

SUPPORTING INFORMATION

Synthesis of *N*-Acyl Triazolyl-Pyrazolines *via* Acylation Initiated by the Hydrazone Moiety with Carboxylic acids

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Experimental

General. All chemicals, reagents, and solvents were of commercially high purity grade purchased from Avra Synthesis Pvt. Ltd. and Merck Ltd. India. Silica gel (60–120 mesh) was used for column chromatographic isolation and purification of the compounds synthesized. Melting points were obtained on electro-thermal apparatus and are uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in CDCl_3 on Bruker Avance (300 MHz) spectrometer and the chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane, with coupling constant (J) values in Hertz

General procedure for the synthesis of pyrazolines⁴⁴

Equimolar quantities of 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1 mmol) and hydrazine hydrate (1 mmol) in ethanol (10 mL) was refluxed for 3 hours. The resulting mixture was poured onto crushed ice. The solid obtained was filtered as the pure product.

General procedure for acylation of 5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole

5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole **1** (1 mmol), was dissolved in carboxylic acids (2 mL) **2** and heated at 110 °C for an hour. After the completion of the reaction (monitored by TLC), the mixture was treated with aqueous sodium bicarbonate to neutralize the excess acid. Then the reaction mixture was extracted with dichloromethane to separate the organic layer and dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography using pet ether: ethyl acetate (93:7) as the eluent to afford the pure products (**3a-3i**) in excellent yields (91-95 %). While compounds **3a**¹⁰, **3b**¹¹, **3f**¹² are known, others are hitherto unknown compounds.

1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3a**)**. Yield: 95%. Pale brown solid. M.p. 106-108 °C. (lit¹), ¹H NMR (300 MHz, CDCl₃): δ 7.81 – 7.69 (m, 2H); 7.43 (s, 3H); 7.16 (d, *J* = 8.5 Hz, 2H); 6.84 (d, *J* = 8.5 Hz, 2H); 5.54 (dd, *J* = 11.7, 4.4 Hz, 1H); 3.76 (s, 3H); 3.74 – 3.62 (m, 1H); 3.15 (dd, *J* = 17.7, 4.4 Hz, 1H); 2.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 168.8; 158.9; 153.8; 134.1; 131.4; 130.2; 128.7; 126.8; 126.5; 114.1; 59.4; 55.2; 42.2; 21.9. Anal. Calcd. for (%) C₁₈H₁₈N₂O₂: C 73.45, H 6.16, N 9.52; Found: C 73.49, H 6.19, N 9.58.

1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (3b**)**. Yield: 92%. White solid. M.p. 85-87 °C. (lit²), ¹H NMR (300 MHz, CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 2H); 7.52 – 7.39 (m, 3H); 7.17 (d, *J* = 8.5 Hz, 2H); 6.84 (d, *J* = 8.5 Hz, 2H); 5.53 (dd, *J* = 11.8, 4.7 Hz, 1H); 3.77 (s, 3H); 3.75 – 3.64 (m, 1H); 3.15 (dd, *J* = 17.7, 4.6 Hz, 1H); 2.81 (q, *J* = 7.5 Hz, 2H); 1.18 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 172.2; 158.9; 153.5; 134.3; 131.5; 130.1; 128.7; 126.8; 126.4; 114.2; 59.5; 55.2; 41.9; 27.5; 8.9. Anal. Calcd. for (%) C₁₉H₂₀N₂O₂: C 74.00, H 6.54, N 9.08; Found: C 74.04, H 6.55, N 9.12.

1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c**)**. Yield: 94%. White solid. M.p. 105-107 °C. FTIR (KBr) ν/cm^{-1} 1658, 1599. ¹H NMR (300 MHz, CDCl₃): δ 7.74 (d, *J* = 6.7 Hz, 2H); 7.47 – 7.37 (m, 3H); 7.15 (d, *J* = 8.7 Hz, 2H); 6.82 (d, *J* = 8.7 Hz, 2H); 5.52 (dd, *J* = 11.8, 4.6 Hz, 1H); 3.74 (s, 3H); 3.71 – 3.61 (m, 1H); 3.11 (dd, *J* = 17.7, 4.6 Hz, 1H); 2.77 (ddd, *J* = 15.0, 9.0 Hz, 2H); 1.79 – 1.66 (m, 2H); 0.98 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 171.0; 158.6; 153.1; 134.0; 131.3; 129.9; 128.4; 126.6; 126.2; 125.1; 113.9; 59.2; 54.8; 41.7; 35.8; 18.1; 13.7. Anal. Calcd. for (%) C₂₀H₂₂N₂O₂: C 74.51, H 6.88, N 8.69; Found : C 74.57, H 6.93, N, 8.74.

1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)-2-phenylethanone (3d**)**. Yield: 91%. Pale brown solid. M.p. 130-132 °C. FTIR (KBr) ν/cm^{-1} 1689, 1597. ¹H NMR (300 MHz, CDCl₃): δ 7.80 – 7.76 (m, 2H); 7.75 – 7.59 (m, 3H); 7.48 – 7.29 (m, 5H); 7.05 (d, *J* = 8.6 Hz, 2H); 6.76 (d, *J* =

8.6 Hz, 2H); 5.50 (dd, J = 11.6, 4.5 Hz, 1H); 4.11 (q, J = 13.8 Hz, 2H); 3.72 (s, 3H); 3.71 – 3.65 (m, 1H); 3.10 (dd, J = 17.7, 4.6 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 169.0; 158.7; 154.1; 135.2; 133.7; 131.2; 130.2; 129.4; 129.2; 128.6; 128.4; 128.2; 126.9; 126.7; 126.5; 125.5; 113.9; 59.5; 55.0; 42.0; 41.1. Anal. Calcd. for (%) $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2$: C 77.81, H 5.99, N 7.56; Found : C 77.86, H 5.93, N 7.59.

1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)-2-phenoxyethanone (3e).

Yield: 93%. Pale brown solid. M.p. 93-95 °C. FTIR (KBr) ν/cm^{-1} 1685, 1598. ^1H NMR (300 MHz, CDCl_3): δ 7.71 (d, J = 6.9 Hz, 2H); 7.48 – 7.30 (m, 3H); 7.28 – 7.06 (m, 5H); 6.88 (d, J = 8.6 Hz, 2H); 6.76 (d, J = 8.6 Hz, 2H); 5.52 (dd, J = 11.8, 4.6 Hz, 1H); 5.21 (d, J = 5.5 Hz, 1H); 5.07 (d, J = 2.7 Hz, 1H); 3.77 (s, 3H); 3.71-3.69 (m, 1H); 3.15 (dd, J = 17.8, 4.6 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.5; 158.9; 158.2; 155.3; 133.1; 130.8; 130.5; 129.2; 128.6; 126.9; 126.6; 121.1; 114.7; 114.1; 66.0; 59.7; 55; 41.5. Anal. Calcd. for (%) $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_3$: C 74.59, H 5.74, N 7.25; Found : C 74.64, H 5.77, N 7.29.

2-Chloro-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3f). Yield: 94%. White solid. M.p. 128-130 °C. (lit³), ^1H NMR (300 MHz, CDCl_3): δ 7.75 (dd, J = 7.2, 2.4 Hz, 2H); 7.74 – 7.45 (m, 3H); 7.17 (d, J = 8.7 Hz, 2H); 6.84 (d, J = 8.7 Hz, 2H); 5.54 (dd, J = 11.7, 4.6 Hz, 1H); 4.57 (s, 2H); 3.86 – 3.82 (m, 1H); 3.76 (s, 3H); 3.21 (dd, J = 17.9, 4.6 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.5; 158.9; 155.3; 132.8; 130.5; 128.5; 126.8; 126.5; 113.7; 59.7; 54.9; 42.1; 41.8.

2-Hydroxy-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3g).

Yield: 91%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1676, 1608. ^1H NMR (300 MHz, CDCl_3): δ 7.73 (s, 2H); 7.45 (s, 3H); 7.18 (d, J = 8.1 Hz, 2H); 6.86 (d, J = 7.9 Hz, 2H); 5.54 (dd, J = 11.1, 4.6 Hz, 1H); 4.58 (s, 1H); 4.29 (s, 1H); 3.77 (d, J = 1.9 Hz, 4H One CH and CH_3 merged); 3.21 (dd, J = 17.8, 4.4 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 169.7; 158.9; 155.7; 132.9; 130.5; 128.5; 126.8; 126.6; 114.0; 60.9;

59.8; 54.9; 41.7. Anal. Calcd. for (%) C₁₈H₁₈N₂O₃: C 69.66, H 5.85, N 9.03; Found: C 69.69, H 5.83, N 9.05.

2-Mercapto-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3h).

Yield: 90%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1720, 1591. ¹H NMR (300 MHz, CDCl₃): δ 7.75 (dd, *J* = 6.1, 2.7 Hz, 2H); 7.53 – 7.39 (m, 3H); 7.18 (d, *J* = 8.4 Hz, 2H); 6.85 (d, *J* = 8.4 Hz, 2H); 5.53 (dd, *J* = 11.6, 4.5 Hz, 1H); 3.75 (s, 3H); 3.76 – 3.66 (m, 1H); 3.47 (d, *J* = 8.4 Hz, 2H); 3.18 (dd, *J* = 17.8, 4.4 Hz, 1H); 1.48 – 1.18 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 167.5; 159.1; 154.6; 133.2; 130.8; 130.4; 128.5; 126.8; 126.6; 126.5; 126.5; 113.9; 59.5; 54.9; 42.1; 26.6. Anal. Calcd. for (%) C₁₈H₁₈N₂O₂S: C 66.23, H 5.56, N 8.58, S 9.82; Found: C 66.27, H 5.53, N 8.54, S 9.84.

3-Mercapto-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (3i).

Yield: 92%. White solid. M.p. 122-124 °C. FTIR (KBr) ν/cm^{-1} 1649, 1525. ¹H NMR (300 MHz, CDCl₃): δ 7.84 – 7.69 (m, 2H); 7.56 – 7.35 (m, 3H); 7.17 (d, *J* = 8.7 Hz, 2H); 6.84 (d, *J* = 8.7 Hz, 2H); 5.54 (dd, *J* = 11.7, 4.6 Hz, 1H); 3.84 (s, 1H); 3.76 (s, 3H); 3.67 – 3.52 (m, 1H); 3.25 – 2.92 (m, 2H); 2.75 (dt, *J* = 13.5, 6.7 Hz, 2H); 1.57 (t, *J* = 8.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 168.8; 158.8; 154.2; 133.7; 131.0; 130.2; 128.5; 126.7; 126.4; 113.9; 59.4; 54.9; 41.9; 38.1; 19.6. Anal. Calcd. for (%) C₁₉H₂₀N₂O₂S : C 67.03, H 5.92, N 8.23, S 9.42; Found: C 67.07, H 5.95, N 8.21, S 9.45.

General procedure for the synthesis of triazole-pyrazoline hybrids

Equimolar quantities of 1-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-4-(4-methoxyphenyl) but-3-en-1-one (1 mmol) and hydrazine hydrate (1 mmol) in Ethanol (10 mL) was refluxed for 3 hours. The resulting mixture was poured onto crushed ice. The solid obtained was filtered as a pure product.

General procedure for the acylation of 1-Benzyl-4-(5-(4-methoxybenzyl)-4,5-dihydro-1*H*-pyrazol-3-yl)-5-methyl-1*H*-1,2,3-triazole

1-Benzyl-4-(5-(4-methoxybenzyl)-4,5-dihydro-1*H*-pyrazol-3-yl)-5-methyl-1*H*-1,2,3-triazole **1** (1 mmol) in carboxylic acids (2 mL) **2** was heated at 110 °C for 1 hour. After the completion of the reaction (as monitored by TLC), the mixture was treated with aqueous sodium bicarbonate to wash the excess of acid. Then the reaction mixture was extracted with dichloromethane to separate the organic layer and dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography using pet ether: ethyl acetate (90:10) as the eluent to afford the pure products (**3j-r**) in excellent yields (89-94 %). While compounds (**3j& 3k**)¹⁷ are known, other compounds are hitherto unknown.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (**3j**). Yield: 92%. White solid. M.p. 142-144 °C. (lit⁴), ¹H NMR (300 MHz, CDCl₃): δ 7.43 – 7.08 (m, 5H); 6.96 (d, *J* = 8.7 Hz, 2H); 6.83 (d, *J* = 8.6 Hz, 2H); 5.55 (s, 2H); 5.50 (dd, *J* = 11.8, 4.6 Hz, 1H); 3.85 (dd, *J* = 11.6, 18.2 Hz, 1H); 3.77 (s, 3H); 3.45 (dd, *J* = 18.5, 4.5 Hz, 1H); 2.51 (s, 3H); 2.32 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 168.5; 158.9; 149.5; 138.1; 134.1; 133.7; 132.9; 129.0; 128.5; 127.2; 126.9; 114.0; 58.3; 55.2; 51.9; 43.1; 21.8; 9.4. Anal. Calcd. for (%) C₂₂H₂₃N₅O₂ : C 67.85, H 5.95, N, 17.98; Found: C 67.87, H 5.96, N 17.97.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (**3k**). Yield: 90%. Colorless solid. M.p. 156-158 °C. (lit⁴), ¹H NMR (300 MHz, CDCl₃): δ 7.44 – 7.05 (m, 5H); 6.96 (d, *J* = 7.4 Hz, 2H); 6.83 (d, *J* = 8.4 Hz, 2H); 5.56 (s, 2H); 5.48 (dd, *J* = 11.8, 4.7 Hz, 1H); 3.86 (dd, *J* = 18.2, 12.0 Hz, 1H); 3.77 (s, 3H); 3.44 (dd, *J* = 18.5, 4.6 Hz, 1H); 2.69 (q, *J* = 7.5 Hz, 2H); 2.51 (s, 3H); 1.14 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 171.9; 158.8; 149.2; 138.4; 134.1; 133.9; 132.5; 128.9; 128.4; 127.2; 127.0; 126.9; 114.1; 58.4; 55.1; 51.8; 42.8; 27.4; 9.4; 8.8. Anal. Calcd. for (%) C₂₃H₂₅N₅O₂: C 68.47, H 6.25, N 17.36; Found: C 68.51, H 6.21, N 17.33

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (**3l**). Yield: 94%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1626, 1568. ^1H NMR (300 MHz, CDCl_3): δ 7.35 (s, 3H); 7.23 – 7.11 (m, 2H); 6.94 (d, $J = 7.4$ Hz, 2H); 6.83 (d, $J = 8.0$ Hz, 2H); 5.55 (s, 2H); 5.49 (dd, $J = 12.0, 4.4$ Hz, 1H); 3.83 – 3.72 (m, 1H); 3.77 (s, 3H); 3.43 (dd, $J = 18.3, 4.4$ Hz, 1H); 2.65 (dd, $J = 14.0, 7.0$ Hz, 2H); 2.52 (s, 3H); 1.83 – 1.54 (m, 2H); 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 170.8; 158.5; 149.0; 137.8; 133.9; 133.6; 132.7; 128.7; 128.1; 126.9; 126.6; 113.8; 58.0; 54.8; 51.5; 42.7; 35.8; 18.0; 13.7; 9.1. Anal. Calcd. for (%) $\text{C}_{24}\text{H}_{27}\text{N}_5\text{O}_2$: C 69.04, H 6.52, N 16.77; Found: C 69.08, H 6.50, N 16.81.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-1*H*-pyrazol-1-yl)-2-phenylethanone (**3m**). Yield: 91%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1654, 1508. ^1H NMR (300 MHz, CDCl_3): δ 7.41 – 7.33 (m, 4H); 7.26 (s, 4H); 7.21 (d, $J = 6.9$ Hz, 2H); 7.08 (d, $J = 8.6$ Hz, 2H); 6.78 (d, $J = 8.6$ Hz, 2H); 5.54 (s, 2H); 5.48 (dd, $J = 11.7, 4.5$ Hz, 1H); 4.01 (d, $J = 3.5$ Hz, 2H); 3.87 – 3.81 (m, 1H); 3.75 (s, 3H); 3.43 (dd, $J = 18.5, 4.7$ Hz, 1H); 2.51 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 168.5; 158.7; 149.7; 137.9; 135.1; 133.9; 133.4; 132.8; 129.0; 128.9; 128.3; 128.1; 127.1; 126.8; 126.4; 113.8; 58.3; 54.9; 51.7; 42.9; 41.0; 9.3. Anal. Calcd. for (%) $\text{C}_{28}\text{H}_{27}\text{N}_5\text{O}_2$: C 72.24, H 5.85, N 15.04; Found: C 72.28, H 5.83, N, 15.09.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-1*H*-pyrazol-1-yl)-2-phenoxyethanone (**3n**). Yield: 89%. Brown solid. M.p. 95–97 °C. FTIR (KBr) ν/cm^{-1} 1685, 1598. ^1H NMR (300 MHz, CDCl_3): δ 7.36 (d, $J = 6.5$ Hz, 4H); 7.23 – 7.16 (m, 6H); 6.98 – 6.89 (m, 2H); 6.88 (d, $J = 8.5$ Hz, 2H); 6.82 (d, $J = 8.6$ Hz, 2H); 5.55 (s, 2H); 5.51 (d, $J = 4.7$ Hz, merged with NCH_2 1H); 5.01 (d, $J = 2.1$ Hz, 2H); 3.90 (dd, $J = 17.7, 10.8$ Hz, 1H); 3.75 (s, 3H); 3.51 (dd, $J = 18.7, 4.7$ Hz, 1H); 2.49 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.0; 158.8; 157.9; 150.6; 137.4; 133.9; 133.1; 132.7; 129.0;

128.7; 128.2; 126.9; 120.9; 114.3; 113.8; 65.8; 58.4; 54.9; 51.5; 42.4; 9.2. Anal. Calcd. for (%) C₂₈H₂₇N₅O₃ : C 69.84, H 5.65, N 14.54; Found: C 69.80, H 5.67, N 14.57.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-2-chloroethanone (**3o**). Yield: 91%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1664, 1610. ¹H NMR (300 MHz, CDCl₃): δ 7.43 – 7.12 (m, 5H); 6.91 (d, *J* = 8.3 Hz, 2H); 6.84 (d, *J* = 8.3 Hz, 2H); 5.55 (s, 2H); 5.49 (dd, *J* = 11.6, 4.6 Hz, 1H); 4.42 (s, 2H); 3.91 (dd, *J* = 18.7, 11.6 Hz, 1H); 3.76 (s, 3H); 3.51 (dd, *J* = 18.7, 4.4 Hz, 1H); 2.51 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 163.5; 158.9; 150.9; 134.4; 133.9; 133.3; 132.5; 128.9; 128.4; 127.1; 127.0; 114.0; 58.7; 55.1; 51.8; 42.9; 41.9; 9.4. Anal. Calcd. for (%) C₂₂H₂₂ClN₅O₂ : C 62.34, H 5.23, N 16.52; Found: C 62.36, H 5.27, N 16.48.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-2-hydroxyethanone (**3p**). Yield: 93%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1662, 1508. ¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.07 (m, 5H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 7.4 Hz, 2H), 5.55 (s, 2H), 5.49 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.47 (s, 1H), 4.28 (s, 1H), 3.87 (dd, *J* = 19.1, 7.7 Hz, 1H), 3.77 (s, 3H), 3.50 (dd, *J* = 18.7, 3.5 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) : δ 169.4, 158.9, 151.2, 137.4, 133.9, 133.3, 132.6, 128.9, 128.3, 127.1, 126.9, 113.9, 60.7, 58.7, 54.9, 51.7, 42.7, 9.2. Anal. Calcd. for (%) C₂₂H₂₃N₅O₃ : C, 65.17; H, 5.72; N, 17.27; Found: C, 65.21; H, 5.75; N, 17.22.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-2-mercaptoethanone (**3q**). Yield: 92%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1647, 1550. ¹H NMR (300 MHz, CDCl₃): δ 7.40 – 7.16 (m, 5H); 6.92 (d, *J* = 8.4 Hz, 2H); 6.83 (d, *J* = 8.4 Hz, 2H); 5.55 (s, 2H); 5.48 (dd, *J* = 11.9, 4.4 Hz, 1H); 3.94–3.85 (m, 1H); 3.75 (s, 3H); 3.60 (d, *J* = 5.0 Hz, 2H); 3.48 (dd, *J* = 14.4, 3.9 Hz, 1H); 2.51 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 167.3; 150.4; 144.1; 137.4; 133.8; 132.8; 128.7; 128.2; 126.9; 126.7; 126.6; 113.8; 58.5; 54.9; 51.5; 42.9; 32.6; 9.2. Anal. Calcd. for (%) C₂₂H₂₃N₅O₂S : C 62.69, H 5.50, N 16.61, S 7.61; Found: C 62.72, H 5.54, N 16.58, S 7.59.

1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-hydroxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-3-mercaptopropan-1-one (**3r**). Yield: 94%. Gummy matter. FTIR (KBr) ν/cm^{-1} 1656, 1577. ^1H NMR (300 MHz, CDCl_3): δ 7.41 – 7.11 (m, 5H); 6.91 (d, J = 8.4 Hz, 2H); 6.83 (d, J = 8.4 Hz, 2H); 5.54 (s, 2H); 5.53 – 5.42 (m, 1H); 3.88 (dd, J = 18.7, 11.7 Hz, 1H); 3.75 (s, 3H); 3.44 (dd, J = 18.5, 4.4 Hz, 1H); 3.15 – 2.92 (m, 2H); 2.81 (s, 2H); 2.52 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 168.5; 158.7; 149.8; 137.7; 133.9; 133.3; 132.9; 128.8; 128.3; 127.0; 126.7; 113.9; 58.3; 54.9; 51.6; 42.9; 37.9; 19.5; 9.3. Anal. Calcd. for (%) $\text{C}_{23}\text{H}_{25}\text{N}_5\text{O}_2\text{S}$: C 63.43, H 5.79, N 16.08, S 7.36; Found: C 63.46, H 5.84, N 16.05, S 7.33.

General procedure for the synthesis of *N*-acyl hyrazones (**8a-i**)

Acetophenone/benzaldehyde or 1-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)ethanone **5** (1 mmol), was dissolved in carboxylic acids (2 mL) **2** to which hydrazine hydrate **6** (1 mmol) was added slowly while the mixture was maintained in ice cold condition with stirring for 30 min. Then the mixture was allowed to reach the room temperature and then heated to reflux for 6 hours. Then it was treated with aqueous NaHCO_3 solution followed by the extraction with dichloromethane. Then, the organic layer was separated and dried over anhydrous Na_2SO_4 . It was then separated by column chromatography using petroleum ether: ethyl acetate (93:7) as the eluent to afford the product (**8a-i**) in excellent yields (90-94 %). While compound **8a**⁴³ is known, others are hitherto unknown.

(*E*)-*N*'-(1-Phenylethylidene) acetohydrazide (**8a**). Yield: 91%. White solid. M.p. 130-132 °C. (lit⁵), ^1H NMR (300 MHz, CDCl_3): δ 9.38 (s, 1H); 7.76 (d, J = 7.7 Hz, 2H); 7.39 (m, 3H); 2.40 (s, 3H); 2.27 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 174.5; 147.6; 138.0; 128.9; 128.1; 126.4; 125.8; 20.5; 13.0. . Anal. Calcd. for (%) $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$: C 68.16, H 6.86, N 15.90; Found: C 68.21, H 6.89, N 15.95.

(E)-N'-(1-Phenylethylidene)propionohydrazide (8b). Yield: 93%. White solid. M.p. 137-139 °C. FTIR (KBr) ν/cm^{-1} 1676, 1560. ^1H NMR (300 MHz, CDCl_3): δ 8.62 (s, 1H); 8.00 – 7.61 (m, 2H); 7.71 – 7.41 (m, 3H); 2.82 (q, $J = 7.5$ Hz, 2H); 2.22 (s, 3H); 1.24 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 177.6; 147.1; 138.1; 128.7; 128.1; 125.8; 26.0; 12.8; 8.6. Anal. Calcd. for (%) $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$: C 69.45; H 7.42, N 14.73; Found: C 69.48, H 7.47, N 14.70.

(E)-N'-(1-Phenylethylidene)butyrohydrazide (8c). Yield: 92%. White solid. M.p. 102-104 °C. FTIR (KBr) ν/cm^{-1} 1676, 1654. ^1H NMR (300 MHz, CDCl_3): δ 9.24 (s, 1H); 7.75 (dd, $J = 7.0, 2.6$ Hz, 2H); 7.68 – 7.40 (m, 3H); 2.78 (t, $J = 7.5$ Hz, 2H); 2.25 (s, 3H); 1.76 (dt, $J = 14.7, 7.4$ Hz, 2H); 1.03 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 176.8; 147.1; 138.2; 128.9; 128.3; 125.9; 34.7; 18.1; 13.9; 12.9. Anal. Calcd. for (%) $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$: C 70.56, H 7.90, N 13.71; Found: C 70.59, H 7.93, N 13.68.

(E)-N'-Benzylideneacetohydrazide (8d). Yield: 93%; White solid, M.p. 135-137 °C. FTIR (KBr) ν/cm^{-1} 1676, 1608. ^1H NMR (300 MHz, CDCl_3): δ 10.05 (s, 1H); 7.84 (s, 1H); 7.68 (dd, $J = 6.6, 2.9$ Hz, 2H); 7.53 – 7.30 (m, 3H); 2.40 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 174.7; 144.3; 133.9; 129.8; 128.5; 126.9; 20.2. Anal. Calcd. for (%) $\text{C}_9\text{H}_{10}\text{N}_2\text{O}$: C, 66.65; H, 6.21; N, 17.27; Found: C, 66.71; H, 6.26; N, 17.21.

(E)-N'-Benzylidenepropionohydrazide (8e). Yield: 90%. White solid. M.p. 116-118 °C. FTIR (KBr) ν/cm^{-1} 1672, 1597. ^1H NMR (300 MHz, CDCl_3): δ 10.19 (s, 1H); 7.85 (s, 1H); 7.81 – 7.60 (m, 2H); 7.41 – 7.38 (m, 3H); 2.80 (q, $J = 7.5$ Hz, 2H); 1.25 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 177.8; 143.9; 134.0; 129.7; 128.5; 126.9; 25.9; 8.8. Anal. Calcd. for (%) $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$: C 68.16, H 6.86, N 15.90; Found: C 68.21, H 6.89, N 15.88.

(E)-N'-Benzylidenebutyrohydrazide (8f). Yield: 94%. White solid. M.p. 89-91 °C. FTIR (KBr) ν/cm^{-1} 1675, 1600. ^1H NMR (300 MHz, CDCl_3): δ 10.91 (s, 1H); 7.92 (s, 1H); 7.76 – 7.61 (m, 2H); 7.45 – 7.32 (m, 3H); 2.77 (t, $J = 7.6$ Hz, 2H); 1.79 (dq, $J = 14.9, 7.4$ Hz, 2H); 1.05 (t, $J = 7.4$ Hz, 3H). ^{13}C

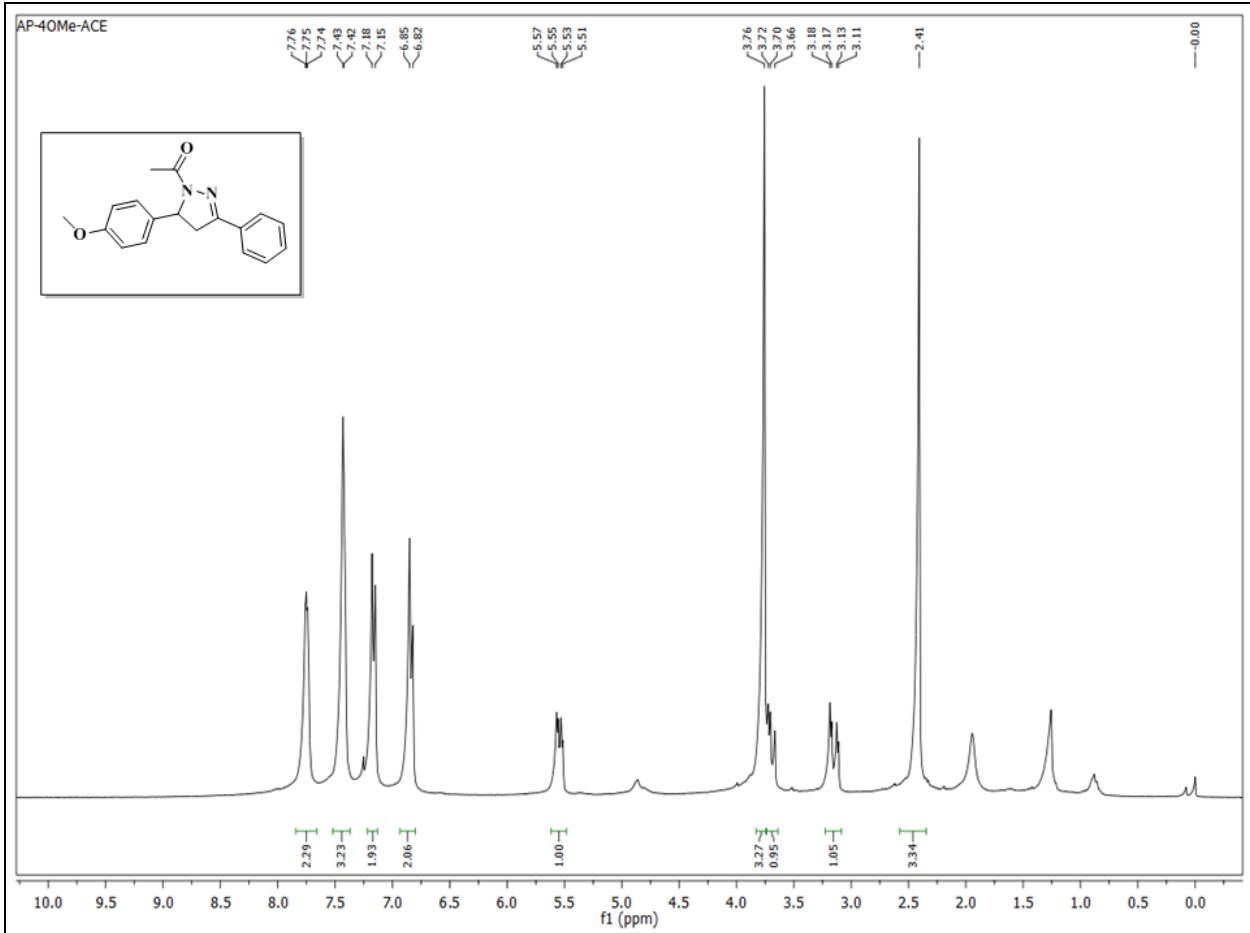
NMR (75 MHz, CDCl₃): δ 176.4; 143.4; 133.9; 129.9; 128.7; 127.1; 34.6; 18.2; 13.9. Anal. Calcd. for (%) C₁₁H₁₄N₂O (190.24): C 69.45, H 7.42, N 14.73; Found: C 69.48, H 7.46, N 14.70.

(E)-N'-(1-(1-Benzyl-5-methyl-1H-1,2,3-triazol-4-yl)ethylidene)acetohydrazide (**8g**). Yield: 93%. Gummy matter. FTIR (KBr) ν/cm⁻¹ 1670, 1560. ¹H NMR (300 MHz, CDCl₃): δ 8.67 (s, 1H); 7.35 (dd, *J* = 8.4, 3.3 Hz, 2H); 7.19 (dd, *J* = 6.6, 4.7 Hz, 2H); 5.54 (s, 2H); 2.43 (s, 3H); 2.42 (s, 3H); 2.28 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 173.4; 144.3; 131.5; 134.2; 128.6; 127.9; 126.7; 51.3; 20.4; 12.7; 9.7. Anal. Calcd. for (%) C₁₄H₁₇N₅O : C 61.98, H 6.32, N 25.81; Found: C 61.95, H 6.35, N 25.77.

