Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

An Effective Promoter for Reductive Coupling Reactions of Nitrodienes with Unactivated Alkenes: Sodium Phosphate Dibasic Heptahydrate

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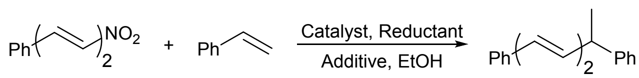
1 Preparation of substrates

The nitrodienes were prepared as reported in respective literature.[1] All characterization data are in accordance with the previous literature.

2 Optimization of Reaction Conditions[a]

Table S1. Catalyst screening [a]

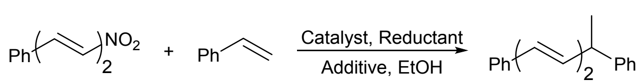


1a **2a**

Entry	Catalyst	Catalyst (mol%)	yield%[b]
1	$Fe(acac)_3$	10	23
2	$Fe(acac)_3$	20	30
3	$Fe(acac)_3$	30	48
4	$Fe(dibm)_3$	30	39
5	$Ni(acac)_3$	30	25
6	$Fe(OX)_3$	30	trace
7	$Nd(acac)_3$	30	N.R.
8	$Co(acac)_2$	30	N.R.
9	$Er(acac)_3$	30	N.R.

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), Styrene (2 equiv), catalyst, $PhSiH_3$ (2 equiv) and $Na_2HPO_4{\cdot}7H_2O$ (2 equiv) was added in 2 mL of EtOH under atmosphere at 40°C for 2 h. [b] Isolated yields are given. N.R.=No reaction.

Table S2. Catalyst loading variation [a]

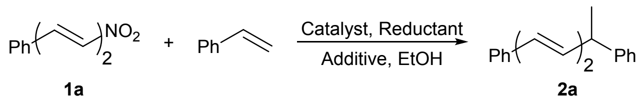


1a **2a**

Entry	Catalyst	Reductant	yield%[b]
1	$Fe(acac)_3$	$PhSiH_3$	48
2[c]	$Fe(acac)_3$	Et_3SiH	N.R.
3	$Fe(acac)_3$	Ph_3SiH	N.R.
4	$Fe(acac)_3$	$(EtO)_3SiH$	34
5	$Fe(acac)_3$	PMHS	43

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), Styrene (2 equiv), $Fe(acac)_3$ (30 mol %), reductant (2 equiv) and $Na_2HPO_4{\cdot}7H_2O$ (2 equiv) was added in 2 mL of EtOH under atmosphere at 40°C for 2 h. [b] Isolated yields are given. N.R.=No reaction.

Table S3. Variation base screening [a]



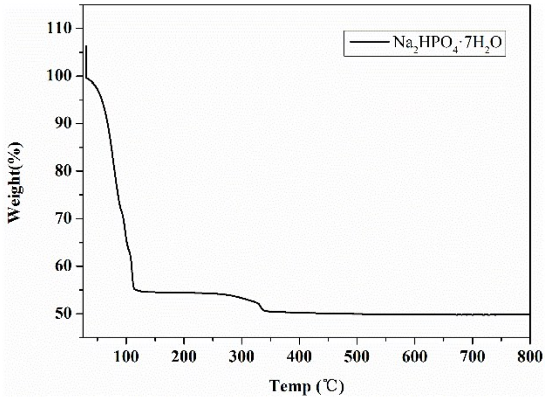
Entry	Catalyst	Additive	Time	Temperature	yield%[b]
1	$Fe(acac)_3$	Na_2CO_3	2h	40	51
2	$Fe(acac)_3$	$NaC_2H_3O_2$	2h	40	47
3	$Fe(acac)_3$	$Na_2S_2O_3$	2h	40	44
4	$Fe(acac)_3$	K_2CO_3	2h	40	45
5	$Fe(acac)_3$	$KC_2H_3O_2$	2h	40	43
6	$Fe(acac)_3$	K_3PO_4	2h	40	42
7	$Fe(acac)_3$	$NaNO_3$	2h	40	33
8	$Fe(acac)_3$	$NH_4C_2H_3O_2$	2h	40	39
9	$Fe(acac)_3$	NH_4NO_3	2h	40	38
10	$Fe(acac)_3$	NH_4Cl	2h	40	34
11	$Fe(acac)_3$	$NaOH$	2h	40	52
12	$Fe(acac)_3$	NaH_2PO_4	2h	40	55
13	$Fe(acac)_3$	Na_2CO_3	2h	40	53
14	$Fe(acac)_3$	Na_2HCO_3	2h	40	51
15	$Fe(acac)_3$	–	2h	40	29
16	$Fe(acac)_3$	NH_4HPO_4	2h	40	45
17	$Fe(acac)_3$	$NaC_2H_3O_2\cdot 2H_2O$	2h	40	55
18	$Fe(acac)_3$	$K_2HPO_4\cdot 2H_2O$	2h	40	57
19	$Fe(acac)_3$	$Na_2HPO_4\cdot 2H_2O$	2h	40	62
20	$Fe(acac)_3$	$Na_2HPO_4\cdot 7\ H_2O$	2h	40	89
21	$Fe(acac)_3$	$Na_2HPO_4\cdot 12\ H_2O$	2h	40	83
22	$Fe(acac)_3$	Na_2HPO_4+7 H_2O	2h	40	12
23	$Fe(acac)_3$	$Na_2HPO_4\cdot 7\ H_2O$	2h	50	71
24	$Fe(acac)_3$	$Na_2HPO_4\cdot 7\ H_2O$	2h	60	58
25	$Fe(acac)_3$	$Na_2HPO_4\cdot 7\ H_2O$	3h	40	65

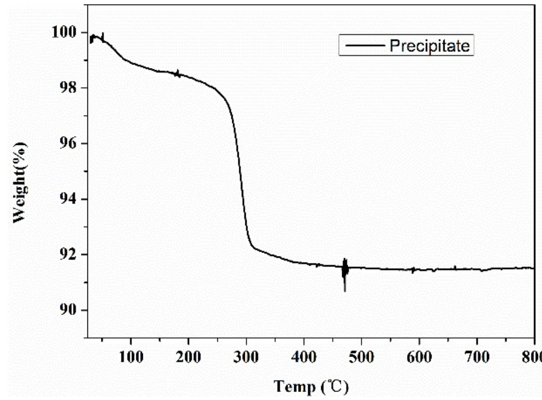
[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), Styrene (2 equiv), $Fe(acac)_3$ (30 mol %), $PhSiH_3$ (2 equiv) and additive (2 equiv) was added in 2 mL of EtOH under atmosphere at 40°C for 2 h. [b] Isolated yields are given. N.R.=No reaction.

3 Mechanistic Investigation

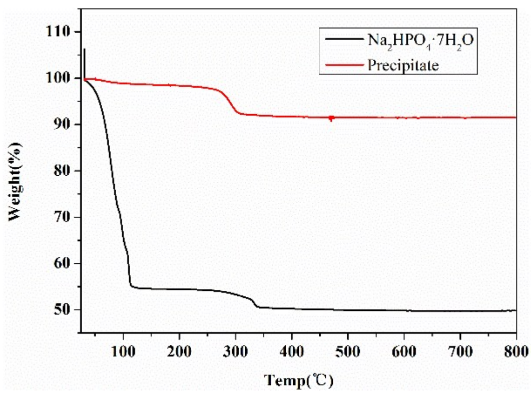
Reaction conditions for GC-MS:

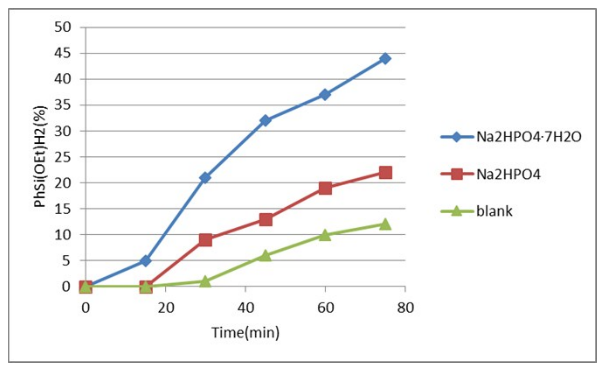
1a (0.2 mmol, 1 equiv), Styrene (2 equiv), $Fe(acac)_3$ (30 mol %), $PhSiH_3$ (2 equiv) and additive (2 equiv) was added in 2 mL of EtOH under Ar protection. After stirring at 40°C for corresponding time, the reaction mixture was quickly cooled in liquid nitrogen under Ar protection before injection. The reaction mixture was allowed to melt under Ar and quickly injected in GC-MS.





a **b**





c **d**

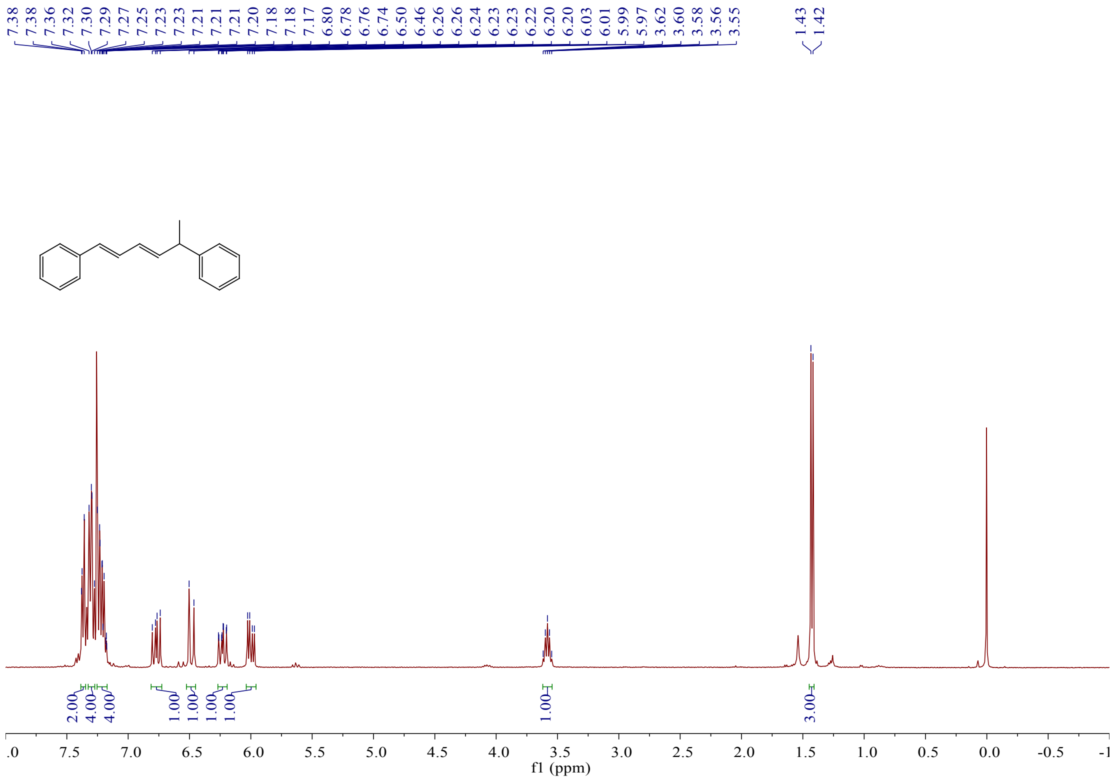
Scheme S1. a: TG-DSC of NaH_2PO_4; b: TG-DSC of resulting precipitate after the reaction; c: comparison of a and b; d: generation of $PhSi(OEt)H_2$ vs time (detected by GC-MS)

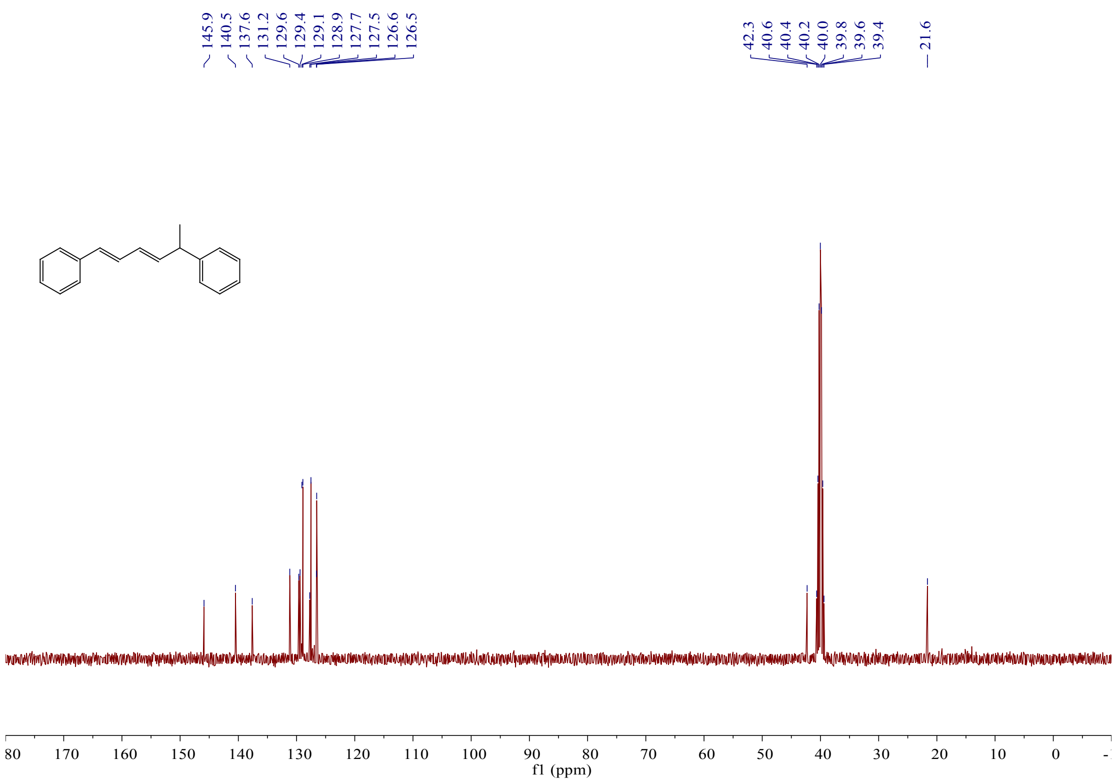
4 References

(1) Dockendorff, C.; Sahli, S.; Olsen, M.; Milhau, L.; Lautens, M. *J. Am. Chem. Soc.* **2005**, 127, 15028–15029.

