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Supplementary Information

Visible-light-enabled oxyazidation of alkenes leading to α-azidoketones in air

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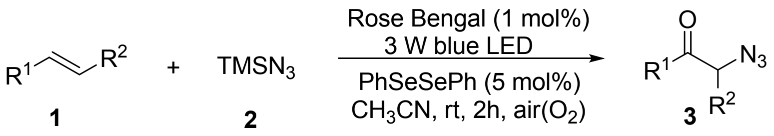
Contents

1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, and Alfa Aesar and used as received without further purification. Solvents (Analytical reagent) were purchased from Tian in Fuyu Fine Chemcial Company and used as received without further purification. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

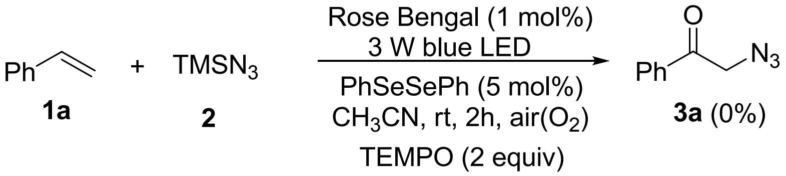
2. General procedure for visible-light-induced oxyazidation of alkenes leading to α-azidoketones.



To a solution of $TMSN_3$ **2** (0.4 mmol), PhSePh (0.01mmol, 5 mol%) and Rose Bengal (0.002 mmol, 1 mol %) in CH_3CN 2 mL was added alkene **1** (0.2 mmol). The reaction mixture was stirred in air under the irradiation of 3w blue LED at room temperature for 2h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.

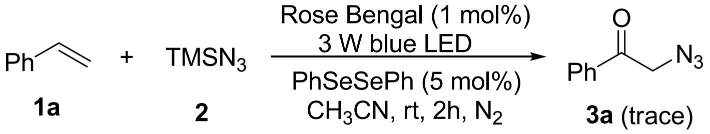
3. Preliminary mechanistic studies

3.1 The addition of TEMPO in the model reaction system.



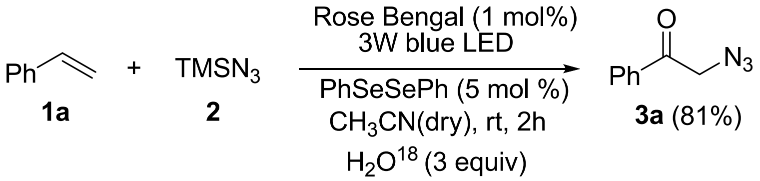
To a solution of $TMSN_3$ **2** (0.4 mmol), TEMPO (0.4 mmol), PhSeSePh (0.01mmol, 5 mol %) and Rose Bengal (0.002 mmol, 1 mol %) in CH_3CN 2 mL was added styrene **1a** (0.2 mmol). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 2h. After completion of the reaction, the solution was concentrated in vacuum, no desired product **3a** was detected.

3.2 The model reaction was carried out under N_2.



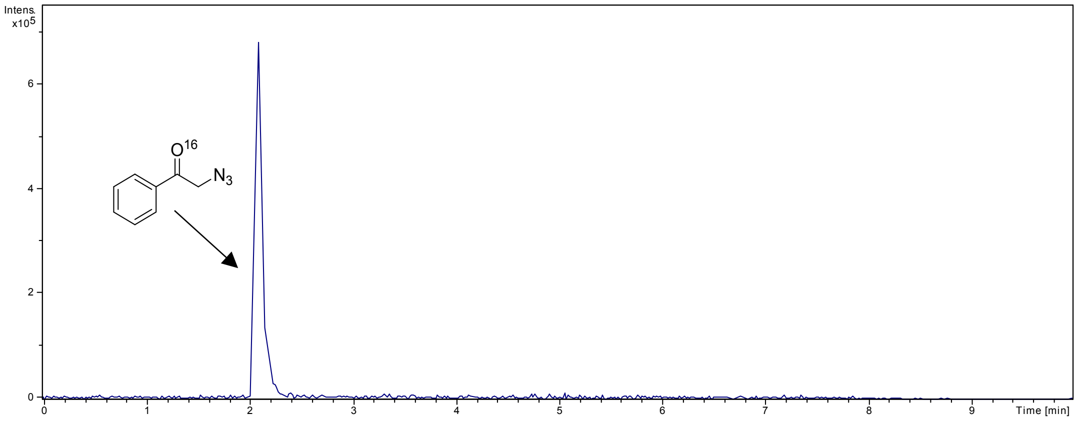
To a solution of $TMSN_3$ **2** (0.4 mmol), PhSeSePh (0.01mmol, 5 mol %) and Rose Bengal (0.002 mmol, 1 mol %) in CH_3CN 2 mL was added styrene **1a** (0.2 mmol). The reaction mixture was stirred in N_2 under the irradiation of 3W blue LED at room temperature for 2h. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of product **3a** was detected.

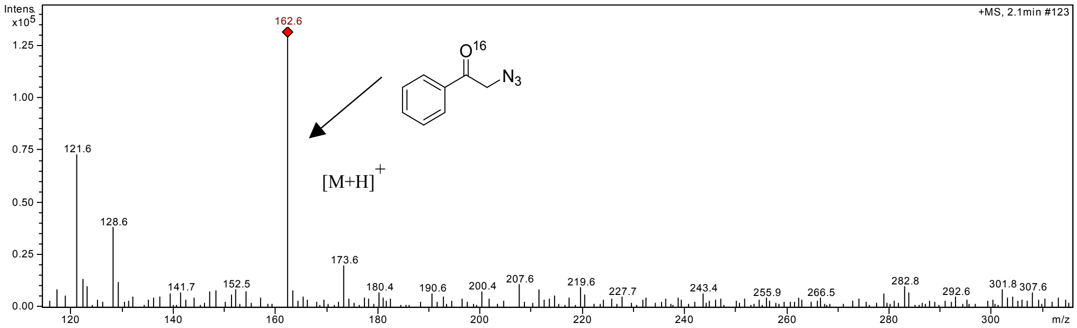
3.3 The model reaction was carried out under H_2O^{18} (^{18}O-labeling experiment).



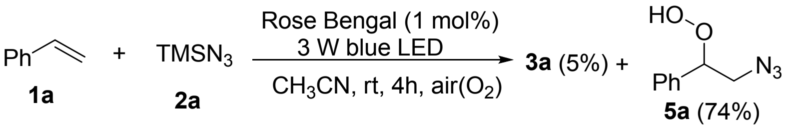
To a solution of $TMSN_3$ **2** (0.4 mmol), PhSeSePh (0.01mmol, 5 mol %), Rose Bengal (0.002 mmol, 1 mol %), and $H_2{}^{18}O$ (3 equiv) in CH_3CN (dry) 2 mL was added styrene **1a** (0.2 mmol). The reaction mixture was stirred in air under the irradiation of

3W blue LED at room temperature for 2h. After completion of the reaction, the solution was concentrated in vacuum, the product O^{16}-**3a** was obtained in 81% yield.



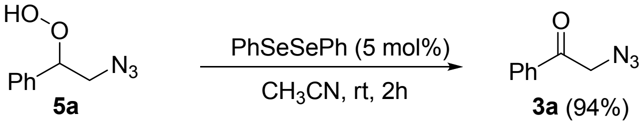


3.4 The model reaction was carried out in the absence of PhSeSePh.



To a solution of $TMSN_3$ **2** (0.4 mmol) and Rose Bengal (0.002 mmol, 1 mol %) in CH_3CN 2 mL was added styrene **1a** (0.2 mmol). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 4h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a** and (2-azido-1-hydroperoxyethyl)benzene **5a** in 5% and 74% yield, respectively.

3.5 The transformation of 5a to product 3a in the presence of PhSeSePh.



To a solution of (2-azido-1-hydroperoxyethyl)benzene **5a** (0.1 mmol) in CH_3CN 2 mL was added PhSePh (0.005mmol, 5 mol %). The reaction mixture was stirred in air at room temperature for 2h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a** in 94% yield.

3.6 The UV-visible spectroscopy and Fluorescence quenching studies (Stern – Volmer Studies)

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing Rose Bengal, PhSeSePh, $TMSN_3$ and styrene with solvent CH_3CN (M[Rose Bengal] = 2.0×10^{-5}mol/L, M[styrene] = 2.0×10^{-3}mol/L, M[$TMSN_3$] = 4.0×10^{-3}mol/L,M[Ph-se-se-Ph] =1.0×10^{-4}mol/L) in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 560 nm. The absorption was collected and the result was listed in Figure S1.

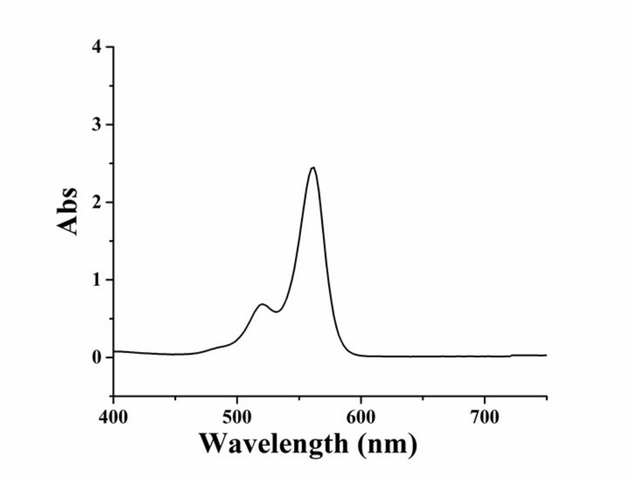


Figure S1. UV–vis spectra of the reaction mixture.

The fluorescence emission intensity of reaction solution was recorded on a Fluoromax-4600 spectrofluorimeter. The excitation wavelength was fixed at 521nm, and the emission wavelength was masured at 583 nm. The sample was prepared by mixing Rose Bengal, styrene, $TMSN_3$, Ph-se-se-Ph with solvent CH_3CN (M[Rose Bengal] = 2.0×10^{-6}mol/L, M[styrene] = 2.0×10^{-4}mol/L, M[$TMSN_3$] = 4.0×10^{-4}mol/L, M[Ph-se-se-Ph] = 1.0×10^{-5}mol/L) in a light path quartz fluoresence cuvette. The emission intensity was collected and the result was listed in Figure S2.

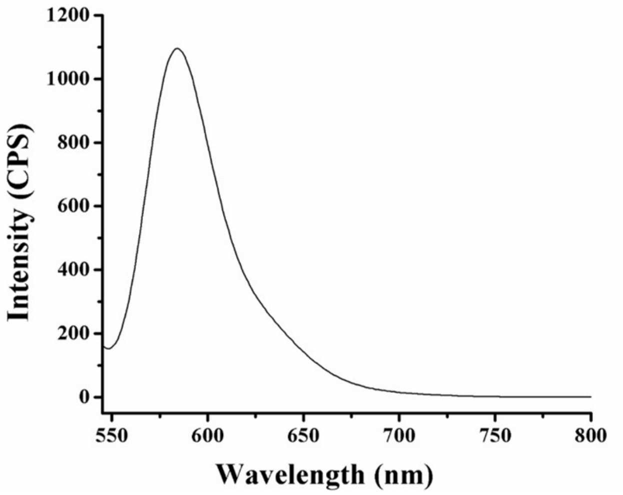


Figure S2. Fluorescence spectra of the reaction mixture

The fluorescence emission intensities were recorded on a Fluormax-4600 spespectrofluorimeter. The excitation wavelength was fixed at 521nm, and the emission wavelength was measured at 571 nm (emission maximum). The samples were prepared by mixing by Rose Bengal (2.0×10^{-6}mol/L) and different amount of $TMSN_3$ in CH_3CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of $TMSN_3$ stock solution is 4.0×10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of $TMSN_3$ stock solution was titrated to a mixed solution of Rose Bengal (0.1mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S3.

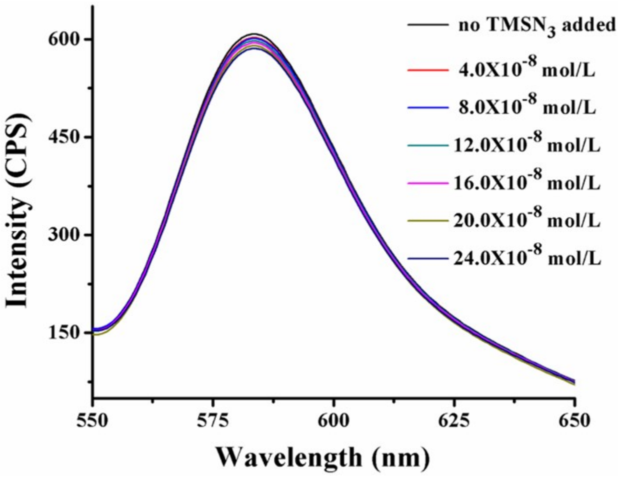


Figure S3. Quenching of Rose Bengal fluorescence emission in the presence of $TMSN_3$

An indeed fluorescence quenching phenomenon of Rose Bengal under various concentrations of $TMSN_3$ was demonstrated in a curve of $[I_0/I]$ vs C $[TMSN_3]$, as shown in Figure S4 (Stern-Volmer plots).

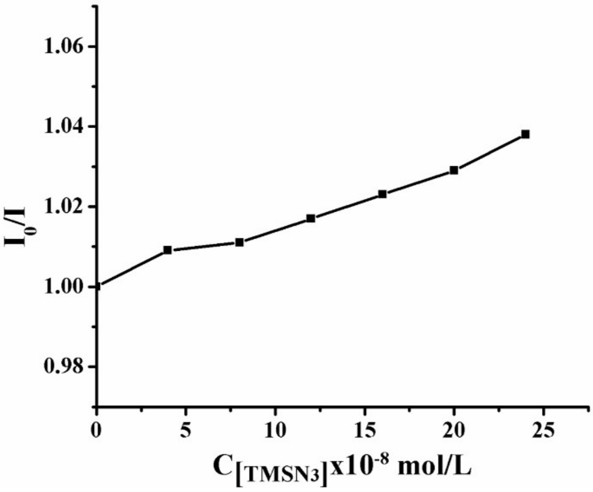


Figure S4. Stern-volmer plots

The fluorescence emission intensities were recorded on a Fluormax-4600 spespectrofluorimeter. The excitation wavelength was fixed at 521nm, and the emission wavelength was measured at 583 nm (emission maximum). The samples were prepared by mixing by Rose Bengal (2.0×10^{-6}mol/L) and different amount of styrene + PhSeSePh in CH_3CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of styrene stock solution is 2.0×10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of styrene stock solution was titrated to a mixed solution of Rose Bengal (0.1mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S5.

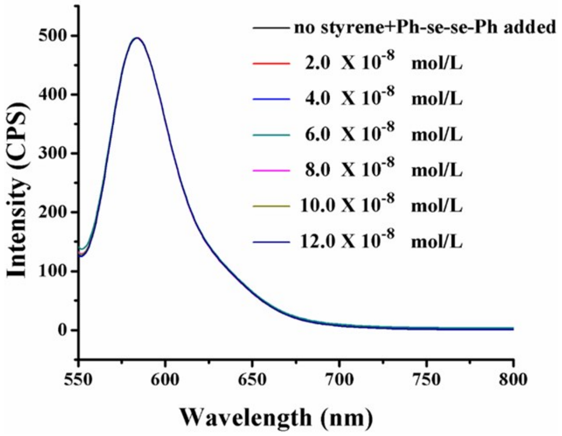


Figure S5. Quenching of Rose Bengal fluorescence emission in the presence of styrene +PhSeSePh

An indeed fluorescence quenching phenomenon of Rose Bengal under various concentrations of styrene +PhSeSePh was demonstrated in a curve of $[I_0/I]$ vs C [styrene + PhSeSePh], as shown in Figure S6 (Stern-Volmer plots).

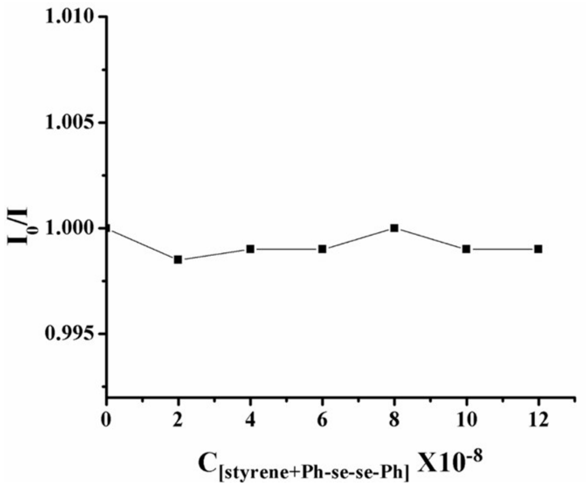
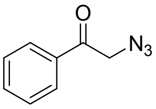
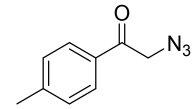


Figure S6 Stern-Volmer plots

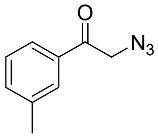
4. Characterization data of products 3a−3u, 5a



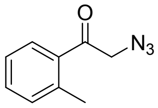
2-azido-1-phenylethanone.[1] Compound **4a** was obtained in 92% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.91 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 4.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 193.2, 134.4, 134.2, 129.0, 127.9, 54.9; HRMS calc. for $C_8H_7N_3ONa$ $(M+Na)^+$, 184.0487; found, 184.0491.



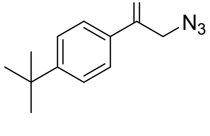
2-azido-1-p-tolylethanone.[2] Compound **4b** was obtained in 97% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.80 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.53 (s, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 192.8, 145.2, 131.9, 129.7, 128.0, 54.8, 21.8; HRMS calc. for $C_9H_9N_3ONa$ $(M+Na)^+$, 198.0643; found, 198.0647.



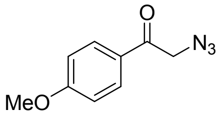
2-azido-1-m-tolylethanone. Compound **4c** was obtained in 96% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.71 (s, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 4.54 (s, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 193.4, 138.9, 134.9, 134.4, 128.8, 128.4, 125.1, 54.9, 21.3; HRMS calc. for $C_9H_9N_3ONa$ $(M+Na)^+$, 198.0643; found, 198.0644.



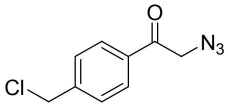
2-**azido-1-o-tolylethanone.** Compound **3d** was obtained in 85% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.57 (d, J = 7.8 Hz, 1H), 7.46-7.42 (m, 1H), 7.31-7.27 (m, 2H), 4.45 (s, 2H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 196.3, 139.5, 134.3, 132.5, 132.5, 128.4, 126.0, 56.4, 21.5; HRMS calc. for $C_9H_9N_3ONa$ $(M+Na)^+$, 198.0643; found, 198.0646.



