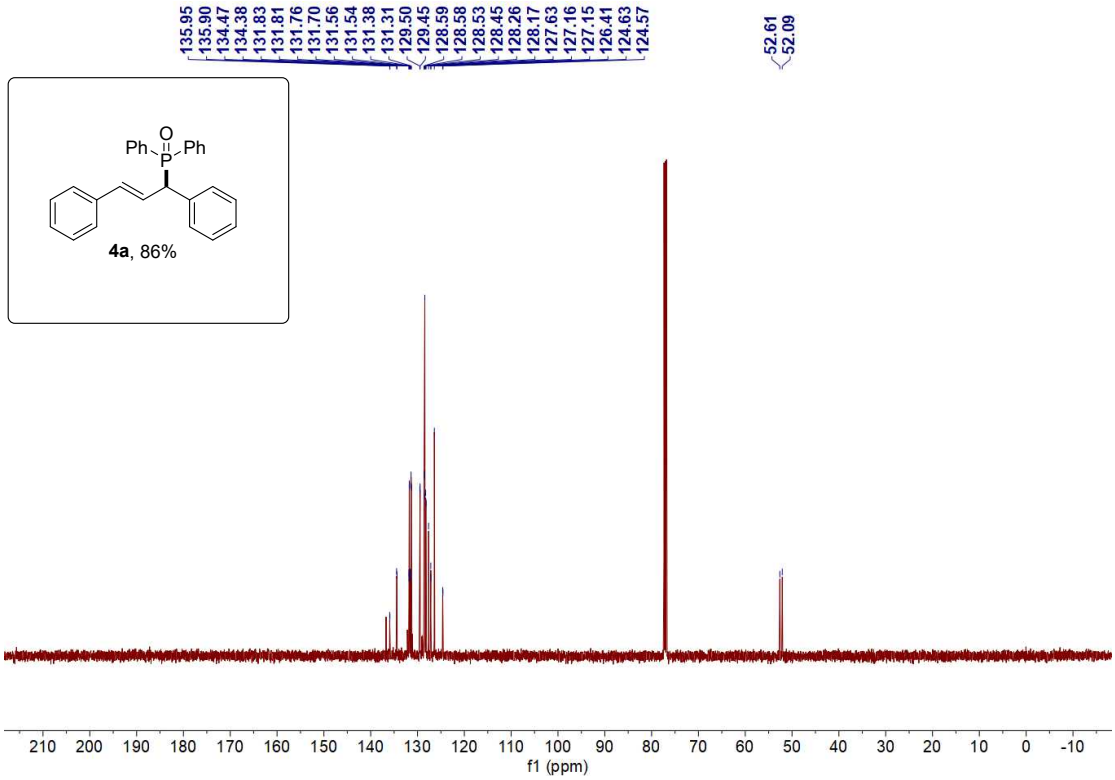


(E)-(1,3-diphenylallyl)diphenylphosphine oxide (4a)

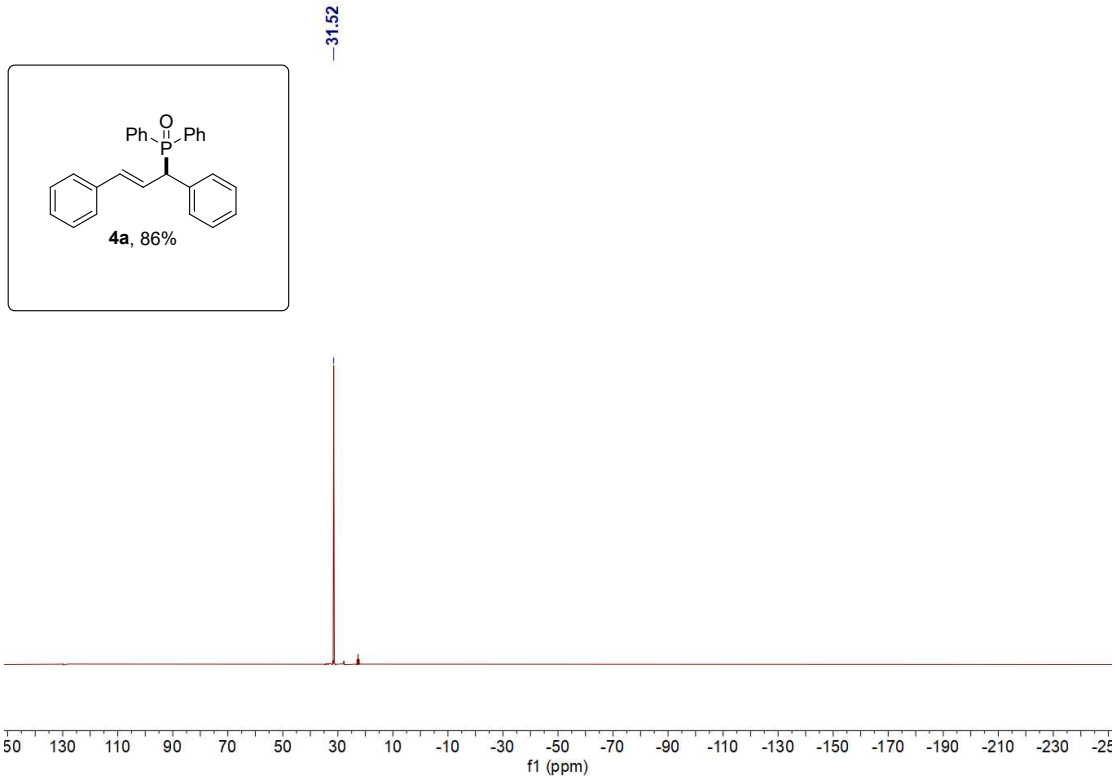
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

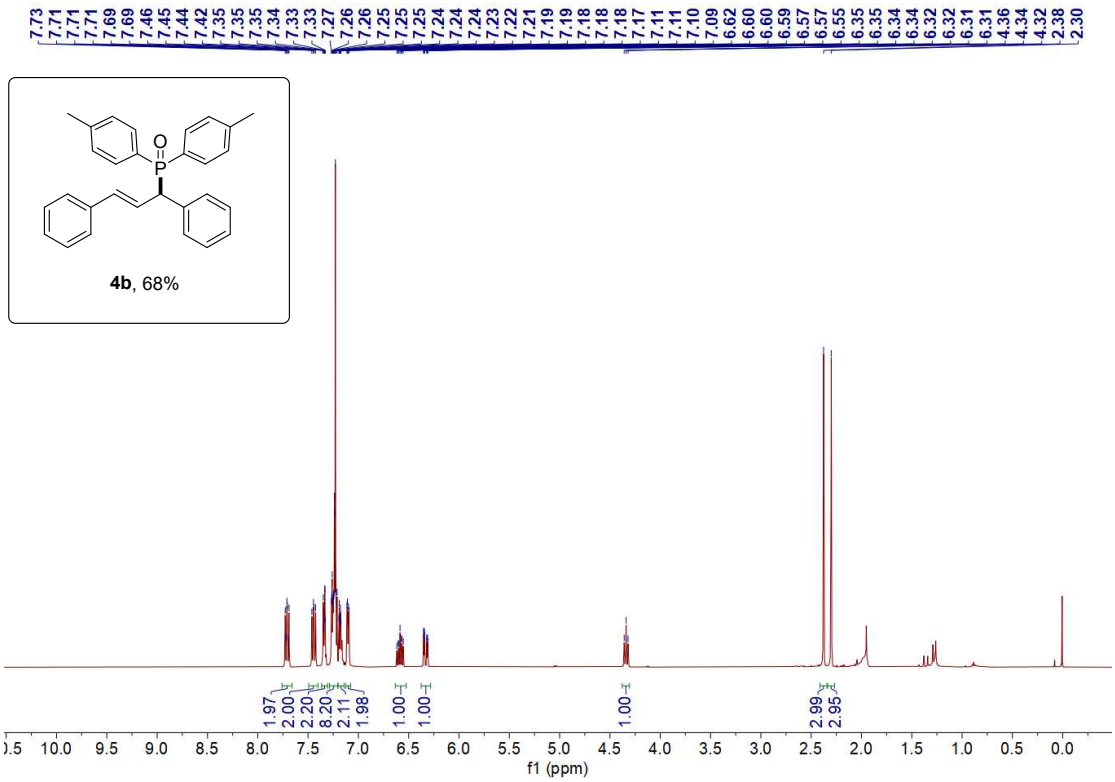


^{31}P NMR (202 MHz, CDCl3)

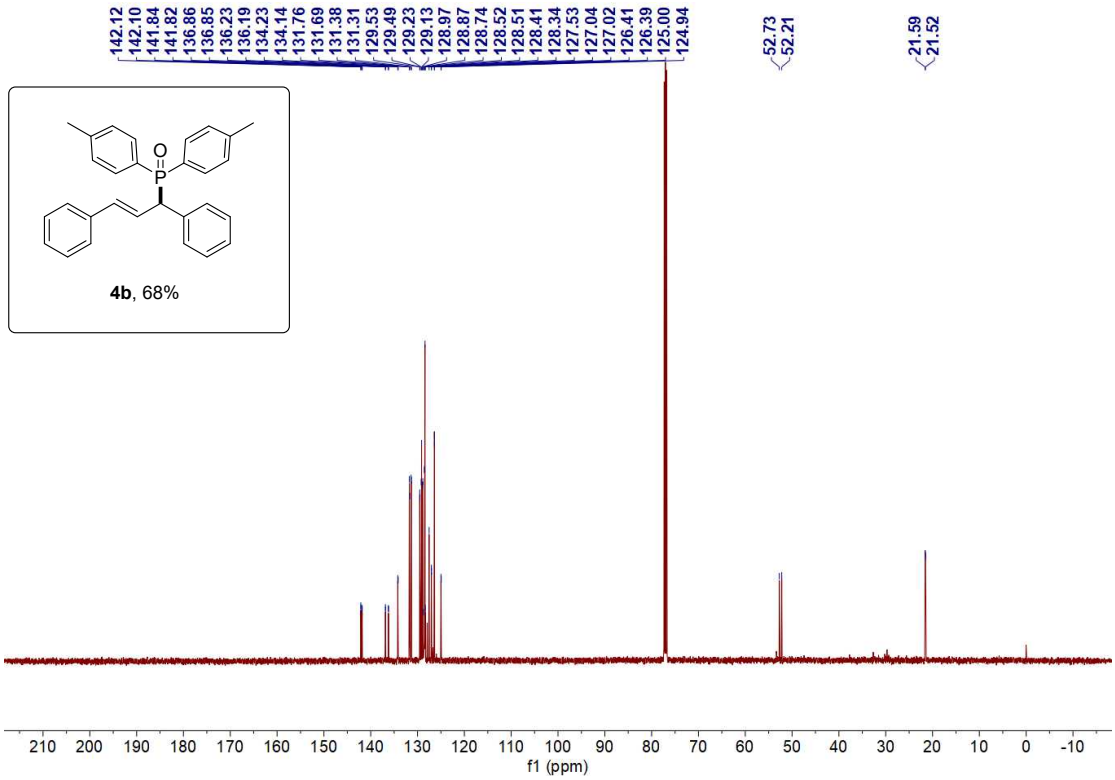


(E)-(1,3-diphenylallyl)di-p-tolylphosphine oxide (4b)

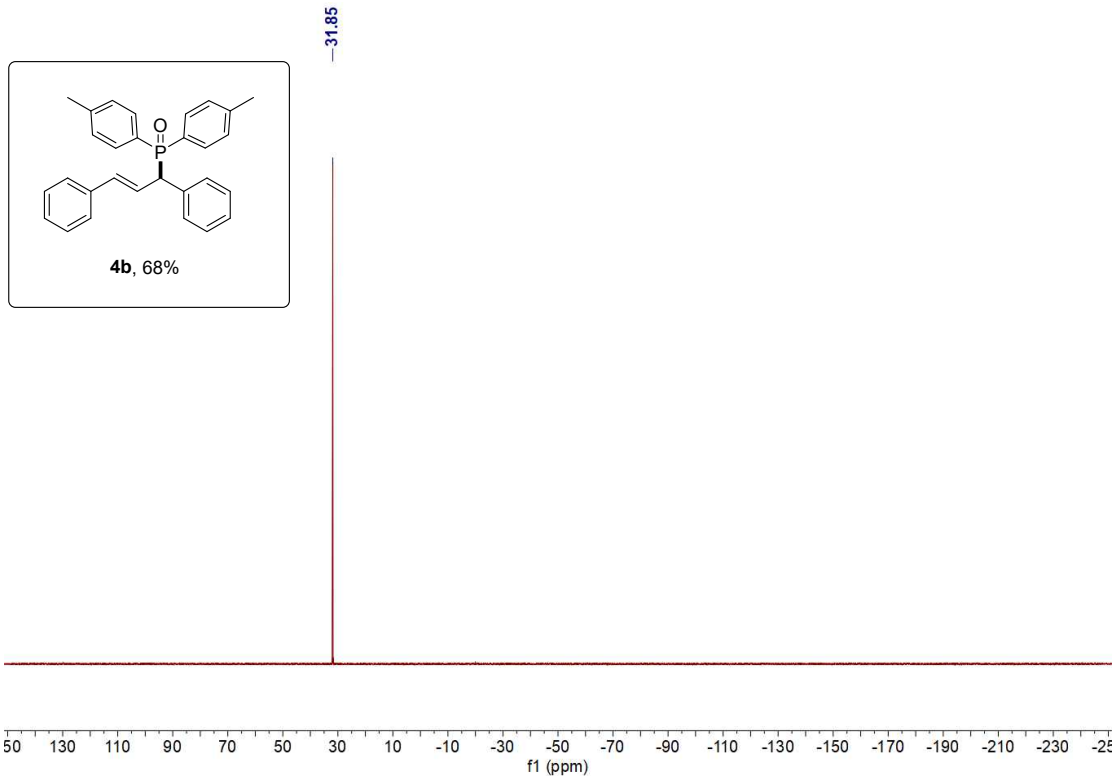
^{1}H NMR (500 MHz, Chloroform-d)


7.73 7.71 7.71 7.71 7.69 7.69 7.46 7.45 7.44 7.42 7.35 7.35 7.35 7.34 7.33 7.33 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.22 7.21 7.19 7.19 7.18 7.18 7.18 7.17 7.11 7.11 7.10 7.09 6.62 6.60 6.60 6.59 6.57 6.57 6.55 6.35 6.35 6.34 6.34 6.32 6.32 6.31 6.31 4.36 4.34 4.32 2.38 2.30
O
P
4b, 68%
1.97 2.00 2.20 8.20 2.11 1.98 1.00 1.00 1.00 2.99 2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C NMR (126 MHz, Chloroform-d)

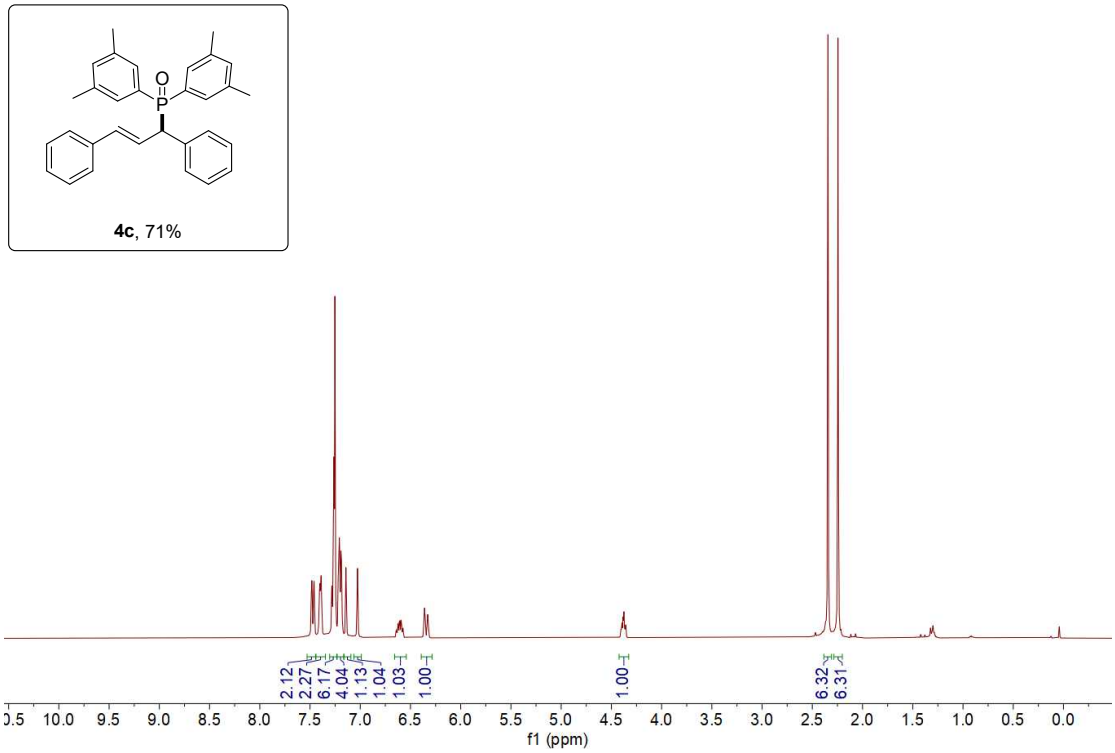


^{31}P NMR (202 MHz, Chloroform-d)

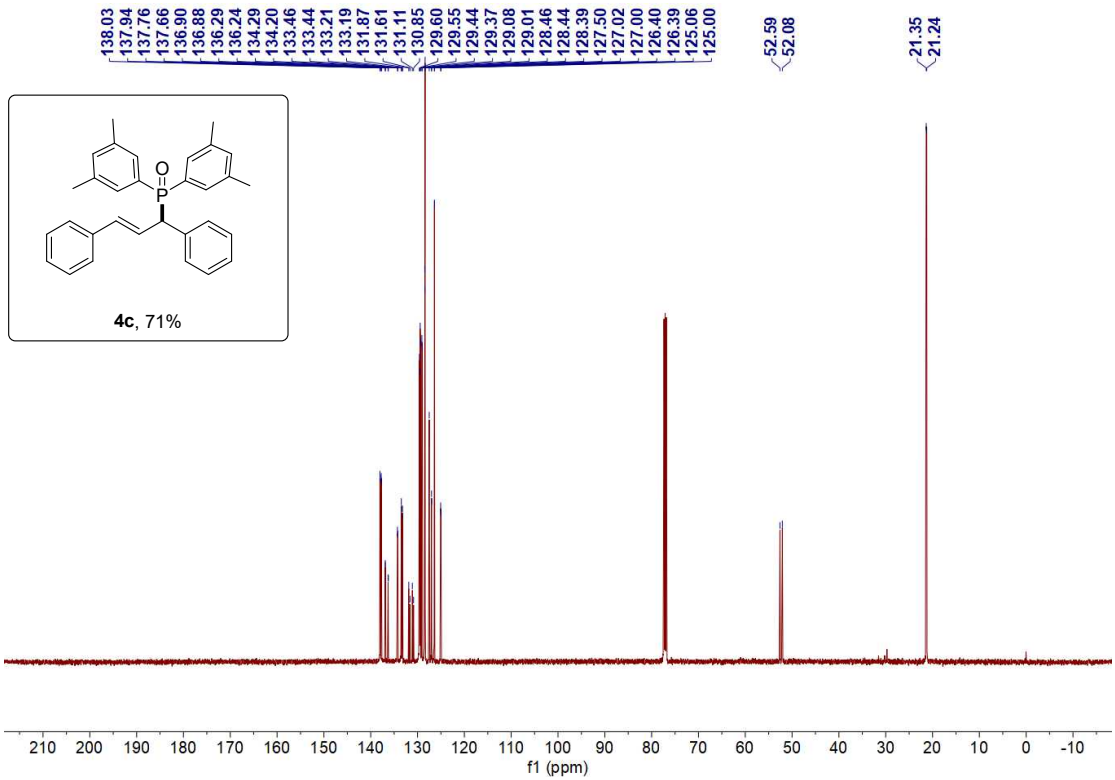


(E)-bis(3,5-dimethylphenyl)(1,3-diphenylallyl)phosphine oxide (4c)

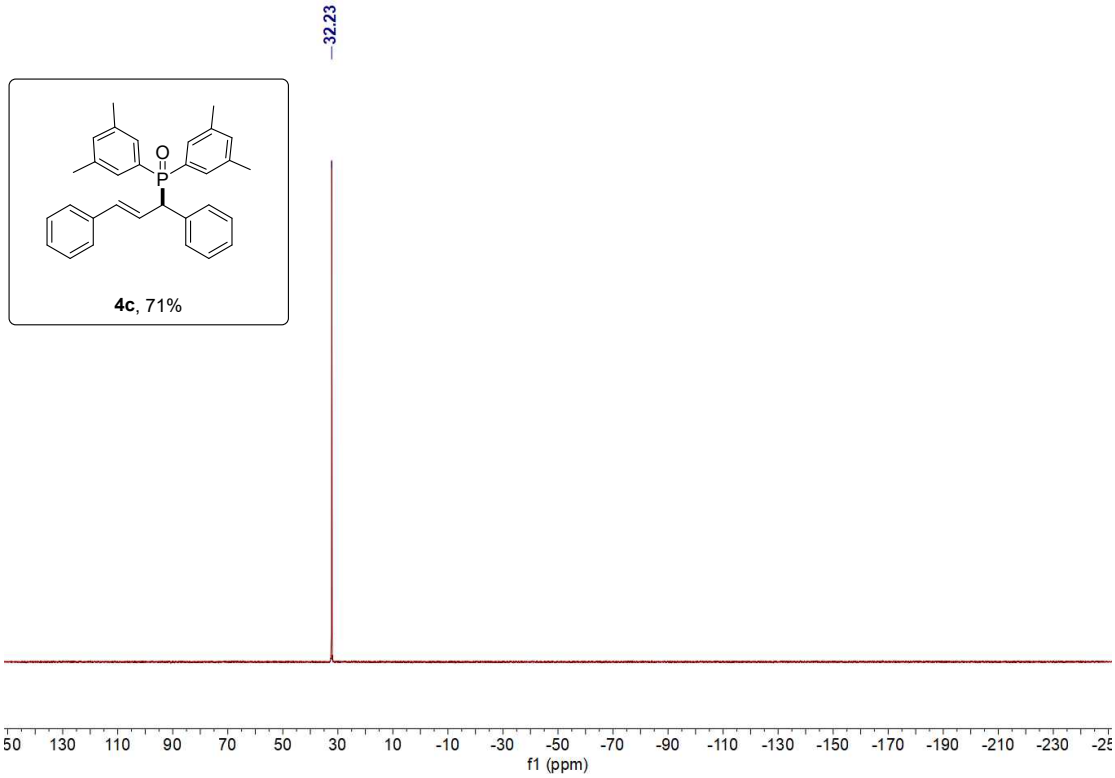
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

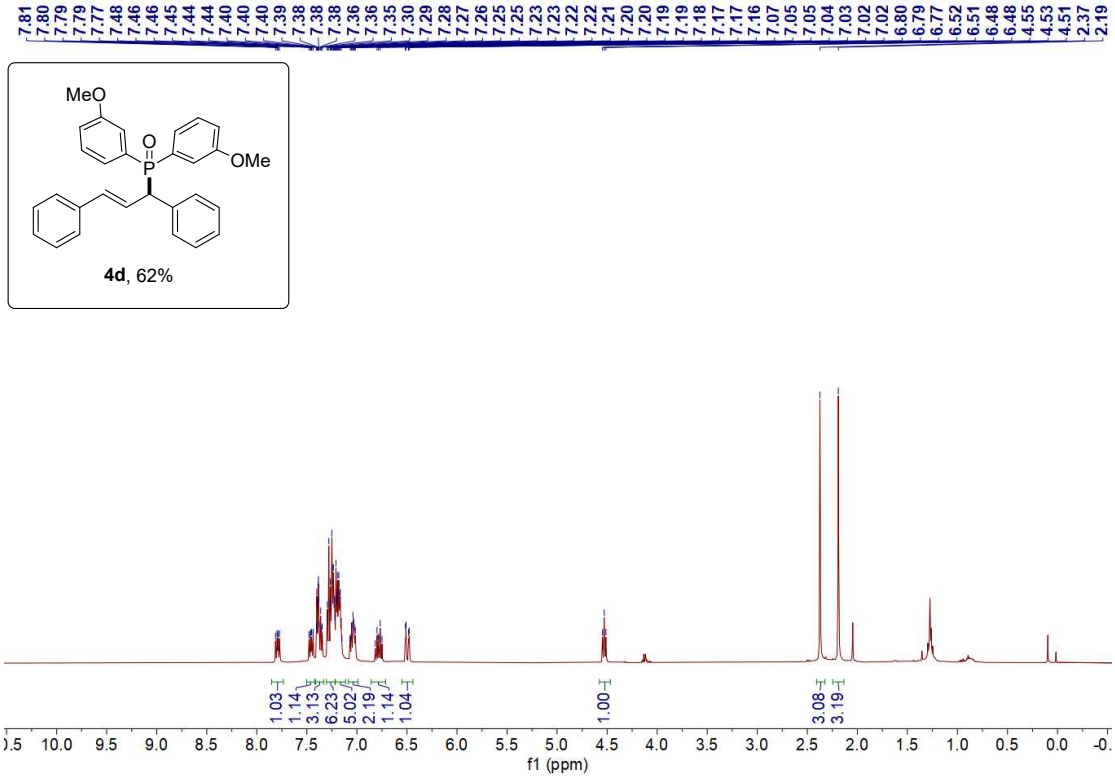


^{31}P NMR (202 MHz, Chloroform-d)

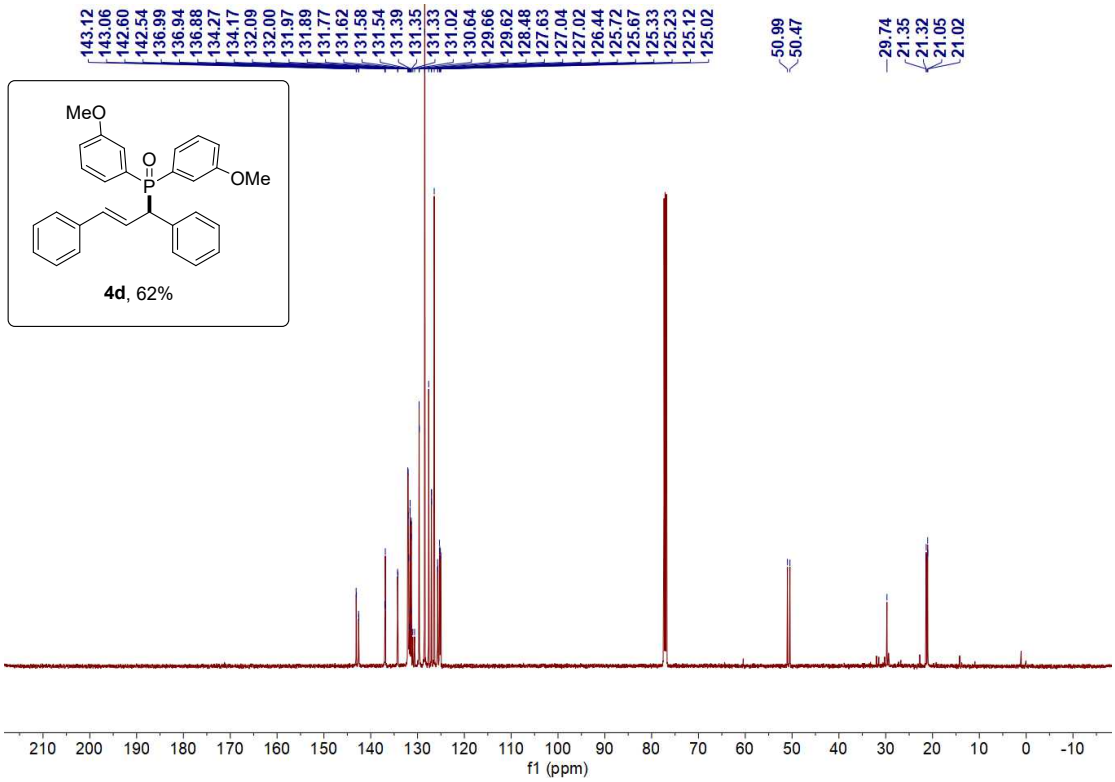


(E)-(1,3-diphenylallyl)bis(3-methoxyphenyl)phosphine oxide (4d)

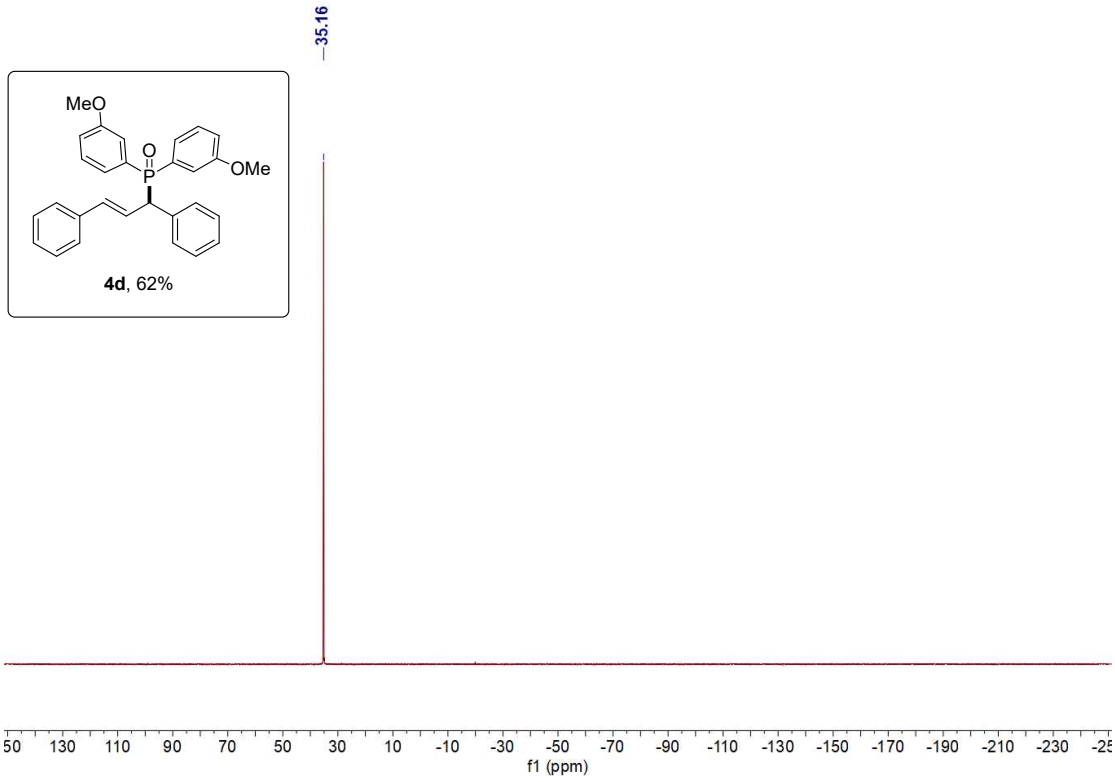
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

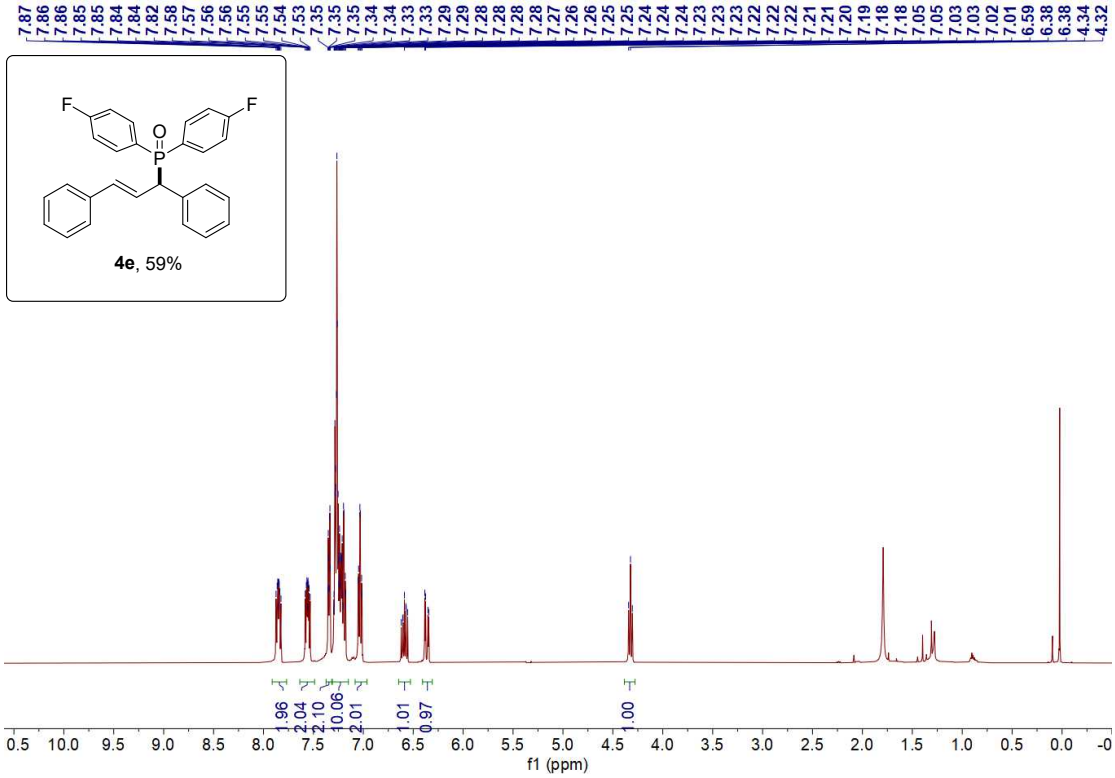


^{31}P NMR (202 MHz, Chloroform-d)

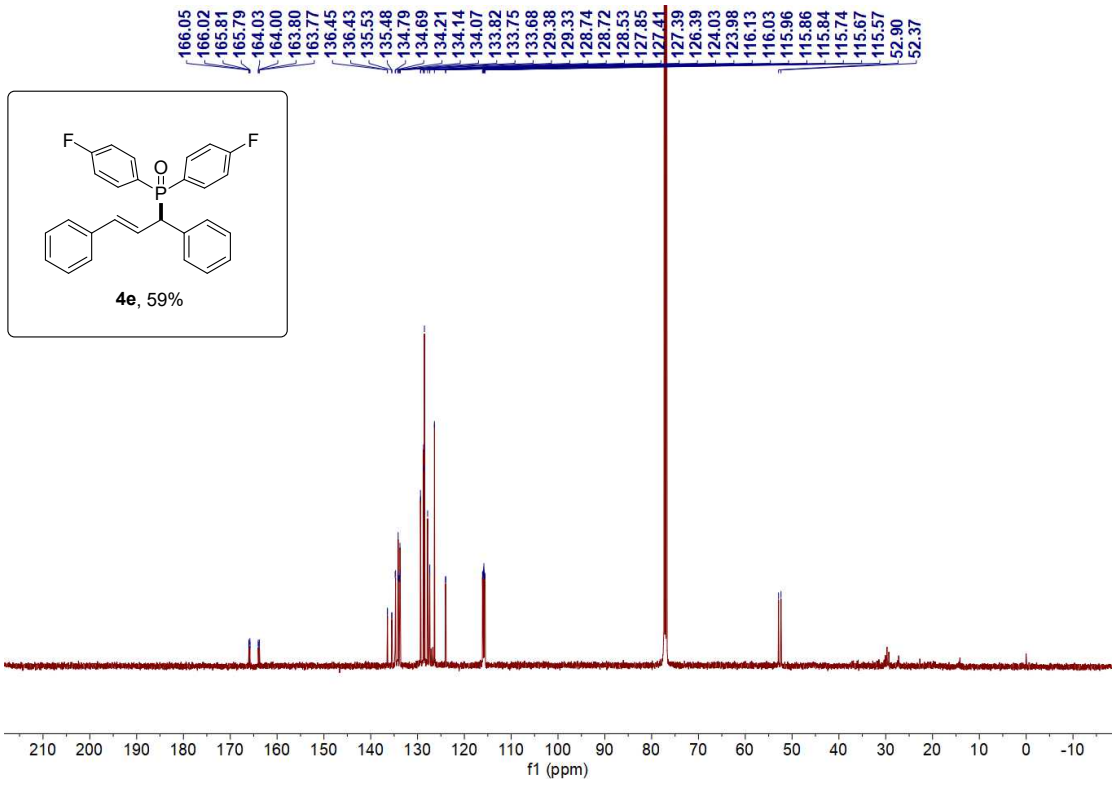


(E)-(1,3-diphenylallyl)bis(4-fluorophenyl)phosphine oxide (4e)

