

Tandem Transformations via Friedel-Crafts Acylation Followed by Ring-Expansion, Ring-Opening, and Cycloisomerization Sequence

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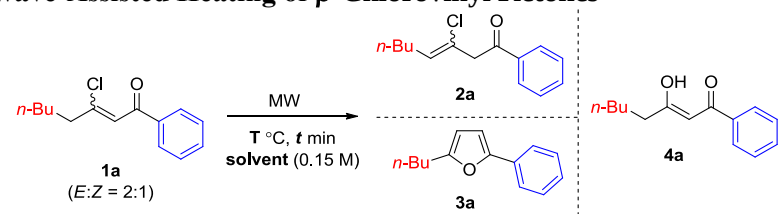
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Reaction Optimization. Our initial assessment established the thermal stability of β -chlorovinyl ketones upto 150 °C in various solvents such as CH₃CN, DCE, PhCH₃, and DMF. To capitalize the microwave-assisted superheating methods, the initially tested solvents were heated under microwave irradiation (Table S1). A 2:1 mixture of (*E/Z*)- β -chlorovinyl ketone **1a** was subjected to the microwave irradiation in CH₃CN at a fixed temperature of 180 °C (entry 1). The analysis of the reaction mixture revealed that the β -chlorovinyl ketone **1a** primarily underwent the alkene isomerization, providing vinyl chlorides **2a** as a 1:4 mixture of (*E/Z*)-isomers in 68% yield. Gratifyingly, the formation of 2,5-disubstituted furan **3a** was observed in 14% yield. While the mechanistic rationale to the formation of the vinyl chlorides **2a** from the β -chlorovinyl ketone **1a** is not clear, given that we previously observed the formation of furans from the α -vinyl enolization of (*E/Z*)- β -chlorovinyl ketone **1a** via allene intermediates,¹ the formation of furan **3a** strongly implied the reaction pathway that involved the α -vinyl enolization of **1a** (*vide infra*). The recovered (*E/Z*)- β -chlorovinyl ketone **1a** remained as a 2:1 mixture, indicating no reactivity difference between (*E*)- and (*Z*)-stereoisomers under the microwave irradiation at 180 °C. The use of DCE as solvent under microwave irradiation at 180 °C resulted in the formation of the vinyl chlorides **2a** and the furan **2a** in 47% and 6% yield, respectively (entry 2). The microwave irradiation of **1a** in 1,4-dioxane at 180 °C led to the formation of the vinyl chlorides **2a** and diketone **4a** in 50% and 21% yield, respectively (entry 3). In DMF solvent the exclusive formation of the diketone **4a** was observed in quantitative yield (entry 4). Given that the heating characteristics of solvents under microwave irradiation are related to their dielectric properties, a mixed solvent system using CH₃CN and protic solvents was tested (entries 5-6). As anticipated, the reaction conversion improved upto 92% upon using a 3:1 mixture of CH₃CN:EtOH (entry 5), leading to the formation of the vinyl chlorides **2a** and diketone **4a**. A mixture of CH₃CN:EtOH solvent, however, led to the exclusive formation of the vinyl chlorides **2a** in a comparable yield of 86% (entry 6). It is conceivable that the hygroscopic nature of 1,4-dioxane, DMF, and EtOH causes the formation of diketone **4a** due to the inadvertent presence of water molecules in the solvents. Next, the reaction solvent was switched to the less hygroscopic, but low microwave absorbing, solvents. The microwave irradiation in PhCH₃ provided the formation of the vinyl chloride **2a** and 2,5-disubstituted furan **3a** in 13% and 31% yield, respectively (entry 7). The reaction in hexanes was less efficient, providing only 17% conversion (entry 8). To further optimize the reaction conditions, the microwave irradiation of **1a** was conducted at 230 °C (entry 9-11). While the formation of the vinyl chlorides **2a** prevailed in CH₃CN and DCE, the furan **3a** was observed as a dominant product in PhCH₃ (entry 11). Further fine-tuning of the reaction optimization was conducted at 250 °C (entry 12-15). With 3 min irradiation, the starting material **1a** displayed 80% conversion, and the products were comprised of 42% yield of vinyl chlorides **2a** and 48% of furan **3a** (entry 12). Upon 10 min irradiation, the starting material **1a** was completely consumed, but with the presence of the vinyl chlorides **2a** in 10% yield, the furan **3a** remained in 90% yield (entry 13). Finally, the irradiation of **1a** for 30 min at 250 °C provided an optimal reaction condition, providing the furan **3a** in an isolated yield of 82% (entry 14). A prolonged irradiation of **1a** gave the furan **3a** in a slightly low yield of 78% (entry 15).

Table S1. Microwave-Assisted Heating of β -Chlorovinyl Ketones^a



entry	solvent	T (°C)	time (min)	conv. (%) ^b	yield (%) ^c
1	CH ₃ CN	180	60	82	2a , 68; 3a , 14
2	DCE	180	60	53	2a , 47; 3a , 6
3	Dioxane	180	60	71	2a , 50; 4a , 21

4	DMF	180	60	100	4a , 100
5 ^d	CH ₃ CN/EtOH	180	60	92	2a , 21; 4a , 71
6 ^d	CH ₃ CN/PhOH	180	60	86	2a , 86
7	PhCH ₃	180	60	43	2a , 13; 3a , 31
8	Hex	180	60	17	2a , 13; 3a , 3
9	CH ₃ CN	230	30	80	2a , 52; 3a , 28
10	DCE	230	30	87	2a , 62; 3a , 23
11	PhCH ₃	230	30	58	2a , 23; 3a , 35
12	PhCH ₃	250	3	80	2a , 42; 3a , 38
13	PhCH ₃	250	10	100	2a , 10; 3a , 90
14	PhCH ₃	250	30	100	3a , 100 (82)
15	PhCH ₃	250	60	100	3a , 100 (78)

^aReaction using **1a** (2:1 E/Z mixture, 0.3 mmol) in solvent (0.15 M). ^bConversion by ¹H NMR analysis of crude mixture. ^cYields calculated by ¹H NMR analysis. Values in parentheses are isolated yields. ^dA 3:1 mixture of CH₃CN:ROH.

Mechanistic Studies. The facile formation of 2,5-disubstituted furan **3a** from β -chlorovinyl ketone **1a** prompted more detailed studies to understand the microwave-assisted heating method (Table S2). The internal temperature of microwave reactor was measured using the built-in IR sensor, and the maximum internal temperature of PhCH₃ solution without the substrate **1a** was 220 °C, after which the microwave reactor shutting down automatically (entry 1). Thus, it was clear that the presence of β -chlorovinyl ketone **1a** in PhCH₃ solution is the key to raise the reaction temperature to 250 °C. The microwave-assisted heating effect was obvious since the conventional heating of 0.15 M PhCH₃ solution of β -chlorovinyl ketone **1a** at 250 °C only led to 47% conversion, yielding the vinyl chlorides **2a** in 26% and 2,5-disubstituted furan **3a** in 21% (entry 2). The effect of the reaction concentration was next investigated using a 0.30 M PhCH₃ solution of β -chlorovinyl ketone **1a** as opposed to our optimized concentration of 0.15 M. The microwave-assisted heating of the 0.30 M PhCH₃ solution of β -chlorovinyl ketone **1a** at 180 °C provided 24% conversion, leading to the vinyl chlorides **2a** and 2,5-disubstituted furan **3a** in 12% and 12% yield, respectively (entry 3). This result suggests that the higher concentration of the substrate **1a** negatively affect the reaction conversion since the 0.15 M PhCH₃ solution of **1a** at 180 °C provided 43% conversion (in Table 1, entry 7). However, such concentration effect was not obvious upon raising the temperature to 250 °C, where the 0.30 M PhCH₃ solution of **1a** provided the desired furan **3a** in 100% yield (entry 4). Thus, the microwave-assisted heating was applied to the 0.03 M PhCH₃ solution of **1a** at 250 °C, and the reaction provided the vinyl chlorides **2a** and 2,5-disubstituted furan **3a** in 9% and 91% yield, respectively (entry 5). The microwave-assisted heating of neat **1a** at 230 °C led to the formation of the furan **3a** in 22% yield in addition to **2a** and **4a** in 39% and 15% yield, respectively (entry 6). Thus, while the overall reaction conversion of neat **1a** improved to 76% as opposed to 58% from the 0.15 M PhCH₃ solution of **1a** (in Table 1, entry 11), upon delineating the formation of the diketone **4a** (15%) the reaction efficiencies became comparable, but the formation of the furan product **3a** was more effective in the PhCH₃ solution of **1a**. Likewise, the microwave-assisted heating of neat **1a** at 250 °C gave the vinyl chlorides **2a** in 13% yield, the furan **3a** in 56% yield, and the diketone **4a** in 31% yield (entry 7). In order to study the possibility of non-thermal effects in the microwave-assisted reaction, the 0.15 M PhCH₃ solution of **1a** was heated with “hit to temperature in time” mode in 110 W to reach the internal temperature of microwave reactor to 250 °C (entry 8). The time required for such setting was 10 min, and the conversion at this point was 75% (**2a** in 41% and **3a** in 34%). The microwave-assisted heating at 250 °C for 10 min using “heat as fast as possible” mode in 250-300 W with an initial pulsed microwave power upto 850 W provided 90% conversion (entry 9); **2a** in 38% and **3a** in 52%. Our results did not provide strong evidences for any specific non-thermal effect, even though a polar substrate **1a** was subjected to a non-polar, microwave transparent, medium. Furthermore, the stirring at 600 rpm of the microwave-assisted heating decreased the conversion to 93%, providing **2a** and **3a** in 19% and 74% yield, respectively (entry 10). Given that the phenomenon of the microwave-assisted

superheating occurs in unstirred liquids, the superheating effects are suppressed by stirring.² This is consistent with the suppressed reaction conversion upon stirring, where the microwave-assisted superheating effect was diminished.

Table S2. Control Experiments for Microwave-Assisted Heating^a

1a (E:Z = 2:1) MW (power W) 2a 3a

T (°C), t (min) PhCH₃ (M)

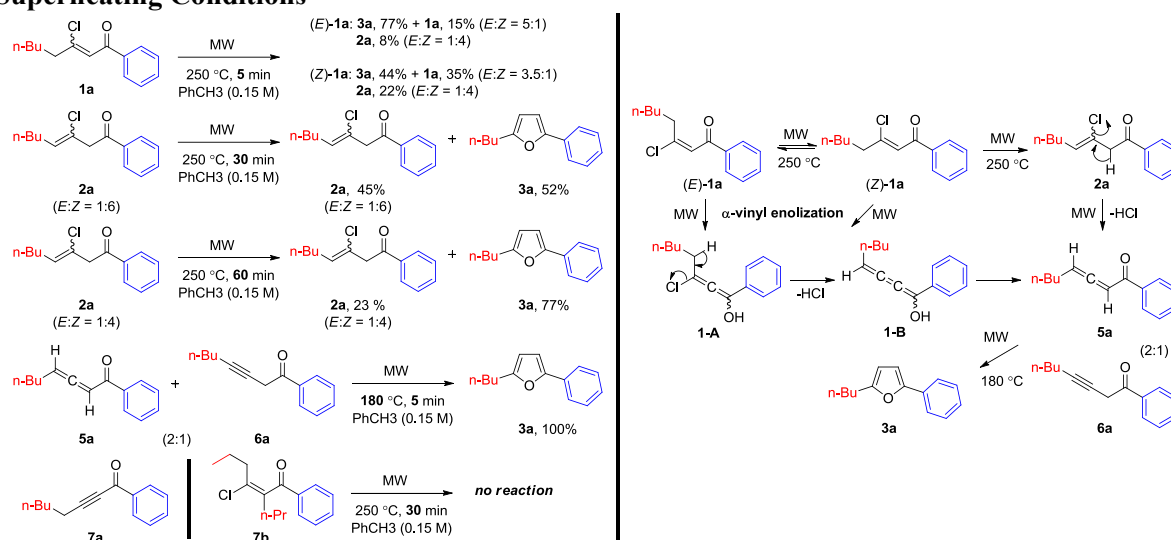
entry	conc'n (M)	T (°C)	time (min)	conv. (%) ^b	yield (%) ^c
1 ^d	PhCH ₃	220	12	-	-
2 ^e	PhCH ₃ (0.15)	250	30	47	2a, 26; 3a, 21
3	PhCH ₃ (0.30)	180	30	24	2a, 12; 3a, 12
4	PhCH ₃ (0.30)	250	30	100	2a, 0; 3a, 100
5	PhCH ₃ (0.03)	250	30	100	2a, 9; 3a, 91
6 ^f	1a (neat)	230	30	76	2a, 39; 3a, 22
7 ^g	1a (neat)	250	30	43	2a, 13; 3a, 56
8 ^h	PhCH ₃ (0.15)	250	10	75	2a, 41; 3a, 34
9 ⁱ	PhCH ₃ (0.15)	250	10	90	2a, 38; 3a, 52
10 ^j	PhCH ₃ (0.15)	250	30	93	2a, 19; 3a, 74

^aReaction using **1a** (2:1 *E/Z* mixture) in solvent (2 mL). ^bConversion by ¹H NMR analysis of crude mixture. ^cYields calculated by ¹H NMR analysis. ^dNo substrate **1a**. ^eUnder conventional heating in a metal jacket. ^fFormation of **4a** in 15% yield. ^gFormation of **4a** in 31% yield. ^hUnder “heat to temperature in time” mode with constant power of 110 W. ⁱUnder “heat as fast as possible” mode in 250-300 W with an initial power upto 850 W. ^jUnder stirring at 600 rpm.

Reaction Pathway. The microwave-assisted heating of stereodefined β-chlorovinyl ketone **1a** at 250 °C revealed that the (*E*)-**1a** underwent the faster reaction to the furan **2a** than (*Z*)-**1a** (Scheme S1). Also, the preferential formation of (*E*)-stereoisomer of **1a** from (*Z*)-**1a** strongly suggested the interconversion between the stereoisomeric β-chlorovinyl ketones **1a** under the microwave-assisted heating conditions at 250 °C. Indeed, our control experiments confirmed that the microwave-assisted heating of stereodefined β-chlorovinyl ketones **1a** at 180-230 °C did not promote the interconversion of β-chlorovinyl ketones **1a**, clearly demonstrating the importance of the reaction temperature of 250 °C. The observation of the vinyl chlorides **2a** suggested that the **2a** might be intermediates to the furan **3a**. To test such reaction pathways, a 1:6 mixture of **2a** was subjected to the microwave-assisted heating conditions (Scheme 2). The conversion of (*E/Z*)-**2a** to **3a** was considerably slow, thus after the 30 min of microwave heating, the conversion to the furan **3a** was only 52% yield. The recovered vinyl chlorides **2a** remained as a 1:6 mixture of stereoisomers, demonstrating the similar reaction rates for the stereoisomeric (*E/Z*)-**2a** to **3a**. To verify that the ratio of the vinyl chlorides did not come from the equilibrium state, a 1:4 mixture of **2a** was heated for 60 min, where the recovered vinyl chlorides retained the ratio of 1:4. Since the conversion of vinyl chlorides **2a** to the β-chlorovinyl ketones **1a** was not observed and the formation of the furan **3a** from the vinyl chlorides **2a** was considerably slower than our optimized conditions, a direct reaction pathway of (*E/Z*)-**2a** to **3a** must be operating. While the presence of other intermediate species was not been observed, the intermediacy of allenyl and propargyl ketones, derived from the thermal α-vinyl enolization of β-chlorovinyl ketone **1a**, was postulated. Thus, the authentic samples of the allenyl ketone **5a** and propargyl ketone **6a** were subjected to our microwave-assisted heating conditions. It turned out that the mixture of **5a** and **6a** underwent the thermal cycloisomerization to **3a** in 5 min at 180 °C. This result explains why the allenyl and propargyl ketone intermediates could not be observed during the reaction due to their facile cycloisomerization pathways with much less energy input. It has been previously reported that the metal-catalyzed [1,3]-prototropic isomerization of alkynyl ketones to allenyl ketones prompted the synthesis of **7a**.³ The subjection of the alkynyl ketone **7a** under our microwave-assisted superheating

conditions did not provide the furan **3a**. Also, the (*E*)- β -chlorovinyl ketone **7b** without α -hydrogen was inert under the microwave-assisted heating condition. Putting all data together, the following conclusion could be made; (1) the α -hydrogen in β -chlorovinyl ketone is needed, (2) the formation of alkynyl ketone via *syn*-/anti-dehydrochlorination of β -chlorovinyl ketone does not occur, (3) the stereoisomeric β -chlorovinyl ketones equilibrate at 250 °C, (4) the vinyl chlorides do not equilibrate nor convert to β -chlorovinyl ketones. As such, β -chlorovinyl ketones are proposed to undergo the α -vinyl enolization to the allenol **1-A**. A subsequent elimination of HCl leads to the formation of the [3]cumulenol **1-B**, spontaneously isomerizing to the allenyl ketone **5a** and propargyl ketone **6a**. Another reaction pathway involves the vinyl chlorides to **5a** and **6a**,⁴ although this reaction pathway to the furan **3a** appears to be a high energy-requiring process. As our control experiment indicated the conversion of the allenyl ketone **5a** and propargyl ketone **6a** proceeds to the furan **3a** with low energy inputs.

Scheme S1. Reaction Pathways of β -Chlorovinyl Ketones to Furan under Microwave-Assisted Superheating Conditions



[1] Kim, H. Y.; Li, J.-Y.; Oh, K. Studies on Elimination Pathways of β -Halovinyl Ketones Leading to Allenyl and Propargyl Ketones and Furans under the Action of Mild Bases. *J. Org. Chem.* **2012**, *77*, 11132-11145.

[2] (a) Chemat, F.; Esveld, E. Microwave Super-Heating Boiling of Organic Liquids: Origin, Effect and Application. *Chem. Eng. Technol.* **2001**, *24*, 735-744. (b) Dudley, G.; Stiegman, A. E.; Rosana, M. R. Correspondence on Microwave Effects in Organic Synthesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 7918-7923.

[3] Kel'I, A. V.; Gevorgyan, V. Efficient Synthesis of 2-Mono- and 2,5-Disubstituted Furans via the CuI-Catalyzed Cycloisomerization of Alkynyl Ketones. *J. Org. Chem.* **2002**, *67*, 95-98.

[4] For the vinyl halide elimination using *t*-BuOK at 220 °C, see: (a) Christi, M.; Groetsch, S. Cyclohexa-1,2,4-triene from 1-Bromocyclohexa-1,4-diene. *Eur. J. Org. Chem.* **2000**, 1871-1874. (b) Kilbas, B.; Azizoglu, A.; Balci, M. Incorporation of an Allene Unit into α -Pinene via β -Elimination. *Helv. Chim. Acta* **2006**, *89*, 1449-1456.

[5] (*E*)/(*Z*)-**2a** was confirmed from ¹H crude NMR. The compound **7a** and **7b** in Scheme S1 were prepared by the same method reported in the previous study.¹

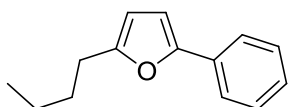
General Methods. All reactions were carried out with oven-dried glassware. The progress of all reactions was monitored by thin-layer chromatography on Dynamic Adsorbent, Inc. precoated silica gel plates (250 μm) and visualized by ultra-violet light or by staining with KMnO_4 stain. HPLC grade dichloromethane and toluene were further dried through alumina columns. Unless otherwise specified, all chemicals were obtained from Alfa Aesar, TCI, or Acros, and all solvents were purchased from Fischer Scientific. The microwave assisted reactions were carried out in Anton Paar microwave 400 synthesis reactor. The ^1H NMR and ^{13}C NMR spectra were obtained on JEOL 600 MHz Fourier transform spectrometers. Chemical Shifts are reported in units of parts per million downfield from tetramethylsilane and all coupling constants are reported in Hertz. The infrared spectra were obtained using a Thermo Nicolet IR 300 Spectrometer. Silica gel (32-64 μ , Dynamic Adsorbent, Inc.) was used for column chromatography. Melting points were recorded on a Buchi-B-450 melting point apparatus and the melting point values were uncorrected.

General Procedure A: Synthesis of β -Chlorovinyl Ketones and Microwave Assisted Reaction

β -Chlorovinyl ketones were synthesized by the literature method.¹ To a stirred suspension of aluminum chloride (47 mg, 0.35 mmol) in dry dichloromethane (1 mL) at 0 $^\circ\text{C}$, were added alkyne (0.3 mmol) and acyl chloride (0.3 mmol) dropwise at the same time. The resulting solution was continued to stir at the same temperature until the reaction was complete by TLC (20-40 min). The reaction was then quenched with several drops of H_2O and concentrated under the reduced pressure. The residue ((*E*)/(*Z*) mixtures of β -chlorovinyl ketones) was dissolved in 5mL of ethyl acetate and hexanes mixture (v:v=10:90) and filtered through short silica gel. Silica gel was further flushed with 5mL of ethyl acetate and hexanes mixture (v:v=10:90). After drying over MgSO_4 , the solution was concentrated under the reduced pressure and transferred into a 10 mL microwave reaction vial with 2 mL toluene. The vial was loaded in a microwave reactor. The reaction mixture was then irradiated to reach the target temperature (250 $^\circ\text{C}$) in 10 min and continued to irradiate at this temperature for 3 -

60 min depending on the reaction with 100-120 W of an initial microwave power. After cooling to ambient temperature, the solvent was removed under the reduced pressure and the product was purified by column chromatography with 0-20% ethyl acetate in hexanes eluent.

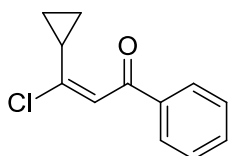
1mmol Scale Reaction:



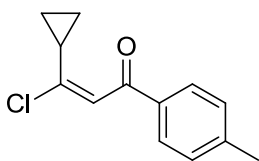
To a stirred suspension of aluminum chloride (160 mg, 1.2 mmol) in dry dichloromethane (5 mL) at 0 °C, were added 1-heptyne (1.0 mmol, 133 μ L) and benzoyl chloride (1.0 mmol, 133 μ L) dropwise at the same time. The resulting solution was continued to stir at same temperature until the reaction was complete by TLC (30 min). The reaction was then quenched with several drops of H₂O and concentrated under the reduced pressure. The residue (a 1:1 (*E*)/(*Z*) mixture of β -chlorovinyl ketones) was dissolved in 15 mL of ethyl acetate and hexanes mixture (v:v=10:90) and filtered through a short silica gel. Silica gel was further flushed with 15 mL of ethyl acetate and hexanes mixture (v:v=10:90). After drying over MgSO₄, the solution was concentrated under the reduced pressure and transferred into a 30 mL microwave reaction vial with 7 mL toluene. The vial was loaded in a microwave reactor. The reaction mixture was then irradiated to reach the target temperature (250 °C) in 10 min and continued to irradiate at this temperature for 30 min with an initial microwave power of 100-120 W. After cooling the vial to ambient temperature, the solvent was removed under the reduced pressure and the product was isolated by column chromatography with hexanes in 79% (158 mg) yield.

Synthesis and Characterization of Compounds (4a-i) in Scheme 4.

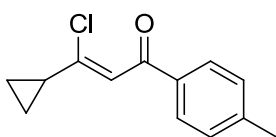
(*E*)-cyclopropyl-substituted β -chlorovinyl ketones (**4a-i**) were synthesized and isolated by the previous method¹ with cyclopropyl acetylene (**2i**). For the microwave-assisted reaction, only (*E*)-cyclopropyl-substituted β -chlorovinyl ketone was employed.



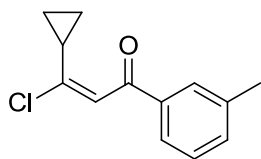
(*E*)-3-Chloro-3-cyclopropyl-1-phenylprop-2-en-1-one (**4a**) : yellow viscous oil; ¹H NMR (CDCl₃, 600 MHz): δ 7.92-7.94 (m, 2H), 7.52-7.55 (m, 1H), 7.44-7.46 (m, 2H), 6.99-7.02 (m, 1H), 4.97-5.01 (m, 1H), 3.29-3.34 (m, 1H), 2.98-3.04 (m, 1H), 2.69-2.75 (m, 1H), 2.32-2.39 (m, 1H); ¹³C NMR (CDCl₃, 150 MHz): δ 190.1, 164.8, 138.2, 132.9, 128.7, 128.3, 117.3, 54.7, 31.4, 30.3; IR (neat): 3020, 2954, 1764, 1651, 1384, 762 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₂H₁₂ClO [M+H]⁺ 207.0570 Found 207.0571.



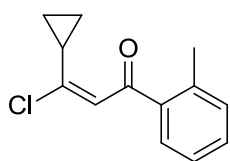
(*E*)-3-Chloro-3-cyclopropyl-1-(*p*-tolyl)prop-2-en-1-one (**4b**): yellow viscous oil; ¹H NMR (CDCl₃, 600 MHz): δ 7.84 (d, 2H, *J* = 7.8 Hz), 7.25 (d, 2H, *J* = 7.8 Hz), 6.97-7.01 (m, 1H), 4.98-5.00 (m, 1H), 3.28-3.38 (m, 1H), 2.98-3.05 (m, 1H), 2.71-2.75 (m, 1H), 2.40 (s, 3H), 2.36-2.40 (m, 1H); ¹³C NMR (CDCl₃, 150 MHz): δ 189.7, 164.4, 143.8, 135.7, 129.4, 128.4, 117.4, 54.7, 31.4, 30.3, 21.7; IR (neat): 3020, 2853, 1786, 1685, 1385, 1023, 801 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₃H₁₄ClO [M+H]⁺ 221.0727 Found 221.0730.



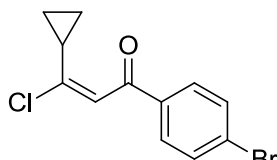
(*Z*)-3-Chloro-3-cyclopropyl-1-(*p*-tolyl)prop-2-en-1-one (**Z-4b**): yellow viscous oil; ¹H NMR (CDCl₃, 600 MHz): δ 7.82 (d, 2H, *J* = 8.4 Hz), 7.25 (d, 2H, *J* = 8.4 Hz), 7.15 (s, 1H), 3.43-3.47 (m, 1H), 2.40 (s, 3H), 1.10-1.12 (m, 2H), 0.96-0.98 (m, 2H); ¹³C NMR (CDCl₃, 150 MHz): δ 188.5, 159.8, 143.7, 136.1, 129.3, 128.4, 122.5, 21.7, 16.1, 9.0 (2C); IR (neat): 3016, 2902, 2896, 1786, 1685, 1254, 1023, 756 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₃H₁₄ClO [M+H]⁺ 221.0727 Found 221.0735.



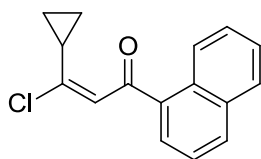
(*E*)-3-Chloro-3-cyclopropyl-1-(*m*-tolyl)prop-2-en-1-one (**4c**): yellow viscous oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.72-7.74 (m, 2H), 7.33-7.35 (m, 2H), 6.19-7.01 (m, 1H), 4.97-5.01 (m, 1H), 3.30-3.35 (m, 1H), 2.98-3.03 (m, 1H), 2.71-2.76 (m, 1H), 2.40 (s, 3H), 2.33-2.40 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 190.3, 164.5, 138.5, 138.3, 133.7, 128.8, 128.6, 125.5, 117.5, 54.7, 31.4, 30.3, 21.4; IR (neat): 3018, 2922, 1768, 1644, 1399, 1070, 774 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClO}$ $[\text{M}+\text{H}]^+$ 221.0727 Found 221.0731.



(*E*)-3-Chloro-3-cyclopropyl-1-(*o*-tolyl)prop-2-en-1-one (**4d**): light yellow solid, m.p. 78-81 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.50-7.52 (m, 1H), 7.34 (t, 1H, $J = 7.8$ Hz), 7.21-7.25 (m, 2H), 6.66-6.70 (m, 1H), 4.92-4.98 (m, 1H), 3.02-3.09 (m, 1H), 2.83-2.86 (m, 1H), 2.67-2.69 (m, 1H), 2.45 (s, 3H), 2.25-2.33 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 194.7, 163.8, 139.4, 137.3, 131.6, 131.0, 128.3, 125.8, 121.5, 54.6, 31.2, 29.9, 20.5; IR (neat): 3020, 2853, 1786, 1685, 1385, 1023, 801 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClO}$ $[\text{M}+\text{H}]^+$ 221.0727 Found 221.0730.

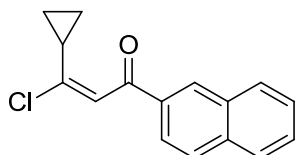


(*E*)-1-(4-Bromophenyl)-3-chloro-3-cyclopropylprop-2-en-1-one (**4e**): yellow solid, m.p. 115-117 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.80 (d, 2H, $J = 9.0$ Hz), 7.59 (d, 2H, $J = 9.0$ Hz), 6.96-6.97 (m, 1H), 4.95-5.01 (m, 1H), 3.28-3.32 (m, 1H), 2.98-3.07 (m, 1H), 2.75-2.77 (m, 1H), 2.39-2.43 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 188.9, 165.7, 136.9, 132.0, 129.8, 128.1, 116.8, 54.6, 31.4, 30.4; IR (neat): 2924, 2853, 1768, 1588, 1478, 1384, 912, 809 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{11}\text{BrClO}$ $[\text{M}+\text{H}]^+$ 284.9676 Found 284.9678.



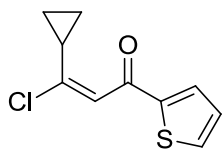
(*E*)-3-Chloro-3-cyclopropyl-1-(naphthalen-1-yl)prop-2-en-1-one (**4f**): sticky material; ^1H NMR (CDCl_3 , 600 MHz): δ 8.44 (d, 1H, $J = 8.4$ Hz), 7.96 (d, 1H,

$J = 8.4$ Hz), 7.87 (d, 1H, $J = 7.8$ Hz), 7.78 (d, 1H, $J = 6.6$ Hz), 7.55-7.58 (m, 1H), 7.49-7.54 (m, 2H), 6.83-6.84 (m, 1H), 4.98-5.01 (m, 1H), 3.09-3.13 (m, 1H), 2.84-2.88 (m, 1H), 2.68-2.73 (m, 1H), 2.33-2.38 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 194.1, 164.3, 137.3, 133.9, 132.2, 130.2, 128.5, 127.7, 127.5, 126.5, 125.6, 124.6, 122.0, 54.6, 31.2, 30.1; IR (neat): 3058, 2954, 1733, 1685, 1359, 1258, 1024, 922 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}$ $[\text{M}+\text{H}]^+$ 257.0727 Found 257.0726.



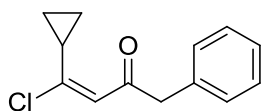
(*E*)-3-Chloro-3-cyclopropyl-1-(naphthalen-2-yl)prop-2-en-1-one (**4g**):

light yellow solid, m.p. 80-82 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.45 (s, 1H), 8.02 (dd, 1H, $J = 7.8, 2.4$ Hz), 7.97 (d, 1H, $J = 8.4$ Hz), 7.90 (d, 1H, $J = 7.8$ Hz), 7.87 (d, 1H, $J = 7.8$ Hz), 7.53-7.60 (m, 2H), 7.19-7.20 (m, 1H), 5.03-5.06 (m, 1H), 3.35-3.39 (m, 1H), 3.06-3.08 (m, 1H), 2.75-2.77 (m, 1H), 2.39-2.43 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.9, 164.7, 135.5, 132.6, 129.9, 129.6(9), 129.6(6), 128.6, 128.5, 127.8, 126.8, 124.1, 117.4, 54.7, 31.4, 30.4; IR (neat): 3058, 2581, 1735, 1616, 1359, 1125, 922, 758 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{14}\text{ClO}$ $[\text{M}+\text{H}]^+$ 257.0727 Found 257.0722.



(*E*)-3-Chloro-3-cyclopropyl-1-(thiophen-2-yl)prop-2-en-1-one (**4h**):

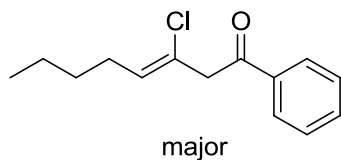
dark yellow gummy material; ^1H NMR (CDCl_3 , 600 MHz): δ 7.74 (d, 1H, $J = 3.0$ Hz), 7.63 (d, 1H, $J = 4.8$ Hz), 7.13 (dd, 1H, $J = 3.0, 4.8$ Hz), 6.85-6.89 (m, 1H), 4.96-5.02 (m, 1H), 3.32-3.34 (m, 1H), 3.02-3.04 (m, 1H), 2.72-2.76 (m, 1H), 2.33-2.41 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 182.3, 164.6, 145.8, 134.0, 131.7, 128.3, 117.2, 54.6, 31.4, 30.3; IR (neat): 3094, 2968, 1654, 1411, 1246, 1022, 801 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{10}\text{ClOS}$ $[\text{M}+\text{H}]^+$ 213.0135 Found 213.0142.



(*E*)-4-Chloro-4-cyclopropyl-1-phenylbut-3-en-2-one (**4i**):

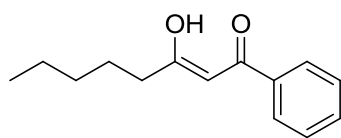
light yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.31-7.34 (m, 2H), 7.25-7.27 (m, 1H), 7.20-7.22 (m, 2H), 6.28-6.29 (m, 1H), 4.84-4.88 (m, 1H), 3.76 (s, 2H), 3.22-3.27 (m, 1H), 2.87-2.92 (m, 1H), 2.66-2.68 (m, 1H), 2.27-2.33 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 197.1, 163.4, 134.0,

129.6, 128.8, 127.1, 120.2, 54.3, 50.7, 31.2, 30.1; IR (neat): 2958, 1685, 1585, 1396, 1220, 1008, 822 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClO}$ $[\text{M}+\text{H}]^+$ 221.0727 Found 221.0737.



(Z)-3-Chloro-1-phenyloct-3-en-1-one (**2a** in Table S1): ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.96 (d, 2H, J

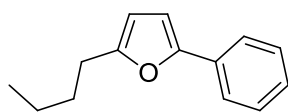
= 8.4 Hz), 7.55-7.60 (m, 1H), 7.45-7.49 (m, 2H), 5.64 (t, 1H, J = 7.2 Hz), 3.96 (s, 2H), 2.21-2.45 (m, 2H), 1.32-1.37 (m, 4H), 0.89 (t, 3H, J = 7.4 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 195.7, 137.5, 134.1, 131.0, 128.7, 128.4, 126.7, 48.5, 30.7, 29.1, 23.0, 14.1.



(Z)-3-Hydroxy-1-phenyloct-2-en-1-one (**4a** in Table S1): ^1H NMR

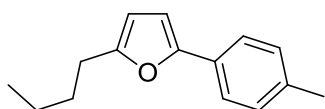
and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.² ^1H NMR (CDCl_3 , 600 MHz): δ 7.86-7.90 (m, 2H), 7.50 (t, 1H, J = 7.0 Hz), 7.43 (t, 2H, J = 7.7 Hz), 6.16 (s, 1H), 2.41 (t, 2H, J = 7.2 Hz), 1.66-1.70 (m, 2H), 1.33-1.35 (m, 4H), 0.90 (t, 3H, J = 7.4 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 197.1, 183.5, 135.1, 132.3, 128.6, 127.0, 96.1, 39.3, 31.5, 25.6, 22.5, 14.0.

Characterization of Compounds in Scheme 3

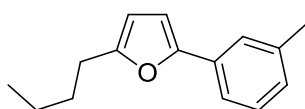


2-Butyl-5-phenylfuran (**3a**): The compound was synthesized using benzoyl chloride (35 μL) and 1-heptyne (40 μL) by the General Procedure A. The

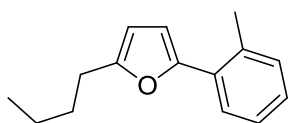
reaction was irradiated at 250 $^\circ\text{C}$ for 30 min. 44 mg (74%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.62-7.65 (m, 2H), 7.34-7.37 (m, 2H), 7.19-7.23 (m, 1H), 6.55 (d, 1H, J = 3.0 Hz), 6.06 (d, 1H, J = 3.0 Hz), 2.69 (t, 2H, J = 7.8 Hz), 1.66-1.71 (m, 2H), 1.39-1.45 (m, 2H), 0.96 (t, 3H, J = 7.4 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.5, 152.1, 131.3, 128.6, 126.7, 123.4, 106.9, 105.7, 30.3, 27.9, 22.4, 13.9.



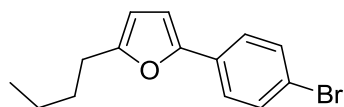
2-Butyl-5-(*p*-tolyl)furan (**3b**): The compound was synthesized using *p*-toluoyl chloride (40 μ L) and 1-heptyne (40 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 45 mg (70%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.51 (d, 2H, J = 8.4 Hz), 7.14 (d, 2H, J = 8.4 Hz), 6.47 (d, 1H, J = 3.0 Hz), 6.03 (d, 1H, J = 3.0 Hz), 2.67 (t, 2H, J = 7.2 Hz), 2.34 (s, 3H), 1.65-1.6 (m, 2H), 1.38-1.42 (m, 2H), 0.94 (t, 3H, J = 7.6 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.1, 152.3, 136.5, 129.3, 128.7, 123.3, 106.7, 104.9, 30.3, 27.9, 22.3, 21.3, 13.9.



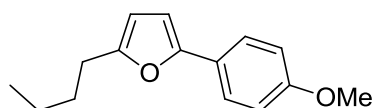
2-Butyl-5-(*m*-tolyl)furan (**3c**): The compound was synthesized using *m*-toluoyl chloride (40 μ L) and 1-heptyne (40 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 46 mg (71%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.³ ^1H NMR (CDCl_3 , 600 MHz): δ 7.41-7.46 (m, 2H), 7.24 (t, 1H, J = 7.2 Hz), 7.02 (d, 1H, J = 7.8 Hz), 6.52 (d, 1H, J = 3.2 Hz), 6.05 (d, 1H, J = 6.05 Hz), 2.68 (t, 2H, J = 7.2 Hz), 2.38 (s, 3H), 1.66-1.71 (m, 2H), 1.40-1.44 (m, 2H), 0.95 (t, 3H, J = 7.2 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.4, 152.3, 138.2, 131.2, 128.5, 127.6, 124.0, 120.6, 106.8, 105.6, 30.3, 27.9, 22.4, 21.6, 13.9.



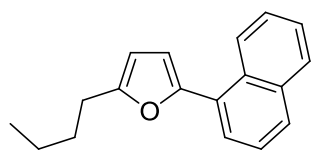
2-Butyl-5-(*o*-tolyl)furan (**3d**): The compound was synthesized using *o*-toluoyl chloride (39 μ L) and 1-heptyne (40 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 42 mg (65%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁴ ^1H NMR (CDCl_3 , 600 MHz): δ 7.69 (dd, 1H, J = 7.8, 1.8 Hz), 7.21-7.25 (m, 2H), 7.15-7.18 (m, 1H), 6.55 (d, 1H, J = 3.0 Hz), 6.09 (d, 1H, J = 3.0 Hz), 2.70 (t, 2H, J = 7.8 Hz), 2.49 (s, 3H), 1.67-1.72 (m, 2H), 1.40-1.44 (m, 2H), 0.96 (t, 3H, J = 7.2 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.0, 151.7, 134.1, 131.1, 130.6, 126.9, 126.6, 126.0, 109.3, 106.6, 30.3, 27.9, 22.4, 22.0, 12.9.



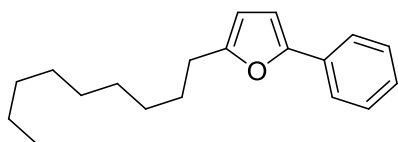
2-(4-Bromophenyl)-5-butylfuran (**3e**): The compound was synthesized using 4-bromobenzoyl chloride (66 mg) and 1-heptyne (40 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 66 mg (79%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.44-7.49 (m, 4H), 6.53 (d, 1H, J = 2.4 Hz), 6.04 (d, 1H, J = 2.4 Hz), 2.66 (t, 2H, J = 7.2 Hz), 1.63-1.67 (m, 2H), 1.37-1.43 (m, 2H), 0.94 (t, 3H, J = 7.8 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.9, 151.1, 131.7, 130.2, 124.8, 120.3, 107.1, 106.3, 30.2, 27.9, 22.3, 13.9.



2-Butyl-5-(4-methoxyphenyl)furan (**3f**): The compound was synthesized using *p*-methoxybenzoyl chloride (41 μ L) and 1-heptyne (40 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 46 mg (67%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.54 (d, 2H, J = 9.0 Hz), 6.89 (d, 2H, J = 9.0 Hz), 6.39 (d, 1H, J = 2.4 Hz), 6.01 (d, 1H, J = 2.4 Hz), 3.81 (s, 3H), 2.66 (t, 2H, J = 7.2 Hz), 1.63-1.67 (m, 2H), 1.39-1.42 (m, 2H), 0.94 (t, 3H, J = 7.6 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 158.6, 155.8, 152.1, 124.8, 124.5, 114.1, 106.7, 104.0, 55.3, 30.3, 27.9, 22.3, 13.9.



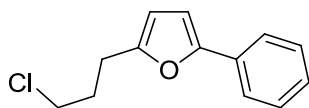
2-Butyl-5-(naphthalen-1-yl)furan (**3g**): The compound was synthesized using 1-naphthoyl chloride (45 μ L) and 1-heptyne (40 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 43 mg (57%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁵ ^1H NMR (CDCl_3 , 600 MHz): δ 8.42 (d, 1H, J = 8.4 Hz), 7.69-7.87 (m, 3H), 7.47-7.53 (m, 3H), 6.61 (d, 1H, J = 3.0 Hz), 6.16 (d, 1H, J = 3.0 Hz), 2.75 (t, 2H, J = 7.8 Hz), 1.70-1.75 (m, 2H), 1.42-1.46 (m, 2H), 0.96 (t, 3H, J = 7.2 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.8, 151.5, 134.0, 130.3, 129.0, 128.5, 128.0, 126.4, 125.8, 125.7, 125.6, 125.4, 110.0, 106.6, 30.3, 28.0, 22.4, 13.9.



2-Nonyl-5-phenylfuran (**3h**): The compound was synthesized using benzoyl chloride (40 μ L) and 1-dodecyne (64 μ L) by the

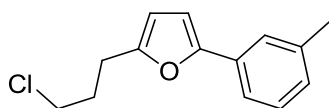
General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for

30 min. 59 mg (73%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.61-7.63 (m, 2H), .35-7.36 (m, 2H), 7.19-7.21 (m, 1H), 6.53 (d, 1H, J = 3.0 Hz), 6.04 (d, 1H, J = 3.0 Hz), 2.67 (t, 2H, J = 7.2 Hz), 1.65-1.69 (m, 2H), 1.27-1.37 (m, 12H), 0.87 (t, 3H, J = 7.4 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 156.5, 152.1, 131.3, 128.6, 126.7, 123.3, 106.8, 106.7, 31.9, 29.6, 29.4(9), 29.4(1), 29.3, 28.3, 28.1, 22.7, 14.2.



2-(3-Chloropropyl)-5-phenylfuran (**3i**): The compound was synthesized using benzoyl chloride (40 μ L) and 6-chloro-1-hexyne (36 μ L) by the

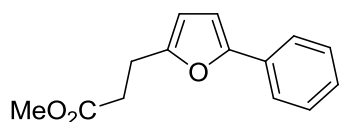
General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 40 mg (61%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data. ^1H NMR (CDCl_3 , 600 MHz): δ 7.61-7.62 (m, 2H), 7.34-7.36 (m, 2H), 7.20-7.23 (m, 1H), 6.54 (d, 1H, J = 3.6 Hz), 6.11 (d, 1H, J = 3.6 Hz), 3.60 (t, 2H, J = 6.6 Hz), 2.86 (t, 2H, J = 7.2 Hz), 2.13-2.28 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.1, 152.7, 131.0, 128.7, 127.0, 123.4, 107.9, 105.7, 44.2, 31.0, 25.4.



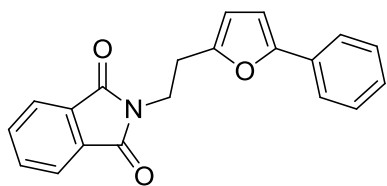
2-(3-Chloropropyl)-5-(*m*-tolyl)furan (**3j**): The compound was synthesized using *m*-toluoyl chloride (40 μ L) and 6-chlorohexyne (36

μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 30 min. 41 mg (58%); yellow liquid; ^1H NMR (CDCl_3 , 600 MHz): δ 7.41-7.44 (m, 2H), 7.23-7.25 (m, 1H), 7.03 (d, 1H, J = 7.8 Hz), 6.52 (d, 1H, J = 3.0 Hz), 6.10 (d, 1H, J = 3.0 Hz), 3.60 (t, 2H, J = 6.6 Hz), 2.86 (t, 2H, J = 7.2 Hz), 2.37 (s, 3H), 2.13-2.18 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.0, 152.9, 138.3, 131.0,

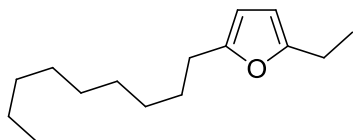
128.6, 127.8, 124.6, 120.6, 107.9, 105.6, 44.2, 31.0, 25.4, 21.5; IR (neat): 2962, 2872, 1694, 1527, 1286, 1064, 736 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{16}\text{ClO}$ $[\text{M}+\text{H}]^+$ 235.0884 Found 235.0890.



Methyl 3-(5-phenylfuran-2-yl)propanoate (**3k**): The compound was synthesized using benzoyl chloride (40 μL) and methyl 5-hexynoate (38 mg) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 30 min. 55 mg (79%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.59-7.61 (m, 2H), 7.30-7.36 (m, 2H), 7.20-7.22 (m, 1H), 6.52 (d, 1H, $J = 3.6$ Hz), 6.10 (d, 1H, $J = 3.6$ Hz), 3.69 (s, 3H), 3.03 (t, 2H, $J = 7.8$ Hz), 2.71 (t, 2H, $J = 7.8$ Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 173.0, 153.8, 152.7, 131.0, 128.6, 127.0, 123.4, 107.6, 105.7, 51.9, 32.6, 23.7.



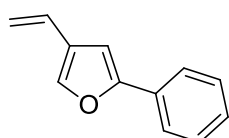
2-(2-(5-Phenylfuran-2-yl)ethyl)isoindoline-1,3-dione (**3l**): The compound was synthesized using benzoyl chloride (40 μL) and N-(4-pentynyl)phthalimide (64 mg) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 30 min. 69 mg (73%); ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.80-7.82 (m, 2H), 7.67-7.69 (m, 2H), 7.50 (d, 2H, $J = 7.8$ Hz), 7.24-7.28 (m, 2H), 7.17-7.18 (m, 1H), 6.49 (d, 1H, $J = 3.6$ Hz), 6.15 (d, 1H, $J = 3.6$ Hz), 4.02 (t, 2H, $J = 7.2$ Hz), 3.09 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 168.2, 153.1, 151.8, 134.0, 132.1, 130.8, 128.6, 127.0, 123.5, 123.3, 108.8, 105.7, 36.8, 27.2.



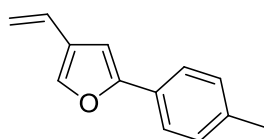
2-Ethyl-5-nonylfuran (**3m**): The compound was synthesized using propionyl chloride (26 μL) and 1-dodecyne (64 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 30 min. 47 mg (71%); pale yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 5.83 (s, 2H), 2.53-2.60 (m, 4H), 1.57-1.60 (m, 2H), 1.25-1.33 (m, 12H), 1.19 (t, 3H, $J = 7.2$ Hz), 0.86 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , 150

MHz): δ 155.9, 154.8, 104.8, 104.1, 31.9, 29.6, 29.4, 29.3(9), 29.3(2), 28.2, 28.1, 22.7, 21.4, 14.2, 12.2; IR (neat): 2925, 2872, 1665, 1608, 1512, 1017, 845 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{27}\text{O}$ $[\text{M}+\text{H}]^+$ 223.2057 Found 223.2064.

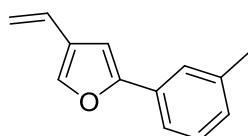
Characterization of Compounds in Scheme 4



2-Phenyl-4-vinylfuran (**5a**): Irradiated the compound (*E*)-**4a** at 250 °C for 60 min. 36 mg (71%); yellow gum; ^1H NMR (CDCl_3 , 600 MHz): δ 7.66 (d, 2H, J = 7.2 Hz), 7.44 (s, 1H), 7.36-7.39 (t, 2H, J = 7.2 Hz), 7.24-7.28 (m 1H), 6.81 (s, 1H), 6.57 (dd, 1H, J = 10.8, 16.8 Hz), 5.52 (d, 1H, J = 16.8 Hz), 5.18 (d, 1H, J = 10.8 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.7, 140.1, 130.6, 128.7, 127.7, 126.7, 126.6, 123.9, 113.7, 102.3; IR (neat): 2924, 2865, 1685, 1384, 1095, 773 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{11}\text{O}$ $[\text{M}+\text{H}]^+$ 171.0804 Found 171.0809.

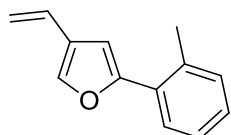


2-(*p*-Tolyl)-4-vinylfuran (**5b**): Irradiated the compound (*E*)-**4b** at 250 °C for 60 min. 39 mg (70%); yellow gum; ^1H NMR (CDCl_3 , 600 MHz): δ 7.55 (d, 2H, J = 7.2 Hz), 7.42 (s, 1H), 7.18 (d, 2H, J = 7.2 Hz), 6.75 (s, 1H), 6.56 (dd, 1H, J = 10.8, 17.4 Hz), 5.51 (d, 1H, J = 17.4 Hz), 5.16 (d, 1H, J = 10.8 Hz), 2.35 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 155.0, 139.8, 137.5, 129.4, 128.0, 126.7, 126.6, 123.9, 113.6, 101.6, 21.3; IR (neat): 2924, 2855, 1768, 1675, 1384, 1071, 6929 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 185.0961 Found 185.0968.

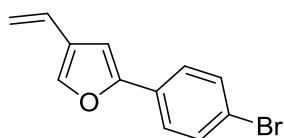


2-(*m*-Tolyl)-4-vinylfuran (**5c**): Irradiated the compound (*E*)-**4c** at 250 °C for 60 min. 40 mg (73%); yellow solid, m.p. 83-85 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.49 (s, 1H), 7.46 (d, 1H, J = 7.2 Hz), 7.43 (s, 1H), 7.26 (t, 1H, J = 7.8 Hz), 7.08 (d, 1H, J = 7.2 Hz), 6.79 (s, 1H), 6.56 (dd, 1H, J = 16.8, 10.8 Hz), 5.51 (d, 1H, J = 16.8 Hz), 5.16 (d, 1H, J = 10.8 Hz), 2.37 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.9, 140.0, 138.3,

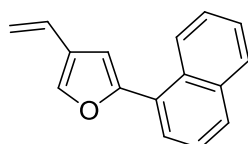
130.6, 128.6, 128.5, 126.7(2), 126.7(0), 124.6, 121.1, 113.6, 102.2, 21.5; IR (neat): 2922, 2854, 1768, 1643, 1384, 1042, 784 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 185.0961 Found 185.0966.



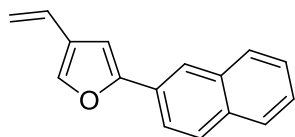
2-(*o*-Tolyl)-4-vinylfuran (**5d**): Irradiated the compound (*E*)-**4d** at 250 °C for 60 min. 38 mg (68%); yellow gum; ^1H NMR (CDCl_3 , 600 MHz): δ 7.66 (d, 1H, J = 7.8 Hz), 7.48 (s, 1H), 7.21-7.24 (m, 3H), 6.67 (s, 1H), 6.59 (dd, 1H, J = 17.4, 10.8 Hz), 5.52 (d, 1H, J = 17.4 Hz), 5.17 (d, 1H, J = 10.8 Hz), 2.50 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.9, 139.7, 134.8, 131.2, 130.0, 127.8, 127.2, 126.8, 126.3, 126.0, 113.5, 105.9, 21.8; IR (neat): 2923, 2851, 1585, 1384, 1399, 1071, 770 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 185.0961 Found 185.0968.



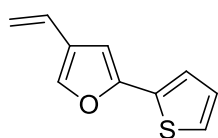
2-(4-Bromophenyl)-4-vinylfuran (**5e**): Irradiated the compound (*E*)-**4e** at 250 °C for 60 min. 49 mg (65%); yellow solid, m.p. 78-79 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.48-7.52 (m, 4H), 7.44 (s, 1H), 6.80 (s, 1H), 6.55 (dd, 1H, J = 18.0, 11.4 Hz), 5.51 (d, 1H, J = 18.0 Hz), 5.18 (d, 1H, J = 11.4 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 153.7, 140.3, 131.9, 129.5, 126.8, 126.4, 125.4, 121.5, 114.0, 102.9; IR (neat): 2942, 2853, 1768, 1585, 1478, 1384, 1399, 912, 809 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{10}\text{BrO}$ $[\text{M}+\text{H}]^+$ 248.9910 Found 248.9918.