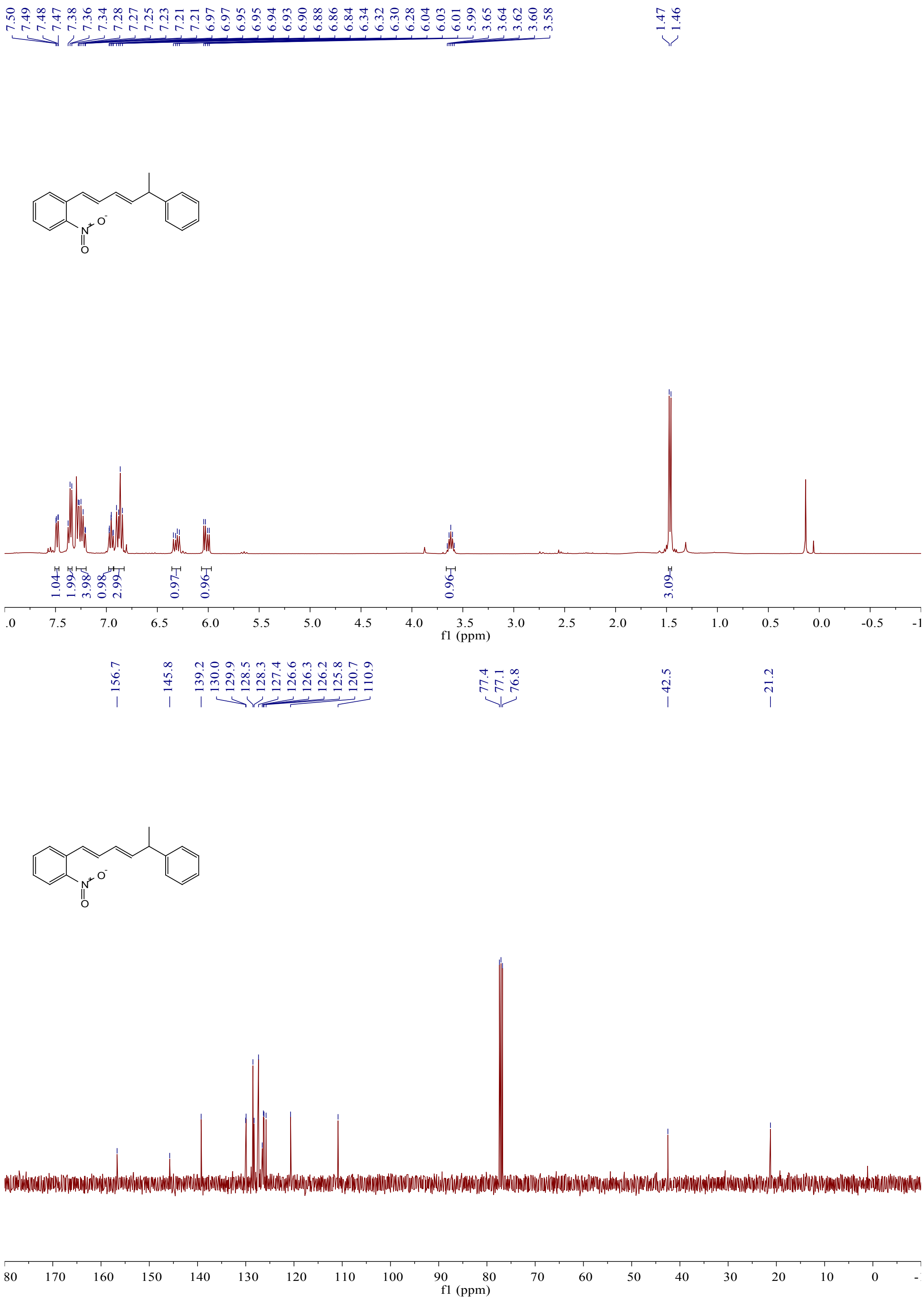
5 ^{1}H and ^{13}C NMR spectra

^{1}H and ^{13}C NMR spectra of **2a**

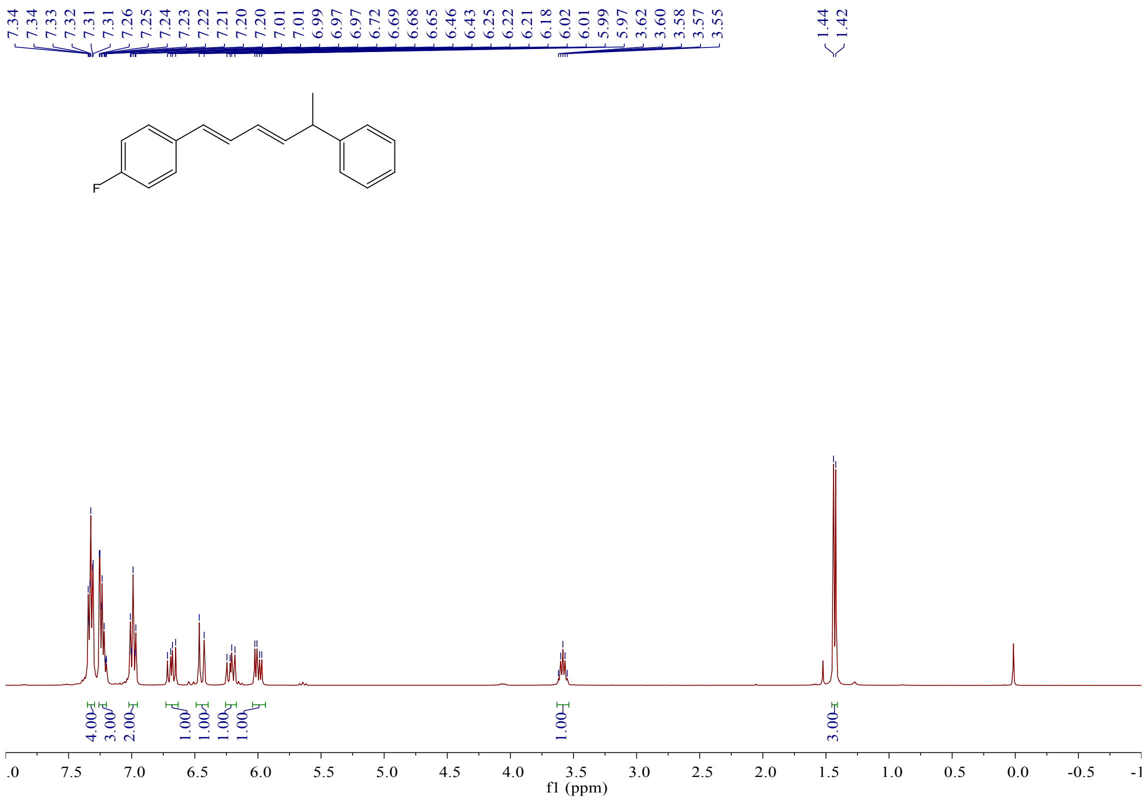


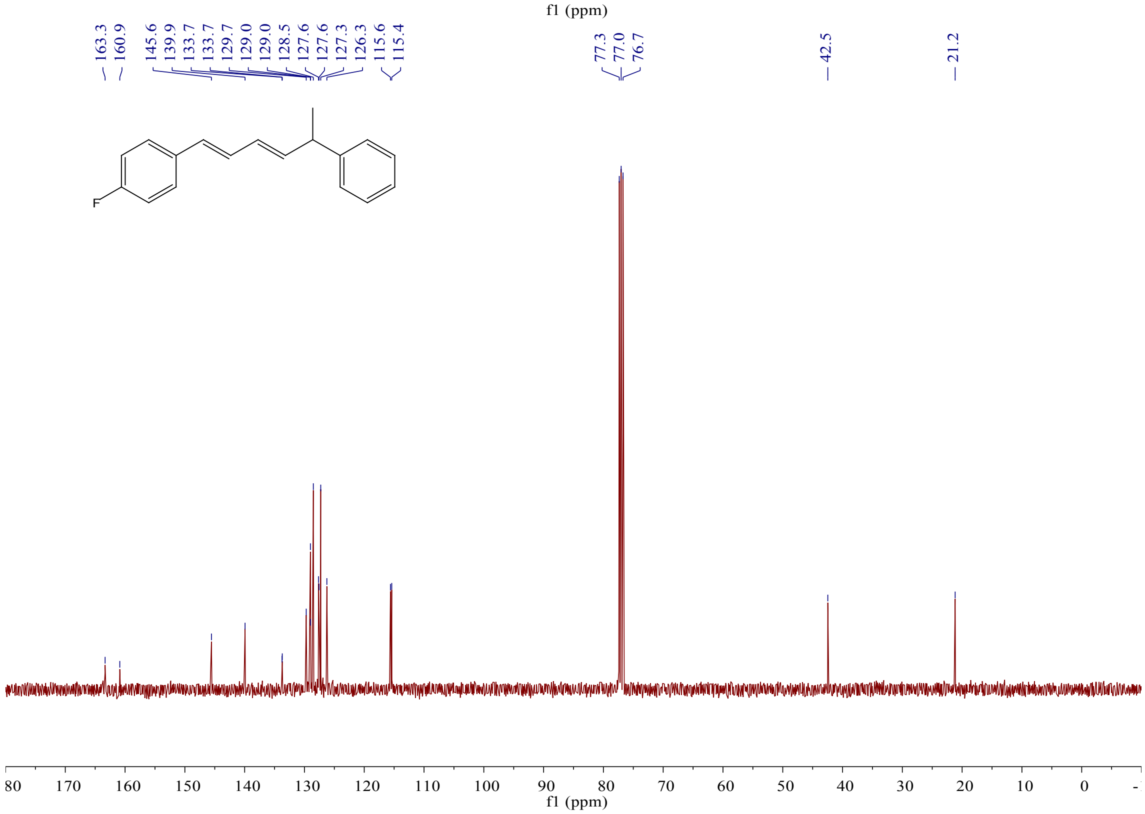


^{1}H and ^{13}C NMR spectra of **2b**

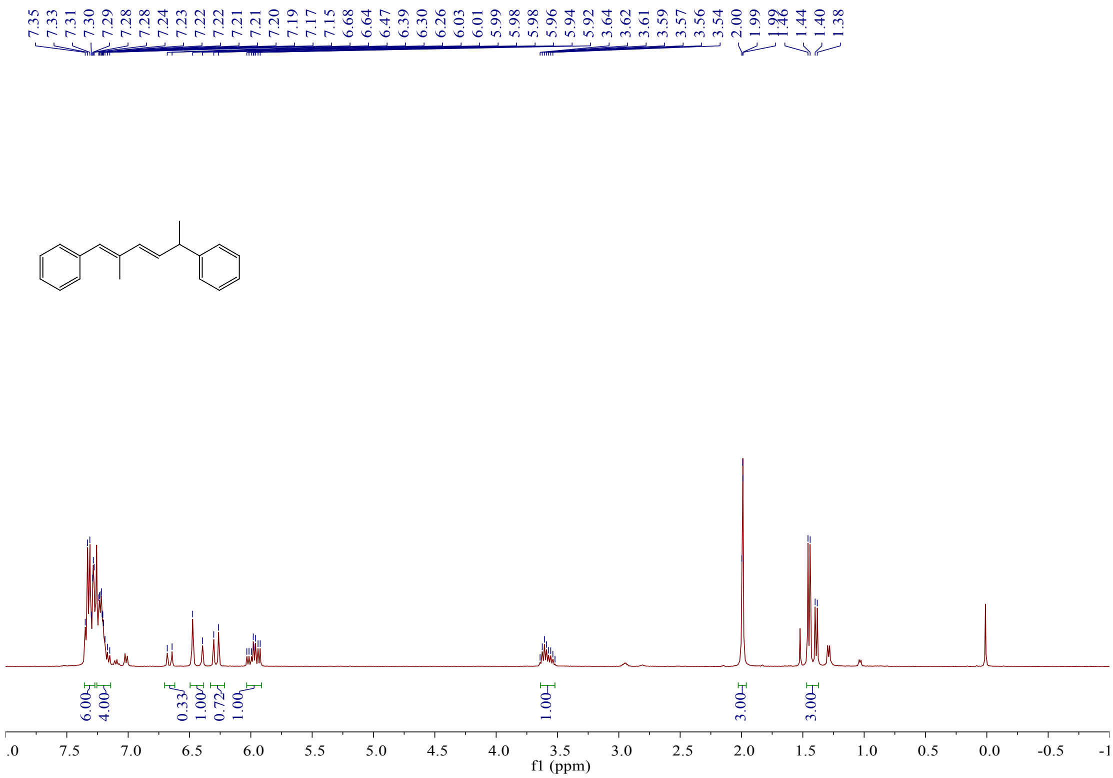


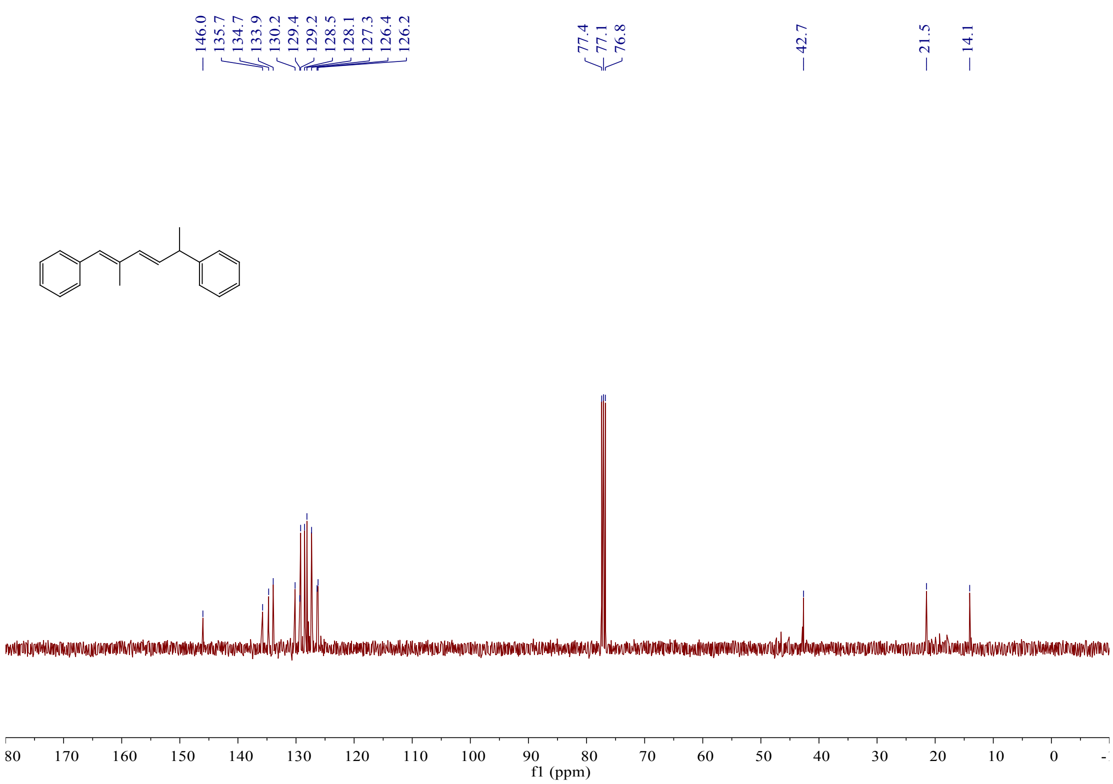
^1H and ^{13}C NMR spectra of **2c**



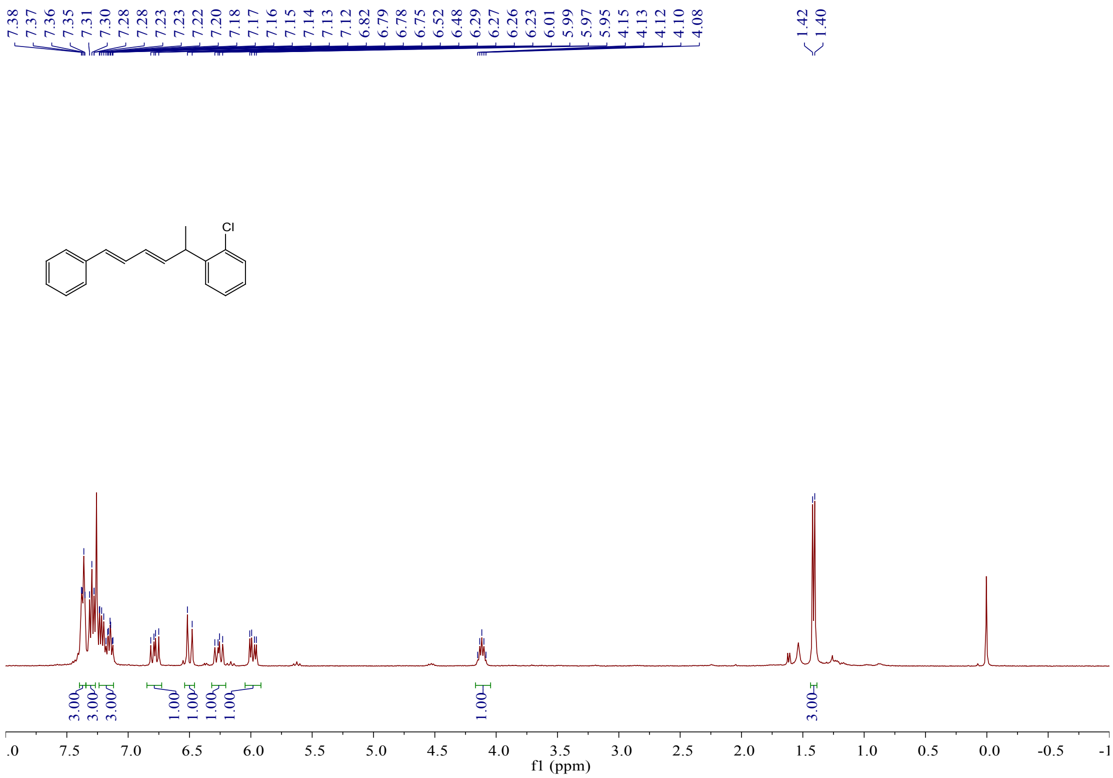


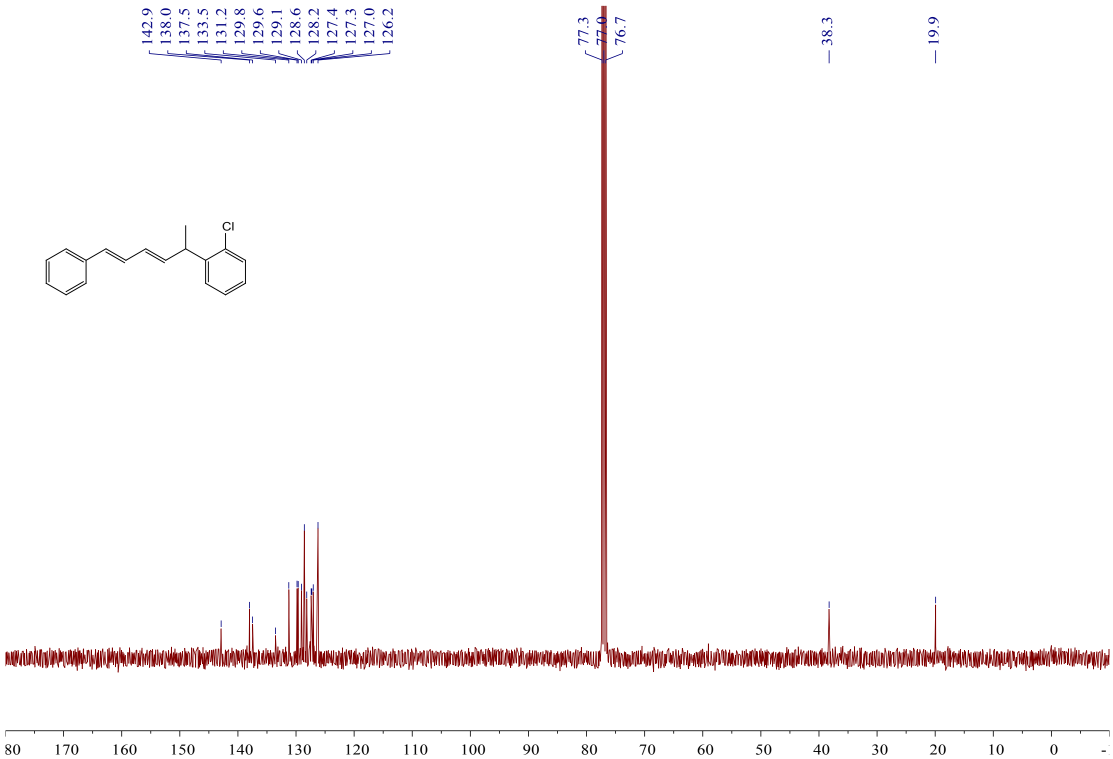
[1]H and [13]C NMR spectra of **2d**