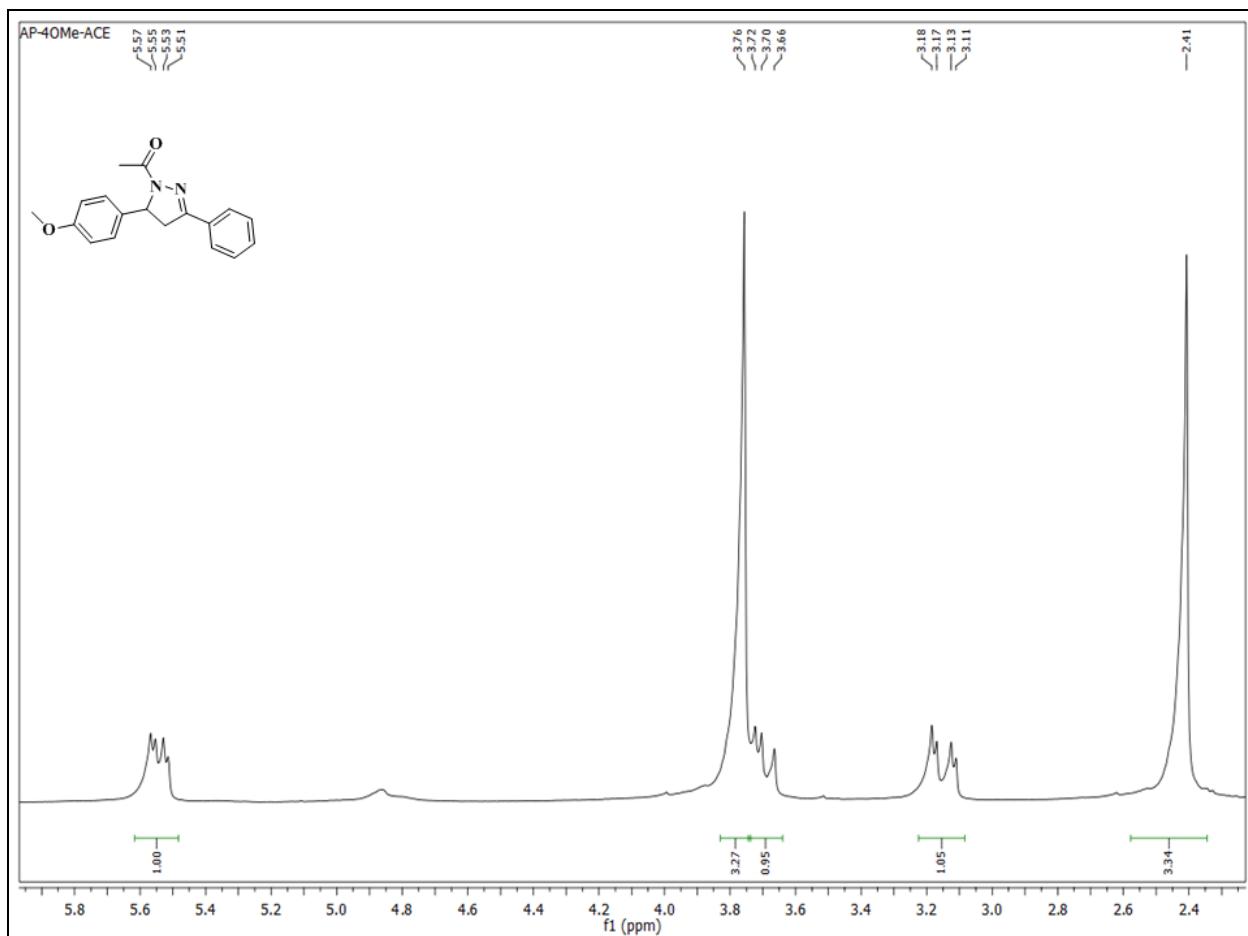
(E)-N'-(1-(1-Benzyl-5-methyl-1H-1,2,3-triazol-4-yl)ethylidene)propionohydrazide (**8h**). Yield: 91%. Gummy matter. FTIR (KBr) ν/cm⁻¹ 1676, 1560. ¹H NMR (300 MHz, CDCl₃): δ 7.36 – 7.29 (m, 4H); 7.22 – 7.20 (m, 1H); 5.53 (s, 2H); 2.53 (s, 3H); 2.50 (s, 3H); 2.45 – 2.38 (m, 2H); 1.17 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 176.4; 143.7; 134.2; 132.8; 128.6; 128.1; 126.8; 51.3; 29.1; 14.8; 9.9; 9.6. Anal. Calcd. for (%) C₁₅H₁₉N₅O : C 63.14, H 6.71, N 24.54; Found: C 63.17, H 6.73, N 24.51.

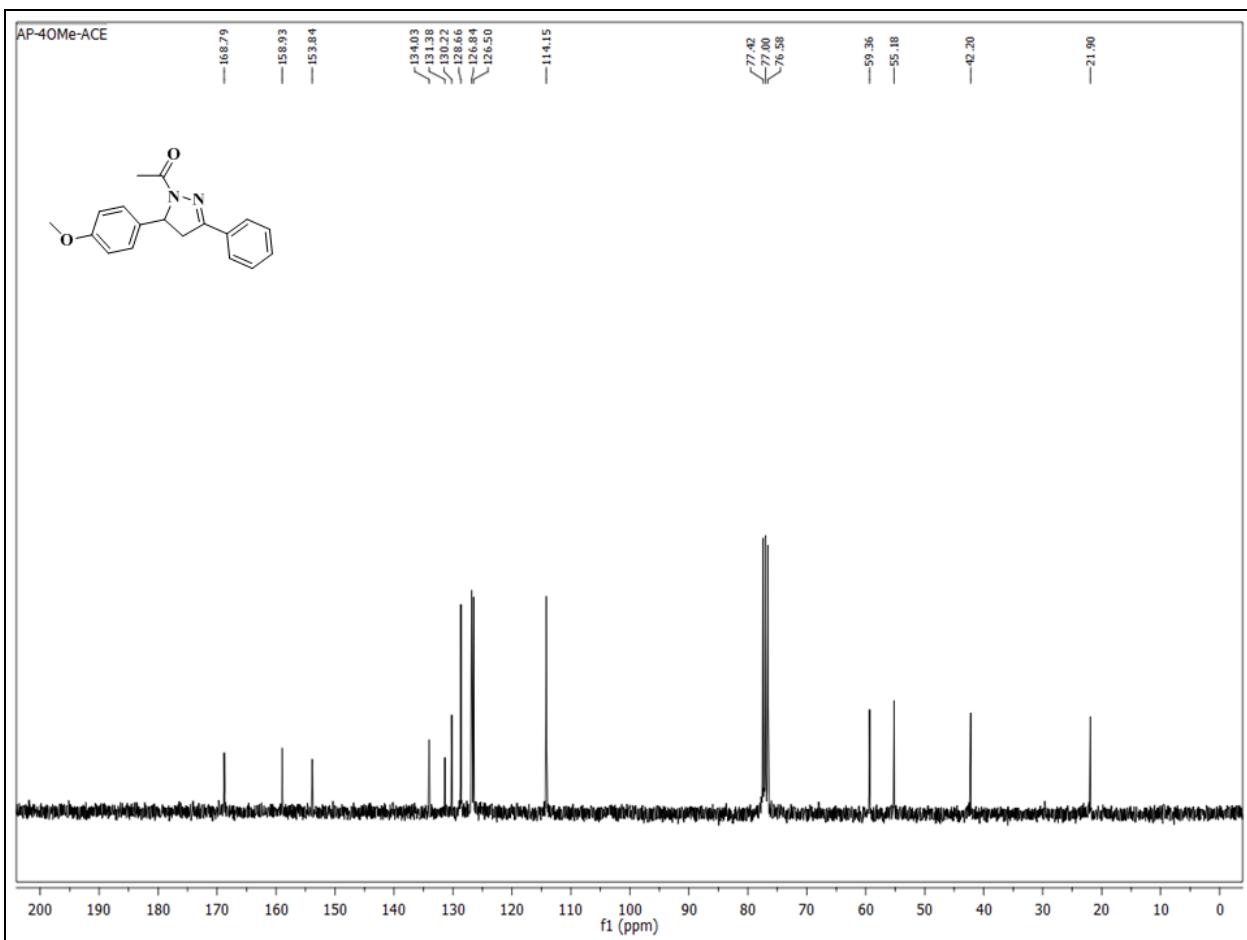
(E)-N'-(1-(1-Benzyl-5-methyl-1H-1,2,3-triazol-4-yl)ethylidene)butyrohydrazide (**8i**). Yield: 90%. Gummy matter. FTIR (KBr) ν/cm⁻¹ 1651, 1608. ¹H NMR (300 MHz, CDCl₃): δ 7.35 – 7.27 (m, 3H); 7.23 – 7.18 (m, 2H); 5.55 (s, 2H); 2.73 – 2.69 (s, 2H); 2.49 (s, 3H); 2.47 (s, 3H); 1.82 – 1.67 (m, 2H); 1.01 (t, *J* = 6.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 173.2; 142.9; 136.3; 133.4; 128.2; 127.6; 126.5; 50.6; 42.4; 19.2; 18.1; 12.9; 8.2. Anal. Calcd. for (%) C₁₆H₂₁N₅O : C 64.19, H 7.07, N 23.39; Found: C 64.22, H 7.09, N 23.35.

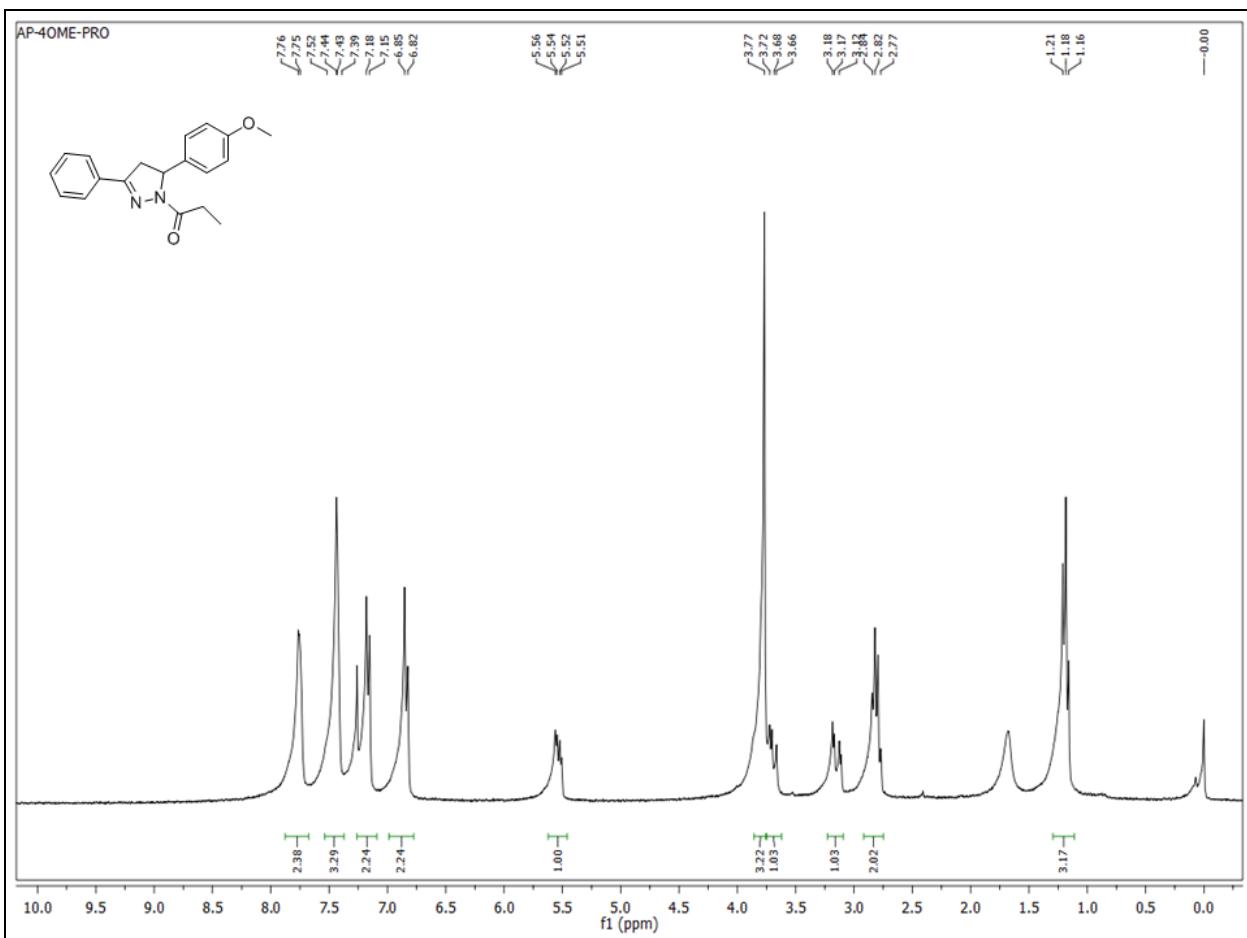
I Copies of ¹H&¹³C NMR of **3a-i**



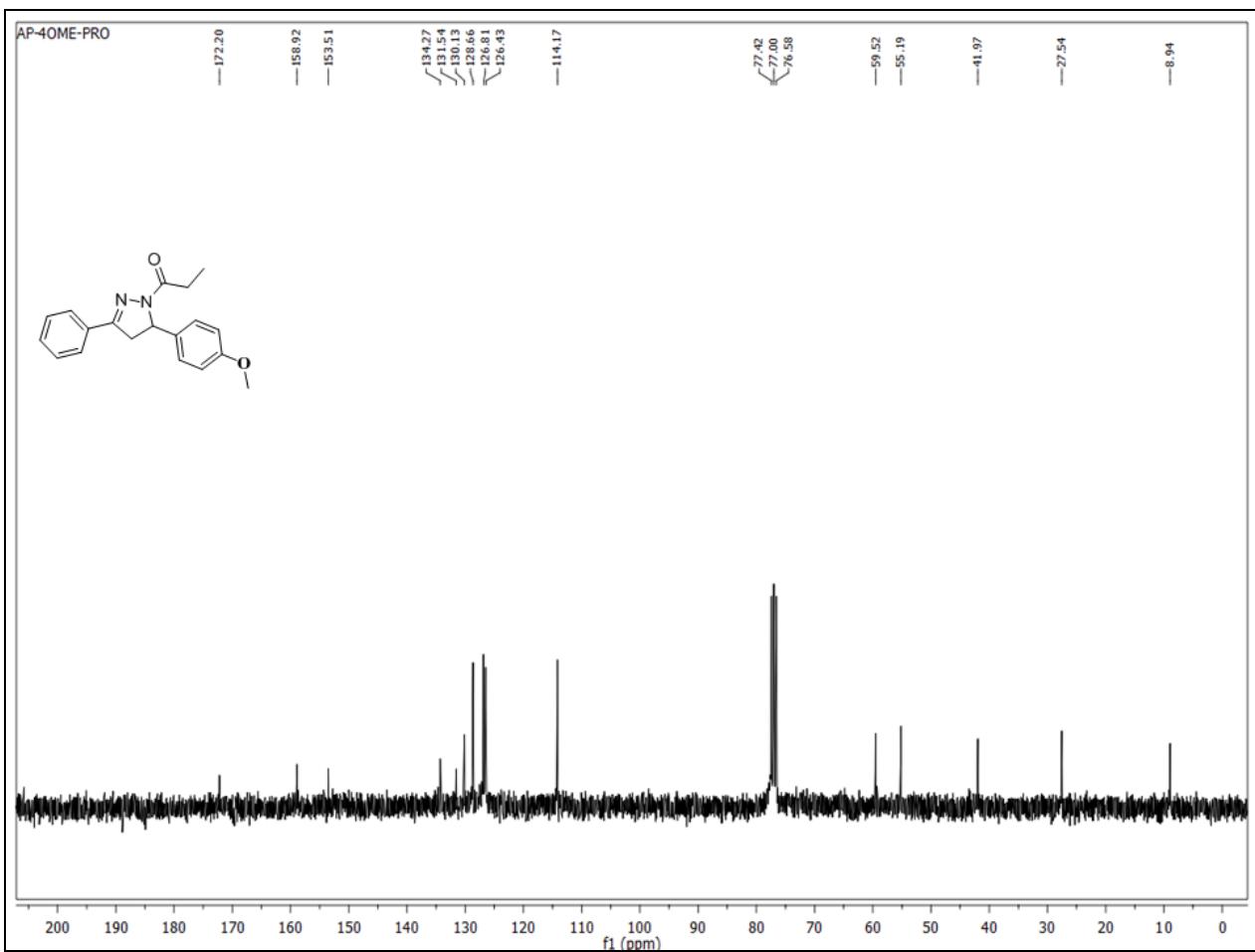
¹H NMR (300 MHz, CDCl₃) : 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl) ethanone (**3a**)



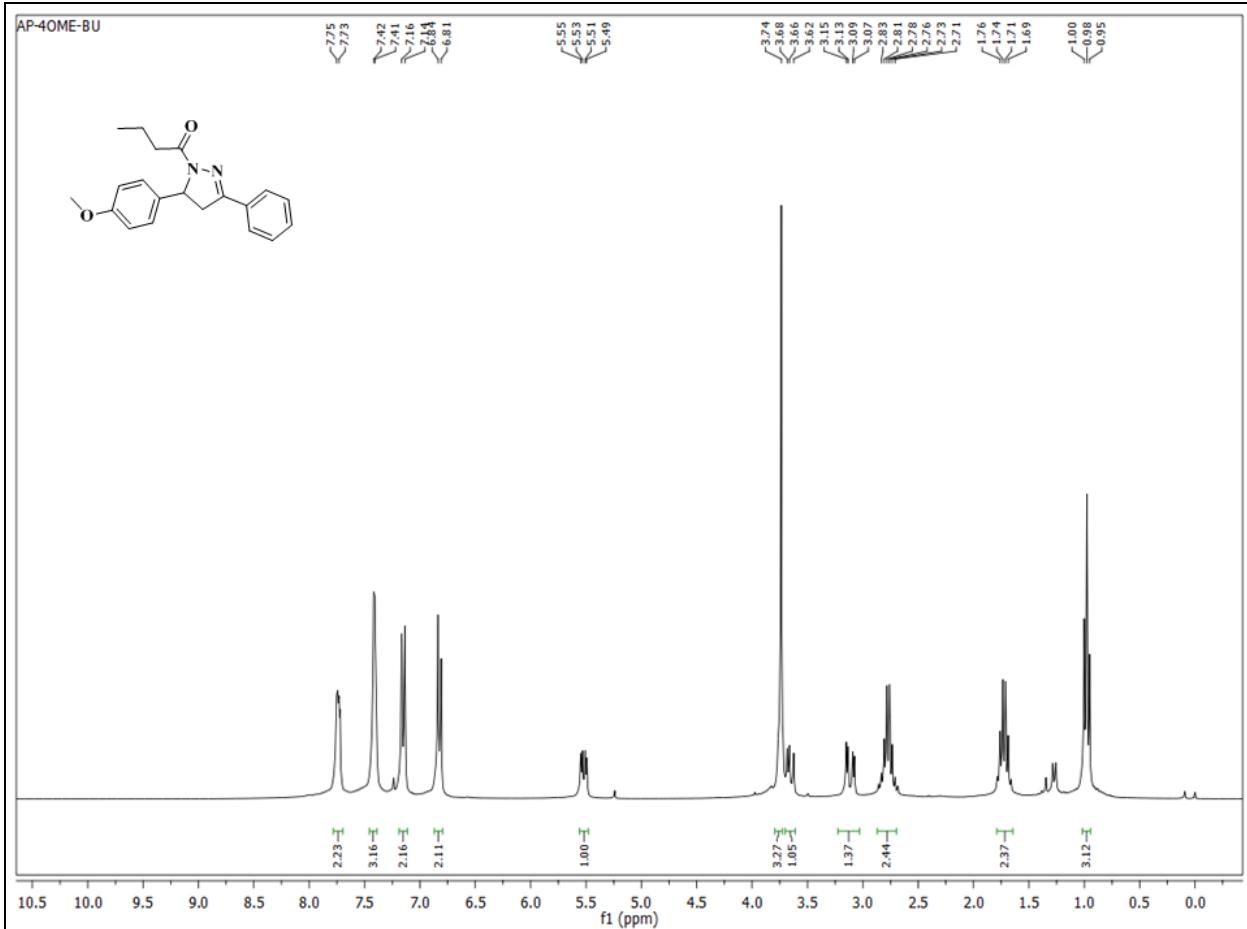




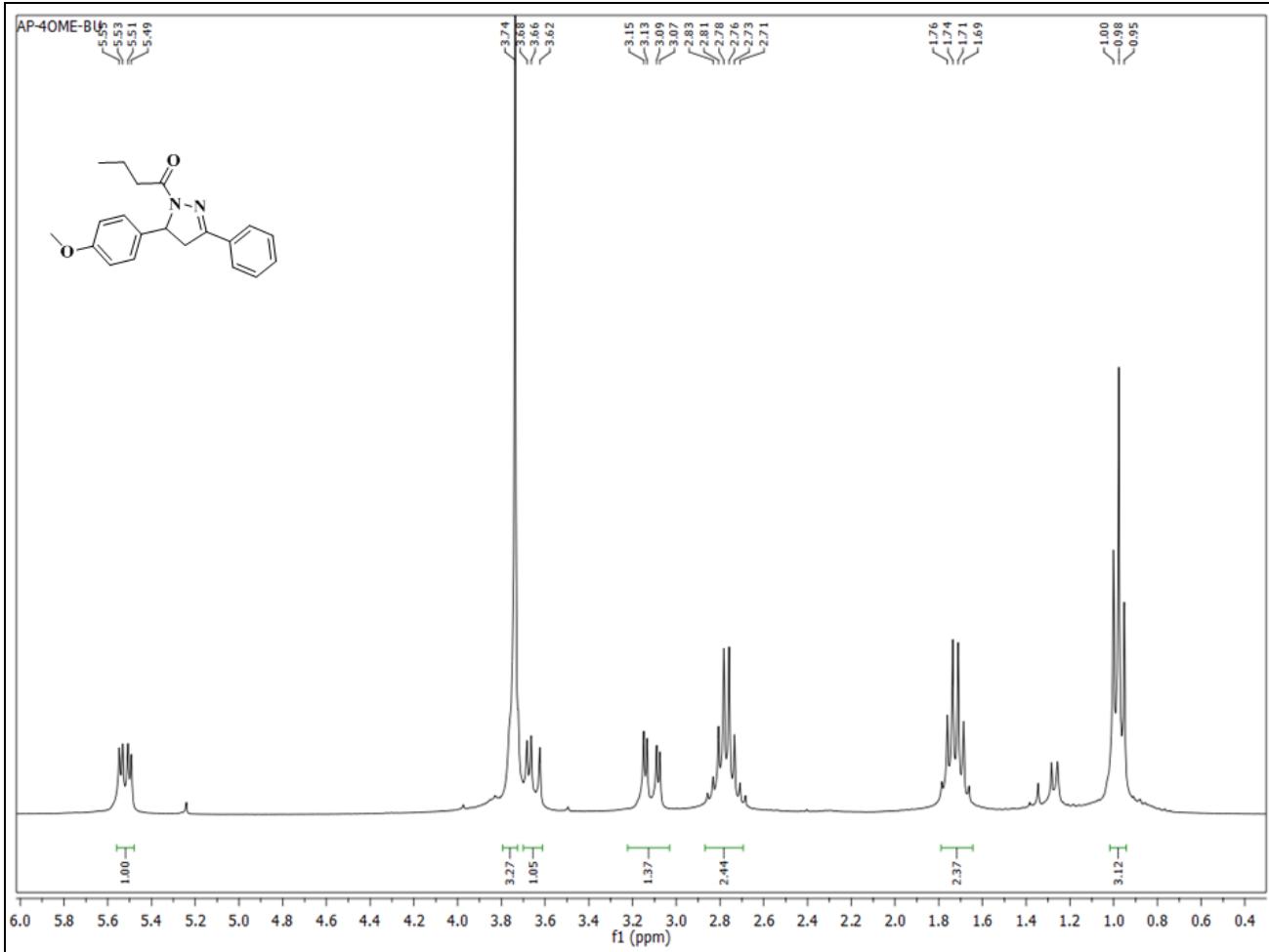
¹H NMR (300 MHz, CDCl₃): 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (3b)

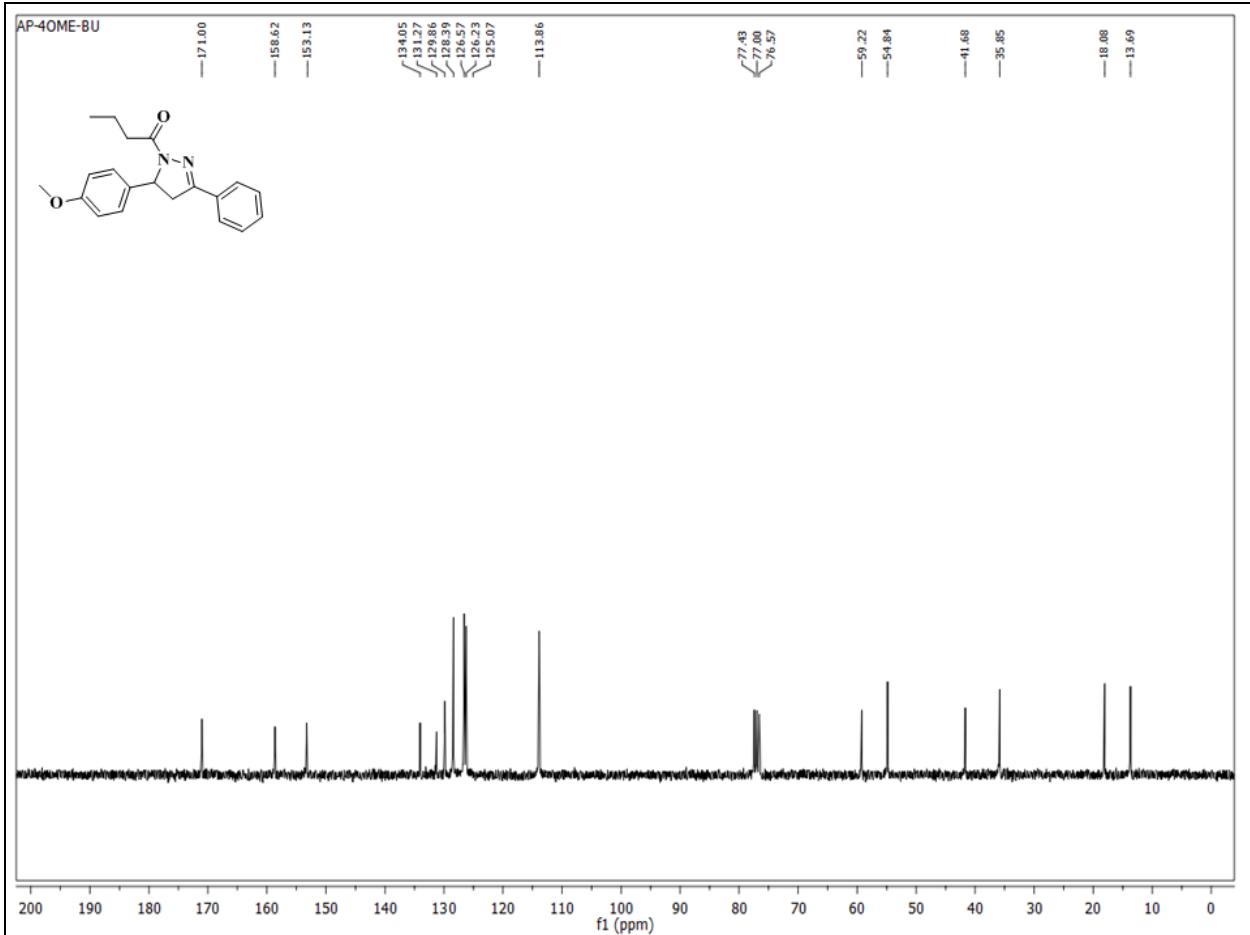


¹³C NMR (75 MHz, CDCl₃): 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (3b)

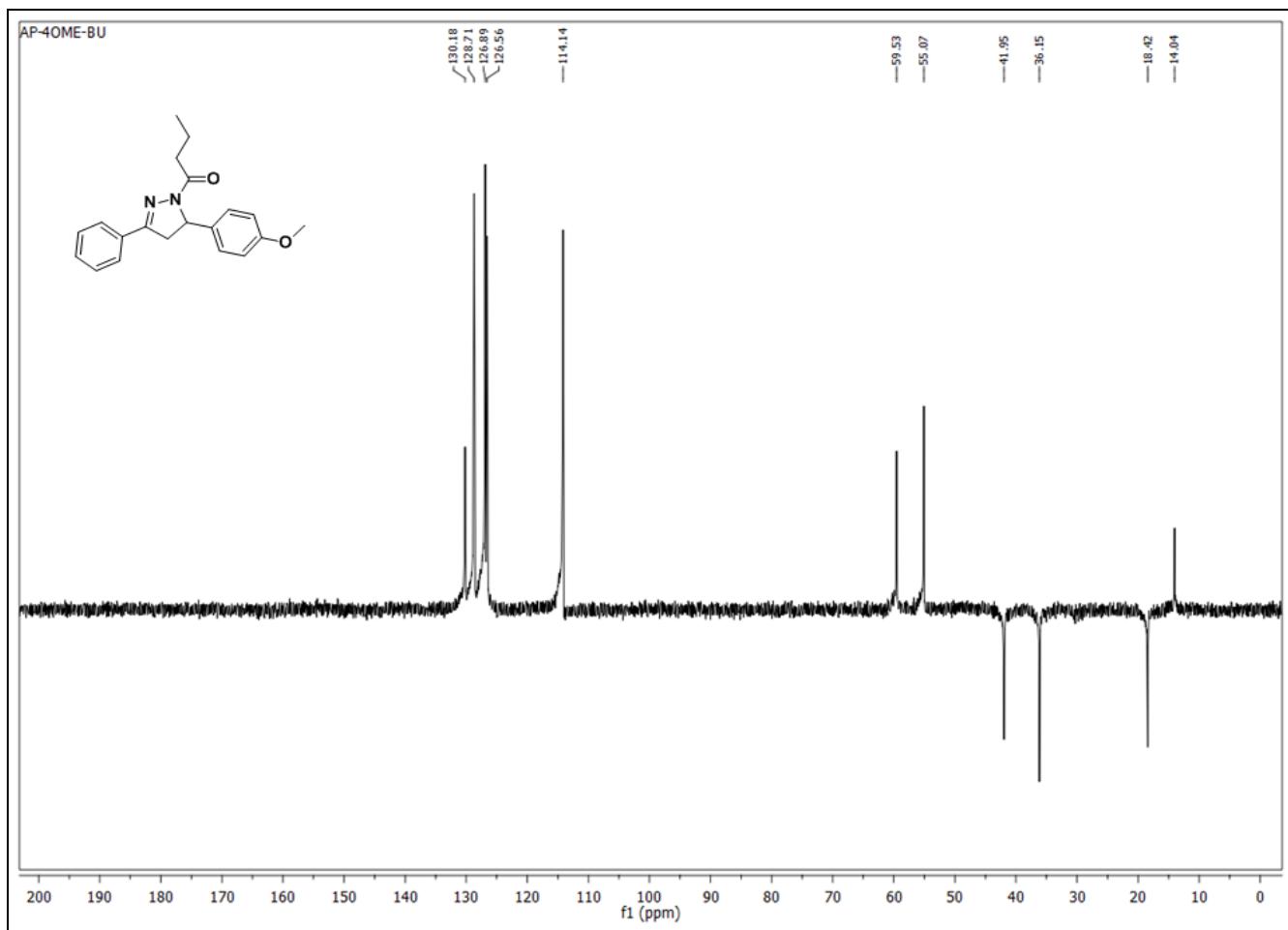


¹H NMR (300 MHz, CDCl₃): 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c)

