Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 48-50

New family of polydentate tetrazole-pyrazoline ligands prepared by the azido-Ugi reaction

Anastasia M. Gorbacheva, Ivan A. Krutov, Nikolay I. Vorozhtsov, Victor N. Khrustalev and Valentine G. Nenajdenko

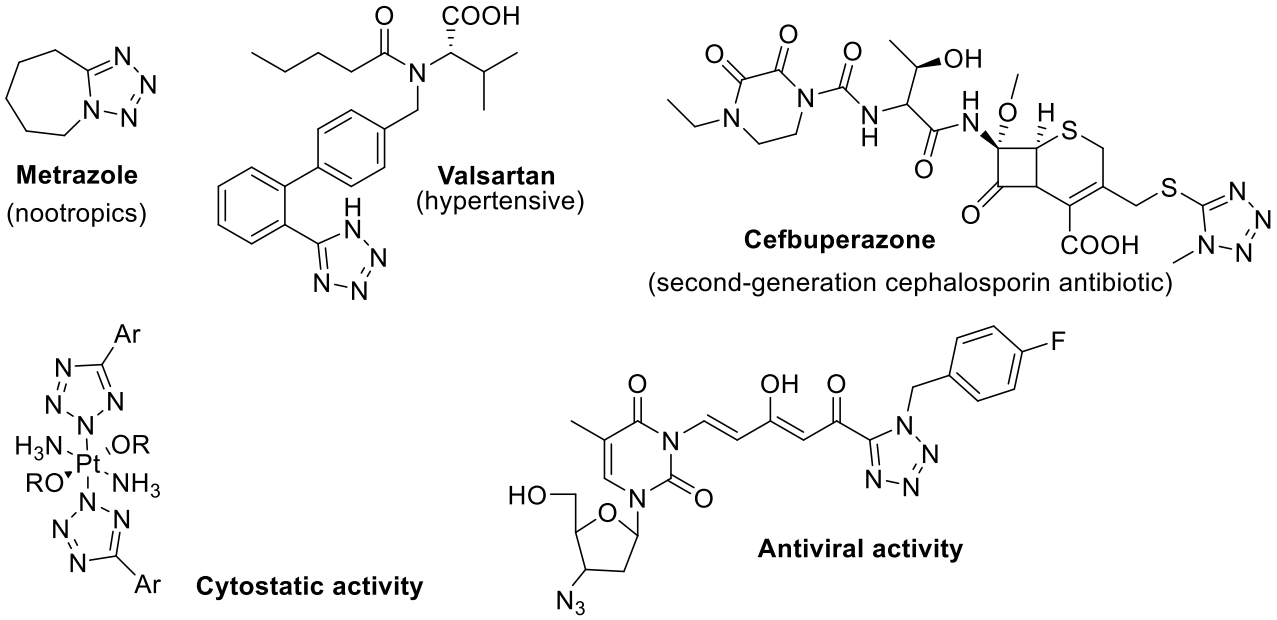


Figure S1 Some tetrazole-derived drugs (se Ref. 2 of the main text).

General procedure for 4,5-dihydro-1H-pyrazoles [A. N. Kost, V. V. Ershov, S. I. Suminov, *J. Gen. Chem. USSR*, 1957, **27**, 25142 (*Zh. Obshch. Khim.*, 1957, **27**, 25142)].

a) To a solution of 98% hydrazine monohydrate (13.7 ml) and 40% sodium hydroxide (6.5 ml) in ethanol (45 ml) heated to 50 °C, the Mannich salt (0.07 mol) is added portionwise with shaking, and this was boiled for 2 hours . The alcohol is distilled off. The obtained crystalline mass* is washed on the filter with water and immediately used in further transformations.* (In the case of 3-phenylpyrazoline: after distillation of ethanol, the residue was extracted with ether (3 x 30 ml), the extract was dried with calcined sodium sulfate in the cold. It was distilled under vacuum in an inert atmosphere).

b) To a hot solution of hydrazine hydrate (0.02 mol) in ethanol (15 ml), chalcone (0.02 mol) and acetic acid (2.4 ml) are added dropwise with stirring. The mixture is refluxed for 2-5 hours until completion of the reaction (TLC control), cooled, partially evaporated and poured onto ice. The precipitate formed is washed with water and immediately used in further reactions.

*General procedure for arylidene salts of 4,5-dihydro-1*H*-pyrazoles* **1** [N. I. Vorozhtsov, G. A. Golubeva, *Chem. Heterocycl. Comp.*, 2005, **10**, 1558 (*Khim. Geterotsikl. Soedin.*, 2005, **10**, 1558)].

Acid HBF_4 (50%, 10 ml) is slowly added to a solution of 4,5-dihydro-1*H*-pyrazole (0.1 mol) in dichloromethane (15 ml). To the resulting solution of the salt of 4,5-dihydro-1*H*-pyrazole, a solution of aldehyde (0.1 mol) in dichloromethane (5 ml) is added with vigorous stirring, and stirring is continued for 2-6 hours. The precipitated crystals are filtered off, washed with water until neutral, then several times with ether. The substance can be further used without additional purification.

General procedure for the azido-Ugi reaction

Method a: The corresponding pyrazolinium salt (1 mmol) is dissolved in methanol (2-4 ml), and benzyl isocyanide (1.2 mmol) and sodium azide (1.2 mmol) are added with stirring. The reaction is carried out at reflux 6 hours. The mixture is then poured into chloroform, and the precipitate formed is filtered off. The filtrate is concentrated, the residue is dissolved in minimum ethyl acetate, and the product is precipitated with hexane, leaving in the cold overnight. The precipitate formed is filtered off and dried.

*1-benzyl-5-((3-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)(phenyl)methyl)-1*H*-tetrazole* **2a.** Yield 56%, mp 181°C. IR (ν/cm^{-1}) : 1600 (C=N).^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.85 (s, 3H, CH_3), 2.66-2.89 (m, 2H, $CH_{2\ pyr}$), 4.35-4.41 (m, 1H, CH_{pyr}), 5.23-5.35 (m, 2H, $CH_{2\ Bn}$), 5.66 (s, 1H, CH), 6.85-7.52 (m, 15H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.0, 45.6, 51.8, 58.1, 68.5, 121.2, 127.4, 127.7, 128.0, 128.2, 128.4, 133.4, 136.1, 139.2, 152.1, 152.3. HRMS (ESI), *m/z*: 409.2137 (calc. for $C_{25}H_{25}N_6^+$ $[M+H]^+$ 409.2135).

*1-benzyl-5-((3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)(p-tolyl)methyl)-1*H*-tetrazole* **2b.** Yield 70%, mp 129°C. IR (ν/cm^{-1}): 1600 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 3H, CH_3), 2.96-3.54 (m, 4H, $CH_{2\ pyr}$), 5.67-5.68 (m, 2H, $CH_{2\ Bn}$), 5.70 (s, 1H, CH), 7.09-7.56 (m, 14H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.1, 32.5, 51.3, 51.4, 62.3, 126.0, 127.7, 128.4, 128.8, 129.3, 133.7, 138.4, 153.5, 154.2. HRMS (ESI), *m/z*: 409.2133 (calc. for $C_{25}H_{25}N_6^+$ $[M+H]^+$ 409.2135).

*1-benzyl-5-((4-methoxyphenyl)(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazole* **2c.** Yield 72%, mp 136°C. IR (ν/cm^{-1}) : 1607 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.92-3.46 (m, 4H, $CH_{2\ pyr}$), 3.72 (s, 3H, OCH_3), 5.59 (s, 2H, $CH_{2\ Bn}$), 5.62 (s, 1H, CH), 6.65 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.03-7.06 (m, 2H, CH_{Ar}),7.20-7.29 (m, 8H, CH_{Ar}), 7.46-7.49 (m, 2H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.5, 51.2, 51.4, 55.2, 61.9, 113.9, 126.0, 127.6, 128.4, 128.8, 130.0, 132.2, 133.7, 153.4, 154.3, 159.7. HRMS (ESI), *m/z*: 425.2085 (calc. for $C_{25}H_{25}N_6O^+$ $[M+H]^+$ 425.2084).

*1-benzyl-5-((4-chlorophenyl)(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazole* **2d.** Yield 58%, mp 118°C. IR (ν/cm^{-1}) : 1530 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.90-3.23 (m, 4H, $CH_{2\ pyr}$), 4.48-4.68 (m, 2H, $CH_{2\ Bn}$), 4.58 (s, 1H, CH), 7.31-7.64 (m, 14H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.9, 42.8, 52.0, 72.7, 125.8, 126.9, 127.2, 128.1, 128.2, 128.3, 128.9, 130.0, 131.8, 133.8, 134.0, 138.1, 153.9, 170.2. HRMS (ESI), *m/z*: 429.1356 (calc. for $C_{24}H_{24}ClN_6^+$ $[M+H]^+$ 429.1589).

*1-benzyl-5-((3-(4-chlorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)(o-tolyl)methyl)-1*H*-tetrazole* **2e.** Yield 62%, mp 127°C. IR (ν/cm^{-1}) : 1582 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.20 (s, 3H, CH_3), 2.94-3.69 (m, 4H, $CH_{2\ pyr}$), 3.58 (q, 2H, CH_2), 5.96 (s, 1H, CH), 7.00-7.02 (m, 2H, CH_{Ar}), 7.11-7.30 (m, 8H, CH_{Ar}), 7.43 (d, $^{3}J_{H,H}$ = 8.6 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.57-7.59 (m, 1H, CH_{Ar}), . ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.39, 32.31, 51.36, 51.45, 58.61, 126.21, 127.18, 127.58, 128.59, 128.76, 130.80, 130.98, 132.66, 133.29, 134.73, 136.94, 151.82, 153.61. HRMS (ESI), *m/z*: 443.1750 (calc. for $C_{25}H_{24}ClN_6^+$ $[M+H]^+$ 443.1745).

*1-benzyl-5-((3-(4-chlorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)(2-methoxyphenyl)methyl)-1*H*-tetrazole* **2f.** Yield 58%, mp 158°C. IR (ν/cm^{-1}) : 1607 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.94 (t, $^{3}J_{H,H}$ = 9.8 Hz, 2H, $CH_{2\ pyr}$), 3.21 (q, $^{3}J_{H,H}$ = 9.9 Hz, 1H, $CH_{2\ pyr}$), 3.49-3.56 (m, 1H, $CH_{2\ pyr}$), 3.57 (s, 3H, OCH_3), 5.60 (s, 2H, $CH_{2\ Bn}$), 6.12 (s, 1H, CH), 6.73 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1H, CH_{Ar}-CH_{Ar}), 6.95-7.11 (m, 3H, CH_{Ar}), 7.19-7.25 (m, 6H, CH_{Ar}), 7.40-7.46 (m, 2H, CH_{Ar}), 7.80-7.82 (m, 1H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.3, 51.1, 51.9, 54.8, 55.2, 69.6, 110.5, 120.8, 123.1, 127.2, 127.6, 128.6, 129.9, 130.9, 133.2, 133.7, 134.7, 152.3, 154.0, 156.6. HRMS (ESI), *m/z*: 459.1698 (calc. for $C_{25}H_{24}ClN_6O^+$ $[M+H]^+$ 459.1695).

*1-benzyl-5-(furan-2-yl)(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazole* **2g.** Yield 77%, yellowish oil. IR (ν/cm^{-1}) : 1595 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.94-3.00 (m, 2H, $CH_{2\ pyr}$), 3.11-3.19 (q, $^{3}J_{H,H}$ = 9.6 Hz, 1H, $CH_{2\ pyr}$), 3.38-3.45 (m, 1H, $CH_{2\ pyr}$), 5.75-5.86 (m, 2H, $CH_{2\ Bn}$), 5.98 (s, 1H, CH), 6.35 (m, 1H, CH_{fur}), 6.55 (s, 1H, CH_{fur}), 7.22-7.55 (m, 11H, 10CH_{Ar}, CH_{fur}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.3, 50.3, 51.3, 56.1, 110.3, 110.7, 125.8, 126.2, 127.5, 128.1, 128.5, 128.6, 129.0, 142.8, 147.2, 153.5. HRMS (ESI), *m/z*: 385.1765 (calc. for $C_{22}H_{21}N_6O^+$ $[M+H]^+$ 385.1771).

*1-benzyl-5-((1,3-dimethyl-1*H*-pyrazol-4-yl)(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1*H*-tetrazole* **2h.** Yield 86%, yellowish oil. IR (ν/cm^{-1}) : 1552 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08 (s, 3H, CH_3), 2.90 (t, $^{3}J_{H,H}$ = 9.7 Hz, 2H, $CH_{2\ pyr}$), 3.14 (q, $^{3}J_{H,H}$ = 9.3 Hz, 1H, $CH_{2\ pyr}$), 3.19-3.30 (m, 1H, CH_2

$_{pyr}$), 3.76 (s, 3H, CH_3), 5.75-5.86 (m, 3H, $CH_{2\ Bn}$, CH), 7.20 (dd, $^3J_{H,H}$ = 3.0 Hz, $^3J_{H,H}$ = 6.6 Hz, 2H, CH_{Ar}), 7.31-7.38 (m, 6H, 5CH_{Ar}, CH_{pyr}), 7.53-7.55 (dd, $^3J_{H,H}$ = 3.0 Hz, $^3J_{H,H}$ = 6.7 Hz, 2H, CH_{Ar}), 7.63 (s, 1H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.8, 32.4, 38.9, 49.2, 51.6, 52.6, 111.8, 126.1, 127.8, 128.6, 128.8, 129.1, 129.2, 129.3, 132.3, 133.8, 147.7, 153.5. HRMS (ESI), *m/z*: 413.2183 (calc. for $C_{23}H_{25}N_8^+$ $[M+H]^+$ 413.2197).

*1-benzyl-5-((1-ethyl-4-methyl-1H-pyrazol-3-yl)(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazole* **2i.** Yield 82%, yellowish oil. IR (ν/cm^{-1}) : 1550 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.42 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.90 (t, $^3J_{H,H}$ = 9.7 Hz, 2H, $CH_{2\ pyr}$), 3.10-3.17 (m, 1H, $CH_{2\ pyr}$), 3.29 (q, $^3J_{H,H}$ = 9.7 Hz, 1H, $CH_{2\ pyr}$), 4.03 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2), 5.76-5.85 (m, 3H, $CH_{2\ Bn}$, CH), 7.20-7.22 (m, 2H, CH_{Ar}), 7.31-7.36 (m, 7H, 6CH_{Ar}, CH_{pyr}), 7.54-7.56 (m, 2H, CH_{Ar}), 7.68 (s, 1H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.9, 15.5, 32.3, 46.9, 49.3, 51.5, 52.6, 111.5, 126.0, 127.8, 128.6, 128.8, 129.1, 129.2, 130.5, 132.3, 133.8, 147.3, 153.5, 153.6. HRMS (ESI), *m/z*: 427.2348 (calc. for $C_{24}H_{27}N_8^+$ $[M+H]^+$ 427.2353).

Method b: 1-(4-Dimethylaminobenzylidene)-3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-ium tetrafluoroborate **1b** (1 mmol) is dissolved in methanol (2-4 ml), and the corresponding isocyanide (1.2 mmol) and sodium azide (1.2 mmol) are added with stirring. The reaction is conducted at reflux 6 hours. The reaction mixture is poured into chloroform, and the precipitate formed is filtered off. The filtrate is concentrated, the residue is dissolved in minimum ethyl acetate, and the product is precipitated with hexane, leaving in the cold overnight. The precipitate formed is filtered off and dried.

*4-((1-benzyl-1*H*-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-N,N-dimethylaniline* **2j.** Yield 65%, mp 177°C. IR (ν/cm^{-1}) : 1615 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.06, 1.10, 1.79 (s, 9H, CH_3), 2.30 (d, $^2J_{H,H}$ = 16.1 Hz, 1H, $CH_{2\ pyr}$), 2.58 (d, $^2J_{H,H}$ = 16.1 Hz, 1H, $CH_{2\ pyr}$), 2.91 (s, 6H, $N(CH_3)_2$), 5.54-5.59 (m, 2H, $CH_{2\ Bn}$), 5.63 (s, 1H, CH), 6.58 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.03 (d, $^3J_{H,H}$ = 3.7 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.20 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.25-7.40 (m, 3H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 22.5, 24.1, 26.7, 40.4, 51.7, 52.3, 56.0, 67.0, 69.6, 112.1, 127.8, 128.5, 129.1, 133.3, 134.5, 150.1, 150.3, 156.8, 178.8. HRMS (ESI), *m/z*: 403.2532 (calc. for $C_{23}H_{30}N_7^+$ $[M+H]^+$ 403.2484).

