Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Copper(I) Complexes as Catalysts for the Synthesis of N-sulfonyl-1,2,3-triazoles from N-sulfonylazides and Alkynes

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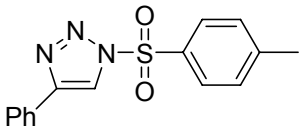
General Methods. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. The chemicals were purchased and used without purification The complexes $[Tpm^{X}Cu(NCMe)]BF_4$[1] and sulfonyl azides[2] were prepared according to literature procedure. ^1H and ^{13}C NMR spectra were recorded on a 400 (^1H)/ 100 (^{13}C) MHz spectrometer. Chemical shifts (δ) are reported relatively to tetramethylsilane as internal standard in ppm. Assignments of some ^1H and ^{13}C signals rely on g-COSY and/or g-HSQC experiments. Elemental Analysis was performed at Unidad de Análisis Elemental of the Universidad de Huelva.

General Catalytic Procedure for [3 + 2] Cycloaddition of Alkyne and Sulfonyl Azide Catalysed by $[Tpm^{*,Br}Cu(NCMe)]BF_4$. The catalyst (18.2 mg, 0.025 mmol, 5 mol%) and sulfonyl azide (0.5 mmol) were dissolved in anhydrous chloroform (1 mL) in an ampoule. The alkyne (0.6 mmol) was added to the solution under a nitrogen atmosphere. The reaction mixture was stirred at a given temperature (40 or 50 ºC) for a given time (24-72 h) (see Scheme 3). The reaction crude was diluted with dicloromethane and filtered through a plug of silica to eliminate the copper catalyst. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (by default 1:3, otherwise indicated) to afford the desired product.

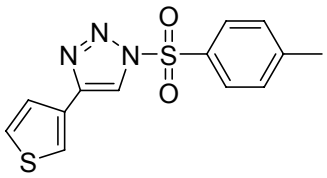
Data of Compounds:



1-(4-Methylbenzensulfonyl)-4-phenyl-1*H*-1,2,3-triazole (Scheme 3, 3a)

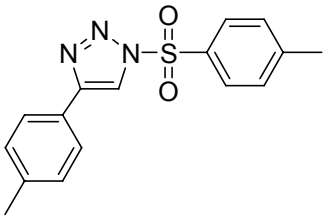
Following the general procedure from phenylacetylene (66 μL) and *p*-toluenesulfonyl azide (98.5 mg) the title compound **3a** was isolated as a white solid (0.136 g, 91%) after purification (AcOEt/PE 1:3, R_f = 0.45) by flash chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.03 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 7.45-7.35 (m, 5H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 133.3, 130.7, 129.3, 129.2, 129.1, 128.9, 126.3, 119.2, 22.1. IR (nujol) ν (cm^{-1}) 3142, 3037, 1594, 1335, 1236,

1197, 1170, 1105, 990, 814, 766, 692, 680. Spectroscopic data for **3a** were consistent with those previously reported for this compound.[3]



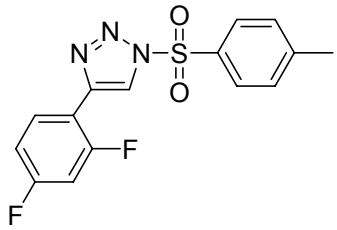
1-(4-Methylbenzensulfonyl)-4-(thien-3-yl)-1*H*-1,2,3-triazole (Scheme 3, 3b)

Following the general procedure from 3-ethynyl-thiophene (59 μL) and *p*-toluenesulfonyl azide (98.5 mg) the title compound **3b** was isolated as a brown solid (0.149 g, 98%) after purification (AcOEt/PE 1:3, R_f = 0.40) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.75-7.76 (m, 1H), 7.47-7.34 (m, 4H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1147.6, 143.7, 133.3, 130.7, 130.2, 128.9, 127.1, 125.8, 122.9, 118.8, 22.1. IR (nujol) ν (cm^{-1}) 3110, 1591, 1297, 1200, 1087, 1034, 1008, 857, 787, 670. Spectroscopic data for **3b** were consistent with those previously reported for this compound.[3]



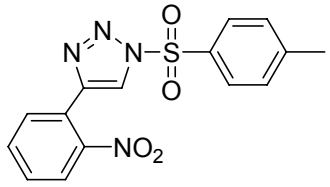
1-(4-Methylbenzensulfonyl)-4-(4-methylphenyl))-1*H*-1,2,3-triazole (Scheme 3, 3c)

Following the general procedure from 1-ethynyl-4-methylbenzene (76 μL)and *p*-toluenesulfonyl azide (98.5 mg) the title compound **3c** was isolated as a white solid (0.131 g, 84%) after purification (AcOEt/PE 1:3, R_f = 0.31) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.02 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147,5, 139.3, 133.3, 130.6, 129.9, 128.9, 126.2, 118.7, 22.1, 21.6. IR (nujol) ν (cm^{-1}) 3167, 1625, 1591, 1156, 947, 815, 722. Spectroscopic data for **3c** were consistent with those previously reported for this compound.[3]



4-(2,4-difluorophenyl)-1-(4-methylbenzenesulfonyl)-1*H*-1,2,3-triazole (Scheme 3, 3d)

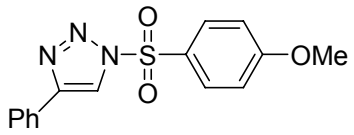
Following the general procedure from 1-ethynyl-2,4-difluorobenzene (82.9 mg) and *p*-toluenesulfonyl azide (98.5 mg) the title compound **3d** was isolated as a white solid (0.149 g, 89%) after purification (AcOEt/PE 1:3, R_f = 0.36) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 3.5 Hz, 1H, NC*H*=), 8.25 (td, *J* = 8.6, 6.5 Hz, 1H, H^{Ar}), 8.04 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 7.40 (d, *J* = 8.2 Hz, 2H, H^{Ar}), 7.00 (m, 1H, H^{Ar}), 6.92 (m, 1H, H^{Ar}), 2.45 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (dd, *J* = 252, 11 Hz, C, C^{Ar}), 159.5 (dd, *J* = 251, 11 Hz, C, C^{Ar}), 147.5 (C, N*C*=), 140.3 (C, C^{Ar}), 133.0 (C, C^{Ar}), 130.5 (CH, C^{Ar}), 129.2 (dd, *J* = 10, 5, CH, C^{Ar}), 128.8 (CH, C^{Ar}), 121.5 (d, *J* = 12 Hz, CH, NC*H*=), 113.6 (dd, *J* = 13, 4 Hz, C, C^{Ar}), 112.2 (dd, *J* = 22, 4 Hz, CH, C^{Ar}), 104.4 (t, *J* = 25 Hz, CH, $C^{Ar,}$), 21.9 (CH_3). IR (nujol) ν (cm^{-1}) 3176, 1620, 1593, 1567, 1120, 1081, 1026, 990, 941, 865, 810, 725, 681, 626. Anal. Calcd. for $C_{15}H_{11}F_2N_3O_2S$: C, 53.73; H, 3.28; N, 12.53. Found: C, 53.66; H, 3.22; N, 12.30.



1-(4-Methylbenzensulfonyl)-4-(2-nitrophenyl)-1*H*-1,2,3-triazole (Scheme 3, 3e)

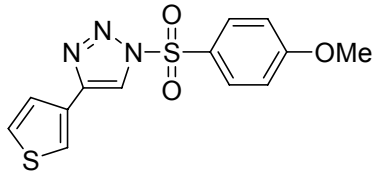
Following the general procedure from 1-ethynyl-2-nitrobenzene (88.3 mg) and *p*-toluenesulfonyl azide (98.5 mg) the title compound **3e** was isolated as a red solid (0.170 g, 99%) after purification (AcOEt/PE 1:3, R_f = 0.16) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H, NC*H*=), 8.04 (d, *J* = 8.5 Hz, 2H, H^{Ar}), 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H, H^{Ar}), 7.89 (dd, *J* = 8.1, 1.2 Hz, 1H, H^{Ar}), 7.68 (td, *J* = 7.6, 1.3 Hz, 1H, H^{Ar}), 7.56 (ddd, *J* = 8.1, 7.5, 1.4 Hz, 1H, H^{Ar}), 7.42 (d, *J* = 8.6 Hz, 2H, H^{Ar}), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4 (C, C^{Ar}), 147.9 (C, N*C*=), 142.1 (C, C^{Ar}), 133.1 (CH, C^{Ar}), 132.9 (C, C^{Ar}), 131.7 (CH, C^{Ar}), 130.8 (CH, C^{Ar}), 130.1 (CH, C^{Ar}), 129.1 (CH, C^{Ar}), 124.7 (CH, C^{Ar}), 123.6 (C, C^{Ar}), 122.9 (CH, N*C*H=), 22.2 (CH_3). IR

(nujol) ν (cm^{-1}) 3138, 1661, 1617, 1592, 1560, 1518, 1196, 1173, 992, 958, 908, 851, 812, 784, 748, 721, 673, 647. Anal. Calcd. for $C_{15}H_{12}N_4O_4S$: C, 52.32; H, 3.49; N, 16.28. Found: C, 51.94; H, 3.34; N, 16.02.



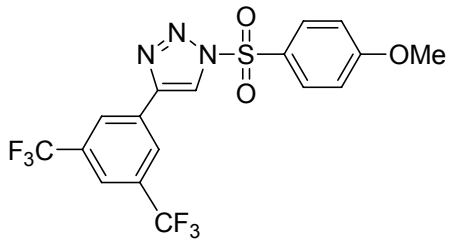
1-(4-Methoxylbenzensulfonyl)-4-phenyl-1*H*-1,2,3-triazole (Scheme 3, 3f)

Following the general procedure from phenylacetylene (66 μL) and 4-methoxybenzenesulfonyl azide (106.5 mg) the title compound **3f** was isolated as a white solid (0.148 g, 94%) after purification (AcOEt/PE 1:3, R_f = 0.33) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H, NC*H*=), 8.07 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 7.82 (d, *J* = 7.1 Hz, 2H, H^{Ar}), 7.45-7.35 (m, 3H, H^{Ar}), 7.03 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (C, C^{Ar}), 147.5 (C, N*C*=), 131.5 (CH, C^{Ar}), 129.3 (CH, C^{Ar}), 129.2 (CH, C^{Ar}), 129.1 (CH, C^{Ar}), 127.2 (C, C^{Ar}), 126.3 (CH, C^{Ar}), 119.1 (CH, N*C*H=), 115.4 (CH, C^{Ar}). IR (nujol) ν (cm^{-1}) 3176, 1589, 1560, 1261, 1166, 973, 942, 847, 767, 723, 674. Anal. Calcd. for $C_{15}H_{13}N_3O_3S$: C, 57.14; H, 4,13; N, 13,33. Found: C, 57,61; H, 4,35; N, 12,84.



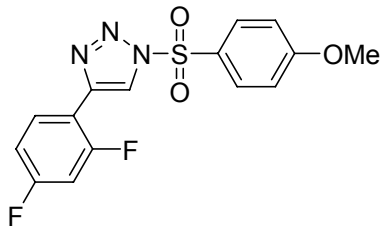
1-(4-Methoxylbenzensulfonyl)-4-(thien-3-yl)-1*H*-1,2,3-triazole (Scheme 3, 3g)

Following the general procedure from 3-ethynyl-thiophene (59 μL) and 4-methoxybenzenesulfonyl azide (106.5 mg) the title compound **3g** was isolated as a white solid (0.159 g, 99%) after purification (AcOEt/PE 1:3, R_f = 0.45) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H, NC*H*=), 8.06 (d, *J* = 9.0 Hz, 2H, H^{Ar}), 7.77-7.74 (m, 1H, H^{thio}), 7.44-7.36 (m, 2H, H^{thio}), 7.03 (d, *J* = 9.0 Hz, 2H H^{Ar}), 3.88 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (C, C^{Ar}), 143.4 (C, N*C*=), 131.2 (CH, C^{Ar}), 130.1 (Cq), 127.0 (Cq), 126.8 (CH, C^{thio}), 125.7 (CH, C^{thio}), 122.7 (CH, C^{thio}), 118.5 (CH, N*C*H=), 115.1 (CH, C^{Ar}), 56.0 (CH_3). IR (nujol) ν (cm^{-1}) 3098, 1589, 1264, 1167, 1007, 838, 785, 722, 677. Calcd. for $C_{13}H_{11}N_3O_3S_2$: C, 48.60; H, 3.34; N, 12.76. Found: C, 48.65; H, 3.61; N, 12.99.



1-(4-methoxylbenzenesulfonyl)-4-(3,5-bis-(trifluoromethyl)benzene)-1*H*-1,2,3-triazole (Scheme 3, 3h)

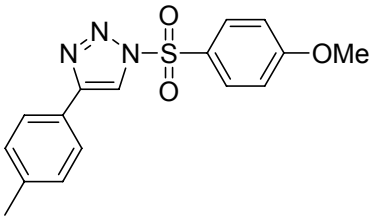
Following the general procedure from 1-ethynyl-3,5-bis-(trifluromethyl)benzene (106 μL) and 4-methoxybenzenesulfonyl azide (106.5 mg) the title compound **3h** was isolated as a white solid (0.214 g, 95%) after purification (AcOEt/PE 1:5, R_f. = 0.17) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H, NC*H*=), 8.28 (s, *2*H, H^{Ar}), 8.11 (d, *J* = 9.1 Hz, 2H, H^{Ar}), 7.85 (s, *1*H, H^{Ar}), 7.06 (d, *J* = 9.1 Hz, 2H, H^{Ar}), 3.90 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9 (C, C^{Ar}), 144.7 (C, N*C*=), 132.7 (q, *J* = 34 Hz, Cq), 131.7 (CH, C^{Ar}), 131.5 (C, C^{Ar}), 126.6 (C, C^{Ar}), 126.3 (CH, C^{Ar}), 123.2 (q, *J* = 273 Hz, CF_3), 122.7 (q, *J* = 4 Hz, CH, C^{Ar}), 120.3 (CH, N*C*H=), 115.5 (CH, C^{Ar}), 56.3 (CH_3). IR (nujol) ν (cm^{-1}) 3166, 3108, 1591, 1495, 1309, 1269, 1169, 1117, 1007, 976, 897, 832, 801, 705, 680. Anal. Calcd. for $C_{17}H_{11}F_6N_3O_3S$: C, 45.23; H, 2.44; N, 9.31. Found: C, 44.92; H, 2.49; N, 9.06.



