Reactions of 1,2-diaza-1,3-butadienes with propargyl alcohol: interesting approaches to novel and fascinating bi-heterocyclic systems

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SUPPORTING INFORMATION

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Experimental Section

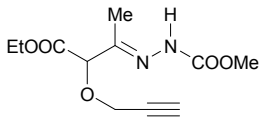
1. General Remarks.

All chemicals and solvents were purchased from commercial suppliers and used as received. 1,2-Diaza-1,3-dienes were prepared as reported[1] and used as EE/EZ isomer mixtures. Melting points were determined in open capillary tubes and are uncorrected. FTIR spectra were obtained as Nujol mulls. All ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Proton and carbon spectra were referenced internally to solvent signals, using values of δ = 2.50 ppm for proton (middle peak) and δ = 39.50 ppm for carbon (middle peak) in DMSO-d6 and δ = 7.27 ppm for proton and δ = 77.00 ppm for carbon (middle peak) in $CDCl_3$. All coupling constants (*J*) are given in Hz. All the NH and OH exchanged with D_2O. Precoated silica gel plates 0.25 mm were employed for analytical thin layer chromatography. All new compounds showed satisfactory elemental analysis. Mass spectra were recorded in the EI mode (70eV). The nomenclature was generated using ACD/IUPAC Name (version 3.50, 5 Apr. 1998), Advanced Chemistry Development Inc., Toronto, ON (Canada).

2. Experimental procedures and spectral data.

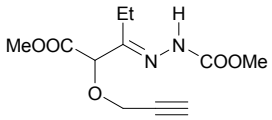
General procedure for the synthesis of α-(prop-2-yn-1-yloxy)hydrazones 3a–f, starting from 1,2-diaza-1,3-dienes 1a–f and propargylic alcohol 2.

A mixture of 1,2-diaza-1,3-diene **1a–f** as a mixture of E/Z isomers[1] (1 mmol), propargylic alcohol **2** (1 mmol), and DBU (0.01 mmol) was stirred at room temperature in CH_2Cl_2 (6 mL) for the appropriate time (24.0–72.0 hours), until the disappearance of the reagent **1** (TLC monitoring). The crude mixture was then purified by column chromatography on silica gel to afford the products **3a–f**, that were crystallized from diethyl ether.



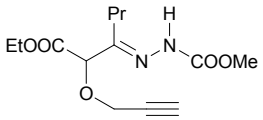
3a

Methyl 2-[3-ethoxy-1-methyl-3-oxo-2-(prop-2-yn-1-yloxy)propylidene]hydrazinecarboxylate (3a): 3a was isolated by column chromatography (acetate/cyclohexane 20:80) in 60% yield. White solid; mp: 115–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.27 (t, J = 7.2 Hz, 3H), 1.84 (s, 3H), 2.47 (t, J_4 = 2.4 Hz, 1H), 3.84 (s, 3H), 4.22–4.30 (m, 4H), 4.80 (s, 1H), 7.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.4 (q), 13.3 (q), 53.3 (t), 57.4 (q), 61.9 (t), 70.0 (d), 78.6 (s), 81.4 (d), 147.4 (s), 154.6 (s), 168.7 (s); IR (nujol): ν_{max} = 3292, 3219, 2119, 1734, 1718, 1705 cm^{-1}; MS *m/z* (%): 256 (M^+) (1), 225 (11), 211 (5), 197 (33), 183 (12), 142 (15), 125 (100); anal. calcd. for $C_{11}H_{16}N_2O_5$ (256.25): C 51.56, H 6.29, N 10.93; found: C 51.78, H 6.32, N 11.11.



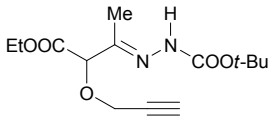
3b

Methyl 2-[1-ethoxy-3-methyl-3-oxo-2-(prop-2-yn-1-yloxy)propylidene]hydrazinecarboxylate (3b): 3b was isolated by column chromatography (acetate/cyclohexane 20:80) in 61% yield. White solid; mp: 114–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.05 (t, J = 7.6 Hz, 3H), 2.20–2.42 (m, 2H), 2.46 (t, J_4 = 2.4 Hz, 1H), 3.74 (s, 3H), 3.80 (s, 3H), 4.21 and 4.27 (dd, J_3 = 15.6 Hz, J_4 = 2.4 Hz, 2H), 4.79 (s, 1H), 8.29 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.7 (q), 18.9 (t), 52.4 (q), 53.0 (q), 57.2 (t), 75.7 (d), 78.3 (s), 80.5 (d), 151.0 (s), 154.7 (s), 169.1 (s); IR (nujol): ν_{max} = 3510, 3455, 3305, 3265, 2120, 1735, 1710, 1680 cm^{-1}; MS *m/z* (%): 256 (M^+) (1), 225 (22), 210 (11), 197 (30), 142 (11), 125 (100); anal. calcd. for $C_{11}H_{16}N_2O_5$ (256.25): C 51.56, H 6.29, N 10.93; found: C 51.39, H 6.19, N 11.01.



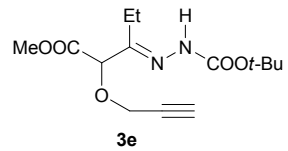
3c

Methyl 2-{1-[2-ethoxy-2-oxo-1-(prop-2-yn-1-yloxy)ethyl]butylidene}hydrazinecarboxylate (3c): 3c was isolated by column chromatography (acetate/cyclohexane 30:70) in 41% yield. White solid; mp: 119–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.95 and 0.99 (2t, J = 7.6 Hz, 3H), 1.27–1.31 (m, 3H), 1.42–1.72 (m, 2H), 2.15–2.33 (m, 1H), 2.39–2.42 (m, 1H), 2.47 and 2.56 (2t, J_4 = 2.4 Hz, 1H), 3.79 and 3.84 (2s, 3H), 4.22–4.32 (m, 4H), 4.80 and 4.92 (2s, 1H), 7.92 and 9.33 (2brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.7 (q), 14.0 (q), 14.1 (q), 14.5 (q), 18.6 (t), 20.0 (t), 28.0 (t), 38.3 (t), 57.2 (q), 61.6 (t), 62.4 (t), 75.2 (d), 75.7 (d), 78.4 (s), 80.7 (d), 147.0 (s), 154.3 (s), 167.2 (s), 168.7 (s); IR (nujol): ν_{max} = 3275, 3228, 2124, 1734, 1705 cm^{-1}; MS *m/z* (%): 284 (M^+) (1), 239 (12), 225 (18), 211 (35), 125 (18), 109 (100); anal. calcd. for $C_{13}H_{20}N_2O_5$ (284.30): C 54.92, H 7.09, N 9.85; found: C 55.15, H 7.18, N 9.68.



3d

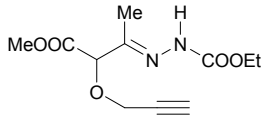
***tert*-Butyl 2-[3-ethoxy-1-methyl-3-oxo-2-(prop-2-yn-1-yloxy)propylidene]hydrazinecarboxylate (3d): 3d** was isolated by column chromatography (acetate/cyclohexane 20:80) in 77% yield. White solid; mp: 123–125 °C; ^{1}H NMR (400 MHz, $DMSO_{d6}$, 25 °C): δ = 1.19 (t, J = 7.2 Hz, 3H), 1.45 (s, 9H), 1.76 (s, 3H), 3.54 (t, J_4 = 2.4 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 4.19–4.20 (m, 2H), 4.59 (s, 1H), 9.82 (s, 1H); ^{13}C NMR (100 MHz, $DMSO_{d6}$, 25 °C): δ = 13.1 (q), 14.7 (q), 28.7 (q), 57.1 (t), 61.6 (t), 78.7 (d), 79.9 (s), 80.3 (s), 81.6 (d), 147.3 (s), 153.5 (s), 169.0 (s); IR (nujol): ν_{max} = 3273, 3238, 2136, 1741, 1707 cm^{-1}; MS *m/z* (%): 298 (M^+) (1), 225 (13), 188 (3), 169 (23), 142 (45), 125 (100); anal. calcd. for $C_{14}H_{22}N_2O_5$ (298.33): C 56.36, H 7.43, N 9.39; found: C 56.58, H 7.49, N 9.52.



3e

***tert*-Butyl 2-[1-ethyl-3-methoxy-3-oxo-2-(prop-2-yn-1-yloxy)propylidene]hydrazinecarboxylate (3e): 3e** was isolated by column chromatography (acetate/cyclohexane 20:80) in 80% yield. White

solid; mp: 114–115 °C; ^{1}H NMR (400 MHz, DMSO$_{d6}$, 25 °C): δ = 0.89 (t, J = 7.6 Hz, 3H), 1.43 (s, 9H), 2.19–2.40 (m, 2H), 3.52 (t, J_4 = 2.4 Hz, 1H), 3.67 (s, 3H), 4.15 and 4.23 (dd, J_2 = 16.0 Hz, J_4 = 2.4 Hz, AB system, 2H), 4.63 (s, 1H), 9.89 (s, 1H); ^{13}C NMR (100 MHz, DMSO$_{d6}$, 25 °C): δ = 9.5 (q), 19.2 (t), 28.0 (q), 51.8 (q), 56.6 (t), 78.0 (d), 79.2 (s), 79.6 (s), 80.1 (d), 150.1 (s), 152.7 (s), 169.1 (s); IR (nujol): ν_{max} = 3256, 3218, 2132, 1756, 1747, 1731, 1711 cm^{-1}; MS *m/z* (%): 298 (M^+) (1), 239 (7), 225 (16), 188 (21), 154 (36), 139 (100), 128 (54), 112 (82); anal. calcd. for $C_{14}H_{22}N_2O_5$ (298.33): C 56.36, H 7.43, N 9.39; found: C 56.03, H 7.31, N 9.49.

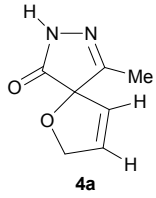


3f

Ethyl 2-[3-methox-3-oxo-2-(prop-2-yn-1-yloxy)propylidene]hydrazinecarboxylate (3f): 3f was isolated by column chromatography (acetate/cyclohexane 20:80) in 60% yield. White solid; mp: 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.30 (t, J = 7.2 Hz, 3H), 1.84 (s, 3H), 2.46 (t, J_4 = 2.4 Hz, 1H), 3.75 (s, 3H), 4.20–4.30 (m, 4H), 4.82 (s, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.5 (q), 15.0 (q), 53.0 (t), 57.8 (q), 62.6 (t), 76.2 (d), 78.8 (s), 81.6 (d), 147.2 (s), 154.5 (s), 169.5 (s); IR (nujol): ν_{max} = 3266, 3217, 2129, 1755, 1748, 1707 cm^{-1}; MS *m/z* (%): 256 (M^+) (1), 202 (12), 197 (52), 168 (27), 151 (7), 129 (74), 101 (100); anal. calcd. for $C_{11}H_{16}N_2O_5$ (256.26): C 51.56, H 6.29, N 10.93; found: C 51.78, H 6.51, N 10.76.

General procedure for the synthesis of 9-alkyl-1-oxa-7,8-diazaspiro[4.4]nona-3,8-dien-6-ones 4a–c, starting from of α-(prop-2-yn-1-yloxy)hydrazones 3a–c.

To magnetically stirred solution of α-(prop-2-yn-1-yloxy)hydrazones **3a–c** (1 mmol) in MeOH (6 mL), four equivalents of K_2CO_3 were added. The mixture was stand in these conditions for 1.0–1.5 hours, until the disappearance of the **3** (TLC monitoring). The crude mixture was purified by column chromatography on silica gel to afford the products **4**, that were crystallized from diethyl ether-light petroleum (bp 40–60 °C).



4a

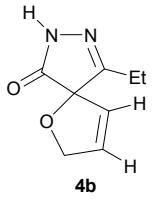
9-Methyl-1-oxa-7,8-diazaspiro[4.4]nona-3,8-dien-6-one (4a): 4a was isolated by column chromatography (acetate/cyclohexane 20:80) in 73% yield. White solid; mp: 125–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.95 (s, 3H), 4.88–4.93 and 5.04–5.09 (2m, 2H), 5.54–5.57 (m, 1H), 6.40–6.42 (m, 1H) 8.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.9 (q), 78.1 (t), 91.6 (s), 123.4 (d), 133.1 (d), 160.1 (s), 175.4 (s); IR (nujol): ν_{max} = 3348, 3165, 1718, 1704 cm^{-1}; MS *m/z* (%): 152 (M^+) (71), 124 (9), 110 (9), 98 (18), 81 (23), 68 (100), 53 (16), 39 (96); anal. calcd. for $C_7H_8N_2O_2$ (152.15): C 55.26, H 5.30, N 18.41; found: C 55.42, H 5.41, N 18.29.

X-ray Crystallography

A single crystal of **4a** was submitted to X-ray data collections by using a Xcalibur, Sapphire3 (Oxford Diffraction Ltd., U.K.) four-circle diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71073Å). The structure was solved by direct methods implemented in SHELXS-2013 program. The refinement was carried out by full-matrix anisotropic least-squares on F^2 for all reflections for non-H atoms by using the SHELXL-2013 program.

$C_7H_8N_2O_2$, M = 152.15, monoclinic, a = 6.4408(8), b = 16.415(2), c = 6.8820(7) Å, β =93.99(1)°, U = 725.85(15)Å^3, T= 293 K, space group P21/n (no. 14), Z = 4, 3007 reflections measured, 1675 unique ($I > 2\sigma_{(I)}$ Rint = 0.021). The final wR_2 was 0.113 (all data).

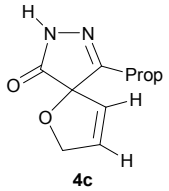
CCDC 1474432 contains the supplementary crystallographic data for compound **4a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



4b

9-Methyl-1-oxa-7,8-diazaspiro[4.4]nona-3,8-dien-6-one (4b): 4b was isolated by column chromatography (acetate/cyclohexane 20:80) in 68% yield. White solid; mp: 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.61 (t, *J* = 7.2 Hz, 3H), 2.21–2.42 (m, 2H), 4.88–4.92 and 5.05–5.09 (2m, 2H), 5.56–5.59 (m, 1H), 6.38–6.40 (m, 1H), 8.55 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.8 (q), 21.3 (t), 78.4 (t), 91.8 (s), 124.1 (d), 133.1 (d), 164.4 (s), 175.7 (s); IR (nujol): ν_{max} = 3163, 3084, 1720, 1684 cm^{-1}; MS *m/z*

(%): 166 (M^+) (1), 137 (1), 111 (2), 97 (3), 69 (5), 28 (100); anal. calcd. for $C_8H_{10}N_2O_2$ (166.17): C 57.82, H 6.07, N 16.86; found: C 57.64, H 5.95, N 16.99.

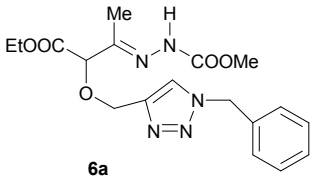


4c

9-Propyl-1-oxa-7,8-diazaspiro[4.4]nona-3,8-dien-6-one (4c): 4c was isolated by column chromatography (acetate/cyclohexane 20:80) in 67% yield. White solid; mp: 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, *J* = 7.2 Hz, 3H), 2.17–2.34 (m, 2H), 4.88–4.93 and 5.05–5.10 (2m, 2H), 5.56–5.59 (m, 1H), 6.39–6.41 (m, 1H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1 (q), 19.1 (t), 30.0 (t), 78.4 (t), 91.7 (s), 124.1 (d), 133.1 (d), 163.3 (s), 175.5 (s); IR (nujol): ν_{max} = 3171, 3093, 1725, 1690 cm^{-1}; MS *m/z* (%): 180 (M^+) (23), 166 (22), 149 (56), 137 (39), 123 (61), 111 (100); anal. calcd. for $C_9H_{11}N_2O_2$ (180.20): C 59.99, H 6.71, N 15.55; found: C 60.22, H 6.80, N 15.68.

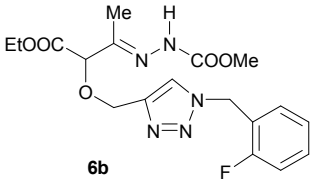
General procedure for the synthesis of α-[(1,2,3-triazol-4-yl)methoxy]hydrazones 6a–f, starting from α-(prop-2-yn-1-yloxy)hydrazones 3a,d–f and benzyl azides 5a,b.