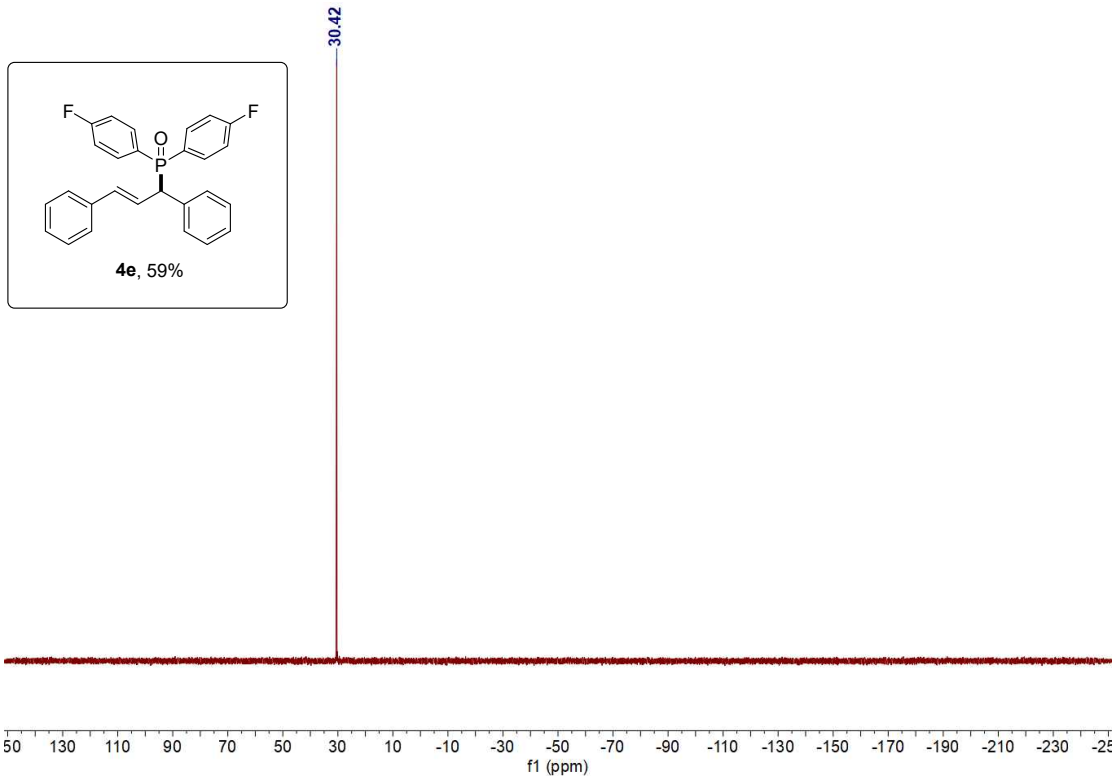
^{1}H NMR (500 MHz, Chloroform-d)



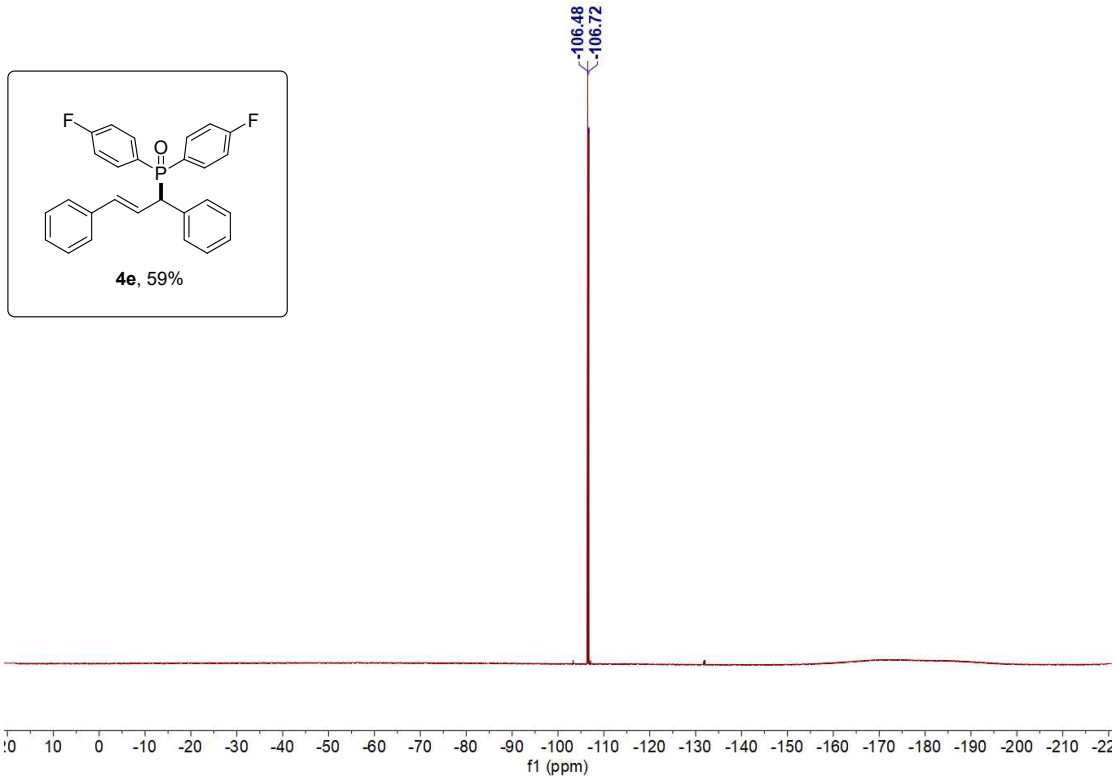
^{13}C NMR (126 MHz, Chloroform-d)



^{31}P NMR (202 MHz, Chloroform-d)

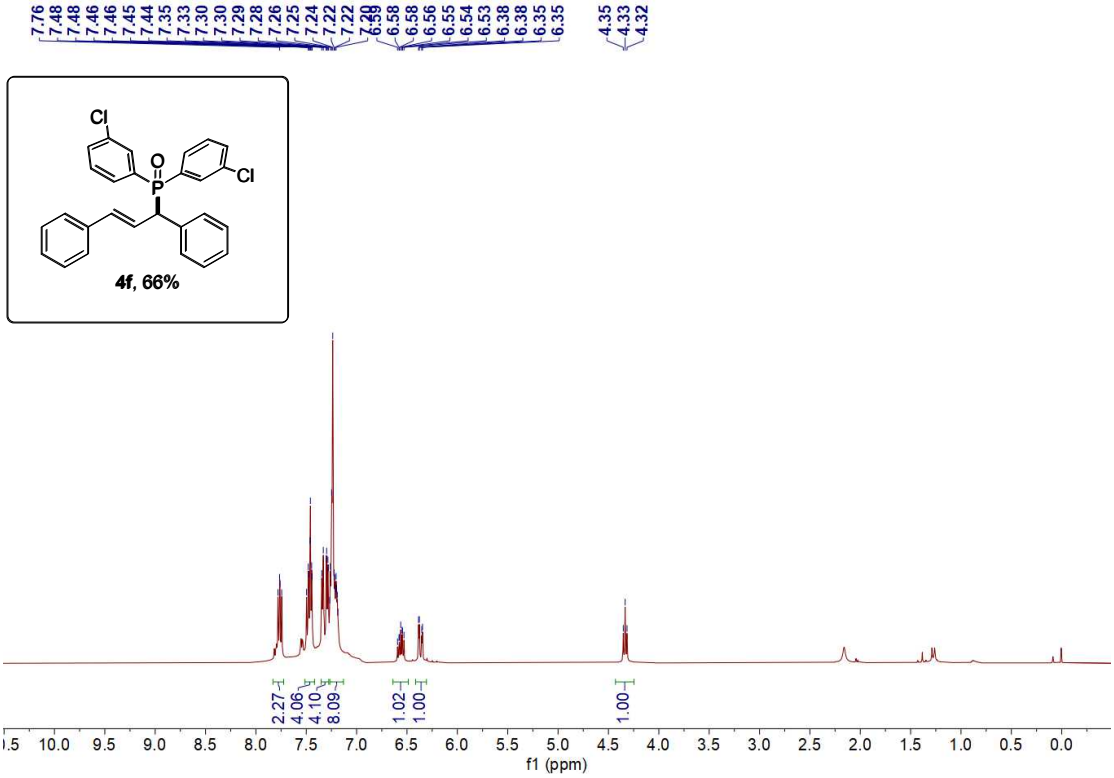


^{19}F NMR (471 MHz, Chloroform-d)

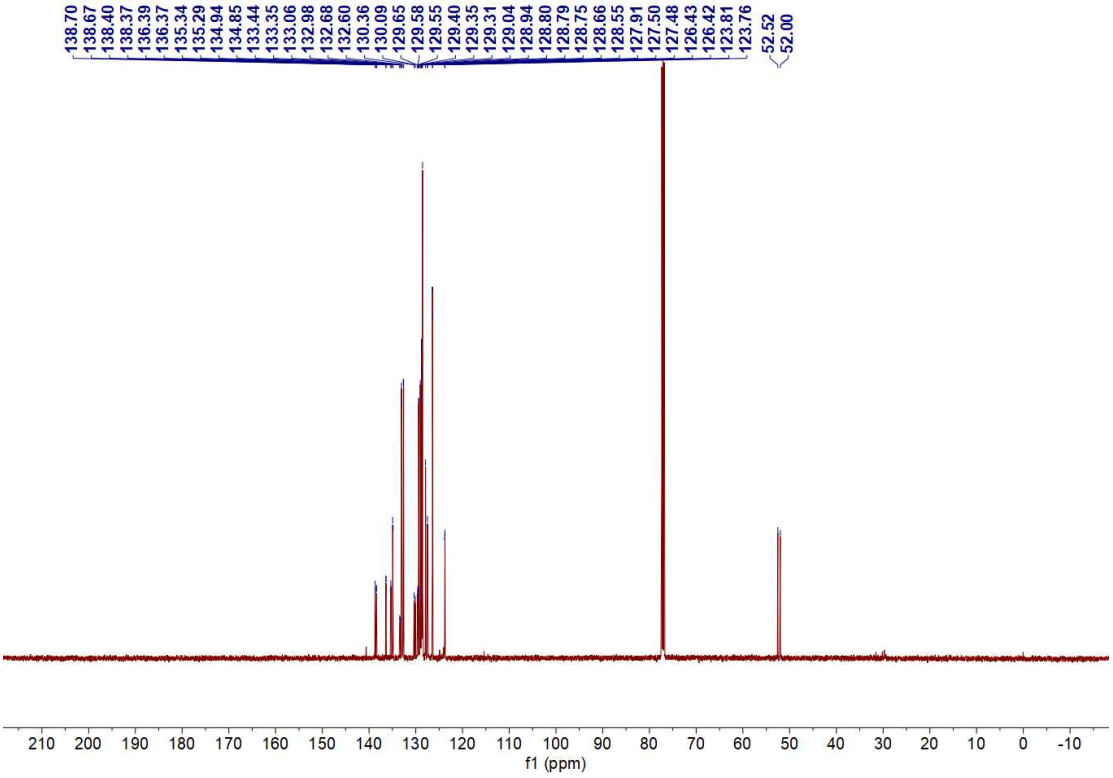


(E)-bis(3-chlorophenyl)(1,3-diphenylallyl)phosphine oxide (4f)

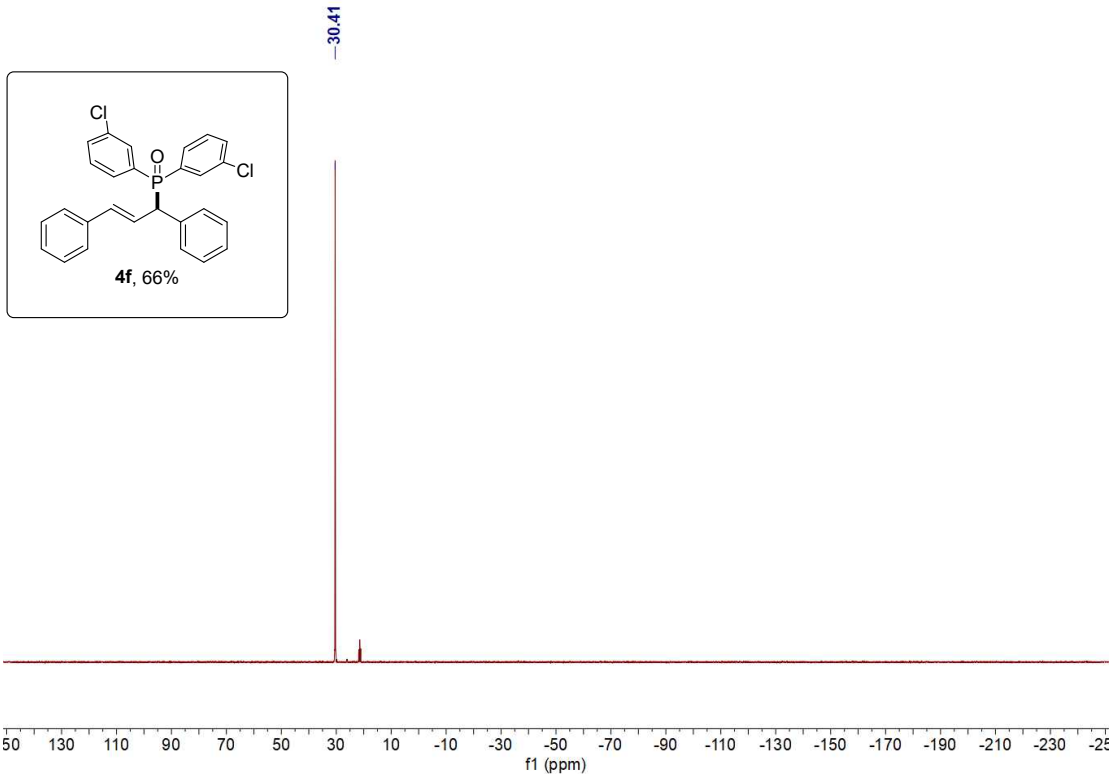
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

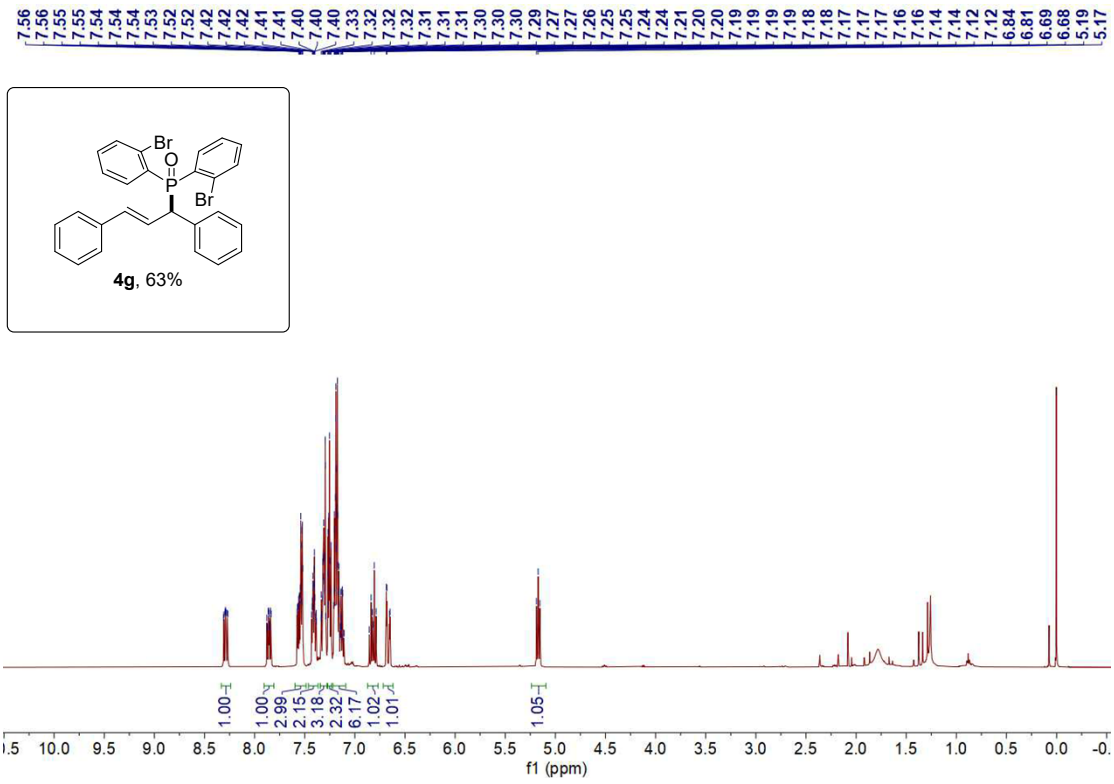


^{31}P NMR (202 MHz, Chloroform-d)

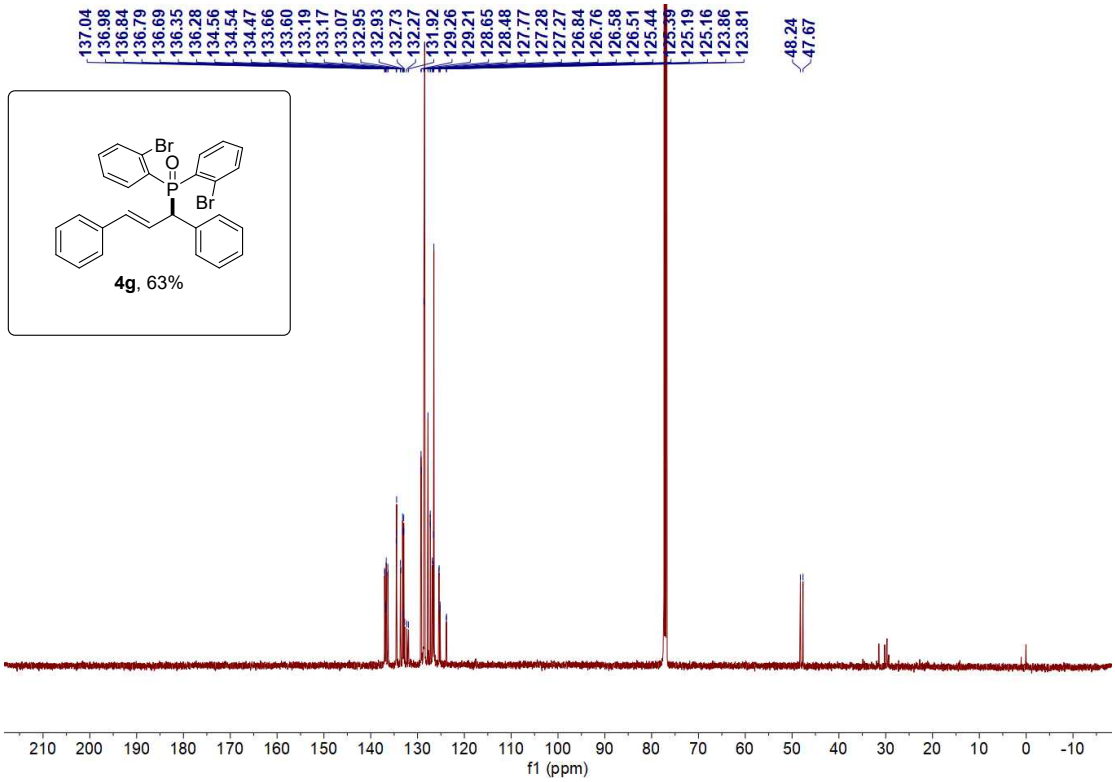


(E)-bis(2-bromophenyl)(1,3-diphenylallyl)phosphine oxide (4g)

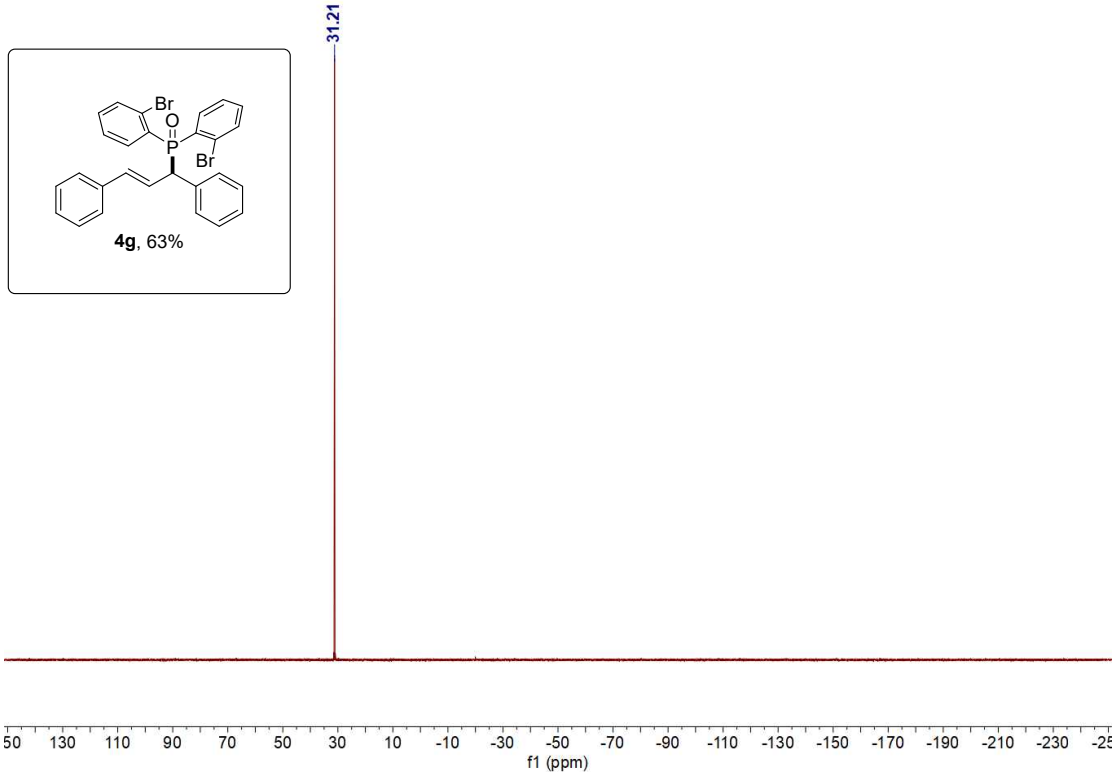
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d).

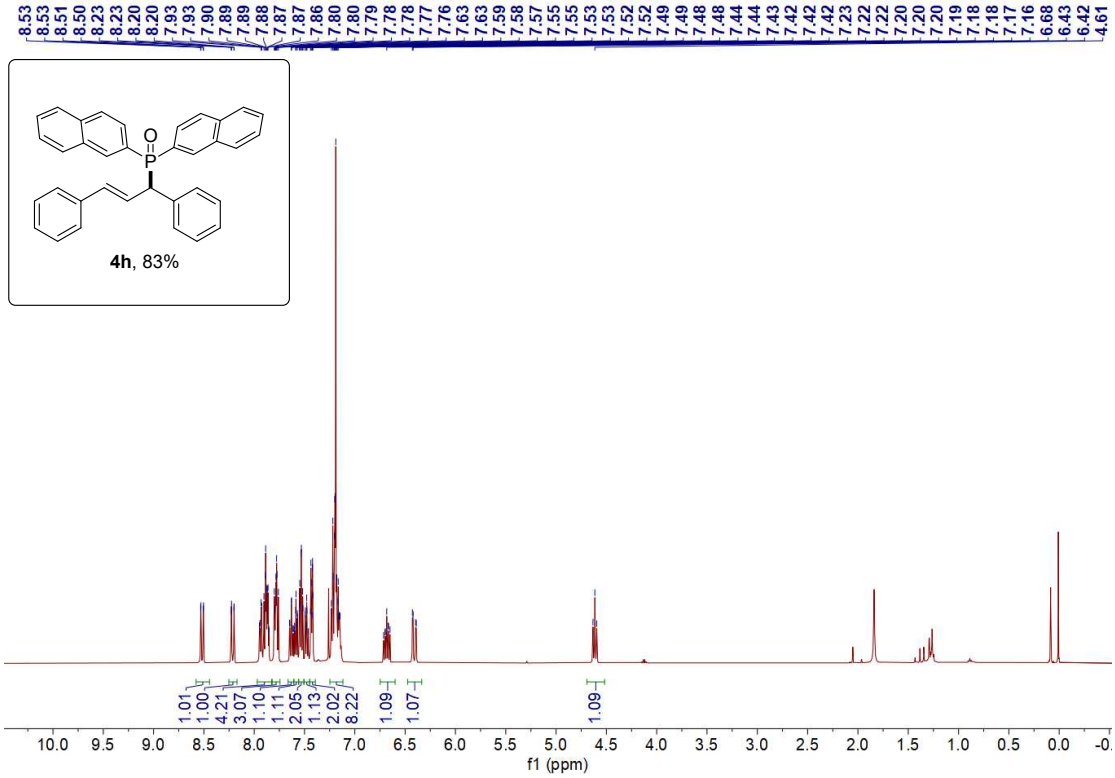


^{31}P NMR (202 MHz, Chloroform-d)

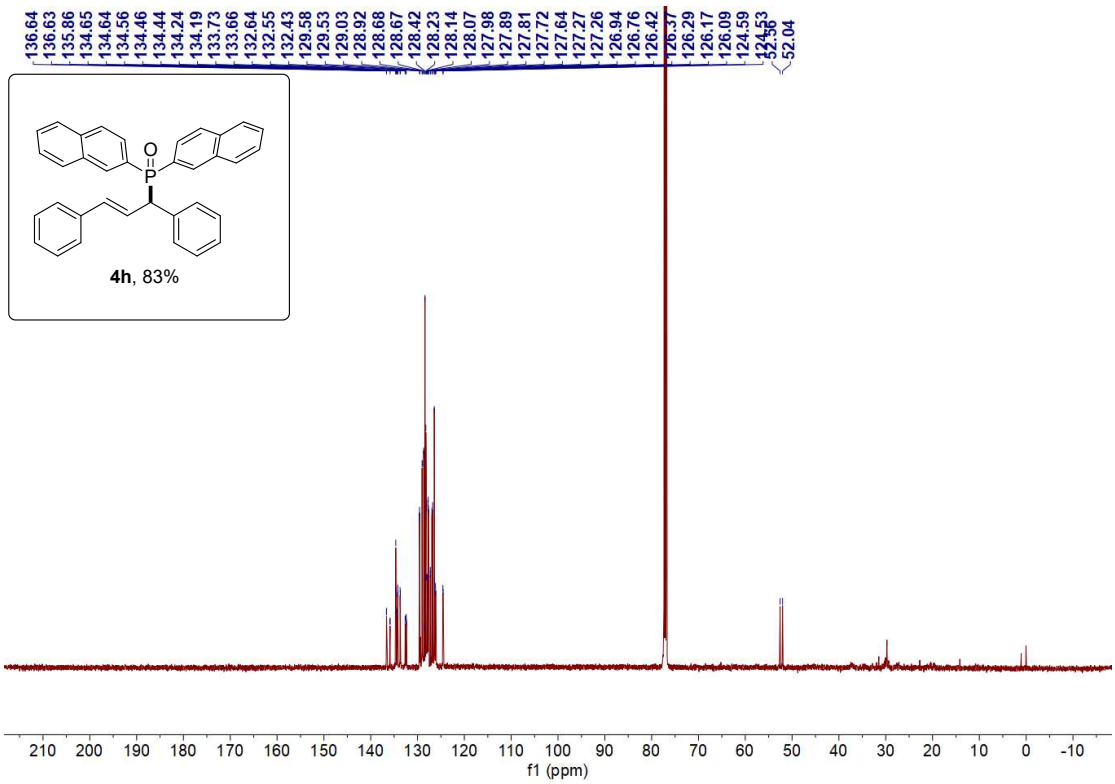


(E)-(1,3-diphenylallyl)di(naphthalen-2-yl)phosphine oxide (4h)

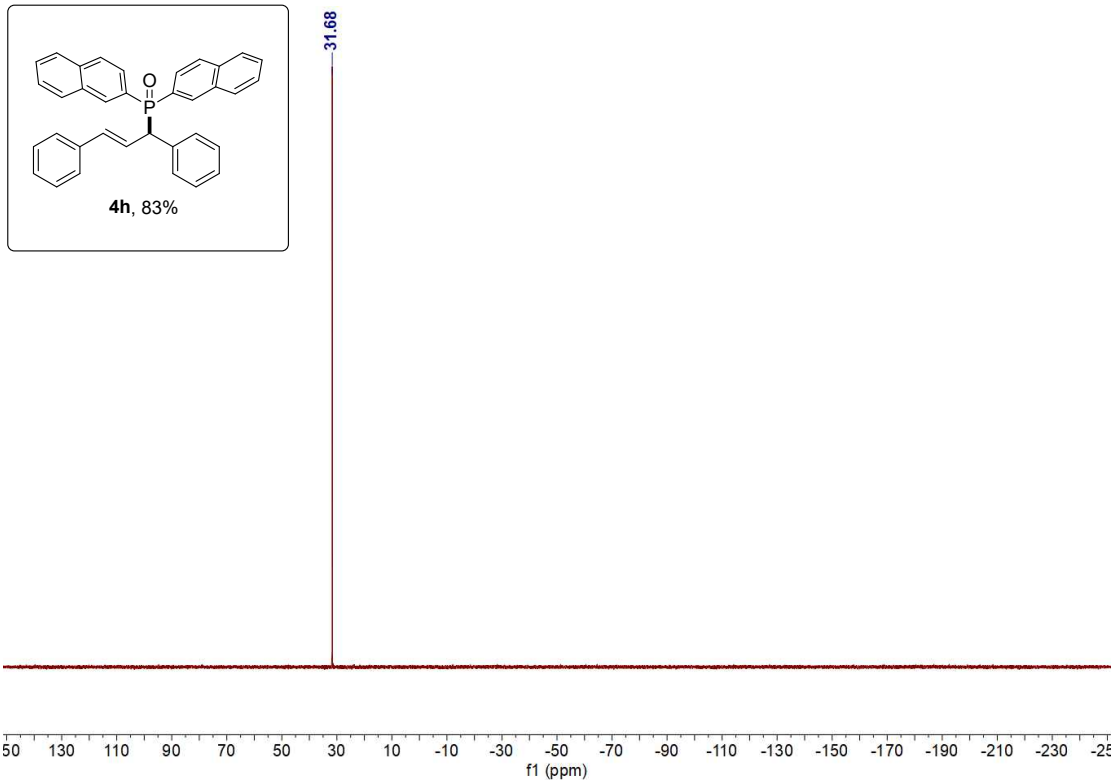
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

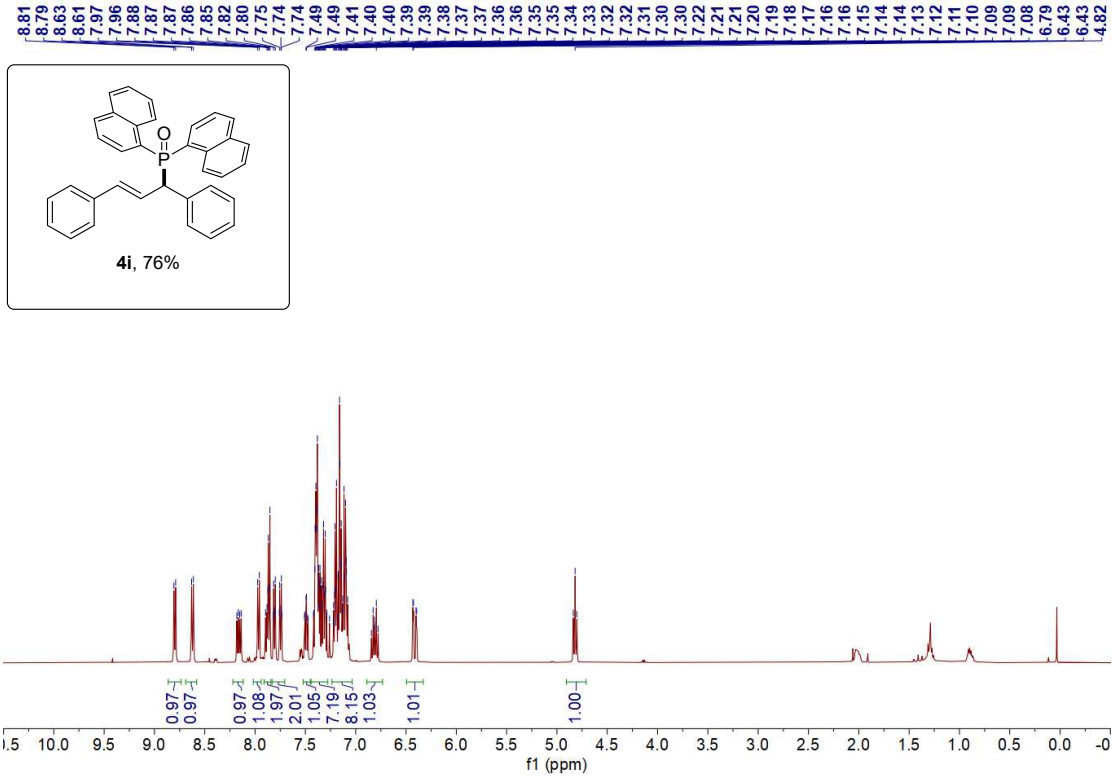


^{31}P NMR (202 MHz, Chloroform-d)

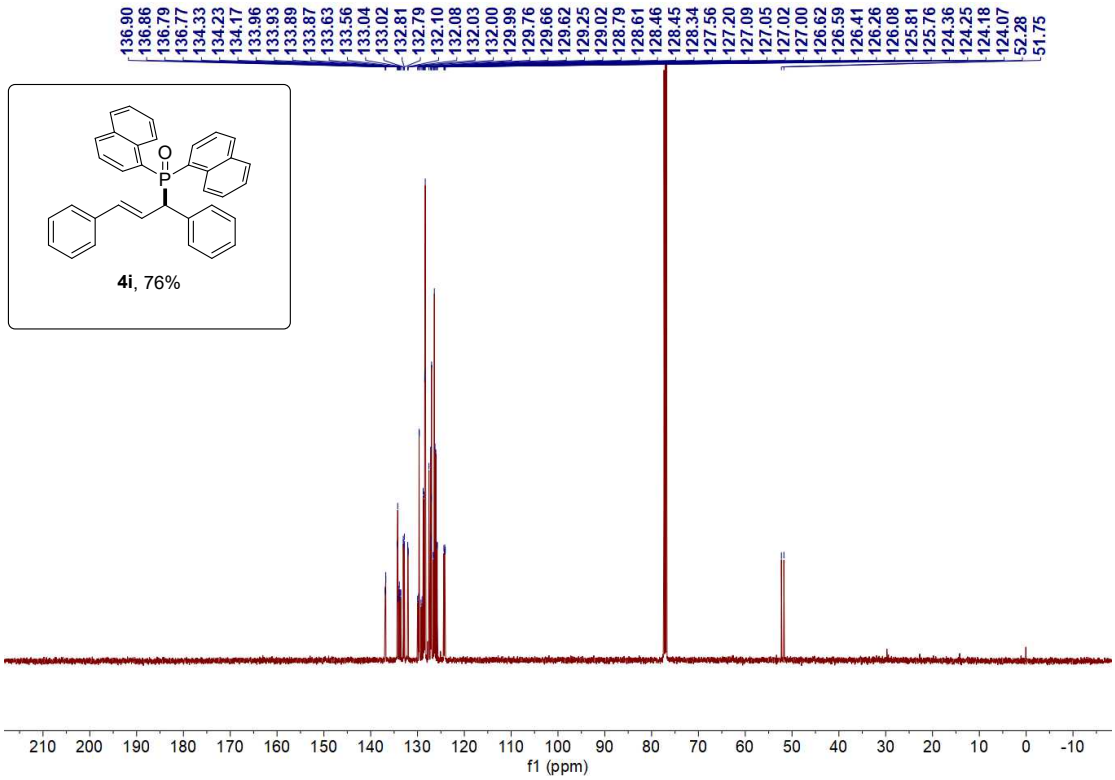


(E)-(1,3-diphenylallyl)di(naphthalen-1-yl)phosphine oxide (4i)

