Supporting Information

Syntheses of 3*H*-1,2,4-Triazol-3-ones by Copper-Promoted Oxidative N-N Bond Formation of Amidines with Isocyanates

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1. General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR and ^{13}C-NMR. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-500 and referenced to 7.28 ppm and 77.16 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (Energy chemical, J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

2. Typical procedure for the synthesis of 3 and 5a

Synthetic procedure for 3

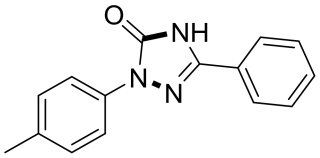
Isocyanate **1** (0.2 mmol), amidine hydrochloride **2** (0.2 mmol), $Cu(OAc)_2$ (0.4 mmol), TBAI (0.2 mmol) and DMSO (2 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 80 ℃ by heating the mantle for 12 h. The combined filtrate was concentrated and purified by a flash column chromatography (EtOAc/petroleumether) on silica gel to afford the products **3**.

Synthetic procedure for 5a

Isocyanate **1a** (0.2 mmol), amidine hydrochloride **2a** (0.2 mmol), $Cu(OAc)_2$ (0.02 mmol), TBAI (0.2 mmol) and DMSO (2 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 80 ℃ by heating the mantle for 4 h. The combined filtrate was concentrated and purified by a flash column chromatography (EtOAc/petroleumether) on silica gel to afford the products **5a**.

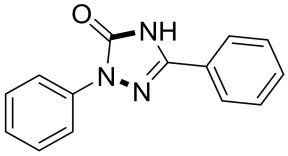
3. Characterization data for all compounds

(1)



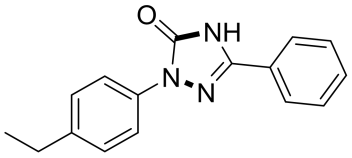
5-Phenyl-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3aa): yellow solid (43.7 mg, 86% yield); mp: 200.0-201.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.65 (s, 1H), 7.92 (dd, J = 7.6, 2.1 Hz, 2H), 7.90 – 7.85 (m, 2H), 7.57 – 7.51 (m, 3H), 7.29 (d, J = 8.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.3, 145.0, 135.9, 134.6, 131.0, 129.9, 129.5, 126.7, 125.7, 118.5, 21.0. HRMS (ESI) m/z: calcd for $C_{15}H_{14}IN_3$ $[M+H]^+$ 252.1131; found 252.1131. HRMS (ESI) m/z: calcd for $C_{15}H_{13}N_3ONa$ $[M+Na]^+$ 274.0950; found 274.0945.

(2)



2,5-Diphenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ab): yellow solid (41.7 mg, 88% yield); mp: 190.9-191.9 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.97 – 7.89 (m, 2H), 7.61 – 7.52 (m, 3H), 7.49 (t, J = 7.9 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.4, 145.3, 138.3, 131.1, 129.5, 129.5, 126.6, 125.8, 125.4, 118.5. HRMS (ESI) m/z: calcd for $C_{14}H_{11}N_3ONa$ $[M+Na]^+$ 260.0794; found 260.0790.

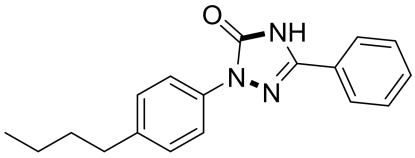
(3)



2-(4-Ethylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ac): yellow solid (39.9 mg, 75% yield); mp: 230.8-231.8 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3:

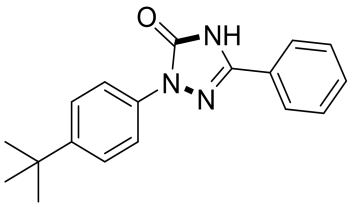
1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.65 (s, 1H), 7.96 – 7.84 (m, 4H), 7.57 – 7.50 (m, 3H), 7.35 – 7.27 (m, 2H), 2.63 (m, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.3, 145.0, 141.0, 136.1, 131.0, 129.5, 128.7, 126.7, 125.7, 118.7, 28.1, 16.1. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3ONa$ $[M+Na]^+$ 288.1107; found 288.1102.

(4)



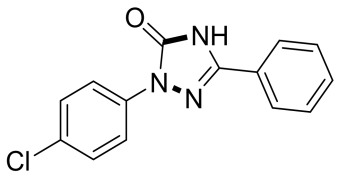
2-(4-Butylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ad): yellow solid (38.1 mg, 65% yield); mp: 150.0-151.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.65 (s, 1H), 7.93 – 7.90 (m, 2H), 7.90 – 7.86 (m, 2H), 7.57 – 7.51 (m, 3H), 7.30 – 7.25 (m, 2H), 2.59 (t, J = 7.7 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.35 – 1.26 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 153.3, 145.0, 139.5, 136.1, 131.0, 129.5, 129.2, 126.7, 125.7, 118.6, 34.7, 33.6, 22.2, 14.2. HRMS (ESI) m/z: calcd for $C_{18}H_{19}N_3ONa$ $[M+Na]^+$ 316.1420; found 316.1415.

(5)



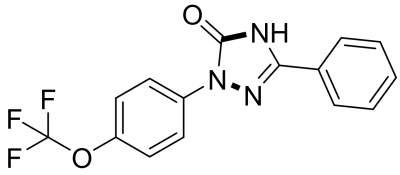
2-(4-(tert-Butyl)phenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ae): yellow solid (43.9 mg, 75% yield); mp: 236.4-237.4 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.64 (s, 1H), 7.93 – 7.87 (m, 4H), 7.57 – 7.52 (m, 3H), 7.51 – 7.47 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.3, 147.9, 145.1, 135.8, 131.0, 129.5, 126.7, 126.1, 125.7, 118.4, 34.7, 31.6. HRMS (ESI) m/z: calcd for $C_{18}H_{19}N_3ONa$ $[M+Na]^+$ 316.1420; found 316.1417.

(6)



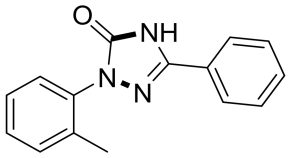
2-(4-Chlorophenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3af): yellow solid (45.0 mg, 83% yield); mp: 284.0-285.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.76 (s, 1H), 8.03 (d, J = 8.9 Hz, 2H), 7.97 – 7.88 (m, 2H), 7.55 (dt, J = 6.4, 3.2 Hz, 5H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.3, 145.6, 137.1, 131.2, 129.6, 129.5, 129.2, 126.5, 125.8, 119.9. HRMS (ESI) m/z: calcd for $C_{14}H_{10}ClN_3ONa$ $[M+Na]^+$ 294.0404; found 294.0400.

(7)



5-Phenyl-2-(4-(trifluoromethoxy)phenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3ag): yellow solid (50.7 mg, 79% yield); mp: 210.0-211.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.78 (s, 1H), 8.17 – 8.08 (m, 2H), 7.97 – 7.89 (m, 2H), 7.56 (dd, J = 5.2, 2.0 Hz, 3H), 7.50 (d, J = 8.5 Hz, 2H) ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.4, 145.7, 145.3, 137.3, 131.3, 129.6, 126.5, 125.8, 122.4, 120.6 (q, J = 255.9 Hz), 119.9. ^{19}F NMR (471 MHz, DMSO-d_6) δ -57.01. HRMS (ESI) m/z: calcd for $C_{15}H_{10}F_3N_3O_2Na$ $[M+Na]^+$ 344.0617; found 344.0613.

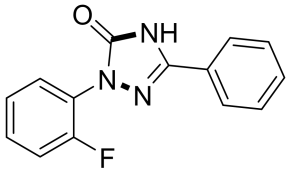
(8)



5-Phenyl-2-(*o*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3ah): yellow solid (23.1 mg, 46% yield); R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz,

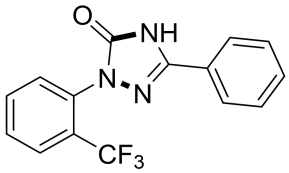
DMSO-d_6) δ 12.50 (s, 1H), 7.89 – 7.83 (m, 2H), 7.56 – 7.49 (m, 3H), 7.42 – 7.30 (m, 4H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 192.1 – 188.7 (m), 153.9, 145.3, 136.1, 135.2, 131.3, 130.8, 129.5, 128.9, 127.6, 127.0, 125.5, 18.3. HRMS (ESI) m/z: calcd for $C_{15}H_{13}N_3ONa$ $[M+Na]^+$ 274.0950; found 274.0945.

(9)



2-(2-Fluorophenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ai): yellow solid (29.6 mg, 58% yield); R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.62 (s, 1H), 7.94 – 7.83 (m, 2H), 7.64 (m, J = 7.8, 1.7 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.44 (m, J = 10.0, 8.3, 1.4 Hz, 1H), 7.36 (m, J = 7.6, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.6 (d, J = 251.4 Hz), 153.9, 146.1, 131.0, 130.6 (d, J = 7.7 Hz), 129.5, 128.6, 126.7, 125.6, 125.3 (d, J = 3.7 Hz), 124.8 (d, J = 11.8 Hz), 117.2 (d, J = 19.2 Hz).^{19}F NMR (471 MHz, DMSO-d_6) δ -120.31. HRMS (ESI) m/z: calcd for $C_{14}H_{10}FN_3ONa$ $[M+Na]^+$ 278.0700; found 278.0696.

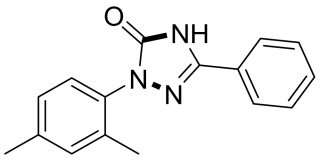
(10)



5-Phenyl-2-(2-(trifluoromethyl)phenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3aj): yellow solid (26.2 mg, 43% yield); mp: 210.0-211.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (dd, J = 7.8, 1.5 Hz, 1H), 7.85 (td, J = 8.1, 2.0 Hz, 3H), 7.72 (d, J = 8.1 Hz, 2H), 7.56 – 7.47 (m, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.2, 146.3, 134.9, 134.0, 130.9, 130.8, 130.0, 129.5, 127.9 (q, J = 5.1 Hz), 127.3, 126.8 (q, J = 30.9 Hz), 125.5, 123.7 (q, J = 273.5 Hz). ^{19}F

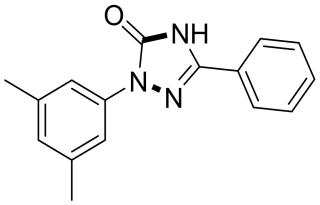
NMR (471 MHz, DMSO-d_6) δ -58.83. HRMS (ESI) m/z: calcd for $C_{15}H_{10}F_3N_3ONa$ $[M+Na]^+$ 328.0668; found 328.0662.

(11)



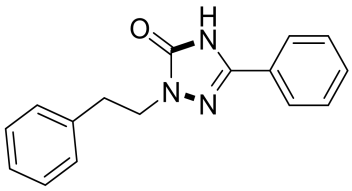
2-(2,4-Dimethylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ak): yellow solid (25.5 mg, 48% yield); mp: 259.8-260.8 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.89 – 7.80 (m, 2H), 7.55 – 7.47 (m, 3H), 7.26 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.12 (dd, J = 8.0, 2.0 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.3, 145.4, 138.3, 135.0, 133.8, 131.7, 130.7, 129.5, 127.5, 127.4, 127.2, 125.4, 21.1, 18.2. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3ONa$ $[M+Na]^+$ 288.1107; found 288.1100.

(12)



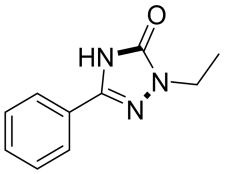
2-(3,5-Dimethylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3al): yellow solid (41.3 mg, 78% yield); mp: 191.8-192.8 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.66 (s, 1H), 7.92 (dd, J = 7.6, 2.2 Hz, 2H), 7.64 (d, J = 1.6 Hz, 2H), 7.54 (dd, J = 5.7, 1.7 Hz, 3H), 6.88 (s, 1H), 2.33 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.5, 145.2, 138.6, 138.3, 131.0, 129.5, 126.8, 126.8, 125.7, 116.2, 21.6. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3ONa$ $[M+Na]^+$ 288.1107; found 288.1103.

(13)



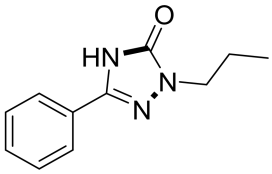
2-Phenethyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3am): yellow solid (43.5 mg, 82% yield); mp: 168.1-169.1 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.19 (s, 1H), 7.84 – 7.76 (m, 2H), 7.53 – 7.44 (m, 3H), 7.28 (dd, *J* = 8.0, 6.8 Hz, 2H), 7.24 – 7.18 (m, 3H), 3.95 (dd, *J* = 8.0, 6.7 Hz, 2H), 3.02 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.7, 143.9, 138.8, 130.5, 129.4, 129.1, 128.8, 127.2, 126.8, 125.3, 45.7, 34.7. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3ONa$ $[M+Na]^+$ 288.1107; found 288.1099.

(14)



2-Ethyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3an): yellow solid (32.1 mg, 83% yield); mp: 180.0-181.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.21 (s, 1H), 7.85 - 7.74 (m, 2H), 7.54 - 7.39 (m, 3H), 3.75 (m, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.4, 143.8, 130.4, 129.4, 127.2, 125.2, 39.5, 14.5. HRMS (ESI) m/z: calcd for $C_{10}H_{12}N_3ONa$ $[M+Na]^+$ 212.0794; found 212.0791.

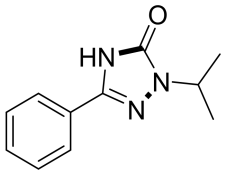
(15)



5-Phenyl-2-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ao): yellow solid (34.5 mg, 85% yield); mp: 175.1-176.1 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.20 (s, 1H), 7.85 – 7.73 (m, 2H), 7.56 – 7.39 (m, 3H),

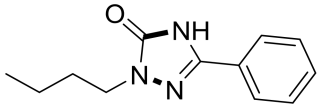
3.67 (t, *J* = 7.0 Hz, 2H), 1.70 (m, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 154.8, 143.8, 130.4, 129.4, 127.2, 125.2, 46.1, 22.2, 11.4. HRMS (ESI) m/z: calcd for $C_{11}H_{13}N_3ONa$ $[M+Na]^+$ 226.0950; found 226.0946.

(16)



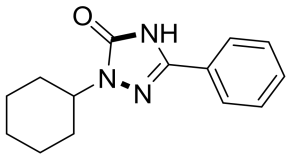
2-Isopropyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ap): yellow solid (32.9 mg,81% yield); mp: 209.5-210.5 ºC; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.17 (s, 1H), 7.83 – 7.77 (m, 2H), 7.51 – 7.43 (m, 3H), 4.35 (p, *J* = 6.7 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.0, 143.8, 130.3, 129.4, 127.3, 125.2, 45.9, 21.6. HRMS (ESI) m/z: calcd for $C_{11}H_{13}N_3ONa$ $[M+Na]^+$ 226.0950; found 226.0947.

(17)



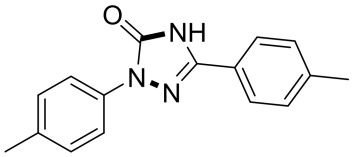
2-Butyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3aq): yellow solid (33.4 mg, 77% yield); mp 212.6-213.6 ºC; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.98 (s, 1H), 7.92 – 7.83 (m, 2H), 7.44 (dd, *J* = 9.2, 7.1 Hz, 3H), 3.90 (t, *J* = 7.2 Hz, 2H), 1.83 (m, *J* = 7.3 Hz, 2H), 1.43 (m, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.3, 145.0, 130.0, 128.9, 126.8, 125.2, 44.9, 30.9, 19.8, 13.7. HRMS (ESI) m/z: calcd for $C_{12}H_{15}N_3ONa$ $[M+Na]^+$ 240.1107; found 240.1102.

(18)



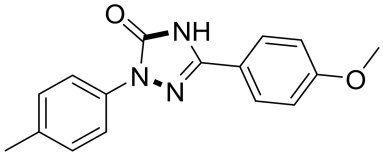
2-Cyclohexyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ar): yellow solid (39.9 mg, 82% yield); mp: 237.6-238.6 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.18 (s, 1H), 7.79 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.57 – 7.29 (m, 3H), 3.95 (m, *J* = 11.7, 3.8 Hz, 1H), 1.81 (m, *J* = 12.3, 4.3, 3.8 Hz, 4H), 1.68 (m, *J* = 27.6, 14.0, 10.4 Hz, 3H), 1.36 (m, *J* = 13.8, 3.7 Hz, 2H), 1.20 m, *J* = 16.3, 13.0, 2.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.1, 143.7, 130.3, 129.4, 127.3, 125.2, 53.2, 31.7, 25.4, 25.4. HRMS (ESI) m/z: calcd for $C_{14}H_{17}N_3ONa$ $[M+Na]^+$ 266.1263; found 266.1266.

(19)



2,5-Di-*p*-tolyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ba): yellow solid (42.9 mg, 81% yield); mp: 160.4-161.4 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.56 (s, 1H), 7.89 – 7.83 (m, 2H), 7.83 – 7.78 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 2H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.3, 145.1, 140.9, 136.0, 134.4, 130.1, 129.8, 125.7, 123.9, 118.5, 21.5, 21.0. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3ONa$ $[M+Na]^+$ 288.1107; found 288.1100.

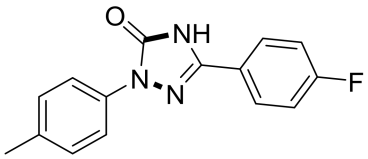
(20)



5-(4-Methoxyphenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bb): yellow solid (42.7 mg, 76% yield); mp: 230.8-231.8 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.90 – 7.81 (m, 4H), 7.29 – 7.23 (m, 2H), 7.12 – 7.06 (m, 2H), 3.83 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.4, 153.4, 145.1, 136.1, 134.3, 129.8, 127.4, 119.2, 118.4,

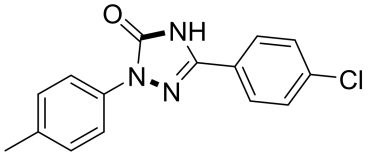
114.9, 55.9, 21.0. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3O_2Na$ $[M+ Na]^+$ 304.1056; found 304.1046.

(21)



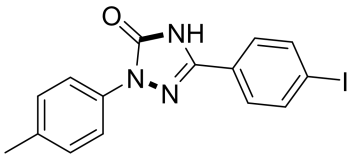
5-(4-Fluorophenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bc): yellow solid (42.0 mg, 78% yield); mp: 282.0-283.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.66 (s, 1H), 7.99 – 7.94 (m, 2H), 7.89 – 7.83 (m, 2H), 7.41 (t, J = 8.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.77 (d, J = 248.4 Hz), 153.25, 144.28, 135.88, 134.60, 129.88, 128.17 (d, J = 8.8 Hz), 123.31 (d, J = 3.1 Hz), 118.52, 116.71 (d, J = 22.3 Hz), 20.96. ^{19}F NMR (471 MHz, DMSO-d_6) δ -109.73. HRMS (ESI) m/z: calcd for $C_{15}H_{12}FN_3ONa$ $[M+Na]^+$ 292.0856; found 292.0850.

(22)



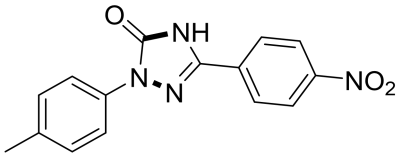
5-(4-Chlorophenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bd): yellow solid (45.6 mg, 80% yield); mp: 175.5-176.5 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.70 (s, 1H), 7.94 – 7.90 (m, 2H), 7.88 – 7.84 (m, 2H), 7.65 – 7.61 (m, 2H), 7.30 – 7.26 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.2, 144.2, 135.8, 135.6, 134.7, 129.9, 129.7, 127.5, 125.6, 118.6, 21.0. HRMS (ESI) m/z: calcd for $C_{15}H_{12}ClONa$ $[M+Na]^+$ 308.0561; found 308.0554.

(23)



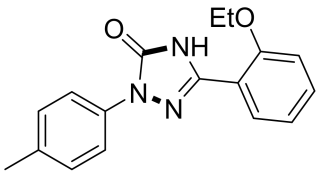
5-(4-Iodophenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3be): yellow solid (53.5 mg, 71% yield); mp: 287.3-288.3 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 2.33 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.2, 144.4, 138.4, 135.8, 134.7, 129.9, 127.5, 126.2, 118.6, 98.0, 21.0. HRMS (ESI) m/z: calcd for $C_{15}H_{12}IN_3ONa$ $[M+Na]^+$ 399.9917; found 399.9908.

(24)



5-(4-Nitrophenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bf): yellow solid (36.7 mg, 62% yield); mp: 324.0-325.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 2: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.94 (s, 1H), 8.38 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 2.33 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 153.8, 148.5, 144.0, 135.8, 134.9, 132.9, 129.9, 126.8, 124.8, 118.7, 21.0. HRMS (ESI) m/z: calcd for $C_{15}H_{12}N_4O_3Na$ $[M+Na]^+$ 319.0801.

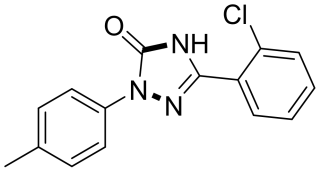
(25)



5-(2-Ethoxyphenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bg): yellow solid (46.6 mg, 79% yield); mp: 191.8-192.8 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92 – 7.83 (m, 2H), 7.75 (dd, J = 7.7, 1.8 Hz, 1H), 7.48 (ddd, J = 8.8, 7.4, 1.8 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 7.16 (d,

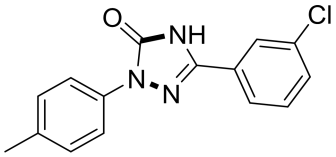
J = 8.4 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 4.16 (m, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 1.38 (t, *J* = 6.9 Hz, 3H). 13C NMR (126 MHz, DMSO-d6) δ 156.6, 153.1, 144.0, 136.0, 134.4, 132.5, 129.8, 129.5, 121.0, 118.5, 115.9, 113.2, 64.3, 20.9, 14.7. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_3O_2Na$ $[M+Na]^+$ 318.1212; found 318.1207.

(26)



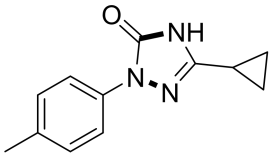
5-(2-Chlorophenyl)-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bh): yellow solid (35.3 mg, 62% yield); mp: 206.2-207.2 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.47 (s, 1H), 7.87 – 7.81 (m, 2H), 7.75 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.58 (m, *J* = 7.7, 1.8 Hz, 1H), 7.52 (m, *J* = 7.5, 1.3 Hz, 1H), 7.30 – 7.25 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.9, 143.8, 135.8, 134.7, 132.5, 132.3, 131.6, 131.0, 129.9, 128.1, 126.3, 118.6, 21.0. HRMS (ESI) m/z: calcd for $C_{15}H_{12}ClN_3ONa$ $[M+Na]^+$ 308.0561; found 308.0554.

(27)



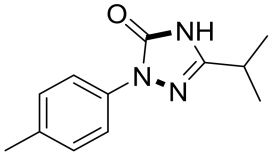
5-(3-Chlorophenyl)-2-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3bi): yellow solid (39.9 mg, 70% yield); R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.80 (s, 1H), 8.10 (t, *J* = 2.1 Hz, 1H), 7.98 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.56 (p, *J* = 3.5 Hz, 3H), 7.52 (t, *J* = 8.1 Hz, 1H), 7.31 (dd, *J* = 8.0, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.9, 153.4, 145.8, 139.5, 133.9, 131.4, 131.3, 129.6, 126.4, 125.9, 125.0, 117.7, 116.6. HRMS (ESI) m/z: calcd for $C_{15}H_{12}ClN_3ONa$ $[M+Na]^+$ 308.0561; found 308.0555.

(28)



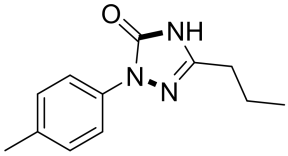
5-Cyclopropyl-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bj): yellow solid (26.2 mg, 61% yield); mp: 214.2-215.2 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.77 – 7.70 (m, 2H), 7.24 – 7.18 (m, 2H), 2.29 (s, 3H), 1.85 (m, *J* = 8.4, 5.1 Hz, 1H), 1.01 – 0.94 (m, 2H), 0.93 – 0.86 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.9, 149.5, 136.0, 133.9, 129.7, 118.1, 20.9, 7.8, 6.9. HRMS (ESI) m/z: calcd for $C_{12}H_{14}N_3O$ $[M+H]^+$ 216.1131; found 216.1130.