4-(2,4-difluorophenyl)-1-(4-methoxybenzenesulfonyl)-1*H*-1,2,3-triazole (Scheme 3, 3i)

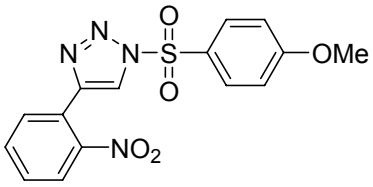
Following the general procedure from 1-ethynyl-2,4-difluorobenzene (82.9 mg) and 4-methoxybenzenesulfonyl azide (106.5 mg) the title compound **3i** was isolated as a white solid (0.172 g, 98%) after purification (AcOEt/PE 1:3, R_f. = 0.35) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 3.5 Hz, 1H, NC*H*=), 8.24 (m, 1H, H^{Ar}), 8.09 (d, *J* = 9.1 Hz, 2H, H^{Ar}), 7.04 (d, *J* = 9.1 Hz, 2H, H^{Ar}), 7.02-6.90 (m, 2H, H^{Ar}), 3.89 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (C, C^{Ar}), 164.8 (dd, *J* = 252, 11 Hz, C, C^{Ar}), 159.5 (dd, *J* = 251, 11 Hz, C, C^{Ar}), 140.1 (C, N*C*=), 131.3 (CH,

C^{Ar}), 129.2 (dd, *J* = 10, 5, CH, C^{Ar}), 126.9 (C, C^{Ar}), 121.3 (d, *J* = 12 Hz, CH, NC*H*=), 115.2 (CH, C^{Ar}), 113.6 (dd, *J* = 13, 4 Hz, C, C^{Ar}), 112.2 (dd, *J* = 22, 3 Hz, CH, C^{Ar}), 104.3 (t, *J* = 25 Hz, CH, $C^{Ar,}$), 55.9 (CH_3). IR (nujol) ν (cm^{-1}) 3175, 1592, 1170, 1000, 947, 841, 807, 719, 682, 624. Anal. Calcd. for $C_{15}H_{11}F_2N_3O_3S$: C, 51.28; H, 3.13; N, 11.97. Found: C, 50.94; H, 3.18; N, 11.97.



1-(4-methoxylbenzenesulfonyl)-4-(4-methylbenzene)-1*H*-1,2,3-triazole (Scheme 3, 3j)

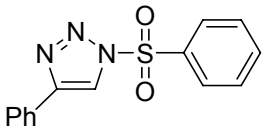
Following the general procedure from 1-ethynyl-4-methylbenzene (76 μL) and 4-methoxybenzenesulfonyl azide (106.5 mg) the title compound **3j** was isolated as a white solid (0.146 g, 89%) after purification (AcOEt/PE 1:3, R_f. = 0.45) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H, NC*H*=), 8.08 (d, *J* = 8.7 Hz, 2H, H^{Ar}), 7.71 (d, *J* = 8.1 Hz, 2H, H^{Ar}), 7.24 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 7.03 (d, *J* = 8.9 Hz, 2H, H^{Ar}), 3.88 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4 (C, C^{Ar}), 147.5 (C, N*C*=), 139.1 (C, C^{Ar}), 131.3 (CH, C^{Ar}), 129.8 (CH, C^{Ar}), 127.1 (C, C^{Ar}), 126.1 (C, C^{Ar}), 126.0 (CH, C^{Ar}), 118.4 (CH, N*C*H=), 115.1 (CH, C^{Ar}), 56.0 (O*C*H_3), 21.4 (CH_3). IR (nujol) ν (cm^{-1}) 3050, 1590, 1263, 1196, 1169, 1088, 1002, 980, 820, 770, 675. Anal. Calcd. for $C_{16}H_{15}N_3O_3S$: C, 58.36; H, 4.56; N, 12.77. Found: C, 57.94; H, 4.77; N, 12.32.



1-(4-methoxylbenzenesulfonyl)-4-(2-nitrobenzene)-1*H*-1,2,3-triazole (Scheme 3, 3k)

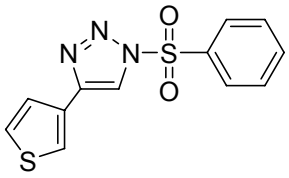
Following the general procedure from 1-ethynyl-2-nitrobenzene (88.3 mg) and 4-methoxybenzenesulfonyl azide (106.5 mg) the title compound **3k** was isolated as a white solid (0.169 g, 89%) after purification (AcOEt/PE 1:3, R_f. = 0.28) by flash

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H, NC*H*=), 8.10 (d, *J* = 8.5 Hz, 2H, H^{Ar}), 7.95 (dd, *J* = 7.8, 1.2 Hz, 1H, H^{Ar}), 7.89 (dd, *J* = 8.1, 1.2 Hz, 1H, H^{Ar}), 7.68 (td, *J* = 7.6, 1.3 Hz, 1H, H^{Ar}), 7.56 (ddd, *J* = 8.1, 7.5, 1.2 Hz, 1H, H^{Ar}), 7.06 (d, *J* = 8.6 Hz, 2H, H^{Ar}), 3.90 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (C, C^{Ar}), 148.5 (C, C^{Ar}), 142.0 (C, N*C*=), 133.0 (CH, C^{Ar}), 131.7 (CH, C^{Ar}), 131.6 (CH, C^{Ar}), 130.0 (CH, C^{Ar}), 126.9 (C, C^{Ar}), 124.7 (CH, C^{Ar}), 123.6 (C, C^{Ar}), 122.8 (CH, N*C*H=), 115.5 (CH, C^{Ar}), 56.2 (CH_3). IR (nujol) ν (cm^{-1}) 3160, 1586, 1532, 1269, 1201, 1156, 1086, 987, 957, 838, 803, 766, 722, 675. Anal. Calcd. for $C_{15}H_{12}N_4O_5S$: C, 50.00; H, 3.33; N, 15.56. Found: C, 49.74; H, 3.47; N, 15.64.



1-Benzenesulfonyl-4-phenyl-1*H*-1,2,3-triazole (Scheme 3, 3l)

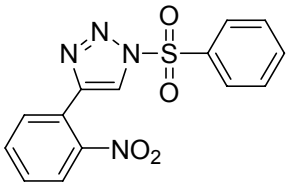
Following the general procedure from phenylacetylene (66 μL) and benzenesulfonyl azide (91.5 mg) the title compound **3l** was isolated as a pale yellow solid (0.122 g, 86%) after purification (AcOEt/PE 1:3, R_f = 0.24) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.16 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.83 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.72 (tt, *J* = 7.5, 1.1 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.47-7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 135.9, 130.1, 129.4, 129.2, 128.9, 128.8, 126.3, 119.2. IR (nujol) ν (cm^{-1}) 3164, 1621, 1595, 1250, 1165, 1071, 947, 767, 722, 690. Spectroscopic data for **3l** were consistent with those previously reported for this compound.[4]



1-Benzensulfonyl-4-(thien-3-yl)-1*H*-1,2,3-triazole (Scheme 3, 3m)

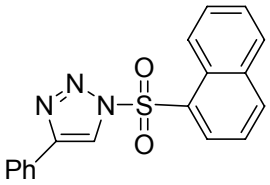
Following the general procedure from 3-ethynyl-thiophene (59 μL) and benzenesulfonyl azide (91.5 mg) the title compound **3m** was isolated as a brown solid (0.141 g, 97%) after purification (AcOEt/PE 1:3, R_f = 0.17) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H, NC*H*=), 8.15 (dd, *J* = 8.7, 1.6 Hz, 2H, H^{Ar}), 7.77 (dd, *J* = 2.8, 1.4 Hz, 1H, H^{thio}), 7.73 (tt, *J* = 7.5, 1.2 Hz, 1H, H^{Ar}), 7.61 (t, *J* = 7.8 Hz, 2H, H^{Ar}), 7.43-7.39 (m, 2H, H^{thio}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7 (C, N*C*=), 136.2 (Cq),

135.7 (Cq), 129.9 (CH, C^{Ar}), 128.6 (CH, C^{Ar}), 126.9 (CH, C^{thio}), 125.7 (CH, C^{thio}), 122.9 (CH, C^{thio}), 118.7 (CH, N*C*H=). IR (nujol) ν (cm^{-1}) 3090, 3048, 1625, 1546, 1244, 1151, 1070, 996, 799, 760, 729, 692, 612. Anal. Calcd. for $C_{12}H_9N_3O_2S_2$: C, 49.48; H, 3.09; N, 14.43. Found: C, 49.25; H, 3.58; N, 14.87.



1-Benzenesulfonyl-4-(2-nitrobenzene)-1*H*-1,2,3-triazole (Scheme 3, 3n)

Following the general procedure from 1-ethynyl-2-nitrobenzene (88.3 mg) and benzenesulfonyl azide (91.5 mg) the title compound **3n** was isolated as a red solid (0.147 g, 89%) after purification (AcOEt/PE 1:3, R_f = 0.22) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H, NC*H*=), 8.17 (dd, *J* = 8.6, 1.2 Hz, 2H, H^{Ar}), 7.96 (dd, *J* = 7.9, 1.4 Hz, 1H, H^{Ar}), 7.90 (dd, *J* = 8.1, 1.2 Hz, 1H, H^{Ar}), 7.79-7.73 (m, 1H, H^{Ar}), 7.71-7.61 (m, 3H, H^{Ar}), 7.56 (ddd, *J* = 8.1, 7.5, 1.5 Hz, 1H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5 (C, C^{Ar}), 142.0 (C, N*C*=), 136.2 (CH, C^{Ar}), 136.1 (C, C^{Ar}), 133.1 (CH, C^{Ar}), 131.7 (CH, C^{Ar}), 130.2 (CH, C^{Ar}), 129.0 (CH, C^{Ar}), 124.7 (CH, C^{Ar}), 123.5 (C, C^{Ar}), 123.0 (CH, N*C*H=). IR (nujol) ν (cm^{-1}) 3169, 1610, 1581, 1538, 1358, 1199, 1188, 1091, 990, 955, 852, 770, 726, 688, 636. Anal. Calcd. for $C_{14}H_{10}N_4O_4S$: C, 50.90; H, 3.03; N, 16.97. Found: C, 50.95; H, 2.95; N, 17.45.



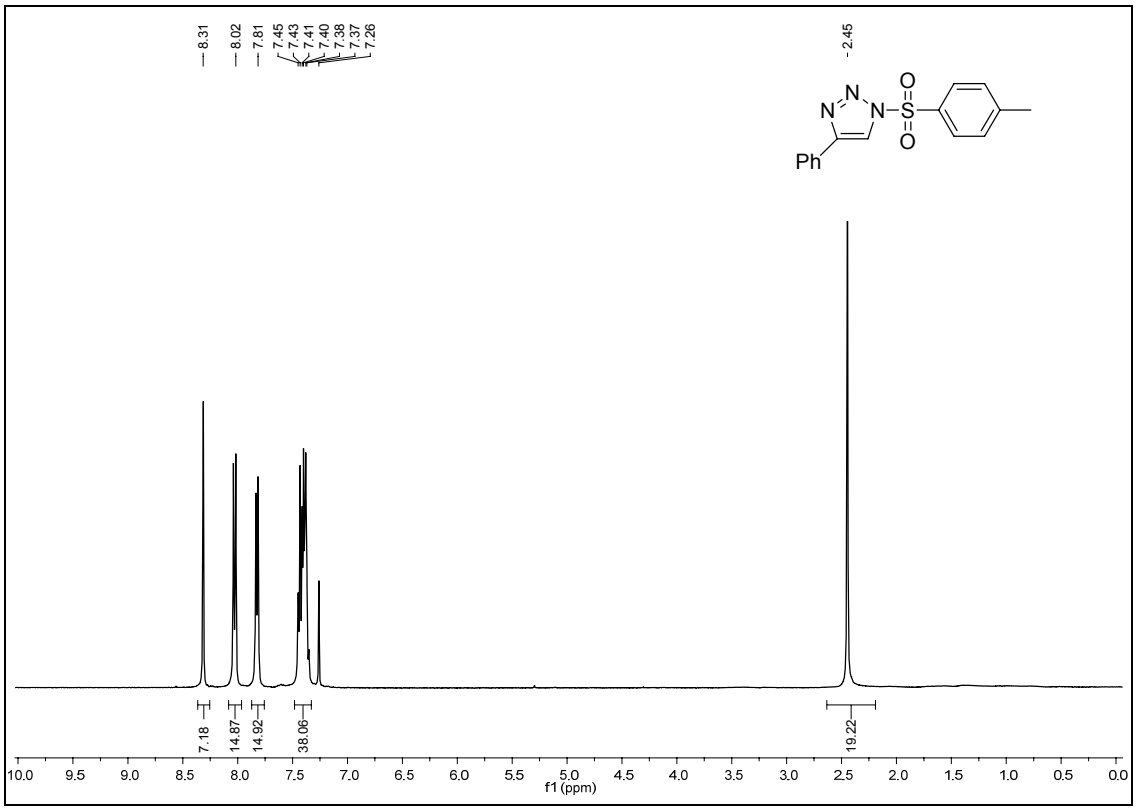
1-(Naphthalene-1-sulfonyl)-4-phenyl-1*H*-1,2,3-triazole (Scheme 3, 3o).

Following the general procedure from 1-phenylacetylene (66 μL) and naphthalene-1-sulfonyl azide (116.5 mg) the title compound **3o** was isolated as a white solid (0.144 g, 86%) after purification (AcOEt/PE 1:3, R_f = 0.38) by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 8.7, 0.8 Hz, 1H, H^{naph}), 8.65 (dd, *J* = 7.5, 1.2 Hz, 1H, H^{naph}), 8.41 (s, 1H, NC*H*=), 8.23 (d, *J* = 8.2, 1H, H^{naph}), 7.96 (dd, *J* = 8.2, 0.5 Hz, 1H, H^{naph}), 7.77 (dd, *J* = 7, 1.5 Hz, 2H, H^{Ar}), 7.72-7.61 (m, 3H, H^{naph}), 7.45-7.32 (m, 3H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 (C, N*C*=), 137.9 (CH, H^{Naph}), 134.4 (Cq), 132.6 (CH, H^{Naph}), 131.3 (Cq), 129.9 (CH, H^{Naph}), 129.5 (CH, H^{Naph}), 129.3 (CH, H^{Ar}),

129.2 (CH, H^{Ar}), 129.0 (Cq), 128.5 (Cq), 127.9 (CH, H^{Naph}), 126.3 (CH, H^{Ar}), 124.5 (CH, H^{Naph}), 124.2 (CH, H^{Naph}), 119.2 (CH, NCH=). IR (nujol) ν (cm^{-1}) 3125, 1591, 1553, 1505, 1196, 1180, 1024, 992, 926, 839, 803, 767, 724, 681, 626. Anal. Calcd. for $C_{18}H_{13}N_3O_2S$: C, 64.48; H, 3.88; N, 12.54. Found: C, 64.93; H, 3.60; N, 12.05.