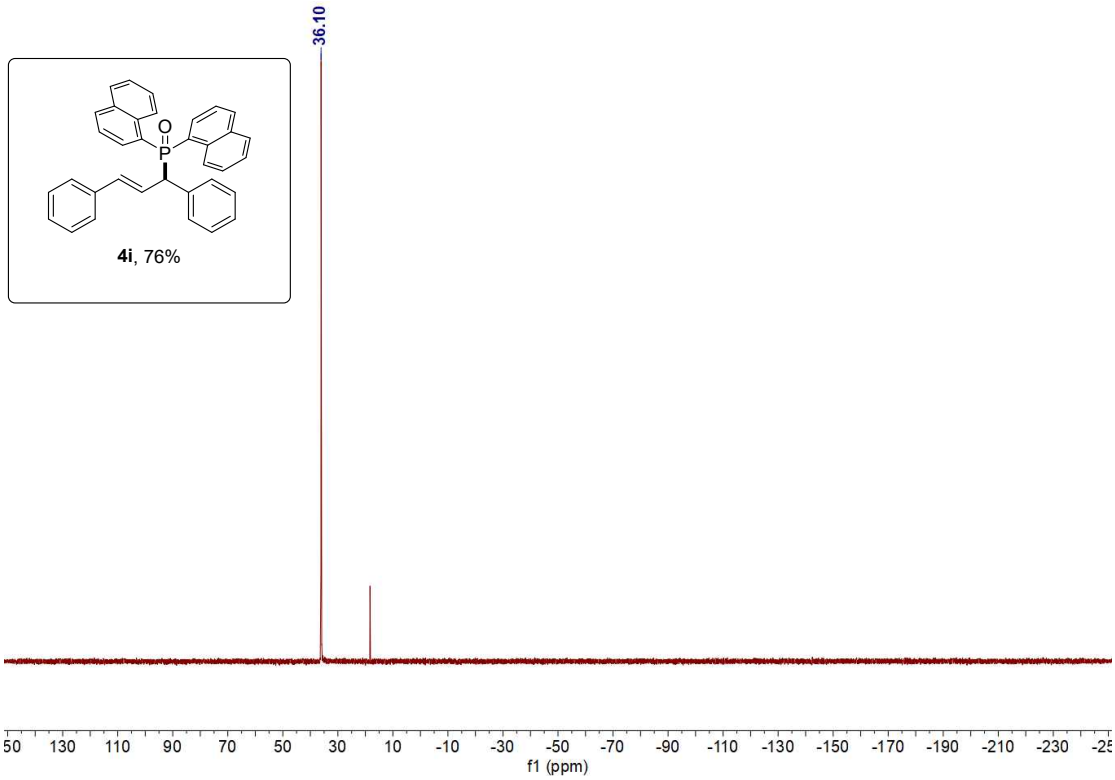
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

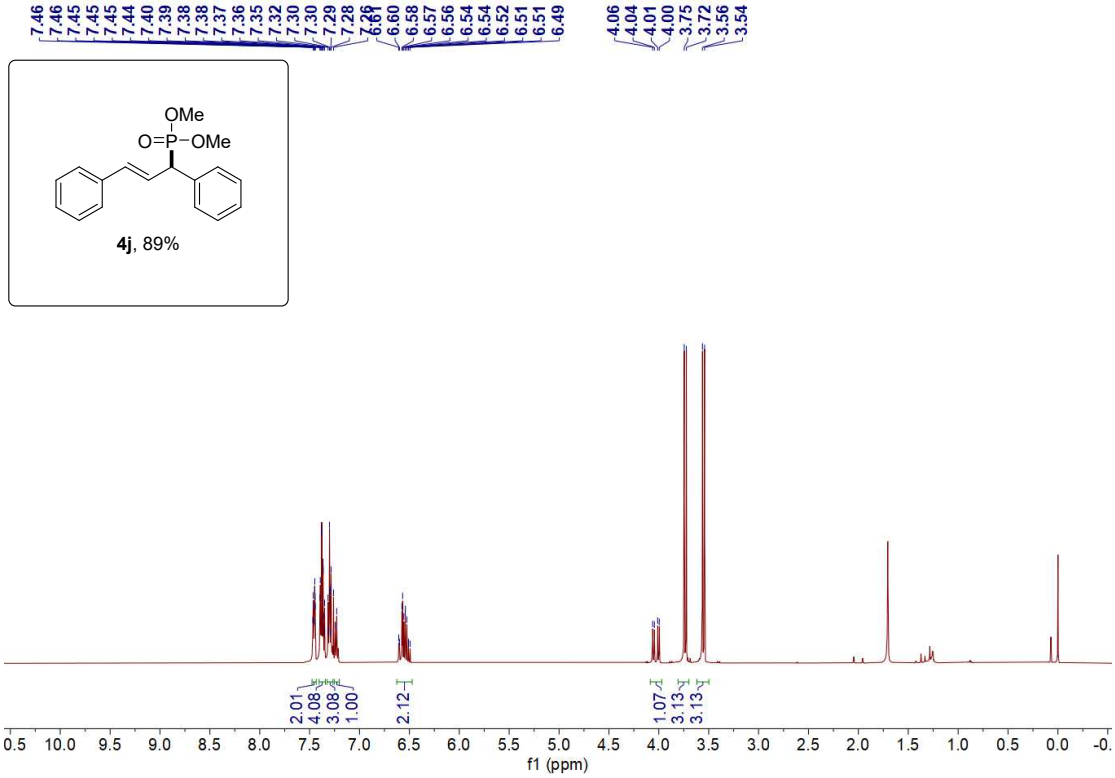


^{31}P NMR (202 MHz, Chloroform-d)

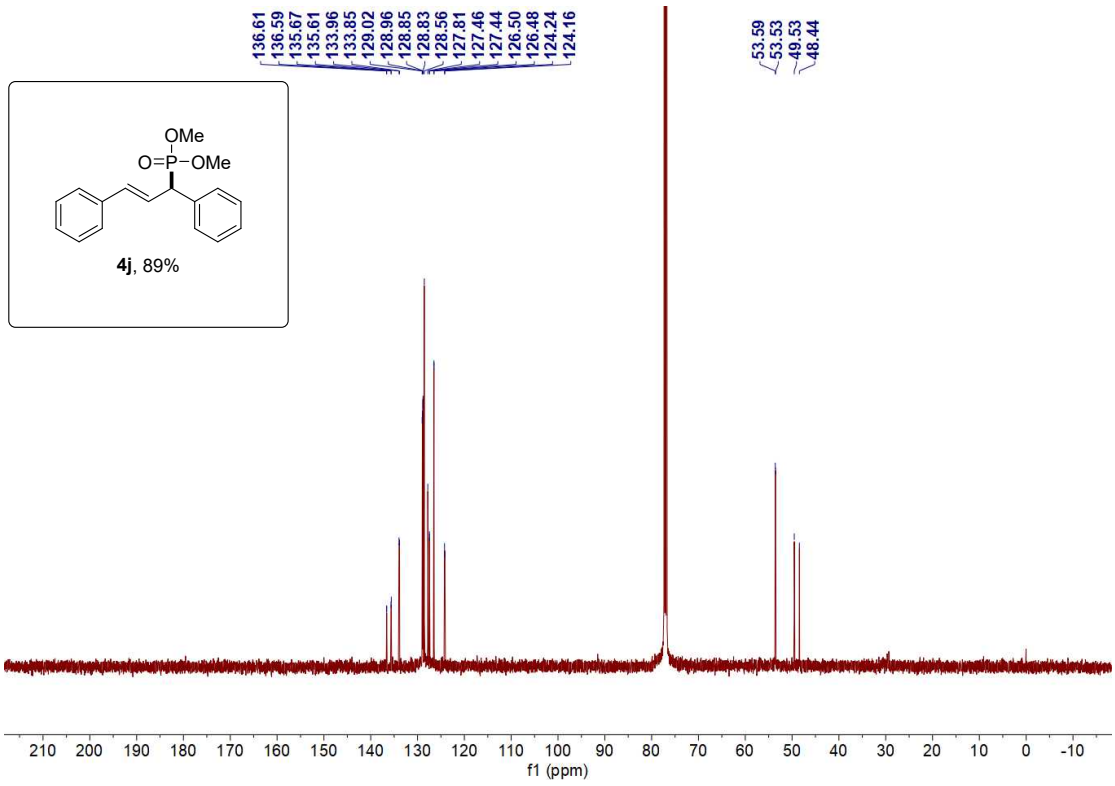


dimethyl (E)-(1,3-diphenylallyl)phosphonate (4j)

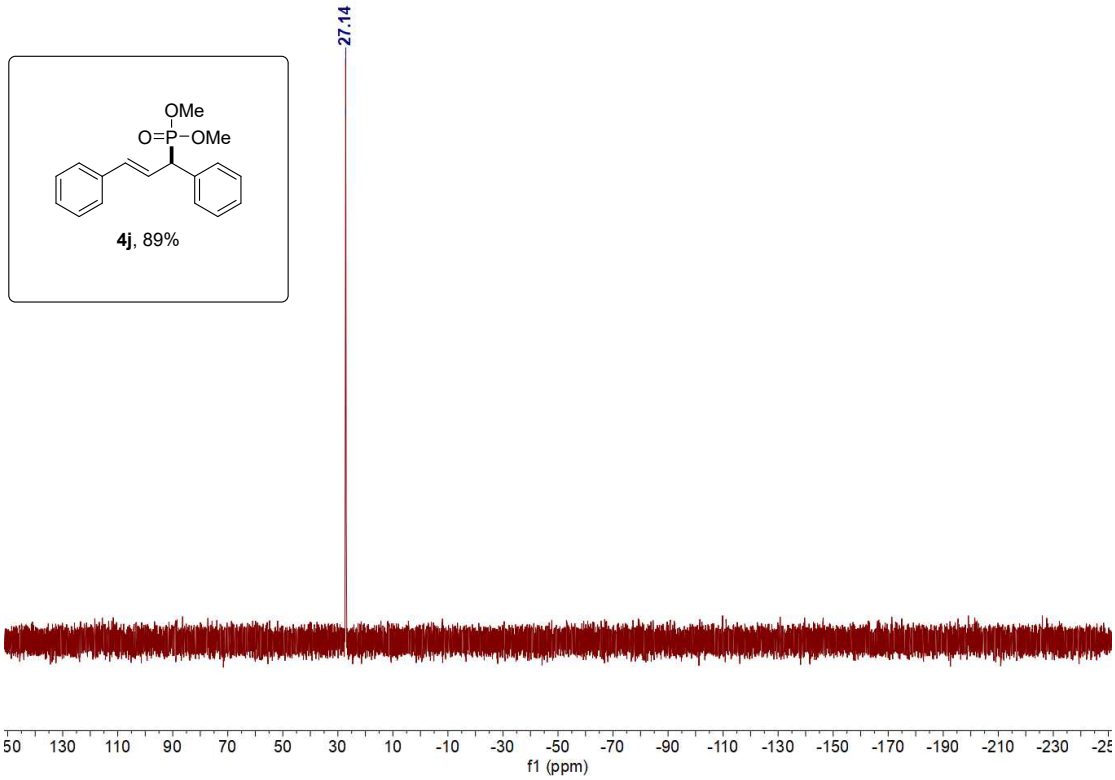
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

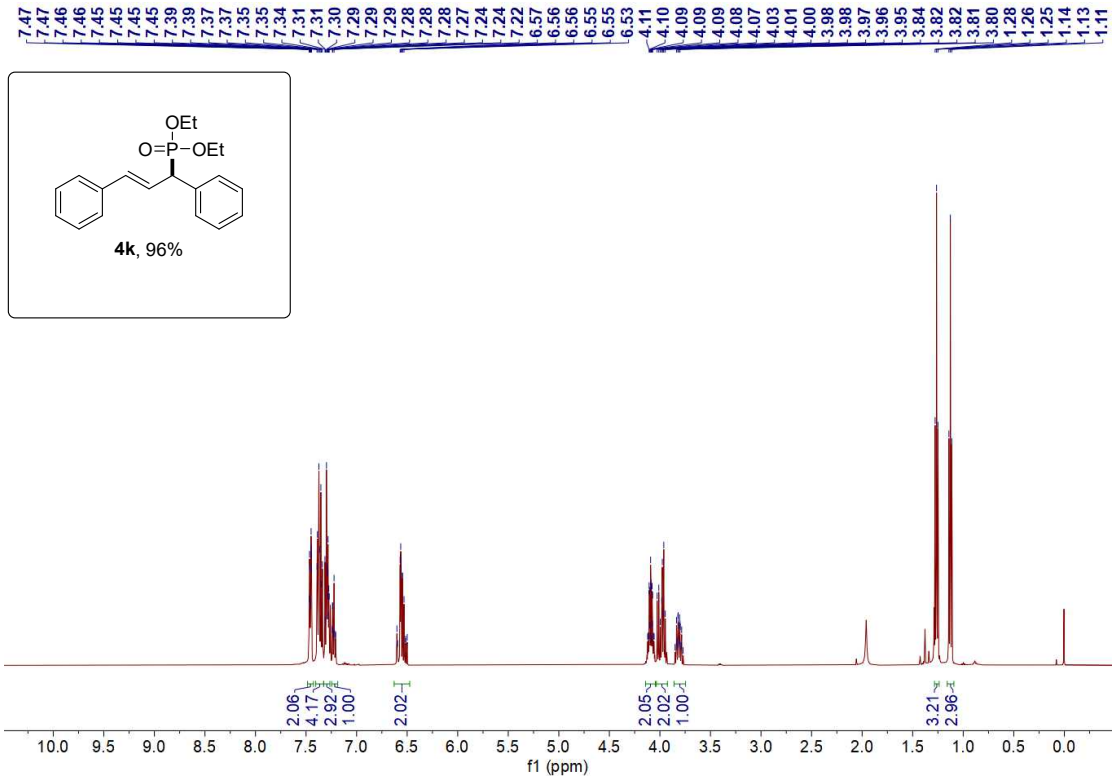


^{31}P NMR (202 MHz, Chloroform-d)

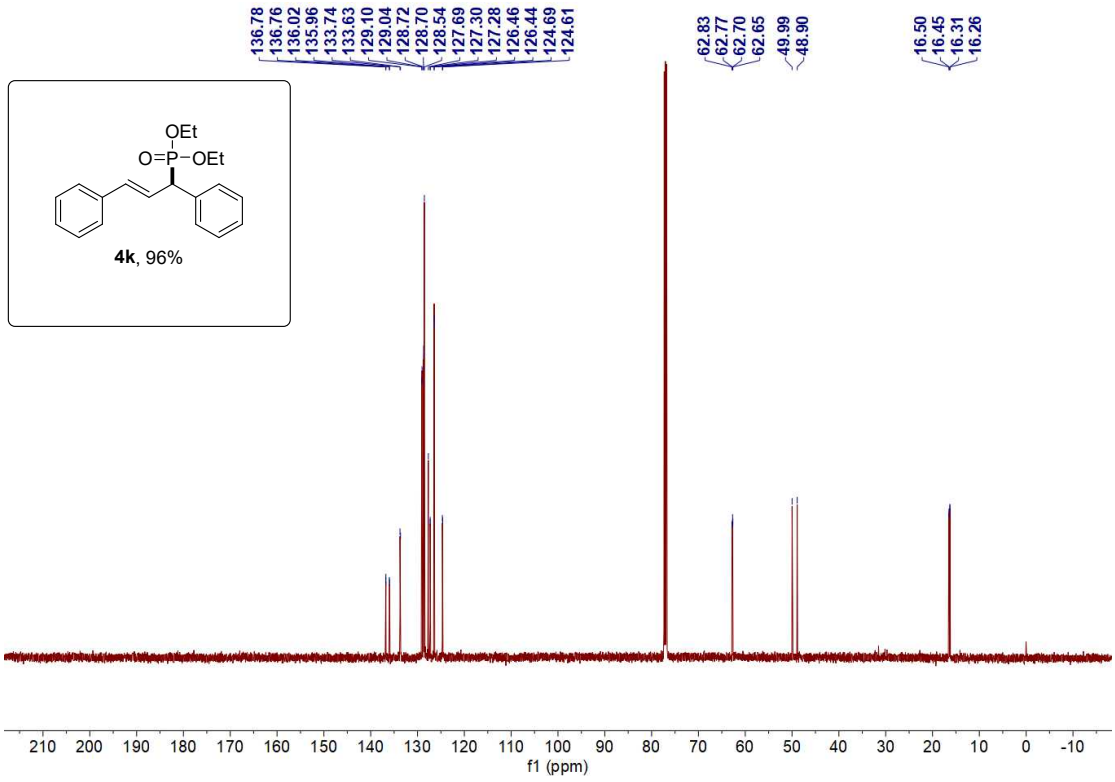

27.14
OMe
O=P–OMe
4j, 89%
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

diethyl (E)-(1,3-diphenylallyl)phosphonate (4k)

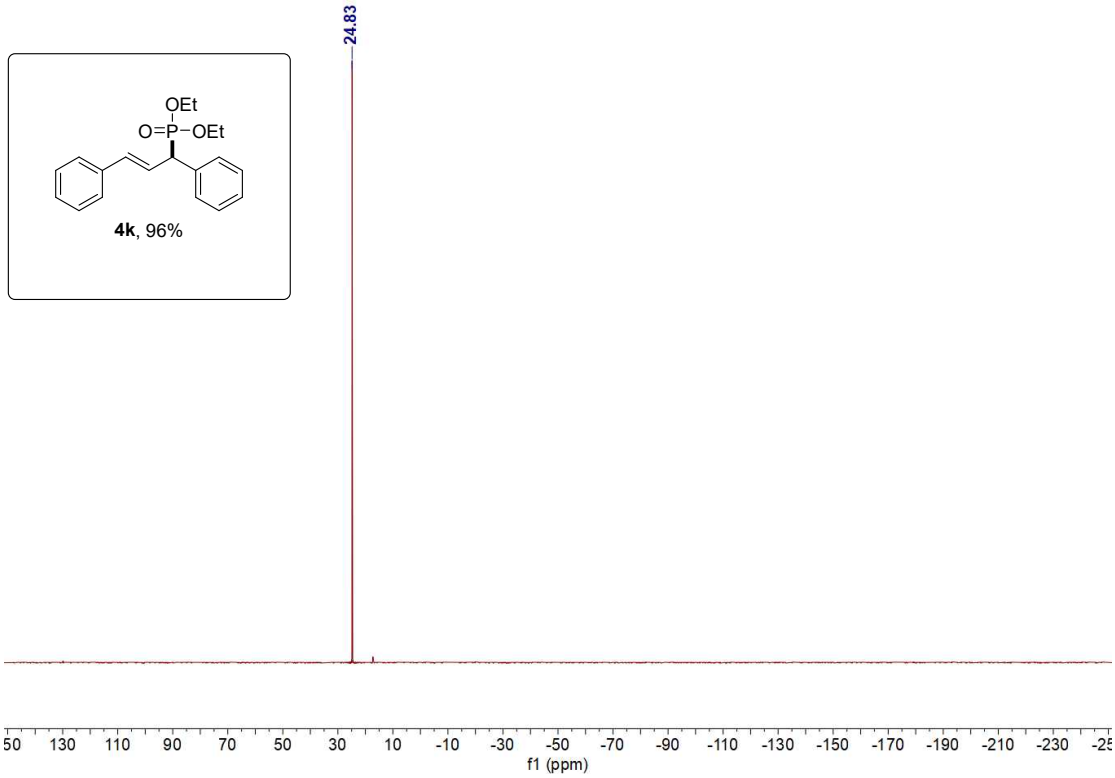
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

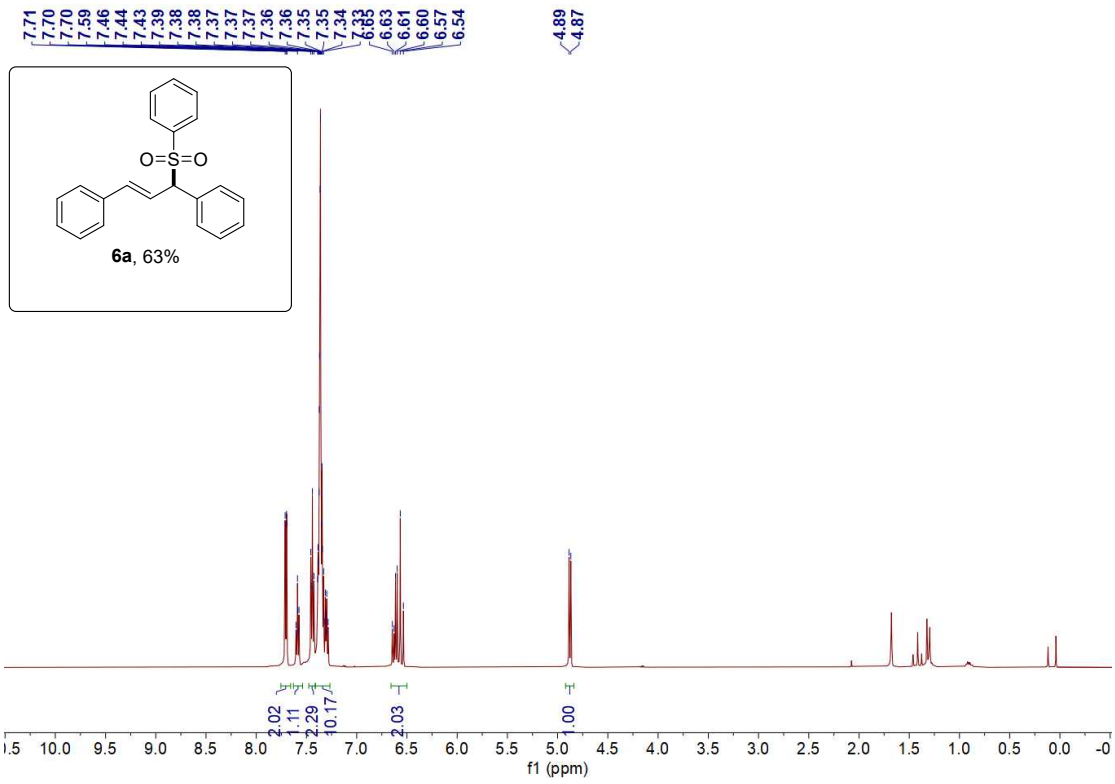


^{31}P NMR (202 MHz, Chloroform-d)

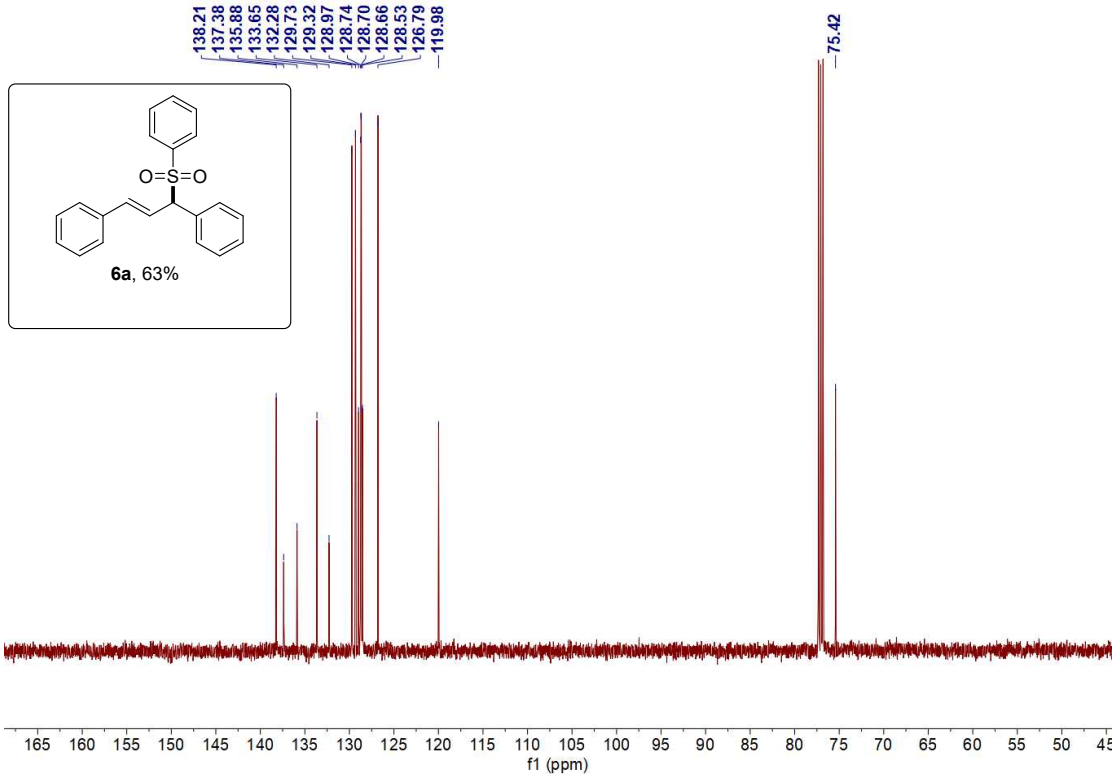


(E)-(3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6a)

^{1}H NMR (500 MHz, Chloroform-d)

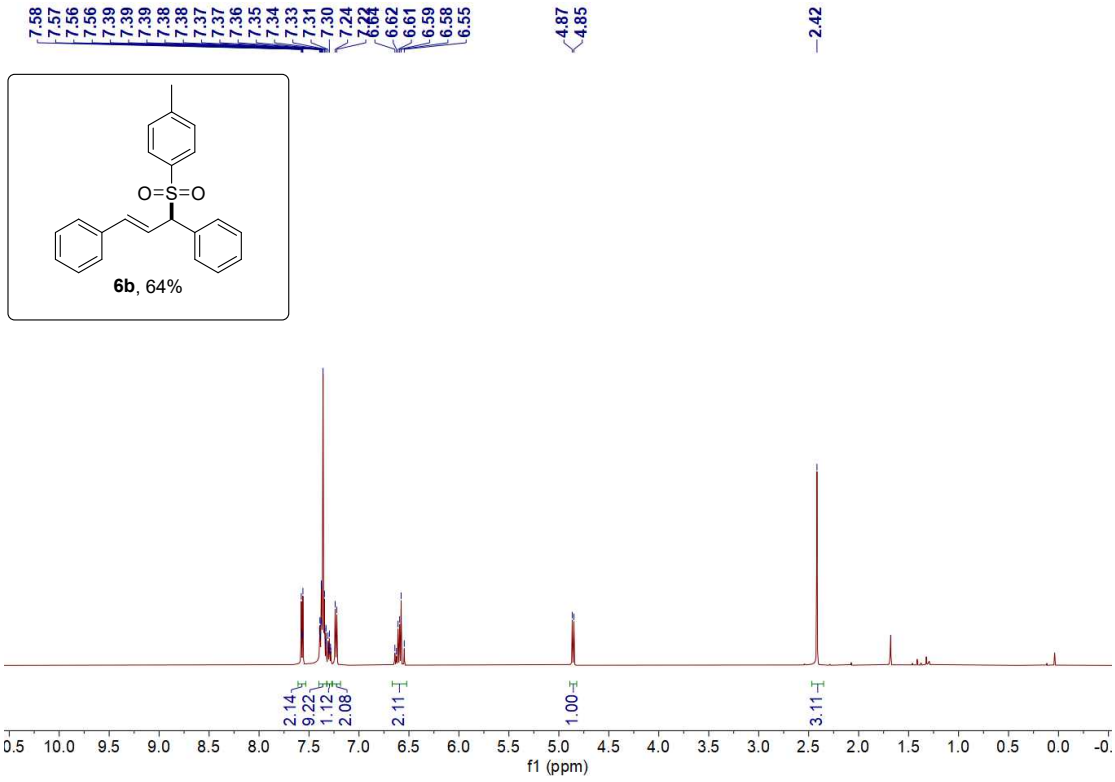


^{13}C NMR (126 MHz, Chloroform-d)

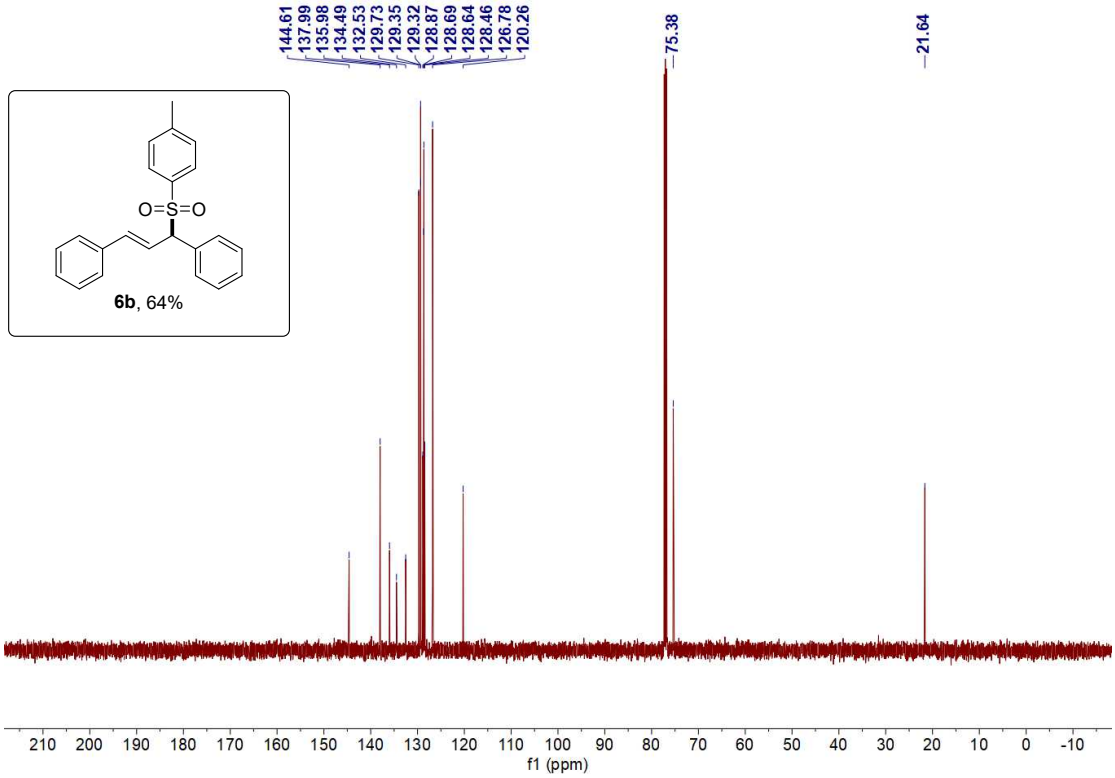


(E)-(3-tosylprop-1-ene-1,3-diyl)dibenzene (6b)

^{1}H NMR (500 MHz, Chloroform-d)

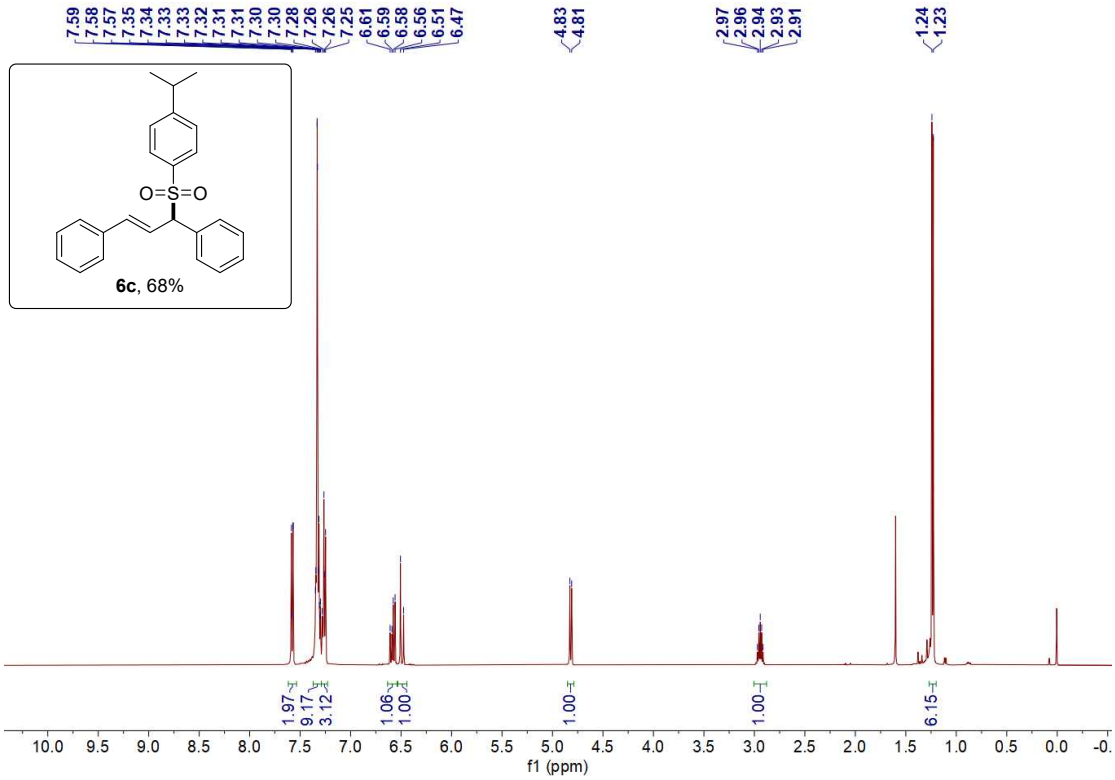


^{13}C NMR (126 MHz, Chloroform-d)

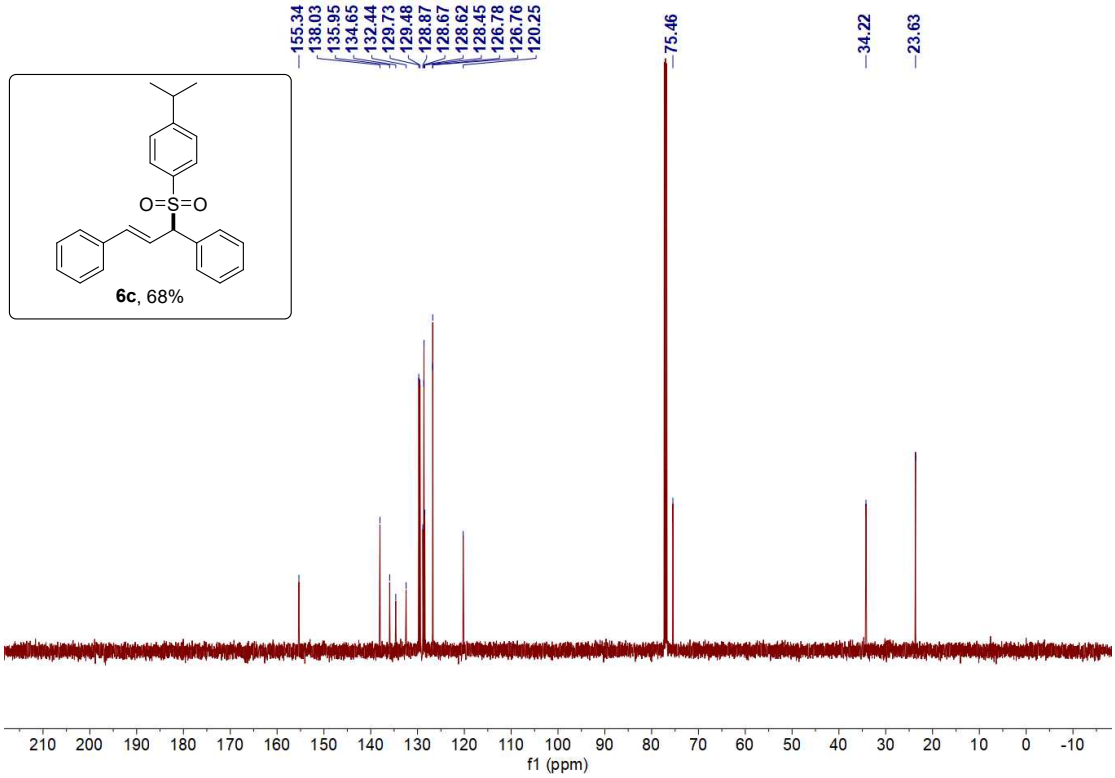


(E)-(3-((4-isopropylphenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6c)

^{1}H NMR (500 MHz, Chloroform-d)

