Electronic Supplementary Information (ESI)

A Facile and Efficient Method for the Synthesis of Alkynone by Carbonylative Sonogashira Coupling Using $CHCl_3$ as CO Source

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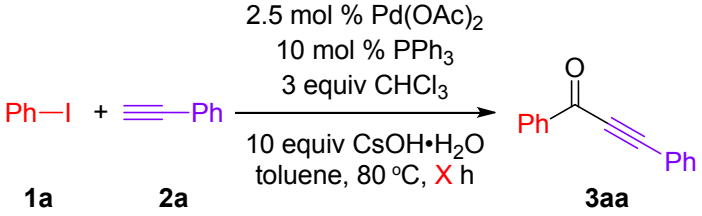
1. General Information

All reactions were performed in flame-dried glassware using sealed tube. Liquids and solutions were transferred with syringes. All solvents and chemical reagents were obtained from commercial sources and used without further purifications. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal reference at 400 MHz and 101 MHz, respectively. Spectra were referenced to the residual solvent peak of $CDCl_3$ unless otherwise noted. Low and high-resolution mass spectra were obtained in the ESI mode. Flash column chromatography on silica gel (200-300 mesh) was used for the routine purification of reaction products. The column output was monitored by analytical thin-layer chromatography (TLC) on silica gel (100-200 mesh) precoated on glass plates (15 x 50 mm), and spots were visualized by ultraviolet light at 254 or 365 nm. Melting points were recorded on a WRS-1B melting point apparatus and are corrected. Commercially available chemicals were obtained from *Acros Organics, Strem Chemicals, Alfa Aesar, Adamas-beta, J&K and TCI*.

2. Select Optimization Results

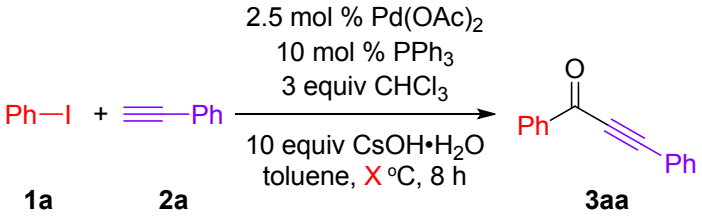
Table S1. Time Screen.[a]



Entry	Time (h)	Yield (%) **3aa**[b]
1	1	60
2	2	73
3	3	78
4	5	82
5	**8**	**96**
6	12	96

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) were stirred in toluene (3 mL) at 80 °C. [b]Yields were determined by LC-MS.

Table S2. Temperature Screen.[a]

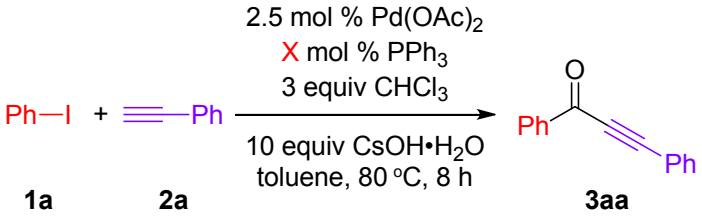


Entry	Temperature (°C)	Yield (%) **3aa**[b]
1	20	0
2	40	18
3	60	75
4	**80**	**96**
5	100	85

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) were stirred in toluene (3 mL) for 8 h. [b]Yields were determined by LC-

MS.

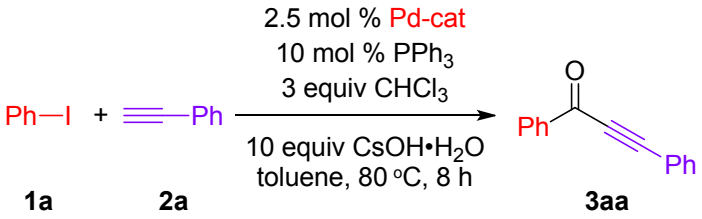
Table S3. Ligand Equivalencies Screen.[a]



Entry	Ligand (mol %)	Yield (%) **3aa**[b]
1	0	15
2	5	86
3	**10**	**96**
4	15	93
5	20	92

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (X mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) were stirred in toluene (3 mL) at 80 °C for 8 h. [b]Yields were determined by LC-MS.

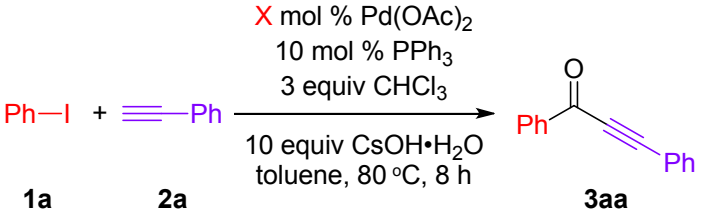
Table S4. Palladium Screen.[a]



Entry	Pd-cat	Yield (%) **3aa**[b]
1	**$Pd(OAc)_2$**	**96**
2	$Pd(CF_3COO)_2$	90
3	$PdSO_4$	54
4	$PdCl_2$	40
5	$Pd_2(dba)_3$	91

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), Pd-cat (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) were stirred in toluene (3 mL) at 80 °C for 8 h. [b]Yields were determined by LC-MS.

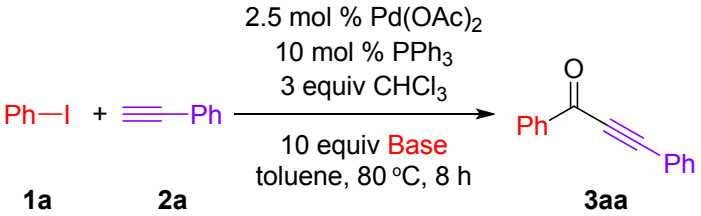
Table S5. Palladium Equivalencies Screen.[a]



Entry	$Pd(OAc)_2$ (mol %)	Yield (%) **3aa**[b]
1	0	0
2	0.5	48
3	1.0	75
4	2.0	88
5	**2.5**	**96**
6	5.0	82

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (X mol %), PPh_3 (10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) were stirred stirred in toluene (3 mL) at 80 °C for 8 h. [b]Yields were determined by LC-MS.

Table S6. Base Screen.[a]

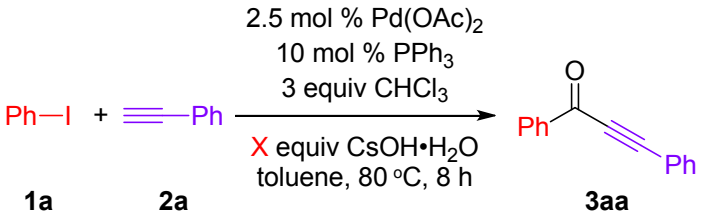


Entry	Base	Yield (%) **3aa**[b]
1	TEA	0
2	K_2CO_3	0
3	LiOH	0
4	NaOH	25
5	KOH	65
6	**$CsOH.H_2O$**	**96**

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and Base (5 mmol, 10 equiv)

were stirred in toluene (3 mL) at 80 °C for 8 h. [b]Yields were determined by LC-MS.

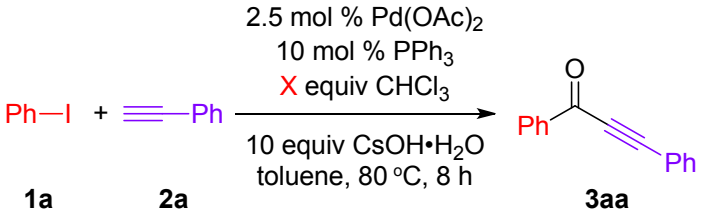
Table S7. Base Equivalencies Screen.[a]



Entry	Equiv $CsOH·H_2O$	Yield (%) **3aa**[b]
1	0	0
2	4	32
3	7	67
4	**10**	**96**
5	15	90
6	20	85

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), and $CsOH·H_2O$ (**0.5X** mmol, **X** equiv) were stirred in toluene (3 mL) at 80 °C for 8 h. [b]Yields were determined by LC-MS.

Table S8. $CHCl_3$ Equivalencies Screen.[a]

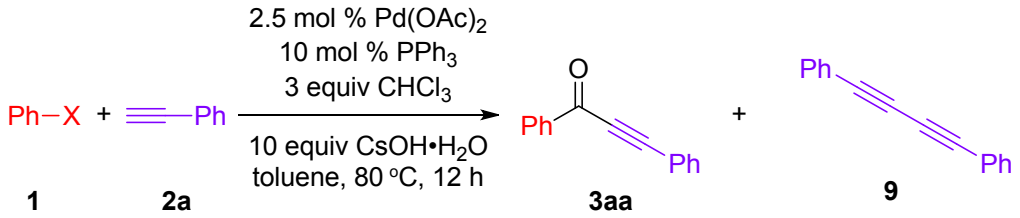


Entry	Equiv $CHCl_3$	Yield (%) **3aa**[b]
1	0	0
2	1	30
3	2	69
4	**3**	**96**
5	6	91
6	15	80
7	30	74

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (**0.5X** mmol, **X** equiv), and $CsOH·H_2O$ (**5** mmol, **10**

equiv) were stirred in toluene (3 mL) at 80 °C for 8 h. [b]Yields were determined by LC-MS.

Table S9. Leaving groups studies.[a]



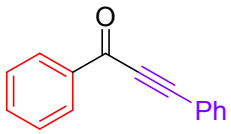
Entry	X	Yield (%) **3aa**[b]	Yield (%) **9**[b]
1	TsO-	0	70
2	TfO-	0	70
3	Br-	0	75
4	Cl-	0	75

[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (2.5 mol %), PPh_3 (10 mol %), $CHCl_3$ (**1.5** mmol, **3** equiv), and $CsOH{\cdot}H_2O$ (**5** mmol, **10** equiv) were stirred in toluene (3 mL) at 80 °C for 12 h. [b]Yields were determined by LC-MS.

3. Experimental procedure and data for compounds

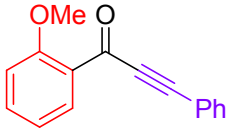
General procedure for 3. In a flame-dried glassware, a 10 mL reaction vial equipped with a stir bar was charged with **1** (0.5 mmol, 1 equiv) and **2** (0.6 mmol, 1.2 equiv), $Pd(OAc)_2$ (3.0 mg, 2.5 mol %), PPh_3 (13.1 mg, 10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) and toluene (3.0 mL). The reaction was then sealed, and heated to 80 °C with stirring until the starting material disappeared (by LC/MS). After cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10/1) as the eluent to afford the corresponding products **3**.

1,3-diphenylpropynone (3aa):



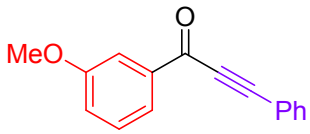
The product was obtained as a yellow solid in 91% yield; mp = 43-44 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.0, 136.9, 134.1, 133.1 (2C), 130.8, 129.6 (2C), 128.7 (2C), 128.6 (2C), 120.1, 93.1, 86.9. **ESI-MS**: m/z 207.5 $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{11}O$, 207.0804; found 207.0809.

1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (3ba):



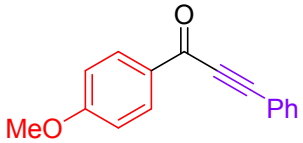
The product was obtained as a yellow solid in 90% yield; mp = 79-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.54-7.58 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.03-7.09 (m, 2H), 3.98 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.7, 159.8, 135.1, 132.9 (2C), 132.6, 130.5, 128.6 (2C), 126.7, 120.6, 120.3, 112.2, 91.6, 89.2, 55.9. **ESI-MS** m/z 237.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{13}O_2$, 237.0910; found 237.0904.

1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-one (3ca):



The product was obtained as a yellow solid in 91% yield; mp = 60-61 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.69-7.72 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41-7.46 (m, 3H), 7.19 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.7, 159.8, 138.2, 133.1 (2C), 130.8, 129.7, 128.7 (2C), 122.8, 120.9, 120.0, 112.8, 93.0, 87.0, 55.4. **ESI-MS** m/z 237.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{13}O_2$, 237.0910; found 237.0904.

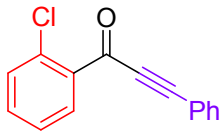
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (3da):



The product was obtained as a white solid in 93% yield; mp = 93-94 °C. **^{1}H**

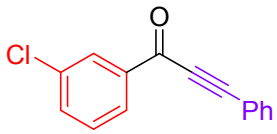
NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.6, 164.5, 132.9 (2C), 132.0 (2C), 130.6, 130.3, 128.6 (2C), 120.3, 113.9 (2C), 92.3, 86.9, 55.6. **ESI-MS** m/z 237.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{13}O_2$, 237.0910; found 237.0915.

1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (3ea):



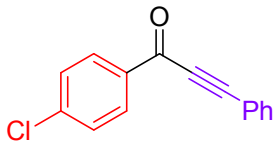
The product was obtained as a yellow solid in 82% yield; mp = 101-102 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.48-7.52 (m, 3H), 7.41-7.45 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.8, 135.8, 133.5, 133.4, 133.1 (2C), 132.6, 131.5, 131.0, 128.7 (2C), 126.8, 120.0, 93.9, 88.3. **ESI-MS** m/z 241.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}ClO$, 241.0415; found 241.0420.

1-(3-chlorophenyl)-3-phenylprop-2-yn-1-one (3fa):



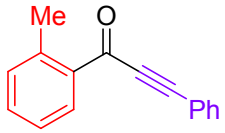
The product was obtained as a yellow solid in 88% yield; mp = 89-90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (t, *J* = 1.6 Hz, 1H), 8.13 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.72 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.63 (dq, *J* = 8.0, 1.2 Hz, 1H), 7.44-7.55 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.5, 138.3, 134.9, 134.0, 133.1 (2C), 131.1, 130.0, 129.4, 128.7 (2C), 127.7, 119.7, 93.9, 86.5. **ESI-MS** m/z 241.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}ClO$, 241.0415; found 241.0413.

1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (3ga):



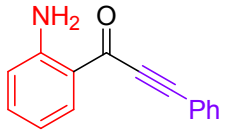
The product was obtained as a yellow solid in 89% yield; mp = 105-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.71 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.51-7.55 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.6, 140.7, 135.3, 133.1 (2C), 131.0, 130.8 (2C), 129.0 (2C), 128.7 (2C), 119.8, 93.6, 86.6. **ESI-MS** m/z 241.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}ClO$, 241.0415; found 241.0410.

1-(2-methylphenyl)-3-phenylprop-2-yn-1-one (3ha):



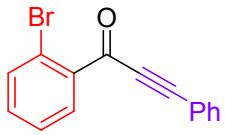
The product was obtained as a light yellow solid in 90% yield; mp = 71-72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.71 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.47-7.51 (m, 2H), 7.37-7.45 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 179.8, 140.5, 135.7, 133.2, 132.9 (2C), 132.2, 130.6, 130.2, 128.6 (2C), 125.9, 120.3, 91.8, 88.3, 21.9. **ESI-MS** m/z 221.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{13}O$, 221.0961; found 221.0966.

1-(2-aminophenyl)-3-phenylprop-2-yn-1-one (3ia):



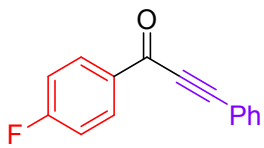
The product was obtained as a orange solid in 80% yield; mp = 63-64 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.71 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.41-7.50 (m, 3H), 7.32-7.36 (m, 1H), 6.73-6.77 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 179.5, 151.1, 135.3, 134.4, 132.8 (2C), 130.4, 128.6 (2C), 120.5, 118.8, 116.8, 116.1, 92.3, 87.1. **ESI-MS**: m/z 222.6 $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{12}NO$, 222.0913; found 222.0919.

1-(2-bromophenyl)-3-phenylprop-2-yn-1-one (3ja):



The product was obtained as a yellow solid in 80% yield; mp = 104-105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.38-7.52 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.5, 137.5, 134.9, 133.4, 133.1 (2C), 132.7, 131.0, 128.7 (2C), 127.4, 121.2, 119.9, 94.2, 87.9. **ESI-MS** m/z 285.4, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}BrO$, 284.9910; found 284.9918.

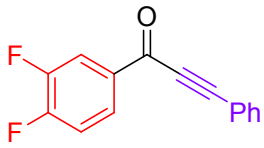
1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one (3ka):



The product was obtained as a yellow solid in 87% yield; mp = 60-62 °C. **^{1}H**

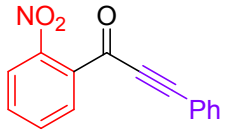
NMR (400 MHz, $CDCl_3$) δ 8.25-8.29 (m, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.3, 167.7 and 165.1 (d, $^1J_{CF}$ = 255.0 Hz, 1C), 133.4 and 133.4 (d, $^4J_{CF}$ = 2.2 Hz, 1C), 133.0 (2C), 132.3 and 132.2 (d, $^3J_{CF}$ = 9.6 Hz, 2C), 130.9, 128.7 (2C), 119.9, 115.9 and 115.7 (d, $^2J_{CF}$ = 21.9 Hz, 2C), 93.3, 86.6. **ESI-MS** m/z 225.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}FO$, 225.0710; found 225.0714.

1-(3,4-difluorophenyl)-3-phenylprop-2-yn-1-one (3la):



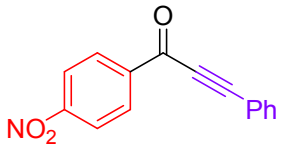
The product was obtained as a yellow solid in 88% yield; mp = 118-119 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-8.06 (m, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.30-7.37 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 175.3, 155.7 and 155.5 and 153.1 and 153.0 (dd, $^1J_{CF}$ = 257.2, 12.9 Hz, 1C), 151.7 and 151.5 and 149.2 and 149.1 (dd, $^1J_{CF}$ = 249.9, 13.2 Hz, 1C), 134.0 and 134.0 and 134.0 and 133.9 (dd, $^3J_{CF}$ = 7.4, 3.6 Hz, 1C), 133.1 (2C), 131.1, 128.7 (2C), 126.7 and 126.7 and 126.7 and 126.6 (dd, $^3J_{CF}$ = 7.7, 3.5 Hz, 1C), 118.5 and 118.4 and 118.3 and 118.3 (dd, $^2J_{CF}$ = 18.3, 1.4 Hz, 1C), 117.7 and 117.7 and 117.5 and 117.5 (dd, $^2J_{CF}$ = 17.9, 1.0 Hz, 1C), 94.0, 88.2. **ESI-MS** m/z 243.5, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_9F_2O$, 243.0616; found 243.0621.

1-(2-nitrophenyl)-3-phenylprop-2-yn-1-one (3ma):



The product was obtained as a yellow solid in 78% yield; mp = 143-144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.59-7.63 (m, 3H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38-7.42 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.3, 149.5, 134.6, 132.8, 132.0 (2C), 129.2, 128.6, 128.5 (2C), 124.7, 122.4, 118.7, 97.1, 84.8. **ESI-MS** m/z 252.5, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}NO_3$, 252.0655; found 252.0650.

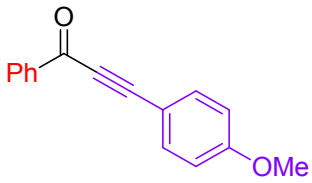
1-(4-nitrophenyl)-3-phenylprop-2-yn-1-one (3na):



The product was obtained as a yellow solid in 84% yield; mp = 161-162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37-8.42 (m, 4H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.56 (t,

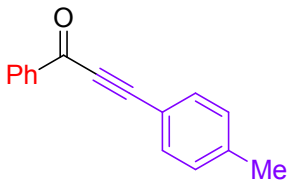
J = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 175.8, 150.8, 141.0, 133.3 (2C), 131.4, 130.4 (2C), 128.8 (2C), 123.8 (2C), 119.4, 95.4, 86.5. **ESI-MS** m/z 252.5, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}NO_3$, 252.0655; found 252.0659.

1-phenyl-3-(4-methoxyphenyl)prop-2-yn-1-one (3ab):



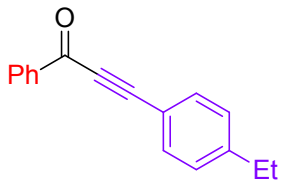
The product was obtained as a yellow solid in 92% yield; mp = 80-81 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.62-7.69 (m, 3H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.0, 161.7, 137.0, 135.1 (2C), 133.9, 129.5 (2C), 128.5 (2C), 114.4 (2C), 111.8, 94.3, 86.9, 55.4. **ESI-MS** m/z 237.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{13}O_2$, 237.0910; found 237.0905.

1-phenyl-3-(4-methylphenyl)prop-2-yn-1-one (3ac):



The product was obtained as a yellow solid in 88% yield; mp = 69-70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.0, 141.6, 136.9, 134.0, 133.1 (2C), 129.6 (2C), 129.5 (2C), 128.6 (2C), 117.0, 93.8, 86.8, 21.8. **ESI-MS** m/z 221.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{13}O$, 221.0961; found 221.0966.

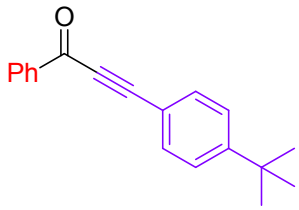
1-phenyl-3-(4-ethylphenyl)prop-2-yn-1-one (3ad):



The product was obtained as a yellow solid in 90% yield; mp = 77-78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.6 Hz, 2H), 7.63-7.67 (m, 3H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.0, 147.8, 137.0, 134.0, 133.2 (2C), 129.5 (2C), 128.6 (2C), 128.3 (2C), 117.2, 93.9, 86.8, 29.0, 15.2. **ESI-MS** m/z 235.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{17}H_{15}O$, 235.1117;

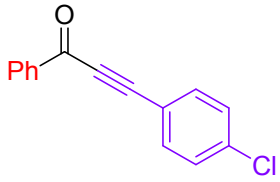
found 235.11121.

1-phenyl-3-(4-tert-butylphenyl)prop-2-yn-1-one (3ae):



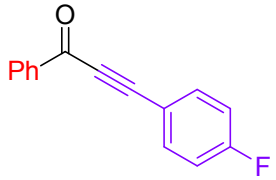
The product was obtained as a yellow solid in 91% yield; mp = 90-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.6 Hz, 2H), 7.63-7.67 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.1, 154.6, 137.0, 134.0, 133.0 (2C), 129.5 (2C), 128.6 (2C), 125.7 (2C), 117.0, 93.8, 86.7, 35.1, 31.0 (3C). **ESI-MS** m/z 263.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{19}H_{19}O$, 263.1430; found 263.1435.

1-phenyl-3-(4-chlorophenyl)prop-2-yn-1-one (3af):



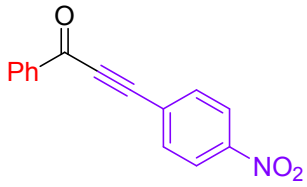
The product was obtained as a white solid in 86% yield; mp = 106-107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.63-7.69 (m, 3H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.7, 137.2, 136.7, 134.2 (3C), 129.5 (2C), 129.1 (2C), 128.7 (2C), 118.5, 91.6, 87.6. **ESI-MS** m/z 241.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}ClO$, 241.0415; found 241.0410.

