Electronic Supplementary Material (ESI) for Chemical Communications.

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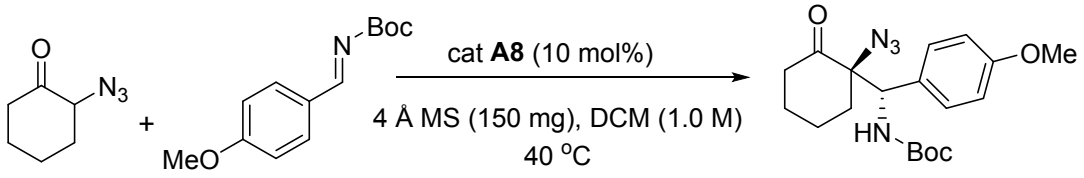
General Information:

Unless otherwise noted, all commercial reagents were used without further purification. Dichloromethane, toluene, ether, THF were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate. Flash column chromatography was carried out on Huanghai Silica Gel HHGJ-300, 300-400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance III HD spectrometer (FT, 500 MHz for ^{1}H, 126 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$; $\delta H = 7.26$ and $\delta C = 77.16$). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. FT-IR spectra were recorded on PerkinElmer Frontier FT-IR Spectrometer, and absorption frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectral data were obtained from the Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^{+}) mode. Optical rotations were measured with an Autopol V Plus/VI digital polarimeter. X-Ray structure analyses were performed using a Bruker D8 Venture X-ray single crystal diffractometer. Enantiomeric excesses were determined on an Agilent 1260 Chiral HPLC using IA, IB, IC, ID columns. Racemic products were synthesized by carrying out the reactions using **(±)-TRIP** as catalyst. General procedure for activating the molecular sieve: 1) weigh 10 g of MS in 250 mL round flask and place the flask under high vacuum; 2) heat the flask all around with heat gun (~300 ^{o}C) for 30 min; 3) after cooled to room temperature, the flask was filled with N_2 and transferred into glove box for further usage.

Table S1. Optimizations of reaction conditions.[a]

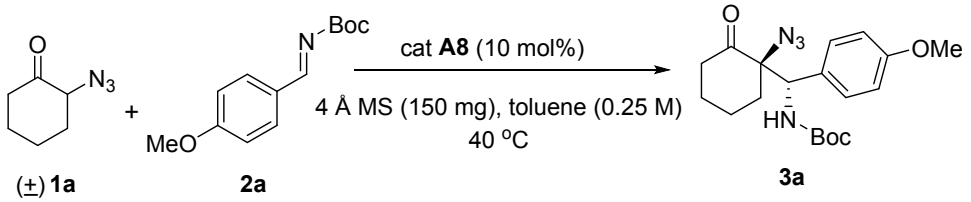


(±) **1a** **2a** **3a**

Entry	Variation from the standard conditions	yield (%)[b]	dr[c]	ee (%)[d]
1	none	93	90:10	95
2	5 Å MS (150 mg)	90	85:15	92
3	3 Å MS (150 mg)	91	87:13	94
4	50 mg 4 Å MS	88	90:10	96
5	100 mg 4 Å MS	91	90:10	96
6	In CCl_4	85	84:16	97
7	In MTBE	82	84:16	96
8	With 5 mol% cat **A8**	58	89:11	97
9	50 °C	91	88:12	95
10	1.0 mmol scale with 500 mg 4 Å MS	96	90:10	96

[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (10 mol%), 4 Å molecular sieves (150 mg) in DCM (0.1 mL) at 40 °C for 16 h. [b]Yields were isolated yields. [c]Dr was determined by ^{1}H NMR. [d]Ee was determined by chiral HPLC analysis.

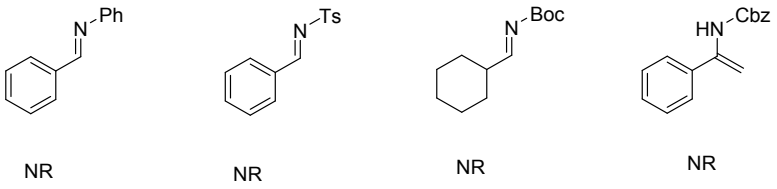
Table S2. Monitor the ee of starting material with different reaction times. [a]



(±) **1a** **2a** **3a**

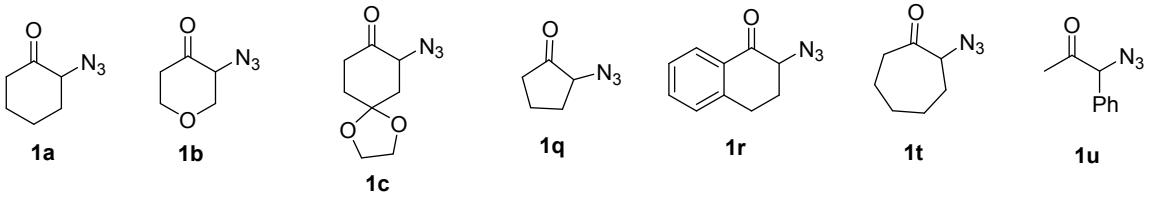
Entry	Reaction Time (h)	Yield of **3a** (%)[b]	Ee of **1a** (%)[c,d]
1	1	49	61
2	2	60	70
3	4	67	59
4	8	72	56

[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), cat **A8** (10 mol%), 4 Å molecular sieves (150 mg) in toluene (0.4 mL) at 40 °C for designated time. [b]Yields were isolated yields. [c]Ee was determined by chiral HPLC analysis. [d]The yields of recovered **1a** couldn't be obtained exactly because it was inseparable with benzaldehyde by column chromatography.

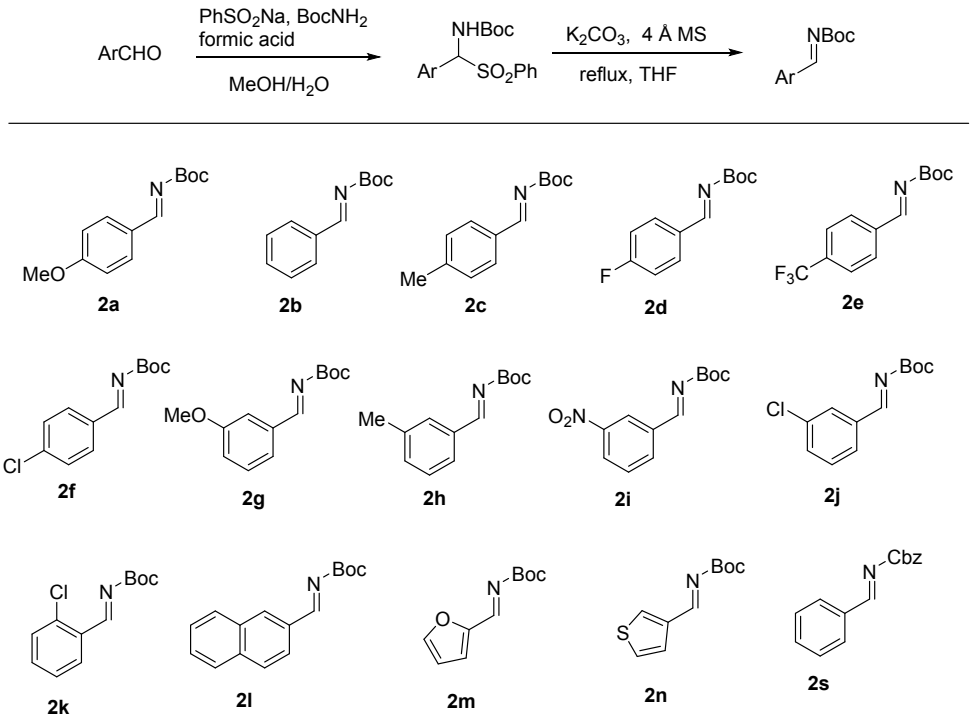


Scheme S1. Incompatible imine substrates.

Synthesis of the substrates:



α-Azido cyclic ketone substrates **1a**[1], **1b**[2], **1c**[2], **1q**[2], **1r**[3], **1t**[2] **and 1u**[2] were synthesized according previous reported procedures.



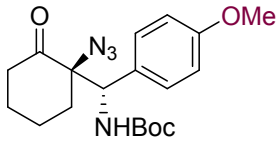
Aldimines **2a-c**[4], **2d-f**[5], **2g**[4], **2h**[5], **2i-j**[6], **2k**[7], **2l-m**[8], **2n**[9] and **2s**[7] were synthesized according previous reported procedures.

Asymmetric synthesis of products:

General procedure for asymmetric synthesis of products: To a 4 ml reaction tube was added α-azido cyclic ketone **1** (0.10 mmol), aldimine **2** (0.20 mmol), (*S*)**-cat A8** (7.1 mg, 0.01 mmol) and 4Å MS (150 mg). Subsequently, DCM (0.1 ml) was added to dissolve the reagents, and the reaction mixture was warmed to 40 ºC under N_2 atmosphere. After heating the reaction mixture at 40 ºC for another 12h (*the DCM was evaporated to leave the mixture as syrup)*, the mixture was cooled to room temperature and directly purified by flash column chromatography to afford the desired product **3**.

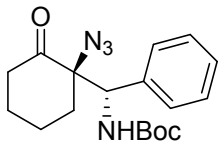
The corresponding racemic products were synthesized with the same procedure using **(±)-TRIP** (10 mol %) as catalyst.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-methoxyphenyl)methyl)carbamate **(3a)**



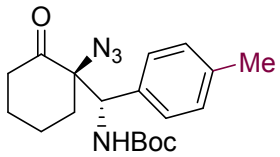
93% yield, 90:10 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 (d, *J* = 8.3 Hz, 1.74H), 7.17 (d, *J* = 8.1 Hz, 0.26H), 6.88 (d, *J* = 8.3 Hz, 1.74H), 6.80 (d, *J* = 8.3 Hz, 0.26H), 5.33 (q, *J* = 9.9 Hz, 2H), 3.80 (s, 2.61H), 3.75 (s, 0.39H), 2.96 (td, *J* = 14.0, 6.2 Hz, 1H), 2.54 (d, *J* = 14.1 Hz, 1H), 2.17 (ddt, *J* = 13.2, 6.4, 3.1 Hz, 1H), 1.99 (d, *J* = 13.8 Hz, 1H), 1.93 – 1.79 (m, 2H), 1.77 – 1.66 (m, 2H), 1.42 (s, 1.17H), 1.34 (s, 7.83H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.9, 159.7, 155.0, 129.7, 128.7, 113.9, 80.3, 76.4, 55.5, 55.4, 39.3, 34.9, 28.3, 27.6, 21.9. IR (cm^{-1}): *f* = 3336, 2934, 2104, 1714, 1511, 1247, 1161, 1032, 800, 751. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{19}H_{26}N_4O_4$ 375.2027, found 375.2011. $[\alpha]_D^{25}$ = 7.80 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 95:05 hexanes/ isopropanol, 1 ml/min; t_R = 9.0 min (minor), 14.2 min (major); 95% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(phenyl)methyl)carbamate **(3b)**



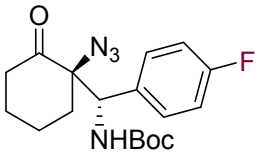
86% yield, 86:14 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 6.99 (m, 5H), 5.31 (q, *J* = 10.1 Hz, 2H), 2.89 (td, *J* = 14.0, 6.2 Hz, 0.86H), 2.47 (d, *J* = 14.1 Hz, 1H), 2.37 (dt, *J* = 13.1, 4.3 Hz, 0.14H), 2.16 – 2.04 (m, 1H), 1.96 (t, *J* = 13.4 Hz, 1H), 1.77 (d, *J* = 13.1 Hz, 2H), 1.71 – 1.53 (m, 2H), 1.34 (s, 1.26H), 1.27 (s, 7.74H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.7, 155.0, 136.6, 128.6, 128.5, 128.2, 80.4, 76.2, 55.9, 39.2, 34.9, 28.3, 27.6, 21.9. IR (cm^{-1}): *f* = 3435, 2962, 2106, 1715, 1490, 1258, 1009, 789, 756, 700. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{18}H_{24}N_4O_3$ 345.1921, found 345.1905. $[\alpha]_D^{25}$ = 10.20 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 6.7 min (minor), 11.9 min (major); 97% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(p-tolyl)methyl)carbamate **(3c)**



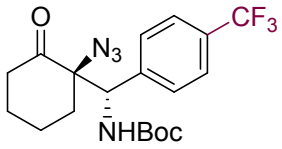
84% yield, 88:12 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.27 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 1.76H), 7.09 (d, *J* = 7.8 Hz, 0.24H), 5.36 (q, *J* = 9.9 Hz, 2H), 2.97 (td, *J* = 14.0, 6.2 Hz, 0.88H), 2.55 (d, *J* = 14.1 Hz, 1H), 2.45 (dt, *J* = 9.1, 5.0 Hz, 0.12H), 2.35 (s, 2.64H), 2.29 (s, 0.36H), 2.23 – 2.13 (m, 1H), 2.05 (dd, *J* = 10.8, 6.8 Hz, 1H), 1.86 (dd, *J* = 10.8, 3.5 Hz, 2H), 1.72 (dd, *J* = 13.1, 4.3 Hz, 2H), 1.42 (s, 1.08H), 1.35 (s, 7.92H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.8, 155.0, 138.3, 133.6, 129.2, 128.4, 80.3, 76.3, 55.7, 39.2, 34.9, 28.3, 27.6, 21.9, 21.3. IR (cm^{-1}): *f* = 2962, 2108, 1716, 1490, 1394, 1258, 1010, 789, 703. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{19}H_{26}N_4O_3$ 359.2078, found 359.2064. $[\alpha]_D^{25}$ = 10.00 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 98:02 hexanes/ isopropanol, 1 ml/min; t_R = 8.7 min (minor), 15.7 min (major); 96% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-fluorophenyl)methyl)carbamate **(3d)**



88% yield, 87: 13 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 1.74H), 6.96 (t, *J* = 8.4 Hz, 0.26H), 5.35 (q, *J* = 9.7 Hz, 2H), 2.92 (td, *J* = 14.0, 6.2 Hz, 0.87H), 2.56 (d, *J* = 14.2 Hz, 1H), 2.48 (d, *J* = 5.2 Hz, 0.13H), 2.18 (dq, *J* = 9.9, 3.2 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.93 – 1.78 (m, 2H), 1.74 (dd, *J* = 13.4, 4.2 Hz, 2H), 1.42 (s, 1.17H), 1.35 (s, 7.83H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.6, 162.8 (d, $J_{C\text{-}F}$ = 247.5 Hz), 154.9, 132.6 (d, $J_{C\text{-}F}$ = 2.9 Hz) , 130.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.6 Hz), 80.5, 76.1, 55.3, 39.2, 34.9, 28.3, 27.5, 21.9. ^{19}F NMR (471 MHz, Chloroform-d) δ -113.48. IR (cm^{-1}): *f* = 2962, 2105, 1715, 1508, 1258, 1012, 793. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{18}H_{23}FN_4O_3$ 363.1827, found 363.1813. $[\alpha]_D^{25}$ = 10.20 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 98:02 hexanes/isopropanol, 1 ml/min; t_R = 7.1 min (minor), 11.9 min (major); 94% ee.

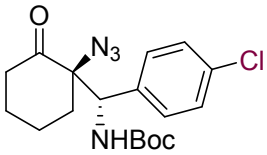
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-(trifluoromethyl)phenyl)methyl)carbamate **(3e)**



76% yield, 81:19 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.1 Hz, 1.52H), 7.53 (dd, *J* = 12.9, 8.1 Hz, 2.28H), 5.41 (m, *J* = 9.7 Hz, 2H), 2.91 (td, *J* = 13.8, 6.2 Hz, 0.81H), 2.64 – 2.54 (m, 0.81H), 2.51, (m *J* = 5.3 Hz, 0.38H), 2.20 (m, *J* = 13.0, 6.2, 3.0 Hz, 1H), 2.11 – 1.99 (m, 1H), 1.88 (d, *J* = 13.1 Hz, 1H), 1.84 – 1.68 (m, 3H), 1.42 (s, 1.71H), 1.35 (s, 7.29H). ***The major diastereomer:*** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.2, 154.9, 140. 8, 129.1, 125.4 (d, $J_{C\text{-}F}$= 3.5 Hz), 80.8, 75.7, 55.6, 39.1, 34.8, 28.3, 27.5, 21.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.67. IR (cm^{-1}): *f* = 3390, 3320, 2956, 2359, 2104, 1718, 1694, 1617, 1558, 1506, 1455, 1424, 1391, 1365, 1323, 1281, 1242, 1159, 1117, 1065, 1037, 1016, 1003, 945, 909, 874, 849, 837, 800, 774, 758, 734, 669, 661, 635, 604. m/z HRMS (ESI) [M] calculated for $C_{19}H_{23}F_3N_4O_3$ 412.1722, found 412.1710. $[\alpha]_D^{25}$ = 14.70 (c 0.1, $CHCl_3$). HPLC: Chiralpak IA column, 95:05 hexanes/ isopropanol, 1 ml/min; t_R = 5.1 min (major), 5.9 min (minor); 86% ee. ***The minor diastereomer:***

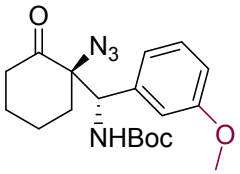
HPLC: Chiralpak IA column, 95:05 hexanes/ isopropanol, 1 ml/min; t_R =8.8 min (major), 9.0 min (minor); 99% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-chlorophenyl)methyl)carbamate **(3f)**



97% yield, 85:15. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.26 (s, 3.4H), 7.18 (d, *J* = 8.0 Hz, 0.6H), 5.26 (tq, *J* = 21.9, 12.3, 10.0 Hz, 2H), 2.84 (td, *J* = 13.9, 6.1 Hz, 0.85H), 2.49 (d, *J* = 14.2 Hz, 0.85H), 2.41 (t, *J* = 5.4 Hz, 0.3H), 2.12 (dq, *J* = 10.1, 3.3 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.86 – 1.71 (m, 2H), 1.66 (td, *J* = 13.8, 4.0 Hz, 2H), 1.35 (s, 1.35H), 1.28 (s, 7.65H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.5, 154.9, 135.3, 134.4, 129.9, 128.7, 80.6, 75.9, 55.4, 39.2, 34.8, 28.3, 27.5, 21.9. IR (cm^{-1}): *f* = 3441, 2963, 2109, 1710, 1484, 1258, 1160, 1089, 798. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{18}H_{23}ClN_4O_3$ 379.1531, found 379.1512. $[\alpha]_D^{25}$ = 8.40 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 98:2 hexanes/ isopropanol, 1 ml/min; t_R = 7.2 min (minor), 11.5 min (major); 93% ee.

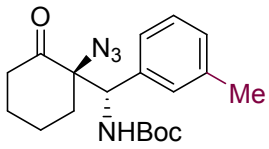
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-methoxyphenyl)methyl)carbamate **(3g)**



91% yield, 85:15 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.14 (m, 0.85H), 7.16 (t, *J* = 7.9 Hz, 0.15H), 7.10 – 6.86 (m, 2H), 6.83 (dd, *J* = 8.3, 2.5 Hz, 0.85H), 6.76 (dd, *J* = 8.3, 2.5 Hz, 0.15H), 5.32 (q, *J* = 9.9 Hz, 2H), 3.78 (s, 2.7H), 3.74 (s, 0.3H), 2.93 (td, *J* = 14.0, 6.1 Hz, 0.85H), 2.52 (d, *J* = 14.2 Hz, 1H), 2.46 – 2.36 (m, 0.15H), 2.15 (ddt, *J* = 13.3, 6.5, 3.2 Hz, 1H), 1.99 (dd, *J* = 18.4, 8.6 Hz, 1H), 1.94 – 1.77 (m, 2H), 1.76 – 1.59 (m, 2H), 1.39 (s, 1.35H), 1.32 (s, 7.65H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.7, 159.6, 155.0, 138.13, 129.47, 121.0, 114.7, 113.5, 80.4, 76.2, 55.9, 55.4, 39.2, 34.9, 28.3, 27.6, 22.0. IR (cm^{-1}): *f* =3675, 2962, 2105, 1716, 1490, 1258, 1010, 789. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{19}H_{26}N_4O_4$

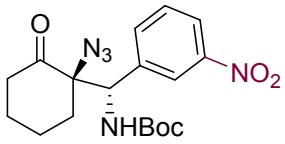
375.2027, found 375.2008. $[\alpha]_D^{25}$ = 3.30 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 10.6 min (minor), 12.8 min (major); 96% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(m-tolyl)methyl)carbamate **(3h)**



89% yield, 87:13 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 1H), 7.30 – 7.16 (m, 2.61H), 7.18 – 7.09 (m, 0.39H), 5.58 – 5.26 (m, 2H), 3.07 (td, *J* = 13.9, 6.2 Hz, 0.87H), 2.75 – 2.57 (m, 1H), 2.57 – 2.50 (m, 0.13H), 2.45 (s, 2.61H), 2.40 (s, 0.39H), 2.26 (m, *J* = 12.9, 6.4, 3.2 Hz, 1H), 2.13 (m, *J* = 15.6, 12.1, 3.3 Hz, 1H), 1.94 (m, *J* = 8.3, 7.4, 2.6 Hz, 2H), 1.87 – 1.72 (m, 2H), 1.44 (s, 7.83H), 1.34 (s, 1.17H). ***The major diastereomer:*** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 154.9, 138.2, 136.5, 129.2, 128.4, 125.6, 125.2, 80.3, 76.2, 55.9, 39.2, 34.9, 28.3, 27.6, 21.9, 21.7. IR (cm^{-1}): *f* = 3321, 2955, 2876, 2104, 1716, 1695, 1668, 1524, 1273, 1250, 1160, 1061, 864, 786, 701, 636. m/z HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{26}N_4O_3$ 381.1897, found 381.1913. $[\alpha]_D^{25}$ = -0.40 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 5.3 min (minor), 7.7 min (major); 96% ee.

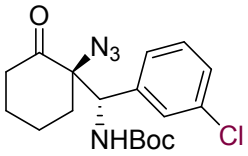
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-nitrophenyl)methyl)carbamate **(3i)**



98% yield, 81:19 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.39 – 8.23 (m, 1H), 8.19 (dd, *J* = 8.2, 2.3 Hz, 0.81H), 8.13 (dd, *J* = 8.1, 2.3 Hz, 0.19H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 0.81H), 7.47 (t, *J* = 8.0 Hz, 0.19H), 5.63 – 5.30 (m, 2H), 2.87 (td, *J* = 13.8, 6.2 Hz, 0.81H), 2.68 – 2.56 (m, 1H), 2.53 (d, *J* = 5.0 Hz, 0.19H), 2.21 (m, *J* = 13.6, 6.3, 3.4 Hz, 1H), 2.12 – 1.98 (m, 1H), 1.91 (dt, *J* = 14.2, 3.8 Hz, 1H), 1.78 (dd, *J* = 9.1, 4.1 Hz, 3H), 1.42 (s, 1.71H), 1.35 (s, 7.29H). ***The major diastereomer:*** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.9, 154.9, 148.3, 139.1, 134.7, 129.4, 123.6, 123.5, 80.9, 75.5, 55.4, 39.1, 34. 9, 28.2, 27.5, 21.9. IR (cm^{-1}): *f* = 3421, 2938, 2869, 2107, 1704, 1529, 1348, 1247, 1158, 1097, 1007, 864, 694. m/z HRMS (ESI) $[M+Na]^+$ calculated

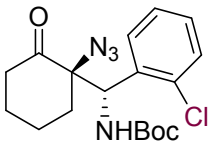
for $C_{18}H_{23}N_5O_5$ 412.1591, found 412.1606. $[\alpha]_D^{25}$ = 9.70 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 8.9 min (minor), 16.9 min (major); 89% ee. ***The minor diastereomer:*** HPLC: Chiralpak IC column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 10.9 min (major), 13.5 min (minor); 77% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-chlorophenyl)methyl)carbamate **(3j)**



96% yield, 83:17 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.19 (m, 3H), 5.49 – 5.18 (m, 2H), 2.91 (td, *J* = 13.9, 6.1 Hz, 0.83H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.50 (d, *J* = 5.2 Hz, 0.17H), 2.19 (ddt, *J* = 13.2, 6.5, 3.3 Hz, 1H), 2.11 – 1.94 (m, 1H), 1.93 – 1.79 (m, 2H), 1.73 (td, *J* = 13.5, 4.4 Hz, 2H), 1.42 (s, 1.53H), 1.35 (s, 7.47H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.4, 154.9, 138.8, 134.5, 130.0, 129.7, 128.7, 126.9, 80.7, 75.9, 55.5, 39.2, 34.9, 28.3, 27.6, 21.9. IR (cm^{-1}): *f* = 3335, 2968, 2105, 1714, 1490, 1258, 1160, 1089, 756, 698. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{18}H_{23}ClN_4O_3$ 379.1531, found 379.1513. $[\alpha]_D^{25}$ = 8.10 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 5.6 min (minor), 7.9 min (major); 94% ee. ***The minor diastereomer:*** HPLC: Chiralpak IC column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 6.1 min (major), 8.5 min (minor); 95% ee.

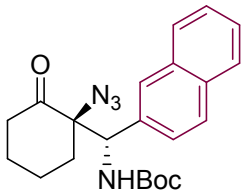
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(2-chlorophenyl)methyl)carbamate **(3k)**



86% yield, 76:24 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 10.9 Hz, 1.24H), 7.28 (d, *J* = 7.1 Hz, 1.76H), 5.98 (d, *J* = 9.8 Hz, 1H), 5.31 (d, *J* = 9.7 Hz, 1H), 2.95 (d, *J* = 15.0 Hz, 1H), 2.60 (d, *J* = 14.0 Hz, 1H), 2.30 (t, *J* = 13.3 Hz, 1H), 2.15 (d, *J* = 13.2 Hz, 1H), 1.96 – 1.68 (m, 4H), 1.35 (s, 9H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.7, 134.4, 130.8, 129.8, 129.6, 127.2, 80.5, 39.7, 35.3, 31.7, 30.3, 29.9, 28.3, 22.4. IR (cm^{-1}): *f* = 3345, 2943, 2105, 1714, 1489, 1250, 1159, 1050, 751. m/z HRMS (ESI)

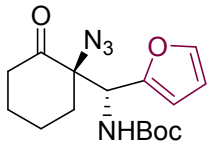
$[M+H]^+$ calculated for $C_{18}H_{23}ClN_4O_3$ 379.1531, found 379.1515. $[\alpha]_D^{25}$ = 11.10 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 98:2 hexanes/ isopropanol, 1 ml/min; t_R = 11.7 min (minor), 31.8 min (major); 85% ee. ***The minor diastereomer:*** HPLC: Chiralpak IC column, 98:2 hexanes/ isopropanol, 1 ml/min; t_R = 11.0 min (major), 15.7 min (minor); 93% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(naphthalen-2-yl)methyl)carbamate **(3l)**



95% yield, 91:9 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.65 (m, 4H), 7.69 – 7.34 (m, 3H), 5.81 – 5.42 (m, 1.82H), 5.35 – 5.05 (m, 0.18H), 3.03 (td, *J* = 13.9, 6.1 Hz, 0.91H), 2.67 – 2.51 (m, 1H), 2.45 (dt, *J* = 13.8, 4.7 Hz, 0.09H), 2.25 – 2.19 (m, 1H), 2.17 – 2.11 (m, 1H), 2.00 – 1.81 (m, 2H), 1.79 – 1.64 (m, 2H), 1.43 (s, 0.81H), 1.36 (s, 8.19H). ***The major diastereomer:*** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 155.0, 134.1, 133.3, 133.0, 128.2, 128.1, 127.8, 126.5, 125.9, 80.4, 76.3, 56.1, 39.2, 34.9, 28.3, 27.6, 22.0. IR (cm^{-1}): *f* = 3852, 3674, 3333, 2936, 2109, 1698, 1488, 1365, 1324, 1270, 1240, 1160, 1128, 1006, 859, 807, 760, 605. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{22}H_{26}N_4O_3$ 395.2078, found 395.2087. $[\alpha]_D^{25}$ = -2.80 (c 0.1, $CHCl_3$). HPLC: Chiralpak IA column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 6.1 min (major), 6.9 min (minor); 96% ee.

