Copper(II)/Copper(I)-catalyzed Aza-Michael addition/Click Reaction of in Situ Generated α-Azidohydrazones: Synthesis of Novel Pyrazolone-Triazole Framework

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SUPPORTING INFORMATION

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Experimental Section

1. General Remarks.

All reactions requiring anhydrous conditions were carried out using oven-dried glassware. All the commercially available reagents and solvents were used without further purification. 1,2-Diaza-1,3-dienes (DDs) **1a–g** were synthesized as a mixture of *E/Z* isomers as previously reported[1,2].

Chromatographic purification of compounds was carried out on silica gel (60–200 μm). TLC analysis was performed on pre-loaded (0.25 mm) glass supported silica gel plates (Kieselgel 60); compounds were visualized by exposure to UV light and by dipping the plates in 1% $Ce(SO_4)\cdot 4H_2O$, 2.5% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 10% sulphuric acid followed by heating on a hot plate. All ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100.56 MHz, respectively. Proton and carbon spectra were referenced internally to solvent signals, using values of δ = 2.49 ppm for proton (middle peak) and δ = 39.50 ppm for carbon (middle peak) in DMSO-d_6 and δ = 7.26 ppm for proton and δ = 77.00 ppm for carbon (middle peak) in $CDCl_3$. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet q = quartet, m = multiplet and br = broad signal. All coupling constants (*J*) are given in Hz. FT-IR spectra were obtained as Nujol mulls. Mass spectra were recorded in the EI mode (70eV). Melting points were determined in open capillary tubes and are uncorrected.

2. Experimental procedures and spectral data.

General procedure for the synthesis of α-triazolehydrazones 3a–n (and 3a'–d', 3h'–n'). To a solution of the DD **1a–g** as a mixture of E/Z isomers[1,2] (1.0 mmol) in CH_2Cl_2 (5 mL), the $TMSN_3$ (1.1 mmol) and $Cu(OAc)_2\cdot H_2O$ (0.2 mmol) were added. The reaction was allowed under magnetic stirring at room temperature for 15 min, until the disappearance of the DD (monitored by TLC). Then, the alkyne **2a–h** (1 mmol for **1a–d** or 0.5 mmol for **1e–g**), sodium ascorbate (0.4 mmol) and H_2O (5 drops) were added. The reaction mixture was allowed under magnetic stirring at room temperature for 0.6**–**5 h, until the disappearance of the α-azidohydrazone intermediate (monitored by TLC). The crude was washed with H_2O (3x10ml) and dried over anhydrous Na_2SO_4. The organic phase was then filtered and concentrated under reduced pressure. The products **3a–n** (and **3a'–d', h'–n'**) were purified by column chromatography on silica gel (elution mixture: ethyl acetate/cyclohexane). During the course of the reactions, the following work-up, and the long standing, compounds **3a'–d', h'–n'** give rise to a partial (or total) transformation to the relevants **3a–d**.

Attention: The main concern about this one-pot procedure may appear a serious safety issue. In fact it is well documented in the literature that ionic azides react with dichloromethane to form explosive azido-chloromethane and/or diazidomethane. See: (a) Conrow, R. E.; Dean, W. D. *Org. Process Res. Dev.* **2008**, *12*, 1285–1286. (b) Hassner, A.; Stern, M.; Gottlieb, H. E. *J. Org. Chem.* **1990**, *55*, 2304–2306. Luckily, under our reaction conditions (short reaction times, stoichiometric amount of $TMSN_3$) the possible competiting nucleophilic substitution on CH_2Cl_2 is effectively suppressed since the Michael addition is the favourite and exclusive pathway.

Caution: organic azides are potentially explosive compounds (when dry) and should be handled with great care. During our studies we used $TMSN_3$ and we encountered no problem.

***tert*-Butyl 3-[(aminocarbonyl)hydrazono]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (3a):**

α-Triazolehydrazone **3a** was isolated by column chromatography (ethyl acetate) in 56% yield as a mixture of desilylated (**a**) and silylated (**a'**) compounds in 53:47 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **a**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.43 (s, 9H), 1.91 (s, 3H), 6.25 (brs, 2H), 6.26 (s, 1H), 7.30–7.34 (m, 1H), 7.39–7.45 (m, 2H), 7.89–7.92 (m, 2H), 8.69 (s, 1H), 9.59 (brs, 1H); minor component **a'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.14 (s, 9H), 1.44 (s, 9H), 1.90 (s, 3H), 5.72 (brs, 1H), 6.33 (s, 1H), 7.30–7.34 (m, 1H), 7.39–7.45 (m, 2H), 7.89–7.92 (m, 2H), 8.66 (s, 1H), 9.81 (brs, 1H).

Ethyl 3-[(aminocarbonyl)hydrazono]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (3b):

α-Triazolehydrazone **3b** was isolated by column chromatography (ethyl acetate) in 53% yield as a mixture of desilylated (**b**) and silylated (**b'**) compounds in 49:51 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Minor component **b**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.21 (t, J = 7.2 Hz, 3H), 1.91 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.28 (brs, 2H), 6.42 (s, 1H), 7.31–7.35 (m, 1H), 7.42–7.45 (m, 2H), 7.88–7.90 (m, 2H), 8.72 (s, 1H), 9.62 (brs, 1H); major component **b'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.14 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H), 1.90 (s, 3H), 4.23 (q, J = 7.2 Hz, 2H), 5.72 (brs, 1H), 6.50 (s, 1H), 7.31–7.35 (m, 1H), 7.42–7.45 (m, 2H), 7.88–7.90 (m, 2H), 8.71 (s, 1H), 9.86 (brs, 1H).

3-[(Aminocarbonyl)hydrazono]-*N*,*N*-dimethyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanamide (3c):

α-Triazolehydrazone **3c** was isolated by column chromatography (ethyl acetate) in 41% yield as a mixture of desilylated (**c**) and silylated (**c'**) compounds in 50:50 ratio (determined by ^{1}H NMR).

Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Component **c**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.83 (s, 3H), 2.89 (s, 6H), 6.17 (brs, 2H), 6.65 (s, 1H), 7.30–7.33 (m, 1H), 7.40–7.44 (m, 2H), 7.89–7.92 (m, 2H), 8.55 (s, 1H), 9.62 (brs, 1H); component **c'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.12 (s, 9H), 1.82 (s, 3H), 2.96 (s, 3H), 2.97 (s, 3H), 6.74 (s, 1H), 7.29–7.33 (m, 1H), 7.40–7.44 (m, 2H), 7.89–7.92 (m, 2H), 8.55 (s, 1H), 9.86 (brs, 1H).

Methyl 3-[(aminocarbonyl)hydrazono]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)pentanoate (3d):

α-Triazolehydrazone **3d** was isolated by column chromatography (ethyl acetate) in 44% yield as a mixture of desilylated (**d**) and silylated (**d'**) compounds in 46:54 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Minor component **d**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.87 (t, J = 7.2 Hz, 3H), 2.17–2.30 (m, 1H), 2.45–2.55 (m, 1H), 3.75 (s, 3H), 6.22 (brs, 2H), 6.53 (s, 1H), 7.31–7.34 (m, 1H), 7.41–7.45 (m, 2H), 7.89–7.91 (m, 2H), 8.76 (s, 1H), 9.76 (brs, 1H); major component **d'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.15 (s, 9H), 0.87 (t, J = 7.2 Hz, 3H), 2.17–2.30 (m, 1H), 2.45–2.55 (m, 1H), 3.75 (s, 3H), 5.71 (brs, 1H), 6.59 (s, 1H), 7.31–7.34 (m, 1H), 7.41–7.45 (m, 2H), 7.89–7.91 (m, 2H), 8.73 (s, 1H), 10.03 (brs, 1H).

2-Methoxyethyl 3-[(anilinocarbonyl)hydrazono]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (3e):

α-Triazolehydrazone **3e** was isolated by column chromatography (ethyl acetate/cyclohexane 50:50) in 43% yield. White solid; mp: 151–153 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.00 (s, 3H), 3.19 (s, 3H), 3.56–3.58 (m, 2H), 4.29–4.45 (m, 2H), 6.61 (s, 1H), 6.96–7.00 (m, 1H), 7.22–7.26 (m, 2H), 7.32–7.36 (m, 1H), 7.43–7.47 (m, 4H), 7.90–7.92 (m, 2H), 8.48 (brs, 1H), 8.81 (s, 1H), 10.11 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.8 (q), 57.9 (q), 65.1 (t), 67.4 (d), 69.4 (t), 118.9 (d), 122.3 (d), 122.6 (d), 125.2 (d), 128.1 (d), 128.7 (d), 128.9 (d), 130.3 (s), 138.5 (s), 141.5 (s), 146.5 (s), 152.8 (s), 166.4 (s); IR (nujol): ν_{max} = 3356, 3205, 3130, 3101, 1765, 1707, 1545 cm^{-1}; MS *m/z* (%): 436 (M^+) (1), 213 (43), 185 (3), 156 (4), 129 (8), 119 (100); anal. calcd. for $C_{22}H_{24}N_6O_4$ (436.46): C 60.54, H 5.54, N 19.25; found: C 60.75, H 5.51, N 19.33.

Ethyl 3-[(anilinocarbonyl)hydrazono]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (3f):

α-Triazolehydrazone **3f** was isolated by column chromatography (ethyl acetate/cyclohexane 50:50) in 44% yield. White solid; mp: 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.36 (t, J = 7.2 Hz, 3H), 2.10 (s, 3H), 4.36 (q, J = 7.2 Hz, 2H), 6.23 (s, 1H), 7.02–7.06 (m, 1H), 7.21–7.26 (m, 2H), 7.34–7.36 (m, 3H), 7.41–7.45 (m, 2H), 7.87–7.89 (m, 2H), 7.95 (brs, 1H), 8.14 (s, 1H), 10.05 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1 (q), 14.5 (q), 62.9 (t), 67.9 (d), 119.0 (d), 120.1 (d), 123.6 (d), 125.8 (d), 128.4 (d), 128.9 (d), 129.0 (d), 130.0 (s), 137.4 (s), 141.6 (s), 148.1

(s), 153.7 (s), 165.8 (s); IR (nujol): ν_{max} = 3408, 3200, 3141, 3096, 1754, 1702, 1528 cm^{-1}; MS *m/z* (%): 406 (M^+) (3), 305 (4), 213 (37), 176 (16), 169 (9), 119 (100); anal. calcd. for $C_{21}H_{22}N_6O_3$ (406.44): C 62.06, H 5.46, N 20.68; found: C 62.21, H 5.41, N 20.59.

Methyl 3-({[(3-fluorophenyl)amino]carbonyl}hydrazono)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (3g):

α-Triazolehydrazone **3g** was isolated by column chromatography (ethyl acetate/cyclohexane 50:50) in 70% yield. White solid; mp: 214–216 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.01 (s, 3H), 3.81 (s, 3H), 6.59 (s, 1H), 6.78–6.83 (m, 1H), 7.17–7.19 (m, 1H), 7.23–7.36 (m, 2H), 7.43–7.51 (m, 3H), 7.89–7.91 (m, 2H), 8.75 (brs, 1H), 8.85 (s, 1H), 10.20 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.8 (q), 53.3 (q), 67.4 (d), 105.5 (d, $^2J_{CF}$ = 26.6 Hz), 108.9 (d, $^2J_{CF}$ = 20.4 Hz), 114.7 (d), 122.3 (d), 125.2 (d), 125.5 (d), 128.1 (d), 128.9 (s), 130.2 (d, $^3J_{CF}$ = 9.1 Hz), 140.5 (s, $^3J_{CF}$ = 10.6 Hz), 142.0 (d), 146.5 (s), 152.7 (s), 161.1 (s), 165.7 (s, $^1J_{CF}$ = 208 Hz); IR (nujol): ν_{max} = 3357, 3207, 3098, 1741, 1713, 1546 cm^{-1}; MS *m/z* (%): 410 (M^+) (8), 323 (20), 300 (9), 213 (57), 194 (34), 169 (21), 137 (100); anal. calcd. for $C_{20}H_{19}N_6O_3F$ (410.40): C 58.53, H 4.67, N 20.48; found: C 58.42, H 4.63, N 20.59.

***tert*-Butyl 3-[(aminocarbonyl)hydrazono]-2-(4-butyl-1*H*-1,2,3-triazol-1-yl)butanoate (3h):**

α-Triazolehydrazone **3h** was isolated by column chromatography (ethyl acetate) in 64% yield as a mixture of desilylated (**h**) and silylated (**h'**) compounds in 62:38 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **h**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.24–1.33 (m, 2H), 1.41 (s, 9H), 1.52–1.60 (m, 2H), 1.84 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 6.11 (s, 1H), 6.25 (brs, 2H), 7.88 (s, 1H), 9.55 (brs, 1H); minor component **h'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.19 (s, 9H), 0.87 (t, *J* = 7.2 Hz, 3H), 1.24–1.33 (m, 2H), 1.41 (s, 9H), 1.52–1.60 (m, 2H), 1.83 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 5.72 (brs, 1H), 6.17 (s, 1H), 7.86 (s, 1H), 9.77 (brs, 1H).

***tert*-Butyl 3-[(aminocarbonyl)hydrazono]-2-[4-(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl]butanoate (3i):**

α-Triazolehydrazone **3i** was isolated by column chromatography (ethyl acetate) in 40% yield as a mixture of desilylated (**i**) and silylated (**i'**) compounds in 71:29 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **i**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.42 (s, 9H), 1.85 (s, 3H), 4.51 (d, *J* = 5.6 Hz, 2H), 5.18 (t, *J* = 5.6 Hz, 1H), 6.10 (brs, 2H), 6.16 (s, 1H), 7.98 (s, 1H), 9.54 (brs, 1H); minor component **i'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.17 (s, 9H), 1.43 (s, 9H), 1.84 (s, 3H), 4.51 (d, *J* = 5.6 Hz, 2H), 5.18 (t, *J* = 5.6 Hz, 1H), 5.72 (brs, 1H), 6.22 (s, 1H), 7.95 (s, 1H), 9.76 (brs, 1H).

***tert*-Butyl 3-[(aminocarbonyl)hydrazono]-2-[4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl]butanoate (3j):**

α-Triazolehydrazone **3j** was isolated by column chromatography (ethyl acetate) in 46% yield as a mixture of desilylated (**j**) and silylated (**j'**) compounds in 68:32 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **j**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.25 (s, 9H), 1.41 (s, 9H), 1.86 (s, 3H), 6.15 (brs, 2H), 6.21 (s, 1H), 8.18 (s, 1H), 9.53 (brs, 1H); minor component **j'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.17 (s, 9H), 0.25 (s, 9H), 1.41 (s, 9H), 1.84 (s, 3H), 5.73 (brs, 1H), 6.25 (s, 1H), 8.15 (s, 1H), 9.74 (brs, 1H).

***tert*-Butyl 3-[(aminocarbonyl)hydrazono]-2-[4-(4-methylphenyl)-1*H*-1,2,3-triazol-1-yl]butanoate (3k):**

α-Triazolehydrazone **3k** was isolated by column chromatography (ethyl acetate) in 51% yield as a mixture of desilylated (**k**) and silylated (**k'**) compounds in 59:41 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **k**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.43 (s, 9H), 1.90 (s, 3H), 2.31 (s, 3H), 6.20 (brs, 2H), 6.24 (s, 1H), 7.23 (d, J = 8 Hz, 2H), 7.78 (d, J = 8 Hz, 2H), 8.62 (s, 1H), 9.60 (brs, 1H); minor component **k'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.14 (s, 9H), 1.43 (s, 9H), 1.88 (s, 3H), 2.31 (s, 3H), 5.73 (brs, 1H), 6.30 (s, 1H), 7.23 (d, J = 8 Hz, 2H), 7.78 (d, J = 8 Hz, 2H), 8.59 (s, 1H), 9.81 (brs, 1H).

***tert*-Butyl 3-[(aminocarbonyl)hydrazono]-2-[4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl]butanoate (3l):**

α-Triazolehydrazone **3l** was isolated by column chromatography (ethyl acetate) in 57% yield as a mixture of desilylated (**l**) and silylated (**l'**) compounds in 81:19 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **l**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.43 (s, 9H), 1.90 (s, 3H), 3.77 (s, 3H), 6.20 (brs, 2H), 6.23 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 8.56 (s, 1H), 9.58 (brs, 1H); minor component **l'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.15 (s, 9H), 1.43 (s, 9H), 1.89 (s, 3H), 3.77 (s, 3H), 5.73 (brs, 1H), 6.29 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 8.53 (s, 1H), 9.80 (brs, 1H).

Ethyl 1-[2-[(aminocarbonyl)hydrazono]-1-(*tert*-butoxycarbonyl)propyl]-1*H*-1,2,3-triazole-4-carboxylate (3m):

α-Triazolehydrazone **3m** was isolated by column chromatography (ethyl acetate) in 39% yield as a mixture of desilylated (**m**) and silylated (**m'**) compounds in 65:35 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **m**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.29 (t, J = 7.2 Hz, 3H), 1.42 (s, 9H),

1.90 (s, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 6.25 (brs, 2H), 6.31 (s, 1H), 8.85 (s, 1H), 9.56 (brs, 1H); minor component **m'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.15 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.42 (s, 9H), 1.89 (s, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 5.68 (brs, 1H), 6.38 (s, 1H), 8.83 (s, 1H), 9.78 (brs, 1H).

