Supporting Information for

Gold-catalysed Cyclisation of *N*-Propargylic *β*-enaminones to Form 3-Methylene-1-pyrroline Derivatives†‡

Kommuru Goutham,[a,b] N. S. V. M. Rao Mangina,[a,b] Surisetti Suresh,[c] Pallepogu Raghavaiah,[d] and Galla V. Karunakar*[a,b]

[a]*Crop protection Chemicals Division,*
CSIR-Indian Institute of Chemical Technology,
Hyderabad, 500007, India.
gallavk@iict.res.in
[b]*Academy of Scientific and Innovative Research,*
New Delhi, 110001, India
[c]*Organic and Biomolecular Chemistry Division,*
CSIR-Indian Institute of Chemical Technology,
Hyderabad, 500007, India.
[d]*School of Chemistry, University of Hyderabad, Hyderabad, 500046, India.*

Contents:

1.1 General

Reactions were carried out in oven dried reaction flasks under nitrogen atmosphere and also solvents and reagents were transferred by oven-dried syringes to ambient temperature. TLC was performed on Merck silica gel aluminium sheets using UV as a visualizing agent and a 0.5% aqueous potassium permanganate solution and heat as developing agents. Solvents were removed under reduced pressure. Columns were packed as slurry of silica gel in hexane and ethyl acetate solvent mixture. The elution was assisted by applying pressure with an air pump. ^{13}C NMR spectra were recorded on 75 and 125 MHz spectrometers. ^{1}HNMR spectra were recorded on 300 and 500 MHz spectrometers in appropriate solvents using TMS as internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet. All reactions were performed under nitrogen atmosphere with freshly distilled and dried solvents. All solvents were distilled using standard procedures. Unless otherwise noted, reagents were obtained from Aldrich, Alfa Aesar, and TCI used without further purification. *N*-propargyl β-enaminones (**1a-1l**) were prepared by following the reported procedure.[1]

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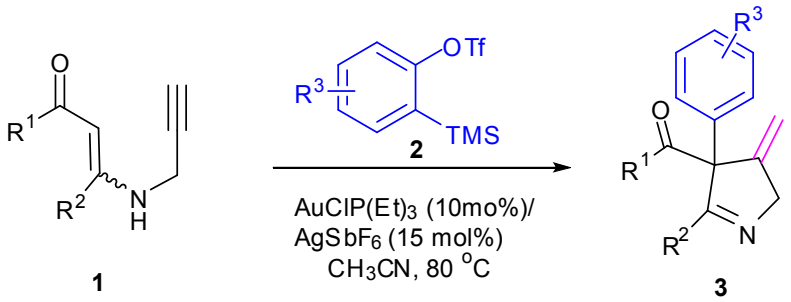
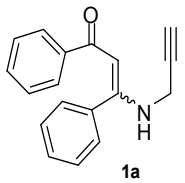
1. A. S. Karpov and T. J. J. Mu1ller, *Org. Lett.,* 2003, **5**, 3451.

1.2. General procedure for synthesis of 3-methylene-1-pyrrolines 3



In a 25 mL round-bottomed two-neck flask CsF (0.174 mg, 1.149 mmol, 3 equiv.) was evacuated and purged with dry nitrogen. To this reaction flask benzyne precursor 2-(trimethylsilyl) phenyl trifluoromethanesulfonate **2a** (0.093 mL, 0.383 mmol, 1 equiv.) was added and stirred for 10 min in CH_3CN (5 mL). To this reaction mixture a solution of *N*-propargyl β-enaminones **1** (0.383 mmol, 1 equiv) in CH_3CN (1 mL), $AuClP(Et)_3$ (13.4 mg, 10 mol%) and $AgSbF_6$ (19.7 mg, 15 mol%) was added. The reaction mixture was allowed to stir at 80 °C for 18 h. The reaction mixture was cooled to room temperature and it was filtered through Celite pad and silica gel. The organic layer was removed under reduced pressure and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with aqueous brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified through a silica gel column using hexane and ethyl acetate as eluent (10/0.7) to give pure 3-methylene-1-pyrrolines **3**.

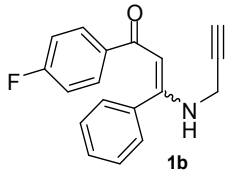
1.3. Spectroscopic data for propargyl β-enaminones (1a-i)



1,3-diphenyl-3-(prop-2-ynylamino)prop-2-en-1-one

1a

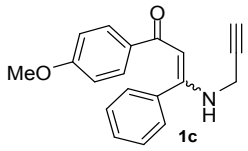
^{1}H NMR (300 MHz, $CDCl_3$): δ 11.33 (t, *J* = 12.1, 6.2 Hz, 1H), 7.93-7.88 (m, 2H), 7.50-7.37 (m, 8H), 5.84 (s, 1H), 3.94 (dd, *J* = 6.2, 2.3 Hz, 2H), 2.31 (t, *J* = 2.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl3) : δ 188.9, 165.6, 139.7, 134.7, 130.8, 129.7, 128.5, 128.1, 127.6, 127.0, 94.5, 79.6, 72.3, 34.0; HRMS (ESI): calcd for $C_{18}H_{16}NO$ [M+H]+ 262.1226; found 262.1222.



1-(4-fluorophenyl)-3-phenyl-3-(prop-2-ynylamino)prop-2-en-1-one

1b

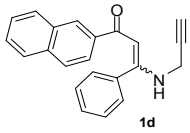
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.28 (t, *J* = 12.1, 6.3, Hz, 1H), 7.93-7.89 (m, 2H), 7.48 (s, 5H), 7.10-7.04 (m, 2H), 5.78 (s, 1H), 3.94 (dd, *J* = 6.3, 2.5 Hz, 2H), 2.31 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.6, 164.5 (d, *J* = 250.8 Hz, 1C), 136.0 (d, *J* = 2.7 Hz, 1C), 134.7, 129.8, 129.3 (d, *J* = 8.7 Hz, 2C), 128.7, 127.7, 115.1 (d, *J* = 21.4 Hz, 2C), 94.1, 79.6, 72.4, 34.2; HRMS (ESI): calcd for $C_{18}H_{15}FNO$ [M+H]+ 280.1132; found 280.1126.



1-(4-methoxyphenyl)-3-phenyl-3-(prop-2-ynylamino)prop-2-en-1-one

1c

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.21 (t, *J* = 12.1, 6.0, Hz, 1H), 7.90-7.87 (m, 2H), 7.50-7.45 (m, 5H), 6.92-6.88 (m, 2H), 5.80 (s, 1H), 3.92 (dd, *J* = 6.0, 2.3 Hz, 2H), 3.84 (s, 3H), 2.29 (t, *J* = 2.3, Hz, 1H); ^{13}C NMR (125, $CDCl_3$): 188.1, 167.3, 165.1, 134.9, 132.4, 129.6, 128.9, 128.7, 128.5, 127.7, 113.3, 94.1, 79.8, 72.2, 55.1, 34.0; HRMS (ESI): calcd for $C_{19}H_{20}NO_2$ [M+H]+ 292.1360; found 292.1357.

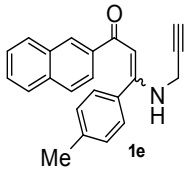


1-(naphthalen-2-yl)-3-phenyl-3-(prop-2-ynylamino)prop-2-en-1-one

1d

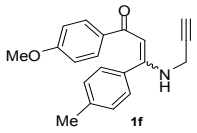
^{1}H NMR (300 MHz, $CDCl_3$): 11.33 (t, *J* = 12.1, 6.2 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 7.91-7.82 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58-7.41 (m, 8H), 5.66 (s, 1H), 4.01 (dd, *J* = 6.2, 2.5 Hz, 2H), 2.36 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 188.4, 165.5, 136.8, 134.4, 134.3, 132.4, 129.5, 128.8, 128.3, 127.6, 127.4, 127.3, 127.2, 126.9, 125.9, 123.7, 94.5, 79.5, 72.3, 33.8; HRMS (ESI): calcd for $C_{22}H_{18}NO$ [M+H]+

312.1578; found 312.1580.



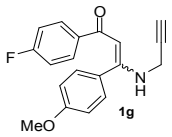
1-(naphthalen-2-yl)-3-(prop-2-ynylamino)-3-*p*-tolylprop-2-en-1-one

^{1}H NMR (300 MHz, $CDCl_3$): 11.31 (t, *J* = 12.1, 6.3 Hz, 1H), 8.27 (s, 1H), 7.91-7.86 (m, 1H), 7.77-7.74 (m, 1H), 7.72-7.66 (m, 3H), 7.38-7.30 (m, 3H), 7.15-7.11 (m, 2H), 5.86 (s, 1H), 3.83 (dd, *J* = 6.3, 2.4 Hz, 2H), 2.26 (s, 3H), 2.19 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) : 188.6, 166.1, 139.9, 137.1, 134.5, 132.6, 131.8, 129.2, 129.0, 127.7, 127.6, 127.4, 127.1, 126.1, 123.9, 94.6, 79.7, 72.3, 34.1, 21.2; HRMS (ESI): calcd for $C_{23}H_{20}NO$[M+H]+ 326.1355; found 326.1352.



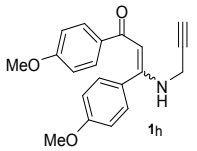
1-(4-methoxyphenyl)-3-(prop-2-ynylamino)-3-*p*-tolylprop-2-en-1-one

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.23 (t, *J* = 12.1, 6.4 Hz, 1H), 7.97-7.81 (m, 2H), 7.42-7.36 (m, 2H), 7.30-7.27 (m, 2H), 6.90-6.88 (m, 2H), 5.80 (s, 1H), 3.94 (dd, *J* = 6.4, 2.5 Hz, 2H), 3.84 (s, 3H), 2.42 (s, 3H), 2.29 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 188.1, 165.5, 161.9, 139.8, 132.7, 132.2, 129.2, 129.0, 127.8, 113.4, 94.2, 80.0, 72.2, 55.3, 34.1, 21.3; HRMS (ESI): calcd for $C_{20}H_{20}NO_2$ [M+H]+ 306.1816; found 306.1811.



1-(4-fluorophenyl)-3-(4-methoxyphenyl)-3-(prop-2-ynylamino)prop-2-en-1-one

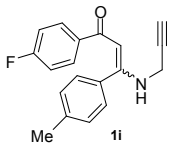
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.31 (t, *J* = 12.1, 6.3 Hz, 1H), 7.98-7.84 (m, 2H), 7.50-7.40 (m, 2H), 7.11-7.04 (m, 2H), 7.01-6.96 (m, 2H), 5.77 (s, 1H), 3.98 (dd, *J* = 6.3, 2.4 Hz, 2H), 3.87 (s, 3H), 2.32 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 187.0, 166.0, 164.2 (d, *J* = 250.6 Hz, 1C),, 160.7, 136.0 (d, *J* = 2.7 Hz, 1C), 132.3 (d, *J* = 9.9 Hz, 2C),129.1, 126.7, 114.9 (d, *J* = 21.7Hz, 2C), 113.9, 93.9, 79.7, 72.3, 55.1, 34.0; HRMS (ESI): calcd for $C_{19}H_{17}FNO_2$ [M+H]+ 310.2331; found 310.2337.



1,3-bis(4-methoxyphenyl)-3-(prop-2-ynylamino)prop-2-en-1-one

^{1}H NMR (500 MHz, $CDCl_3$): 11.23 (t, *J* = 12.1, 6.4 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.9 Hz,

2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.80 (s, 1H), 3.96 (dd, *J* = 6.4, 2.4 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.30 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : 187.9, 165.2, 161.8, 160.6, 132.6, 129.3, 128.9, 127.2, 113.9, 113.3, 94.0, 80.0, 72.1, 55.2, 55.1, 34.0; HRMS (ESI): calcd for $C_{20}H_{20}NO_3$ [M+H]+ 322.1772; found 322.1769.

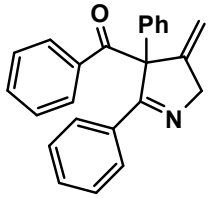


1i

1-(4-fluorophenyl)-3-(prop-2-ynylamino)-3-*p*-tolylprop-2-en-1-one

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.30 (t, *J* = 12.1, 6.8, Hz, 1H), 7.94-7.87 (m, 2H), 7.40-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.11-7.03 (m, 2H), 5.77 (s, 1H), 3.96 (dd, *J* = 6.8, 3.0 Hz, 2H), 2.43 (s, 3H), 2.31 (t, *J* = 3.0 Hz, 1H); ^{13}C NMR (125, $CDCl_3$): 187.3, 166.1, 164.3 (d, *J*=251.5Hz, 1C), 140.0, 136.1 (d, *J*=3.6Hz, 1C), 131.7, 129.3, 129.2 (d, *J*=2.7Hz, 2C), 127.6, 114.9 (d, *J*=20.8Hz, 2C), 93.9, 79.7, 72.3, 34.1, 21.2; HRMS (ESI): calcd for $C_{19}H_{17}FNO$ [M+H]+ 294.1288; found 294.1284.

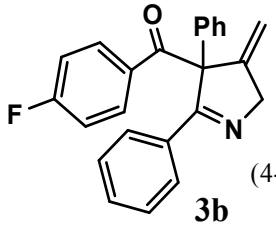
1.4 Spectroscopic data for 3,4 –Dihydro-2H-Pyrroles (3a-m)



3a

(3-methylene-4,5-diphenyl-3,4-dihydro-2*H*-pyrrol-4-yl)(phenyl)methanone

R_f: 0.3; Hexane: Ethyl acetate mixture(10:0.7); Yield: 78%; White solid; Melting Point: 168-170 ^{o}C; IR (CH_2Cl_2): ῡ = 2962, 2853, 1679, 1600, 1446, 1229, 1028 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.70 (m, 2H), 7.69-7.64 (m, 2H), 7.43-7.33 (m, 3H), 7.32-7.17 (m, 8H), 5.18 (s, 1H), 5.12 (s, 1H), 4.97(d, *J* =21.1 Hz, 1H), 4.79 (d, *J* =21.1 Hz, 1H); ^{13}C NMR (125, $CDCl_3$) : δ 196.4, 174.1, 153.1, 138.5, 136.7, 133.5, 132.2, 130.5, 129.1, 128.6, 128.2, 128.0, 127.9, 127.2, 109.4, 75.5, 64.6; HRMS (ESI): calcd for $C_{24}H_{20}NO$ [M+H]+ 338.1539; found 338.1533.

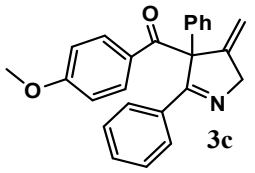


3b

(4-fluorophenyl)(3-methylene-4,5-diphenyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

R_f: 0.3; Hexane: Ethyl acetate mixture(10:0.7); Yield: 58%; Colourless oil; IR (CH_2Cl_2): ῡ = 2922**,** 2851, 1637, 1462, 1278, 1157, 875 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.74 (m, 2H), 7.69-7.63 (m, 2H),

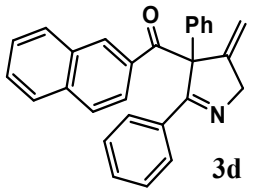
7.40-7.36 (m, 2H), 7.34 -7.17 (m, 6H), 6.96-6.88 (m, 2H), 5.18 (s, 1H), 5.12 (s, 1H), 4.99(d, *J* =21.1 Hz, 1H), 4.77 (d, *J* =21.1 Hz, 1H);^{13}C NMR (75, $CDCl_3$): δ 194.7, 174.2, 164.8 (d, *J*=254.6Hz, 1C), 153.0, 131.8 (d, *J*=8.7Hz, 1C), 130.6, 128.5 (d, *J*=6.5Hz, 2C), 128.3, 127.8, 127.3, 115.1 (d, *J*=21.9Hz, 2C), 109.3, 75.2, 64.4; HRMS (ESI): calcd for $C_{24}H_{19}FNO$ [M+H]+ 356.1445; found 356.1439.



3c

(4-methoxyphenyl)(3-methylene-4,5-diphenyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

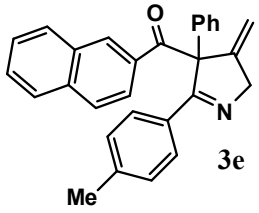
R_f: 0.3; Hexane: Ethyl acetate mixture(10:0.7); Yield: 66%; Pale yellow oil; IR (CH_2Cl_2): ῡ = 2924, 2851, 1599, 1305, 1241, 1170, 1027 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79-7.76 (m, 2H), 7.69-7.65 (m, 2H), 7.38-7.35(m, 2H), 7.29-7.24 (m, 4H), 7.22-7.18 (m, 2H), 6.74-6.70(m, 2H), 5.17 (s, 1H), 5.11 (s, 1H), 4.96(d, *J* =21.0 Hz, 1H), 4.76 (d, *J* =21.0 Hz, 1H); ^{13}C NMR (75, $CDCl_3$) : δ 194.5, 174.7, 162.7, 153.4, 138.5, 133.7, 131.8, 130.5, 129.0, 128.8, 128.6, 128.2, 127.8, 127.1, 113.2, 109.1, 75.3, 64.5, 55.2; HRMS (ESI): calcd for $C_{25}H_{22}NO_2$ [M+H]+ 368.1645; found 368.1639.



3d

(3-methylene-4,5-diphenyl-3,4-dihydro-2*H*-pyrrol-4-yl)(naphthalen-2-yl)methanone

R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 67%; white solid; Melting Point: 218-200 ^{o}C; IR (CH_2Cl_2): ῡ = 2924, 2853, 1588, 1425, 1295, 1122, 1026 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 8.30 (s, 1H), 7.84-7.78 (m, 2H), 7.72-7.68 (m, 3H), 7.54-7.48 (m, 1H), 7.47-7.41 (m, 3H), 7.34-7.28 (m, 3H), 7.25-7.20 (m, 2H), 7.19-7.15 (m, 2H), 5.19 (s, 1H), 5.15 (s, 1H), 5.05(d, *J* =21.0 Hz, 1H), 4.84 (d, *J* =21.0 Hz, 1H); ^{13}C NMR (125, $CDCl_3$): 196.1, 174.4, 153.2, 138.5, 134.8, 133.8, 133.6, 132.0, 130.9, 130.6, 129.7, 128.7, 128.6, 128.3, 127.9, 127.7, 127.4, 127.3, 126.5, 125.1, 109.6, 75.7, 64.7; HRMS (ESI): calcd for $C_{28}H_{22}NO$[M+H]+ 388.1695, found 388.1692.

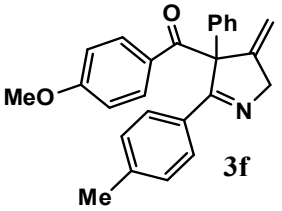


3e

(3-methylene-4-phenyl-5-*p*-tolyl-3,4-dihydro-2*H*-pyrrol-4-yl)(naphthalen-2-yl)methanone

R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 64%; white solid; Melting Point: 208-210 ^{o}C; IR (CH_2Cl_2): ῡ = 2923, 2851, 1675, 1494, 1301, 1189, 900 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.86-7.78 (m, 2H), 7.76-7.60 (m, 4H), 7.53-7.39 (m, 4H), 7.35-7.26 (m, 3H), 7.01-6.95 (d, *J* = 9.2 Hz, 2H), 5.17 (s, 1H), 5.12 (s, 1H), 5.03(d, *J* =21.1 Hz, 1H), 4.81 (d, *J* =21.1 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (75,

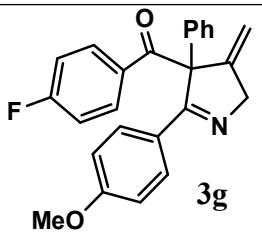
$CDCl_3$): δ 196.2, 174.0, 153.5, 141.0, 138.6, 134.8, 133.9, 132.0, 130.9, 129.7, 129.1, 128.7, 128.6, 128.3, 127.9, 127.7, 127.4, 127.2, 126.4, 125.1, 109.3, 75.5, 64.6, 21.2; HRMS (ESI): calcd for $C_{29}H_{24}NO$[M+H]+ 402.1852, found 402.1849.



