Supporting Information

Biogenic Synthesis of Pd-Nanoparticle Using Areca Nut Husk Extract: A Greener Approach to Access *α*-keto imides and Stilbenes

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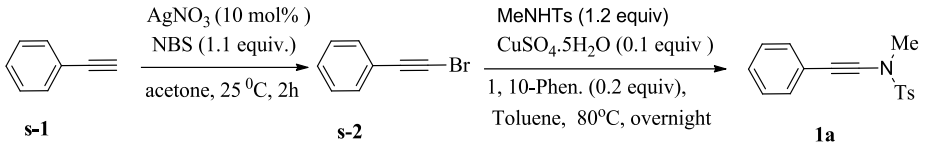
1.0 . General Considerations:

Unless otherwise specified, the presence of phytochemicals in Areca nut Husk (ANH) extract was analyzed using GC-MS data using SHIMADZU GC-MS QP 2010SE system. The presence of functional groups in ANH extract and palladium Nanoparticles **(**PdNPs) was done by using Fourier Transform Infrared Spectroscopy (FT-IR) in a Perkin Elmer FT-IR instrument by KBr pellets method in the range of 4000 to 500 cm^{-1}. UV-Visible analysis was carried out with the help of PerkinElmer Lambda 360 UV-Visible spectrophotometer. The crystallographic nature and the phase of the PdNPs was examined and confirmed using powder X-ray diffraction spectroscopy (XRD) noted on a Rigaku X-Ray Diffraction Ultima IV (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan rate of 2^{o} min^{-1} and theta value range of 10- 80° at 30 kV voltage and 15 mA current. The surface area analysis of PdNPs was performed using Brunauer Emmet and Teller (BET) method on Belsorp-Max (M/s. Microtrac BEL, Japan) under N_2 atmosphere at a temperature of -196 ºC. The corresponding pore size distribution of the catalysts was analyzed using Barrett Joyner Halenda (BJH) method. The catalysts were degassed at 180 ºC for 2h under vacuum prior to analysis in order to push out absorbed moisture. The thermal degradation of PdNPs was determined by a thermal analyzer within the temperature window of 40 ºC to 800 ºC under continuous N_2 flow with a heating rate of 10 ºC min^{-1}.The surface morphology and structural identity of PdNPs was investigated using Field Emission Scanning Electron Microscope (JEOL JSM-7100F, Singapore) coupled with energy dispersive X-Ray spectroscopy (EDX). The carbon tape on the aluminum metal stub was adequately covered with the powdered sample and subjected to sputtering using gold nanoparticles. To know more information about size, shape and surface morphology of PdNPs was investigated using HR-TEM analysis. The palladium loading in PdNPs was estimated through ICP-OES technique.All reactions were carried out in oven dried vials or sealed tubes with magnetic stirring under nitrogen atmosphere. All other reagents were directly used as purchased without further purification unless otherwise specified. All experiments were monitored by analytical thin layer chromatography (TLC) on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (60–120 mesh) using a proper eluent. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak ($CHCl_3$ in $CDCl_3$: 7.26 ppm). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). ^{13}C {^{1}H} NMR was recorded on Agilent Technologies DD2 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of $CDCl_3$. All analytical and spectral data are given for newly synthesized products while for reported compounds; the corresponding references are cited.[S1-S3]

2.0. Preparation of starting materials:

2.1. Preparation of ynamide (1a)



Scheme 1. Synthetic route for ynamide preparation

Synthesis of (bromoethynyl)benzene (s-2): To a oven dried 50 mL round bottom flask containing solution of phenylacetylene (**s-1**) (400 mg, 3.92 mmol) in acetone (50 mL) was added NBS (836 mg, 4.71 mmol) and $AgNO_3$(66.5 mg, 0.392 mmol), the resulting solution was stirred under nitrogen at room temperature for 3 hours. After removing excess acetone the reaction was quenched with water, and the organic layer was extracted with hexane (30mL×3), dried over Na_2SO_4, and concentrated under reduced pressure to obtain pure colorless oil of bromoalkyne**s-2**(574.25 mg, 81%) [S4]

Synthesis of ynamide (1a): To a dried flask was added *N*-methylmethanesulfonamide (363 mg, 3.34 mmol),$CuSO_4 \cdot 5H_2O$ (69.3 mg, 0.281 mmol), 1,10-phenanthroline (100 mg, 0.562 mmol) and K_2CO_3 (767 mg, 5.55 mmol), and this mixture was subsequently treated with anhydrous toluene (3mL) and **s-2** (500 mg, 2.78 mmol) and subsequently heated at 80 °C overnight nitrogen atmosphere. After complete consumption of starting material (indicated by TLC), reaction mixture was cooled to room temperatures, filtered through Celite$_{TM}$, and concentrated *in vacuo*. Purification of the crude residue using silica gel column chromatography (eluent: 10–12% EA/Hexane) gave the pure ynamide**1a** as pale yellow solid(630.56 mg, 80%).[S4]

3.0. Synthesis of PdNPs using ANH extract:

3.1. Preparation of ANH extract:

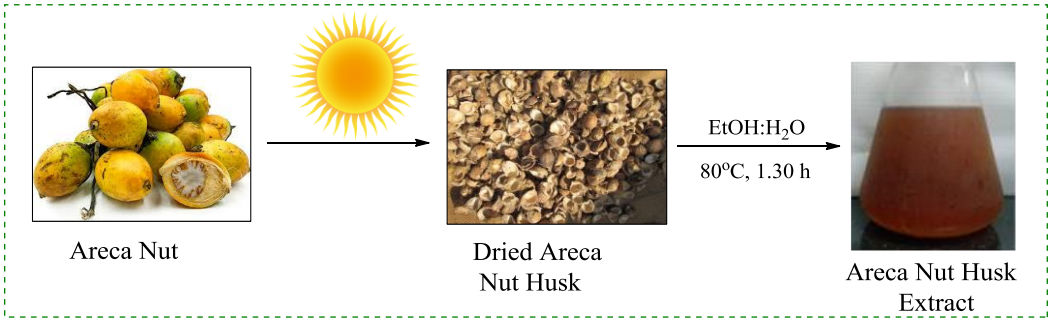


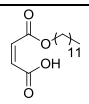
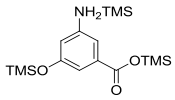
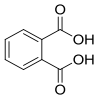
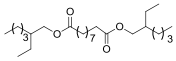
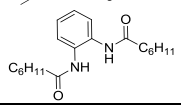
Fig. 1: Preparation of Areca nut husk (Areca catechu) extract from Areca nut Husk

ANH is collected from the local area of Sirsi, Uttara Kannada, India and rinsed with double distilled water, cut into small pieces and completely air dried. Then, 10g of dried husk taken in a 250 mL Erlenmeyer flask containing 150 mL solvent (EtOH: H_2O, 1:1,).The mixture was heated to 80^oC for 1.30 h to extract the phytochemicals present in ANH and then cooled, centrifuged, filtered and stored at 4^oC.[S1-S2]

3.2. Gas Chromatography –Mass Spectroscopic (GC-MS) Analysis of ANH [S5]:

Initially, the Areca nut husk (Areca catechu) extract was subjected to GC-MS analysis to confirm the presence of phytochemicals in extract (Table 1).This analysis helps us to find out the presence of phytochemicals and their percentage so as to understand the role of different phytochemicals in the bio-reduction process. The GC–MS chromatogram of ethyl acetate extract of the areca nut husk showed the qualitative presence of compounds having acid groups, OH, NH_2 etc are the major components present in it (**Table 1**) which is directly involved in bio-reduction process.

Table-1: Phytochemicals identification using GC–MS

RT	Area (%)	Structure	Name of the compound
6.88	2.03		(Z)-4-(dodecyloxy)-4-oxobut-2-enoic acid
8.18	2.41		trimethylsilyl 3-((trimethylsilyl)amino)-5-((trimethylsilyl)oxy)benzoate
8.53	3.08		nonadecan-1-ol
8.80	46.40		1,2-benzenedicarboxylic
12.01	4.36		Decanedioic acid orbis(2-ethylhexyl) decanedioate
12.78	3.65		N,N'-(1,2-phenylene)dicyclohexanecarboxamide

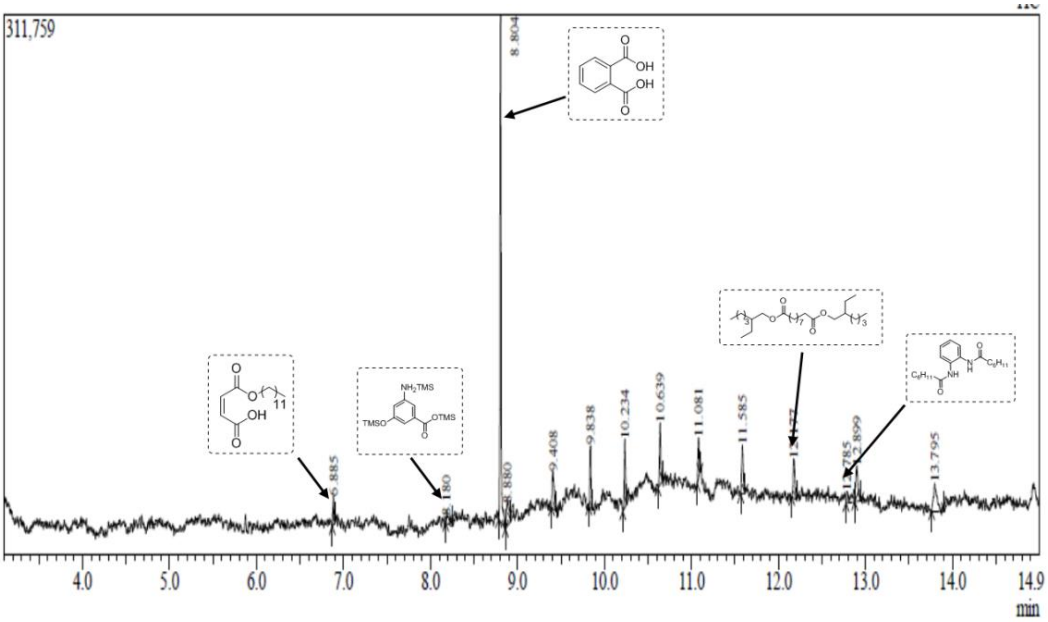


Fig. 2: The GC–MS chromatogram of ethyl acetate extract of the ANH extract

3.3. Preparation of PdNPs Using Areca Nut Husk (Areca catechu) extract:

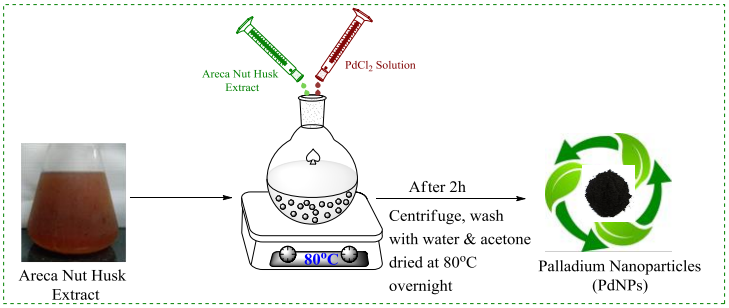


Fig. 3: Preparation of PdNPs Using Areca nut husk (Areca catechu) extract

An aqueous solution of 100 mL $PdCl_2$ (10 mM) is taken in 250 mL round bottom flask and sonicated for 10 min. It is then kept stirring at 80°C and ANH extract (15-20 mL) were added drop wise. The reduction of Pd (II) to Pd(0) were monitored by observing a gradual change in color of the solution from initial light brown to black over the time. However, the complete reduction of Pd (II) was confirmed by UV-visible spectroscopic analysis of the reaction mixture indicating the formation of PdNPs. At this stage, the reaction mixture was cooled to room temperature and newly formed PdNPs were collected by centrifugation at 4000 rpm for 15 min. It is then washed with double distilled water and acetone, then dried at 80 °C for 8 h and characterized by various spectroscopic techniques.[S1-S2]

4.0. Spectroscopic and microscopic analysis of Palladium Nanoparticles (PdNPs):

4.1. Fourier Transform Infrared (FT-IR) spectroscopy:

The presence of various functional groups in ANH extract was confirmed by FT-IR analysis Fig 4(b). The peaks at 3467, 2987, 2898,1637, 1394 and 1046cm^{-1} are due to stretching and bending vibrations of functional groups like –OH, –NH, aromatic and aliphatic –C–H,–C=O, C–O and –C=C present in ANH extract. Further, FT-IR analysis of PdNPs were subsequently performed (Fig 4a) and similar peaks was identified indicating that, the phytochemicals are adsorbed on the surface of PdNPs during the reduction of Pd(II) to Pd(0).

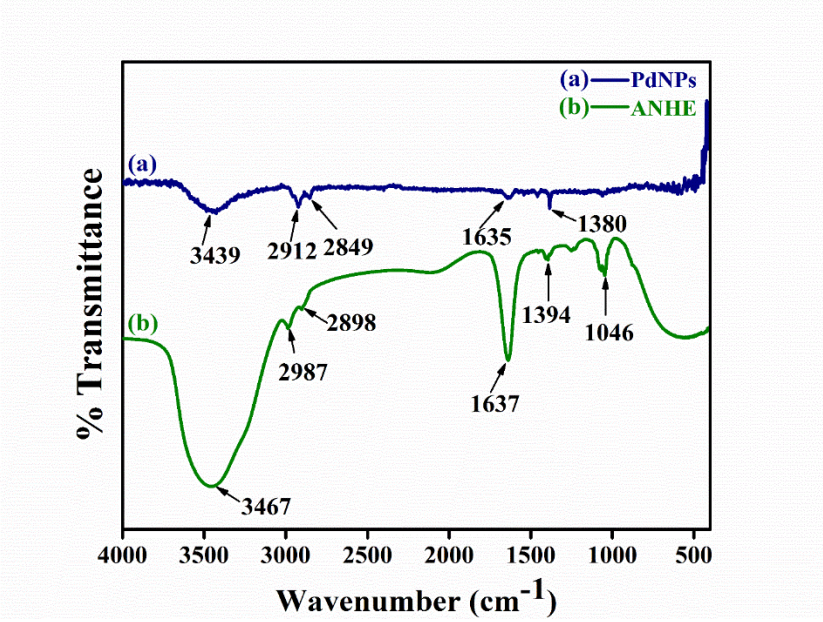


Fig.4. FT-IR spectrum of (a) Biogenically synthesized PdNPs (b) Fresh Areca Nut Husk extract

4.2. Field Emission-Scanning Electron Microscopic (FE-SEM) analysis:

The surface morphological study and size distribution of the PdNPs were examined by FE-SEM technique (Fig. 5).It indicates that, all particles are in nanometer size and agglomerated with spherical morphology. S1-S2

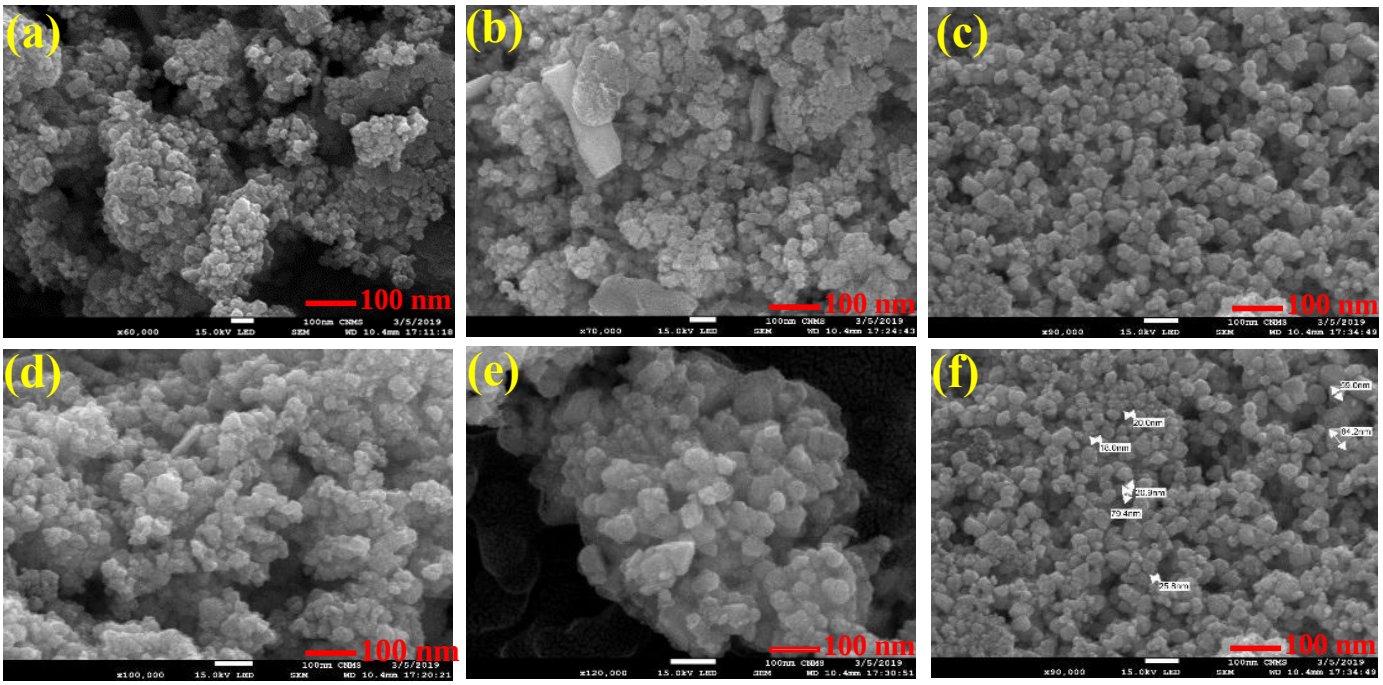


Fig. 5.(a) to(f) FE-SEM images of freshly prepared PdNPs

4.3. Energy Dispersive X-ray Spectroscopy (EDX) analysis:

In order to study the chemical composition and elemental distribution, PdNPs was subjected toEDX analysis (Fig. 6). The EDX spectrum exhibits characteristic signals corresponding to C, N, O, and Pd atoms evidenced the attachment of functional groups of phytochemicals to the PdNPs.[S1-S2]Furthermore, elemental mapping demonstrate the uniform distribution of the elements present in the PdNPs (Fig.7). The percentage of C, N, O, and Pd found to be 8.54 %, 2.49 %, 4.90 %, 84.07 % respectively.

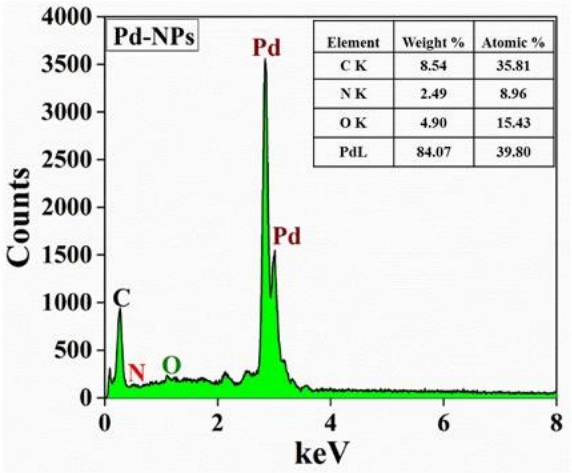


Fig.6. EDX spectrum of PdNPs

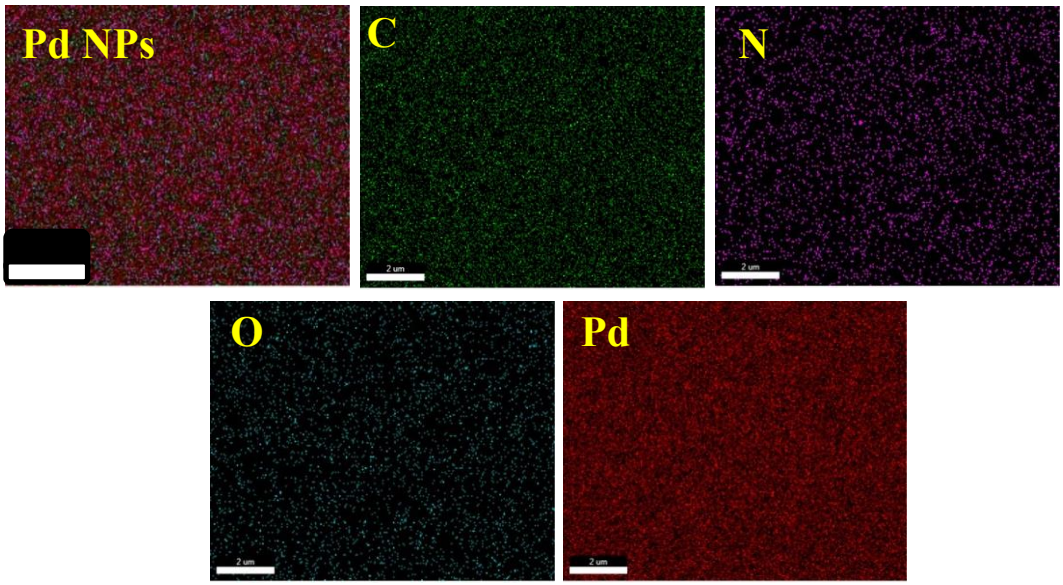


Fig.7. Elemental Mapping of PdNPs

4.4 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis:

The exact quantity of palladium loading was estimated through ICP-OES technique and loading of 63.37 % (w/w) palladium was observed.