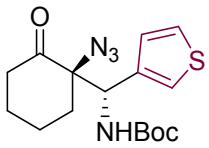
tert-butyl ((R)-((R)-1-azido-2-oxocyclohexyl)(furan-2-yl)methyl)carbamate **(3m)**



90% yield, 78:22 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (s, 0.78H), 7.30 (s, 0.22H), 6.41 – 6.32 (m, 1.56H), 6.30 – 6.23 (m, 0.44H), 5.55 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 2.90 (td, *J* = 13.6, 6.1 Hz, 0.78H), 2.68 (td, *J* = 12.9, 5.6 Hz, 0.22H), 2.55 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.20 – 2.08 (m, 1H), 2.00 (td, *J* = 15.6, 15.2, 7.7 Hz, 2H), 1.92 – 1.70 (m, 3H), 1.46 (s, 1.98H), 1.38 (s, 7.02H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.0, 155.0,

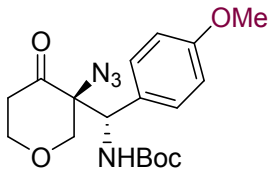
150.2, 142.6, 110.6, 108.9, 80.7, 75.7, 51.0, 39.2, 34.9, 28.3, 27.5, 21.7. IR (cm^{-1}): *f* = 3449, 2958, 2109, 1708, 1497, 1158, 1012, 813, 740. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{16}H_{22}N_4O_4$ 335.1714, found 335.1697. $[\alpha]_D^{25}$ = -11.50 (c 0.1, $CHCl_3$).HPLC: Chiralpak IC column, 98:2 hexanes/ isopropanol, 1 ml/min; t_R = 10.9 min (minor), 22.1 min (major); 90% ee. ***The minor diastereomer:*** Chiralpak IC column, 98:2 hexanes/ isopropanol, 1 ml/min; t_R = 11.9 min (minor), 12.6 min (major); 80% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(thiophen-3-yl)methyl)carbamate **(3n)**



98% yield, 85:15 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.26 (m, 1.85H), 7.25 (dd, *J* = 5.0, 2.9 Hz, 0.15H), 7.21 – 7.04 (m, 0.85H), 7.12 – 7.03 (m, 0.15H), 5.53 (d, *J* = 10.0 Hz, 0.85H), 5.47 (d, *J* = 10.2 Hz, 0.15H), 5.28 (d, *J* = 10.6 Hz, 1H), 2.98 (td, *J* = 13.8, 6.3 Hz, 0.85H), 2.55 (ddd, *J* = 15.1, 5.1, 2.7 Hz, 1H), 2.49 (d, *J* = 5.7 Hz, 0.15H), 2.16 (dq, *J* = 10.0, 3.1 Hz, 1H), 2.08 – 1.93 (m, 1H), 1.93 – 1.80 (m, 2H), 1.81 – 1.68 (m, 2H), 1.45 (s, 1.35H), 1.37 (s, 7.65H). ***The major diastereomer:*** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 154.9, 137.2, 127.4, 126.0, 124.1, 80.4, 76.2, 52.2, 39.2, 35.0, 28.3, 27.5, 21.7. IR (cm^{-1}): *f* = 3318, 3084, 2978, 2947, 2103, 1697, 1506, 1453, 1365, 1261, 1234, 1159, 1003, 794, 692, 633. m/z HRMS (ESI) [M] calculated for $C_{16}H_{22}N_4O_3S$ 350.1413, found 350.1374. $[\alpha]_D^{25}$ = 23.10 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 95:05 hexanes/ isopropanol, 1 ml/min; tR = 6.7 min (minor), 11.1 min (major); 95% ee.

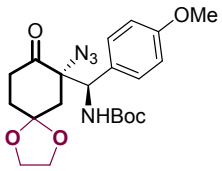
tert-butyl ((S)-((S)-3-azido-4-oxotetrahydro-2H-pyran-3-yl)(4-methoxyphenyl)methyl)carbamate **(3o)**



81% yield, 83:17 dr. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 5.48 (d, *J* = 10.1 Hz, 1H), 5.32 (t, *J* = 13.0 Hz, 1H), 4.39 (t, *J* = 9.6 Hz, 1H), 3.81 (s, 3H),

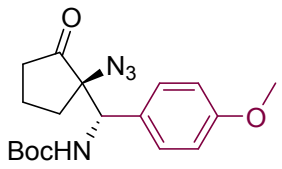
3.73 (d, *J* = 11.3 Hz, 2H), 3.45 (q, *J* = 13.4, 12.7 Hz, 1H), 3.35 (d, *J* = 11.8 Hz, 1H), 2.54 (d, *J* = 14.5 Hz, 1H), 1.37 (s, 9H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-d) δ 203.1, 159.8, 154.9, 129.9, 127.7, 113.9, 80.5, 75.0, 72.00, 69.2, 64.5, 55.4, 40.6, 28.3. IR (cm^{-1}): *f* = 3418, 3316, 2962, 2112, 1701, 1505, 1256, 1161, 1020, 792. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{18}H_{24}N_4O_5$ 377.1819, found 377.1810. $[\alpha]_D^{25}$ = -1.70 (c 0.1, $CHCl_3$). HPLC: Chiralpak IA column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 8.6 min (major), 9.3 min (minor); 82% ee. ***The minor diastereomer:*** HPLC: Chiralpak IA column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 14.4 min (major), 16.2 min (minor); 74% ee.

tert-butyl-((R)-((S)-7-azido-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)(4-methoxyphenyl)methyl)carbamate**(3p)**



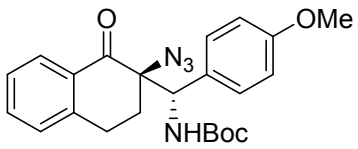
90% yield, 95:5 dr. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (d, *J* = 8.0 Hz, 1.9H), 7.30 (d, *J* = 8.4 Hz, 0.1H), 7.19 (d, *J* = 8.1 Hz, 0.1H), 6.87 (dd, *J* = 7.7, 4.1 Hz, 1.9H), 5.67 (d, *J* = 10.1 Hz, 0.95H), 5.38 (d, *J* = 10.7 Hz, 0.05H), 5.24 (d, *J* = 10.1 Hz, 0.95H), 5.12 (s, 0.05H), 4.07 (ddt, *J* = 20.5, 14.9, 6.8 Hz, 2H), 3.93 (dt, *J* = 28.7, 5.9 Hz, 2H), 3.80 (t, *J* = 2.8 Hz, 3H), 3.49 – 3.16 (m, 0.95H), 2.88 (s, 0.05H), 2.50 (d, *J* = 14.2 Hz, 1H), 2.26 – 2.10 (m, 1H), 2.00 (t, *J* = 15.7 Hz, 3H), 1.35 (d, *J* = 3.7 Hz, 9H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.7, 159.4, 154.9, 130.8, 113.6, 107.1, 80.2, 75.1, 65.4, 64.7, 55.9, 55.4, 41.8, 35.6, 35.4, 28.3. IR (cm-1): *f* = 3367, 2968, 2098, 1697, 1505, 1235, 1029, 843, 84. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{21}H_{28}N_4O_6$ 433.2082, found 433.2066. $[\alpha]_D^{25}$ = -8.10 (c 0.1, CHCl3). HPLC: Chiralpak IA column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 11.1 min (major), 14.0 min (minor); 96% ee.

tert-butyl ((S)-((R)-1-azido-2-oxocyclopentyl)(4-methoxyphenyl)methyl)carbamate **(3q)**



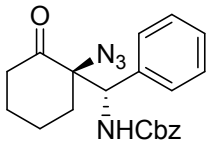
99% yield, 89:11 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 (d, *J* = 8.2 Hz, 1.89H), 7.17 – 7.06 (m, 0.11H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.32 (d, *J* = 8.6 Hz, 0.89H), 5.23 (d, *J* = 8.6 Hz, 0.11H), 5.00 (d, *J* = 8.6 Hz, 0.89H), 4.87 – 4.71 (m, 0.11H), 3.80 (s, 3H), 2.93 – 2.63 (m, 0.22H), 2.60 – 2.21 (m, 1.78H), 1.95 (d, *J* = 14.4 Hz, 3H), 1.87 – 1.71 (m, 1H), 1.39 (s, 9H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-*d*) δ 211.6, 159.6, 155.3, 129.3, 128.9, 114.1, 80.3, 73.2, 55.4, 54.7, 35.7, 31.0, 28.4, 17.2. IR (cm^{-1}): *f* = 3376, 2965, 2104, 1697, 1511, 1246, 1155, 1022, 788, 756. m/z HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{24}N_4O_4$ 383.1690, found 383.1674. $[\alpha]_D^{25}$ = -41.00 (c 0.1, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; tR = 10.8 min (major), 11.8 min (minor); 90% ee.

tert-butyl-((S)-((R)-2-azido-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)(4-methoxyphenyl)methyl)carbamate **(3r)**



40% yield, >96:4 dr. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.53 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 (q, *J* = 7.4 Hz, 3H), 7.25 (d, *J* = 9.3 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 2H), 5.44 (d, *J* = 9.0 Hz, 1H), 5.12 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 3.24 (d, *J* = 13.9 Hz, 1H), 3.01 (dt, *J* = 17.8, 4.7 Hz, 1H), 2.27 (td, *J* = 13.7, 12.7, 5.4 Hz, 1H), 1.98 (dt, *J* = 13.8, 4.5 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-d) δ 177.6, 159.6, 154.8, 141.9, 134.4, 131.3, 129.7, 128.8, 128.8, 127.5, 114.0, 80.0, 55.4, 29.8, 28.3, 25.6, 22.8, 14.3. IR (cm^{-1}): *f* = 3351, 2928, 1694, 1610, 1512, 1455, 1391, 1366, 1299, 1278, 1243, 1162, 1033, 910, 834, 796, 731.28, 648. m/z HRMS (ESI) $[M+Na]^+$ calculated for $C_{23}H_{26}N_4O_4$ 446.1880, found 446.1878. $[\alpha]_D^{25}$ = 0.60 (c 0.1, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 12.8 min (minor), 18.0 min (major); 97% ee.

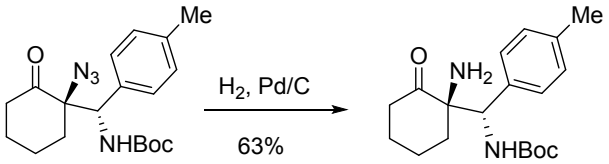
benzyl ((S)-((R)-1-azido-2-oxocyclohexyl)(phenyl)methyl)carbamate **(3s)**



47% yield, >96:4 dr, ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.27 (m, 10H), 5.67 (dd, *J* = 18.5, 9.9 Hz, 1H), 5.37 (dd, *J* = 21.3, 9.9 Hz, 1H), 5.20 – 5.03 (m, 1H), 5.00 (s, 1H), 2.73 – 2.50 (m, 1H), 2.42 – 2.23 (m, 1H), 2.15 – 1.99 (m, 2H), 1.85 (m, 2H), 1.80 – 1.68 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 206.5, 155.6, 136.3, 136.1, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 76.0, 67.3, 56.6, 39.3, 35.0, 27.6, 21.9. IR (cm^{-1}): *f* = 3327, 2947, 2104, 1715, 1496, 1453, 1308, 1224, 1126, 10815, 1021, 908, 853, 804, 771, 732, 698, 673, 647. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{21}H_{22}N_4O_3$ 380.1798, found 380.1797. $[\alpha]_D^{25}$ = 24.90 (c 0.1, $CHCl_3$). HPLC: Chiralpak ID column, 70:30 hexanes/ isopropanol, 1 ml/min; t_R = 9.4 min (major), 14.7 min (minor); 96% ee.

Transformation of the products:

tert-butyl ((S)-((R)-1-amino-2-oxocyclohexyl)(p-tolyl)methyl)carbamate **(4a)**



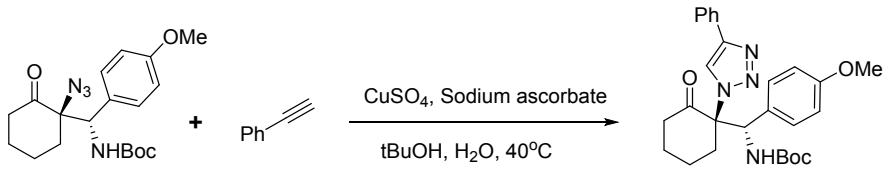
3c
88:12 dr, 96% ee

4c
89:11 dr, 96% ee

To a solution of **3c** (39 mg, 0.11 mmol) in 2 mL of anhydrous EA was added 10% Pd/C (23 mg, 0.02 mmol). After stirring under hydrogen atmosphere for 2 days, the reaction mixture was filtered through celite and then purified by flash column chromatography (2:1, Petroleum Ether /Ethyl Acetate) to give **4c** (22.4 mg, 63% yield, 89:11 dr) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 7.6 Hz, 1.68H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 0.32H), 5.98 (d, *J* = 9.6 Hz, 0.16H), 5.72 (d, *J* = 9.6 Hz, 0.84H), 5.30 (d, *J* = 9.5 Hz, 0.84H), 4.98 (s, 0.16H), 2.95 (dt, *J* = 13.8, 6.8 Hz, 0.84H), 2.80 (td, *J* = 13.6, 5.8 Hz, 0.16H), 2.44 (d, *J* = 14.4 Hz, 1H), 2.30 (d, *J* = 24.4 Hz, 3H), 2.24 – 1.97 (m, 2H), 1.73 (d, *J* = 39.3 Hz, 5H), 1.42 (s, 1.5H), 1.34 (s, 7.5H). ***The major diastereomer:*** ^{13}C NMR (126 MHz, Chloroform-d) δ 212.6, 155.3, 137.6,

129.1, 128.2, 127.0, 79.7, 56.4, 41.9, 38.4, 31.6, 28.7, 28.4, 22.2, 21.2. IR (cm^{-1}): *f* = 3305, 2928, 1698, 1497, 1363, 1233, 1162, 798, 694. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{19}H_{28}N_2O_3$ 333.2173, found 333.2159. $[\alpha]_D^{25}$ = -28.60 (c 0.1, $CHCl_3$). HPLC: Chiralpak IB column, 95:5 hexanes/ isopropanol, 1 ml/min; t_R = 5.8 min (minor), 7.3min (major); 96% ee.

tert-butyl-((S)-(4-methoxyphenyl)((R)-2-oxo-1-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclohexyl)methyl)carbamate **(5a)**

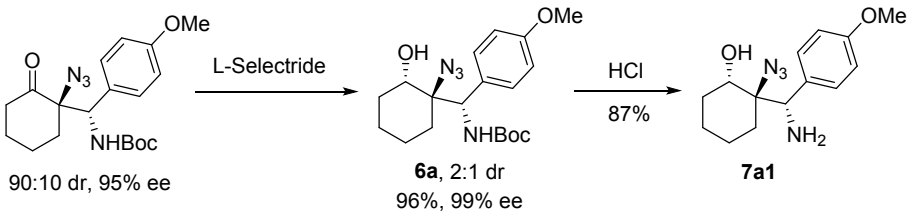


3a
90:10 dr, 95% ee

5a, 69%, 95% ee

To a solution of **3a** (17.8 mg, 0.05 mmol) in *t*-BuOH/H_2O (1 mL, 1:1) was added phenylacetylene (48.6 mg, 0.5 mmol), $CuSO_4$•$5H_2O$ (24 mg, 0.1 mmol) and sodium ascorbate (38 mg, 0.19 mmol) at room temperature. After stirring for two days, the reaction mixture was filtered, and the collected solid was dissolved in DCM and purified by flash column chromatography (3:1, Petroleum Ether /Ethyl Acetate) to give **5a** (16 mg, 69% yield) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.43 (dd, *J* = 18.0, 10.4 Hz, 3H), 7.34 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 3H), 5.67 (d, *J* = 9.5 Hz, 1H), 3.70 (s, 3H), 2.92 (s, 1H), 2.55 (dt, *J* = 12.3, 5.4 Hz, 1H), 2.36 (t, *J* = 5.3 Hz, 2H), 2.17 (d, *J* = 30.5 Hz, 2H), 1.90 (q, *J* = 13.5 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 204.2, 159.5, 155.5, 146.9, 130.4, 129.2, 129.0, 128.5, 125.9, 119.6, 113.9, 80.3, 55.3, 39.2, 35.9, 31.7, 30.3, 28.4, 28.1, 21.5. IR (cm^{-1}): *f* = 3418, 2964, 2240, 1701, 1502, 1250, 1162, 1025, 726. m/z HRMS (ESI) $[M+H]^+$ calculated for $C_{28}H_{34}N_4O_3$ 477.2496, found 477.2480. $[\alpha]_D^{25}$ = -7.00 (c 0.1, $CHCl_3$). HPLC: Chiralpak ID column, 60:40 hexanes/ isopropanol, 1 ml/min; tR = 20.8 min (major), 29.8 min (minor); 95% ee.

tert-butyl ((1S)-((1R)-1-azido-2-hydroxycyclohexyl)(4-methoxyphenyl)methyl)carbamate **(6a)**



90:10 dr, 95% ee

6a, 2:1 dr
96%, 99% ee

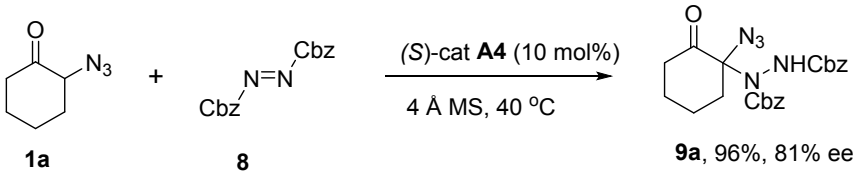
7a1

To a solution of **3a** (14 mg, 0.04 mmol) in THF (2.5 mL) was added L-selectride (1 N, 200 μL, 0.2 mmol) at -78°C. After stirring at this temperature for 2.5 h, the reaction mixture was quenched by adding a saturated solution of NH_4Cl. The layers were separated and aqueous layer was extracted with DCM for three times. The combined organic layers were then washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum to give a residue, which was purified flash column chromatography (9:1, Petroleum Ether /Ethyl Acetate) to afford **6a1** as the major diastereomer (8.9 mg, 64% yield) with **6a2** (4.5 mg, 32% yield). Data for **6a1:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.29 (d, *J* = 9.4 Hz, 1H), 4.81 (d, *J* = 9.5 Hz, 1H), 4.68 (d, *J* = 4.4 Hz, 1H), 3.81 (s, 3H), 3.67 (s, 1H), 1.88 (d, *J* = 12.5 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.43 (s, 9H), 1.27 (d, *J* = 11.3 Hz, 3H), 1.05 (d, *J* = 14.3 Hz, 1H), 0.93 – 0.81 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.6, 157.3, 129.3, 114.2, 81.1, 68.4, 67.0, 58.8, 55.4, 28.8, 28. 6, 28.4, 27.6, 21. 6, 18.3. IR (cm^{-1}): *f* = 3314, 2934, 2113, 1666, 1612, 1585, 1528, 1511, 1456, 1391, 1366, 1277, 1241, 1155, 1078, 1064, 1033, 1018, 995, 915, 890, 867, 850, 832, 801, 787, 764, 723, 656, 633. m/z HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{28}N_4O_4$ 399.2003, found 399.2017. $[\alpha]_D^{25}$ = -25.80 (c 0.1 , $CHCl_3$). HPLC: Chiralpak IC column, 95:05 hexanes/ isopropanol, 1 ml/min; t_R = 7.1 min (minor), 12 min (major); 99% ee.

To a solution of the major diastereomer **6a1** in ethyl acetate (1 mL) was added a solution of HCl in EA (0.33 N, 2 mL) at room temperature. After stirring for 4 h, the reaction mixture was concentrated under vacuum to give a residue, which was dissolved in DCM (1 mL) and added $NH_3.H_2O$ (1 mL). The reaction mixture was stirred for 0.5 h at room temperature and then the solvent was removed by vacuum evaporation to get the product **7a1** (6.5 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.22 (s, 1H), 3.93 – 3.61 (m, 4H), 3.22 (s, 3H), 1.89 (dt, *J* = 11.6, 4.8 Hz, 1H), 1.83 – 1.59 (m, 3H), 1.47 (t, *J* = 5.8 Hz, 2H), 1.43 – 1.32 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.48, 133.02, 128.91, 114.03, 72.38, 67.21, 59.00, 55.41, 31.59, 30.85, 21.90, 21.81. IR (cm^{-1}): *f* = 3360, 2933, 2861, 2097, 1609, 1582,

1511, 1456, 1303, 1246, 1178, 1111, 1083, 1032, 997, 909, 875, 832, 751, 654, 627. m/z HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}N_4O_2$ 299.1478, found 299.1494. $[\alpha]_D^{25}$ = -0.10 (c 0.1 , $CHCl_3$).

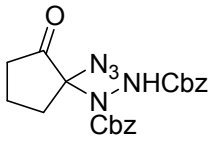
Asymmetric aminations with azodicarboxylate:



1a **8** **9a**, 96%, 81% ee

To a 4 ml reaction tube was added substrate **1a** (14 mg, 0.1 mmol), azodicarboxylate **8** (60 mg, 0.20 mmol), (*S*)**-cat A4** (7 mg, 0.01 mmol) and 4Å MS (150 mg). Subsequently, DCM (0.1 mL) was added to dissolve the reagents, and the mixture was warmed to 40 ºC under N_2 atmosphere. After approximate 30min, the DCM was evaporated to leave the mixture as syrup. After stirring at 40 ºC for another 12h, the mixture was cooled to rt and directly purified by flash column chromatography (20:1, Petroleum Ether /Ethyl Acetate) to afford the desired product **9** (42 mg, 96% yield**)**. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 6.91 (m, 10H), 6.70 (d, *J* = 83.8 Hz, 1H), 5.17 (dq, *J* = 37.5, 12.0, 11.2 Hz, 4H), 2.89 (td, *J* = 13.1, 5.7 Hz, 0.5H), 2.68 – 2.27 (m, 2H), 2.06 (d, *J* = 18.1 Hz, 1H), 2.01 – 1.91 (m, 0.5H), 1.80 – 1.50 (m, 3.5H), 1.44 (td, *J* = 9.2, 8.4, 4.4 Hz, 0.5H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.24, 156.06, 135.40, 134.69, 128.90, 128.80, 128.77, 128.76, 128.74, 128.33, 85.00, 69.70, 68.60, 68.27, 53.56, 39.45, 39.07, 37.81, 28.99, 28.53, 21.60. IR (cm^{-1}): *ƒ* = 3648, 3292, 2945, 2106, 1716, 1516, 1455, 1393, 1329, 1232, 1214, 1116, 1058, 1028, 946, 737, 695, 589. m/z HRMS (ESI) [M] calculated for $C_{22}H_{23}N_5O_5$ 437.1699, found 437.1667. $[\alpha]_D^{25}$ = -11.00 (c 0.1, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R =17 min (major), 19 min (minor); 81% ee.

dibenzyl 1-(1-azido-2-oxocyclopentyl)hydrazine-1,2-dicarboxylate **(9b)**



81% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.28 (m, *J* = 5.0, 3.9 Hz, 9H), 7.25 (d, *J* = 5.7 Hz, 1H), 5.28 – 4.95 (m, 5H), 2.65 – 2.49 (m, 2H), 2.36 (dd, *J* = 18.7, 7.8 Hz, 1H), 2.06 (m, 2H), 1.78 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 206.40, 156.38, 154.68, 135.29, 134.93, 128.77, 128.74, 128.35, 128.27, 82.50, 69.03, 68.40, 34.67, 31.49, 18.16. IR (cm^{-1}): *f* = 3179, 3031, 2950, 2106, 1746, 1711, 1586, 1514, 1499, 1458, 1406, 1350, 1321, 1292, 1260, 1240, 1218, 1158, 1099, 1042, 988, 914, 813, 754.10, 725, 691. m/z HRMS (ESI) $[M+Na]^{+}$ calculated for $C_{21}H_{21}N_5O_5$ 447.1468, found 447.1464. $[\alpha]_D^{25}$ = -17.80 (c 0.1, $CHCl_3$). HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R =11.6 min (major), 13.5 min (minor); 52% ee.