To a solution of α-(prop-2-yn-1-yloxy)hydrazones **3a,d–f** (1.0 mmol) and benzyl azides **5a,b** (1.1 mmol) in CH_2Cl_2 (1 mL)–H_2O (1 mL), $Cu(OAc)_2 \cdot H_2O$ (0.55 mmol) and sodium ascorbate (0.15 mmol) were added. The reaction was allowed under magnetic stirring at room temperature for the appropriate time (2.0–12.0 h), until the disappearance of the hydrazone **3** (monitored by TLC). After the adding of further amount of CH_2Cl_2 (4 mL), the crude was washed with aqueous saturated solution of NH_4Cl (2x10ml) and then with H_2O (2x10ml) and dried over anhydrous Na_2SO_4. The organic phase was then filtered and concentrated under reduced pressure. The products **6a–f** were purified by column chromatography on silica gel (elution mixture: ethyl acetate/cyclohexane).



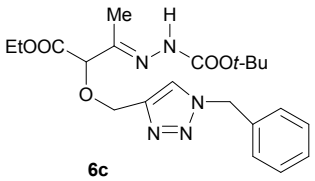
6a

Methyl 2-{2-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-3-ethoxy-1-methyl-3-oxopropylidene}hydrazinecarboxylate (6a): 6a was isolated by column chromatography (acetate/cyclohexane 20:80) in 62% yield. White solid; mp: 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.17 (t, *J* = 7.2 Hz, 3H), 1.78 (s, 3H), 3.74 (s, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.58–4.66 (m, 3H), 5.44 (s, 2H), 7.20–7.22 (m, 2H$_{ar}$), 7.29–7.32 (m, 3H$_{ar}$), 7.51 (s, 1H$_{ar}$), 8.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.5 (q), 14.4 (q), 53.3 (q), 54.4 (t), 61.9 (t), 63.6 (t), 82.2 (d), 123.5 (d), 128.5 (d), 129.0 (d), 129.2 (d), 129.4 (d), 134.8 (s), 144.5 (s), 147.9 (s), 154.8 (s), 168.9 (s); IR (nujol): ν_{max} = 3245, 3140, 1720, 1705 cm^{-1}; MS *m/z* (%): 389 (M^+) (1), 344 (1), 315 (11), 188 (4), 173 (100), 156 (13); anal. calcd. for $C_{18}H_{23}N_5O_5$ (389.40): C 55.52, H 5.95, N 17.98; found: C 55.39, H 5.88, N 18.21.



6b

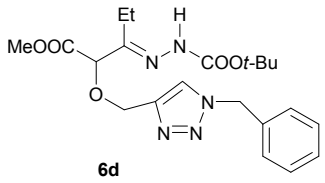
Methyl 2-(3-ethoxy-2-{[1-(2-fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methoxy}-1-methyl-3-oxopropylidene)hydrazinecarboxylate (6b): 6b was isolated by column chromatography (acetate/cyclohexane 20:80) in 79% yield. White solid; mp: 99–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.23 (t, *J* = 7.2 Hz, 3H), 1.82 (s, 3H), 3.83 (s, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.64–4.73 (m, 3H), 5.56 (s, 2H), 7.04–7.16 (m, 2H$_{ar}$), 7.23–7.41 (m, 2H$_{ar}$), 7.62 (s, 1H$_{ar}$), 7.88 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.4 (q), 14.6 (q), 48.1 (t), 53.6 (q), 62.1 (t), 63.8 (t), 82.4 (d), 116.2 (d), 116.4 (d), 122.2 (s), 123.7 (d), 125.3 (d), 131.2 (d), 131.4 (d), 131.7 (s), 144.8 (s), 147.9 (s), 154.9 (s), 159.8 (s), 162.2 (s), 169.1 (s); IR (nujol): ν_{max} = 3247, 3145, 1725, 1702 cm^{-1}; MS *m/z* (%): 407 (M^+) (2), 333 (8), 246 (2), 191 (72), 162 (27), 109 (100); anal. calcd. for $C_{18}H_{22}FN_5O_5$ (407.40): C 53.07, H 5.44, N 17.19; found: C 53.35, H 5.56, N 17.08.



6c

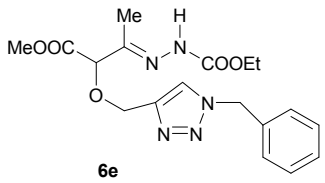
***tert*-Butyl 2-{2-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-3-ethoxy-1-methyl-3-oxopropylidene}hydrazinecarboxylate (6c): 6c** was

isolated by column chromatography (acetate/cyclohexane 20:80) in 78% yield. White solid; mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.21 (t, *J* = 7.2 Hz, 3H), 1.46 (s, 9H), 1.76 (s, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.63 (s, 2H), 4.64 (s, 1H), 5.45 (s, 2H), 7.23–7.26 (m, $2H_{ar}$), 7.30–7.32 (m, $3H_{ar}$), 7.54 (s, $1H_{ar}$), 7.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.3 (q), 14.5 (q), 28.6 (q), 54.5 (t), 61.9 (t), 63.6 (t), 81.8 (s), 82.4 (d), 123.6 (d), 128.5 (d), 129.1 (d), 129.2 (d), 129.4 (d), 134.9 (s), 144.6 (s), 146.7 (s), 152.7 (s), 169.1 (s); IR (nujol): ν_{max} = 3247, 3145, 1720, 1701 cm^{-1}; MS *m/z* (%): 431 (M^+) (1), 410 (5), 358 (4), 303 (6), 188 (5), 173 (100), 144 (48); anal. calcd. for $C_{21}H_{29}N_5O_5$ (431.48): C 58.45, H 6.77, N 16.23; found: C 58.68, H 6.89, N 16.09.



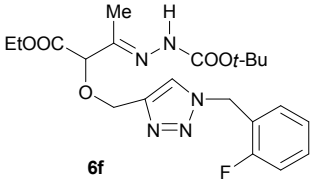
6d

***tert*-Butyl 2-{2-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-1-ethyl-3-methoxy-3-oxopropylidene}hydrazinecarboxylate (6d): 6d** was isolated by column chromatography (acetate/cyclohexane 20:80) in 69% yield. White solid; mp: 118–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.03–1.07 (m, 3H), 1.47 and 1.50 (2s, 9H), 2.14–2.48 (m, 2H), 3.72 and 3.74 (2s, 3H), 4.68–4.79 (m, 3H), 5.51–5.23 (m, 2H), 7.26–7.29 (m, $2H_{ar}$), 7.34–7.38 (m, $3H_{ar}$), 7.50 and 7.59 (2s, $1H_{ar}$), 7.70 and 9.27 (2brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 9.9 (q), 11.2 (q), 19.4 (t), 28.7 (q), 52.8 (q), 53.3 (q), 54.7 (t), 54.8 (t), 63.5 (t), 63.8 (t), 76.7 (d), 81.4 (s), 82.0 (d), 123.5 (d), 123.7 (d), 128.6 (d), 128.7 (d), 129.2 (d), 129.3 (d), 129.4 (d), 129.6 (d), 129.7 (d), 134.7 (s), 135.0 (s), 144.2 (s), 144.7 (s), 153.4 (s), 165.5 (s), 170.0 (s); IR (nujol): ν_{max} = 3234, 3135, 1754, 1704 cm^{-1}; MS *m/z* (%): 431 (M^+) (1), 315 (18), 242 (6), 229 (6), 188 (9), 173 (100), 144 (43); anal. calcd. for $C_{21}H_{29}N_5O_5$ (431.48): C 58.45, H 6.77, N 16.23; found: C 58.23, H 6.65, N 16.51.



6e

Methyl 2-{2-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-3-ethoxy-1-methyl-3-oxopropylidene}hydrazinecarboxylate (6e): 6e was isolated by column chromatography (acetate/cyclohexane 20:80) in 81% yield. Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.26 (t, *J* = 7.2 Hz, 3H), 1.79 (s, 3H), 3.68 (s, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.64–4.68 (m, 3H), 5.47 (s, 2H), 7.23–7.25 (m, $2H_{ar}$), 7.26–7.33 (m, $3H_{ar}$), 7.53 (s, $1H_{ar}$), 8.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.5 (q), 14.9 (q), 52.8 (q), 54.5 (t), 62.5 (t), 63.6 (t), 82.2 (d), 123.6 (d), 128.5 (d), 129.1 (d), 129.5 (d), 129.9 (d), 134.9 (s), 144.5 (s), 147.6 (s), 154.4 (s), 169.6 (s); IR (nujol): ν_{max} = 3253, 3145, 1743 cm^{-1}; MS *m/z* (%): 389 (M^+) (1), 301 (18), 228 (3), 202 (4), 188 (4), 173 (100), 144 (33); anal. calcd. for $C_{18}H_{23}N_5O_5$ (389.40): C 55.52, H 5.95, N 17.98; found: C 55.80, H 6.03, N 17.81.



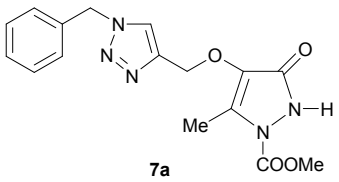
6f

***tert*-Butyl 2-(3-ethoxy-2-{[1-(2-fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methoxy}-1-methyl-3-oxopropylidene)hydrazinecarboxylate (6f): 6f** was isolated by column chromatography (acetate/cyclohexane 20:80)

in 81% yield. White solid; mp: 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.24 (t, *J* = 7.2 Hz, 3H), 1.50 (s, 9H), 1.79 (s, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.64–4.72 (m, 3H), 5.56 (s, 2H), 7.08–7.16 (m, $2H_{ar}$), 7.26–7.35 (m, $2H_{ar}$), 7.62 (s, $1H_{ar}$), 7.66 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.4 (q), 14.6 (q), 28.7 (q), 48.1 (t), 62.1 (t), 63.7 (t), 82.1 (s), 82.5 (d), 116.2 (d), 116.4 (d), 122.3 (s), 123.8 (d), 125.3 (d), 131.1 (d), 131.3 (d), 131.4 (s), 144.8 (s), 146.7 (s), 152.7 (s), 160.0 (s), 162.2 (s), 169.2 (s); IR (nujol): ν_{max} = 3330, 3245, 1749, 1725, 1701 cm^{-1}; MS *m/z* (%): 449 (M^+) (1), 339 (2), 303 (4), 207 (4), 191 (13), 162 (8), 149 (6), 122 (9), 109 (100); anal. calcd. for $C_{21}H_{28}FN_5O_5$ (449.47): C 56.12, H 6.28, N 15.58; found: C 56.35, H 6.37, N 15.40.

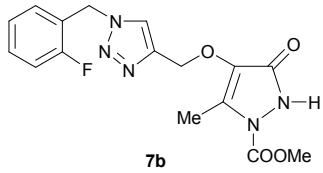
General procedure for the synthesis of α-[(1,2,3-triazol-4-yl)methoxy]pyrazolones 7a–e, starting from of α-[(1,2,3-triazol-4-yl)methoxy]hydrazones 6a–f.

To magnetically stirred solution of α-[(1,2,3-triazol-4-yl)methoxy]hydrazones **6a–f** (1 mmol) in MeOH (6 mL), four equivalents of K_2CO_3 were added. The mixture was stand in these conditions for 0.3–0.5 hours, until the disappearance of the **6** (TLC monitoring). The crude mixture was purified by column chromatography on silica gel to afford the products **7**, that were crystallized from diethyl ether-light petroleum (bp 40–60 °C).



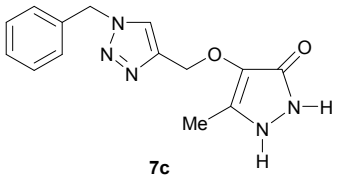
7a

Methyl 4-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-3-methyl-5-oxo-2,5-dihydro-1*H*-pyrazole-1-carboxylate (7a): 7a was isolated by column chromatography (acetate/methanol 90:10) in 83% yield. White solid; mp: 130–132 °C; ^{1}H NMR (400 MHz, DMSO$_{d6}$, 25 °C): δ = 1.99 (s, 3H), 3.83 (s, 3H), 4.98 (s, 2H), 5.60 (s, 2H), 7.24–7.38 (m, 5H$_{ar}$), 8.18 (s, 1H$_{ar}$), 11.21 (brs, 1H); ^{13}C NMR (100 MHz, DMSO$_{d6}$, 25 °C): δ = 11.1 (q), 53.2 (t), 54.2 (q), 65.6 (t), 125.4 (d), 128.2 (d), 128.5 (d), 129.1 (d), 130.4 (s), 133.4 (s), 136.6 (s), 143.3 (s), 150.8 (s), 157.1 (s); IR (nujol): ν_{max} = 3201, 3134, 3092, 2982, 1737, 1707, 1609 cm^{-1}; MS *m/z* (%): 343 (M$^+$) (7), 285 (3), 173 (84), 144 (100); anal. calcd. for $C_{16}H_{17}N_5O_4$ (343.33): C 55.97, H 4.99, N 20.40; found: C 55.75, H 4.78, N 20.29.



7b

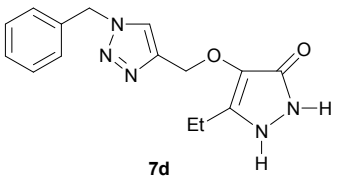
Methyl 4-{[1-(2-fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methoxy}-3-methyl-5-oxo-2,5-dihydro-1*H*-pyrazole-1-carboxylate (7b): 7b was isolated by column chromatography (acetate/methanol 90:10) in 86% yield. White solid; mp: 126–129 °C; ^{1}H NMR (400 MHz, DMSO$_{d6}$, 25 °C): δ = 1.73 (s, 3H), 3.85 (s, 3H), 4.94 (s, 2H), 5.66 (s, 2H), 7.19–7.30 (m, 3H$_{ar}$), 7.39–7.45 (m, 1H$_{ar}$), 8.20 (s, 1H$_{ar}$), 10.80 (brs, 1H); ^{13}C NMR (100 MHz, DMSO$_{d6}$, 25 °C): δ = 9.4 (q), 46.8 (t), 53.7 (q), 64.3 (t), 115.5 (d), 115.7 (d), 122.8 (s), 123.0 (s), 124.8 (d), 125.1 (d), 130.5 (d), 130.7 (d), 143.1 (s), 144.7 (s), 148.7 (s), 158.7 (s), 161.2 (s); IR (nujol): ν_{max} = 3202, 3133, 3095, 2983, 1737, 1710, 1611 cm^{-1}; MS *m/z* (%): 361 (M$^+$) (1), 317 (3), 191 (15), 162 (19), 109 (100); anal. calcd. for $C_{16}H_{16}FN_5O_4$ (361.32): C 53.18, H 4.46, N 19.38; found: C 53.35, H 4.25, N 19.20.



7c

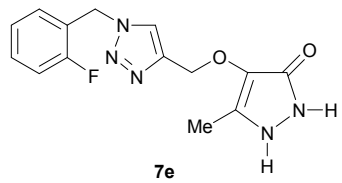
4-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (7c): 7c was isolated by column chromatography (acetate/methanol 80:20) in 62% yield from **6c** and 60% yield from **6e**. Pale pink solid; mp: 136–138 °C; ^{1}H NMR (400 MHz, DMSO$_{d6}$, 25 °C): δ = 1.74 (s, 3H), 4.83 (s, 2H), 5.57 (s, 2H), 7.25–7.35 (m, 5H$_{ar}$), 8.11 (s, 1H$_{ar}$), 10.27 (brs, 2H); ^{13}C NMR (100 MHz, DMSO$_{d6}$, 25 °C): δ = 8.5 (q), 52.7 (t), 65.7 (t), 125.1 (d), 125.2 (d), 128.5 (d), 128.7 (d), 129.4 (d), 130.1 (s), 136.8 (s), 144.5 (s), 153.2 (s); IR (nujol): ν_{max} = 3204, 3134, 3090,

2981, 1738, 1708, 1610 cm^{-1}; MS *m/z* (%): 285 (M^+) (1), 173 (16), 144 (4), 91 (100); anal. calcd. for $C_{14}H_{15}N_5O_2$ (285.30): C 58.94, H 5.30, N 24.55; found: C 59.21, H 5.18, N 24.67.



7d

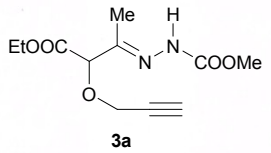
4-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-5-ethyl-1,2-dihydro-3H-pyrazol-3-one (7d): 7d was isolated by column chromatography (acetate/methanol 80:20) in 63% yield. Red oil; ^{1}H NMR (400 MHz, $DMSO_{d6}$, 25 °C): δ = 1.24–1.62 (m, 5H), 4.48 (s, 2H), 5.56 (s, 2H), 7.22–7.41 (m, $5H_{ar}$), 8.02 (s, $1H_{ar}$), 11.41 (brs, 2H); ^{13}C NMR (100 MHz, $DMSO_{d6}$, 25 °C): δ = 12.4 (q), 30.0 (t), 53.0 (t), 123.3 (d), 128.2 (d), 128.4 (d), 128.6 (d), 129.1 (d), 129.2 (d), 136.7 (s), 143.4 (s), 148.7 (s), 153.4 (s); IR (nujol): ν_{max} = 3210, 3142, 3092, 2981, 1741, 1710, 1615 cm^{-1}; MS *m/z* (%): 299 (M^+) (1), 209 (18), 110 (9), 91 (100); anal. calcd. for $C_{15}H_{17}N_5O_2$ (299.32): C 60.19, H 5.72, N 23.40; found: C 60.32, H 5.85, N 23.28.