References

1. (a) Tpm^X = Tpm*: Reger, D. L.; Collins, J. E.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1996**, *15*, 2029. (b) Tpm^X = $Tpm^{*,Br}$: Cvetkovic, M.; Batten, S. R.; Moubaraki, B.; Murray, K. S.; Spiccia, L. *Inorg. Chim. Acta*, **2001**, *324*, 131. (c) Tpm^X = Tpm^{Ms}: Rodríguez, P.; Álvarez, E.; Nicasio, M. C.; Pérez, P. J. *Organometallics* **2007**, *26*, 6661.
2. 4-Methylbenzenesulfonyl azide, 4-methoxybenzene sulfonyl azide and benzenesulfonyl azide were prepared as described in: Ruppel, J. V.; Jones, J. E.; Huff, C. A.; Kamble, R. M.; Chen, Y.; Zhang, X. P. *Org. Lett*. **2008**, *10*, 1995. 2-Nitrobenzenesulfonyl azide and naphthalene-1-sulfonyl azide were prepared as published in Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc*. **2006**, *128*, 11693.
3. Yoo, E. J.; Ahlquist, M.; Kim, S. H.; Bae, I.; Fokin, V. V.; Sharpless, K. B.; Chang, S. *Angew. Chem. Int. Ed*. **2007**, *46*, 1730.
4. Whitting, M.; Fokin, V. V. *Angew. Chem. Int. Ed*. **2006**, *45*, 3157.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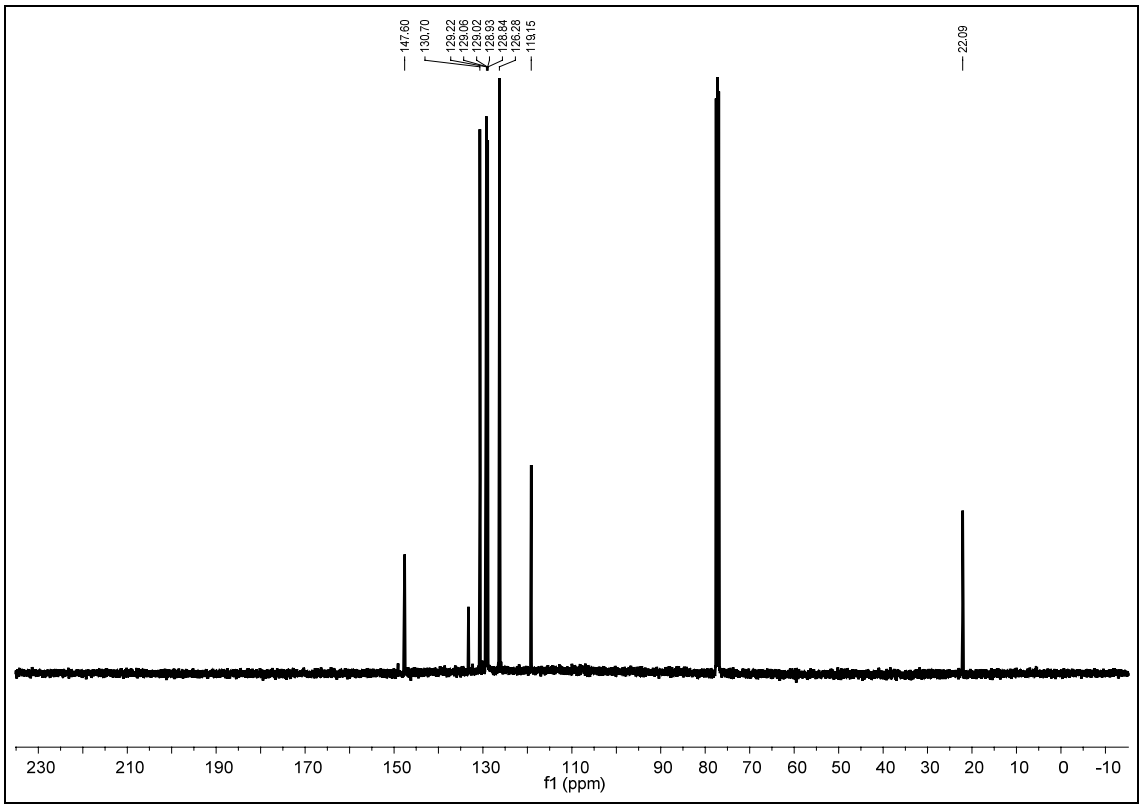
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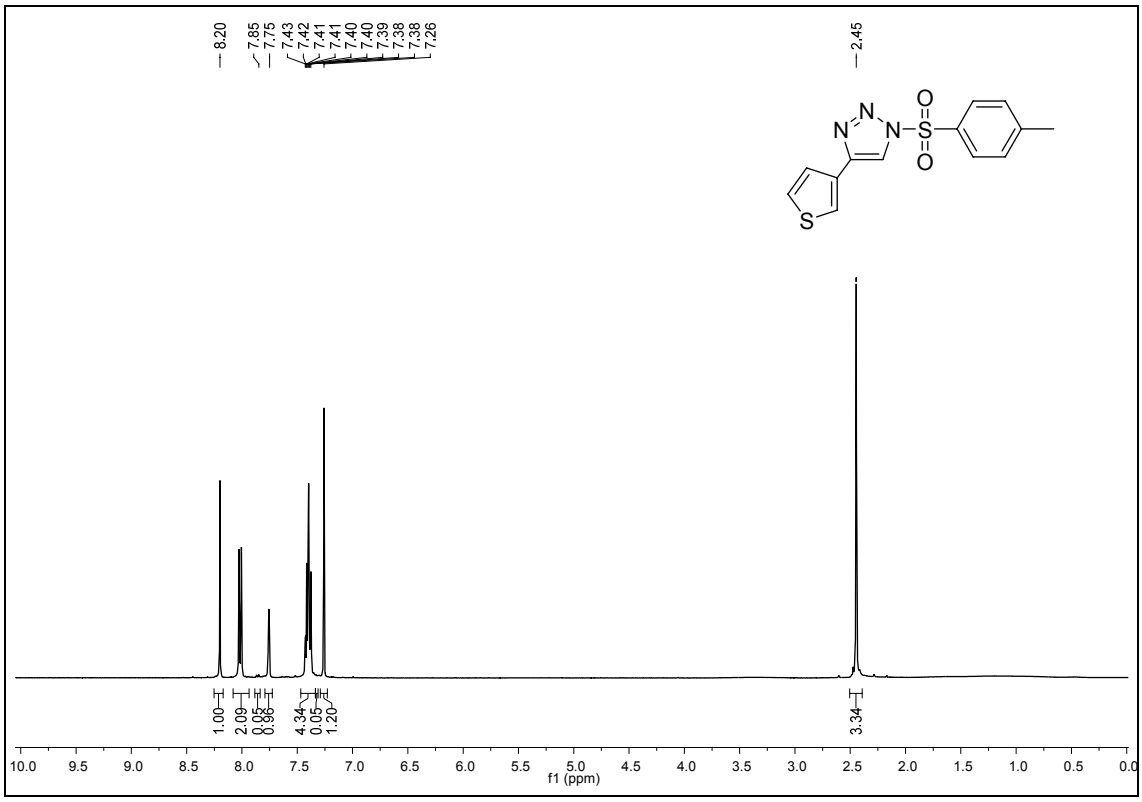
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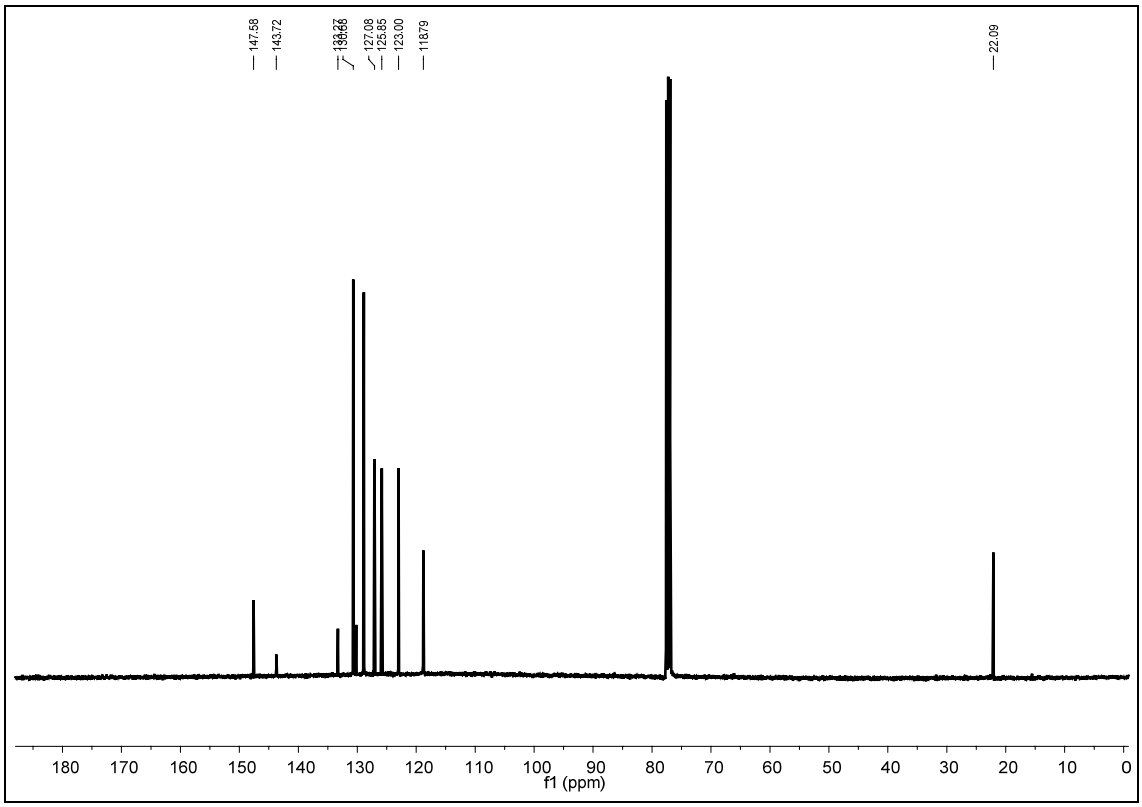
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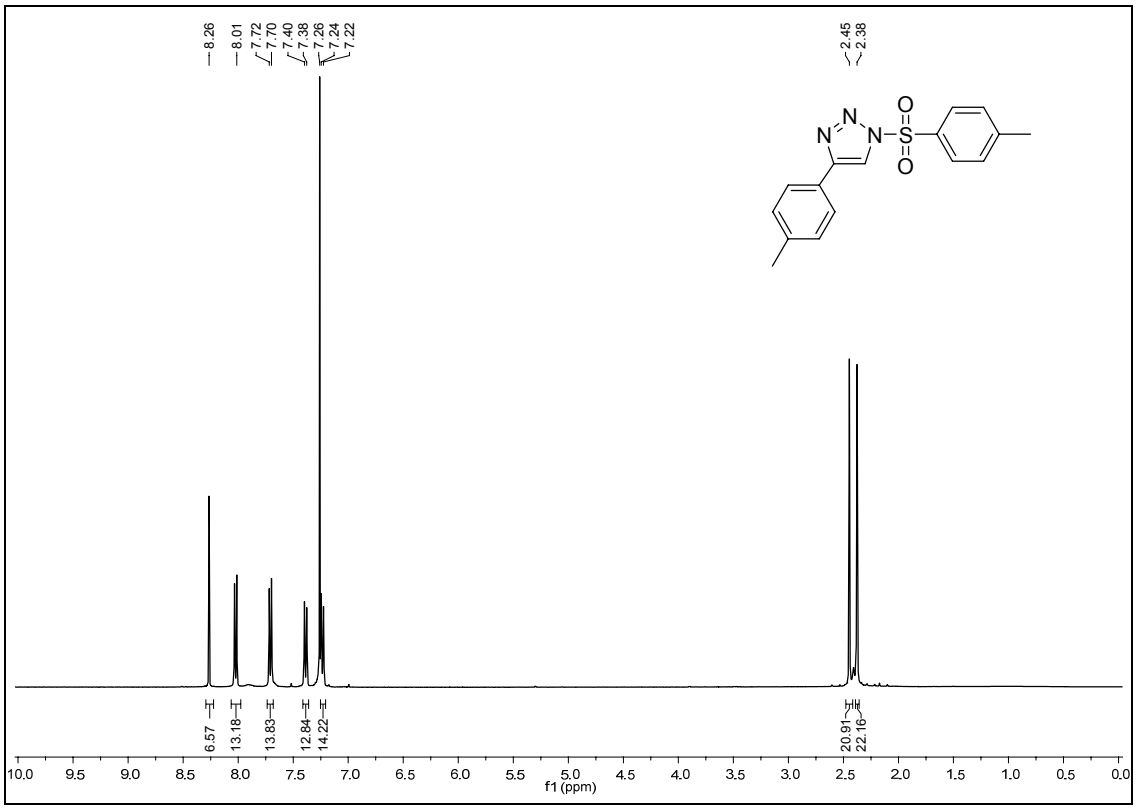
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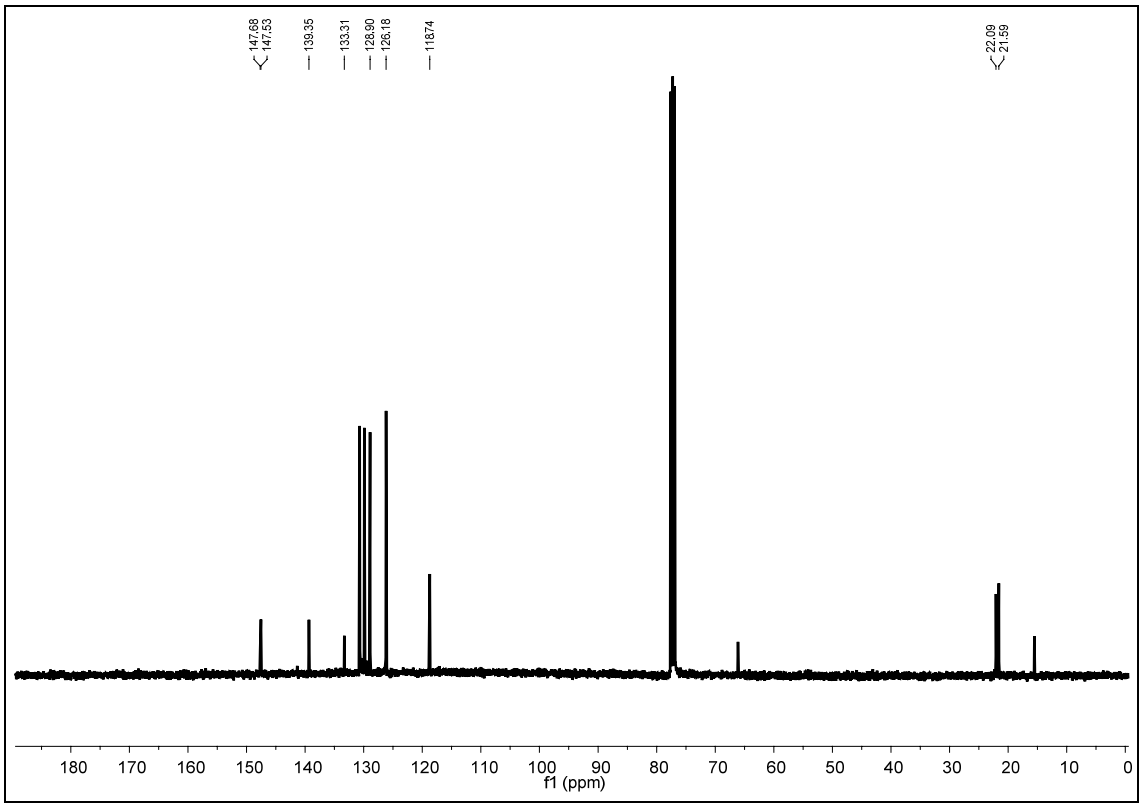
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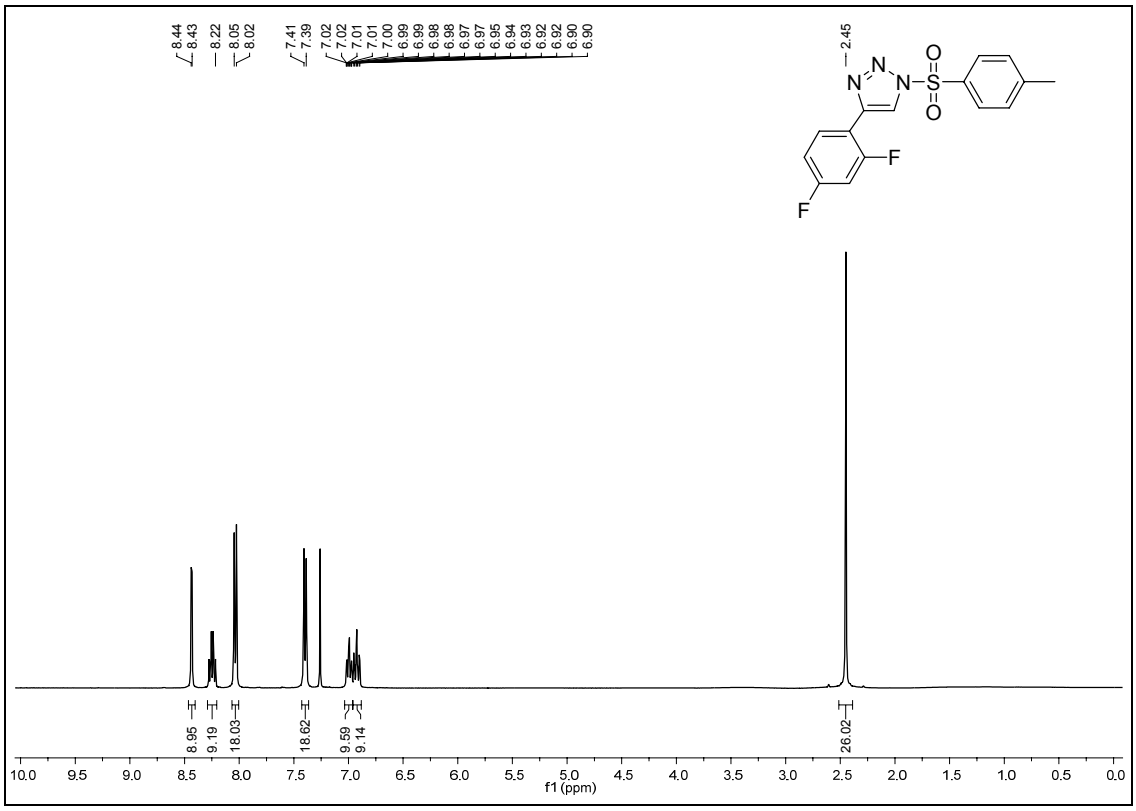
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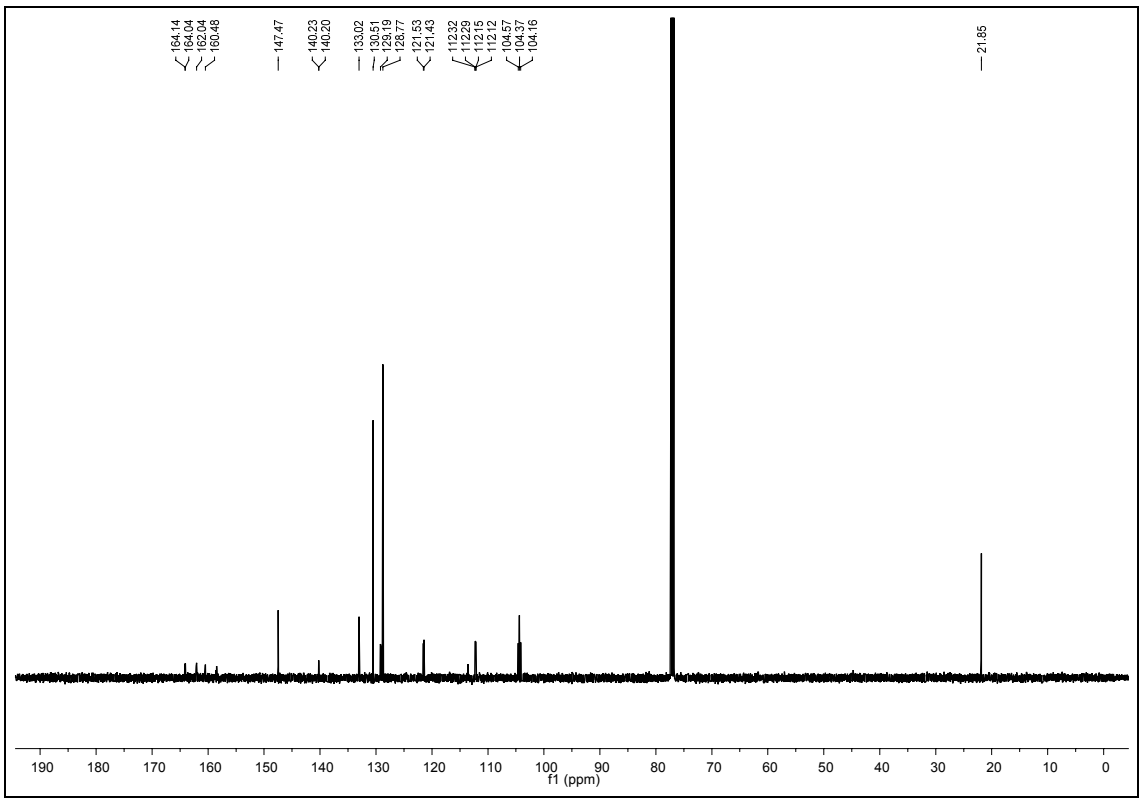
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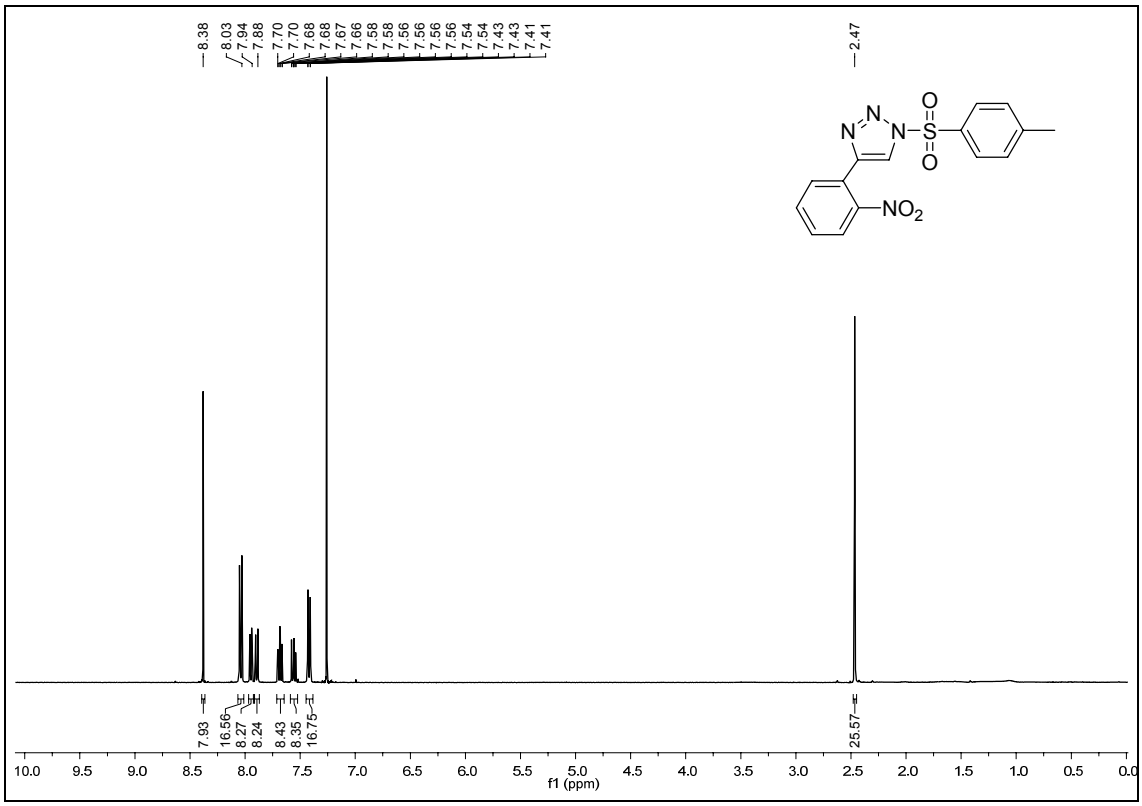
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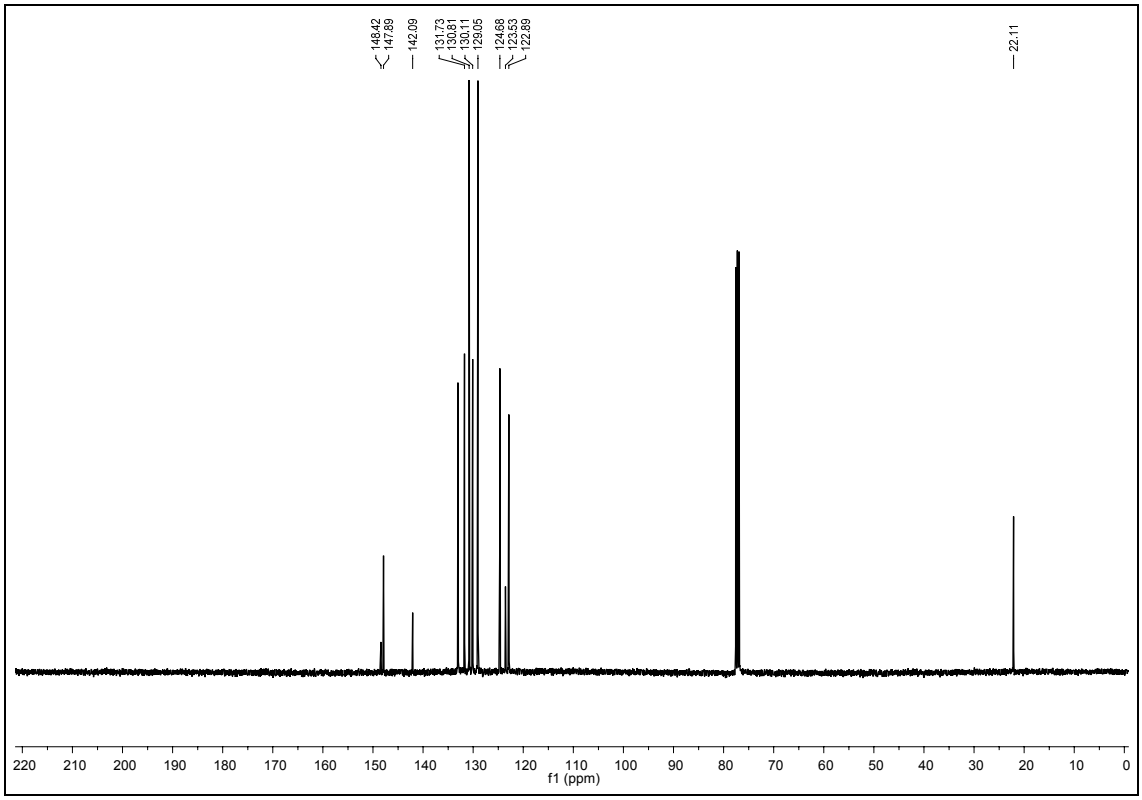
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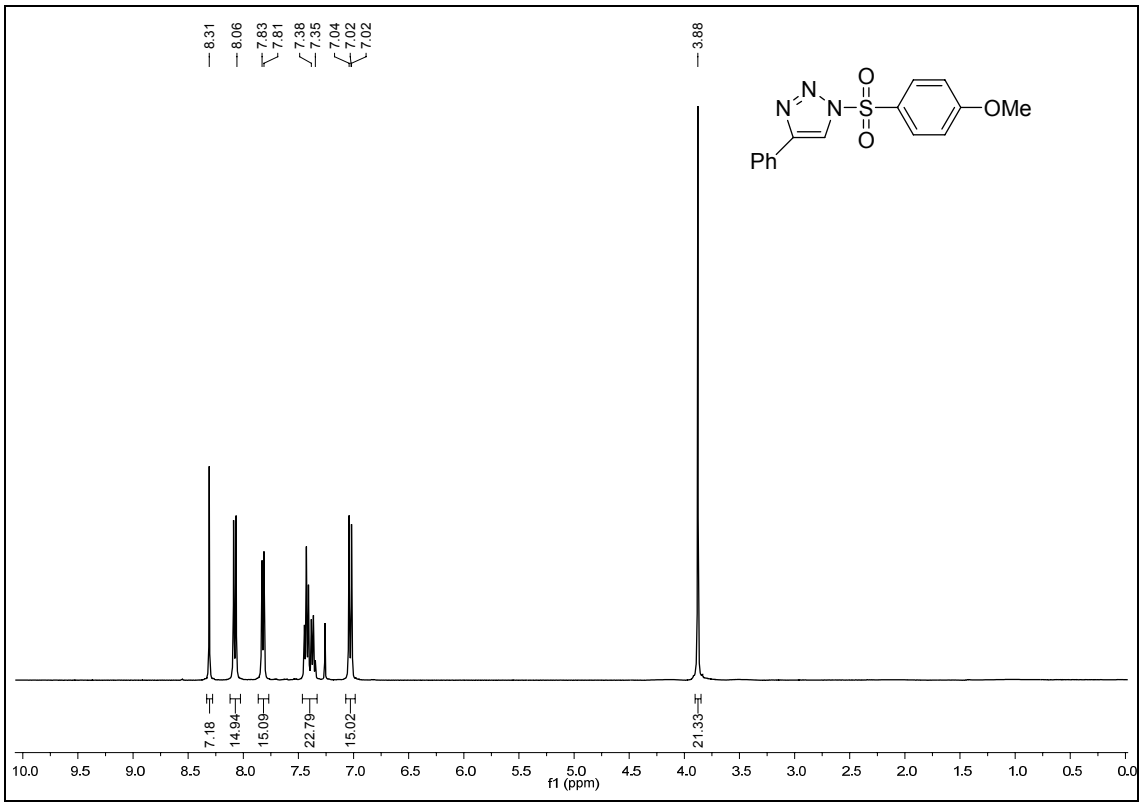
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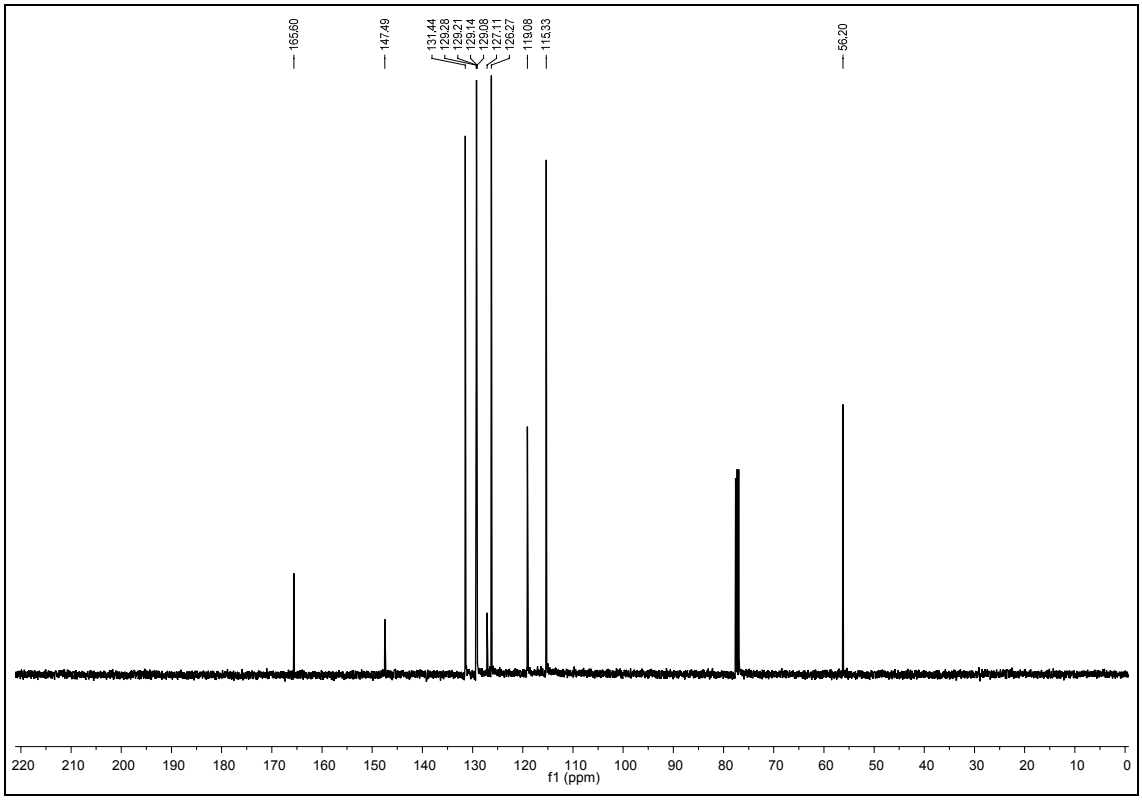
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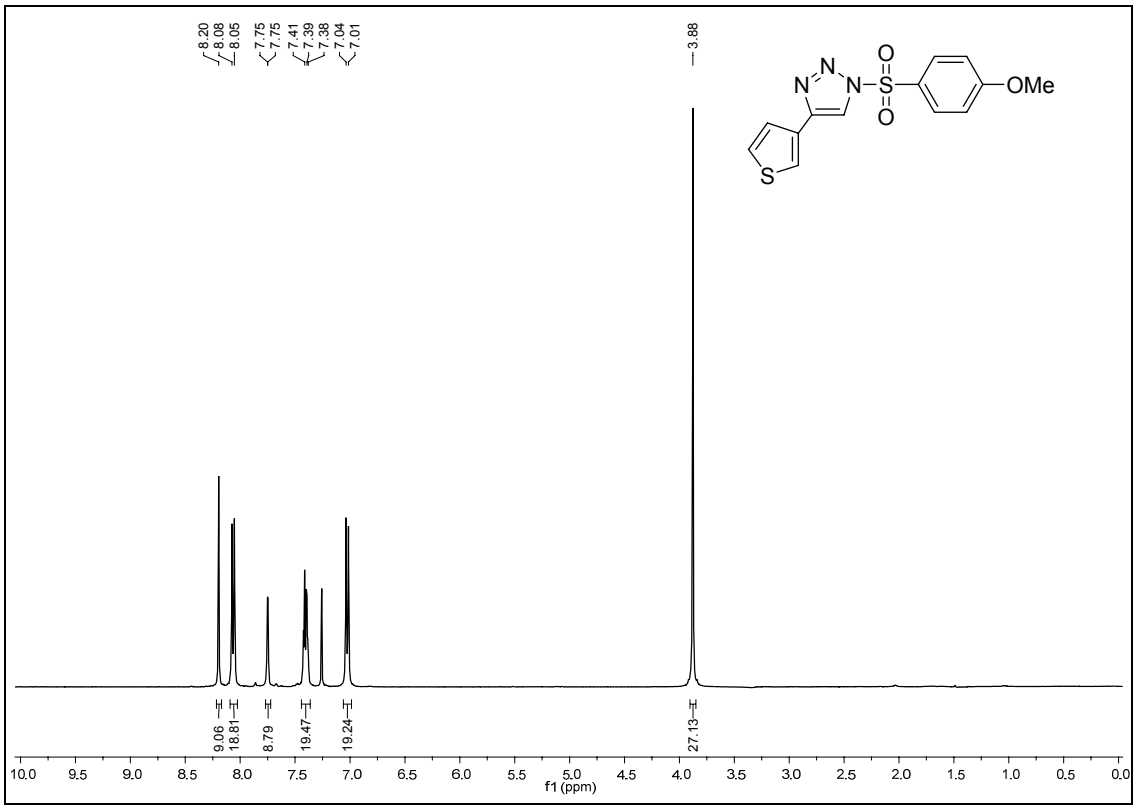
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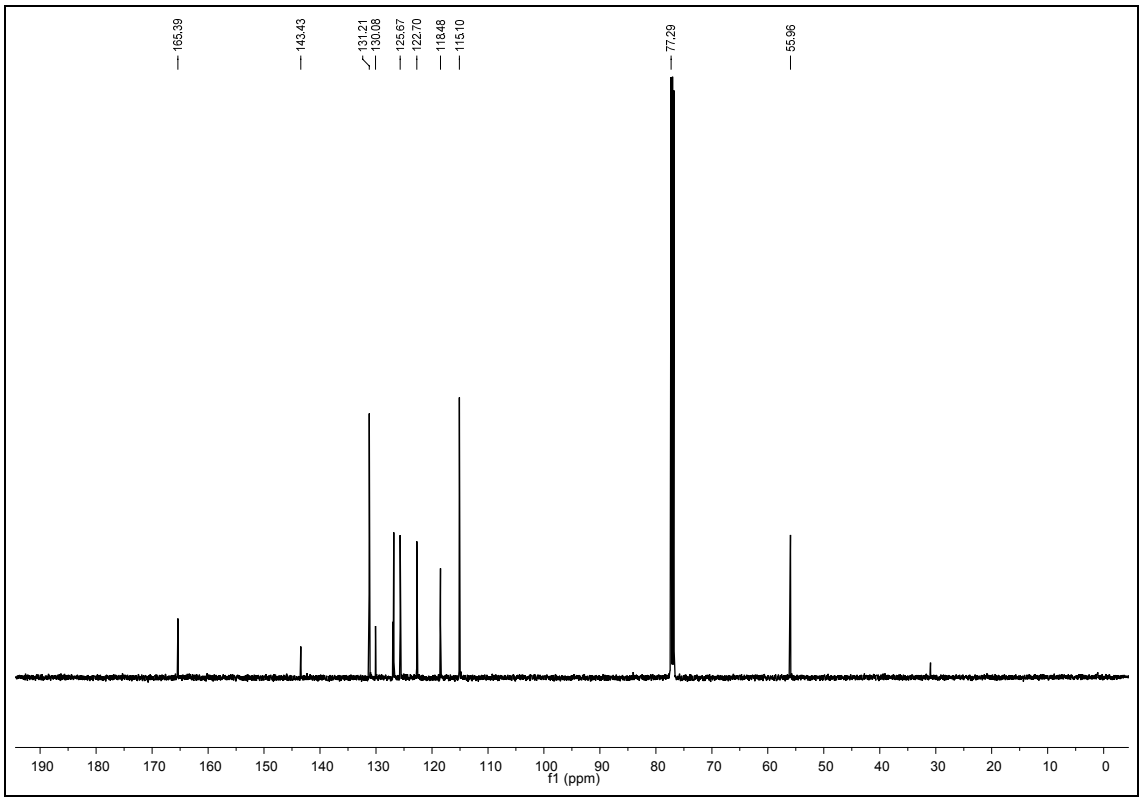
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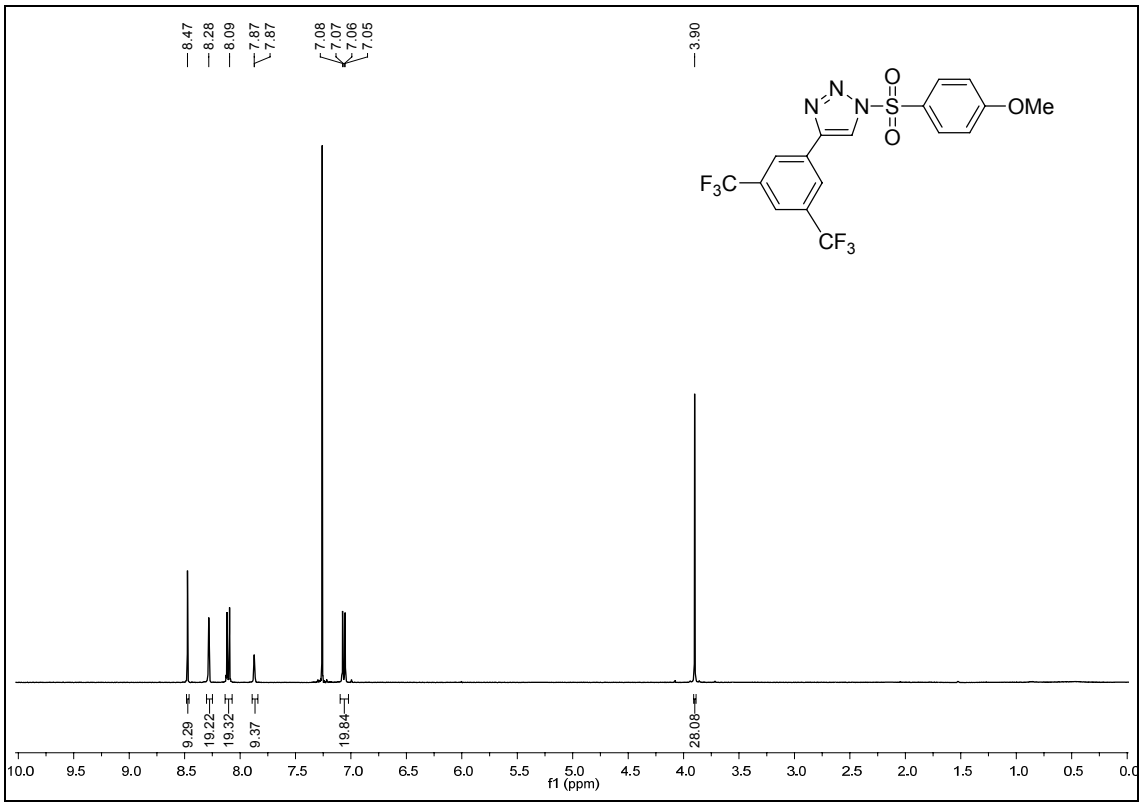
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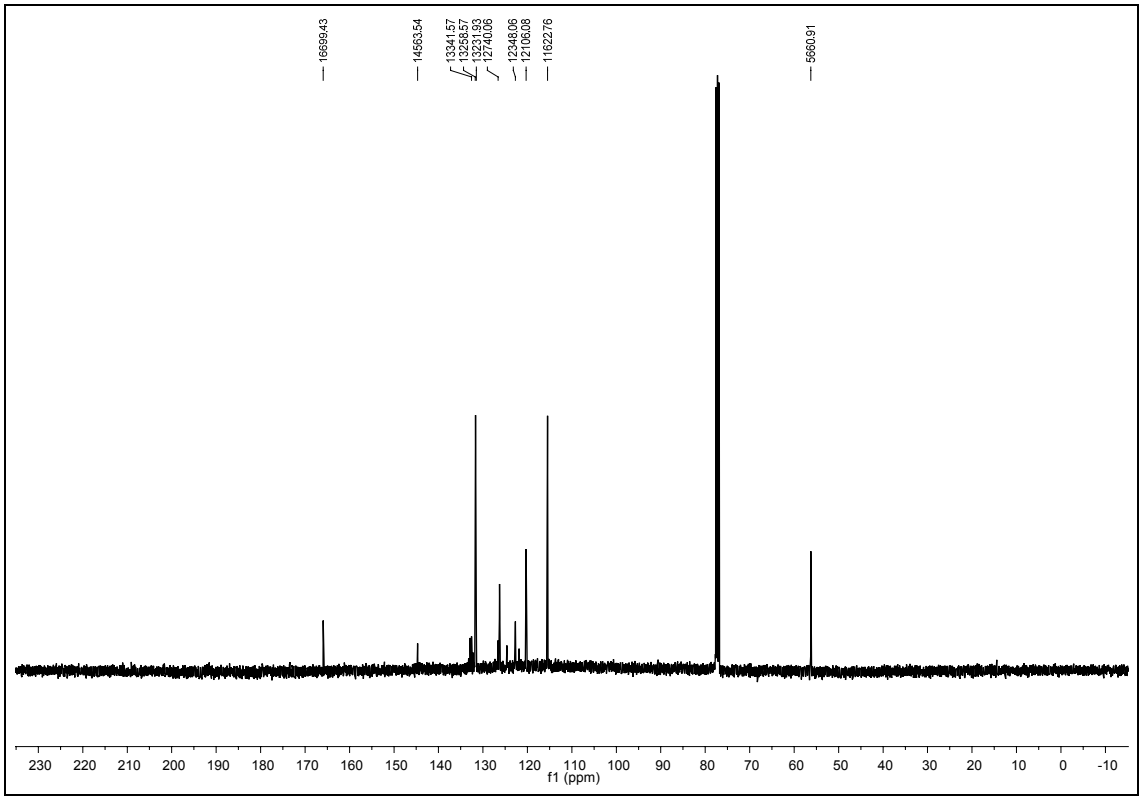
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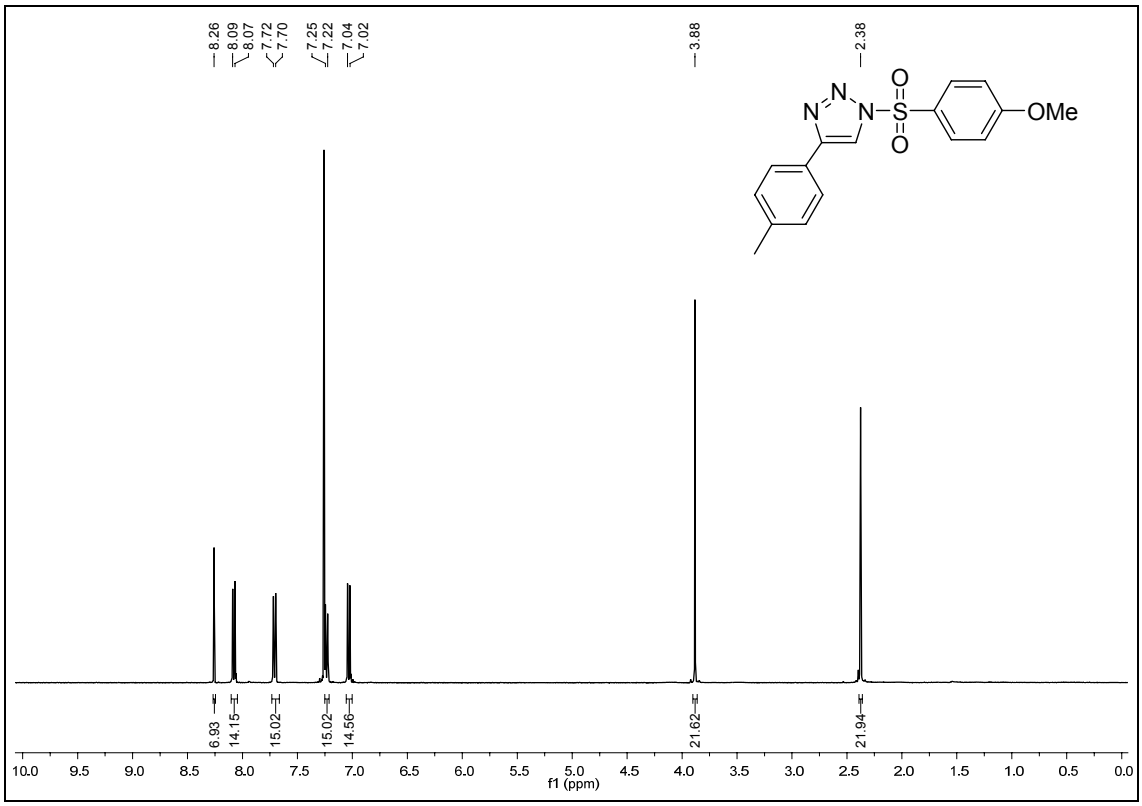
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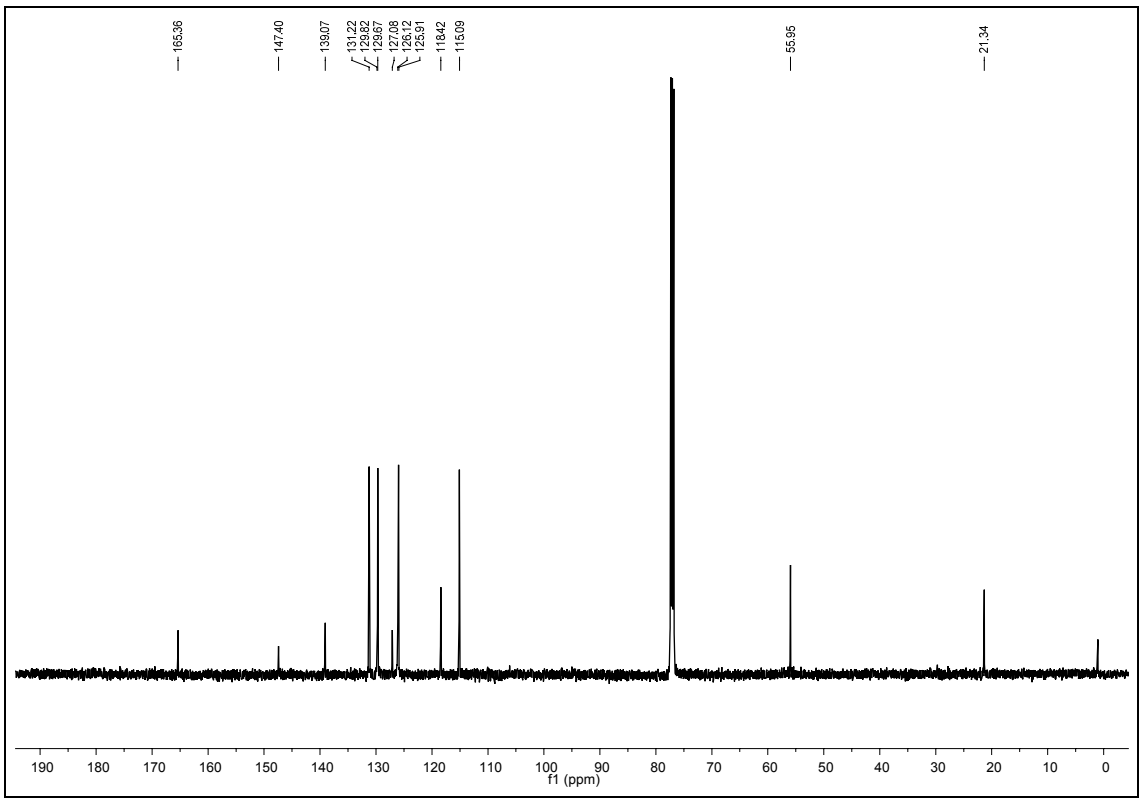
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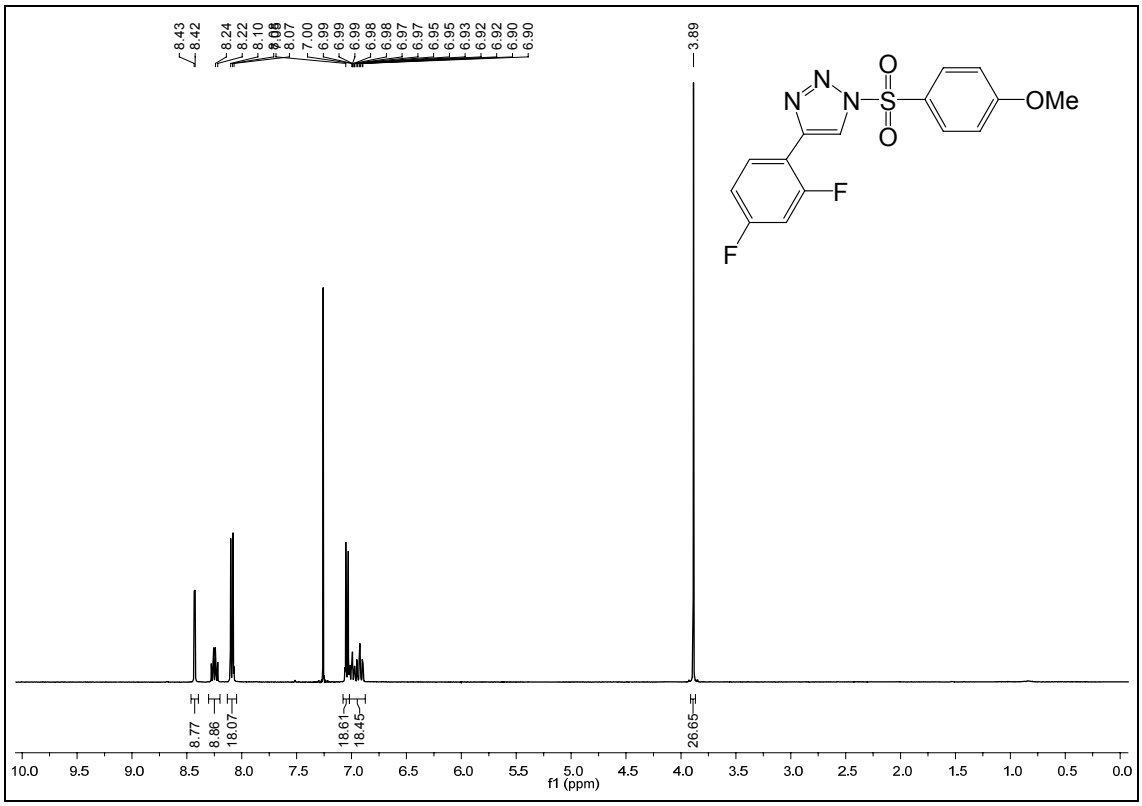
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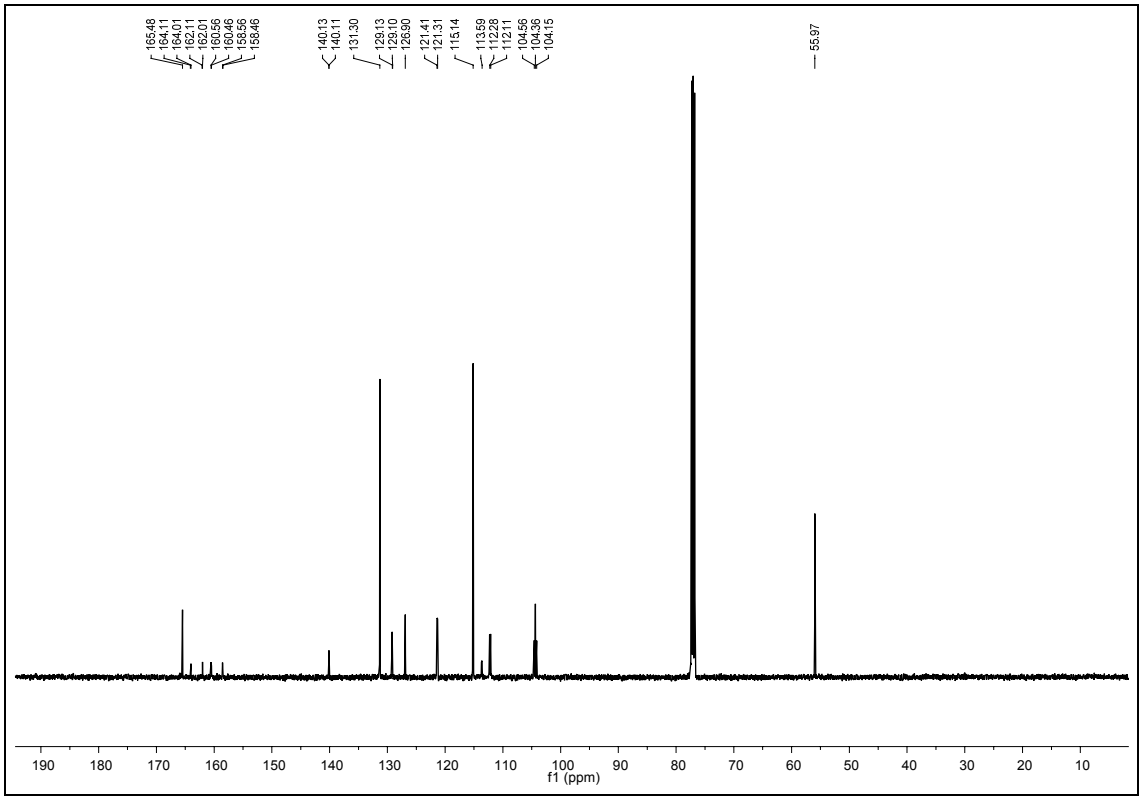
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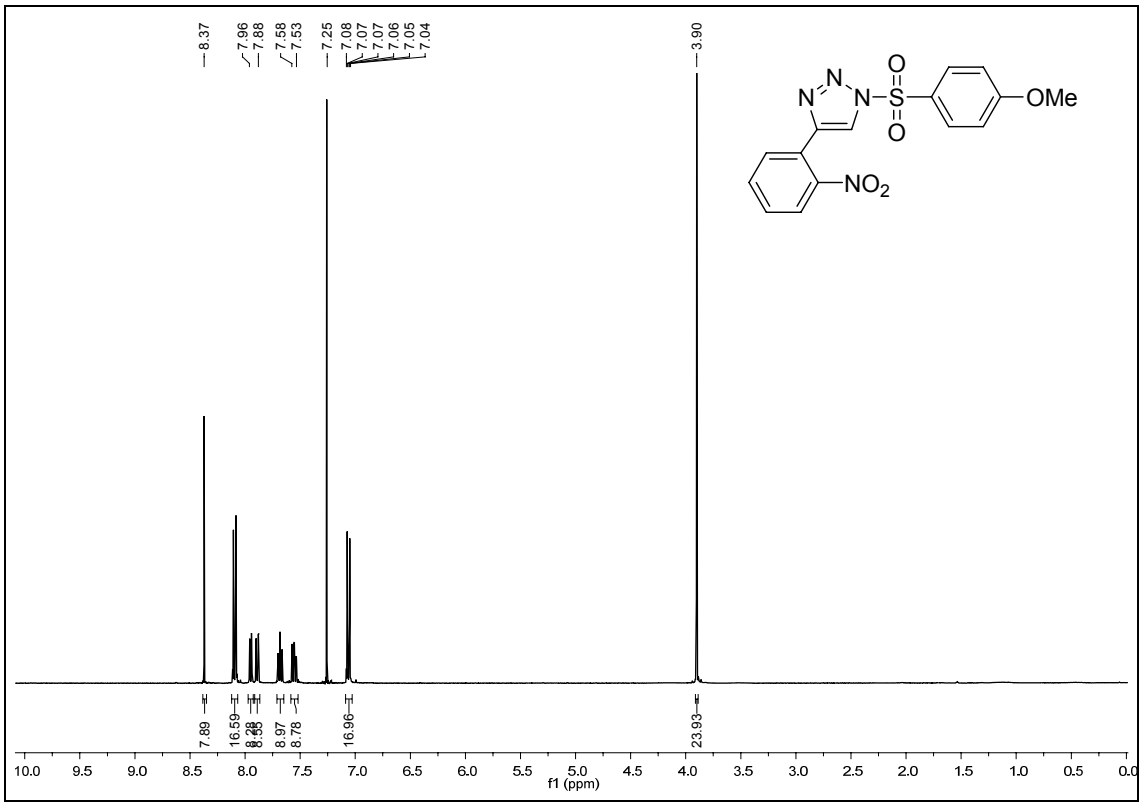
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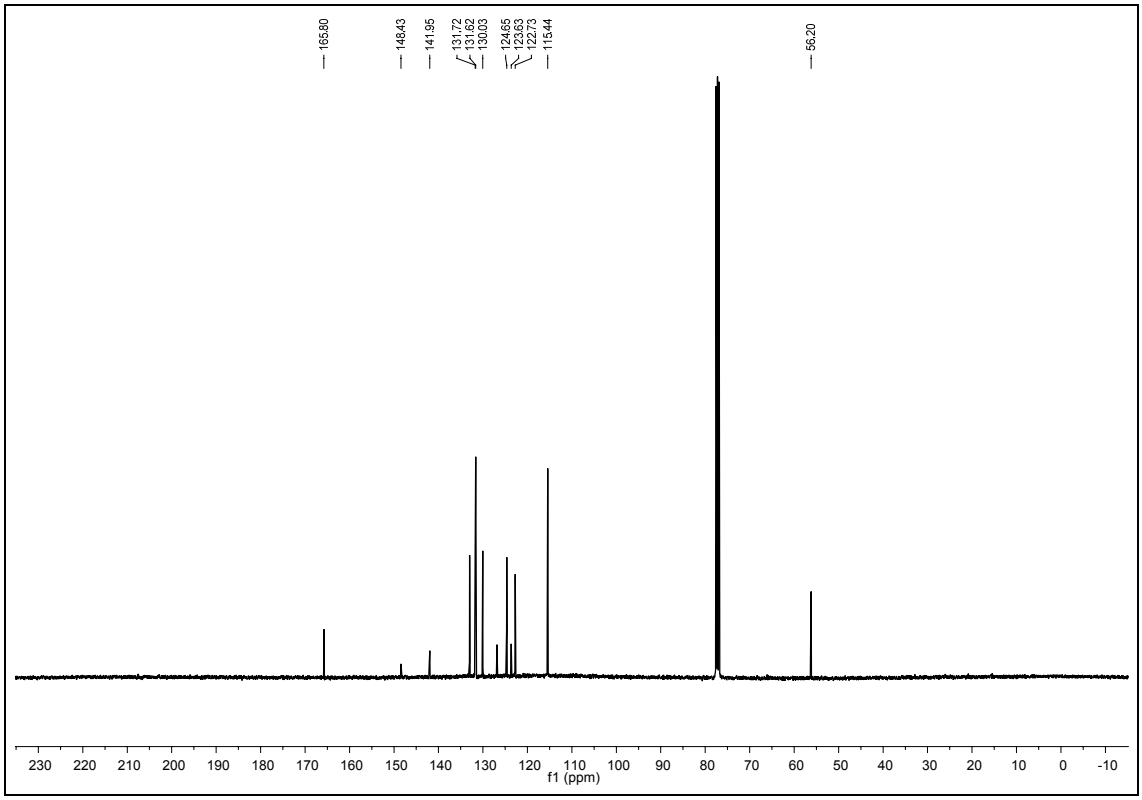
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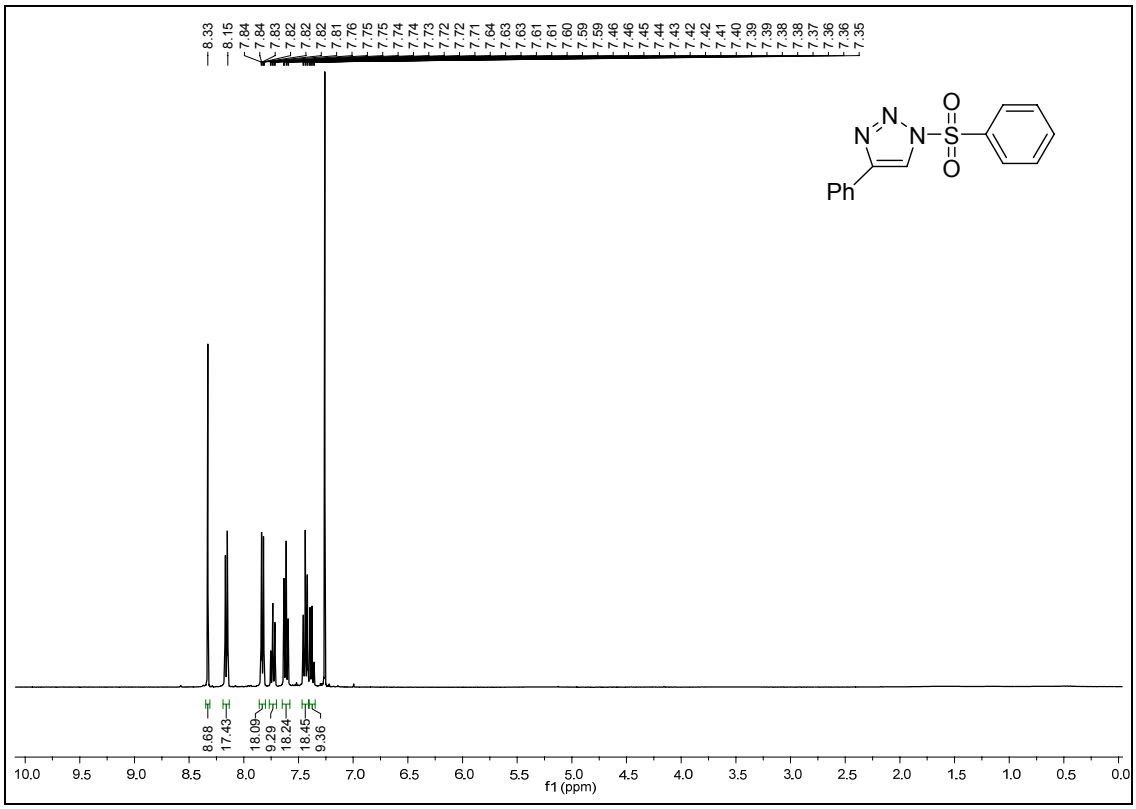
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9.0
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8.0
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7.0
6.5
6.0
5.5
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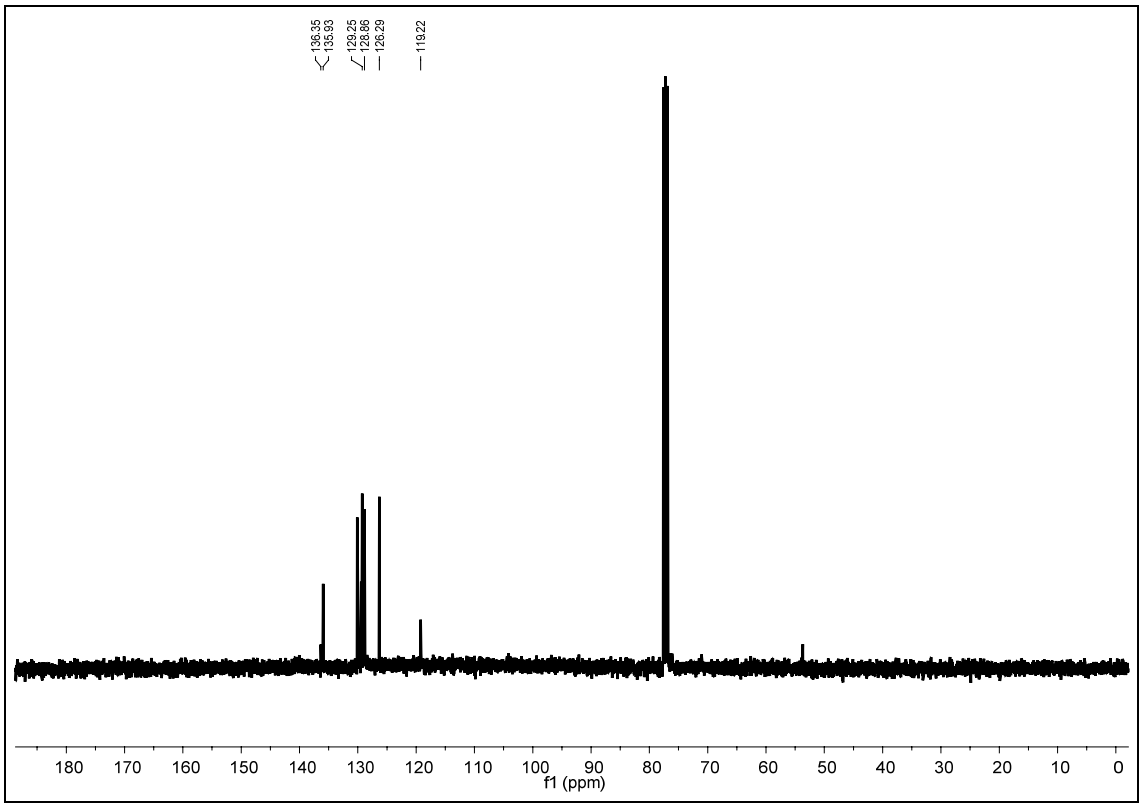
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129.25
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126.29
119.22
180
170
160
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140
130
120
110
100
90
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70
60
50
40
30
20
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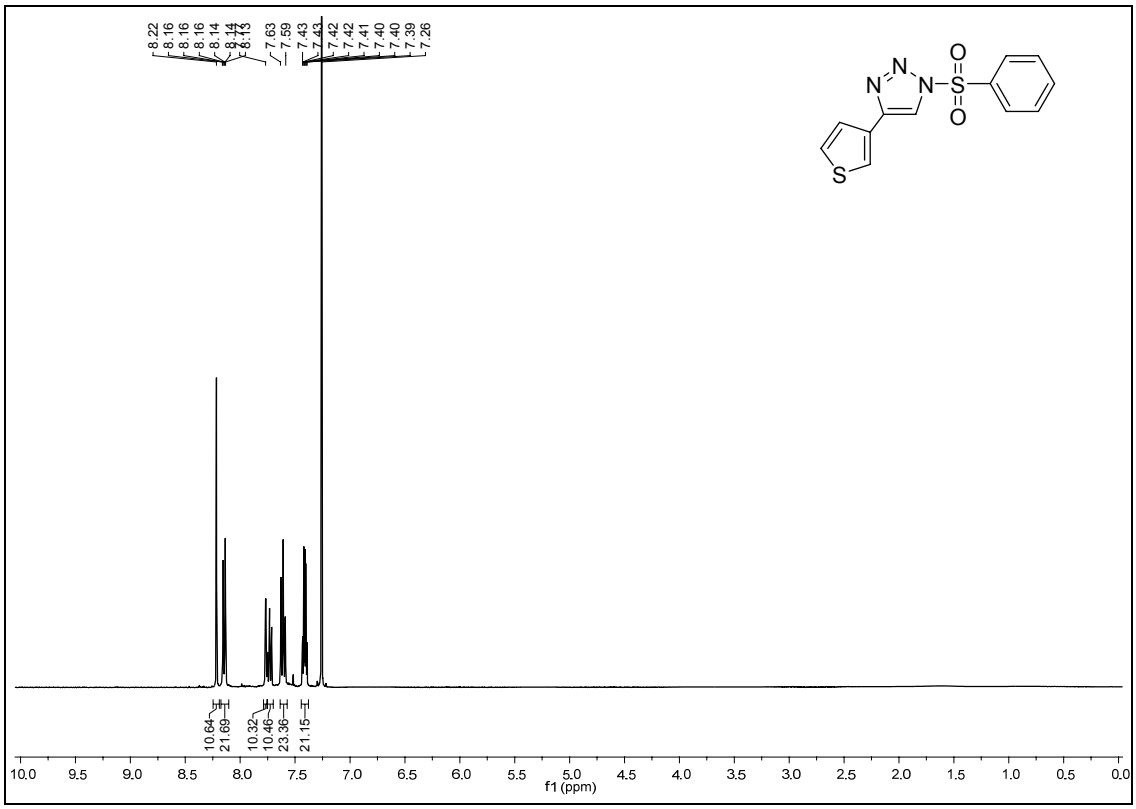
f1 (ppm)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7.43
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7.42
7.41
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7.39
7.26
10.64
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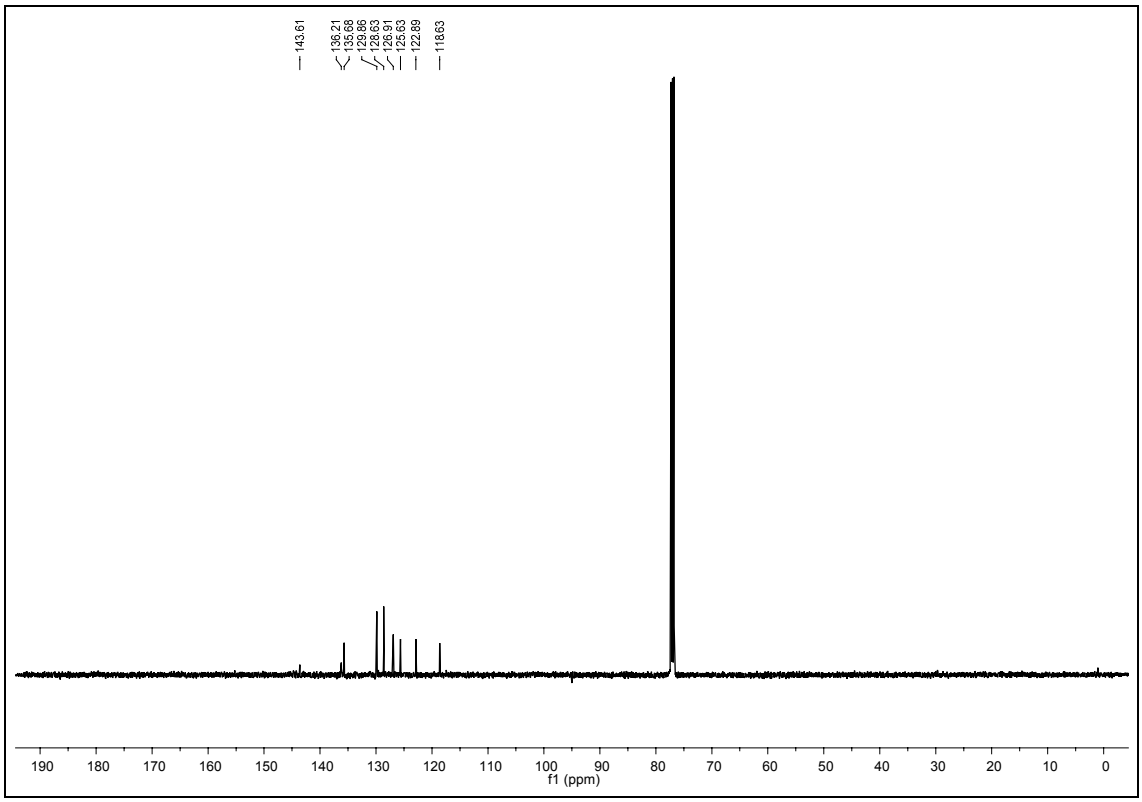
10.32
10.46
23.36
21.15
f1 (ppm)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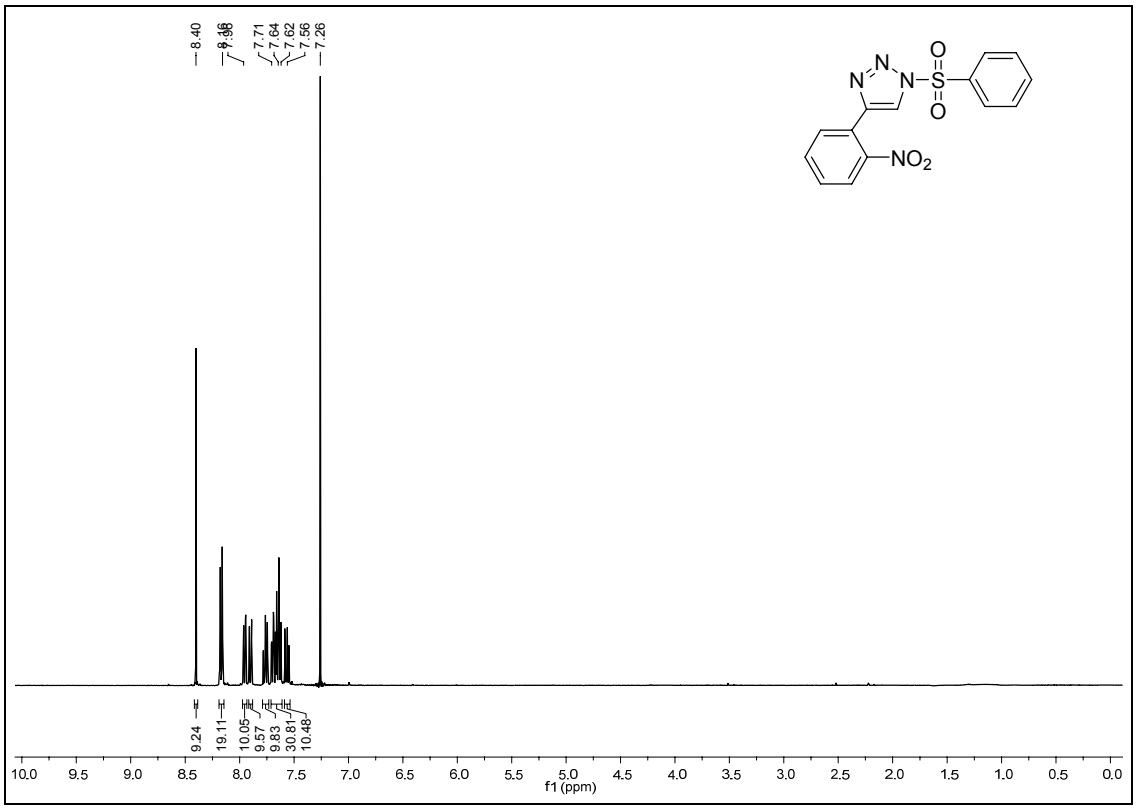
126.91
125.63
122.89
118.63
f1 (ppm)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7.64
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9.57
9.83
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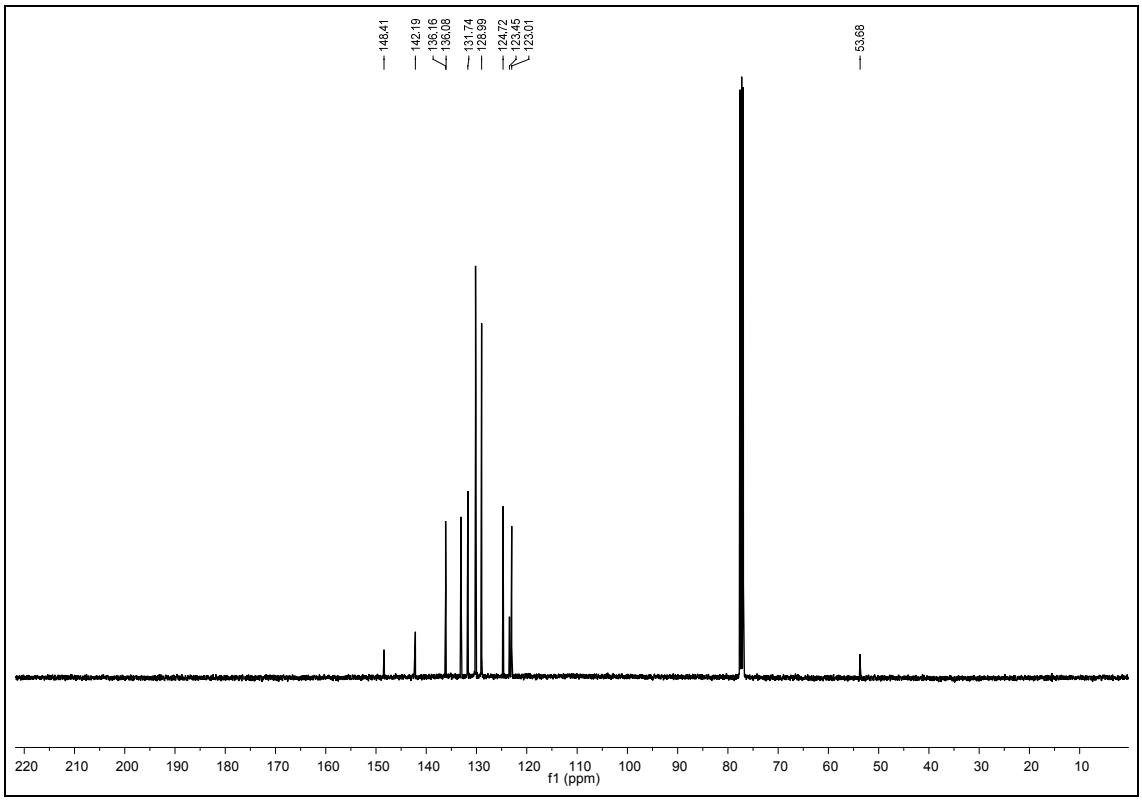
10.48
f1 (ppm)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123.45
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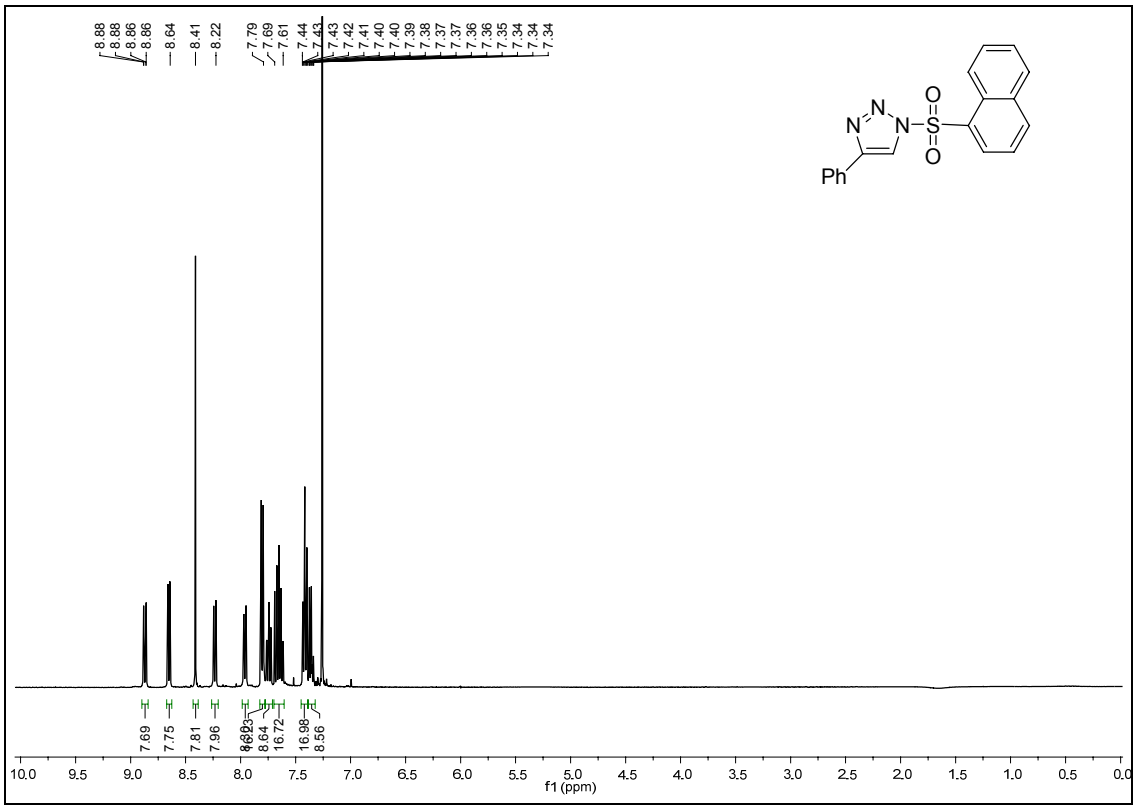
53.68
f1 (ppm)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8.86
8.86
8.64
8.41
8.22
7.79
7.69
7.61
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.34
O
N
N
N
S
O
Ph
7.69
7.75
7.81
7.96
8.64
16.72
16.98
8.56
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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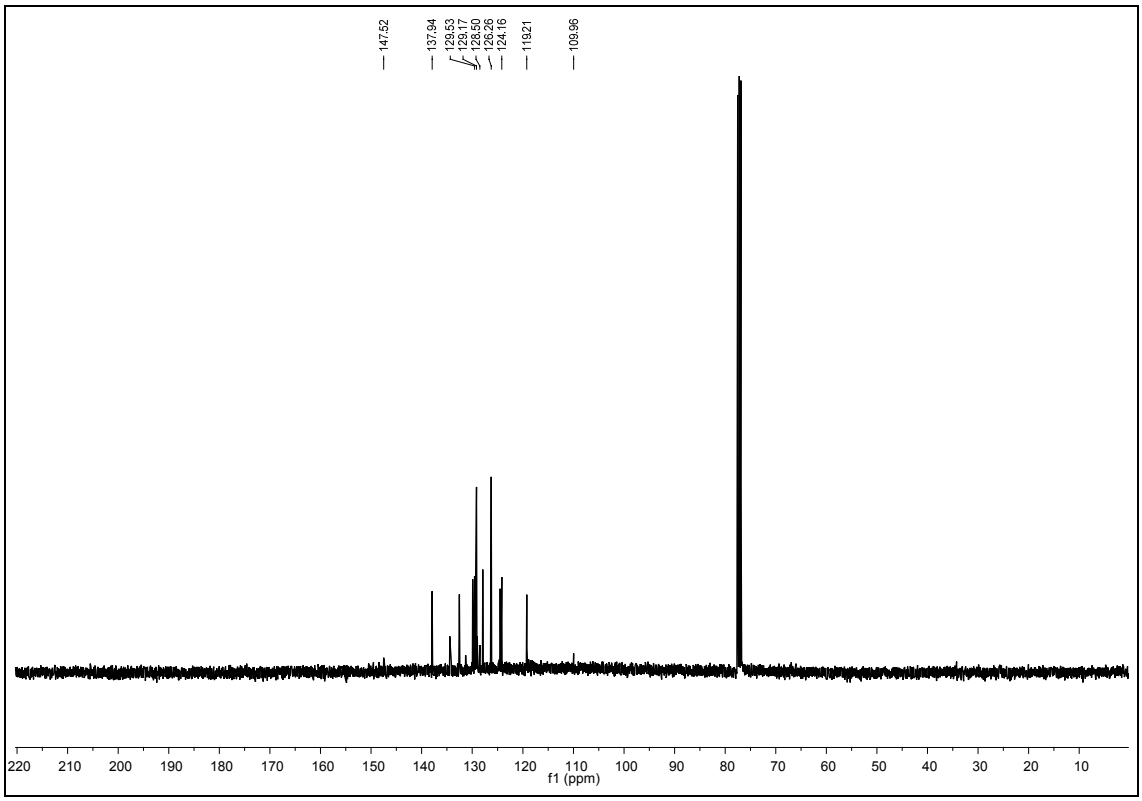
0.0
f1 (ppm)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126.26
124.16
119.21
109.96
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200
190
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)