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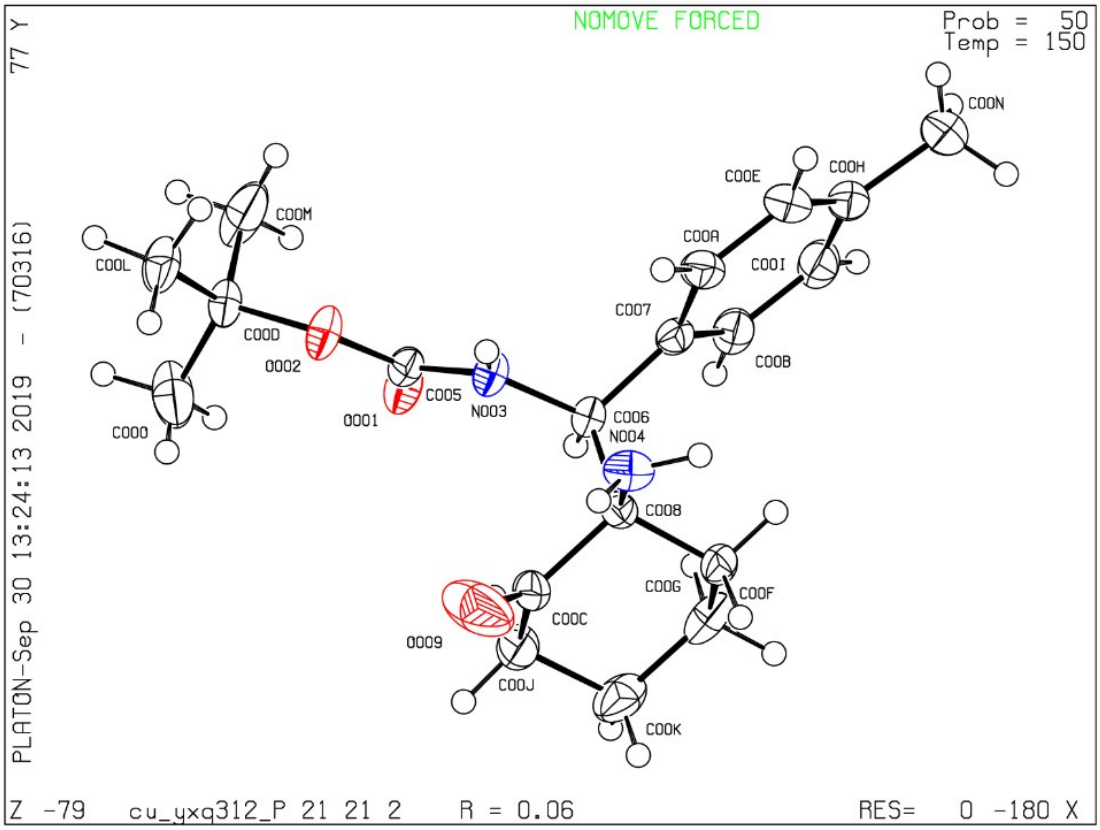
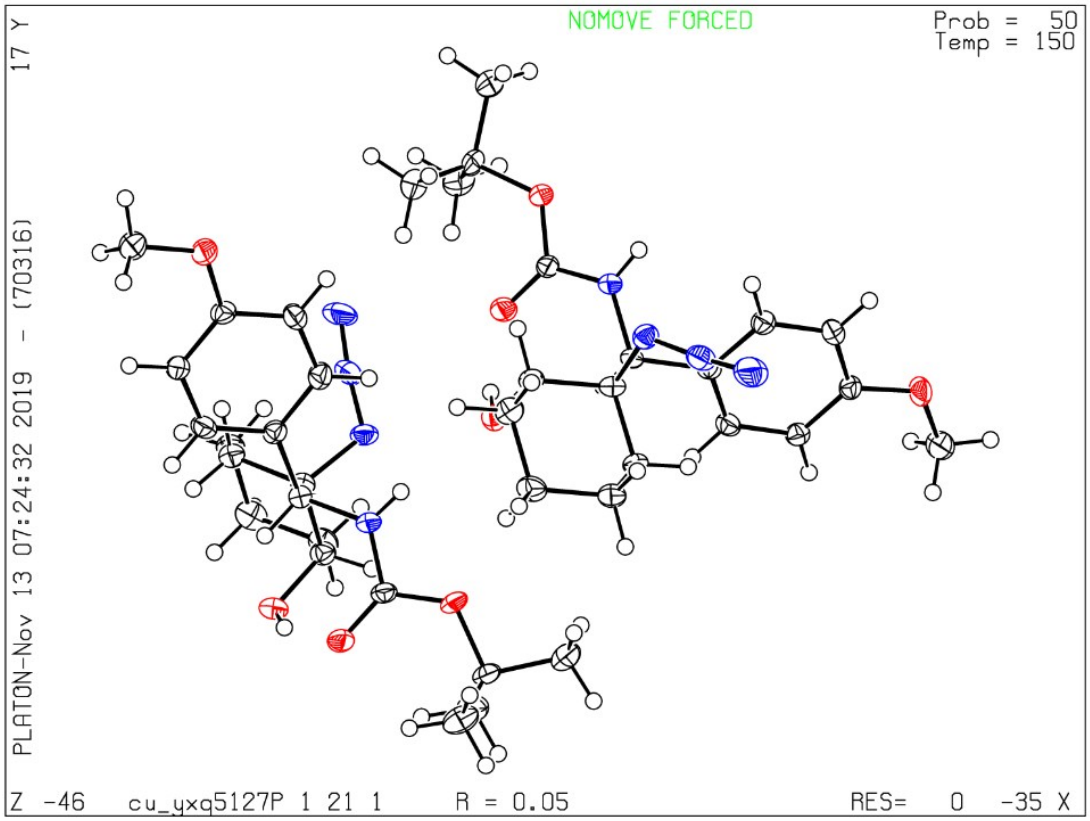
X-Ray Structures



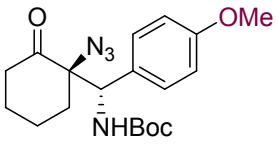
X-ray structure of 4c

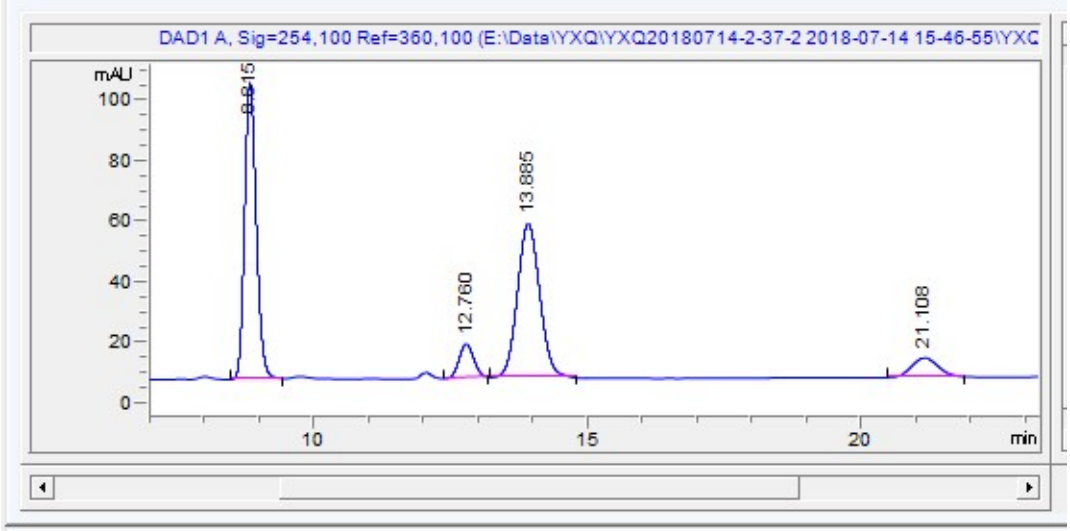


X-Ray structure of 6a1

HPLC traces:

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-methoxyphenyl)methyl)carbamate **(3a)**





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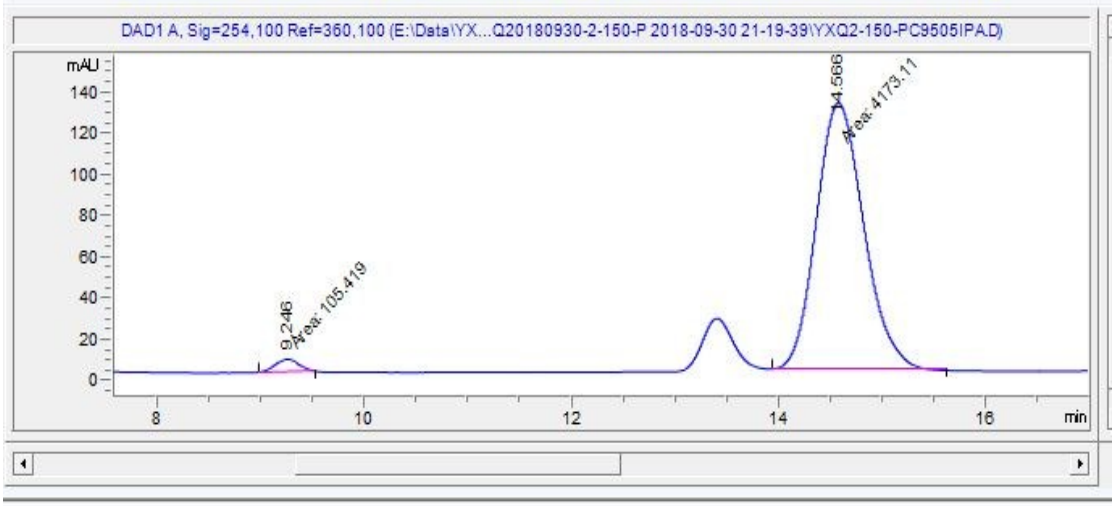
3	13.885	BB	1448.8	51.2	0.3479	43.609	0.921
4	21.108	BB	215.1	6.4	0.3924	6.473	0.916



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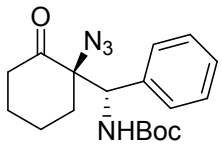
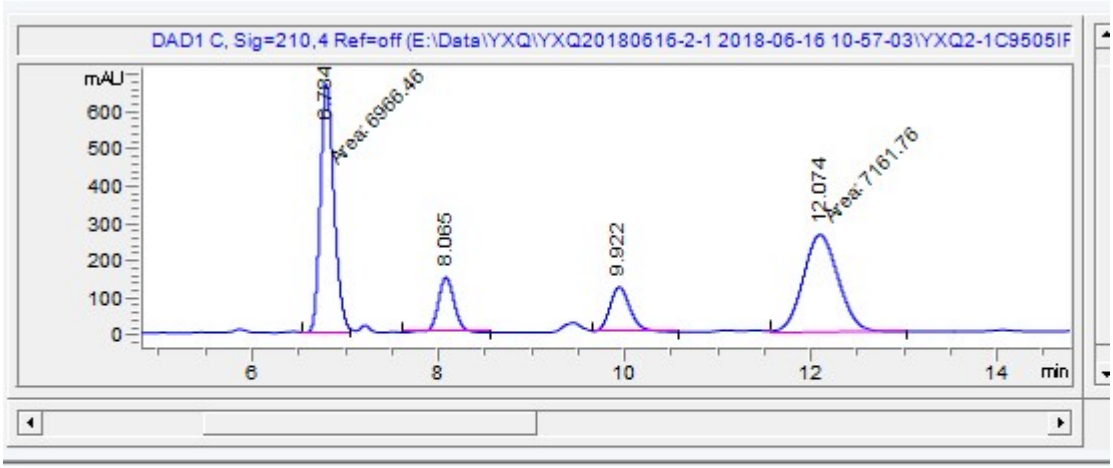
2	14.566	MM	4173.1	130.2	0.5342	97.536	0.825

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(phenyl)methyl)carbamate **(3b)**





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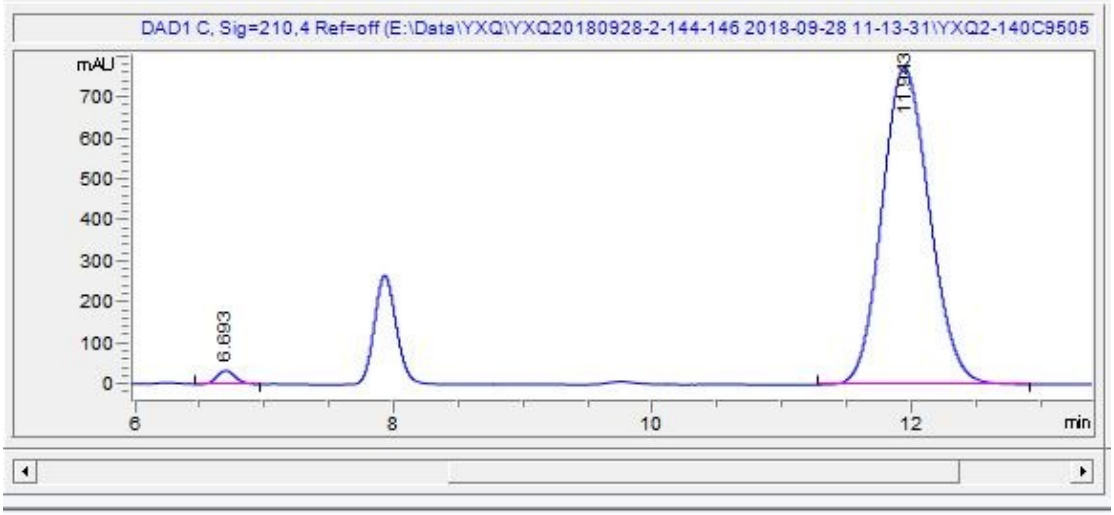
3	9.922	VB	1889.2	122.7	0.2367	10.583	0.801
4	12.074	MM	7161.8	267.4	0.4465	40.120	0.894



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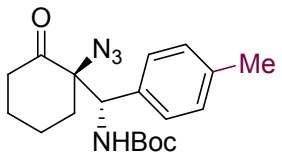
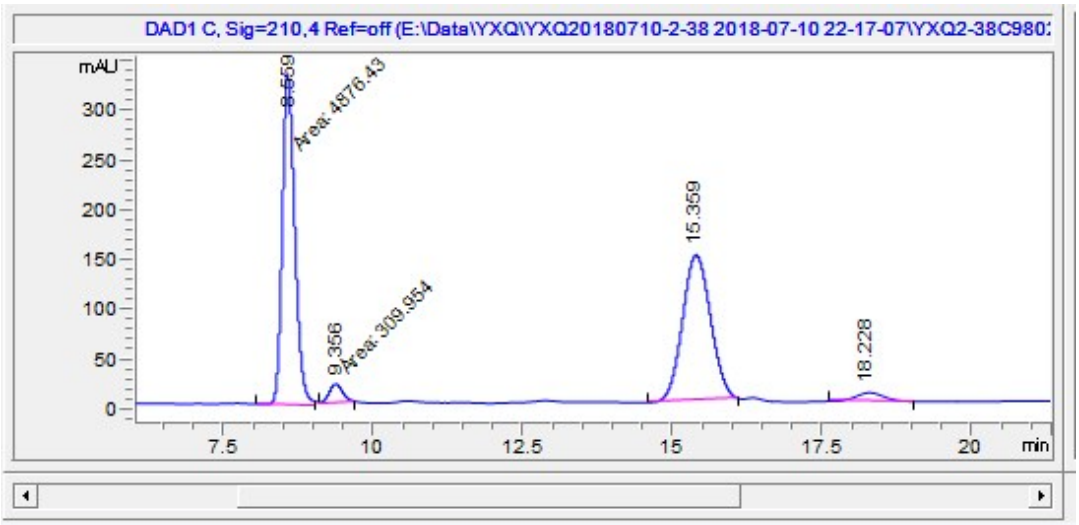
2	11.943	BB	19624.4	766.2	0.3863	98.360	0.86

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(p-tolyl)methyl)carbamate **(3c)**





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2	9.356	MM	310	19.5	0.2655	3.017	0.908
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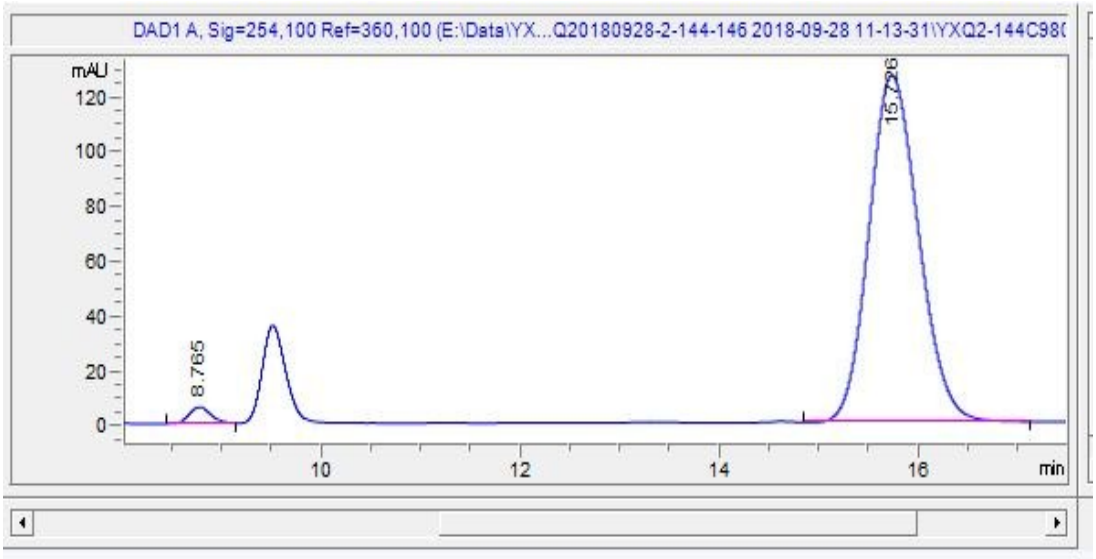
4	18.228	BV R	284.4	8.7	0.384	2.768	0.861



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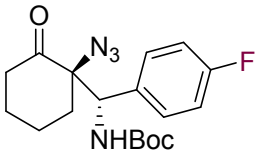
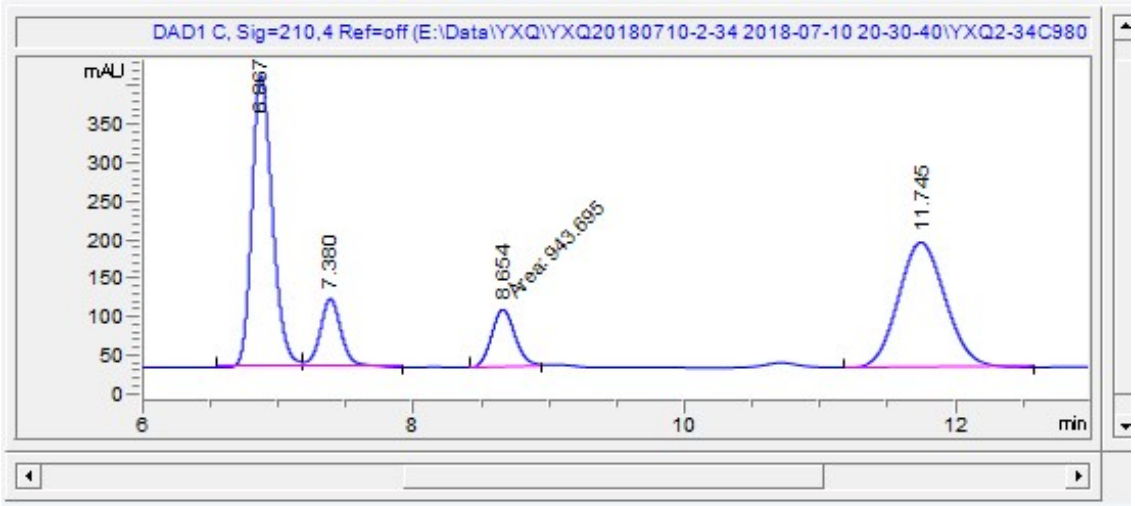
2	15.726	BB	4365.5	125.9	0.4994	98.004	0.827

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-fluorophenyl)methyl)carbamate **(3d)**





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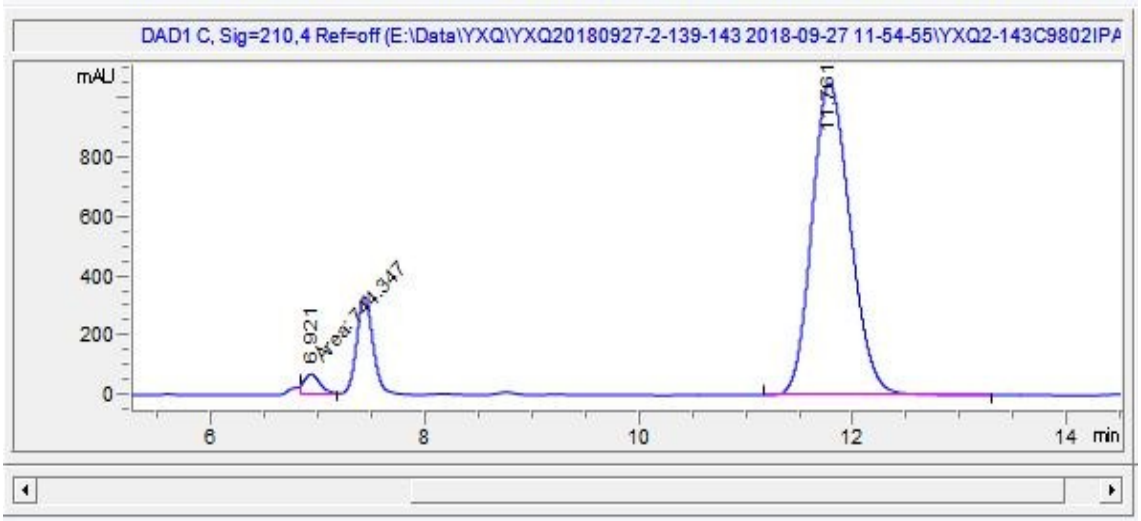
3	8.654	MM	943.7	75.9	0.2072	9.540	0.896
4	11.745	BB	3940.6	162.5	0.3149	39.834	0.879



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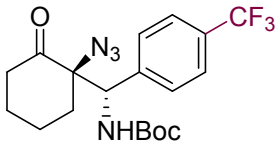
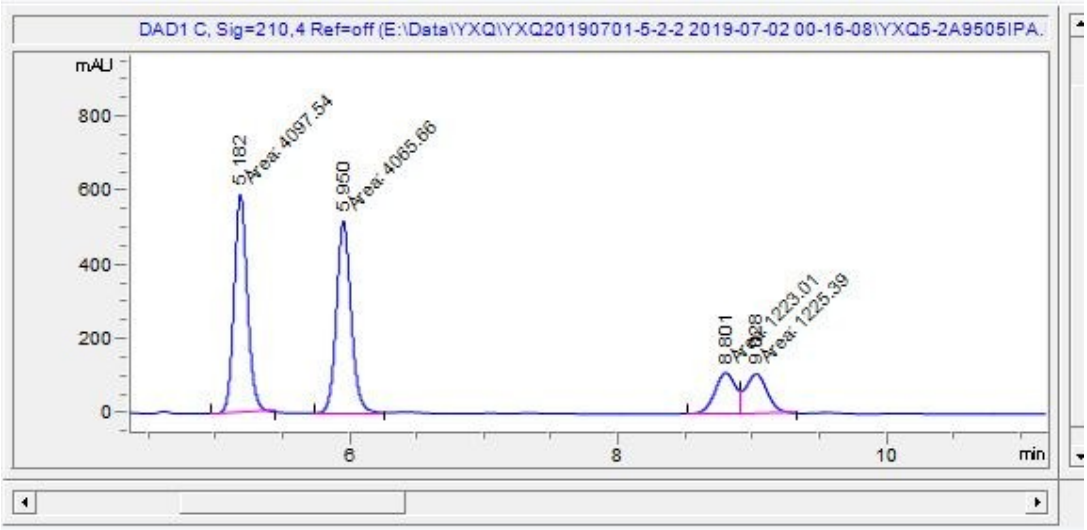
2	11.761	BB	26419.6	1059.2	0.3855	97.260	0.812

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-(trifluoromethyl)phenyl)methyl)carbamate **(3e)**





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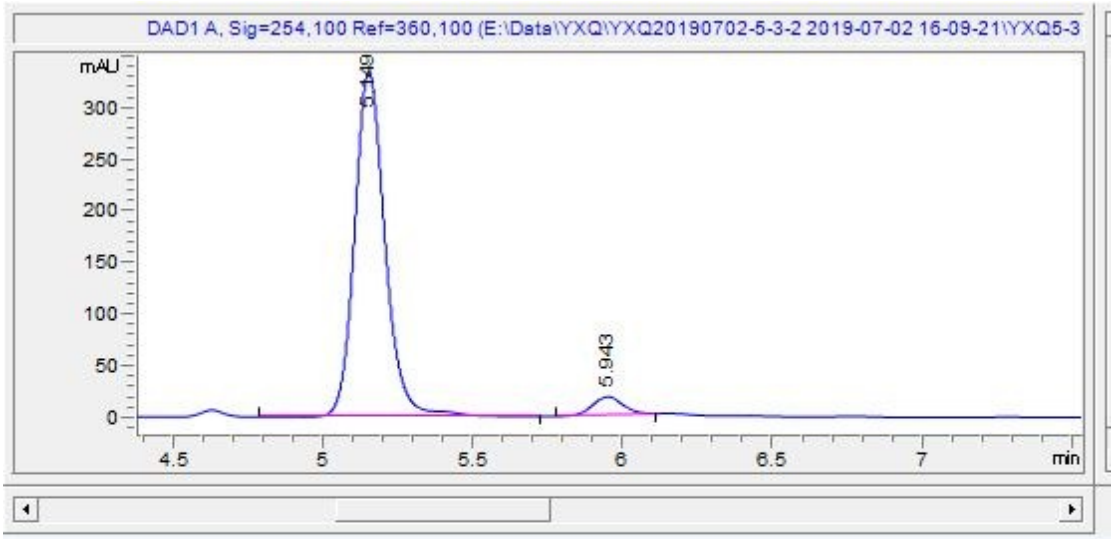
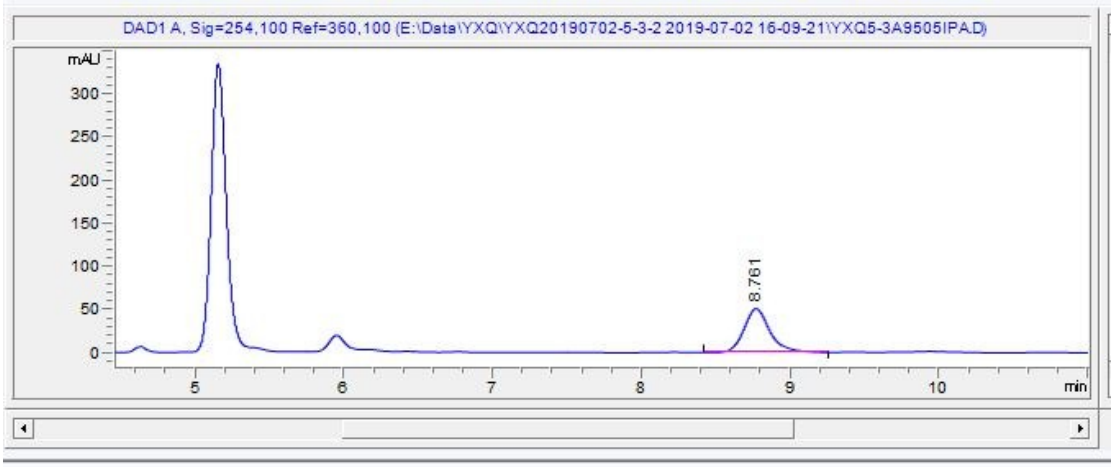
3	8.801	MF	1223	111.9	0.1821	11.525	1.154
4	9.028	FM	1225.4	107.8	0.1894	11.548	0.939



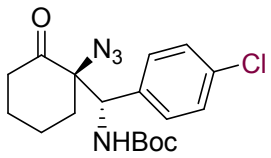
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.149	BB	2357.7	332.6	0.1082	95.046	0.816
2	5.943	BB	122.9	17.5	0.1098	4.954	0.955

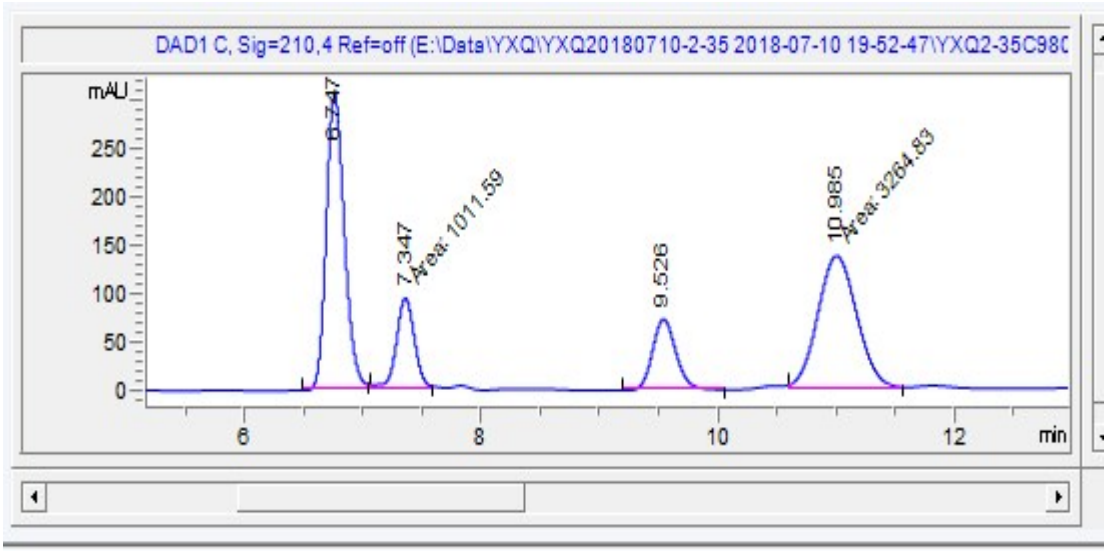
The minor diastereomer **3e':**



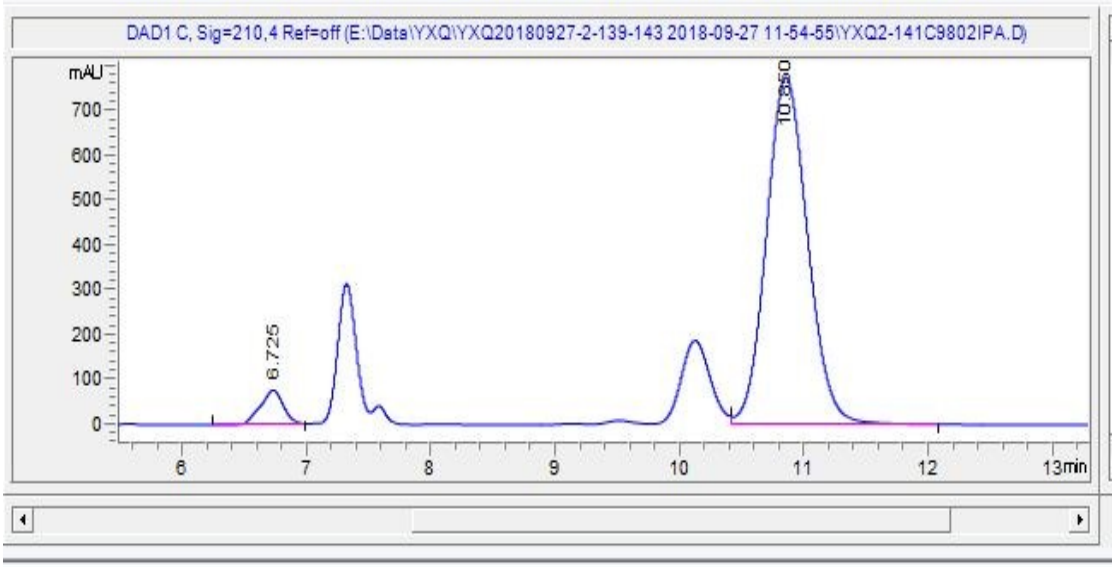
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.761	BB	616.6	50.5	0.1835	100.000	0.821