*4-((1-allyl-1*H*-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-N,N-dimethylaniline* **2k.** Yield 59%, mp 129°C. IR (ν/cm^{-1}) : 1525 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10, 1.13, 1.83 (s, 9H, CH_3), 2.33 (d, $^2J_{H,H}$ = 16.2 Hz, 1H, $CH_{2\ pyr}$), 2.60 (d, $^2J_{H,H}$ = 16.1 Hz, 1H, $CH_{2\ pyr}$), 2.91 (s, 6H, $N(CH_3)_2$), 4.88 (dd, $^2J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 15.4 Hz, 1H, CH=$CH_{2\ allyl}$), 5.00 (dd, $^2J_{H,H}$ = 5.7 Hz, $^3J_{H,H}$ = 15.5 Hz, 1H, CH=$CH_{2\ allyl}$), 5.13 (d, $^3J_{H,H}$ = 19.5 Hz, 1H, CH-CH_2), 5.15 (d, $^3J_{H,H}$ = 19.5 Hz, 1H, CH-CH_2), 5.71 (s, 1H, CH), 5.80-5.83 (m, 1H, CH_{allyl}), 6.65 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.29 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, CH_{Ar}-CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.1, 22.2, 26.3, 40.0, 50.5, 51.8, 55.5, 66.7, 111.8, 118.8, 124.7, 128.5, 130.6, 149.7, 149.9, 156.0. HRMS (ESI), *m/z*: 354.1528 (calc. for $C_{19}H_{28}N_7^+$ $[M+H]^+$ 354.2401).

*4-((1-(tert-butyl)-1*H*-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-N,N-dimethylaniline* **2l.** Yield 72%, mp 173°C. IR (ν/cm^{-1}) : 1608 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.85, 1.16 (s, 6H, CH_3), 1.74 (s, 12H, CH_3),), 2.23 (d, $^2J_{H,H}$ = 16.1 Hz, 1H, $CH_{2\ pyr}$), 2.64 (d, $^2J_{H,H}$ = 15.0 Hz, 1H, $CH_{2\ pyr}$), 2.90 (s, 6H, $N(CH_3)_2$), 5.67 (s, 1H, CH), 6.63 (d, $^3J_{H,H}$ = 8.9 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.64 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, CH_{Ar}-CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 20.7, 26.9, 30.1, 39.9, 52.9, 58.1, 60.2, 66.5, 111.3, 123.2, 130.8, 150.0, 157.4. HRMS (ESI), *m/z*: 370.2905 (calc. for $C_{20}H_{32}N_7^+$ $[M+H]^+$ 370.2714).

*Methyl 3-(5-((4-dimethylaminophenyl)(3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazol-1-yl)propanoate* **2m.** Yield 64%, mp 108°C. IR (ν/cm^{-1}) : 1616 (C=N), 1736 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12, 1.15, 1.84 (s, 9H, CH_3), 2.35 (d, $^2J_{H,H}$ = 16.3 Hz, 1H, $CH_{2\ pyr}$), 2.59 (d, $^2J_{H,H}$ = 16.2 Hz, 1H, $CH_{2\ pyr}$), 2.70-2.81 (m, 2H, $CH_2C(O)$), 2.92 (s, 6H, $N(CH_3\text{-})_2$), 3.68 (s, 3H, OCH_3), 4.51-4.72 (m, 2H, N-CH_2), 5.79 (s, 1H, CH), 6.65 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, CH_{Ar}-CH_{Ar}), 7.29 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, CH_{Ar}-CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.1, 22.3, 26.3, 30.0, 33.1, 40.1, 43.5, 51.6, 55.4, 66.8, 111.9, 124.7, 128.3, 149.8, 149.9, 150.0, 170.5. HRMS (ESI), *m/z*: 400.2460 (calc. for $C_{20}H_{30}N_7O_2^+$ $[M+H]^+$ 400.2455).

*N,N-dimethyl-4-((1-(2-(pyridin-4-yl)ethyl)-1*H*-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)aniline* **2n.** Yield 75%, mp 132°C. IR (ν/cm^{-1}) : 1606 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10, 1.22, 1.83 (s, 9H, CH_3), 2.35 (d, $^2J_{H,H}$ = 16.2 Hz, 1H, $CH_{2\ pyr}$), 2.60 (d, $^2J_{H,H}$ = 16.2 Hz, 1H, $CH_{2\ pyr}$), 2.80-2.83, 3.05-3.11 (m, 2H, CH_2), 2.93 (s, 6H, $N(CH_3)_2$), 4.45-4.52 (m, 2H, N-CH_2), 5.81 (s, 1H, CH), 6.65 (d, $^3J_{H,H}$ = 8.9 Hz, 2H, CH_{Ar}-CH_{Ar}), 6.94 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, CH_{pyr}-CH_{pyr}), 7.23 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, CH_{Ar}-CH_{Ar}), 8.47 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, CH_{pyr}-CH_{pyr}). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.8, 23.1, 26.8, 34.8, 40.7, 48.9, 52.1, 55.3, 67.6, 110.2, 112.5, 124.3, 128.5, 146.6, 150.1, 150.5, 156.4. HRMS (ESI), *m/z*: 419.2662 (calc. for $C_{23}H_{31}N_8^+$ $[M+H]^+$ 419.2666).

Synthesis of metal complexes

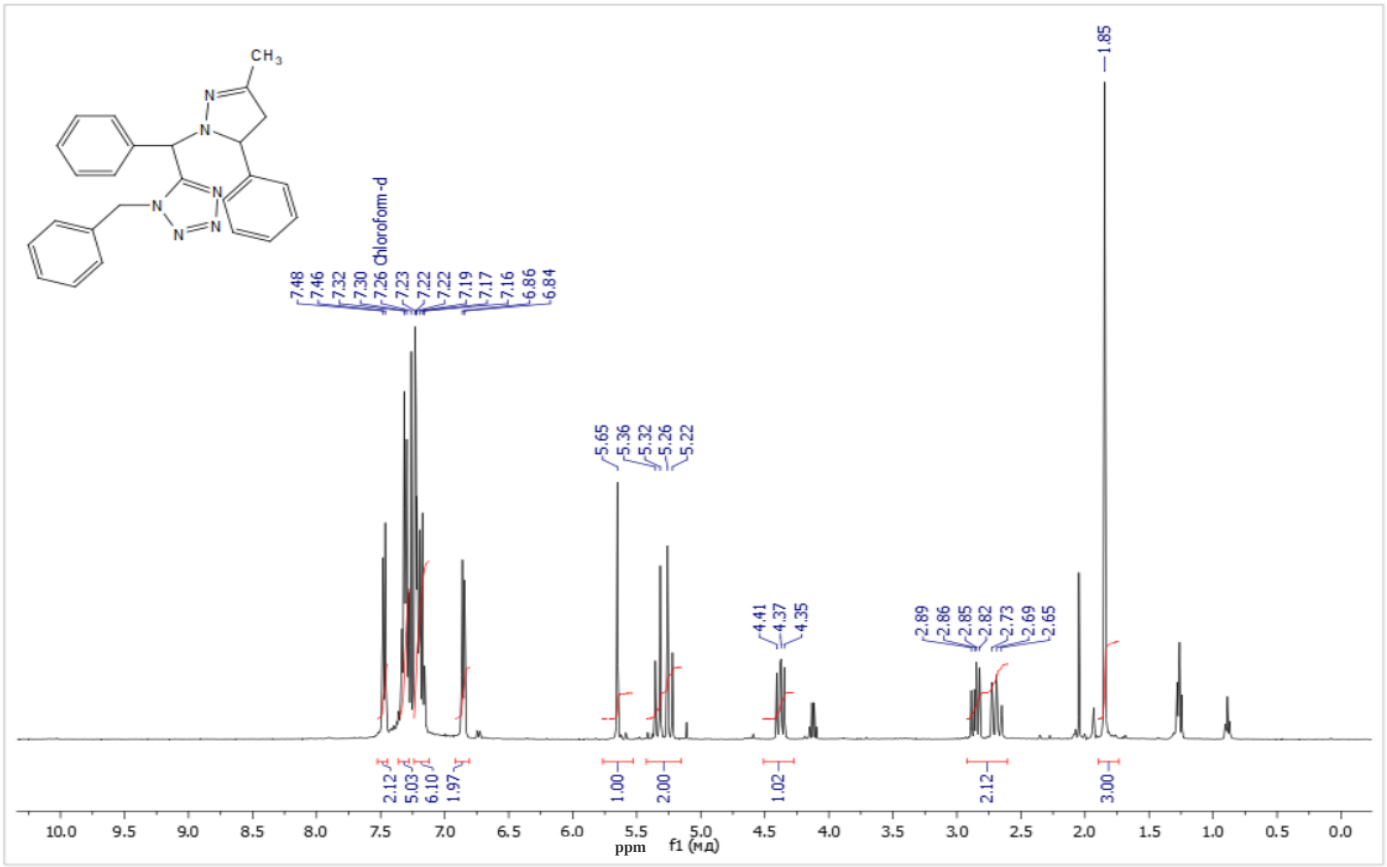
Complex **2c**·$PdCl_2$ To a solution of 1-benzyl-5-((4-methoxyphenyl)(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazole (0.028 mmol, 2 equiv.) in acidified methanol (4 ml), a solution of palladium(II) chloride (0.014 mmol, 1 equiv.) in acidified methanol (2 ml) is poured. The reaction mixture is left for precipitation.

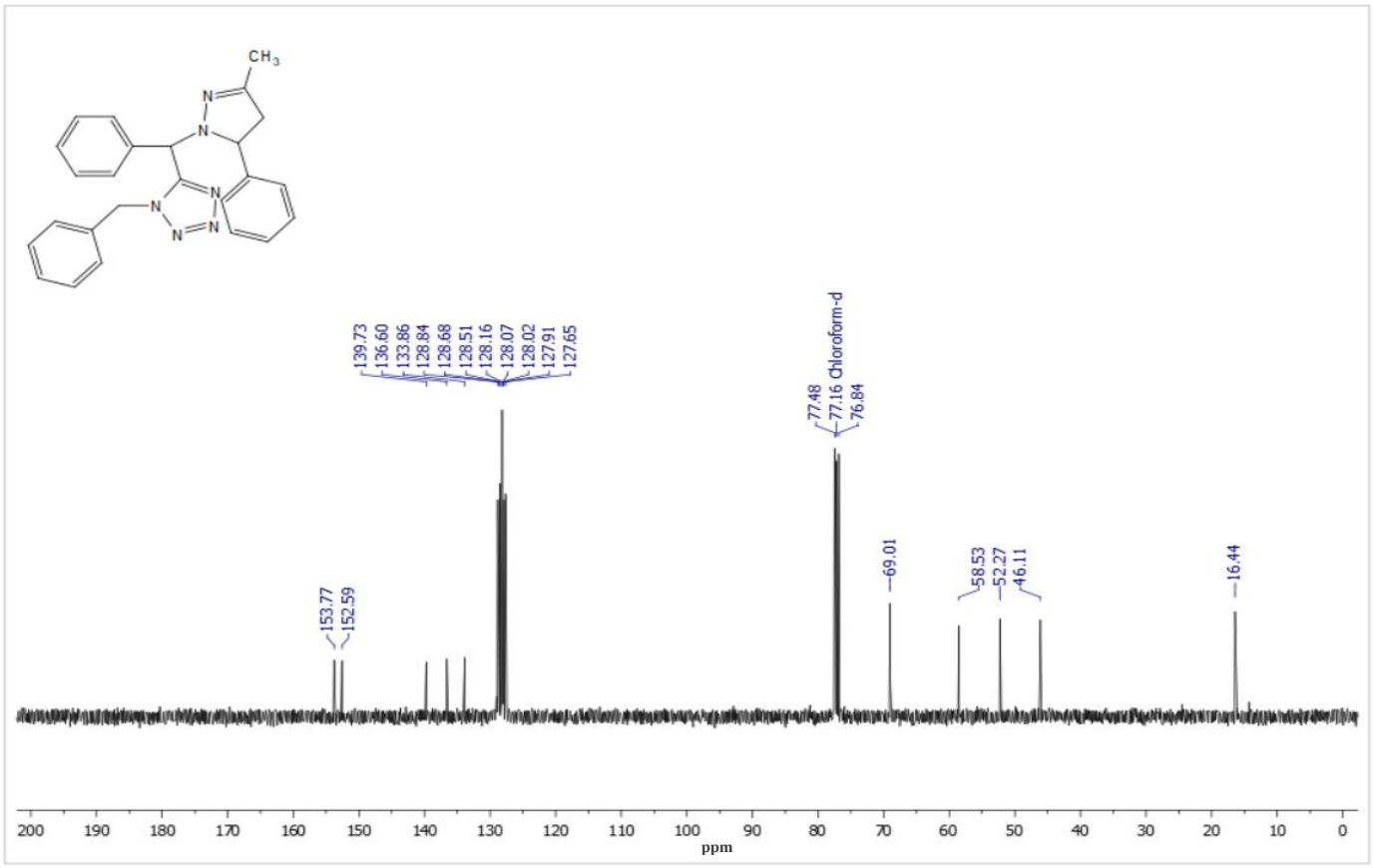
Complex **2c**·0.25Cu_3Cl_4 To a solution of 1-benzyl-5-((4-methoxyphenyl)(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)methyl)-1*H*-tetrazole (0.032 mmol, 1 equiv.) in methanol (2 ml), a solution of copper (II) chloride dihydrate (0.031 mmol, 1 equiv.) in methanol (1 ml) is poured. The reaction mixture is left for precipitation.

Table S1 Hydrogen bonds for complex **2c**·0.25Cu_3Cl_4 [Å and °].

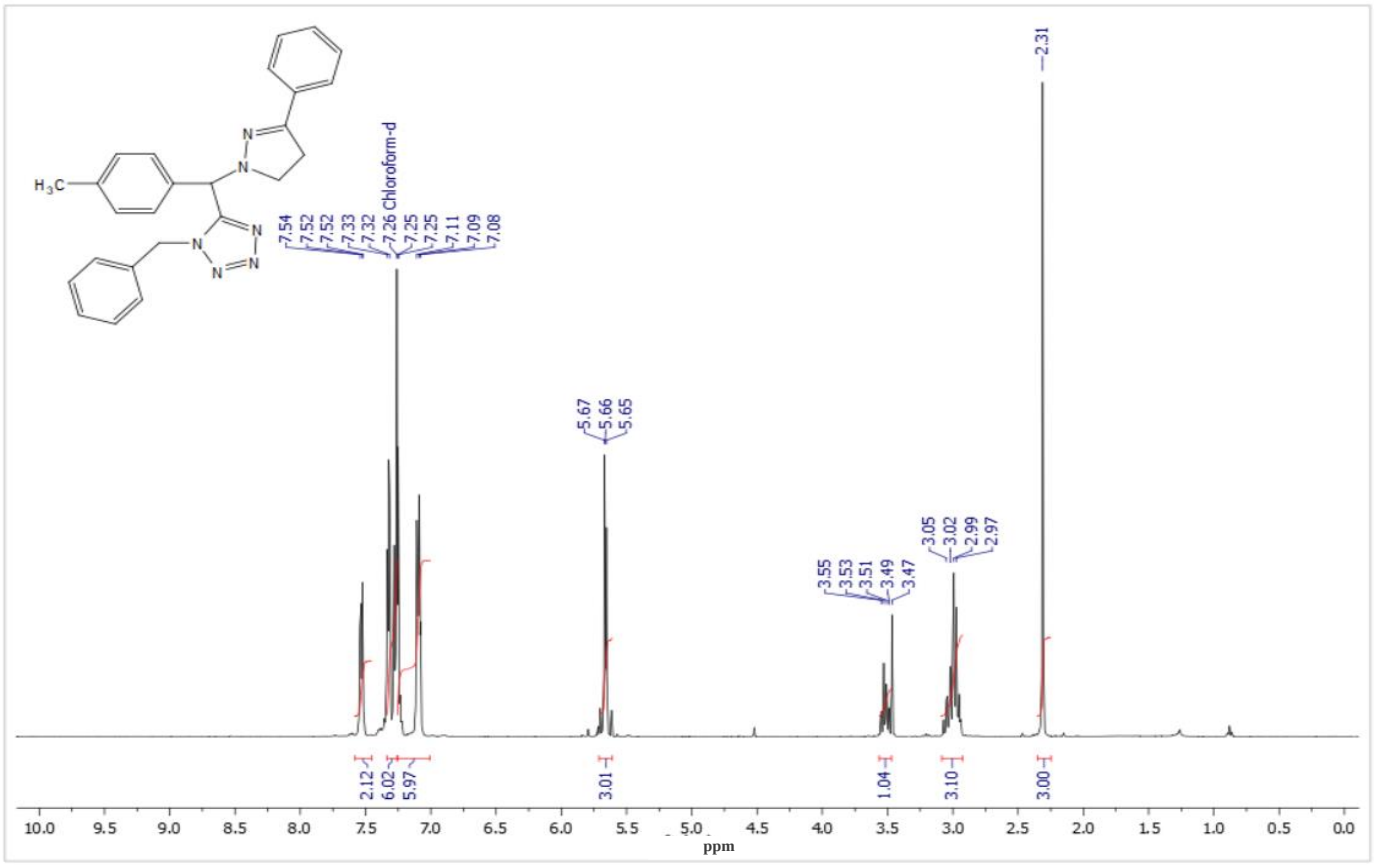
D─H···A	d(D─H)	d(H···A)	d(D···A)	∠(D─H···A)
C6─H6B···Cl4[a]	0.99	2.55	3.525(12)	167
C31─H31B···Cl3	0.99	2.58	3.537(13)	162
C56─H56A···Cl1[b]	0.99	2.57	3.535(12)	165
C81─H81A···Cl2	0.99	2.53	3.504(12)	168