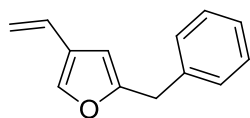
2-(Naphthalen-1-yl)-4-vinylfuran (**5f**): Irradiated the compound (*E*)-**4f** at 250 °C for 60 min. 43 mg (65%); yellow gum; ^1H NMR (CDCl_3 , 600 MHz): δ 8.39 (d, 1H, J = 8.4 Hz), 7.88 (d, 1H, J = 7.2 Hz), 7.84 (d, 1H, J = 7.8 Hz), 7.72 (d, 1H, J = 7.2 Hz), 7.60 (s, 1H), 7.49-7.55 (m, 3H), 6.87 (s, 1H), 6.65 (dd, 1H, J = 16.8, 10.2 Hz), 5.58 (d, 1H, J = 16.8 Hz), 5.22 (d, 1H, J = 10.2 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.3, 140.4, 134.0, 130.5, 128.9, 128.6, 128.4, 126.7(7), 126.7(1), 126.5, 126.3, 126.0, 125.5, 125.3, 113.8, 106.7; IR (neat): 3050, 2959, 2853, 1793, 1685, 1385, 1095, 800 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 221.0961 Found 221.0966.



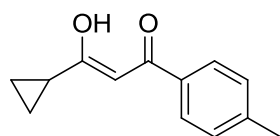
2-(Naphthalen-2-yl)-4-vinylfuran (**5g**): Irradiated the compound (*E*)-**4g** at 250 °C for 60 min. 46 mg (70%); yellow solid, m. p. 83-87 °C; ¹H NMR (CDCl₃, 600 MHz): δ 8.13 (s, 1H), 7.84 (t, 2H, *J* = 7.8 Hz), 7.80 (d, 1H, *J* = 7.2 Hz), 7.75-7.77 (m, 1H), 7.50 (s, 1H), 7.43-7.49 (m, 2H), 6.93 (s, 1H), 6.60 (dd, 1H, *J* = 17.4, 10.8 Hz), 5.56 (d, 1H, *J* = 17.4 Hz), 5.20 (d, 1H, *J* = 10.8 Hz); ¹³C NMR (CDCl₃, 150 MHz): δ 154.8, 140.3, 133.5, 132.8, 128.4, 128.2, 127.9, 127.8, 126.9, 126.6, 126.5, 126.1, 122.4, 122.3, 113.8, 103.0; IR (neat): 3050, 2924, 1684, 1504, 1259, 1023, 801, 773 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₆H₁₃O [M+H]⁺ 221.0961 Found 221.0969.



2-(Thiophen-2-yl)-4-vinylfuran (**5h**): Irradiated the compound (*E*)-**4h** at 250 °C for 60 min. 25 mg (48%); yellow sticky material; ¹H NMR (CDCl₃, 600 MHz): δ 7.37 (s, 1H), 7.25 (d, 1H, *J* = 6.0 Hz), 7.22 (d, 1H, *J* = 4.8 Hz), 7.03 (dd, 1H, *J* = 6.0, 4.8 Hz), 6.65 (s, 1H), 6.53 (dd, 1H, *J* = 16.8, 10.8 Hz), 5.49 (d, 1H, *J* = 16.8 Hz), 5.17 (d, 1H, *J* = 10.8 Hz); ¹³C NMR (CDCl₃, 150 MHz): δ 150.2, 139.6, 133.5, 127.7, 126.7, 126.4, 124.5, 123.0, 113.9, 102.4; IR (neat): 3295, 2906, 1711, 1602, 1466, 1385, 1016, 775 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₀H₉OS [M+H]⁺ 177.0369 Found 177.0382.



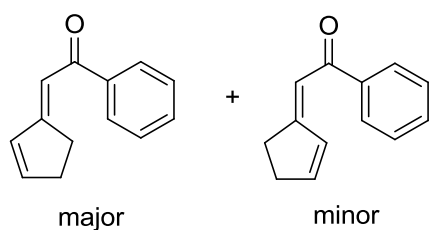
2-Benzyl-4-vinylfuran (**5i**): Irradiated the compound (*E*)-**4i** at 250 °C for 60 min. 32 mg (57%); yellow oil; ¹H NMR (CDCl₃, 600 MHz): δ 7.30 (t, 2H, *J* = 8.4 Hz), 7.29 (s, 1H), 7.21-7.24 (m, 3H), 6.49 (dd, 1H, *J* = 18.0, 10.8 Hz), 6.16 (s, 1H), 5.37 (d, 1H, *J* = 18.0 Hz), 5.06 (d, 1H, *J* = 10.8 Hz), 3.92 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz): δ 155.7, 139.6, 137.8, 128.8, 128.6, 126.8, 126.6, 125.6, 113.6, 103.9, 34.6; IR (neat): 3010, 2856, 1698, 1574, 1324, 1023 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₃H₁₃O [M+H]⁺ 185.0961 Found 185.0954.



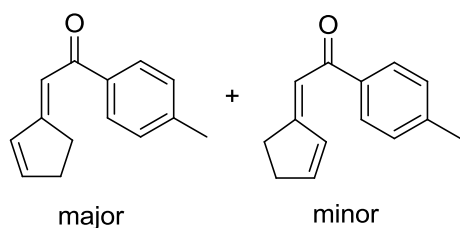
(*Z*)-3-Cyclopropyl-3-hydroxy-1-(*p*-tolyl)prop-2-en-1-one (**4ba**): Irradiated the compound (*Z*)-**4b** at 250 °C for 60 min. yellow oil; ¹H NMR (CDCl₃,

600 MHz): δ 7.83 (d, 2H, J = 8.4 Hz), 7.25 (d, 2H, J = 8.4 Hz), 6.98 (s, 1H), 2.40 (s, 3H), 1.88-1.92 (m, 1H), 1.56 (brs, 1H), 1.02-1.05 (m, 2H), 0.88-0.90 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 188.5, 150.0, 143.8, 135.6, 129.3, 118.6, 119.3, 21.7, 20.3, 7.6 (2C); IR (neat): 3310, 2954, 2836, 1724, 1524, 1294, 1104, 924 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$ 203.1068 Found 203.1064.

Characterization of Compounds in Scheme 5

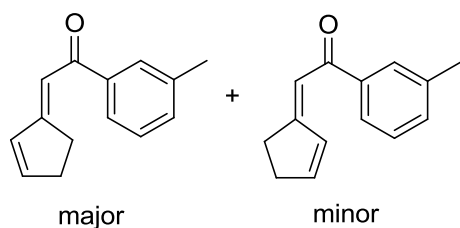


2-(Cyclopent-2-en-1-ylidene)-1-phenylethanone (**6a**): The compound was synthesized using benzoyl chloride (40 μL) and **2j** (25 mg) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 34 mg (61%); yellow viscous oil; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.94 (d, 2H, J = 8.6 Hz), 7.50 (t, 1H, J = 7.8 Hz), 7.42-7.45 (m, 2H), 6.97 (s, 1H), 6.77-6.79 (m, 1H), 6.43-6.45 (m, 1H), 3.18-3.20 (m, 2H), 2.66-2.69 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): 190.8, 169.8, 150.2, 139.7, 135.6, 131.9, 128.4, 127.9, 112.9, 33.8, 31.3; minor (*Z*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.93 (d, 2H, J = 7.8 Hz), 7.63 (m, 1H), 7.50 (t, 1H, J = 7.8 Hz), 7.42-7.45 (m, 2H), 6.79-6.82 (m, 1H), 6.30 (s, 1H), 2.77-2.78 (m, 2H), 2.56-2.57 (m, 2H) ^{13}C NMR (CDCl_3 , 150 MHz): δ 190.8, 169.8, 151.7, 139.7, 133.1, 132.0, 138.4, 128.0, 112.0, 31.9, 31.3; IR (neat): 2985, 2921, 1698, 1534, 1422, 1264, 1011, 755 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 185.0961 Found 185.0960.



2-(Cyclopent-2-en-1-ylidene)-1-(*p*-tolyl)ethanone (**6b**): The compound was synthesized using *p*-toluoyl chloride (40 μL) and **2j** (25 mg) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 39 mg (65%); yellow viscous oil; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.85 (d, 2H, J = 8.4 Hz), 7.23 (d, 2H, J = 8.4 Hz), 6.96 (s, 1H), 6.74-6.76 (m, 1H), 6.42-6.43 (m, 1H), 3.17-3.19 (m, 2H), 2.66-2.67 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): 190.5, 169.3, 149.9, 142.6, 137.2, 133.1, 129.2, 128.0, 112.9, 33.8,

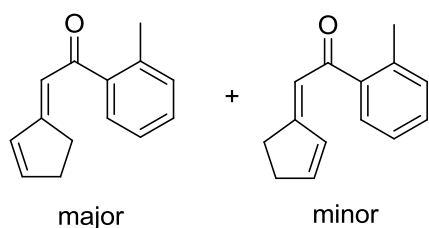
31.3, 21.6; minor (*Z*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.84 (d, 2H, $J = 8.2$ Hz), 7.61-7.62 (m, 1H), 7.24 (d, 2H, $J = 8.2$ Hz), 6.76-6.78 (m, 2H), 2.75-2.77 (m, 2H), 2.56-2.57 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.7, 166.8, 151.3, 142.6, 137.1, 133.1, 129.4, 129.1, 128.6, 31.8, 31.3, 21.6; IR (neat): 3001, 2967, 2954, 1643, 1584, 1413, 1265, 1022, 771 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O} [\text{M}+\text{H}]^+$ 199.1118 Found 199.1120.



2-(Cyclopent-2-en-1-ylidene)-1-(*m*-tolyl)ethanone (**6c**):

The compound was synthesized using *m*-toluoyl chloride (40 μL) and **2j** (25 mg) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 31 mg (52%);

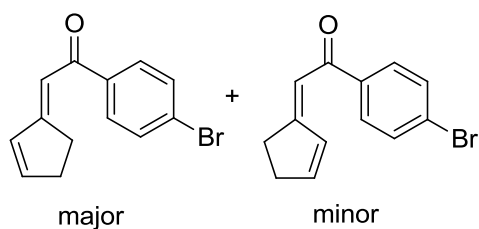
yellow viscous oil; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.72-7.76 (m, 2H), 7.31-7.34 (m, 2H), 6.94 (s, 1H), 6.76-6.78 (m, 1H), 6.43-6.45 (m, 1H), 3.17-3.19 (m, 2H), 2.67-2.68 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): 191.4, 169.6, 150.4, 139.8, 138.2, 136.6, 132.7, 128.5, 128.3, 125.0, 113.2, 33.8, 31.3, 21.5; minor (*Z*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.72-7.75 (m, 2H), 7.61-7.62 (m, 1H), 7.32-7.36 (m, 2H), 6.79-6.80 (m, 1H), 6.77 (s, 1H), 2.77-2.78 (m, 2H), 2.56-2.57 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 190.3, 169.6, 151.5, 139.8, 138.2, 133.2, 132.8, 128.7, 128.3, 125.3, 112.2, 31.9, 31.3, 21.4; IR (neat): 3015, 1925, 1854, 1695, 1584, 1414, 1264, 1004, 801 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O} [\text{M}+\text{H}]^+$ 199.1118 Found 199.1118.



2-(Cyclopent-2-en-1-ylidene)-1-(*o*-tolyl)ethanone (**6d**): The compound was synthesized using *o*-toluoyl chloride (39 μL) and **2j** (25 mg) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 36 mg (60%); yellow viscous

oil; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.48 (d, 1H, $J = 7.8$ Hz), 7.28-7.31 (m, 1H), 7.19-7.22 (m, 2H), 6.74-6.76 (m, 1H), 6.60 (s, 1H), 6.36-6.37 (m, 1H), 3.09-3.11 (m, 2H), 2.65-2.66 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): 195.7, 168.7, 150.1, 141.4, 136.6, 135.5, 131.3,

130.0, 127.6, 125.6, 117.0, 33.8, 31.0, 20.4; minor (Z)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.45-7.47 (m, 1H), 7.36-7.38 (m, 1H), 7.28-7.31 (m, 1H), 7.19-7.22 (m, 2H), 6.74-6.76 (m, 1H), 6.40 (s, 1H), 2.72-2.74 (m, 2H), 2.54-2.55 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 195.0, 166.4, 151.5, 141.4, 136.6, 135.5, 131.5, 131.3, 127.7, 125.6, 116.2, 31.8, 31.2, 20.3; IR (neat): 2998, 2923, 1654, 1587, 1445, 1246, 1032, 771 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$ 199.1118 Found 199.1125.

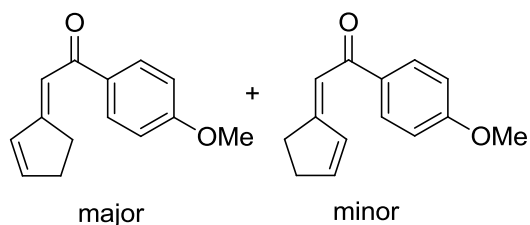


1-(4-Bromophenyl)-2-(cyclopent-2-en-1-ylidene)

ethanone (**6e**): The compound was synthesized using *p*-bromobenzoyl chloride (66 mg) and **2j** (25 mg) by the

General Procedure A. The reaction was irradiated at 250 °C

for 10 min. 45 mg (57%); yellow sticky gum; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.80 (d, 2H, $J = 7.8$ Hz), 7.56 (d, 2H, $J = 7.8$ Hz), 6.90 (s, 1H), 6.80-6.81 (m, 1H), 6.43-6.44 (m, 1H), 3.16-3.18 (m, 2H), 2.67-2.68 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): 189.6, 170.7, 150.9, 138.5, 135.5, 131.7, 129.5, 126.9, 112.4, 33.9, 31.5; minor (Z)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.78-7.80 (m, 2H), 7.60-7.62 (m, 1H), 7.55-7.58 (m, 2H), 6.83-6.84 (m, 1H), 6.71 (s, 1H), 2.76-2.78 (m, 2H), 2.56-2.58 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 188.8, 168.1, 152.4, 138.4, 133.1, 131.7, 129.7, 127.0, 111.4, 32.0, 31.3; IR (neat): 3010, 2962, 2821, 1704, 1582, 1453, 1264, 940, 697 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{BrO}$ $[\text{M}+\text{H}]^+$ 263.0066 Found 263.0070.



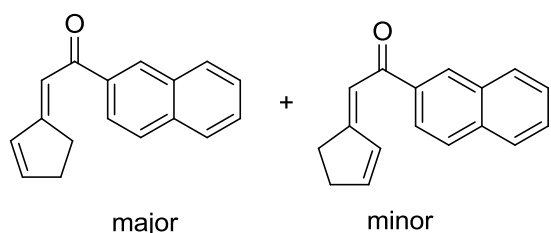
2-(Cyclopent-2-en-1-ylidene)-1-(4-methoxyphenyl)

ethanone (**6f**): The compound was synthesized using *p*-methoxybenzoyl chloride (41 μL) and **2j** (25 mg) by

the General Procedure A. The reaction was irradiated

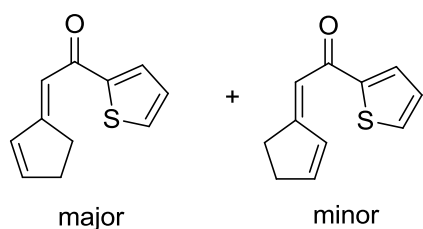
at 250 °C for 10 min. 46 mg (72%); yellow viscous oil; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.94 (d, 2H, $J = 8.2$ Hz), 6.94 (s, 1H), 6.92 (d, 2H, $J = 8.2$ Hz), 6.76-6.74 (m, 1H), 6.41-6.43 (m, 1H),

3.87 (s, 3H), 3.17-3.18 (m, 2H), 2.65-2.66 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): 189.5, 169.0, 162.9, 149.6, 135.6, 132.7, 130.1, 113.6, 112.8, 55.4, 33.8, 31.2; minor (*Z*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.92-9.94 (m, 2H), 7.60-7.61 (m 1H), 6.90-6.92 (m, 2H), 6.75-6.77 (m, 2H), 3.87 (s, 3H), 2.75-2.77 (m, 2H), 2.54-2.56 (m, 2H) ; ^{13}C NMR (CDCl_3 , 150 MHz): δ 188.8, 166.3, 162.7, 151.0, 145.8, 133.1, 130.4, 113.6, 111.9, 55.4, 31.8, 31.2; IR (neat): 3044, 2978, 2821, 1735, 1638, 1566, 1356, 1063, 892 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$ 215.1067 Found 215.1072.



2-(Cyclopent-2-en-1-ylidene)-1-(naphthalen-2-yl)ethanone (**6g**): The compound was synthesized using 2-naphthoyl chloride (57 mg) and **2j** (25 mg) by the General Procedure A. The reaction was irradiated at

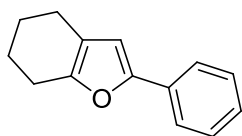
250 °C for 10 min. 46 mg (66%); yellow amorphous gum; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 8.45 (s, 1H), 8.04-8.06 (m, 1H), 7.95 (d, 1H, $J = 7.8$ Hz), 7.85-7.89 (m, 2H), 7.51-7.57 (m, 2H), 7.14 (s, 1H), 6.79-6.81 (m, 1H), 6.49-6.57 (m, 1H), 3.23-3.25 (m, 2H), 2.73-2.75 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): 190.7, 169.9, 150.3, 137.1, 135.7, 135.1, 132.7, 129.5, 128.9, 128.3, 127.9, 127.8, 126.5, 124.4, 113.0, 33.9, 31.4; minor (*Z*)- ^1H NMR (CDCl_3 , 600 MHz): δ 8.45 (s, 1H), 8.03-8.05 (m, 1H), 7.95 (d, 1H, $J = 7.8$ Hz), 7.85-7.89 (m, 2H), 7.67-7.68 (m, 1H), 7.51-7.57 (m, 2H), 6.95 (s, 1H), 6.82-6.84 (m, 1H), 2.82-2.84 (m, 2H), 2.59-2.60 (m, 2H) ; ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.9, 167.3, 151.8, 137.1, 135.1, 133.2, 132.7, 130.2, 129.5, 129.2, 129.1, 128.3, 127.9, 124.5, 112.1, 32.0, 31.3; IR (neat): 3044, 2968, 2934, 1654, 1584, 1432, 1246, 1022, 775 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$ 235.1117 Found 235.1125.



2-(Cyclopent-2-en-1-ylidene)-1-(thiophen-2-yl)ethanone (**6h**): The compound was synthesized using 2-thienoyl chloride (32 μL) and **2j** (25 mg) by the General Procedure A. The reaction was irradiated at 250 °C for 10 min. 27 mg (48%); yellow

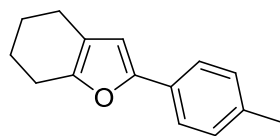
amorphous gum; major (*E*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.68 (d, 1H, J = 3.8 Hz), 7.55 (d, 1H, J = 4.2 Hz), 7.09 (dd, 1H, J = 4.2, 3.8 Hz), 6.82 (s, 1H), 6.76-6.77 (m, 1H), 6.41-6.42 (m, 1H), 3.16-3.21 (m, 2H), 2.66-2.67 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): 183.2, 169.6, 150.5, 147.3, 136.4, 132.4, 130.1, 128.0, 112.8, 33.9, 31.3; minor (*Z*)- ^1H NMR (CDCl_3 , 600 MHz): δ 7.69 (d, 1H, J = 3.8 Hz), 7.64-7.66 (m, 1H), 7.55 (d, 1H, J = 4.2 Hz), 7.09 (dd, 1H, J = 4.2, 3.8 Hz), 6.77-6.79 (m, 1H), 6.65 (s, 1H), 2.75-2.77 (m, 2H), 2.55-2.56 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 182.1, 167.2, 151.8, 147.1, 133.2, 132.6, 130.4, 128.0, 111.6, 31.8, 31.3; IR (neat): 3099, 2962, 2922, 2854, 1631, 1566, 1414, 1246, 1063, 801, 717 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{OS}$ $[\text{M}+\text{H}]^+$ 191.0525 Found 191.0529.

Characterization of Compounds in Scheme 6



2-Phenyl-4,5,6,7-tetrahydrobenzofuran (**7a**): The compound was synthesized using benzoyl chloride (40 μL) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^\circ\text{C}$ for 10 min. 42 mg (70%); yellow solid;

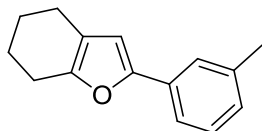
^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁶ ^1H NMR (CDCl_3 , 600 MHz): δ 7.61 (d, 2H, J = 7.2 Hz), 7.33 (t, 2H, J = 7.2 Hz), 7.17-7.21 (m, 1H), 6.46 (s, 1H), 2.65 (t, 2H, J = 6.2 Hz), 2.45 (t, 2H, J = 6.0 Hz), 1.84-1.88 (m, 2H), 1.72-1.76 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.6, 150.8, 131.5, 128.6, 126.6, 123.3, 119.0, 106.0, 23.3, 23.2, 23.1, 22.2.



2-(*p*-Tolyl)-4,5,6,7-tetrahydrobenzofuran (**7b**): The compound was synthesized using *p*-toluoyl chloride (40 μL) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^\circ\text{C}$ for 10 min. 39 mg

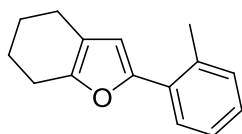
(62%); yellow solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁶ ^1H NMR (CDCl_3 , 600 MHz): δ 7.51 (d, 2H, J = 8.4 Hz), 7.15 (d, 2H, J = 8.4 Hz), 6.41 (s, 1H), 2.66 (t, 2H, J = 6.2 Hz), 2.45 (t, 2H, J = 6.2 Hz), 2.34 (s, 3H), 1.83-1.87

(m, 2H), 1.74-1.77 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.9, 150.4, 136.3, 129.3, 128.8, 123.3, 118.9, 105.3, 23.3, 23.2(6), 23.2(2), 22.2, 21.3.



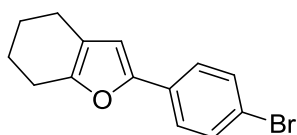
2-(*m*-Tolyl)-4,5,6,7-tetrahydrobenzofuran (**7c**): The compound was synthesized using *m*-toluoyl chloride (40 μL) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 44 mg (69%);

yellow amorphous gum; ^1H NMR (CDCl_3 , 600 MHz): δ 7.44 (s, 1H), 7.40 (d, 1H, J = 7.8 Hz), 7.23-7.25 (m, 1H), 7.01 (d, 1H, J = 7.2 Hz), 6.44 (s, 1H), 2.65 (t, 2H, J = 6.2 Hz), 2.45 (t, 2H, J = 6.0 Hz), 2.36 (s, 3H), 1.83-1.87 (m, 2H), 1.72-1.76 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.8, 150.7, 138.2, 131.4, 128.5, 127.4, 123.9, 120.5, 119.0, 105.9, 23.3, 23.2, 23.1, 22.4, 21.5; IR (neat): 2934, 2860, 1676, 1448, 1384, 761 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 213.1274 Found 213.1278.



2-(*o*-Tolyl)-4,5,6,7-tetrahydrobenzofuran (**7d**): The compound was synthesized using *o*-toluoyl chloride (39 μL) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 39 mg (62%); yellow

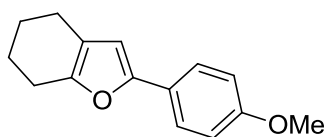
amorphous gum; ^1H NMR (CDCl_3 , 600 MHz): δ 7.68 (d, 1H, J = 8.2 Hz), 7.21-7.23 (m, 2H), 7.14-7.16 (m, 1H), 6.35 (s, 1H), 2.67 (t, 2H, J = 6.0 Hz), 2.48 (t, 2H, J = 6.0 Hz), 2.48 (s, 3H), 1.85-1.89 (m, 2H), 1.75-1.79 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.1, 150.3, 134.0, 131.1, 130.8, 126.7, 126.5, 125.9, 118.7, 109.8, 23.3, 23.2(7), 23.2(2), 22.2, 22.1; IR (neat): 2956, 2854, 1631, 1449, 1187, 746 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 213.1274 Found 213.1281.



2-(4-Bromophenyl)-4,5,6,7-tetrahydrobenzofuran (**7e**): The compound was synthesized using *p*-bromobenzoyl chloride (66 mg) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10

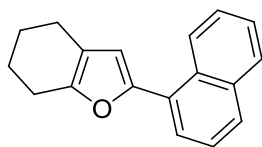
min. 49 mg (59%); yellow solid, m.p. 113-115 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.43-7.48 (m, 4H),

6.45 (s, 1H), 2.63 (t, 2H, $J = 6.0$ Hz), 2.44 (t, 2H, $J = 6.0$ Hz), 1.83-1.87 (m, 2H), 1.72-1.76 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.3, 150.6, 131.7, 130.4, 124.7, 120.1, 119.3, 106.7, 23.3, 23.1(7), 23.1(1), 22.1; IR (neat): 2930, 2848, 1477, 1393, 1300, 822, 806 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{BrO}$ $[\text{M}+\text{H}]^+$ 277.0223 Found 277.0229.



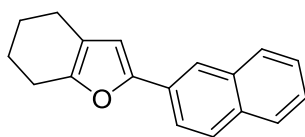
2-(4-Methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran (**7f**): The compound was synthesized using *p*-methoxybenzoyl chloride (41 μL) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$

for 10 min. 48 mg (70%); yellow solid, m.p. 108-110 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.54 (d, 2H, $J = 8.6$ Hz), 6.88 (d, 2H, $J = 8.6$ Hz), 6.33 (s, 1H), 3.81 (s, 3H), 2.64 (t, 2H, $J = 6.2$ Hz), 2.44 (t, 2H, $J = 6.2$ Hz), 1.84-1.86 (m, 2H), 1.73-1.75 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 158.6, 151.7, 150.0, 124.7(8), 124.7(3), 118.9, 114.1, 104.5, 55.3, 23.3, 23.2(7), 23.2(3), 22.2; IR (neat): 2926, 2849, 1609, 1498, 1252, 1026, 831, 771 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 229.1223 Found 229.1229.

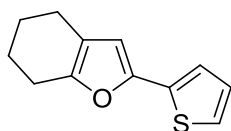


2-(Naphthalen-1-yl)-4,5,6,7-tetrahydrobenzofuran (**7g**): The compound was synthesized using 1-naphthoyl chloride (45 μL) and **2k** (35 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 10 min. 43

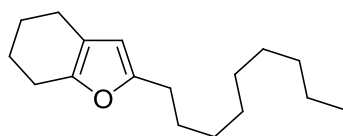
mg (58%); yellow amorphous gum; ^1H NMR (CDCl_3 , 600 MHz): δ 8.46 (d, 1H, $J = 7.8$ Hz), 7.86 (d, 1H, $J = 7.8$ Hz), 7.78 (d, 1H, $J = 8.0$ Hz), 7.70 (d, 1H, $J = 7.6$ Hz), 7.46-7.53 (m, 3H), 6.55 (s, 1H), 2.73 (t, 2H, $J = 6.6$ Hz), 2.54 (t, 2H, $J = 6.6$ Hz), 1.89-1.93 (m, 2H), 1.79-1.83 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.1, 151.0, 134.1, 130.3, 129.2, 128.5, 127.9, 126.3, 125.8(2C), 125.5, 125.4, 118.8, 110.5, 23.4, 23.2(8), 23.2(4), 22.3; IR (neat): 2931, 2849, 1591, 1442, 1396, 918, 773 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 249.1274 Found 249.1281.



2-(Naphthalen-2-yl)-4,5,6,7-tetrahydrobenzofuran (**7h**): The compound was synthesized using 2-naphthoyl chloride (57 mg) and **2k** (35 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 10 min. 44 mg (62%); yellow gum; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁷ ^1H NMR (CDCl_3 , 600 MHz): δ 8.02 (s, 1H), 7.83 (d, 1H, J = 8.4 Hz), 7.93 (t, 2H, J = 8.4 Hz), 7.70-7.73 (m, 1H), 7.40-7.47 (m, 2H), 6.59 (s, 1H), 2.71 (t, 2H, J = 6.6 Hz), 2.49 (t, 2H, J = 6.6 Hz), 1.87-1.90 (m, 2H), 1.74-1.79 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 151.7, 151.2, 133.7, 132.4, 128.8, 128.3, 128.1, 127.8, 126.4, 125.5, 122.3, 121.2, 119.3, 106.8, 23.4, 23.2(4), 23.2(0), 22.2.



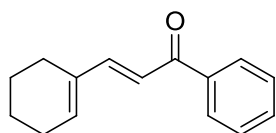
2-(Thiophen-2-yl)-4,5,6,7-tetrahydrobenzofuran (**7i**): The compound was synthesized using 2-thienoyl chloride (32 μ L) and **2k** (35 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 10 min. 33 mg (54%); yellow amorphous gum; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁸ ^1H NMR (CDCl_3 , 600 MHz): δ 7.15 (d, 1H, J = 3.6 Hz), 7.14 (d, 1H, J = 4.8 Hz), 6.98 (dd, 1H, J = 4.8, 3.6 Hz), 6.31 (s, 1H), 2.62 (t, 2H, J = 6.0 Hz), 2.42 (t, 2H, J = 6.0 Hz), 1.83-1.85 (m, 2H), 1.72-1.74 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 150.5, 147.2, 134.6, 127.5, 123.2, 121.4, 119.0, 106.1, 23.3, 23.1(5), 23.1(2), 22.1.n



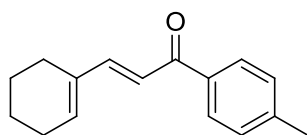
2-Nonyl-4,5,6,7-tetrahydrobenzofuran (**7j**): The compound was synthesized using decanoyl chloride (62 μ L) and **2k** (35 μ L) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}$ C for 10 min. 51 mg (69%); yellow amorphous gum; ^1H NMR (CDCl_3 , 600 MHz): δ 5.77 (s, 1H), 2.53-2.56 (m, 4H), 2.36-2.37 (m, 2H), 1.79-1.81 (m, 2H), 1.69-1.70 (m, 2H), 1.58-1.61 (m, 2H), 1.26-1.34 (m, 12H), 0.88 (t, 3H, J = 7.2 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 154.3, 148.6, 117.1, 105.4, 31.9, 29.6, 29.5,

29.4, 29.3, 28.4, 28.2, 23.3(4), 23.3(0), 23.2, 22.7, 22.2, 14.2; IR (neat): 2925, 2815, 1678, 1458, 1220, 1096, 989, 758 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}$ $[\text{M}+\text{H}]^+$ 249.2213 Found 249.2221.

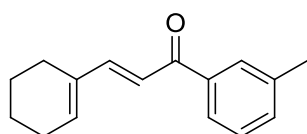
Characterization of Compounds in Scheme 7



(*E*)-3-(Cyclohex-1-en-1-yl)-1-phenylprop-2-en-1-one (**8a**): The compound was synthesized using benzoyl chloride (40 μL) and **2I** (39 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 3 min. 52 mg (81%); yellow solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.92-7.94 (m, 2H), 7.52-7.54 (m, 1H), 7.45 (t, 2H, $J = 7.8$ Hz), 7.40 (d, 1H, $J = 15.6$ Hz), 6.83 (d, 1H, $J = 15.6$ Hz), 6.27-6.29 (m, 1H), 2.23-2.26 (m, 4H), 1.70-1.74 (m, 2H), 1.63-1.66 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 191.3, 148.6, 140.9, 138.6, 135.6, 132.4, 128.5, 128.4, 118.9, 26.8, 24.4, 22.1(6), 22.6(1).

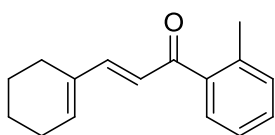


(*E*)-3-(Cyclohex-1-en-1-yl)-1-(*p*-tolyl)prop-2-en-1-one (**8b**): The compound was synthesized using *p*-toluoyl chloride (40 μL) and **2I** (39 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 3 min. 47 mg (69%); yellow solid, m. p. 115-117 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.84 (d, 2H, $J = 7.8$ Hz), 7.40 (d, 1H, $J = 15.6$ Hz), 7.24 (d, 2H, $J = 7.8$ Hz), 6.83 (d, 1H, $J = 15.6$ Hz), 6.26-6.27 (m, 1H), 2.39 (s, 3H), 2.21-2.26 (m, 4H), 1.70- 1.73 (m, 2H), 1.62-1.65 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 190.8, 148.1, 143.2, 140.5, 136.0, 135.6, 129.2, 128.6, 118.8, 26.7, 24.4, 22.1(8), 22.1(4), 21.7; IR (neat): 3039, 2025, 2865, 1660, 1564, 1278, 775 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$ 227.1430 Found 227.1435.



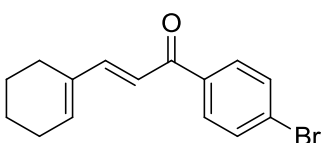
(*E*)-3-(cyclohex-1-en-1-yl)-1-(*m*-tolyl)prop-2-en-1-one (**8c**): The compound was synthesized using *m*-toluoyl chloride (40 μL) and **2I** (39

μL) by the General Procedure A. The reaction was irradiated at 250 °C for 3 min. 47 mg (69%); yellow solid, m. p. 120-122 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.71-7.73 (m, 2H), 7.39 (d, 1H, J = 15.6 Hz), 7.32-7.34 (m, 2H), 6.82 (d, 1H, J = 15.6 Hz), 6.27-6.28 (m, 1H), 2.40 (s, 3H), 2.23-2.27 (m, 4H), 1.71-1.75 (m, 2H), 1.62-1.66 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 191.5, 148.4, 140.6, 138.7, 138.3, 135.6, 133.2, 128.9, 128.3, 125.6, 119.0, 26.8, 24.4, 22.1(0), 22.1(3), 21.4; IR (neat): 3021, 1954, 1894, 1669, 1497, 1230, 769 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$ 227.1430 Found 227.1431.



(*E*)-3-(Cyclohex-1-en-1-yl)-1-(*o*-tolyl)prop-2-en-1-one (**8d**): The compound was synthesized using *o*-toluoyl chloride (39 μL) and **2I** (39 μL) by the General Procedure A. The reaction was irradiated at 250 °C for 3 min.

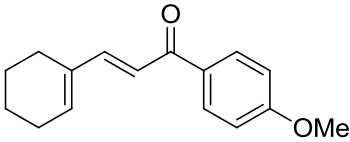
52 mg (77%); yellow amorphous gum; ^1H NMR (CDCl_3 , 600 MHz): δ 7.36 (d, 1H, J = 7.2 Hz), 7.32 (dd, 1H, J = 7.2, 1.8 Hz), 7.20-7.23 (m, 2H), 7.02 (d, 1H, J = 15.6 Hz), 6.42 (d, 1H, J = 15.6 Hz), 6.13-6.16 (m, 1H), 2.37 (s, 3H), 2.19-2.21 (m, 4H), 1.68-1.71 (m, 2H), 1.60-1.63 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 197.7, 149.9, 140.8, 139.6, 136.5, 135.5, 131.1, 130.0, 127.9, 125.4, 123.9, 26.7, 24.3, 22.1, 22.0, 20.1; IR (neat): 3020, 2929, 2858, 1669, 1584, 1292, 769 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$ 227.1430 Found 227.1440.

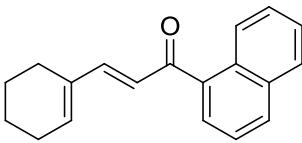


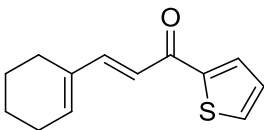
(*E*)-1-(4-Bromophenyl)-3-(cyclohex-1-en-1-yl)prop-2-en-1-one (**8e**):

The compound was synthesized using *p*-bromobenzoyl chloride (66 mg) and **2I** (39 μL) by the General Procedure A. The reaction was irradiated at 250 °C for 3 min. 57 mg (65%); yellow solid, m. p. 124-126 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.79 (d, 2H, J = 9.0 Hz), 7.59 (d, 2H, J = 9.0 Hz), 7.40 (d, 1H, J = 15.0 Hz), 6.77 (d, 1H, J = 15.0 Hz), 6.29-6.30 (m, 1H), 2.24-2.25 (m, 4H), 1.70-1.74 (m, 2H), 1.63-1.66 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 190.1, 149.1, 141.5, 137.3, 135.5, 131.8, 130.0, 127.4, 118.2, 26.8, 24.4, 22.1, 22.0; IR (neat):

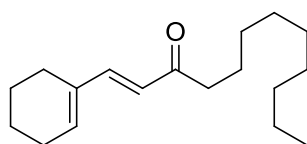
3029, 2922, 2853, 1603, 1445, 1235, 769 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{BrO}$ $[\text{M}+\text{H}]^+$ 291.0379 Found 291.0381.

(*E*)-3-(Cyclohex-1-en-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one
**(8f):** The compound was synthesized using *p*-methoxybenzoyl chloride (41 μL) and **2I** (40 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 3 min. 49 mg (68%); yellow solid, m. p. 98-101 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.94-7.95 (m, 2H), 7.39(d, 1H, J = 15.0 Hz), 6.92-6.94 (m, 2H), 6.84 (d, 1H, J = 15.0 Hz), 6.26-6.27 (m, 1H), 3.85 (s, 3H), 2.22-2.26 (m, 4H), 1.71-1.73 (m, 2H), 1.62-1.64 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.5, 163.1, 147.7, 140.2, 136.6, 131.5, 130.7, 118.5, 113.7, 55.5, 26.7, 24.4, 22.1(9), 22.1(5); IR (neat): 3021, 1965, 2896, 1669, 1445, 1396, 1058, 954 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 243.1380 Found 243.1383.

(*E*)-3-(Cyclohex-1-en-1-yl)-1-(naphthalen-1-yl)prop-2-en-1-one **(8g)**:

The compound was synthesized using 1-naphtholyl (45 μL) and **2I** (39 μL) by the General Procedure A. The reaction was irradiated at 250 $^{\circ}\text{C}$ for 3 min. 56 mg (71%); yellow amorphous gum; ^1H NMR (CDCl_3 , 600 MHz): δ 8.44 (s, 1H), 8.03 (dd, 1H, J = 9.0, 1.8 Hz), 7.96 (d, 1H, J = 8.4 Hz), 7.89 (d, 1H, J = 9.0 Hz), 7.26 (d, 1H, J = 7.8 Hz), 7.52-7.58 (m, 2H), 7.47 (d, 1H, J = 15.0 Hz), 5.99 (d, 1H, J = 15.0 Hz), 6.30-6.31 (m, 1H), 2.24-2.33 (m, 4H), 1.74-1.78 (m, 2H), 1.62-1.67 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 191.1, 148.5, 140.8, 136.0, 135.7, 135.4, 132.6, 129.6, 129.5, 128.4, 128.2, 127.8, 126.7, 124.6, 118.9, 26.8, 24.5, 22.2, 22.1; IR (neat): 3058, 3016, 2928, 2860, 1602, 1446, 1260, 775 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$ 263.1431 Found 263.1438.

(*E*)-3-(Cyclohex-1-en-1-yl)-1-(thiophen-2-yl)prop-2-en-1-one **(8h)**: The compound was synthesized using 2-thienoyl chloride (32 μL) and **2I** (39 μL)


by the General Procedure A. The reaction was irradiated at 250 °C for 3 min. 44 mg (67%); yellow solid, m. p. 112-115 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.75 (d, 1H, J = 4.2 Hz), 7.61 (d, 1H, J = 4.8 Hz), 7.44 (d, 1H, J = 15.0 Hz), 7.13 (dd, 1H, J = 4.8, 4.2 Hz), 6.74 (d, 1H, J = 15.0 Hz), 6.29-6.30 (m, 1H), 2.24-2.25 (m, 4H), 1.71-1.74 (m, 2H), 1.62-1.66 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 182.7, 147.7, 145.9, 141.1, 135.4, 133.3, 131.3, 128.1, 118.3, 26.8, 24.4, 22.1(4), 22.1(0); IR (neat): 3025, 2959, 2906, 1627, 1318, 1124, 820, 724 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{15}\text{OS}$ $[\text{M}+\text{H}]^+$ 219.0838 Found 219.0844.



(*E*)-1-(Cyclohex-1-en-1-yl)dodec-1-en-3-one (**8i**): The compound was synthesized using decanoyl chloride (62 μL) and **2l** (39 μL) by the General Procedure A. The reaction was irradiated at 250 °C for 3 min. 59

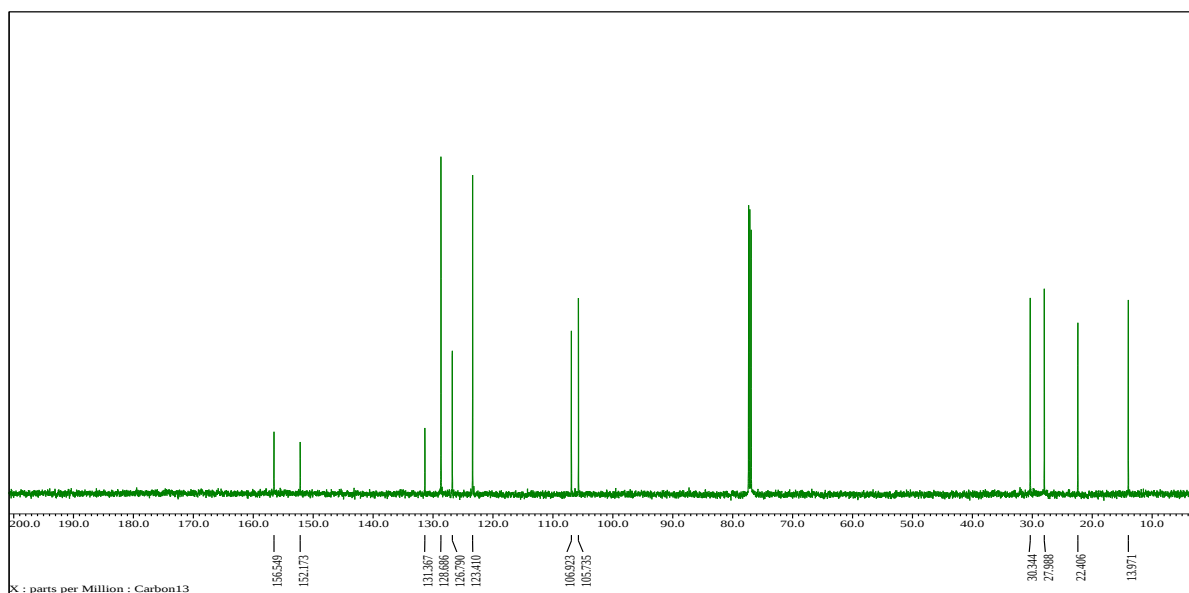
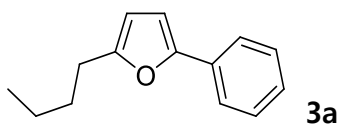
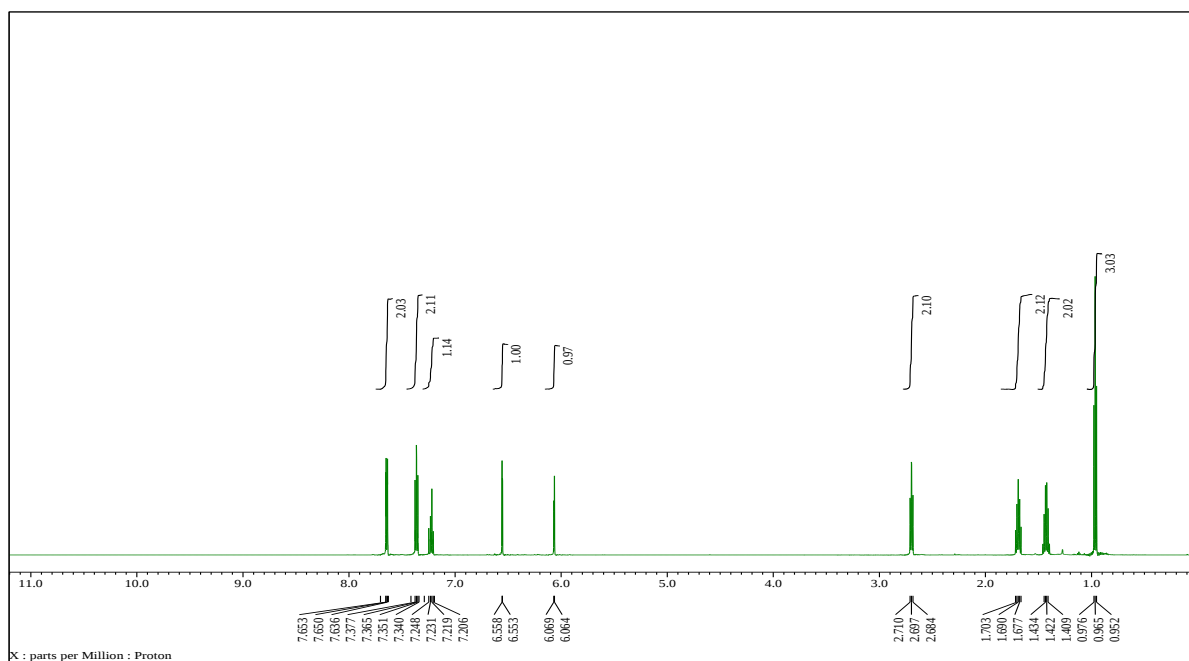
mg (75%); yellow amorphous solid; ^1H NMR (CDCl_3 , 600 MHz): δ 7.13 (d, 1H, J = 16.2 Hz), 6.19-6.20 (m, 1H), 6.05 (d, 1H, J = 16.2 Hz), 2.53 (t, 2H, J = 7.2 Hz), 2.12-2.21 (m, 4H), 1.66-1.69 (m, 2H), 1.60-1.62 (m, 4H), 1.23-1.28 (m, 12H), 0.85 (t, 3H, J = 7.2 Hz); ^{13}C NMR (CDCl_3 , 150 MHz): δ 201.5, 146.0, 139.7, 135.3, 123.3, 40.6, 31.9, 29.5 (2C), 29.4, 29.3, 26.7, 24.6, 24.2, 22.7, 22.1(4), 22.1(1), 14.1; IR (neat): 2926, 2854, 1677, 1629, 1458, 1260, 992, 758 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{31}\text{O}$ $[\text{M}+\text{H}]^+$ 263.2369 Found 263.2375.