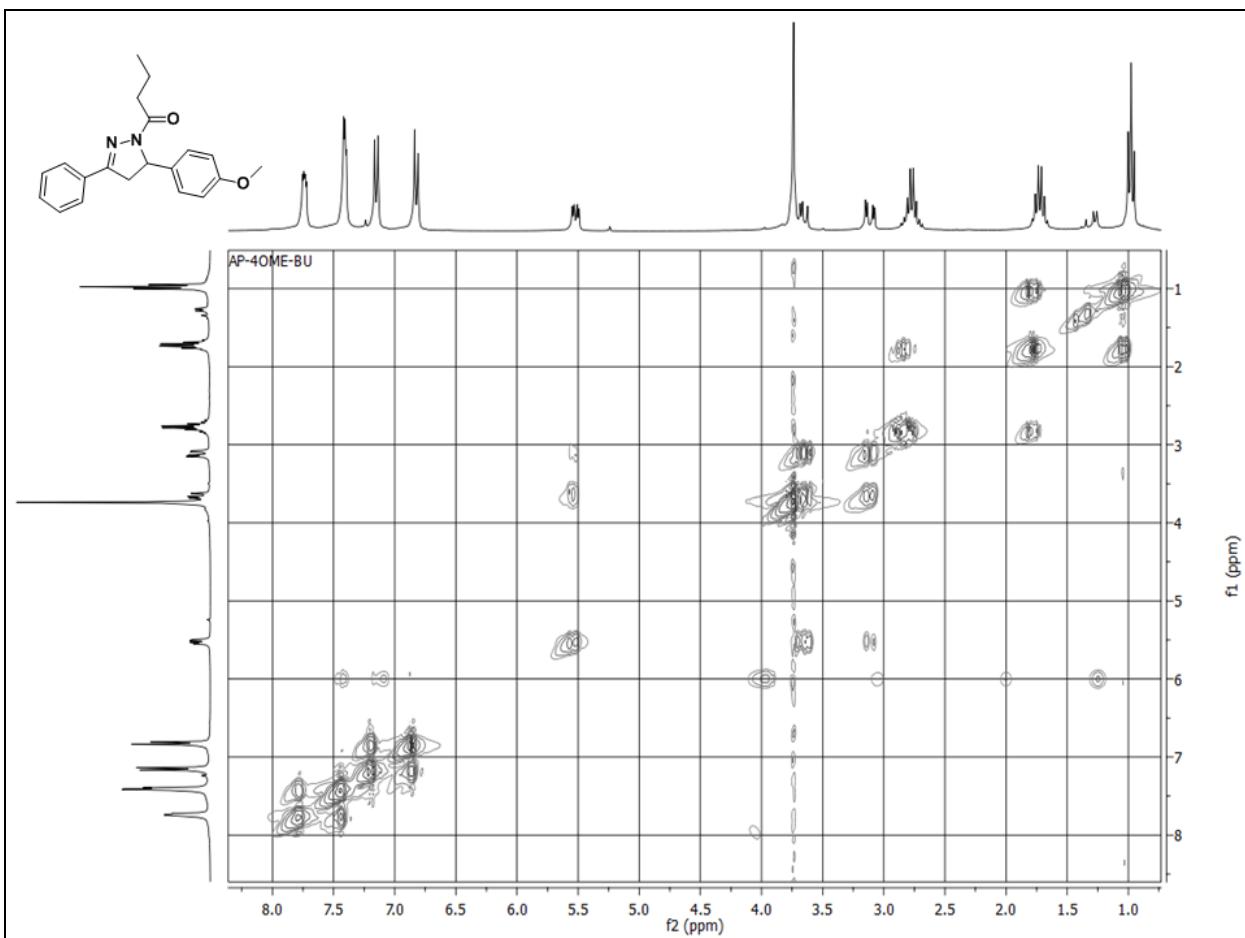




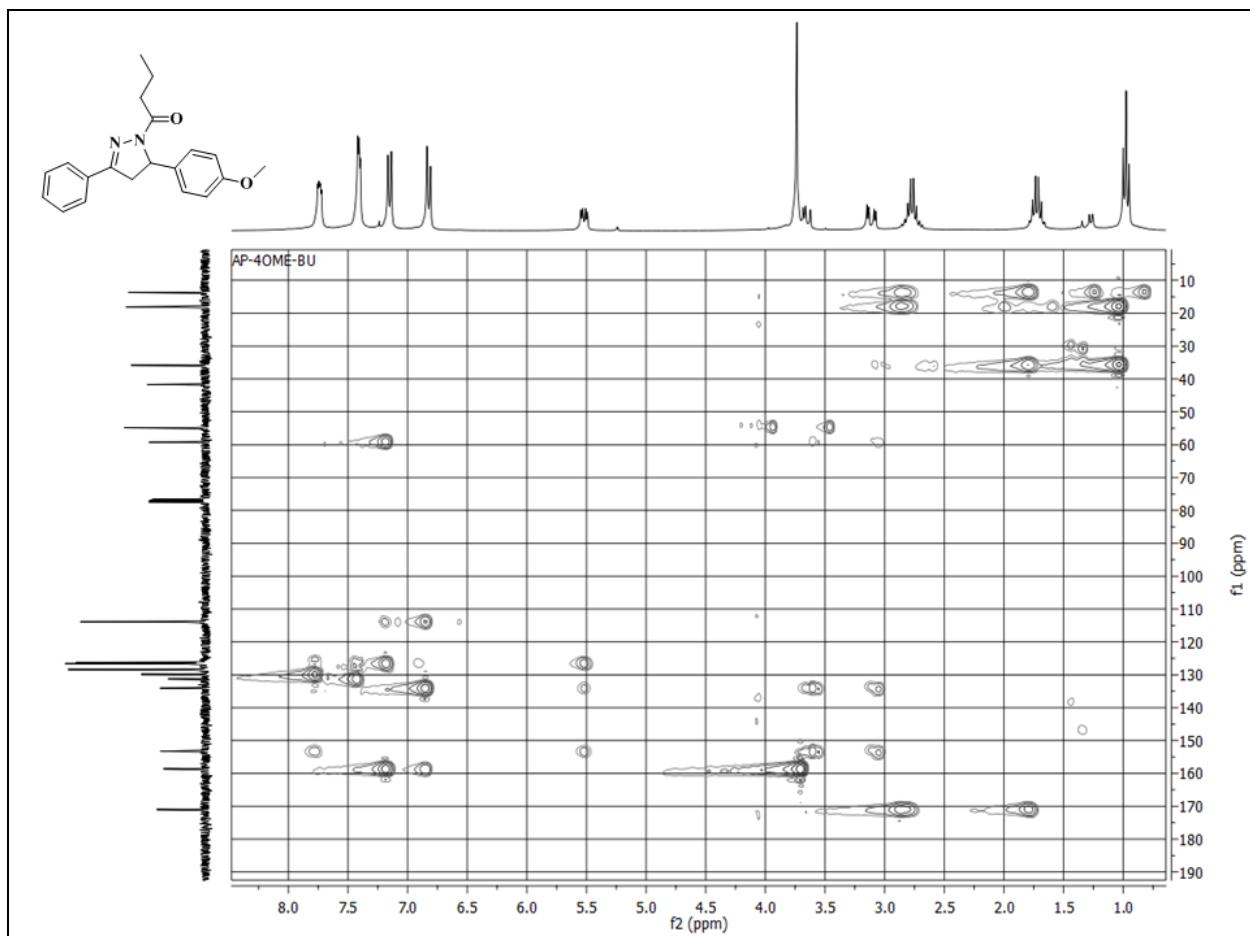
¹³C NMR (75 MHz, CDCl₃): 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c)



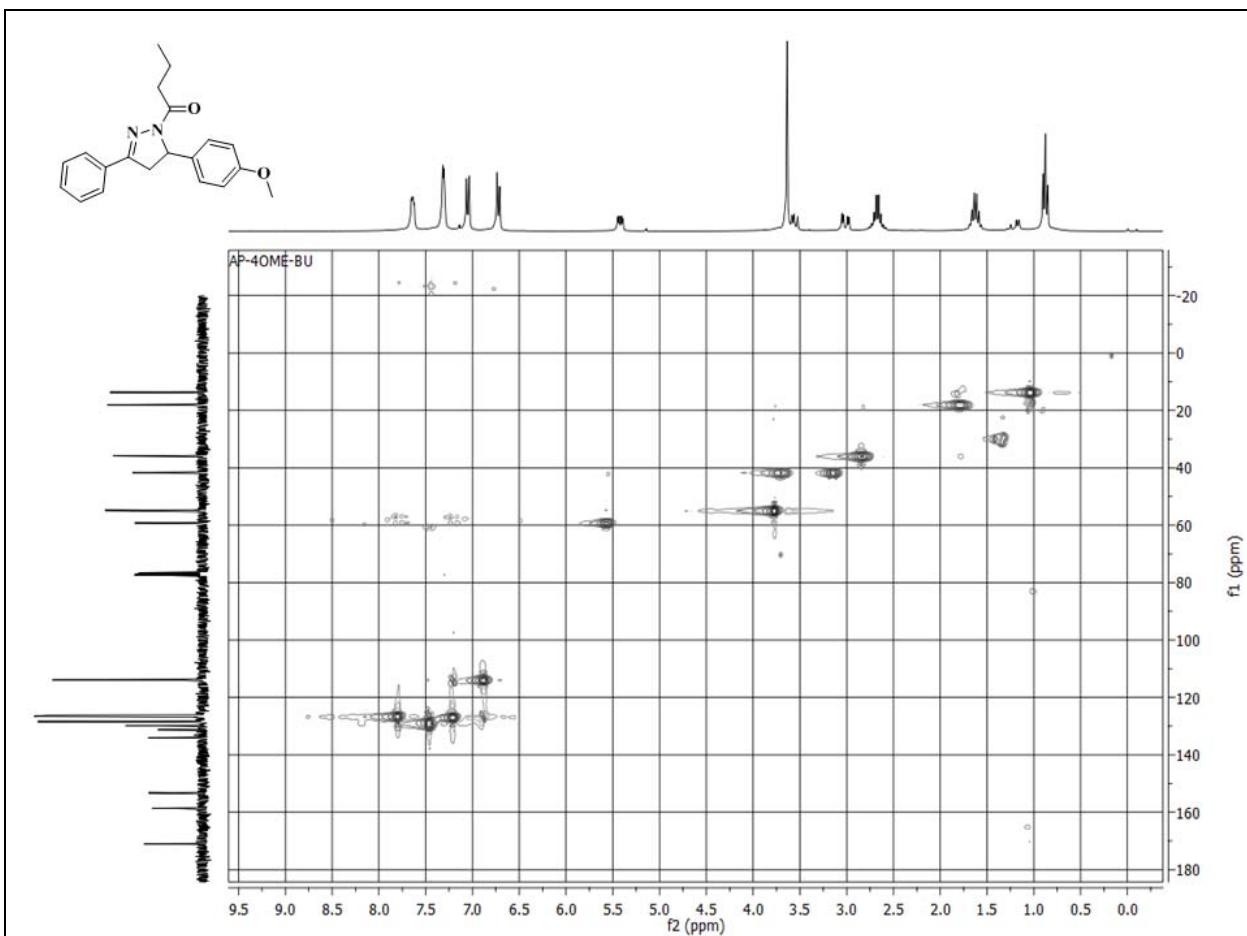
DEPT-135:1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c)



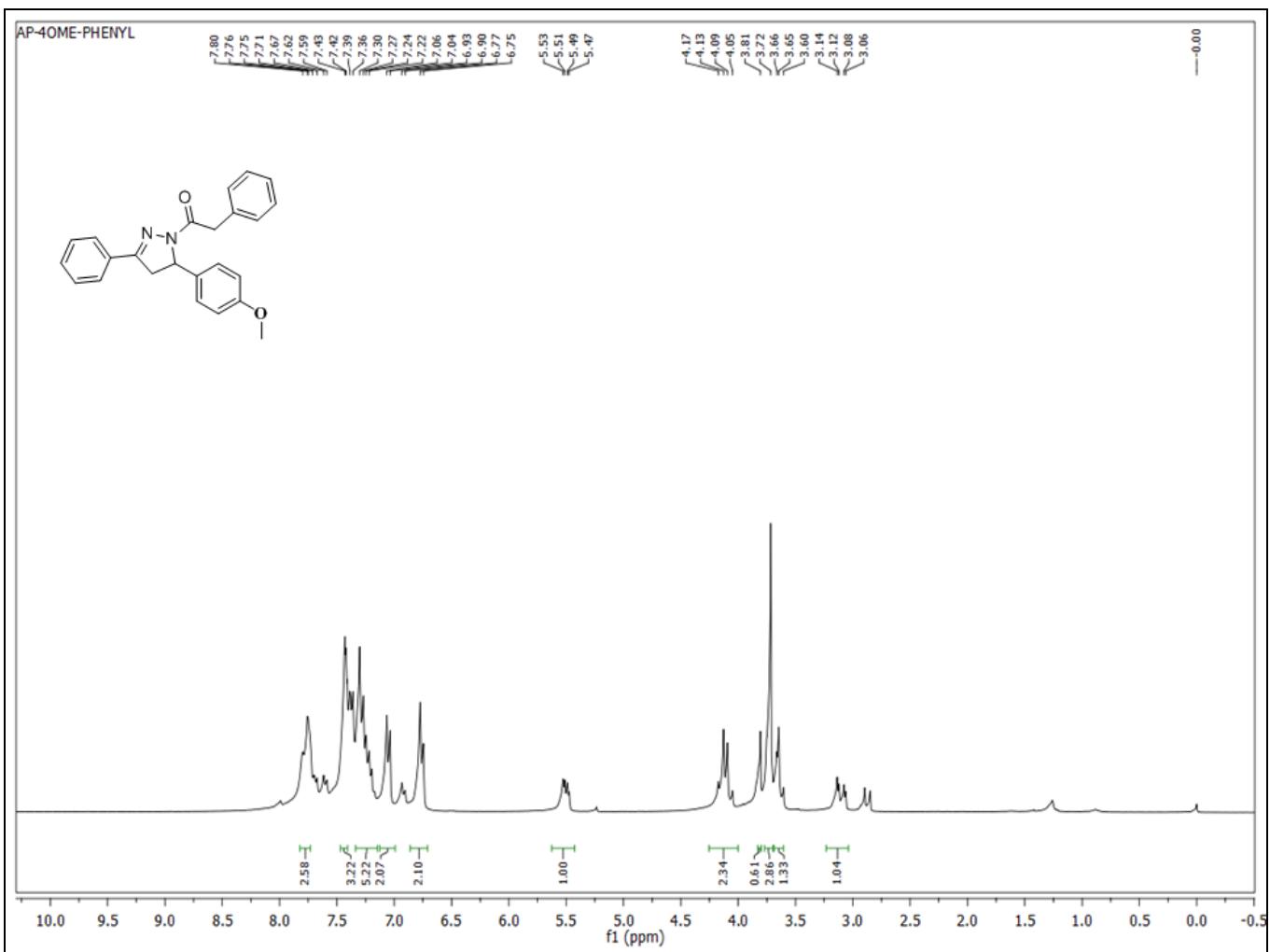
H,H COSY Spectrum of 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c)



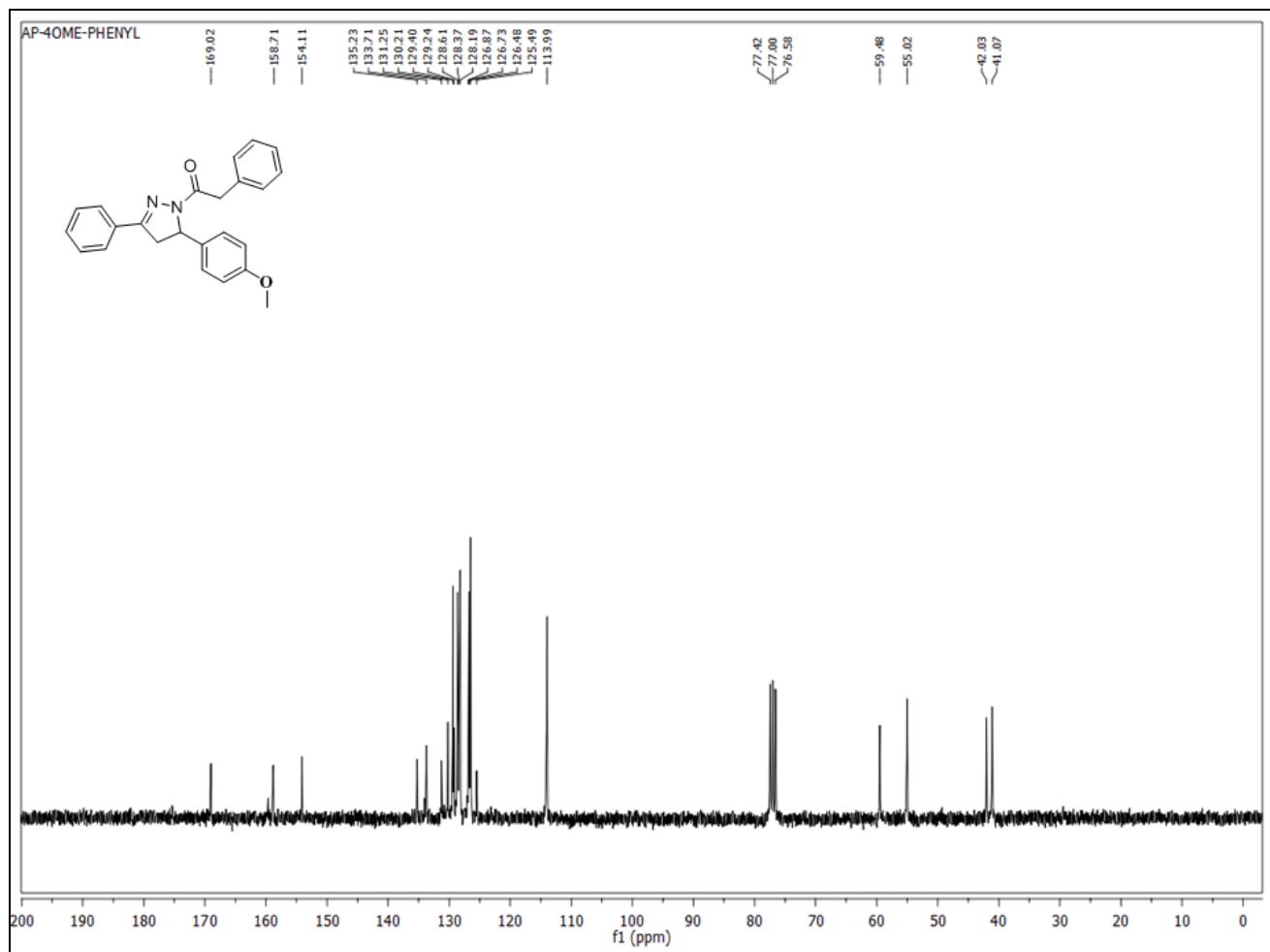
HMBC Spectrum of 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c)

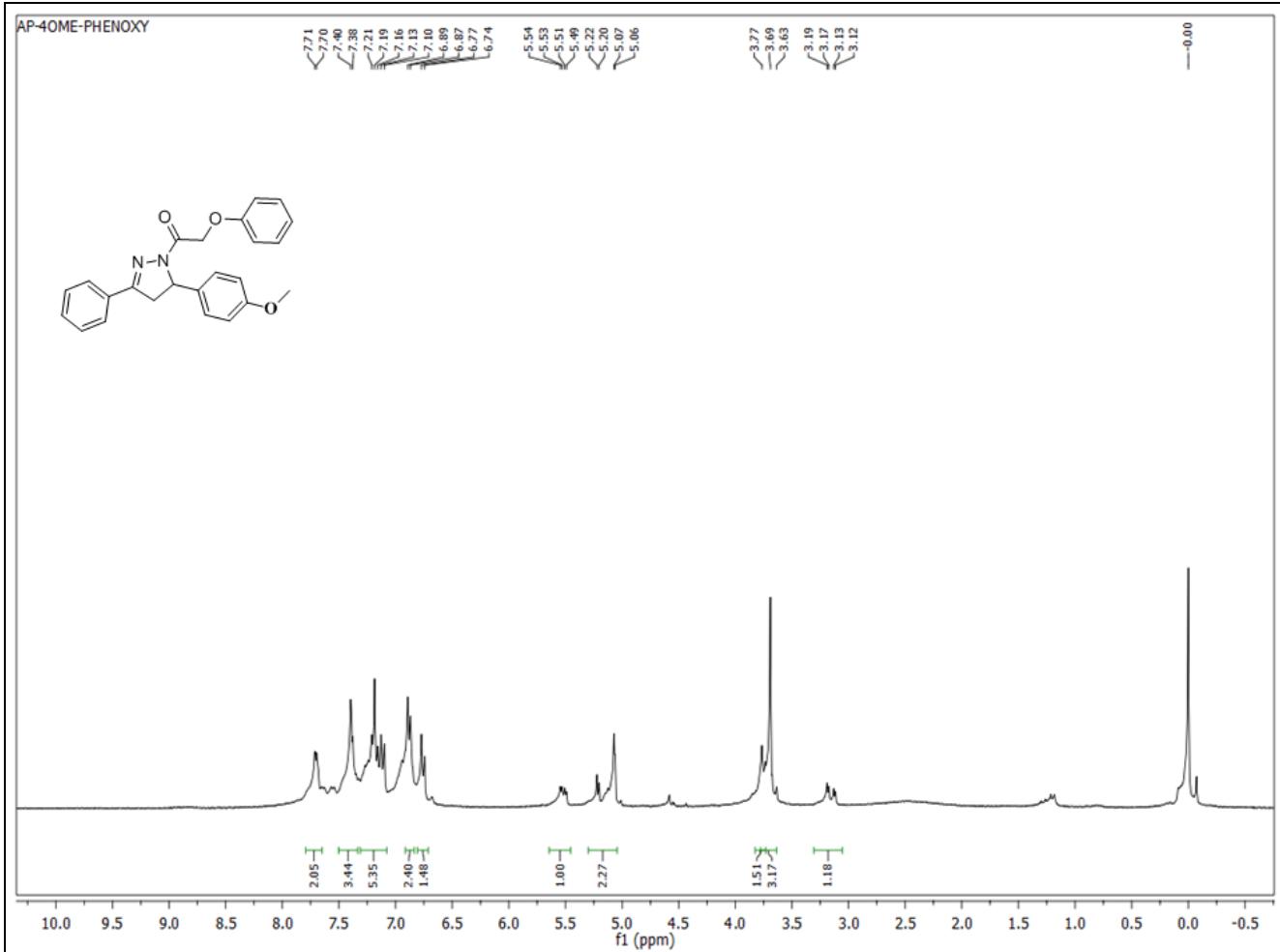


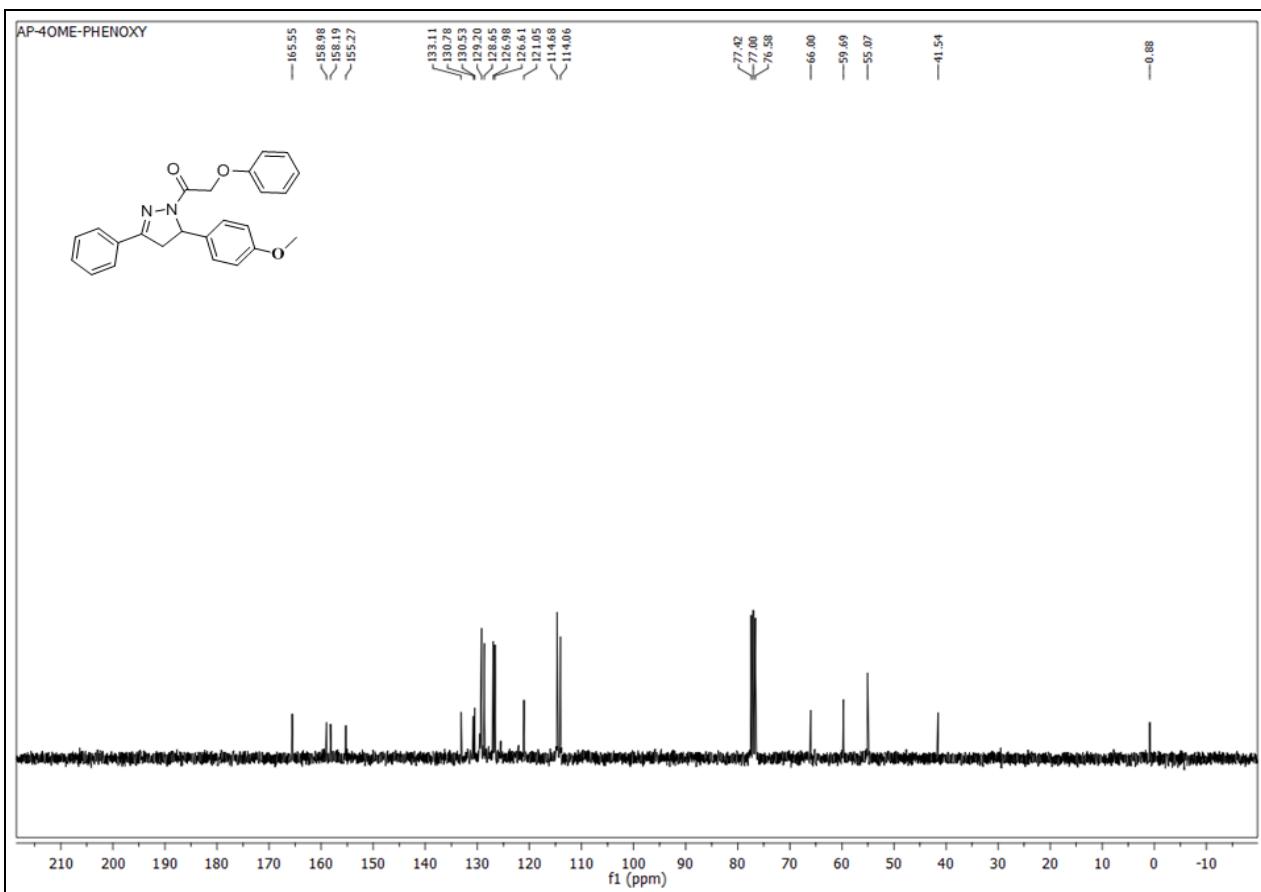
C,H COSY Spectrum of 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3c)



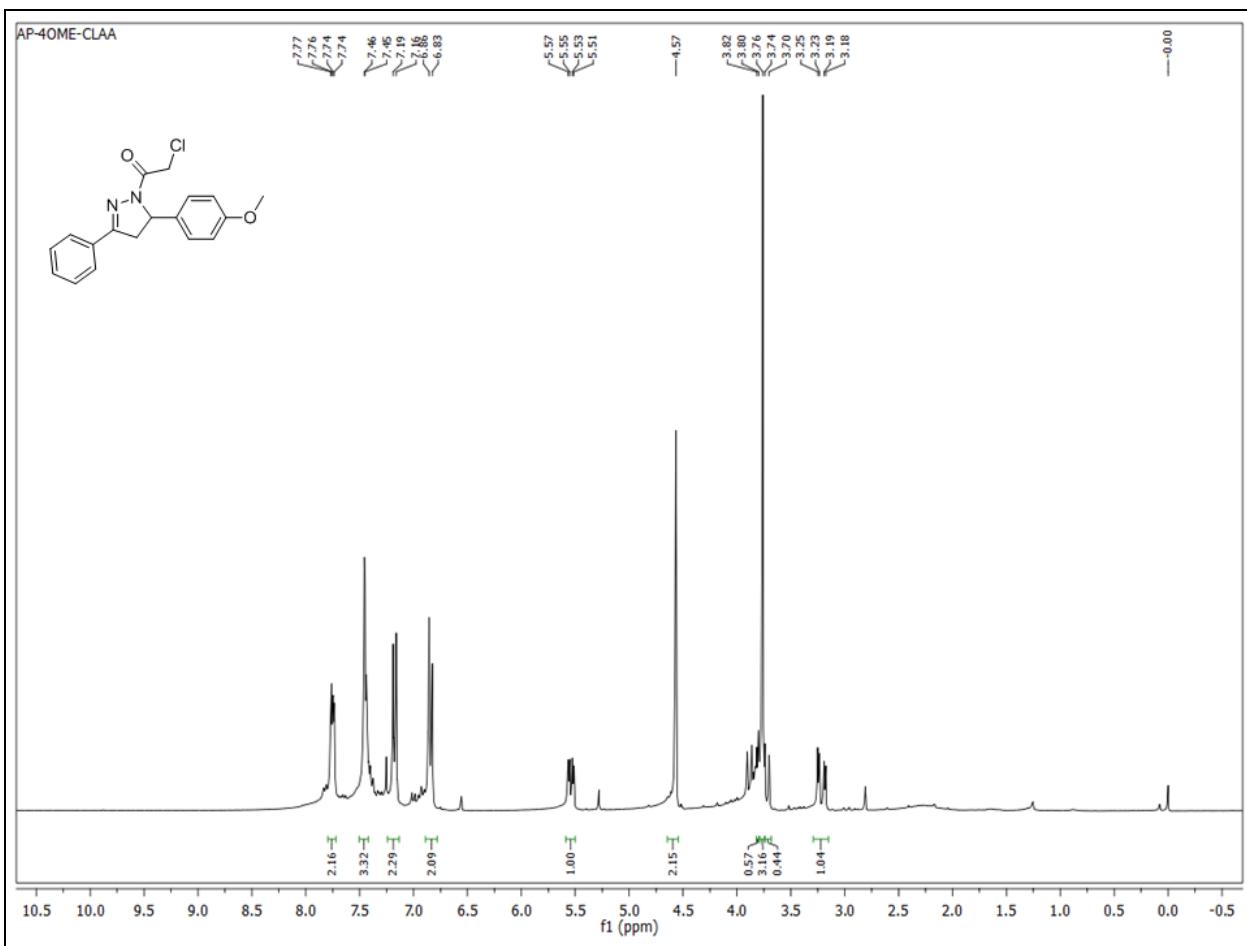
¹H NMR (300 MHz, CDCl₃): 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)-2-phenylethanone (3d)



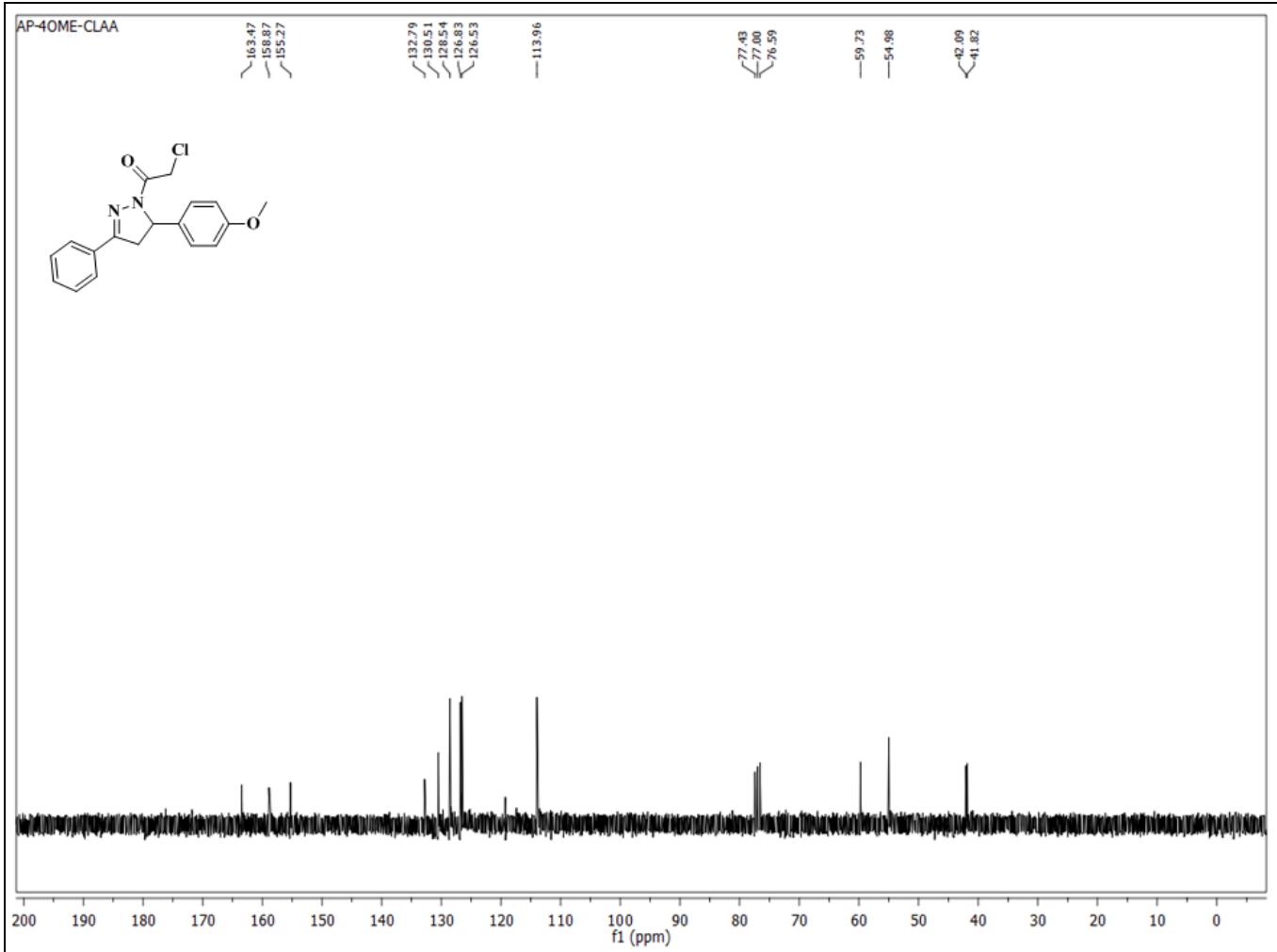




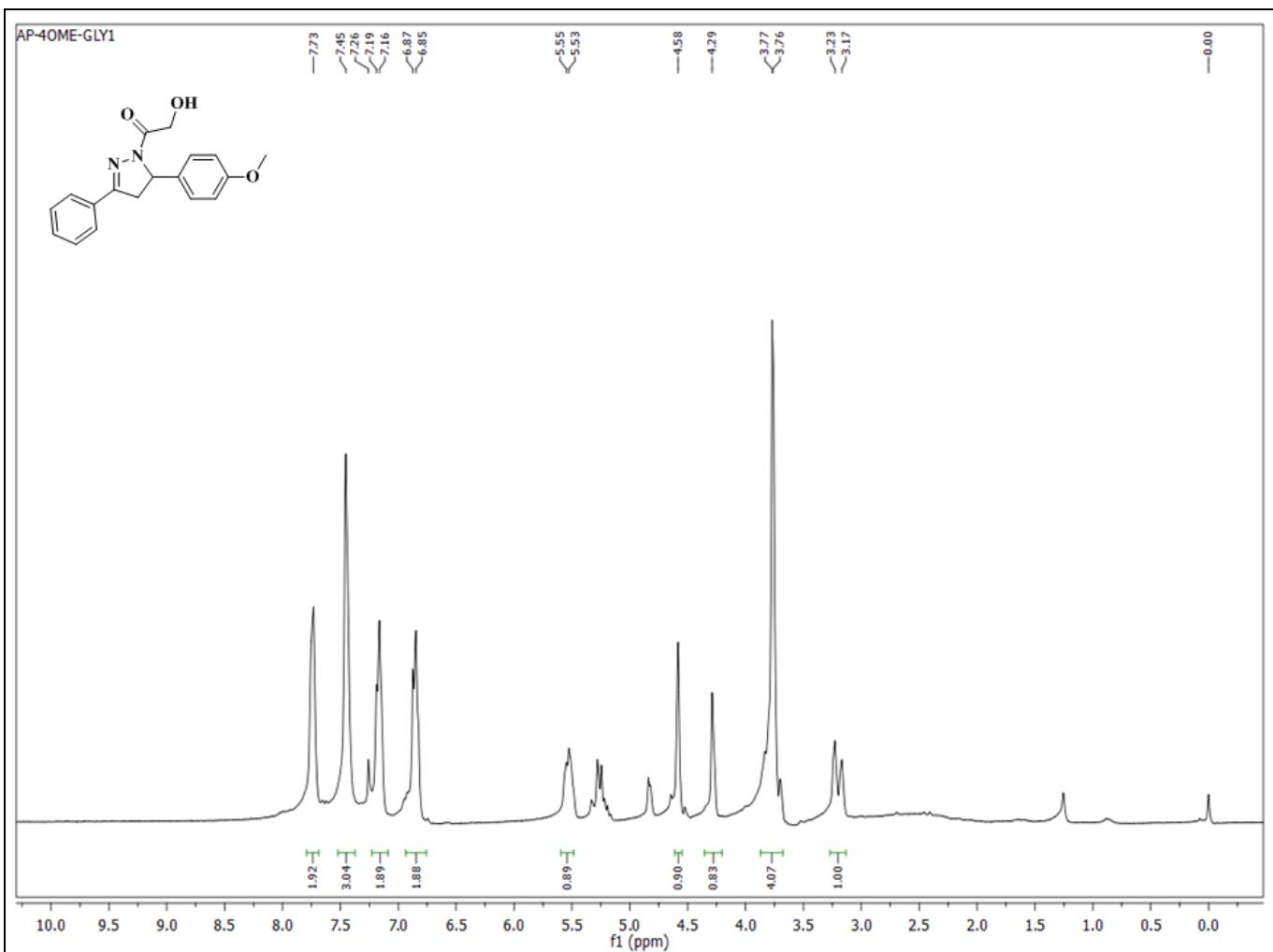
¹³C NMR (75 MHz, CDCl₃): 1-(5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)-2-phenoxyethanone (3e)