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-chlorophenyl)methyl)carbamate **(3f)**



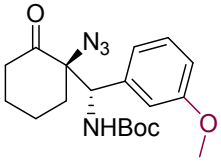


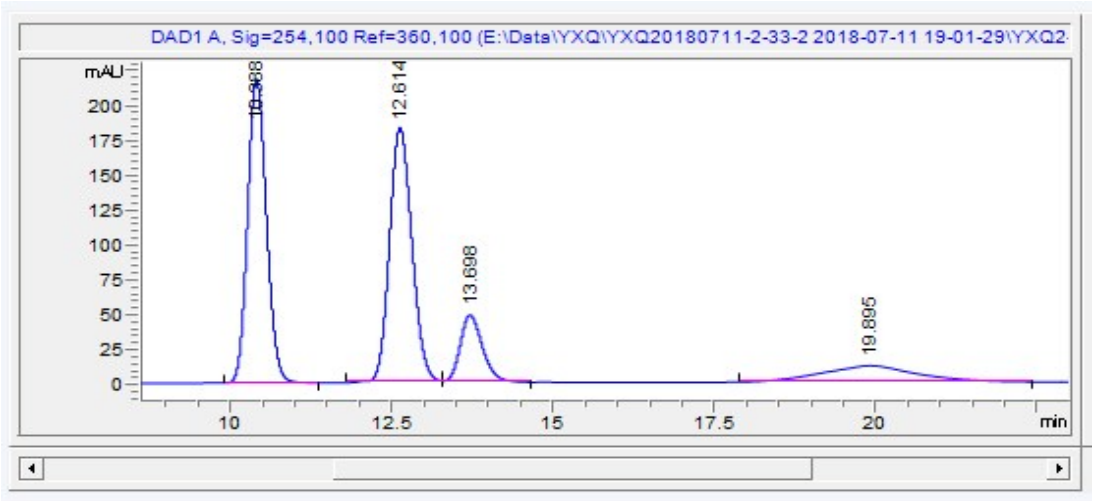
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.747	BV	3285.8	306.3	0.1657	38.328	0.768
2	7.347	MM	1011.6	93.8	0.1798	11.800	0.959
3	9.526	BB	1010.7	73.2	0.1981	11.789	0.844
4	10.985	MM	3264.8	139	0.3916	38.083	0.871



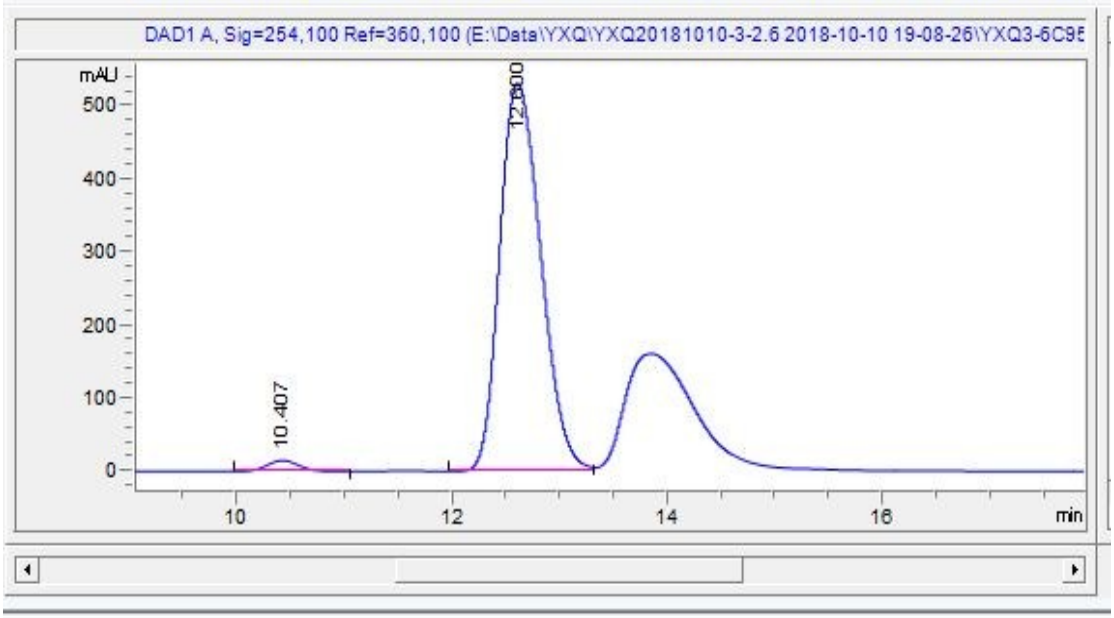
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.725	BV	1004.7	76.4	0.1915	5.340	1.204
2	10.85	VB	17808.9	771.8	0.3507	94.660	0.874

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-methoxyphenyl)methyl)carbamate **(3g)**



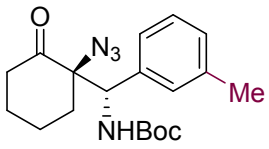


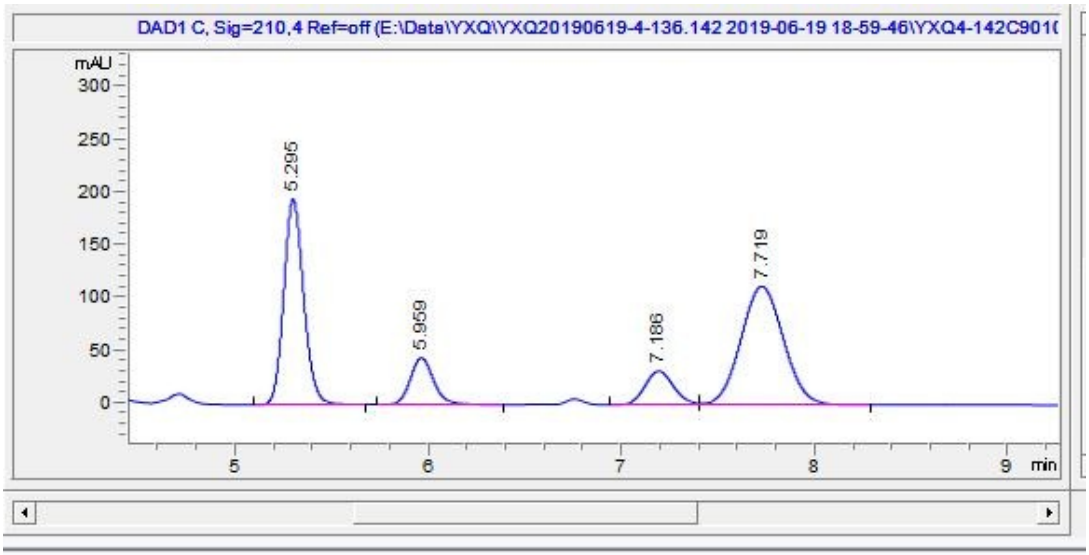
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.388	BB	4418.7	218.4	0.3145	39.418	0.841
2	12.614	BV	4428	183.2	0.3695	39.502	0.85
3	13.698	VB	1172.9	48.3	0.3606	10.463	0.747
4	19.895	BB	1190.2	11.7	1.1898	10.617	1.028



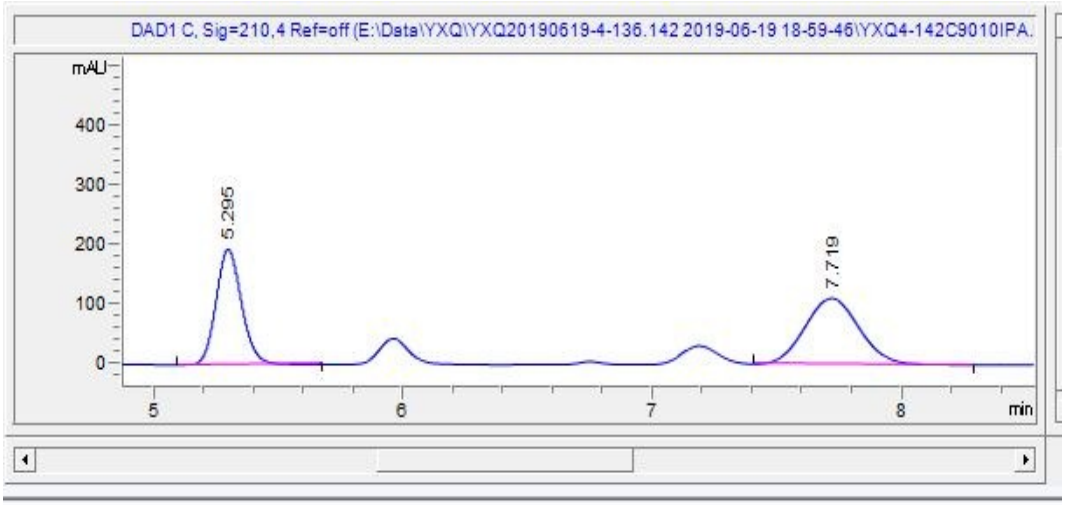
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.407	BB	311.6	15.2	0.2489	2.164	0.948
2	12.6	BV	14092.1	530.4	0.319	97.836	0.736

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(m-tolyl)methyl)carbamate **(3h)**



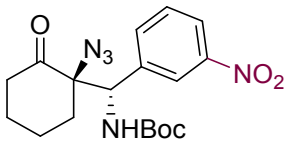


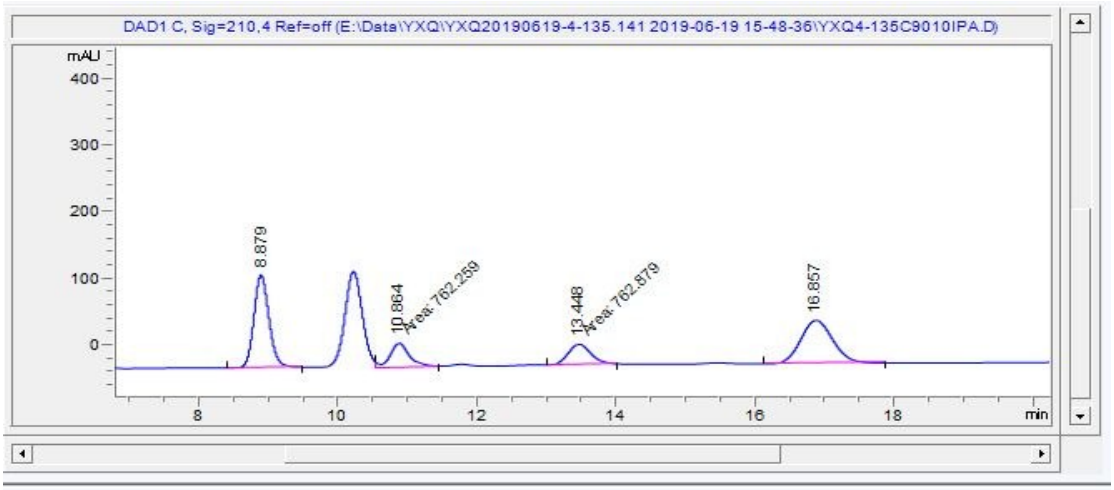
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.295	BB	1387.9	194.1	0.1104	36.511	0.844
2	5.959	BB	370.8	44	0.1298	9.754	0.848
3	7.186	BV	329.5	31.8	0.1601	8.668	0.878
4	7.719	VB	1713.2	111.8	0.2408	45.068	0.931



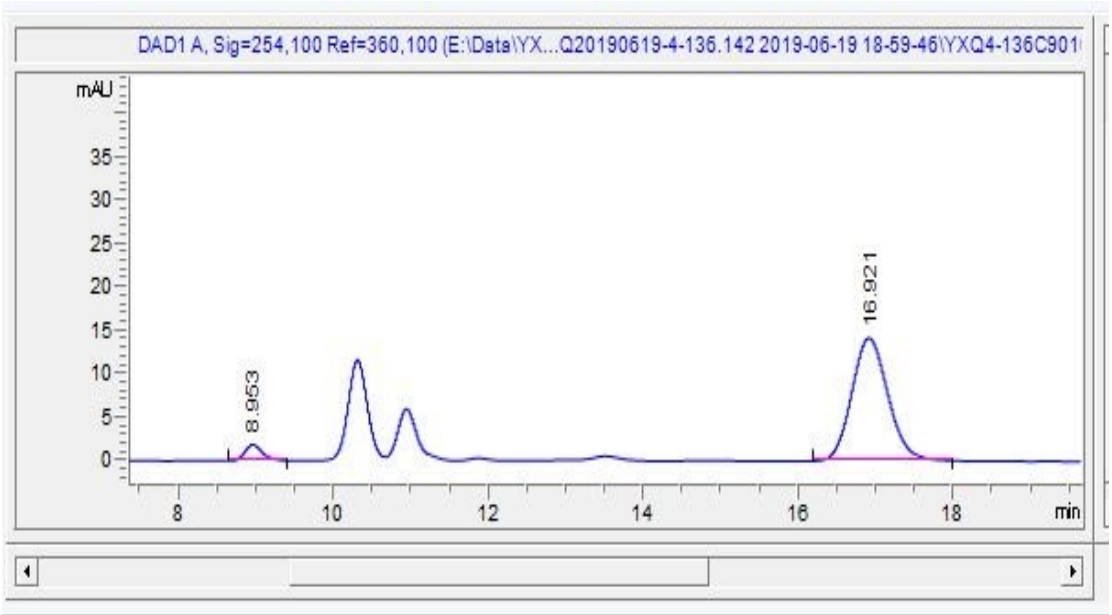
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.295	BB	1387.9	194.1	0.1104	44.755	0.844
2	7.719	VB	1713.2	111.8	0.2408	55.245	0.931

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-nitrophenyl)methyl)carbamate **(3i)**



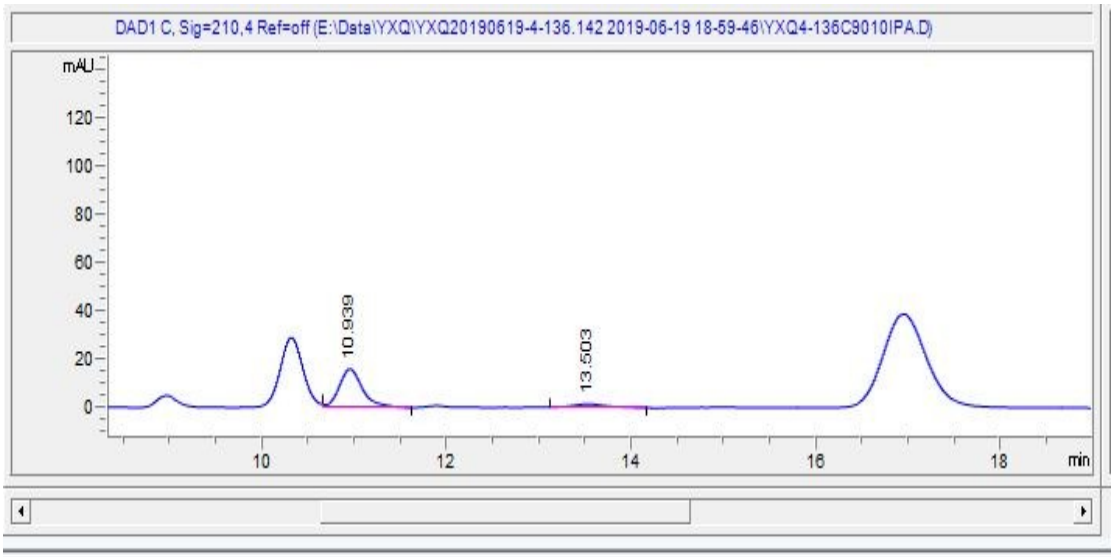


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.879	BB	2095.1	139.2	0.2341	36.708	0.846
2	10.864	MM	762.3	37.6	0.3375	13.356	0.842
3	13.448	MM	762.9	31.6	0.4023	13.367	0.865
4	16.857	BB	2087.2	65	0.4278	36.570	0.875



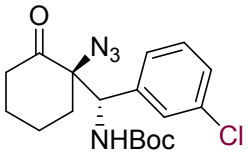
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.953	BB	28.7	1.8	0.2082	5.873	0.811
2	16.921	BB	460.2	14.1	0.3826	94.127	0.877

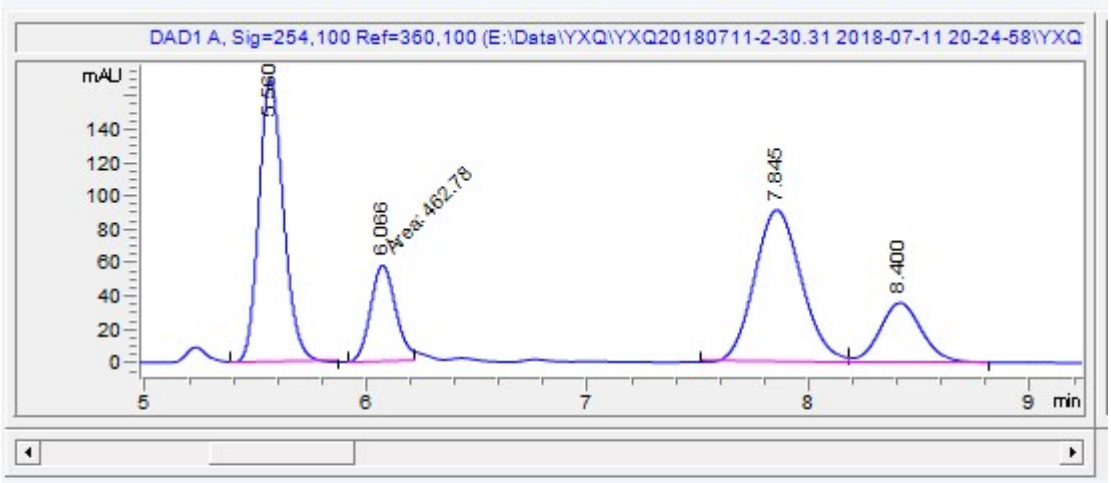
The minor diastereomer **3i'**:



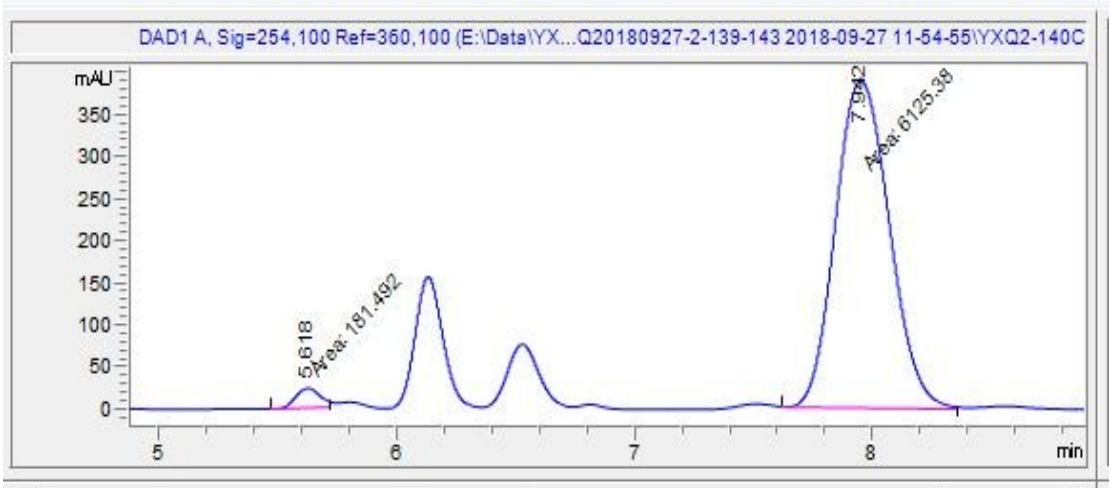
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.939	VB	279.6	16	0.2294	88.697	0.779
2	13.503	BB	35.6	1.4	0.2997	11.303	0.678

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-chlorophenyl)methyl)carbamate **(3j)**



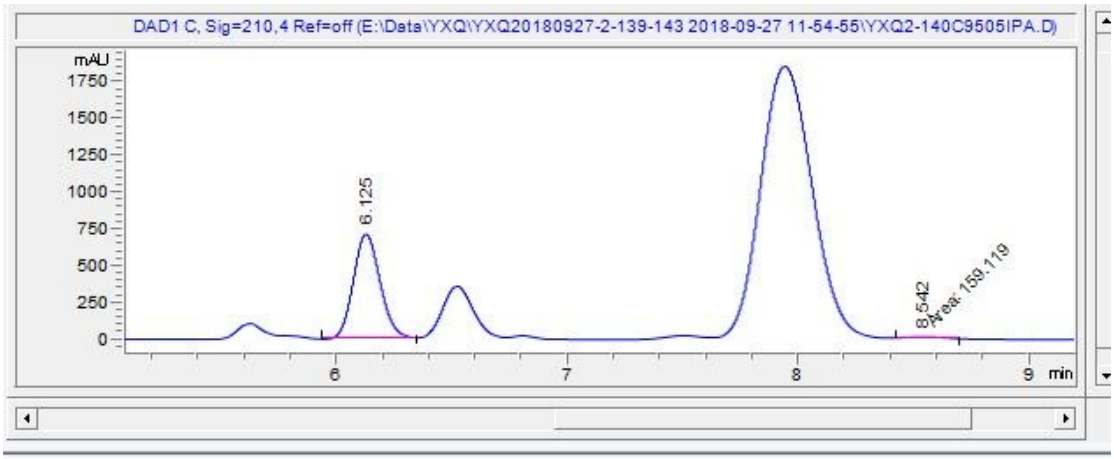


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.56	VB	1311.7	169.3	0.1204	36.557	0.801
2	6.066	MM	462.8	58	0.133	12.898	0.879
3	7.845	BV	1347.3	91.2	0.2303	37.550	0.875
4	8.4	VB	466.3	35.7	0.2015	12.996	0.893



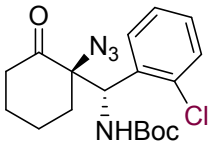
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.618	MM	181.5	24.2	0.1252	2.878	1.02
2	7.942	MM	6125.4	386.4	0.2642	97.122	0.855

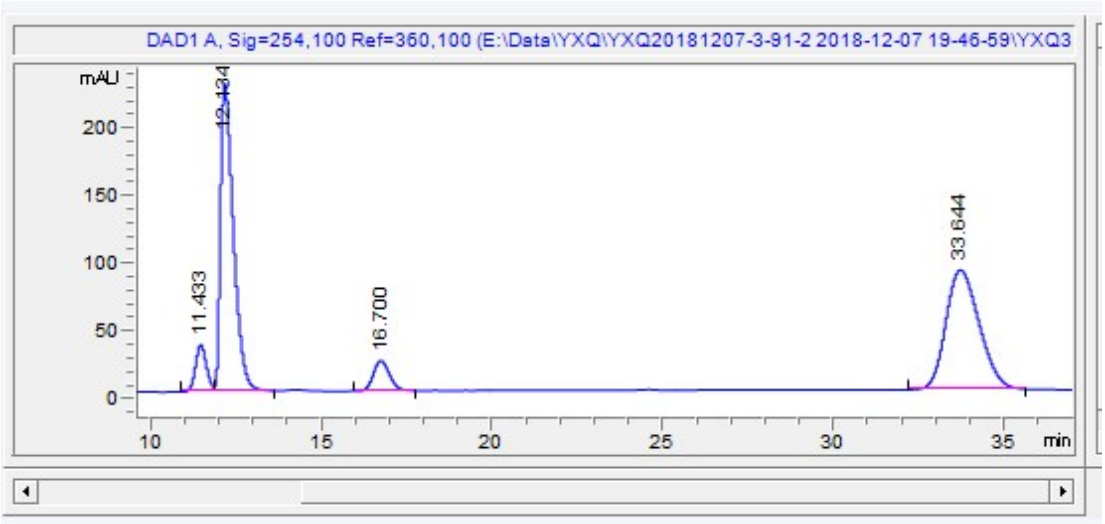
The minor diastereomer **3j'**:



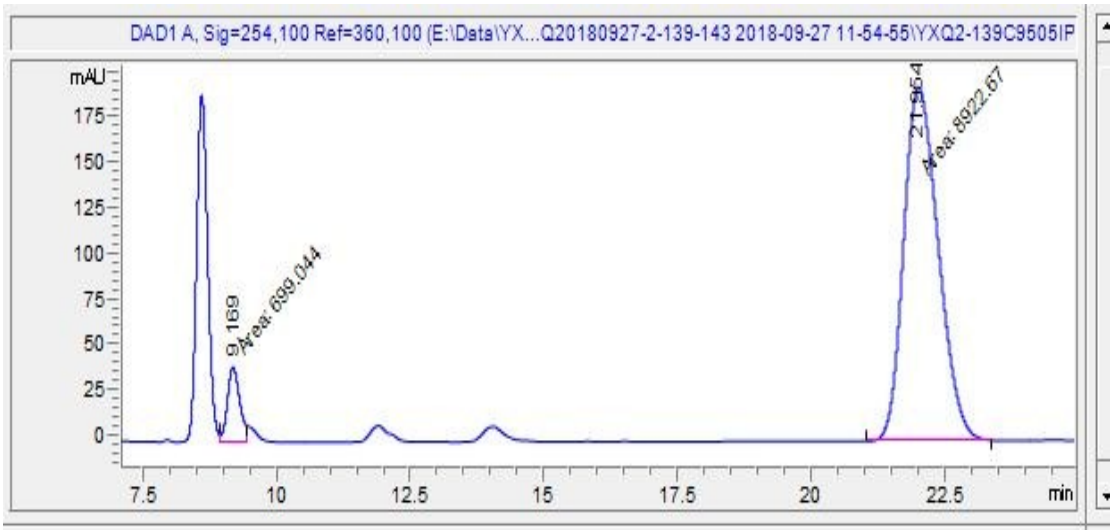
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.125	BV	5857	719	0.1265	97.355	0.85
2	8.542	MM	159.1	14.2	0.1868	2.645	0.964

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(2-chlorophenyl)methyl)carbamate **(3k)**