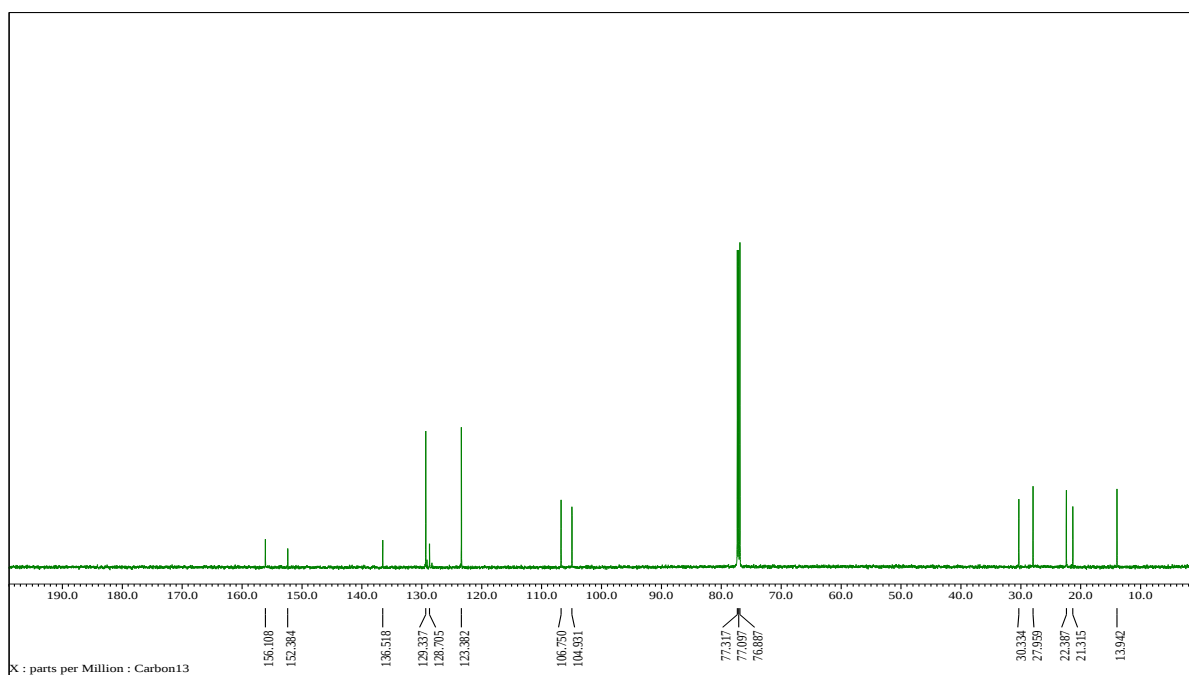
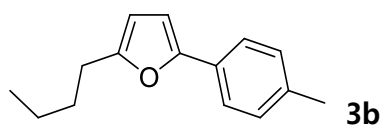
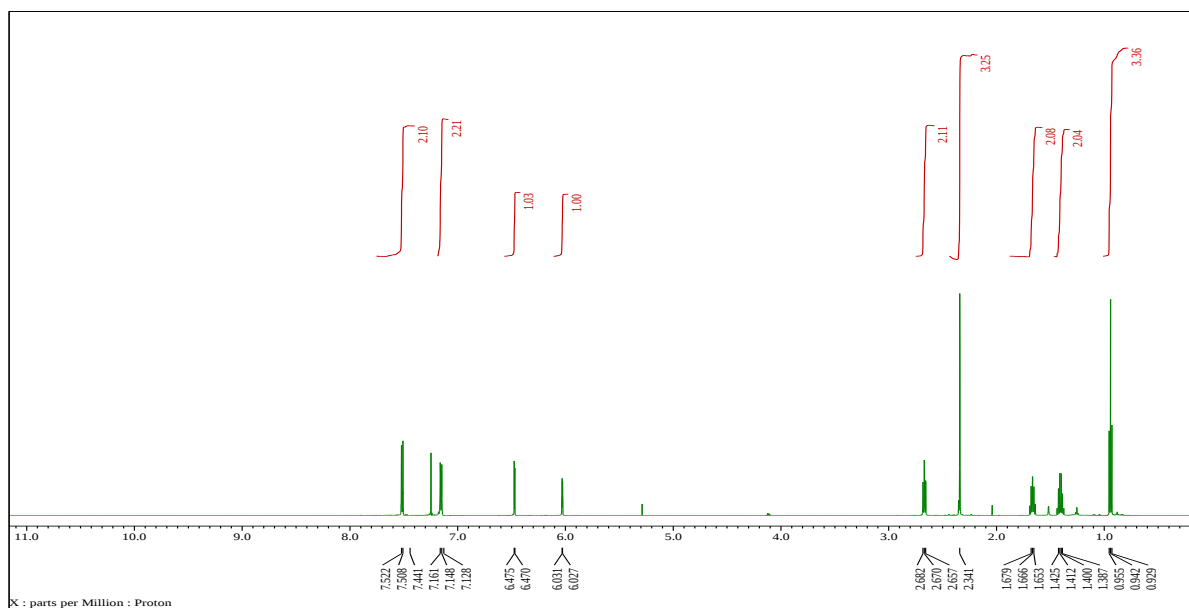
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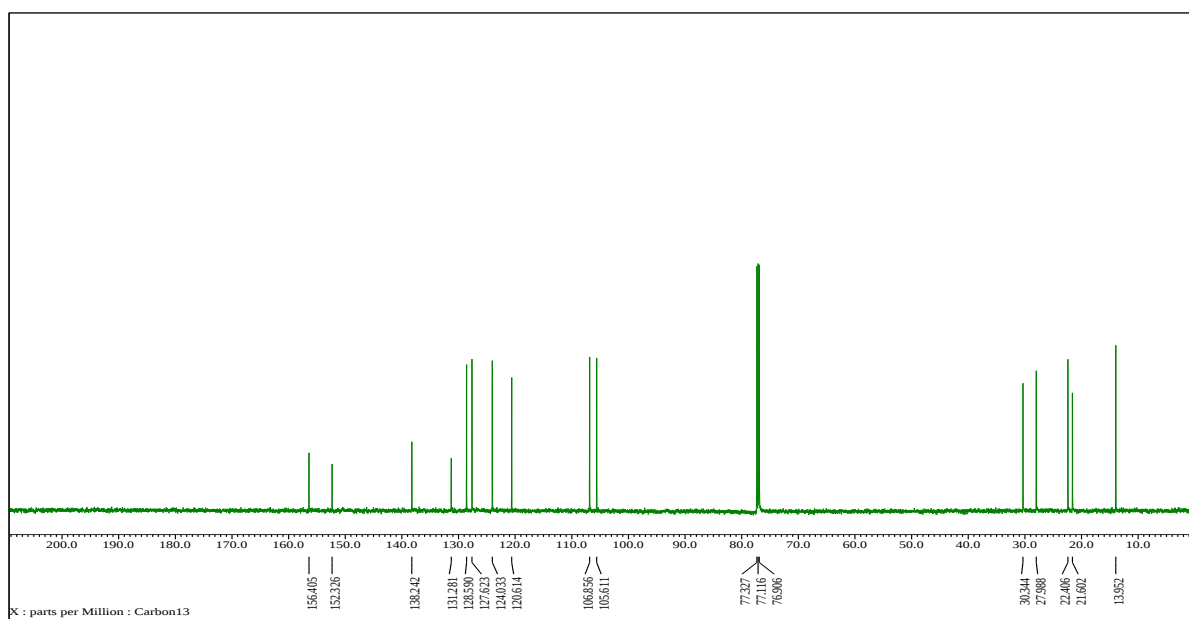
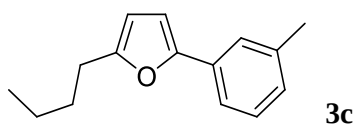
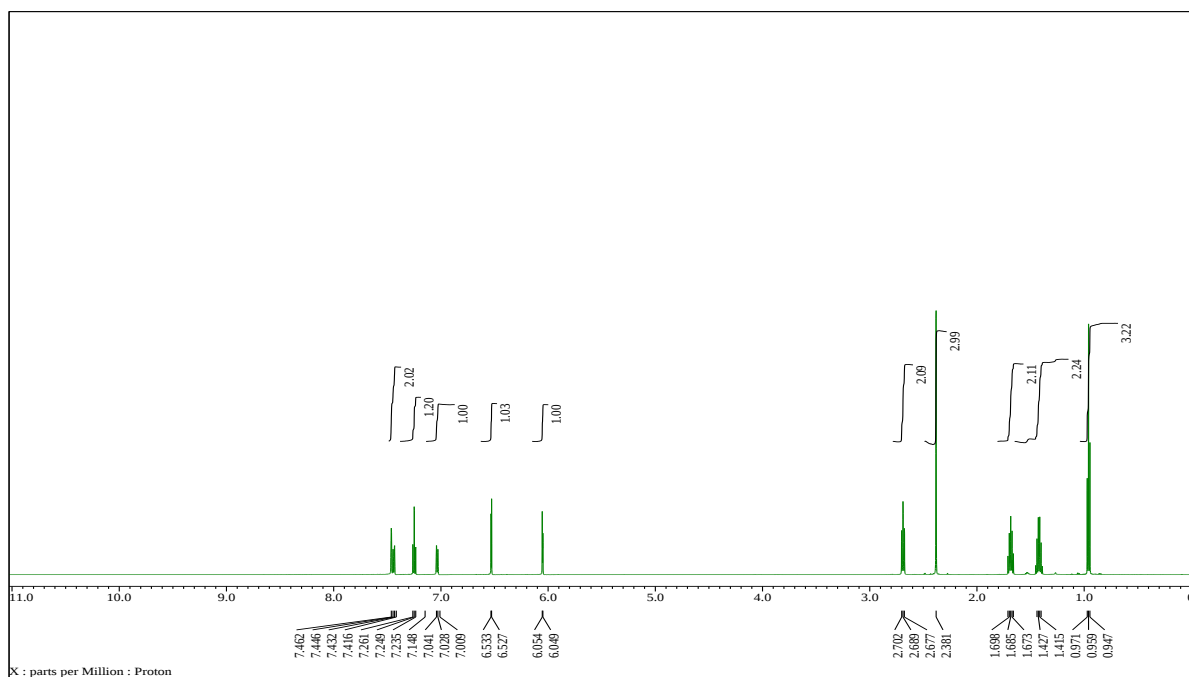
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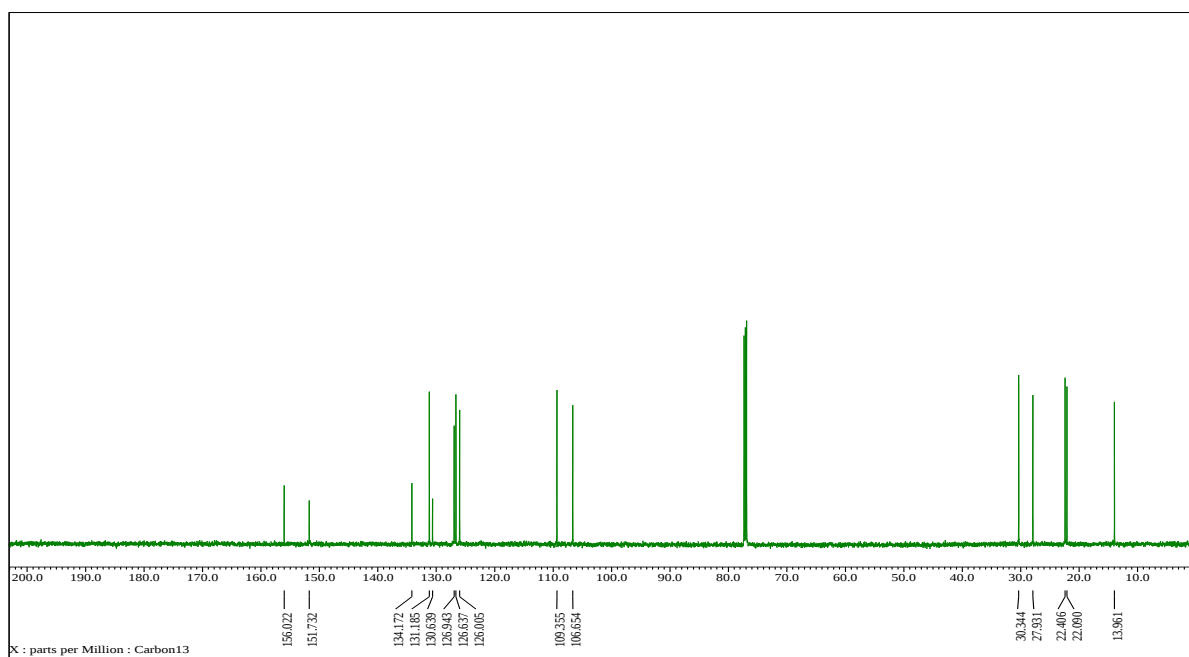
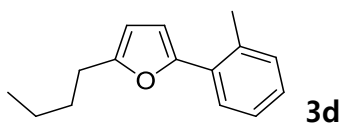
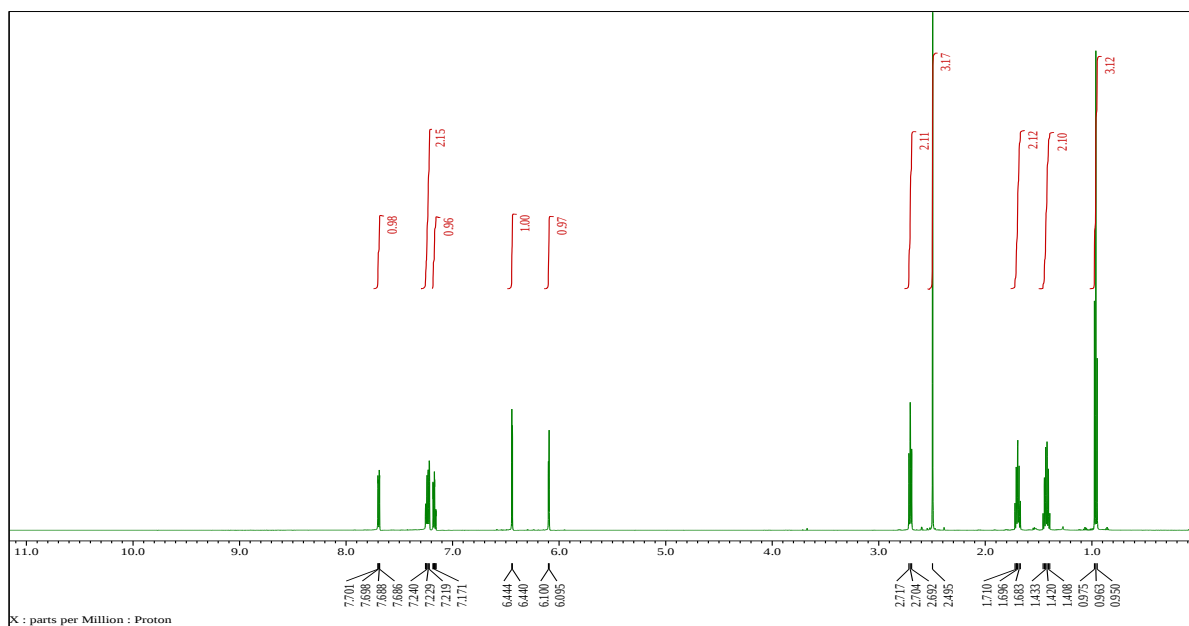
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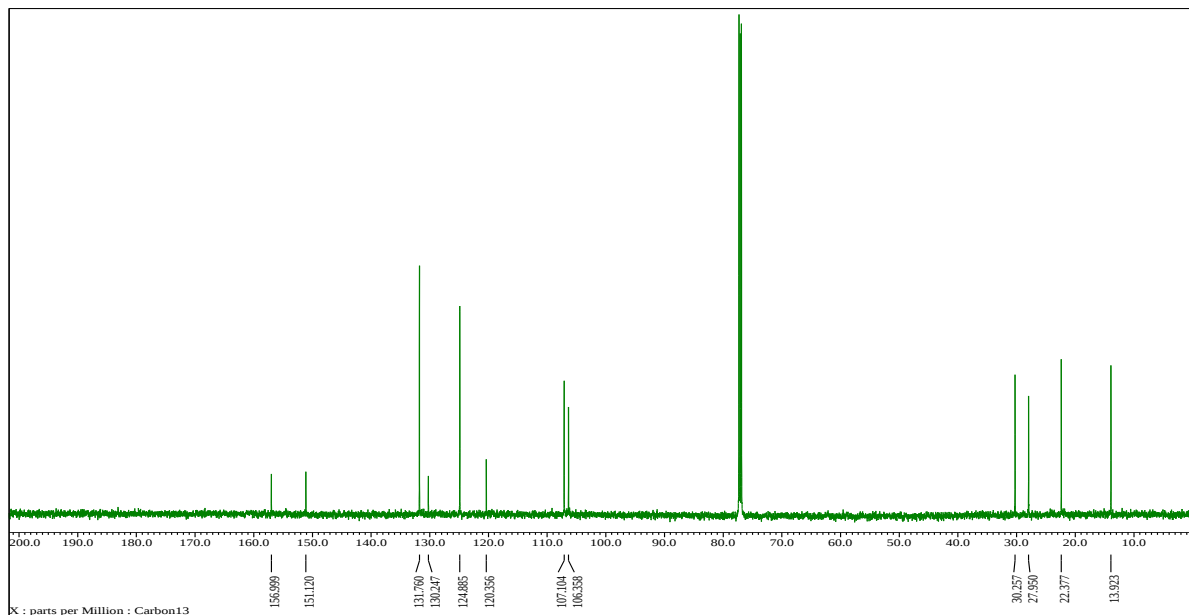
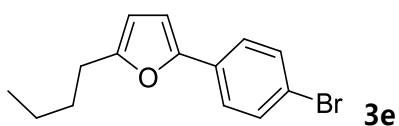
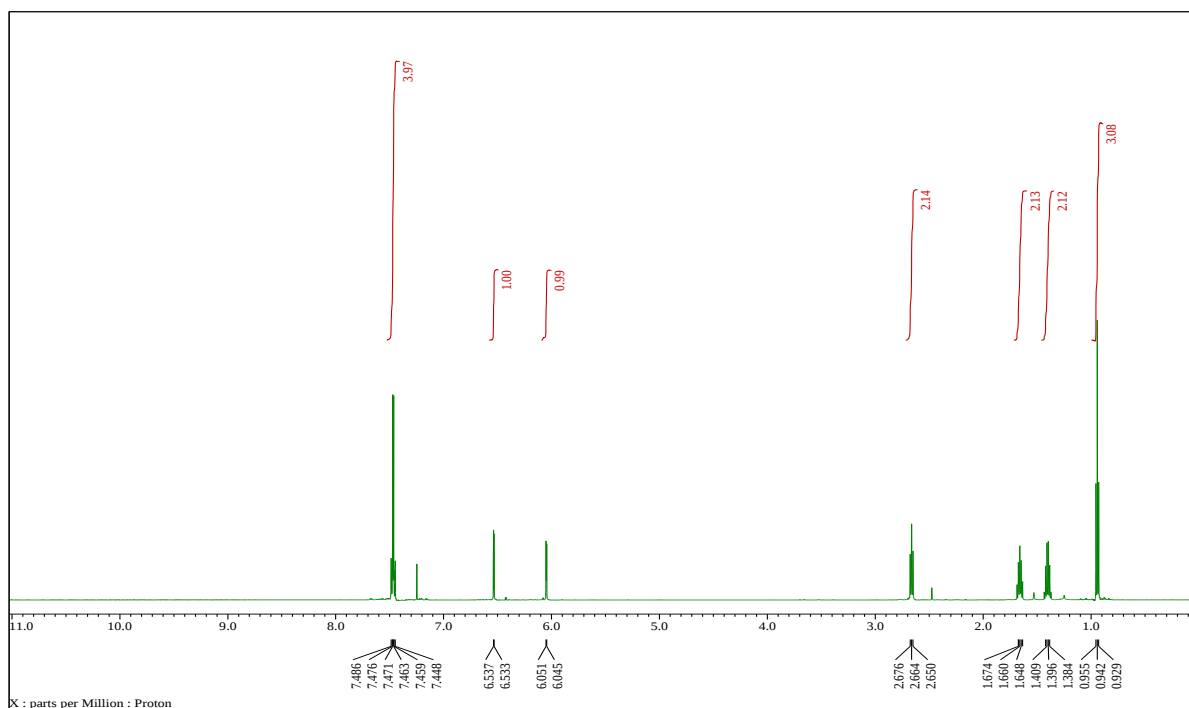
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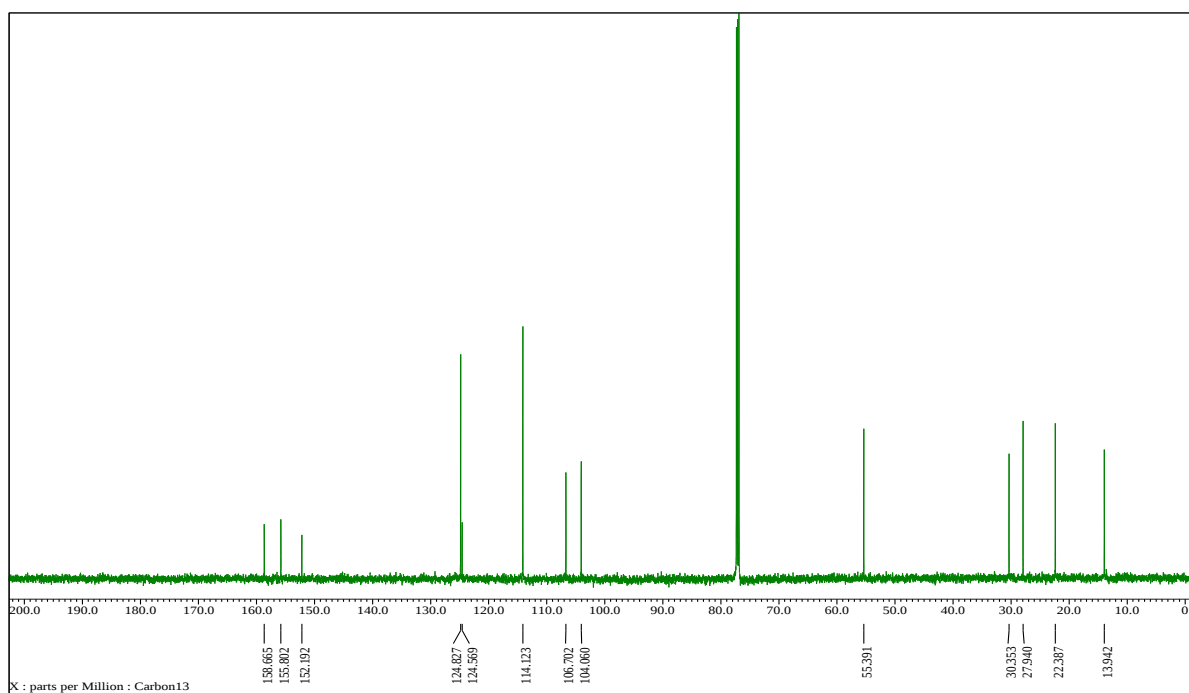
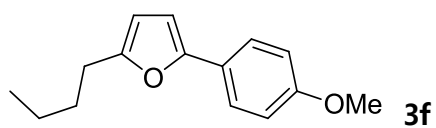
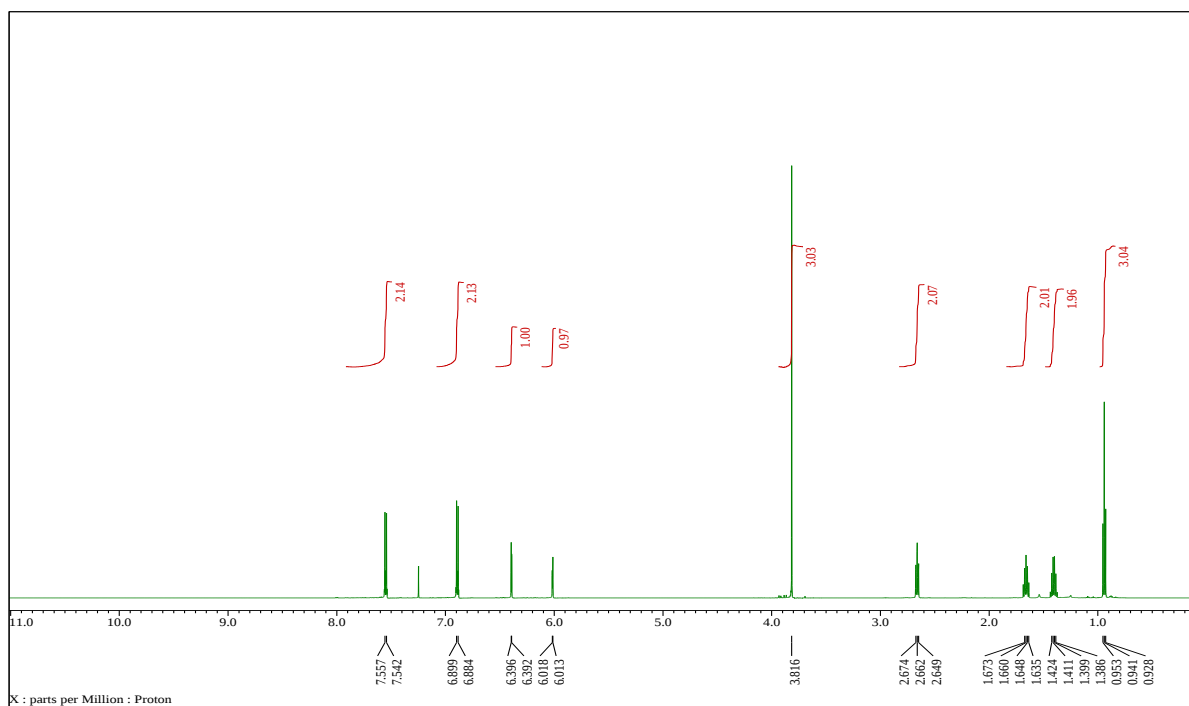


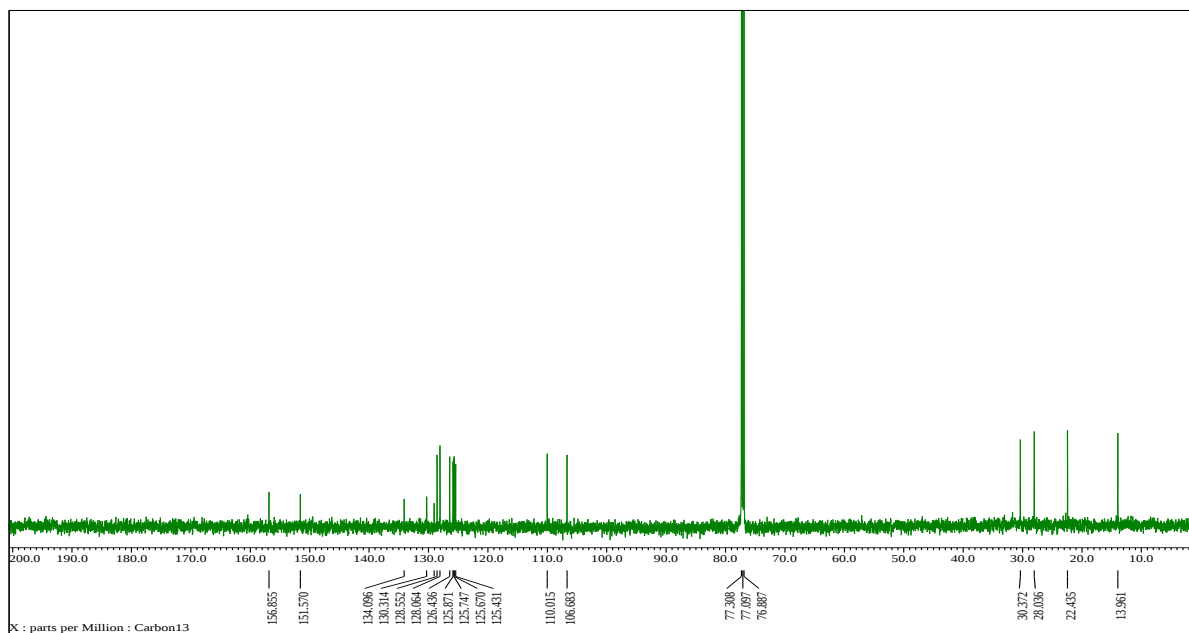
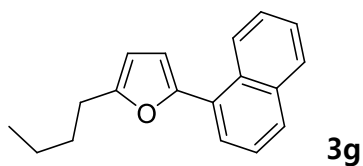
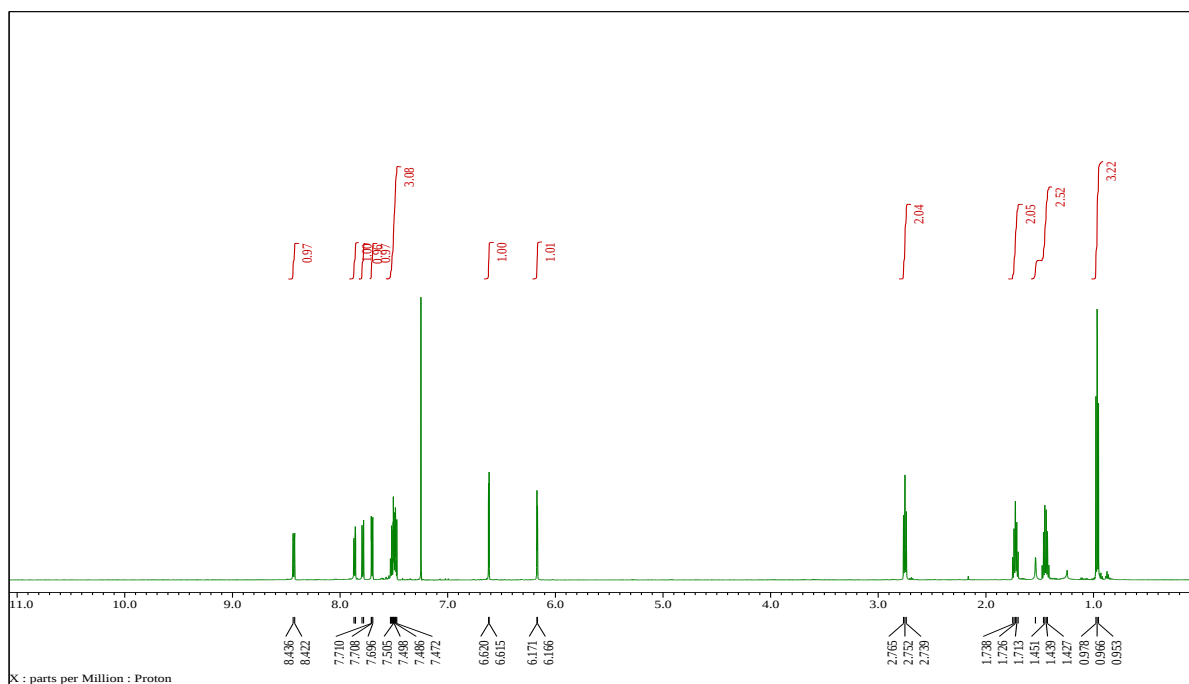


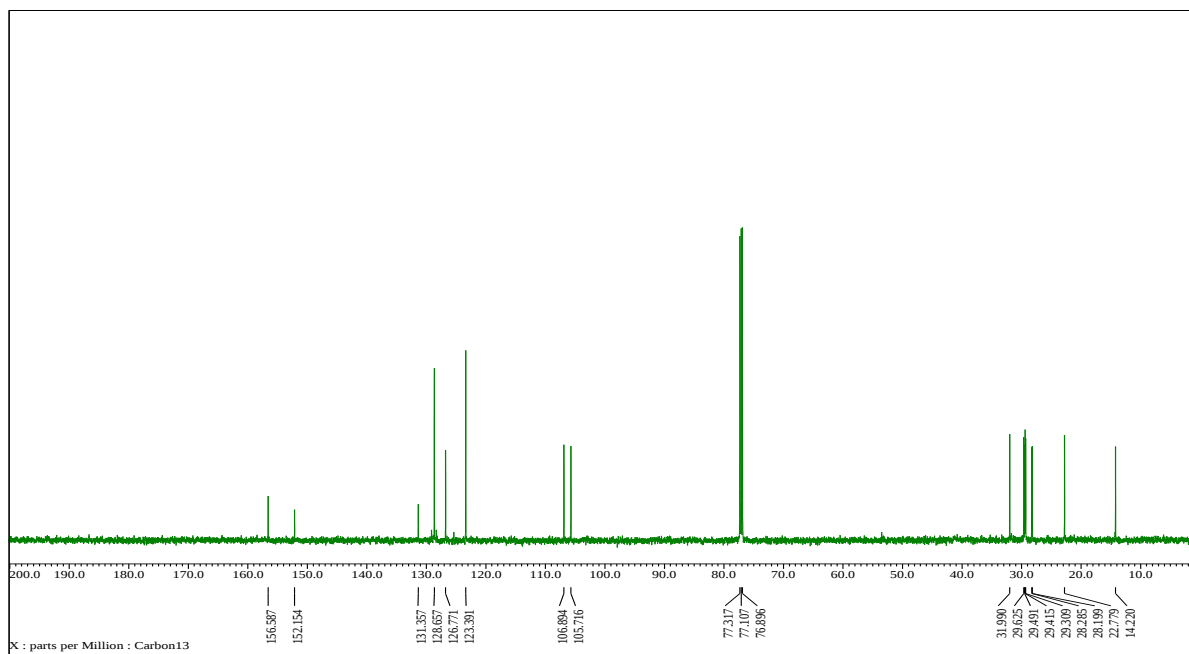
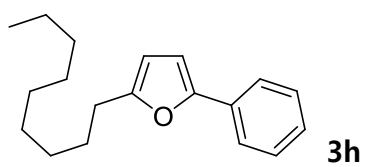
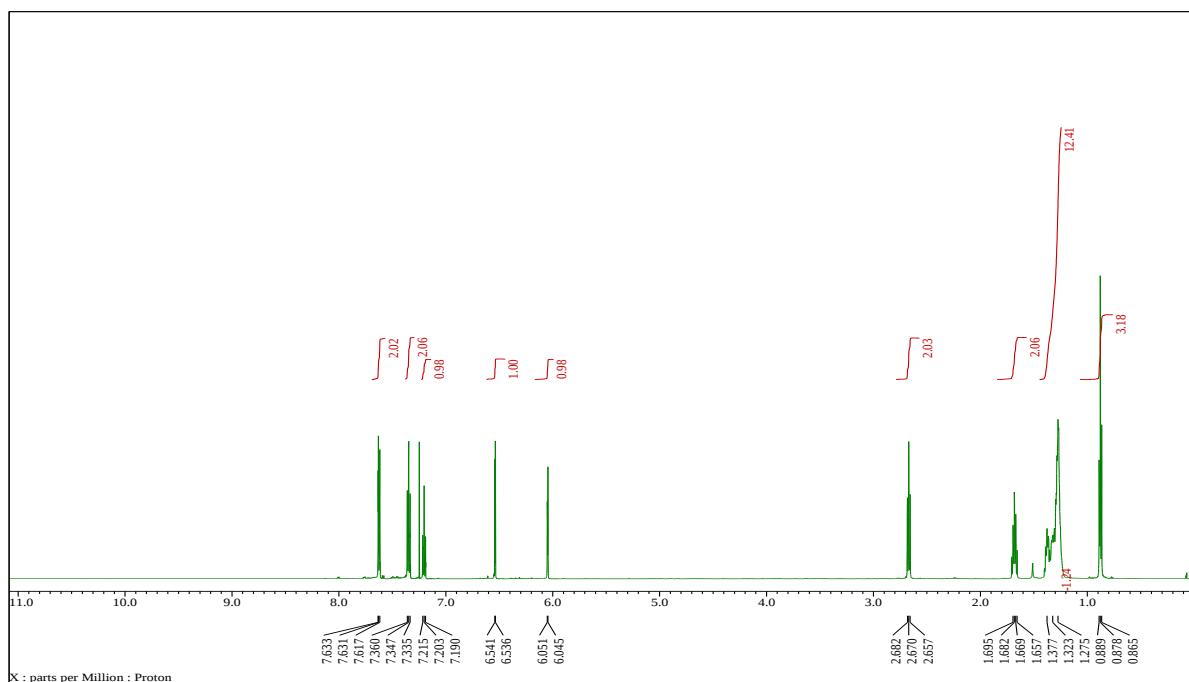


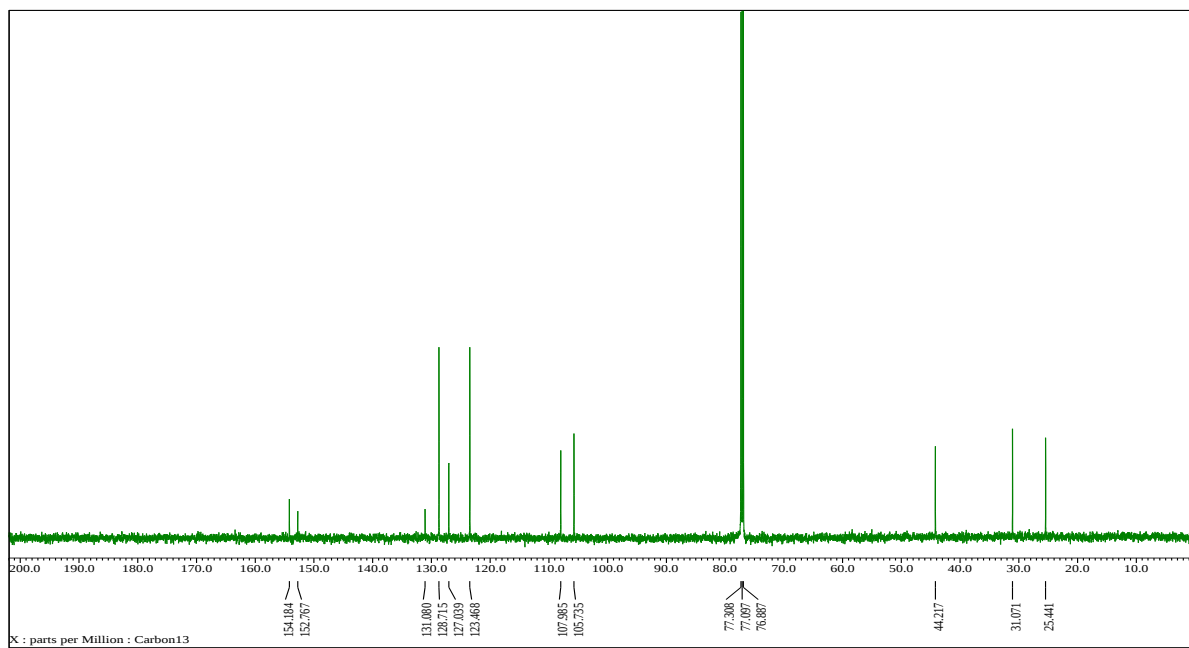
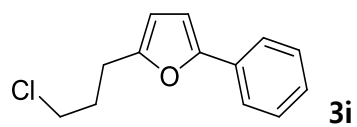
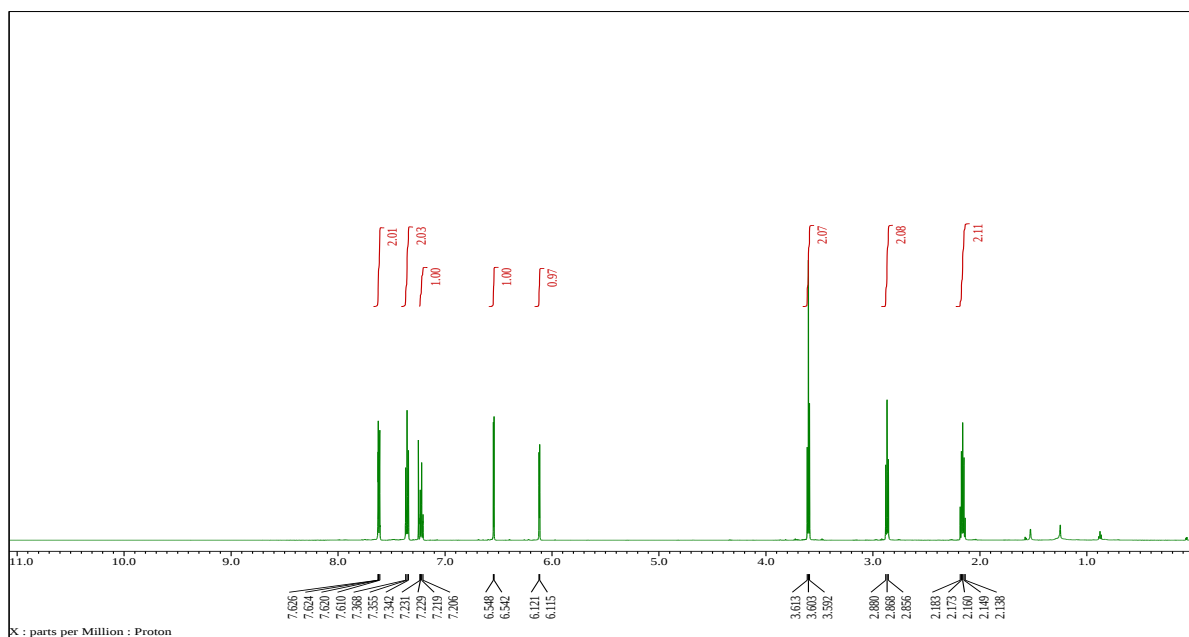


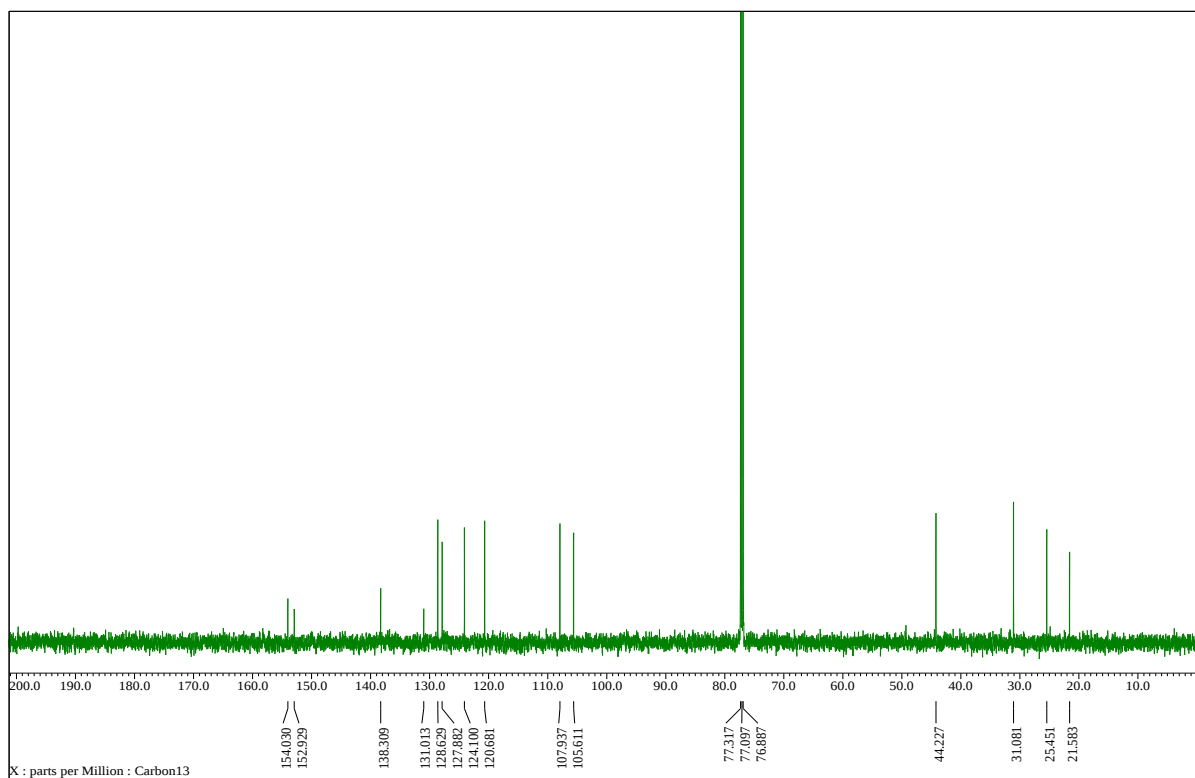
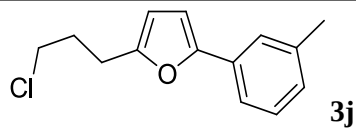
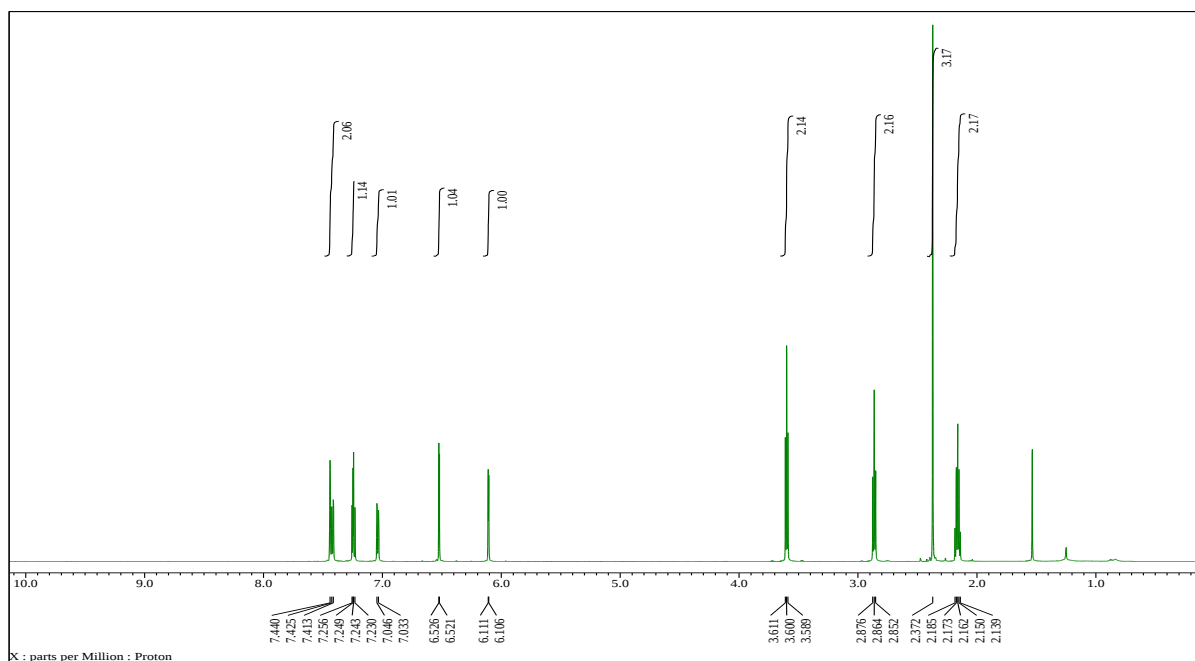


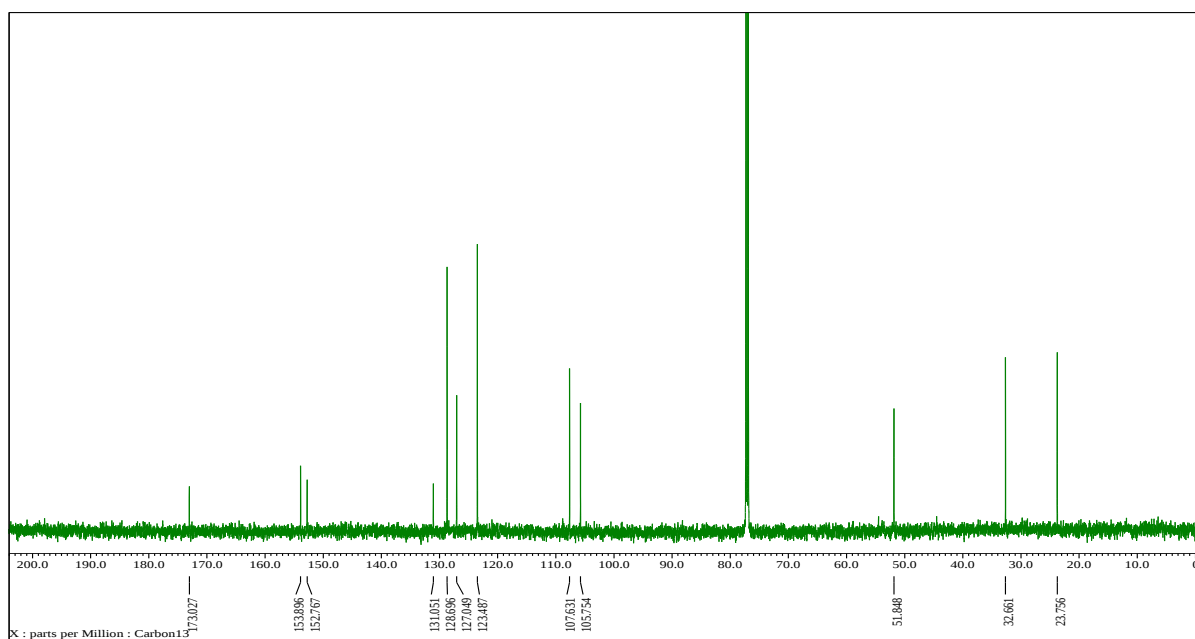
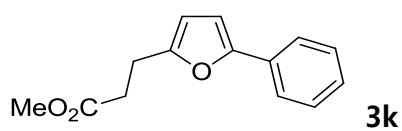
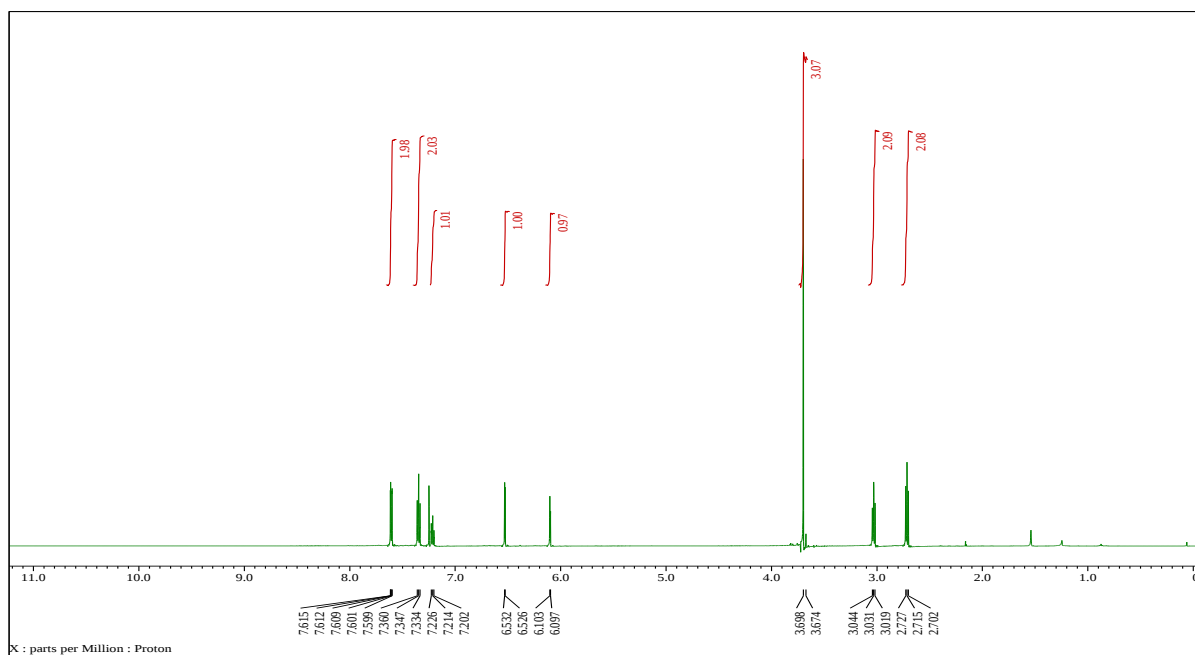


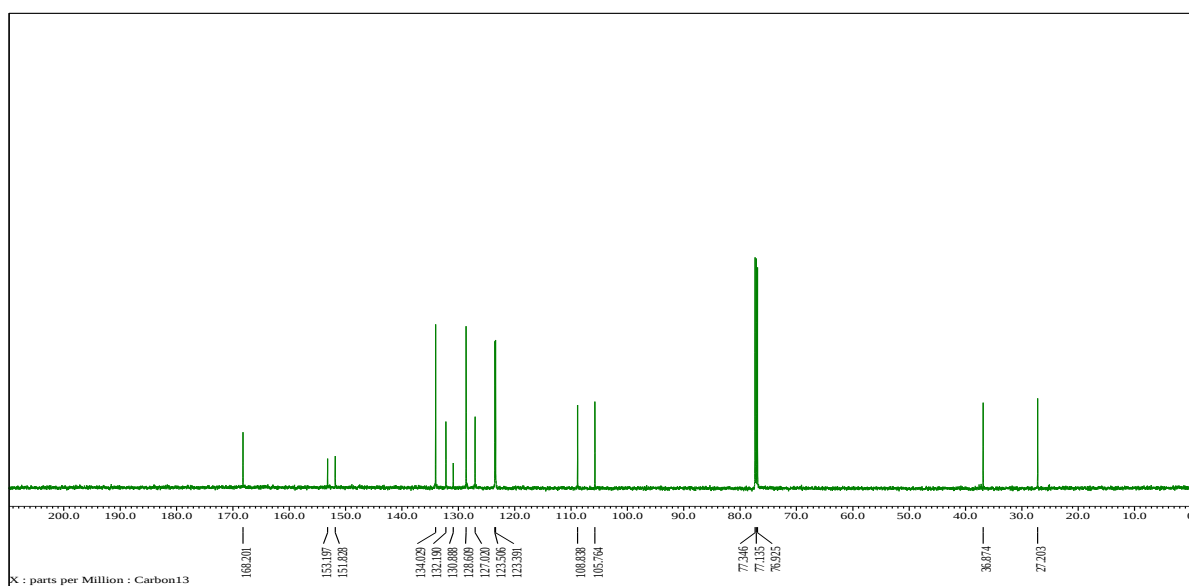
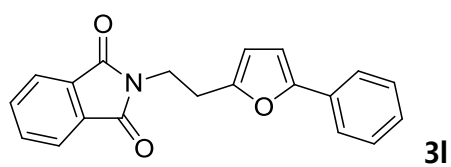
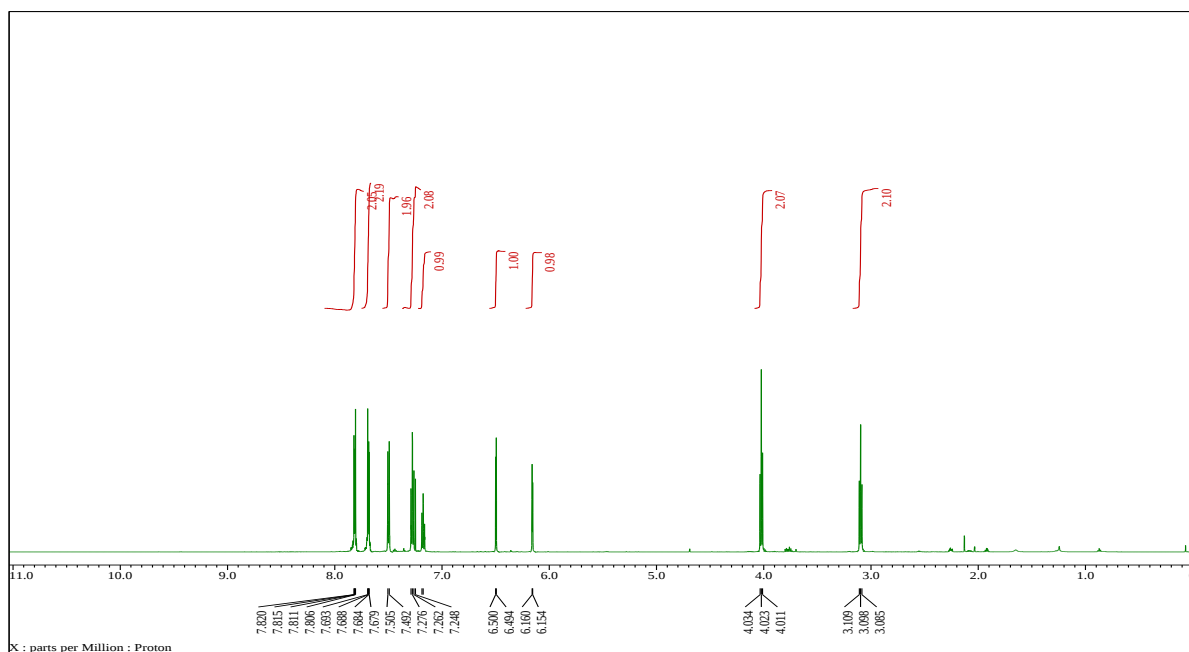


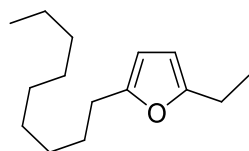
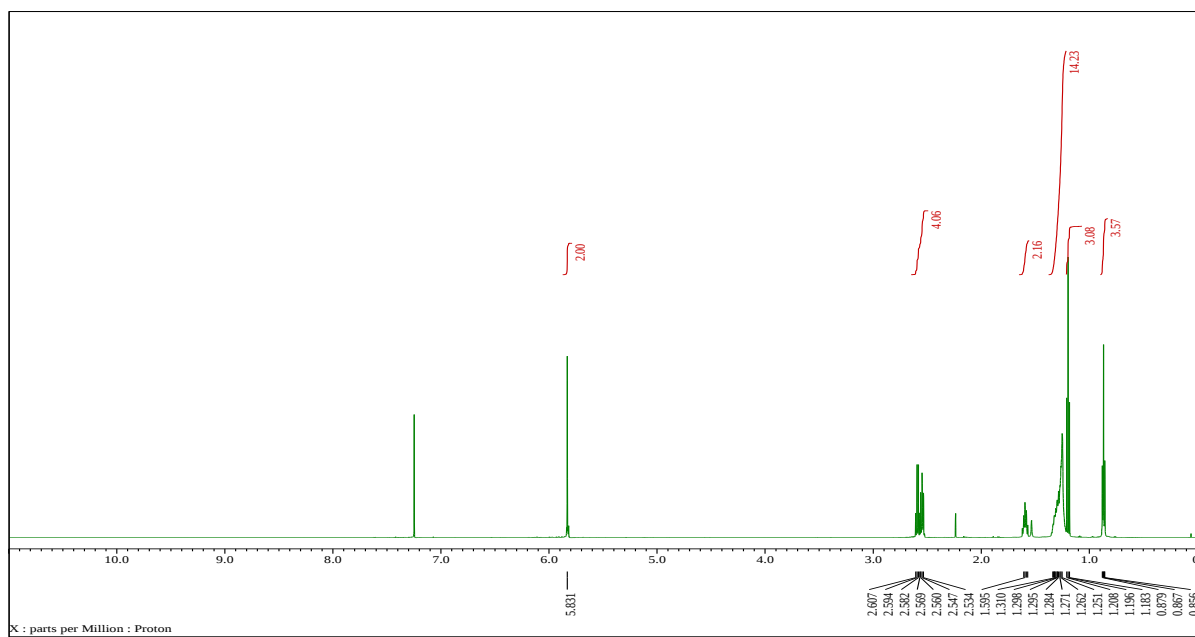