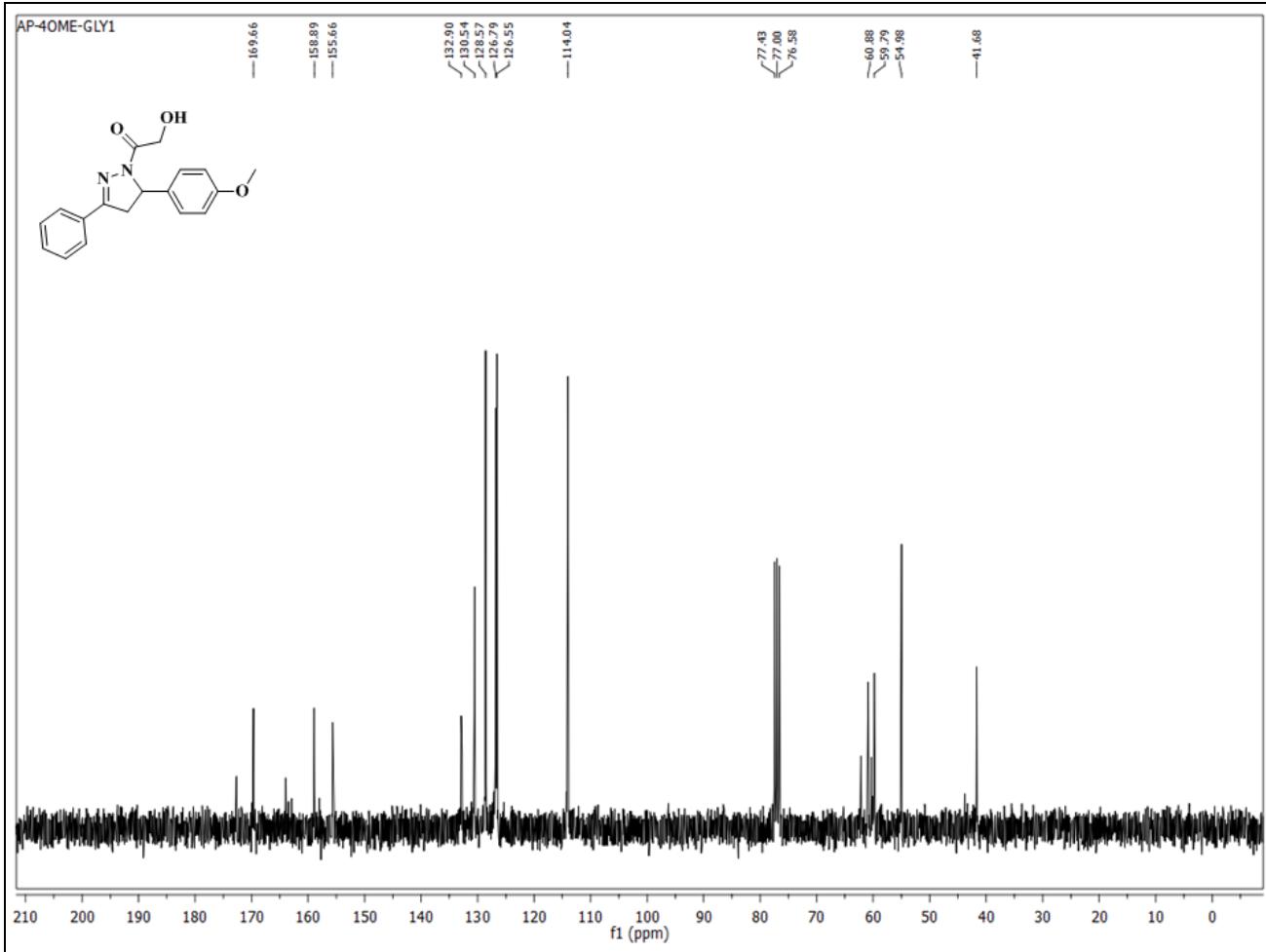
^1H NMR (300 MHz, CDCl_3): 2-Chloro-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (**3f**)

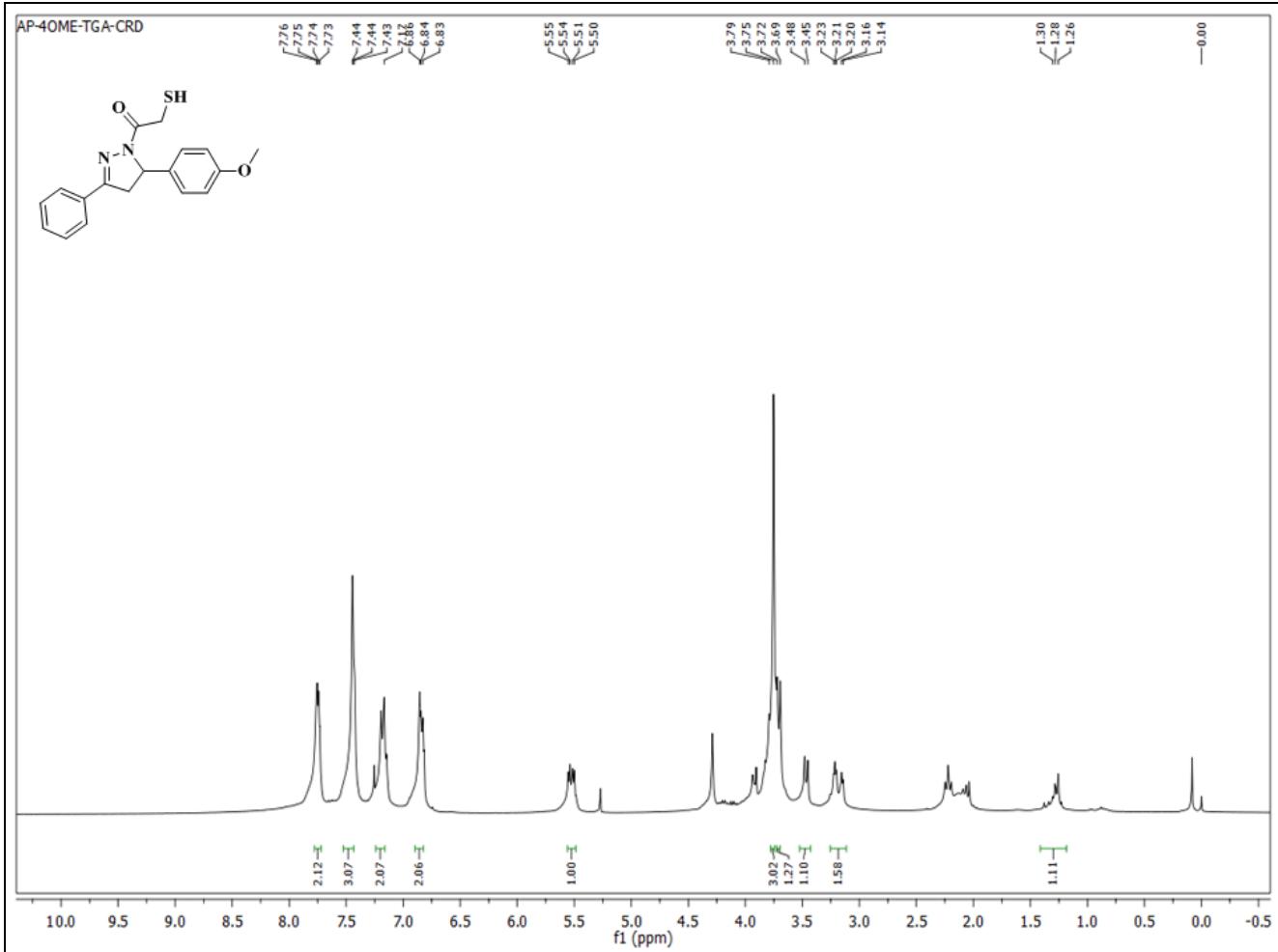


¹³C NMR (75 MHz, CDCl₃): 2-Chloro-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (**3f**)

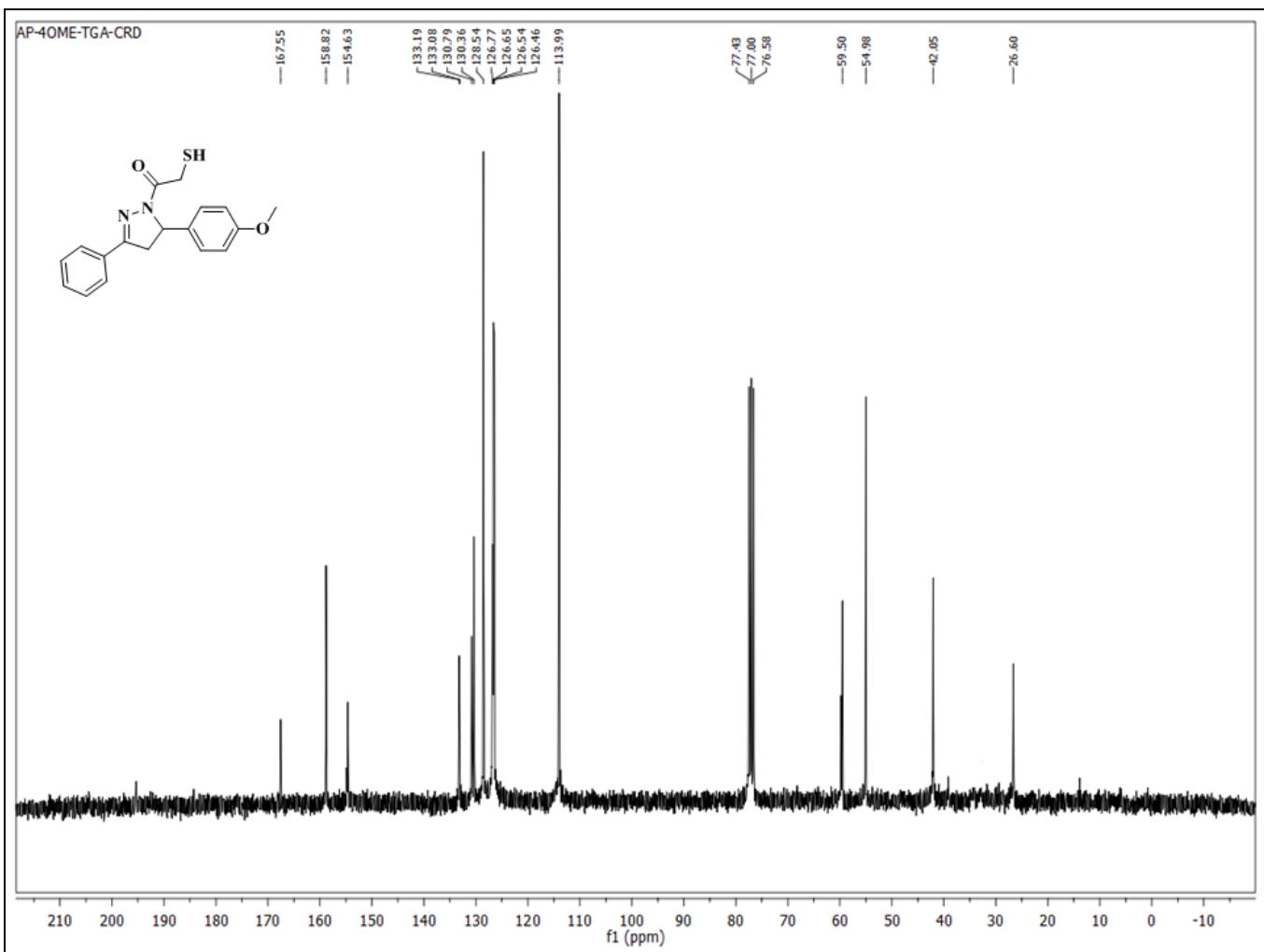


^1H NMR (300 MHz, CDCl_3): 2-Hydroxy-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3g)

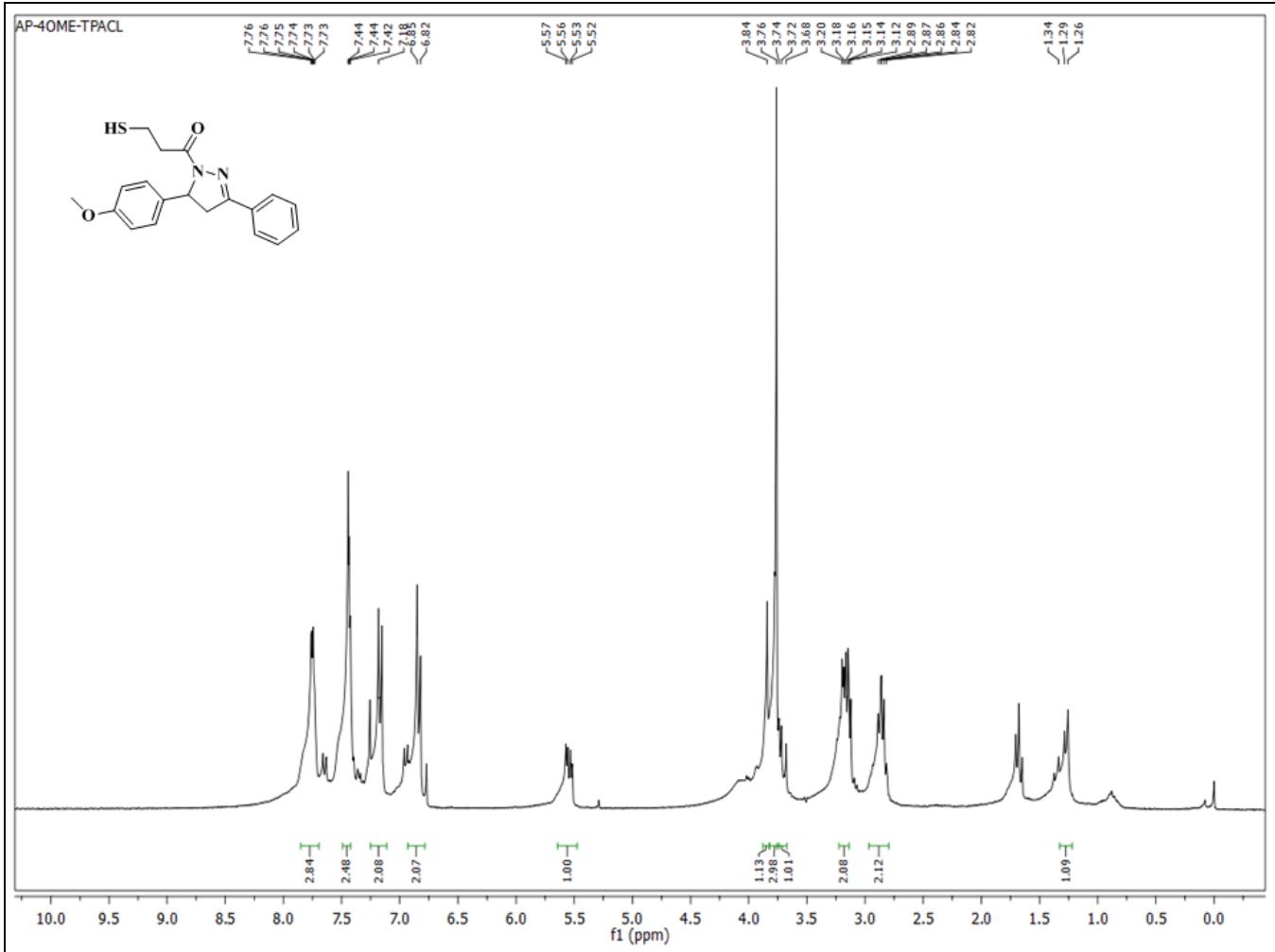




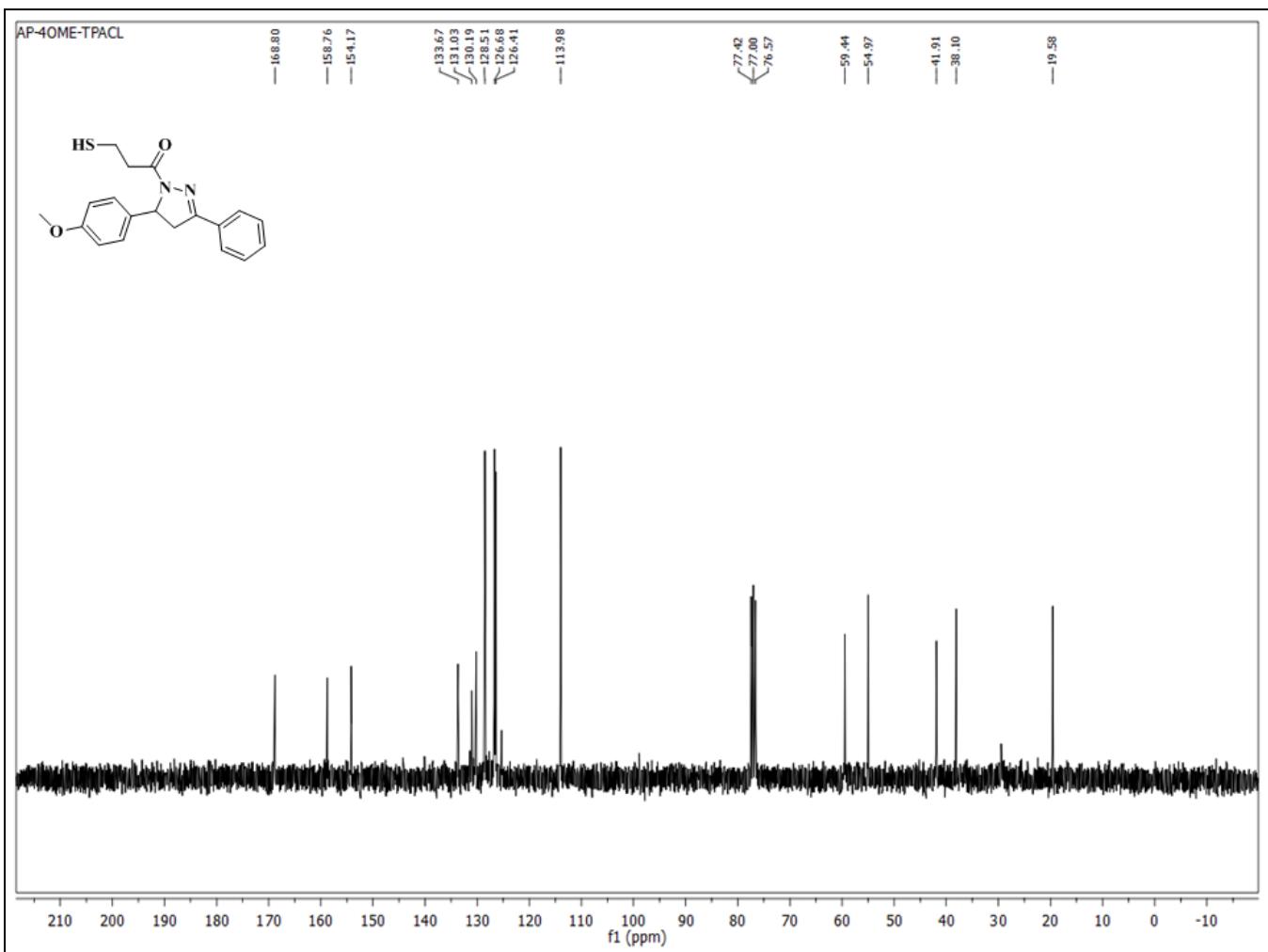
¹H NMR (300 MHz, CDCl₃): 2-Mercapto-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3h)



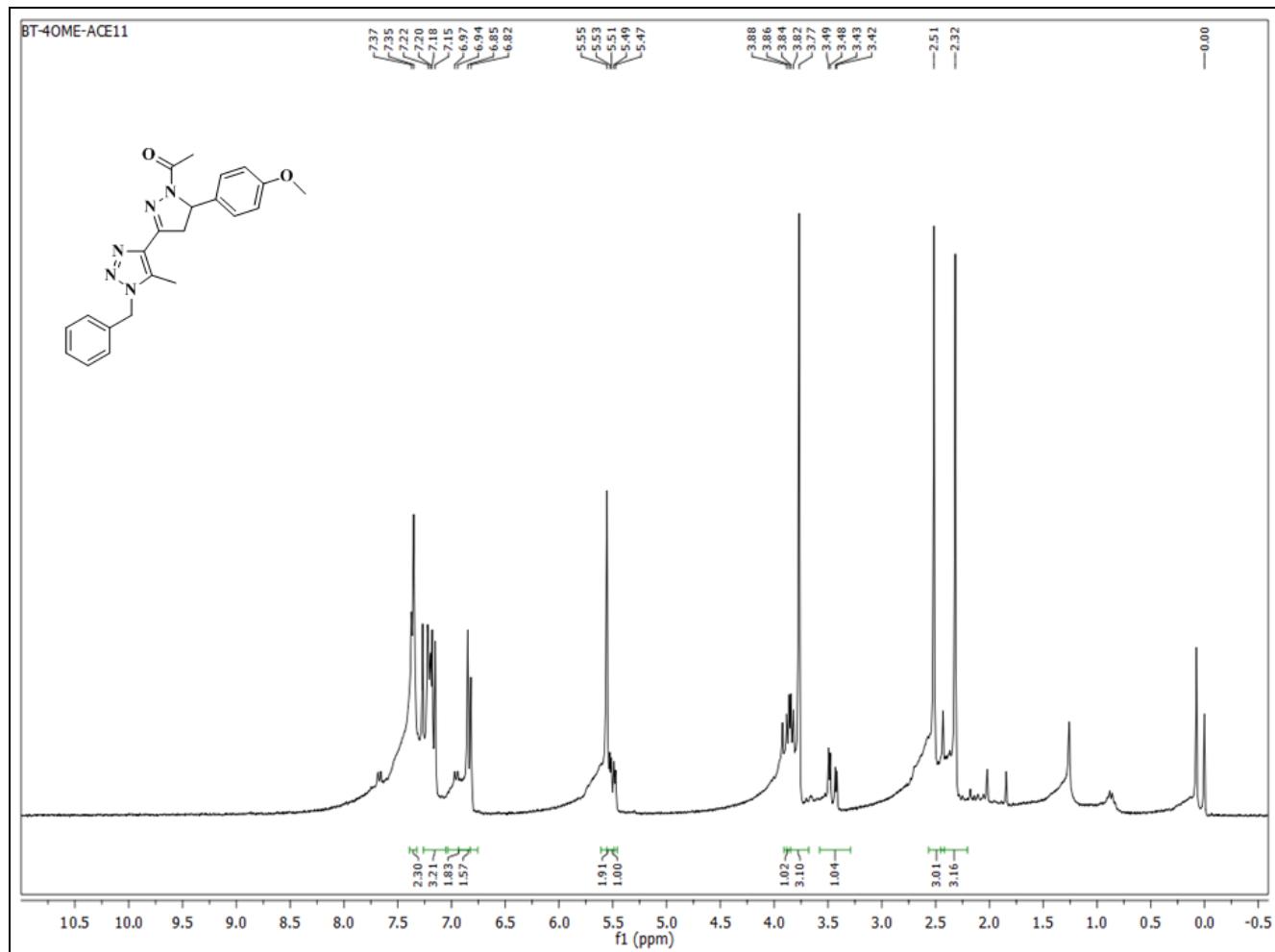
^{13}C NMR (75 MHz, CDCl_3): 2-Mercapto-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanone (3h)

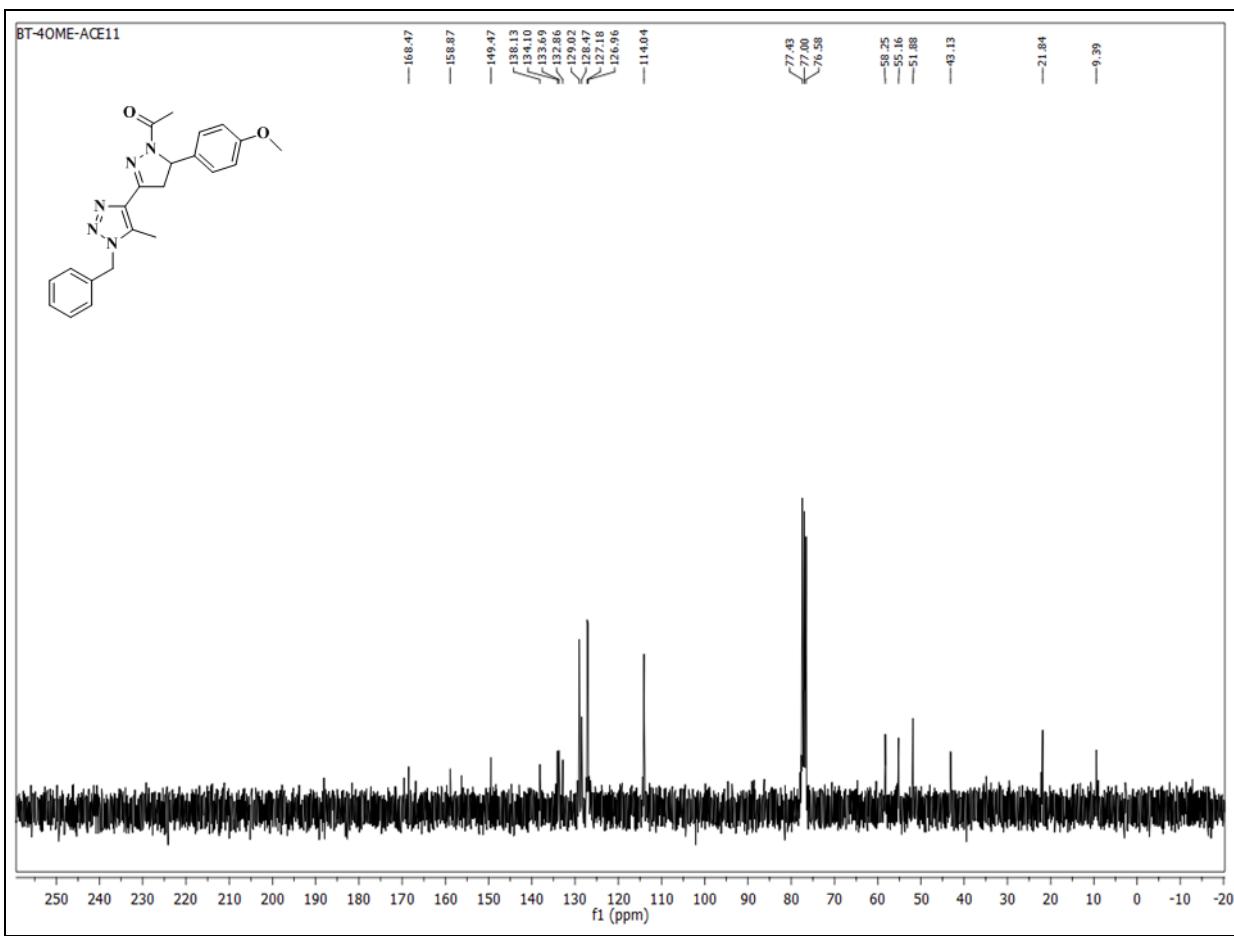


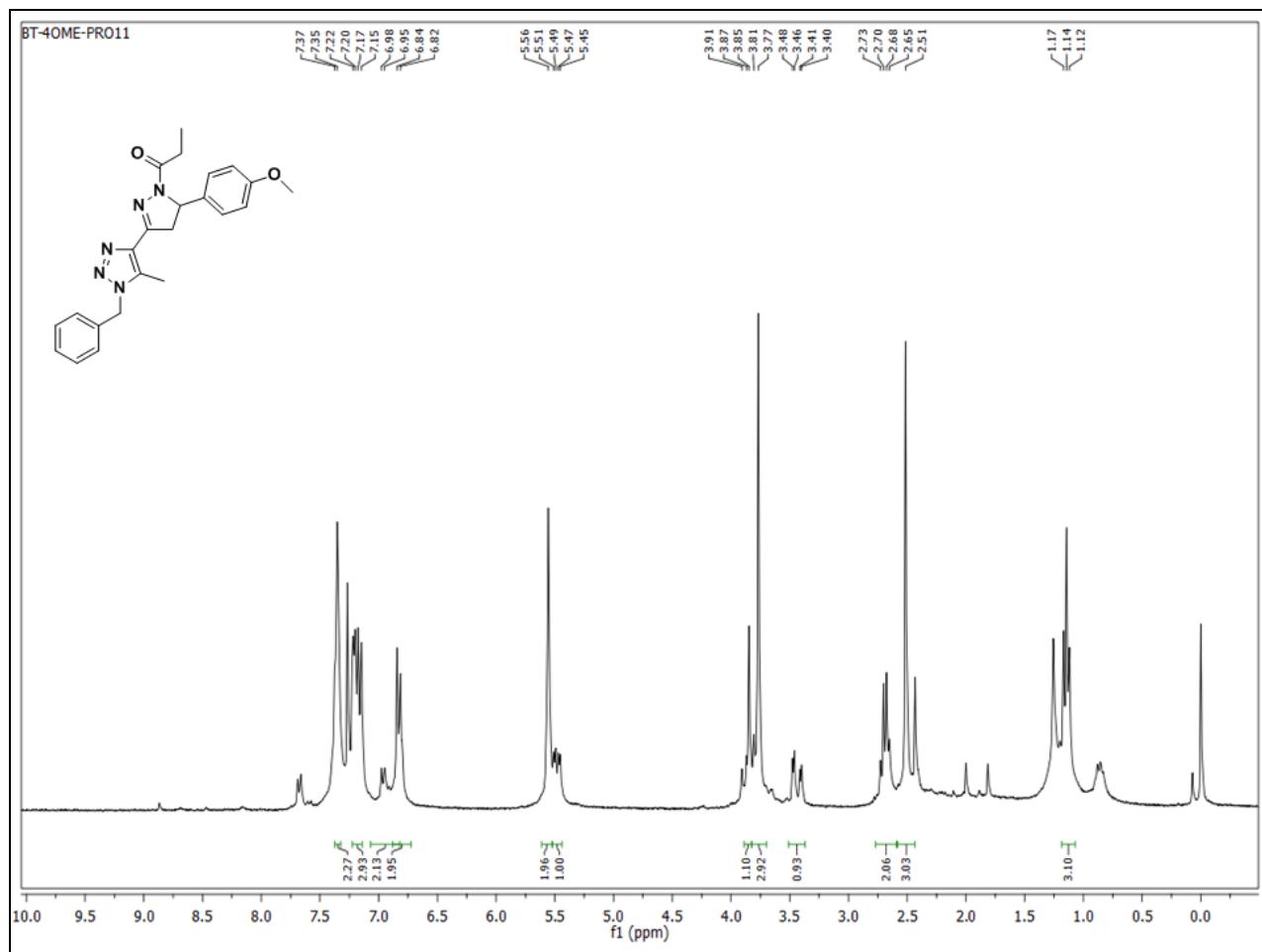
¹H NMR (300 MHz, CDCl₃): 3-Mercapto-1-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (3i)