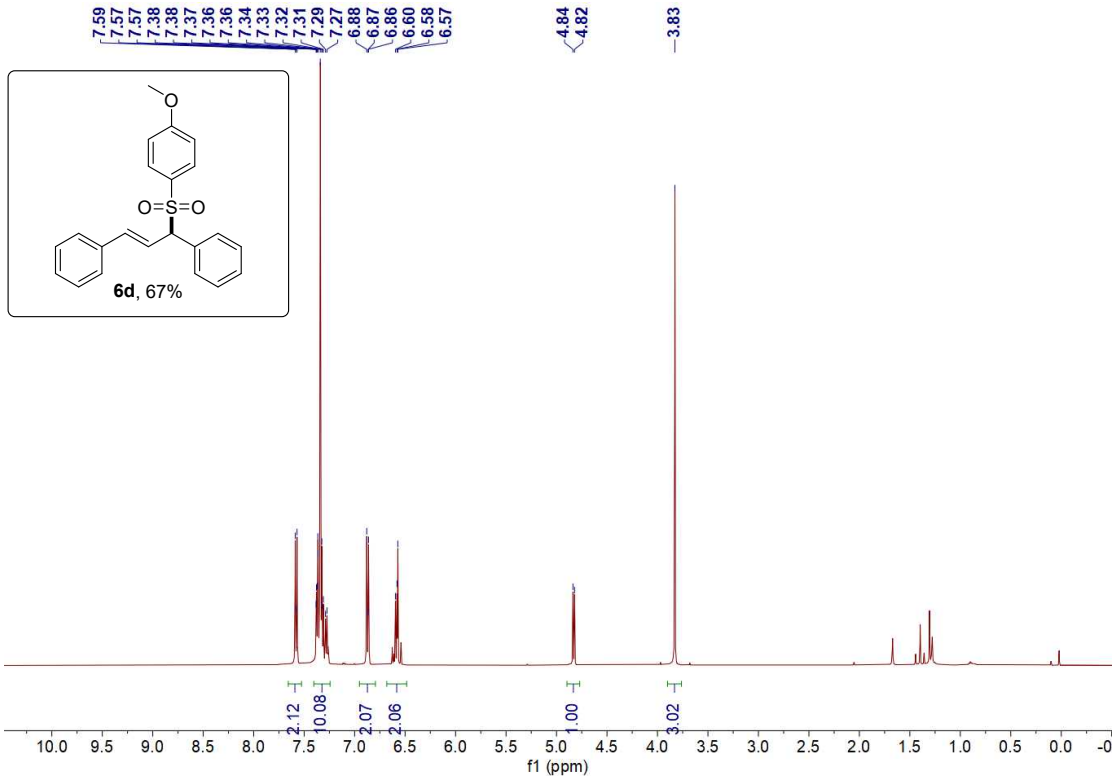


^{13}C NMR (126 MHz, Chloroform-d)

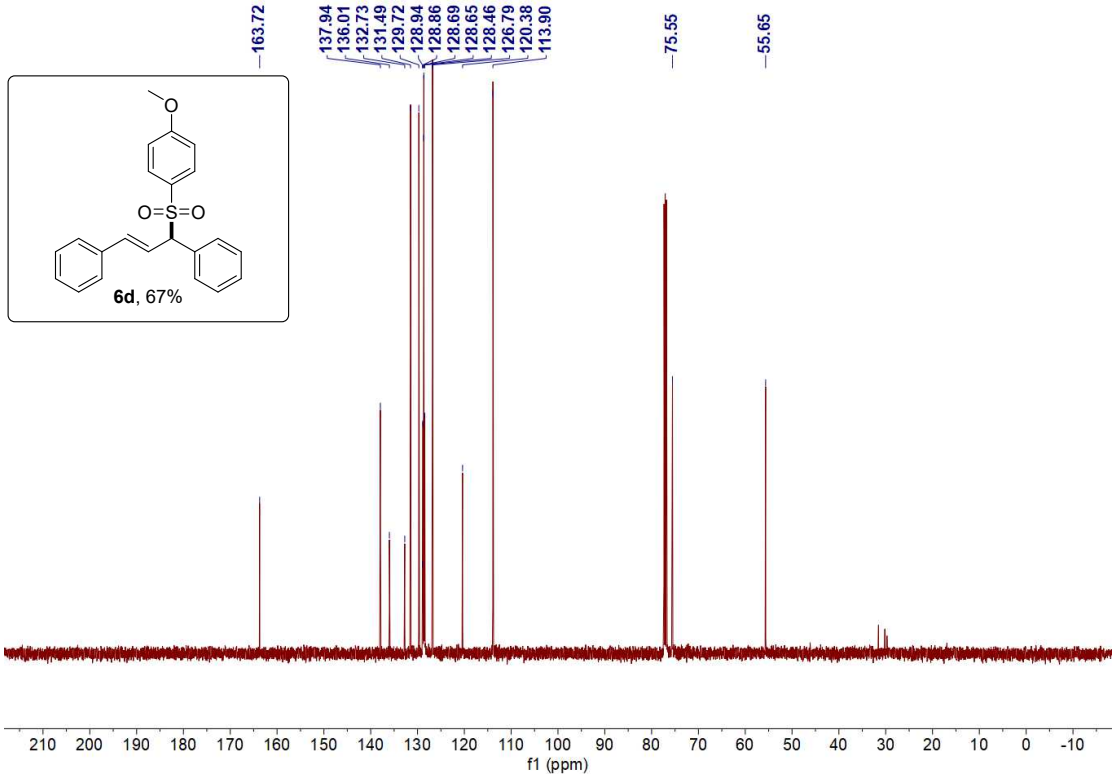


(E)-(3-((4-methoxyphenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6d)

^{1}H NMR (500 MHz, Chloroform-d)

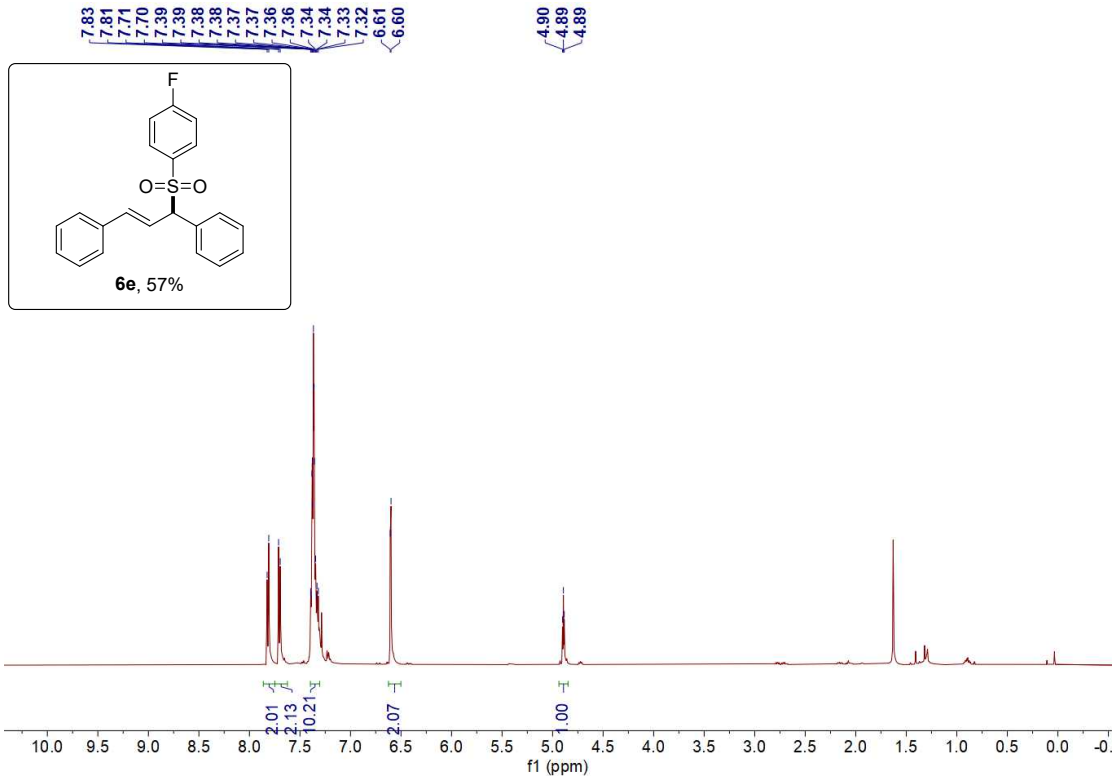


^{13}C NMR (126 MHz, Chloroform-d)

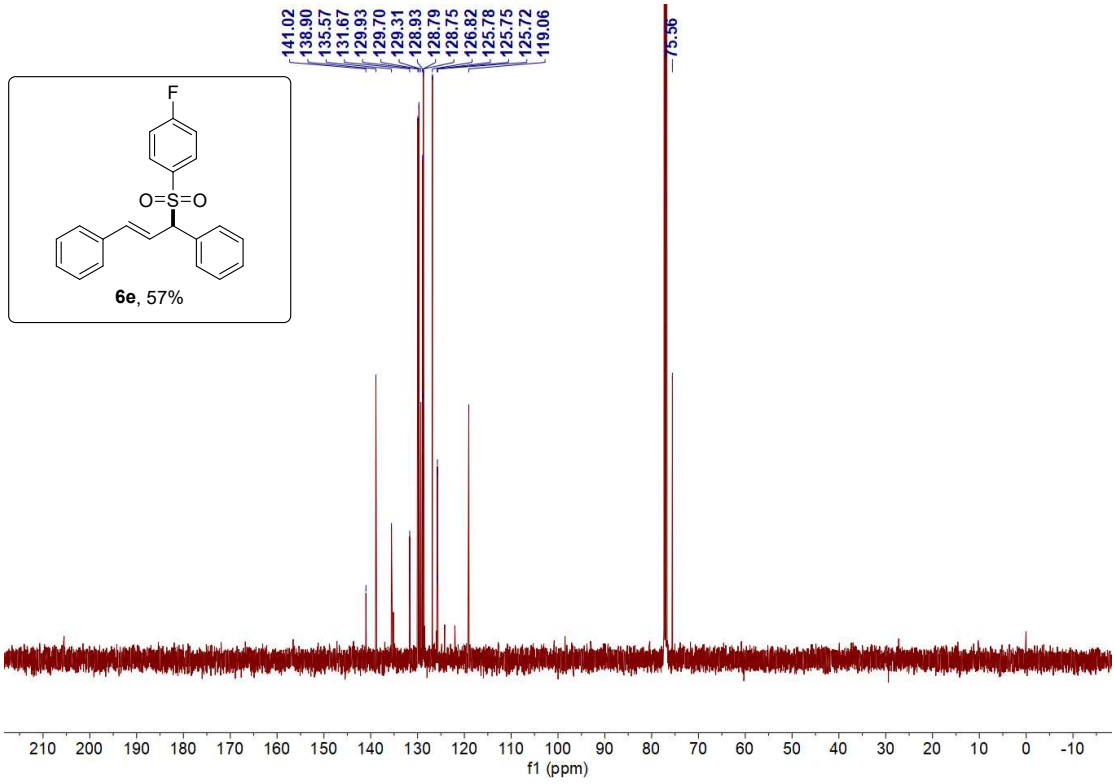


(E)-(3-((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6e)

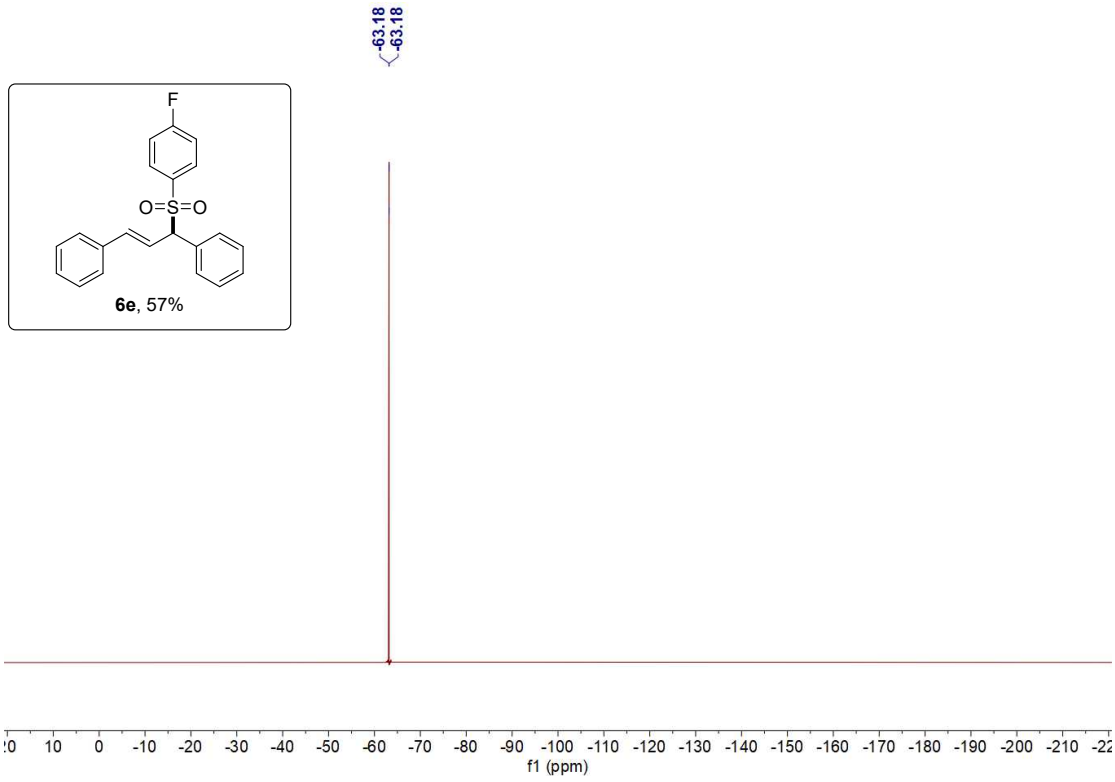
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

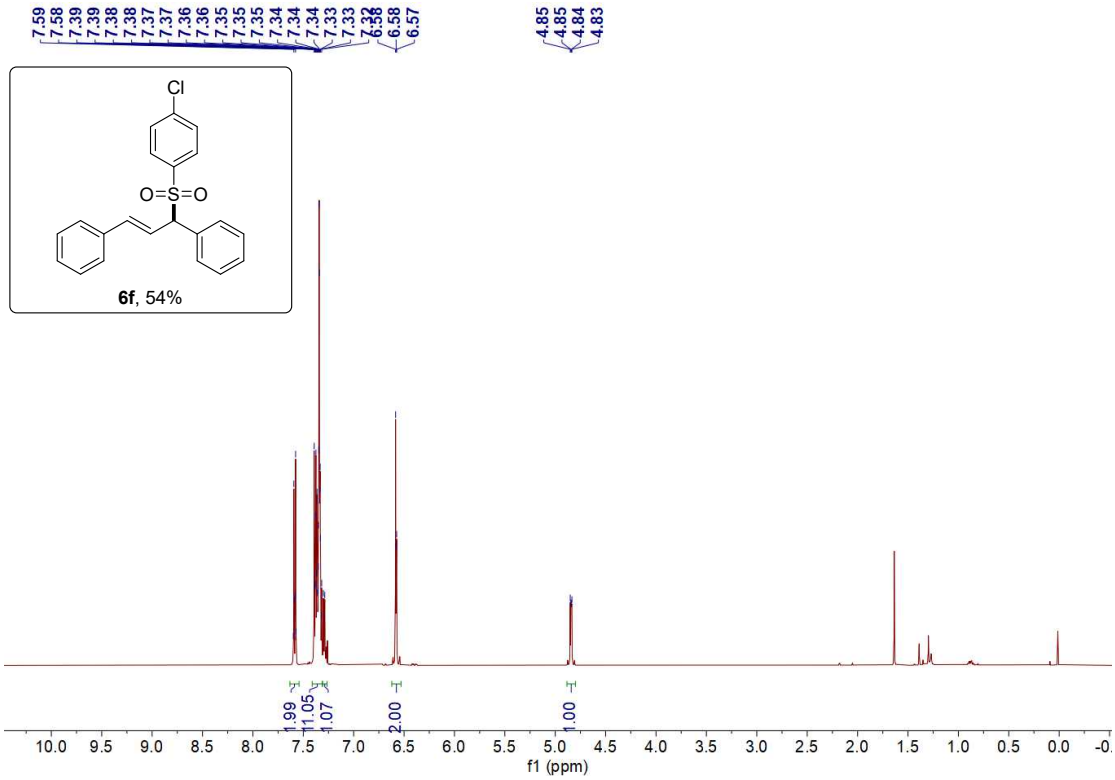


^{19}F NMR (471 MHz, Chloroform-d)

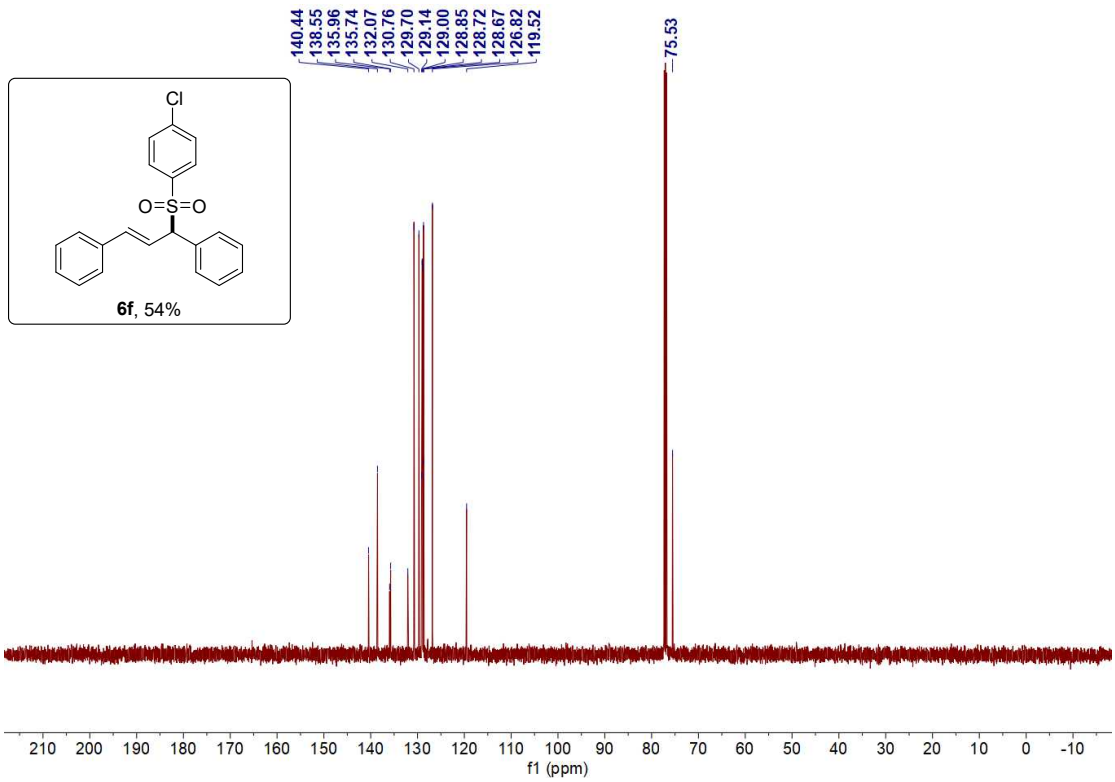


(E)-(3-((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6f)

^{1}H NMR (500 MHz, Chloroform-d)

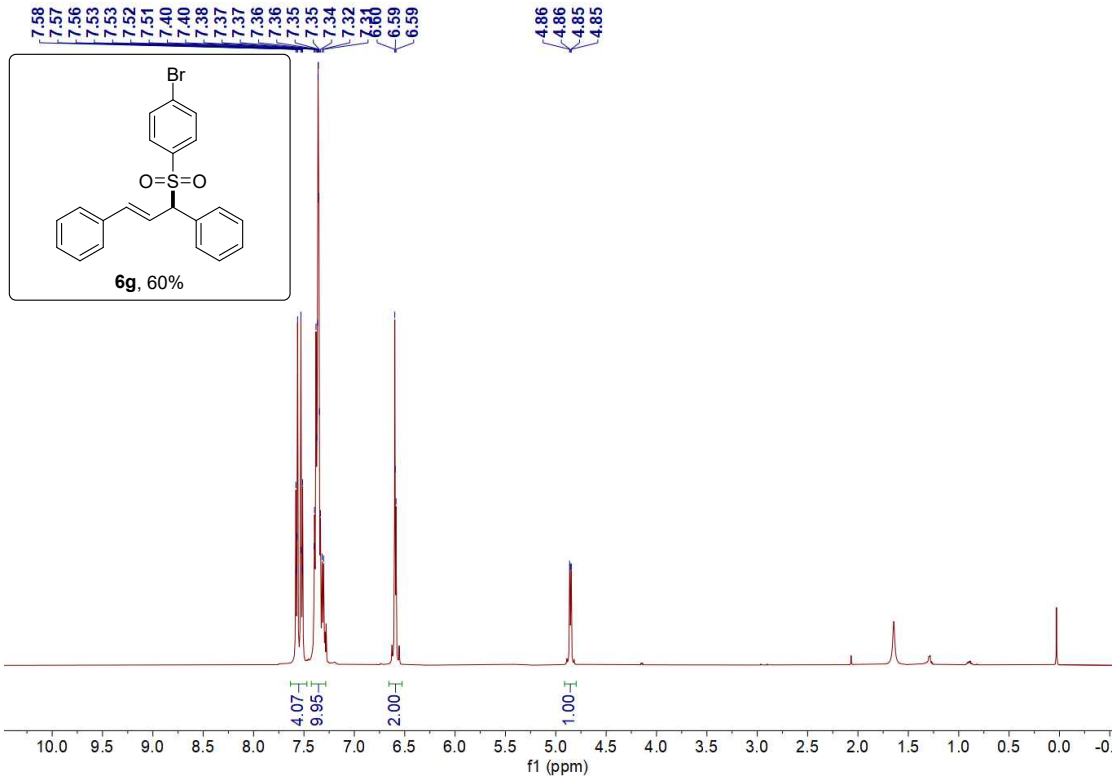


^{13}C NMR (126 MHz, Chloroform-d)

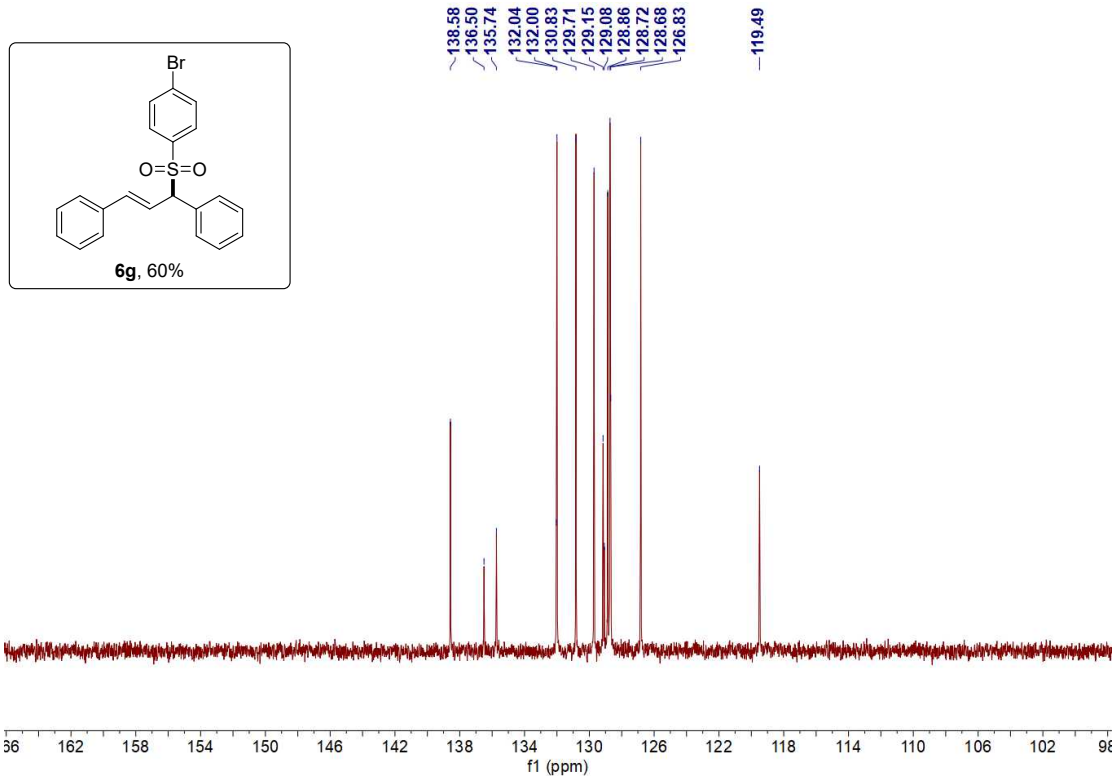


(E)-(3-((4-bromophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6g)

^{1}H NMR (500 MHz, Chloroform-d)

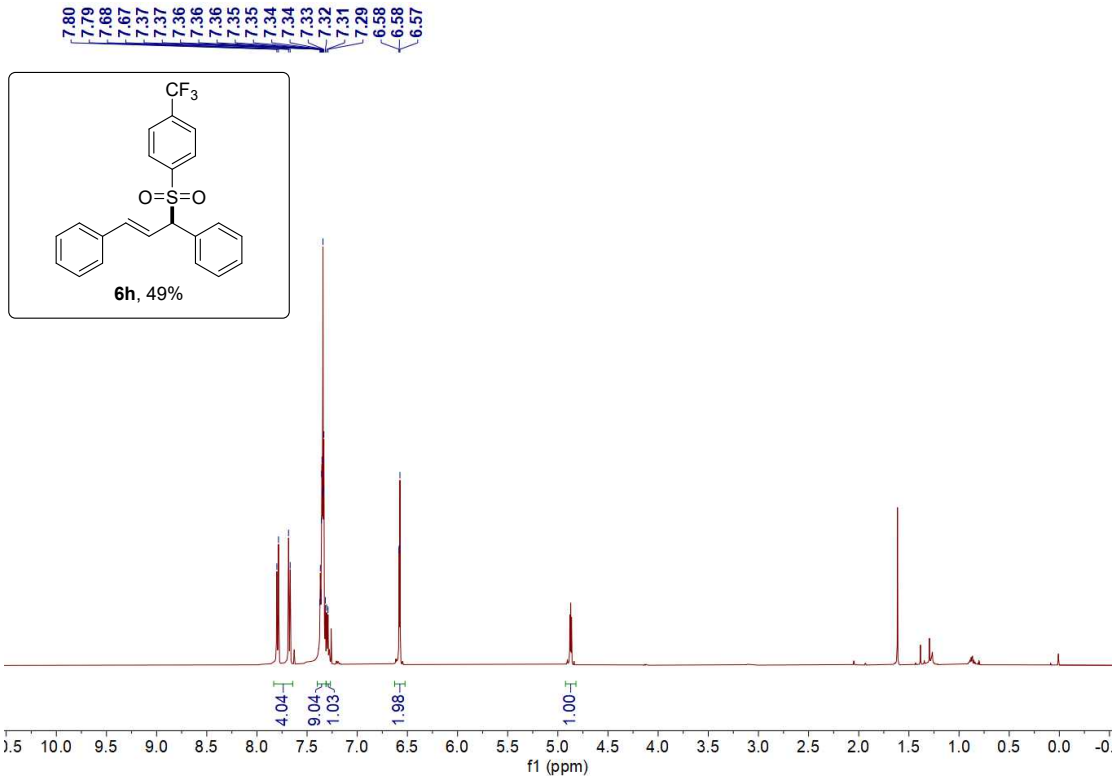


^{13}C NMR (126 MHz, Chloroform-d)

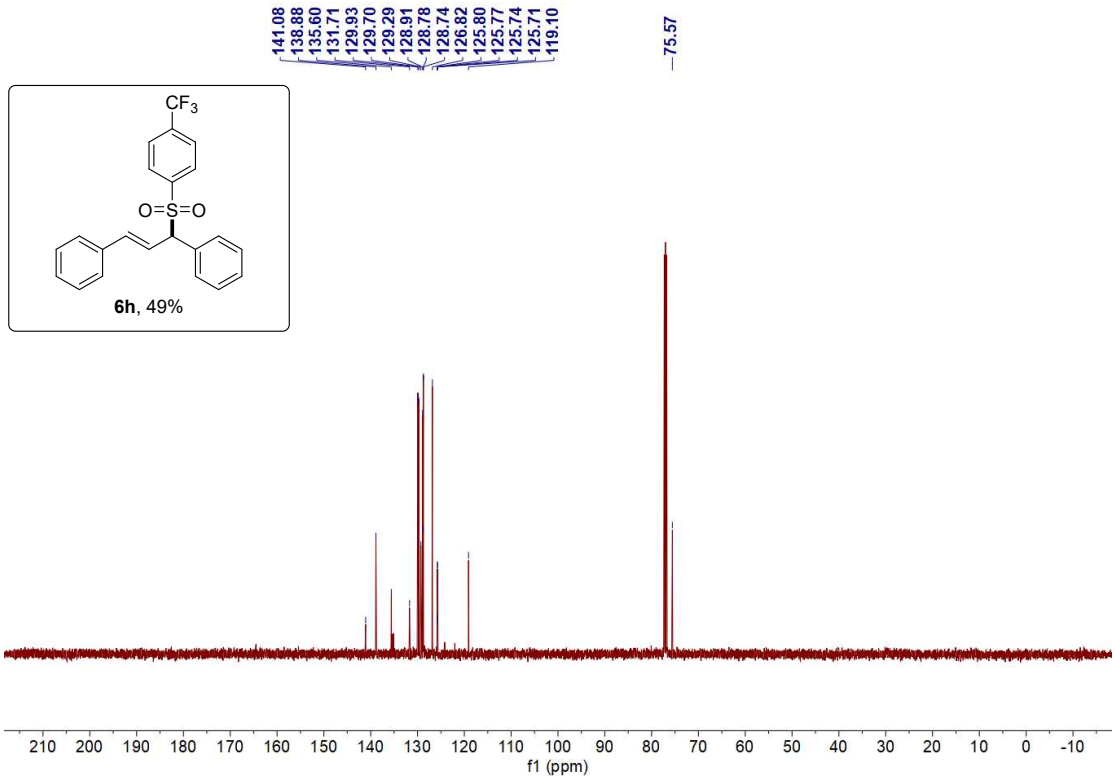


(E)-(3-((4-(trifluoromethyl)phenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6h)

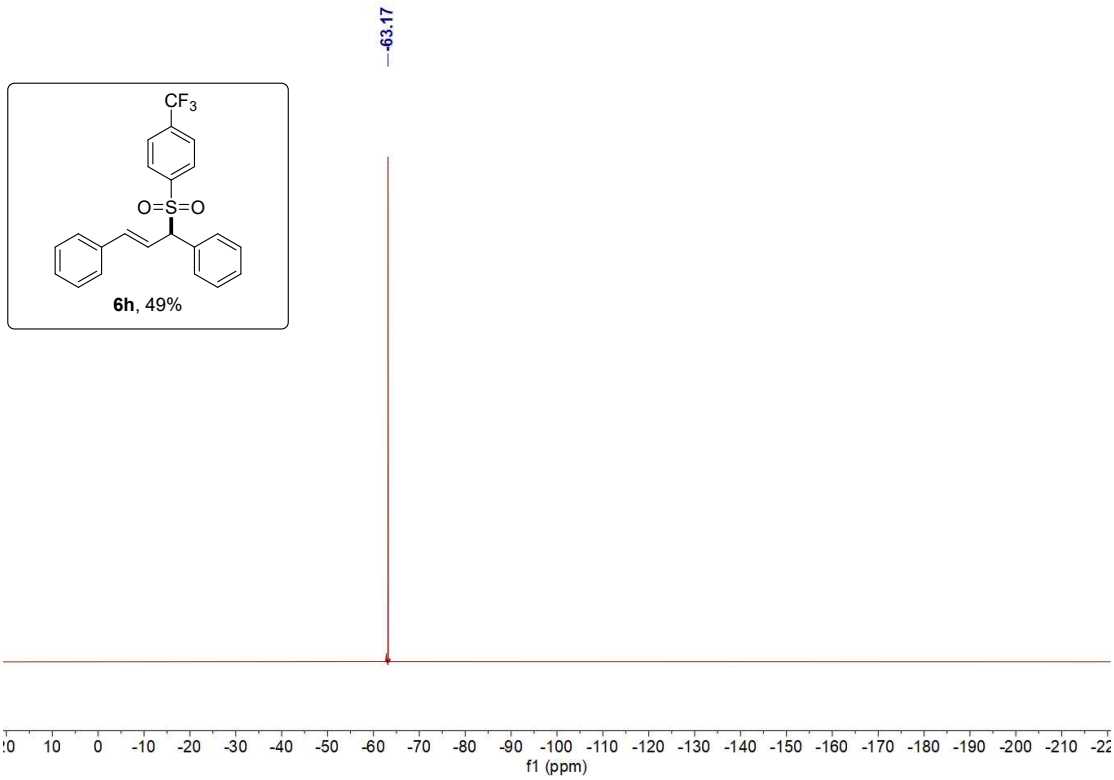
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

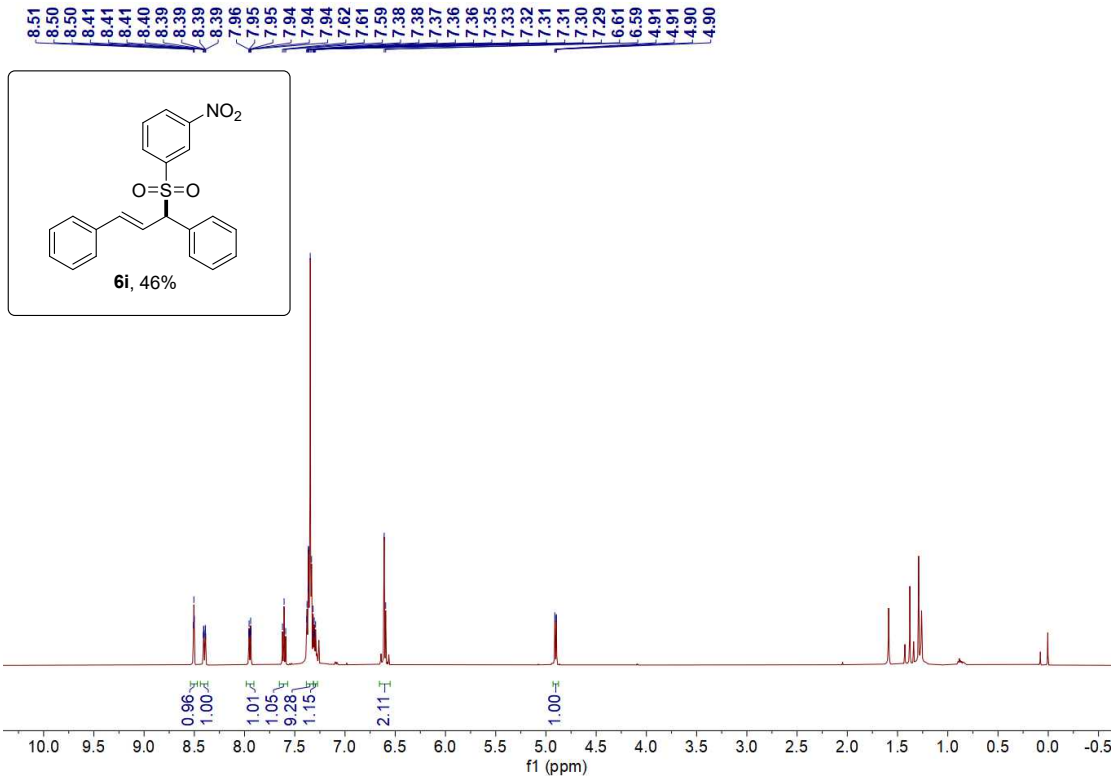


^{19}F NMR (471 MHz, Chloroform-d)

