Supporting Information

Electrooxidative C(sp3)−H Amination of Azoles via Intermolecular Oxidative C(sp3)−H/N−H Cross-Coupling

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1. General information

All glassware was oven dried at 110 ^{o}C for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anode electrode and cathode electrode all are Pt (1.5×1.5 cm^2). Cyclic voltammograms were obtained on a CHI 605E potentiostat. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ^{o}C). GC-MS spectra were recorded on Varian GC MS 3900-2100T or SHIMADZU GC MS-2010. ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C).

2. Experimental Proceduces

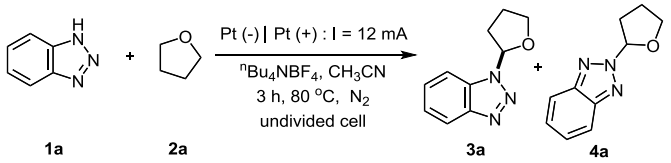
2.1 General procedure for the electrooxidative C(sp3)−H amination of azoles with tetrahydrofuran: In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, azoles (0.3 mmol) and $^{n}Bu_4NBF_4$ (65.85 mg, 0.2 mmol) were combined and added. The bottle was equipped with platinum electrodes (1.5 × 1.5 cm^2) as both the anode and cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (8 mL) and tetrahydrofuran (2 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at 80 ^{o}C for 3-5 h. When the reaction was finished, the reaction mixture was washed with water and extracted with diethyl ether (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

2.2 General procedure for the electrooxidative C(sp3)−H amination of 1H-benzotriazole with other C(sp3)-H sources: In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 1H-benzotriazole (35.74 mg, 0.3 mmol) and $^{n}Bu_4NBF_4$ (65.85 mg, 0.2 mmol) were combined and added. The bottle was equipped with platinum electrodes (1.5×1.5 cm^2) as both the anode and cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (10 mL) and other C(sp3)-H sources (10 equiv.) were injected respectively into the tubes via syringes.

The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at 80 °C for 3 h. When the reaction was finished, the reaction mixture was washed with water and extracted with diethyl ether (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

Procedure for gram scale synthesis: In an oven-dried undivided three-necked bottle (250 mL) equipped with a stir bar, 1H-benzotriazole (1.19 g, 10 mmol) and $^nBu_4NBF_4$ (987.81 mg, 3 mmol) were combined and added. The bottle was equipped with platinum electrodes (1.5×1.5 cm^2) as both the anode and cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (60 mL) and tetrahydrofuran (40 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 60 mA at 80 °C for 24 h. When the reaction was finished, the reaction mixture was washed with water and extracted with diethyl ether (100 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

Table S1. Optimization of the reaction conditions.[a]



1a 2a 3a 4a

Entry	Variation from the standard conditions	Yield of **3a** (%)[b]
1	Pt (-) | C (+) instead of Pt (-) | Pt (+)	51
2	C (-) | C (+) instead of Pt (-) | Pt (+)	trace
3	Ni (-) | C (+) instead of Pt (-) | Pt (+)	38
4	$^nBu_4NClO_4$ instead of $^nBu_4NBF_4$	84
5	$^nBu_4NHSO_4$ instead of $^nBu_4NBF_4$	69
6	$^nBu_4NI$ instead of $^nBu_4NBF_4$	n.d.
7	$^nEt_4NBF_4$ instead of $^nBu_4NBF_4$	88
8	DCE instead of CH_3CN	71
9	DMSO instead of CH_3CN	trace
10	H_2O instead of CH_3CN	n.d.
11	EtOH instead of CH_3CN	n.d.

[a] Reaction conditions: Pt anode, Pt cathode, constant current = 12 mA, **1a** (0.3 mmol), **2a** (2.0 mL), $^nBu_4NBF_4$ (0.2 mmol), in 8.0 mL CH_3CN at 80 °C under N_2 for 3 h. [b] Yields shown are of isolated products. RT = room temperature. n.d. = not detected.

3. Additional experiments

3.1 Cyclic voltammetry of 1a, 3a and 2a.

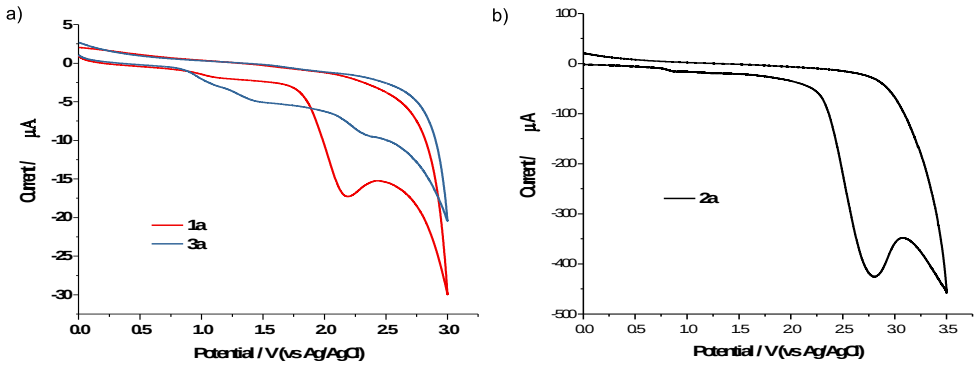
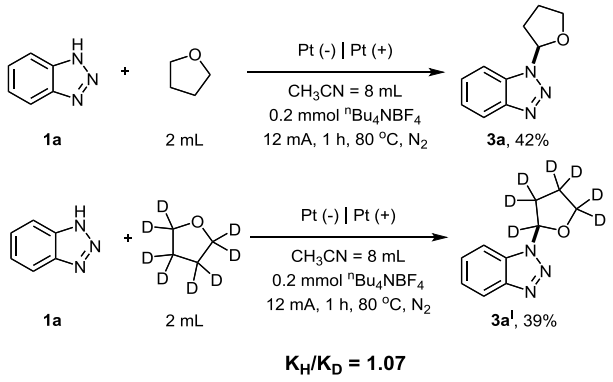


Figure S1. a) Cyclic voltammetry of **1a** and **3a** in CH_3CN with $^nBu_4NBF_4$ (0.2 mmol) under nitrogen at a platinum-disk electrode at a scan rate of v = 0.1 Vs^{-1}. b) Cyclic voltammetry of **2a** in CH_3CN with $^nBu_4NBF_4$ (0.2 mmol) under nitrogen at a platinum-disk electrode at a scan rate of v = 0.1 Vs^{-1}.

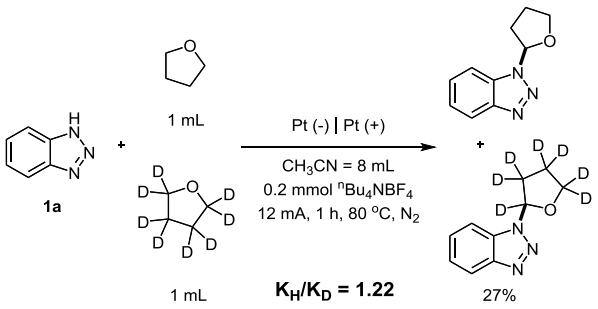
3.2 KIE Determined with Two Parallel Reactions:

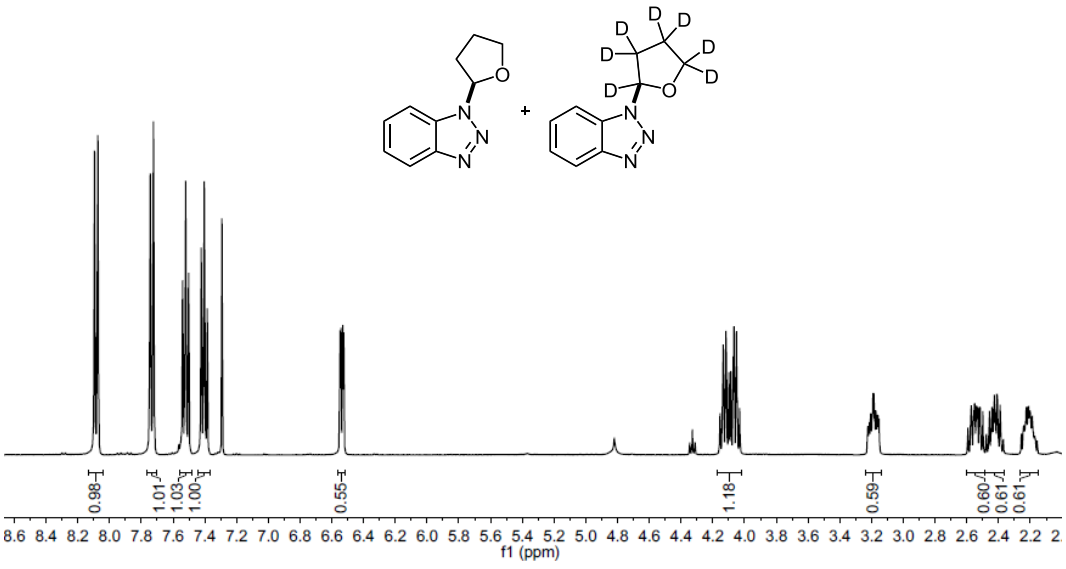
General procedure and results: In two oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 1H-benzotriazole (35.74 mg, 0.3 mmol), $^nBu_4NBF_4$ (65.85 mg, 0.2 mmol) and were combined and added. The bottle was equipped with platinum electrodes (1.5×1.5 cm^2) as both the anode and cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (8 mL) tetrahydrofuran (2 mL) and d_8-tetrahydrofuran (2 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at 80 ^oC for 1 h. When the reaction was finished, the reaction mixture was washed with water and extracted with diethyl ether (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel. As a result, the desired coupling products were obtained in 42% and 39% yields, respectively, in which k_H/k_D = 1.07.



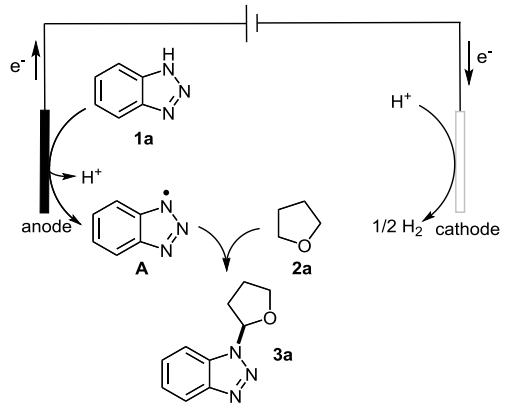
3.3 Intermolecular Kinetic Isotopic Effect (KIE)

General procedure and characterization spectrum: In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 1H-benzotriazole (35.74 mg, 0.3 mmol), $^{n}Bu_4NBF_4$ (65.85 mg, 0.2 mmol) and were combined and added. The bottle was equipped with platinum electrodes (1.5×1.5 cm^2) as both the anode and cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (8 mL), tetrahydrofuran (1 mL) and d_8-tetrahydrofuran (1 mL) were injected into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at 80 ^{o}C for 1 h. When the reaction was finished, the reaction mixture was washed with water and extracted with diethyl ether (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel with a total yield of 27% and detected by ^{1}H NMR to determine the exact KIE value. From the following ^{1}H NMR spectrum, we can calculate the KIE value to be $k_H/k_D = 0.55/0.45 = 1.22$



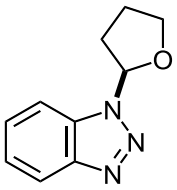


4. Proposed mechanism



Scheme S1. Proposed mechanism.

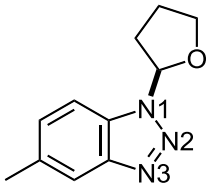
5. Detail descriptions for products



1-(Tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3a)[1]: 52.2 mg, yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 6.51 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.14 – 3.99 (m, 2H), 3.19 – 3.10 (m, 1H), 2.57 – 2.46 (m, 1H), 2.45 – 2.33 (m, 1H), 2.23 – 2.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.37, 132.82, 127.53, 124.15, 119.86, 110.45, 87.89, 69.32, 30.83, 24.44.

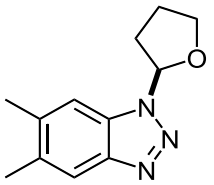


5-Methyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole and **6-Methyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole** (**3b,** N1/N3 = 1/1.6): 56.7 mg, yield: 93%**.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 1.00H), 7.81 (s, 0.64H), 7.58 (d, *J* = 8.5 Hz, 0.67H), 7.47 (s, 1.00H), 7.32 (d, *J* = 7.5 Hz, 0.66H), 7.20 (d, *J* = 8.5 Hz, 1.02H), 6.47 (t, *J* = 7.0 Hz, 1.67H), 4.12 – 3.99 (m, 3.49H), 3.21 – 3.09 (m, 1.74H), 2.52 (d, *J* = 8.6 Hz, 5.89H), 2.47 – 2.35 (m, 2.81H), 2.23 – 2.12 (m, 1.78H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.99, 145.06, 138.17, 134.15, 133.31, 131.32, 129.68, 126.43, 119.29, 118.78, 109.95, 109.61, 87.91, 87.65, 69.25, 30.81, 30.65, 24.48, 24.45, 22.07, 21.54.

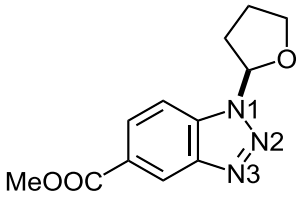
HRMS (ESI) calculated for $C_{11}H_{13}N_3O$ [M+Na]$^+$: 226.0951; found: 226.0956.



5,6-Dimethyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3c)[1]: 54.1 mg, yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.45 (s, 1H), 6.45 (dd, *J* = 6.7, 2.5 Hz, 1H), 4.12 – 4.05 (m, 1H), 4.04 – 3.97 (m, 1H), 3.20 – 3.10 (m, 1H), 2.54 – 2.35 (m, 8H), 2.21 – 2.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.66, 137.86, 133.89, 131.88, 118.91, 109.84, 87.68, 69.18, 30.63, 24.48, 21.00, 20.48.

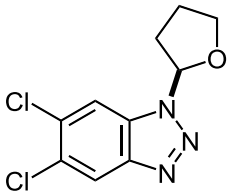


Methyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole-5-carboxylate and **Methyl 1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole-6-carboxylate** (**3d,** N1/N3 = 1/3.7): 44.5 mg, yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1.00H), 8.49 (s, 0.27H), 8.19 (d, *J* = 8.7 Hz, 1.11H), 8.08 (q, *J* = 8.7 Hz, 0.59H), 7.75 (d, *J* = 8.7 Hz, 1.13H), 6.57 (dd, *J* = 6.7, 1.9 Hz, 0.32H), 6.53 (dd, *J* = 6.7, 1.9 Hz, 1.09H), 4.16 – 4.03 (m, *J* = 28.1, 7.9 Hz, 3.19H), 3.99 (s, 4.29H), 3.21 – 3.14 (m, 1.49H), 2.61 – 2.48 (m, 1.49H), 2.44 – 2.33 (m, 1.64H), 2.23 – 2.16 (m, 1.52H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 148.42, 146.16, 135.21, 132.64, 129.31, 128.39, 126.56, 124.96, 122.81, 119.79, 113.32, 110.50, 88.33, 69.57, 52.55, 31.06, 24.37.

HRMS (ESI) calculated for $C_{12}H_{13}N_3O_3$ $[M+Na]^+$: 270.0849; found: 270.0855.

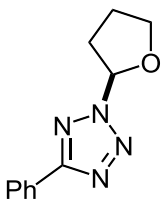


5,6-Dichloro-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3e): 33.2 mg, yield: 43%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.91 (s, 1H), 6.44 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.13 (q, *J* = 7.8 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.23 –3.16 (m, 1H), 2.60 – 2.48 (m, 1H), 2.37 – 2.29 (m, 1H), 2.27 – 2.14 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.34, 132.70, 131.94, 129.03, 120.76, 112.22, 88.80, 69.62, 31.03, 24.18.

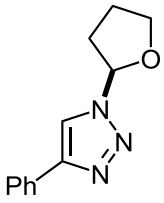
HRMS (EI) calculated for $C_{10}H_9Cl_2N_3O$ (M): 257.0123; found: 257.0132.



5-Phenyl-2-(tetrahydrofuran-2-yl)-2H-tetrazole (3f)[2]: 54.5 mg, yield: 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.51 (dq, *J* = 7.3, 2.7, 2.1 Hz, 3H), 6.61 (dd, *J* = 6.5, 2.1 Hz, 1H), 4.34 – 4.27 (m, 1H), 4.20 – 4.13 (m, 1H), 2.77 – 2.67 (m, 1H), 2.60 – 2.47 (m, 2H), 2.25 – 2.14 (m, 1H).

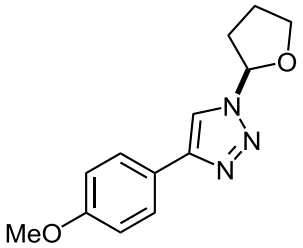
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.26, 130.47, 128.96, 127.45, 127.04, 91.77, 70.35, 31.96, 24.15.



4-Phenyl-1-(tetrahydrofuran-2-yl)-1H-1,2,3-triazole (3g)[3]: 57.4 mg, yield: 89%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.83 (d, *J* = 7.1 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.37 (dd, *J* = 6.7, 2.5 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.12 – 4.06 (m, 1H), 2.77 – 2.69 (m, 1H), 2.52 – 2.41 (m, 2H), 2.17 – 2.10 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.12, 131.48, 130.38, 128.89, 128.58, 126.09, 92.39, 69.65, 31.43, 24.56.