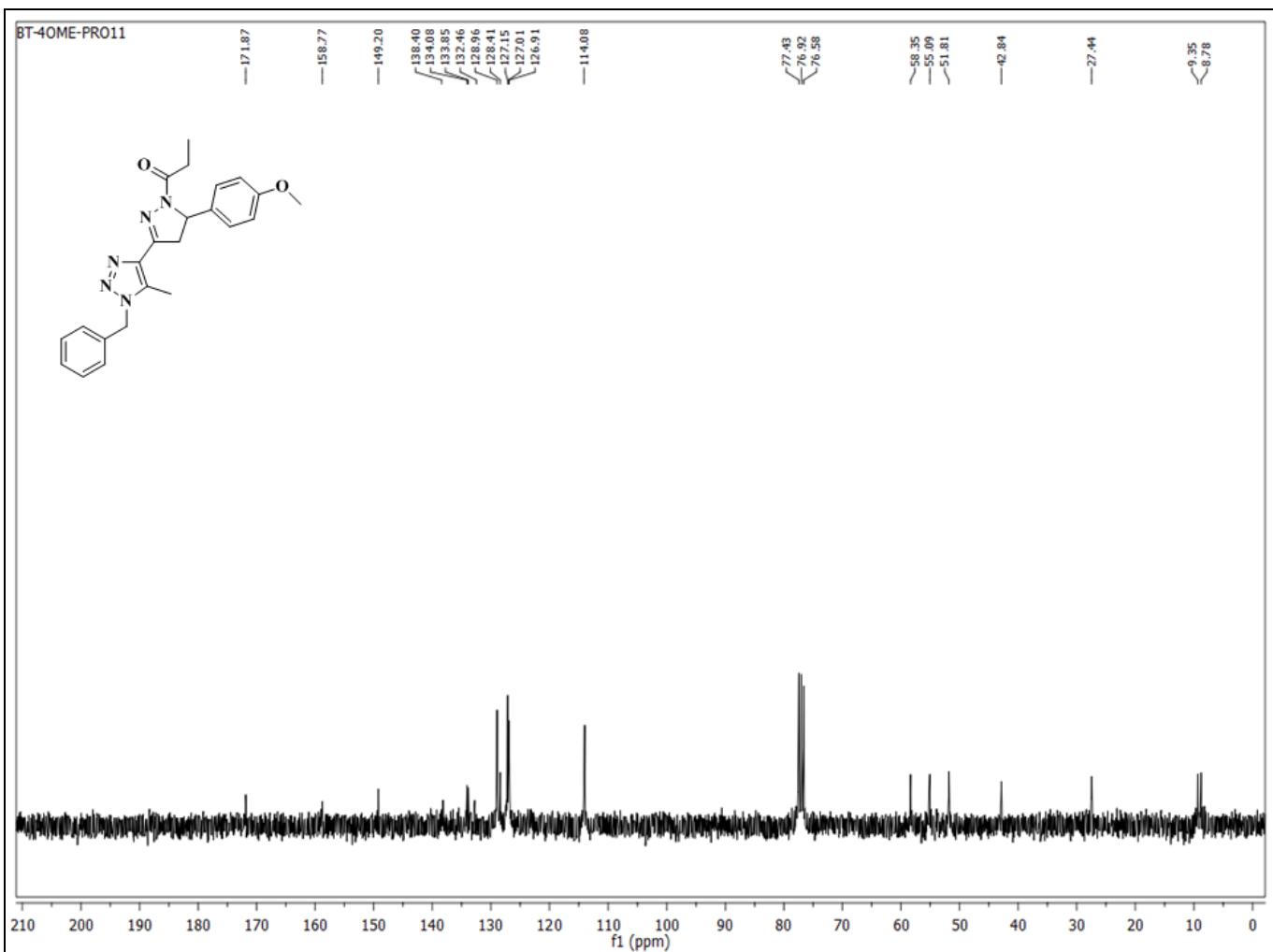


II Copies of ^1H & ^{13}C NMR of 3j-r

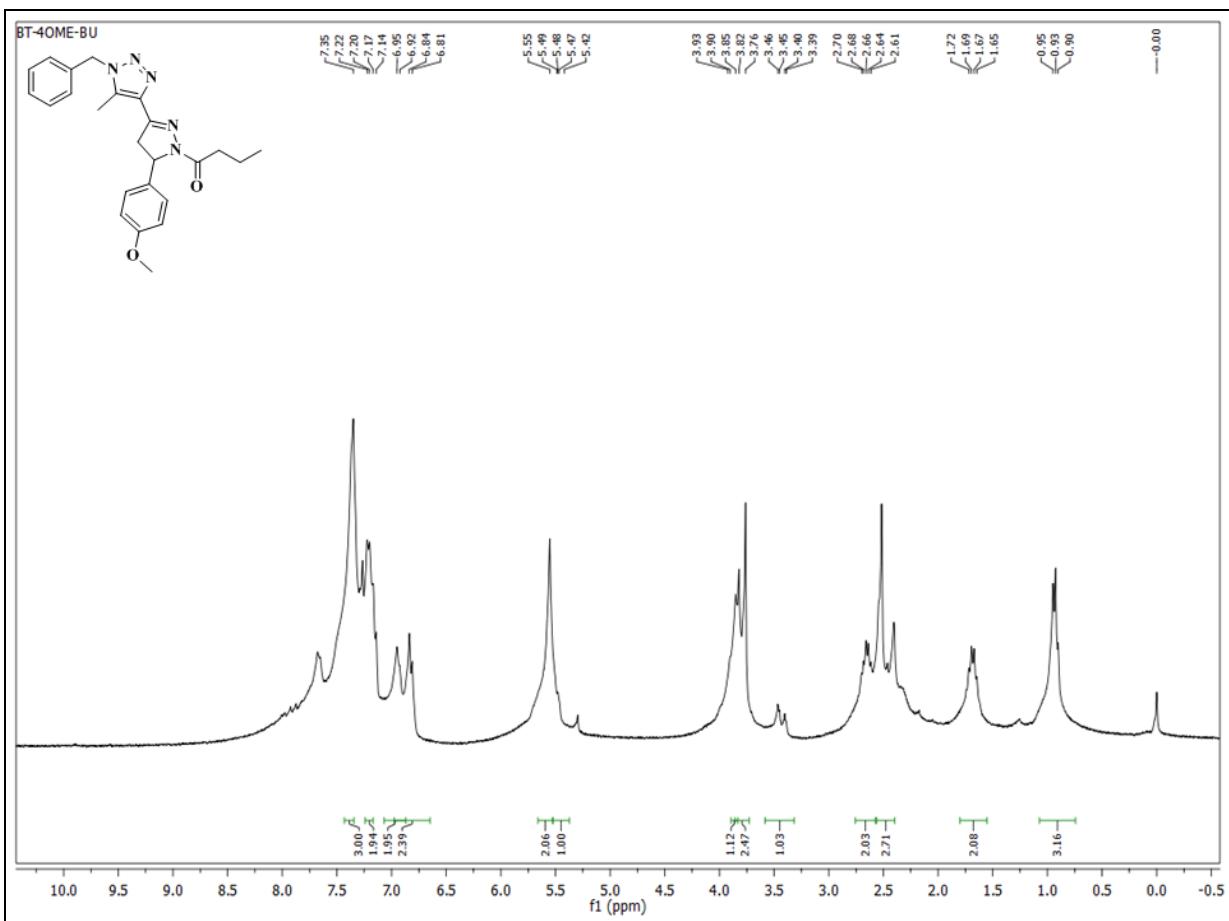




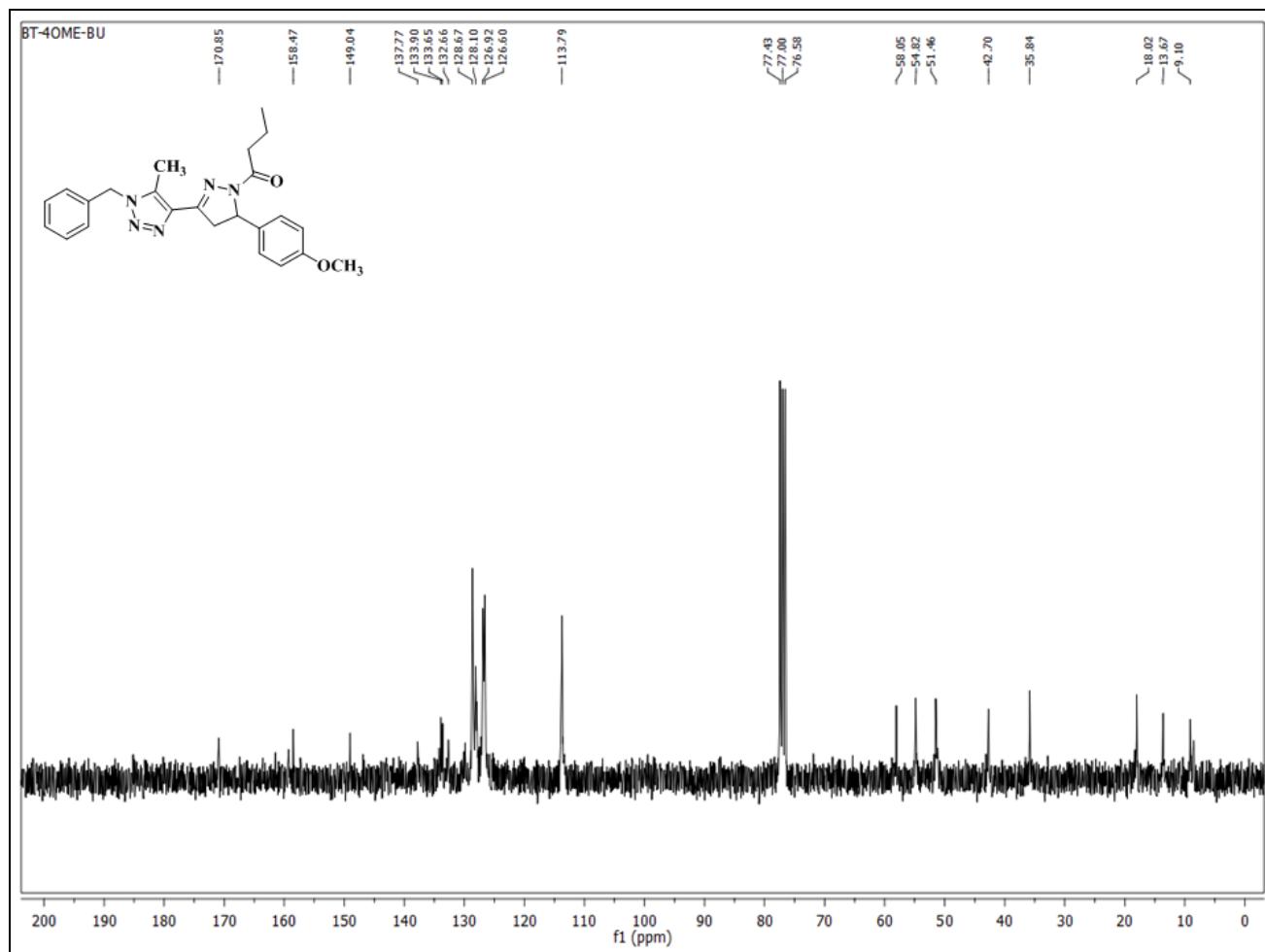




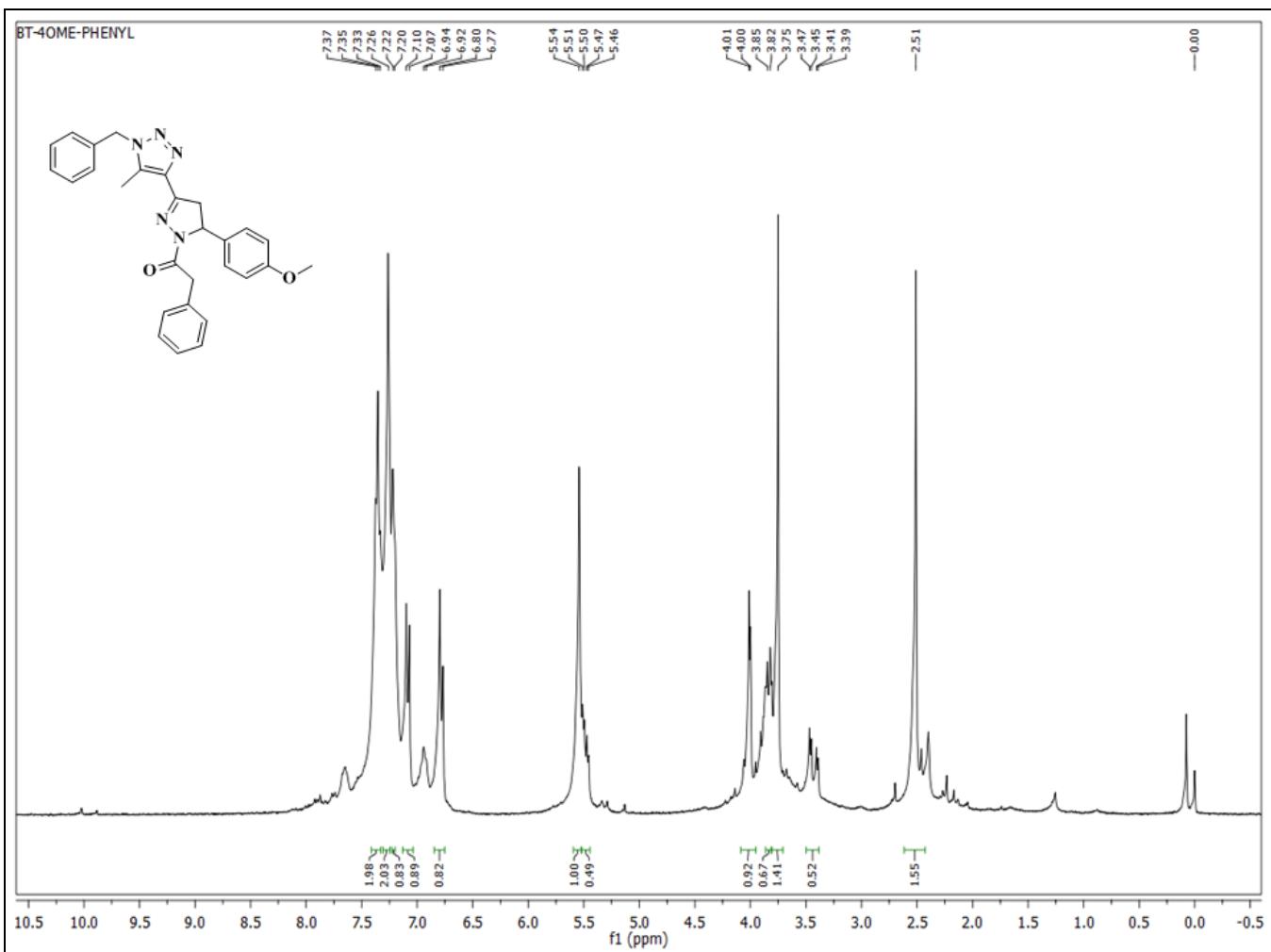
¹³C NMR (75 MHZ, CDCl₃): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)propan-1-one (3k)



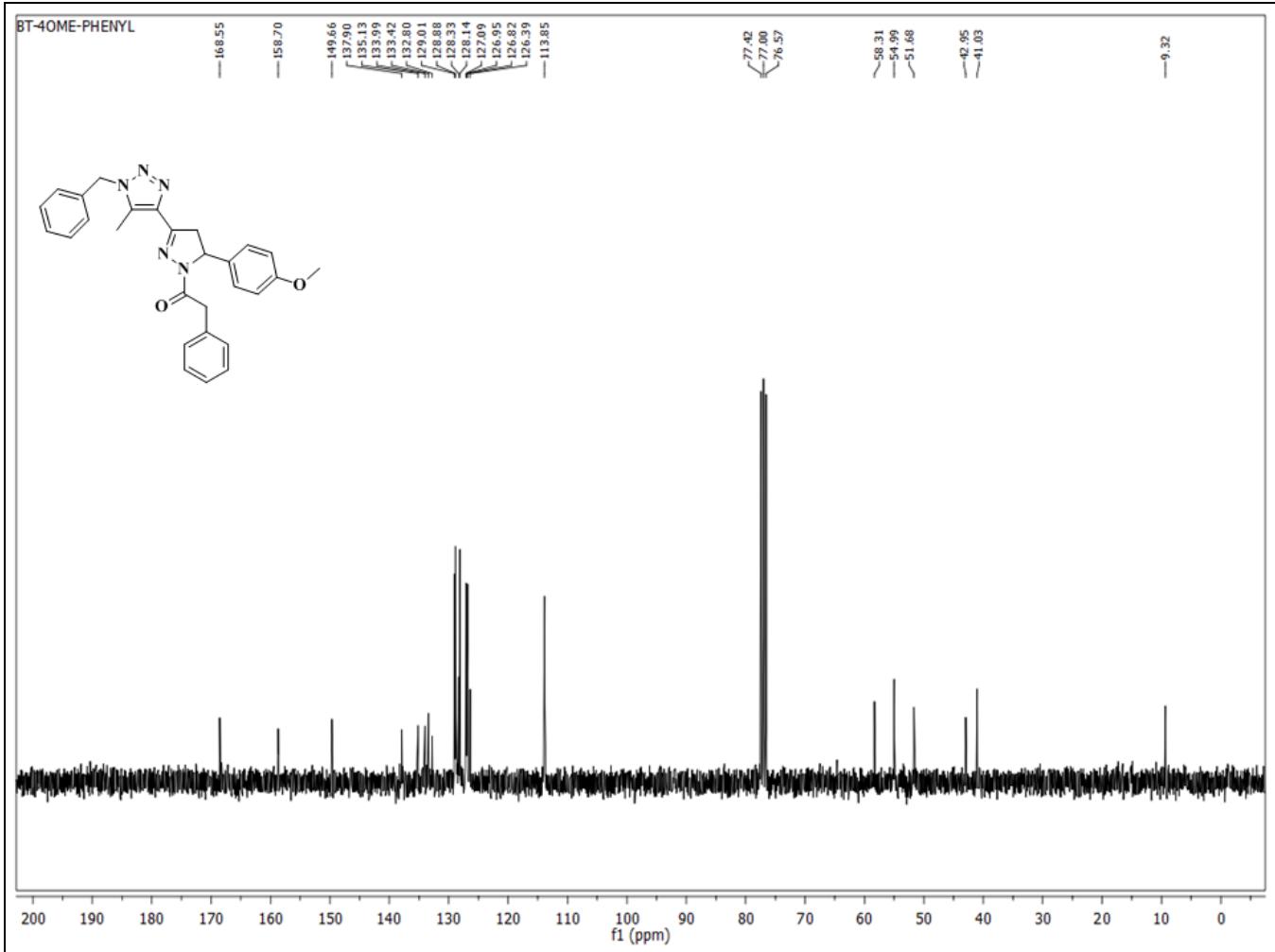
¹H NMR (300 MHZ, CDCl₃): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3l)

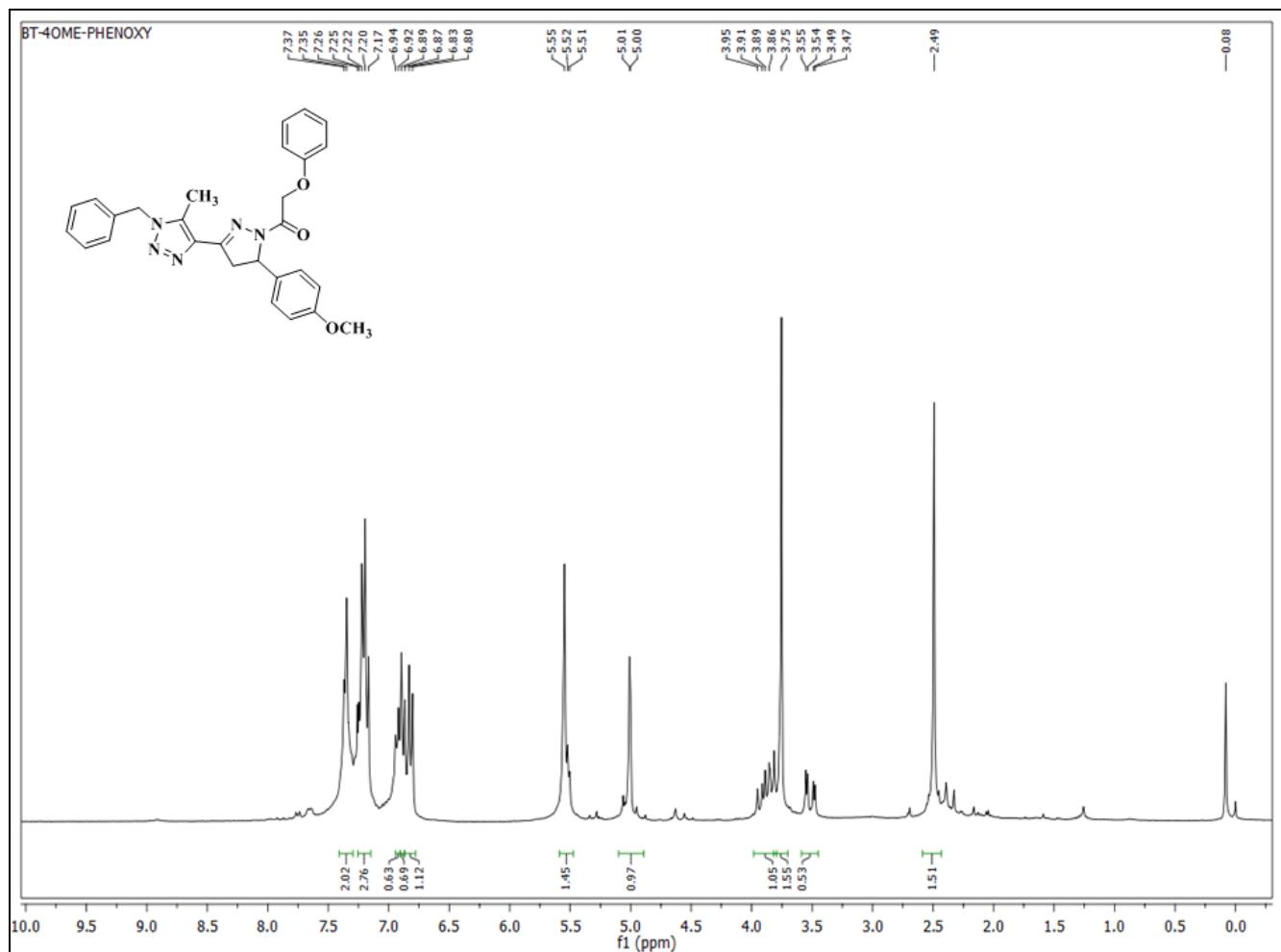


^{13}C NMR (75 MHz, CDCl_3): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)butan-1-one (3l)

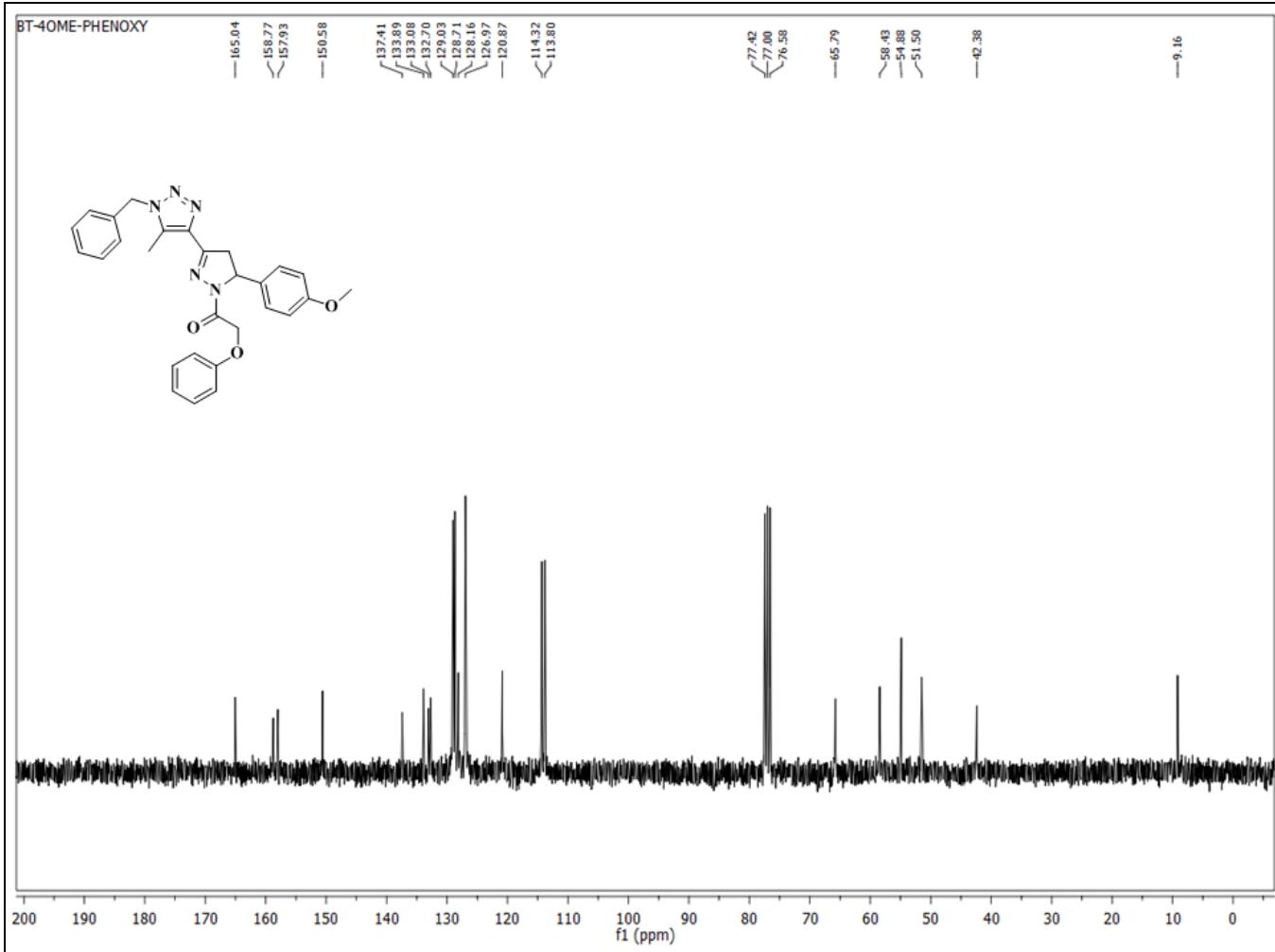


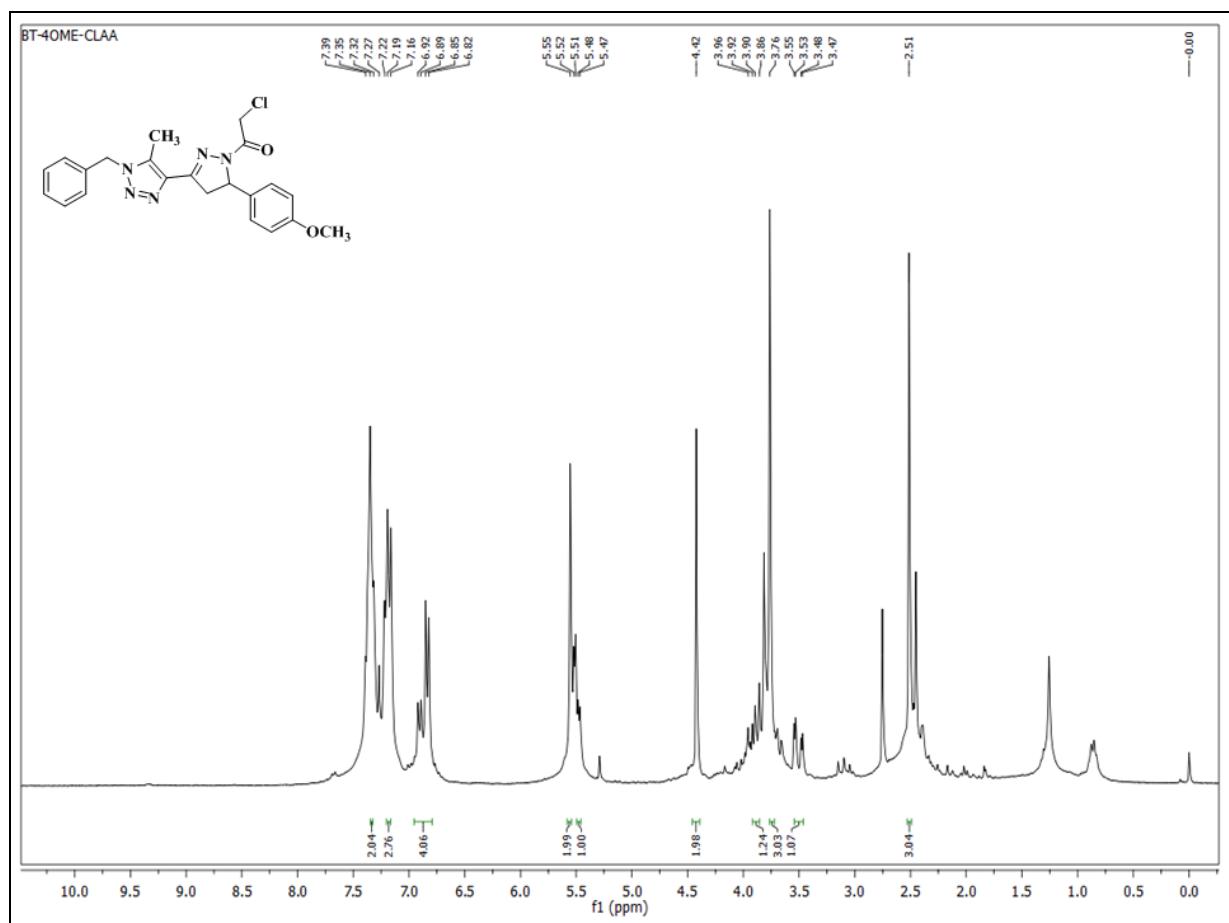
¹H NMR (300 MHz, CDCl₃): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-1*H*-pyrazol-1-yl)-2-phenyl ethanone (3m)

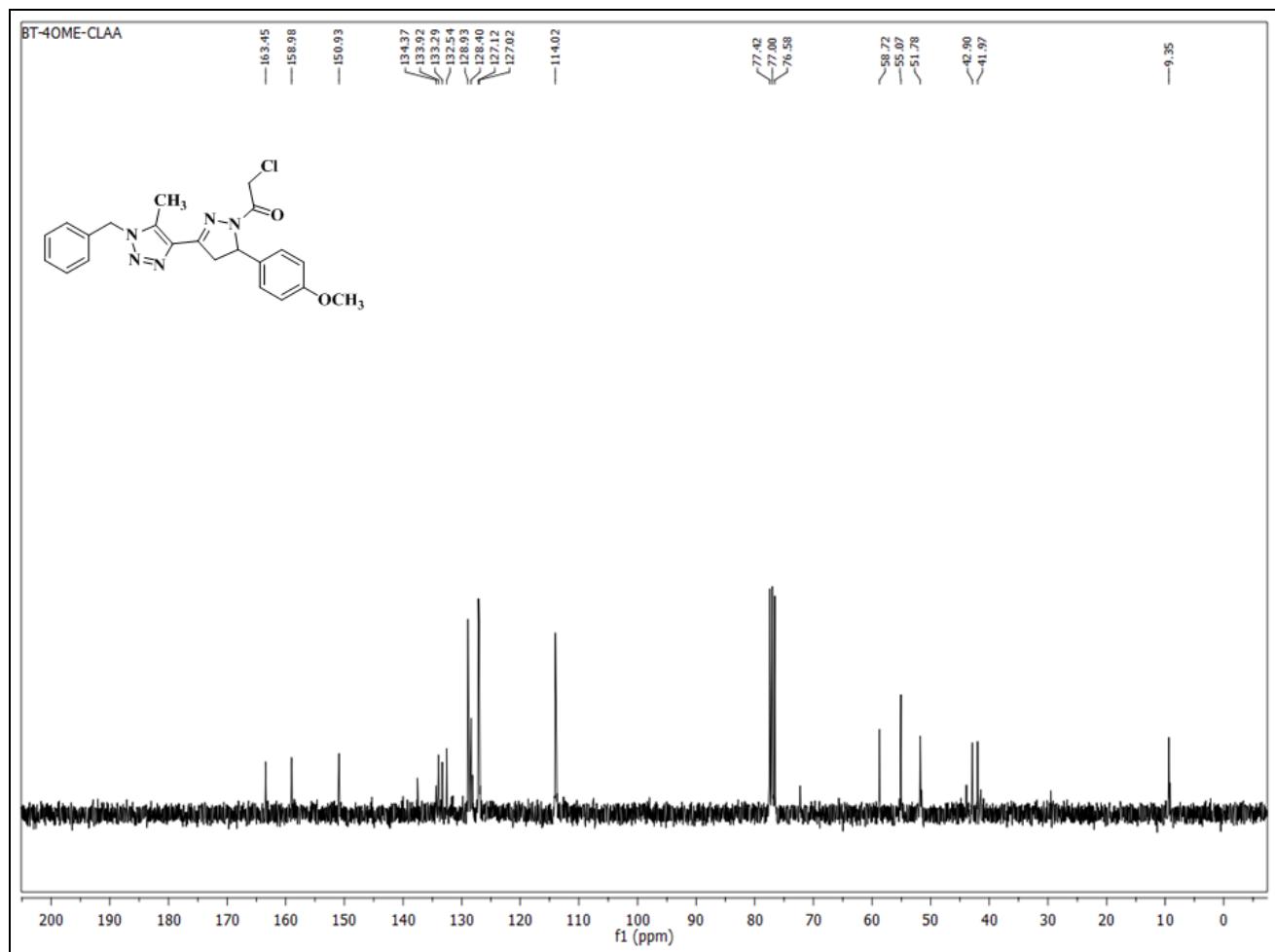


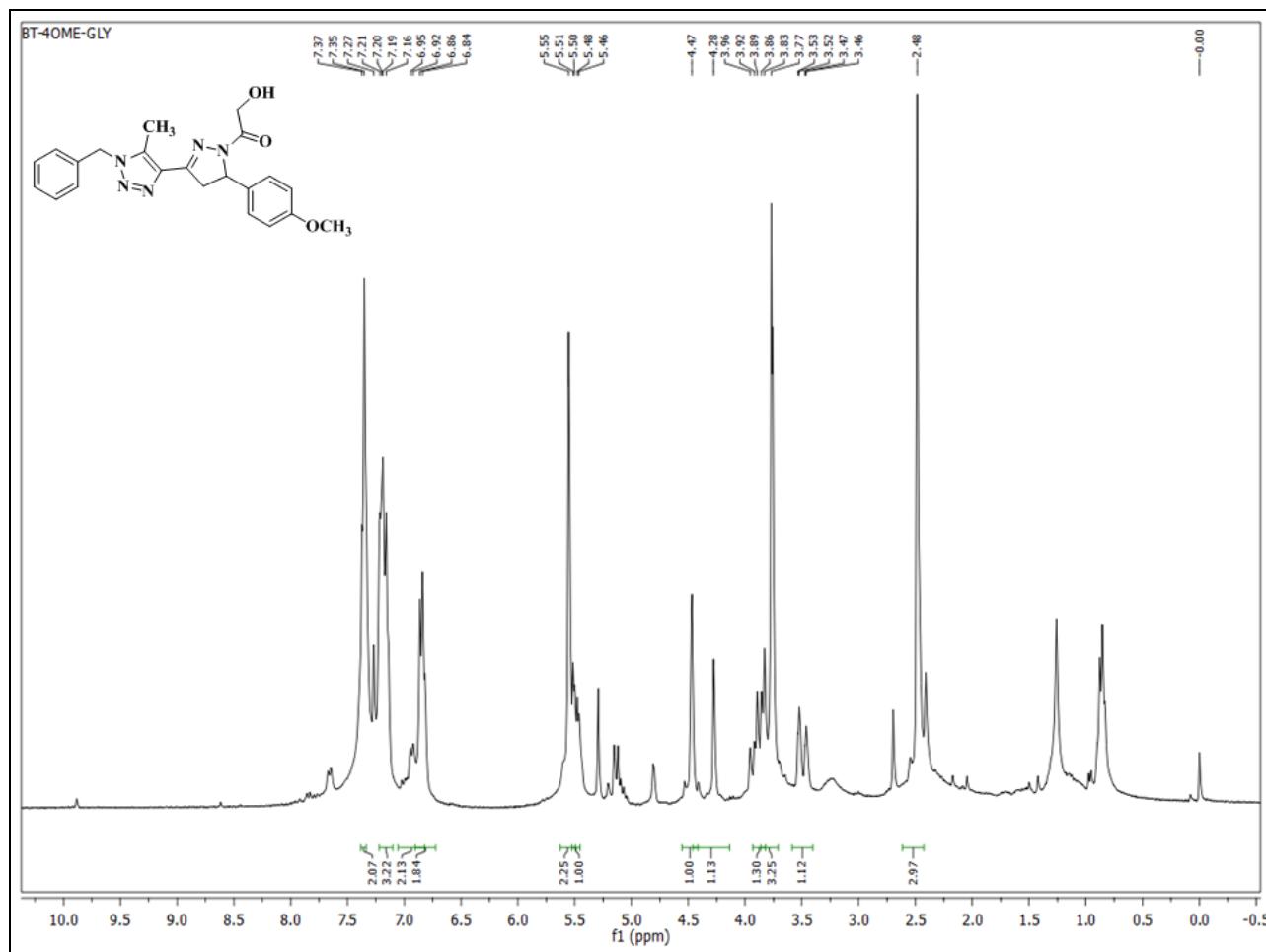


^1H NMR (300 MHz, CDCl_3): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-1*H*-pyrazol-1-yl)-2-phenoxyethanone (**3n**)