4.5. High Resolution Transmission Electron Microscopic (HR-TEM) analysis:

To know more information about size, shape and surface morphology of PdNPs HR-TEM analysis was performed and the resulting HR-TEM images were demonstared in Fig. 8. indicates quasi-spherical shaped nanoparticles with an average diameter of 16nm in size. Also, selected area electron diffraction(SAED) pattern evidences the polycrystalline nature of PdNPs (Fig. 8f).

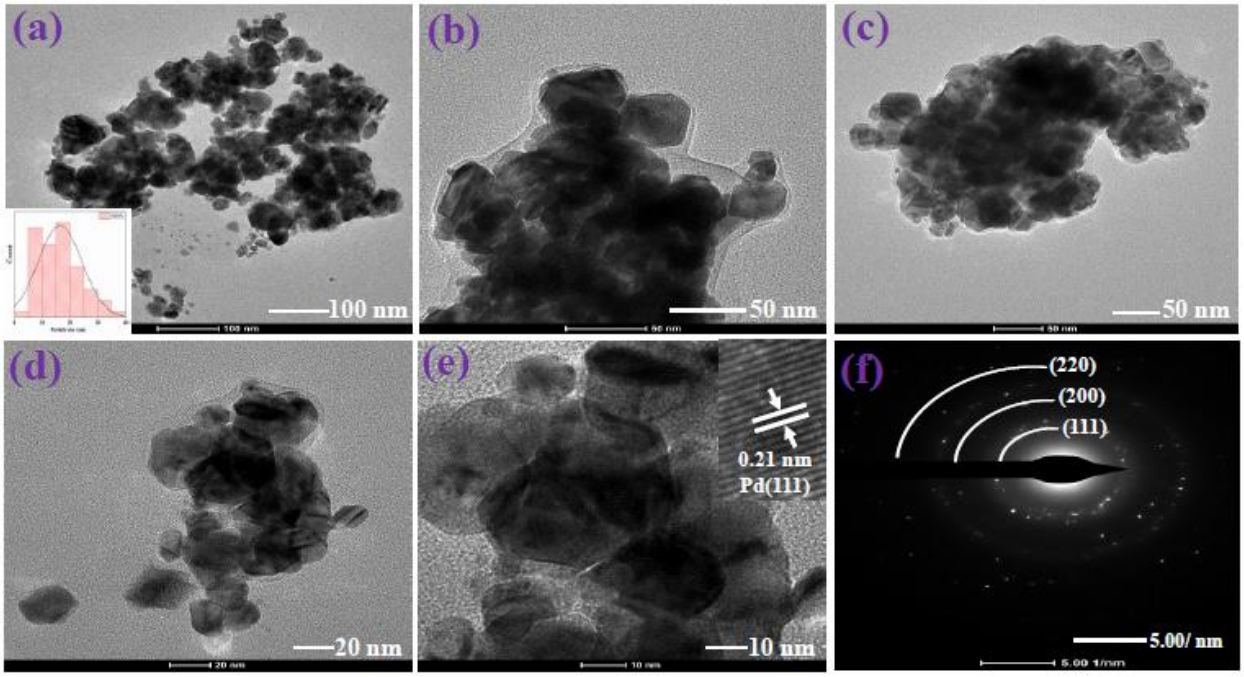


Fig. 8.HR-TEM images (a) to (e),and(f)SAED pattern of Palladium Nanoparticles.

4.6. Brunauer–Emmett–Teller (BET) surface area analysis:

Surface modification and specific surface area and porosity of PdNPs was assessed by BET and the N_2 adsorption-desorption curves. The surface area of PdNPs is found 8.782$m^2g^{-1}$was estimated which evidence the high amount of N_2 adsorbed on the surface of PdNPs. In addition, hysteresis loop values for Pd NPs at $P/P_0 \geq 0.925$ and mean pore diameter of 16.685 nm for Pd NPs was achieved which reveals the mesoporus characteristics with type-II BET isotherm.

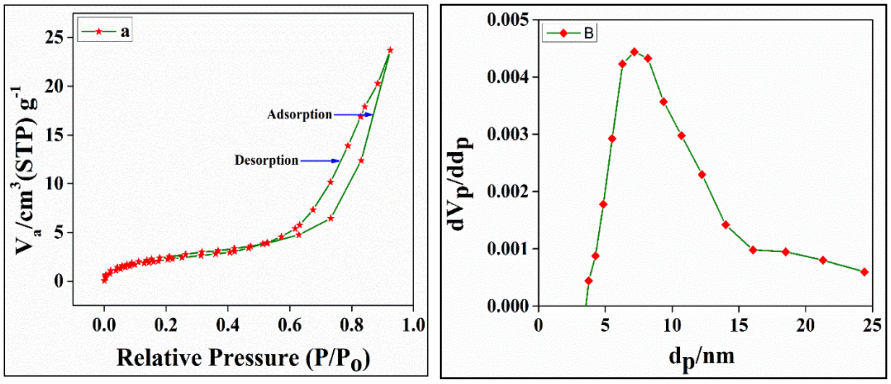


Fig. 9.(a)Nitrogen adsorption-desorption curves of Pd NPs. (b) Barrett-Joyner-Halenda (BJH) plot forPd NPs

4.7. Thermogravimetric analysis and Differential Thermal Analysis (TGA–DTA):

Thermal stability of palladium Nanoparticles was determined by TGA under N_2atmosphere at the heating rate of 10 °C/minute from the range of 35 °C to 750 °C. TGA graph of Pd NPs (Fig. 10a) shows theweight

loss of 5% can be attributed to moisture, removal of functional group of phytochemicals and carbonization confirms the presence of phytochemicals in PdNPs.DTA (Fig 10b) shows that at 275ºC there is a maximum weight loss and by this we can say that our catalyst is stable up to 275ºC.

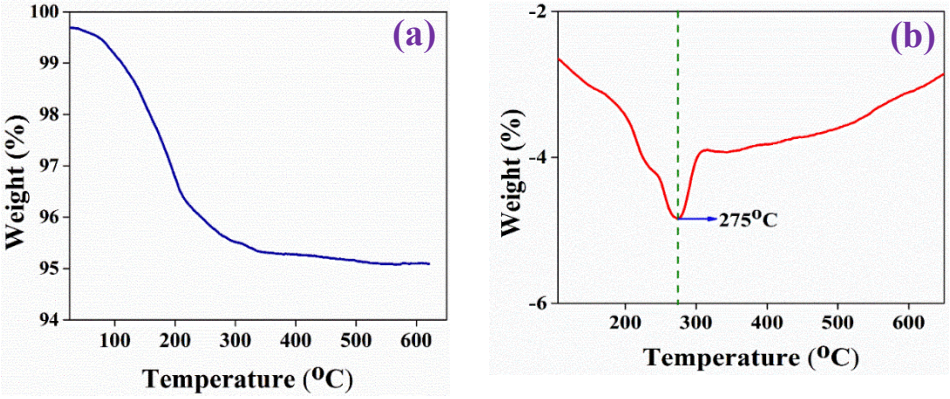


Fig. 10.(a) TGA Graph of PdNPs. (b) DTA Graph of PdNPs

4.8. X-ray diffraction analysis (PXRD):

The freshly synthesized PdNPs was characterized by PXRD to confirm the crystallographic nature and the phase (Fig.11). Palladium shows three peaks at 2θ=40.03°, 46.51° and 68.03° analogous to lattice planes (111), (200) and (220) respectively, which confirms the face centered cubic (fcc) crystal structure for Pd NPs.

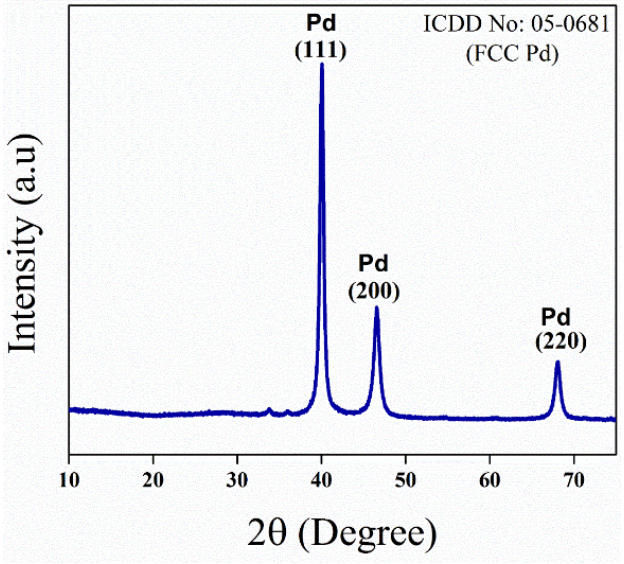


Fig. 11.X-ray diffraction pattern of Pd NPs

4.9. UV-Visible Analysis:

The UV analysis of $PdCl_2$ and Pd NPs were performed separately. The signal at wavelength 415 nm indicates presence of Pd (II) which is completely absent in the cases of UV analysis of Pd NPs clearly indicates that, the absence of Pd (II)(Fig. 12). This eventually confirms the reduction of palladium by the phytochemicals present in the Areca nut husk (Areca catechu) extract.

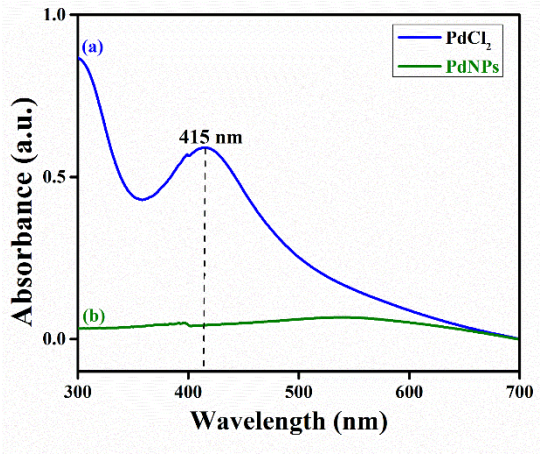
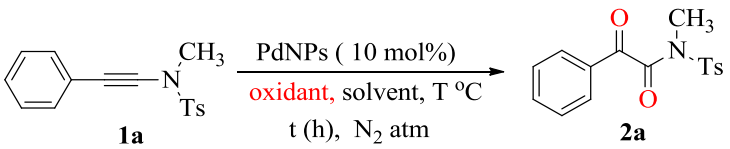


Fig 12: UV-Vis spectrum of a) pure $PdCl_2$,b) PdNPs

5.0 General experimental procedure for optimization study of oxidation of *N*-sulfonylynamides to α-keto imides:

The PdNPs (0-10mol%, Pd content: 63.37 w/w) was added in an oven dried 15mL sealed tube containing compound **1a** (0.5 mmol, 1 equiv), then the Oxidant (A-E) (1.1mmol, 2.2equiv) was added and dry DCE (1-2mL) is added to the tube in N_2atmosphere. The reaction mixture was stirred at 25–80 °C for 5–24 h. After complete conversion of starting material (indicated by TLC), the reaction was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 8–10% EA/Hexane) to get the compound **2**. The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

Table 2. Optimization of reaction condition[a]



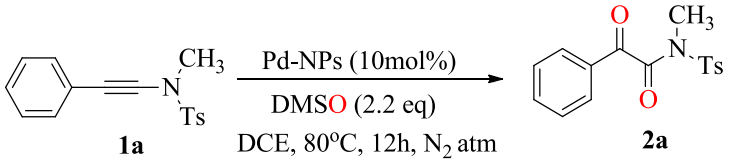
1a **2a**

Entry	Catalyst (mol %)	Oxidant (2.2 equiv)	Solvent	T (°C)/t (h)	[c]Yield (%) 2

1	Pd NPs (10)	A	DCE	25/24	N.R
2	Pd NPs(10)	A	DCE	50/24	41
3	Pd NPs(10)	A	DCE	80/15	63
4	**Pd NPs(10)**	**B**	**DCE**	**80/12**	**81**
5	Pd NPs(10)	B	DCE	50/24	55
6	Pd NPs(10)	B	THF	80/12	48
7	Pd NPs(10)	B	CH_3CN	80/12	51
8	Pd NPs(10)	B	1,4 dioxane	80/12	43
9	Pd NPs(10)	B	Toluene	80/12	trace
14	Pd NPs (5)	B	DCE	80/12	67
15	Pd NPs(10)	B (1.5equiv)	DCE	80/12	55
7	Pd NPs(10)	C	DCE	80/12	31
8	Pd NPs(10)	D	DCE	80/12	trace
9	Pd NPs(10)	E	DCE	80/12	22
10	-	B	DCE	80/12	0

[a]Reaction condition: **1a** (0.5 mmol), oxidant (0-2.2 equiv), PdNPs (0-10 mol%, 63.37 w/w), solvent, at 25-80 °C for 5-24h. [b]Oxidant Used:A:8-methyl quinoline N-oxide, B-dimethyl sulphoxide, C: quinolone *N*-Oxide D: nitrone, E:pyridine *N*-oxide; [c]yields after purification from silica gel column chromatography (average of two run).

6.0. Exact experimental procedure for the synthesis of N-methyl-2-oxo-2-phenyl-N-tosylacetamide (2a):



1a **2a**

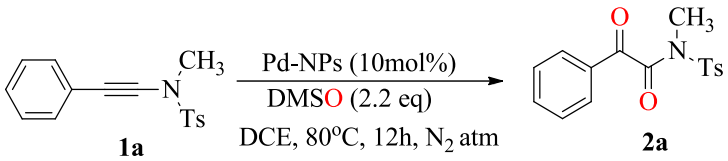
The PdNPs (8.39mg, 10mol%, Pd content: 63.37 w/w) was added in an oven dried 15mL sealed tube containing compound **1a** (142.68 mg, 0.5 mmol, 1 equiv), then the DMSO (85.94mg, 1.1 mmol, 2.2 equiv) was added and dry DCE (2mL) is added to the tube in N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After complete conversion of starting material (indicated by TLC), the reaction was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 8–10% EA/Hexane) to get the compound N-methyl-2-oxo-2-phenyl-N-tosylacetamide**2a**(128.54mg, 81%).The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

7.0.Calculation of Turn over Number (TON) for compound N-methyl-2-oxo-2-phenyl-N-tosylacetamide (2a):

$$TON = \frac{\text{(Moles reactant } \mathbf{1)} \text{ x (\% yield of } \mathbf{2})}{\text{(Moles of catalyst) x } 100 \times 10^{-3}} = \frac{0.000497617 \text{ X } 81}{0.00005 \times 100 \times 10^{-3}} = 8061$$

$$TOF = \frac{TON}{Time} = \frac{8061}{12} = 672$$

8.0 Representative procedure of gram scale reaction:



1a **2a**

The Pd NPs (58.84mg, 10mol%, Pd content: 63.37 w/w) was added in an oven dried 15mL sealed tube containing compound **1a** (1g, 3.50mmol, 1 equiv), then the DMSO (0.602 g, 7.70mmol, 2.2 equiv) was added. Then dry DCE (8 mL) is added to the tube in N_2 atmosphere. The reaction mixture was stirred at 80 ^oC for 12 h. After complete conversion of starting material (indicated by TLC), the reaction was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 8–10% EA/Hexane) to get the compound N-methyl-2-oxo-2-phenyl-N-tosylacetamide **2a** (0.86g, 78%). The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

9.0.Catalyst recyclability for oxidation of N-sulfonylynamides:

The recyclability of freshly synthesized the PdNPs was examined for oxidation of N-sulfonylynamides under optimized condition. After the completion of reaction, the desired product is purified by column chromatography and yield was determined. However, the heterogeneous PdNPs catalyst is separated from reaction mixture by centrifugation, washed with water (2 x 10 mL) followed by ethanol (2 x 10 mL) and dried at 45 $^\circ C$ for 12 hrs. It is then further used for second cycle and so on. As shown in Fig.13 (a), PdNPs catalyst used up to ten cycle and the yield was determined. As indicated by FESEM images (Fig. 13 (b-e), only slight change in morphology was observed after the ten cycles as the activity of PdNPs goes on decreasing steadily. However, the agglomeration was increased as compared to the fresh catalyst.

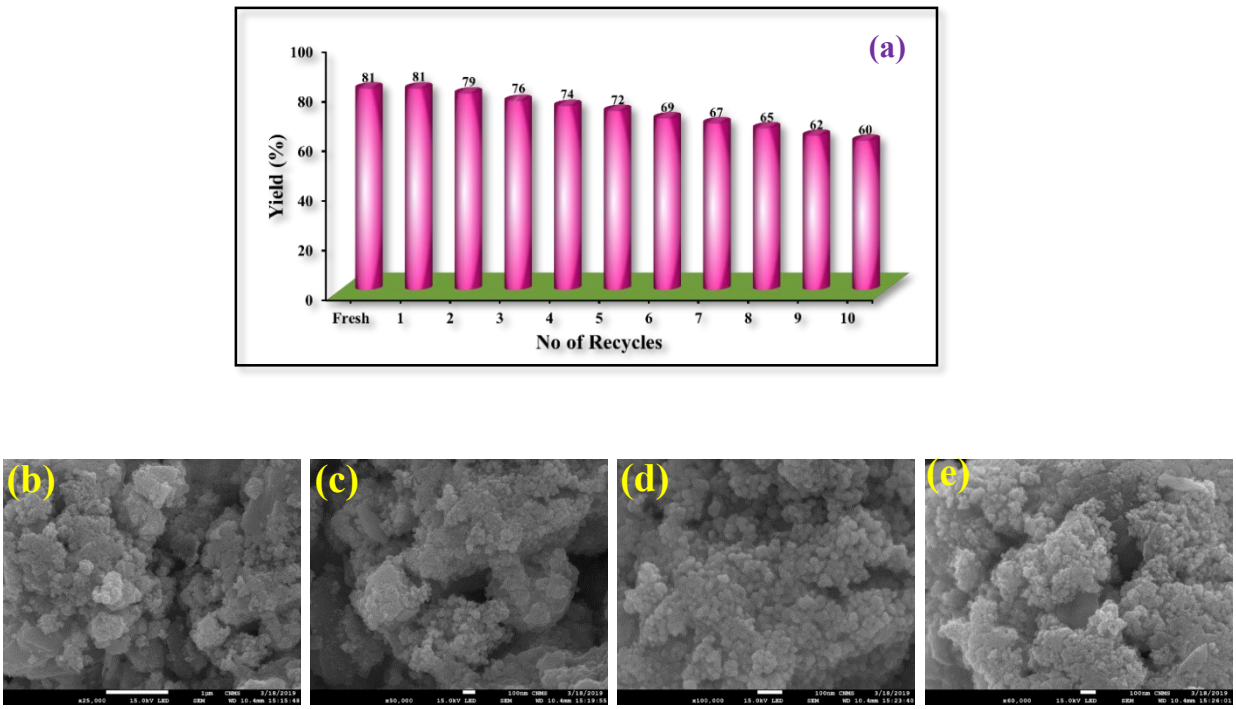
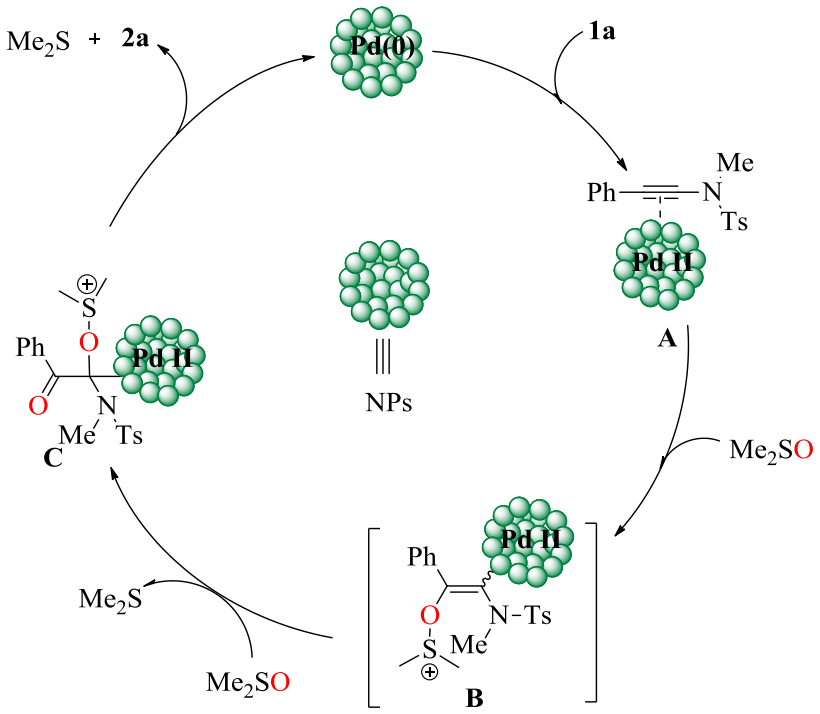
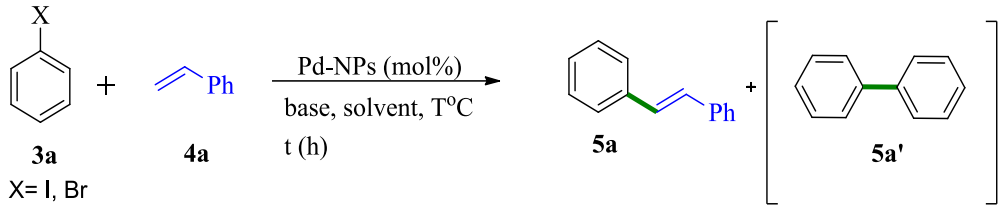


Fig.13. a) Recycling efficiency of PdNPs in ynamide oxidation
b-e) FESEM Images PdNPs after 10thcycle

10.0 Reaction Mechanism for oxidation of N-sulfonylynamides:



11.0. General experimental procedure for optimization study for Heck Coupling:



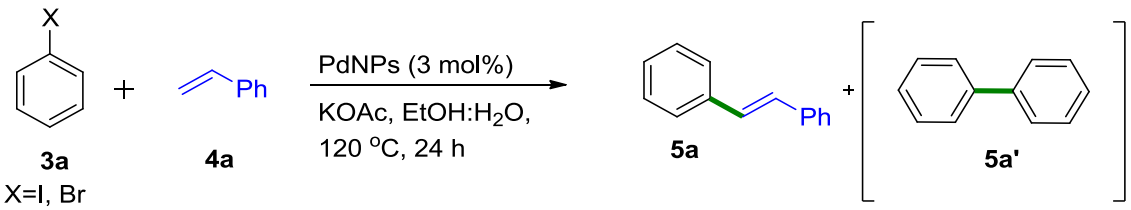
The Pd NPs (0-3mol%, Pd content: 63.37 w/w) was added in an oven dried 15mL sealed tube containing compound **3a**(0.5 mmol, 1 equiv), KOAc (0.6mmol, 1.2 equiv), compound **4a** (2.5 mmol, 5 equiv) was added followed by EtOH: H_2O (1:1) (1-2mL) is added to the tube. The reaction mixture was stirred at 25–120 °C for 12–48 h. After complete conversion of starting material (indicated by TLC), the reaction was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: Hexane) to get the compound **5a**. The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

Table 3. Optimization of reaction condition[a]

S. N	PdNPs(x mol %)	Solvent	Base	T (°C)/t (h)	[c]Yield 3 (%)
1	3	EtOH:H_2O	KOAc	25/48	N.R
2	3	EtOH:H_2O	KOAc	50/12	45
3	**3**	**EtOH:H_2O**	**KOAc**	**120/24**	**88**
4	3	EtOH	KOAc	120/24	81
5	3	H_2O	KOAc	120/24	79
6	3	NMP	KOAc	120/24	54
7	3	ACN	KOAc	120/24	62
8	3	EtOH:H_2O	NaOAc	120/24	61
9	3	EtOH:H_2O	Cs_2CO_3	120/24	71
10	3	EtOH:H_2O	K_2CO_3	120/24	58
11	3	EtOH:H_2O	KOH	120/24	49
12	2	EtOH:H_2O	KOAc	120/36	51
13	1	EtOH:H_2O	KOAc	120/36	32
14	0	EtOH:H_2O	KOAc	120/36	N.R

[a]Reaction condition: **3a** (0.5 mmol), **4a** (2.5mmol, 5 equiv), Base (0-1.5 equiv), Pd NPs (0-3 mol%, 63.37 w/w), solvent, at 25-120°C for 5-24h. [c]yields after purification from silica gel column chromatography (average of two run).