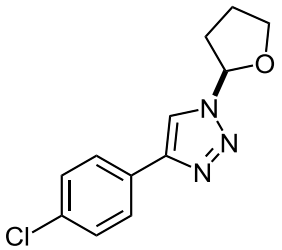


4-(4-Methoxyphenyl)-1-(tetrahydrofuran-2-yl)-1H-1,2,3-triazole (3h): 44.1mg, yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.34 (dd, *J* = 6.7, 2.5 Hz, 1H), 4.25 – 4.17 (m, 1H), 4.12 – 4.03 (m, 1H), 3.86 (s, 3H), 2.77 – 2.67 (m, 1H), 2.54 – 2.37 (m, 2H), 2.18 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.92, 148.01, 131.01, 127.42, 123.06, 114.29, 92.28, 69.61, 55.40, 31.37, 24.61.

HRMS (ESI) calculated for $C_{13}H_{15}N_3O_2$ $[M+Na]^+$: 268.1056; found: 268.1071.

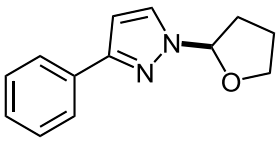


4-(4-Chlorophenyl)-1-(tetrahydrofuran-2-yl)-1H-1,2,3-triazole (3i): 55.3 mg, yield: 74%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.35 (dd, *J* = 6.6, 2.4 Hz, 1H), 4.22 (q, *J* = 7.7 Hz, 1H), 4.09 (q, *J* = 7.7 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.55 – 2.39 (m, 2H), 2.20 – 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.14, 134.41, 131.46, 129.16, 128.94, 127.38, 92.52, 69.76, 31.49, 24.59.

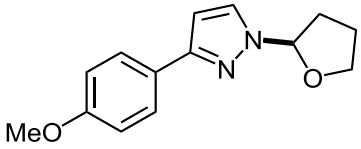
HRMS (ESI) calculated for $C_{12}H_{12}ClN_3O$ $[M+Na]^+$: 273.0561; found: 273.0567.



3-Phenyl-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3j)[3]: 58.5 mg, yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 6.06 (dd, *J* = 6.6, 2.5 Hz, 1H), 4.24 – 4.19 (m, 1H), 4.04 (q, *J* = 7.3 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.43 – 2.32 (m, 1H), 2.30 – 2.21 (m, 1H), 2.13 – 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.95, 133.68, 129.25, 128.62, 127.70, 125.76, 102.96, 90.32, 69.39, 32.02, 24.44.

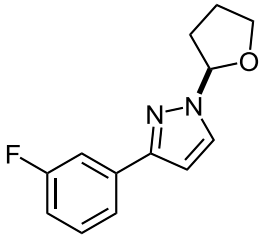


3-(4-Methoxyphenyl)-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3k): 67.4 mg, yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.04 (dd, *J* = 6.6, 2.6 Hz, 1H), 4.20 (td, *J* = 7.9, 5.5 Hz, 1H), 4.03 (q, *J* = 7.4 Hz, 1H), 3.86 (s, 3H), 2.73 – 2.64 (m, 1H), 2.43 – 2.30 (m, 1H), 2.30 – 2.19 (m, 1H), 2.13 – 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.35, 151.85, 129.20, 127.03, 126.57, 114.01, 102.50, 90.27, 69.37, 55.40, 32.00, 24.50.

HRMS (ESI) calculated for $C_{14}H_{14}N_2O_2$ $[M+H]^+$: 245.1285; found: 245.1284



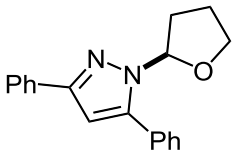
3-(3-Fluorophenyl)-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3l): 57.8 mg, yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 3H), 7.37 (q, *J* = 7.8, 7.1 Hz, 1H), 7.01 (t, *J* = 8.4 Hz, 1H), 6.61 – 6.56 (m, 1H), 6.04 (d, *J* = 6.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 1H), 2.75 – 2.64 (m, 1H), 2.42 – 2.33 (m, 1H), 2.31 – 2.25 (m, 1H), 2.14 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.26 (d, *J* = 244.6 Hz), 150.87, 135.99 (d, *J* = 8.4 Hz), 130.13 (d, J = 8.4 Hz), 129.52, 121.39 (d, *J* = 2.9 Hz), 114.46 (d, *J* = 21.3 Hz), 112.58 (d, *J* = 22.5 Hz), 103.18, 90.40, 69.50, 32.05, 24.46.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.53.

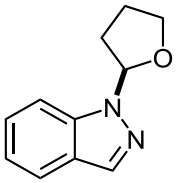
HRMS (ESI) calculated for $C_{13}H_{13}FN_2O$ $[M+H]^+$: 233.1085; found: 233.1085.



3,5-Diphenyl-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3m)[4]: 52.2 mg, yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.0 Hz, 2H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.04 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.36 – 4.29 (m, 1H), 4.08 – 4.00 (m, 1H), 2.92 – 2.83 (m, 1H), 2.72 – 2.60 (m, 1H), 2.32 – 2.23 (m, 1H), 2.15 – 2.05 (m 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.91, 145.79, 133.68, 130.57, 129.39, 128.79, 128.71, 128.64, 127.81, 125.85, 103.73, 86.69, 69.26, 31.11, 25.68.

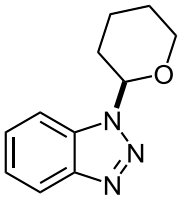


1-(Tetrahydrofuran-2-yl)-1H-indazole (3n): 41.2 mg, yield: 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.43 (dd, *J* = 6.7, 3.2 Hz, 1H), 4.12 – 4.00 (m, 2H), 3.03 – 2.93 (m, 1H), 2.51 – 2.38 (m, 2H), 2.20 – 2.08 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.94, 134.03, 126.65, 124.75, 121.23, 121.09, 109.74, 86.91, 68.86, 30.33, 25.17.

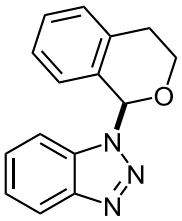
HRMS (ESI) calculated for $C_{11}H_{12}N_2O$ $[M+Na]^+$: 211.0842; found: 211.0843.



1-(Tetrahydro-2H-pyran-2-yl)-1H-benzo[d][1,2,3]triazole (3o)[1]: 30.5 mg, yield: 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.05 (dd, *J* = 8.3, 2.9 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.84 – 3.75 (m, 1H), 2.69 – 2.57 (m, 1H), 2.27 – 2.14 (m, 2H), 1.91 – 1.69 (m, 3H).

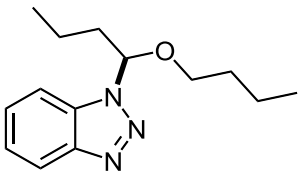
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.41, 132.50, 127.54, 124.23, 119.96, 111.18, 85.74, 66.97, 29.37, 24.99, 21.72.



1-(Isochroman-1-yl)-1H-benzo[d][1,2,3]triazole (3p)[1]: 67.8 mg, yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 6.3, 3.1 Hz, 1H), 7.44 (s, 1H), 7.42 – 7.33 (m, 4H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.03 (dq, *J* = 6.9, 3.3 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 4.15 – 4.08 (m, 2H), 3.16 (dt, *J* = 14.3, 6.9 Hz, 1H), 3.07 –3.01 (m, 1H).

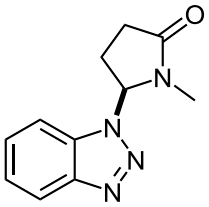
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.48, 134.80, 132.72, 130.26, 129.17, 127.74, 127.11, 126.95, 124.18, 120.14, 110.84, 83.51, 62.11, 27.89.



1-(1-Butoxybutyl)-1H-benzo[d][1,2,3]triazole (3q)[5]: 22.2 mg, yield: 30%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 6.08 (t, *J* = 6.8 Hz, 1H), 3.52 – 3.44 (m, 1H), 3.27 – 3.18 (m, 1H), 2.34 – 2.22 (m, 1H), 2.17 – 2.06 (m, 1H), 1.56 – 1.43 (m, 3H), 1.36 – 1.27 (m, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H).

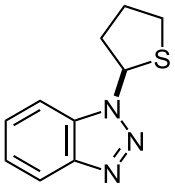
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.93, 131.36, 127.45, 124.29, 120.17, 111.47, 91.05, 69.03, 36.85, 31.38, 19.28, 18.38, 13.83, 13.63.



5-(1H-benzo[d][1,2,3]triazol-1-yl)-1-methylpyrrolidin-2-one (3r)[1]: 55.1 mg, yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 – 7.43 (m, 2H), 6.52 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.01 – 2.81 (m, 2H), 2.70 (s, 4H), 2.53 – 2.44 (m, 1H).

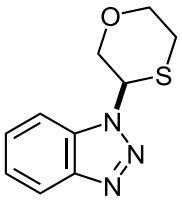
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.51, 146.69, 131.34, 128.47, 124.71, 120.78, 109.05, 74.69, 29.37, 27.73, 25.16.



1-(Tetrahydrothiophen-2-yl)-1H-benzo[d][1,2,3]triazole (3s)[3]: 30.8 mg, yield: 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 6.48 (dd, *J* = 6.4, 3.9 Hz, 1H), 3.37 – 3.29 (m, 1H), 3.16 – 3.10 (m, 1H), 2.98 – 2.93 (m, 1H), 2.64 – 2.47 (m, 2H), 2.39 – 2.32 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.52, 132.18, 127.23, 124.13, 120.18, 110.38, 65.97, 37.28, 33.97, 29.96.

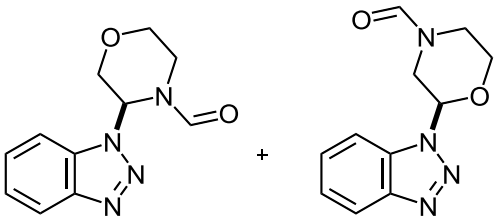


1-(1,4-Oxathian-3-yl)-1H-benzo[d][1,2,3]triazole (3t): 41.8 mg, yield: 63%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 5.79 (dd, *J* = 5.8, 3.1 Hz, 1H), 4.67 (dd, *J* = 12.1, 5.8 Hz, 1H), 4.46 (dd, *J* = 12.1, 3.1 Hz, 1H), 4.19 – 4.13 (m, 2H), 3.11 (dt, *J* = 13.8, 5.3 Hz, 1H), 2.86 (dt, *J* = 13.8, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.13, 132.46, 127.75, 124.41, 120.38, 110.51, 70.85, 68.24, 54.28, 26.77.

HRMS (ESI) calculated for $C_{10}H_{11}N_3OS$ $[M+Na]^+$: 244.0515; found: 244.0518.

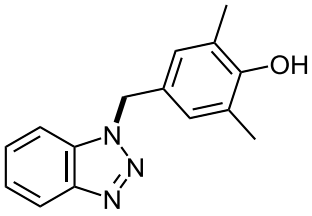


3-(1H-benzo[d][1,2,3]triazol-1-yl)morpholine-4-carbaldehyde and **2-(1H-benzo[d][1,2,3]triazol-1-yl)morpholine-4-carbaldehyde** (**3u/3u^{I} =** 2.3/1): 63.4 mg, yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 0.43H), 8.18 (s, 1.00H), 8.12 – 8.06 (m, 1.44H), 7.90 (d, *J* = 8.5 Hz, 0.45H), 7.82 (d, *J* = 8.4 Hz, 1.02H), 7.56 – 7.48 (m, 1.47H), 7.40 (q, *J* = 8.1 Hz, 1.48H), 6.85 (d, *J* = 3.6 Hz, 1.00H), 6.41 (d, *J* = 3.4 Hz, 0.45H), 4.85 – 4.76 (m, 1.50H), 4.26 – 4.15 (m, 2.42H), 4.10 (dd, *J* = 12.6, 3.7 Hz, 1.07H), 3.82 – 3.63 (m, 2.59H), 3.48 (d, *J* = 13.3 Hz, 1.06H), 3.16 – 3.05 (m, 0.47H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.55, 174.43, 146.61, 144.49, 131.26, 128.39, 127.06, 124.63, 120.70, 118.43, 108.97, 80.59, 74.62, 29.29, 28.84, 27.65, 25.81, 25.08, 23.85.

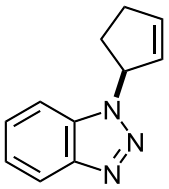
HRMS (ESI) calculated for $C_{11}H_{12}N_4O_2$ $[M+Na]^+$: 255.0852; found: 255.0858.



4-((1H-Benzo[d][1,2,3]triazol-1-yl)methyl)-2,6-dimethylphenol (**3v**): 51.7 mg, yield: 68%.

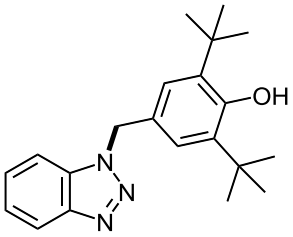
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 3.6 Hz, 2H), 7.38 – 7.34 (m, 1H), 6.97 (s, 2H), 5.73 (s, 2H), 5.34 (s, 1H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.57, 146.23, 132.73, 128.14, 127.29, 126.03, 123.93, 123.85, 119.89, 110.00, 52.07, 16.06.

HRMS (ESI) calculated for $C_{15}H_{15}N_3O$ $[M+H]^+$: 254.1288; found: 254.1296.



1-(Cyclopent-2-en-1-yl)-1H-benzo[d][1,2,3]triazole (**3w**)[6]: 23.3mg, yield: 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.49 – 7.42 (m, 1H), 7.40 – 7.36 (m, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.34 -6.31 (m, 1H), 6.20 – 6.18 (m, 1H), 6.01 - 5.99 (m, 1H), 2.90 – 2.78 (m, 1H), 2.78 – 2.61 (m, 2H), 2.29 – 2.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.70, 137.07, 131.96, 128.45, 126.87, 123.77, 120.11, 110.26, 65.84, 32.05, 30.16.

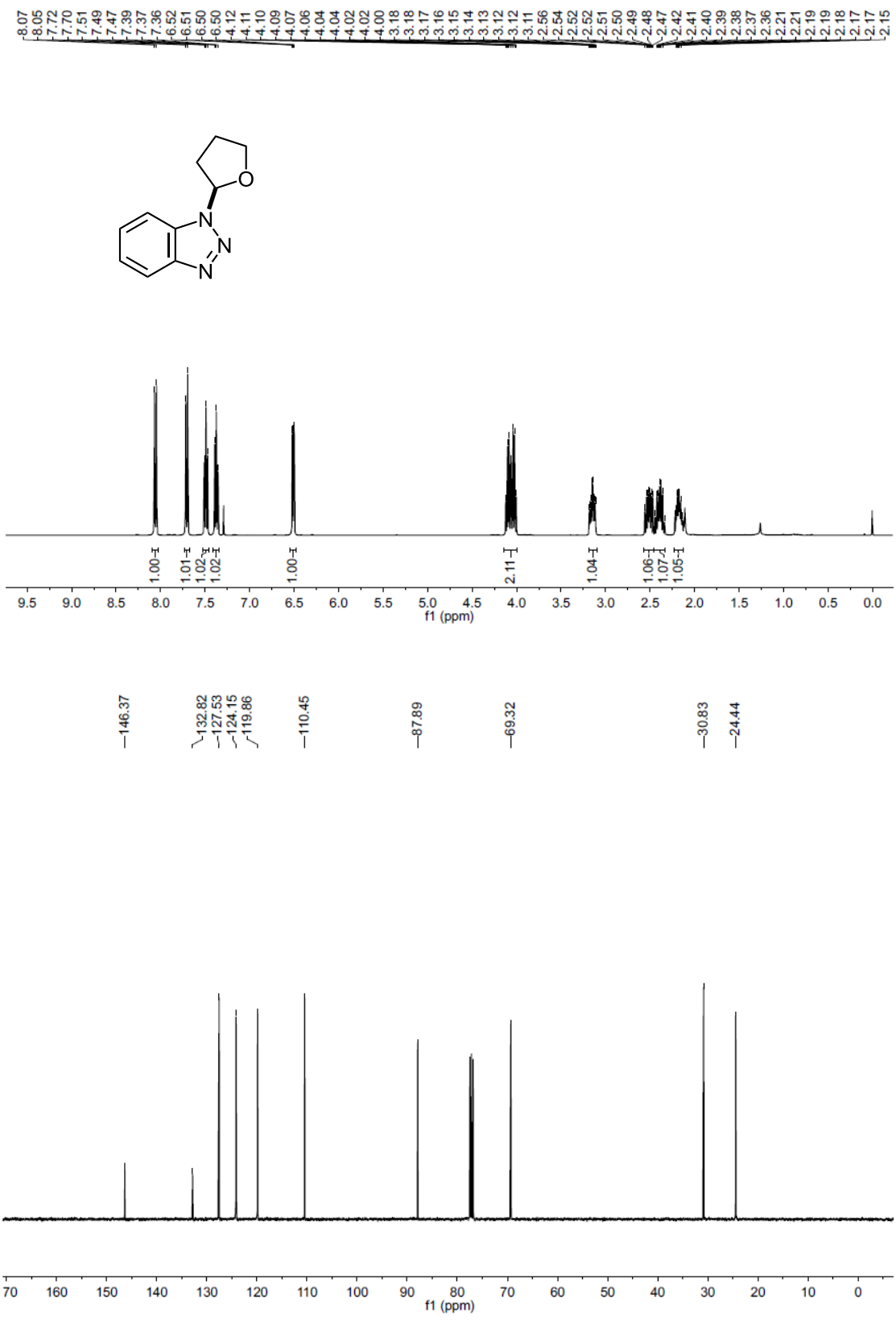


4-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)-2,6-di-tert-butylphenol (5a): 76.8 mg, yield: 76%.