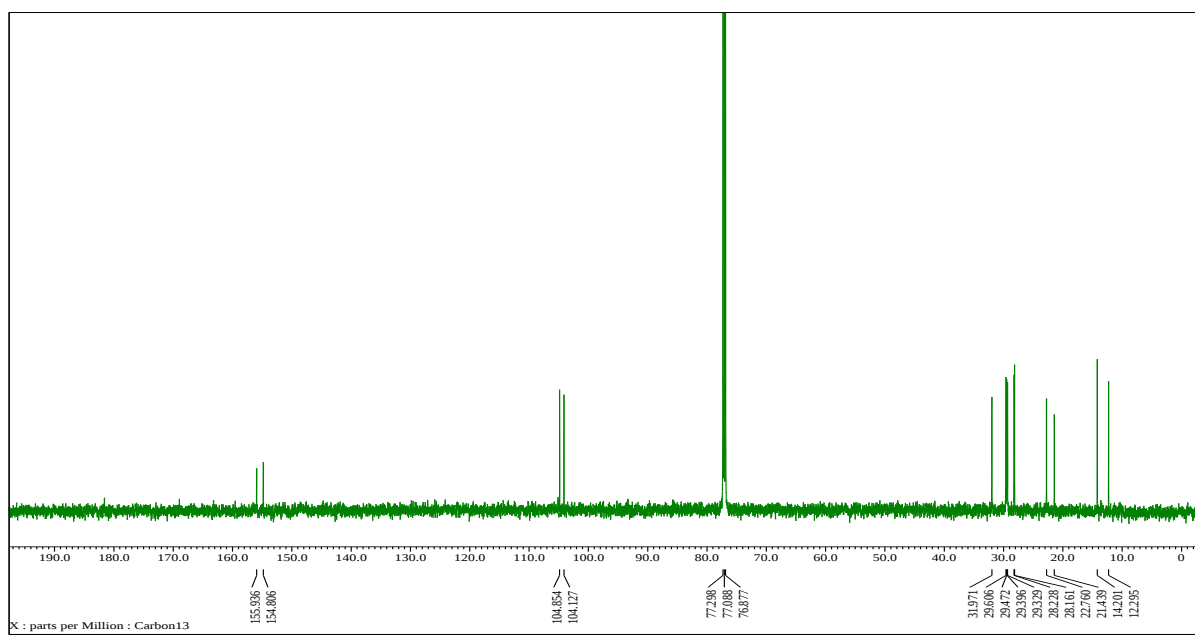


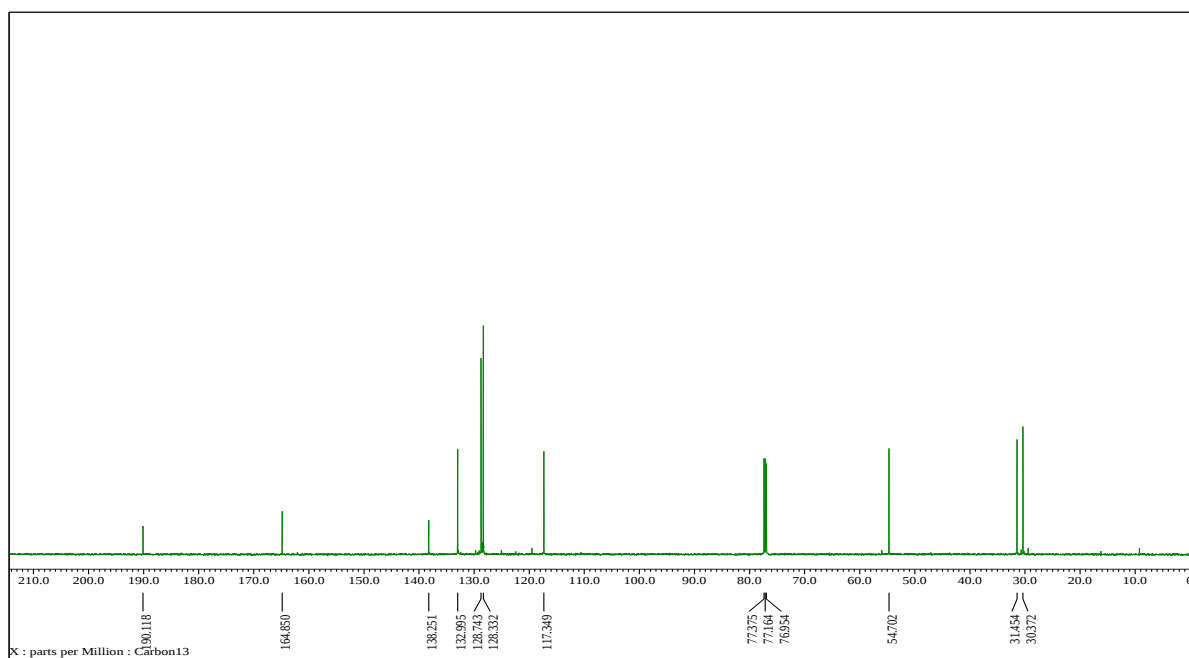
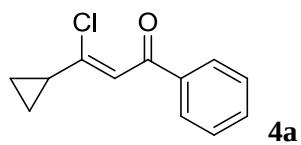
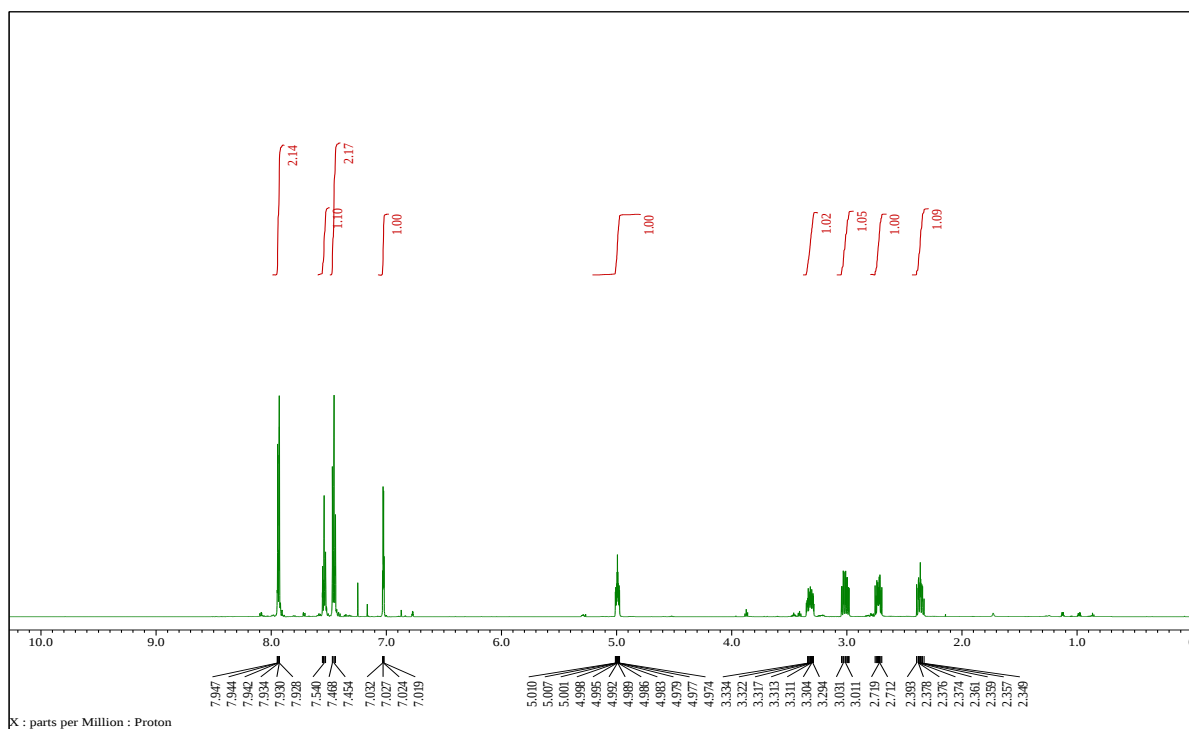


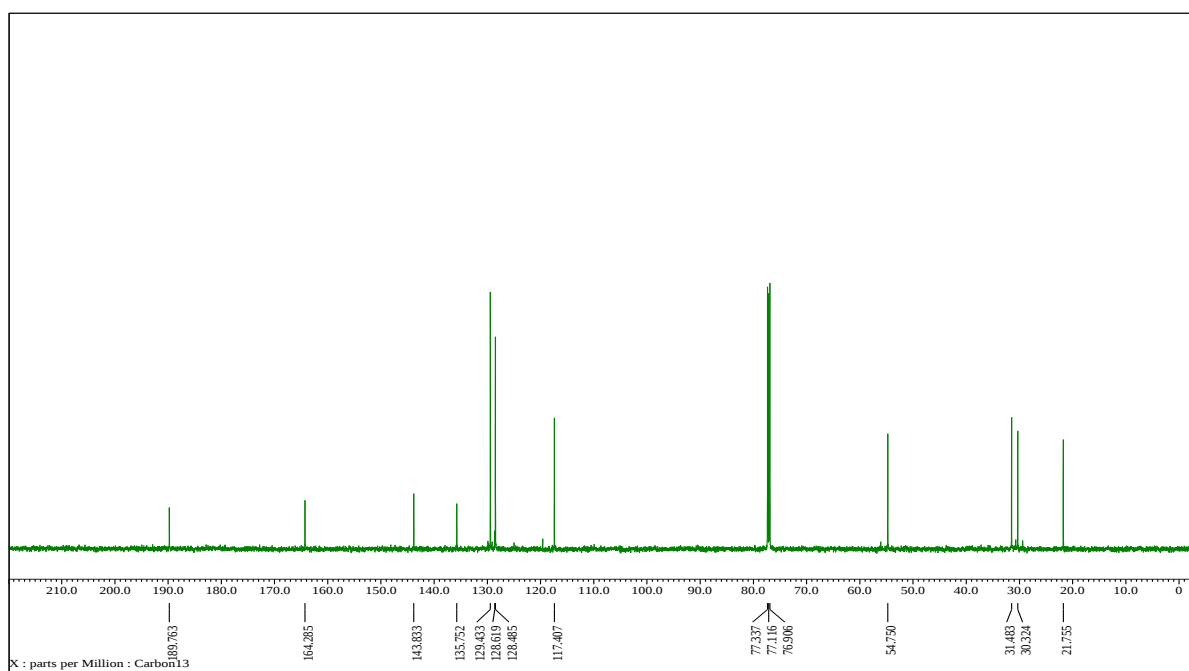
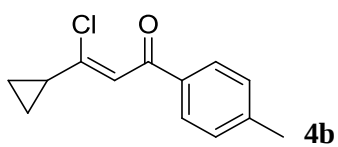
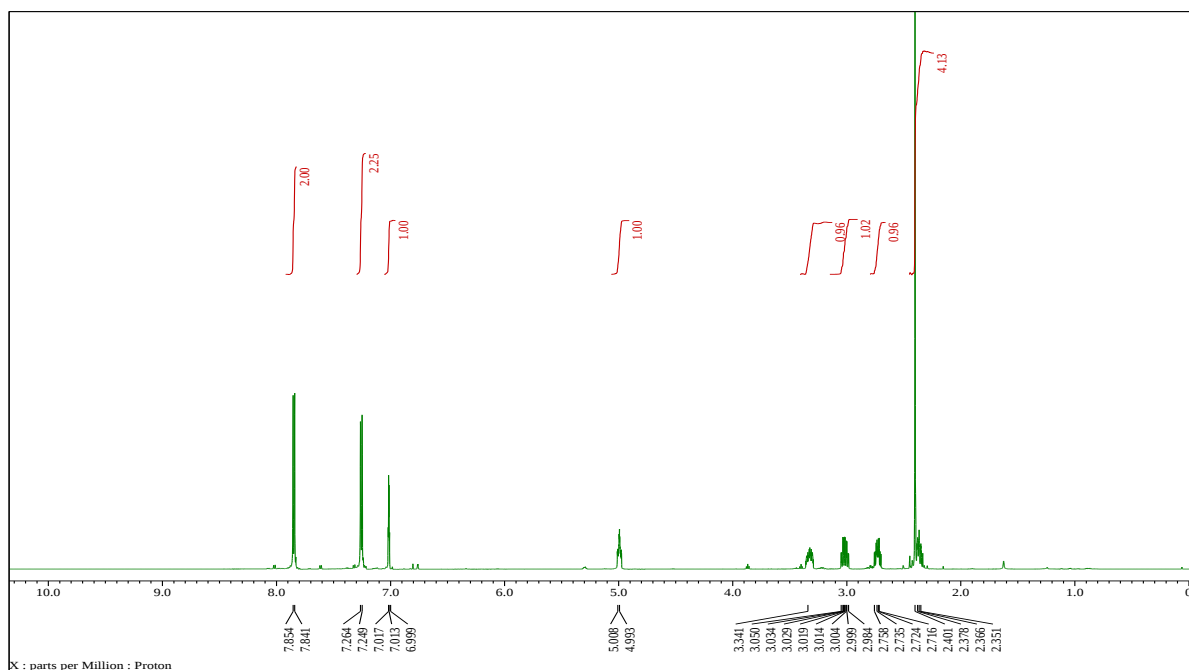


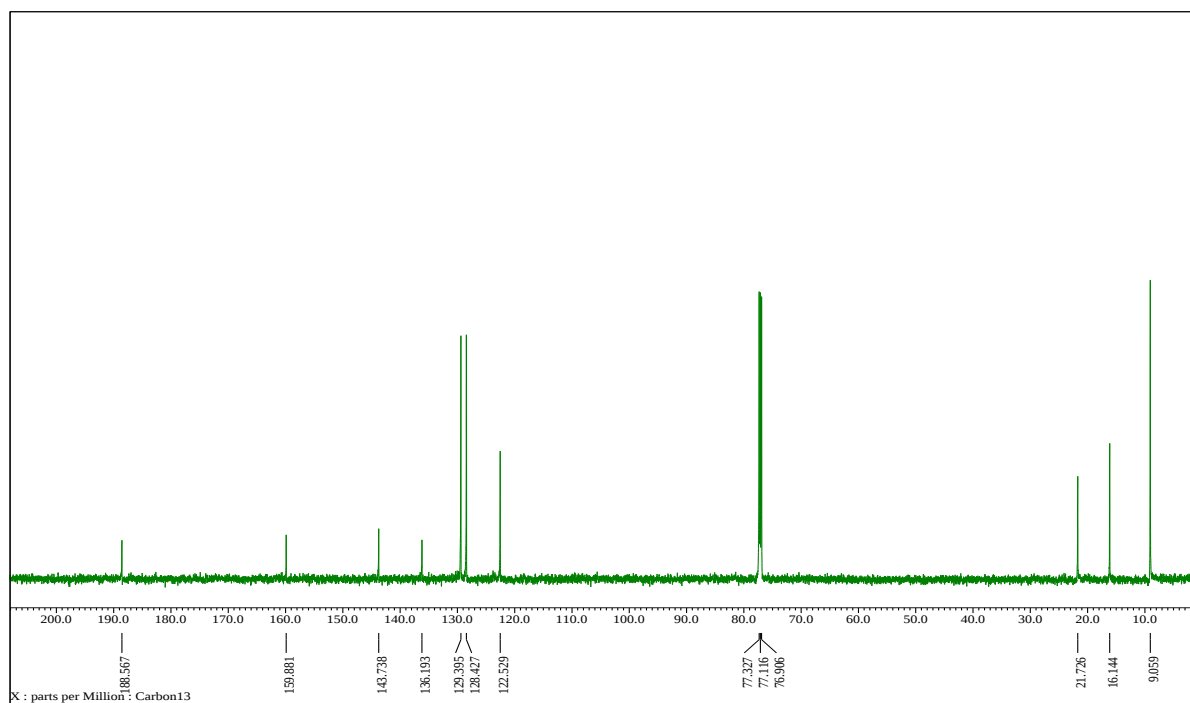
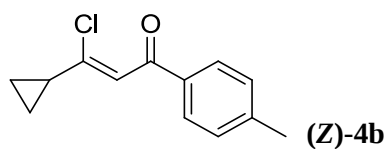
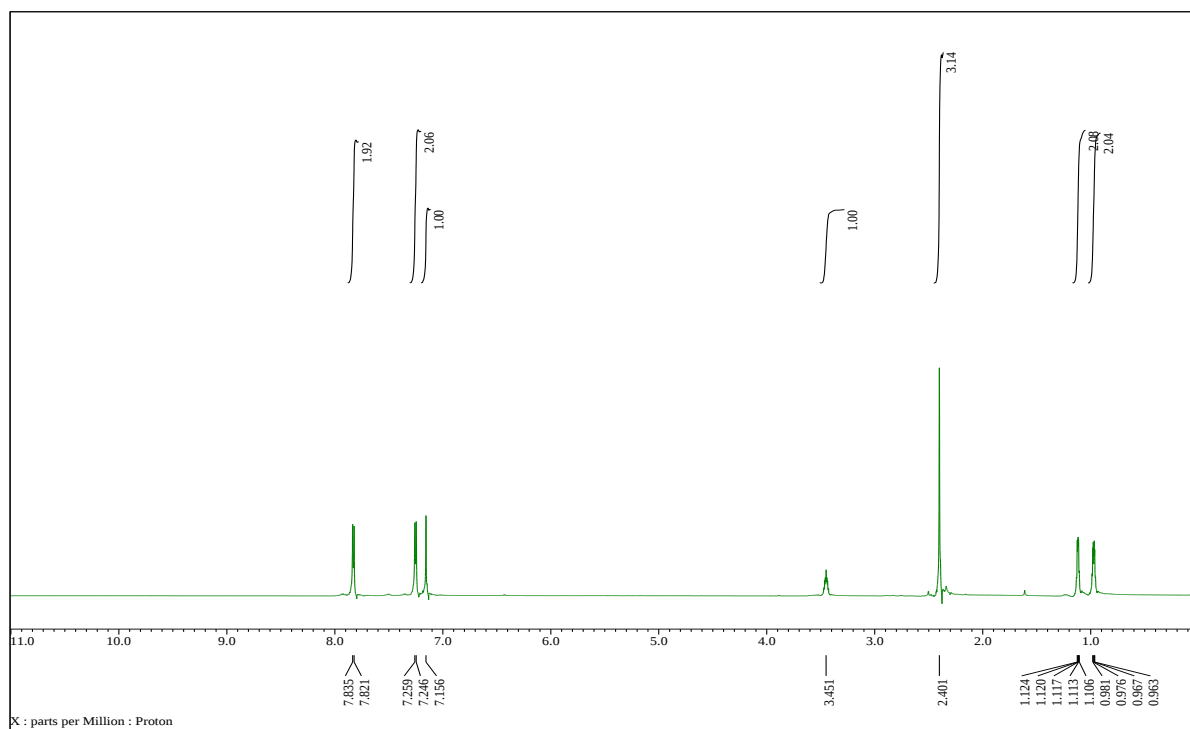


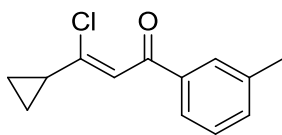
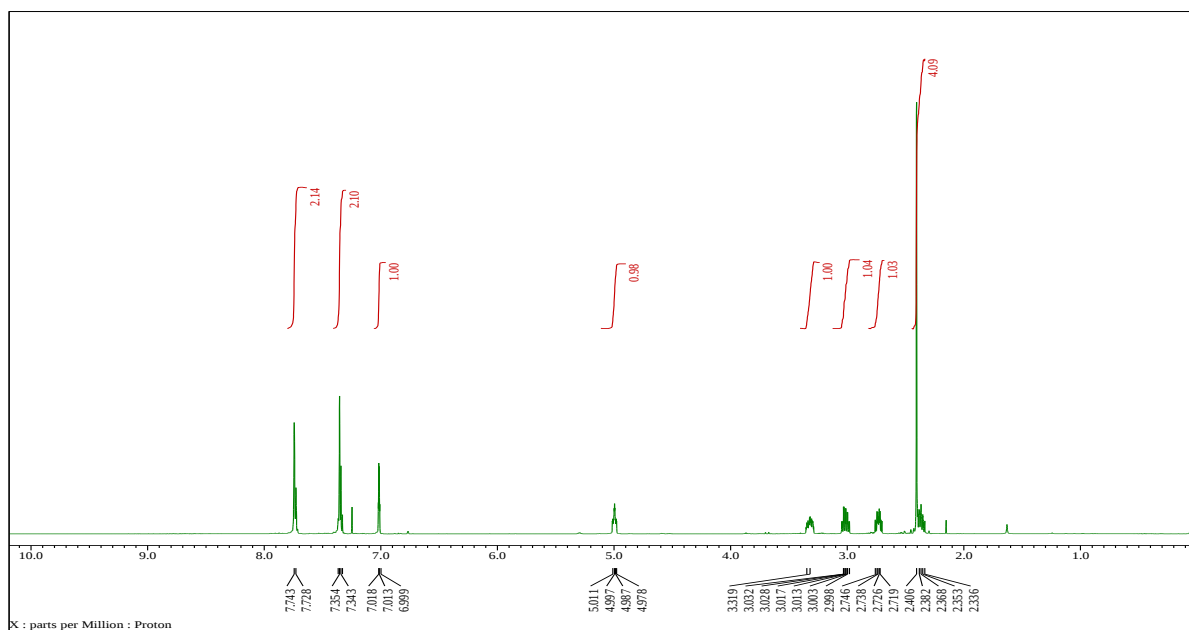
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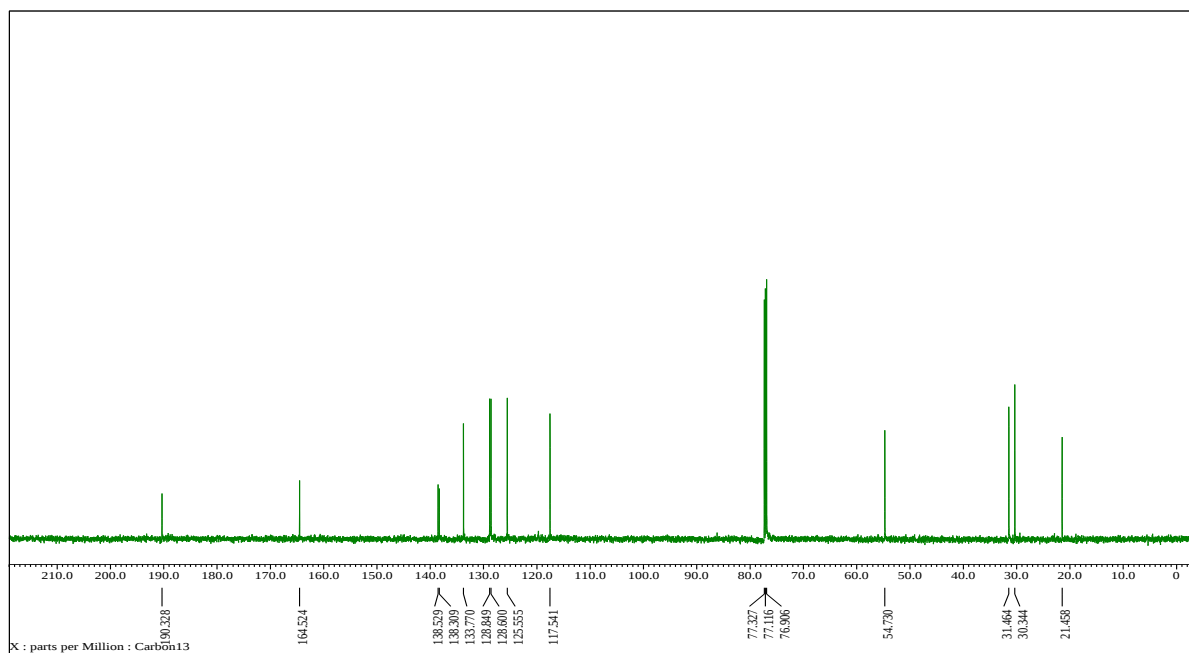


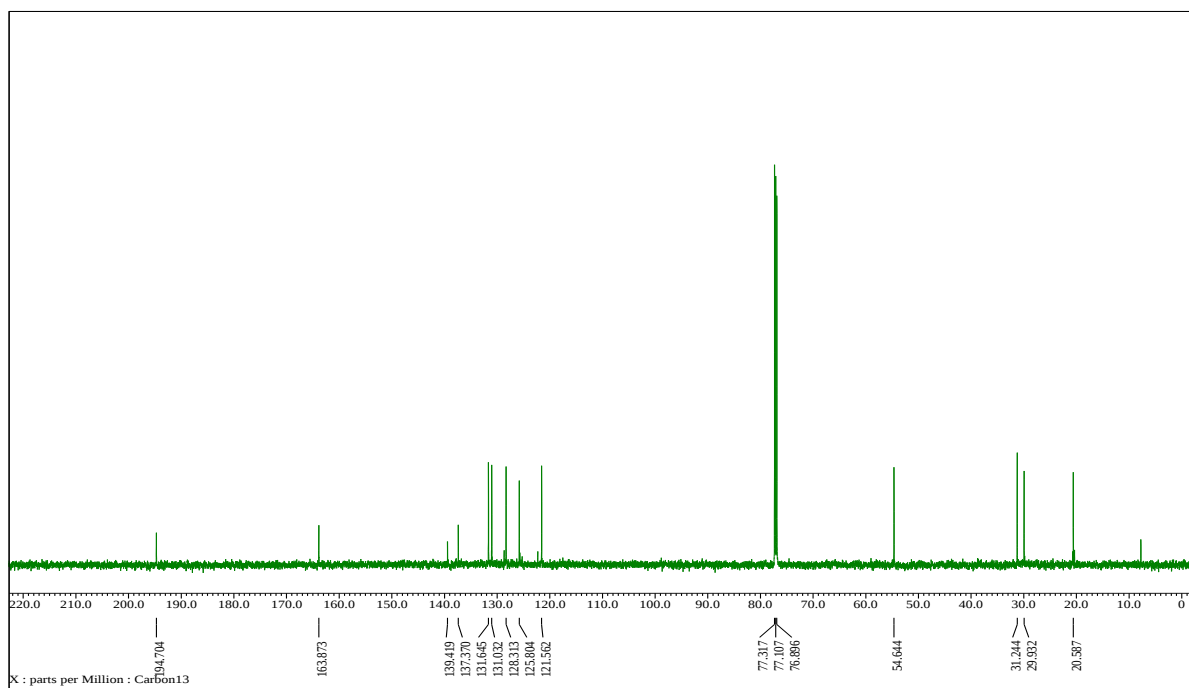
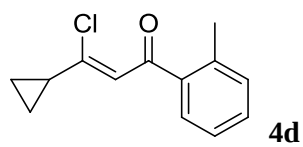
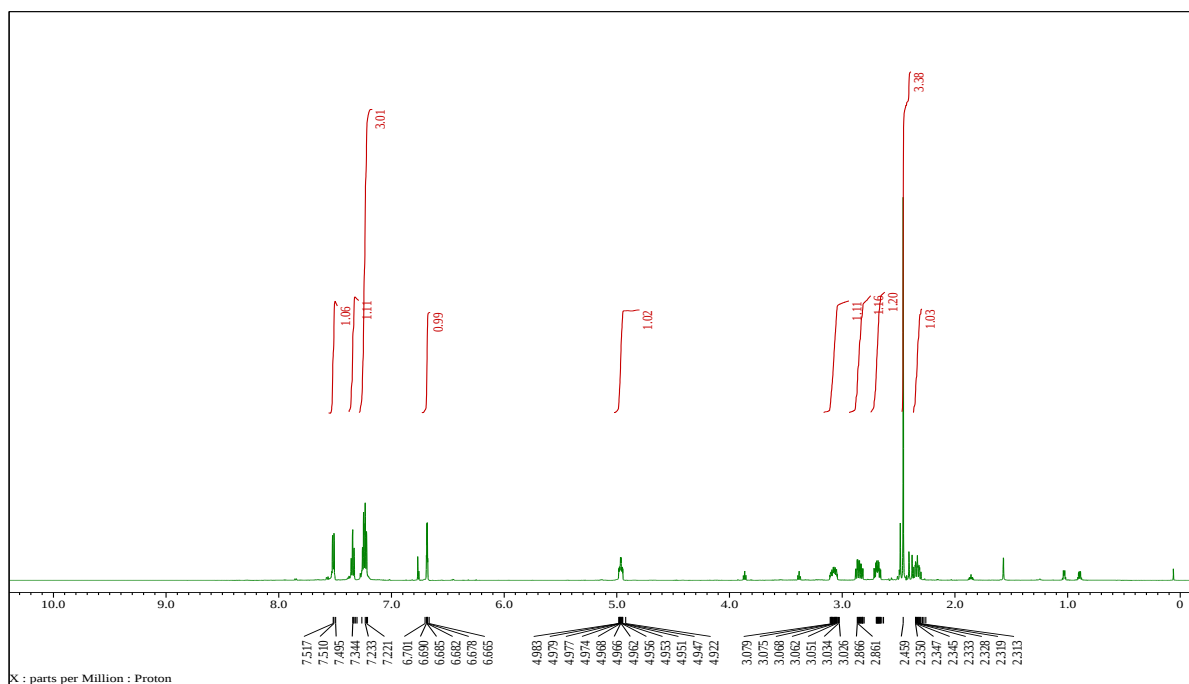


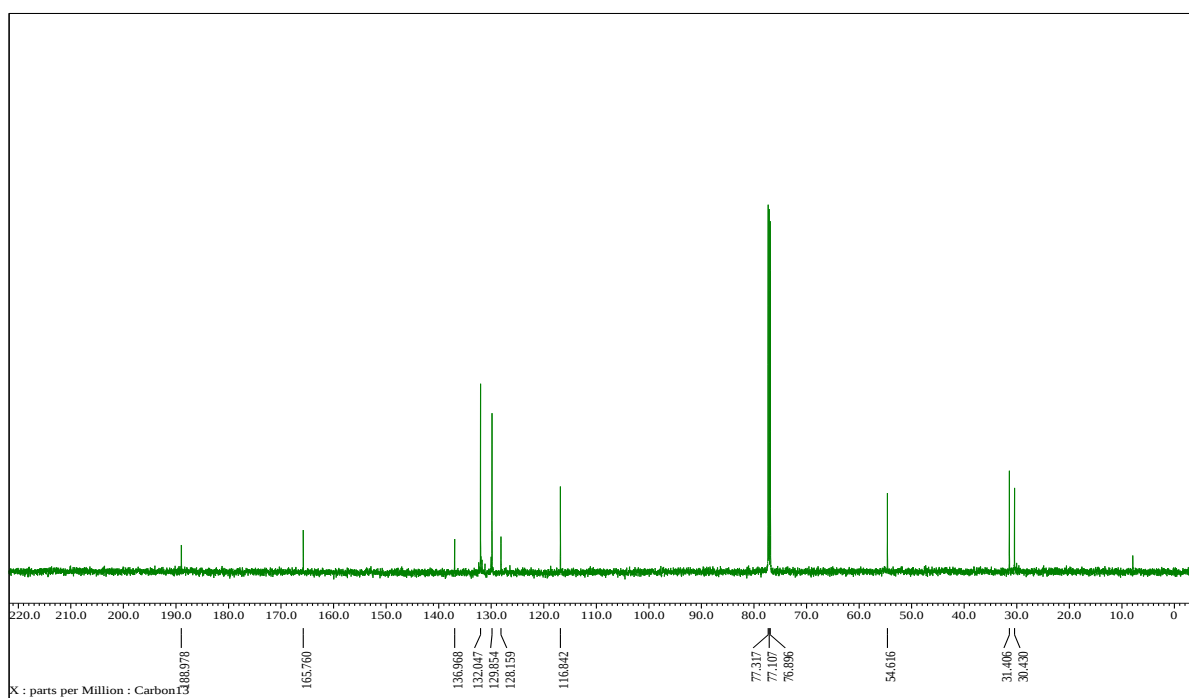
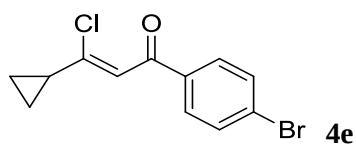
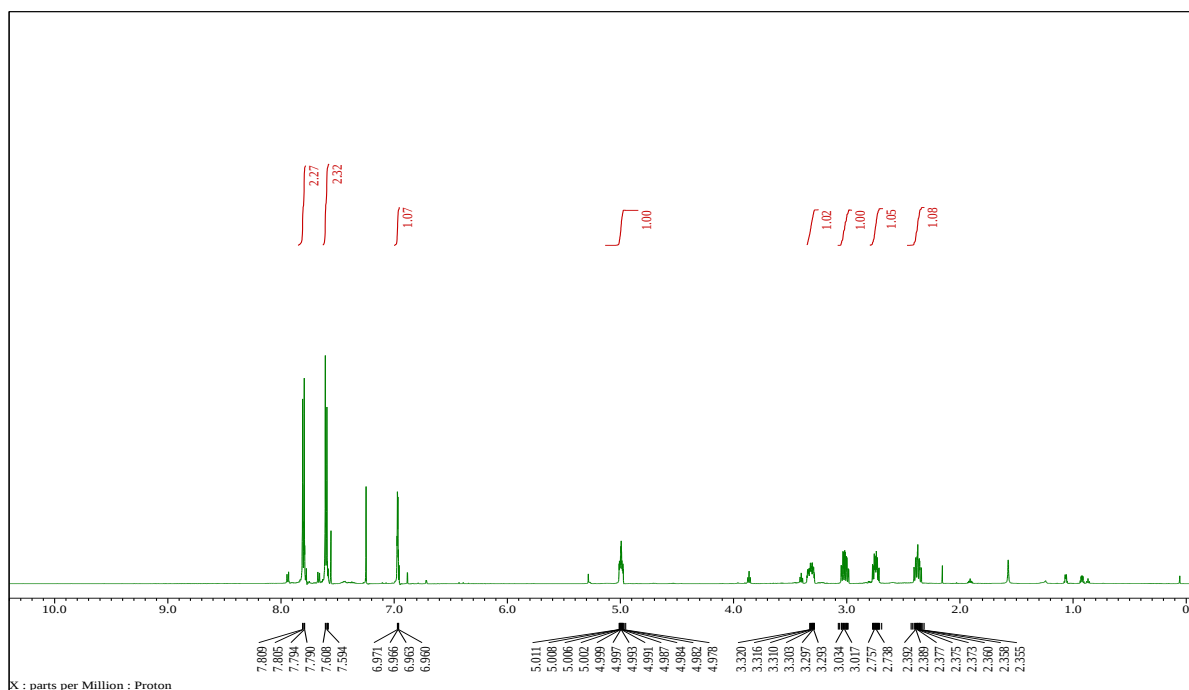


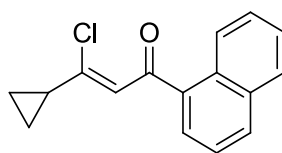
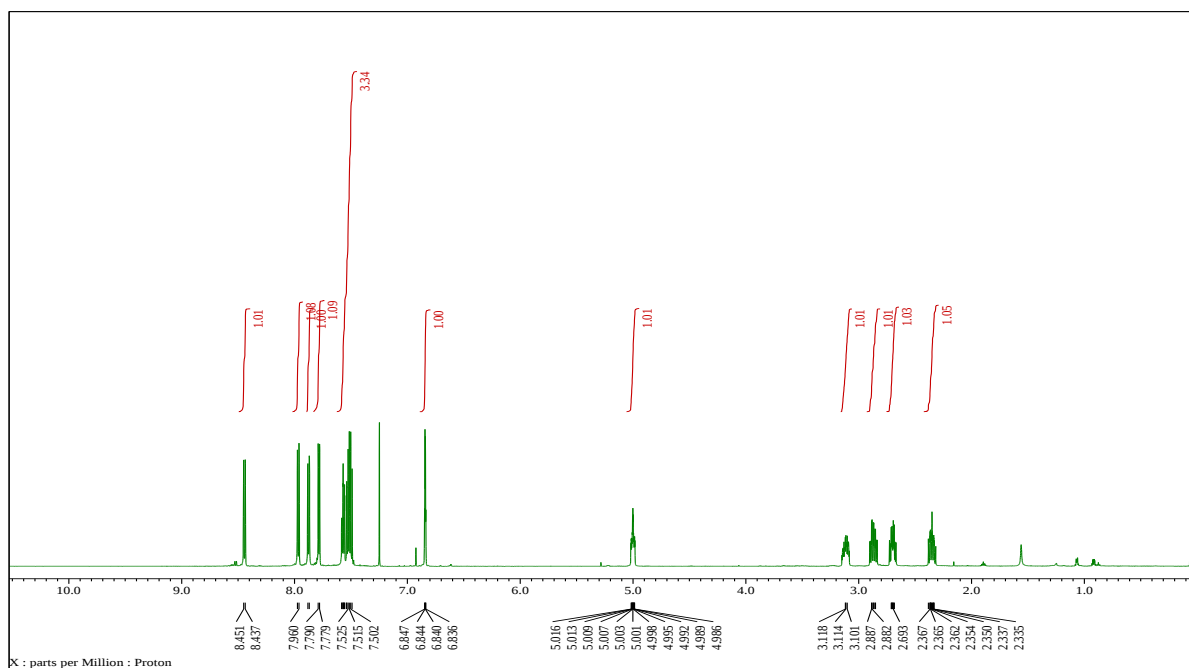


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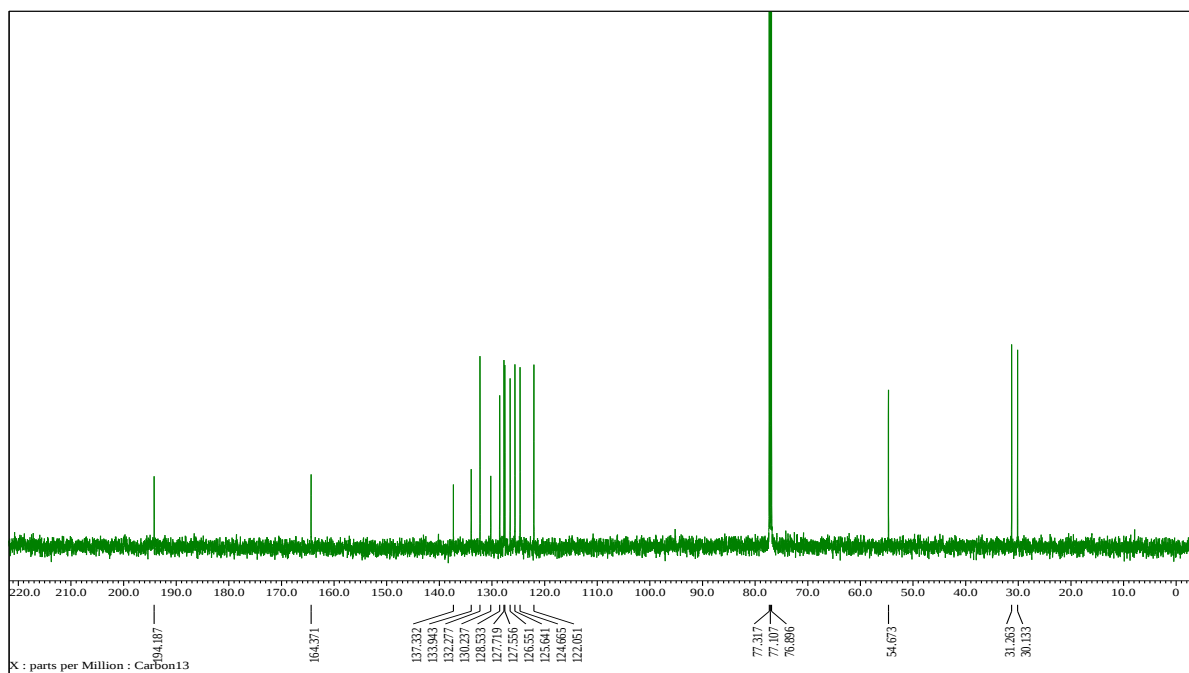


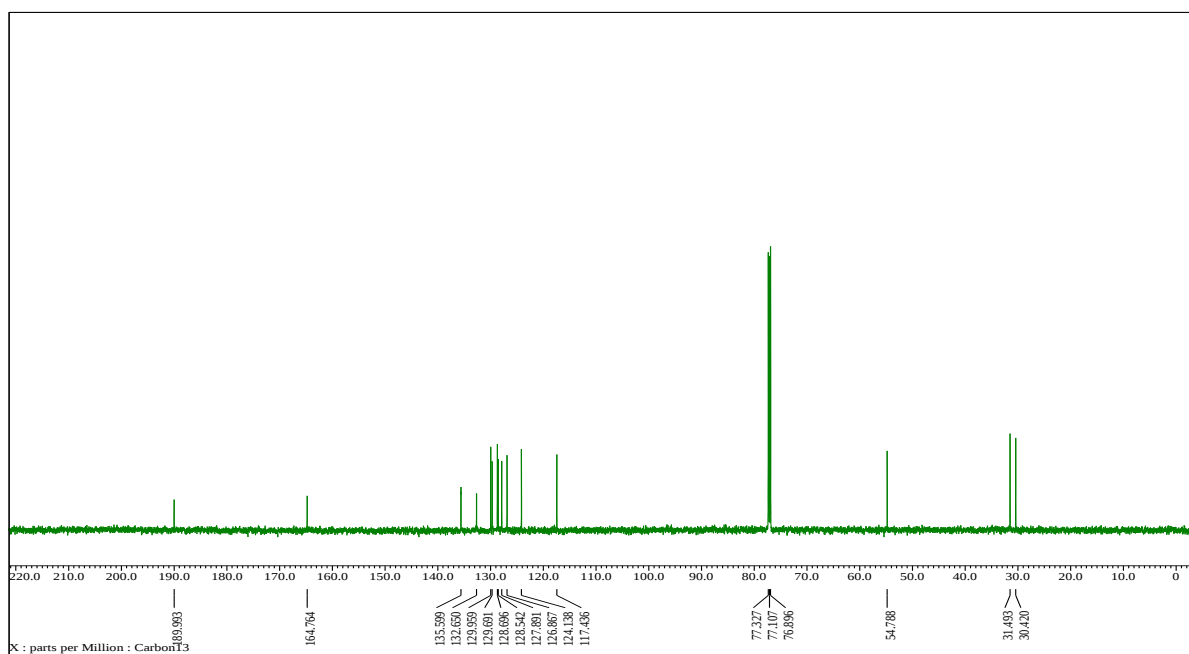
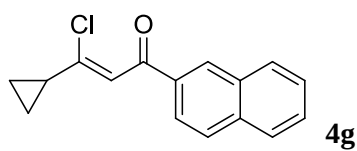
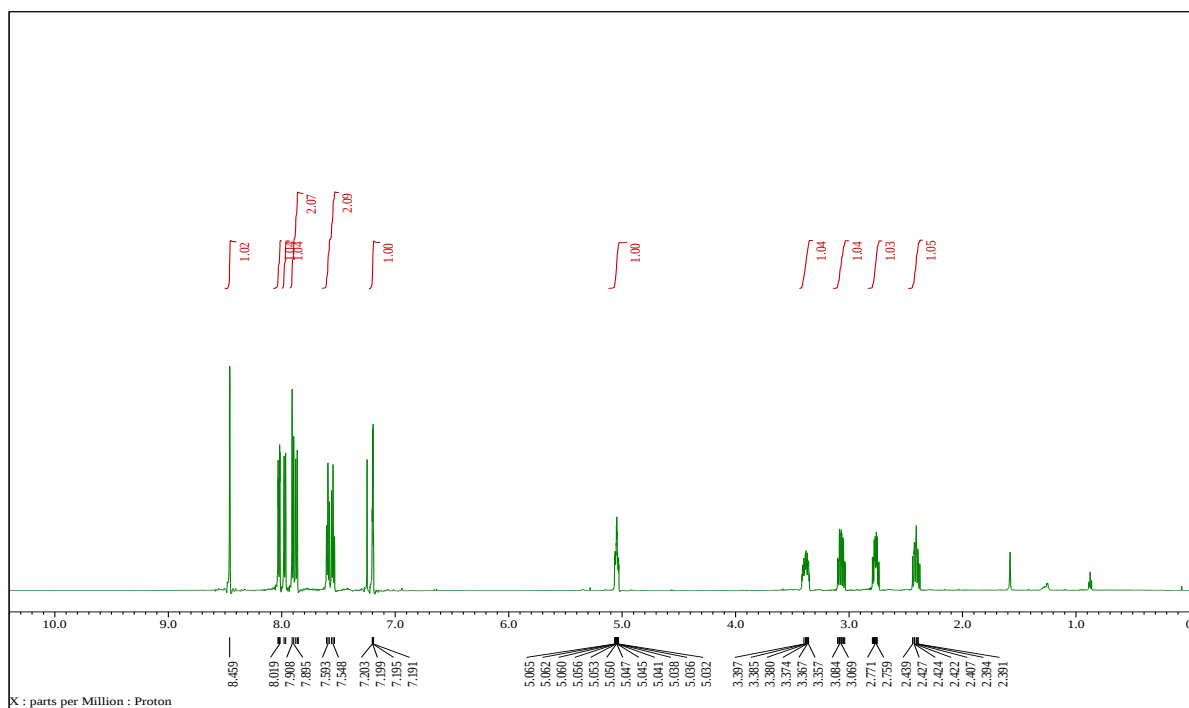


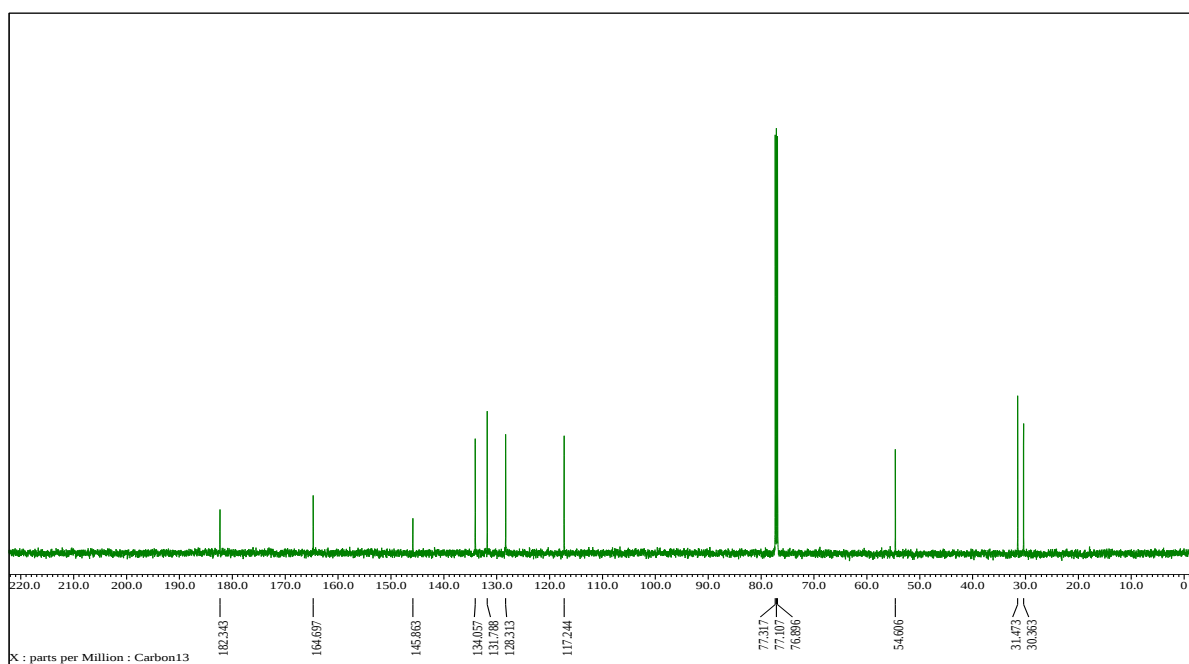
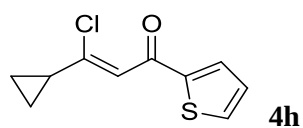
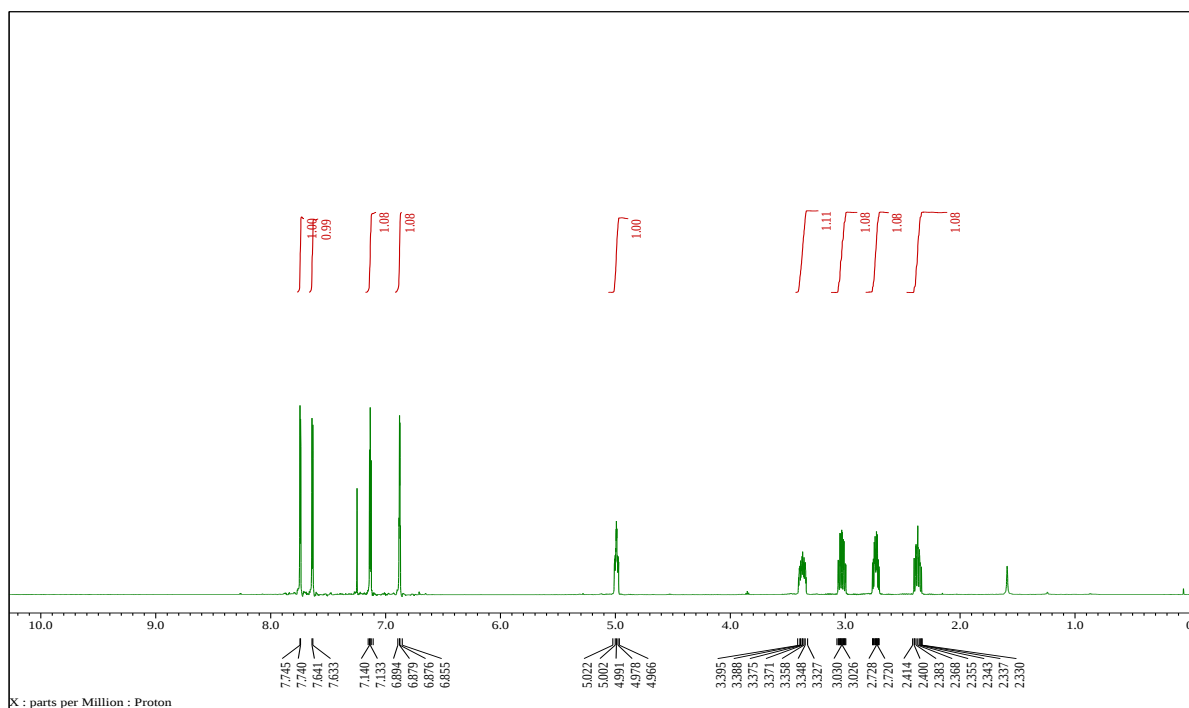