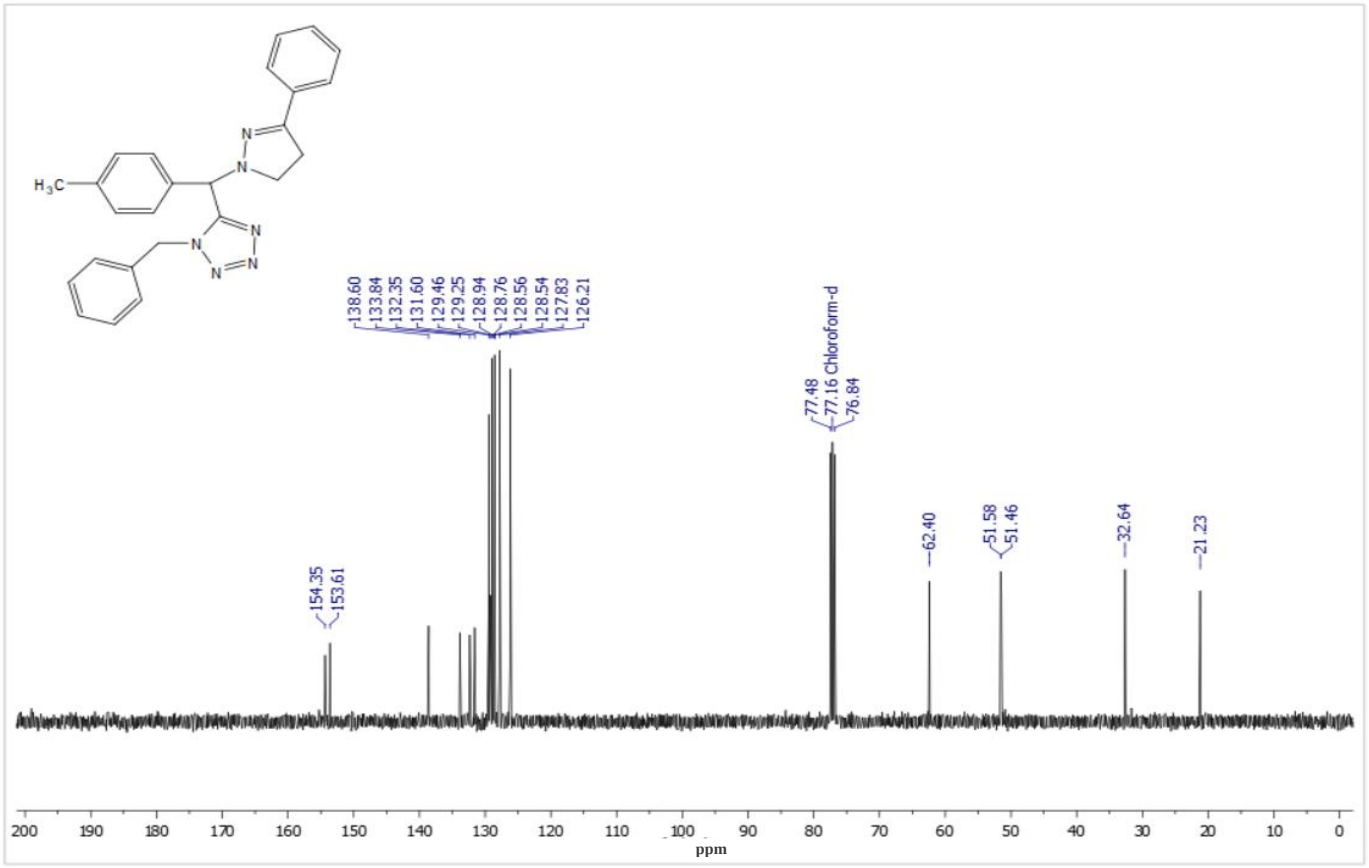
Symmetry transformations used to generate equivalent atoms:
[a] x+1/2, y+1/2, z; [b] x-1/2, y+1/2, z



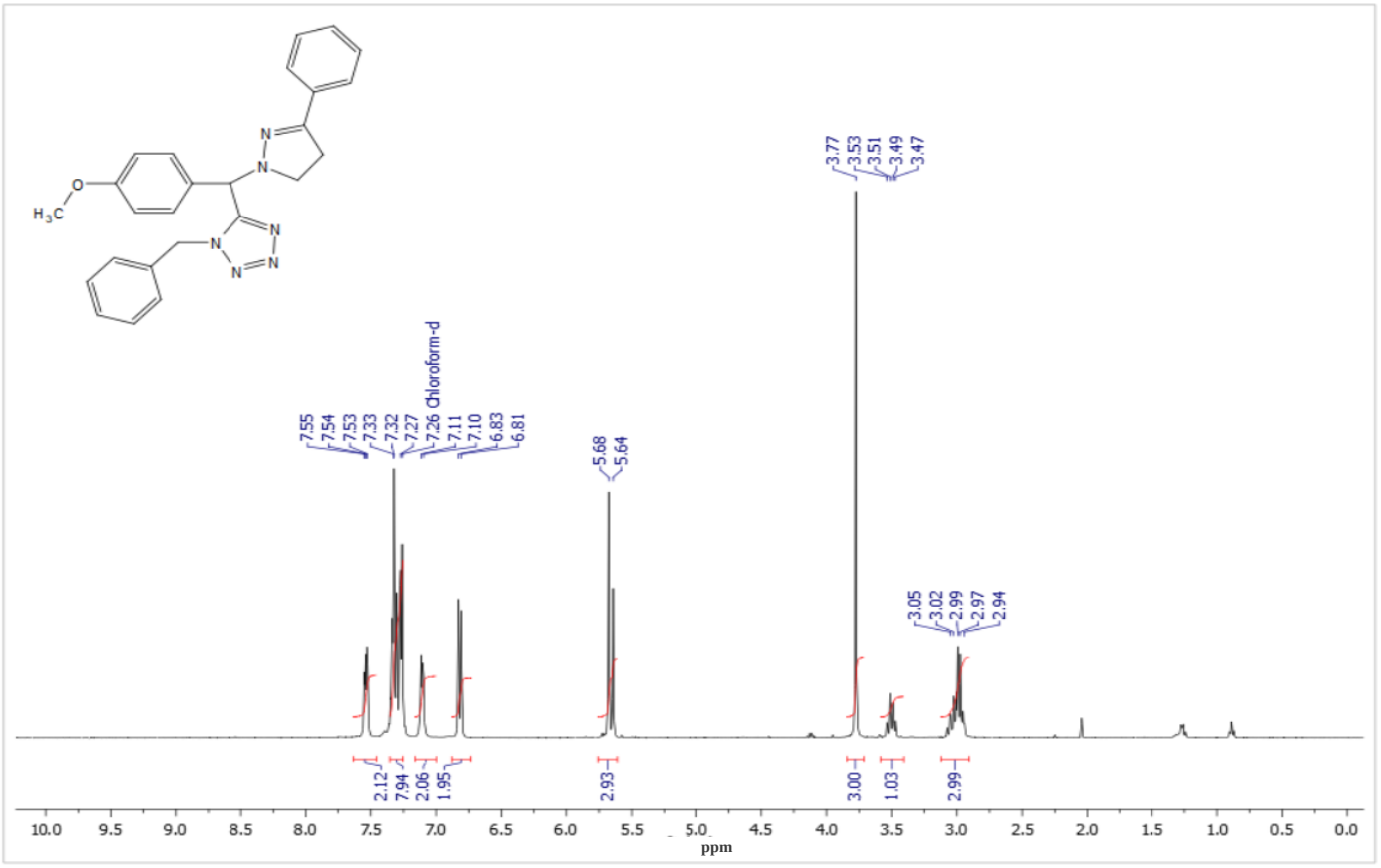


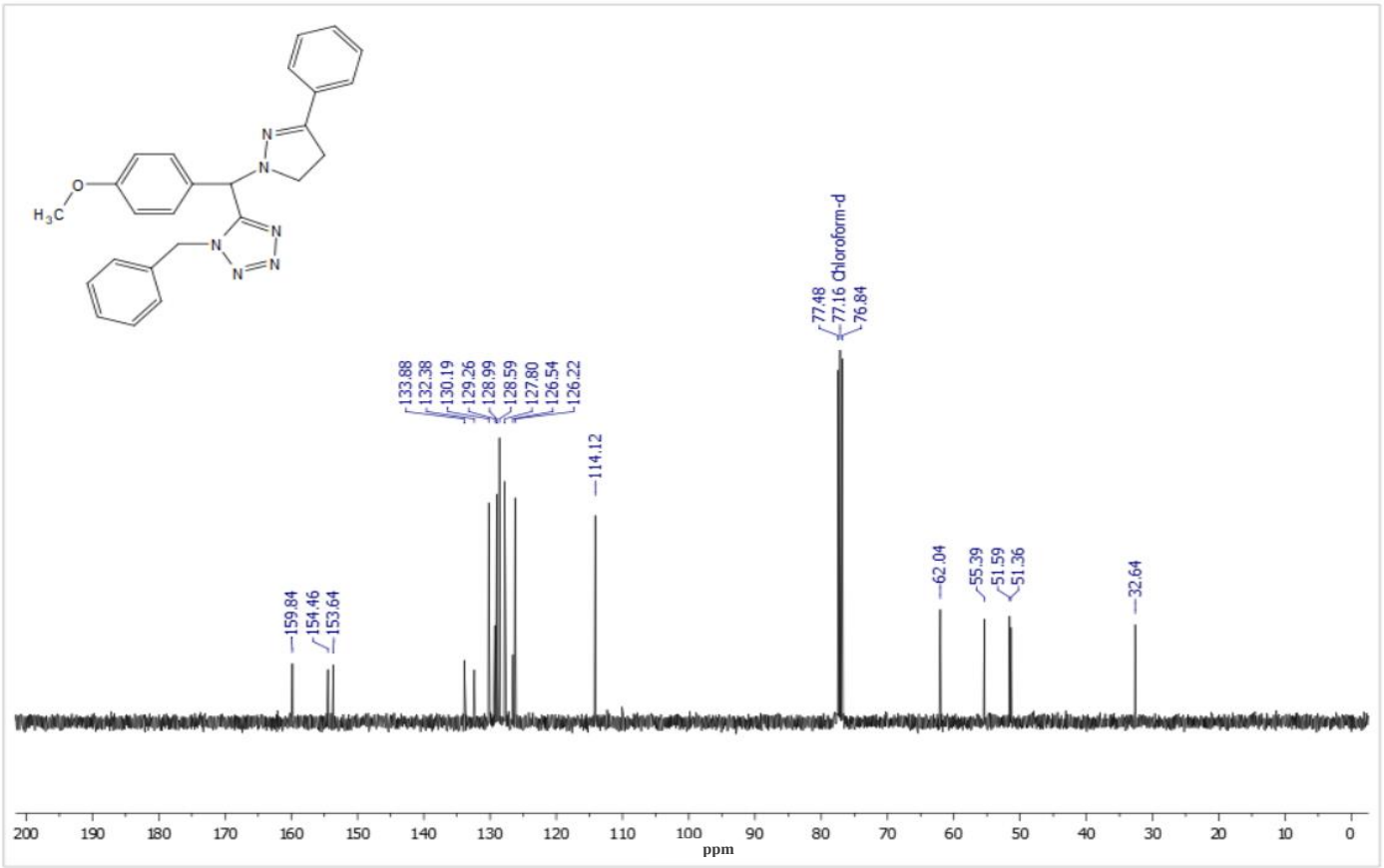
1-Benzyl-5-((3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)(phenyl)methyl)-1H-tetrazole 2a.



