Hypervalent iodine(III)-promoted rapid cascade reaction for the synthesis of unsymmetric azo compounds

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Supporting Information

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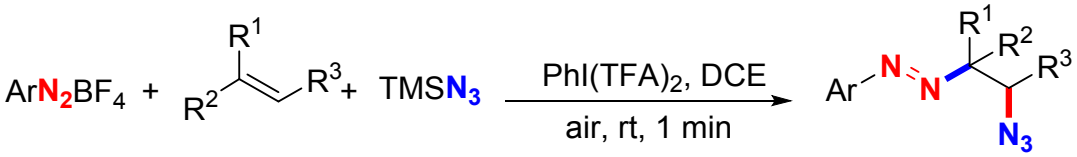
1. General Information

All reagents and deuterated solvents were commercially available and used without further purification. All products were separated by silica gel (200-300 mesh) column chromatography with petroleum ether (PE) (60-90°C) and ethyl acetate (EA). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 spectrometer at ambient temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer.

2. Experimental Section

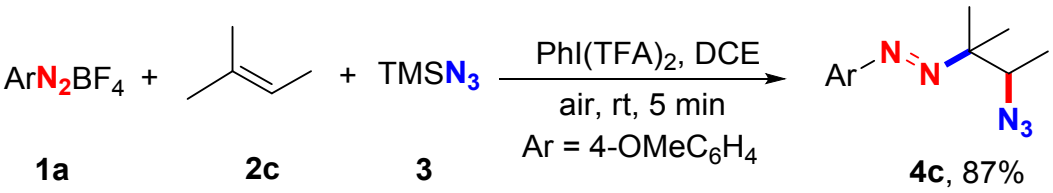
2.1 General procedure for the synthesis of products 4



1 **2** **3** **4**

A mixture of aryl diazonium (**1**) (0.2 mmol), alkenes (**2**) (0.4 mmol), $TMSN_3$ (0.4 mmol), and DCE (1.0 mL) in a 10 mL tube was stirred at room temperature. Then, $PhI(TFA)_2$ (0.2 mmol in 0.5 mL DCE) was added dropwise. After the completion (as indicated by TLC), the reaction mixture was quenched with saturated $NaHCO_3$ solution, and extracted with EtOAc (5 mL x 3). The collected organic layer was washed with brine and dried with $MgSO_4$. Finally, the organic solvent was removed under reduced pressure, and the obtained residue was purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 10:1) to provide the products **4**.

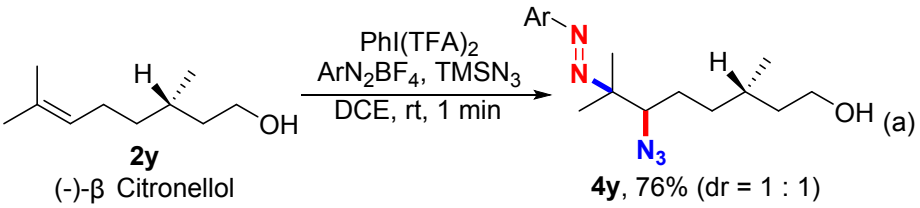
2.2 General procedure for gram-scale synthesis of product 4c

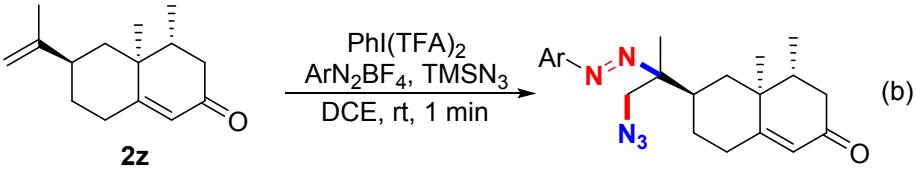


1a **2c** **3** **4c**, 87%

A mixture of 4-methoxybenzenediazonium tetrafluoroborate (**1a**) (4.0 mmol), 2-methylbut-2-ene (**2d**) (8.0 mmol), $TMSN_3$ (8.0 mmol) and DCE (10 mL) in a 50 mL tube was stirred at room temperature. Then, $PhI(TFA)_2$ (6.0 mmol in 5 mL DCE) was added dropwise. After the completion (as indicated by TLC), the reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution, and extracted with EtOAc (20 mL × 3). The collected organic layer was washed with brine, and dried with $MgSO_4$. Finally, the organic solvent was removed under reduced pressure, and the obtained residue was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 10:1) to provide product **4c** in 76% yield (0.75 g).

2.3 Modification of natural products

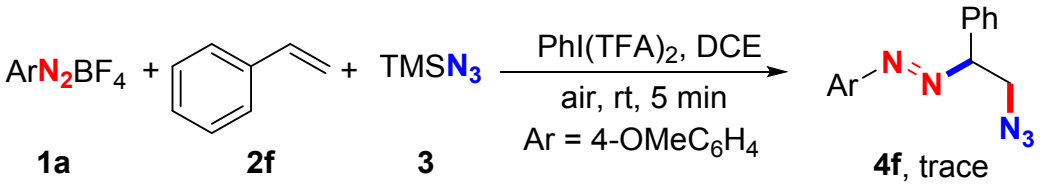




3.

A mixture of aryl diazonium (**1a**) (0.2 mmol), **2y-z** (0.4 mmol), $TMSN_3$ (0.4 mmol) and DCE (1.0 mL) in a 10 mL tube was stirred at room temperature. Then, $PhI(TFA)_2$ (0.2 mmol in 0.5 mL DCE) was added dropwise. After the completion (as indicated by TLC), the reaction mixture was quenched with saturated $NaHCO_3$ solution, and extracted with EtOAc (5 mL x 3). The collected organic layer was washed with brine and dried with $MgSO_4$. Finally, the organic solvent was removed under reduced pressure, and the obtained residue was purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 10:1) to provide the products **4y-z**.

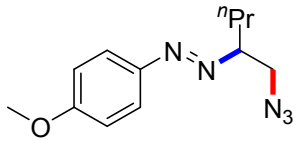
2.4 Modification of styrene



A mixture of aryl diazonium (**1a**) (0.2 mmol), **2ak-l** (0.26 mmol), $TMSN_3$ (0.26 mmol), and DCE (1.0 mL) in a 10 mL tube was stirred at room temperature. Then, PhI(TFA)2 (0.2 mmol in 0.5 mL DCE) was added dropwise. After the completion (as indicated by TLC), no desired product was detected.

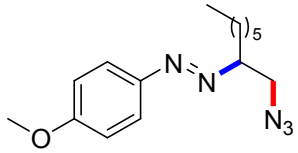
4. Characterization of the products

1-(1-Azidopentan-2-yl)-2-(4-methoxyphenyl)diazene (4a)



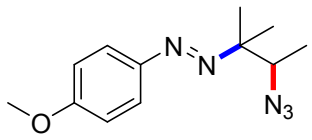
Obtained as a yellow oil (40 mg, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 6.98 – 6.93 (m, 2H), 3.86 (s, 3H), 3.84 – 3.80 (m, 1H), 3.78 (d, J = 12.4 Hz, 1H), 3.59 – 3.53 (m, 1H), 1.90 (dd, J = 13.7, 7.7 Hz, 1H), 1.78 – 1.71 (m, 1H), 1.32 (d, J = 7.7 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.79, 146.10, 124.26, 114.06, 76.41, 55.55, 53.74, 33.11, 19.10, 13.96; HRMS (ESI): $[M+H]^+$ Calculated for $C_{12}H_{17}N_5OH$: 248.1506, Found 248.1506.

1-(1-Azidooctan-2-yl)-2-(4-methoxyphenyl)diazene (4b)



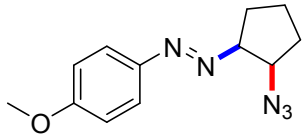
Obtained as a yellow oil (49 mg, 85% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 3.82 – 3.75 (m, 2H), 3.59 – 3.54 (m, 1H), 1.89 (dd, J = 8.2, 5.9 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.30 – 1.23 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.79, 146.11, 124.26, 114.05, 76.65, 55.55, 53.73, 31.61, 31.02, 29.15, 25.78, 22.55, 14.03; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{15}H_{23}N_5ONa$: 312.1795, Found 312.1790.

1-(3-Azido-2-methylbutan-2-yl)-2-(4-methoxyphenyl)diazene (4c)



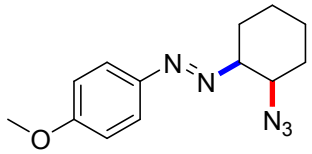
Obtained as a yellow oil (43 mg, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 3.95 (q, J = 6.8 Hz, 1H), 3.85 (s, 3H), 1.33 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 14.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.62, 146.22, 124.08, 114.01, 72.75, 64.81, 55.55, 21.78, 21.28, 14.56; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{17}N_5ONa$: 270.1325, Found 270.1325.

1-(2-Azidocyclopentyl)-2-(4-methoxyphenyl)diazene (4d)



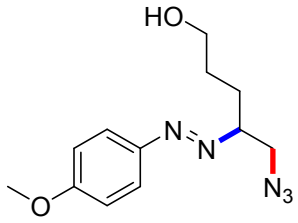
Obtained as a yellow oil, 9:1 dr (32 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.28 (q, J = 6.5 Hz, 1H), 4.10 (dt, J = 8.0, 6.2 Hz, 1H), 3.87 (s, 3H), 2.28 – 2.20 (m, 1H), 2.16 – 2.09 (m, 1H), 2.07 – 2.01 (m, 1H), 1.94 – 1.84 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.05, 139.43, 124.17, 114.04, 82.58, 65.76, 55.56, 31.07, 29.26, 22.22; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{15}N_5ONa$: 268.1175, Found 268.1174.

1-(2-Azidocyclohexyl)-2-(4-methoxyphenyl)diazene (4e)



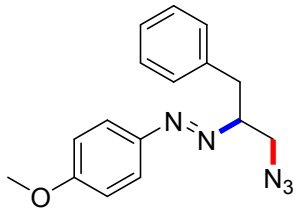
Obtained as a yellow oil, 4:6 dr (32 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 9.1 Hz, 2H), 6.96 (dd, J = 9.0, 2.1 Hz, 2H), 4.00 (d, J = 4.3 Hz, 1H), 3.86 (s, 3H), 3.79 (d, J = 9.0 Hz, 0.4H), 3.57 – 3.49 (m, 0.6H), 2.20 (d, J = 4.8 Hz, 1H), 1.87 (d, J = 2.3 Hz, 2H), 1.78 (d, J = 4.1 Hz, 2H), 1.74 – 1.58 (m, 1H), 1.46 (d, J = 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.77, 146.20, 124.27, 114.06, 80.04, 63.07, 55.55, 30.39, 29.77, 24.39, 23.59; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{13}H_{17}N_5ONa$: 282.1325, Found 282.1328.

5-azido-4-((4-methoxyphenyl)diazenyl)pentan-1-ol (4f)



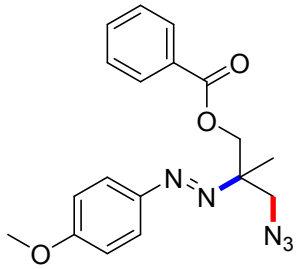
Obtained as a yellow oil (43 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.87 (m, 4H), 3.81 – 3.76 (m, 1H), 3.66 (td, J = 6.3, 1.6 Hz, 2H), 3.60 (m, 1H), 2.05 – 1.98 (m, 1H), 1.93 – 1.85 (m, 1H), 1.59 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.96, 145.97, 124.35, 114.11, 76.07, 62.45, 55.58, 53.73, 28.89, 27.45; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{17}N_5O_2Na$: 286.1274, Found 286.1285.

1-(1-Azido-3-phenylpropan-2-yl)-2-(4-methoxyphenyl)diazene (4g)



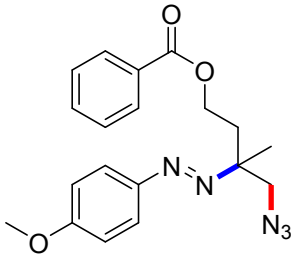
Obtained as a yellow oil (42 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.9 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.0 Hz, 3H), 6.96 (d, J = 9.0 Hz, 2H), 4.11 (dd, J = 7.1, 3.7 Hz, 1H), 3.85 (s, 3H), 3.71 (dd, J = 12.8, 7.3 Hz, 1H), 3.58 (dd, J = 12.7, 3.7 Hz, 1H), 3.13 (dd, J = 16.6, 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.93, 146.08, 137.30, 129.54, 128.55, 126.60, 124.32, 114.10, 77.36, 55.56, 52.77, 37.29; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{16}H_{17}N_5ONa$: 318.1325, Found 318.1328.

3-Azido-2-((4-methoxyphenyl)diazenyl)-2-methylpropyl benzoate (4h)



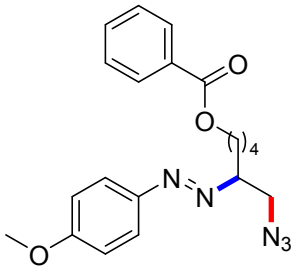
Obtained as a yellow oil (59 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 6.9 Hz, 2H), 7.73 (d, J = 8.9 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.74 – 4.60 (m, 2H), 3.86 (s, 3H), 3.81 (s, 2H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.11, 162.08, 145.93, 133.12, 129.90, 129.60, 128.44, 124.32, 114.09, 72.20, 66.88, 55.67, 55.58, 19.06; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{18}H_{19}N_5O_3Na$: 376.1386, Found 376.1386.

4-Azido-3-((4-methoxyphenyl)diazenyl)-3-methylbutyl benzoate (4i)



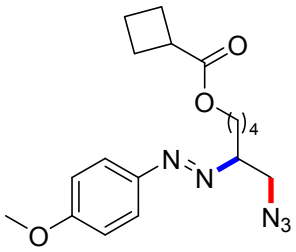
Obtained as a yellow oil (59 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 6.9 Hz, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.44 (td, J = 6.8, 1.1 Hz, 2H), 3.85 (s, 3H), 3.67 (d, J = 1.8 Hz, 2H), 2.44 – 2.23 (m, 2H), 1.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.47, 161.88, 145.84, 132.92, 130.10, 129.55, 128.33, 124.29, 114.03, 71.63, 61.09, 58.17, 55.57, 35.27, 20.94; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{19}H_{21}N_5O_3Na$: 390.1542, Found 390.1542.

6-Azido-5-((4-methoxyphenyl)diazenyl)hexyl benzoate (4j)



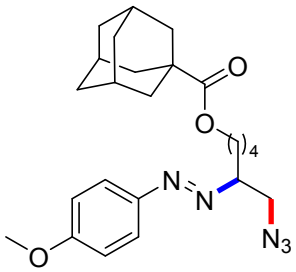
Obtained as a yellow oil (61 mg, 80% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.70 (d, J = 8.9 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.30 (td, J = 6.5, 2.7 Hz, 2H), 3.86 (s, 4H), 3.80 – 3.75 (m, 1H), 3.58 (dd, J = 12.5, 4.0 Hz, 1H), 2.00 (d, J = 7.7 Hz, 1H), 1.86 – 1.76 (m, 3H), 1.46 (t, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.59, 161.89, 146.03, 132.84, 130.34, 129.51, 128.32, 124.31, 114.09, 76.25, 64.57, 55.56, 53.70, 30.57, 28.51, 22.41; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{20}H_{23}N_5O_3Na$: 404.1693, Found 404.1703.

6-Azido-5-((4-methoxyphenyl)diazenyl)hexyl cyclobutanecarboxylate (4k)



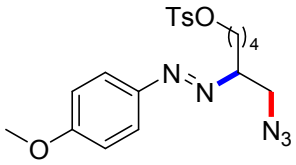
Obtained as a yellow oil (58 mg, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 4.07 – 4.02 (m, 2H), 3.86 (s, 3H), 3.82 – 3.74 (m, 2H), 3.57 (dd, J = 12.3, 3.7 Hz, 1H), 3.08 (td, J = 8.5, 1.0 Hz, 1H), 2.27 – 2.20 (m, 2H), 2.19 – 2.13 (m, 2H), 1.99 – 1.91 (m, 2H), 1.89 – 1.78 (m, 2H), 1.68 – 1.63 (m, 2H), 1.36 (p, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.52, 161.90, 146.02, 124.30, 114.07, 76.30, 63.87, 55.56, 53.67, 38.11, 30.57, 28.48, 25.25, 22.29, 18.40; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{18}H_{25}N_5O_3Na$: 382.1850, Found 382.1845.

6-Azido-5-((4-methoxyphenyl)diazenyl)hexyl-adamantane-1-carboxylate (4l)



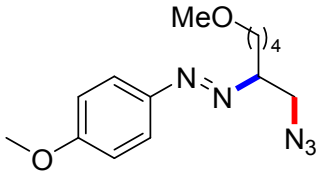
Obtained as a yellow oil (64 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.9 Hz, 2H), 6.97 – 6.93 (m, 2H), 4.02 (td, J = 6.4, 1.3 Hz, 2H), 3.86 (s, 3H), 3.84 – 3.80 (m, 1H), 3.78 (d, J = 12.3 Hz, 1H), 3.58 (d, J = 3.7 Hz, 1H), 1.95 (d, J = 7.0 Hz, 3H), 1.82 (d, J = 3.0 Hz, 6H), 1.72 – 1.63 (m, 10H), 1.36 (d, J = 7.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.69, 161.89, 146.03, 124.28, 114.06, 76.29, 63.58, 55.56, 53.71, 40.69, 38.82, 36.48, 30.57, 28.46, 27.93, 22.29; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{24}H_{33}N_5O_3Na$: 462.2476, Found 462.2469.

6-Azido-5-((4-methoxyphenyl)diazenyl)hexyl 4-methylbenzenesulfonate (4m)



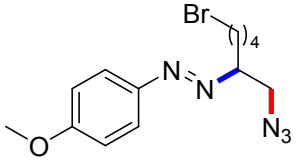
Obtained as a yellow oil (61 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.86 (s, 3H), 3.77 – 3.68 (m, 2H), 3.52 (dd, J = 12.1, 3.5 Hz, 1H), 2.43 (s, 3H), 1.92 – 1.84 (m, 1H), 1.71 – 1.64 (m, 3H), 1.32 (d, J = 7.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.96, 145.97, 144.73, 133.06, 129.83, 127.85, 124.33, 114.10, 76.10, 70.09, 55.58, 53.58, 30.25, 28.64, 21.83, 21.62; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{20}H_{25}N_5O_4SNa$: 454.1519, Found 454.1518.

1-(1-Azido-6-methoxyhexan-2-yl)-2-(4-methoxyphenyl)diazene (4n)



Obtained as a yellow oil (49 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 3.81 (s, 1H), 3.77 (d, J = 12.3 Hz, 1H), 3.59 (d, J = 3.6 Hz, 1H), 3.35 (t, J = 6.5 Hz, 2H), 3.30 (s, 3H), 1.92 (d, J = 7.2 Hz, 1H), 1.80 (s, 1H), 1.61 – 1.57 (m, 2H), 1.37 (d, J = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.84, 146.07, 124.30, 114.05, 76.51, 72.45, 58.55, 55.55, 53.67, 30.87, 29.50, 22.55; HRMS (ESI): $[M+Na]^+$Calculated for $C_{14}H_{21}N_5O_2Na$: 314.1587, Found 314.1582.

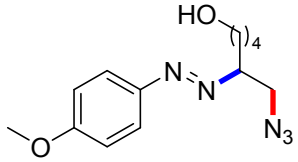
1-(1-Azido-6-bromohexan-2-yl)-2-(4-methoxyphenyl)diazene (4o)



Obtained as a yellow oil (52 mg, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 3.83 – 3.81 (m, 1H), 3.77 (d, J = 12.4 Hz, 1H), 3.58 (dd, J = 12.4, 3.9 Hz, 1H), 3.38 (t, J = 6.8 Hz, 2H), 1.98 – 1.93 (m, 1H), 1.90 – 1.85 (m, 2H), 1.79 (m, 1H), 1.50 – 1.43 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.93, 146.02, 124.33, 114.10, 76.17,

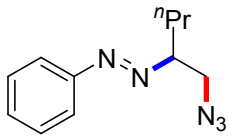
55.57, 53.63, 33.31, 32.46, 30.08, 24.45; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{13}H_{18}BrN_5ONa$: 362.0587, Found 362.0592.

6-Azido-5-((4-methoxyphenyl)diazenyl)hexan-1-ol (4p)



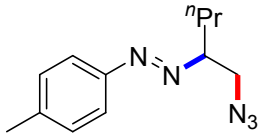
Obtained as a yellow oil (39 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.85 – 3.80 (m, 1H), 3.80 – 3.75 (m, 1H), 3.63 (t, J = 6.5 Hz, 2H), 3.58 (dd, J = 12.4, 3.8 Hz, 1H), 1.95 (d, J = 7.7 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.63 – 1.56 (m, 3H), 1.38 (t, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.88, 146.03, 124.31, 114.09, 76.45, 62.61, 55.57, 53.70, 32.51, 30.76, 22.11; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{13}H_{19}N_5O_2Na$: 300.1431, Found 300.1429.

1-(1-Azidopentan-2-yl)-2-phenyldiazene (4q)



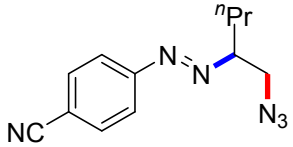
Obtained as a yellow oil (32 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.49 – 7.43 (m, 3H), 3.89 (dd, J = 4.9, 3.6 Hz, 1H), 3.84 – 3.78 (m, 1H), 3.60 (dd, J = 12.5, 3.8 Hz, 1H), 1.96 – 1.89 (m, 1H), 1.79 – 1.72 (m, 1H), 1.33 (q, J = 7.6 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.87, 130.80, 129.02, 122.42, 76.82, 53.61, 33.01, 19.07, 13.94; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{15}N_5Na$: 240.122, Found 240.1221.

1-(1-Azidopentan-2-yl)-2-(p-tolyl)diazene (4r)



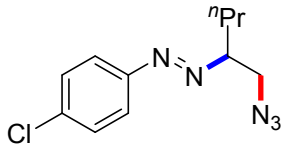
Obtained as a yellow oil (33 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 4.7 Hz, 2H), 3.86 (dd, J = 4.9, 3.6 Hz, 1H), 3.82 – 3.76 (m, 1H), 3.58 (dd, J = 12.4, 3.8 Hz, 1H), 2.40 (s, 3H), 1.95 – 1.86 (m, 1H), 1.78 – 1.71 (m, 1H), 1.32 (d, J = 7.7 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.94, 141.25, 129.63, 122.42, 76.66, 53.67, 33.05, 21.39, 19.08, 13.95; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{17}N_5Na$: 254.1376, Found 254.1378.

4-((1-Azidopentan-2-yl)diazenyl)benzonitrile (4s)



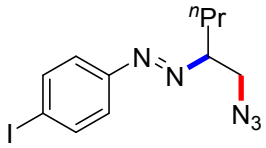
Obtained as a yellow oil (33 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 4H), 3.94 (s, 1H), 3.88 – 3.80 (m, 1H), 3.63 (dd, J = 12.7, 3.6 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.80 – 1.73 (m, 1H), 1.35 – 1.29 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.62, 133.24, 123.04, 114.16, 77.46, 53.40, 32.89, 19.06, 13.87; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{14}N_6Na$: 265.1172, Found 265.1174.

1-(1-Azidopentan-2-yl)-2-(4-chlorophenyl)diazene (4t)



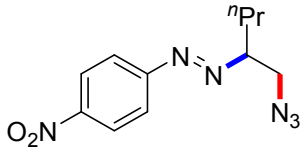
Obtained as a yellow oil (50 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 3.89 (dd, J = 4.9, 3.5 Hz, 1H), 3.81 (d, J = 12.6 Hz, 1H), 3.61 (d, J = 3.7 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.79 – 1.71 (m, 0H), 1.32 (q, J = 7.6 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.13, 136.84, 129.26, 123.77, 77.21, 53.54, 32.96, 19.06, 13.91; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}ClN_5Na$: 274.0830, Found 274.0840.

1-(1-Azidopentan-2-yl)-2-(4-iodophenyl)diazene (4u)



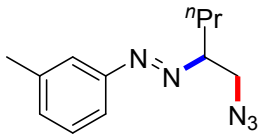
Obtained as a yellow oil (50 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 3.87 (dd, J = 4.9, 3.5 Hz, 1H), 3.79 (dd, J = 12.6, 8.1 Hz, 1H), 3.58 (dd, J = 12.6, 3.7 Hz, 1H), 1.89 (d, J = 8.0 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.31 (q, J = 7.6 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.10, 138.28, 124.12, 97.45, 76.95, 53.50, 32.93, 19.06, 13.91; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{14}IN_5Na$: 366.0186, Found 366.0195.

1-(1-Azidopentan-2-yl)-2-(4-nitrophenyl)diazene (4v)



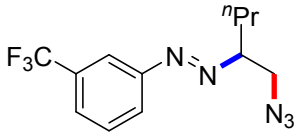
Obtained as a yellow oil (38 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.9 Hz, 2H), 7.82 (d, J = 8.9 Hz, 2H), 3.97 (s, 1H), 3.90 – 3.82 (m, 1H), 3.65 (dd, J = 12.8, 3.7 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.79 (d, J = 7.6 Hz, 1H), 1.37 – 1.31 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ154.79, 148.83, 124.72, 123.15, 77.64, 53.38, 32.89, 19.07, 13.87; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{14}N_6O_2Na$: 285.1070, Found 285.1045.

1-(1-Azidopentan-2-yl)-2-(m-tolyl)diazene (4w)



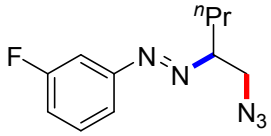
Obtained as a yellow oil (31 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.26 (m, 2H), 3.87 (m, 1H), 3.82 (d, J = 12.5 Hz, 1H), 3.64 – 3.57 (m, 1H), 2.42 (s, 3H), 1.93 (dd, J = 13.8, 7.5 Hz, 1H), 1.75 (d, J = 8.0 Hz, 1H), 1.35 – 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.97, 138.97, 131.53, 128.83, 122.56, 119.94, 77.21, 53.62, 33.01, 21.32, 19.07, 13.93; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{17}N_5Na$: 254.1376, Found 254.1376.

1-(1-azidopentan-2-yl)-2-(3-(trifluoromethyl)phenyl)diazene (4x)



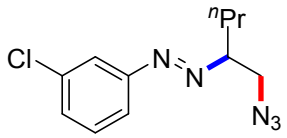
Obtained as a yellow oil (39 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.84 (dd, J = 12.6, 8.2 Hz, 1H), 3.63 (dd, J = 12.7, 3.7 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.77 (m, 1H), 1.33 (q, J = 7.6 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.71, 131.66 (d, J = 33.0 Hz), 129.68, 127.23 (q, J = 3.4 Hz), 125.82, 123.76 (d, J = 272.6 Hz), 119.35 (q, J = 3.8 Hz), 77.08, 53.47, 32.92, 19.06, 13.88; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.72; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{12}H_{14}F_3N_5Na$: 308.1099, Found 308.1095.

1-(1-Azidopentan-2-yl)-2-(3-fluorophenyl)diazene (4y)



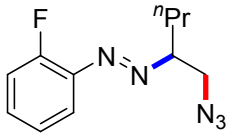
Obtained as a yellow oil (31 mg, 66% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 1H), 7.45 (td, J = 8.1, 5.8 Hz, 1H), 7.38 (dt, J = 9.6, 2.2 Hz, 1H), 7.16 (td, J = 8.4, 2.2 Hz, 1H), 3.91 (dd, J = 4.9, 3.6 Hz, 1H), 3.81 (dd, J = 12.6, 8.1 Hz, 1H), 3.61 (dd, J = 12.6, 3.8 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.80 – 1.72 (m, 1H), 1.33 (s, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.17 (d, J = 247.9 Hz), 153.24 (d, J = 6.8 Hz), 130.25 (d, J = 8.3 Hz), 119.85 (d, J = 3.0 Hz), 117.65 (d, J = 22.1 Hz), 108.04 (d, J = 23.1 Hz), 53.50, 32.95, 19.05, 13.91; ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.94; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}FN_5Na$: 258.1125, Found 258.1126.