1-phenyl-3-(4-fluorophenyl)prop-2-yn-1-one (3ag):



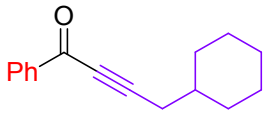
The product was obtained as a yellow solid in 87% yield; mp = 78-79 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25-8.29 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.43-7.54 (m, 3H), 7.21 (t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.9, 165.3 and 162.7 (d, $^1J_{CF}$ = 252.2 Hz, 1C), 136.8 and 133.4 (d, $^3J_{CF}$ = 8.9 Hz, 2C), 134.2, 129.5 (2C), 128.6 (2C), 116.3 and 116.1 (d, $^2J_{CF}$ = 22.2 Hz, 2C), 116.2 and 116.2 (d, $^4J_{CF}$ = 3.6 Hz, 1C), 92.0, 86.8. **ESI-MS** m/z 225.5, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}FO$, 225.0710; found 225.0716.

1-phenyl-3-(4-nitrophenyl)prop-2-yn-1-one (3ah):



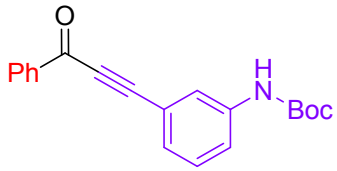
The product was obtained as an orange solid in 89% yield; mp = 147-148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.4, 148.5, 136.3, 134.7, 133.6 (2C), 129.6 (2C), 128.8 (2C), 126.8, 123.8 (2C), 89.8, 89.2. **ESI-MS** m/z 252.5, $[M+Na]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{10}NO_3$, 252.0655; found 252.0660.

1-phenyl-4-cyclohexyl-2-butin-1-one (3ai):



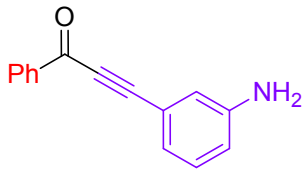
The product was obtained as a yellow liquid in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.42 (d, *J* = 6.8 Hz, 2H), 1.67-1.92 (m, 5H), 1.10-1.32 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.3, 136.9, 133.8, 129.5 (2C), 128.5 (2C), 96.0, 80.6, 36.9, 32.8 (2C), 26.9, 26.1, 26.0 (2C). **ESI-MS** m/z 227.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{16}H_{19}O$, 227.1430; found 227.1436.

1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-one (3aj):



The product was obtained as a yellow solid in 86% yield; mp = 77-78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.46-7.49 (m, 1H), 7.33-7.39 (m, 2H), 6.61 (s, 1H), 1.55 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.0, 152.5, 138.8, 136.8, 134.1, 129.6 (2C), 129.3, 128.6 (2C), 127.6, 122.3, 120.8, 120.7, 92.9, 86.7, 81.0, 28.3 (3C). **ESI-MS** m/z 322.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{20}H_{20}NO_3$, 322.1438; found 322.1444.

1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-one (3ak):

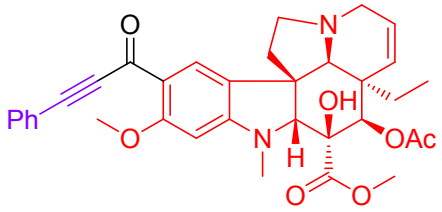


The product was obtained as a yellow solid in 81% yield; mp = 60-61 °C. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09-7.11 (m, 1H), 6.99 (t, *J* = 1.6 Hz, 1H), 6.80-6.82 (m, 1H), 3.83 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.1, 146.6, 136.9, 134.1, 129.7 (2C), 129.6, 128.6 (2C), 123.3, 120.7, 118.8, 117.7, 93.8, 86.3. **ESI-MS** m/z 222.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{12}NO$, 222.0913; found 222.0908.

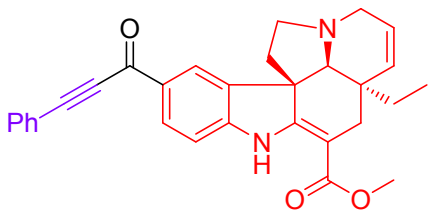
General procedure for 7 and 8. In a flame-dried glassware, a 10 mL reaction vial equipped with a stir bar was charged with **5** or **6** (0.5 mmol, 1 equiv) and **2a** (0.6 mmol, 1.2 equiv), $Pd(OAc)_2$ (3.0 mg, 2.5 mol %), PPh_3 (13.1 mg, 10 mol %), $CHCl_3$ (1.5 mmol, 3 equiv), $CsOH{\cdot}H_2O$ (5 mmol, 10 equiv) and toluene (3.0 mL). The reaction was then sealed, and heated to 80 °C with stirring for 12 h. After cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) as the eluent to afford the corresponding products **7** or **8**.

15-phenylethynylvindoline (7):



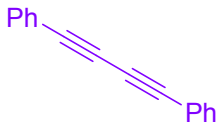
The product was obtained as a yellow solid in 79% yield; mp = 137-138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.81 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.37-7.45 (m, 3H), 5.99 (s, 1H), 5.89 (dd, *J* = 10.0, 4.0 Hz, 1H), 5.36 (s, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 1H), 3.81 (s, 3H), 3.42-3.53 (m, 2H), 2.83-2.90 (m, 5H), 2.59-2.66 (m, 1H), 2.30-2.35 (m, 2H), 2.08 (s, 3H), 1.59-1.68 (m, 1H), 1.09-1.18 (m, 1H), 0.57 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 173.4, 171.7, 170.6, 164.0, 157.9, 132.7 (2C), 130.1, 129.9, 128.5 (2C), 126.2, 124.9, 124.3, 121.5, 117.8, 90.9, 90.5, 90.1, 83.1, 79.3, 75.9, 66.5, 55.9, 52.4, 52.2, 51.3, 50.8, 43.7, 42.8, 36.3, 31.0, 21.0, 7.5. **ESI-MS** m/z 585.8, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{34}H_{37}N_2O_7$, 585.2595; found 585.2606.

10-phenylethynyltabersonine (8):



The product was obtained as a yellow solid in 75% yield; mp = 116-117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.19 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.08 (d, *J* = 1.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.38-7.52 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.83 (dd, *J* = 10.0, 4.4 Hz, 1H), 5.72 (d, *J* = 10.0 Hz, 1H), 3.81 (s, 3H), 3.51 (dd, *J* = 16.0, 4.8 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.09 (t, *J* = 8.0 Hz, 1H), 2.78-2.84 (m, 2H), 2.59 (dd, *J* = 15.2, 1.6 Hz, 1H), 2.49 (d, *J* = 15.2 Hz, 1H), 2.05-2.13 (m, 1H), 1.84 (dd, *J* = 11.6, 4.4 Hz, 1H), 0.97-1.03 (m, 1H), 0.85-0.92 (m, 1H), 0.66 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.6, 168.7, 164.9, 148.6, 138.6, 133.1, 132.9 (2C), 132.5, 130.5, 128.6 (2C), 125.1, 121.8, 120.4, 108.5, 95.3, 92.2, 87.1, 69.8, 54.4, 51.3, 50.9, 50.5, 44.7, 41.3, 28.5, 26.9, 7.5. **ESI-MS** ((m/z) 465.7, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{30}H_{29}N_2O_3$, 465.2173; found 465.2184.

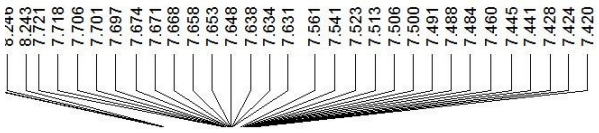
diphenylbutadiyne (9):

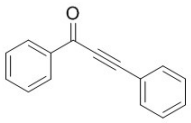


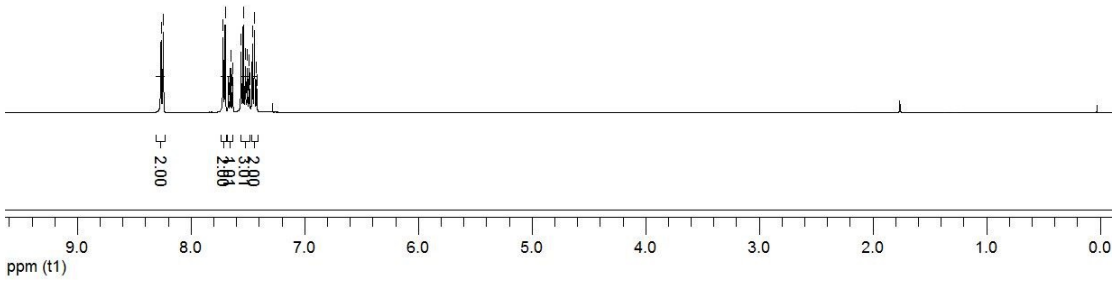
The product was obtained as a yellow solid in 70% yield; mp = 87-88 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.34-7.42 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 132.5 (4C), 129.2 (2C), 128.4 (4C), 121.8 (2C), 81.5 (2C), 73.9 (2C). **ESI-MS** m/z 203.6, $[M+H]^+$; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{15}H_{11}$, 203.0855; found 203.0859.

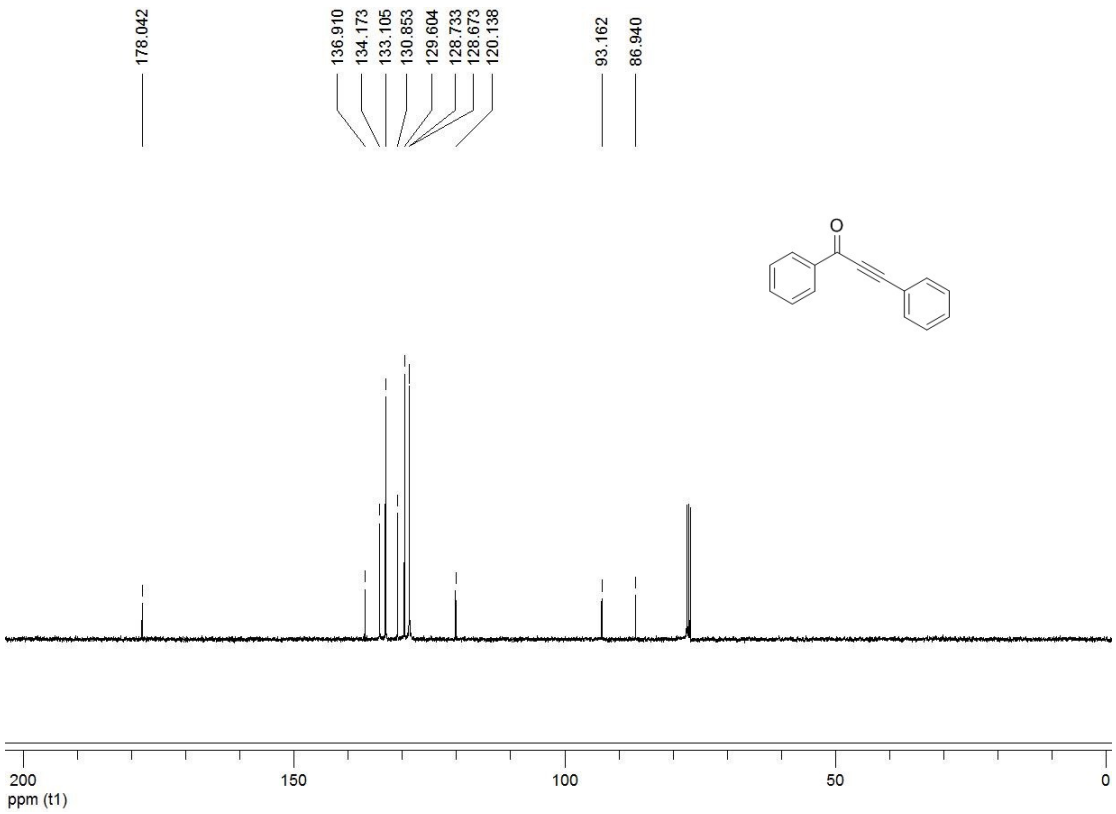
4. Copies of NMR Spectra Data

^{1}H NMR and ^{13}C NMR spetra of compound **3aa**

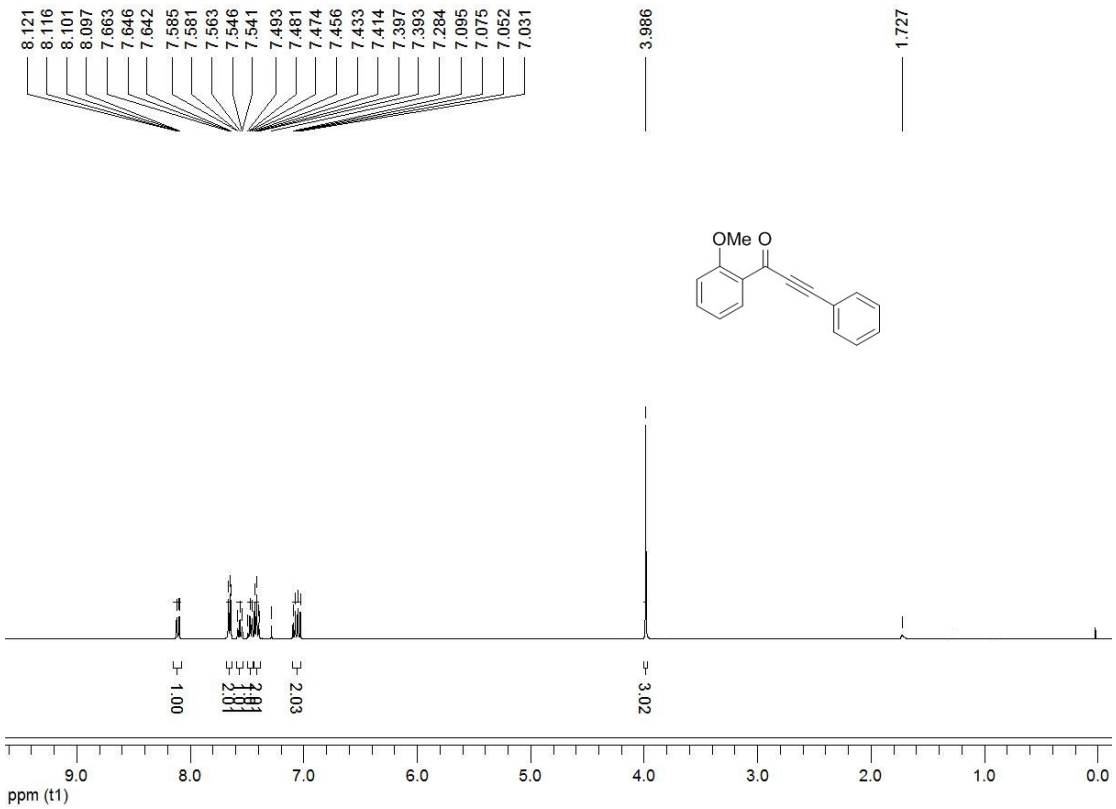


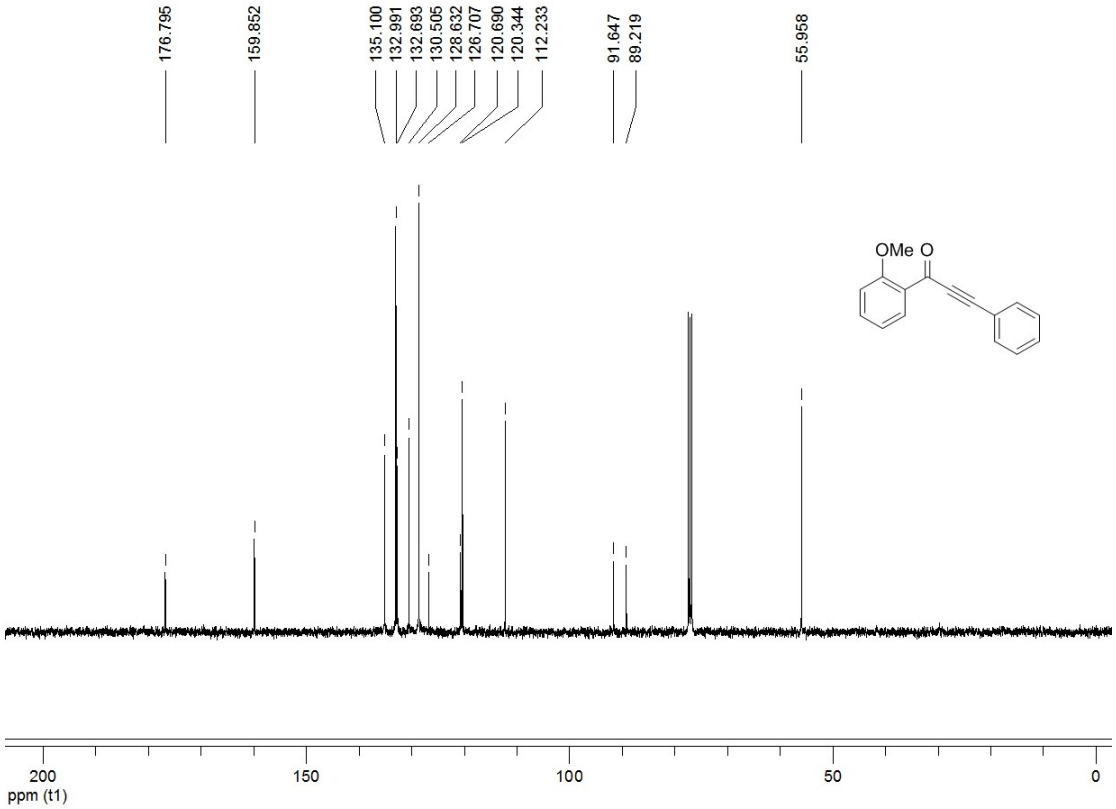




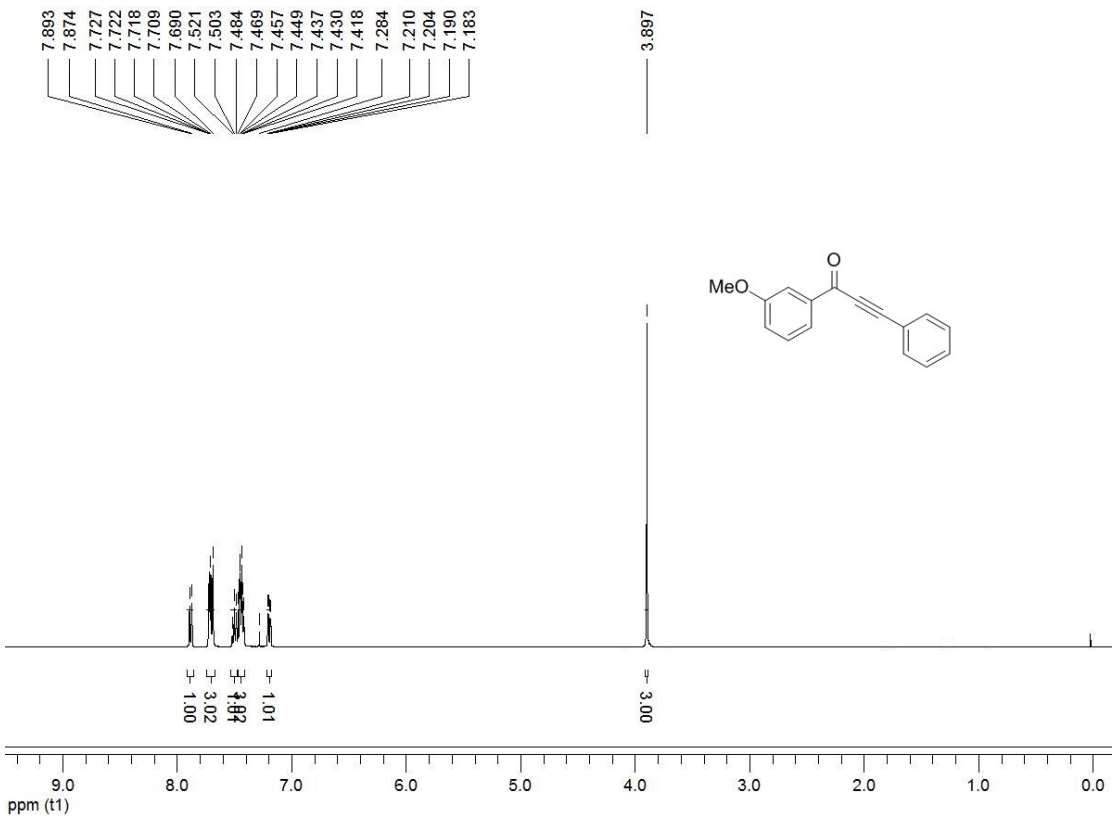


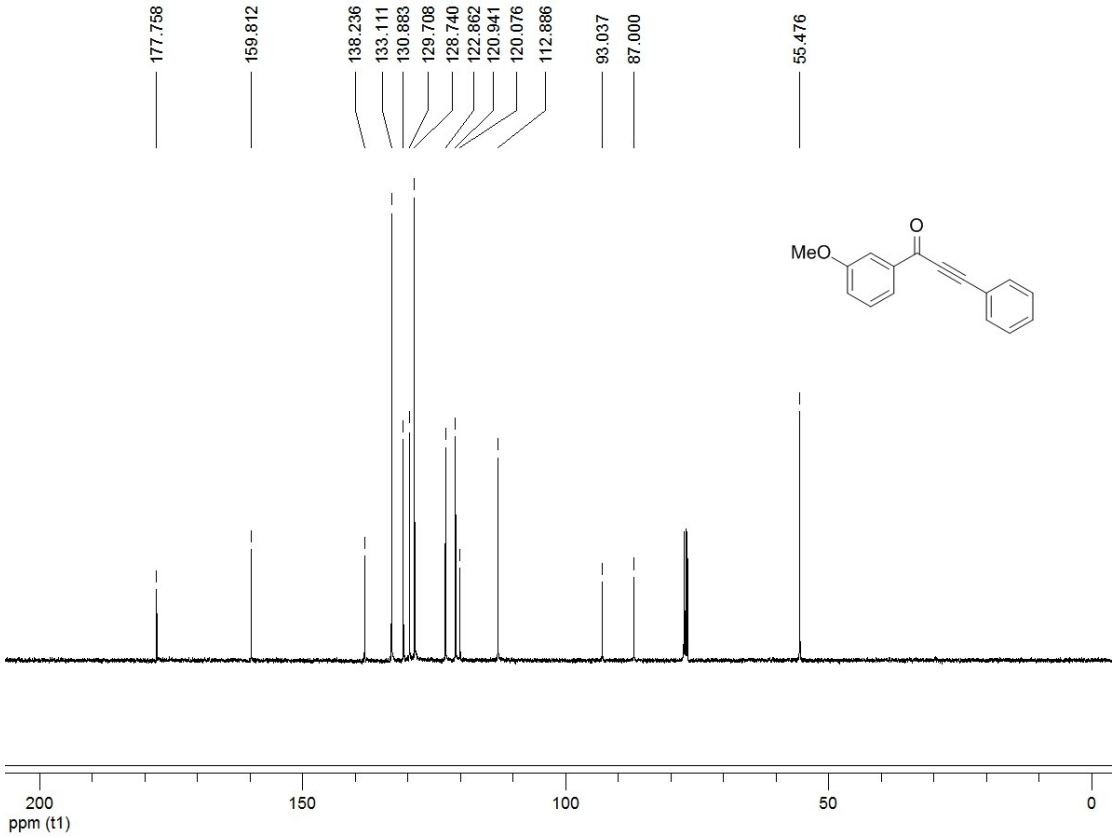
^{1}H NMR and ^{13}C NMR spetra of compound **3ba**