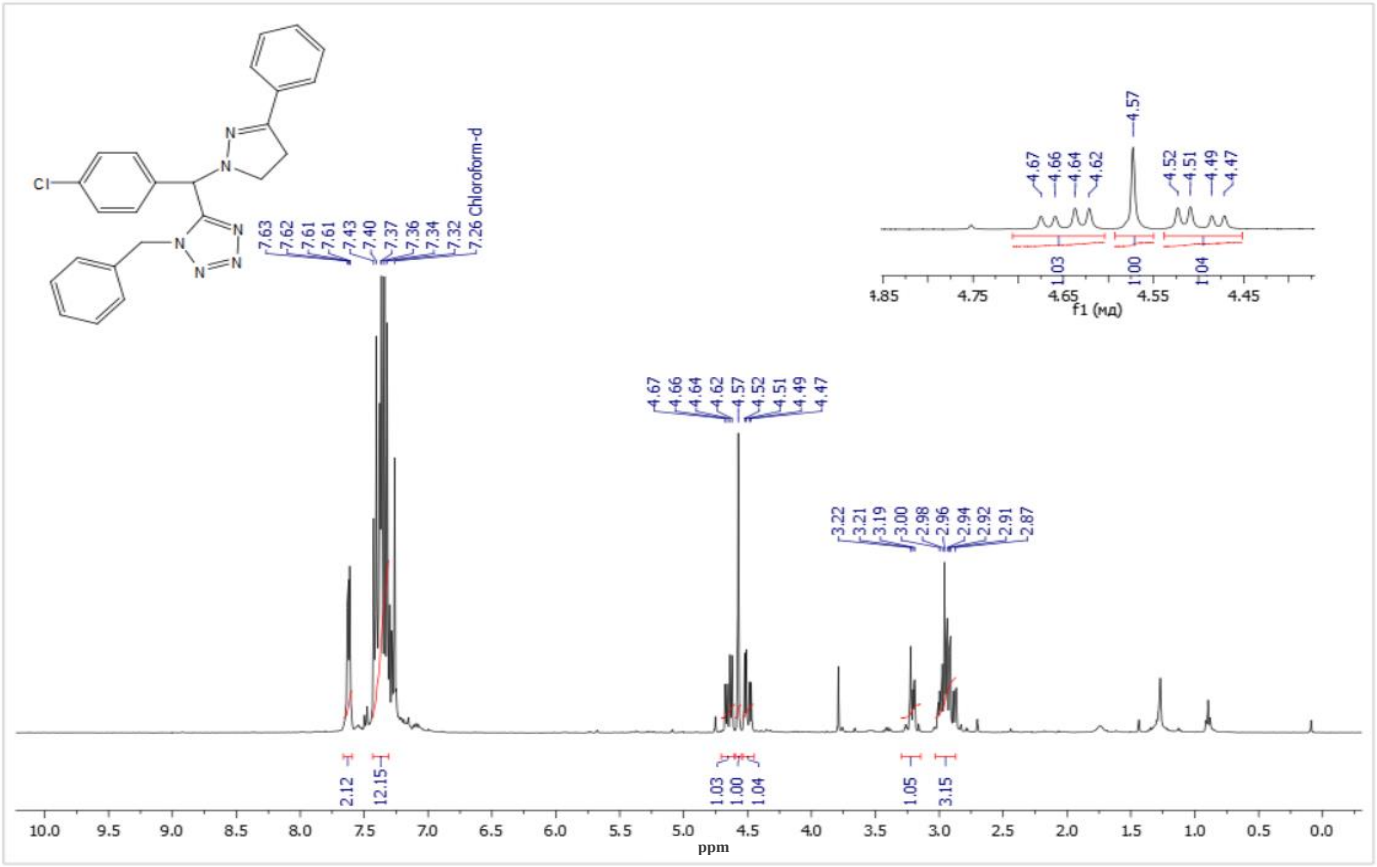


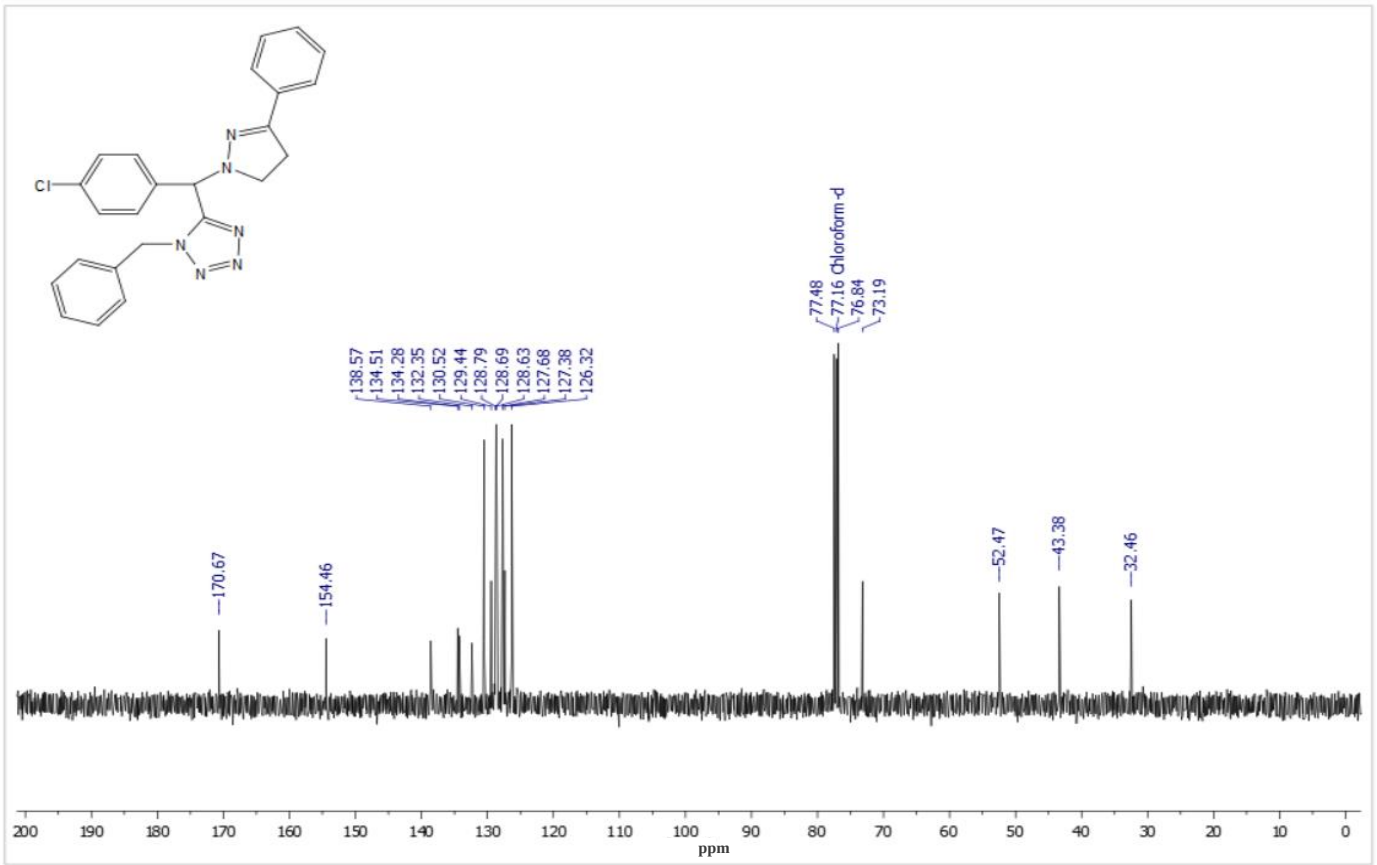
1-Benzyl-5-((3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)(p-tolyl)methyl)-1H-tetrazole **2b.**



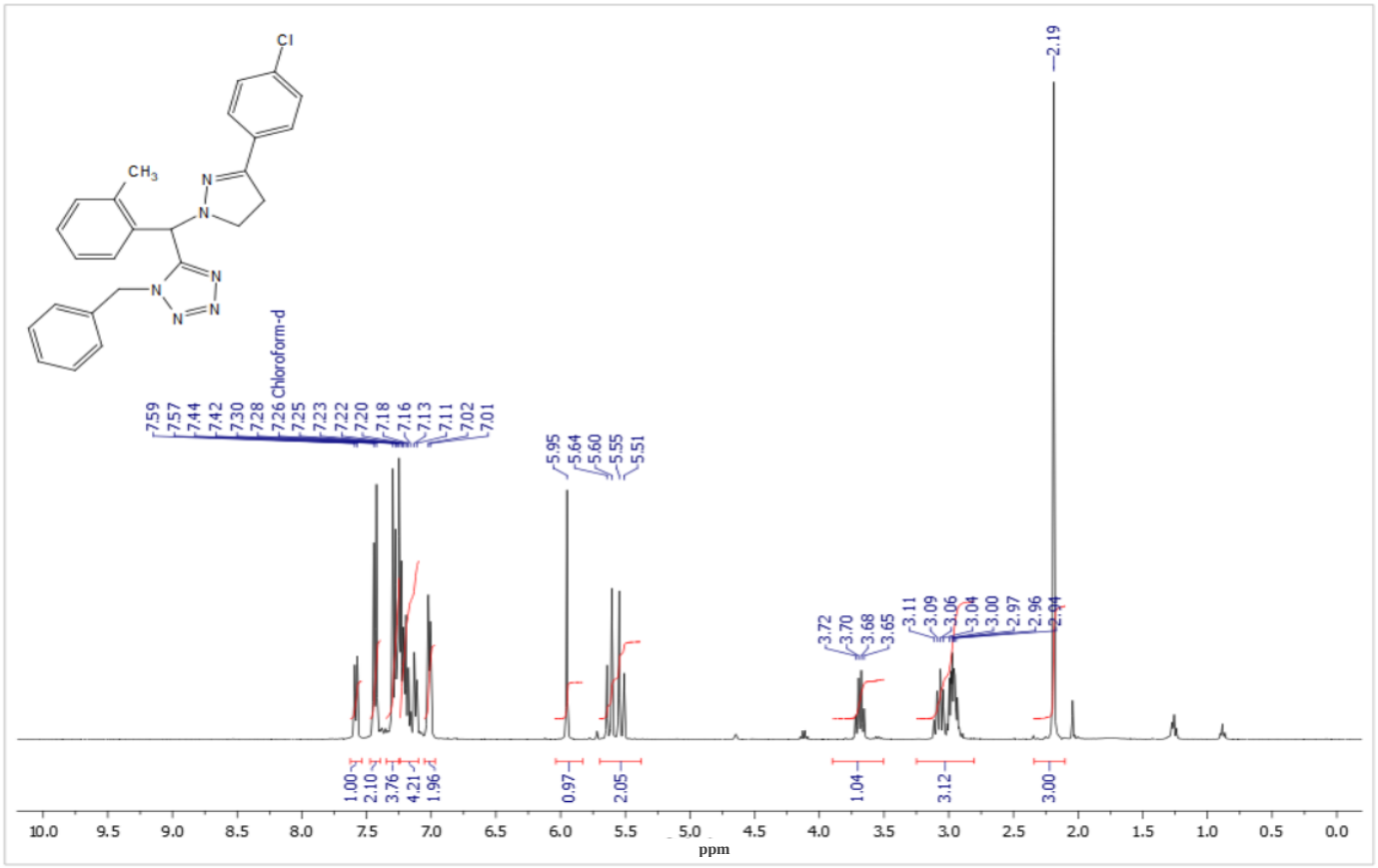


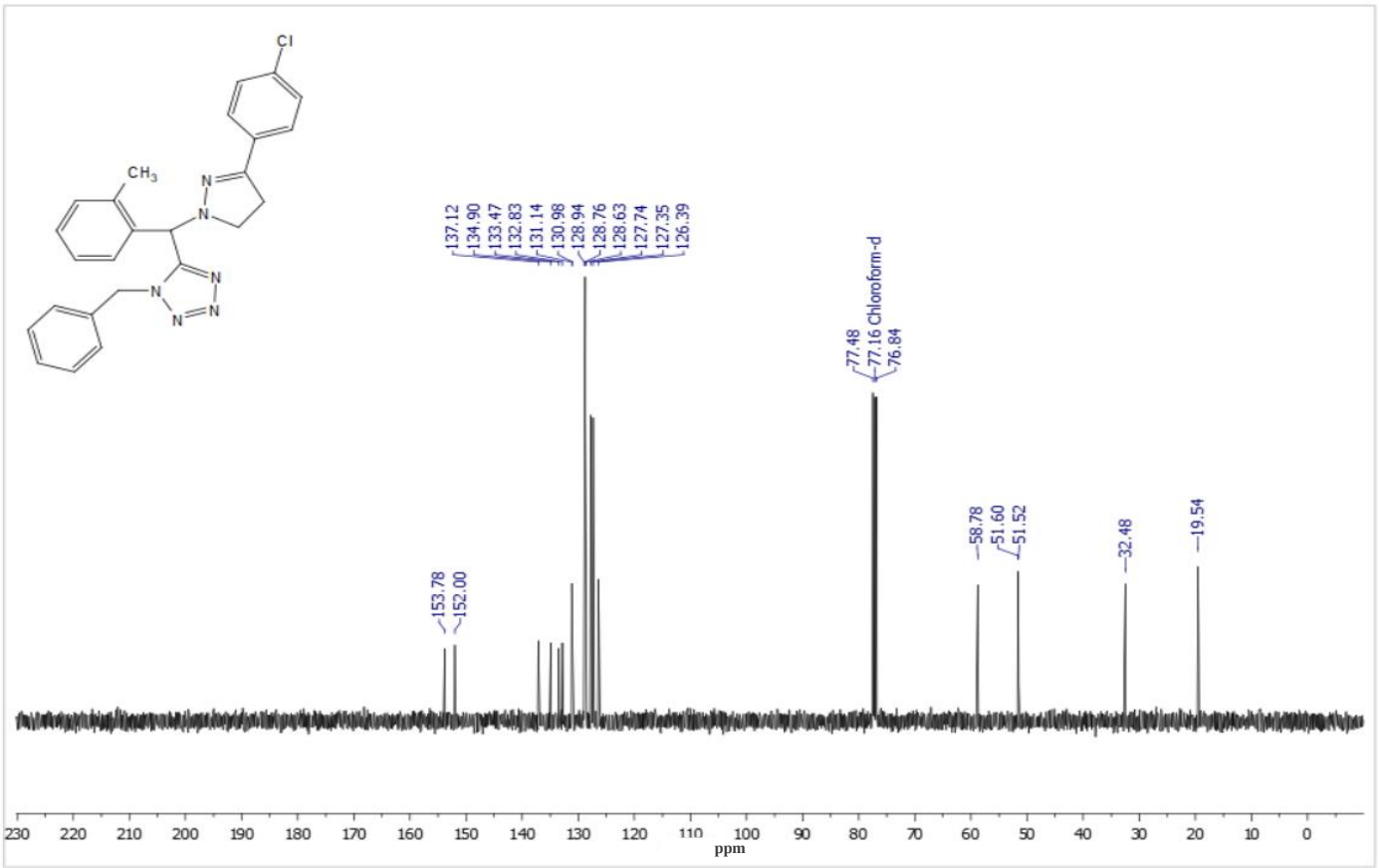
1-Benzyl-5-((4-methoxyphenyl)(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1H-tetrazole **2c.**