12.0. Exact experimental procedure for Heck Coupling:



The PdNPs (2.51mg, 3mol%, Pd content: 63.37 w/w %) was added in an oven dried 15mL sealed tube containing compound **3a** (102.00 mg, 0.5 mmol, 1 equiv), then KOAc (58.88 mg, 0.6 mmol, 1.2 equiv) then added compound **4a**. (260.37mg, 2.5 mmol, 5 equiv) was added. Then EtOH: H_2O (1:1) (1-2mL) is added to the tube. The reaction mixture was stirred at 120°C for 24 h. After complete conversion of starting material (indicated by TLC), the reaction was quenched with water and the organic layer was extracted with EtOAc (25×3) the combined organic layer was dried over anhydrous Na_2SO_4then the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: Hexane) to get the compound **5a**(E)-1,2-diphenylethene (79.30 mg,88%). The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

13.0 Catalyst recyclability study for Heck Coupling:

The recyclability of freshly synthesized the Pd NPs was examined for Heck Coupling under optimized condition. After the completion of reaction, the desired product is purified by column chromatography and yield was determined. However, the heterogeneous PdNPs catalyst is separated from reaction mixture by centrifugation, washed with water (2 x 10 mL) followed by ethanol (2 x 10 mL) and dried at 45 °C for 12 hrs. It is then further used for second cycle and so on. As shown in Fig. 14(a), Pd NPs catalyst used up to five cycle and the yield was determined.As indicated by FESEM images (Fig. 14(b-i), only slight change in morphology was observed after the five cycles as the activity of PdNPs goes on decreasing steadily. However, the agglomeration was increased as compared to the fresh catalyst.

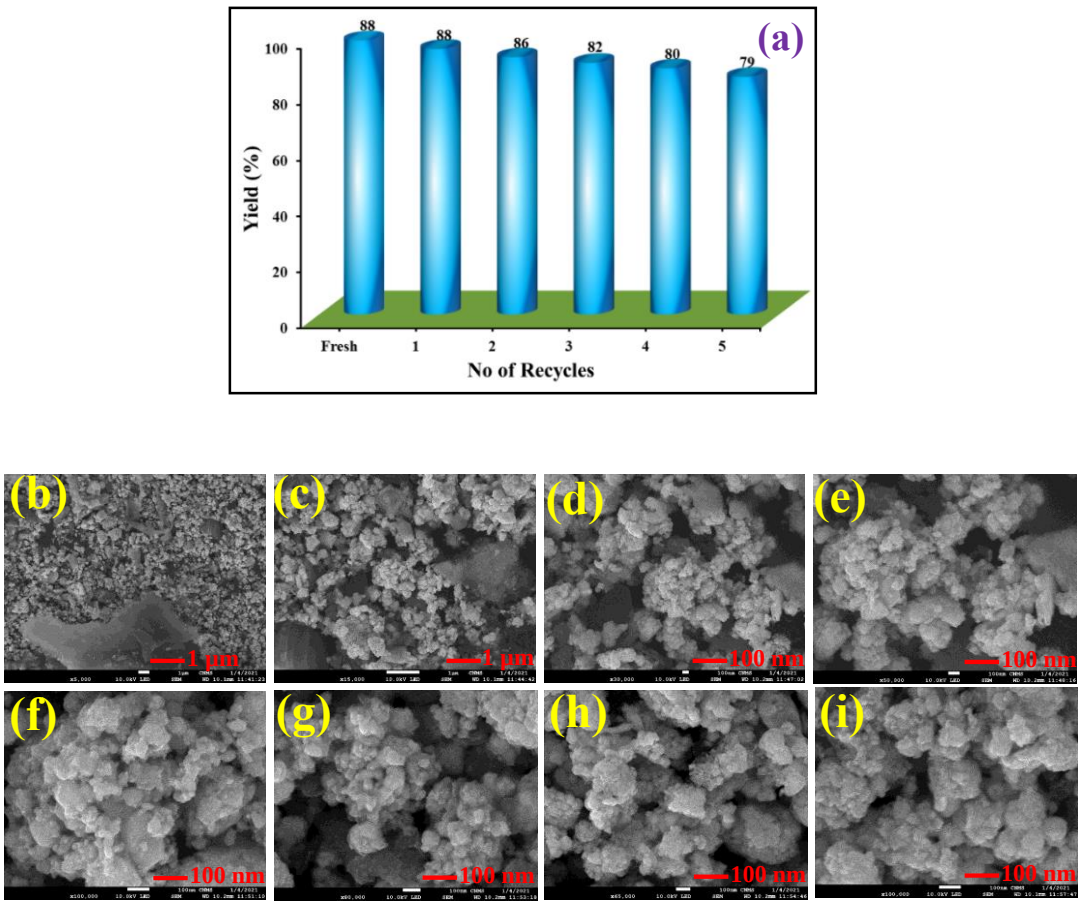
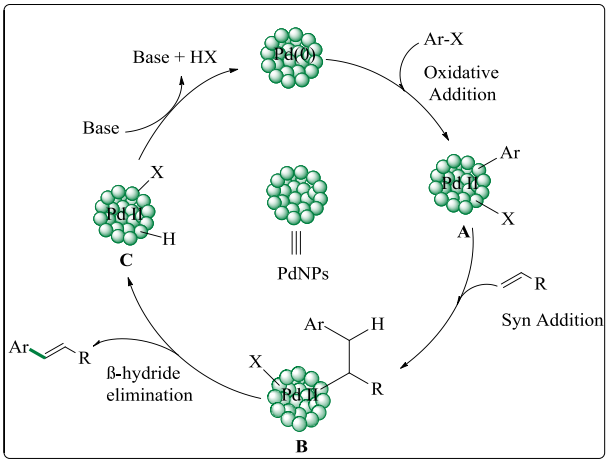


Fig.14.a) Recycling efficiency of PdNPs in Heck Coupling b-i) FESEM Images PdNPs after 5thcycle

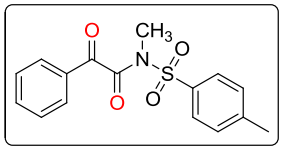
14.0. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis of reaction mixture and recovered catalyst: In order to check leaching of palladium from the catalyst we have carried out the ICP-OES analysis of reaction mixture after separating the catalyst from it and also the ICP-OES analysis of recovered catalyst. We found that the palladium lost in reaction mixture was less than 0.01 ppm and the palladium content of final PdNPs was 62.50 w/w%. This result shows that catalyst leaching was very less in biogenically synthesized PdNPs.

15.0. Reaction Mechanism for Heck Coupling:



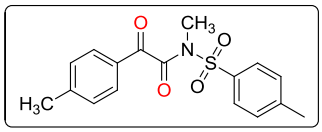
16.0.Spectroscopic data of newly obtained Diketo products:

N-methyl-2-oxo-2-phenyl-N-tosylacetamide (2a)



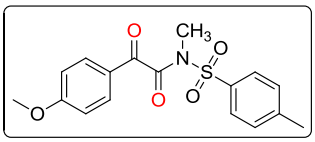
Pale yellow solid; m.p. 130 – 132°C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 –7.96 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.58 – 7.54 (m,2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.27 (s, 3H), 2.49 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ188.1, 167.3, 146.0, 134.5, 133.5, 132.8, 130.1, 129.7, 128.9, 128.4, 30.7, 21.7;IR (cm^{-1}): 2917, 2849, 1681, 1372, 1232, 1166, 947, 717, 664, 594; HRMS (ESI) calcd.for $C_{16}H_{15}NNaO_4S$ $[M + Na]^+$: 340.0614; found: 340.0615.

N-methyl-2-oxo-2-(p-tolyl)-N-tosylacetamide(2b)



Yellow solid; m.p. 137– 139°C; ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.23 (s, 3H), 2.46 (s, 3H), 2.46 (s, 3H); 2.44 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 167.6, 146.0, 145.9, 133.8, 130.6, 130.3, 130.0, 129.8, 128.6, 31.0, 22.1, 21.9; IR (cm^{-1}): 3066, 2923, 1678, 1605, 1372, 1177, 1033, 694, 669, 591;

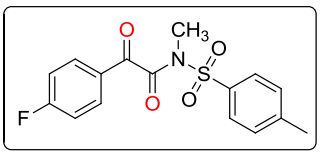
2-(4-methoxyphenyl)-N-methyl-2-oxo-N-tosylacetamide (2c)



Yellow solid; m.p. 92–95°C;^{1}H NMR (400 MHz, $CDCl_3$)δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.39 (d, 8.4 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.00(d,*J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.90

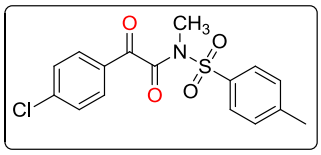
(s, 3H), 3.24 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 171.8, 167.6, 164.8, 145.9, 133.7, 132.2, 130.5, 130.2, 130.0, 128.5, 127.6, 125.9, 114.4, 55.8, 30.9, 21.8;IR (cm^{-1}): 3068, 2935, 1668, 1598, 1371, 1172, 1030, 816, 695, 667; HRMS (ESI) calcd.for $C_{17}H_{17}NO_5S$ $[M]^+$: 347.0827; found for $C_{17}H_{17}NO_5NaS$ $[M+Na]^+$: 370.0723

2-(4-fluorophenyl)-N-methyl-2-oxo-N-tosylacetamide(2d)



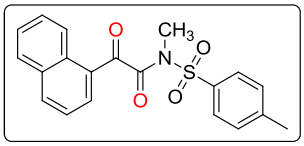
Yellow solid; m.p. 141 – 143ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 2H), 3.23 (s, 3H), 2.46 (s, 3H).;^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 167.6 (d, J_{C-F}= 73.4 Hz), 165.4, 146.2, 133.6, 132.6 (d, J_{C-F}= 9.7 Hz), 130.4, 129.8 (d, J_{C-F}= 10.9 Hz), 128.6, 116.5 (d, J_{C-F}= 22.2 Hz) 31.0, 22.0; IR (cm^{-1}): 3070, 2925, 1682, 1598, 1372, 1237, 1033, 957, 669, 590;

2-(4-chlorophenyl)-N-methyl-2-oxo-N-tosylacetamide (2e)



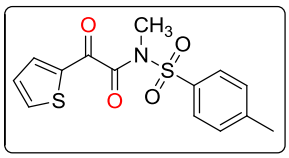
Pale yellow solid; m.p. 150 – 152 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 3H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 1H), 3.23 (s, 3H), 2.46 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 167.0, 146.2, 141.1, 133.4, 131.4, 131.0, 130.3, 129.4, 128.5, 30.8, 21.7; IR (cm^{-1}): 3065, 2927, 1676, 1590, 1372, 1173, 1034, 759, 666, 579;

N-methyl-2-(naphthalen-1-yl)-2-oxo-N-tosylacetamide (2f)



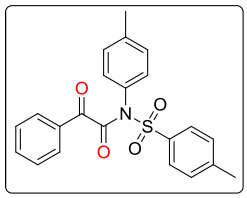
Yellow solid; m.p. 156 – 158 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.09(t, *J* = 8.6 Hz, 1H), 3.28 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 167.2, 146.0, 135.7, 134.5, 134.2, 131.3,130.2, 129.7, 129.3, 128.9, 128.5, 127.9, 127.0, 126.0, 124.5, 31.0, 21.8; IR (cm^{-1}):3072, 2931, 1721, 1640, 1547, 640, 592; HRMS (ESI) calcd.for $C_{20}H_{17}NO_4S$ $[M]^+$: 367.0878; found: 367.0882.

N-methyl-2-oxo-2-(thiophen-2-yl)-N-tosylacetamide (2g)



Paleyellowsolid.m.p. 138– 140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 4.8 Hz, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 4.2 Hz, 1H), 3.24 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 166.1, 146.0, 139.7, 136.1, 136.0 133.7, 130.2, 128.7128.6,31.2, 21.9; IR (cm^{-1}): 3072, 2931, 1721, 1647, 645, 590; HRMS (ESI) calcd.for $C_{14}H_{13}NO_4S_2$ [M] $^{+}$: 323.0286; found $C_{14}H_{13}NO_4NaS_2$ [M + Na] $^{+}$: 346.0187.

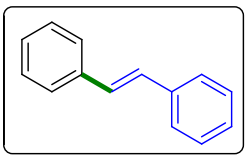
2-oxo-2-phenyl-N-(p-tolyl)-N-tosylacetamide (2h)



Yellow solid; m.p. 164 – 166°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.28 (m, 3H), 3.24 (s, 3H), 2.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 167.5, 146.1, 134.6, 133.7, 133.0, 130.3, 130.1, 129.9, 129.6, 129.1, 128.8, 128.6, 127.7, 30.9, 21.9;IR (cm^{-1}): 3066, 2923, 1682, 1596, 1371, 1172, 957, 715, 655, 590; HRMS (ESI) calcd.for $C_{22}H_{19}NNaO_4S$[M + Na]$^{+}$: 416.0926;found: 416.0926.[S4]

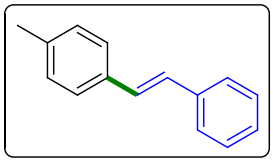
17.0. Spectroscopic data of newly obtained Heck Coupled product:

(E)-1,2-diphenylethene (5a)



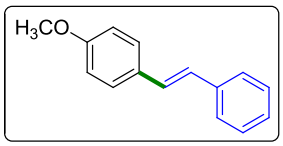
White solid; m.p. 122 – 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $cdcl_3$) δ 7.53 (d, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 4H), 7.29 – 7.24 (m, 2H), 7.12 (s,2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.6, 127.6, 126.5;IR (cm^{-1}): 2922, 1737, 1450;MS (EI) m/z 180, 77;[S6]

(E)-1-methyl-4-styrylbenzene (5b)



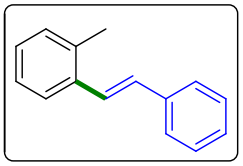
White solid; m.p. 119 – 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 2.4 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 137.4, 134.5, 129.3, 128.6, 127.7, 127.3, 126.4, 126.3,21.2;IR (cm^{-1}):3020, 1592, 1508, 1448; MS (EI) m/z 194, 91, 77; [S6]

(E)-1-methoxy-4-styrylbenzene (5c)



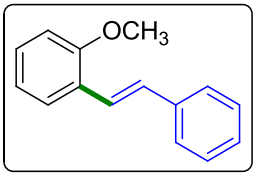
White solid; m.p. 131 – 134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.48 (q, *J* = 8.0 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.03 (q, *J* =16.2 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.6, 130.1, 128.6, 128.1, 127.6, 127.1, 126.5, 126.2, 114.1, 55.2;IR (cm^{-1}):2935, 1599, 1509; MS (EI) m/z 210, 107, 104, 77; [S6]

(E)-1-methyl-2-styrylbenzene (5d)



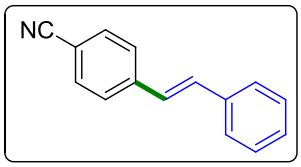
Yellowish solid; m.p.115 – 118°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 (d,*J* =7.2Hz,1H), 7.23-7.19 (m, 3H), 7.01 d,*J* =16Hz,1H), (2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.3, 135.7, 130.3, 130.0, 128.6, 127.5, 126.5, 126.1, 125.3, 19.8;IR (cm^{-1}):3023, 1511,1494; MS (EI) m/z 194, 91, 77; [S6]

(E)-1-methoxy-2-styrylbenzene (5e)



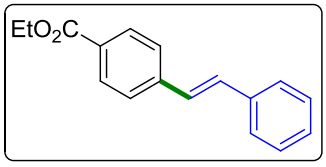
White solid; m.p. 125 – 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.59-7.52 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 16.4 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 137.9,129.1, 128.6, 128.5, 128.0, 127.3, 126.5, 126.4, 123.5, 120.7, 110.9, 55.5; IR (cm^{-1}): 2945, 1589, 1513; MS (EI) m/z 210, 107, 104, 77; [S6]

(E)-4-styrylbenzonitrile (5f)



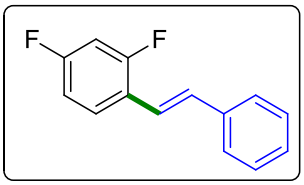
White solid; m.p. 126-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$)δ ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 16.0 Hz,1H), 7.08 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 136.2, 132.4, 132.3, 128.8, 128.6, 126.8, 126.8, 126.6, 118.9, 110.5;IR (cm^{-1}): 2923, 1596, 1371, 1172;

(E)-ethyl 4-styrylbenzoate (5g)



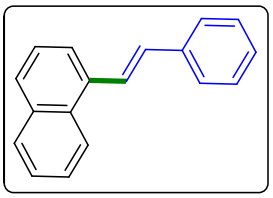
Whitish Yellow solid; m.p. 128-131 ºC; ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 9.2Hz, 4H), 7.38 (t, *J*= 7.4 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.15(t, *J* = 18.2 Hz, 2H), 4.38 (q, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 141.6, 136.7, 131.0, 129.9, 129.2, 128.7, 128.1, 127.5, 126.7, 126.2, 60.8, 14.3;IR (cm^{-1}): 2909, 1745, 1443;

(E)-2,4-difluoro-1-styrylbenzene (5h)



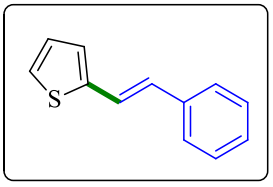
Yellow semi solid; m.p. 164 – 166ºC; ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.60-7.51 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 16.4 Hz, 1H), 7.10 (d, *J* = 16.8 Hz, 1H), 6.91-6.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ162.5 (dd, $J_{C\text{-}F}$= 180.0 Hz and 13 Hz), 160.0 (dd, $J_{C\text{-}F}$ = 185.0 Hz, 13.0 Hz), 143.5, 137.0, 130.5, 128.7, 128.0, 127.8 (dd, $J_{C\text{-}F}$= 14.0 Hz and 8 Hz), 126.5, 111.5 (dd, *J* = 22.0 Hz and 0 Hz), 104.6 (t, *J* = 25 Hz); IR (cm^{-1}):1769, 1643, 1629, 1140, 1178, 1018;

(E)-1-styrylnaphthalene (5i)



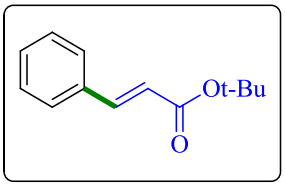
Yellow solid; m.p. 70–71 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 135.0, 133.7, 131.7, 131.4, 128.7, 128.6, 128.0, 127.7, 126.6, 126.0, 125.8, 125.6, 123.7, 123.6; IR (cm^{-1}): 3055, 3022, 1493, 957; MS (EI) m/z 230, 127, 103, 77; [S6]

(E)-2-styrylthiophene (5j)



Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8^{1}H NMR (400 MHz, cdcl$_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.09 (d, *J* = 3.2 Hz, 1H), 7.02 (q,*J* = 3.8 Hz 1H), 6.95 (d, *J* = 16 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.0, 128.7, 128.3, 127.6, 126.3, 126.1, 124.3, 121.8;

tert-butyl cinnamate (5k)



Brownish solid; m.p. 154 – 156ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.50 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.38 – 7.34 (m, 3H), 6.37 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 143.5, 134.6, 129.9, 128.8, 127.9, 120.2, 80.4, 28.2; IR (cm^{-1}): 3069, 2944, 2841, 1718, 1641, 1458, 1205, 1167, 770, 685;

18.0 References:

[S1] V. Kandathil, R. B. Dateer, B. S. Sasidhar, S. A. Patil, S. A. Patil, *Catal. Lett*. 2018, **148**, 1562–1578.