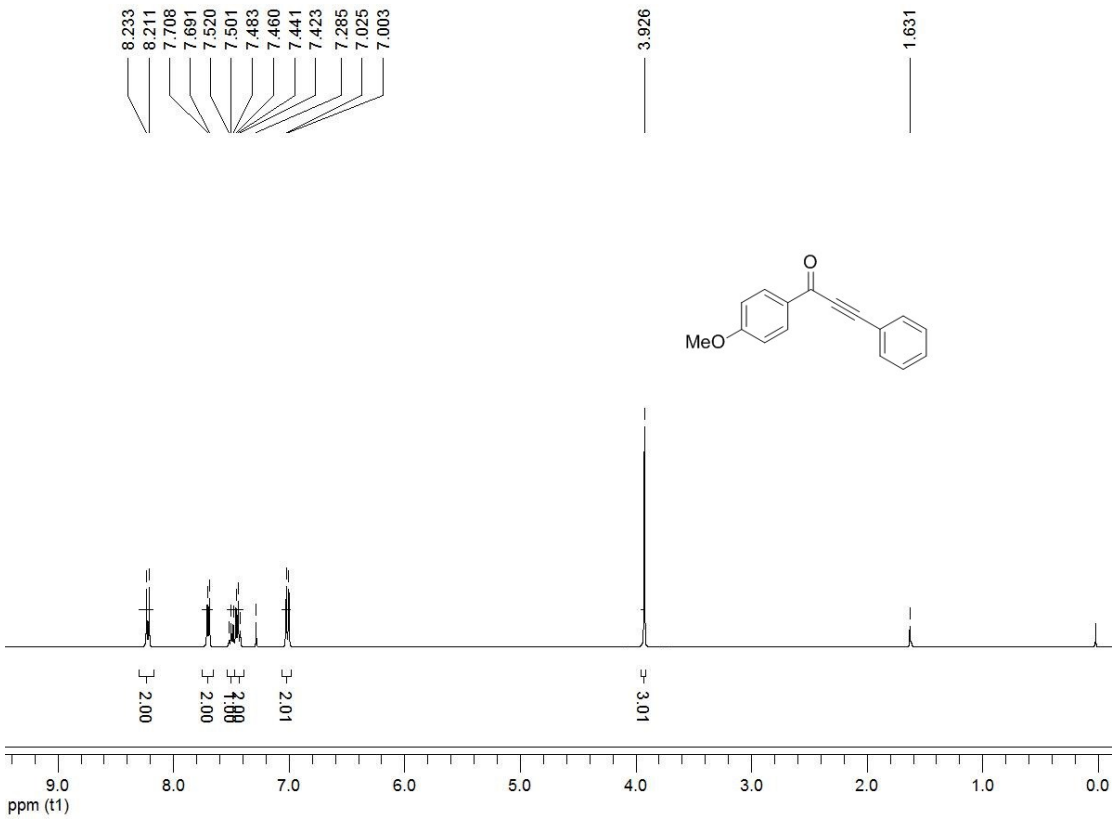


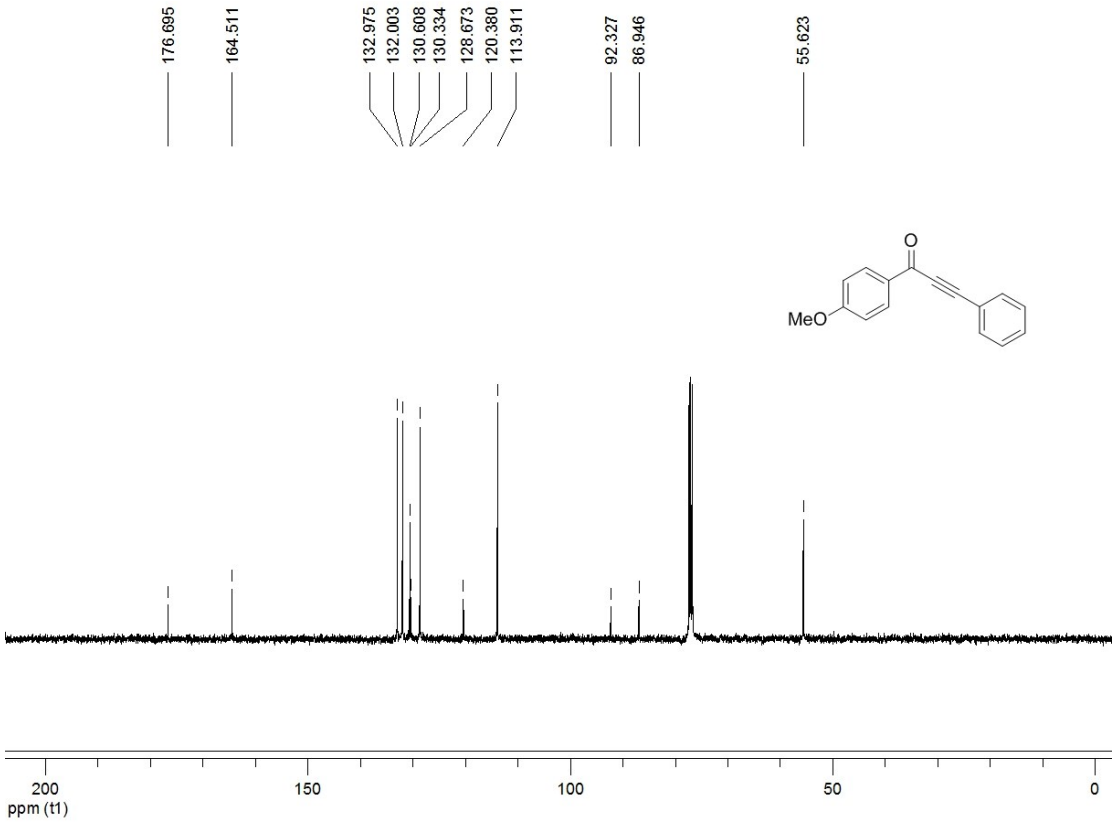
^{1}H NMR and ^{13}C NMR spetra of compound **3ca**



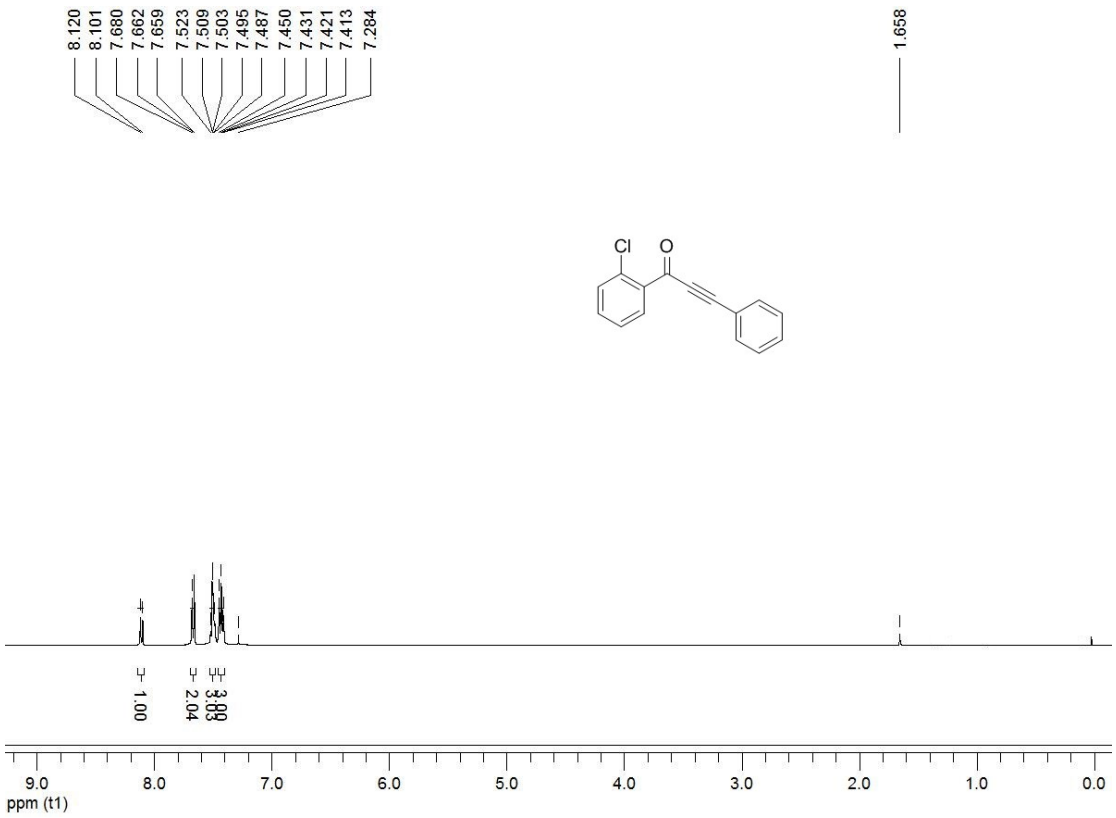


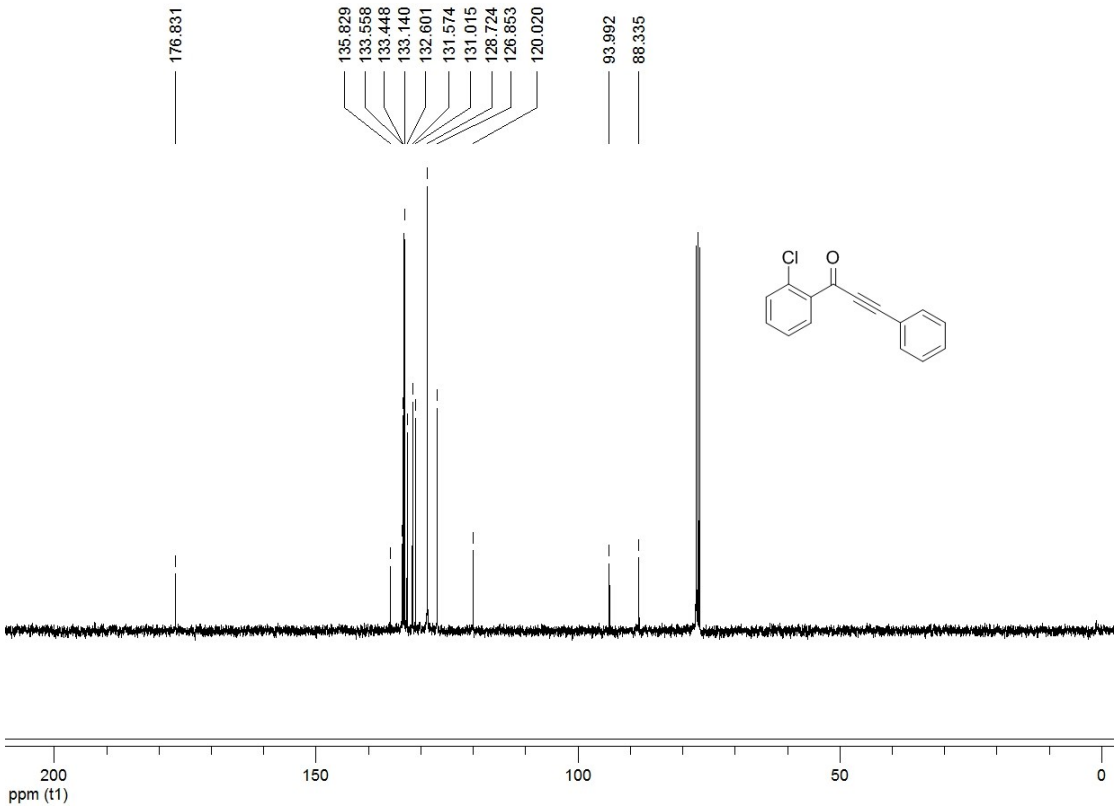
^{1}H NMR and ^{13}C NMR spetra of compound **3da**



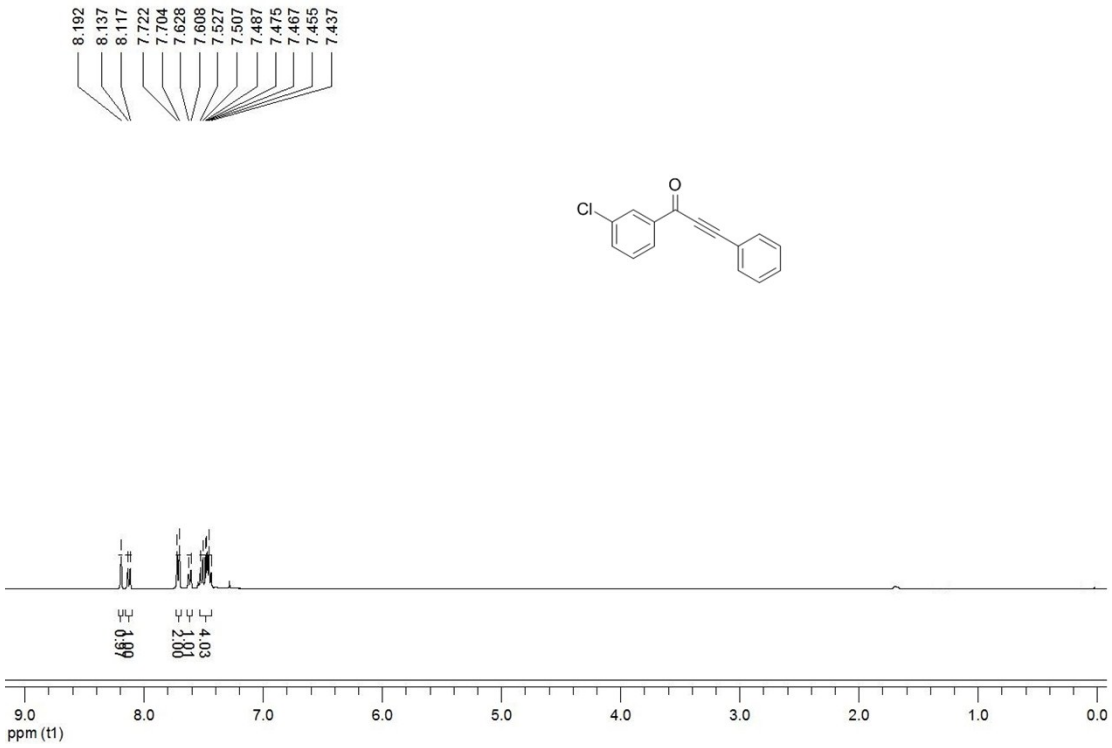


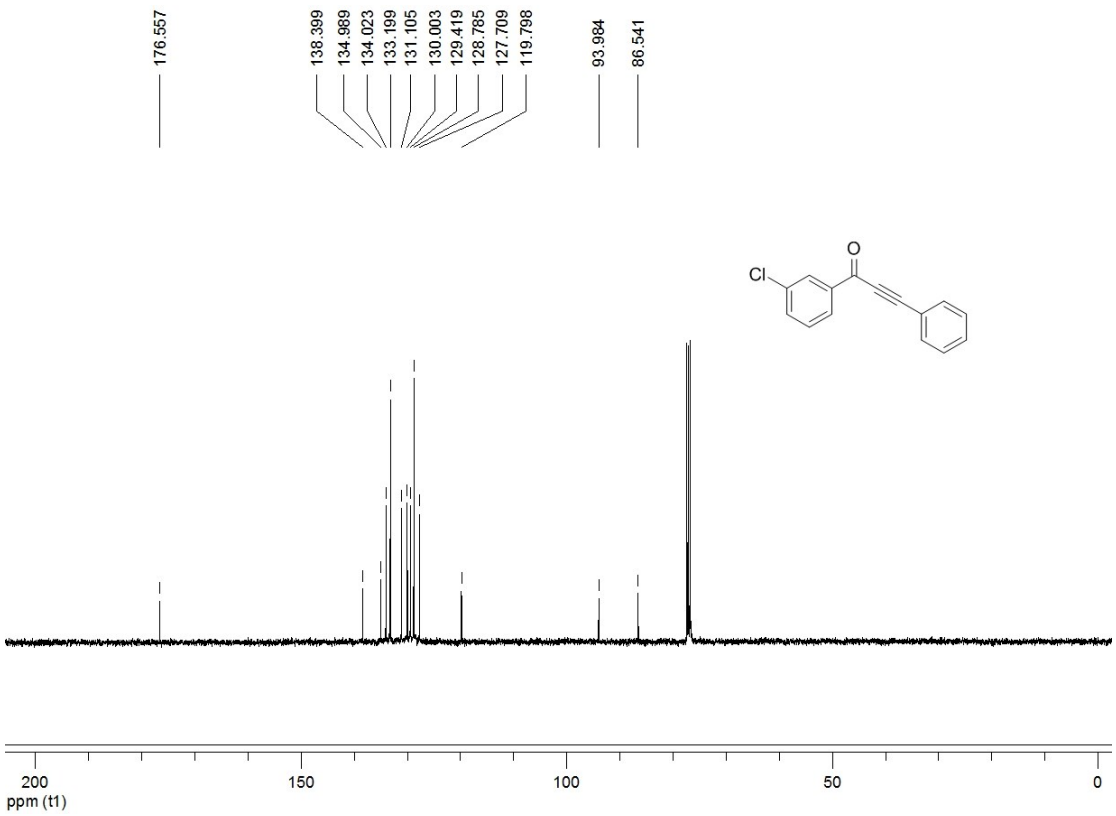
^{1}H NMR and ^{13}C NMR spetra of compound **3ea**



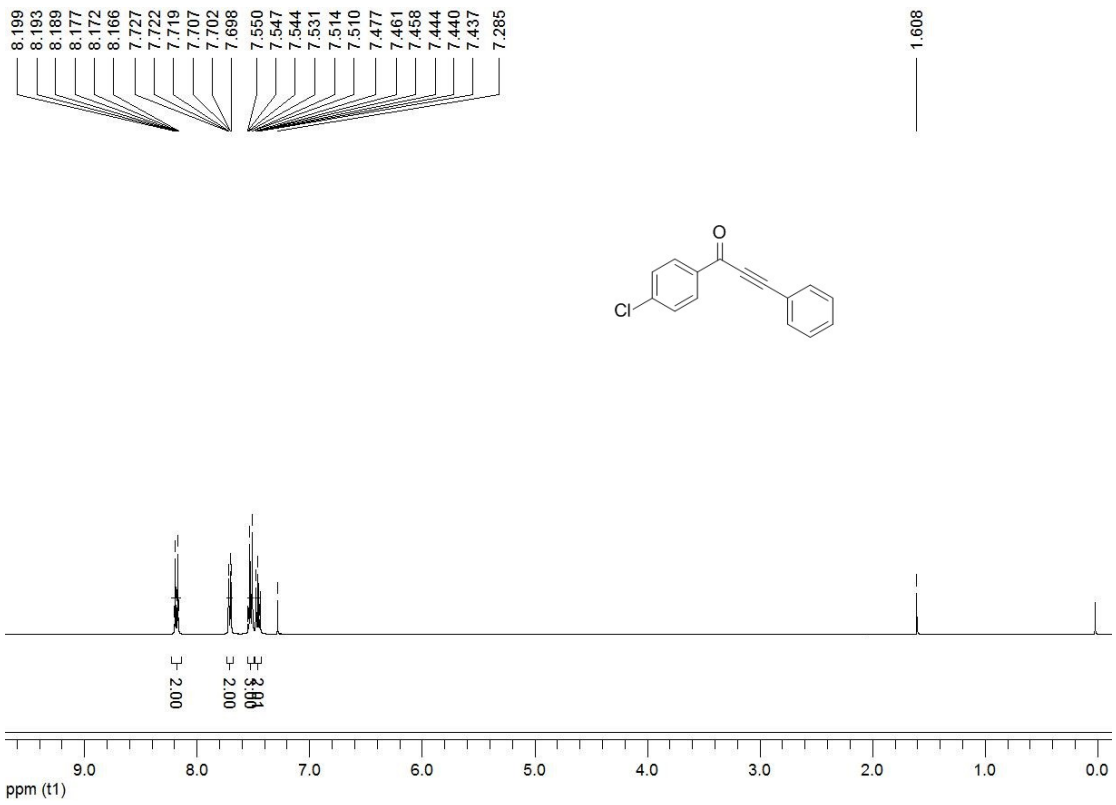


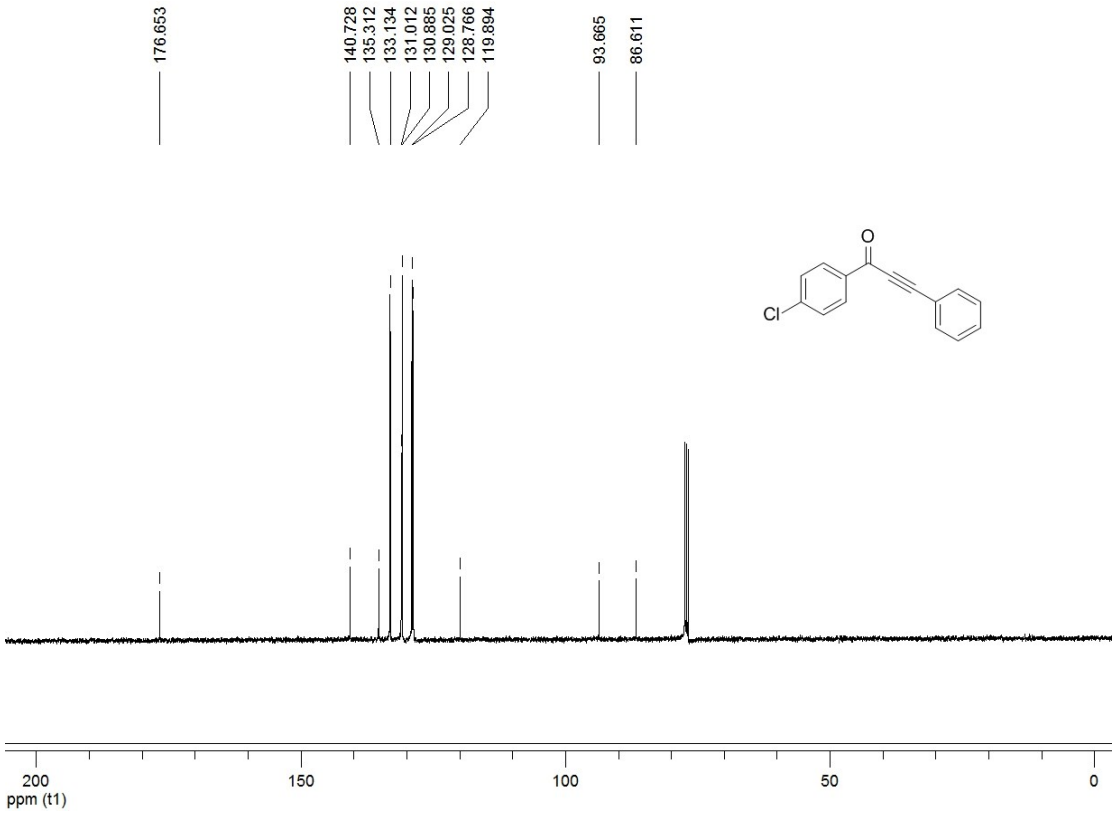
^{1}H NMR and ^{13}C NMR spetra of compound **3fa**