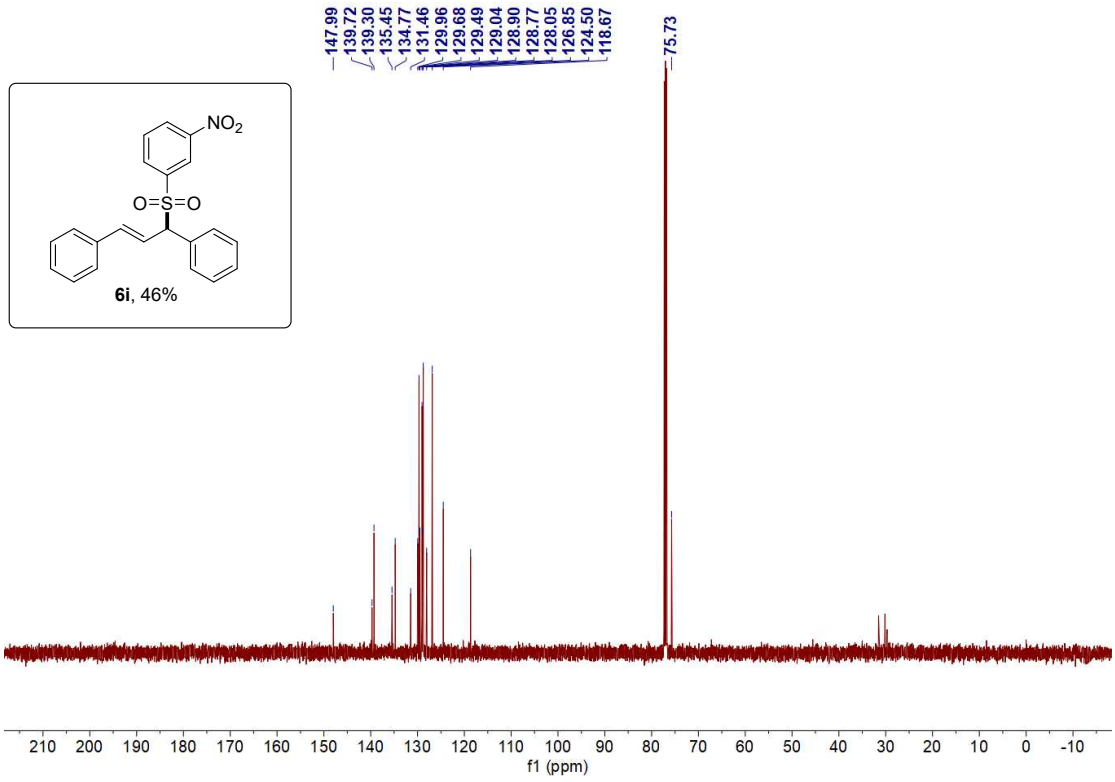


(E)-(3-((3-nitrophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6i)

^{1}H NMR (500 MHz, Chloroform-d)

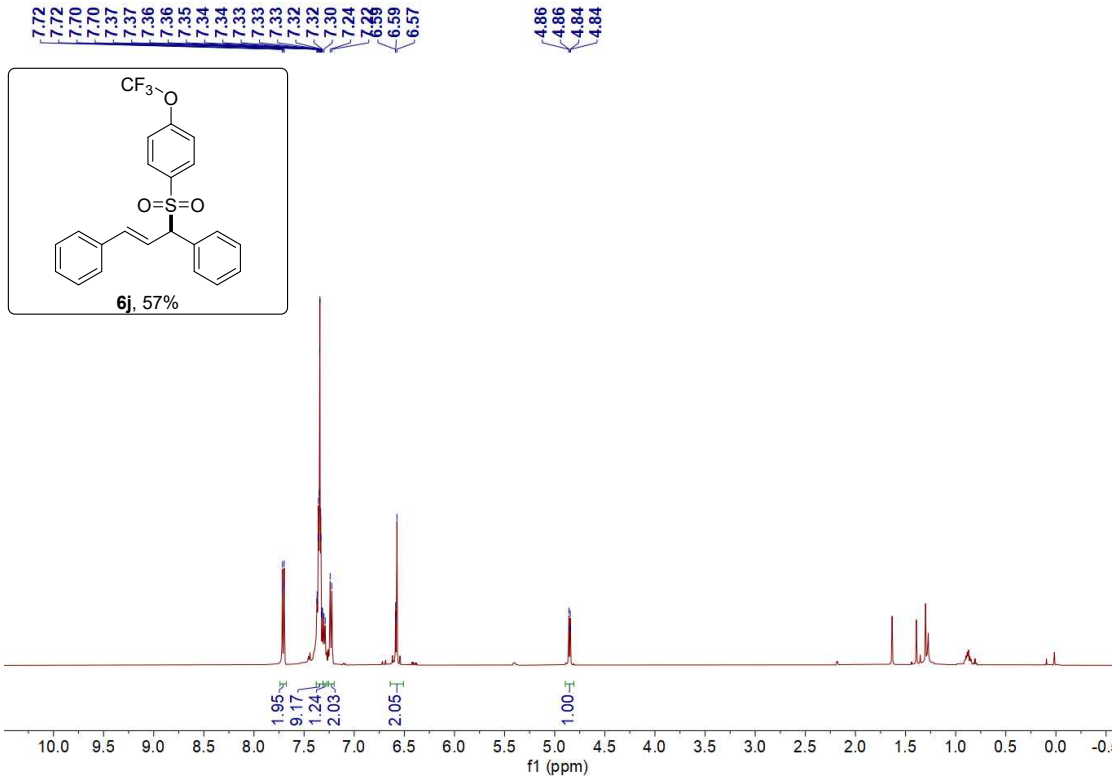


^{13}C NMR (126 MHz, Chloroform-d)

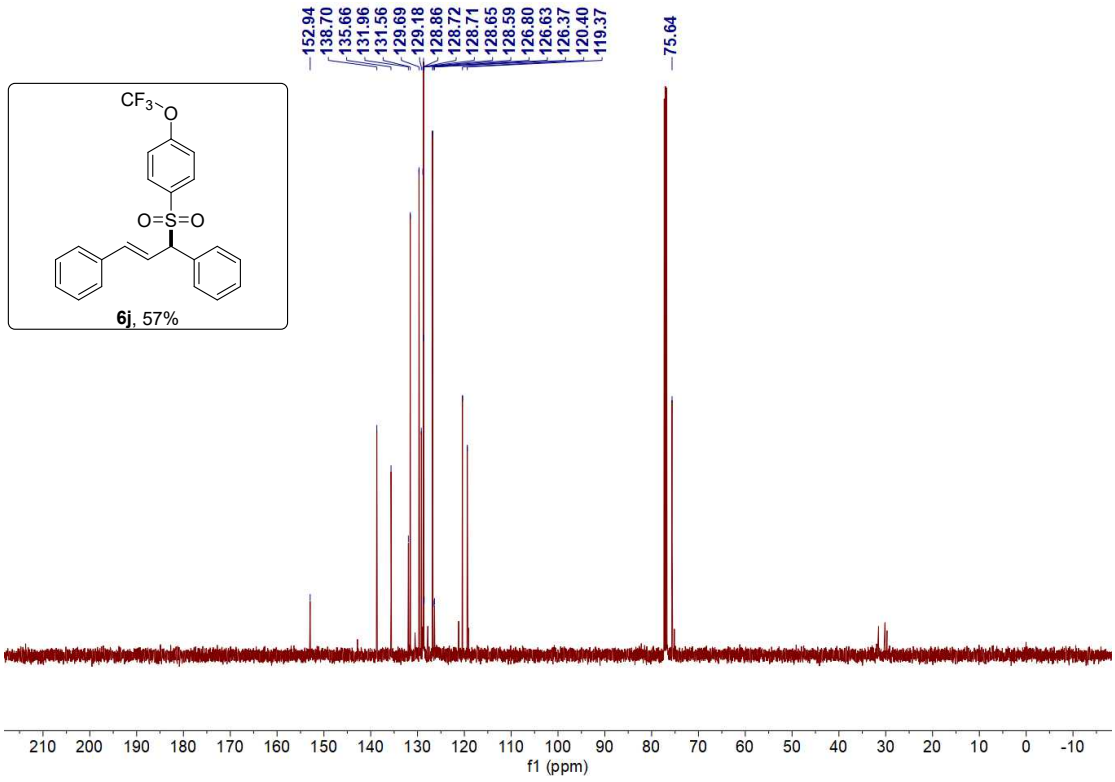


(E)-(3-((4-(trifluoromethoxy)phenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (6j)

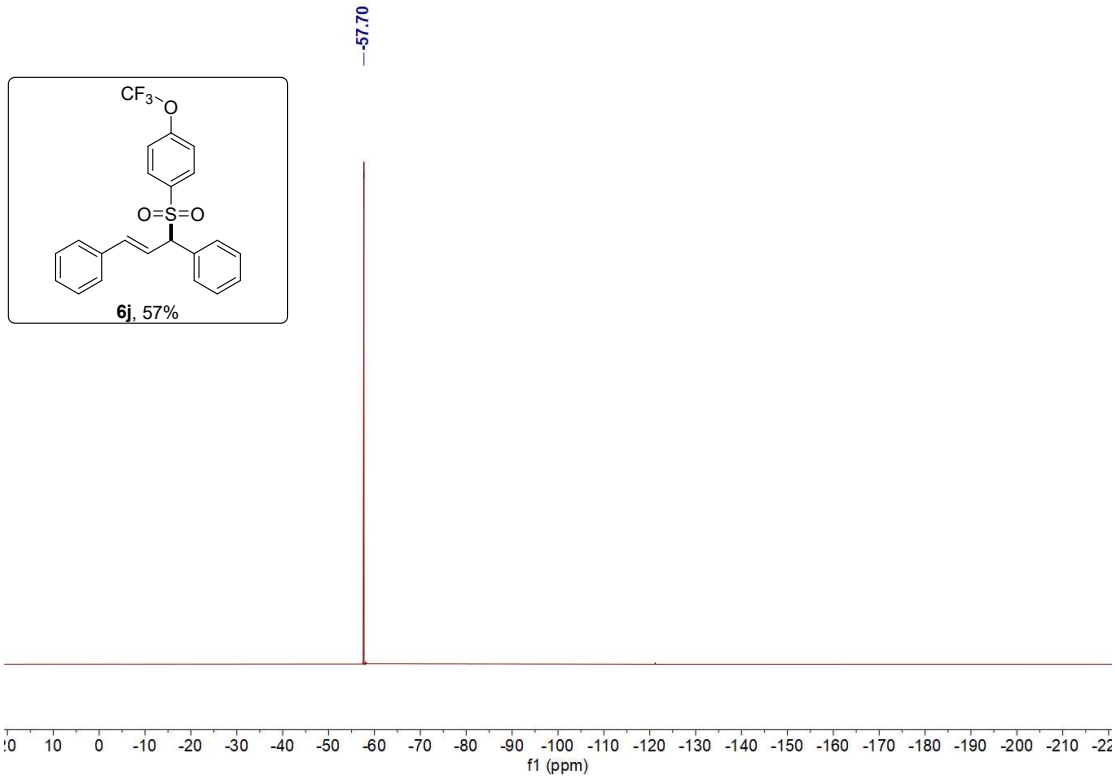
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

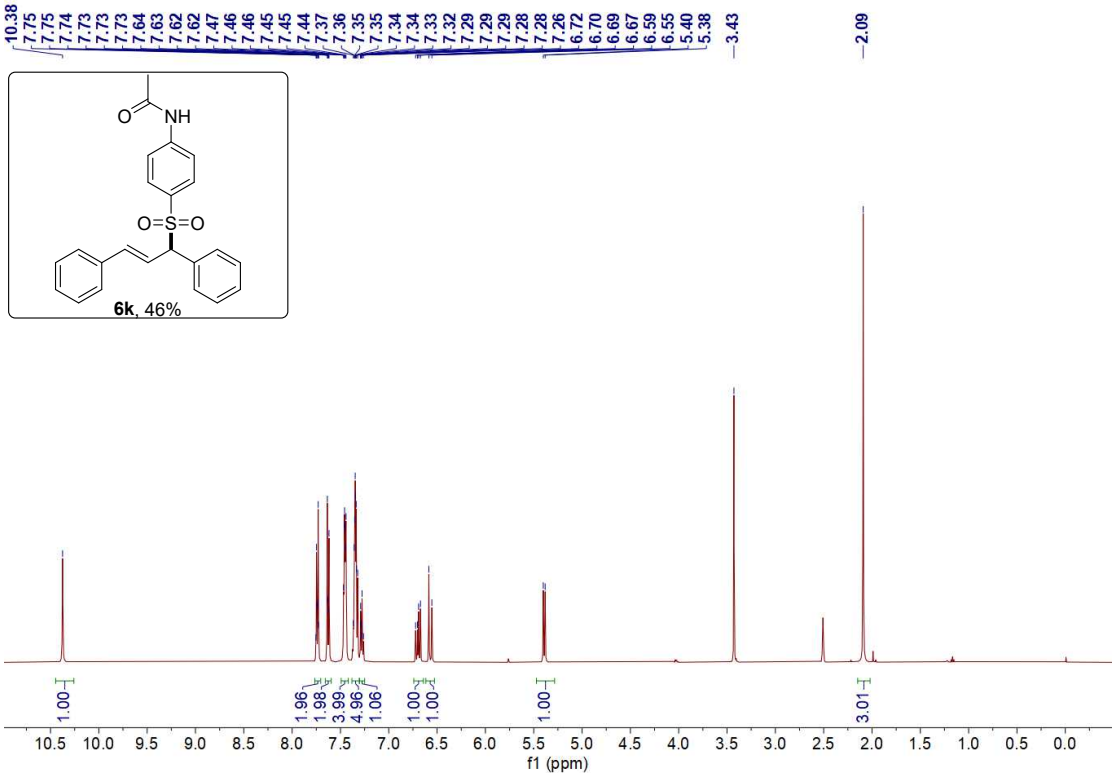


^{19}F NMR (471 MHz, Chloroform-d)

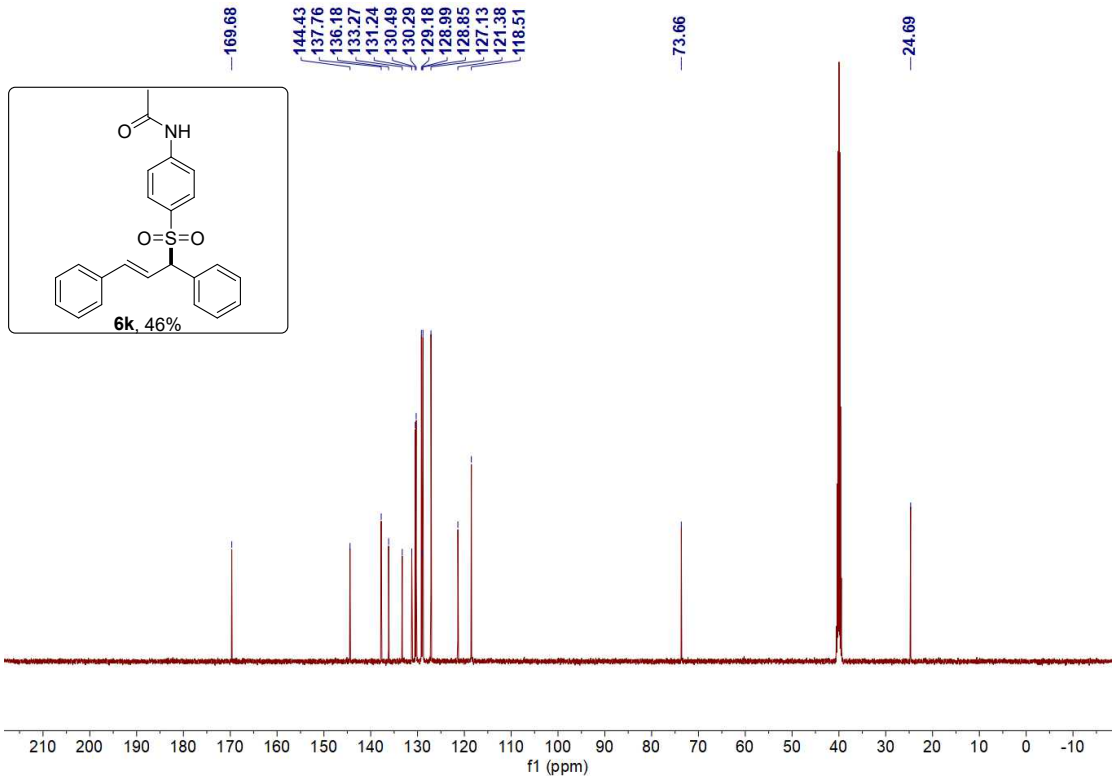


(E)-N-(4-((1,3-diphenylallyl)sulfonyl)phenyl)acetamide (6k)

^{1}H NMR (500 MHz, DMSO-d6)

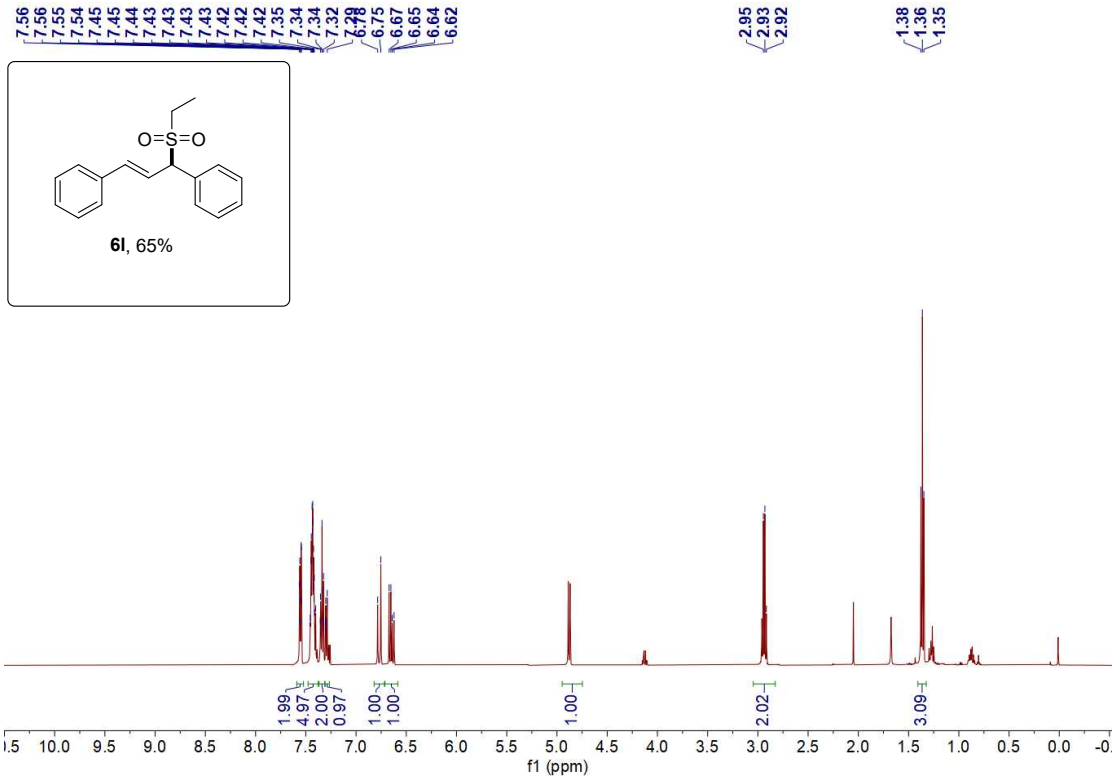


^{13}C NMR (126 MHz, DMSO-d6)

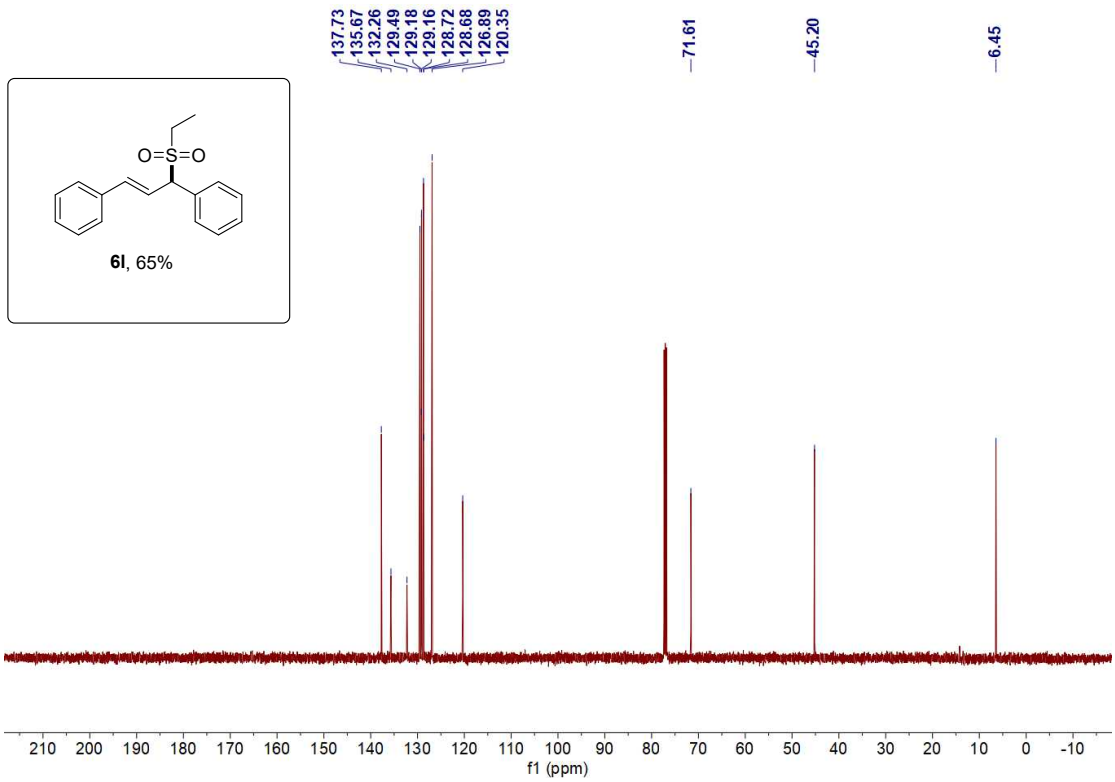


(E)-(3-(ethylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6l)

^{1}H NMR (500 MHz, Chloroform-d)

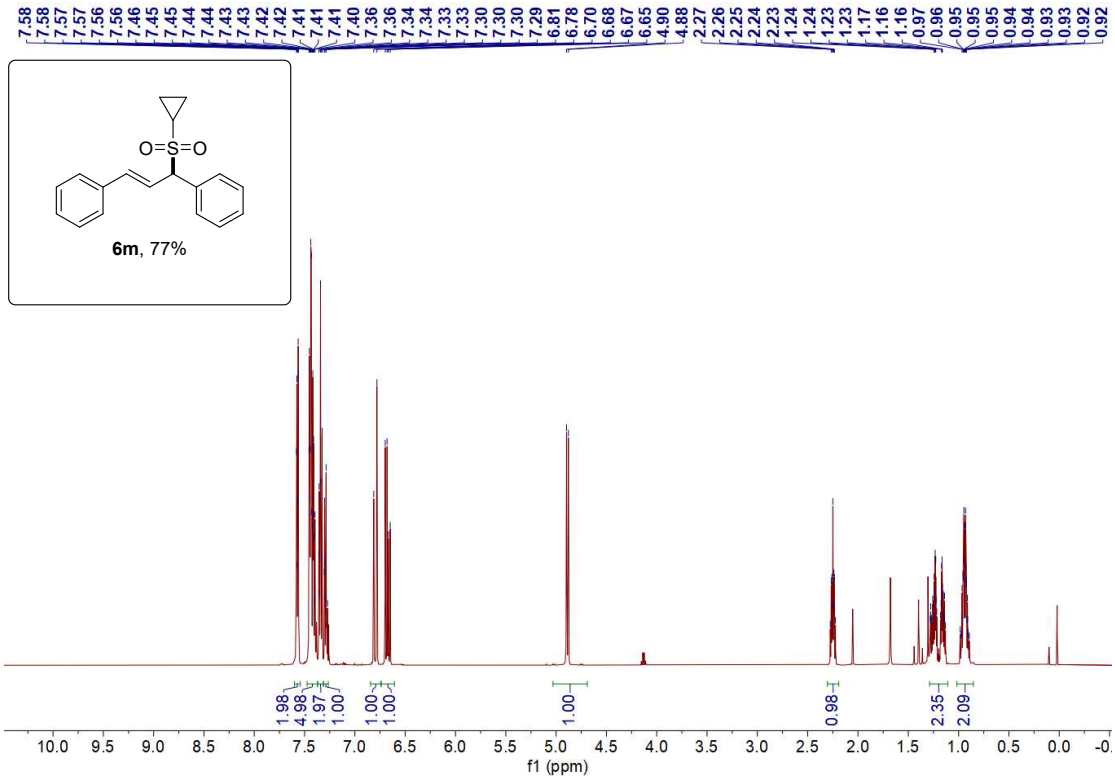


^{13}C NMR (126 MHz, Chloroform-d)

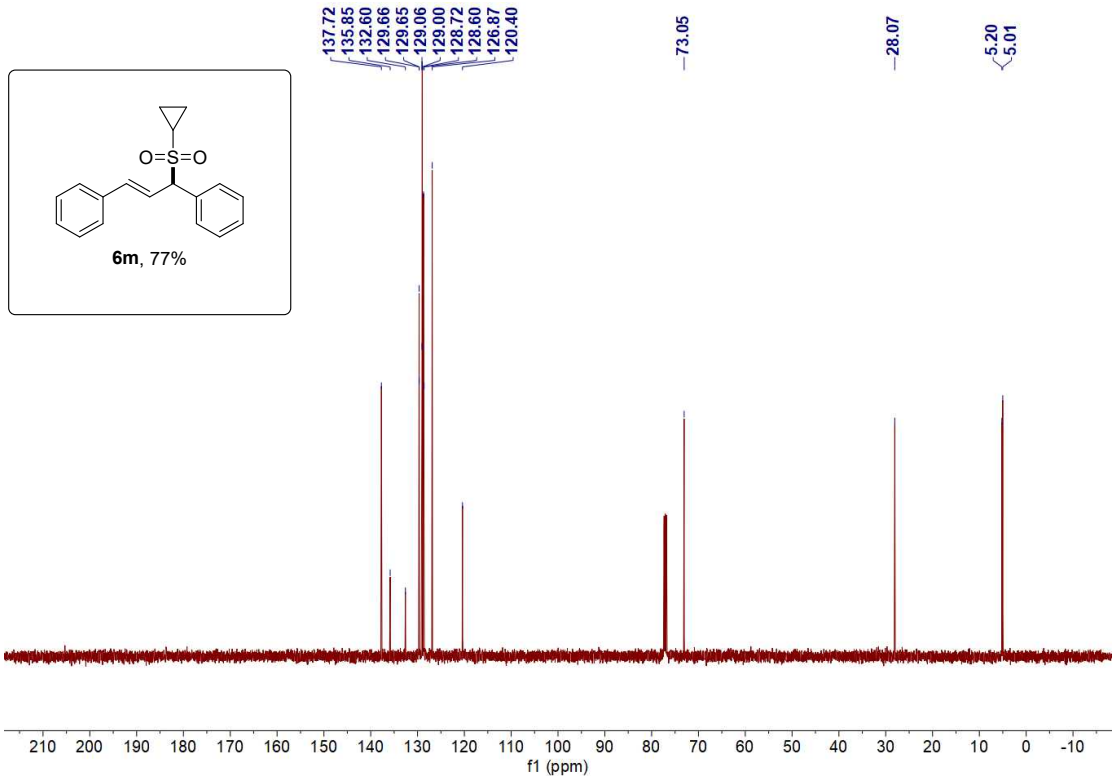


(E)-(3-(cyclopropylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6m)

^{1}H NMR (500 MHz, Chloroform-d)

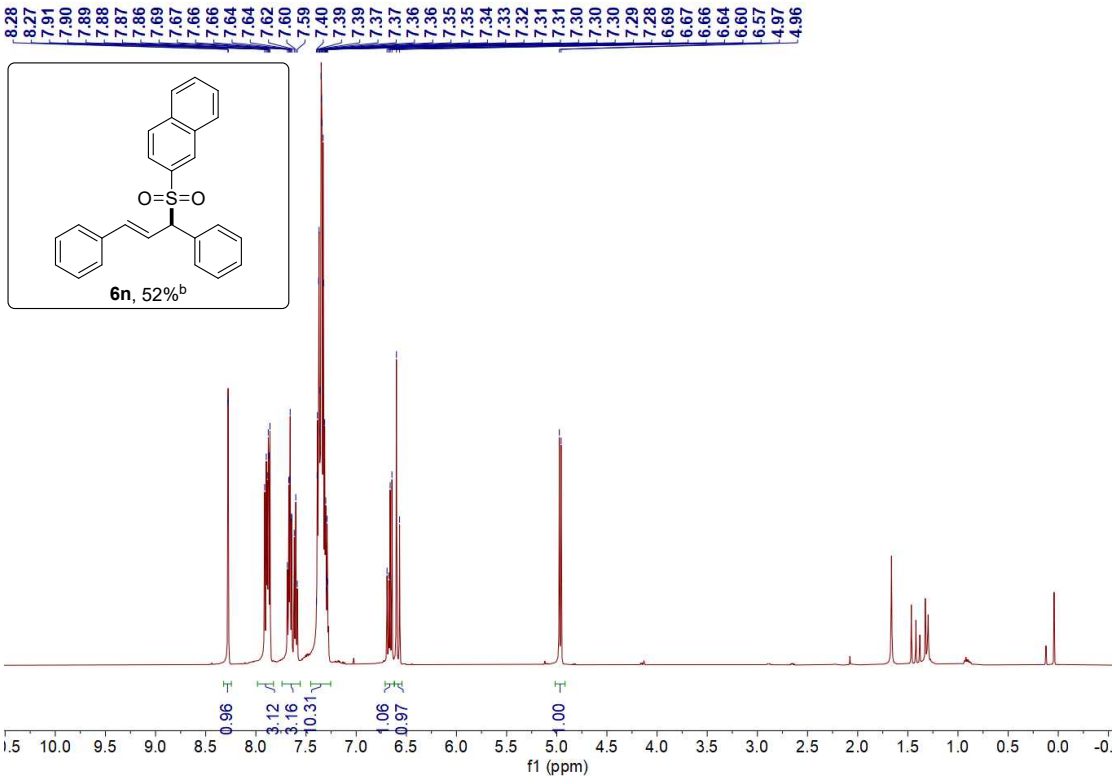


^{13}C NMR (126 MHz, Chloroform-d)

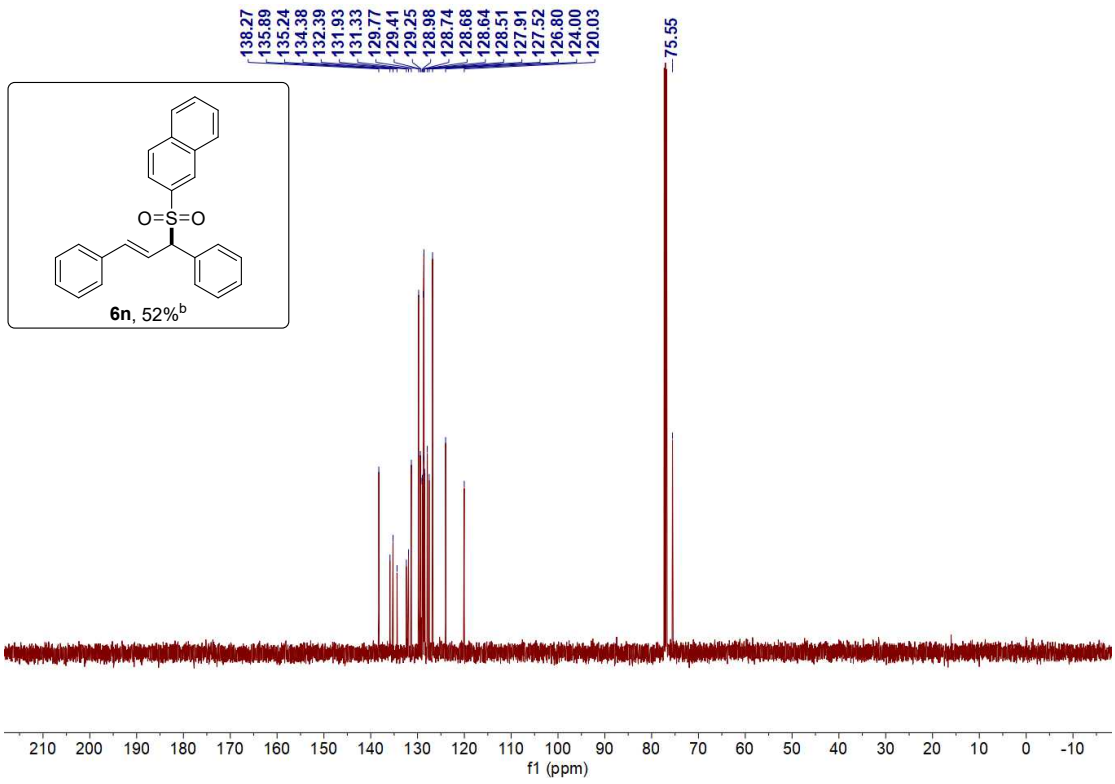


(E)-2-((1,3-diphenylallyl)sulfonyl)naphthalene (6n)

^{1}H NMR (500 MHz, Chloroform-d)

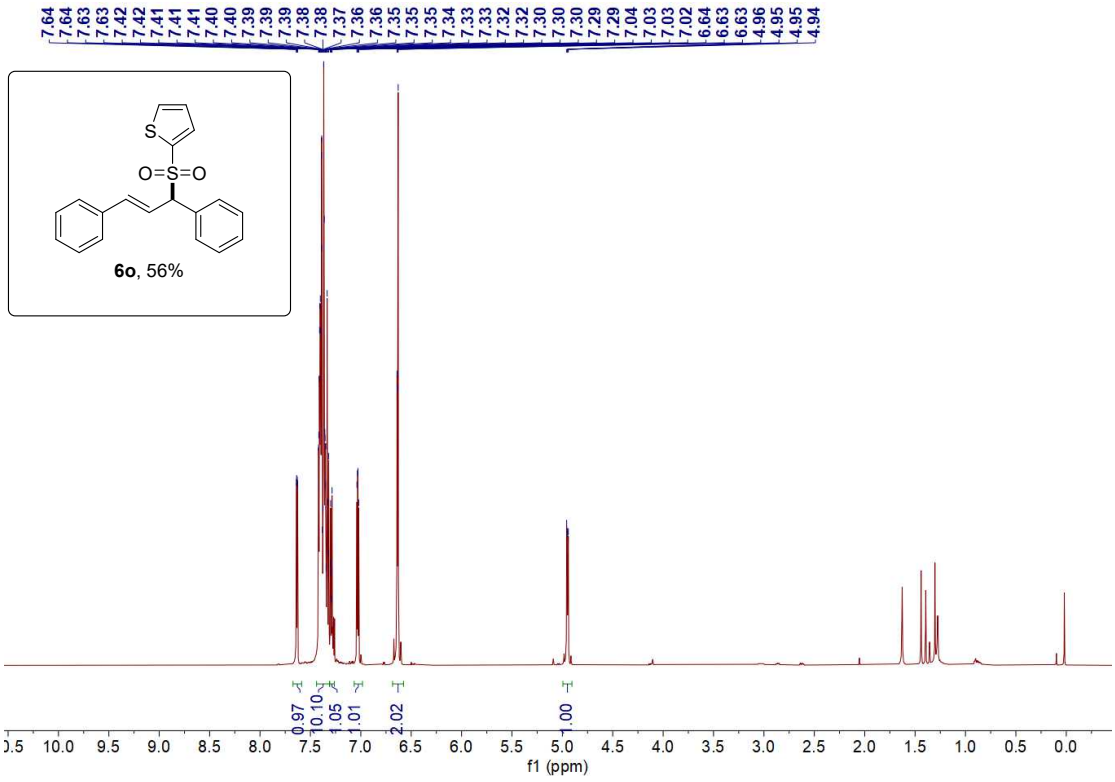


^{13}C NMR (126 MHz, Chloroform-d)

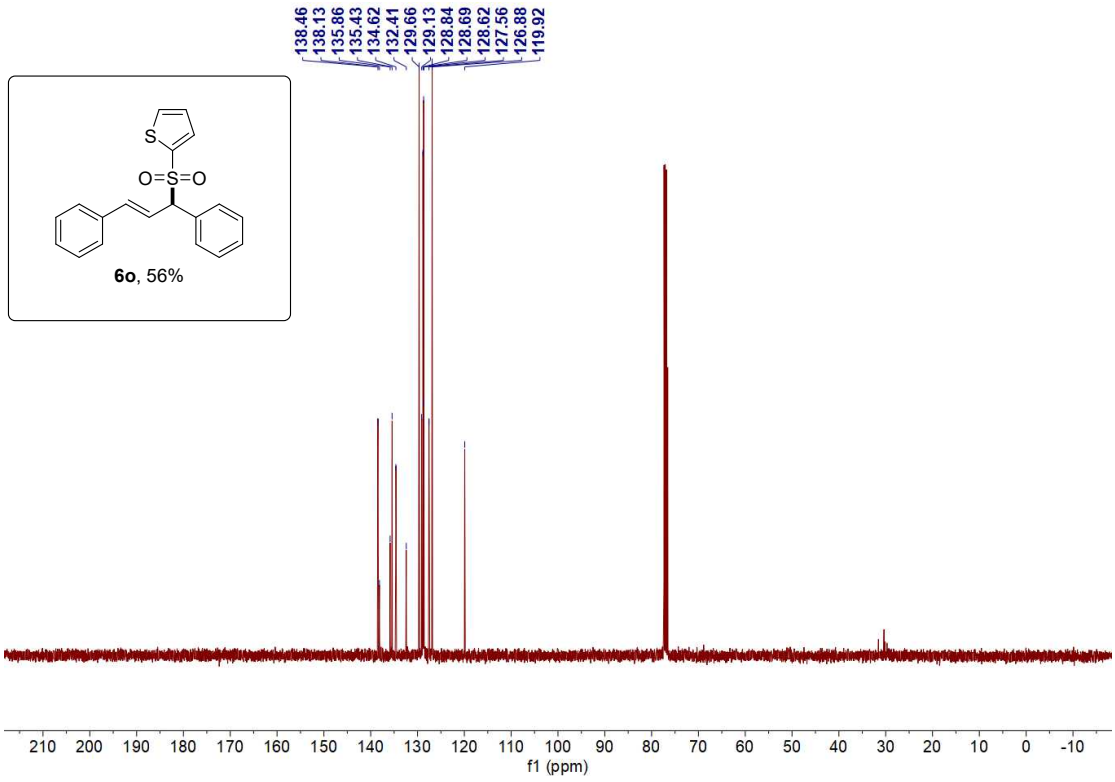


(E)-2-((1,3-diphenylallyl)sulfonyl)thiophene (6o)