[S2] R. V. Hegde, A. Ghosh, S. A. Patil, R. B. Dateer, *Tetrahedron.* 2019, **75**,13077.

[S3] X. Liu, Z. –X. Zhang, B. Zhou, Z. –S. Wang, R. –H. Zheng, L. –W. Ye, *Org. Biomol. Chem*. 2017, **15**, 10156–10159.

[S4] R. B. Dateer, B. S. Shaibu, R. –S. Liu, *Angew. Chem. Int. Ed.* 2012, **51**, 113–117.

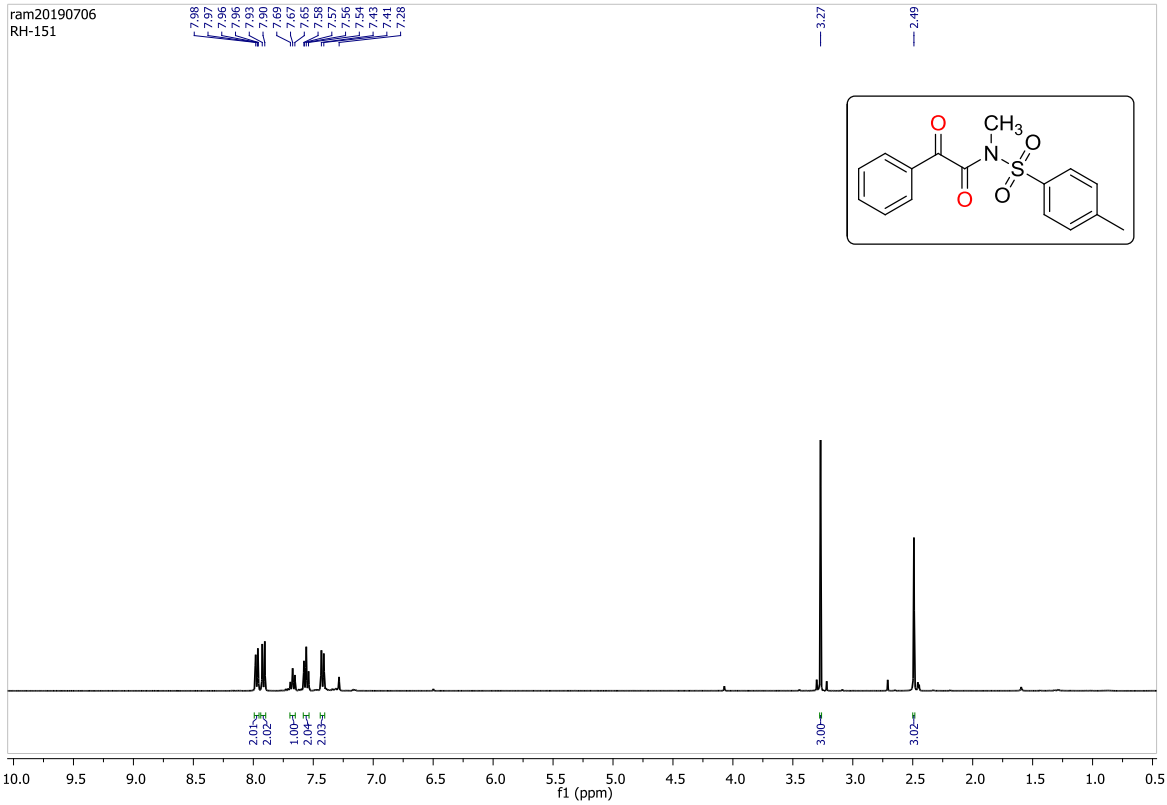
[S5] K. Sumalatha, J. IshwaraBhat, *Iranian (Iranica) Journal of Energy and Environment*. 2019, **10**, 136–146.

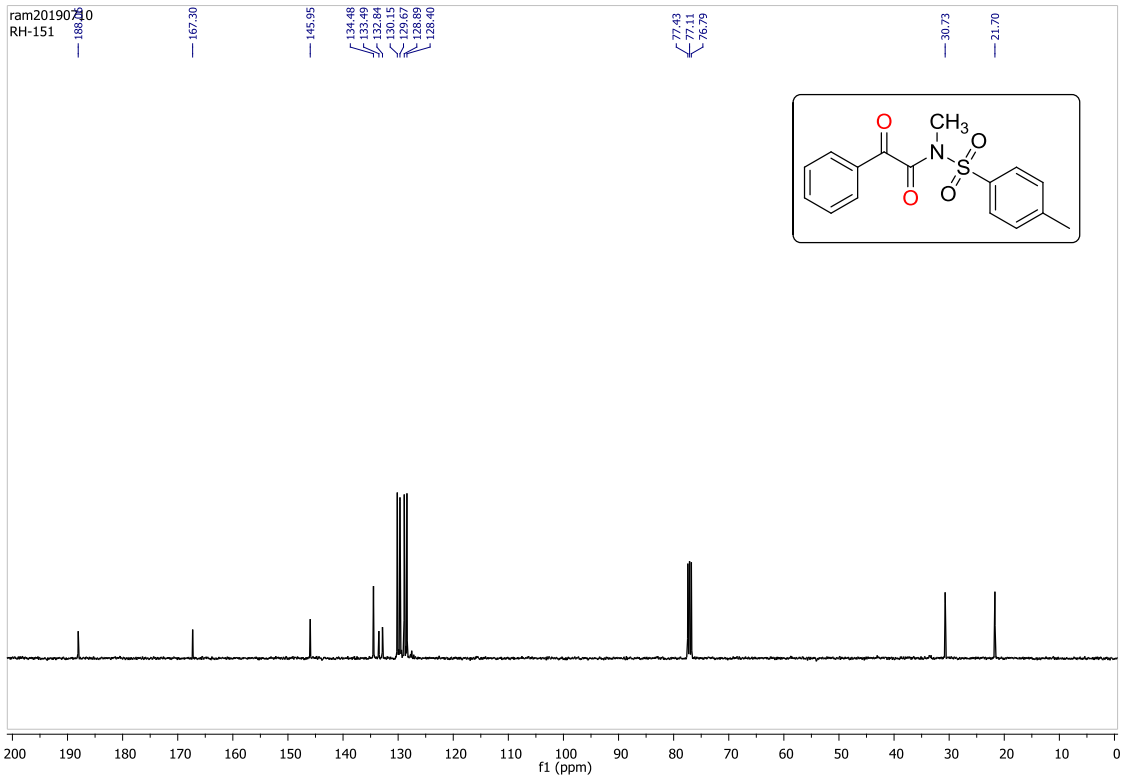
[S6] M. B. Andrus, C. Song, J. Zhang, *Org. Lett*. 2002, **12**, 2079–2082.

Appendix

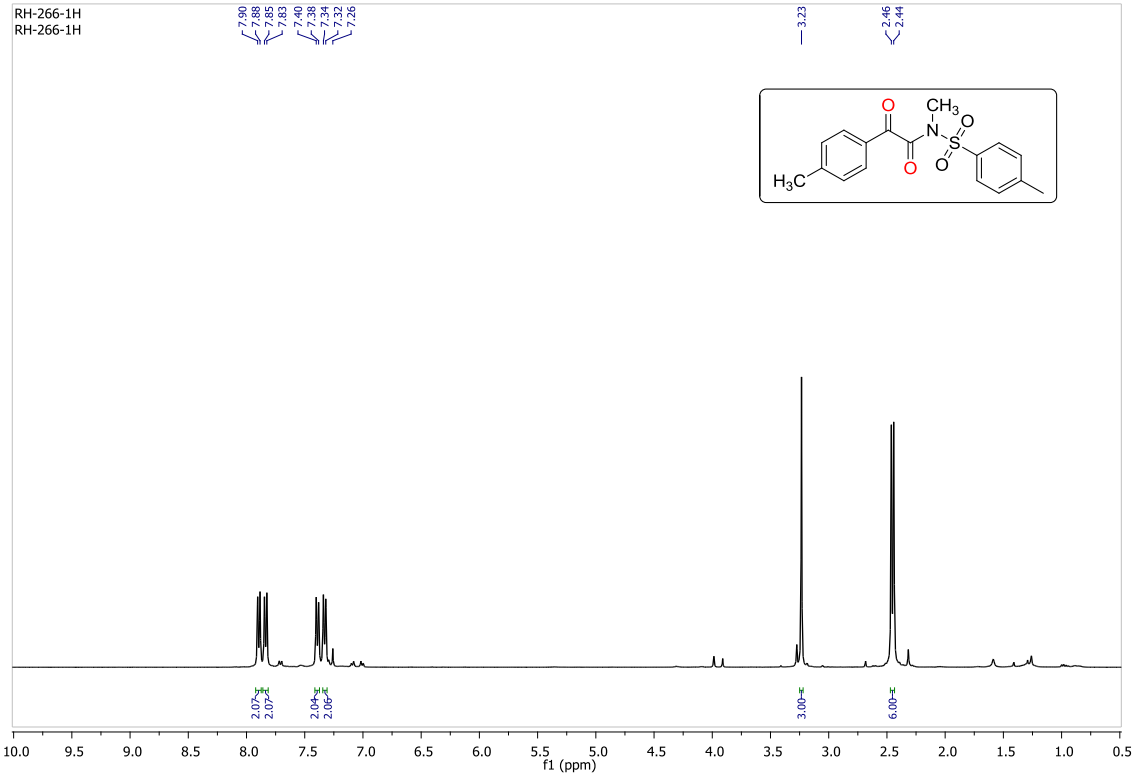
Spectral copies of ^{1}H and ^{13}C NMR of compounds obtained in this study

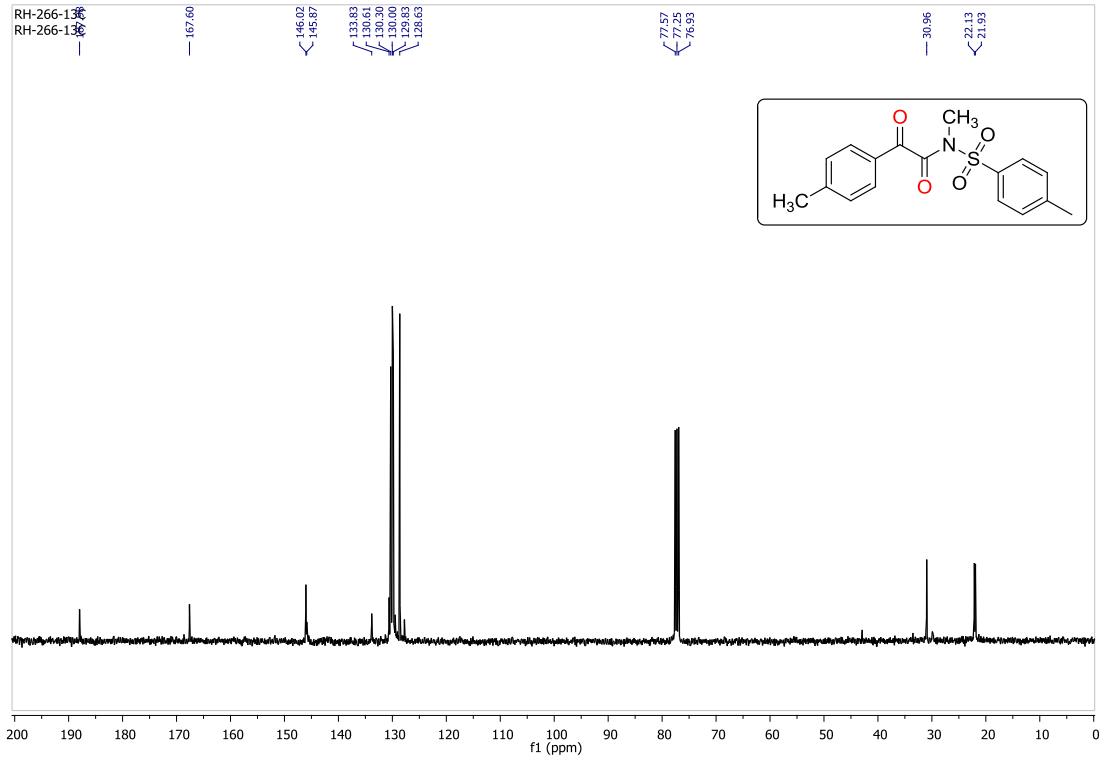
N-methyl-2-oxo-2-phenyl-N-tosylacetamide (2a)



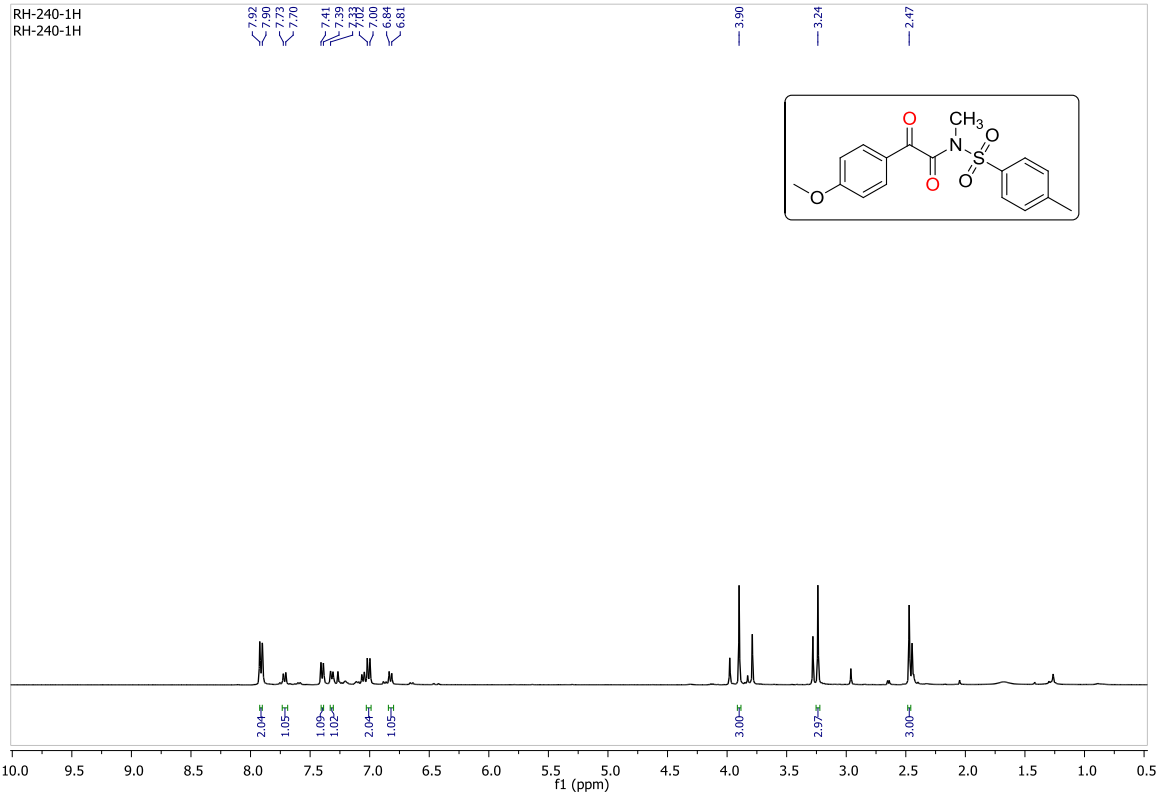


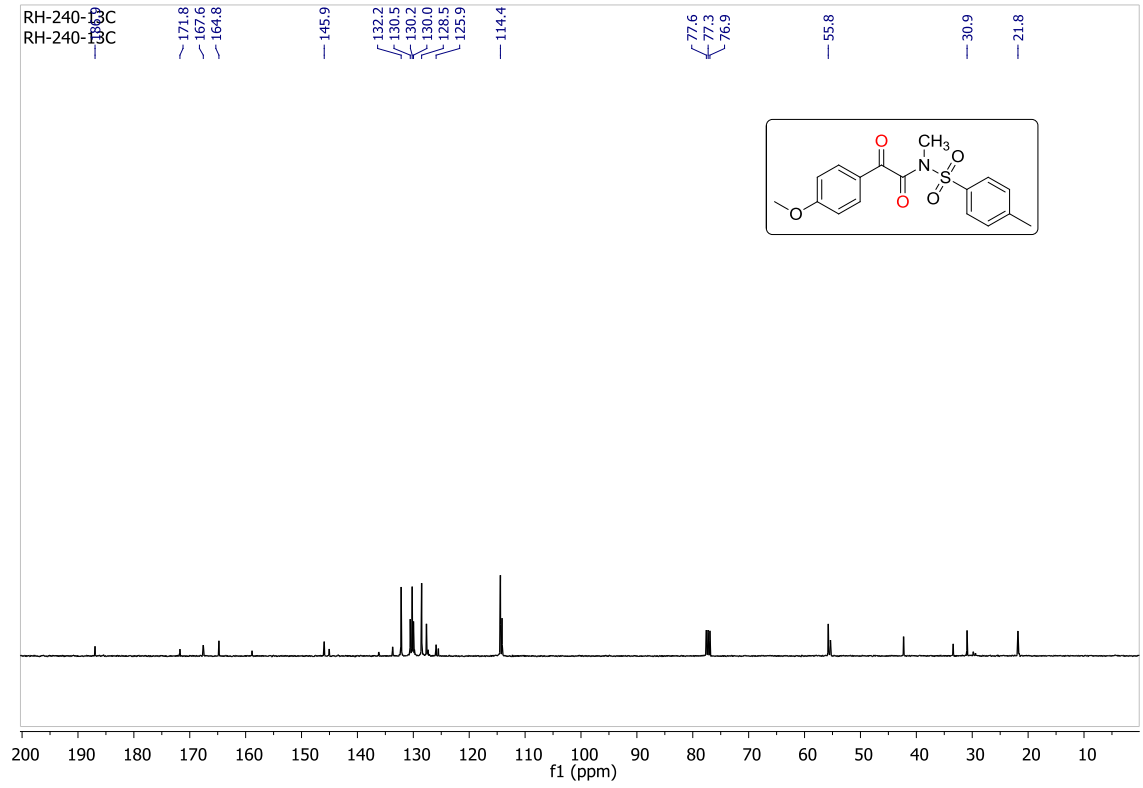
N-methyl-2-oxo-2-(p-tolyl)-N-tosylacetamide (2b)



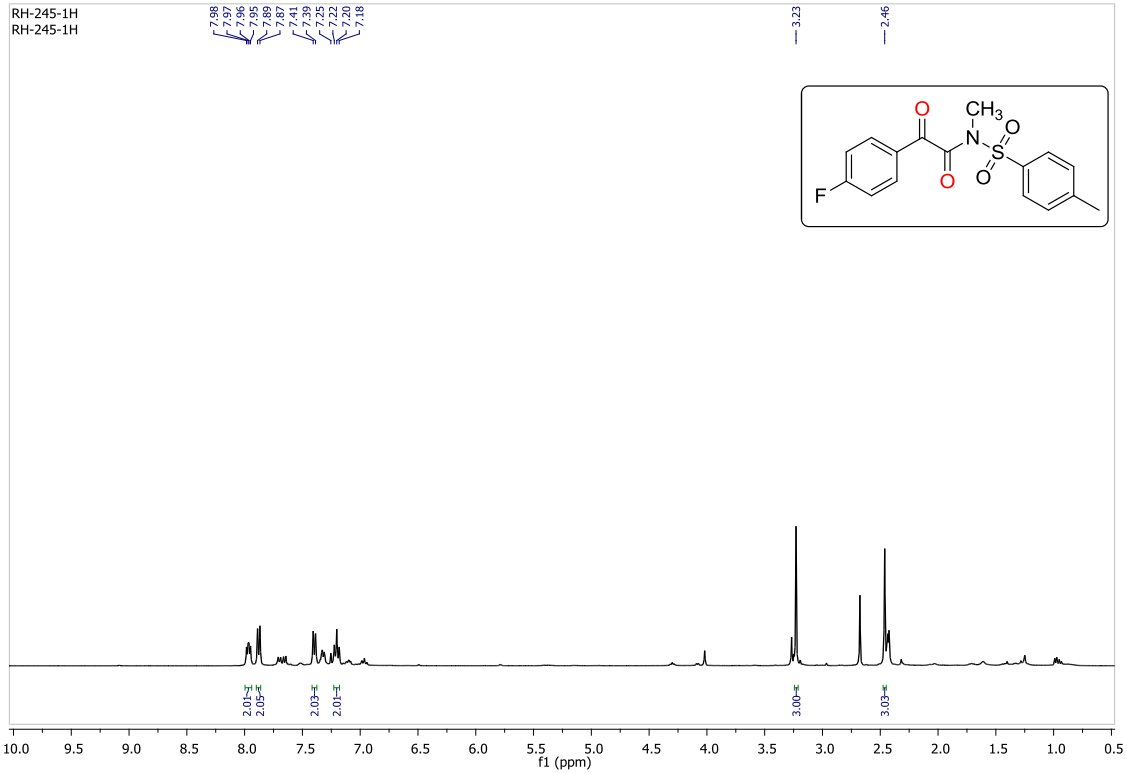


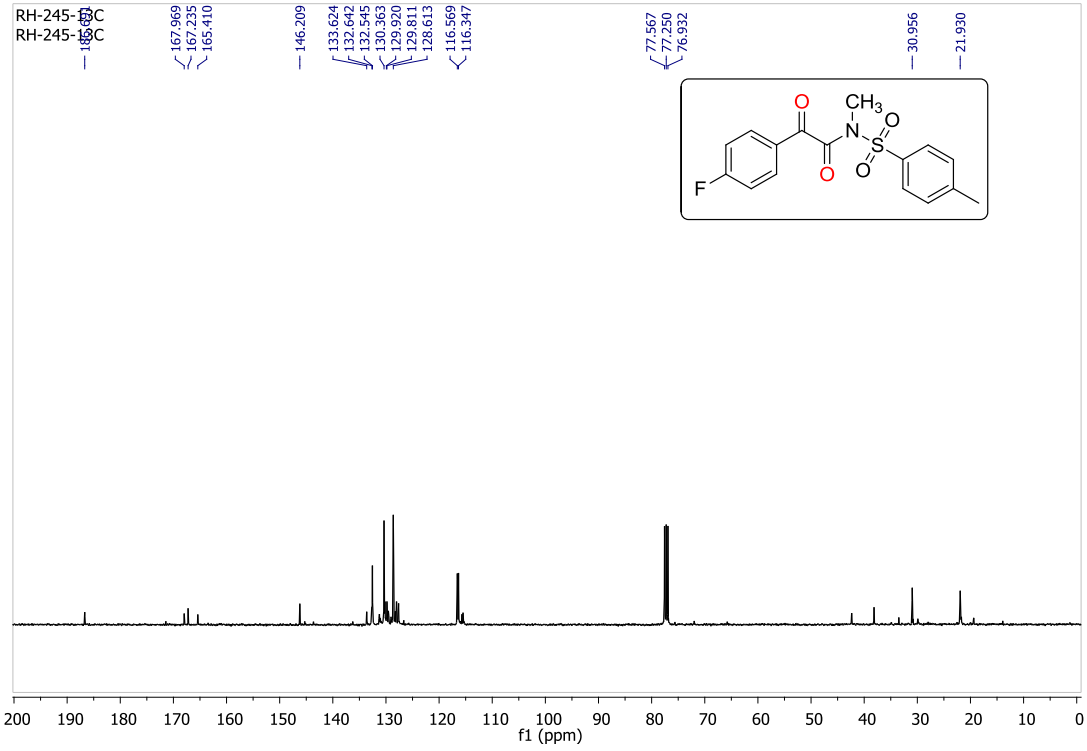
2-(4-methoxyphenyl)-N-methyl-2-oxo-N-tosylacetamide (2c)