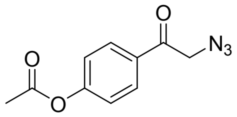
2-azido-1-(4-tert-butylphenyl)ethanone.[3] Compound **3e** was obtained in 86% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.85 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 4.54 (s, 2H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 192.8, 158.1, 131.8, 127.9, 126.0, 54.8, 35.3, 31.0.; HRMS calc. for $C_{12}H_{15}N_3ONa$ $(M+Na)^+$, 240.1113; found, 240.1117.



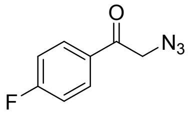
2-azido-1-(4-methoxyphenyl)ethanone.[4] Compound **3f** was obtained in 76% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.89 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 4.50 (s, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 191.7, 164.3, 130.3, 127.4, 114.2, 55.6, 54.6; HRMS calc. for $C_9H_9N_3O_2Na$ $(M+Na)^+$, 214.0592; found, 214.0591.



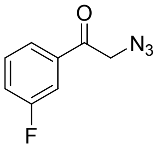
2-azido-1-(4-(chloromethyl)phenyl)ethanone. Compound **3g** was obtained in 93% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.90 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 4.62 (s, 2H), 4.55 (s, 2H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 192.7, 143.6, 134.2, 129.1, 128.4, 54.9, 45.1; HRMS calc. for $C_9H_8ClN_3ONa$ $(M+Na)^+$, 232.0254; found, 232.0256.



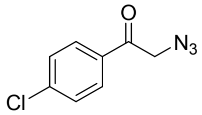
4-(2-azidoacetyl)phenyl acetate.[5] Compound **3h** was obtained in 87% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.94 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 4.54 (s, 2H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 192.1, 168.7, 155.1, 131.9, 129.6, 122.3, 54.8, 21.1; HRMS calc. for $C_{10}H_9N_3O_3Na$ $(M+Na)^+$, 242.0542; found, 242.0548.



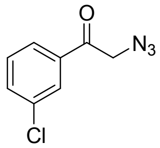
2-azido-1-(4-fluorophenyl)ethanone.[4] Compound **3i** was obtained in 77% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.97-7.94 (m, 2H), 7.18 (t, J = 8.5 Hz, 2H), 4.54 (s, 2H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 191.7, 167.3, 165.3, 130.7 (d, J = 9.5 Hz), 116.3 (d, J = 22.0 Hz), 54.8; HRMS calc. for $C_8H_6FN_3ONa$ $(M+Na)^+$, 202.0393; found, 202.0395.



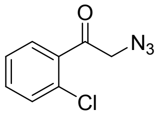
2-azido-1-(3-fluorophenyl)ethanone. Compound **3j** was obtained in 73% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.68 (d, J = 7.8 Hz, 1H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 1H), 7.35-7.32 (m, 1H), 4.55 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.1 (d, J = 2.2 Hz), 162.9 (d, J = 247.8 Hz), 136.3 (d, J = 6.3 Hz), 130.8 (d, J = 7.6 Hz), 123.7 (d, J = 3.1 Hz), 121.3 (d, J = 21.3 Hz), 114.8 (d, J = 22.4 Hz), 55.0; HRMS calc. for $C_8H_6FN_3ONa$ (M+Na)$^+$, 202.0393; found, 202.0396.



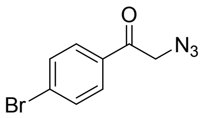
2-azido-1-(4-chlorophenyl)ethanone.[4] Compound **3k** was obtained in 74% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.85 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 4.53 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.1, 140.7, 132.7, 129.4, 129.4, 54.8; HRMS calc. for $C_8H_6ClN_3ONa$ (M+Na)$^+$, 218.0097; found, 218.0099.



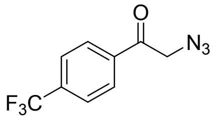
2-azido-1-(3-chlorophenyl)ethanone.[6] Compound **3l** was obtained in 85% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.89 (t, J = 1.7 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.61-7.59 (m, 1H), 7.45 (t, J = 7.9 Hz, 1H), 4.54 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.1, 135.8, 135.4, 134.1, 130.4, 128.1, 126.0, 55.0; HRMS calc. for $C_8H_6ClN_3ONa$ (M+Na)$^+$, 218.0097; found, 218.0094.



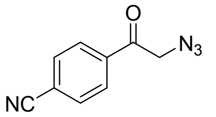
2-azido-1-(2-chlorophenyl)ethanone. Compound **3m** was obtained in 84% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.58 (d, J = 7.2 Hz, 1H), 7.48--7.44 (m, 2H), 7.39-7.36 (m, 1H), 4.52 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.3, 136.1, 133.1, 131.6, 130.8, 129.9, 127.3, 57.9; HRMS calc. for $C_8H_6ClN_3ONa$ (M+Na)$^+$, 218.0097; found, 218.0096.



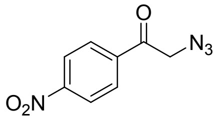
2-**azido-1-(4-bromophenyl)ethanone.**[3] Compound **3n** was obtained in 85% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.78 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 4.53 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.3, 133.1, 132.4, 129.5, 129.4, 54.8; HRMS calc. for $C_8H_6BrN_3ONa$ (M+Na)$^+$, 261.9592; found, 261.9593.



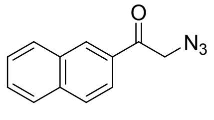
2-azido-1-(4-(trifluoromethyl)phenyl)ethanone. Compound **3o** was obtained in 56% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.03 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 4.59 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.1, 137.0, 135.4 (q, J = 32.9 Hz), 128.4, 126.1(q, J = 3.7 Hz), 123.3 (q, J = 271.2 Hz), 55.1; HRMS calc. for $C_9H_6F_3N_3ONa$ (M+Na)$^+$, 252.0361; found, 252.0366.



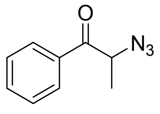
3-**(2-azidoacetyl)benzonitrile.**[7] Compound **3p** was obtained in 41% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.02 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 4.58 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.2, 137.3, 132.8, 128.5, 117.6, 117.5, 55.1; HRMS calc. for $C_9H_6N_4ONa$ (M+Na)$^+$, 209.0436; found, 209.0433.



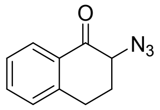
2-azido-1-(4-nitrophenyl)ethanone. Compound **3q** was obtained in 55% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.36 (d, J = 8.9 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 4.62 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 192.0, 150.9, 138.7, 129.1, 124.2, 55.3; HRMS calc. for $C_8H_6N_4O_3Na$ (M+Na)$^+$, 229.0338; found, 229.0341.



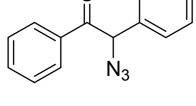
2-azido-1-(naphthalen-2-yl)ethanone.[3] Compound **3r** was obtained in 82% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.36 (s, 1H), 7.96-7.87 (m, 4H), 7.64-7.55 (m, 2H), 4.67 (s, 2H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 193.2, 136.0, 132.4, 131.7, 129.8, 129.6, 129.1, 129.0, 127.9, 127.2, 123.3, 55.0; HRMS calc. for $C_{12}H_9N_3ONa$ (M+Na)$^+$, 234.0643; found, 234.0644.



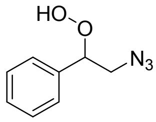
2-azido-1-phenylpropan-1-one. Compound **3s** was obtained in 63% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.95 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 4.73-4.69 (q, J = 7.0 Hz, 1H), 1.58 (d, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 196.7, 134.3, 133.9, 128.9, 128.7, 58.4, 16.5; HRMS calc. for $C_9H_9N_3ONa$ (M+Na)$^+$, 198.0643; found, 198.0645.



2-azido-3,4-dihydronaphthalen-1(2H)-one. Compound **3t** was obtained in 78% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.07 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 6.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 3.1 Hz, 1H), 4.23 (dd, J_1 = 4.7 Hz, J_2 = 12.1 Hz, 1H), 3.09-3.07 (m, 2H), 2.40-2.35 (m, 1H), 2.18-2.10 (m, 1H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 193.8, 143.4, 134.2, 131.1, 128.8, 128.0, 127.1, 64.3, 29.4, 27.6; HRMS calc. for $C_{10}H_9N_3ONa$ (M+Na)$^+$, 210.0643; found, 210.0647.



2-azido-1,2-diphenylethanone.[8] Compound **3u** was obtained in 69% yield according to the general procedure. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.88 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.40-7.37 (m, 7H), 5.72 (s, 1H); ^{13}C NMR (CDCl$_3$, 125MHz, ppm): δ 194.4, 134.4, 133.8, 133.8, 129.6, 129.4, 128.9, 128.8, 128.3, 67.9; HRMS calc. for $C_{14}H_{11}N_3ONa$ $(M+Na)^+$, 260.0800; found, 260.0807.



5a

(2-azido-1-hydroperoxyethyl)benzene,[9] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.34 (s, 1H), 7.42-7.35 (m, 5H), 5.12 (dd, J_1 = 4.2 Hz, J_2 = 7.8 Hz, 1H), 3.63(dd, J_1 = 7.9 Hz, J_2 = 13.4 Hz, 1H), 3.47 (dd, J_1 = 4.2 Hz, J_2 = 13.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): δ 136.9, 129.1, 128.9, 126.9, 86.5, 53.3.

References:

(1) Su, Y.; Petersen, J. L.; Gregg, T. L.; Shi, X. *Org. Lett.* **2015**, *17*, 1208-1211.

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(5) Nair, V.; Nair, L. G.; George, T. G.; Augustine, A.*Tetrahedron* **2000**, *56*,7607-7611.

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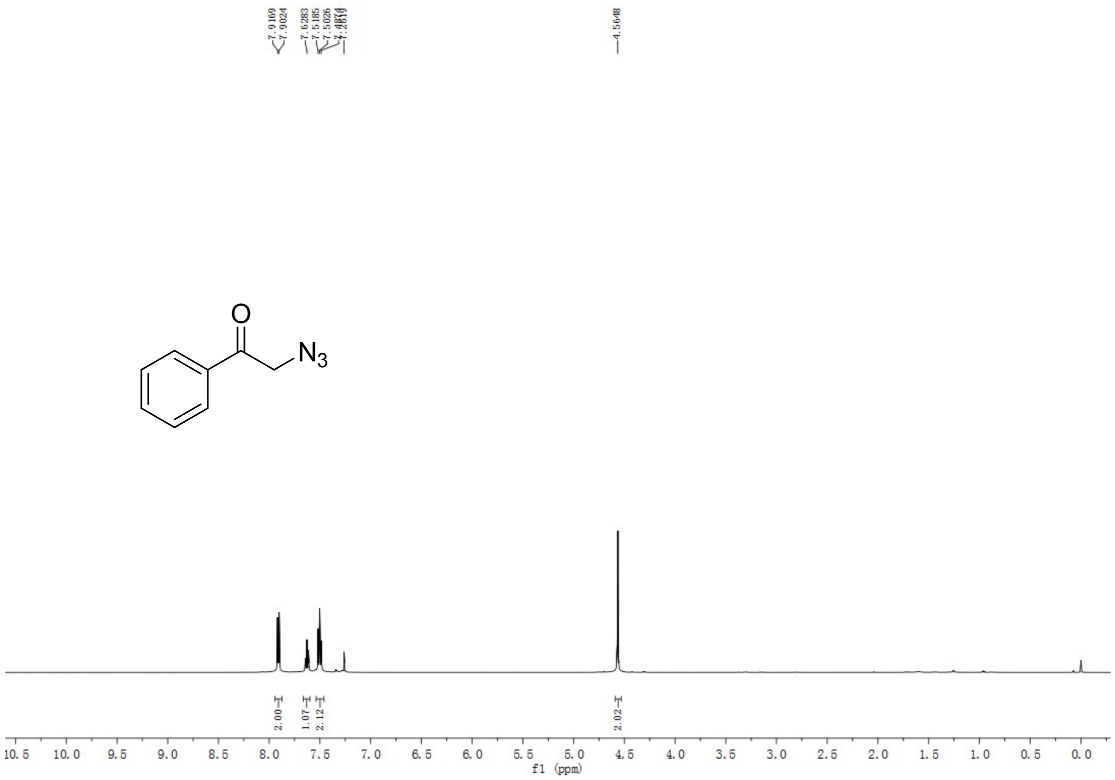
(8) Soltani Rad, M. N.; Behrouz, S.; Khalafi-Nezhad, A. *Tetrahedron Lett.* **2007**, *48*, 3445-3449.

(9) X. Sun, X. Li, S. Song, Y. Zhu, Y.-F. Liang and N. Jiao, *J. Am. Chem. Soc.* **2015**, 137, 6059;