1-(1-Azidopentan-2-yl)-2-(3-chlorophenyl)diazene (4z)



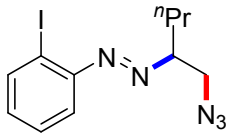
Obtained as a yellow oil (37 mg, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.63 (m, 1H), 7.42 (dd, *J* = 4.9, 1.6 Hz, 2H), 3.94 – 3.88 (m, 1H), 3.81 (dd, *J* = 12.6, 8.1 Hz, 1H), 3.61 (dd, *J* = 12.6, 3.7 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.80 – 1.72 (m, 1H), 1.34 – 1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.59, 135.07, 130.67, 130.11, 121.85, 121.62, 76.94, 53.49, 32.94, 19.05, 13.90; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{14}ClN_5Na$: 274.0830, Found 274.0821.

1-(1-Azidopentan-2-yl)-2-(2-fluorophenyl)diazene (4aa)



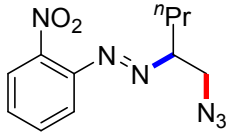
Obtained as a yellow oil (31 mg, 66% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.23 (m, 1H), 7.19 – 7.15 (m, 1H), 3.99 – 3.92 (m, 1H), 3.83 (dd, *J* = 12.7, 7.8 Hz, 1H), 3.62 (dd, *J* = 12.7, 4.0 Hz, 1H), 1.92 (d, *J* = 7.2 Hz, 1H), 1.79 (s, 1H), 1.34 (td, *J* = 7.5, 6.0 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ159.30 (d, J = 256.6 Hz), 139.82 (d, J = 7.3 Hz), 132.32 (d, J = 8.2 Hz), 124.29 (d, J = 4.0 Hz), 118.24, 116.99 (d, J = 19.8 Hz), 77.36, 53.62, 32.97, 19.01, 13.93; ^{19}F NMR (471 MHz, $CDCl_3$) δ -125.60; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{14}FN_5Na$: 258.1125, Found 258.1131.

1-(1-Azidopentan-2-yl)-2-(2-iodophenyl)diazene (4ab)



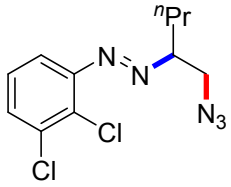
Obtained as a yellow oil (44 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.9 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.24 (m, 1H), 7.13 (m, 1H), 4.08 – 4.01 (m, 1H), 3.84 (dd, J = 12.7, 7.9 Hz, 1H), 3.63 (dd, J = 12.7, 4.1 Hz, 1H), 1.96 (m, 1H), 1.80 – 1.73 (m, 1H), 1.41 – 1.34 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.36, 139.63, 131.82, 128.98, 117.79, 99.49, 76.47, 53.65, 32.93, 19.05, 13.94; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{14}IN_5Na$: 366.0186, Found 366.0195.

1-(1-Azidopentan-2-yl)-2-(2-nitrophenyl)diazene (4ac)



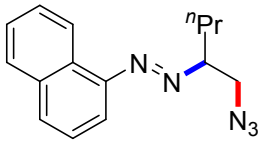
Obtained as a yellow oil (33 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.1, 1.3 Hz, 1H), 7.59 (m, 1H), 7.48 (m, 1H), 7.23 (dd, J = 7.9, 1.4 Hz, 1H), 3.97 – 3.90 (m, 1H), 3.78 (dd, J = 12.7, 8.0 Hz, 1H), 3.59 (dd, J = 12.7, 3.9 Hz, 1H), 1.96 – 1.87 (m, 1H), 1.76 – 1.66 (m, 1H), 1.36 – 1.27 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.69, 133.57, 130.14, 124.18, 119.30, 77.49, 53.41, 32.78, 19.01, 13.91; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{11}H_{14}N_6O_2Na$: 285.1070, Found 285.1045.

1-(1-Azidopentan-2-yl)-2-(2,3-dichlorophenyl)diazene (4ad)



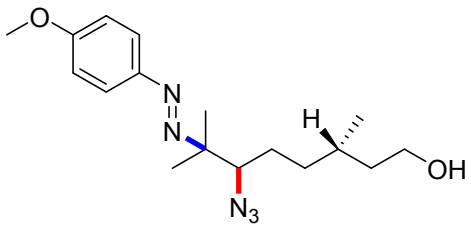
Obtained as a yellow oil (38 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 2.2 Hz, 1H), 7.62 – 7.54 (m, 2H), 3.93 – 3.88 (m, 1H), 3.81 (dd, J = 12.6, 8.1 Hz, 1H), 3.60 (dd, J = 12.6, 3.7 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.79 – 1.72 (m, 1H), 1.34 – 1.28 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.55, 134.95, 133.43, 130.85, 123.75, 122.42, 53.44, 32.91, 19.05, 13.88; HRMS (ESI): $[M+H]^+$ Calculated for $C_{11}H_{13}Cl_2N_5H$: 286.0621, Found 286.0626.

1-(1-Azidopentan-2-yl)-2-(naphthalen-1-yl)diazene (4ae)



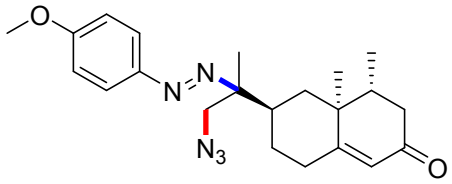
Obtained as a yellow oil (43 mg, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.9 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.63 (t, J = 6.9 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.53 – 7.46 (m, 2H), 4.12 – 4.06 (m, 1H), 3.91 (dd, J = 12.7, 8.2 Hz, 1H), 3.69 (dd, J = 12.7, 4.0 Hz, 1H), 2.02 (d, J = 6.4 Hz, 1H), 1.81 (d, J = 7.7 Hz, 1H), 1.44 – 1.36 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.37, 134.12, 130.85, 130.34, 127.89, 126.87, 126.45, 125.54, 123.17, 112.26, 77.17, 53.79, 33.05, 19.14, 13.94; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{15}H_{17}N_5Na$: 290.1376, Found 290.1374.

6-Azido-7-((4-methoxyphenyl)diazenyl)-3,7-dimethyloctan-1-ol (4af)



Obtained as a yellow oil 1:1 dr (51 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.73 – 3.67 (m, 3H), 1.68 – 1.59 (m, 5H), 1.46 (d, J = 2.0 Hz, 2H), 1.28 (s, 3H), 1.25 (s, 3H), 0.93 (dd, J = 7.4, 5.6 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) Mixture of diastereomers is observed. Ratio: 5/5. Major diastereomer: δ 161.62, 146.18, 124.08, 114.03, 73.48, 71.28, 60.99, 55.55, 40.04, 34.88, 29.55, 27.08, 22.10, 21.60, 19.84; Minor diastereomer: δ 161.62, 146.18, 124.08, 114.03, 73.44, 70.89, 60.96, 55.55, 39.46, 34.52, 29.17, 26.89, 22.10, 21.60, 19.37; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{17}H_{27}N_5O_2Na$: 356.2057, Found 356.2060.

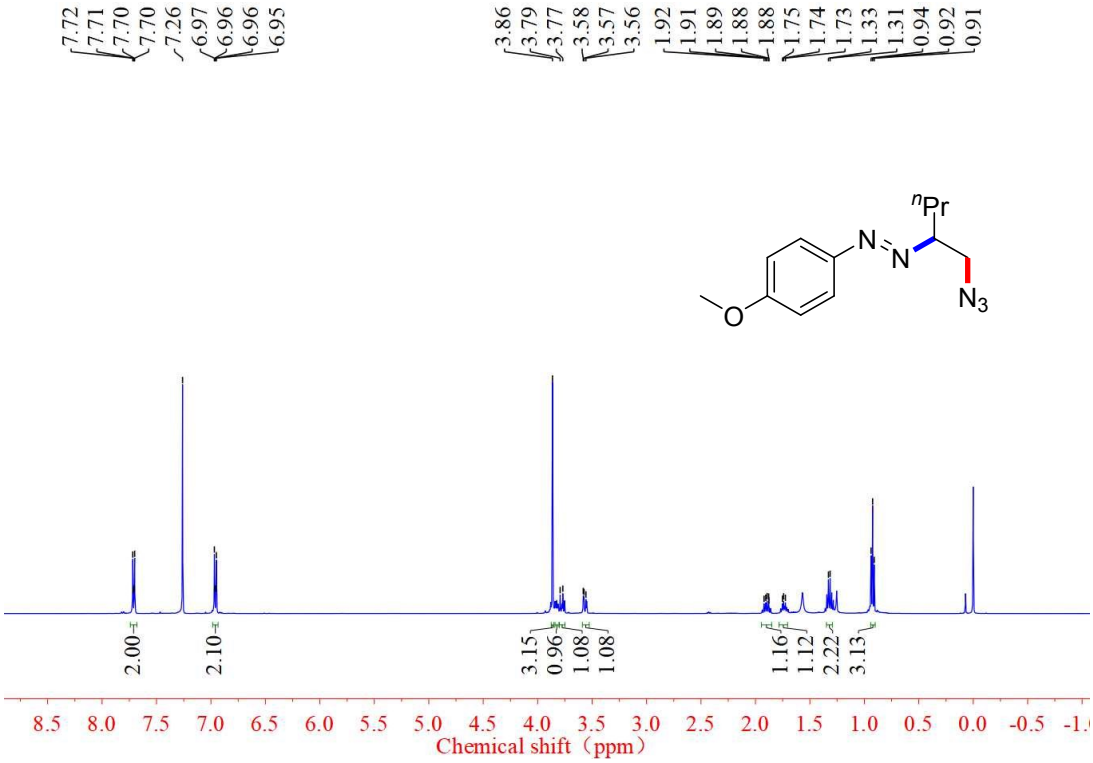
1-Azido-2-((4-methoxyphenyl)diazenyl)propan-2-yl)-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (4ag)



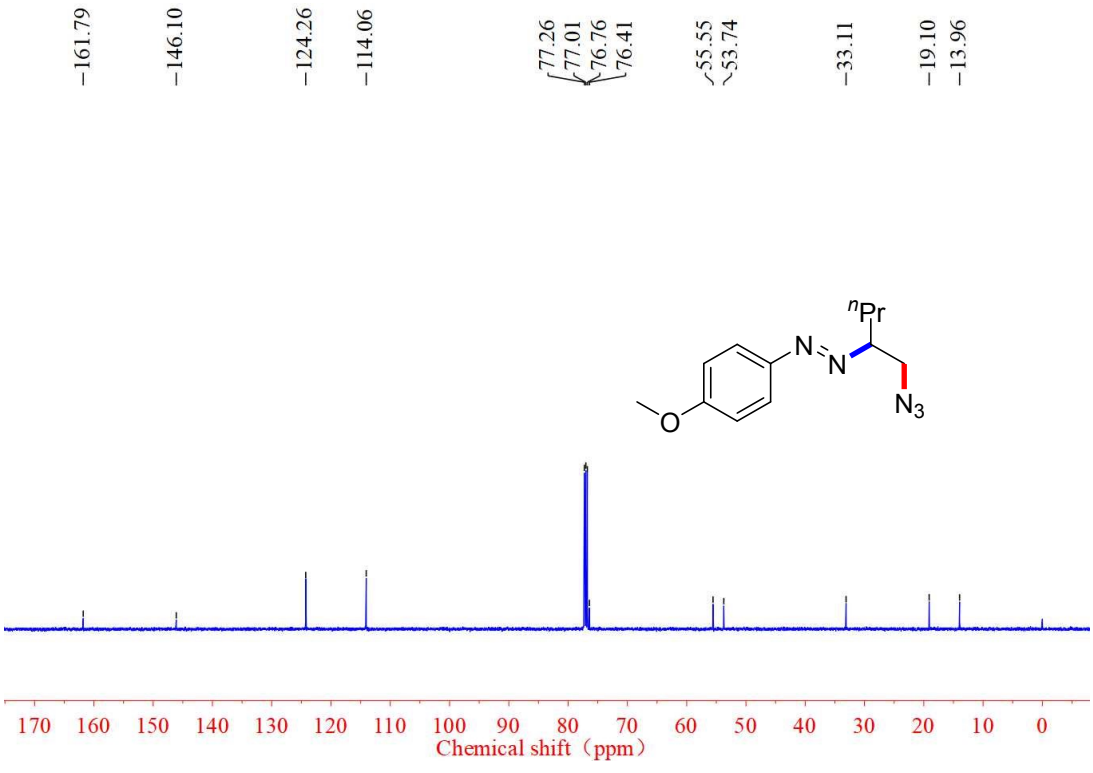
Obtained as a yellow oil 1:1 dr (56 mg, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 6.97 (d, J = 9.1 Hz, 2H), 5.76 (s, 1H), 3.87 (s, 3H), 3.67 – 3.52 (m, 2H), 2.58 – 2.20 (m, 6H), 2.04 – 1.92 (m, 3H), 1.34 – 1.27 (m, 1H), 1.24 – 1.20 (m, 3H), 1.15 (s, 3H), 1.00 – 0.95 (m, 2H), 0.92 – 0.91 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) Mixture of diastereomers is observed. Ratio: 5/5. Major diastereomer: δ 199.47, 170.23, 161.82, 145.90, 124.55, 124.16, 114.10, 74.32, 56.68, 55.57, 42.05, 40.53, 39.41, 39.31, 38.51, 32.94, 27.45, 17.74, 16.84, 15.03; Minor diastereomer: δ 199.45, 170.18, 161.82, 145.87, 124.55, 124.10, 114.09, 74.10, 56.61, 55.57, 45.98, 42.01, 40.46, 39.34, 38.97, 38.34, 27.02, 17.32, 16.80, 15.00; HRMS (ESI): $[M+Na]^+$ Calculated for $C_{22}H_{29}N_5O_2Na$: 418.2213, Found 418.2214.

Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

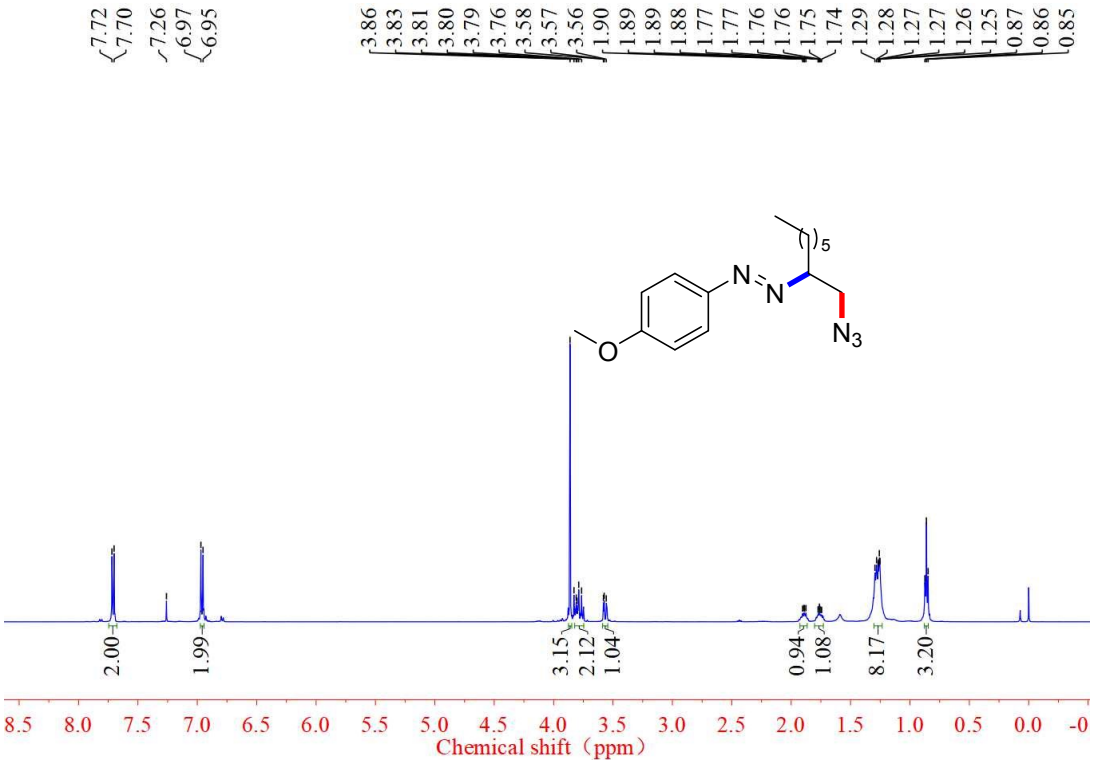
4a ^{1}H NMR



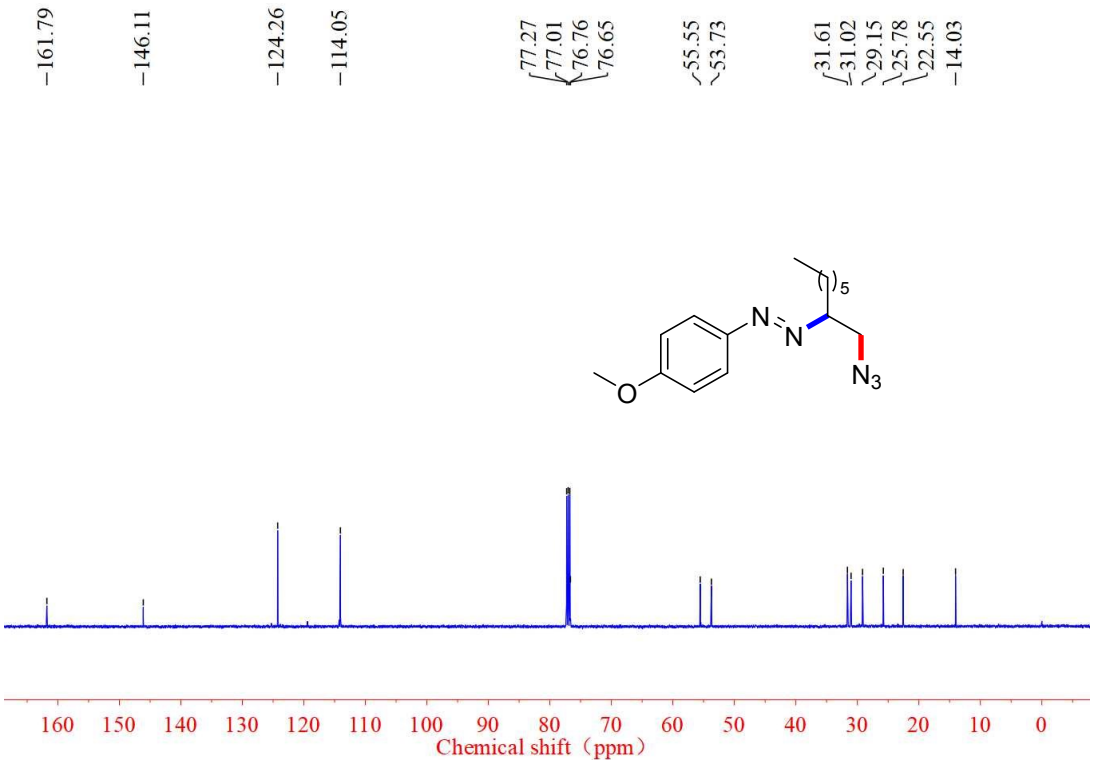
4a ^{13}C NMR



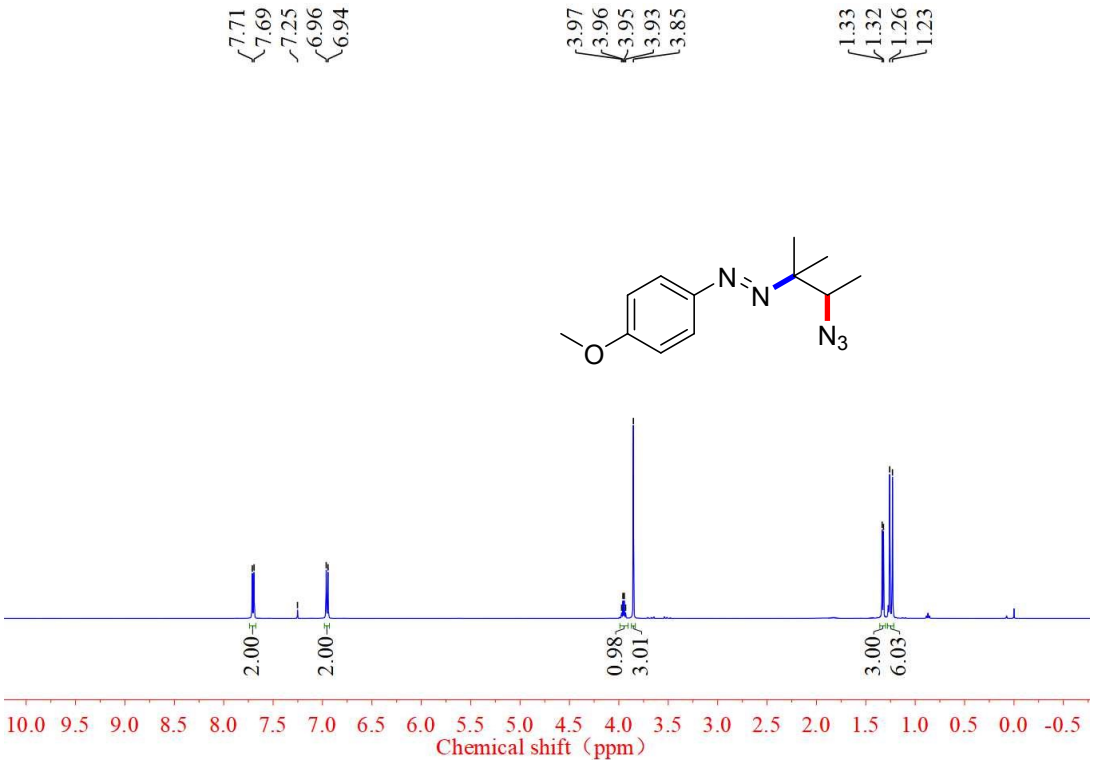
4b ^{1}H NMR



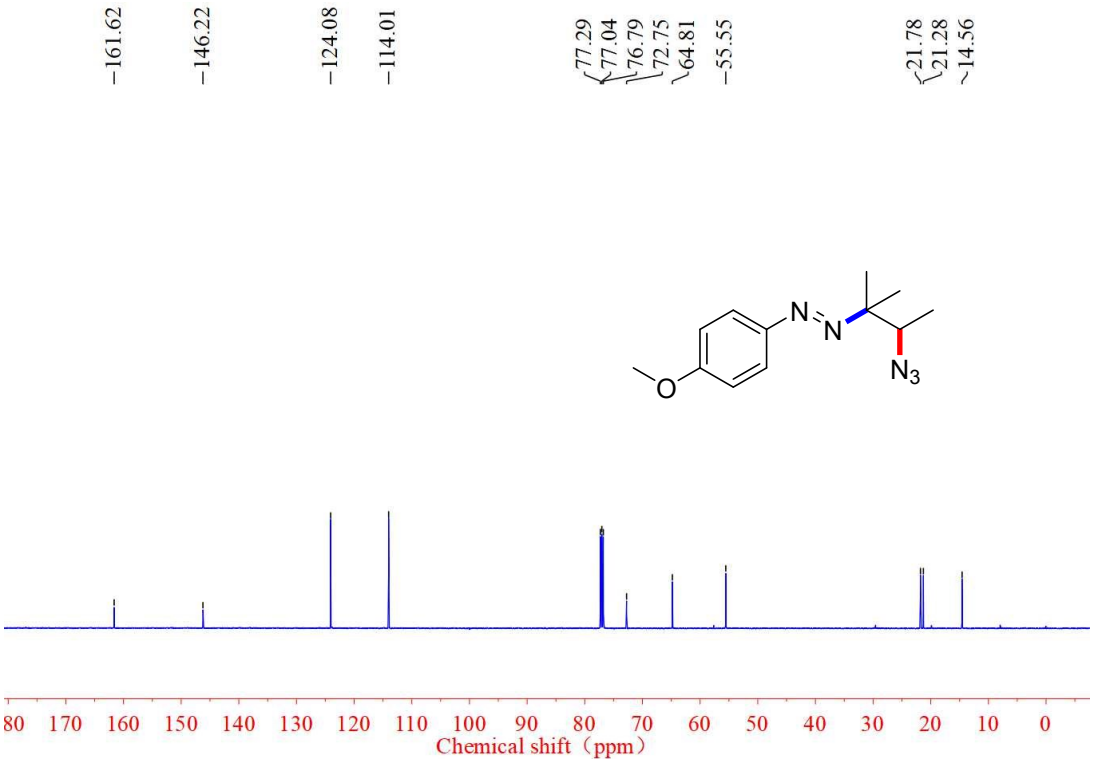
4b ^{13}C NMR



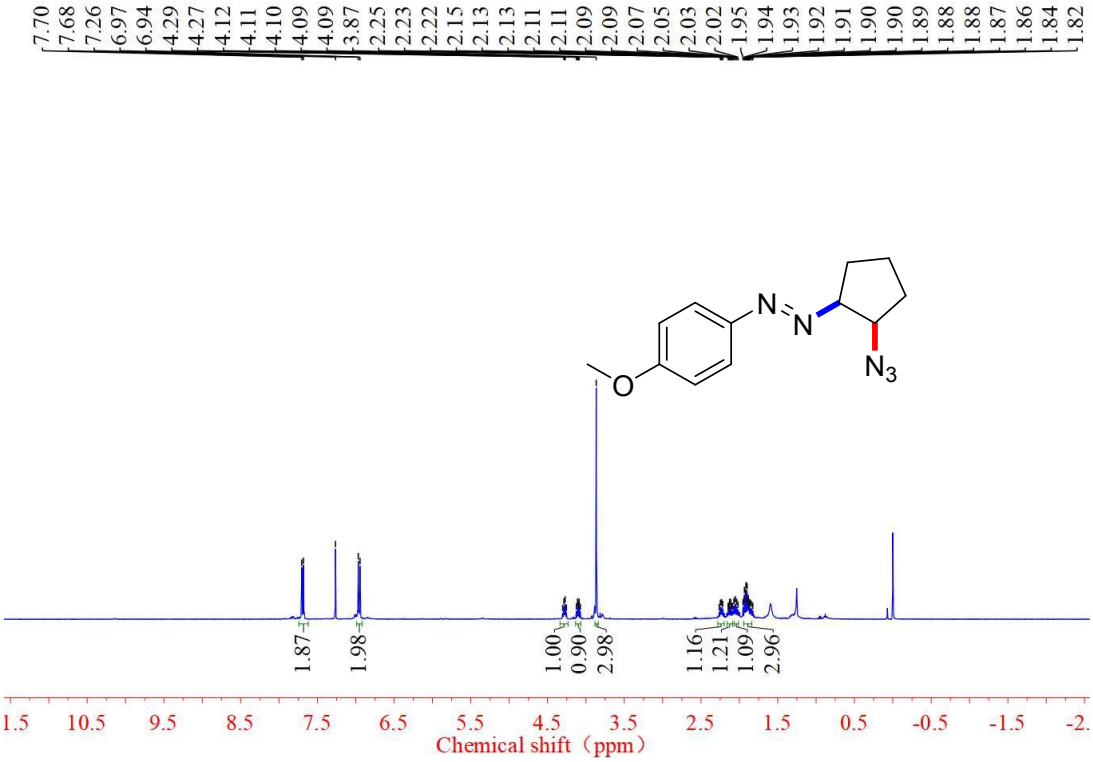
4c ^{1}H NMR



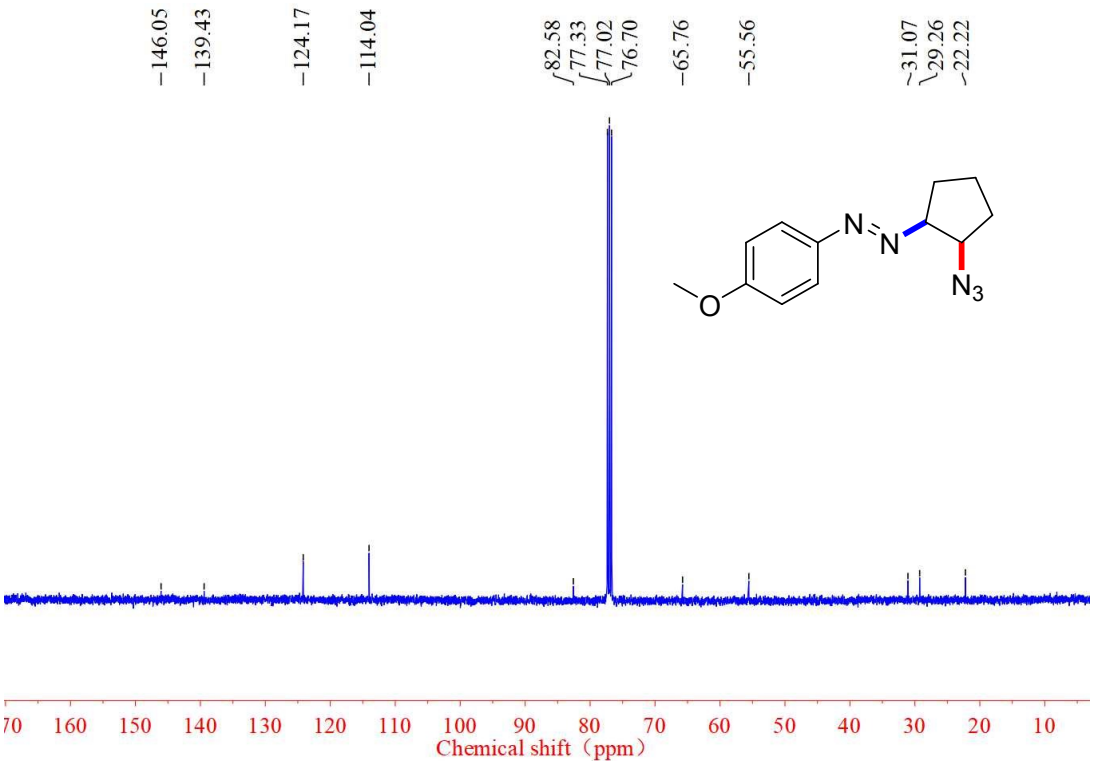
4c ^{13}C NMR



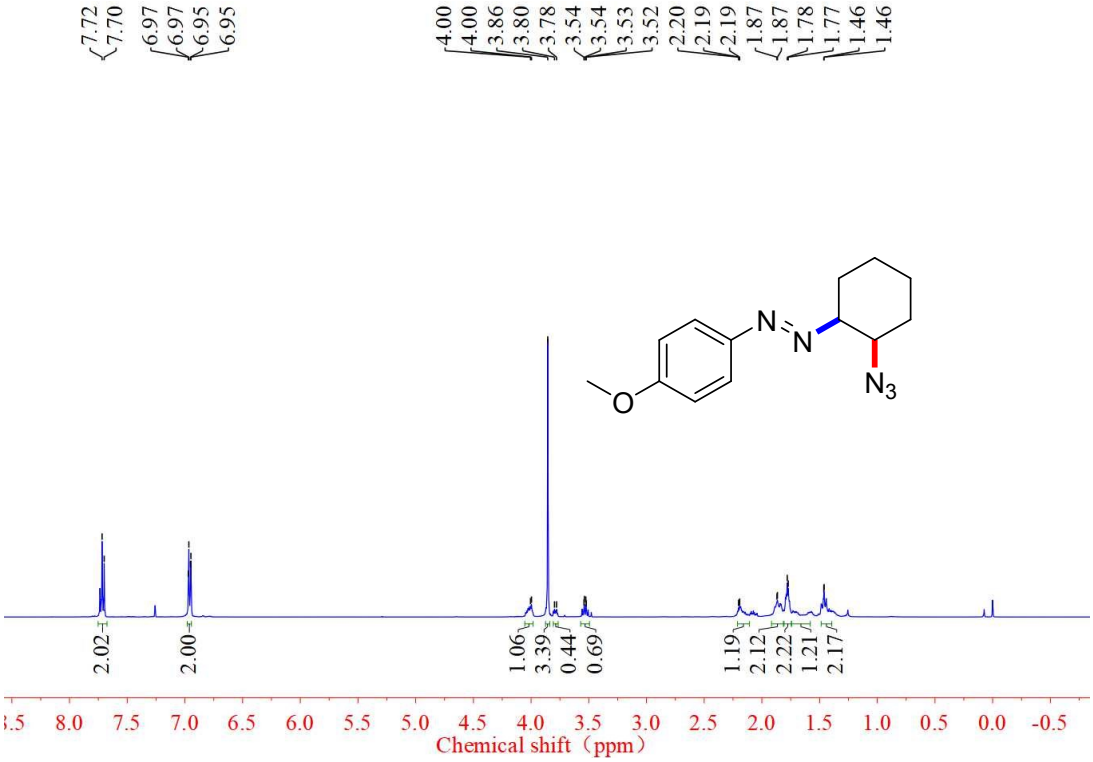
4d ^{1}H NMR



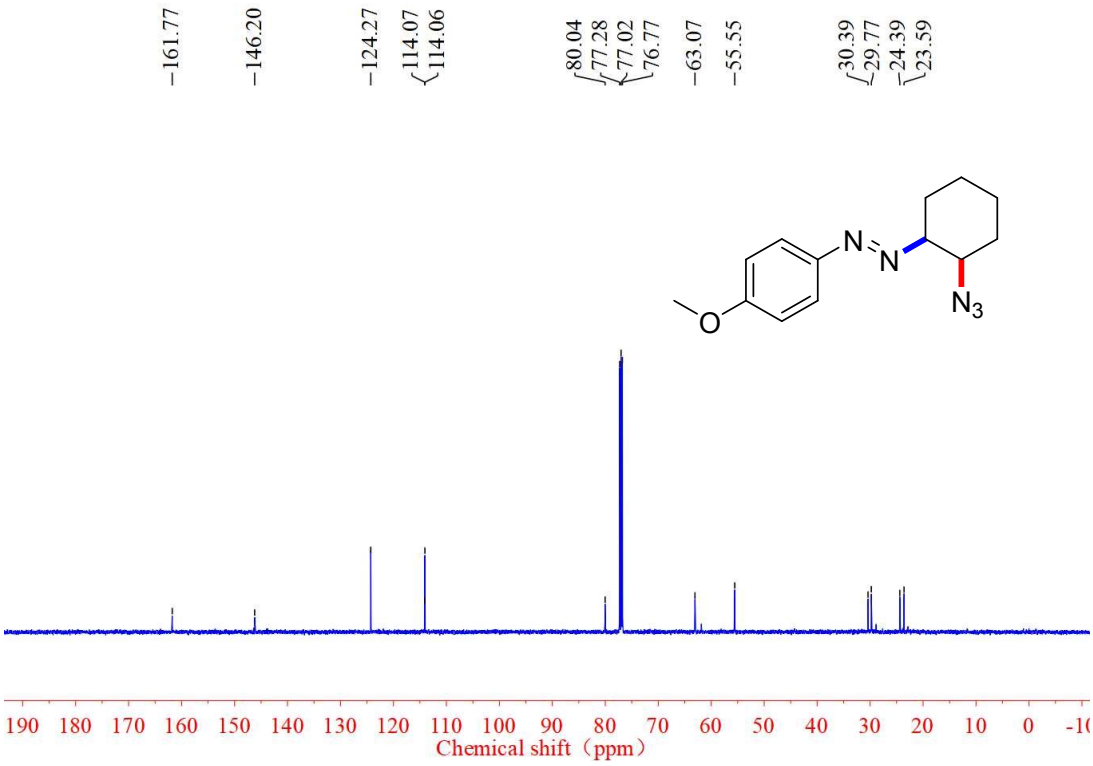
4d ^{13}C NMR



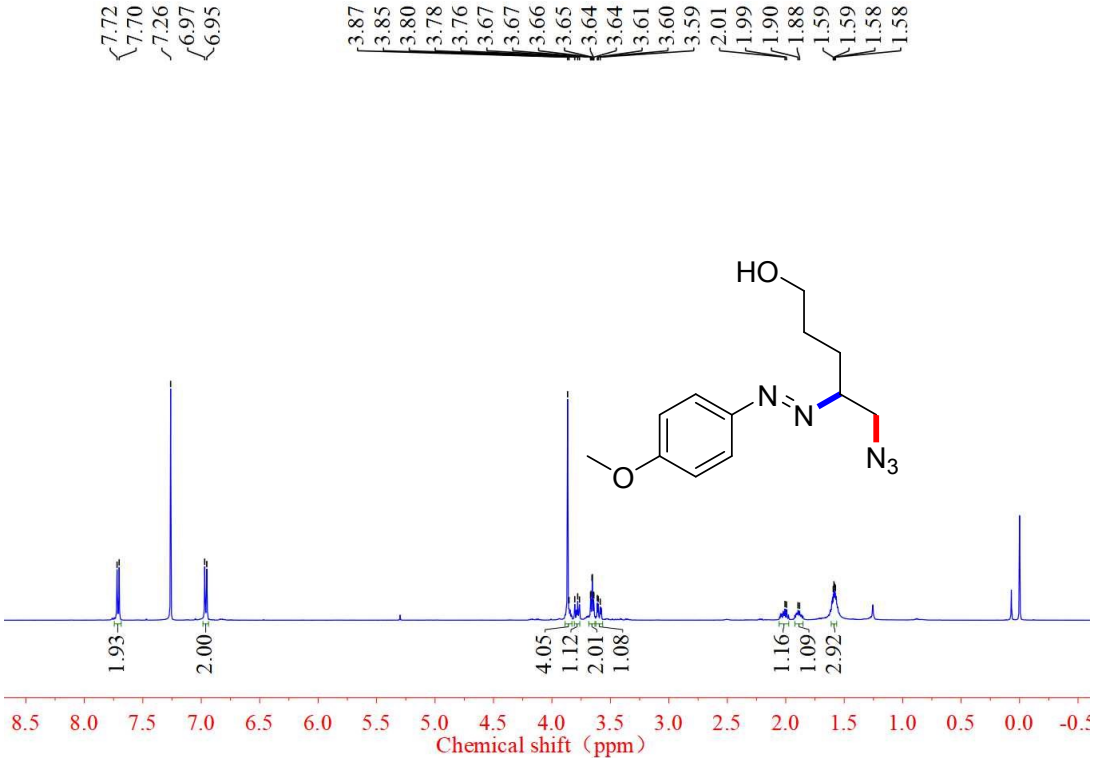
4e ^{1}H NMR



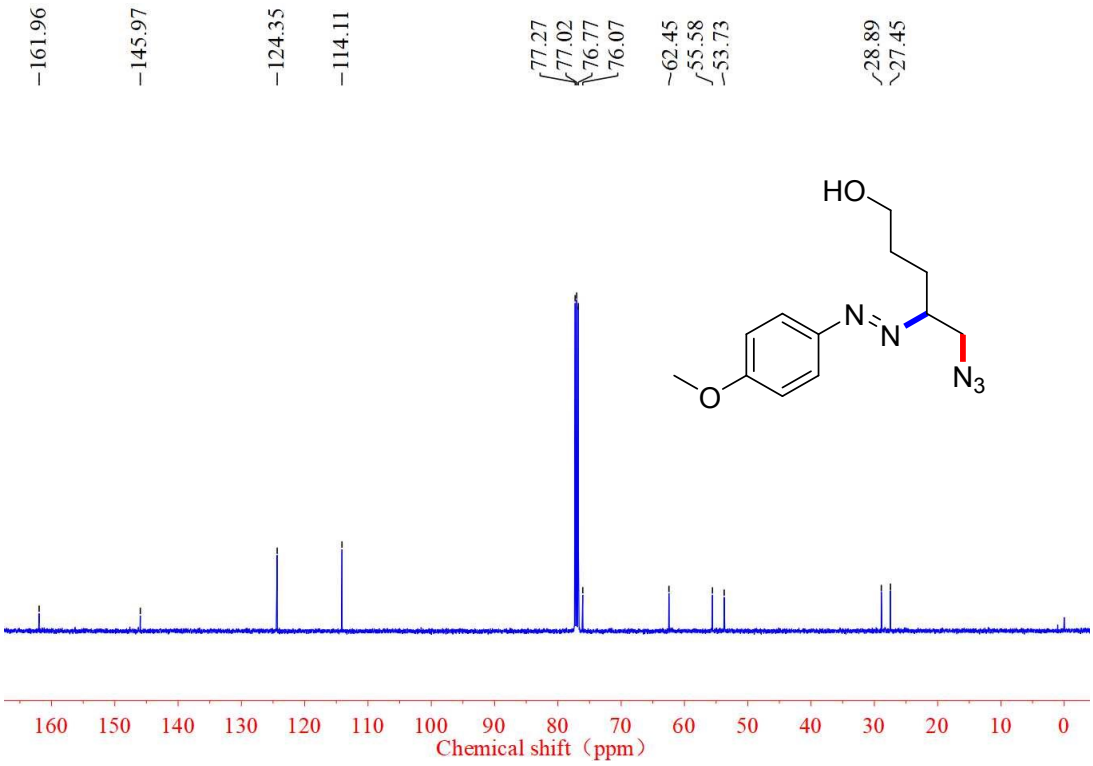
4e ^{13}C NMR



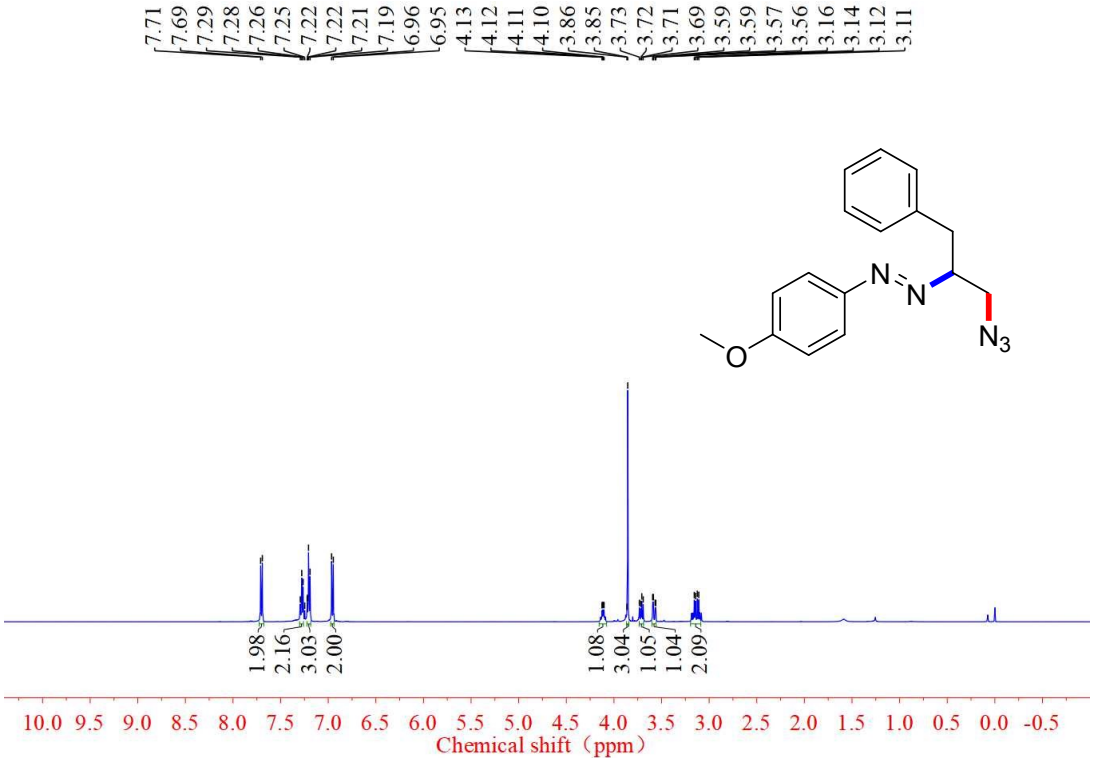
4f ^{1}H NMR



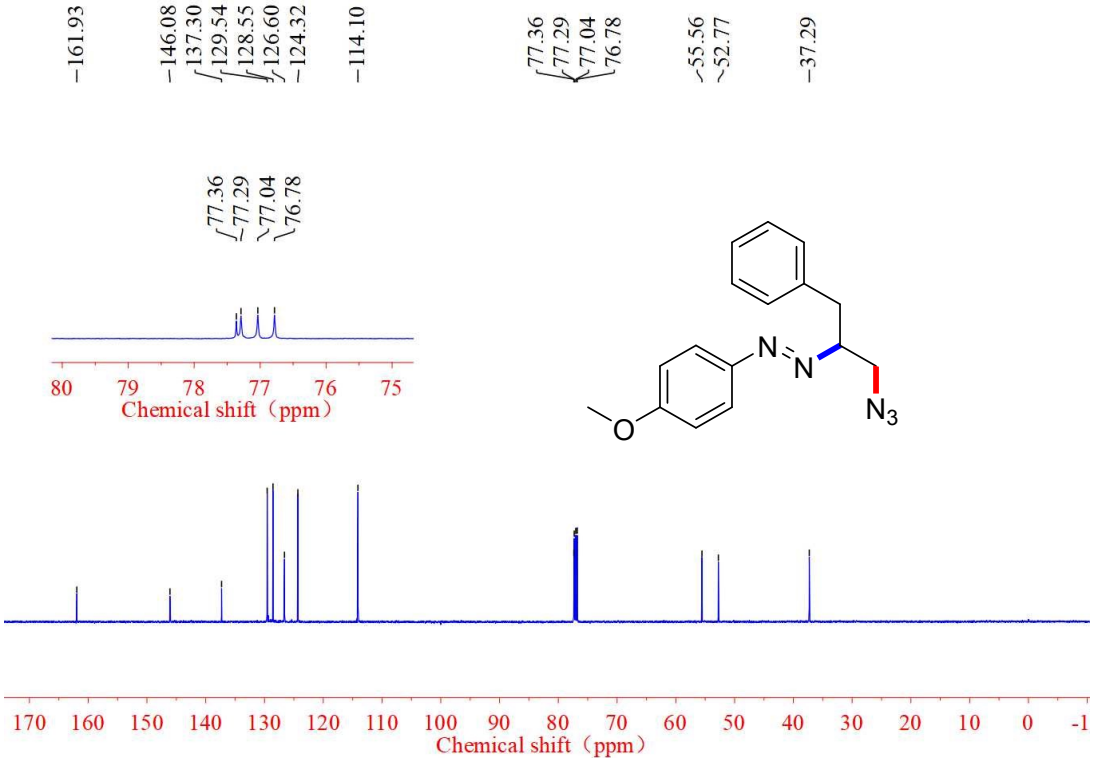