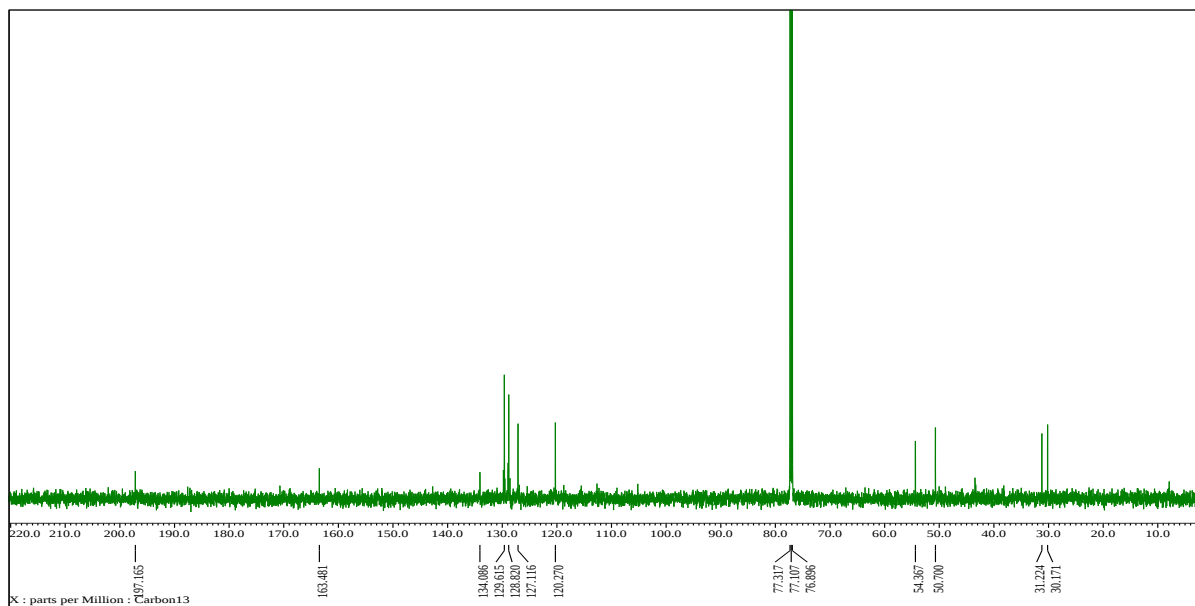
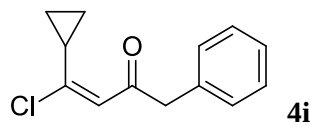
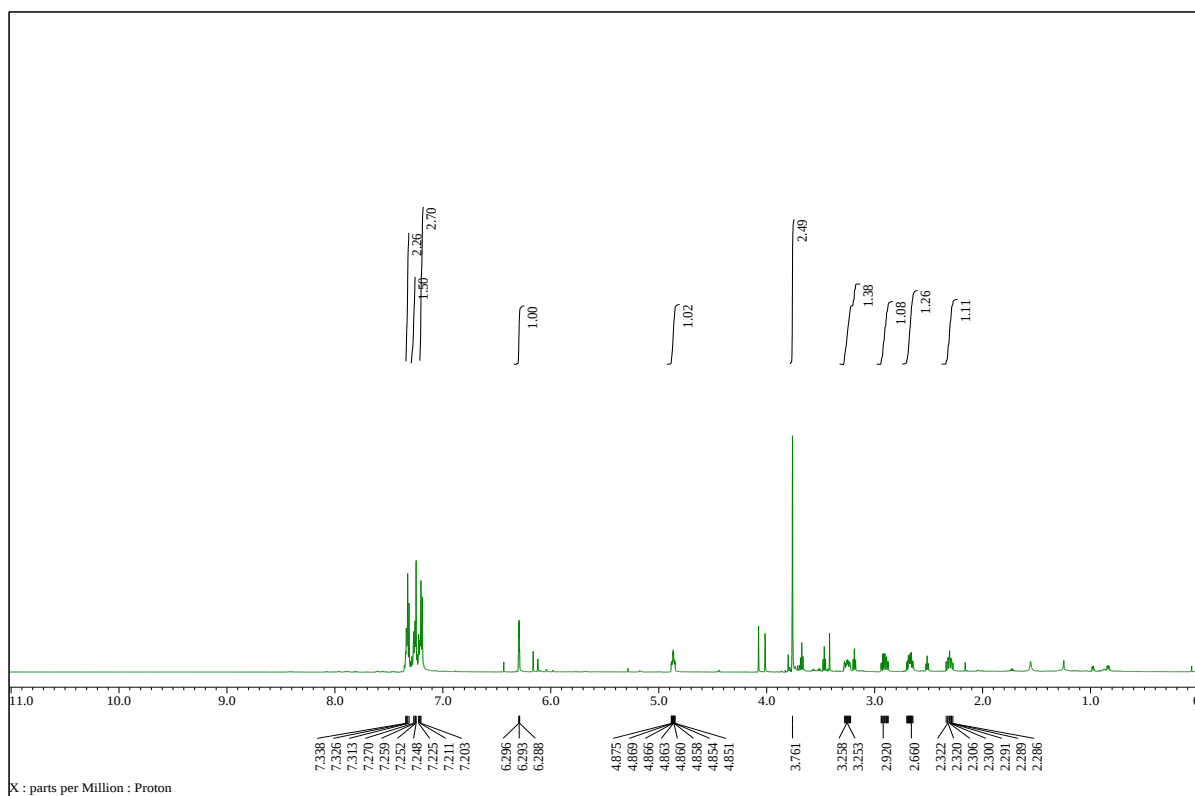


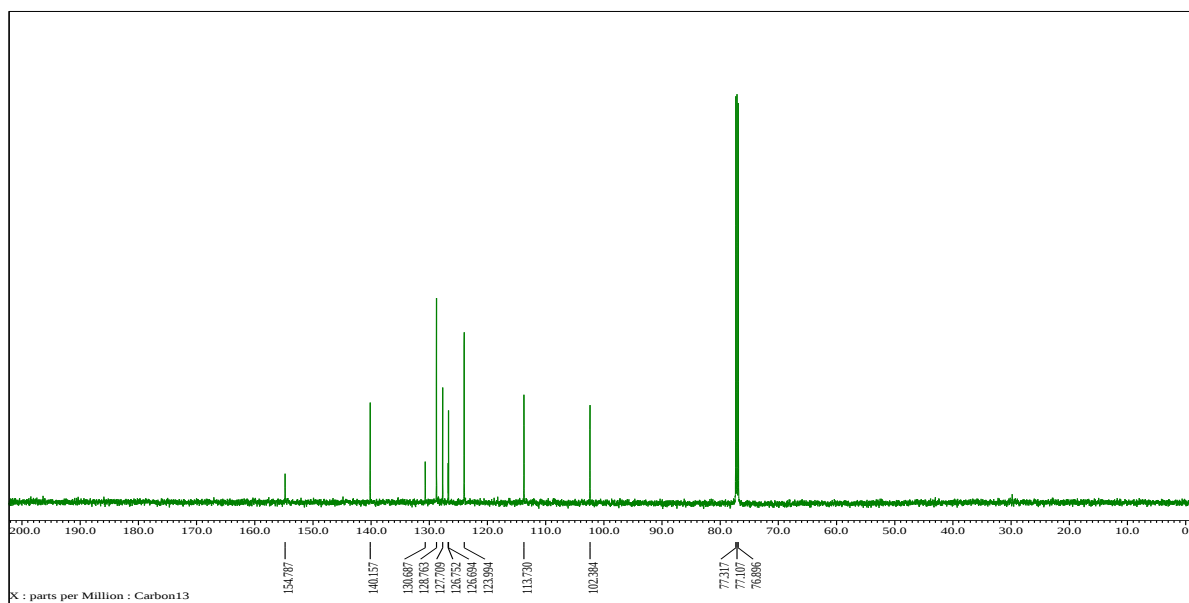
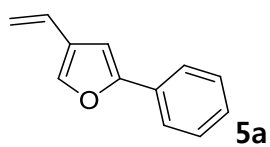
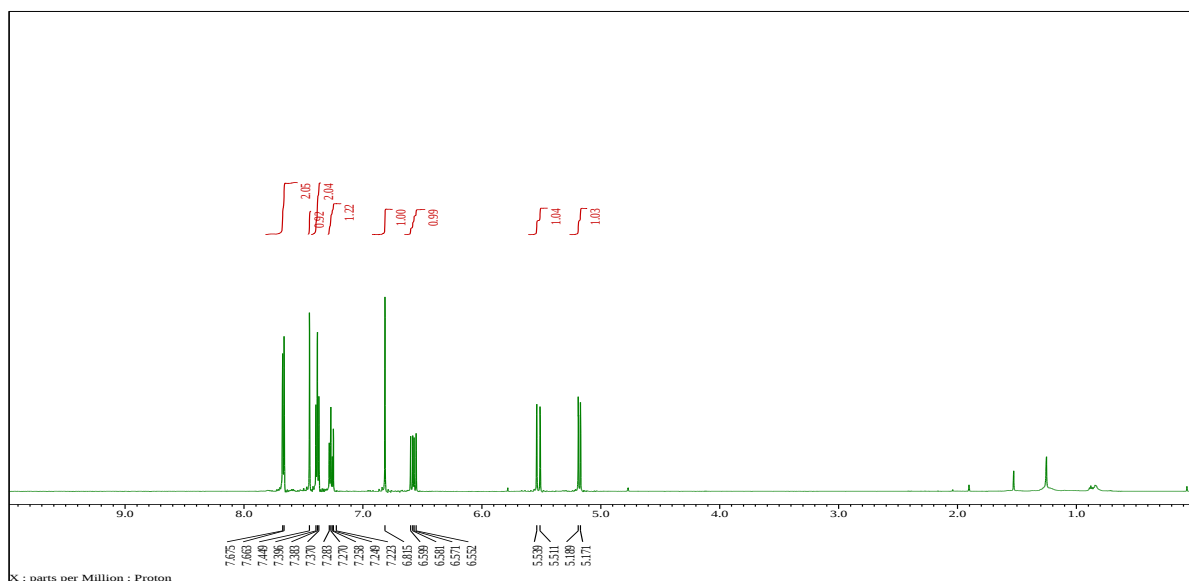
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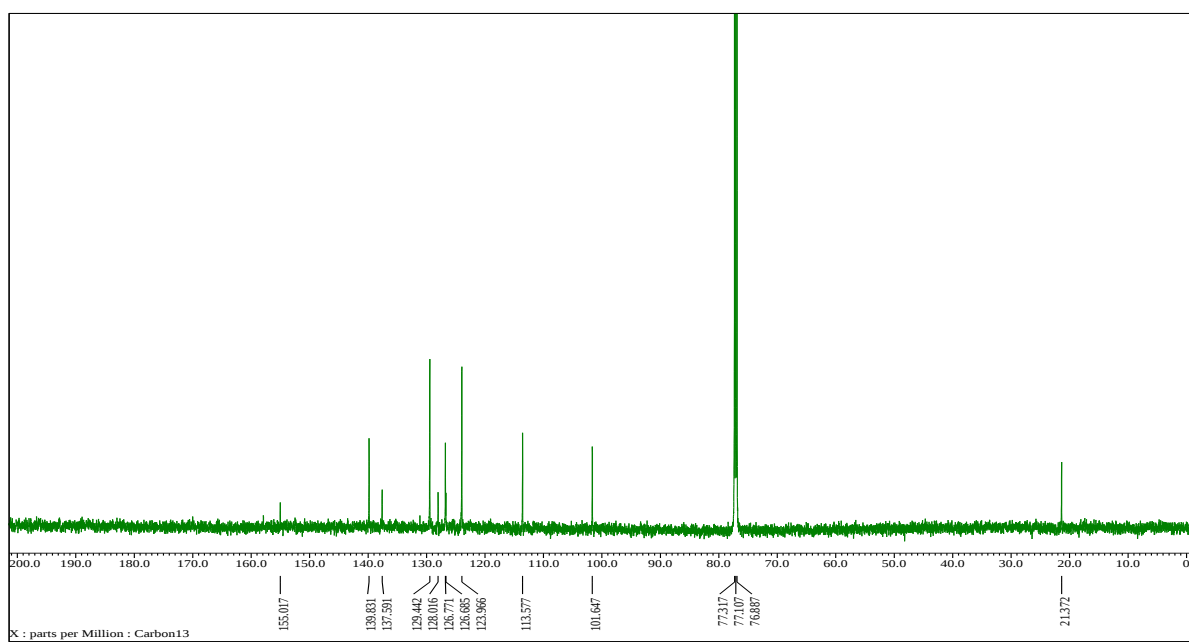
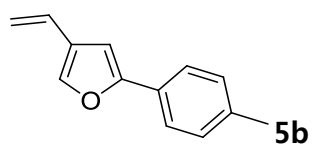
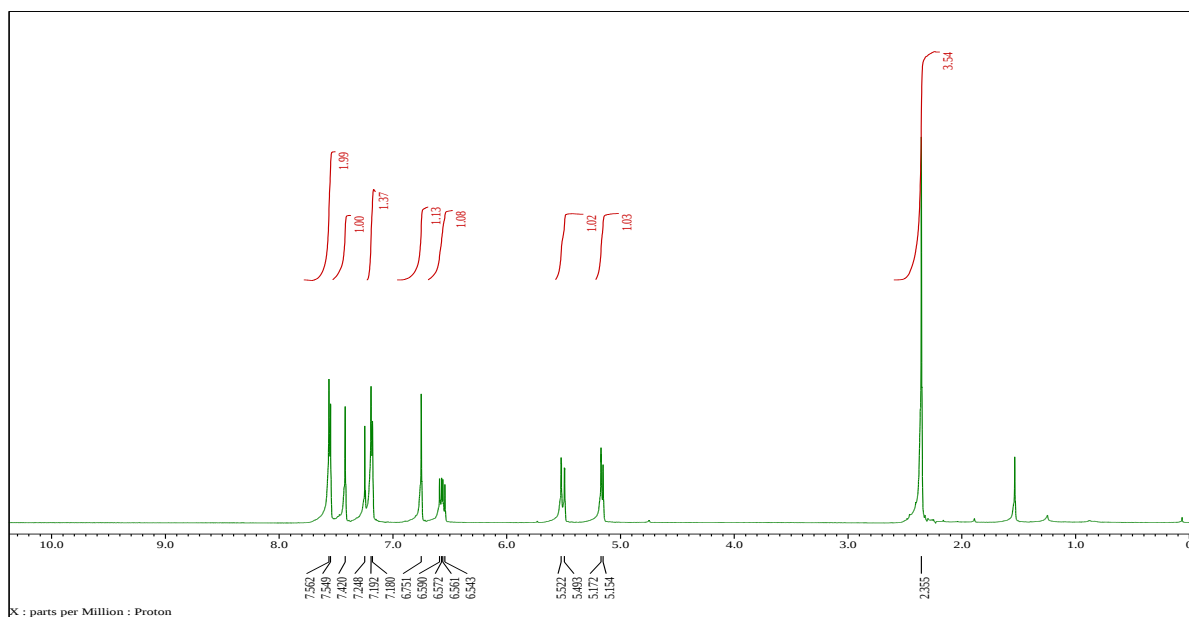


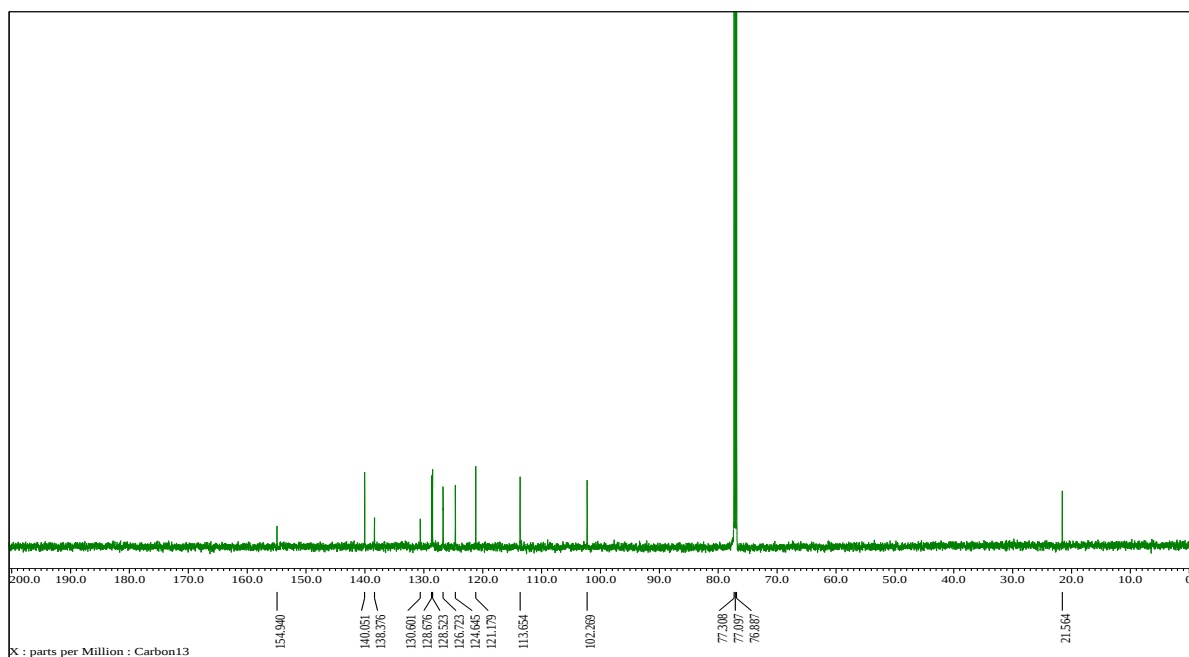
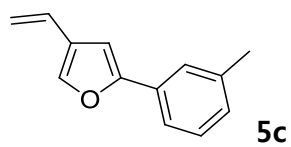
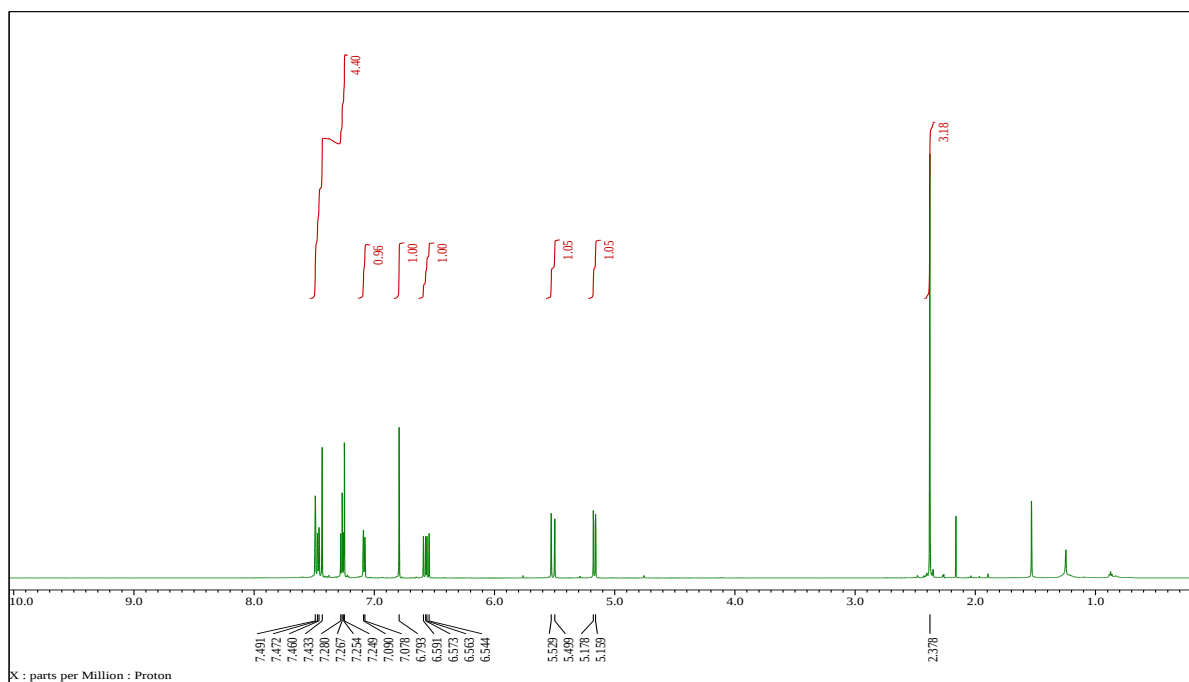


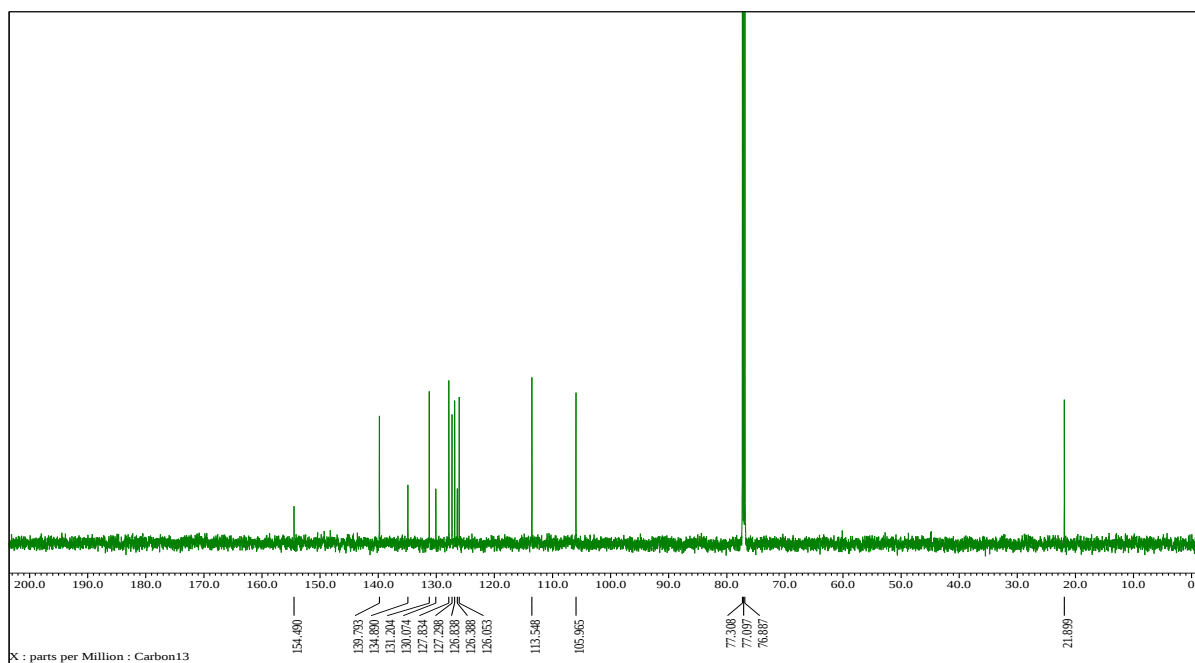
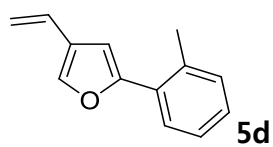
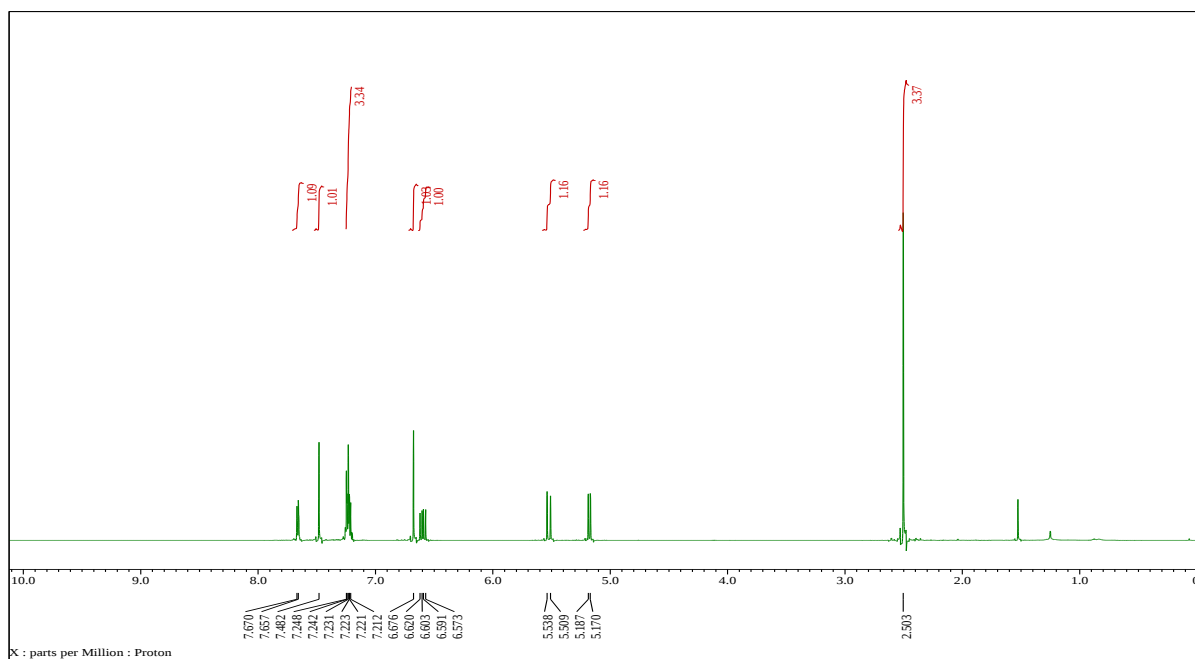


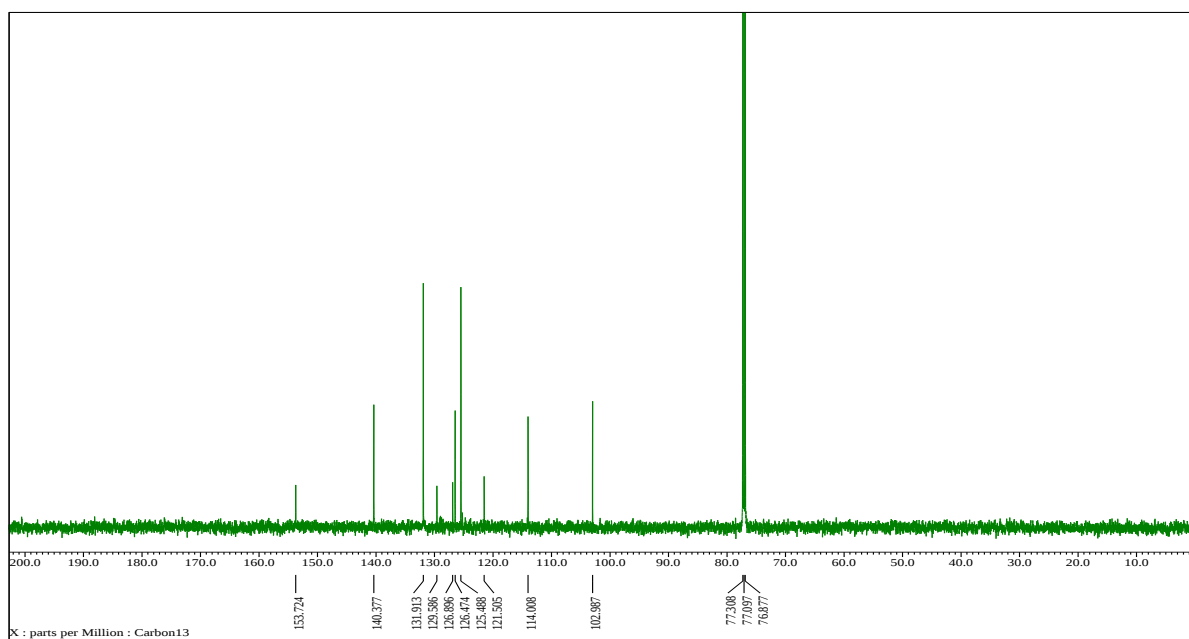
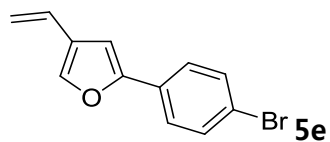
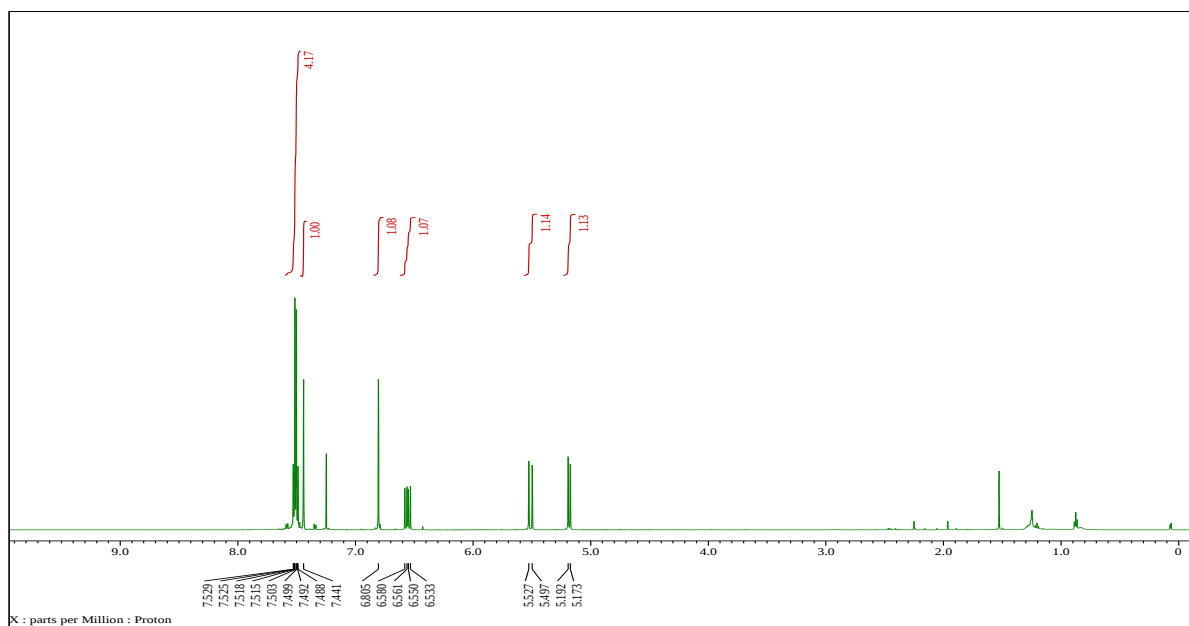


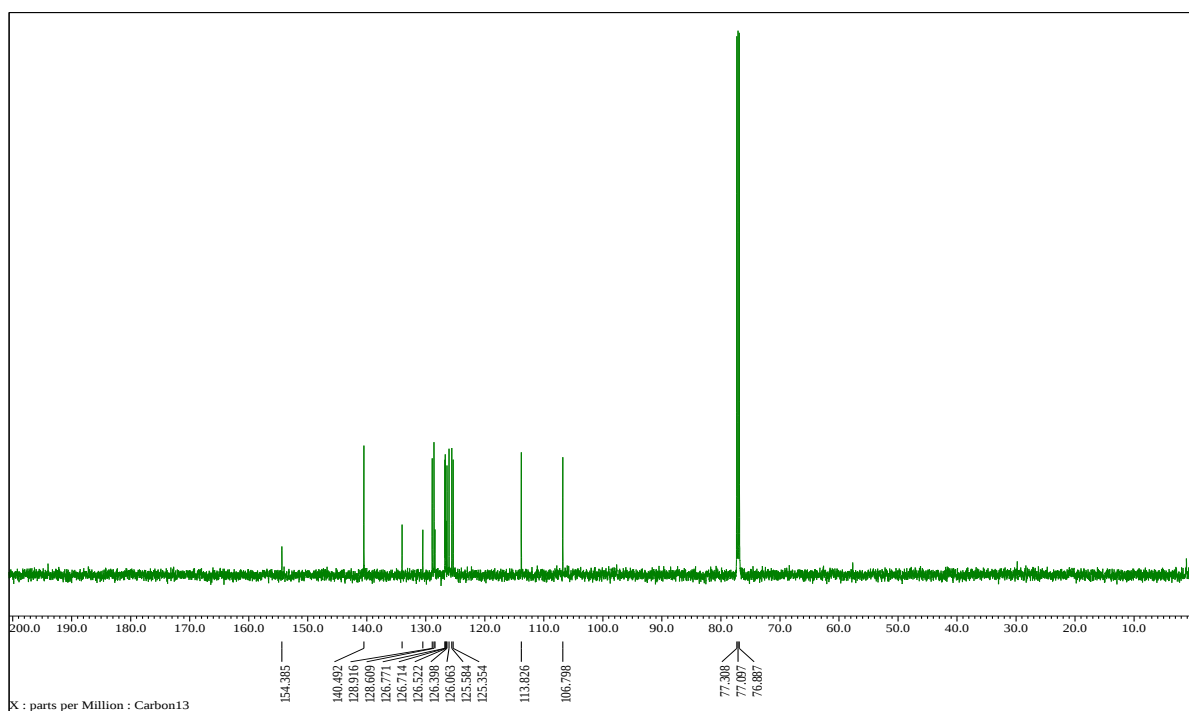
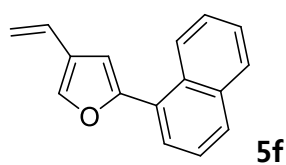
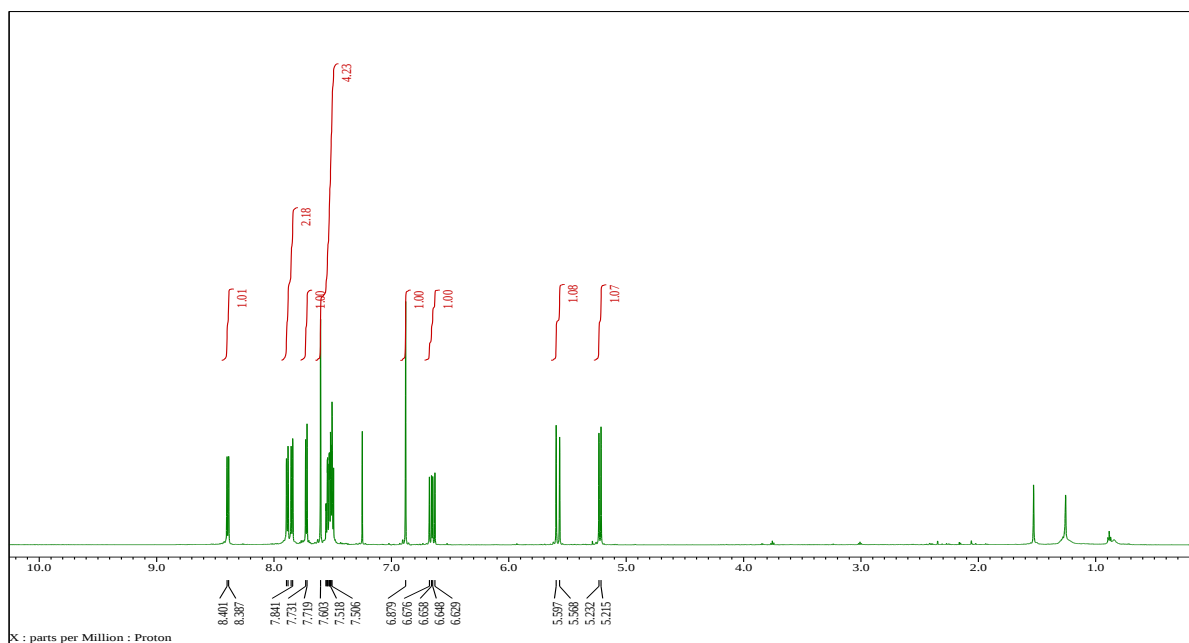


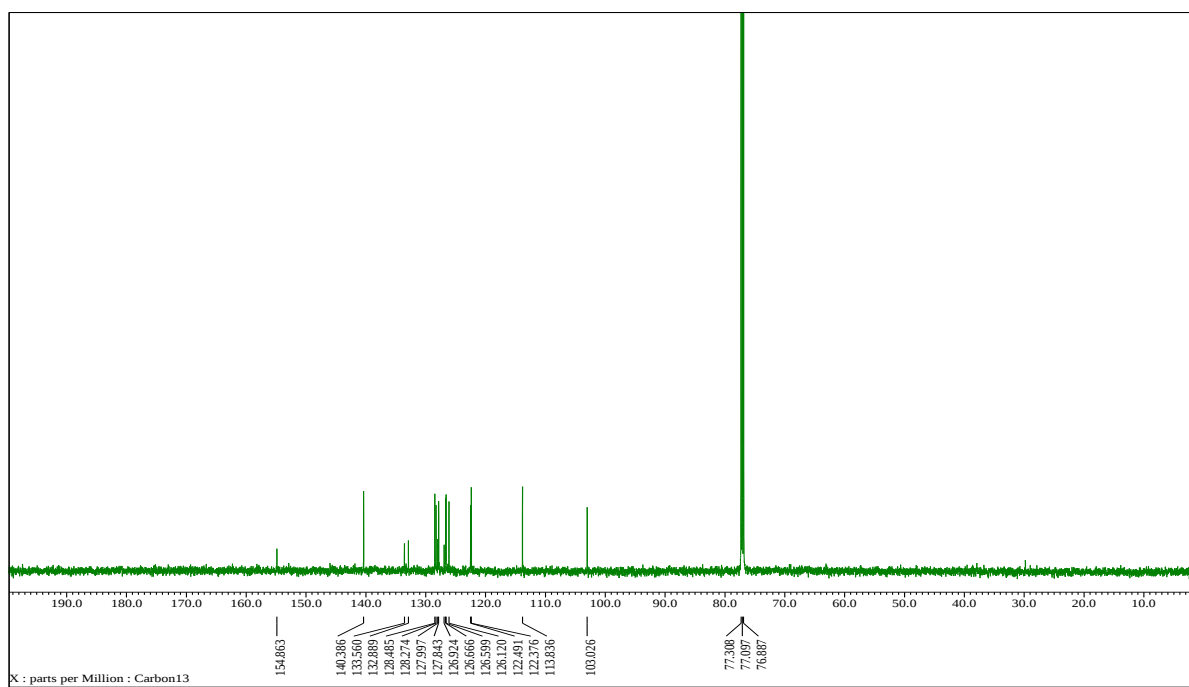
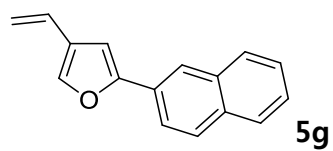
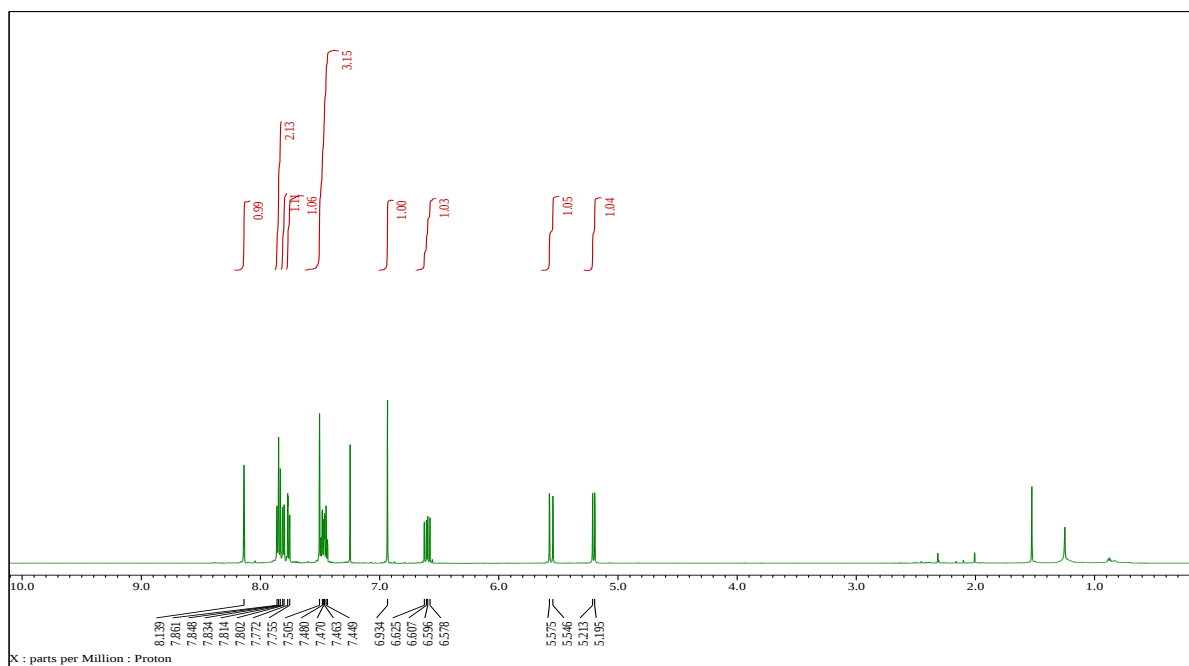


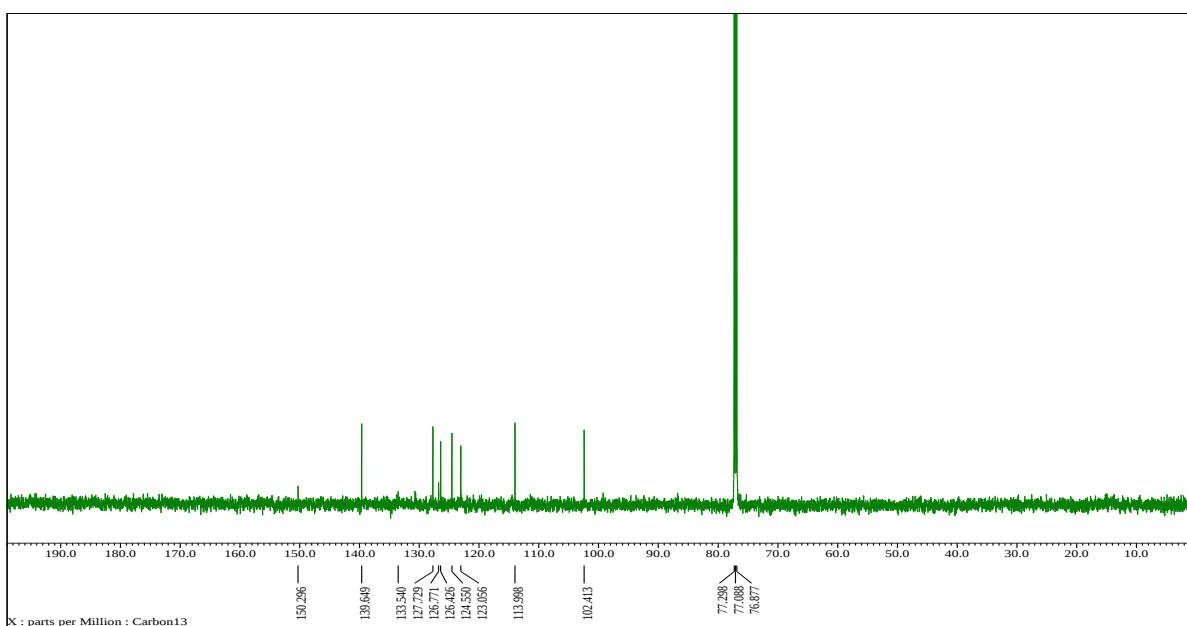
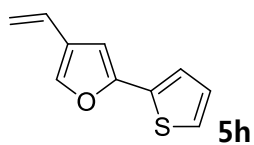
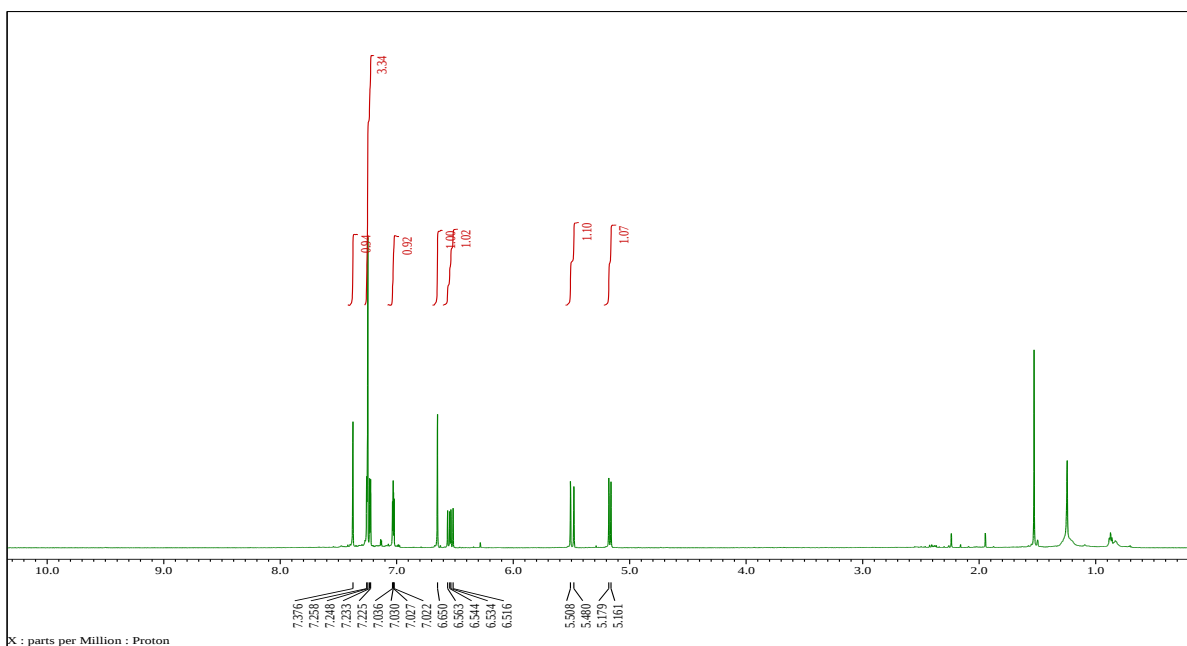


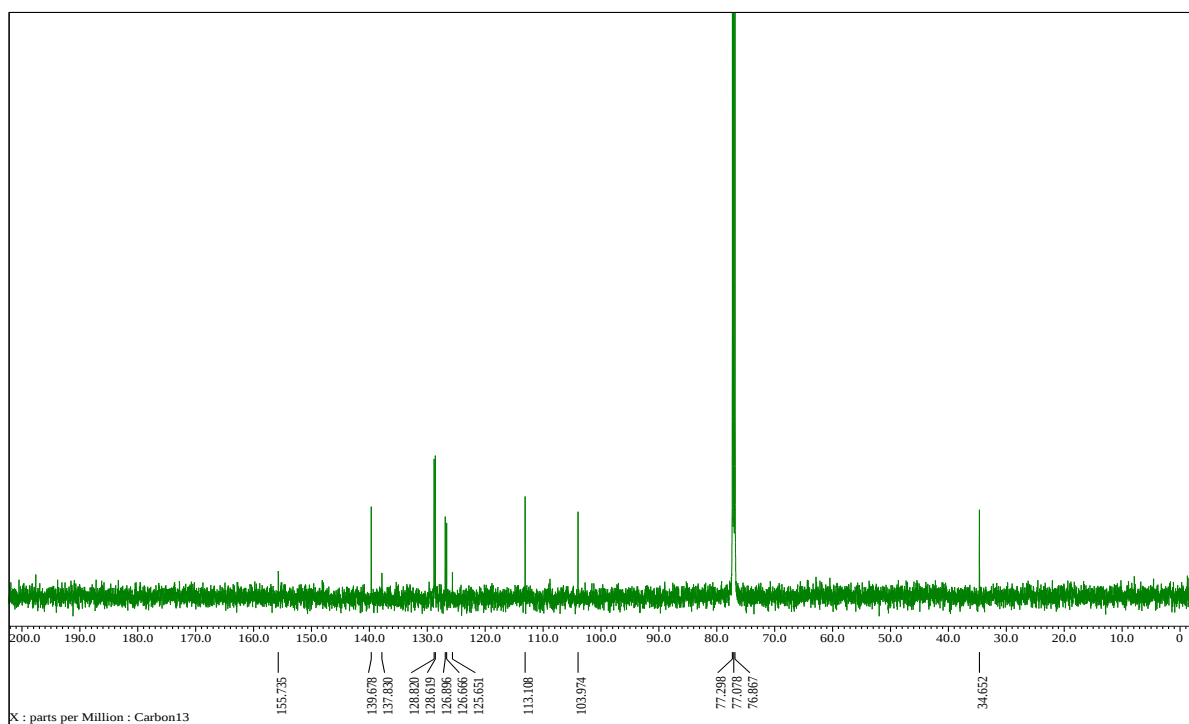
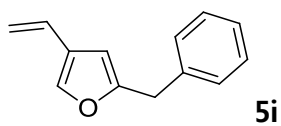
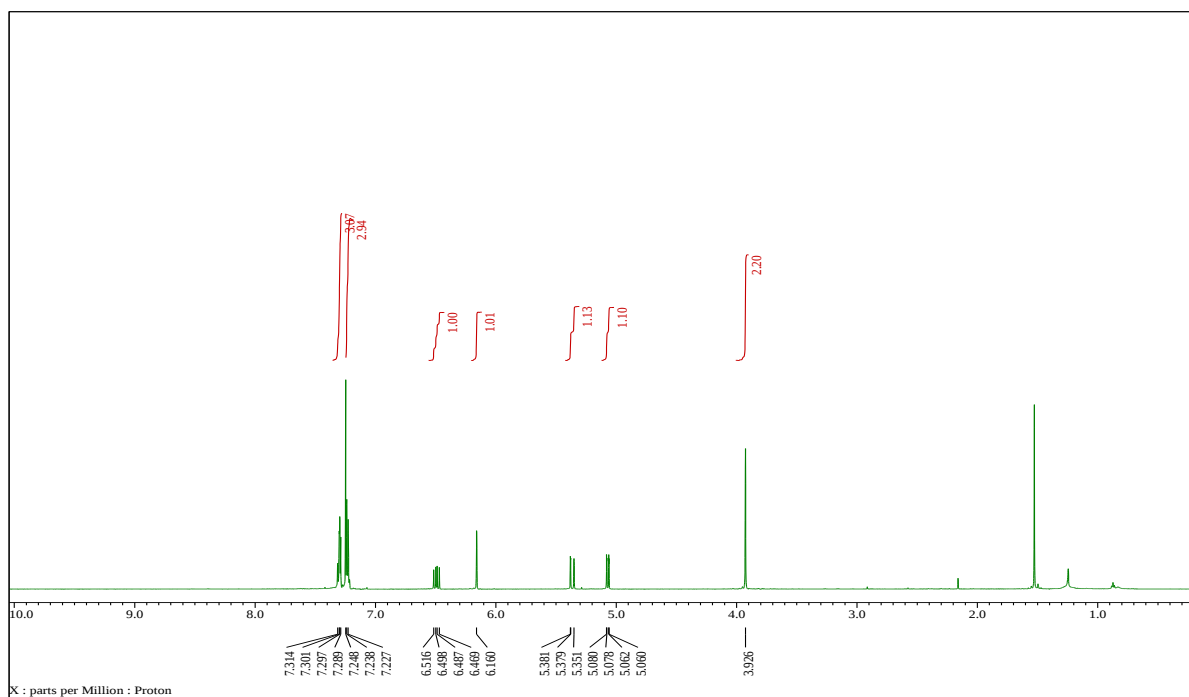


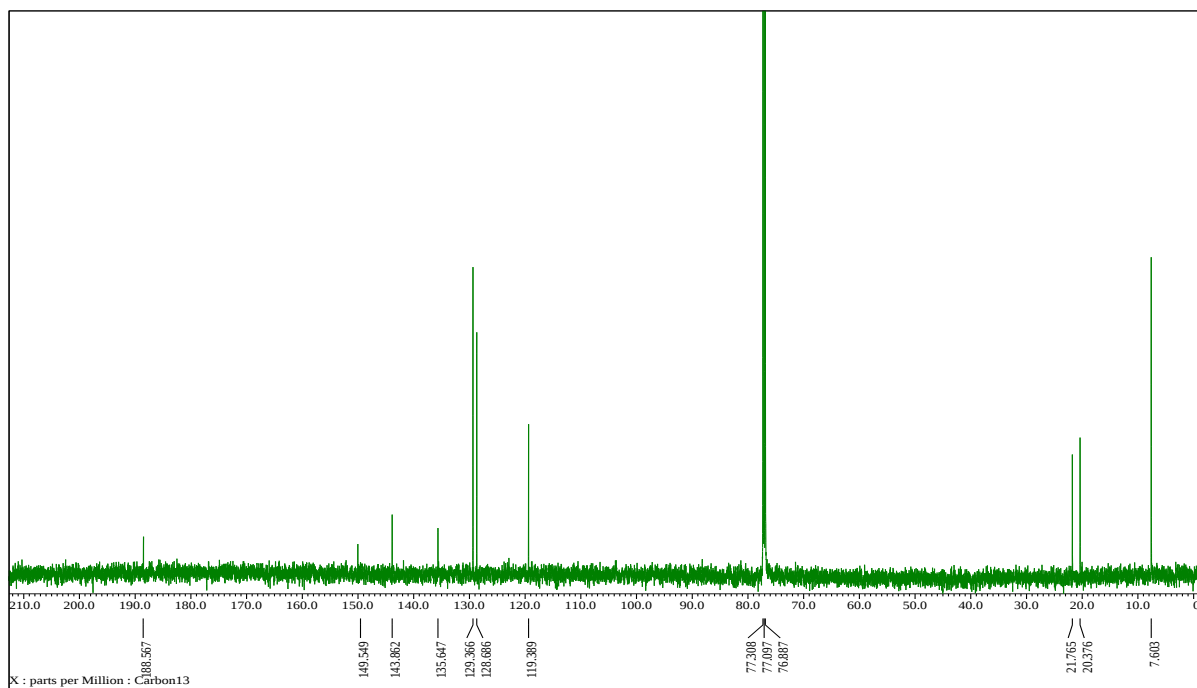
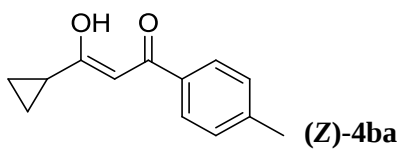
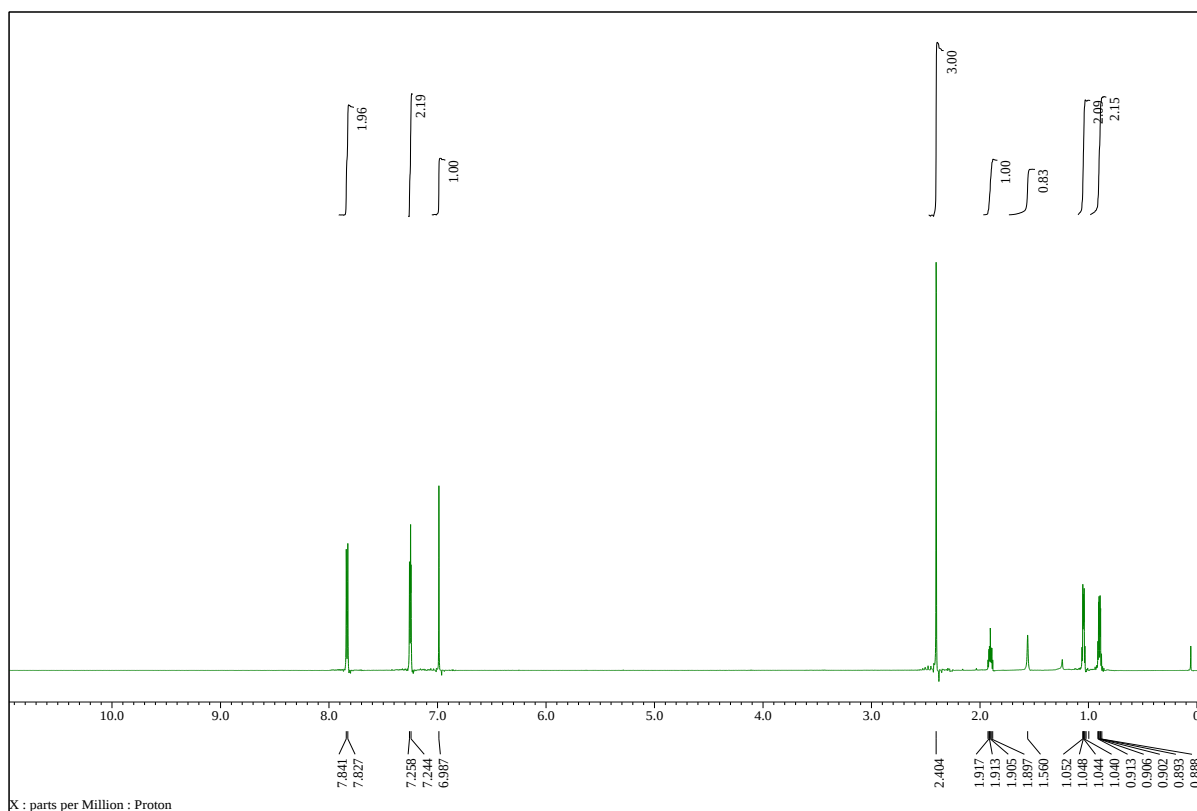