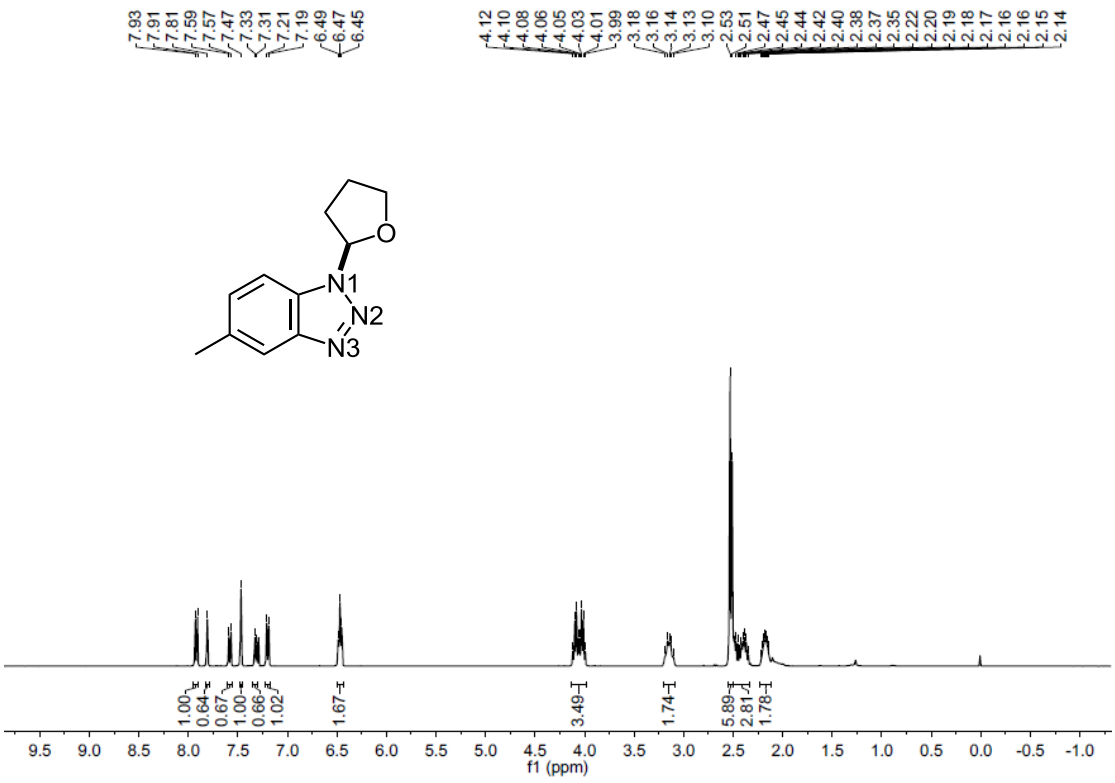
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 1H), 7.46 (q, *J* = 8.7 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.20 (s, 2H), 5.77 (s, 2H), 5.34 (d, *J* = 2.9 Hz, 1H), 1.41 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.95, 146.22, 136.50, 132.82, 127.20, 125.42, 124.86, 123.81, 119.95, 109.93, 52.71, 34.33, 30.17.
HRMS (ESI) calculated for $C_{21}H_{27}N_3O$ $[M+H]^+$: 338.2227; found: 338.2230.

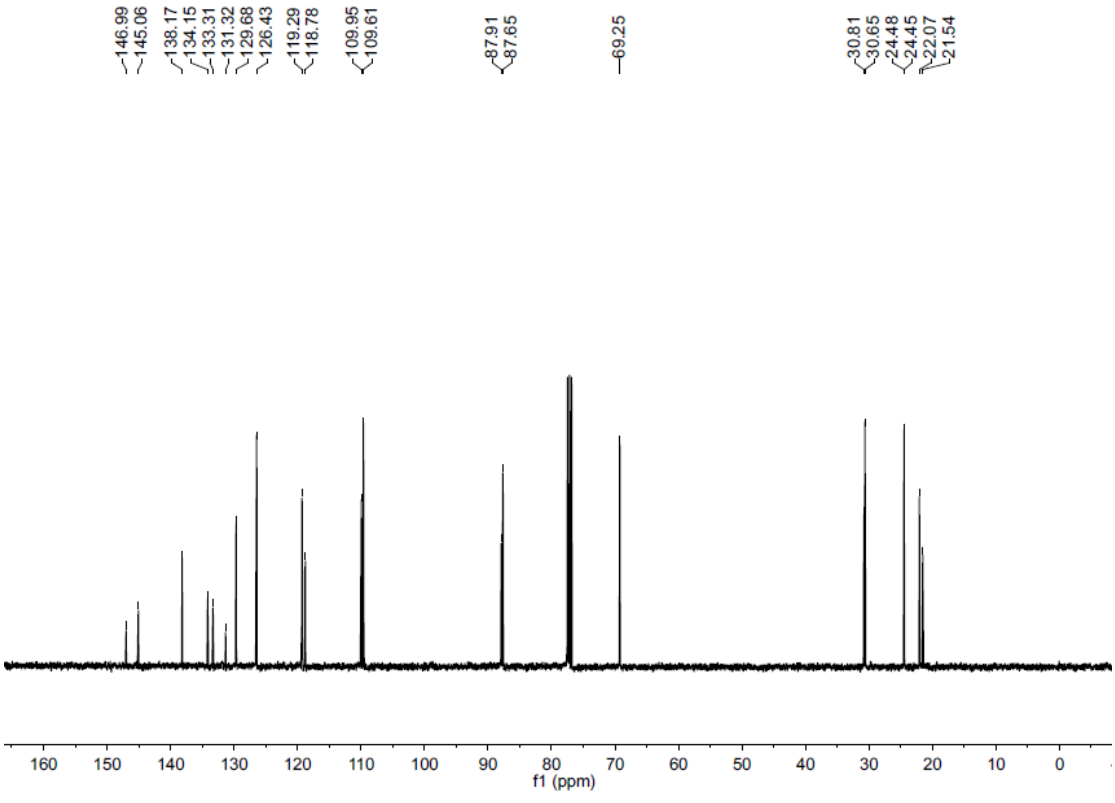
6. Copies of product NMR spectra

1-(Tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3a)

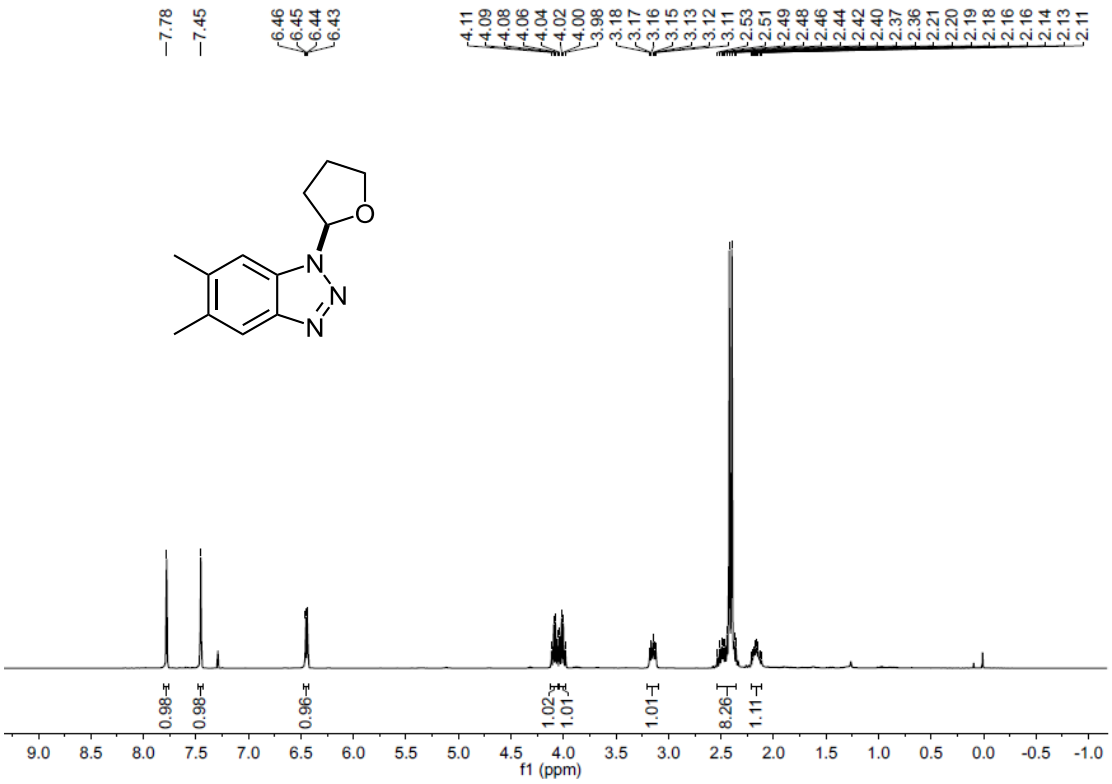


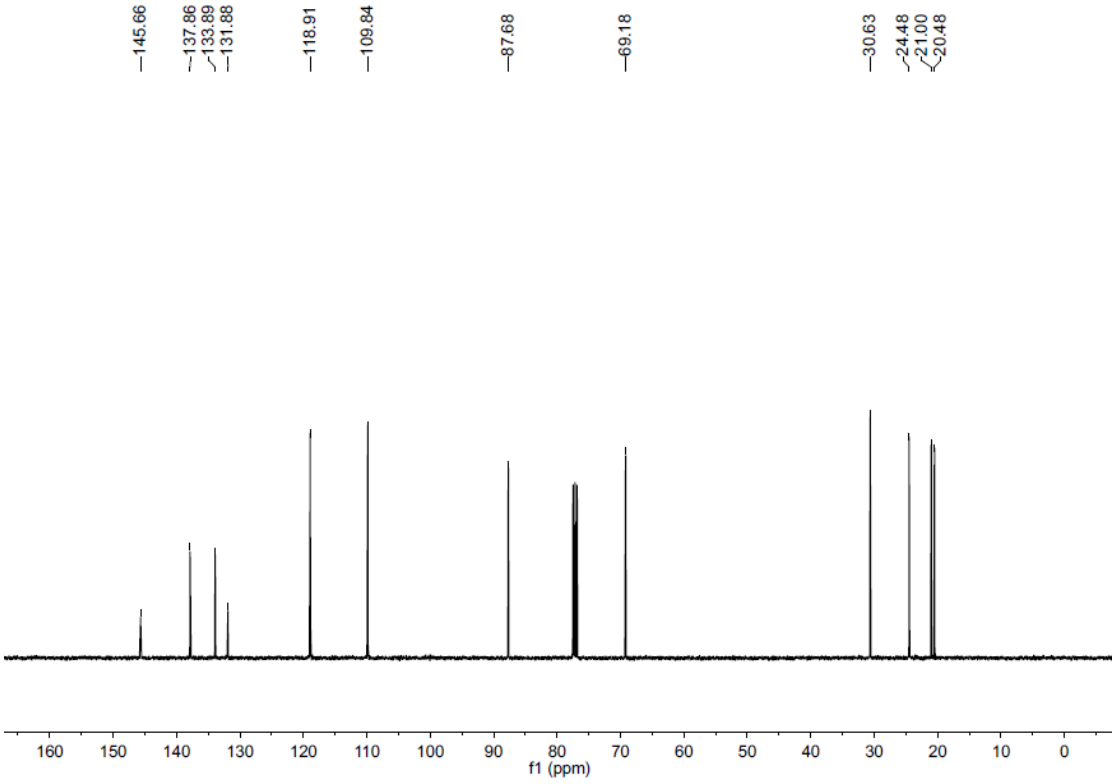
5-Methyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole and **6-Methyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole** (**3b**, N1/N3 = 1/1.6)



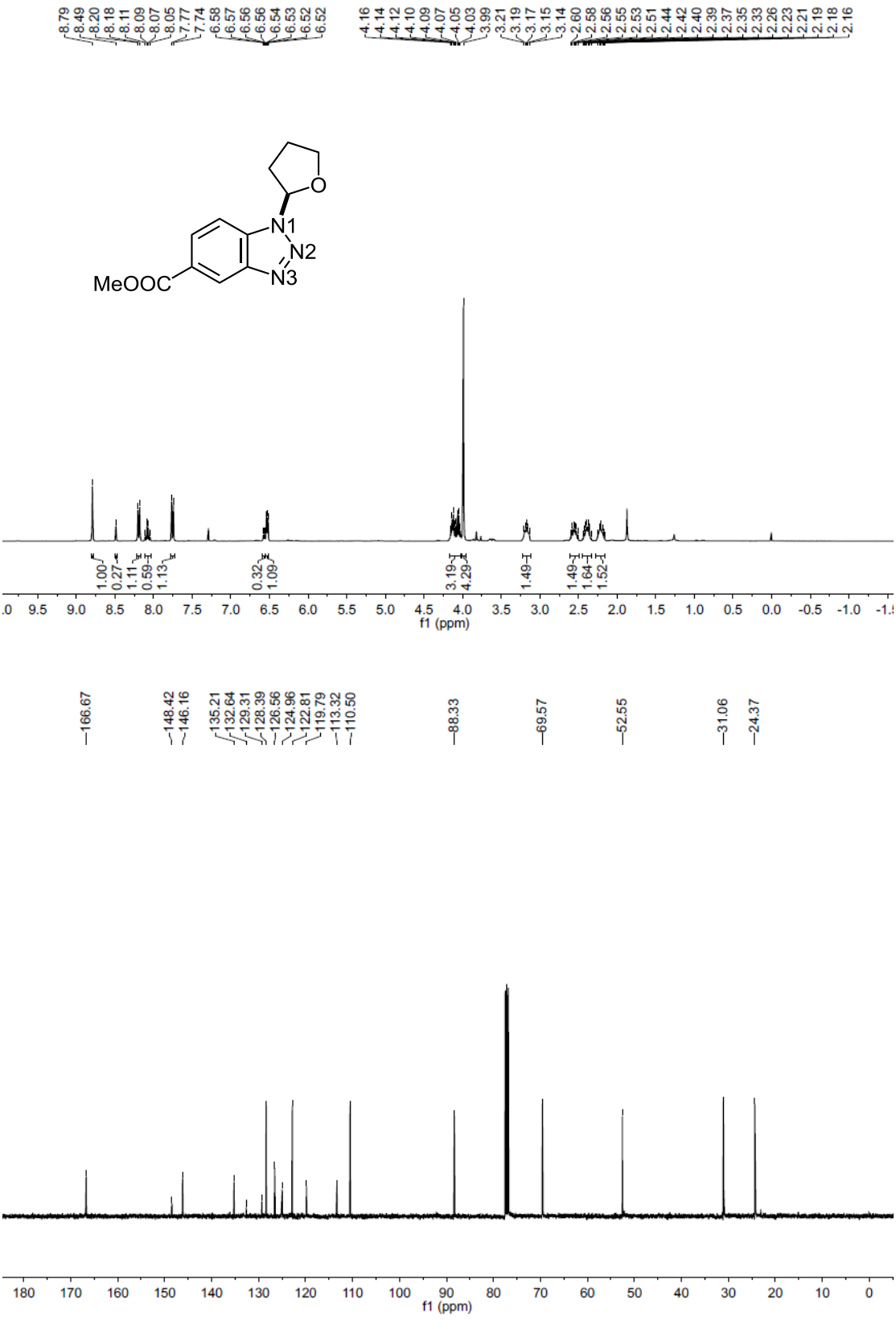


5,6-Dimethyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3c)

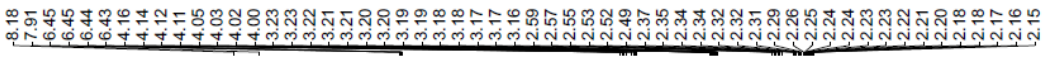


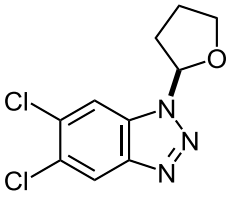


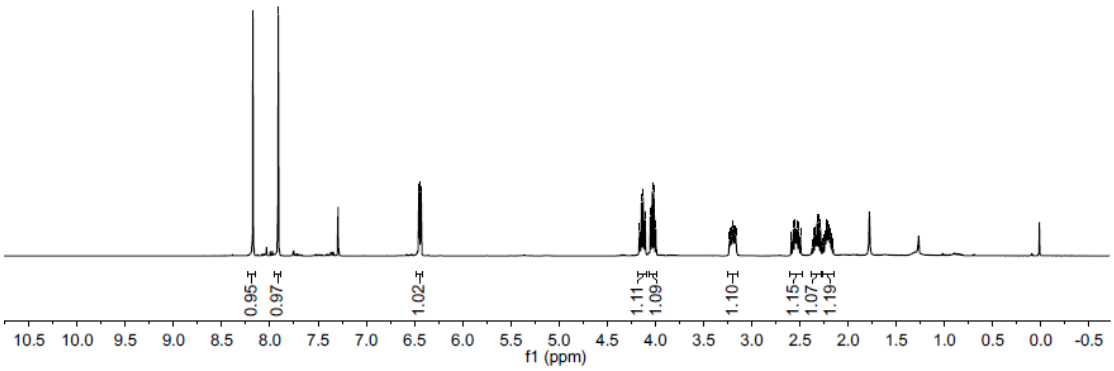
Methyl-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole-5-carboxylate and **Methyl 1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole-6-carboxylate** (**3d,** N1/N3 = 1/3.7)