(29)



5-Isopropyl-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bk): yellow solid (26.0 mg, 60% yield); mp: 167.7-168.7 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.86 (s, 1H), 7.78 – 7.73 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 2.83 (m, *J* = 6.9 Hz, 1H), 2.30 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.2, 152.3, 136.1, 133.9, 129.8, 118.1, 26.9, 20.9, 20.1. HRMS (ESI) m/z: calcd for $C_{11}H_{13}N_3O$ $[M+H]^+$ 226.0950; found 226.0943.

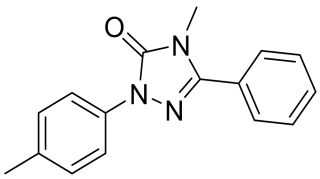
(30)



5-Propyl-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bl): yellow solid (29.5 mg, 68% yield); mp: 149.0-150.0 °C; R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.81 (s, 1H), 7.78 – 7.72 (m, 2H), 7.24 – 7.20 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 1.66 (m, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.4

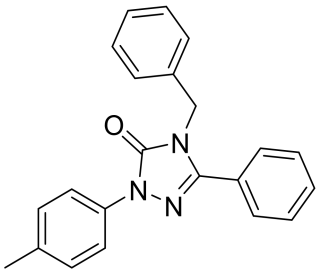
Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.1, 147.9, 136.1, 133.9, 129.8, 118.1, 28.5, 20.9, 19.9, 13.8. HRMS (ESI) m/z: calcd for $C_{12}H_{15}N_3ONa$ $[M+Na]^+$ 240.1107; found 240.1099.

(31)

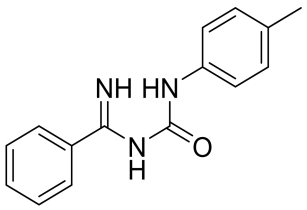


4-Methyl-5-phenyl-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (4a) yellow oily (37.6 mg, 71% yield); R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1);^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.73 – 7.66 (m, 2H), 7.57 – 7.50 (m, 3H), 7.25 (d, *J* = 8.1 Hz, 2H), 3.45 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.7, 146.4, 135.5, 135.1, 130.6, 129.5, 129.0, 128.1, 126.8, 118.8, 29.4, 21.0. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_2O$ $[M+Na]^+$ 288.1107; found 288.1100.

(32)



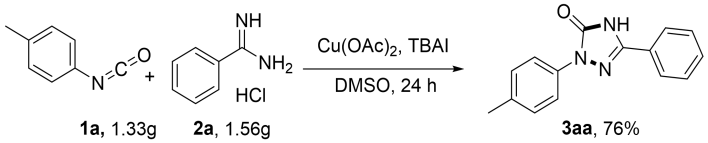
4-Benzyl-5-phenyl-2-(*p*-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (4b): yellow oily (56.6 mg, 83% yield); R_f = 0.3 (petroleum ether: ethyl acetate = 3: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 7.97 (m, 2H), 7.57 – 7.54 (m, 2H), 7.53 – 7.50 (m, 1H), 7.46 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.25 – 7.20 (m, 2H), 5.04 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.7, 146.7, 136.1, 135.5, 135.2, 130.7, 129.5, 129.0, 128.9, 128.4, 127.9, 127.1, 126.7, 118.8, 45.8, 21.0. HRMS (ESI) m/z: calcd for $C_{16}H_{15}N_3O$ $[M+Na]^+$ 364.1420; found 364.1413.



***N*-(*p*-tolylcarbamoyl)benzimidamide** (**5a**): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 7.95 – 7.82 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.47 (td, *J* = 7.7, 7.2, 1.8 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.7, 163.5, 136.3, 135.5, 132.7, 131.8, 129.4, 128.8, 127.0, 119.2, 20.8. HRMS (ESI) m/z: calcd for $C_{15}H_{15}N_3ONa$ $[M+Na]^+$ 276.1107; found 276.1101.

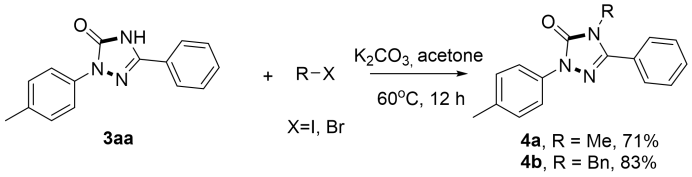
4. Gram-scale reaction and further transformations of 3aa

(a)



1-isocyanato-4-methylbenzene **1a** (10 mmol), benzamidine hydrochloride **2a** (10 mmol), $Cu(OAc)_2$ (20 mmol), TBAI (10 mmol) and DMSO (50 mL) were introduced in a 100mL roundbottomed, successively. Then the roundbottomed was closed and the resulting mixture was stirred at 80 ℃ by heating the mantle for 24 h. The combined filtrate was concentrated and purified by a flash column chromatography (EtOAc/petroleumether) on silica gel to afford the products **3aa**.

(b)

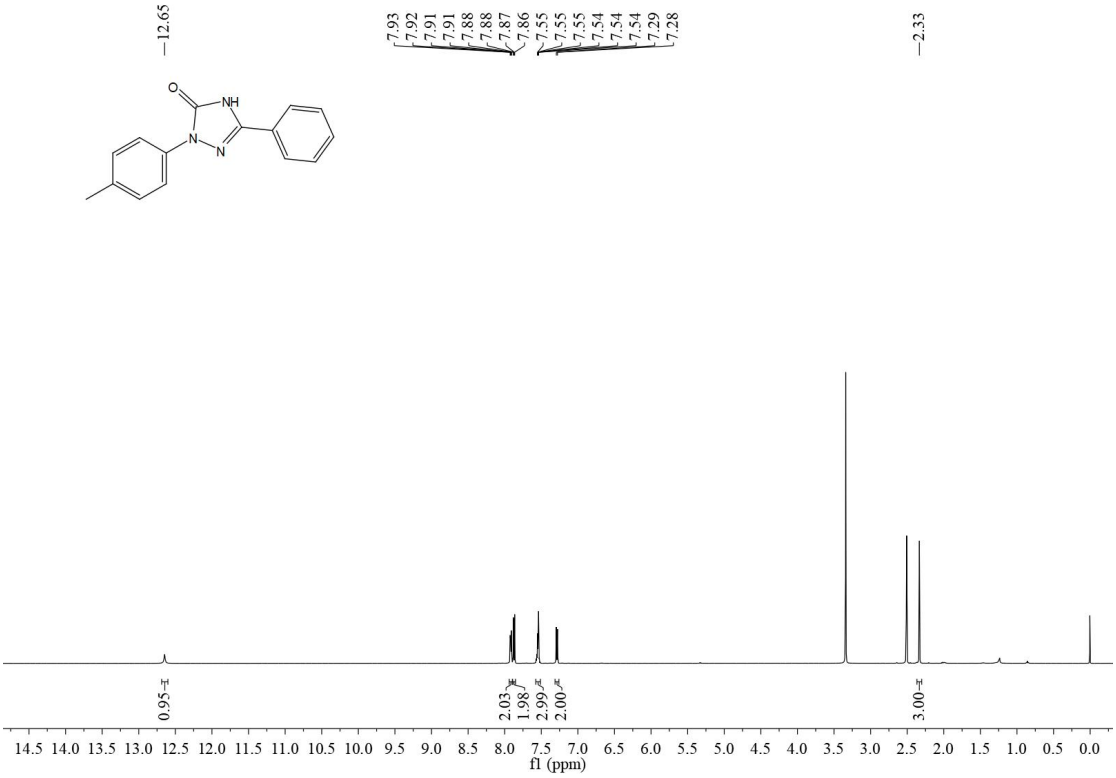


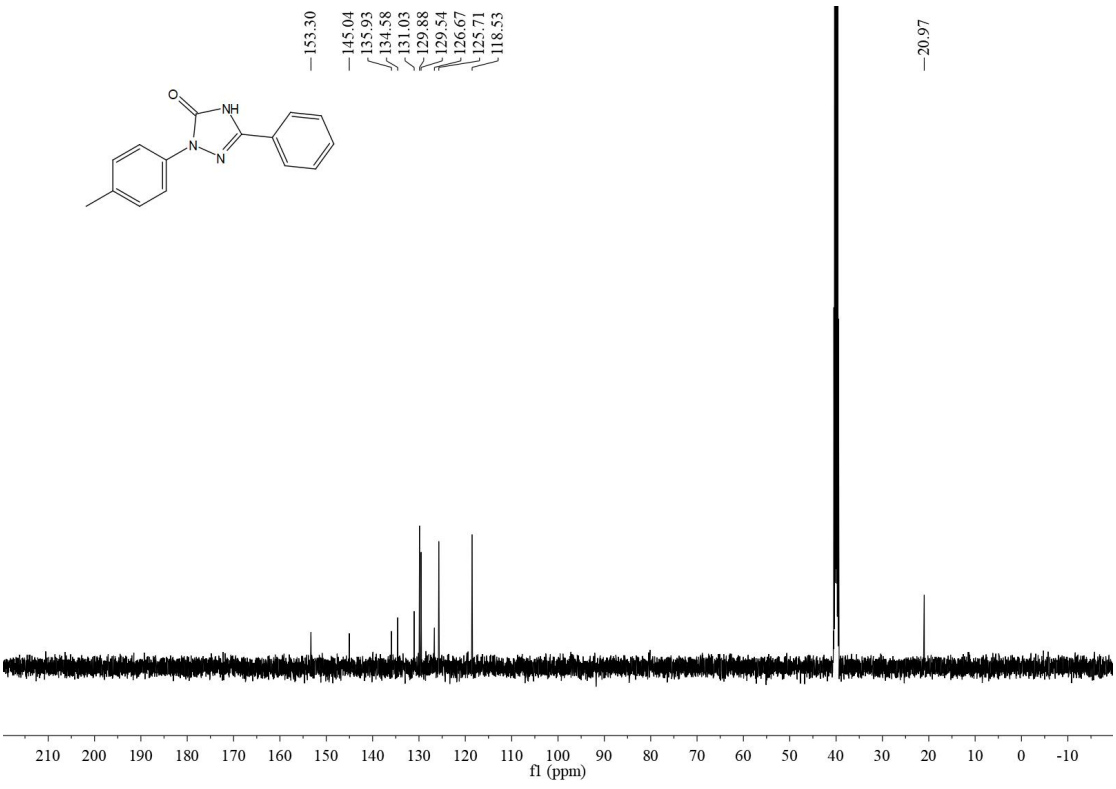
Stir a mixture of 1 equiv. of **3aa** (0.2 mmol), halide (0.6 mmol) and K_2CO_3 (0.4 mmol) in acetone (2 mL) at 60°C for 12 hours in a Schlenk tube. Cool the mixture. Evaporate

the solvent under vacuum. Add 5 ml of water to the reaction mixture. Extract the reaction mixture with ethyl acetate (2 mL x 2). Dry the combined organic fractions over anhydrous sodium sulfate. Concentrate the organic fractions under vacuum. Purify the crude product by column chromatography using a mixture of dichloromethane/ethano(98:2) as eluent to obtain **4**.

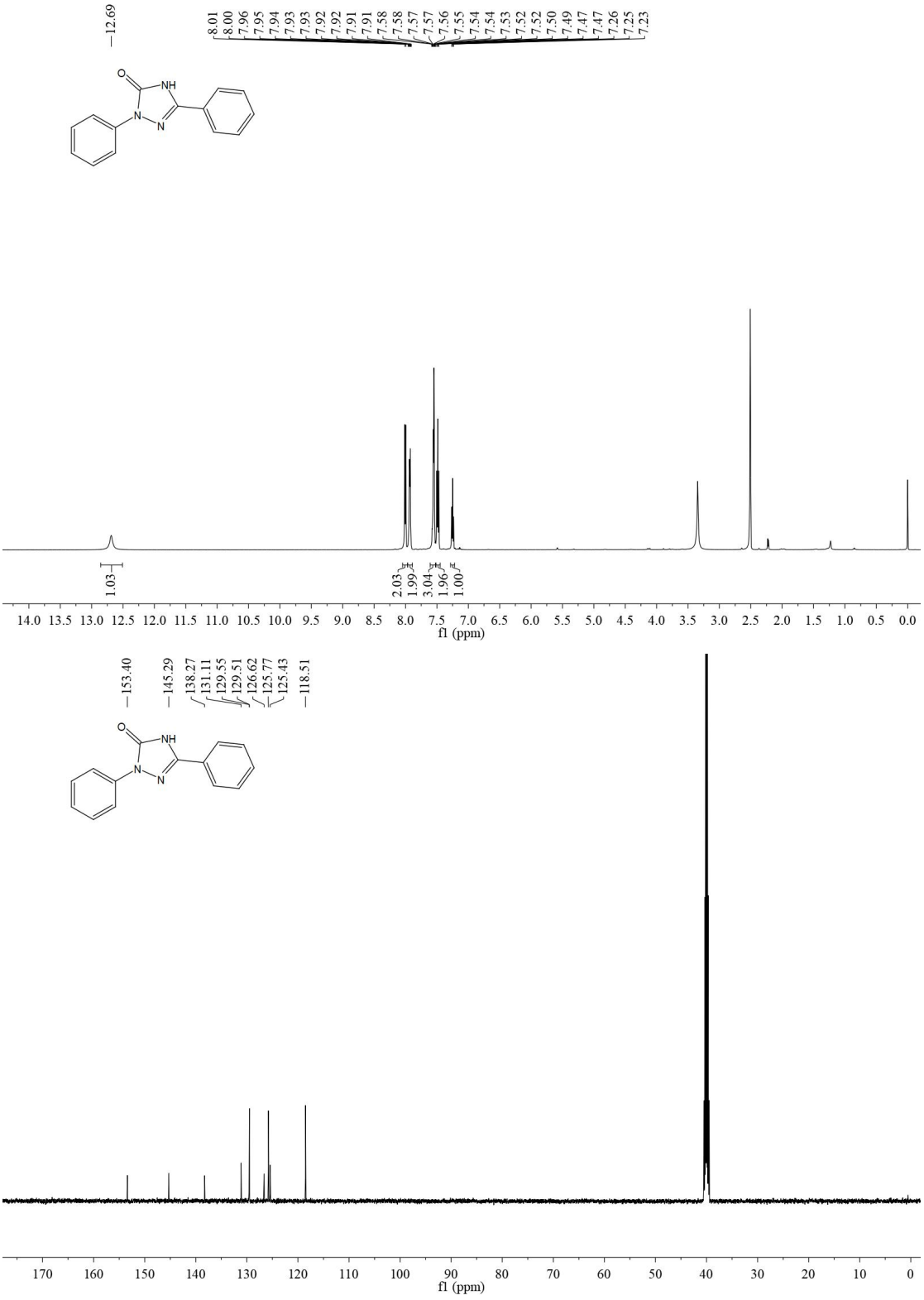
5. NMR spectra of the obtained compounds

^{1}H and ^{13}C NMR spectra of 5-Phenyl-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3aa) (500 MHz, DMSO-d_6)

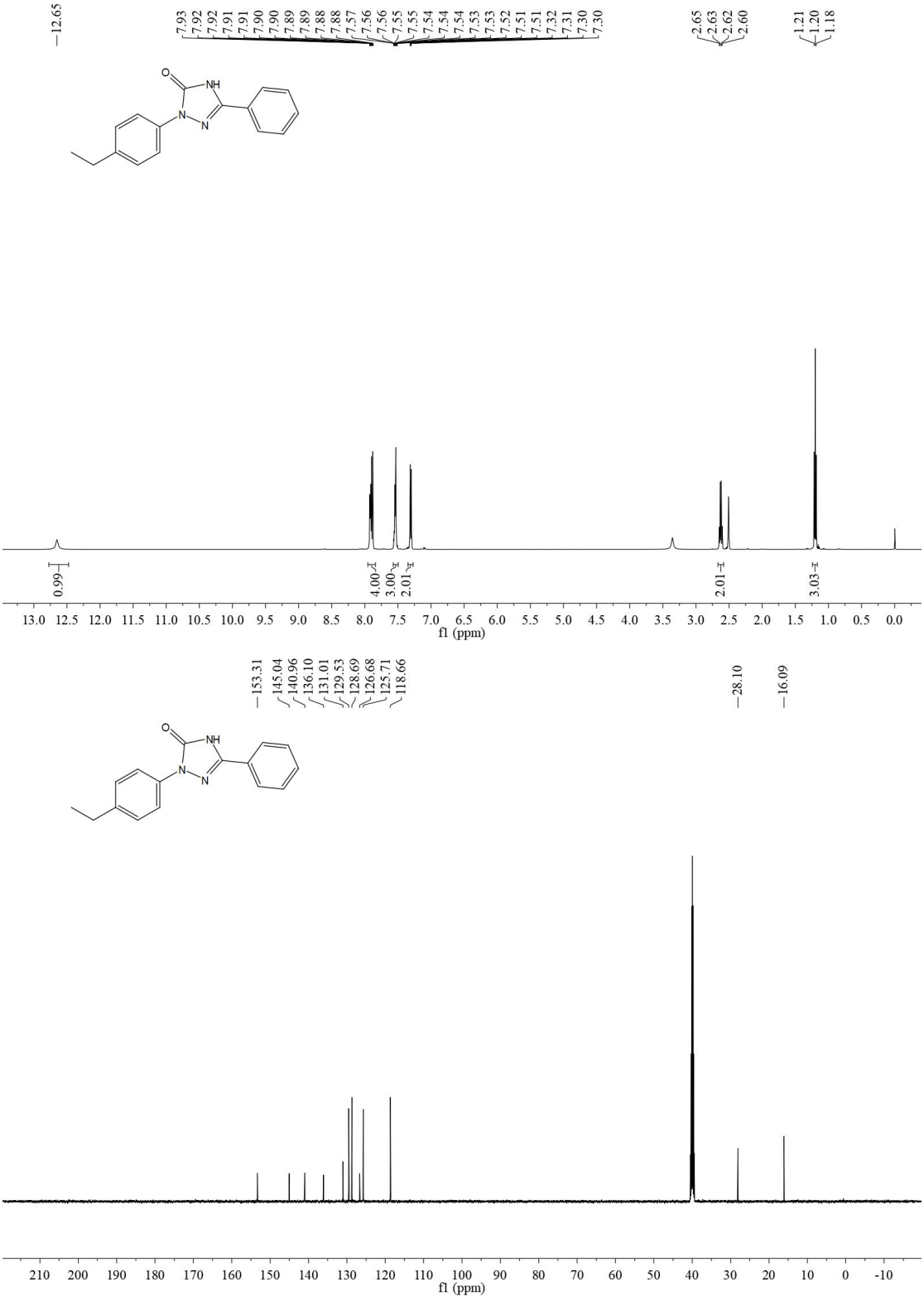




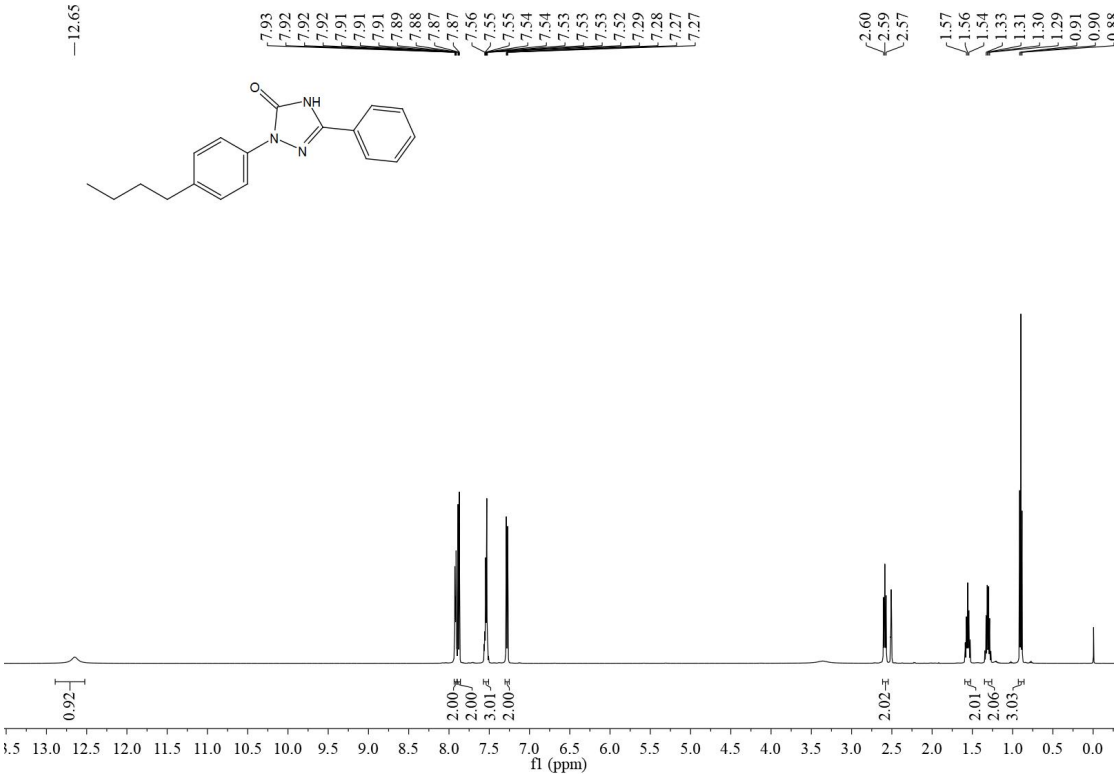
^{1}H and ^{13}C NMR spectra of 2,5-Diphenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ab) (500 MHz, DMSO-d_6)

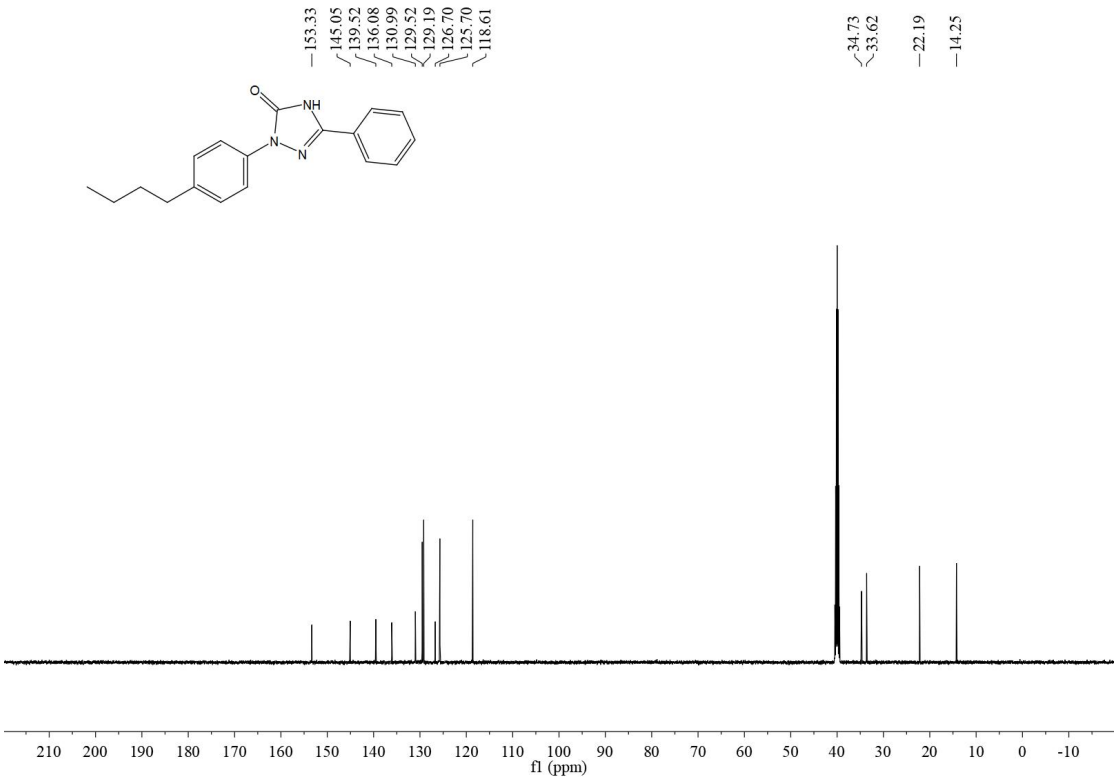


^{1}H and ^{13}C NMR spectra of 2-(4-Ethylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ac) (500 MHz, DMSO-d_6)