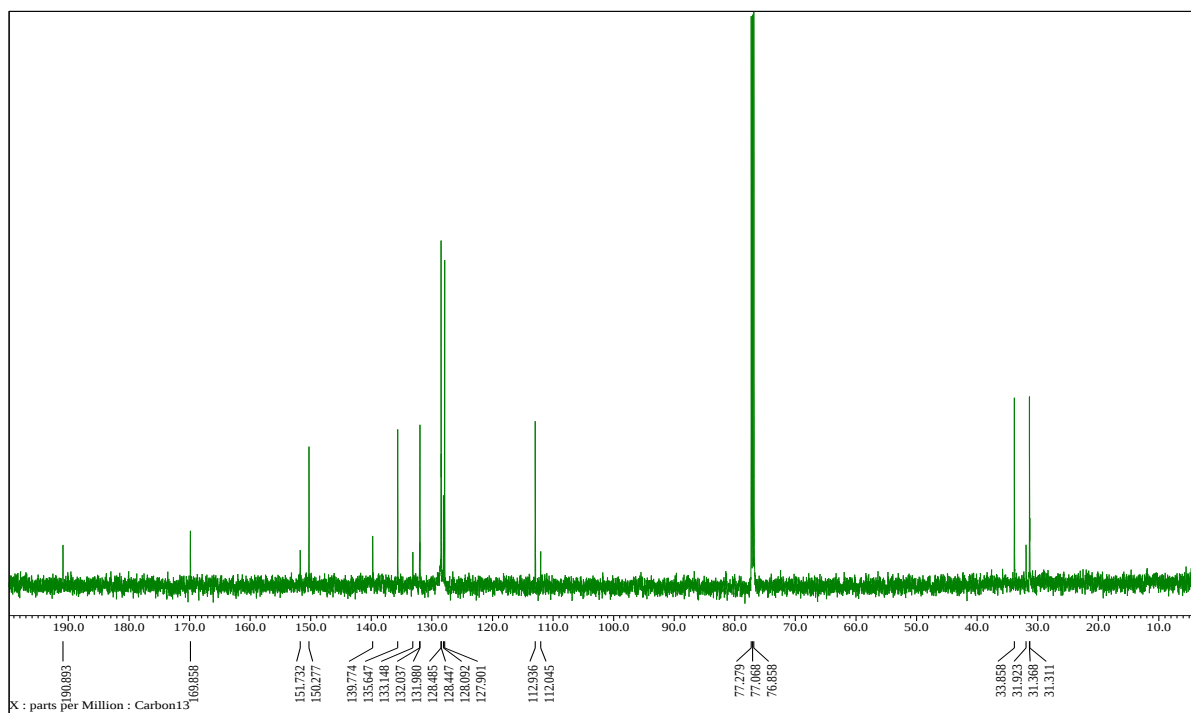
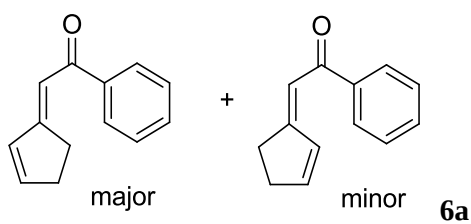
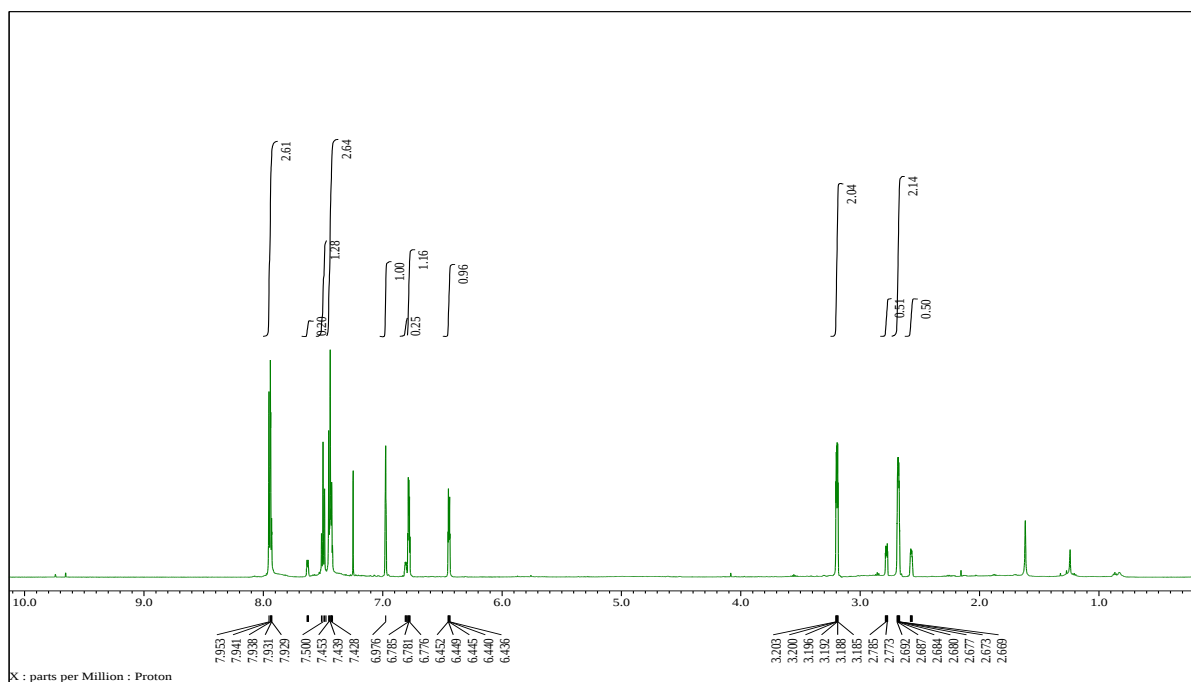


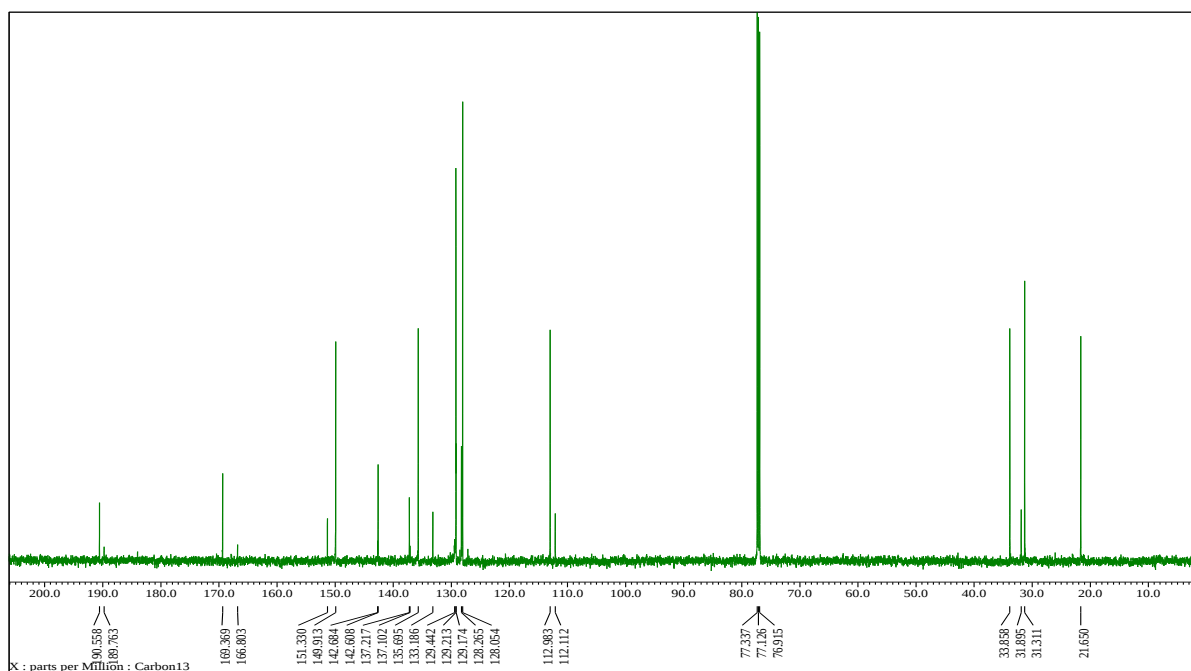
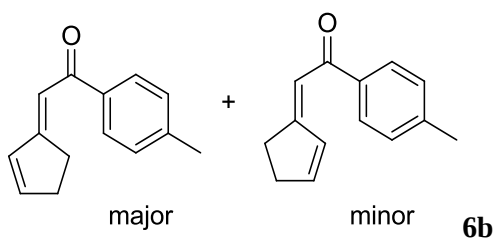
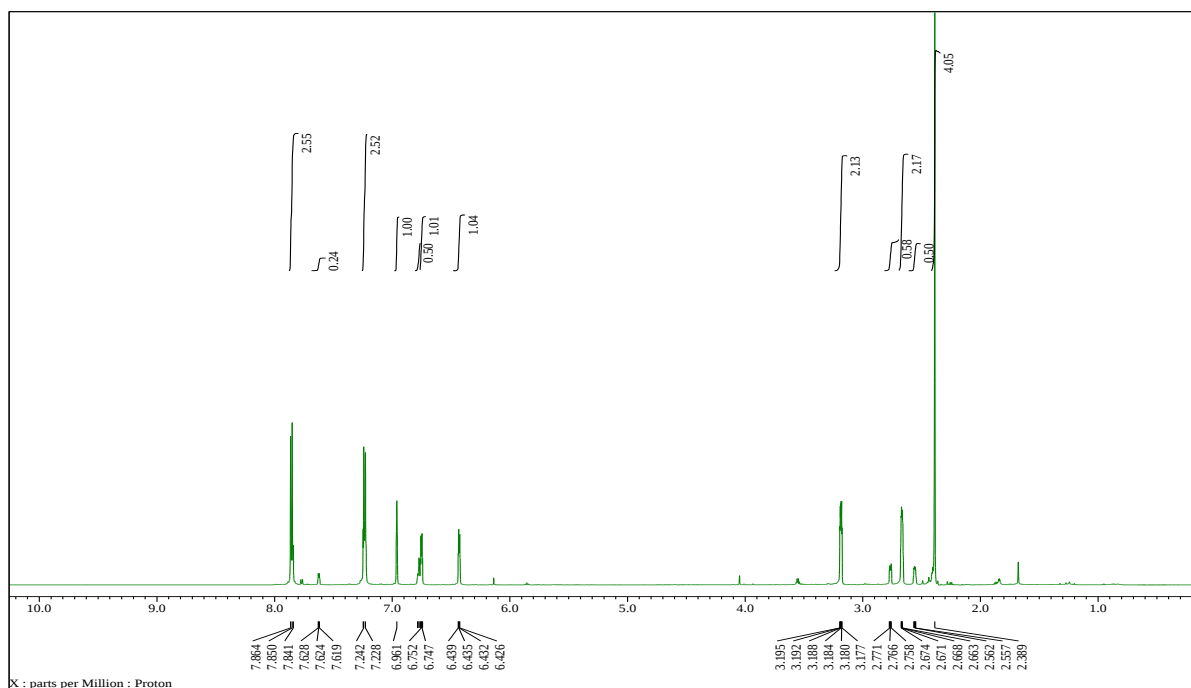


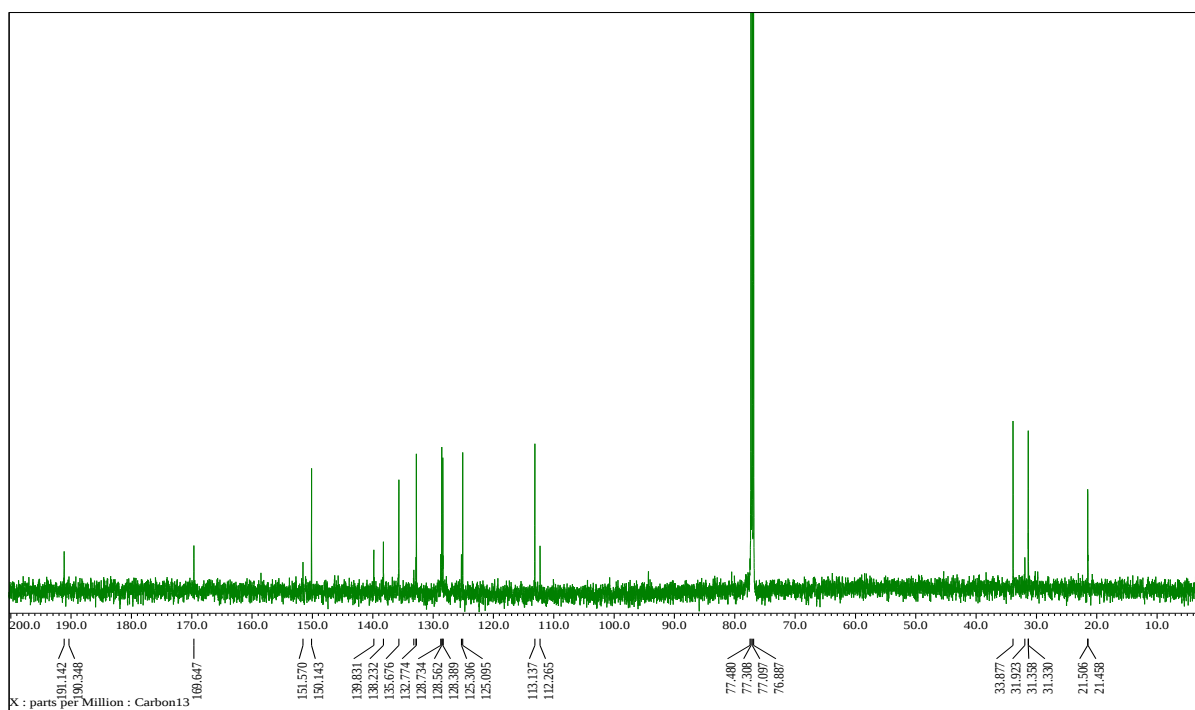
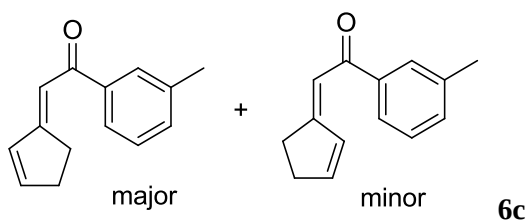
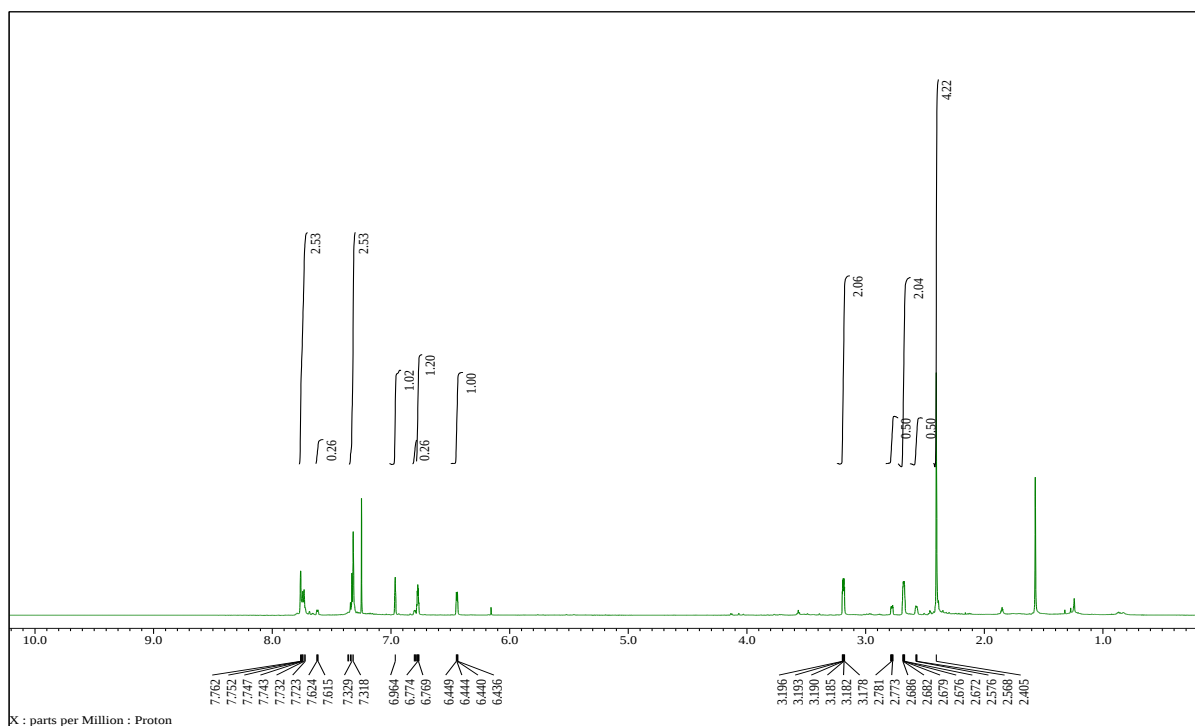


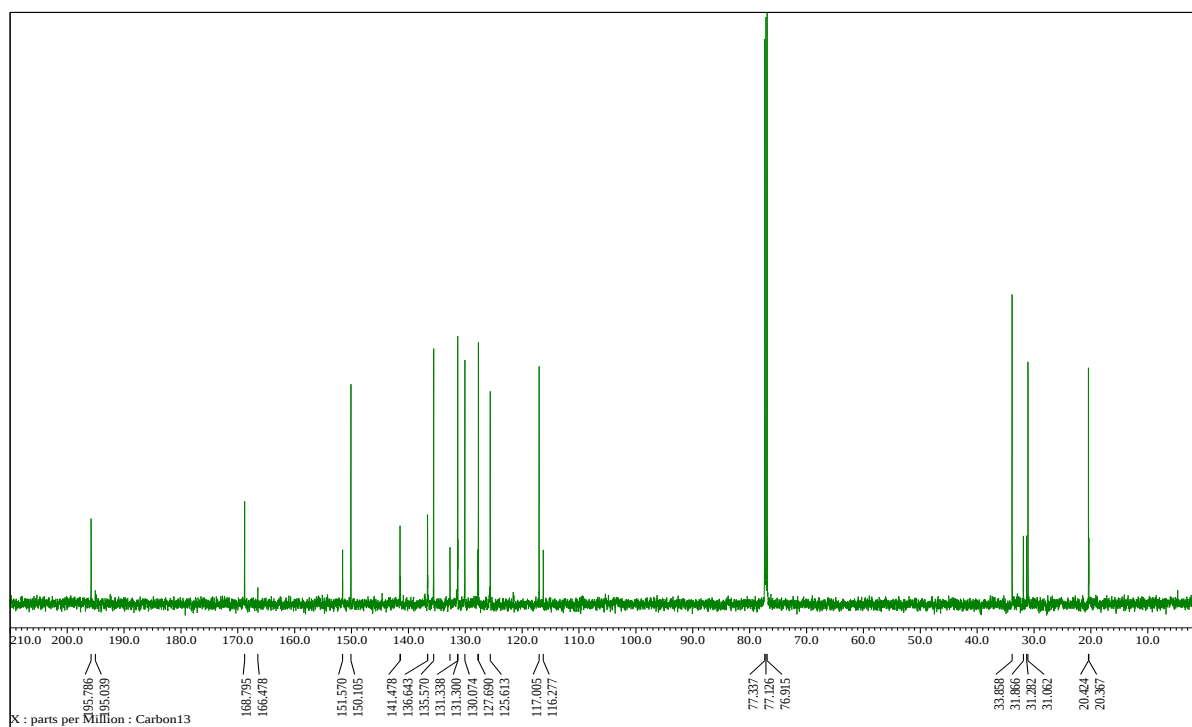
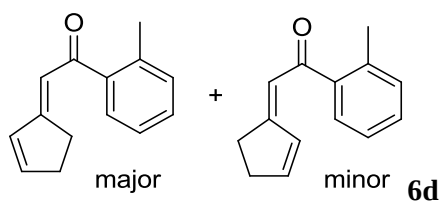
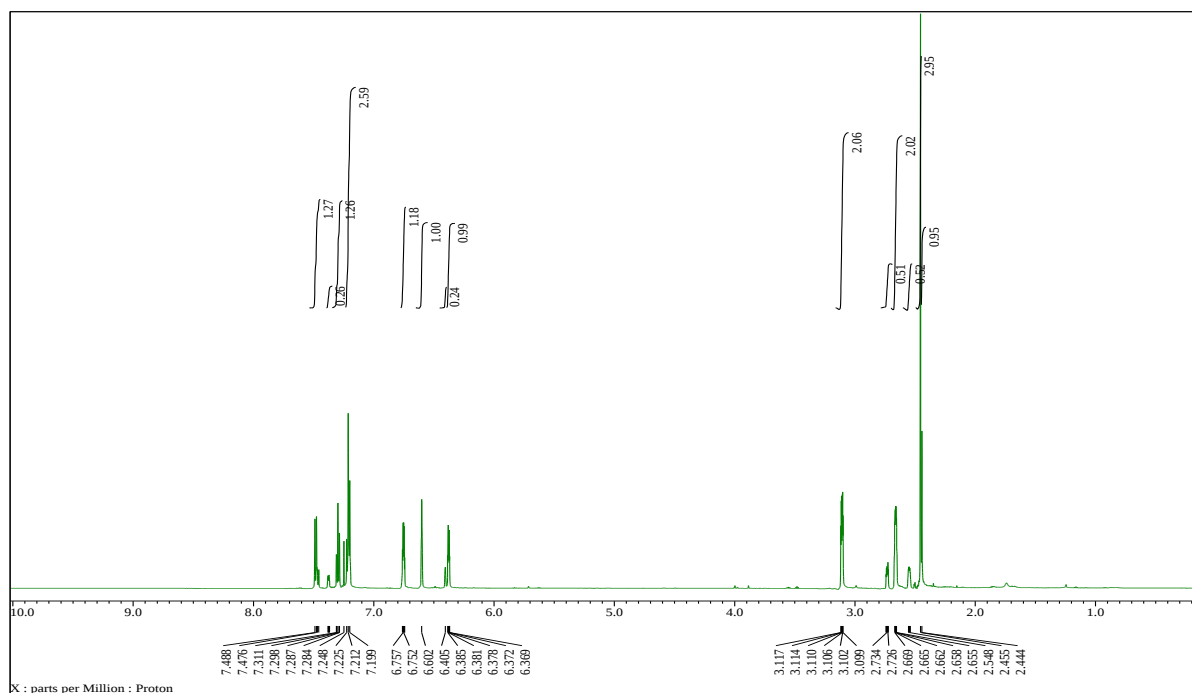


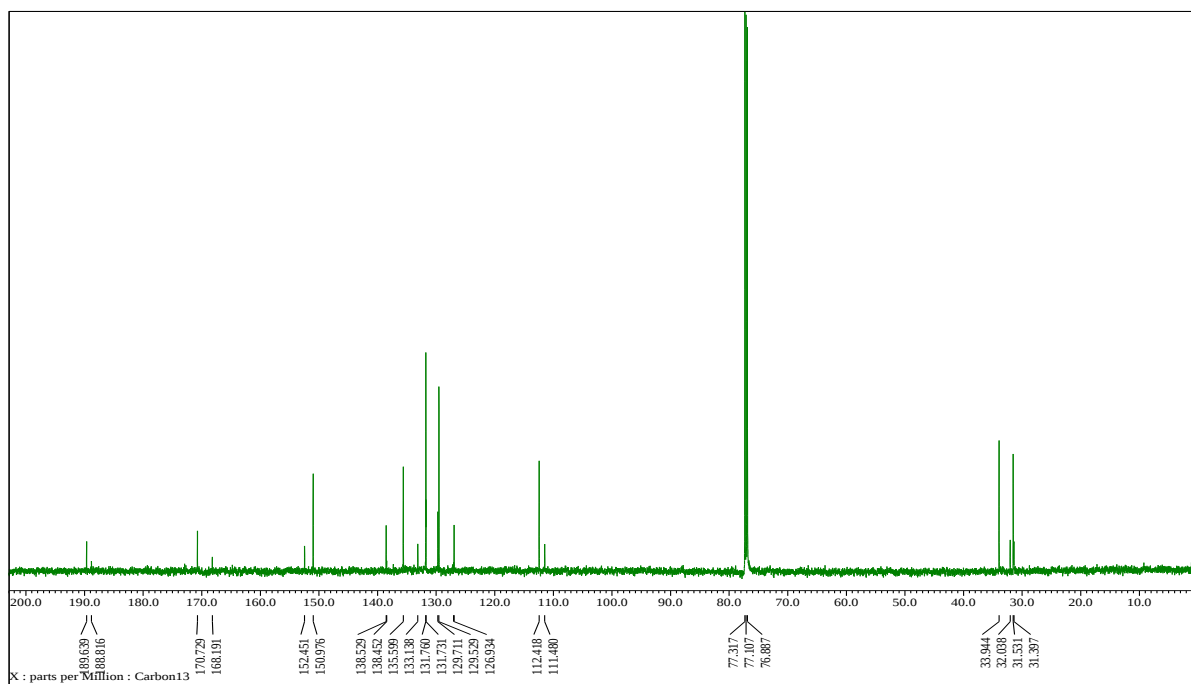
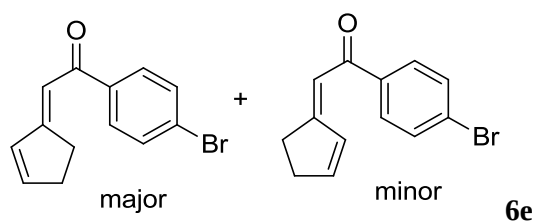
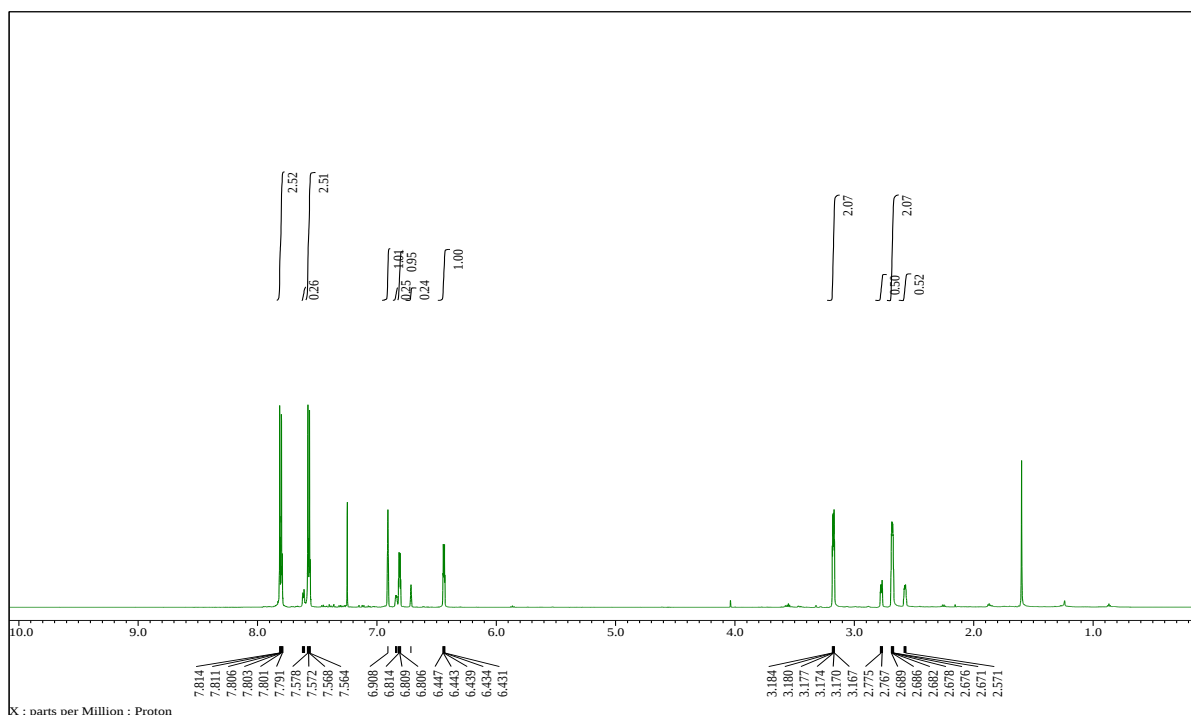


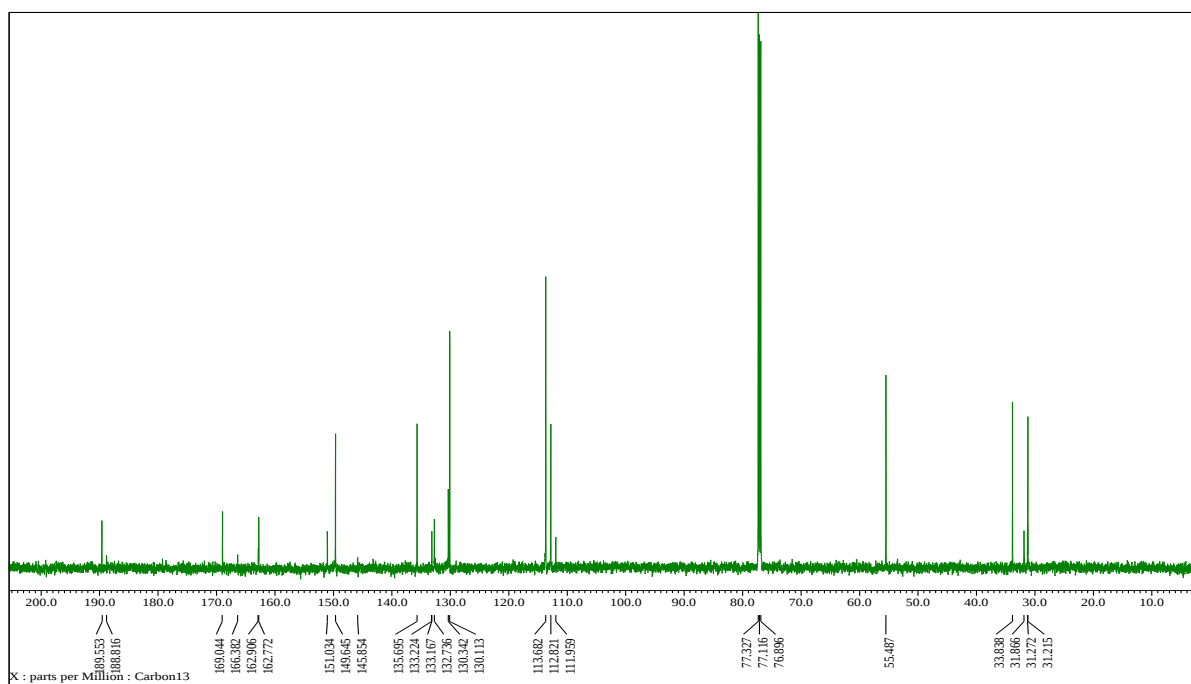
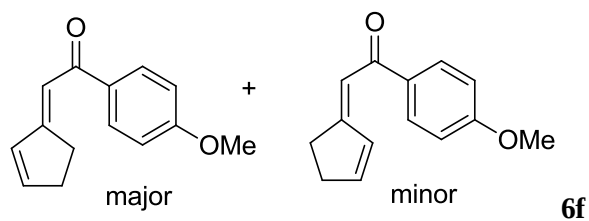
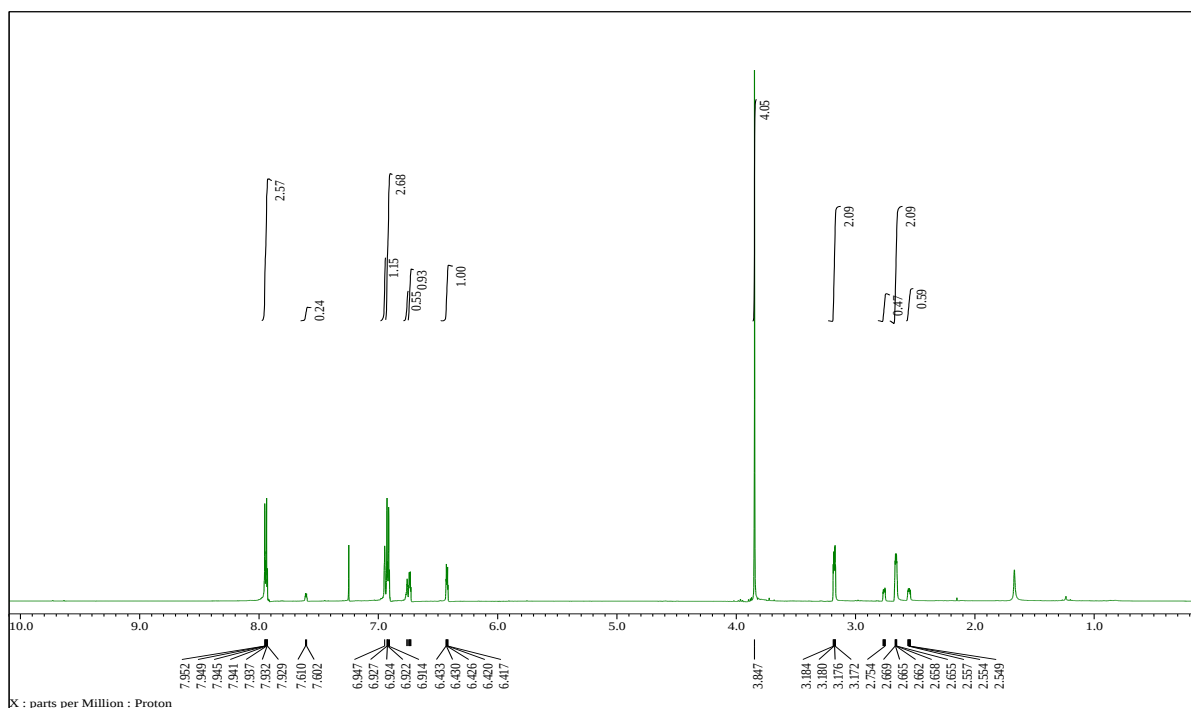


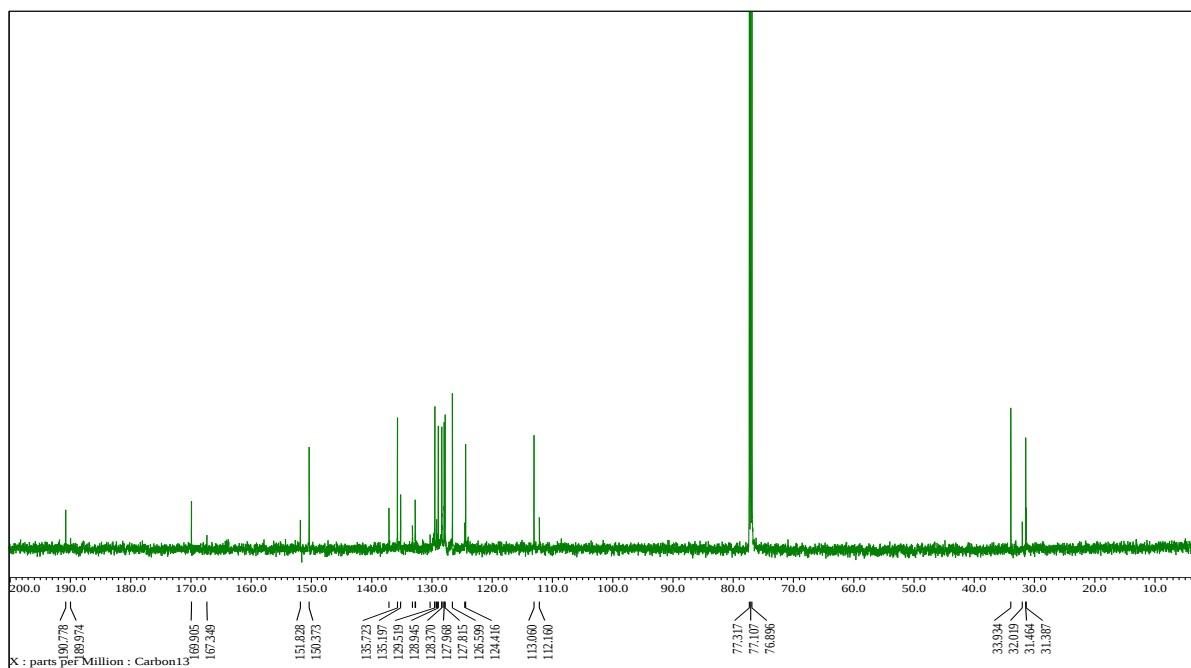
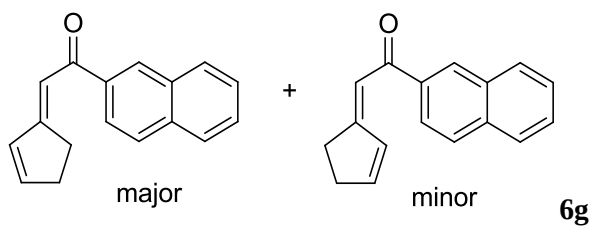
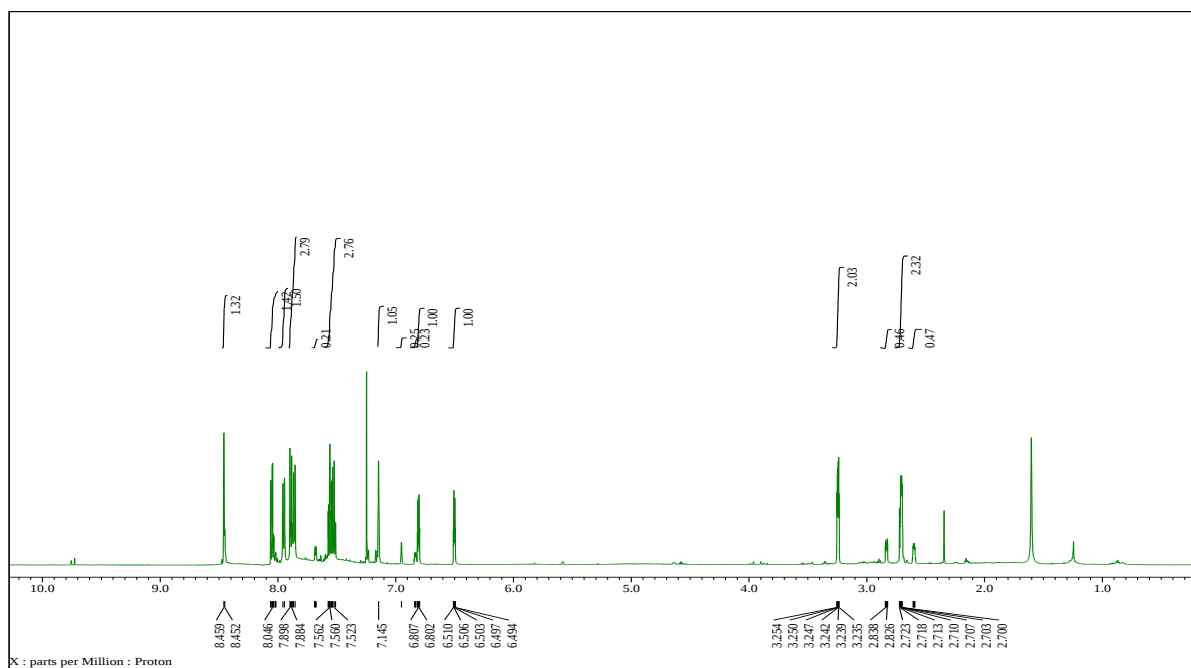


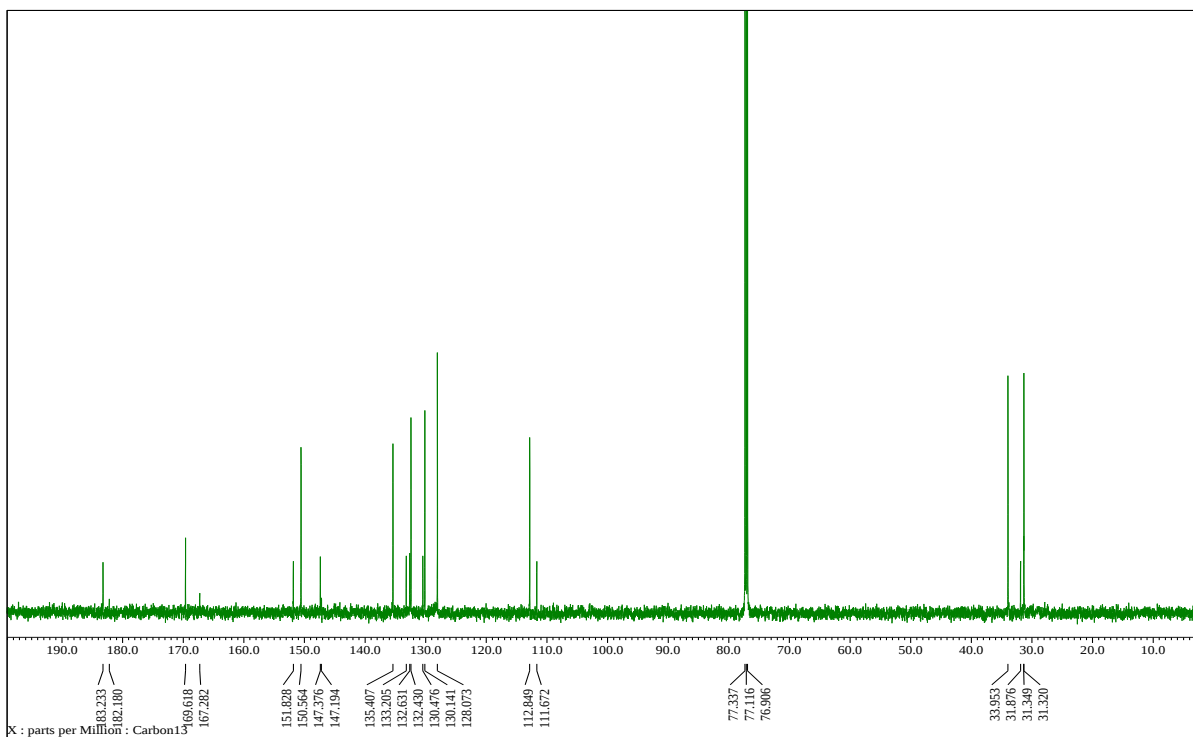
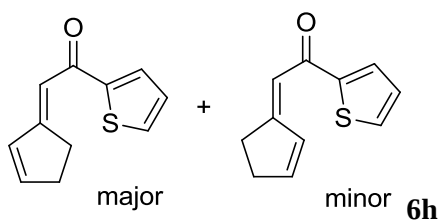
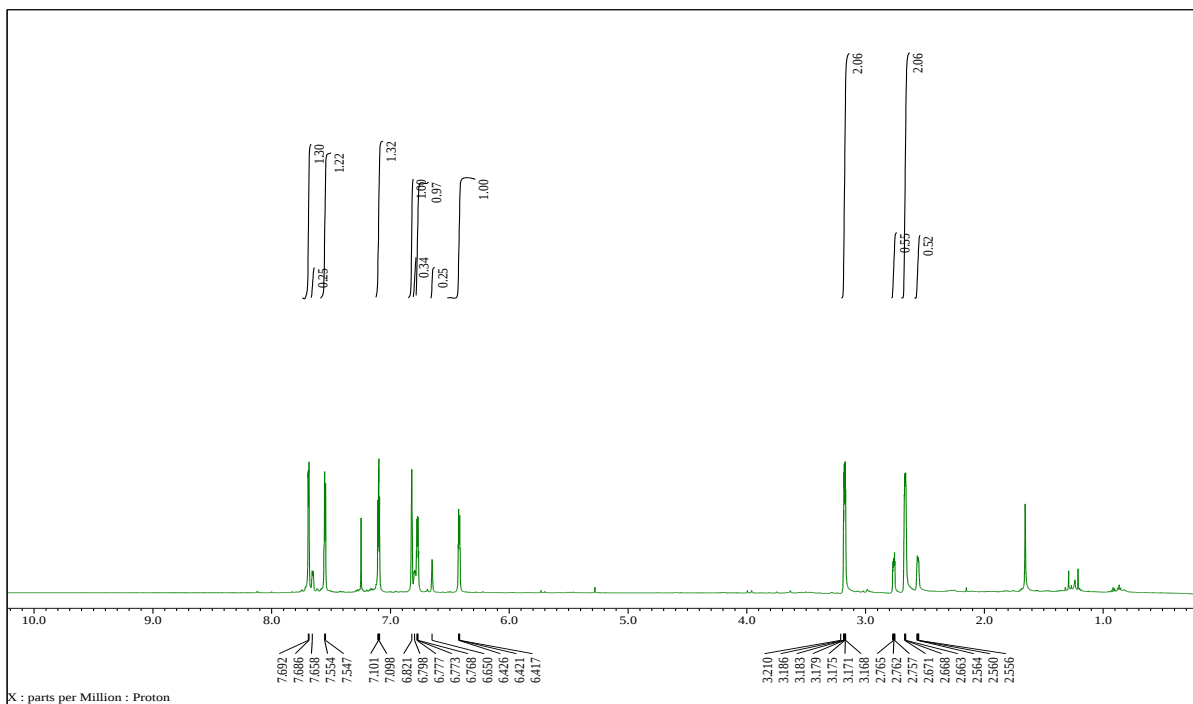


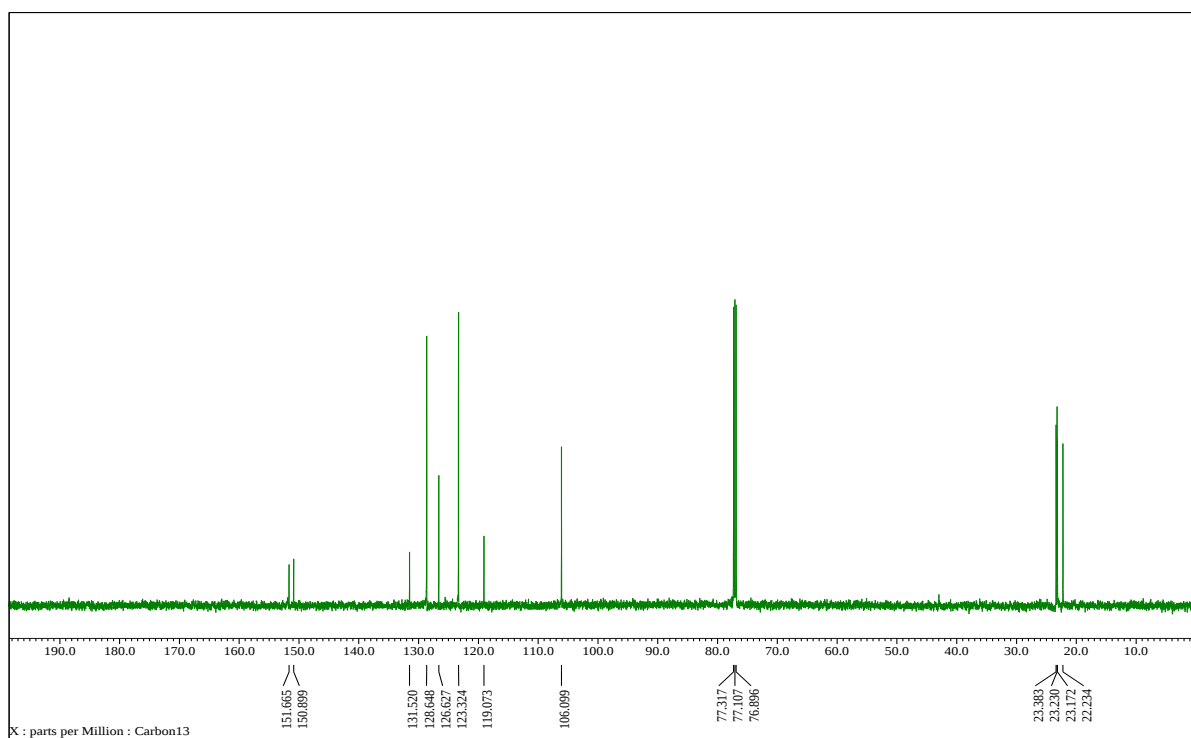
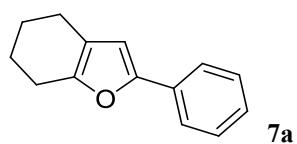
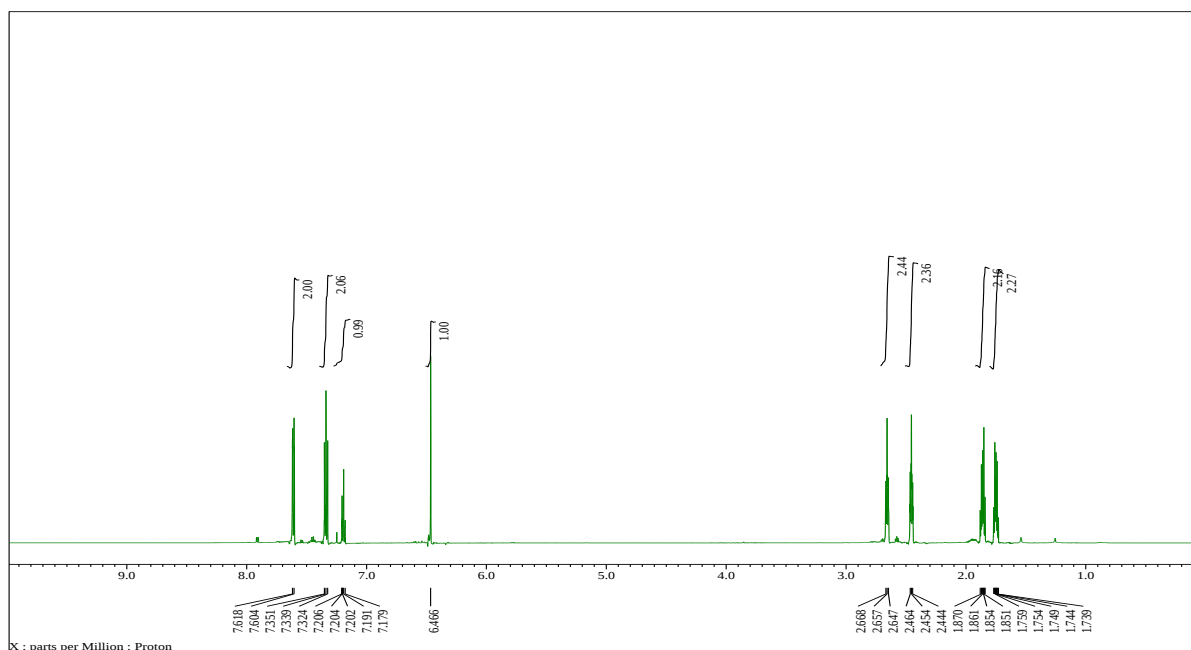