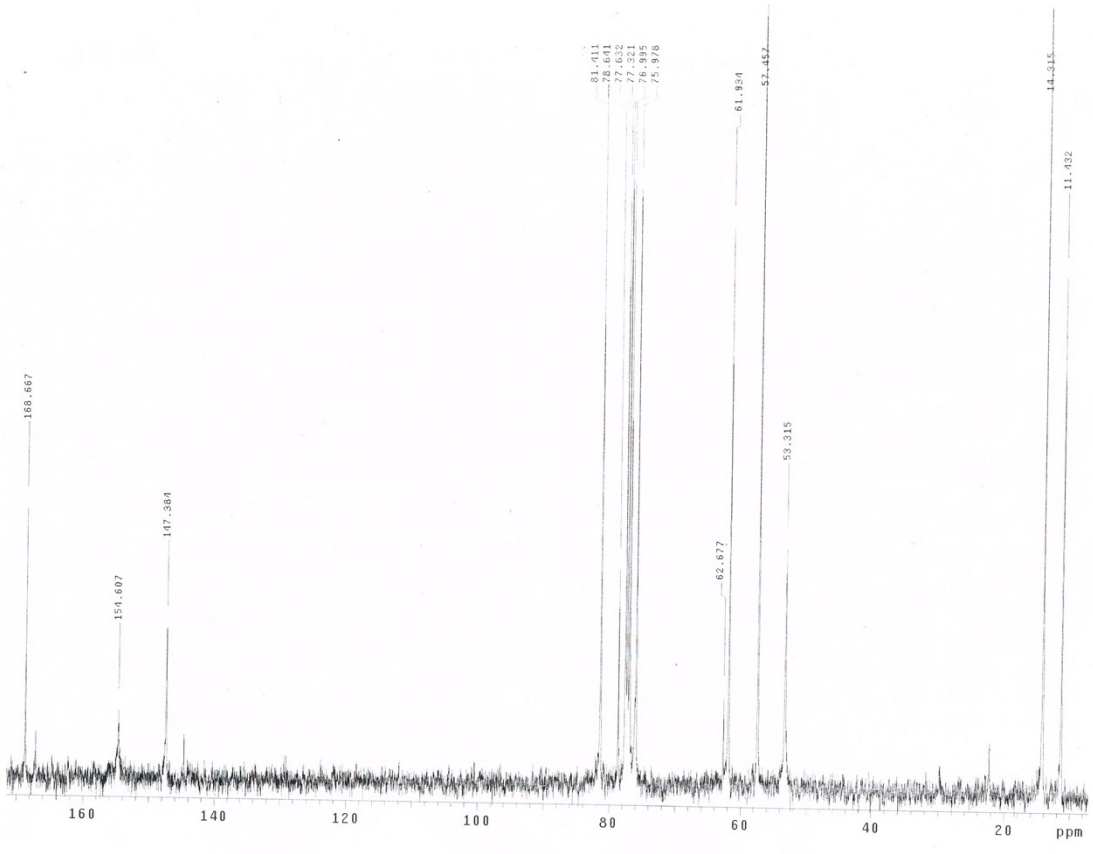
7e

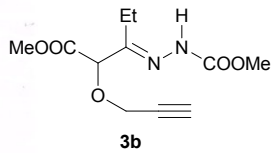
4-{[1-(2-Fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methoxy}-5-methyl-1,2-dihydro-3*H*-pyrazole-3-one (7e): 7e was isolated by column chromatography (acetate/methanol 80:00) in 67% yield. Red oil; ^{1}H NMR (400 MHz, $DMSO_{d6}$, 25 °C): δ = 1.93 (s, 3H), 4.83 (s, 2H), 5.64 (s, 2H), 7.18–7.40 (m, $4H_{ar}$), 8.10 (s, $1H_{ar}$), 10.52 (brs, 2H); ^{13}C NMR (100 MHz, $DMSO_{d6}$, 25 °C): δ = 8.5 (q), 46.8 (t), 65.7 (t), 116.2 (d), 116.4 (d), 123.6 (s), 125.0 (s), 125.4 (d), 125.5 (d), 130.1 (s), 131.3 (d), 131.4 (d), 144.5 (s), 153.2 (s), 159.5 (s), 161.9 (s); IR (nujol): ν_{max} = 3208, 3132, 3093, 2980, 1735, 1710, 1611 cm^{-1}; MS *m/z* (%): 303 (M^+) (2), 281 (3), 207 (21), 191 (14), 162 (11), 109 (100); anal. calcd. for $C_{14}H_{14}FN_5O_2$ (303.29): C 55.44, H 4.65, N 23.09; found: C 55.22, H 4.45, N 23.21.

3. ^{1}H and ^{13}C NMR spectra of products.



3a

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H
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N
N
COOMe
O

3b

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3.736
3.788
1.073
1.053
1.034
4.252
4.245
4.223
4.789
4.291
4.285
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2.451
2.445
2.328
2.463
2.308
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1.244
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8.78
1
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7
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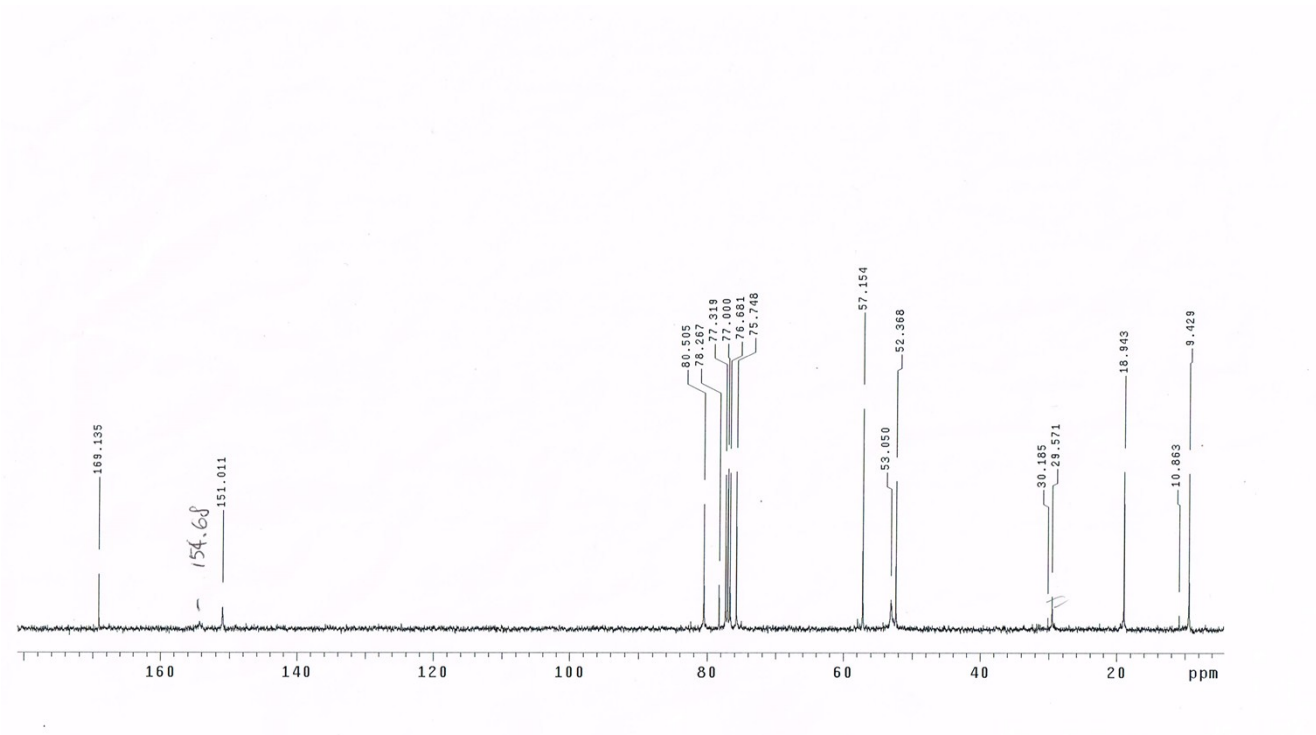
3.00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140
120
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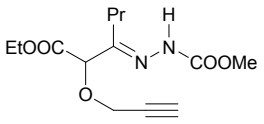
80
60
40
20
ppm


Pr
H
EtOOC
N
N
COOMe
O

3c

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4.802
3.840
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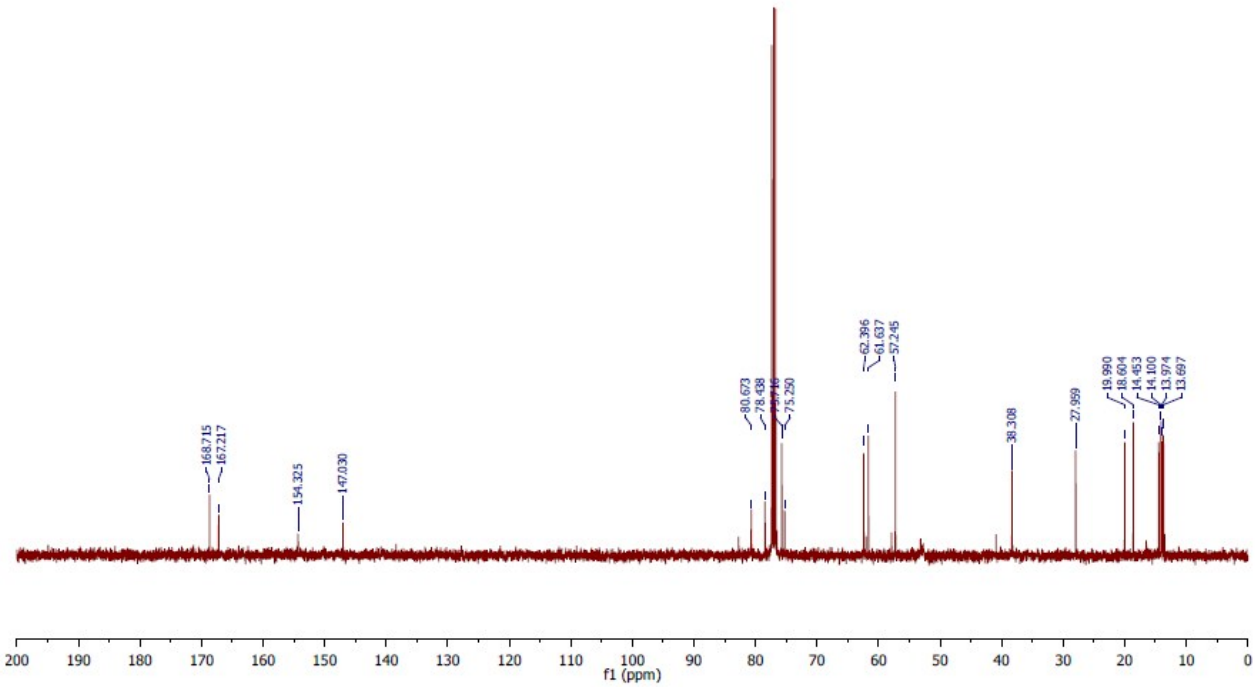
1.006
0.987
0.970
0.953
0.934
1.25
1.07
4.09
3.00
0.96
0.97
1.13
2.29
3.01
3.06
f1 (ppm)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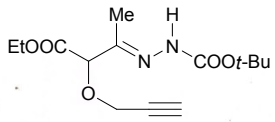
f1 (ppm)


Me
H
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N
N
COO*t*-Bu
O

3d

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1.190
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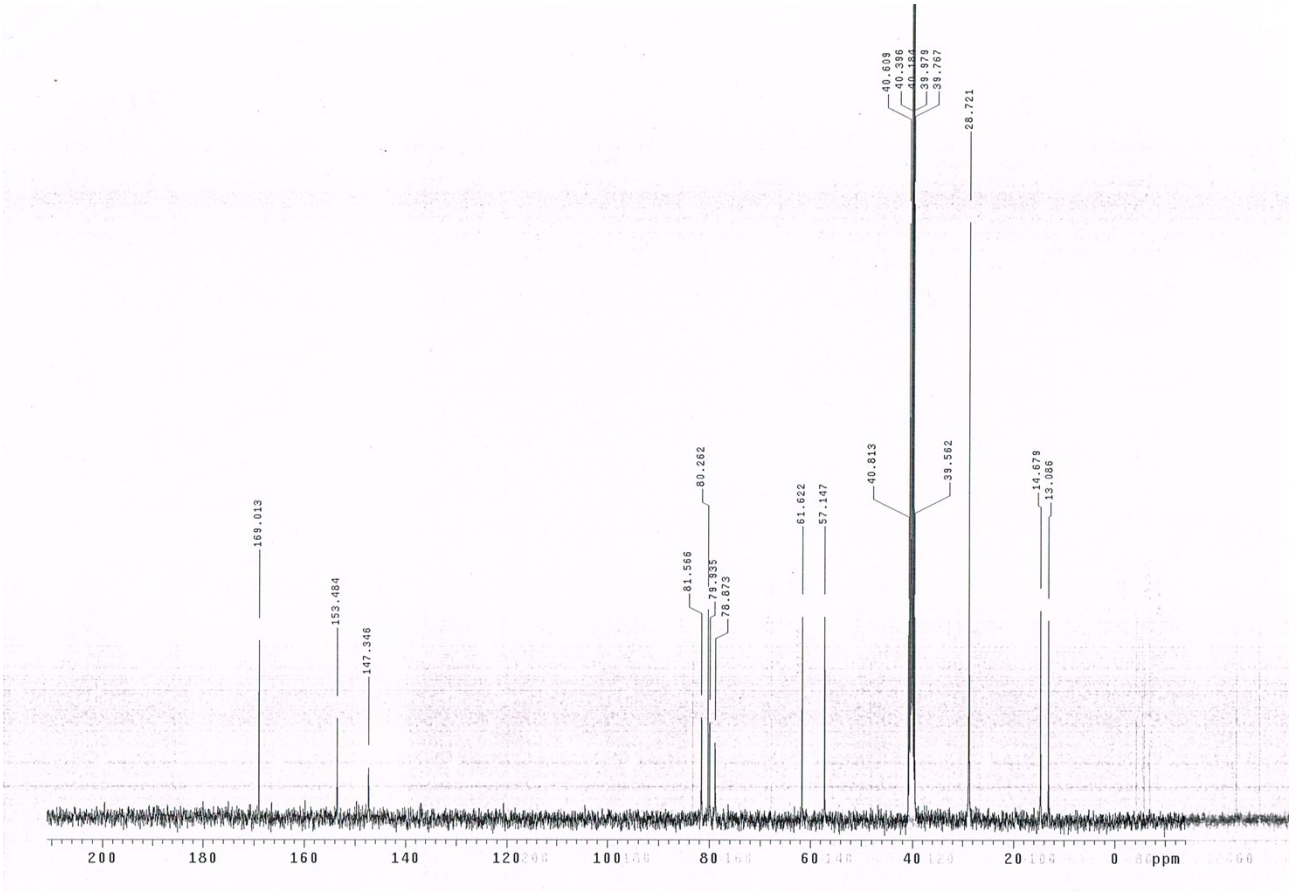
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39.979
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120
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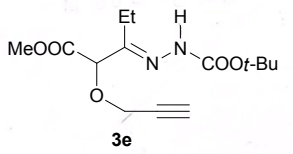
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N
COO*t*-Bu
O