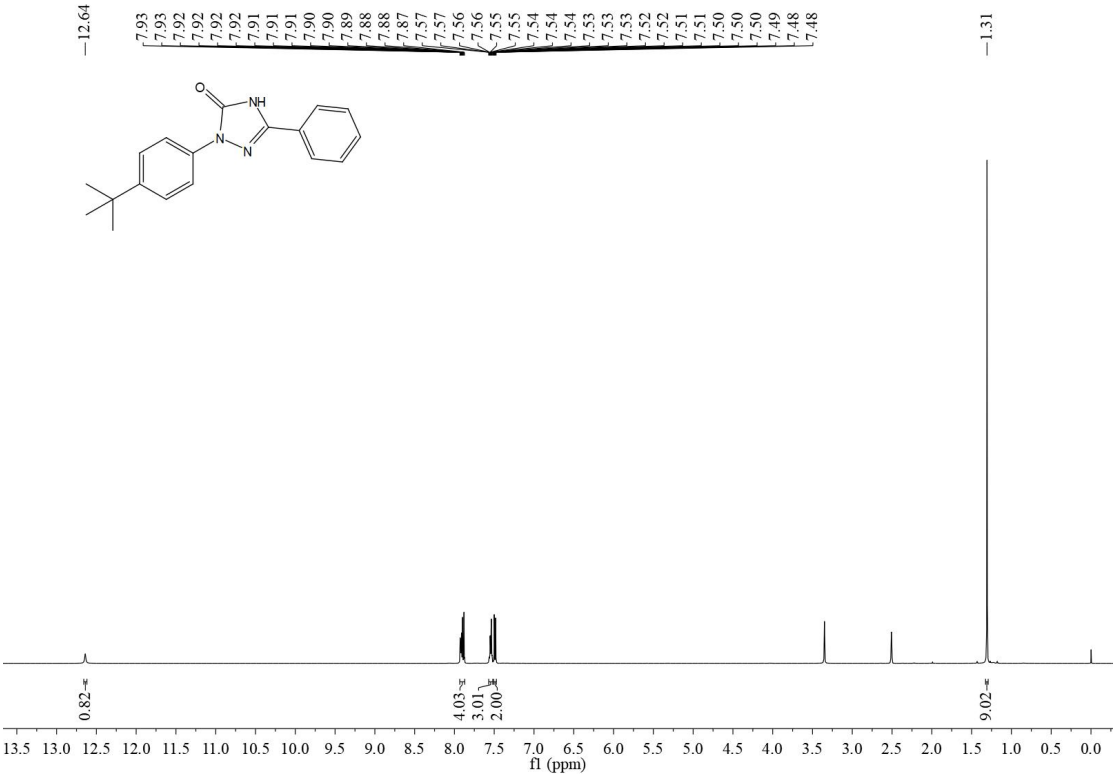


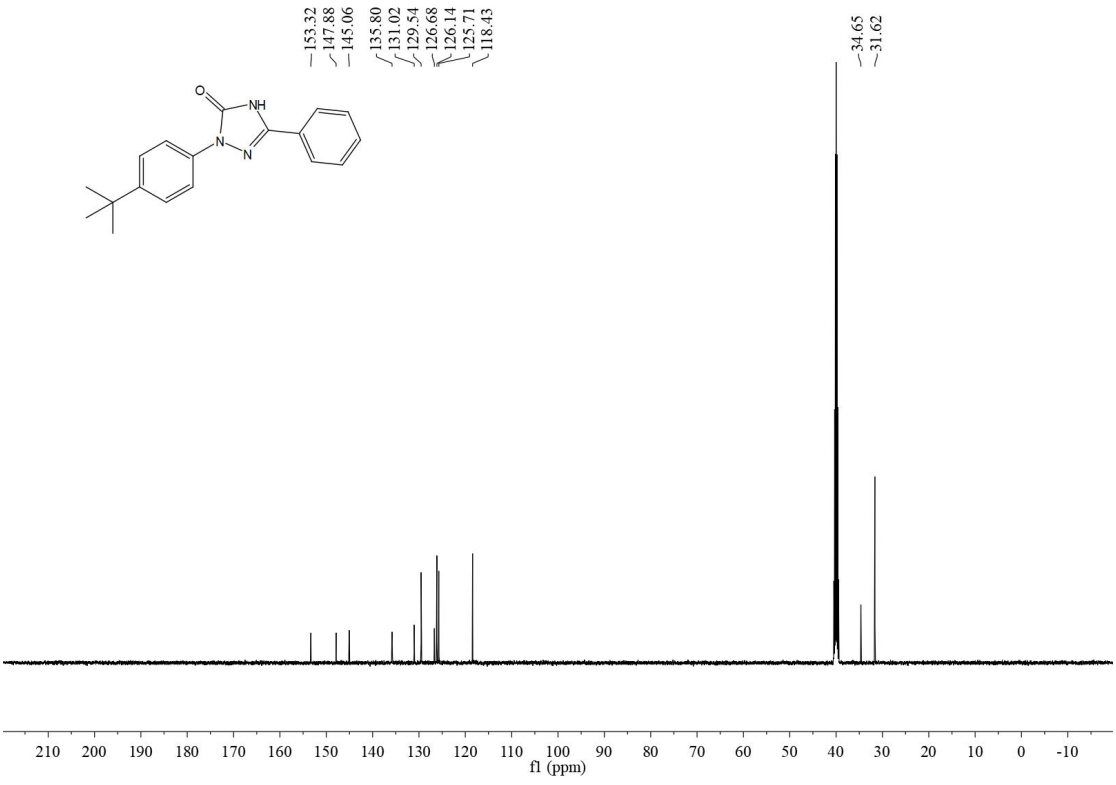
^{1}H and ^{13}C NMR spectra of 2-(4-Butylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ad) (500 MHz, DMSO-d_6)



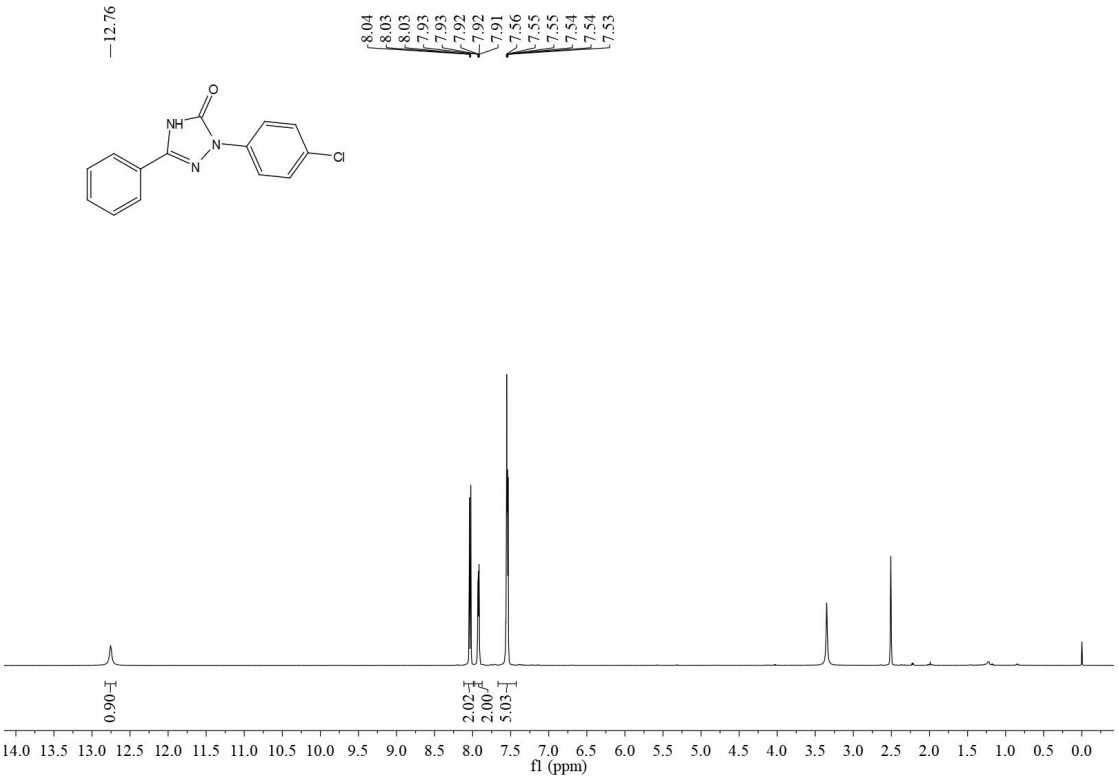


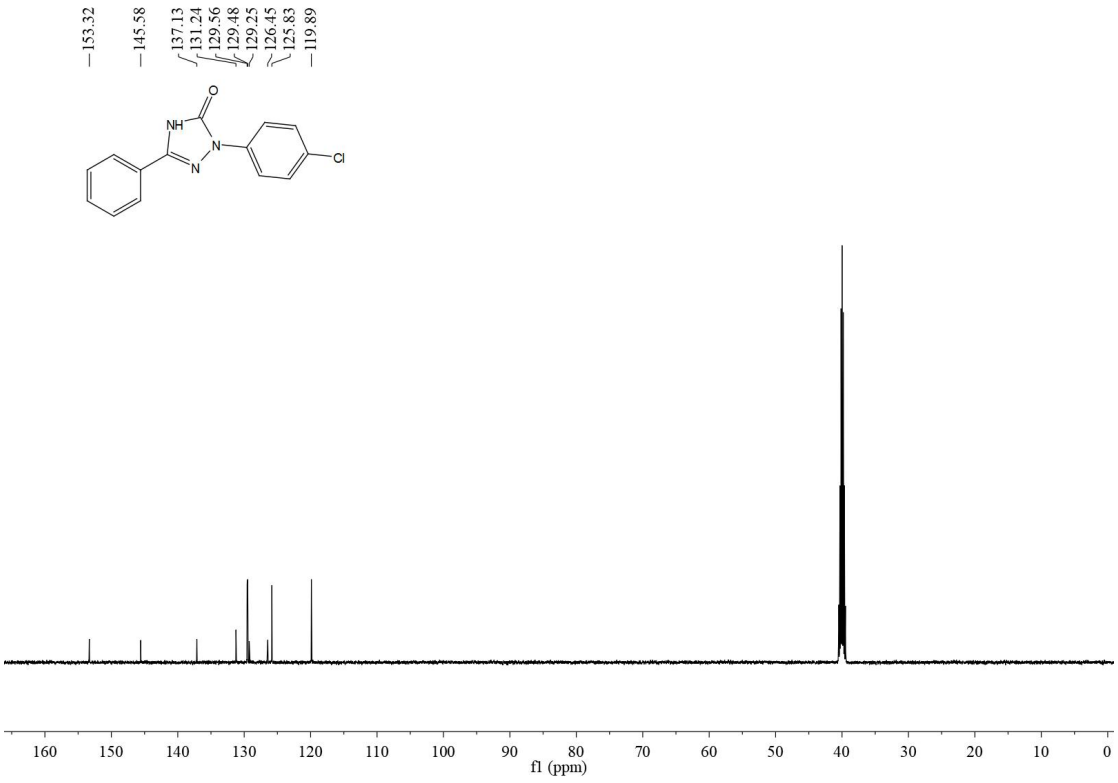
^{1}H and ^{13}C NMR spectra of 2-(4-(Tert-butyl)phenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ae) (500 MHz, DMSO-d_6)



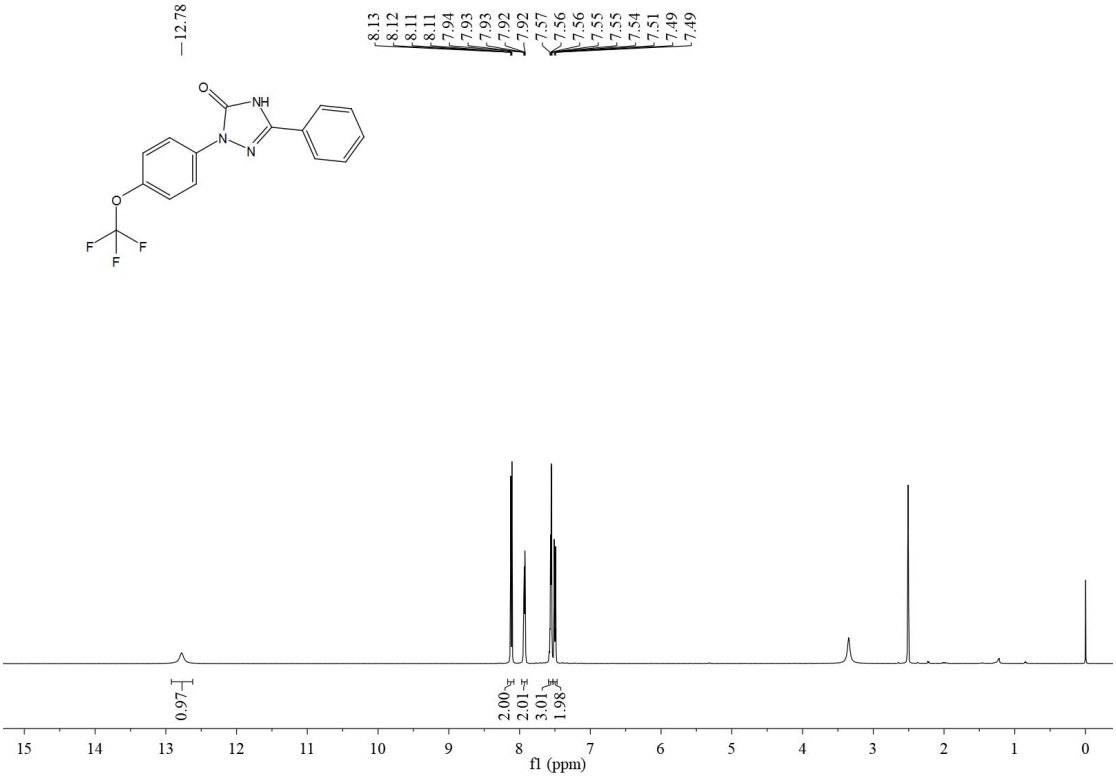


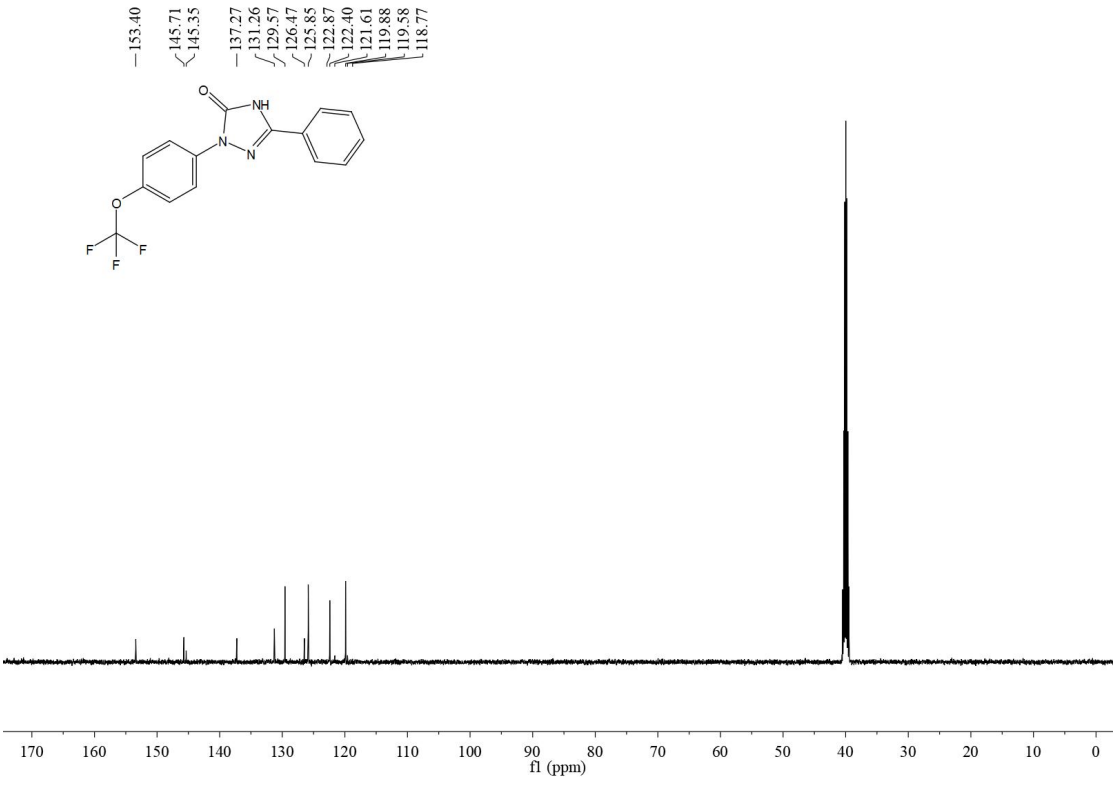
^{1}H and ^{13}C NMR spectra of 2-(4-Chlorophenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3af) (500 MHz, DMSO-d_6)

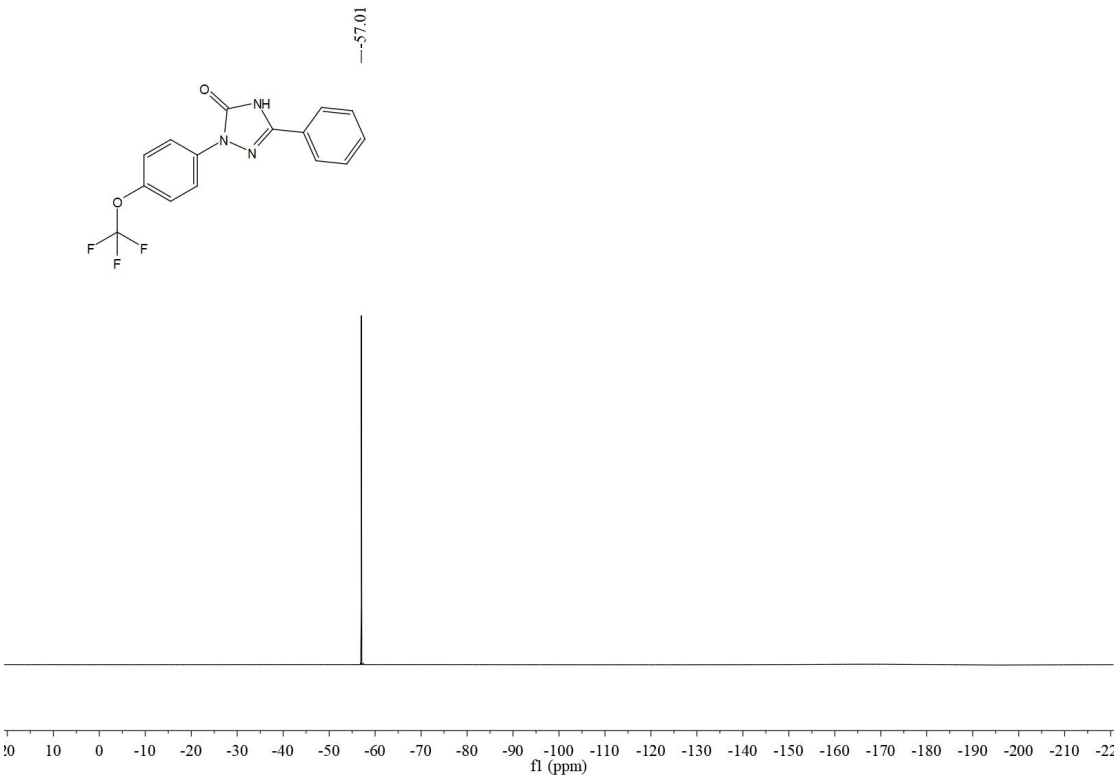




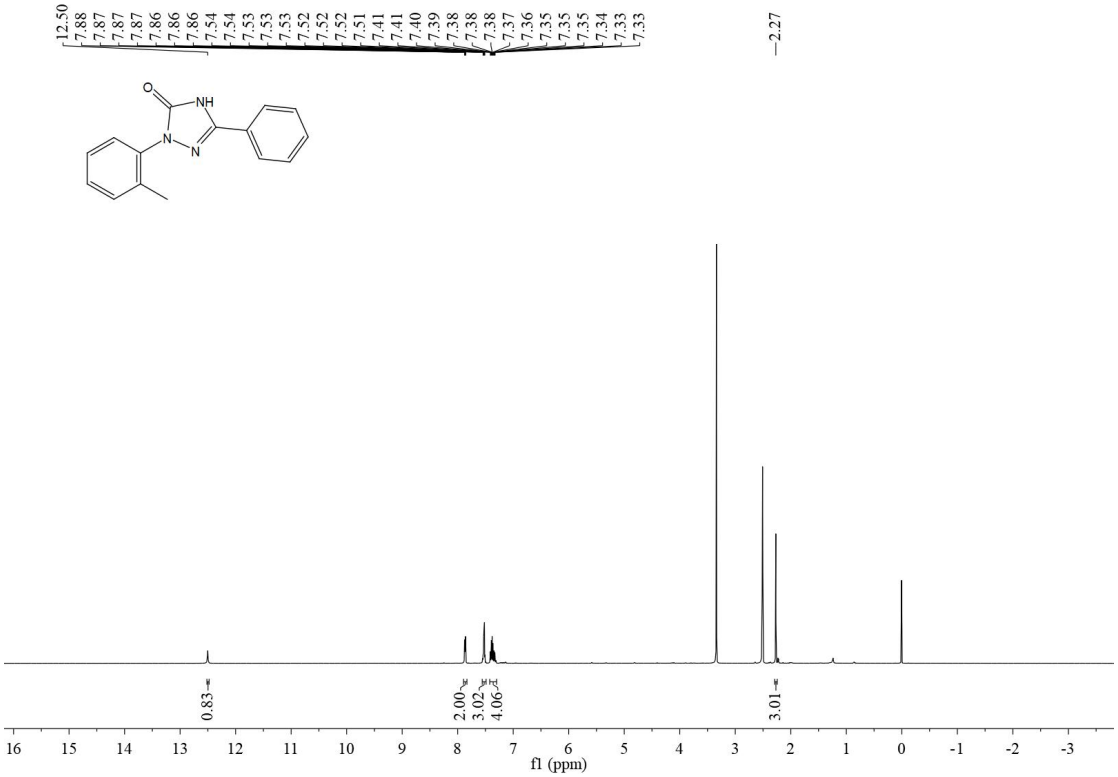
^{1}H and ^{13}C NMR spectra of 5-Phenyl-2-(4-(trifluoromethoxy)phenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3ag) (500 MHz, DMSO-d_6)