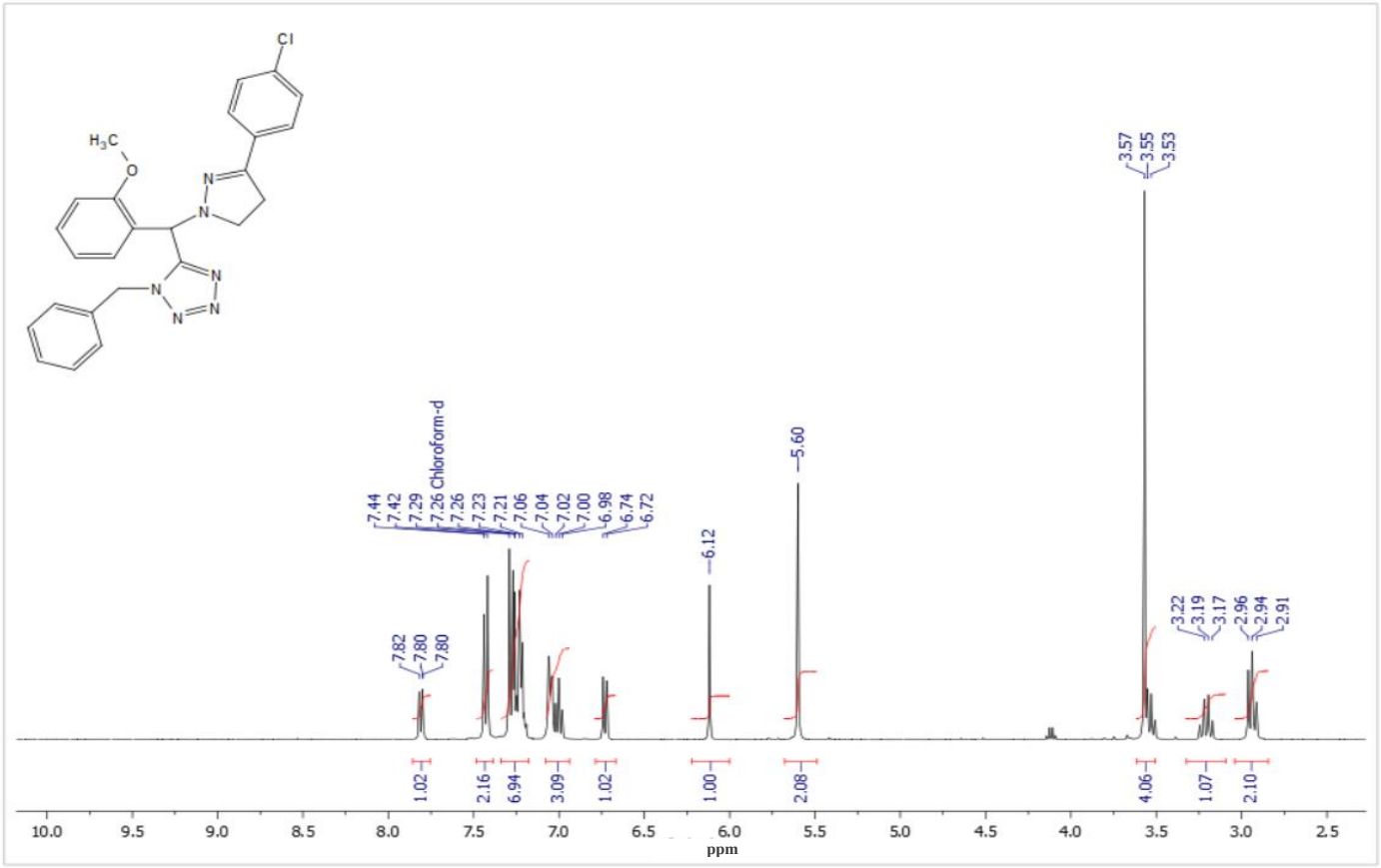


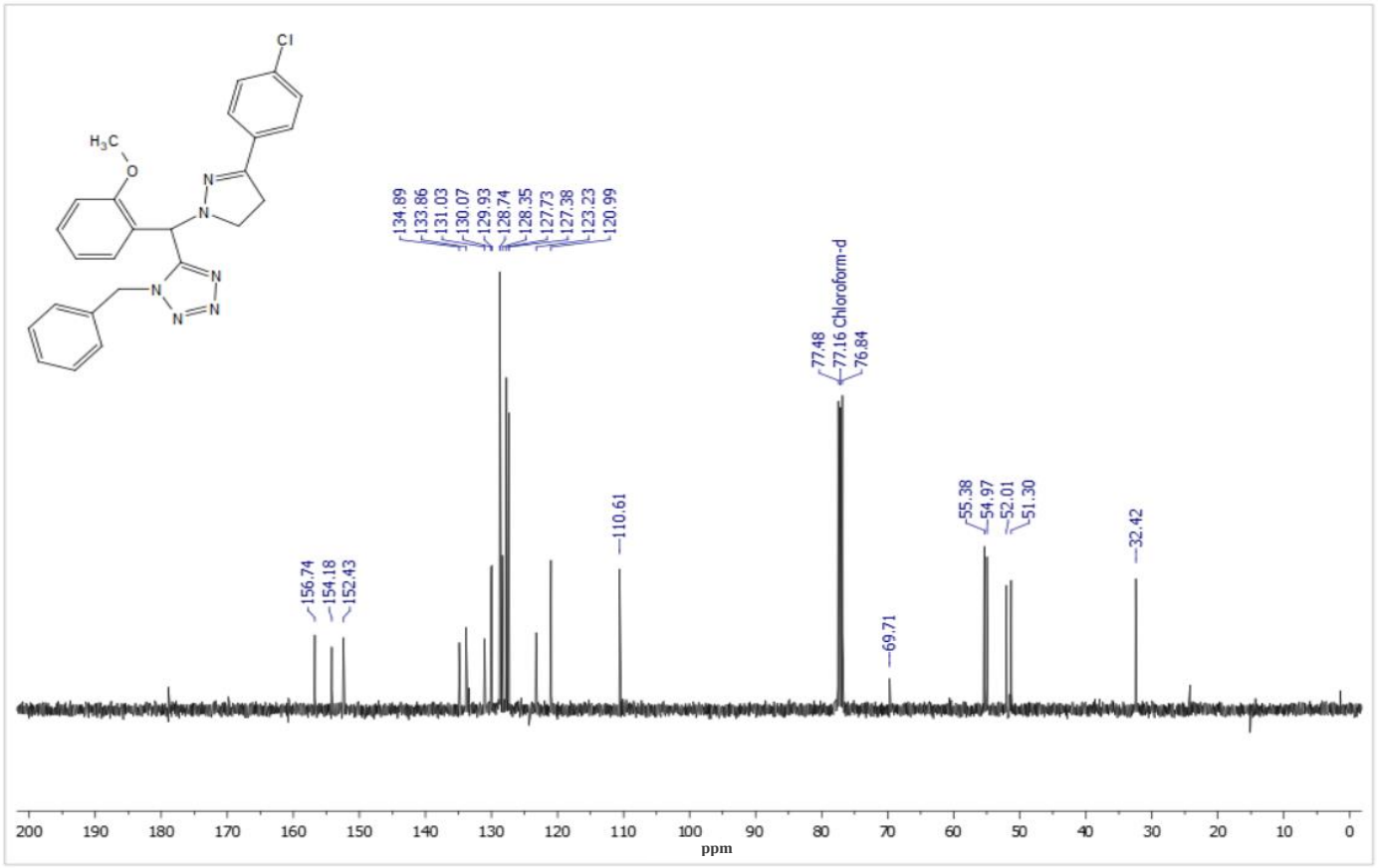
1-Benzyl-5-((4-chlorophenyl)(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1H-tetrazole **2d.**



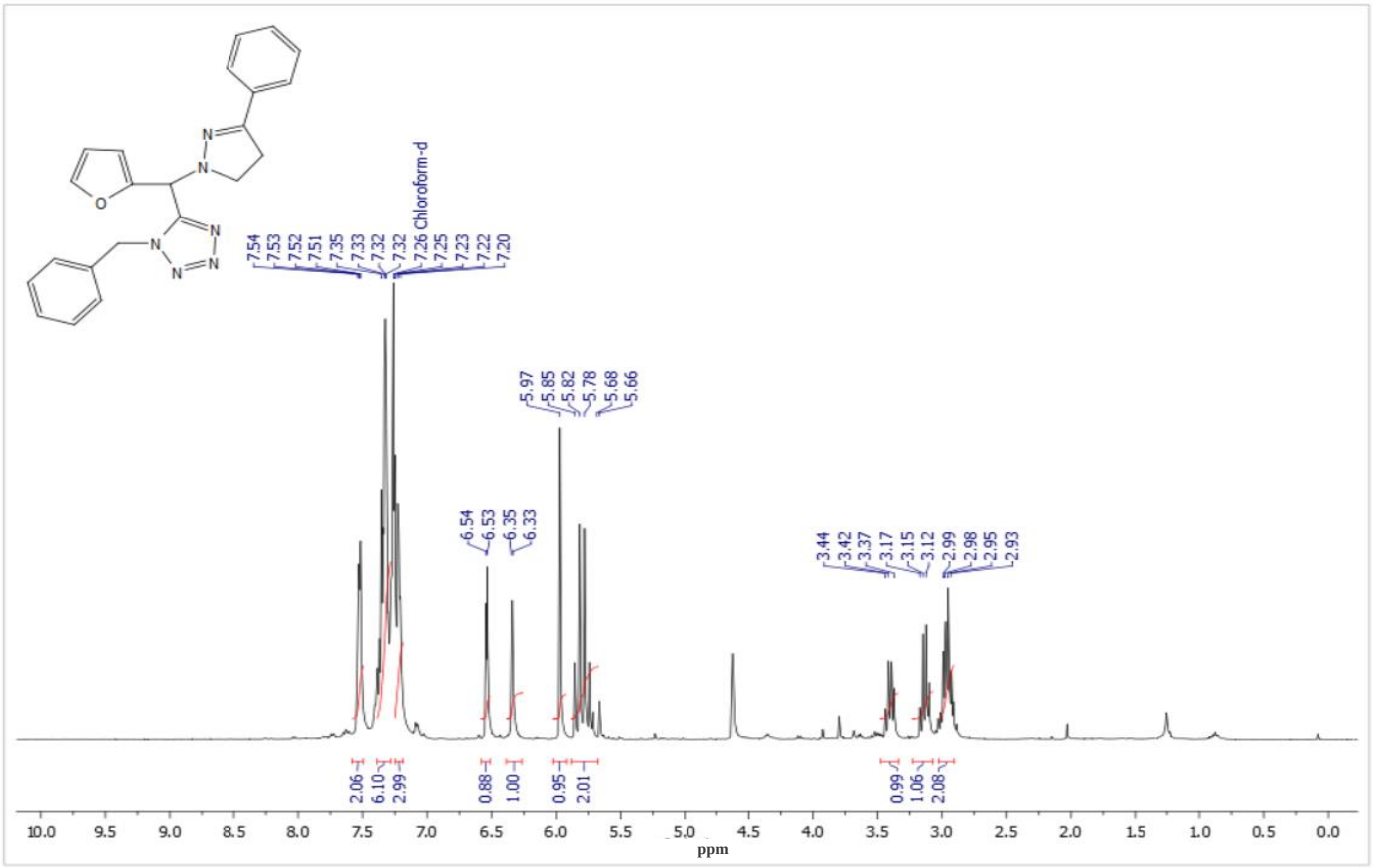


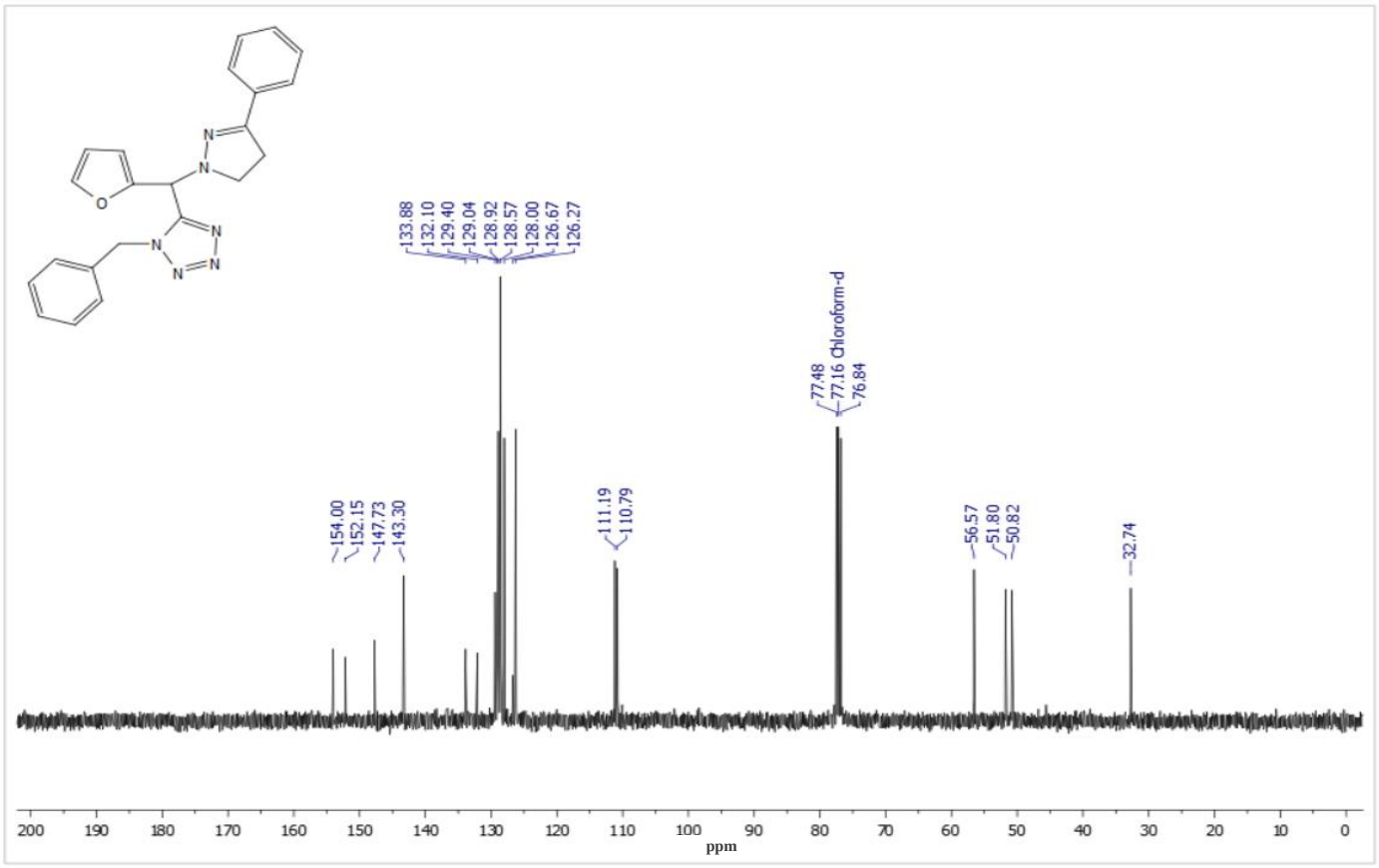
1-Benzyl-5-((3-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-1-yl)(o-tolyl)methyl)-1H-tetrazole 2e.