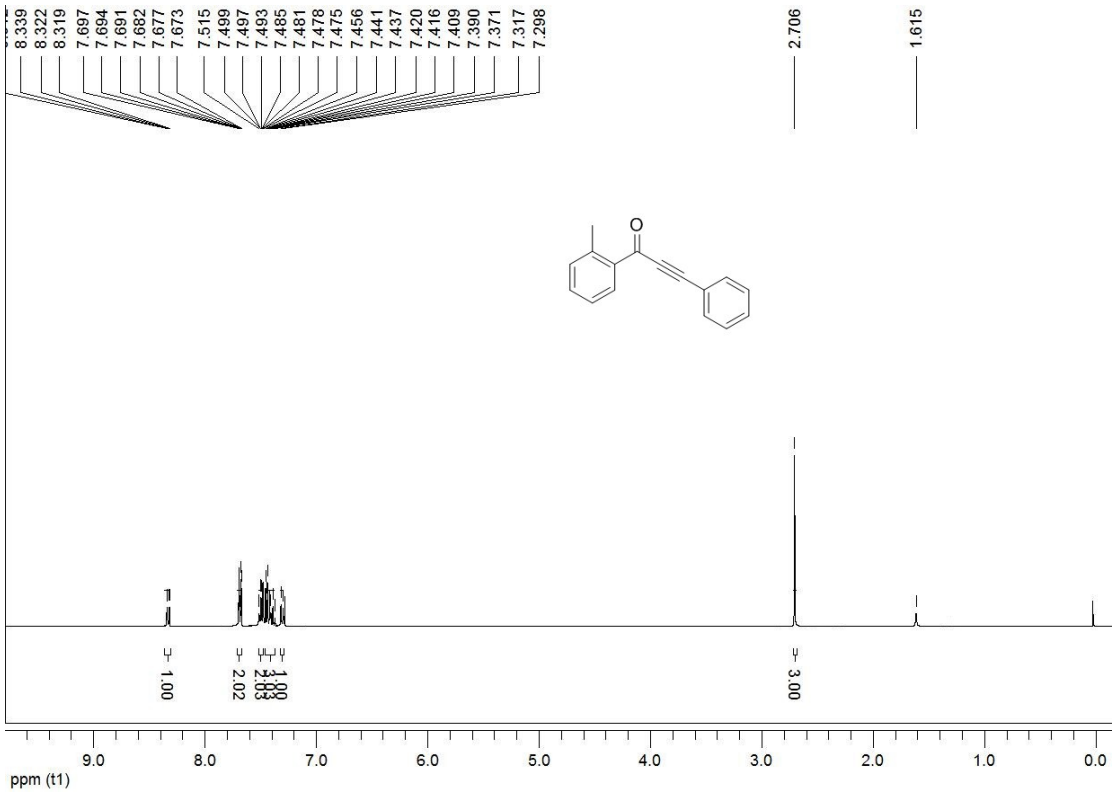


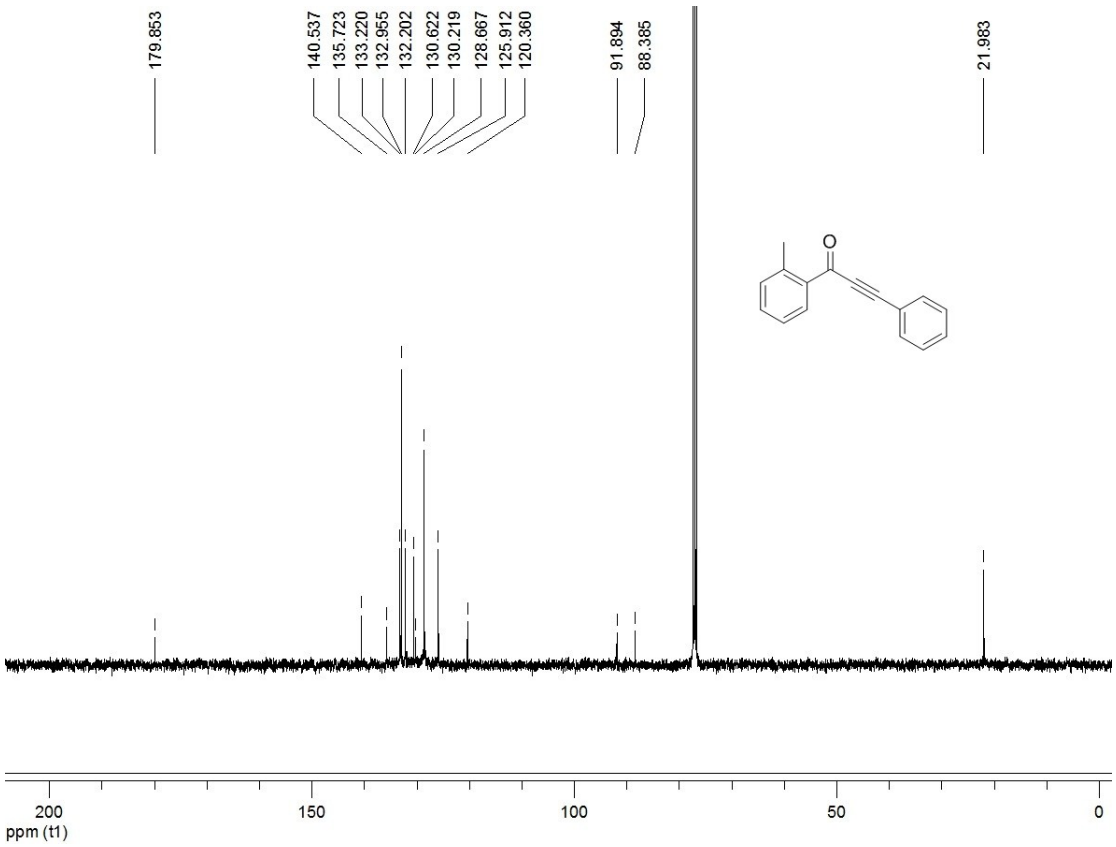
^{1}H NMR and ^{13}C NMR spetra of compound **3ga**



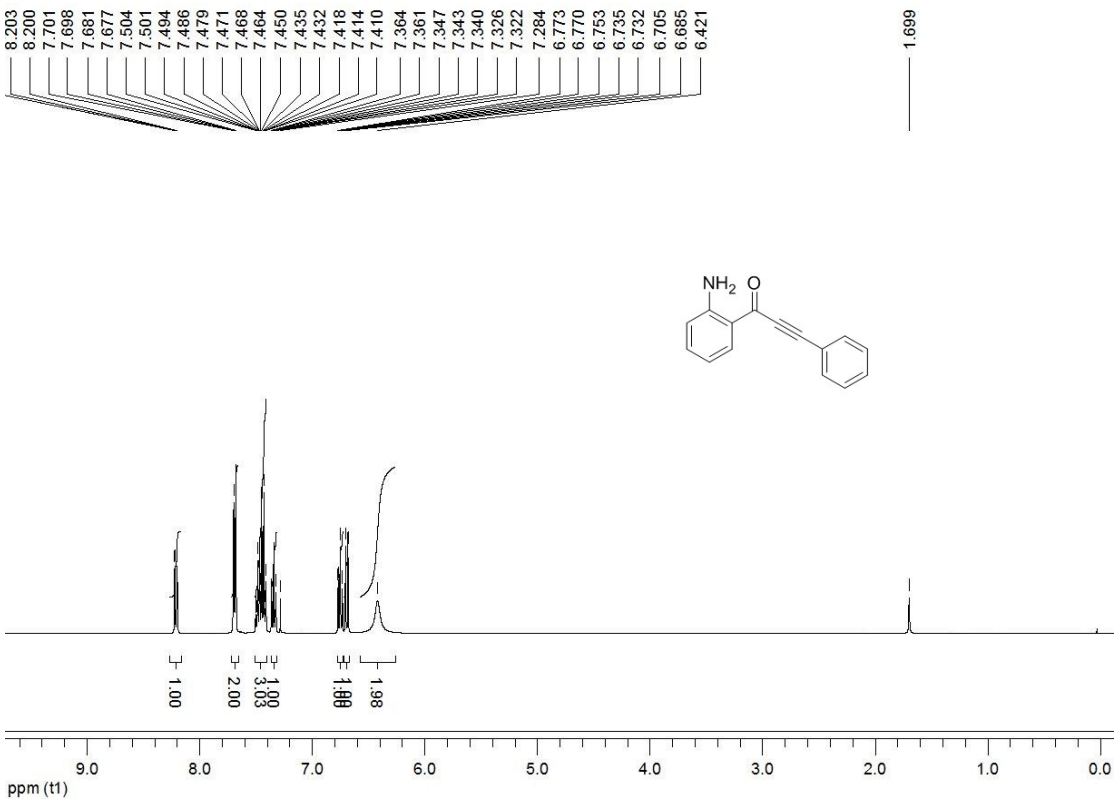


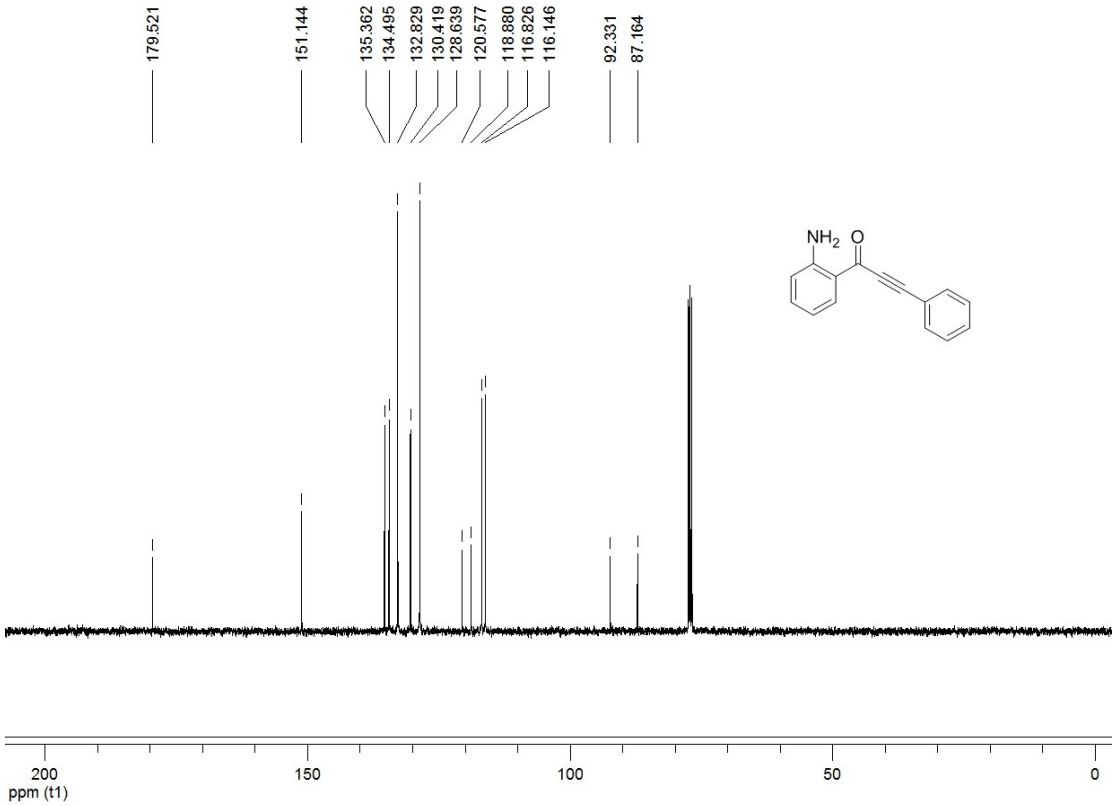
^{1}H NMR and ^{13}C NMR spetra of compound **3ha**



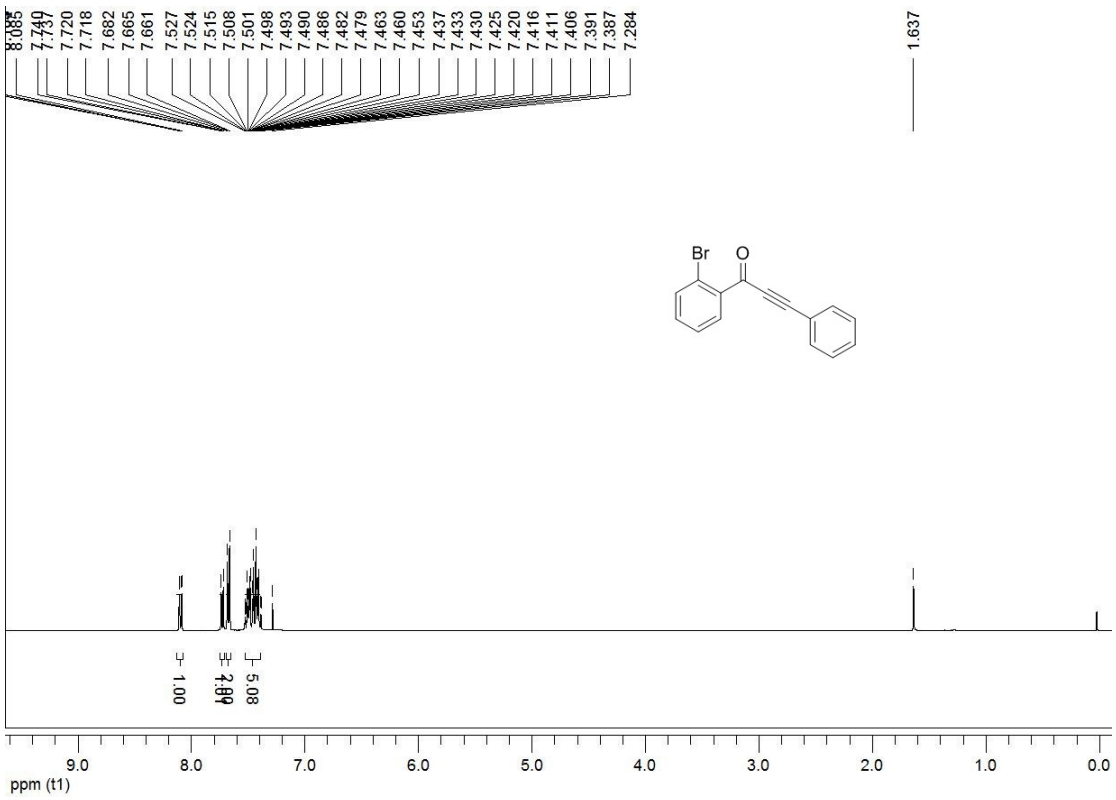


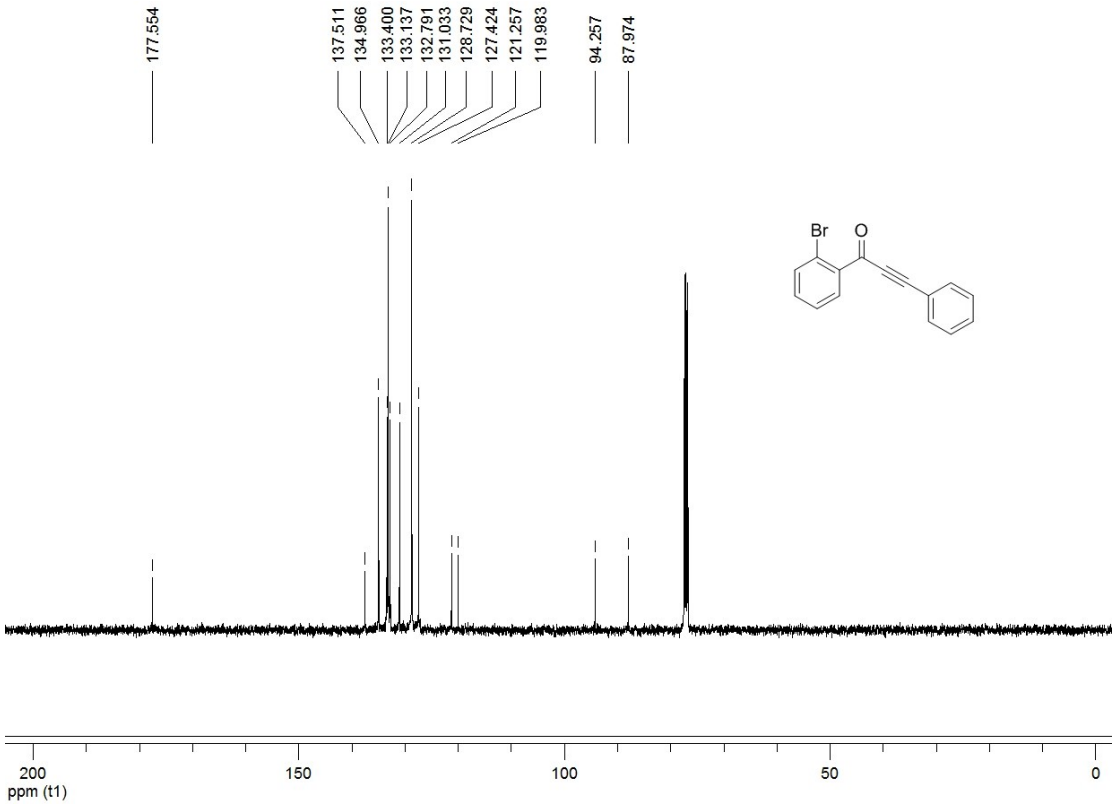
^{1}H NMR and ^{13}C NMR spetra of compound **3ia**



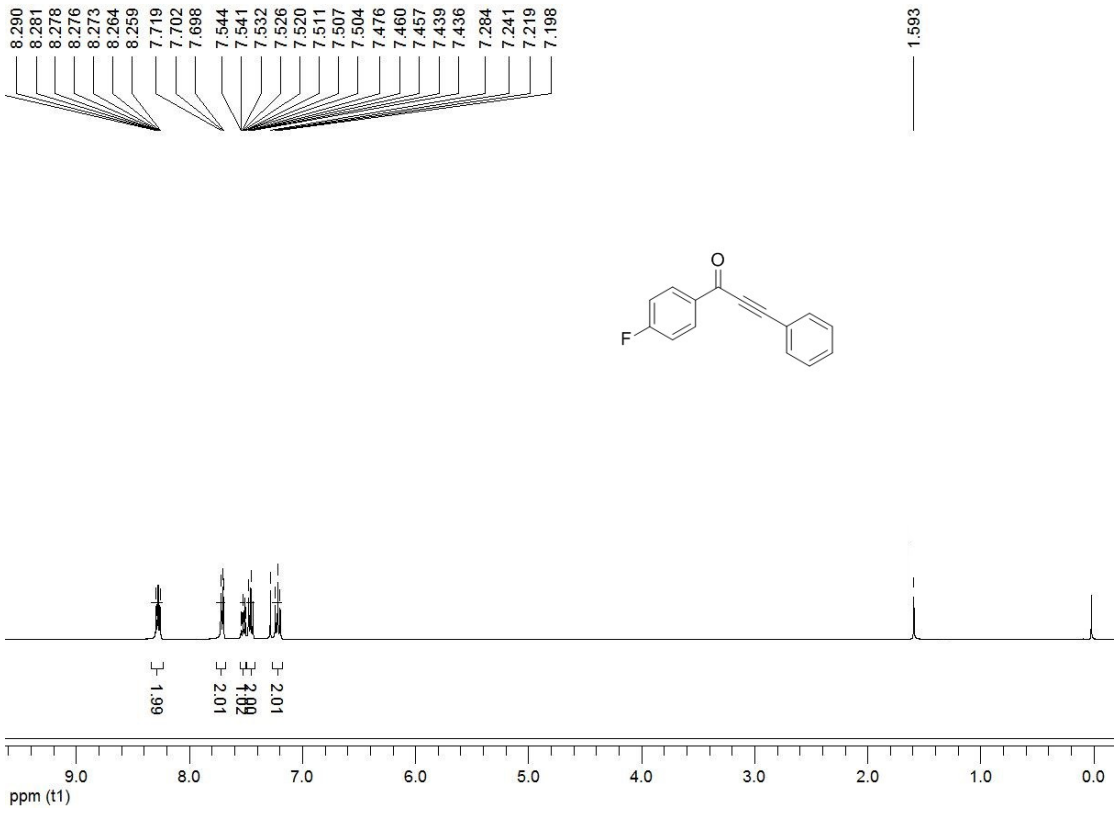


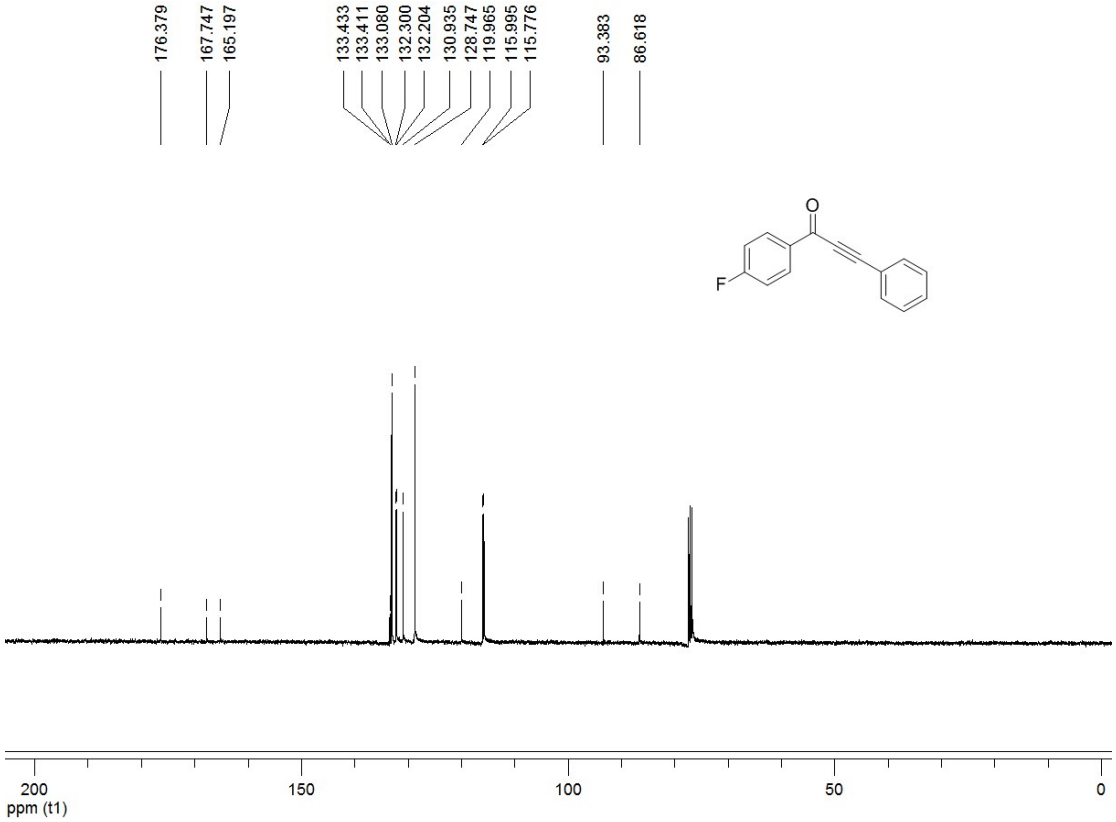
^{1}H NMR and ^{13}C NMR spetra of compound **3ja**