3e

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3.297
2.490
2.481
2.486
2.476
2.472
2.326
2.308
2.231
1.428
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0.889
0.870
10
9
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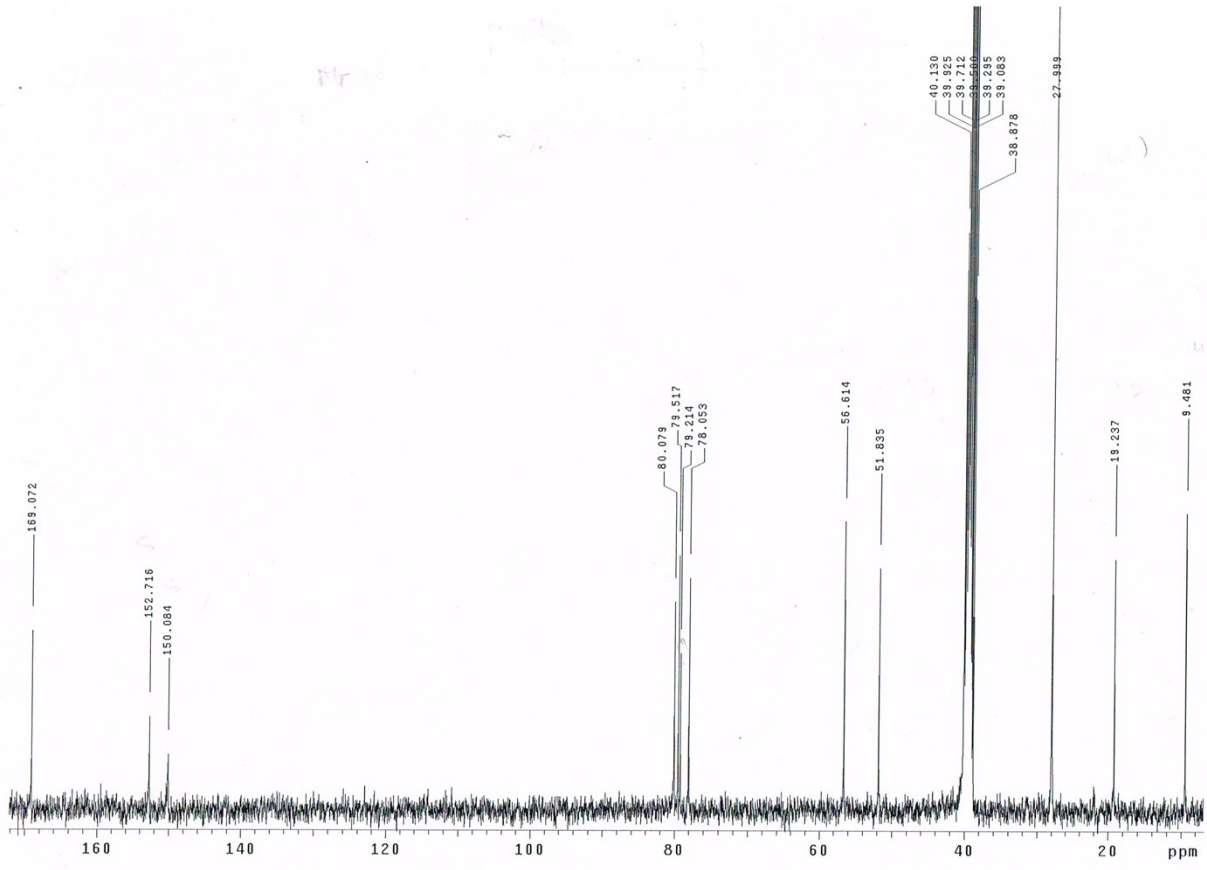
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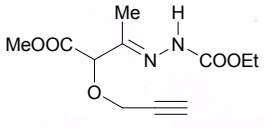
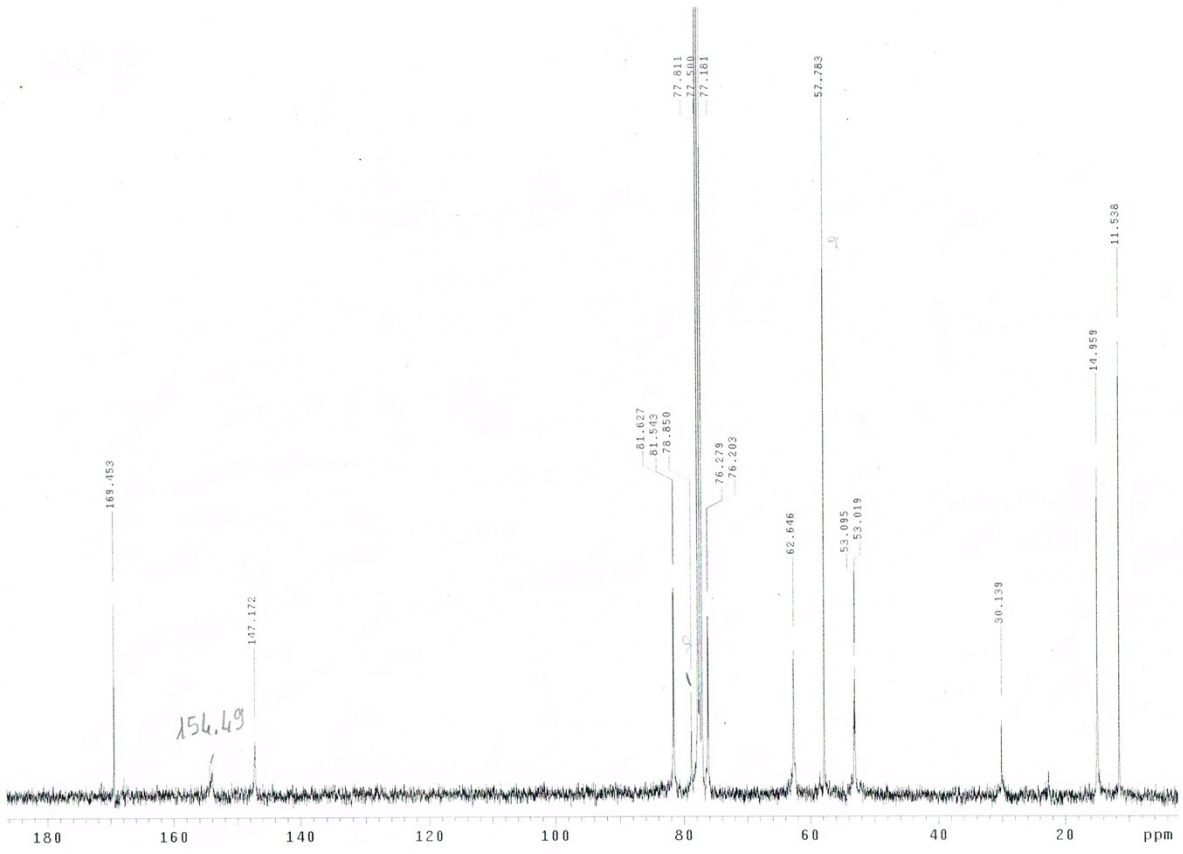
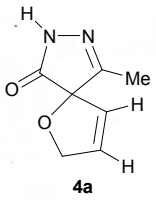
160
140
120
100
80
60
40
20
ppm


Me
H
MeOOC
N
N
COOEt
O

3f

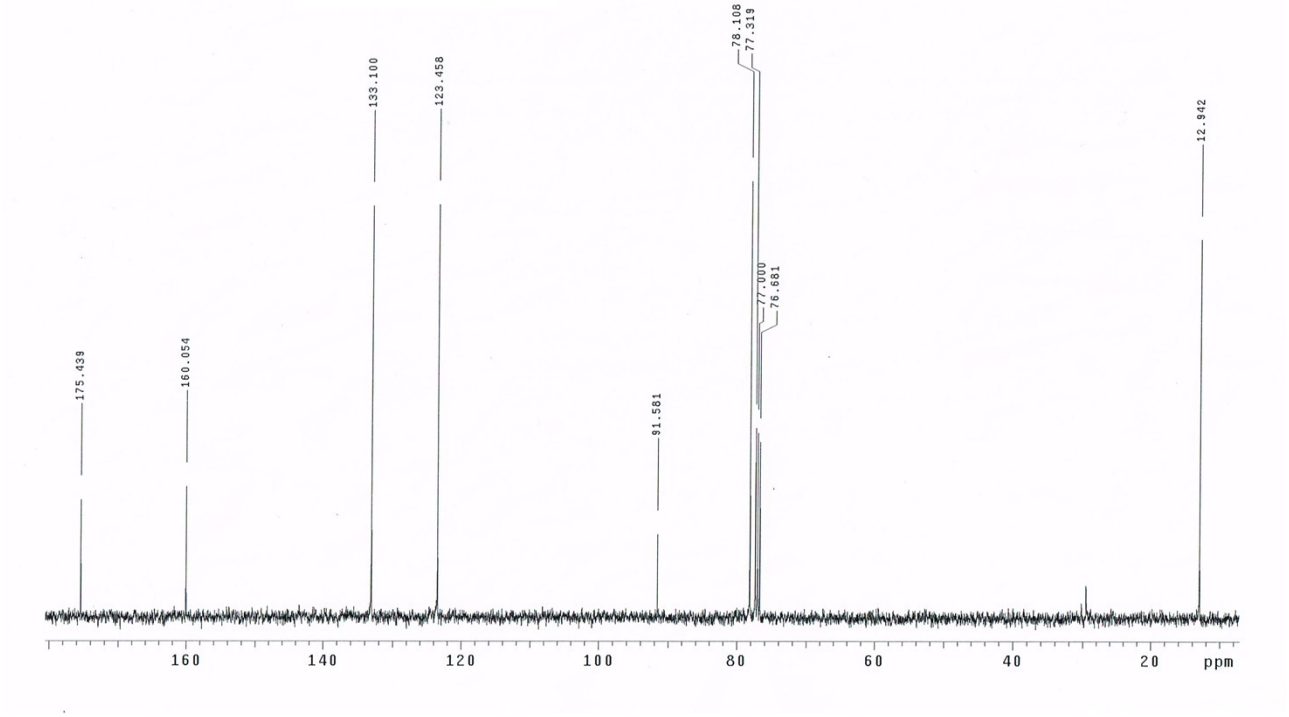
4.239
4.205
4.199
3.803
3.801
3.755
1.837
4.264
4.258
4.245
4.819
4.303
4.297
4.279
2.465
1.303
2.472
2.460
2.448
2.118
1.320
1.265
1.406
1.232
7.830
7.256
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.89
0.97
4.55
3.57
3.00
4.70

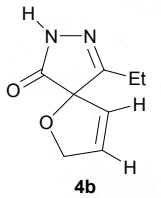

77.611
77.300
77.161
57.783
81.627
81.543
78.850
76.279
76.203
62.646
53.095
53.019
14.959
11.538
30.139
169.453
147.172
154.49
180
160
140
120
100
80
60
40
20
ppm


H
N
N
Me
O
H
O
H

4a

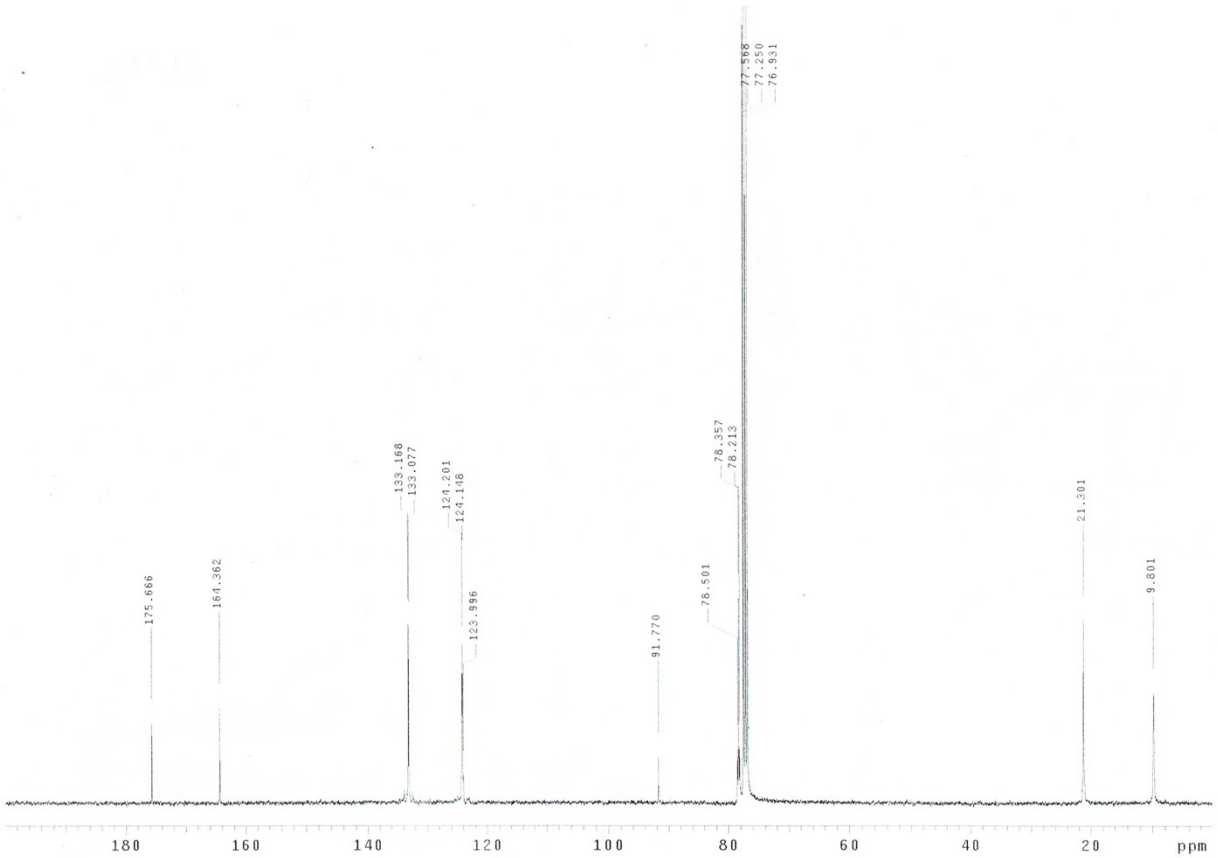
8.752
7.260
6.421
6.417
6.413
6.405
6.402
6.398
5.568
5.562
5.558
5.556
5.553
5.549
5.547
5.543
5.540
5.088
5.084
5.082
5.078
5.055
5.051
5.049
4.927
4.922
4.321
4.916
4.893
4.889
4.887
4.883
1.954
1.946
11
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.01
1.00
2.30
3.81

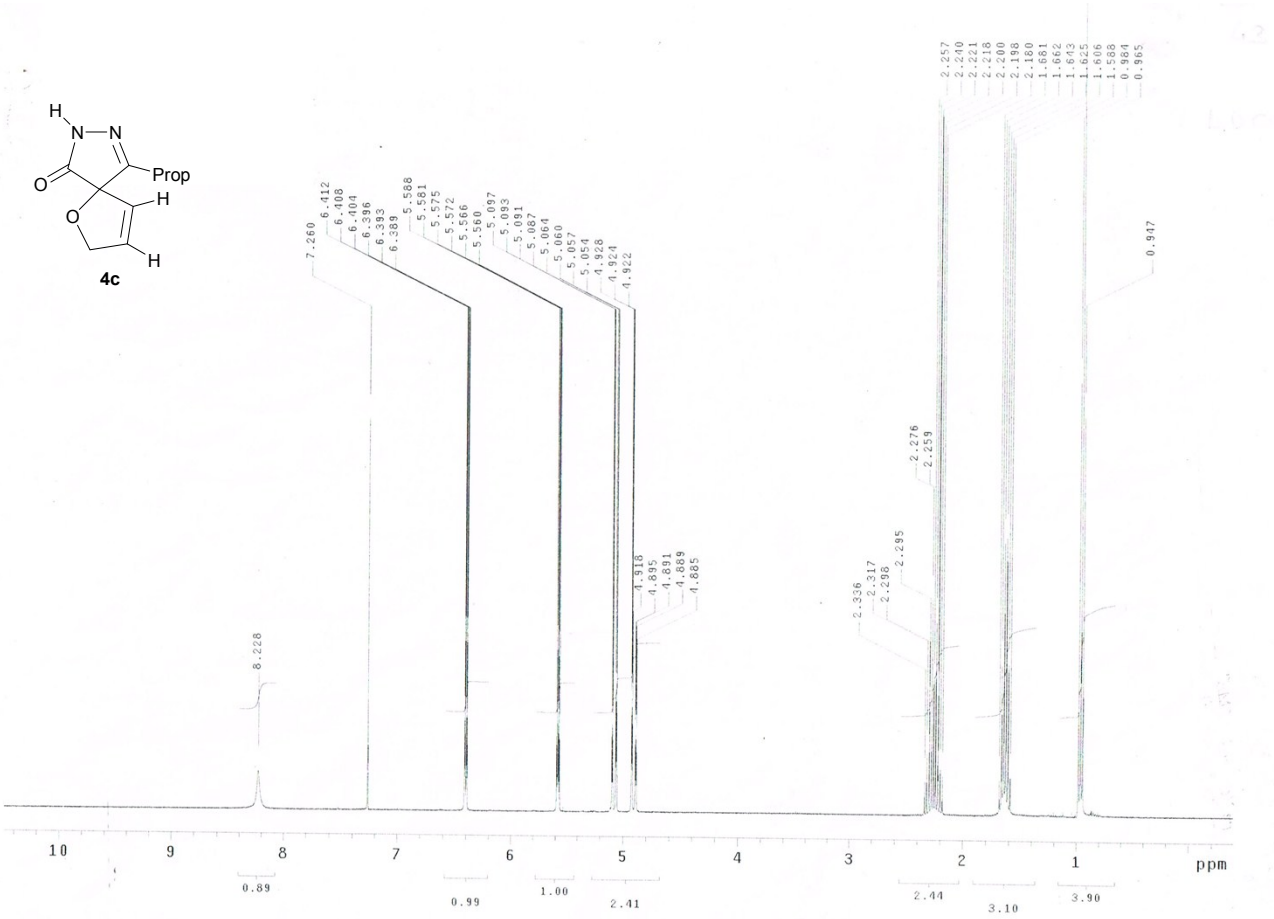

175.439
160.054
133.100
123.458
91.581
78.108
77.319
77.000
76.681
12.942
160
140
120
100
80
60
40
20
ppm