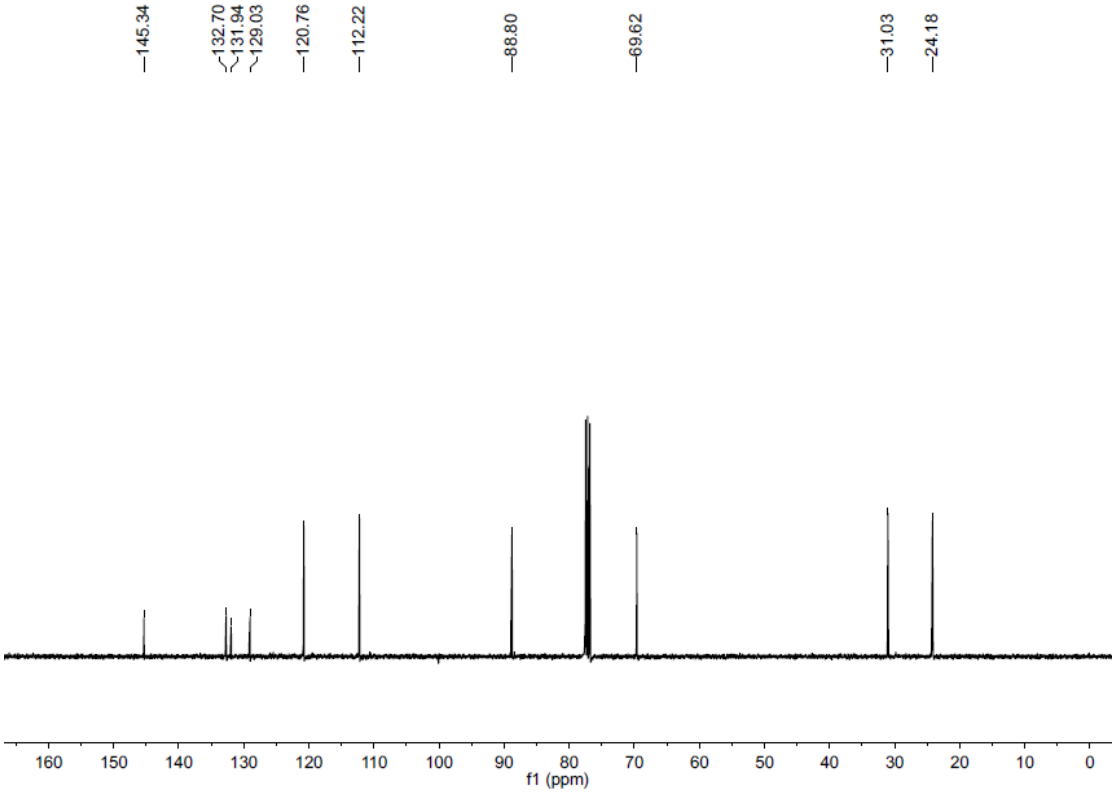


5,6-Dichloro-1-(tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3e)

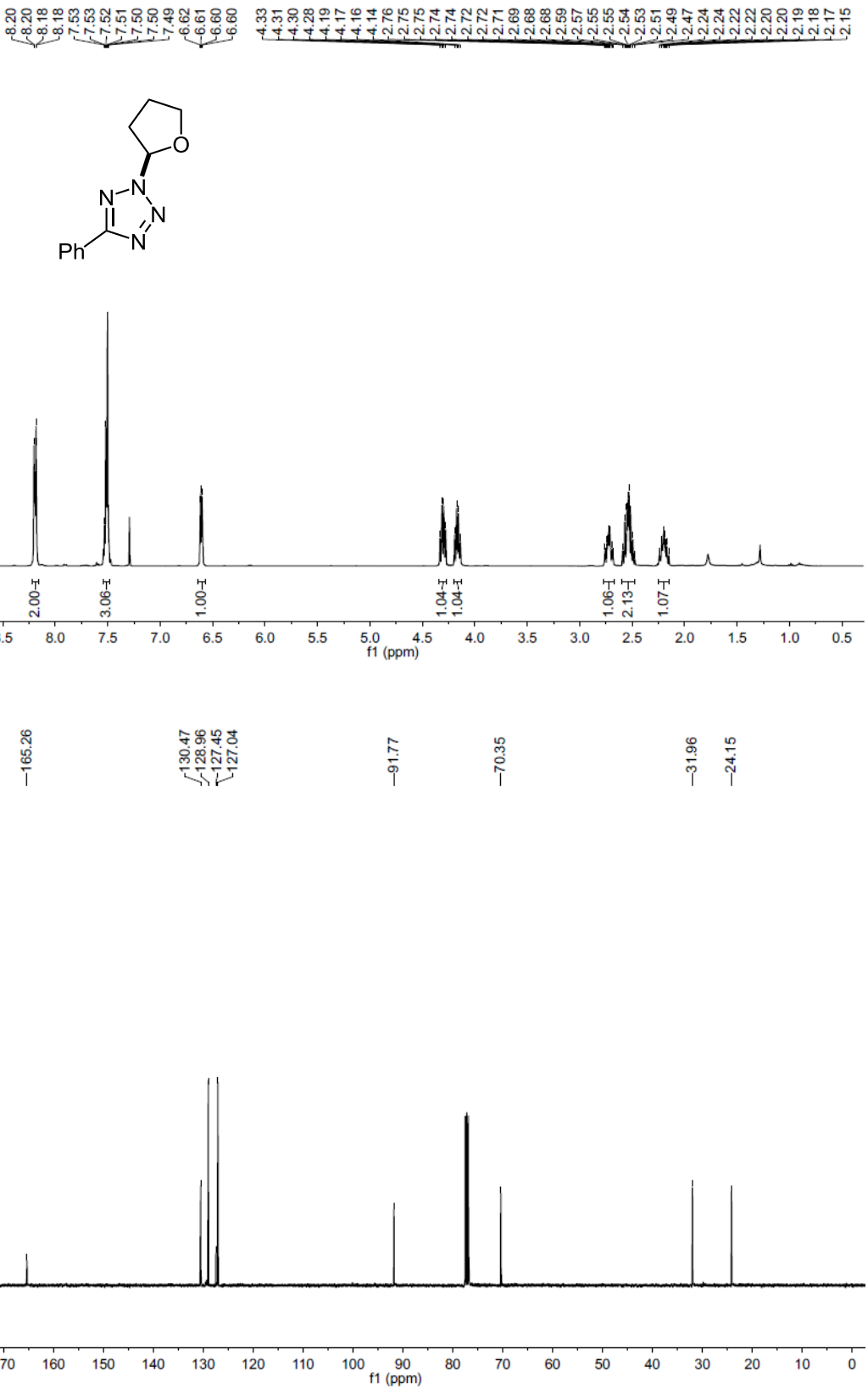




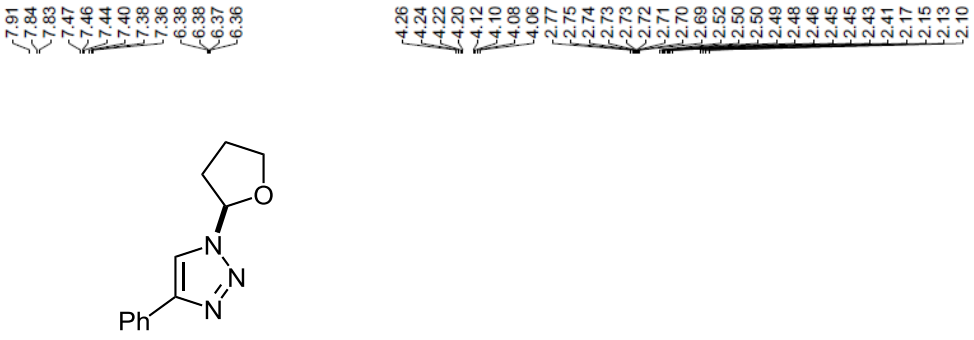


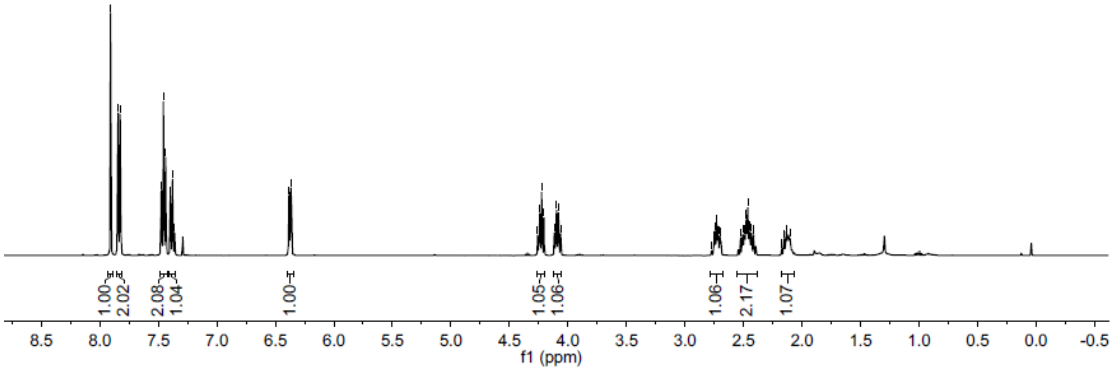


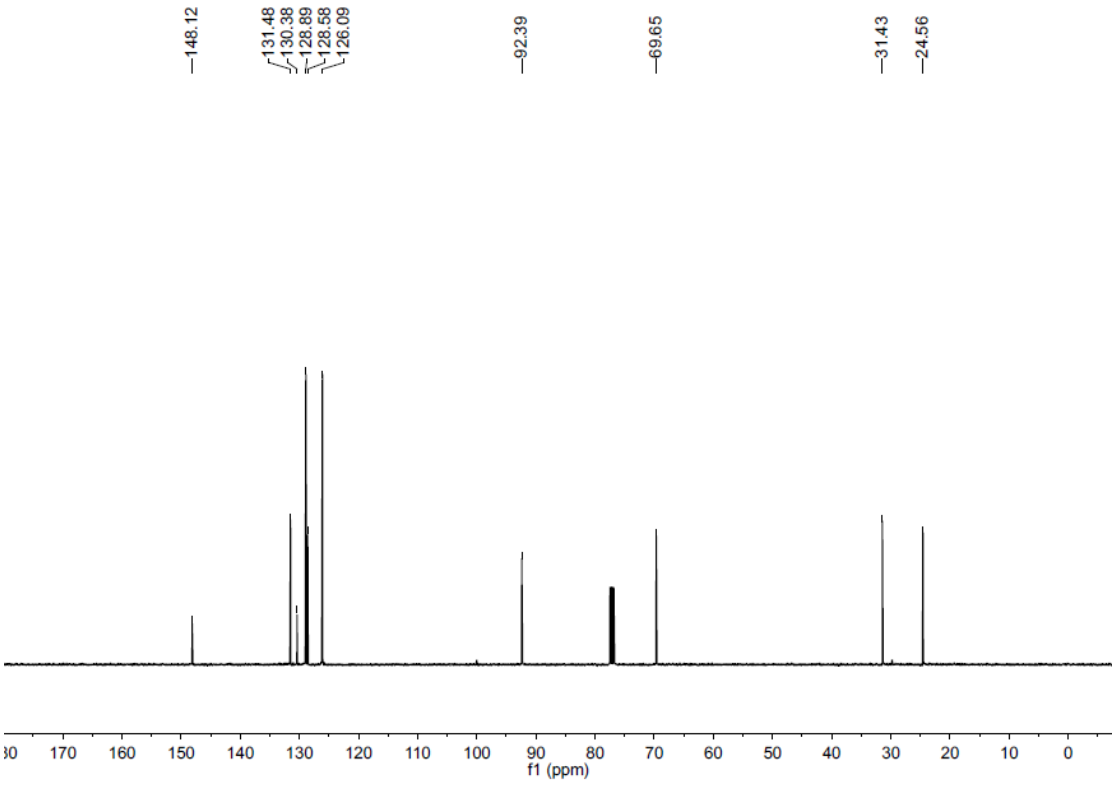
5-Phenyl-2-(tetrahydrofuran-2-yl)-2H-tetrazole (3f)



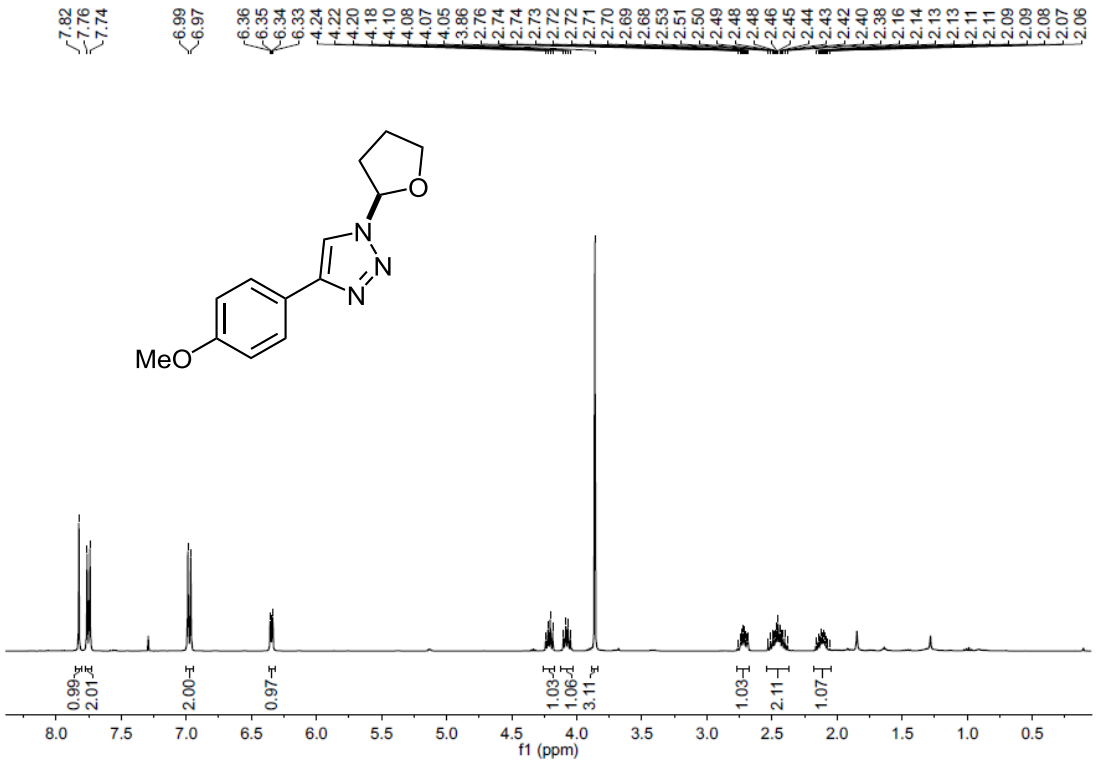
4-Phenyl-1-(tetrahydrofuran-2-yl)-1H-1,2,3-triazole (3g)