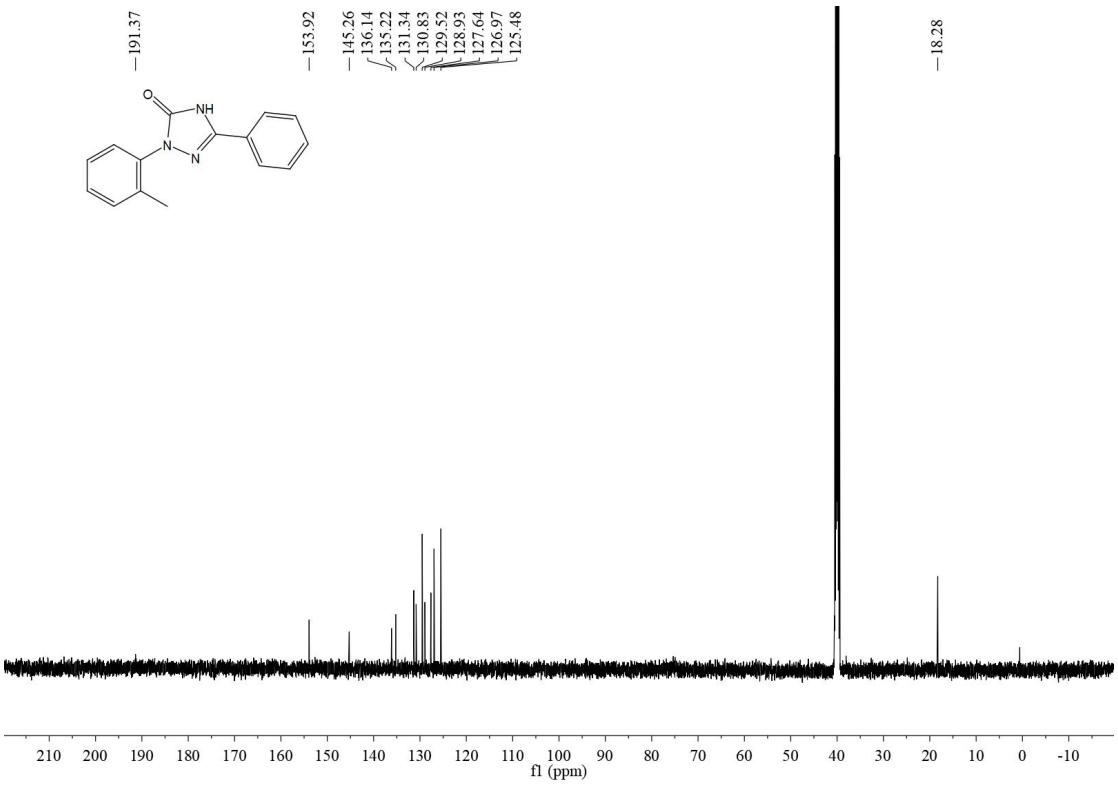




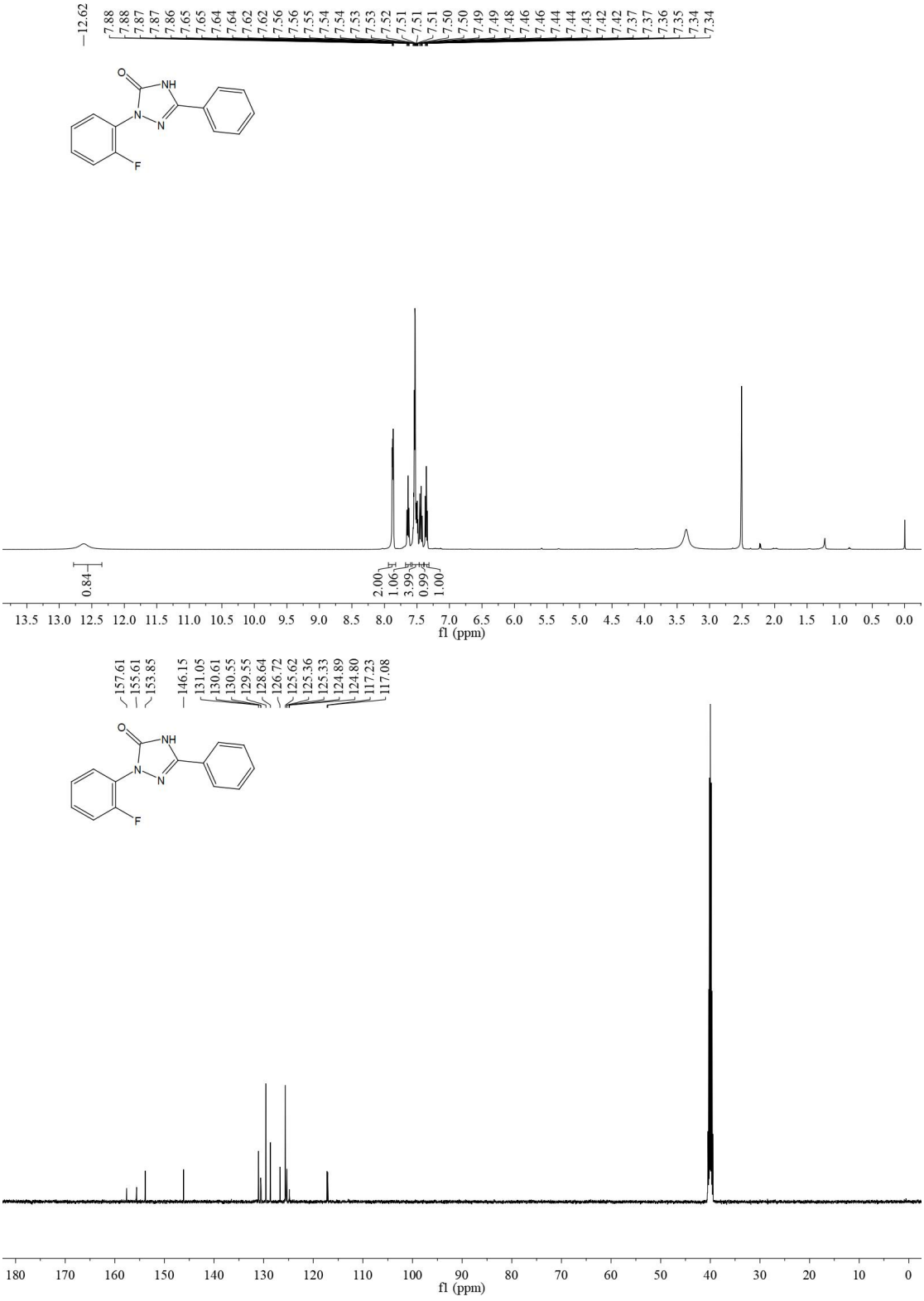

-57.01
O
NH
N
N
O
F
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

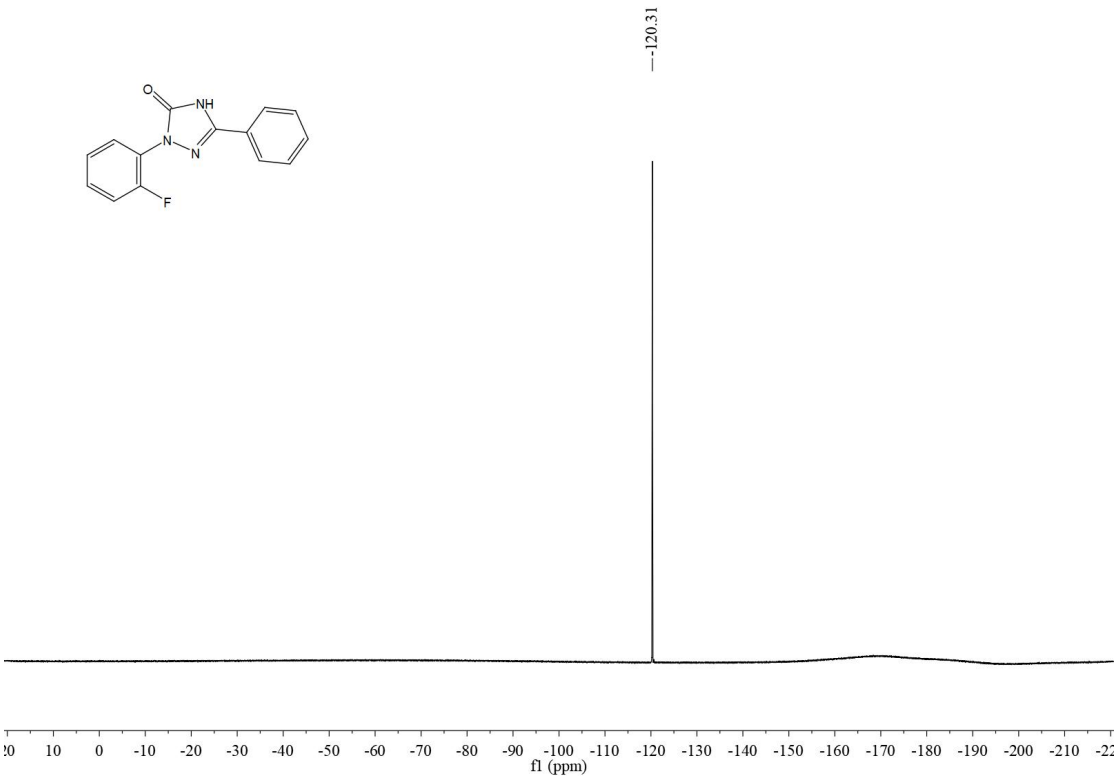
^{1}H and ^{13}C NMR spectra of 5-Phenyl-2-(o-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3ah) (500 MHz, DMSO-d_6)



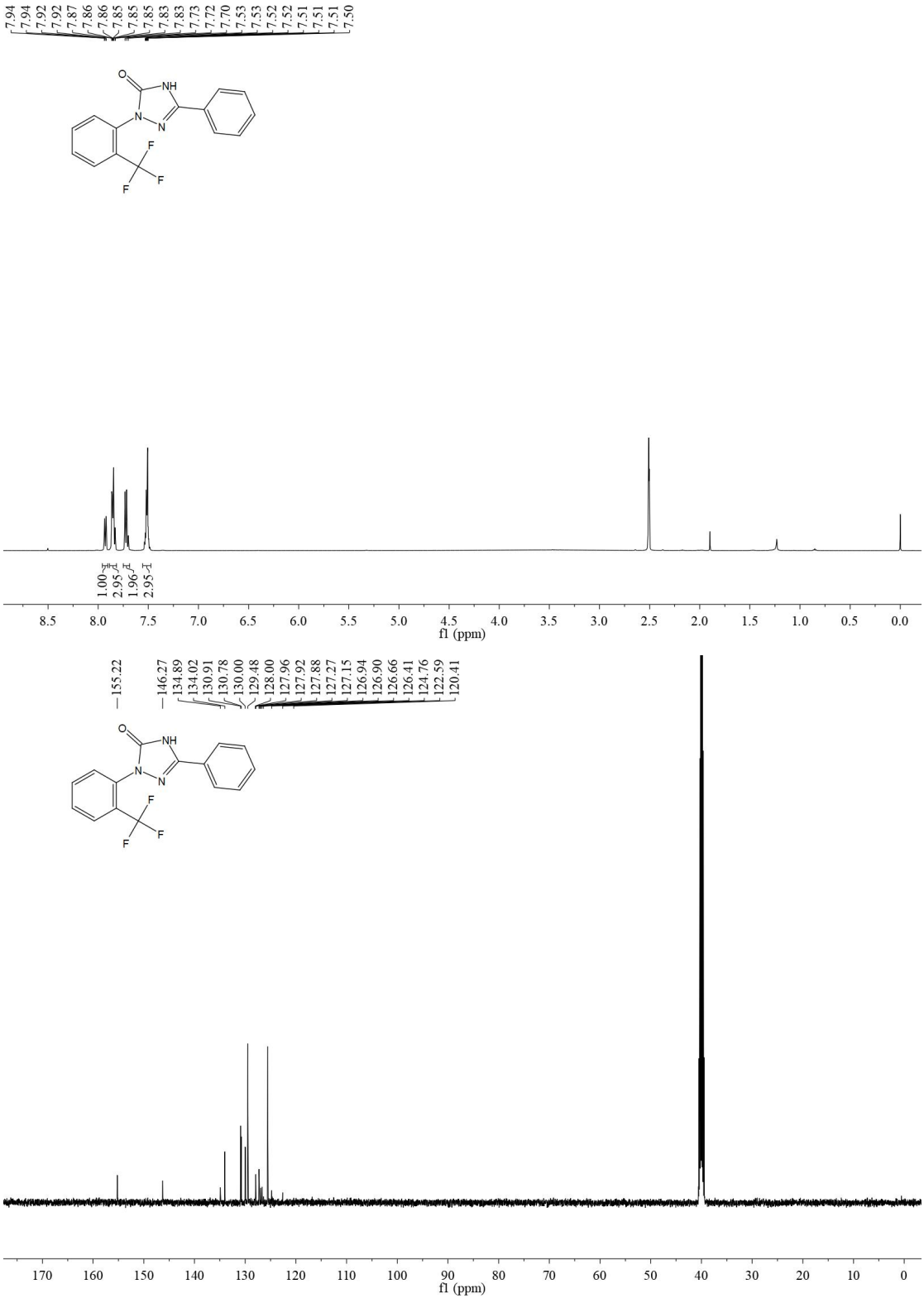


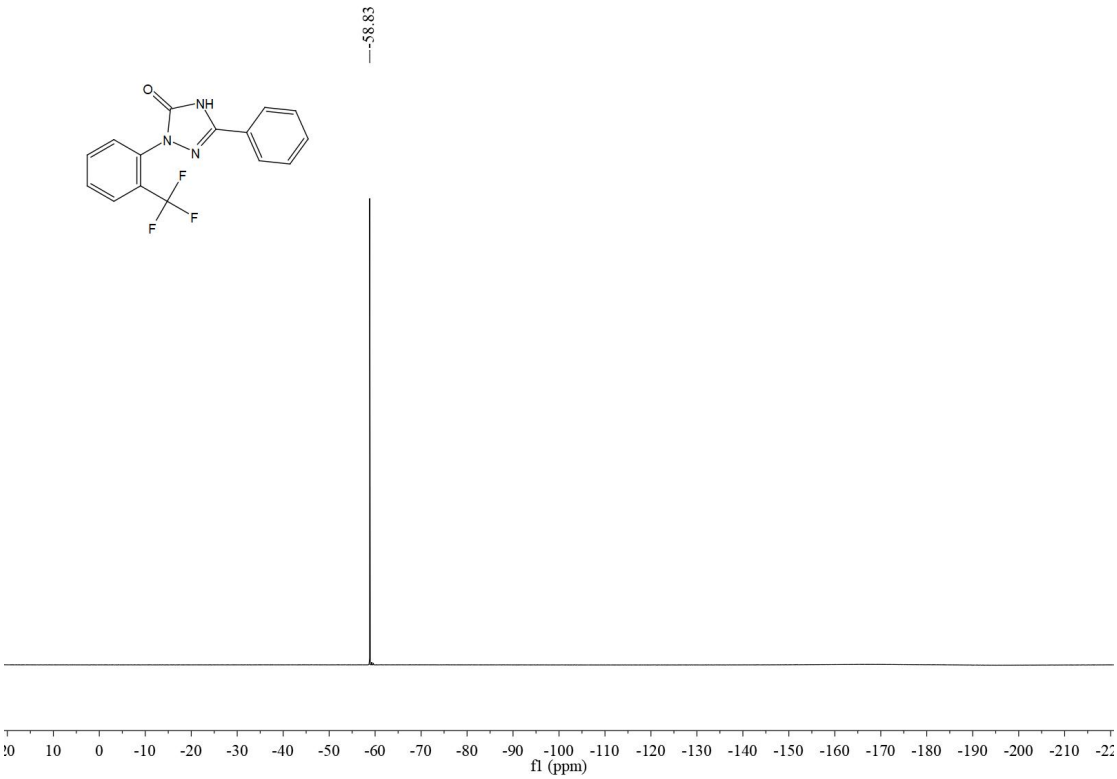
^{1}H and ^{13}C NMR spectra of 2-(2-Fluorophenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ai) (500 MHz, DMSO-d_6)



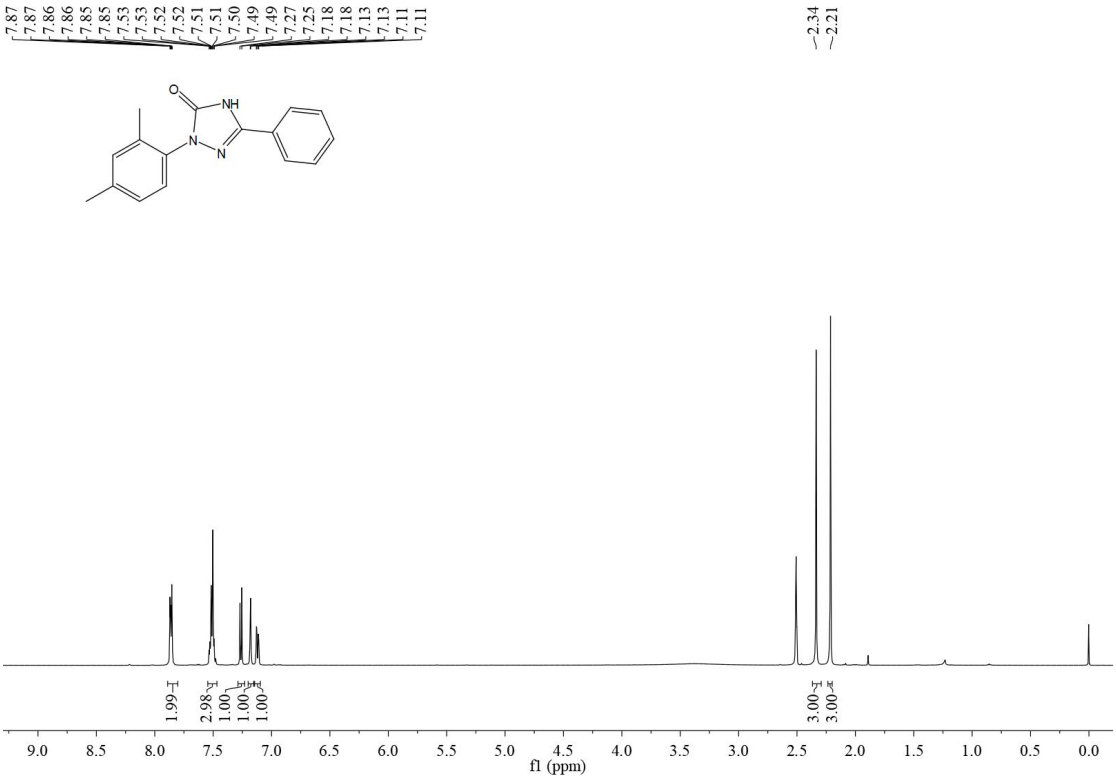

-120.31
O
NH
N
N
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

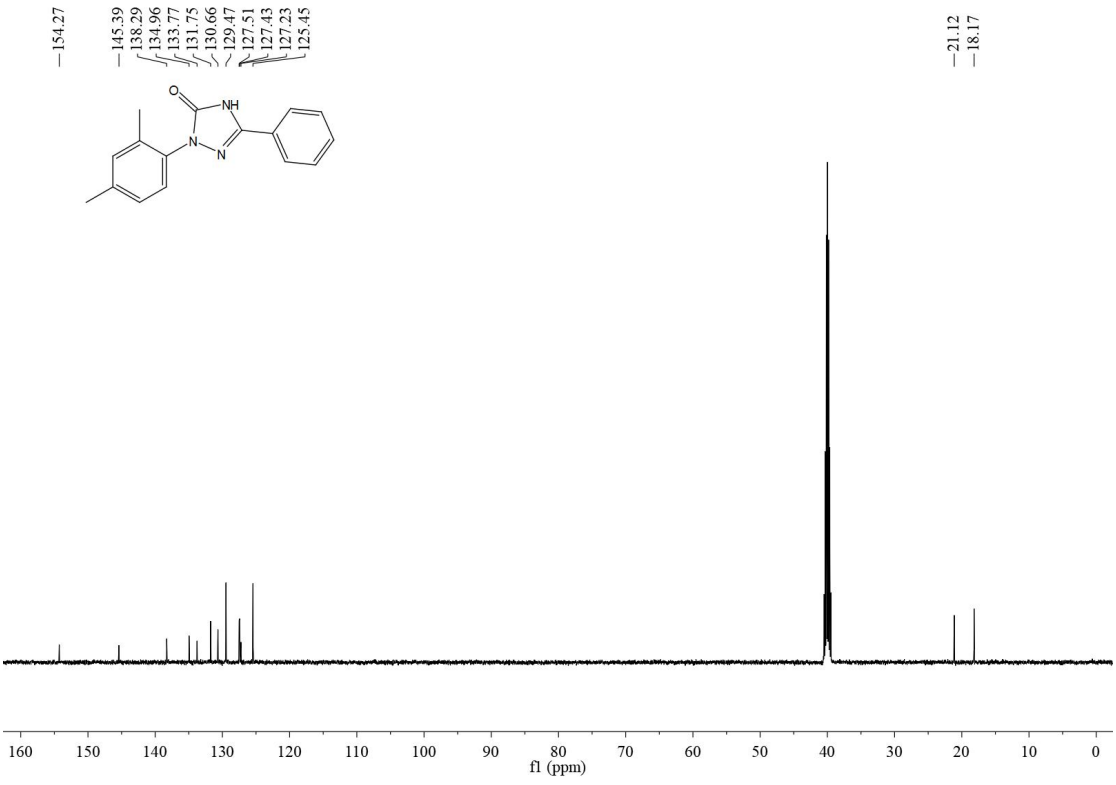
^{1}H and ^{13}C NMR spectra of 5-Phenyl-2-(2-(trifluoromethyl)phenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3aj) (500 MHz, DMSO-d_6)



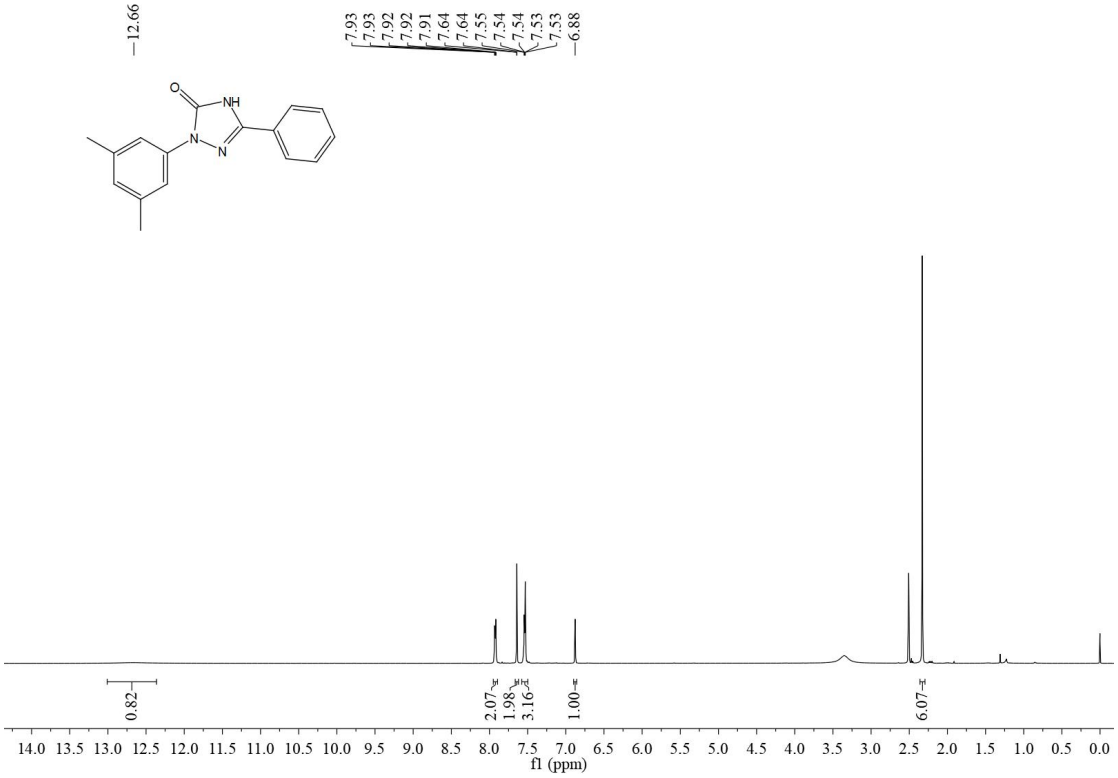

-58.83
O
NH
N
N
F
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

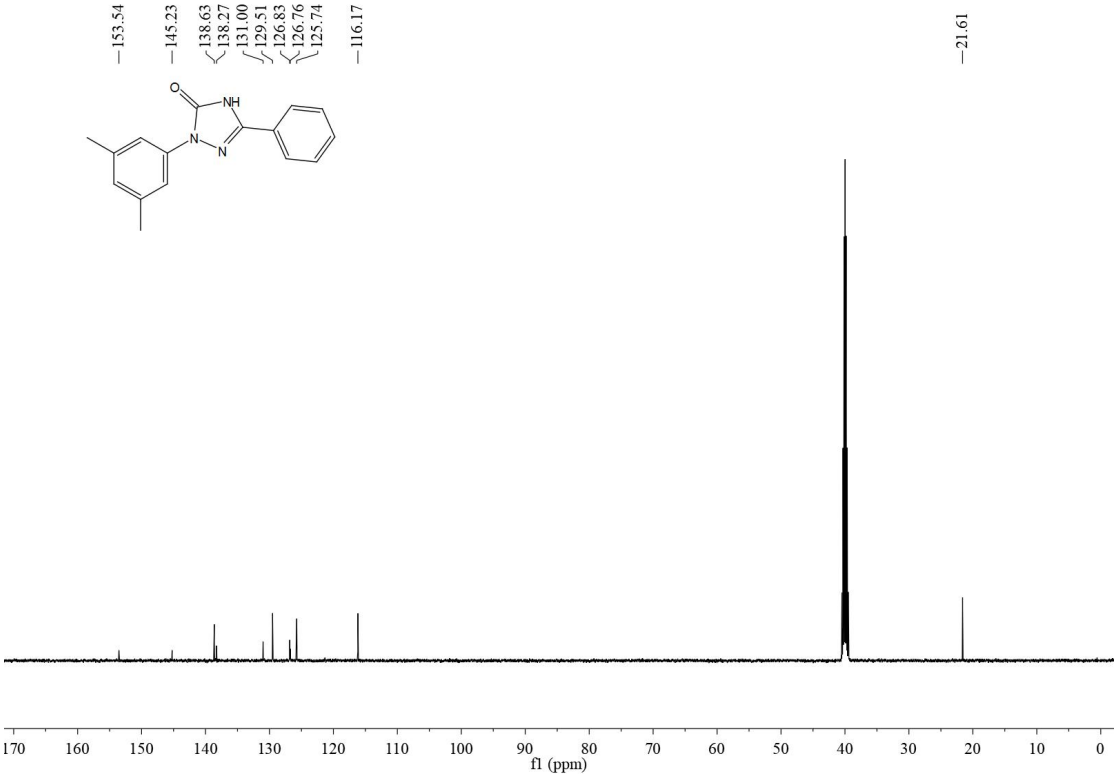
^{1}H and ^{13}C NMR spectra of 2-(2,4-Dimethylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ak) (500 MHz, DMSO-d_6)