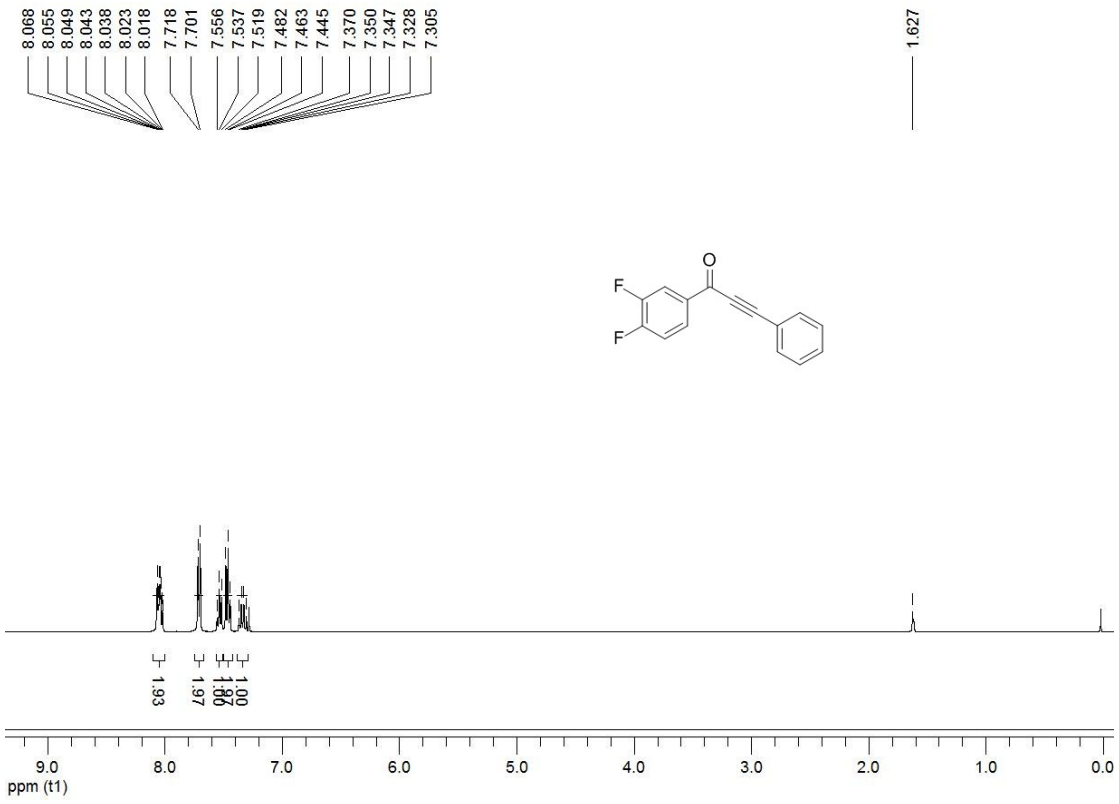


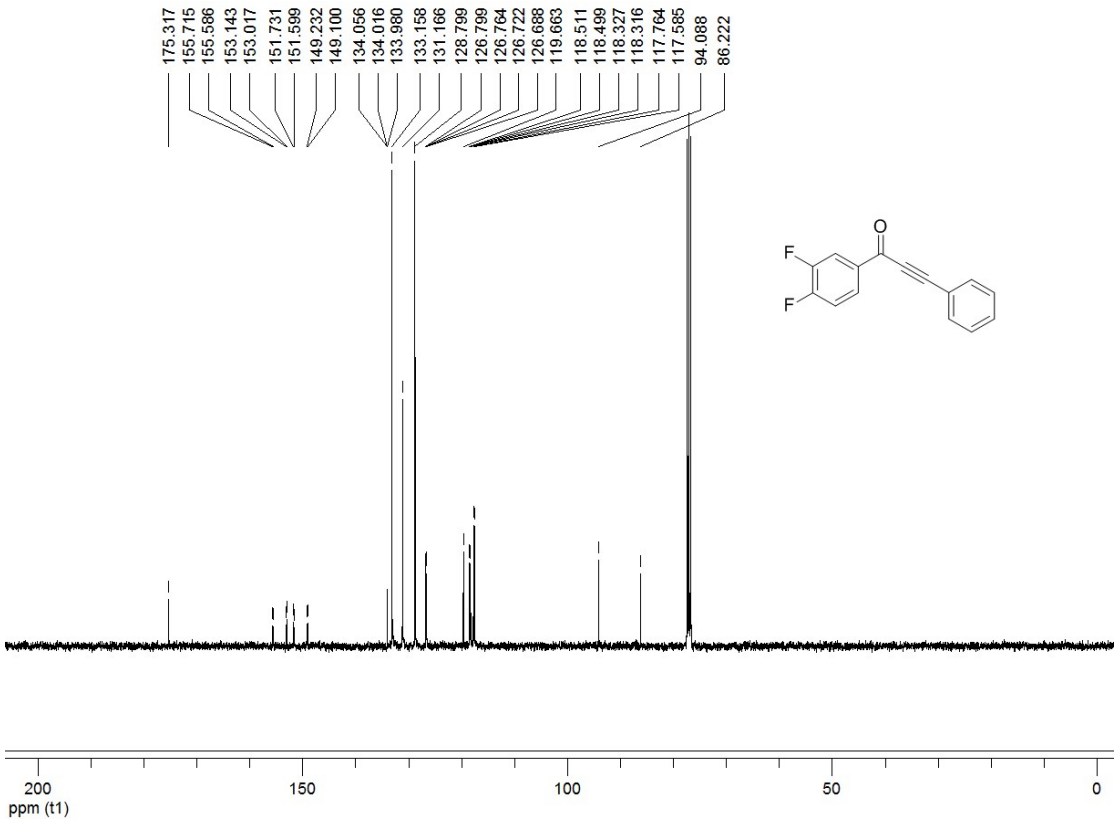
^{1}H NMR and ^{13}C NMR spetra of compound **3ka**



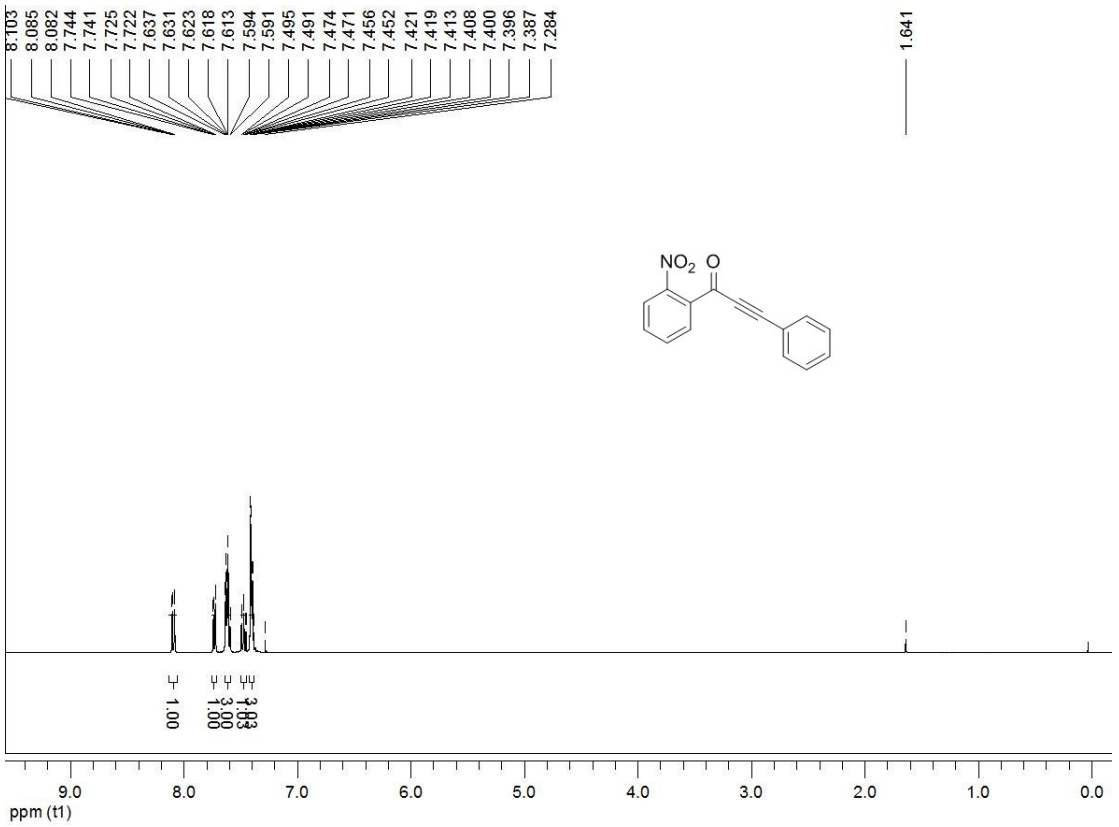


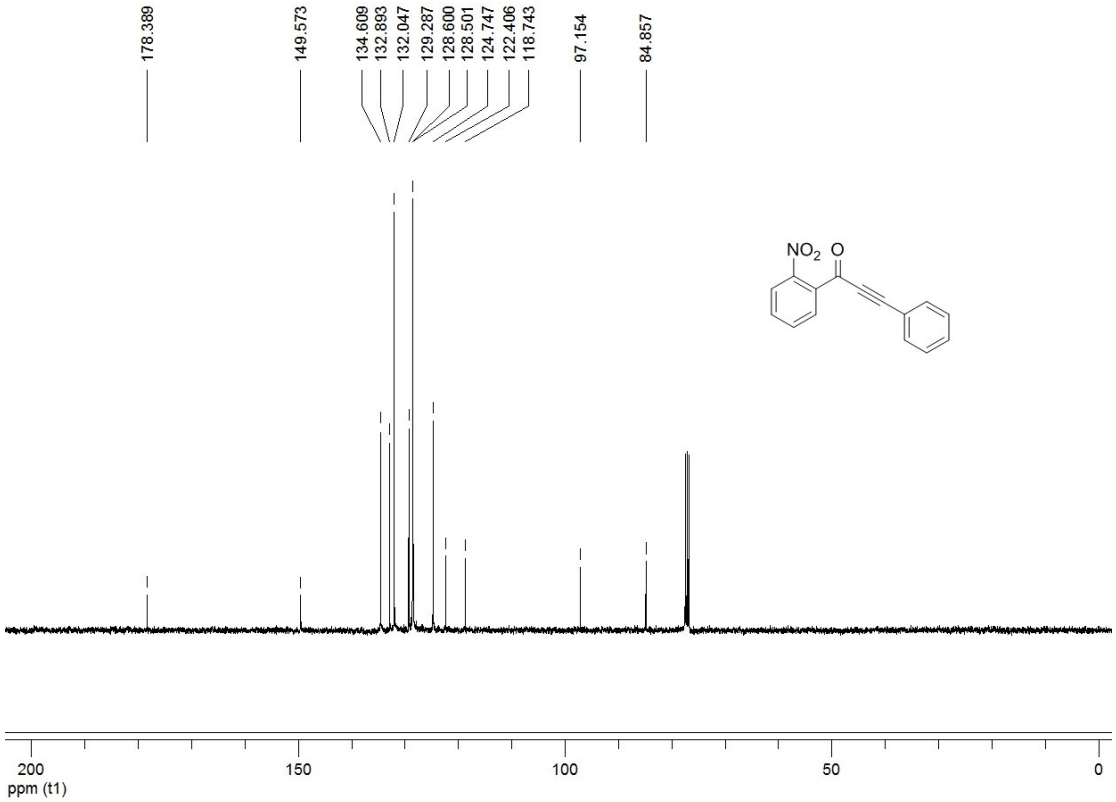
^{1}H NMR and ^{13}C NMR spetra of compound **3la**



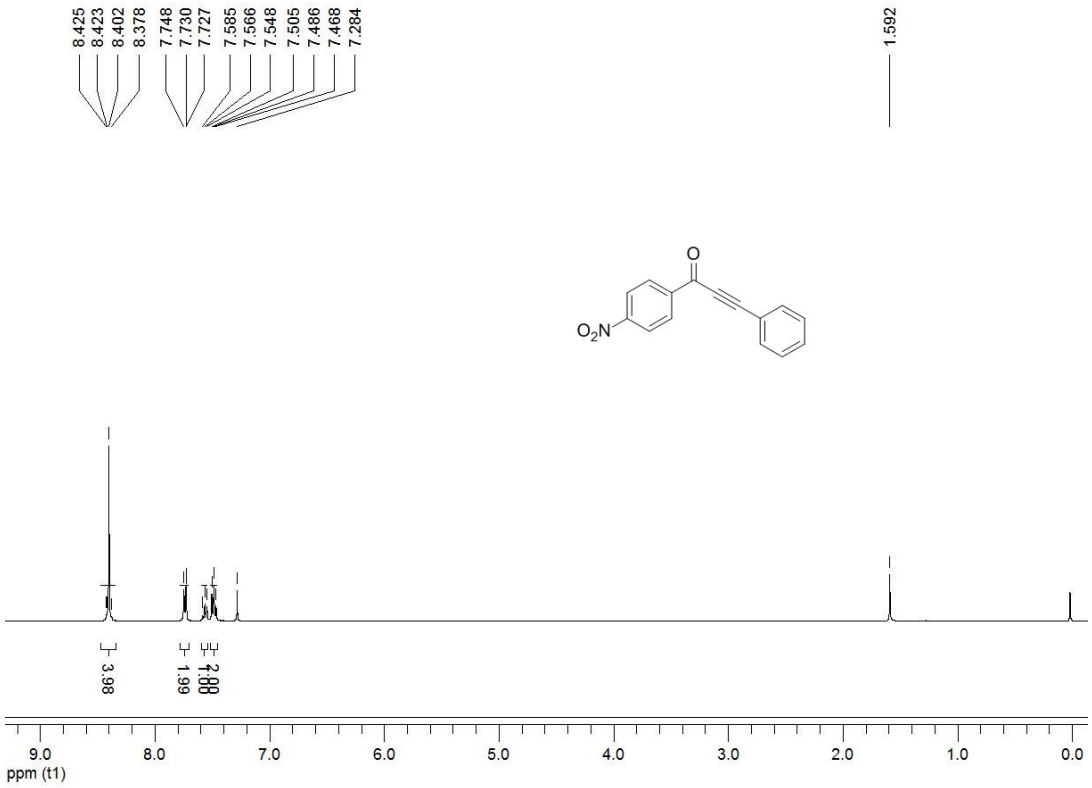


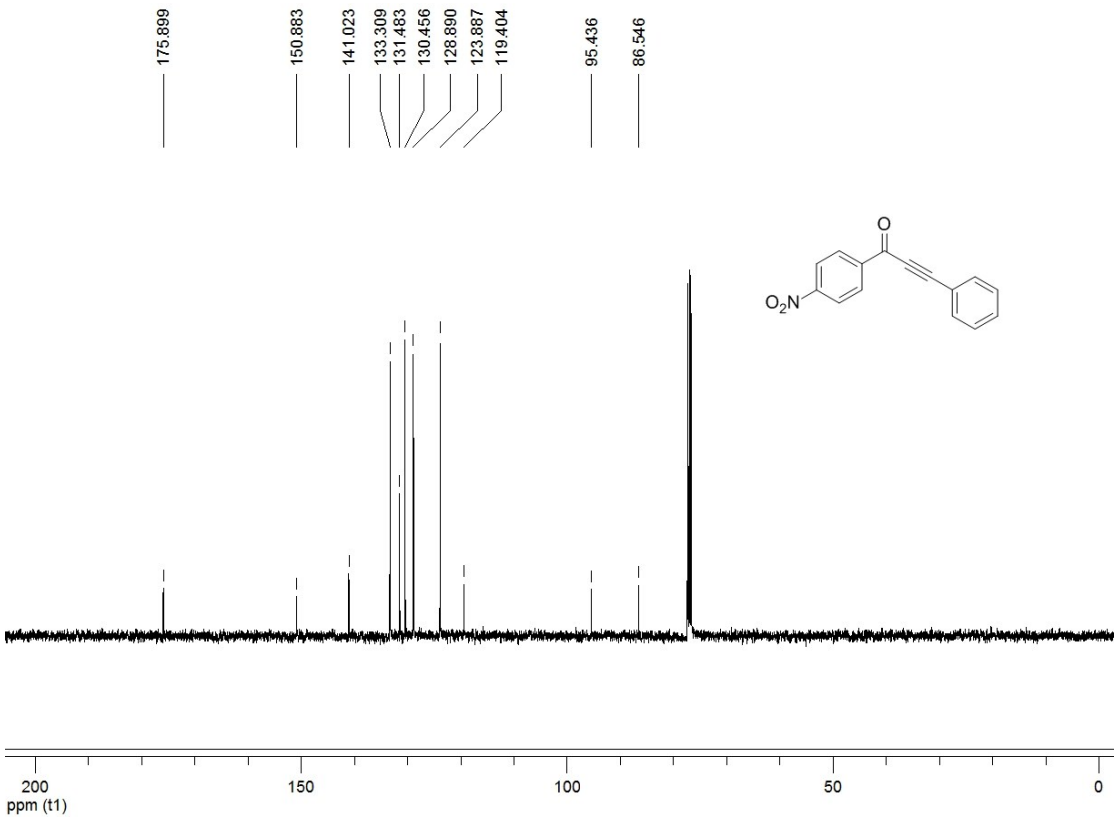
^{1}H NMR and ^{13}C NMR spetra of compound **3ma**



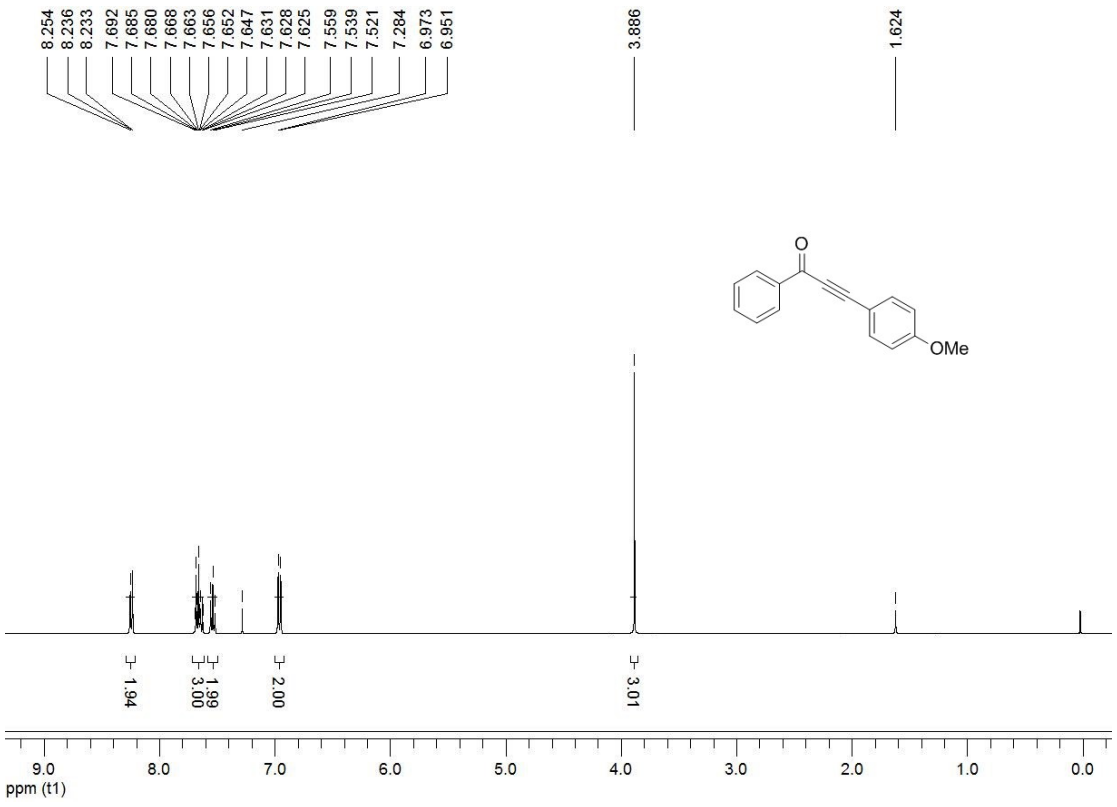


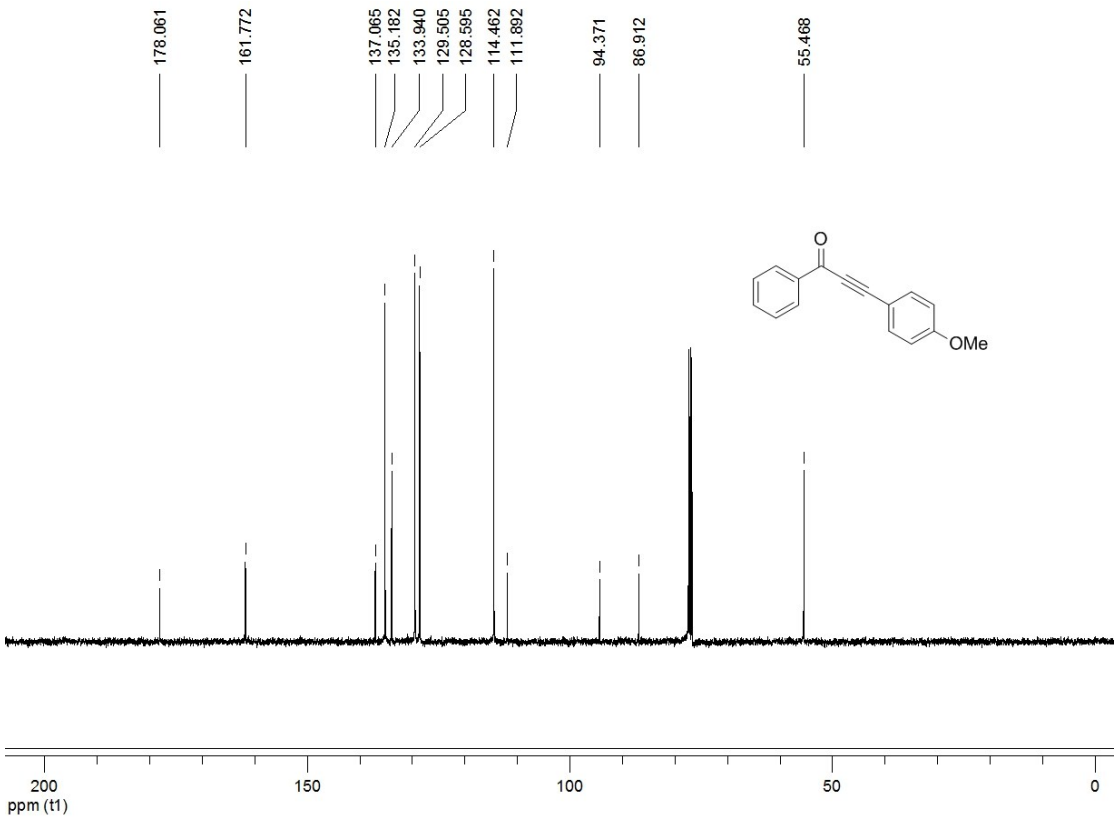
^{1}H NMR and ^{13}C NMR spetra of compound **3na**