***tert*-Butyl 2-(4-acetyl-1*H*-1,2,3-triazol-1-yl)-3-[(aminocarbonyl)hydrazono]butanoate (3n):** α-Triazolehydrazone **3n** was isolated by column chromatography (ethyl acetate) in 50% yield as a mixture of desilylated (**n**) and silylated (**n'**) compounds in 78:22 ratio (determined by ^{1}H NMR). Pale yellow foam. For clarity sake the NMR values are given separately for each compound. Major component **n**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.42 (s, 9H), 1.90 (s, 3H), 2.55 (s, 3H), 6.25 (brs, 2H), 6.32 (s, 1H), 8.86 (s, 1H), 9.55 (brs, 1H); minor component **n'**: ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.16 (s, 9H), 1.42 (s, 9H), 1.89 (s, 3H), 2.55 (s, 3H), 5.69 (brs, 1H), 6.38 (s, 1H), 8.82 (s, 1H), 9.77 (brs, 1H).

General procedure for the synthesis of 1-(3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)-1,2,3-triazoles 4a–k. The α-triazolehydrazone **3a–n** and **3a'–d, h'–n'** (1 mmol) was dissolved in methanol (5 mL) and a stoichiometric amount of the potassium carbonate (1 mmol) was added. The reaction mixture was magnetically stirred for 0.1–2 h (see Table 3) until the disappearance of the starting material (monitored by TLC). The solvent was then evaporated under reduced pressure. The products **4a–k** were obtained by elution with methanol of the crude mixture on acidic resin column (cation–exchange resin [Dowex HCRS(E)] from Dow Chemicals, USA, treated with HCl 1M) and crystallized from methanol. In the case of pyrazolone-triazole **4j** the acidic treatment with cation–exchange resin was avoided to prevent the formation of byproducts.

1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-phenyl-1*H*-1,2,3-triazole (4a): White solid from methanol; mp: 226–228 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.27 (s, 3H), 7.33–7.36 (m, 1H), 7.44–7.47 (m, 2H), 7.89–7.91 (m, 2H), 8.07 (brs, 1H) and 8.14 (brs, 1H), 8.77 (s, 1H), 13.48 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.3 (q), 103.3 (s), 122.8 (d), 125.3 (d), 128.0 (d), 128.9 (d), 130.3 (s), 144.3 (s), 146.0 (s), 148.6 (s), 156.0 (s); IR (nujol): ν_{max} = 3315, 1751, 1680, 1597, 1360 cm^{-1}; MS *m/z* (%): 285 (M^++1) (1), 241 (2), 213 (100), 207 (5), 185 (7), 156 (9), 129 (17), 117 (15), 102 (45); anal. calcd. for $C_{13}H_{12}N_6O_2$ (284.27): C 54.93, H 4.25, N 29.56; found: C 55.15, H 4.33, N 29.44.

1-[2-(Aminocarbonyl)-5-ethyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-phenyl-1*H*-1,2,3-triazole (4b): White solid from methanol; mp: 221–223 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.08 (t, *J* = 7.6 Hz, 3H), 2.60 (q, *J* = 7.6 Hz, 2H), 7.32–7.36 (m, 1H), 7.43–7.47 (m, 2H), 7.89–7.91 (m, 2H), 8.09 (brs, 1H) and 8.14 (brs, 1H), 8.78 (s, 1H), 13.47 (brs, 1H); ^{13}C NMR (100 MHz,

DMSO-d_6, 25 °C): δ = 12.4 (q), 18.1 (t), 102.6 (s), 123.3 (d), 125.3 (d), 128.1 (d), 129.0 (d), 130.3 (s), 146.1 (s), 148.6 (s), 149.4 (s), 156.3 (s); IR (nujol): ν_{max} = 3376, 3323, 3129, 1719, 1672, 1589, 1372 cm^{-1}; MS *m/z* (%): 299 (M^++1) (1), 252 (3), 227 (100), 226 (21), 212 (16), 198 (9), 155 (11), 130 (21), 102 (44). anal. calcd. for $C_{14}H_{14}N_6O_2$ (298.30): C 56.37, H 4.73, N 28.17; found: C 56.25, H 4.76, N 27.96.

1-[2-(Anilinocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-phenyl-1*H*-1,2,3-triazole (4c): White solid from methanol; mp: 152**–**154 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.33 (s, 3H), 7.13**–**7.17 (m, 1H), 7.33–7.48 (m, 5H), 7.54**–**7.56 (m, 2H), 7.91**–**7.93 (m, 2H), 8.81 (s, 1H), 11.01 (brs, 1H), 13.79 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.5 (q), 103.3 (s), 119.8 (d), 122.7 (d), 124.4 (d), 125.3 (d), 128.1 (d), 129.0 (d), 129.3 (d), 130.3 (s), 136.7 (s), 145.1 (s), 145.9 (s), 146.1 (s), 156.2 (s); IR (nujol): ν_{max} = 3153, 1713, 1613, 1572 cm^{-1}; MS *m/z* (%): 241 (3), 213 (95), 185 (6), 156 (8), 130 (15), 119 (100), 102 (43); anal. calcd. for $C_{19}H_{16}N_6O_2$ (360.37): C 63.32, H 4.48, N 23.32; found: C 63.43, H 4.50, N 23.16.

1-{2-[(3-Fluorophenyl)aminocarbonyl]-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl}-4-phenyl-1*H*-1,2,3-triazole (4d): White solid from methanol; mp: 227**–**229 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.33 (s, 3H), 6.96**–**7.00 (m, 1H), 7.28–7.57 (m, 6H), 7.90**–**7.92 (m, 2H), 8.80 (s, 1H), 11.16 (brs, 1H), 13.38 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.6 (q), 103.1 (s), 106.7 (d, $^2J_{CF}$ = 26.6 Hz), 110.9 (d, $^2J_{CF}$ = 21.9 Hz), 115.7 (d), 122.6 (d), 125.3 (d), 128.1 (d), 129.0 (d), 130.3 (s), 130.9 (d, $^3J_{CF}$ = 9.1 Hz), 138.5 (s, $^3J_{CF}$ = 11.0 Hz), 145.5 (s), 146.0 (s), 146.1 (s), 156.2 (s), 162.3 (s, $^1J_{CF}$ = 241 Hz); IR (nujol): ν_{max} = 3194, 3159, 1725, 1621, 1574 cm^{-1}; MS *m/z* (%): 252 (3), 213 (33), 179 (3), 137 (100), 117 (6), 109 (52); anal. calcd. for $C_{19}H_{15}N_6O_2F$ (378.36): C 60.31, H 4.00, N 22.21; found: C 60.24, H 4.03, N 22.16.

1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-butyl-1*H*-1,2,3-triazole (4e): White solid from methanol; mp: 169**–**171 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.89 (t, *J* = 7.6 Hz, 3H), 1.28**–**1.37 (m, 2H), 1.56**–**1.63 (m, 2H), 2,21 (s, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 8.03 (s, 1H), 8.13 (brs, 2H), 13.34 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.4 (q), 13.7 (q), 21.7 (t), 24.6 (t), 31.0 (t), 103.5 (s), 123.0 (d), 144.0 (s), 146.5 (s), 148.6 (s), 156.0 (s); IR (nujol): ν_{max} = 3326, 3164, 1775, 1679, 1600, 1355 cm^{-1}; MS *m/z* (%): 264 (M^+) (2), 213 (15), 192 (13), 178 (12), 164 (10), 150 (100), 137 (18), 124 (13), 112 (21); anal. calcd. for $C_{11}H_{16}N_6O_2$ (264.28): C 49.99, H 6.10, N 31.80; found: C 55.28, H 6.04, N 31.62.

1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-hydroxymethyl-1*H*-1,2,3-triazole (4f): White solid from methanol; mp: 188**–**190 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.23 (s, 3H), 4.50 (brs, 1H), 4.56 (s, 2H), 8.05 (brs, 1H) and 8.11 (brs, 1H), 8.14 (s, 1H), 13.36 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.8 (q), 54.9 (t), 102.7 (s), 123.8 (d),

144.0 (s), 147.5 (s), 149.2 (s), 156.3 (s); IR (nujol): ν_{max} = 3344, 3222, 1773, 1681, 1593 cm^{-1}; MS *m/z* (%): 239 (M^++1) (1), 213 (18), 207 (13), 195 (8), 166 (10), 149 (100), 129 (20), 124 (21), 111 (29); anal. calcd. for $C_8H_{10}N_6O_3$ (238.20): C 40.34, H 4.23, N 35.28; found: C 40.20, H 4.28, N 35.40.

1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-trimethylsilyl-1*H*-1,2,3-triazole (4g): White solid from methanol; mp: 150**–**152 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 0.28 (s, 9H), 2.21 (s, 3H), 8.06 (brs, 1H) and 8.12 (brs, 1H), 8.31 (s, 1H), 13.40 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = -1.0 (q), 10.4 (q), 103.2 (s), 131.6 (d), 144.0 (s), 144.5 (s), 148.6 (s), 156.0 (s); IR (nujol): ν_{max} = 3300, 3233, 3149, 1733, 1599, 1383, 1358 cm^{-1}; MS *m/z* (%): 281 (M^++1) (1), 266 (3), 209 (31), 194 (100), 167 (25), 154 (7), 141 (19), 125 (10), 100 (70); anal. calcd. for $C_{10}H_{16}N_6O_2$,Si (280.36): C 42.84, H 5.75, N 29.98; found: C 42.95, H 5.68, N 29.83.

1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-(4-methylphenyl)-1*H*-1,2,3-triazole (4h): White solid from methanol; mp: 241**–**243 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.25 (s, 3H), 2.32 (s, 3H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 8.09 (brs, 1H) and 8.13 (brs, 1H), 8.70 (s, 1H), 13.51 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.5 (q), 20.9 (q), 102.8 (s), 122.2 (d), 125.3 (d), 127.7 (d), 129.5 (s), 137.3 (s), 144.2 (s), 146.0 (s), 149.0 (s), 156.2 (s); IR (nujol): ν_{max} = 3346, 3213, 1718, 1660, 1578, 1395 cm^{-1}; MS *m/z* (%): 252 (3), 227 (100), 222 (15), 179 (23), 166 (10), 138 (46), 115 (43); anal. calcd. for $C_{14}H_{14}N_6O_2$ (298.30): C 56.37, H 4.73, N 28.17; found: C 56.51, H 4.68, N 28.11.

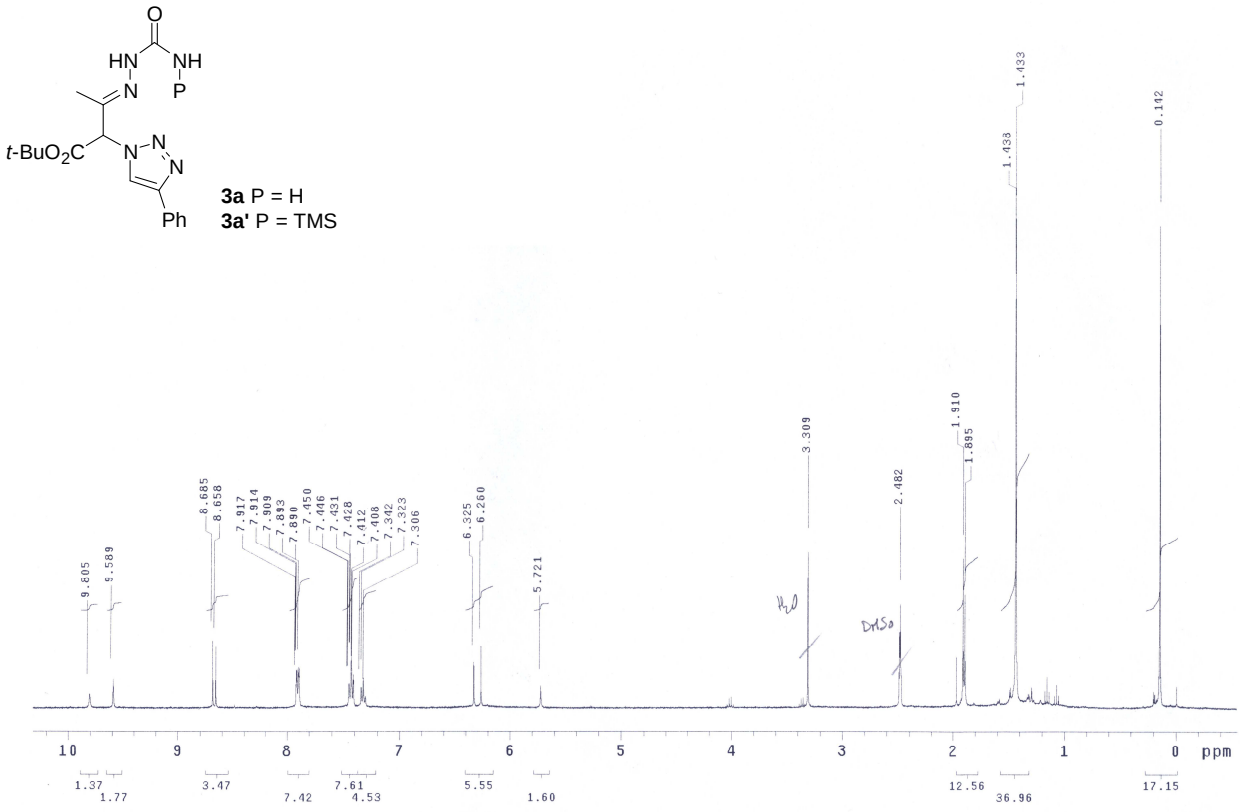
1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (4i): White solid from methanol; mp: 201**–**203 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.26 (s, 3H), 3.78 (s, 3H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 8.08 (brs, 1H) and 8.14 (brs, 1H), 8.65 (s, 1H), 13.46 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.3 (q), 55.2 (q), 103.4 (s), 114.4 (d), 121.8 (d), 122.9 (d), 126.6 (s), 144.2 (s), 146.0 (s), 148.6 (s), 156.0 (s), 159.1 (s); IR (nujol): ν_{max} = 3353, 3149, 1721, 1675, 1579, 1392, 1242 cm^{-1}; MS *m/z* (%): 306 (7), 285 (11), 243 (73), 228 (65), 207 (26), 135 (98), 119 (100), 104 (74). anal. calcd. for $C_{14}H_{14}N_6O_3$ (314.30): C 53.50, H 4.49, N 26.74; found: C 53.41, H 4.53, N 26.68.

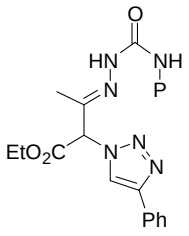
Ethyl 1-[2-(aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-2,3-dihydro-1*H*-1,2,3-triazole-4-carboxylate (4j): White solid from methanol; mp: 230**–**232 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.29 (t, *J* = 7.2 Hz, 3H), 2.09 (s, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.85 (brs, 1H), 8.75 (s, 1H), 9.03 (brs, 1H), 13.22 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 14.0 (q), 14.2 (q), 60.3 (q), 97.4 (s), 126.5 (d), 137.4 (s), 142.8 (s), 152.5 (s), 157.9 (s), 160.5 (s); IR (nujol): ν_{max} = 3343, 3129, 1703, 1652, 1591 cm^{-1}; MS *m/z* (%): 279 (10), 263 (9), 236 (12), 219

(84), 203 (38), 189 (35), 161 (30), 149 (82), 139 (34), 125 (66), 111 (100). anal. calcd. for $C_{10}H_{12}N_6O_4$ (280.24): C 42.86, H 4.32, N 29.99; found: C 42.63, H 4.19, N 30.13.

1-[2-(Aminocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-4-acetyl-1*H*-1,2,3-triazole (4k): White solid from methanol; mp: 132 °C burn; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.25 (s, 3H), 2.58 (s, 3H), 8.08 (brs, 2H), 8.91 (s, 1H), 13.62 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 10.3 (q), 27.3 (q), 102.6 (s), 128.4 (d), 144.2 (s), 146.6 (s), 148.4 (s), 155.7 (s), 191.3 (s); IR (nujol): ν_{max} = 3390, 3327, 3096, 1748, 1689, 1589, 1354 cm^{-1}; MS *m/z* (%): 250 (M^+) (8), 235 (4), 219 (2), 207 (15), 179 (100), 164 (53), 136 (56), 108 (28); anal. calcd. for $C_9H_{10}N_6O_3$ (250.21): C 43.20, H 4.03, N 33.59; found: C 43.31, H 4.07, N 33.48.