5. Copies of NMR spectra for 3a−3u,5a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2.12
2.02
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9.0
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8.0
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7.0
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6.0
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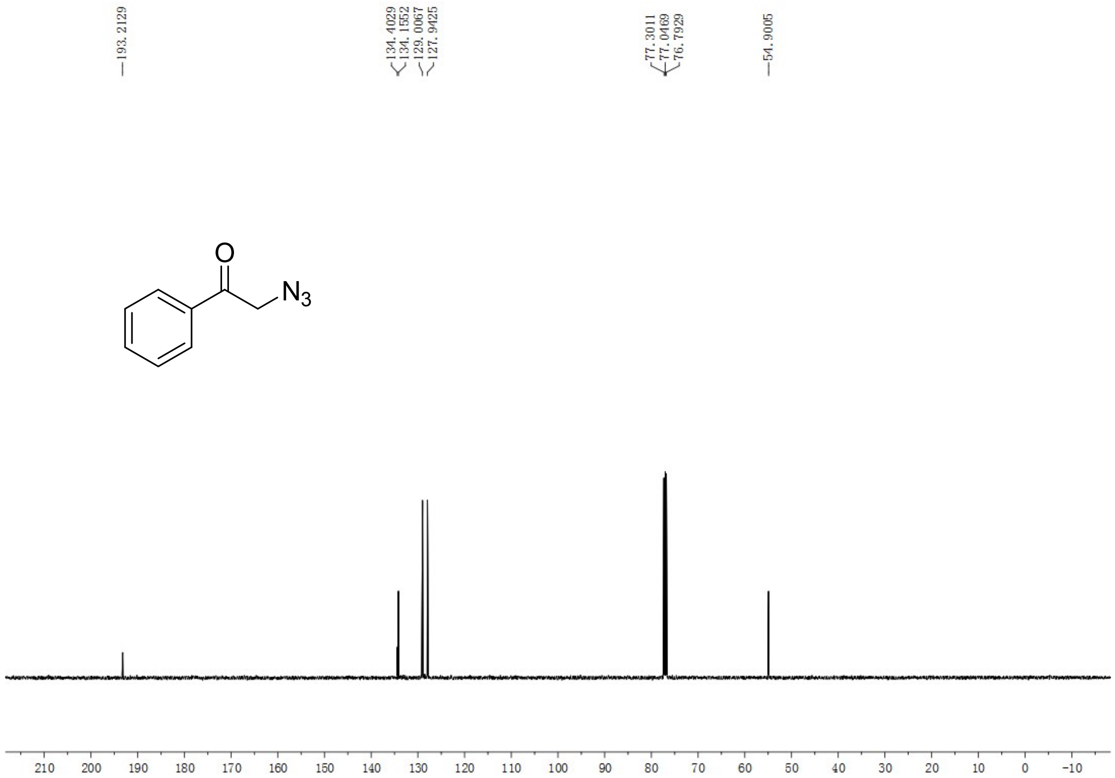
f1 (ppm)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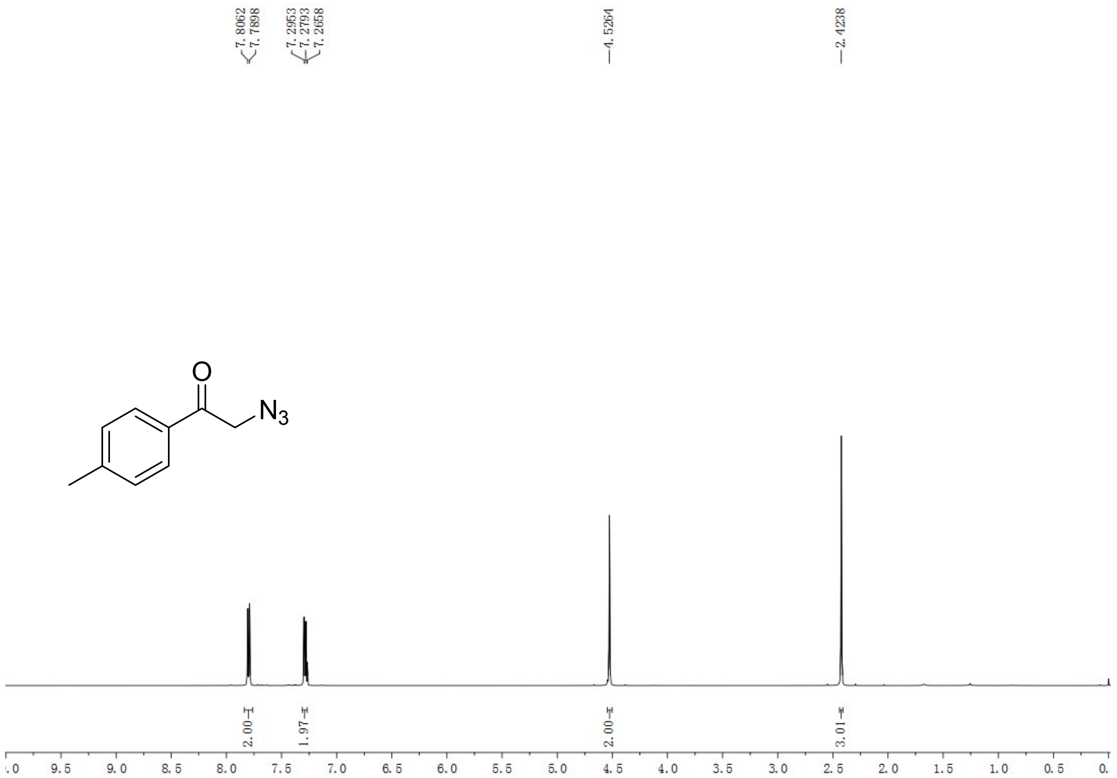
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8.0
7.5
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6.5
6.0
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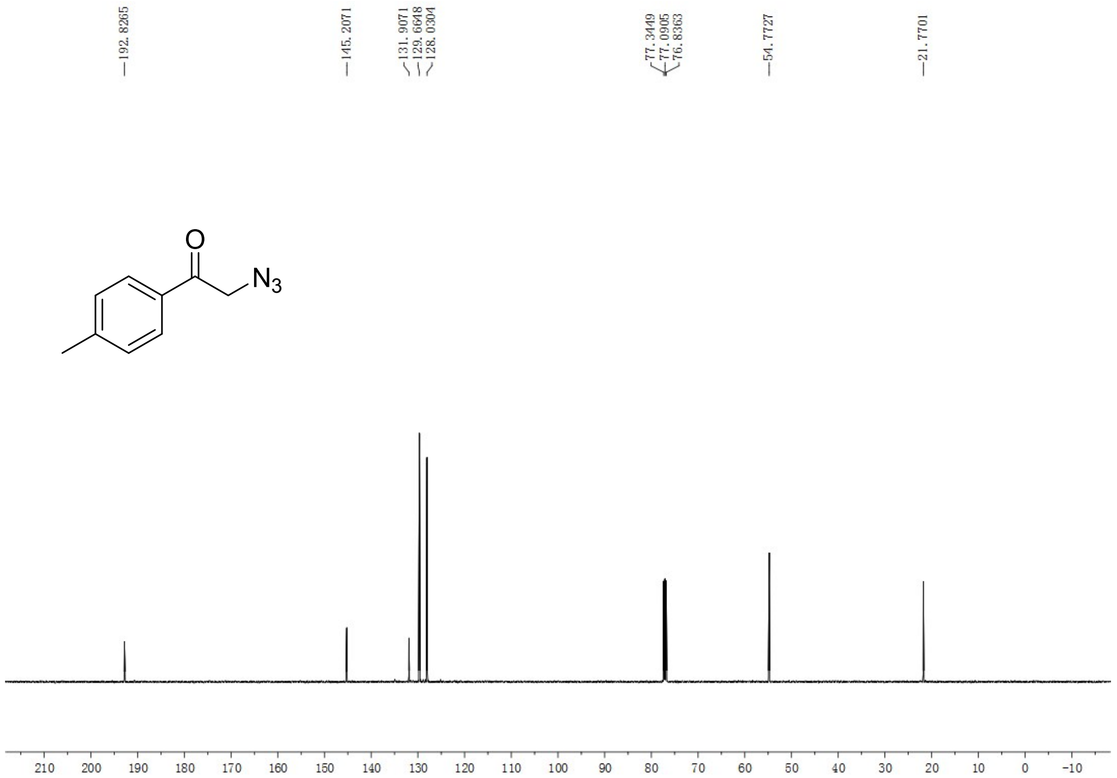
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200
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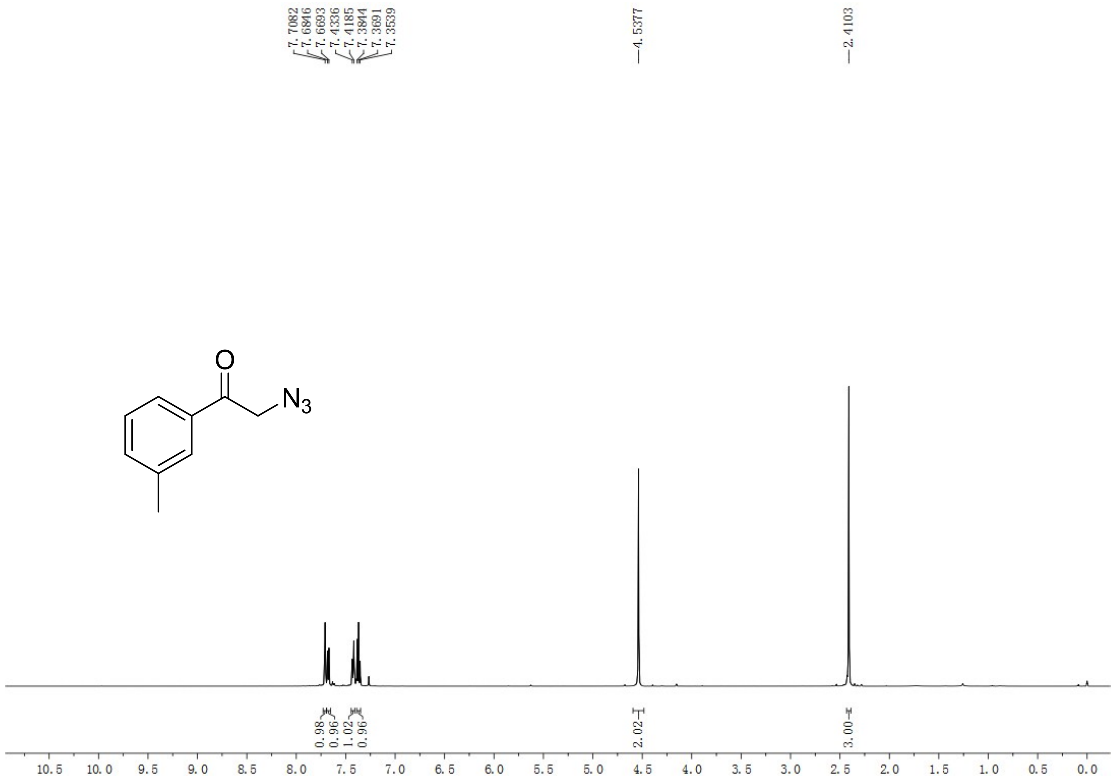