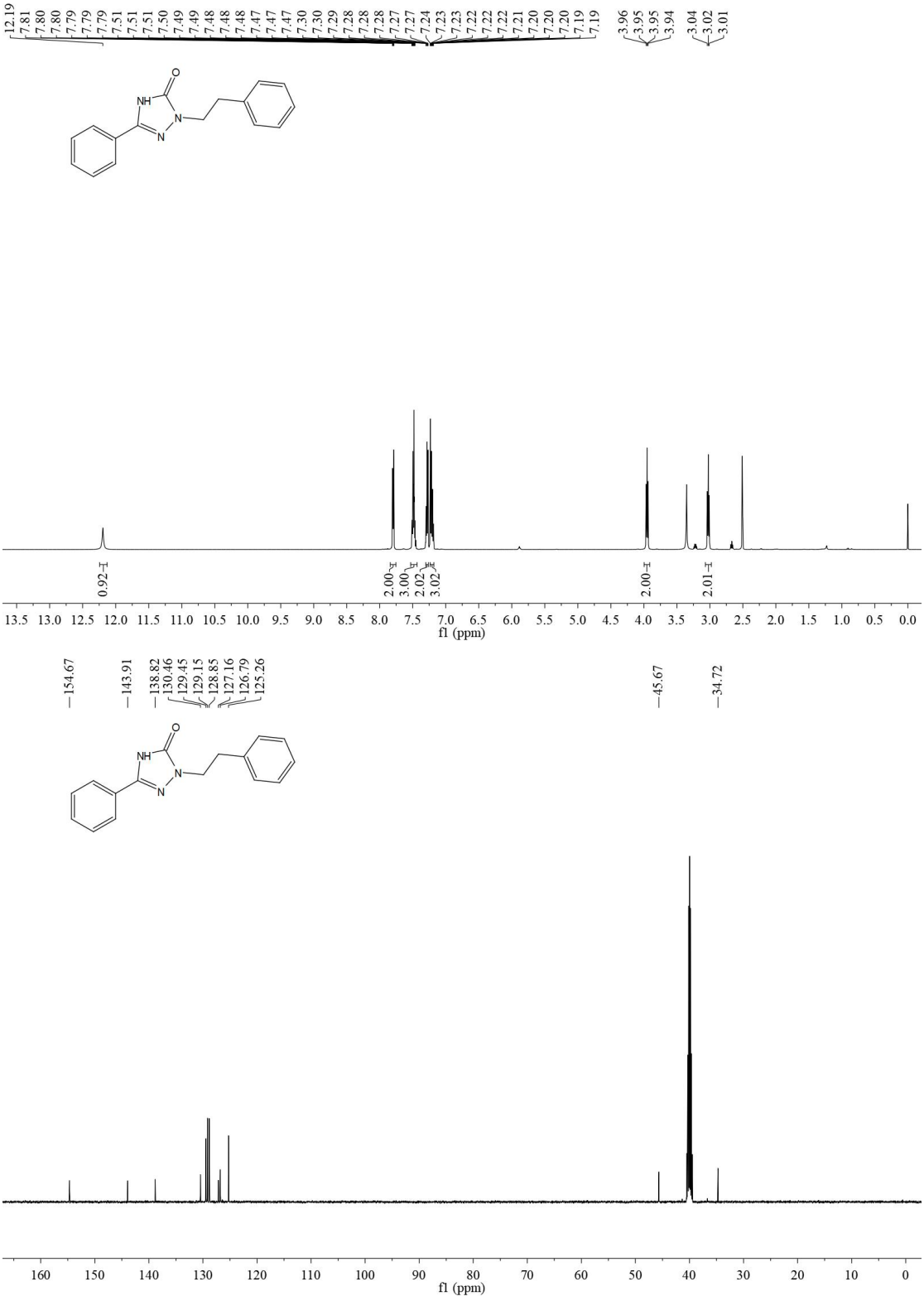


^{1}H and ^{13}C NMR spectra of 2-(3,5-Dimethylphenyl)-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3al) (500 MHz, DMSO-d_6)

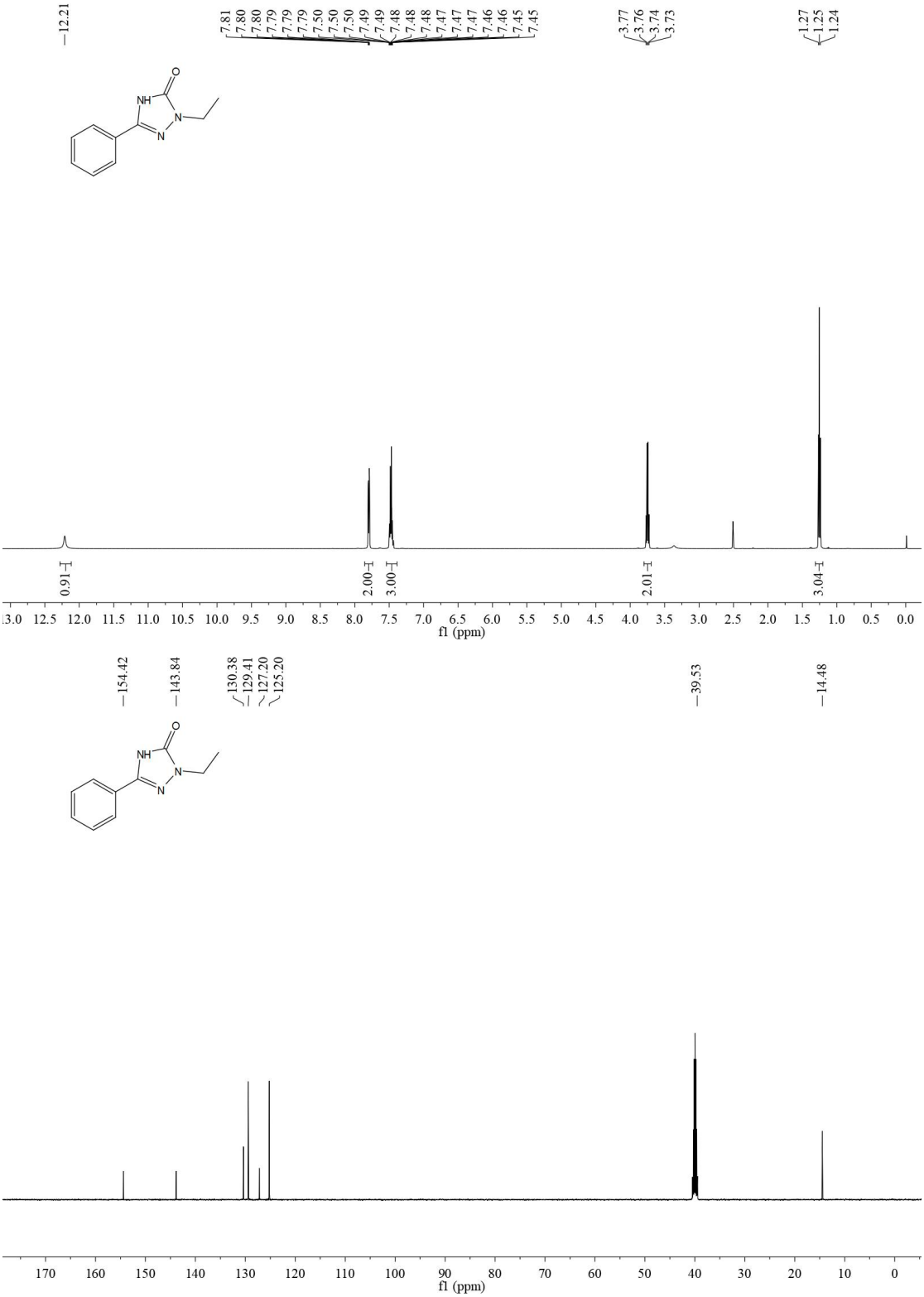




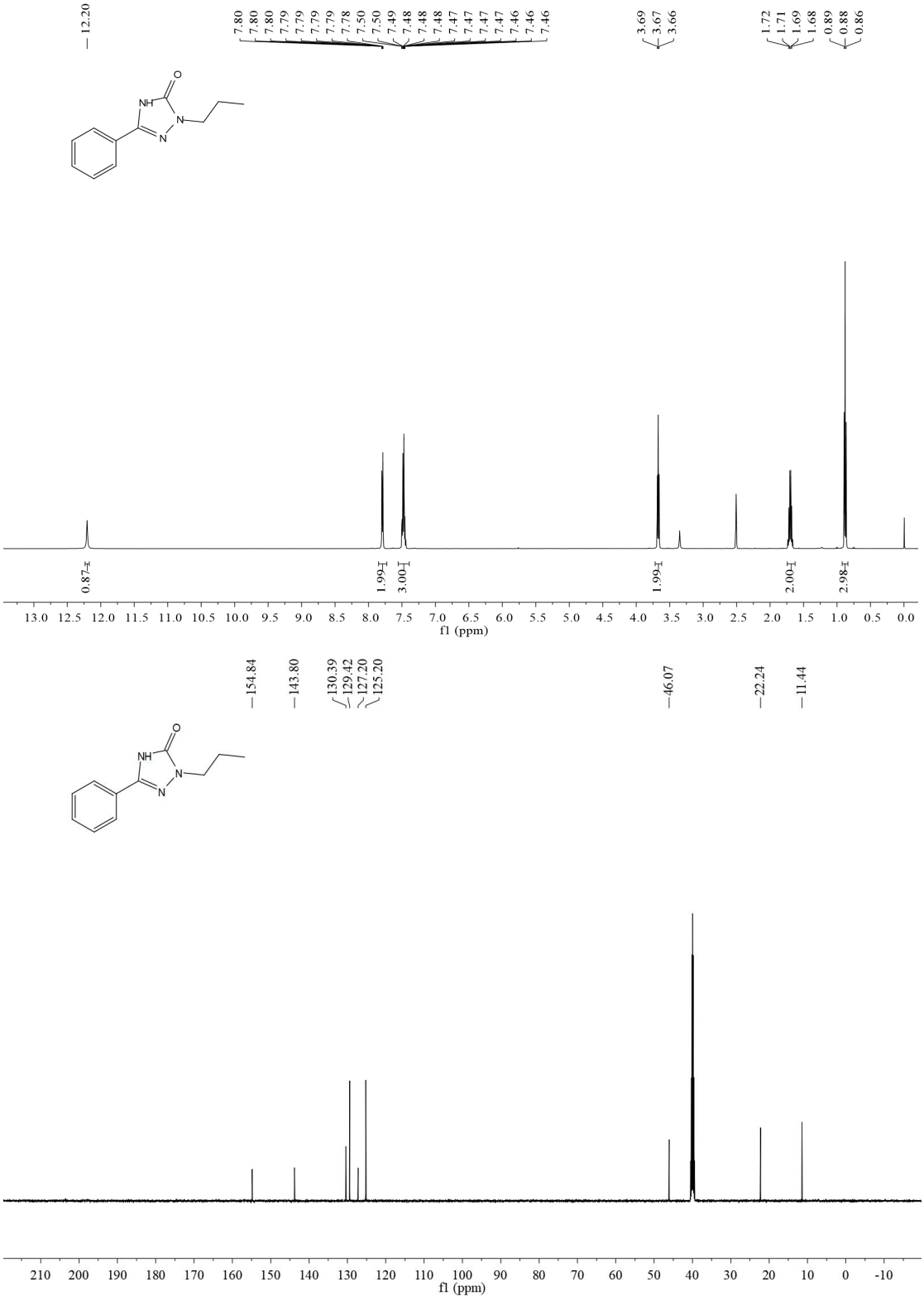
^{1}H and ^{13}C NMR spectra of 2-Phenethyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3am) (500 MHz, DMSO-d_6)



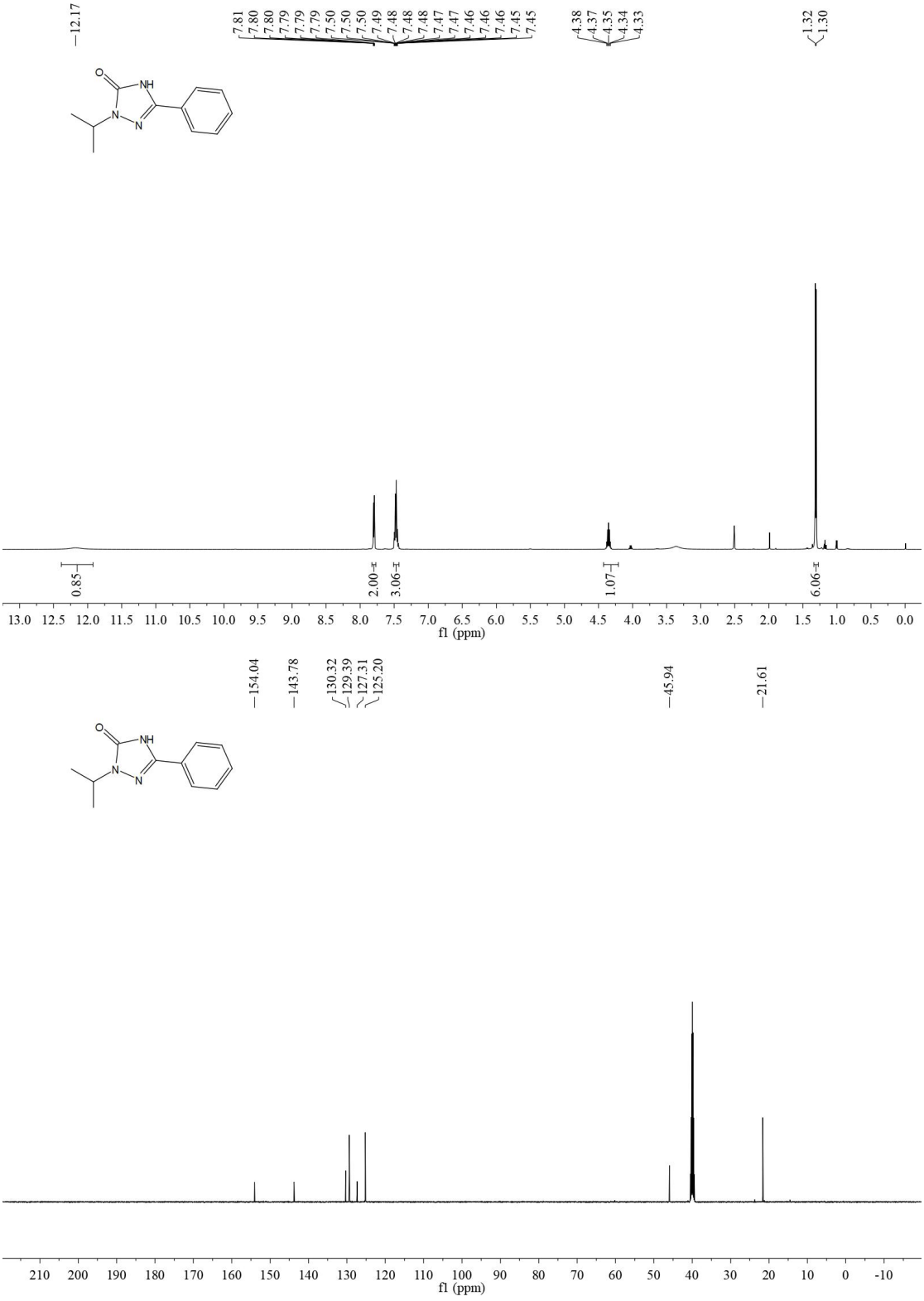
^{1}H and ^{13}C NMR spectra of 2-Ethyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3an) (500 MHz, DMSO-d_6)



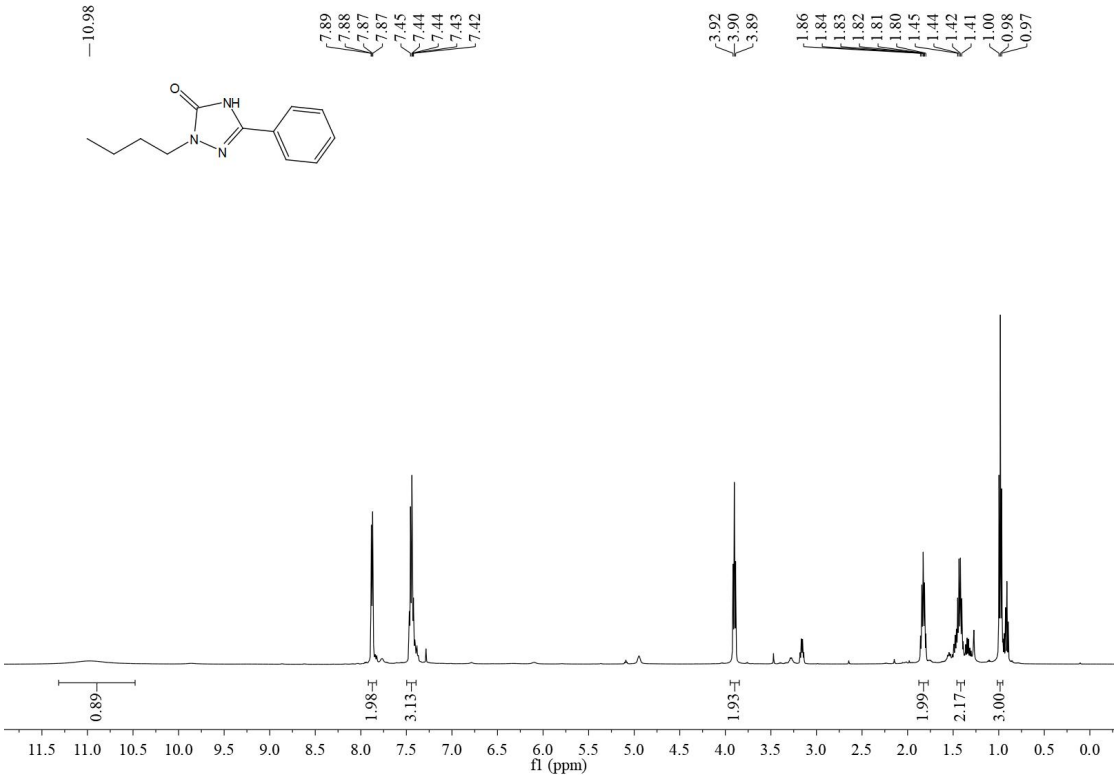
^{1}H and ^{13}C NMR spectra of 5-Phenyl-2-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ao) (500 MHz, DMSO-d_6)

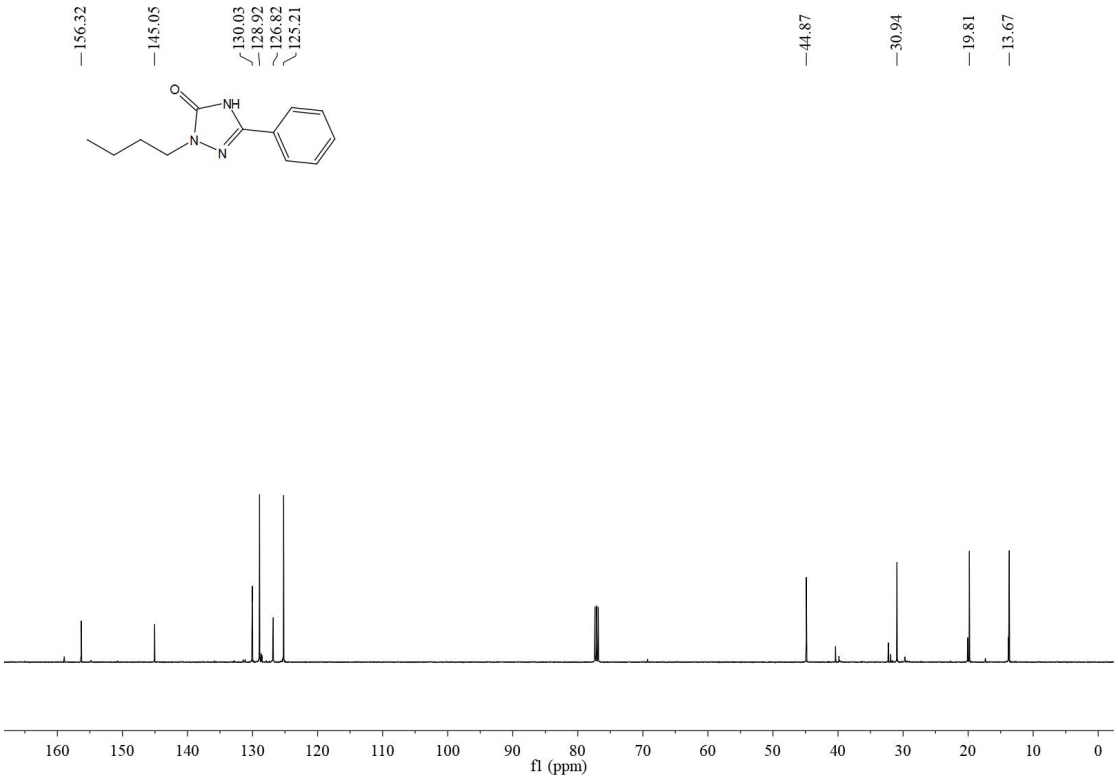


^{1}H and ^{13}C NMR spectra of 2-Isopropyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ap) (500 MHz, DMSO-d_6)

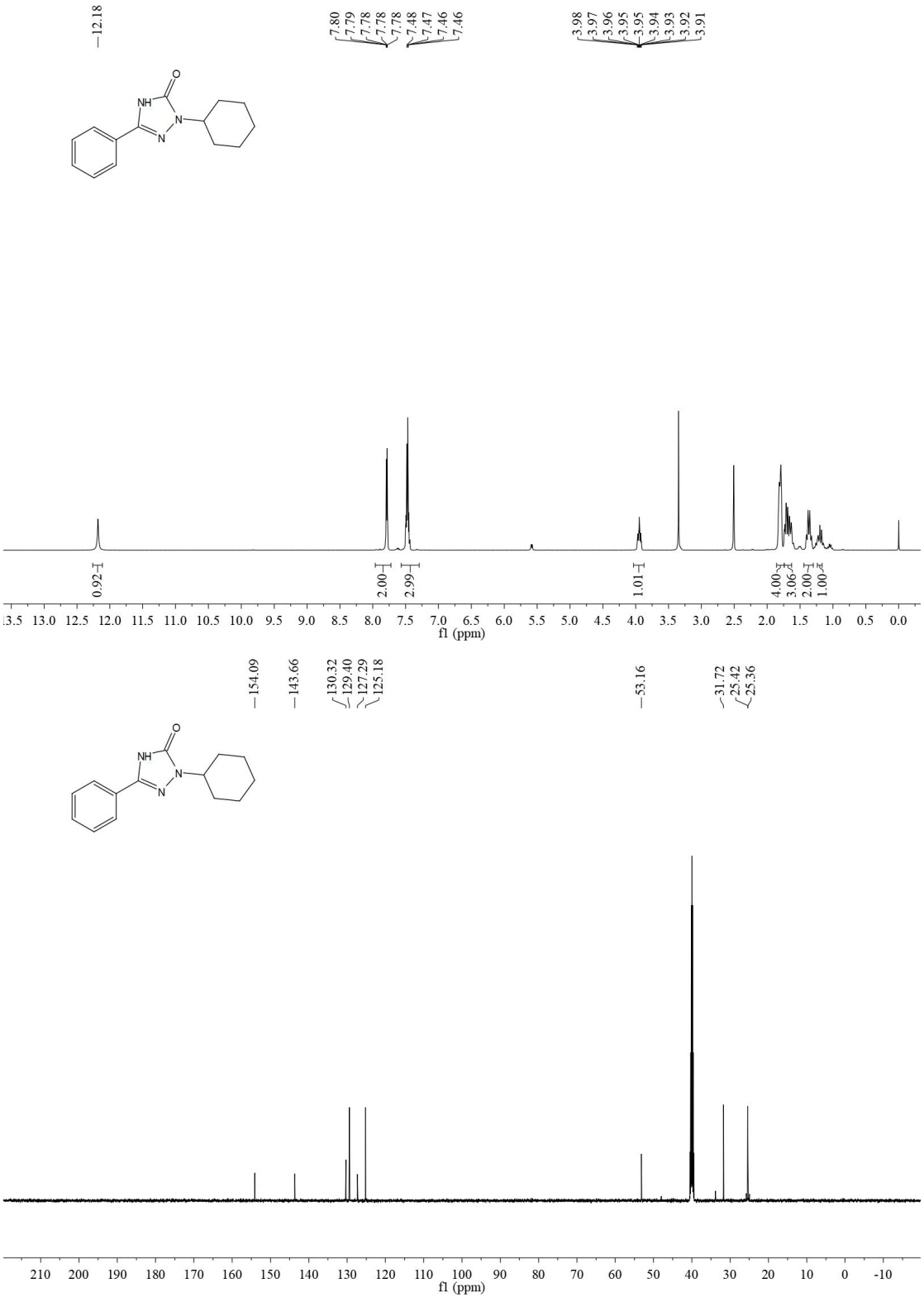


^{1}H and ^{13}C NMR spectra of 2-Butyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3aq) (500 MHz, $CDCl_3$)