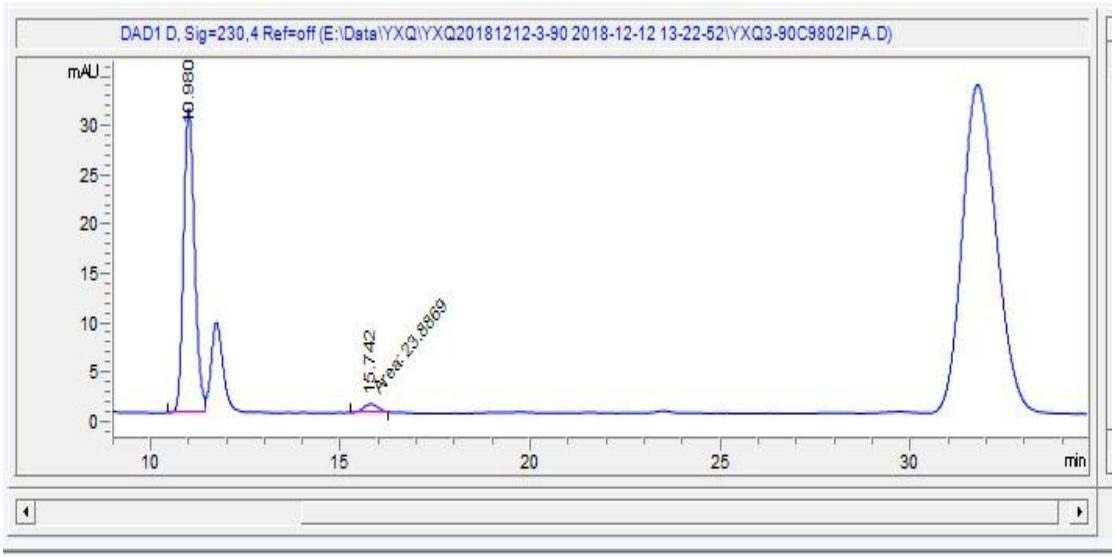


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.433	BV E	773.5	34.7	0.2869	5.721	0.853
2	12.134	VB R	6012.9	227.3	0.3666	44.472	0.862
3	16.7	BB	737	22.4	0.3948	5.451	0.85
4	33.644	BB	5997.1	88.3	0.7975	44.356	0.755



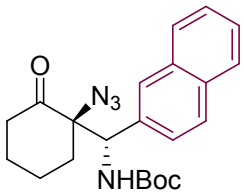
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.169	MM	699	42.5	0.2742	7.265	0.763
2	21.954	MM	8922.7	197.2	0.7543	92.735	0.724

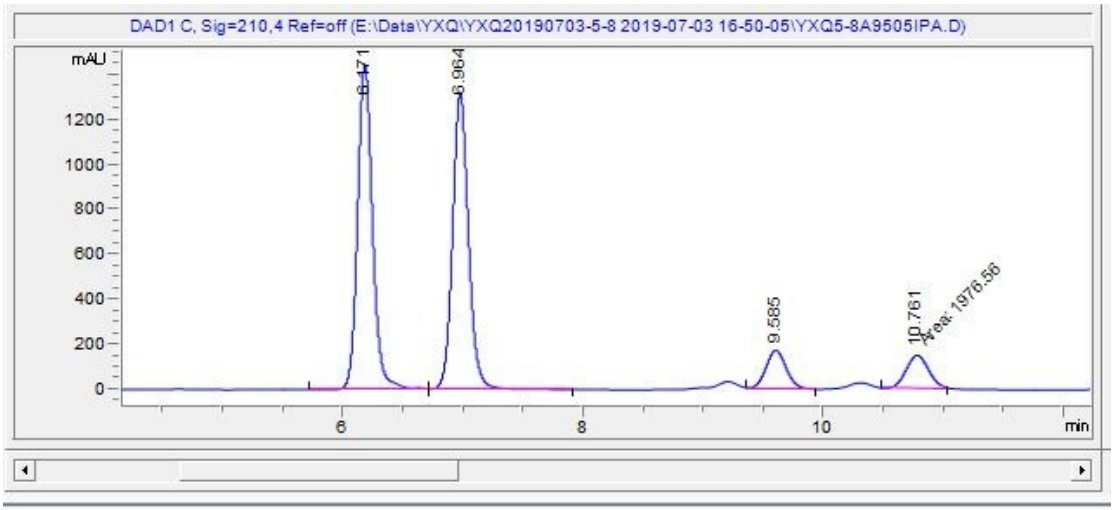
The minor diastereomer **3k'**:



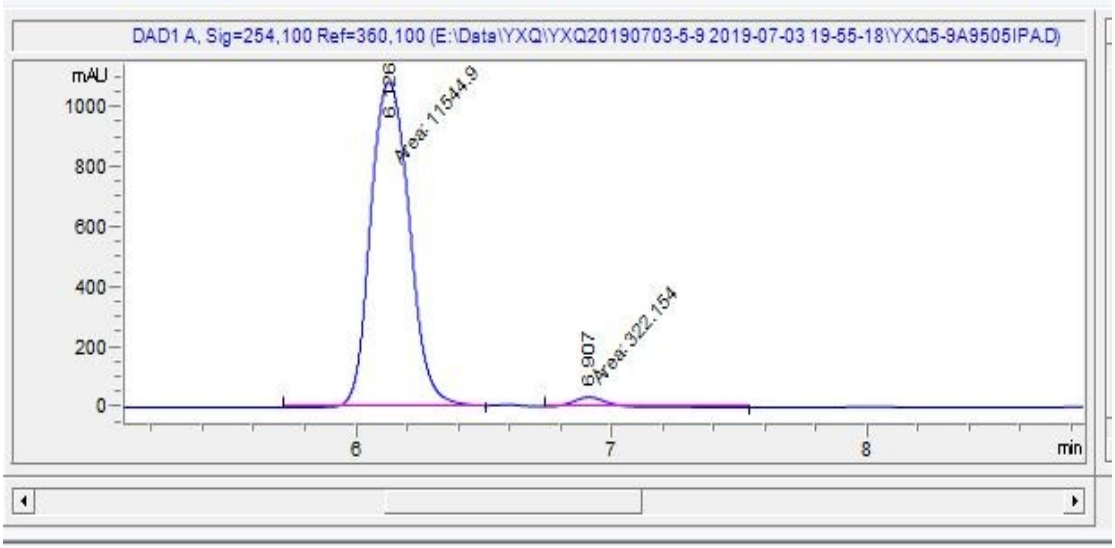
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.98	BV	619.2	30.7	0.313	96.286	0.806
2	15.742	MM	23.9	8.6E-1	0.4641	3.714	0.756

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(naphthalen-2-yl)methyl)carbamate **(3l)**



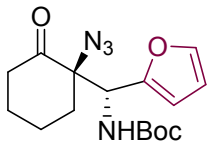


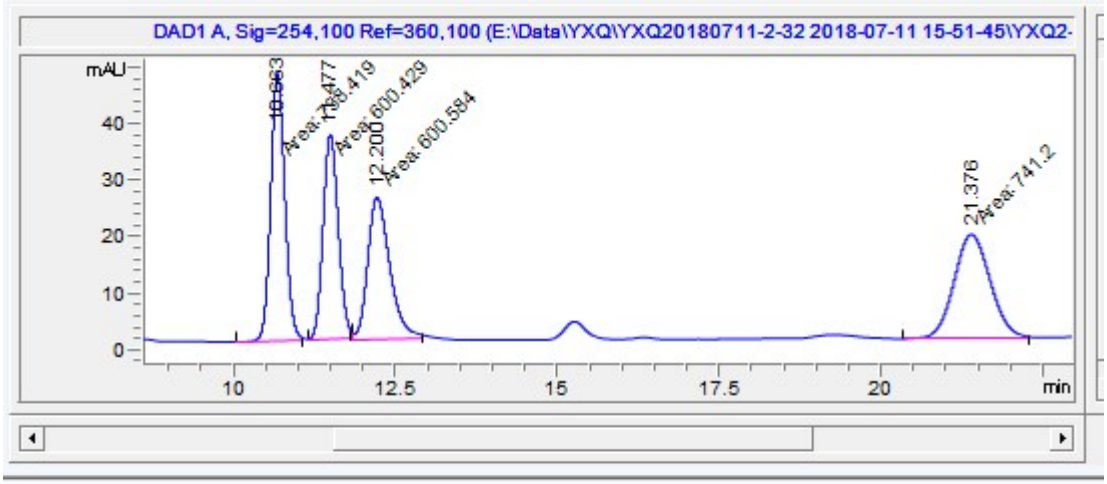
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.171	BV R	12454.6	1438.4	0.1322	43.627	0.838
2	6.964	VV R	12055.3	1316	0.1401	42.228	0.859
3	9.585	VB	2061.5	172.5	0.1845	7.221	0.925
4	10.761	MM	1976.6	148.3	0.2221	6.924	0.895



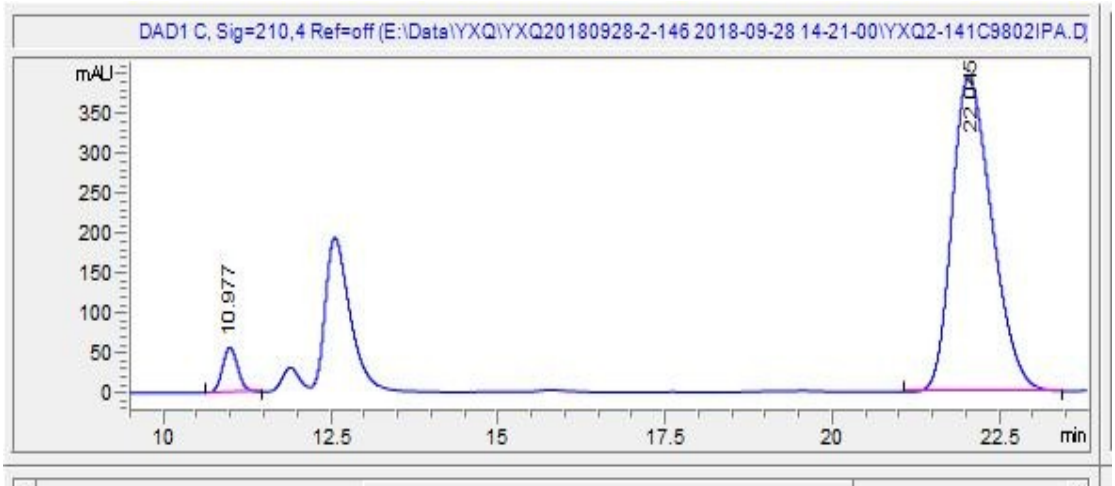
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.126	MF	11544.9	1086.8	0.1771	97.285	0.858
2	6.907	FM	322.2	33.5	0.1605	2.715	0.889

tert-butyl ((R)-((R)-1-azido-2-oxocyclohexyl)(furan-2-yl)methyl)carbamate **(3m)**



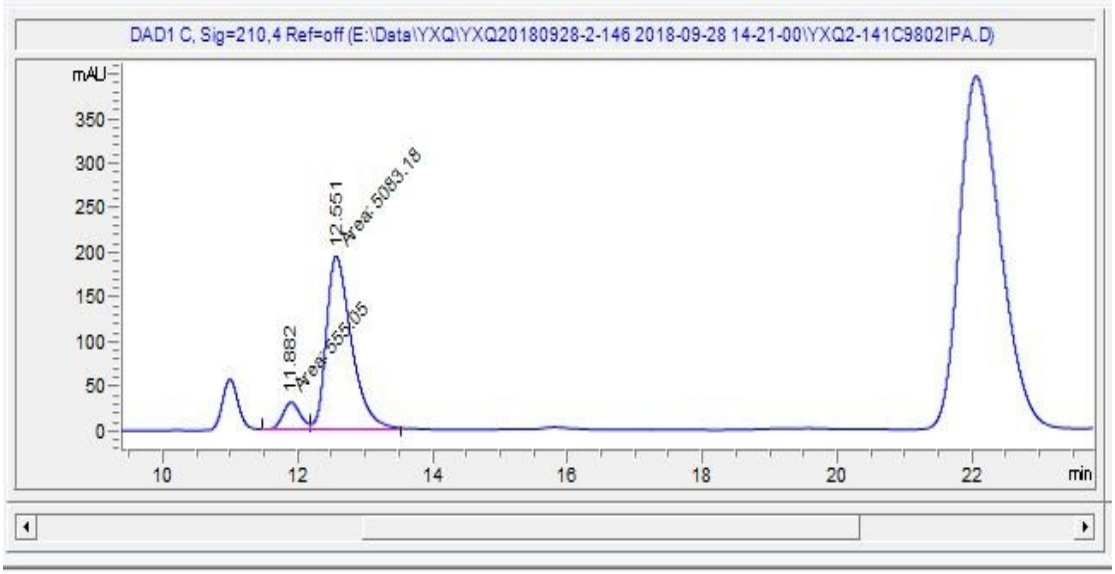


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.663	MM	738.4	47.6	0.2585	27.546	0.904
2	11.477	MM	600.4	36.5	0.2738	22.399	0.885
3	12.2	MM	600.6	25.2	0.3964	22.405	0.72
4	21.376	MM	741.2	18.6	0.6648	27.650	0.918



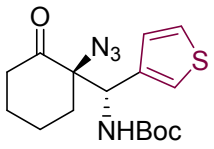
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.977	BV R	898.9	56.6	0.1933	5.179	0.878
2	22.045	BB	16457.4	393.1	0.4965	94.821	0.677

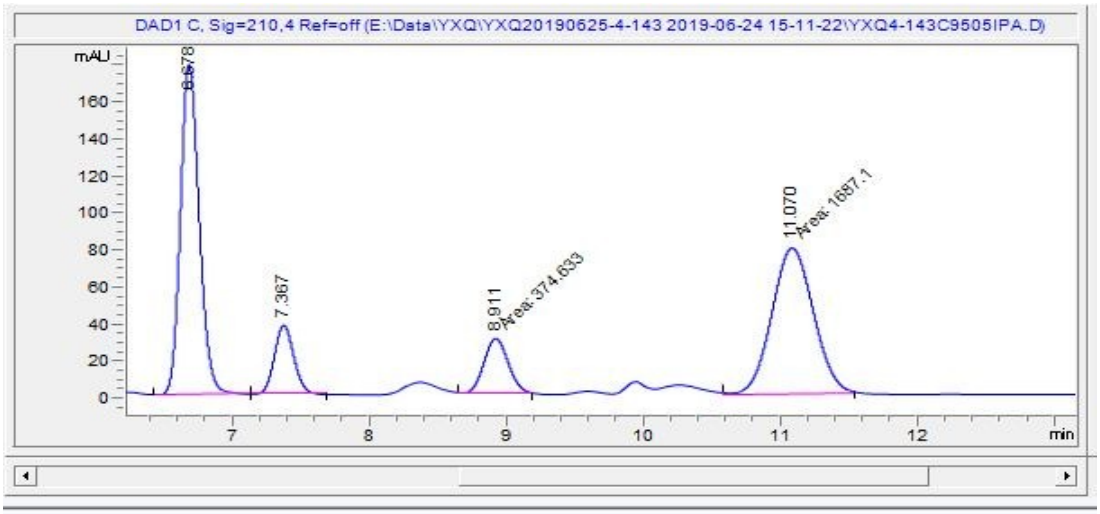
The minor diastereomer **3m'**:



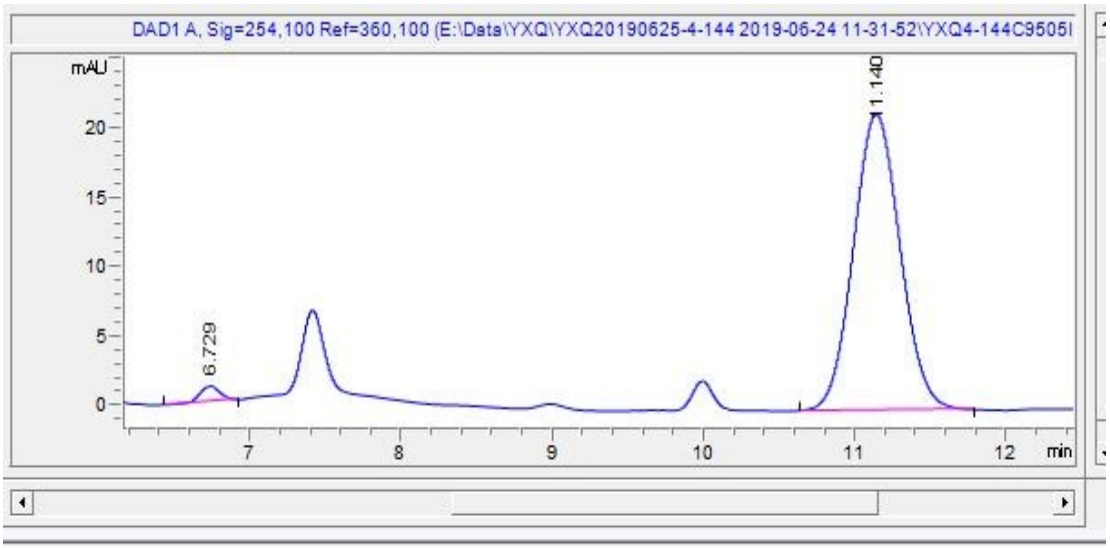
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.882	MM	555	30.4	0.3047	9.844	0.846
2	12.551	MM	5083.2	193.7	0.4374	90.156	0.585

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(thiophen-3-yl)methyl)carbamate **(3n)**





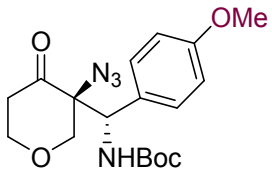
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.678	BB	1691.9	178.3	0.1462	41.030	0.811
2	7.367	BB	370	37.4	0.1534	8.972	0.872
3	8.911	MM	374.6	30	0.2081	9.085	0.915
4	11.07	MM	1687.1	79.3	0.3547	40.913	0.932

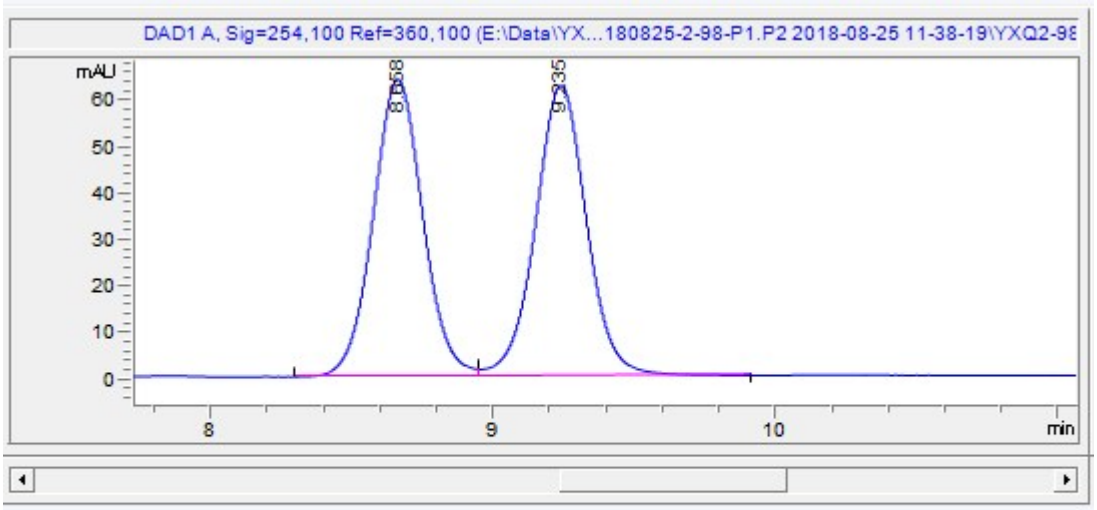


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.729	BB	10.2	1.1	0.1086	2.175	0.97
2	11.14	BB	459.2	21.4	0.2859	97.825	0.944

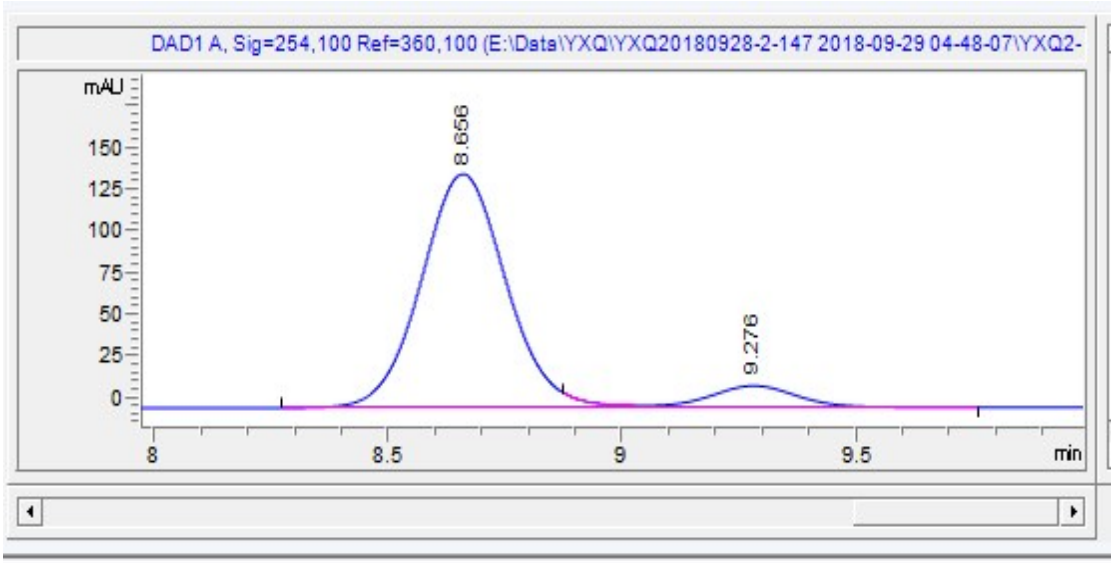
tert-butyl ((S)-((S)-3-azido-4-oxotetrahydro-2H-pyran-3-yl)(4-methoxyphenyl)methyl)carbamate

(3o)



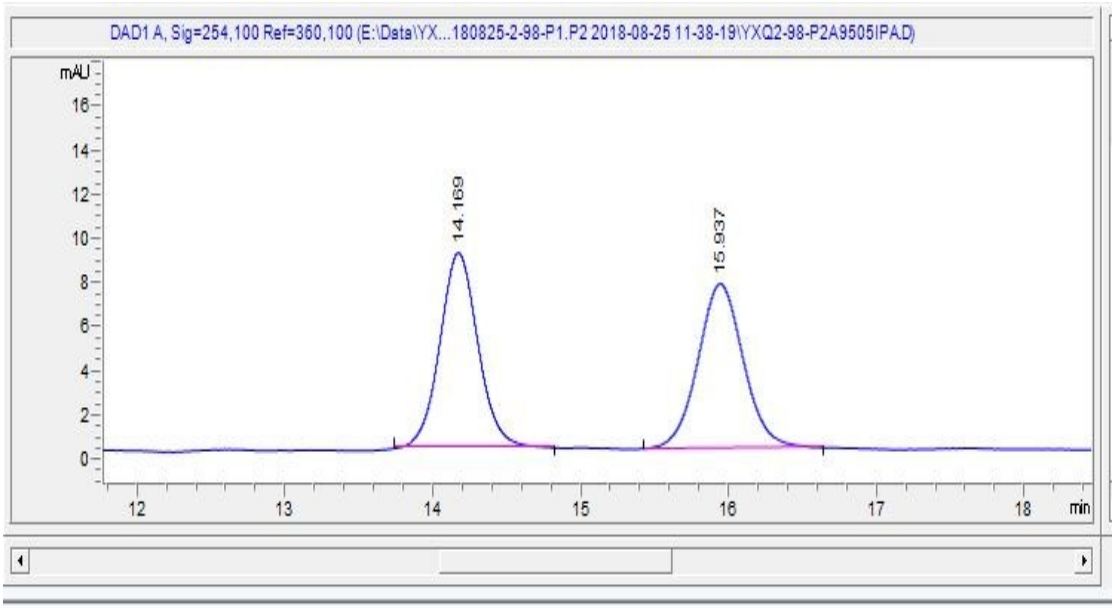


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.658	BV	788.7	64.4	0.1894	49.804	0.951
2	9.235	VB	794.9	63	0.1922	50.196	0.966

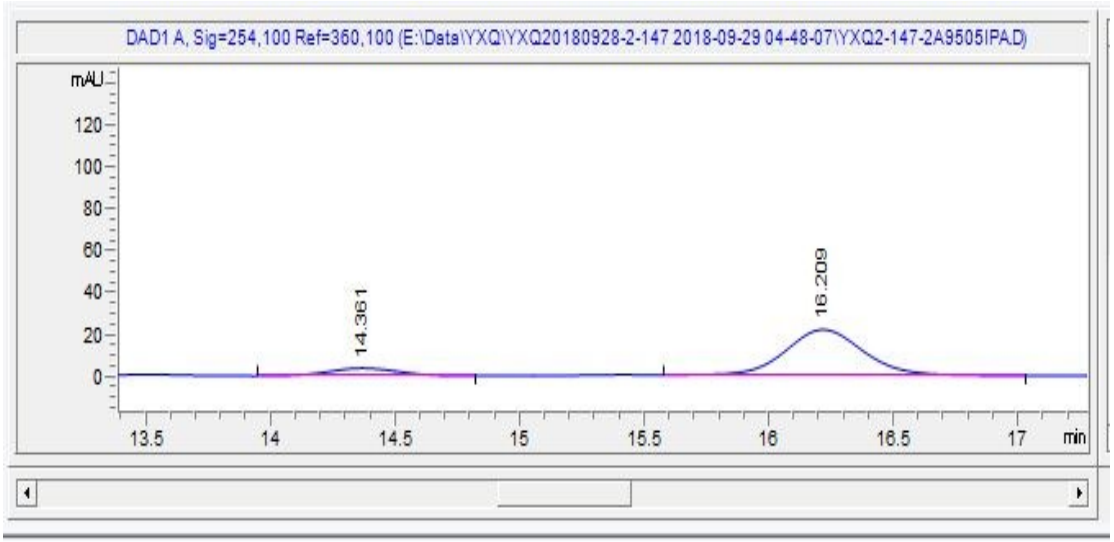


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.656	BV R	1768.5	139.7	0.1952	90.867	0.933
2	9.276	VB E	177.7	13.1	0.1976	9.133	1.014

The minor diastereomer **3o'**:

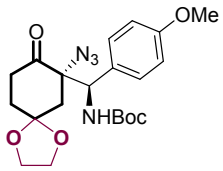


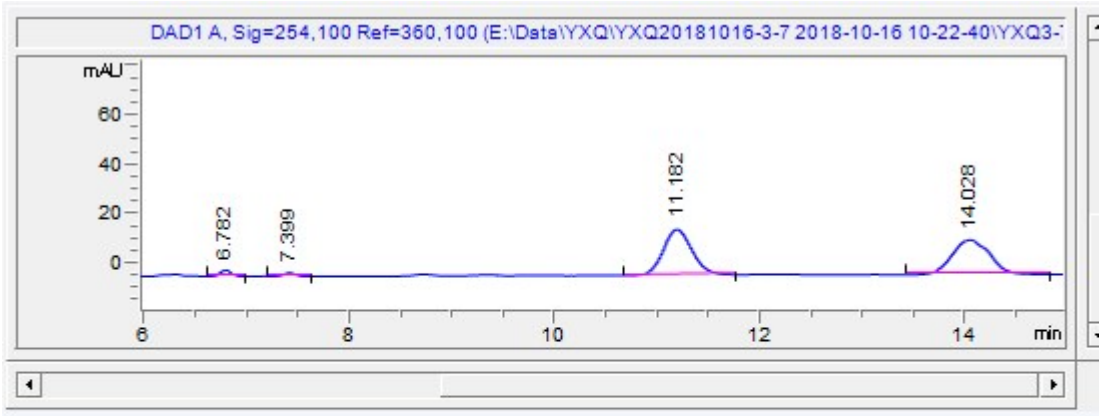
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.169	BB	160.3	8.8	0.235	50.137	0.948
2	15.937	BB	159.4	7.4	0.2535	49.863	0.918