3f

(4-methoxyphenyl)(3-methylene-4-phenyl-5-*p*-tolyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

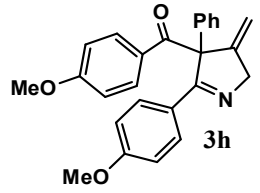
R_f: 0.3; Hexane: Ethyl acetate mixture(10:0.7); Yield: 67%; colourless oil; [1] IR (CH_2Cl_2): ῡ = 2924, 2852, 1601, 1510, 1242, 1171, 1028 cm^{-1}; H NMR (500 MHz, $CDCl_3$): 7.80-7.76 (m, 2H), 7.60-7.57 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.21 (m, 3H), 7.05-6.98 (m, 2H), 6.76-6.71 (m, 2H), 5.14 (s, 1H), 5.09 (s, 1H), 4.94(d, *J* =20.9 Hz, 1H), 4.74 (d, *J* =20.9 Hz, 1H), 3.77 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75, $CDCl_3$): 194.5, 174.5, 162.6, 153.5, 140.8, 138.5, 131.7, 128.9, 128.7, 128.5, 127.7, 127.0, 113.1, 108.8, 75.0, 64.2, 55.1, 21.2; HRMS (ESI): calcd for $C_{26}H_{24}NO_2$ [M+H]+ 382.1801; found 382.1800.



3g

(4-fluorophenyl)(5-(4-methoxyphenyl)-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

R_f: 0.2; Hexane: Ethyl acetate mixture(10:0.7); Yield: 57%; colourless oil; IR (CH_2Cl_2): ῡ = 2928, 2851, 1625, 1503, 1399, 1220, 1023 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : 7.84-7.75 (m, 2H), 7.69-7.58 (m, 2H), 7.44-7.35 (m, 2H), 7.35-7.27 (m, 3H), 6.99-6.86 (m, 2H), 6.76-6.66 (m, 2H), 5.13 (s, 1H), 5.08 (s, 1H), 4.92(d, *J* =20.9 Hz, 1H), 4.74 (d, *J* =20.9 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (125, $CDCl_3$): 195.0, 173.3, 164.8 (d, *J*=255.2Hz, 1C), 161.4, 153.5, 138.3, 132.8 (d, *J*=3.63Hz, 1C), 131.8 (d, *J*=9.0Hz, 2C), 130.3, 128.6, 127.9, 127.2, 126.1, 115.1(d, *J*=21.7Hz, 2C), 113.7, 109.0, 75.1, 64.3, 55.1; HRMS (ESI): calcd for $C_{25}H_{21}FNO_2$ [M+H]+ 386.1524, found 386.1521.

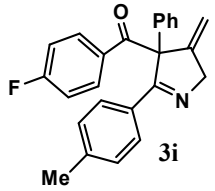


3h

(4-methoxyphenyl)(5-(4-methoxyphenyl)-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

R_f: 0.2; Hexane: Ethyl acetate mixture(10:0.7); Yield: 72%; white solid; Melting Point: 252-254 °C; IR (CH_2Cl_2): ῡ = 2918, 2850, 1599, 1420, 1256, 1158, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.73-7.65(m, 4H), 7.31-7.27(m, 2H), 7.23-7.19 (m, 3H), 6.75-6.59 (m, 4H) 5.10 (d, J =20.5Hz, 2H), 4.89 (d, *J*

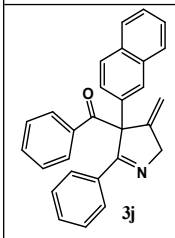
=20.7 Hz, 1H), 4.68 (d, *J* =20.7 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125, $CDCl_3$): 194.8, 173.9, 162.7, 153.8, 141.3, 138.7, 131.7,130.3, 129.1, 128.8, 127.8, 127.1, 113.7, 108.8, 75.0, 64.2, 55.2, 55.1; HRMS (ESI): calcd for $C_{26}H_{24}NO_3$ [M+H]+ 398.1270, found 398.1267.



3i

(4-fluorophenyl)(3-methylene-4-phenyl-5-*p*-tolyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

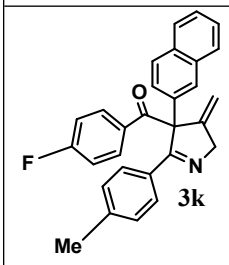
R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 55%; Yellow oil; IR (CH_2Cl_2): ῡ = 2924, 2854, 1681, 1505, 1234, 1158, 864 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83-7.75 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.41-7.36 (m, 2H), 7.33-7.27 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.96-6.87 (m, 2H), 5.14 (s, 1H), 5.08 (s, 1H), 4.94(d, *J* =21.1 Hz, 1H), 4.75 (d, *J* =21.1 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75, $CDCl_3$): δ 194.7, 173.9, 164.8 (d, *J*=255.2Hz, 1C), 153.2, 141.0, 138.2 , 132.9, 132.8, 131.8 (d, *J*=8.2Hz, 1C), 130.7, 129.0, 128.5 (d, *J*=8.2Hz, 2C), 127.8, 127.2, 115.0 (d, *J*=21.4Hz, 2C), 109.1, 75.1, 64.3, 21.2; HRMS (ESI): calcd for $C_{25}H_{21}FNO$ [M+H]+ 370.1601, found 370.1600.



3j

(3-methylene-4-(naphthalen-2-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-4-yl)(phenyl)methanone

R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 66%; white solid; Melting Point: 218-220 ^{o}C; IR (CH_2Cl_2): ῡ = 2922, 2851, 1624, 1443, 1359, 1176, 968 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85-7.60 (m, 8H), 7.51-7.35 (m, 3H), 7.32-7.16 (m, 6H), 5.22 (s, 1H), 5.18 (s, 1H), 5.0 (d, *J* =21.1 Hz, 1H), 4.82 (d, *J* =21.1 Hz, 1H); ^{13}C NMR (75, $CDCl_3$): δ 196.7, 174.2, 152.9, 136.7, 136.1, 133.5, 132.8, 132.3, 130.6, 129.2, 128.7, 128.3, 128.2, 128.0, 127.4, 127.3, 127.1, 127.0, 126.2, 125.8, 109.7, 75.8, 64.6; HRMS (ESI): calcd for $C_{28}H_{22}NO$ [M+H]+ 388.1695, found 388.1698.

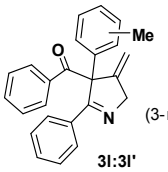


3k

(4-fluorophenyl)(3-methylene-4-(naphthalen-2-yl)-5-*p*-tolyl-3,4-dihydro-2*H*-pyrrol-4-yl)methanone

R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 60%; brown oil; IR (CH_2Cl_2): ῡ = 2923, 2853, 1680, 1505, 1234, 1158, 754 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84-7.78 (m, 4H), 7.70-7.61 (m, 5H), 7.47-7.38 (m, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.93 (t, *J* = 8.5 Hz, 2H), 5.19 (s, 1H), 5.15 (s, 1H), 4.96(d, *J* =21.0

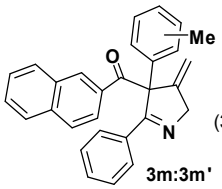
Hz, 1H), 4.79 (d, *J* =21.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (125, $CDCl_3$): δ 195.1, 174.0, 164.9 (d, *J* = 255.2 Hz, 1C), 153.1, 141.2, 135.8, 132.8 (d, *J* = 2.7 Hz, 1C), 132.3, 132.0 (d, *J* = 9.9 Hz, 2C), 130.7, 129.2, 128.6, 128.2, 127.36, 127.32, 127.1, 127.0, 126.2, 125.9, 115.2 (d, *J* = 21.7 Hz, 2C), 109.4, 75.4, 64.4, 21.3; HRMS (ESI): calcd for $C_{29}H_{23}NOF$ [M+H]+ 420.1758, found 420.1747.



(3-methylene-5-phenyl-4-p/*m*-tolyl-3,4-dihydro-2*H*-pyrrol-4-yl)(phenyl)methanone

3l:3l'

R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 64%; pale yellow solid; Melting Point: 133-135 °C; IR (CH_2Cl_2): ῡ = 2923, 2846, 1673, 1446, 1227, 1026, 897 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.62 (m, 4H), 7.40-7.33 (m, 1H), 7.30-7.10 (m, 9H), 5.18 (s, 1H), 5.12 (s, 1H), 4.96(d, *J* =21.1 Hz, 1H), 4.79 (d, *J* =21.1 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (75, $CDCl_3$): δ 196.5, 174.3, 153.2, 153.1, 138.5, 137.4, 137.0, 136.8, 135.6, 133.6, 132.1, 130.4, 129.3, 129.1, 128.6, 128.5, 128.2, 127.9, 127.7, 125.6, 109.4, 109.2, 75.5, 75.2, 64.6, 21.5, 20.9; HRMS (ESI): calcd for $C_{25}H_{22}NO$ [M+H]+ 352.1695, found 352.1692.



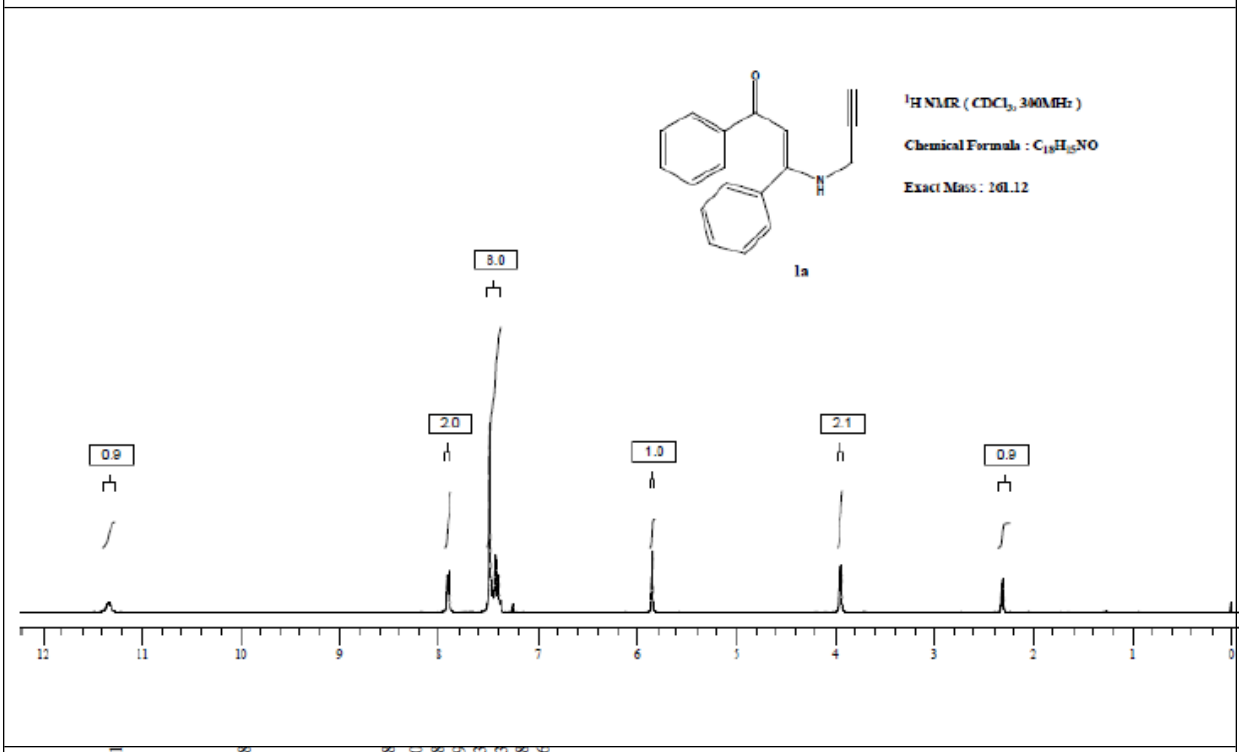
(3-methylene-5-phenyl-4-*p/m*-tolyl-3,4-dihydro-2*H*-pyrrol-4-yl)(naphthalen-2-yl)methanone

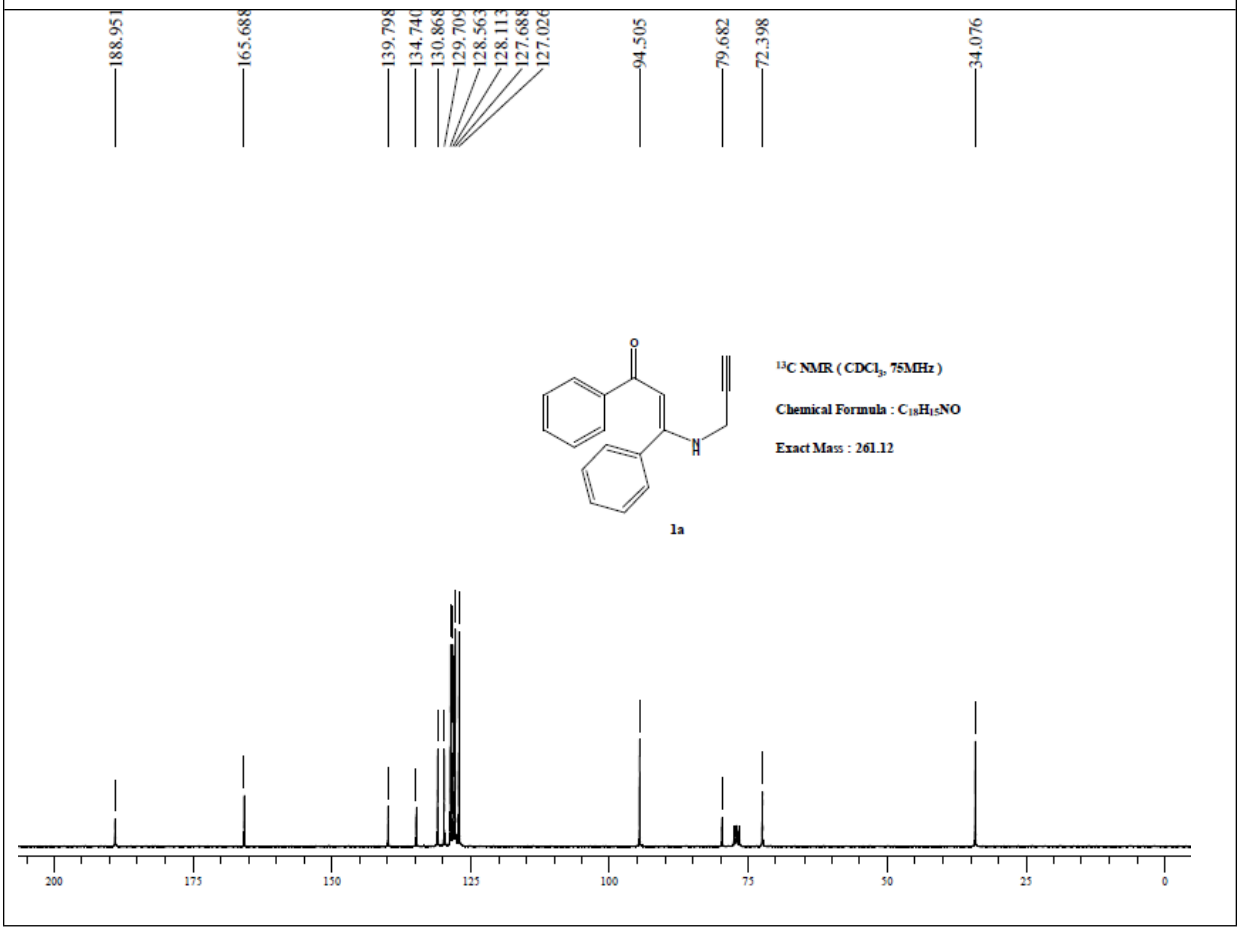
3m:3m'

R_f: 0.4; Hexane: Ethyl acetate mixture(10:0.7); Yield: 68%; white solid; Melting Point: 201-203 °C; IR (CH_2Cl_2): ῡ = 2918, 2850, 1591, 1423, 1294, 1116, 930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 8.30 (s, 1H), 7.98-7.88 (m, 1H), 7.85-7.77 (m, 2H), 7.74-7.68 (m,3H), 7.55-7.42 (m, 2H), 7.34-7.27 (m, 2H), 7.22-7.16 (m, 3H), 7.15-7.10 (m, 2H), 5.18 (s, 1H), 5.11 (s, 1H), 4.97(d, *J* =21.1 Hz, 1H), 4.79 (d, *J* =21.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75, $CDCl_3$): 196.0, 174.2, 153.2, 153.0, 138.3, 136.8, 135.4, 134.5, 133.6, 133.4, 132.2, 131.8, 130.6, 130.3, 129.4, 129.1, 128.4, 128.0, 127.6, 127.5, 127.1, 126.2, 125.4, 124.9, 109.3, 109.0, 75.5, 75.1, 64.4, 21.3, 20.7. HRMS (ESI): calcd for $C_{29}H_{24}NO$[M+H]+ 402.1852, found 402.1845.