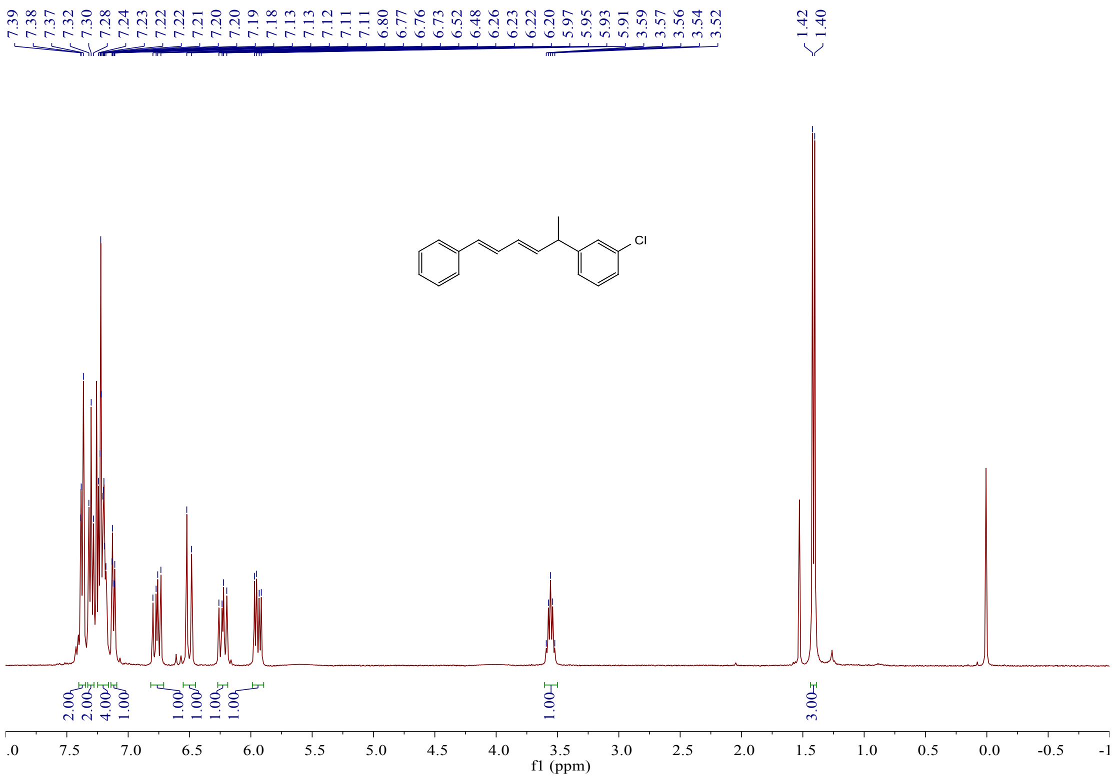


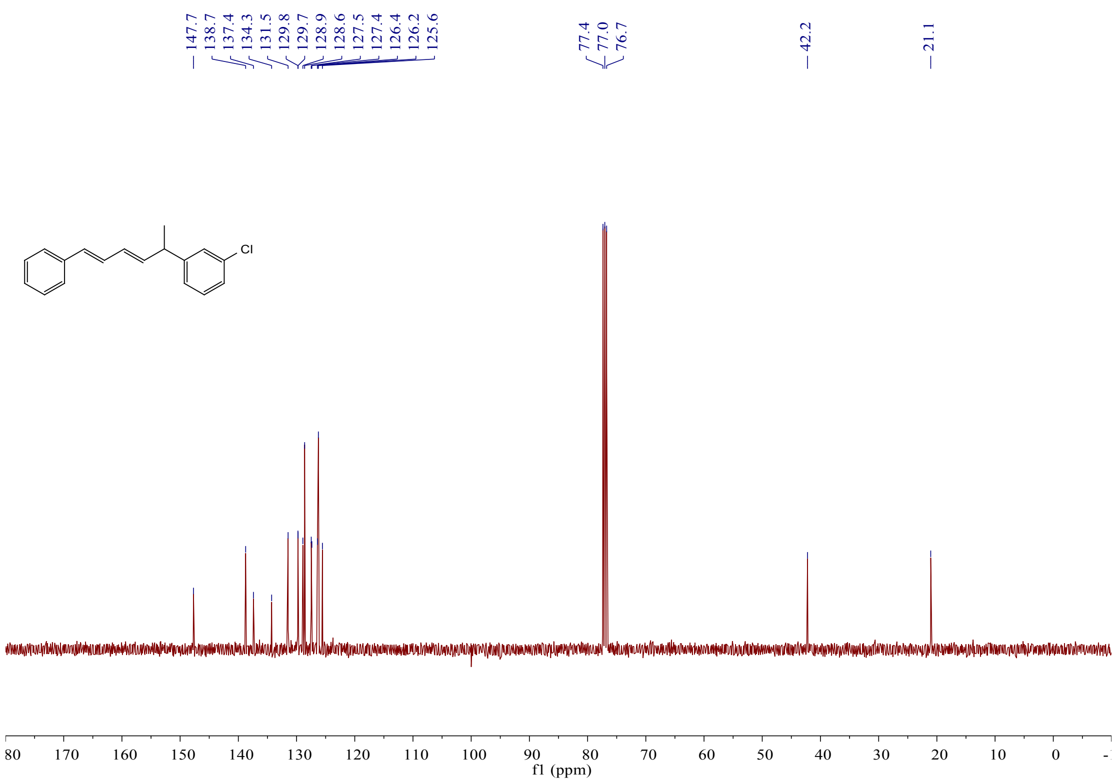
[1]H and [13]C NMR spectra of **2e**



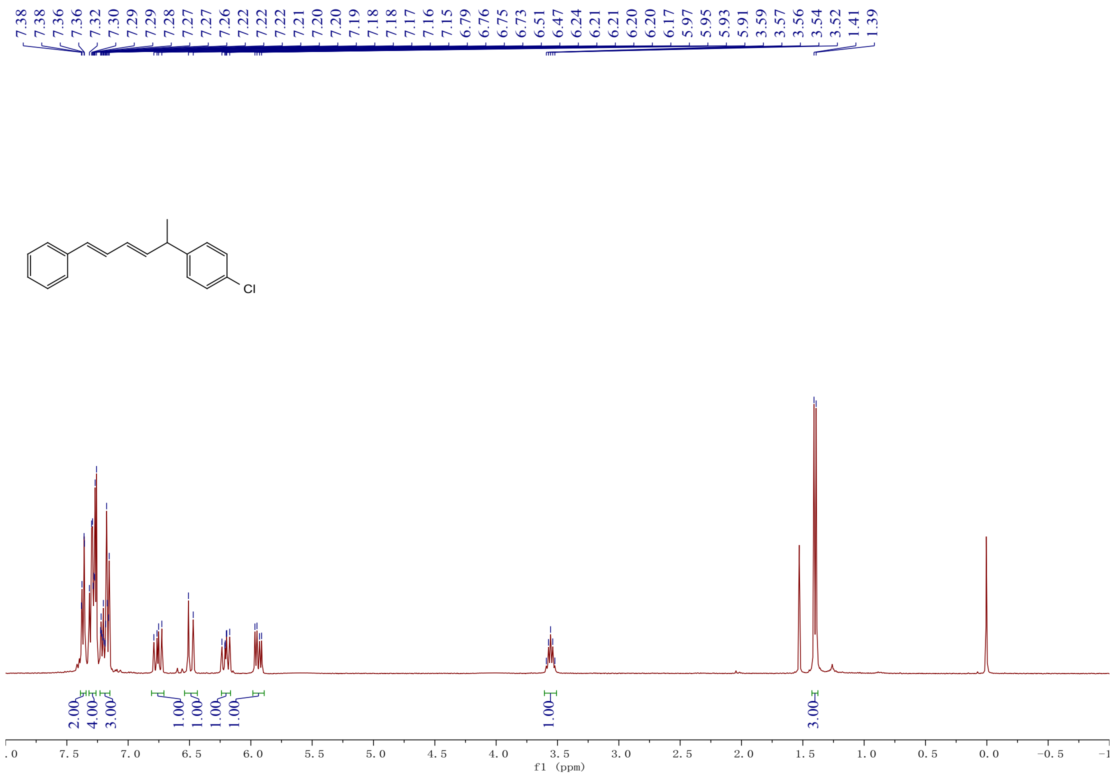


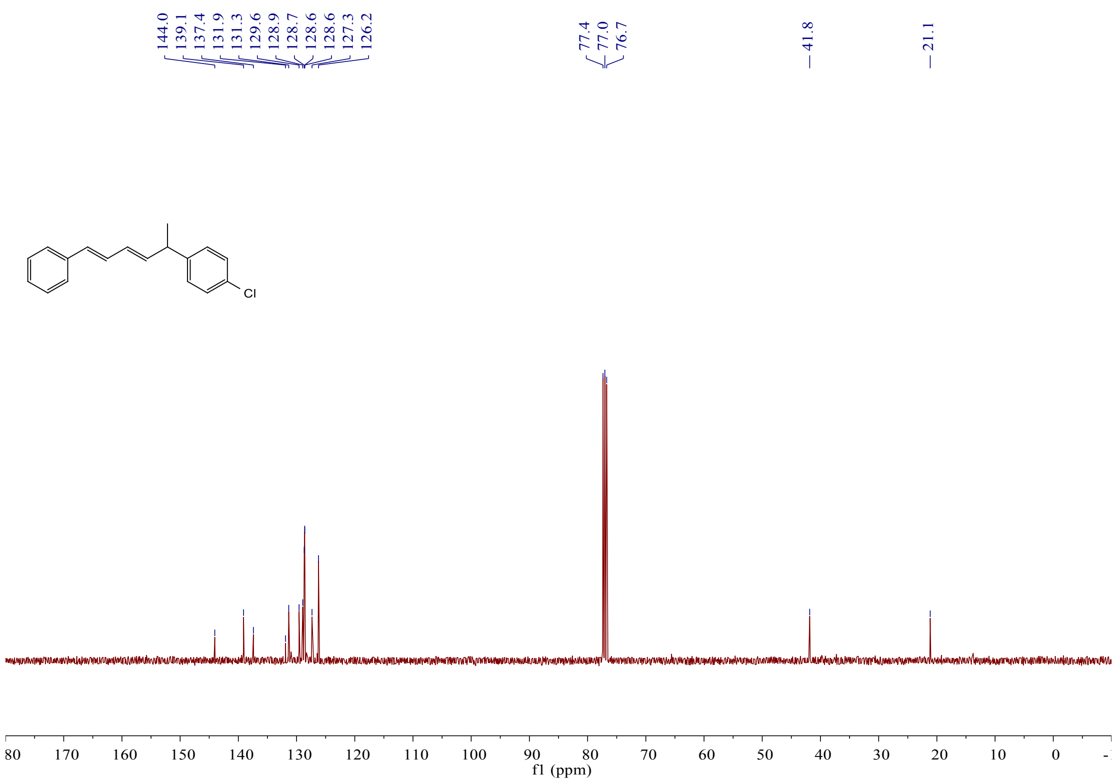
^{1}H and ^{13}C NMR spectra of 2f



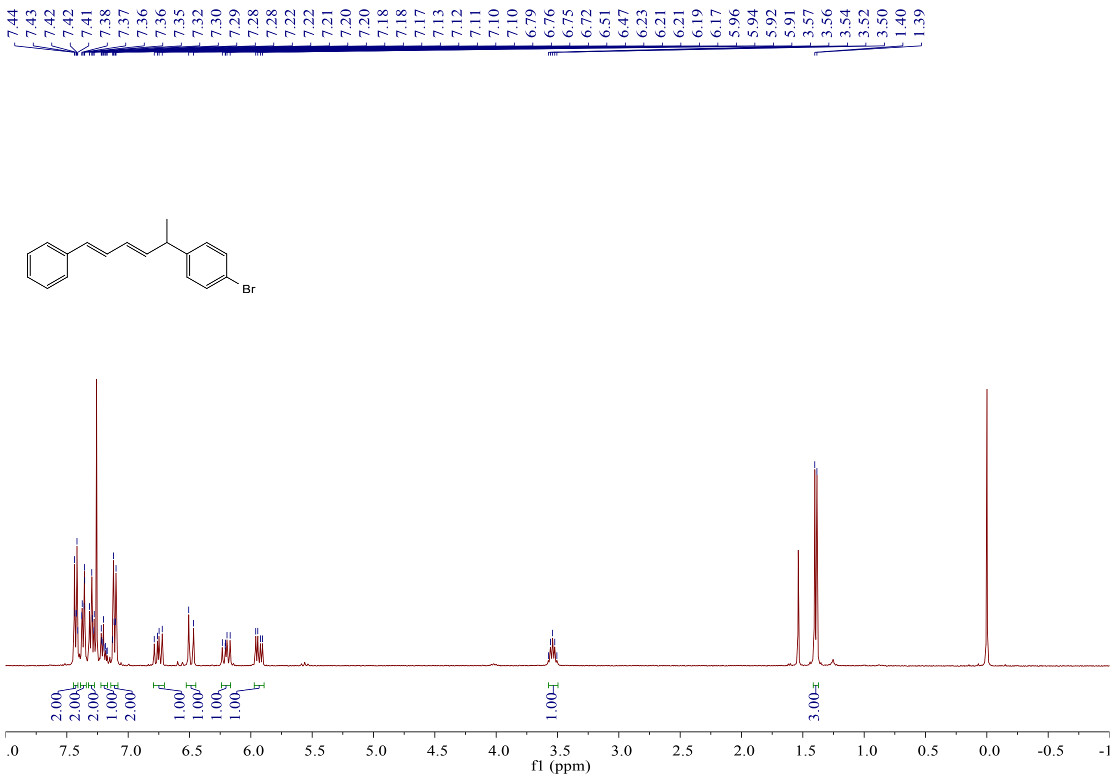


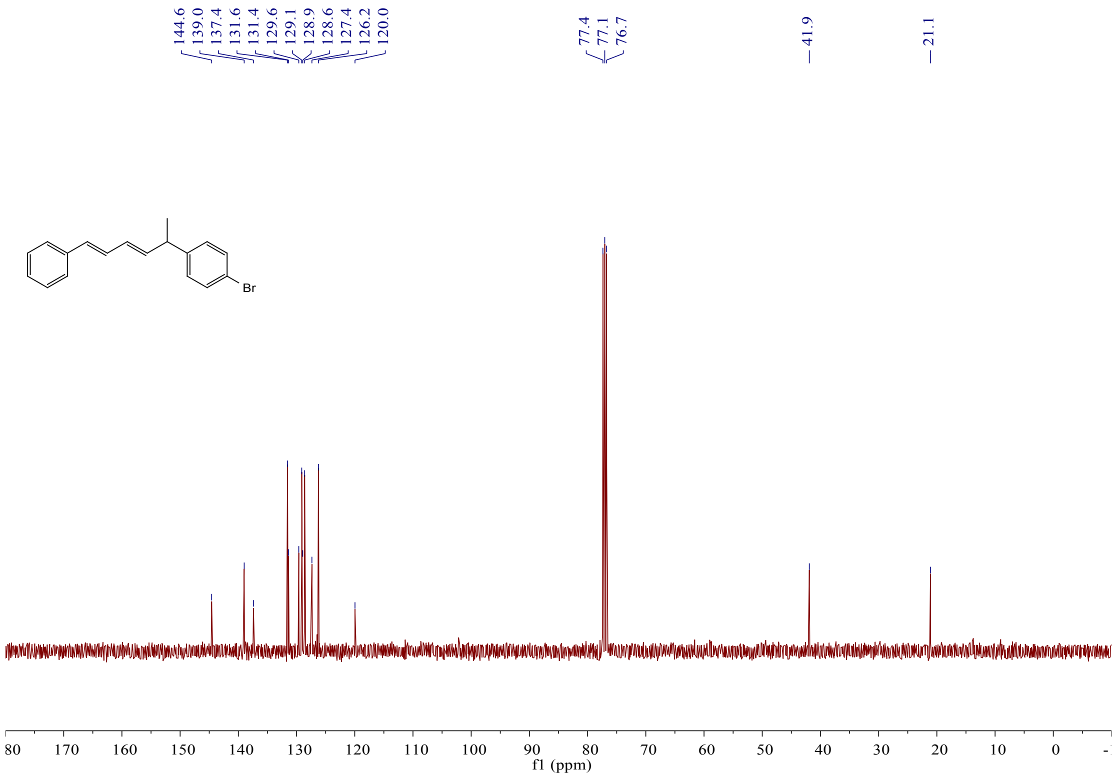
^{1}H and ^{13}C NMR spectra of **2g**



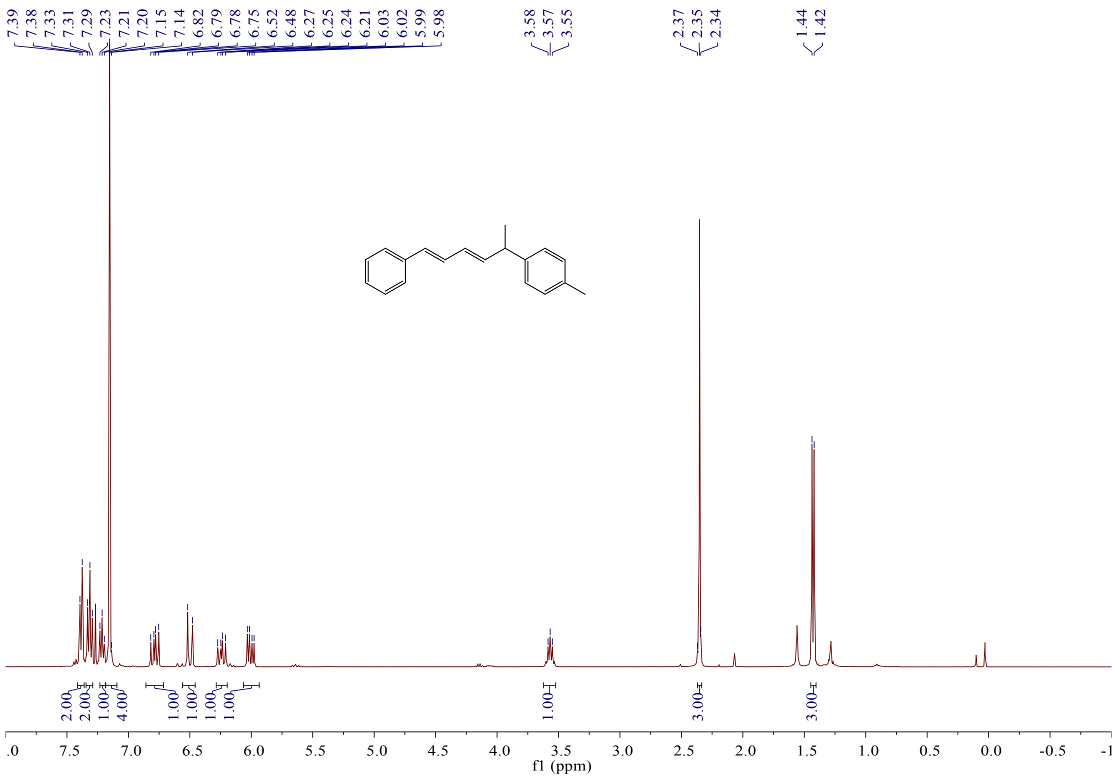


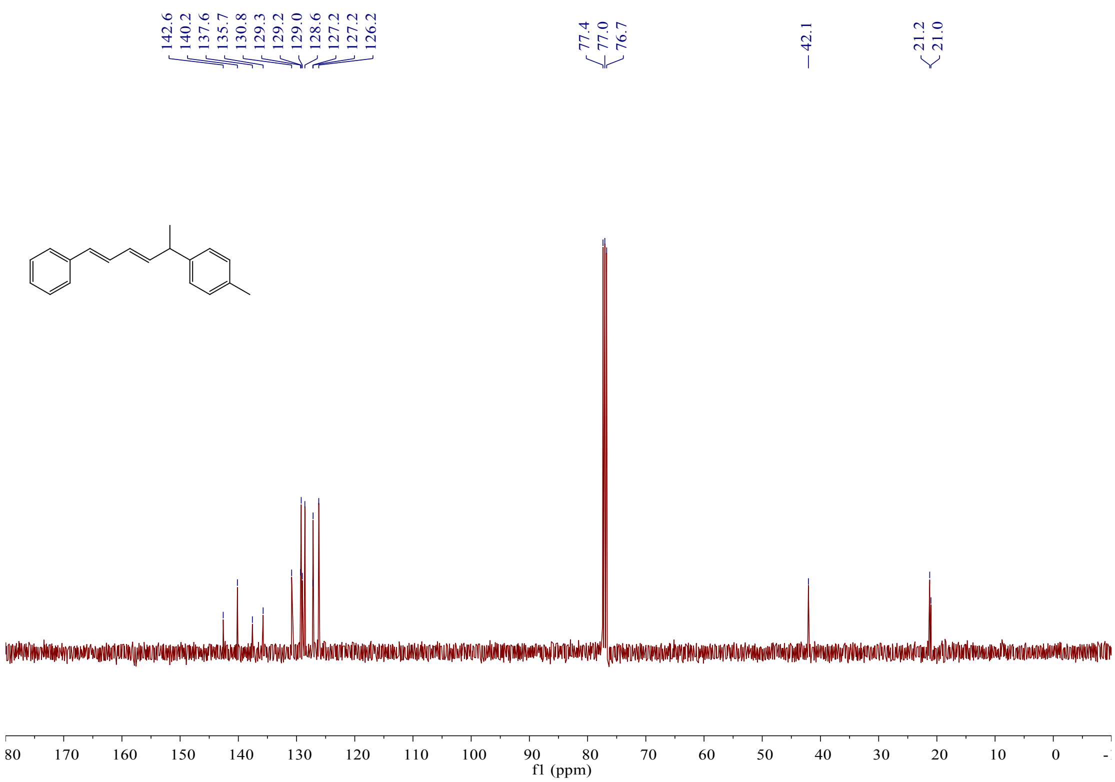