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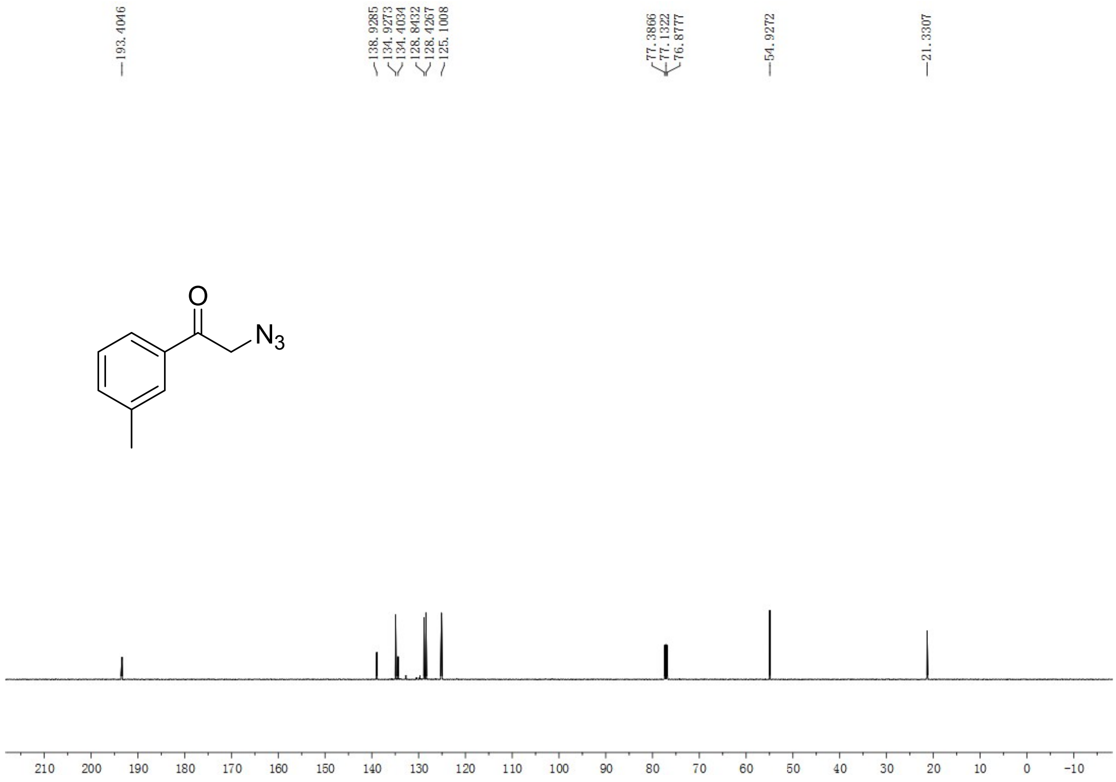
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N3
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200
190
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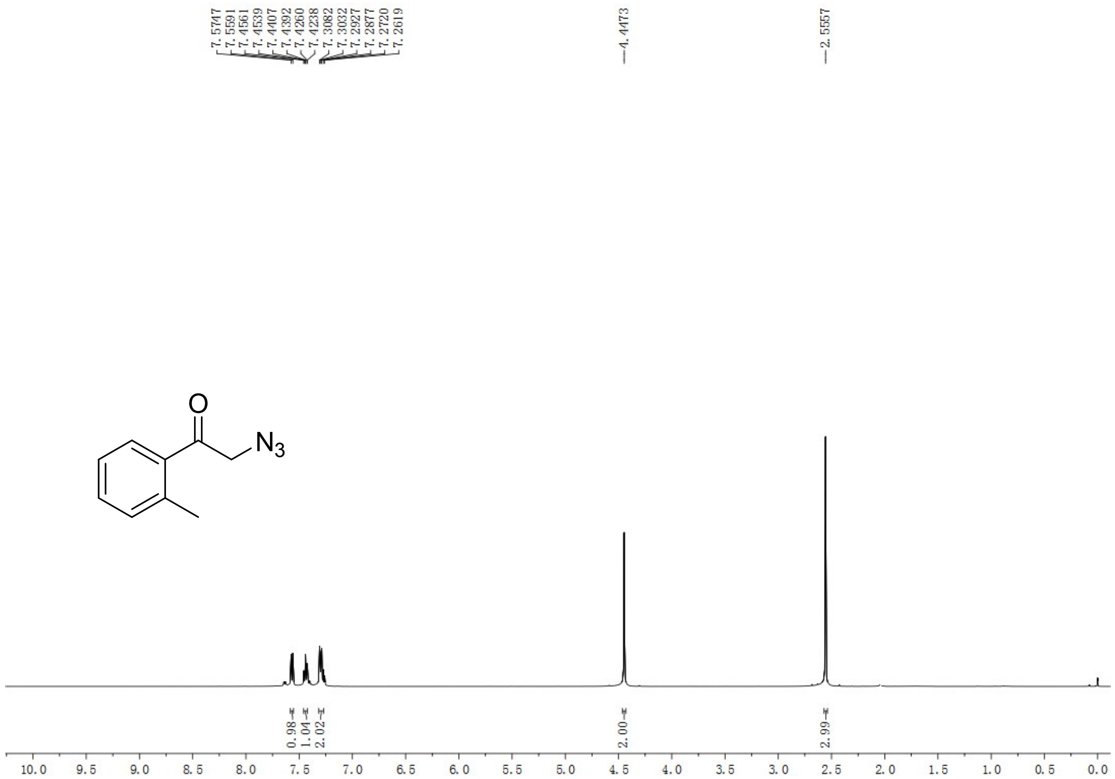
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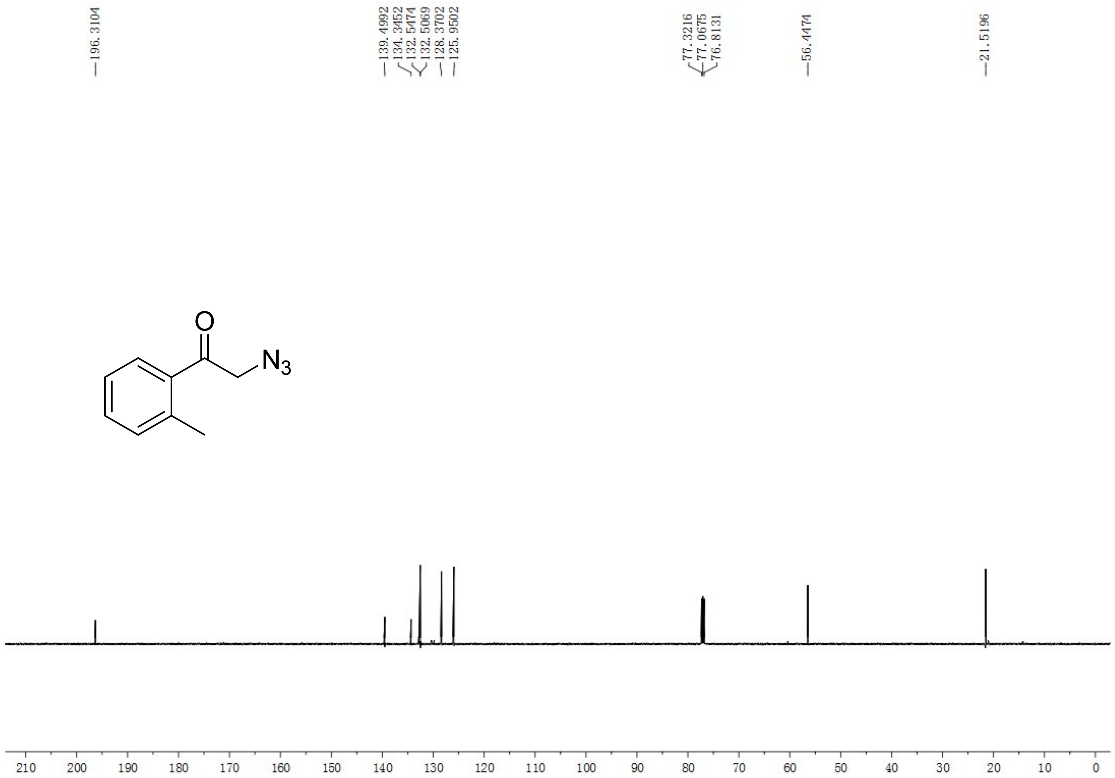
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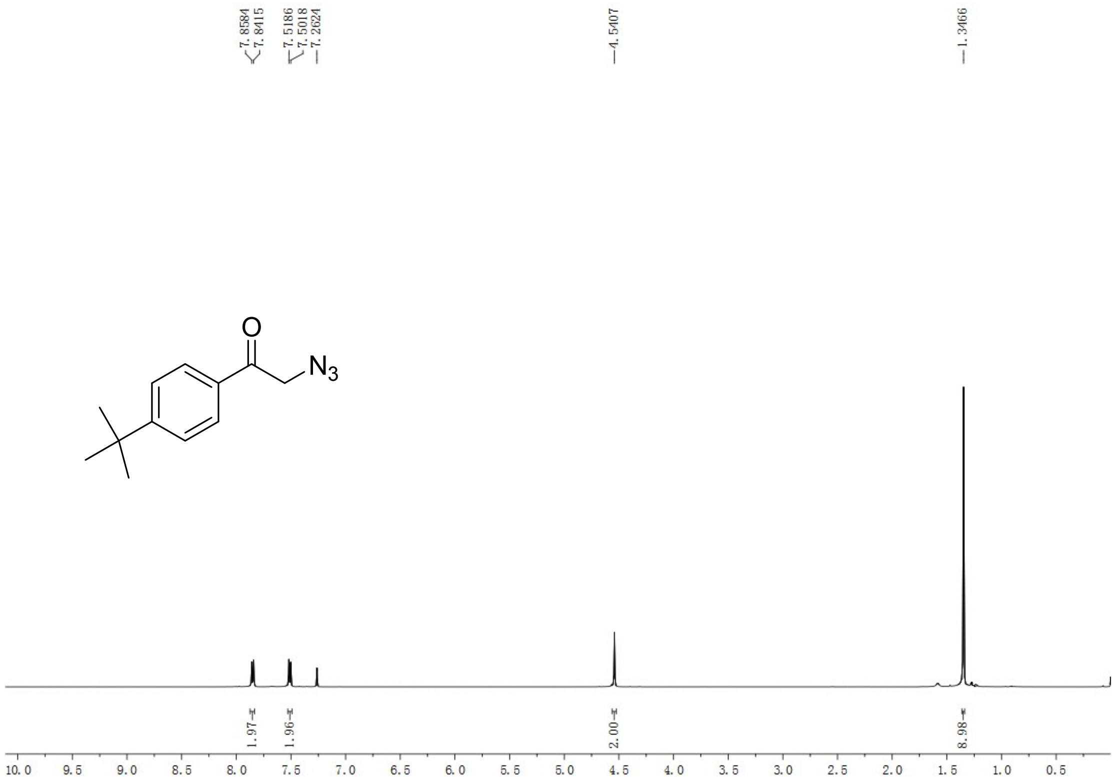
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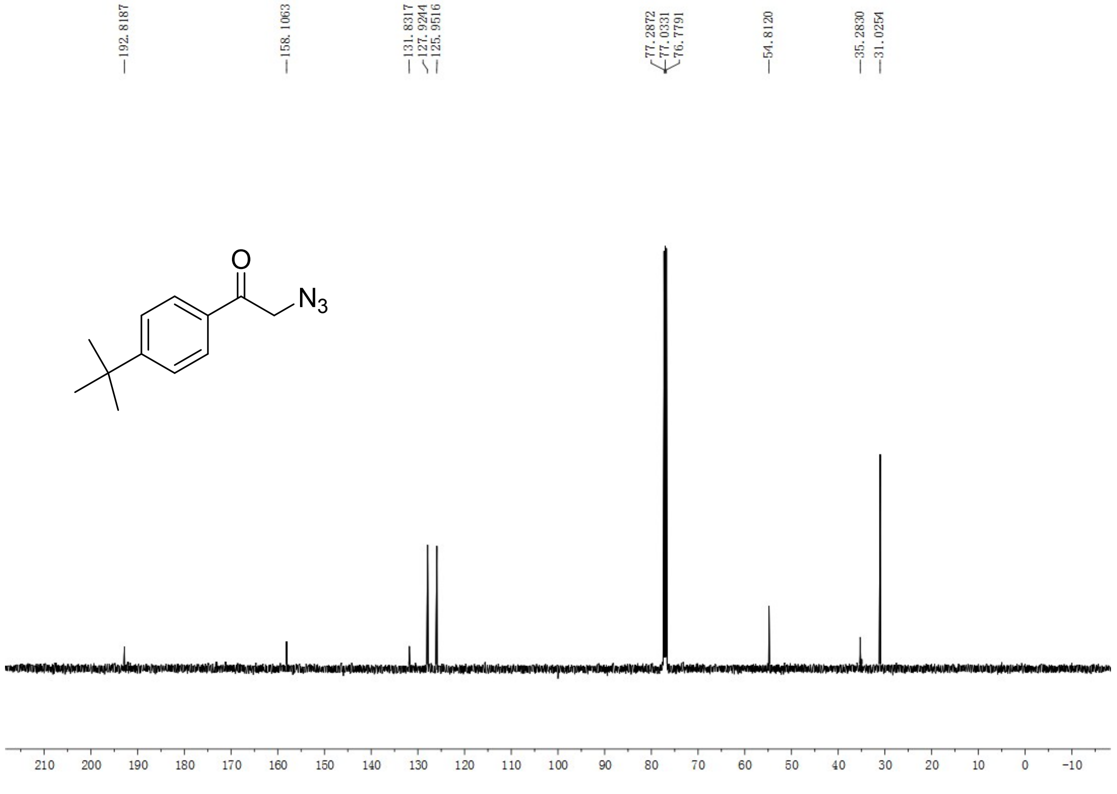
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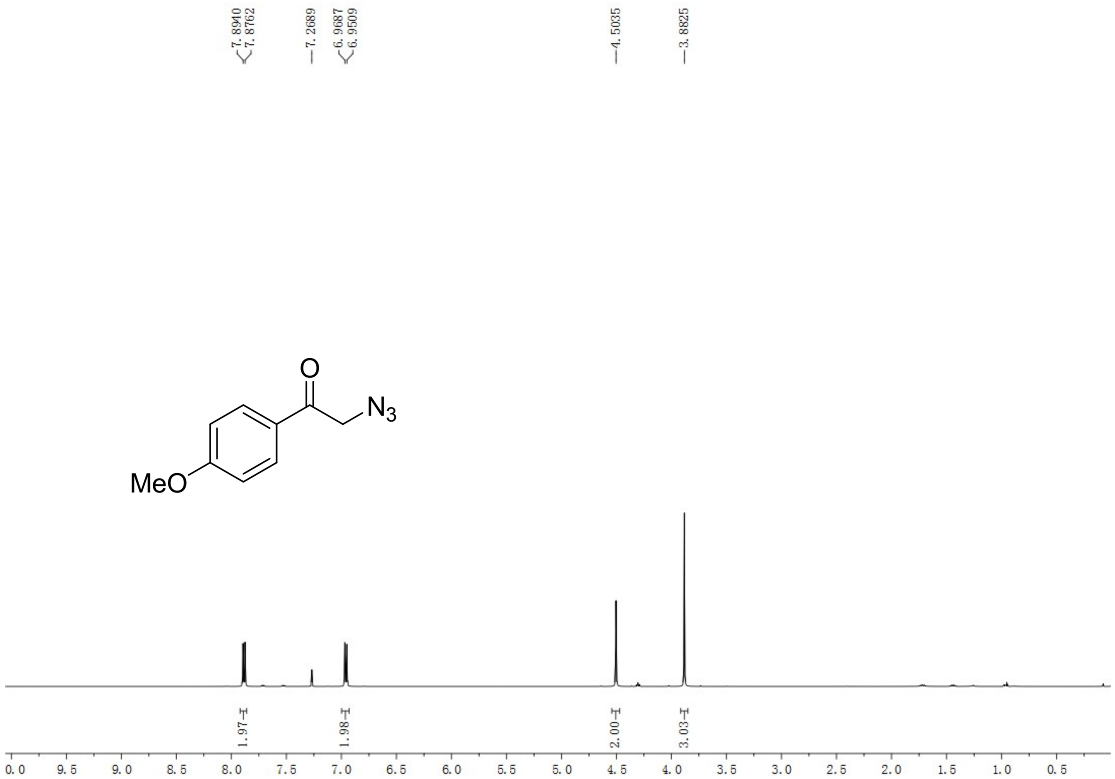
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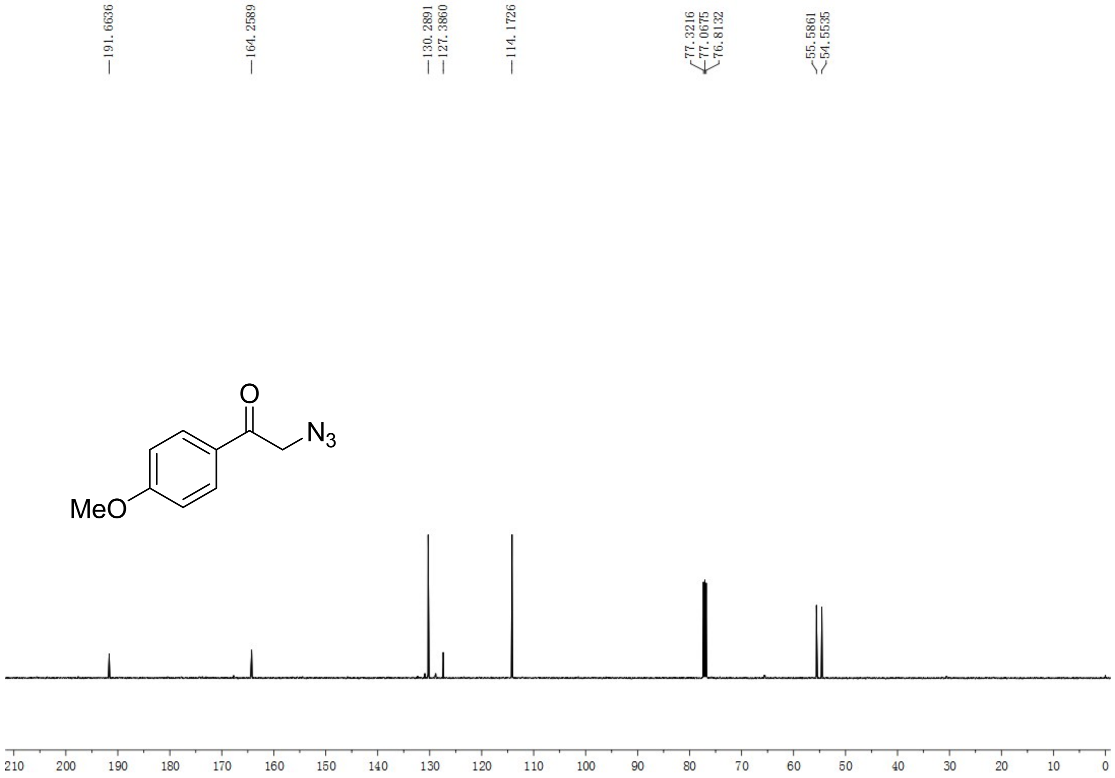
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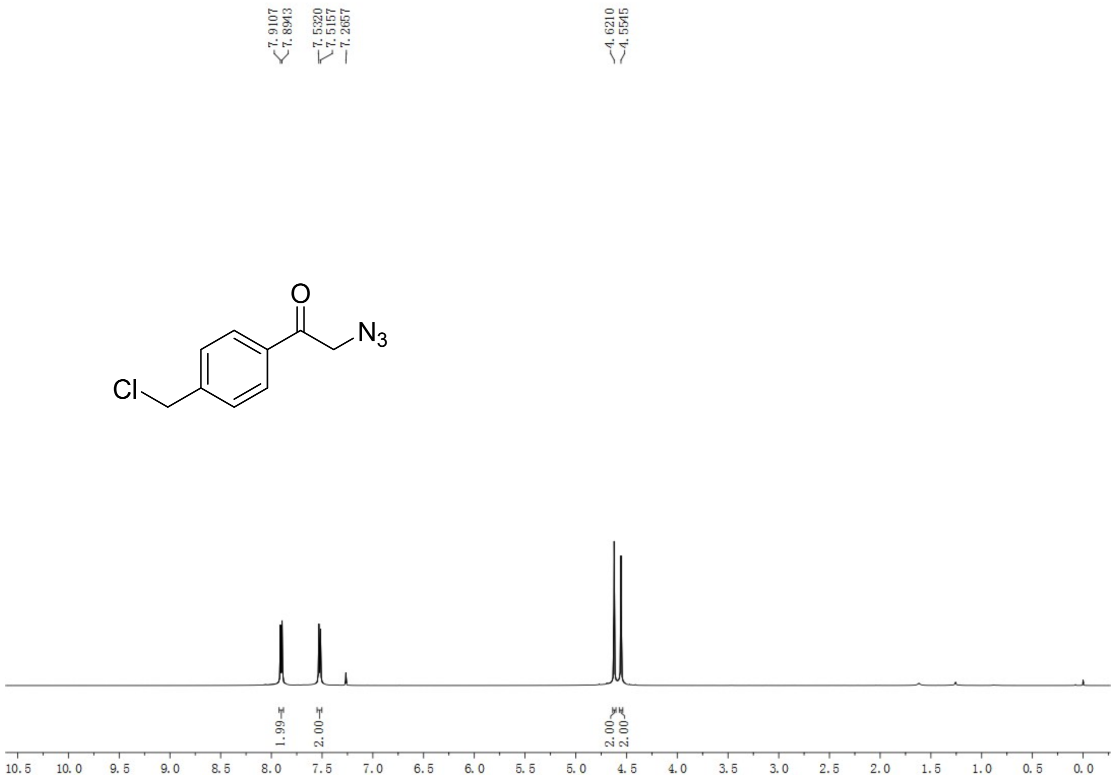