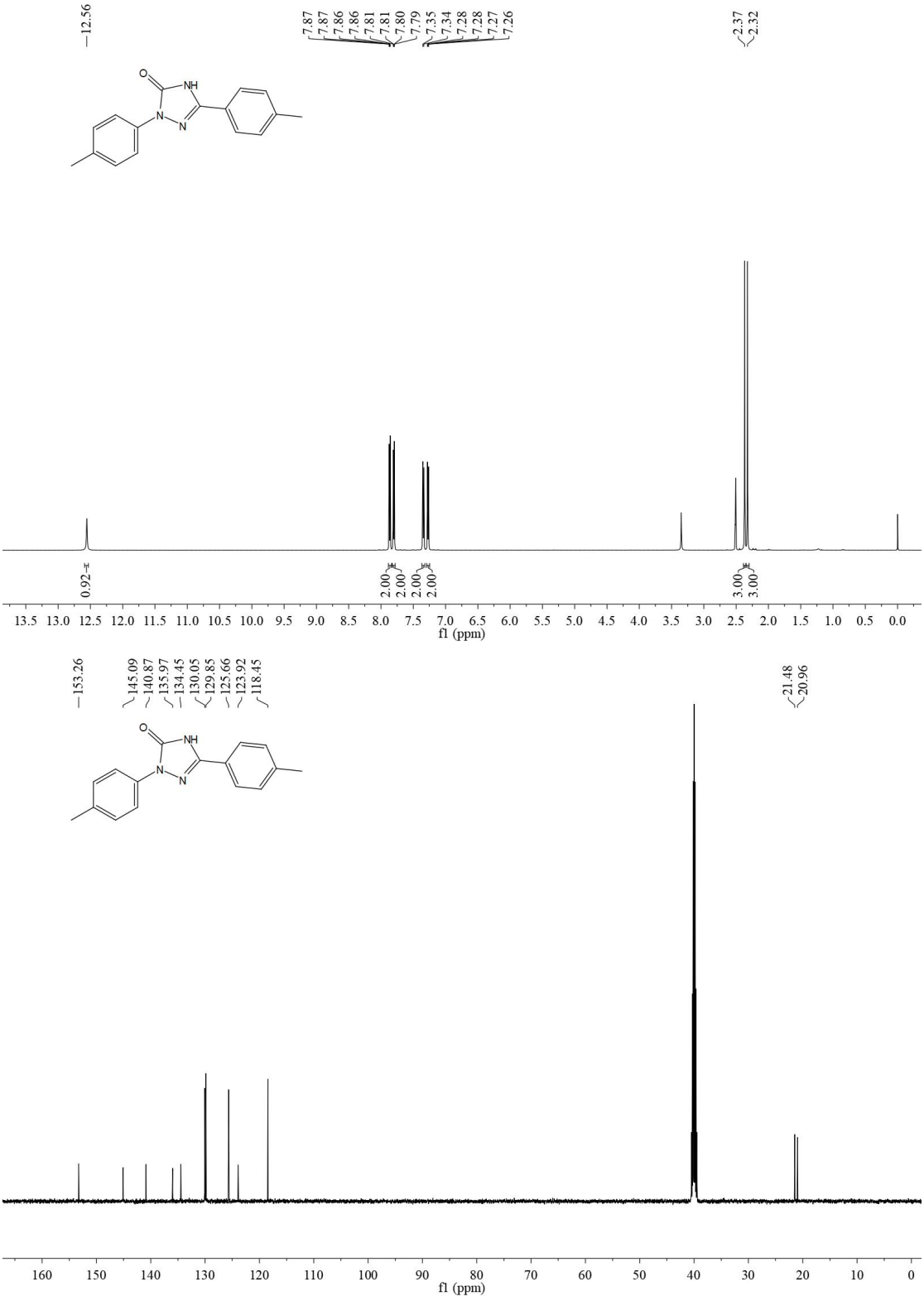




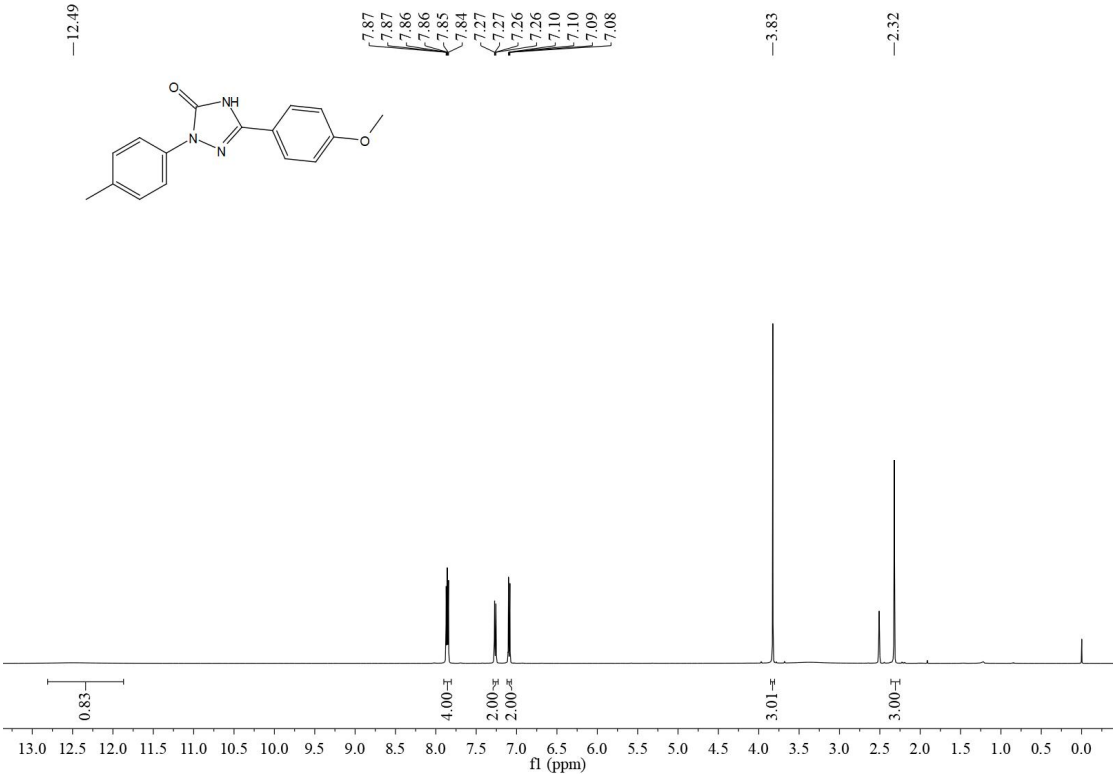
^{1}H and ^{13}C NMR spectra of 2-Cyclohexyl-5-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ar) (500 MHz, DMSO-d_6)

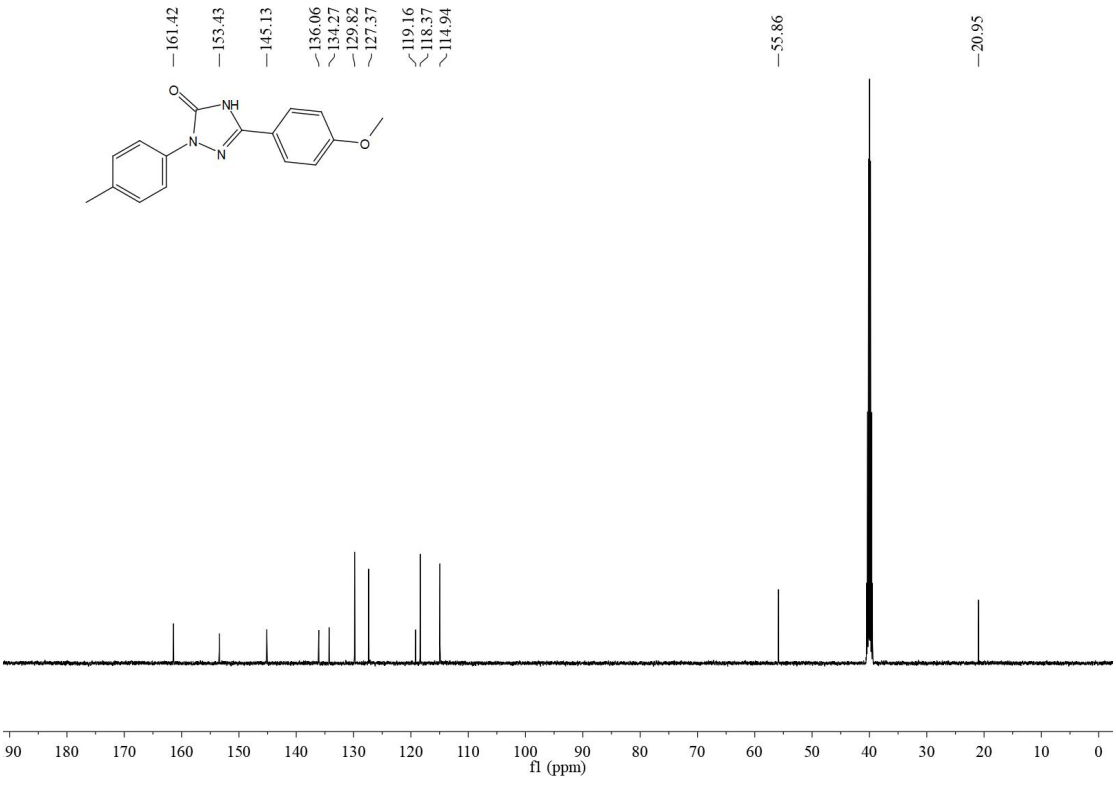


^{1}H and ^{13}C NMR spectra of 2,5-Di-p-tolyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3ba) (500 MHz, DMSO-d_6)

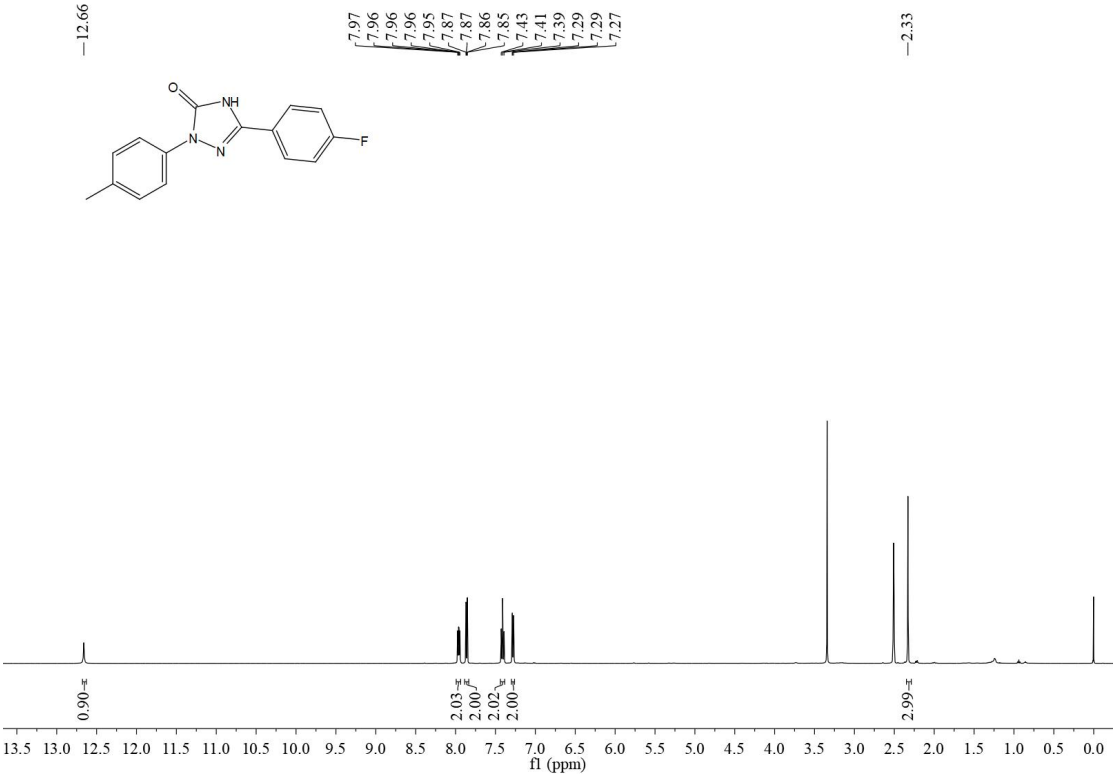


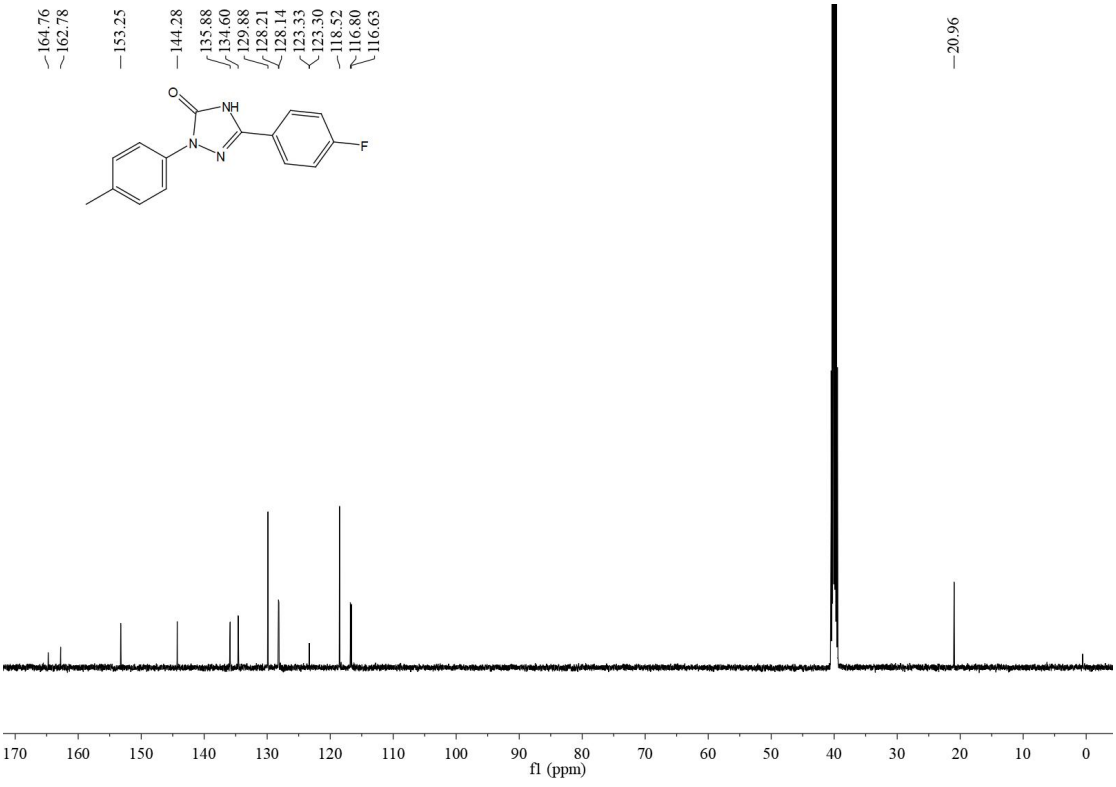
^{1}H and ^{13}C NMR spectra of 5-(4-Methoxyphenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bb) (500 MHz, DMSO-d_6)

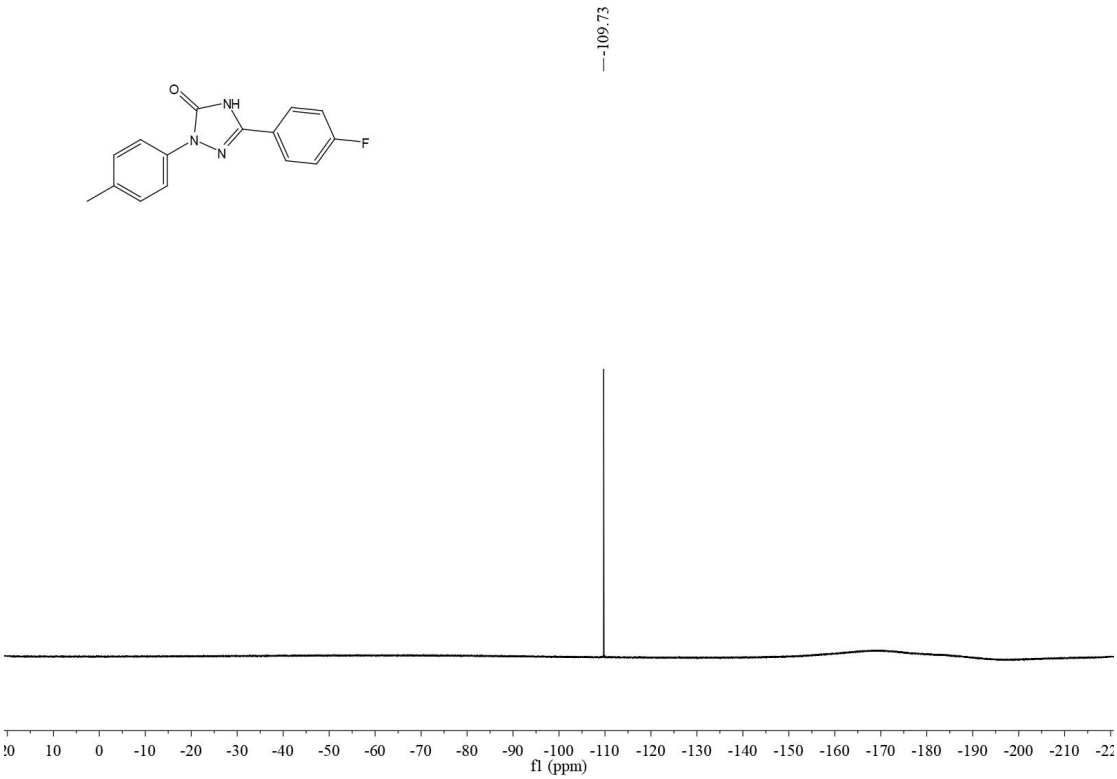




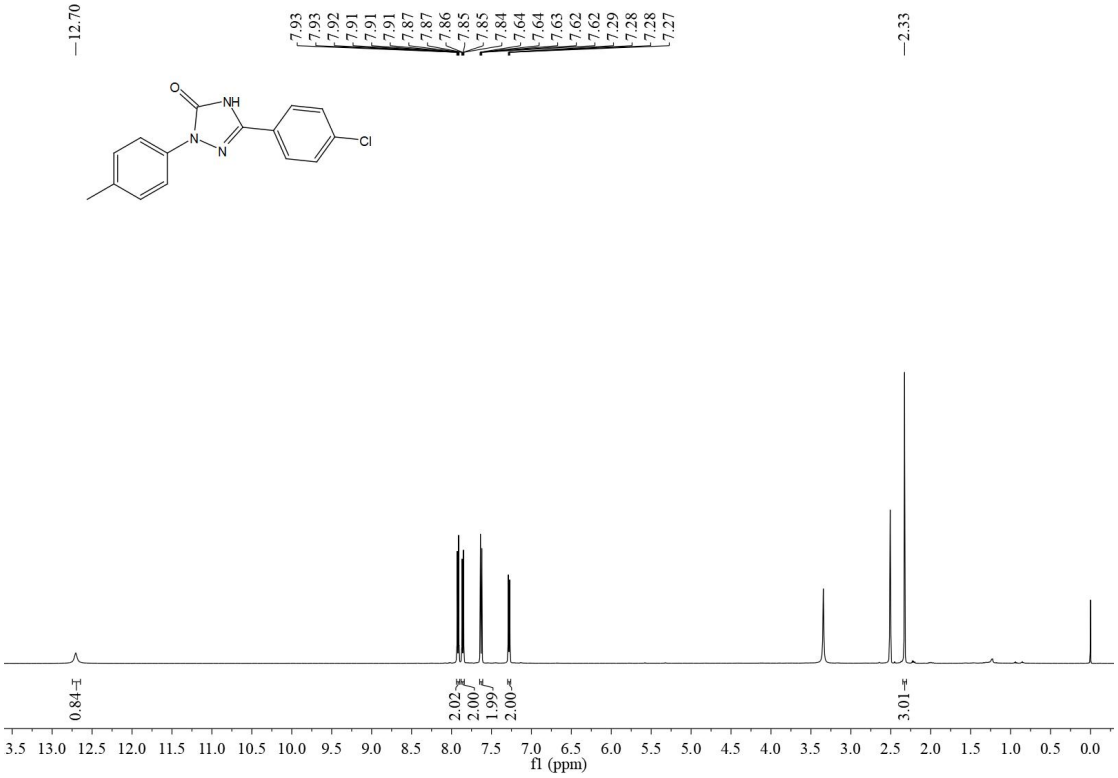
^{1}H and ^{13}C NMR spectra of 5-(4-Fluorophenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bc) (500 MHz, DMSO-d_6)