[1]H and [13]C NMR spectra of **2h**



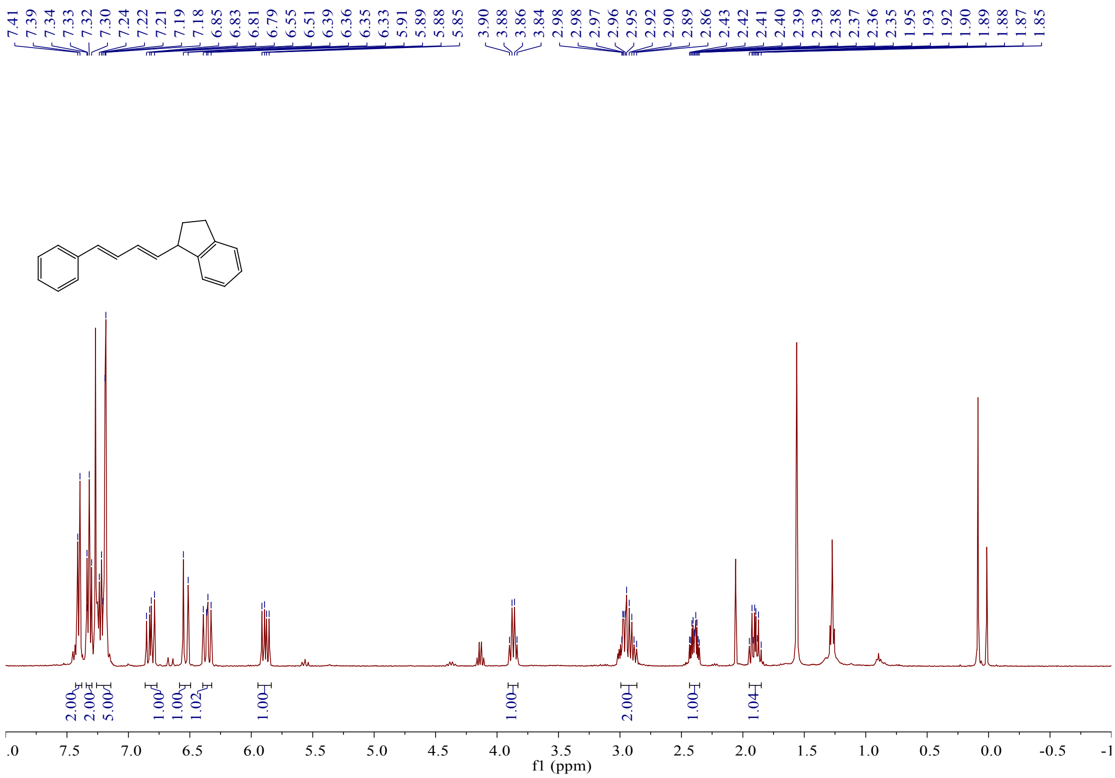


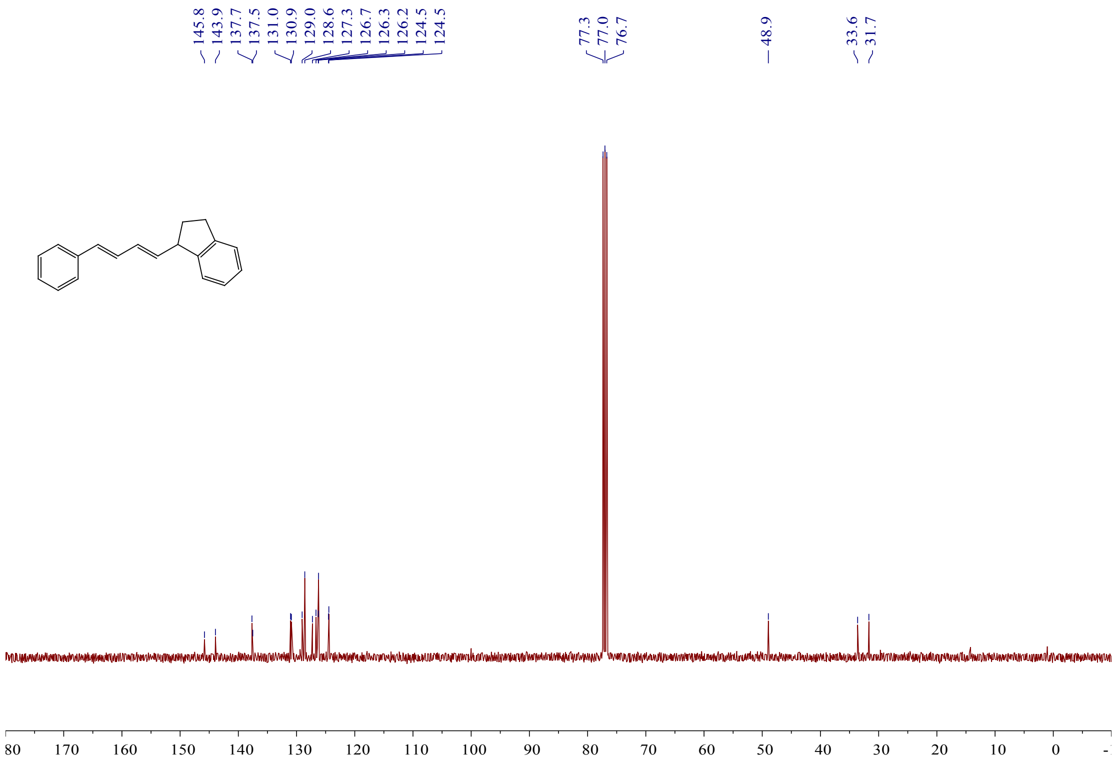
[1]H and [13]C NMR spectra of **2i**



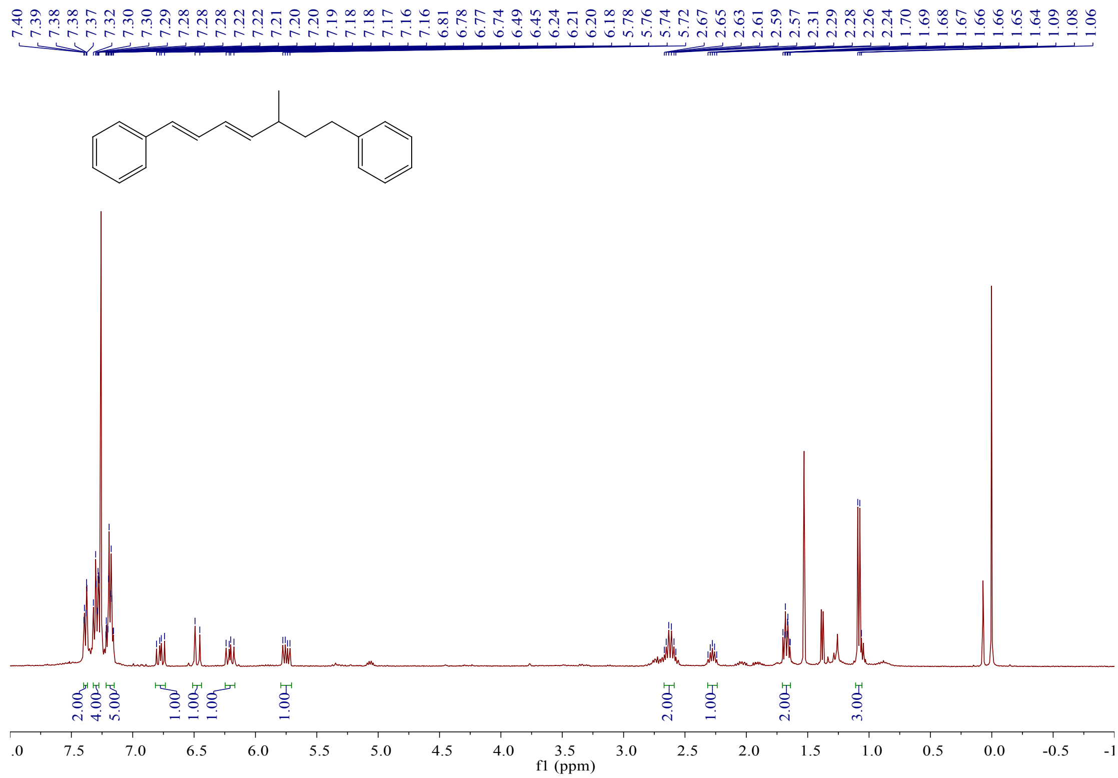


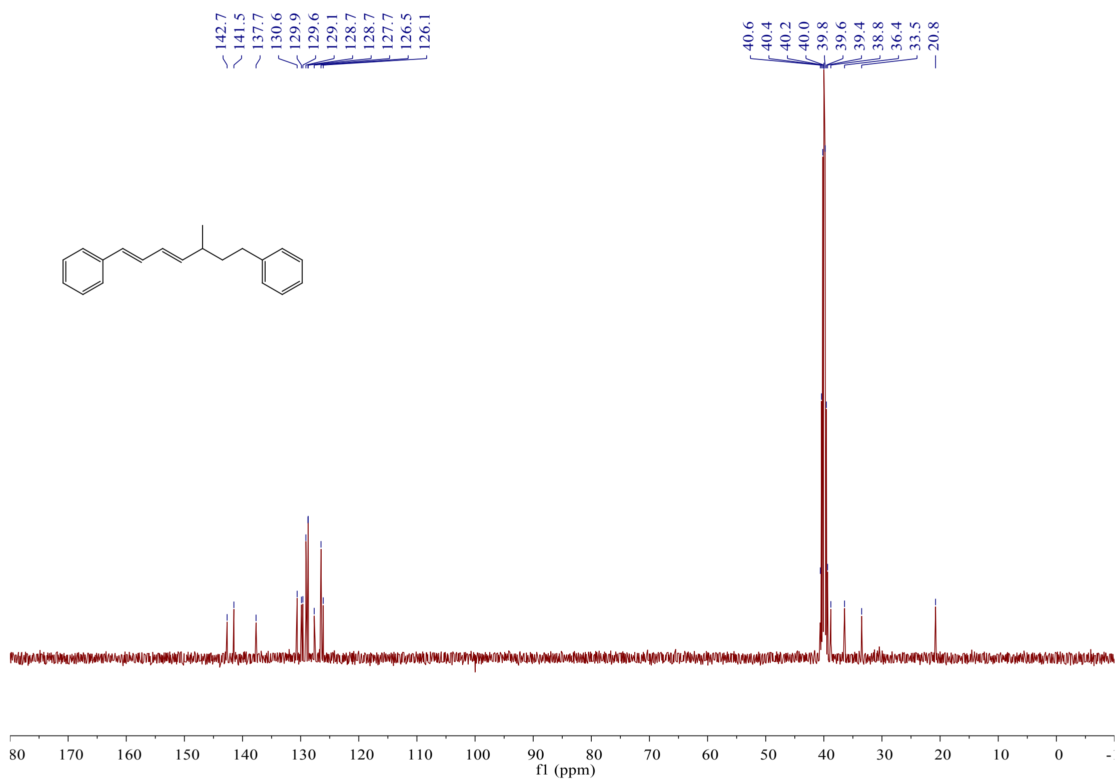
^{1}H and ^{13}C NMR spectra of **2j**



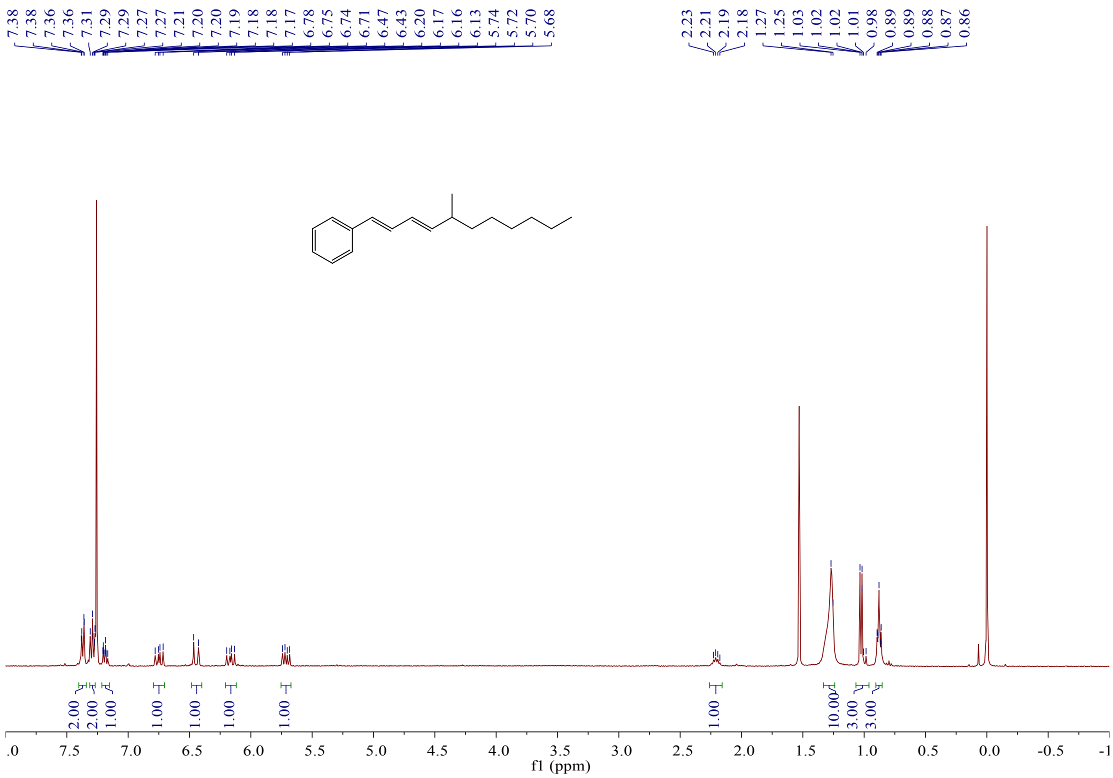


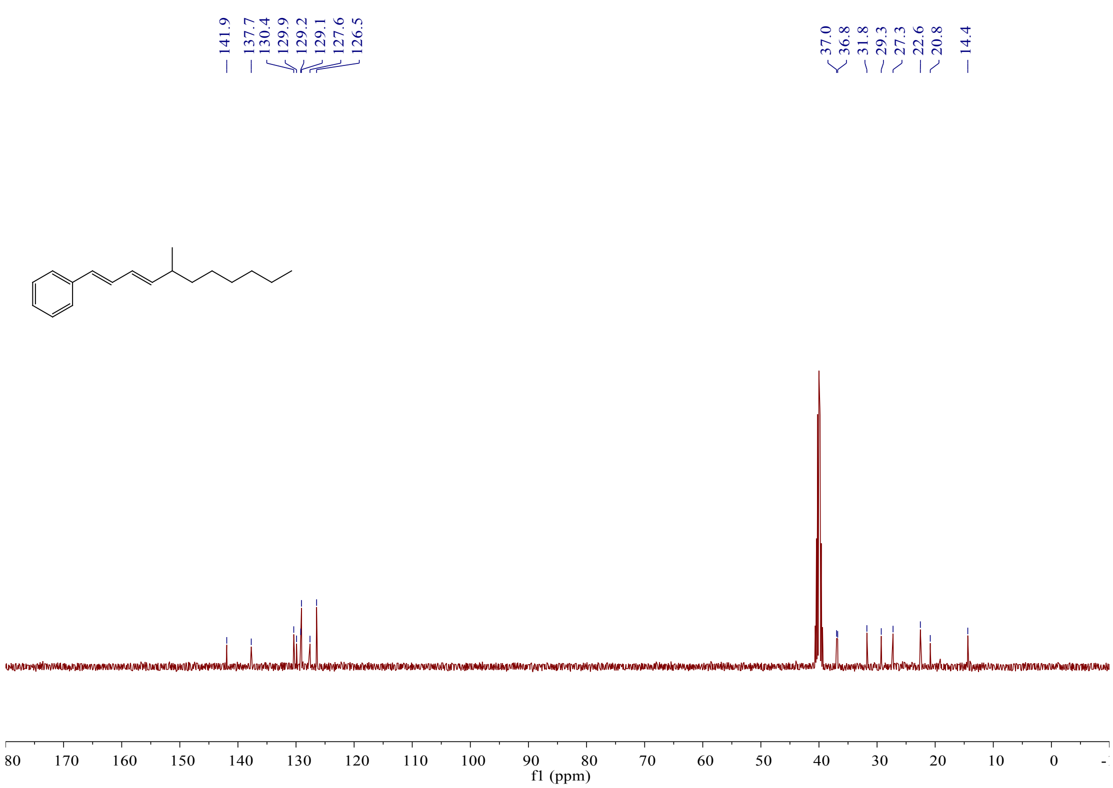
H and ^{13}C NMR spectra of **2k**



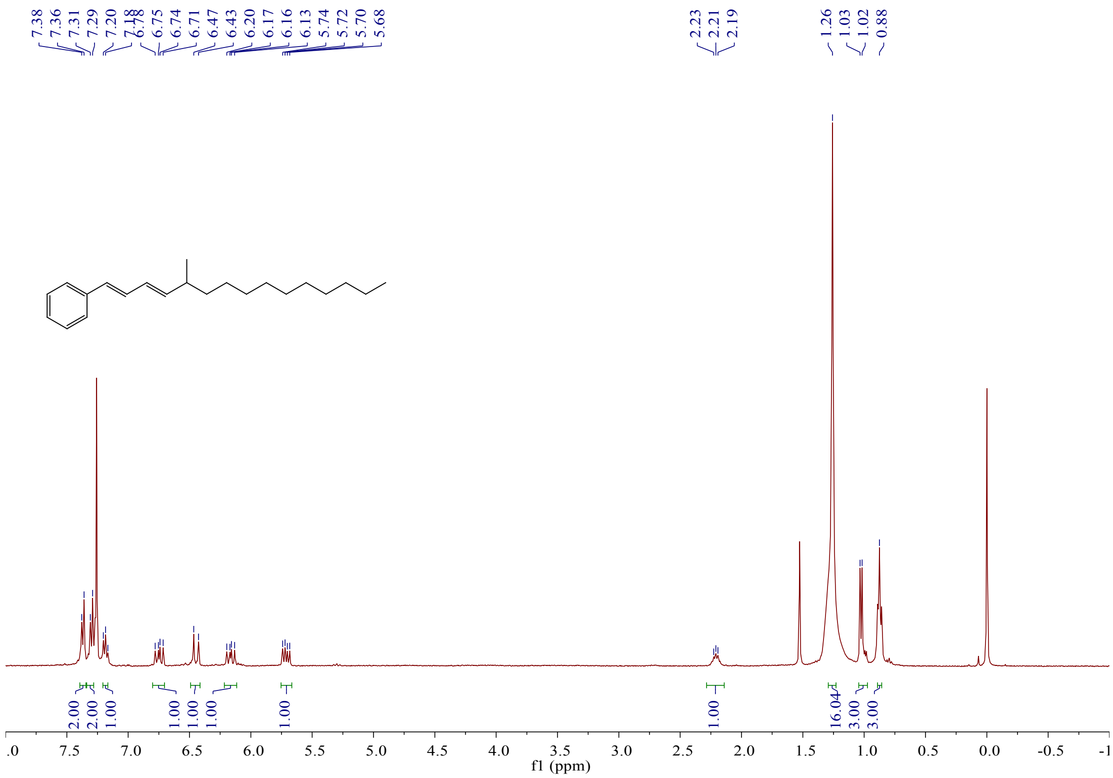


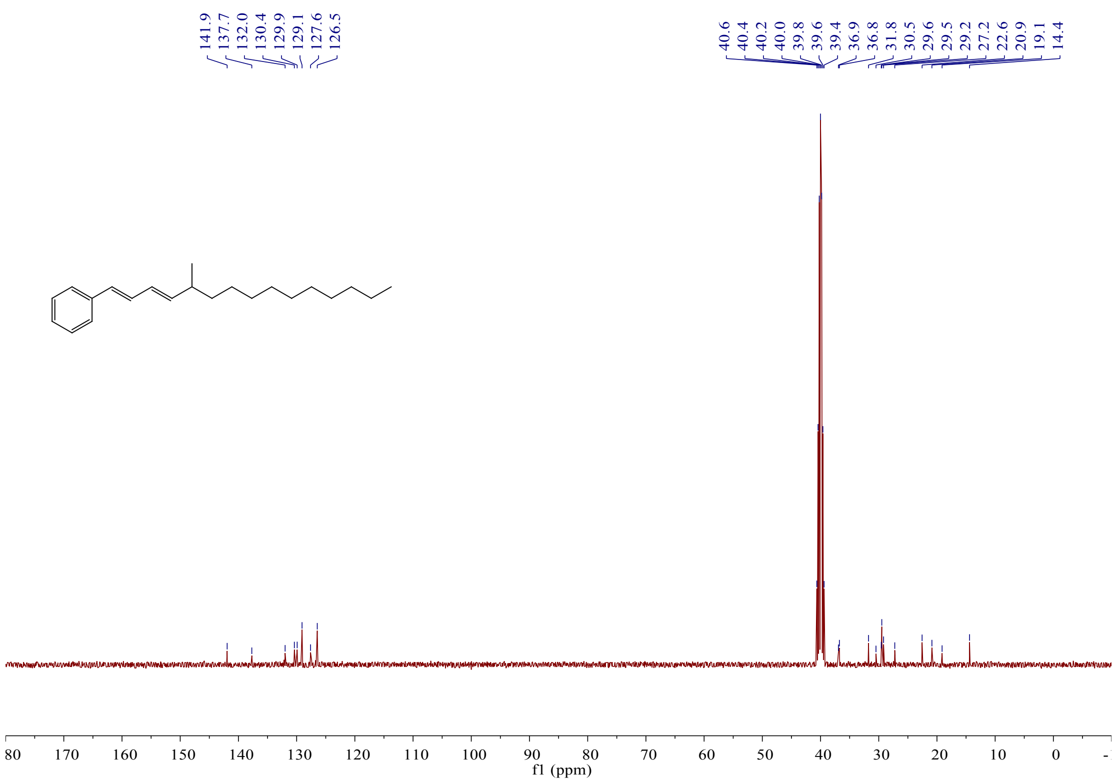