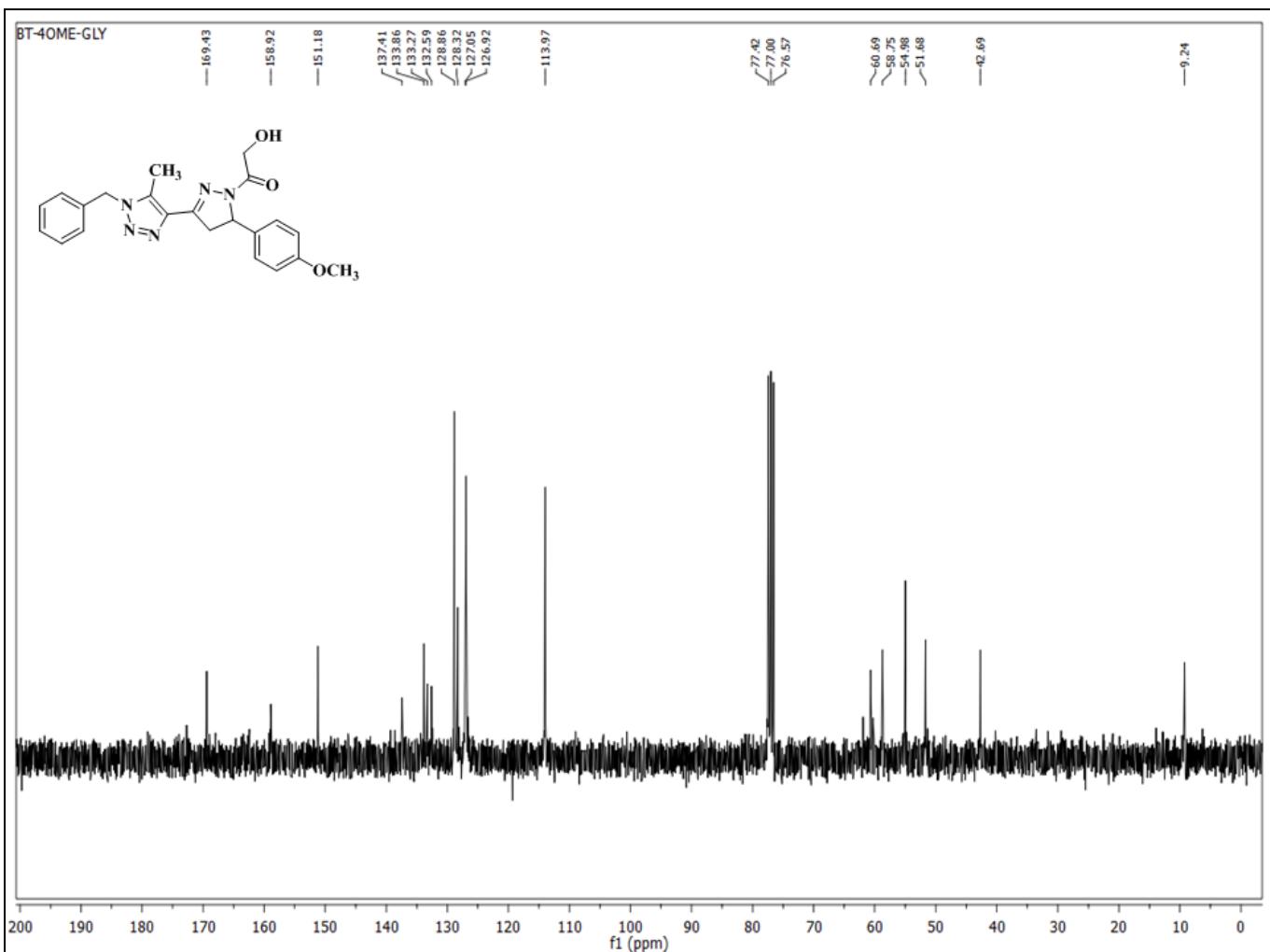




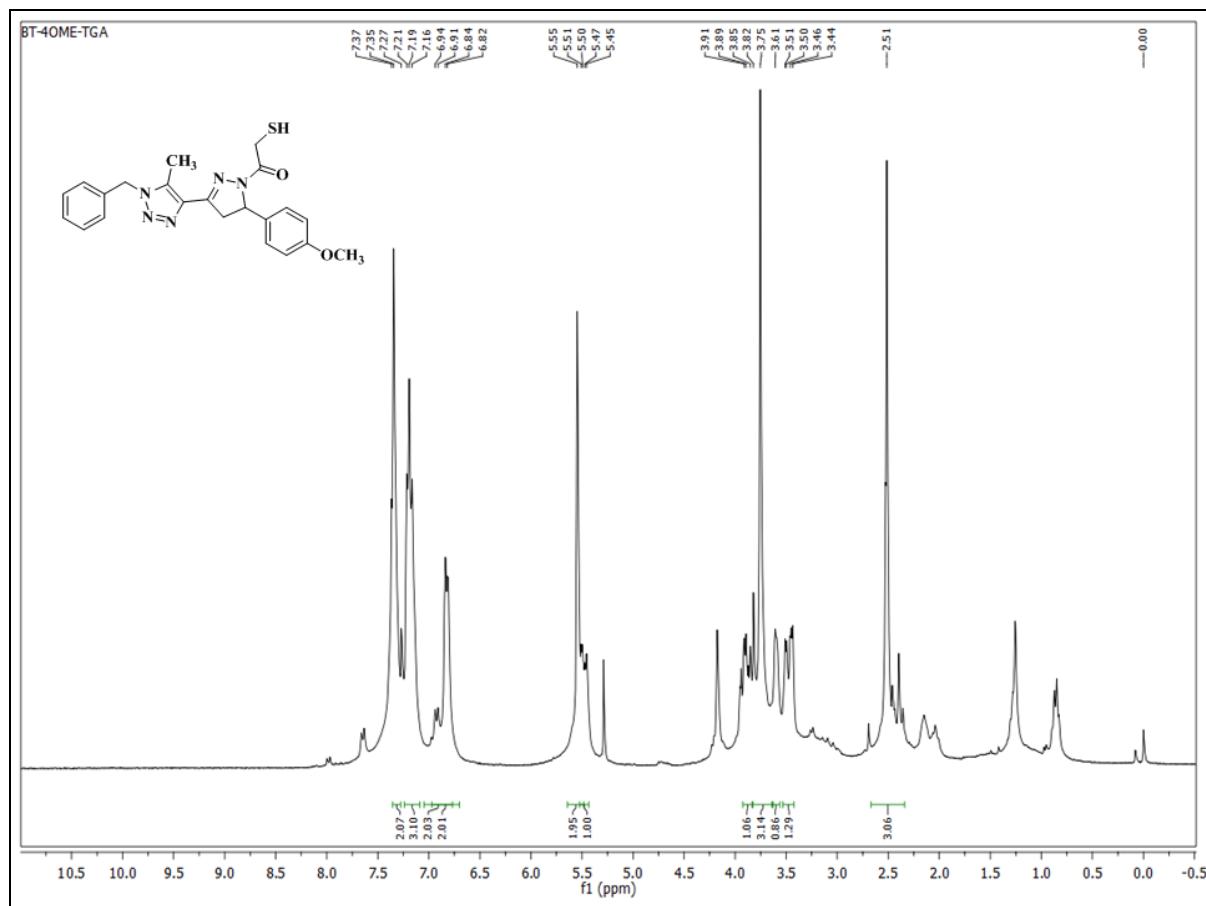


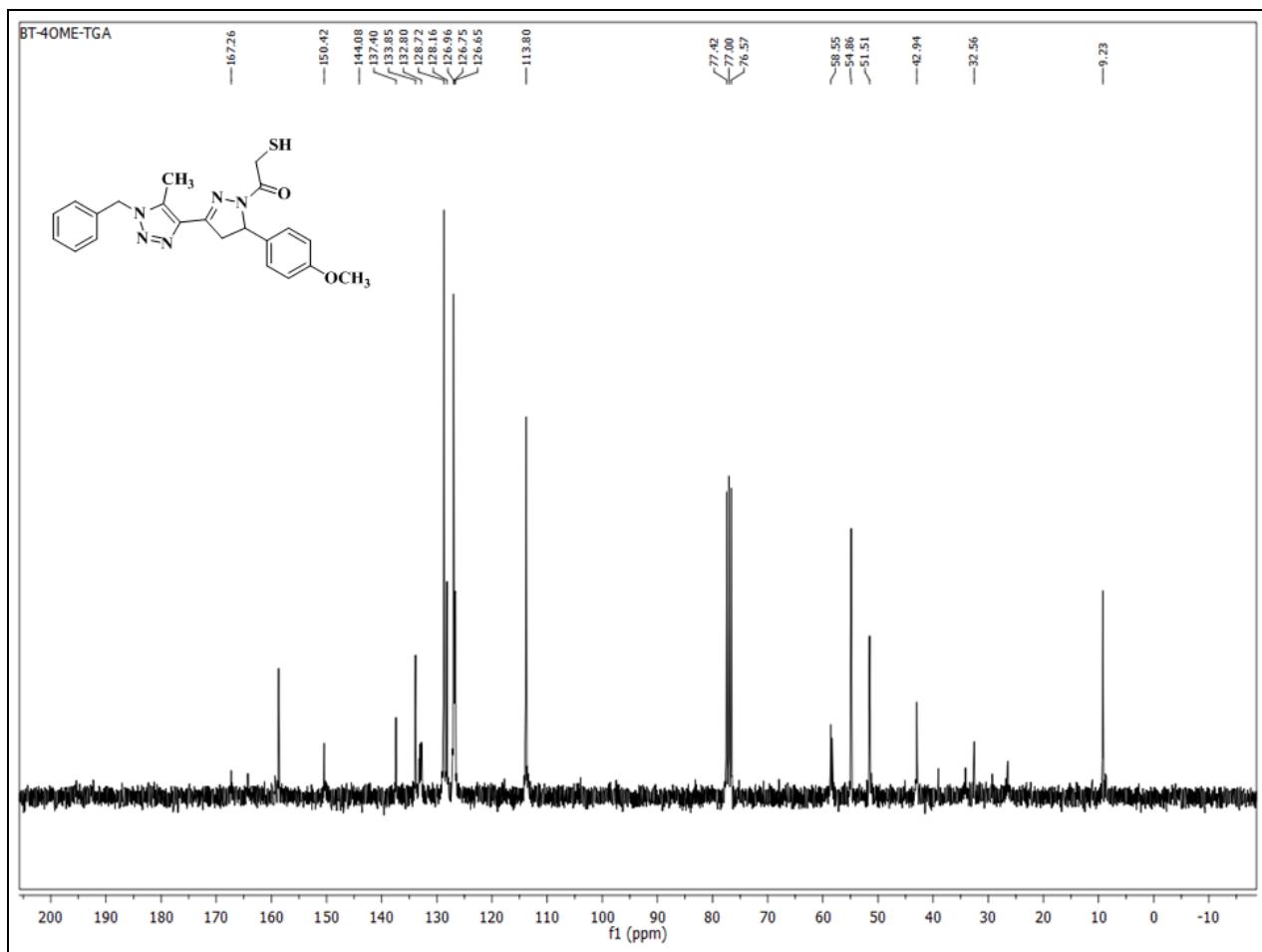


¹H NMR (300 MHz, CDCl₃): 1-(3-(1-Benzyl-5-methyl-1H-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)-2-hydroxyethanone (3p)

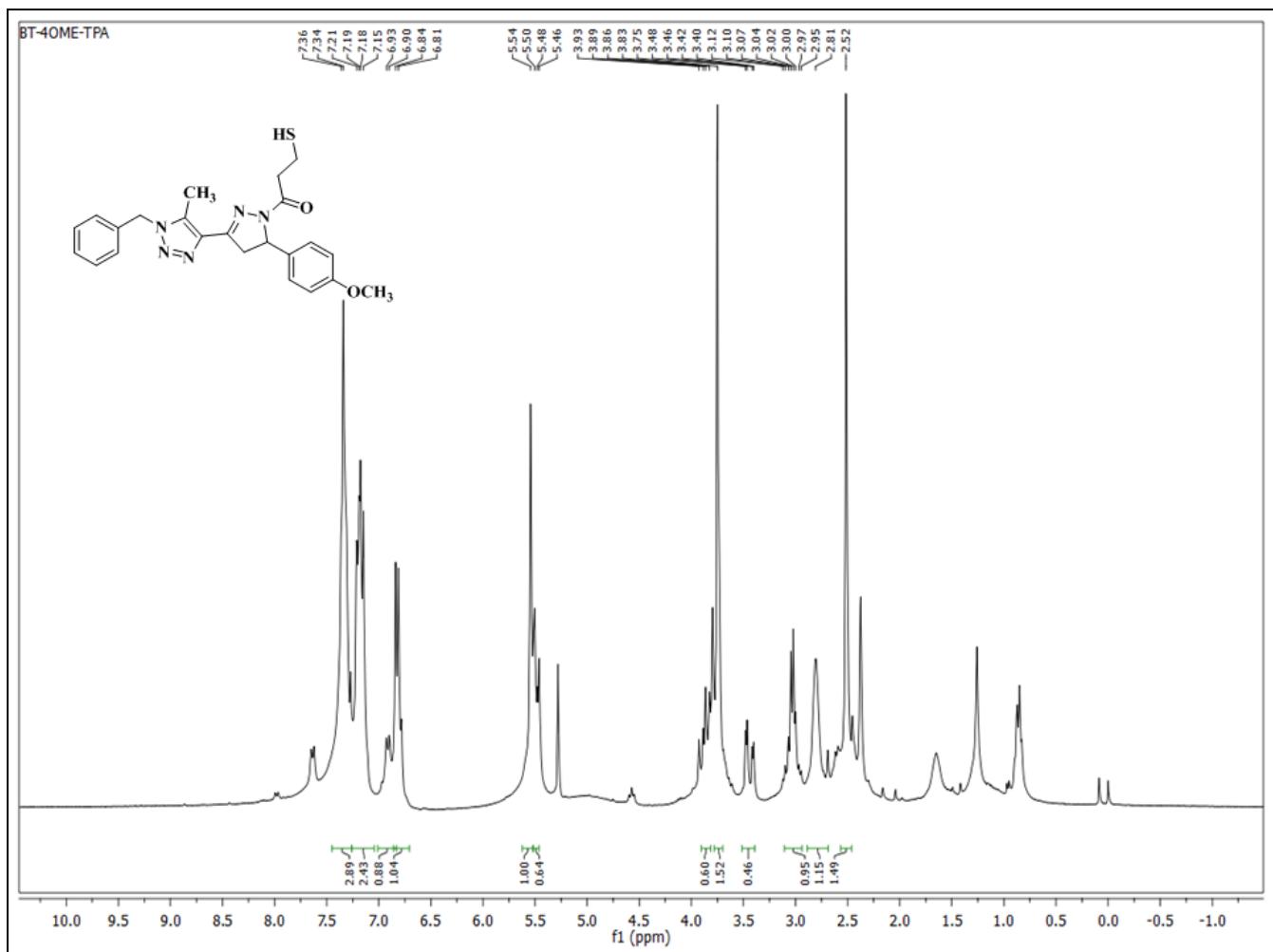


^{13}C NMR (75 MHz, CDCl_3): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-2-hydroxyethanone (3p)

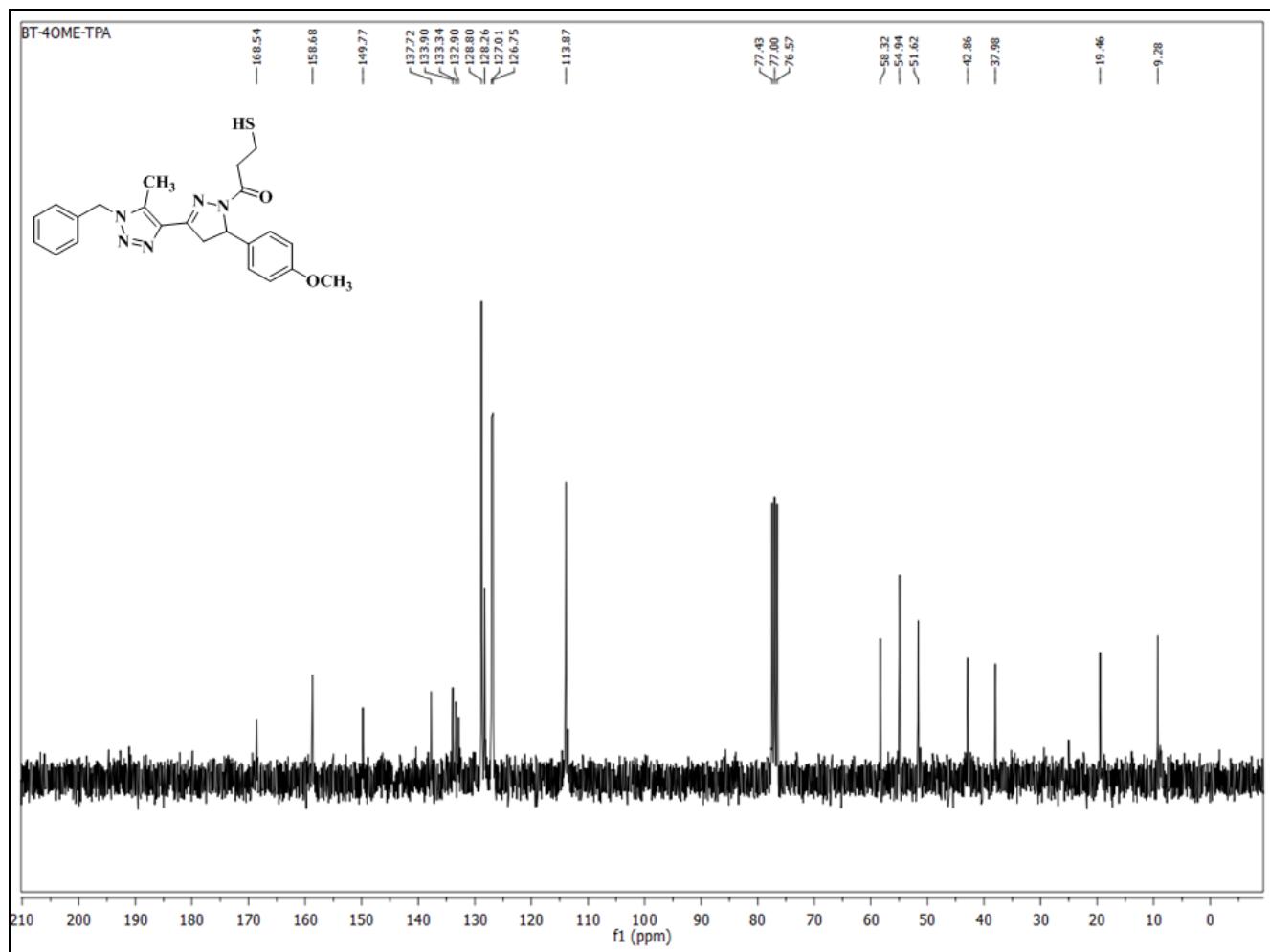




^{13}C NMR (75MHz, CDCl_3): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-2-mercaptopropanone (**3q**)

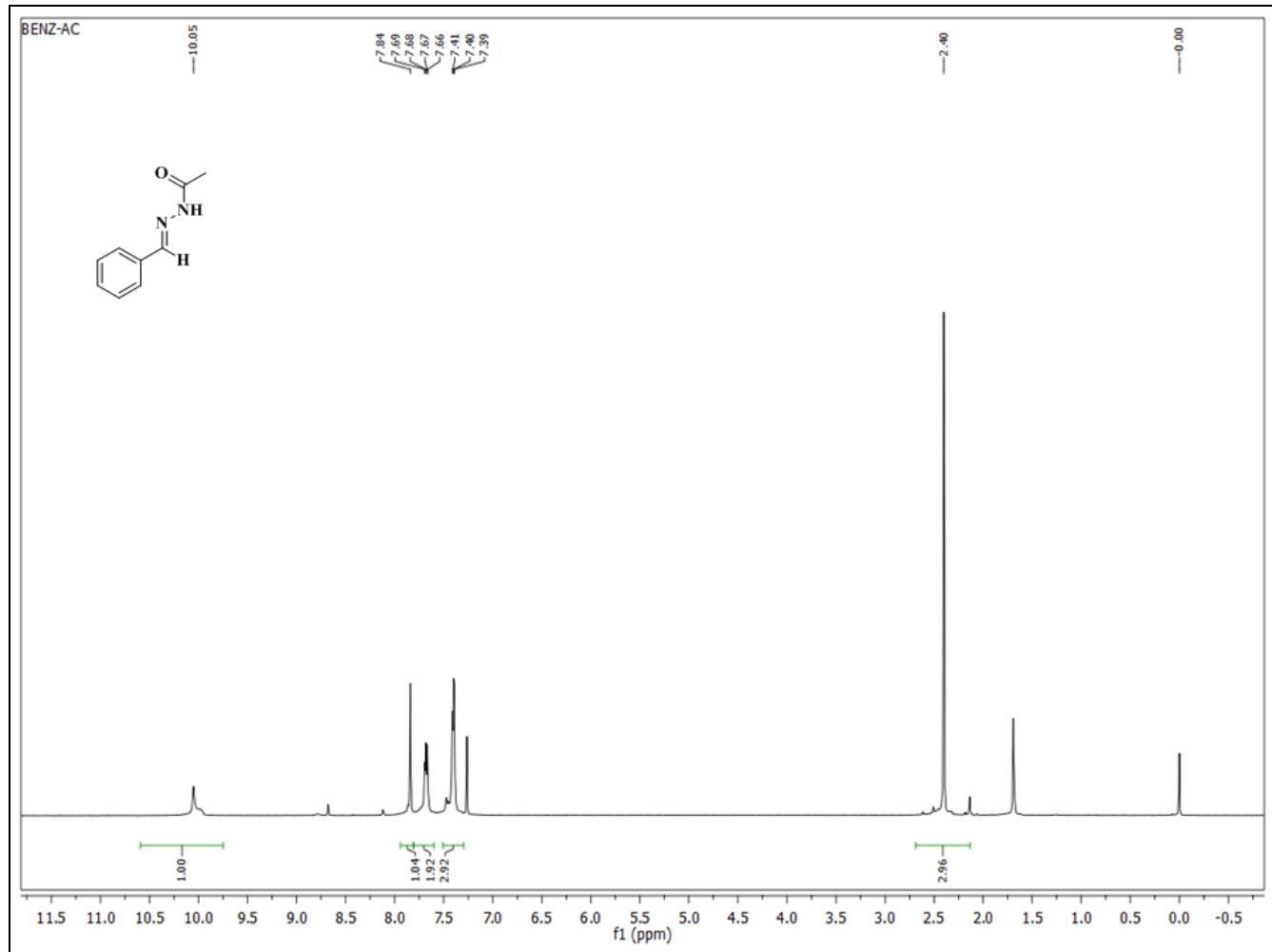


¹H NMR (300 MHz, CDCl₃): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-hydroxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-3-mercaptopropan-1-one (3r)

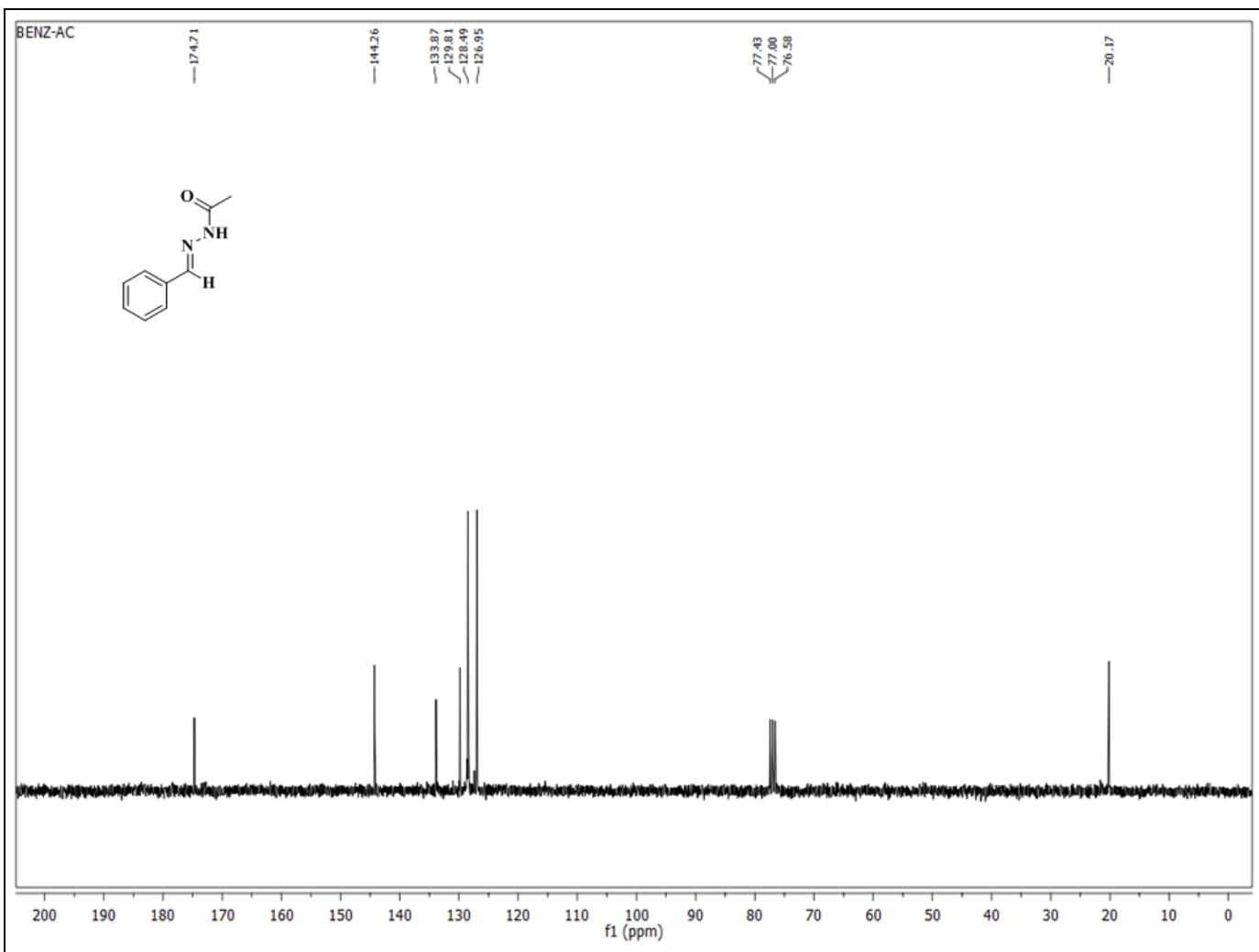


¹³C NMR (75 MHz, CDCl₃): 1-(3-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-5-(4-hydroxyphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-3-mercaptopropan-1-one (3r)

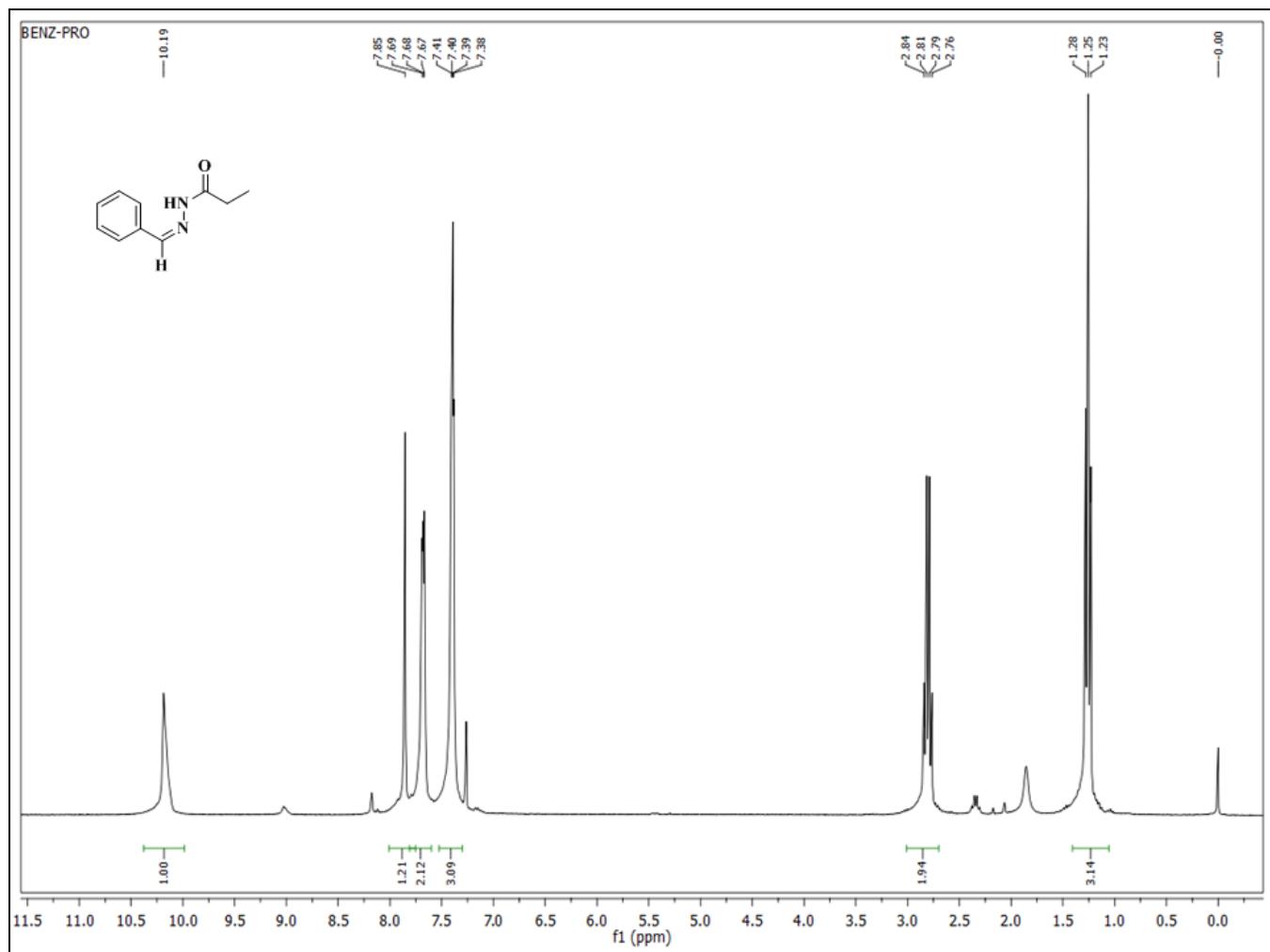
III Copies of ^1H & ^{13}C NMR of **8a-i**