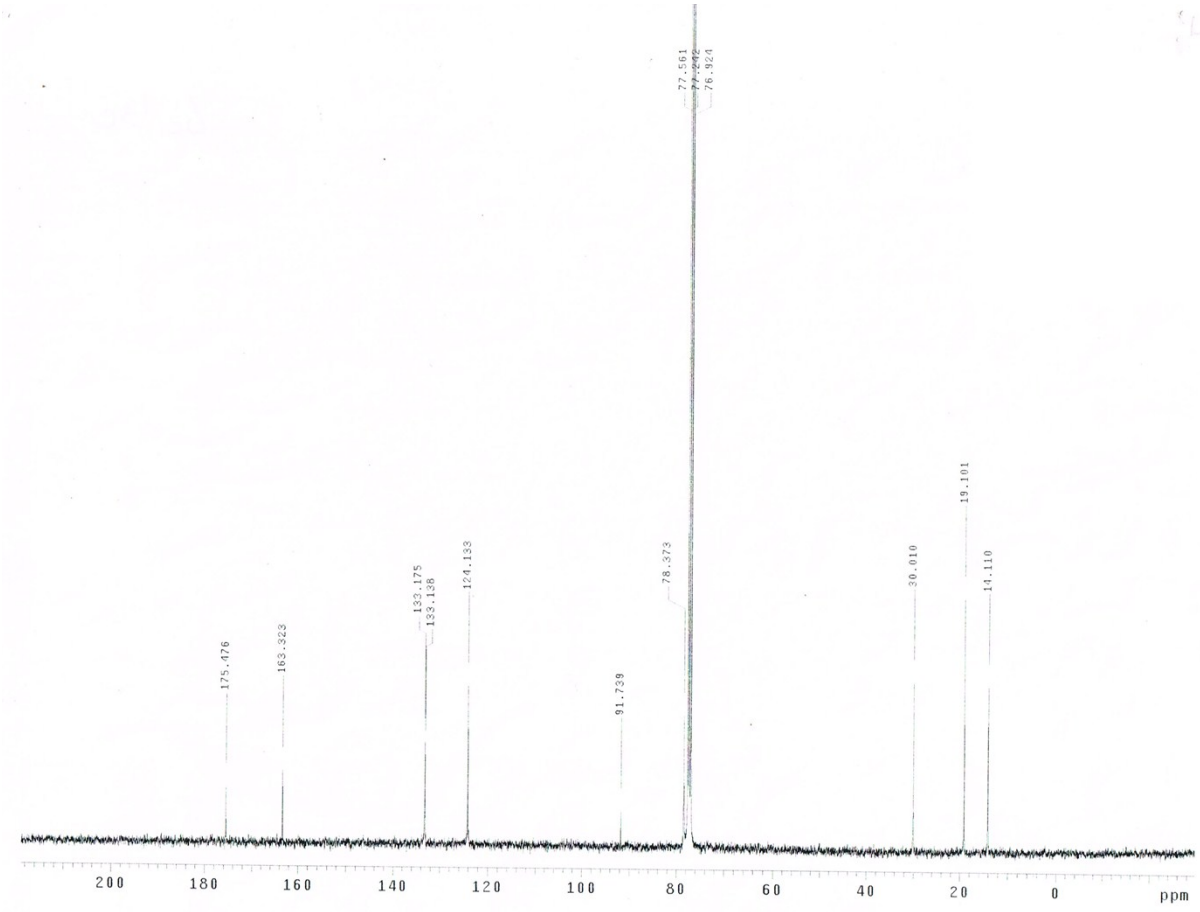

H
N
N
Et
O
H
O
H

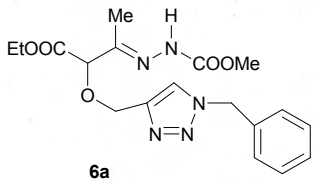
4b

1.161
1.180
1.143
7.260
6.403
6.400
6.388
6.384
5.580
5.574
5.565
5.067
5.058
5.054
5.052
5.048
5.020
4.916
4.883
2.359
2.340
2.289
2.271
10
9
8
7
6
5
4
3
2
1
ppm
0.66
0.77
0.75
1.78
1.84
3.00


77.568
77.250
76.931
133.168
133.077
124.201
124.148
78.357
78.213
175.668
164.362
123.996
91.770
78.501
21.301
9.801
180
160
140
120
100
80
60
40
20
ppm

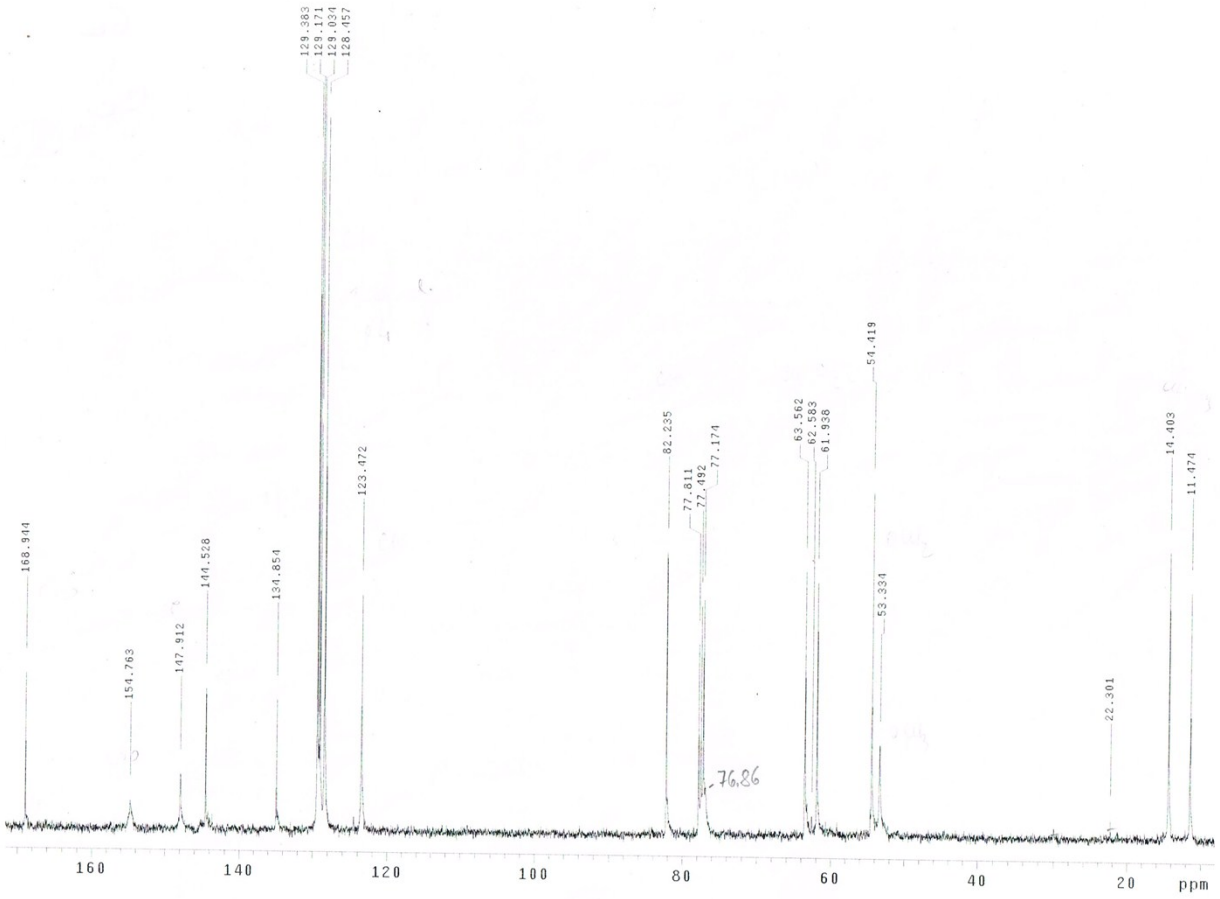

H
N
N
O
Prop
H
O
H
4c
7.260
6.412
6.408
6.404
6.396
6.393
6.389
5.588
5.581
5.575
5.572
5.566
5.560
5.097
5.093
5.091
5.087
5.064
5.060
5.057
5.054
4.928
4.924
4.922
4.918
4.895
4.891
4.889
4.885
8.228
2.336
2.317
2.298
2.295
2.276
2.259
2.257
2.240
2.221
2.218
2.200
2.198
2.180
1.661
1.662
1.643
1.625
1.606
1.588
0.984
0.965
0.947
10
9
8
7
6
5
4
3
2
1
ppm
0.89
0.99
1.00
2.41
2.44
3.10
3.90

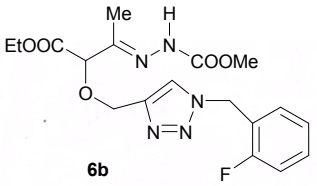

77.561
77.242
76.924
175.476
163.323
133.175
133.138
124.133
91.739
78.373
30.010
19.101
14.110
200
180
160
140
120
100
80
60
40
20
0
ppm


Me
H
EtOOC
N
N
COOMe
O
N
N=N

6a

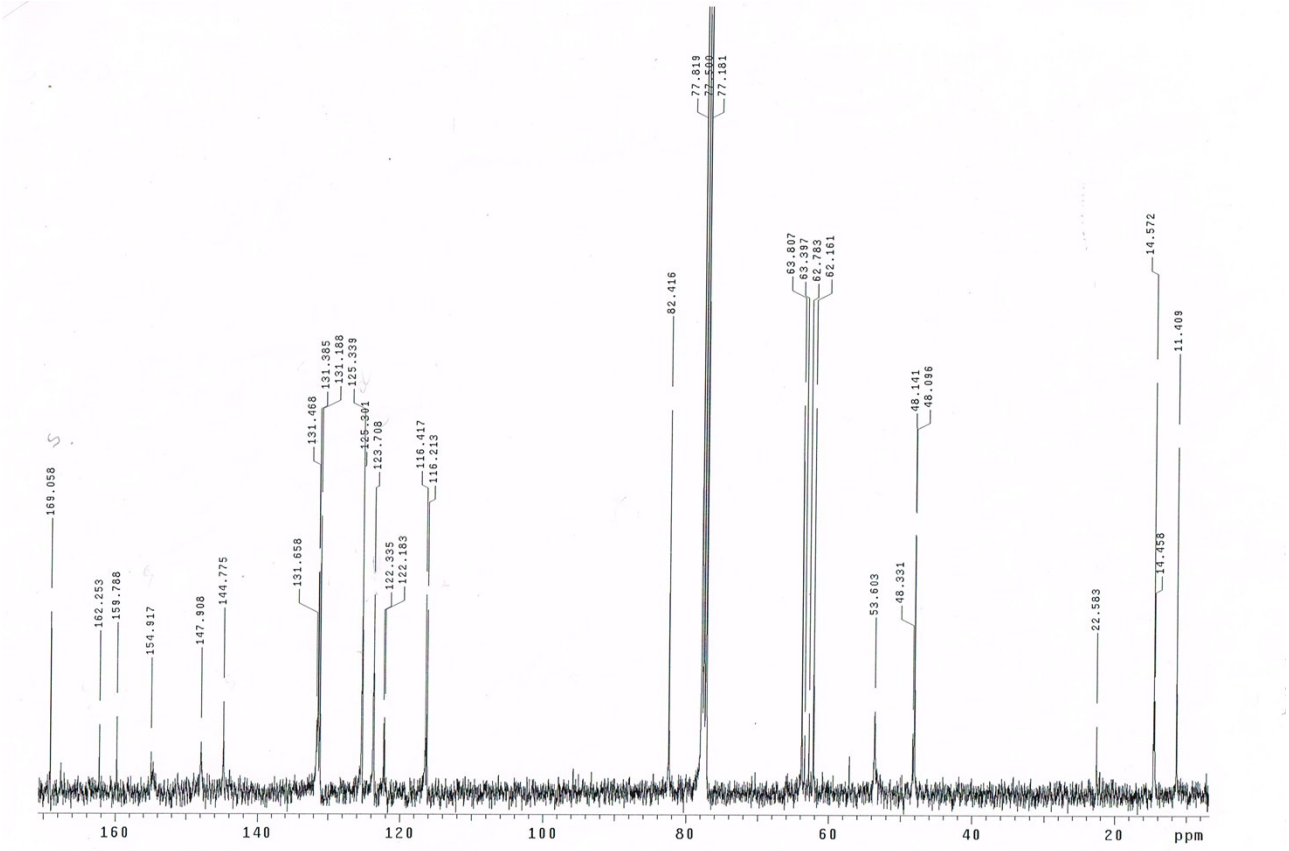
7.508
7.320
7.306
7.289
7.224
7.218
7.205
5.448
5.443
5.477
4.663
4.633
4.615
4.584
4.156
4.138
4.121
4.103
3.740
2.009
1.977
1.760
1.214
1.210
1.193
1.175
1.158
8.27
8
7
6
5
4
3
2
ppm
1.35
0.99
2.94
2.07
2.17
3.05
2.46
3.27
3.00
3.83

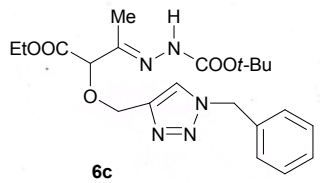

168.944
154.763
147.912
144.528
134.854
129.383
129.171
129.034
128.457
123.472
82.235
77.811
77.492
77.174
63.562
62.583
61.938
54.419
53.334
22.301
14.403
11.474
76.86
160
140
120
100
80
60
40
20
ppm