^{1}H and ^{13}C NMR spectra of **2l**



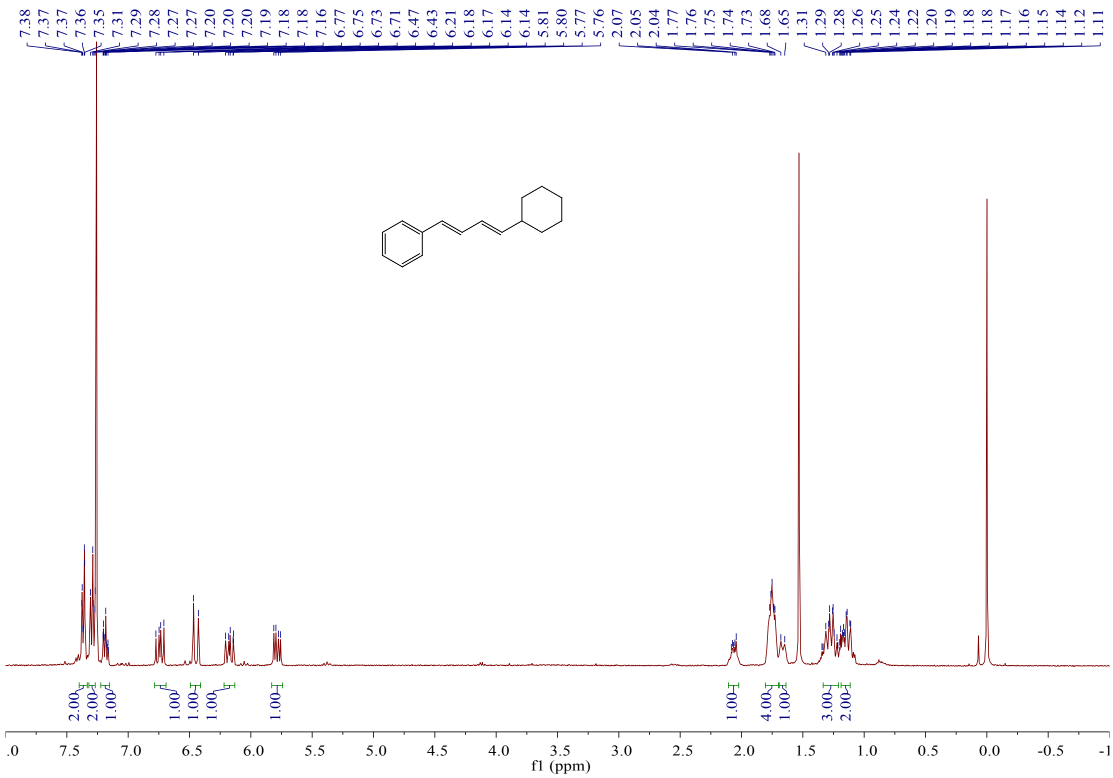


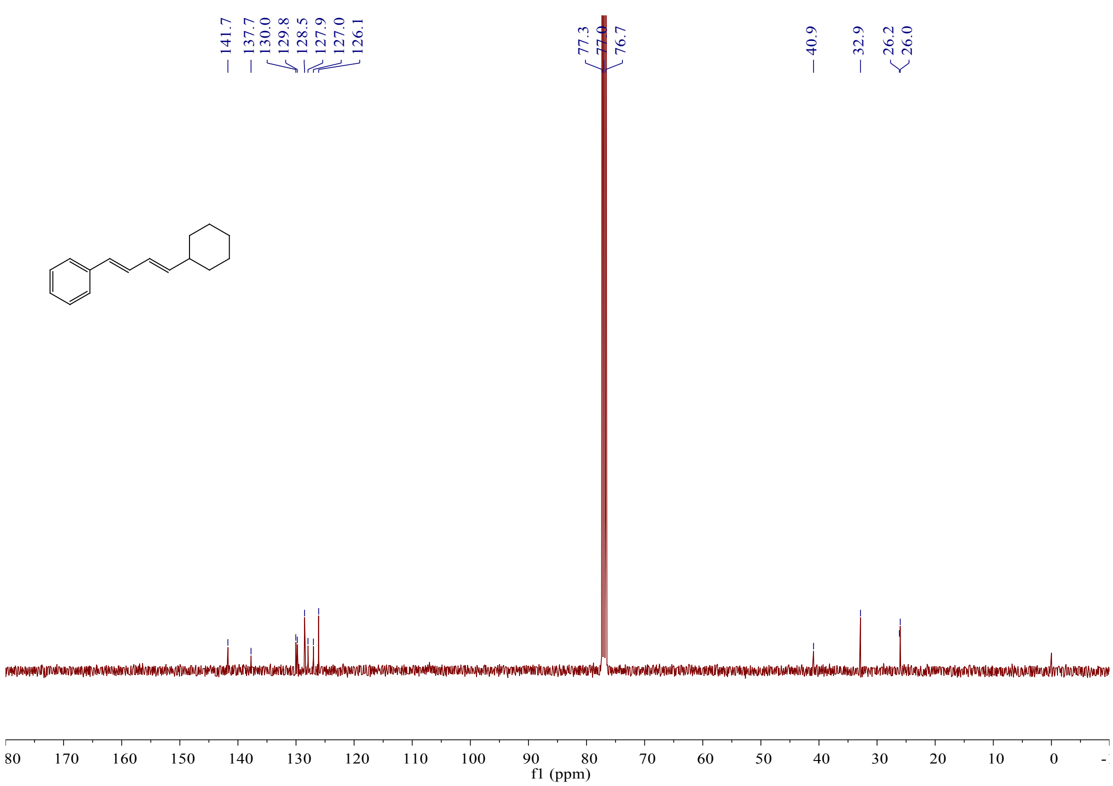
^{1}H and ^{13}C NMR spectra of **2m**



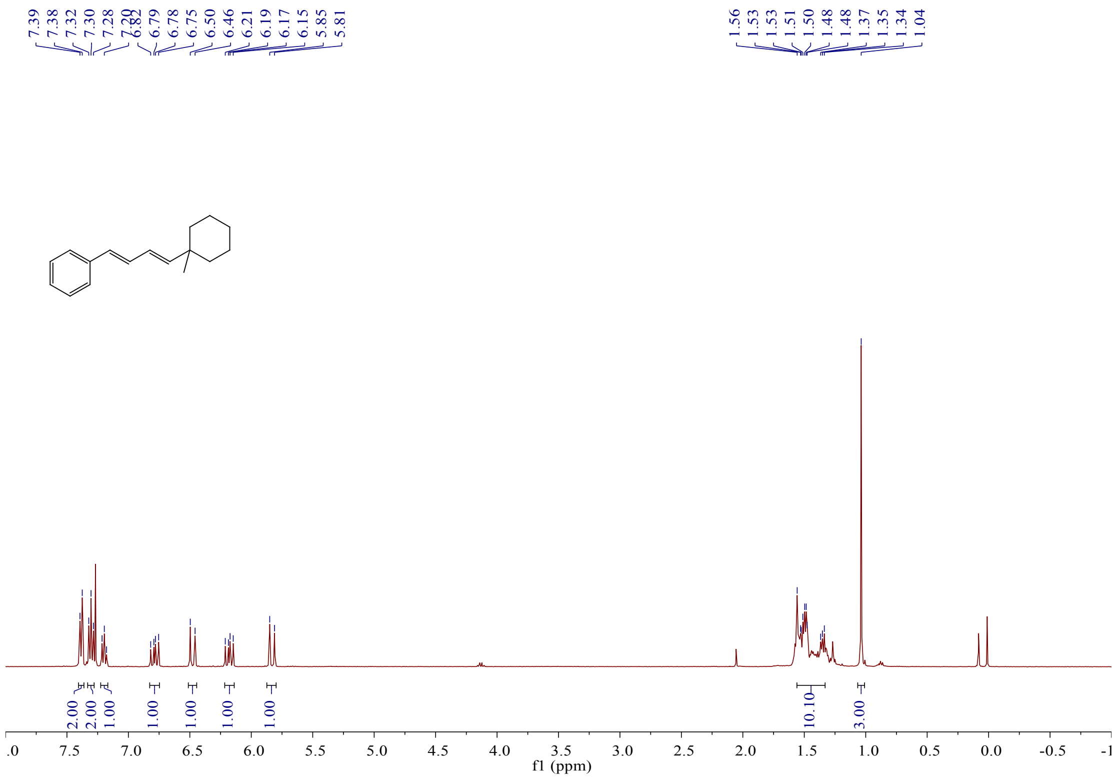


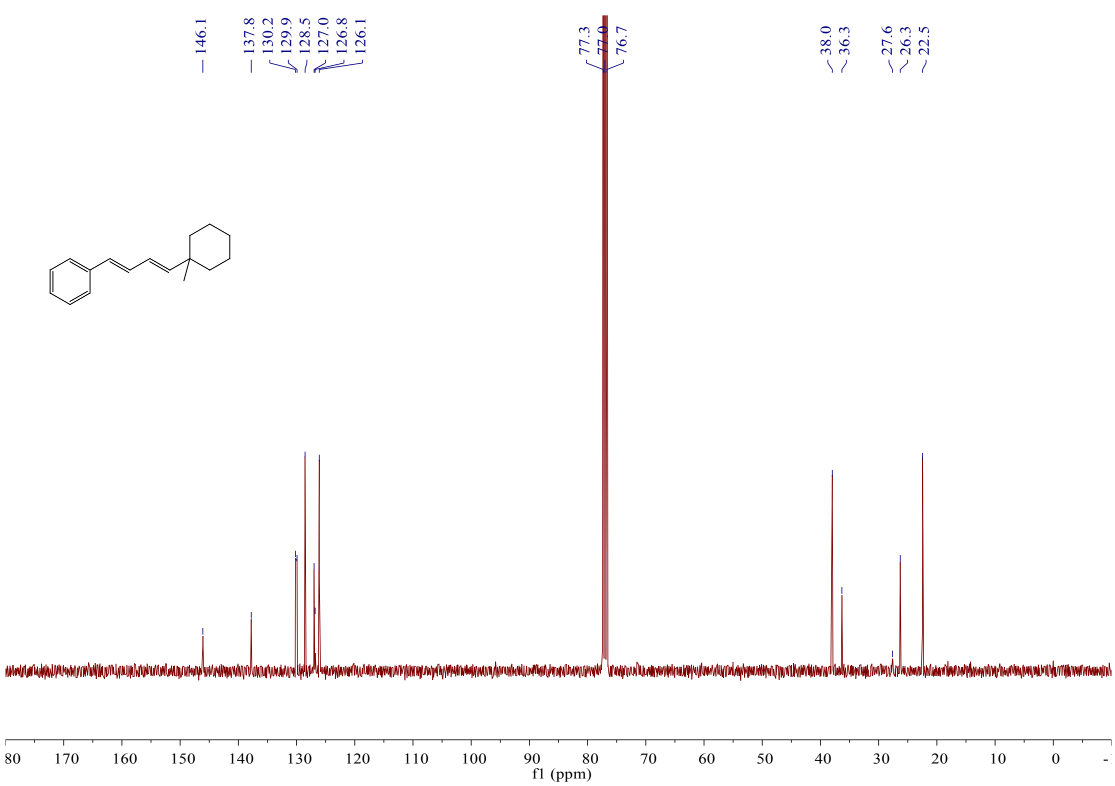
[1]H and [13]C NMR spectra of **2n**



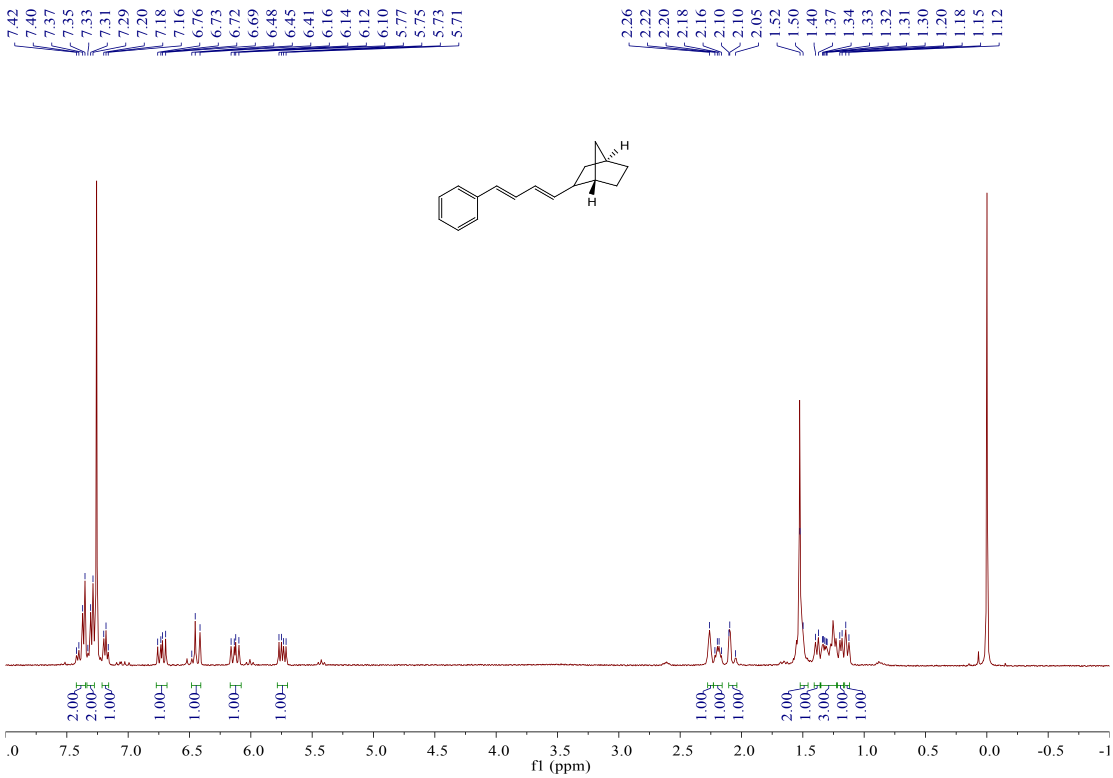


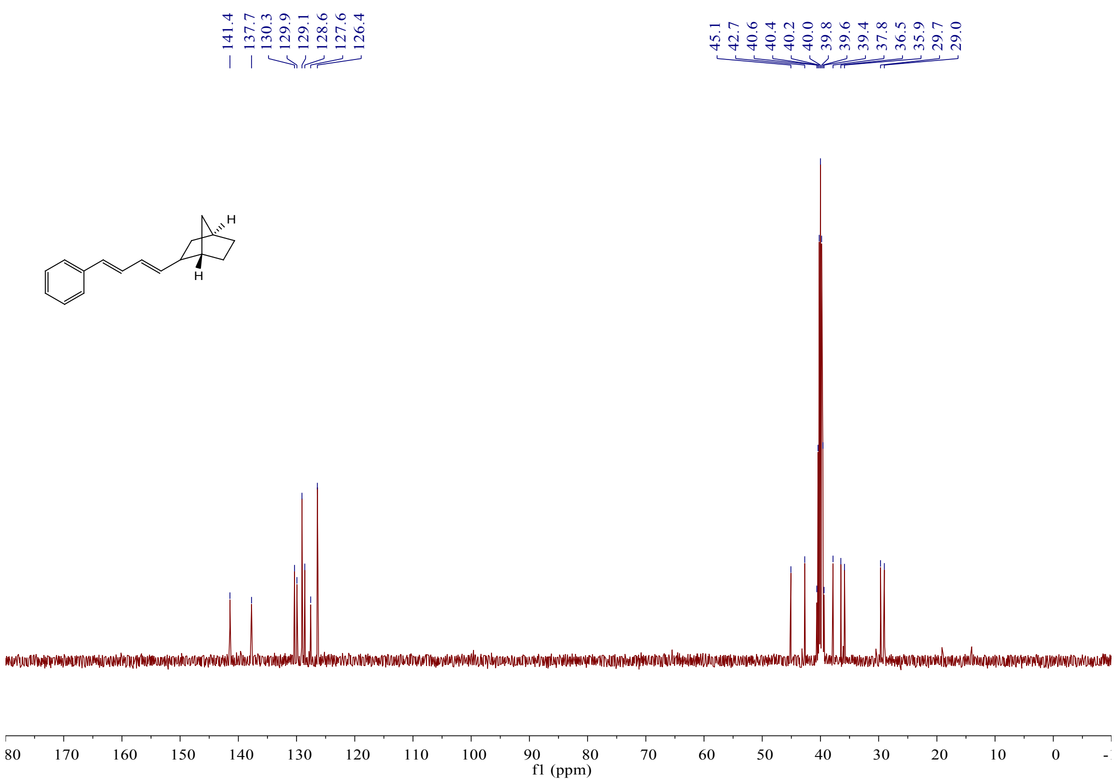
[1]H and [13]C NMR spectra of **2o**



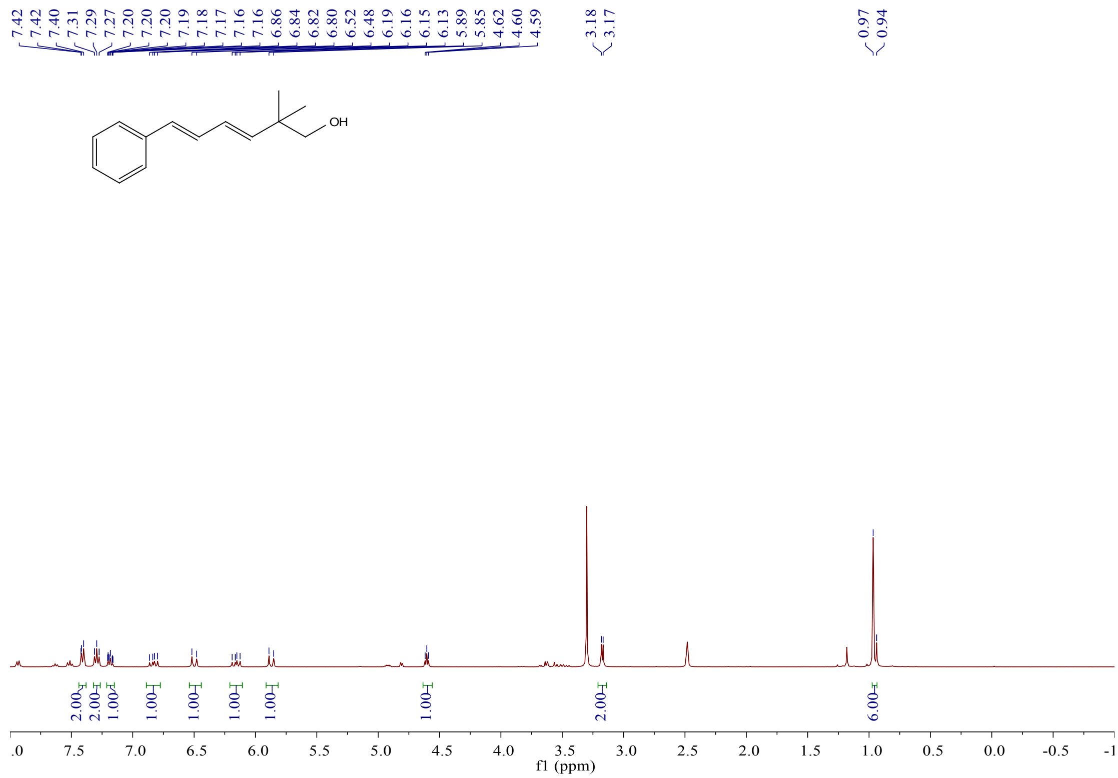