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





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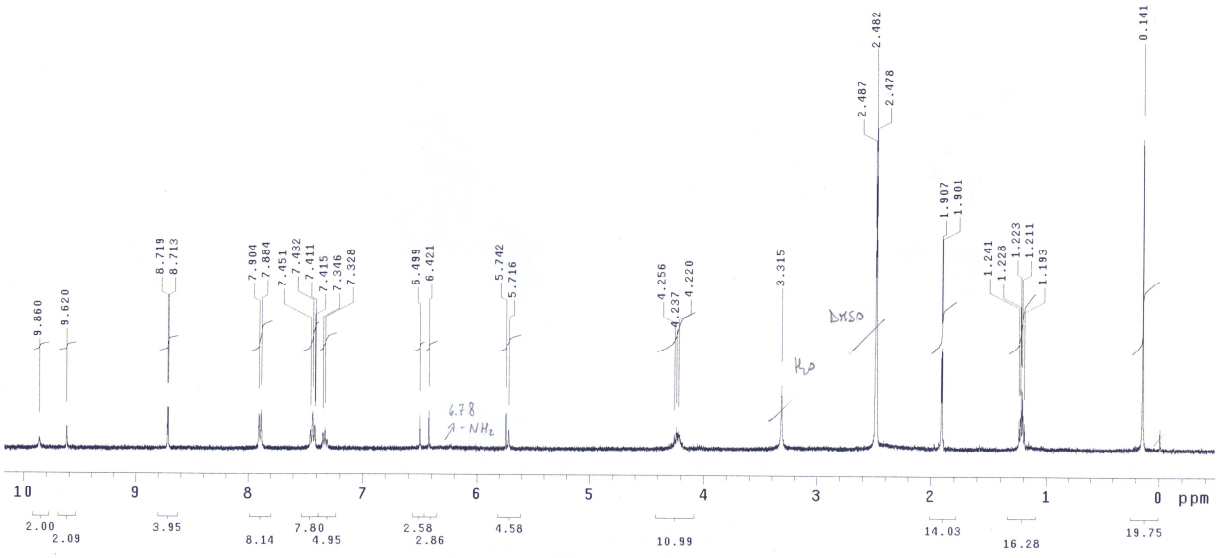

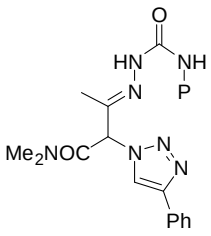

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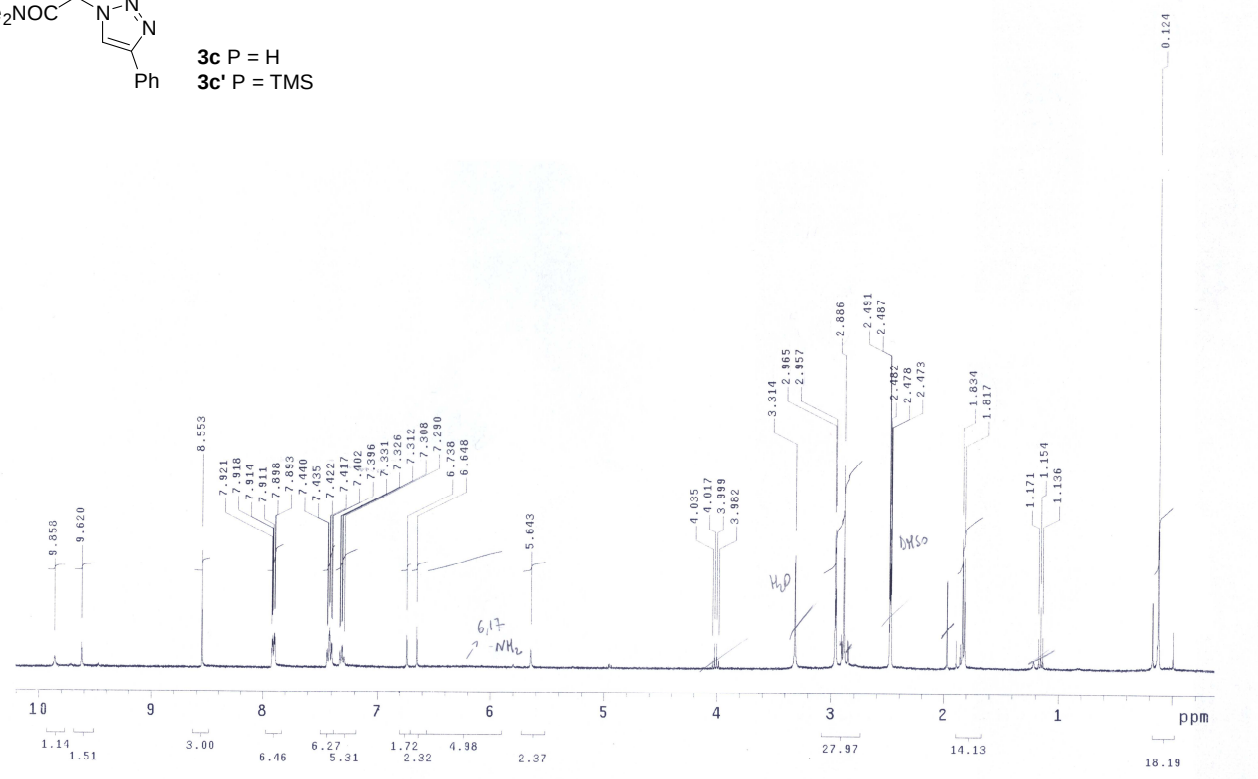

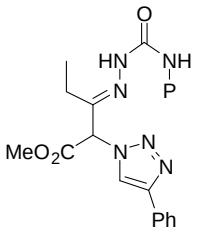

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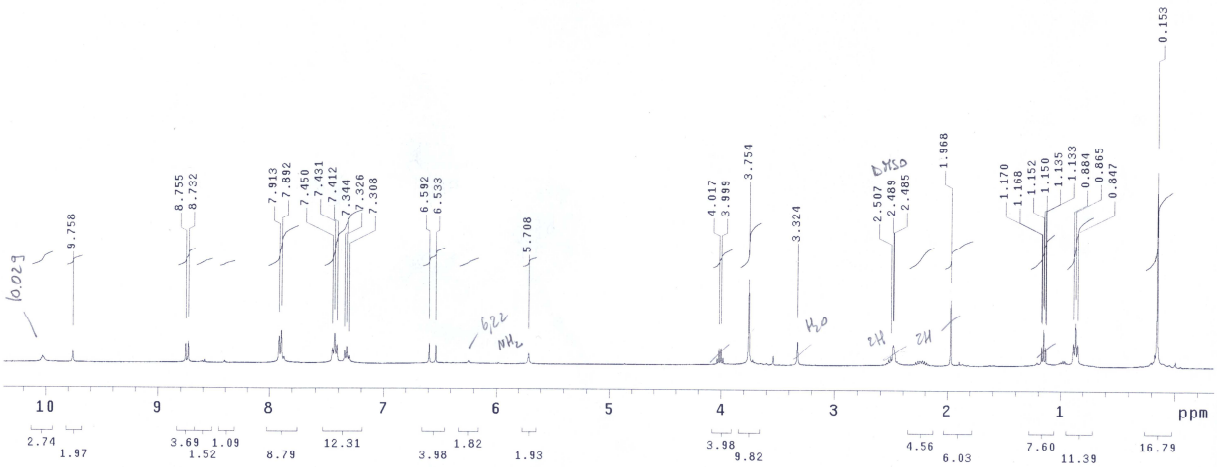

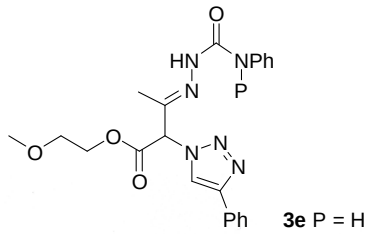

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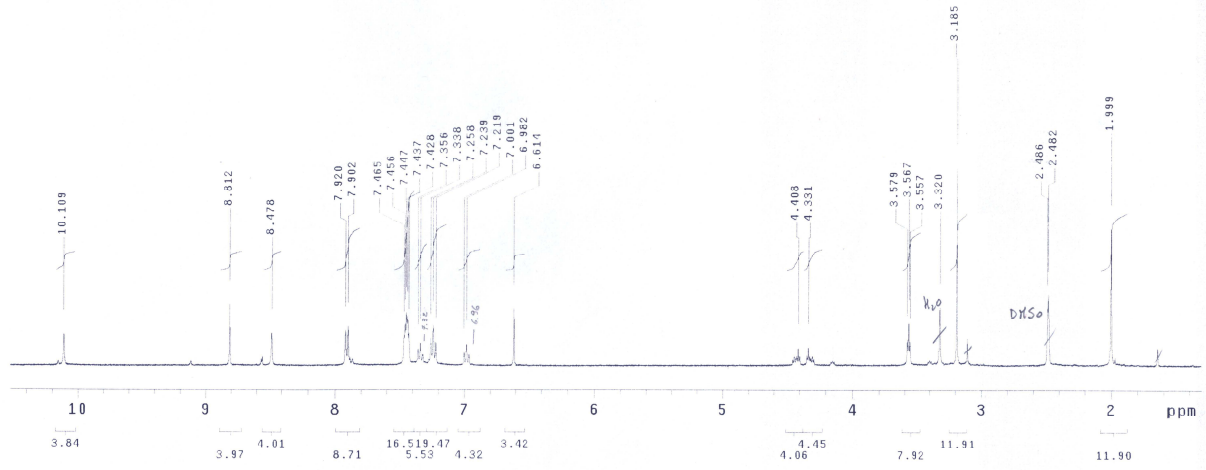

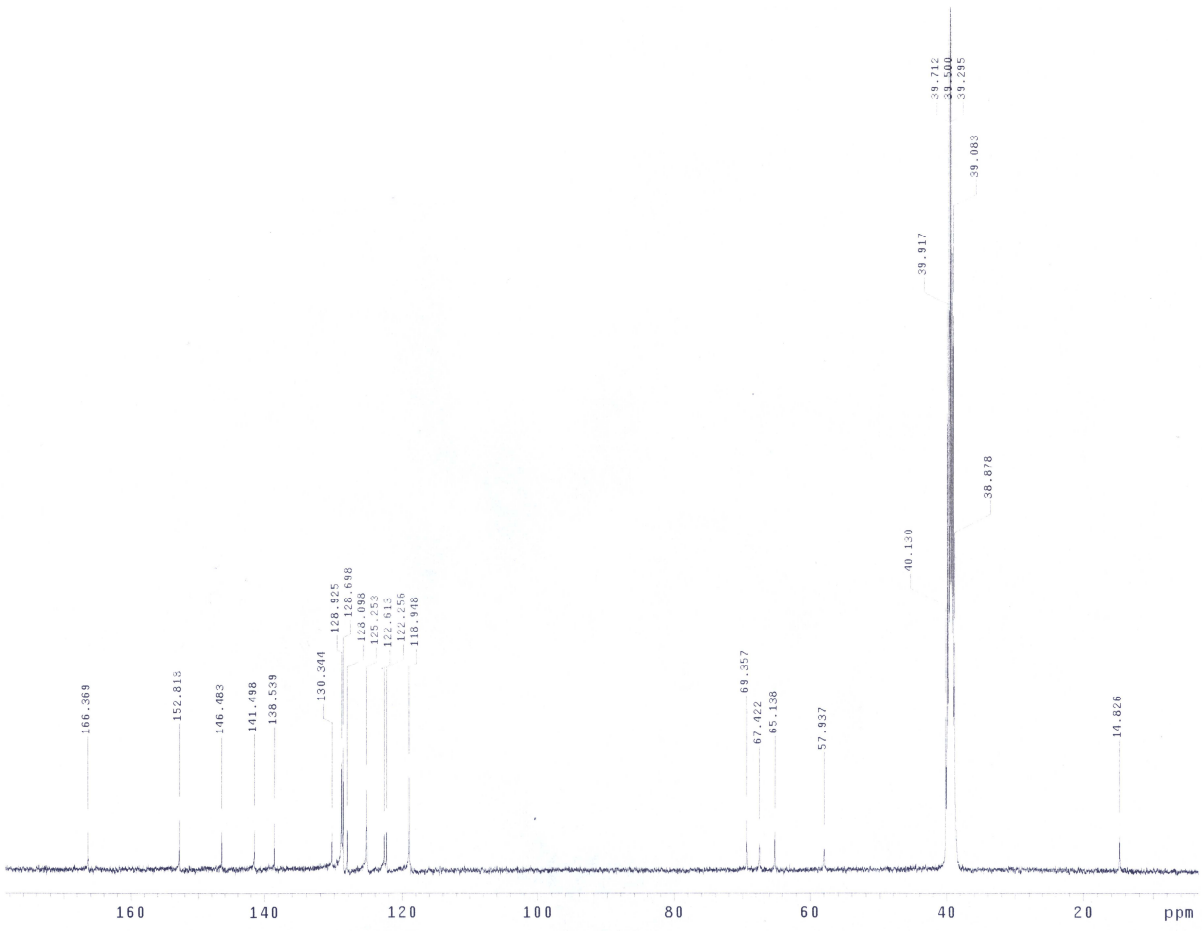
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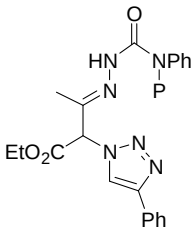
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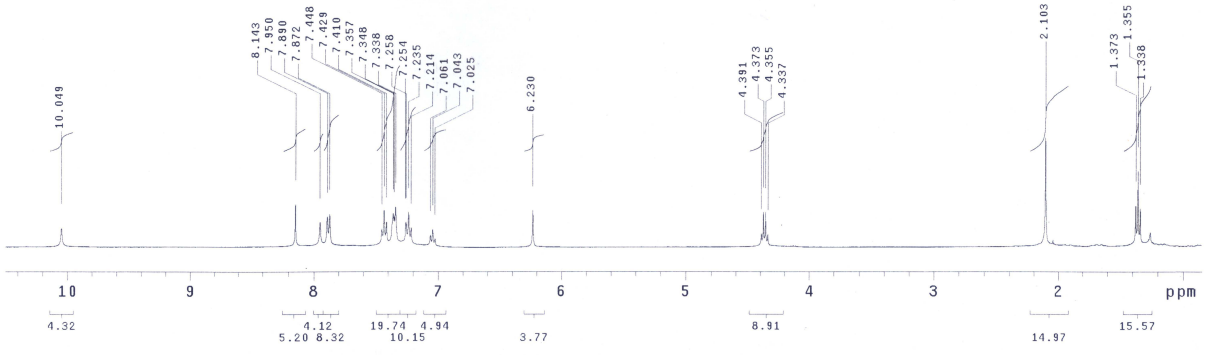
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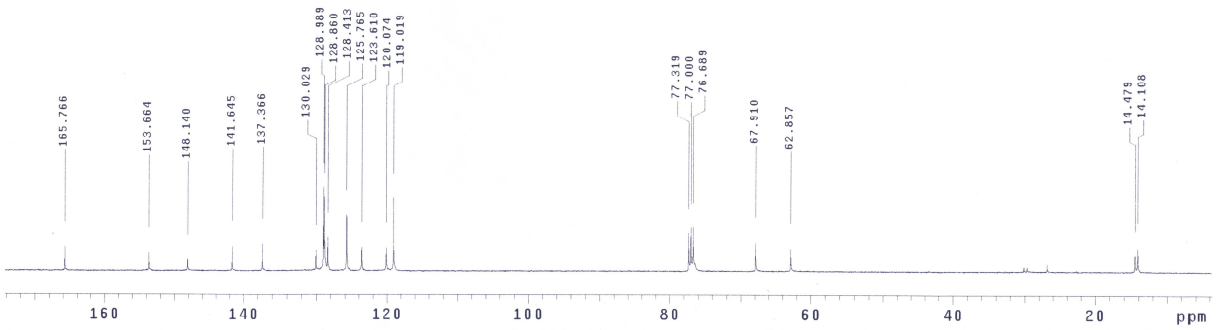
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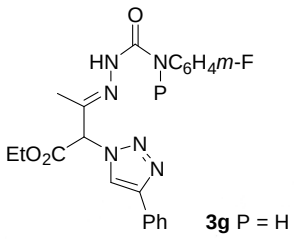
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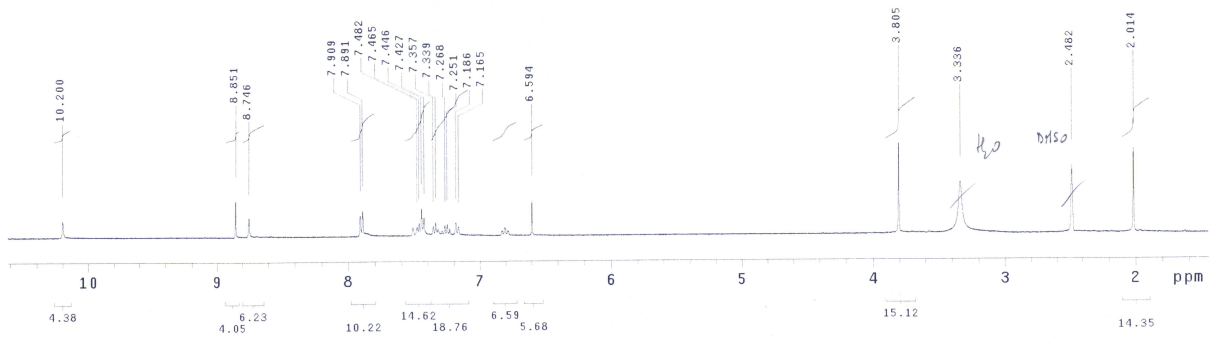
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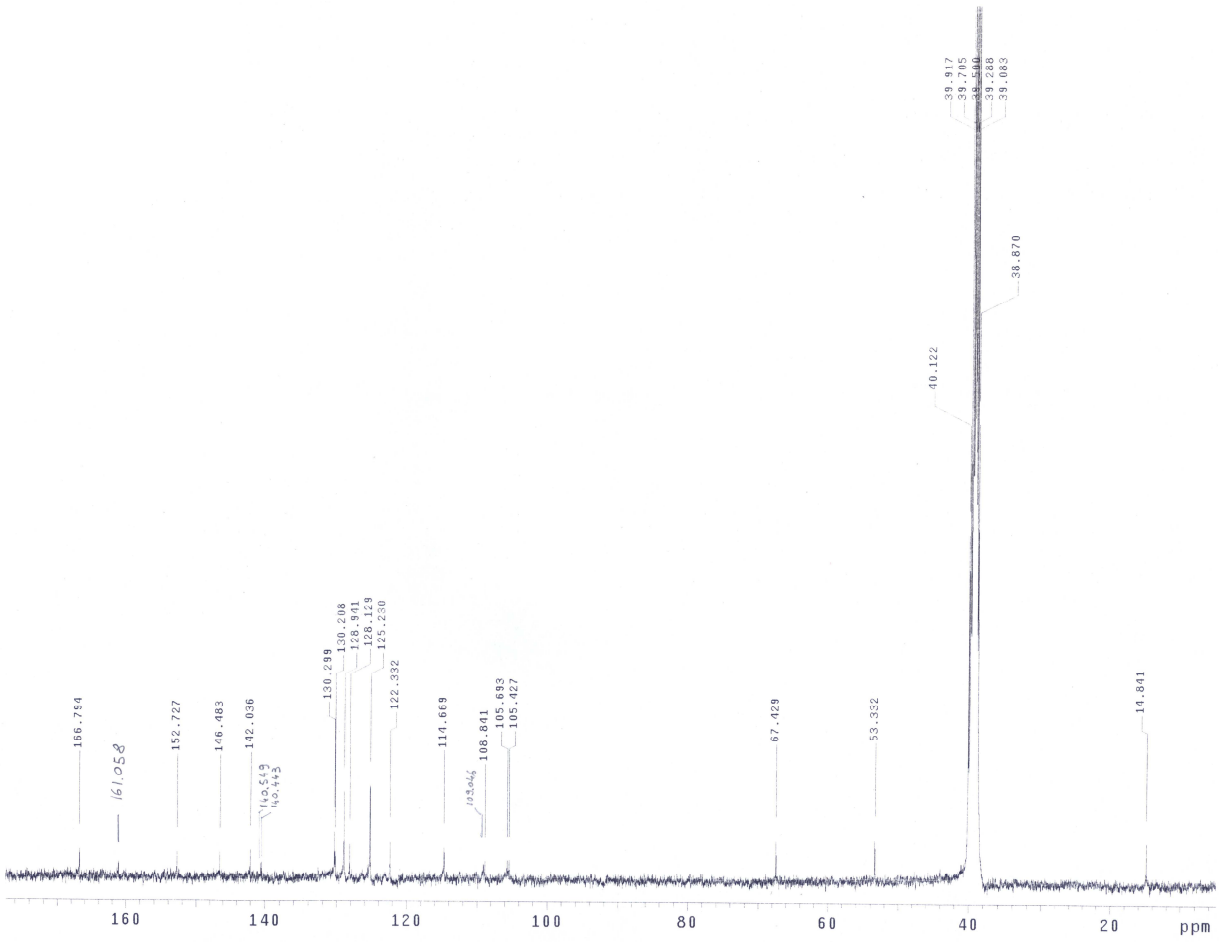
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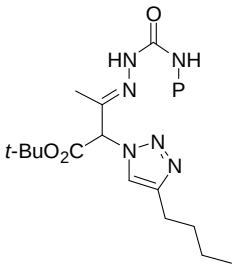
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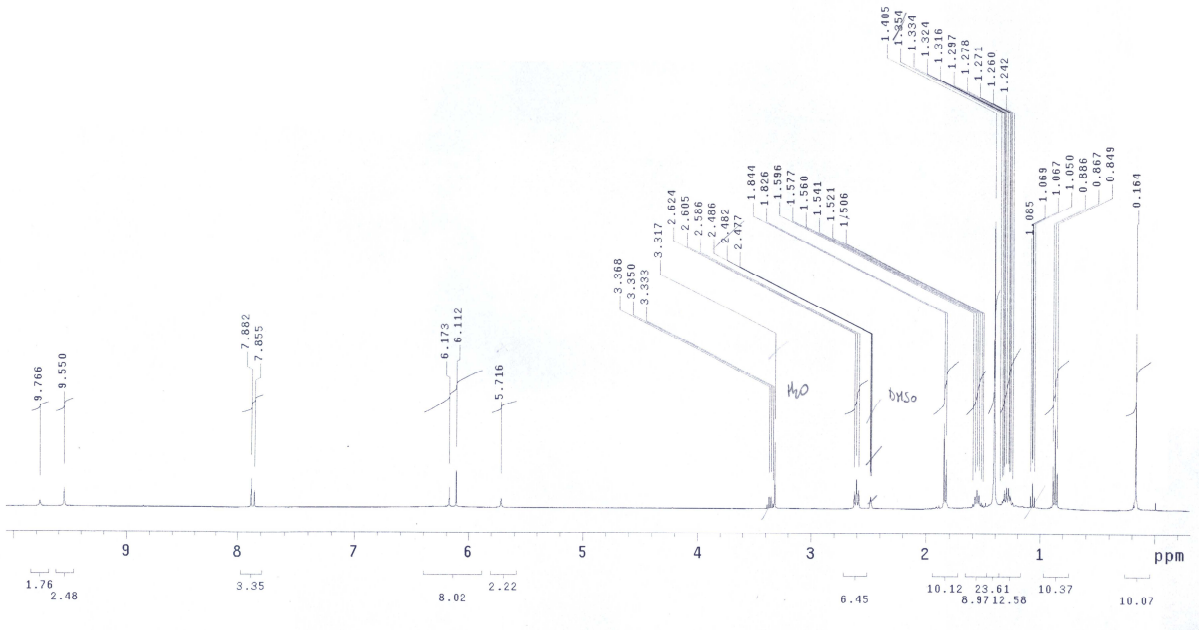
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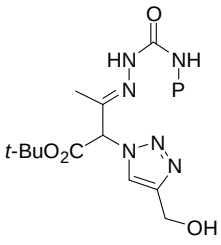