^{1}H NMR (500 MHz, Chloroform-d)

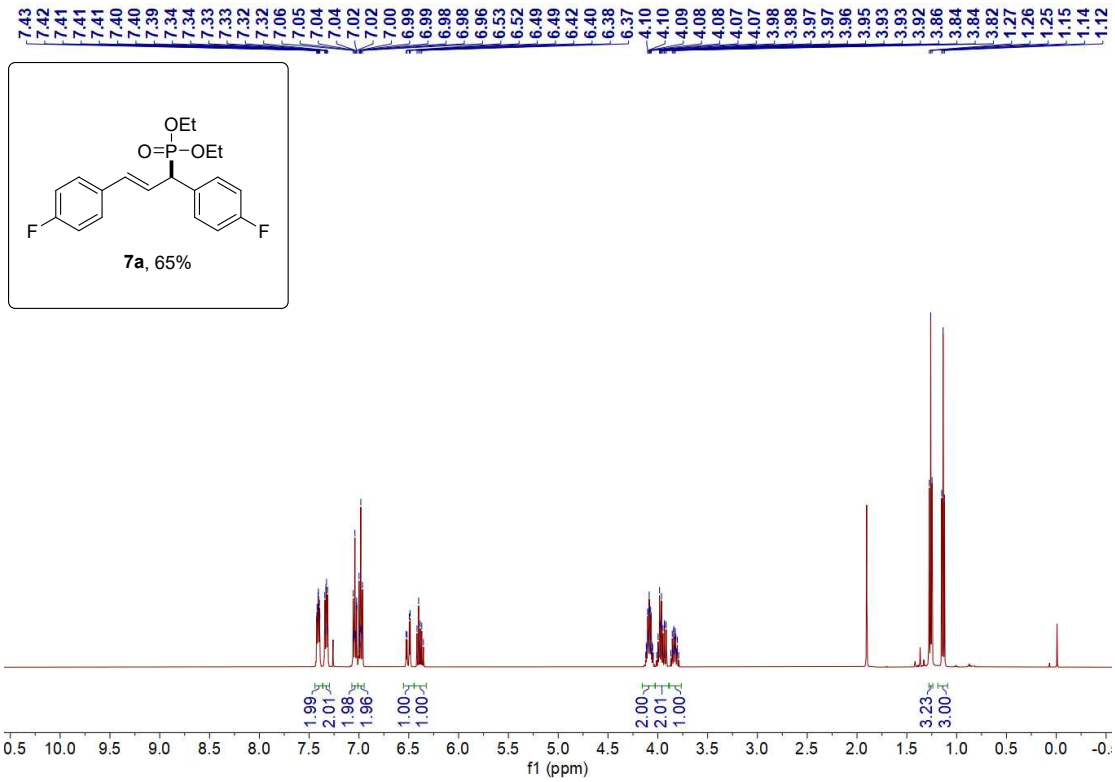


^{13}C NMR (126 MHz, Chloroform-d)

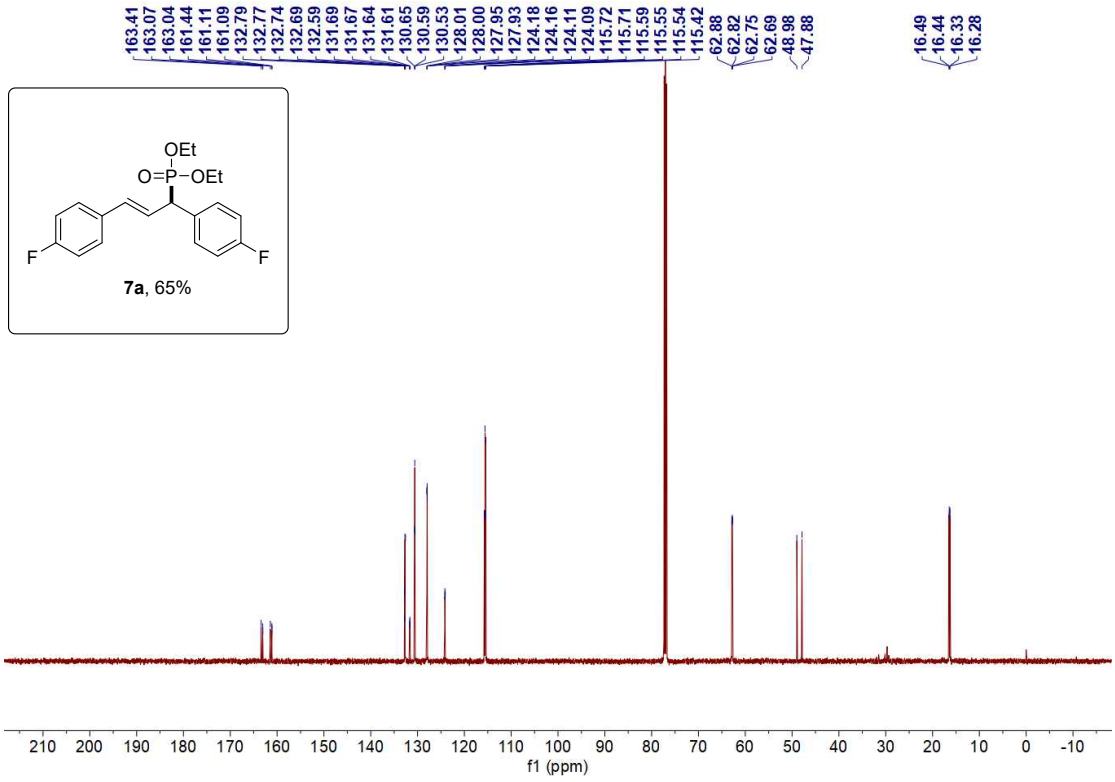


diethyl (E)-(1,3-bis(4-fluorophenyl)allyl)phosphonate (7a)

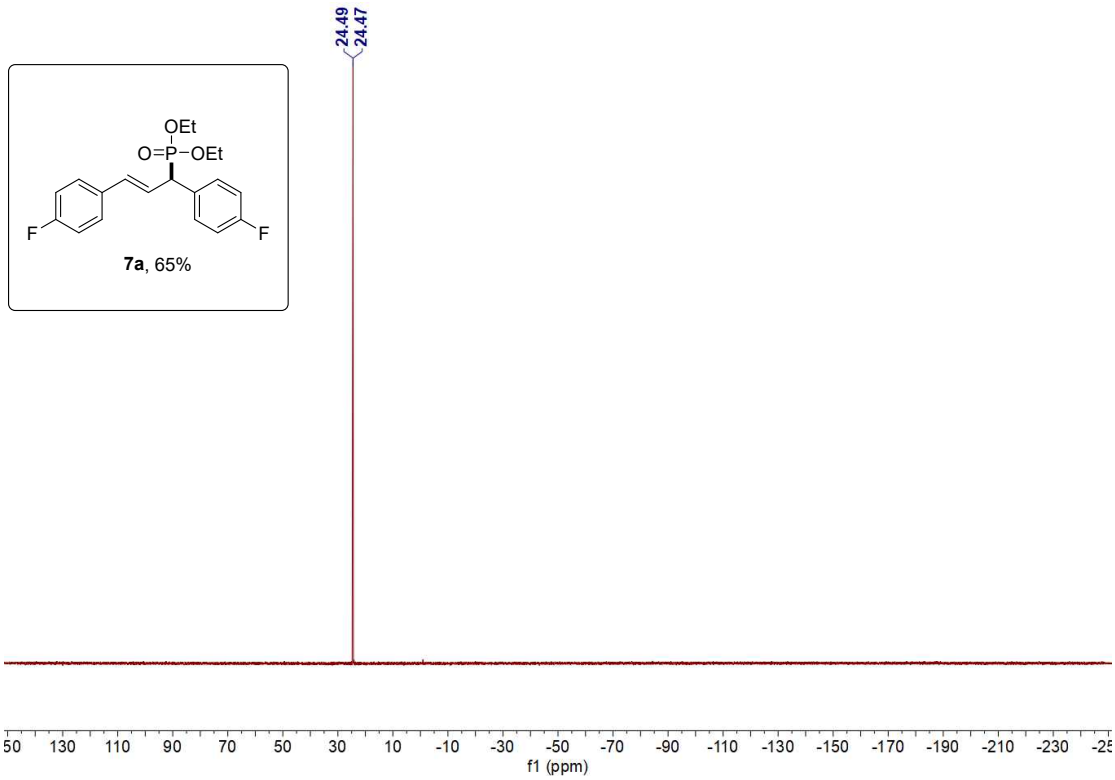
^{1}H NMR (500 MHz, Chloroform-d)



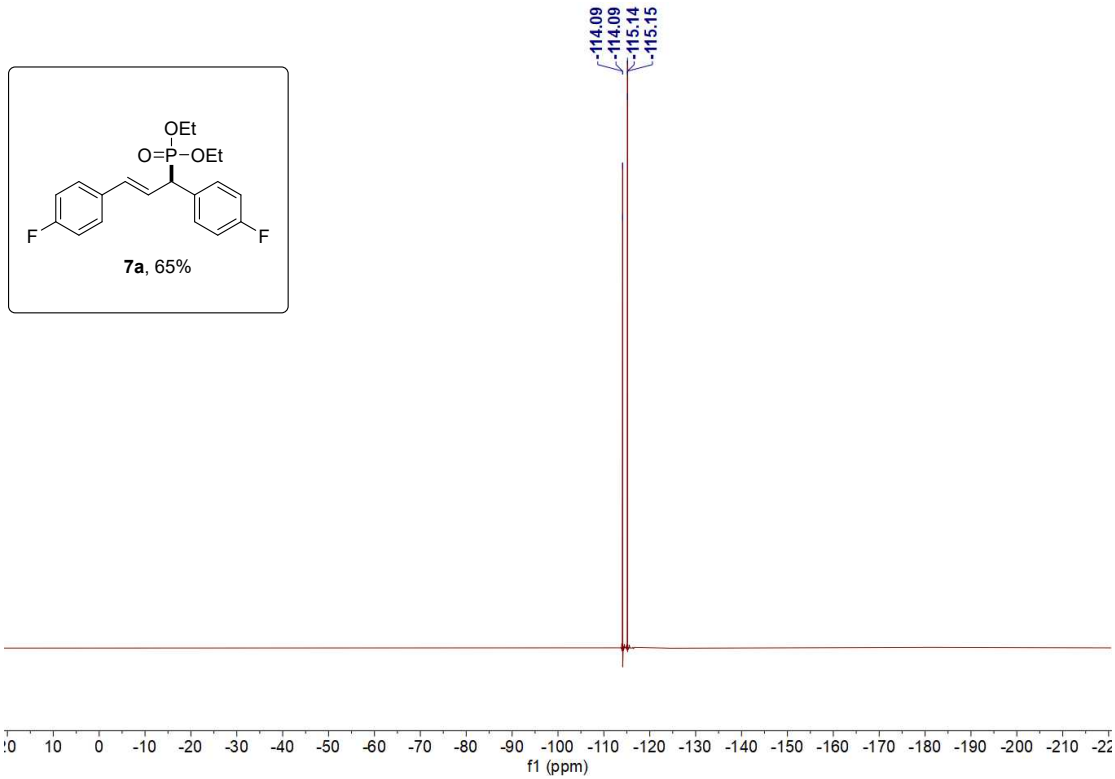
^{13}C NMR (126 MHz, Chloroform-d)



^{31}P NMR (202 MHz, Chloroform-d)

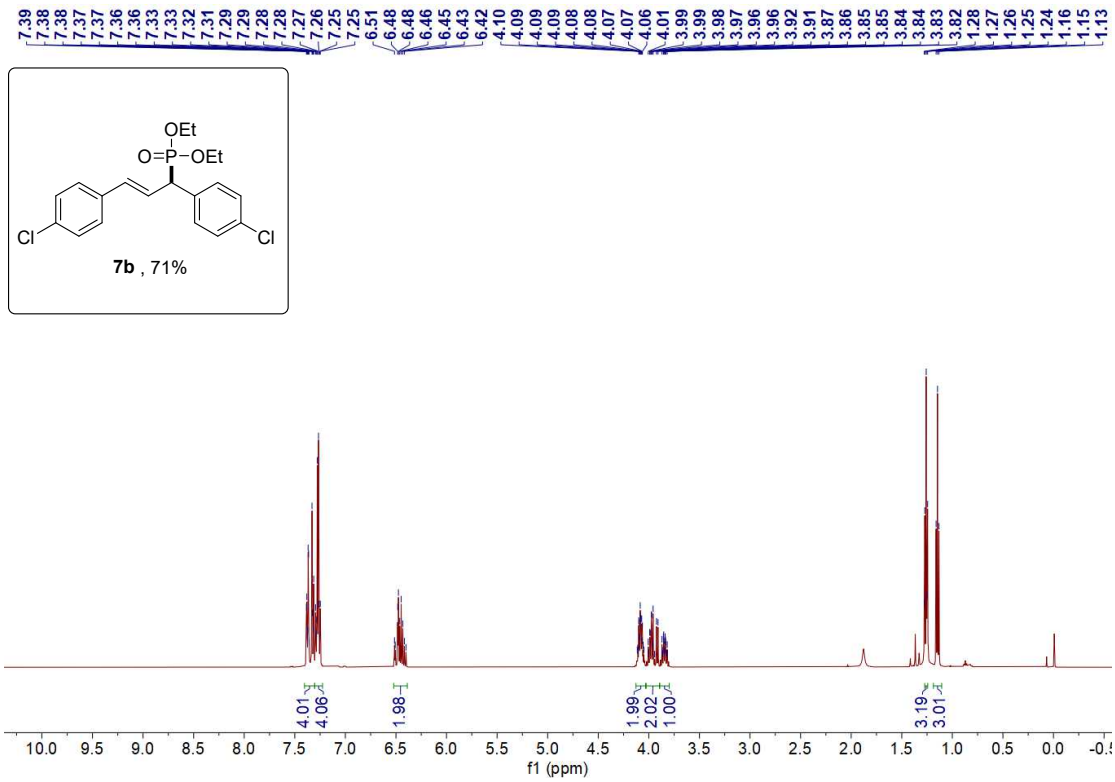


^{19}F NMR (471 MHz, Chloroform-d)

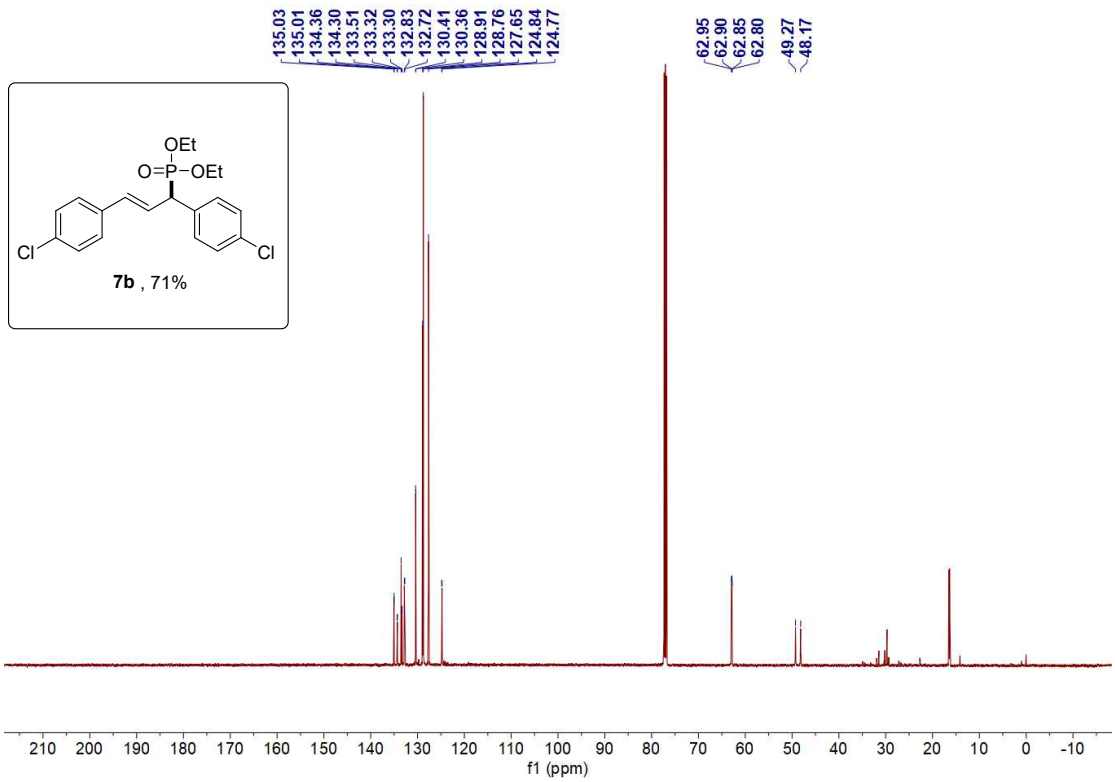


diethyl (E)-(1,3-bis(4-chlorophenyl)allyl)phosphonate (7b)

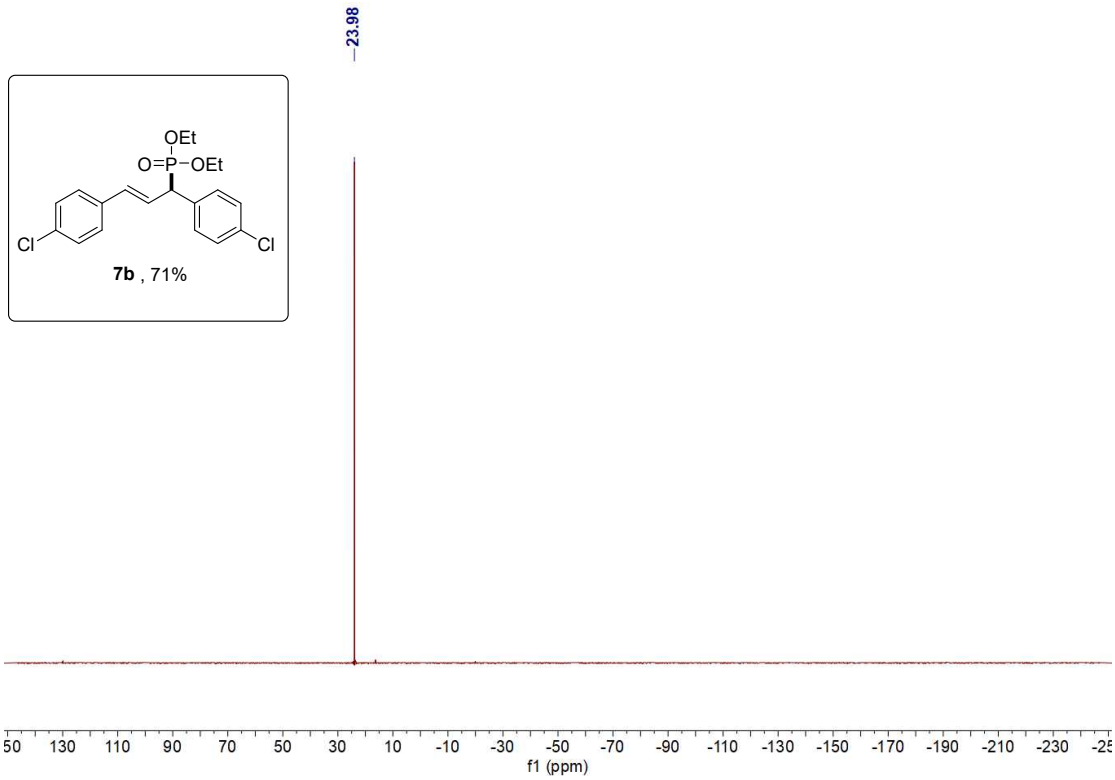
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

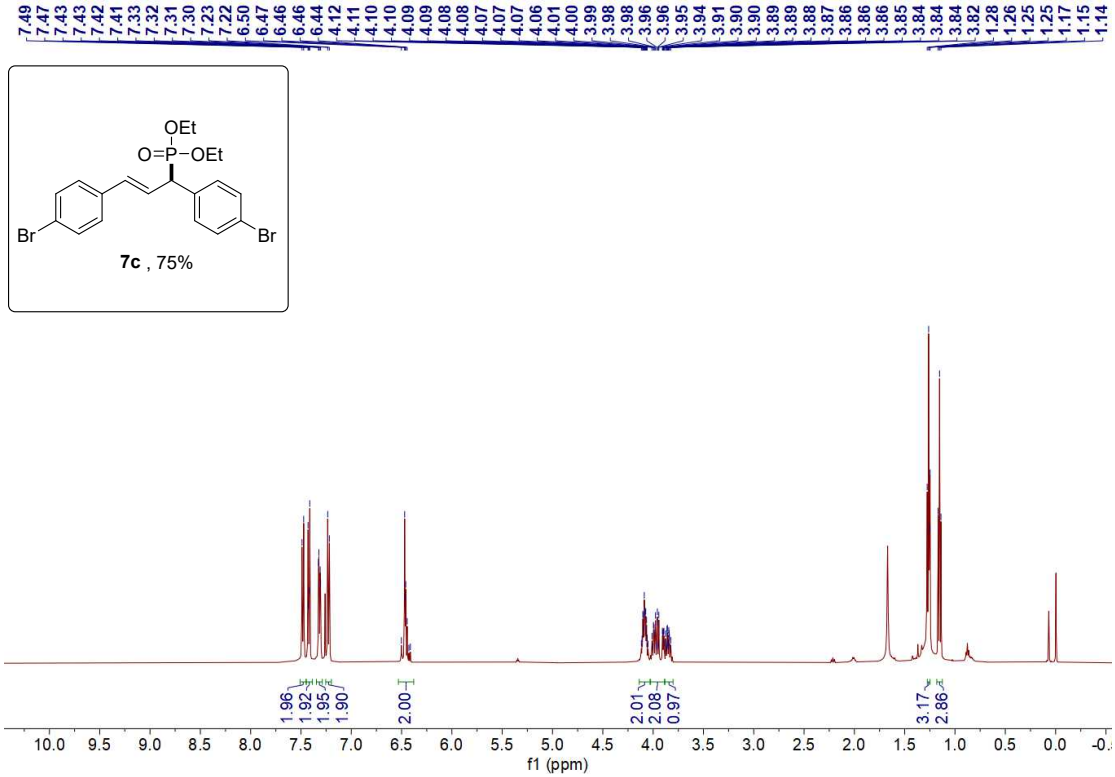


^{31}P NMR (202 MHz, Chloroform-d)

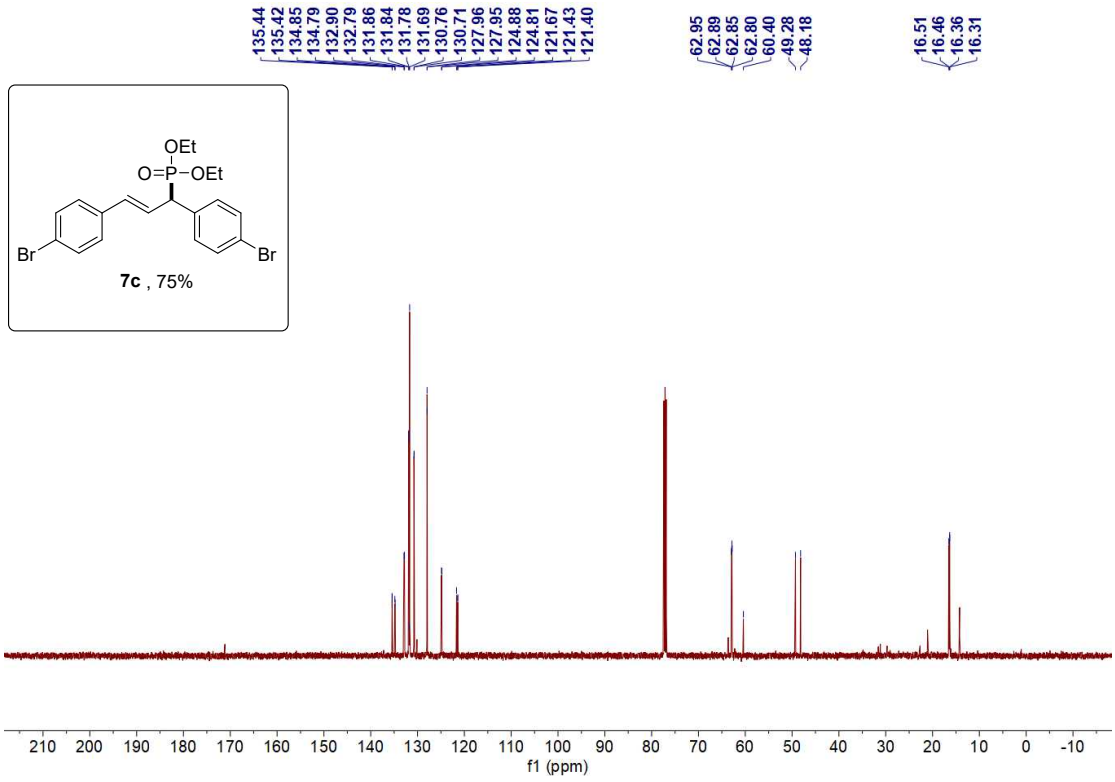


diethyl (E)-(1,3-bis(4-bromophenyl)allyl)phosphonate (7c)

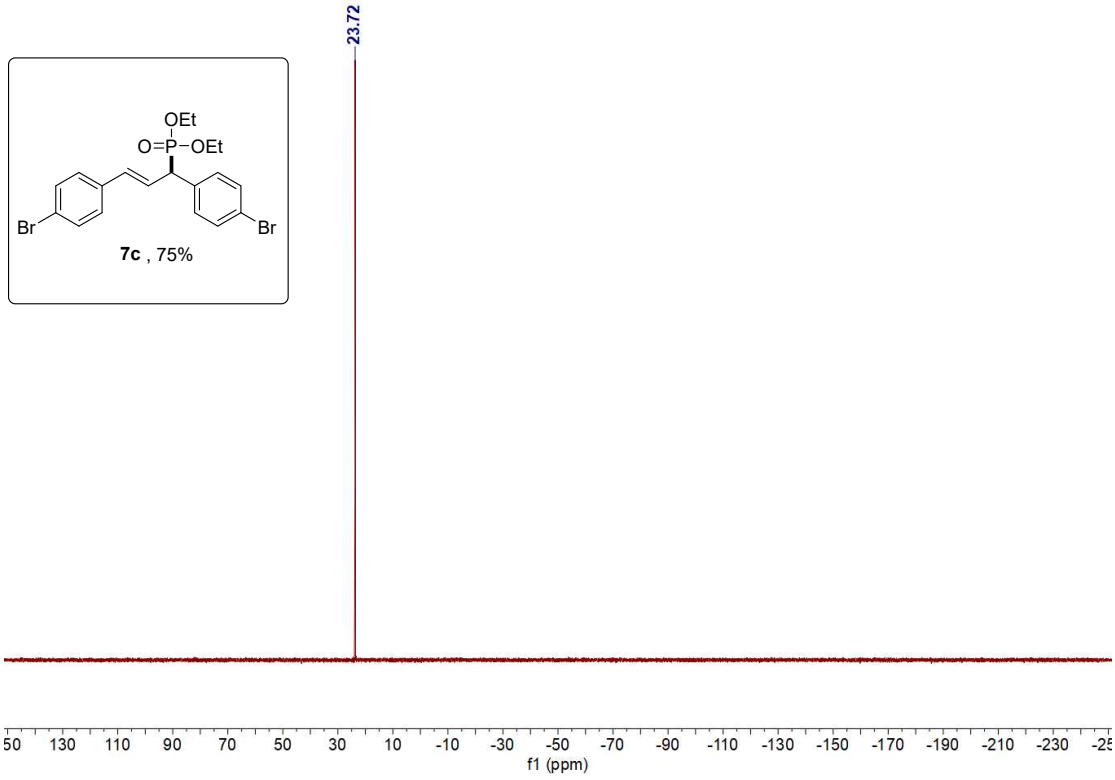
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

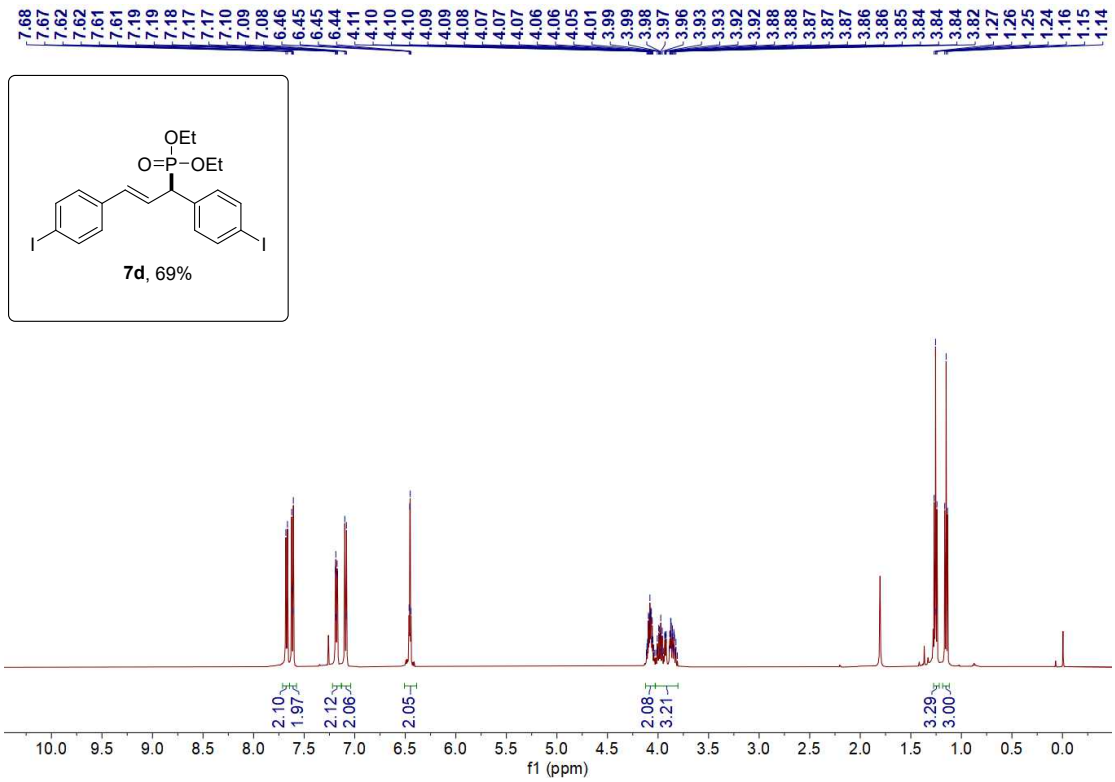


^{31}P NMR (202 MHz, Chloroform-d)

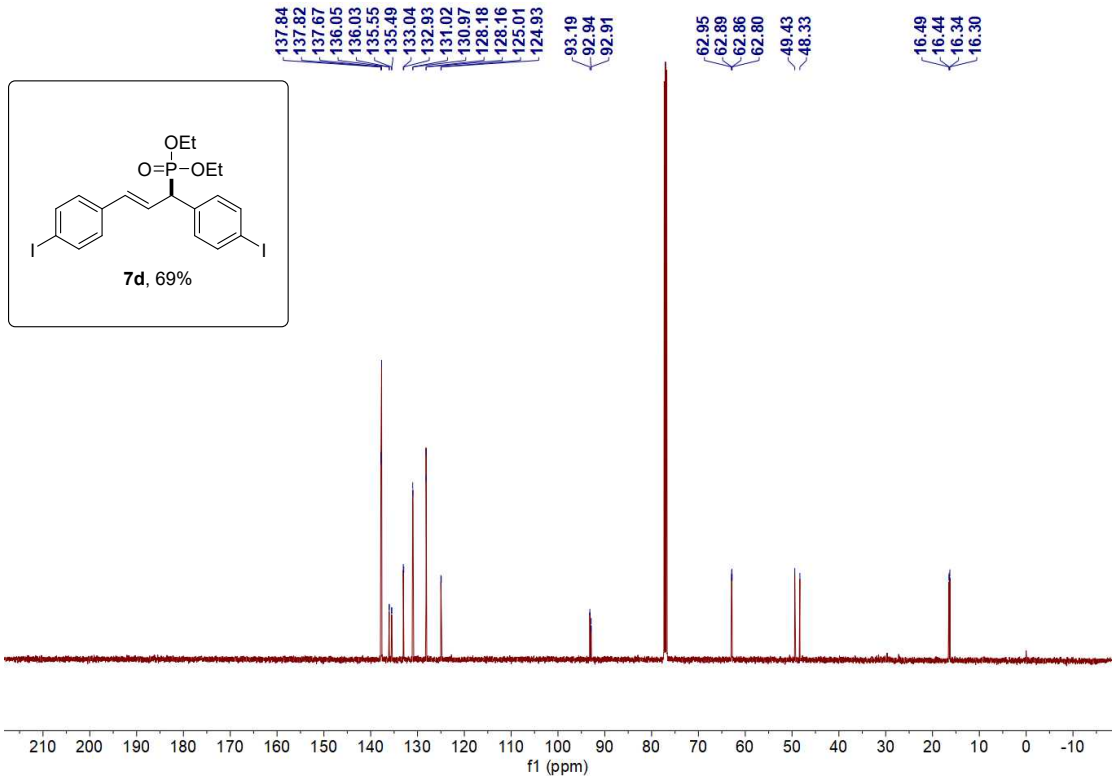


diethyl (E)-(1,3-bis(4-iodophenyl)allyl)phosphonate (7d)

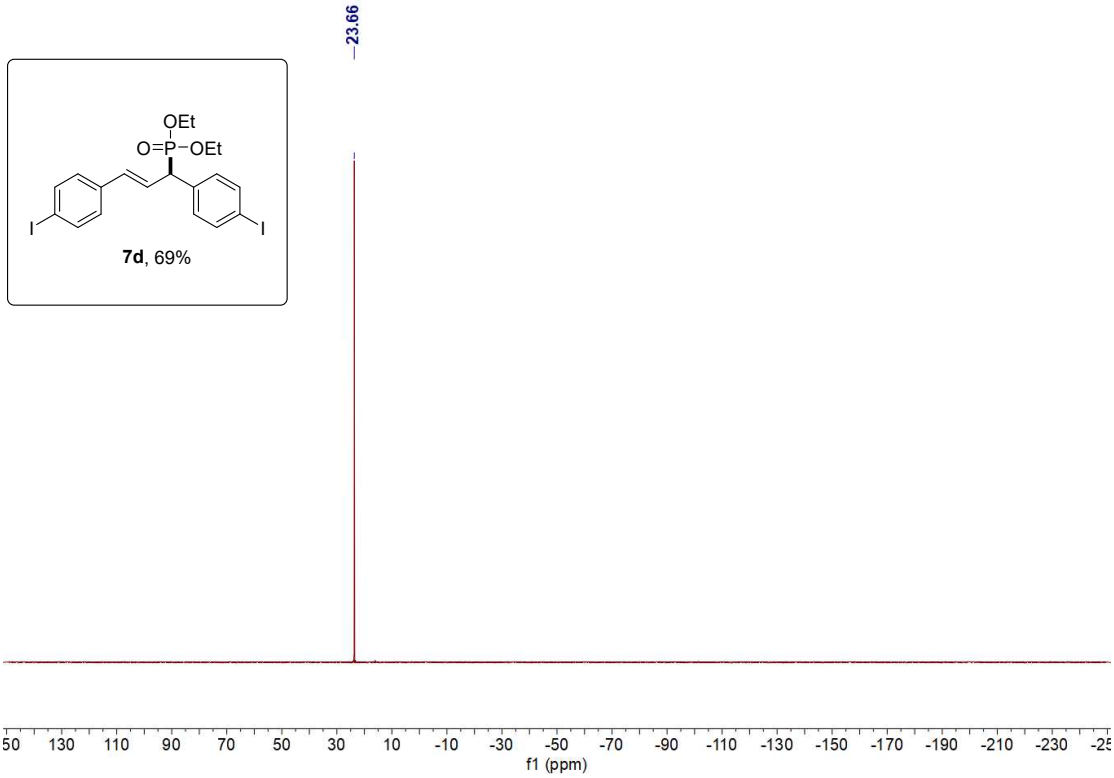
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