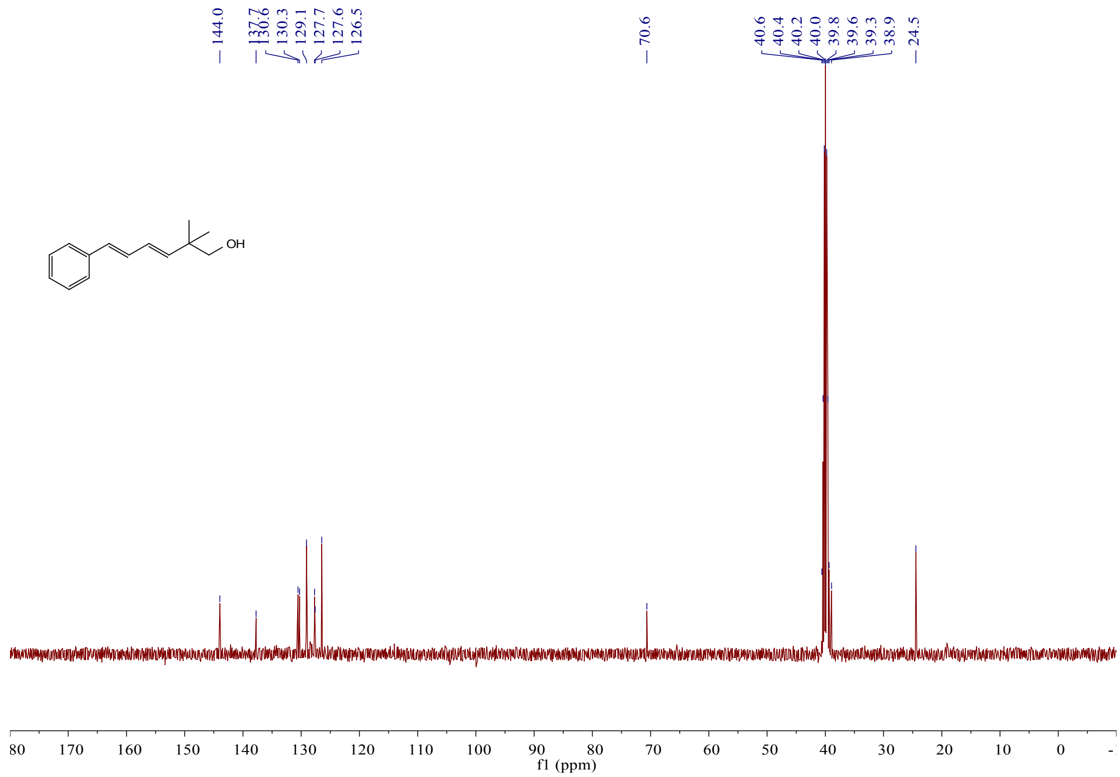
[1]H and [13]C NMR spectra of **2p**



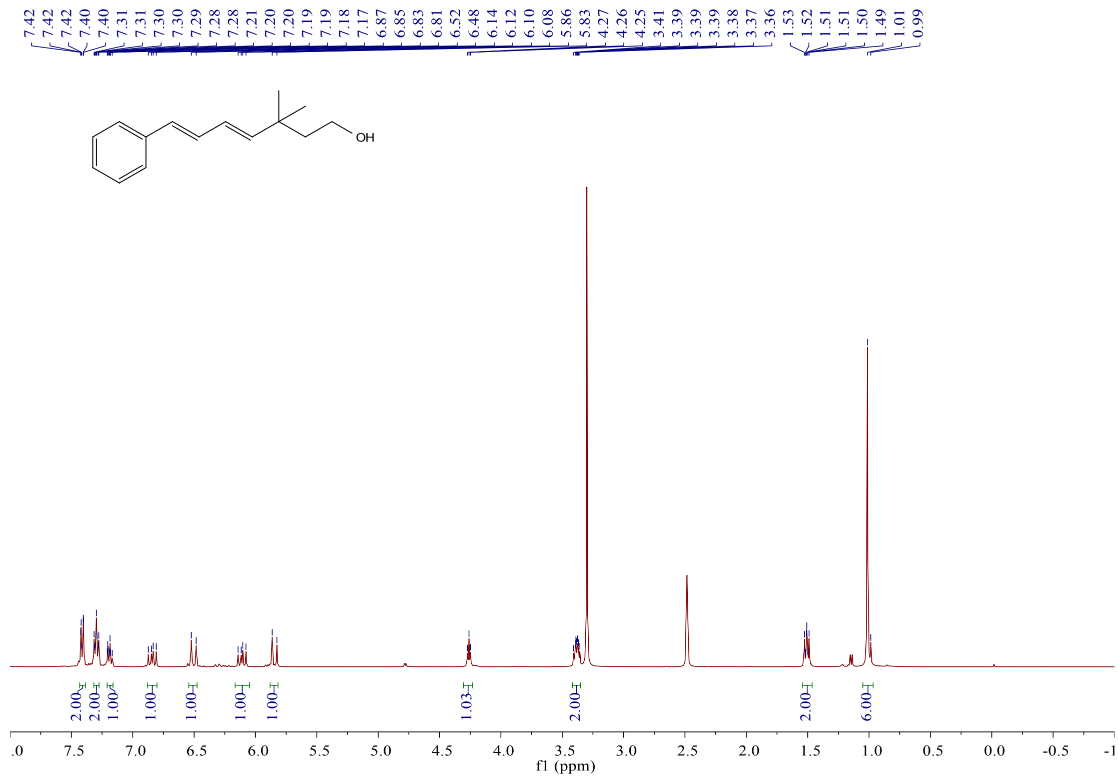


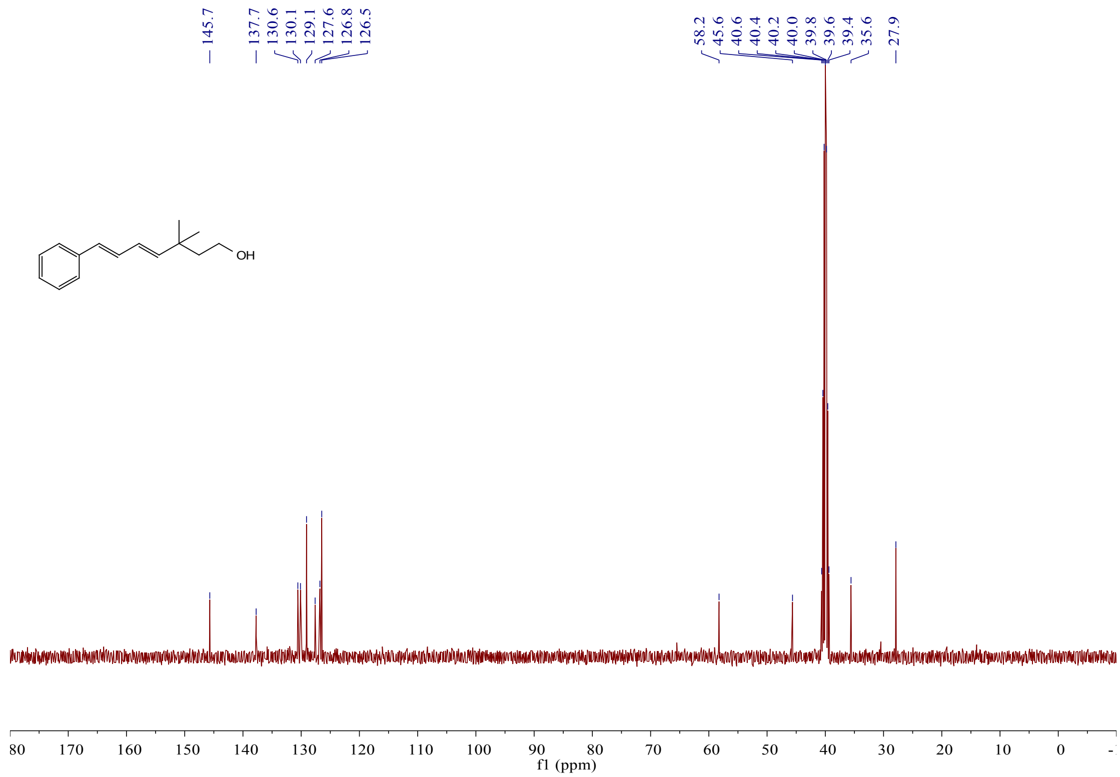
^{1}H and ^{13}C NMR spectra of **2q**



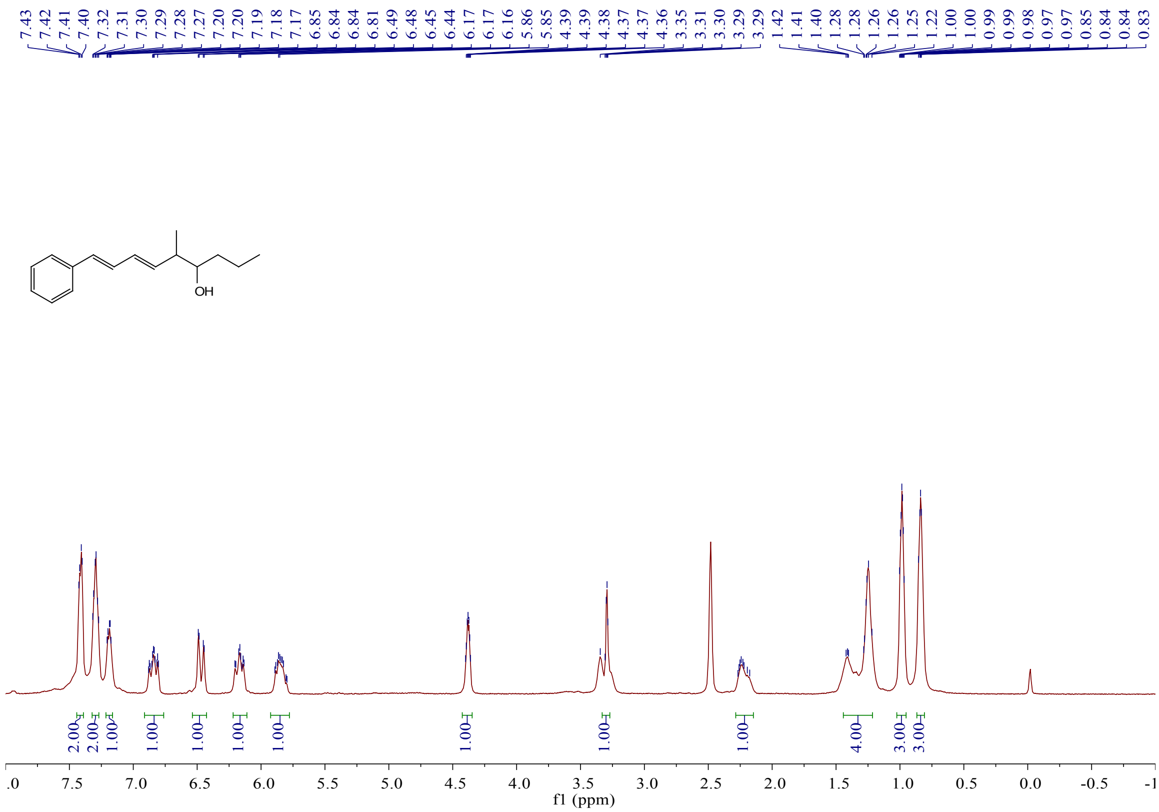


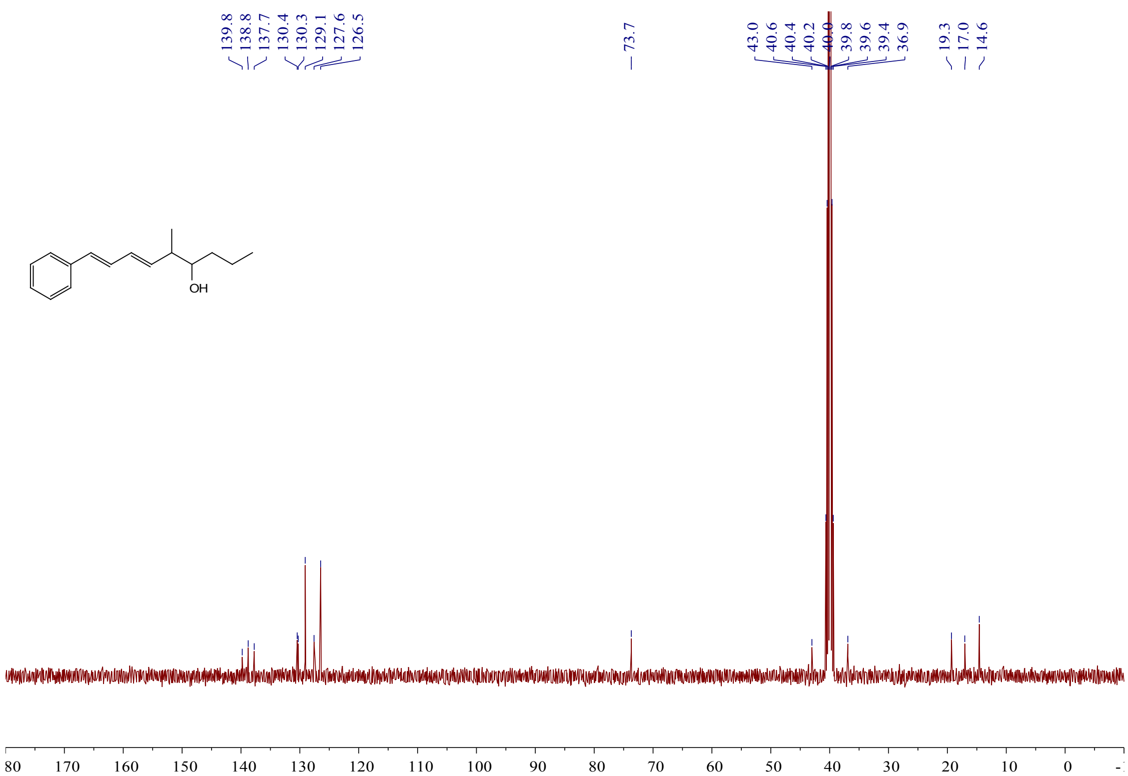
[1]H and [13]C NMR spectra of **2r**



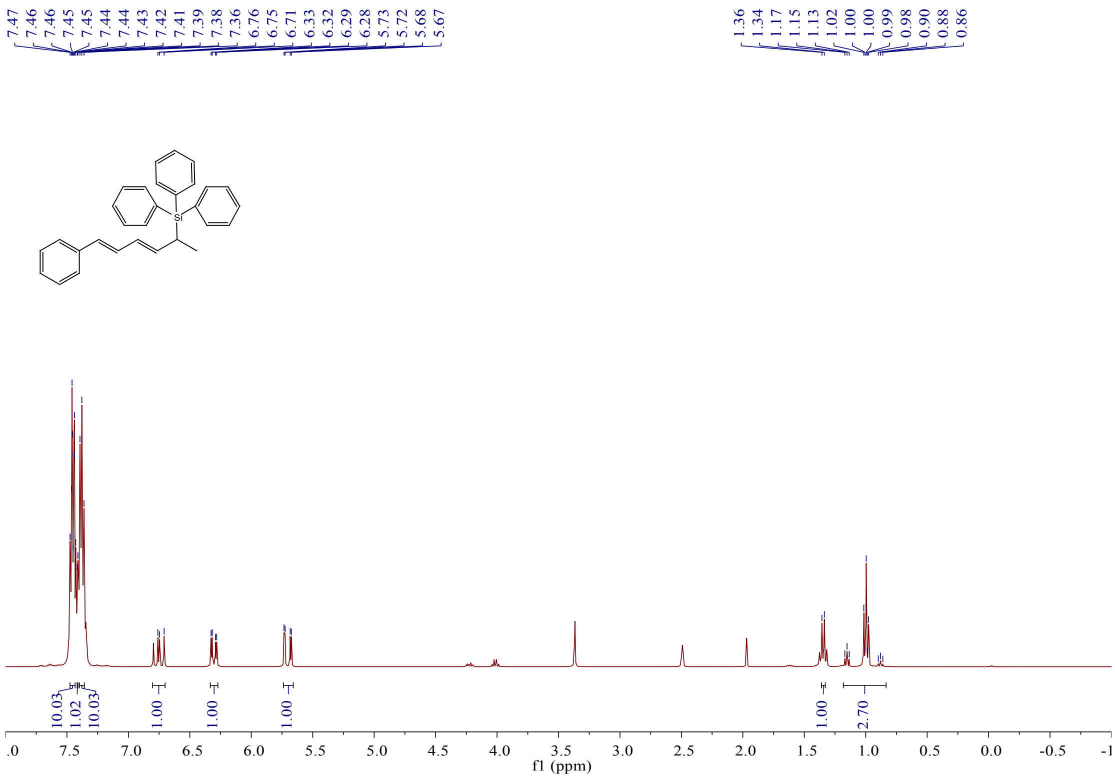


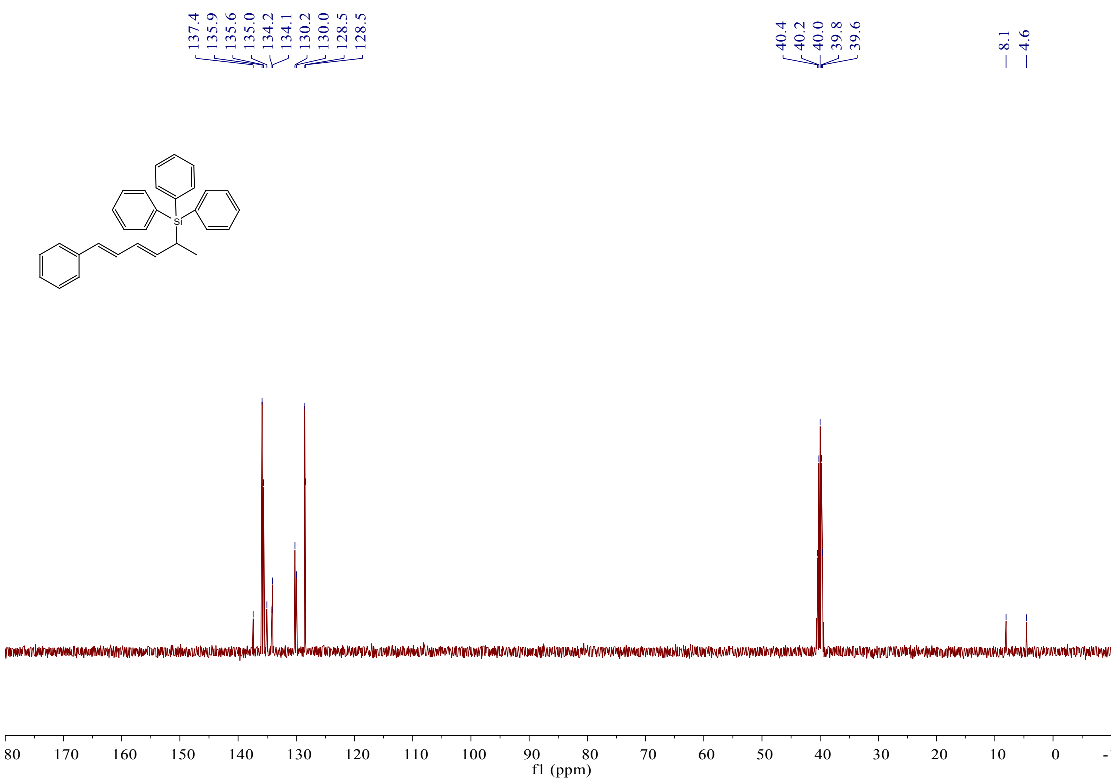
^{1}H and ^{13}C NMR spectra of **2s**