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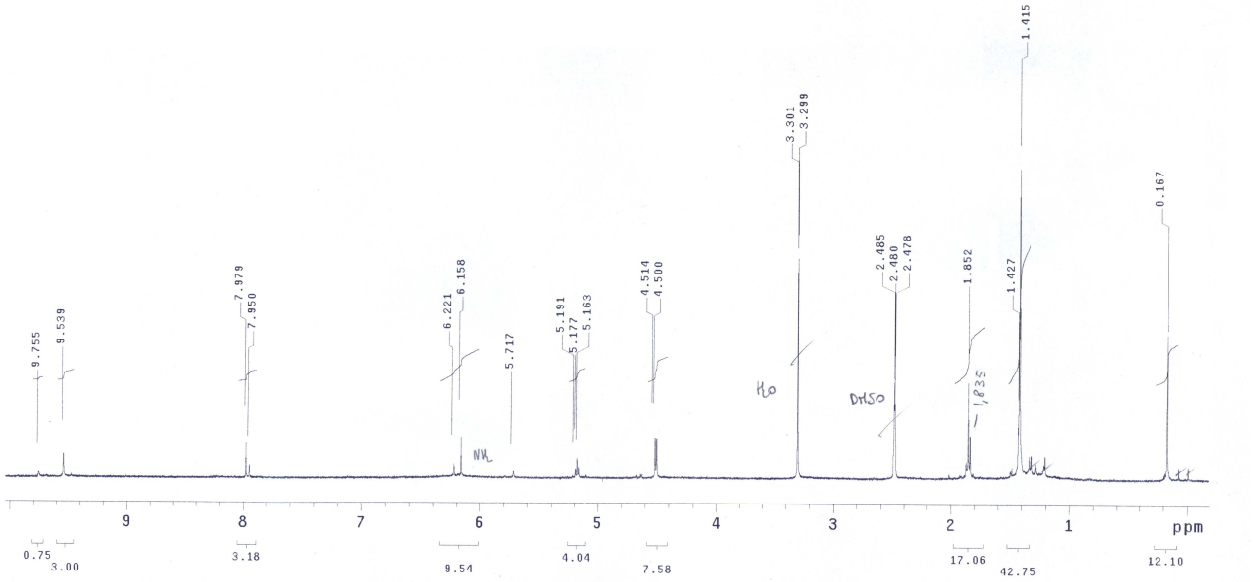
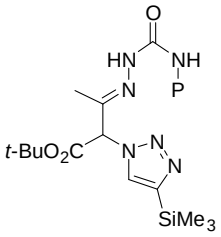
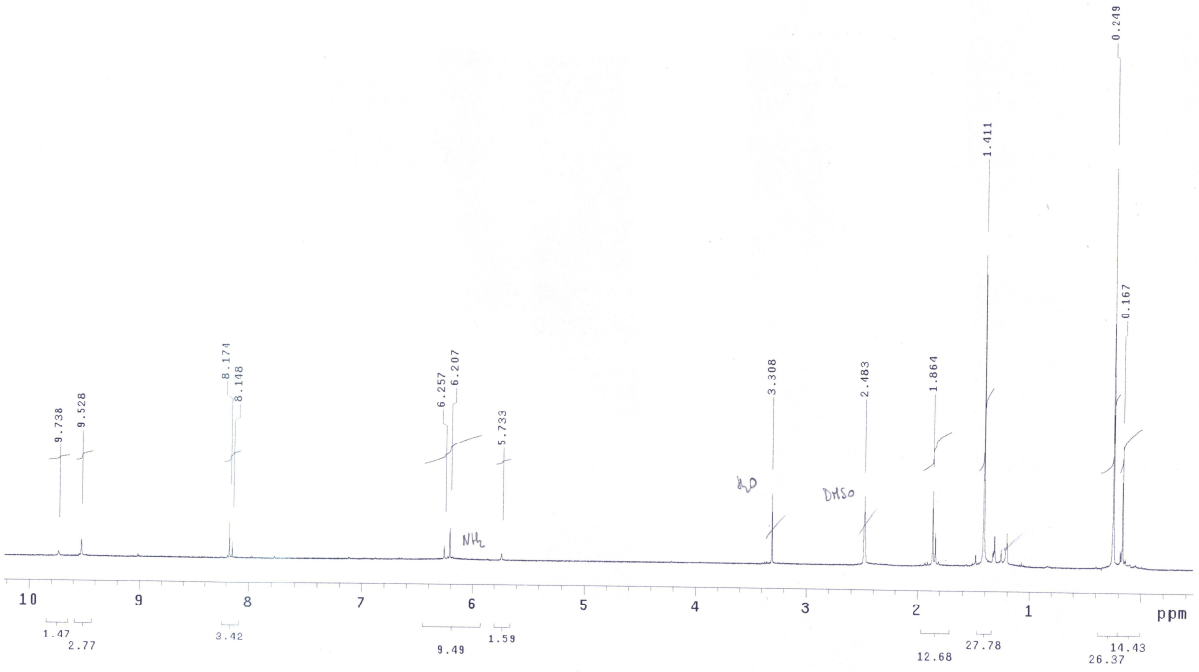
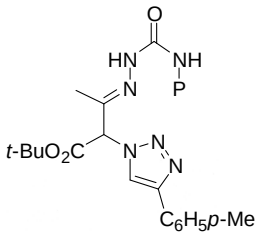
3i' P = TMS