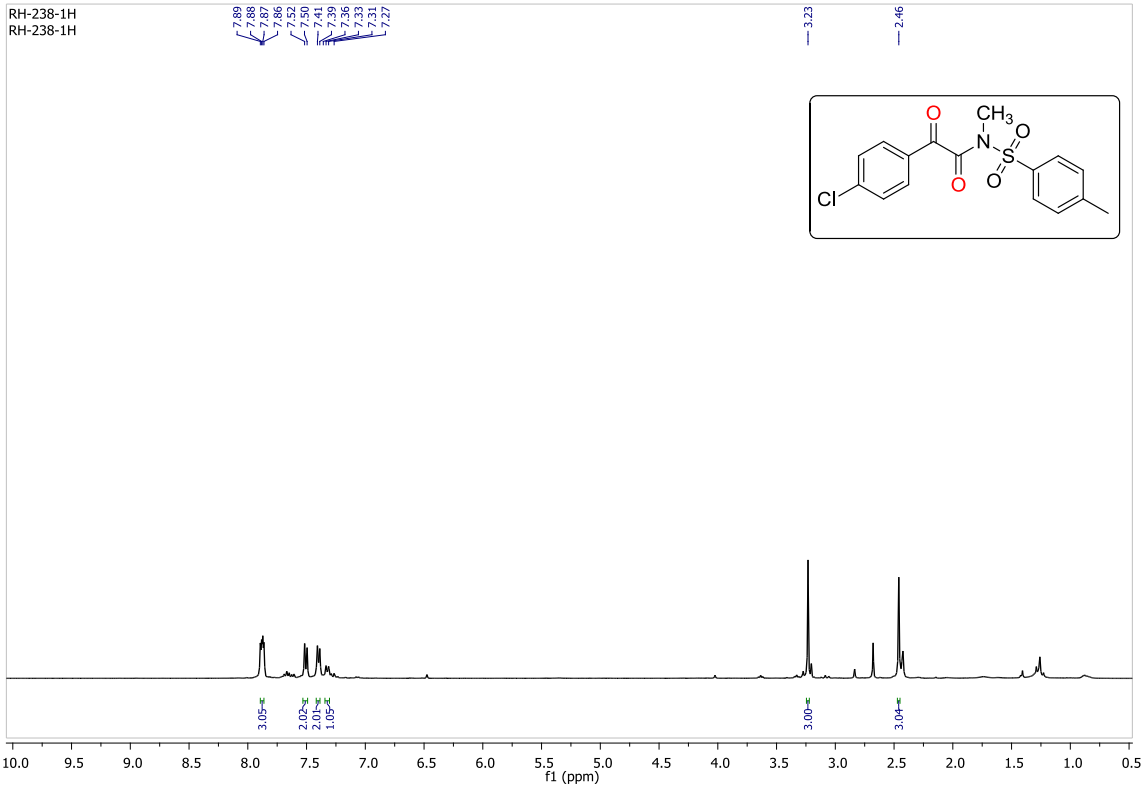


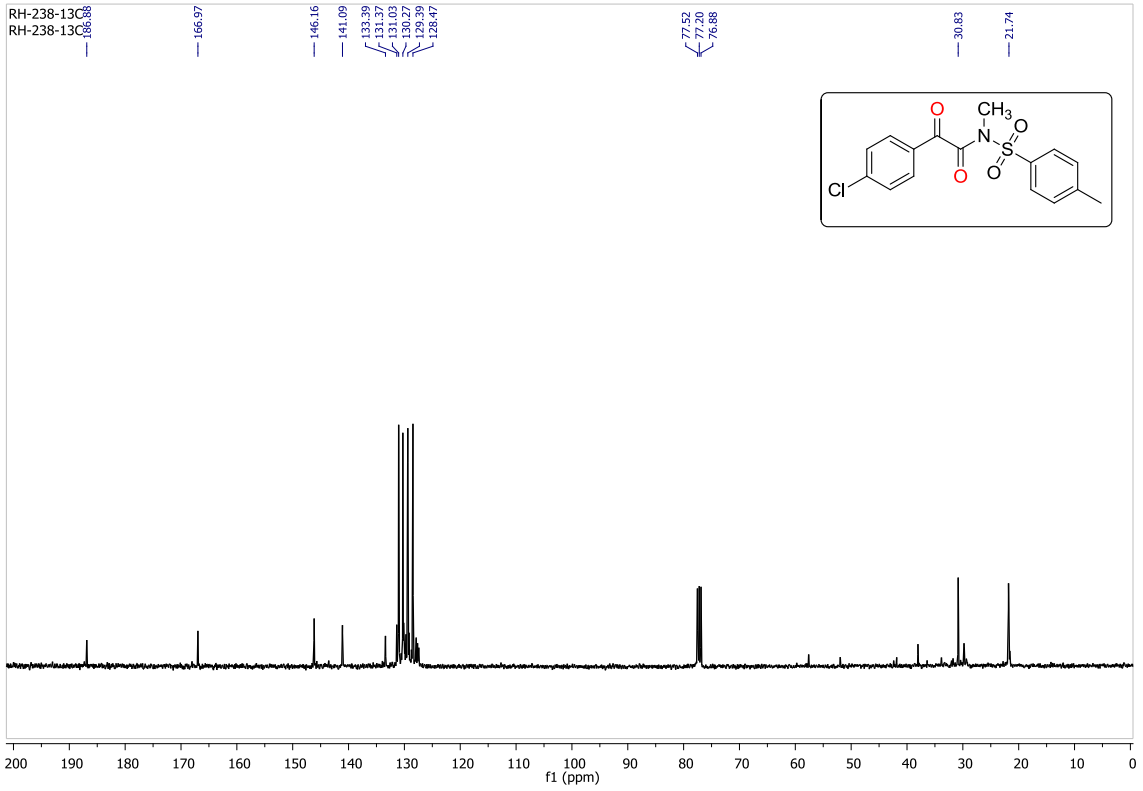
2-(4-fluorophenyl)-N-methyl-2-oxo-N-tosylacetamide (2d)



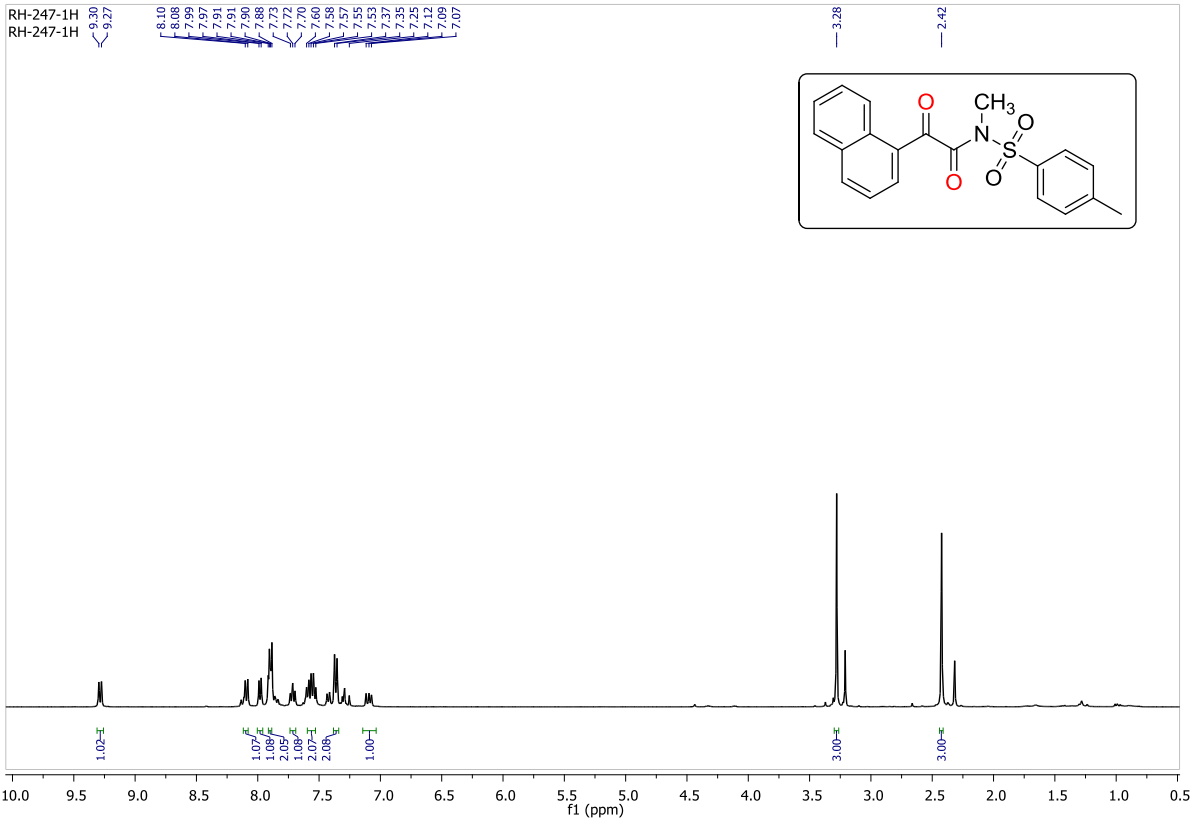


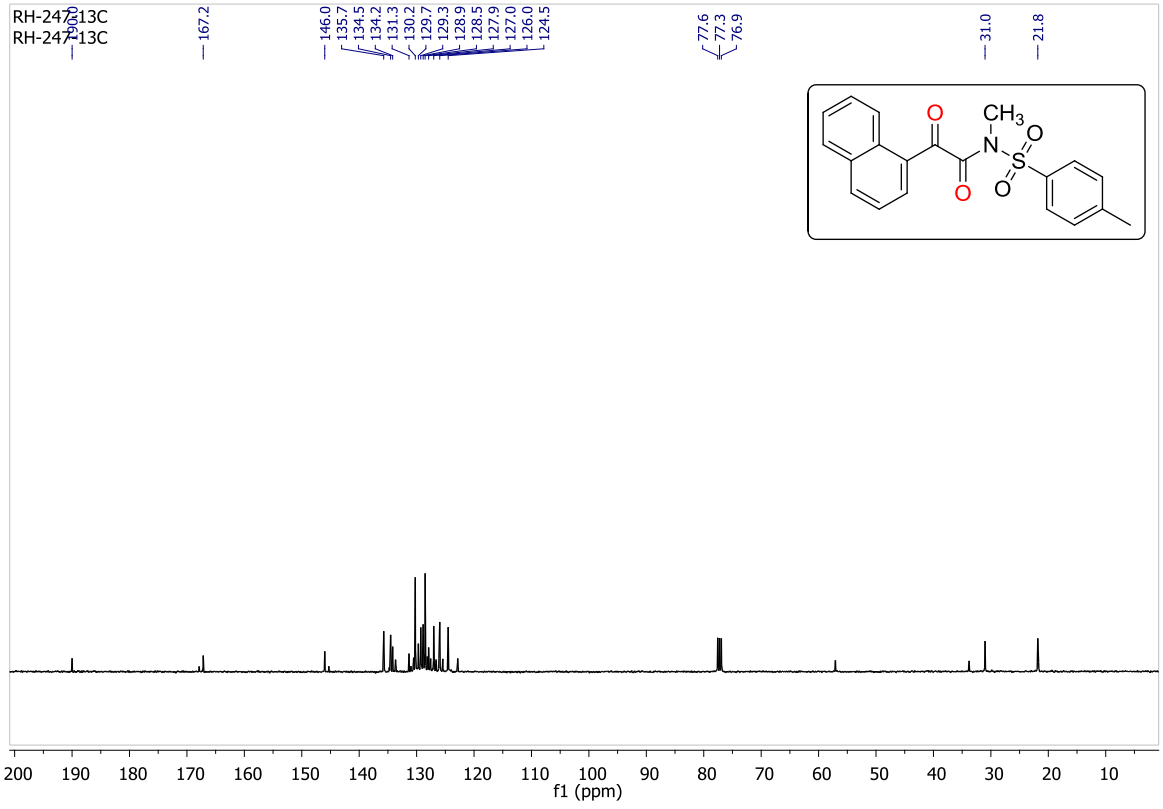
2-(4-chlorophenyl)-N-methyl-2-oxo-N-tosylacetamide (2e)



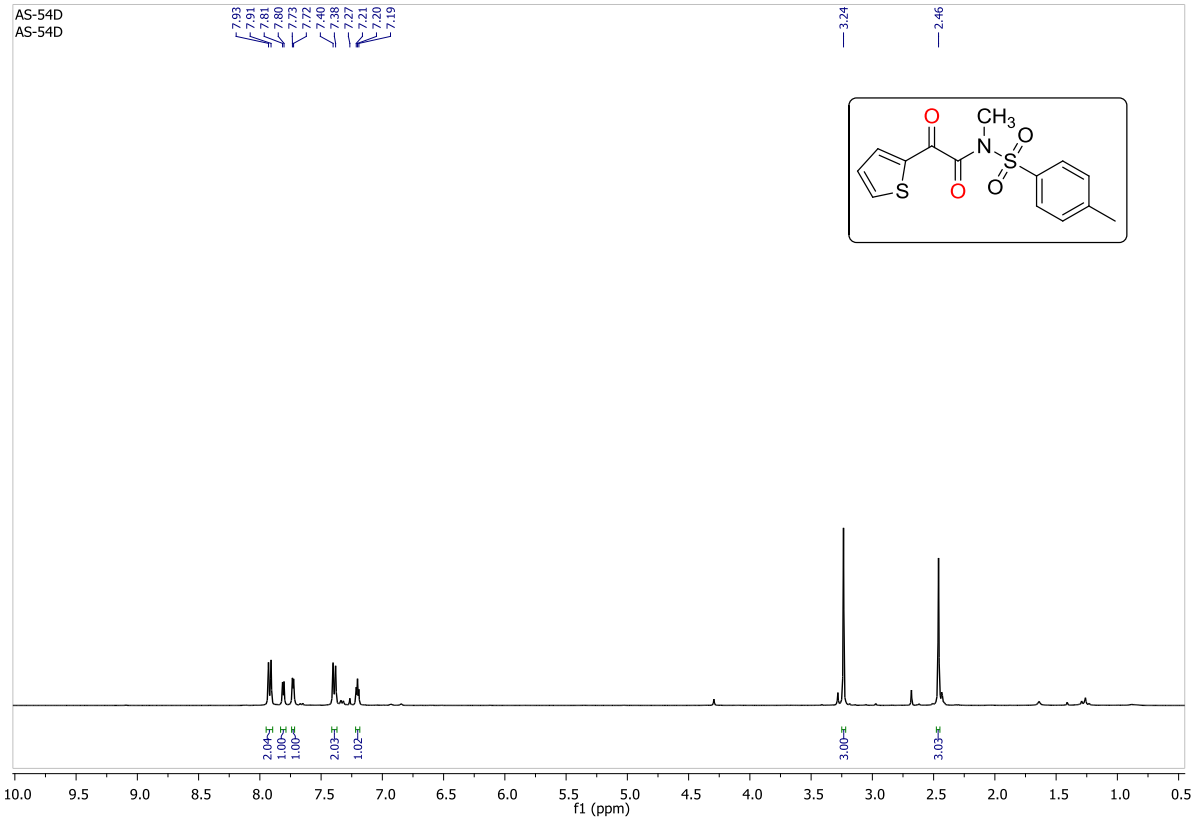


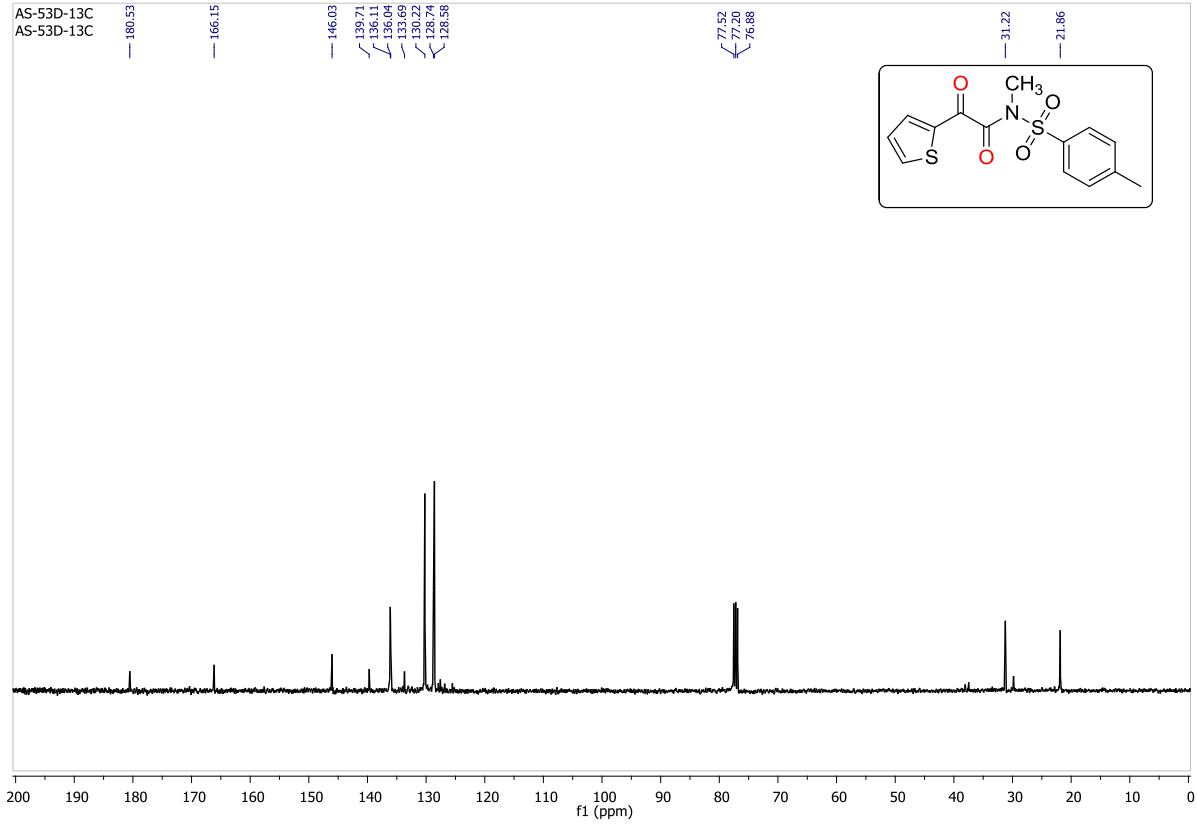
N-methyl-2-(naphthalen-1-yl)-2-oxo-N-tosylacetamide (2f)