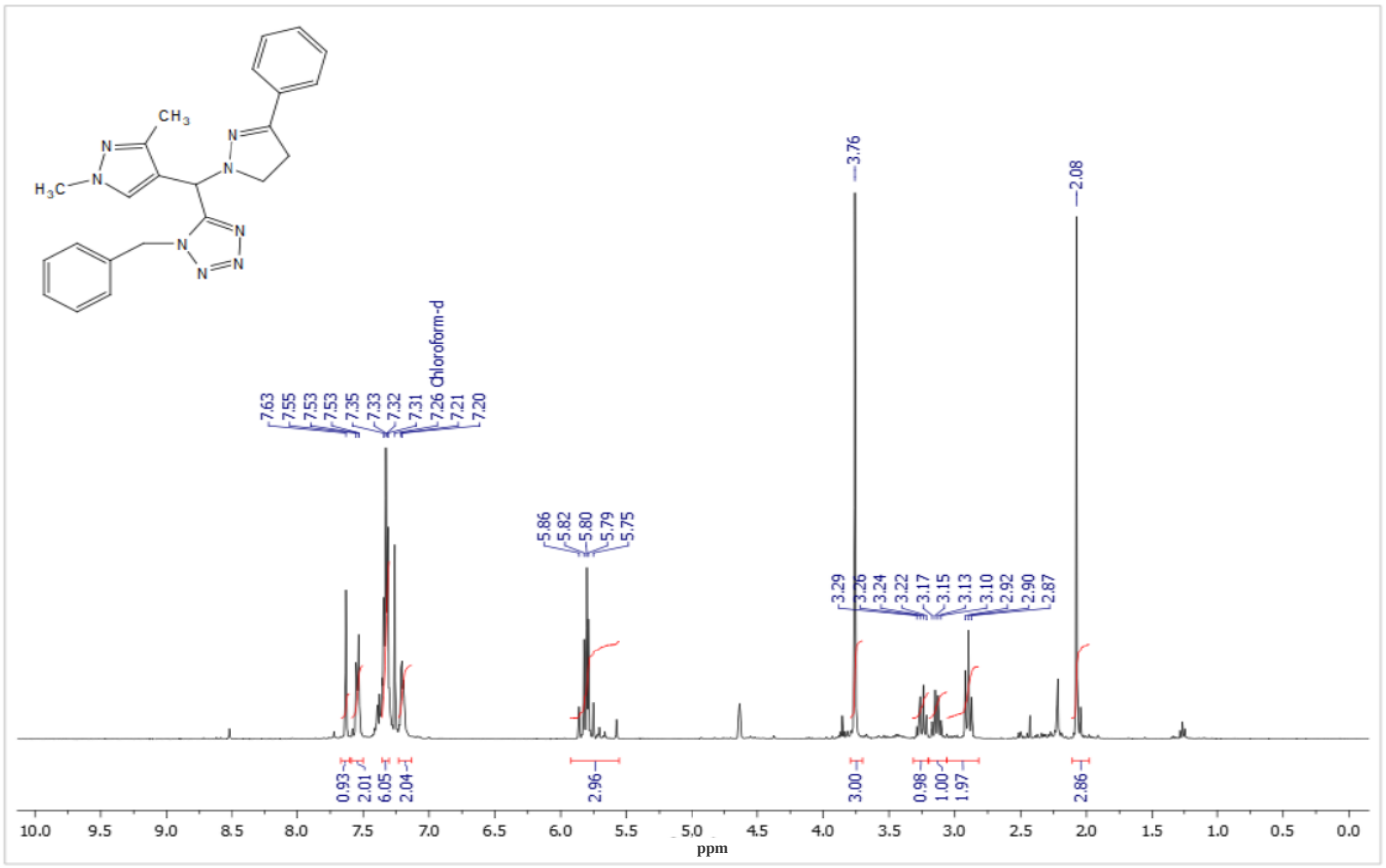


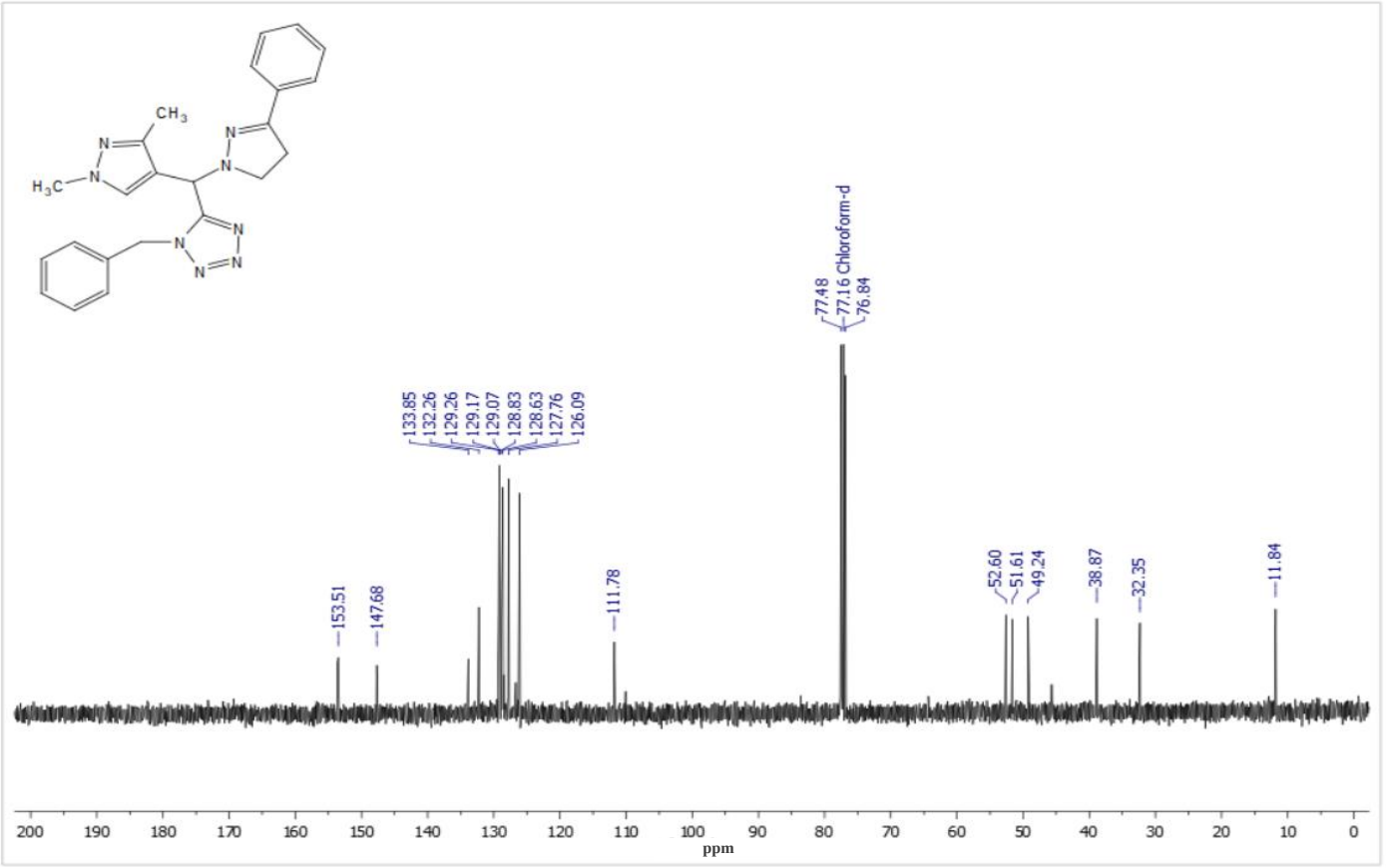
1-Benzyl-5-((3-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-1-yl)(2-methoxyphenyl)methyl)-1H-tetrazole **2f.**



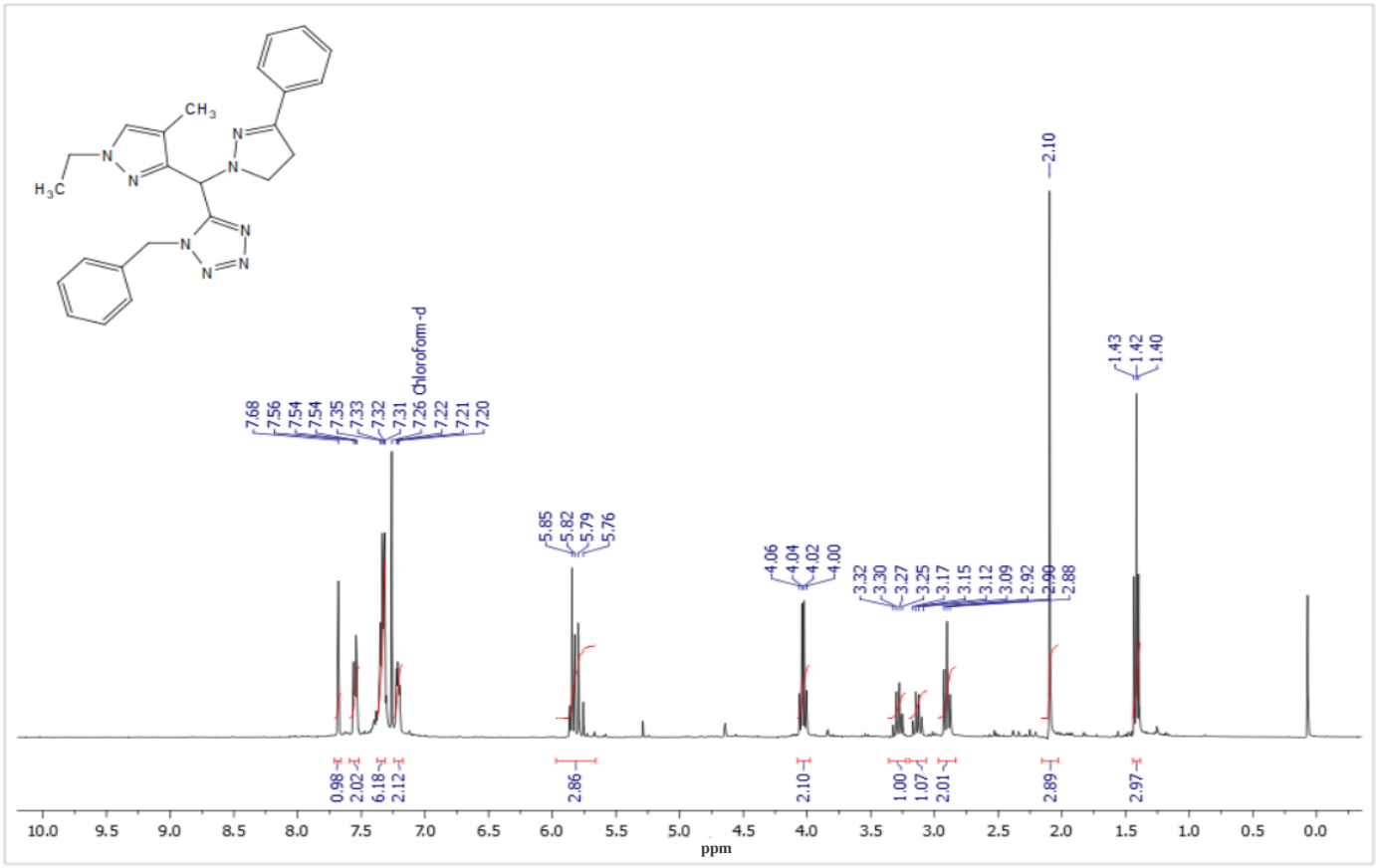


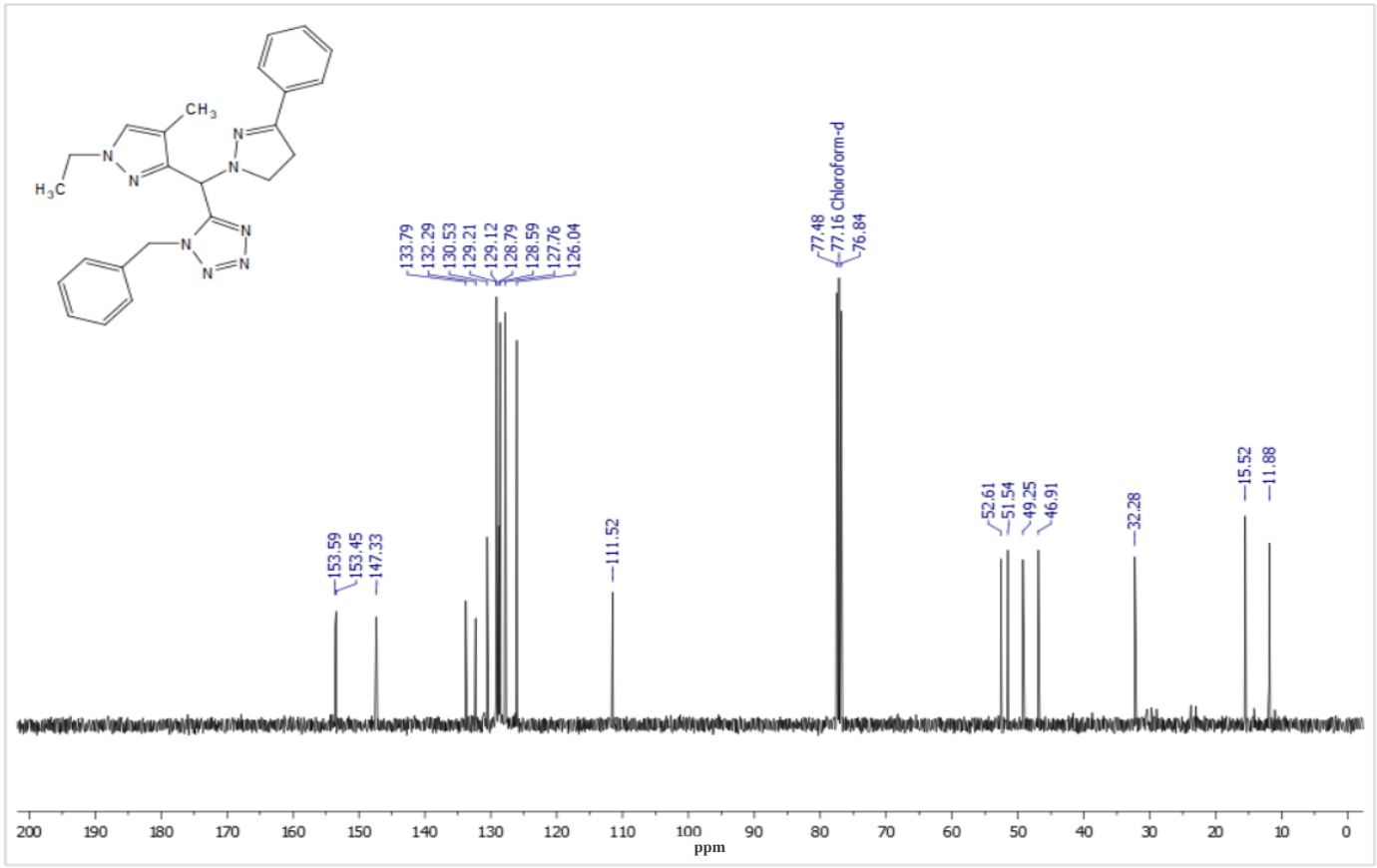
1-Benzyl-5-(furan-2-yl)(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1H-tetrazole **2g.**



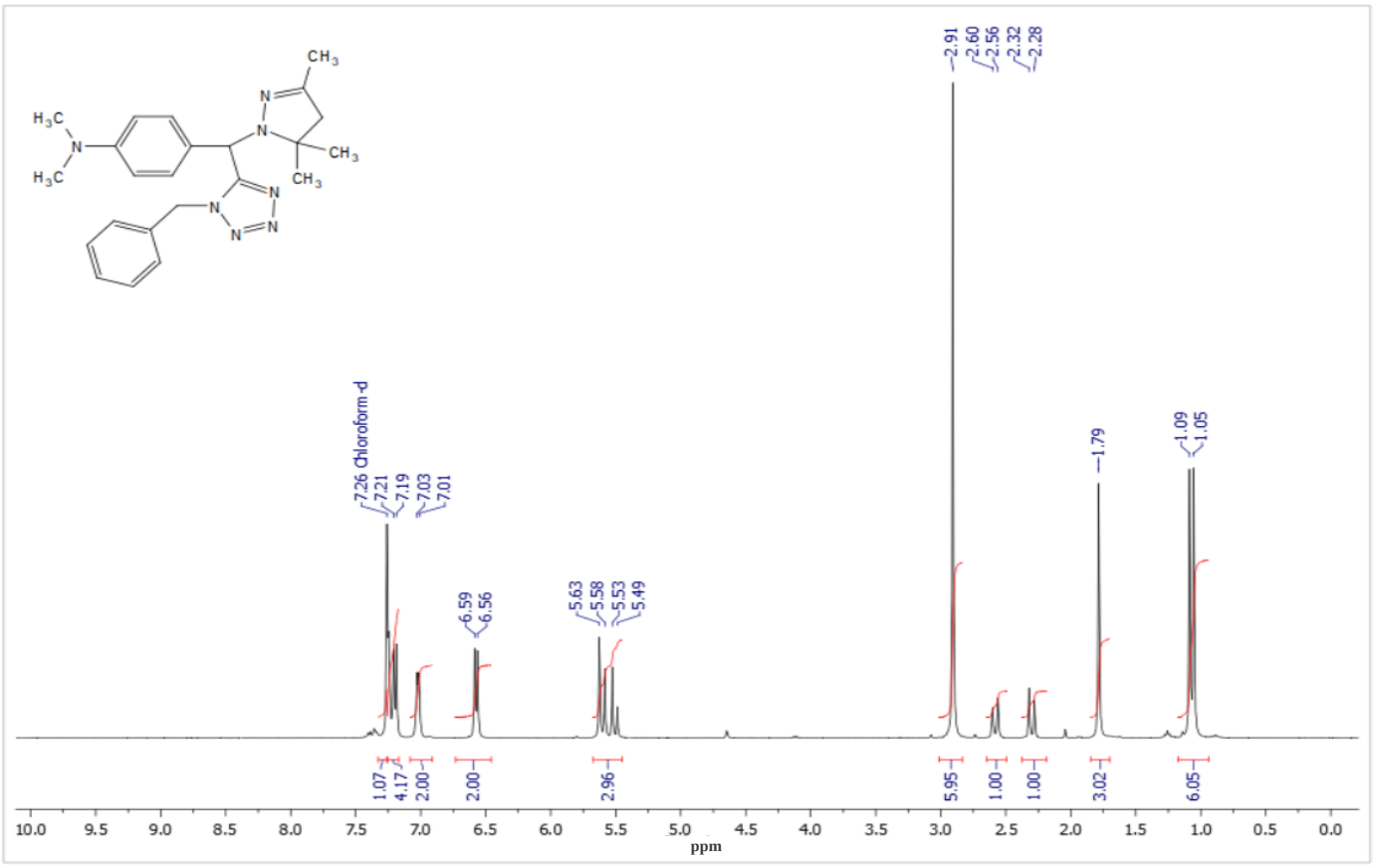


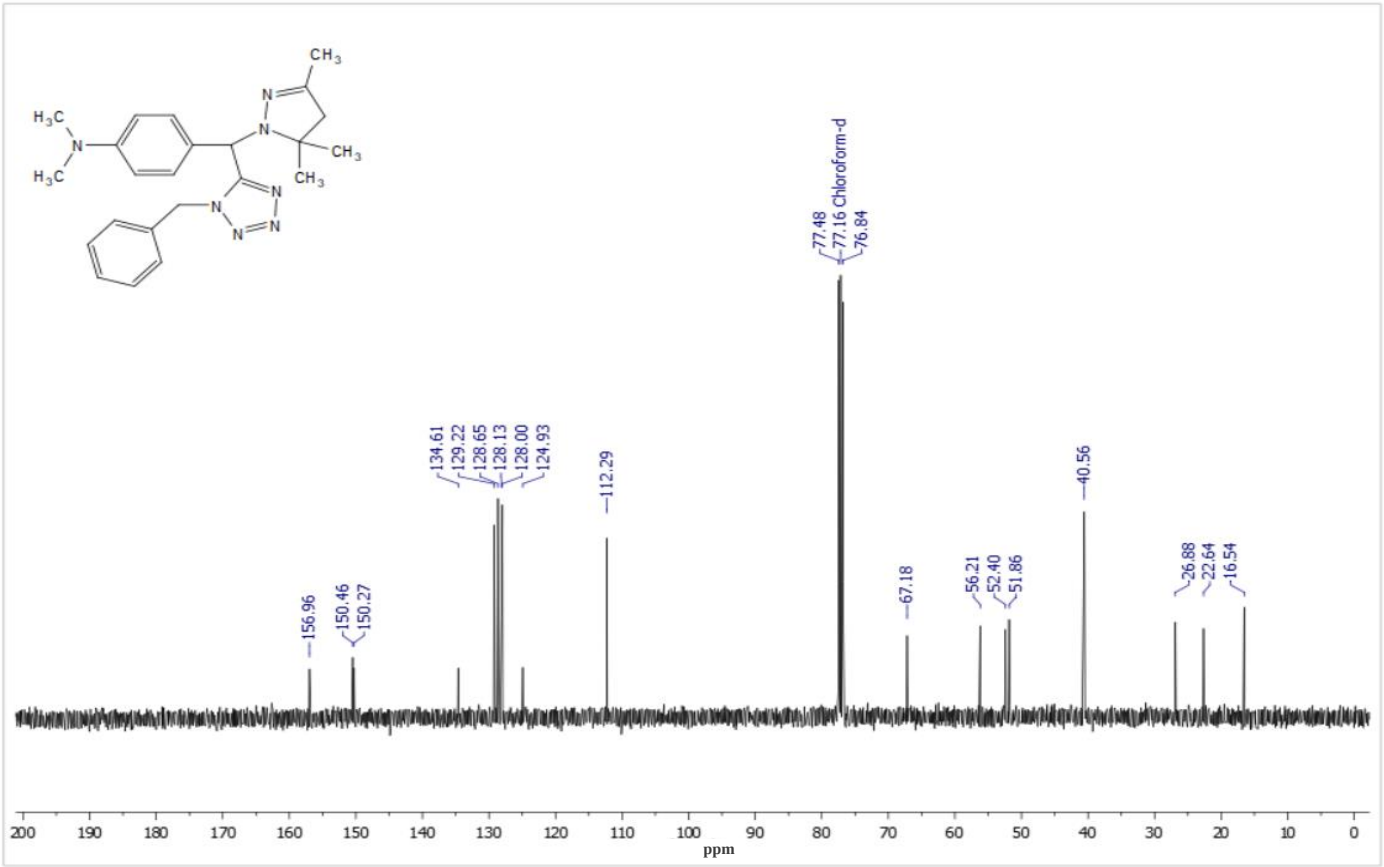
1-Benzyl-5-((1,3-dimethyl-1H-pyrazol-4-yl)(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1H-tetrazole **2h**.