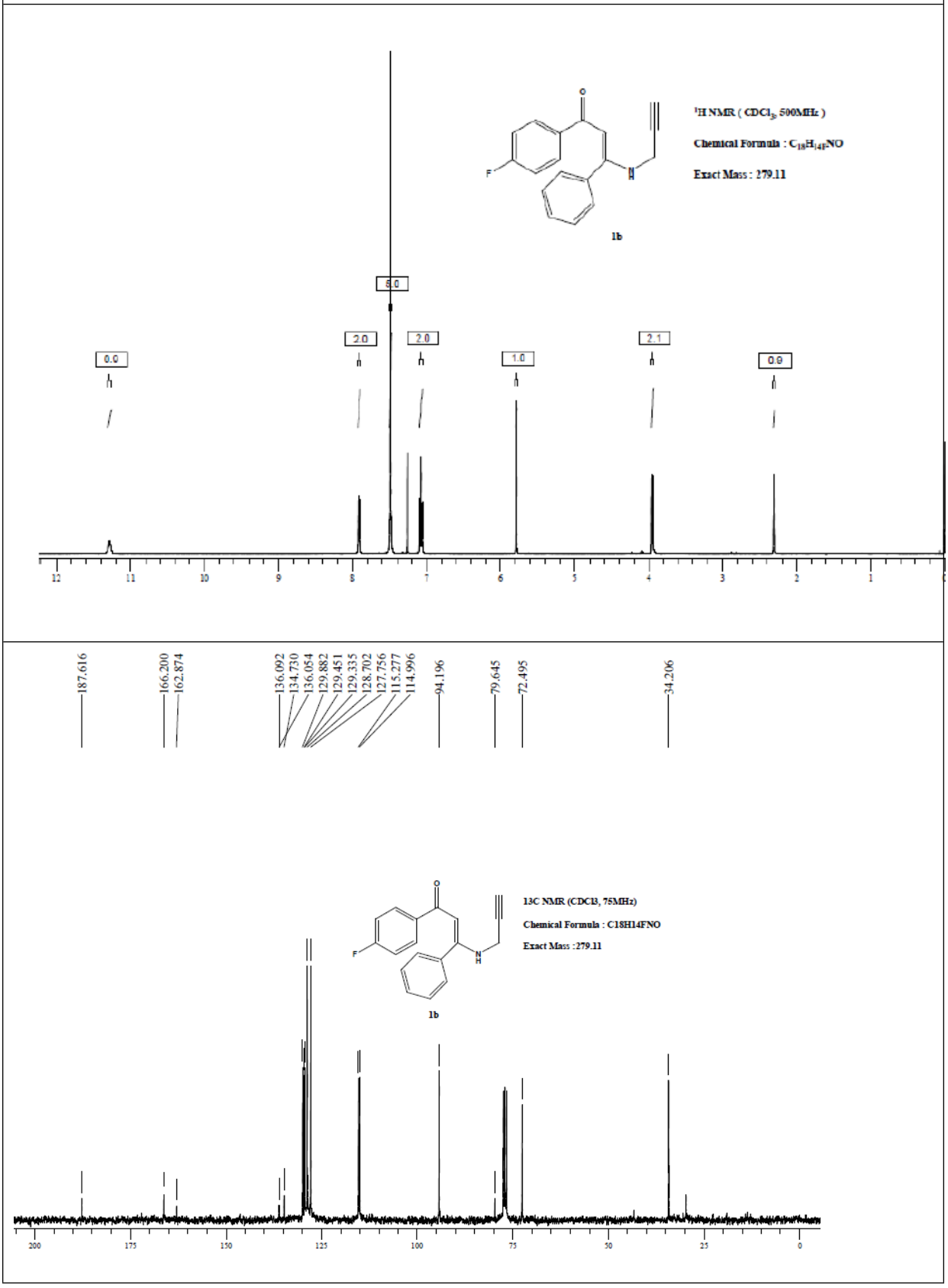
1.5 Representative spectral data

1,3-diphenyl-3-(prop-2-ynylamino)prop-2-en-1-one **1a**

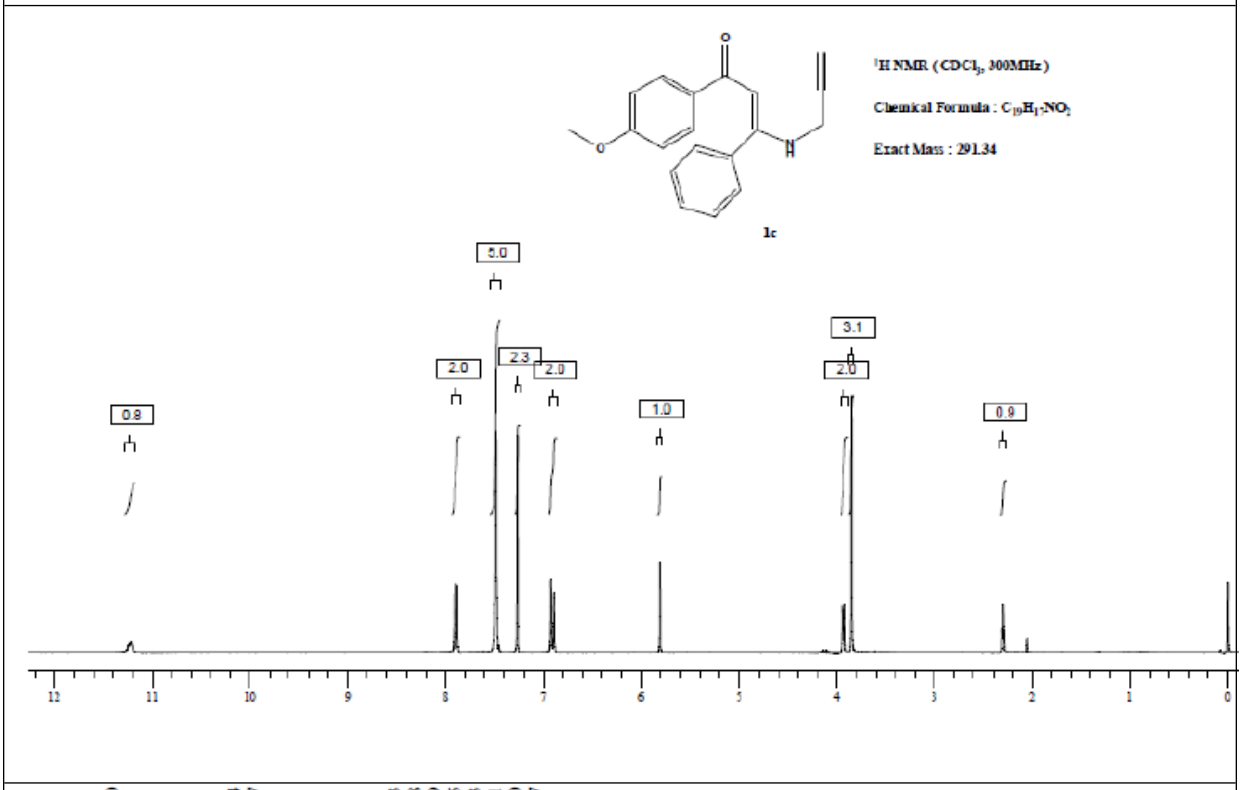


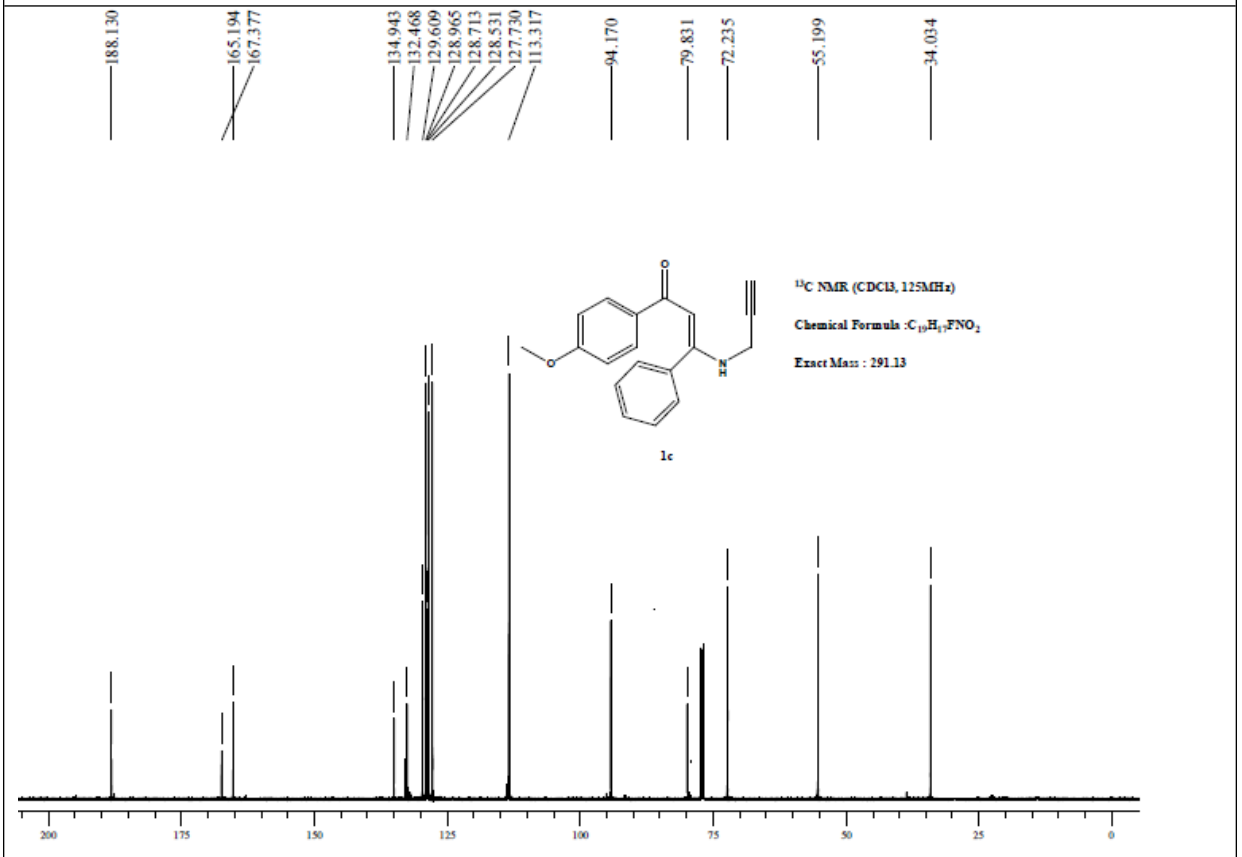


1-(4-fluorophenyl)-3-phenyl-3-(prop-2-ynylamino)prop-2-en-1-one **1b**

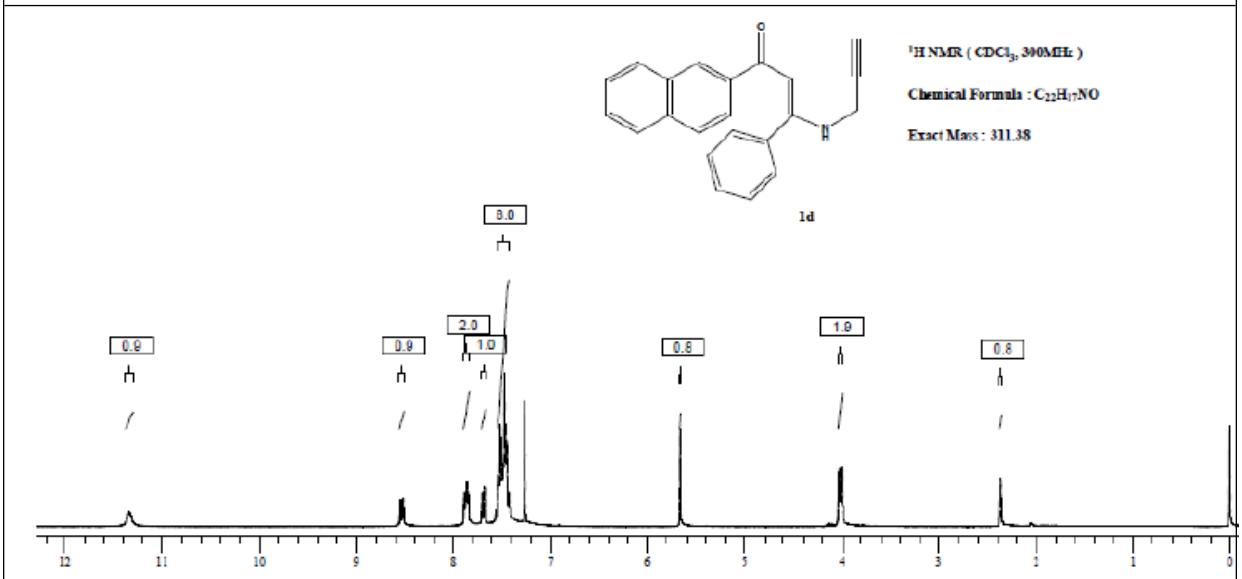


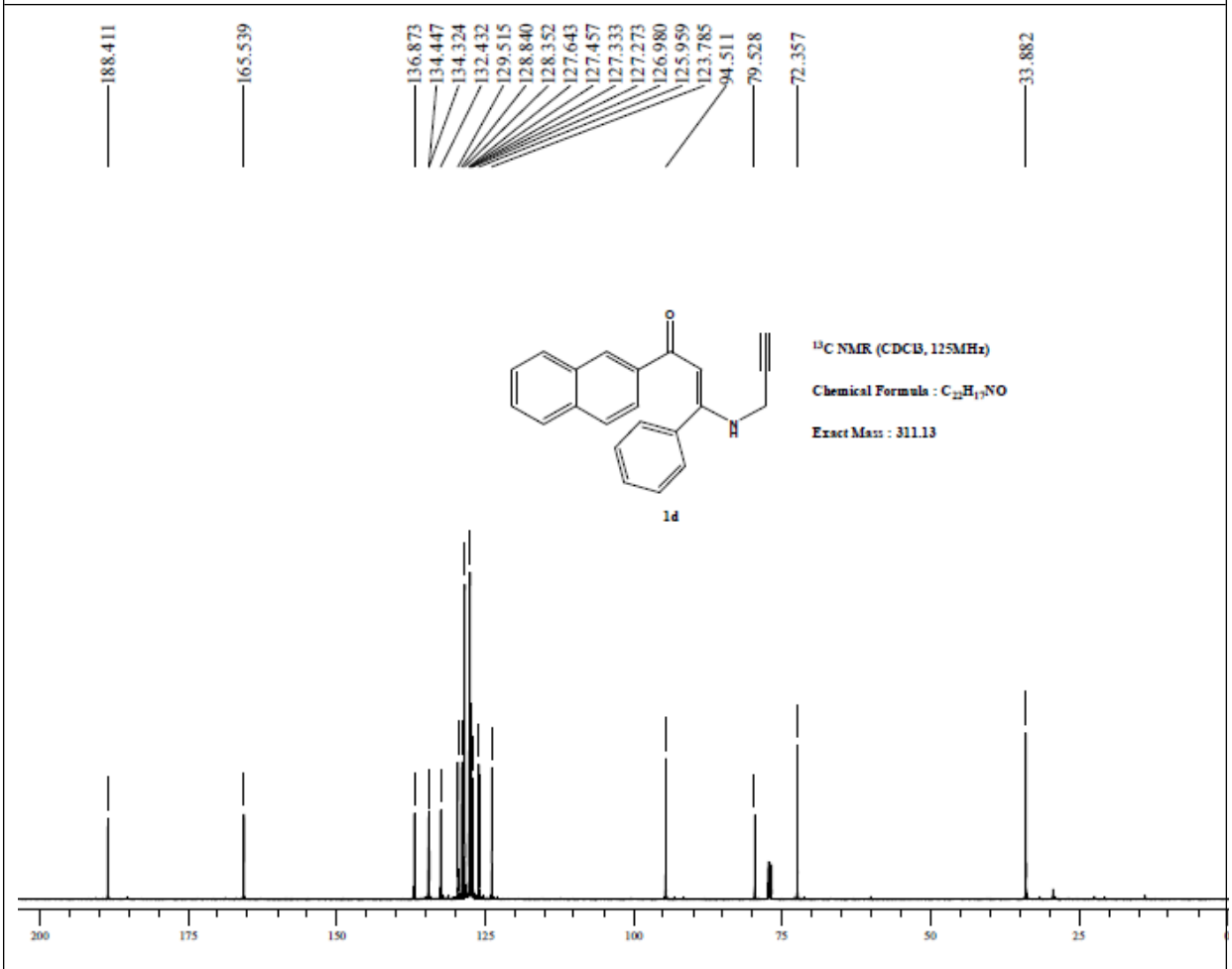
1-(4-methoxyphenyl)-3-phenyl-3-(prop-2-ynylamino)prop-2-en-1-one **1c**



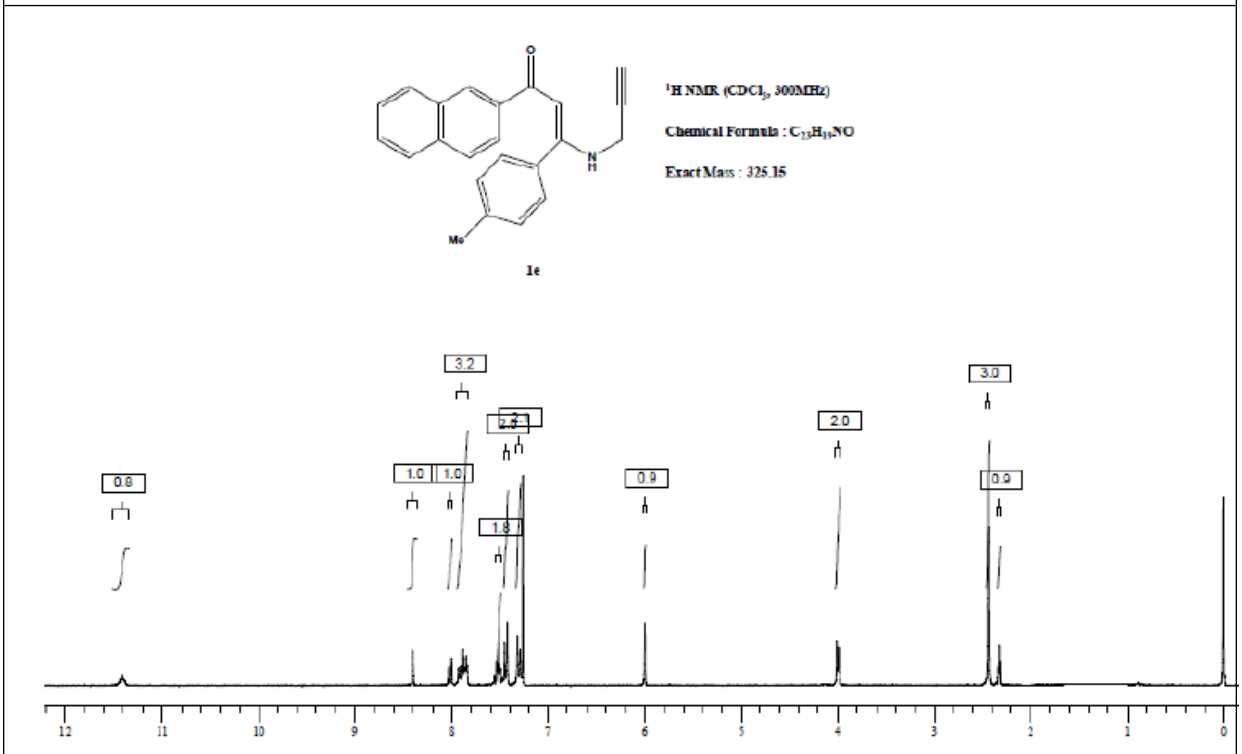


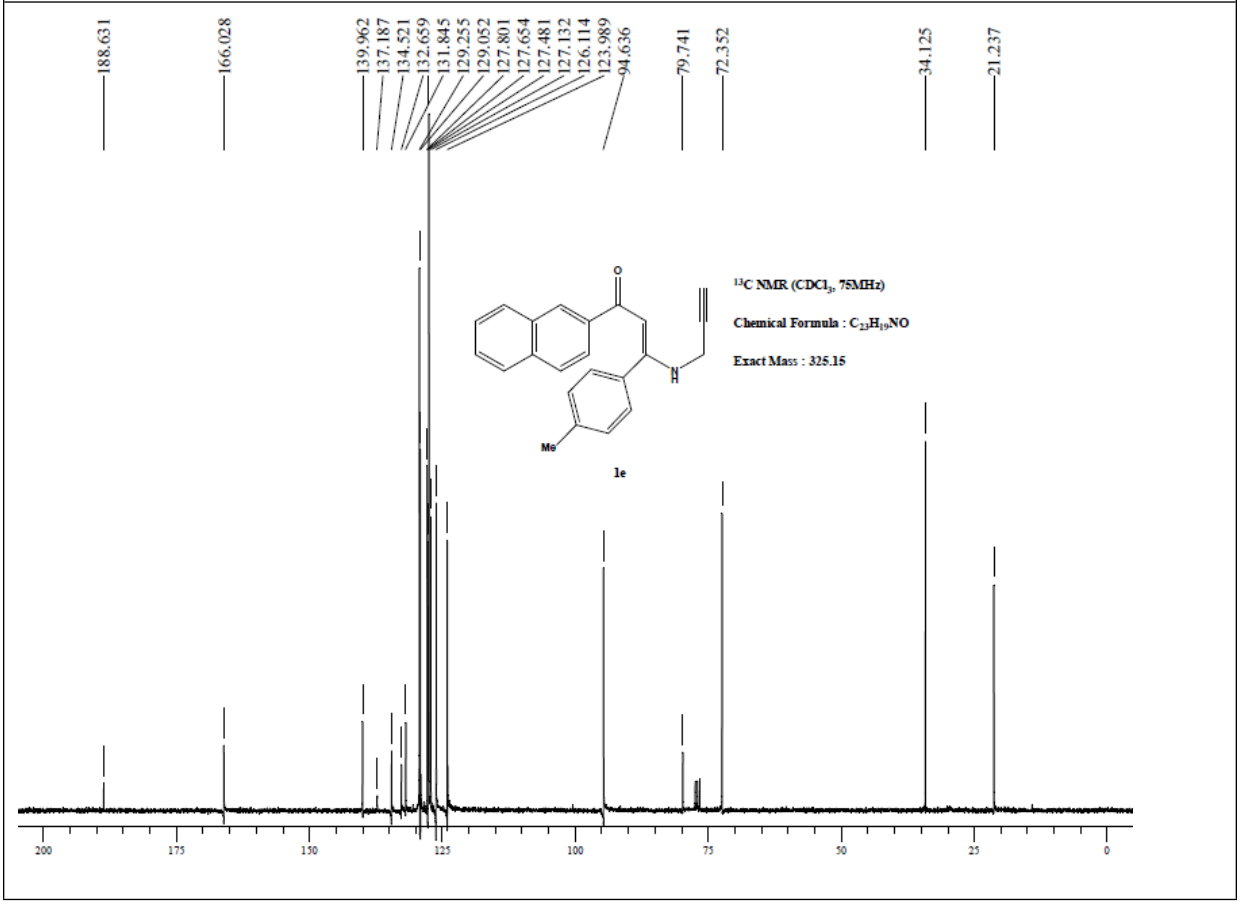
1-(naphthalen-2-yl)-3-phenyl-3-(prop-2-ynylamino)prop-2-en-1-one **1d**