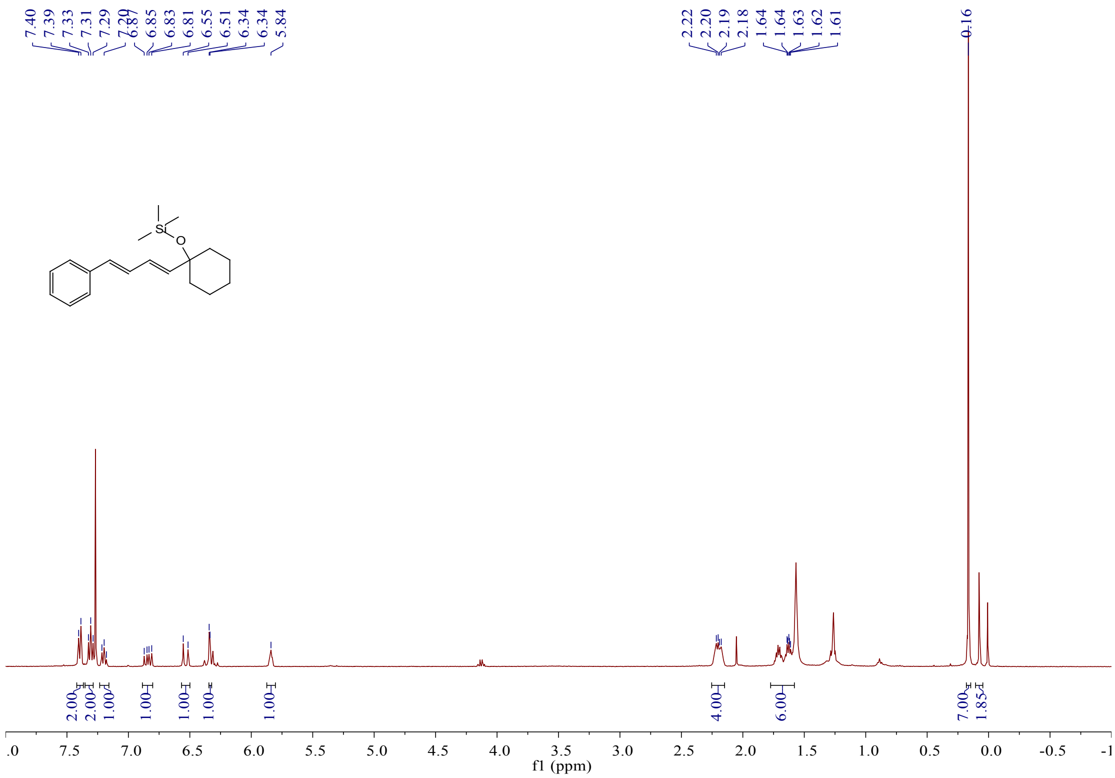


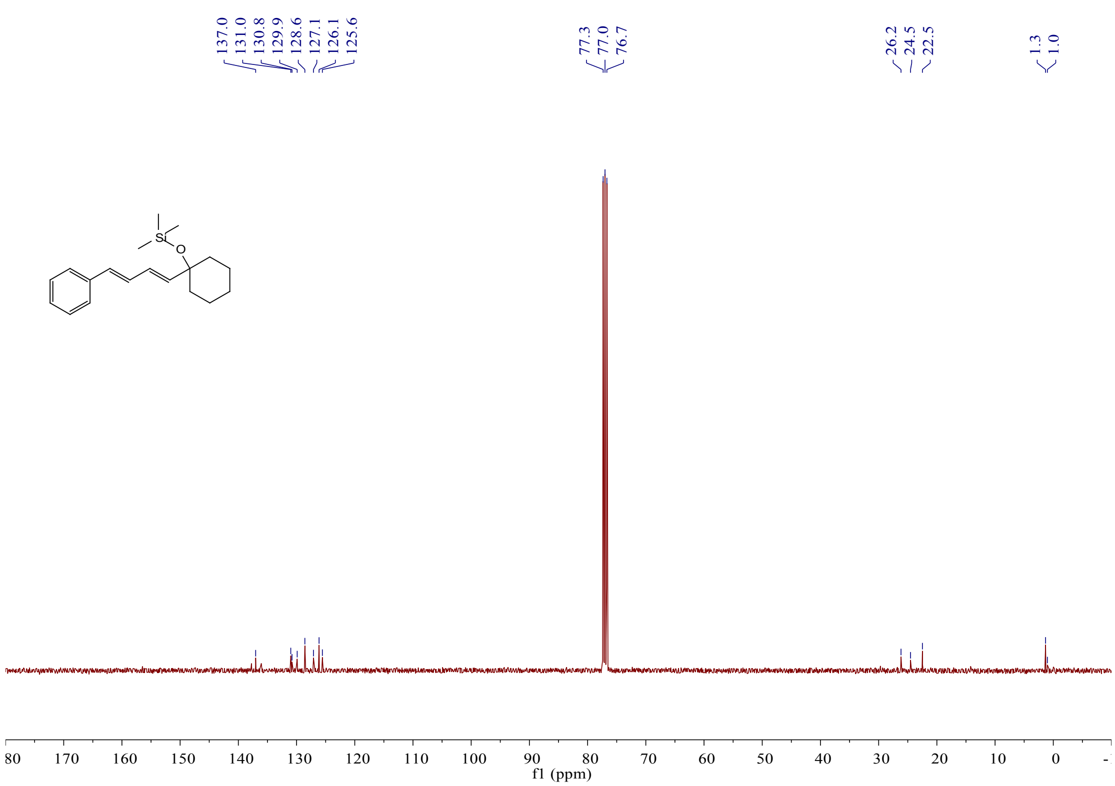
^{1}H and ^{13}C NMR spectra of **2t**



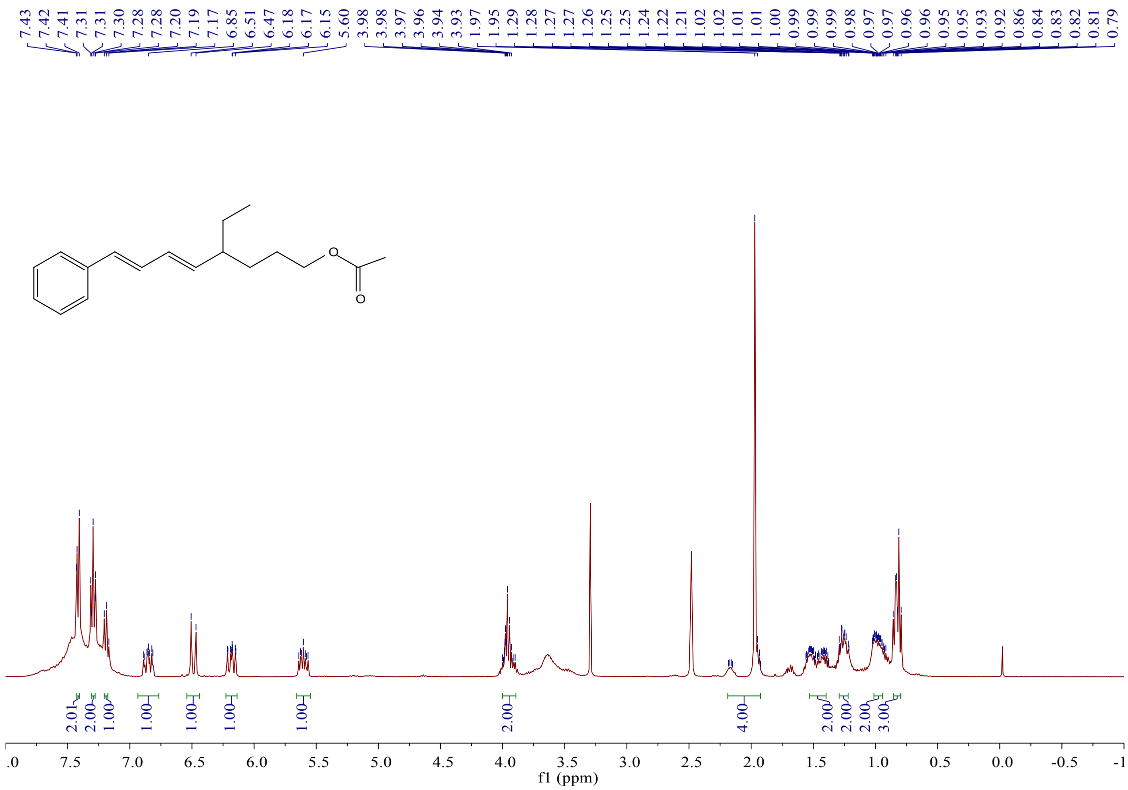


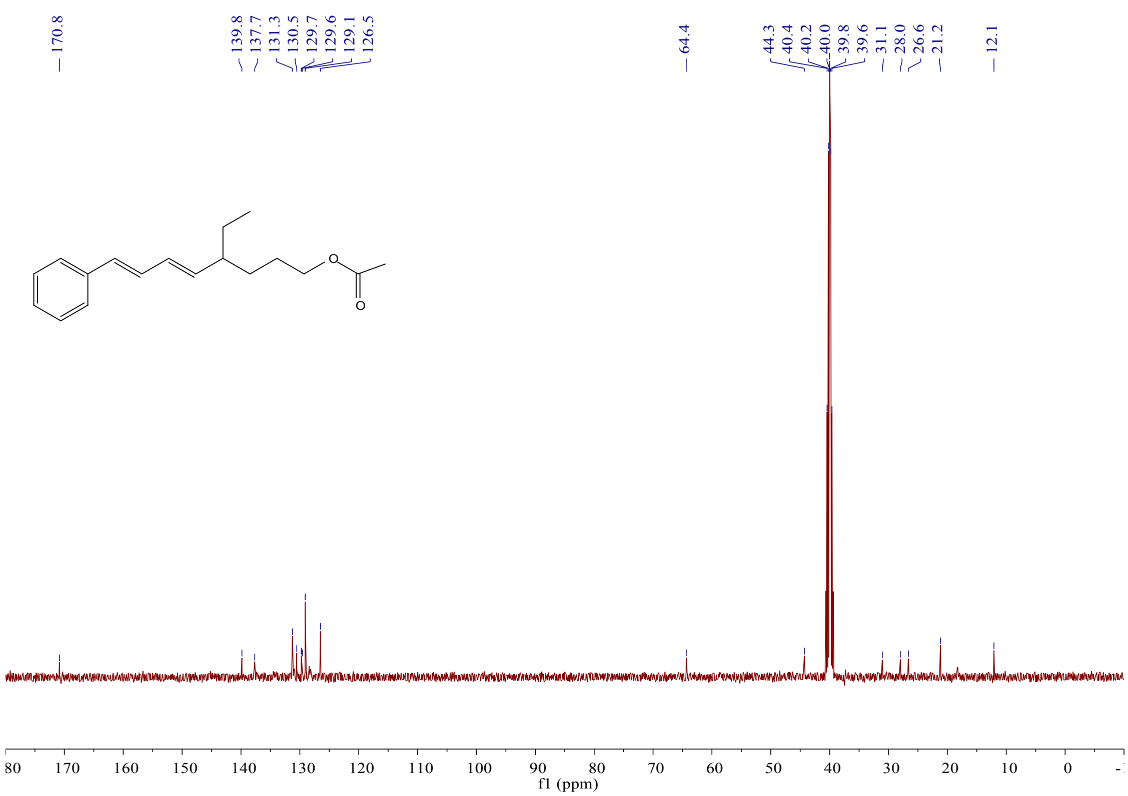
^{1}H and ^{13}C NMR spectra of **2u**



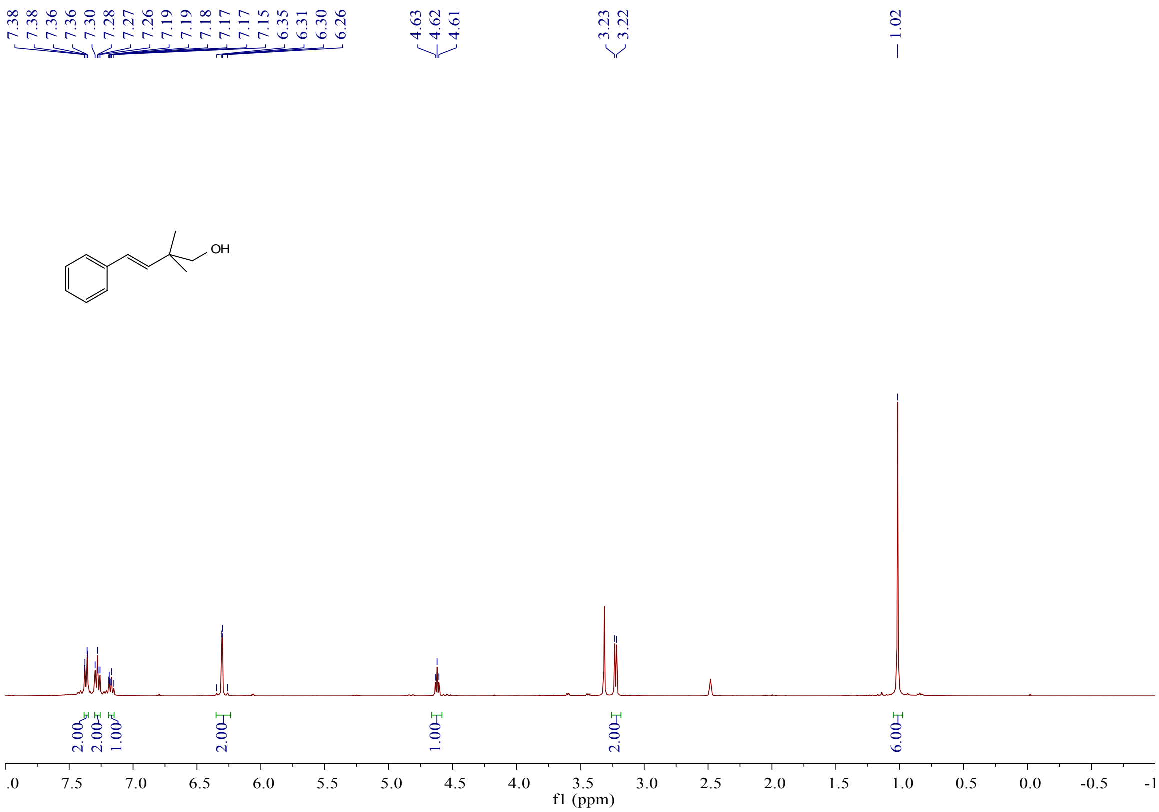


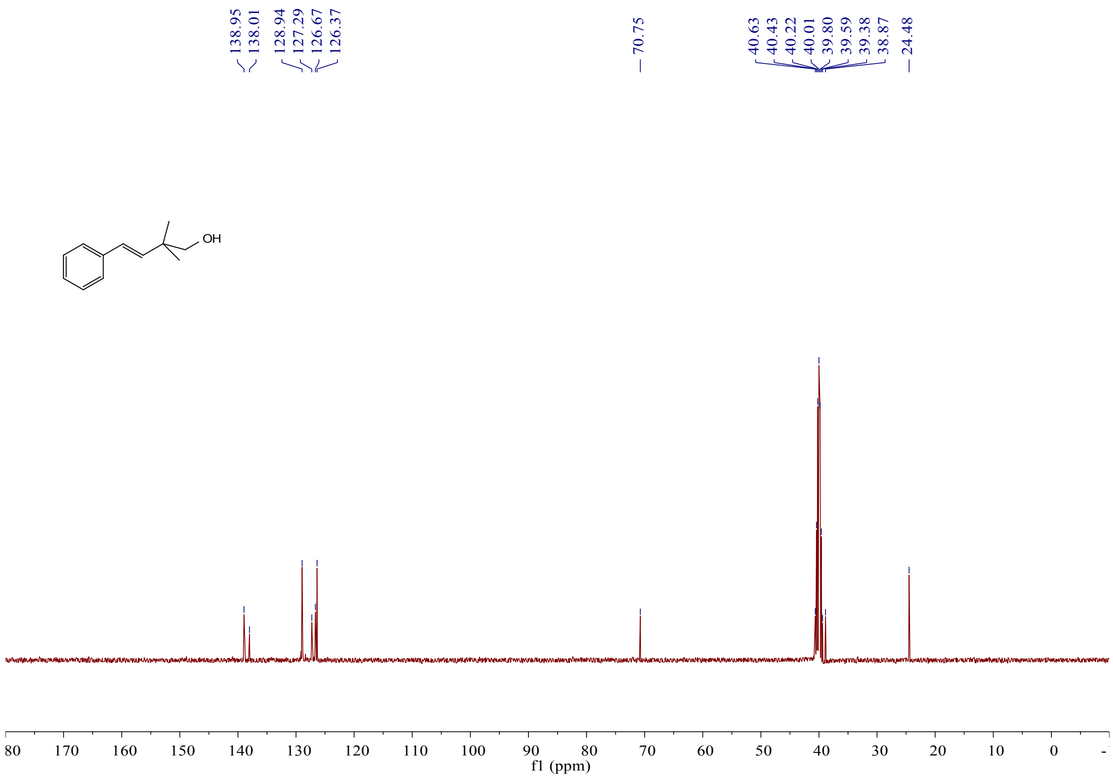
^{1}H and ^{13}C NMR spectra of **2v**



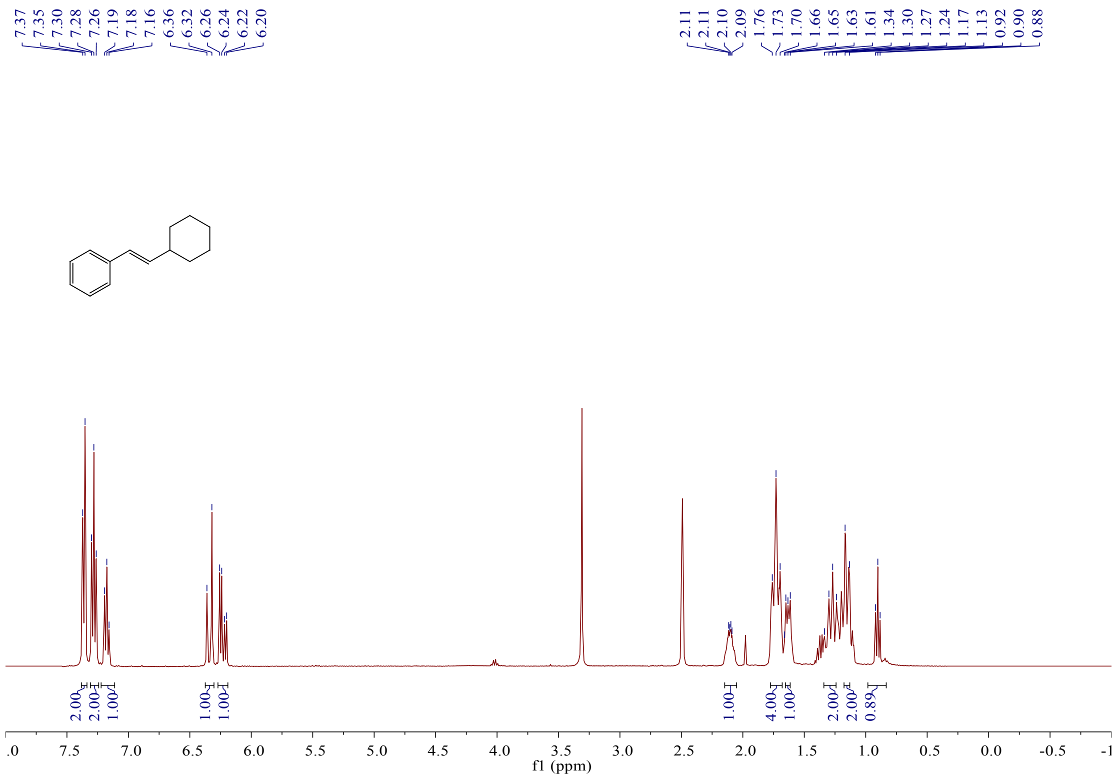


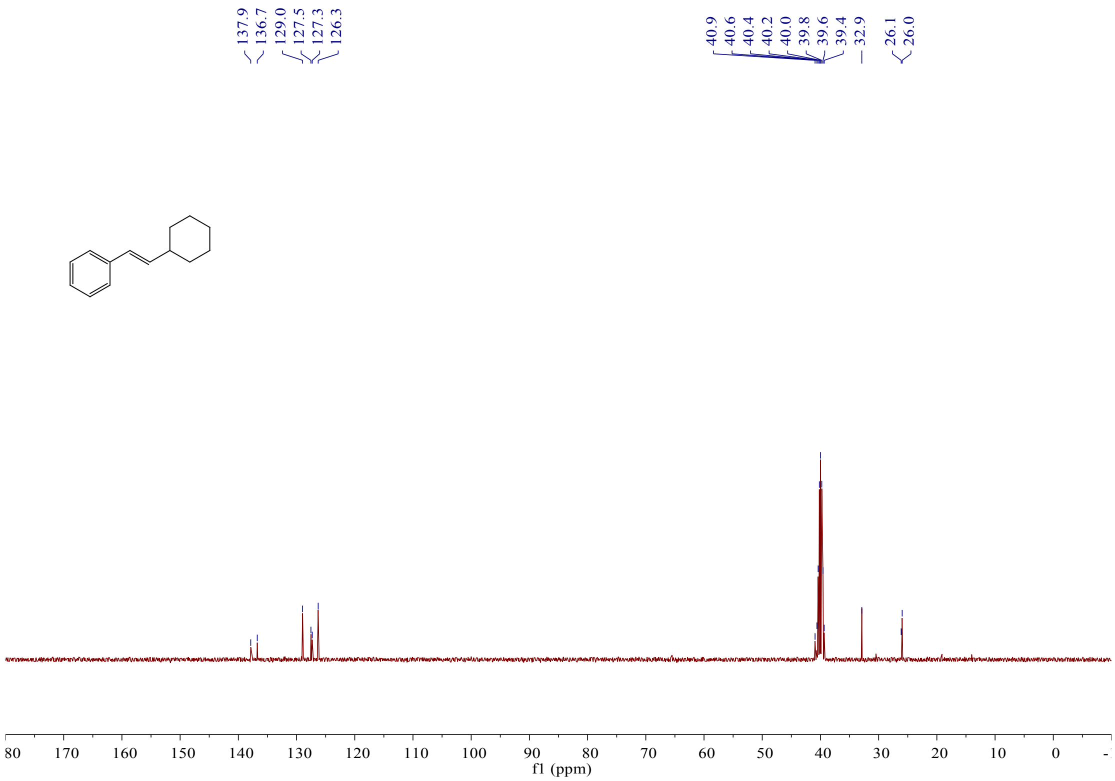
^{1}H and ^{13}C NMR spectra of **4a**