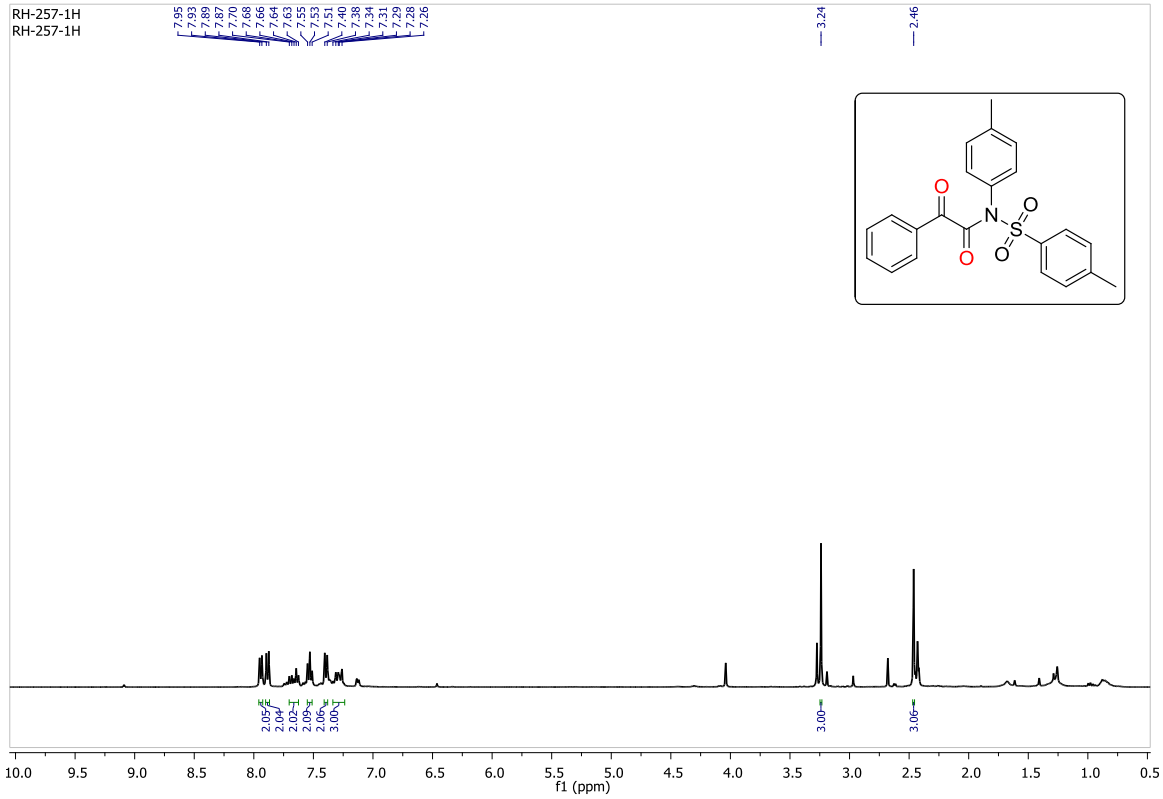


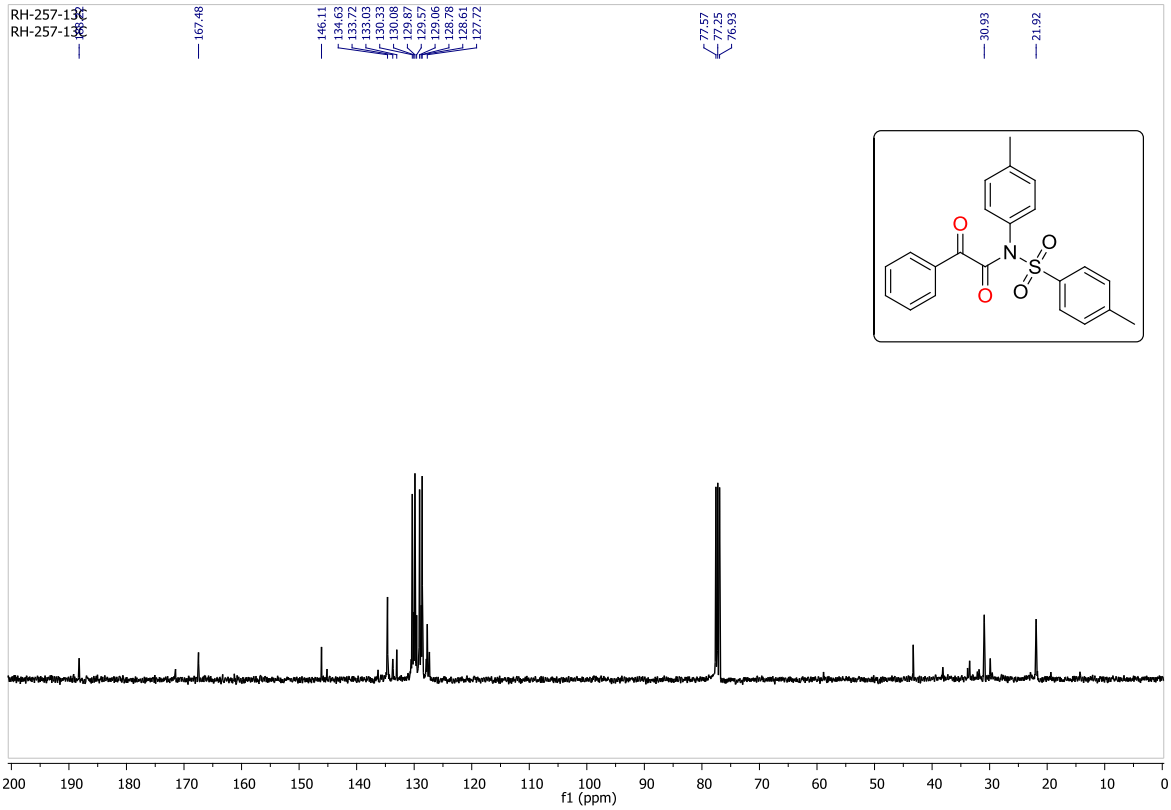
N-methyl-2-oxo-2-(thiophen-2-yl)-N-tosylacetamide (2g)



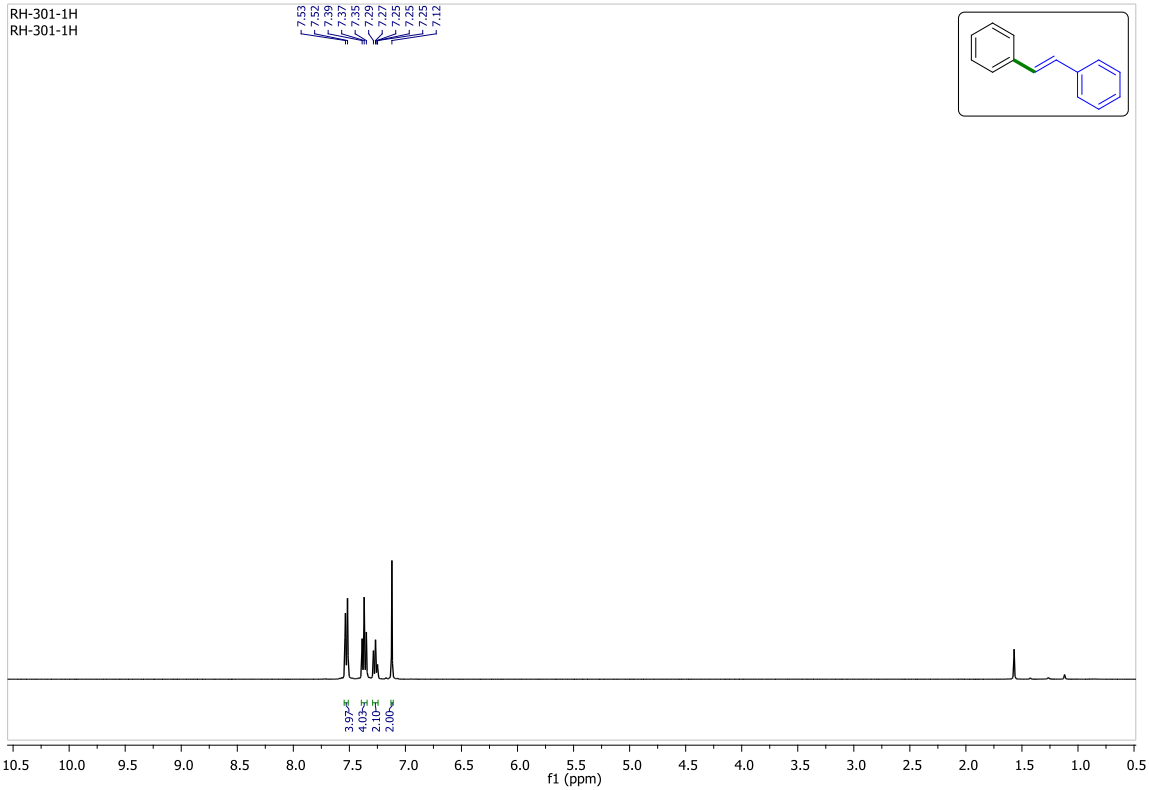


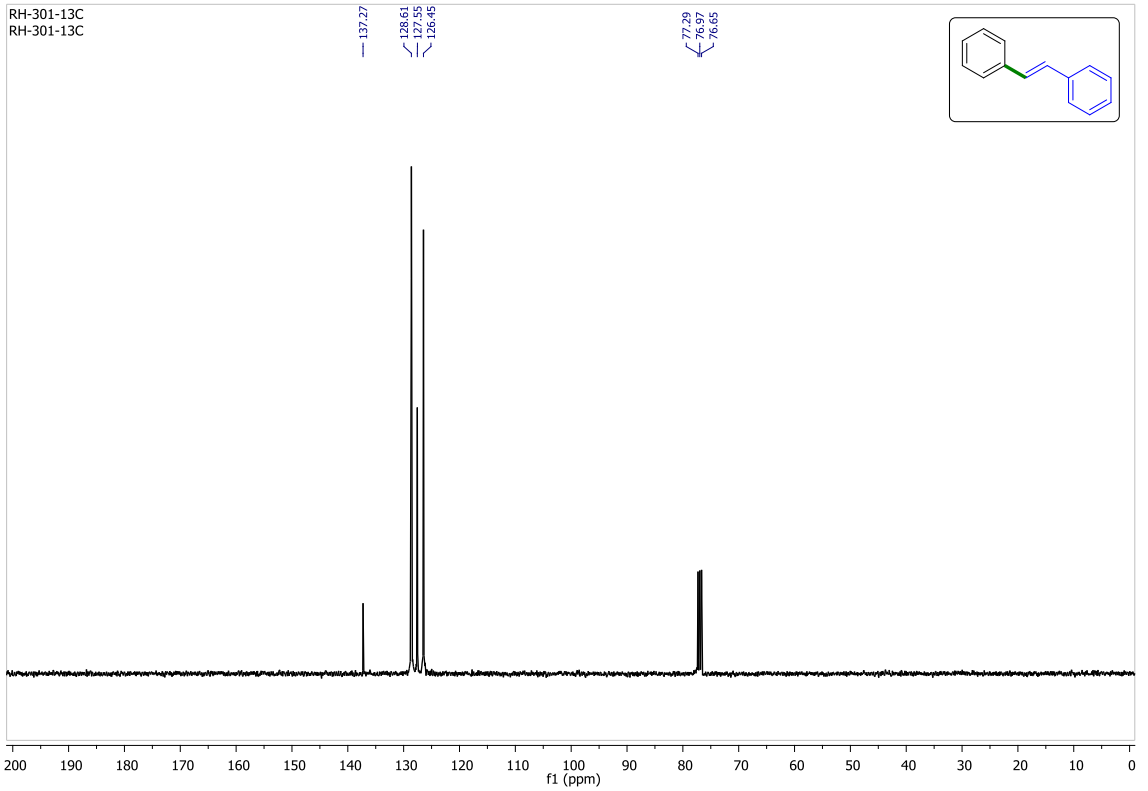
2-oxo-2-phenyl-N-(p-tolyl)-N-tosylacetamide (2h)



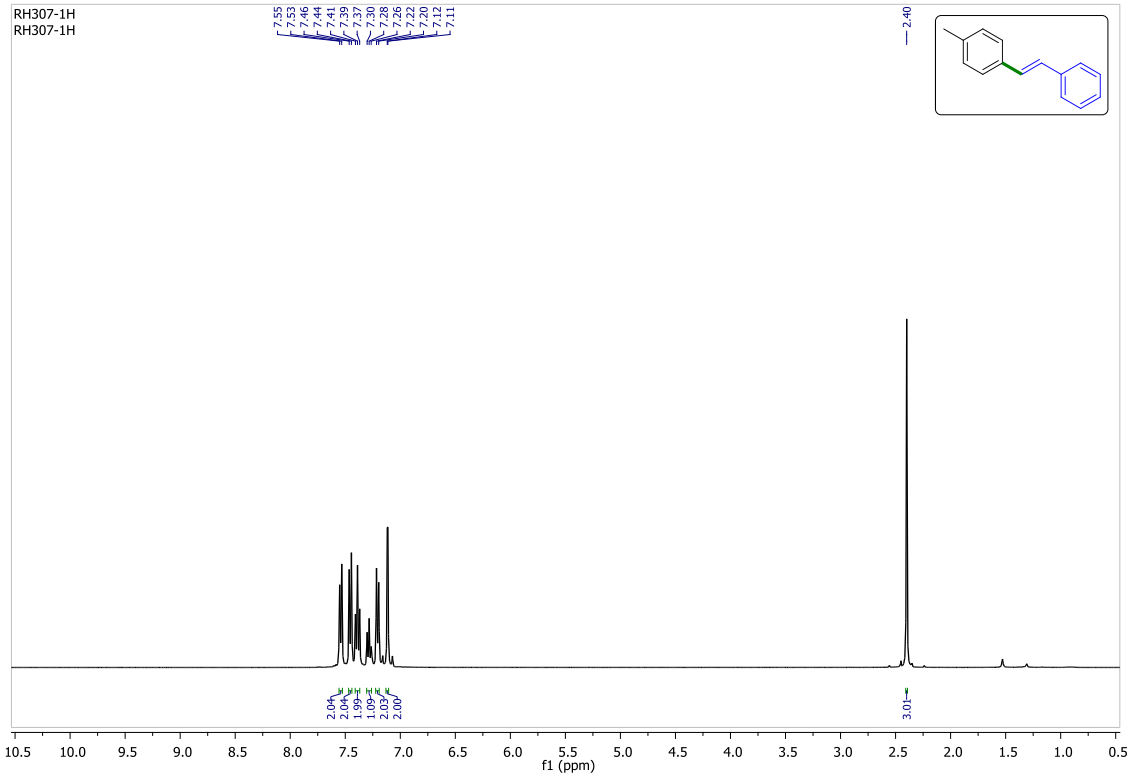


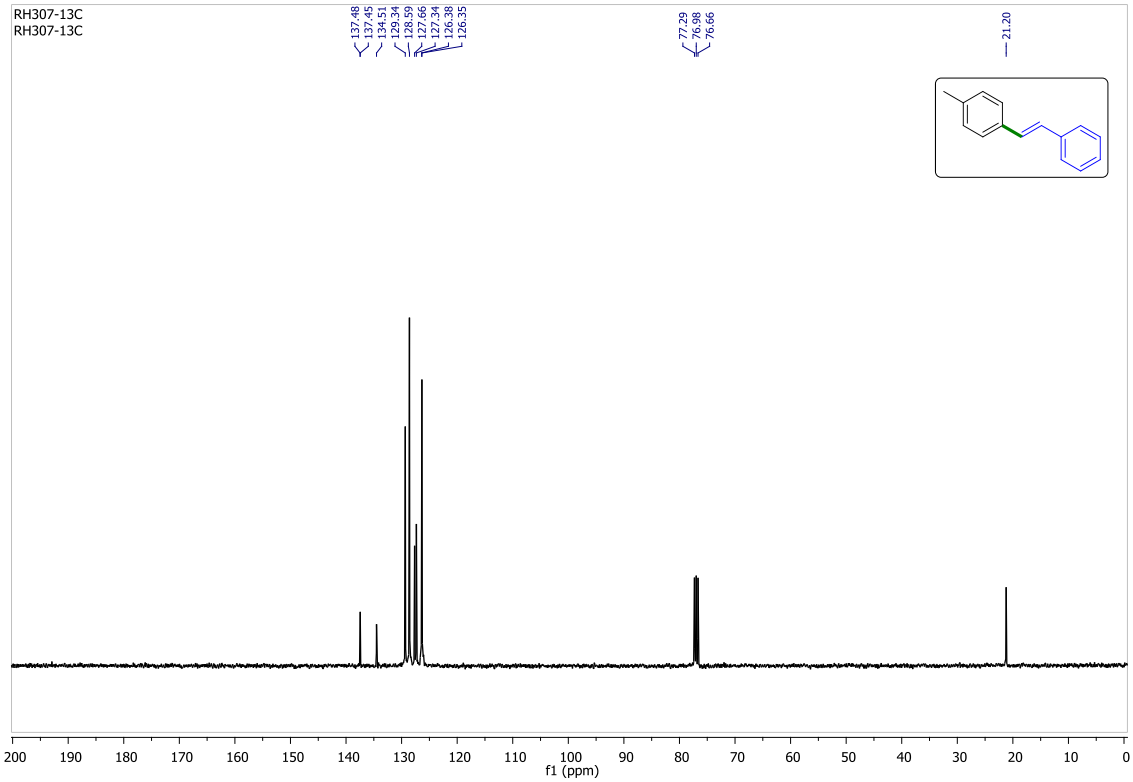
(E)-1,2-diphenylethene (5a)



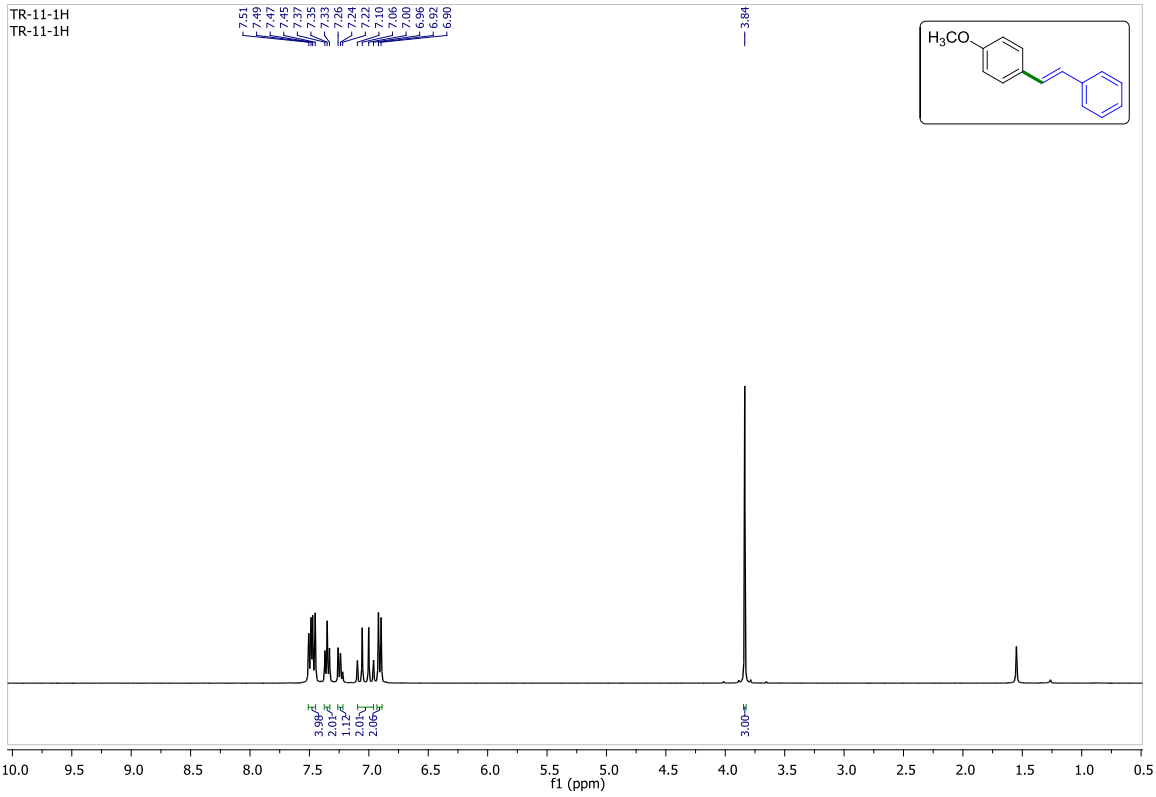


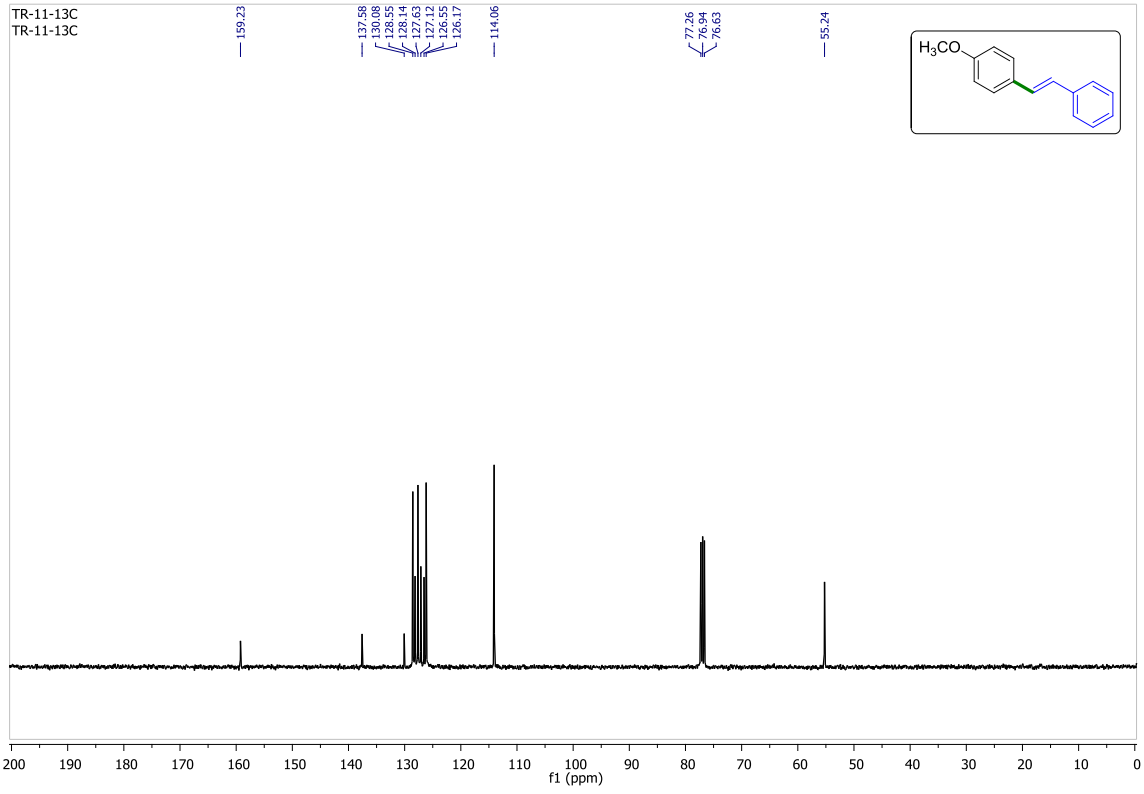
(E)-1-methyl-4-styrylbenzene (5b)