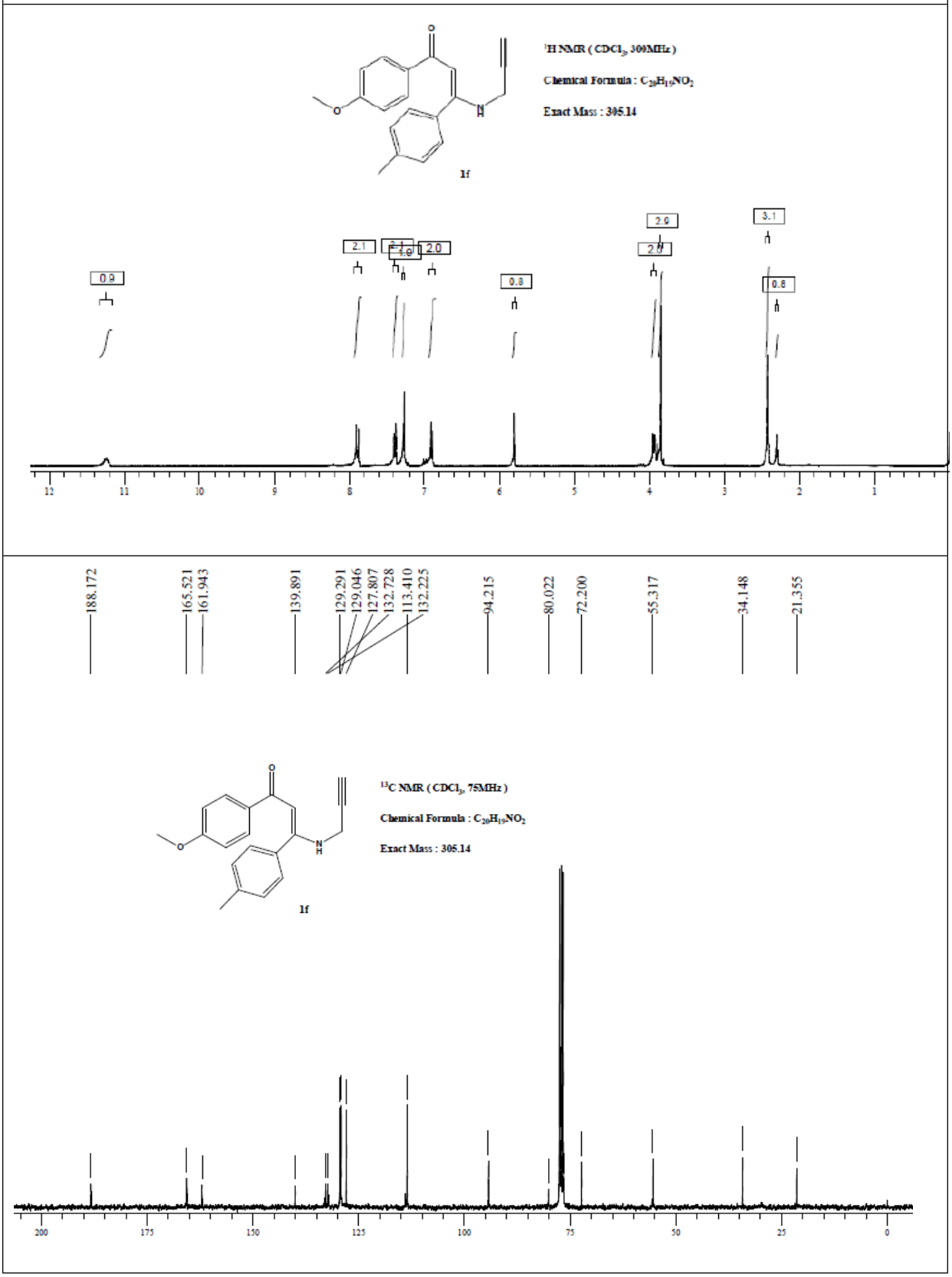


1-(naphthalen-2-yl)-3-(prop-2-ynylamino)-3-p-tolylprop-2-en-1-one **1e**

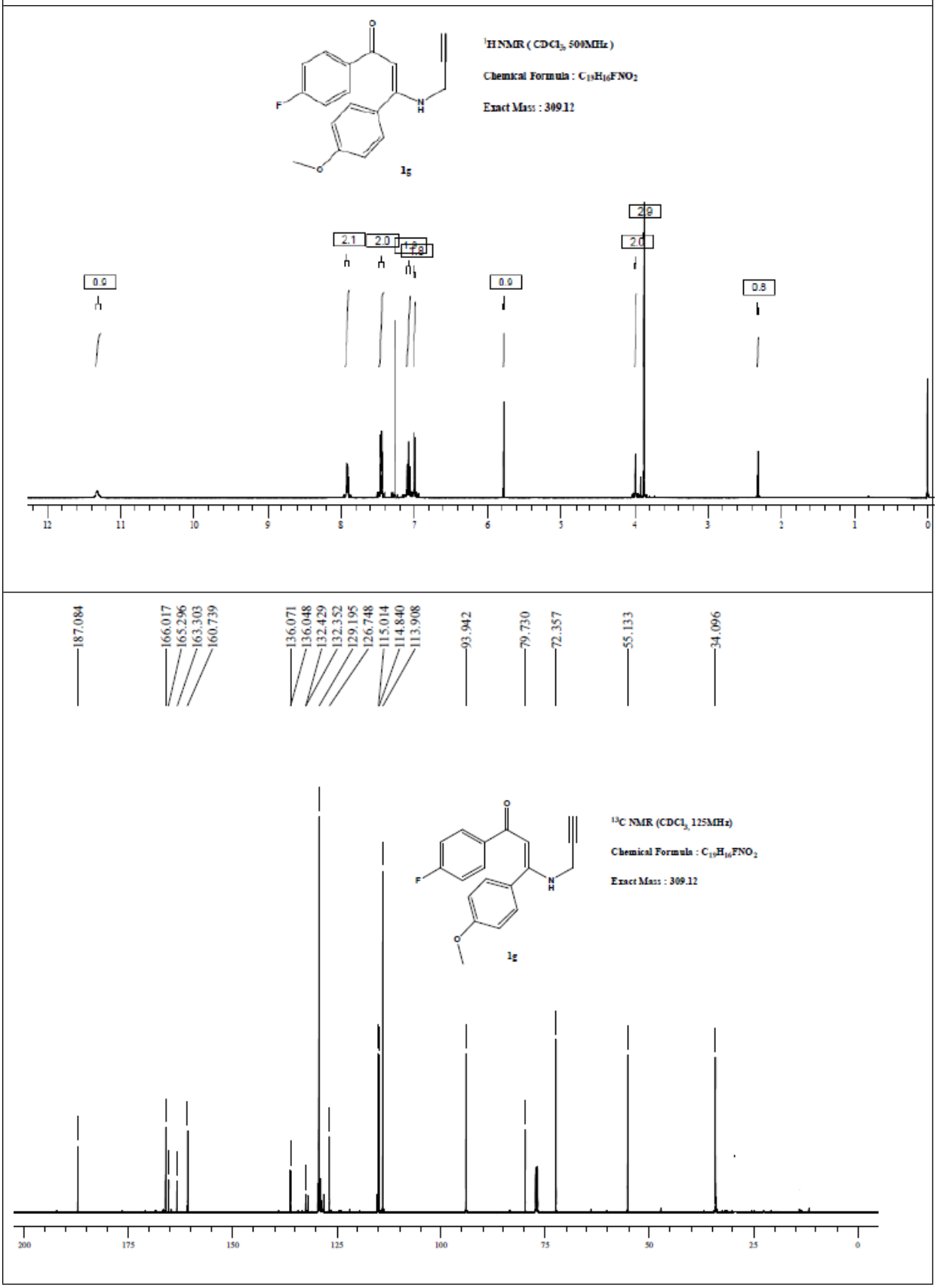




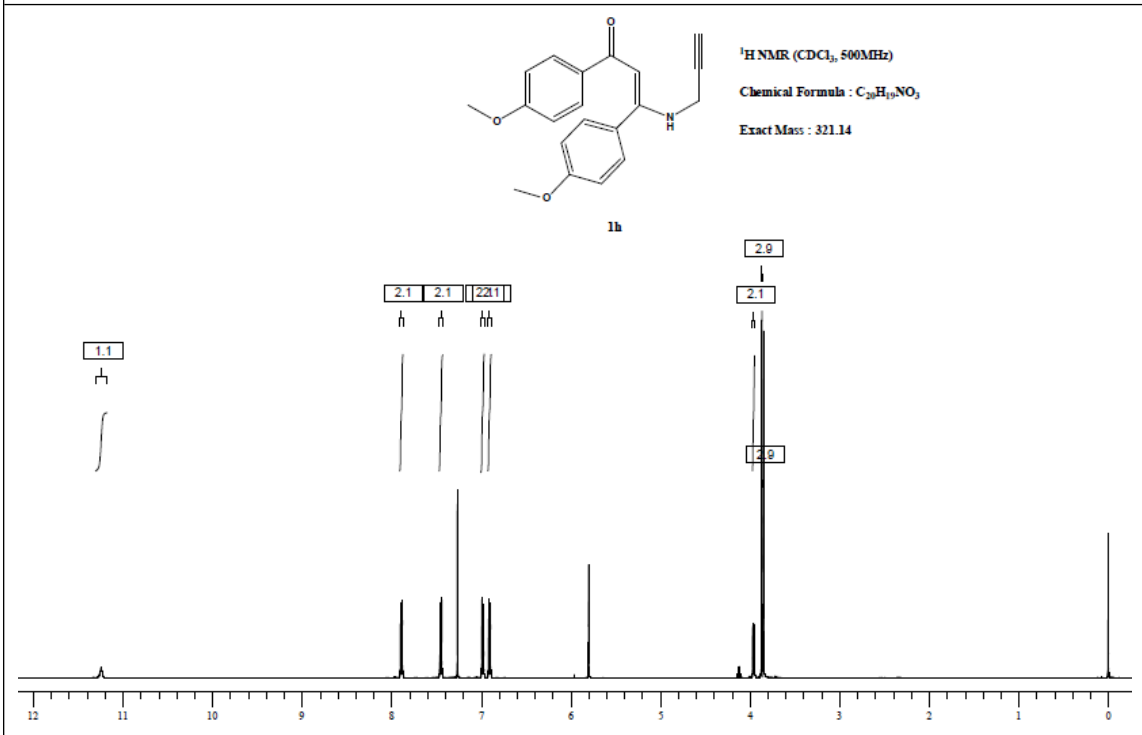
1-(4-methoxyphenyl)-3-(prop-2-ynylamino)-3-p-tolylprop-2-en-1-one **1f**

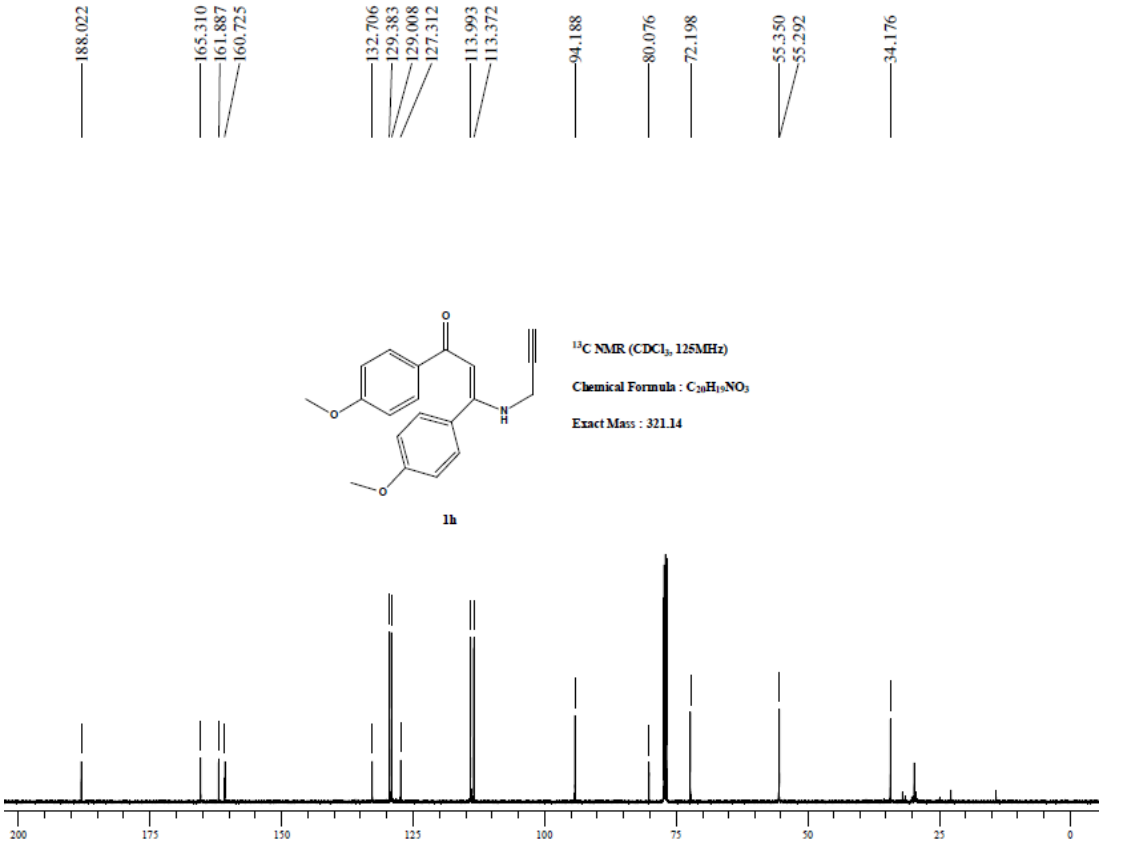


1-(4-fluorophenyl)-3-(4-methoxyphenyl)-3-(prop-2-ynylamino)prop-2-en-1-one **1g**