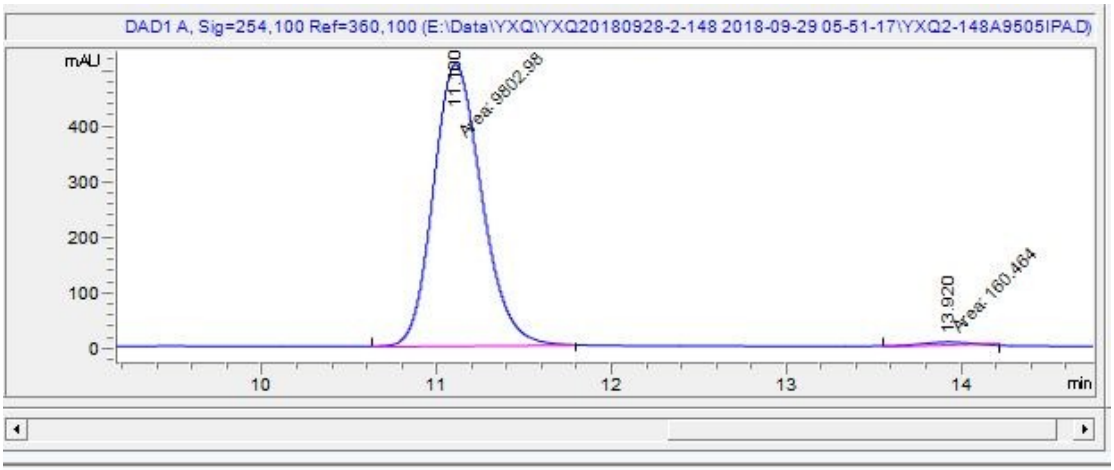
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.361	BB	71.7	3.7	0.2304	13.161	0.928
2	16.209	BB	472.8	21.7	0.3044	86.839	0.914

tert-butyl-((R)-((S)-7-azido-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)(4-methoxyphenyl)methyl)carbamate**(3p)**



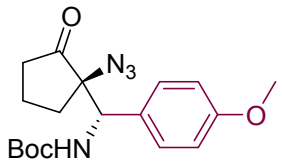


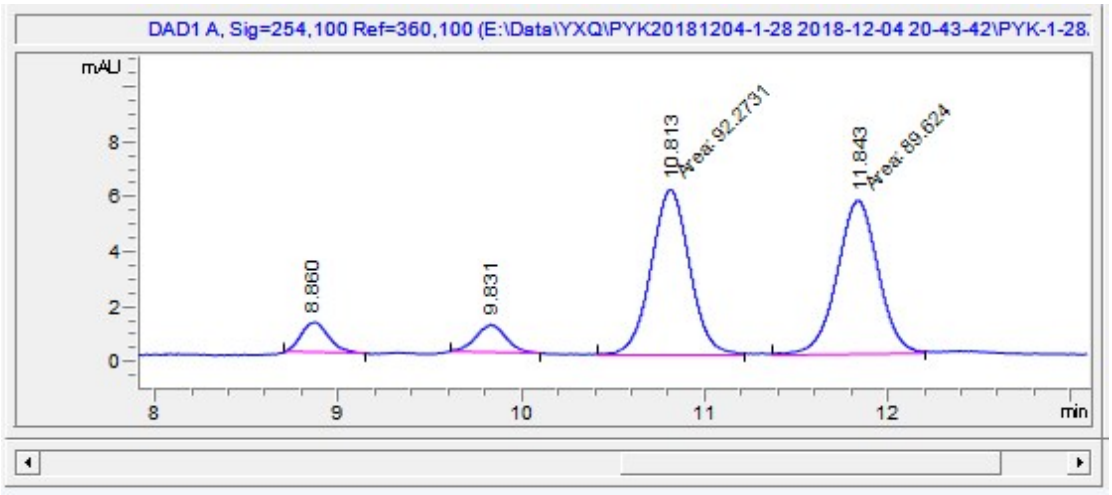
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.782	BB	19.4	2.6	0.1064	2.540	0.928
2	7.399	BB	11.6	1.5	0.096	1.525	0.983
3	11.182	BB	365.6	18.7	0.2589	47.927	0.855
4	14.028	BB	366.2	14.3	0.3128	48.009	0.823



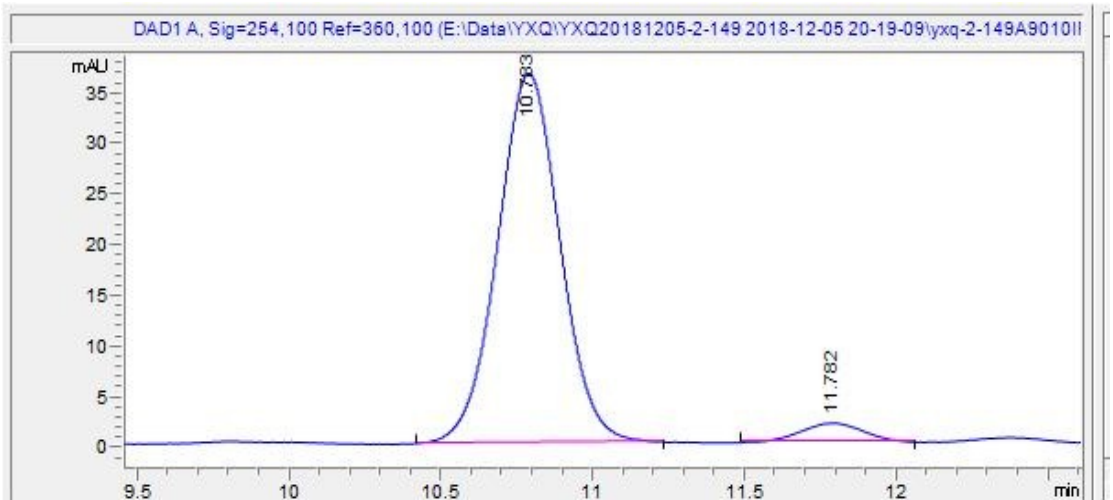
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.1	MM	9803	505.6	0.3231	98.389	0.818
2	13.92	MM	160.5	7.1	0.268	1.611	1.602

tert-butyl ((S)-((R)-1-azido-2-oxocyclopentyl)(4-methoxyphenyl)methyl)carbamate **(3q)**



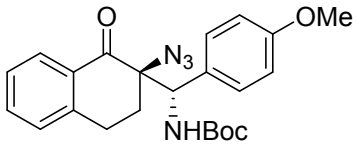


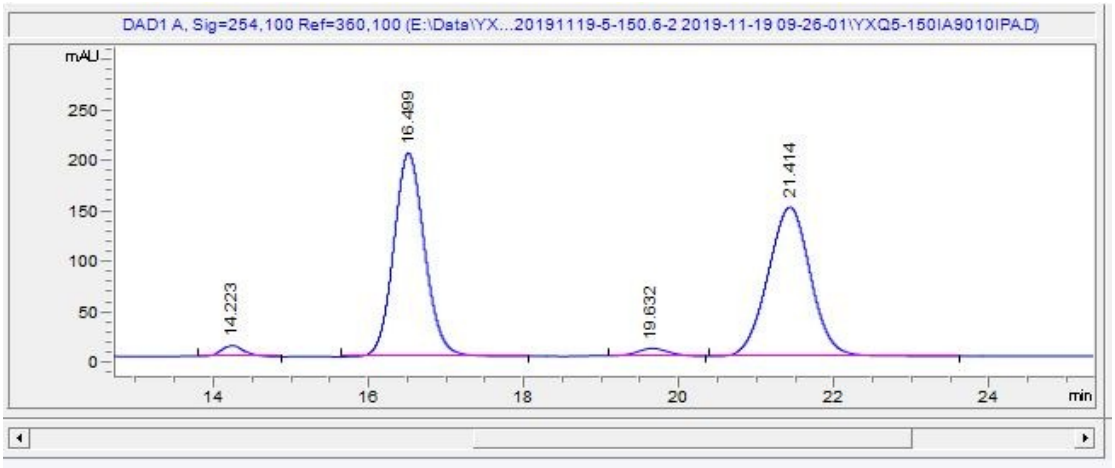
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.86	BB	11.9	1.1	0.1254	5.771	0.784
2	9.831	BB	11.8	1	0.137	5.729	0.969
3	10.813	MM	92.3	6.1	0.2525	44.894	0.962
4	11.843	MM	89.6	5.6	0.2655	43.605	1.08



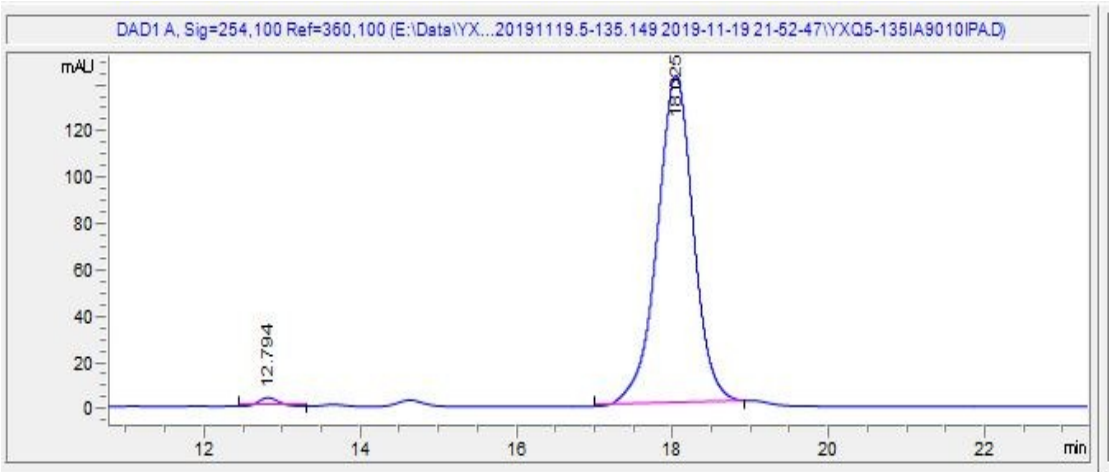
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.783	BB	520.5	36.3	0.2006	94.966	0.956
2	11.782	BB	27.6	1.9	0.1739	5.034	1.008

tert-butyl-((S)-((R)-2-azido-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)(4-methoxyphenyl)methyl)carbamate **(3r)**



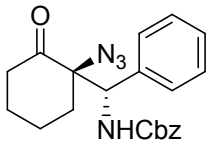


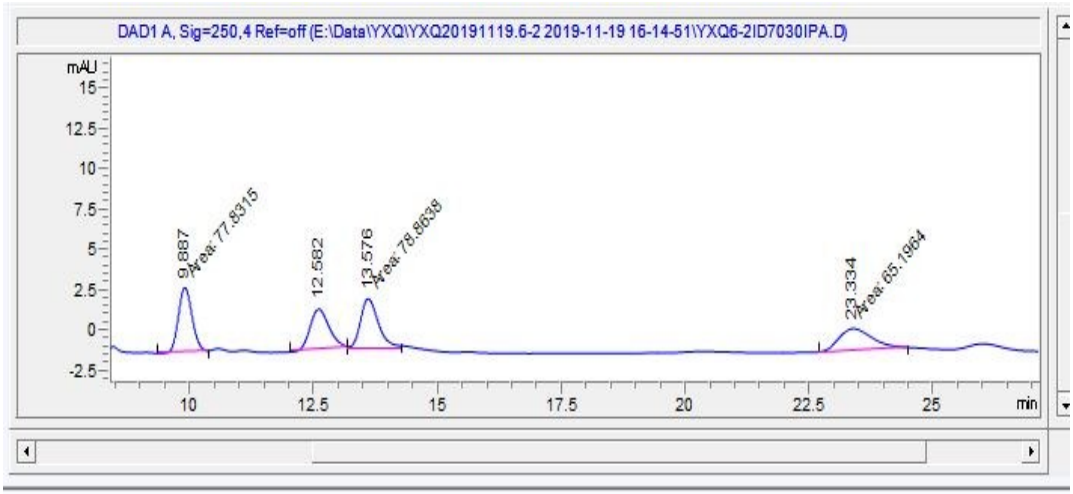
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.223	BB	220.6	10.7	0.3134	1.888	0.823
2	16.499	BB	5608.9	202.4	0.4263	48.004	0.872
3	19.632	BB	205.1	7.4	0.4151	1.755	0.861
4	21.414	BB	5649.6	148.2	0.5897	48.352	1.025



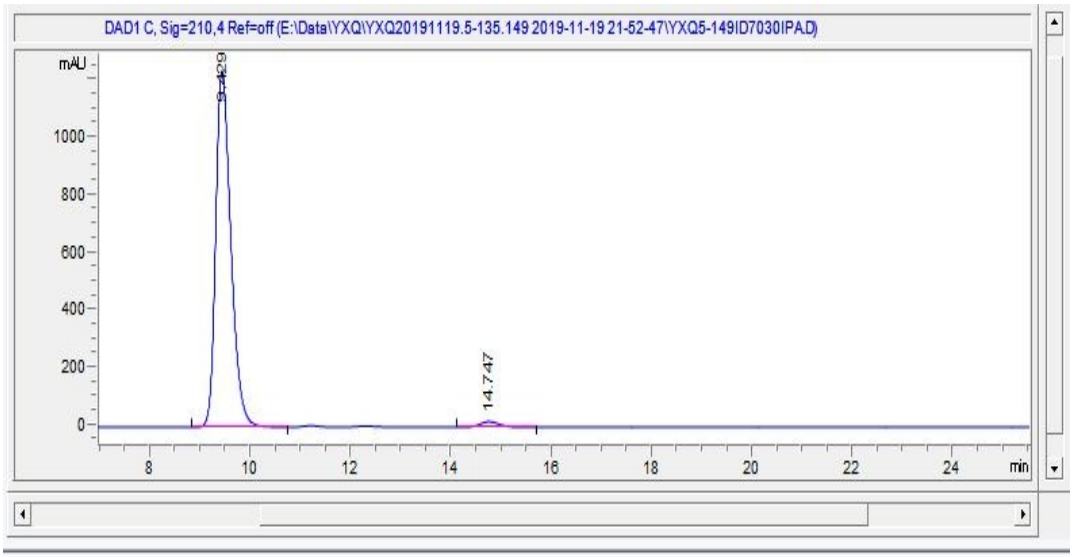
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.794	BB	65.9	3.7	0.2111	1.418	0.851
2	18.025	BB	4579.9	142.5	0.48	98.582	1.062

benzyl ((S)-((R)-1-azido-2-oxocyclohexyl)(phenyl)methyl)carbamate **(3s)**



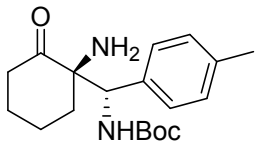


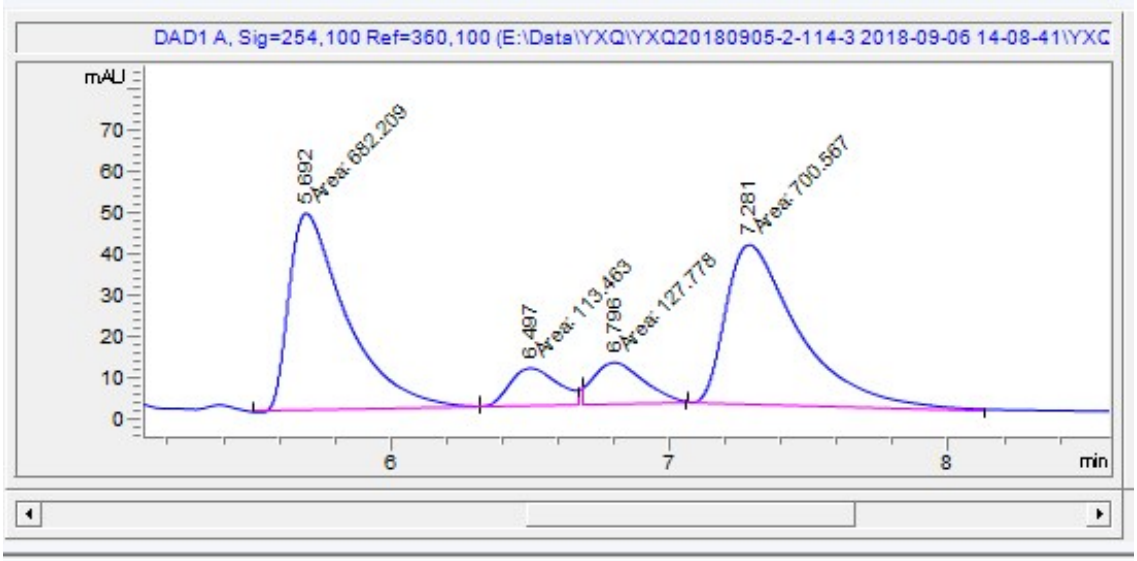
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.887	MM	77.8	4	0.3217	27.010	0.853
2	12.582	BB	66.3	2.5	0.3902	22.997	0.821
3	13.576	MM	78.9	3.1	0.4234	27.368	0.708
4	23.334	MM	65.2	1.4	0.7852	22.625	0.737



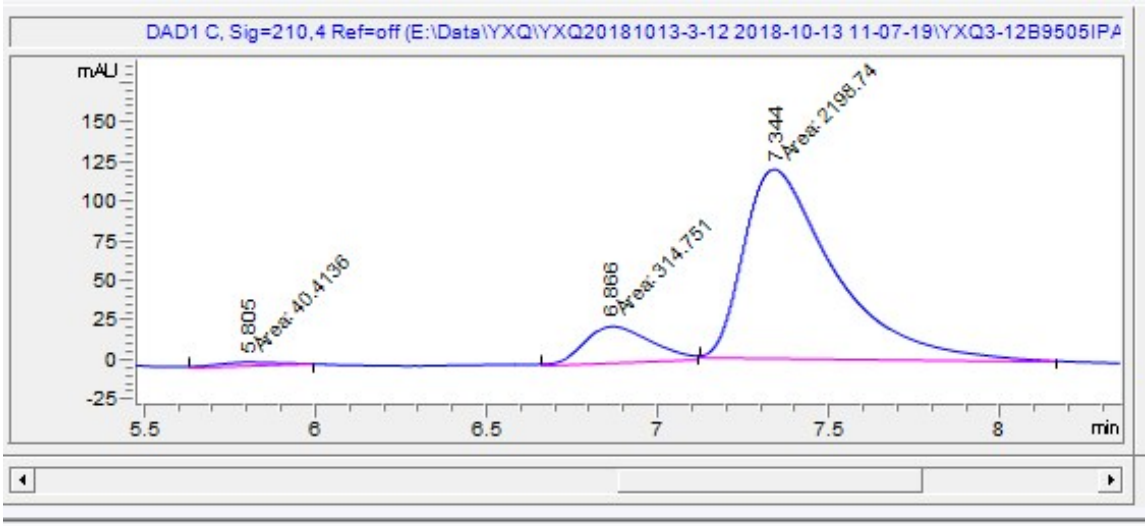
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.429	BB	25874.1	1235.5	0.3203	97.988	0.661
2	14.747	BB	531.4	19.7	0.4152	2.012	0.86

tert-butyl ((S)-((R)-1-amino-2-oxocyclohexyl)(p-tolyl)methyl)carbamate **(4c)**



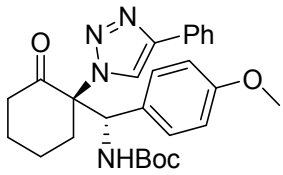


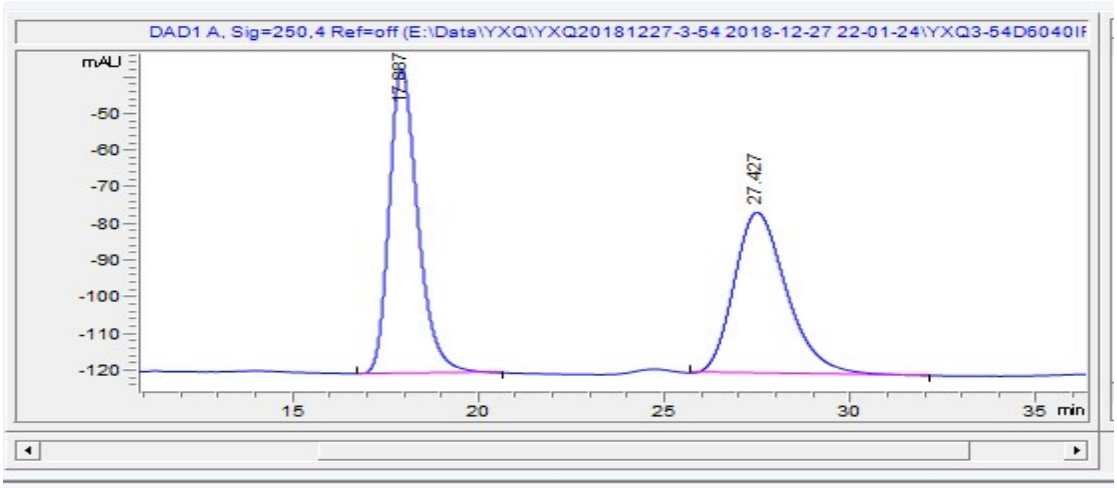
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.692	MM	682.2	47.6	0.239	42.008	0.417
2	6.497	MM	113.5	9.2	0.206	6.987	0.715
3	6.796	MM	127.8	10.2	0.2082	7.868	0.684
4	7.281	MM	700.6	38.4	0.3045	43.138	0.455



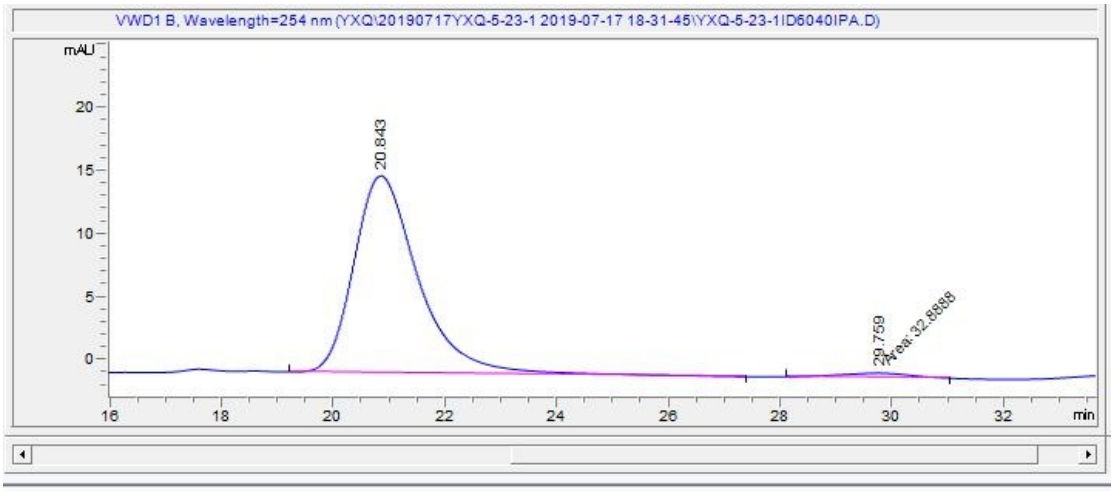
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.805	MM	40.4	2.8	0.2392	1.582	1.604
2	6.866	MM	314.8	23.2	0.2262	12.324	0.735
3	7.344	MM	2198.7	118.8	0.3085	86.093	0.5

tert-butyl-((S)-(4-methoxyphenyl)((R)-2-oxo-1-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclohexyl)methyl)carbamate **(5a)**



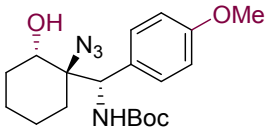


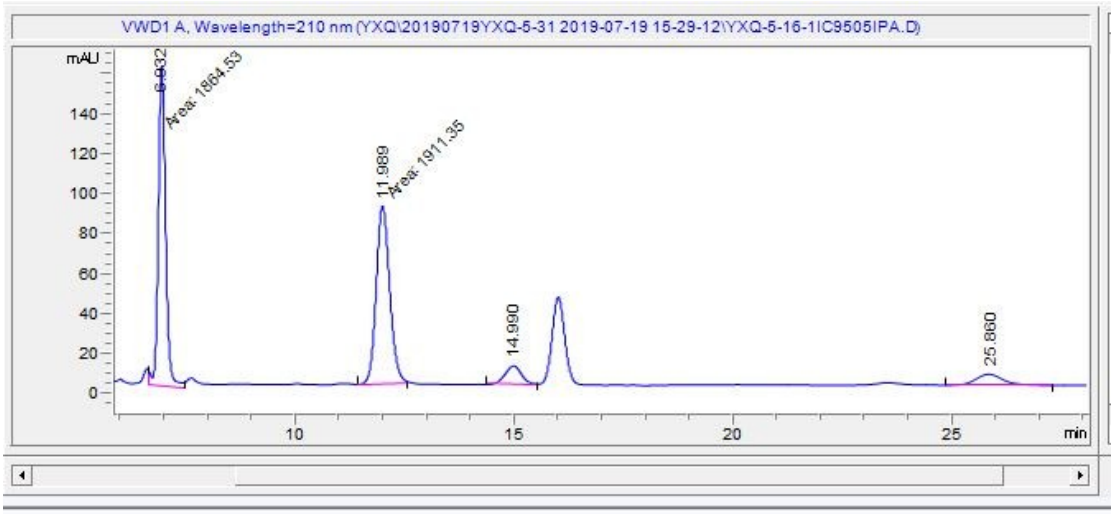
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.887	BB	4443.1	82.9	0.8229	50.740	0.715
2	27.427	BB	4313.5	43.9	1.3532	49.260	0.733



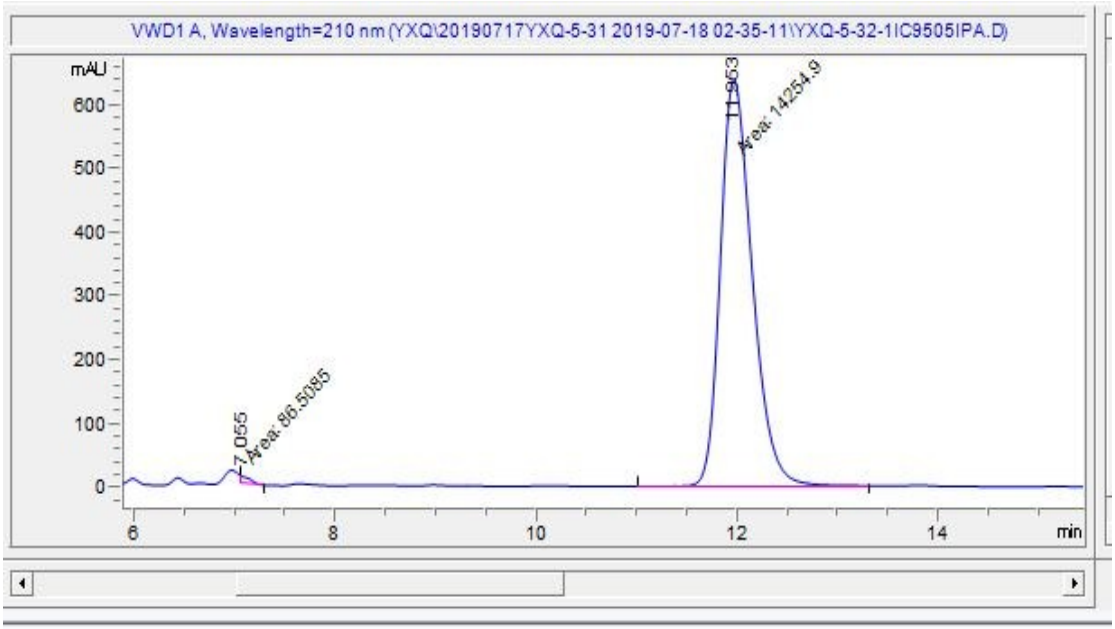
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.843	BB	1253.2	15.6	1.2197	97.443	0.665
2	29.759	MM	32.9	3.7E-1	1.4854	2.557	1.242

tert-butyl ((1S)-((1R)-1-azido-2-hydroxycyclohexyl)(4-methoxyphenyl)methyl)carbamate **(6a1)**