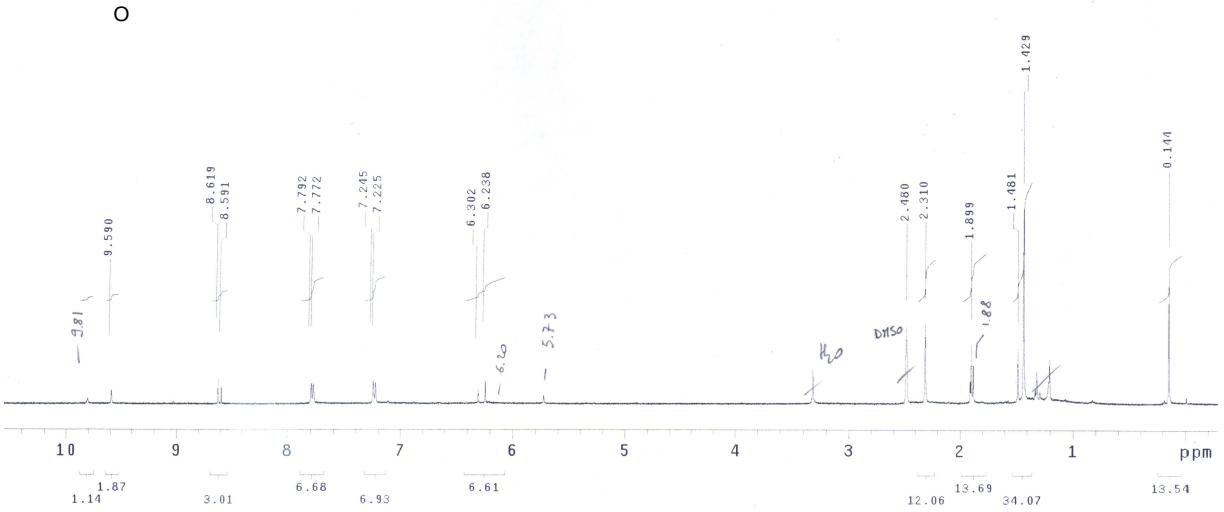


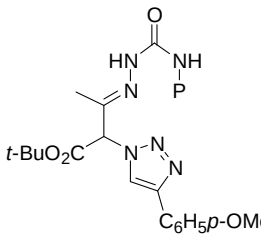
3j P = H
3j' P = TMS



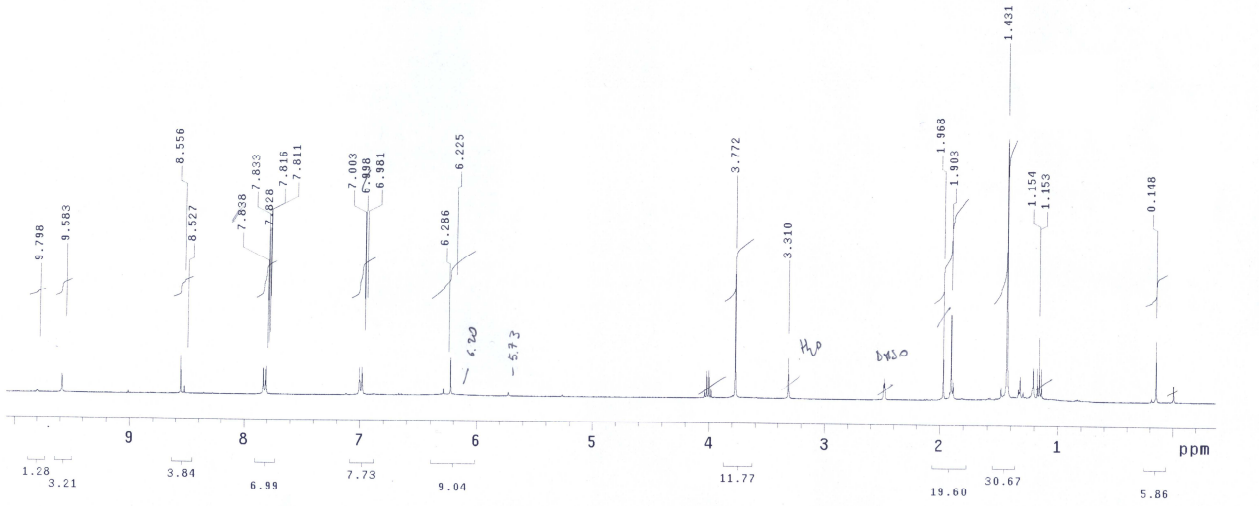


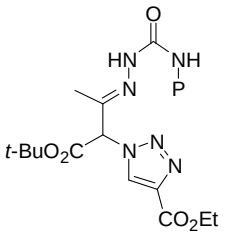
3k P = H
3k' P = TMS



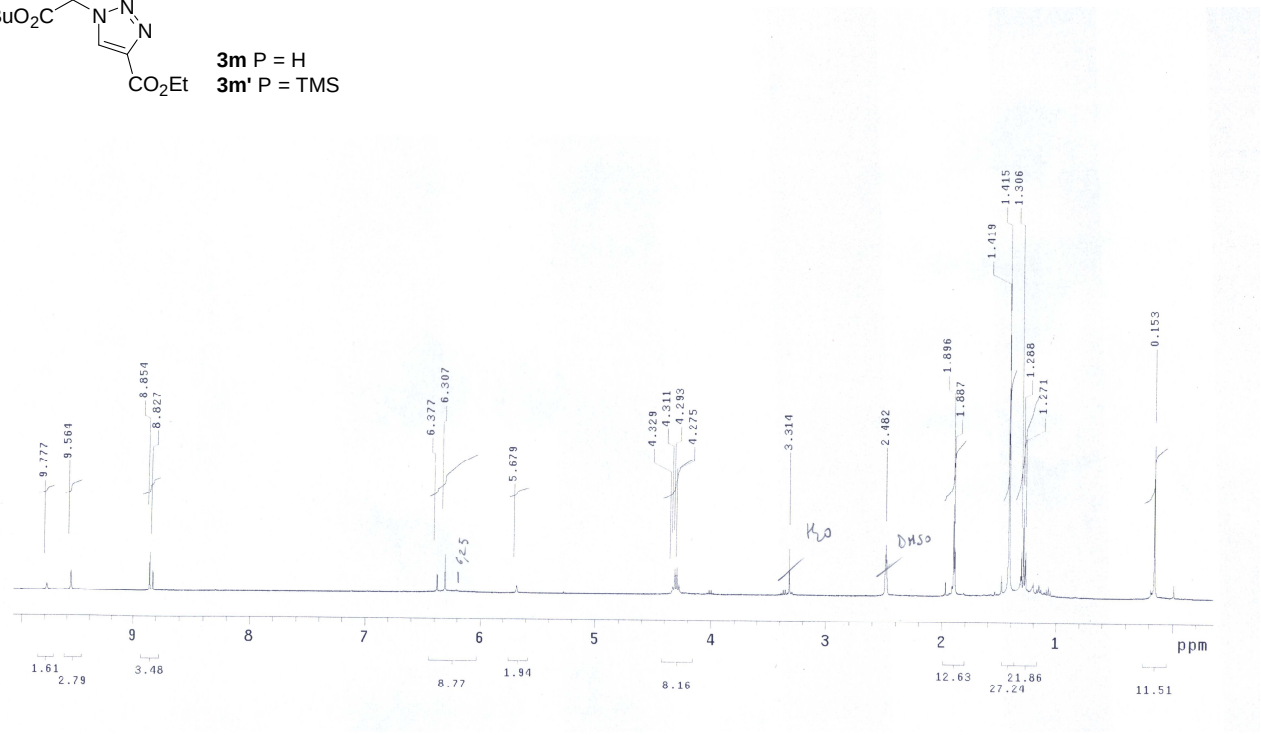


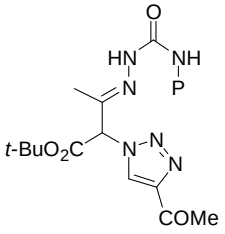
3l P = H
3l' P = TMS



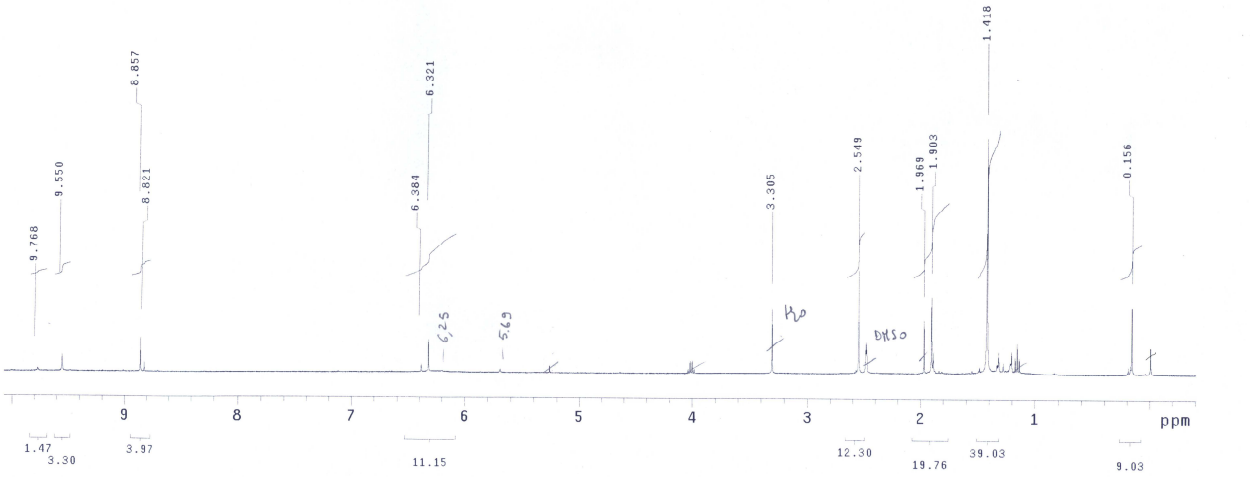


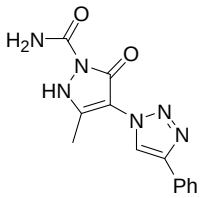
3m P = H
3m' P = TMS



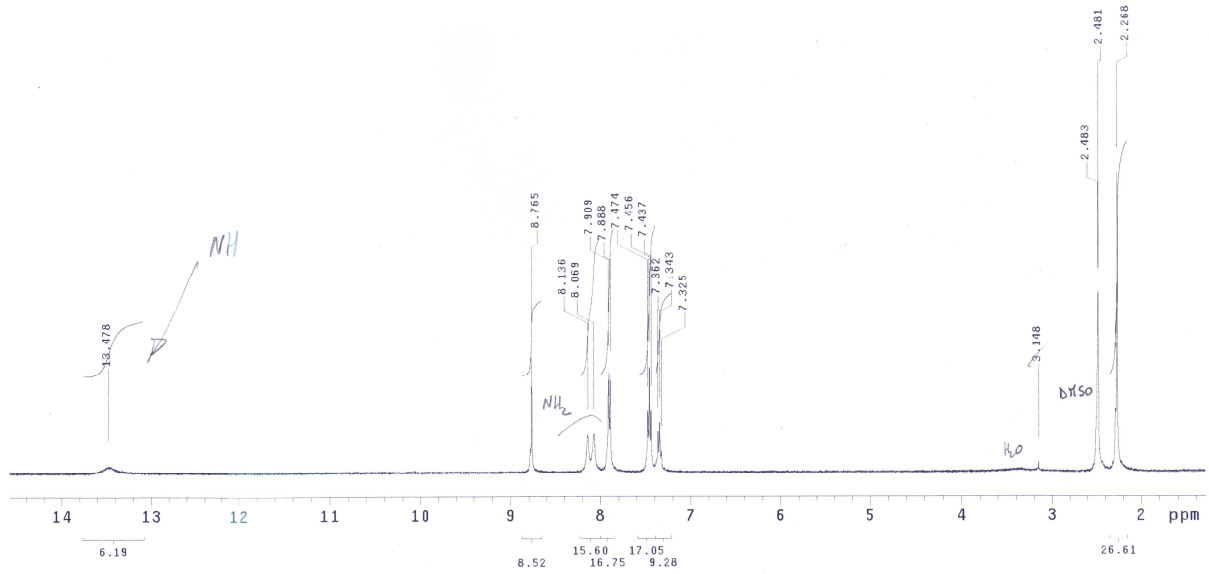


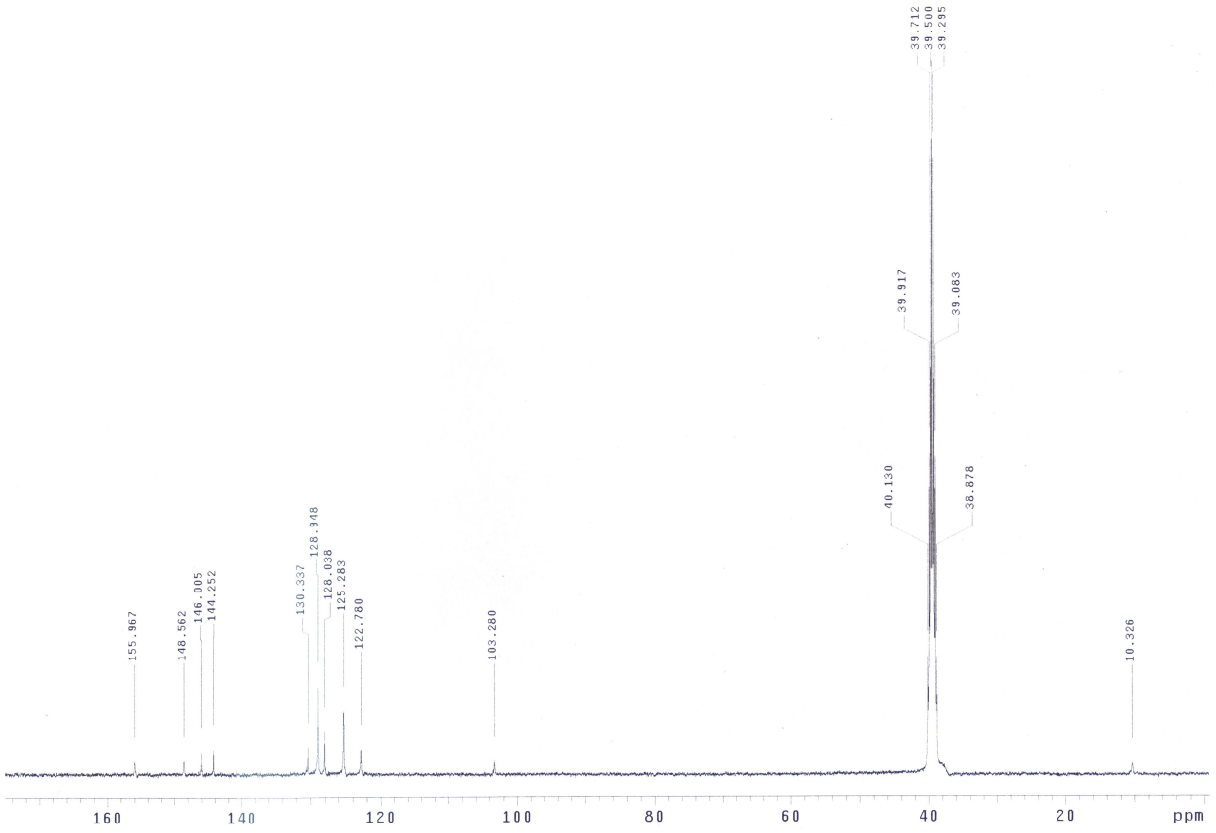
3n P = H
3n' P = TMS

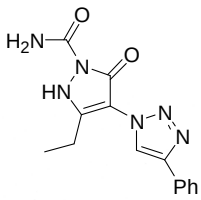



O
H2N
N
O
HN
N
N
N
Ph

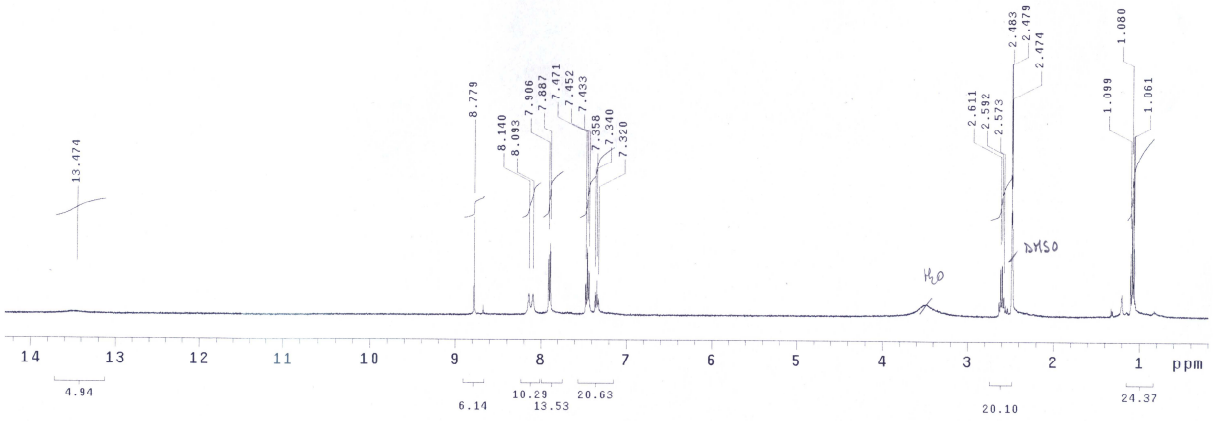
4a

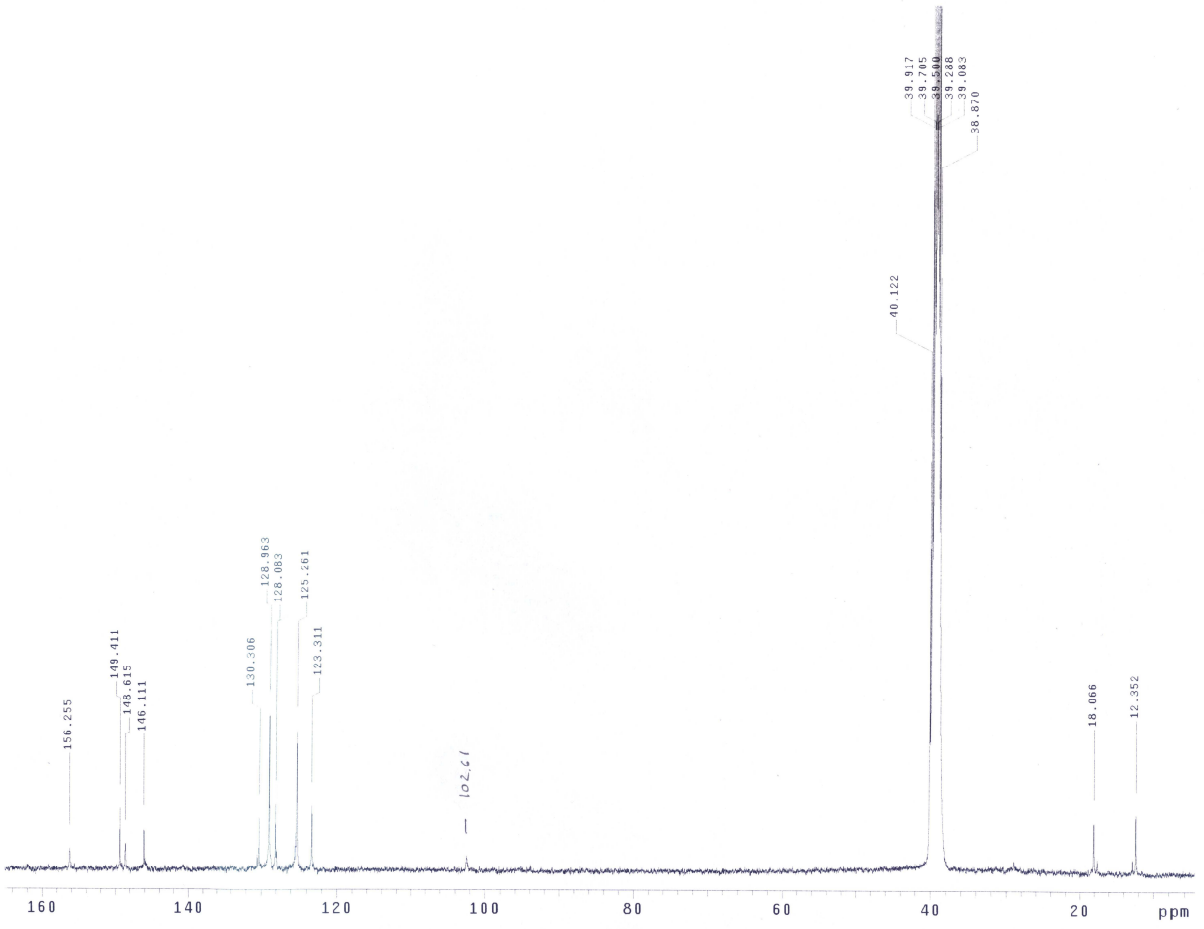

13.478
NH
8.765
7.909
7.888
7.474
7.456
7.437
8.136
8.069
7.362
7.343
7.325
NH2
3.148
H2O
DMSO
2.481
2.268
2.483
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
6.19
8.52
15.60
16.75
17.05
9.28
26.61

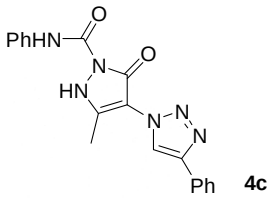

155.967
148.562
146.305
144.252
130.337
128.348
128.008
125.283
122.780
103.280
39.712
39.500
39.295
39.917
39.083
40.130
38.878
10.326
160
140
120
100
80
60
40
20
ppm