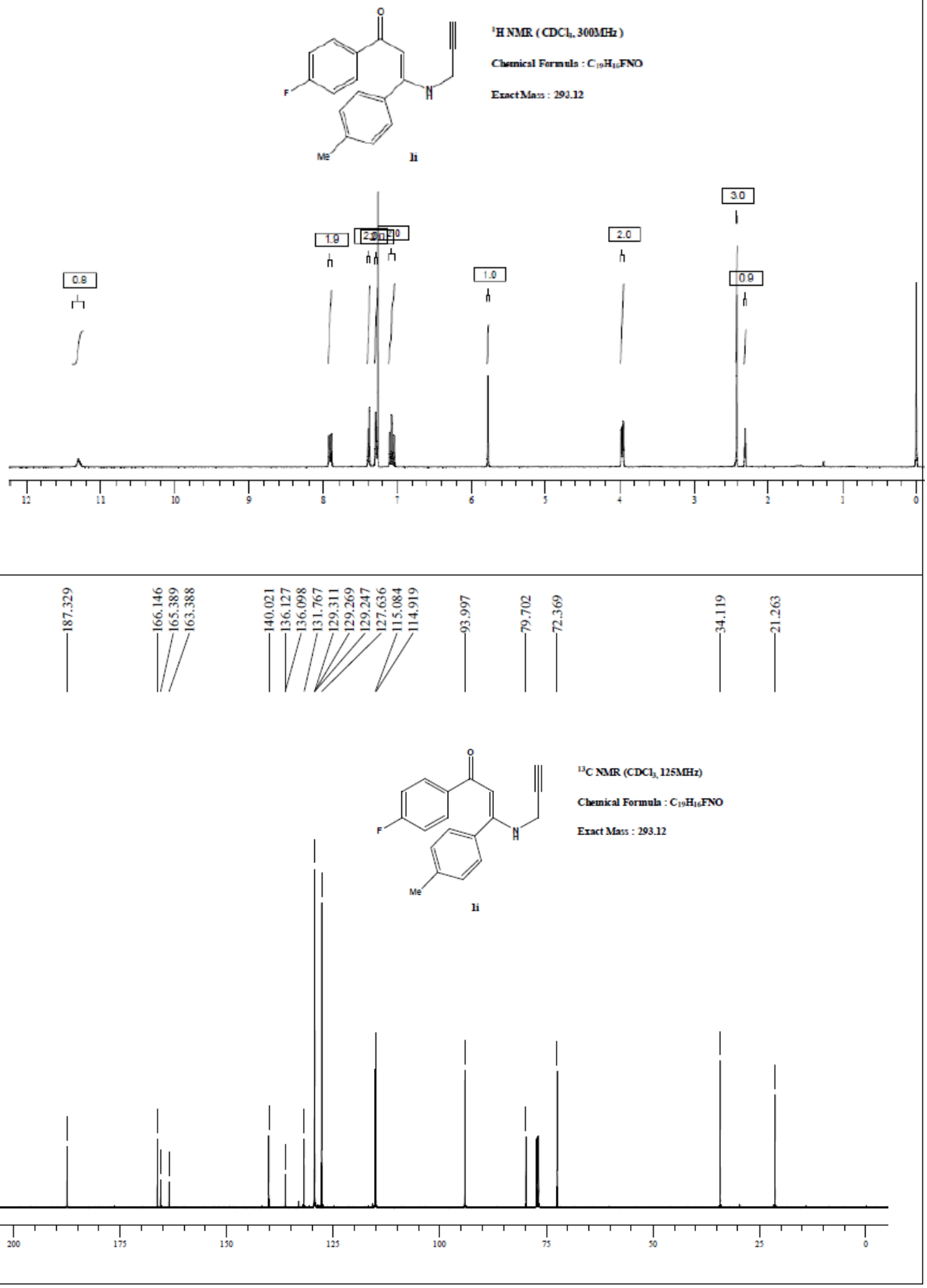


1,3-bis(4-methoxyphenyl)-3-(prop-2-ynylamino)prop-2-en-1-one **1h**

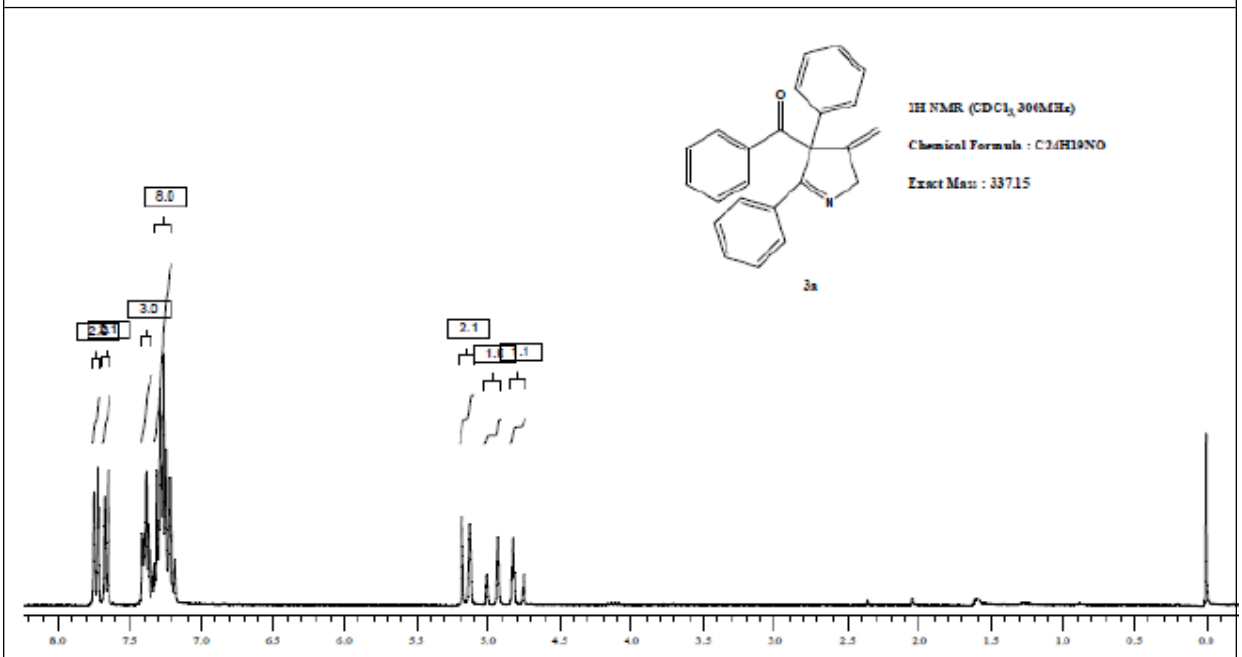


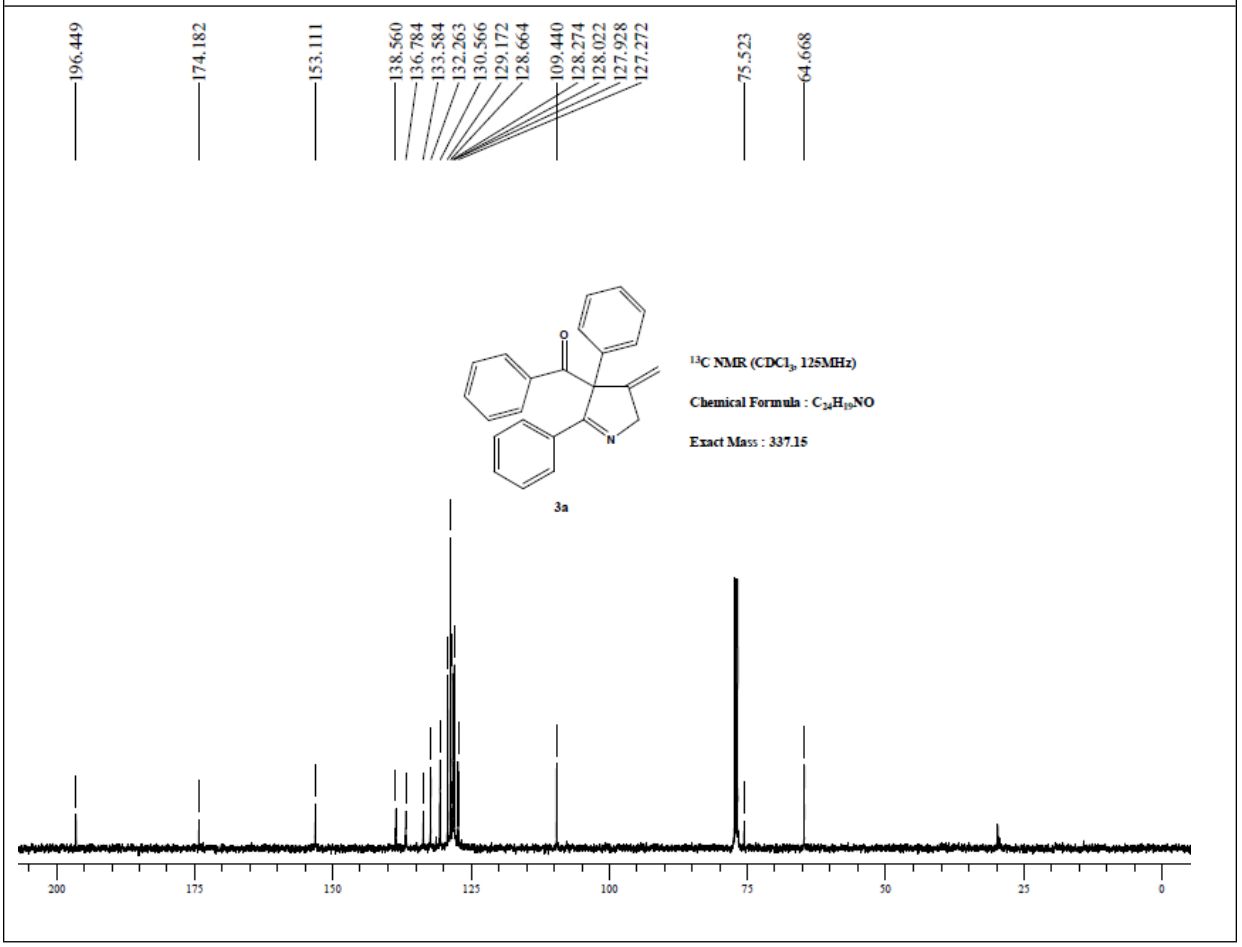


1-(4-fluorophenyl)-3-(prop-2-ynylamino)-3-p-tolylprop-2-en-1-one **1i**

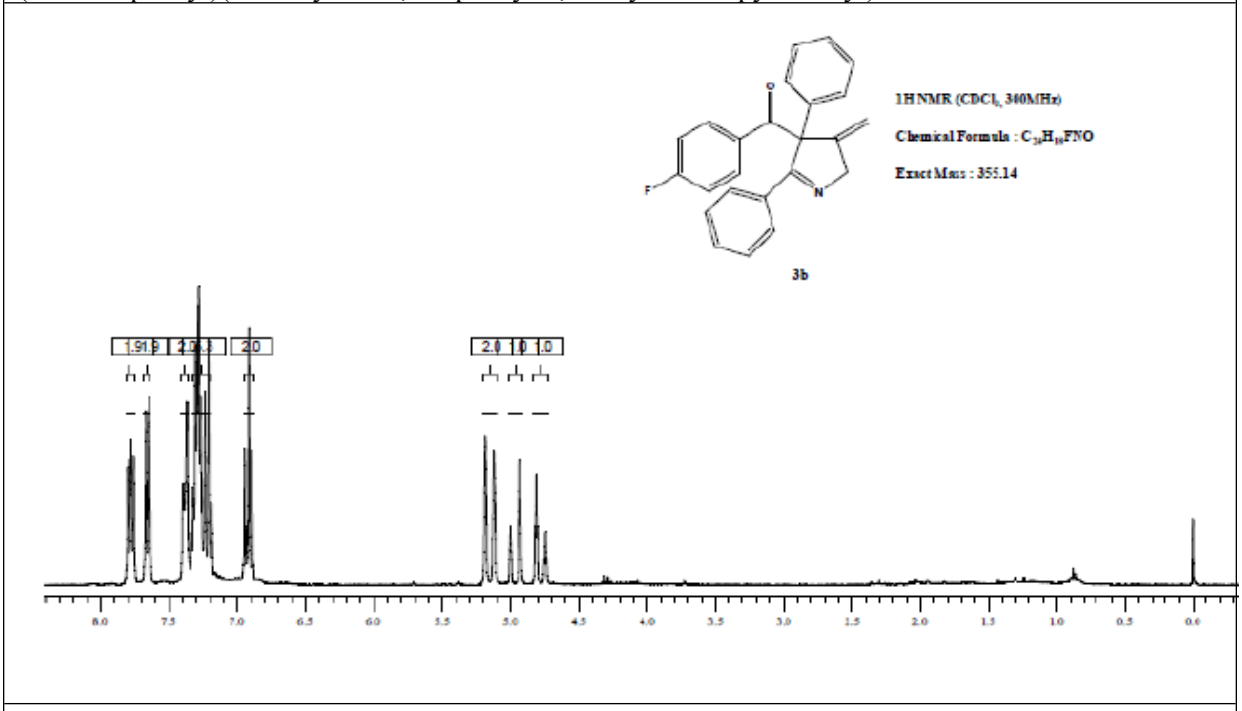


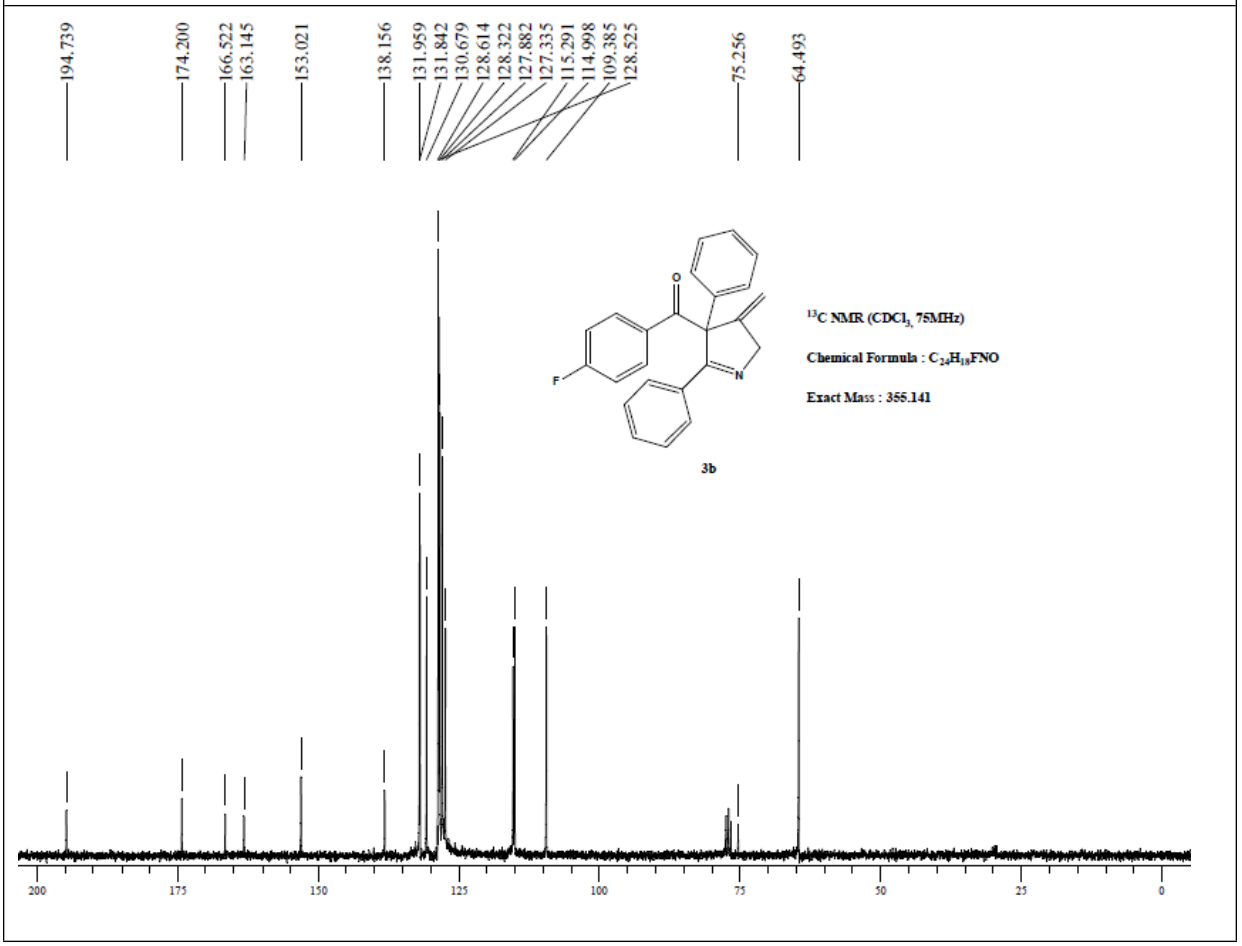
(3-methylene-4,5-diphenyl-3,4-dihydro-2H-pyrrol-4-yl)(phenyl)methanone **3a**



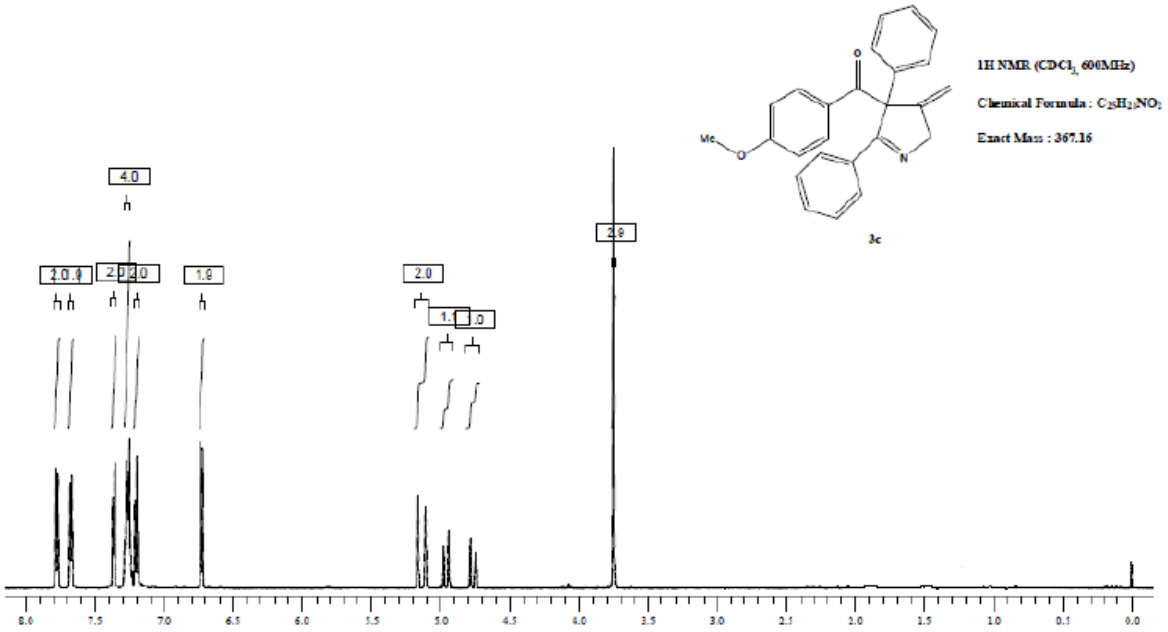


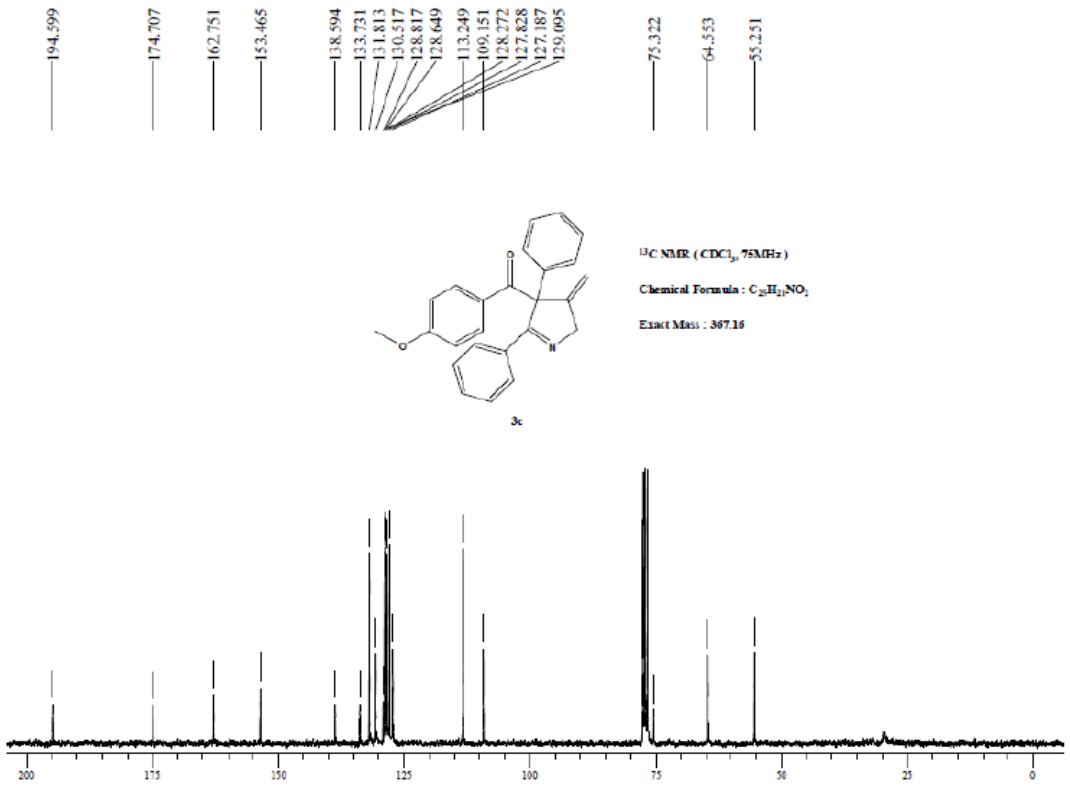
(4-Fluorophenyl)(3-methylene-4,5-diphenyl-3,4-dihydro-2H-pyrrol-4-yl)methanone **3b**



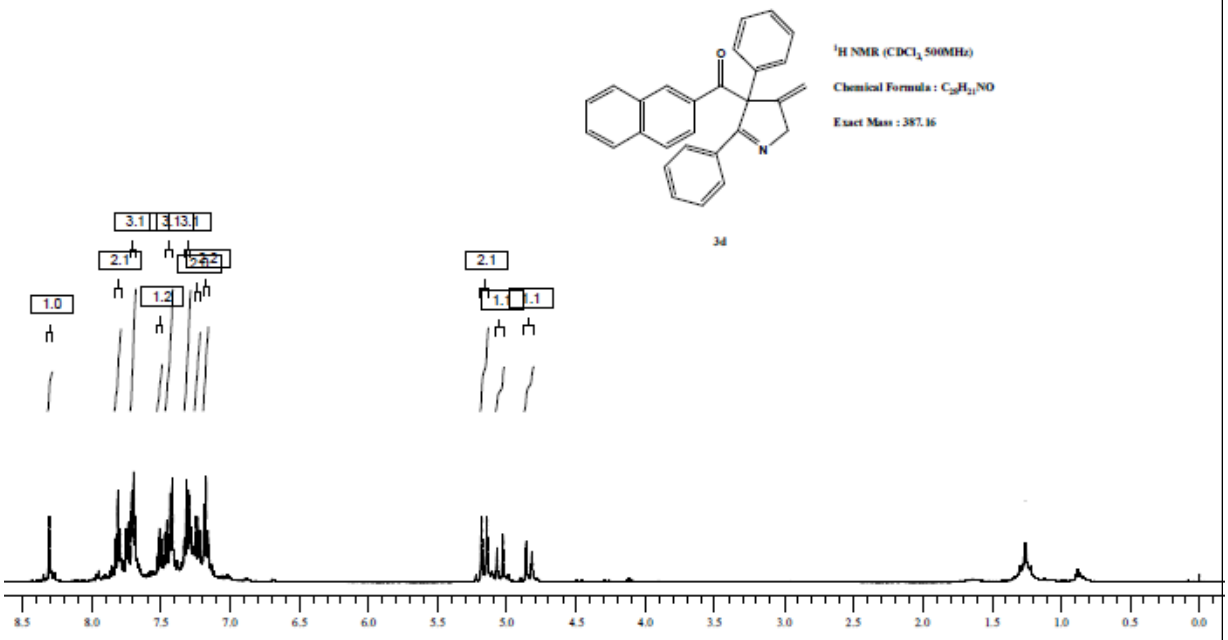


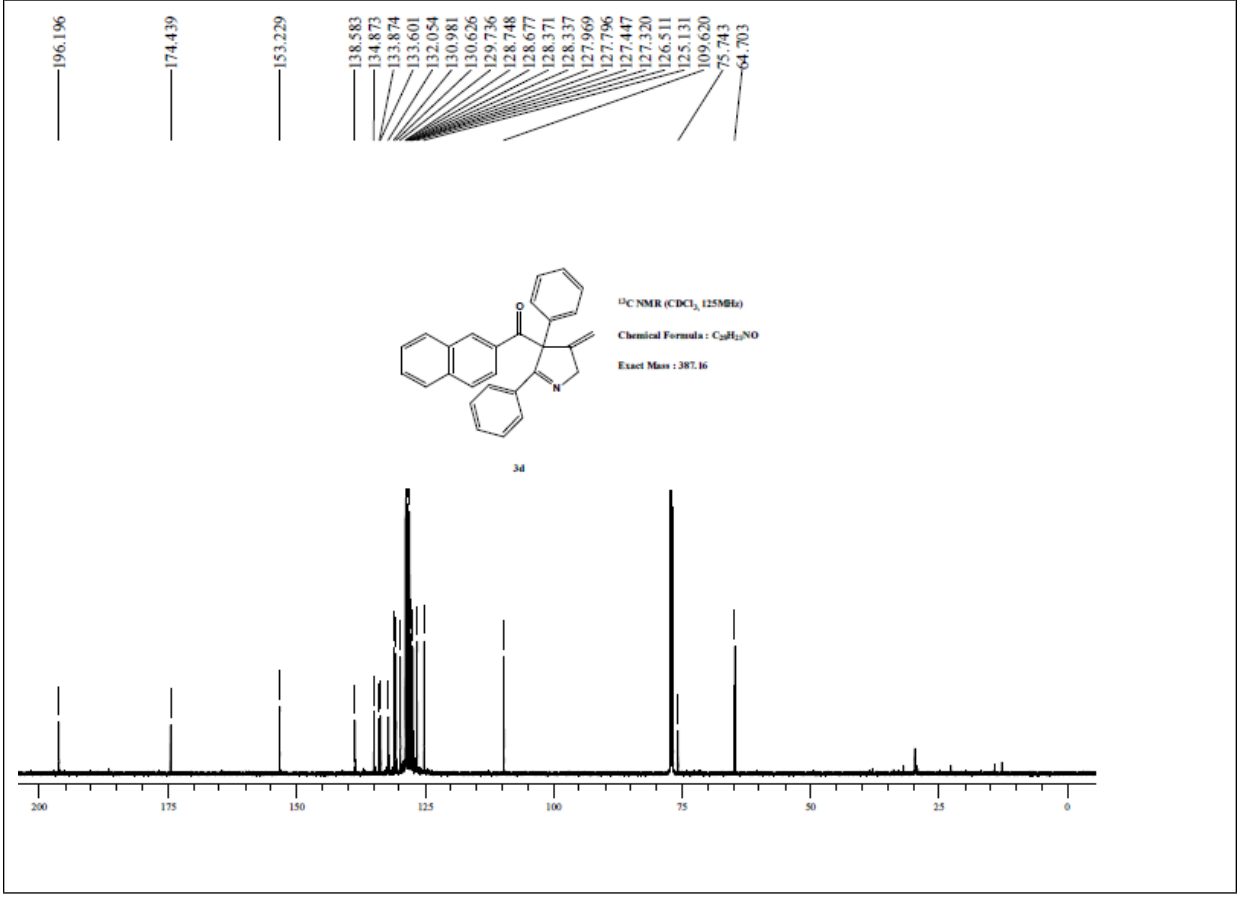
(4-Methoxyphenyl)(3-methylene-4,5-diphenyl-3,4-dihydro-2H-pyrrol-4-yl)methanone **3c**