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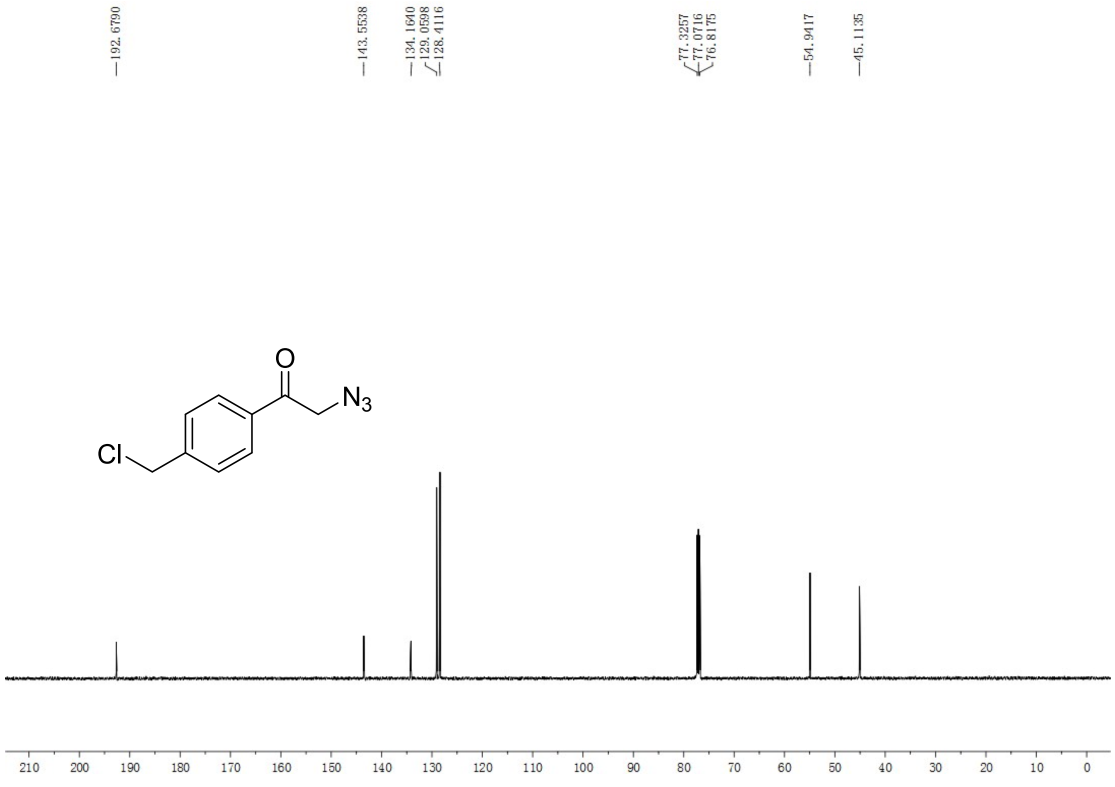
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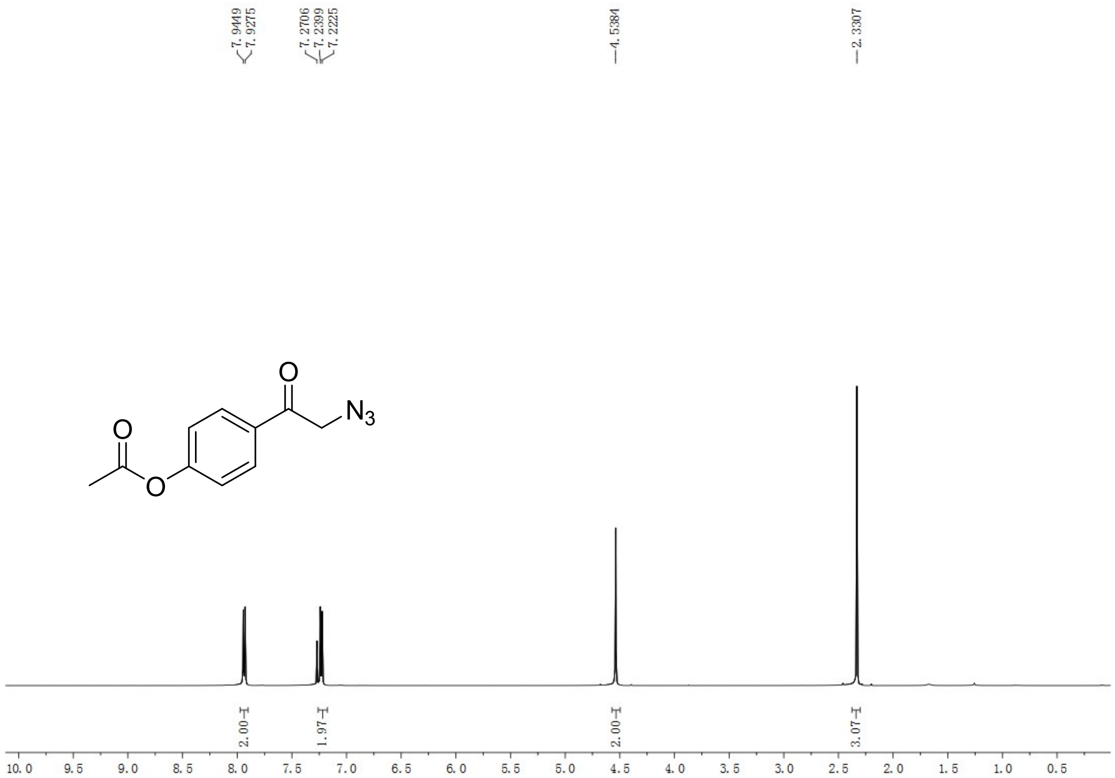
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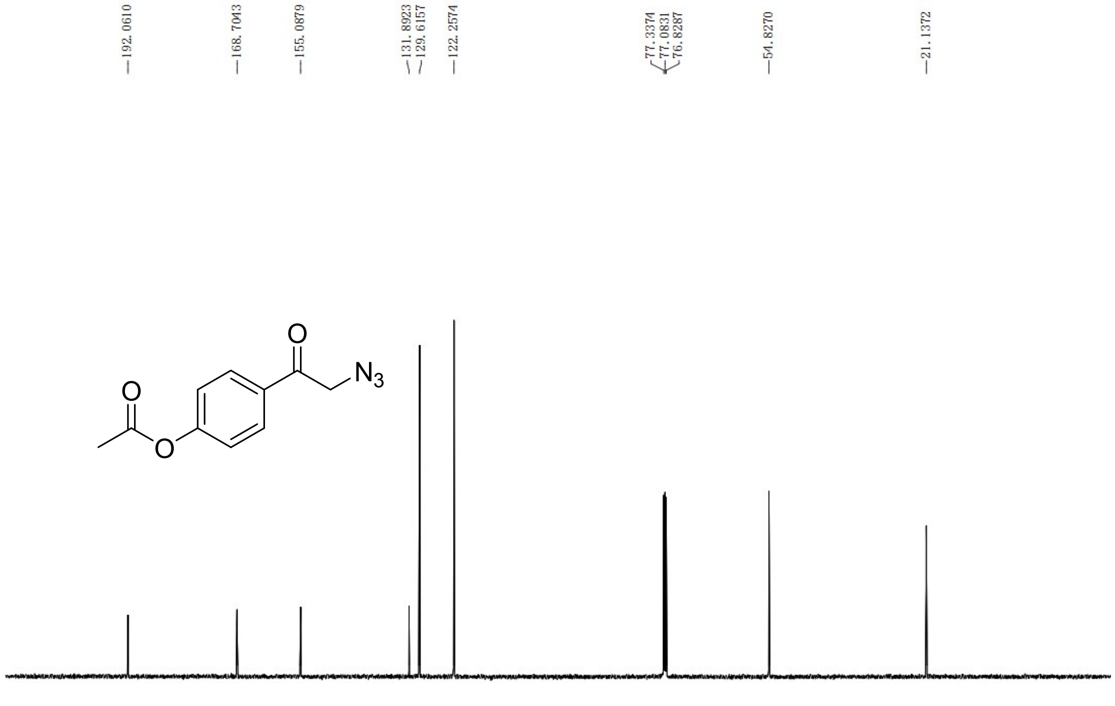
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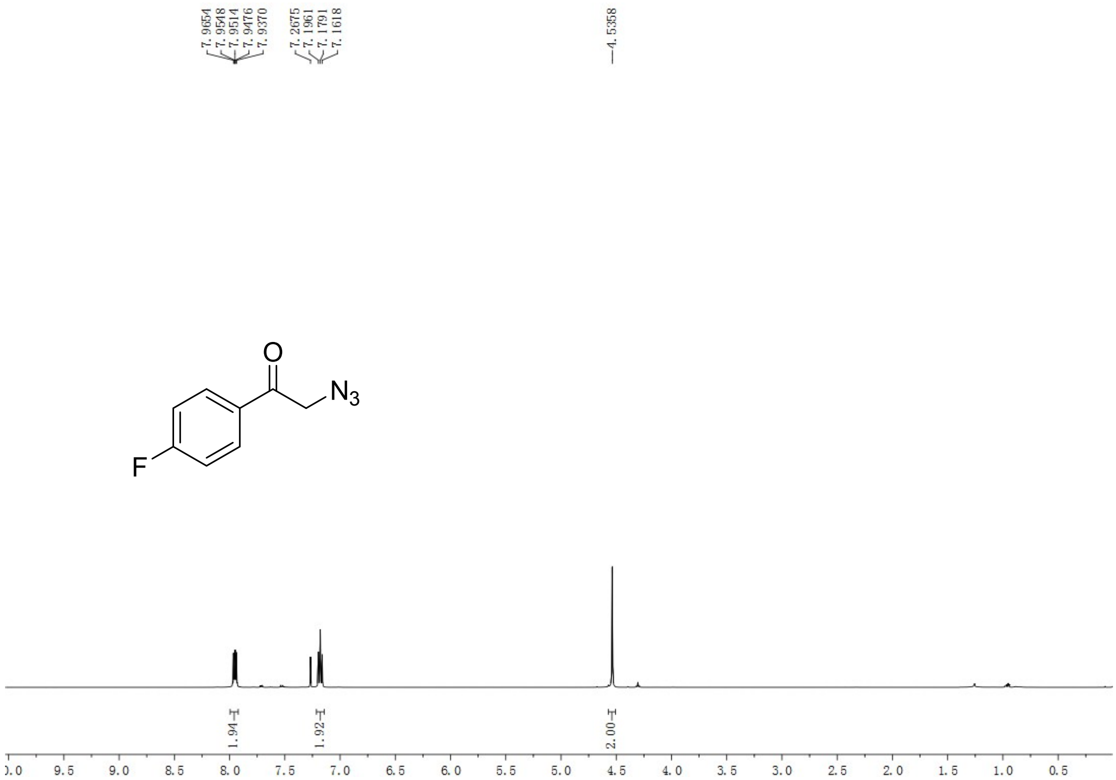
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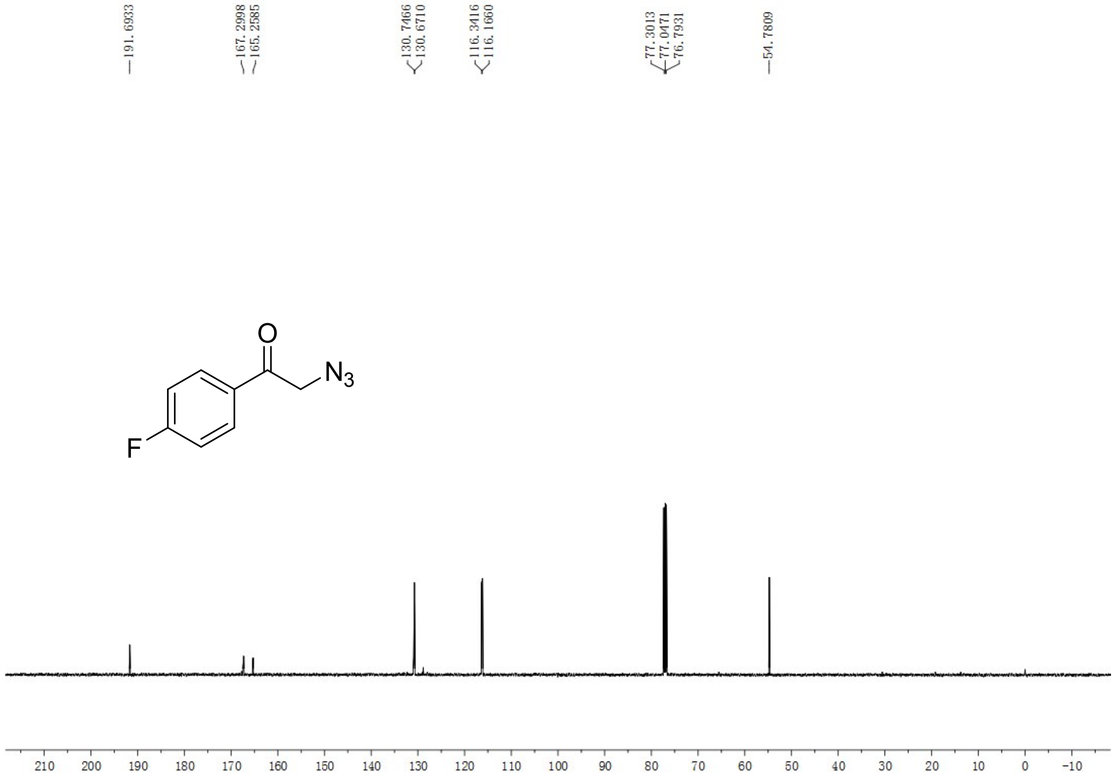
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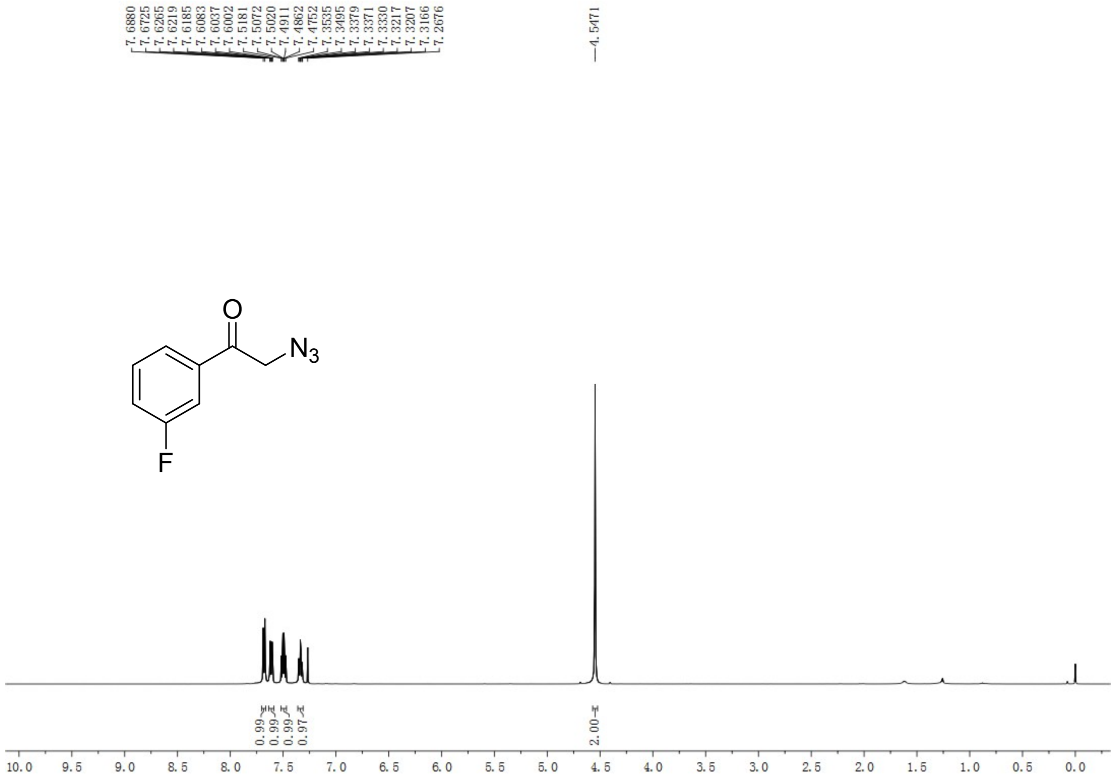
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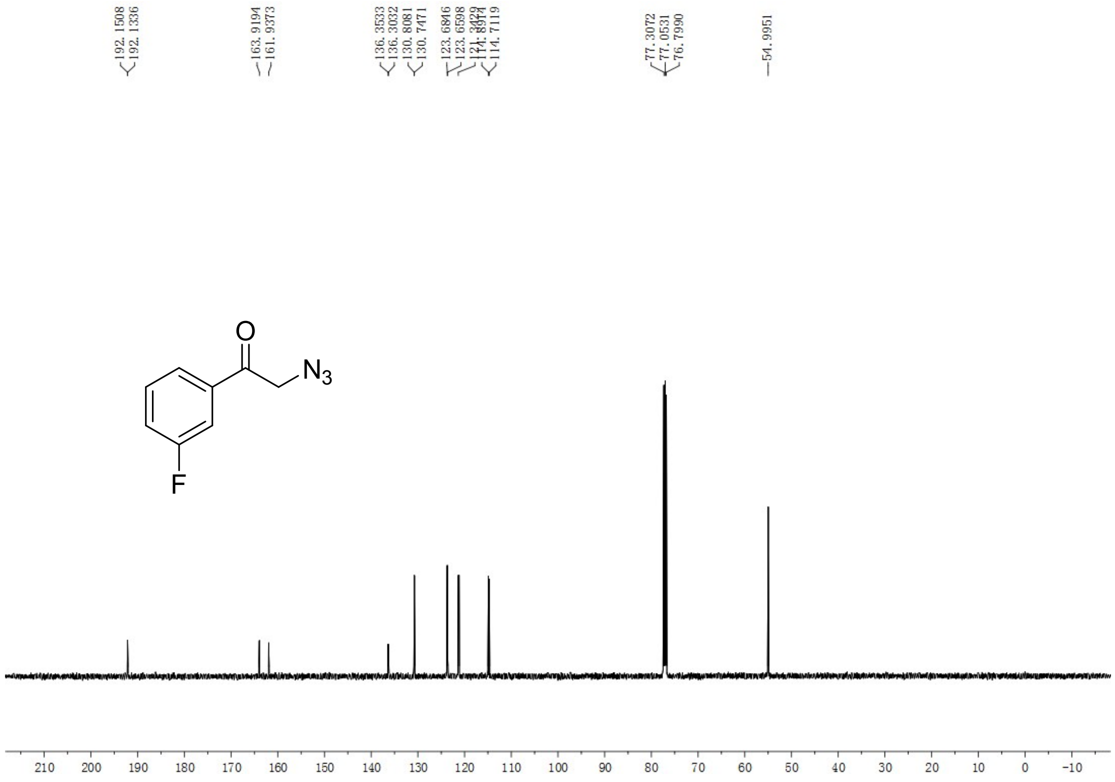
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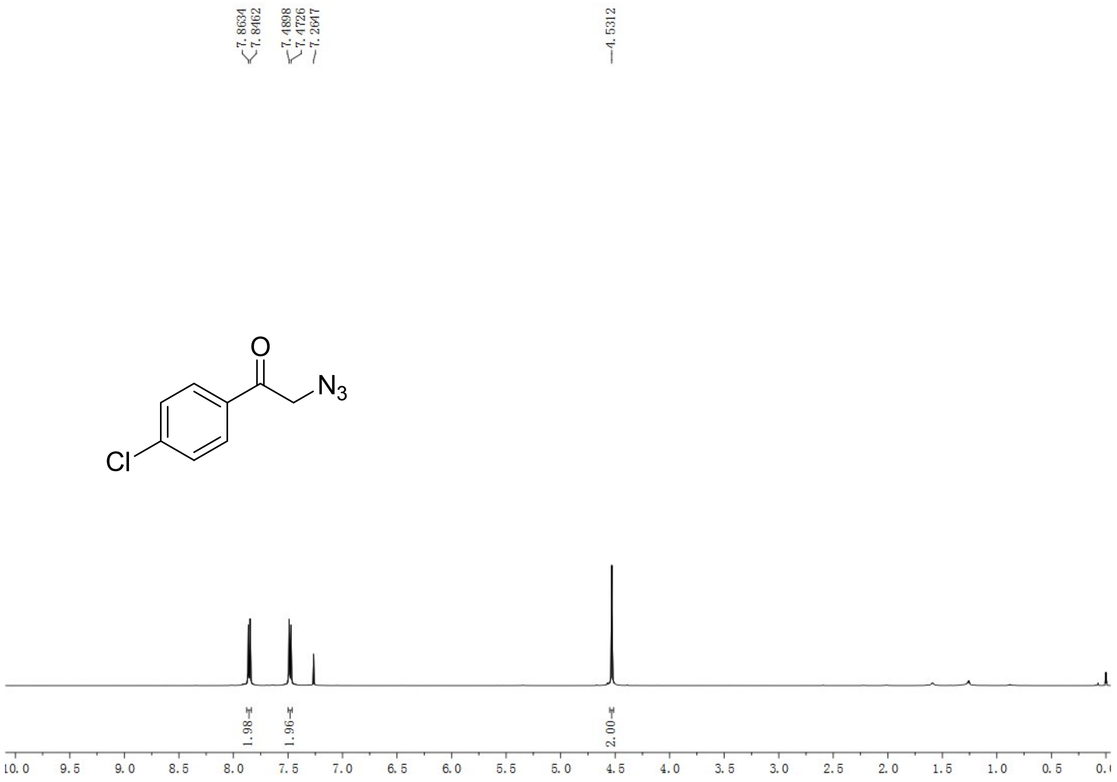
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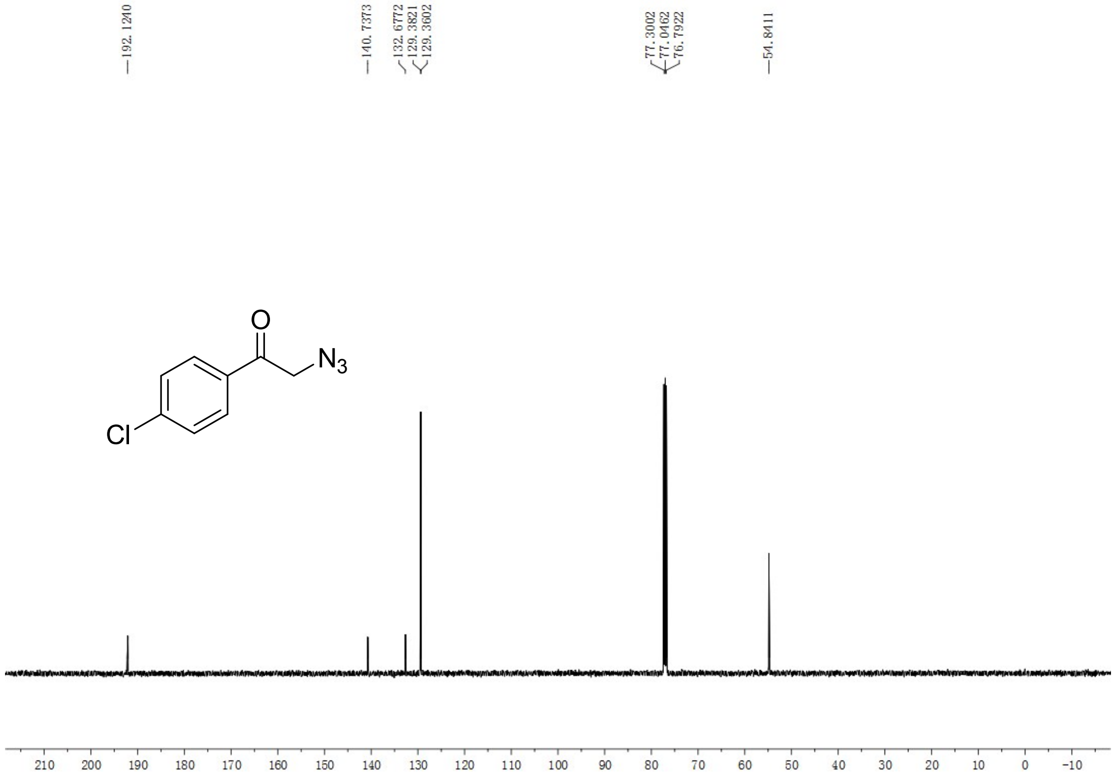