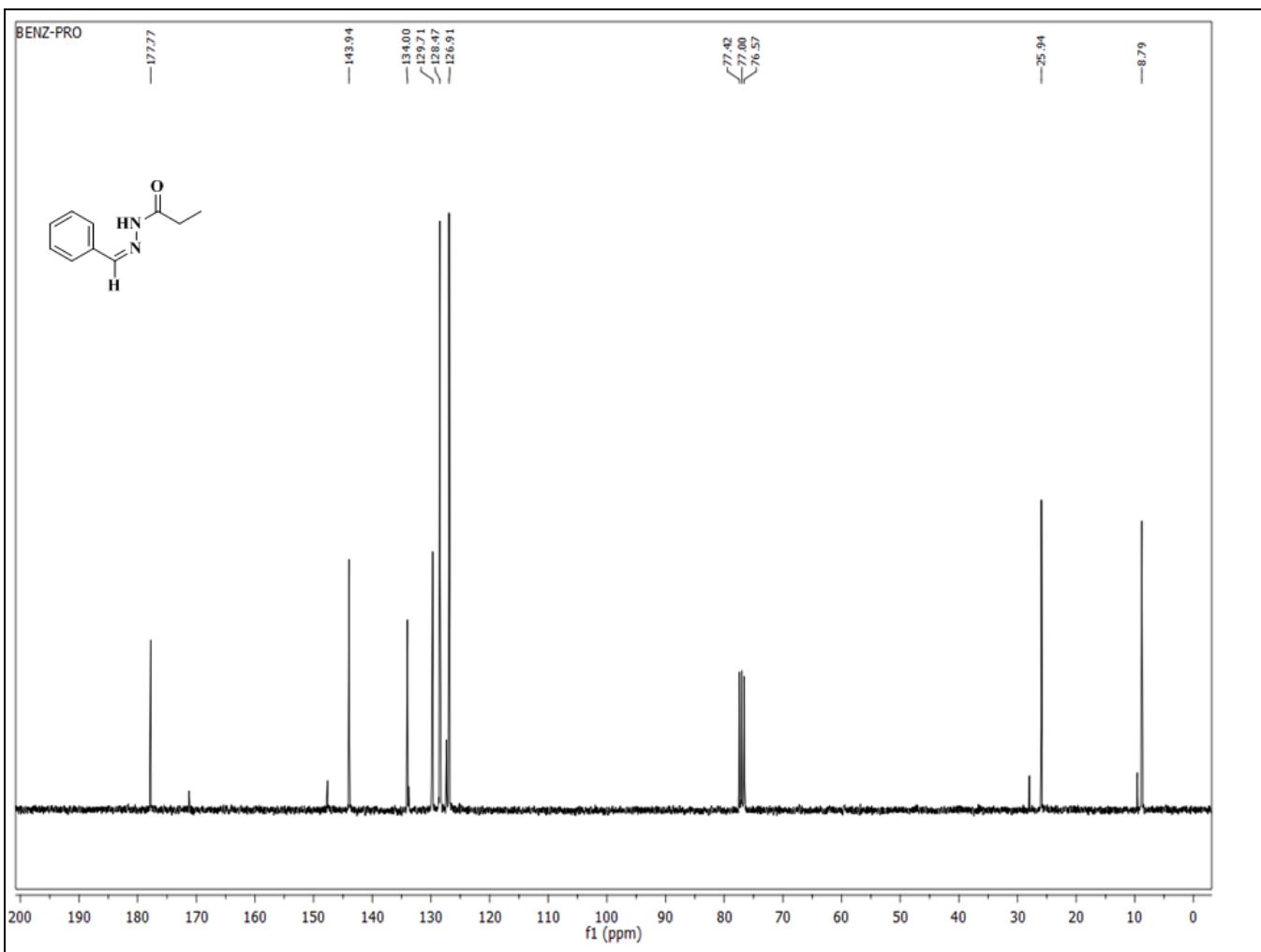
^1H NMR (300 MHz, CDCl_3): (*E*)-N'-Benzylideneacetohydrazide (**8a**)



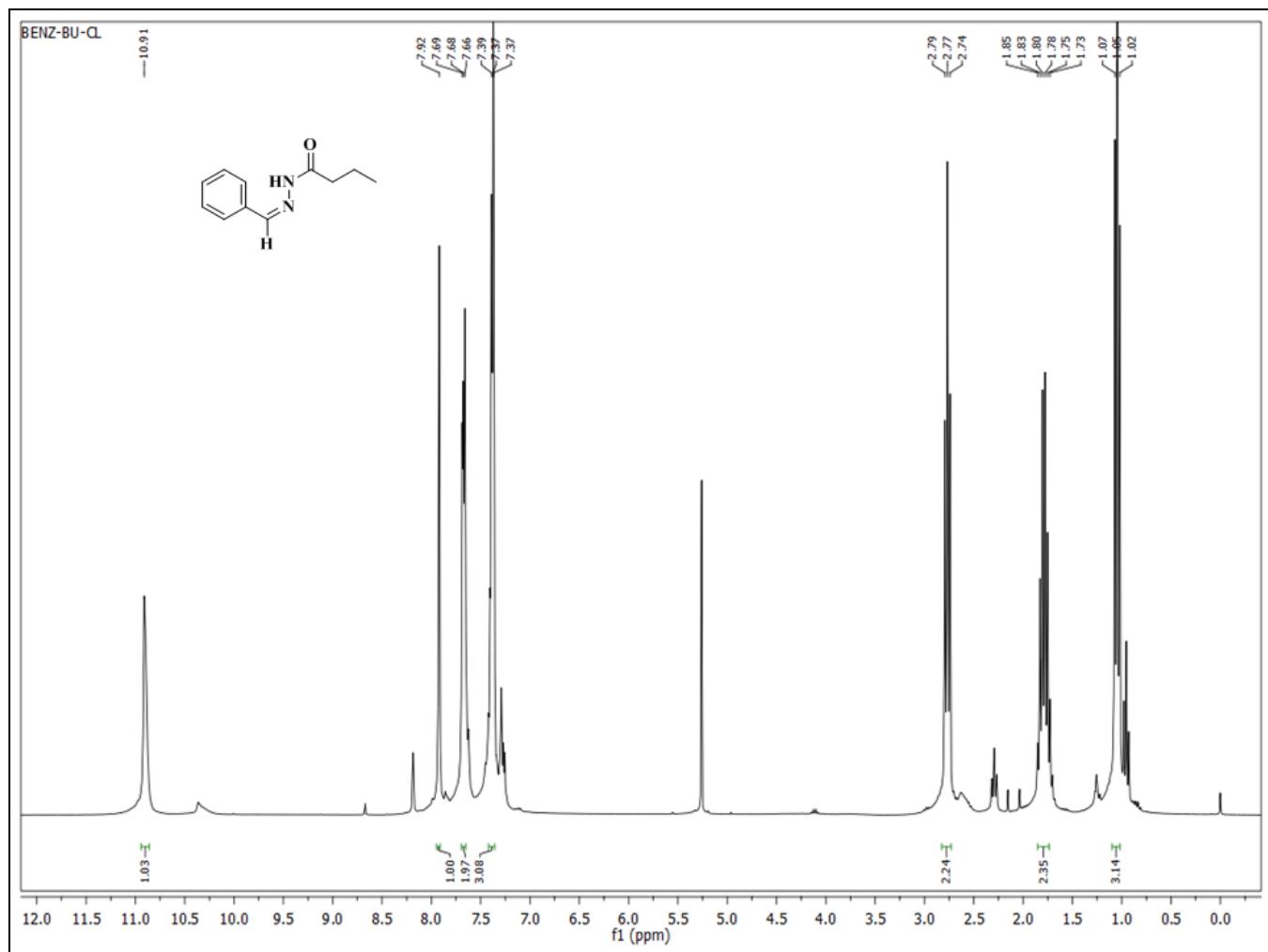
^{13}C NMR (75 MHz, CDCl_3): (*E*)-*N'*-Benzylideneacetohydrazide (8a)



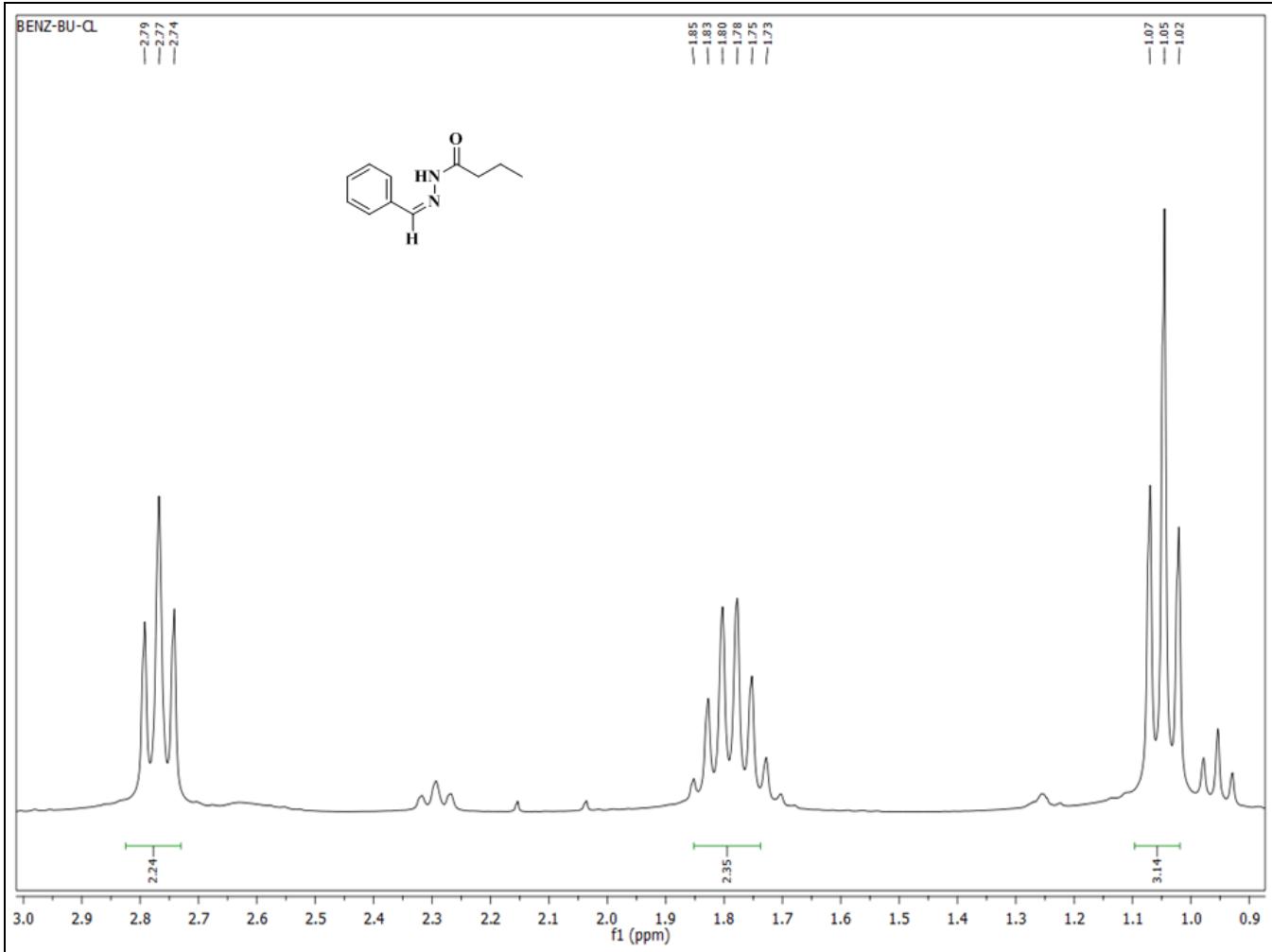
¹H NMR (300 MHz, CDCl₃): (E)- N'-Benzylidenepropionohydrazide (8b)



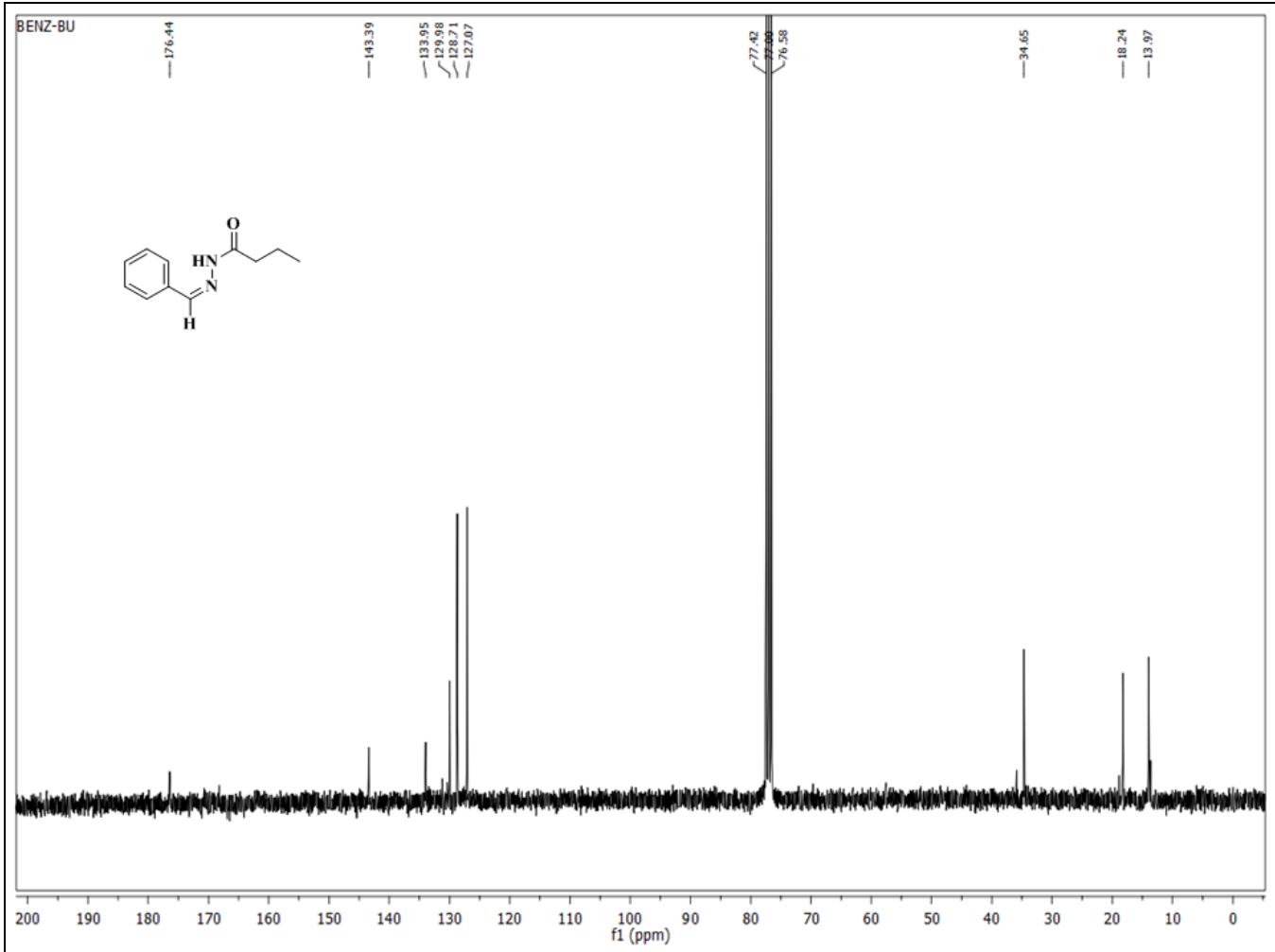
^{13}C NMR (75 MHz, CDCl_3): (*E*)-*N'*-Benzylidenepropionohydrazide (8b)

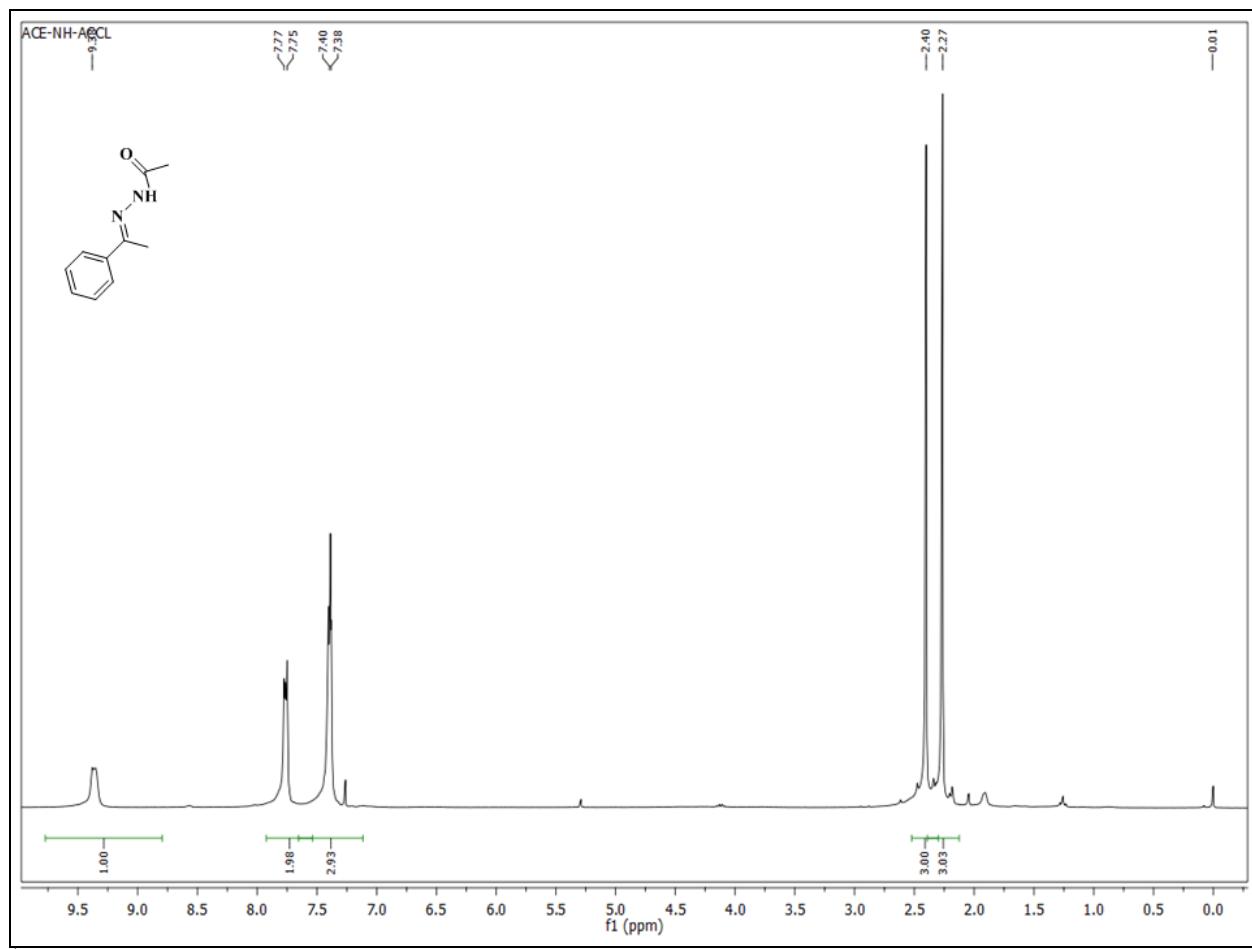


¹H NMR (300 MHz, CDCl₃): (E)-N'-Benzylidenebutyrohydrazide (8c)

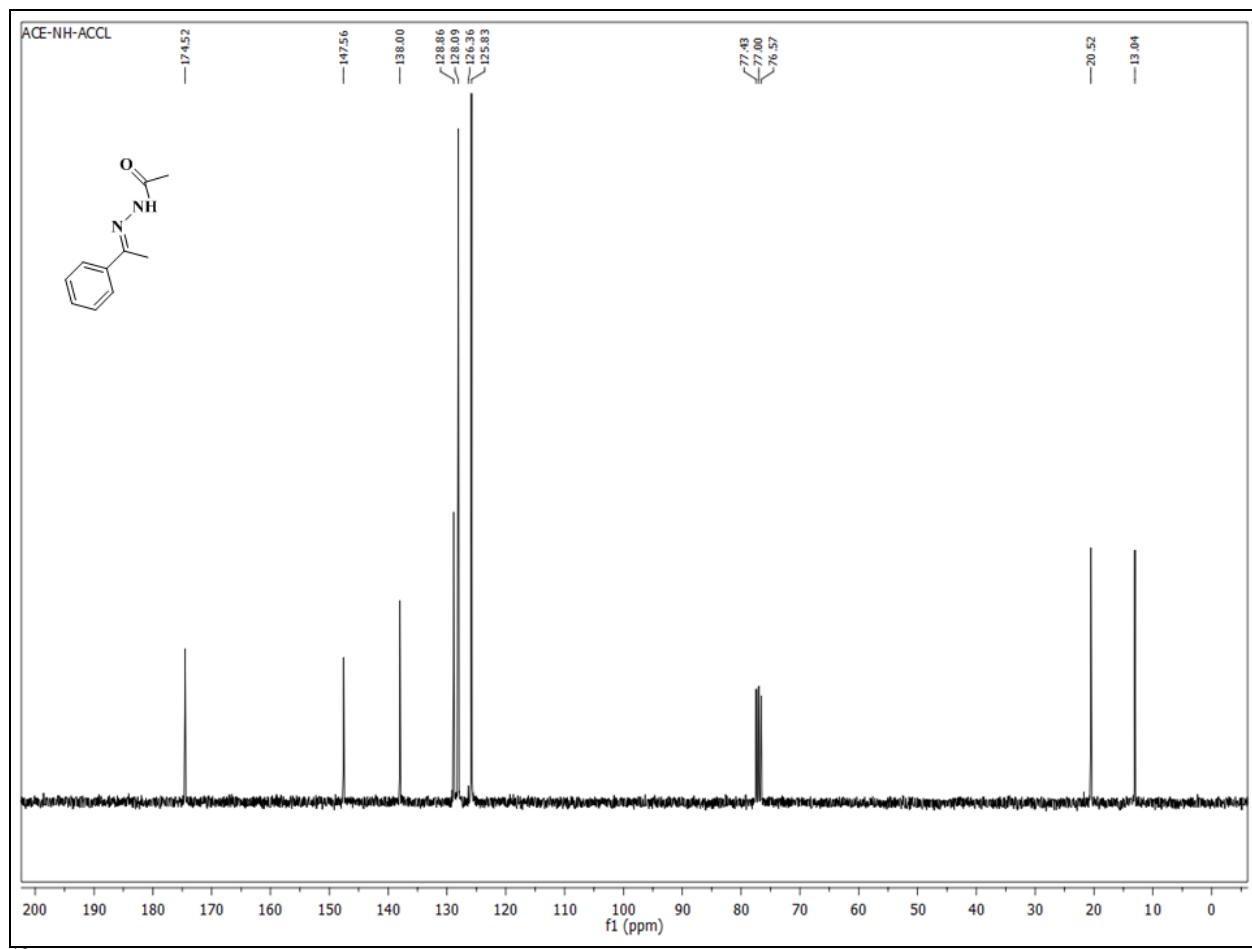


¹H NMR (300 MHz, CDCl₃): [Expansion] (E)-N'-Benzylidenebutyrohydrazide (8c)

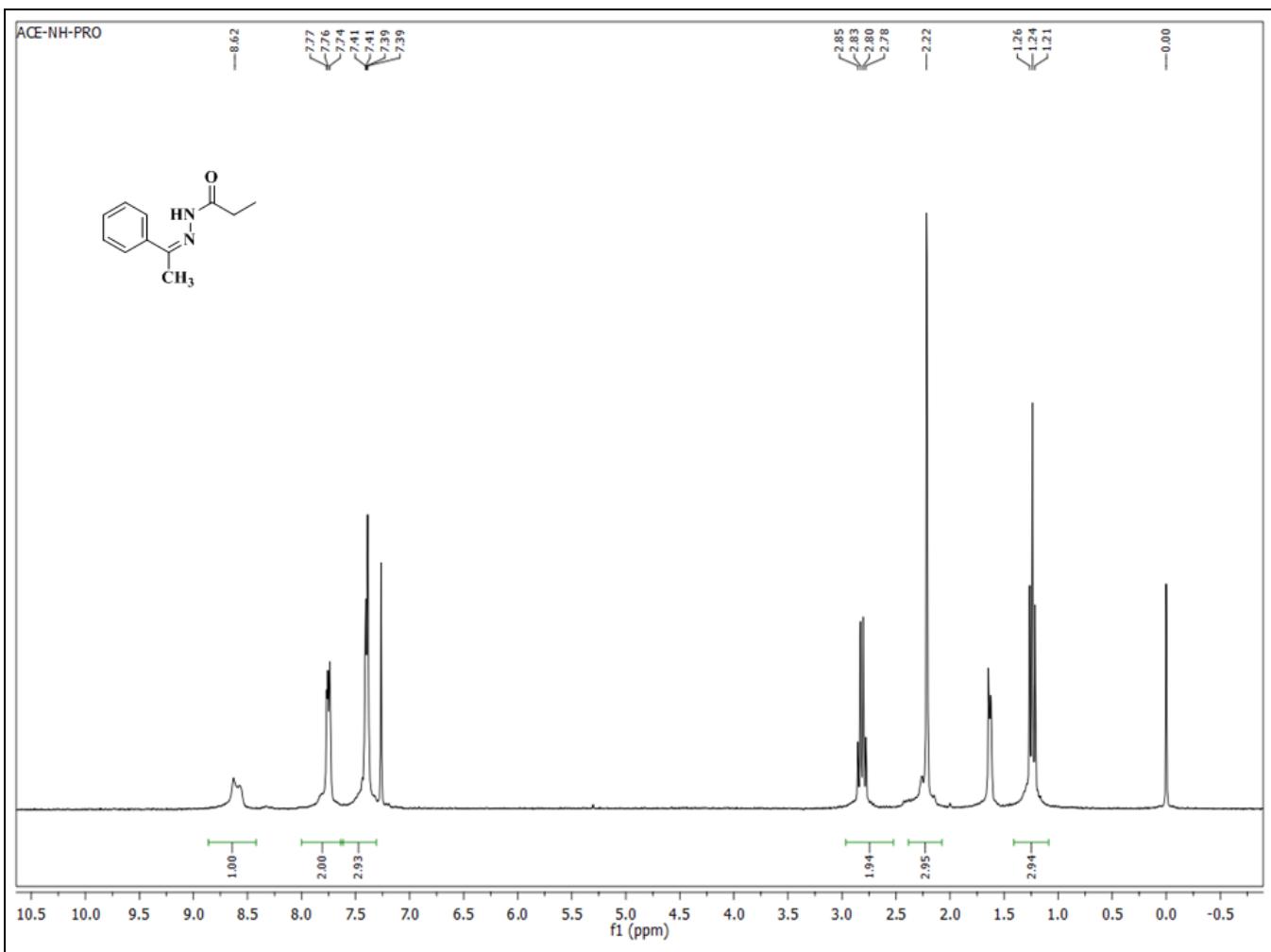


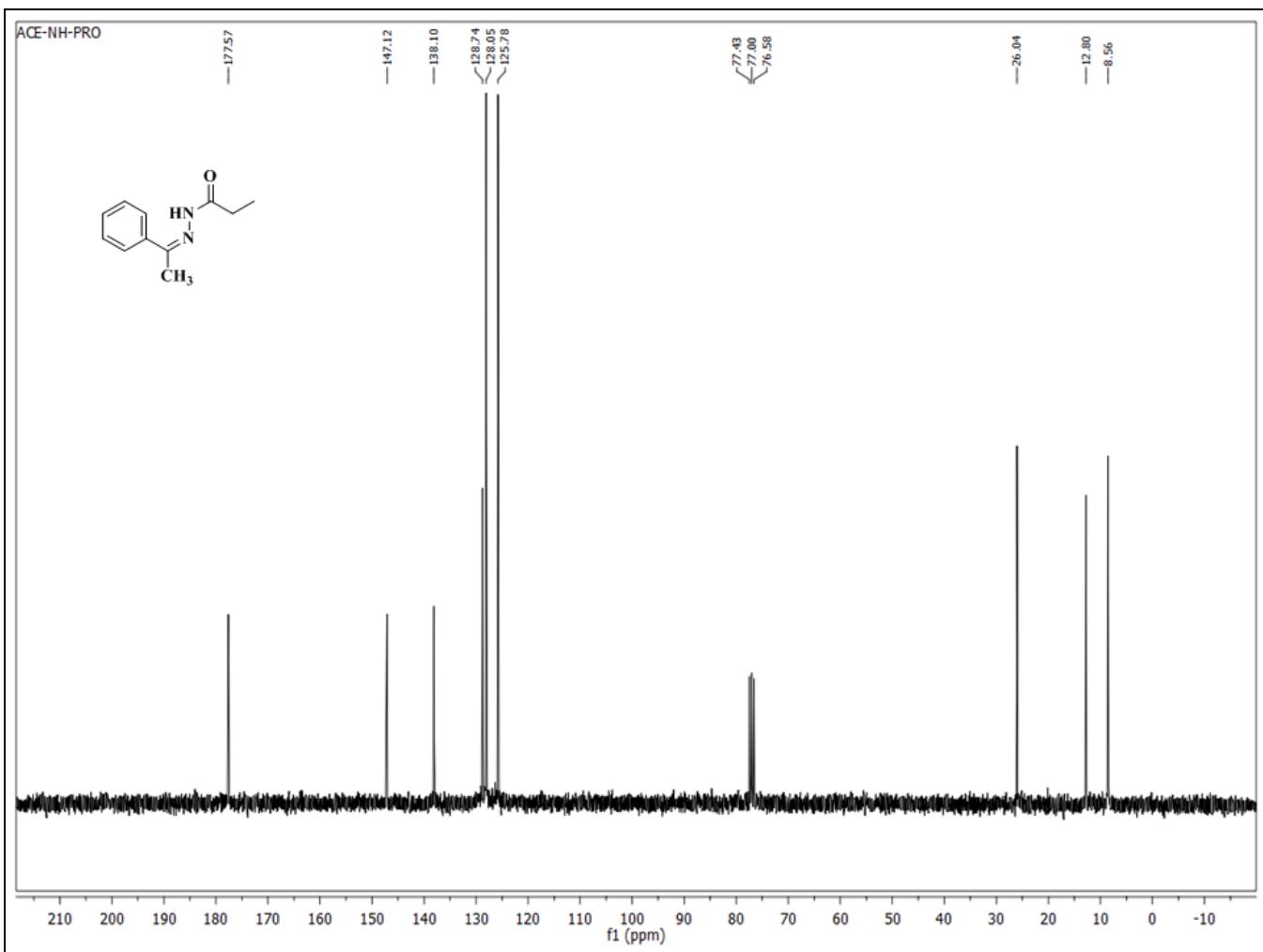


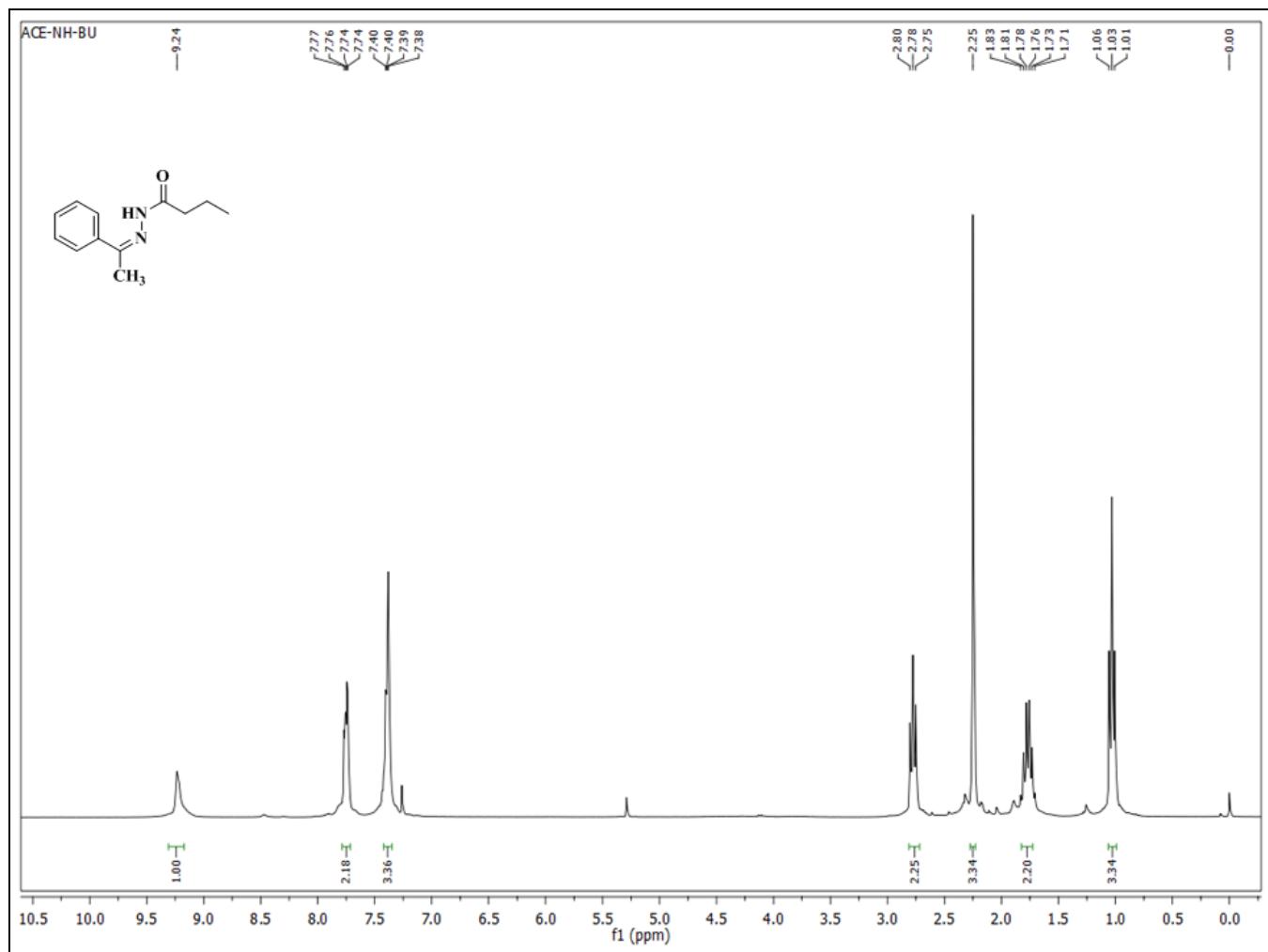
¹H NMR (300 MHz, CDCl₃): (E)-N'-(1-Phenylethylidene)acetohydrazide (8d)