Me
H
EtOOC
N
N
COOMe
O
N
N=N
F

6b

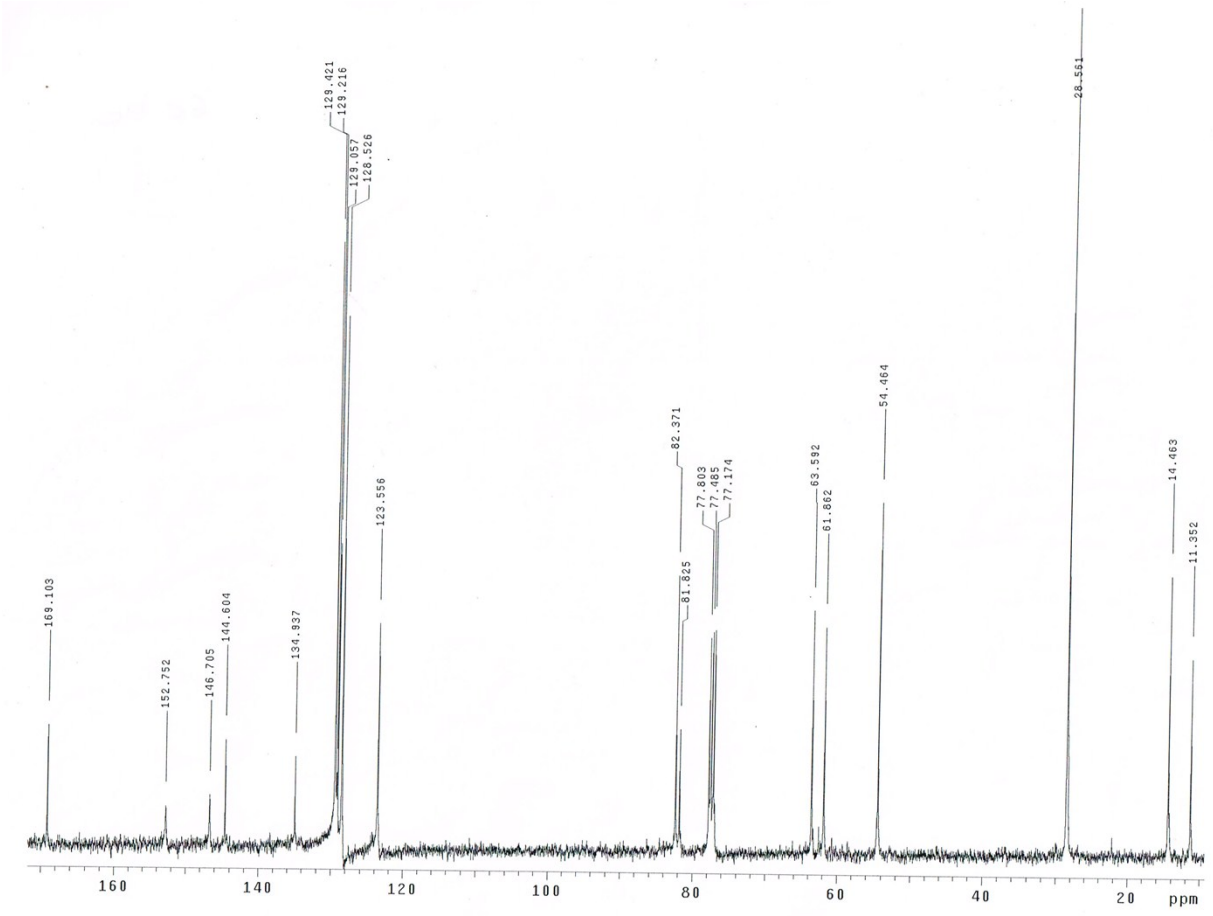
7.623
7.281
7.266
7.262
7.259
7.161
7.158
7.142
7.140
7.109
5.565
5.589
4.700
4.690
4.673
4.223
4.206
4.188
3.827
2.074
1.816
1.258
1.255
1.244
1.241
1.237
1.223
7.88
4.73
4.64
4.17
4.82
7.04
7.41
7.23
8
7
6
5
4
3
2
ppm
0.80
1.00
2.60
2.20
2.50
3.41
2.22
3.45
3.00
3.63

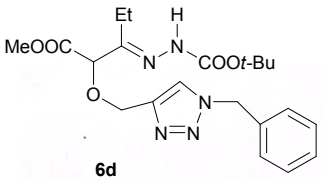

169.058
162.253
159.788
154.917
147.908
144.775
131.658
131.468
131.385
131.188
125.339
125.301
123.708
116.417
116.213
122.335
122.183
82.416
77.619
77.500
77.181
63.807
63.397
62.783
62.161
53.603
48.331
48.141
48.096
22.583
14.572
14.458
11.409
160
140
120
100
80
60
40
20
ppm


Me
H
EtOOC
N
N
COOt-Bu
O
N
N=N

6c

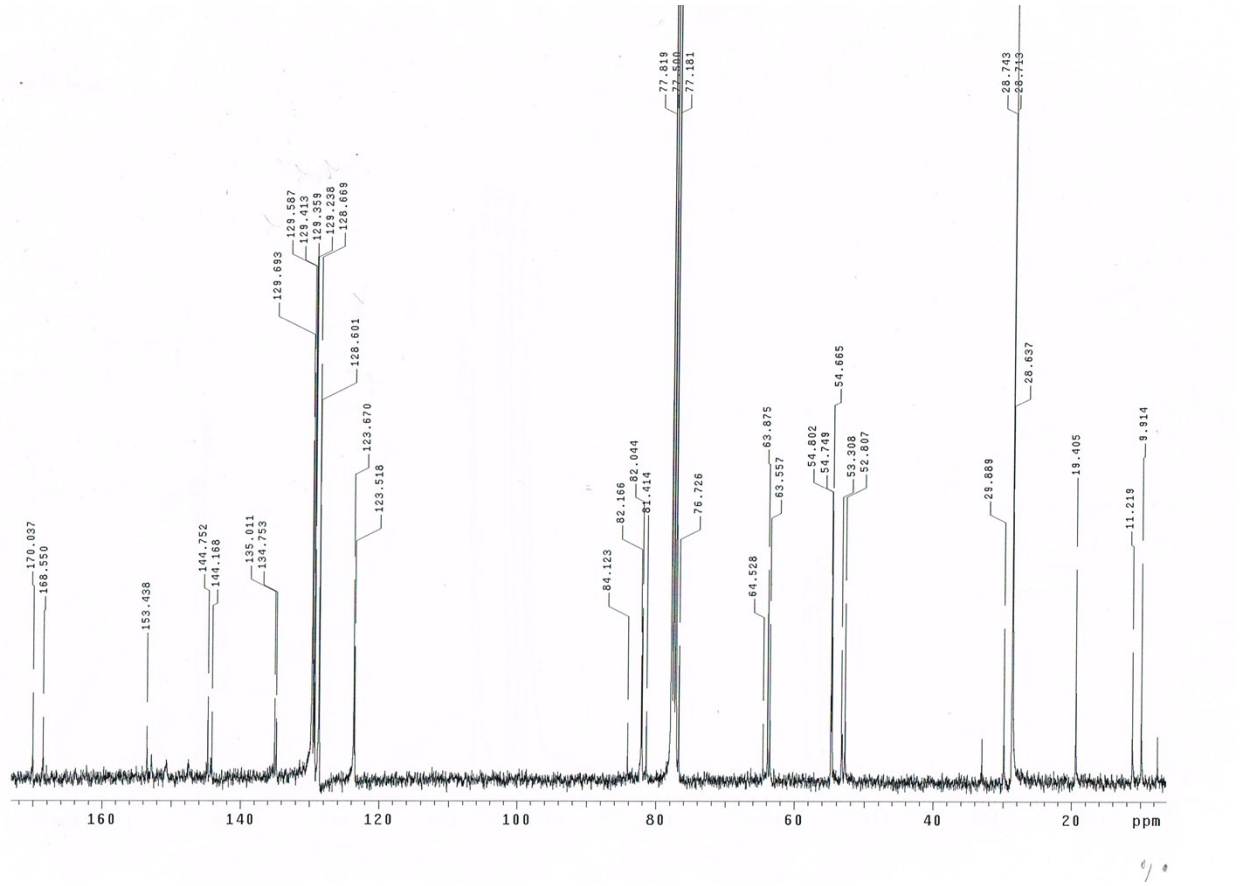
7.769
7.536
7.321
7.305
7.258
7.247
7.242
7.228
5.465
5.458
4.640
4.629
4.149
4.131
2.009
1.992
1.761
1.459
1.439
1.218
1.208
1.192
1.174
ppm
0.90
0.89
3.14
2.48
2.17
3.12
2.46
3.00
10.82
3.98

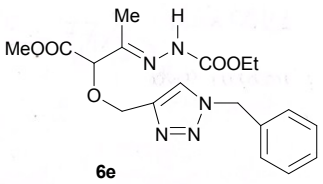

169.103
152.752
146.705
144.604
134.937
129.421
129.216
129.057
128.526
123.556
82.371
81.825
77.803
77.485
77.174
63.592
61.862
54.464
28.561
14.463
11.352
ppm


Et
H
MeOOC
N
N
COOt-Bu
O
N
N=N

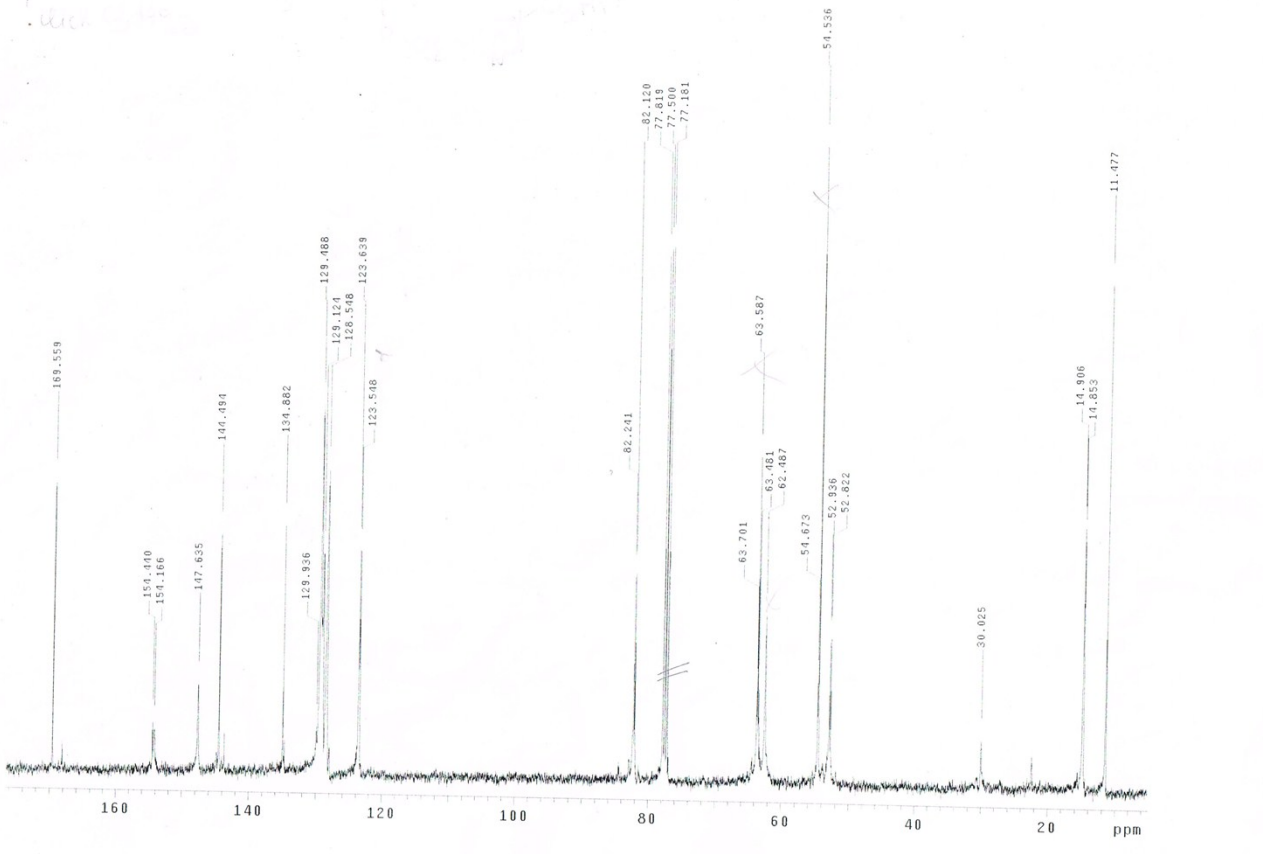
6d

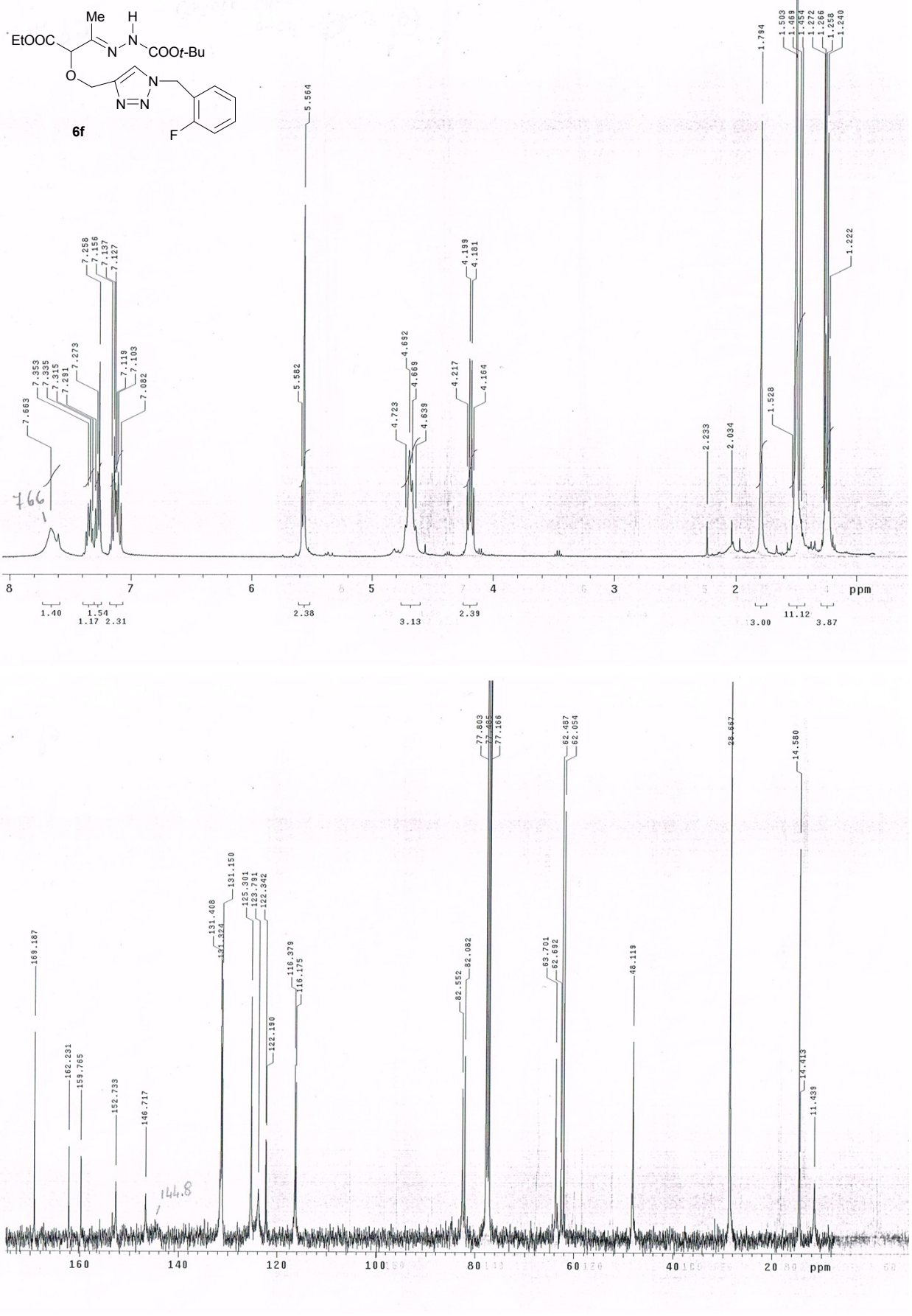
7.285
7.279
7.272
7.268
7.259
7.367
7.362
7.355
7.343
7.291
7.588
7.500
7.380
5.529
5.523
5.517
5.507
4.786
4.723
4.702
4.695
4.684
3.744
3.724
3.751
1.505
1.071
1.056
1.052
1.046
1.034
1.027
1.533
2.341
2.202
9.27
1.70
2.14
2.48
ppm
0.18
0.522.66
0.400.331.55
1.95
2.44
0.39
2.86
2.41
9.63
3.00