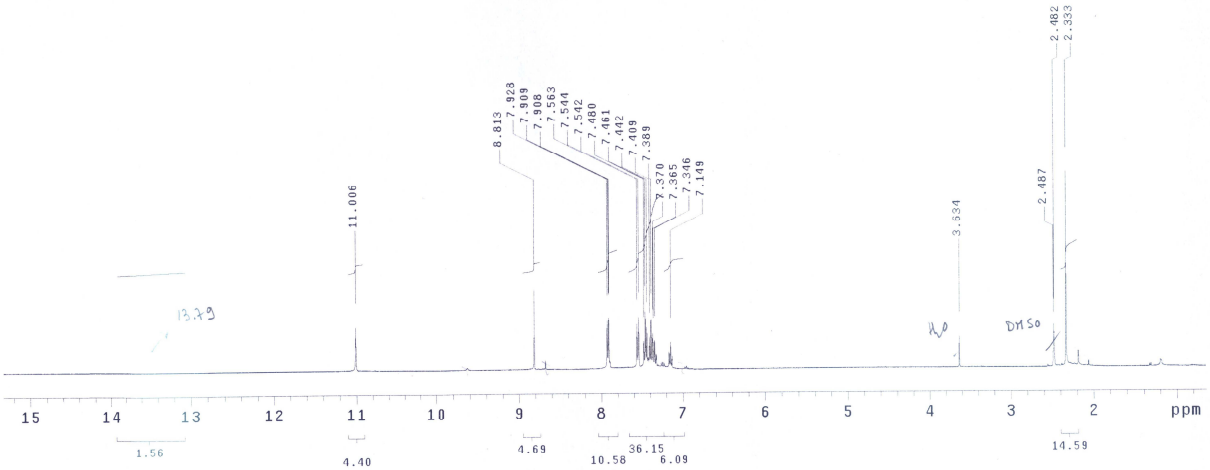
4b

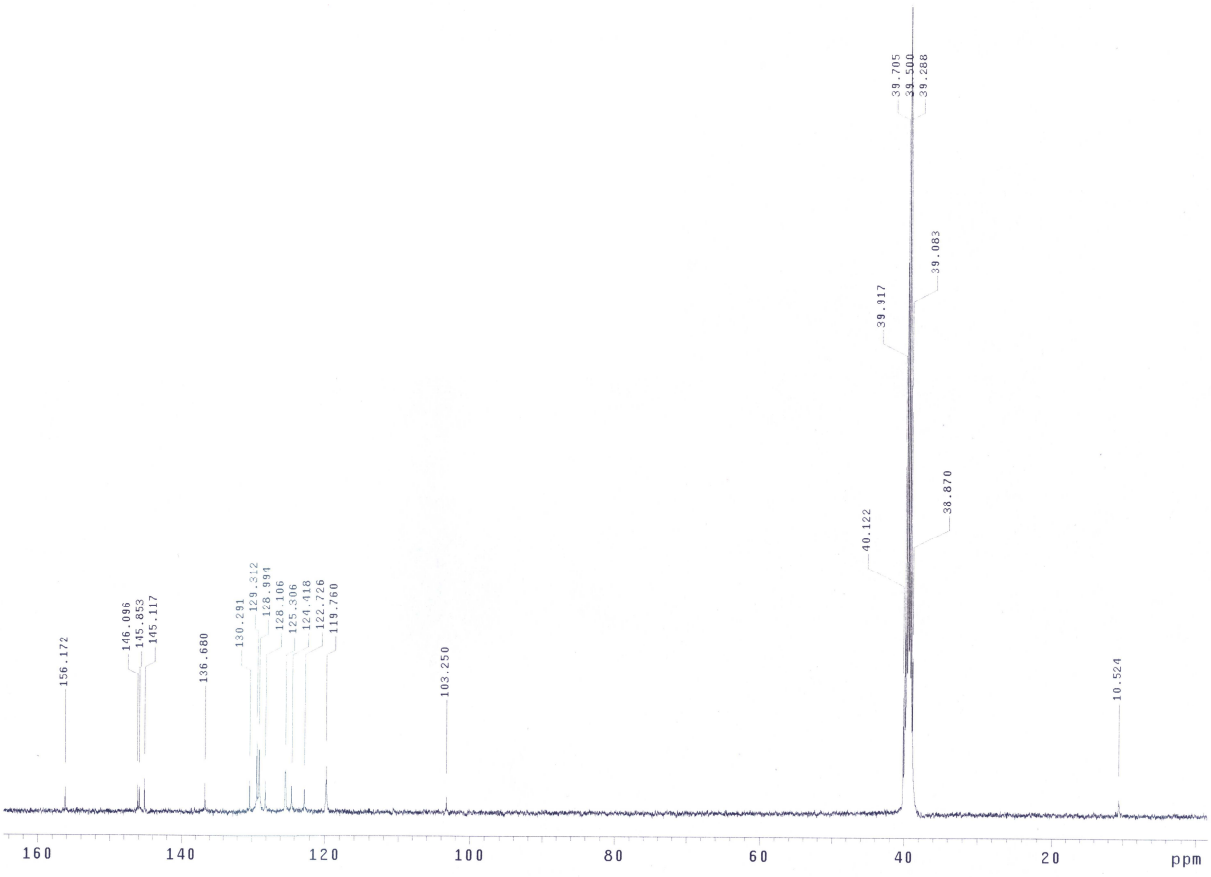

13.474
8.779
8.140
8.093
7.906
7.887
7.471
7.452
7.433
7.358
7.340
7.320
2.611
2.592
2.573
2.483
2.479
2.474
1.099
1.080
1.061
H2O
DMSO
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
4.94
6.14
10.29
13.53
20.63
20.10
24.37

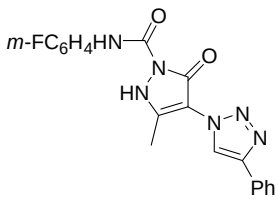

156.255
149.411
148.615
146.111
130.306
128.963
128.083
125.261
123.311
102.641
40.122
39.917
39.705
39.288
39.083
38.870
18.066
12.352
160 140 120 100 80 60 40 20 ppm


PhHN
O
O
N
HN
N
N
N
Ph

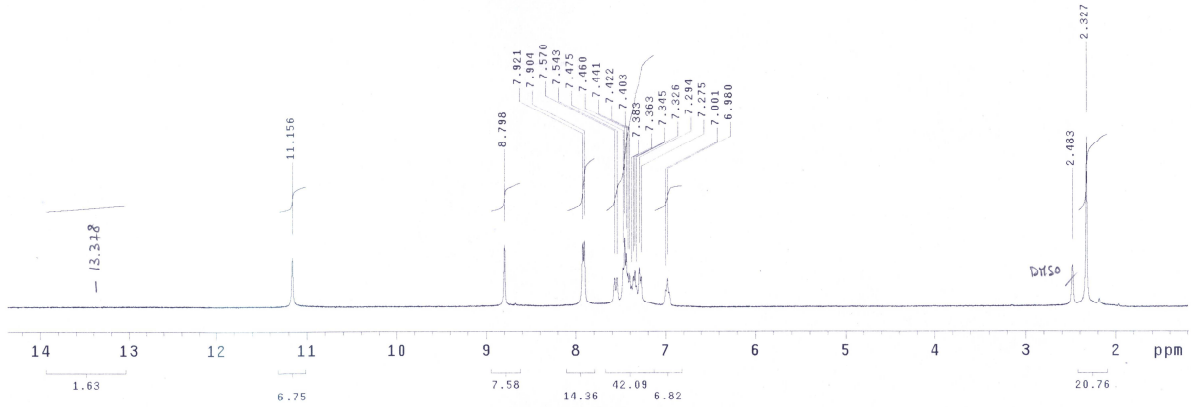
4c

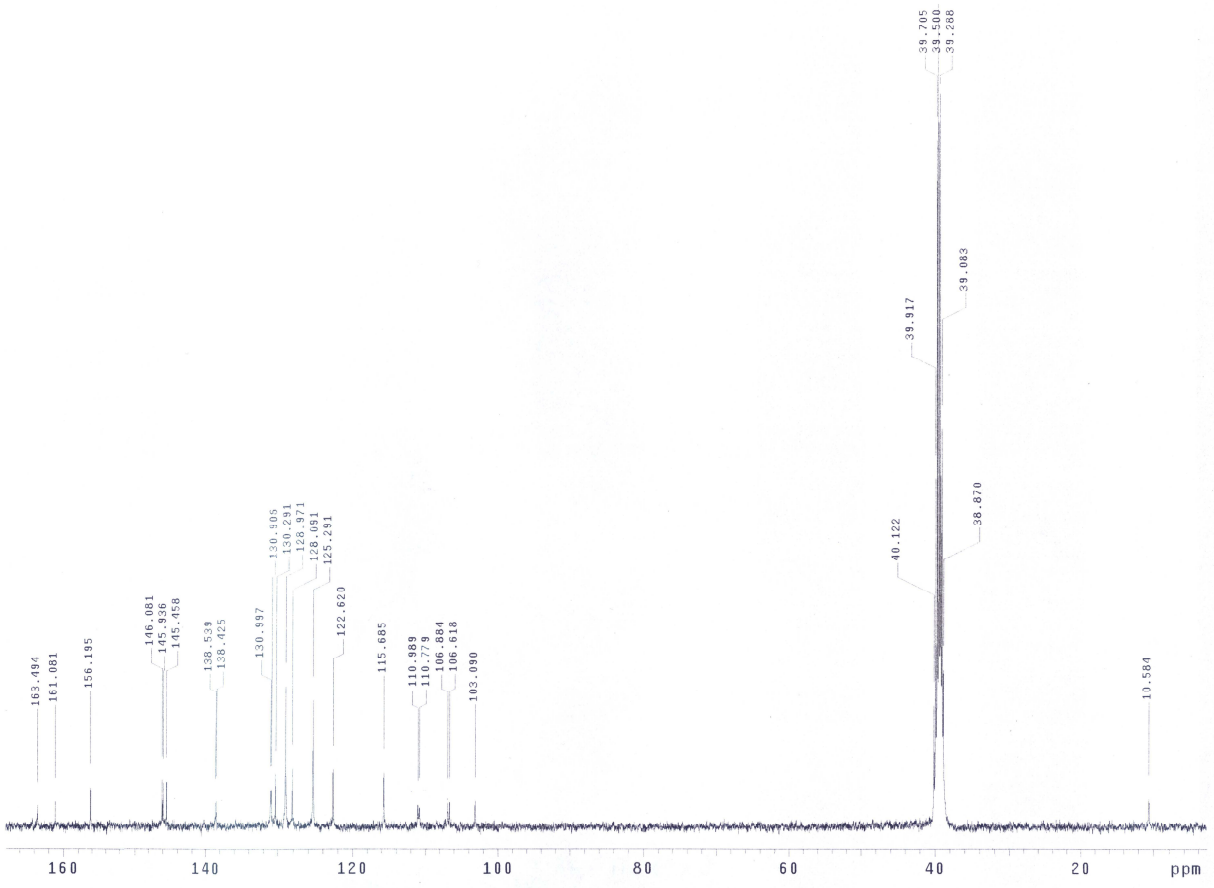

11.006
8.813
7.923
7.908
7.908
7.563
7.544
7.542
7.480
7.461
7.442
7.409
7.389
7.370
7.365
7.346
7.149
3.534
2.487
2.482
2.333
DMSO
15
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
1.56
4.40
4.69
10.58
36.15
6.09
14.59

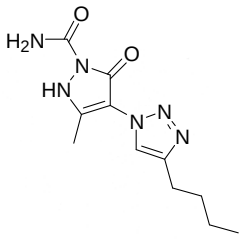

156.172
146.096
145.853
145.117
136.680
130.291
129.312
128.994
128.106
125.306
124.418
122.726
119.760
103.250
39.705
39.500
39.288
39.083
38.917
38.870
40.122
10.524
160
140
120
100
80
60
40
20
ppm


m-FC6H4HN
O
N
O
HN
N
N
N
Ph

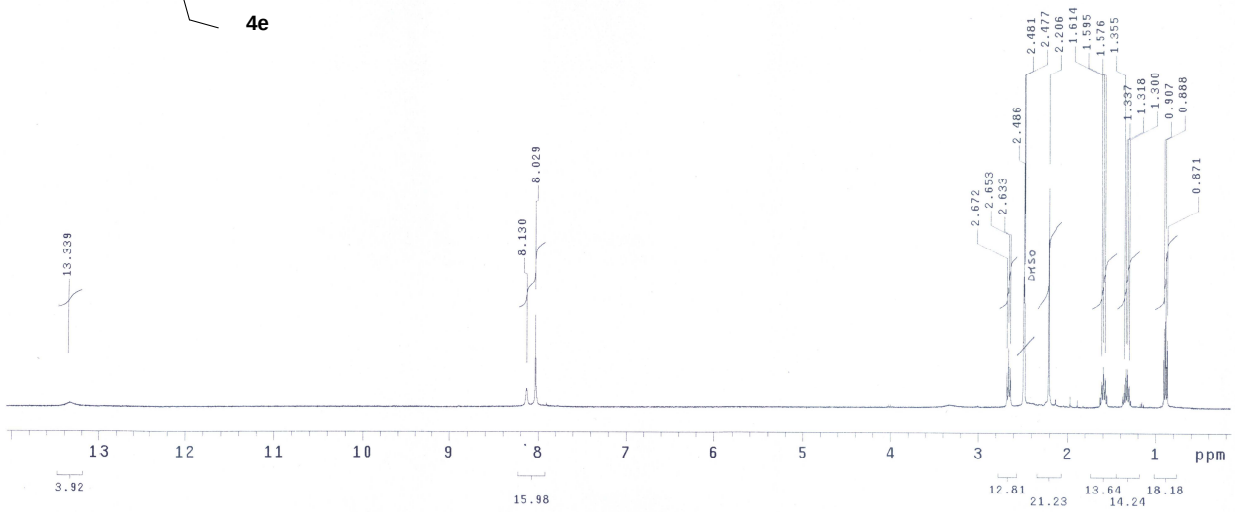
4d

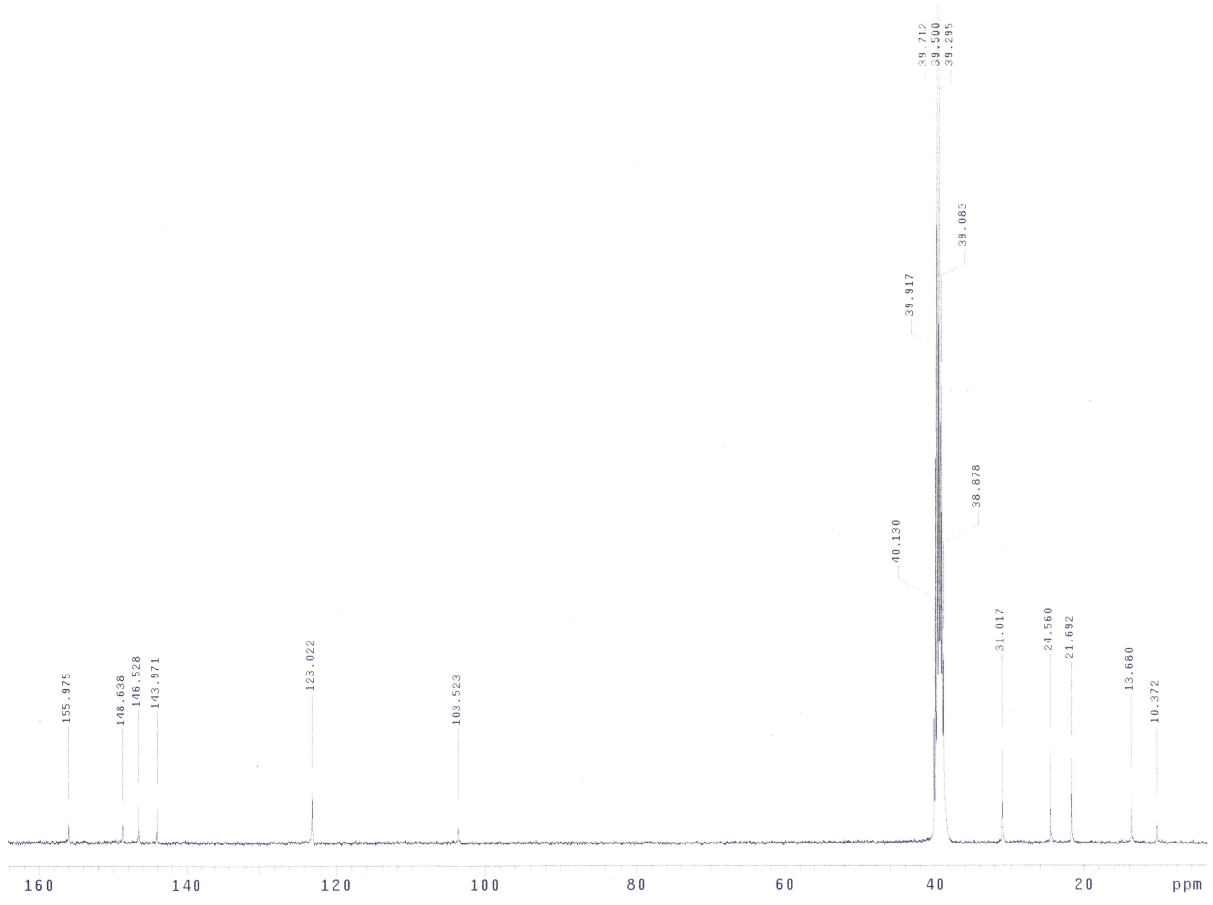

13.318
11.156
8.798
7.921
7.904
7.570
7.543
7.475
7.460
7.441
7.422
7.403
7.385
7.363
7.345
7.326
7.294
7.275
7.001
6.980
2.483
2.327
DMSO
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
1.63
6.75
7.58
14.36
42.09
6.82
20.76

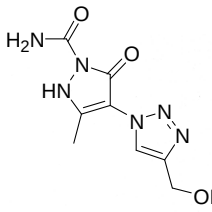

163.494
161.081
156.195
146.081
145.936
145.458
138.539
138.425
130.597
130.406
130.291
128.971
128.051
125.291
122.623
115.685
110.989
110.779
106.884
106.618
103.090
39.705
39.500
39.288
39.917
39.083
40.122
38.870
10.584
160
140
120
100
80
60
40
20
ppm