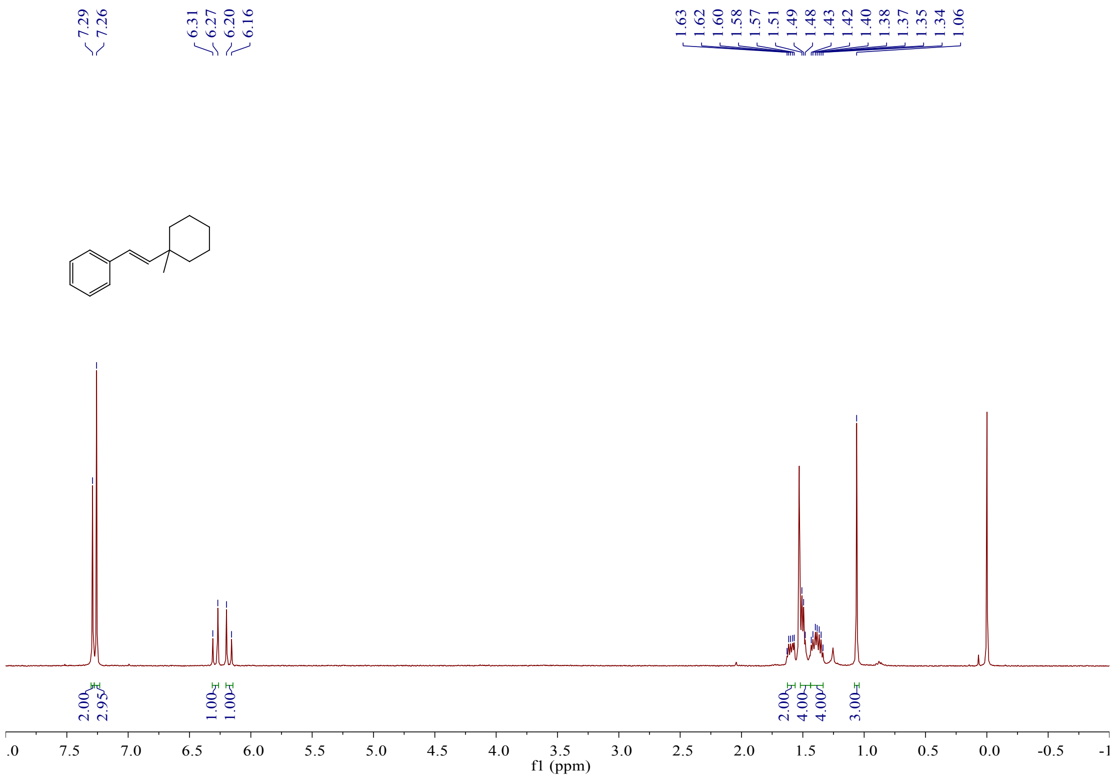


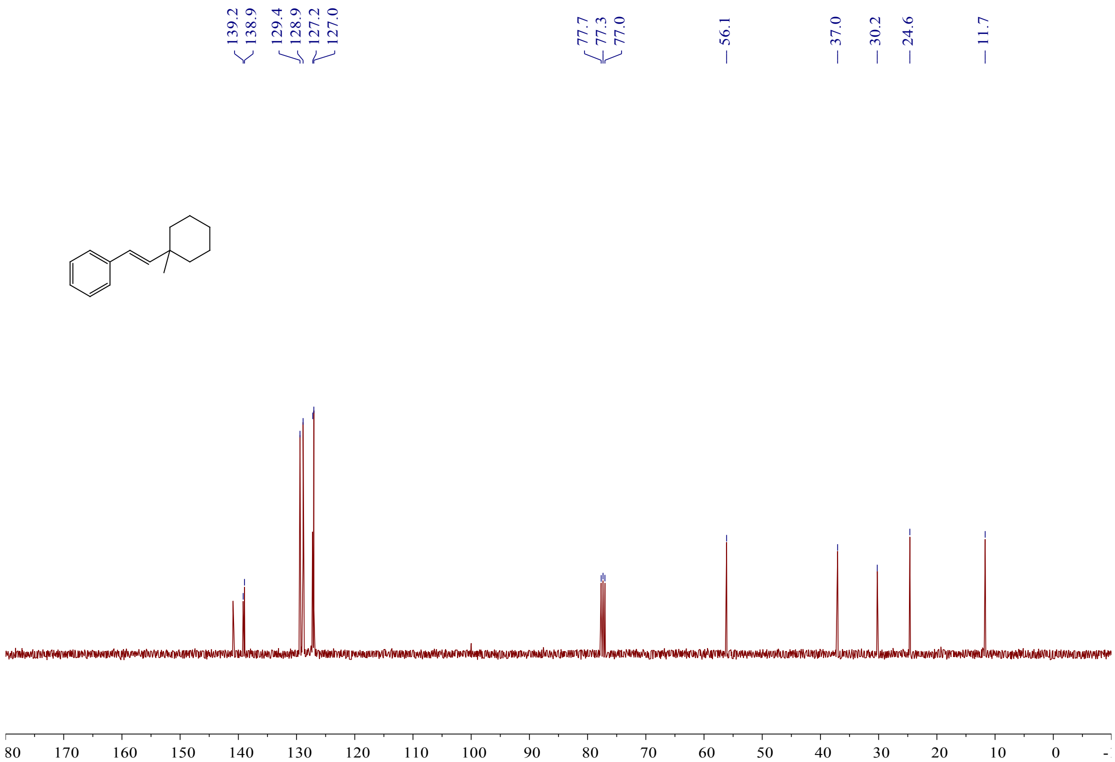
^{1}H and ^{13}C NMR spectra of **4b**



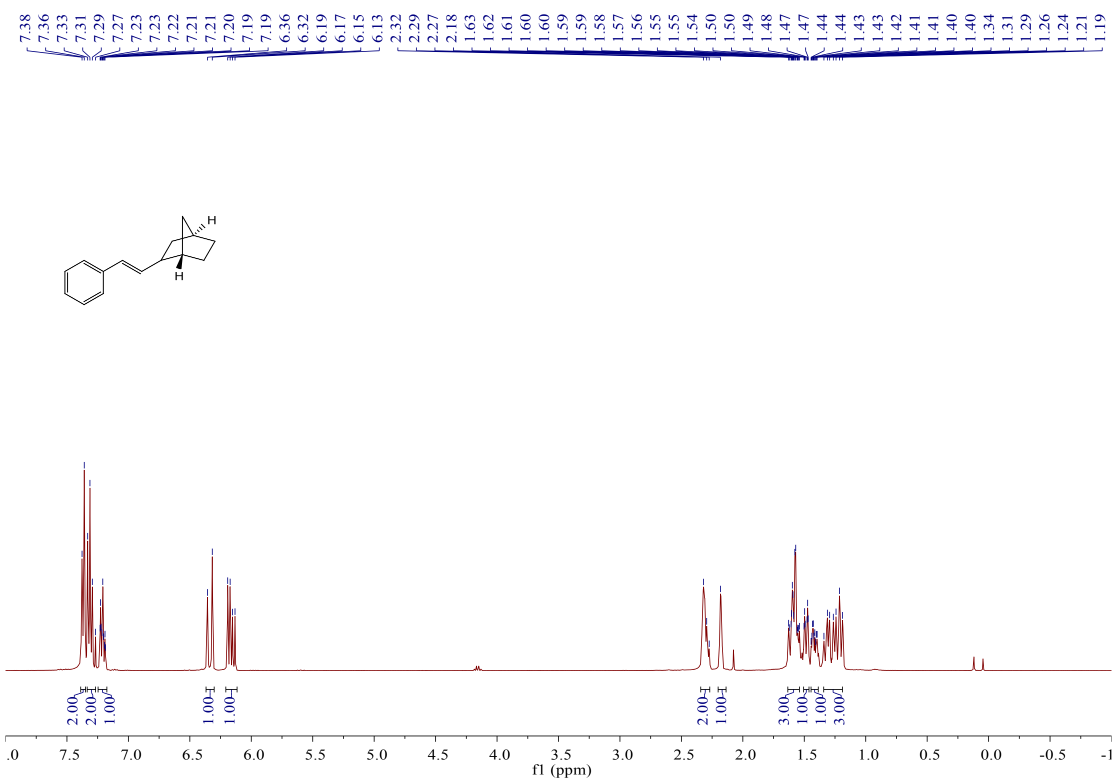


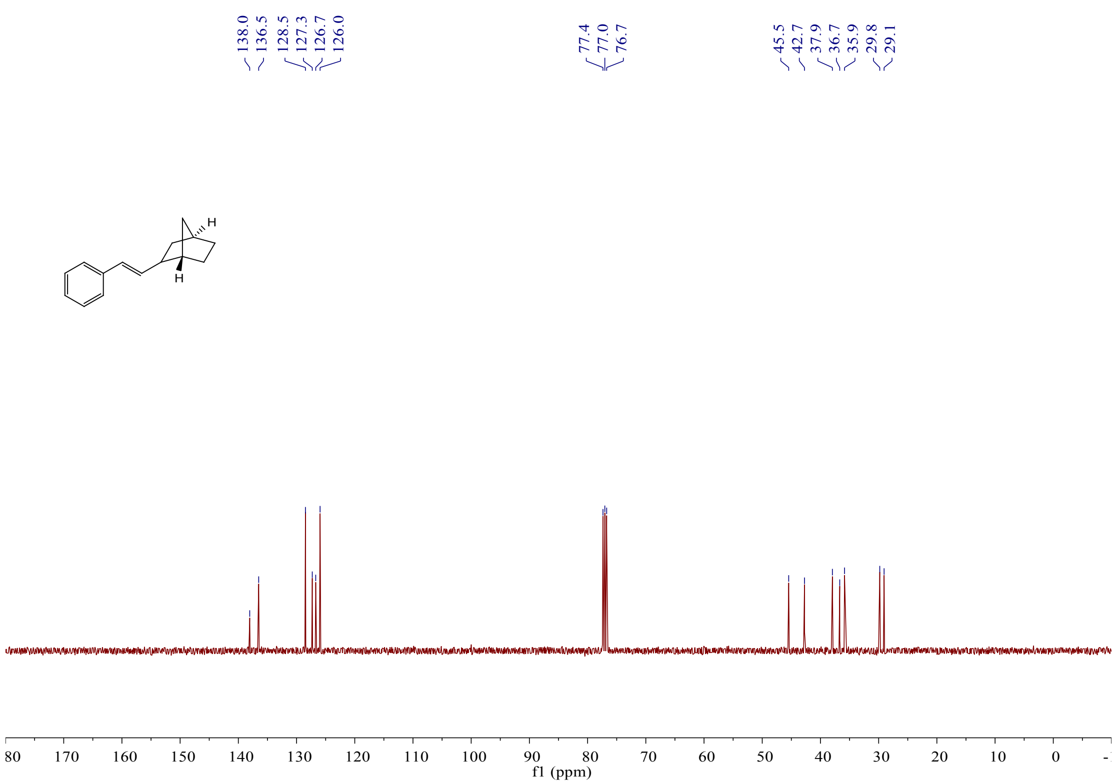
^{1}H and ^{13}C NMR spectra of **4c**



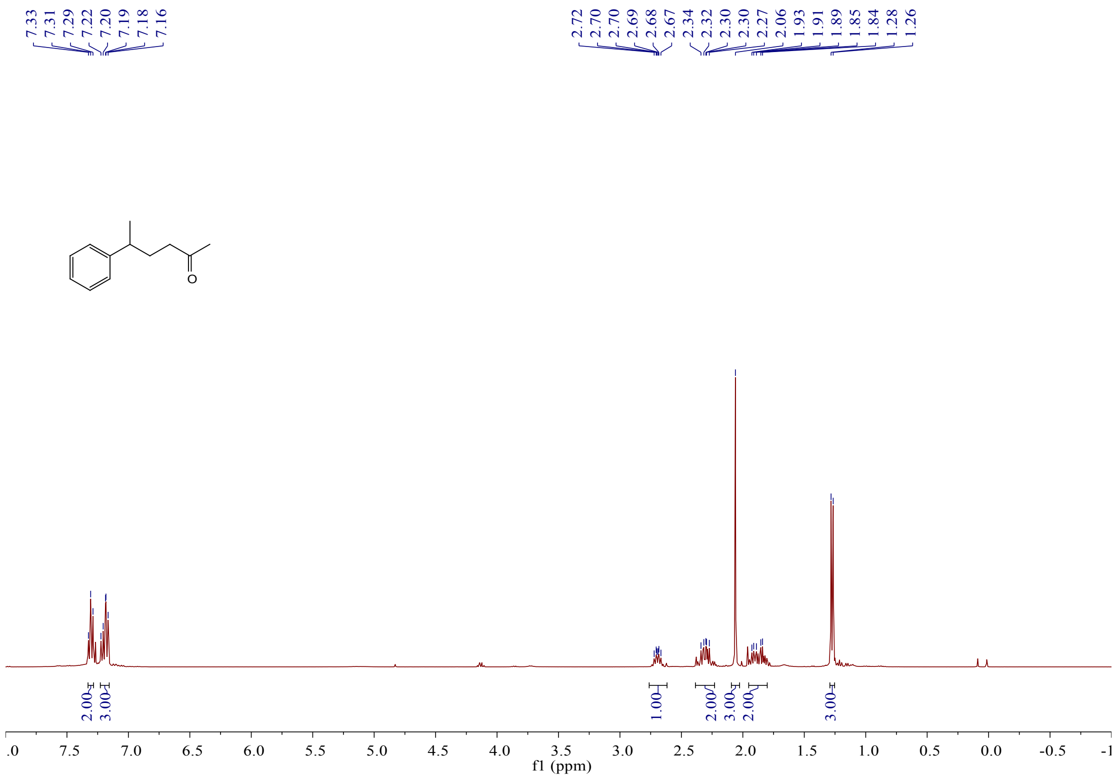


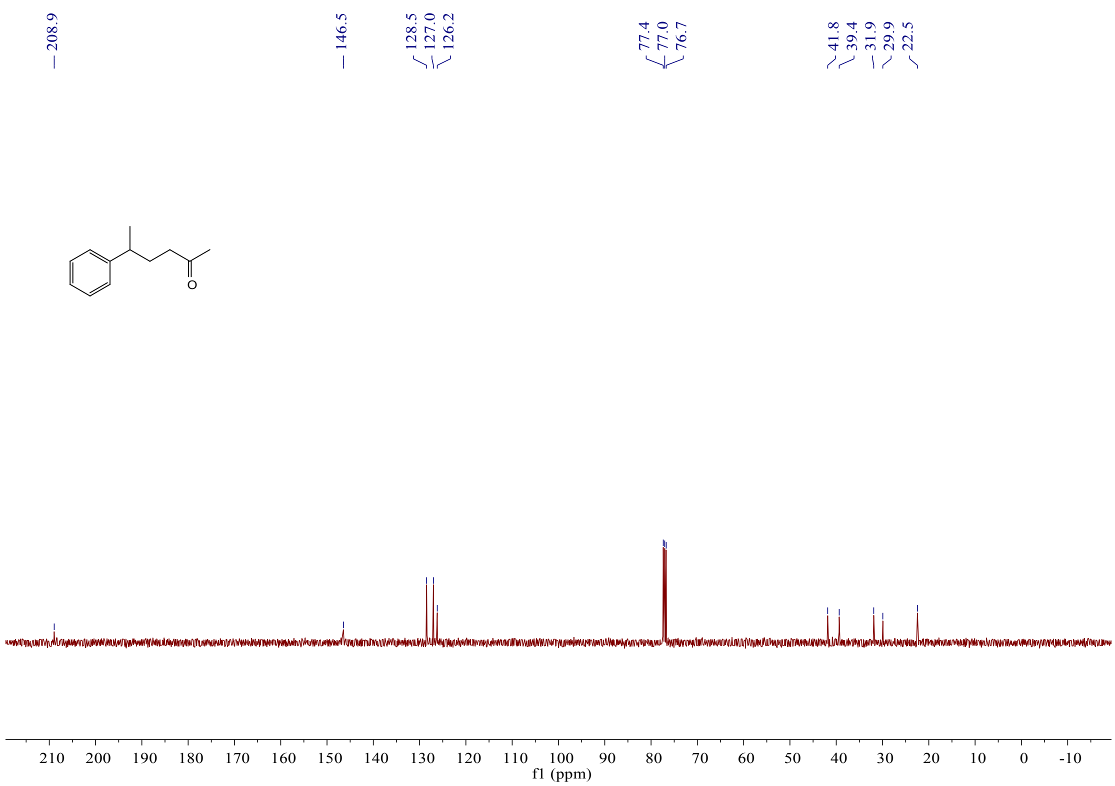
[1]H and [13]C NMR spectra of **4d**





^{1}H and ^{13}C NMR spectra of **4e**





^{1}H and ^{13}C NMR spectra of **4f**