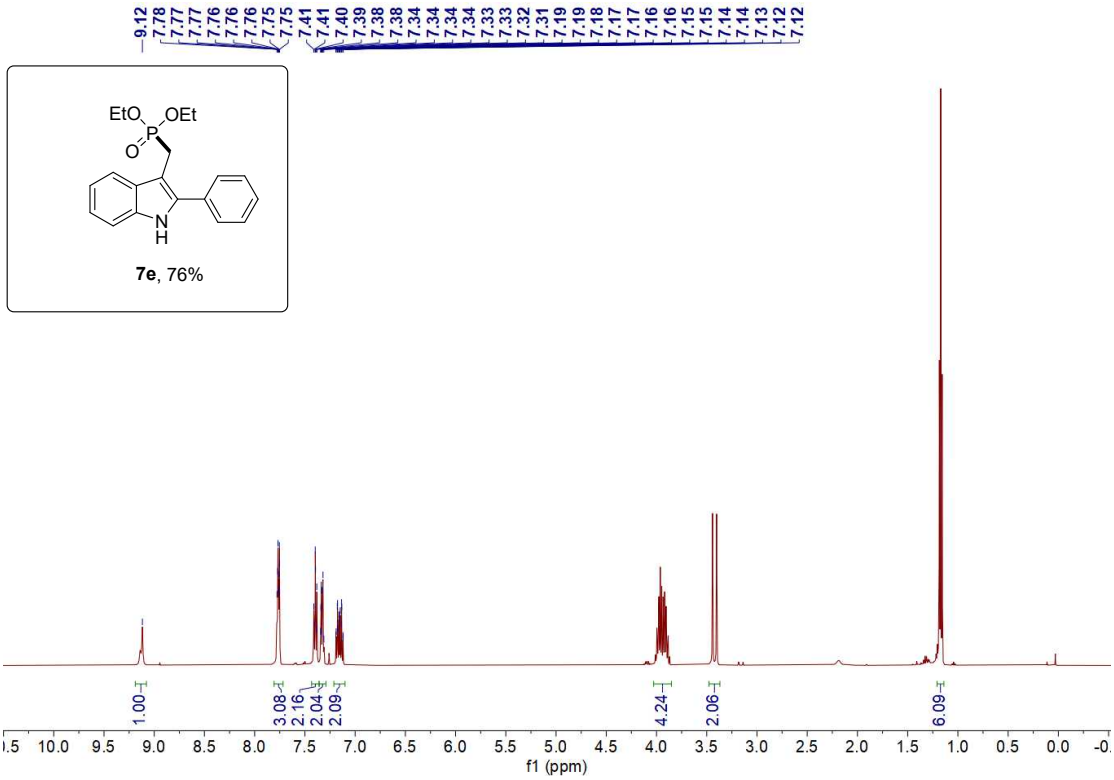


^{31}P NMR (202 MHz, Chloroform-d)

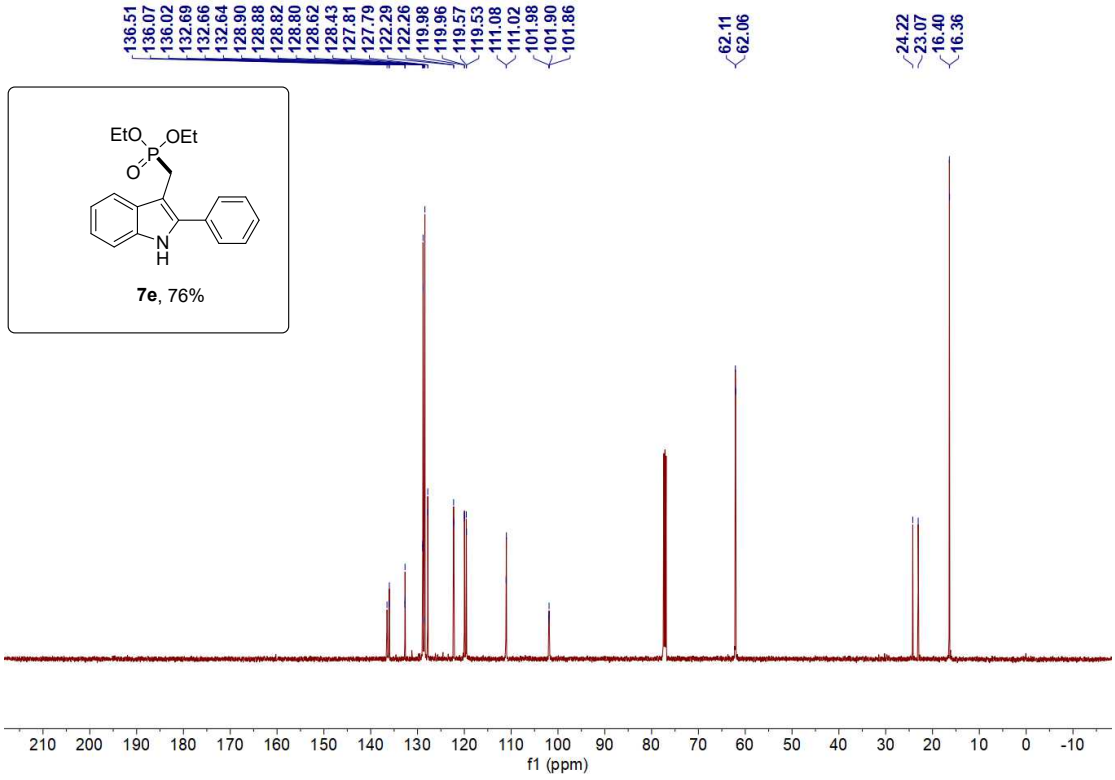


diethyl ((2-phenyl-1H-indol-3-yl)methyl)phosphonate (7e)

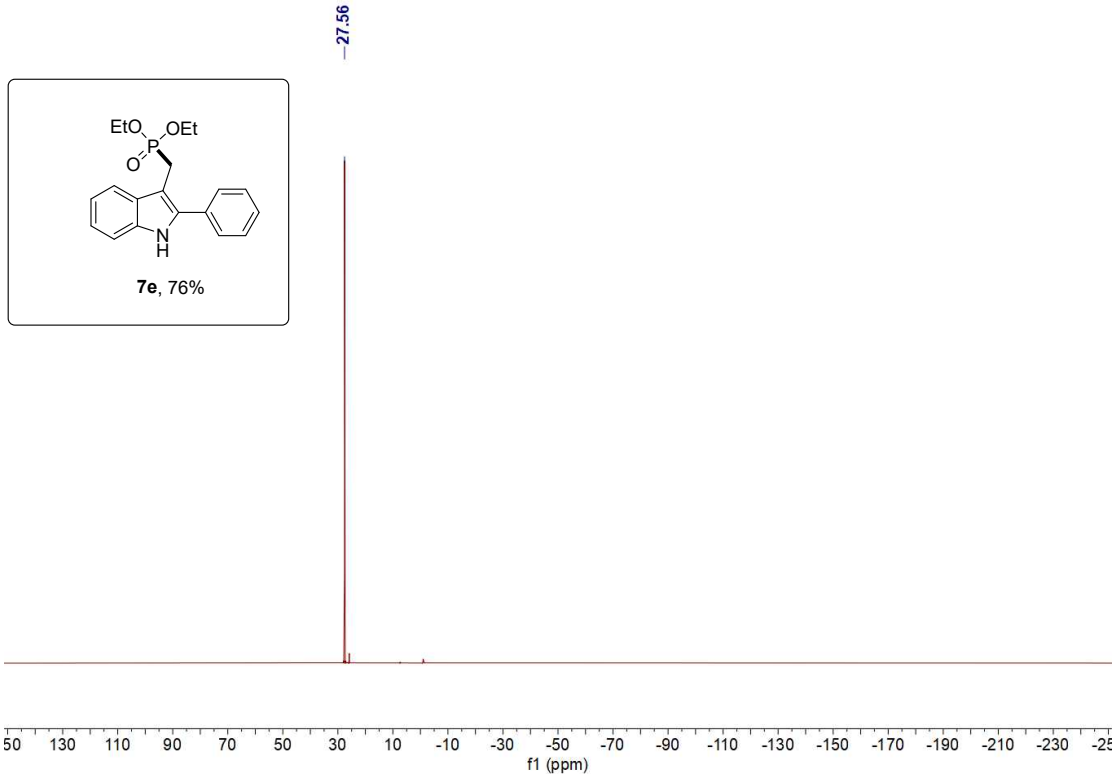
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

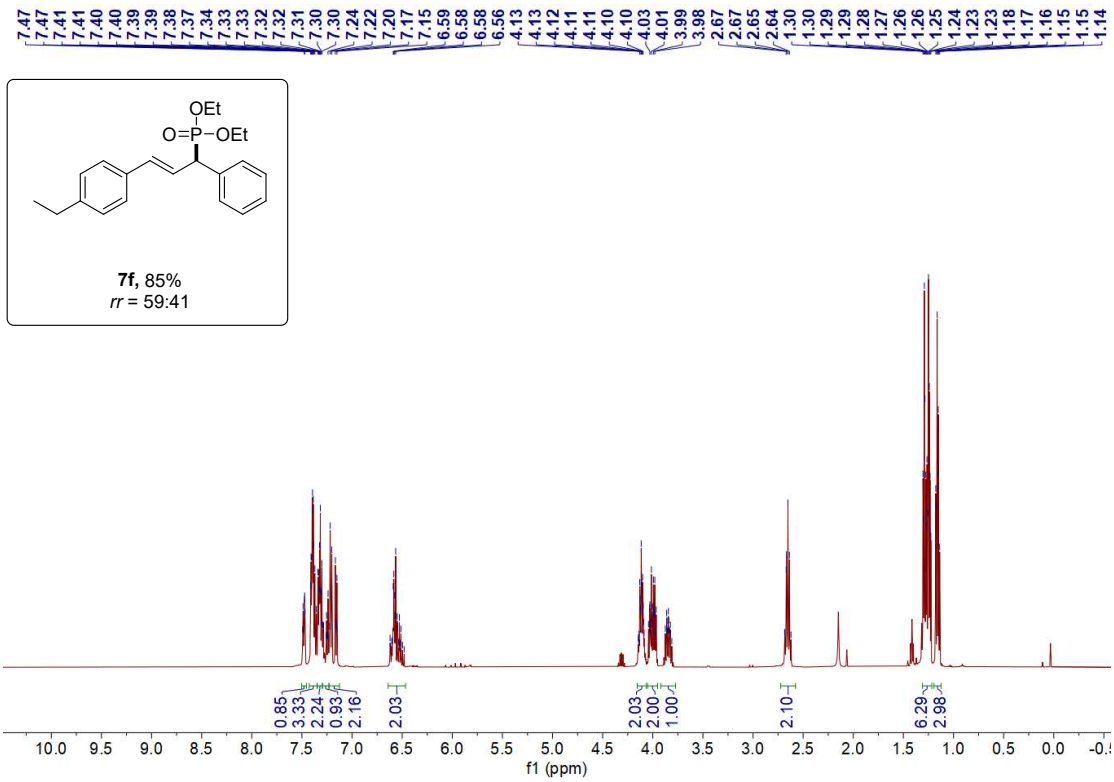


^{31}P NMR (202 MHz, Chloroform-d)

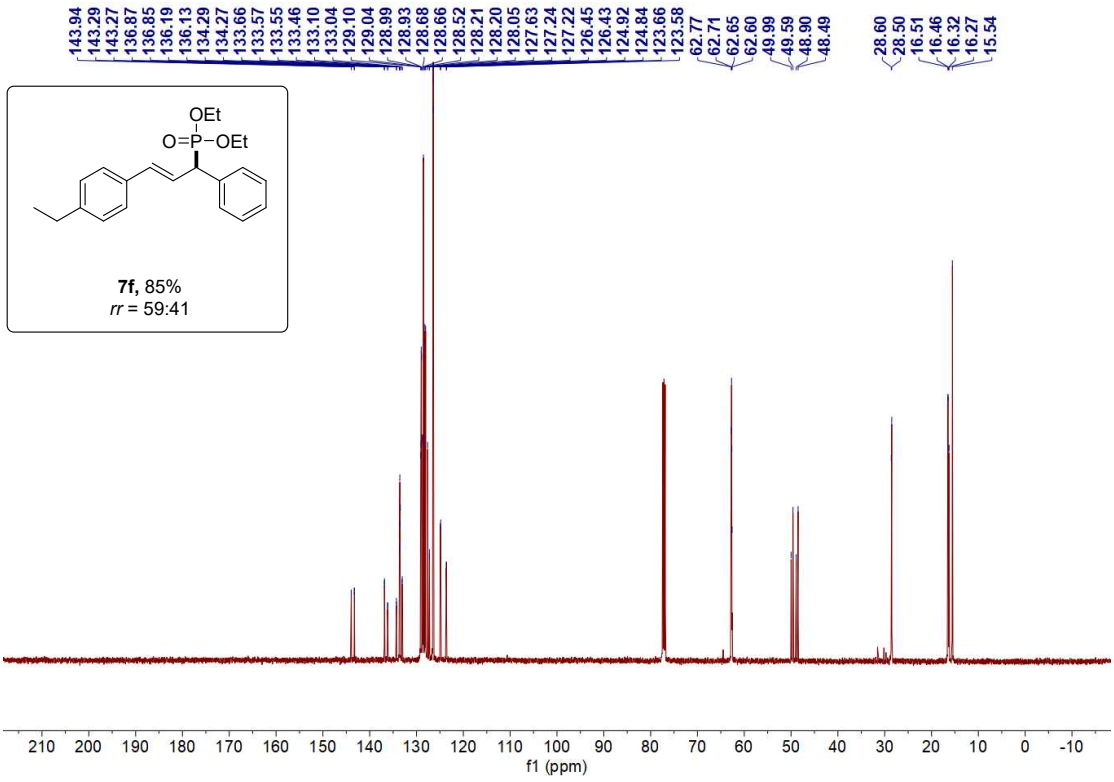


diethyl (E)-(3-(4-ethylphenyl)-1-phenylallyl)phosphonate (7f)

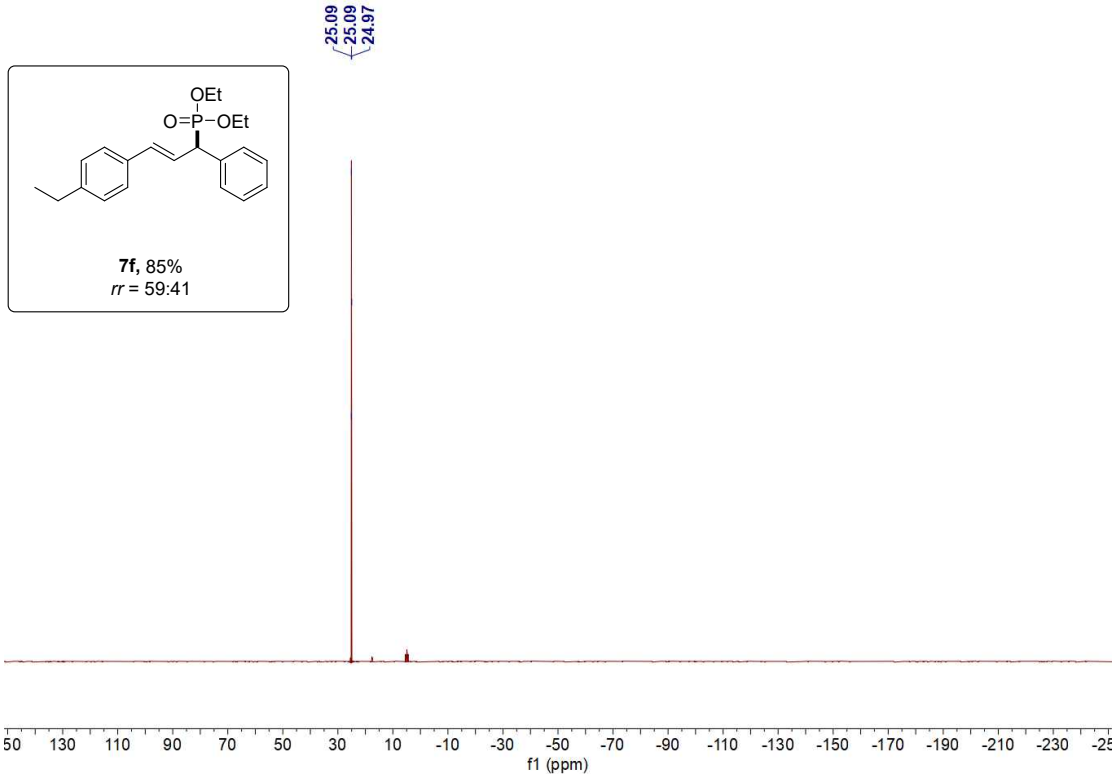
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

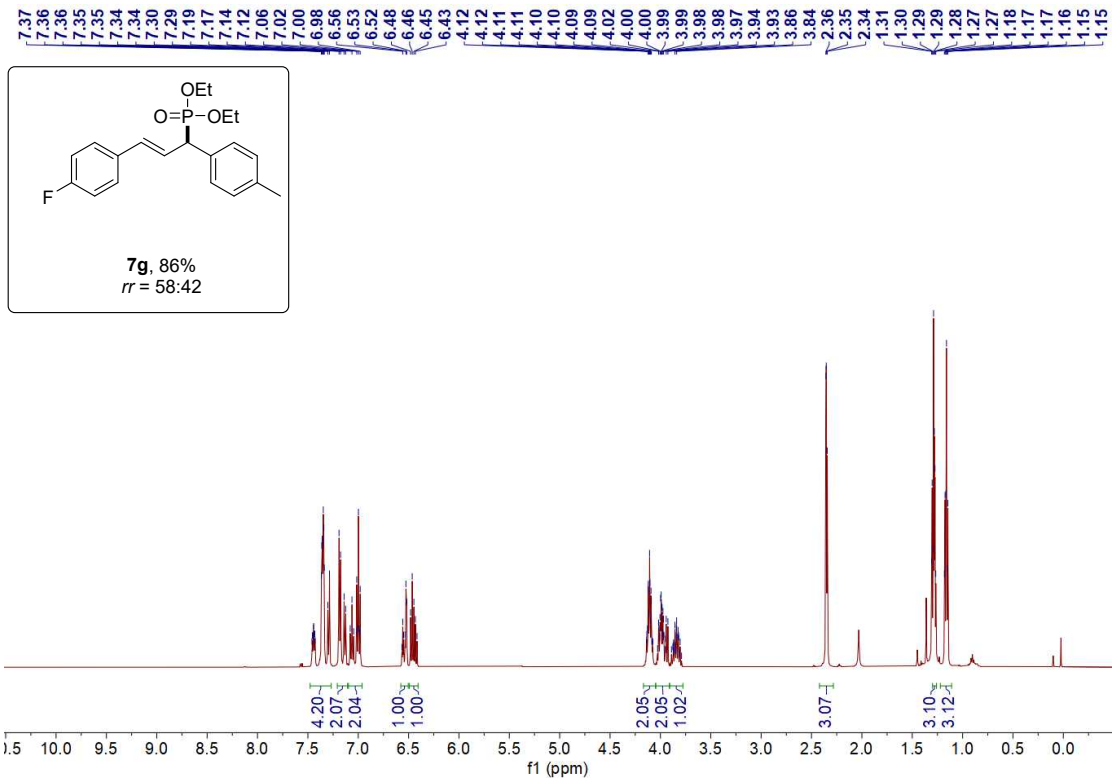


^{31}P NMR (202 MHz, Chloroform-d)

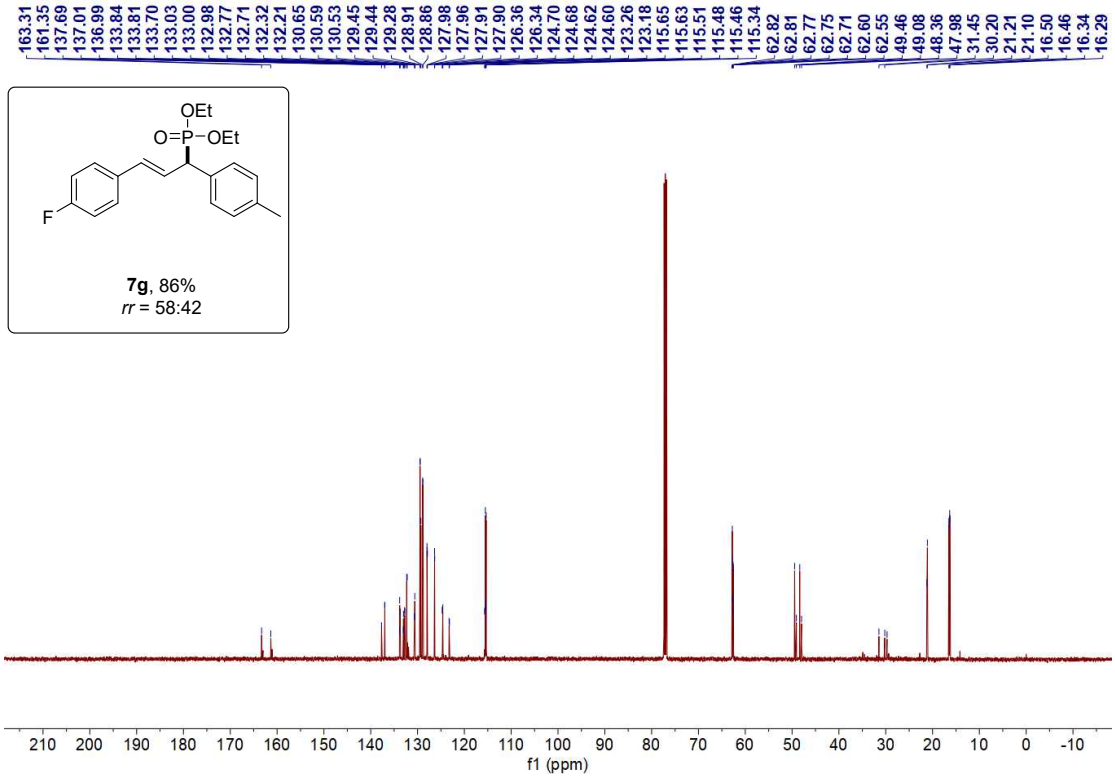


diethyl (E)-(3-(4-fluorophenyl)-1-(p-tolyl)allyl)phosphonate (7g)

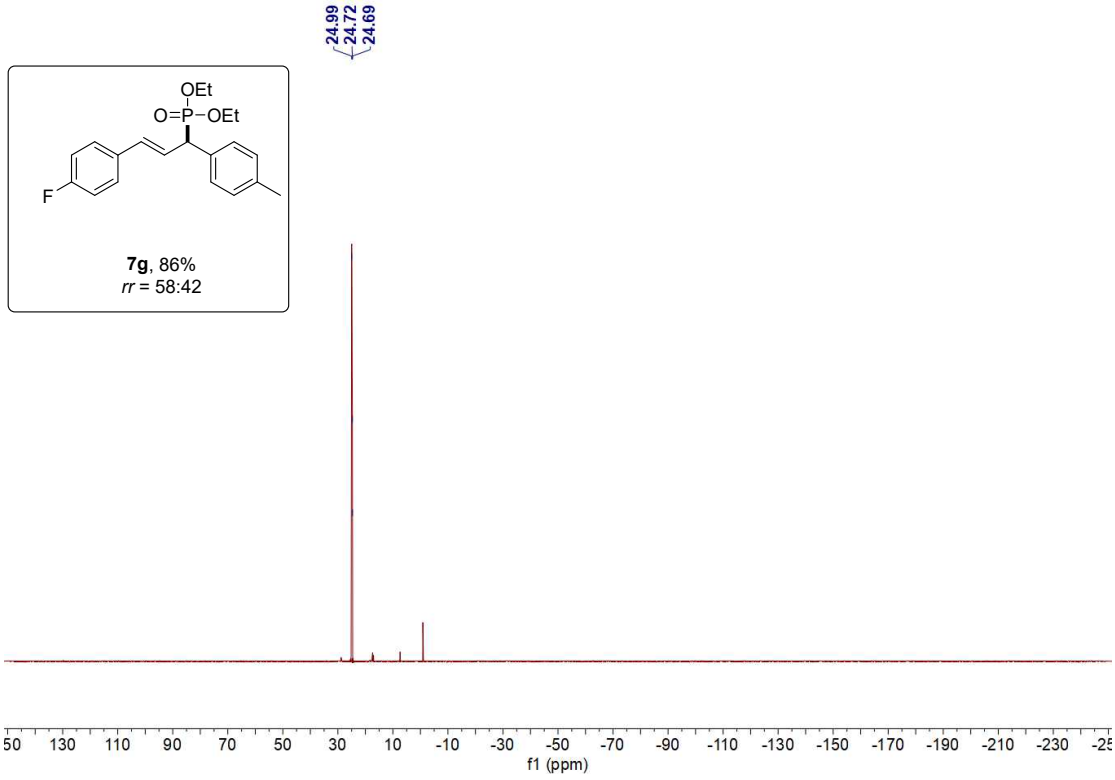
^{1}H NMR (500 MHz, Chloroform-d)



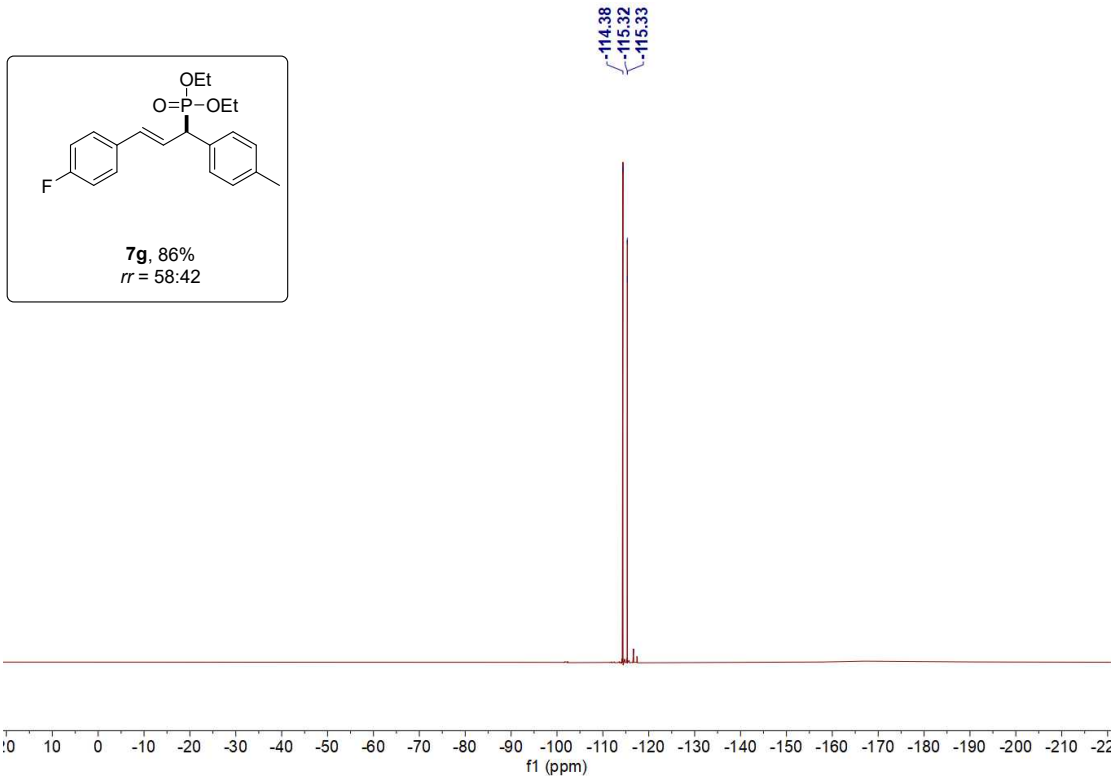
^{13}C NMR (126 MHz, Chloroform-d)



^{31}P NMR (202 MHz, Chloroform-d)

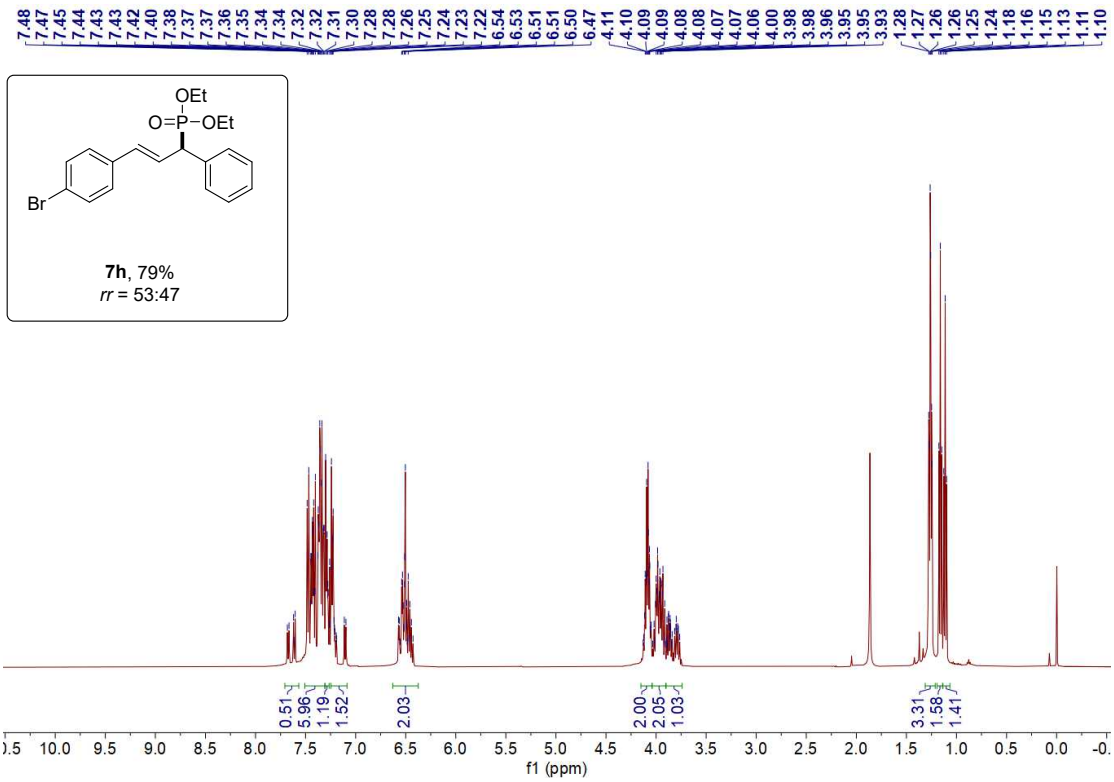


^{19}F NMR (471 MHz, Chloroform-d)

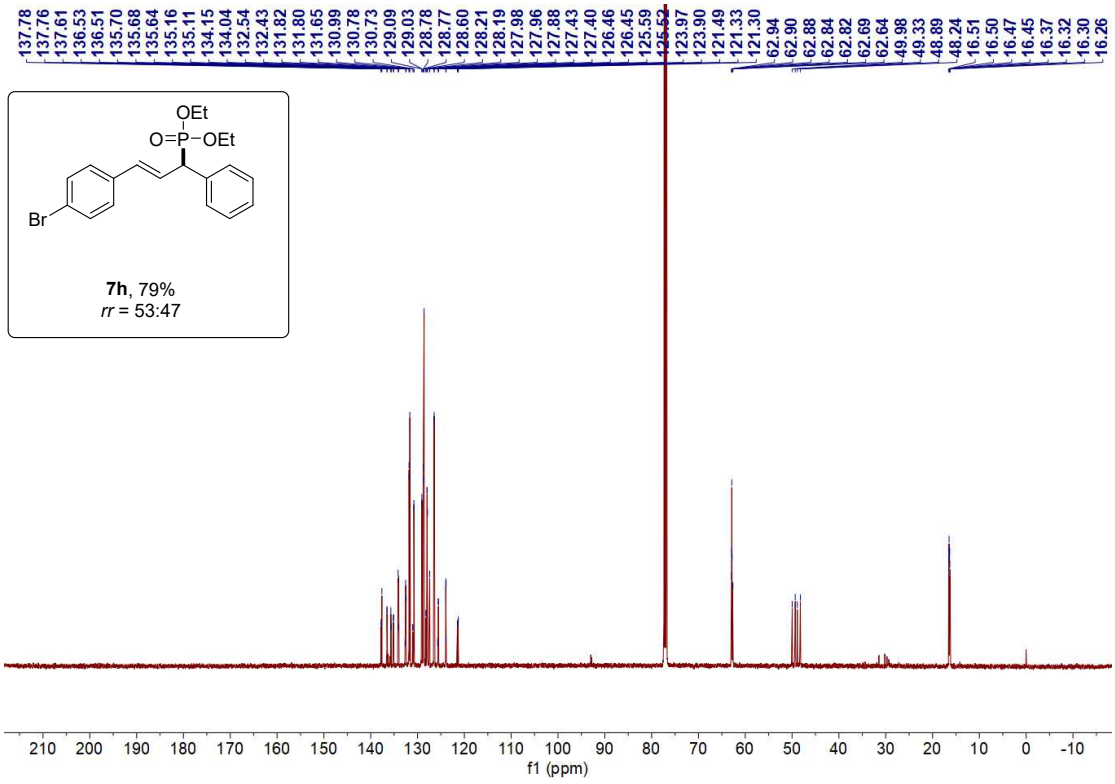


diethyl (E)-(3-(4-bromophenyl)-1-phenylallyl)phosphonate (7h)

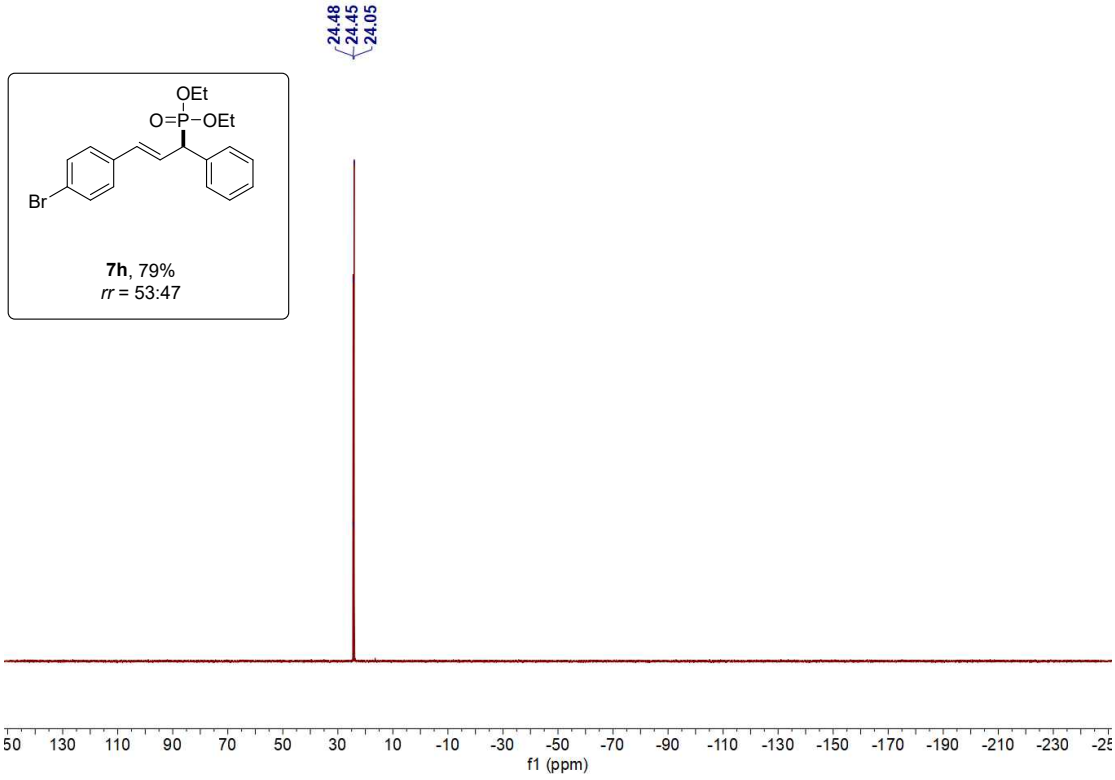
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