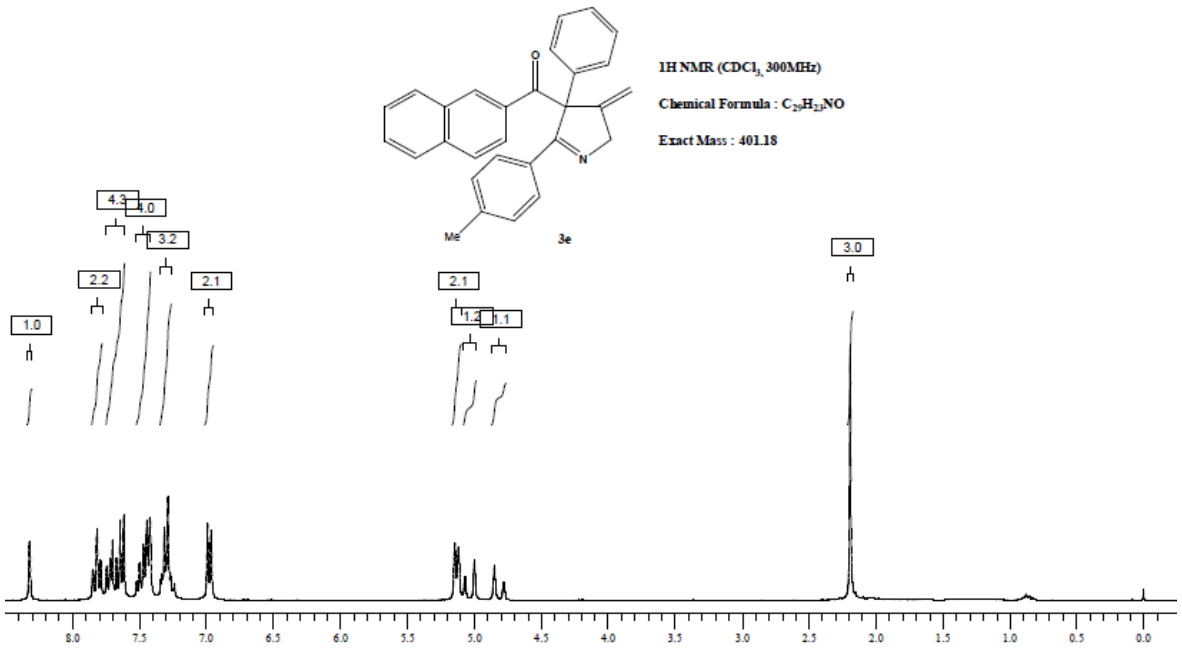


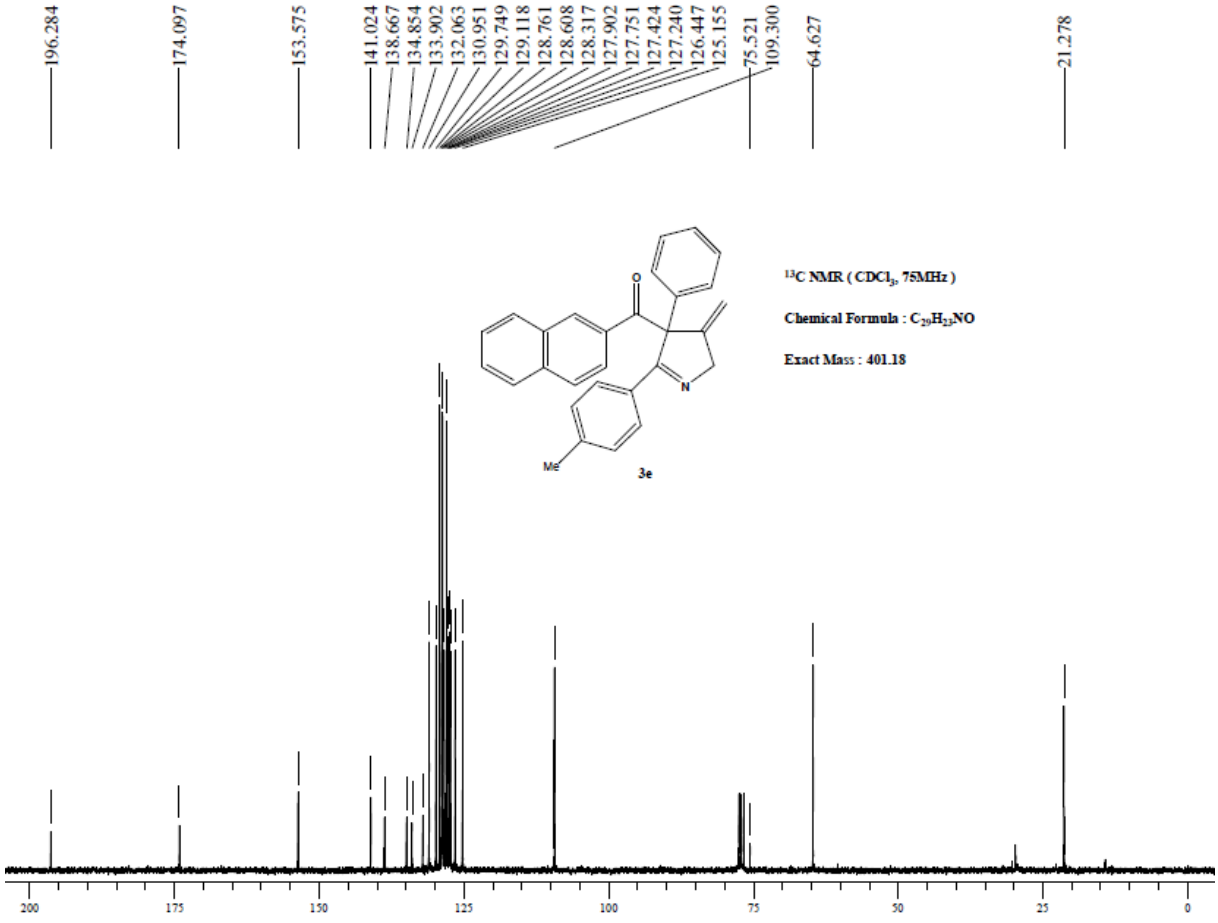
(3-Methylene-4,5-diphenyl-3,4-dihydro-2H-pyrrol-4-yl)(naphthalen-2-yl)methanone **3d**



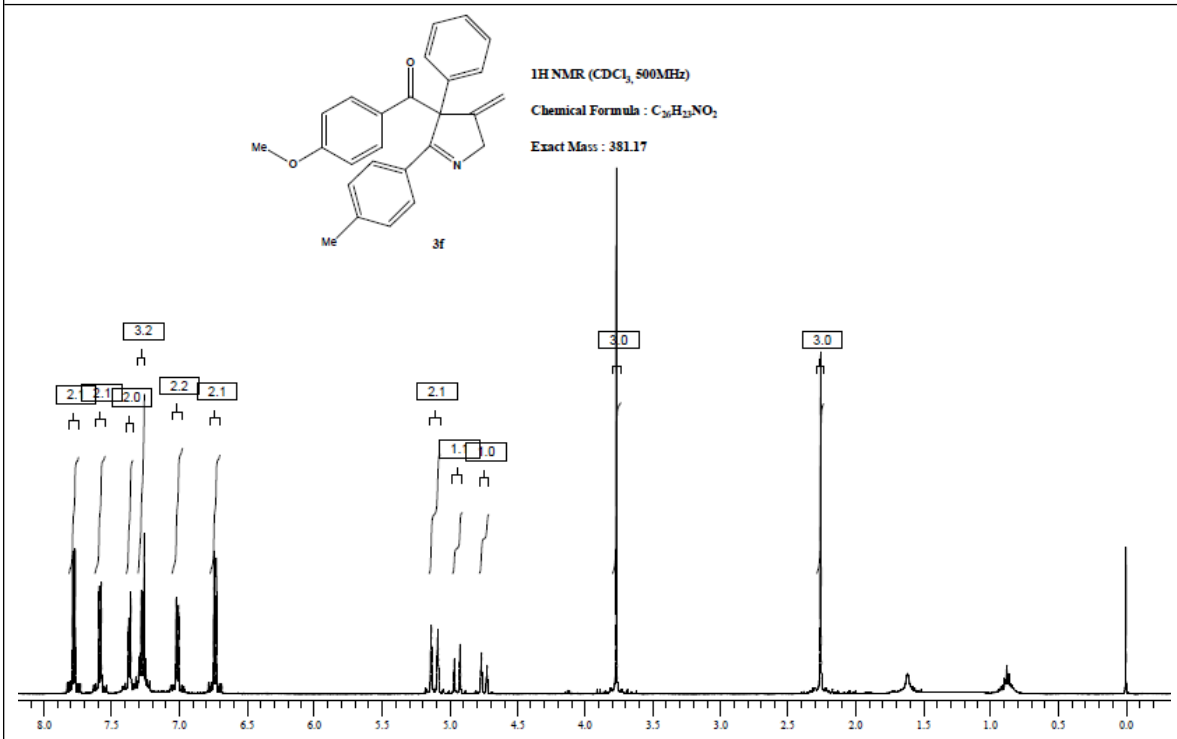


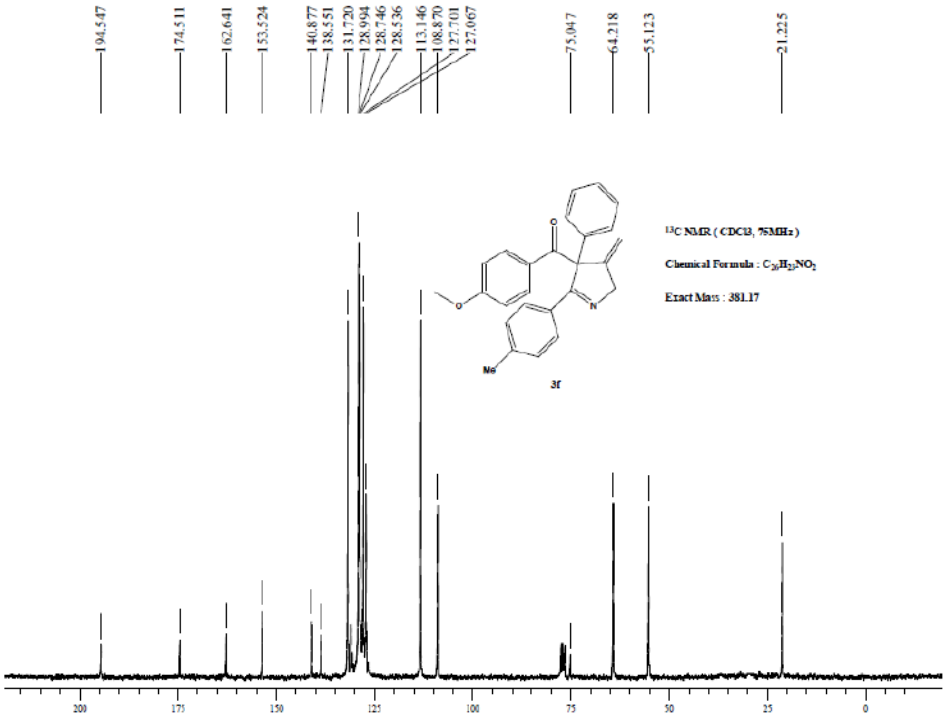
(3-Methylene-4-phenyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-4-yl)(naphthalen-2-yl)methanone **3e**





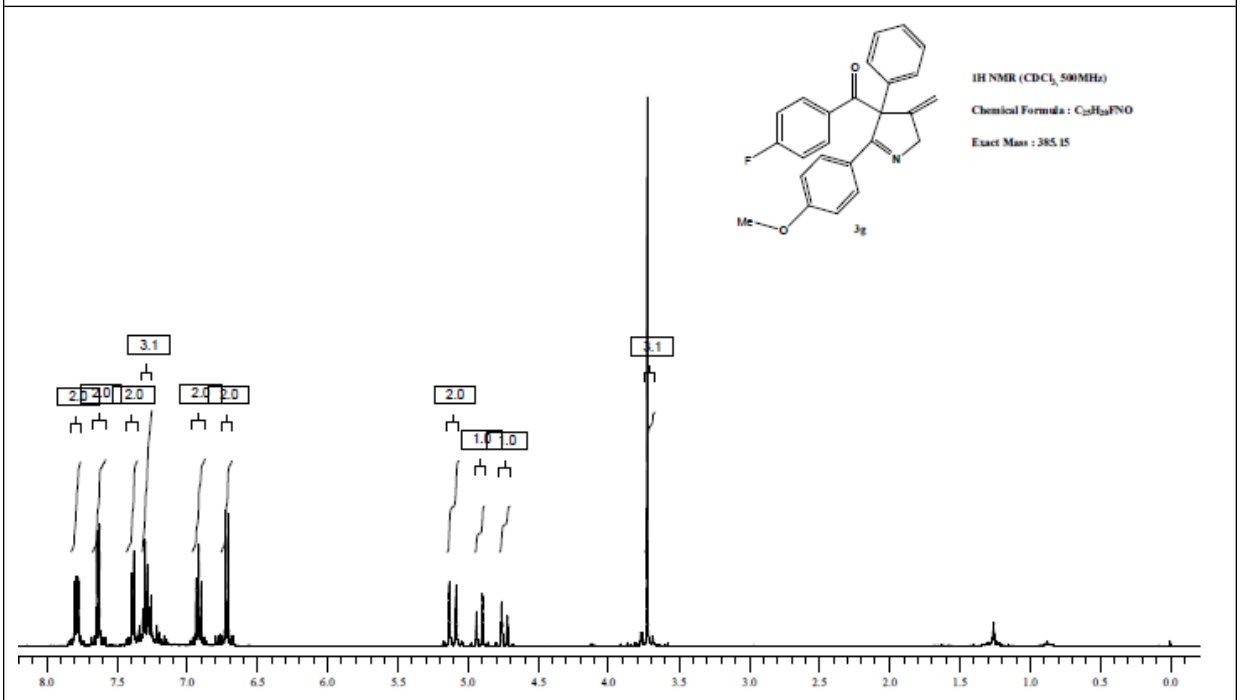
(4-Methoxyphenyl)(3-methylene-4-phenyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-4-yl)methanone **3f**

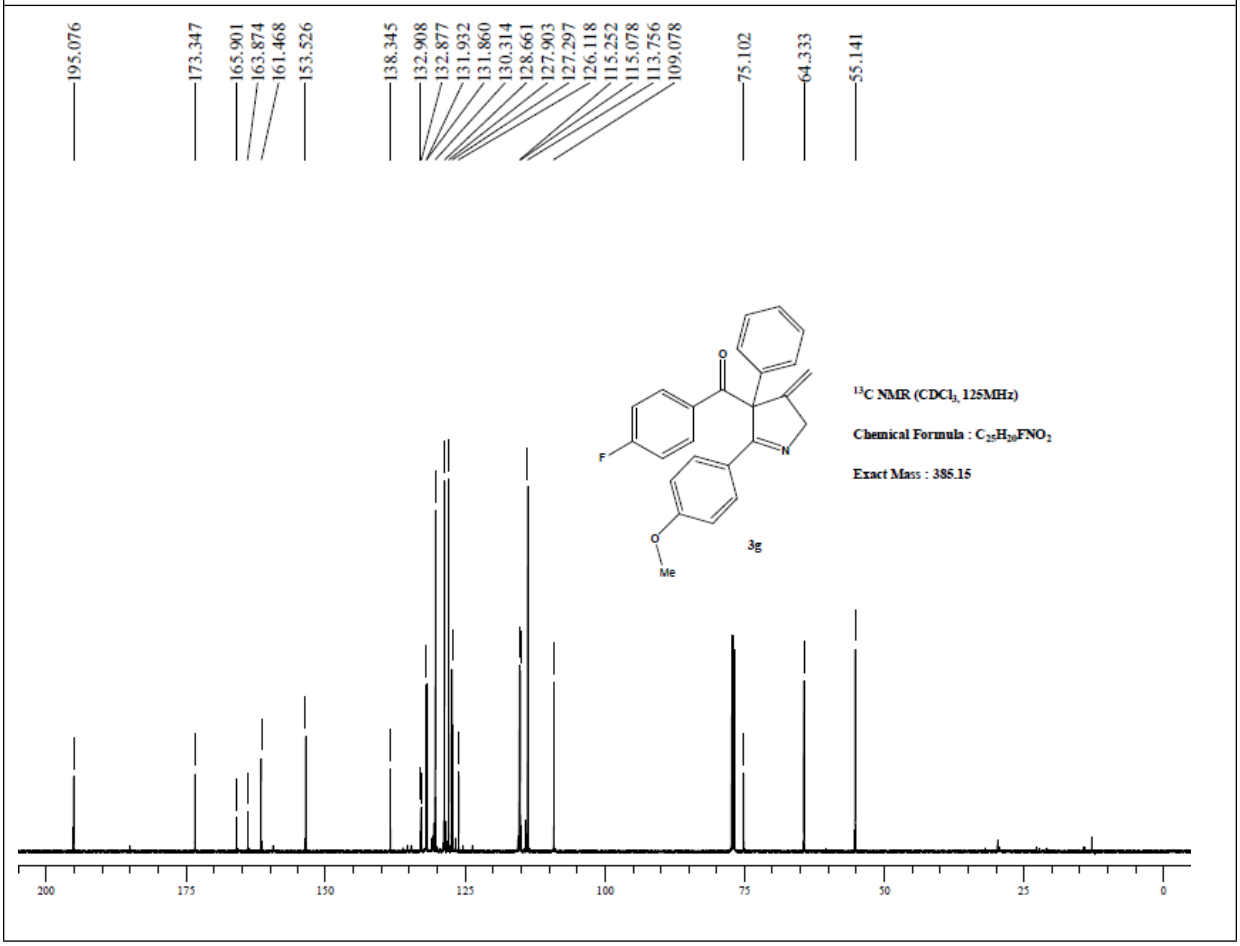




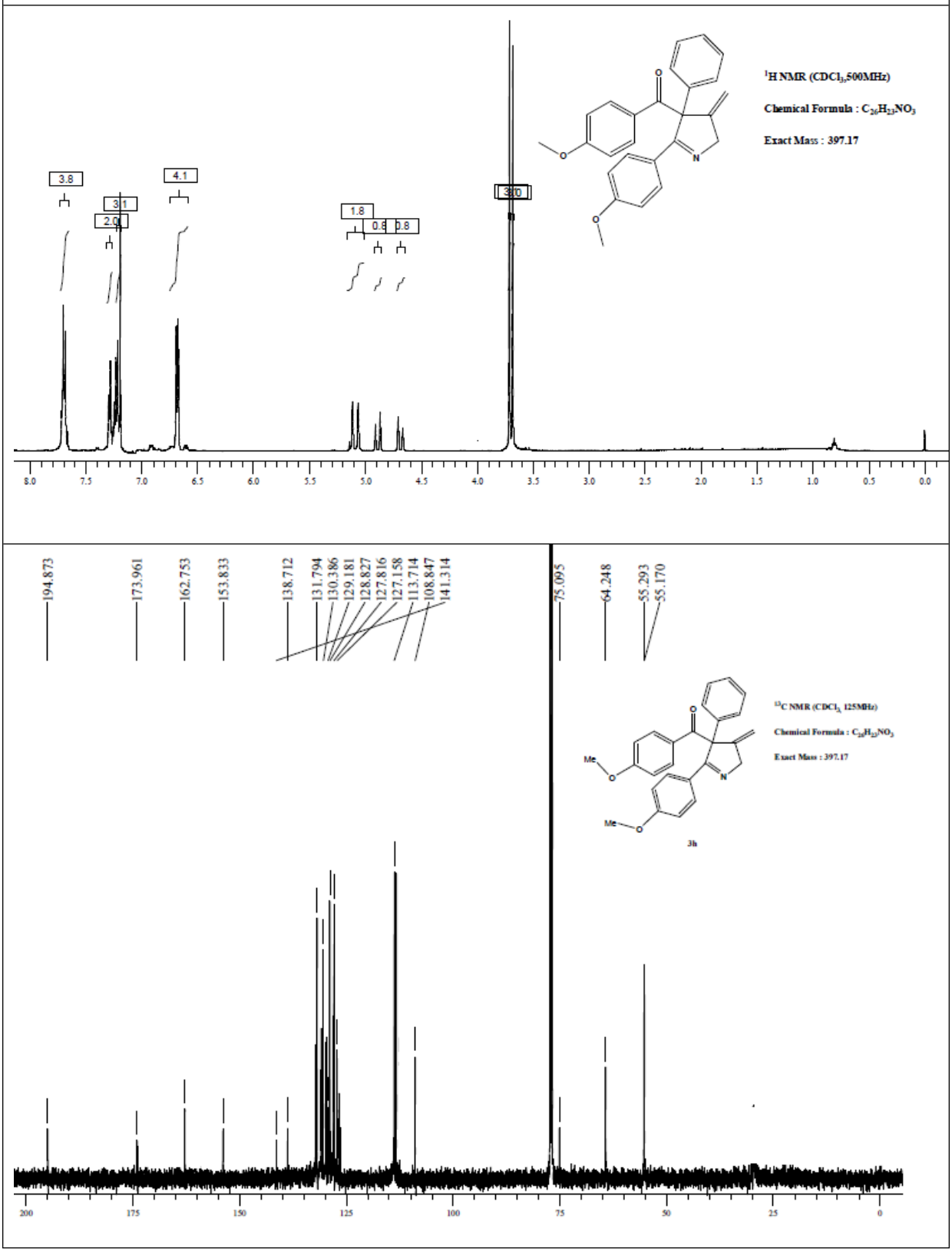
(4-fluorophenyl)(5-(4-methoxyphenyl)-3-methylene-4-phenyl-3,4-dihydro-2H-pyrrol-4-yl)methanone