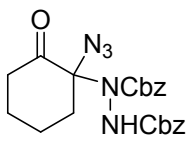


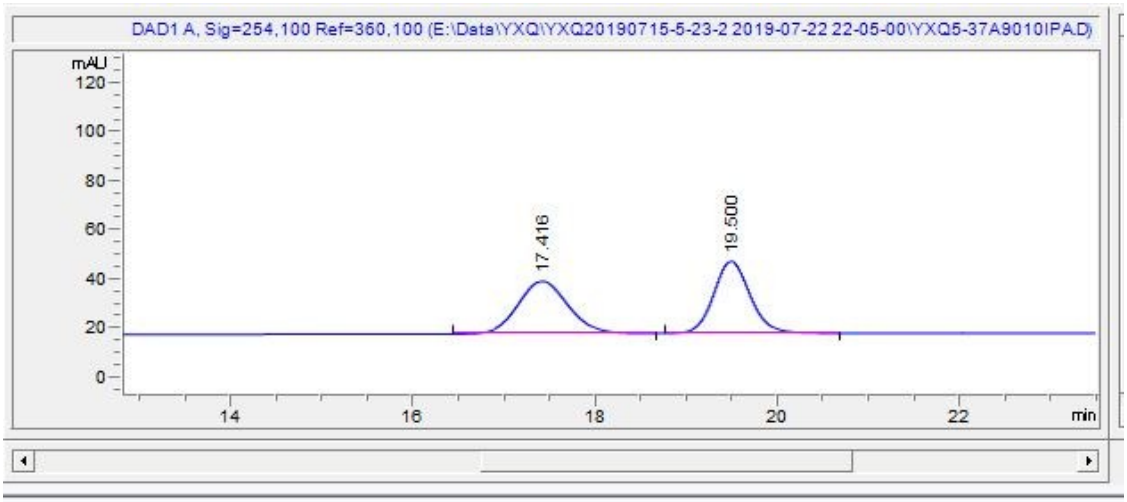
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.932	MM	1864.5	160.2	0.194	43.669	0.83
2	11.989	MM	1911.4	88.7	0.359	44.765	0.848
3	14.99	BV	251.9	9.4	0.4061	5.900	1.027
4	25.86	BB	241.9	5.5	0.6771	5.666	0.844



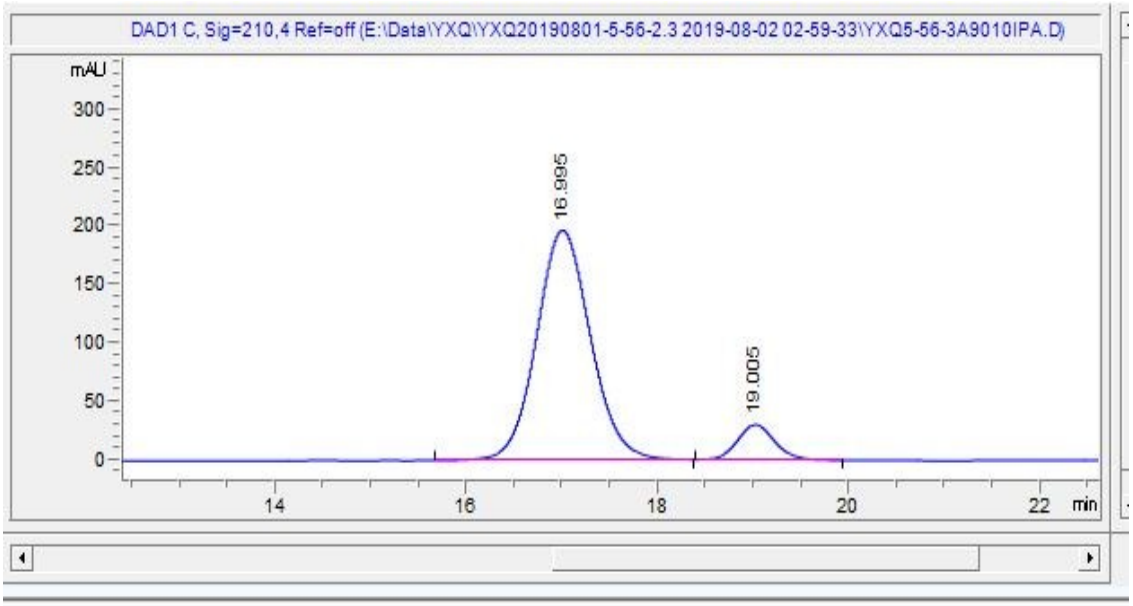
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.055	MM	86.5	13.3	0.083	0.603	0
2	11.953	MM	14254.9	639.9	0.3713	99.397	0.699

dibenzyl 1-(1-azido-2-oxocyclohexyl)hydrazine-1,2-dicarboxylate **(9a)**



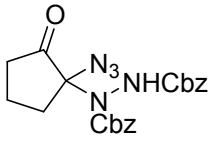


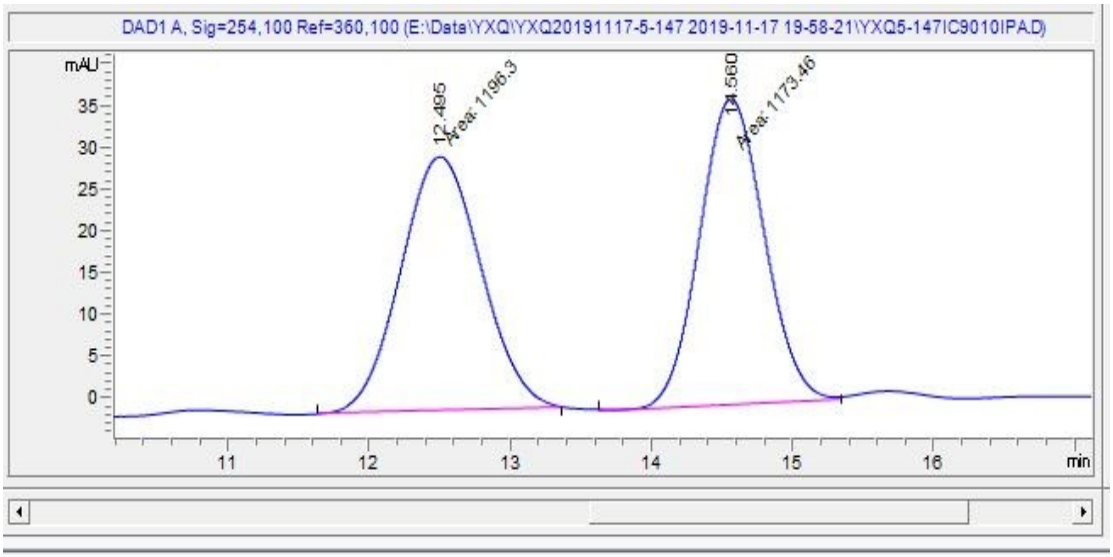
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.416	BB	819.1	21.4	0.5148	50.120	0.898
2	19.5	BB	815.2	29.3	0.4165	49.880	0.883



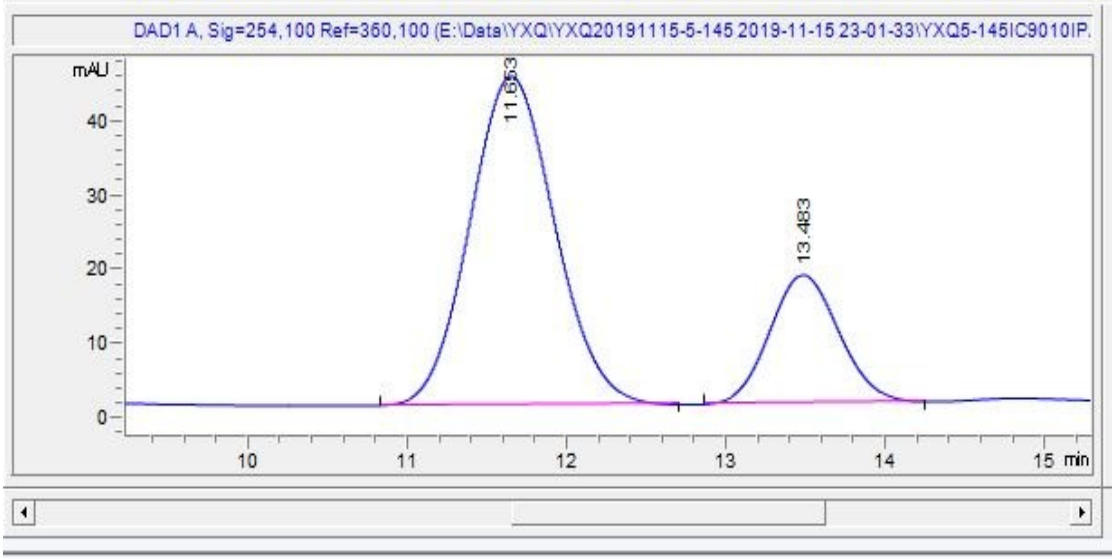
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.995	BB	7657.4	195.6	0.5748	90.468	0.914
2	19.005	BB	806.8	29.9	0.3299	9.532	0.893

dibenzyl 1-(1-azido-2-oxocyclopentyl)hydrazine-1,2-dicarboxylate (**9b**)



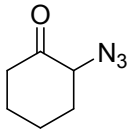


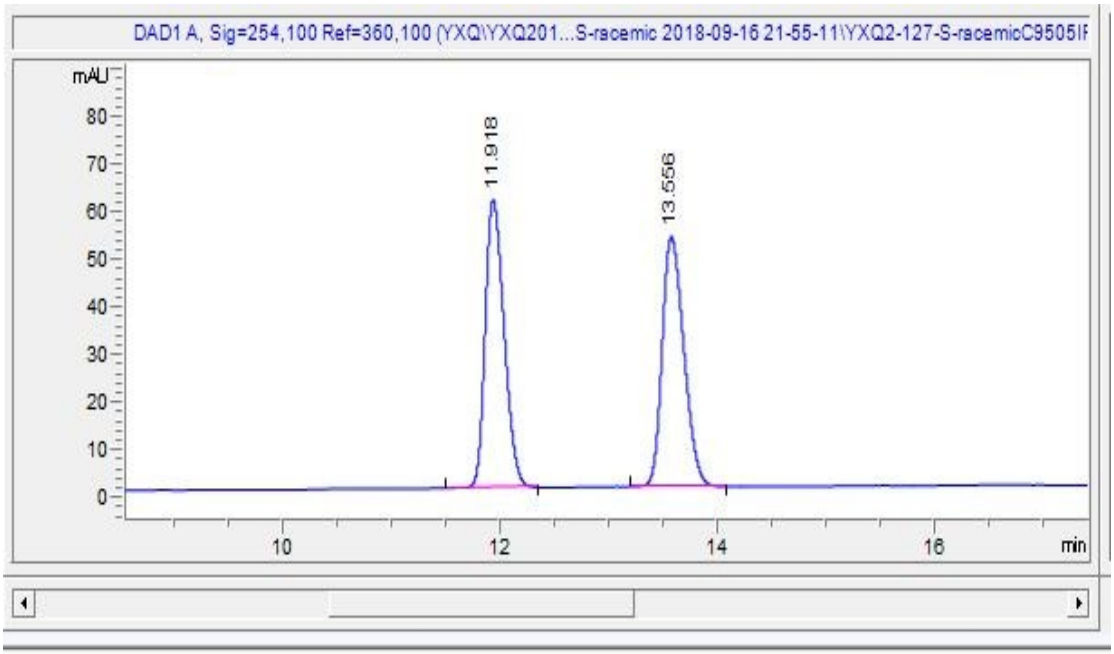
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.495	MM	1196.3	30.3	0.6577	50.482	0.921
2	14.56	MM	1173.5	36.6	0.5339	49.518	0.931



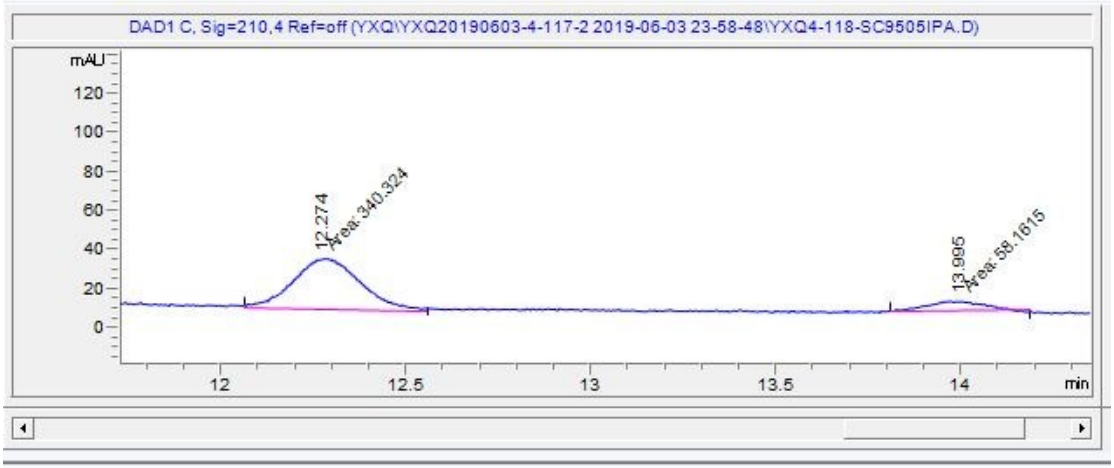
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.653	BB	1646.1	44.3	0.4364	75.826	0.934
2	13.483	BB	524.8	17.3	0.3559	24.174	0.892

2-azidocyclohexan-1-one **(1a)**





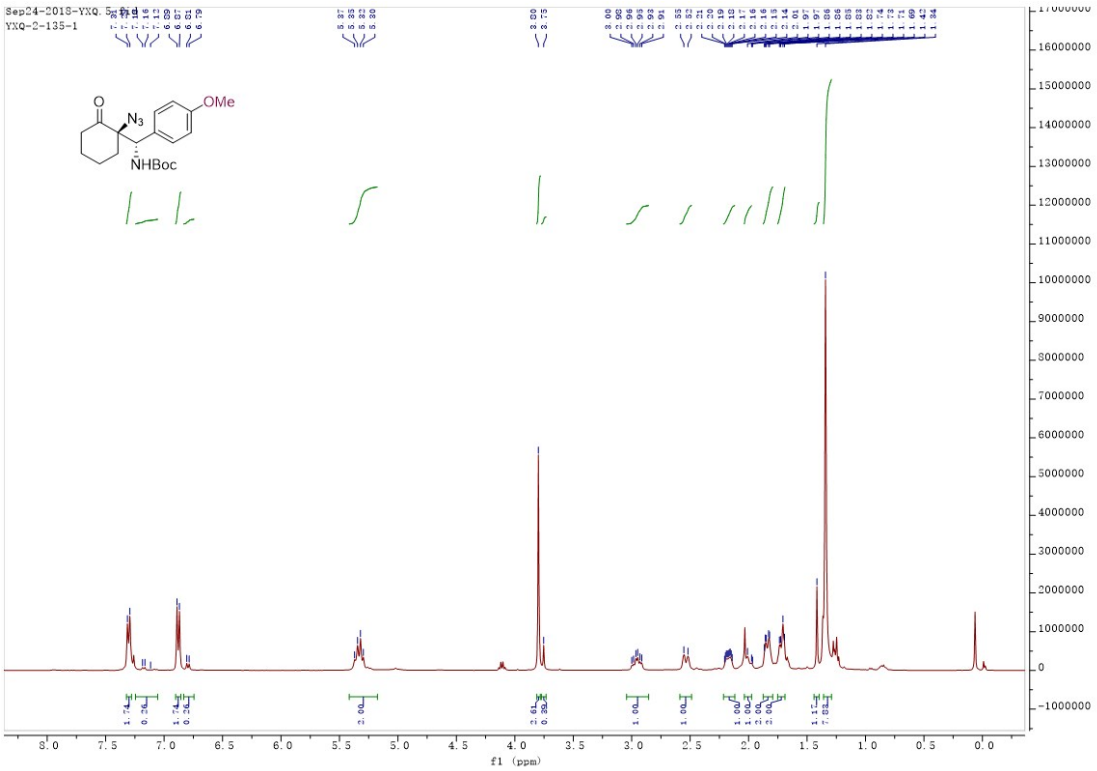
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.918	BB	728.2	60.2	0.1866	50.116	0.691
2	13.556	BB	724.8	52.2	0.2104	49.884	0.699

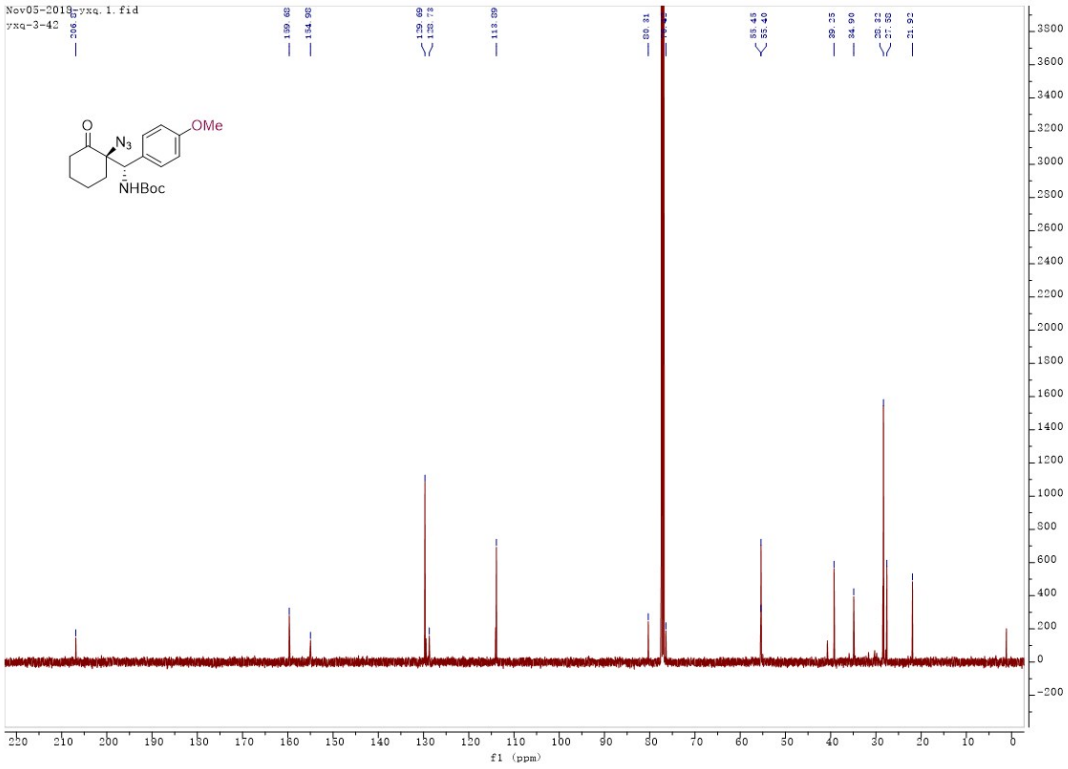


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.274	MM	340.3	26.2	0.2167	85.404	0.805
2	13.995	MM	58.2	5.1	0.1885	14.596	1.297

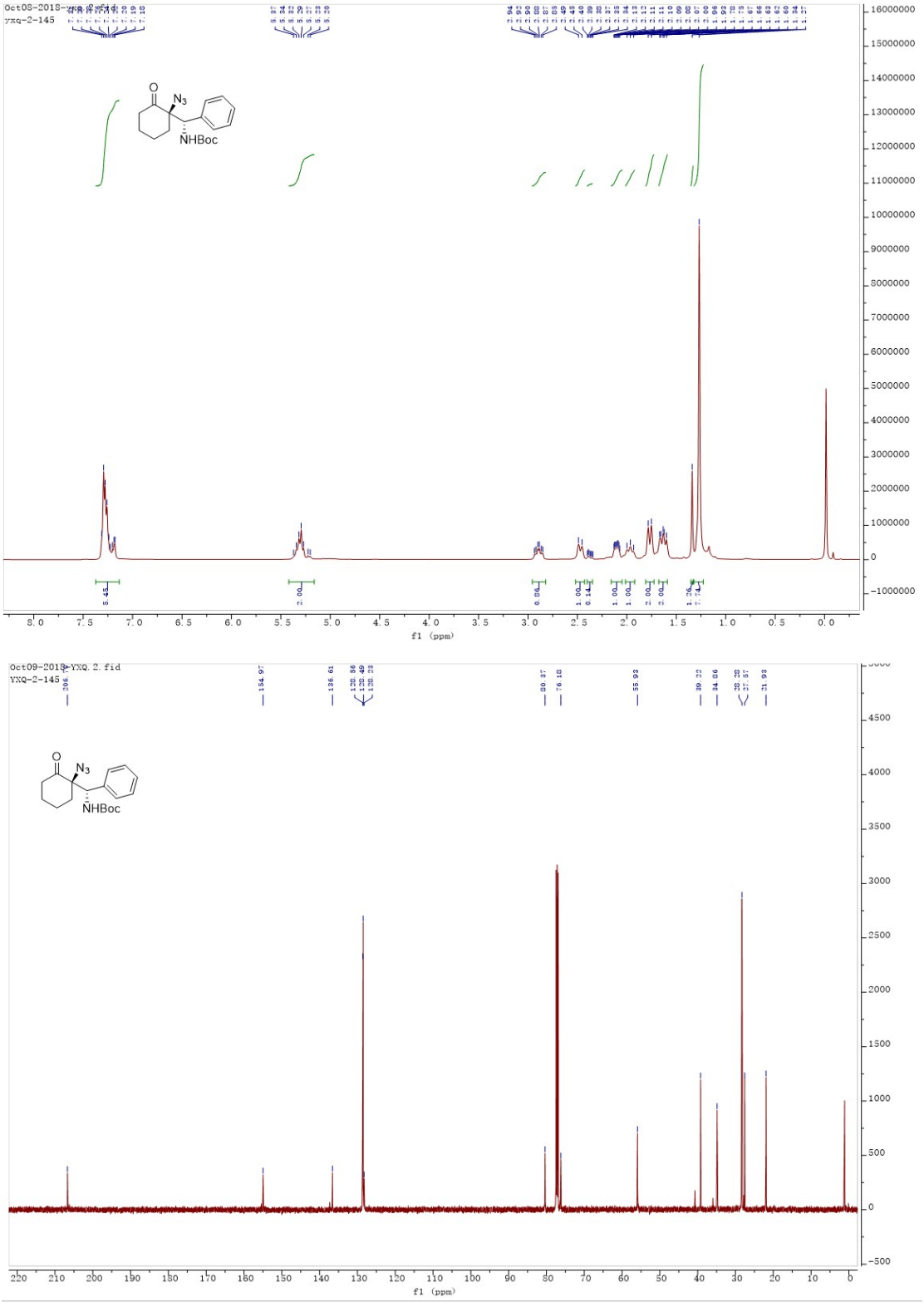
NMR spectrums:

tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-methoxyphenyl)methyl)carbamate **(3a)**

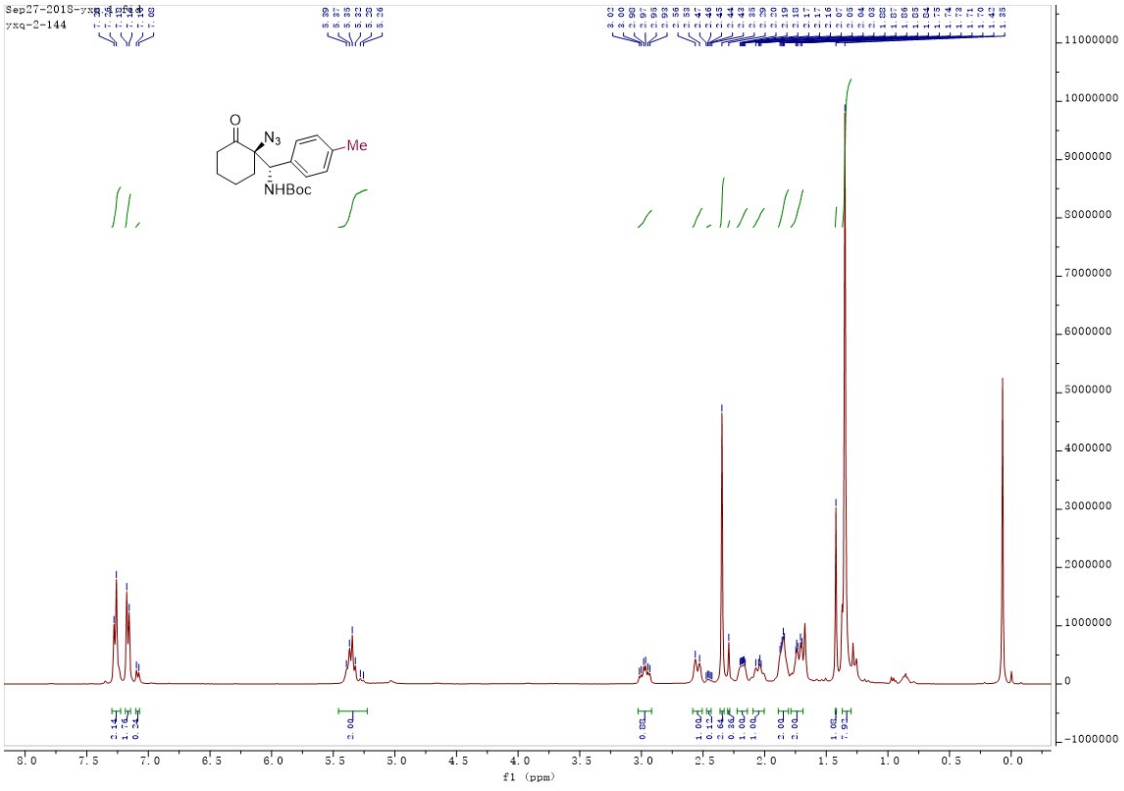


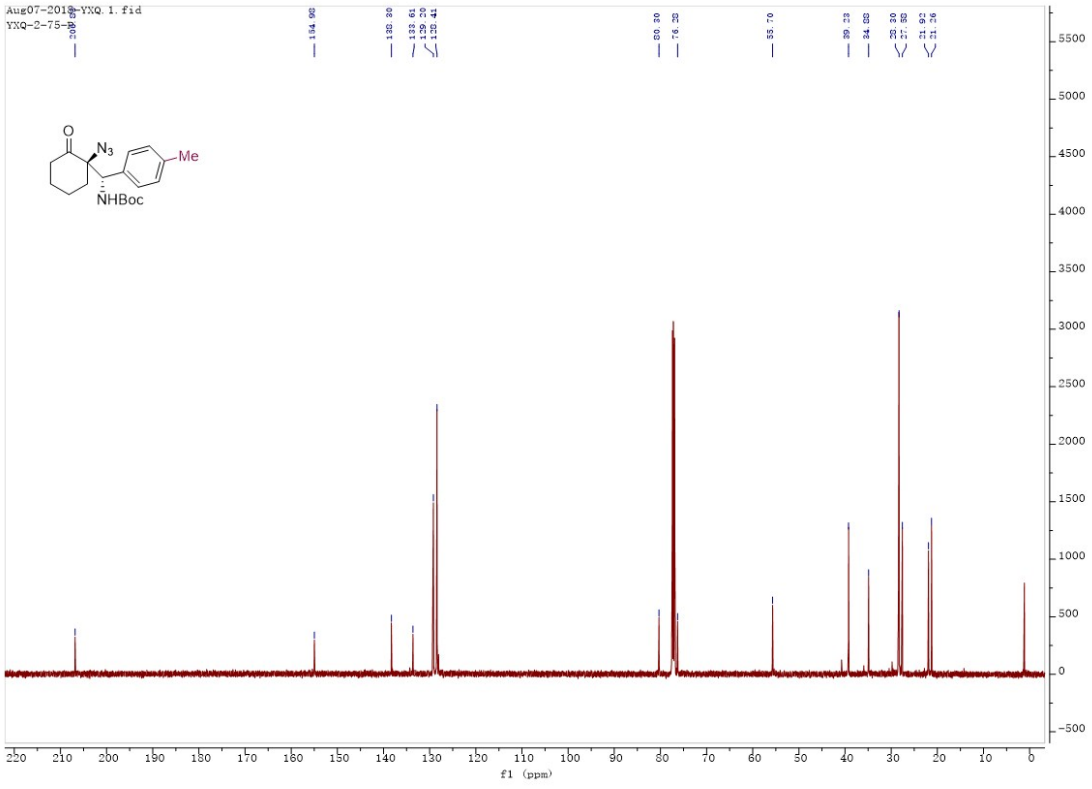


tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(phenyl)methyl)carbamate **(3b)**