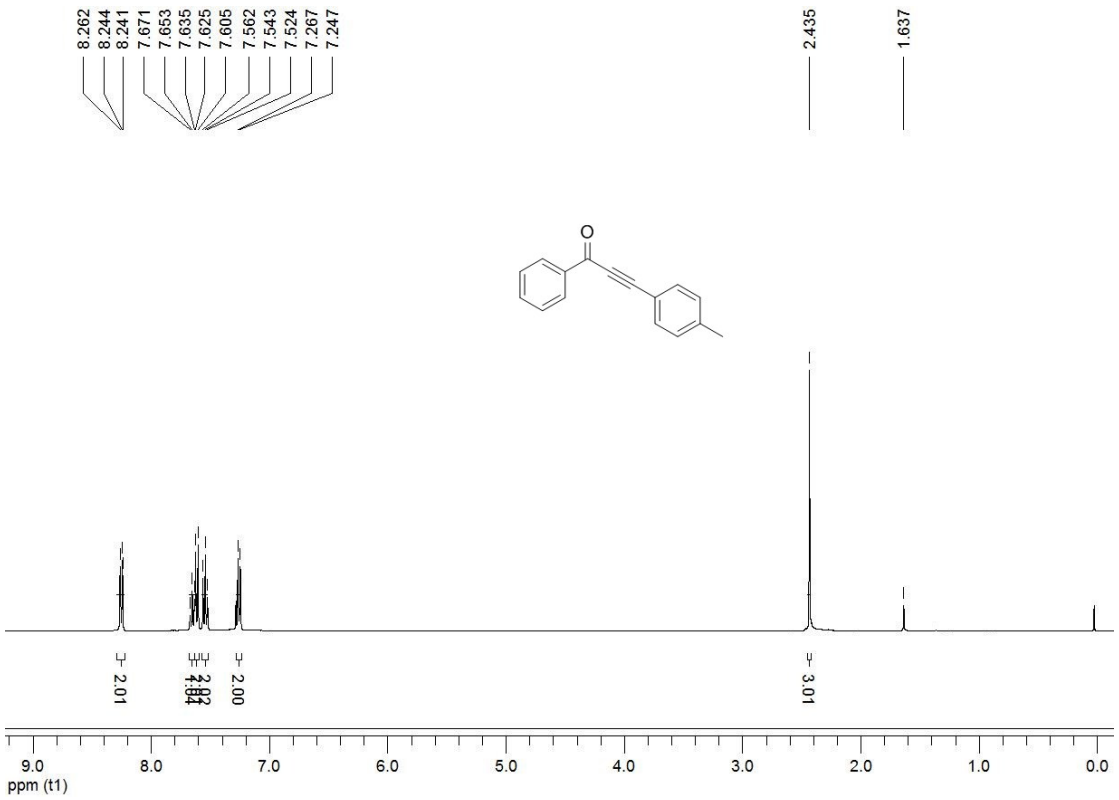


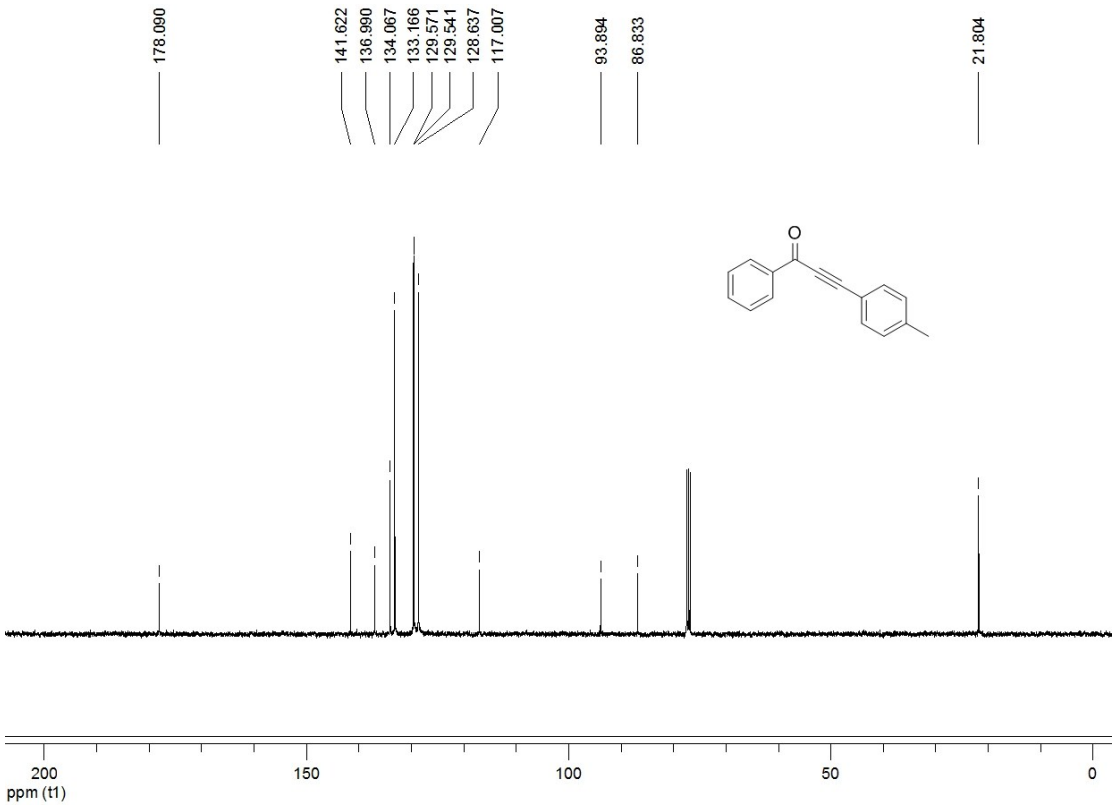
^{1}H NMR and ^{13}C NMR spetra of compound **3ab**



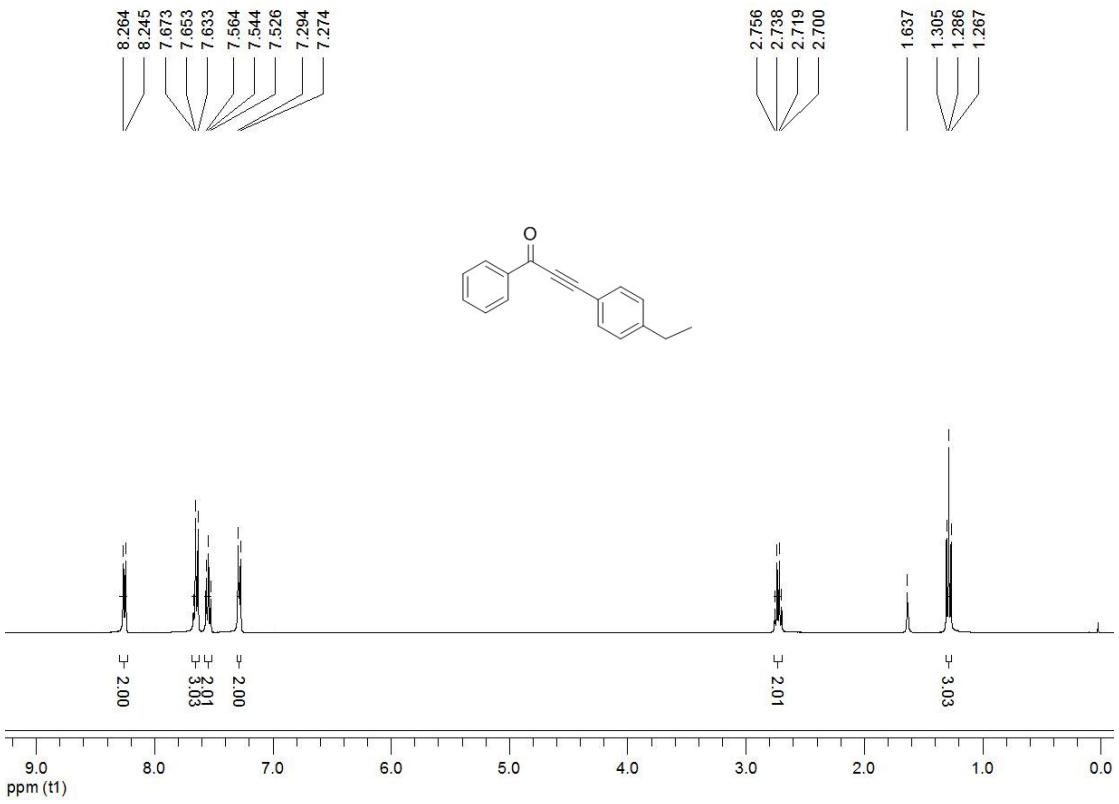


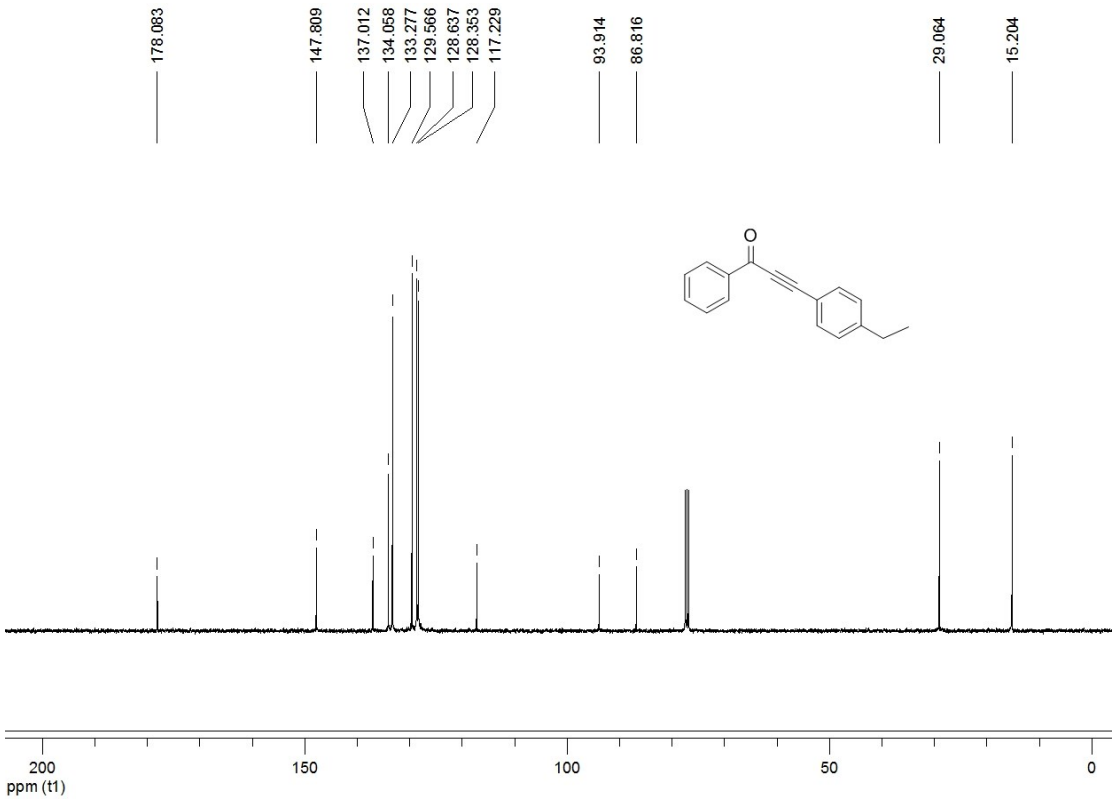
^{1}H NMR and ^{13}C NMR spetra of compound **3ac**



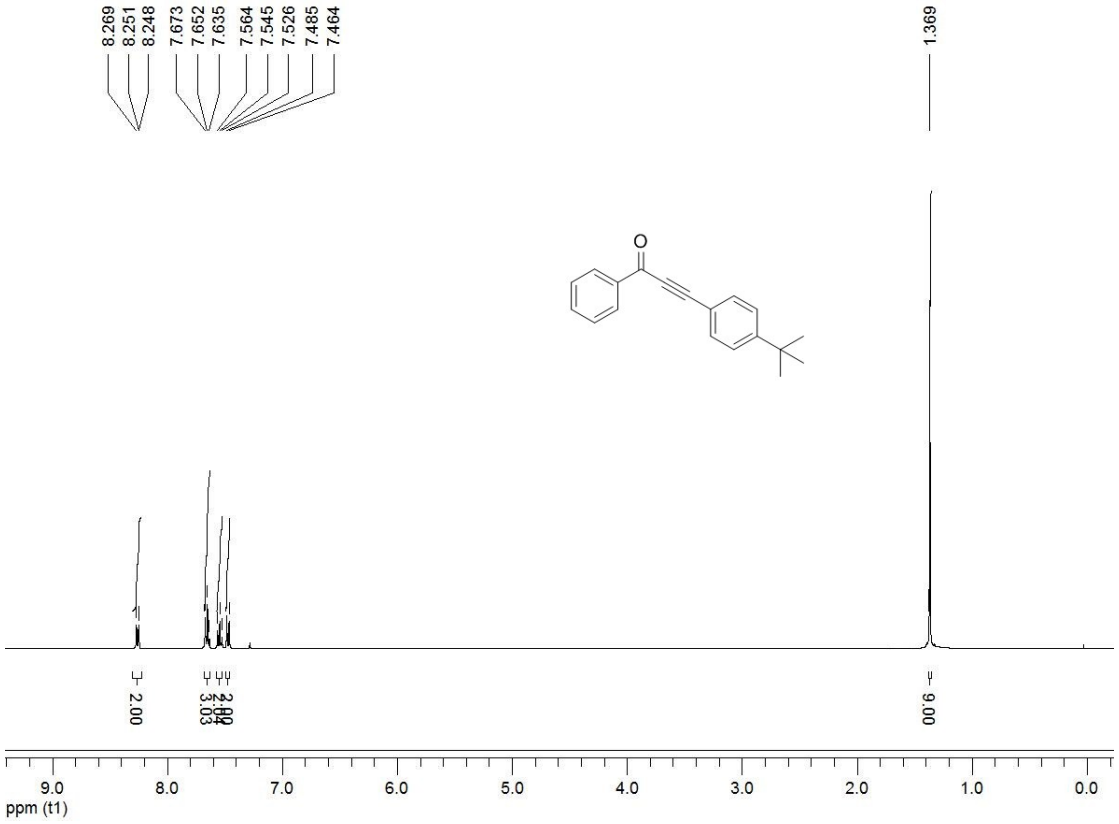


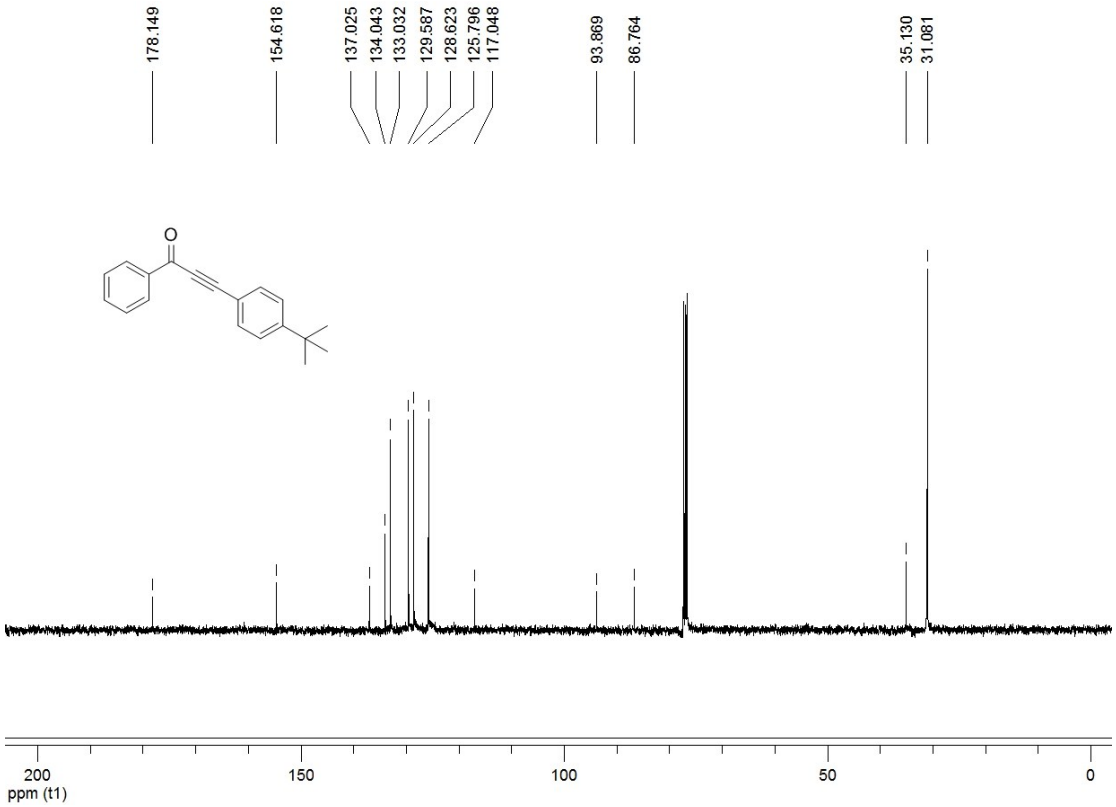
^{1}H NMR and ^{13}C NMR spetra of compound **3ad**



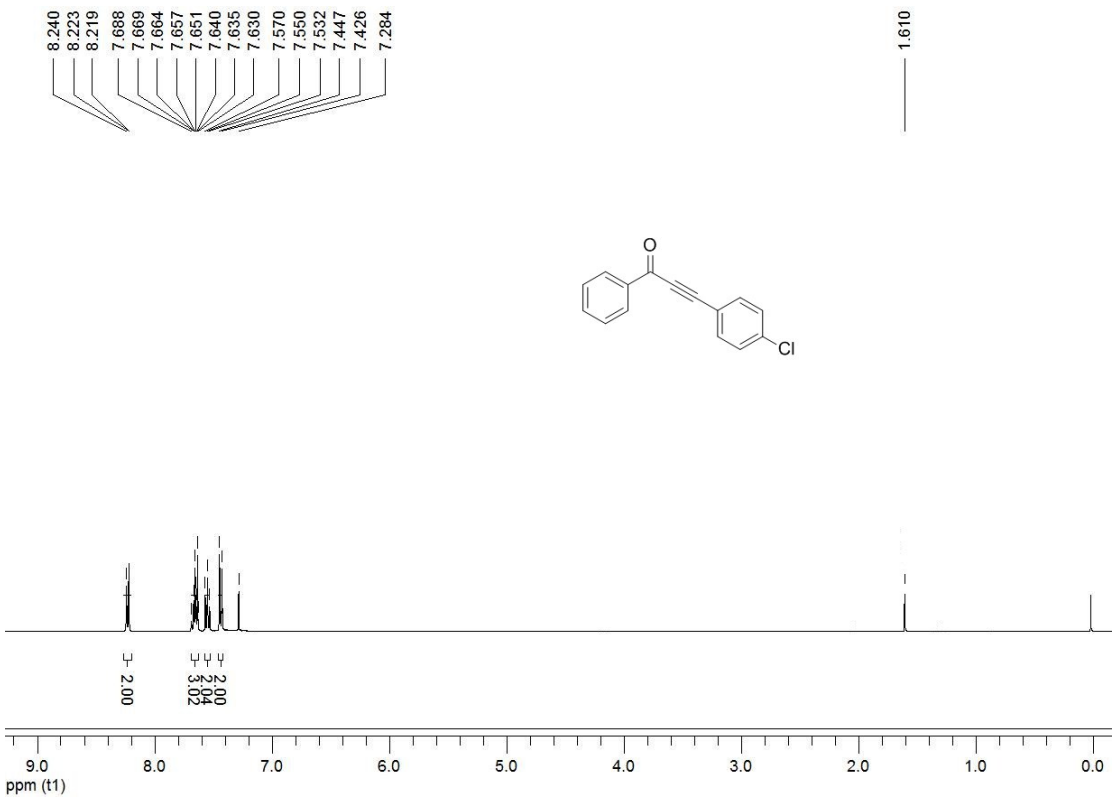


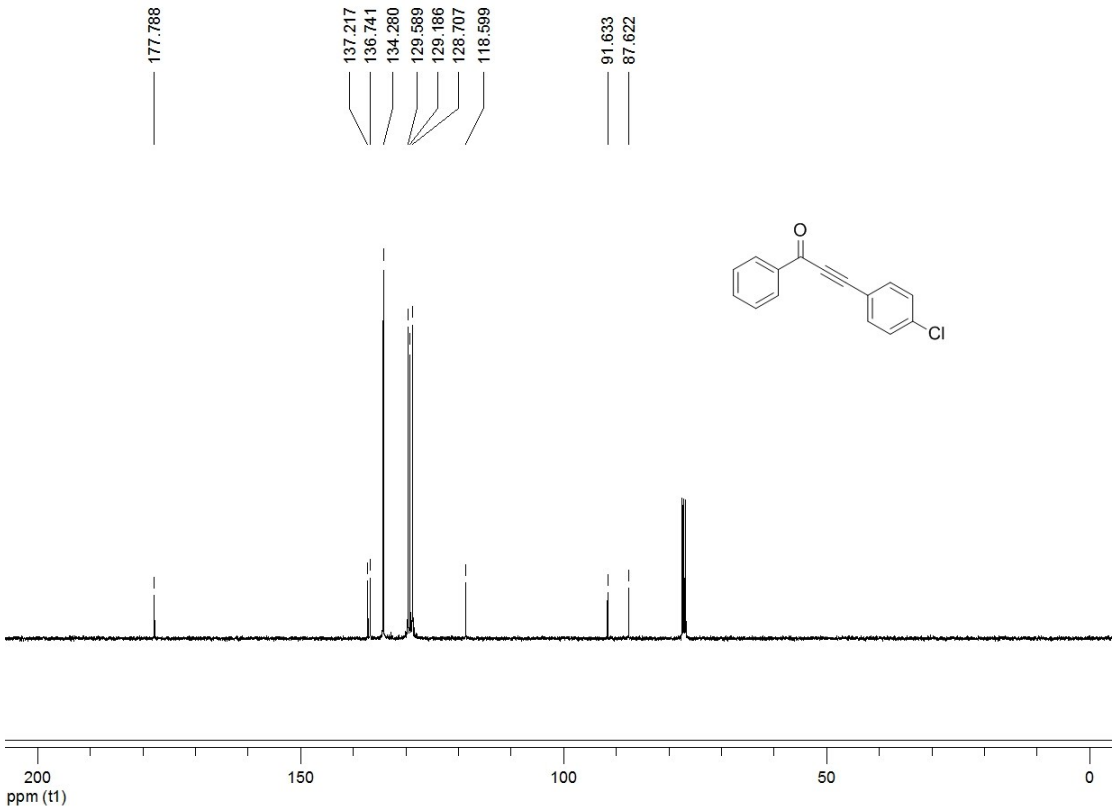
^{1}H NMR and ^{13}C NMR spetra of compound **3ae**