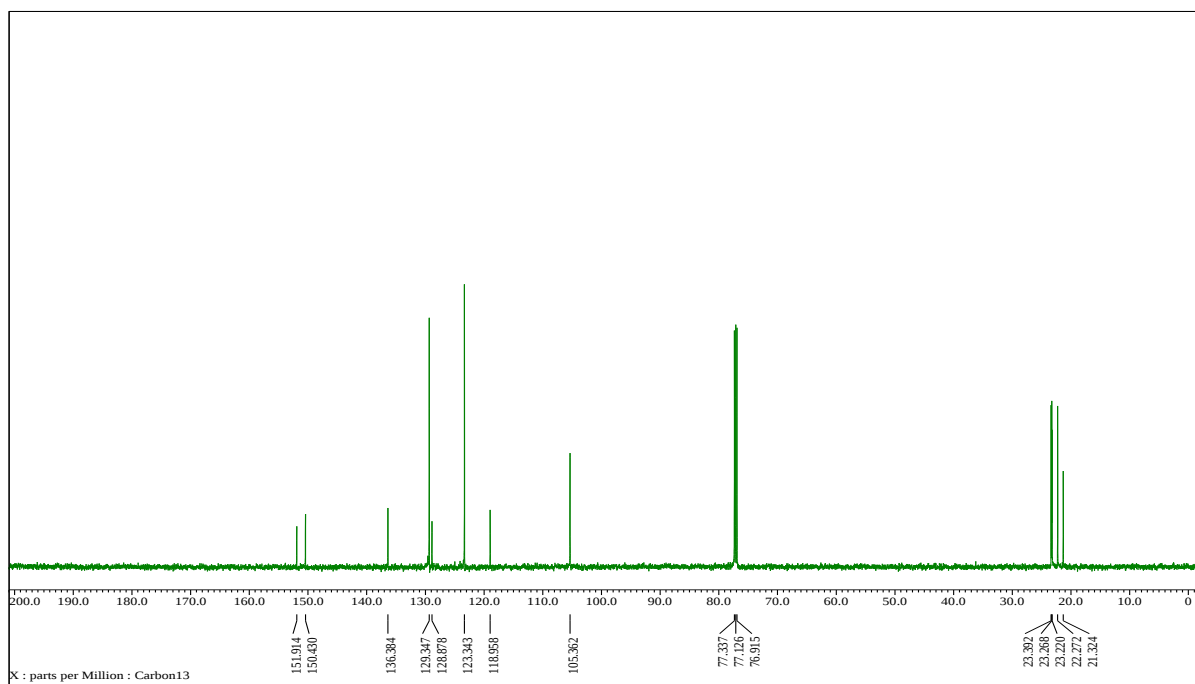
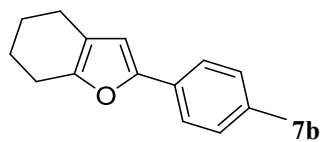
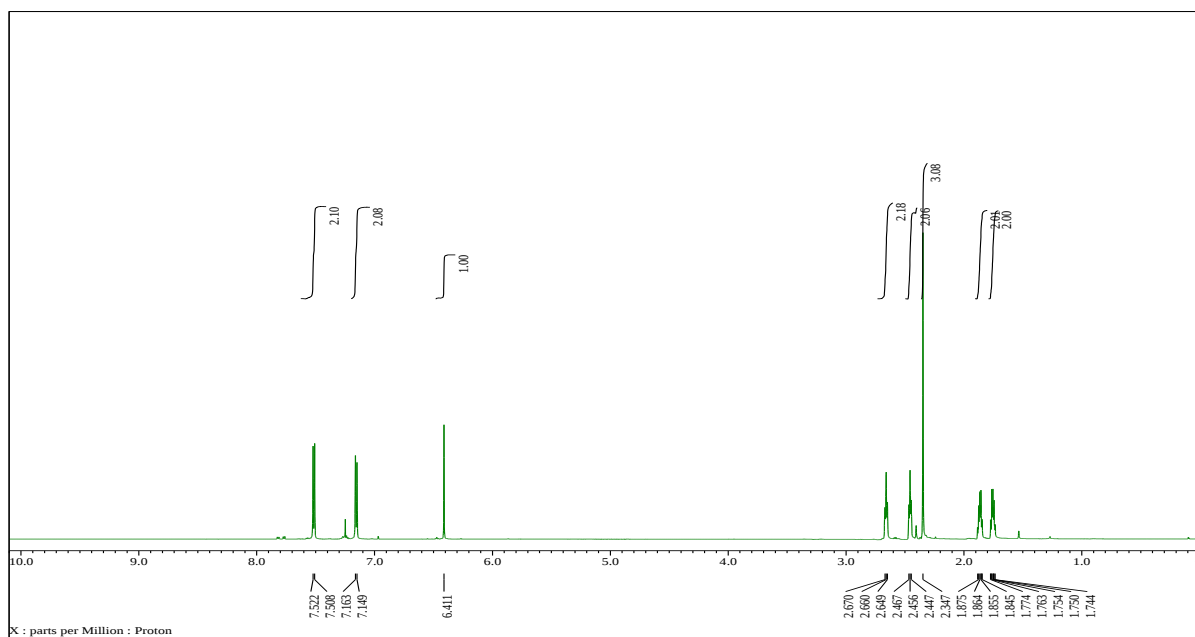


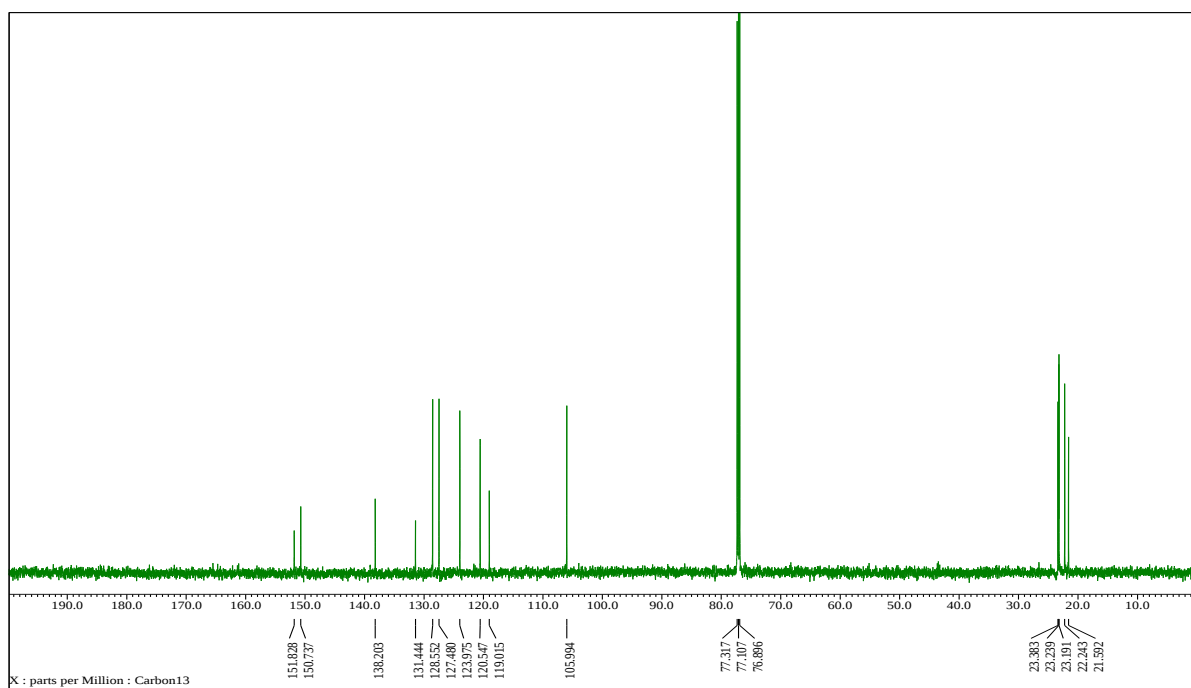
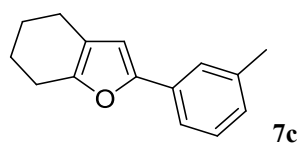
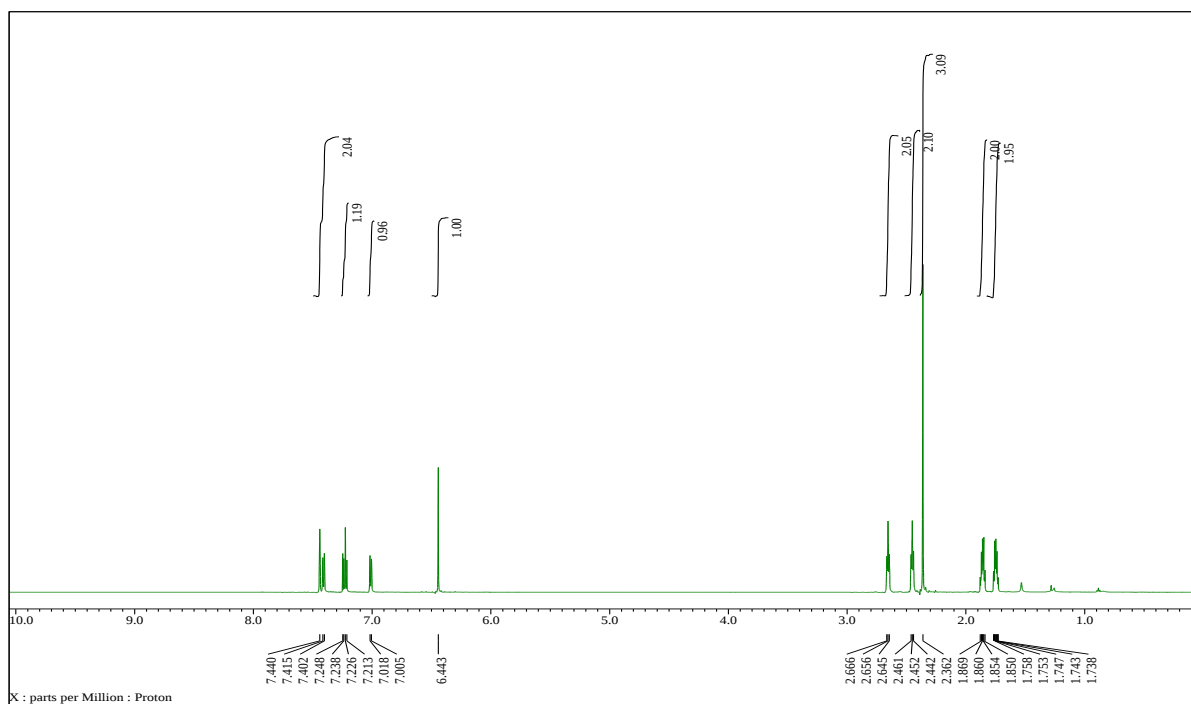


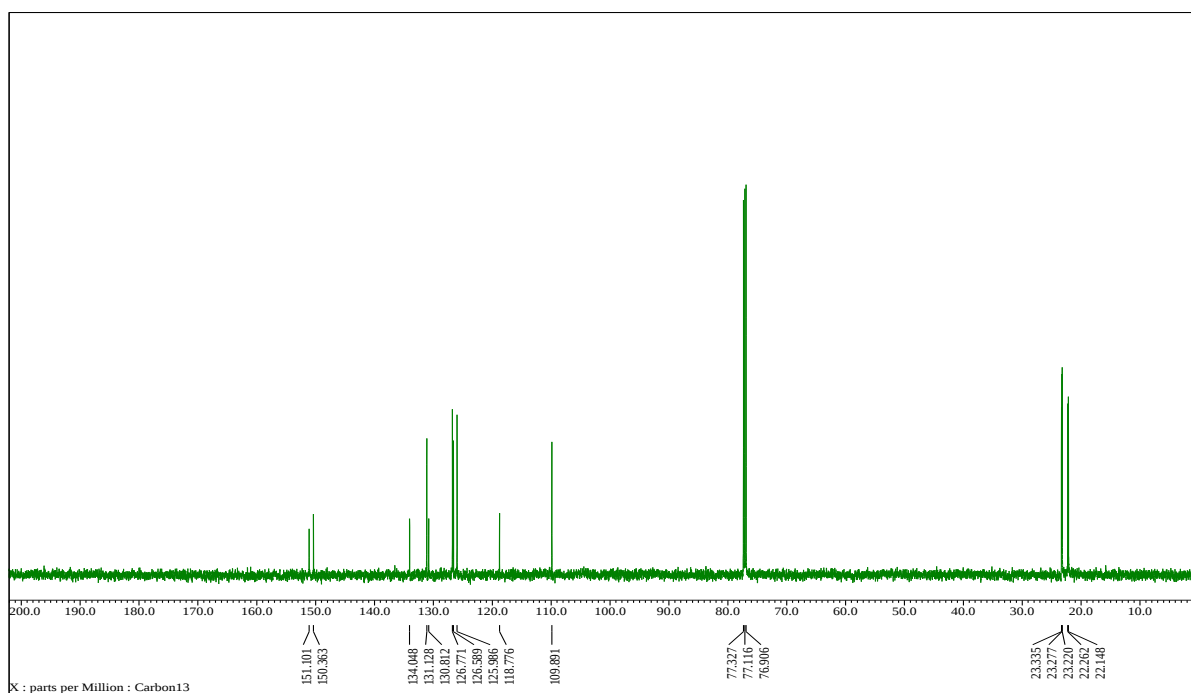
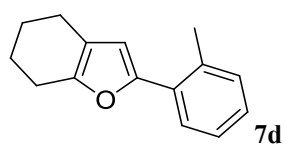
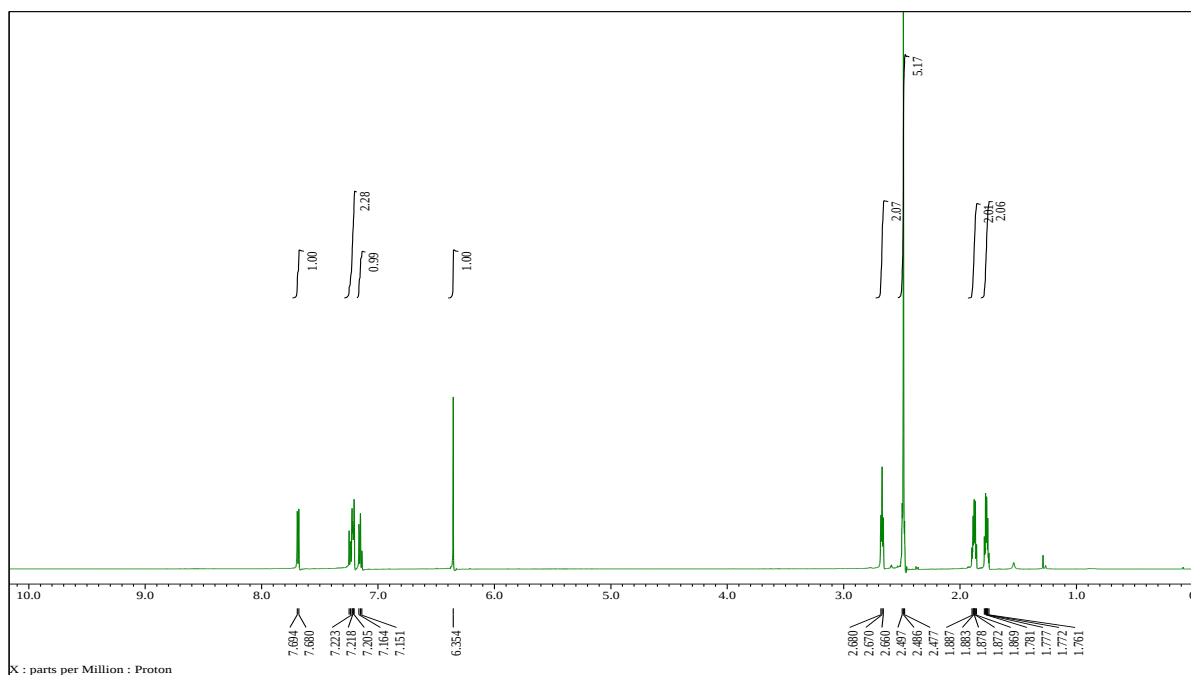


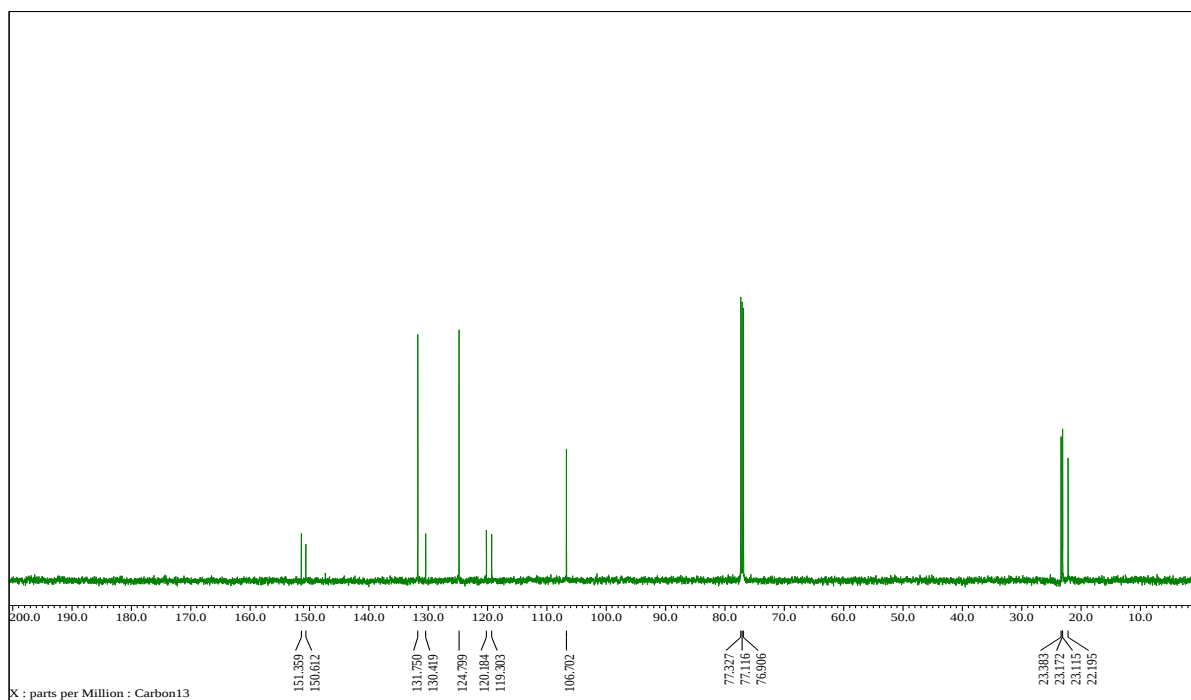
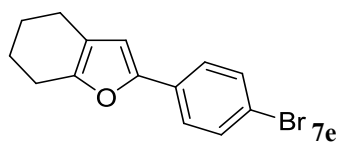
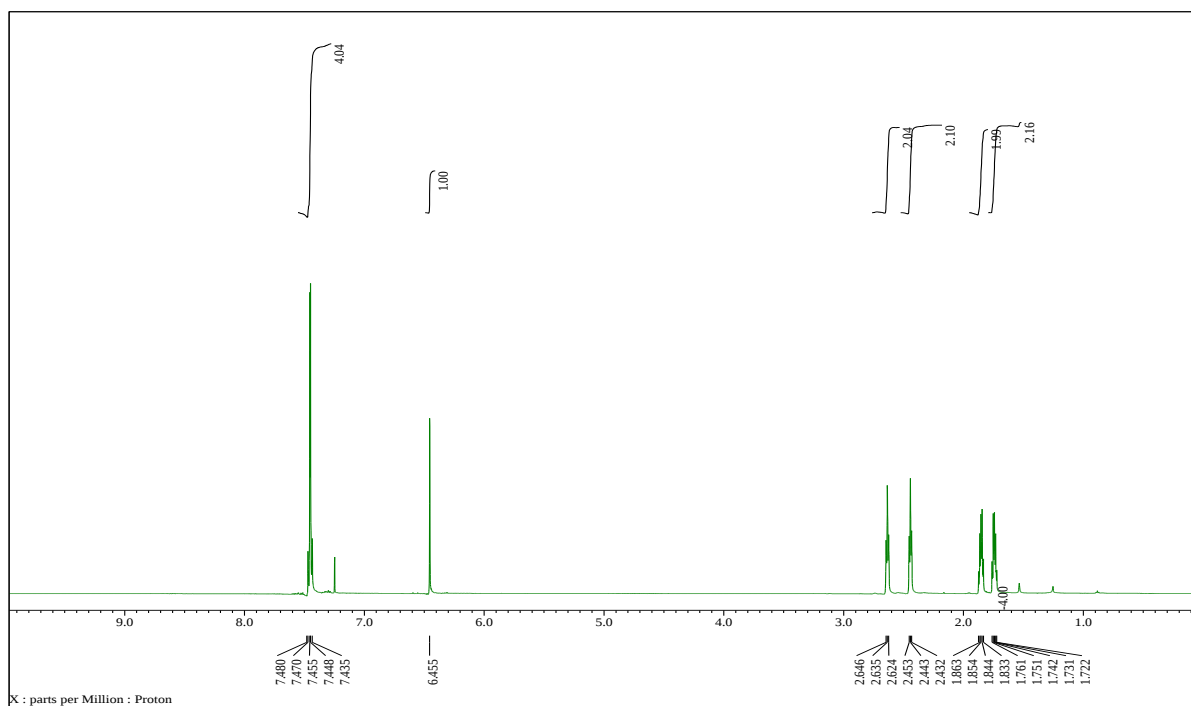


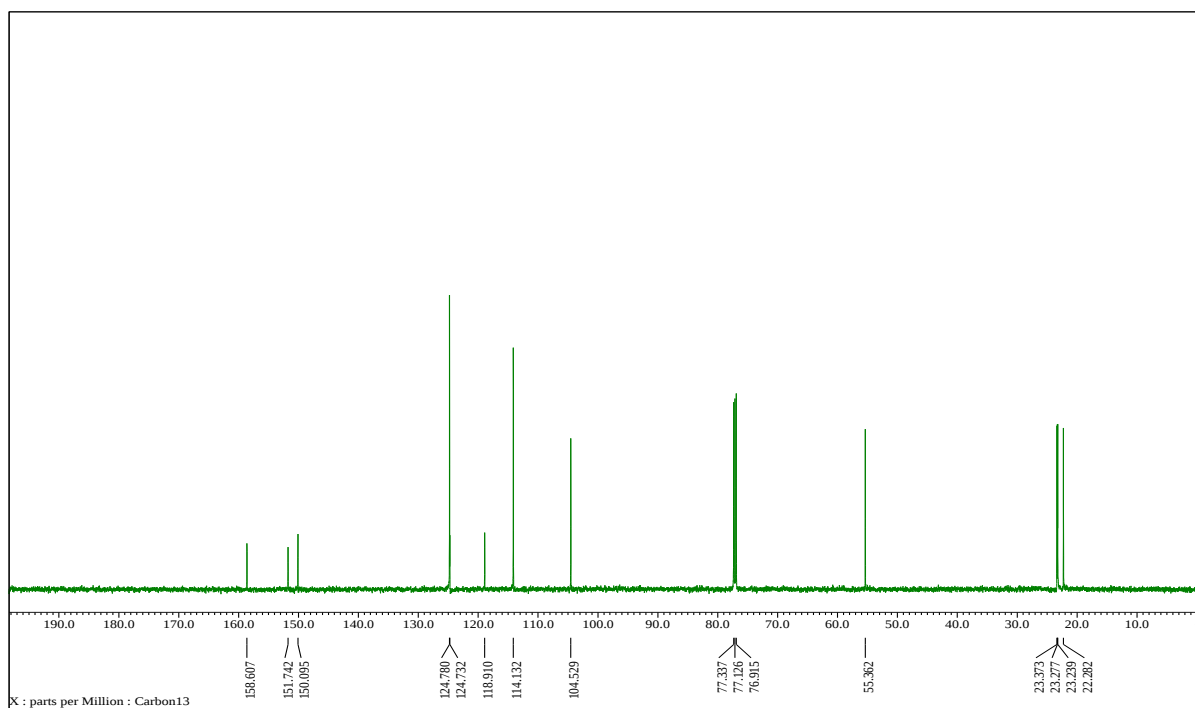
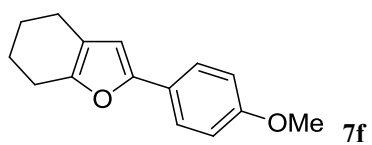
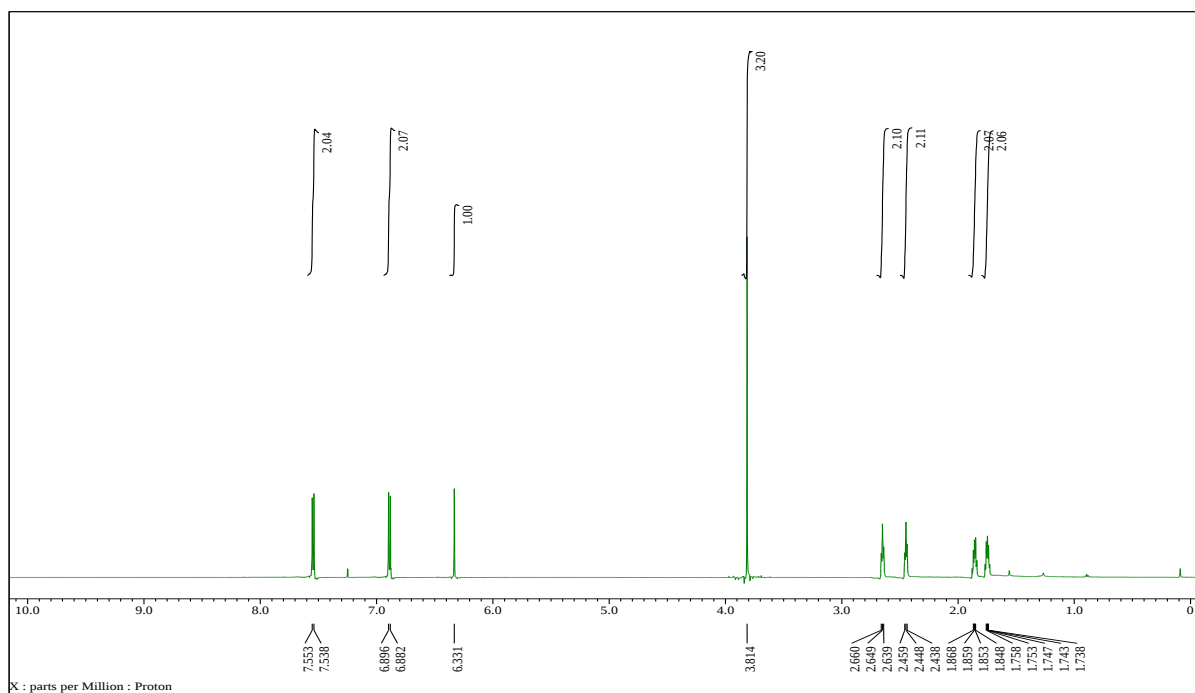


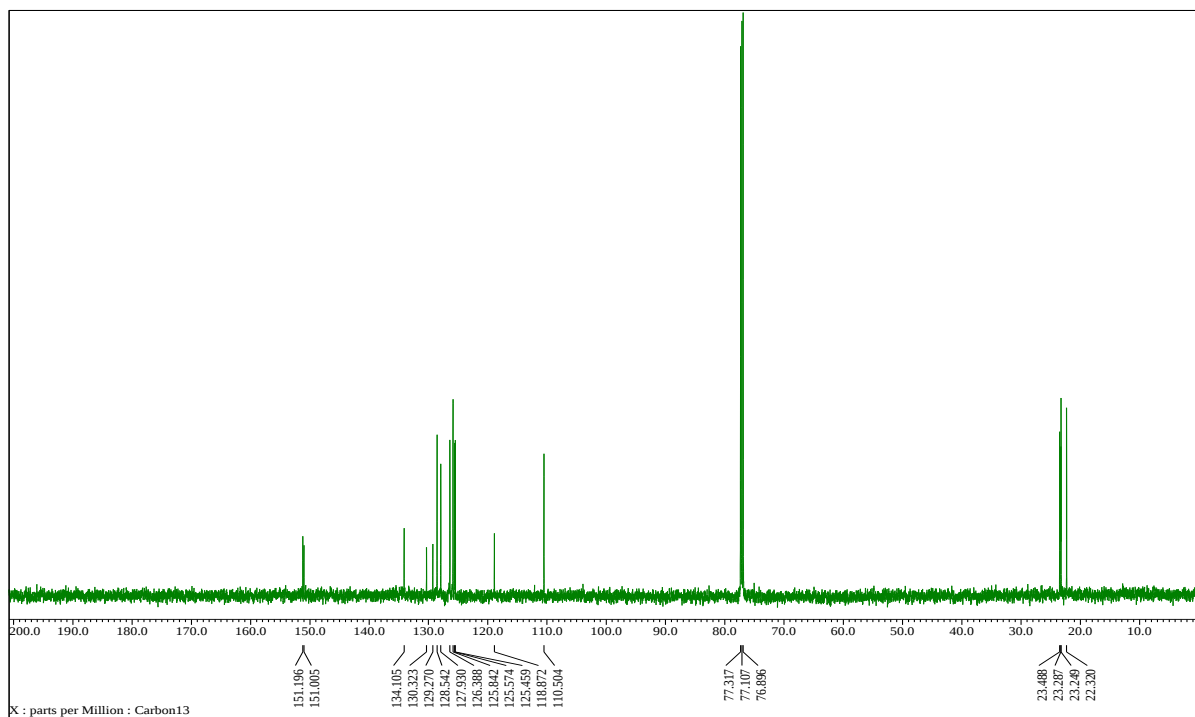
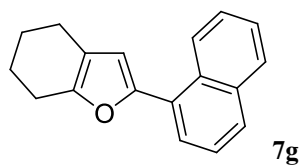
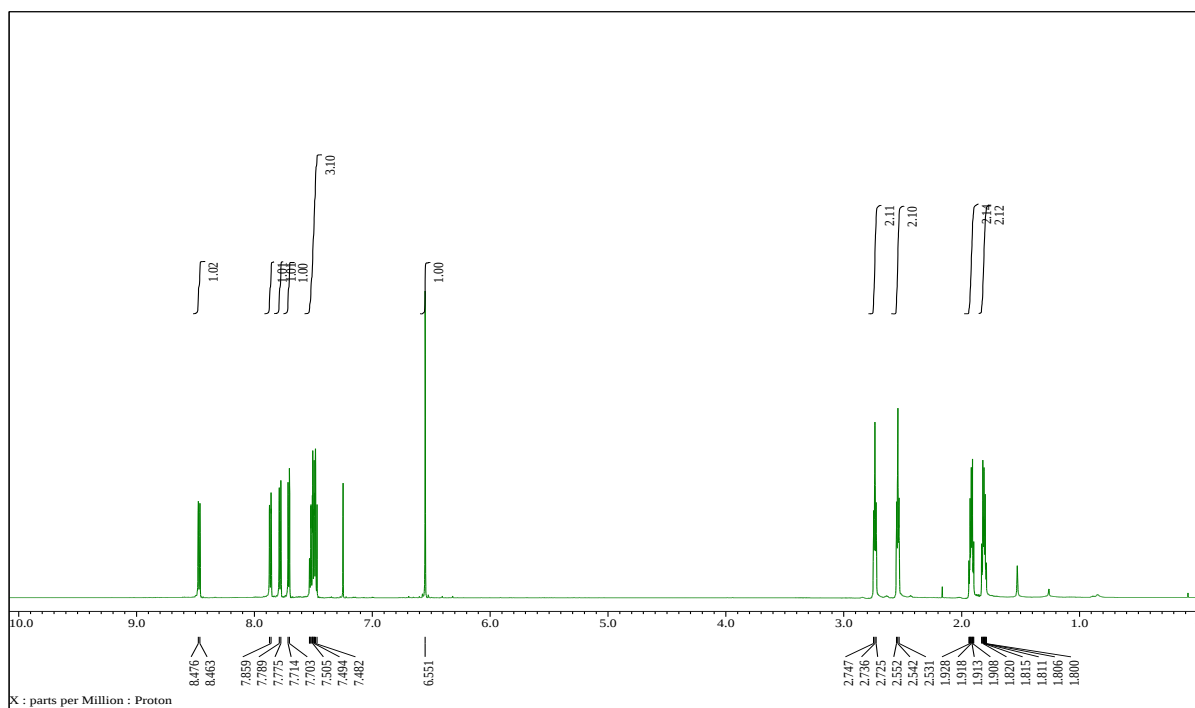


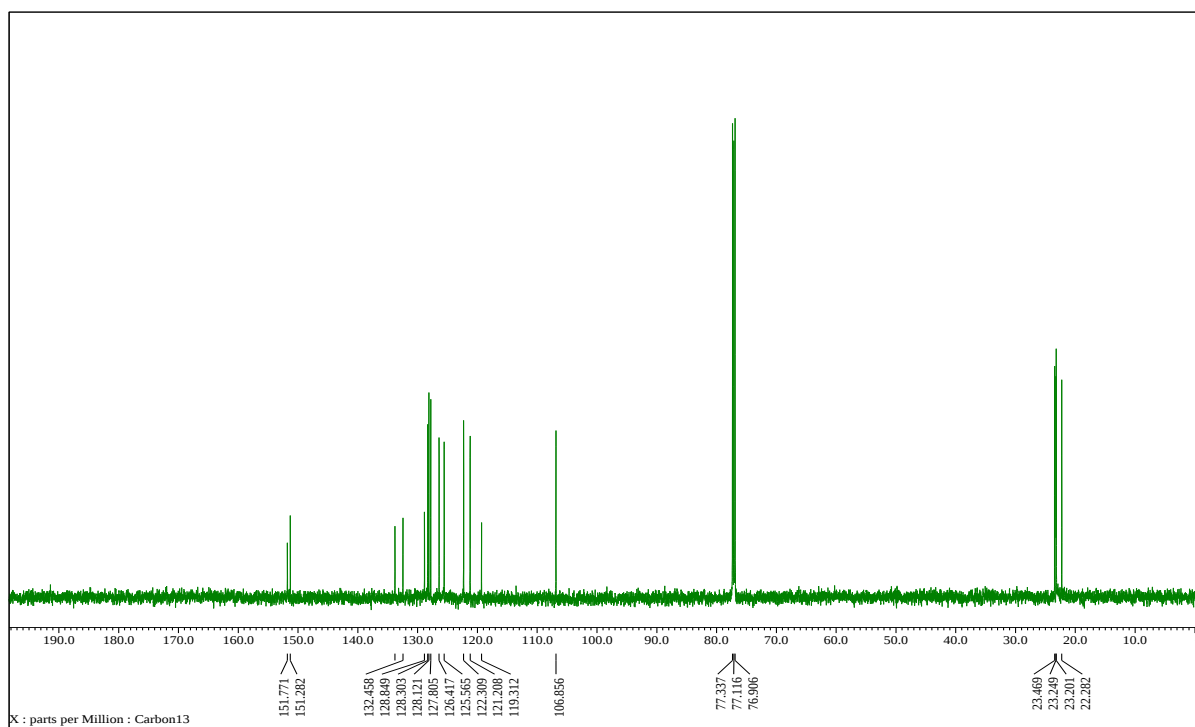
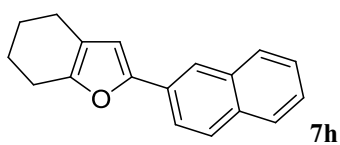
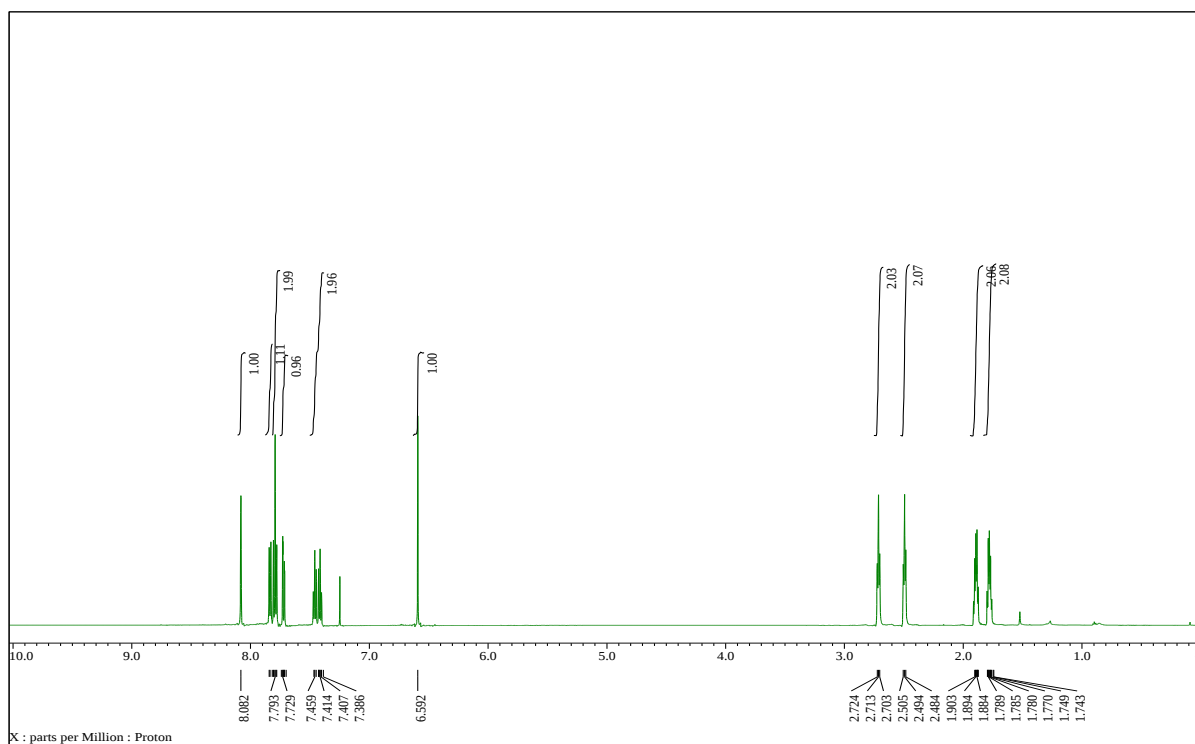


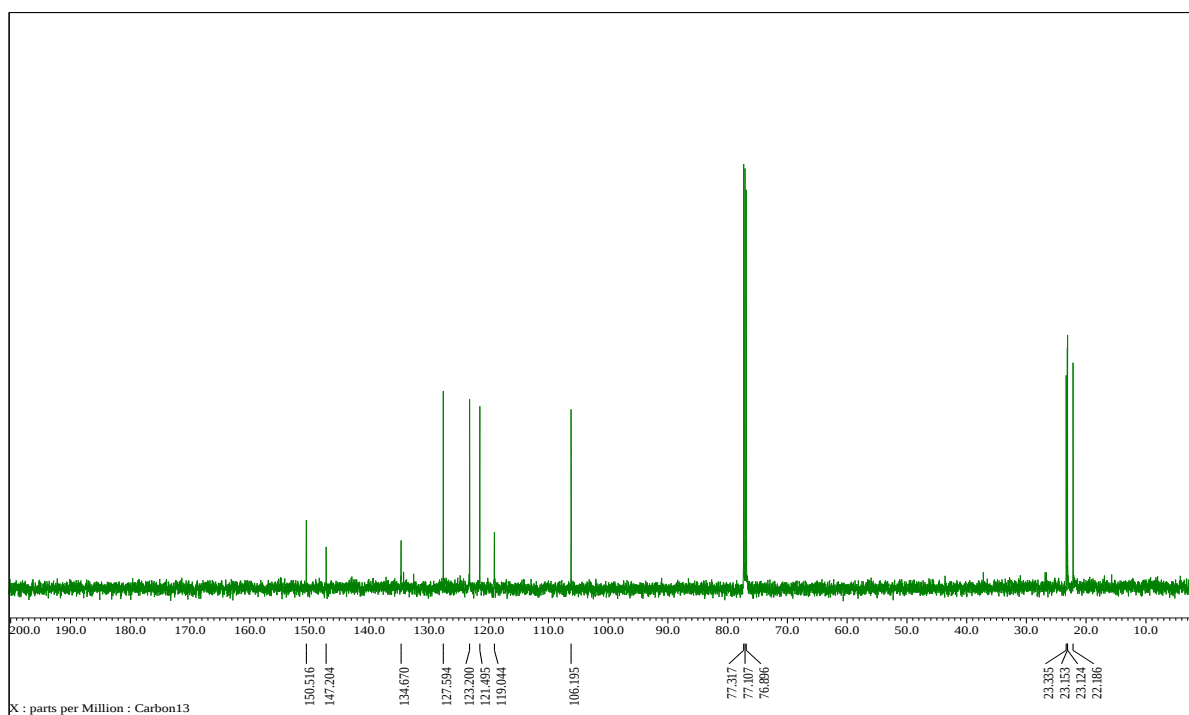
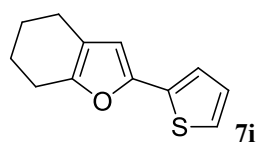
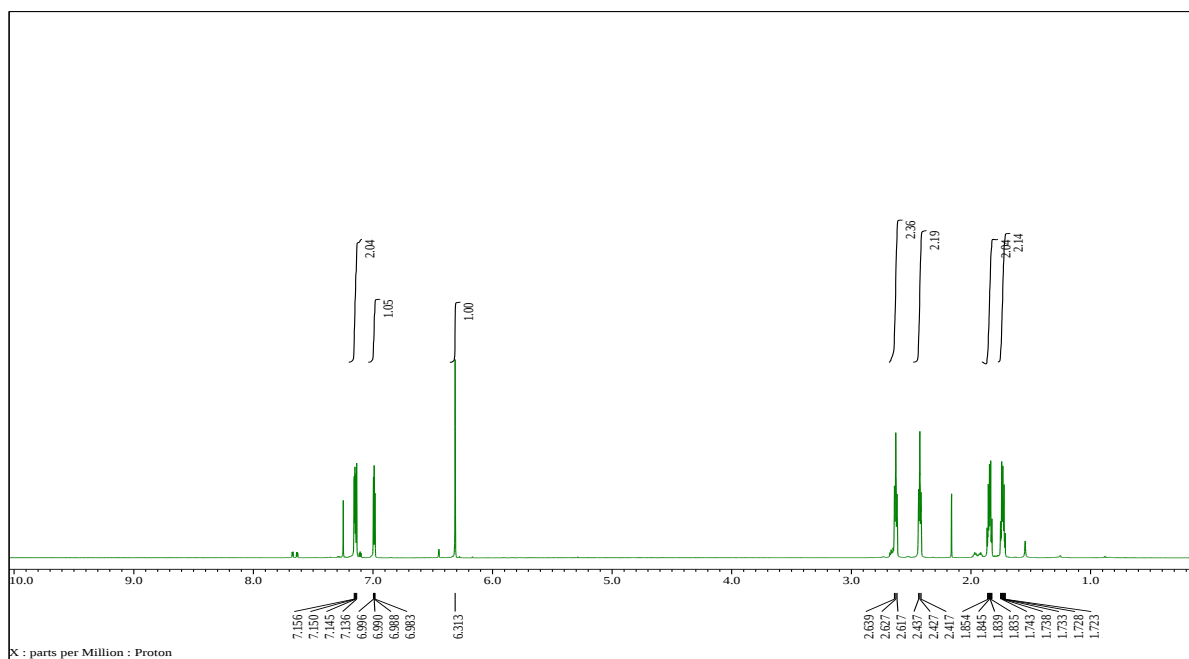


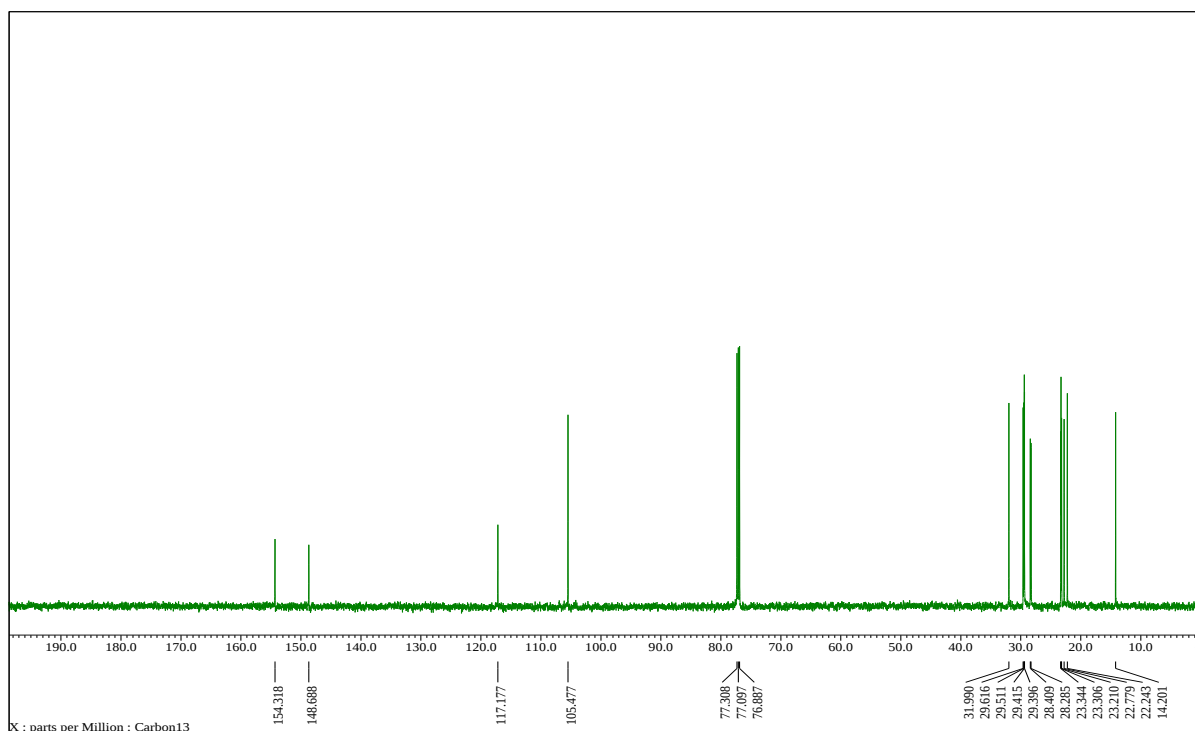
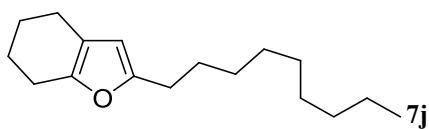
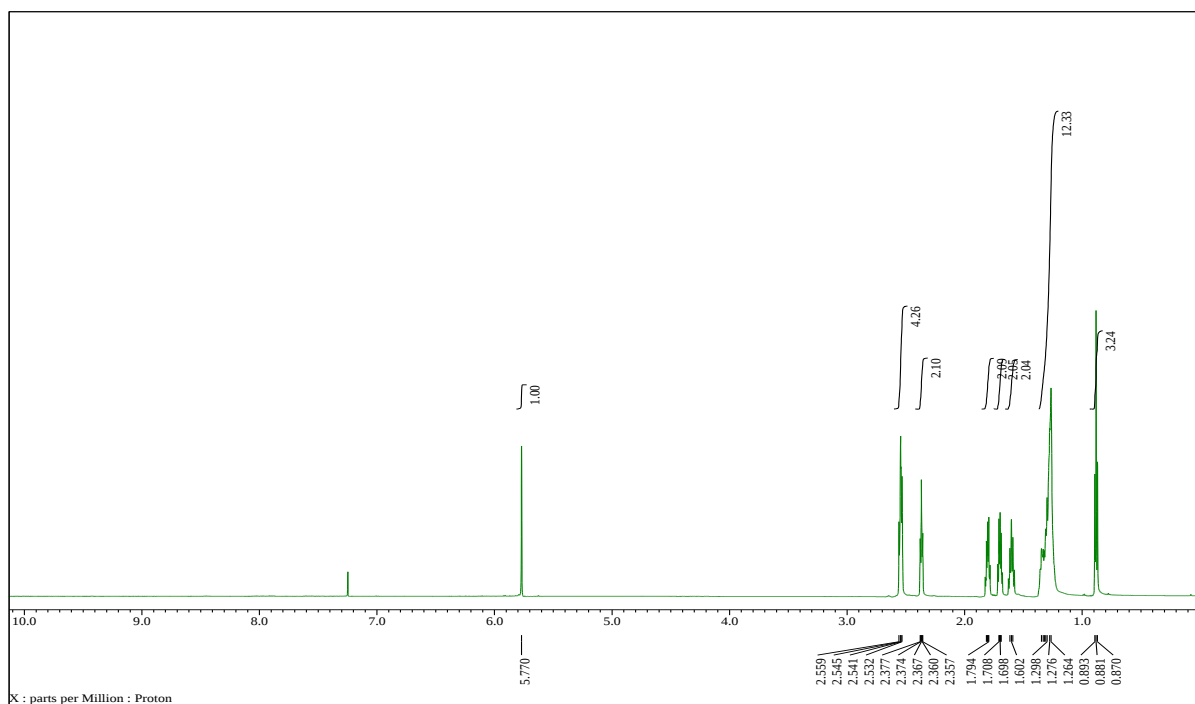


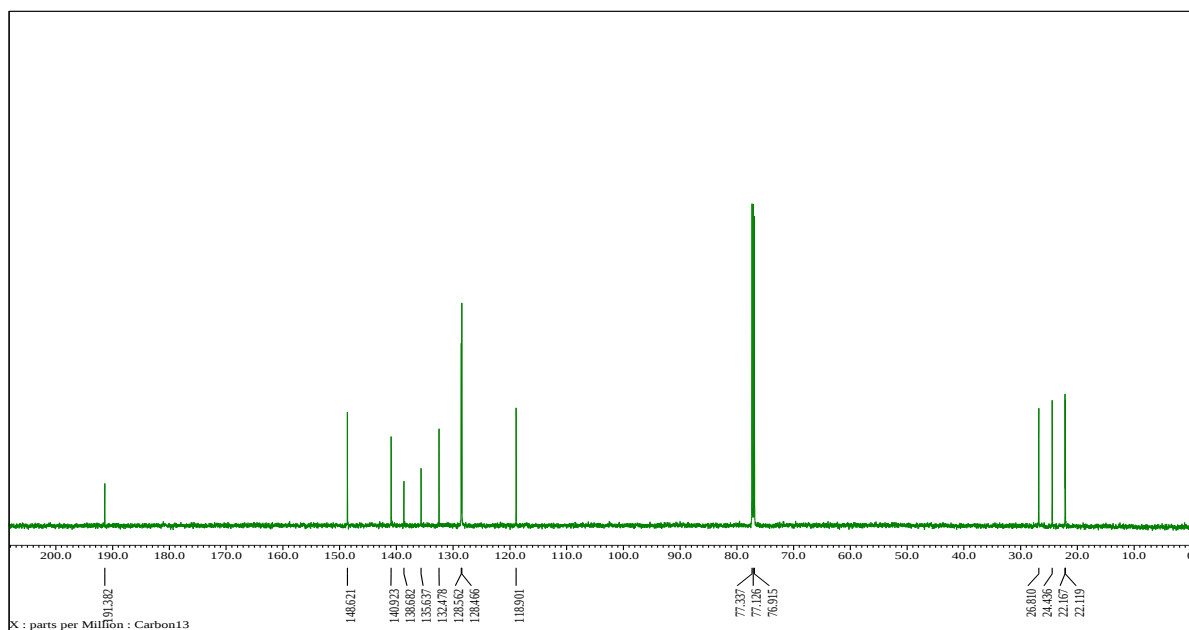
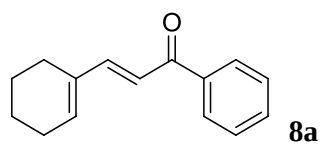
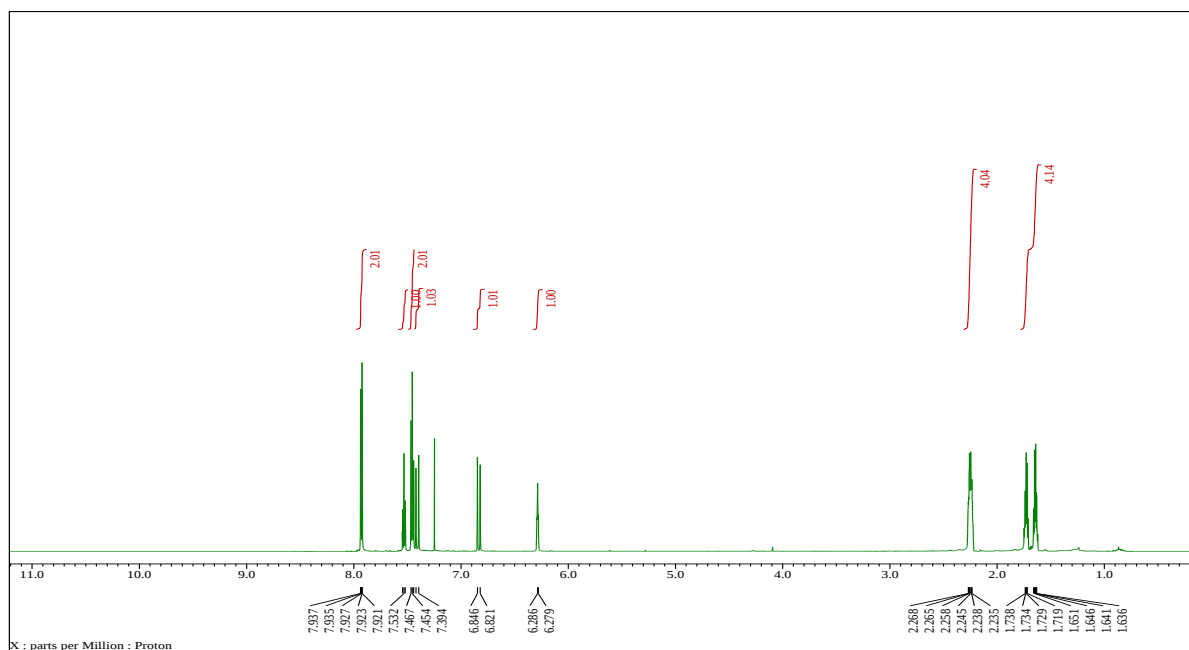