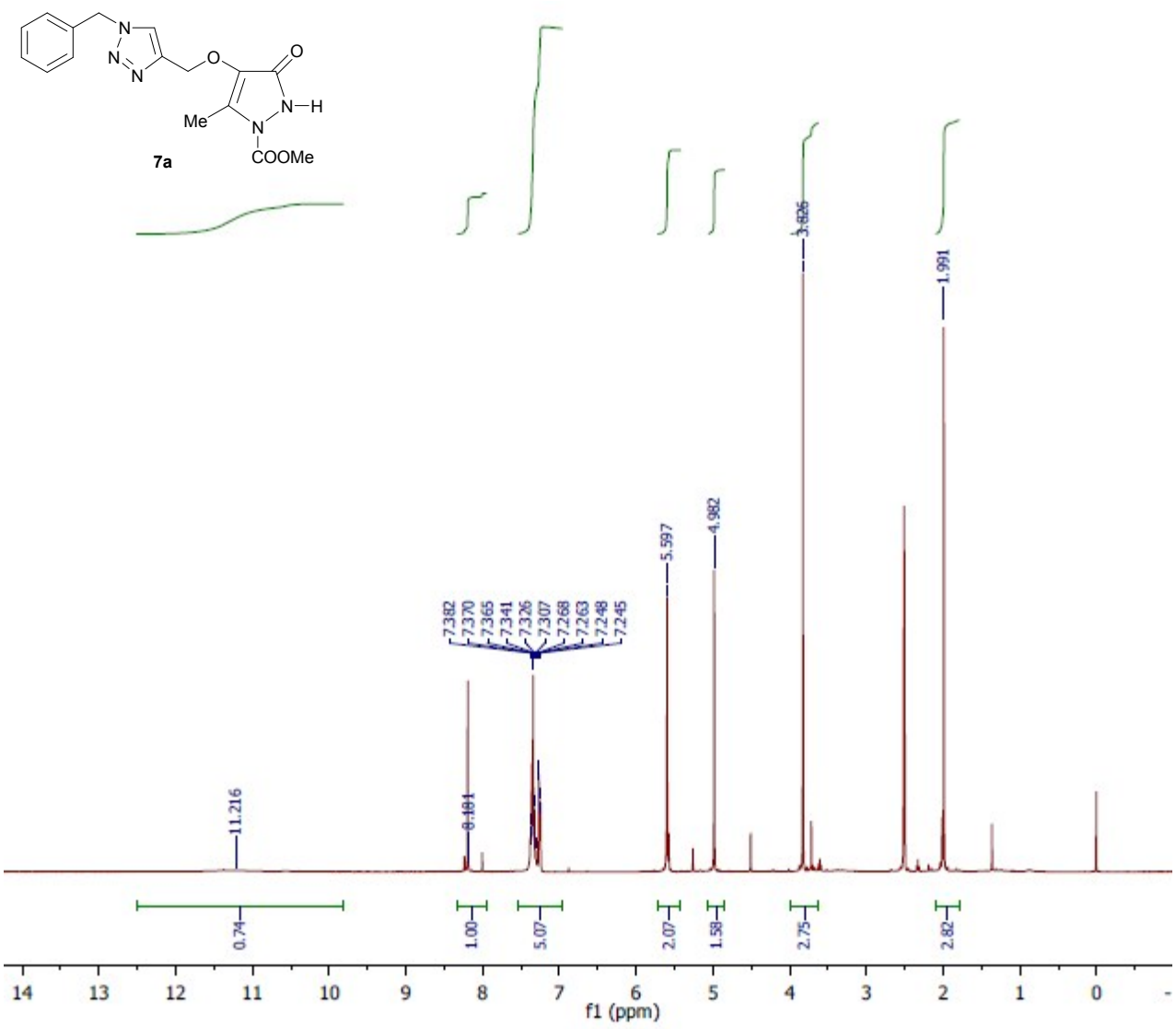

170.037
168.550
153.438
144.752
144.168
135.011
134.753
129.693
129.587
129.413
129.359
128.238
128.669
128.601
123.670
123.518
84.123
82.166
82.044
81.414
77.819
77.500
77.181
76.726
64.528
63.875
63.557
54.802
54.749
54.665
53.308
52.807
29.889
28.743
28.713
28.637
19.405
11.219
9.914
ppm

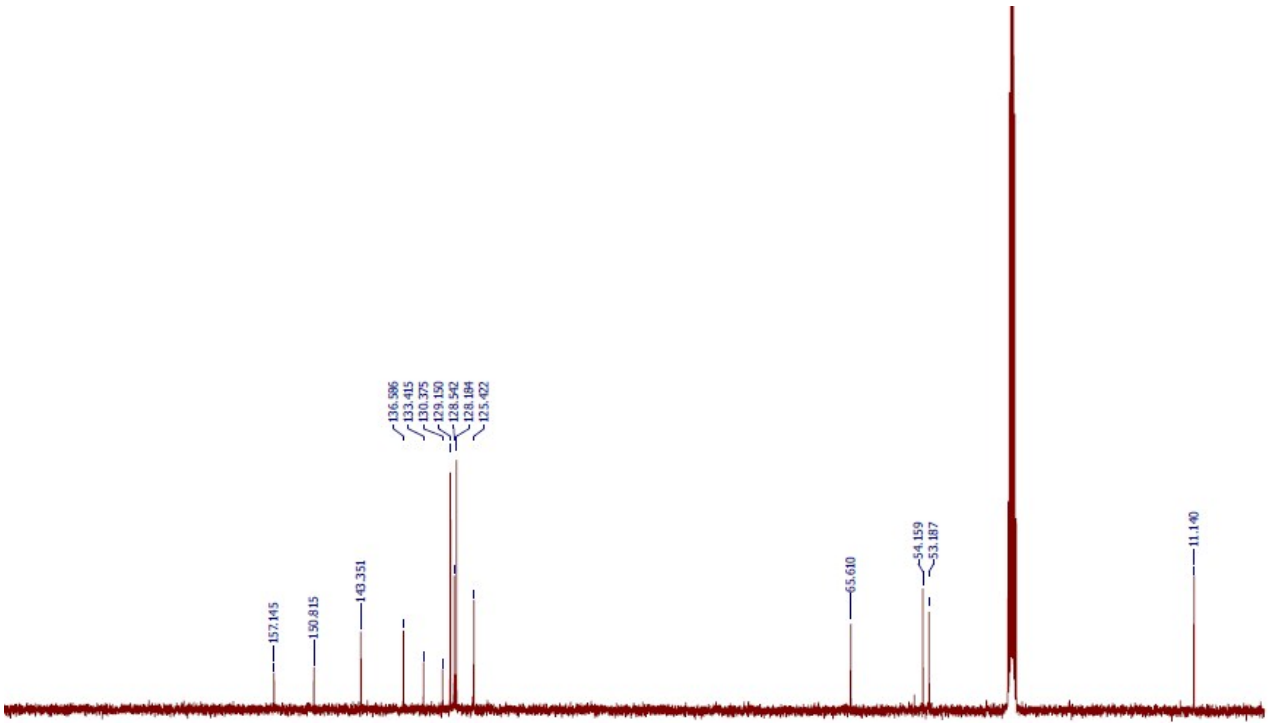


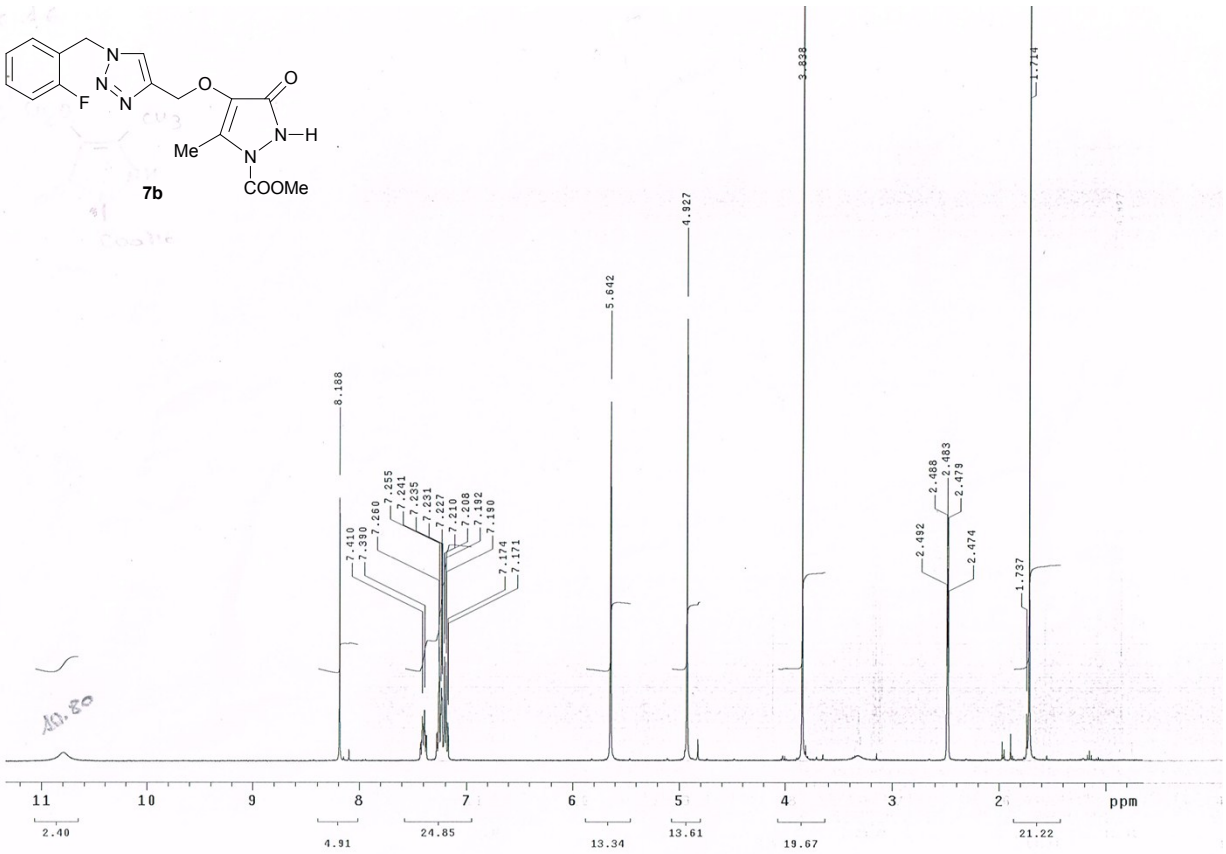
6e

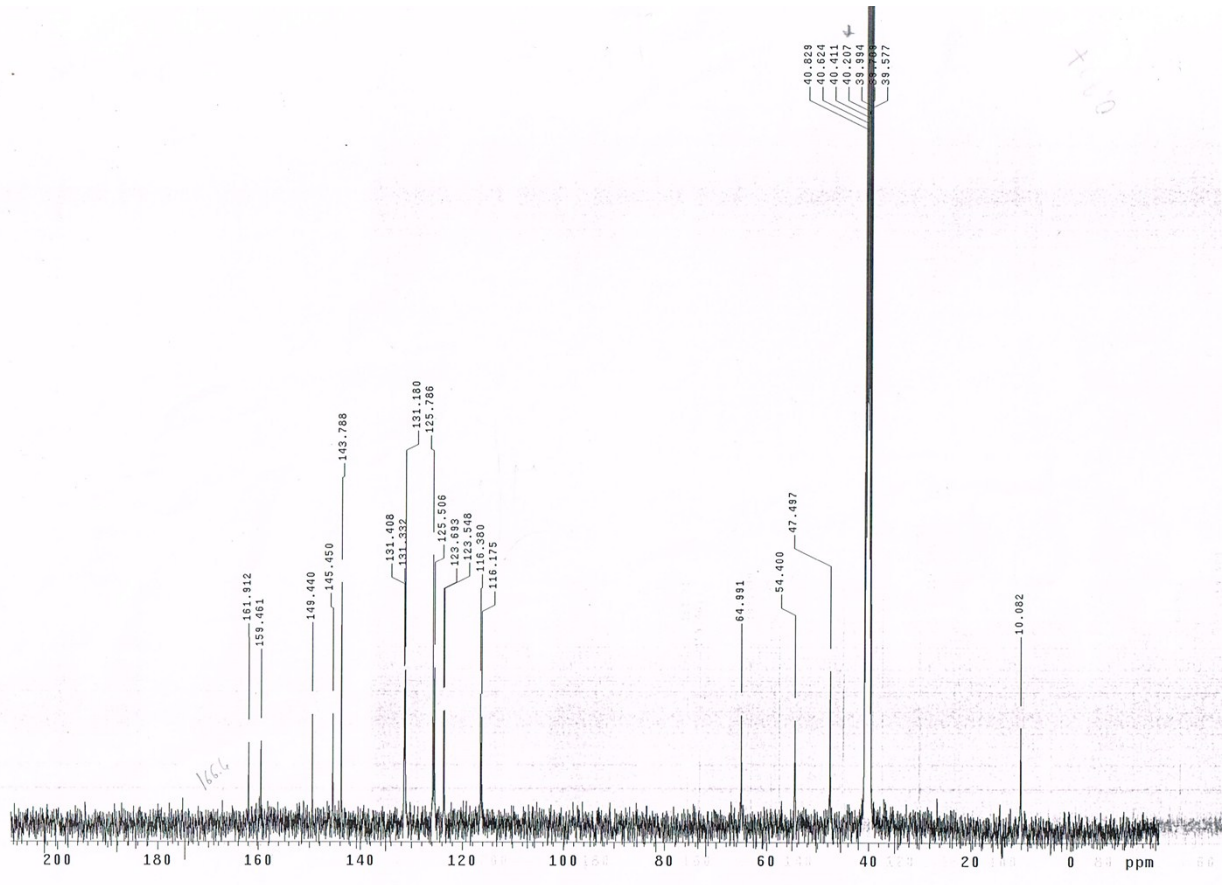



Me
H
EtOOC
N
N
COOt-Bu
O
N
N=N
F
6f
7.766
1.40
1.54
1.17
2.31
2.38
3.13
2.39
3.00
11.12
3.87
ppm
144.8

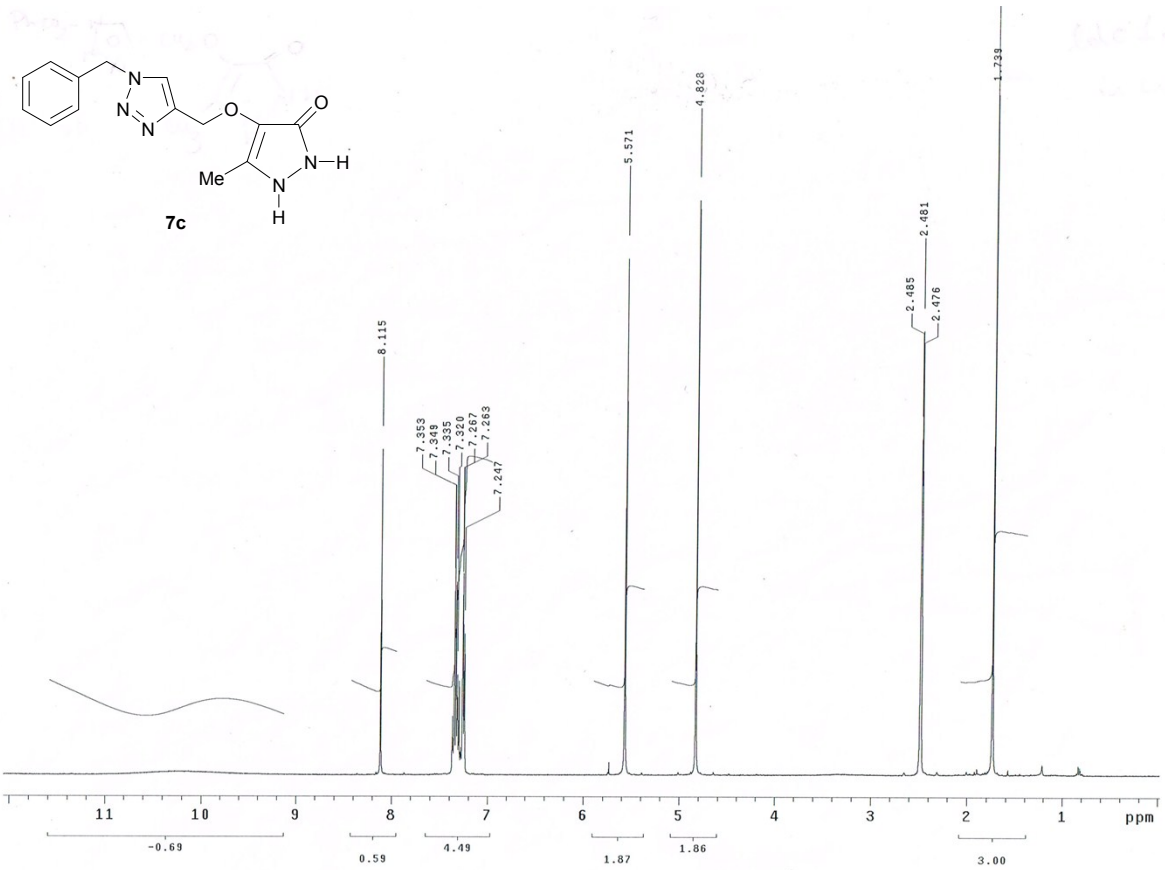

7a
Me
COOMe
11.216
8.181
7.382
7.370
7.365
7.341
7.326
7.307
7.268
7.263
7.248
7.245
5.597
4.982
3.826
1.991
0.74
1.00
5.07
2.07
1.58
2.75
2.82
f1 (ppm)


157.145
150.815
143.351
136.586
133.415
130.375
129.150
128.542
128.184
125.422
65.610
54.159
53.187
11.140