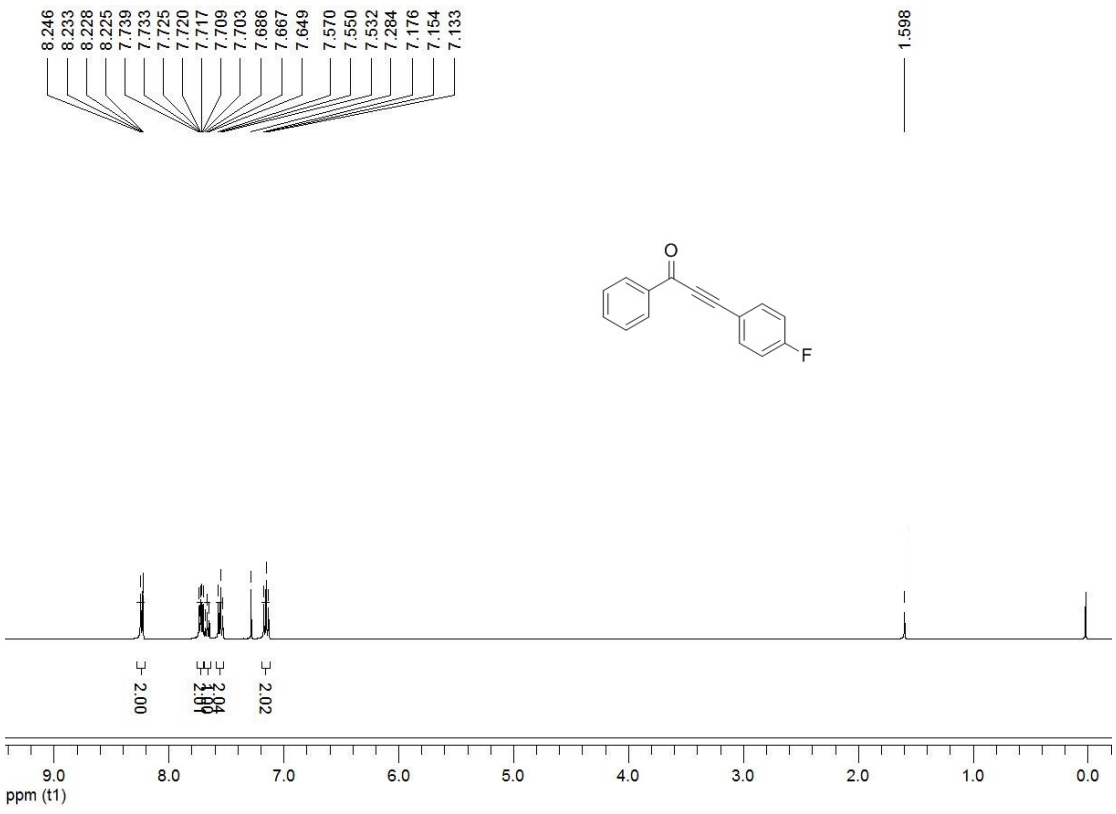


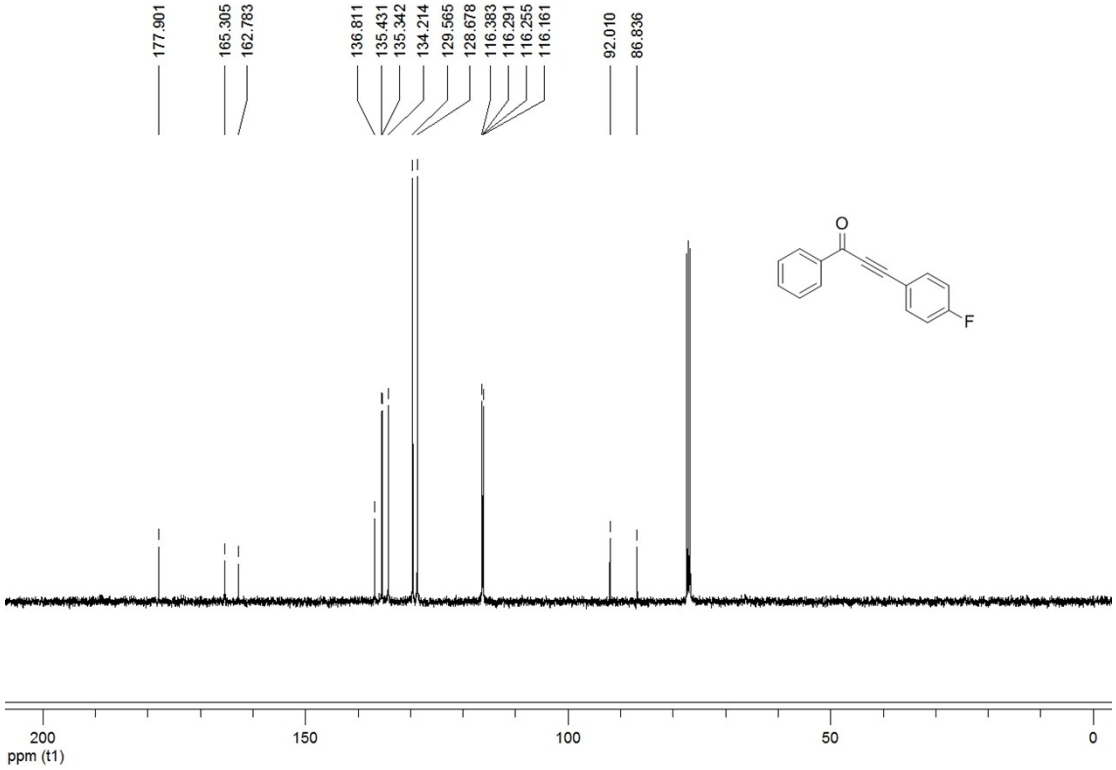
^{1}H NMR and ^{13}C NMR spetra of compound **3af**



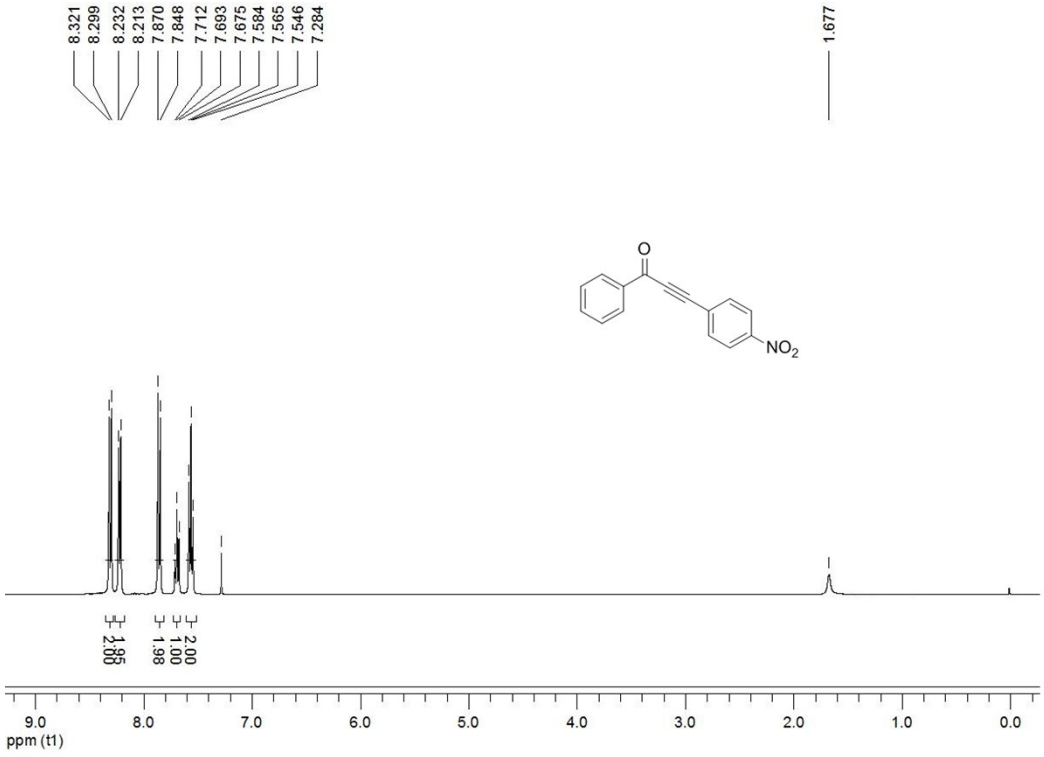


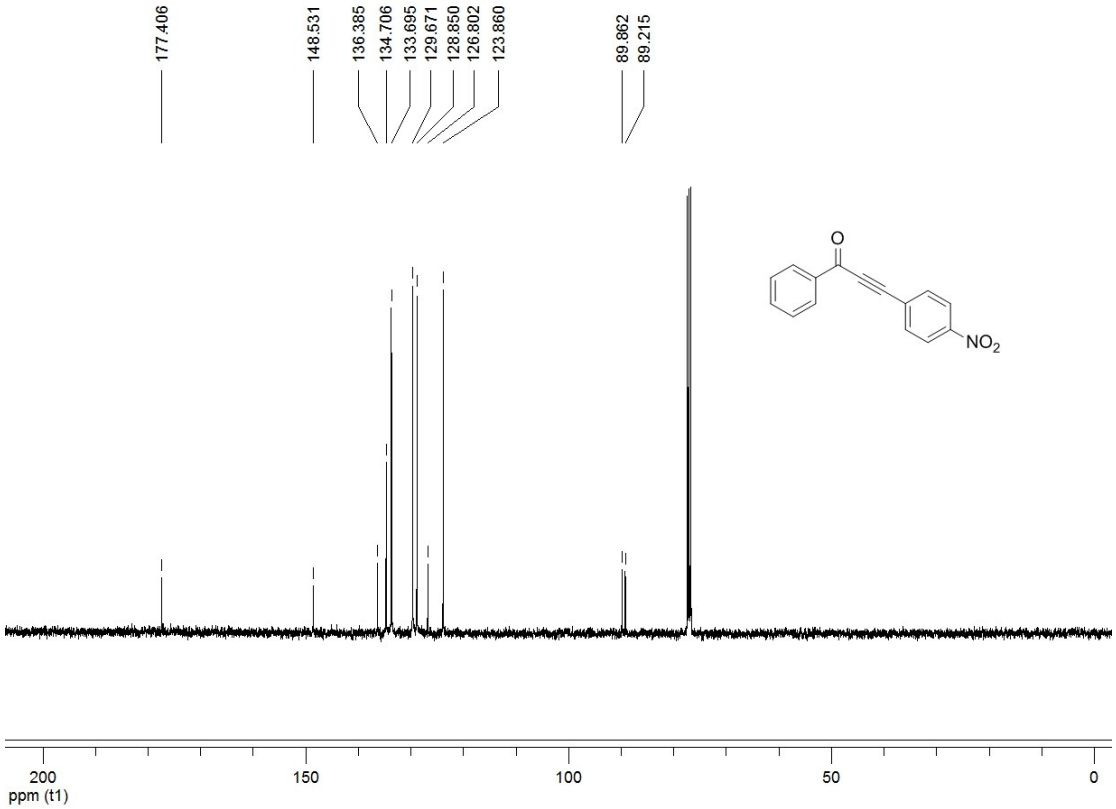
^{1}H NMR and ^{13}C NMR spetra of compound **3ag**



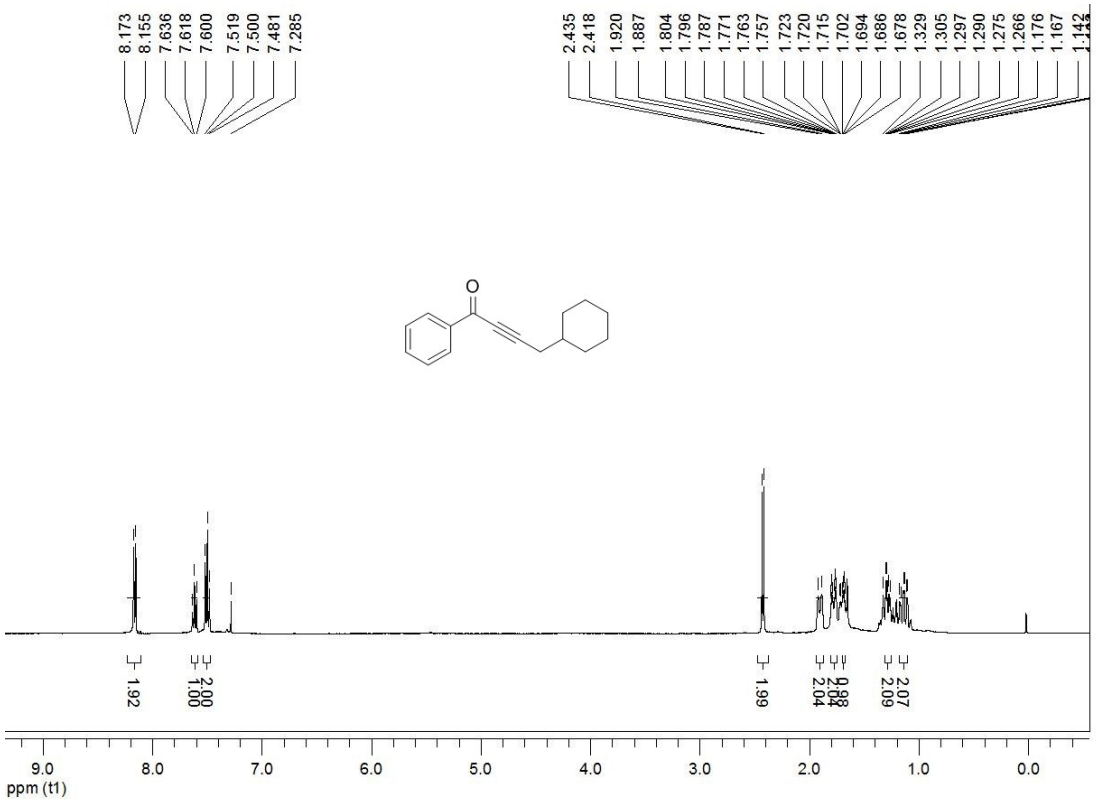


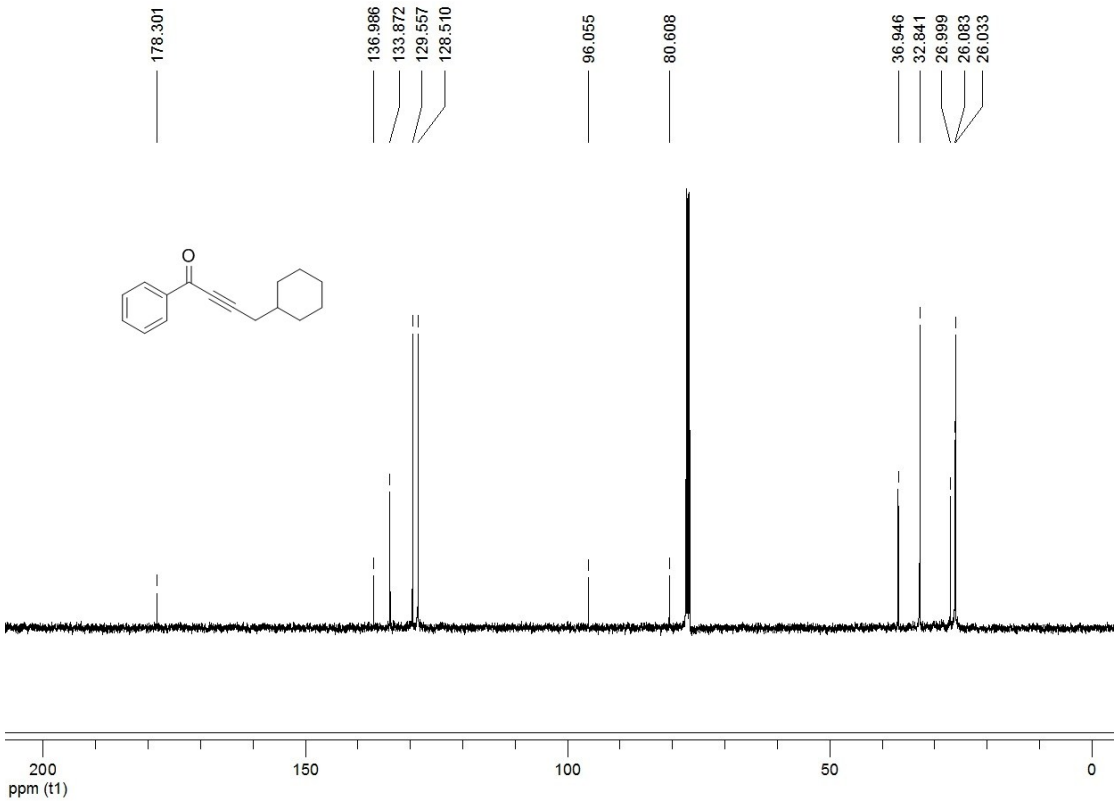
^{1}H NMR and ^{13}C NMR spetra of compound **3ah**



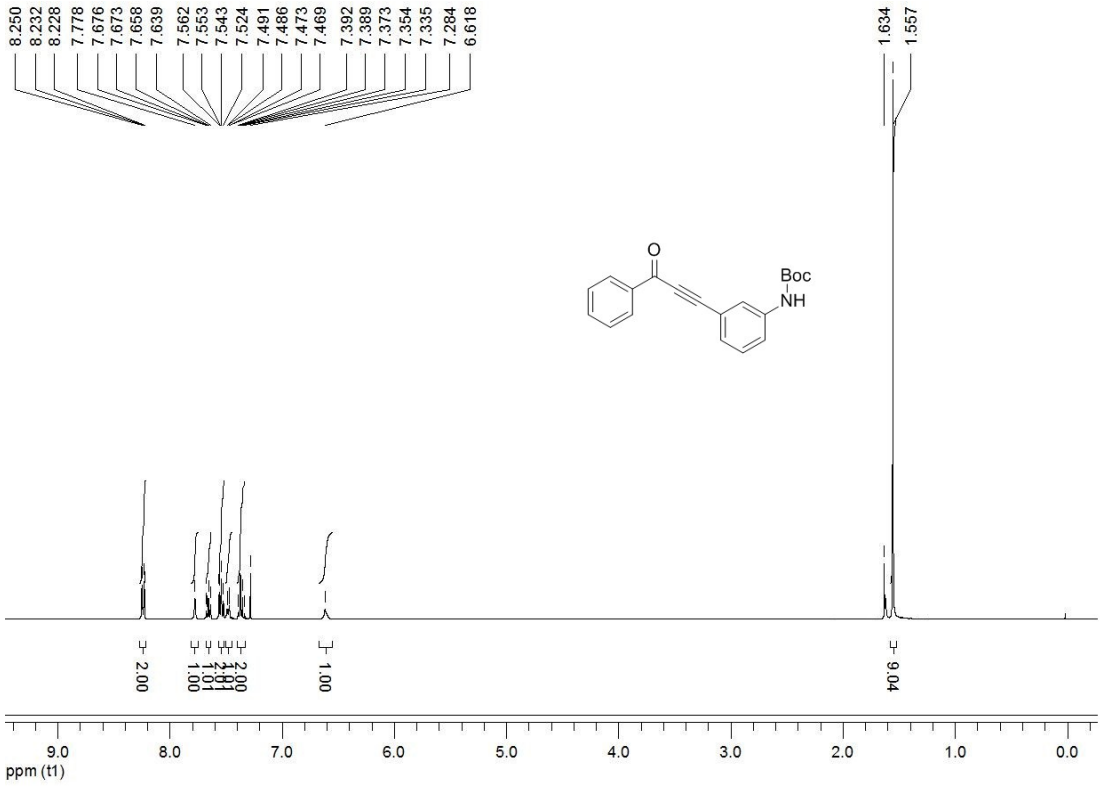


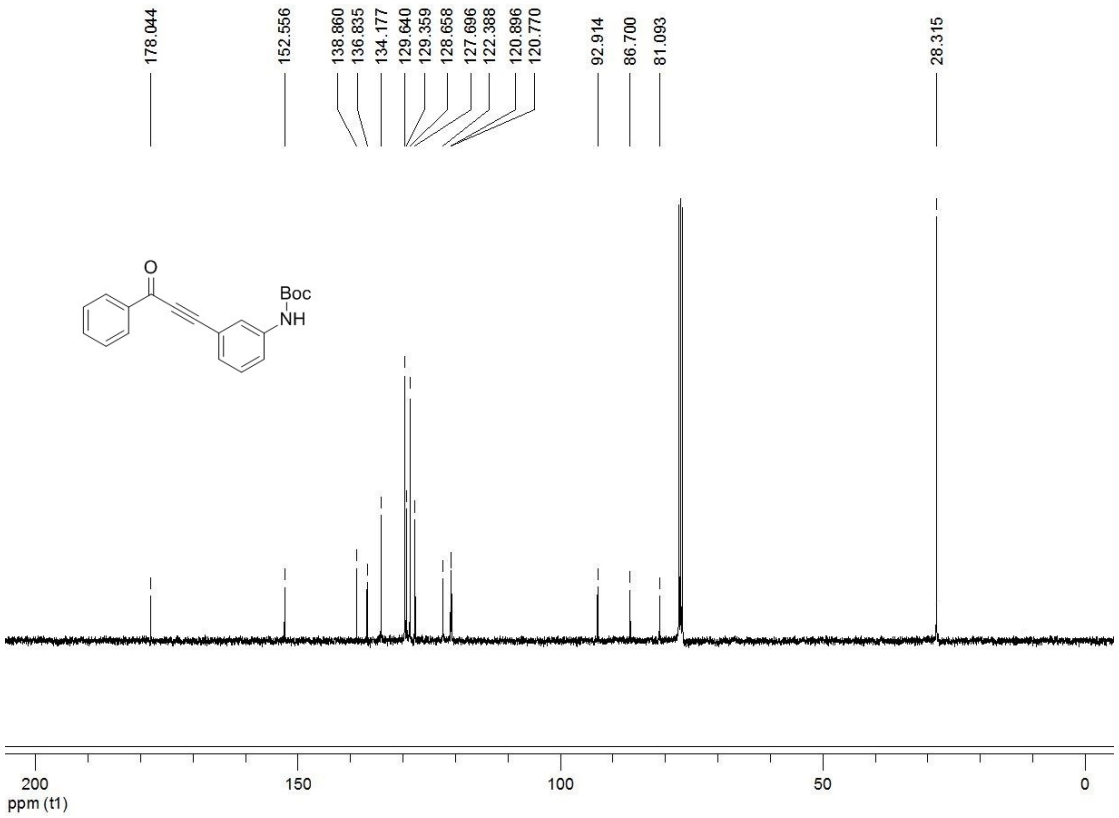
^{1}H NMR and ^{13}C NMR spetra of compound **3ai**