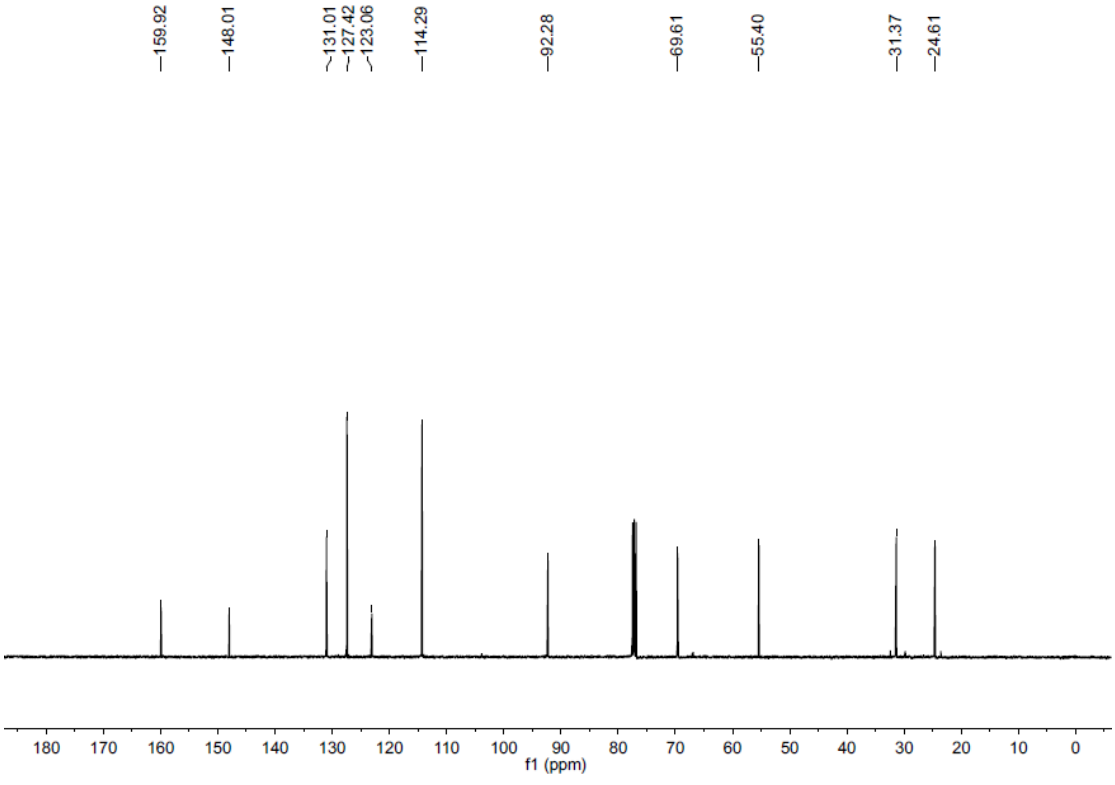




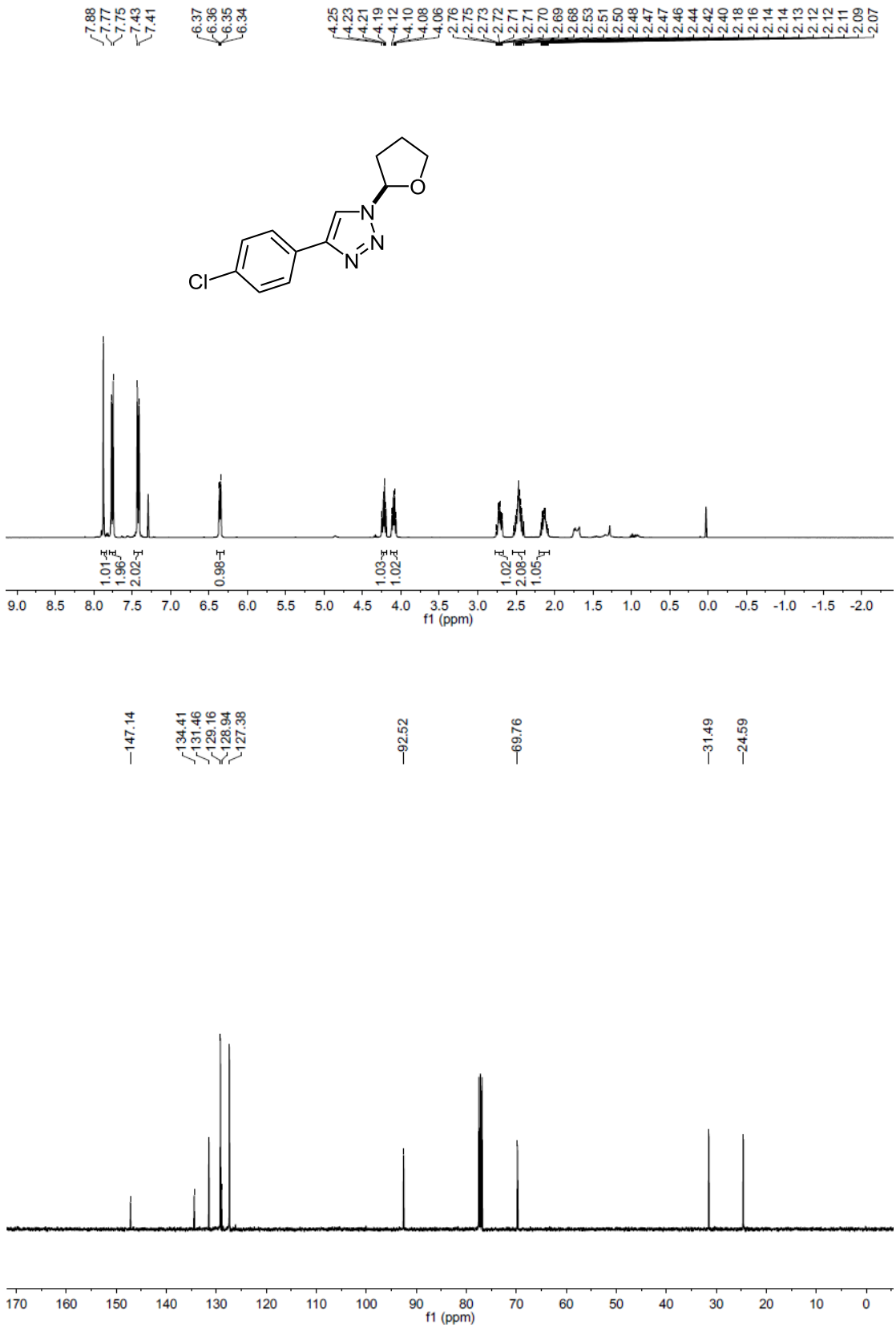


4-(4-Methoxyphenyl)-1-(tetrahydrofuran-2-yl)-1H-1,2,3-triazole (3h)

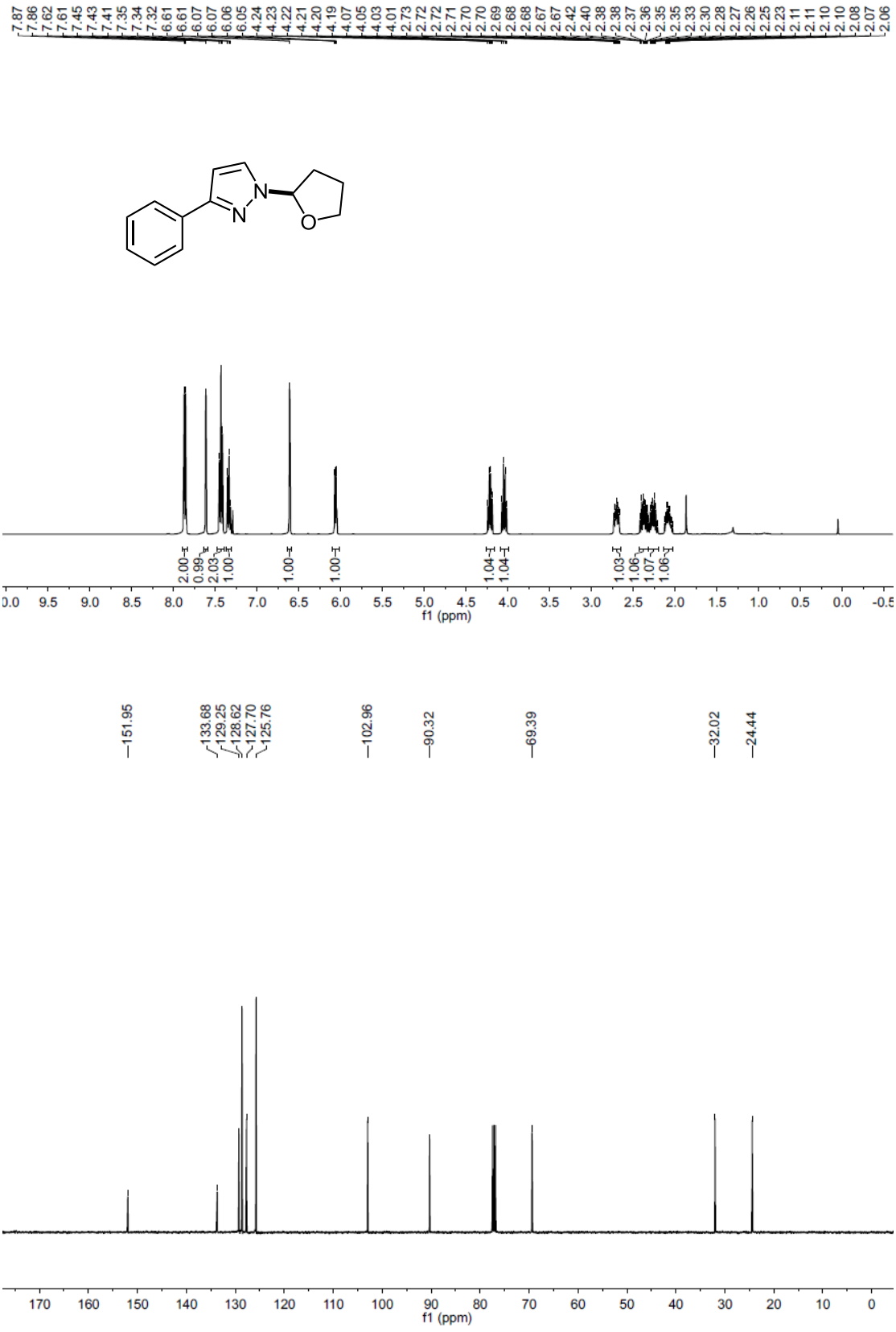




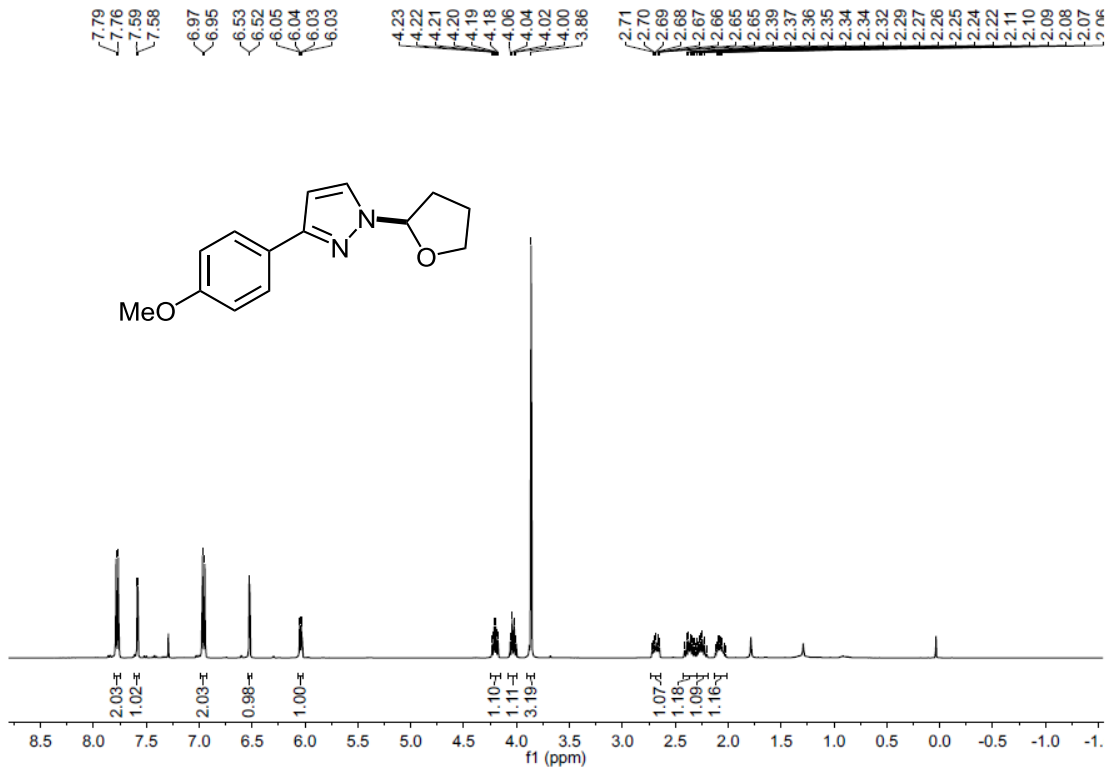
4-(4-Chlorophenyl)-1-(tetrahydrofuran-2-yl)-1H-1,2,3-triazole (3i)

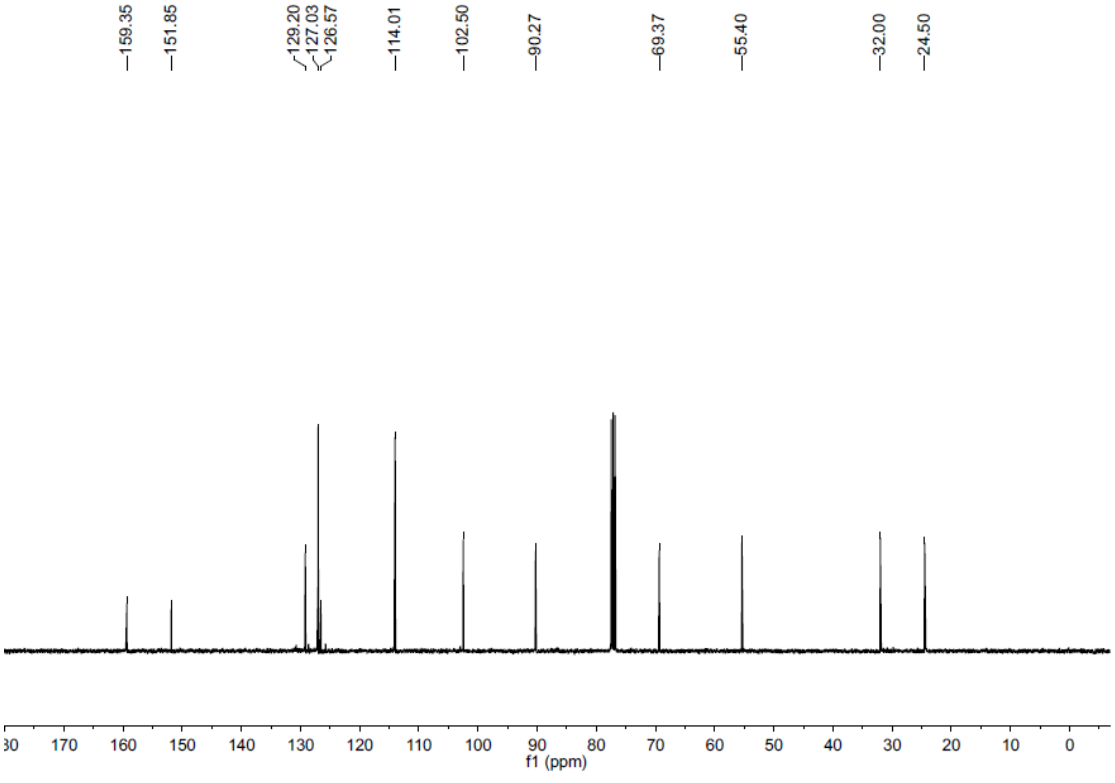


3-Phenyl-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3j)

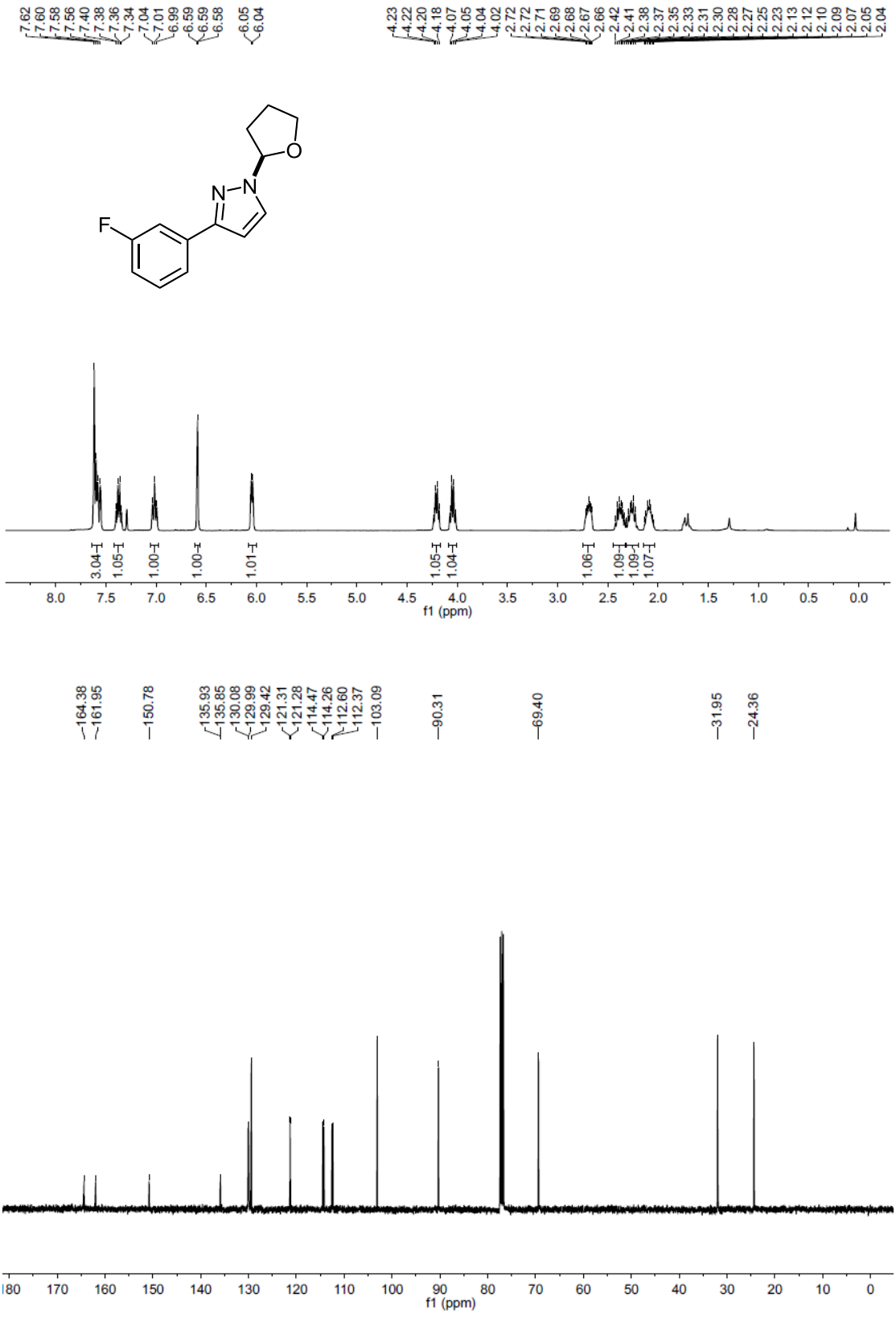


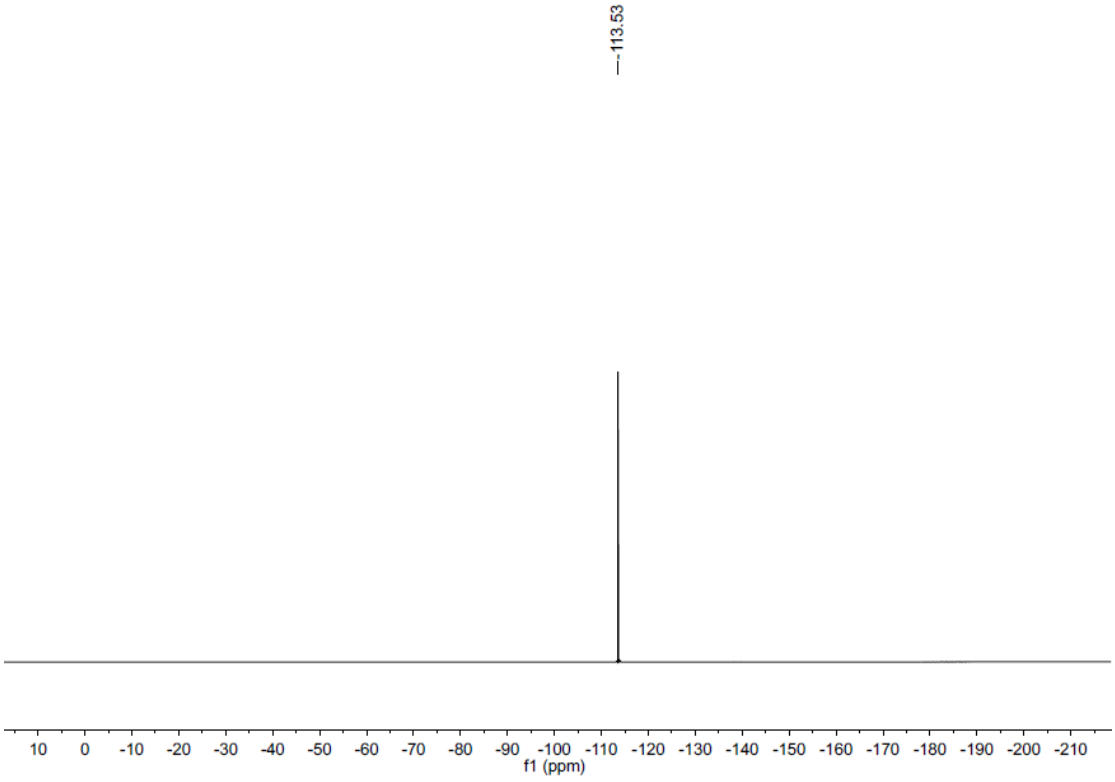
3-(4-Methoxyphenyl)-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3k)