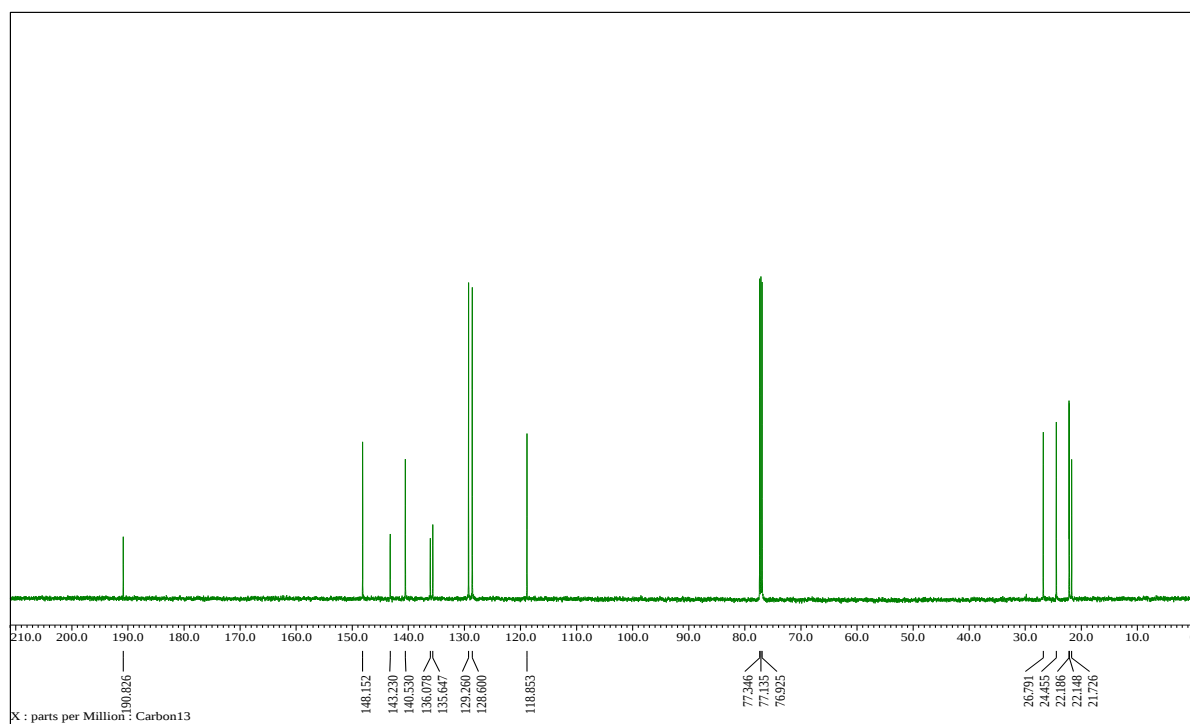
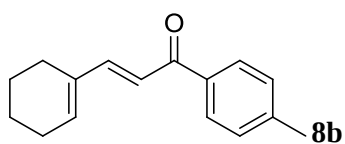
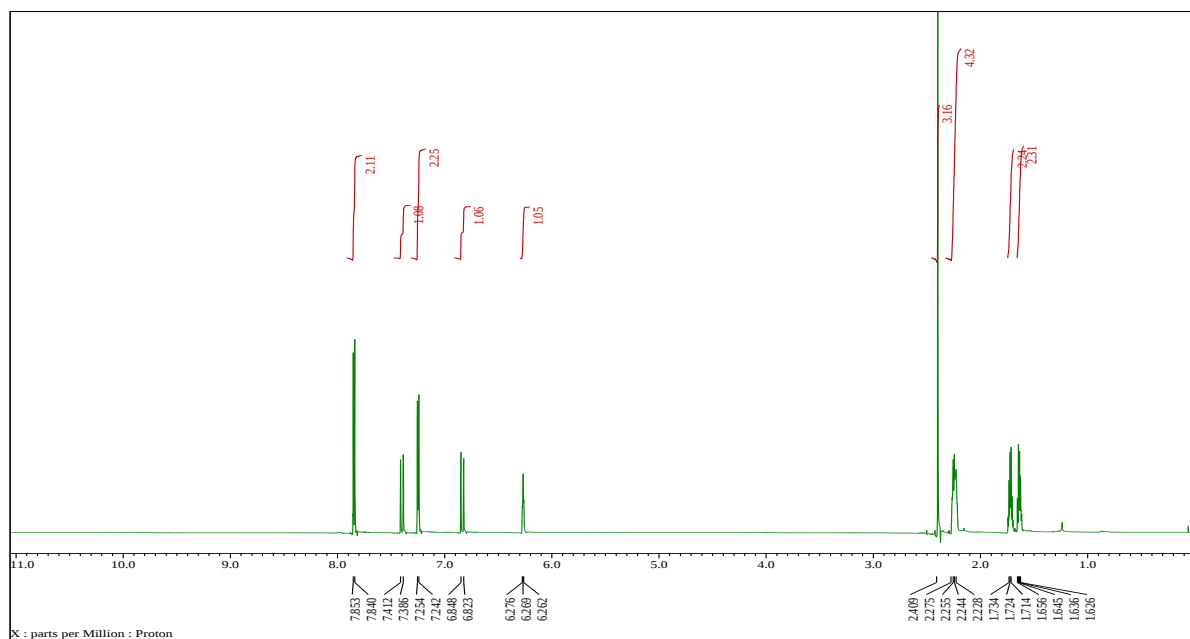


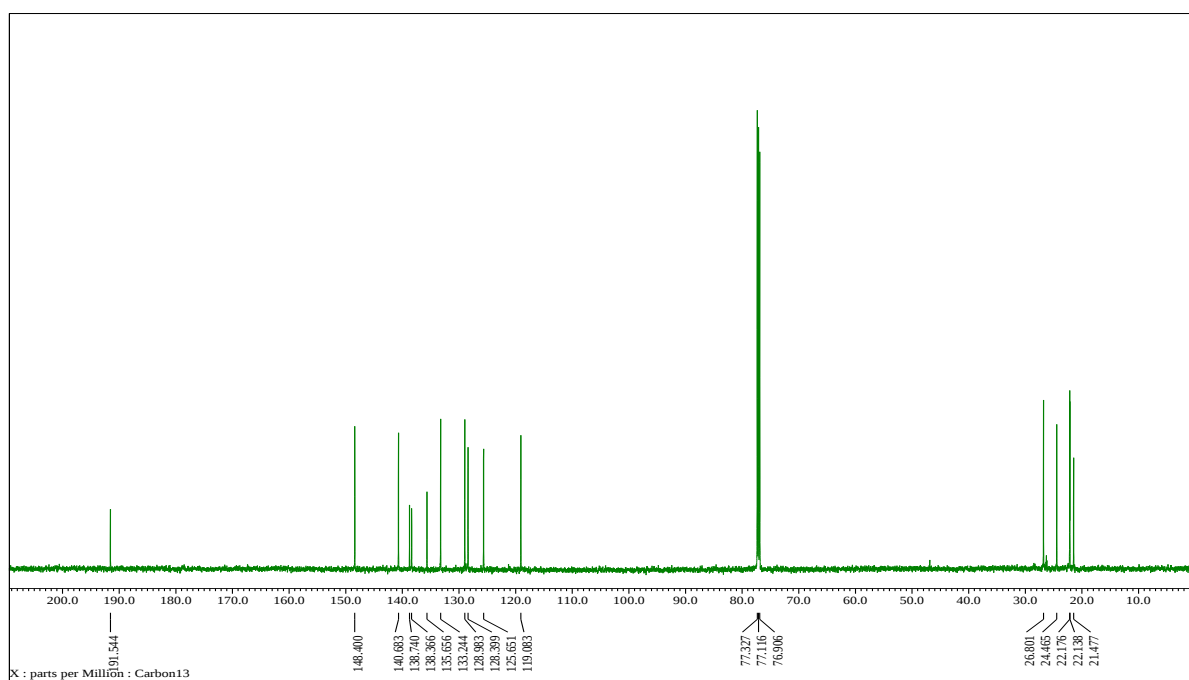
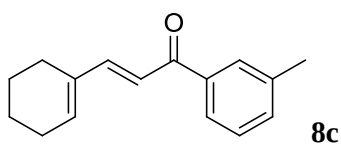
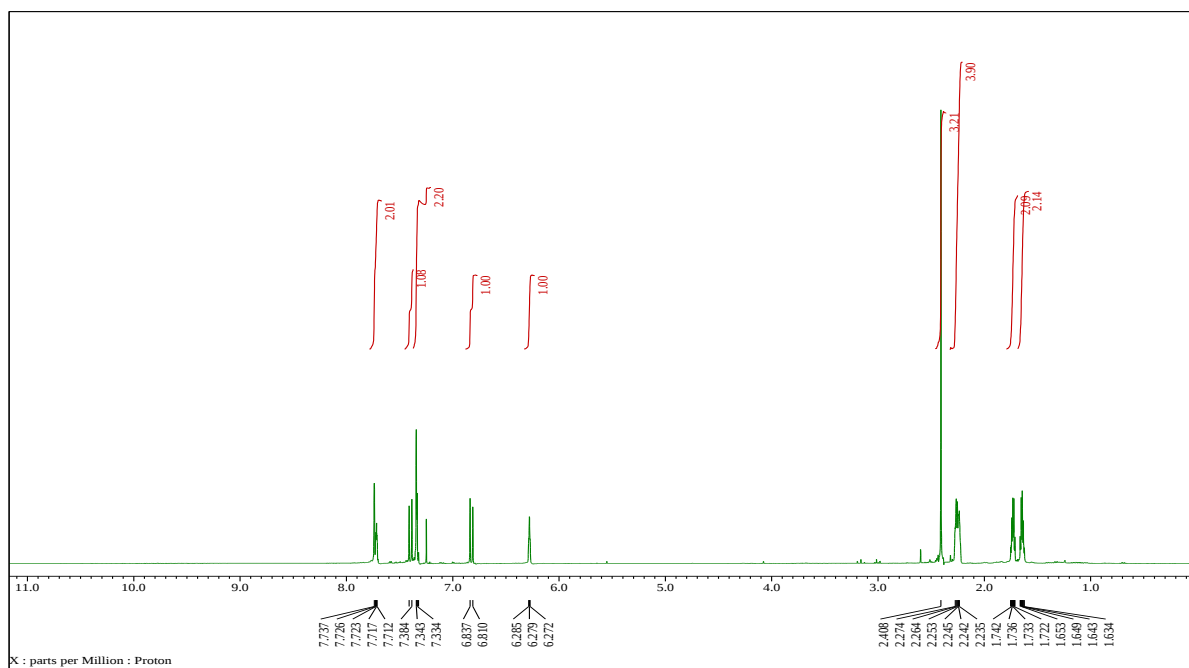


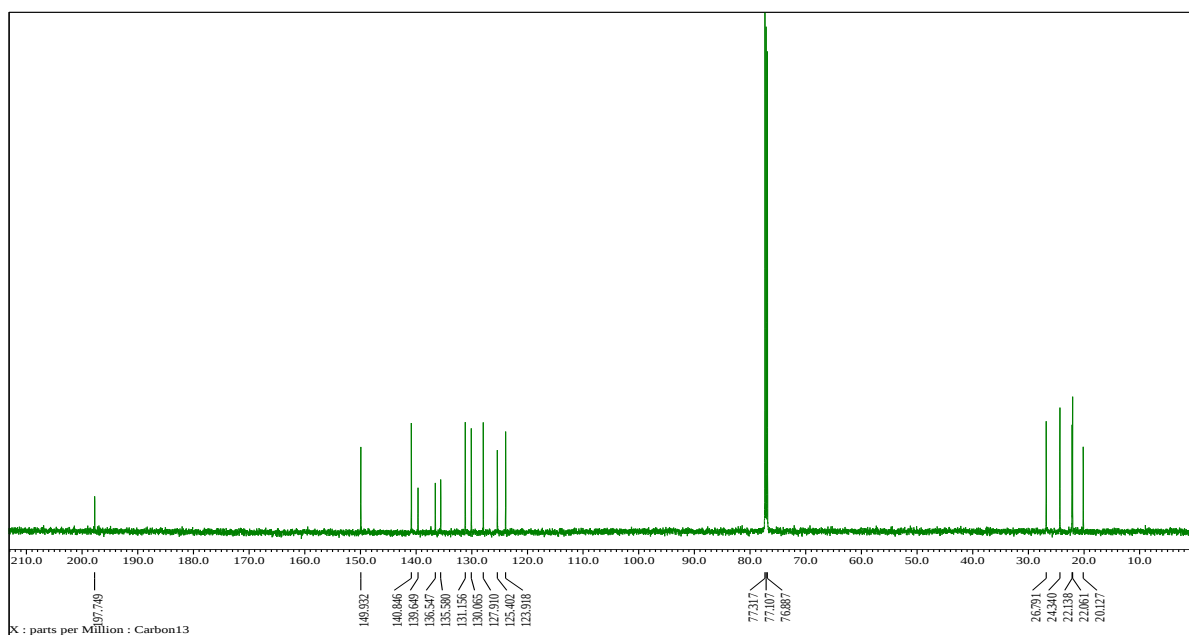
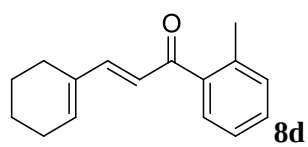
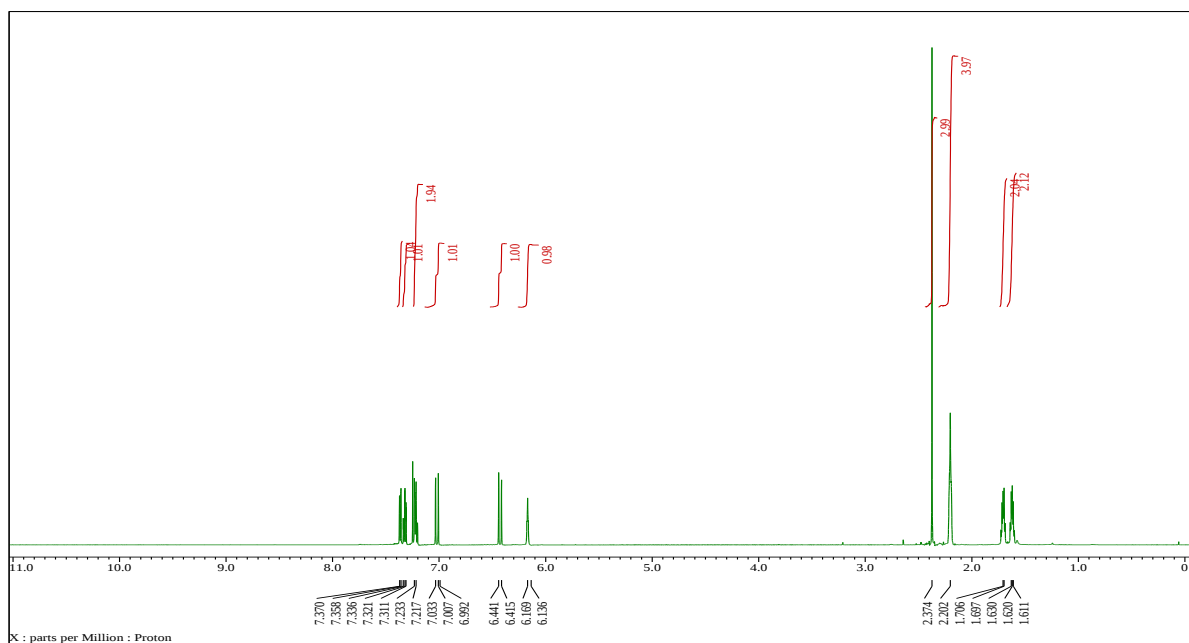


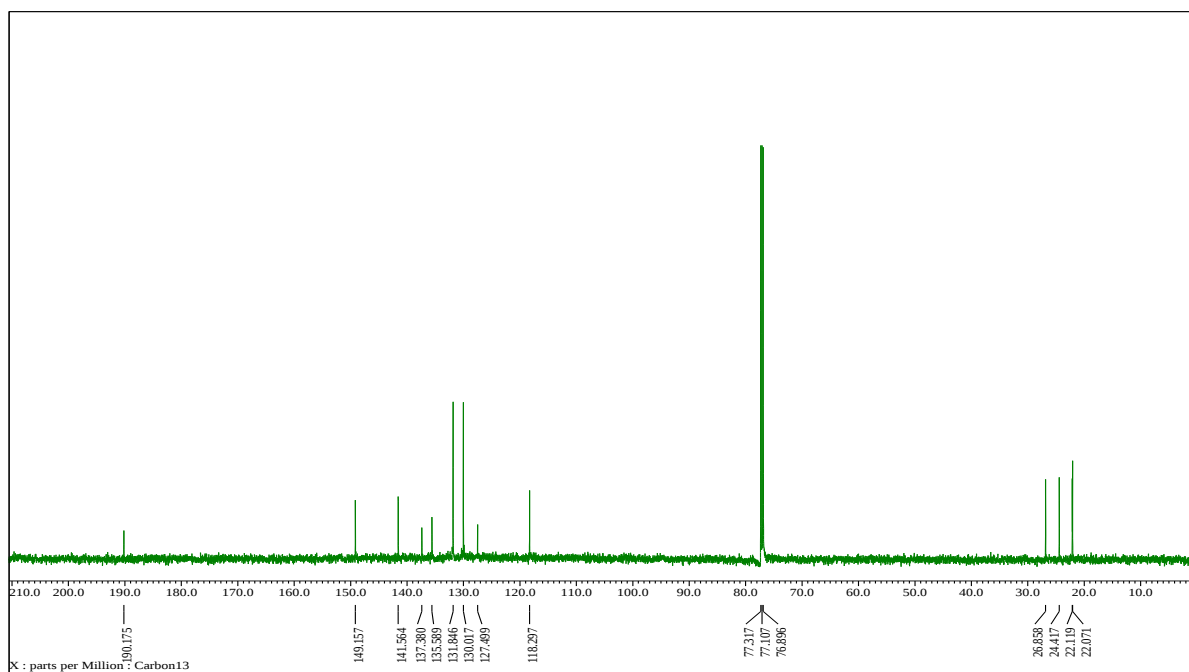
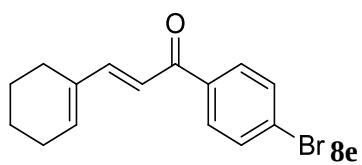
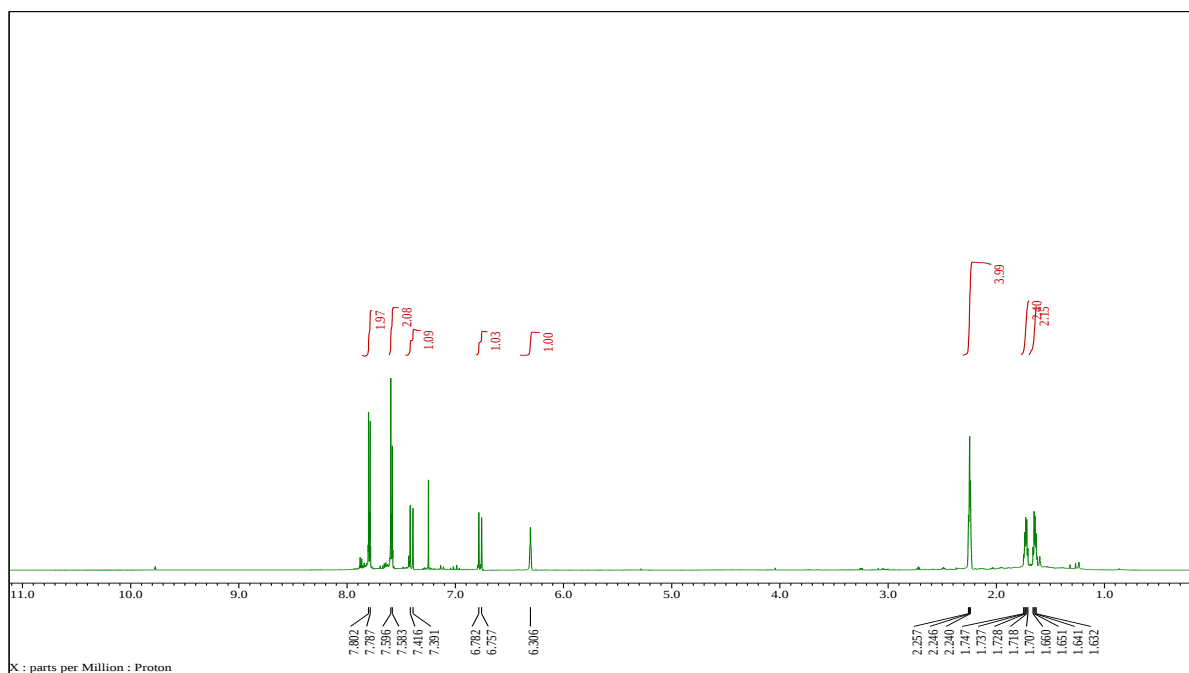


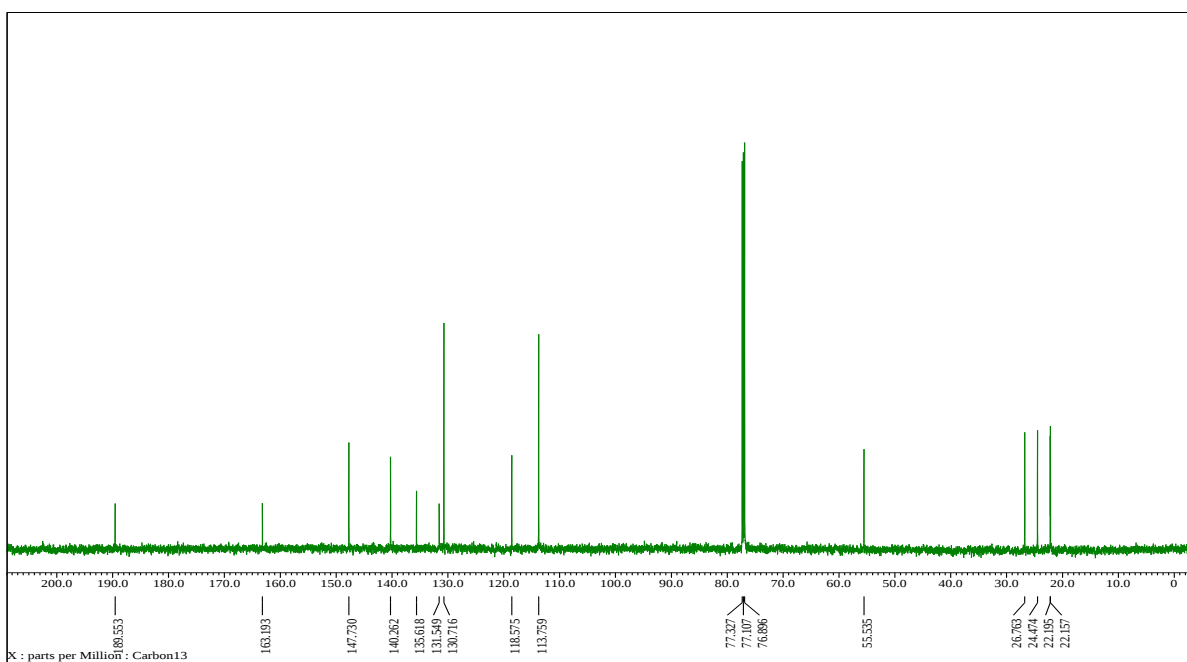
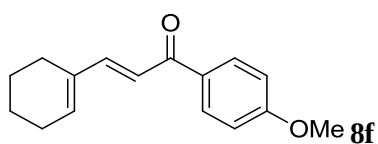
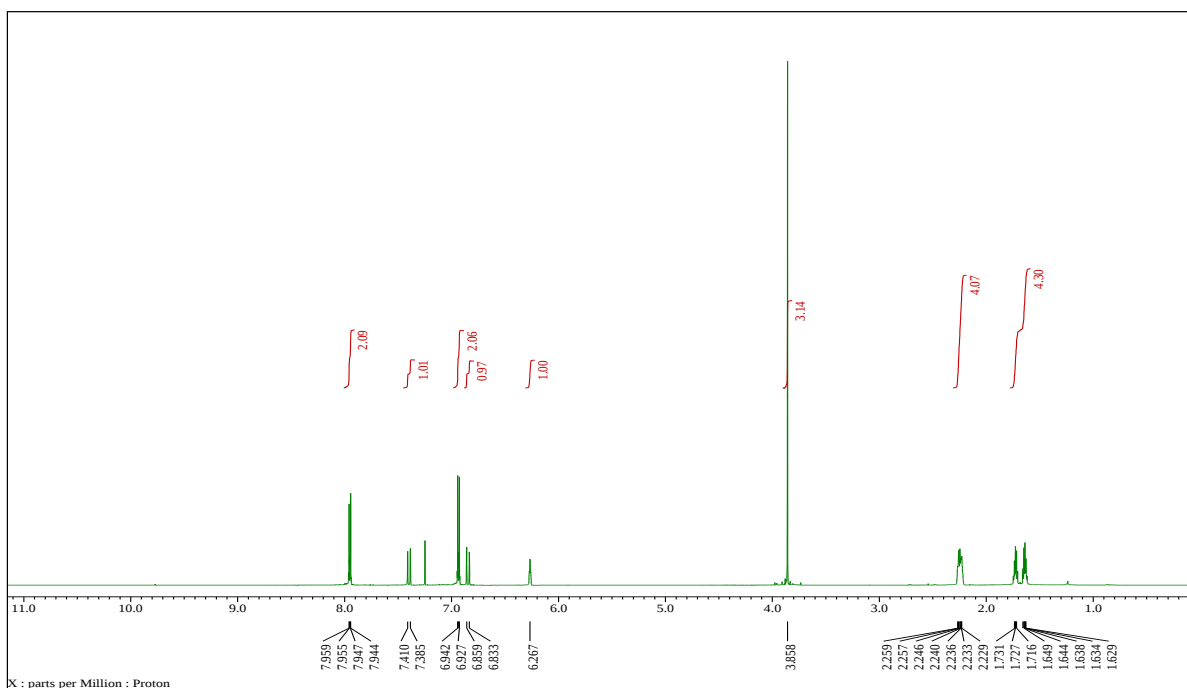


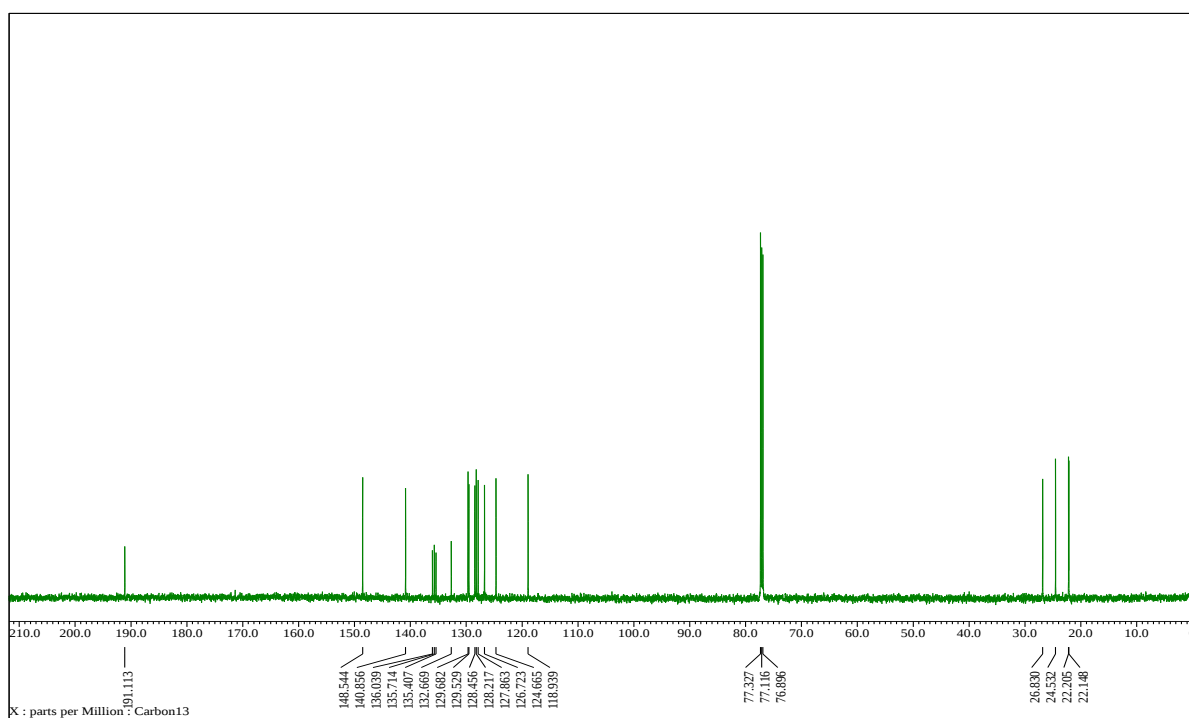
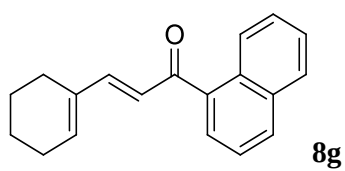
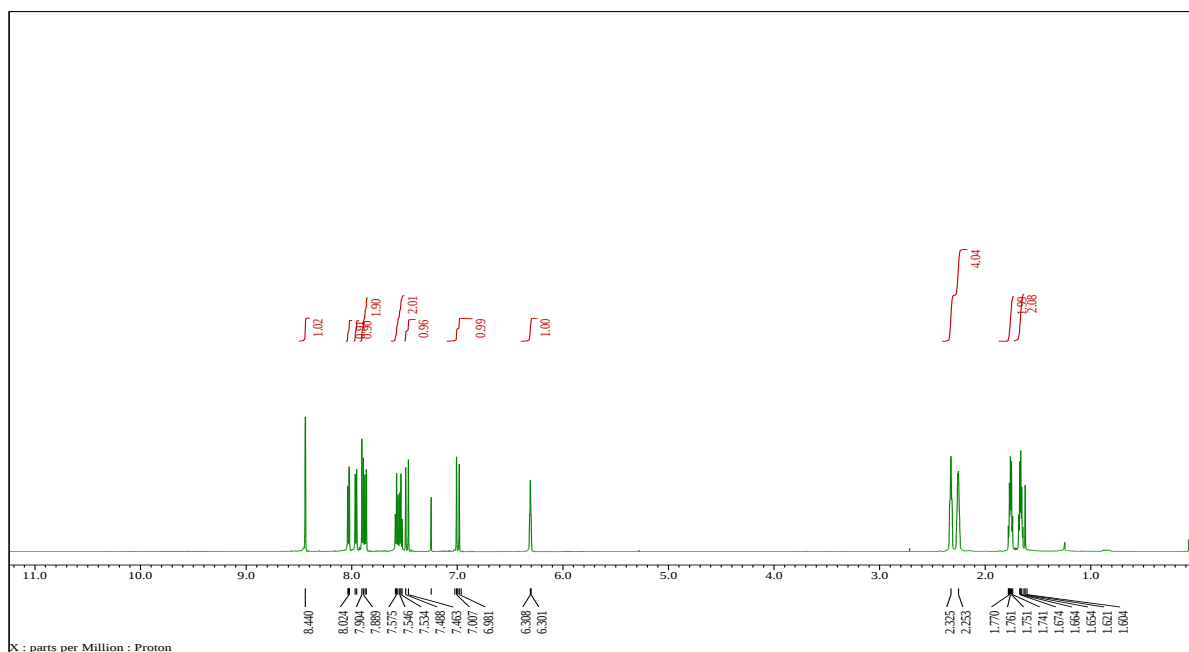


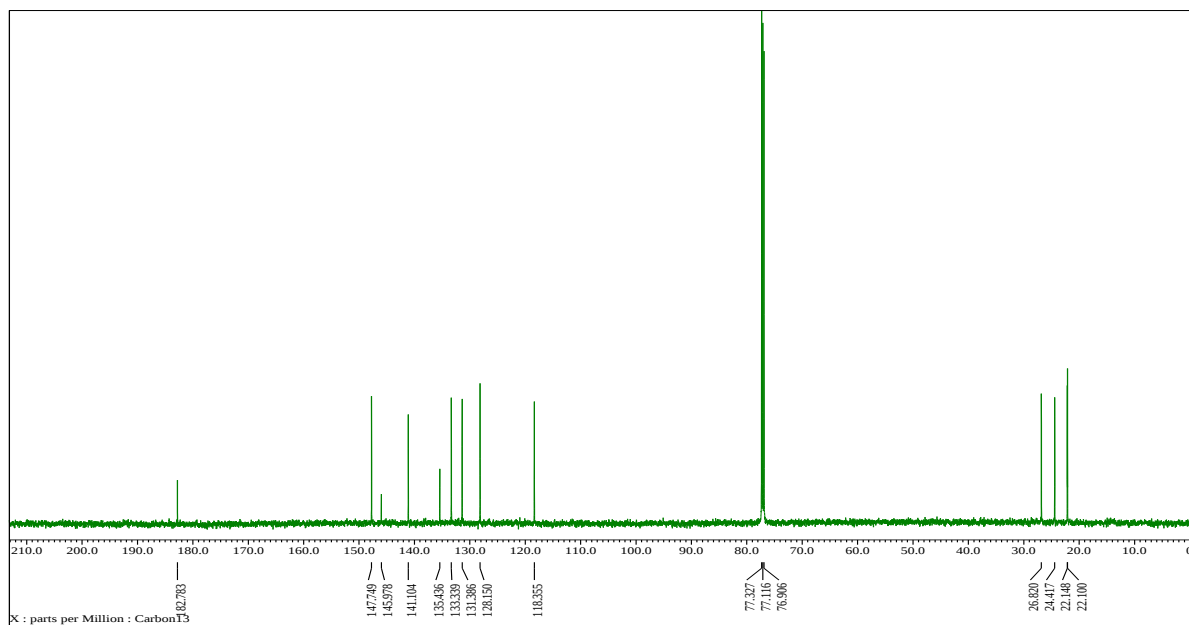
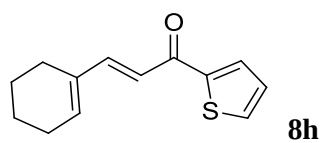
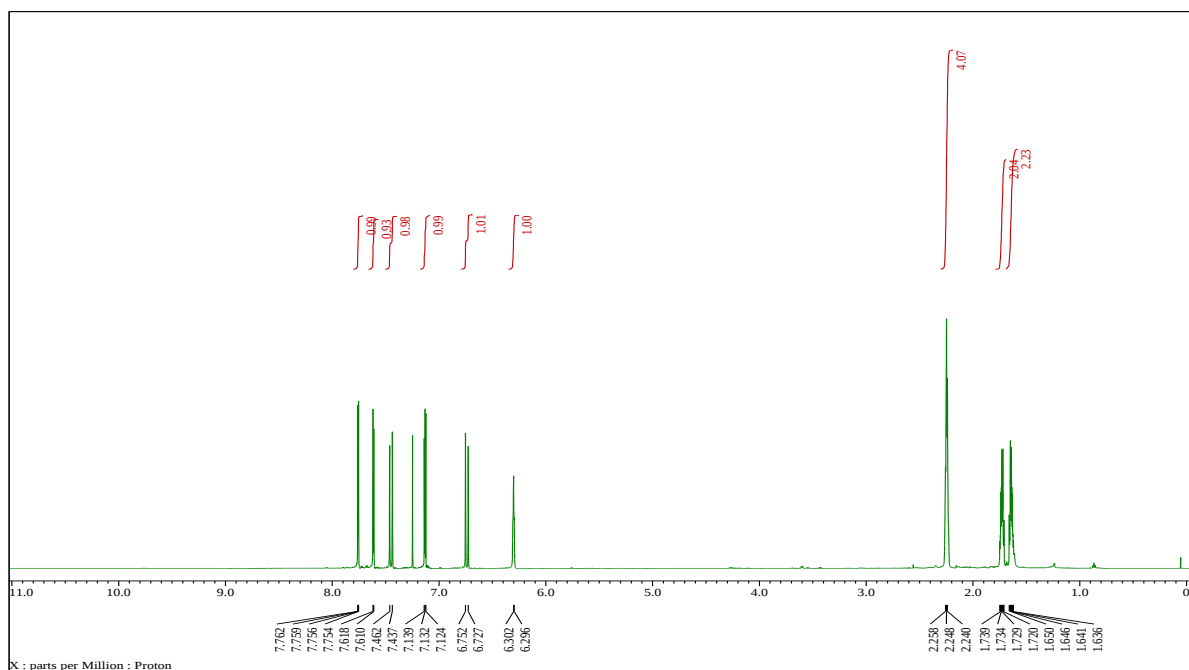


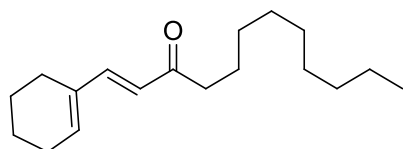
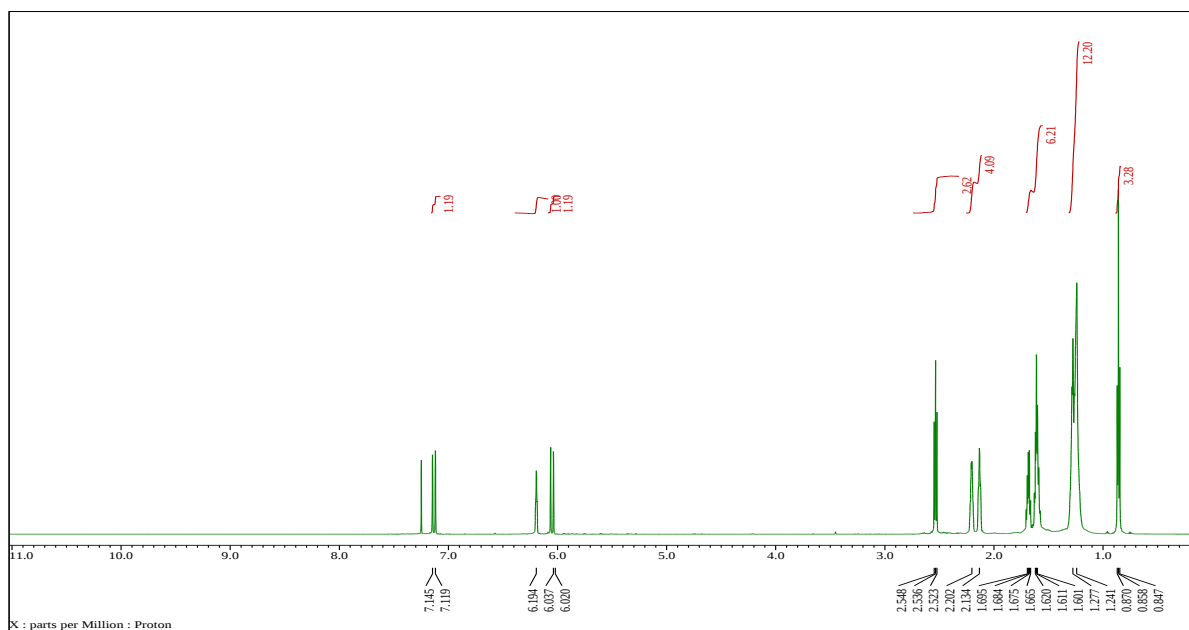




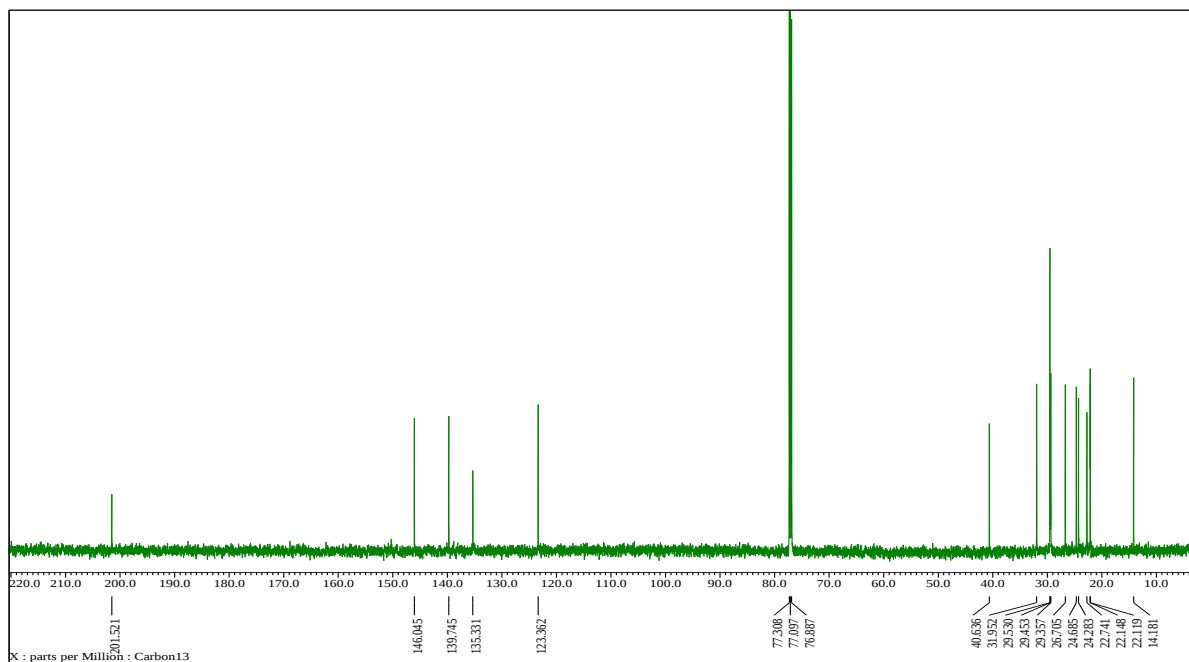


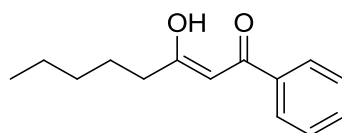
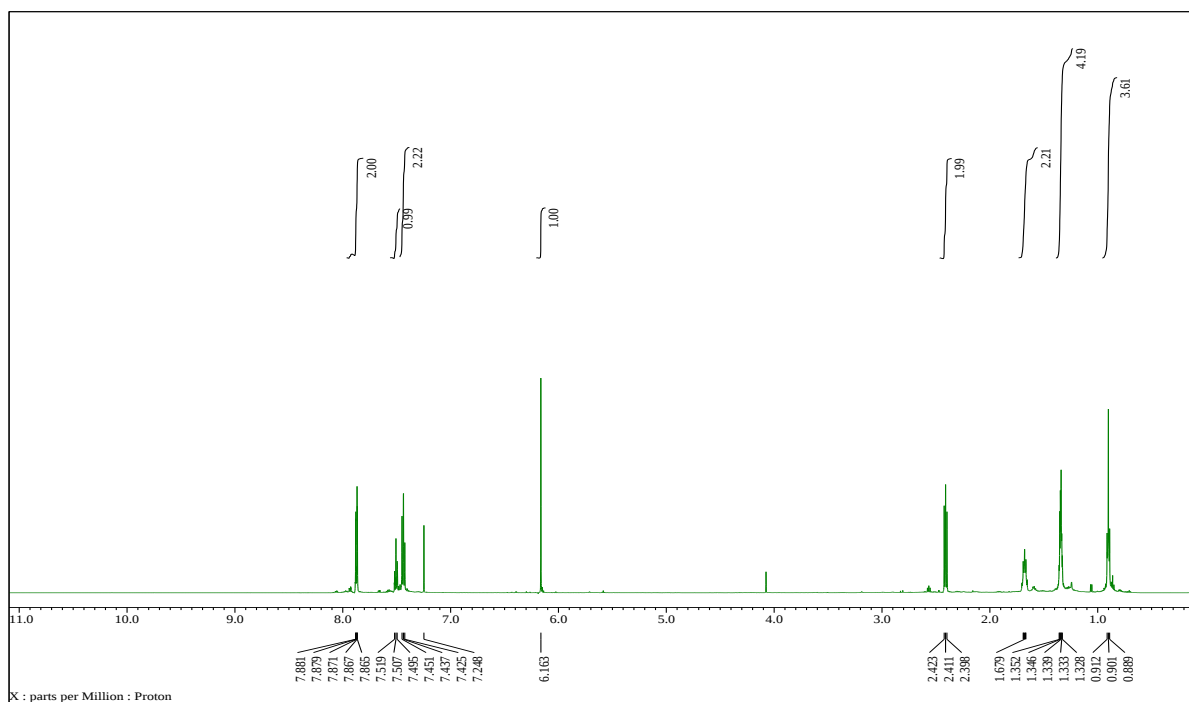




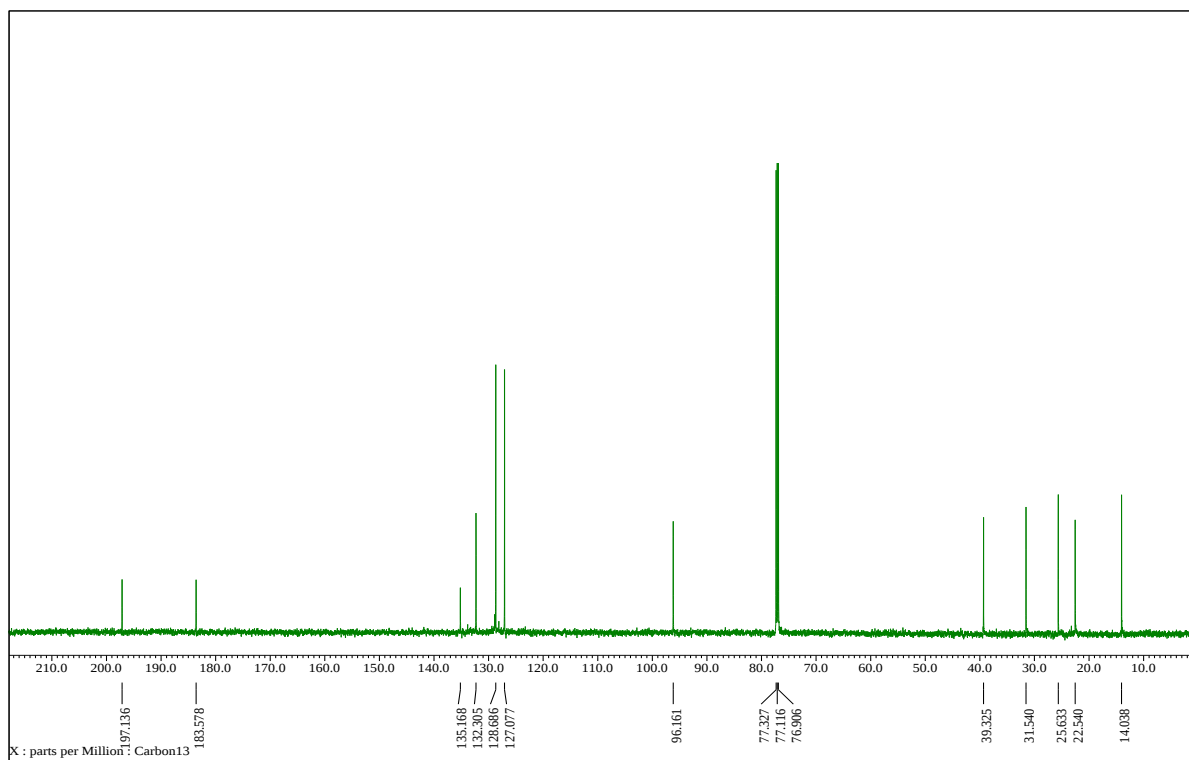


8i

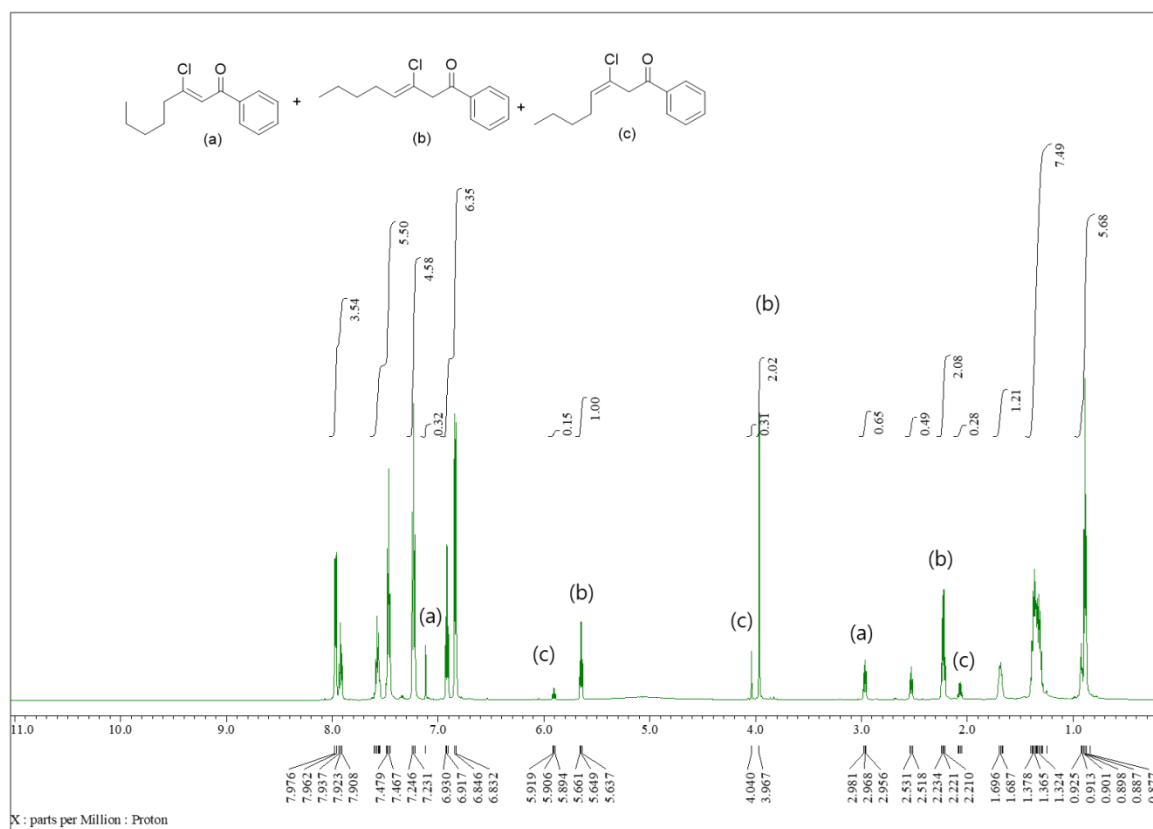




4a (in Table S-1)



Crude ^1H NMR (2a Z(b)/E(c)) in Table S-1



Stereochemistry Determination