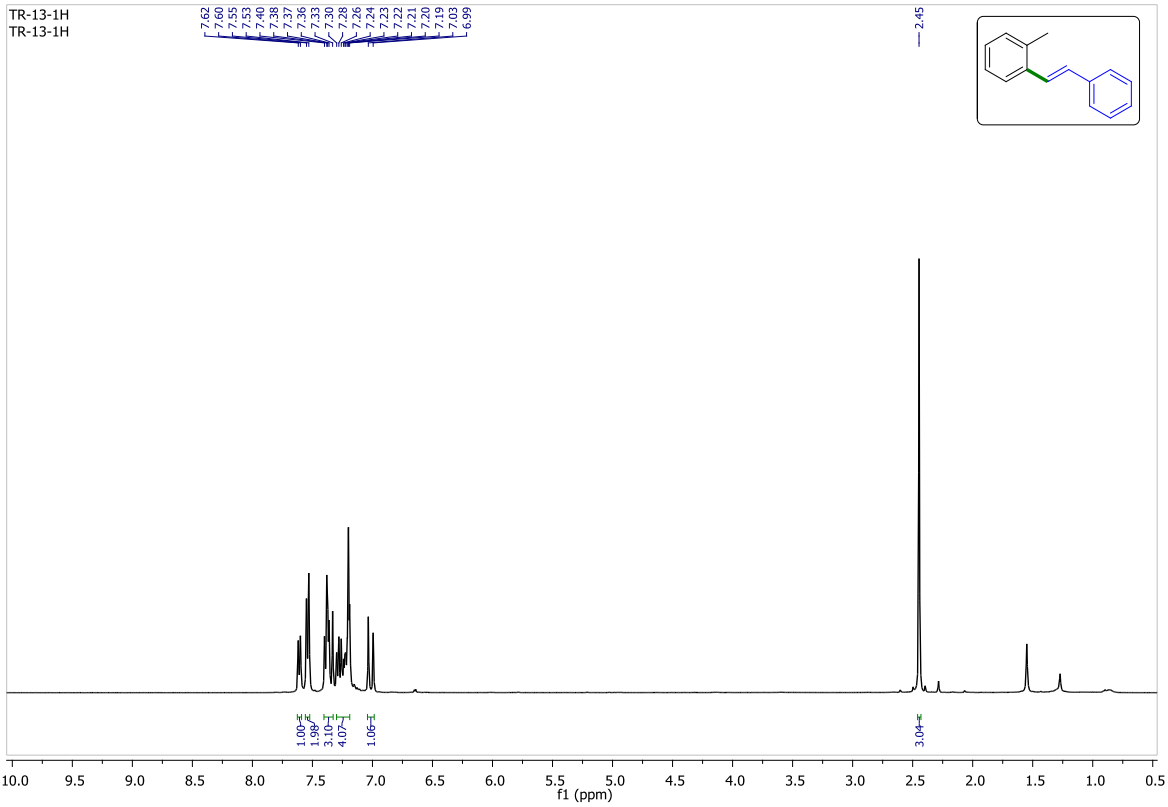


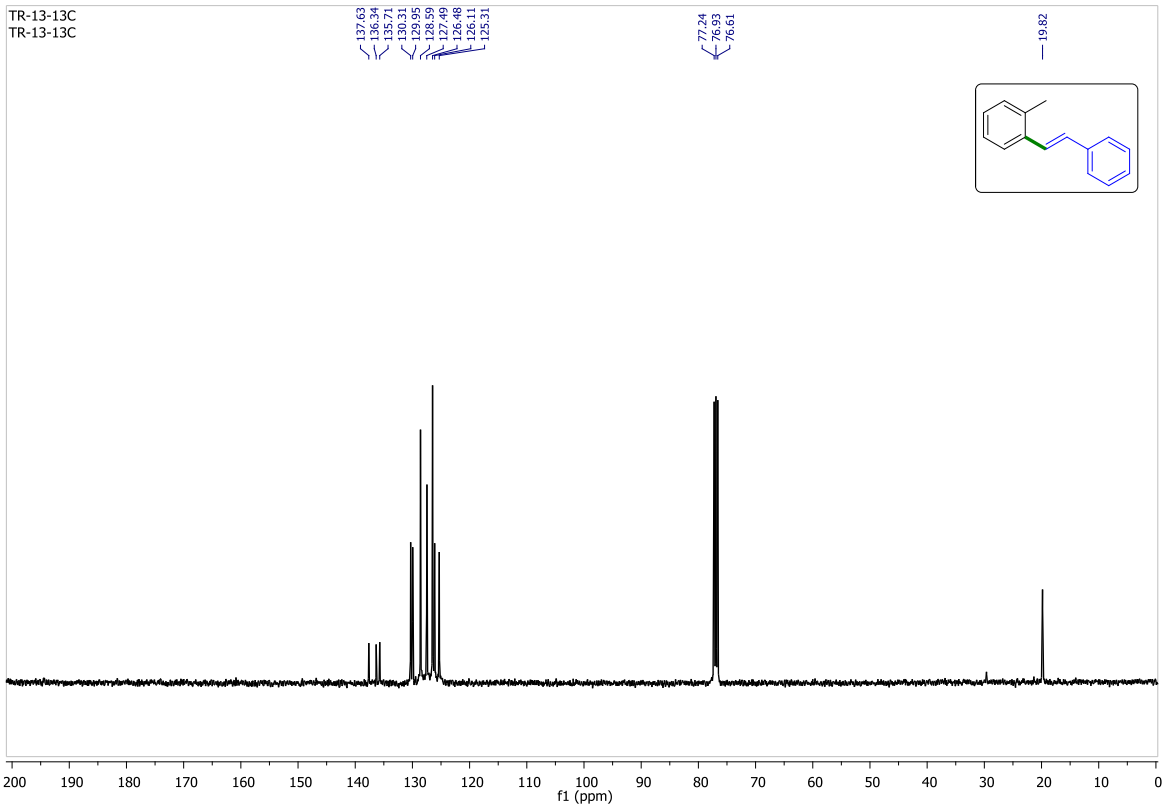
(E)-1-methoxy-4-styrylbenzene (5c)



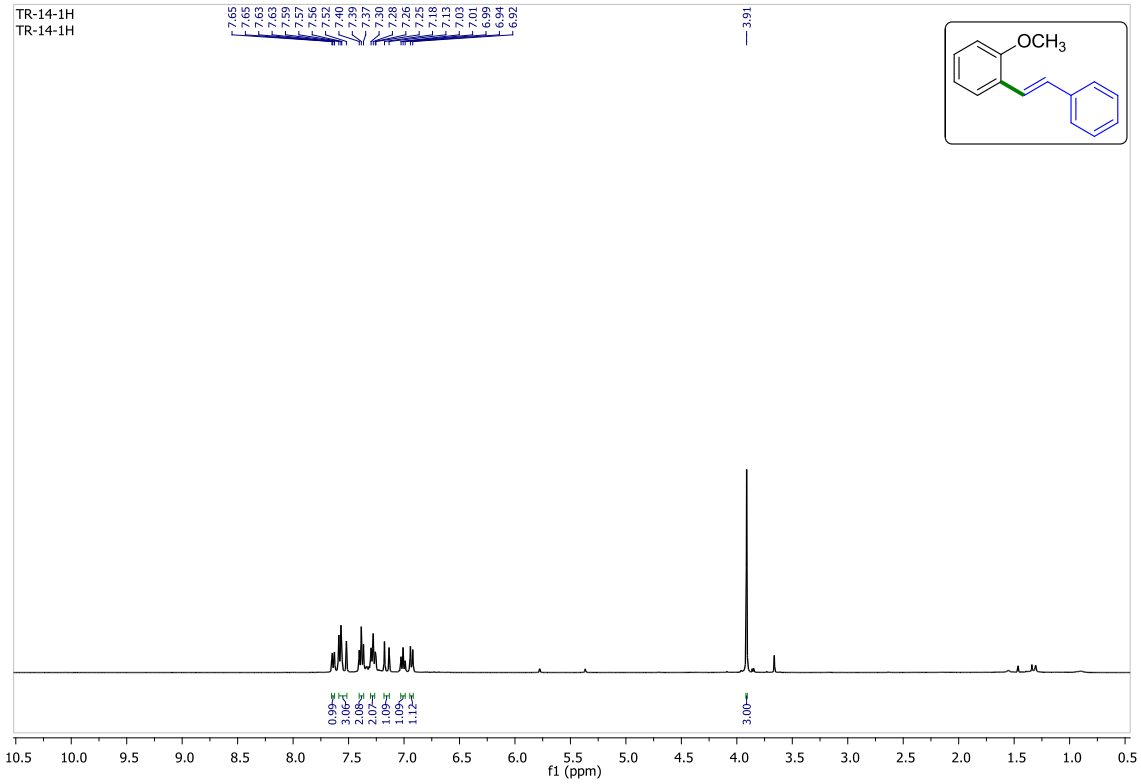


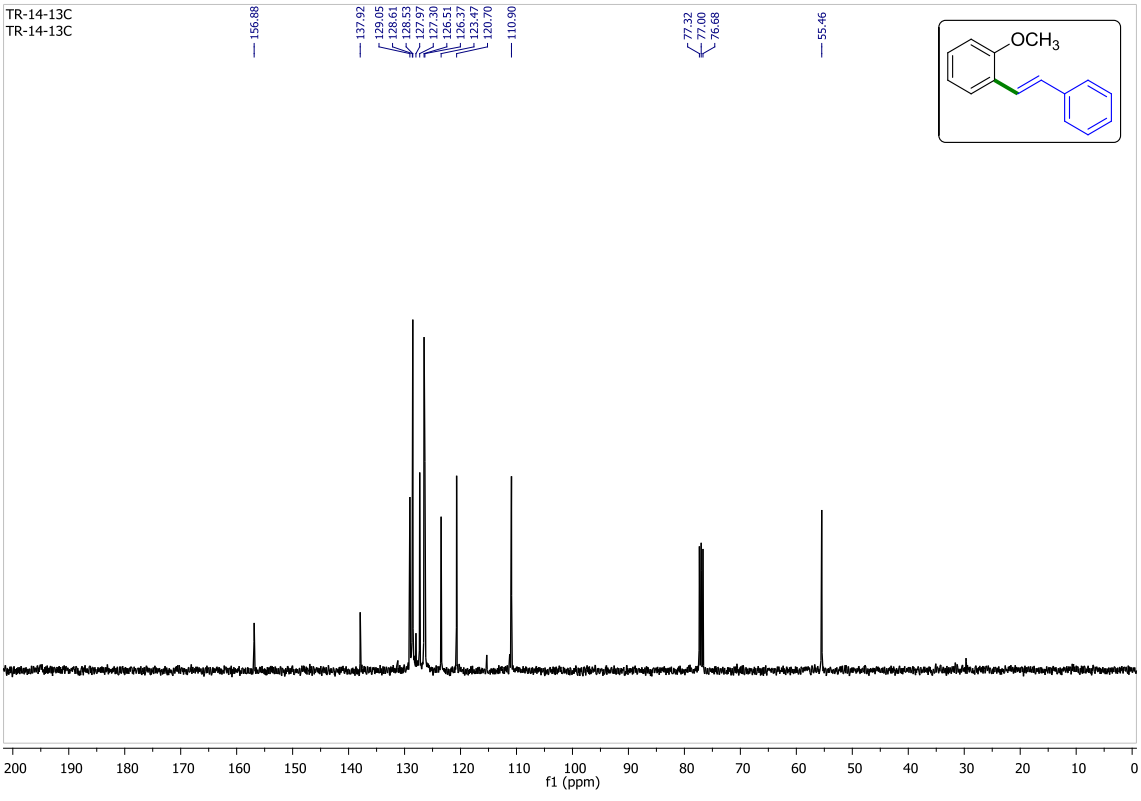
(E)-1-methyl-2-styrylbenzene (5d)



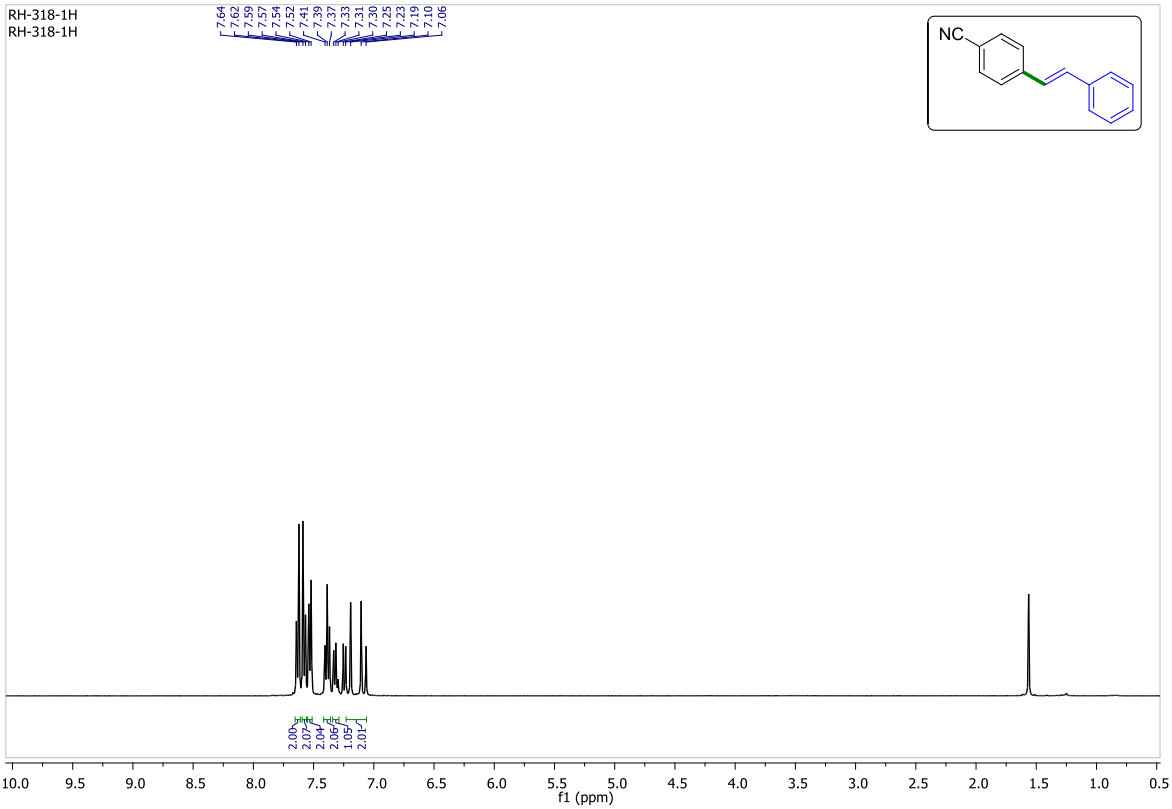


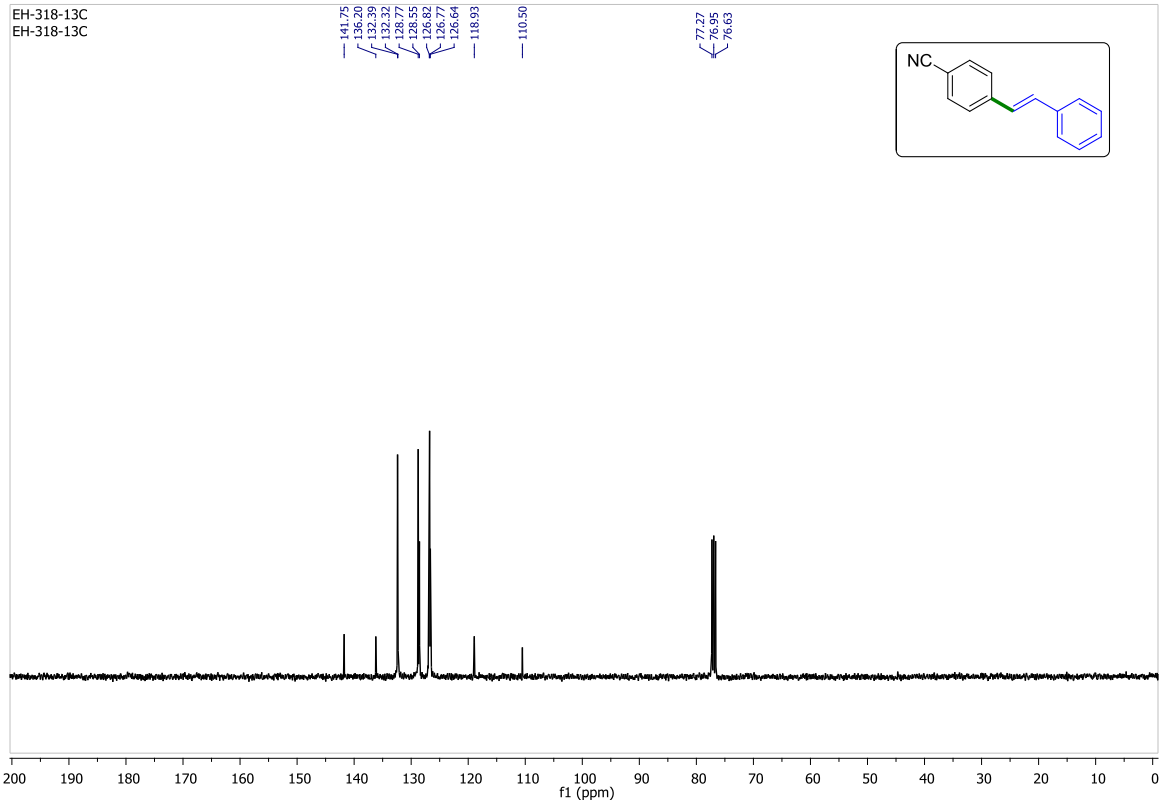
(E)-1-methoxy-2-styrylbenzene (5e)