3g

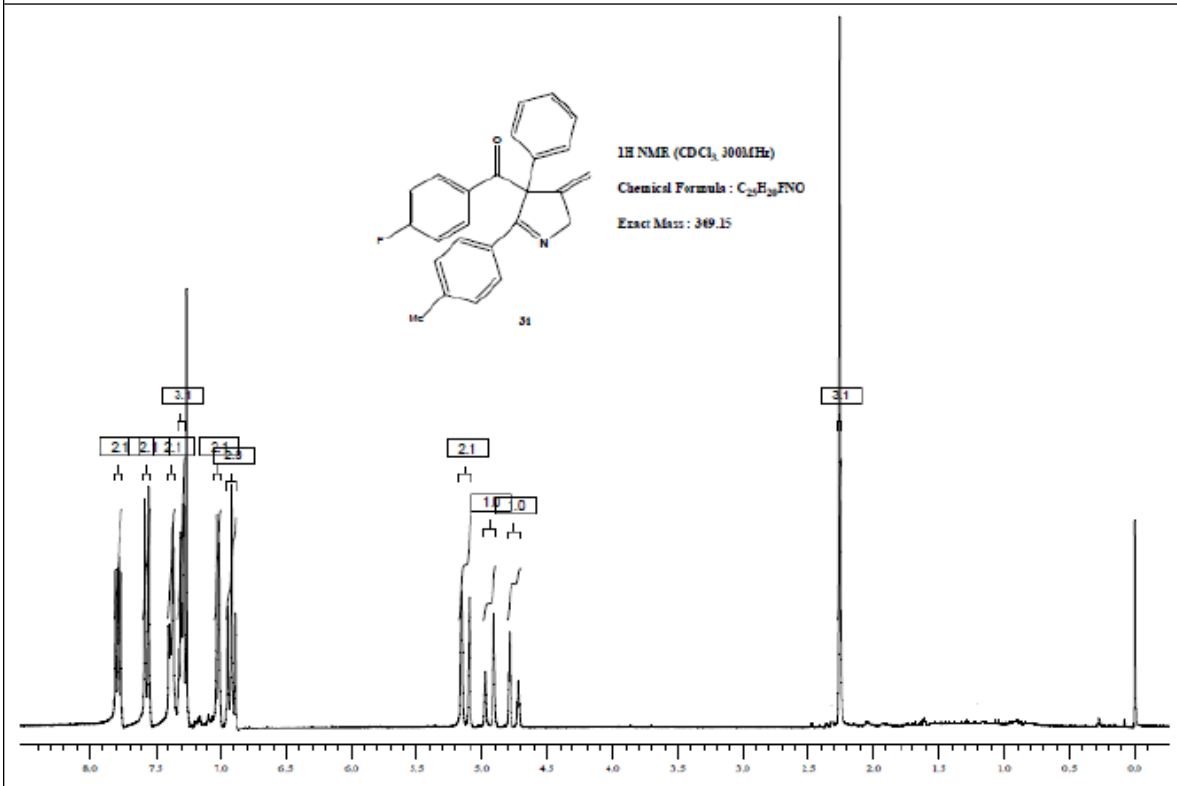


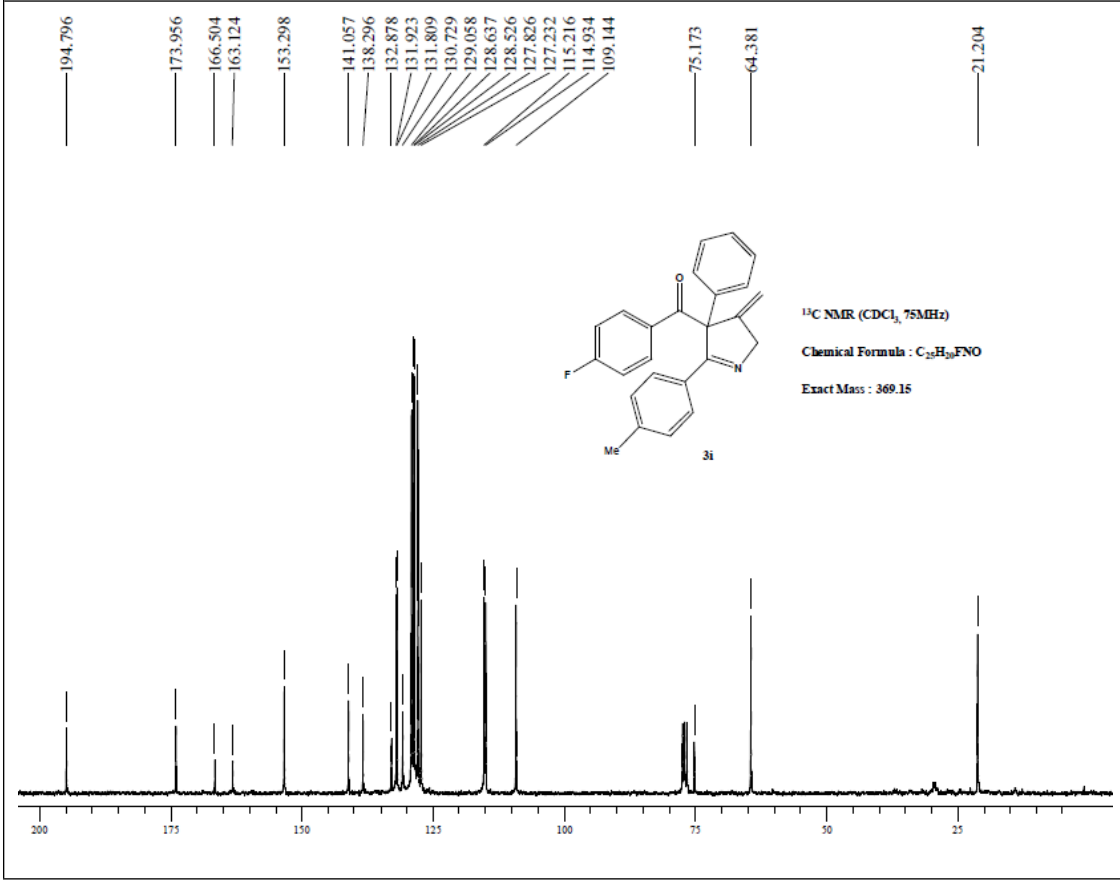


(4-Methoxyphenyl)(5-(4-methoxyphenyl)-3-methylene-4-phenyl-3,4-dihydro-2H-pyrrol-4-yl)methanone **3h**

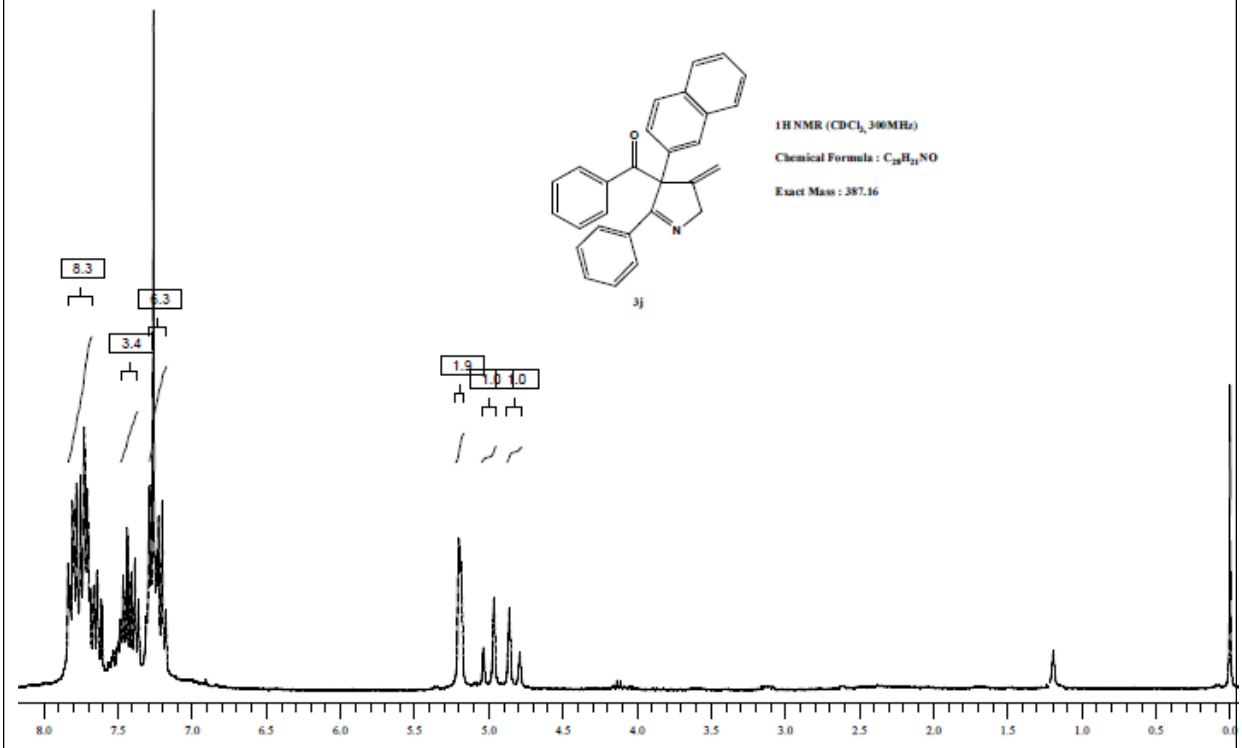


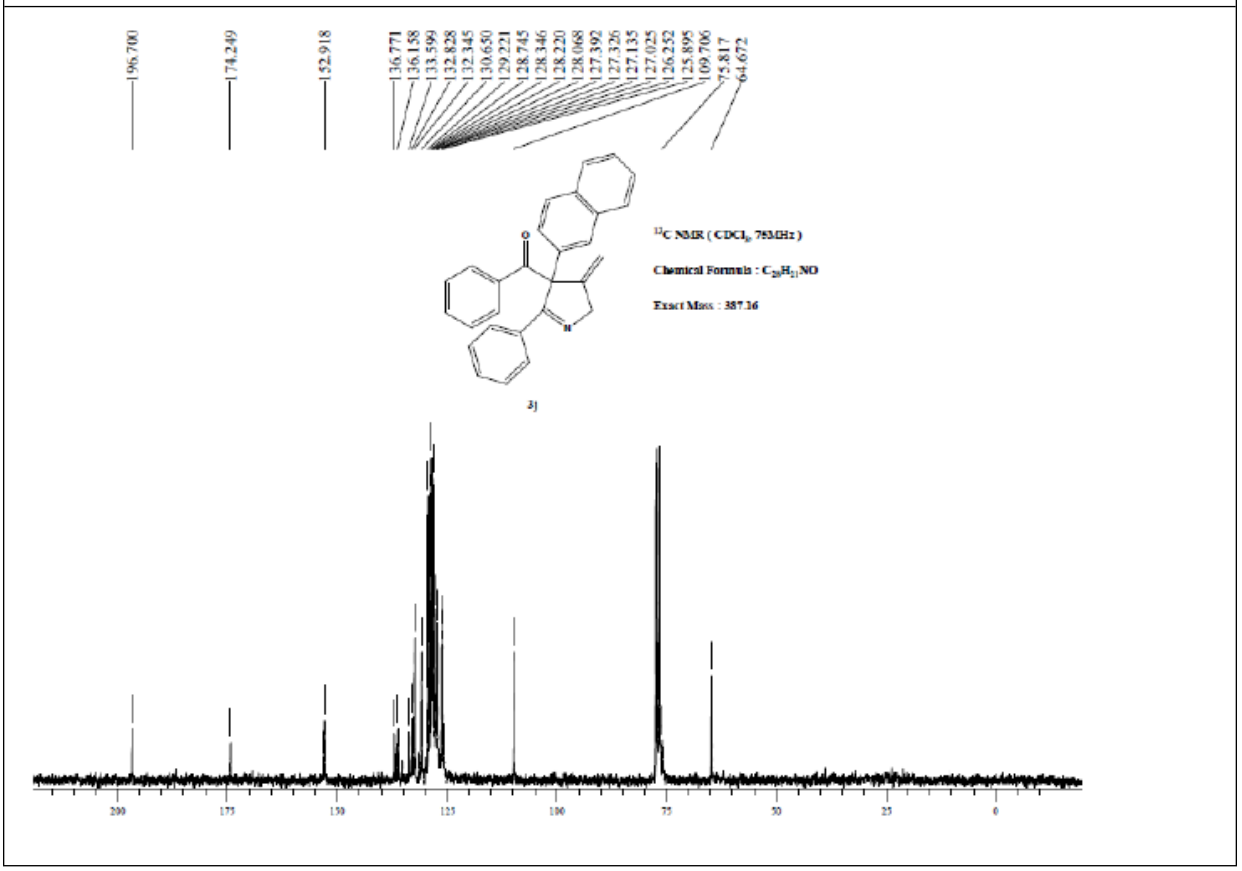
(4-Fluorophenyl)(3-methylene-4-phenyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-4-yl)methanone **3i**





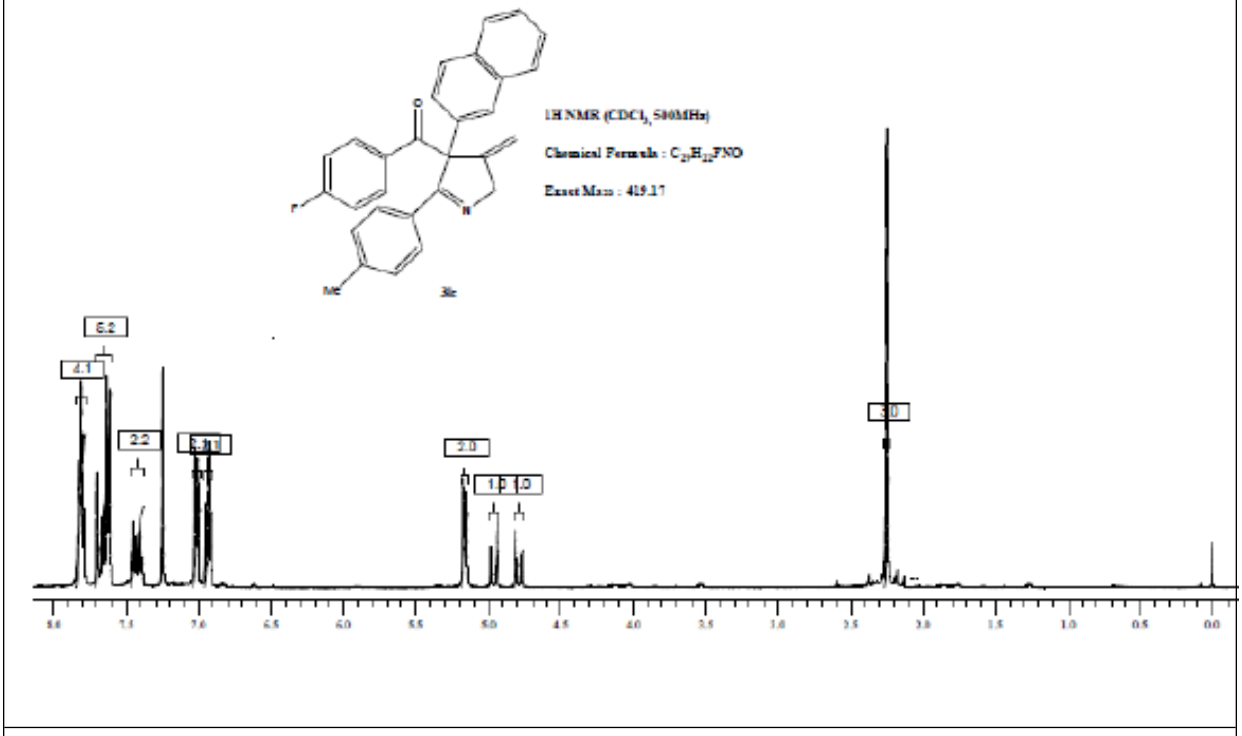
(3-Methylene-4-(naphthalen-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrol-4-yl)(phenyl)methanone **3j**

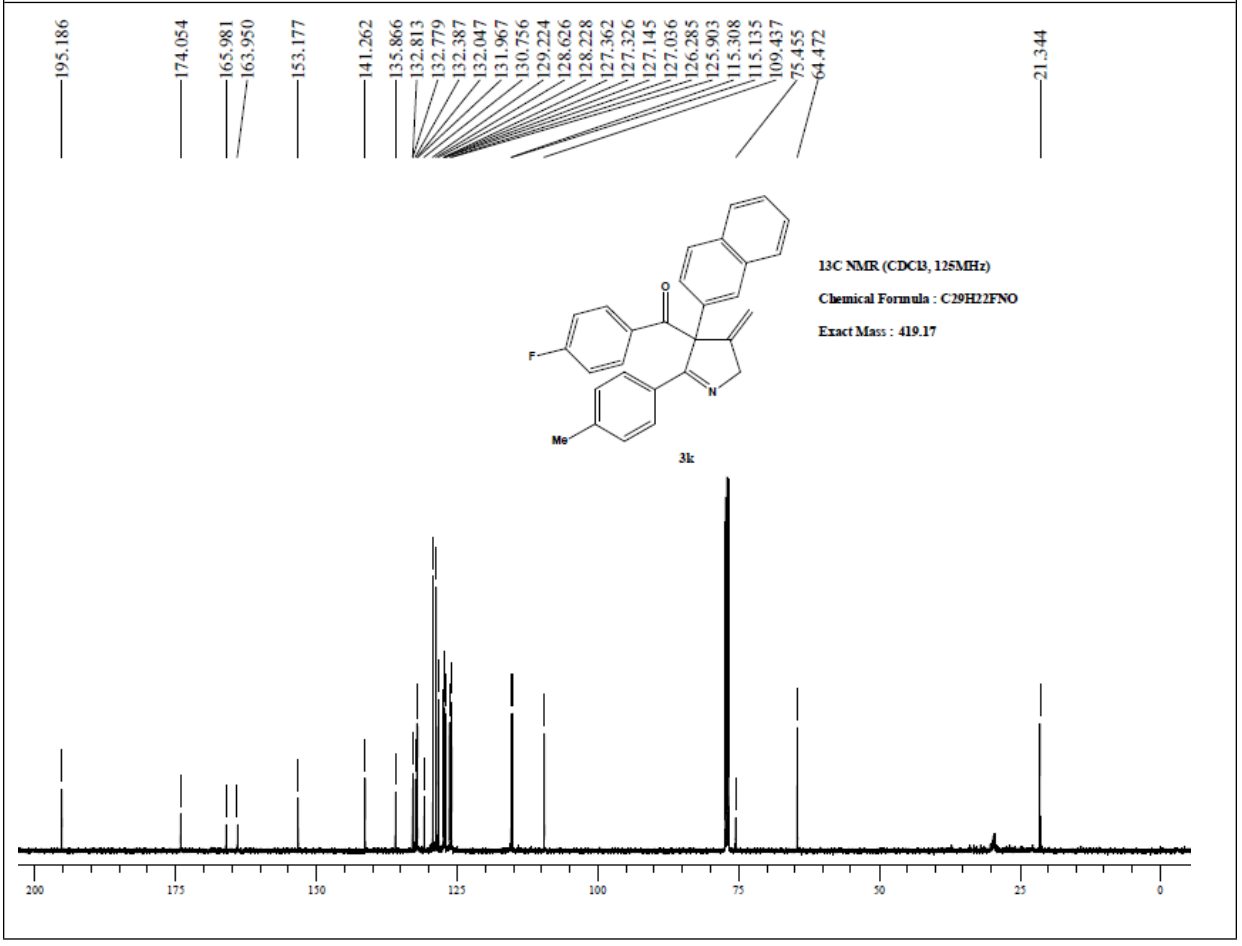




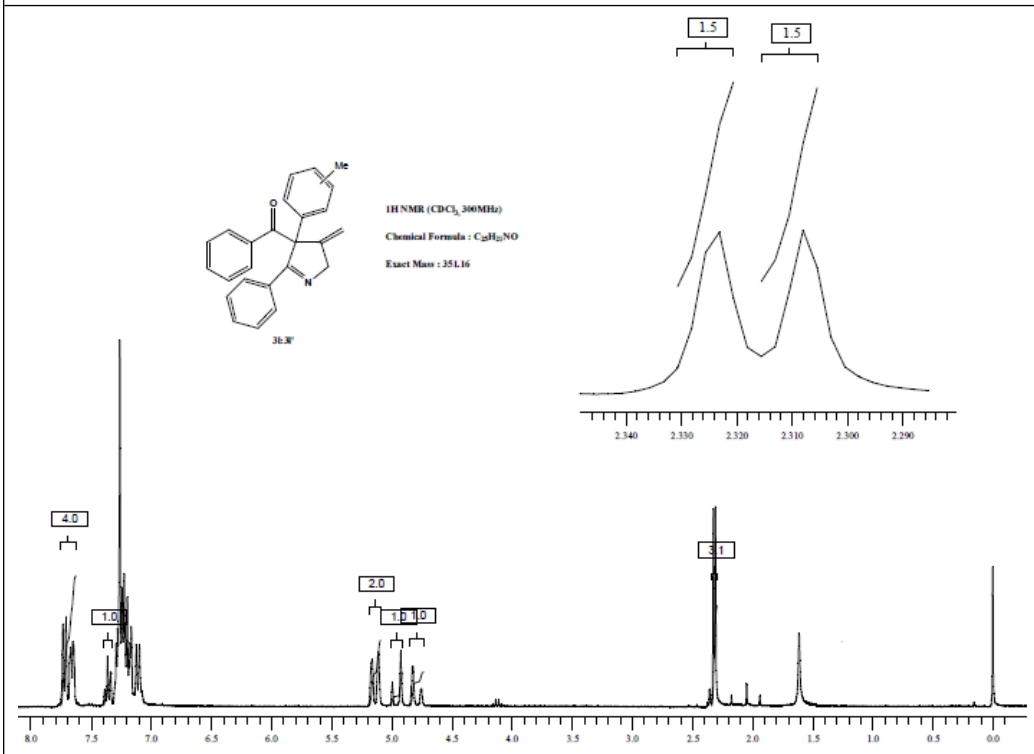
(4-Fluorophenyl)(3-methylene-4-(naphthalen-2-yl)-5-p-tolyl-3,4-dihydro-2H-pyrrol-4-yl)methanone