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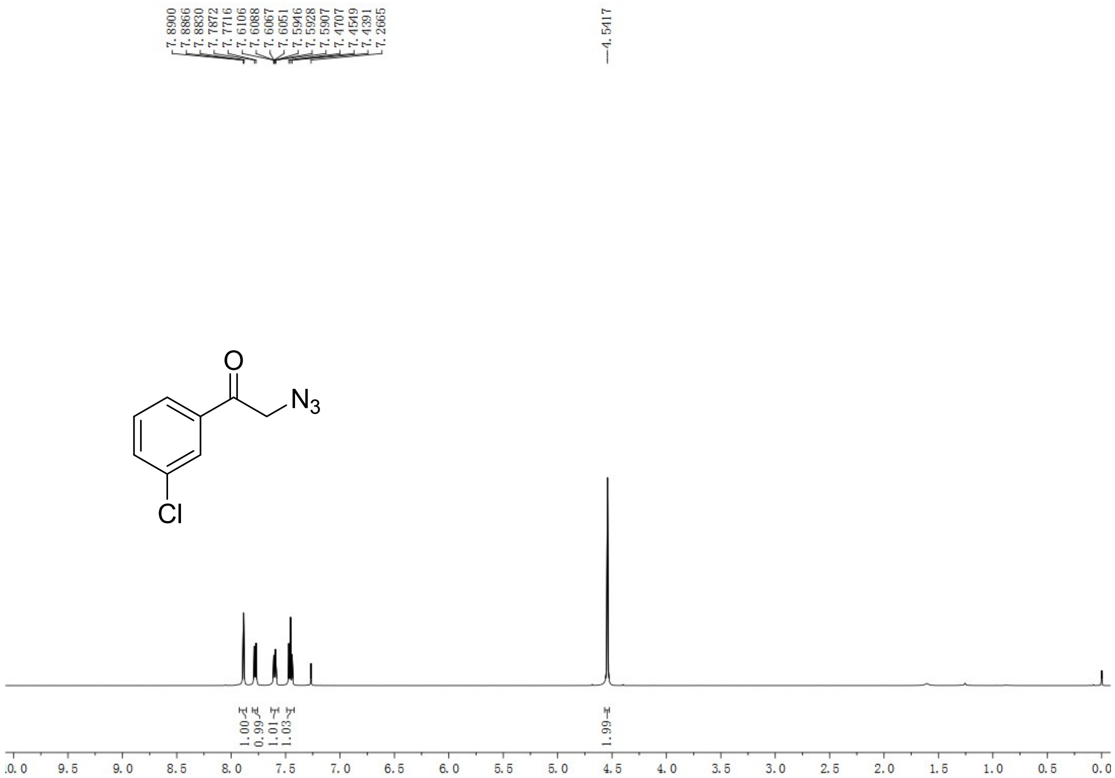
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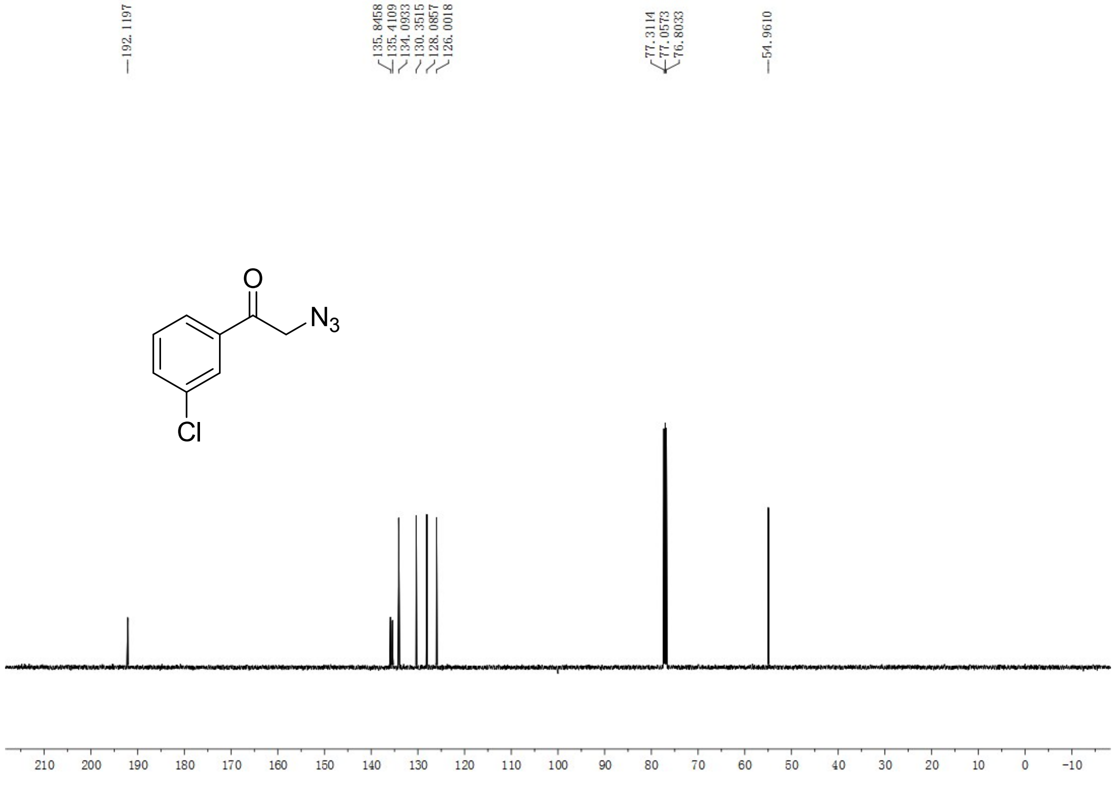
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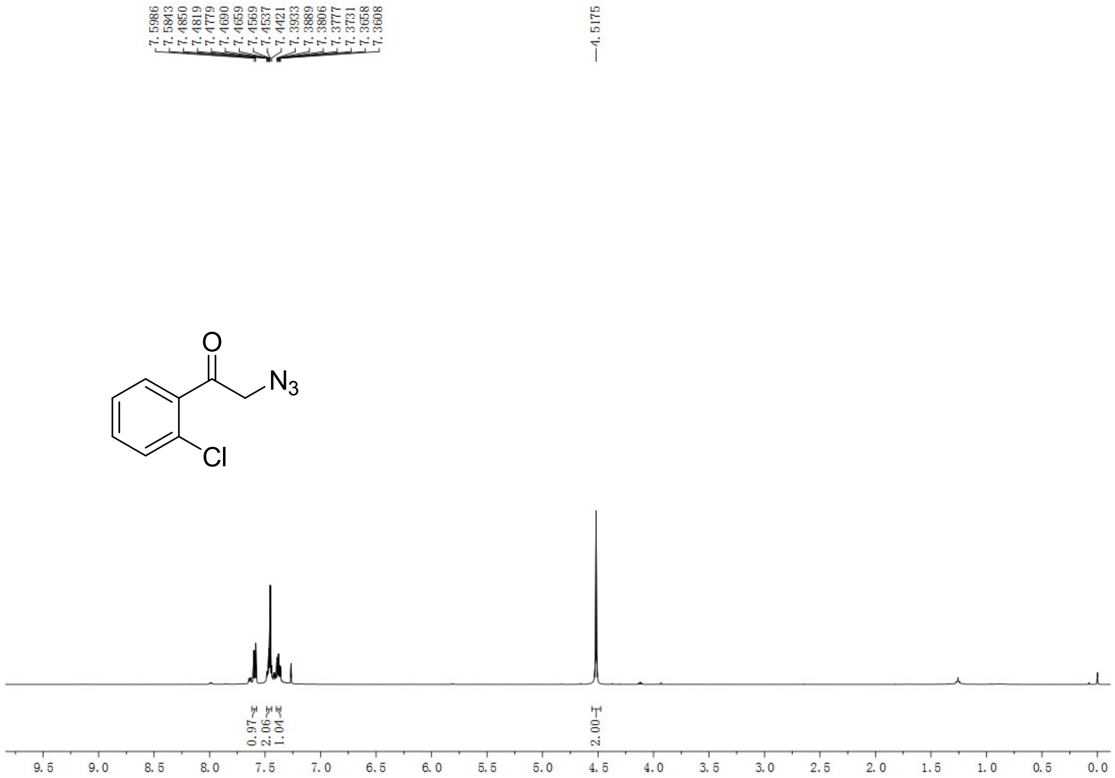
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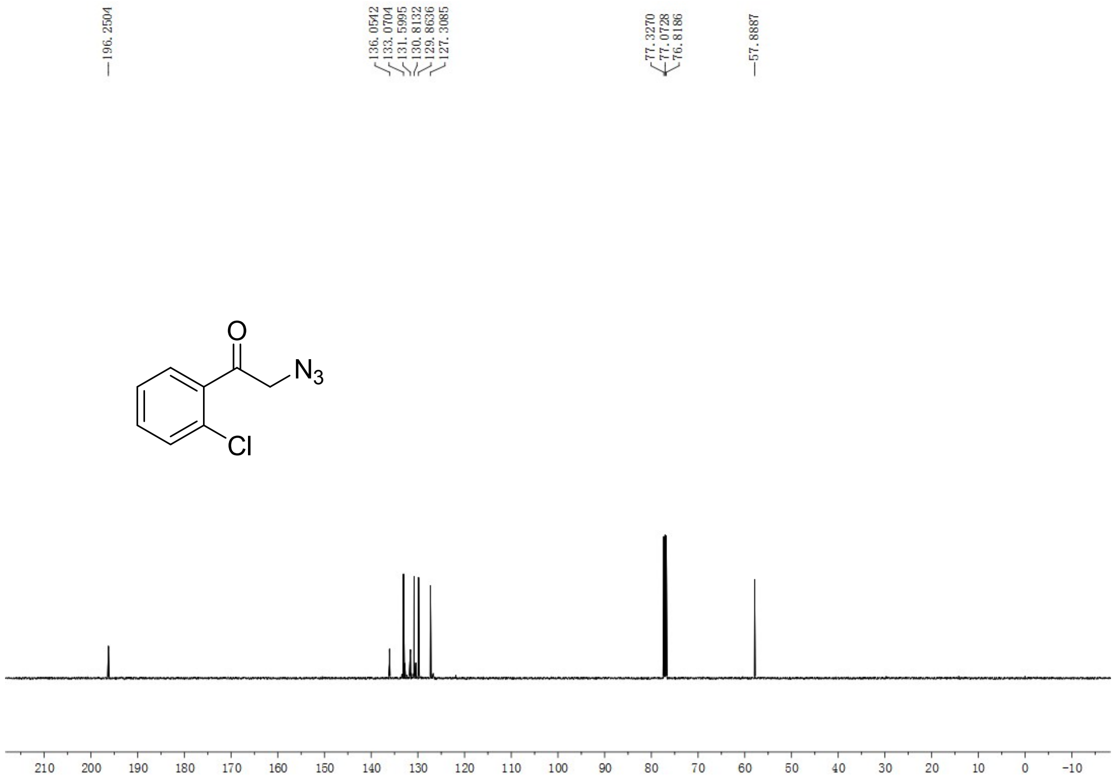
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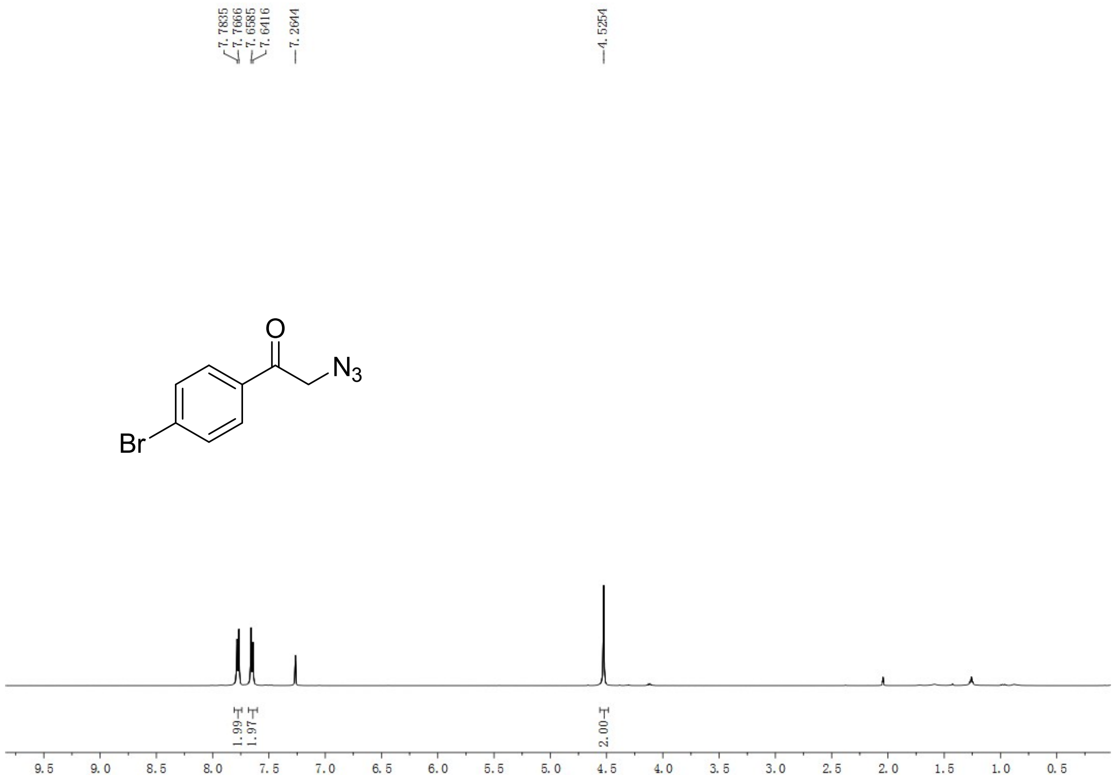
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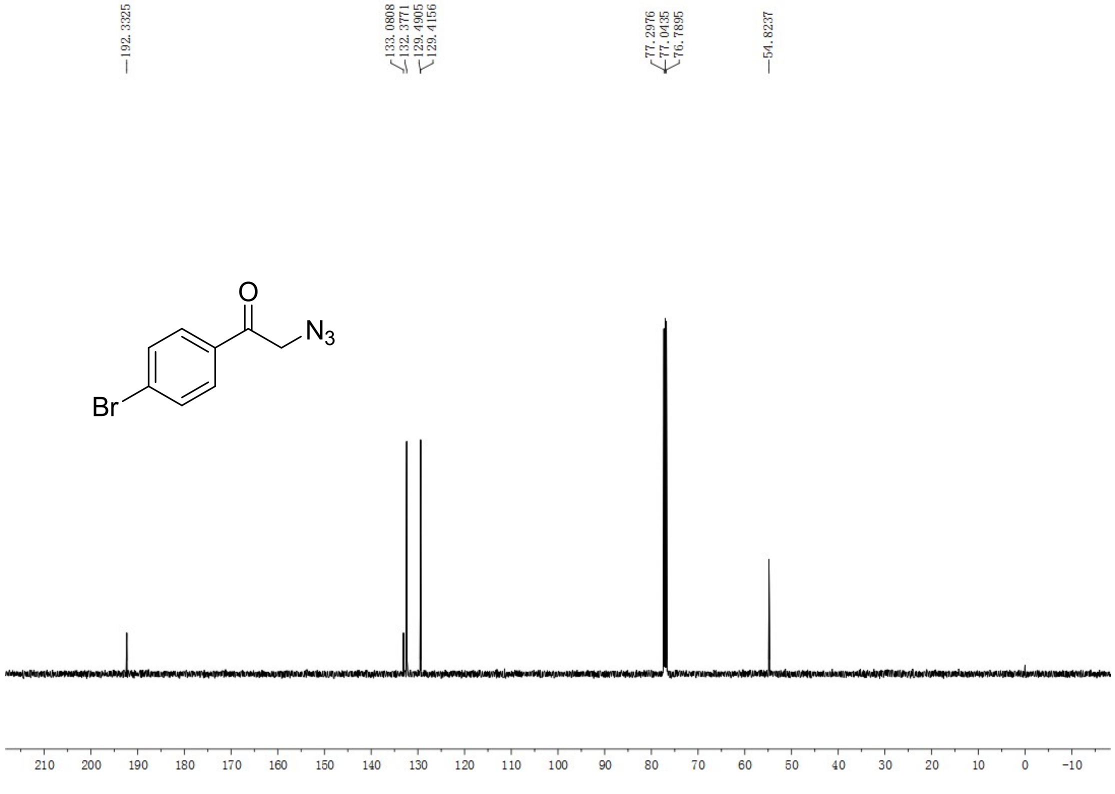
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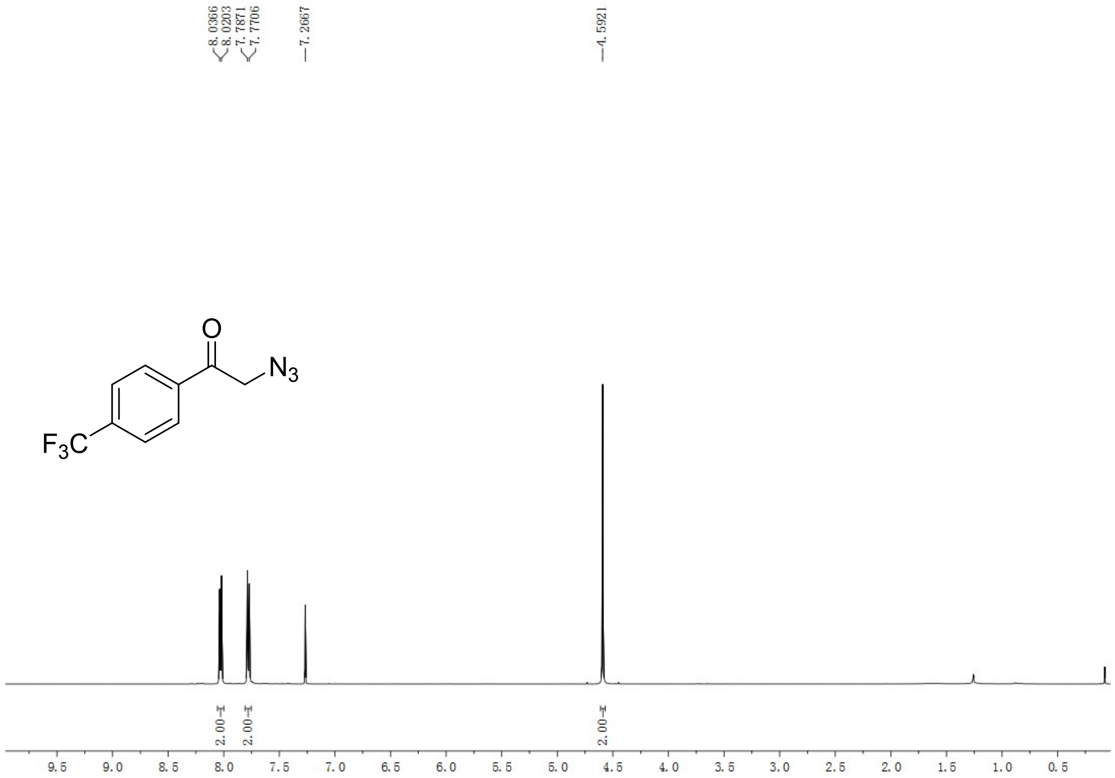
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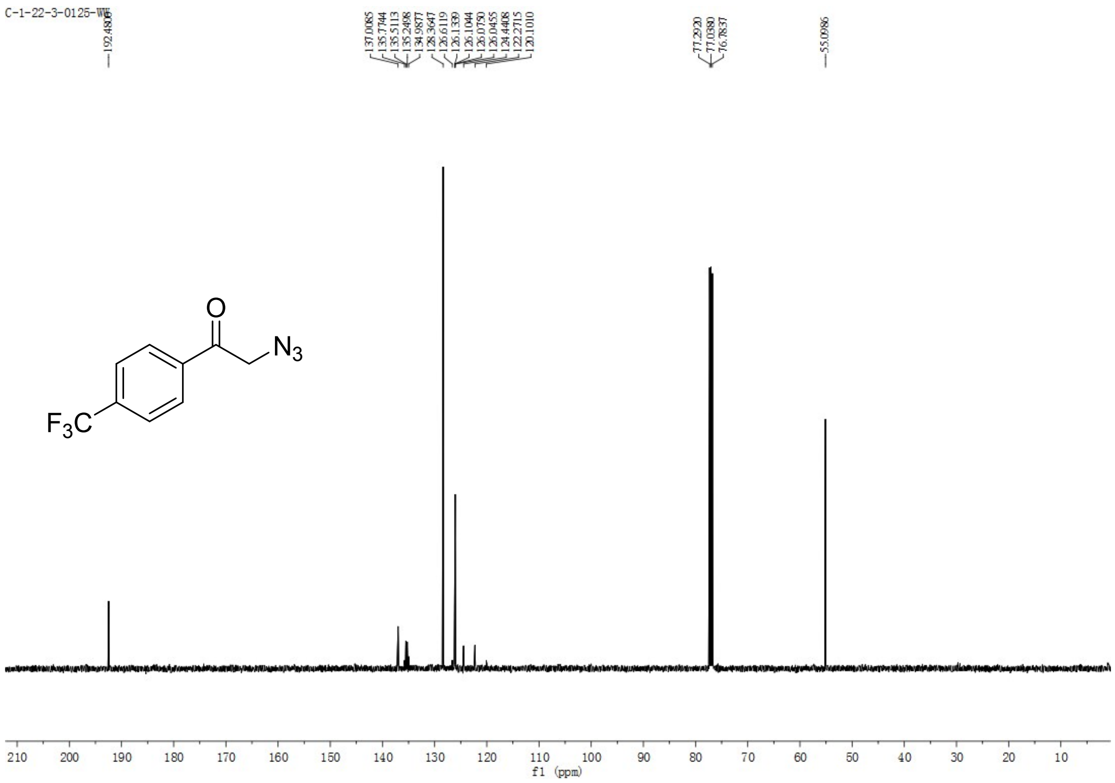
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124.4408
122.2715
120.1010
77.2920
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76.7837
55.0986
O
N3
F3C
210
200
190
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100
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20
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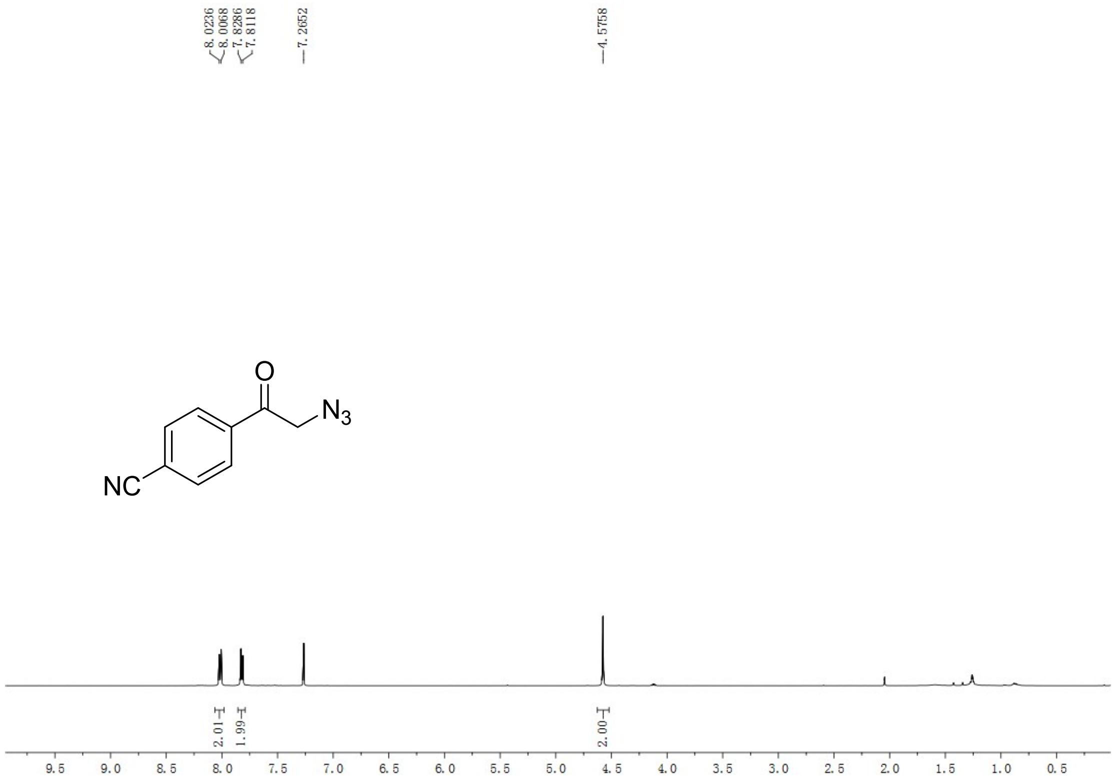
f1 (ppm)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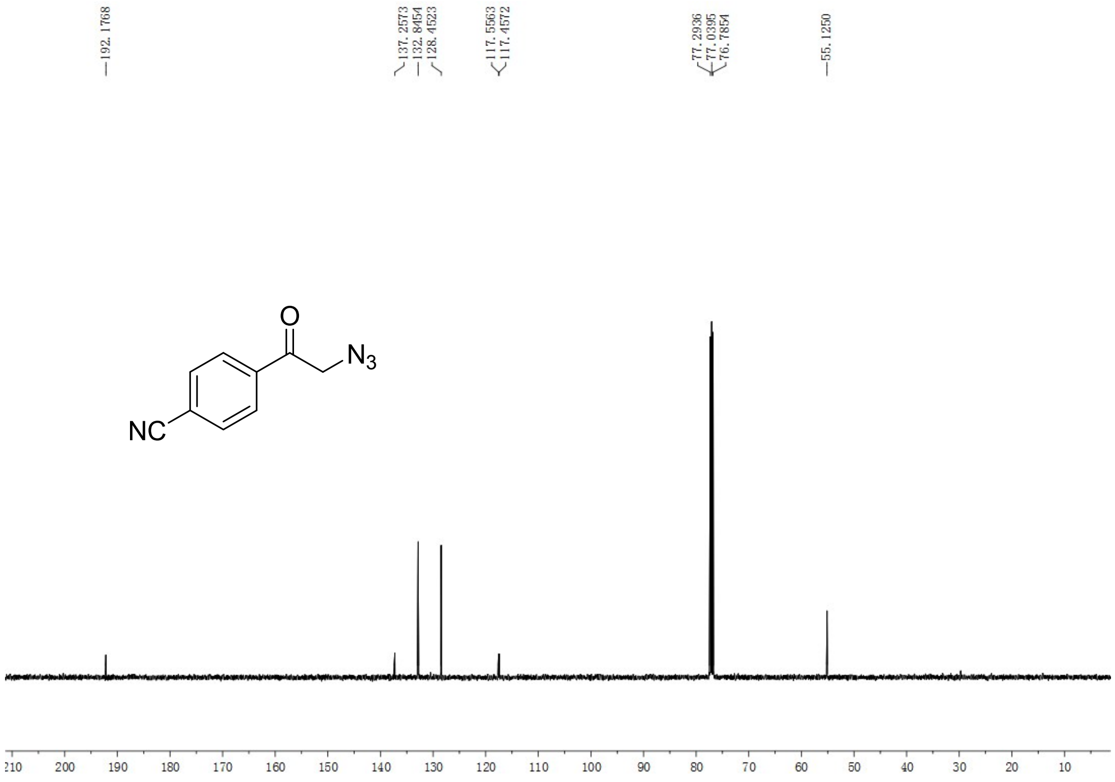
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NC
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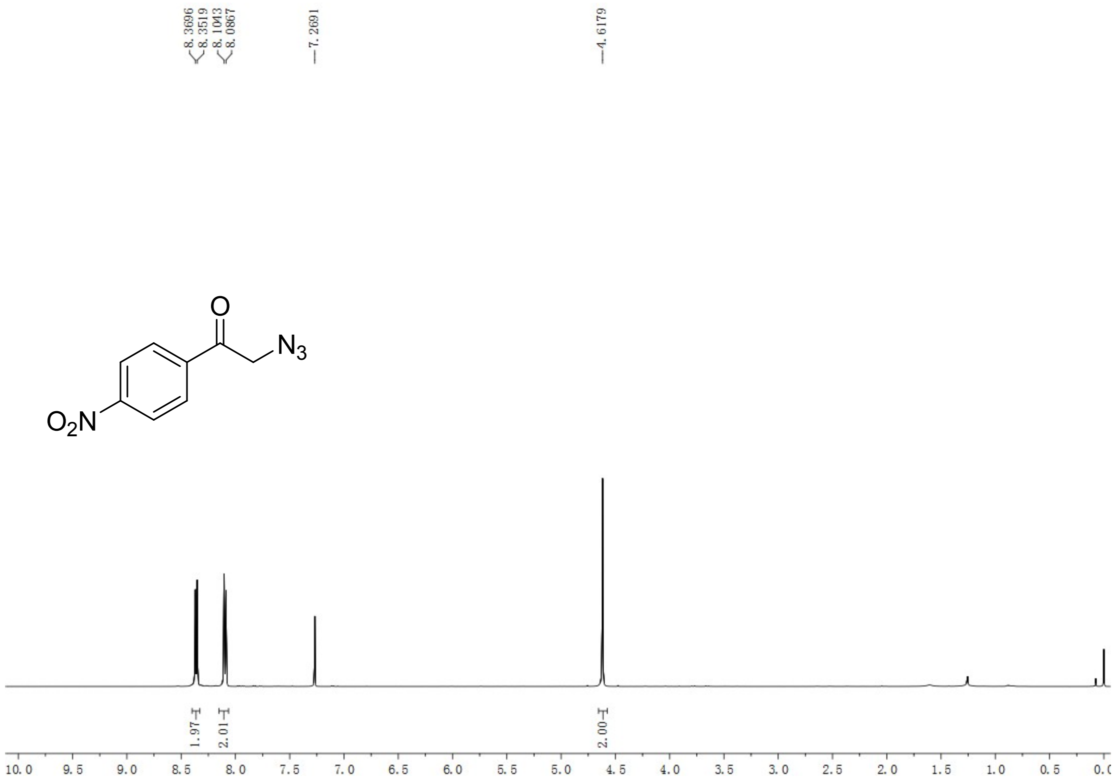
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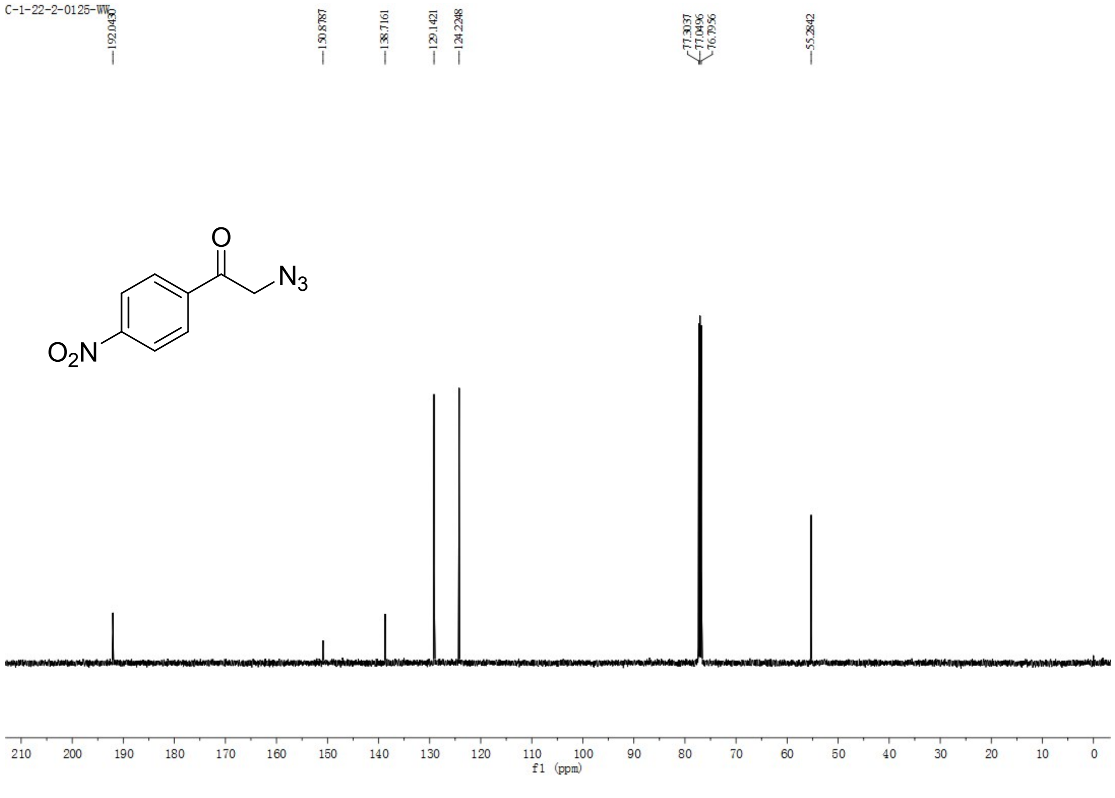
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O2N
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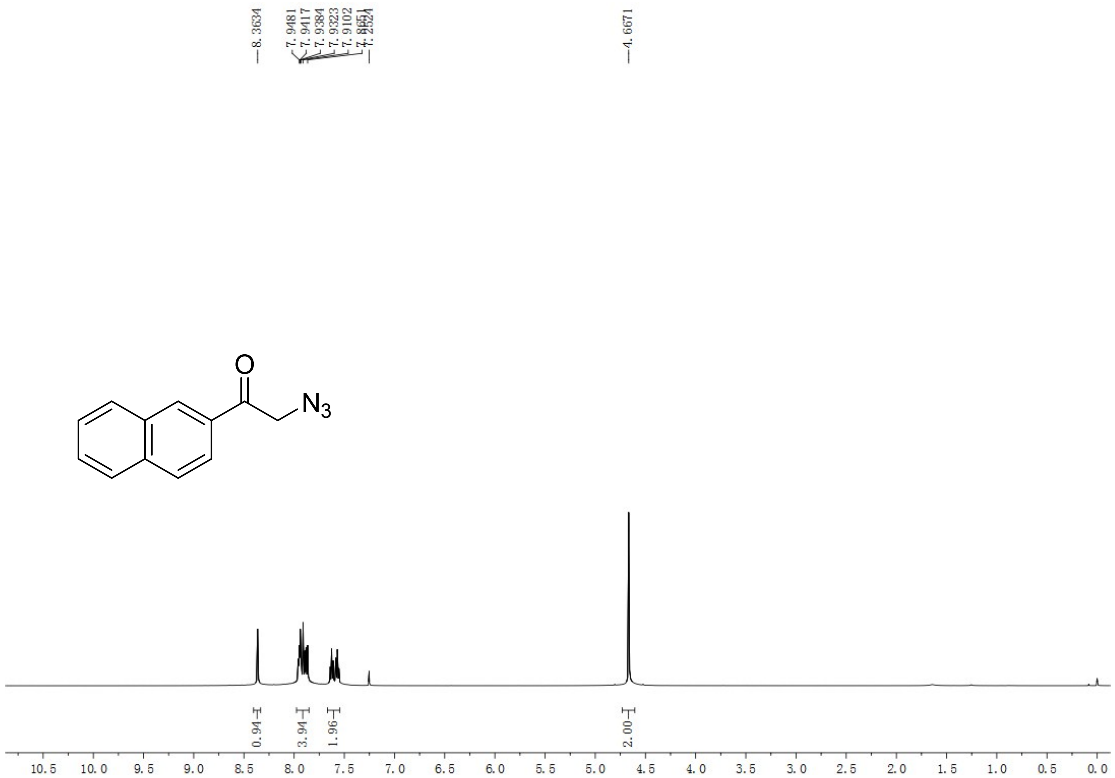
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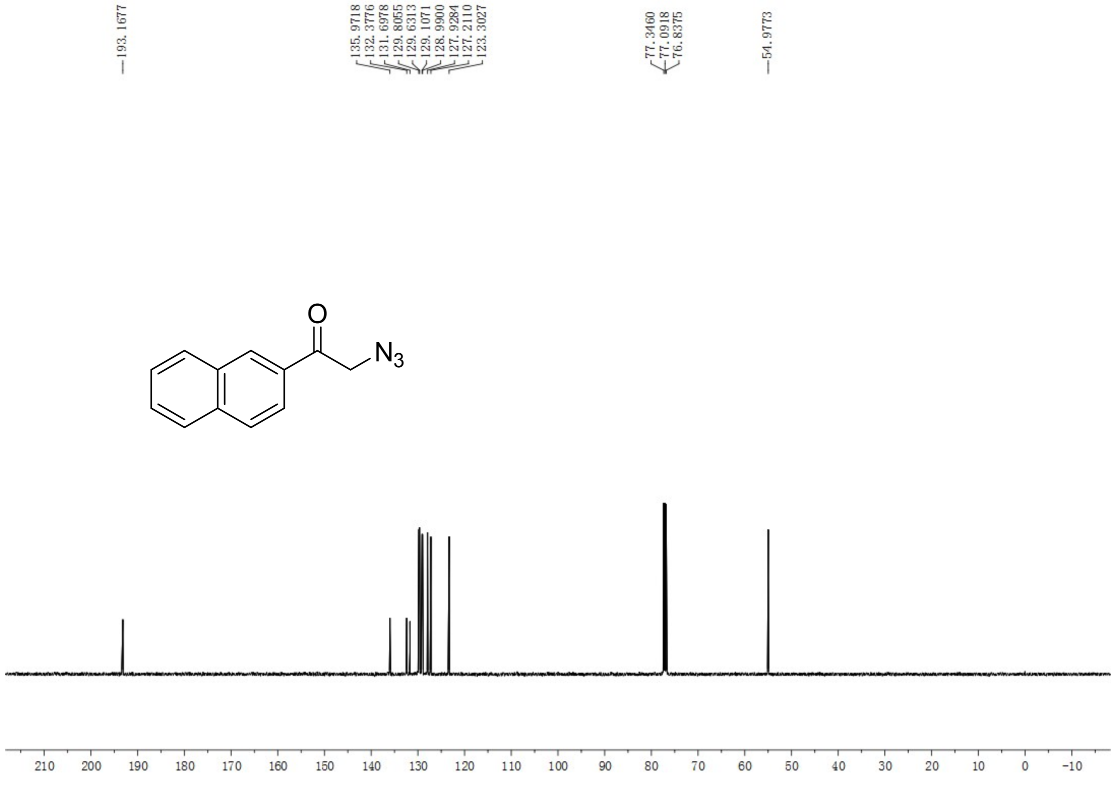
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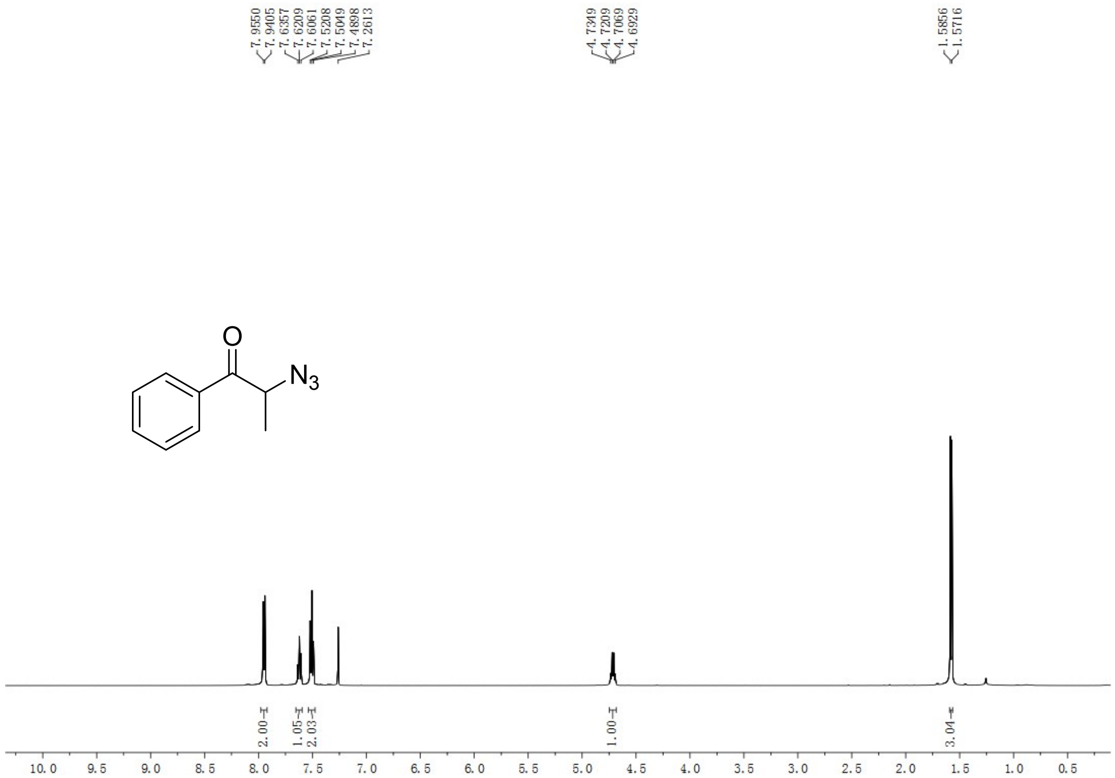
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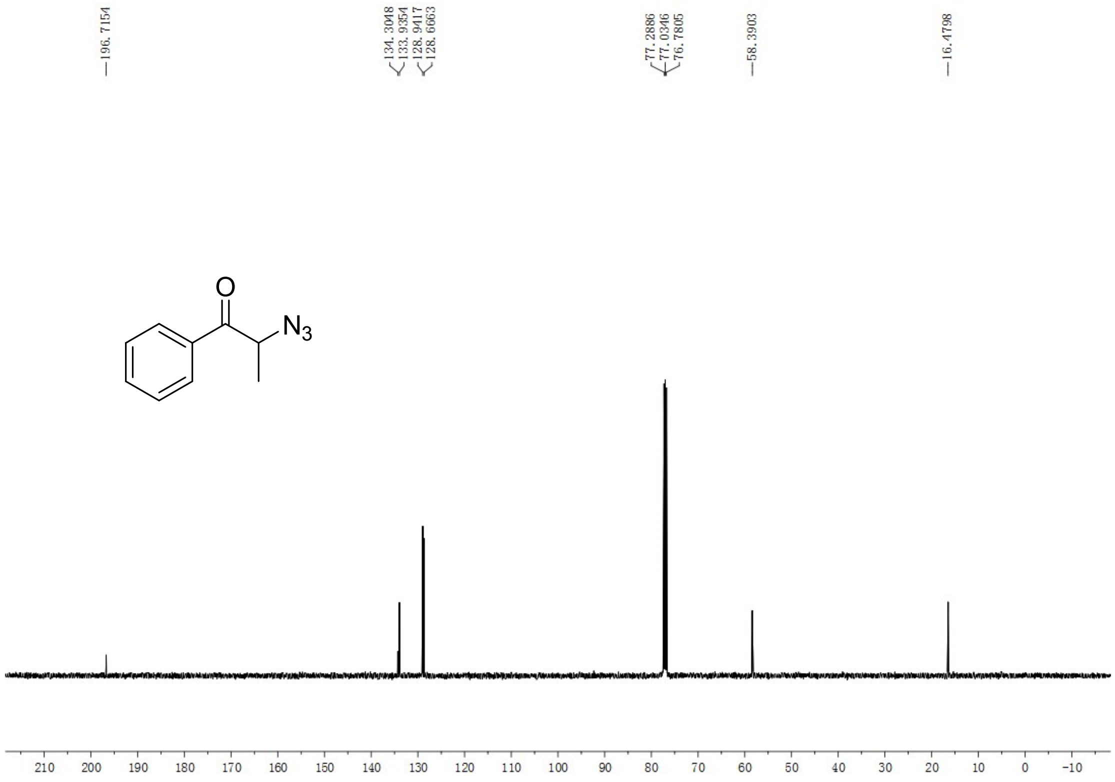
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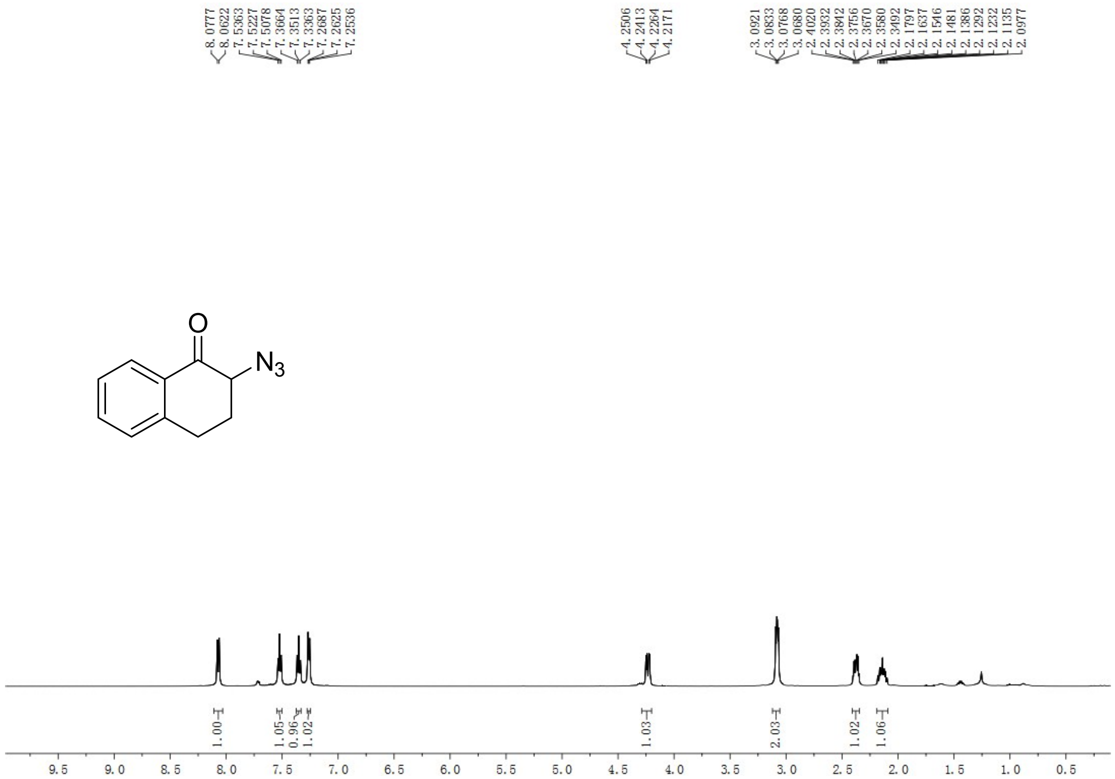
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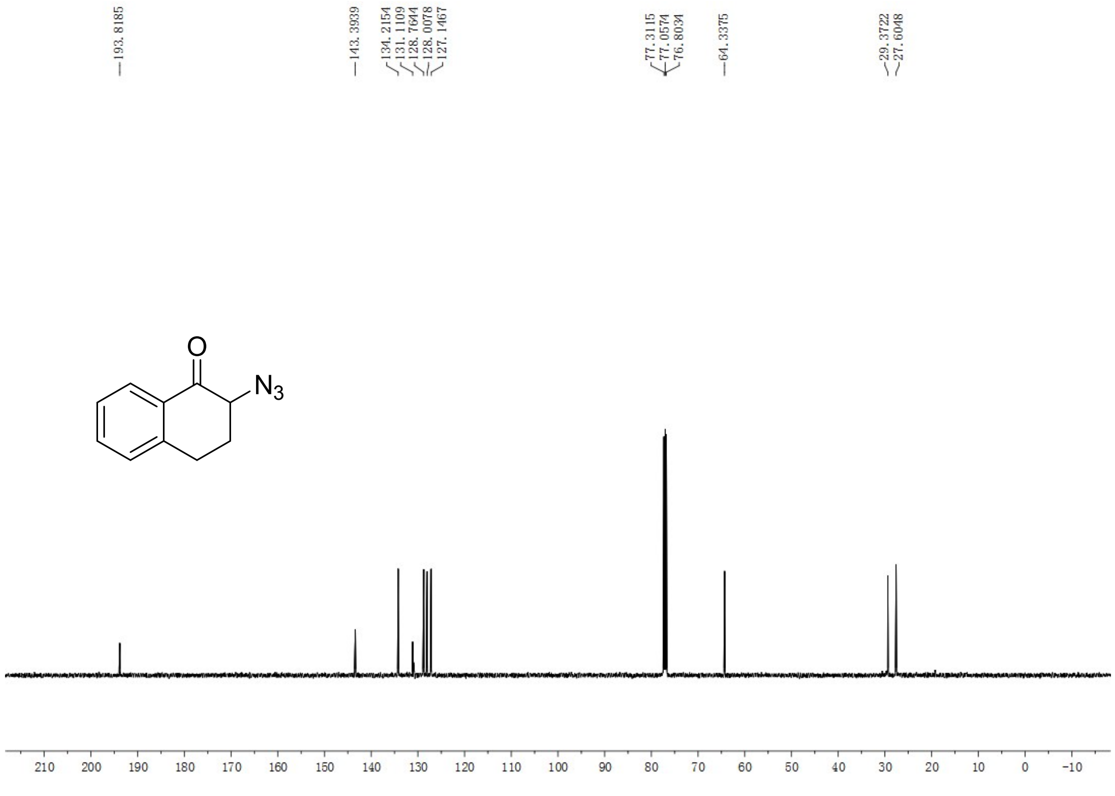
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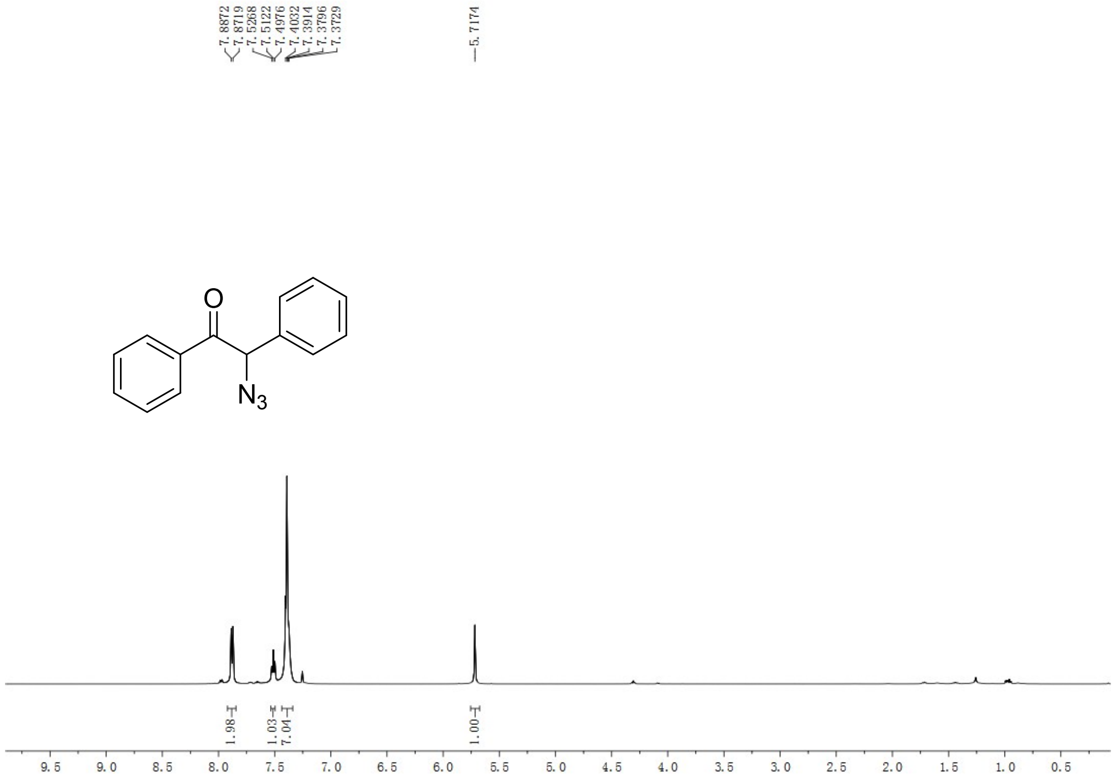
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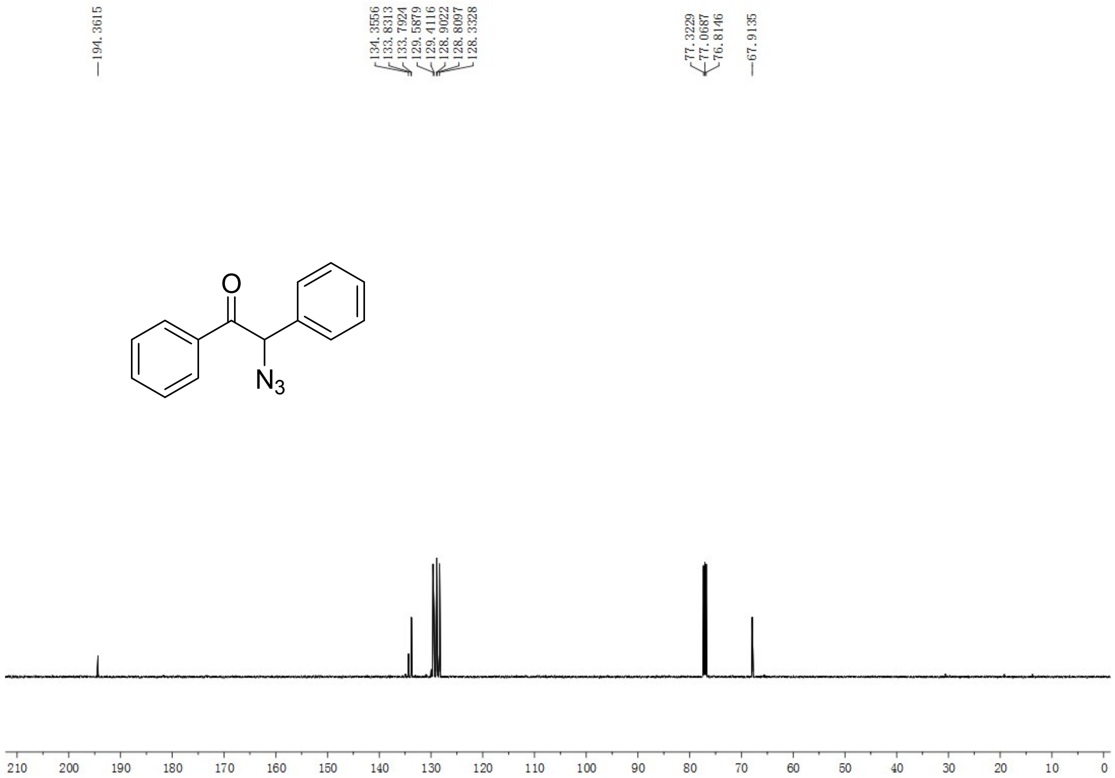
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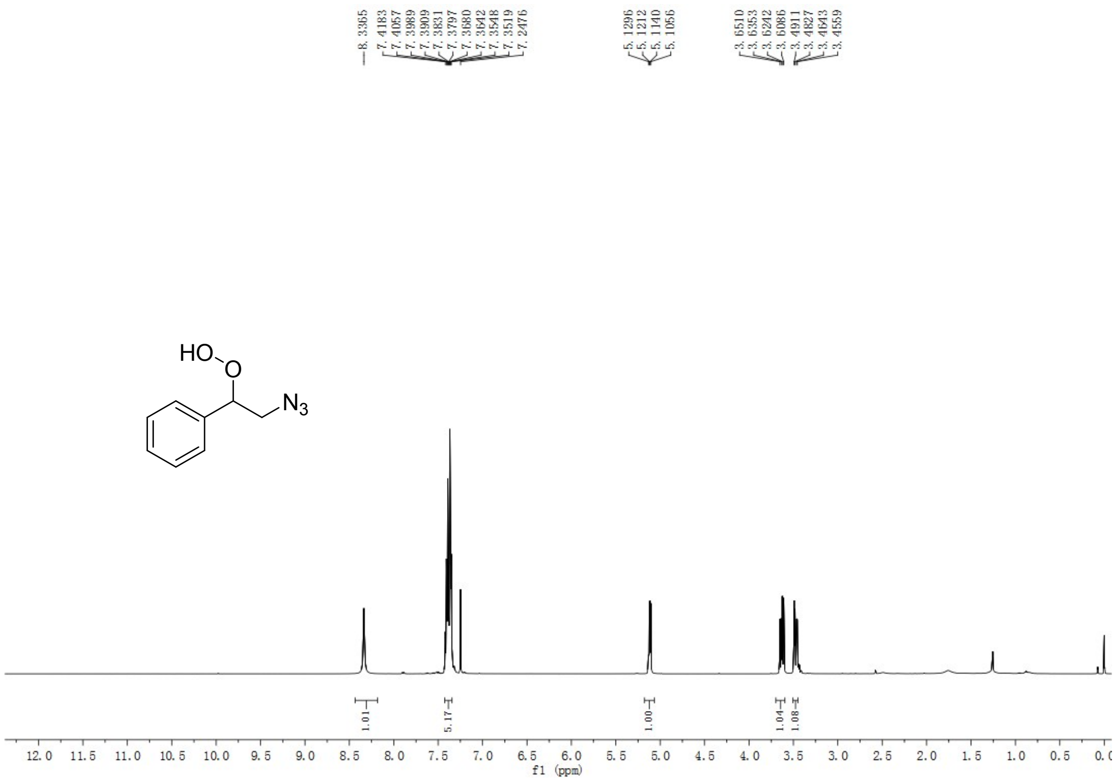
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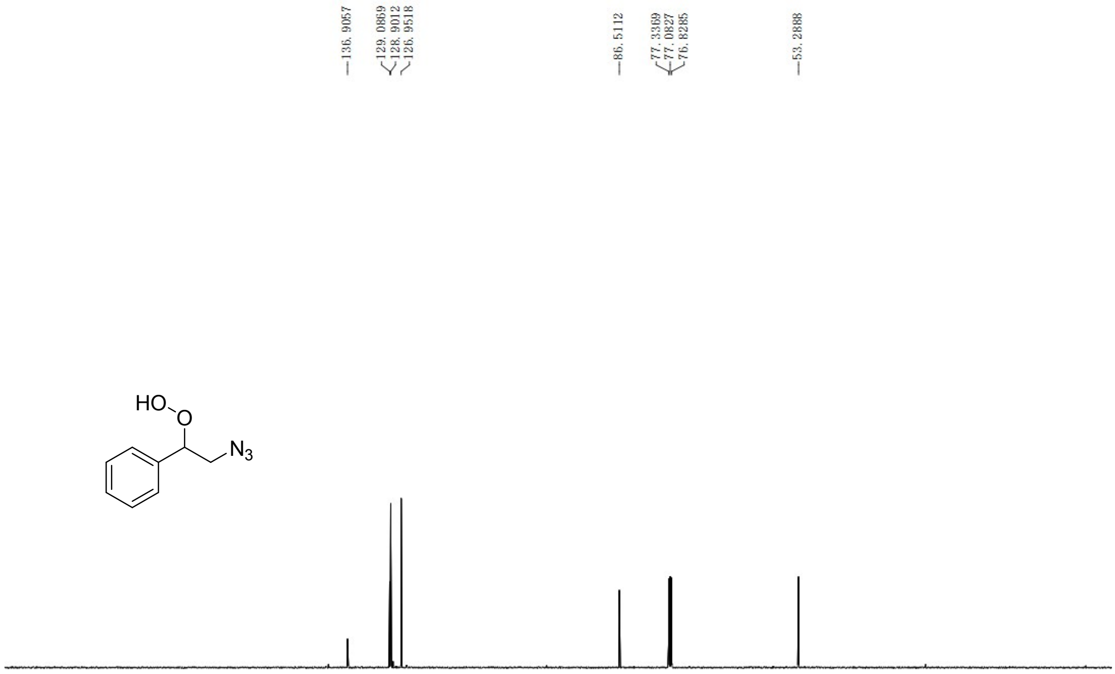
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f1 (ppm)