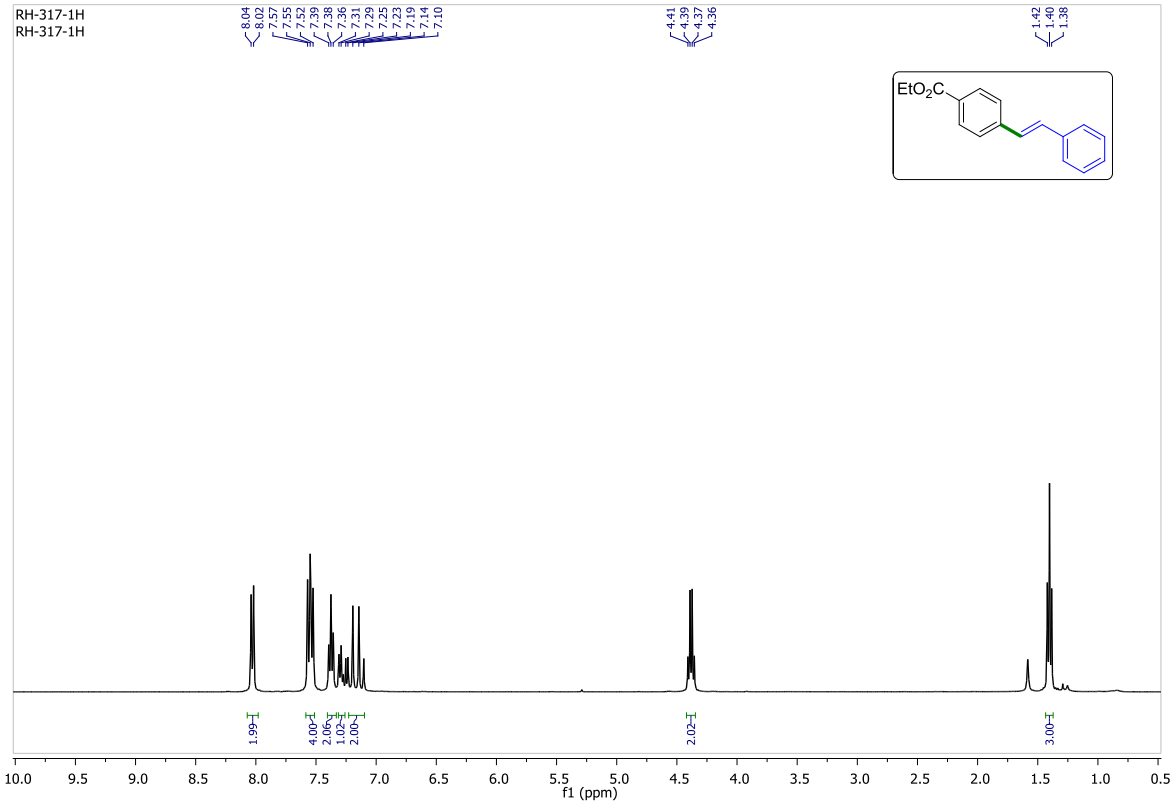


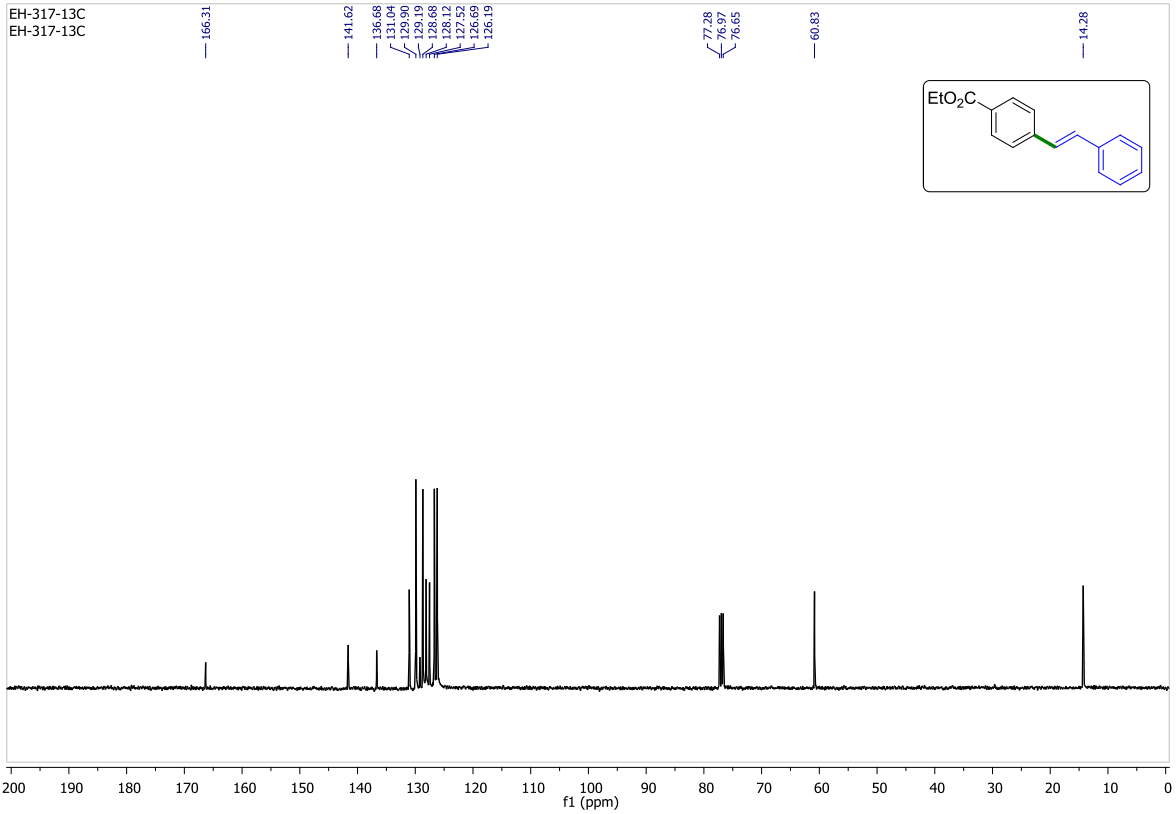
(E)-4-styrylbenzonitrile (5f)



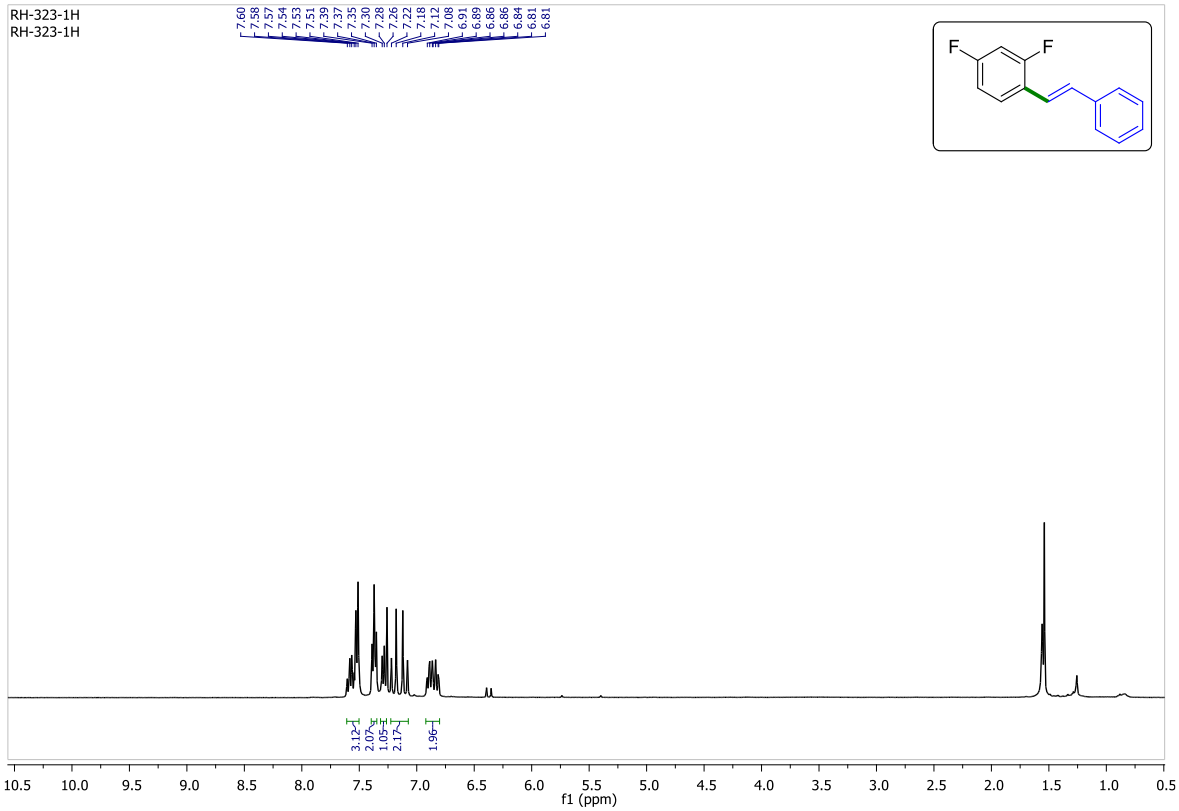


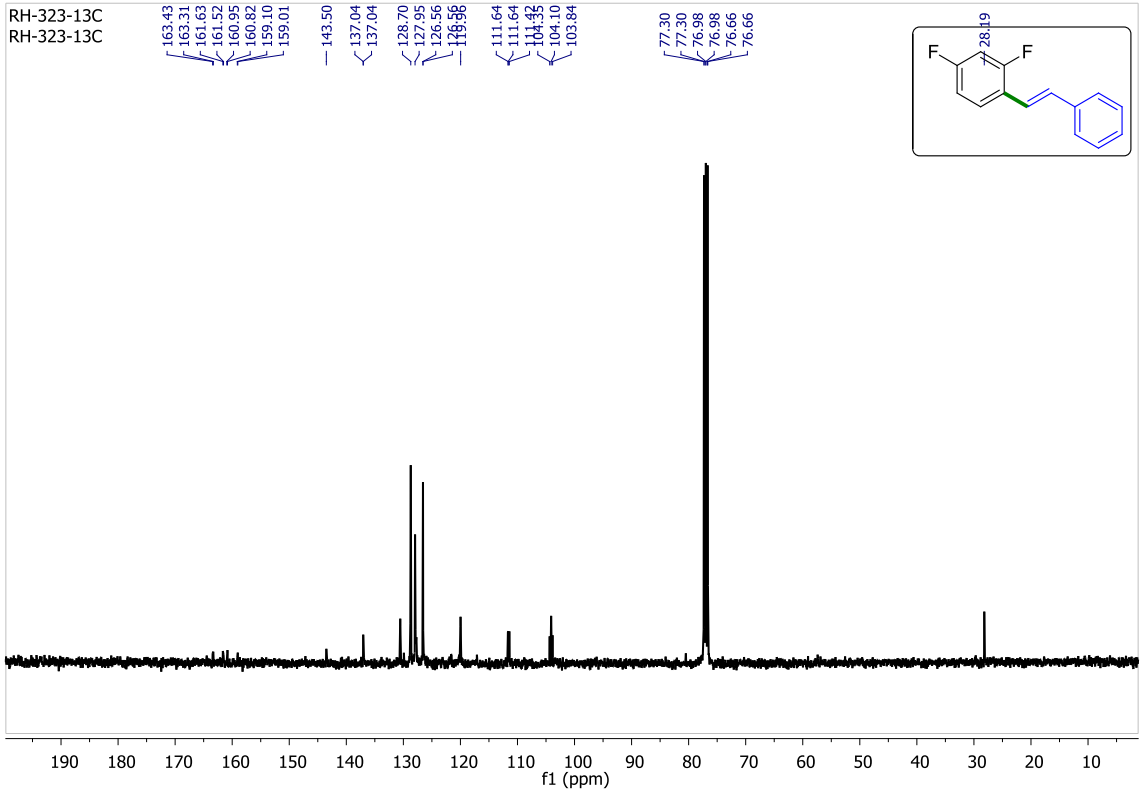
(E)-ethyl 4-styrylbenzoate (5g)



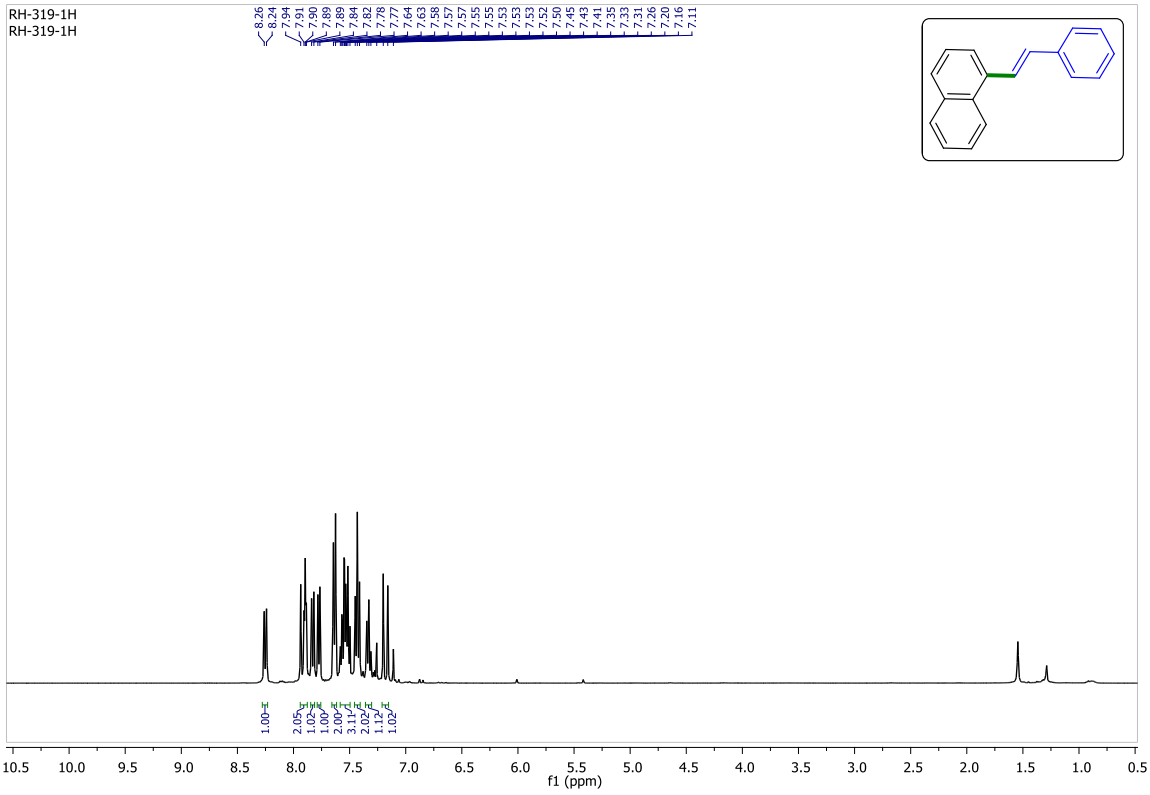


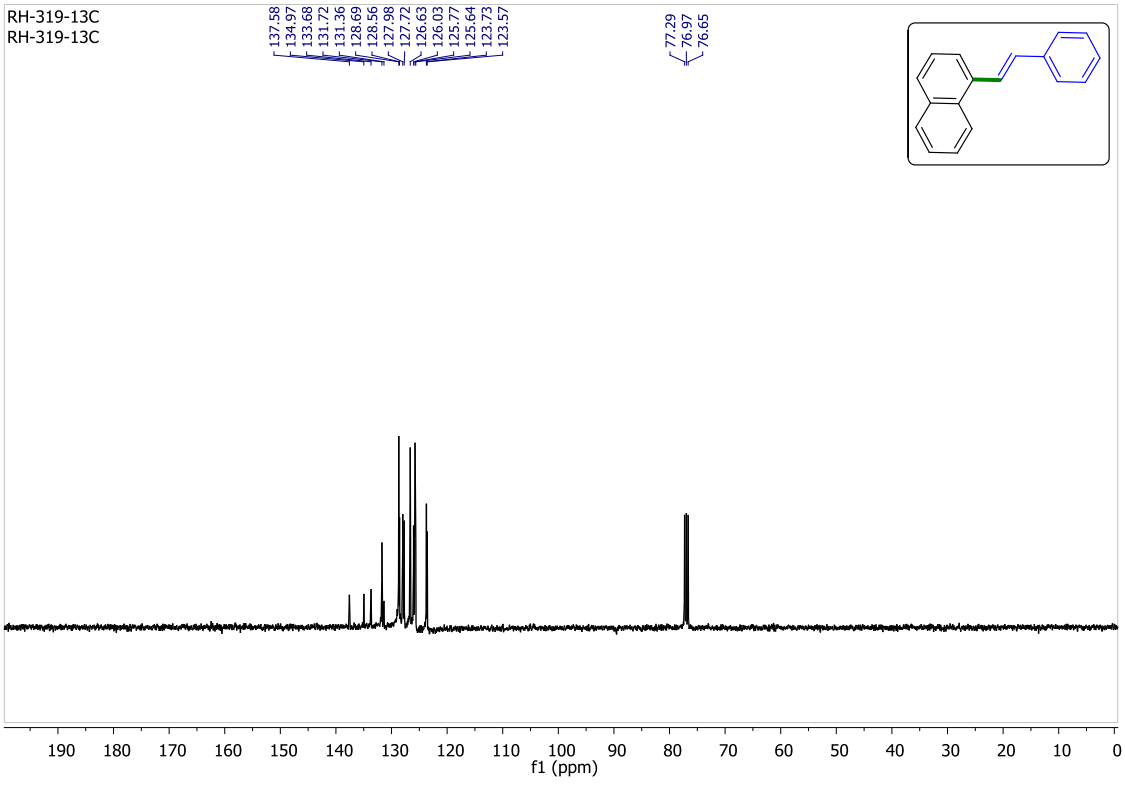
(E)-2,4-difluoro-1-styrylbenzene (5h)



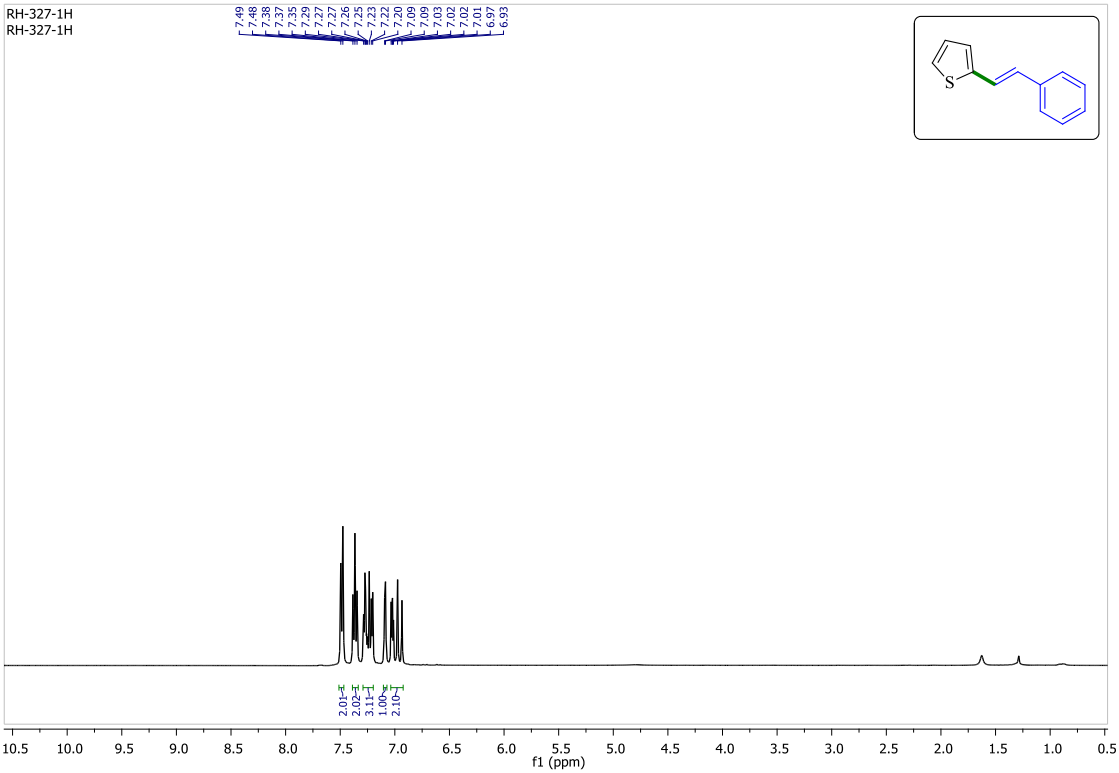


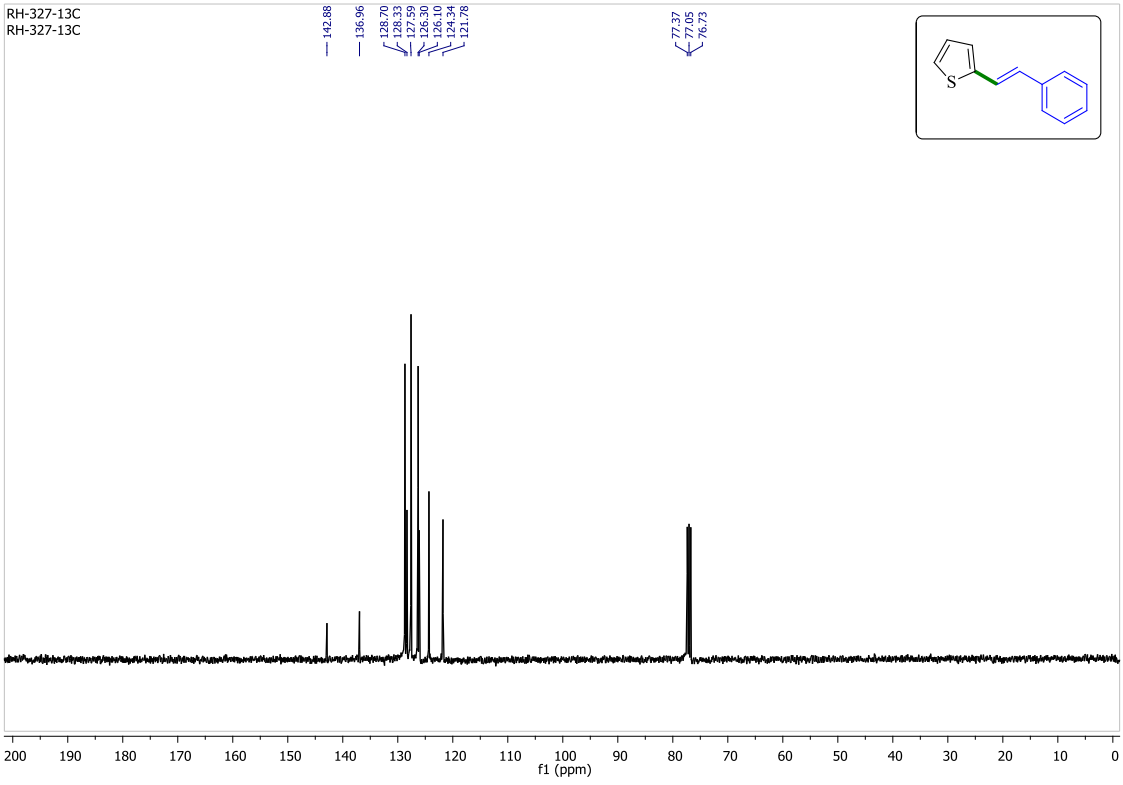
(E)-1-styrylnaphthalene (5i)





(E)-2-styrylthiophene (5j)





tert-butyl cinnamate (5k)