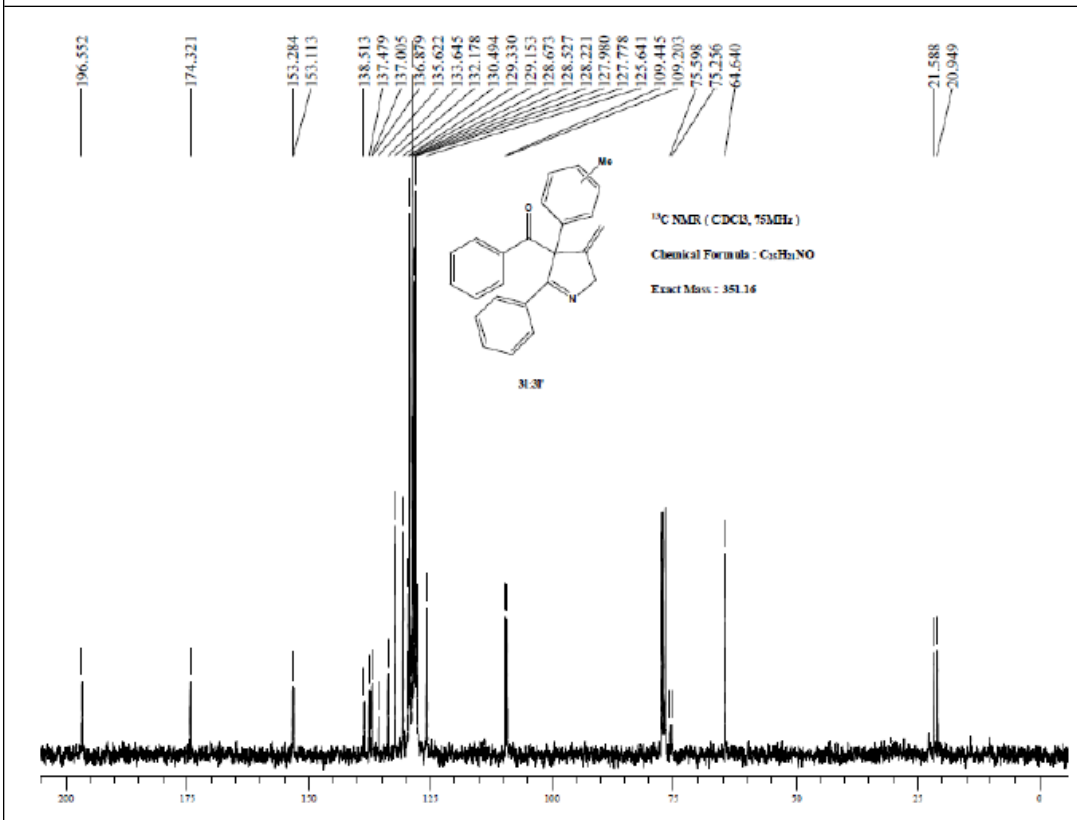
3k



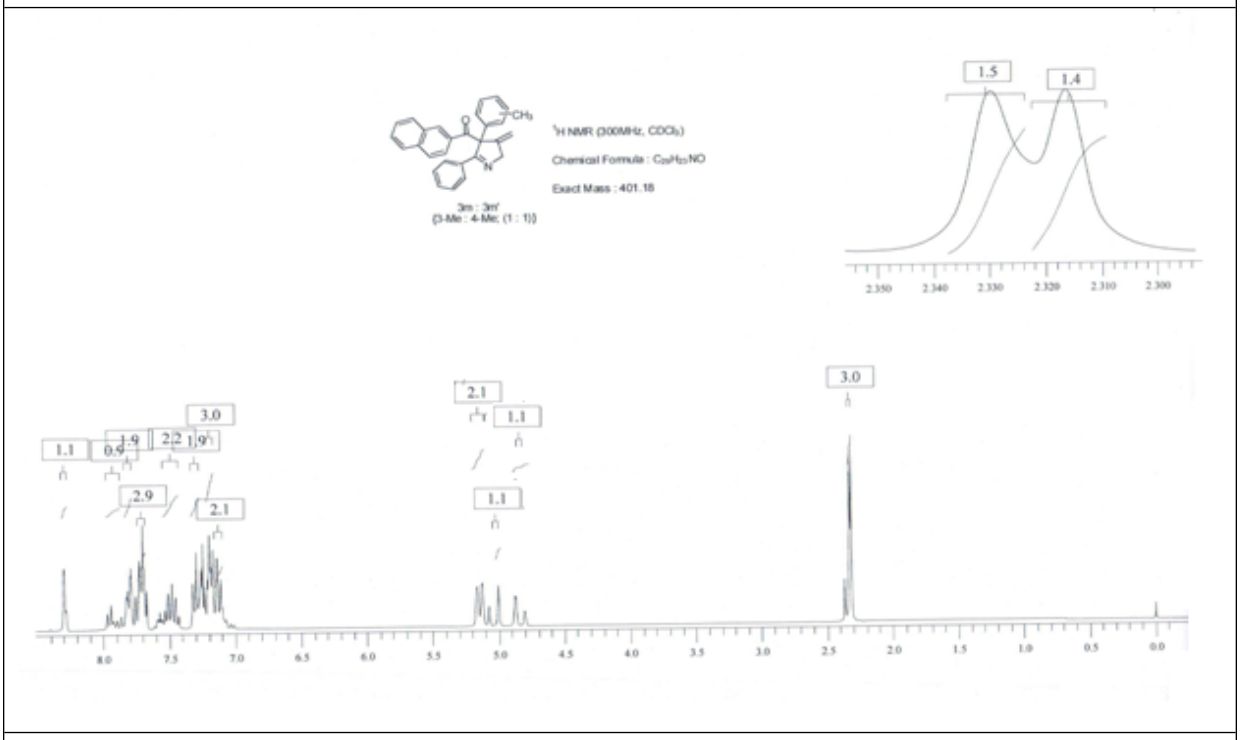


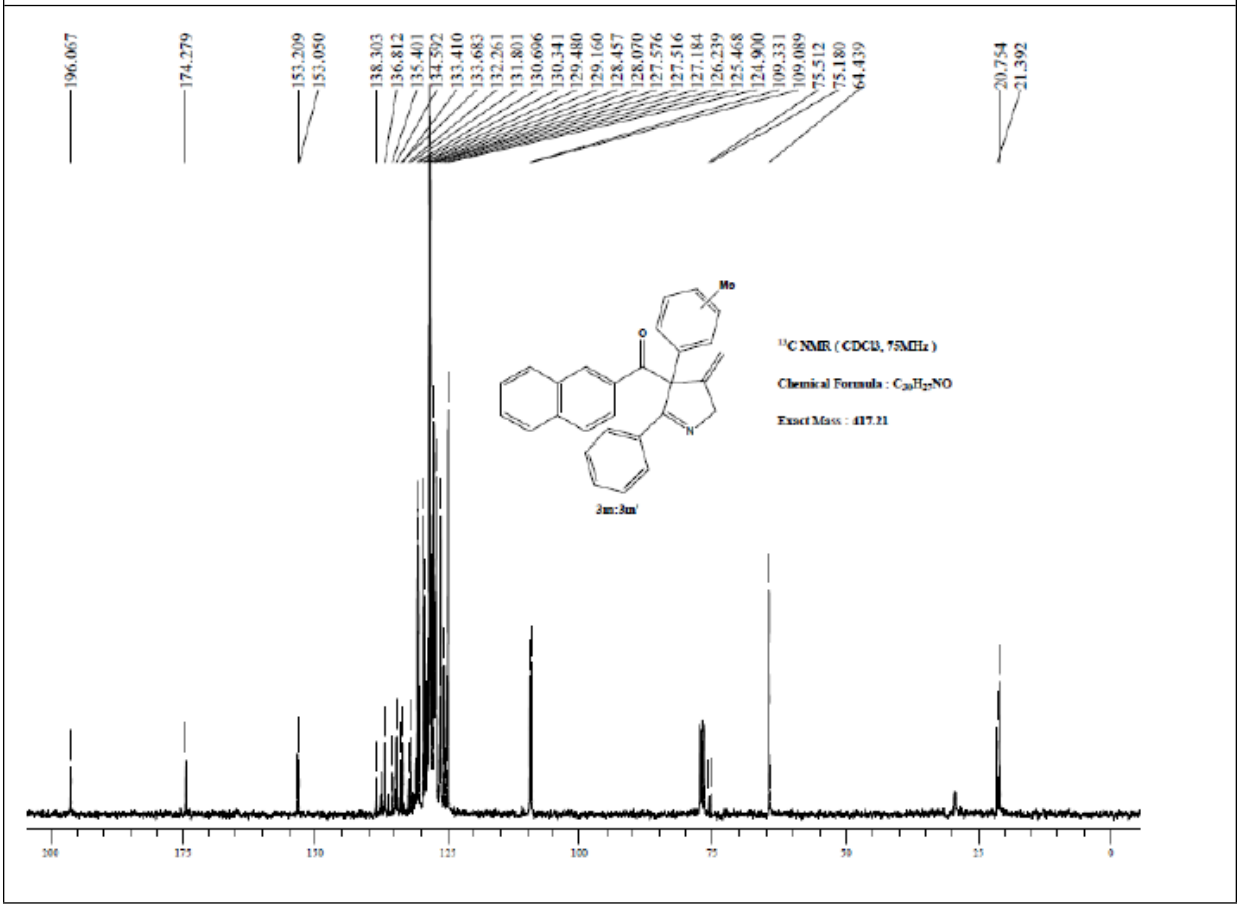
(4-Fluorophenyl)(3-methylene-5-phenyl-*m/p*-tolyl-3,4-dihydro-2H-pyrrol-4-yl)methanone **3l:3l'**





(3-Methylene-5-phenyl-*m/p*-tolyl-3,4-dihydro-2H-pyrrol-4-yl)(naphthalen-2-yl)methanone **3m:3m'**





X-ray crystallography data

Cambridge Crystallographic Data Centre

CCDC

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Crystal structure data of 3a: Crystal structure deposition no: CCDC 932648.

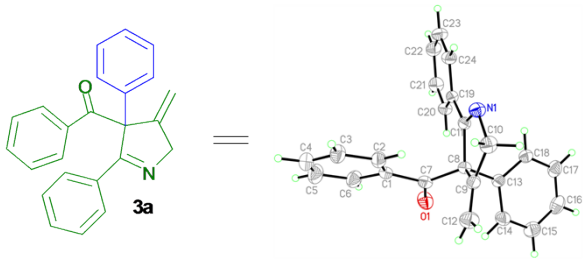

Figure 1. ORTEP diagram of the methylene-3,4 -dihydro-2*H*-pyrrole **3a**

Table 1. Crystal data and structure refinement for 3a

Identification code	epr105gk	
Empirical formula	C_{24} H_{19} N O	
Formula weight	337.40	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.2718(19) Å	□= 73.388(13)°.
	b = 9.5841(14) Å	□= 84.716(14)°.
	c = 10.4920(15) Å	□ = 79.196(15)°.
Volume	876.9(3) Å^3	
Z	2	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	356	
Crystal size	0.42 x 0.22 x 0.20 mm^3	
Theta range for data collection	2.89 to 25.00°.	
Index ranges	-10<=h<=11, -11<=k<=11, -10<=l<=12	
Reflections collected	5558	
Independent reflections	3086 [R(int) = 0.0332]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9847 and 0.9682	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3086 / 0 / 243	
Goodness-of-fit on F^2	0.978	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.0894	
R indices (all data)	R1 = 0.0961, wR2 = 0.1096	
Largest diff. peak and hole	0.138 and -0.185 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for epr105gk. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3160(2)	5806(2)	2701(2)	38(1)
C(2)	4311(3)	5508(3)	1824(2)	47(1)
C(3)	4748(3)	6637(3)	805(2)	57(1)
C(4)	4062(3)	8050(3)	647(3)	65(1)
C(5)	2905(3)	8365(3)	1491(3)	74(1)
C(6)	2458(3)	7250(3)	2514(2)	58(1)
C(7)	2652(2)	4698(2)	3902(2)	39(1)
C(8)	3059(2)	3024(2)	4058(2)	34(1)
C(9)	4717(2)	2487(2)	4038(2)	38(1)
C(10)	5019(2)	1525(3)	3106(2)	50(1)
C(11)	2670(2)	2615(2)	2826(2)	34(1)
C(12)	5689(3)	2804(3)	4700(3)	57(1)
C(13)	2389(2)	2126(2)	5362(2)	36(1)
C(14)	2645(3)	2345(3)	6565(2)	53(1)
C(15)	2130(3)	1508(3)	7750(2)	62(1)
C(16)	1347(3)	425(3)	7767(3)	59(1)
C(17)	1115(3)	164(3)	6597(3)	56(1)
C(18)	1636(2)	1002(2)	5402(2)	44(1)
C(19)	1208(2)	3075(2)	2234(2)	33(1)
C(20)	0(2)	3766(2)	2827(2)	40(1)
C(21)	-1347(3)	4125(3)	2244(2)	50(1)
C(22)	-1493(3)	3806(3)	1074(3)	55(1)
C(23)	-299(3)	3138(3)	466(2)	51(1)
C(24)	1044(3)	2772(2)	1039(2)	42(1)
N(1)	3705(2)	1810(2)	2345(2)	43(1)
O(1)	1903(2)	5143(2)	4761(2)	59(1)

Table 3. Bond lengths [Å] and angles [°] for epr105gk.

C(1)-C(6)	1.381(3)
C(1)-C(2)	1.386(3)
C(1)-C(7)	1.500(3)
C(2)-C(3)	1.379(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.355(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.372(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.376(3)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-O(1)	1.213(2)
C(7)-C(8)	1.542(3)
C(8)-C(9)	1.527(3)
C(8)-C(13)	1.539(3)
C(8)-C(11)	1.544(3)
C(9)-C(12)	1.313(3)
C(9)-C(10)	1.501(3)
C(10)-N(1)	1.458(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-N(1)	1.275(3)
C(11)-C(19)	1.481(3)
C(12)-H(12A)	1.01(3)
C(12)-H(12B)	0.99(3)
C(13)-C(18)	1.379(3)
C(13)-C(14)	1.385(3)
C(14)-C(15)	1.371(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.369(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.364(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.381(3)
C(17)-H(17)	0.9300

C(18)-H(18)	0.9300
C(19)-C(20)	1.381(3)
C(19)-C(24)	1.393(3)
C(20)-C(21)	1.382(3)
C(20)-H(20)	0.9300
C(21)-C(22)	1.371(3)
C(21)-H(21)	0.9300
C(22)-C(23)	1.371(3)
C(22)-H(22)	0.9300
C(23)-C(24)	1.374(3)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(6)-C(1)-C(2)	118.4(2)
C(6)-C(1)-C(7)	116.1(2)
C(2)-C(1)-C(7)	125.4(2)
C(3)-C(2)-C(1)	120.3(2)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	120.6(3)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.0(3)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	120.1(3)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	120.7(3)
C(5)-C(6)-H(6)	119.7
C(1)-C(6)-H(6)	119.7
O(1)-C(7)-C(1)	118.6(2)
O(1)-C(7)-C(8)	119.93(19)
C(1)-C(7)-C(8)	121.5(2)
C(9)-C(8)-C(13)	108.11(17)
C(9)-C(8)-C(7)	112.79(16)
C(13)-C(8)-C(7)	111.41(18)
C(9)-C(8)-C(11)	99.60(17)
C(13)-C(8)-C(11)	112.55(15)

C(7)-C(8)-C(11)	111.81(17)
C(12)-C(9)-C(10)	126.7(2)
C(12)-C(9)-C(8)	127.0(2)
C(10)-C(9)-C(8)	106.29(17)
N(1)-C(10)-C(9)	106.92(19)
N(1)-C(10)-H(10A)	110.3
C(9)-C(10)-H(10A)	110.3
N(1)-C(10)-H(10B)	110.3
C(9)-C(10)-H(10B)	110.3
H(10A)-C(10)-H(10B)	108.6
N(1)-C(11)-C(19)	120.9(2)
N(1)-C(11)-C(8)	115.08(19)
C(19)-C(11)-C(8)	124.0(2)
C(9)-C(12)-H(12A)	120.6(15)
C(9)-C(12)-H(12B)	118.5(15)
H(12A)-C(12)-H(12B)	121(2)
C(18)-C(13)-C(14)	117.40(19)
C(18)-C(13)-C(8)	122.34(19)
C(14)-C(13)-C(8)	120.02(18)
C(15)-C(14)-C(13)	121.4(2)
C(15)-C(14)-H(14)	119.3
C(13)-C(14)-H(14)	119.3
C(16)-C(15)-C(14)	120.3(2)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(17)-C(16)-C(15)	119.3(2)
C(17)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(16)-C(17)-C(18)	120.5(2)
C(16)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(13)-C(18)-C(17)	121.0(2)
C(13)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(20)-C(19)-C(24)	118.8(2)
C(20)-C(19)-C(11)	122.90(19)
C(24)-C(19)-C(11)	118.3(2)
C(19)-C(20)-C(21)	120.0(2)

C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0
C(22)-C(21)-C(20)	120.4(2)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	120.2(2)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-H(22)	119.9
C(22)-C(23)-C(24)	119.9(2)
C(22)-C(23)-H(23)	120.1
C(24)-C(23)-H(23)	120.1
C(23)-C(24)-C(19)	120.6(2)
C(23)-C(24)-H(24)	119.7
C(19)-C(24)-H(24)	119.7
C(11)-N(1)-C(10)	109.75(19)

Symmetry transformations used to generate equivalent atoms: