Electronic Supporting Information (ESI)

Silver-Catalyzed Regioselective Cycloaddition of Isocyanides with Diazo Compounds: Access to 1,4-Disubstituted-1,2,3-triazoles

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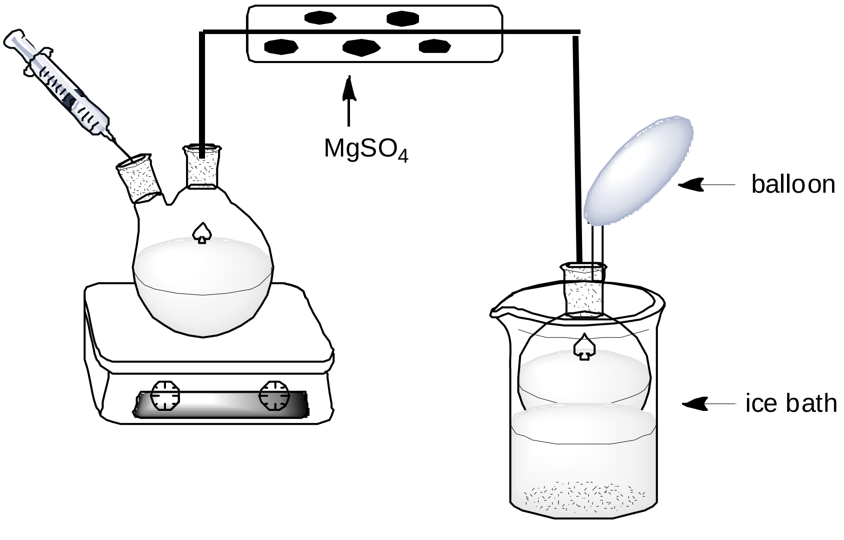
General information:

^{1}H, ^{13}C and ^{19}F NMR were recorded at Bruker AVANCE III 600 M spectrometer. Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points (MP) were measured on a WRS-1A digital melting point apparatus and are uncorrected. X-ray structural analysis was conducted on the XtaLAB mini instrument.

Materials:

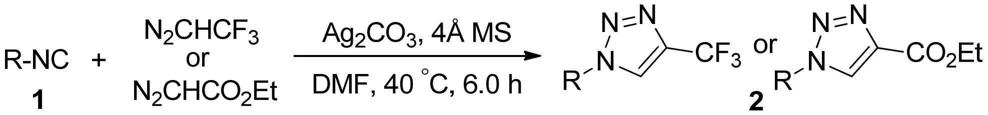
N,N-Dimethylformamide (DMF) was dried by CaH_2. Analytical thin layer chromatography was performed on 0.20 mm silica gel plates. Silica gel (200–300 mesh) was used for flash chromatography. All the isocyanides were prepared according to literatures.[1] 2,2,2-Trifluorodiazoethane (CF_3CHN_2) in different solutions was prepared as flows.



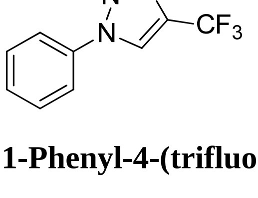
As shown in the figure: A solution of 6.1 g $NaNO_2$ in 15 mL water was added slowly to the stirring solution of 10.8 g of tritluoroethylamine hydrochloride in 25 mL water at rt. And then the rapidly generated yellow gas was gradually blown off through a drying tube ($MgSO_4$) into a gas absorber containing 100 mL anhydrous solvent equipped with an ice bath. After about 2 hours later, there would be no gas bubbling any more. Then the apparatus was removed carefully. Finally the concentration of the stock solution was determined by ^{19}F-NMR analysis with dispersion method.

Experimental part

General procedure for the cycloaddition of diazo compound with isocyanides

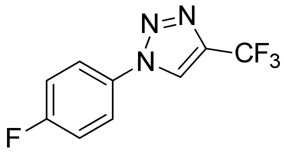


Isocyanobenzene (**1a**, 20.6 mg, 0.2 mmol), Ag_2CO_3 (5.5 mg, 0.02 mmol), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well and 2,2,2-trifluorodiazoethane (26.4 mg, 0.24 mmol, 12 μL of 0.02 M in DMF) was added at room temperature. The reaction mixture was stirred at 40 °C for 6 h. After the reaction mixture was cooled down to room temperature, 10 mL water was added and extracted with EtOAc (8 mL × 3). The organic phases were collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether / ethyl acetate (25:1, v:v) afforded pure 1-phenyl-4-(trifluoromethyl)-1*H*-1,2,3-triazole (**2a**) as a white solid.



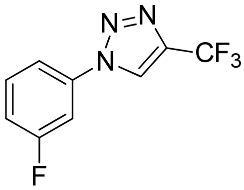
1-Phenyl-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2a).

White solid (36.2 mg, mp: 76–78 ºC, yield: 85%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.18 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.55 (q, *J* = 39.5 Hz), 136.20, 130.12, 129.90, 121.71, 120.99, 120.44 (q, *J* = 267.9 Hz). **HRMS (ESI):** calcd. for $C_9H_6F_3N_3[M+Na]^+$: 236.0406, found: 236.0410. **IR (KBr)** ν 3105, 1596, 1571, 1505, 1380, 1335, 1256, 1134, 1042, 995, 852, 755, 687 cm^{-1}.



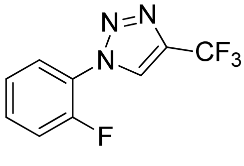
1-(4-Fluorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2b).

White solid (43.0 mg, mp: 83–85 ºC, yield: 93%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.77 – 7.73 (m, 2H), 7.30 – 7.24 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.28 (s), –110.33 ~ –110.38 (m). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.14 (d, *J* = 250.9 Hz), 139.73 (q, *J* = 39.7 Hz), 132.54, 123.21 (d, *J* = 8.8 Hz), 121.90, 120.41 (q, *J* = 267.8 Hz), 117.19 (d, *J* = 23.4 Hz). **HRMS (ESI):** calcd. for $C_9H_5F_4N_3[M+Na]^+$: 254.0312, found: 254.0313. **IR (KBr)** ν 3145, 3114, 1571, 1519, 1378, 1303, 1262, 1240, 1172, 1126, 1101, 1039, 996, 836 cm^{-1}.



1-(3-Fluorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2c).

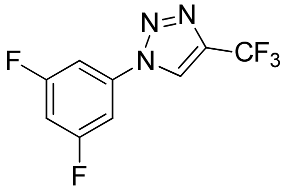
White solid (38.8 mg, mp: 82–84 ºC, yield: 84%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.57 – 7.52 (m, 3H), 7.21 (ddd, *J* = 11.5, 5.4, 3.2 Hz, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.39 (s), –108.99 ~ –109.04 (m). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.19 (d, *J* = 249.8 Hz), 139.80 (q, *J* = 39.6 Hz), 137.33 (d, *J* = 10.0 Hz), 131.69 (d, *J* = 8.9 Hz), 121.79, 120.34 (q, *J* = 268.0 Hz), 116.89 (d, *J* = 21.1 Hz), 116.35 (d, *J* = 3.4 Hz), 108.88 (d, *J* = 26.4 Hz). **HRMS (ESI):** calcd. for $C_9H_5F_4N_3[M+Na]^+$: 254.0312, found: 254.0312. **IR (KBr)** ν 3145, 3115, 1610, 1573, 1484, 1380, 1267, 1222, 1179, 1150, 1042, 977, 870, 848, 780, 679 cm^{-1}.



1-(2-Fluorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2d).

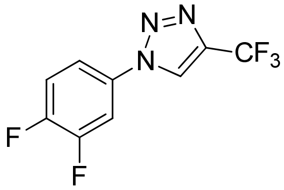
White solid (46.1 mg, mp: 55–57 ºC, yield: 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.39

(s, 1H), 8.02 – 7.94 (m, 1H), 7.54 – 7.48 (m, 1H), 7.42 – 7.31 (m, 2H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.22 (s), –123.74 (ddd, *J* = 11.4, 7.5, 2.4 Hz). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 153.50 (d, *J* = 251.5 Hz), 139.48 (q, *J* = 39.7 Hz), 131.40 (d, *J* = 8.0 Hz), 125.68 (d, *J* = 3.8 Hz), 125.14, 124.55, 120.43 (q, *J* = 267.9 Hz), 117.35 (d, J = 19.8 Hz). **HRMS (ESI):** calcd. for $C_9H_5F_4N_3[M+H]^+$: 232.0492, found: 232.0496. **IR (KBr)** ν 3027, 1538, 1522, 1498, 1455, 1399, 1388, 1243, 1138, 1098, 1022, 937, 774, 672 cm^{-1}.



1-(3,5-Difluorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2e).

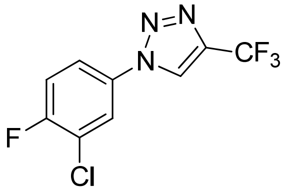
White solid (40.3 mg, mp: 66–68 ºC, yield: 81%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.38 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.99 (tt, *J* = 8.5, 2.2 Hz, 1H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.48 (s), –105.12 (dd, *J* = 8.6, 7.4 Hz). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 163.66 (dd, *J* = 252.2, 13.7 Hz), 140.14 (q, *J* = 40.0 Hz), 137.81 (t, *J* = 12.5 Hz), 121.67 (d, *J* = 2.5 Hz), 120.19 (q, *J* = 268.2 Hz), 105.35 (t, *J* = 25.2 Hz), 104.89 – 104.57 (m). **HRMS (ESI):** calcd. for $C_9H_4F_5N_3[M+H]^+$: 250.0398, found: 250.0404. **IR (KBr)** ν 3122, 3074, 1616, 1514, 1500, 1480, 1428, 1379, 1268, 1233, 1171, 1136, 1029, 997, 977, 855 cm^{-1}.



1-(3,4-Difluorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2f).

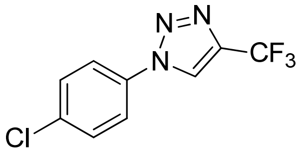
White solid (39.3 mg, mp: 85–87 ºC, yield: 79%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.72 – 7.67 (m, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.39 (q, *J* = 8.8 Hz, 1H)**.** ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.43 (s), –132.56 ~ –132.76 (m), –134.18 ~ –134.77 (m). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 151.74 (dd, *J* = 35.7, 13.0 Hz), 150.06 (dd, *J* =

35.3, 13.1 Hz), 139.86 (q, *J* = 39.7 Hz), 132.43 (dd, *J* = 7.8, 3.4 Hz), 121.97 (d, *J* = 2.3 Hz), 120.22 (q, *J* = 267.9 Hz), 118.86 (d, *J* = 18.9 Hz), 117.17 (dd, *J* = 6.7, 4.0 Hz), 111.31 (d, *J* = 21.8 Hz). **HRMS (ESI):** calcd. for $C_9H_4F_5N_3[M+H]^+$: 250.0398, found: 250.0405. **IR (KBr)** ν 3149, 3115, 1622, 1576, 1527, 1479, 1380, 1282, 1260, 1225, 1210, 1176, 1122, 1040, 979, 879, 845, 821, 782, 746, 645, 605 cm^{-1}



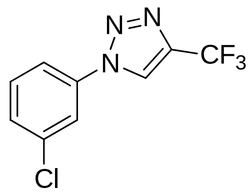
1-(3-Chloro-4-fluorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2g).

White solid (45.1 mg, mp: 70–72 ºC, yield: 85%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.87 (dd, *J* = 6.1, 2.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.36 (t, *J* = 8.5 Hz, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.36 (s), –111.19 ~ –114.89 (m). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.72 (d, *J* = 253.5 Hz), 139.95 (q, *J* = 39.8 Hz), 132.80, 123.75, 123.13 (d, *J* = 19.4 Hz), 121.89 (d, *J* = 2.5 Hz), 120.96 (d, *J* = 7.7 Hz), 120.26 (q, *J* = 268.0 Hz), 118.10 (d, *J* = 23.0 Hz). **HRMS (ESI):** calcd. for $C_9H_4ClF_4N_3[M+H]^+$: 266.0103, found: 266.0109. **IR (KBr)** ν 3143, 3108, 1603, 1566, 1511, 1455, 1407, 1373, 1277, 1256, 1181, 1126, 1065, 1040, 980, 879, 830, 750, 720 cm^{-1}.



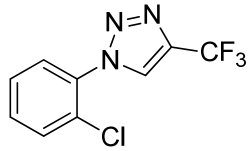
1-(4-Chlorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2h).

White solid (39.0 mg, mp: 126–128 ºC, yield: 79%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.29 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.80 (q, *J* = 39.7 Hz), 135.87, 134.74, 130.33, 122.23, 121.70, 120.35 (q, *J* = 268.0 Hz). **HRMS (ESI):** calcd. for $C_9H_5ClF_3N_3[M+Na]^+$: 270.0016, found: 270.0015. **IR (KBr)** ν 3005, 1555, 1507, 1446, 1397, 1256, 1142, 1040, 933 cm^{-1}.



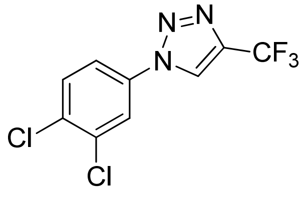
1-(3-Chlorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2i).

White solid (40.0 mg, mp: 79–81 ºC, yield: 81%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.80 (s, 1H), 7.66 (d, J = 7.4 Hz, 1H), 7.51 (q, J = 8.0 Hz, 2H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.29 (s). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 139.78 (q, J = 39.7 Hz), 136.99, 135.96, 131.24, 130.00, 121.75, 121.27, 120.27 (q, J = 267.9 Hz), 118.96. **HRMS (ESI):** calcd. for $C_9H_5ClF_3N_3[M+Na]^+$: 270.0016, found: 270.0022. **IR (KBr)** ν 3139, 3113, 1600, 1579, 1566, 1423, 1420, 1384, 1243, 1199, 1162, 1033, 976, 866, 847, 776, 743, 669 cm^{-1}.



1-(2-Chlorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2j).

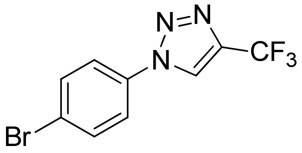
Oil (32.6 mg, yield: 66%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.53 – 7.49 (m, 2H), 7.41 (dt, J = 23.9, 7.2 Hz, 2H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.14 (s). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 138.73 (q, J = 39.6 Hz), 133.91, 131.77, 130.99, 128.76, 128.26, 127.87, 125.43 (d, J = 2.6 Hz), 120.42 (q, J = 267.9 Hz). **HRMS (ESI):** calcd. for $C_9H_5ClF_3N_3[M+Na]^+$: 270.0016, found: 270.0018. **IR (KBr)** ν 3023, 1532, 1500, 1441, 1372, 1301, 1243, 1141, 1037, 931 cm^{-1}.



1-(3,4-Dichlorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2k).

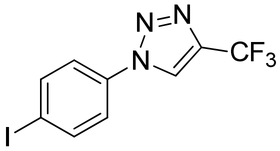
White solid (42.3 mg, mp: 97–99 ºC, yield: 75%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.91 (s, 1H), 7.64 (s, 2H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.37 (s). ^{13}**C**

NMR (150 MHz, $CDCl_3$) δ 139.96 (q, *J* = 39.8 Hz), 135.20, 134.45, 134.26, 131.85, 122.83, 121.76 (d, *J* = 2.6 Hz), 120.21 (q, *J* = 268.0 Hz), 119.95. **HRMS (ESI):** calcd. for $C_9H_4Cl_2F_3N_3[M+Na]^+$: 303.9627, found: 303.9631. **IR (KBr)** ν 3112, 1568, 1488, 1440, 1400, 1373, 1263, 1177, 1137, 1040, 1014, 977, 882, 852, 817,741, 675 cm^{-1}.



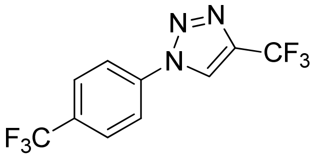
1-(4-Bromophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2l).

White solid (39.4 mg, mp: 139–141 ºC, yield: 68%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.28 (s). ^{13}**C NMR** (150MHz, $CDCl_3$) δ 139.82 (q, *J* = 39.6 Hz), 135.22, 133.31, 123.77, 122.42, 121.62. 120.34 (q, *J* = 267.9 Hz). **HRMS (ESI):** calcd. for $C_9H_5BrF_3N_3[M+Na]^+$: 313.9511, found: 313.9517. **IR (KBr)** ν 3135, 3027, 1561, 1278, 1253, 1212, 1201, 1143, 1111, 1022, 996, 832 cm^{-1}



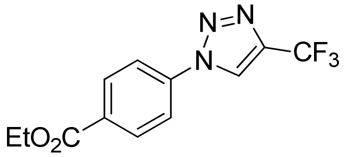
1-(4-Iodophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2m).

White solid (35.3 mg, mp: 159–161 ºC, yield: 52%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H). ^{19}**F NMR** (565 MHz, CDCl3) δ –61.25 (s). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 139.88 (q, *J* = 39.7 Hz), 139.29, 135.92, 122.49, 121.46, 120.34 (q, *J* = 267.8 Hz), 95.12. **HRMS (ESI):** calcd. for $C_9H_5F_3IN_3[M+H]^+$: 339.9553, found: 339.9560. **IR (KBr)** ν 3136, 3106, 1588, 1564, 1493, 1374, 1256, 1168, 1135, 1040, 989, 851, 821, 748 cm^{-1}.



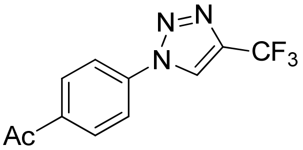
4-(Trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (2n).

White solid (47.8 mg, mp: 139–141 ºC, yield: 85%). **^{1}H NMR** (600 MHz, DMSO) δ 9.72 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 2H). **^{19}F NMR** (565 MHz, DMSO) δ –60.28 (s), –61.55 (s). **^{13}C NMR** (150 MHz, DMSO) δ 138.80, 138.08 (q, *J* = 38.8 Hz), 129.76 (q, *J* = 32.6 Hz), 127.30 (q, *J* = 3.7 Hz), 124.70, 123.76 (q, *J* = 272.4 Hz), 121.29, 120.68 (q, *J* = 267.3 Hz). **HRMS (ESI):** calcd. for $C_{10}H_5F_6N_3[M+Na]^+$: 304.0280, found: 304.0286. **IR (KBr)** ν 3145, 3112, 1572, 1525, 1380, 1336, 1260, 1175, 1071, 1038, 994, 847 cm^{-1}.



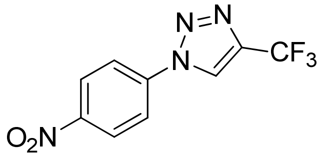
1-(4-Ethoxycarbonylphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2o).

White solid (49.6 mg, mp: 126–128 ºC, yield: 87%). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.45 (s, 1H), 8.21 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (565 MHz, CDCl$_3$) δ –61.36 (s). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 165.23, 139.87 (q, *J* = 39.8 Hz), 139.19, 131.71, 131.51, 121.74, 120.45, 120.31 (q, *J* = 268.0 Hz), 61.70, 14.30. **HRMS (ESI):** calcd. for $C_{12}H_{10}F_3N_3O_2[M+H]^+$: 286.0798, found: 286.0801. **IR (KBr)** ν 3143, 3112, 2996, 1714, 1568, 1376, 1286, 1257, 1145, 1038, 001, 851, 769 cm^{-1}.



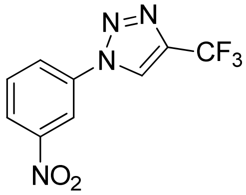
1-(4-Acetylphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2p).

White solid (43.3 mg, mp: 198–200 ºC, yield: 85%). **^{1}H NMR** (600 MHz, DMSO) δ 9.71 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 2.64 (s, 3H). **^{19}F NMR** (565 MHz, DMSO) δ –59.99 (s). **^{13}C NMR** (150 MHz, DMSO) δ 196.95, 138.87, 137.91 (q, *J* = 38.7 Hz), 137.16, 130.03, 124.54, 120.63 (q, *J* = 267.4 Hz), 120.58, 26.86 (q, *J* = 8.8 Hz). **HRMS (ESI):** calcd. for $C_{11}H_8F_3N_3O[M+Na]^+$: 278.0512, found: 278.0513. **IR (KBr)** ν 3106, 3070, 1683, 1601, 1515, 1459, 1403, 1364, 1259, 1145, 1083, 1038, 994, 846, 802, 760, 620, 592 cm^{-1}



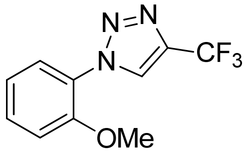
1-(4-Nitrophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2q).

White solid (42.3 mg, mp: 193–195 ºC, yield: 82%). **^{1}H NMR** (600 MHz, DMSO) δ 9.78 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H). **^{19}F NMR** (565 MHz, DMSO) δ –60.15 (s). **^{13}C NMR** (150 MHz, DMSO) δ 147.38, 140.13, 138.05 (q, *J* = 38.7 Hz) 125.49, 124.98, 121.47, 120.52 (q, *J* = 267.7 Hz). **HRMS (ESI):** calcd. for $C_9H_5F_3N_4O_2[M+H]^+$: 259.0437, found: 259.0444. **IR (KBr)** ν 3121, 3092, 1528, 1396, 1350, 1294, 1262, 1150, 1114, 860 cm^{-1}.



1-(3-Nitrophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2r).

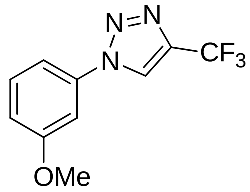
White solid (48.0 mg, mp: 142–144 ºC, yield: 93%). **^{1}H NMR** (600 MHz, DMSO) δ 9.76 (s, 1H), 8.74 (s, 1H), 8.39 (d, *J* = 7.6 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 7.88 (td, *J* = 8.2, 2.1 Hz, 1H). **^{19}F NMR** (565 MHz, DMSO) δ –60.34 (s). **^{13}C NMR** (150 MHz, DMSO) δ 148.40, 137.97 (q, *J* = 38.7 Hz), 136.51, 131.48, 126.58, 124.75, 123.85, 120.50 (q, *J* = 267.4 Hz), 115.43. **HRMS (ESI):** calcd. for $C_{12}H_{10}F_3N_3O_2[M+H]^+$: 259.0437, found: 259.0441. **IR (KBr)** ν 3149, 3120, 3068, 1574, 1539, 1495, 1381, 1352, 1297, 1261, 1180, 1141, 1040, 1010, 976, 902, 869, 844, 814, 751, 667 cm^{-1}.



1-(2-Methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2s).

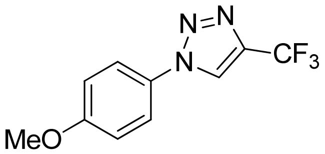
White solid (38.8 mg, mp: 63–65 ºC, yield: 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.43

(s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 8.3 Hz, 2H), 3.92 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -61.00 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.06, 138.52 (q, *J* = 39.4 Hz), 131.08, 125.56, 125.44, 125.41, 121.52, 120.74 (q, *J* = 267.6 Hz), 112.48, 56.21. **HRMS (ESI):** calcd. for $C_{10}H_8F_3N_3O[M+Na]^+$: 266.0512, found: 266.0515. **IR (KBr)** ν 3175, 2947, 1605, 1569, 1510, 1477, 1380, 1258, 1234, 1139, 1029, 981, 940, 837, 762, 673 cm^{-1}.



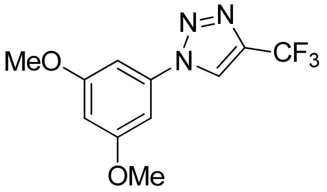
1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2t).

White solid (46.2 mg, mp: 63–65 ºC, yield: 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 2.2 Hz, 1H), 7.26 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.9 Hz, 1H), 3.88 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.25 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.84, 139.49 (q, *J* = 39.5 Hz), 137.23, 130.90, 121.76, 120.47 (q, *J* = 267.8 Hz), 115.55, 112.77, 106.93, 55.76. **HRMS (ESI):** calcd. for $C_{10}H_8F_3N_3O[M+H]^+$: 244.0692, found: 266.0699. **IR (KBr)** ν 3121, 3011, 1610, 1573, 1483, 1449, 1410, 1376, 1211, 1150, 1066, 1018, 972, 921, 822 cm^{-1}.



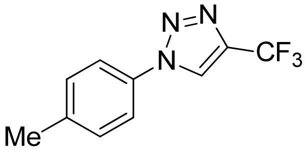
1-(4-Methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2u).

White solid (39.3 mg, mp: 121–123 ºC, yield: 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.18 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.65, 139.34 (q, *J* = 39.4 Hz) 129.56, 122.67, 121.75, 120.54 (q, *J* = 267.8 Hz), 115.09, 55.75. **HRMS (ESI):** calcd. for $C_{10}H_8F_3N_3O[M+Na]^+$: 266.0512, found: 266.0517. **IR (KBr)** ν 3104, 1568, 1517, 1466, 1425, 1380, 1261, 1174, 1137, 1043, 826 cm^{-1}.



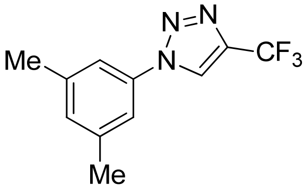
1-(3,5-Dimethoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2v).

White solid (39.2 mg, mp: 65–67 ºC, yield: 72%). ^{1}**H NMR** (600 MHz, CDCl$_3$) δ 8.31 (s, 1H), 6.87 (s, 2H), 6.54 (s, 1H), 3.85 (s, 6H). ^{19}**F NMR** (565 MHz, CDCl$_3$) δ –61.24. ^{13}**C NMR** (150 MHz, CDCl$_3$) δ161.69, 139.35 (q, J = 39.5 Hz), 137.61, 121.78, 120.40 (q, J = 267.8), 101.27, 99.33, 55.81. **HRMS (ESI):** calcd. for $C_{11}H_{10}F_3N_3O$ $[M+H]^+$: 274.0798, found: 274.0804. **IR (KBr)** ν 3113, 3010, 1616, 1495, 1462, 1377, 1231, 1210, 1150, 1062, 1020, 976, 924, 826, 675 cm^{-1}.



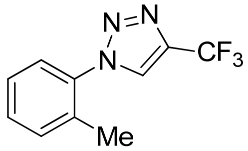
1-(*p*-Tolyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2w).

White solid (25.4 mg, mp: 95–97 ºC, yield: 56%). ^{1}**H NMR** (600 MHz, CDCl$_3$) δ 8.27 (s, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H). ^{19}**F NMR** (565 MHz, CDCl3) δ –61.20 (s). ^{13}**C NMR** (150 MHz, CDCl$_3$) δ 140.22, 139.45 (q, J = 39.6 Hz), 133.98, 130.59, 121.61, 120.88, 120.54 (q, J = 267.2 Hz), 21.18. **HRMS (ESI):** calcd. for $C_{10}H_8F_3N_3[M+Na]^+$: 250.0563, found: 250.0566. **IR (KBr)** ν 3111, 3049, 1569, 1522, 1379, 1259, 1166, 1134, 1041, 994, 853, 818 cm^{-1}.



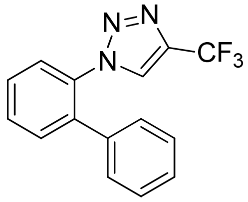
1-(3,5-Dimethylphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2x).

White solid (36.2 mg, mp: 63–65 ºC, yield: 75%). ^{1}**H NMR** (600 MHz, CDCl$_3$) δ 8.21 (s, 1H), 7.22 (s, 2H), 6.99 (s, 1H), 2.26 (s, 6H). ^{19}**F NMR** (565 MHz, CDCl$_3$) δ –61.25 (s). ^{13}**C NMR** (150 MHz, CDCl$_3$) δ 140.12, 139.26 (q, J = 39.4 Hz), 136.09, 131.34, 121.72 (d, *J* = 2.6 Hz), 120.54 (q, *J* = 267.7 Hz), 118.59, 21.14. **HRMS (ESI):** calcd. for $C_{11}H_{10}F_3N_3[M+H]^+$: 242.0900, found: 242.0905. **IR (KBr)** ν 3144, 3113, 1618, 1597, 1571, 1489, 1436, 1378, 1290, 1255, 1225, 1169, 1133, 1036, 988, 945, 896, 846 cm^{-1}



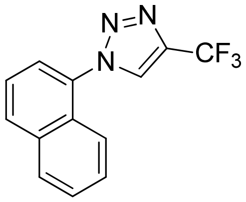
1-(*o*-Tolyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2y).

Oil (32.7 mg, yield: 72%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 2.19 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.04 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.78 (q, *J* = 39.5 Hz), 135.53, 133.77, 131.77, 130.71, 127.15, 125.97, 124.84, 120.56 (q, *J* = 267.8 Hz), 17.70. **HRMS (ESI):** calcd. for $C_{10}H_8F_3N_3[M+H]^+$: 250.0563, found: 250.0570. **IR (KBr)** ν 3121, 3099, 1567, 1522, 1441, 1422, 1399, 1379, 1263, 1200, 1173, 1122, 1019, 987, 877, 815, 760 cm^{-1}.



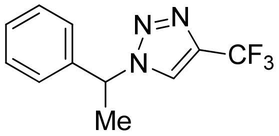
1-([1,1'-Biphenyl]-2-yl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2z).

White solid (38.2 mg, mp: 67–69 ºC, yield: 66%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 15.5, 7.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.47 (s, 1H), 7.32 (p, J = 6.0 Hz, 3H), 7.10 – 7.04 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.22 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.66 (q, *J* = 39.5 Hz), 137.37, 136.69, 134.23, 131.36, 130.79, 129.02, 128.91, 128.50, 128.45, 126.63, 125.34 (d, *J* = 2.6 Hz), 120.33 (q, *J* = 267.8 Hz). **HRMS (ESI):** calcd. for $C_{15}H_{10}F_3N_3[M+Na]^+$: 312.0719, found: 312.0720. **IR (KBr)** ν 3146, 3114, 1592, 1565, 1506, 1486, 1465, 1447, 1435, 1423, 1394, 1295, 1261, 1230, 1131, 1084, 1037, 1009, 997, 979, 910, 840, 780, 765, 737 cm^{-1}.



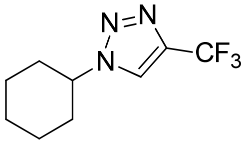
1-(Naphthalen-1-yl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2a').

White solid (46.3 mg, mp: 94–96 ºC, yield: 88%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.05 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 5.2 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.51 (d, *J* = 8.4 Hz, 1H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –60.89 (s). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 138.98 (q, *J* = 39.6 Hz), 134.22, 132.63, 131.32, 128.55, 128.42, 128.28, 127.46, 125.86, 125.00, 123.92, 121.74, 120.61 (q, *J* = 267.9 Hz). **HRMS (ESI):** calcd. for $C_{13}H_8F_3N_3[M+H]^+$: 264.0743, found: 264.0749. **IR (KBr)** ν 3134, 3100, 1599, 1567, 1376, 1269, 1246, 1216, 1148, 1038, 985, 861, 803, 772, 741 cm^{-1}.



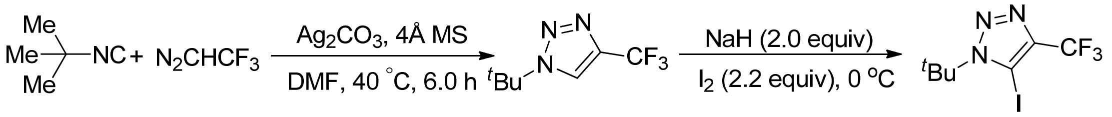
1-(1-Phenylethyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2b').

White solid (20.8 mg, mp: 54–56 ºC, yield: 43%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.40 (dd, *J* = 15.5, 8.3 Hz, 3H), 7.30 (d, *J* = 7.0 Hz, 2H), 5.87 (q, *J* = 6.8 Hz, 1H), 2.03 (d, *J* = 7.0 Hz, 3H). ^{19}**F NMR** (565 MHz, $CDCl_3$) δ –61.08 (s). ^{13}**C NMR** (150 MHz, $CDCl_3$) δ 138.97 (q, *J* = 39.3 Hz), 138.78, 129.45, 129.24, 126.77, 122.07, 120.60 (q, *J* = 267.7 Hz), 61.19, 21.35. **HRMS (ESI):** calcd. for $C_{11}H_{10}F_3N_3[M+Na]^+$: 264.0719, found: 264.0718. **IR (KBr)** ν 3141, 3104, 3033, 3005, 1566, 1496, 1455, 1384, 1259, 1229, 1157, 1041, 994, 855, 778, 749, 706 cm^{-1}.



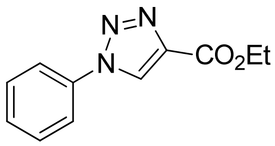
1-Cyclohexyl-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2c').

White solid (12.3 mg, mp: 34–36 ºC, yield: 28%). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.83 (s, 1H), 4.51 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.25 (dd, *J* = 13.2, 1.8 Hz, 2H), 1.96 (dd, *J* = 10.9, 3.0 Hz, 2H), 1.77 (ddd, *J* = 25.0, 12.6, 3.6 Hz, 3H), 1.53 – 1.45 (m, 2H), 1.35 – 1.26 (m, 1H). **^{19}F NMR** (565 MHz, CDCl$_3$) δ –61.06 (s). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 138.72 (q, *J* = 39.2 Hz), 120.91, 120.81 (q, *J* = 267.6 Hz), 60.93, 33.63, 25.18, 25.16. **HRMS (ESI):** calcd. for $C_9H_{12}F_3N_3[M+Na]^+$: 242.0876, found: 242.0881. **IR (KBr)** ν 3119, 2961, 1537, 1440, 1212, 1147, 1030, 990, 889, 766 cm^{-1}.



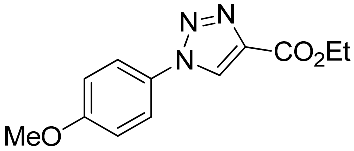
2d': 26% yield of two steps: 21%

Ag$_2$CO$_3$ (0.04 mmol, 0.10 equiv), isocyanide **1** (0.40 mmol, 1.0 equiv), 4Å MS (100.0 mg), and trifluoromethylbenzene (0.4 mmol, 1.0 equiv) were added into a 10.0 mL Schlenk tube. The tube was sealed well and diazo compound (0.48 mmol, 1.2 equiv) in DMF (1.0 mL) was added. The reaction mixture was conducted at 40 °C for 6.0 h, and cooled at room temperature. A little sample (~ 40 μL) was used for the ^{19}F NMR spectroscopic analysis and the determination of yield (**2d'**: 26%). To the reaction mixture was added sodium hydride (0.8 mmol, 2.0 equiv) at 0 ºC. After stirring for 1 h at the same temperature, I$_2$ (0.88 mmol, 2.2 equiv) was added and stirred overnight at room temperature. The reaction was quenched with water and extracted with ether (8.0 mL × 3). The organic phases were collected, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexane / ethyl acetate =50:1) afforded the corresponding iodotriazole: 1-(*tert*-butyl)-5-iodo-4-(trifluoromethyl)-1*H*-1,2,3-triazole, white solid (26.8 mg, mp: 84–86 ºC, yield: 21%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 1.17 (s, 9H). **^{19}F NMR** (376 MHz, CDCl$_3$) δ –59.46 (s). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 126.57, 120.31 (q, *J* = 267.4 Hz), 54.12, 29.89. **IR (KBr)** ν 3445, 3179, 2975, 2925, 1581, 1418, 1141, 971, 768, 610, 432 cm^{-1}. **HRMS (EI):** calcd. for $C_7H_9F_3IN_3[M]^+$: 318.9788, found: 318.9793.



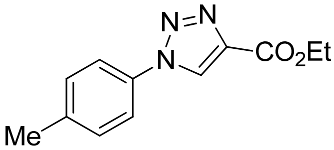
Ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (2e'). [2]

White solid (31.2 mg, mp: 83–85 ºC, yield: 72%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.64, 140.84, 136.38, 129.95, 129.52, 125.59, 120.81, 61.48, 14.34.



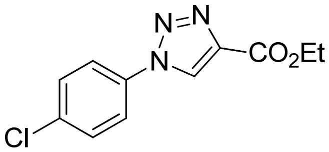
Ethyl 1-(4-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (2f'). [2]

White solid (41.0 mg, mp: 110–112 ºC, yield: 83%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.62 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.77, 160.40, 140.69, 129.76, 125.65, 122.50, 114.98, 61.47, 55.74, 14.39.



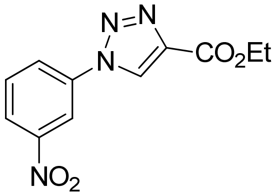
Ethyl 1-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (2g'). [2]

White solid (39.3 mg, mp: 96–98 ºC, yield: 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.64, 140.63, 139.70, 134.03, 130.37, 125.49, 120.62, 61.36, 21.09, 14.30.



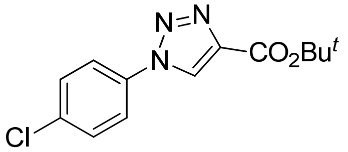
Ethyl 1-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (2h'). [2]

White solid (37.3 mg, mp: 170–172 ºC, yield: 74%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.57, 141.17, 135.55, 134.95, 130.27, 125.53, 122.10, 61.70, 14.43.



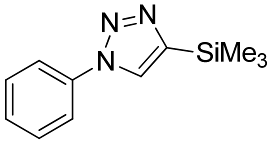
Ethyl 1-(3-nitrophenyl)-1*H*-1,2,3-triazole-4-carboxylate (2i'). [2]

White solid (31.9 mg, mp: 142–144ºC, yield: 61%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (s, 2H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 1H), 4.48 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.29, 149.13, 141.63, 137.22, 131.40, 126.38, 125.58, 124.12, 115.80, 61.93, 14.44.



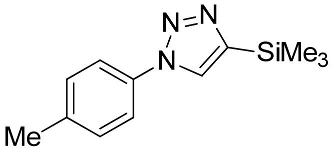
***Tert*-butyl 1-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (2j').**

White solid (36.9 mg, mp: 169–171 ºC, yield: 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 1.58 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.66, 142.29, 135.23, 134.98, 130.11, 125.20, 122.01, 82.69, 28.25. **HRMS (ESI):** calcd. for $C_{13}H_{14}ClN_3O_2[M+Na]^+$: 302.0667, found: 302.0668. **IR (KBr)** ν 3408, 3145, 3110, 2983, 2935, 1713, 1543, 1498, 1400, 1264, 1038, 836, 800, 516 cm^{-1}.



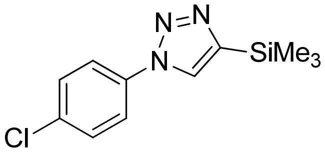
1-Phenyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (2k').

White solid (13.9 mg, mp: 96–98 ºC, yield: 32%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 0.37 (s, 9H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 147.45, 137.21, 129.78, 128.58, 127.25, 120.92, –1.01. **HRMS (ESI):** calcd. for $C_{11}H_{15}N_3Si[M+Na]^+$: 240.0927, found: 240.0930. **IR (KBr)** ν 3444, 3137, 2957, 2226, 1674, 1399, 1245, 1207, 839, 749, 687, 513 cm^{-1}.



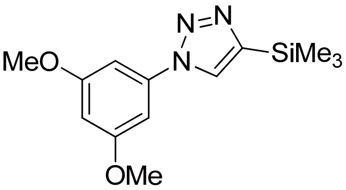
1-(*p*-Tolyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (2l').

White solid (16.2 mg, mp: 95–97 ºC, yield: 35%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H), 0.37 (s, 9H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 147.25, 138.61, 134.94, 130.26, 127.23, 120.82, 21.19, –1.00. **HRMS (ESI):** calcd. for $C_{12}H_{17}N_3Si[M+Na]^+$: 254.1084, found: 254.1090. **IR (KBr)** ν 3130, 3046, 2959, 2226, 1721, 1519, 1249, 1205, 842, 815, 755, 517 cm^{-1}.



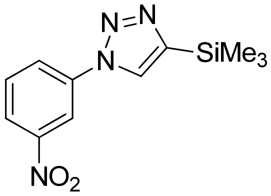
1-(4-Chlorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (2m').

White solid (20.6 mg, mp: 123–125 ºC, yield: 41%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.91 (s, 1H), 7.69 (d, *J* = 6.9 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 0.37 (s, 9H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 147.86, 135.73, 134.32, 129.98, 127.09, 122.04, –1.03. **HRMS (ESI):** calcd. for $C_{11}H_{14}ClN_3Si[M+Na]^+$: 274.0538, found: 274.0539. **IR (KBr)** ν 3448, 3117, 2980, 2902, 2231, 1677, 1502, 1248, 1201, 1038, 983, 840, 761, 514 cm^{-1}.



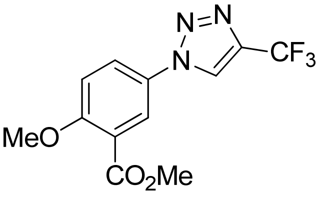
1-(3,5-Dimethoxyphenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (2n').

Colorless oil (23.3 mg, yield: 42%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 6.87 (s, 2H), 6.47 (s, 1H), 3.82 (s, 6H), 0.35 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.52, 147.32, 138.65, 127.36, 100.36, 99.31, 55.76, –1.06. **HRMS (ESI):** calcd. for $C_{13}H_{19}N_3O_2Si[M+Na]^+$: 300.1139, found: 300.1140. **IR (KBr)** ν 3122, 3005, 2958, 2843, 1608, 1492, 1203, 1157, 1065, 843, 759, 632 cm^{-1}.



1-(3-Nitrophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (2o').

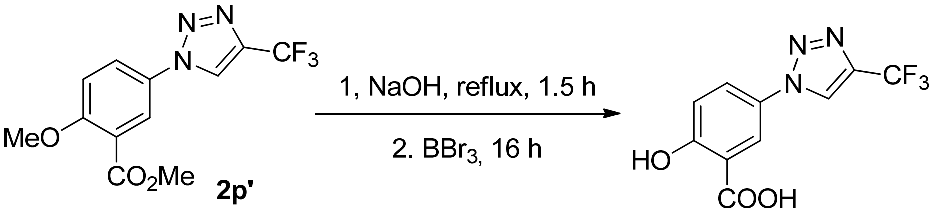
White solid (19.9 mg, mp: 107–109 ºC, yield: 38%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.74 (t, *J* = 8.2 Hz, 1H), 0.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.00, 148.58, 137.94, 131.05, 127.07, 126.43, 123.03, 115.44, –1.08. **HRMS (ESI):** calcd. for $C_{11}H_{14}N_4O_2Si[M+Na]^+$: 285.0778, found: 285.0782. **IR (KBr)** ν 3742, 3125, 2961, 1743, 1698, 1535, 1399, 1349, 1248, 840, 735, 667 cm^{-1}.



Methyl 2-methoxy-5-(4-(trifluoromethyl)-1*H*-1,2,3-triazol-1-yl)benzoate (2p').

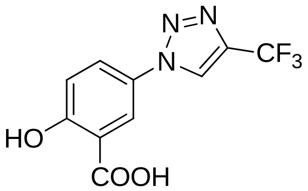
White solid (45.2 mg, mp: 126–128 ºC, yield: 75%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.10 (d, *J* = 2.8 Hz, 1H), 7.86 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.24 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.09, 159.93, 139.54 (q, *J* = 39.6 Hz), 128.89, 126.22, 124.43, 121.79 (d, J = 2.5 Hz), 121.09, 120.40 (q, J = 267.8 Hz), 113.42, 56.60, 52.53. **HRMS (ESI):** calcd. for $C_{12}H_{10}F_3N_3O_3[M+Na]^+$: 324.0566, found: 324.0566. **IR (KBr)** ν 3113, 2960, 1687, 1614, 1510, 1323, 1262, 1194, 1138, 1044, 1018, 983, 912, 847, 822, 785, 747 cm^{-1}.

The preparation of Mesalazine-derived 1,2,3-triazole



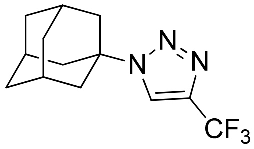
To a solution of **2p'**(0.29 mmol, 87.3 mg) in methanol (5.0 mL) was added 2 N aqueous sodium hydroxide solution (4.5 mL) and the mixture heated at reflux for 1.5 h. The reaction was cooled to ambient temperature, filtered and the filtrate concentrated *in vacuo* to remove the methanol. The residual aqueous phase was washed with diethyl ether, acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. The organic extracts were dried ($MgSO_4$) and the solvent removed in vacuo to give 2-methoxy-5-(4-(trifluoromethyl)-1*H*-1,2,3-triazol-1-yl)benzoic acid as a white solid (82.7 mg), which was used without further purification.

A solution of boron tribromide (0.66 mmol) in dichloromethane (1.0 mL) was added dropwise to a solution of 2-methoxy-5-(4-(trifluoromethyl)-1*H*-1,2,3-triazol-1-yl)-benzoic acid (82.7 mg, 0.29 mmol) in dried dichloromethane (2.0 mL) under argon at 0 °C. The reaction was stirred for 1 hour at 0 °C and allowed to warm to ambient temperature and stirred for further 16 hours. It was then poured into ice water and extracted with dichloromethane then with ethyl acetate. The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate and the aqueous phase acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. The ethyl acetate extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography on silica gel afforded the corresponding product.



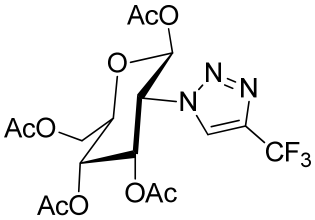
2-Hdroxy-5-(4-(trifluoromethyl)-1*H*-1,2,3-triazol-1-yl)benzoic acid (3).

White solid [75.2 mg, mp: 222–224 ºC, yield: 95% (two steps)]. **^{1}H NMR** (600 MHz, DMSO) δ 9.55 (s, 1H), 8.28 (d, *J* = 2.3 Hz, 1H), 8.04 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 1H). **^{19}F NMR** (565 MHz, DMSO) δ –59.83 (s). **^{13}C NMR** (150 MHz, DMSO) δ 170.68, 161.37, 137.51 (q, *J* = 38.4 Hz), 128.14, 127.79, 124.31, 122.77, 120.70 (q, *J* = 267.3 Hz), 118.62, 113.90. **HRMS (ESI):** calcd. for $C_{10}H_6F_3\ N_3O_3[M-H]^-$: 272.0288, found: 272.0289. **IR (KBr)** ν 3247, 3053, 3011, 2955, 1660, 1613, 1502, 1312, 1260, 1182, 1022, 1000, 982, 903,843, 822, 773 cm^{-1}.



1-(Adamantan-1-yl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (2q').

White solid (28.2 mg, mp: 148–150 ºC, yield: 52%). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.90 (s, 1H), 2.26 (d, *J* = 19.4 Hz, 6H), 2.23 (s, 3H) 1.79 (q, *J* = 12.5 Hz, 6H). **^{19}F NMR** (565 MHz, CDCl$_3$) δ –60.96 (s). **^{13}C NMR** (150 MHz, CDCl$_3$) δ 138.06 (q, *J* = 38.8 Hz), 120.87 (q, *J* = 267.5 Hz), 119.80, 60.91, 43.00, 35.81, 29.50. **HRMS (ESI):** calcd. for $C_{13}H_{16}F_3N_3[M+Na]^+$: 294.1189, found: 294.1190. **IR (KBr)** ν 3146, 3109, 2914, 2859, 1566, 1453, 1380, 1308, 1253, 1227, 1196, 1161, 1135, 1053, 1016, 983 cm^{-1}.



(2*S*,3*R*,5*S*,6*R*)-6-(Acetoxymethyl)-3-(4-(trifluoromethyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (2r').

White solid (34.5 mg, mp: 174–176 ºC, yield: 37%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 5.80 (t, *J* = 8.8 Hz, 1H), 5.22 (t, *J* = 8.5 Hz, 1H), 4.72 (t, *J* = 8.5 Hz, 1H) 4.39 (d, *J* = 9.5 Hz, 1H), 4.17 (d, *J* = 11.9 Hz, 1H), 4.08 (d, *J* = 5.0 Hz, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.20 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.57, 169.68, 169.14, 168.02, 139.19 (q, *J* = 39.8 Hz), 123.90, 120.25 (q, *J* = 268.2 Hz), 91.59, 73.25, 72.07, 68.18, 63.36, 61.47, 20.76, 20.60, 20.54, 20.24. **HRMS (ESI):** calcd. for $C_9H_{12}F_3N_3[M+Na]^+$: 490.1044, found: 490.1045. **IR (KBr)** ν 2995, 1770, 1759, 1383, 1245, 1103, 1056, 764, 750 cm^{-1}.

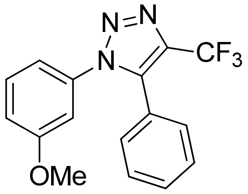
Pd-catalyzed arylation of 1,4-disubstituted 1,2,3-triazoles:[3]

Typical Preparative Procedure A

1-(3-methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole **2t** (36.4 mg, 0.15 mmol, 1.0 equiv), $Pd(Ph_3P)_2Cl_2$ (5.26 mg, 0.05 equiv), tetrabutylammonium acetate (90.3 mg, 2.0 equiv) were added into a 10.0 mL Schlenk tube under Ar atmosphere. 1.0 mL of NMP was then added, followed by the addition of aryl bromine (1.5 equiv), and the reaction mixture was stirred at 100°C for 2 h. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (10 mL), washed twice with 10 mL portions of water and brine, dried over Na_2SO_4, concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 15:1) afforded the corresponding product.

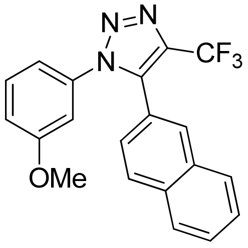
Typical Preparative Procedure B

1-(3-methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (36.4 mg, 0.15 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.34 mg, 0.04 equiv), PCy_3 (3.36 mg, 0.08 equiv), chlorobenzene or aryl trifluoromethanesulfonate (1.50 equiv), and K_2CO_3 (41.4 mg, 2.0 equiv) were added into a 10.0 mL Schlenk tube under Ar atmosphere. 1.0 mL of PhMe was then added and the reaction mixture was stirred for 22 h. at 120 °C. Et_2O (5.0 mL) and H_2O (5.0 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 5.0 mL). The combined organic layers were washed with aqueous NH_4Cl (5.0 mL), H_2O (5.0 mL) and brine (5.0 mL), dried over Na_2SO_4 and concentrated in vacuum. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 15:1) afforded the corresponding product.



1-(3-Methoxyphenyl)-5-phenyl-4-(trifluoromethyl)-1*H*-1,2,3-triazole (4a).

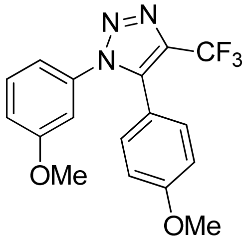
Prepared according to Procedure **A**, white solid (41.0 mg, mp: 82–84 ºC, yield: 86%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 3H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 3.71 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –59.10 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.23, 137.31, 136.53, 136.43 (q, *J* = 38.3 Hz), 130.45, 130.25, 129.85, 128.99, 124.77, 120.94 (q, *J* = 268.7 Hz), 117.32, 115.98, 110.75, 55.59. **HRMS (ESI):** calcd. for $C_{16}H_{12}F_3N_3O_2[M+Na]^+$: 342.0825, found: 342.0824. **IR (KBr)** ν 3064, 2957, 2926, 2833, 1597, 1500, 1488, 1455, 1427, 1377, 1246, 1147, 1030, 987, 863, 831, 770 cm^{-1}.



1-(3-Methoxyphenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (4b).

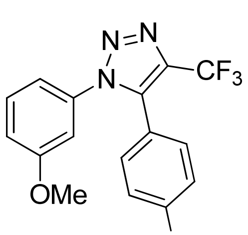
Prepared according to Procedure **B**, white solid (39.3 mg, mp: 101–103 ºC, yield: 71%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 18.1, 9.0 Hz, 4H), 7.60 – 7.54 (m, 2H), 7.25 – 7.18 (m, 2H), 6.93 (dd, *J* = 8.6, 1.6 Hz, 2H), 6.83 – 6.80 (m, 1H), 3.68 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –58.97 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ

160.29, 137.39, 137.38, 136.65 (q, *J* = 38.0 Hz), 136.61, 133.69, 132.81, 130.27, 128.86, 128.55, 127.97, 127.93, 127.24, 126.04, 122.02, 121.02 (q, *J* = 268.8 Hz), 117.32, 115.88, 110.91, 55.57. **HRMS (ESI):** calcd. for $C_{20}H_{14}F_3N_3O[M+Na]^+$: 392.0981, found: 392.0985. **IR (KBr)** ν 3056, 3006, 2962, 1493, 1472, 1262, 1197, 1162, 1134, 1092, 843 cm^{-1}.



1-(3-Methoxyphenyl)-5-(4-methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (4c).

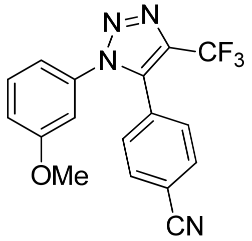
Prepared according to Procedure **A**, oil (37.8 mg, yield: 73%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.93 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.85 (t, *J* = 2.2 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.1 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –59.14 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.19, 160.34, 137.33, 136.80, 136.23 (q, *J* = 37.9 Hz), 131.30, 130.24, 121.10 (q, *J* = 268.6 Hz), 117.46, 116.64, 115.89, 114.55, 111.00, 55.66, 55.48. **HRMS (ESI):** calcd. for $C_{17}H_{14}F_3N_3O_2[M+Na]^+$: 372.0930, found: 372.0935. **IR (KBr)** ν 3076, 2961, 2931, 2841, 1613, 1584, 1512, 1494, 1469,1451, 1443, 1386, 1252, 1157, 1090,1032, 989, 863, 834, 780 cm^{-1}.



1-(3-Methoxyphenyl)-5-(4-nitrophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (4d)

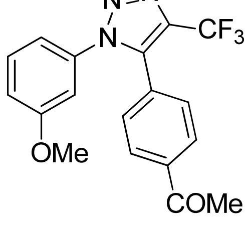
Prepared according to Procedure **B**, white solid (35.4 mg, mp: 128–130 ºC, yield: 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.88 (s, 1H), 6.73 (dd, *J* =

7.9, 0.9 Hz, 1H), 3.77 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –59.03 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.59, 148.97, 137.05 (q, *J* = 38.7 Hz), 135.94, 135.14, 131.25, 131.11, 130.66, 124.16, 120.63 (q, *J* = 268.9 Hz), 117.34, 116.17, 111.38, 55.76. **HRMS (ESI):** calcd. for $C_{16}H_{11}F_3N_4O_3$ $[M+Na]^+$: 387.0675, found: 387.0679. **IR (KBr)** ν 3117, 3015, 2967, 2845, 1609, 1520, 1493, 1443, 1388, 1345, 1290, 1242, 1201, 1168, 1132, 1077, 1044, 1005, 858, 770, 700, 680 cm^{-1}.



4-(1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazol-5-yl)benzonitrile (4e).

Prepared according to Procedure **A**, white solid (28.5 mg, mp: 99–101 ºC, yield: 55%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.85 (t, *J* = 2.1 Hz, 1H), 6.73 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.76 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –59.04 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.53, 136.88 (q, *J* = 38.5 Hz), 135.97, 135.41, 132.68, 130.66, 130.59, 129.46, 120.64 (q, *J* = 268.9 Hz), 117.74, 117.31, 116.15, 114.56, 111.25, 55.72. **HRMS (ESI):** calcd. for $C_{17}H_{11}F_3N_4O$ $[M+Na]^+$: 367.0777, found: 367.0778. **IR (KBr)** ν 2963, 2925, 2839, 2228, 1610, 1590, 1469, 1443, 1388, 1258, 1200, 1173, 1159, 1138, 1076, 1047, 1013, 993, 875, 840 cm^{-1}.



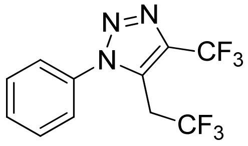
1-(4-(1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazol-5-yl)phenyl)ethanone (4f).

Prepared according to Procedure **B**, white solid (44.4 mg, mp: 91–93 ºC, yield: 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.84 (t, *J* = 2.1 Hz, 1H), 6.73 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.72 (s, 3H), 2.59 (s, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –59.06 (s). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 197.19, 160.43, 138.36, 136.77 (q, *J* = 38.4 Hz), 136.28, 130.45, 130.26, 129.31, 128.75, 120.79 (q, *J* = 268.7 Hz), 117.36, 116.05, 111.14, 55.69, 26.81. **HRMS (ESI):** calcd. for $C_{18}H_{14}F_3N_3O_2[M+Na]^+$: 384.0930, found: 384.0933. **IR (KBr)** ν 3058, 3014, 1688, 1606, 1498, 1475, 1425, 1260, 1202, 1165, 1132, 1095, 1067, 1038, 843 cm^{-1}.

1-Phenyl-5-(2,2,2-trifluoroethyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (5) was also detected when excessive CF_3CHN_2 were used

Ag_2CO_3 (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide **1** (20.6 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg) were added into a 10.0 mL Schlenk tube. The tube was sealed well and 2,2,2-trifluorodiazoethane in DMF (178 mg, 2.0 M, 8.0 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 25:1) afforded the corresponding product **2** (23.4 mg, yield: 55%) and the product **5** (7.1 mg, yield: 12%).



White solid (mp: 102–104 ºC). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 16.3, 8.4 Hz, 3H), 7.42 (d, *J* = 7.2 Hz, 2H), 3.67 (q, *J* = 9.1 Hz, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ –61.02 (d, *J* = 3.7 Hz, 3F), –64.35 (dt, *J* = 9.2, 4.4 Hz, 3F). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.26 (q, *J* = 38.7 Hz), 134.45, 131.43, 130.20, 127.56, 126.50, 123.36 (q, *J* = 278.1 Hz), 120.61 (q, *J* = 268.7 Hz), 28.62 (q, *J* = 33.6 Hz). **HRMS**

(ESI): calcd. for $C_{11}H_7F_6N_3[M+Na]^+$: 318.0436, found: 318.0440. **IR (KBr)** ν 3105, 3075, 2994, 2958, 1761, 1558, 1530, 1467, 1426, 1396, 1368, 1251, 1164, 1141, 1115, 1091, 997, 909, 844, 771, 699, 651 cm^{-1}.

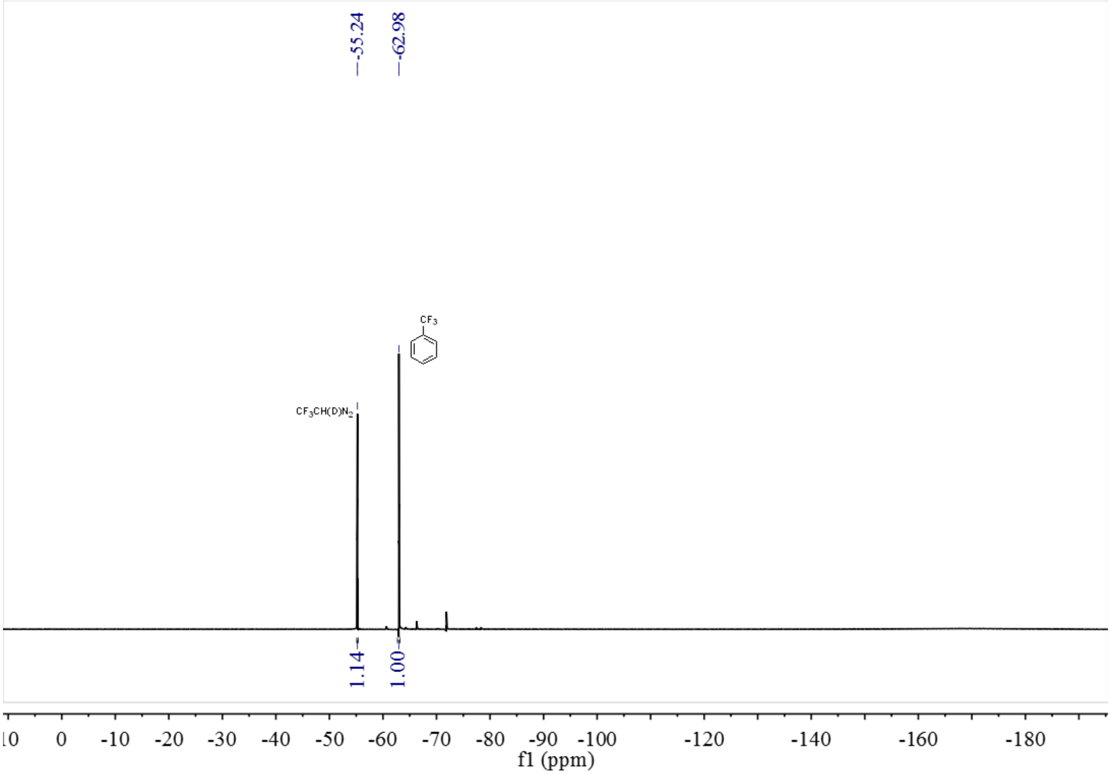
Cross-coupling experiment of the cycloadduct 2a with CF_3CHN_2

Ag_2CO_3 (5.50 mg, 0.02 mmol, 0.10 equiv), cycloadduct **2a** (42.6 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg) were added into a 10.0 mL Schlenk tube. The tube was sealed well and CF_3CHN_2 in DMF (44.0 mg, 0.20 M, 2.0 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After cooling the tube to room temperature, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel afforded the product. The ^1H NMR spectrogram of product indicated this reaction could not undergo and the starting reagent **2a** was 99% recovered.

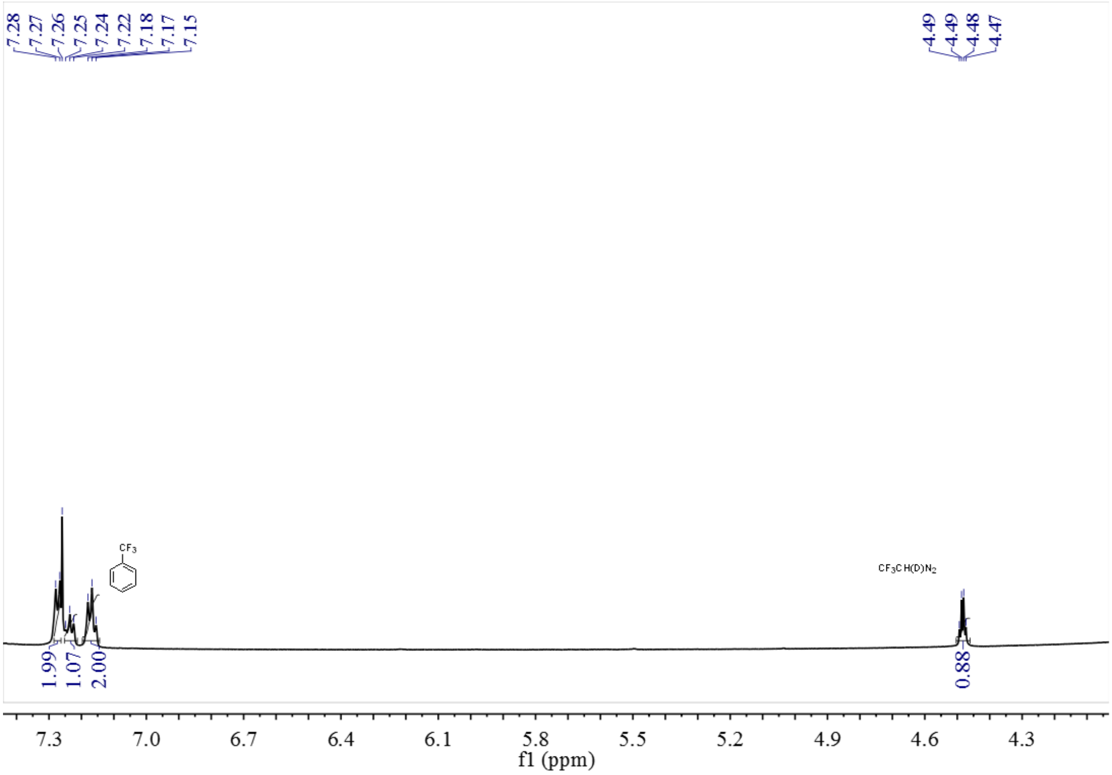
General procedure for isotopic labeling experiments

The preparation of $CF_3CH(D)N_2$

As shown in the figure: A solution of 610 mg $NaNO_2$ in 1.5 mL deuterium oxide was added slowly to the stirring solution of 1.08 g of tritluoroethylamine hydrochloride in 2.5 mL deuterium oxide at rt. And then the rapidly generated yellow gas was gradually blown off through a drying tube ($MgSO_4$) into a gas absorber containing 10.0 mL anhydrous solvent equipped with an ice bath. After about 0.5 hour later, there would be no gas bubbling any more. Then the apparatus was removed carefully. Add the $PhCF_3$ (25 uL) to 1.0 mL of DMF solvent (containing $CF_3CH(D)N_2$) and then detected by NMR. From the $CF_3CH(D)N_2$–^{19}F NMR spectrogram, the concentration of $CF_3CH(D)N_2$ in DMF is 0.22 mmol/mL. Combined the $CF_3CH(D)N_2$–^{19}F NMR spectrogram and the $CF_3CH(D)N_2$ –^1H NMR spectrogram, the ratio of hydrogen to deuterium of $CF_3CH(D)N_2$ is 76:24.



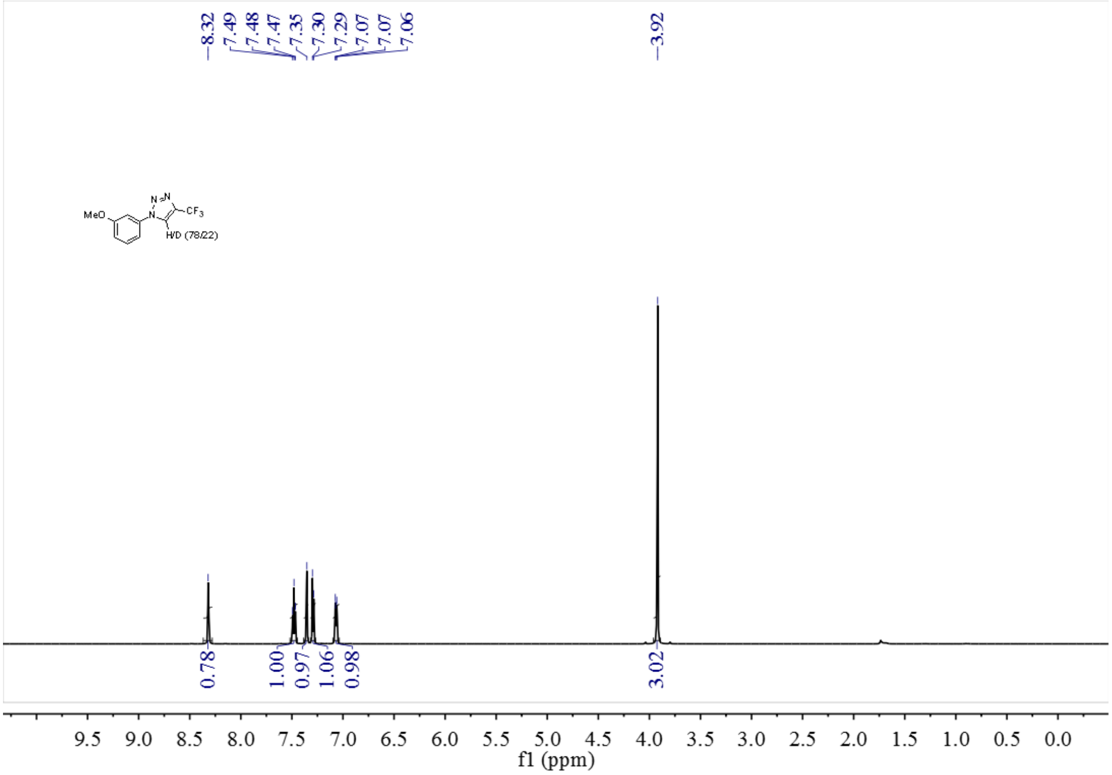
$CF_3CH(D)N_2$ –^{19}F NMR



$CF_3CH(D)N_2$ –^{1}H NMR

The Procedure for the cycloaddition of $CF_3CH(D)N_2$ with 3-methoxyphenyl isocyanide

Having the $CF_3CH(D)N_2$ in hand, we then undergo the silver-catalyzed cycloaddition. Ag_2CO_3 (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide (20.6 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg) were added into a 10.0 mL Schlenk tube. The tube was sealed well and $CF_3CH(D)N_2$ (26.4 mg, 1.2 equiv) in DMF was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 25:1) afforded the product. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring is 78:22 by ^1H NMR, which is almost identical to that in $CF_3CH(D)N_2$.

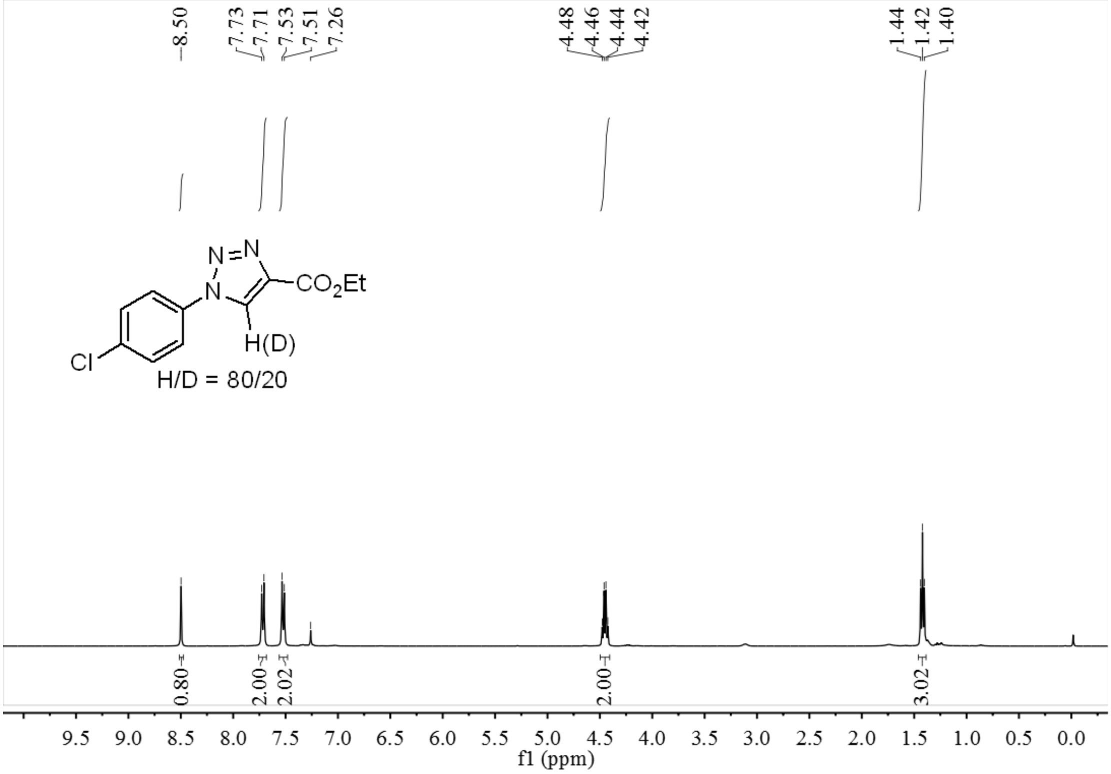


1,2,3-triazole ^1H NMR

The Procedure for the cycloaddition of $N_2CH(D)CO_2Et$ (H/D = 15/85) with

4-chlorophenyl isocyanide

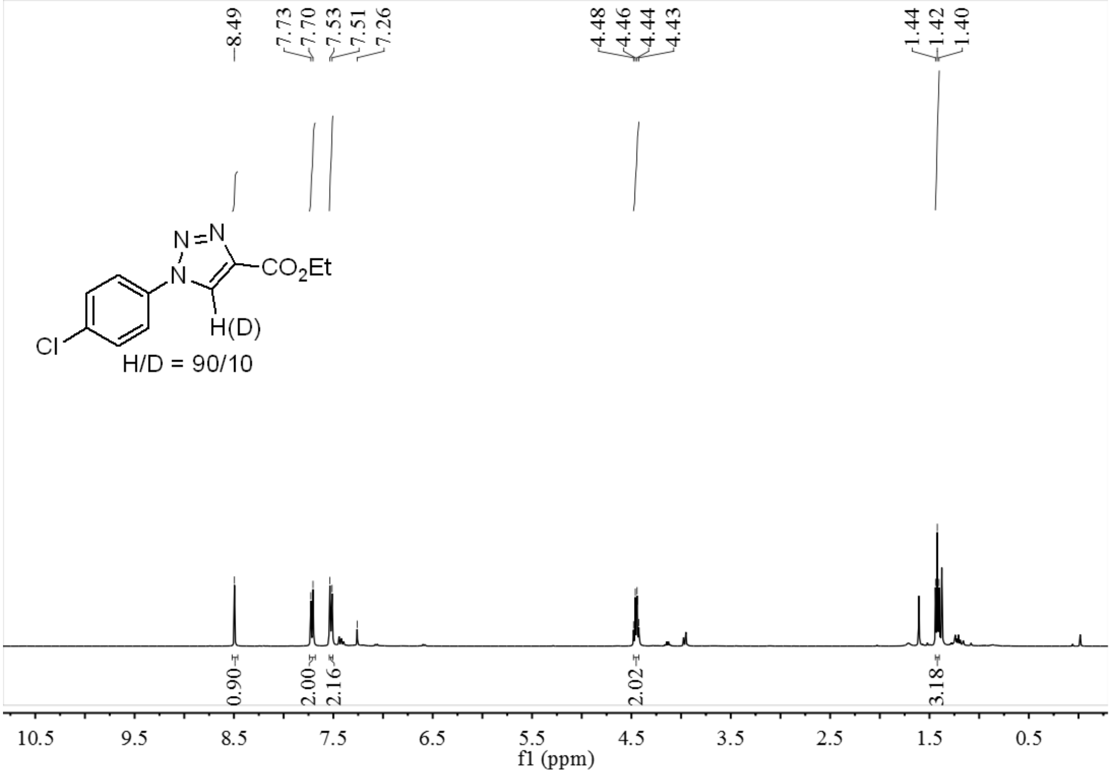
Ag_2CO_3 (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide (26.5 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well and $N_2CH(D)CO_2Et$ (H/D = 15/85), 27.4 mg, 0.24 mmol, 1.2 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 5:1) afforded the product. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring is 80:20 by ^1H NMR analysis.

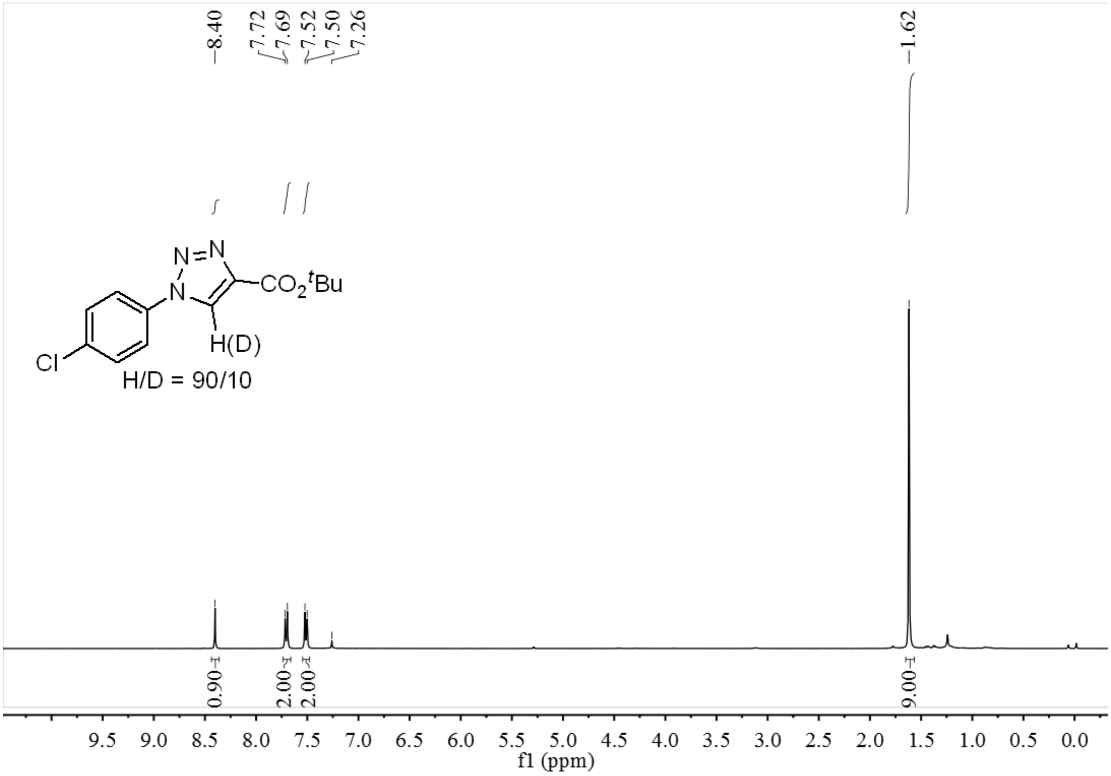


The Procedure for the cross-over cycloaddition of $N_2CH(D)CO_2Et$ (H/D = 15/85) and $N_2CHCO_2Bu^t$ with 4-chlorophenyl isocyanide

Ag_2CO_3 (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide (26.5 mg, 0.20 mmol, 1.0

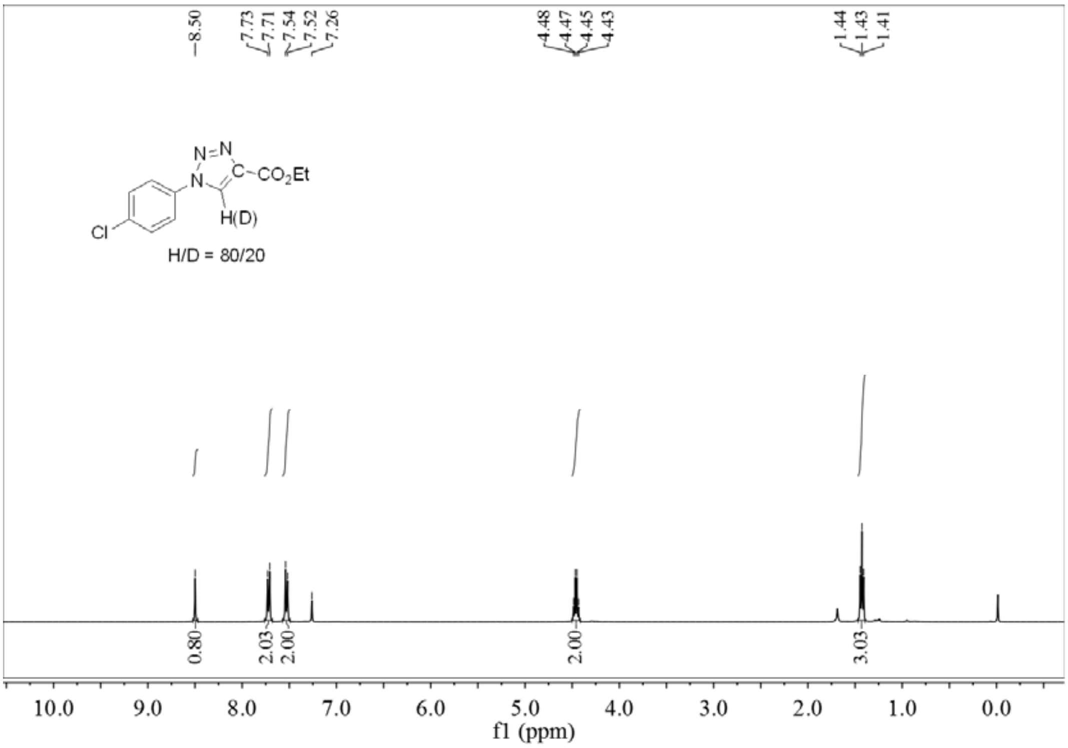
equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well. $N_2CH(D)CO_2Et$ (H/D = 15/85, 13.7 mg, 0.12 mmol) and $N_2CHCO_2Bu^t$ (17.0 mg, 0.12 mmol) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 8:1) afforded the corresponding products. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring was analyzed by ^1H NMR.

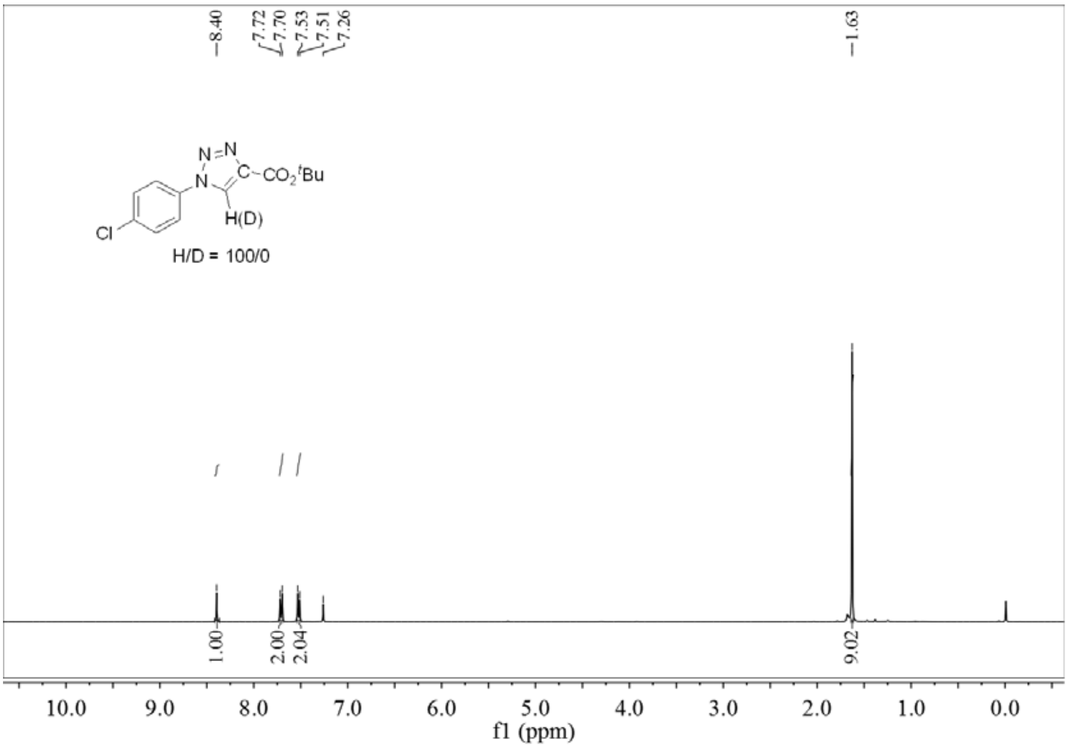




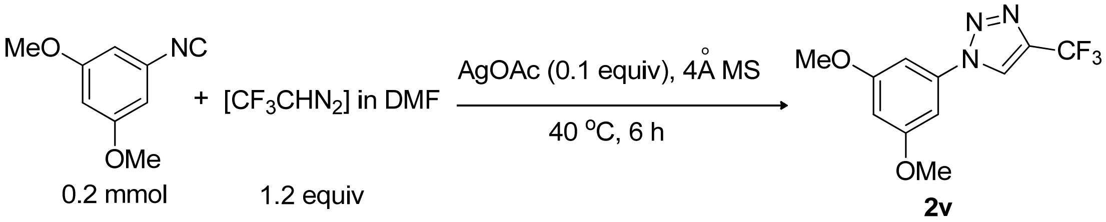
The Procedure for the cross-over control experiment

Ethyl 1-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (H/D = 80/20, 25.0 mg, 0.1 mmol) and *tert*-butyl 1-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (28.0 mg, 0.1 mmol), Ag_2CO_3 (5.50 mg, 0.02 mmol, 0.10 equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well and conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 8:1) recovered the corresponding triazoles in quantitative yields. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring was analyzed by ^{1}H NMR.


8.50
7.73
7.71
7.54
7.52
7.26
4.48
4.47
4.45
4.43
1.44
1.43
1.41
N=N
N
C
CO2Et
H(D)
Cl
H/D = 80/20
0.80
2.03
2.00
2.00
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

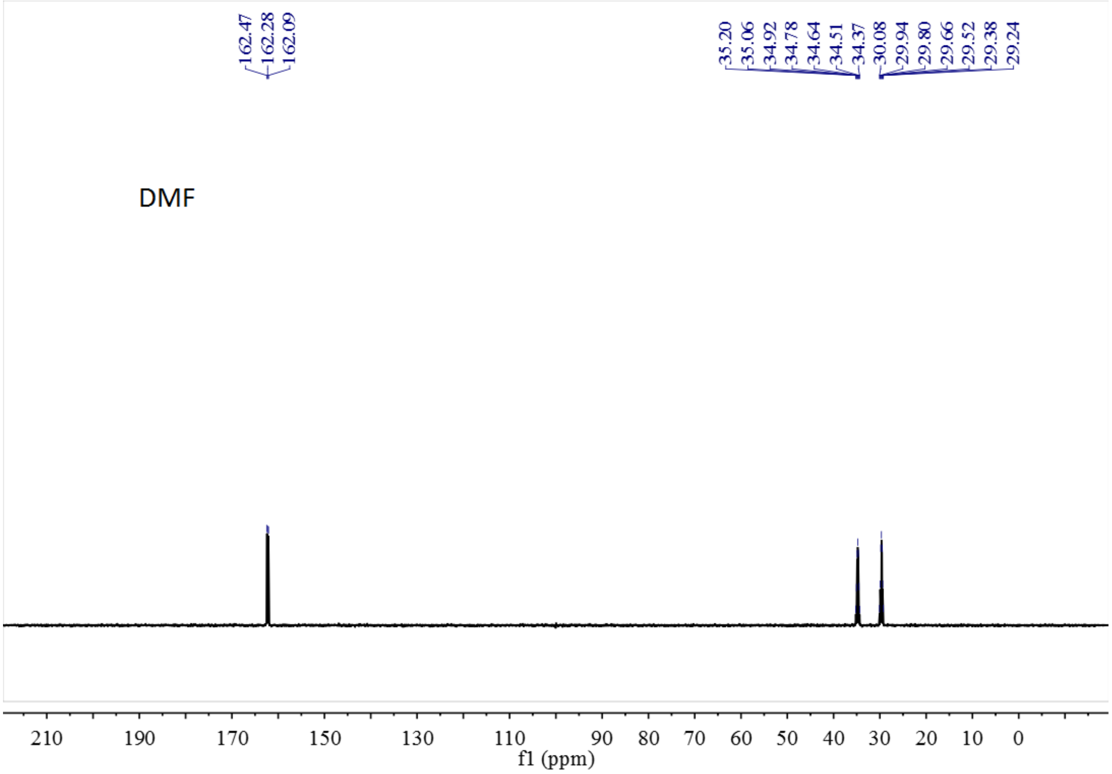

8.40
7.72
7.70
7.53
7.51
7.26
1.63
N=N
N
C
CO2tBu
H(D)
Cl
H/D = 100/0
1.00
2.00
2.04
9.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

The research of interaction between isocyanide and Ag(I)

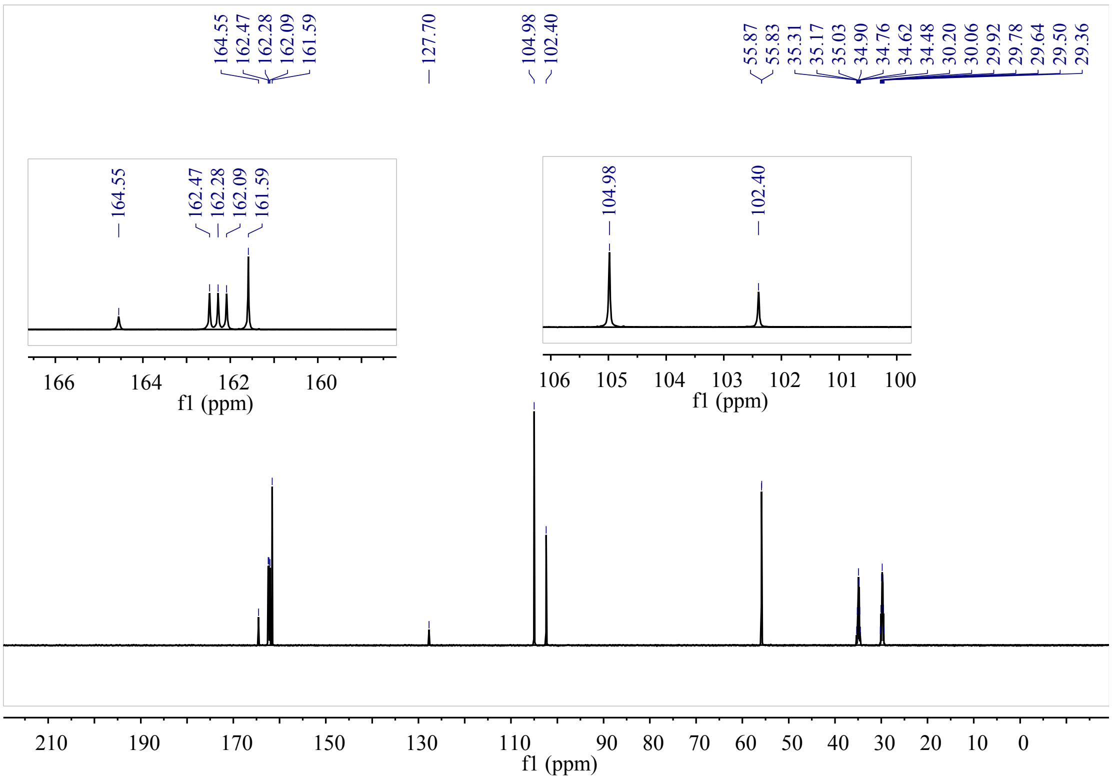


AgOAc (0.1 equiv) can also promote this reaction well and 1-(3,5-Dimethoxylphenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazole (**2v**) was obtained in 58% yield. In view of the poor solubility of Ag_2CO_3 in DMF, AgOAc was chosen as the catalyst to do **NMR** and **IR** experiments to study the interaction between isocyanide and Ag(I).

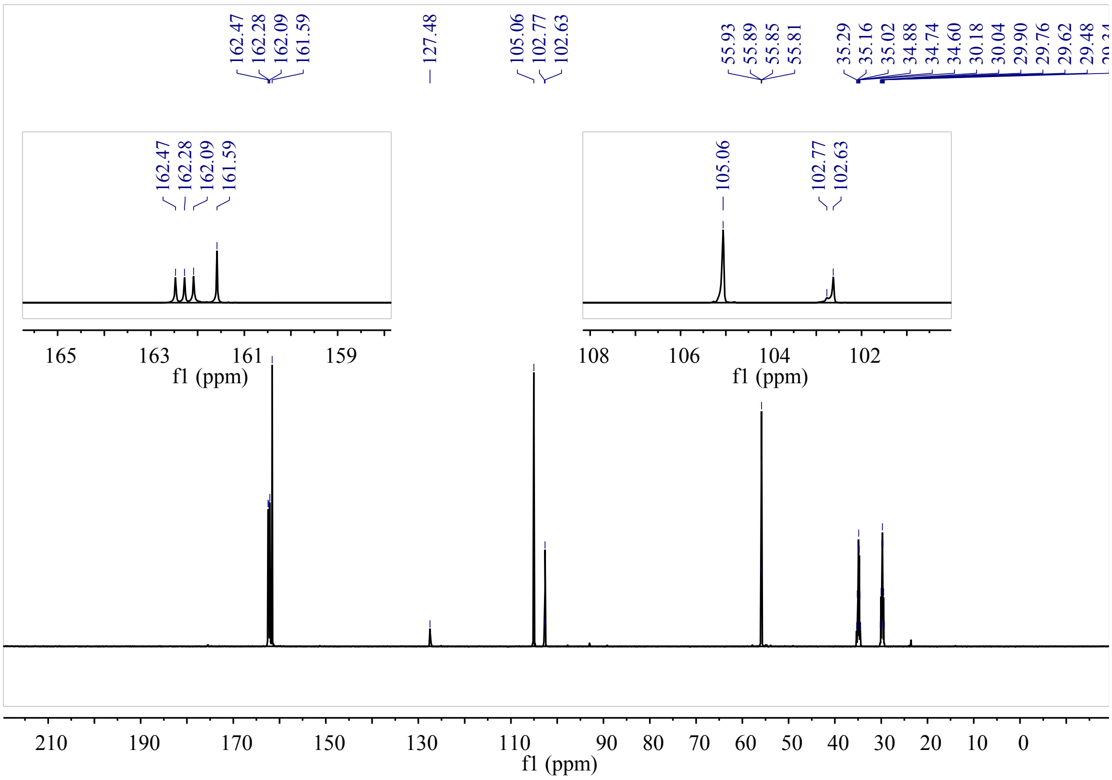
1-Isocyano-3,5-dimethoxybenzene (0.4 mmol, 65.2 mg) was dissolved in 0.5 mL DMF-d_7 in NMR tube, then AgOAc (1 equiv) was added to tube. After 10 minutes, interaction between isocyanide and Ag(I) was detected by **^{13}C NMR**.



DMF-^{13}C NMR

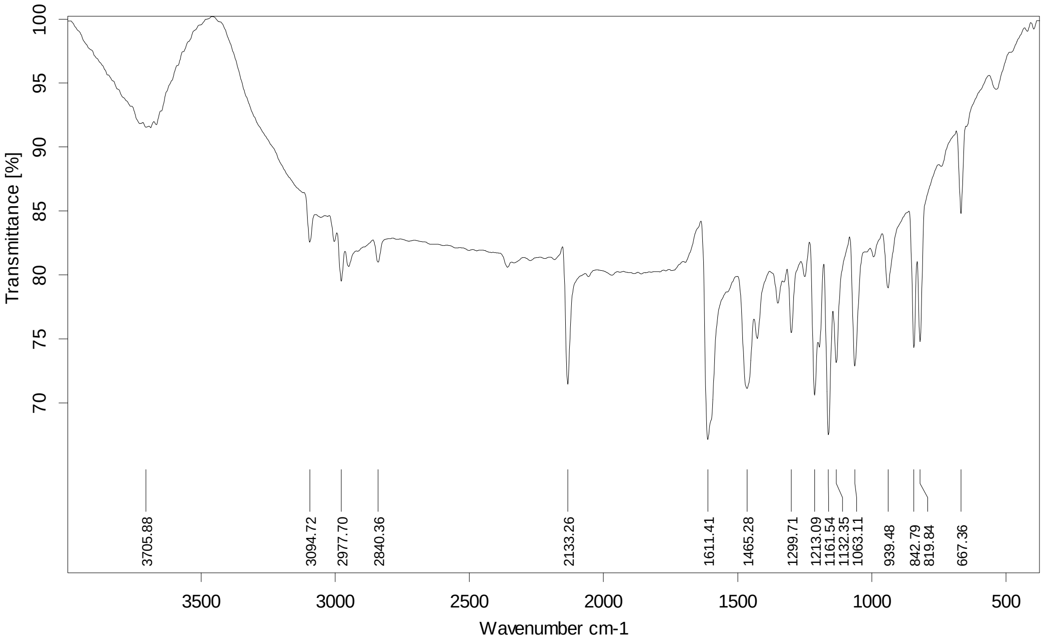


1-isocyano-3,5-dimethoxybenzene in DMF-d_7 –^{13}C NMR

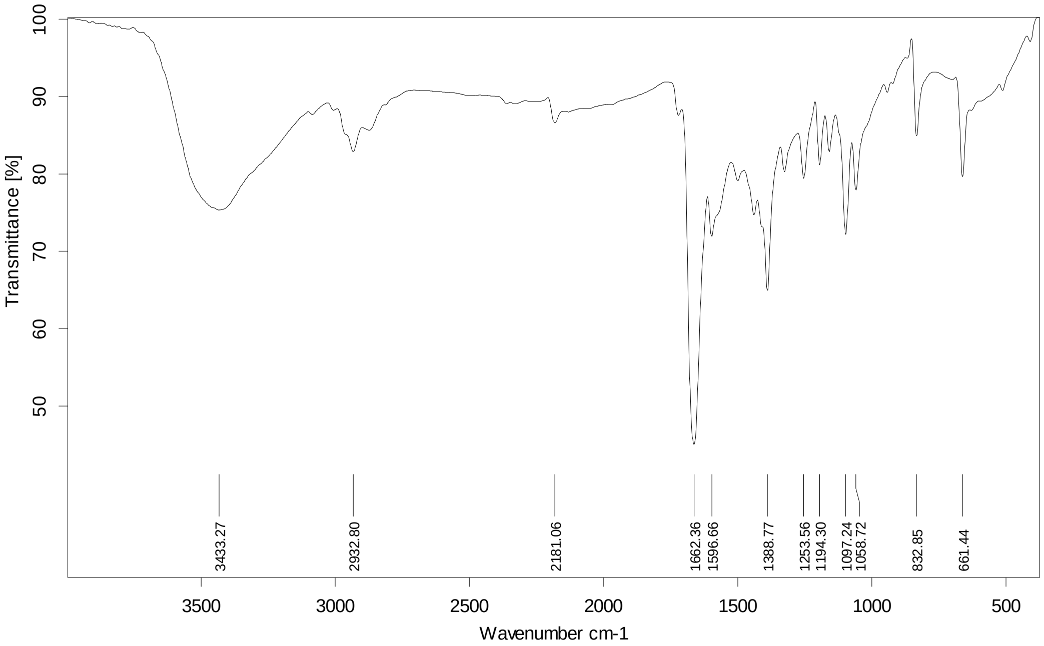


1-isocyano-3,5-dimethoxybenzene and Ag(I) in DMF-d_7 –^{13}C NMR

1-Isocyano-3,5-dimethoxybenzene (0.2 mmol, 32.6 mg), AgOAc (55 mg, 0.2 mmol), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. After stiring for 10 minutes, the interaction between isocyanide and Ag(I) was detected by IR (KBr).



1-isocyano-3,5-dimethoxybenzene-IR



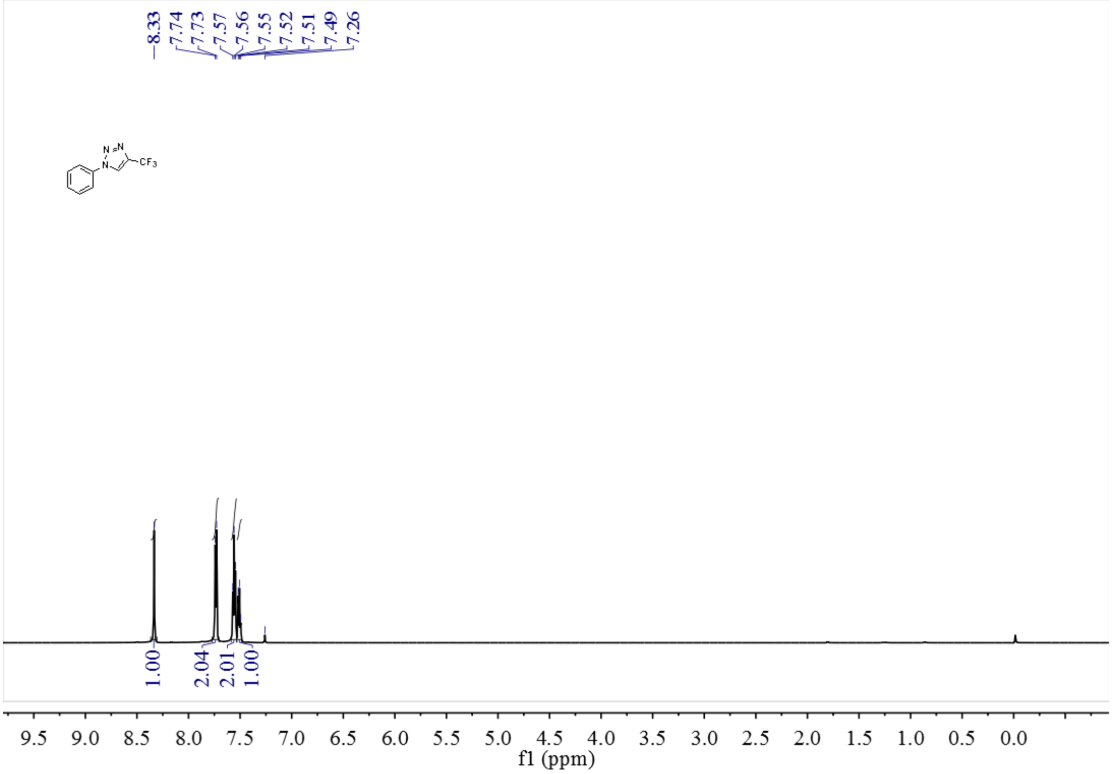
1-isocyano-3,5-dimethoxybenzene and AgOAc in DMF-IR

[1] (*a*) J. H. Rigby, S. Laurent, *J. Org. Chem.*, **1998**, *63,* 6742; (*b*) B. Janza, A. Studer, *Org. Lett.*, **2003**, *5*, 1079; (*c*) O. Lopez, S. Maza, V. Ulgar, I. Maya, J. G. Bolanos. *Tetrahedron*, **2009**, *65* 2556.

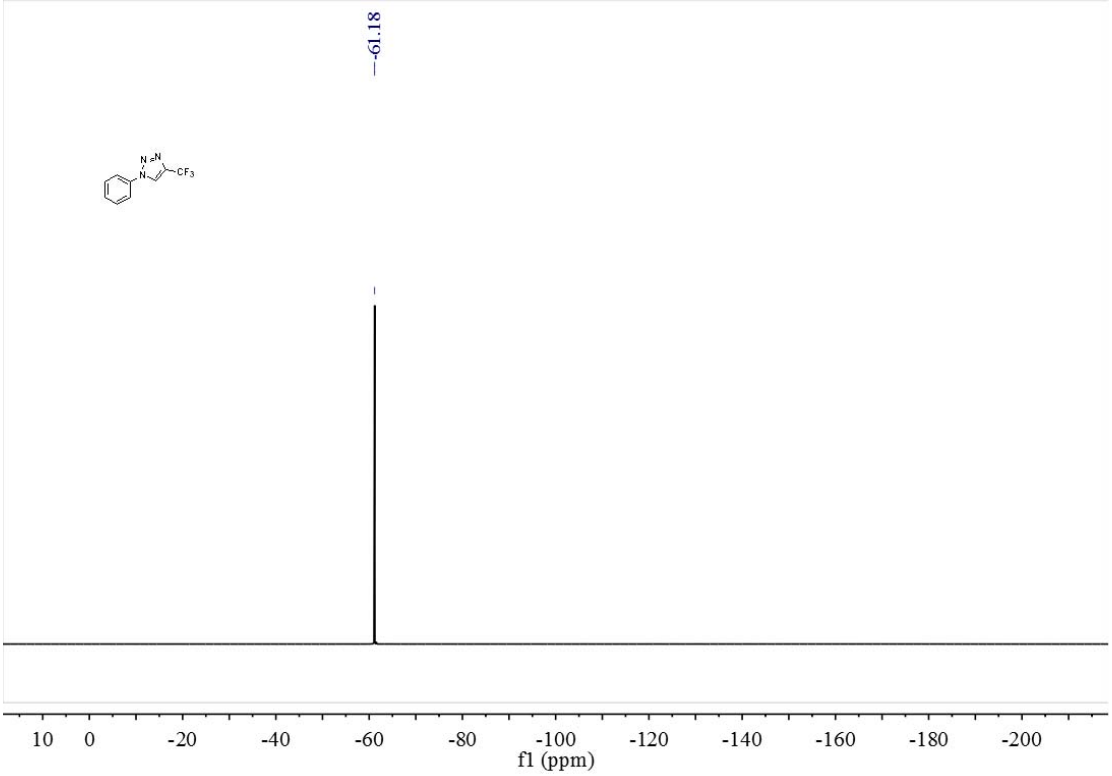
[2] (*a*) K. Dabak, O. Sezer, A. Akar, O Anac, *Eur. J. Med. Chem.*, **2003**, *38*, 2154; (*b*) I. S. Park, M. S. Kwon, Y. Kim, J. S. Lee, J. Park, *Org. Lett.*, **2003**, *10*, 497; (*c*) Z. X. Wang, H. L. Qin, *Chem. Commun.*, **2003**, 2450.

[3] (*a*) L. Ackermann, H. K. Potukuchi, *Org. Biomol. Chem.*, **2010**, *8*, 4503; (*b*) S. Chuprakov, N. Chernyak, A. S. Dudnik, V. Gevorgyan , *Org. Lett.*, **2007**, *9*, 2333; (*c*) L. Ackermann, R. Vicente, R. Borna, *Adv. Synth. Catal.*, **2008**, *350*, 741.

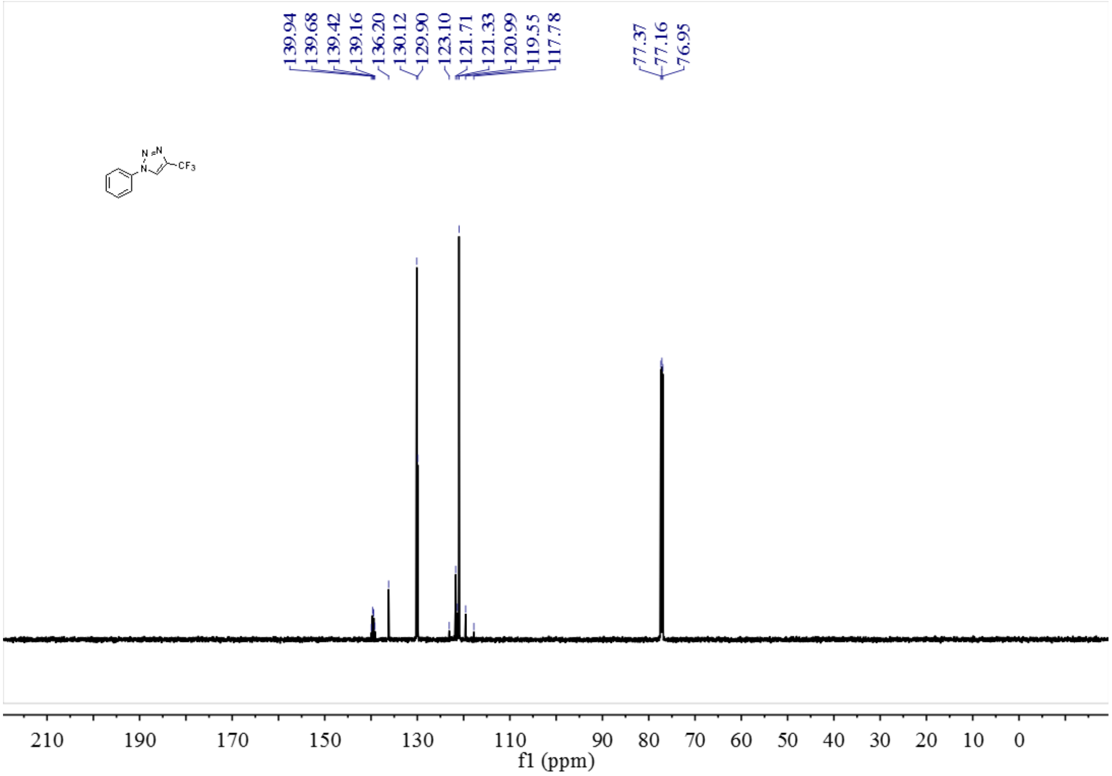
NMR Spectra of Products



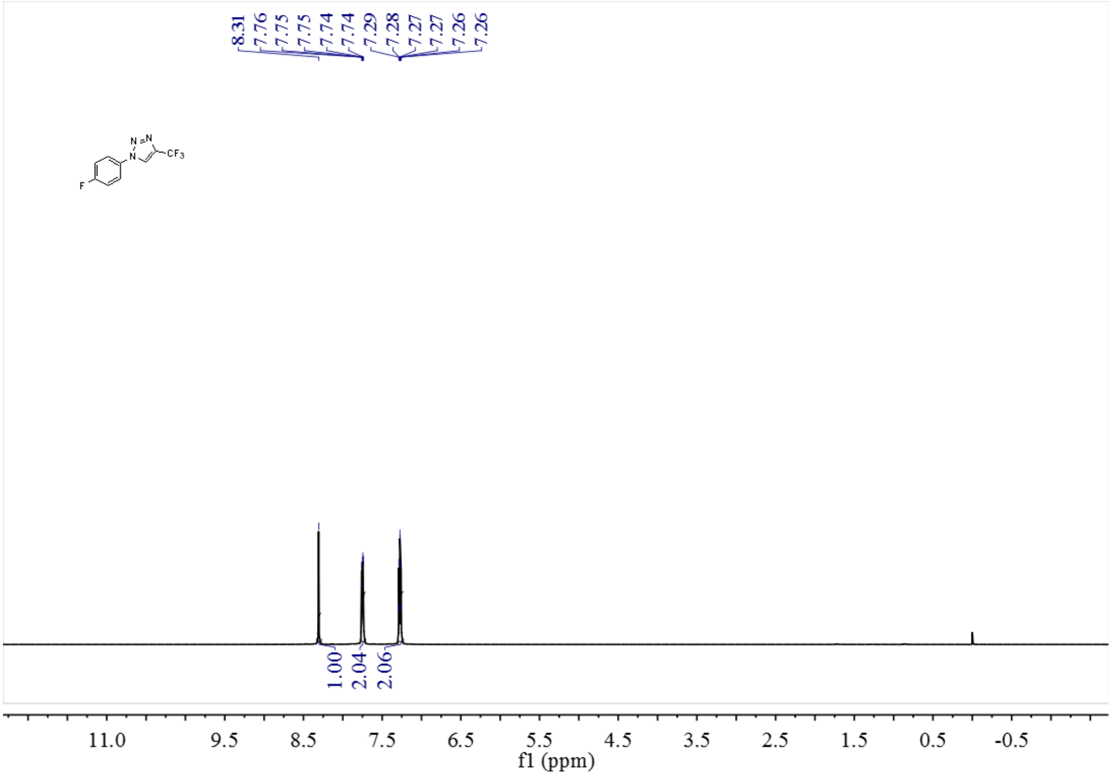
2a-^{1}H NMR



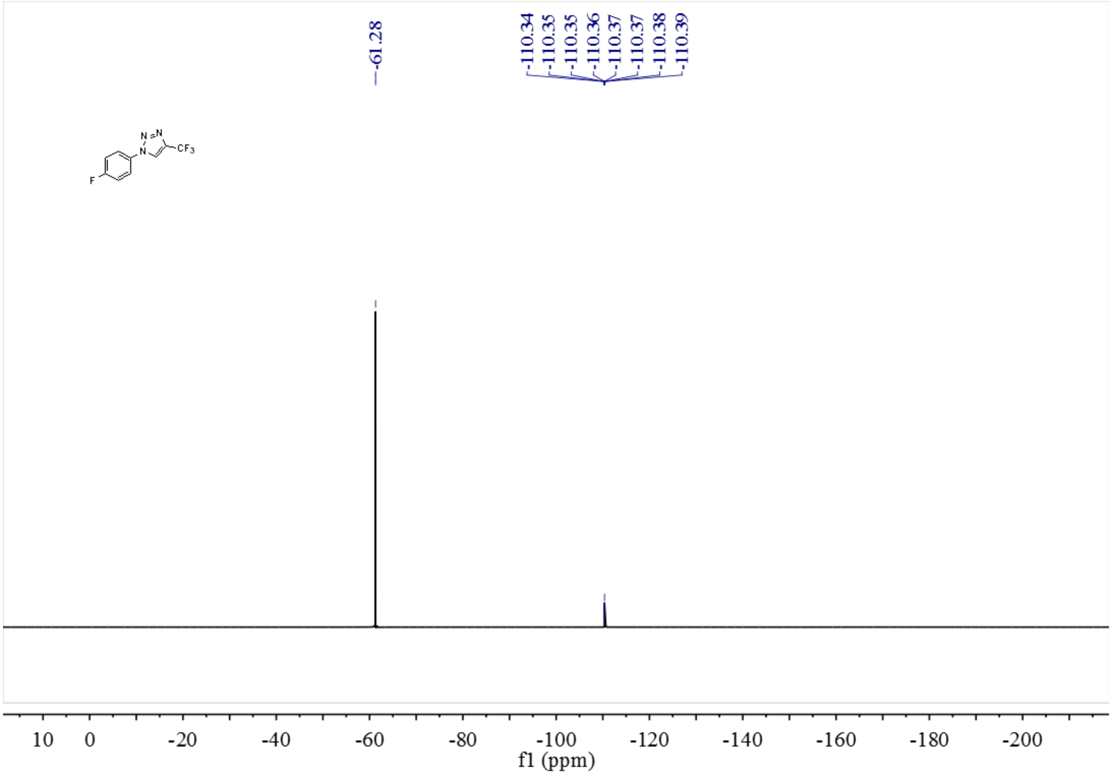
2a-^{19}F NMR



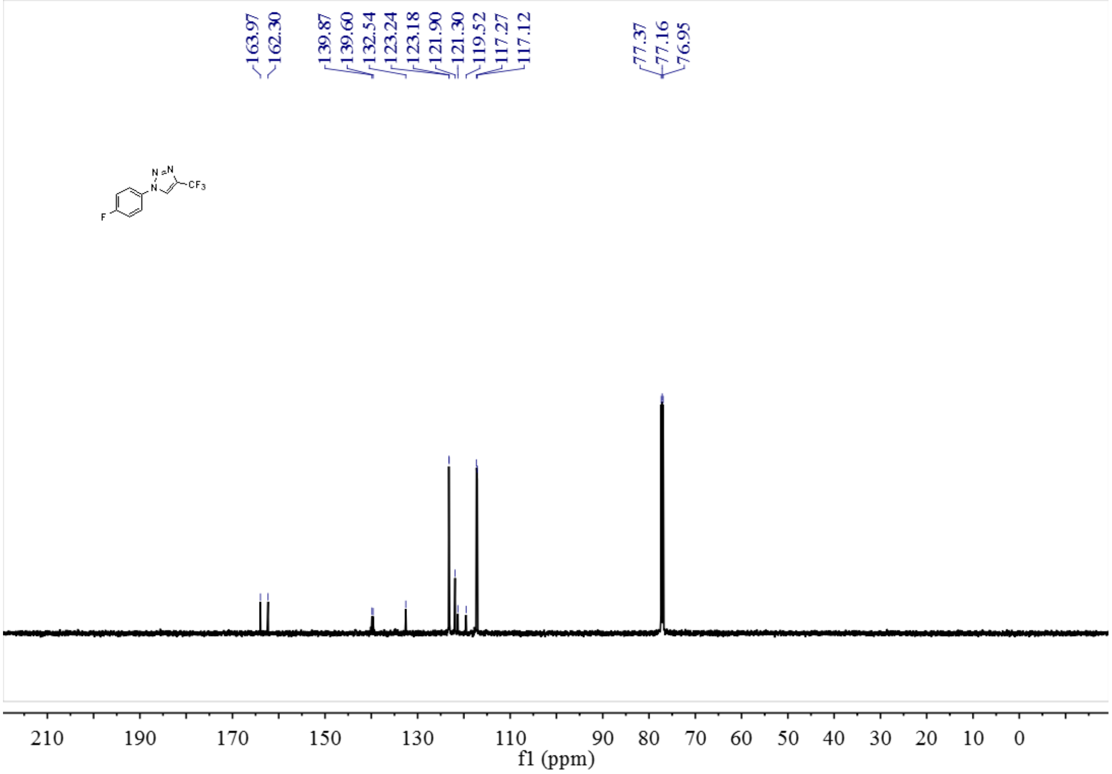
2a-^{13}C NMR



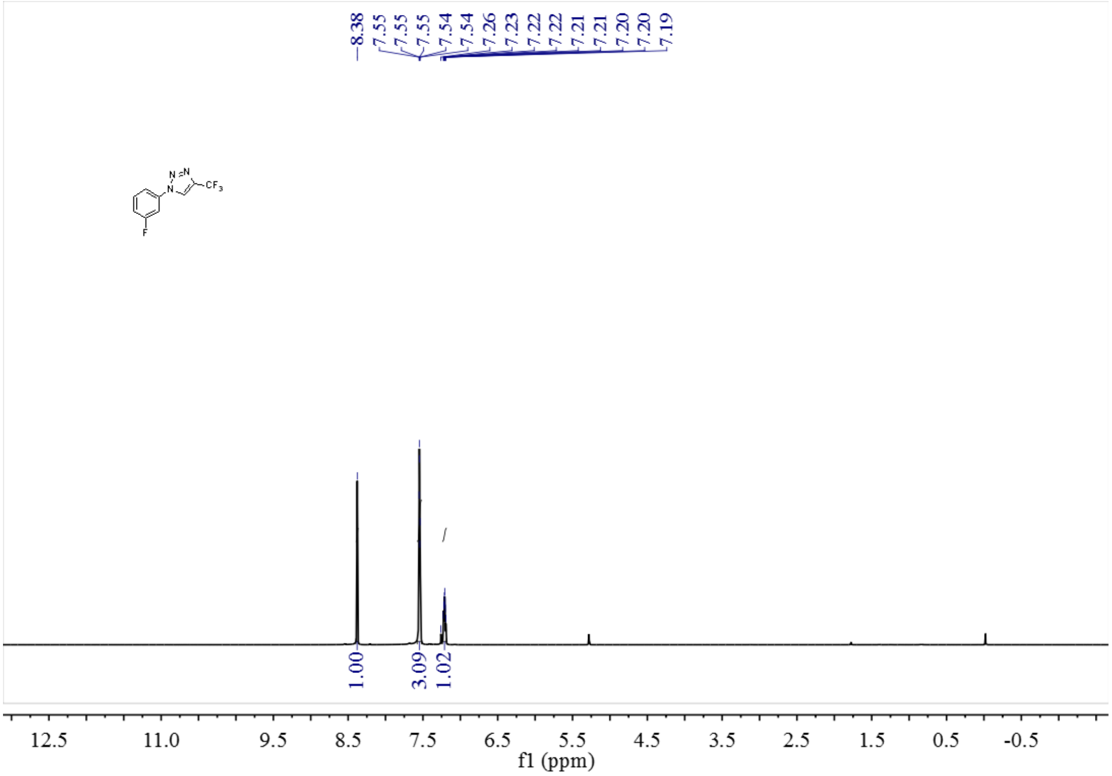
2b-^{1}H NMR



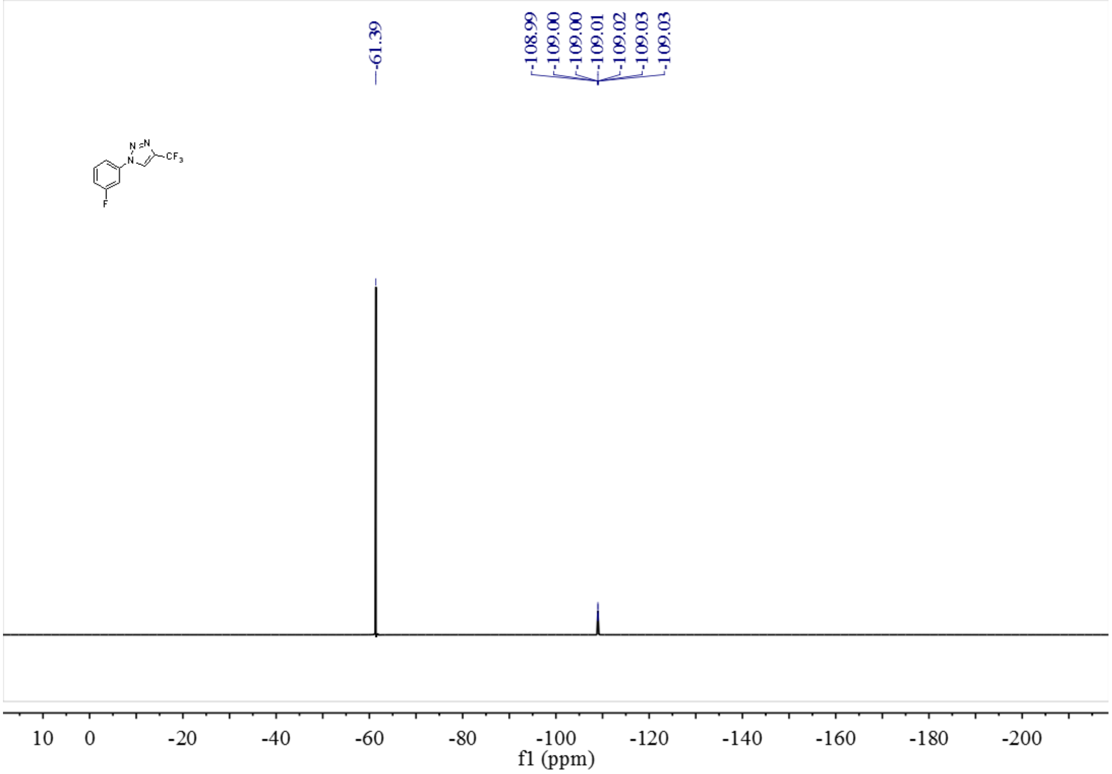
2b-^{19}F NMR



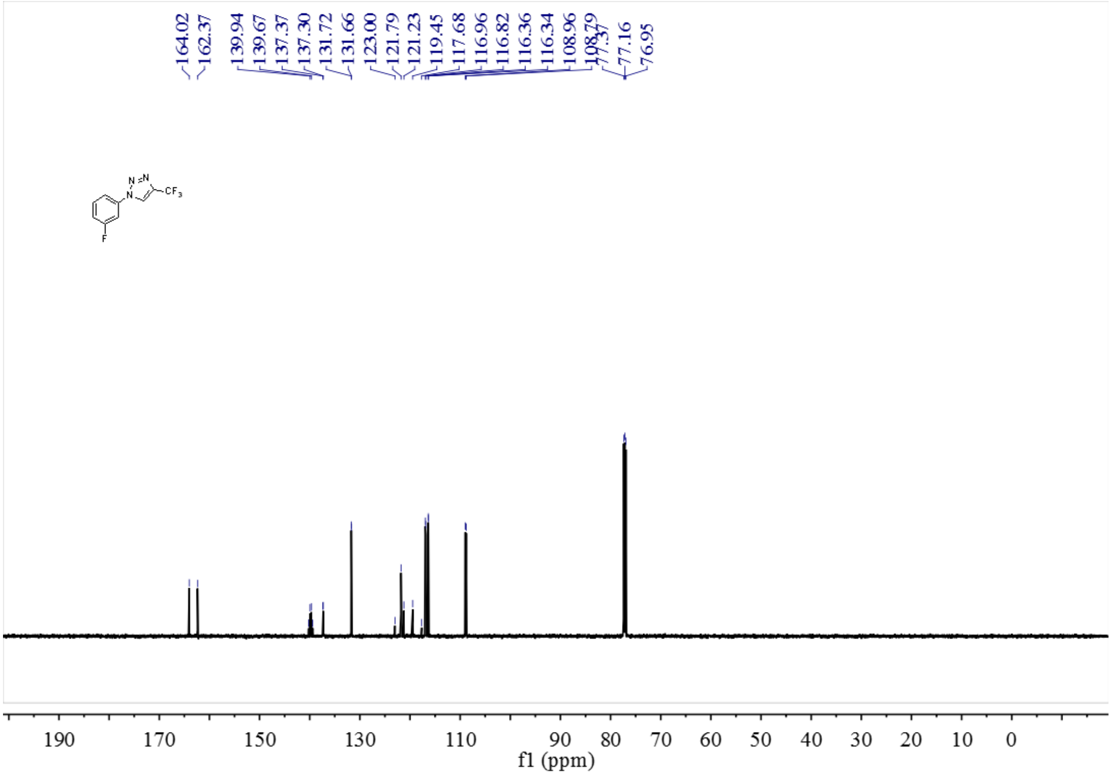
2b-^{13}C NMR



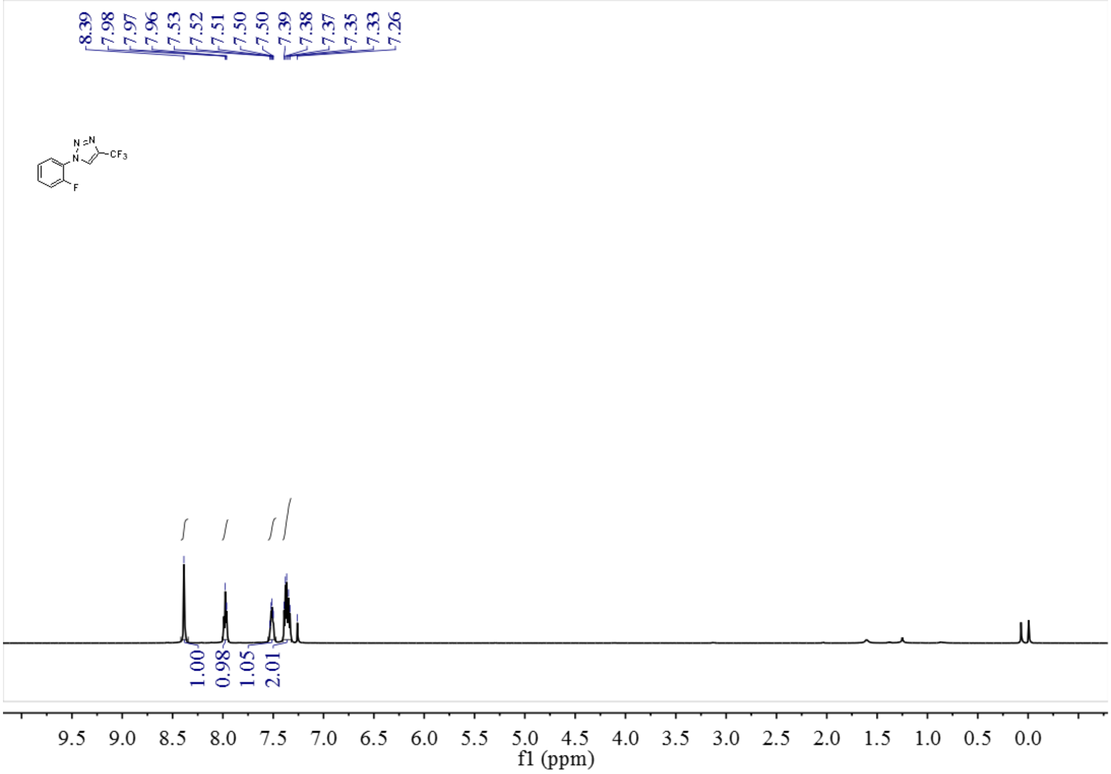
2c-^{1}H NMR



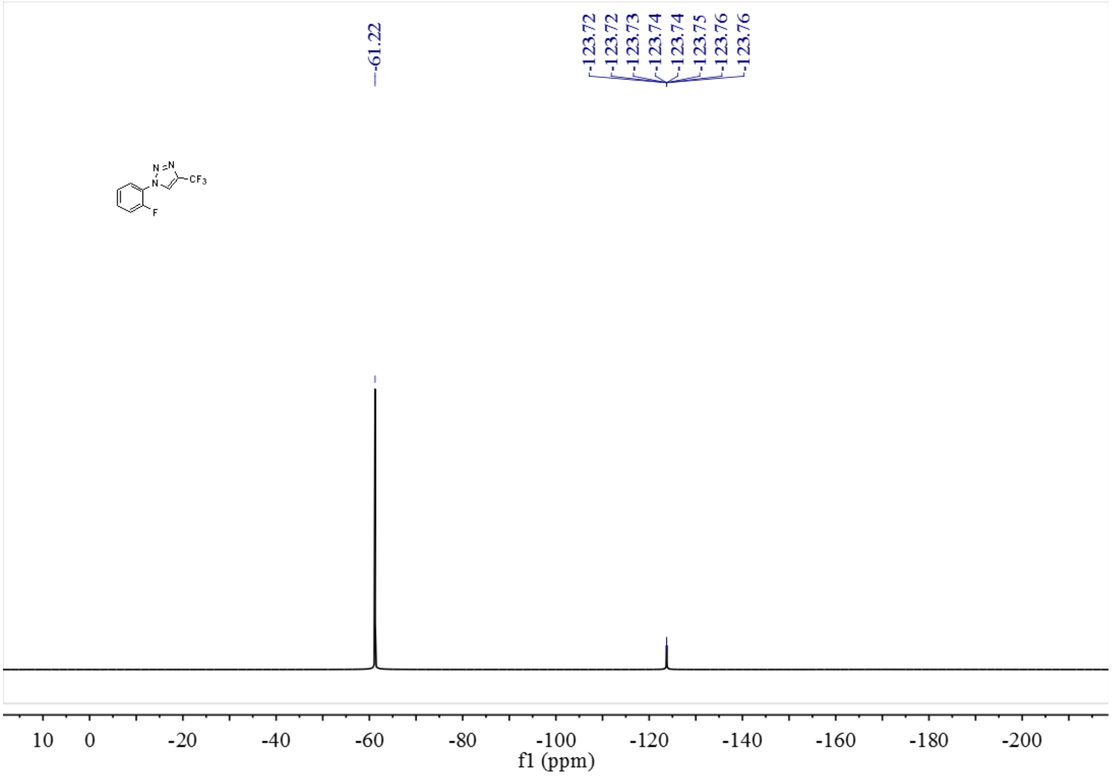
2c-^{19}F NMR



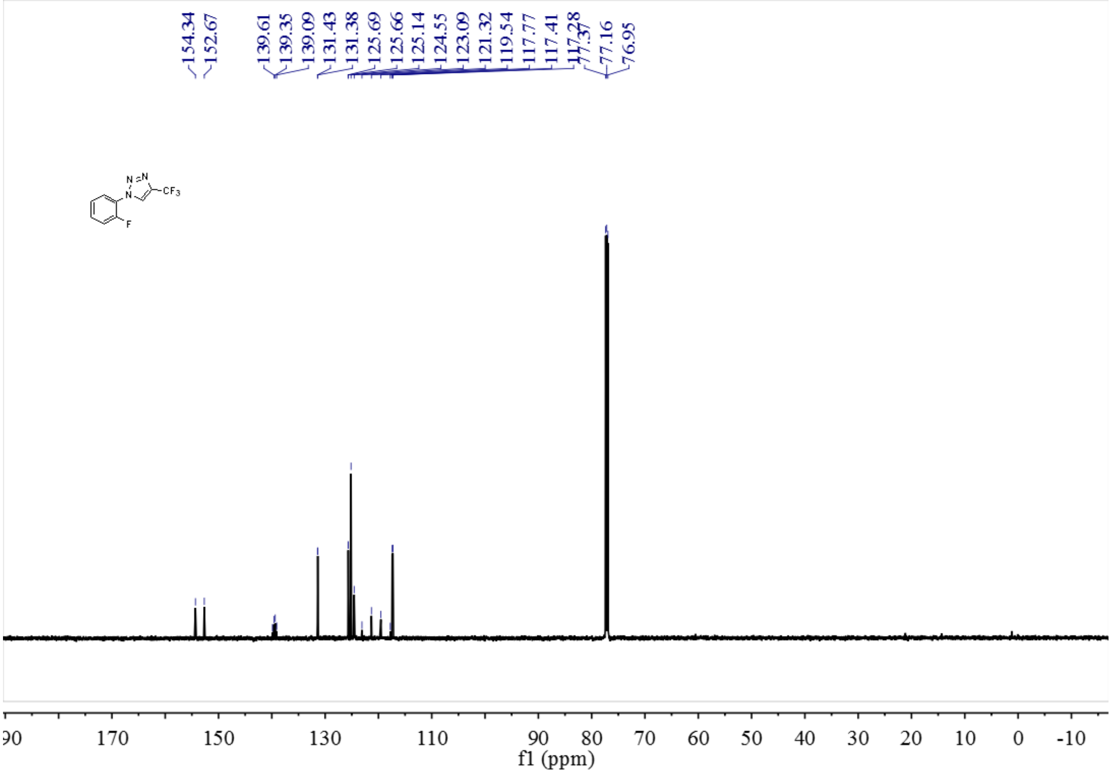
2c-^{13}C NMR



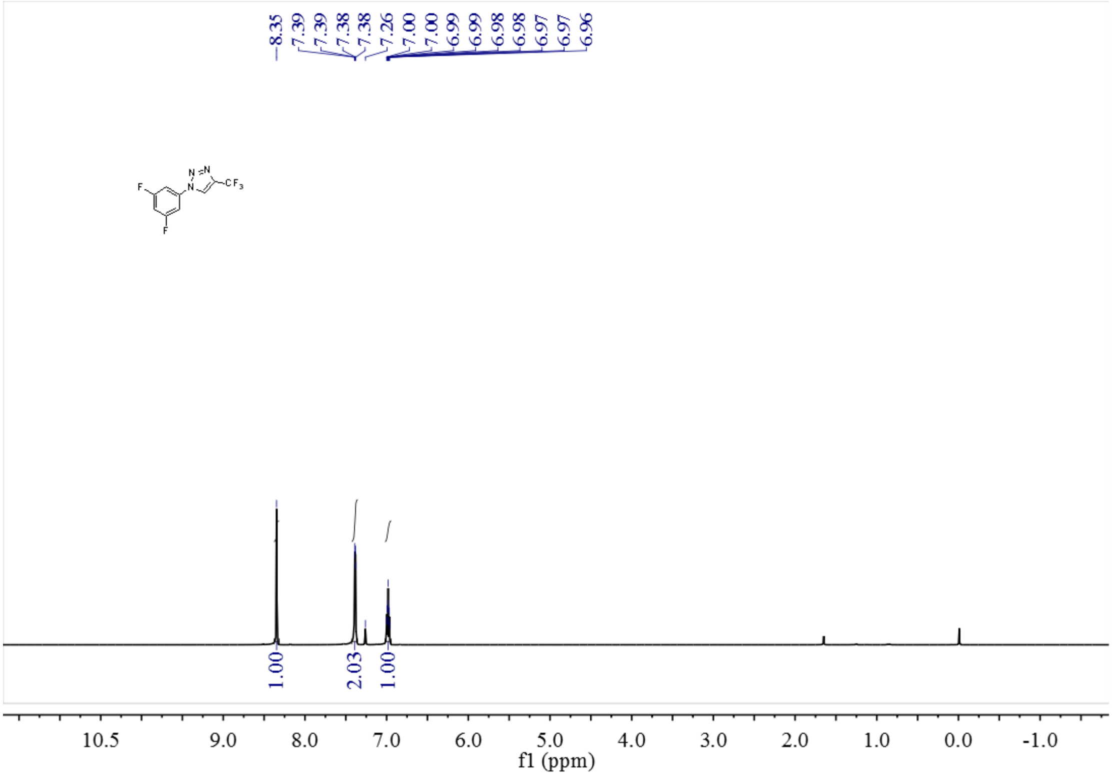
2d-^{1}H NMR



2d-^{19}F NMR



2d-^{13}C NMR



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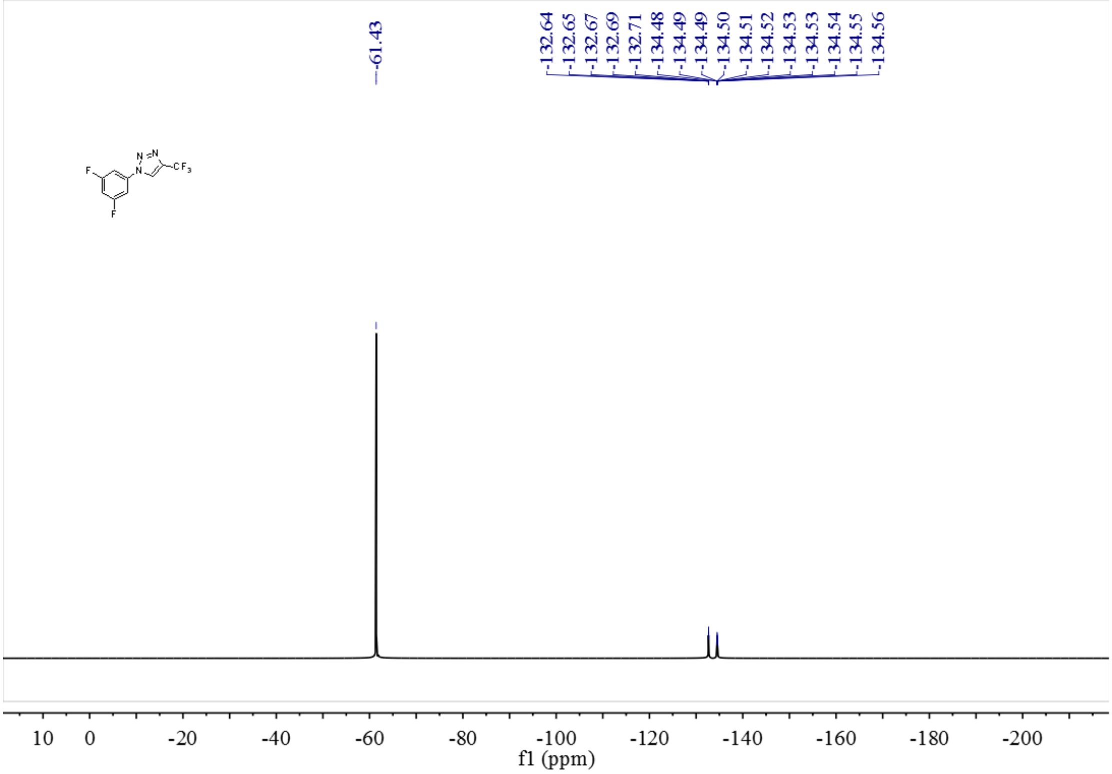

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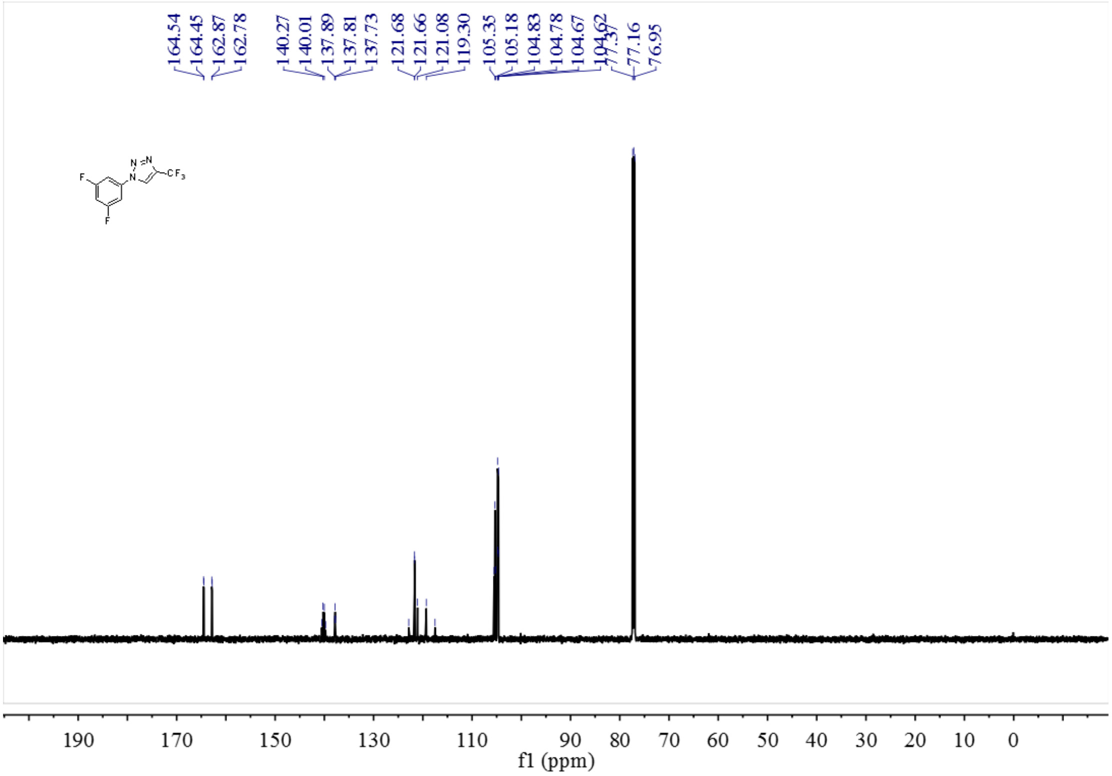

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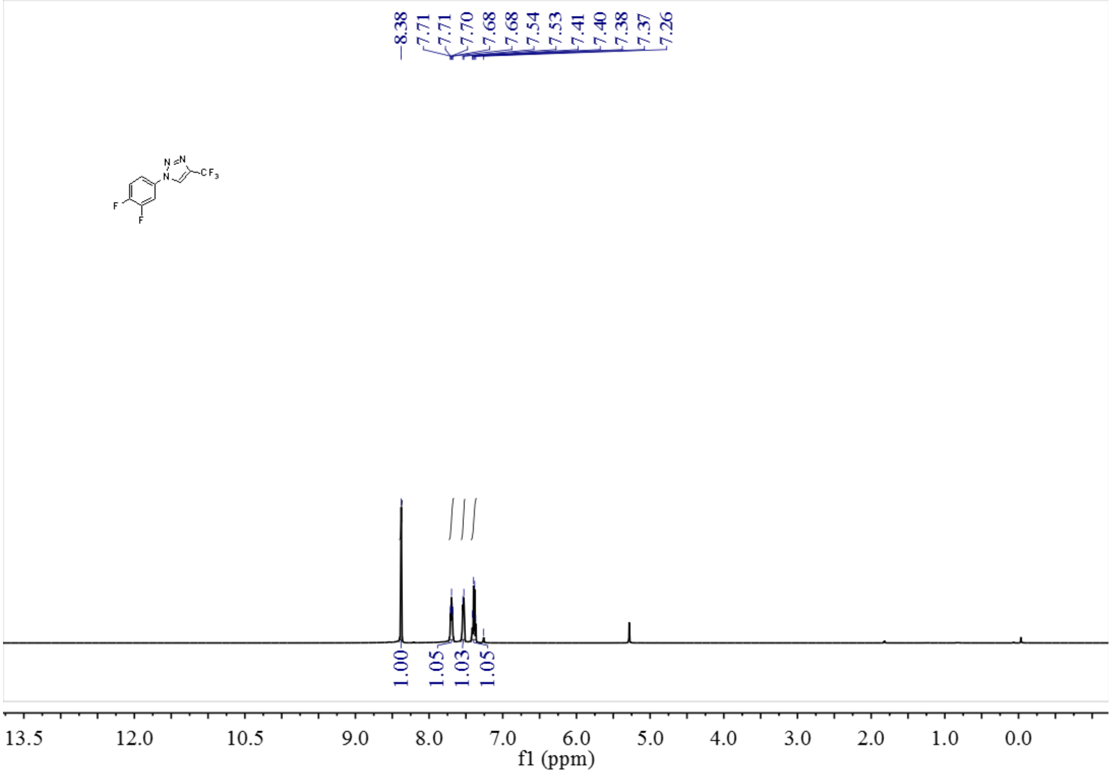

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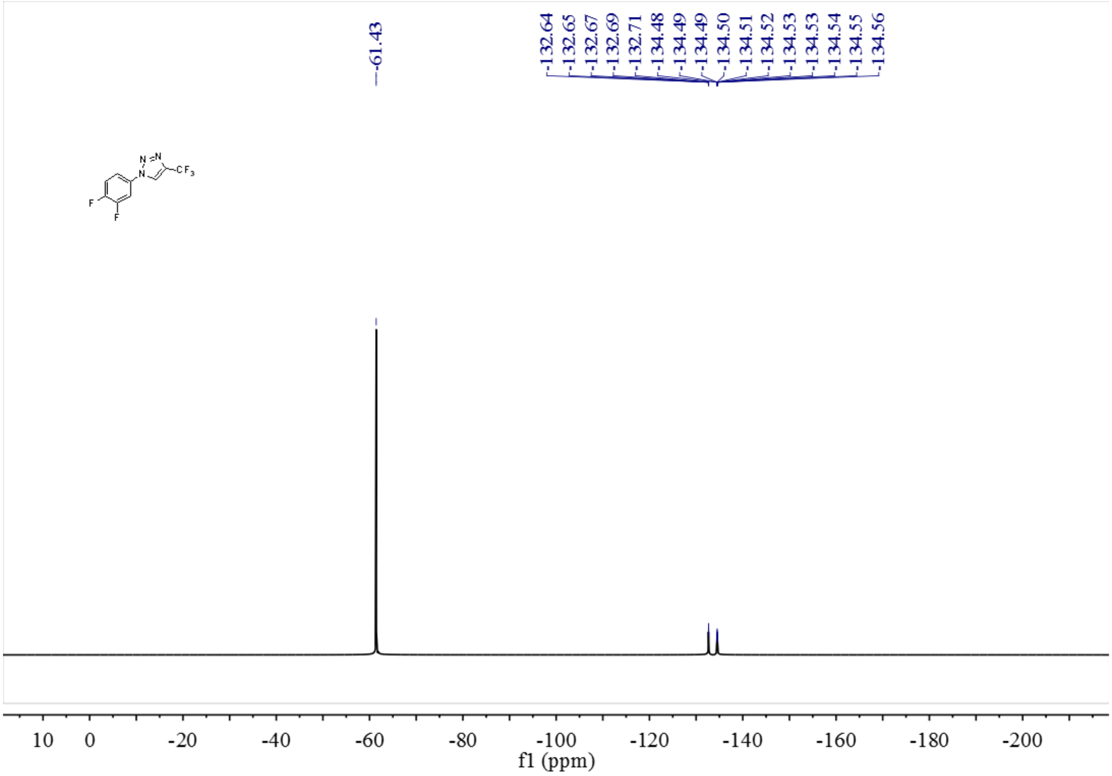

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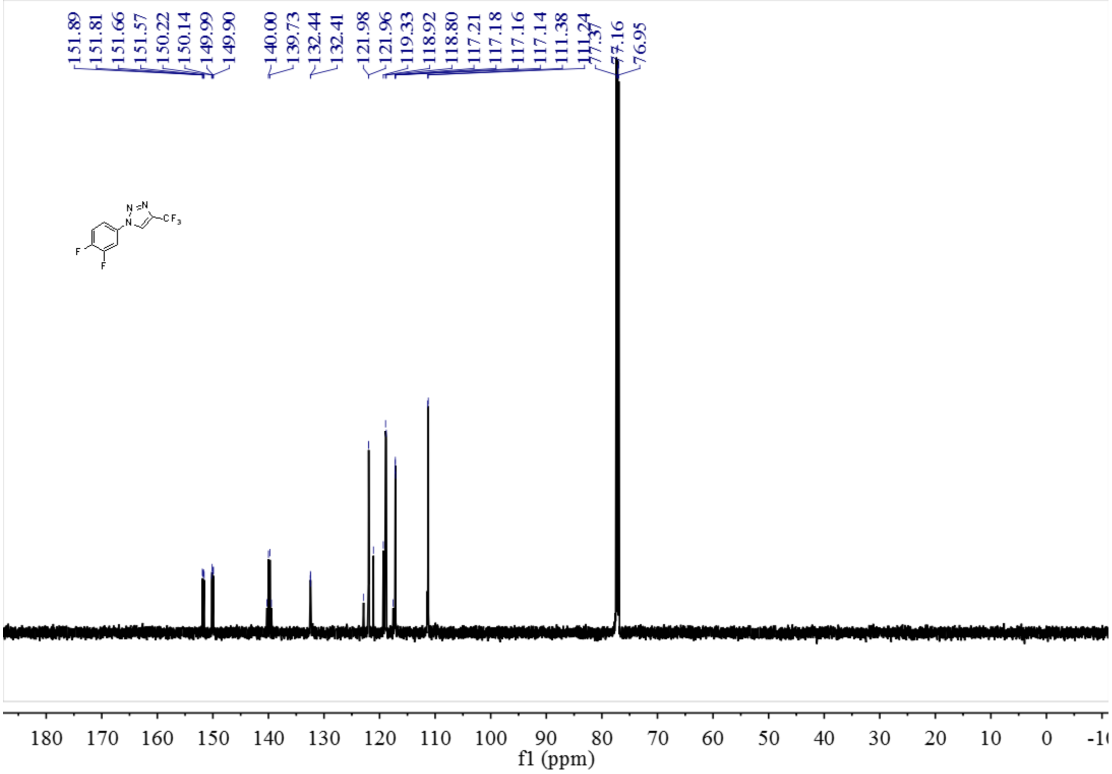

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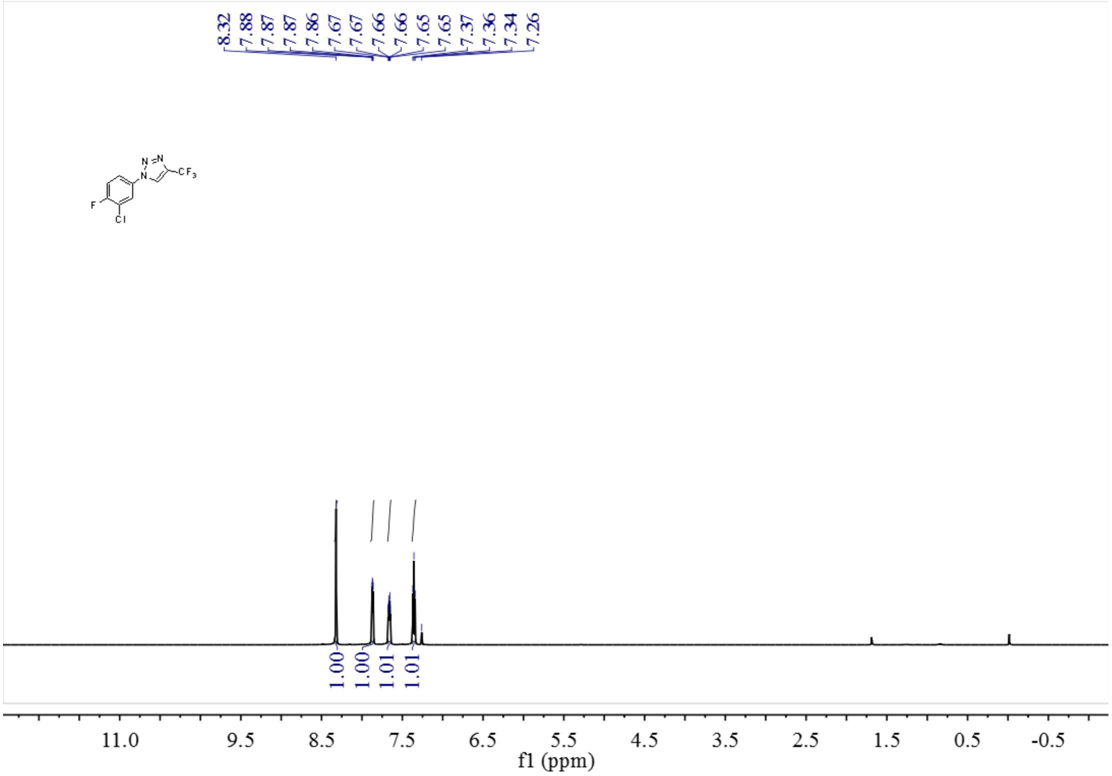

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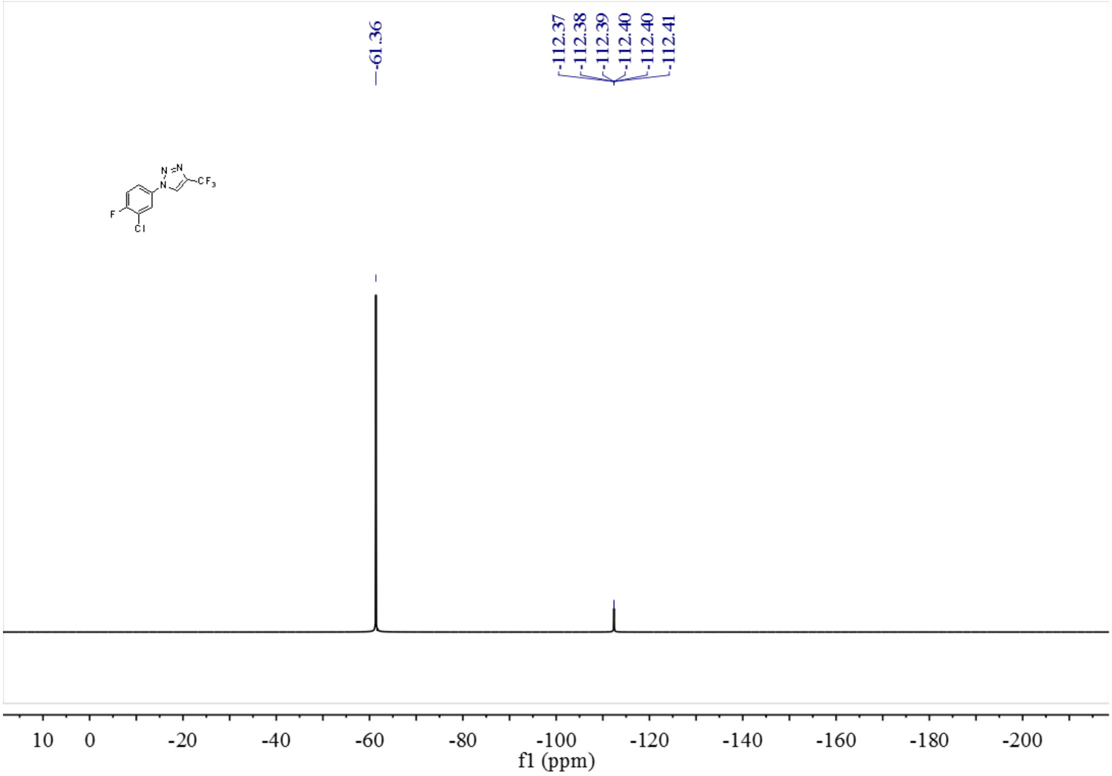

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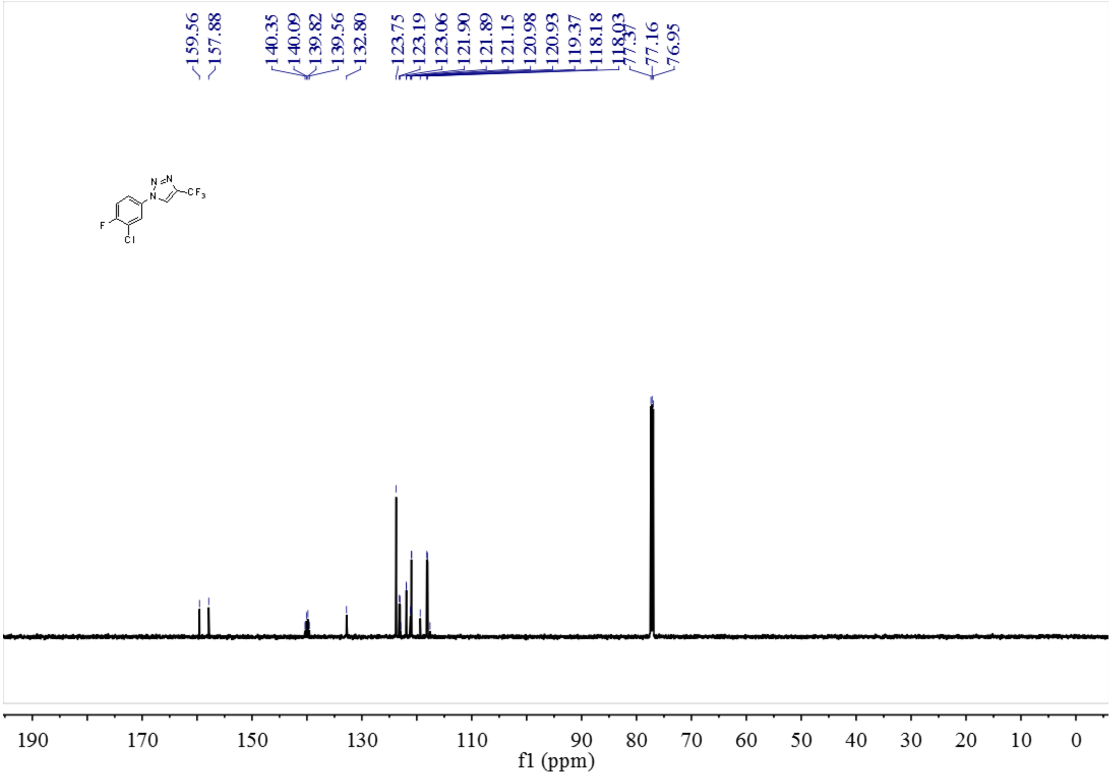

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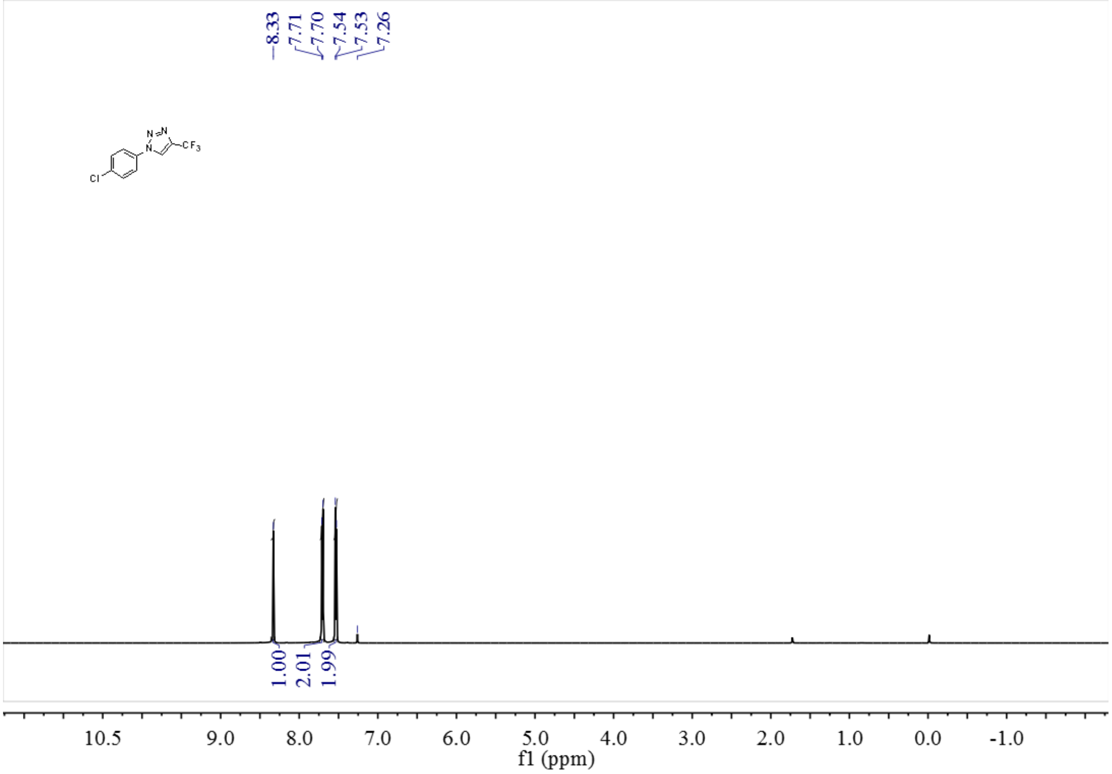

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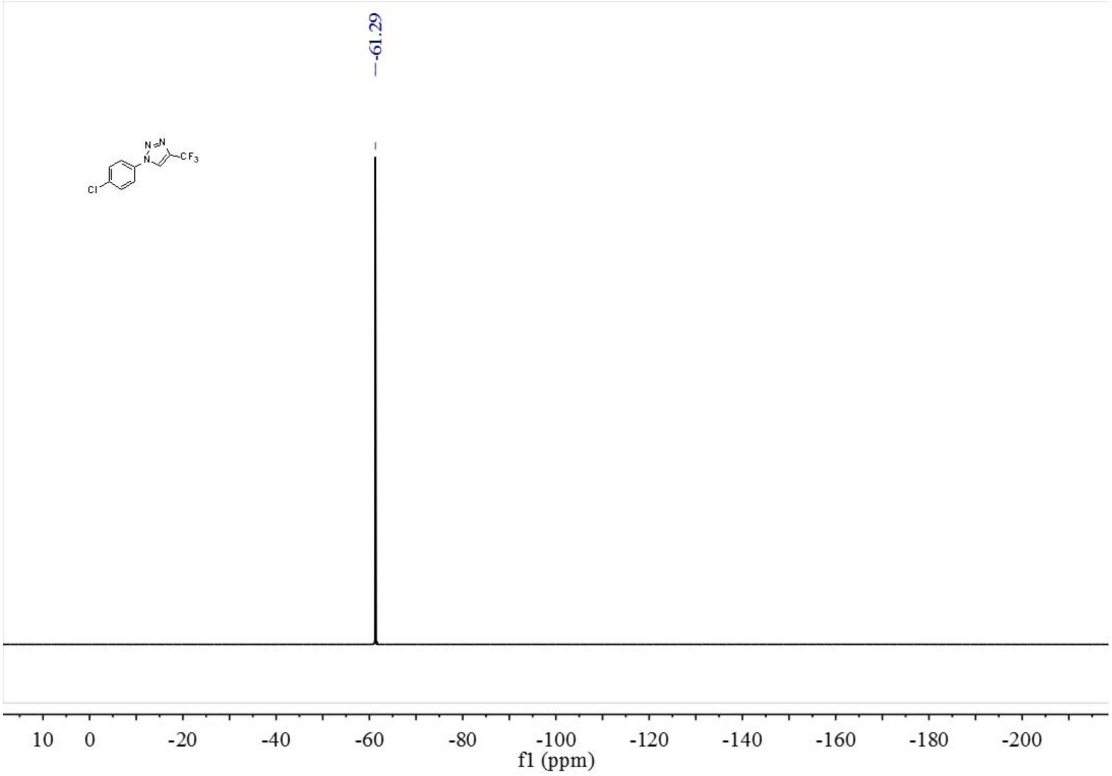

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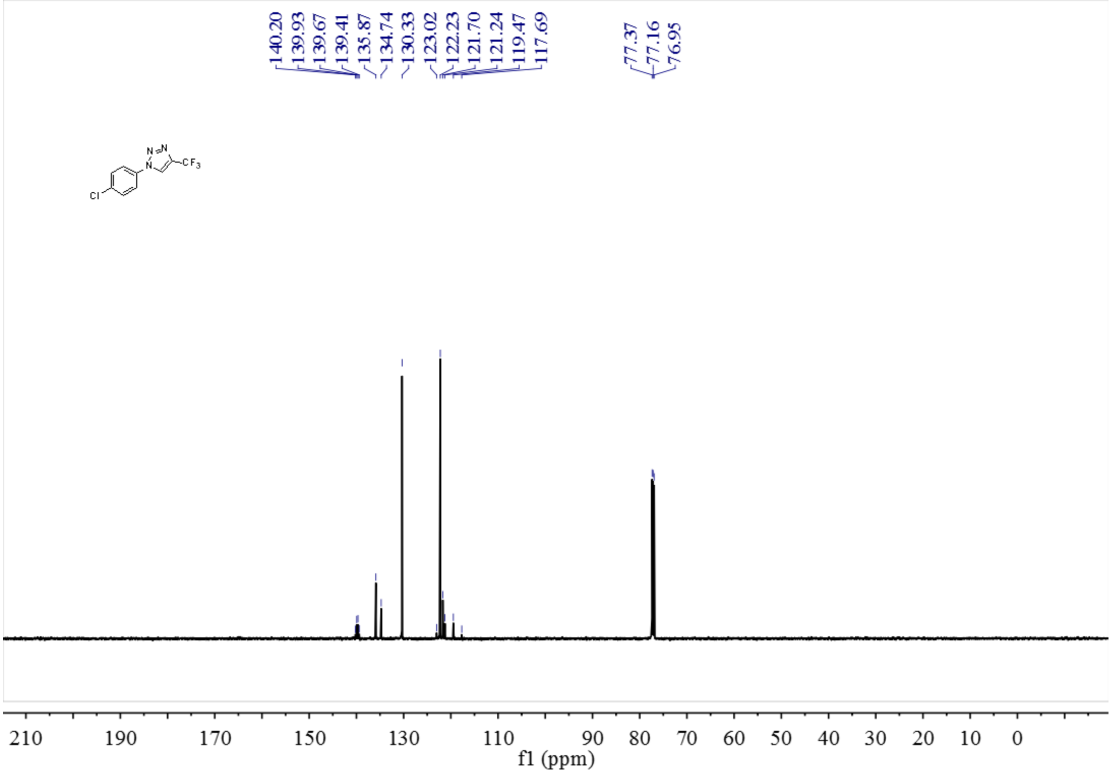

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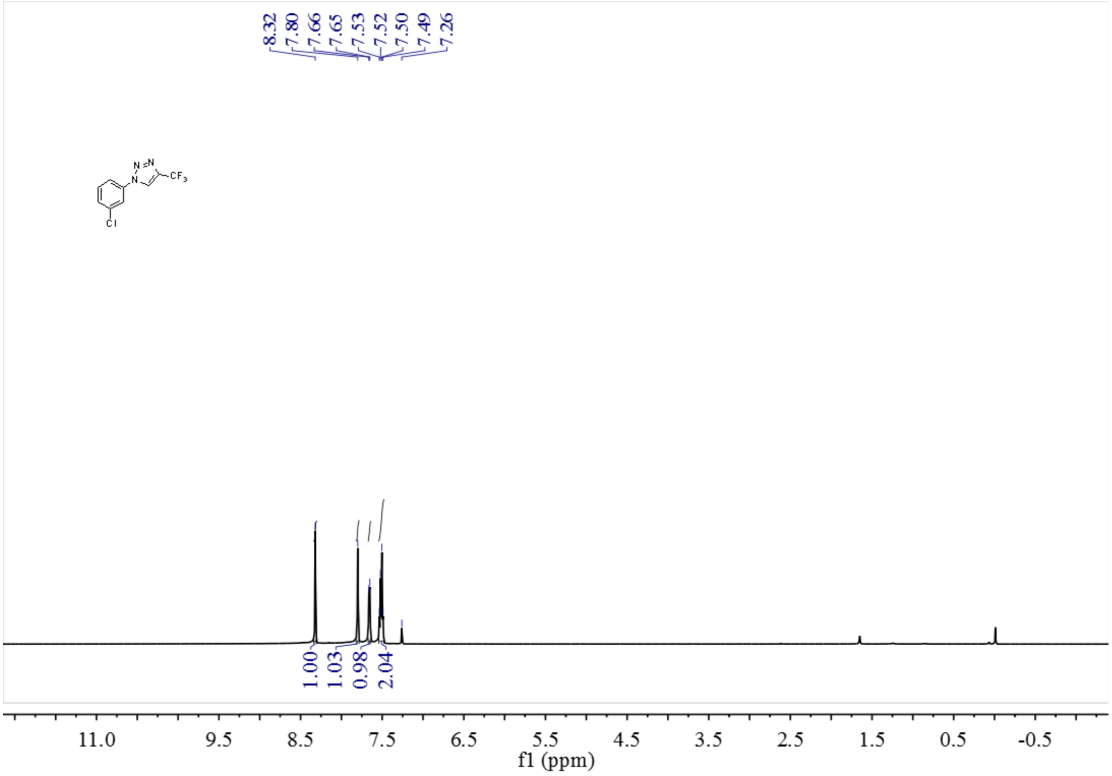

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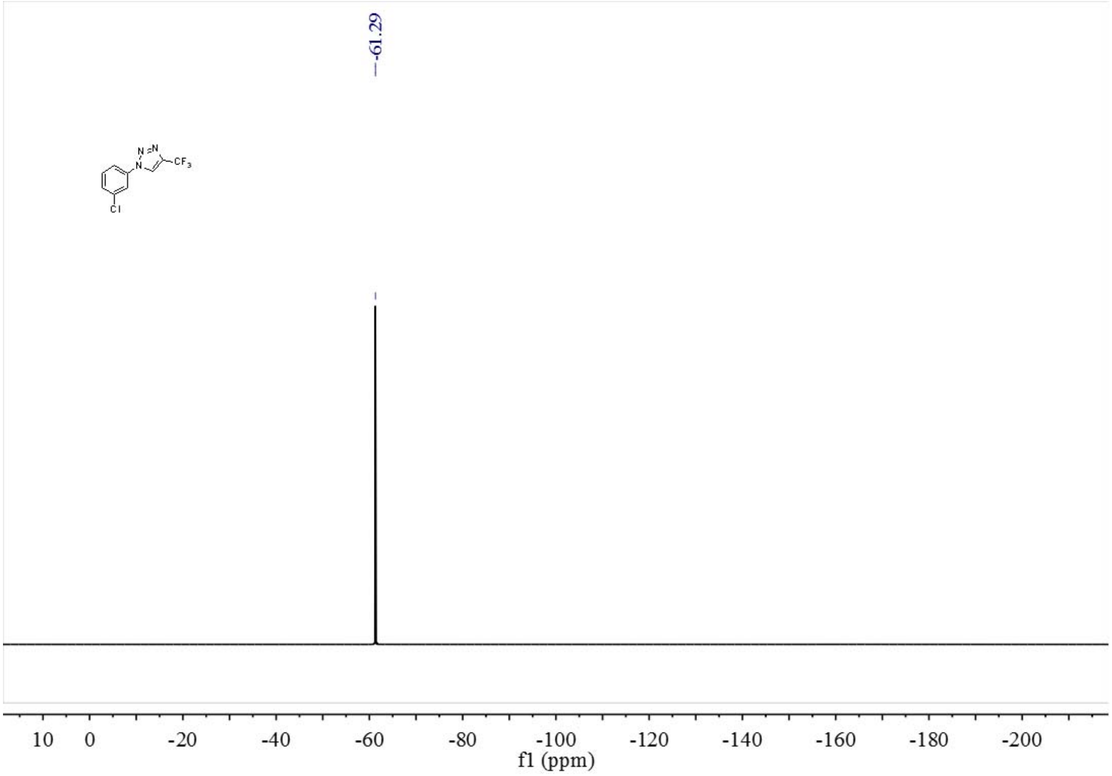

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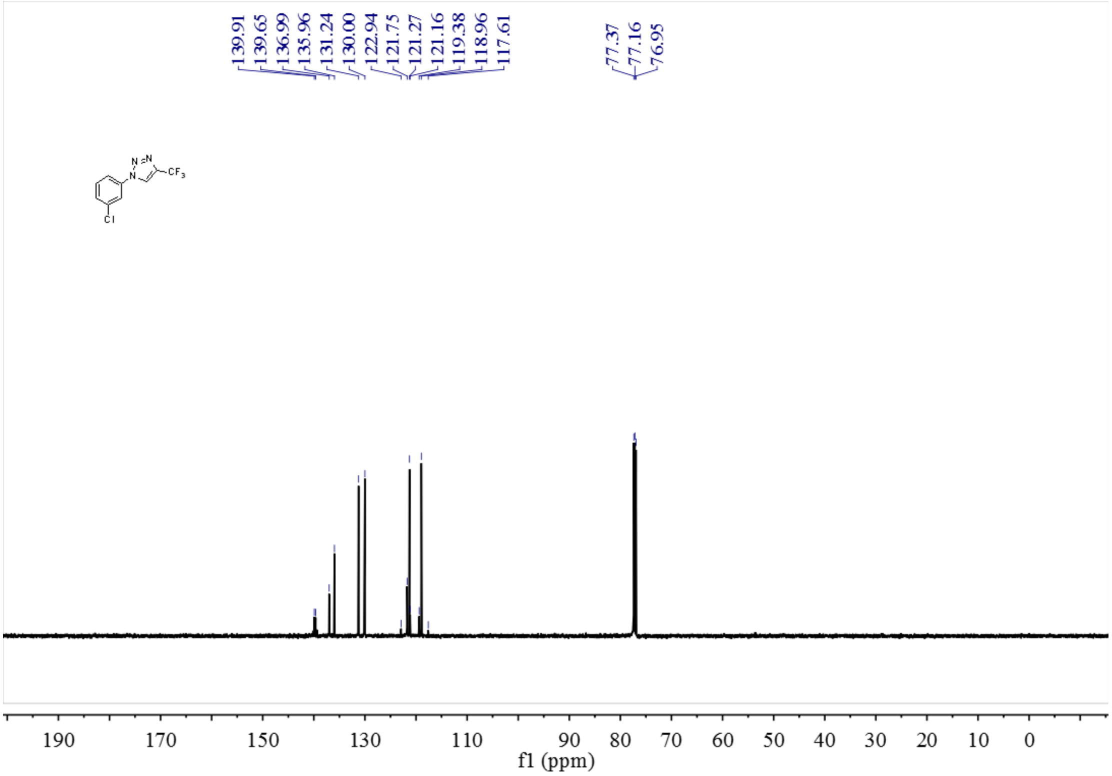

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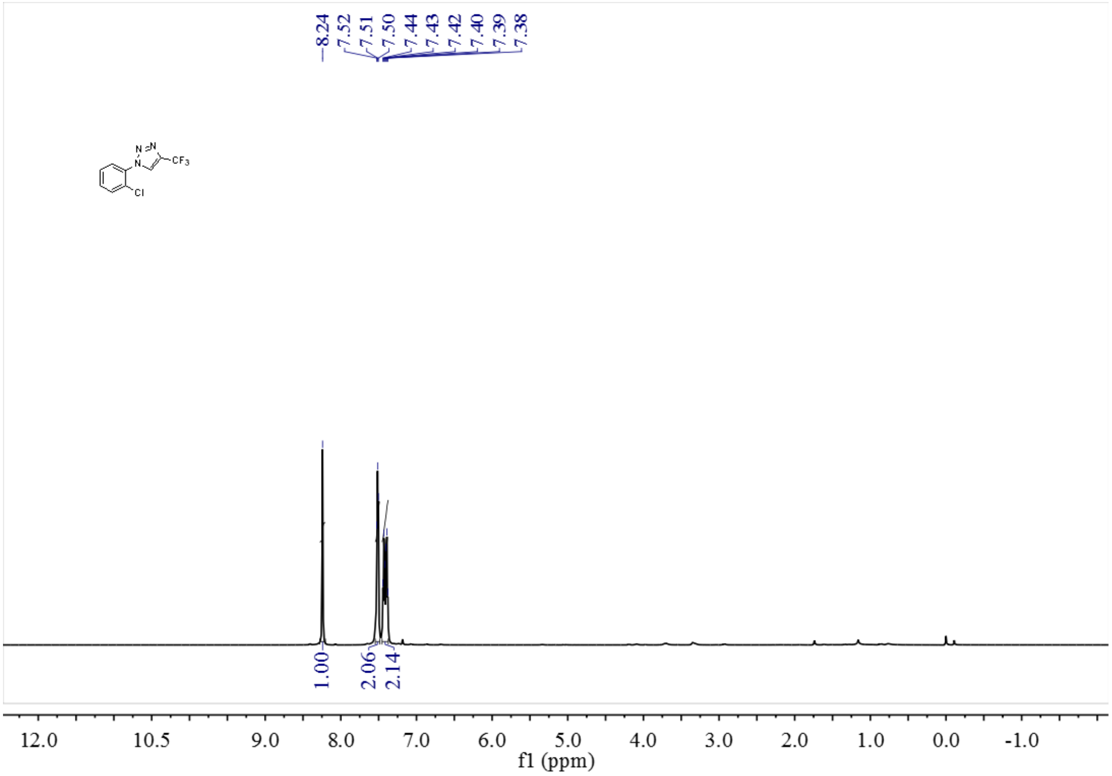

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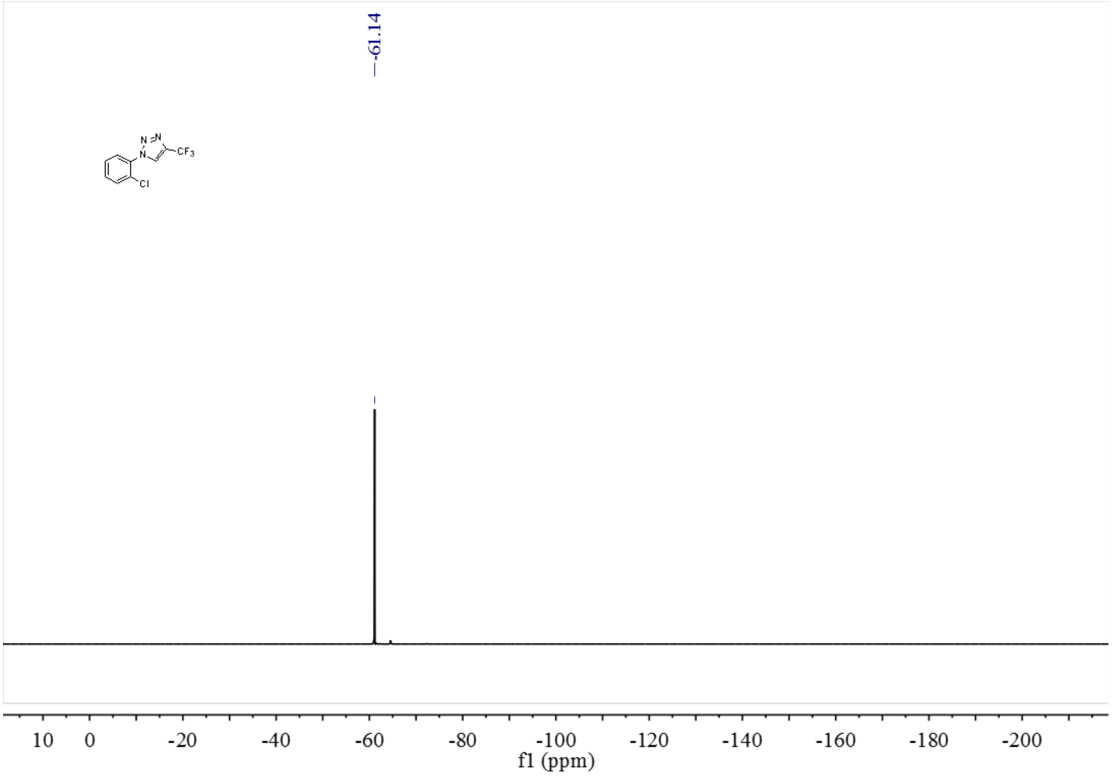

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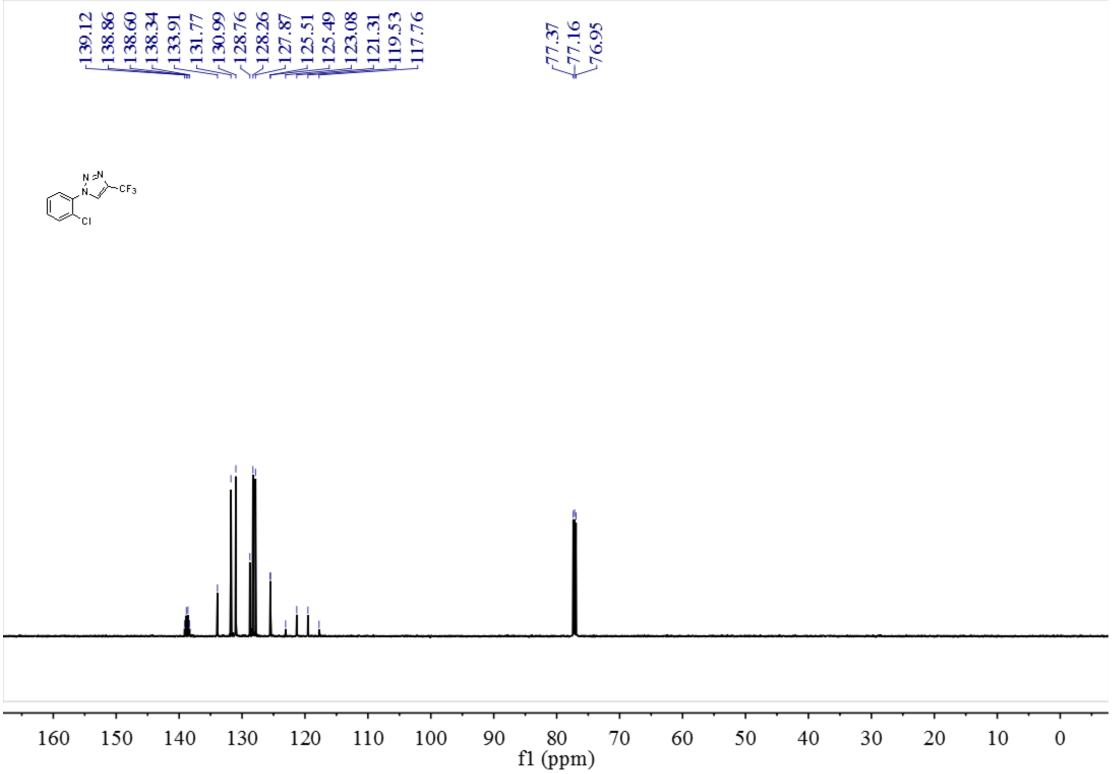

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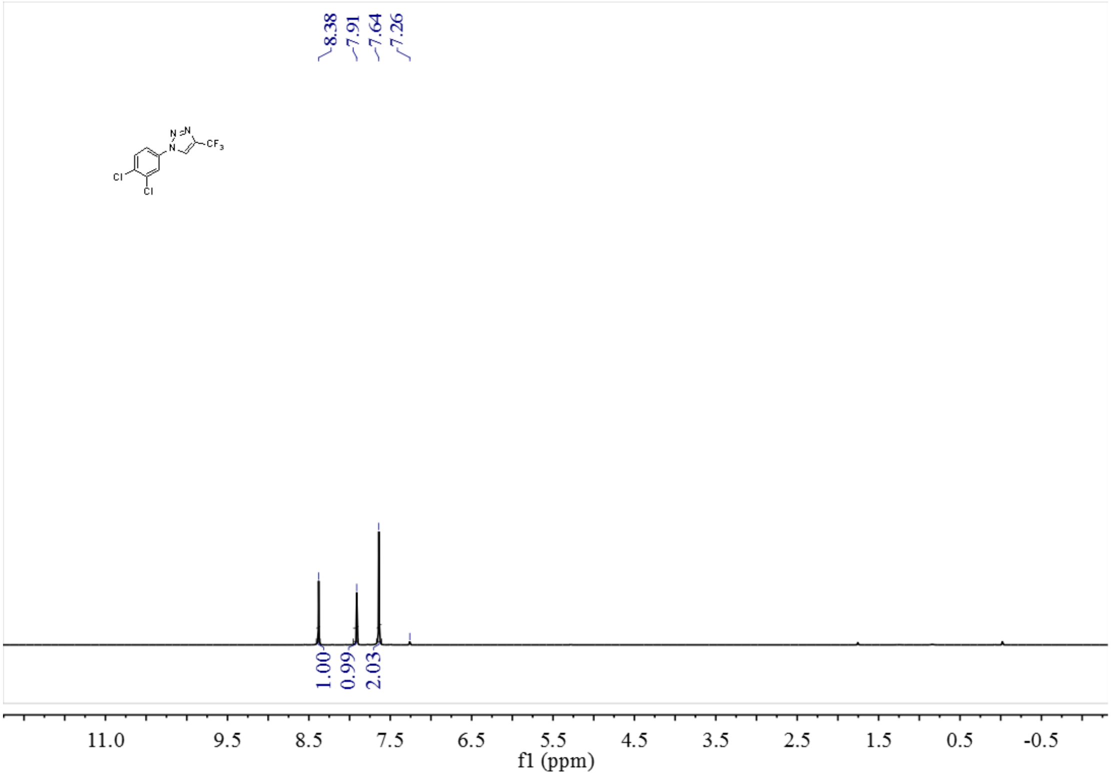

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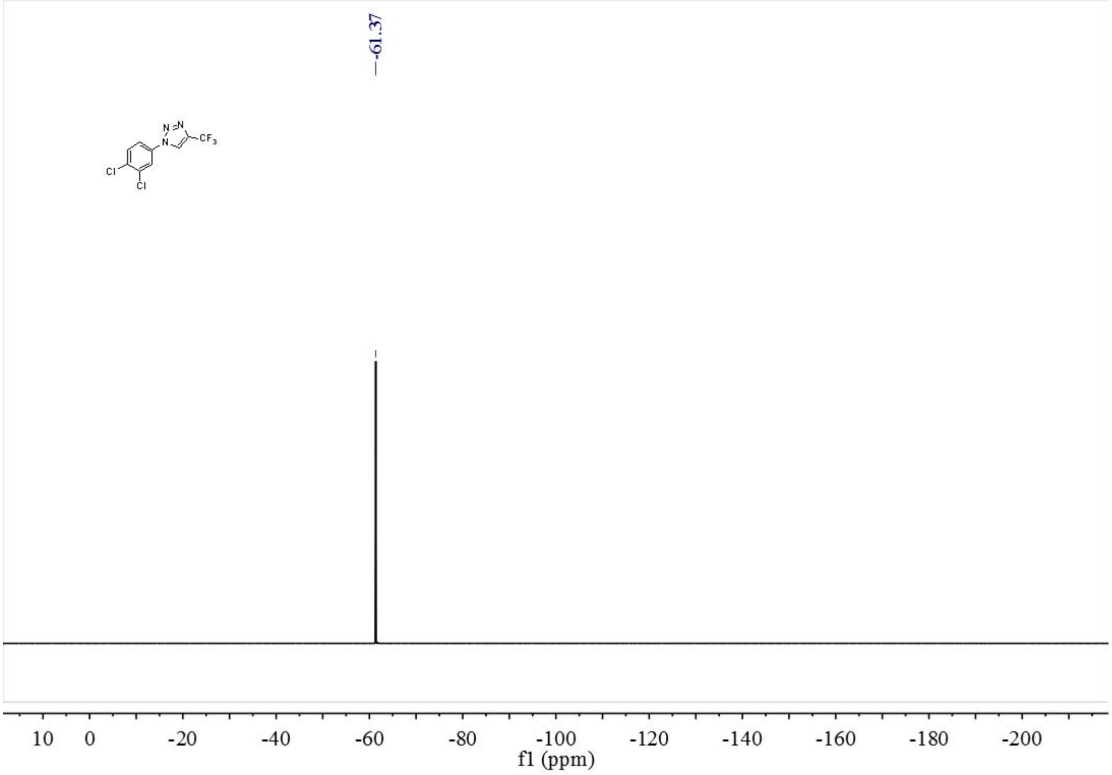

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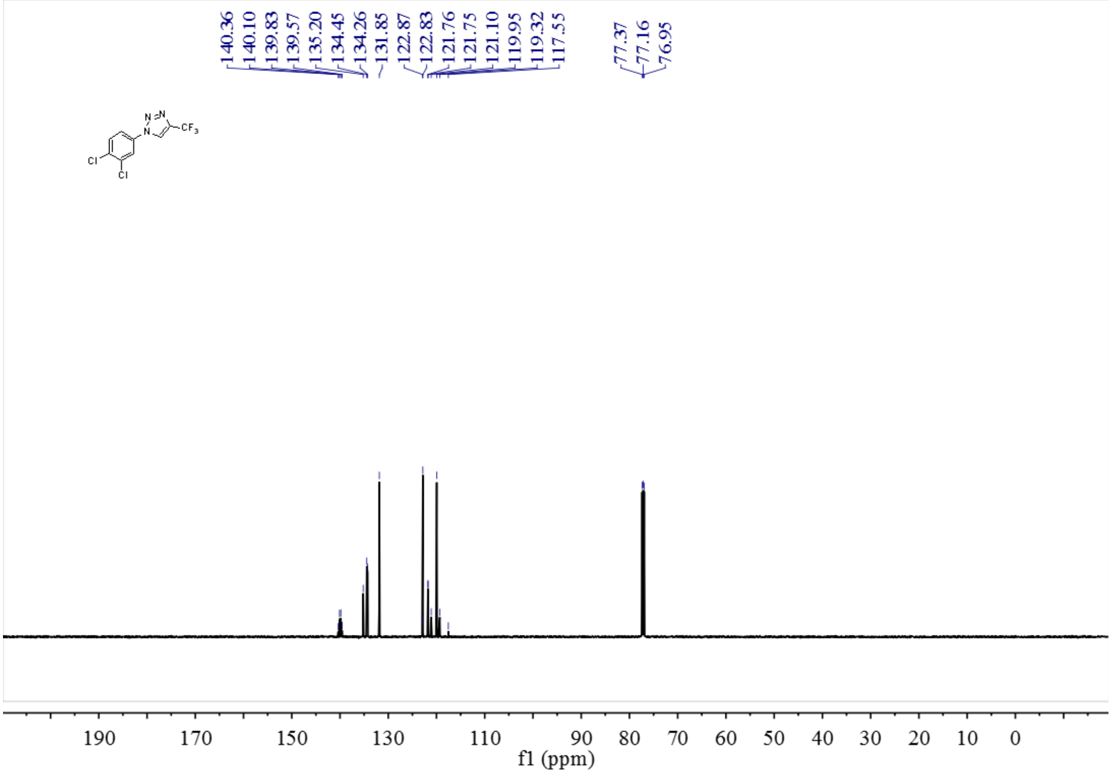

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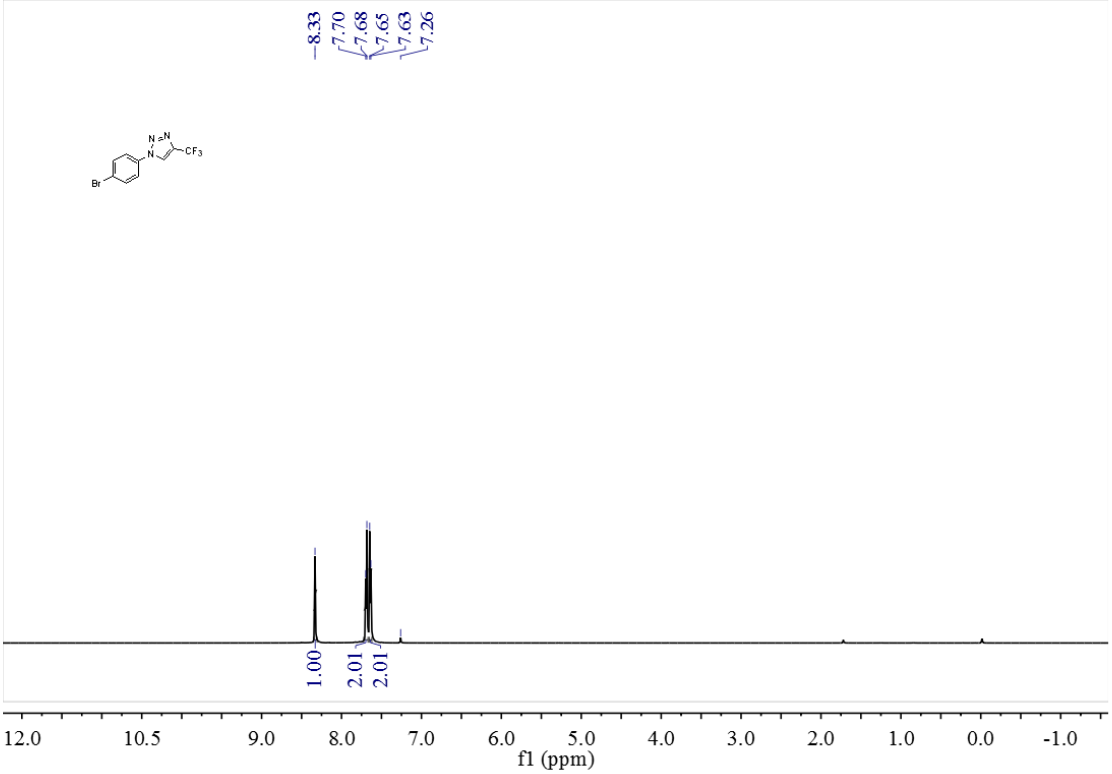

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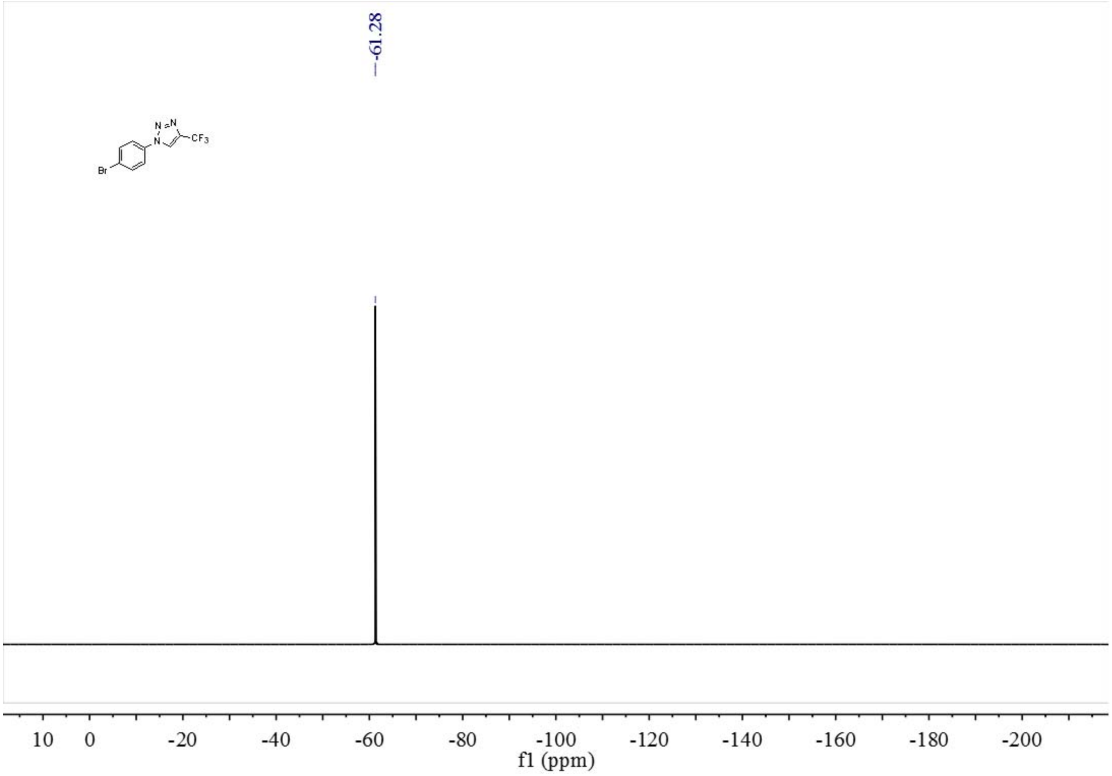

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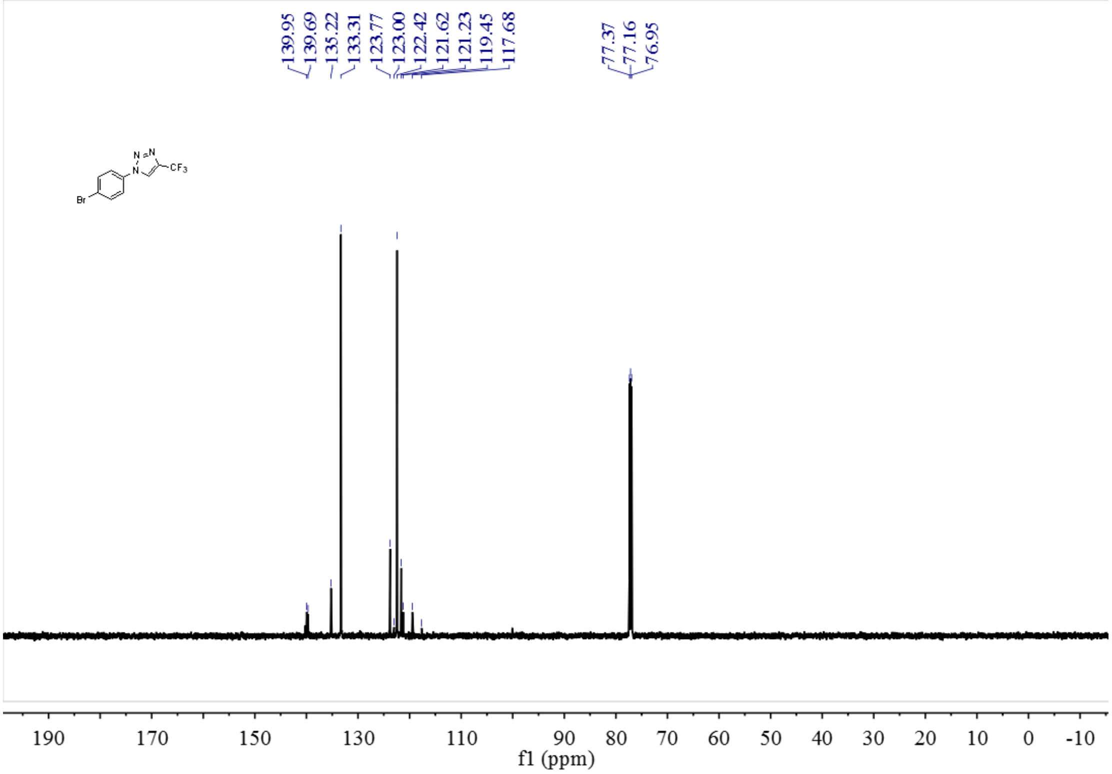

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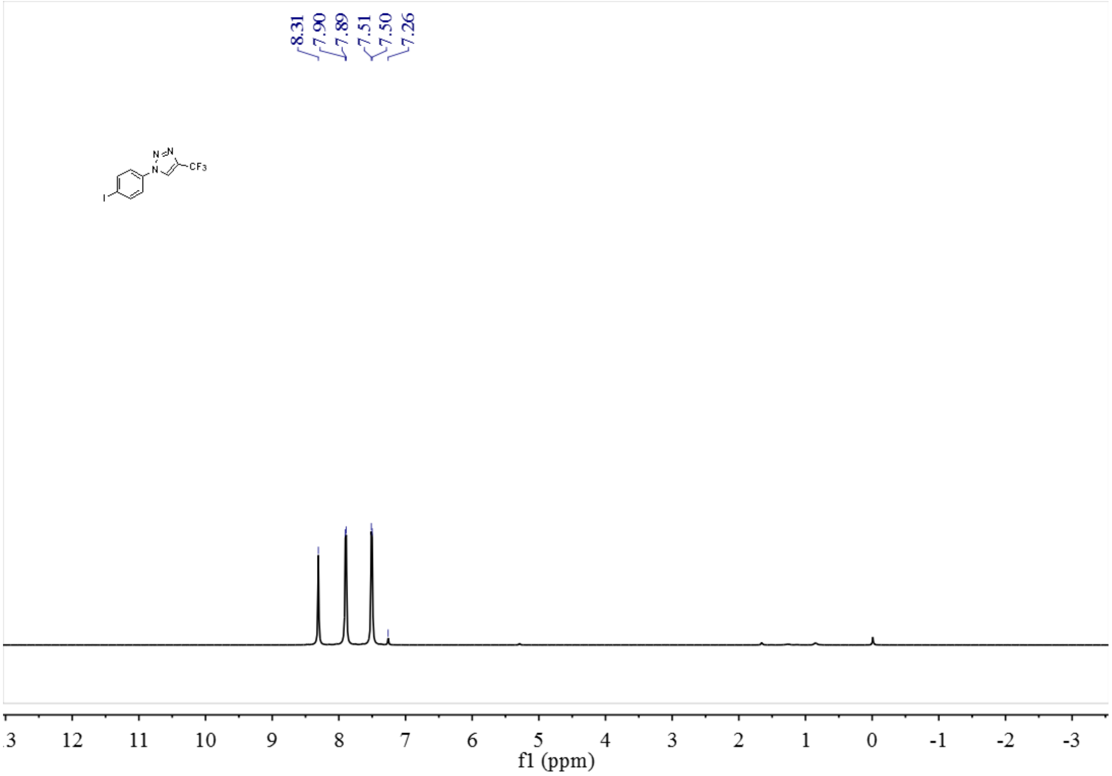

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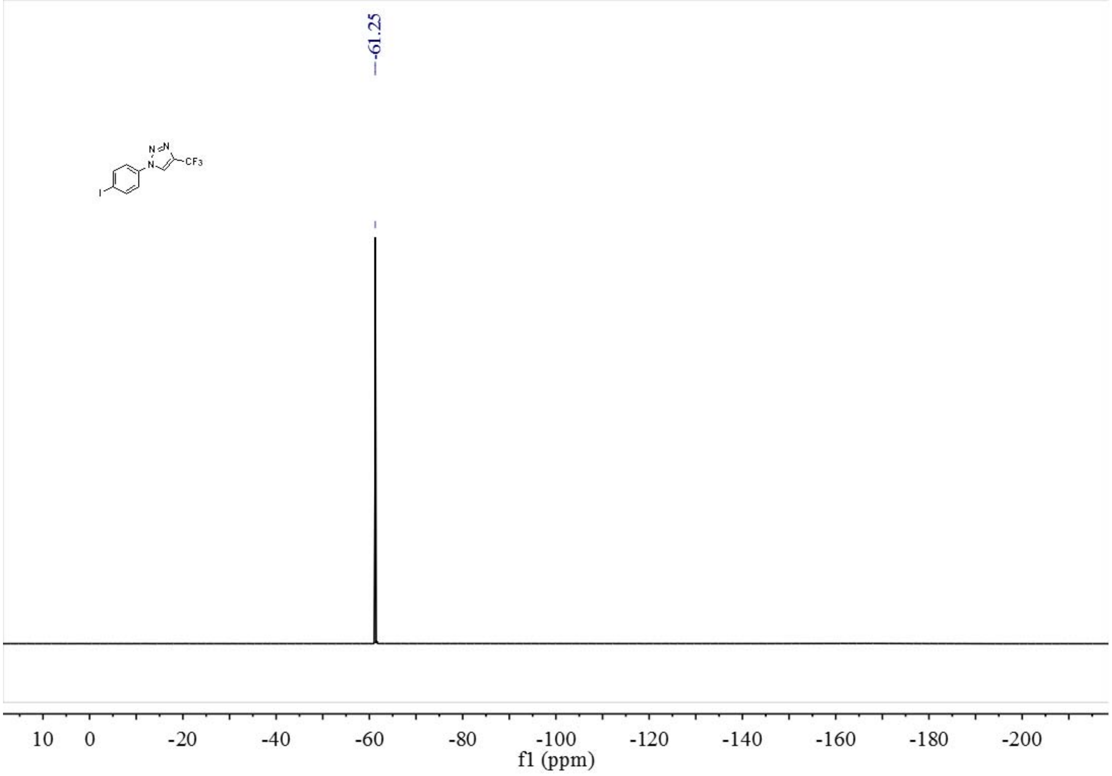

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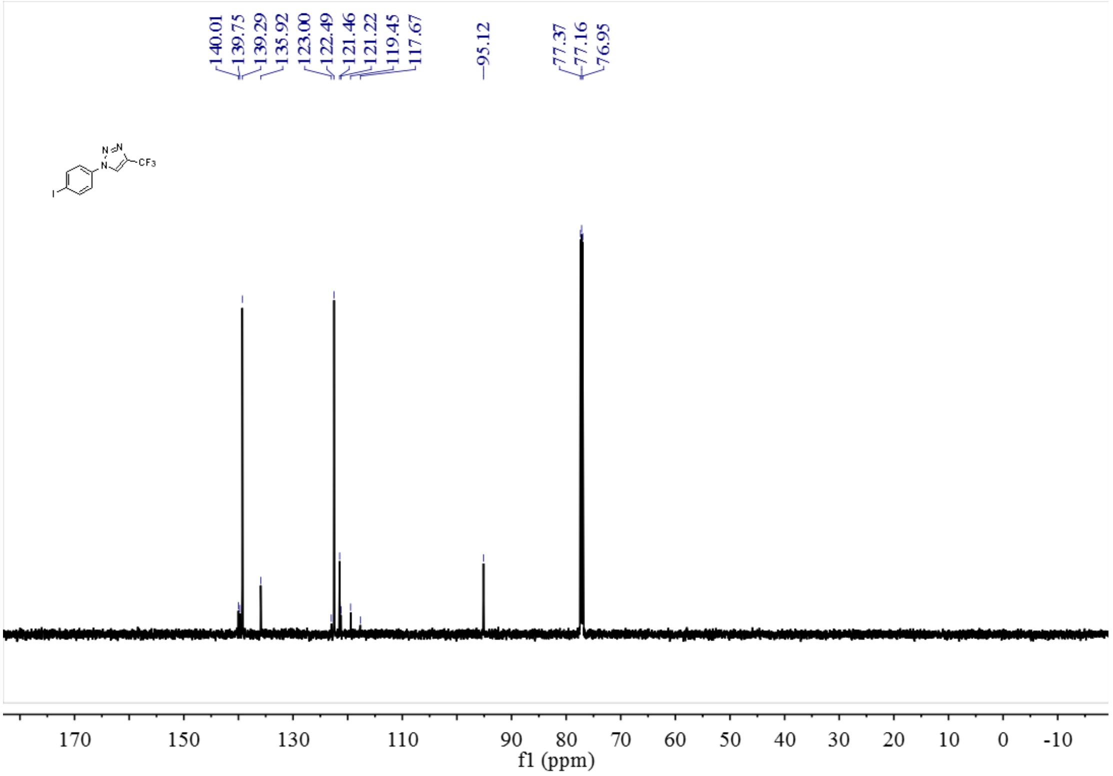

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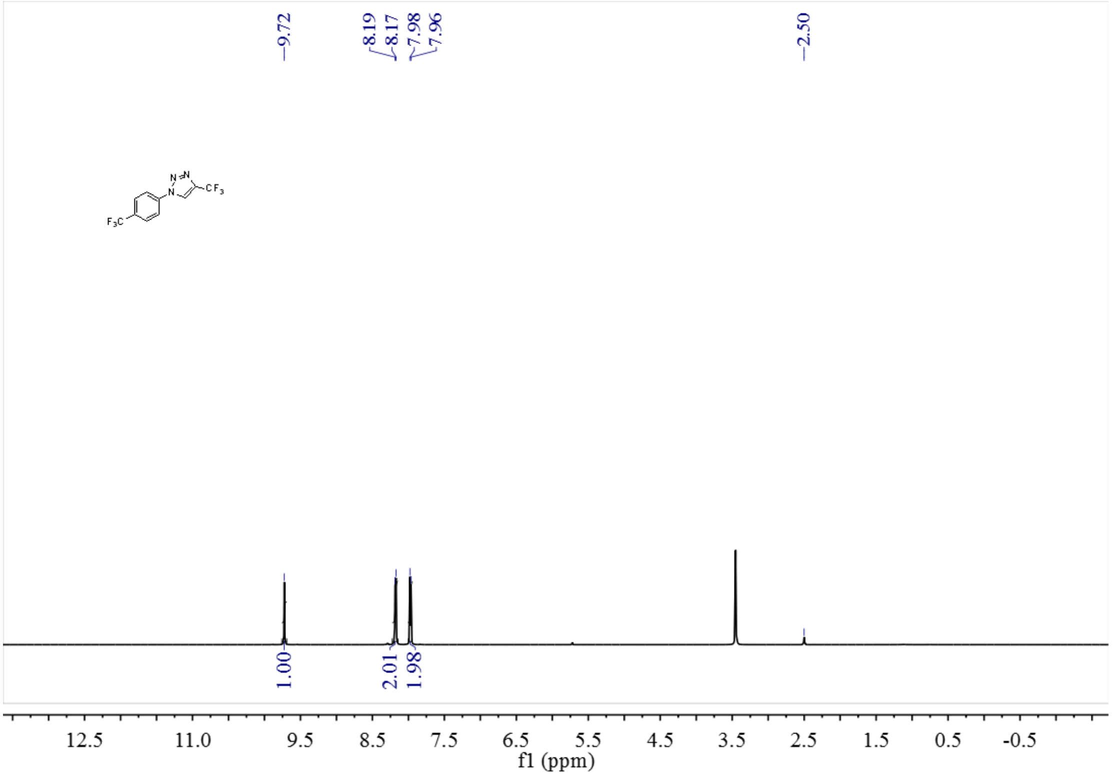

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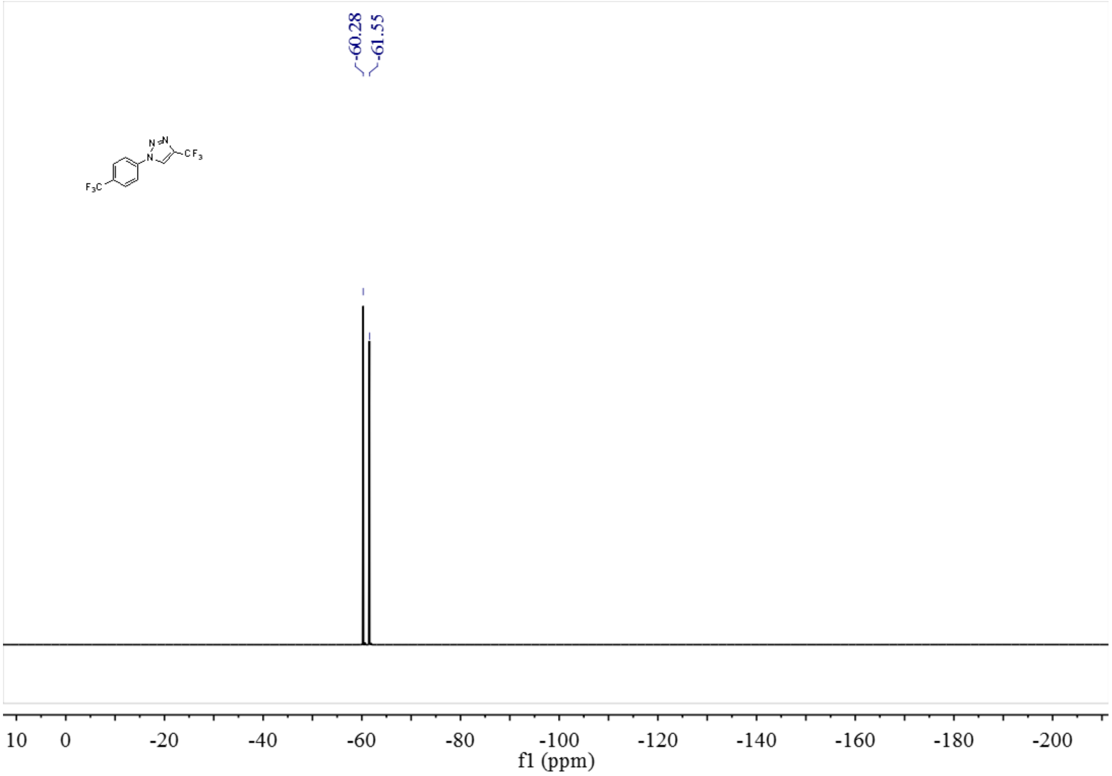

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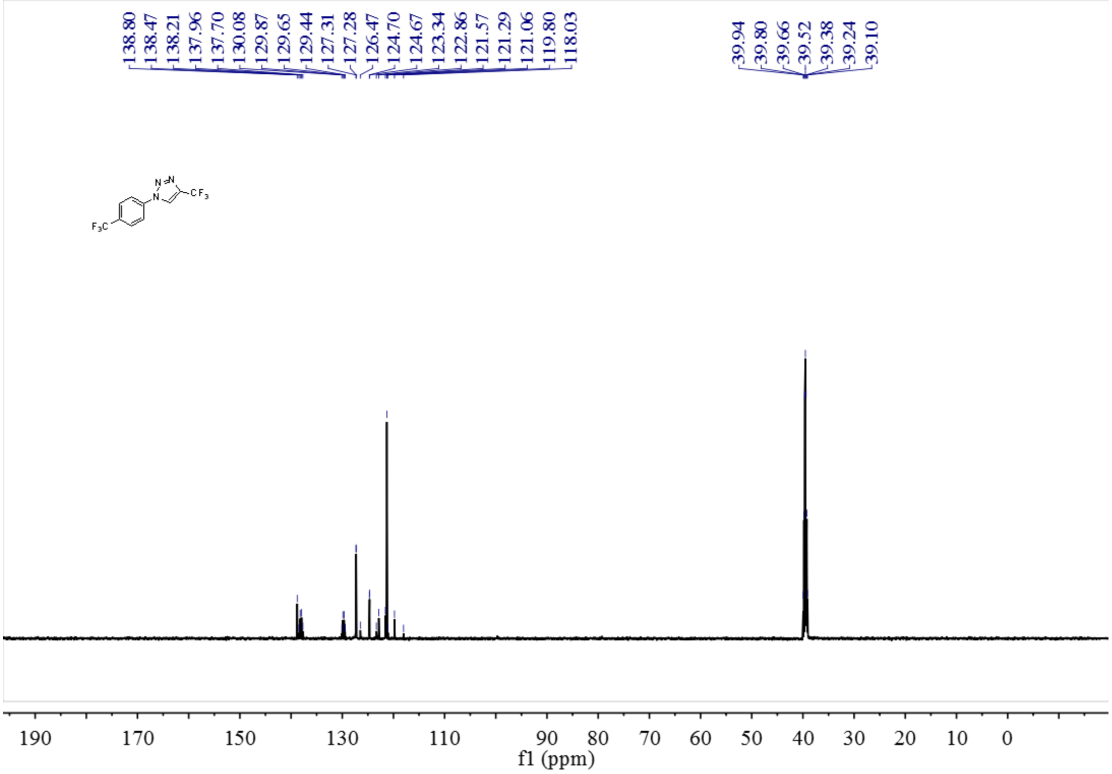

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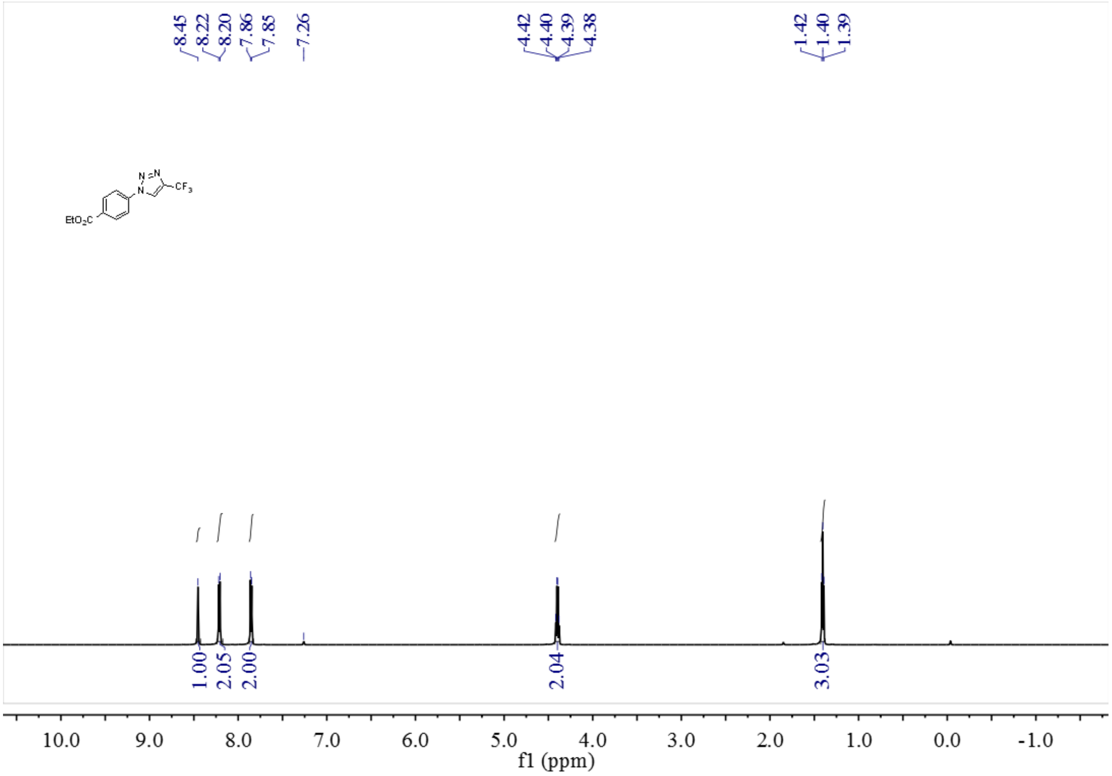

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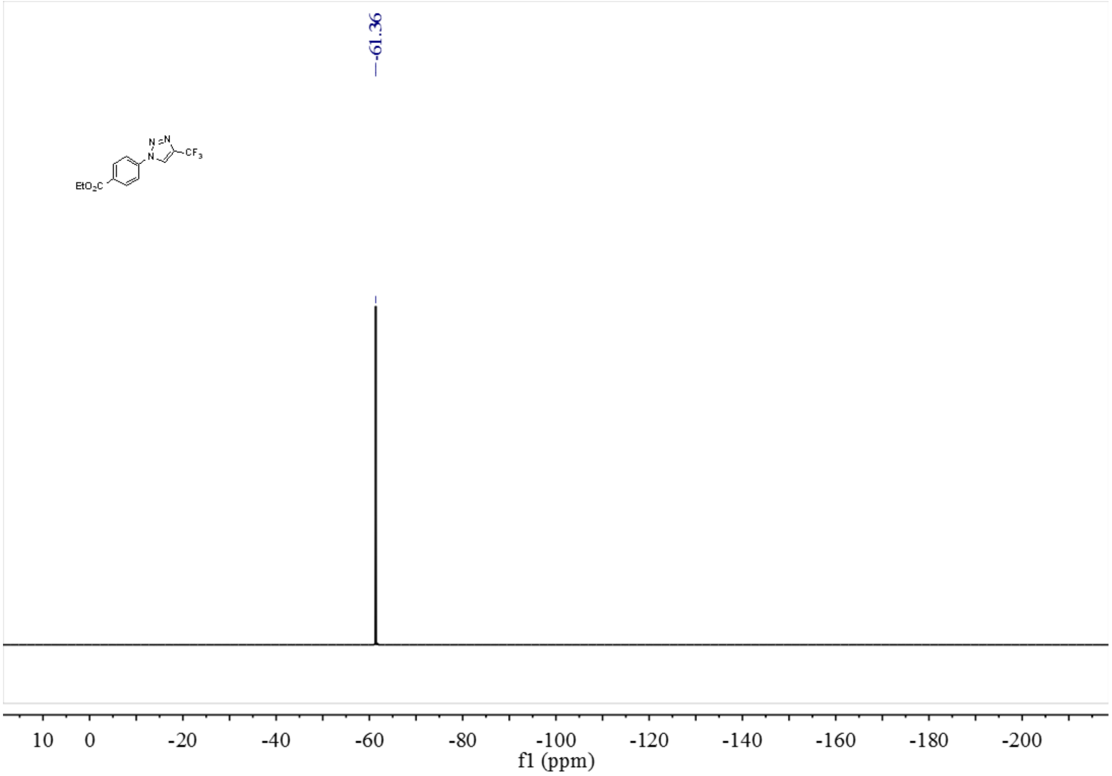

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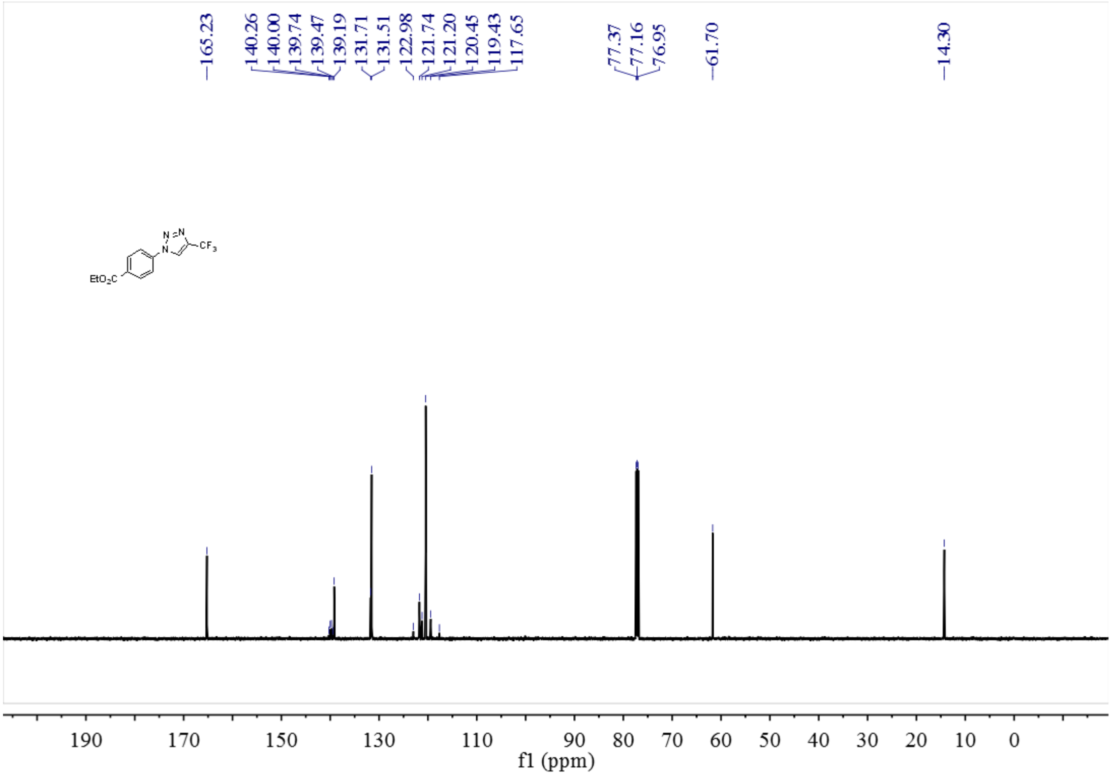

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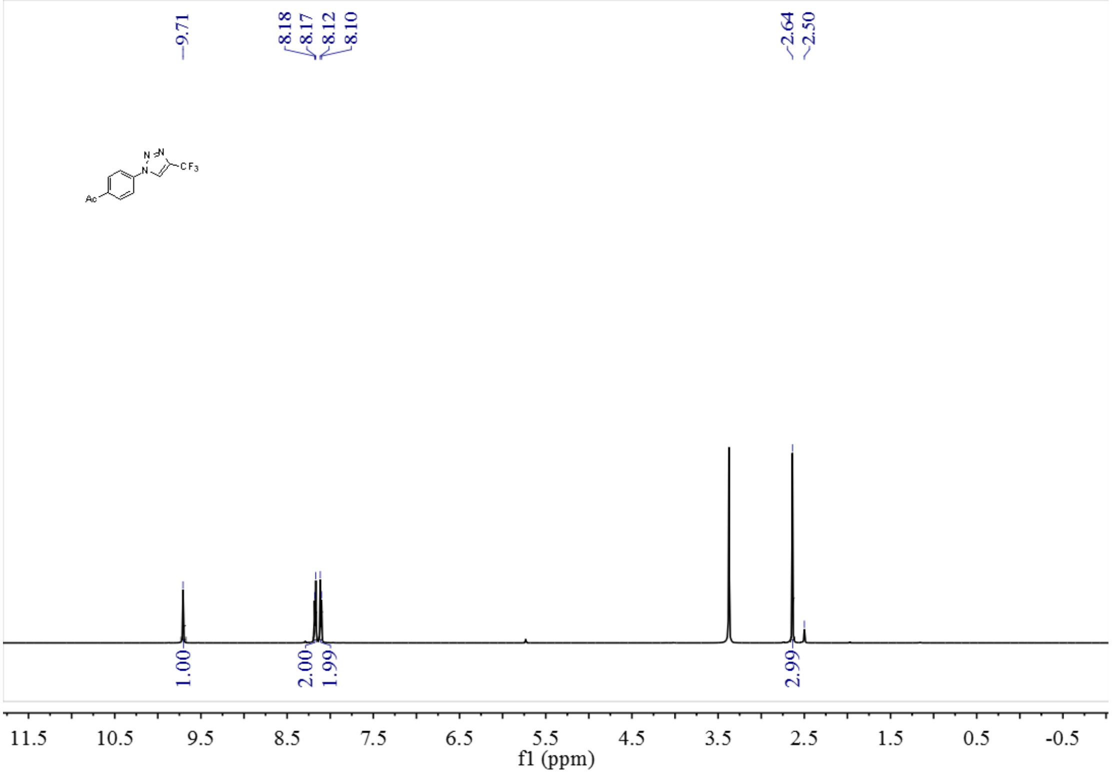

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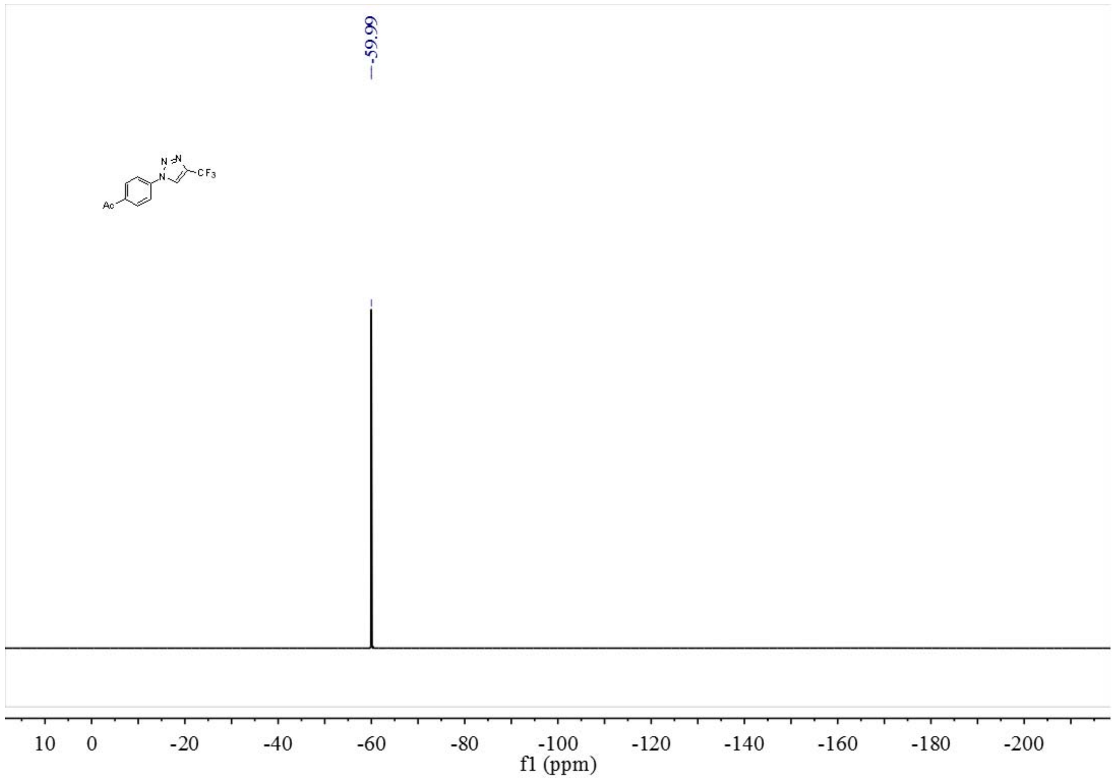

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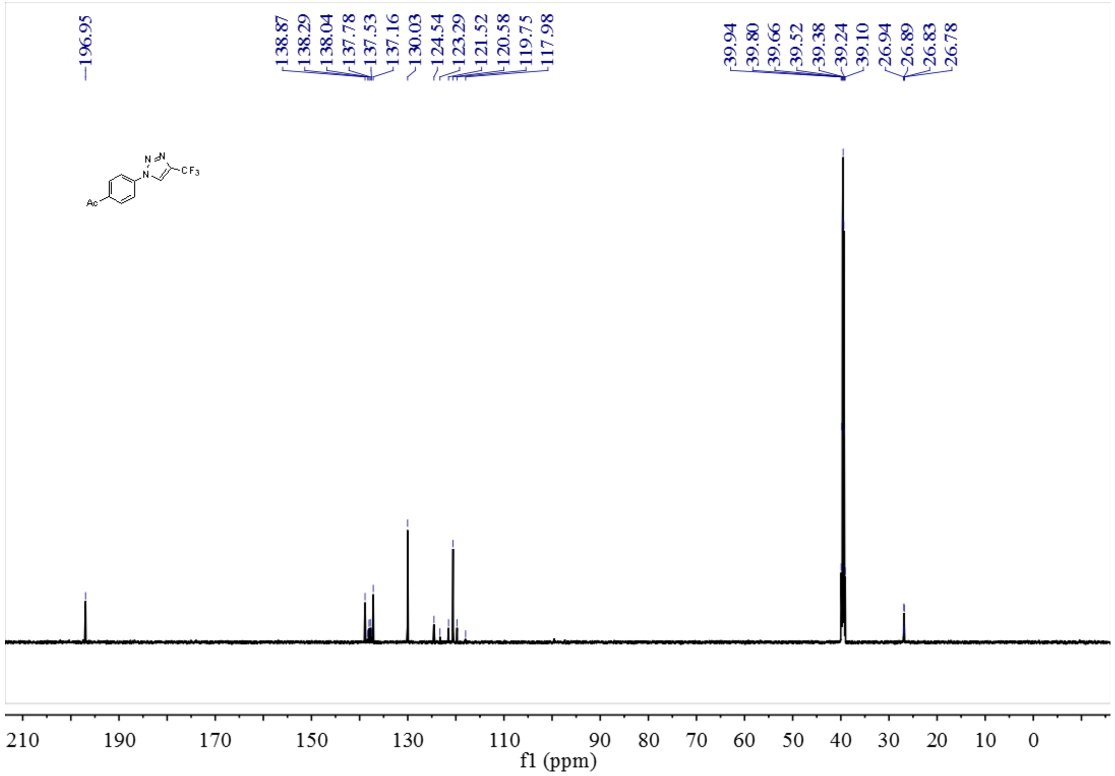

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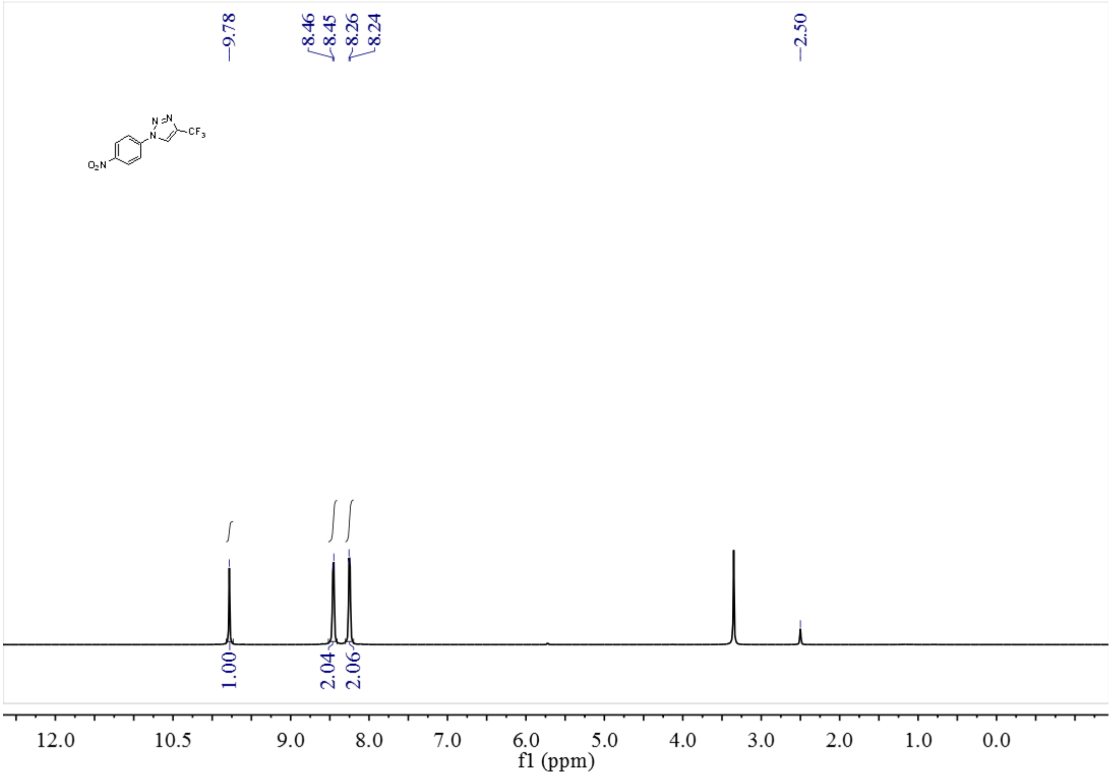

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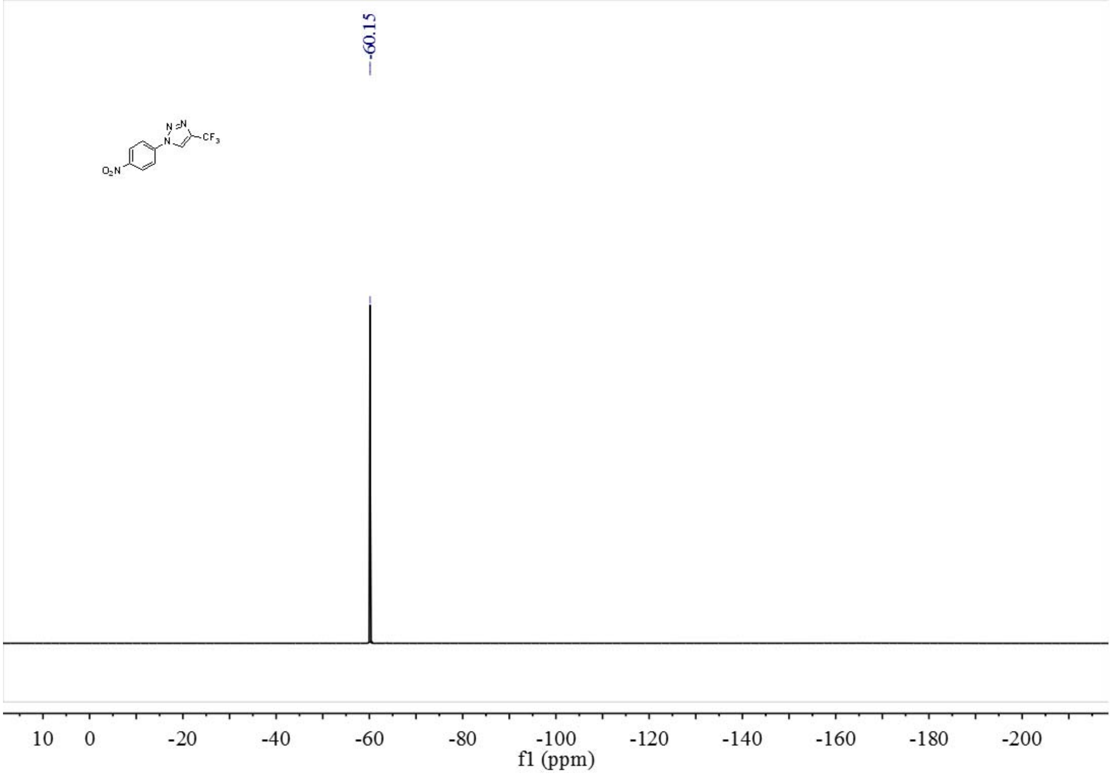

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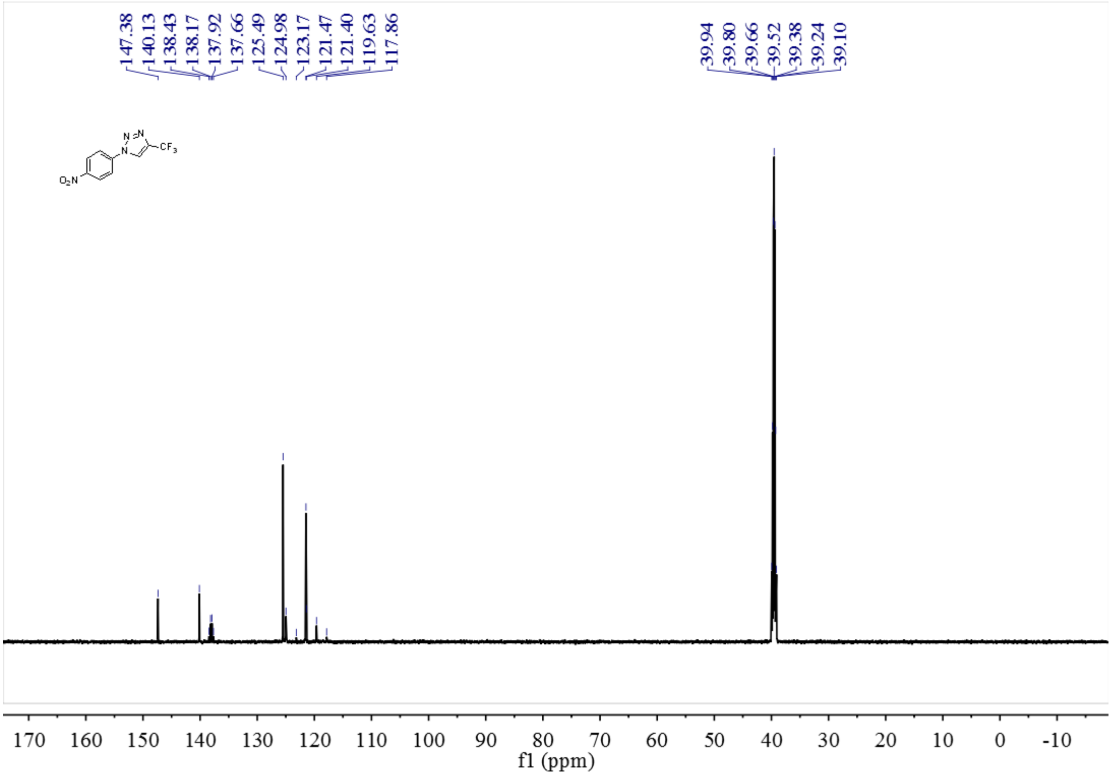

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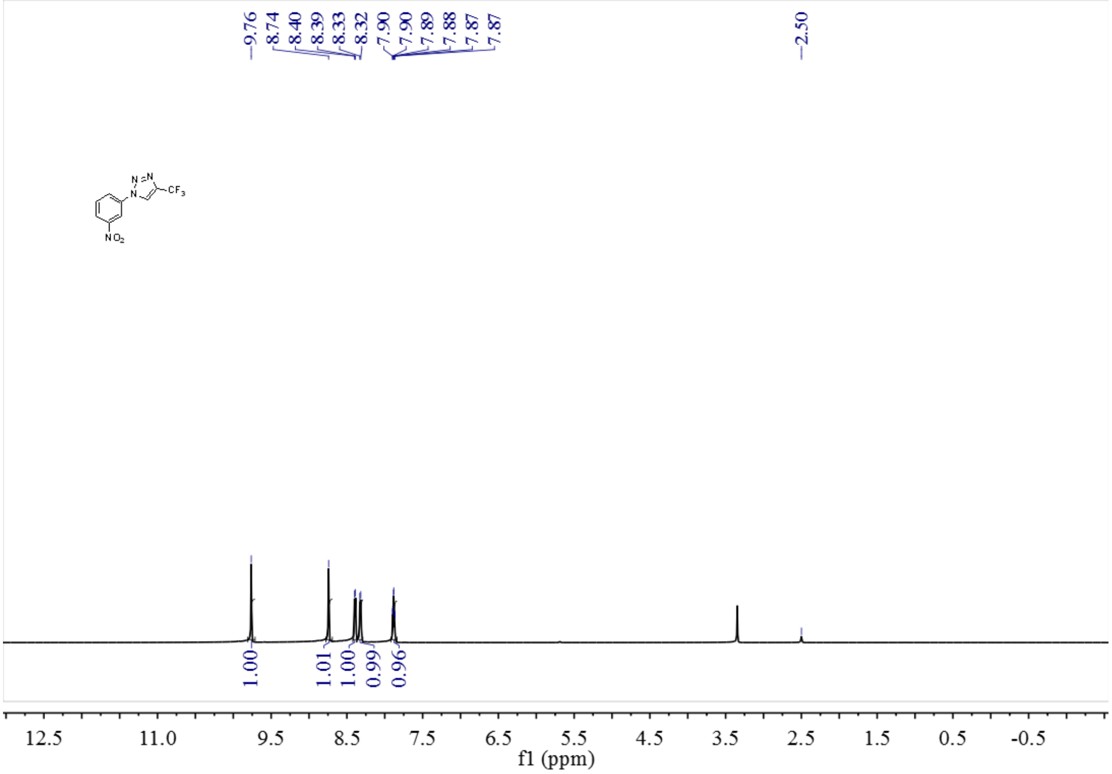

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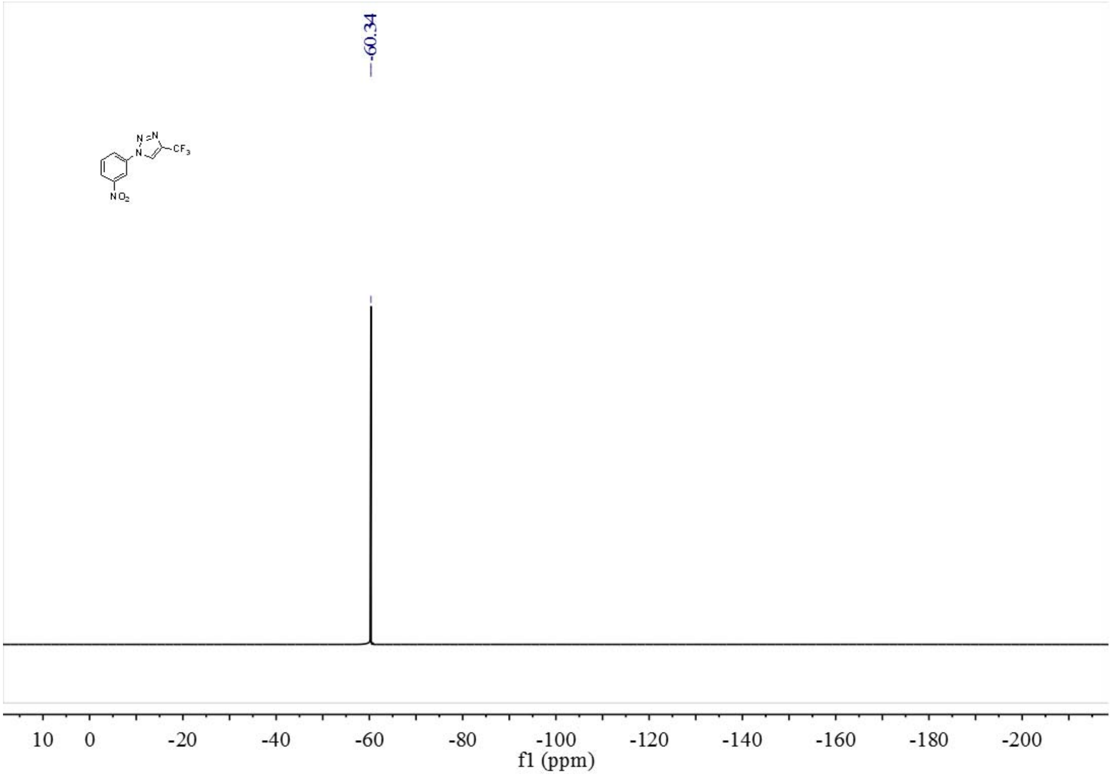

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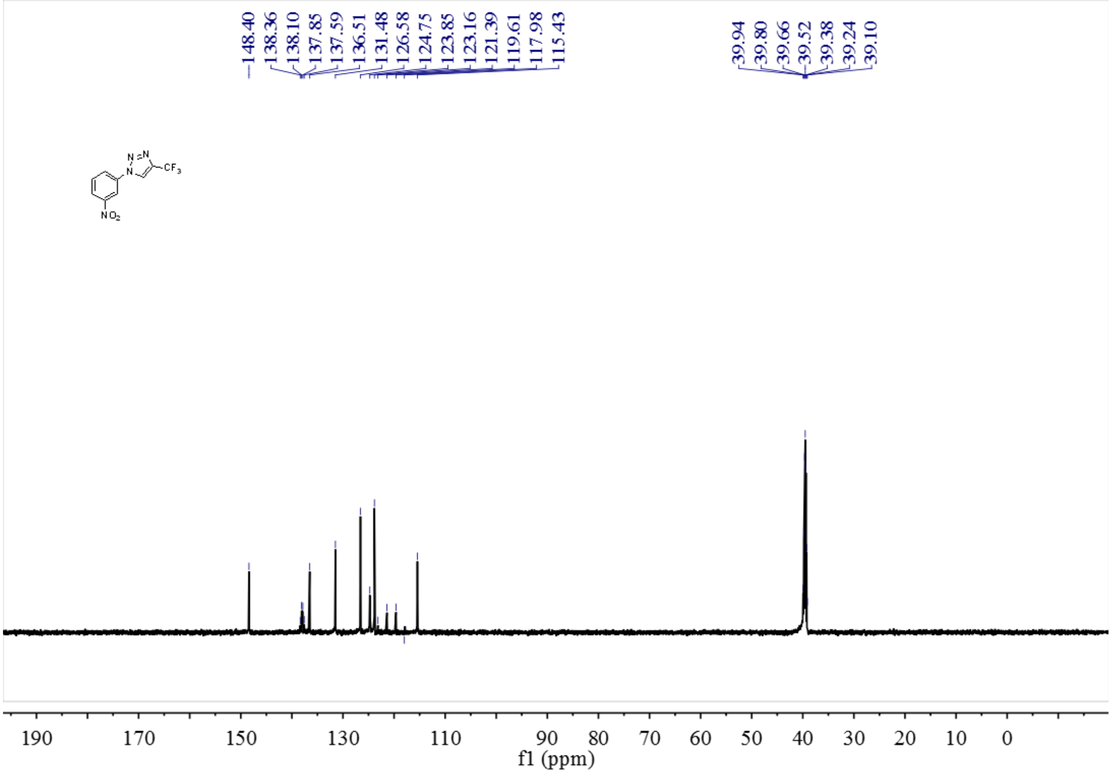

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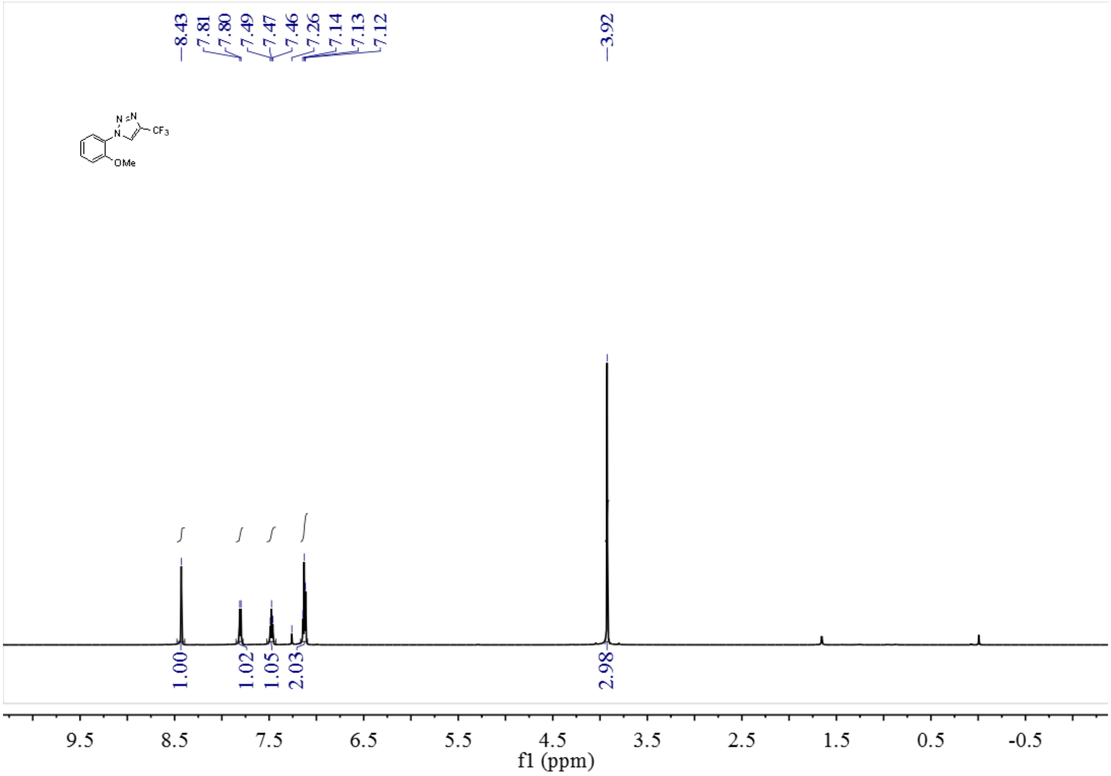

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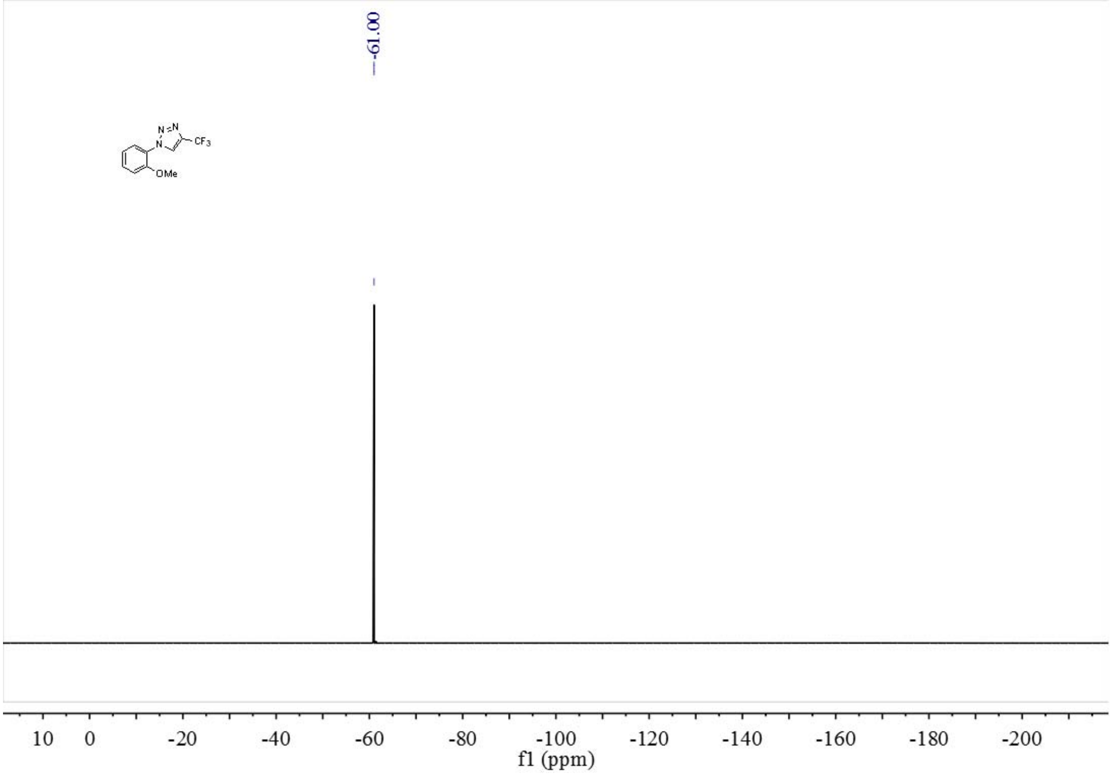

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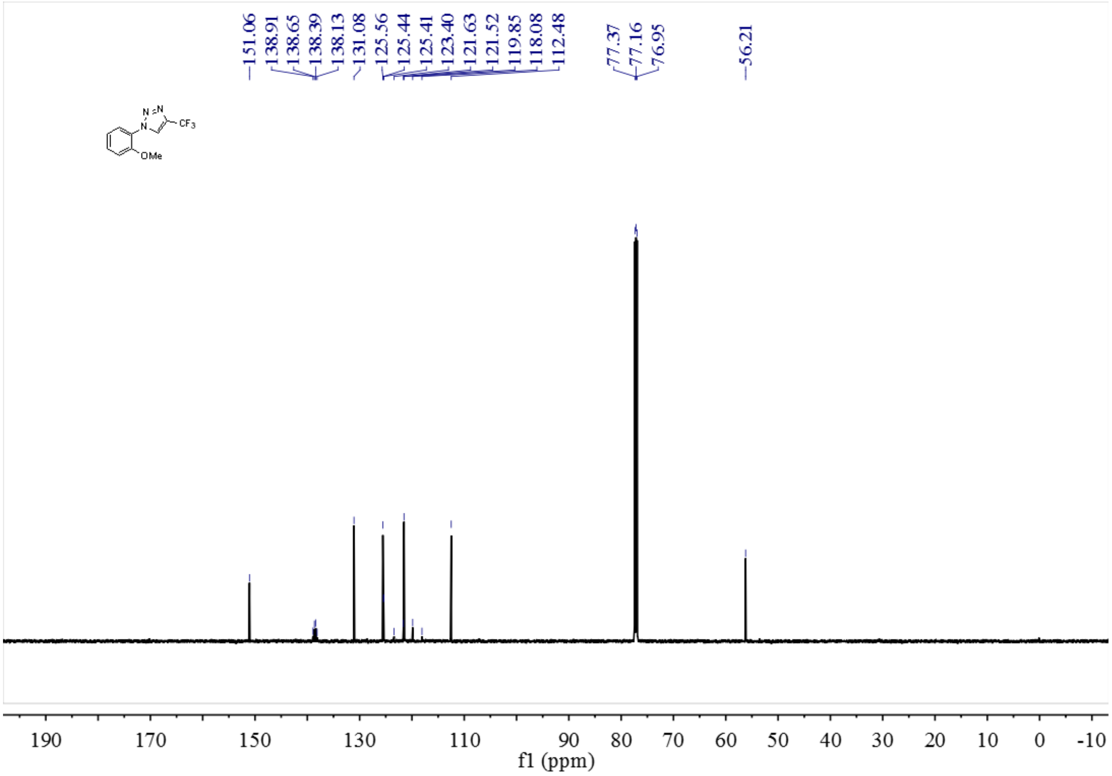

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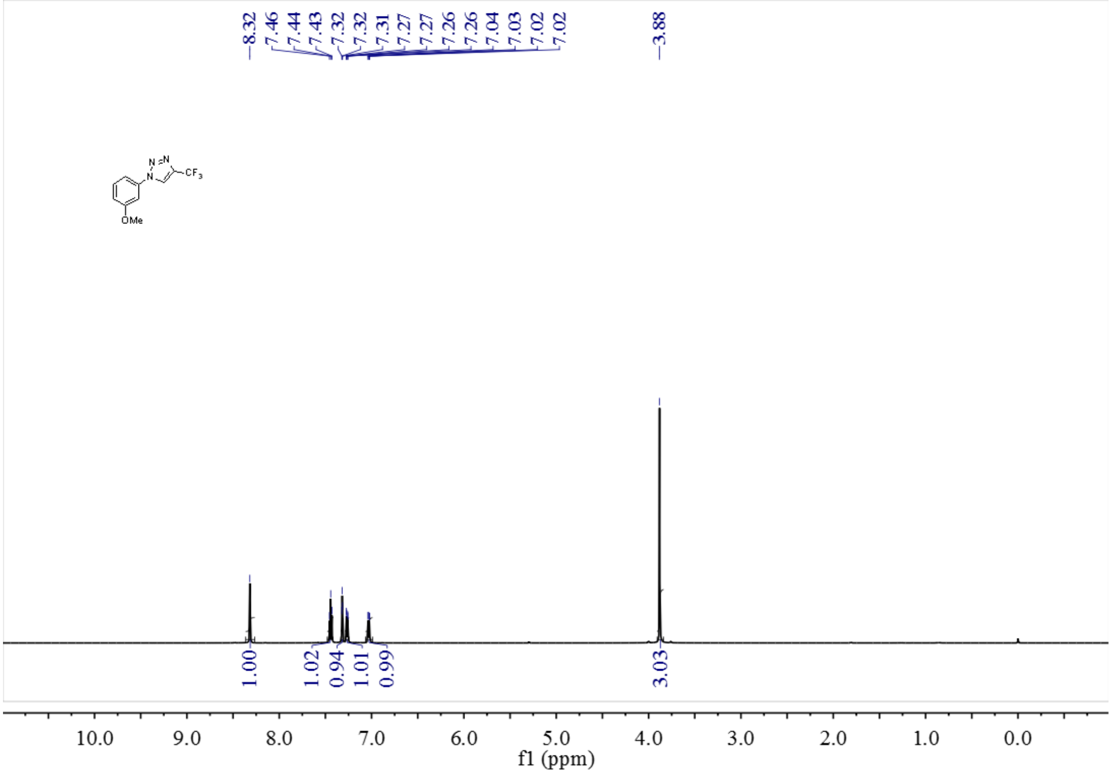

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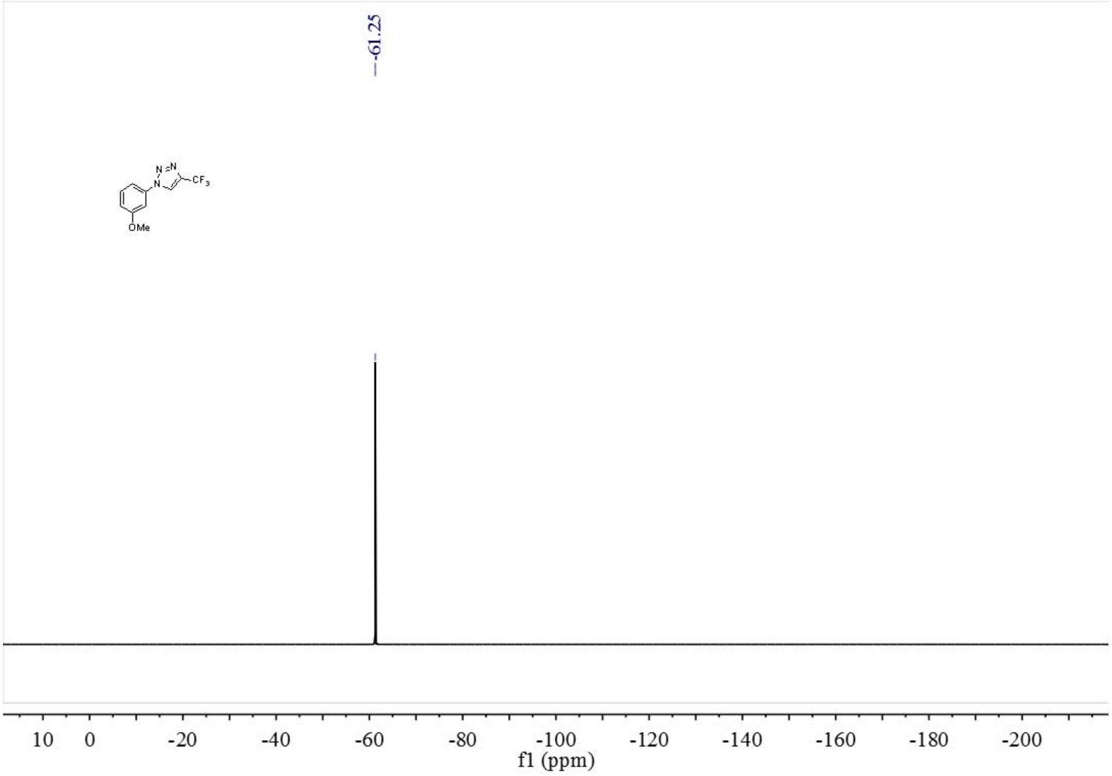

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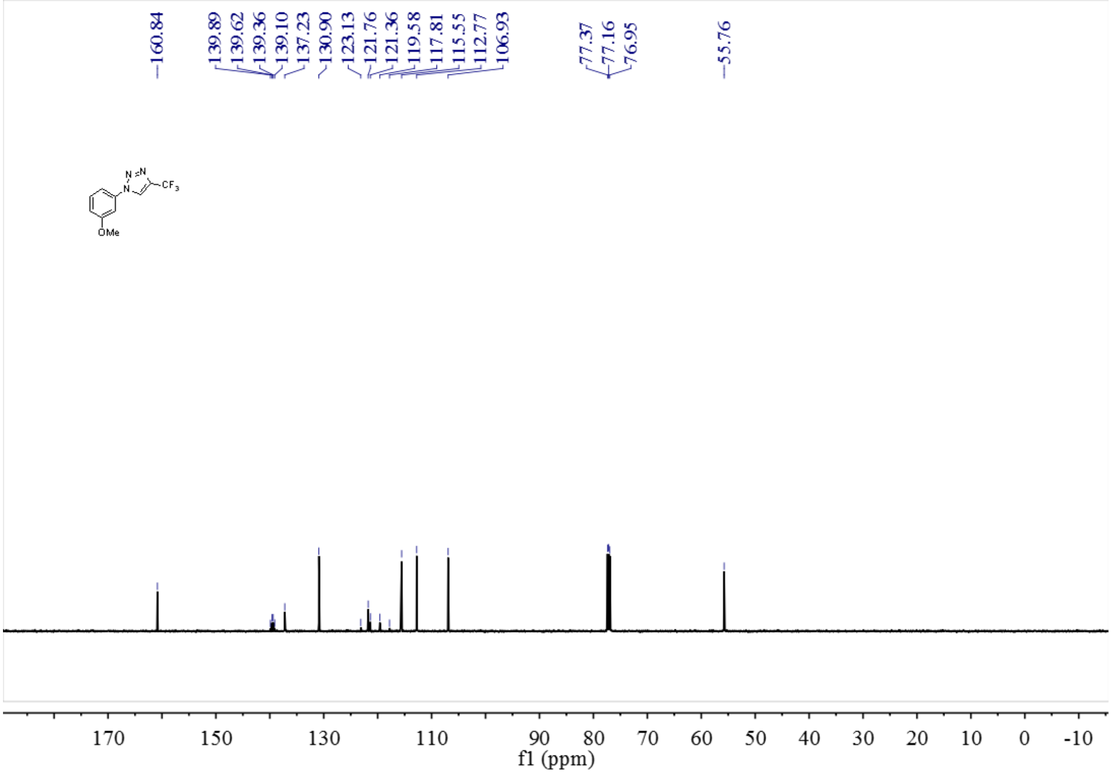

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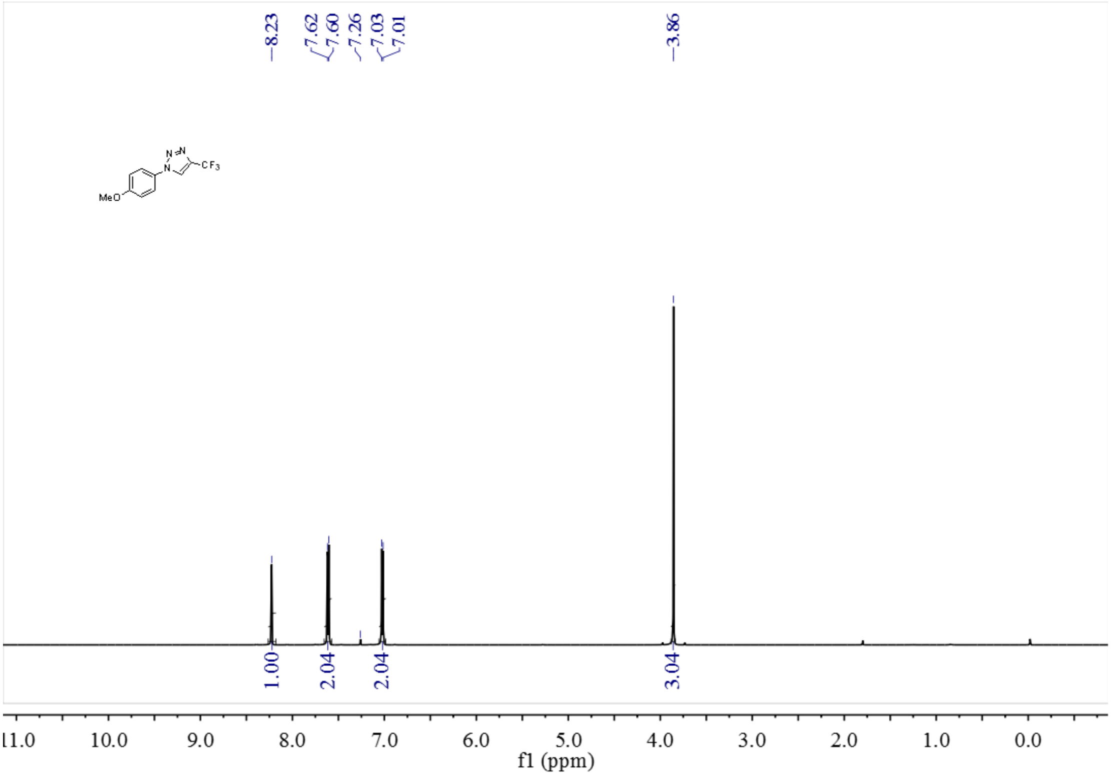

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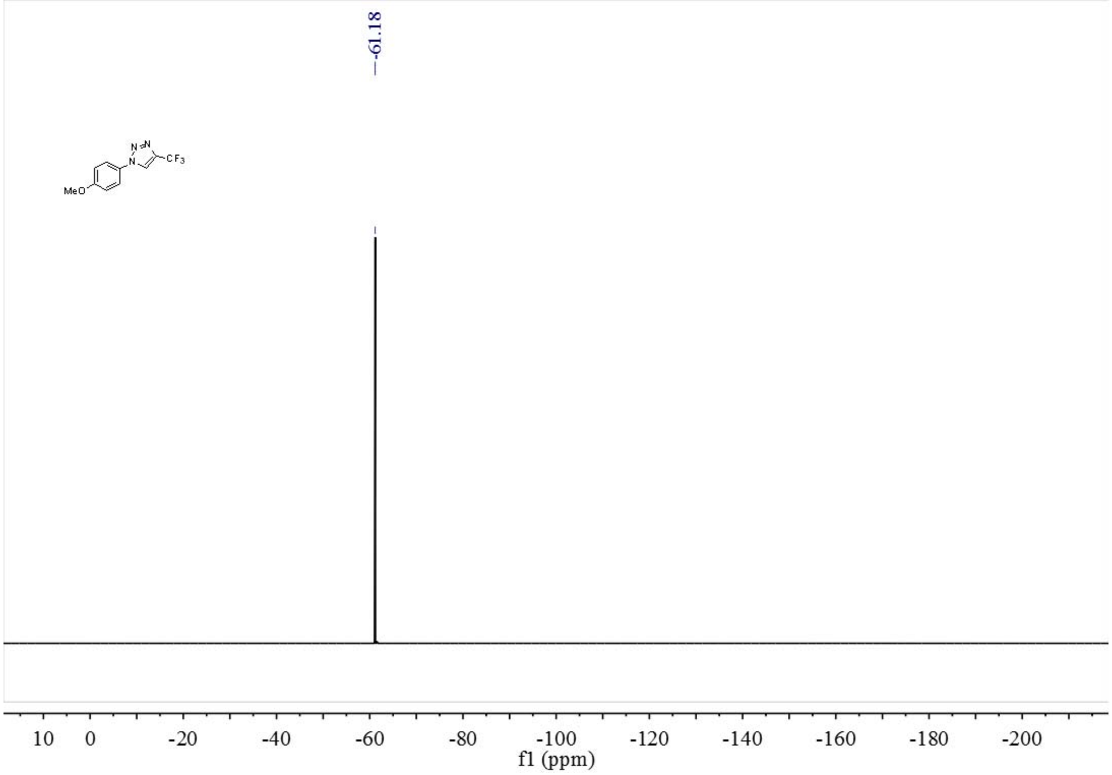

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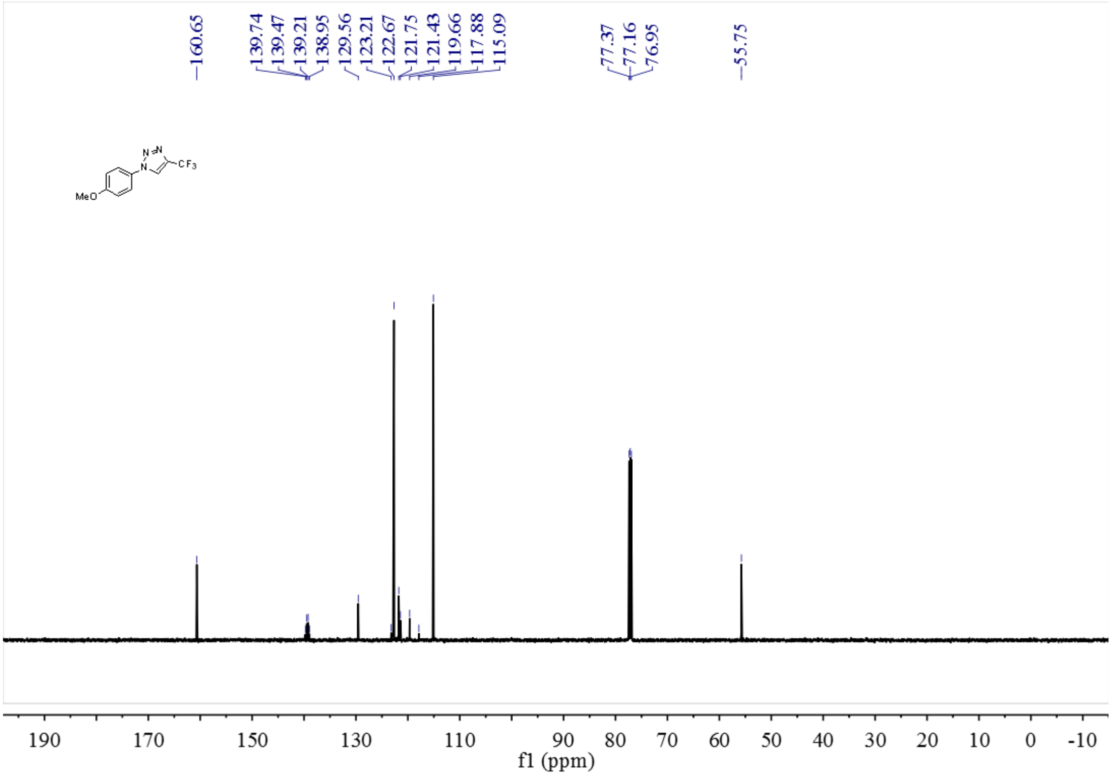

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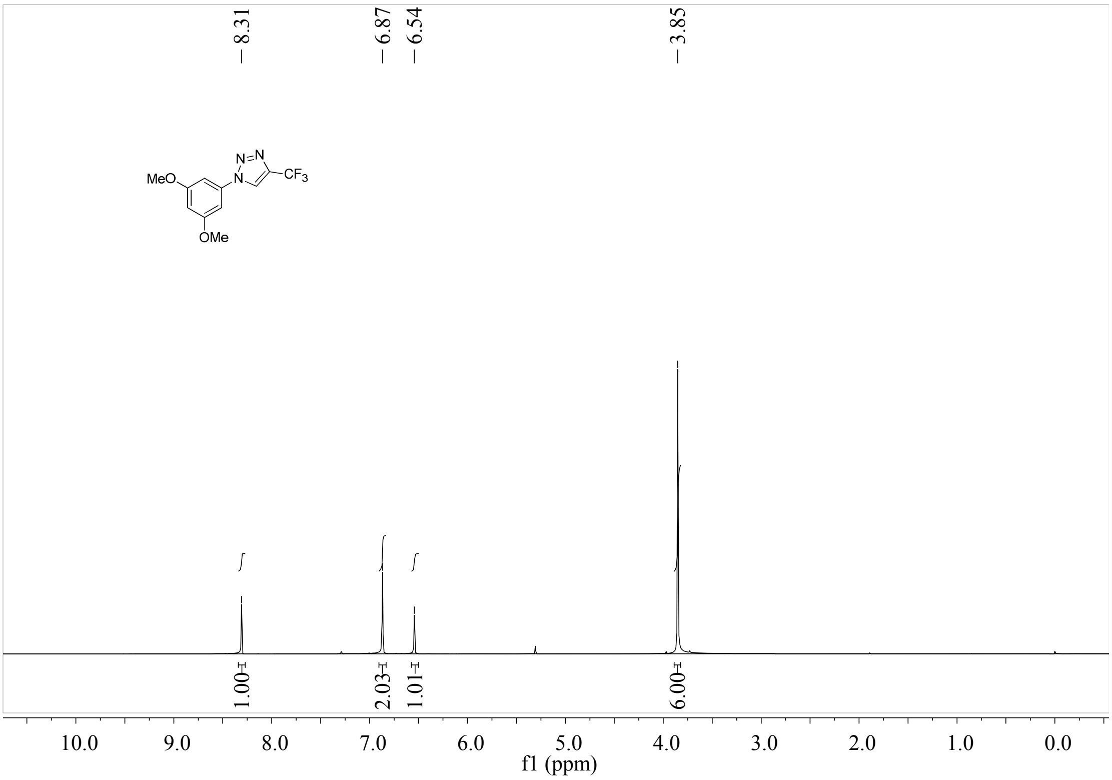

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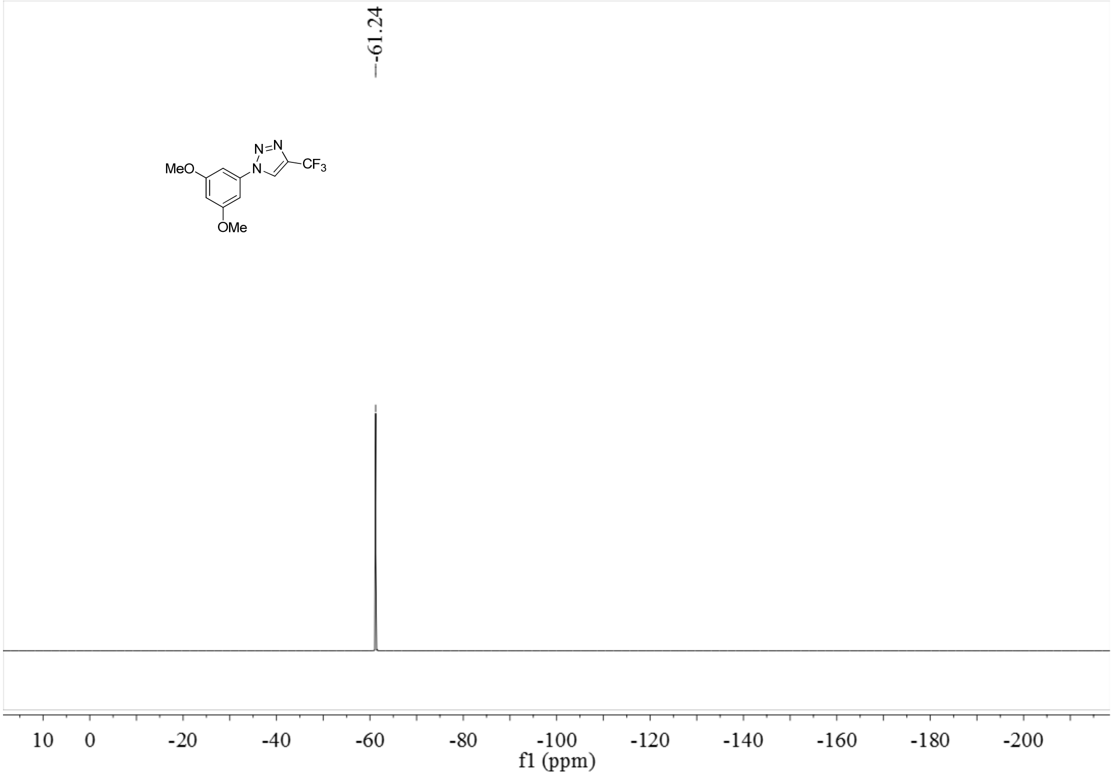

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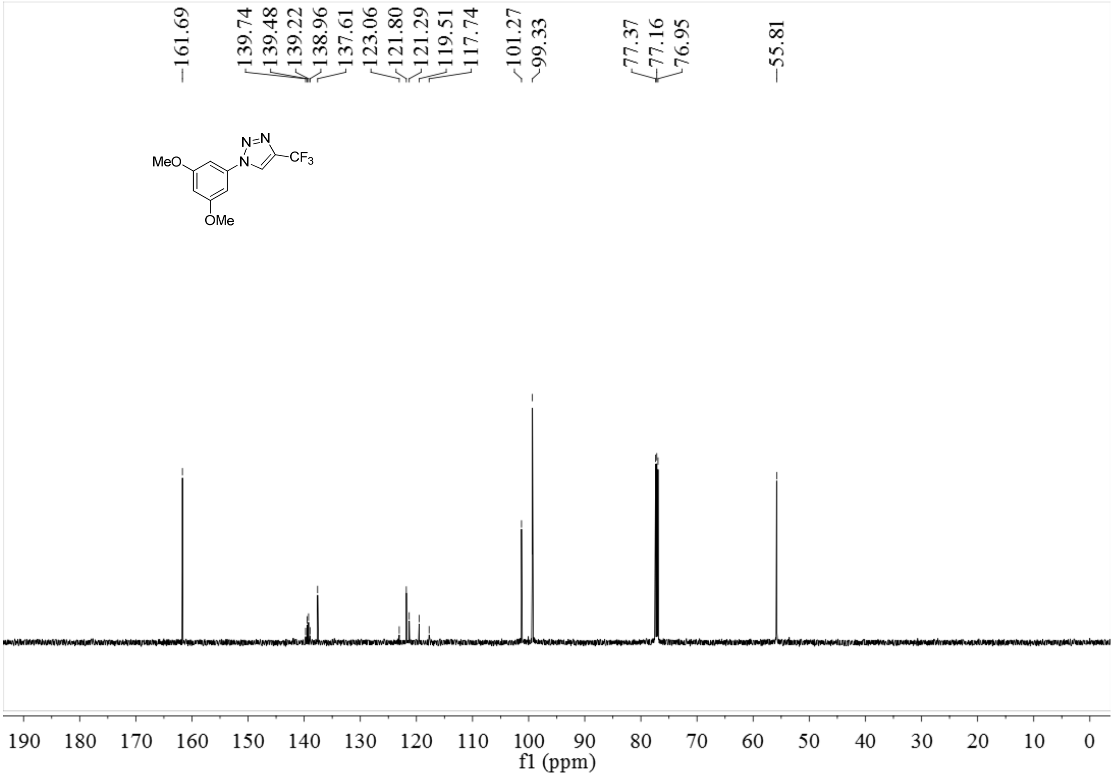

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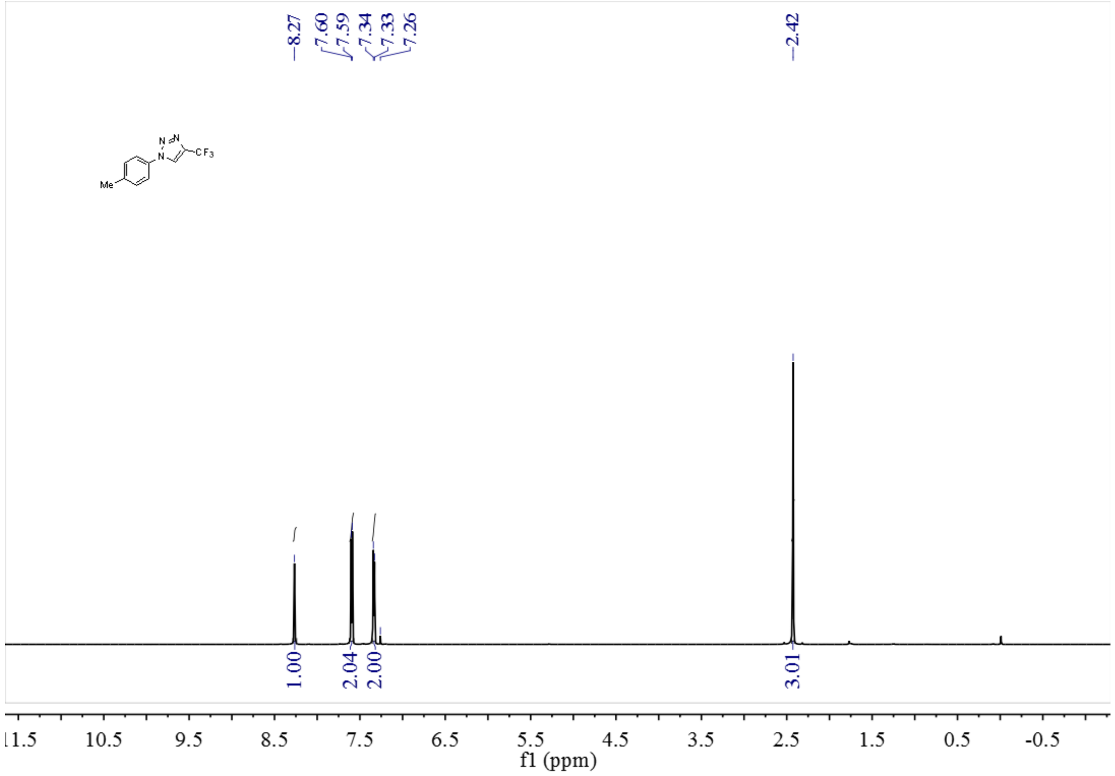

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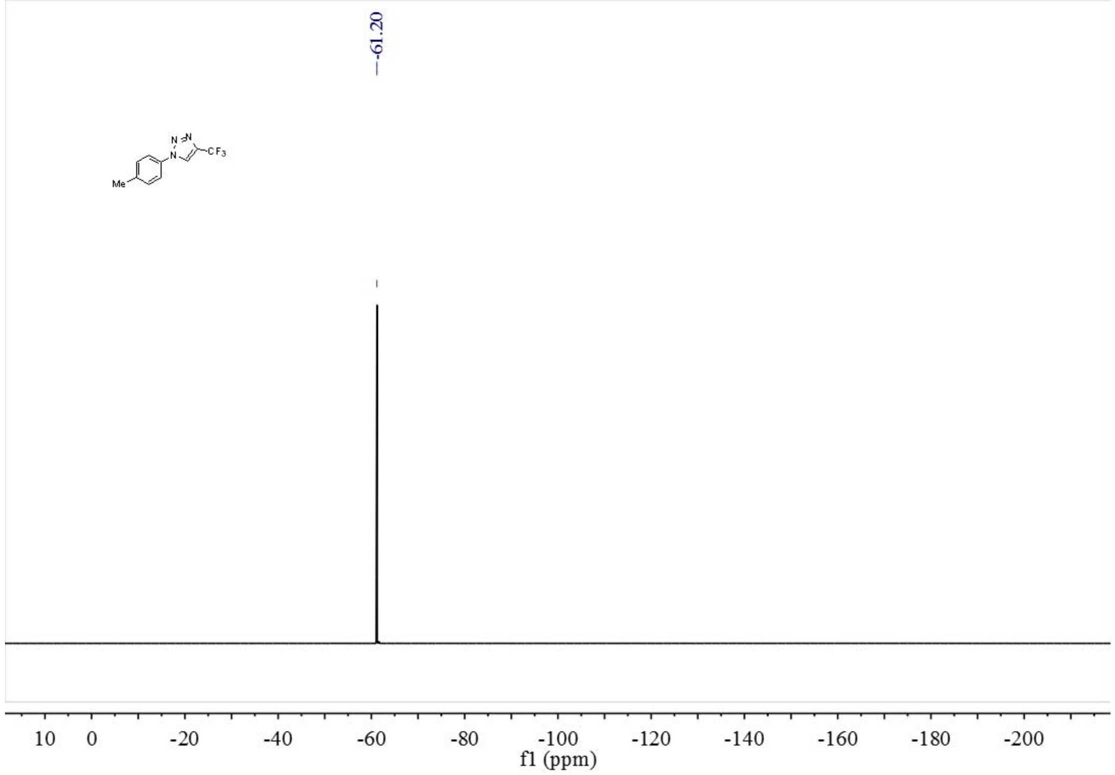

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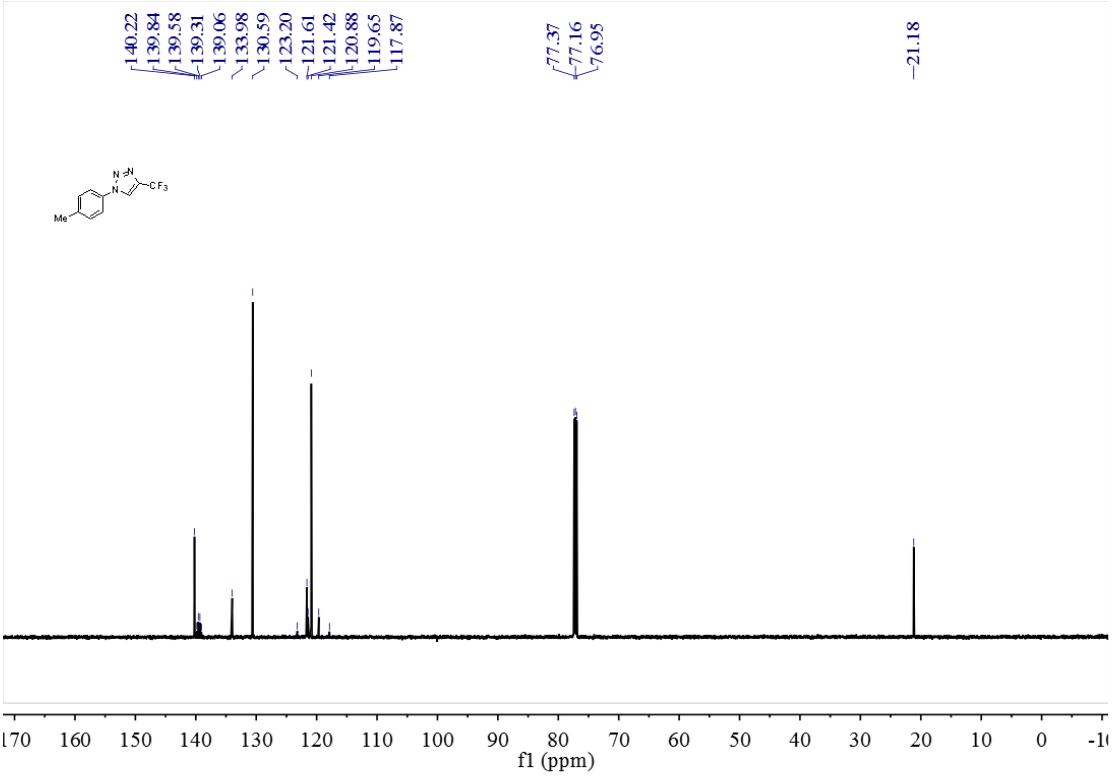

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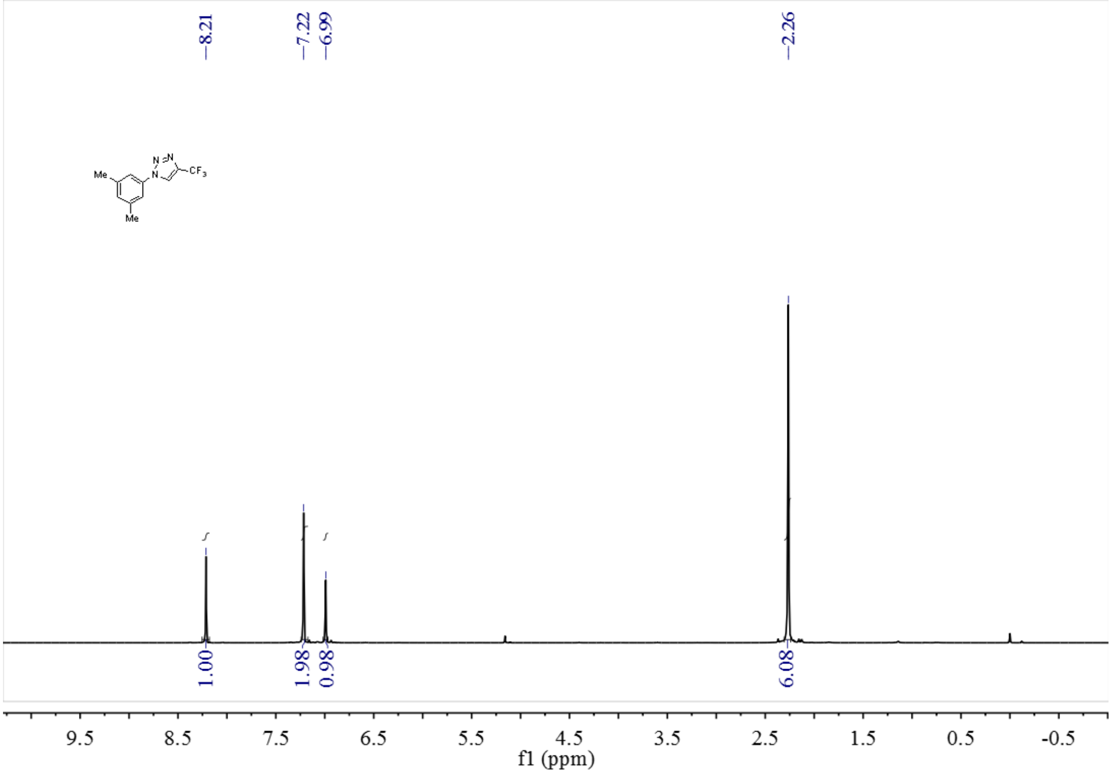

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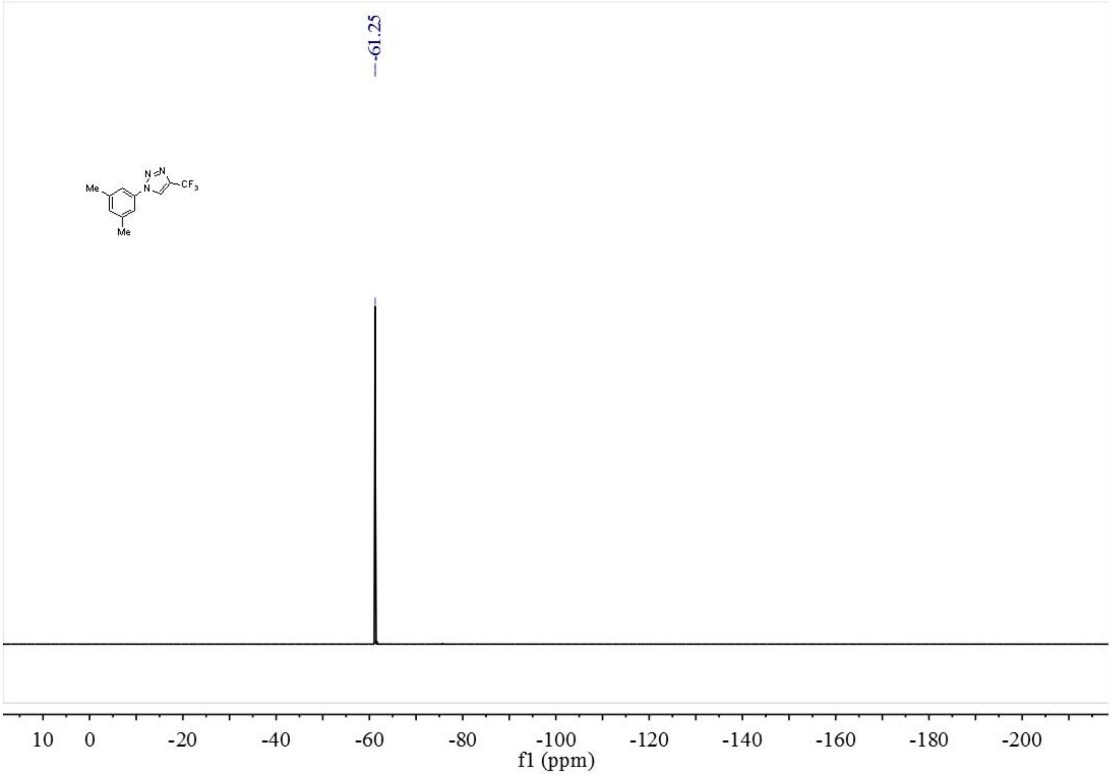

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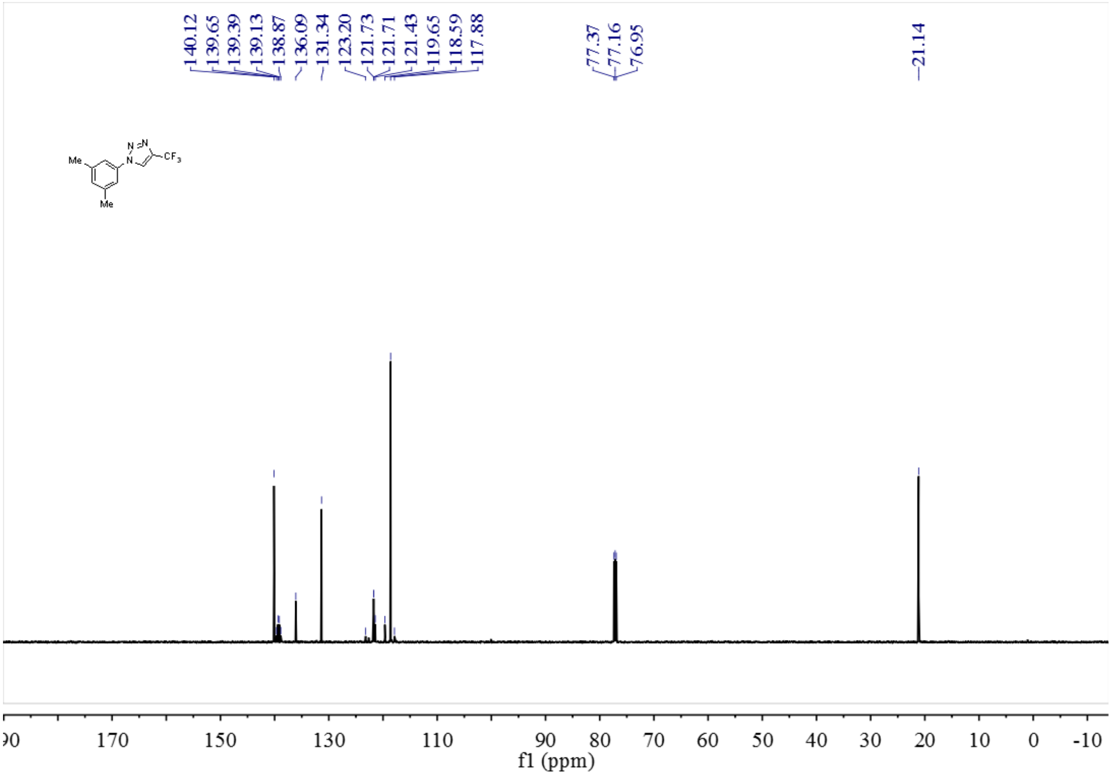

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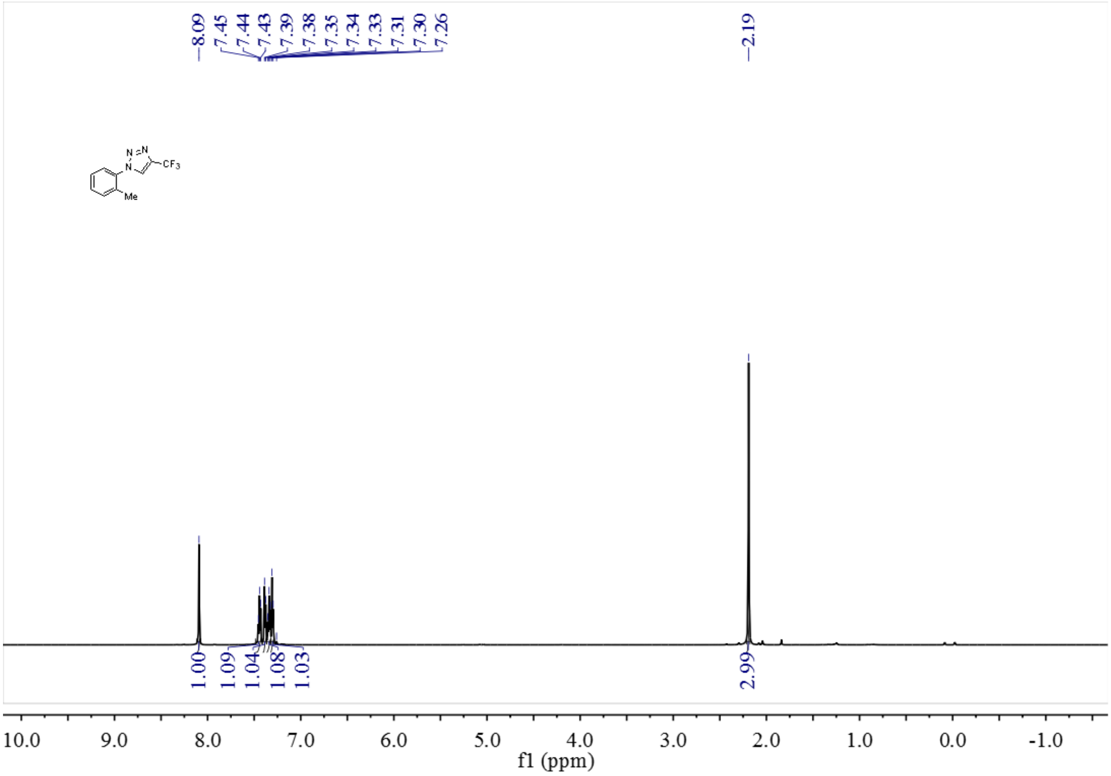

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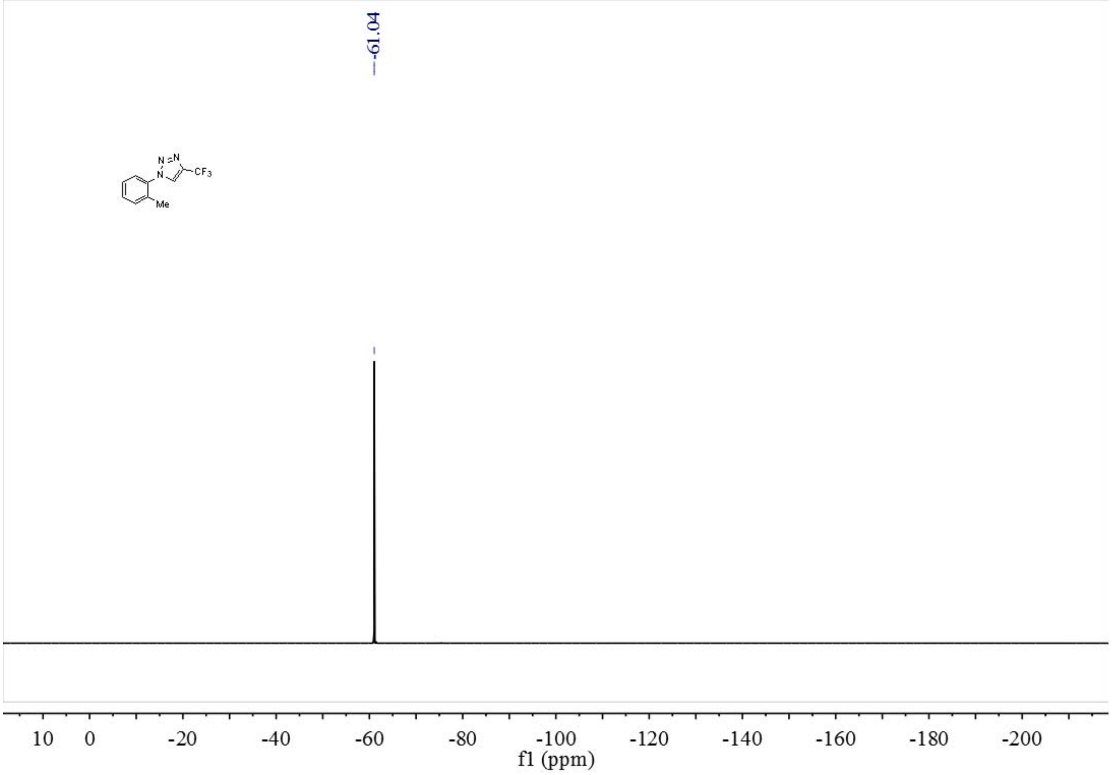

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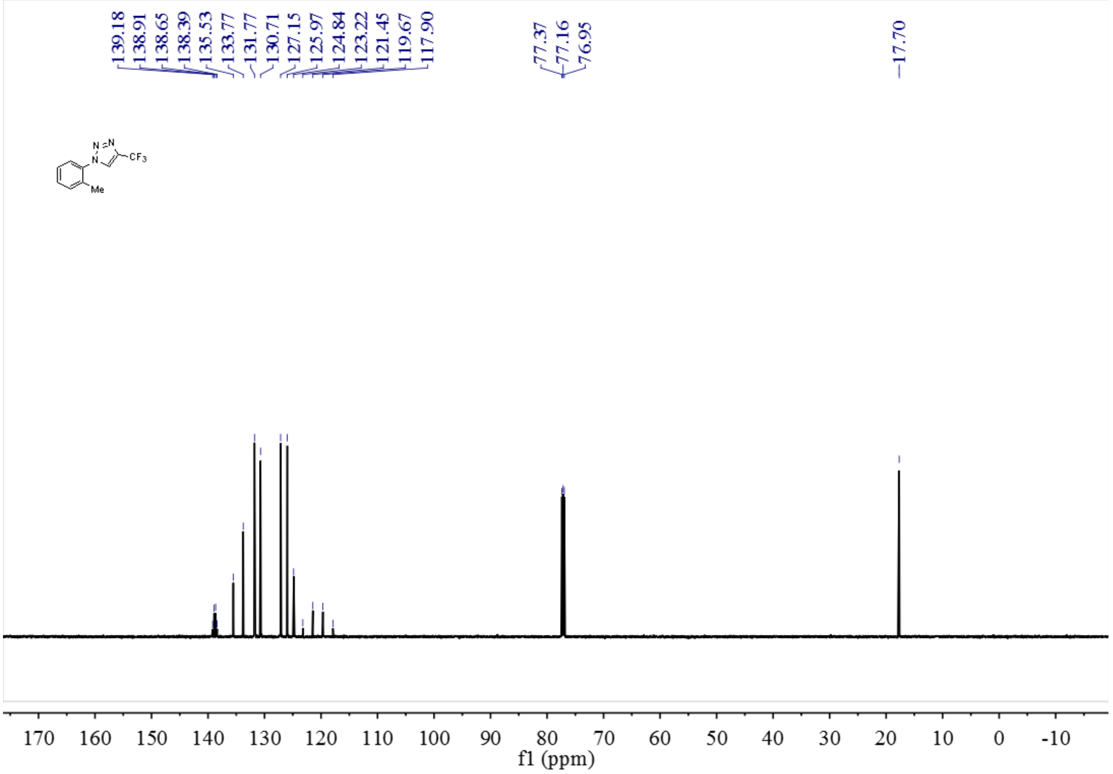

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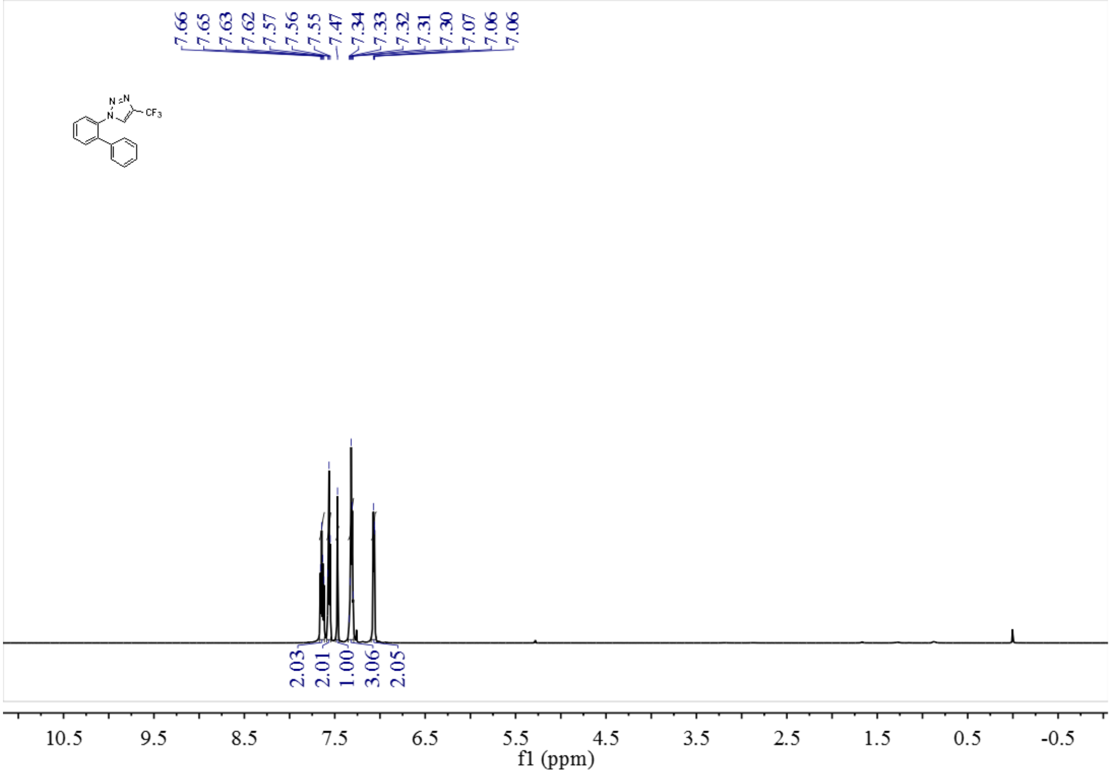

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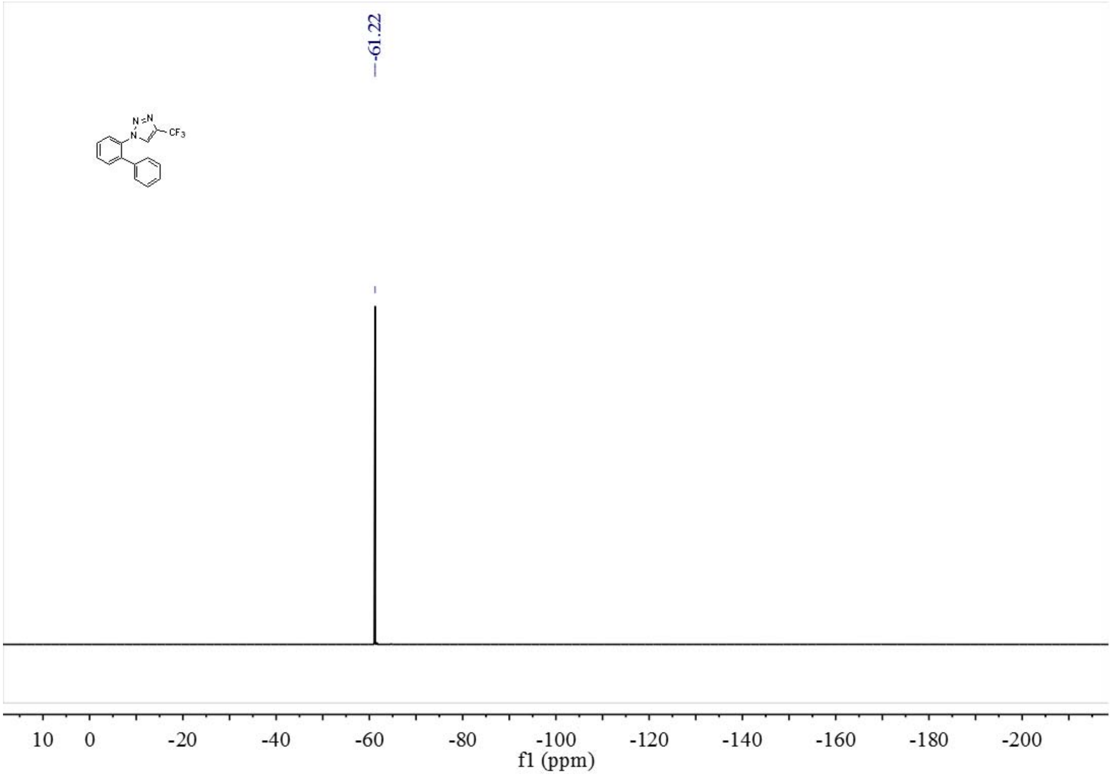

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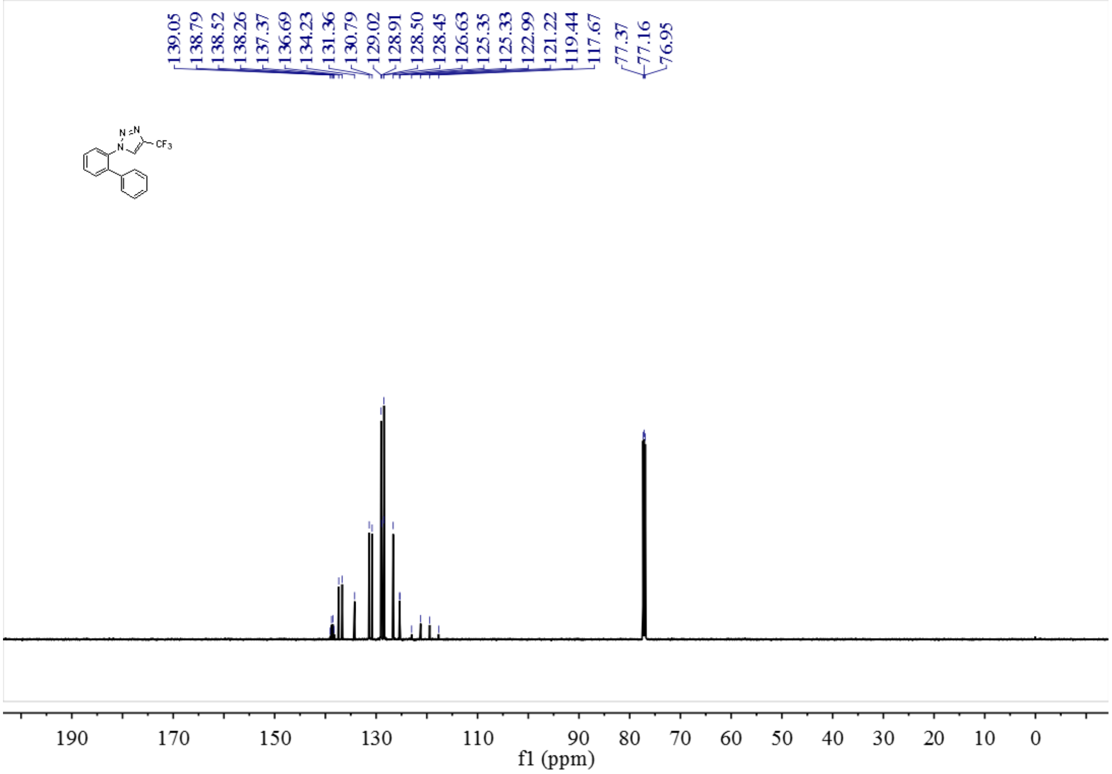

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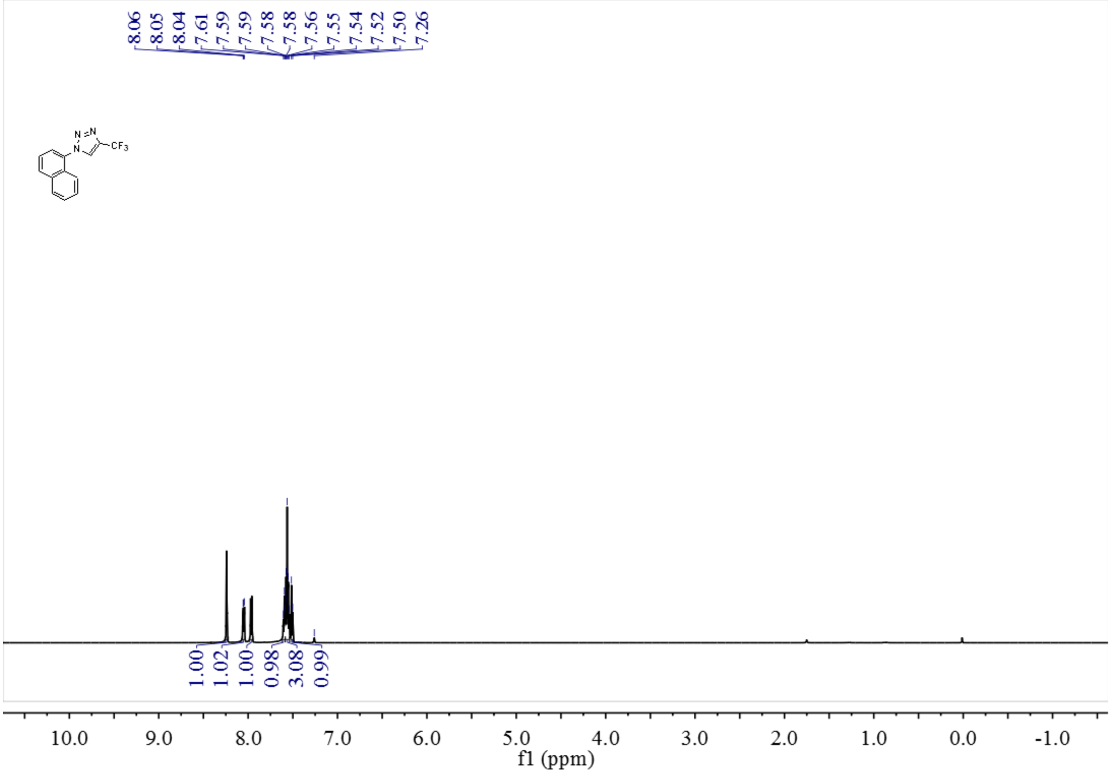

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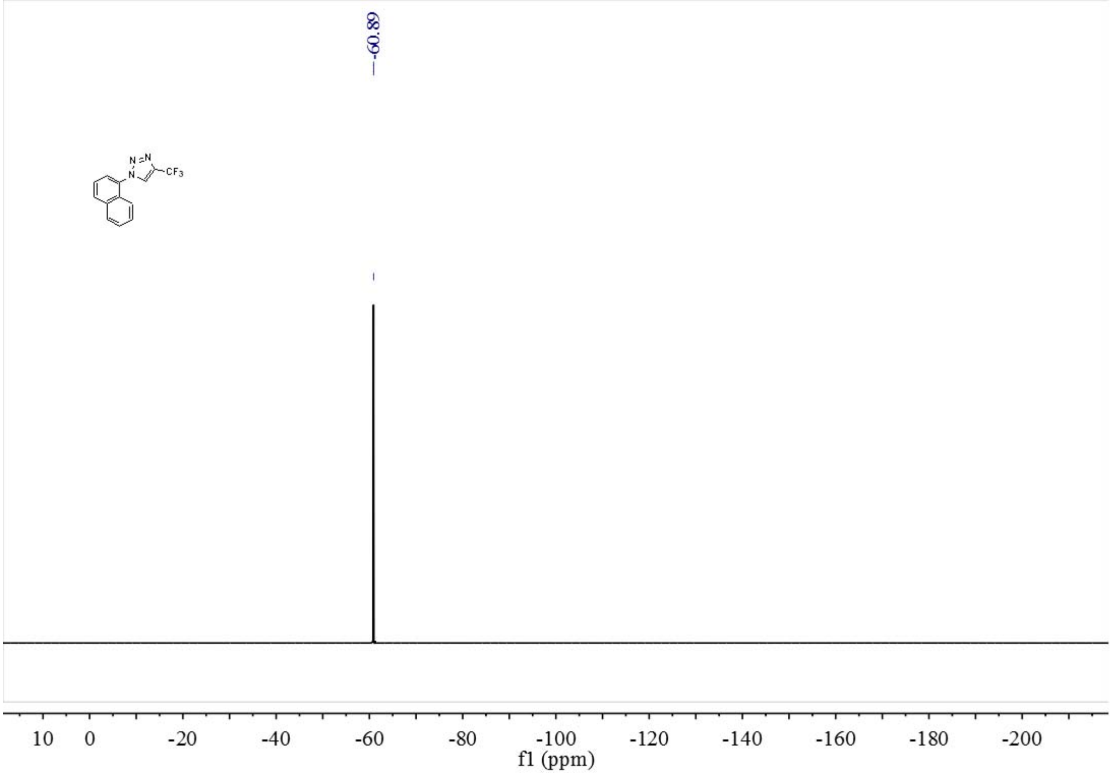

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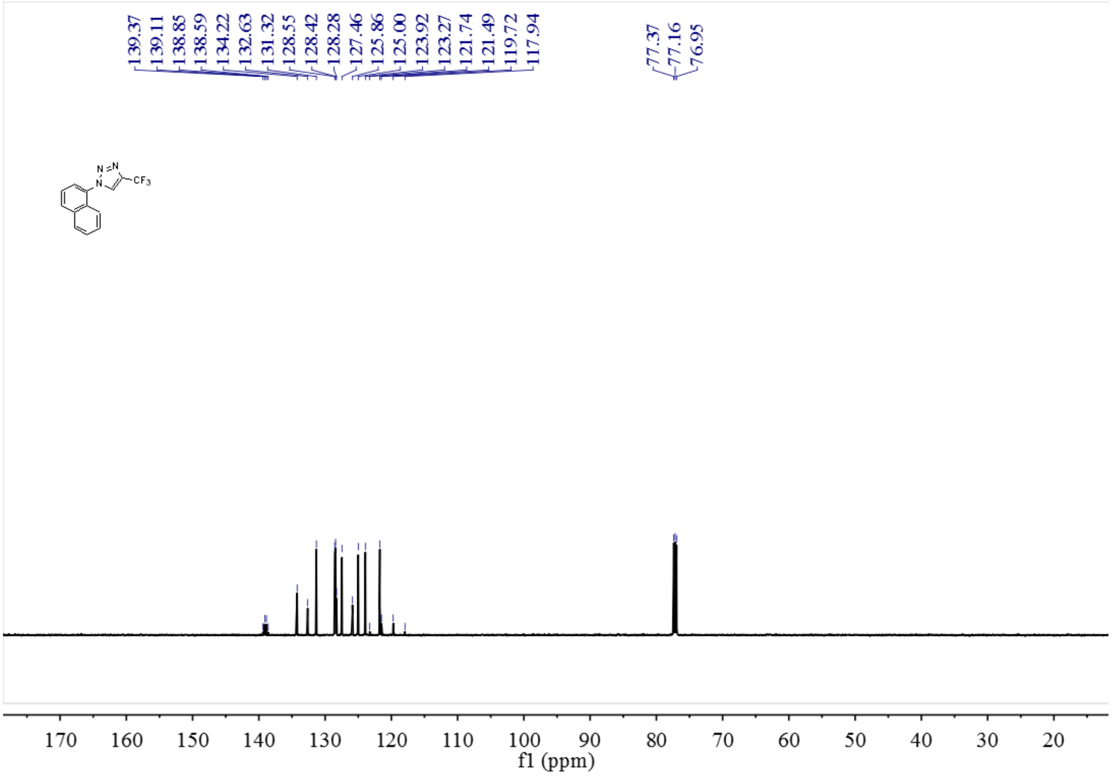

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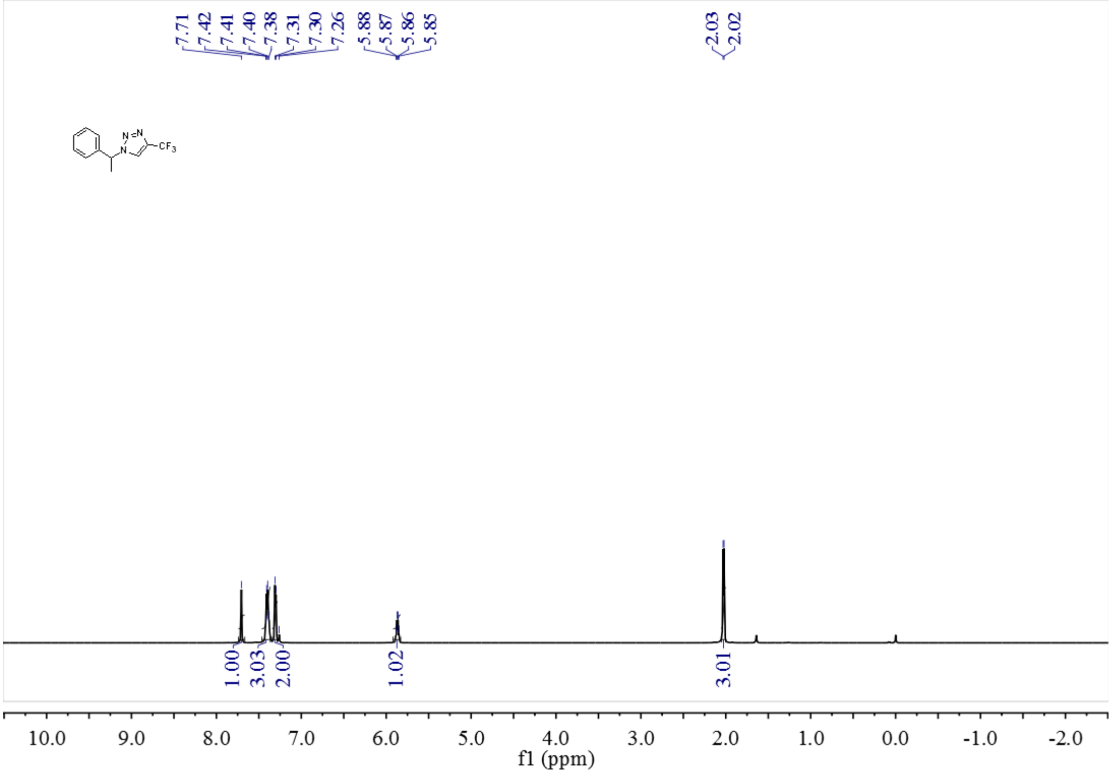

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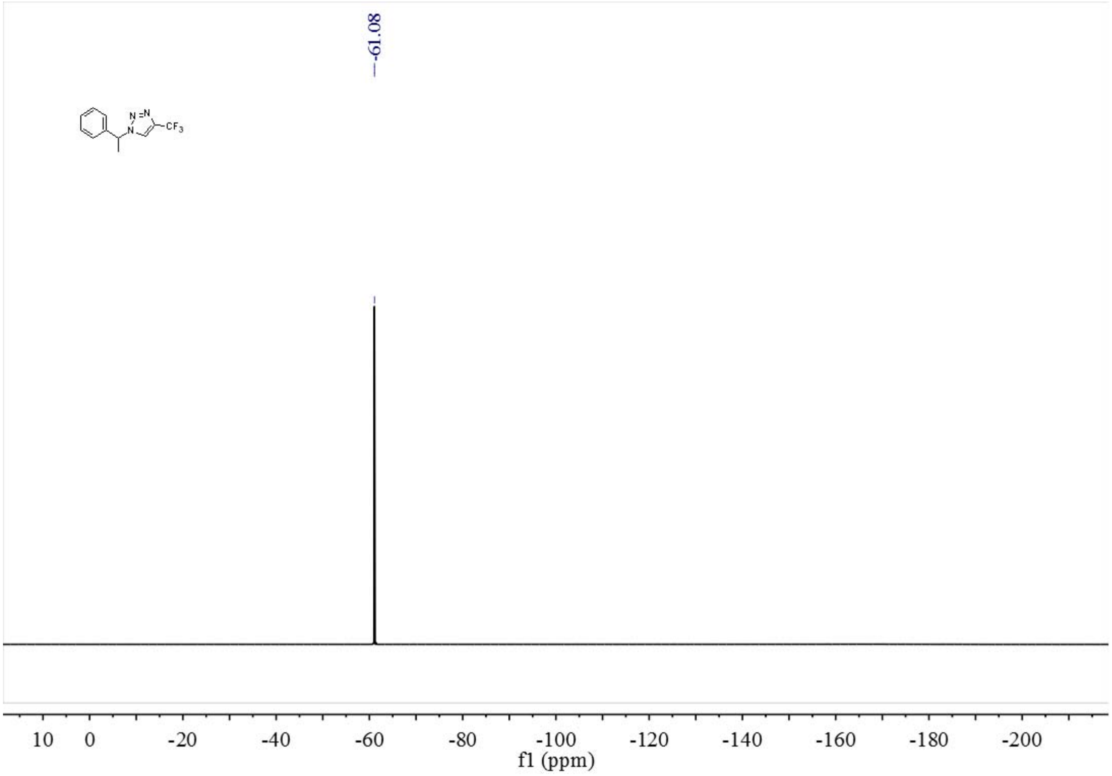

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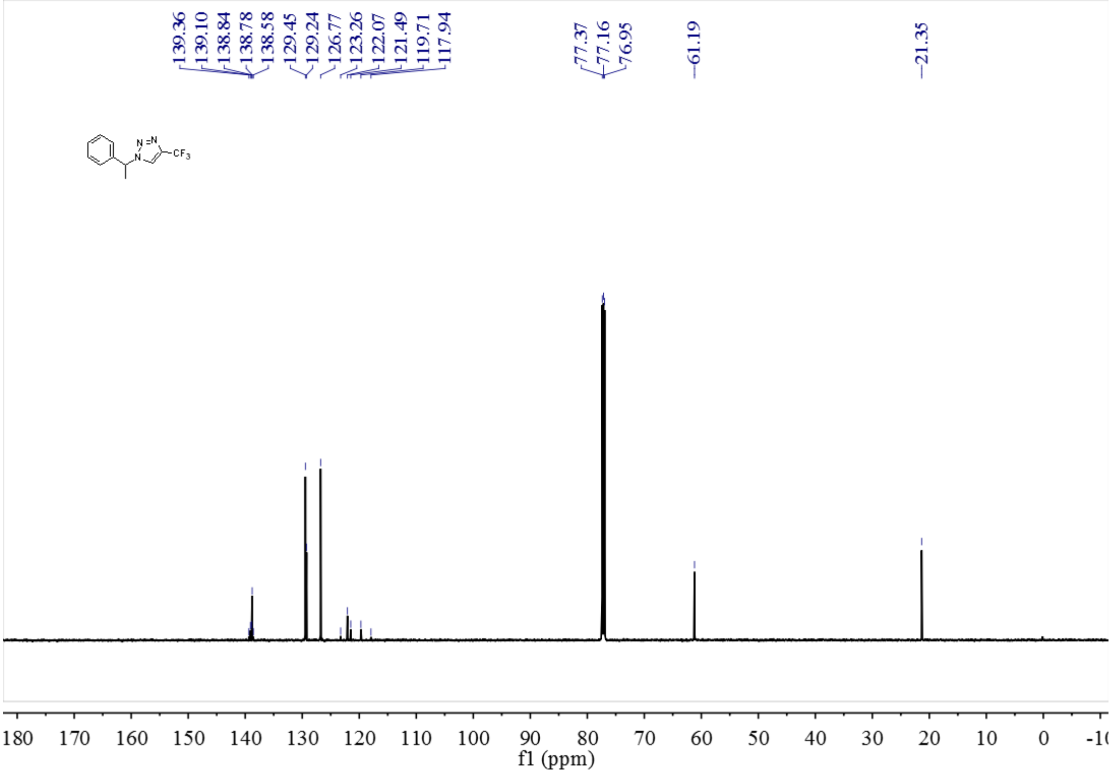

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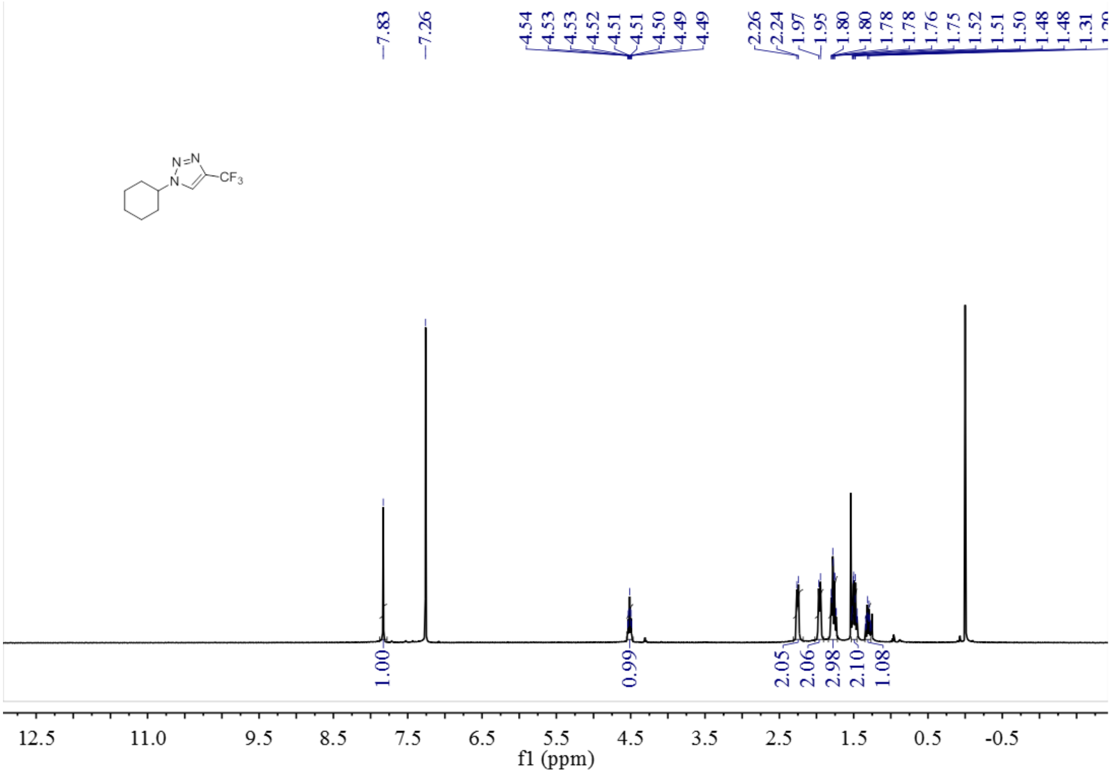

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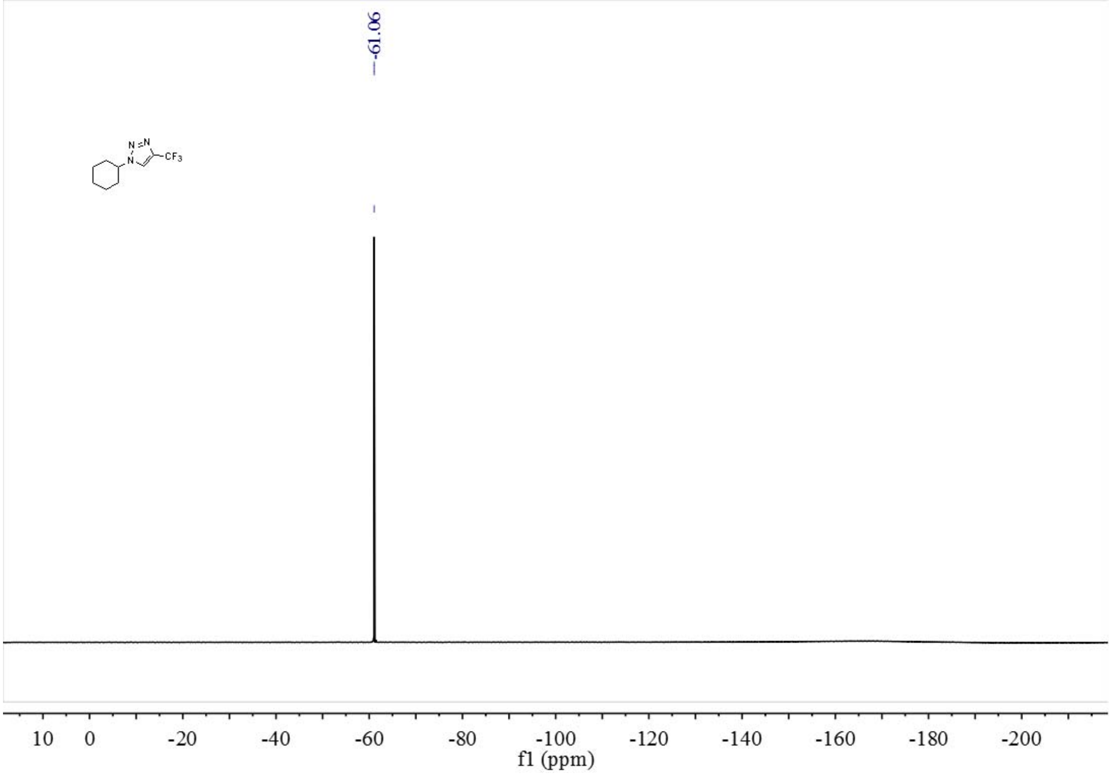

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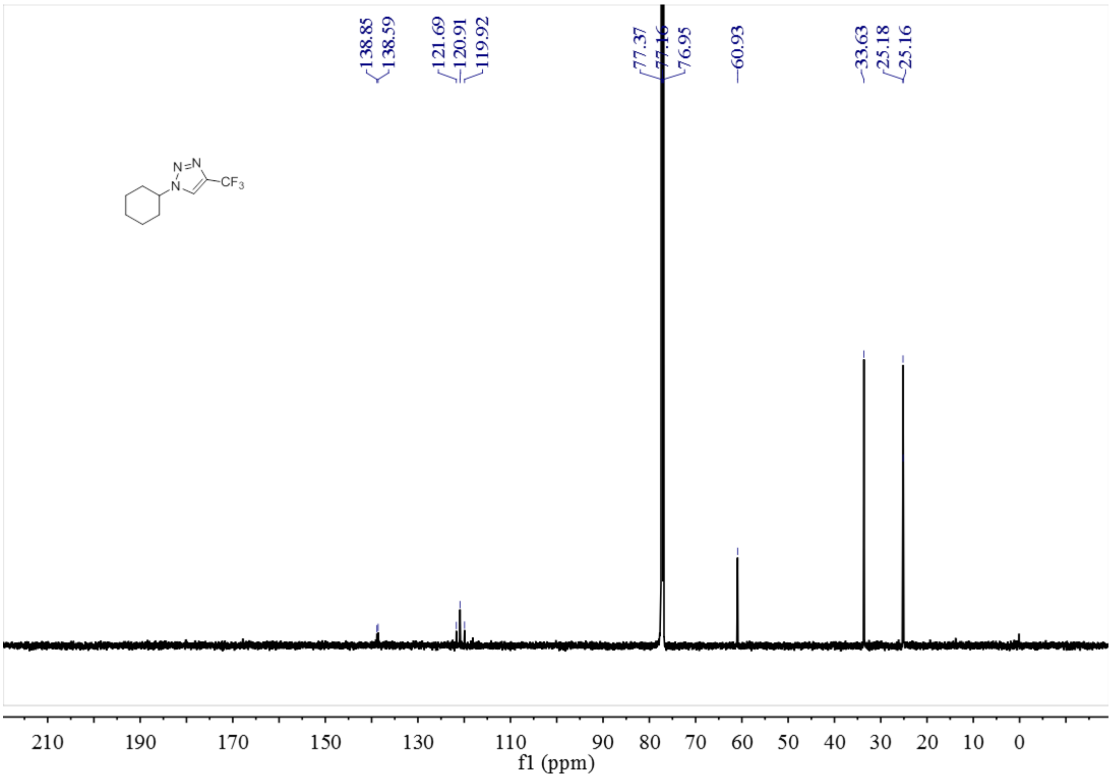

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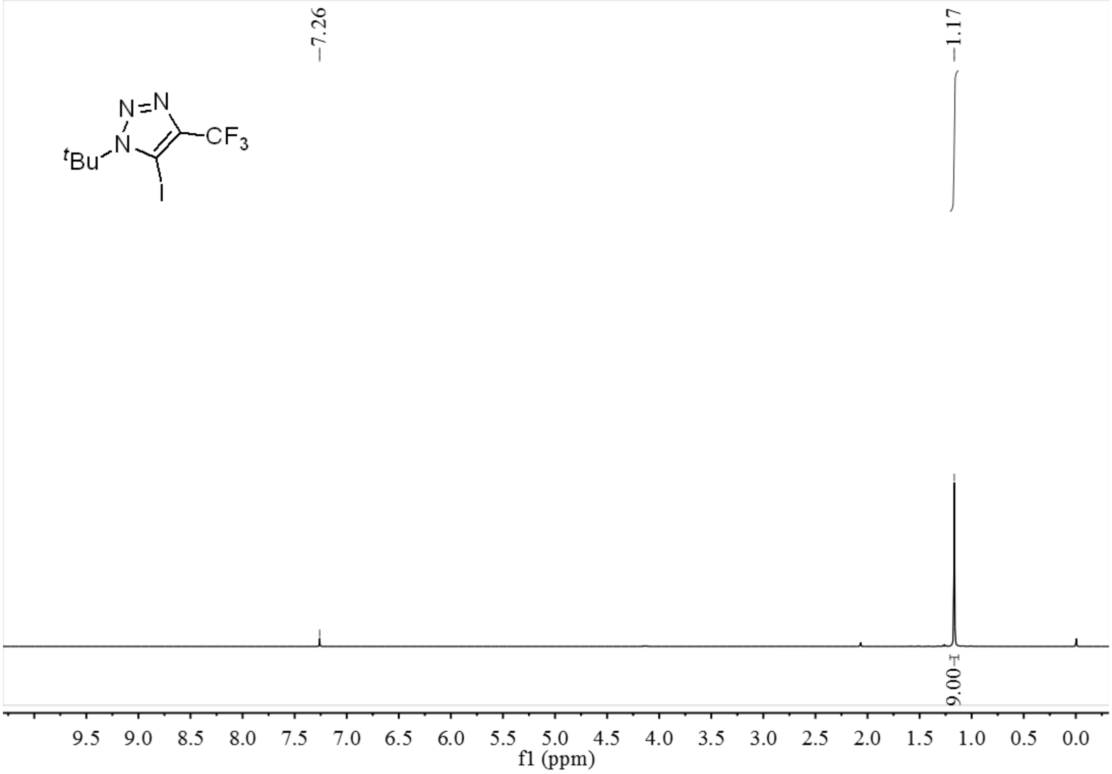

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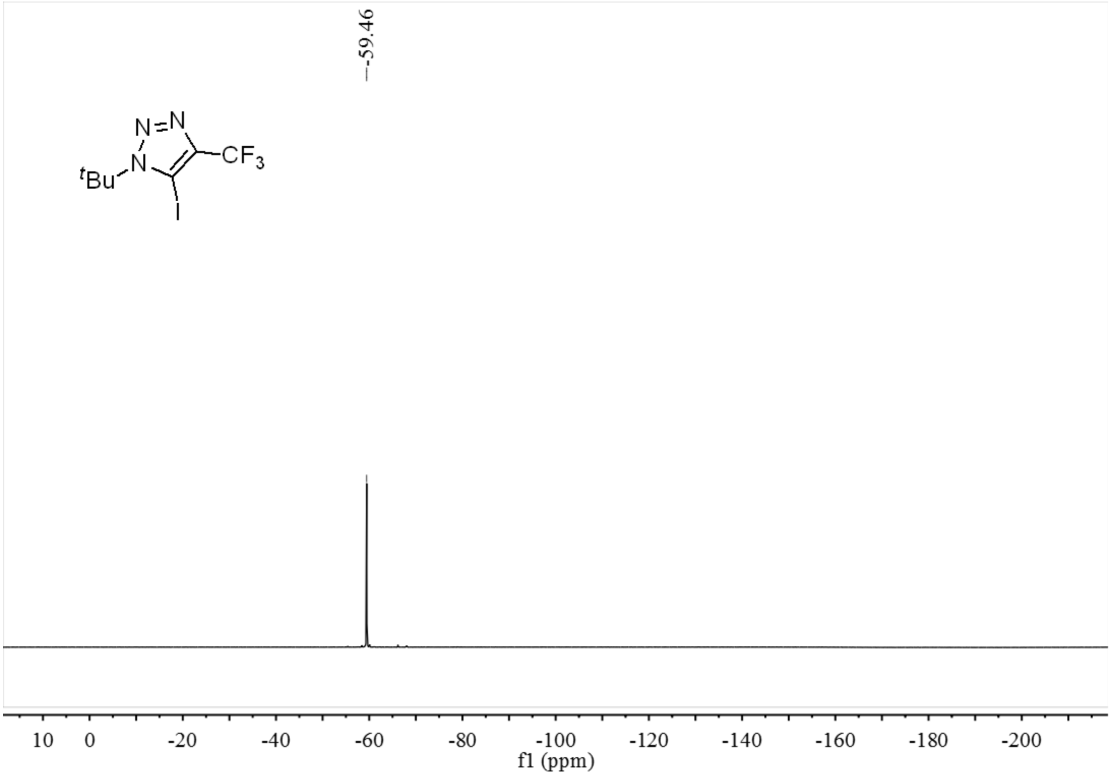

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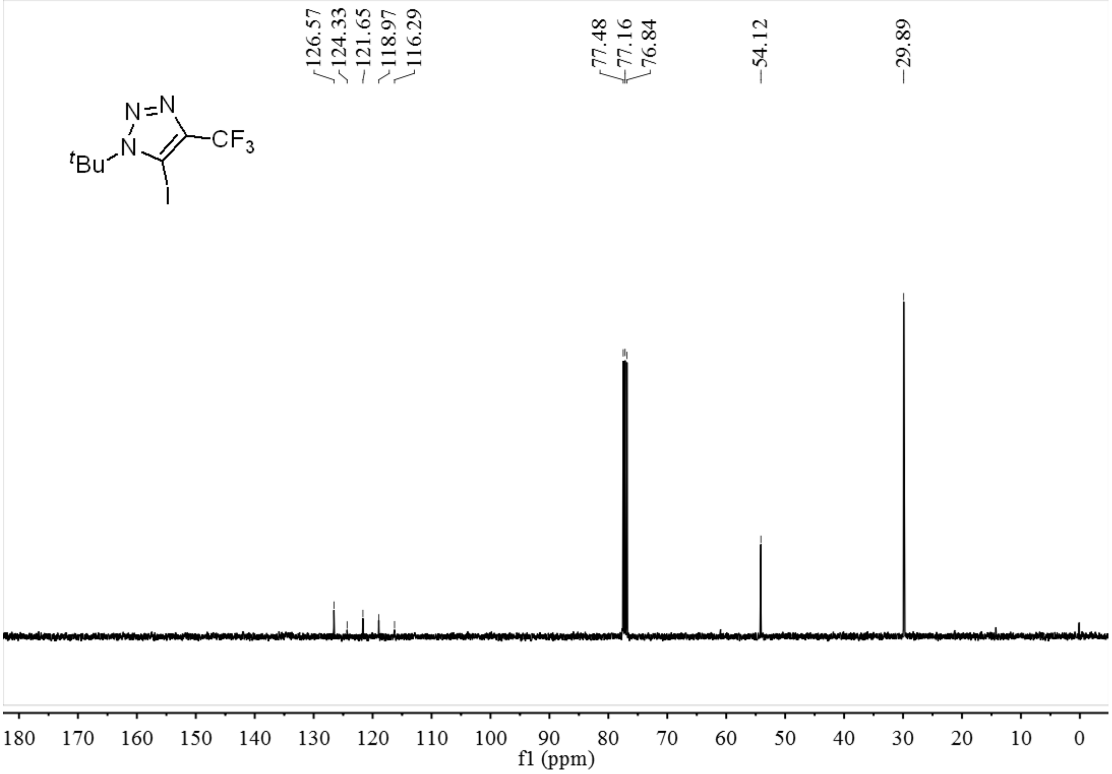

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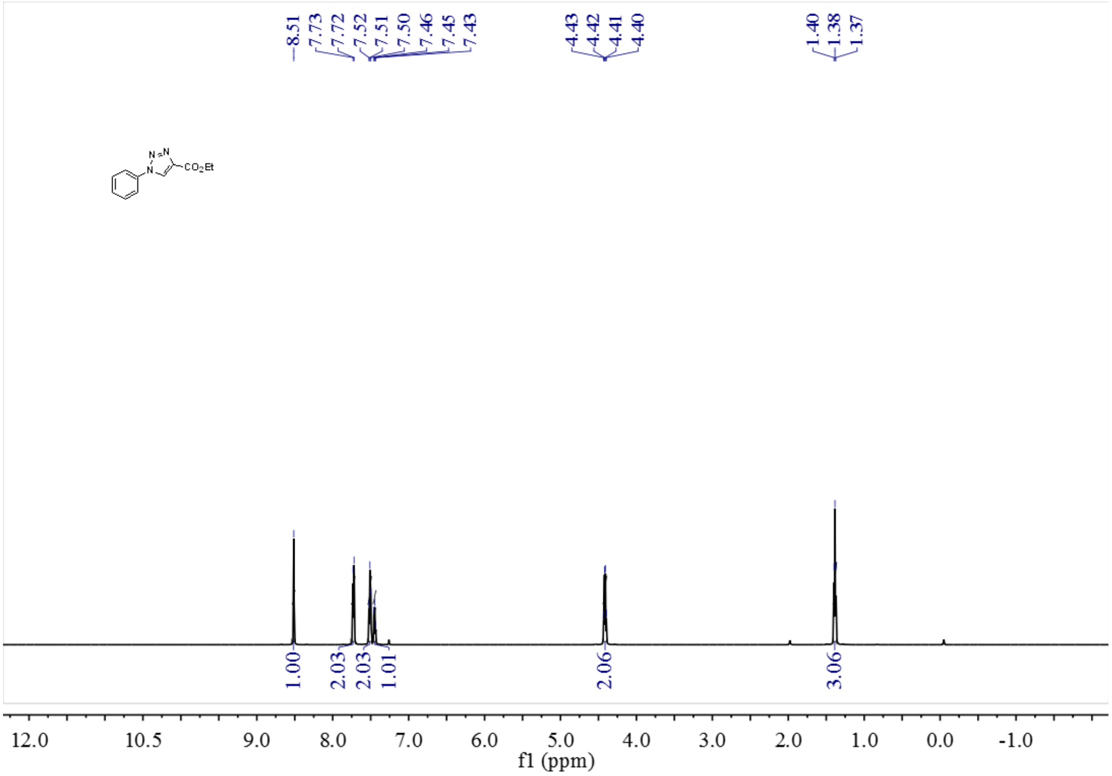

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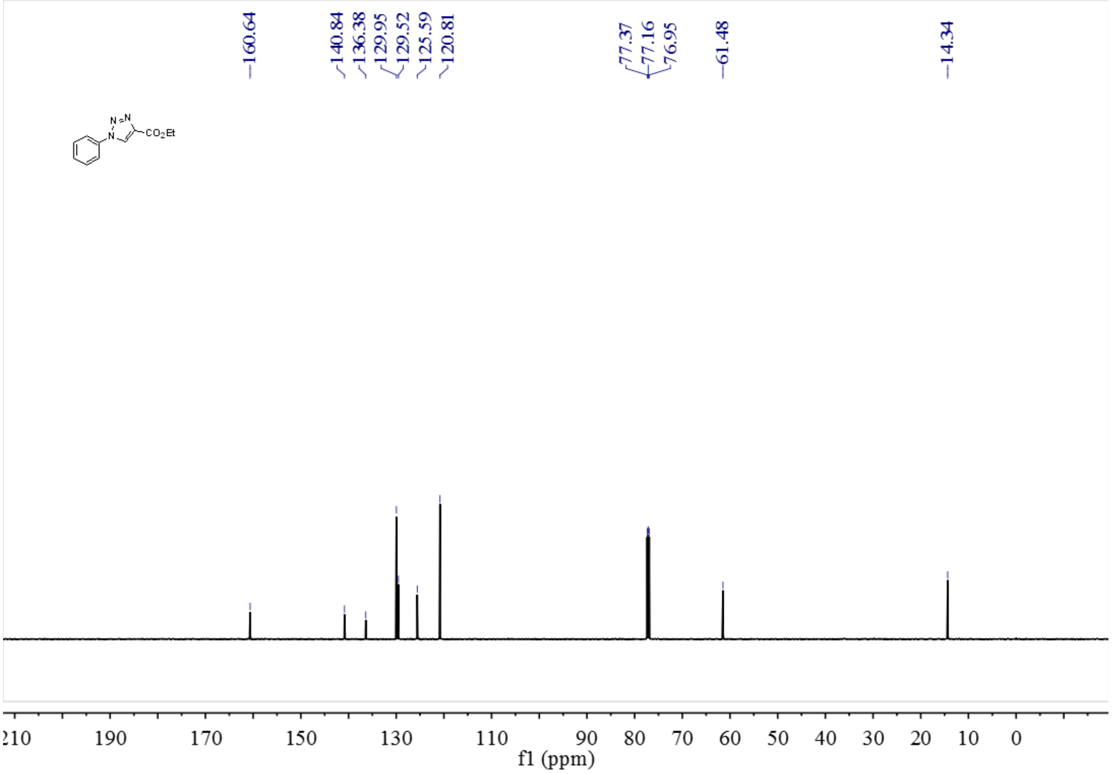

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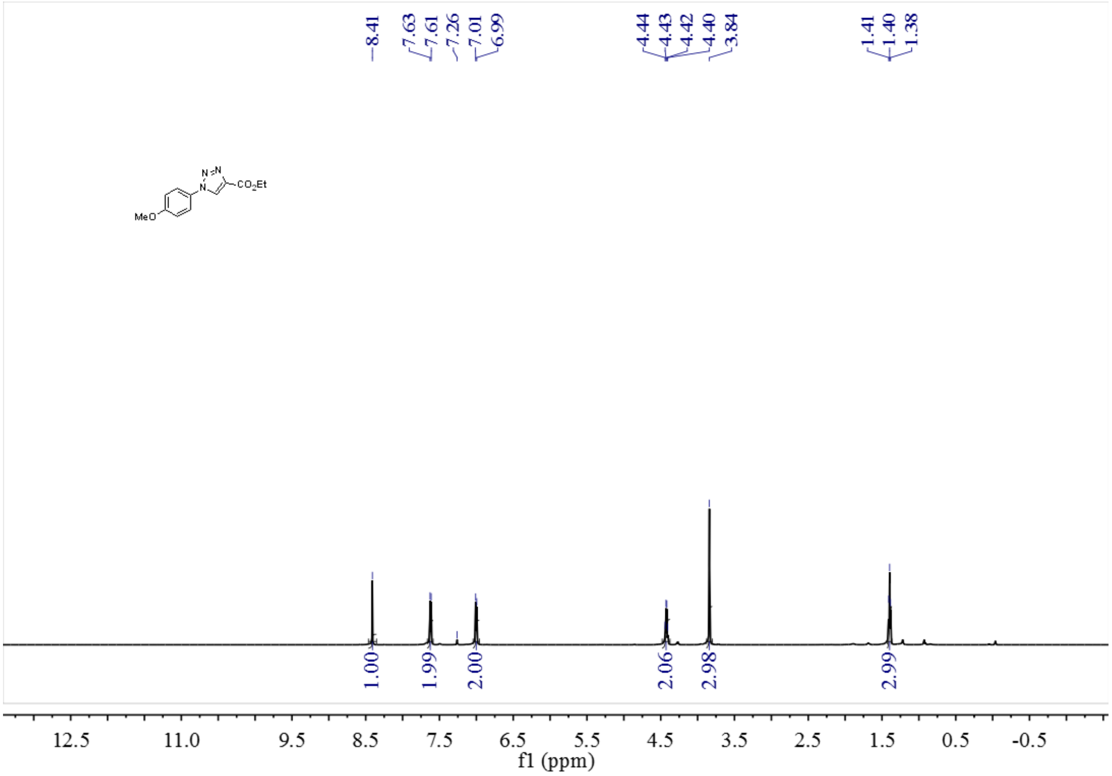

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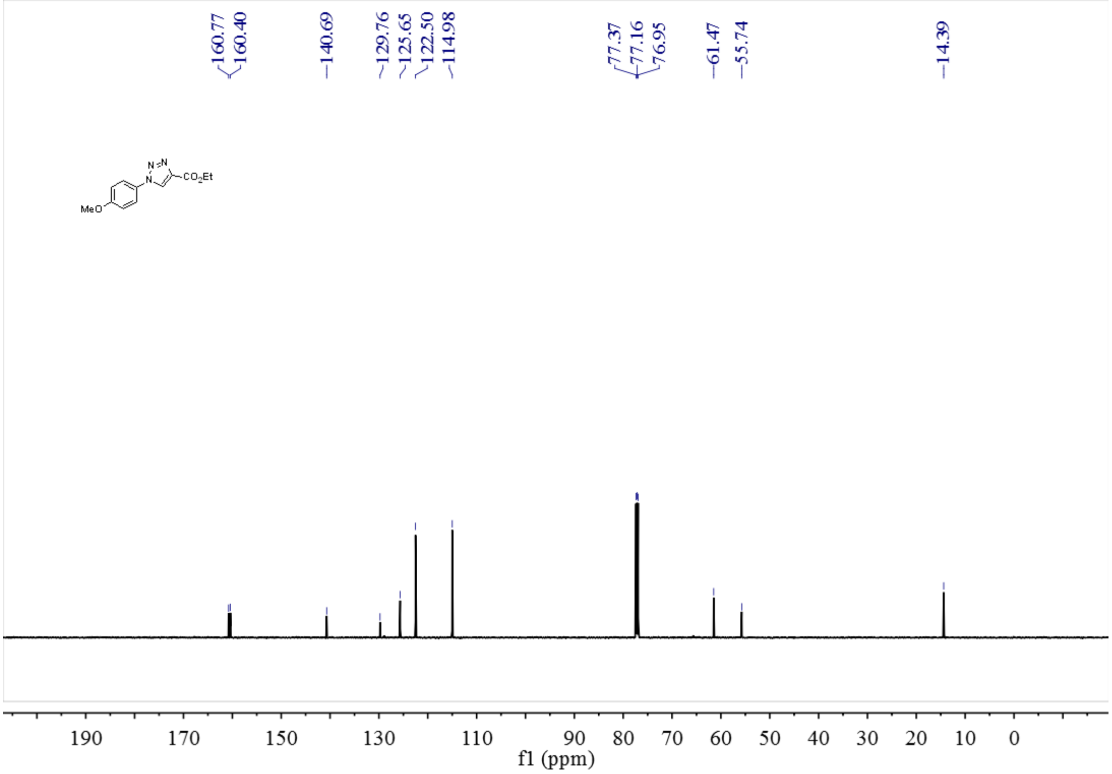

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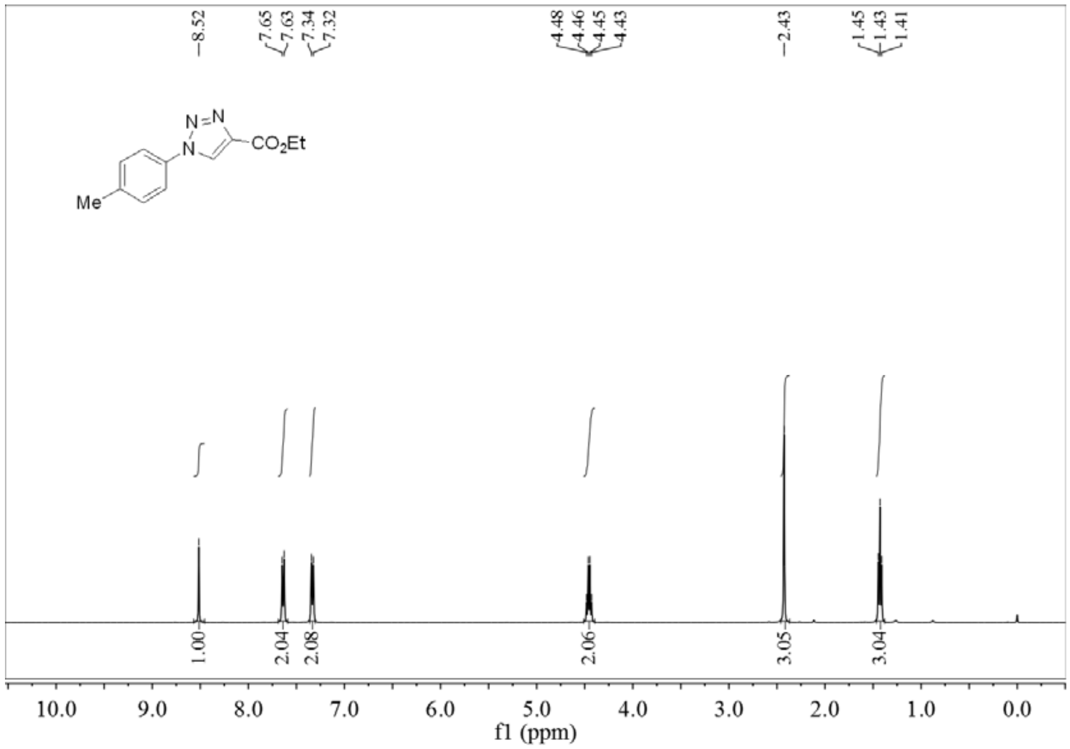

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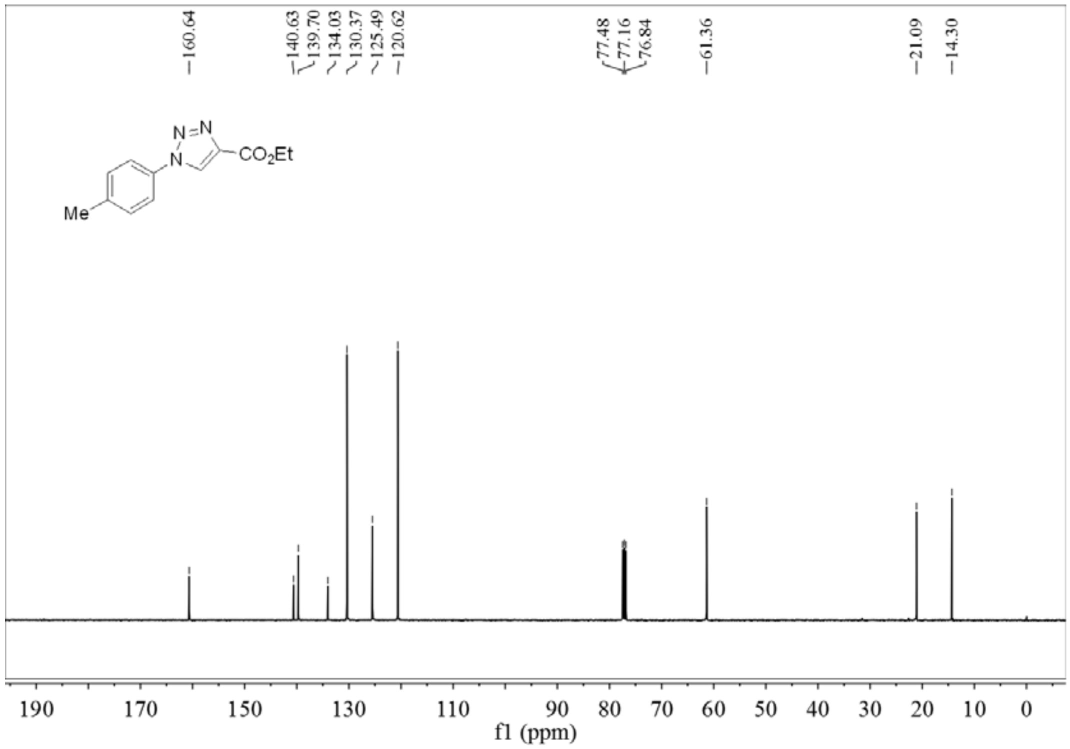

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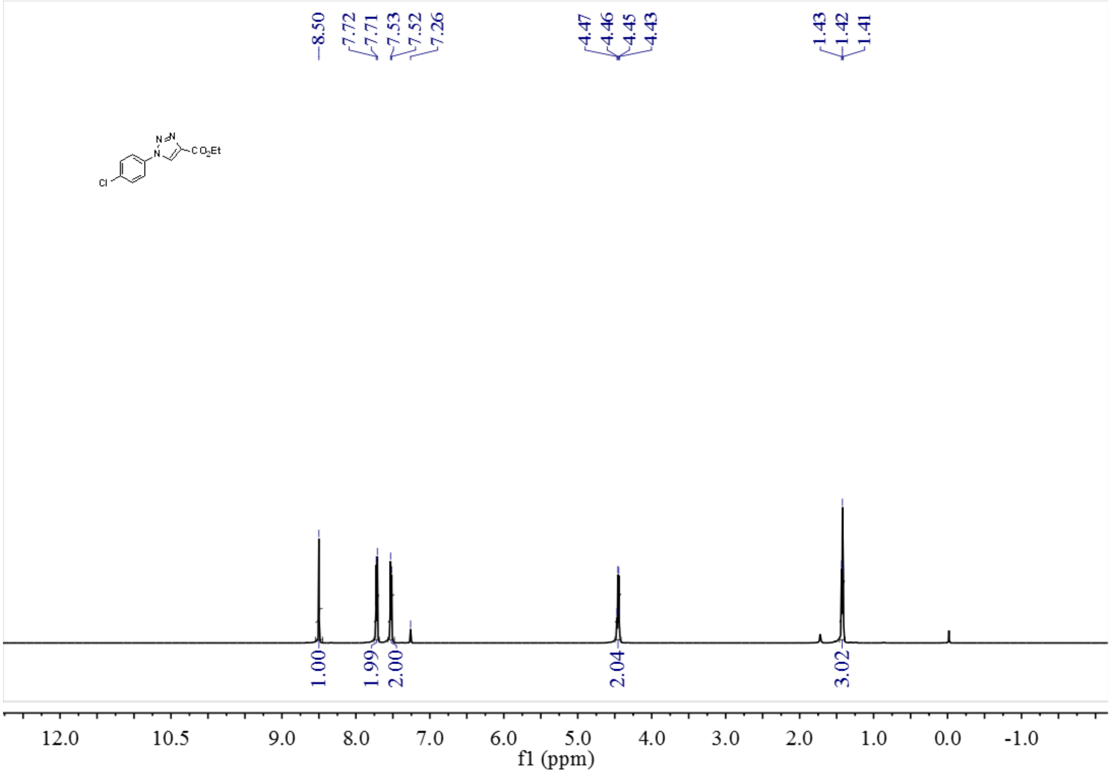

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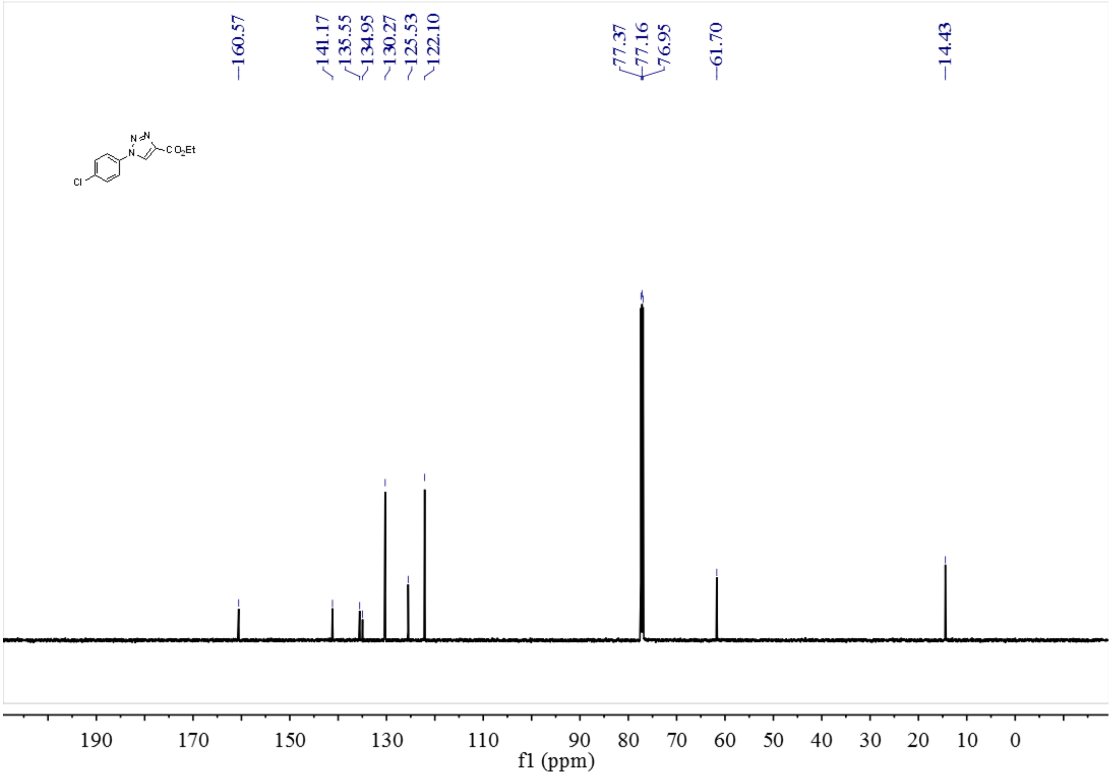

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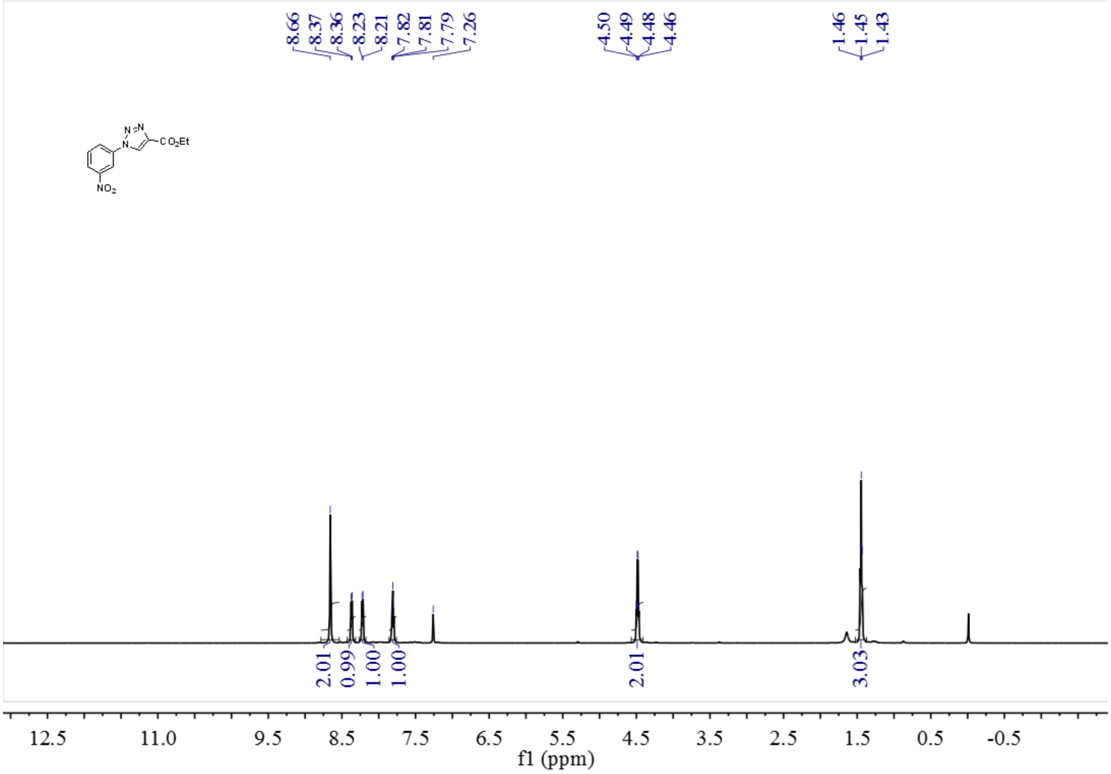

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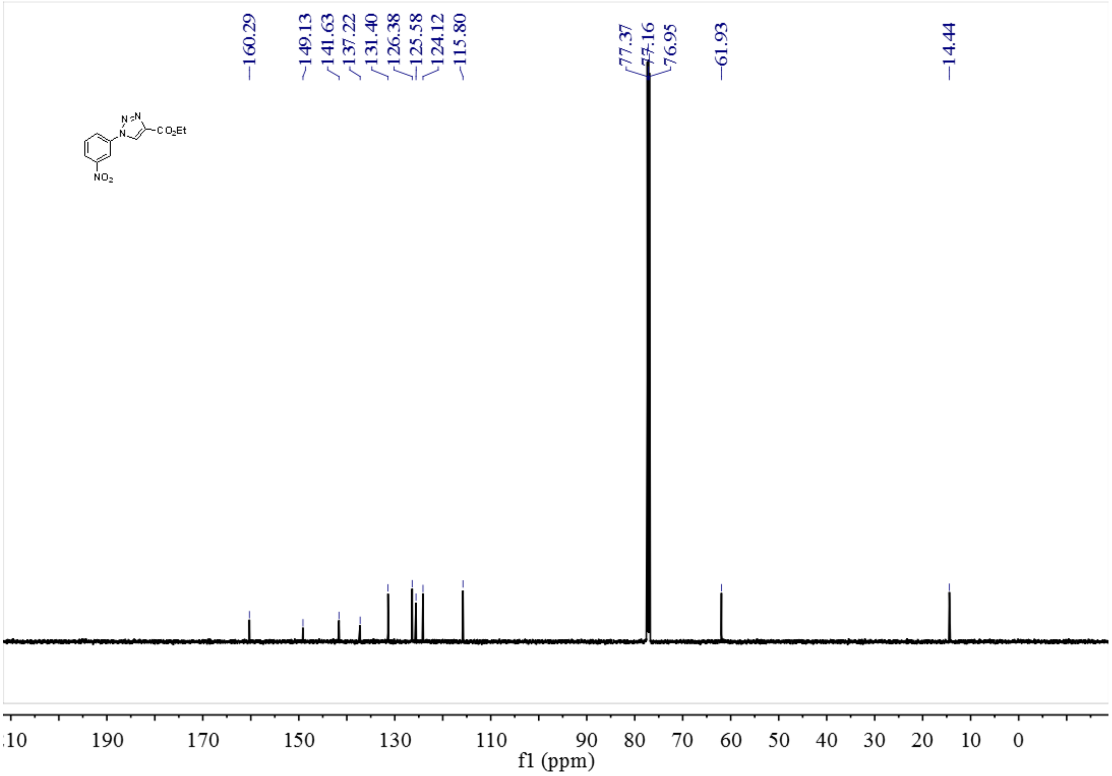

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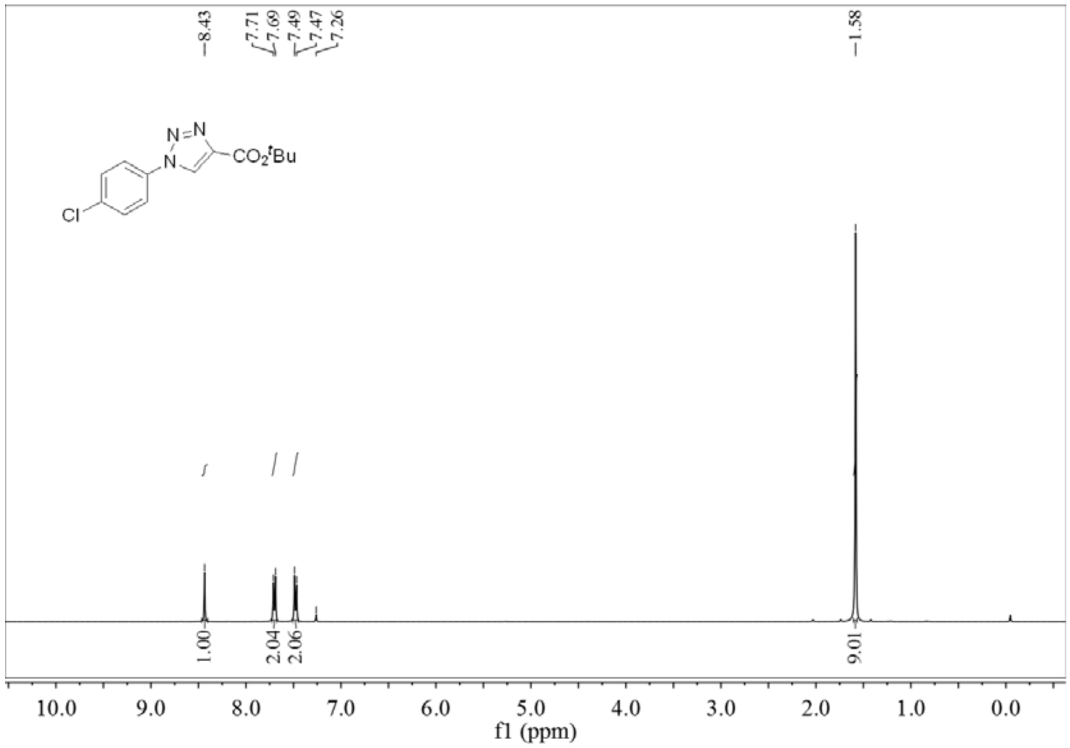

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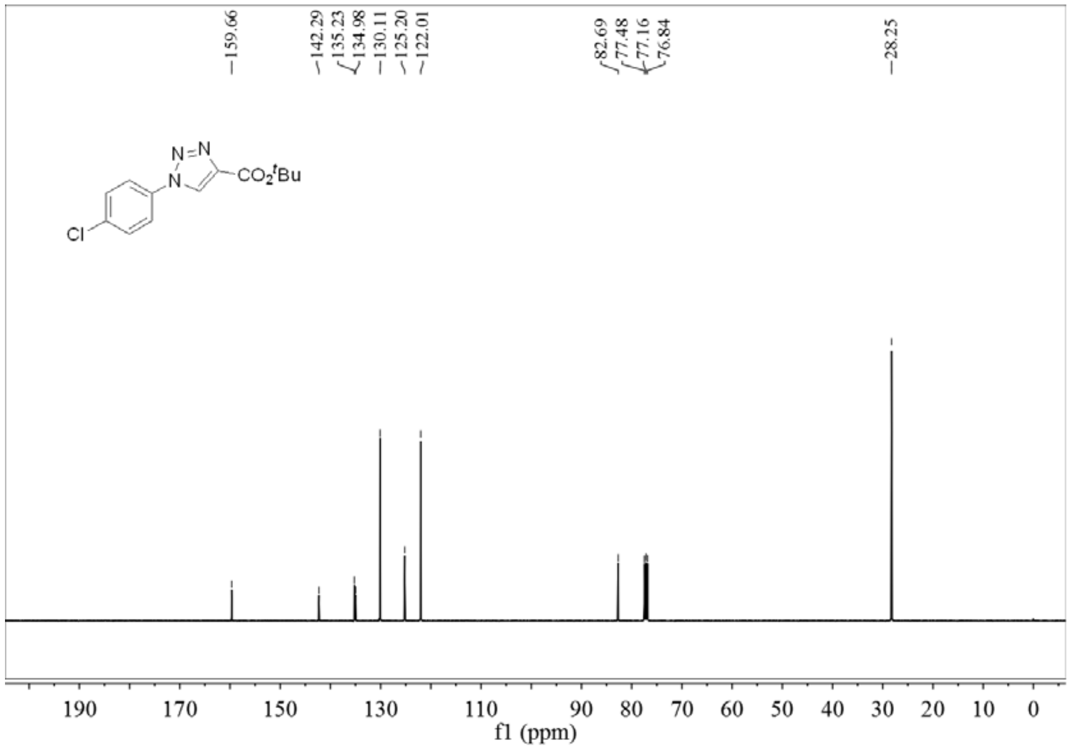

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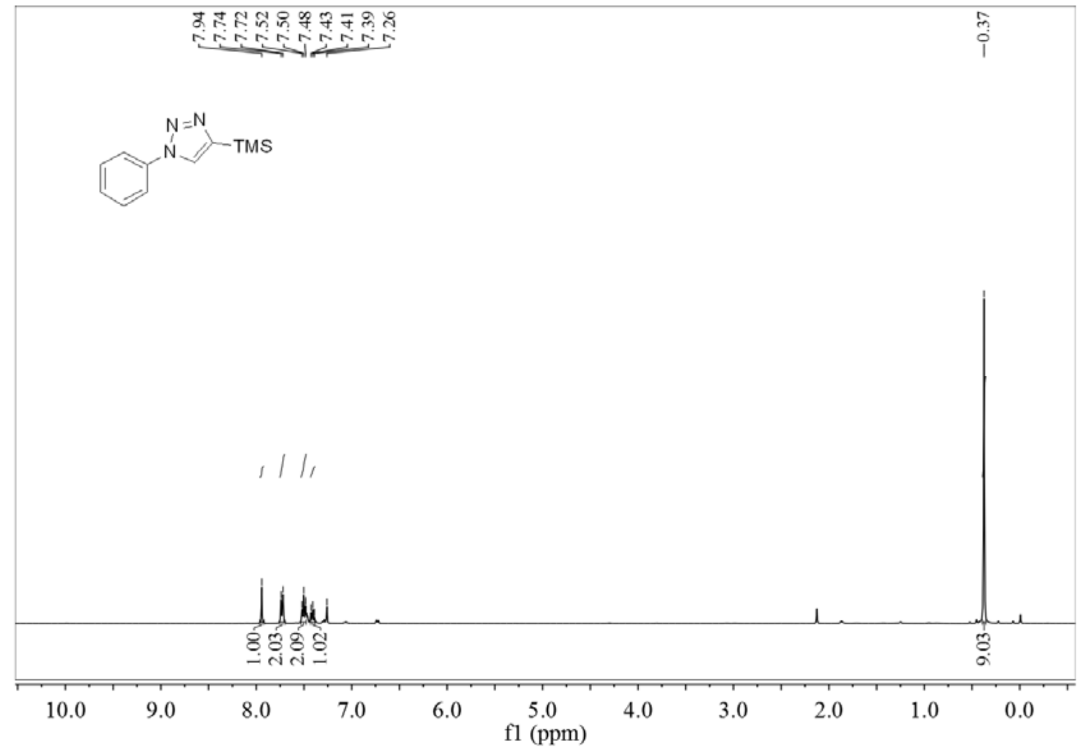

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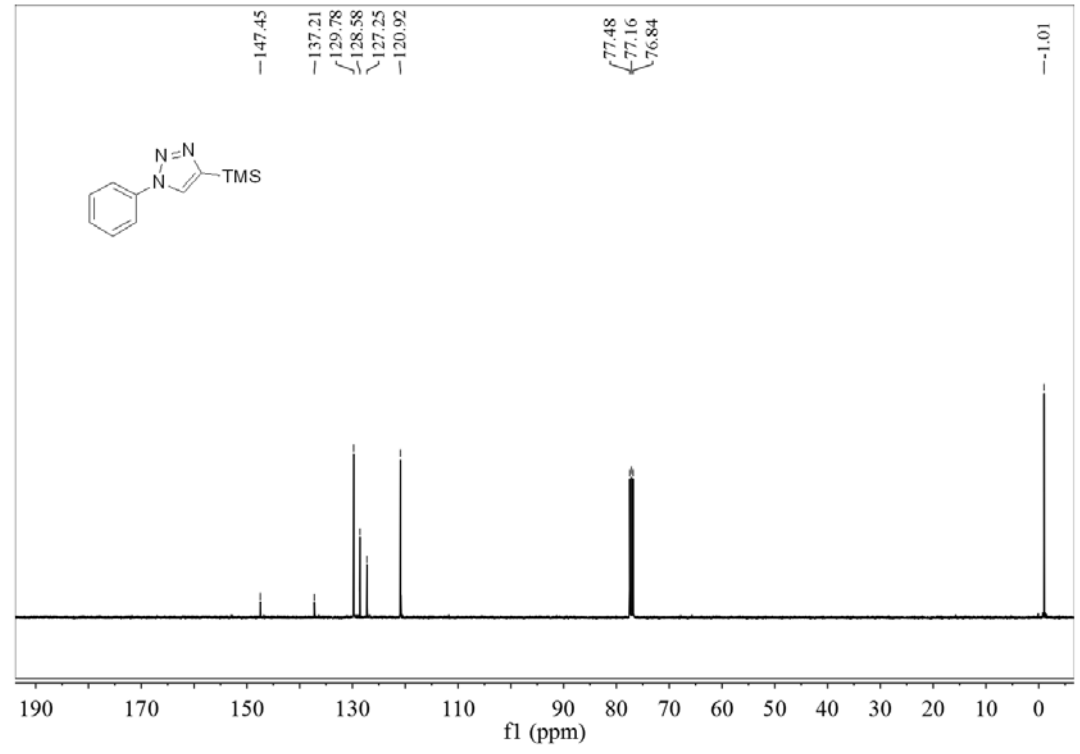

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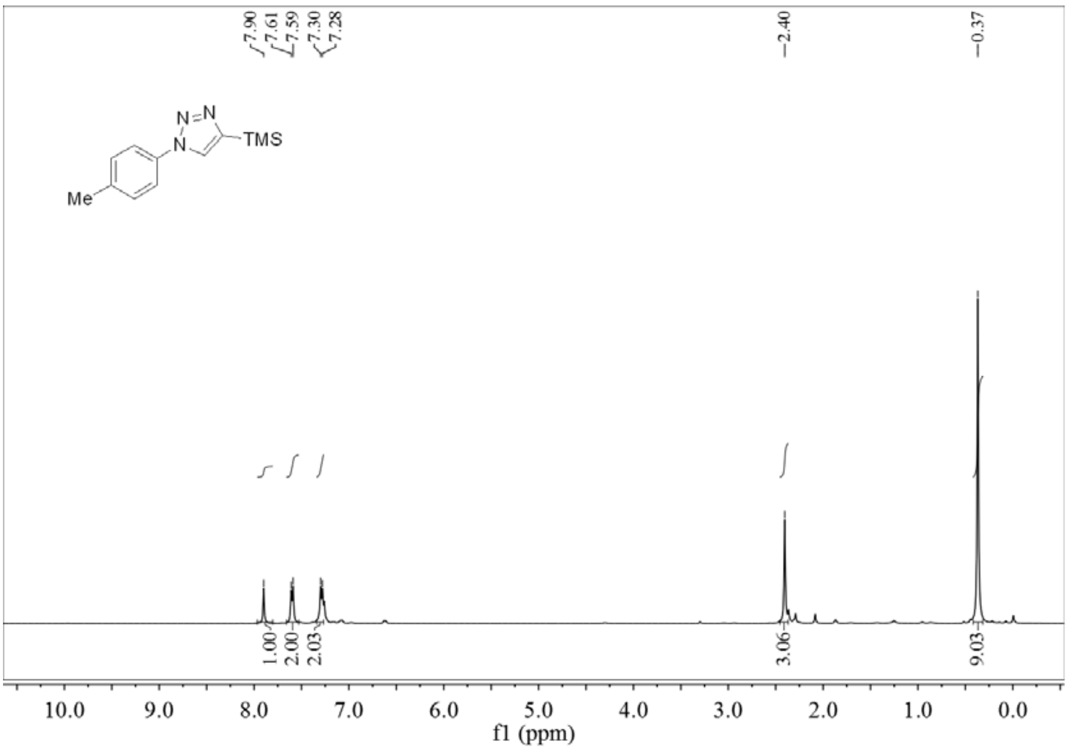

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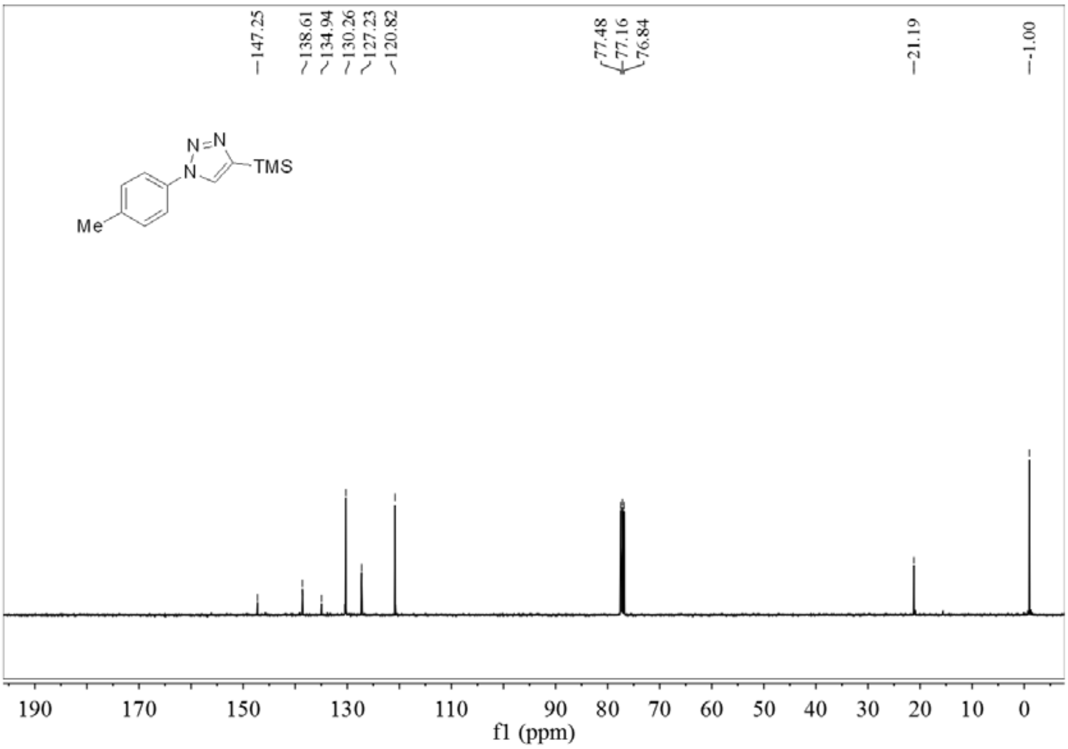

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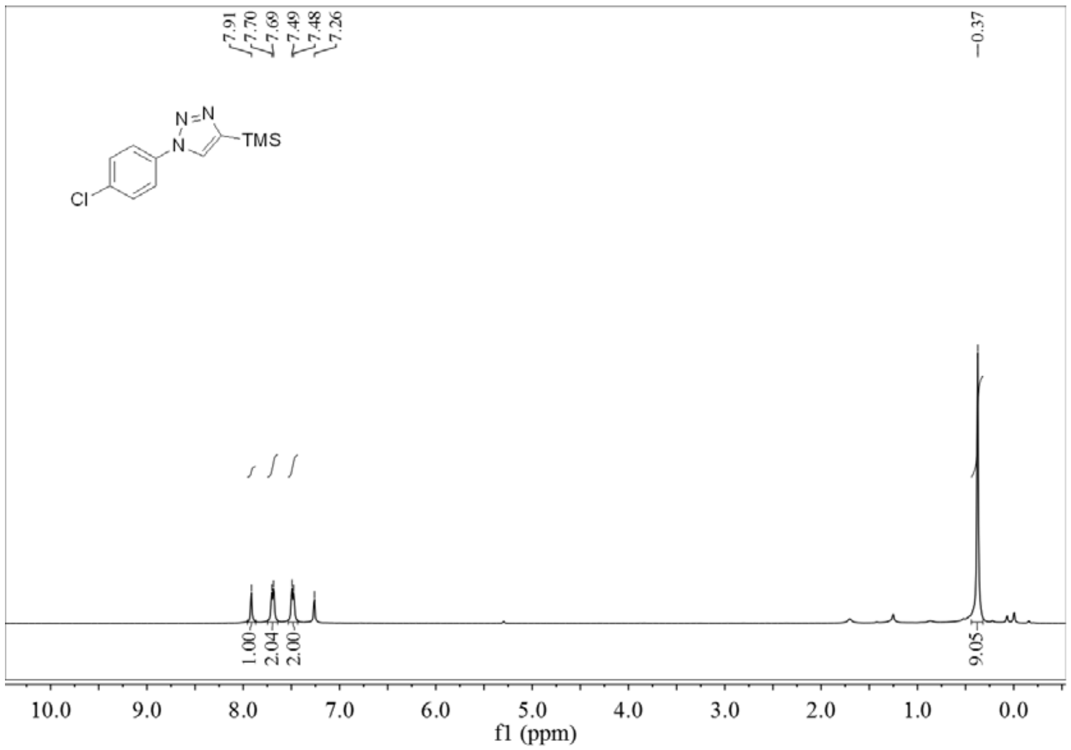

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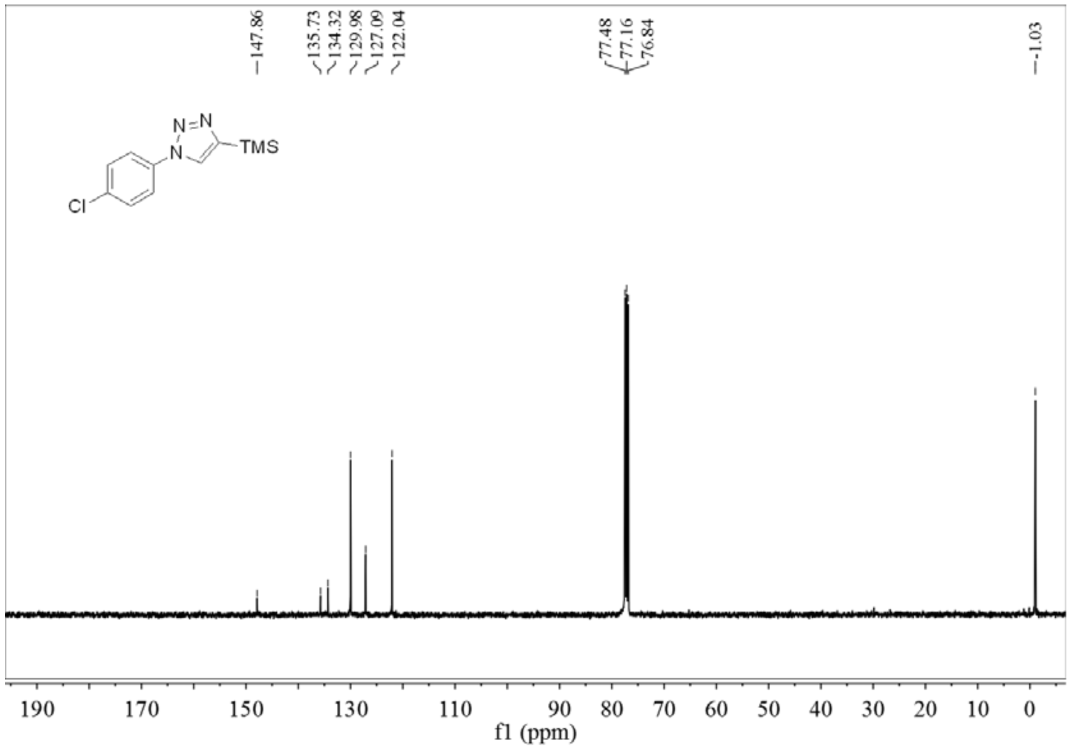

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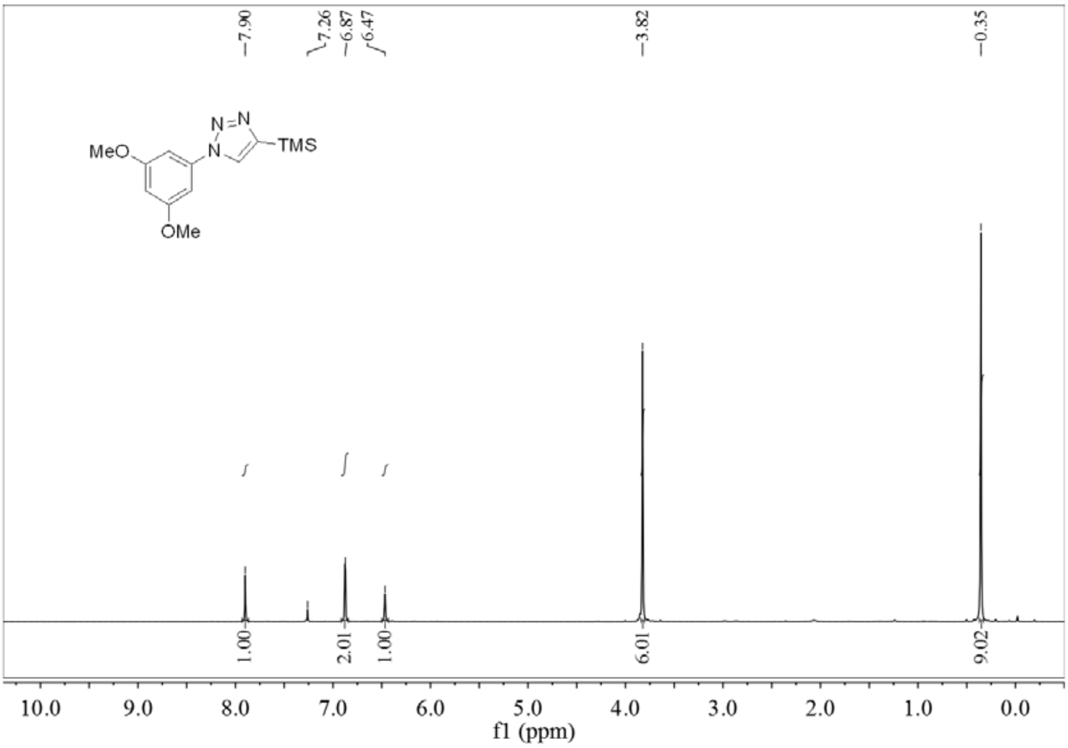

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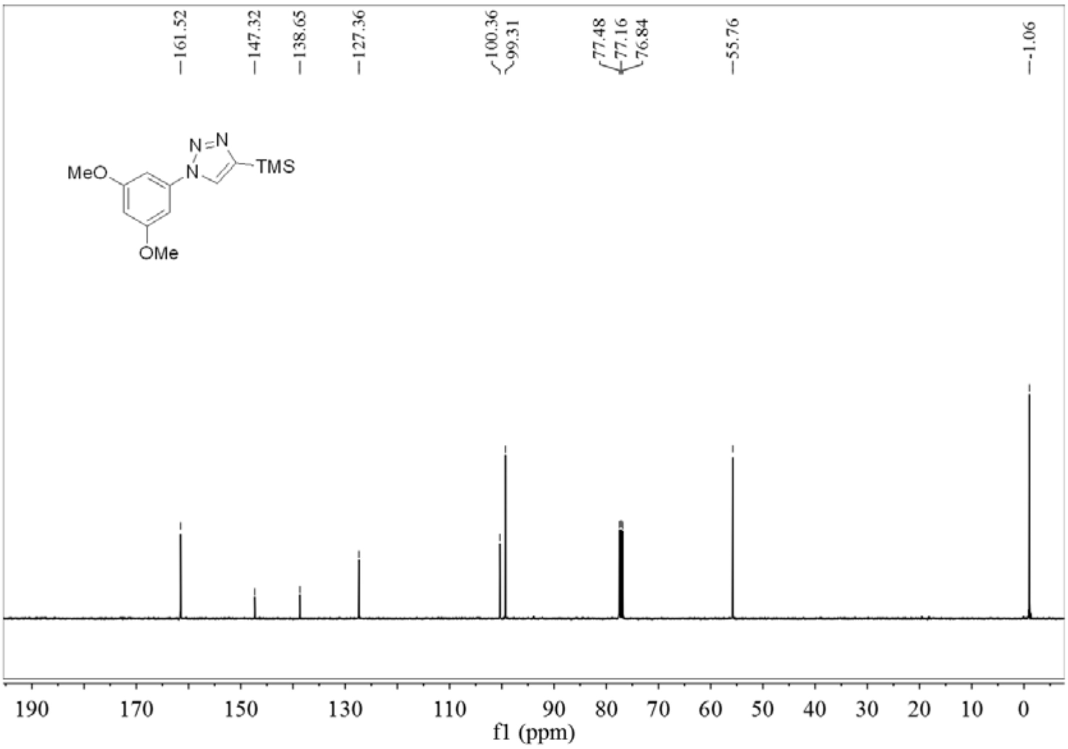

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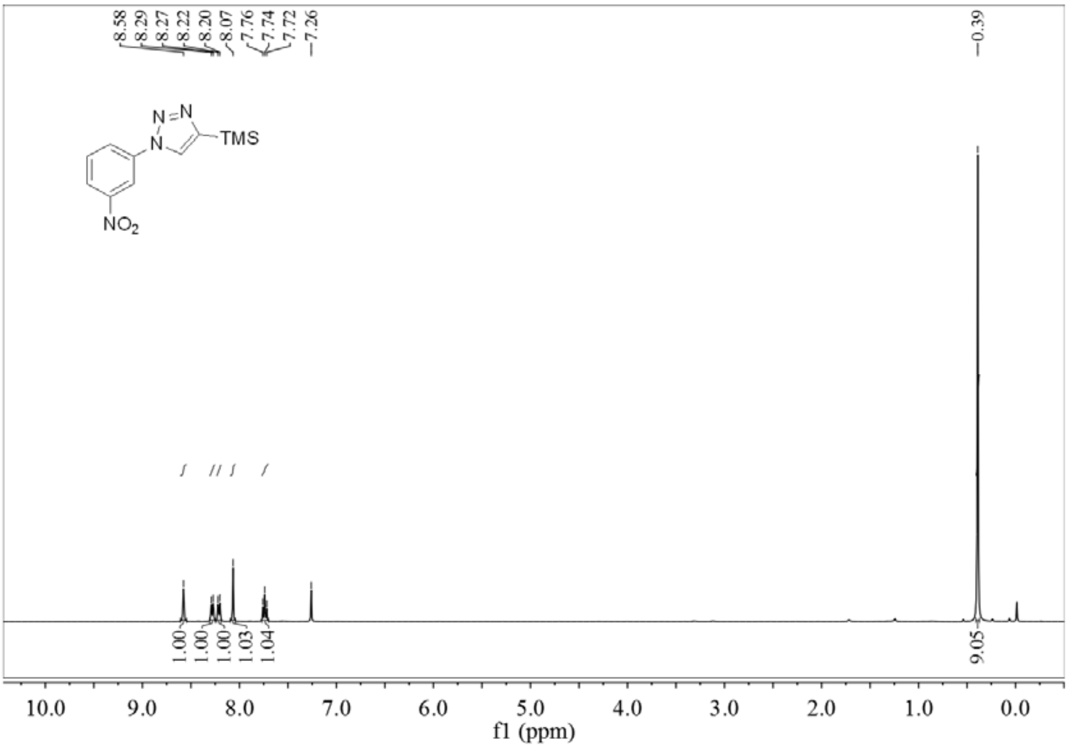

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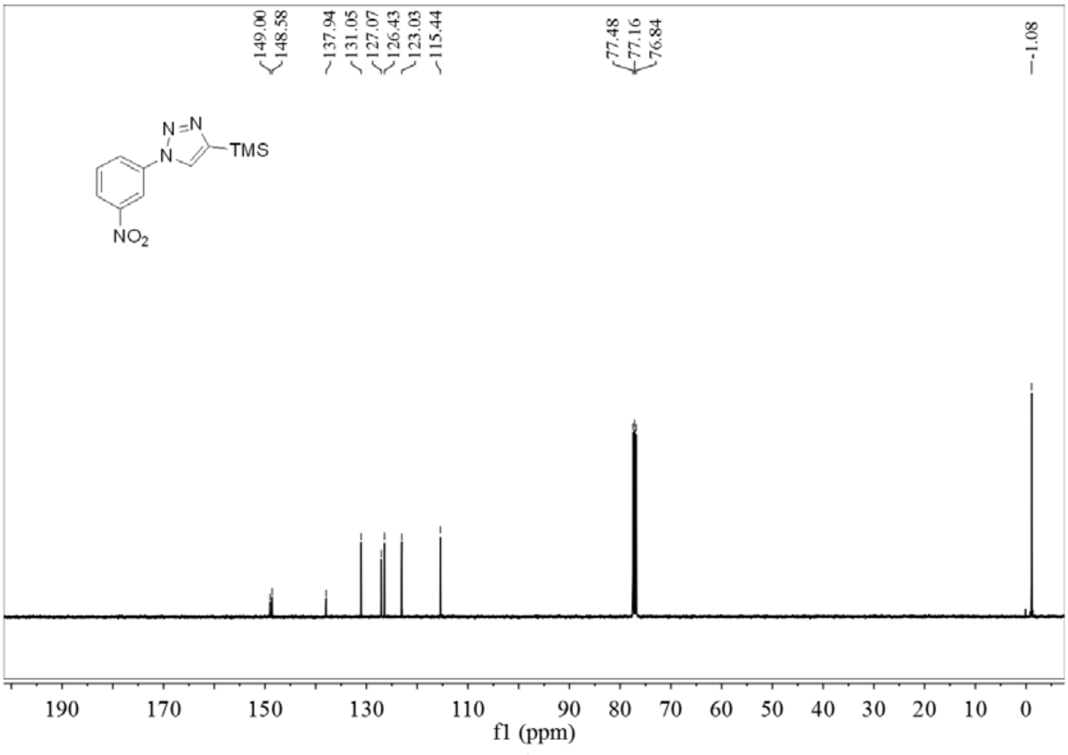

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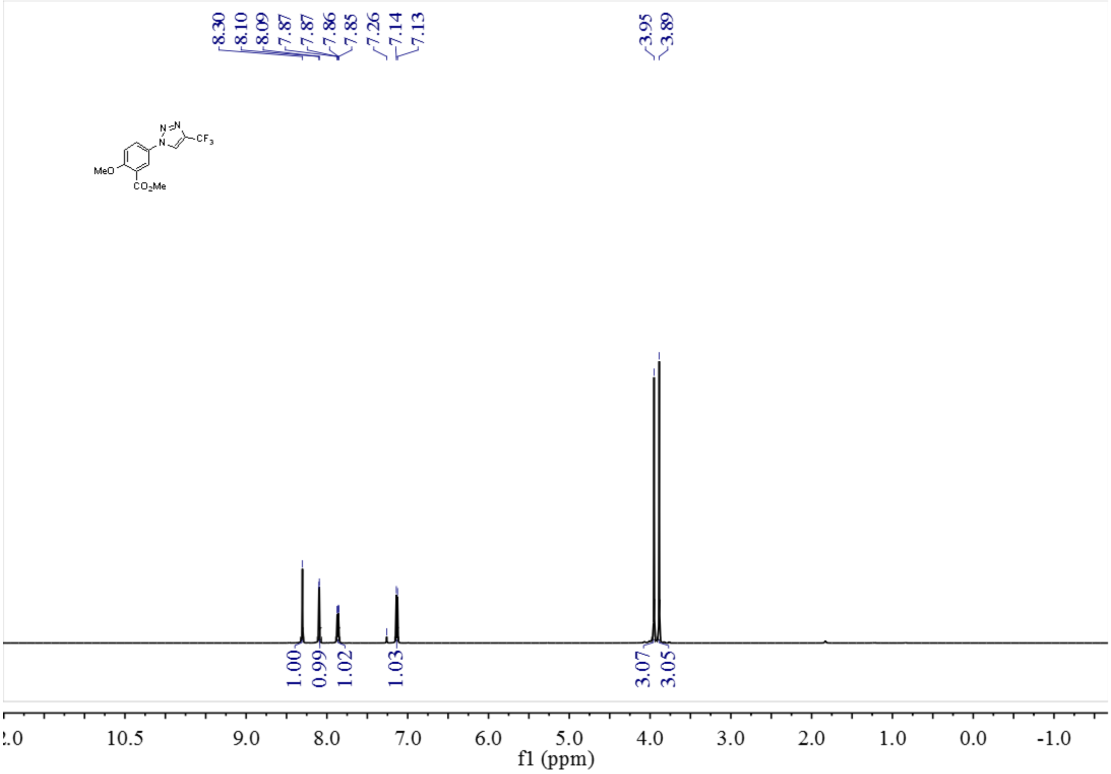

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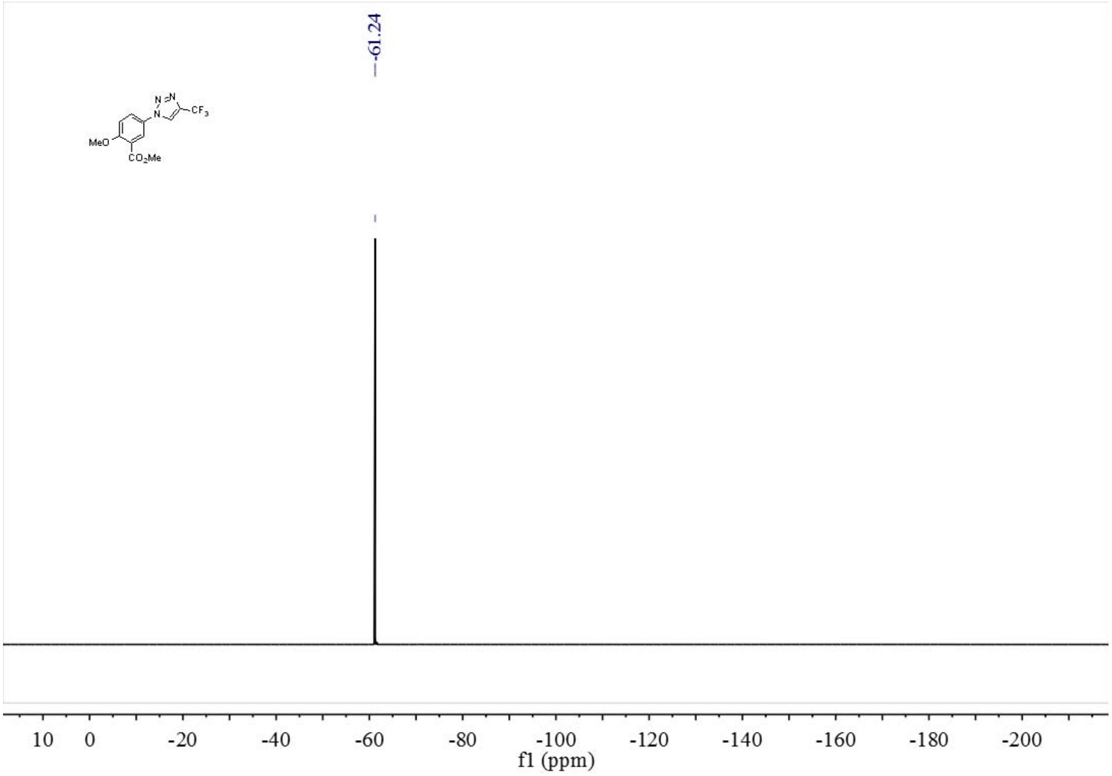

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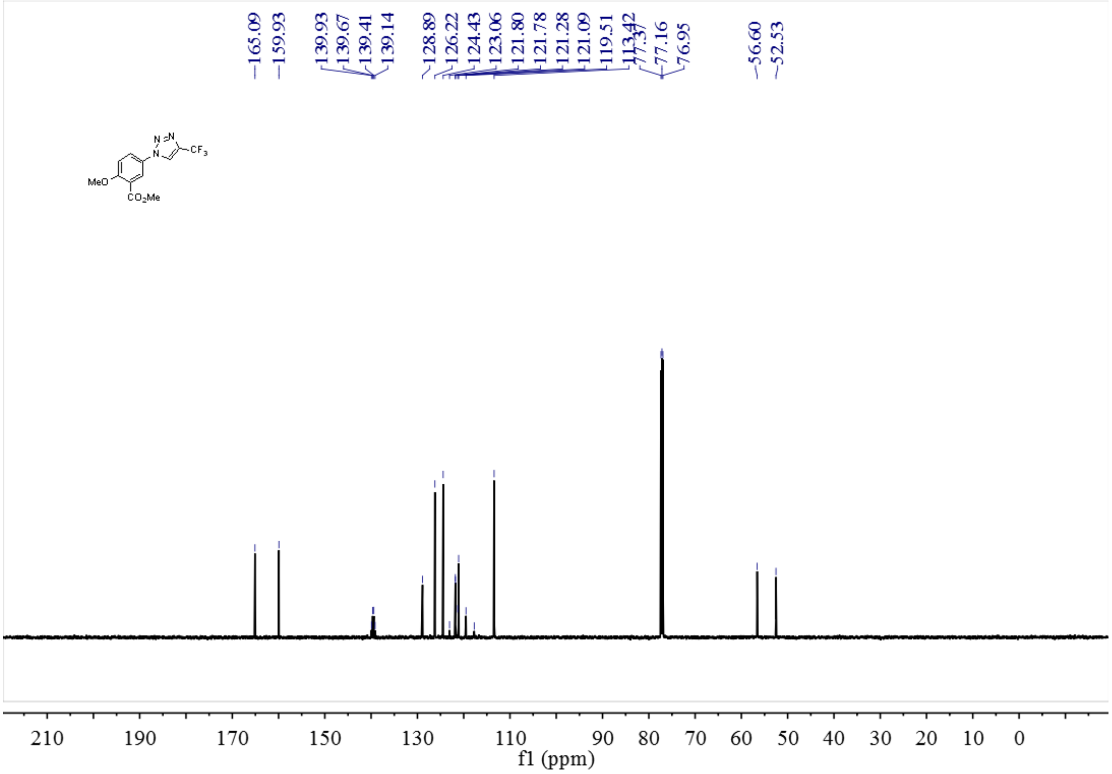

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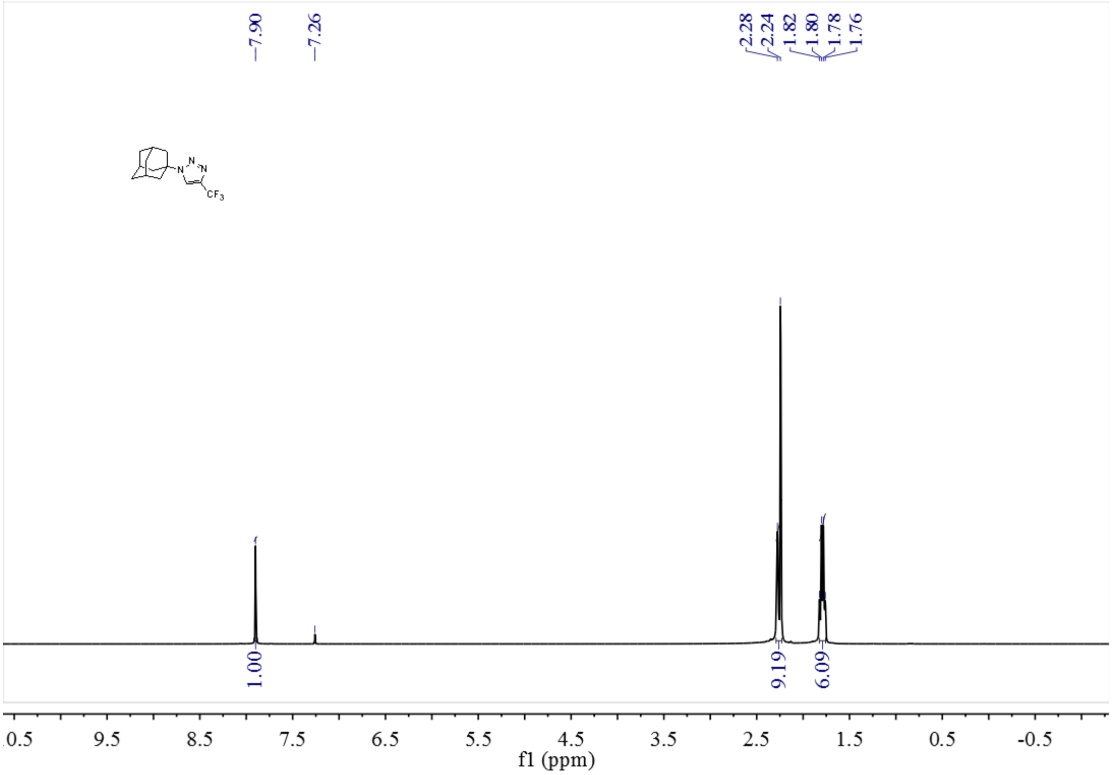

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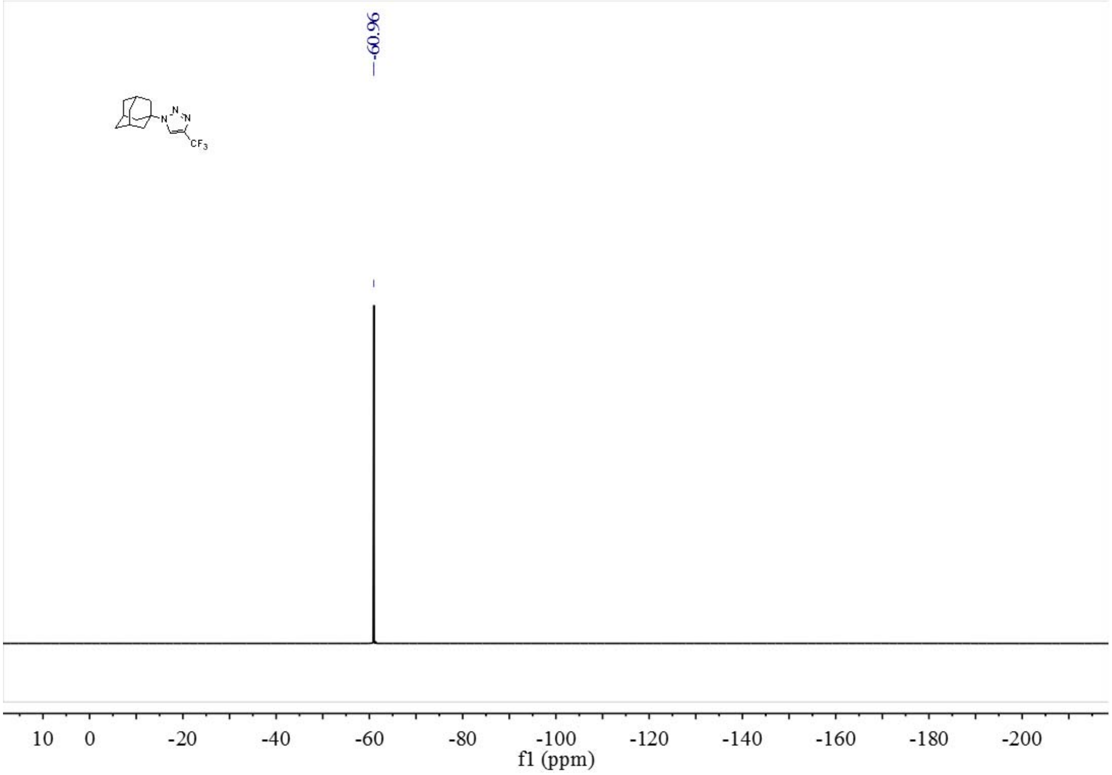

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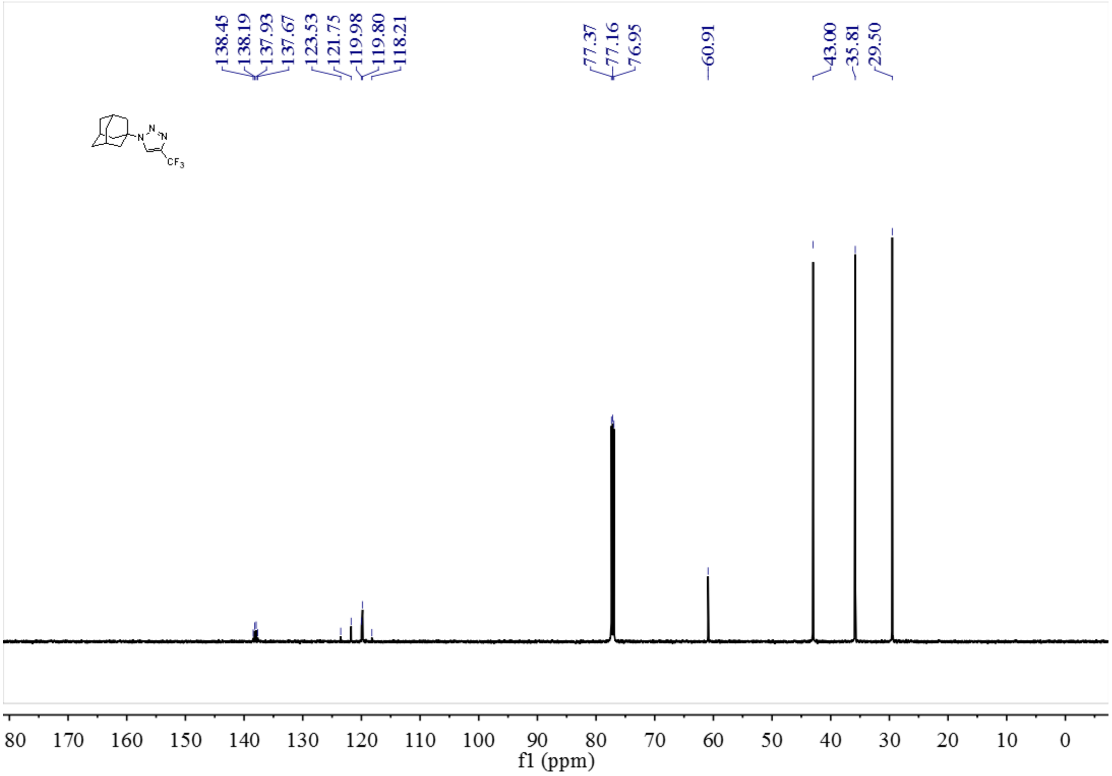

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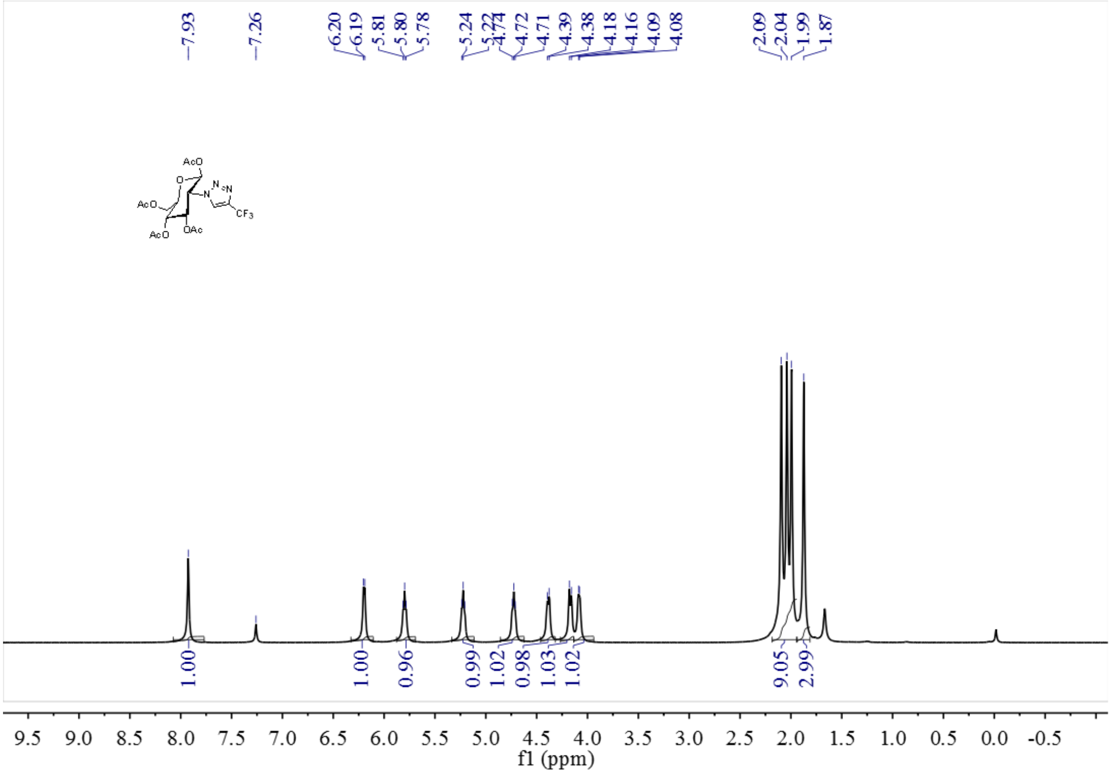

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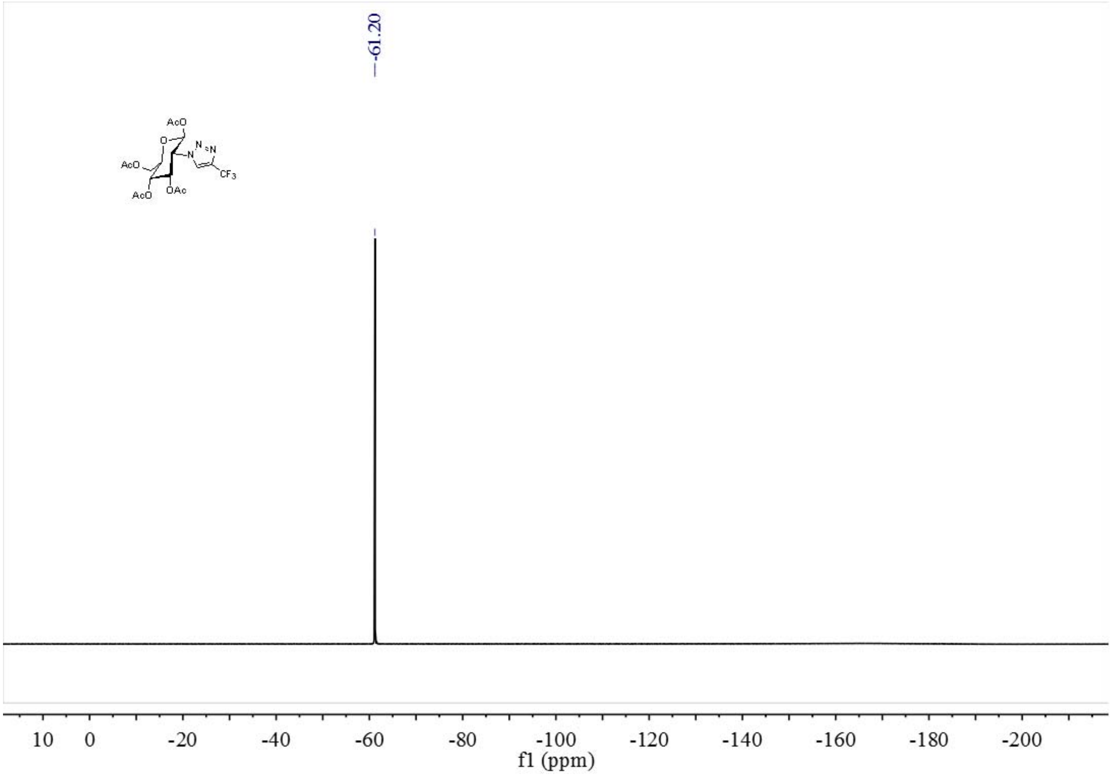

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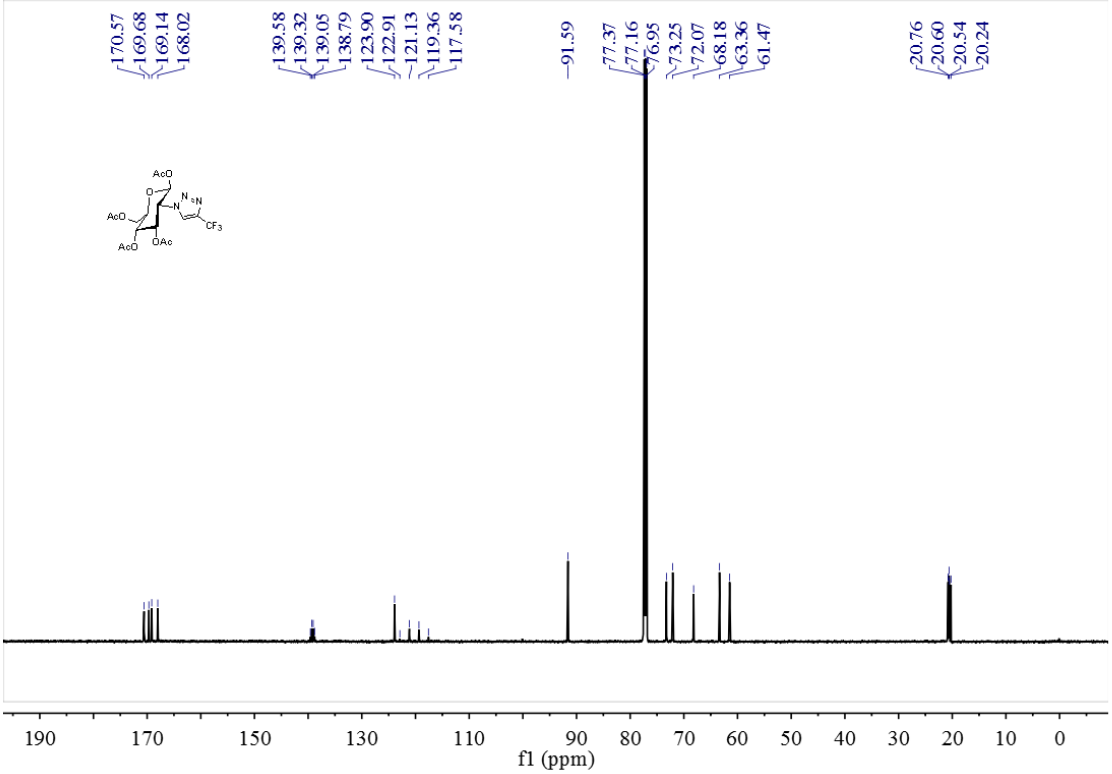

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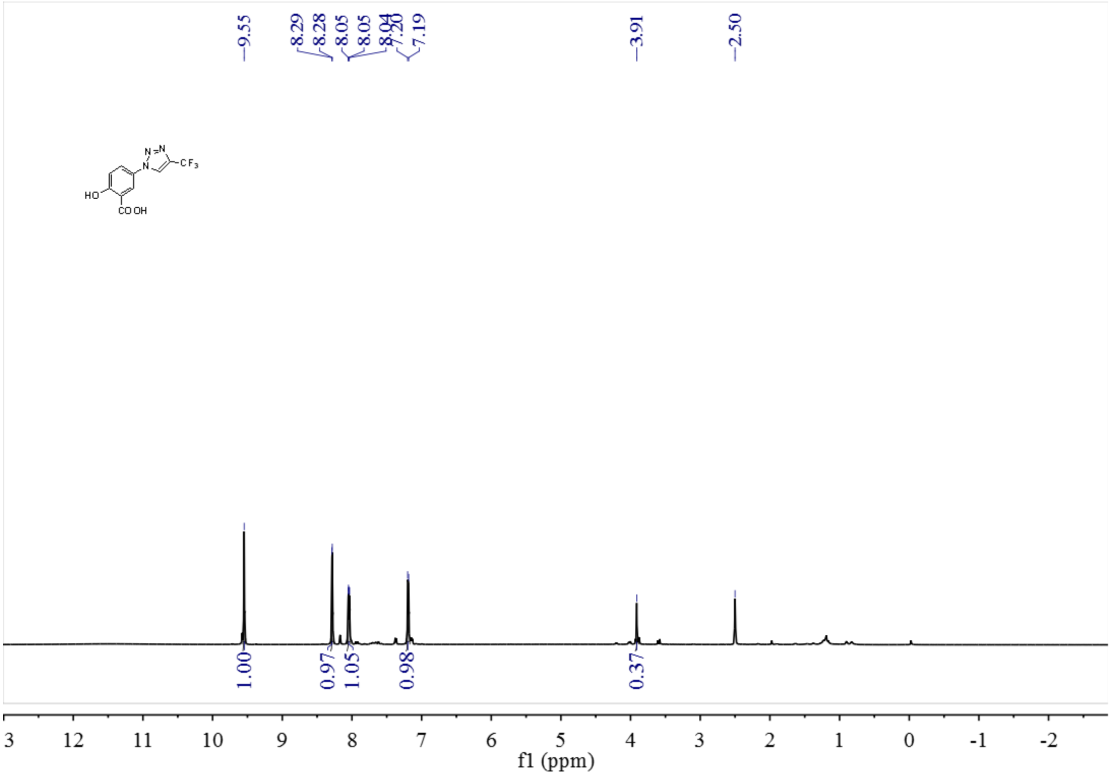

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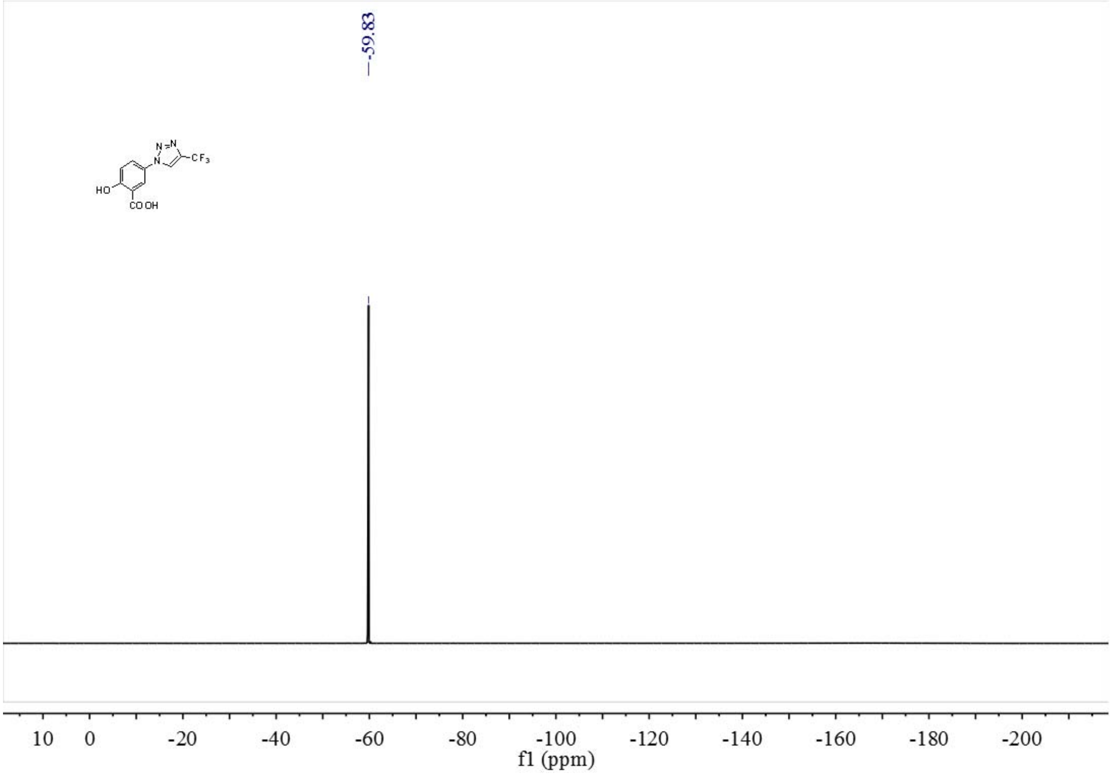

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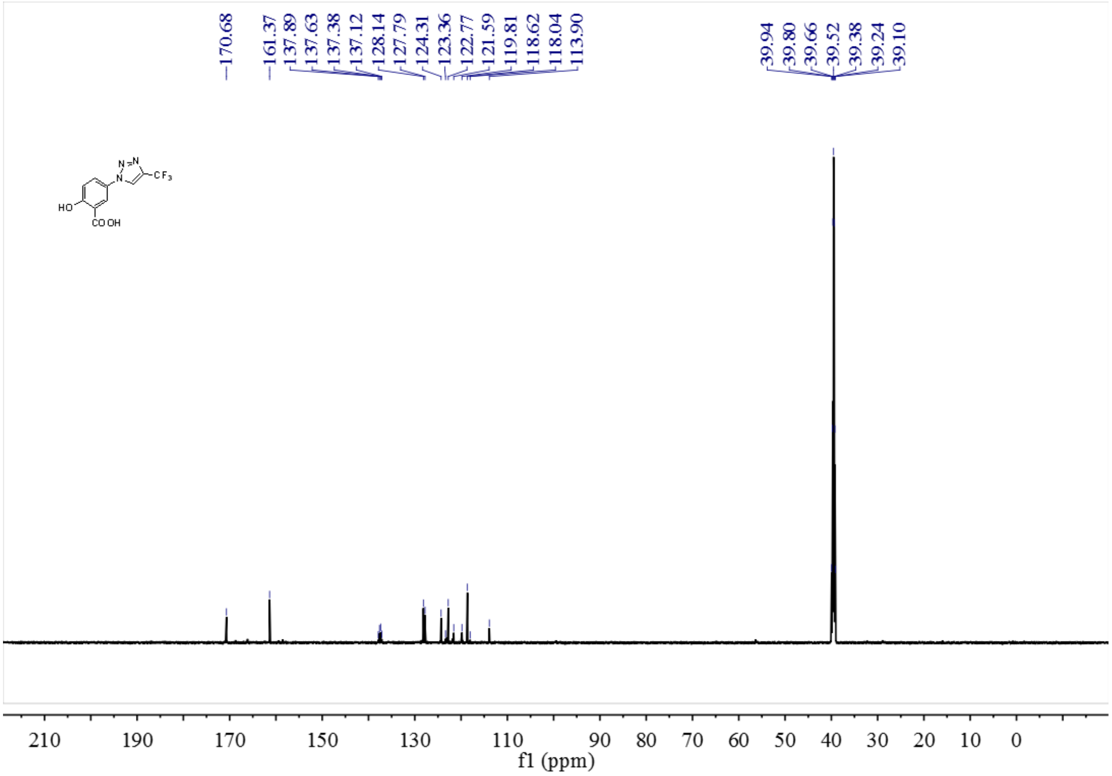

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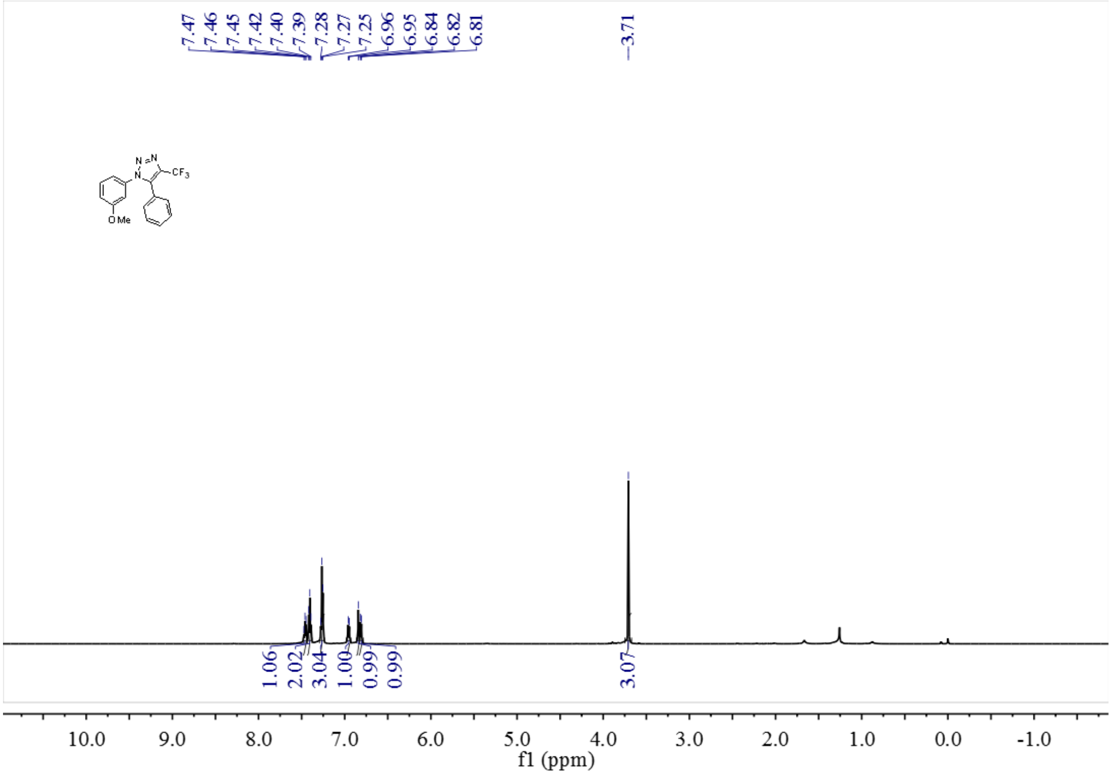

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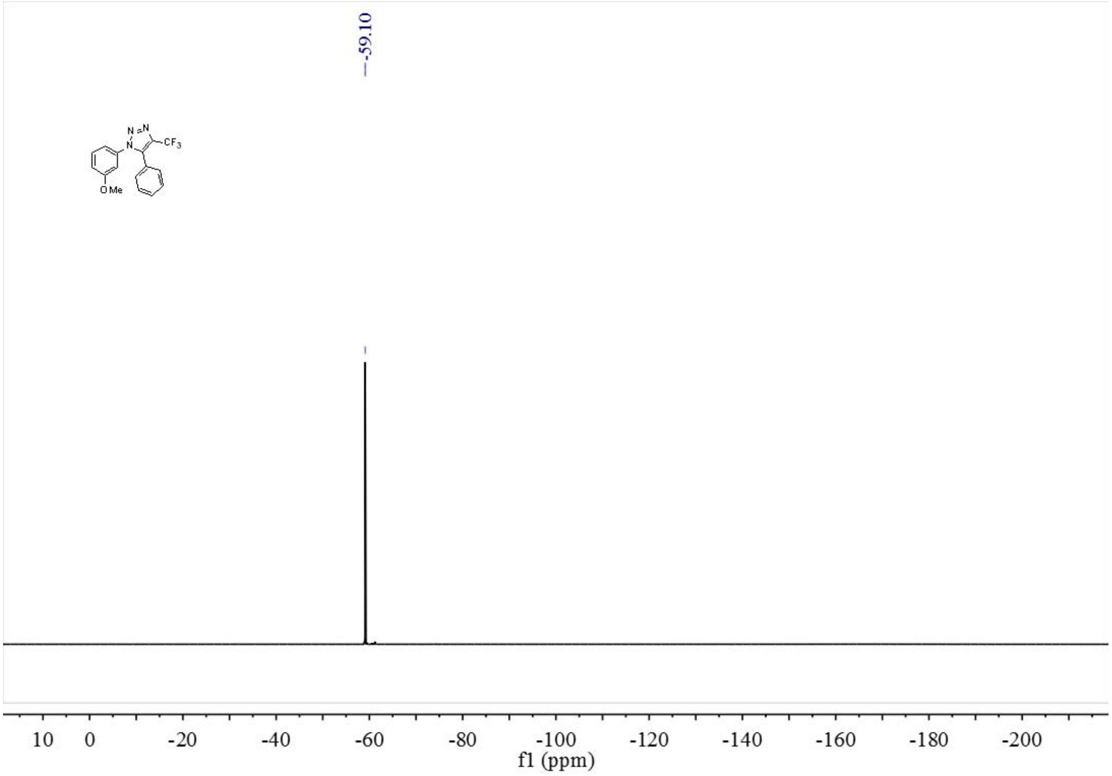

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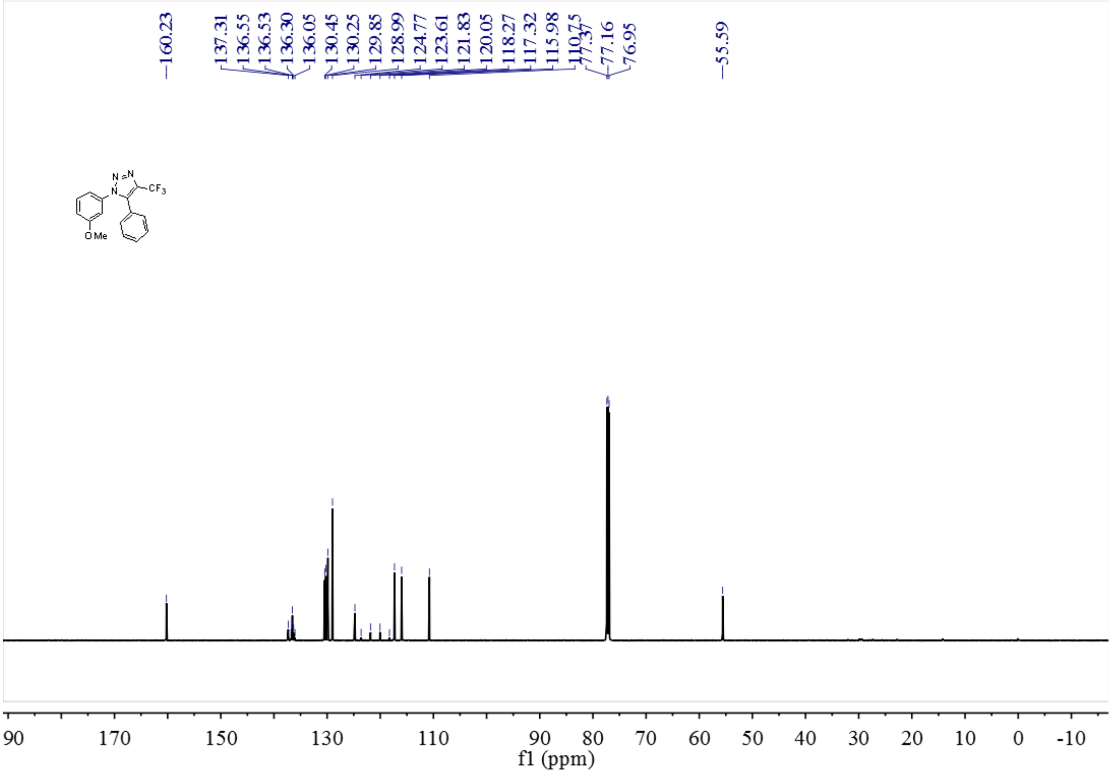

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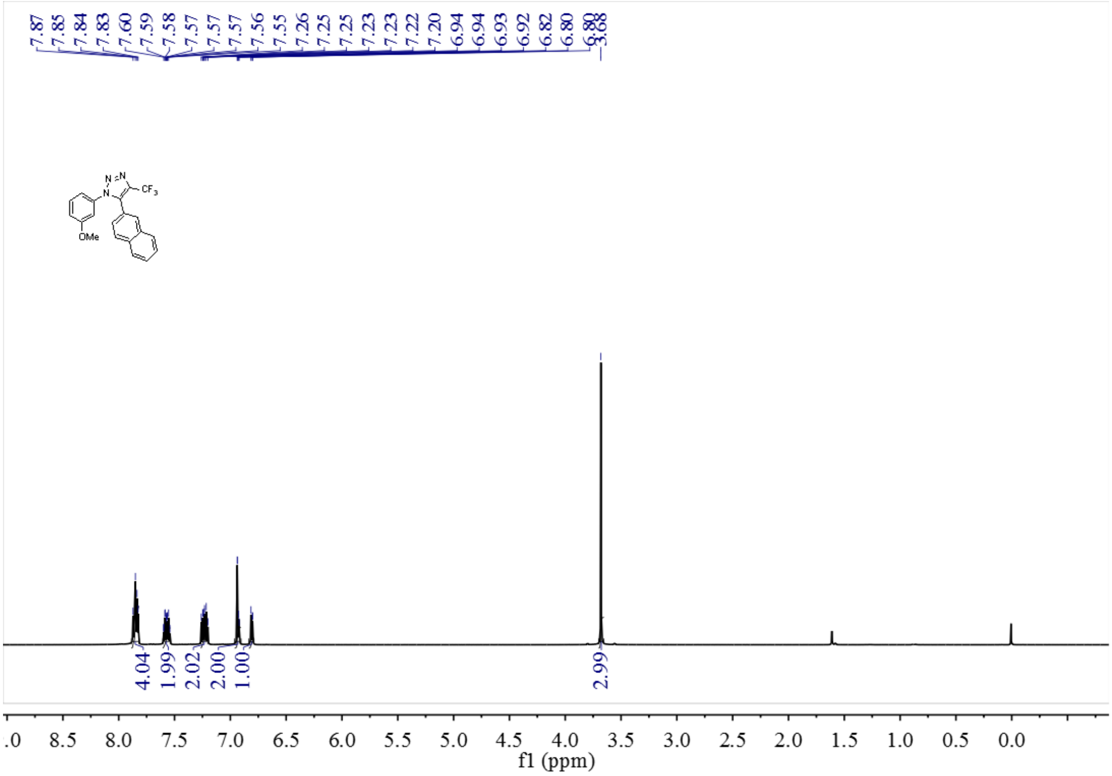

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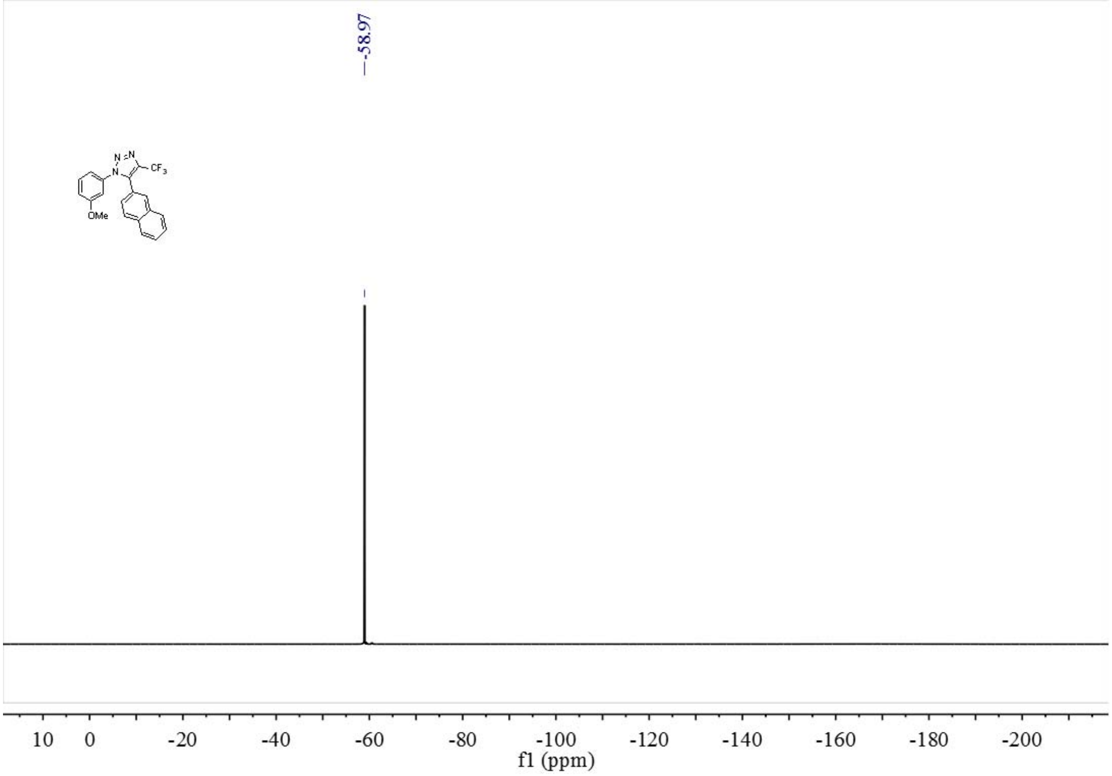

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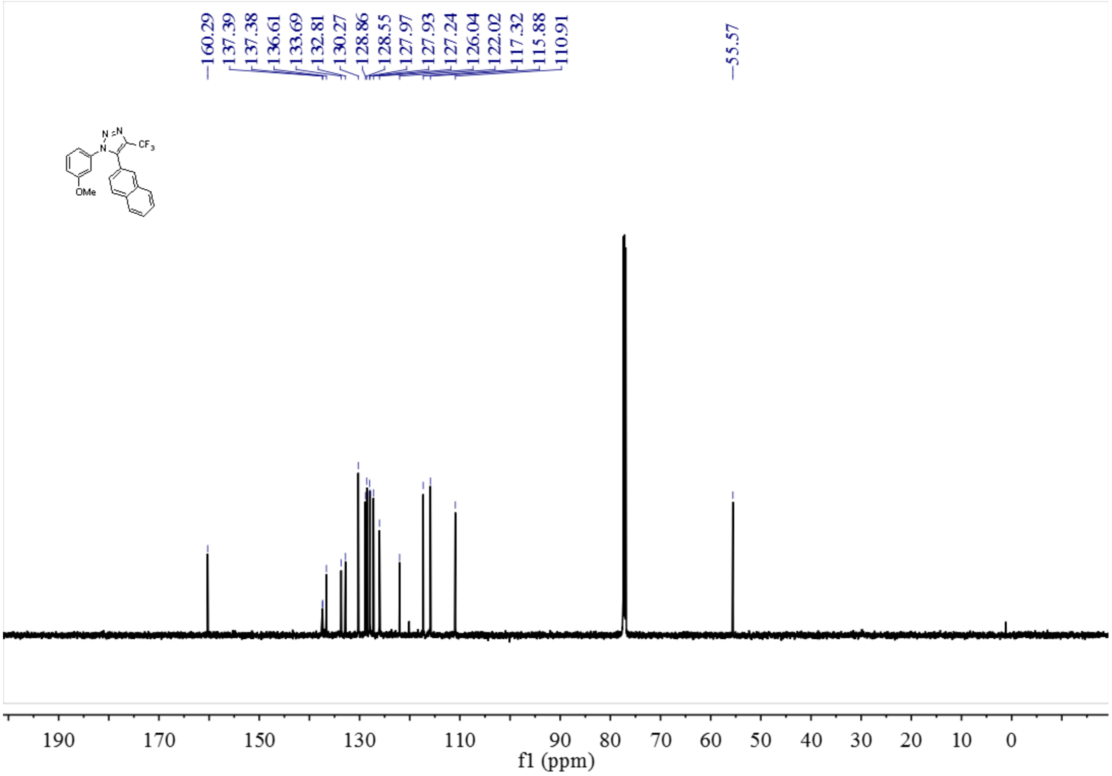

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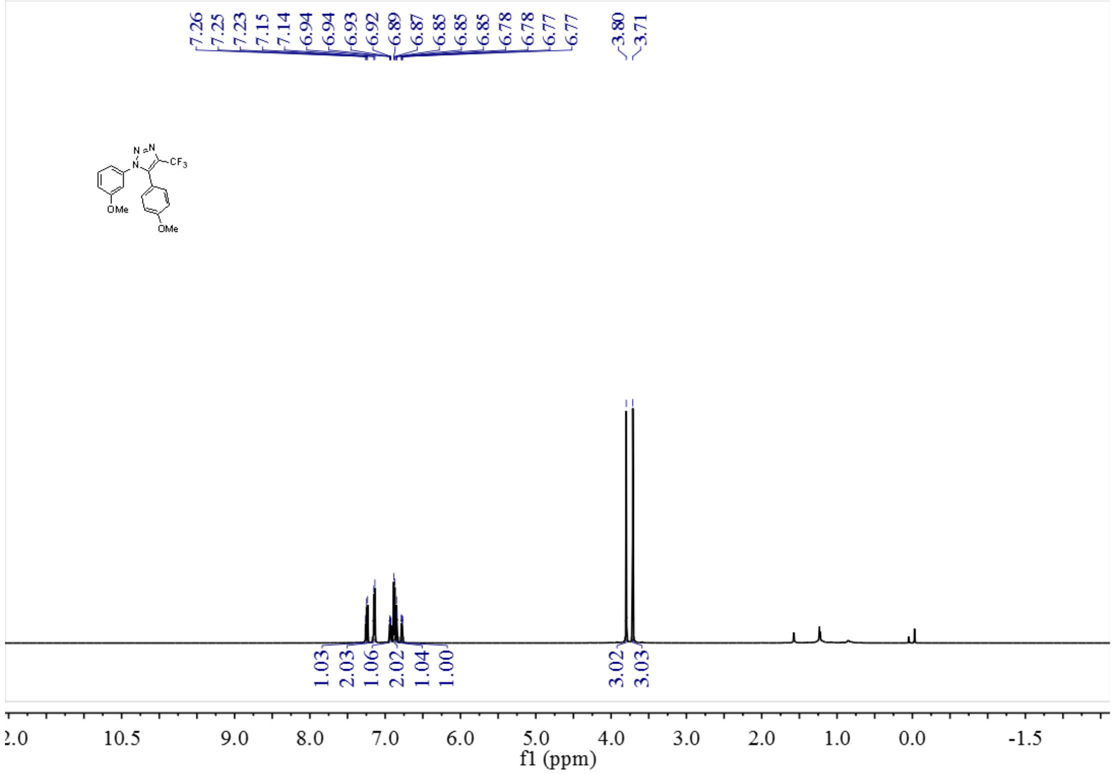

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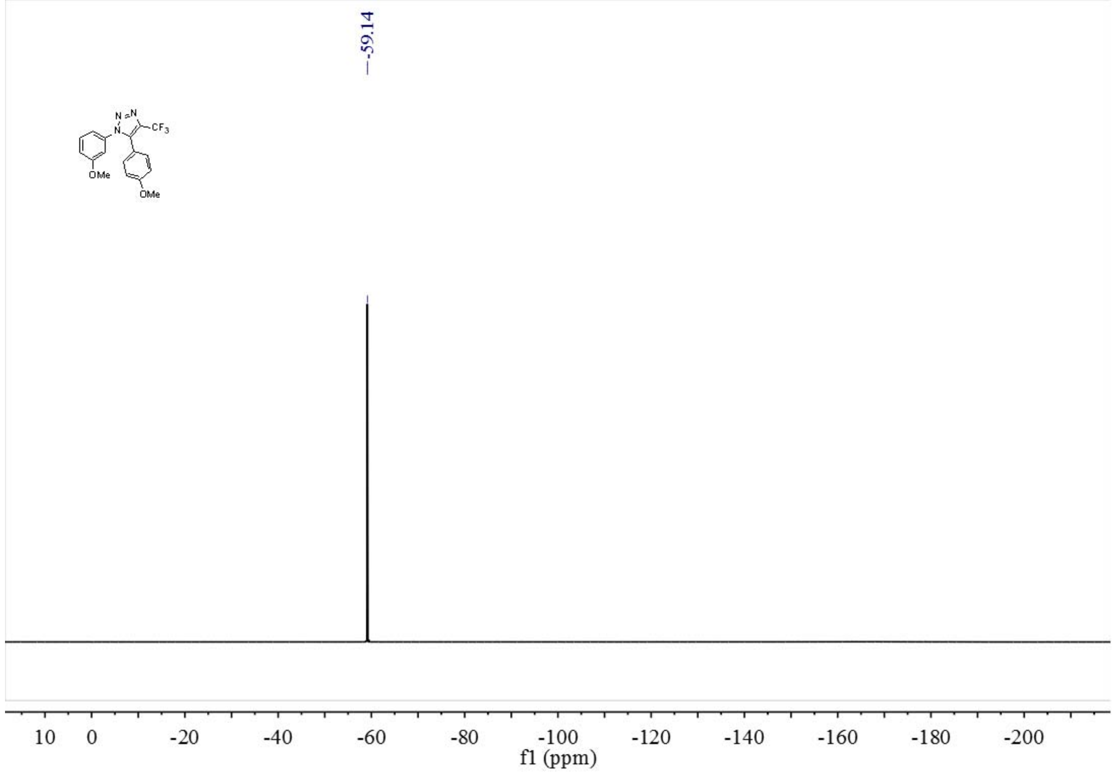

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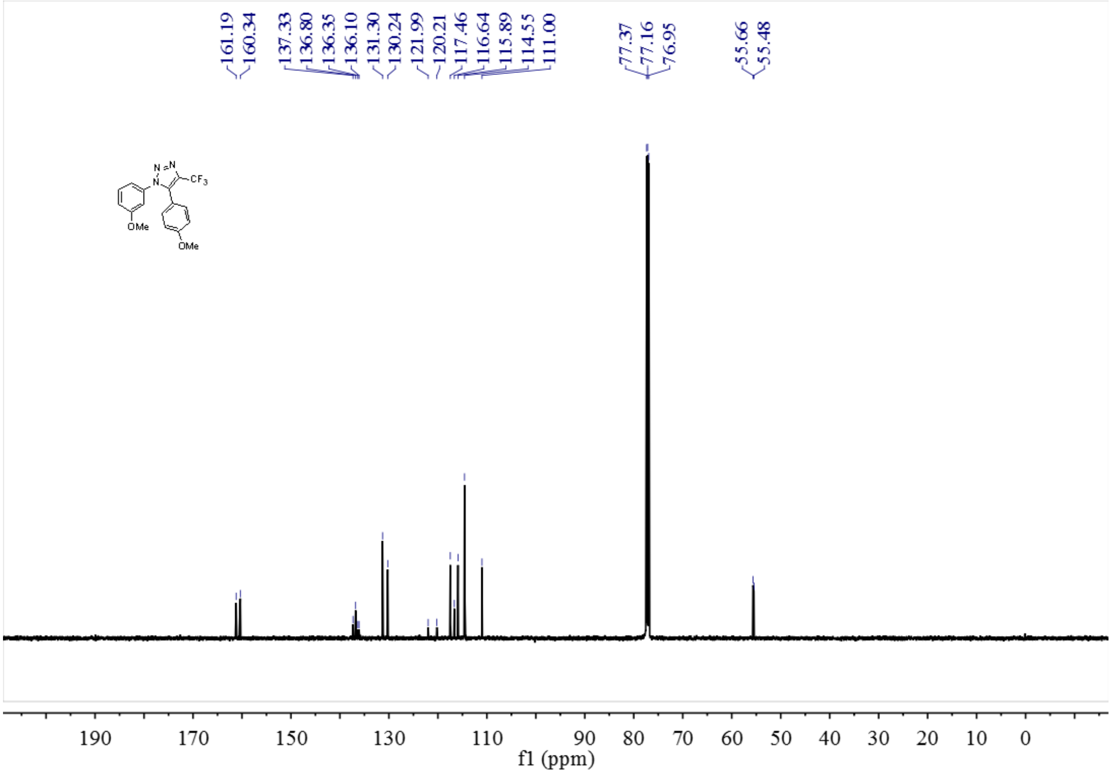

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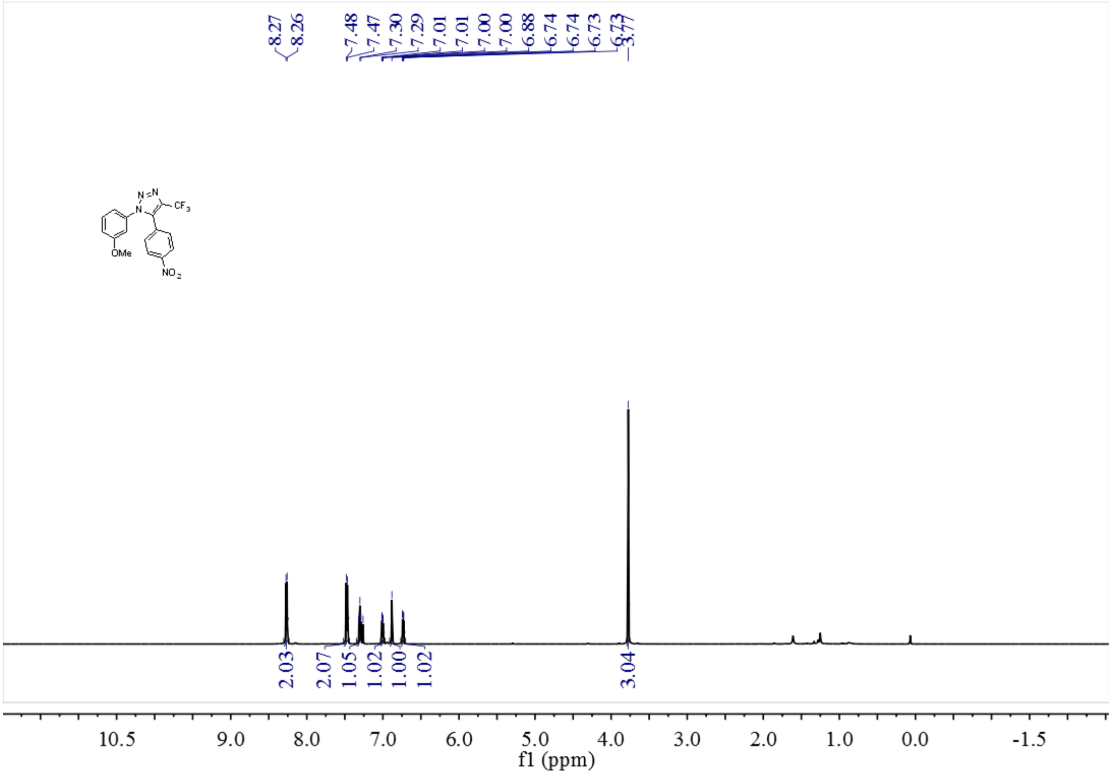

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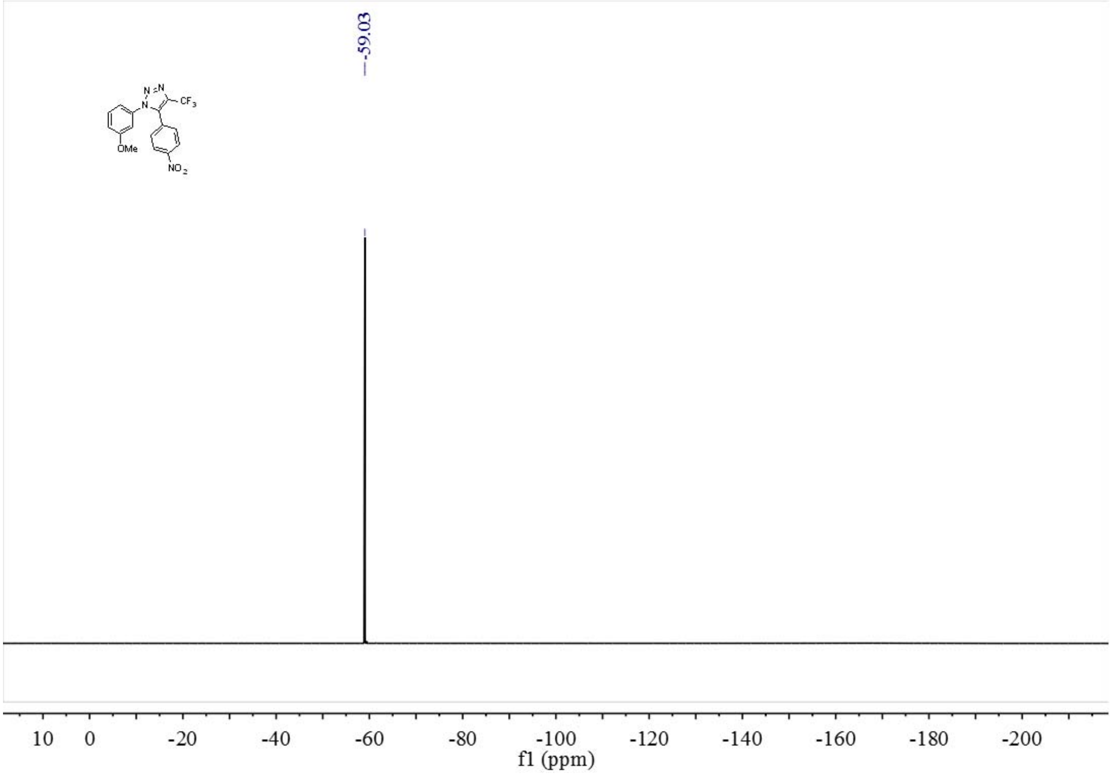

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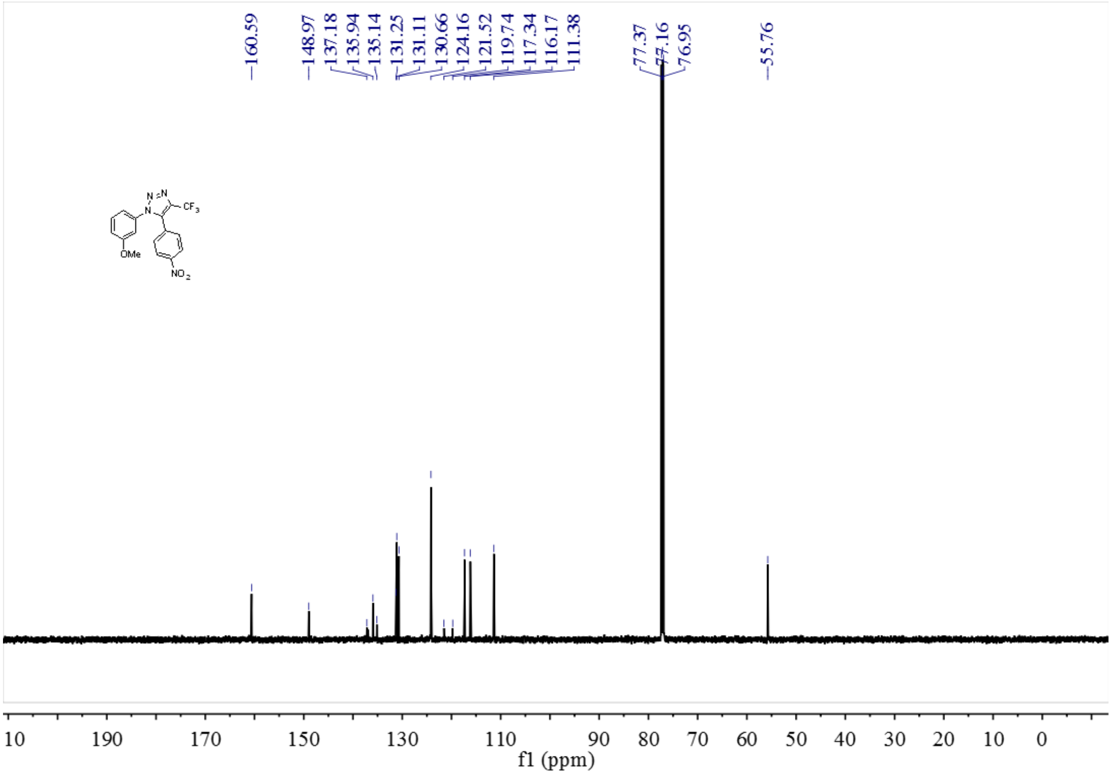

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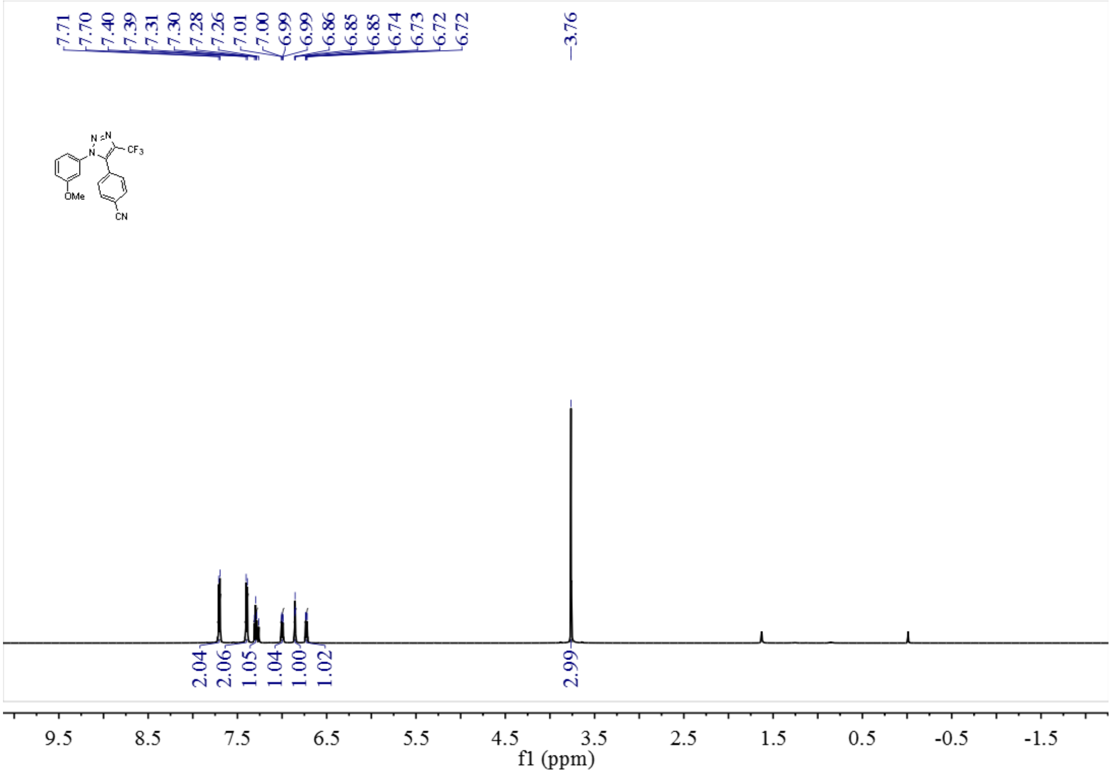

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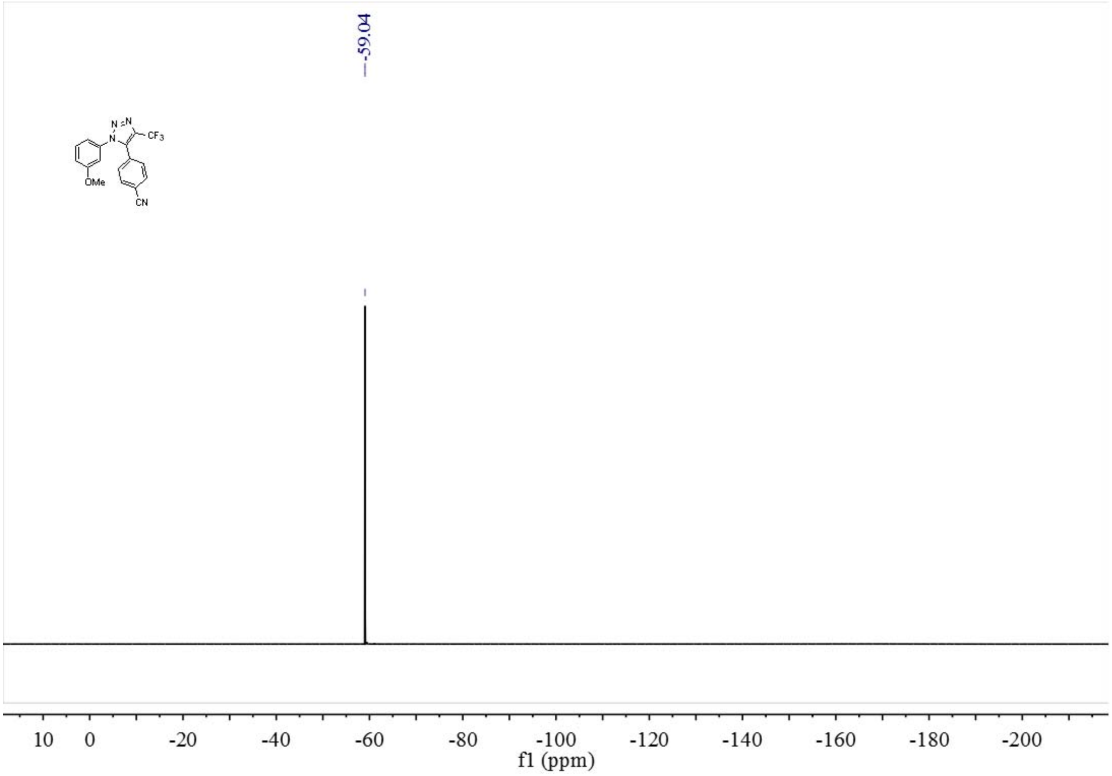

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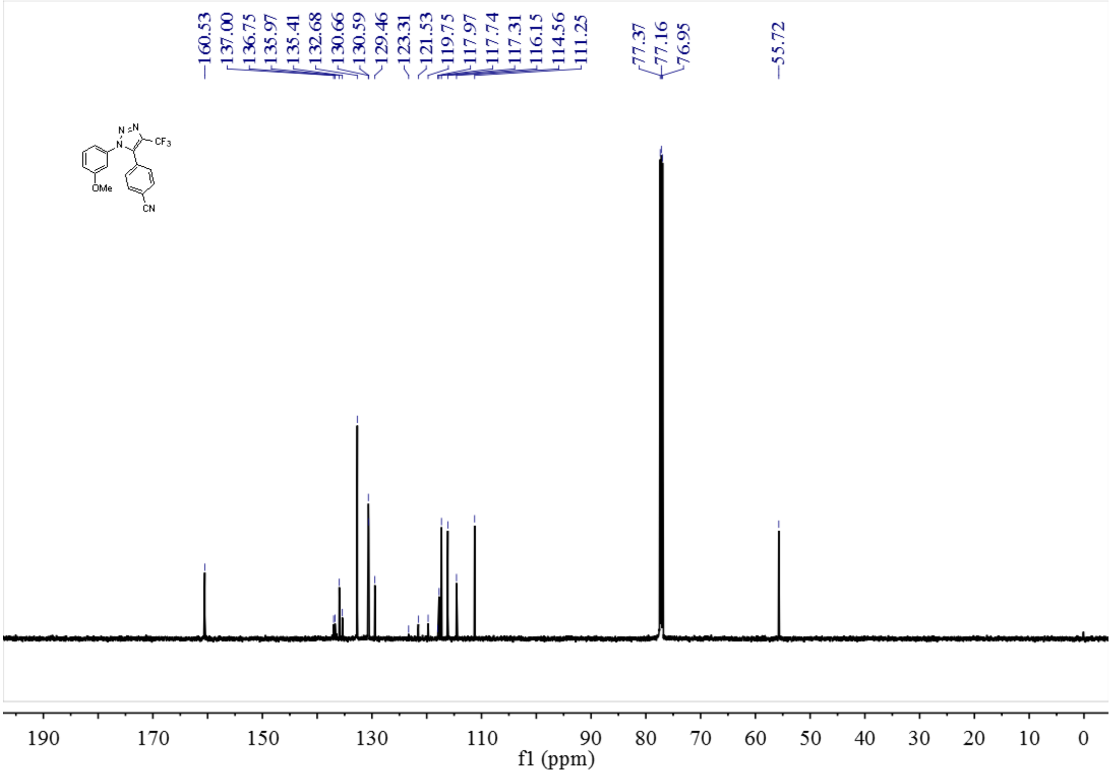

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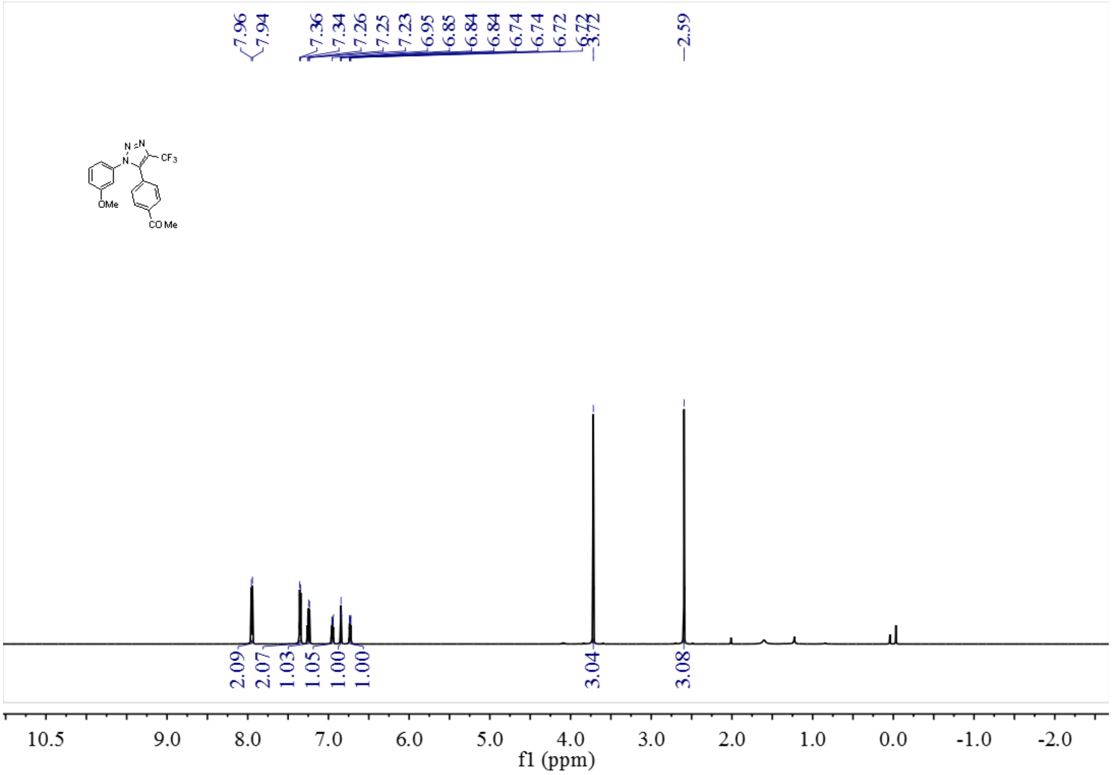

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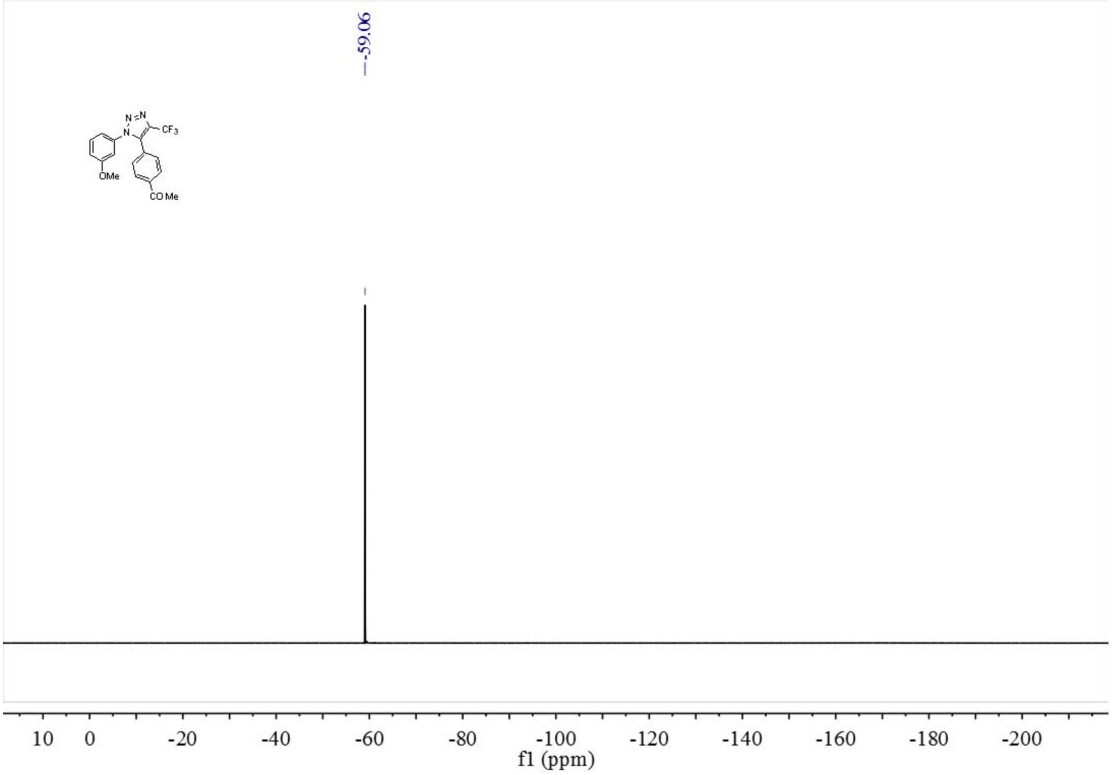

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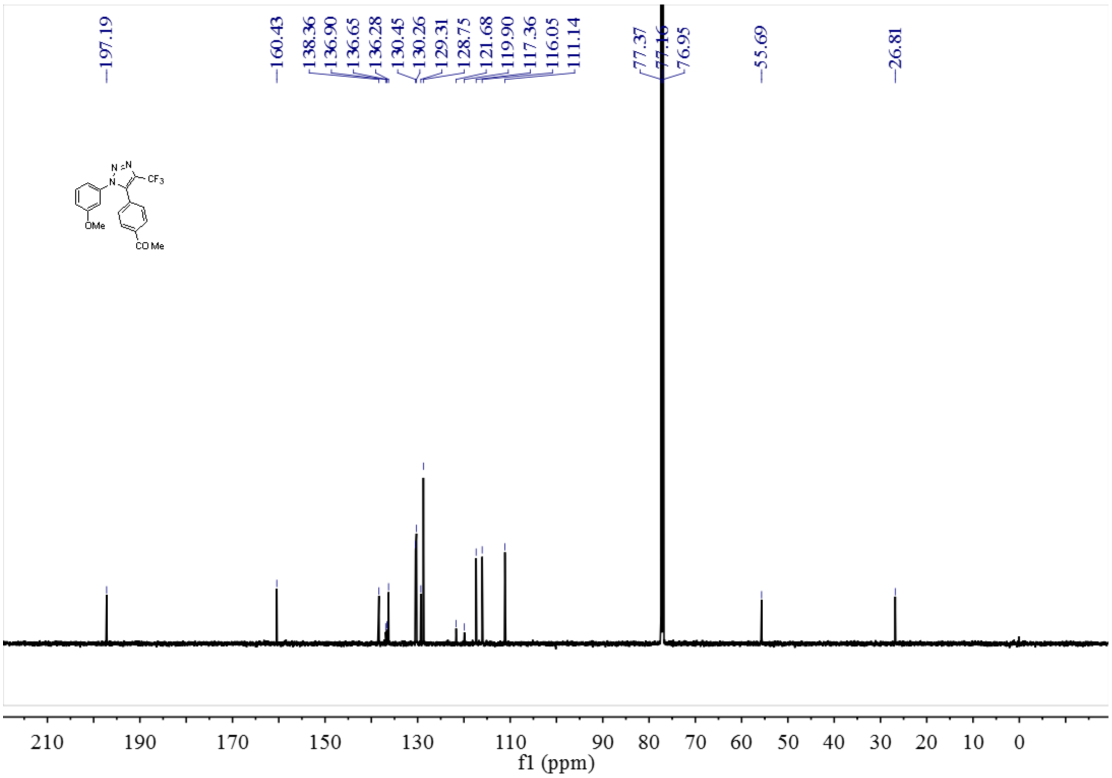

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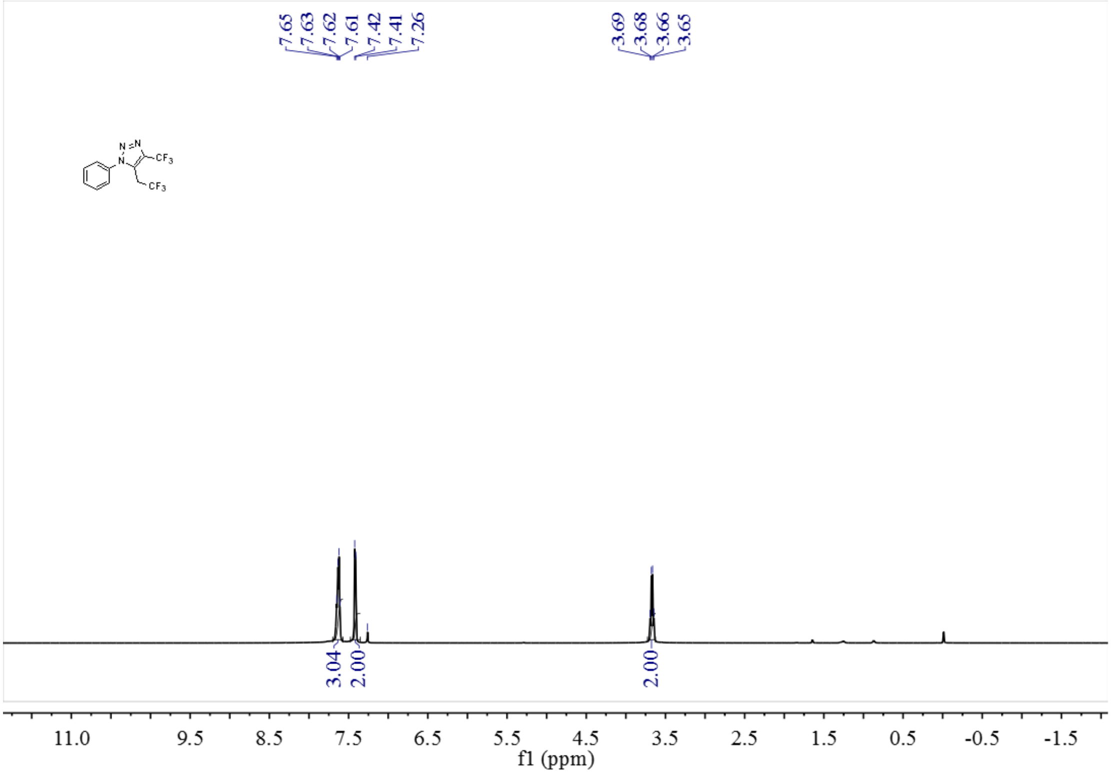

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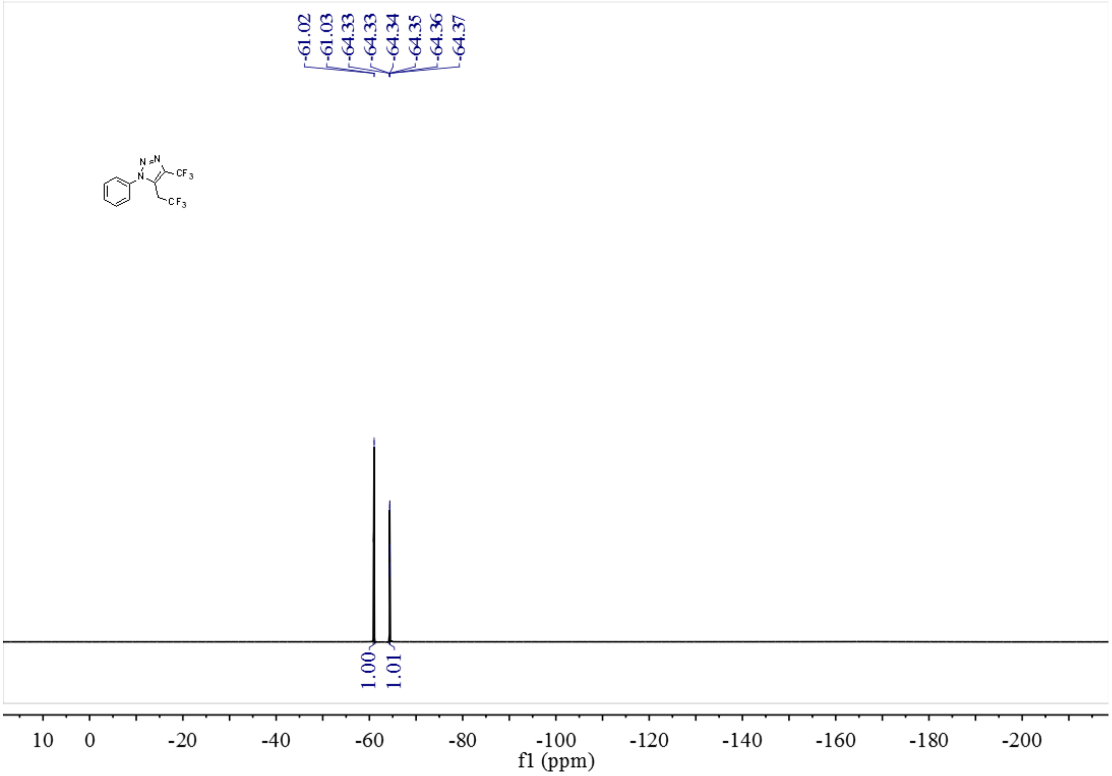

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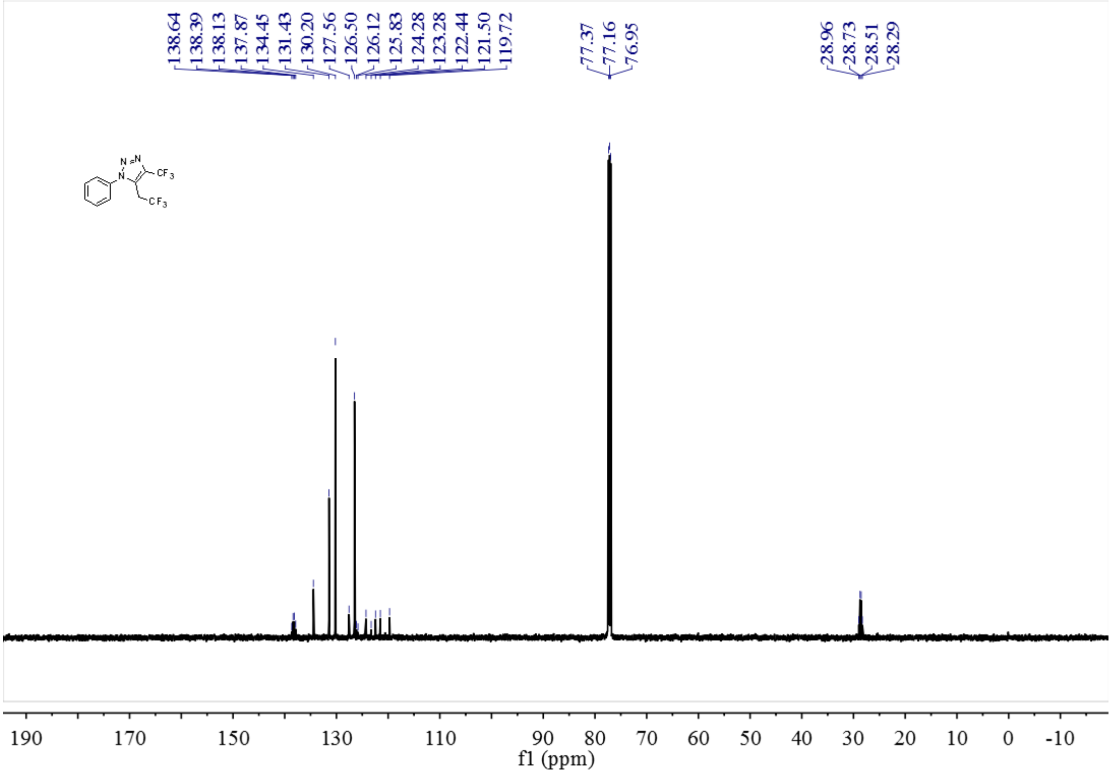
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28.96
28.73
28.51
28.29
N
N
N
CF3
CF3
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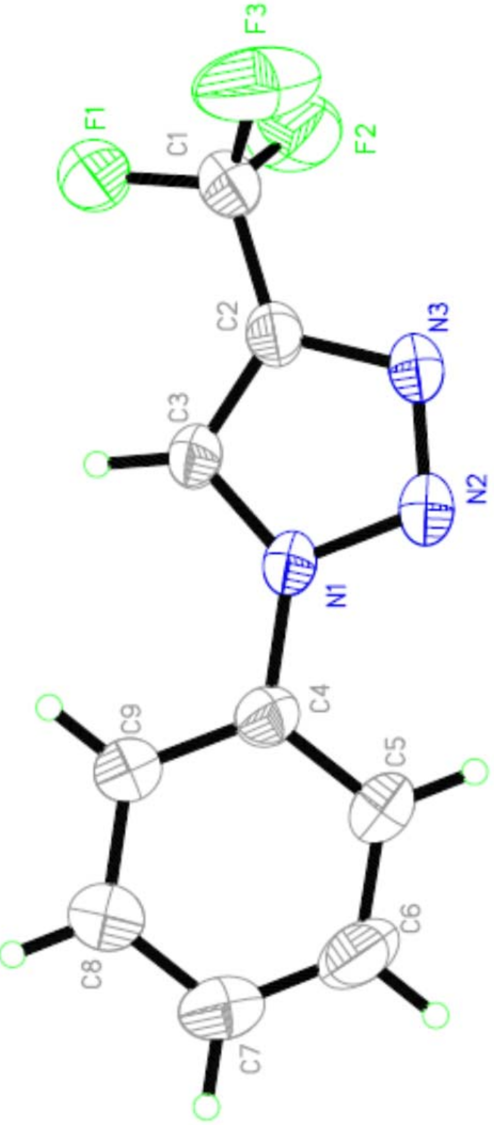
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5-^{13}C NMR

X-Ray Analysis for the product 2a

CCDC 1024377 contains the supplementary crystallographic data for the product **2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk /data_request/cif.



X-Ray Analysis for the product 5

CCDC 1024379 contains the supplementary crystallographic data for the product **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk /data_request/cif.