4f ^{13}C NMR



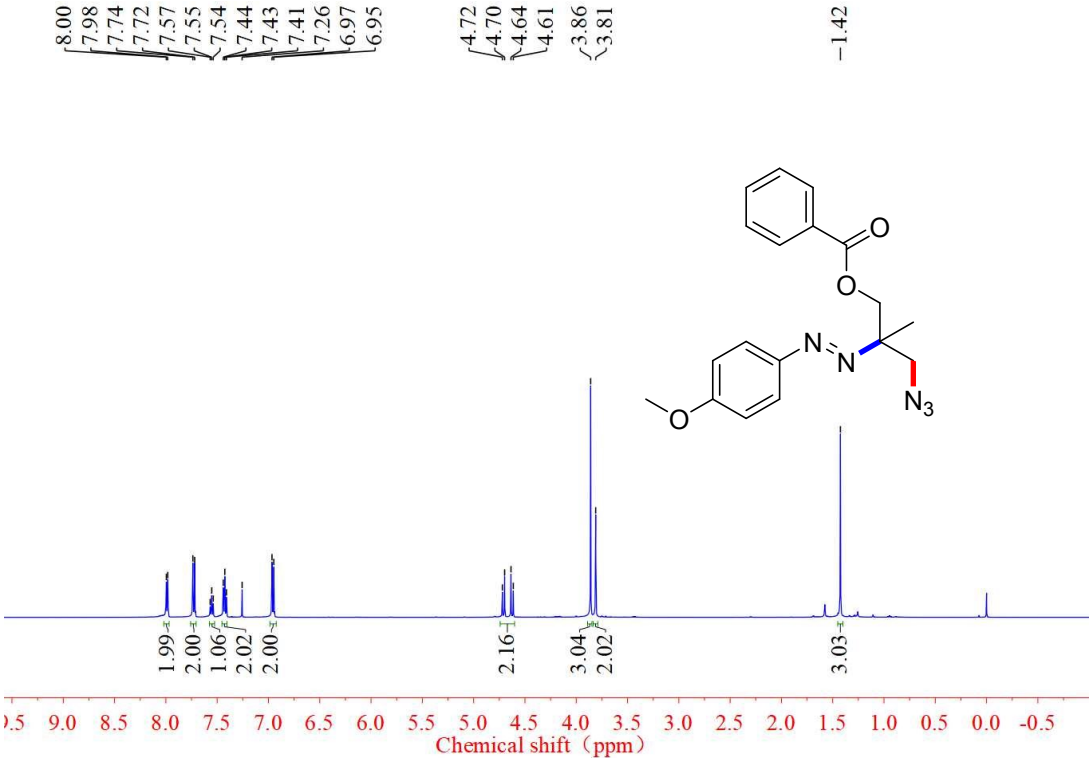
4g ^{1}H NMR



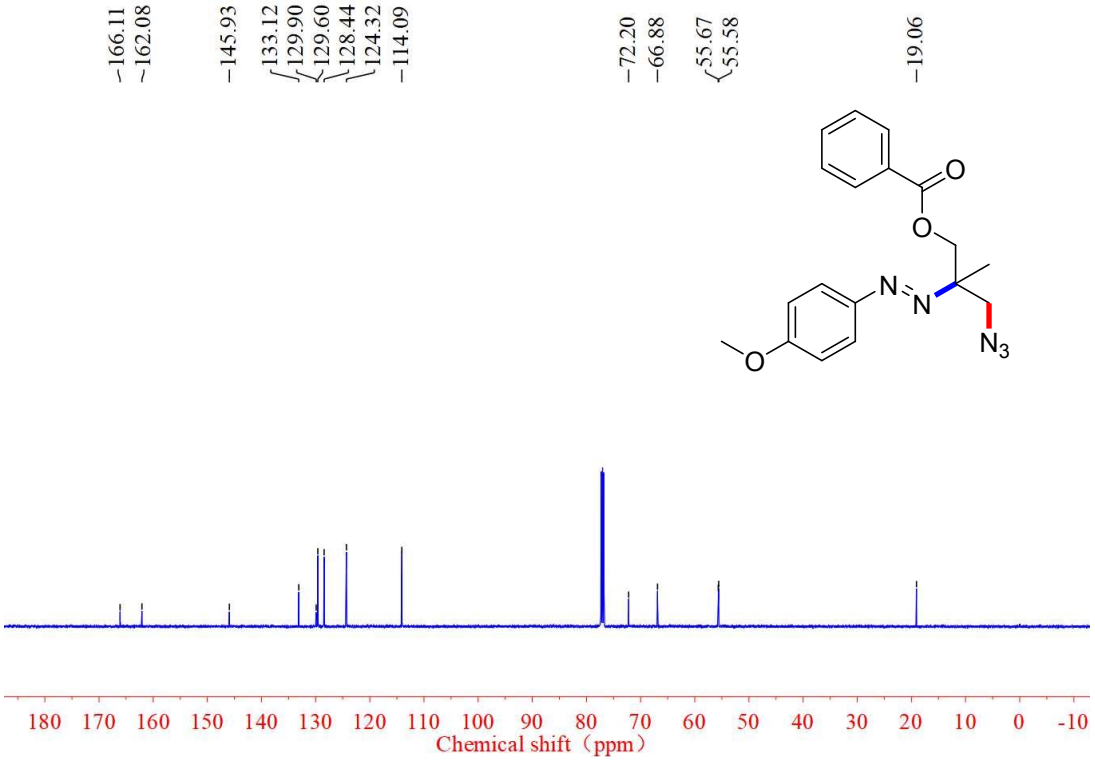
4g ^{13}C NMR



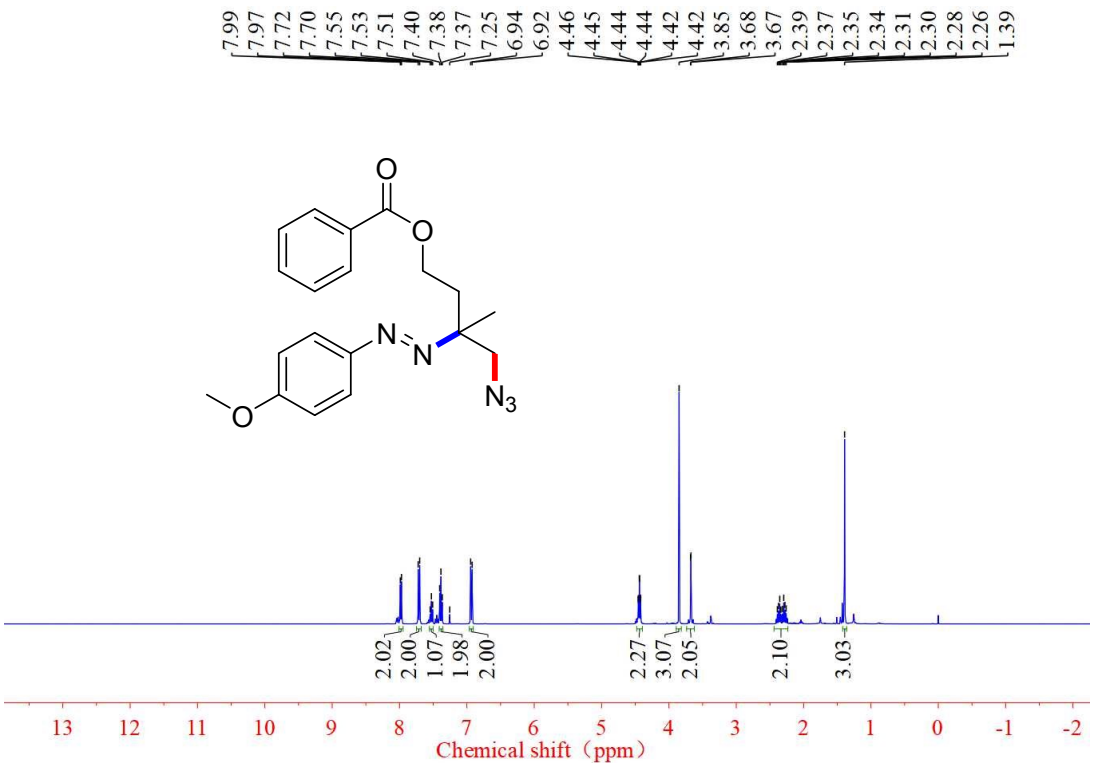
4h ^{1}H NMR



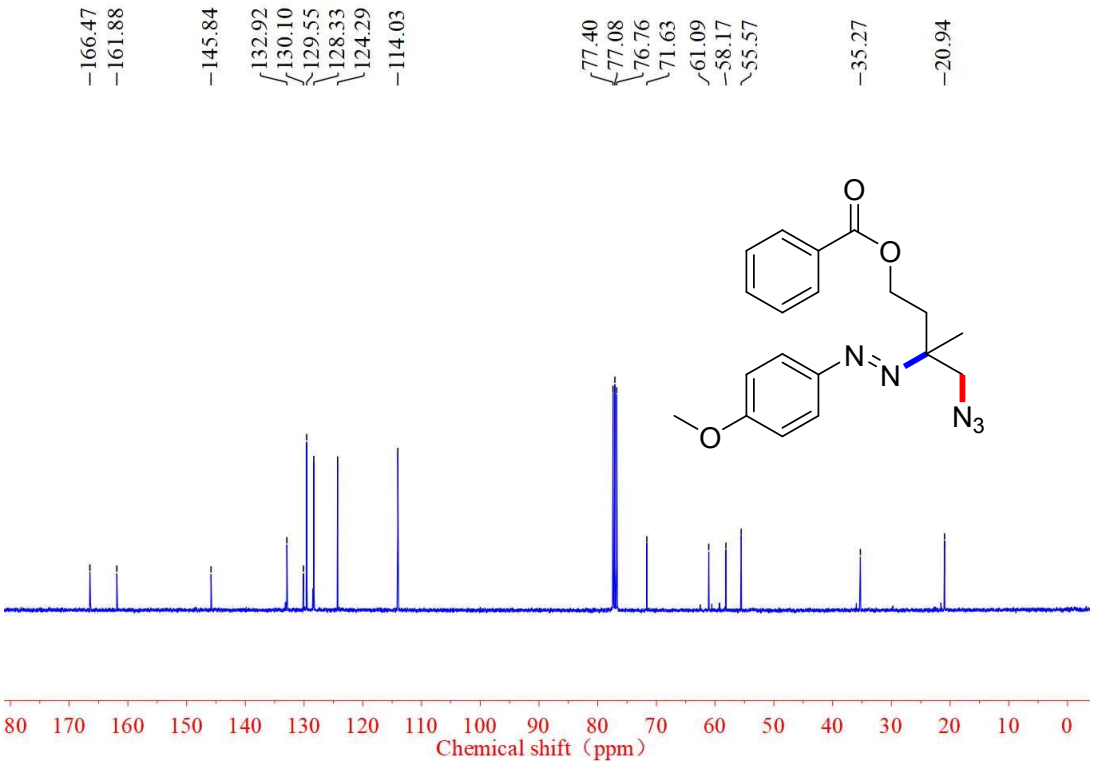
4h ^{13}C NMR



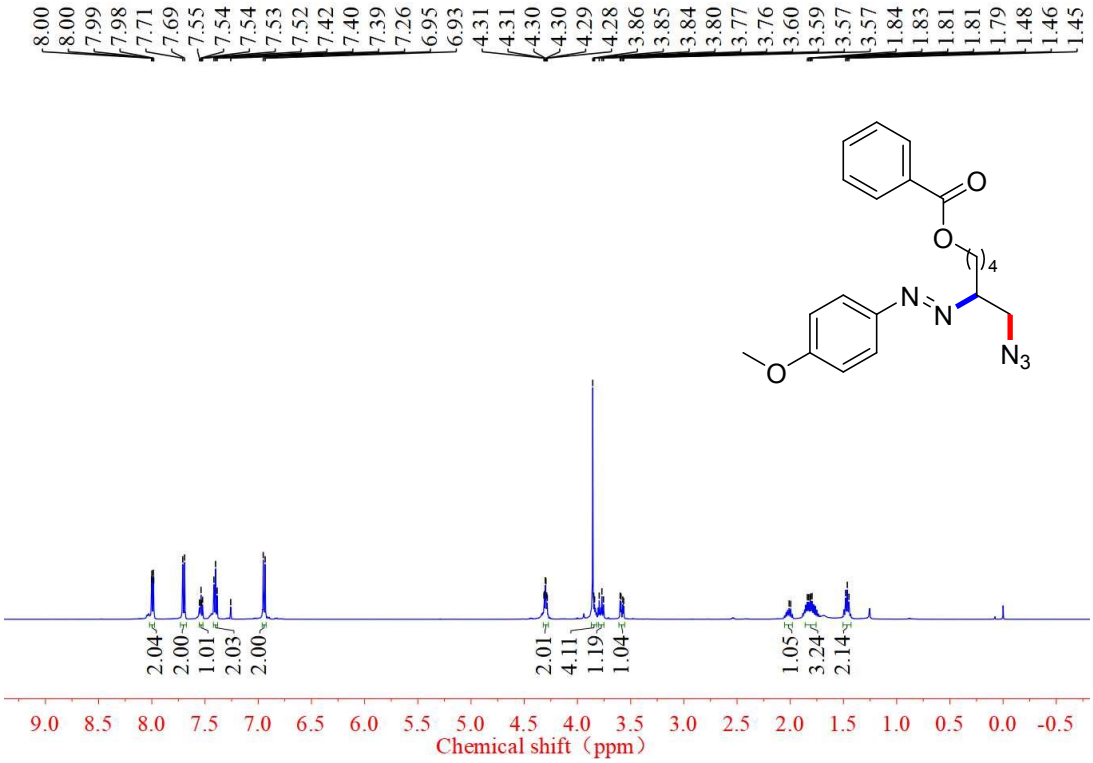
4i ^{1}H NMR



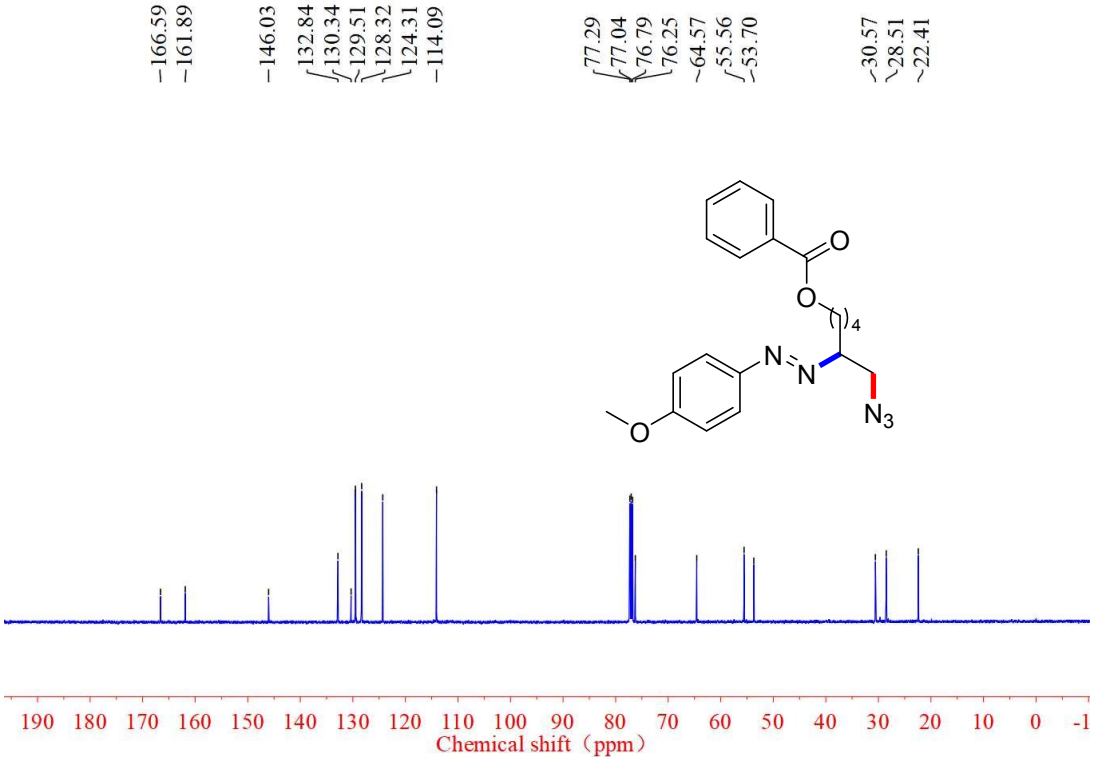
4i ^{13}C NMR



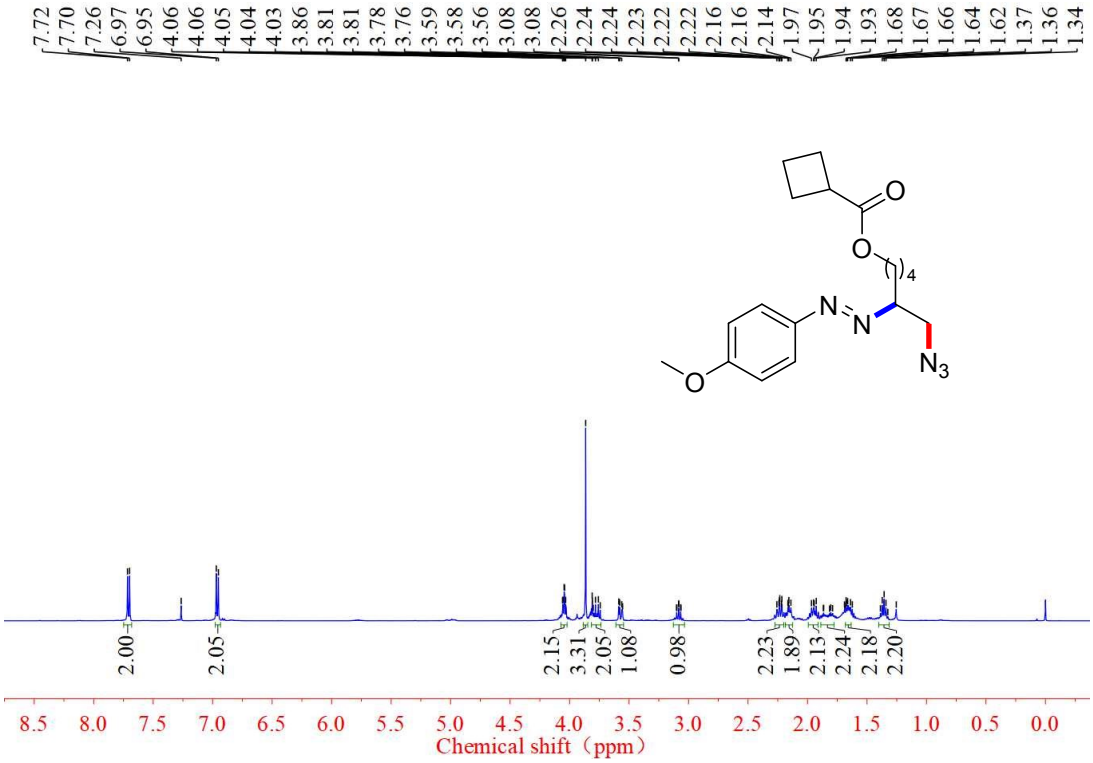
4j ^{1}H NMR



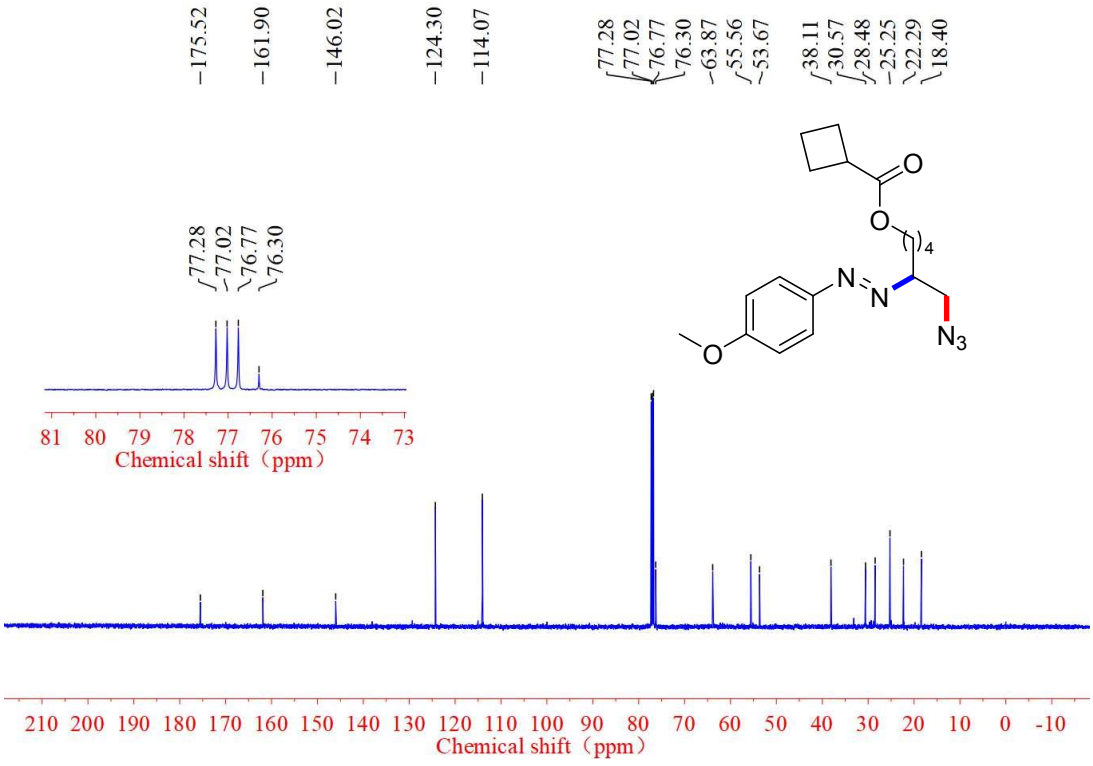
4j ^{13}C NMR



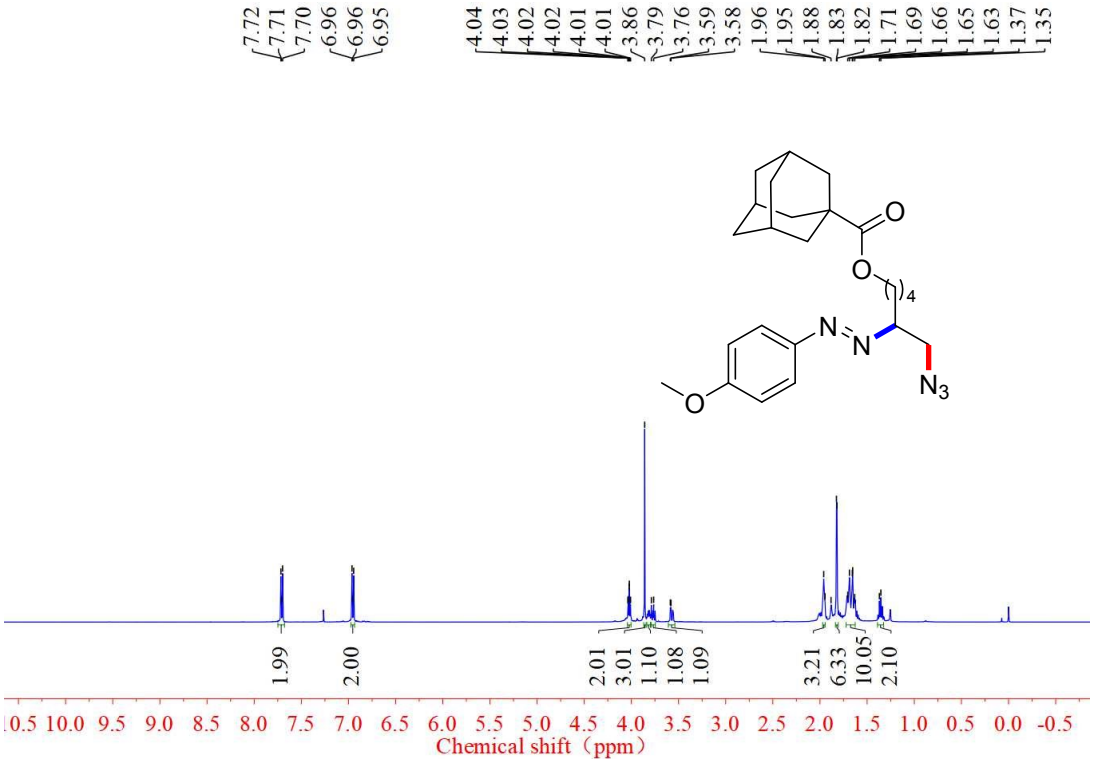
4k ^{1}H NMR



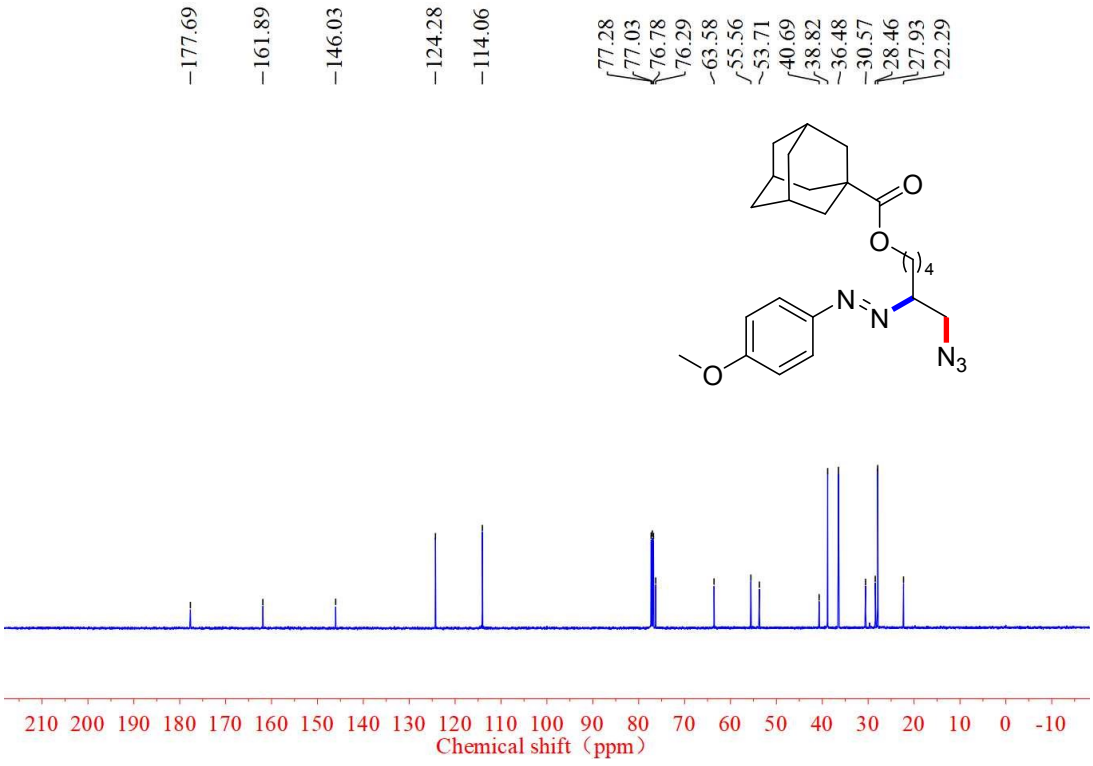
4k ^{13}C NMR



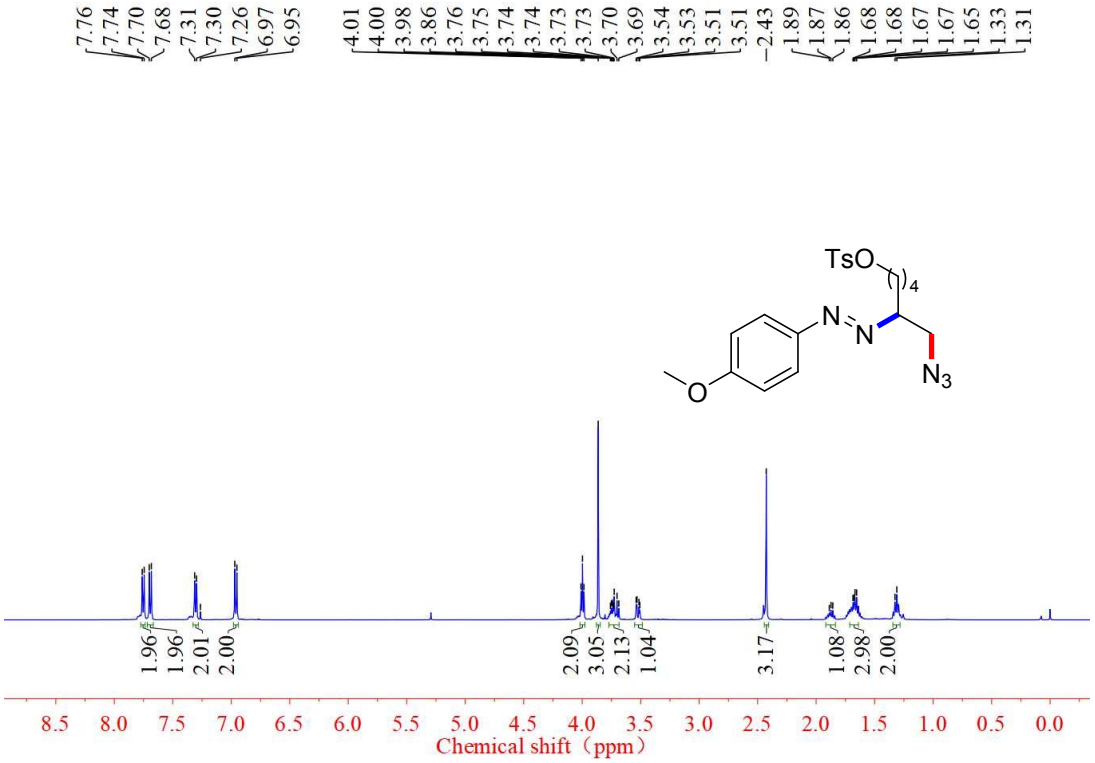
4l ^{1}H NMR



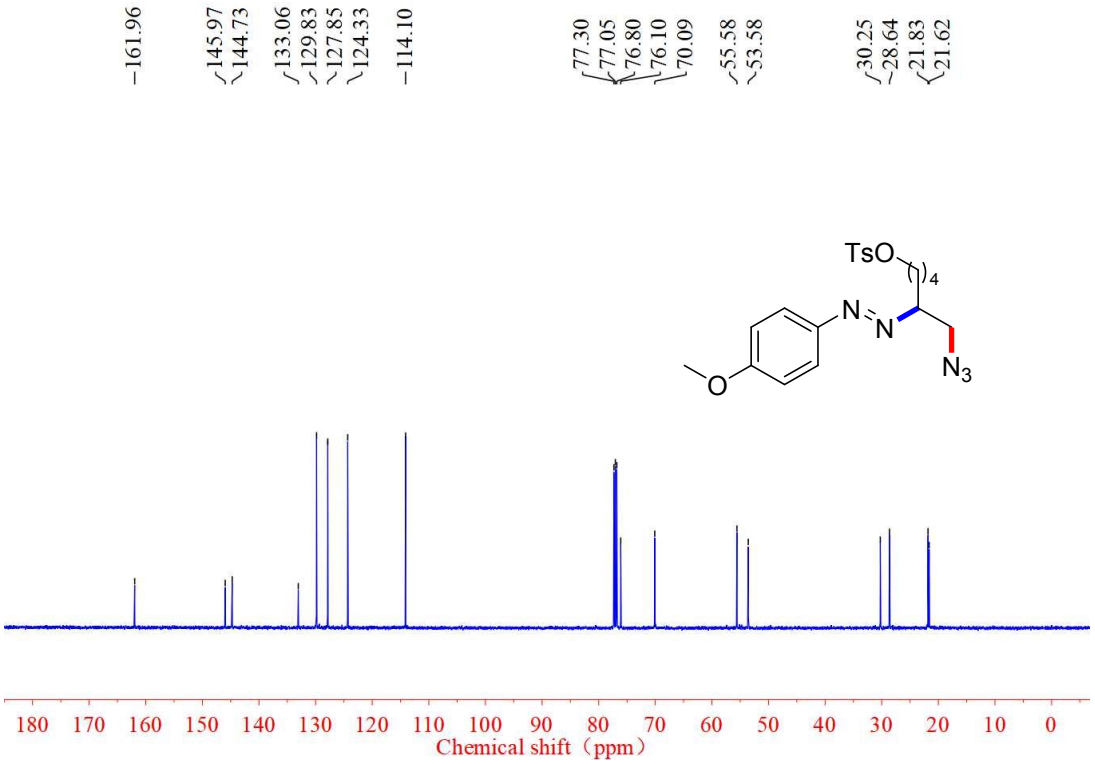
4l ^{13}C NMR



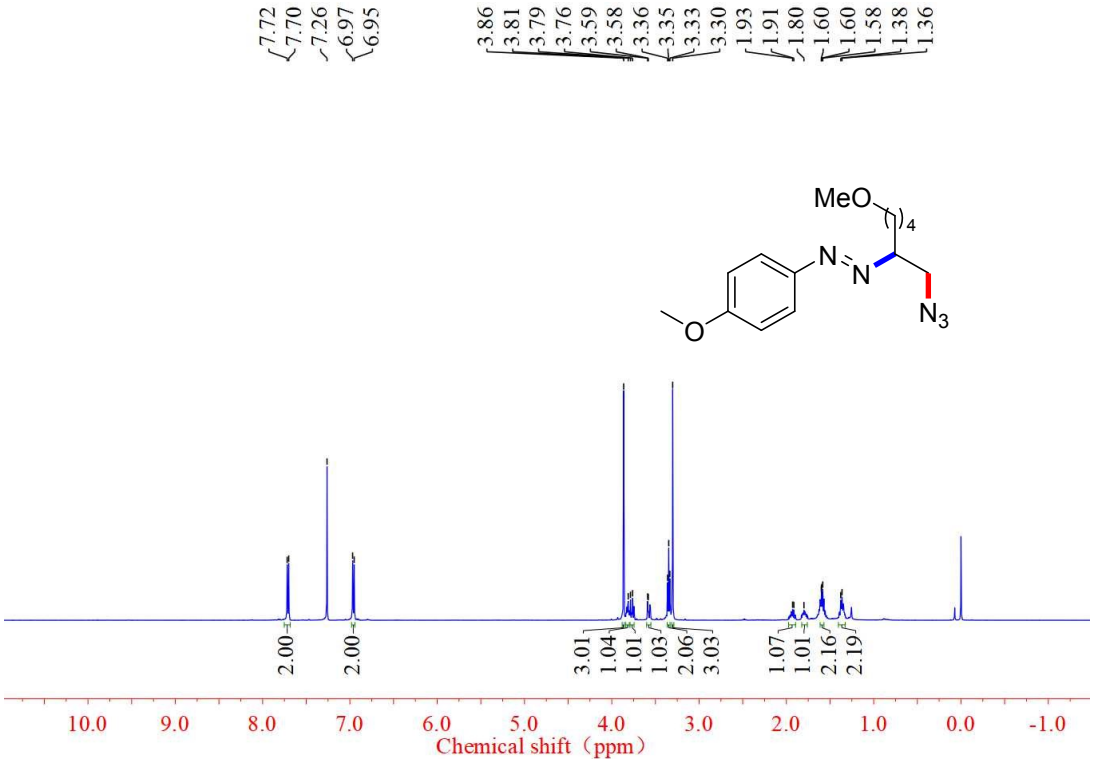
4m ^{1}H NMR



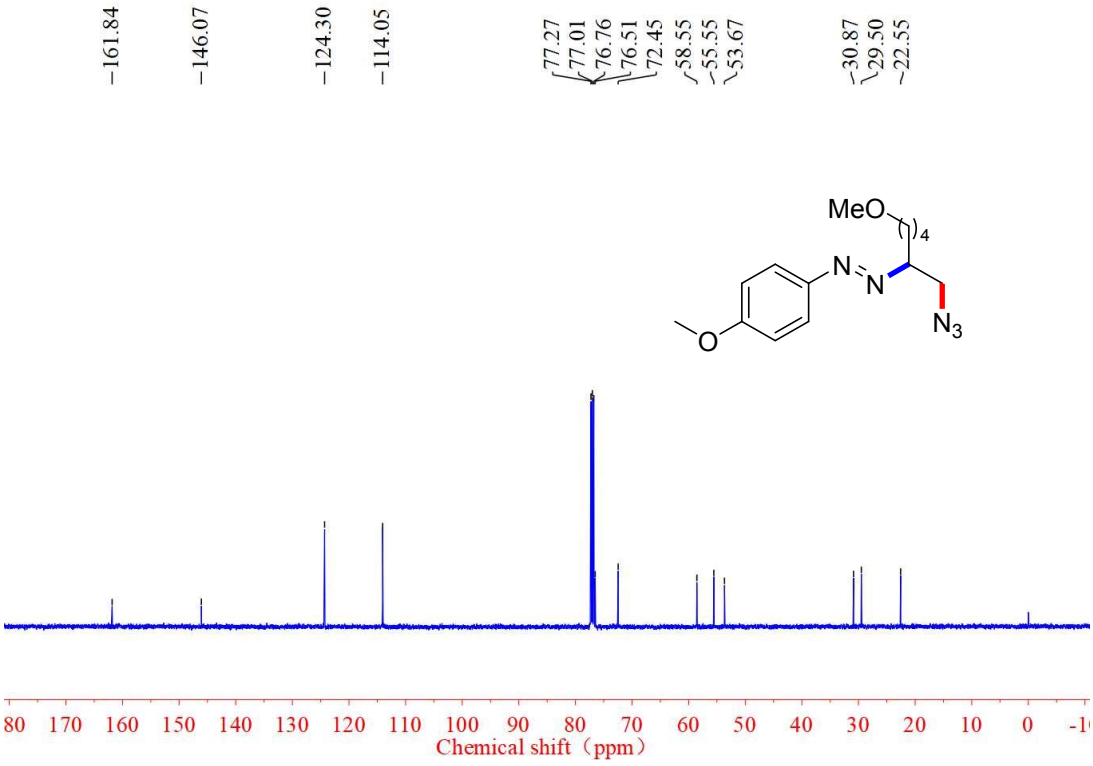
4m ^{13}C NMR



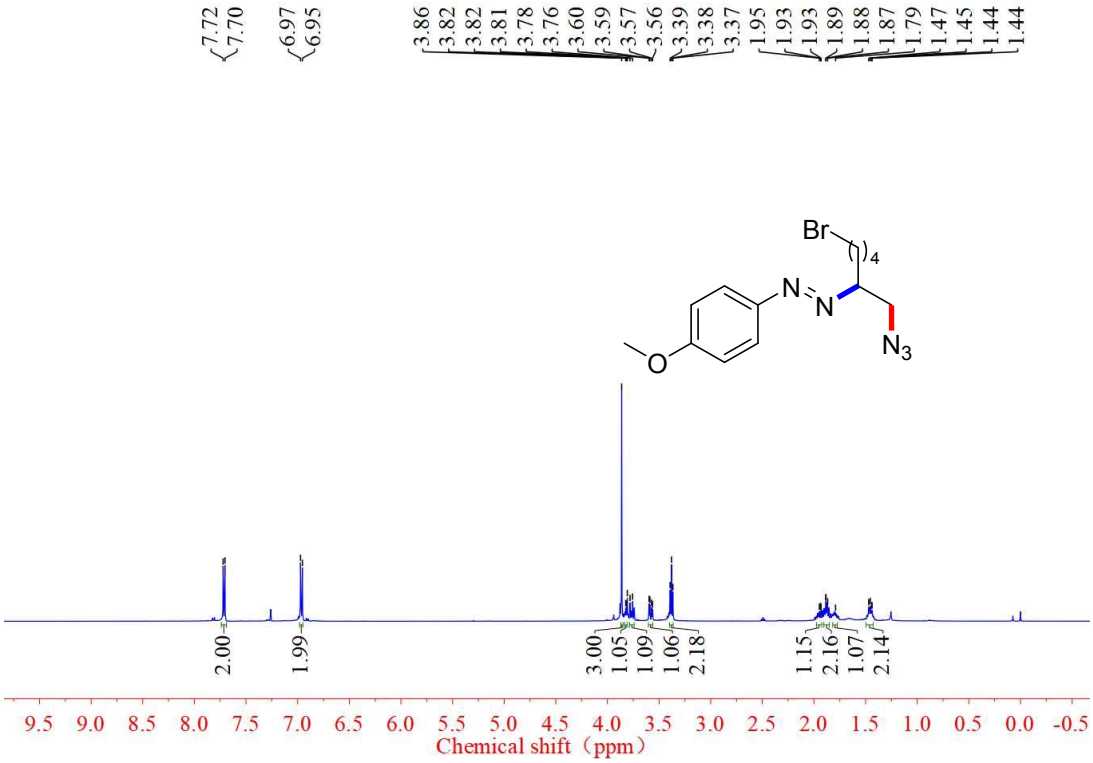
4n ^{1}H NMR



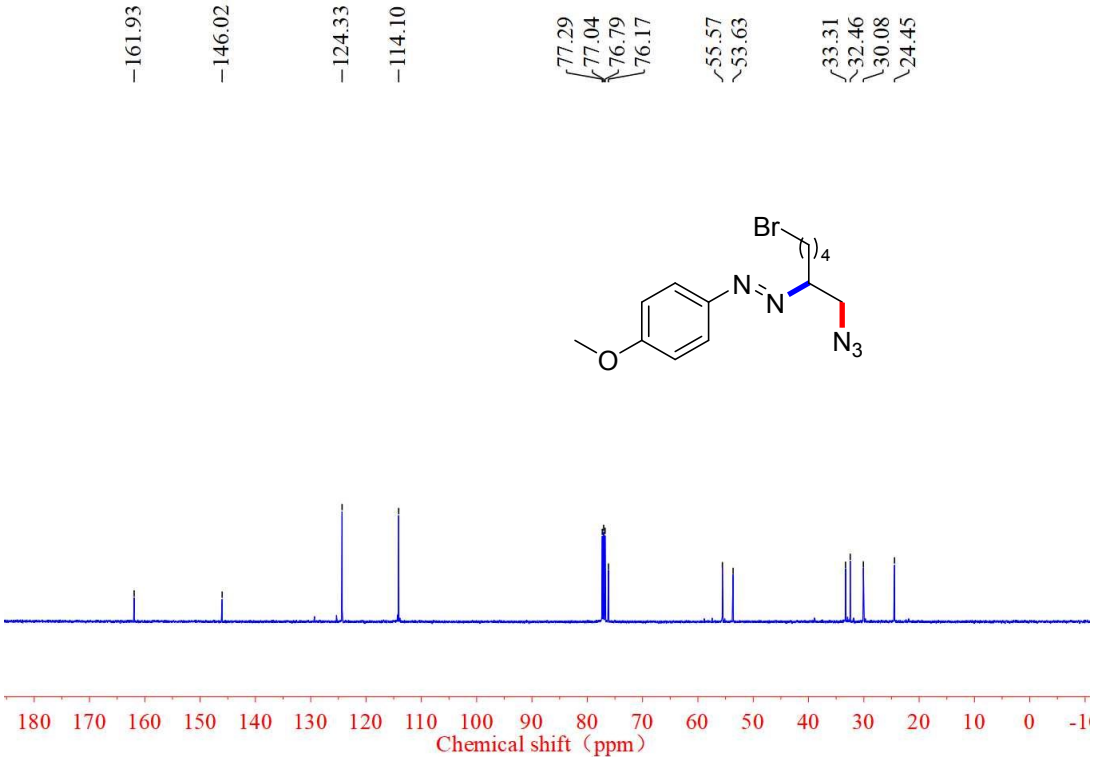
4n ^{13}C NMR



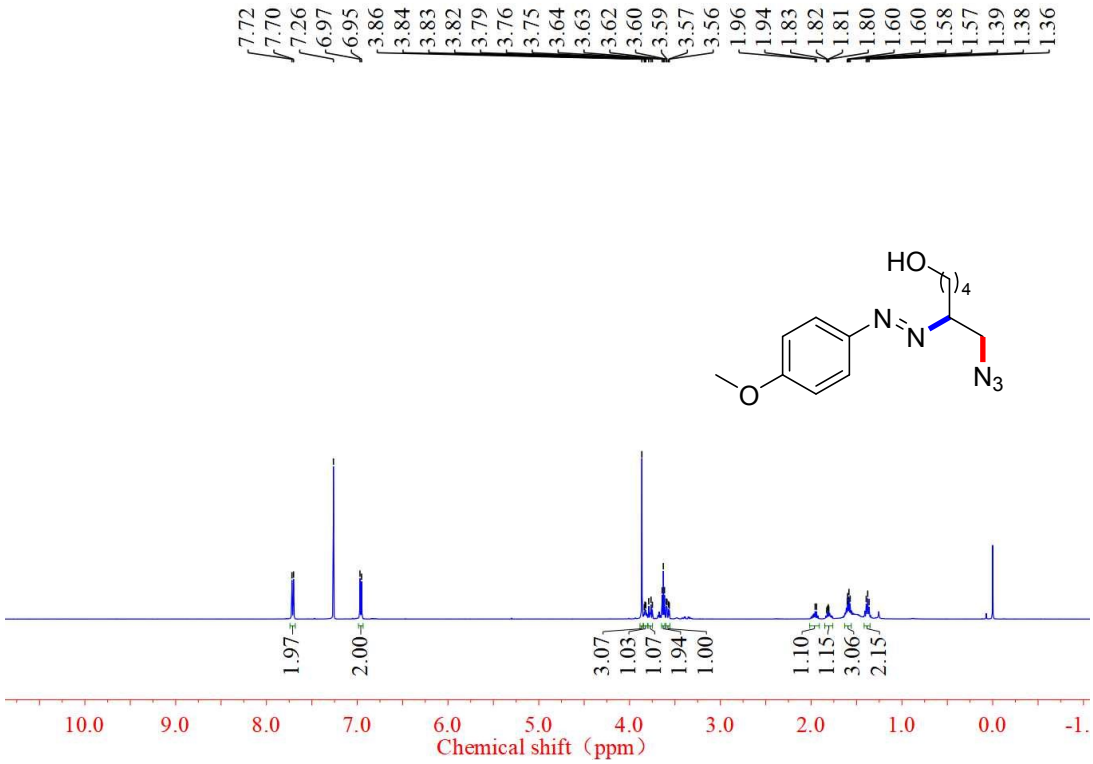
4o ^{1}H NMR



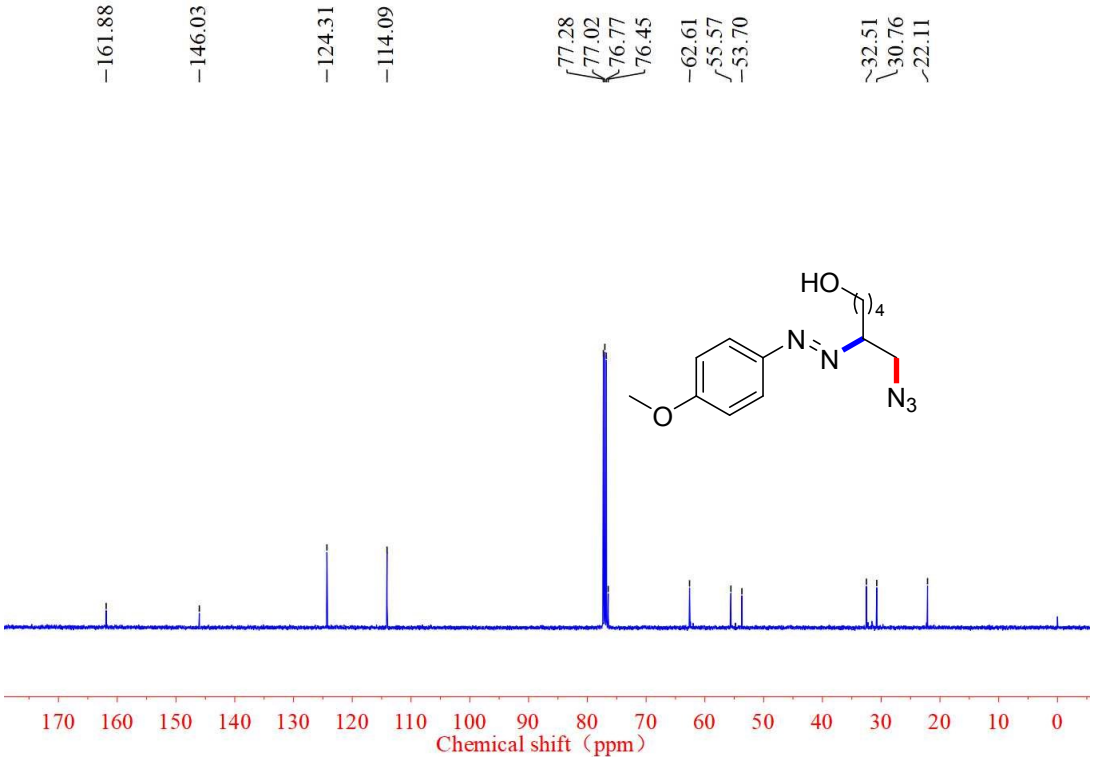
4o ^{13}C NMR



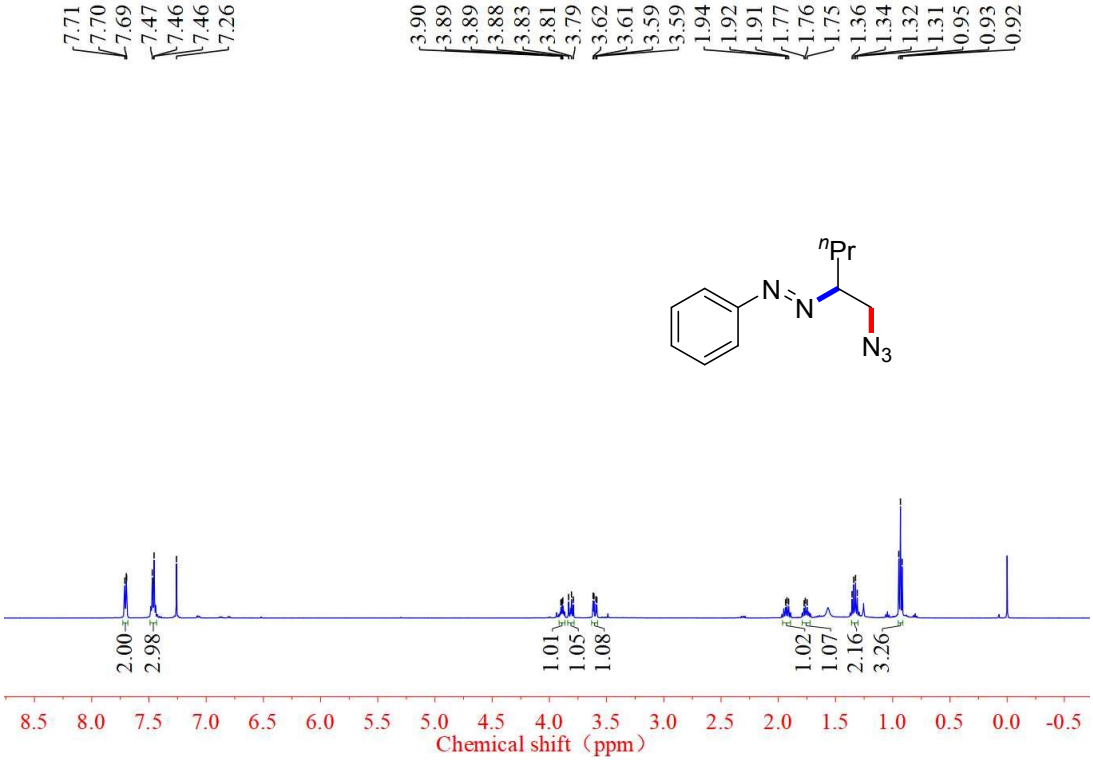
4p ^{1}H NMR



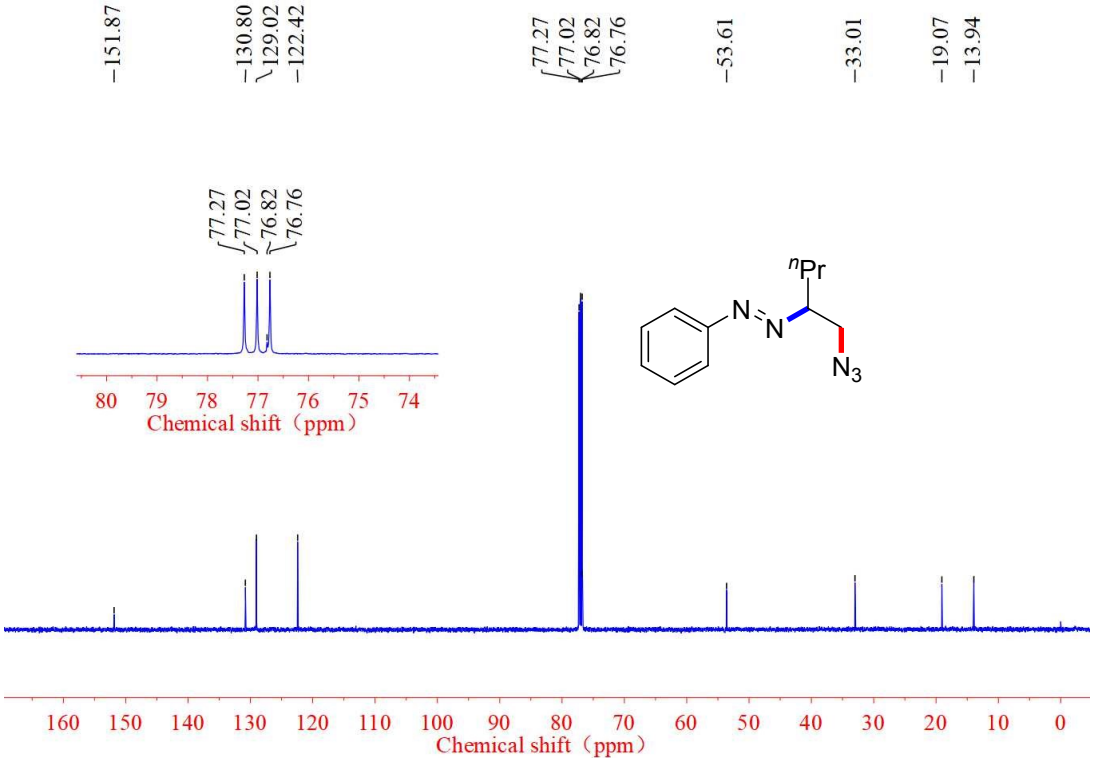
4p ^{13}C NMR



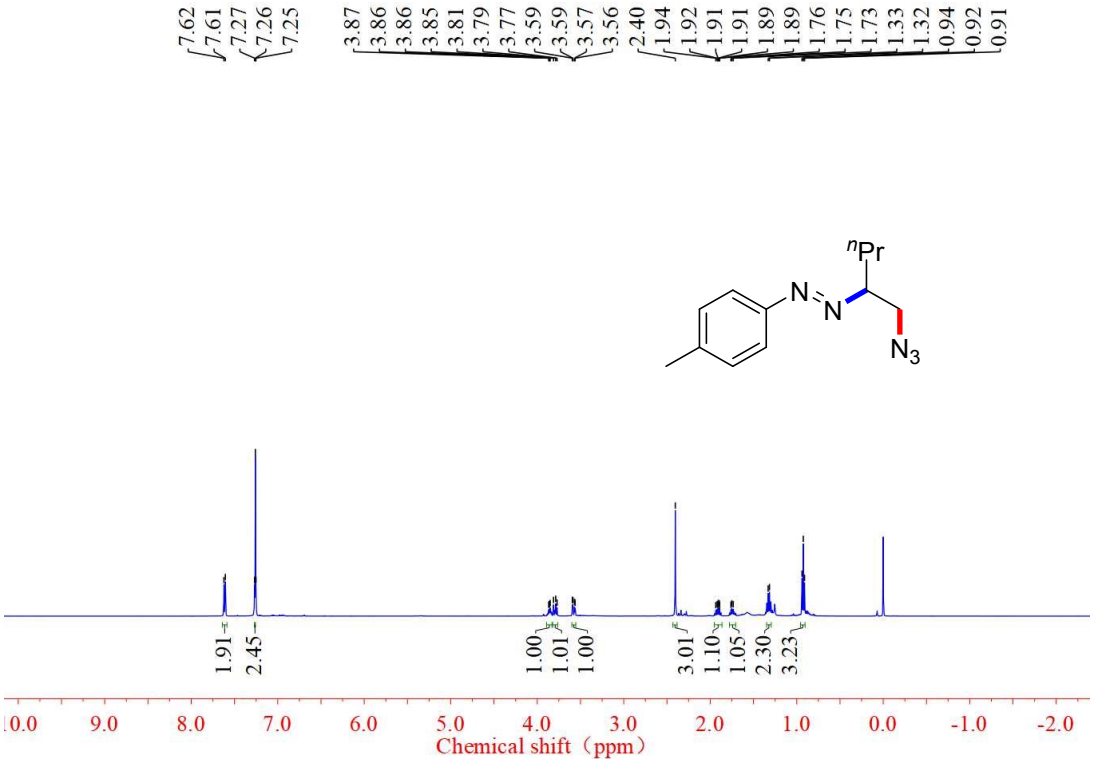
4q ^{1}H NMR



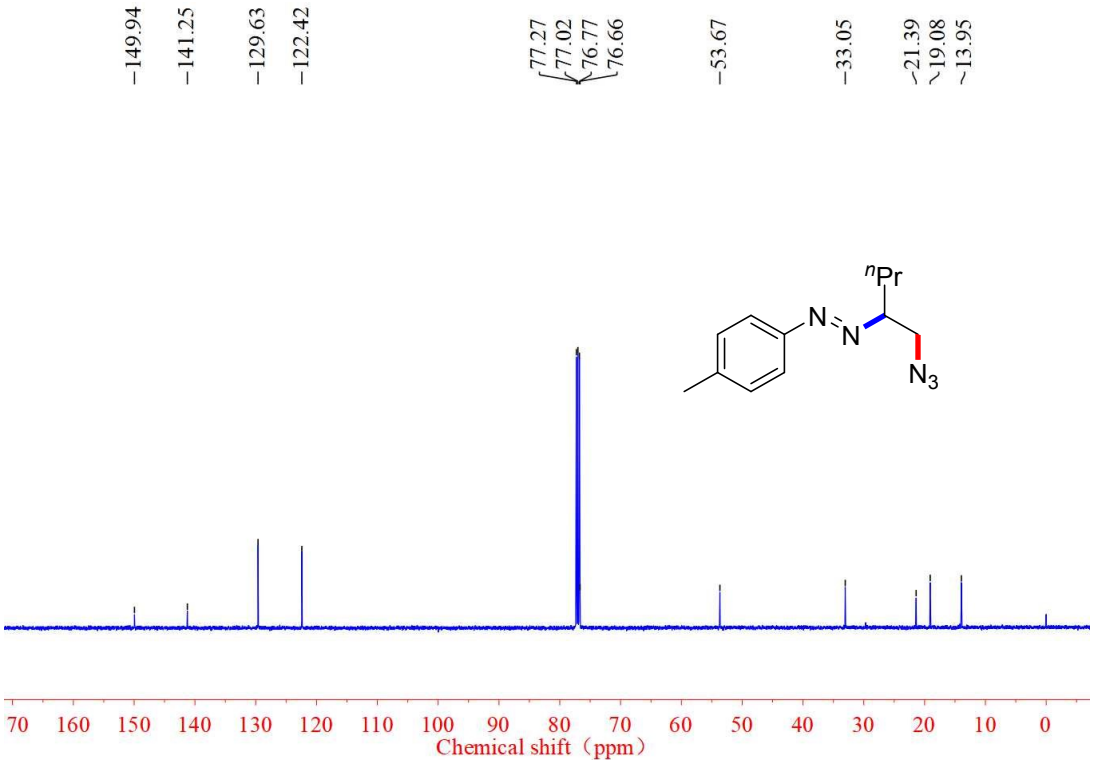
4q ^{13}C NMR



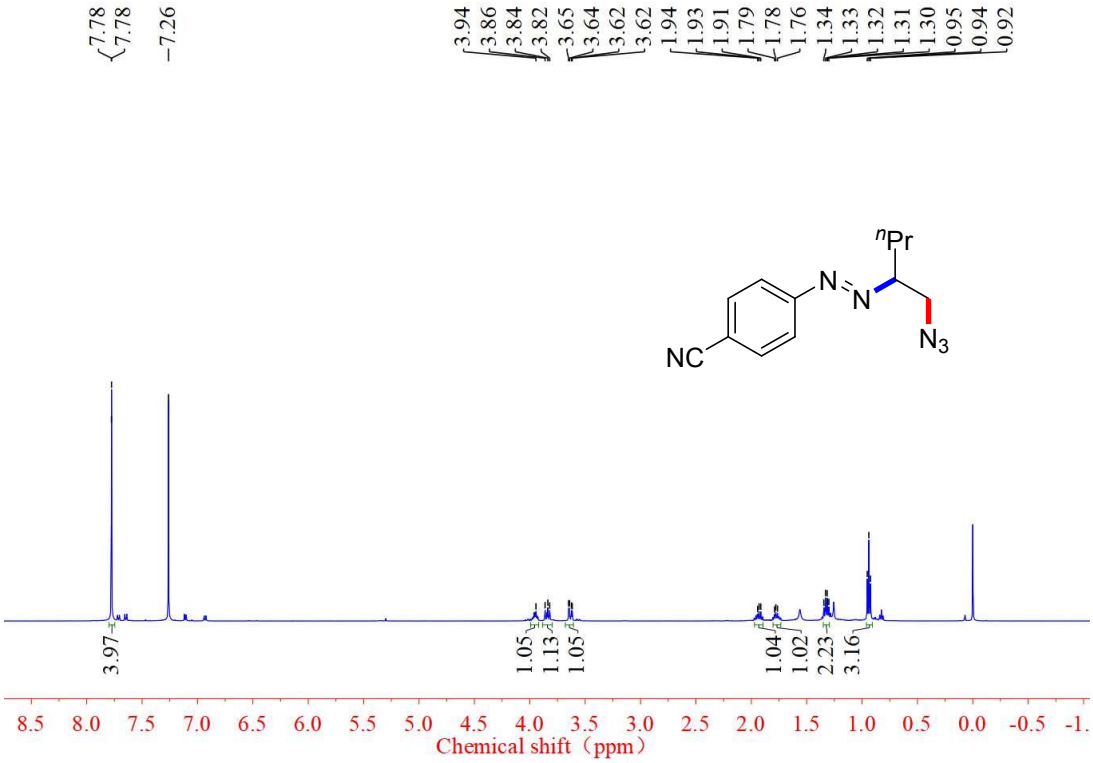
4r ^{1}H NMR



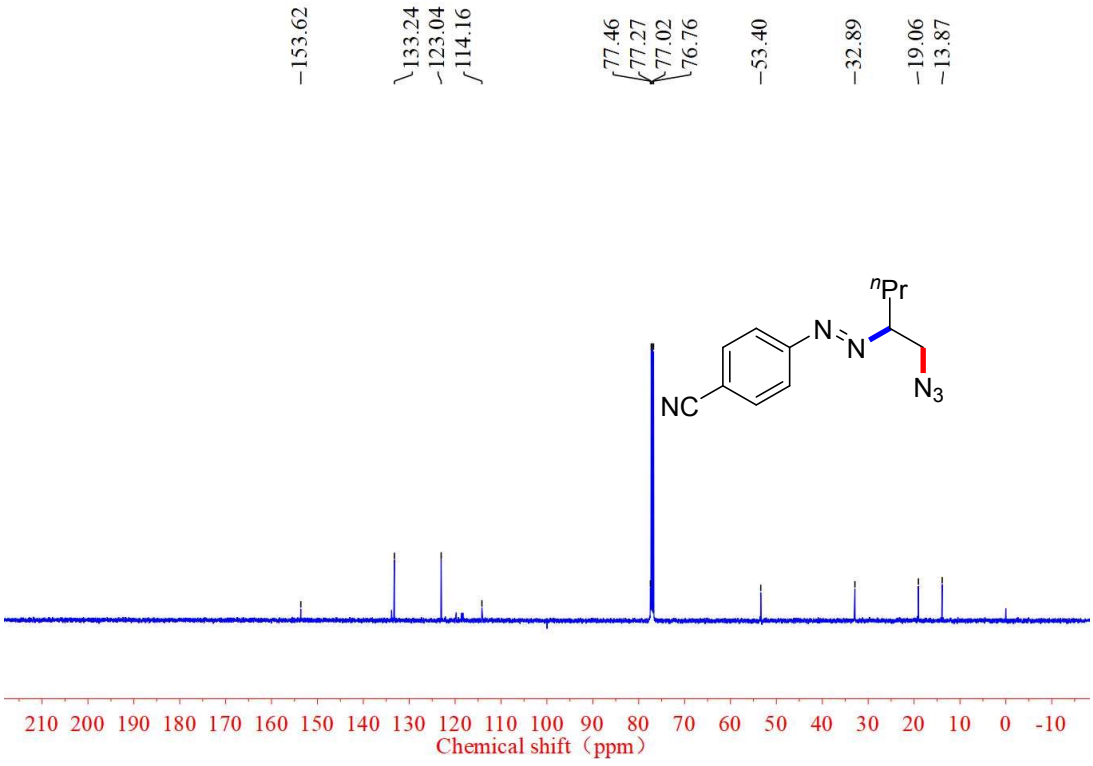
4r ^{13}C NMR



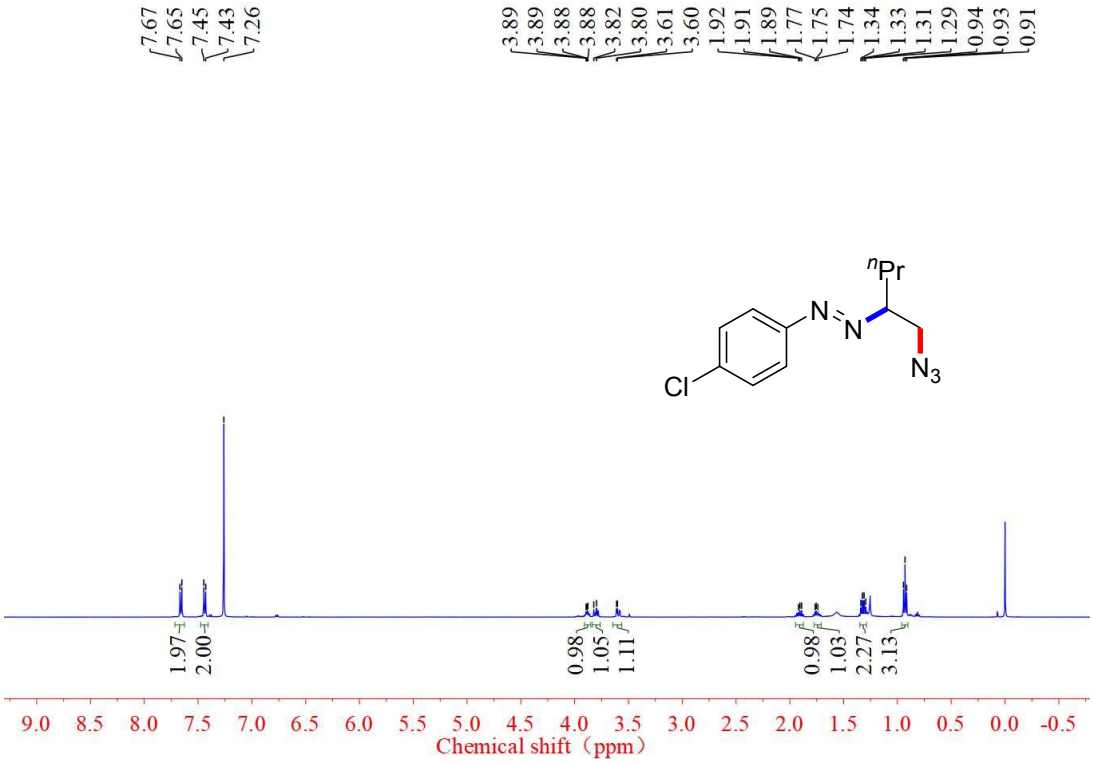
4s ^{1}H NMR



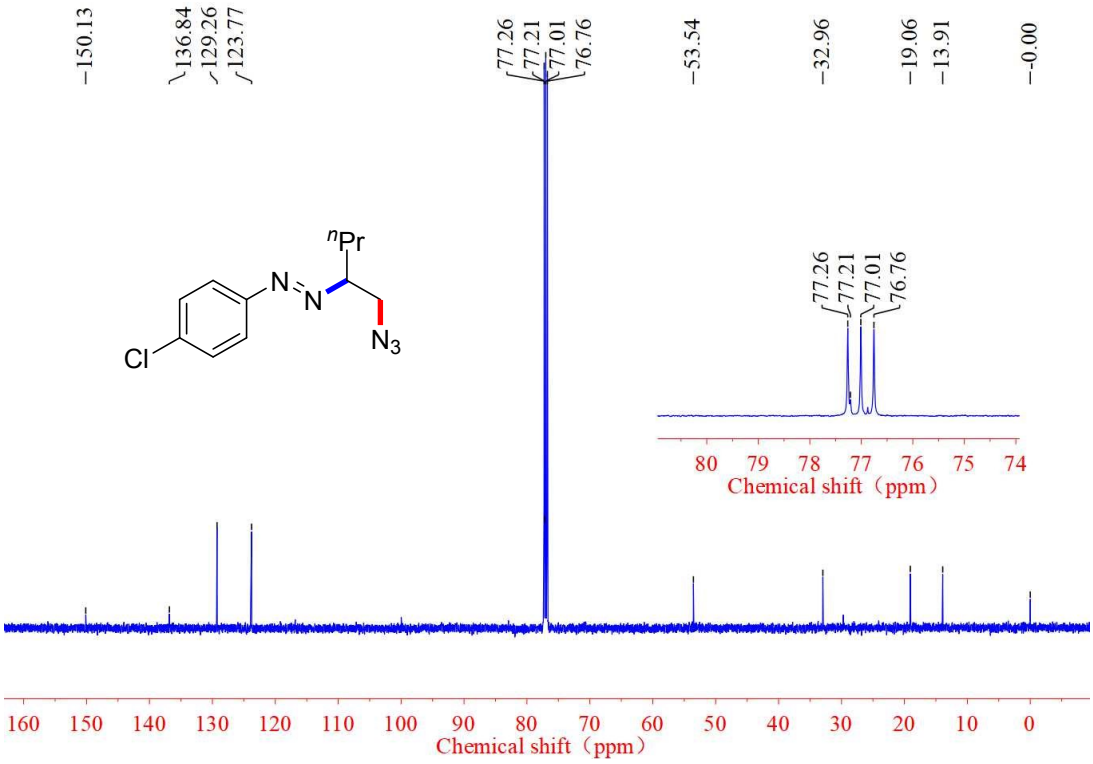
4s ^{13}C NMR



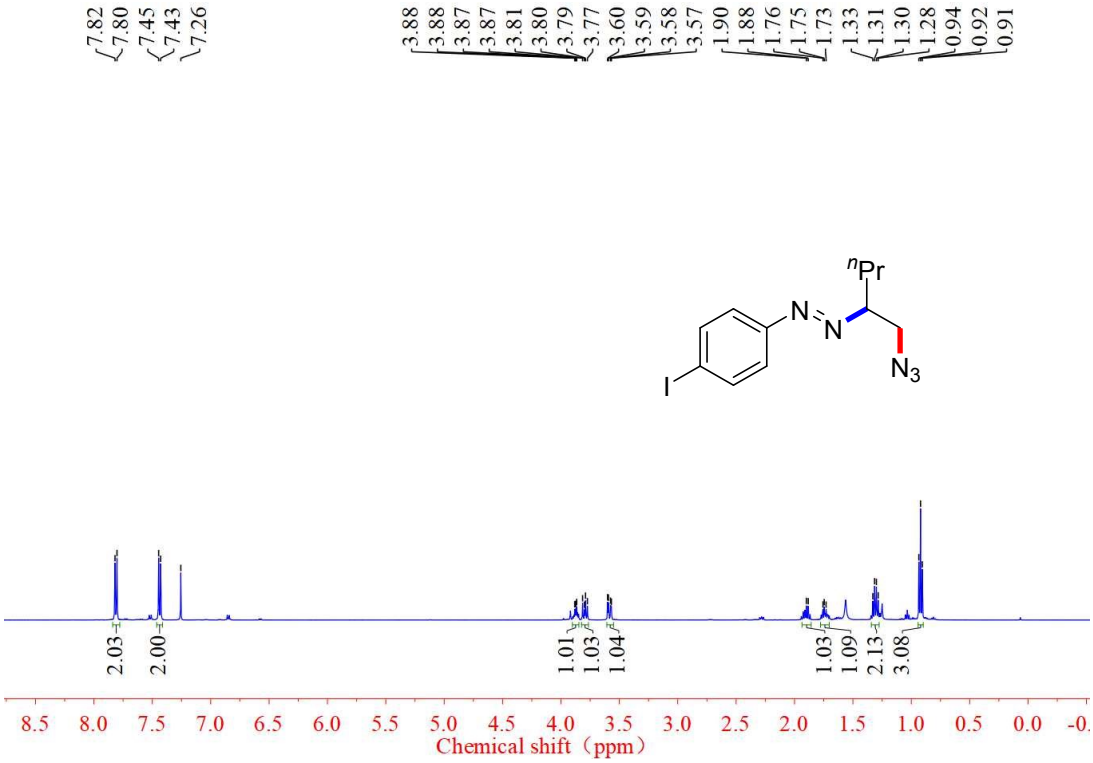
4t ^{1}H NMR



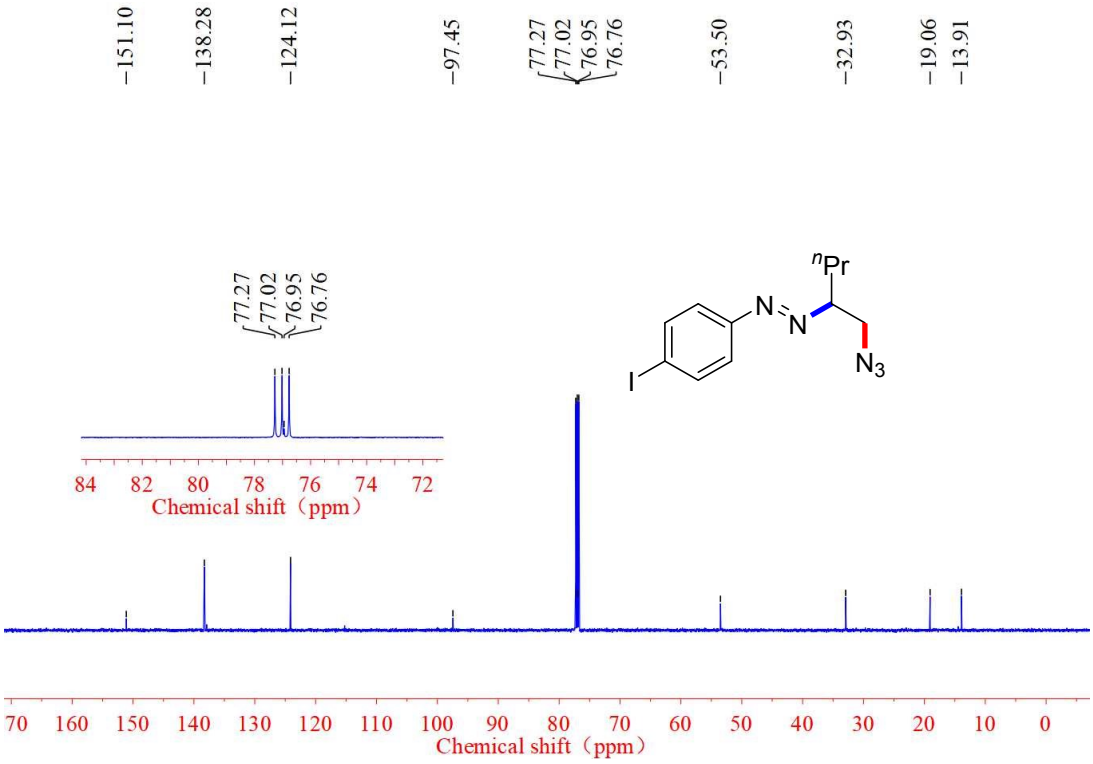
4t ^{13}C NMR



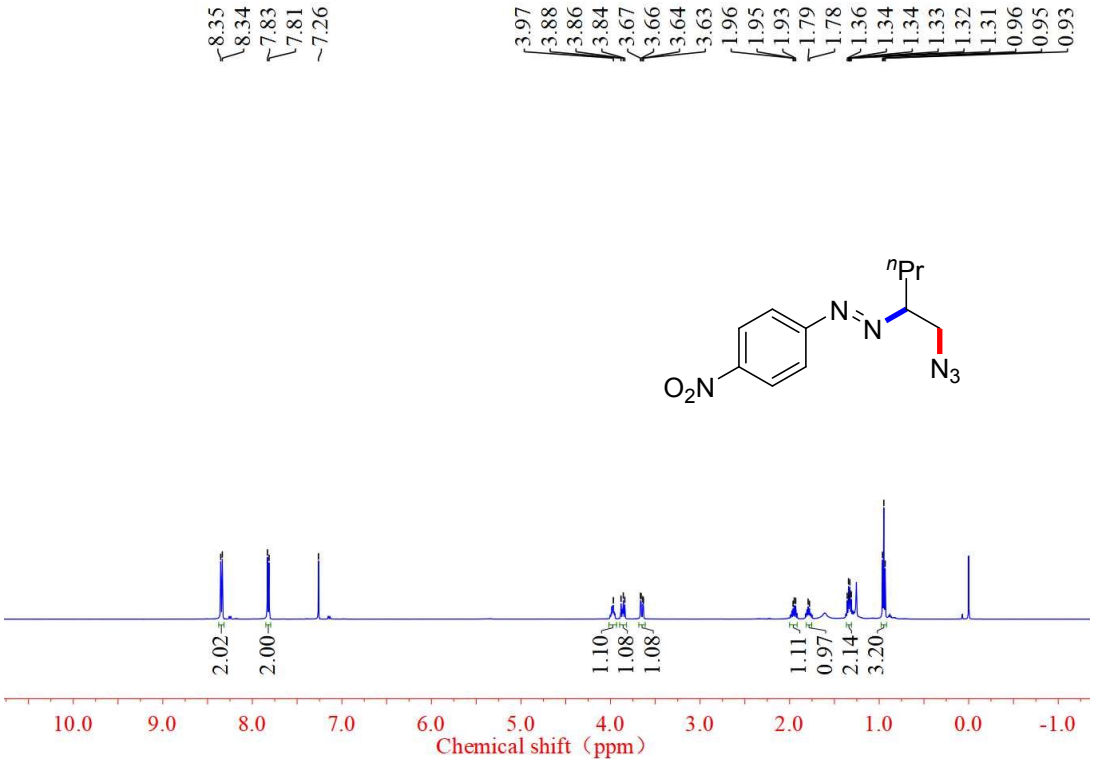
4u ^{1}H NMR



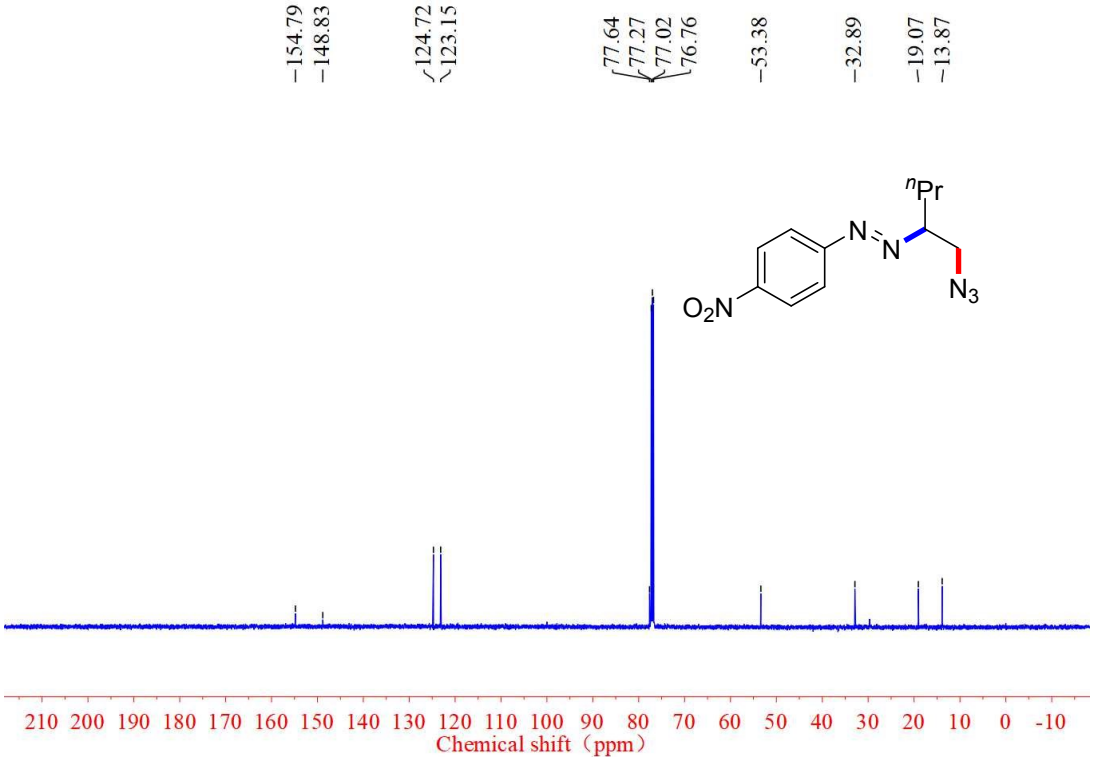
4u ^{13}C NMR



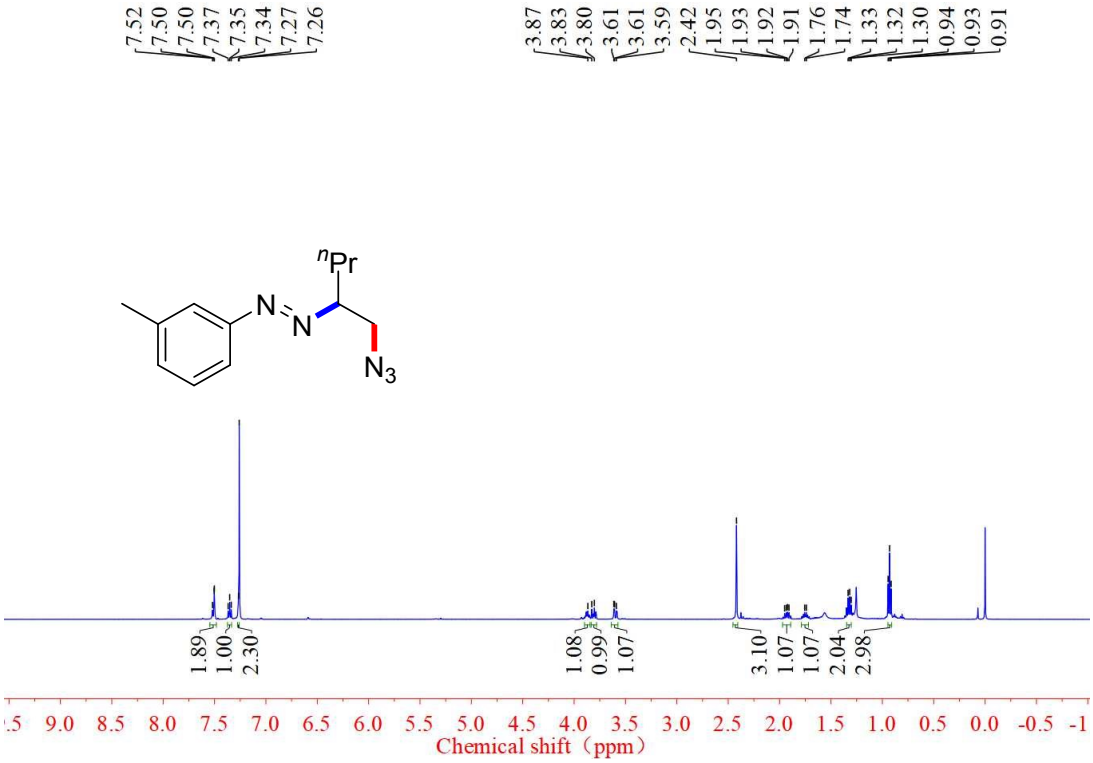
4v ^{1}H NMR



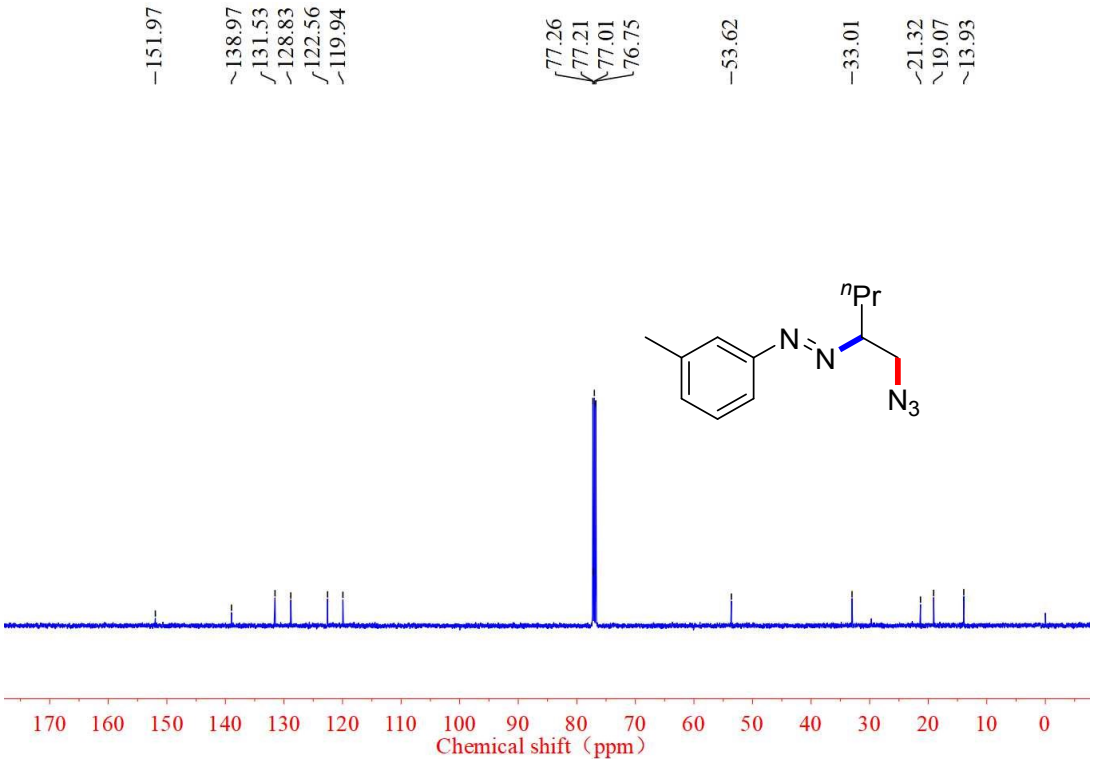
4v ^{13}C NMR



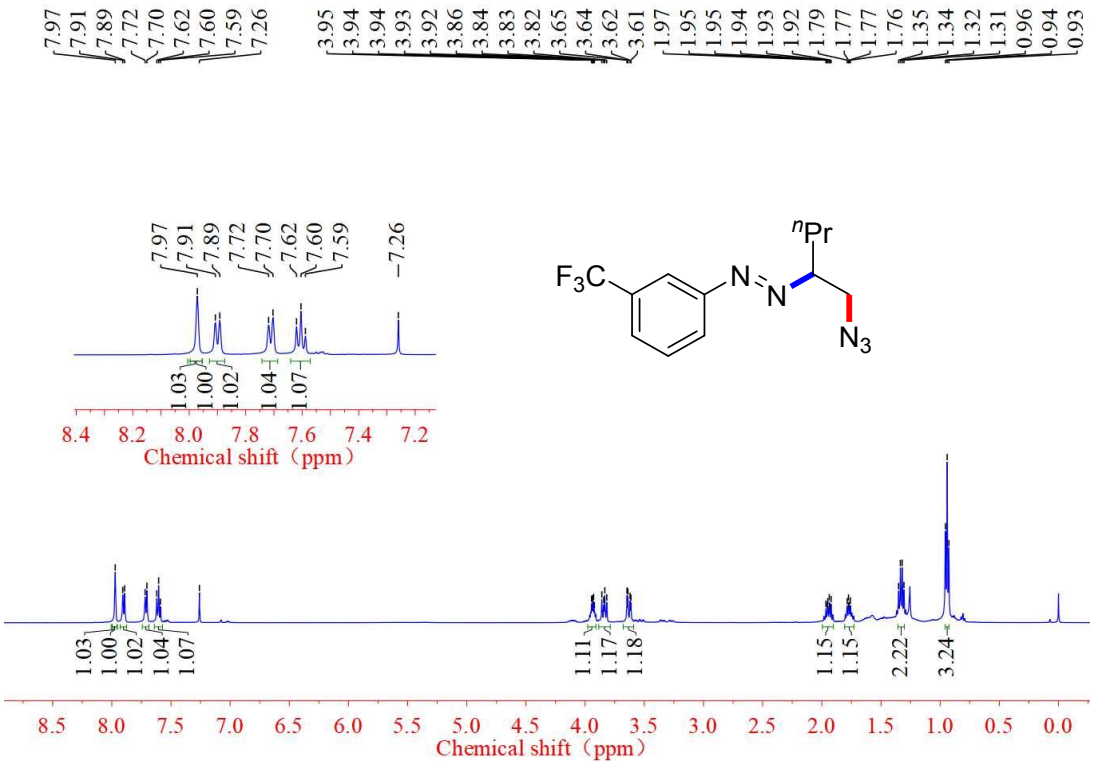
4w ^{1}H NMR



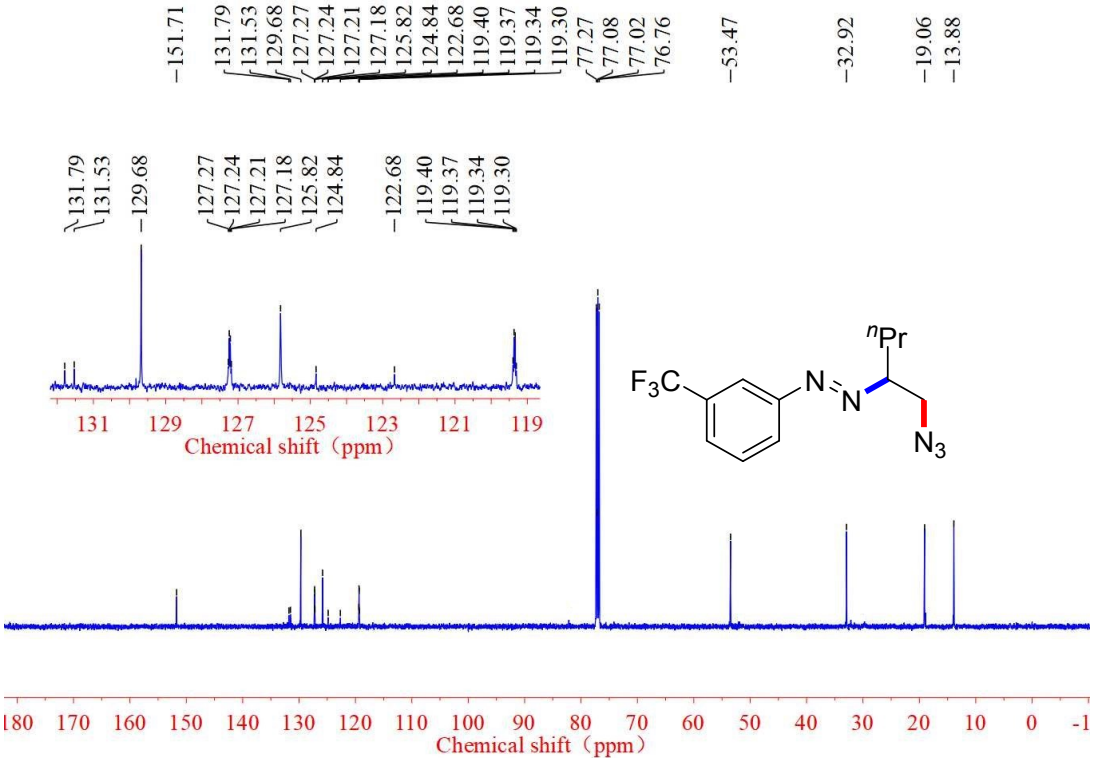
4w ^{13}C NMR



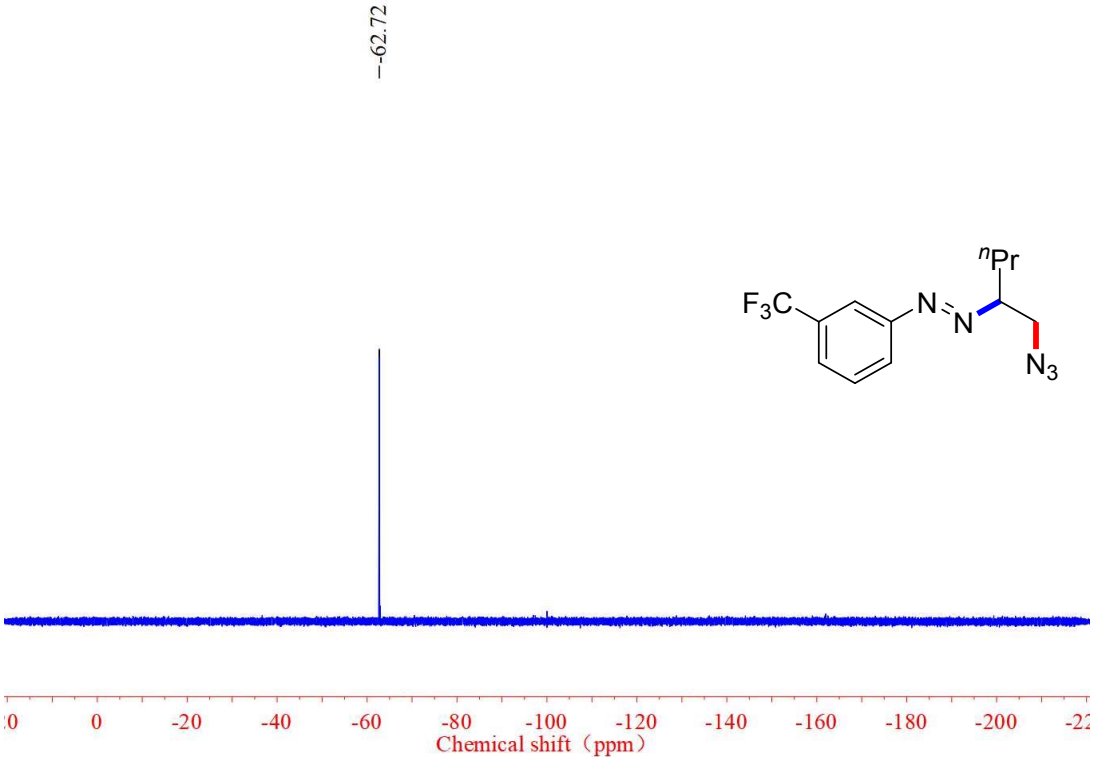
4x ^{1}H NMR



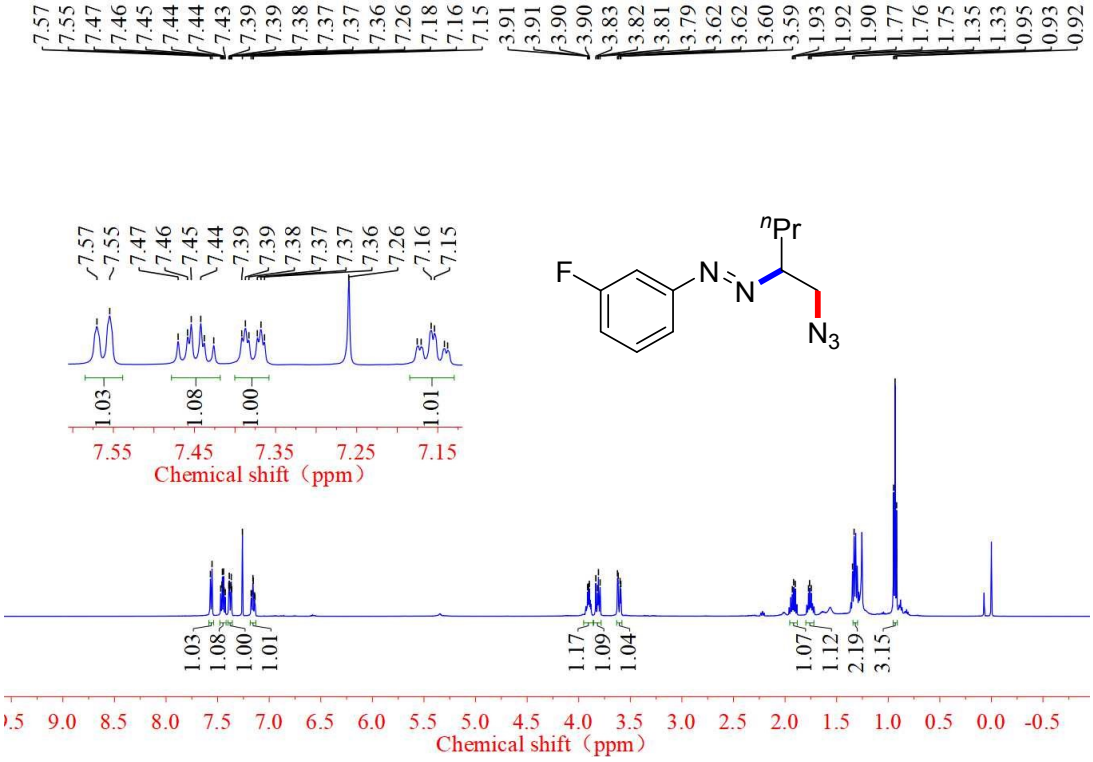
4x ^{13}C NMR



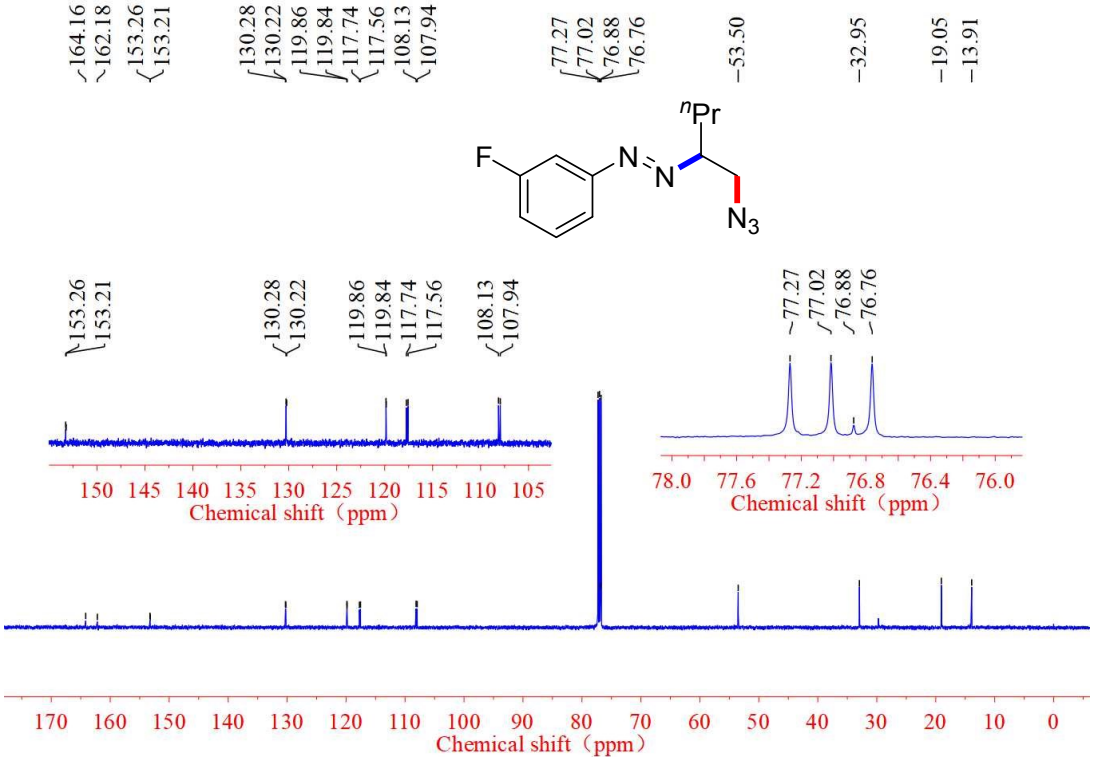