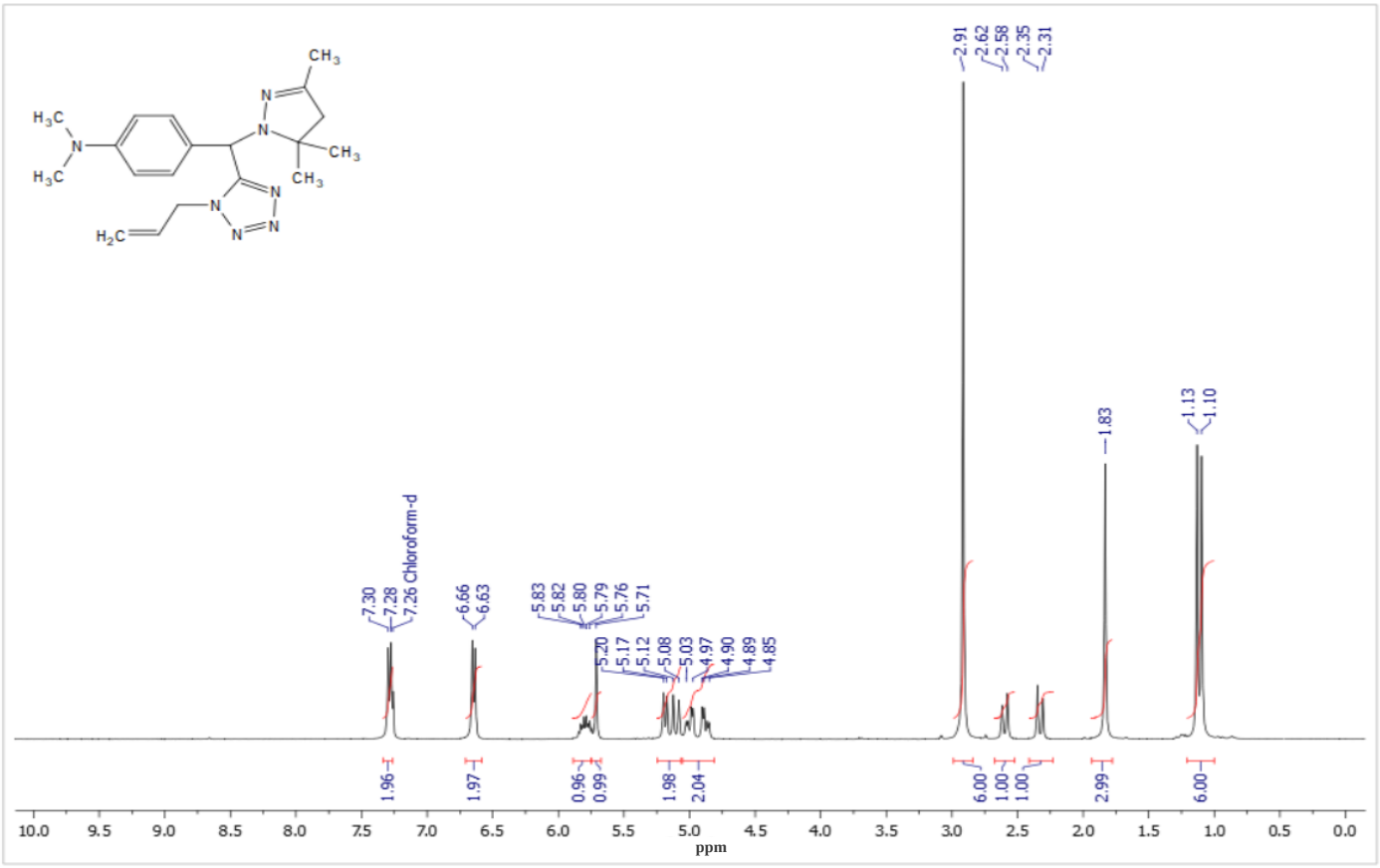


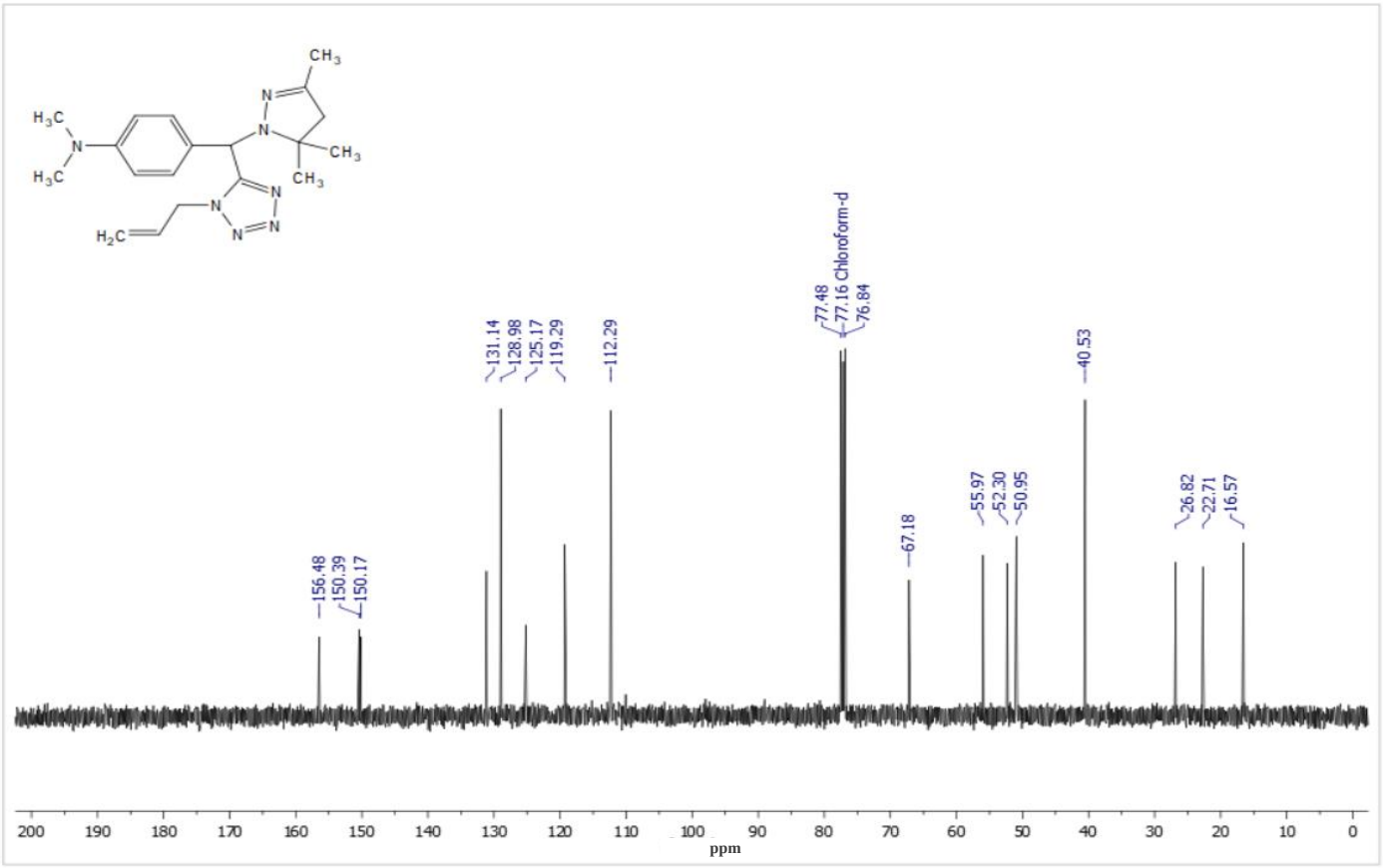
1-Benzyl-5-((1-ethyl-4-methyl-1H-pyrazol-3-yl)(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1H-tetrazole **2i.**



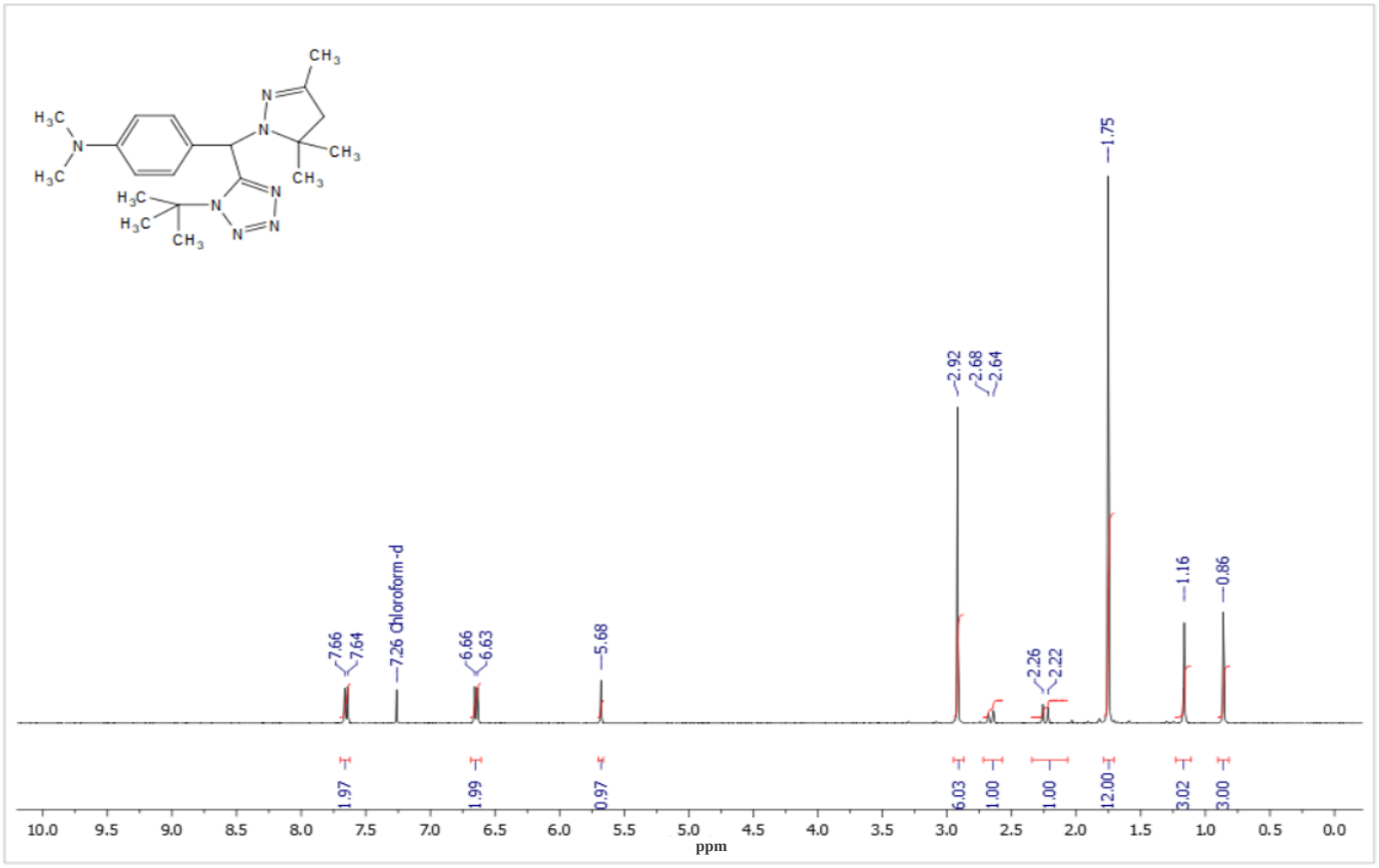


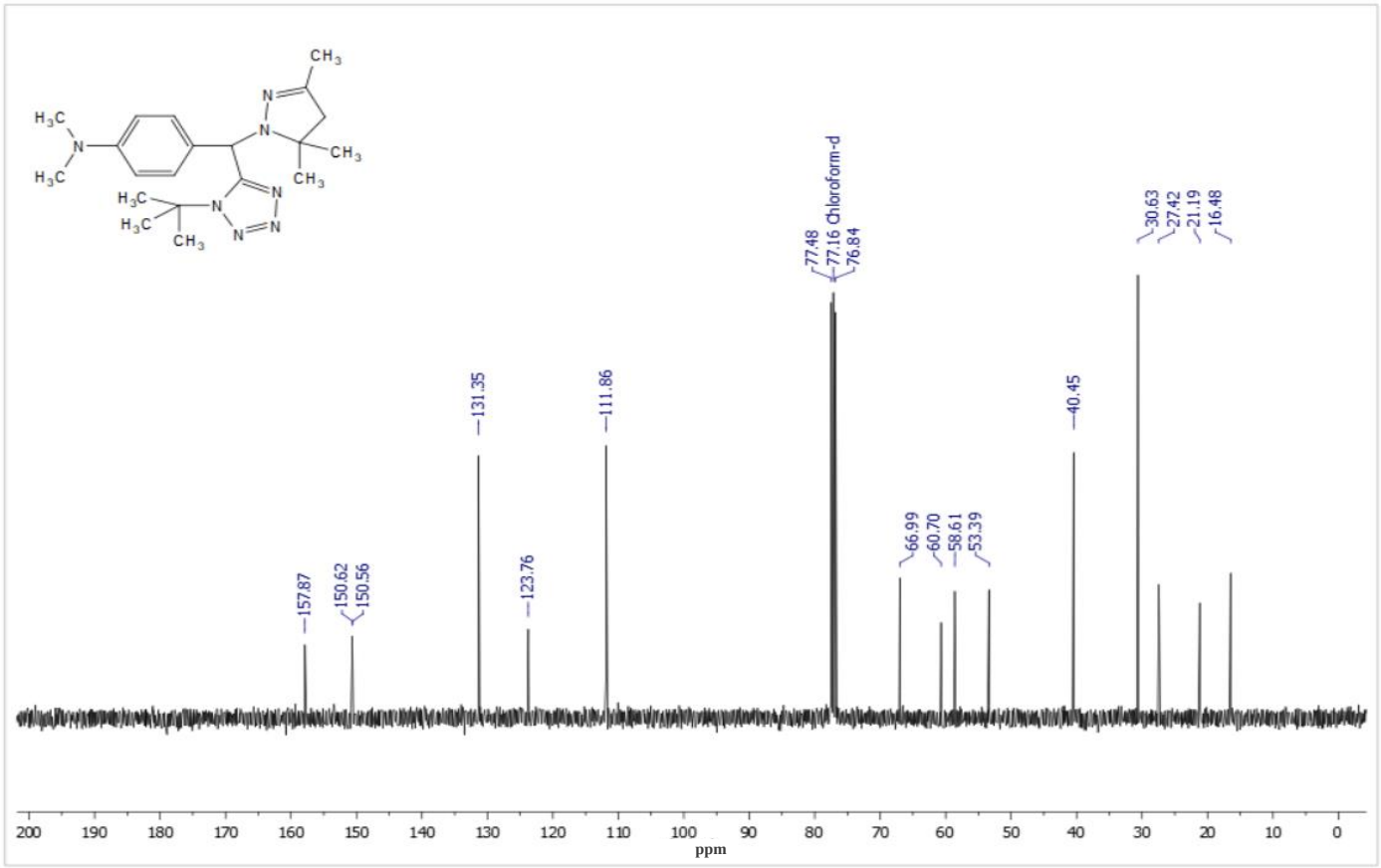
4-((1-Benzyl-1H-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-N,N-dimethylaniline **2j.**