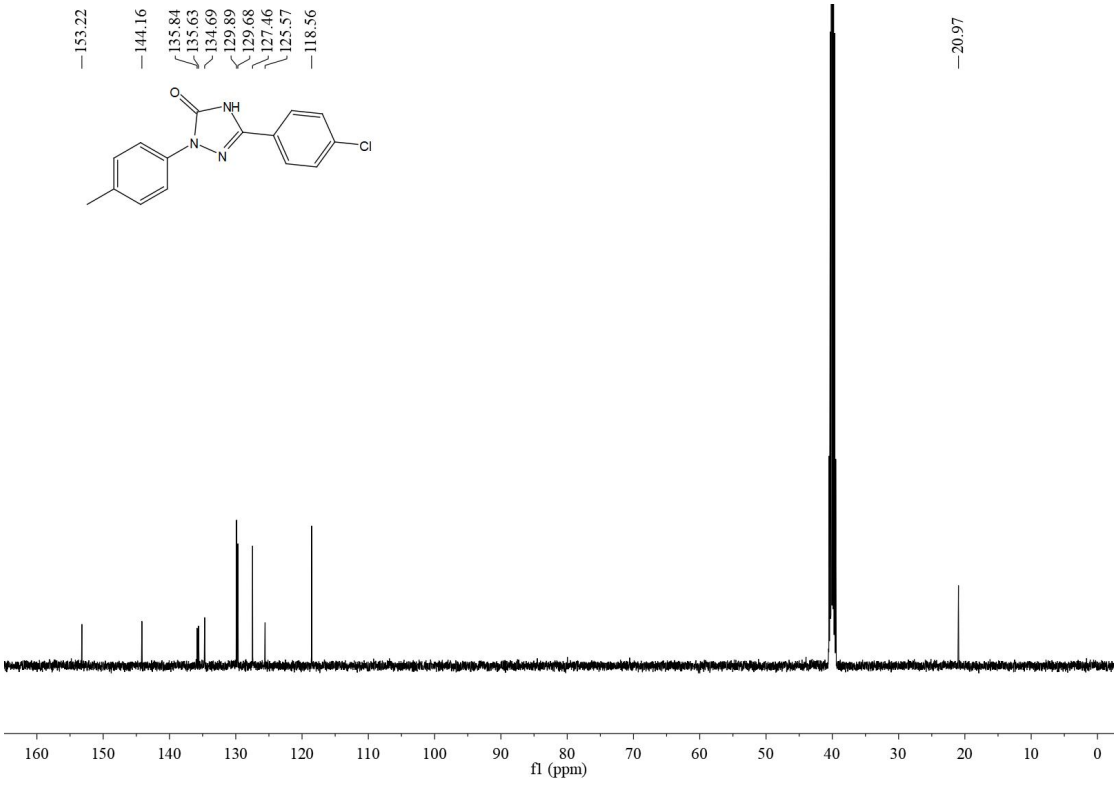




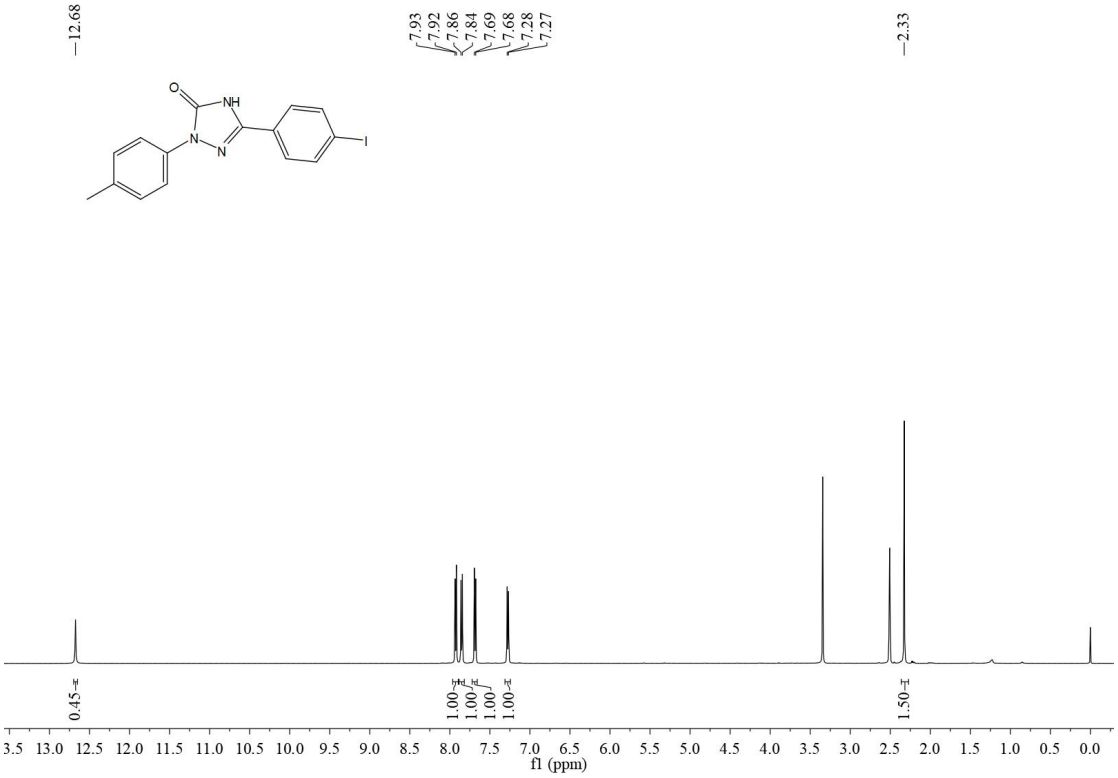

-109.73
O
NH
N
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

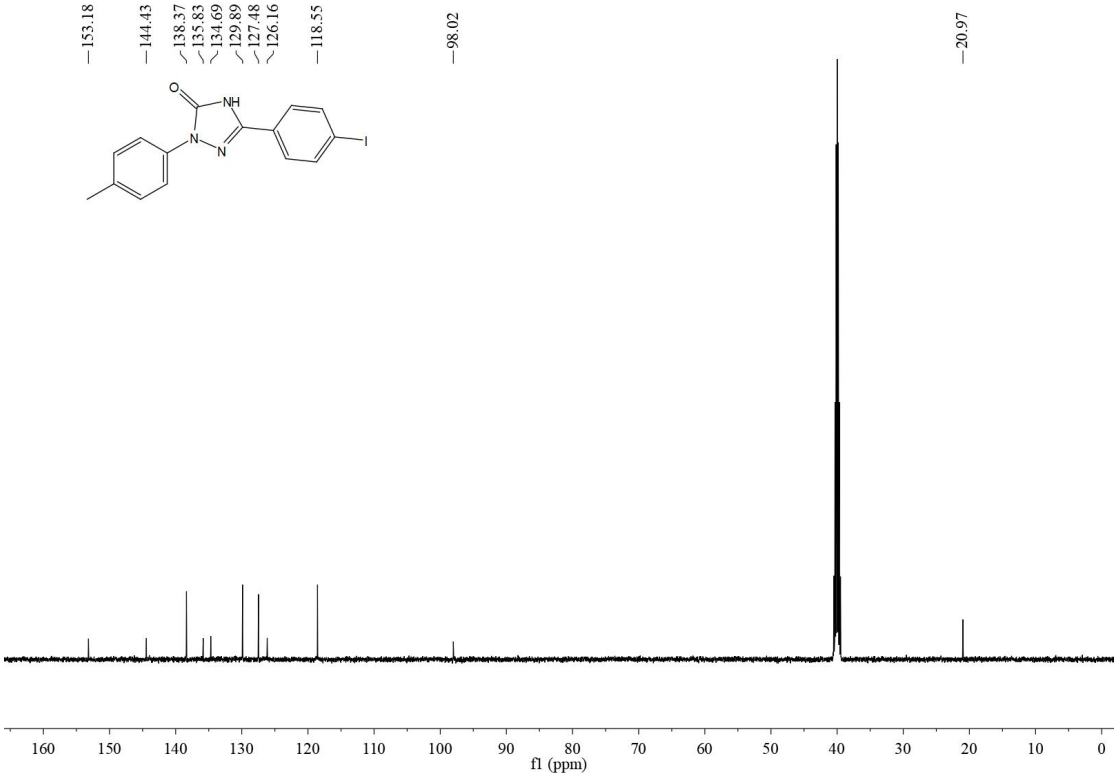
^{1}H and ^{13}C NMR spectra of 5-(4-Chlorophenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bd) (500 MHz, DMSO-d_6)



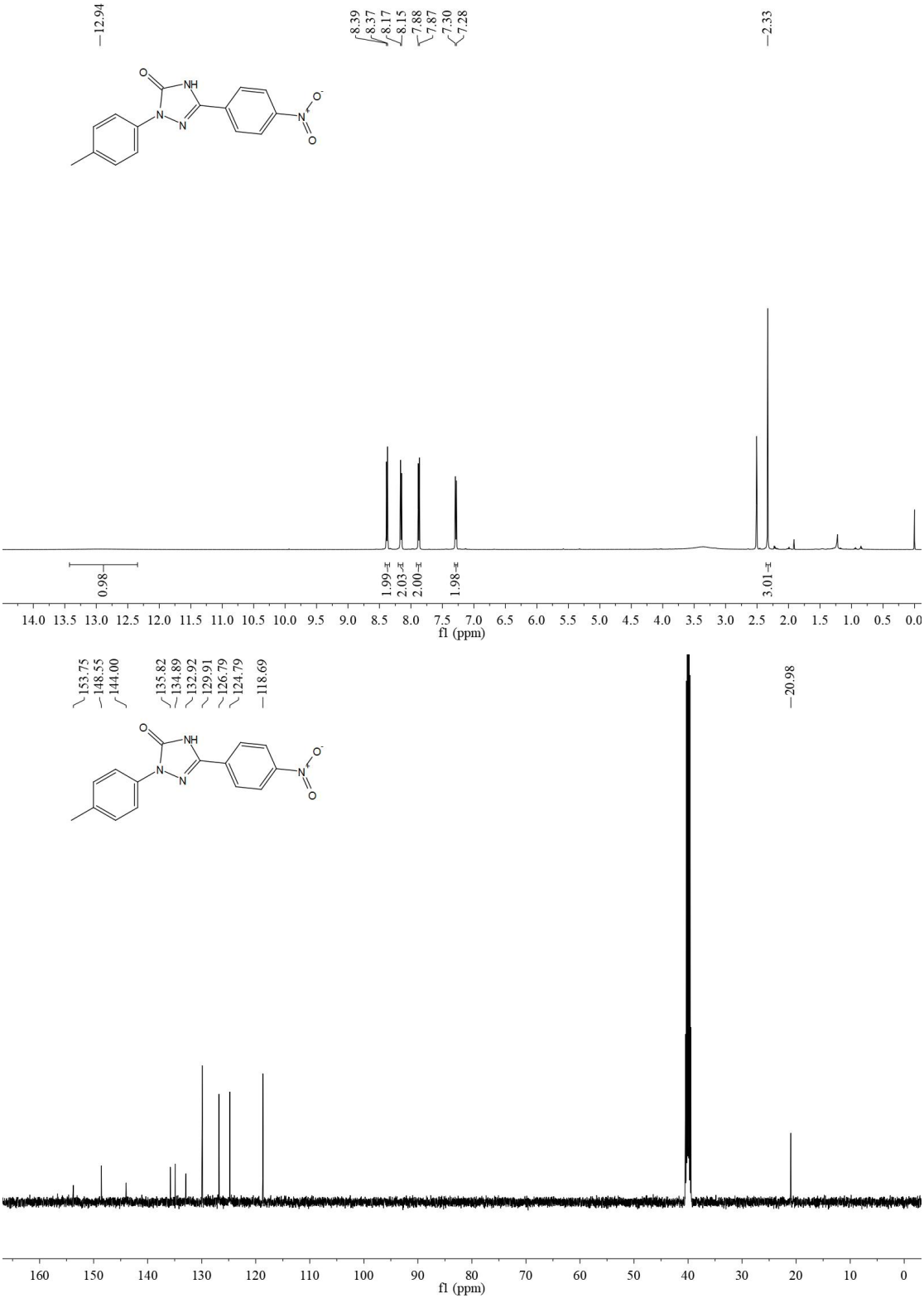


^{1}H and ^{13}C NMR spectra of 5-(4-Iodophenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3be) (500 MHz, DMSO-d_6)

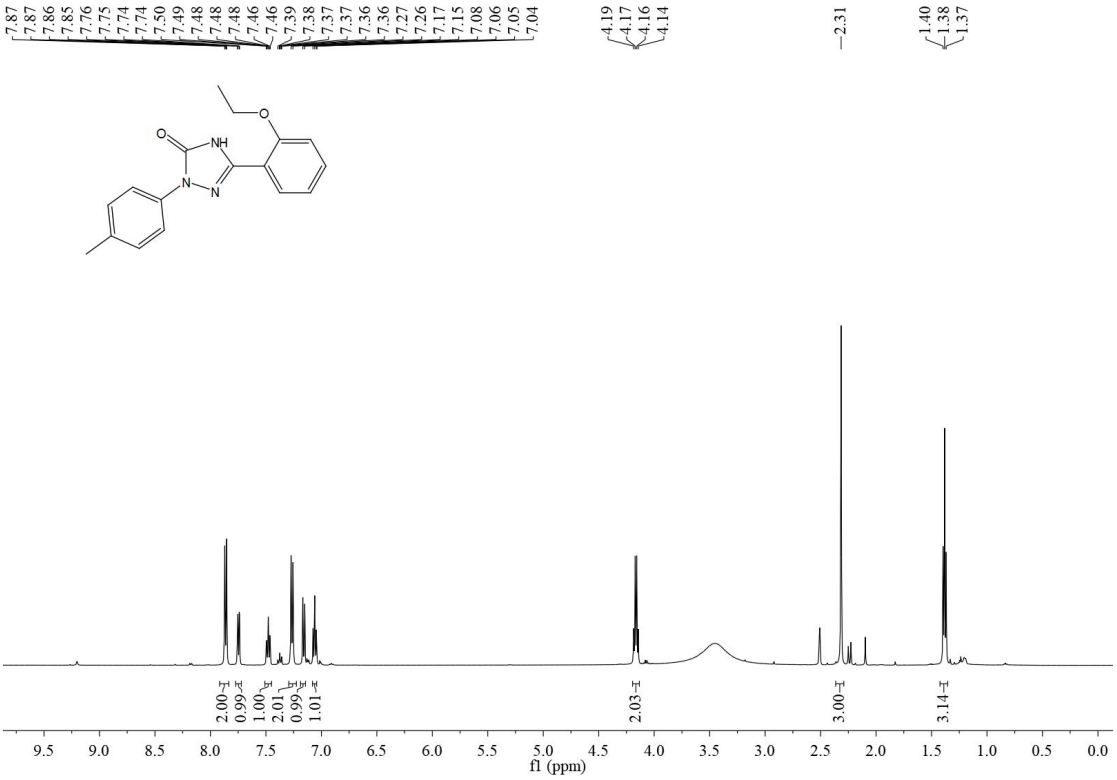


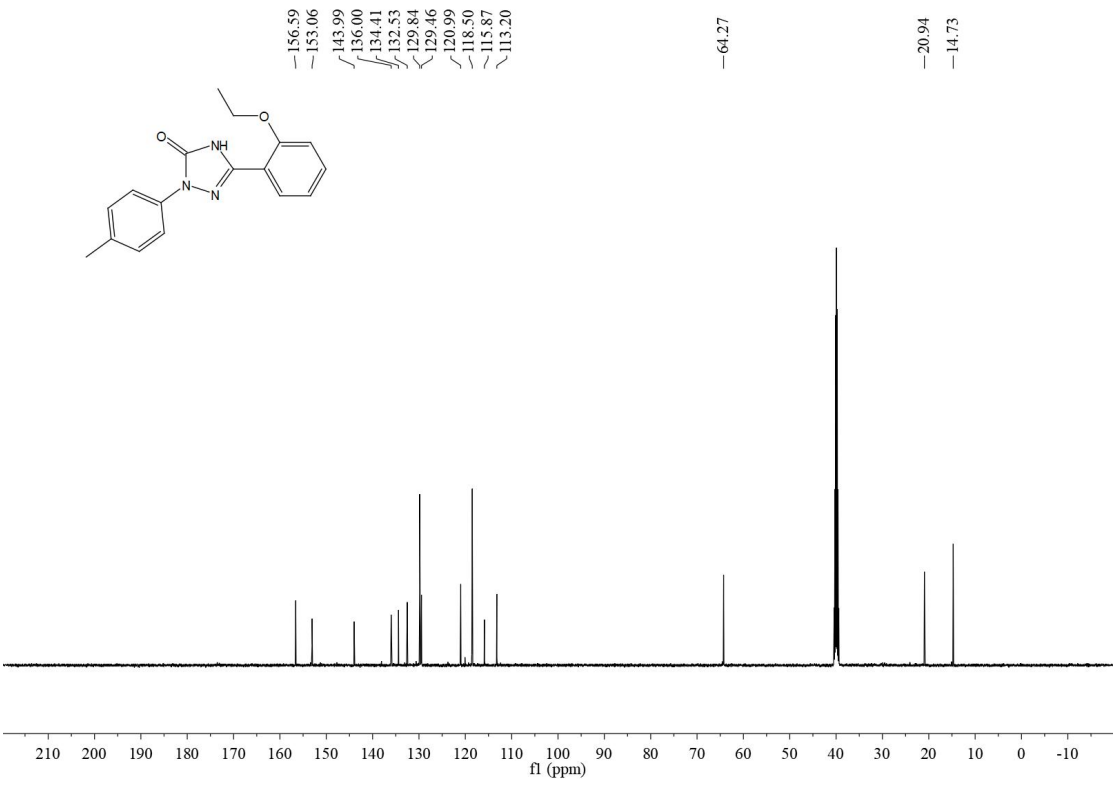


^{1}H and ^{13}C NMR spectra of 5-(4-Nitrophenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bf) (500 MHz, DMSO-d_6)

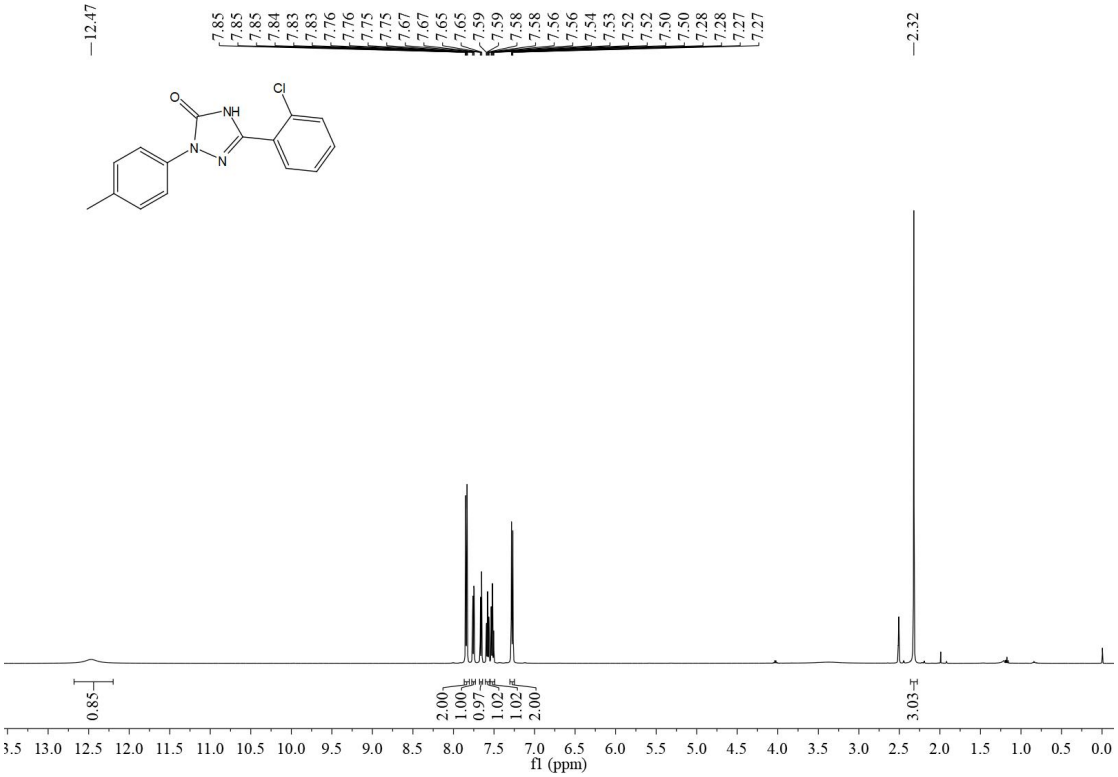


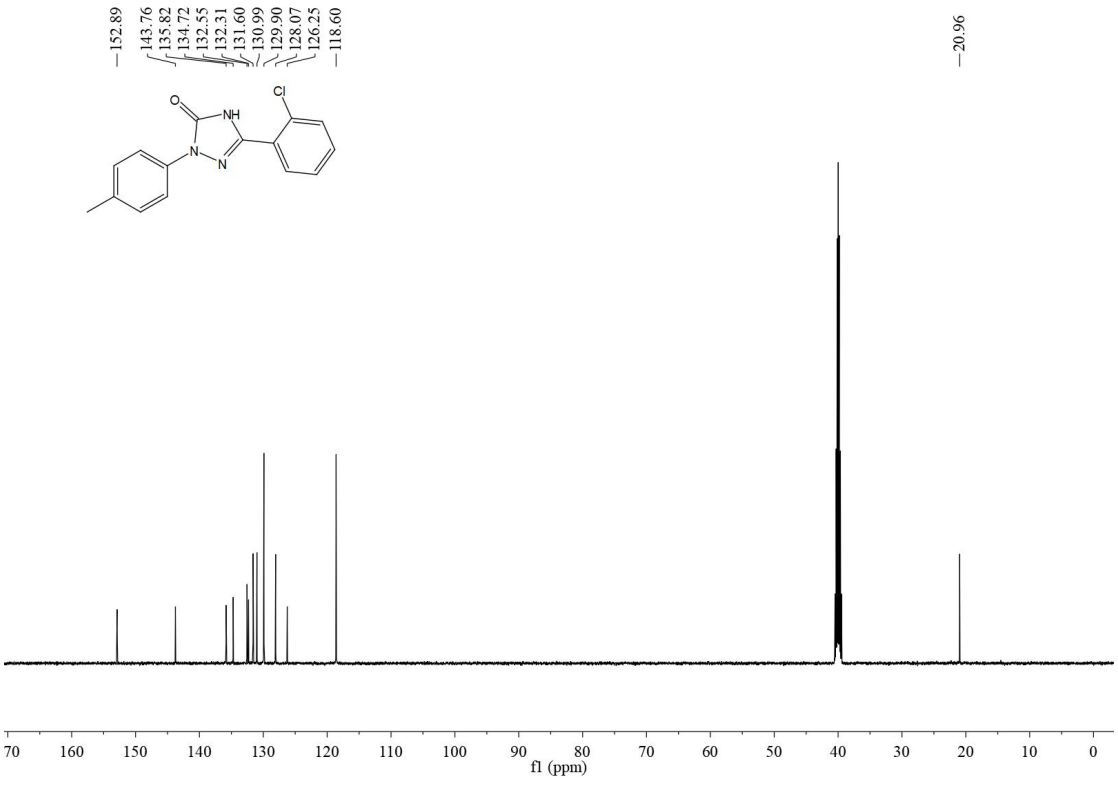
^{1}H and ^{13}C NMR spectra of 5-(2-Ethoxyphenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bg)) (500 MHz, DMSO-d_6)



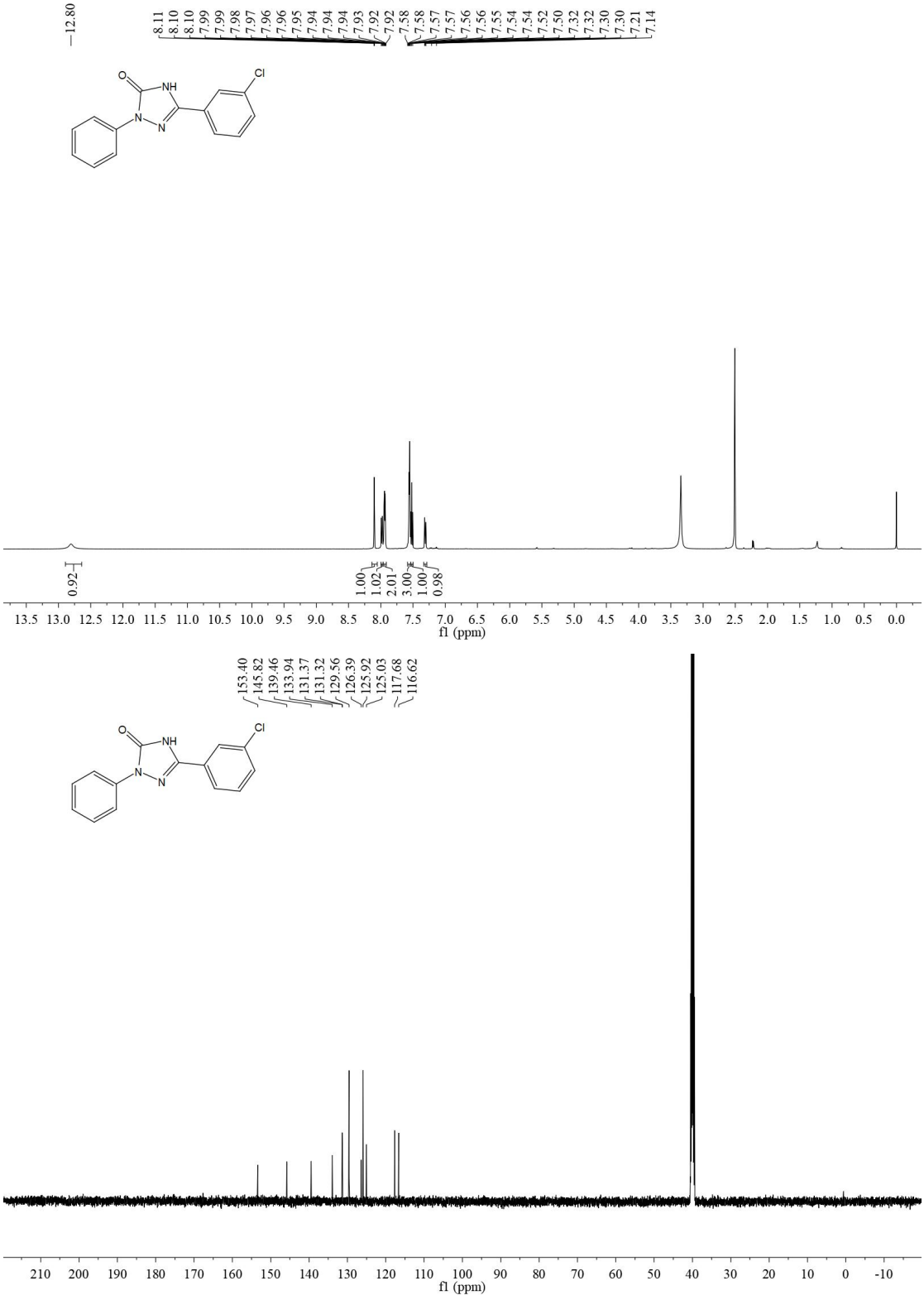


^{1}H and ^{13}C NMR spectra of 5-(2-Chlorophenyl)-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bh) (500 MHz, DMSO-d_6)

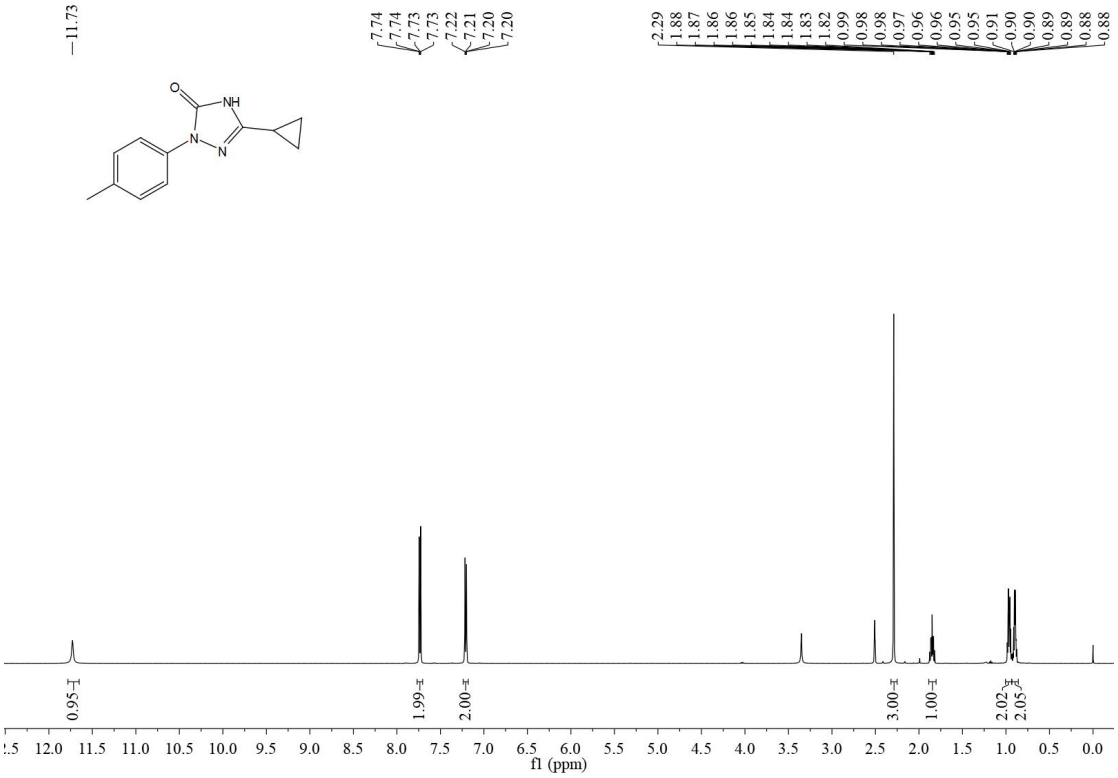


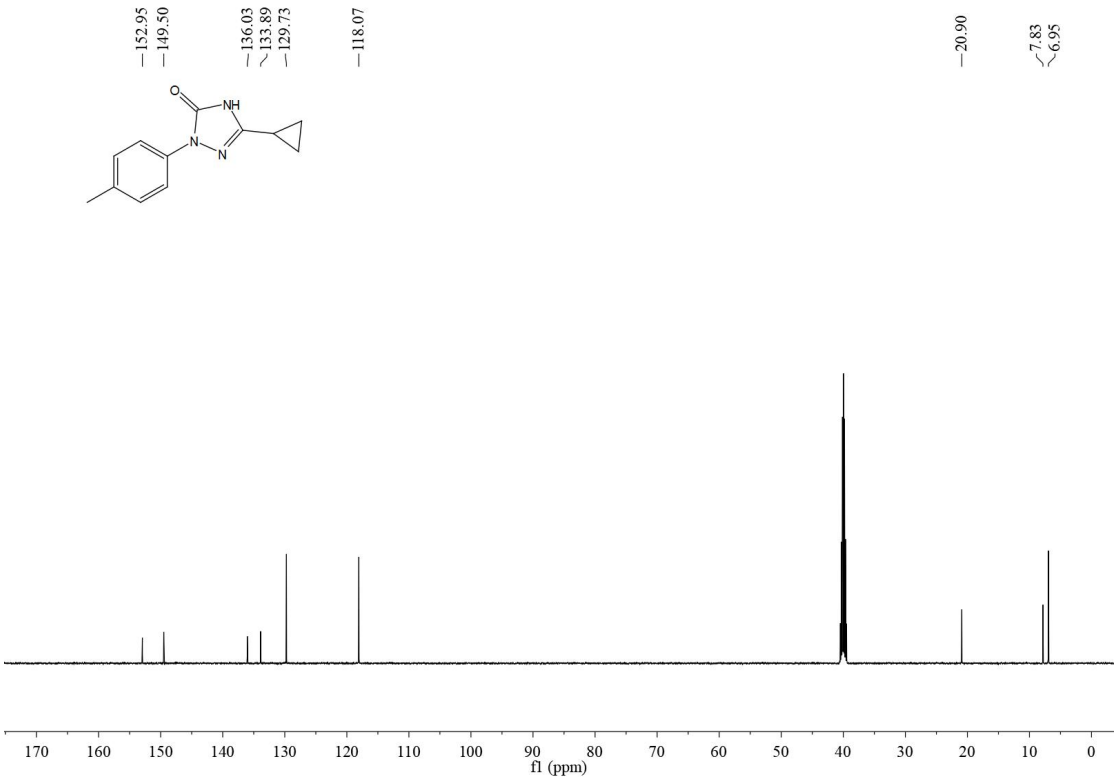


^{1}H and ^{13}C NMR spectra of 5-(3-Chlorophenyl)-2-phenyl-2,4-dihydro-3H-1,2,4-triazol-3-one (3bi) (500 MHz, DMSO-d_6)

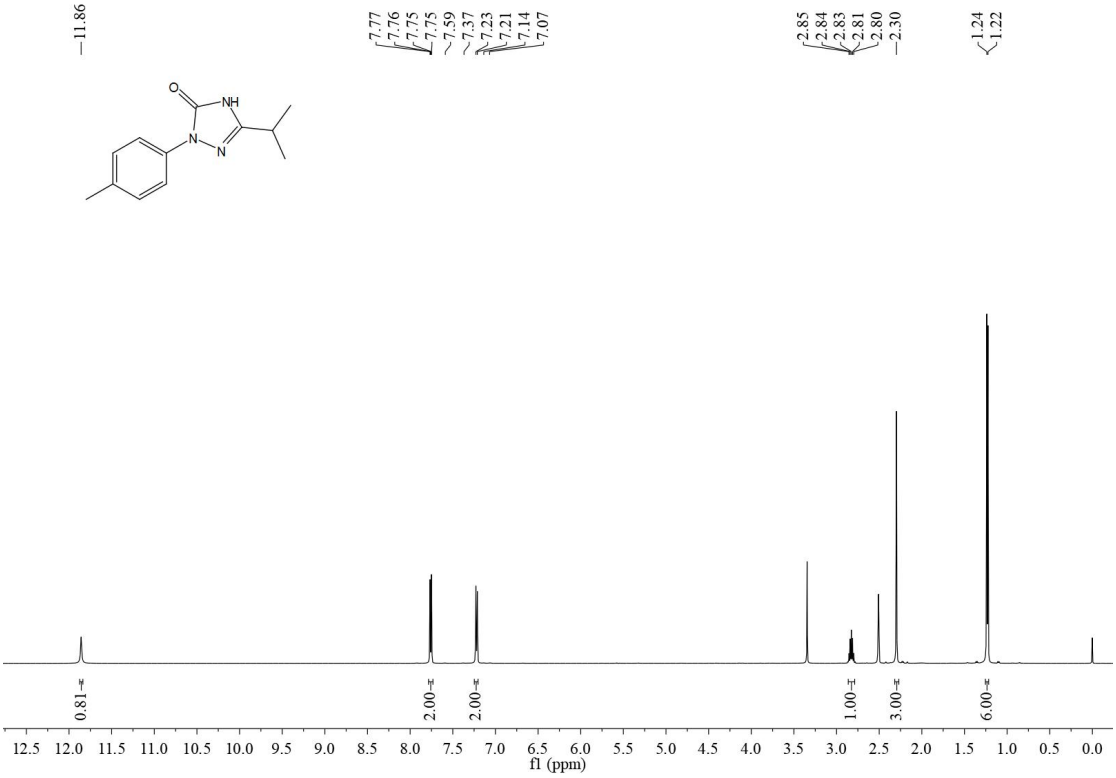


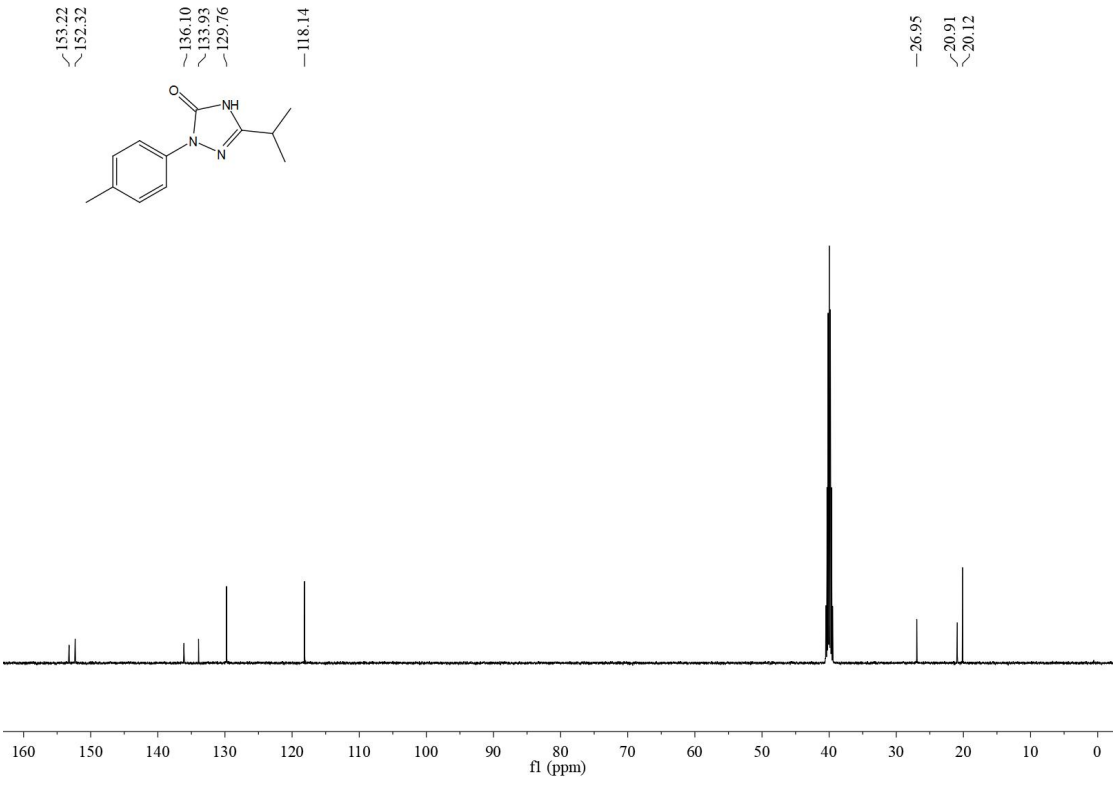
^{1}H and ^{13}C NMR spectra of 5-Cyclopropyl-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bj) (500 MHz, DMSO-d_6)



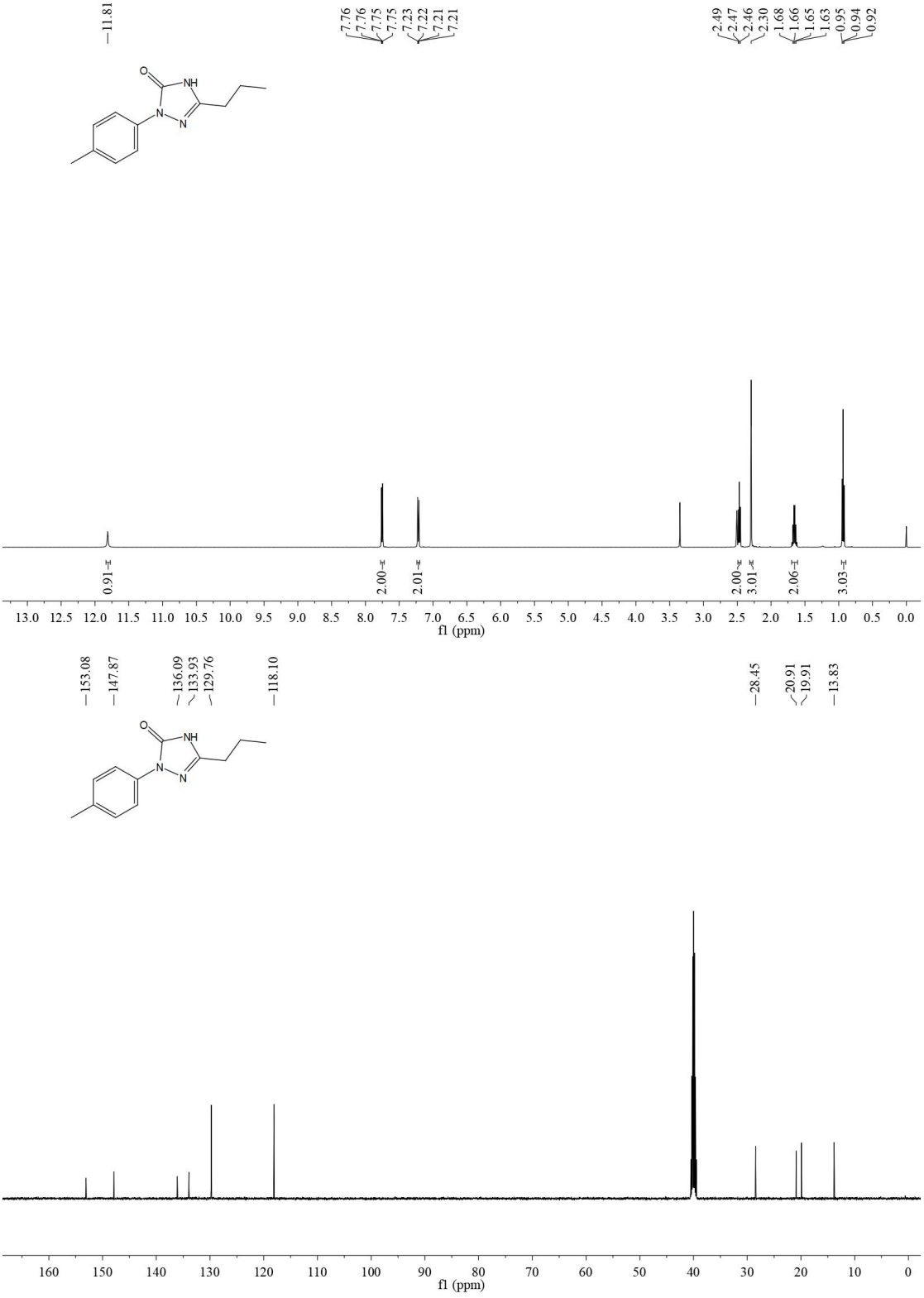


^{1}H and ^{13}C NMR spectra of 5-Isopropyl-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bk) (500 MHz, DMSO-d_6)

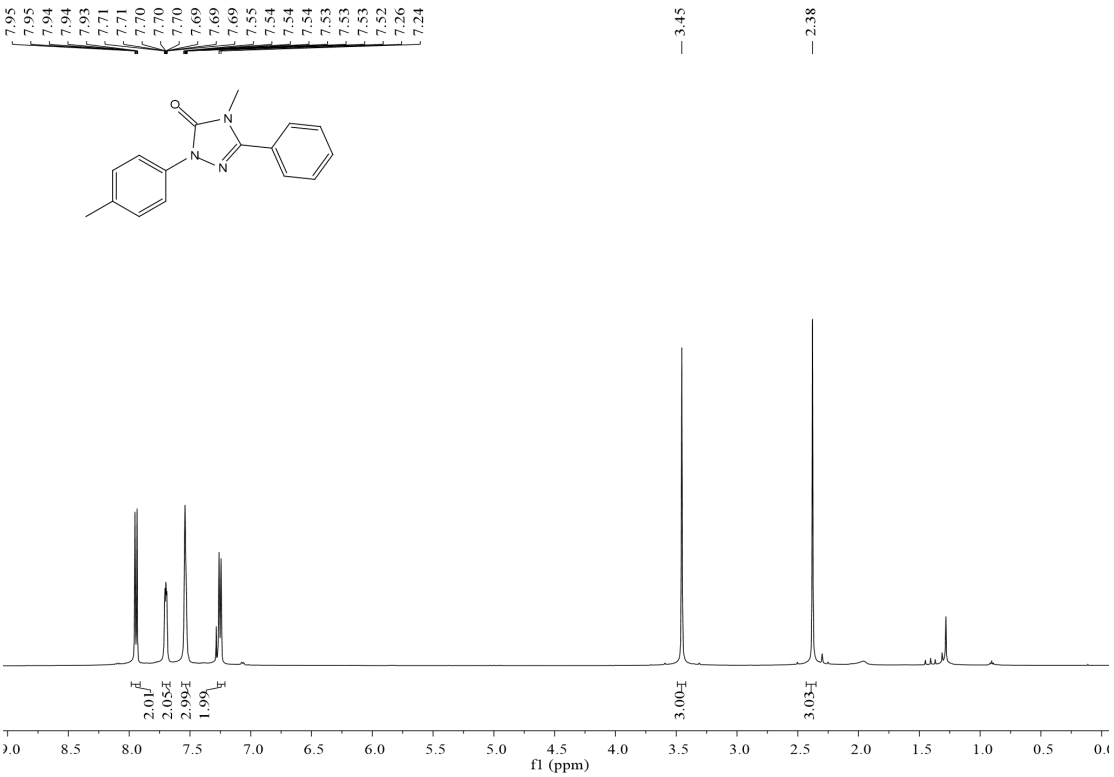


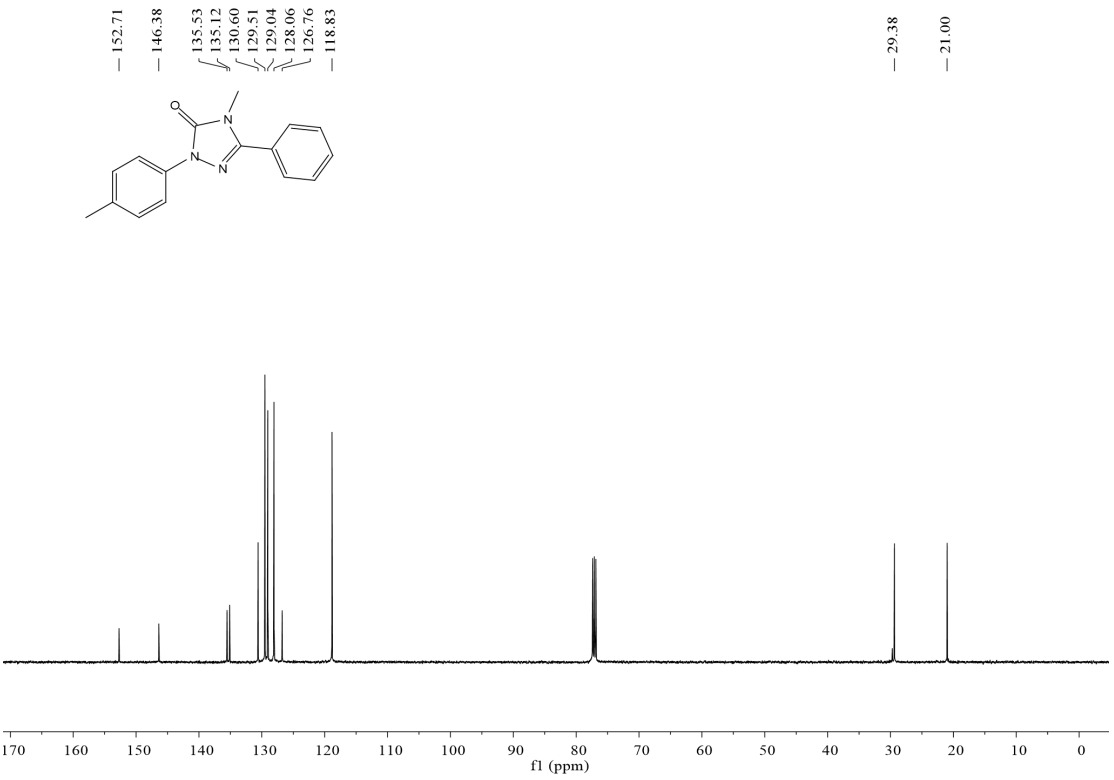


^{1}H and ^{13}C NMR spectra of 5-Propyl-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (3bl) (500 MHz, DMSO-d_6)

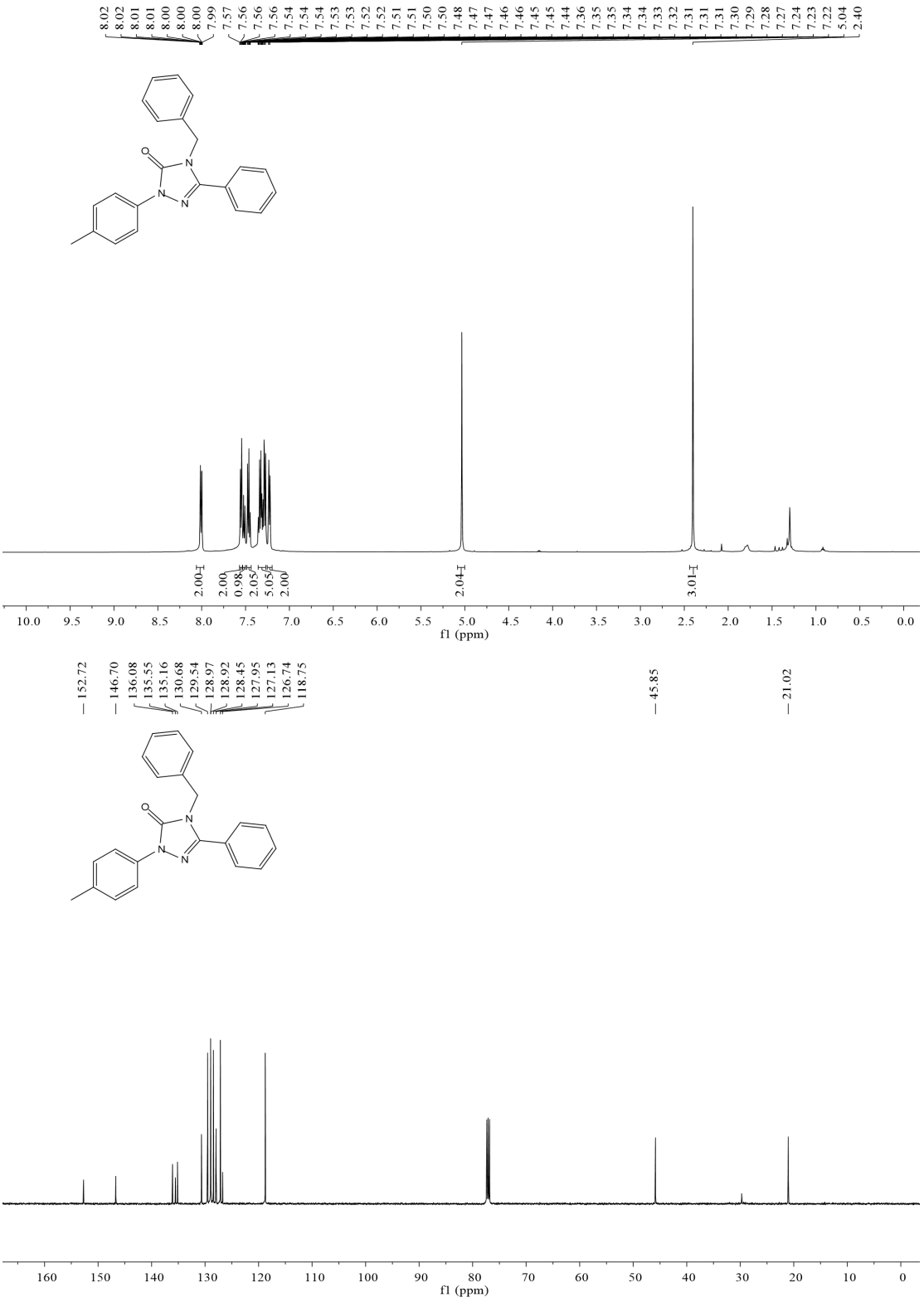


^{1}H and ^{13}C NMR spectra of 4-Methyl-5-phenyl-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (4a) (500 MHz, $CDCl_3$)





^{1}H and ^{13}C NMR spectra of 4-Benzyl-5-phenyl-2-(p-tolyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (4b) (500 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR spectra of N-(p-tolylcarbamoyl)benzimidamide (5a) (500 MHz, $CDCl_3$)