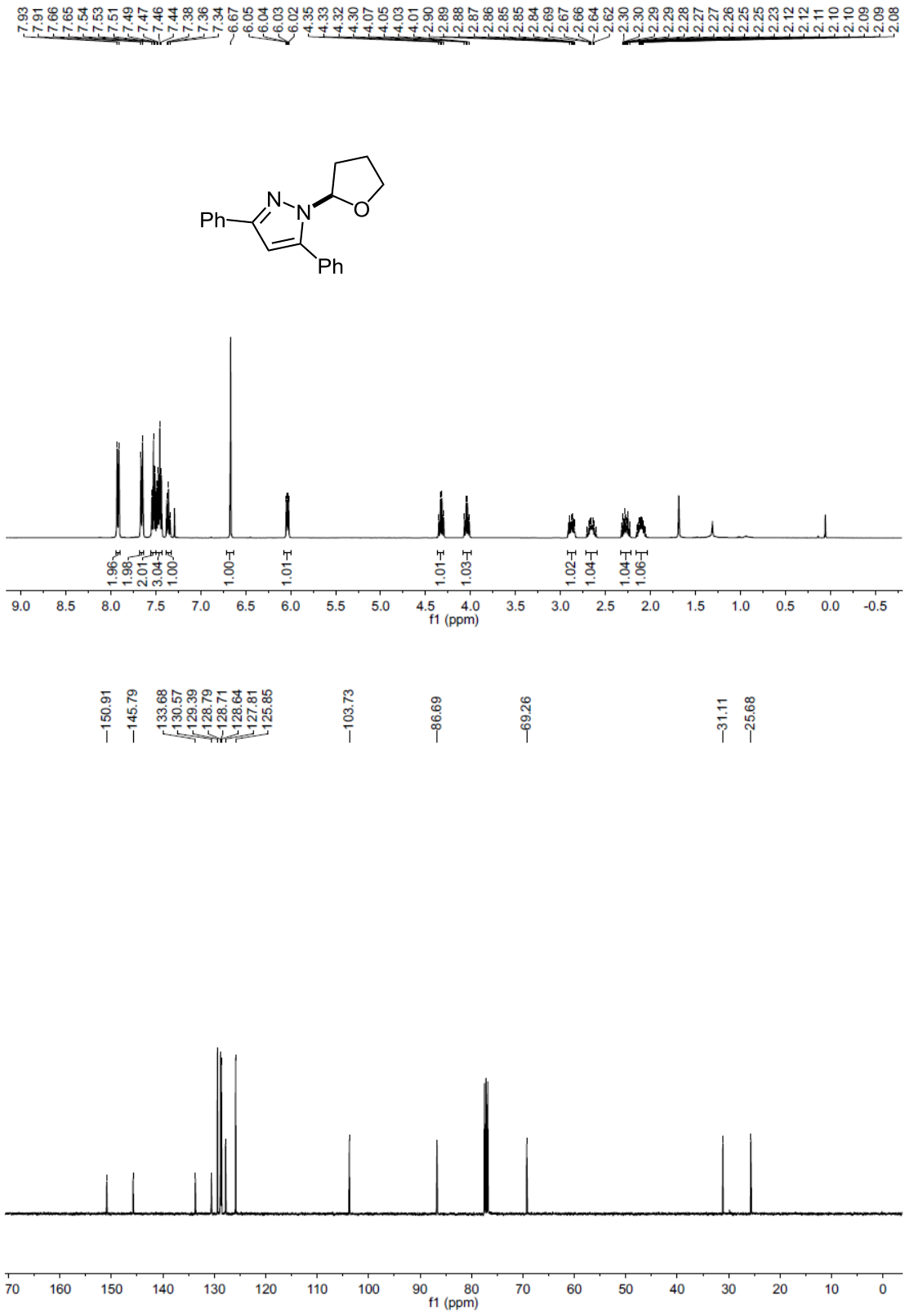


3-(3-Fluorophenyl)-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3l)

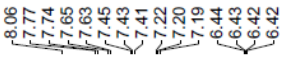


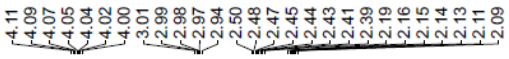

-113.53
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

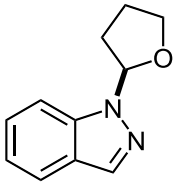
3,5-diphenyl-1-(tetrahydrofuran-2-yl)-1H-pyrazole (3m)

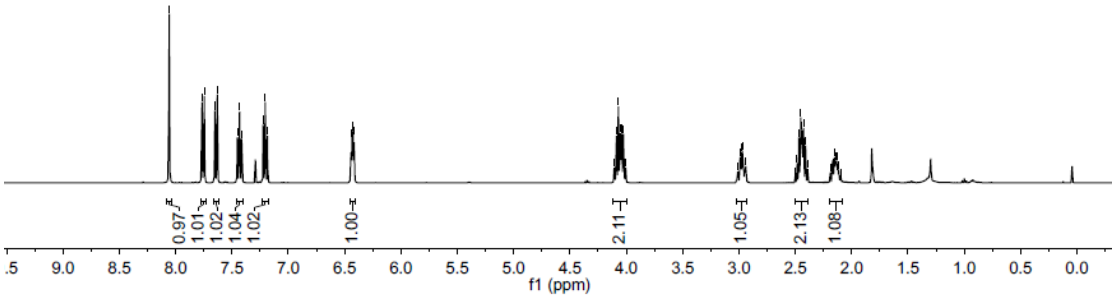


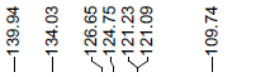
1-(Tetrahydrofuran-2-yl)-1H-indazole (3n)

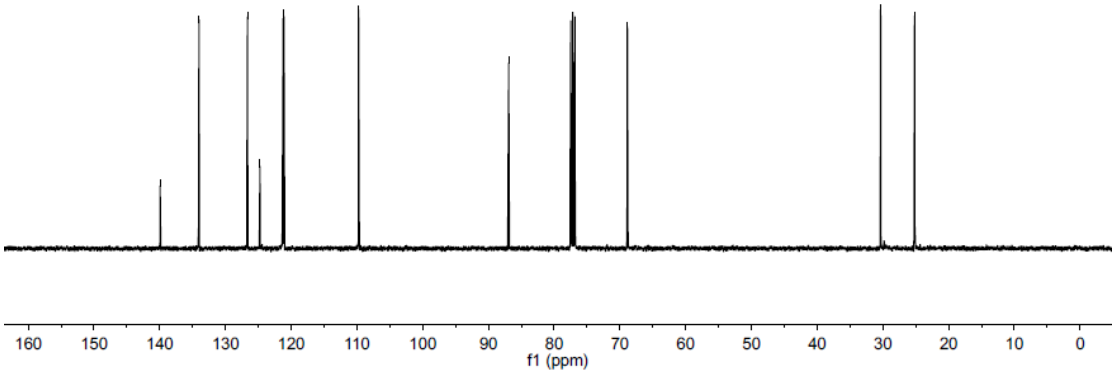




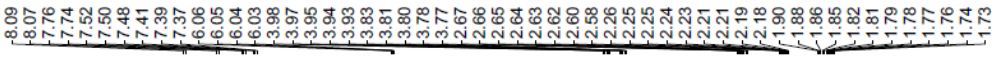


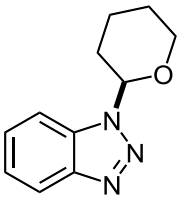


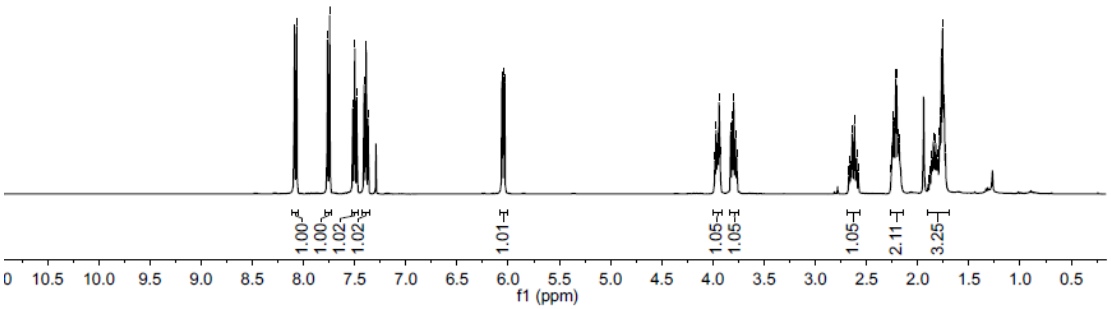


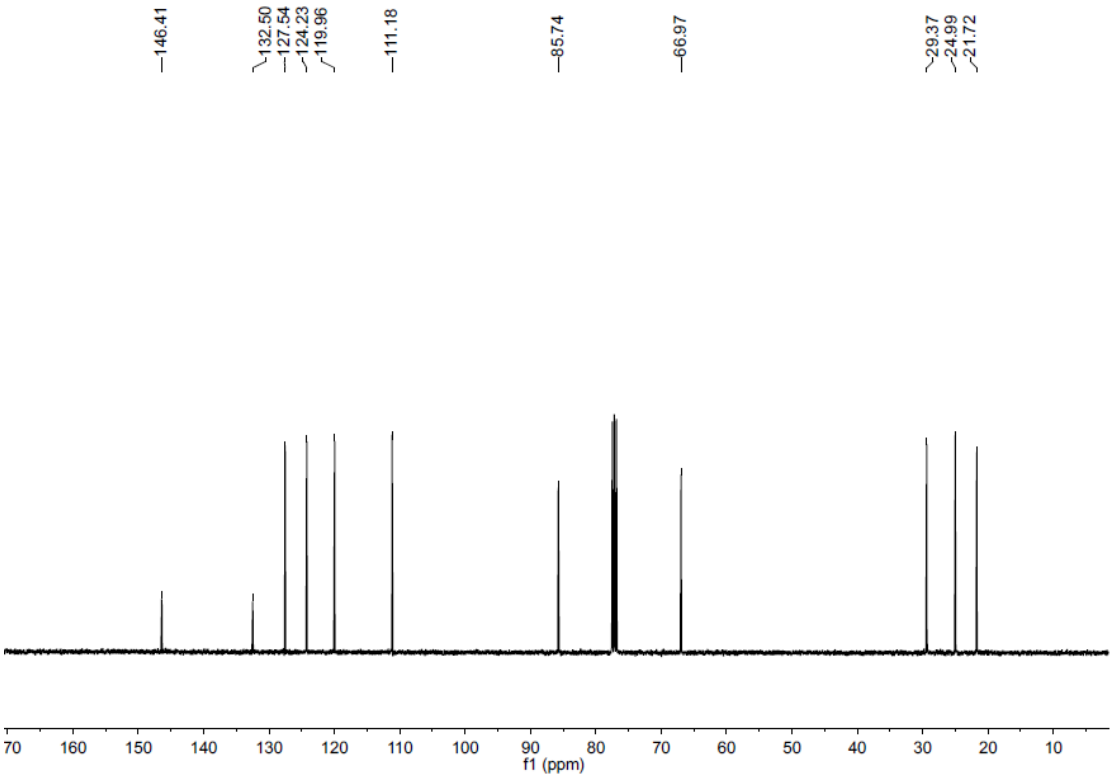


1-(Tetrahydro-2H-pyran-2-yl)-1H-benzo[d][1,2,3]triazole (3o)

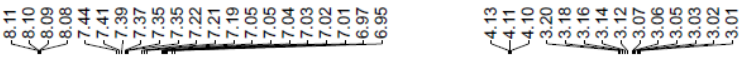


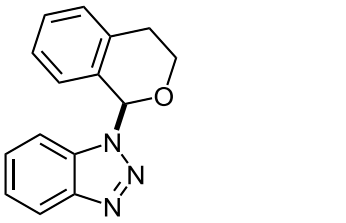


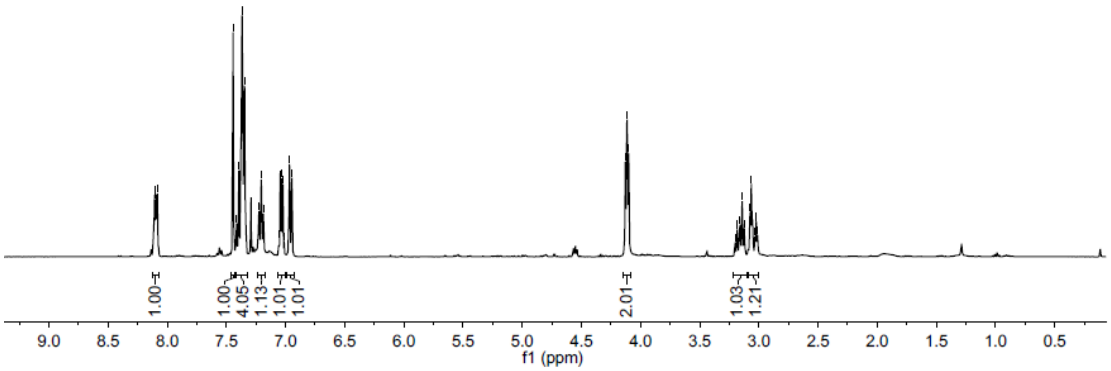


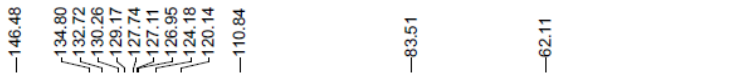


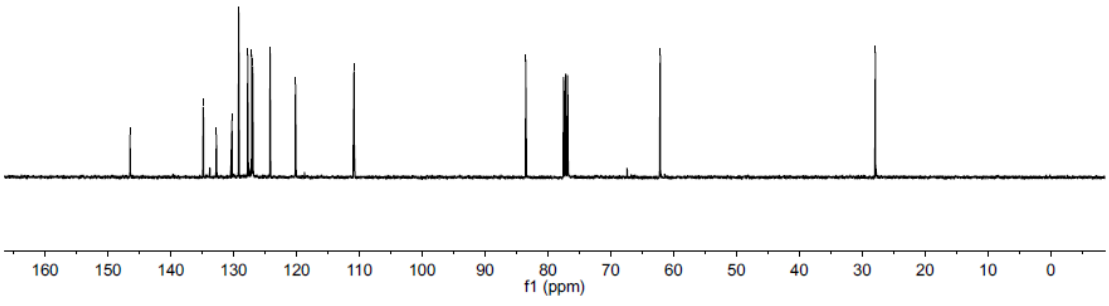
1-(Isochroman-1-yl)-1H-benzo[d][1,2,3]triazole (3p)