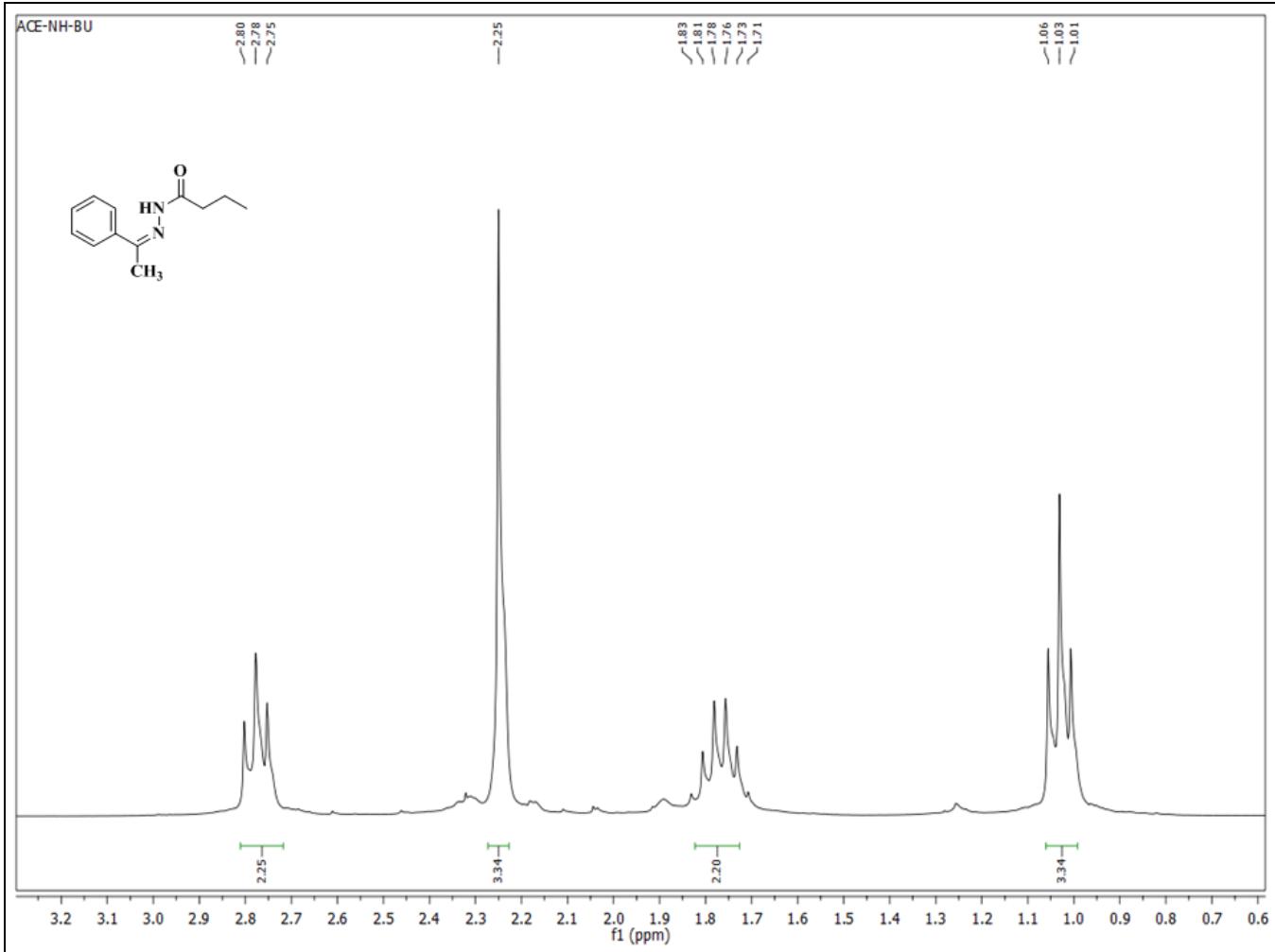
¹³C NMR (75 MHz, CDCl₃): (E)-N'-(1-Phenylethylidene)acetohydrazide (8d)



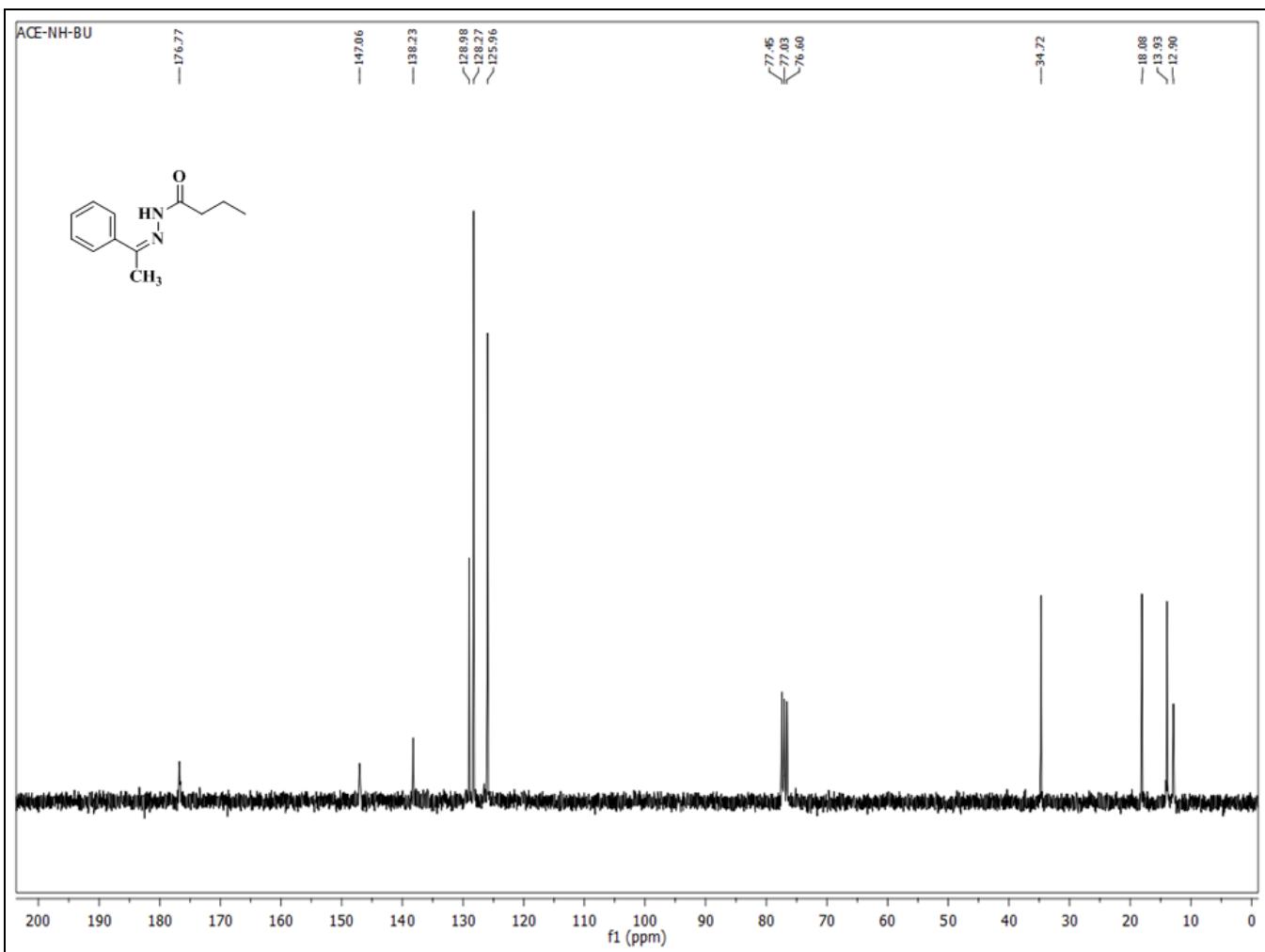


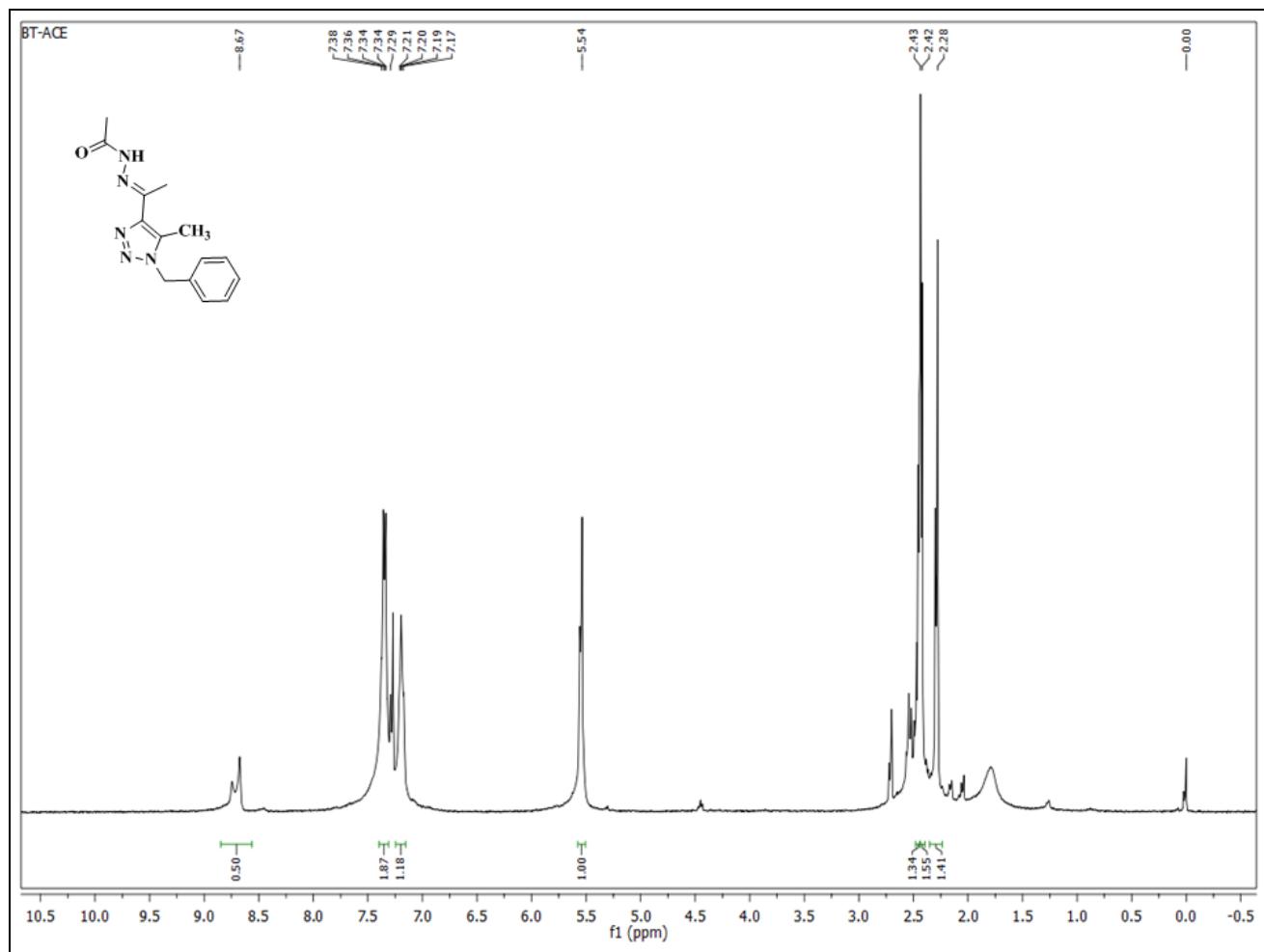


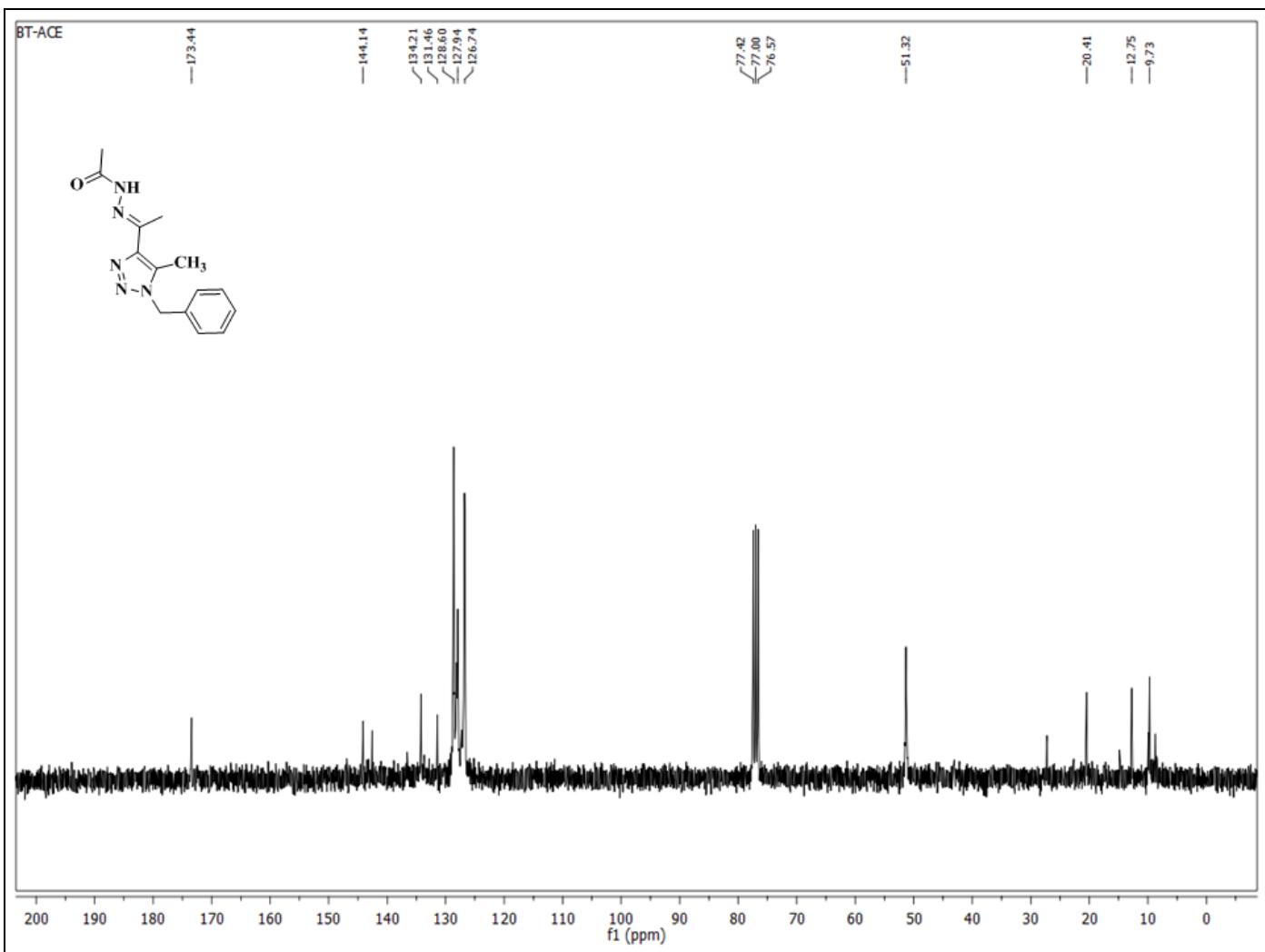
¹H NMR (300 MHz, CDCl₃): (E)-N'-(1-Phenylethylidene)butyrohydrazide (8f)



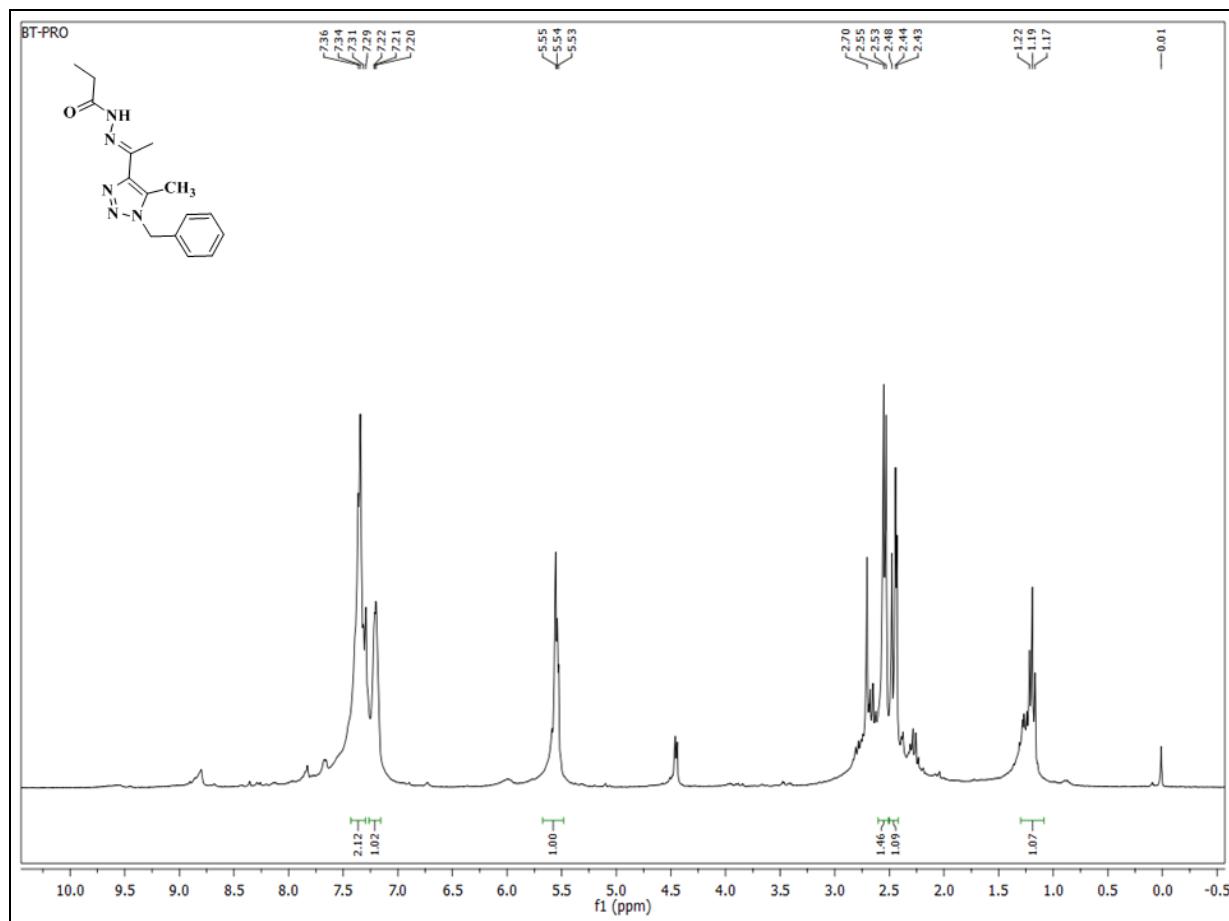
¹H NMR (300 MHz, CDCl₃): [Expantion] (E)-N'-(1-Phenylethylidene)butyrohydrazide (8f)

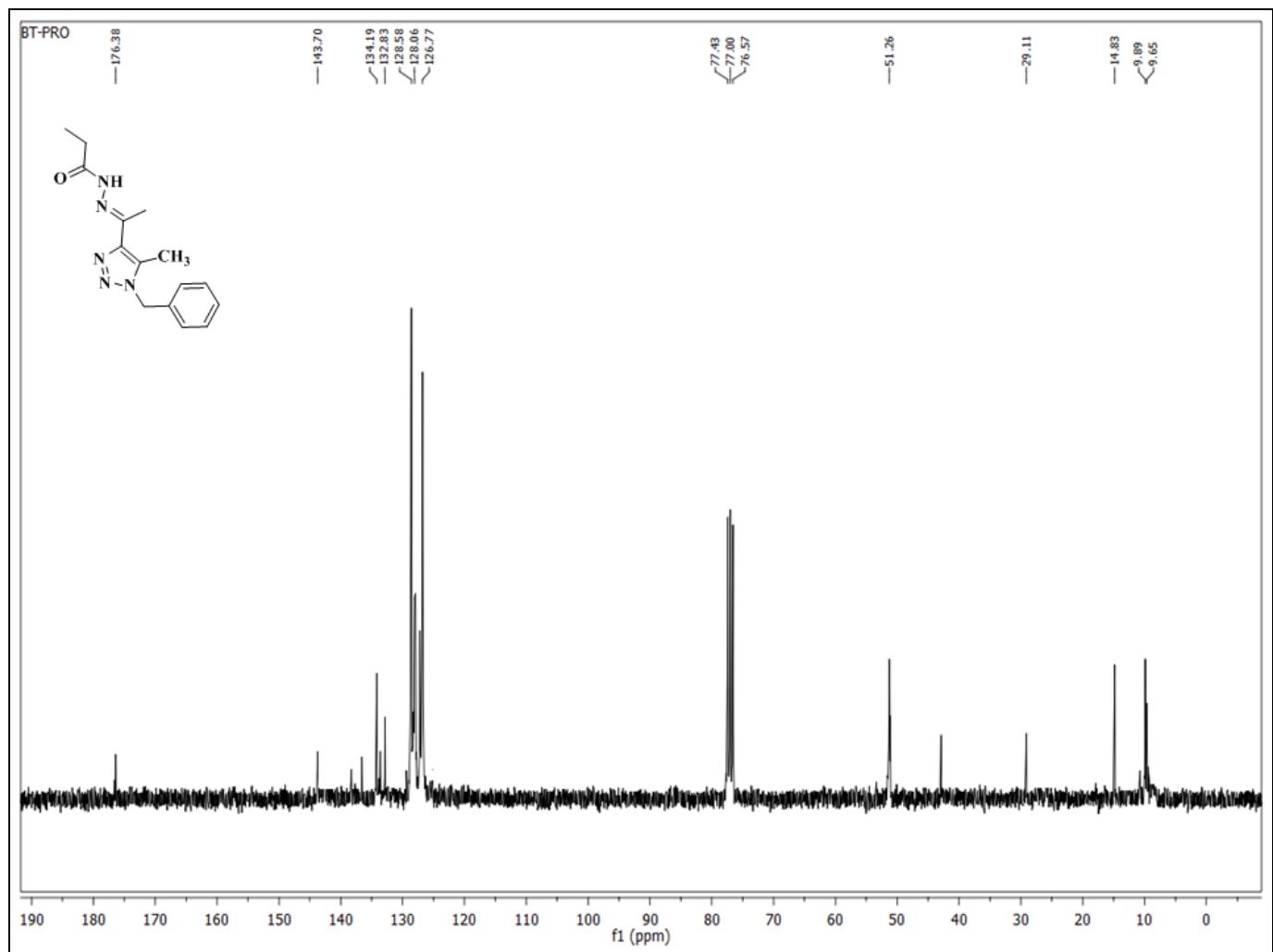


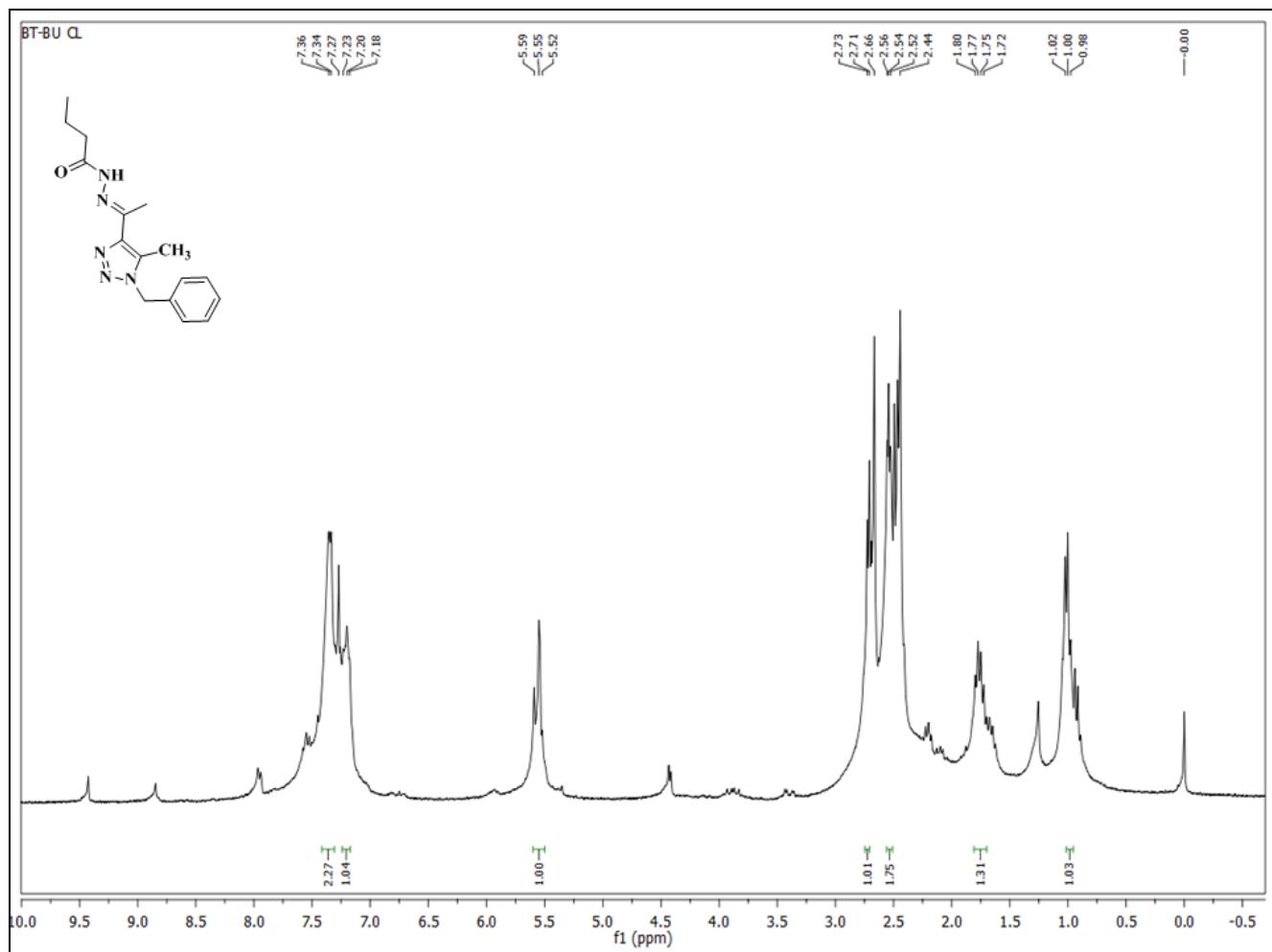




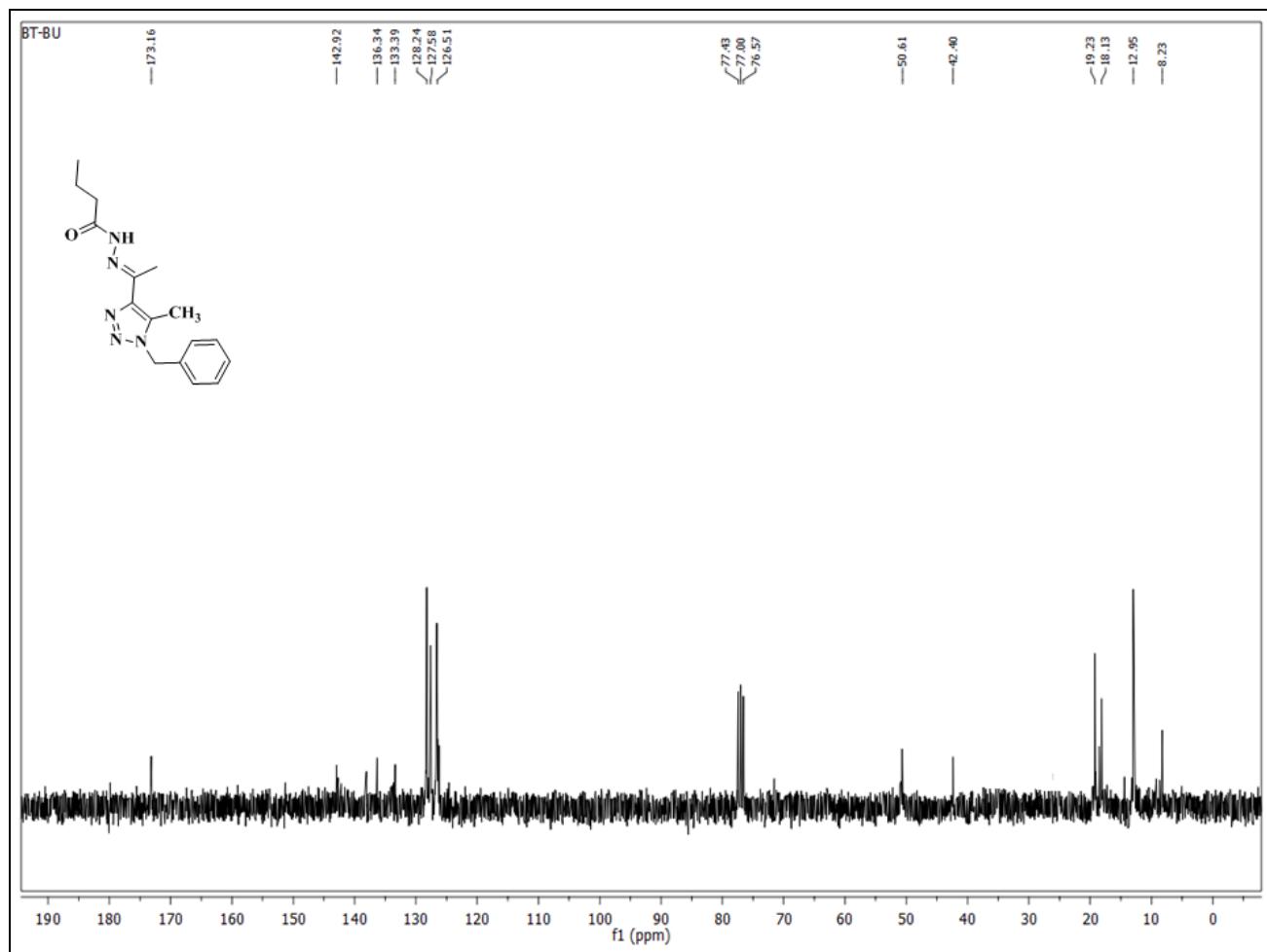
¹³C NMR (75 MHz, CDCl₃): (E)-N'-(1-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)ethylidene)acetohydrazide (**8g**)







¹H NMR (300 MHz, CDCl₃): (E)-N'-(1-(1-Benzyl-5-methyl-1*H*-1,2,3-triazol-4-yl)ethylidene)butyrohydrazide (**8i**)



¹³C NMR (75 MHz, CDCl₃): (E)-N'-(1-(1-Benzyl-5-methyl-1H-1,2,3-triazol-4-yl)ethyldene)butyrohydrazide (**8i**)

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