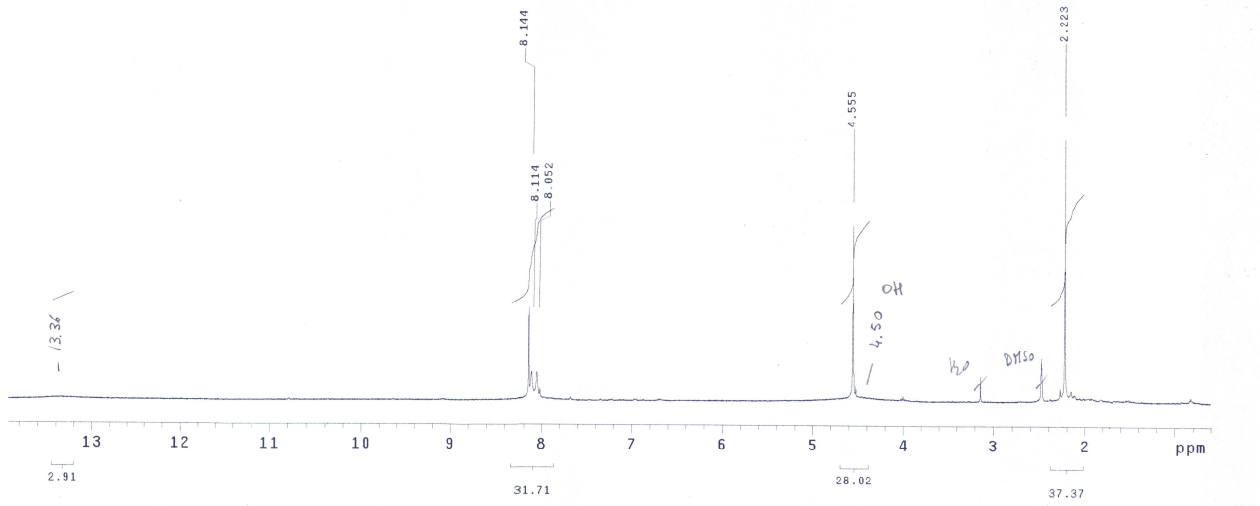
4e

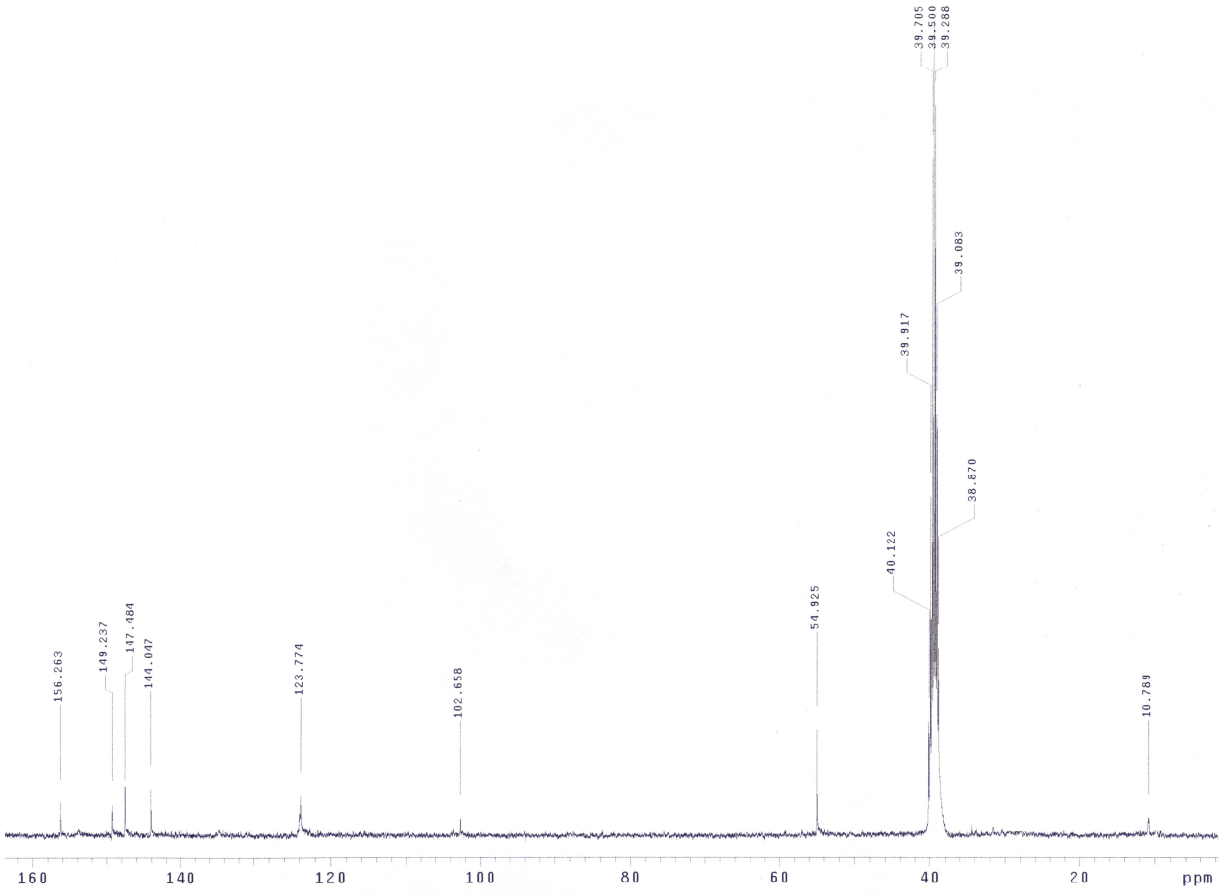

13.339
8.130
8.029
2.672
2.653
2.633
2.486
DMSO
2.481
2.477
2.206
1.614
1.595
1.576
1.355
1.337
1.318
1.300
0.907
0.888
0.871
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
3.92
15.98
12.81
21.23
13.64
14.24
18.18

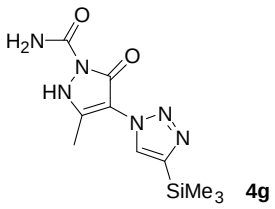

39.712
39.500
39.295
39.083
38.917
38.878
40.130
155.975
148.638
146.528
143.971
123.022
103.523
31.017
24.560
21.692
13.660
10.372
160 140 120 100 80 60 40 20 ppm


O
H2N
N
O
HN
N
N
N
OH

4f

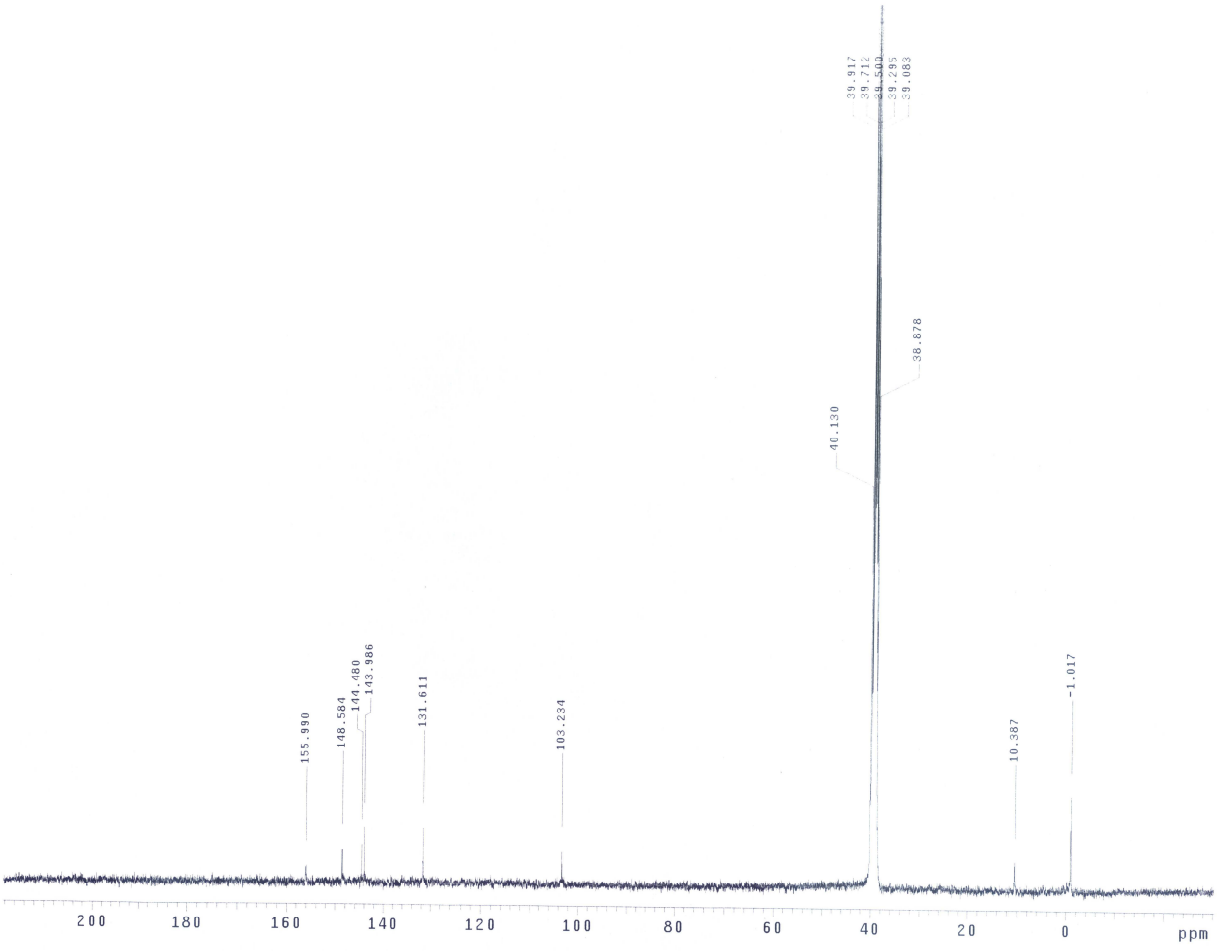

8.144
8.114
8.052
4.555
2.223
13.36
OH
4.50
H2O
DMSO
13
12
11
10
9
8
7
6
5
4
3
2
ppm
2.91
31.71
28.02
37.37

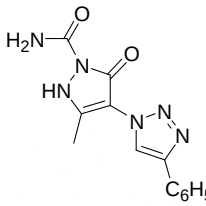

39.705
39.500
39.288
39.083
39.917
38.870
40.122
156.263
149.237
147.484
144.047
123.774
102.658
54.925
10.789
160
140
120
100
80
60
40
20
ppm


O
H2N
N
O
HN
N
N
N
SiMe3

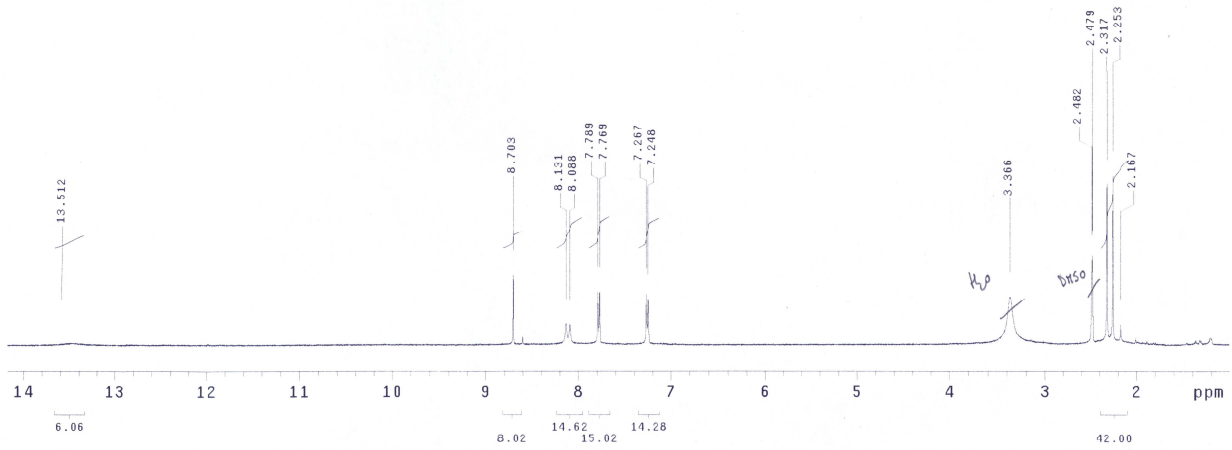
4g

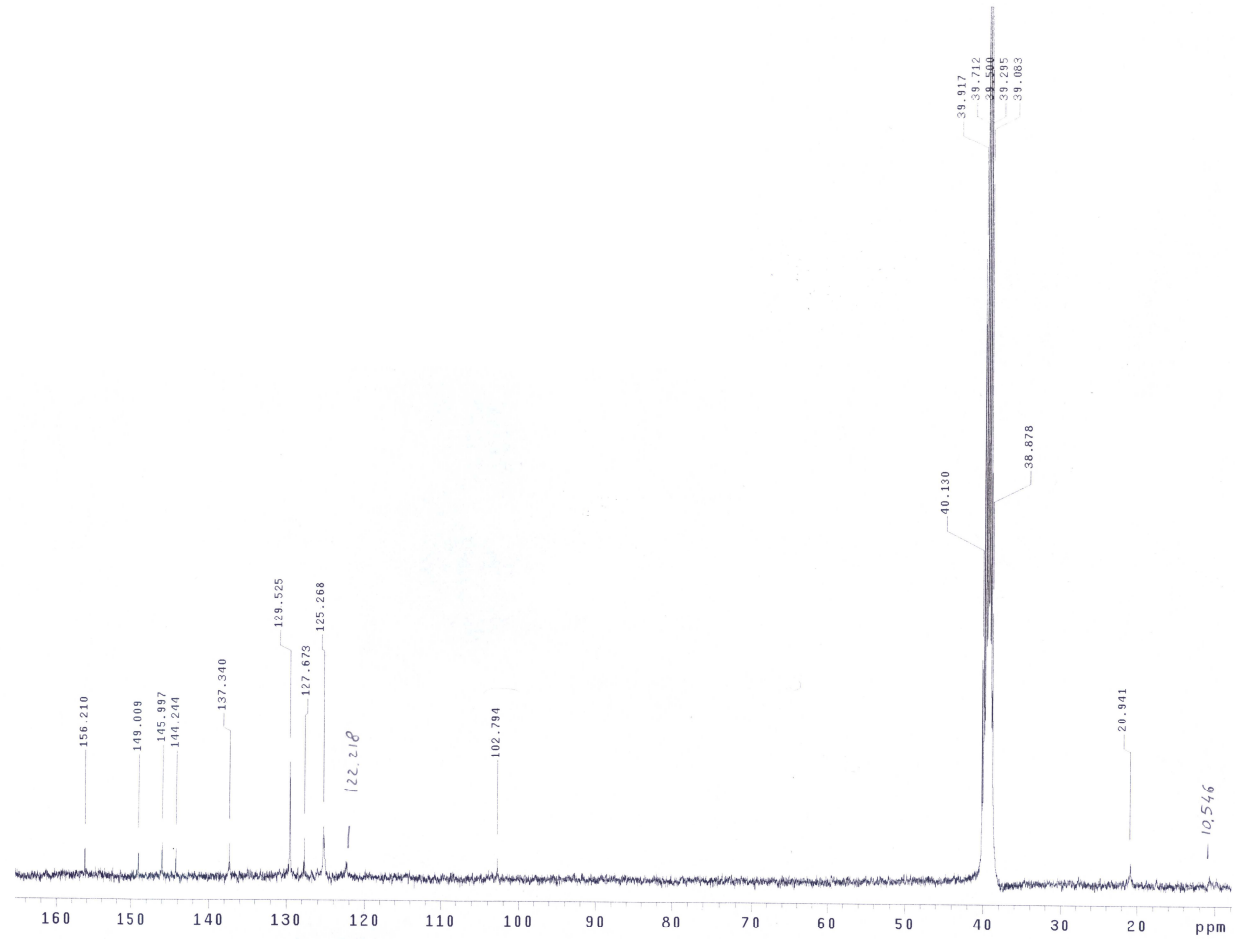
0.277
8.312
8.124
8.057
3.372
2.486
2.482
2.478
2.213
13.40
H2O
DMSO
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
5.21
12.99
7.02
23.51
51.26

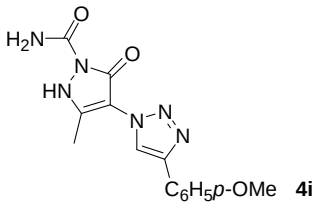

39.917
39.712
39.508
39.295
39.083
38.878
40.130
155.990
148.584
144.480
143.986
131.611
103.234
10.387
-1.017
200
180
160
140
120
100
80
60
40
20
0
ppm