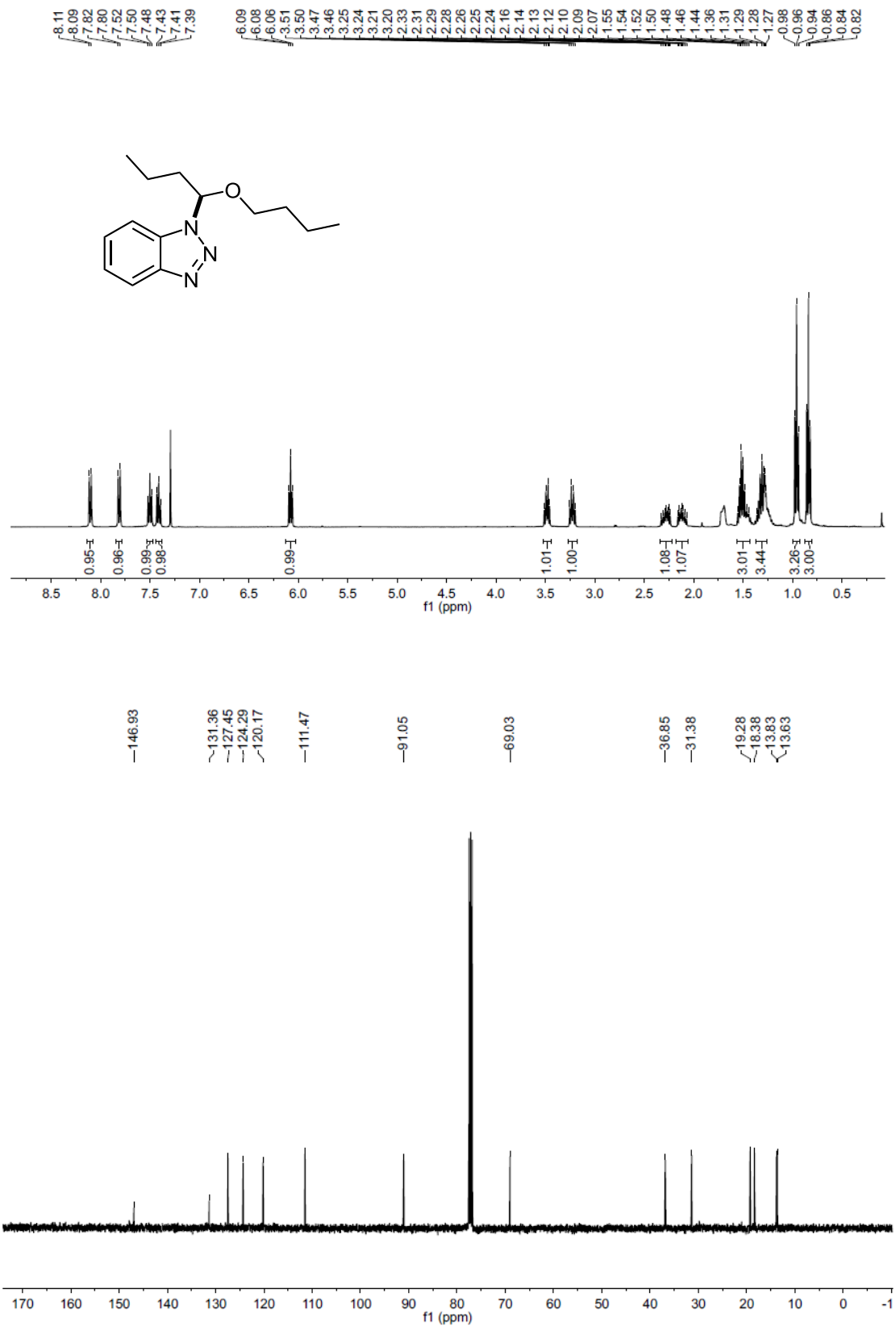




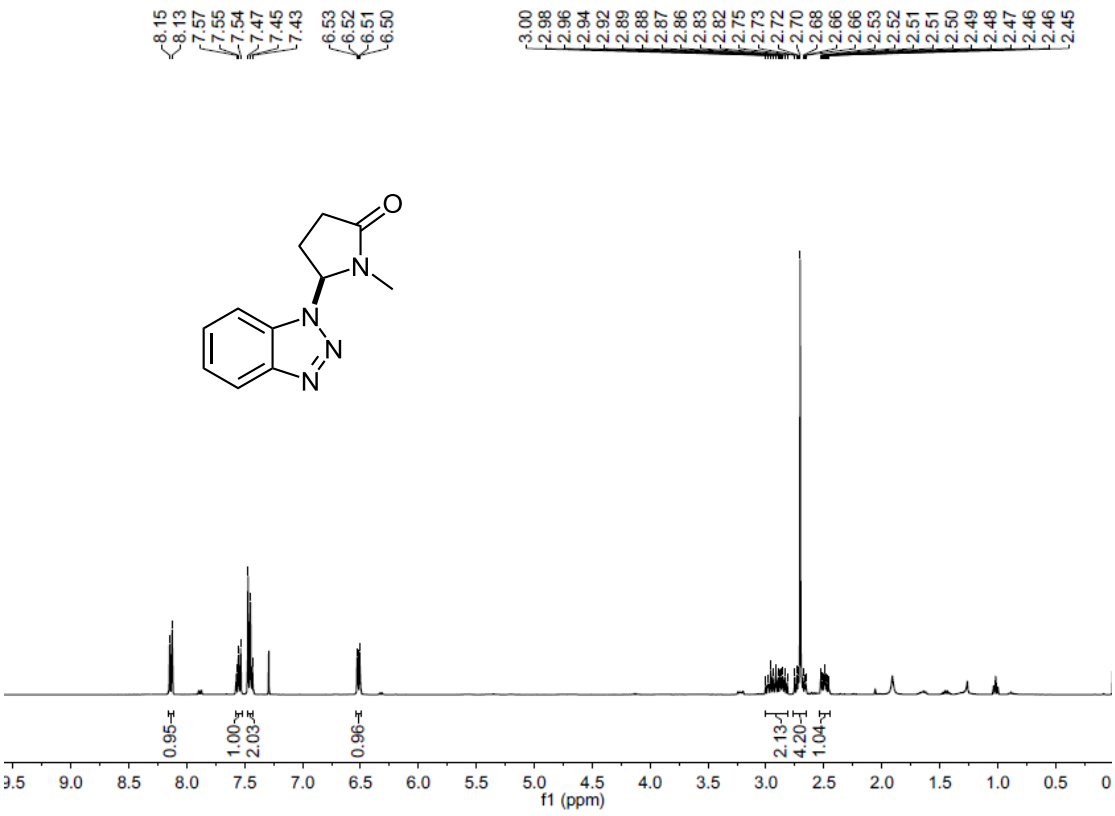


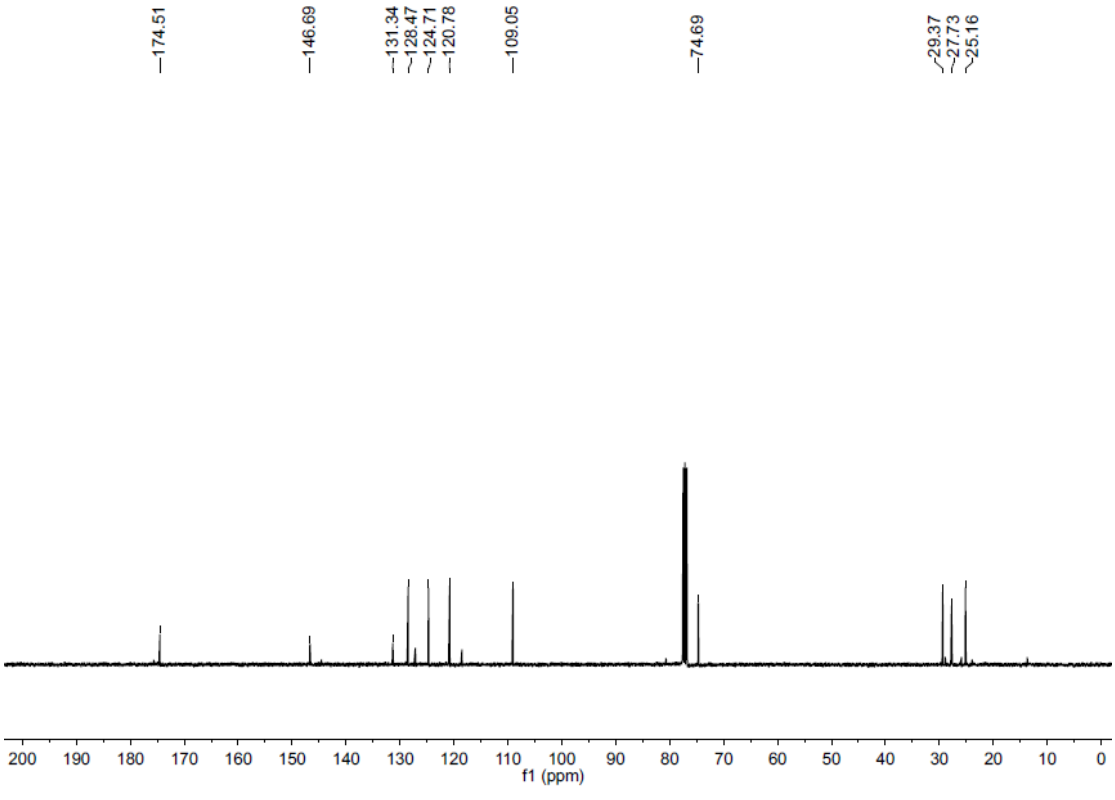


1-(1-Butoxybutyl)-1H-benzo[d][1,2,3]triazole (3q)

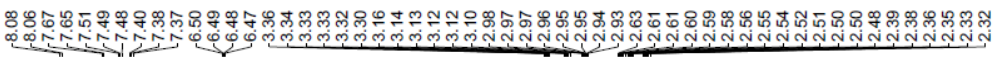


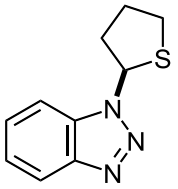
5-(1H-benzo[d][1,2,3]triazol-1-yl)-1-methylpyrrolidin-2-one (3r)

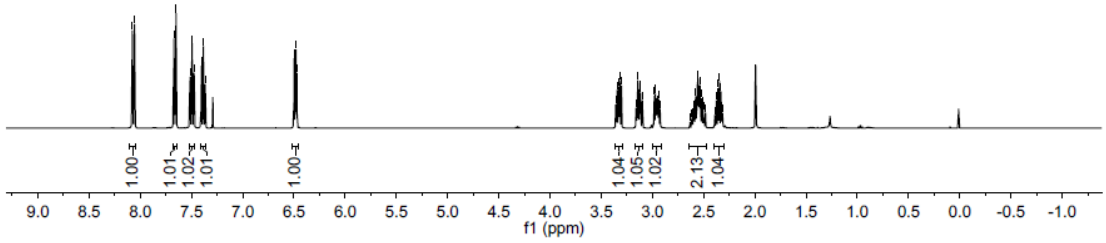


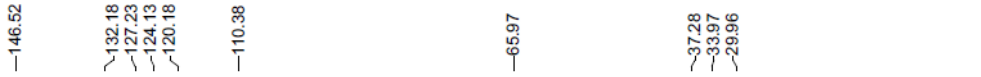


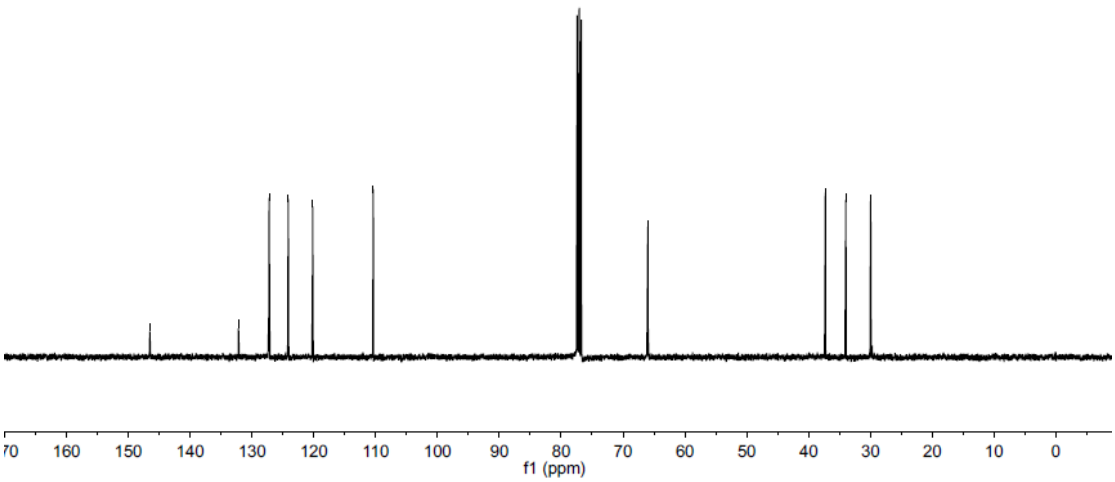
1-(Tetrahydrothiophen-2-yl)-1H-benzo[d][1,2,3]triazole (3s)



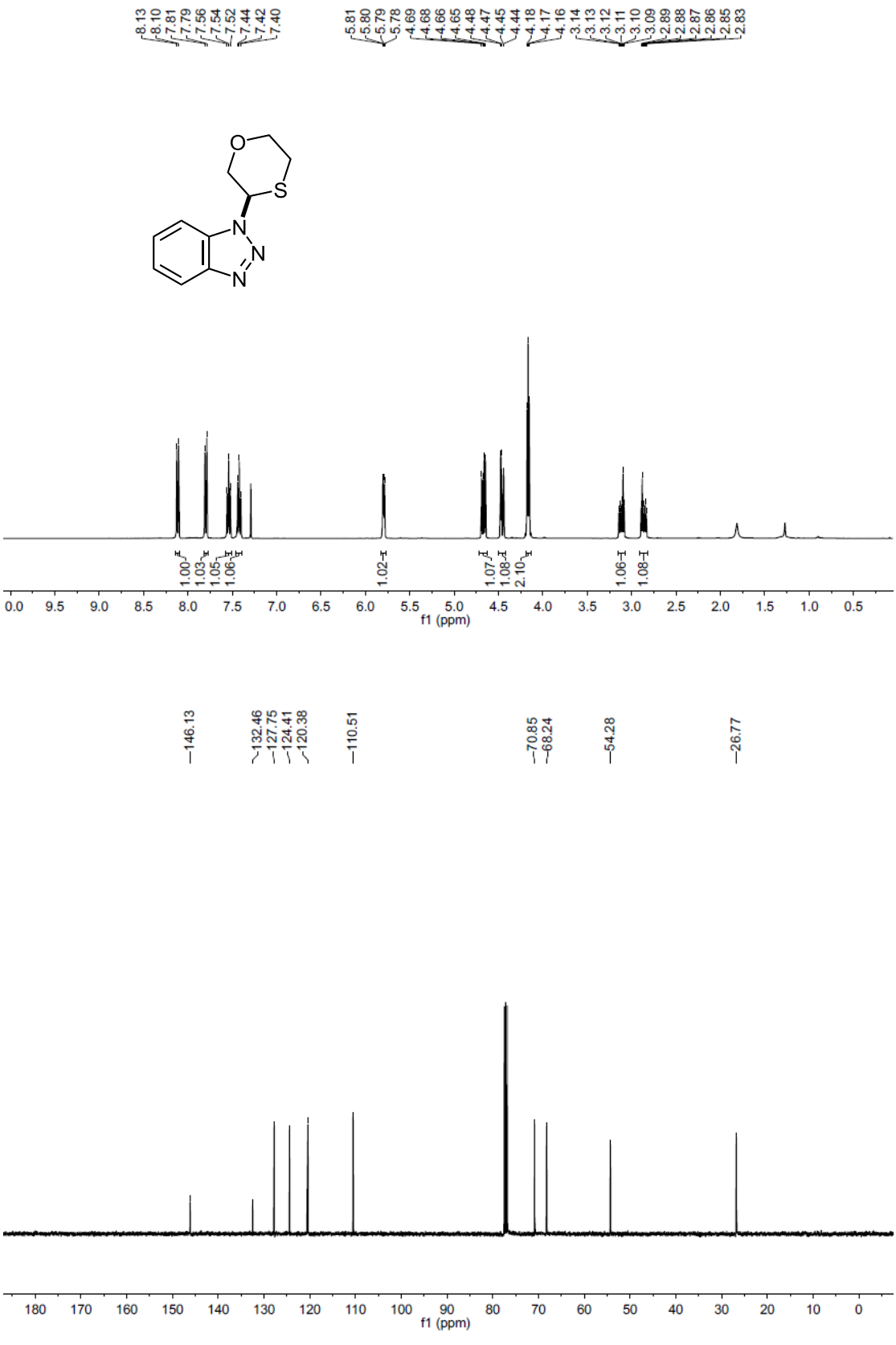




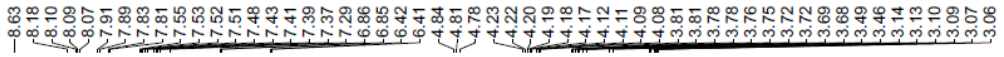


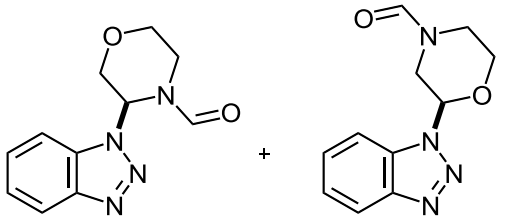


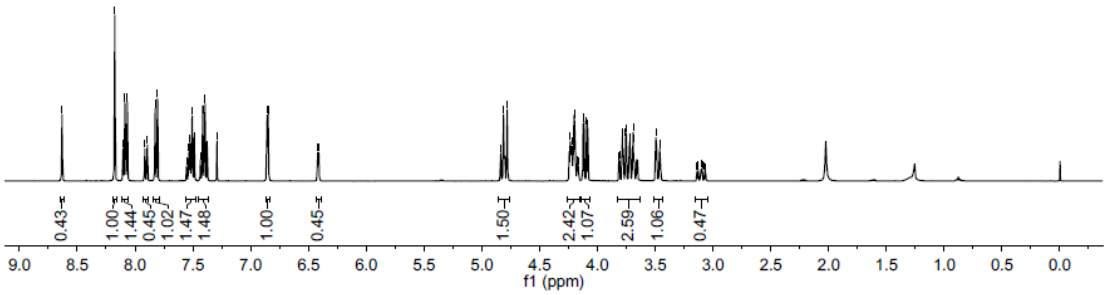
1-(1,4-Oxathian-3-yl)-1H-benzo[d][1,2,3]triazole (3t)