4x ^{19}F NMR



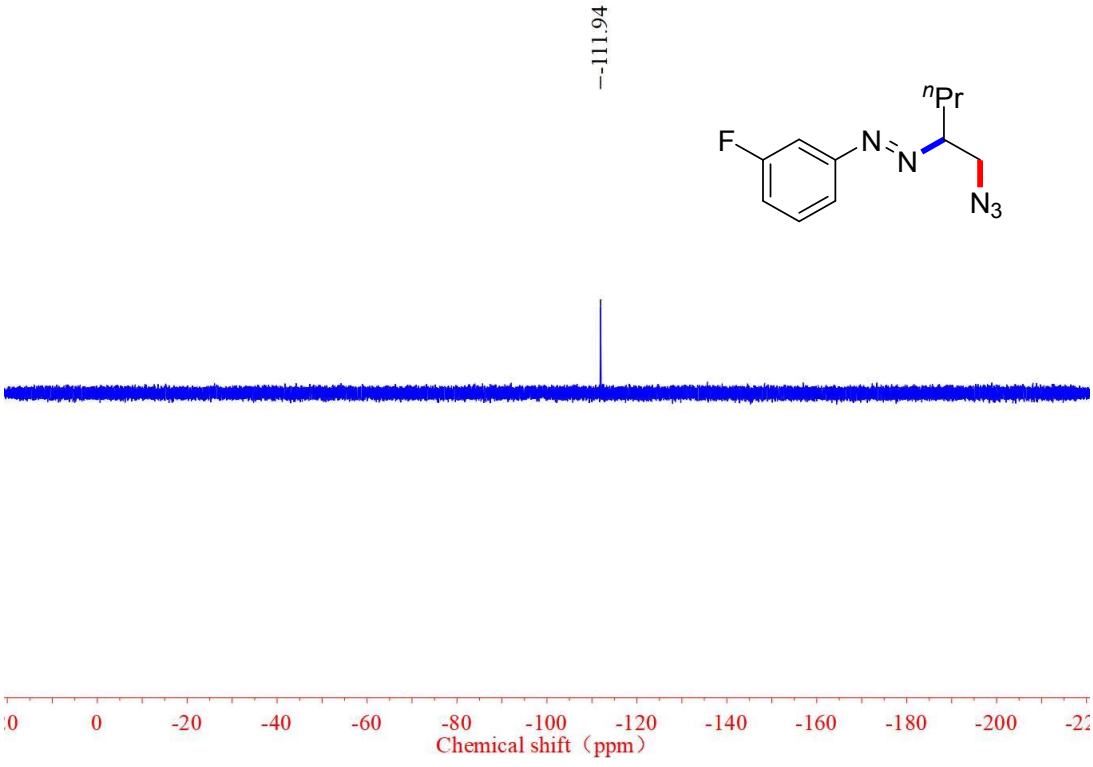
4y ^{1}H NMR



4y ^{13}C NMR



4y ^{19}F NMR



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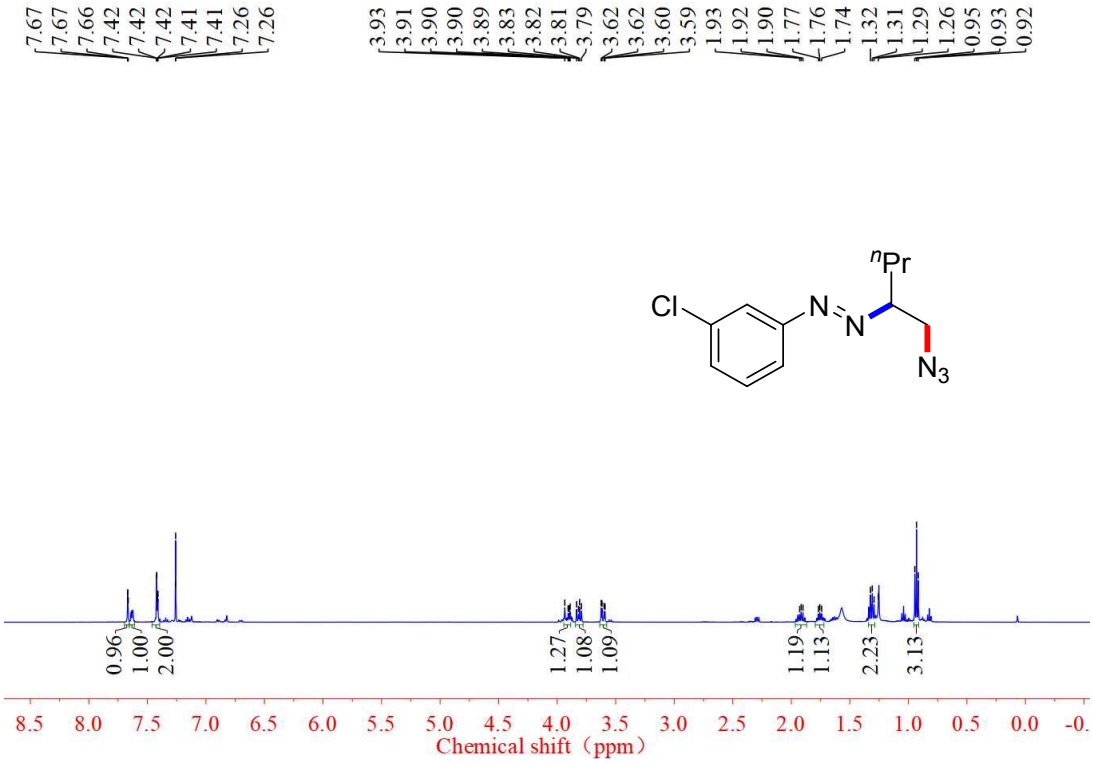

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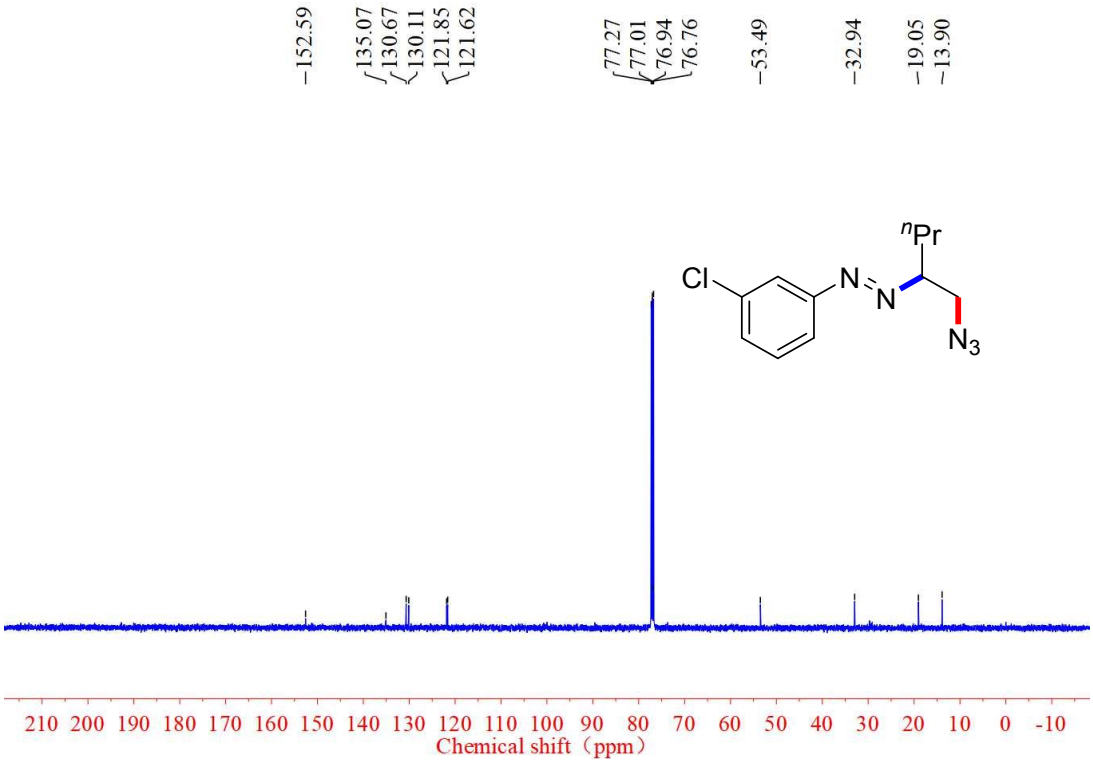

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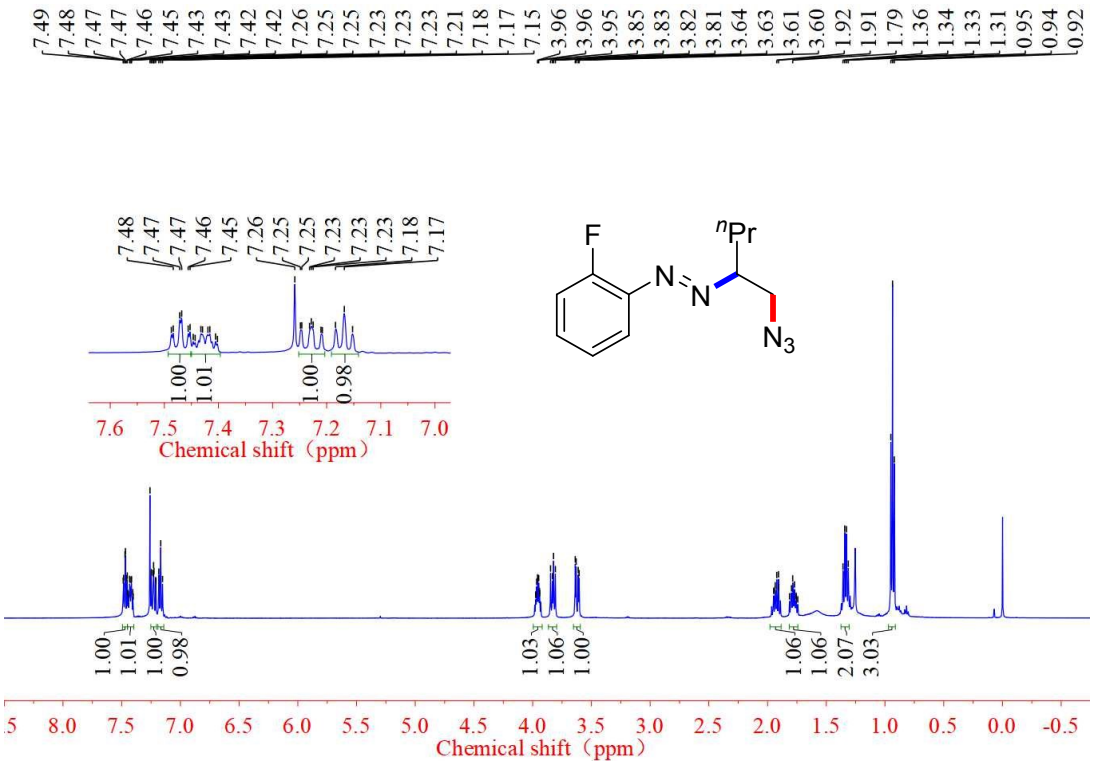
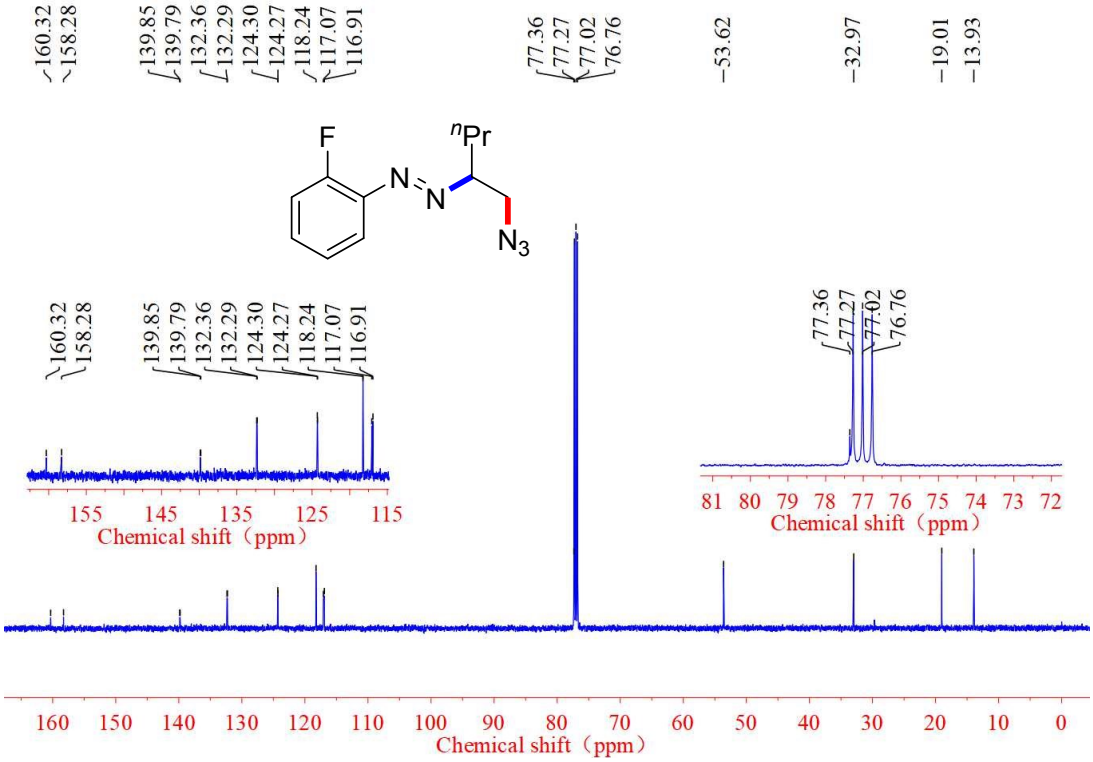
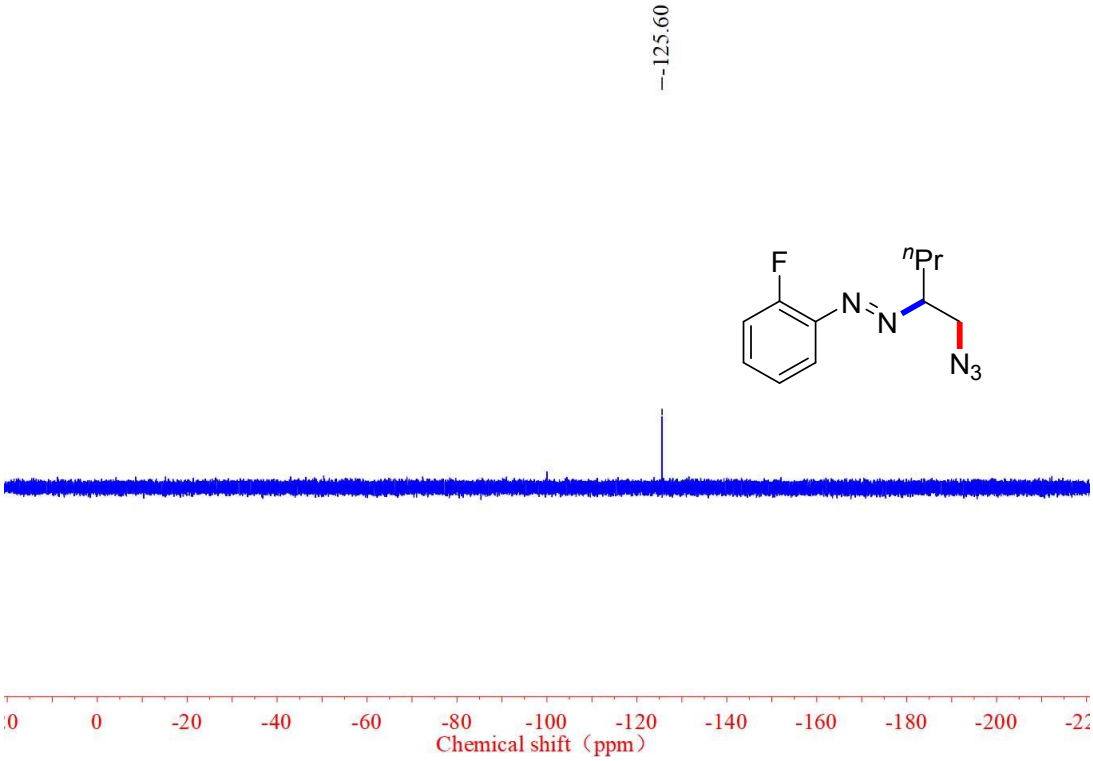


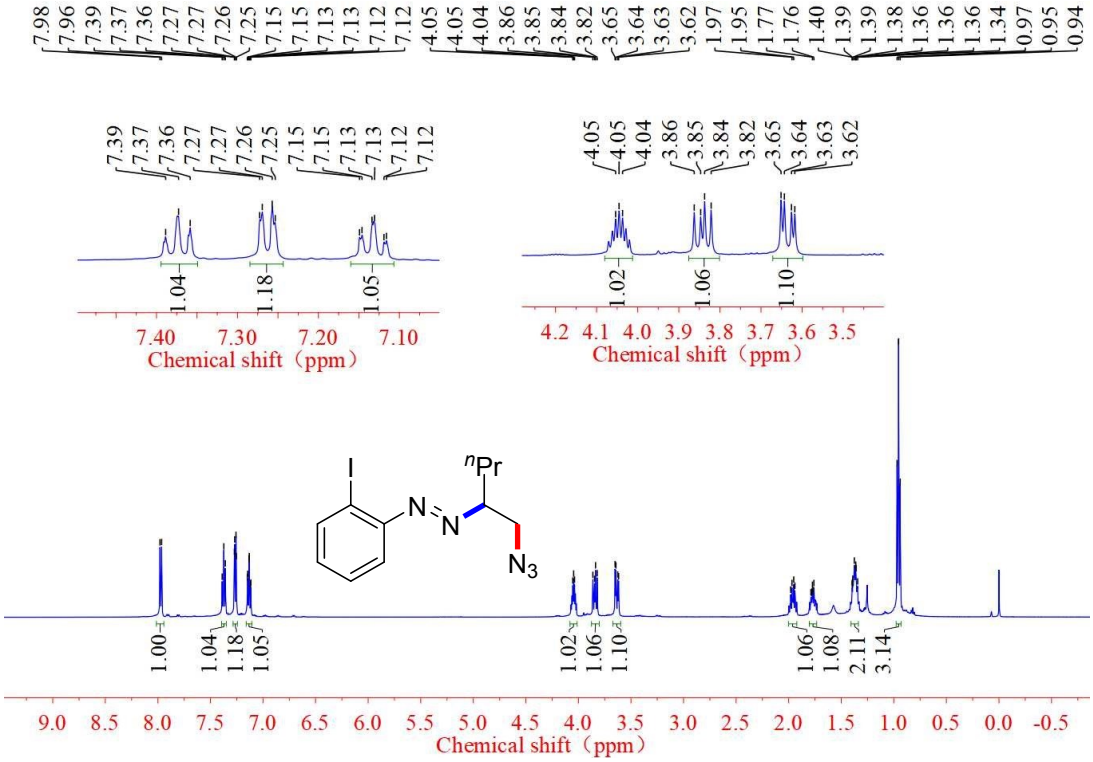
4aa ^{13}C NMR



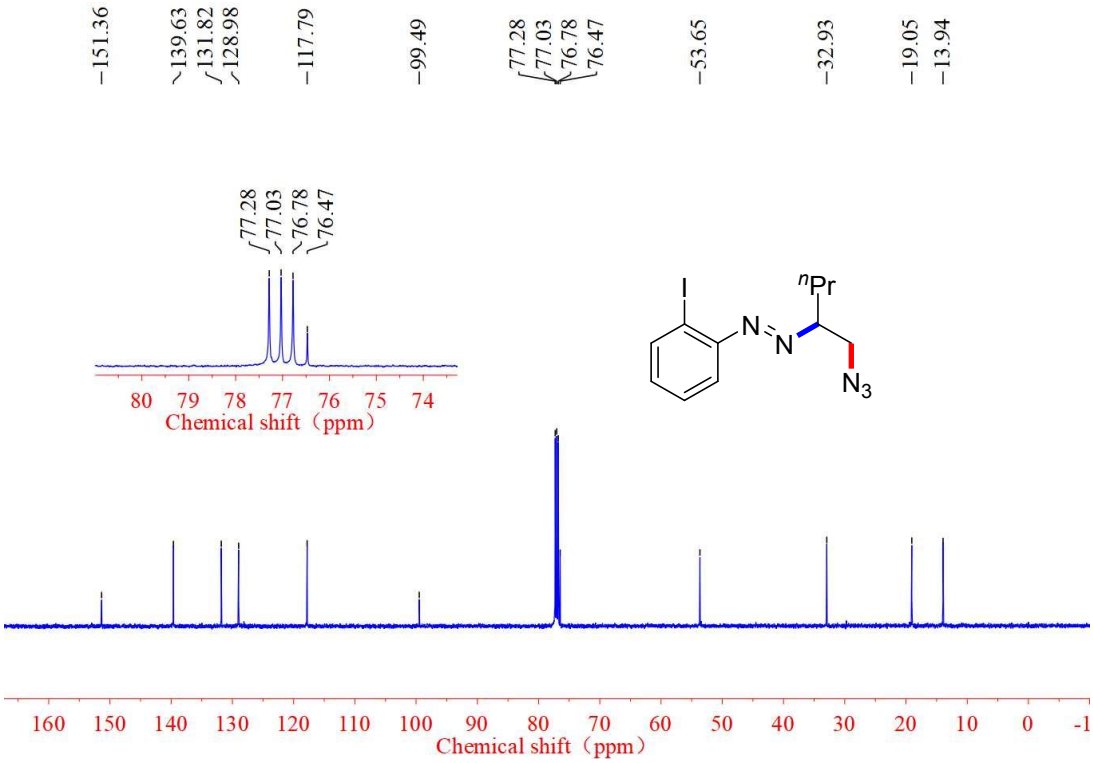
4aa ^{19}F NMR



4ab ^{1}H NMR



4ab ^{13}C NMR



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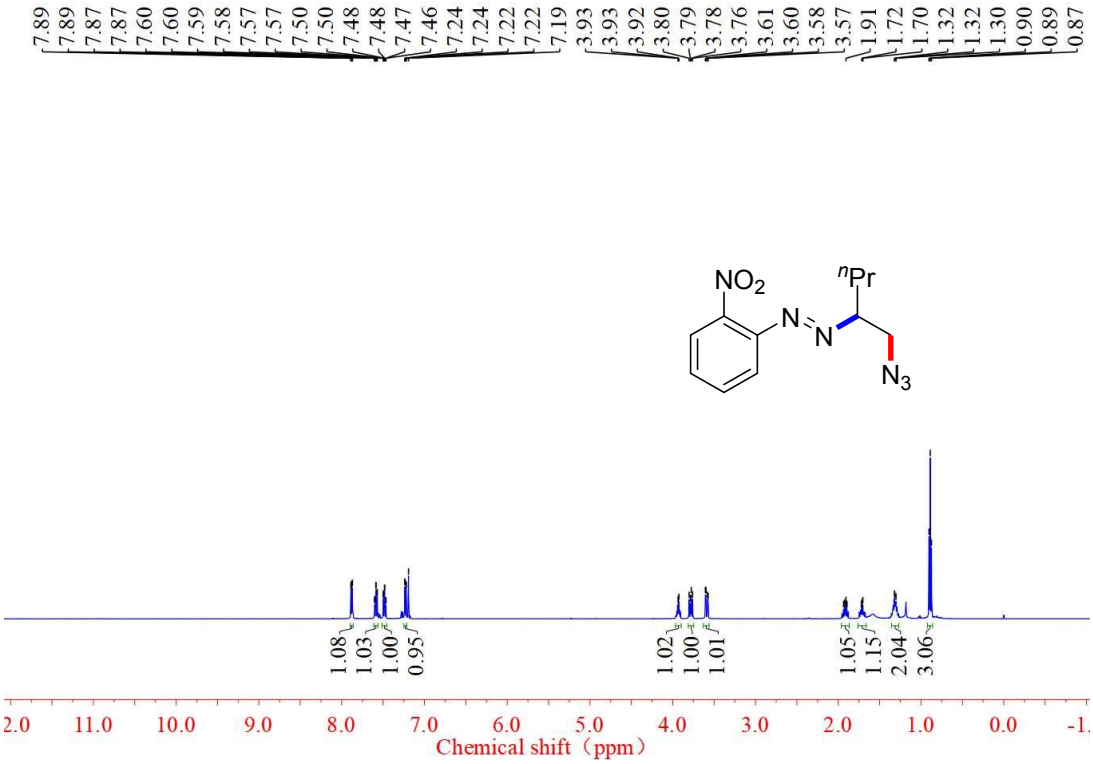

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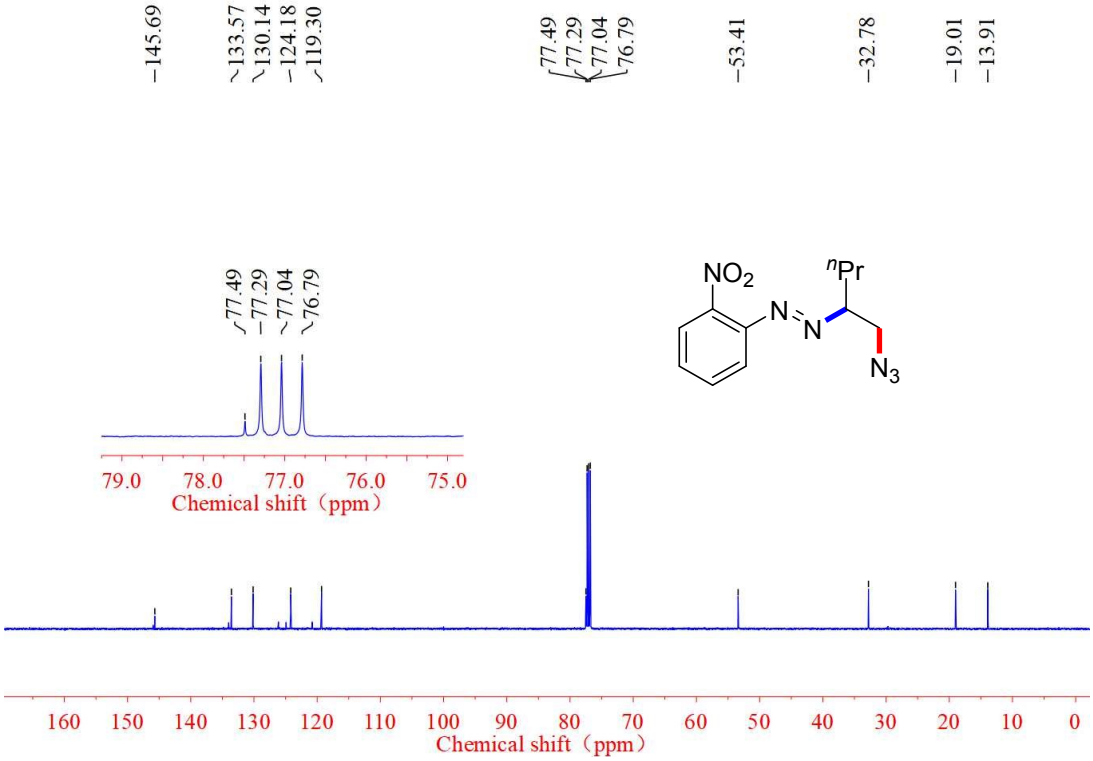
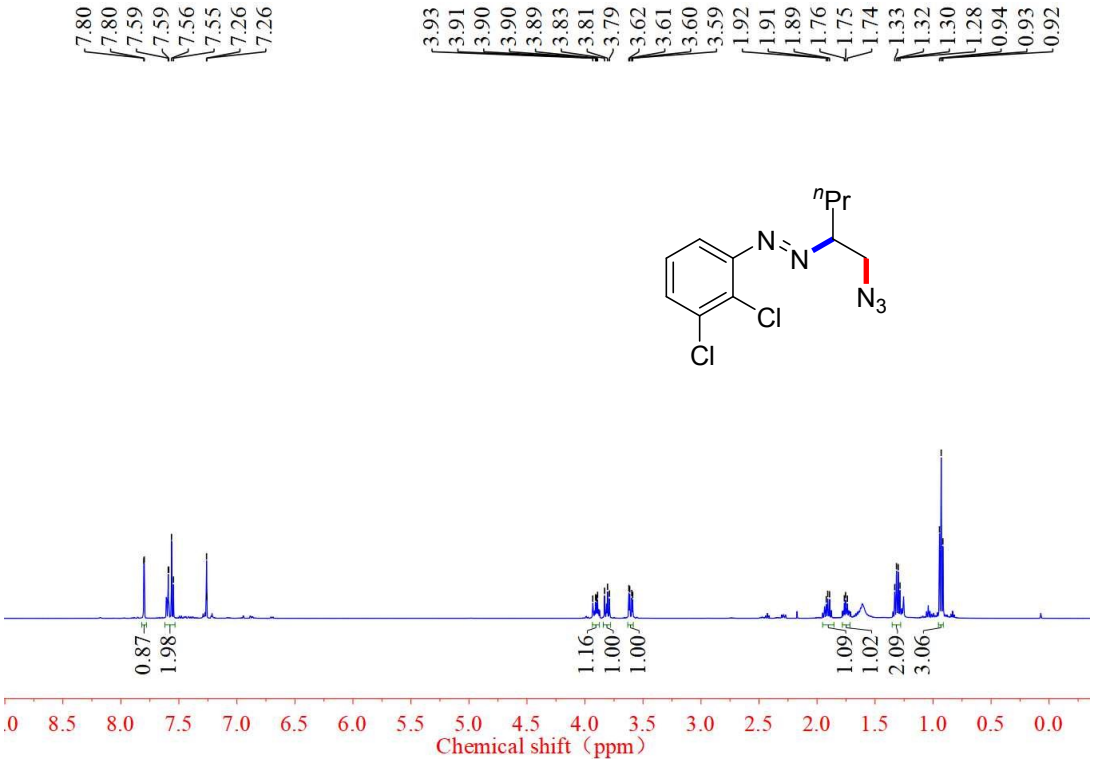


4ad ^{1}H NMR



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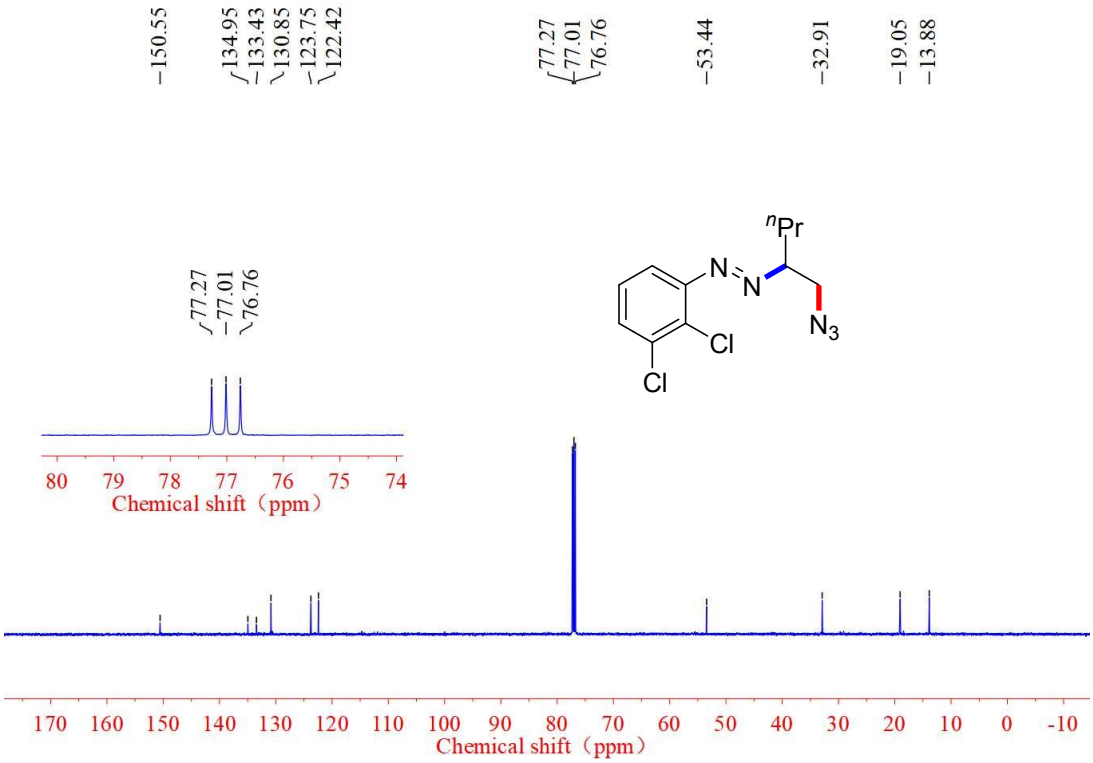
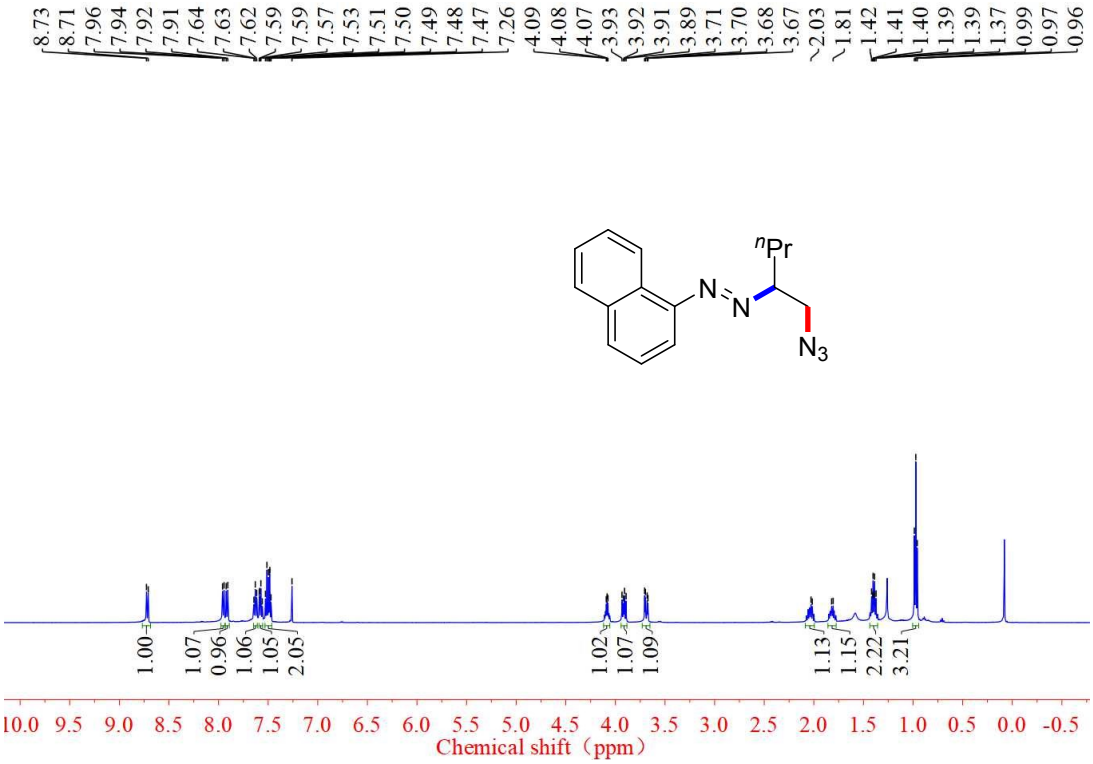
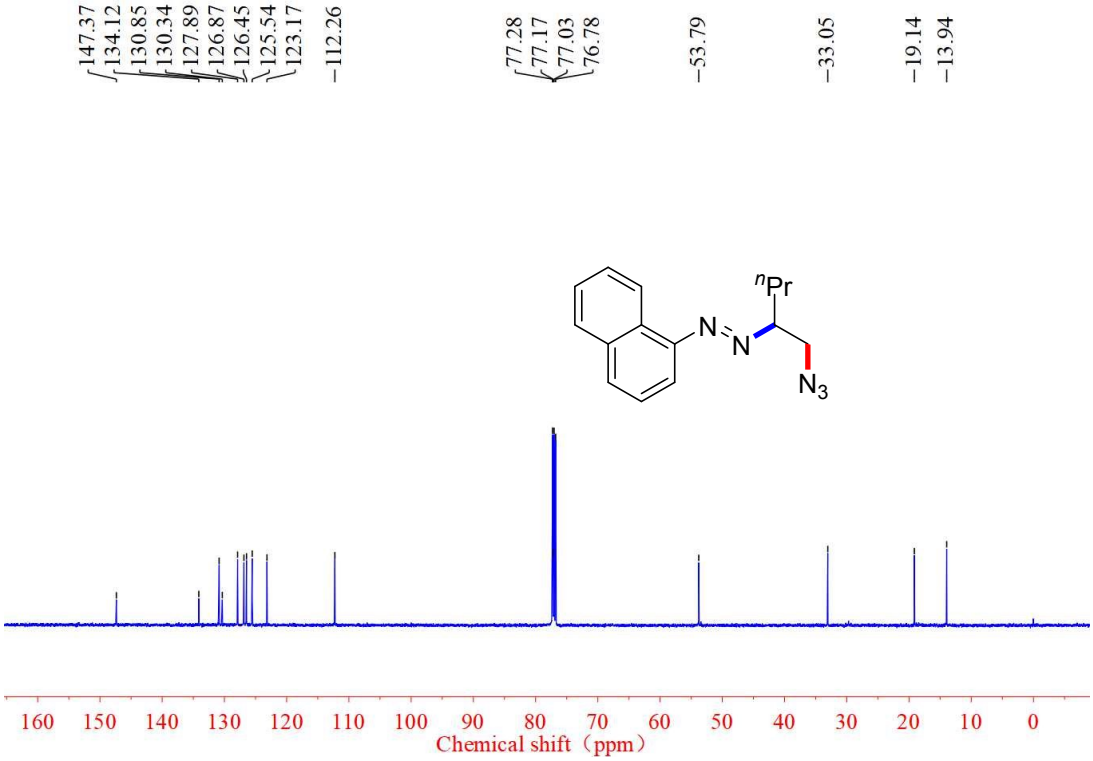


4ae ^{1}H NMR



4ae ^{13}C NMR



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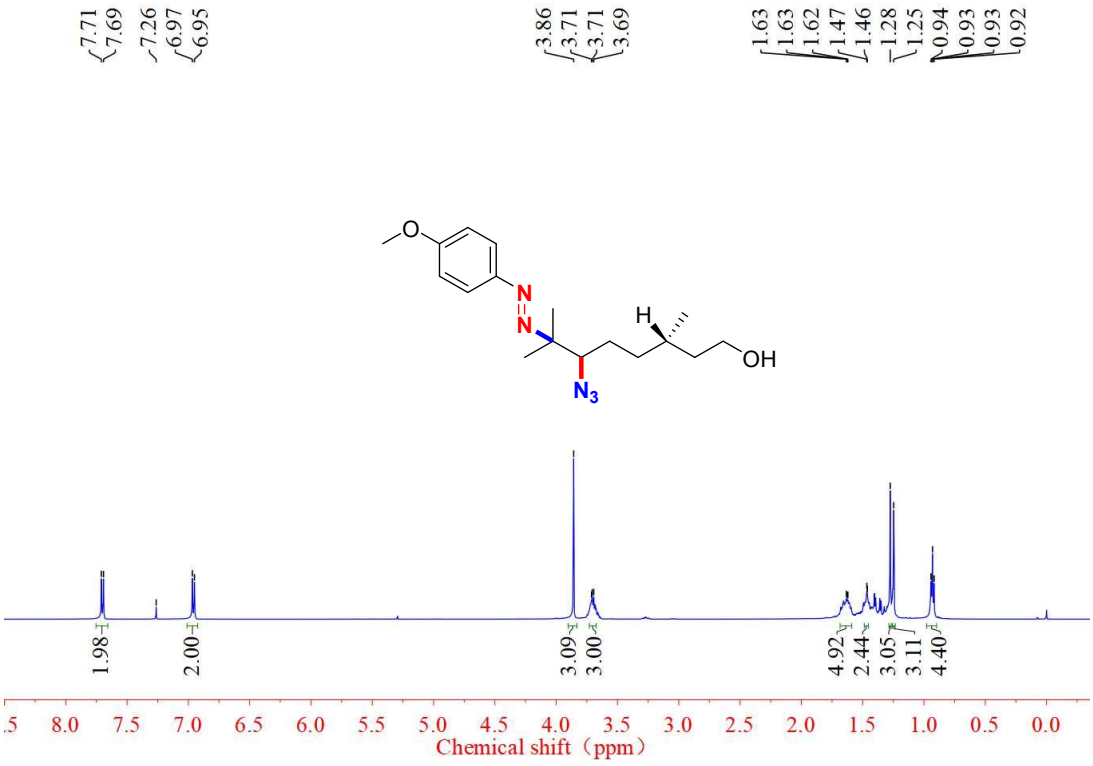

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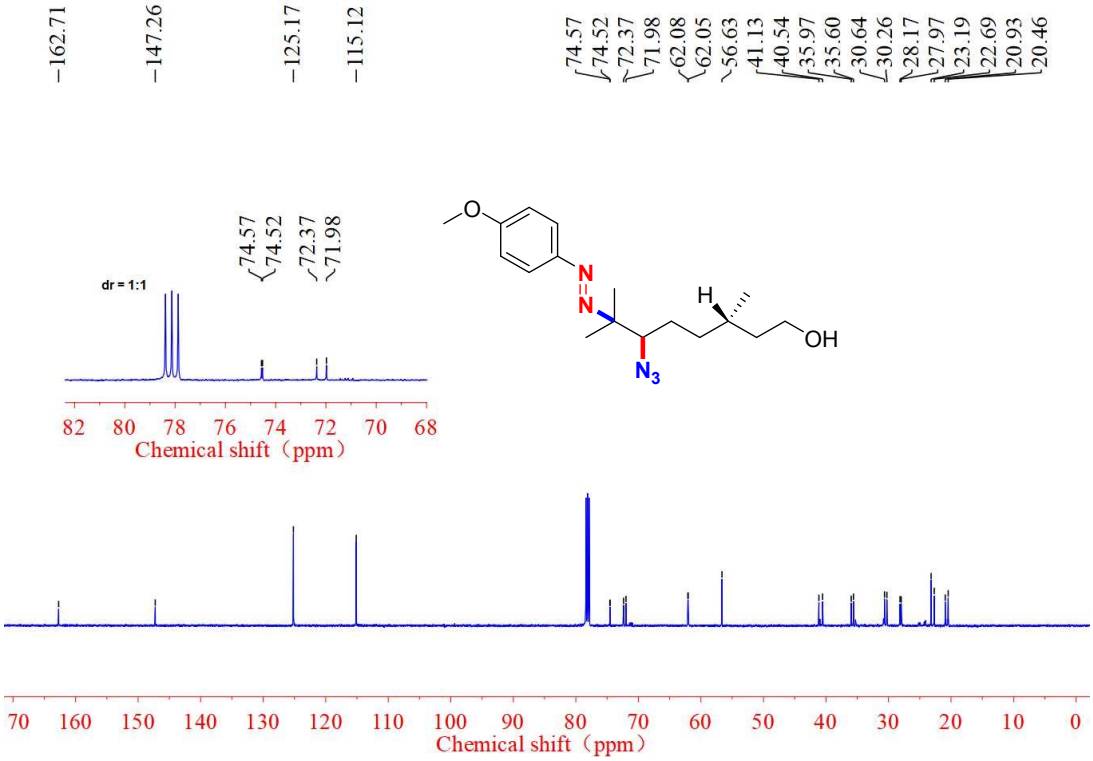

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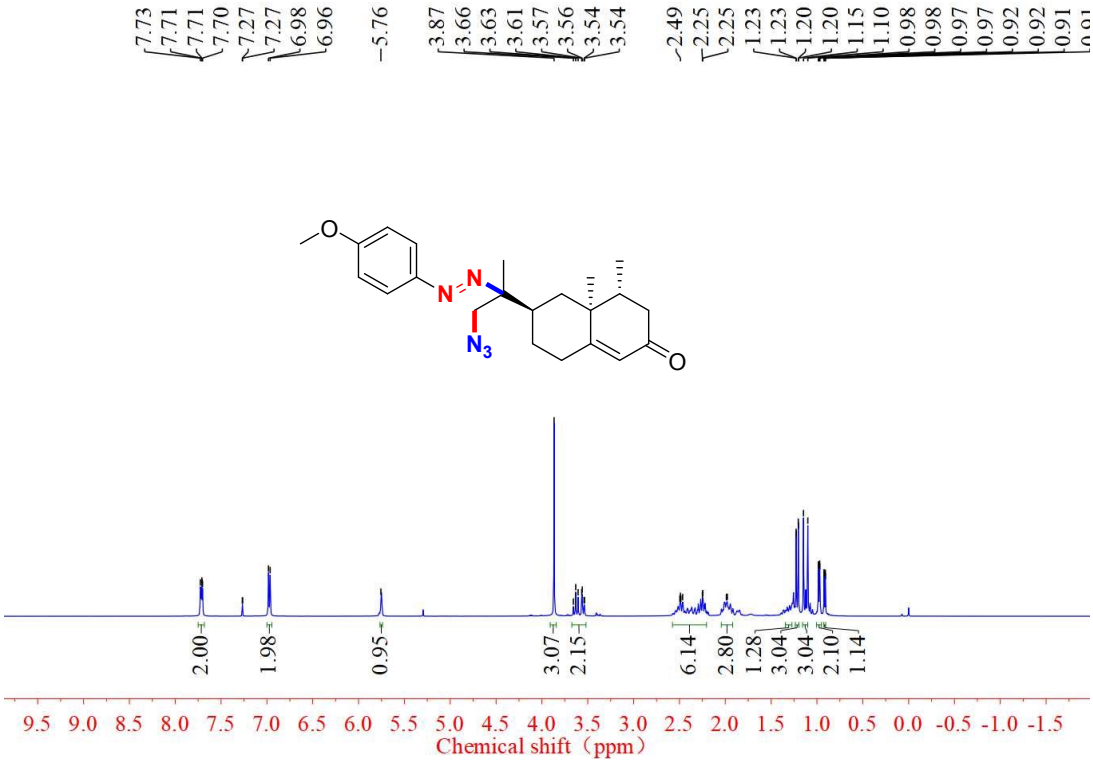
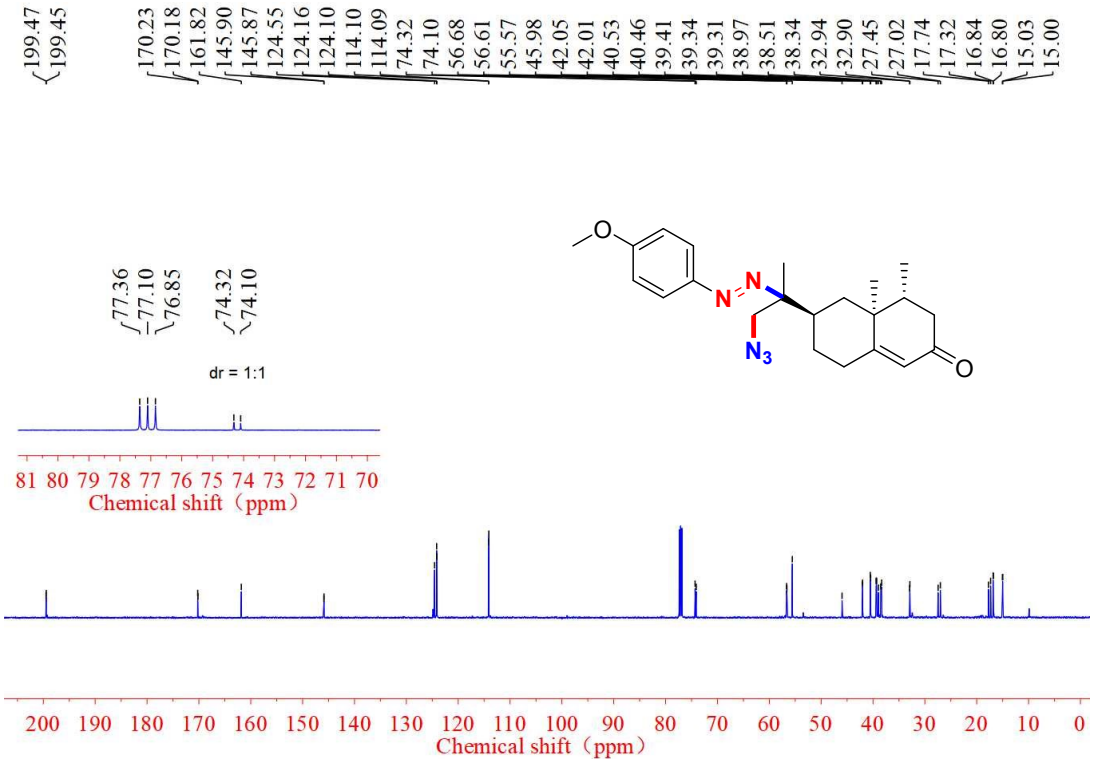


4ag ^{13}C NMR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124.10
114.10
114.09
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74.10
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15.03
15.00
77.36
77.10
76.85
74.32
74.10
dr = 1:1
81 80 79 78 77 76 75 74 73 72 71 70
Chemical shift（ppm）
O
N
N
N3
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift（ppm）