O
H2N
N
O
HN
N
N
N

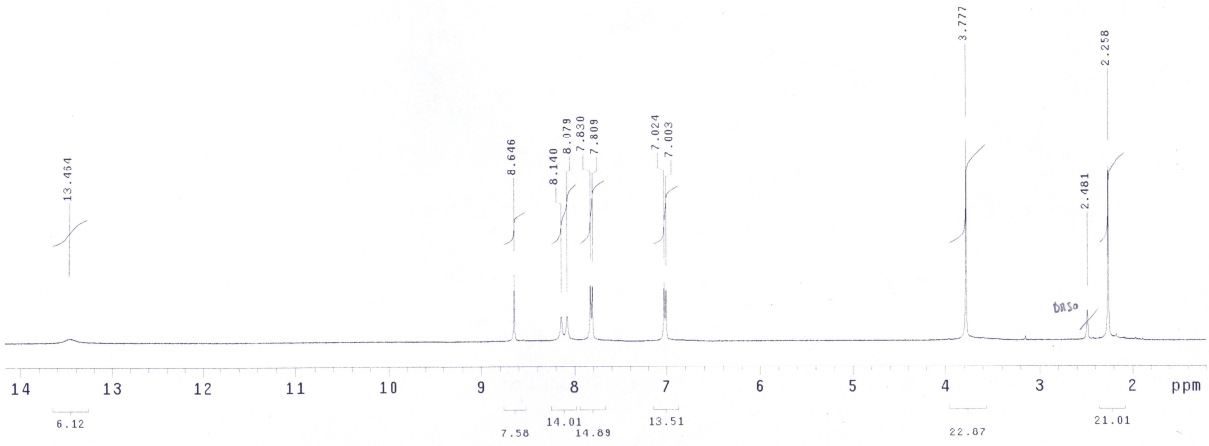
C_6H_5*p*-Me **4h**

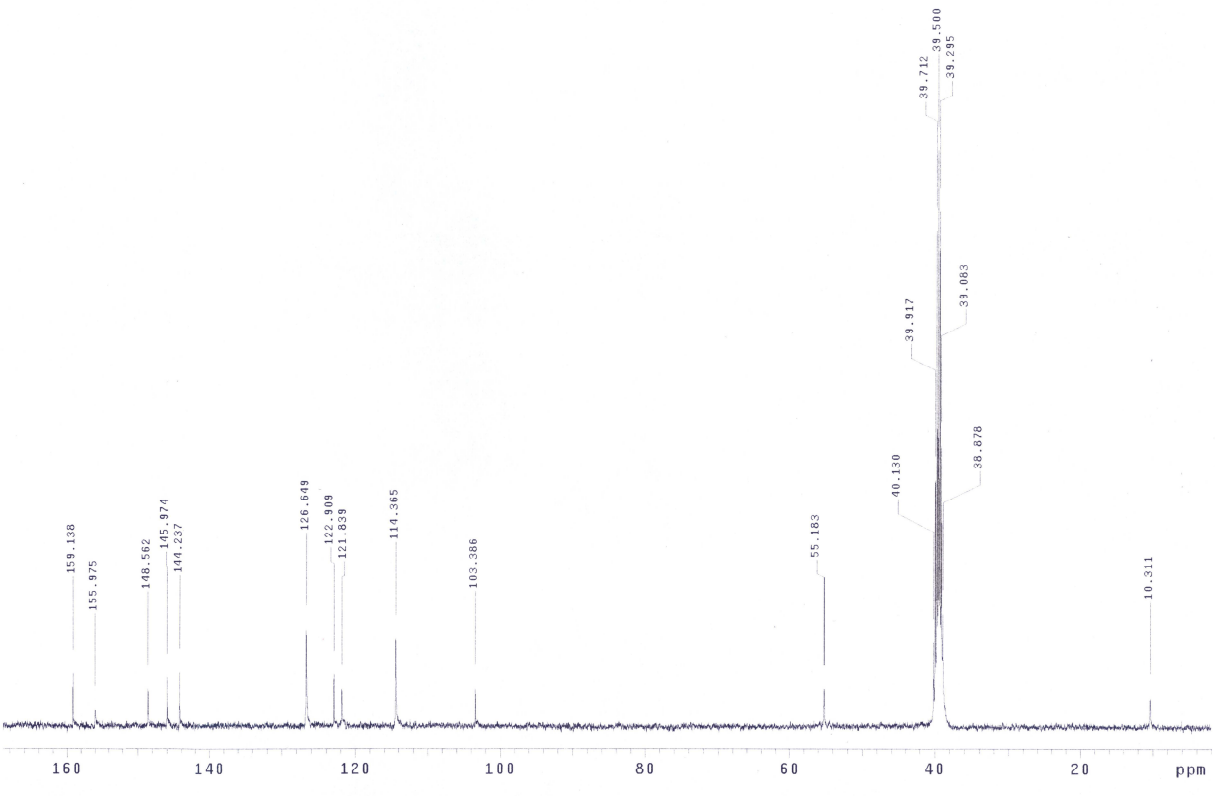

13.512
8.703
8.131
8.088
7.789
7.769
7.267
7.248
3.366
2.482
2.479
2.317
2.253
2.167
H2O
DMSO
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
6.06
8.02
14.62
15.02
14.28
42.00

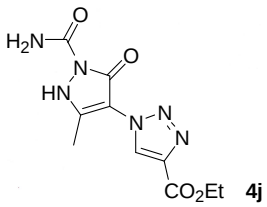

39.917
39.712
39.500
39.295
39.083
40.130
38.878
156.210
149.009
145.997
144.244
137.340
129.525
127.673
125.268
122.218
102.794
20.941
10.546
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


H2N
O
N
O
HN
N
N
N
C6H5p-OMe

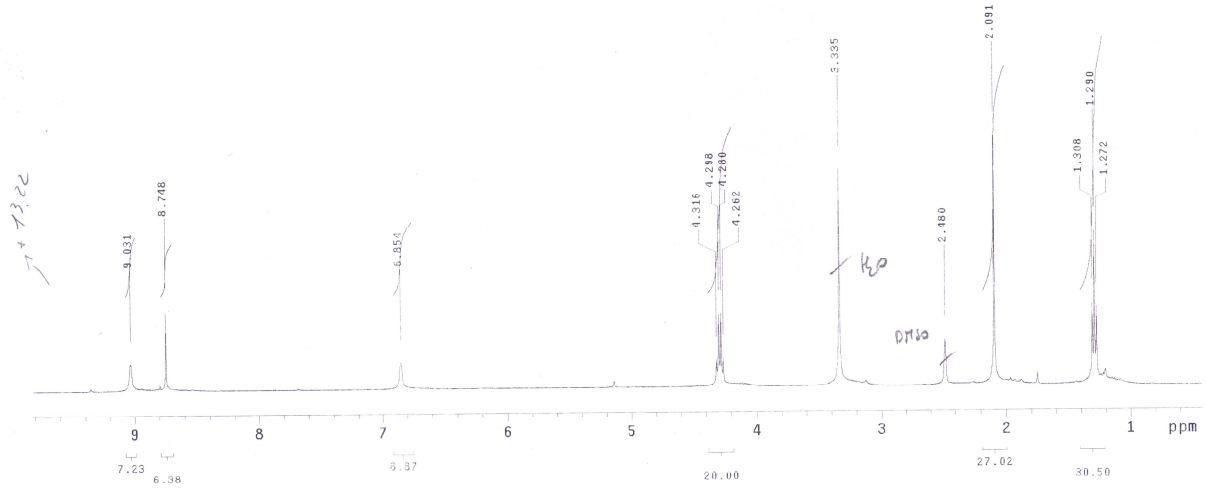
4i

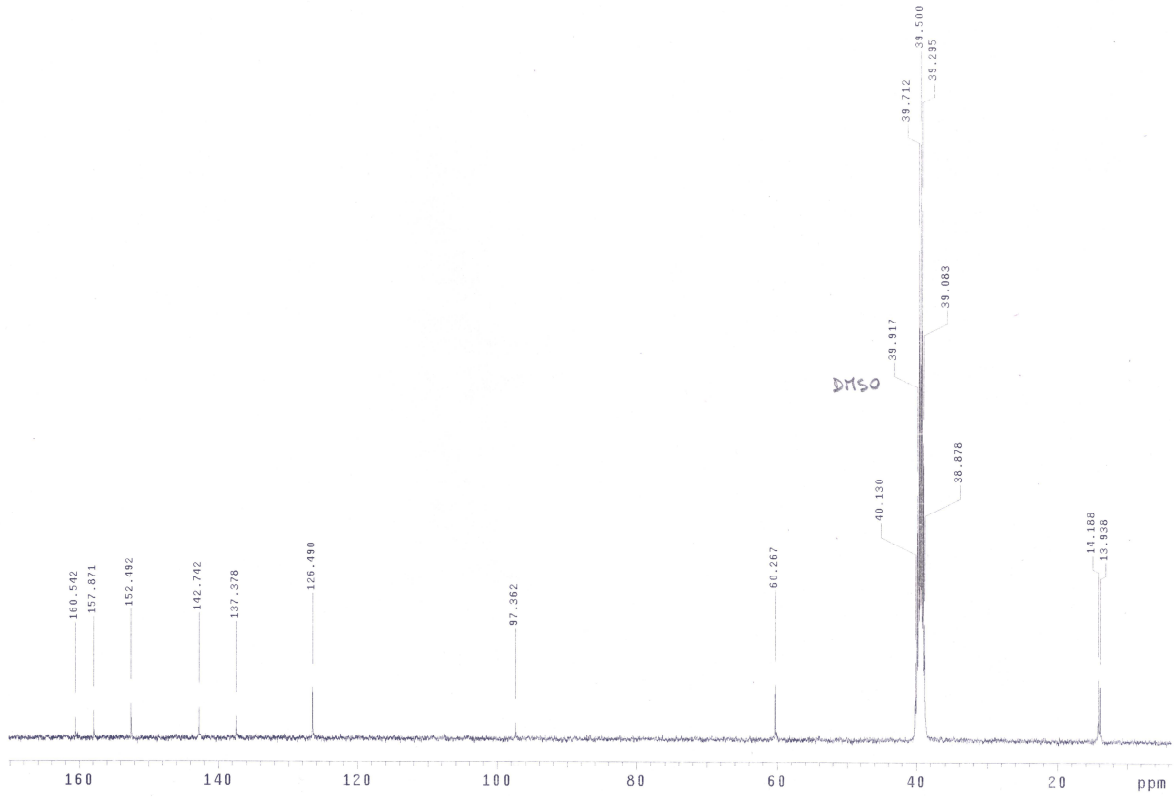

13.464
8.646
8.140
8.079
7.830
7.809
7.024
7.003
3.777
2.481
2.258
DMSO
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
6.12
7.58
14.01
14.89
13.51
22.67
21.01

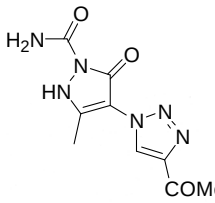

159.138
155.975
148.562
145.974
144.237
126.649
122.909
121.839
114.365
103.386
55.183
40.130
39.917
39.712
39.500
39.295
39.083
38.878
10.311
160
140
120
100
80
60
40
20
ppm


H2N
O
N
O
HN
N
N
N
CO2Et

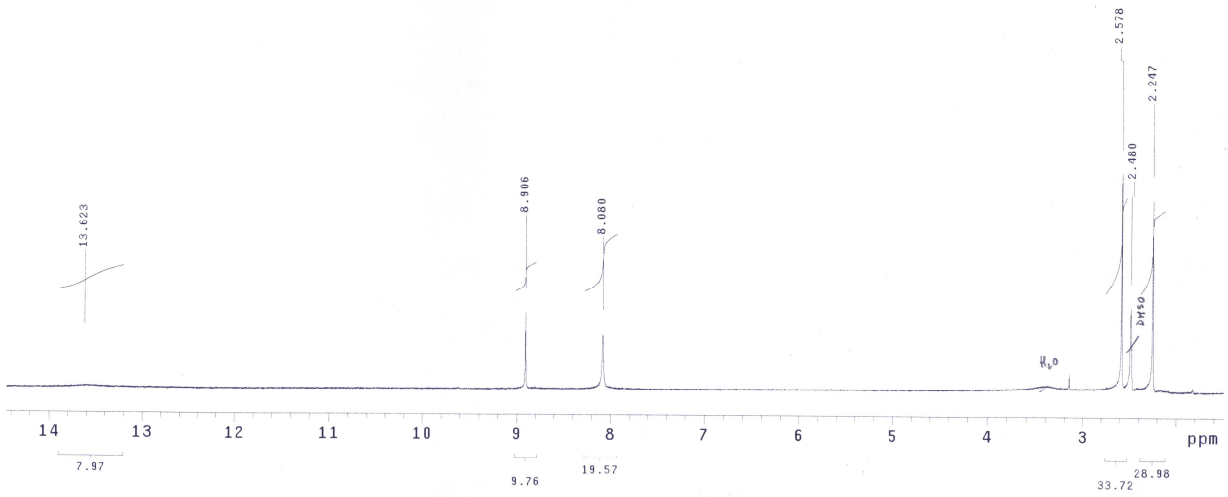
4j

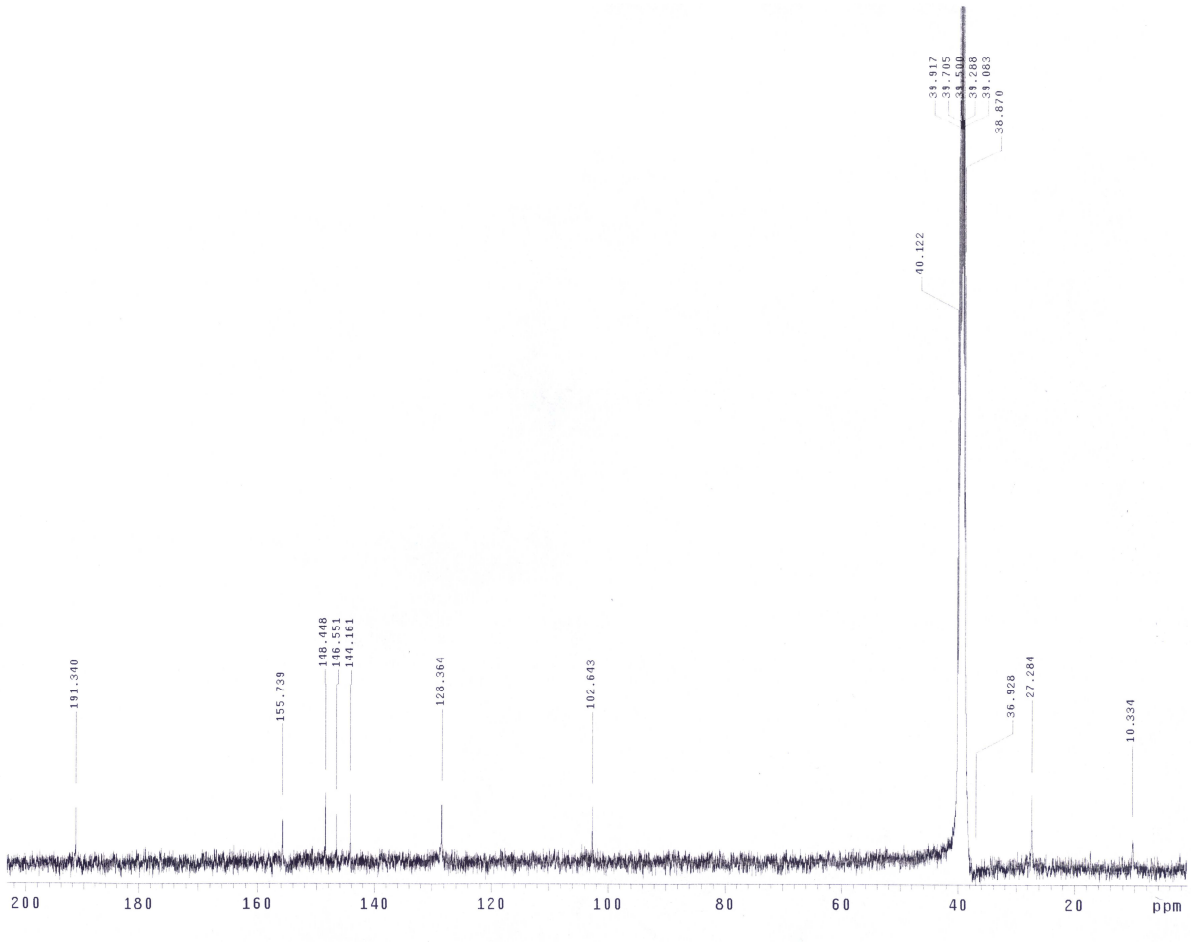

9.031
8.748
6.854
4.316
4.288
4.260
4.262
5.335
2.480
2.091
1.290
1.308
1.272
DMSO
ppm
7.23
6.38
6.87
20.00
27.02
30.50


160.542
157.871
152.192
142.742
137.378
126.490
97.362
66.267
40.130
39.917
39.712
39.500
39.295
39.083
38.876
DMSO
14.188
13.938
ppm


O
H2N
N
O
HN
N
N
N
COMe

4k


13.623
8.906
8.080
2.578
2.480
2.247
DMSO
H2O
14
13
12
11
10
9
8
7
6
5
4
3
ppm
7.97
9.76
19.57
33.72
28.98


191.340
155.739
148.448
146.551
144.161
128.364
102.643
40.122
39.917
39.705
39.500
39.288
39.083
38.870
36.928
27.284
10.334
200
180
160
140
120
100
80
60
40
20
ppm

4. References.

(1) Sommer, S. *Tetrahedron Lett.* **1977**, *18*, 117–120.

(2) (a) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 671–672.

(b) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 873–874.