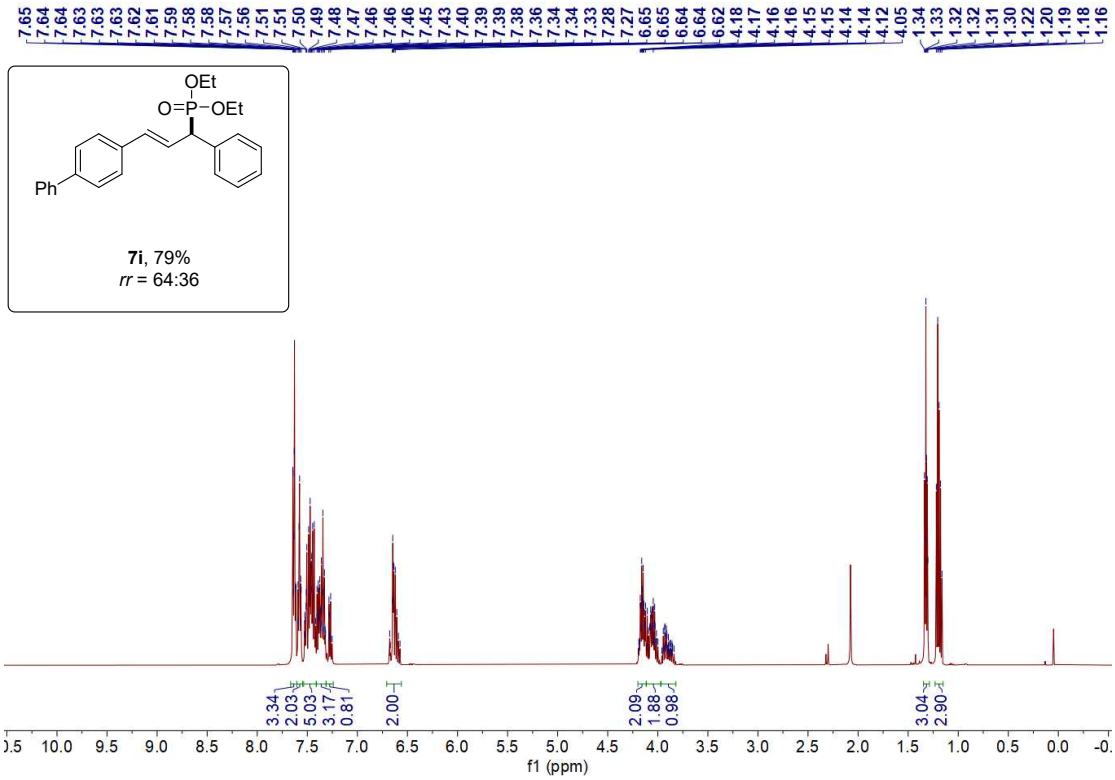


^{31}P NMR (202 MHz, Chloroform-d)

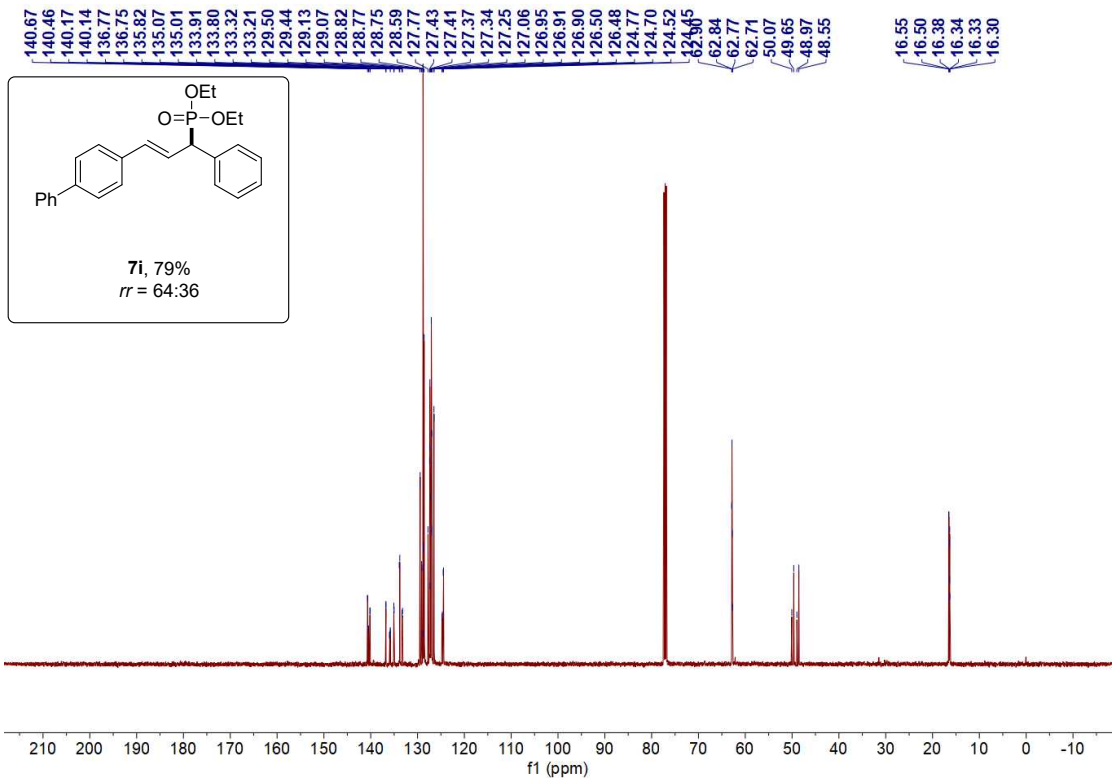


diethyl (E)-(3-([1,1'-biphenyl]-4-yl)-1-phenylallyl)phosphonate (7i)

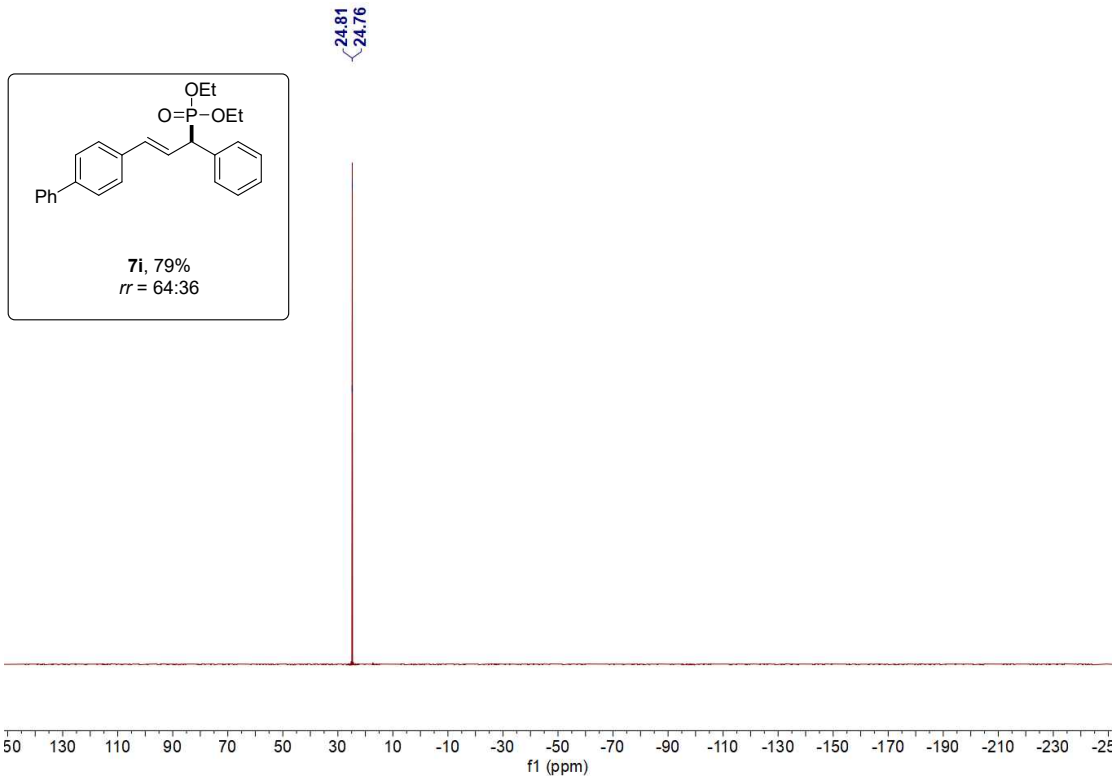
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

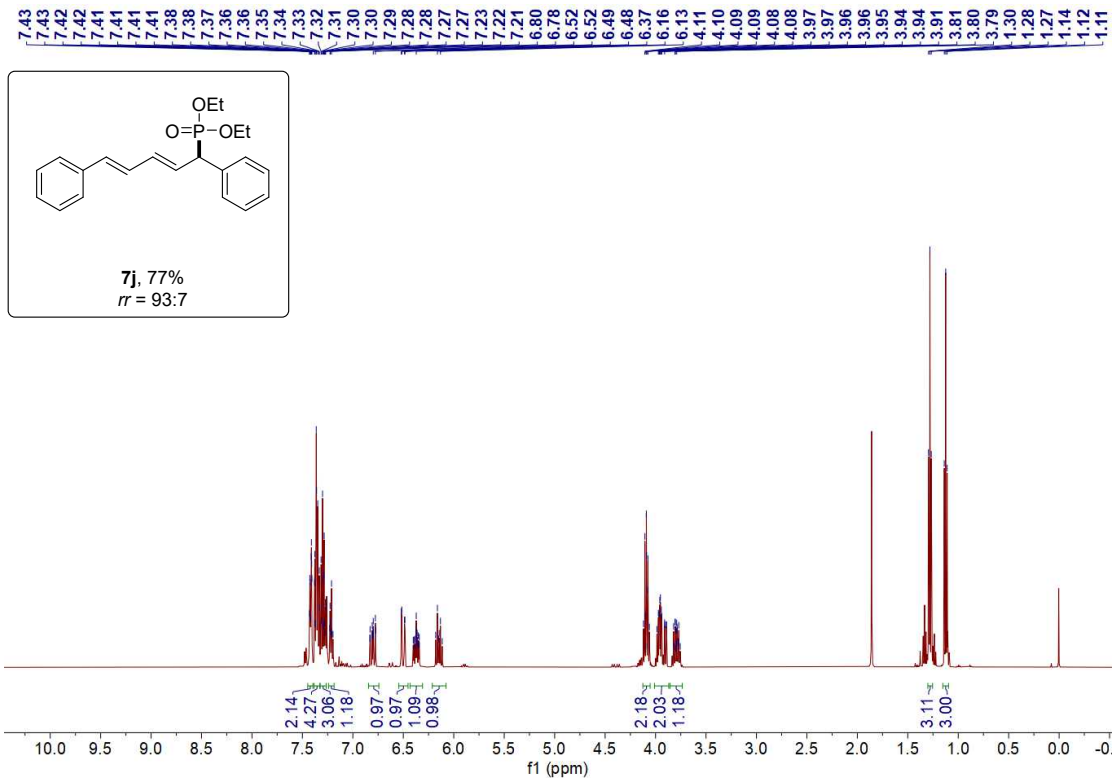


^{31}P NMR (202 MHz, Chloroform-d)

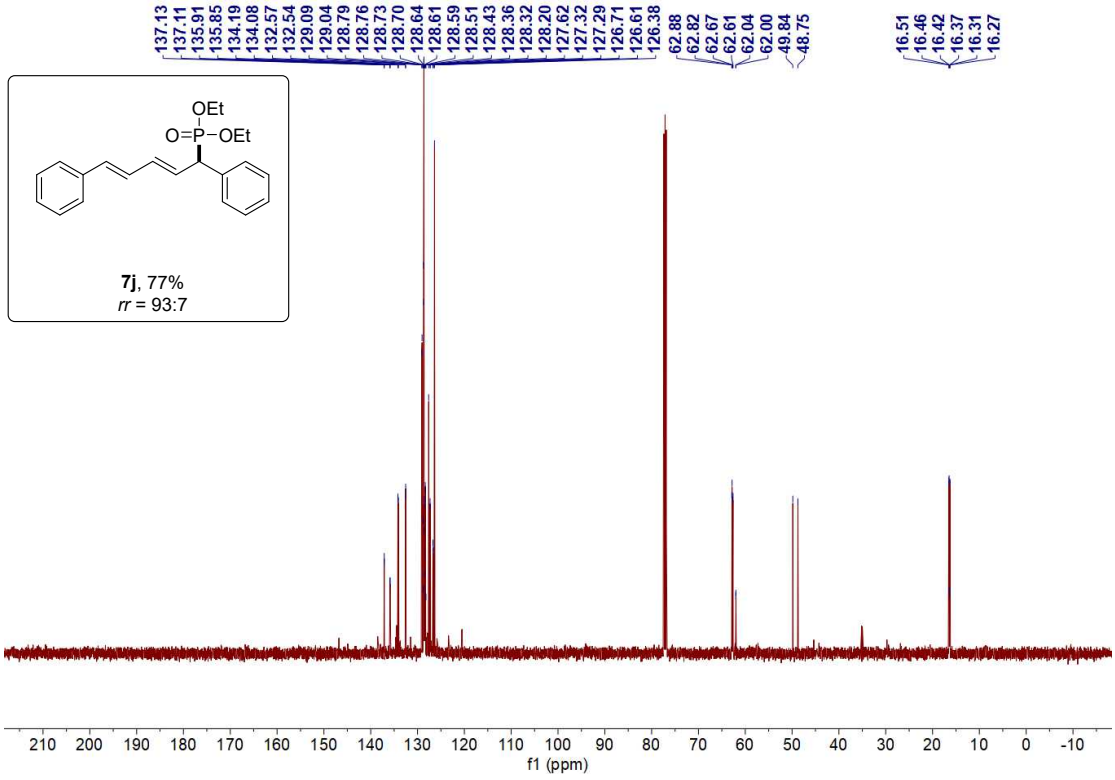


diethyl ((2E,4E)-1,5-diphenylpenta-2,4-dien-1-yl)phosphonate (7j)

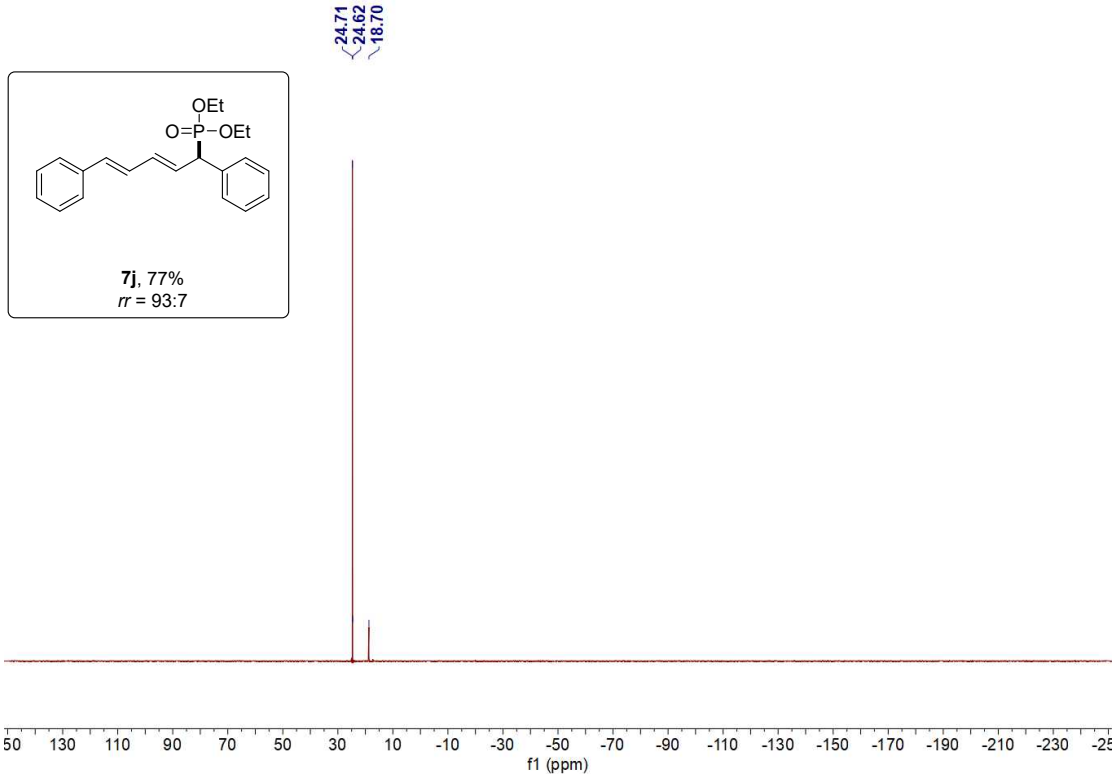
^{1}H NMR (500 MHz, Chloroform-d)



^{13}C NMR (126 MHz, Chloroform-d)

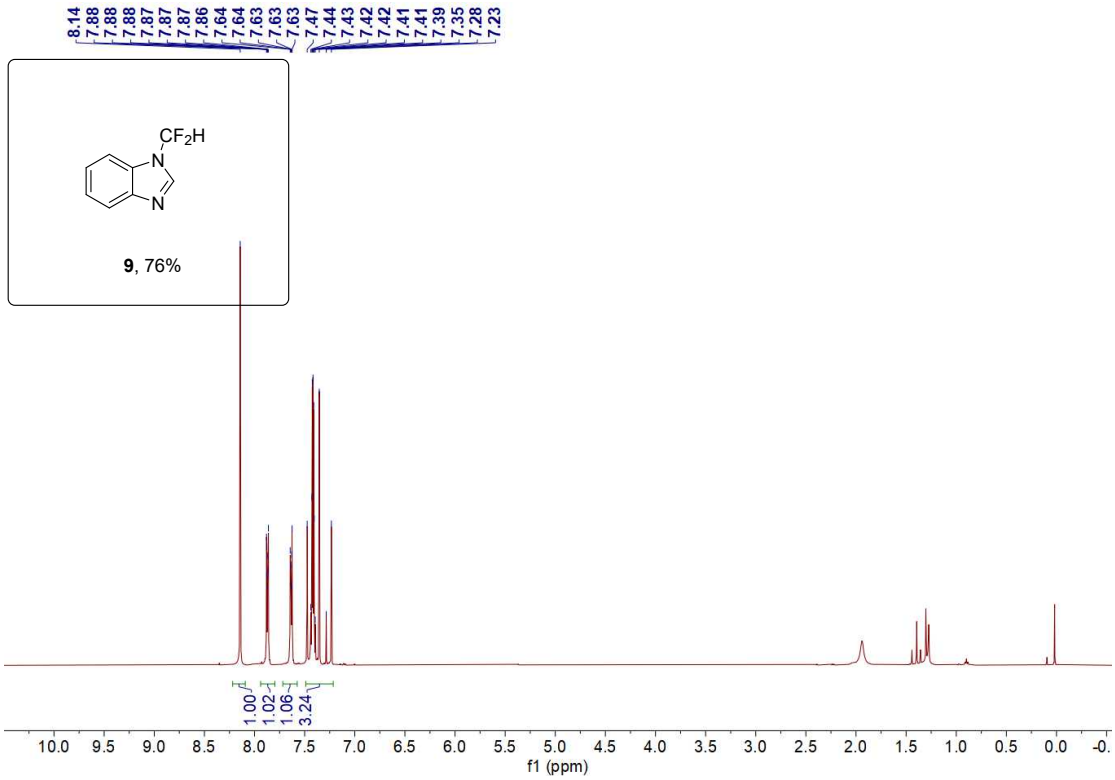


^{31}P NMR (202 MHz, Chloroform-d)

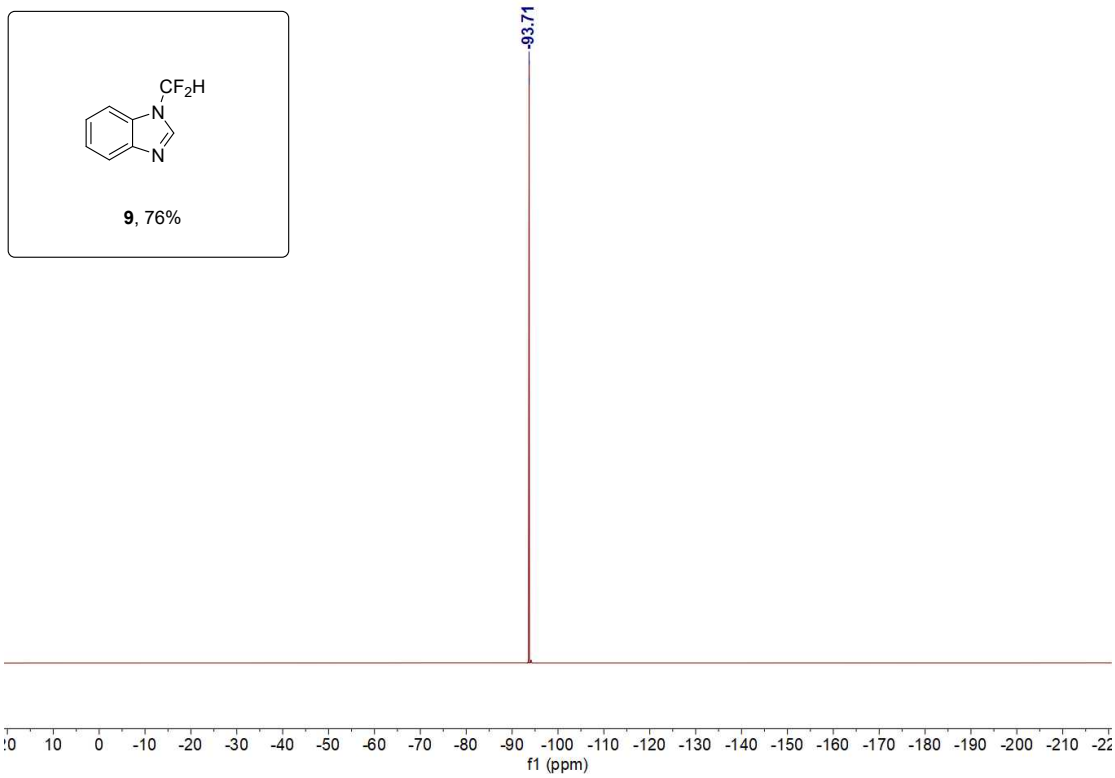


1-(difluoromethyl)-1H-benzo[d]imidazole

^{1}H NMR (500 MHz, Chloroform-d)

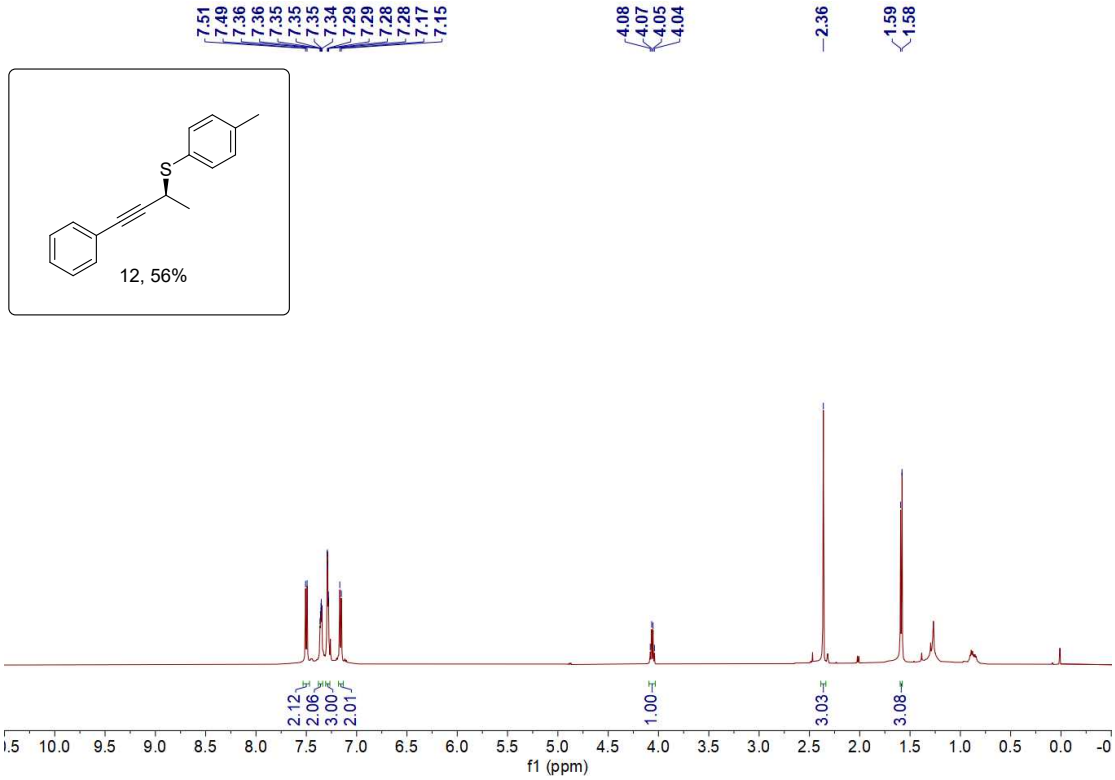


^{13}C NMR (126 MHz, Chloroform-d)

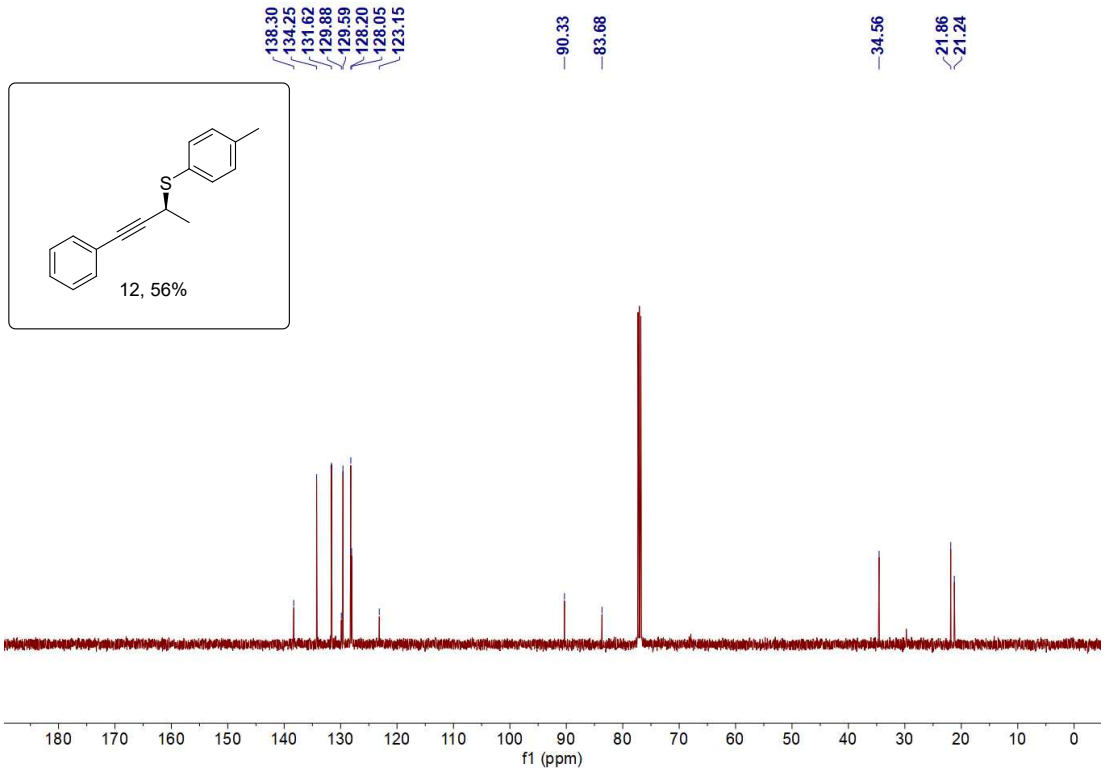


(S)-(4-phenylbut-3-yn-2-yl)(p-tolyl)sulfane

^{1}H NMR (126 MHz, Chloroform-d)

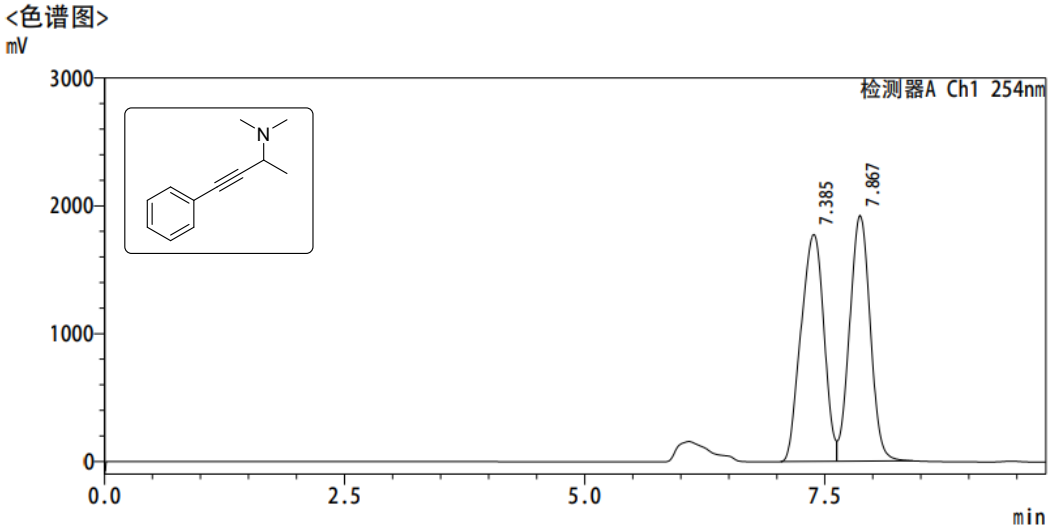


^{13}C NMR (126 MHz, Chloroform-d)



2.5 HPLC spectra

<色谱图>



<峰表>

检测器A Ch1 254nm

峰号	保留时间	面积%
1	7.385	50.814
2	7.867	49.186
总计		100.000

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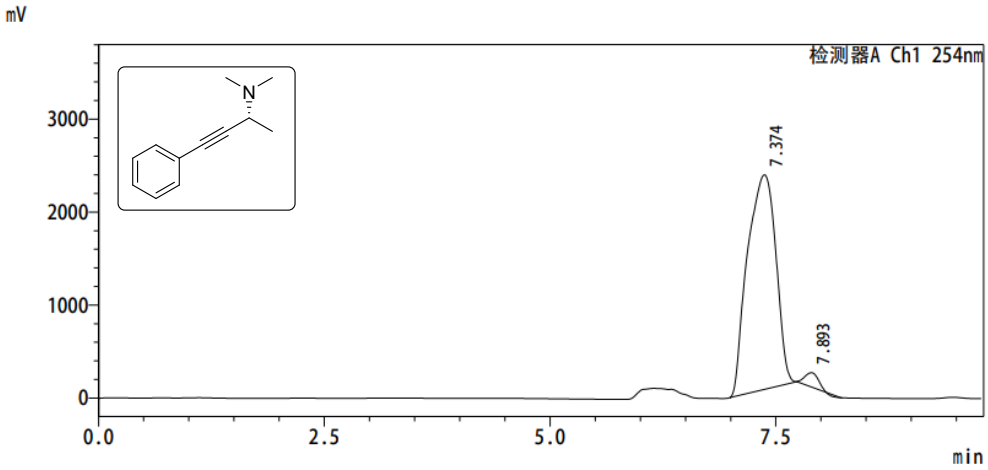
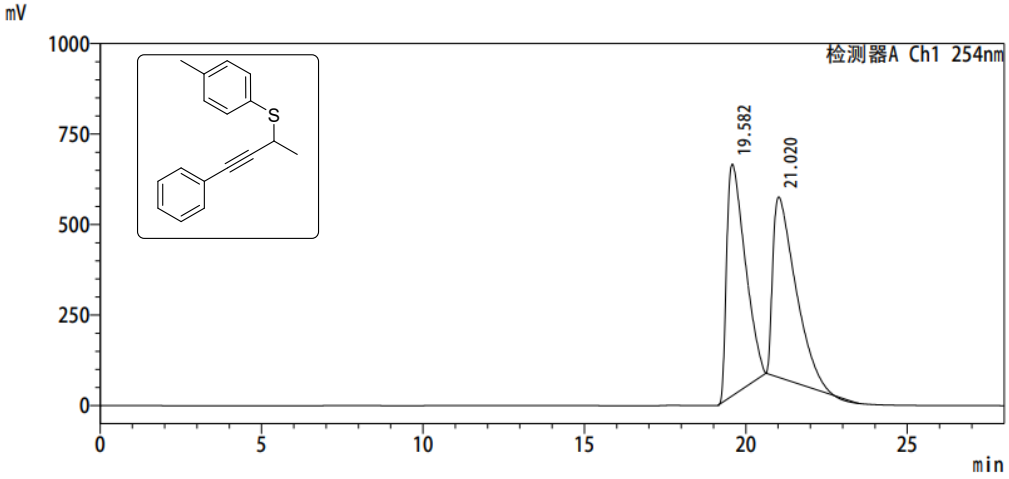


<峰表>

检测器A Ch1 254nm

峰号	保留时间	面积%
1	7.374	97.259
2	7.893	2.741
总计		100.000

<色谱图>



<峰表>

检测器A Ch1 254nm

峰号	保留时间	面积%
1	19.582	50.635
2	21.020	49.365
总计		100.000

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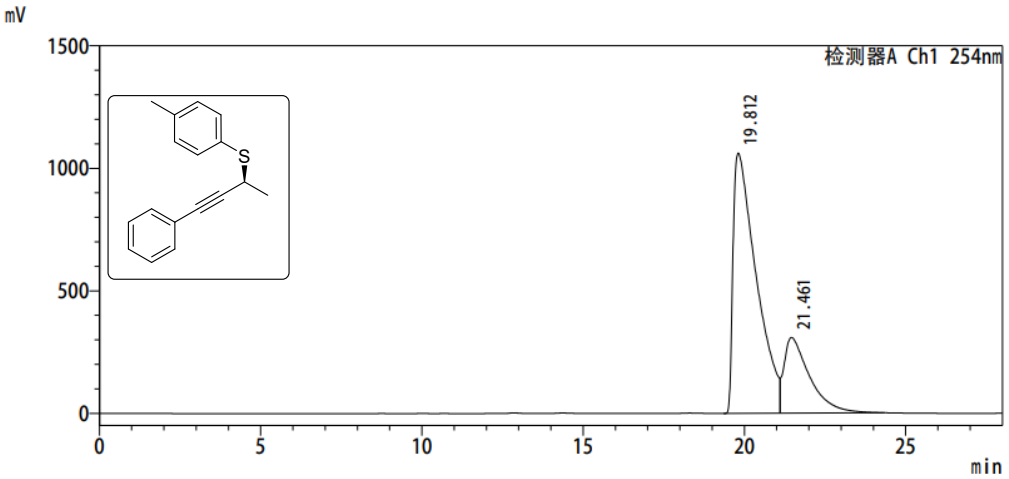

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检测器A Ch1 254nm

峰号	保留时间	面积%
1	19.812	75.632
2	21.461	24.368
总计		100.000

2.6 References

[1]. Zhou, X.; Zhang, G.; Huang, R.; Huang, H., Palladium-Catalyzed Allyl–Allyl Reductive Coupling of Allylamines or Allylic Alcohols with H2 as Sole Reductant. *Org Lett* **2021,** *23*, 365-369.

[2]. Guisán-Ceinos, M.; Martín-Heras, V.; Tortosa, M., Regio- and Stereospecific Copper-Catalyzed Substitution Reaction of Propargylic Ammonium Salts with Aryl Grignard Reagents. *J. Am. Chem. Soc.* **2017,** *139*, 8448-8451.

[3]. Zhu, M.; Zheng, C.; Zhang, X.; You, S.-L., Synthesis of Cyclobutane-Fused Angular Tetracyclic Spiroindolines via Visible-Light-Promoted Intramolecular Dearomatization of Indole Derivatives. *Journal of the American Chemical Society* **2019,** *141*, 2636-2644.

[4]. Zhang, X.; Xu, A.; Ran, Y.; Wei, C.; Xie, F.; Wu, J., Design, synthesis and biological evaluation of phenyl vinyl sulfone based NLRP3 inflammasome inhibitors. *Bioorganic Chemistry* **2022,** *128*, 106010.