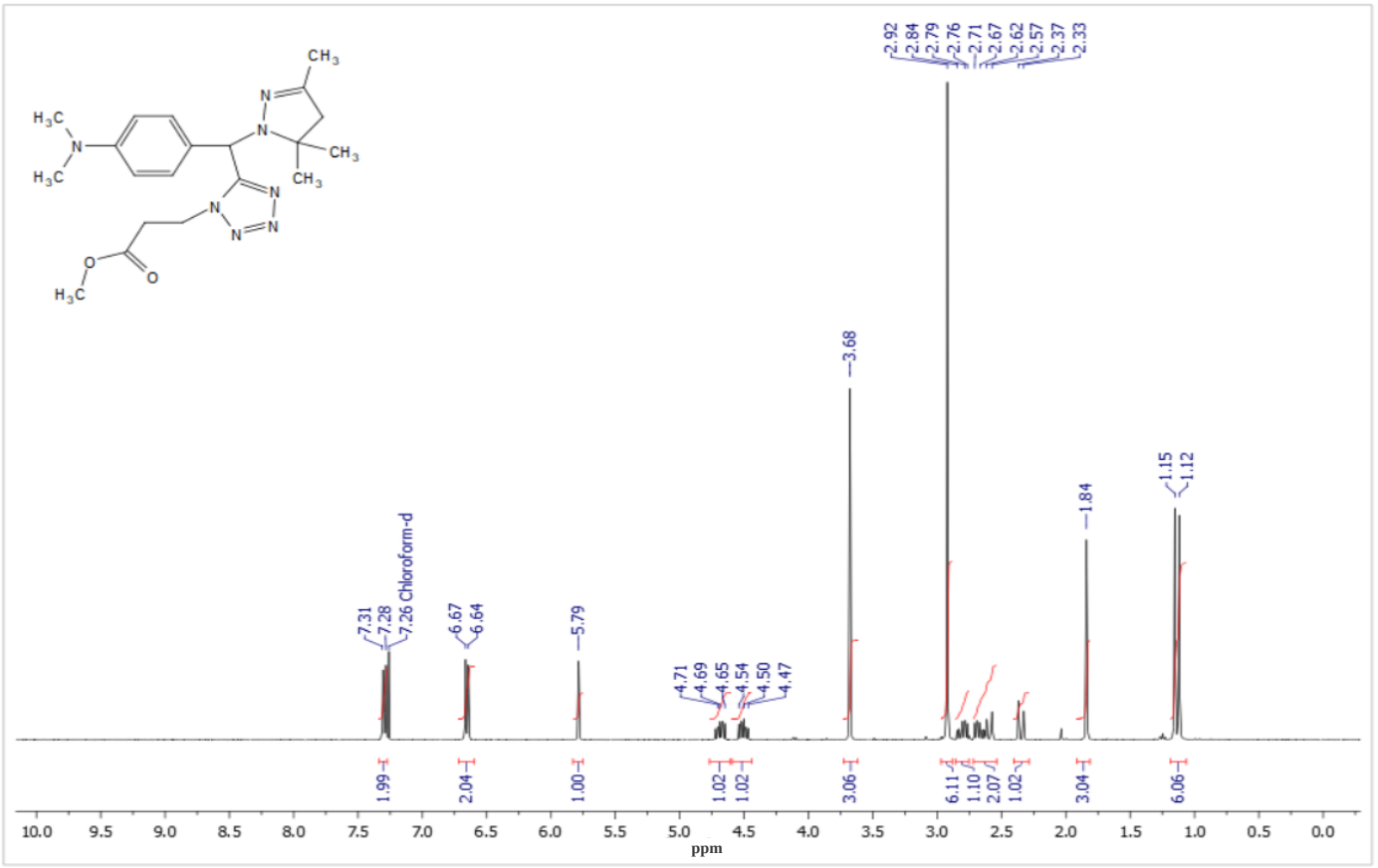


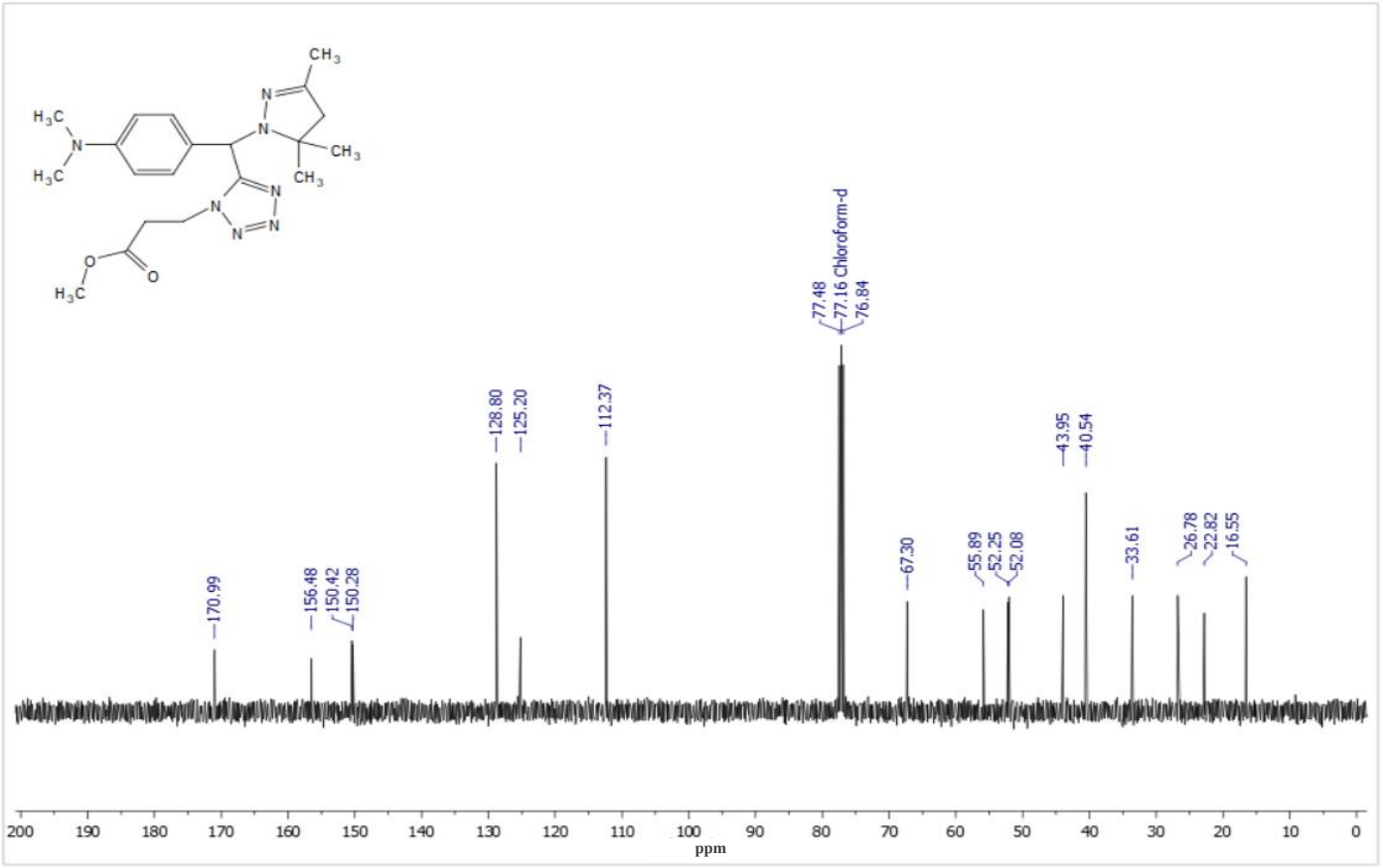
4-((1-Allyl-1H-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-N,N-dimethylaniline **2k.**



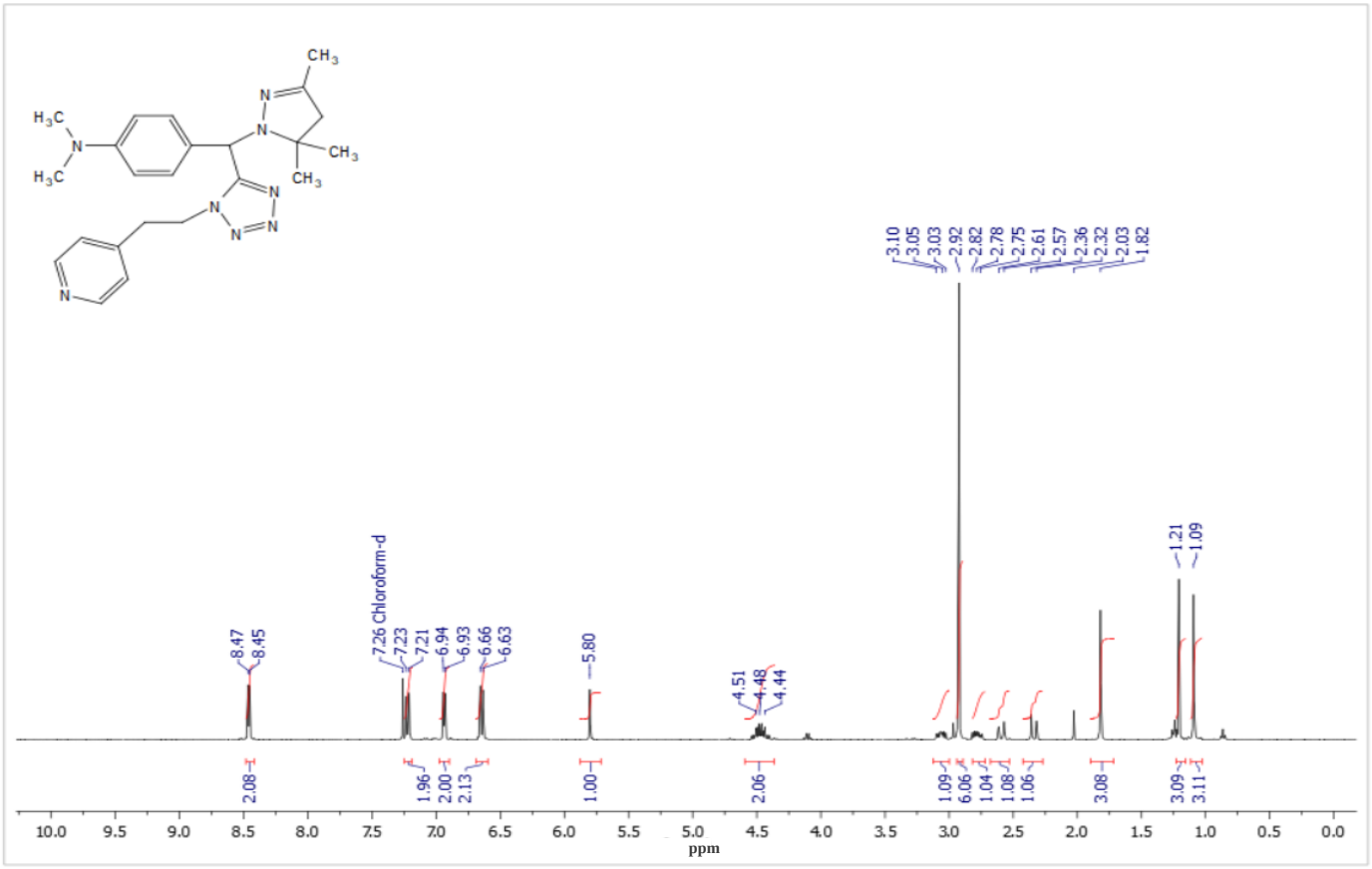


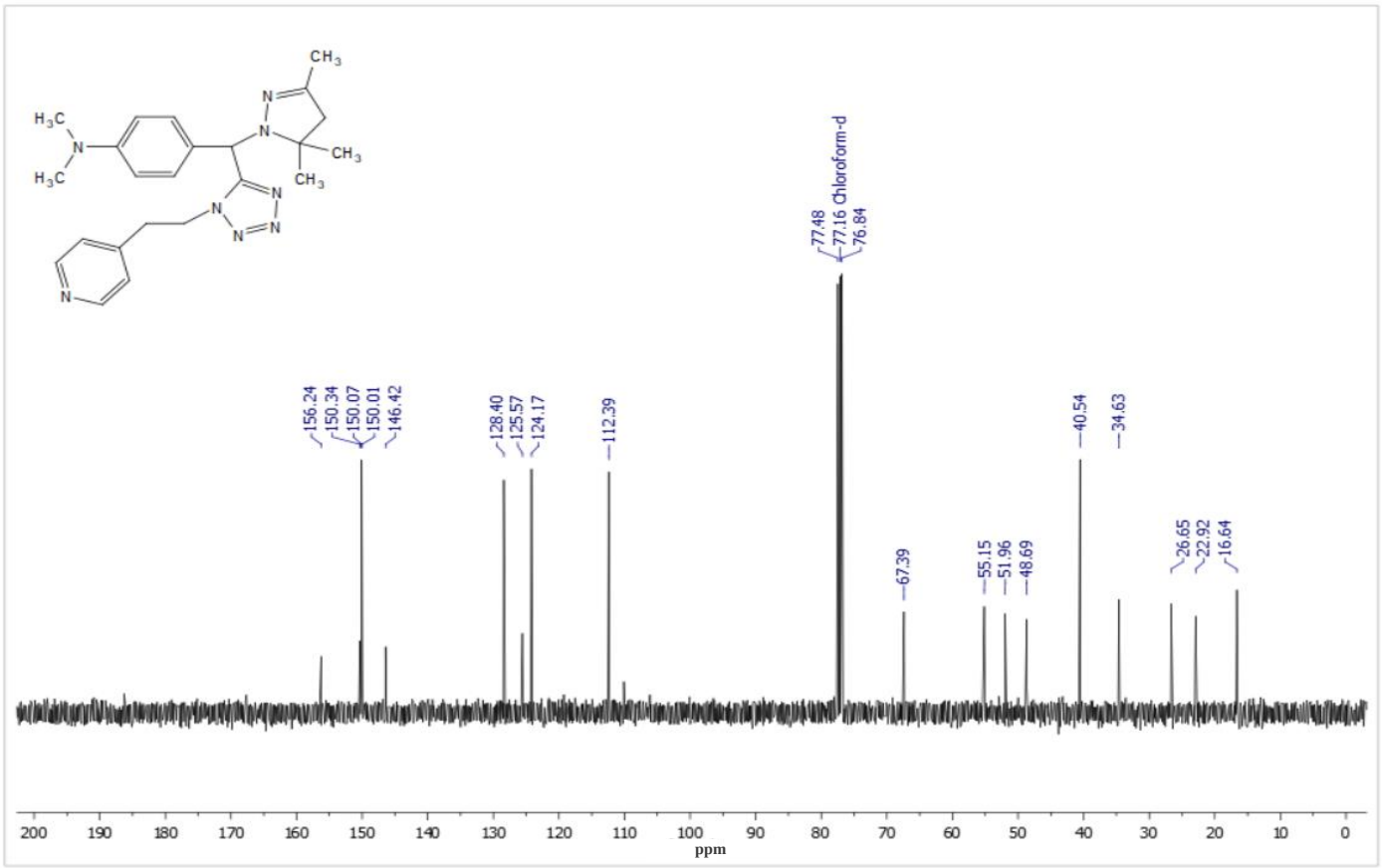
4-((1-(tert-Butyl)-1H-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-N,N-dimethylaniline **2l.**





Methyl 3-(5-((4-(dimethylamino)phenyl)(3,5,5-trimethyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)-1H-tetrazol-1-yl)propanoate **2m.**





N,N-dimethyl-4-((1-(2-(pyridin-4-yl)ethyl)-1H-tetrazol-5-yl)(3,5,5-trimethyl-4,5-dihydro-1H-pyrazol-1-yl)methyl)aniline **2n.**