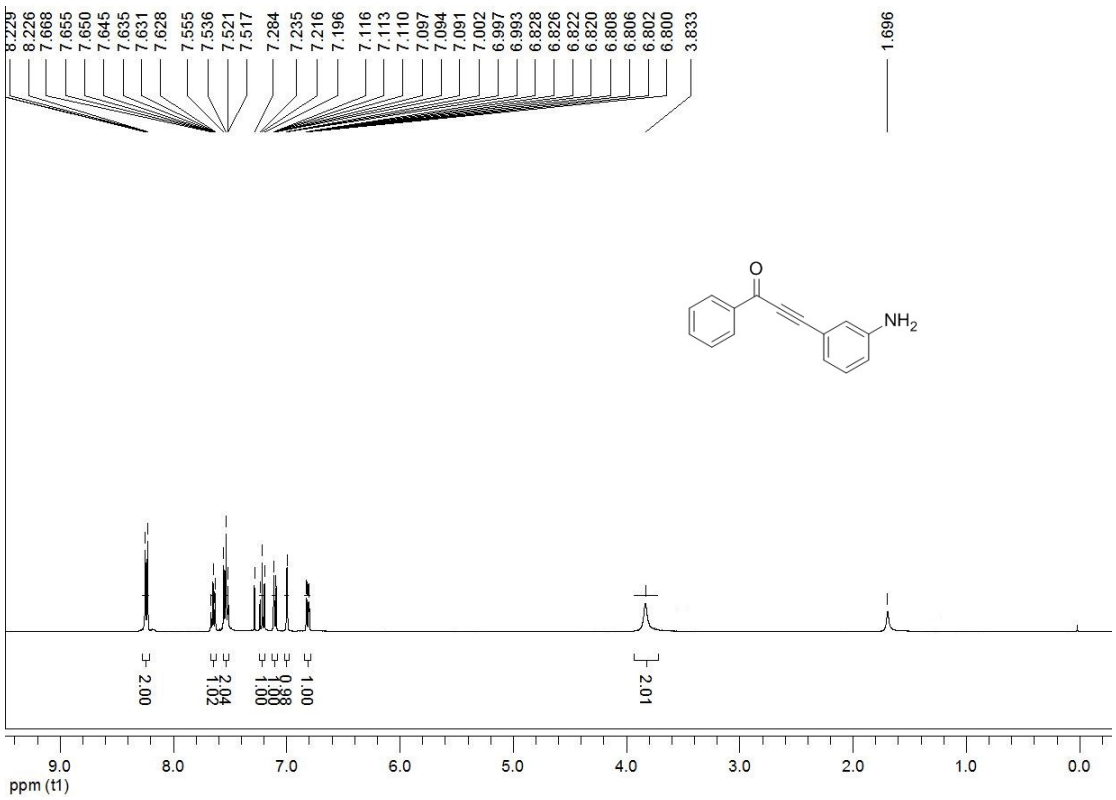


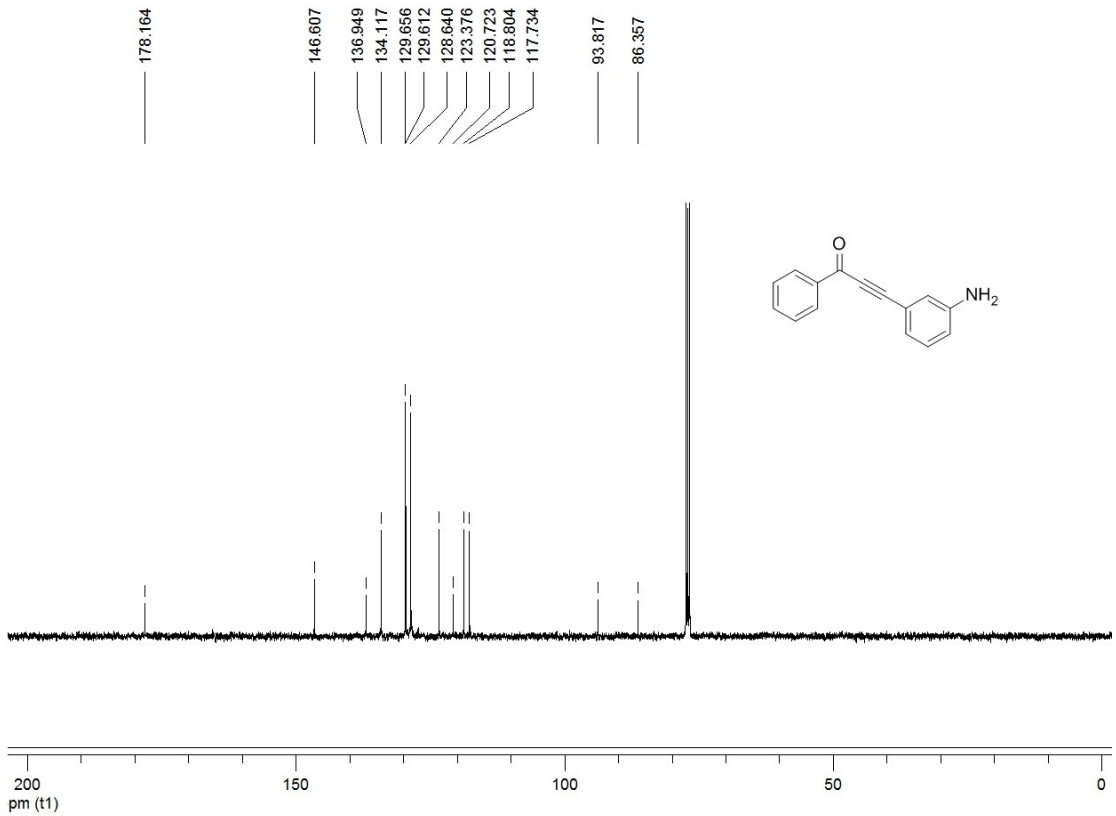
^{1}H NMR and ^{13}C NMR spetra of compound **3aj**



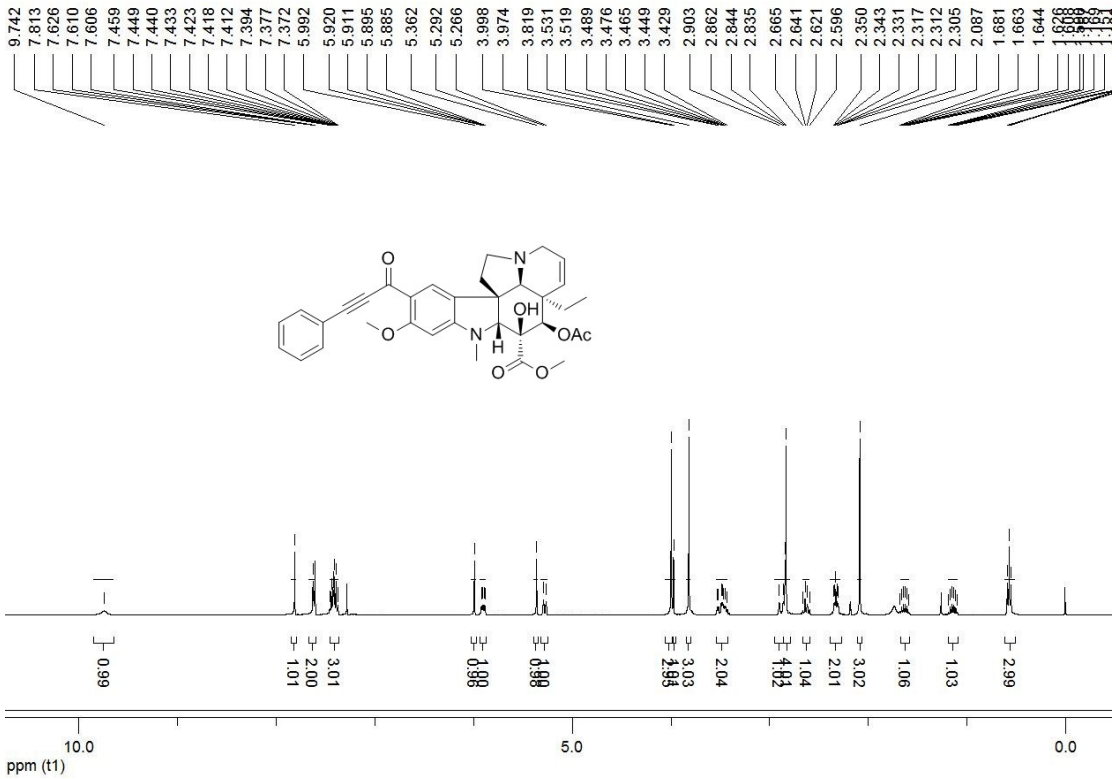


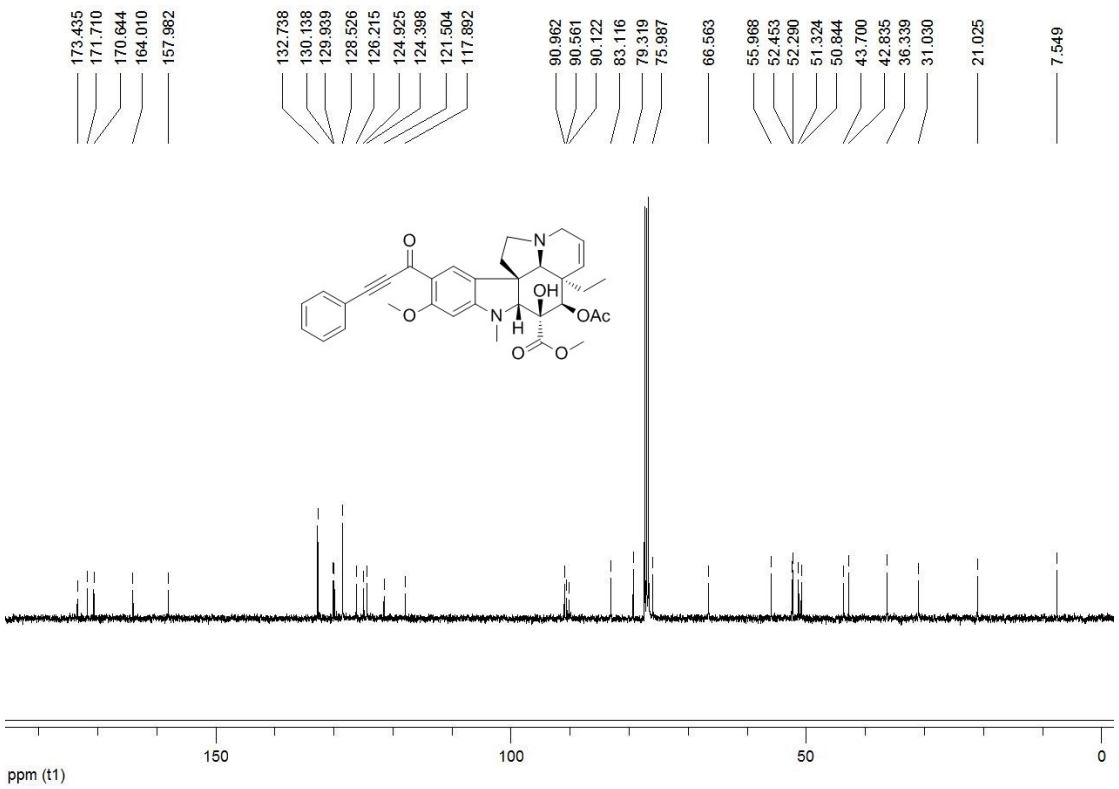
^{1}H NMR and ^{13}C NMR spetra of compound **3ak**



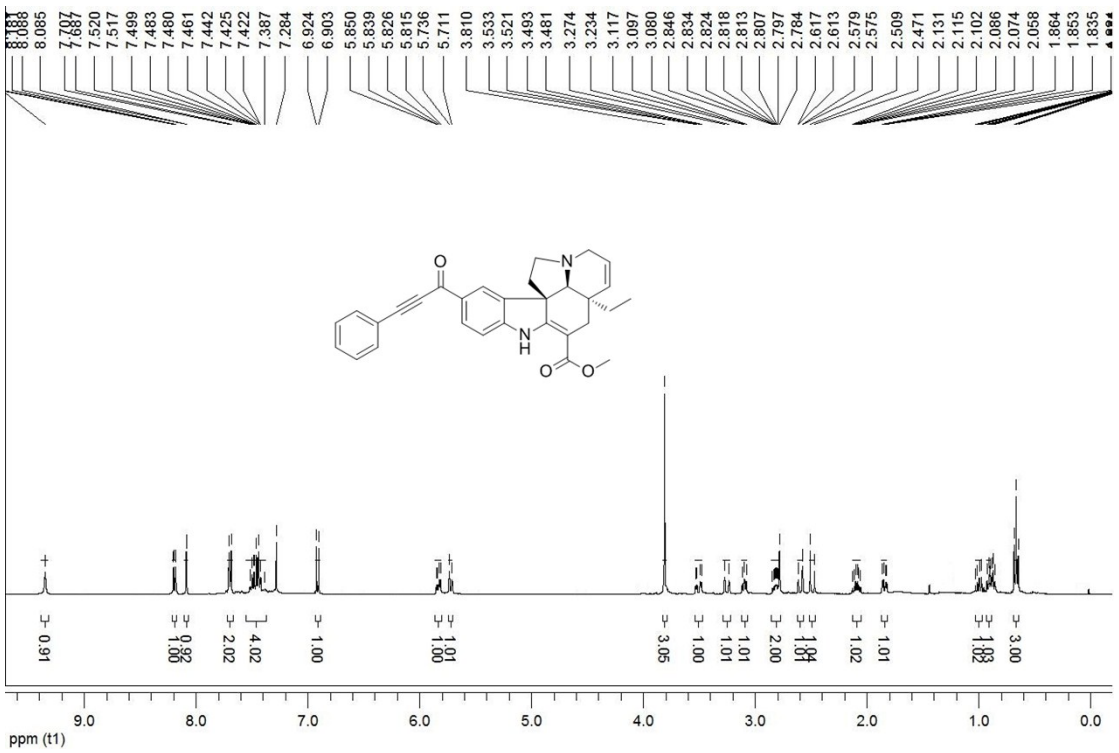


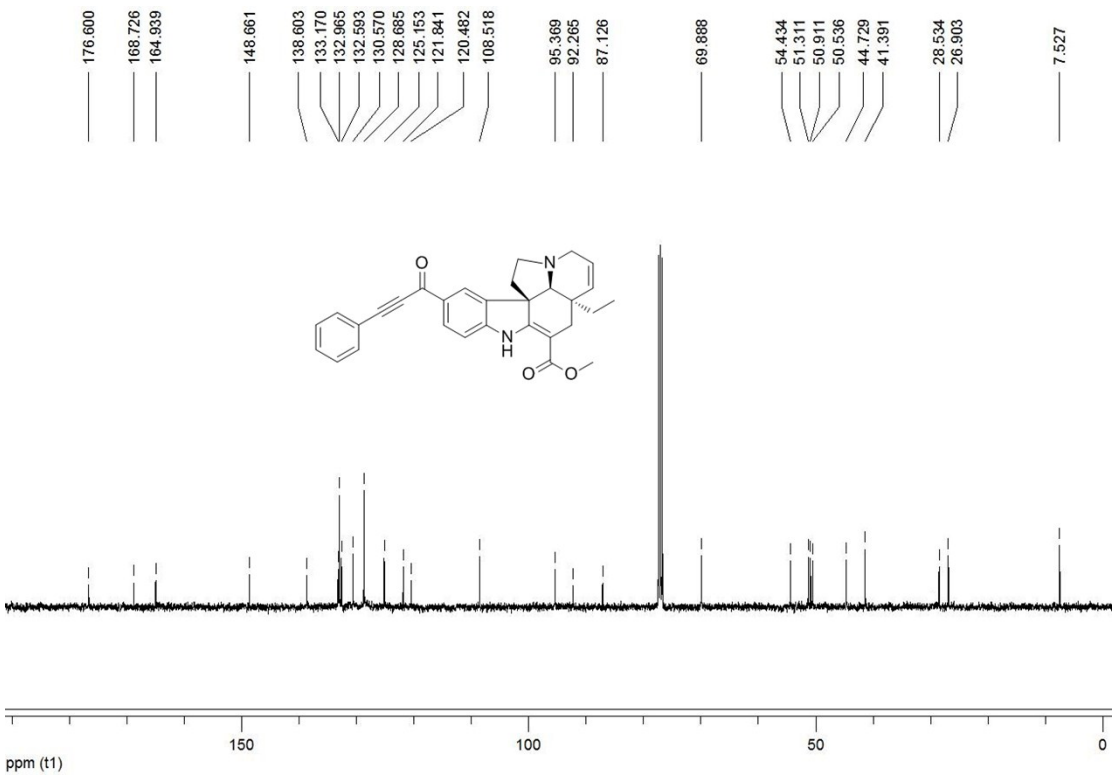
^{1}H NMR and ^{13}C NMR spetra of compound **7**



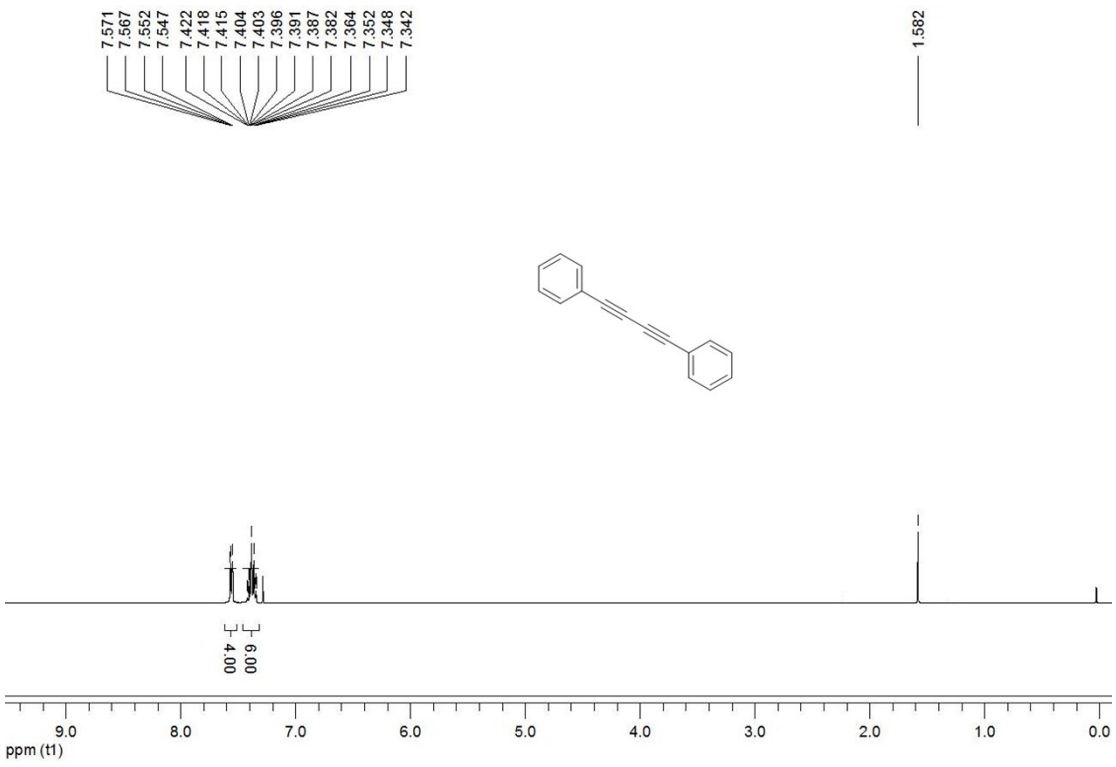


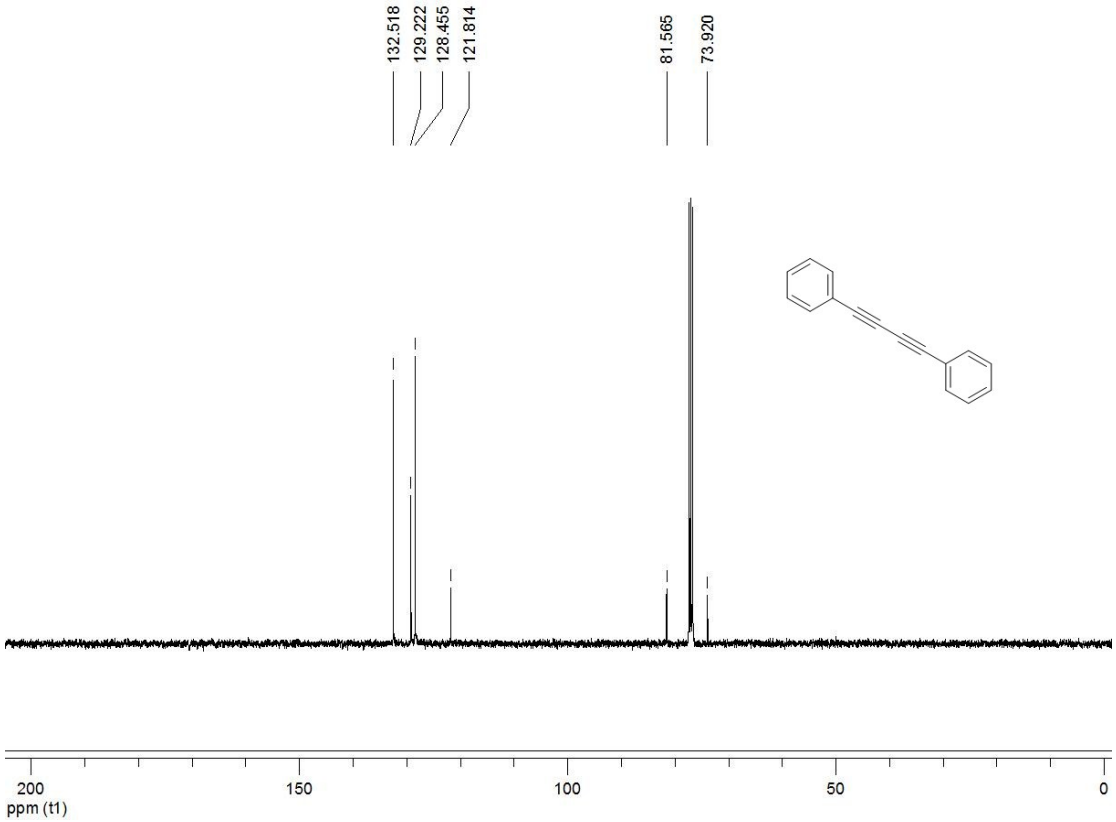
^{1}H NMR and ^{13}C NMR spetra of compound **8**





^{1}H NMR and ^{13}C NMR spetra of compound **9**




132.518
129.222
128.455
121.814
81.565
73.920
200
150
100
50
0
ppm (t1)