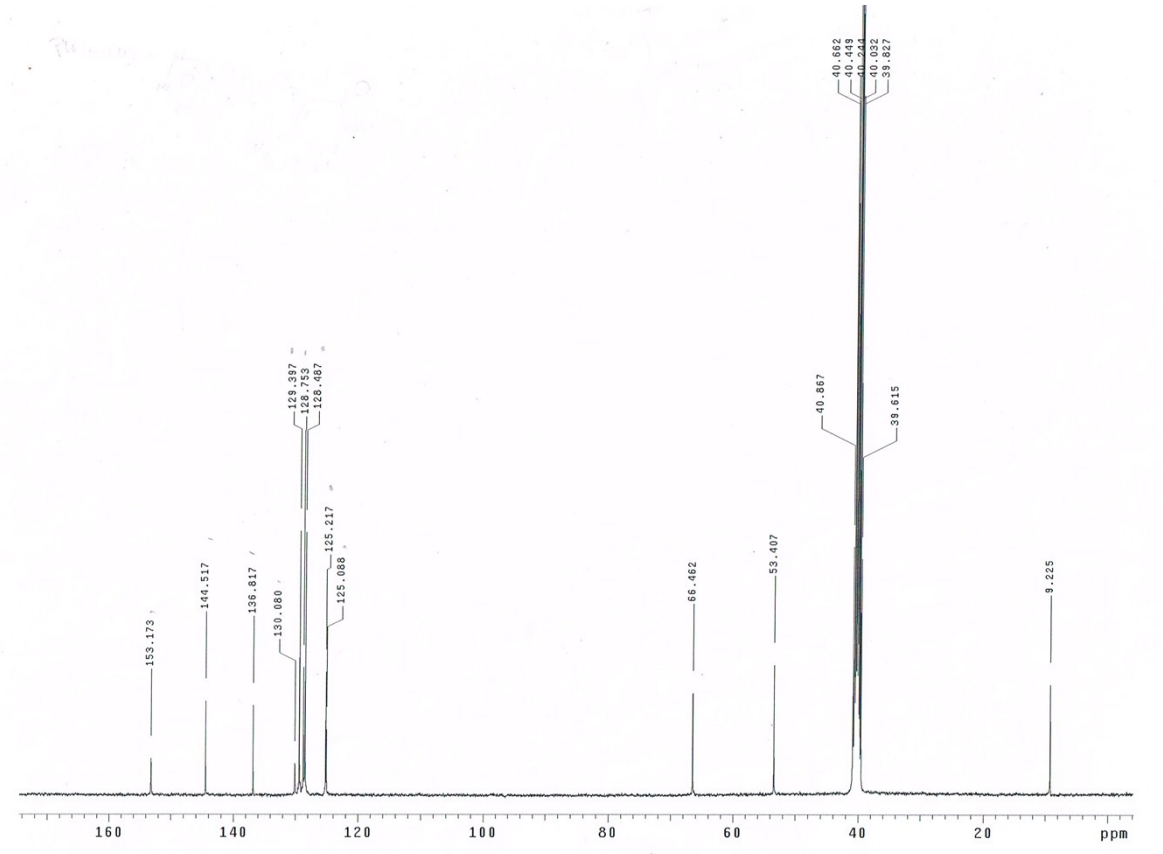

F
N
N
N
O
O
N
H
Me
N
COOMe
8.188
7.410
7.390
7.260
7.255
7.241
7.235
7.231
7.227
7.210
7.208
7.192
7.180
7.174
7.171
5.642
4.927
3.838
2.492
2.488
2.483
2.479
2.474
1.737
1.714
11
10
9
8
7
6
5
4
3
2
ppm
2.40
4.91
24.85
13.34
13.61
19.67
21.22

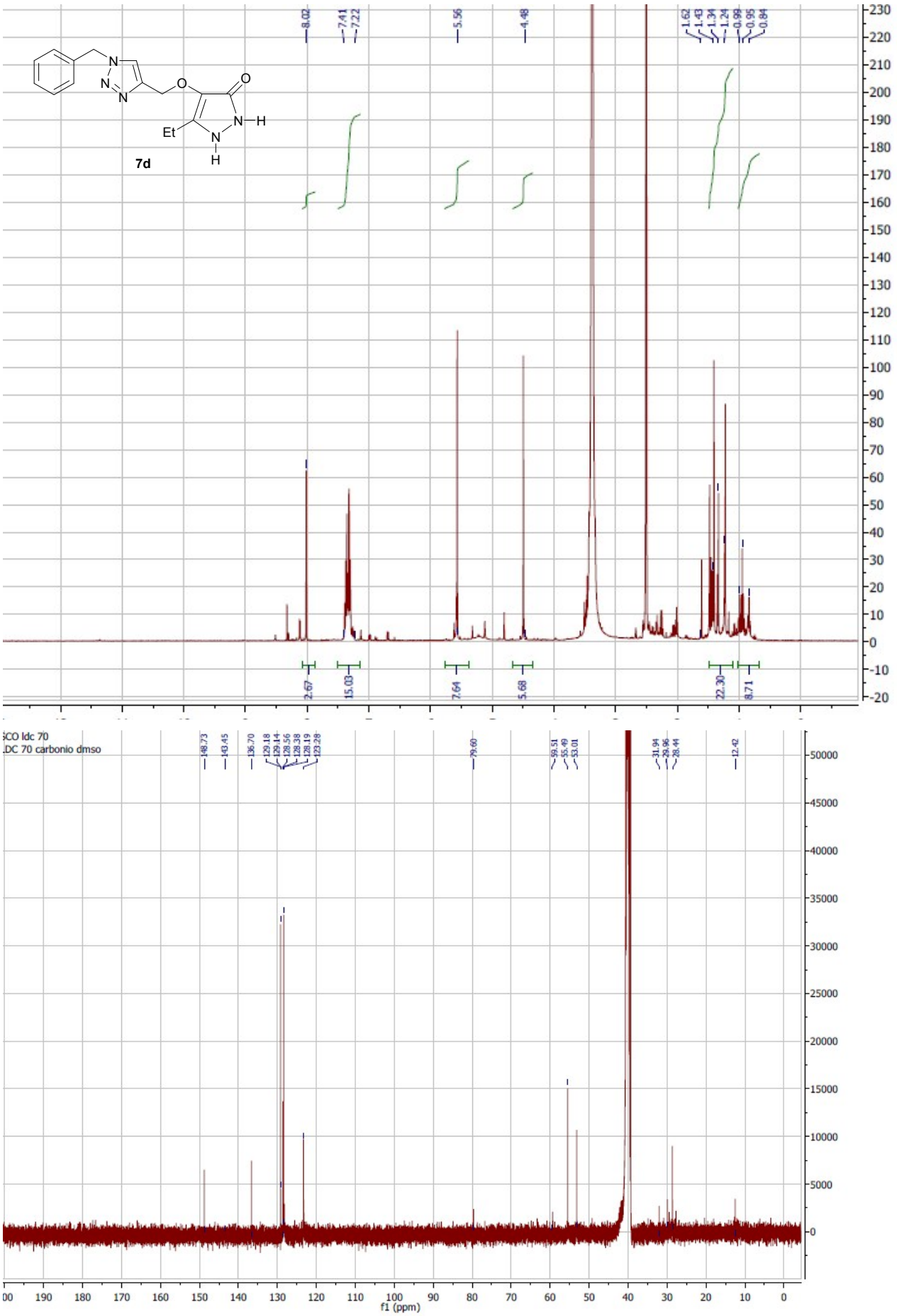

161.912
159.461
149.440
145.450
143.788
131.408
131.332
131.180
125.786
125.506
123.693
123.548
116.380
116.175
64.991
54.400
47.497
40.828
40.624
40.411
40.207
39.994
39.577
10.082
200
180
160
140
120
100
80
60
40
20
0
ppm

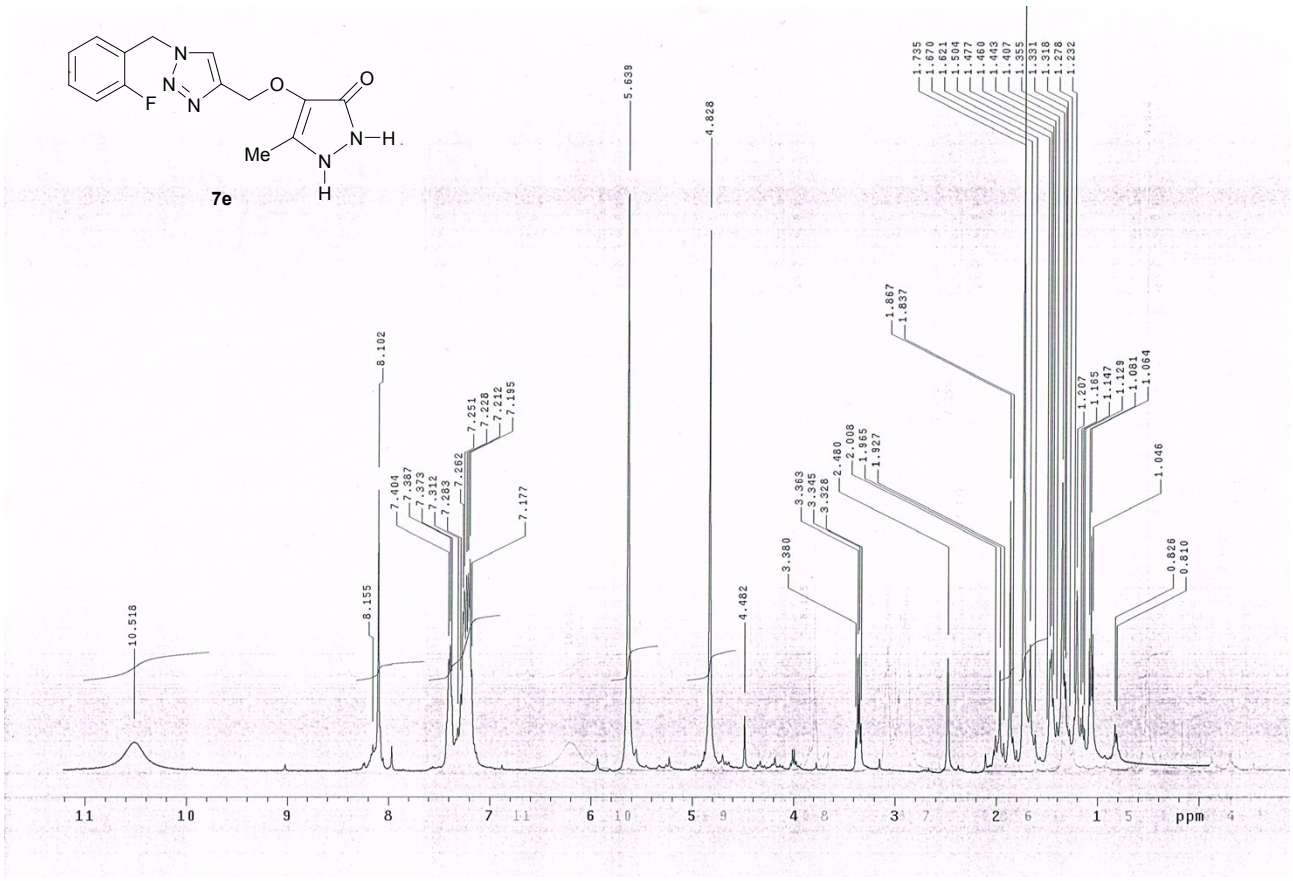
7b

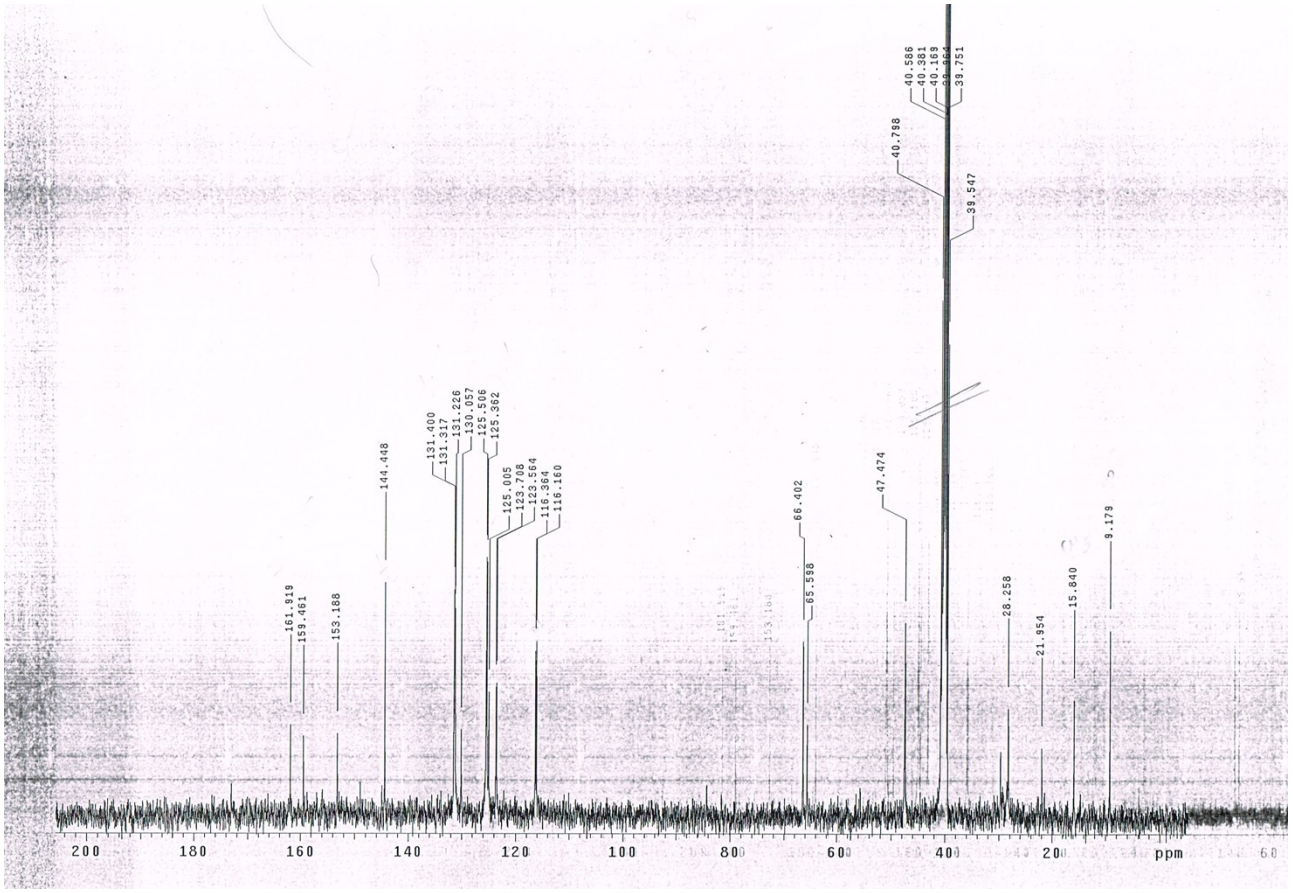

8.115
7.353
7.349
7.335
7.320
7.267
7.263
7.247
5.571
4.828
2.485
2.481
2.476
1.739
11
10
9
8
7
6
5
4
3
2
1
ppm
-0.69
0.59
4.49
1.87
1.86
3.00

7c


153.173
144.517
136.817
130.080
129.397
128.753
128.487
125.217
125.088
66.462
53.407
40.662
40.449
40.244
40.032
39.827
40.867
39.615
8.225
160
140
120
100
80
60
40
20
ppm


7d
8.02
7.41
7.22
5.56
4.48
1.62
1.43
1.34
1.24
0.99
0.95
0.84
2.67
15.03
7.64
5.68
22.30
8.71
148.73
143.45
136.70
129.18
129.14
128.56
128.38
128.19
123.28
79.60
59.51
55.49
53.01
31.94
29.96
28.44
12.42
f1 (ppm)


7e
10.518
8.155
8.102
7.404
7.387
7.373
7.312
7.283
7.262
7.251
7.228
7.212
7.195
7.177
5.639
4.828
4.482
3.380
3.363
3.345
3.328
2.480
2.008
1.965
1.927
1.867
1.837
1.735
1.670
1.621
1.504
1.477
1.460
1.443
1.407
1.355
1.331
1.318
1.278
1.232
1.207
1.165
1.147
1.129
1.081
1.064
1.046
0.826
0.810
ppm


161.919
159.461
153.188
144.448
131.400
131.317
131.226
131.137
129.507
125.362
125.005
123.708
123.564
116.384
116.160
66.402
65.588
47.474
40.788
40.586
40.381
40.169
39.751
39.547
28.258
21.954
15.840
9.179
ppm

4. References

(1) (a) O. A. Attanasi, P. Filippone, A. Mei, S. Santeusanio, *Synthesis* 1984, 671. (b) O. A. Attanasi, P. Filippone, A. Mei, S. Santeusanio, *Synthesis* 1984, 873. (c) L. Preti, O. A. Attanasi, E. Caselli, G. Favi, C. Ori, P. Davoli, F. Felluga, F. Prati, *Eur. J. Org. Chem.* 2010, 4312.