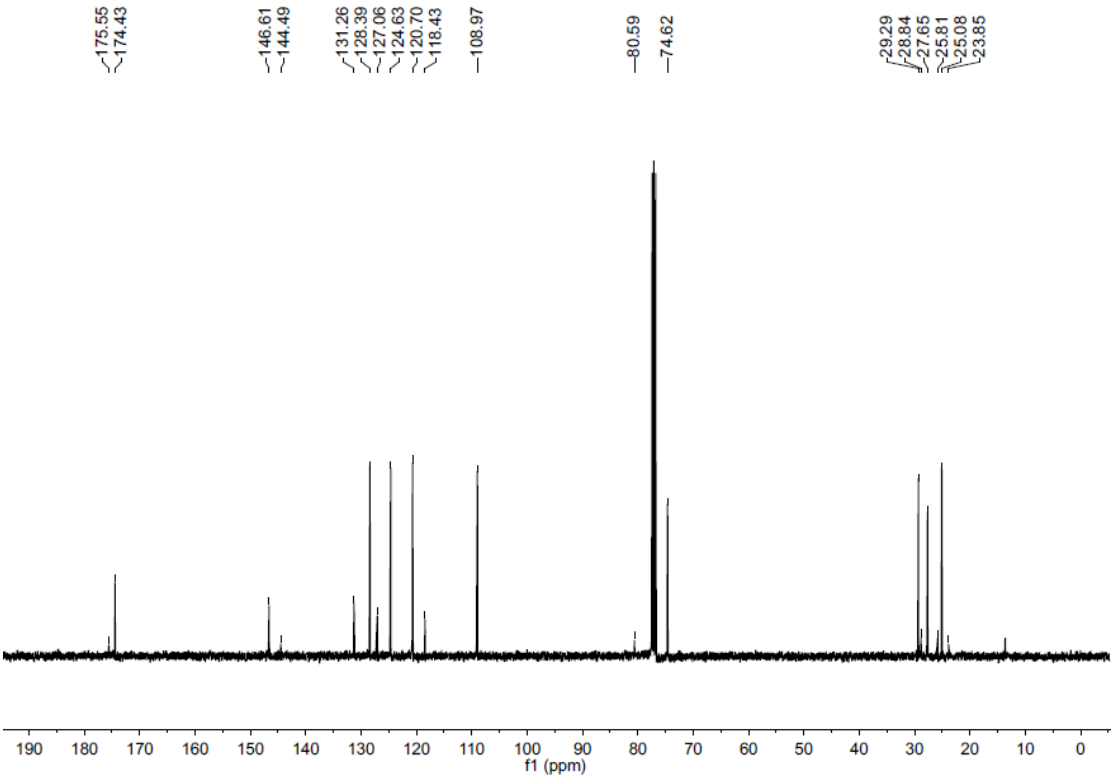


3-(1H-benzo[d][1,2,3]triazol-1-yl)morpholine-4-carbaldehyde and **2-(1H-benzo[d][1,2,3]triazol-1-yl)morpholine-4-carbaldehyde** (**3u/3u^{I}** = 2.3/1)

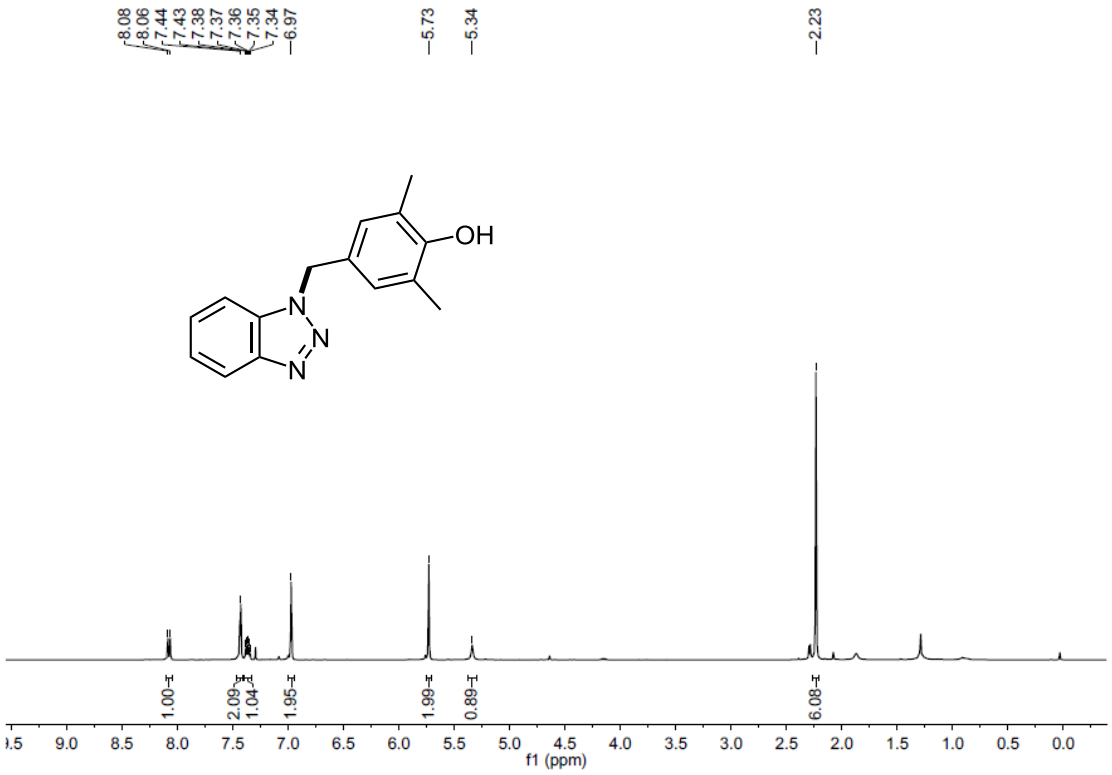


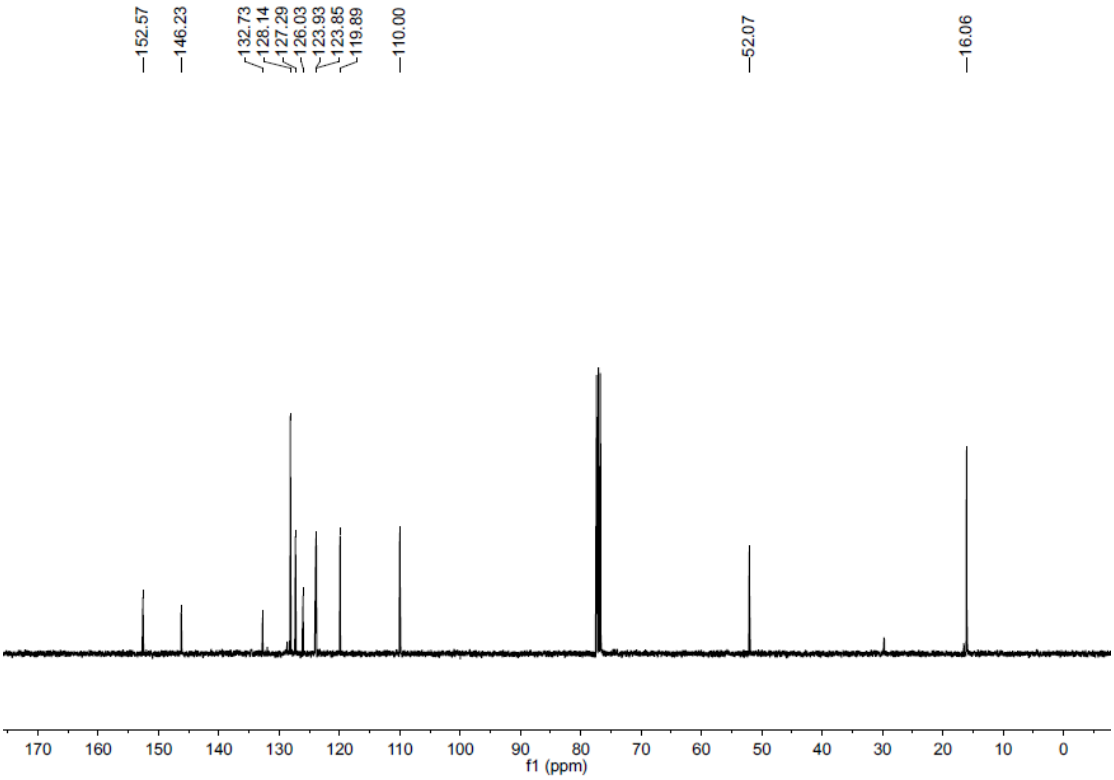




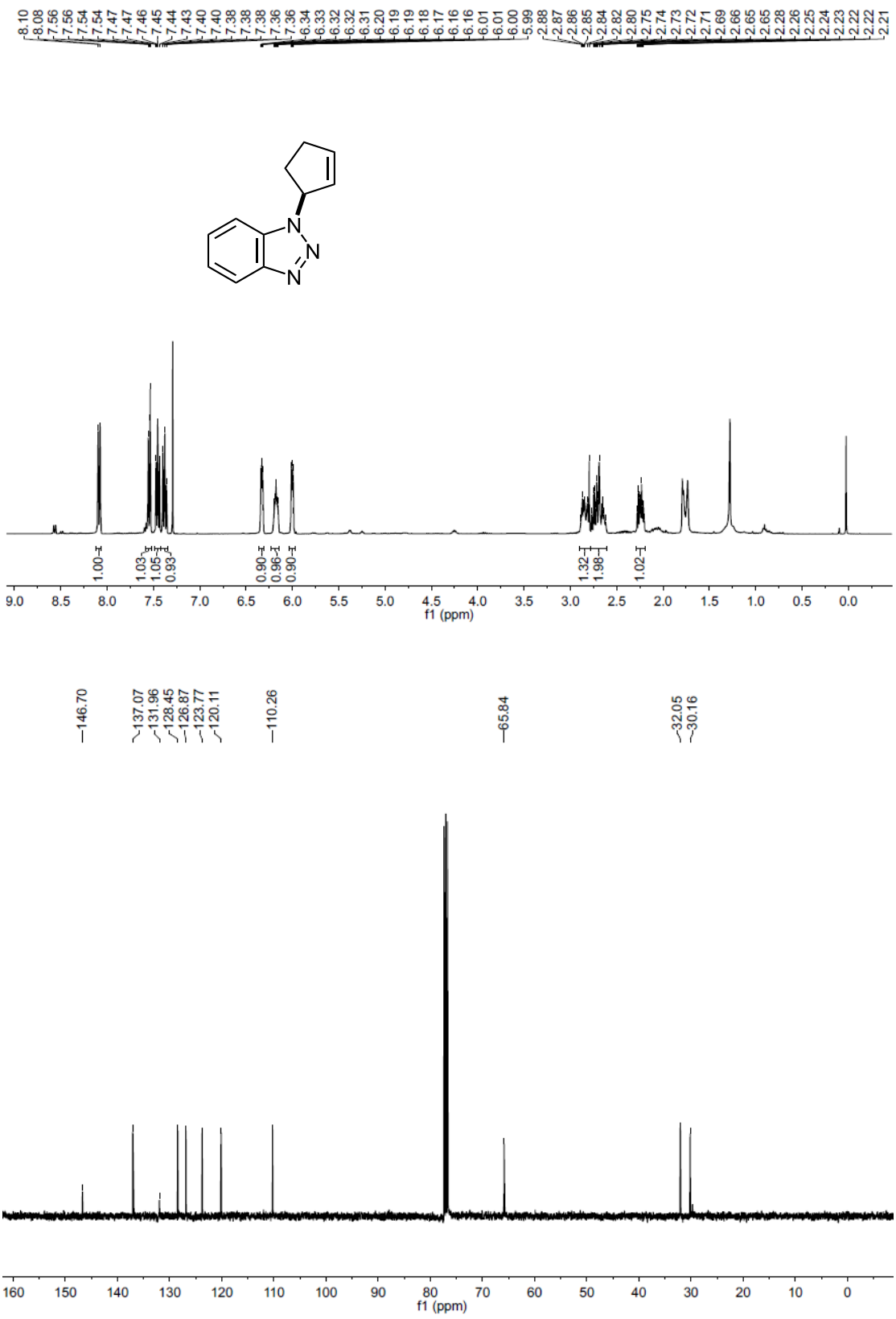


4-((1H-Benzo[d][1,2,3]triazol-1-yl)methyl)-2,6-dimethylphenol (3v)

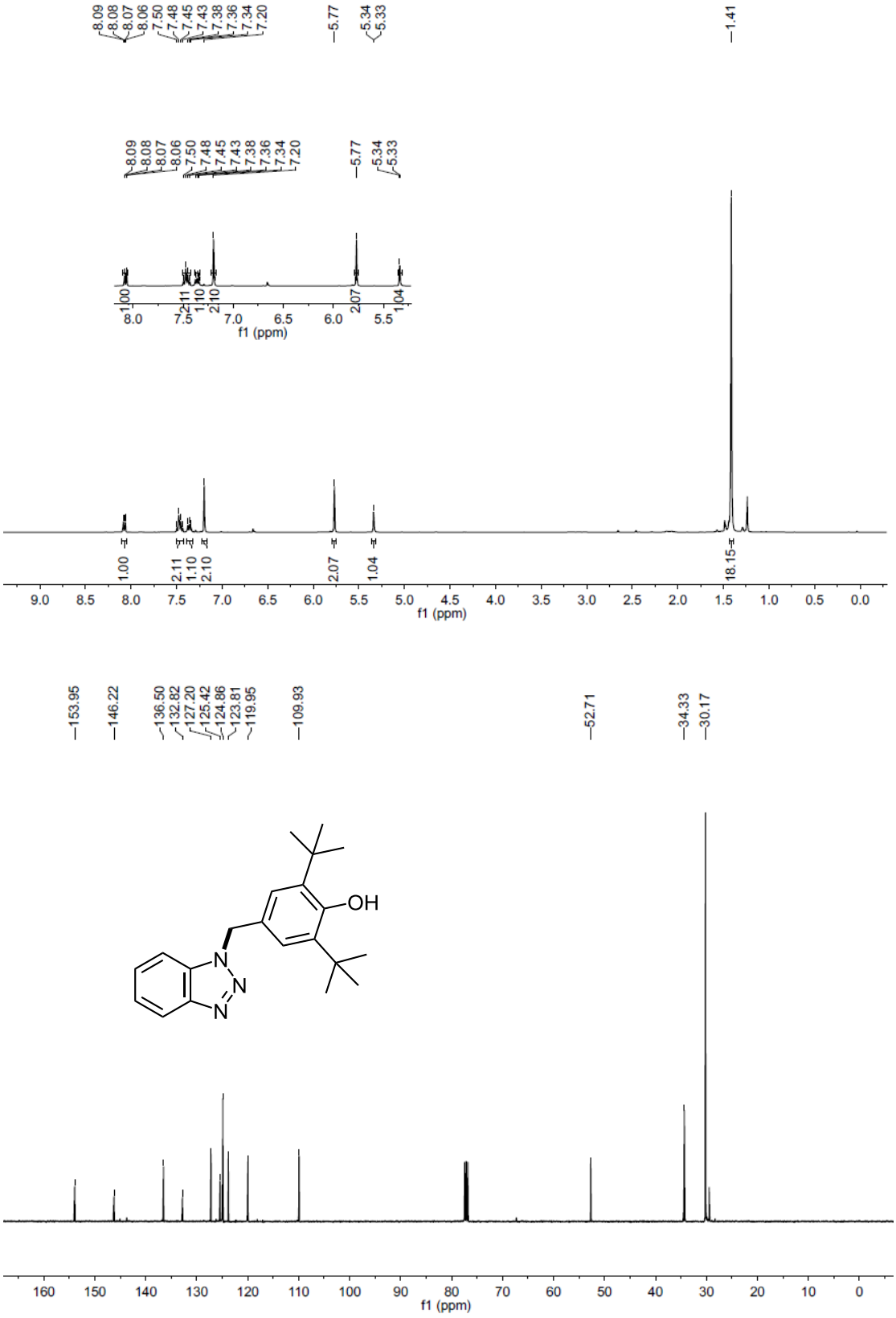




1-(Cyclopent-2-en-1-yl)-1H-benzo[d][1,2,3]triazole (**3w**)



4-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)-2,6-di-tert-butylphenol (5a)



7 References

[1] Singh, M. K.; Akula, H. K.; Satishkumar, S.; Stahl, L.; Lakshman, M. K. *ACS Catal.* **2016**, 6, 1921−1928.

[2] Wang, L.; Zhu, K.; Wu, W.; Chen, Q.; He, M. *Catal. Sci. Technol.* **2015**, 5, 2891–2896.

[3] Aruri, H.; Singh, U.; Sharma, S.; Gudup, S.; Bhogal, M.; Kumar, S.; Singh, D.; Gupta, V. K.; Kant, R.; Vishwakarma, R. A.; Singh, P. P. *J. Org. Chem.* **2015**, 80, 1929−1936.

[4] Sha, Q.; Liu, H.; Wei, Y. *Eur. J. Org. Chem.* **2014**, 79, 7707–7715.

[5] Sun, J.; Zhang, Y.; Mathan, S.; Wang, Y.; Pan, Y. *J. Org. Chem.* **2016**, 81, 3380−3385.

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