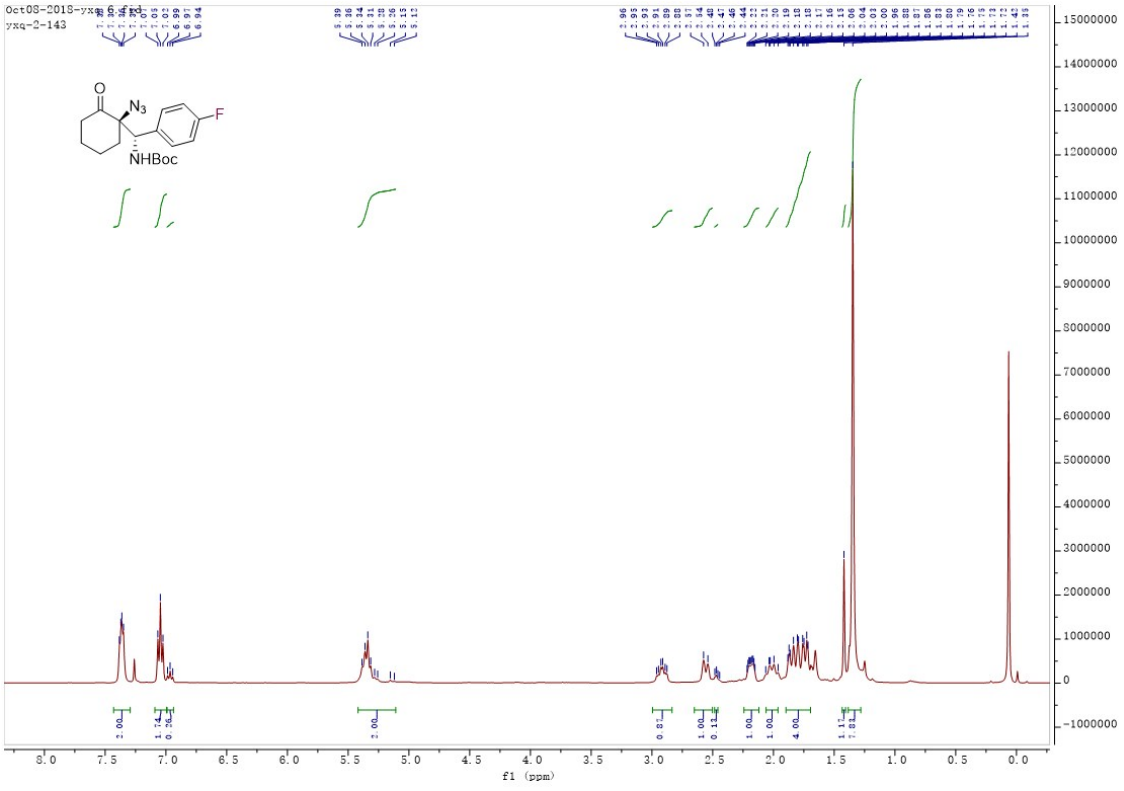


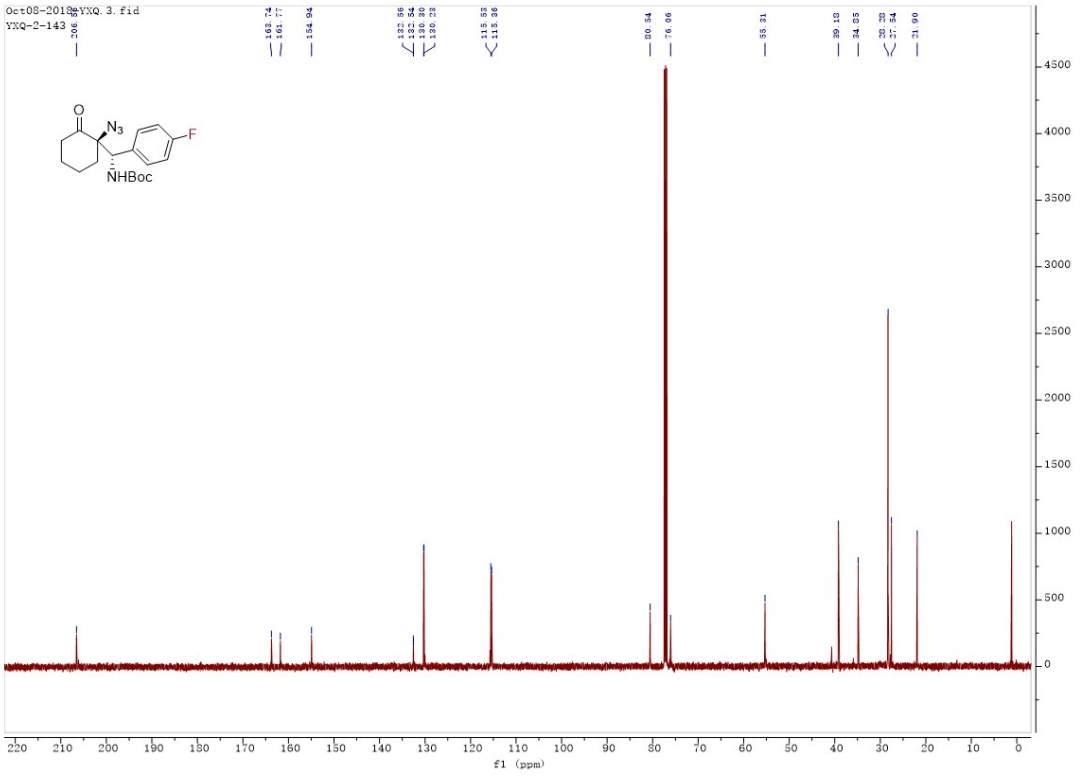
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(p-tolyl)methyl)carbamate **(3c)**

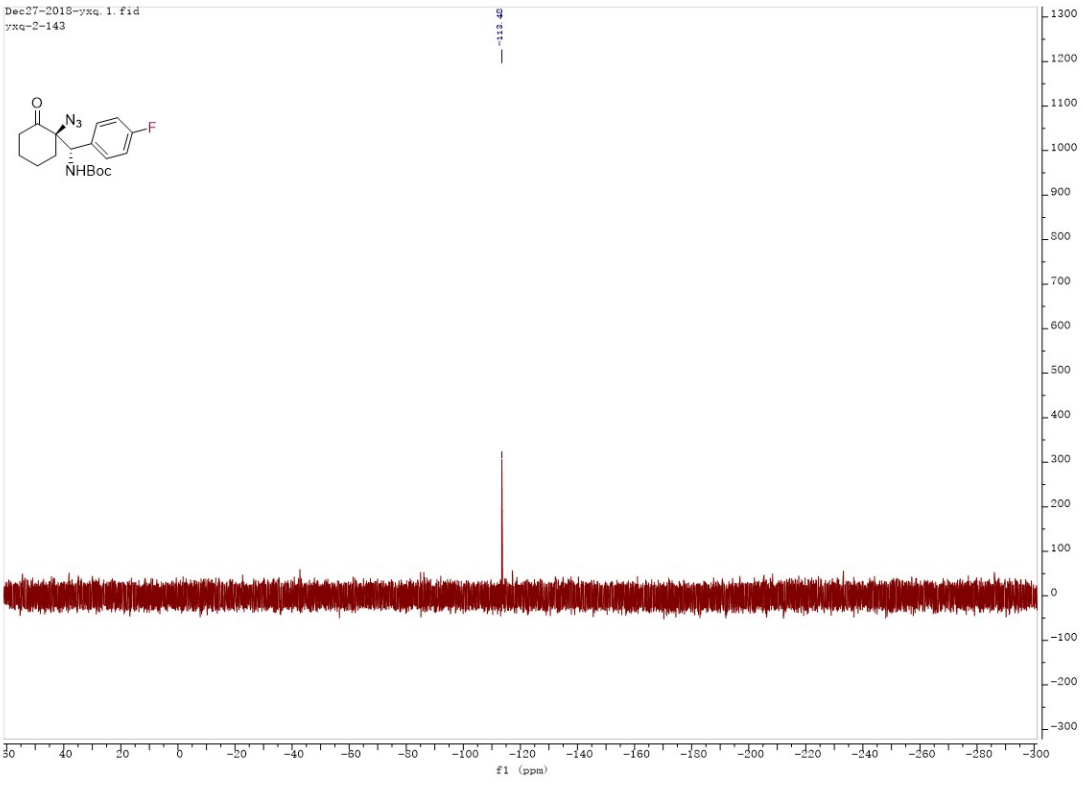




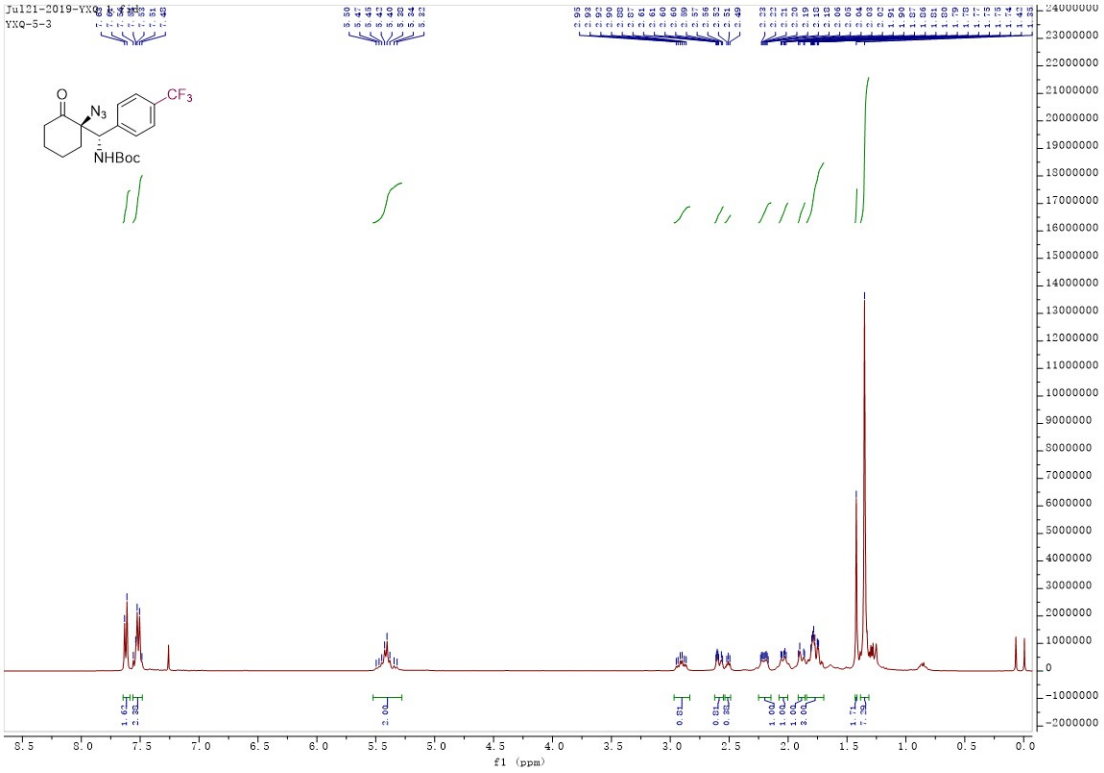
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-fluorophenyl)methyl)carbamate **(3d)**

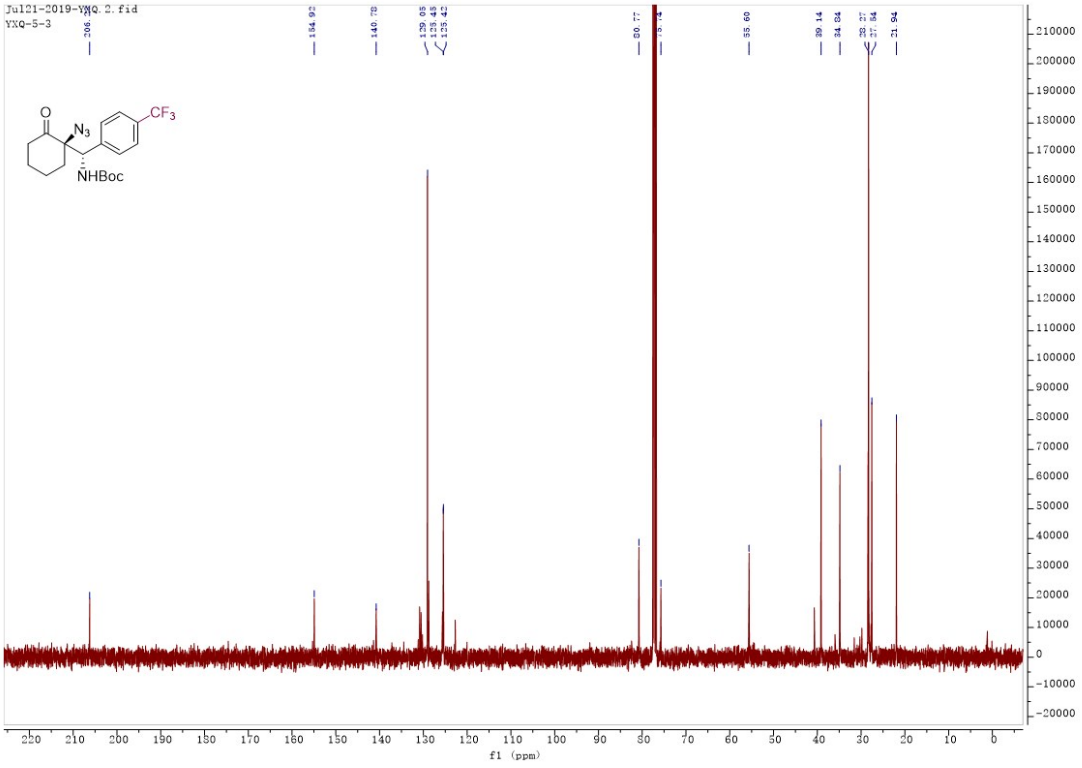

yxq-2-143
N3
F
NHBoc
f1 (ppm)

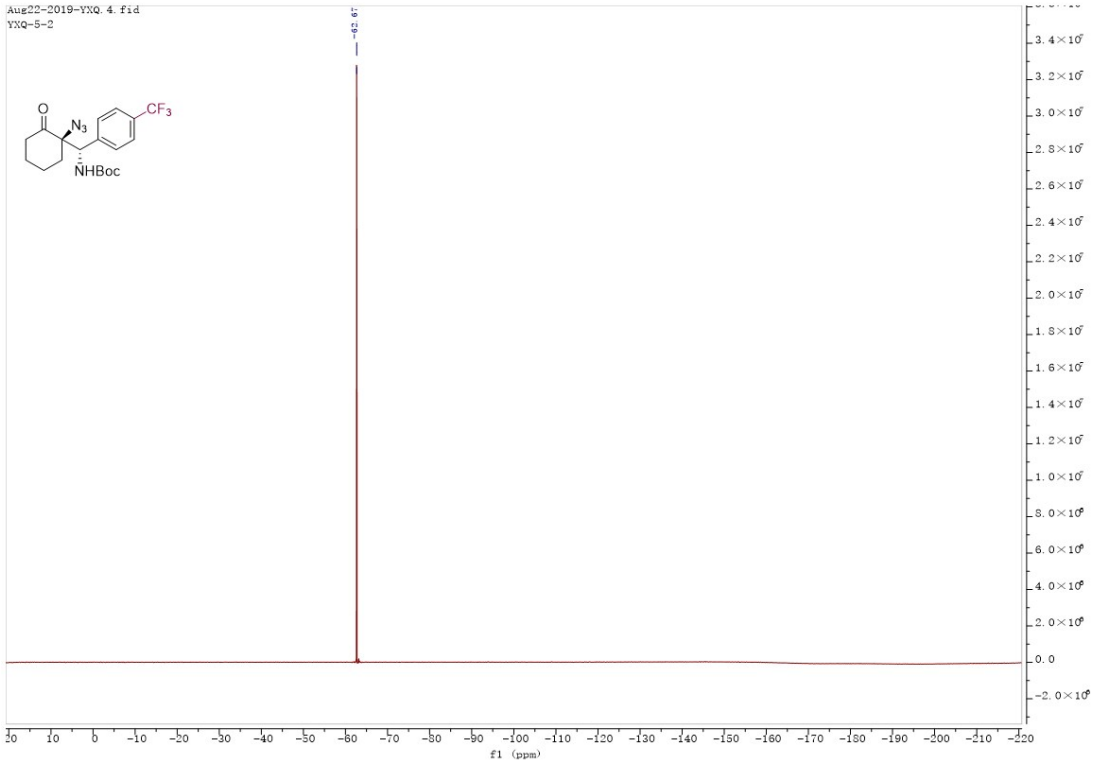

YXQ-2-143
N3
F
NHBoc
f1 (ppm)



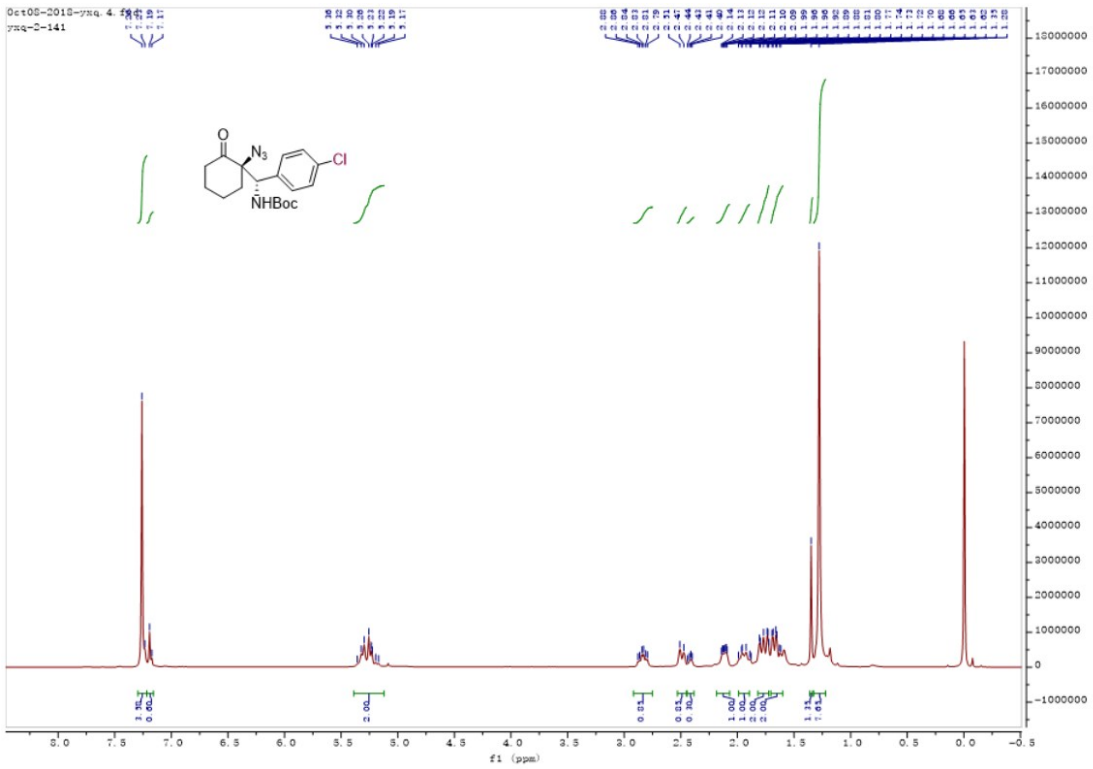
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-(trifluoromethyl)phenyl)methyl)carbamate **(3e)**

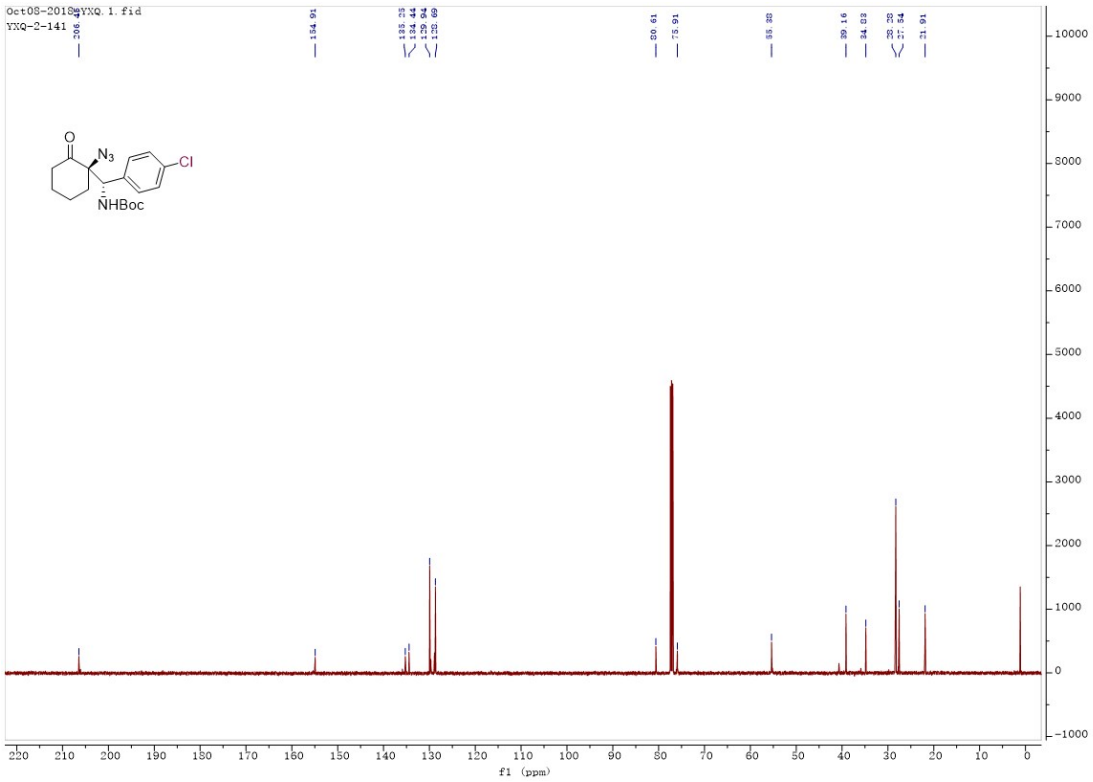

YXQ-5-3
O
N3
CF3
NHBoc
f1 (ppm)


YXQ-5-3
O
N3
CF3
NHBoc
f1 (ppm)

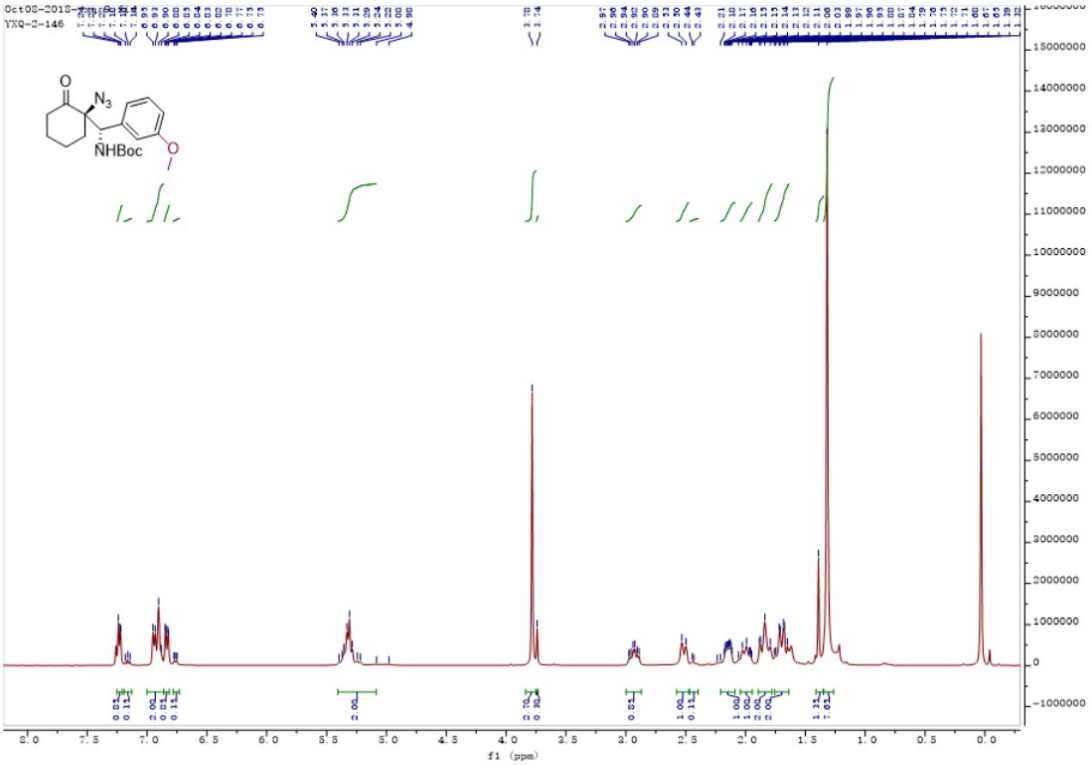


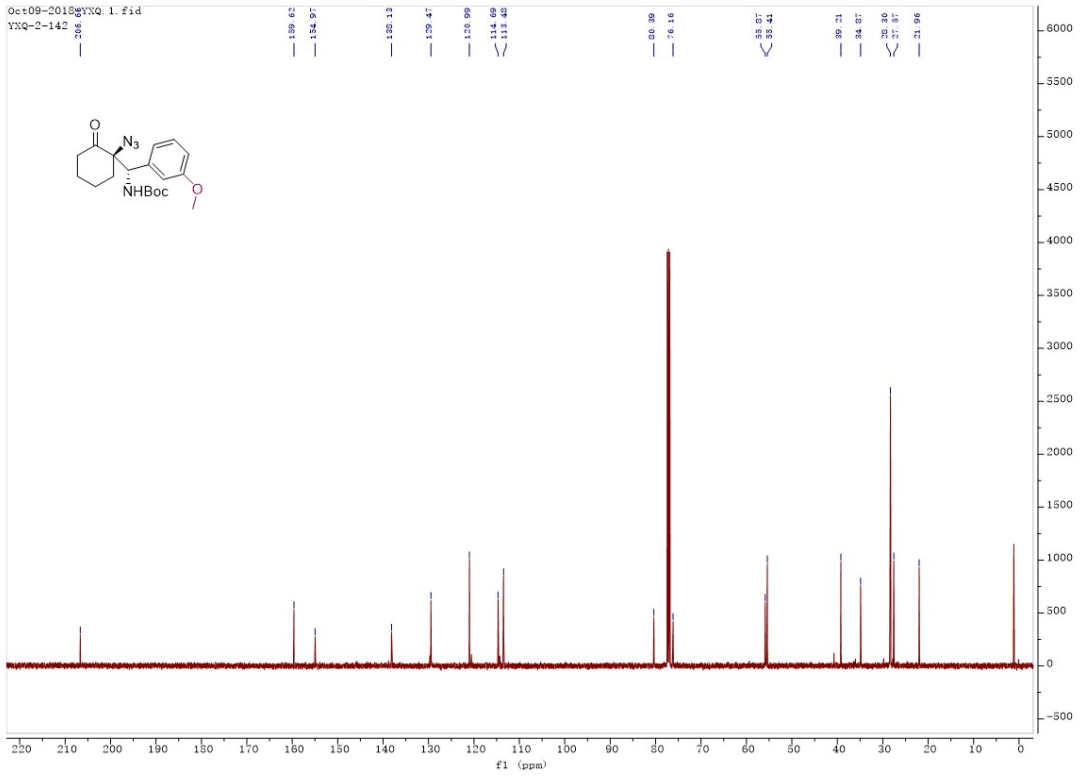
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(4-chlorophenyl)methyl)carbamate **(3f)**



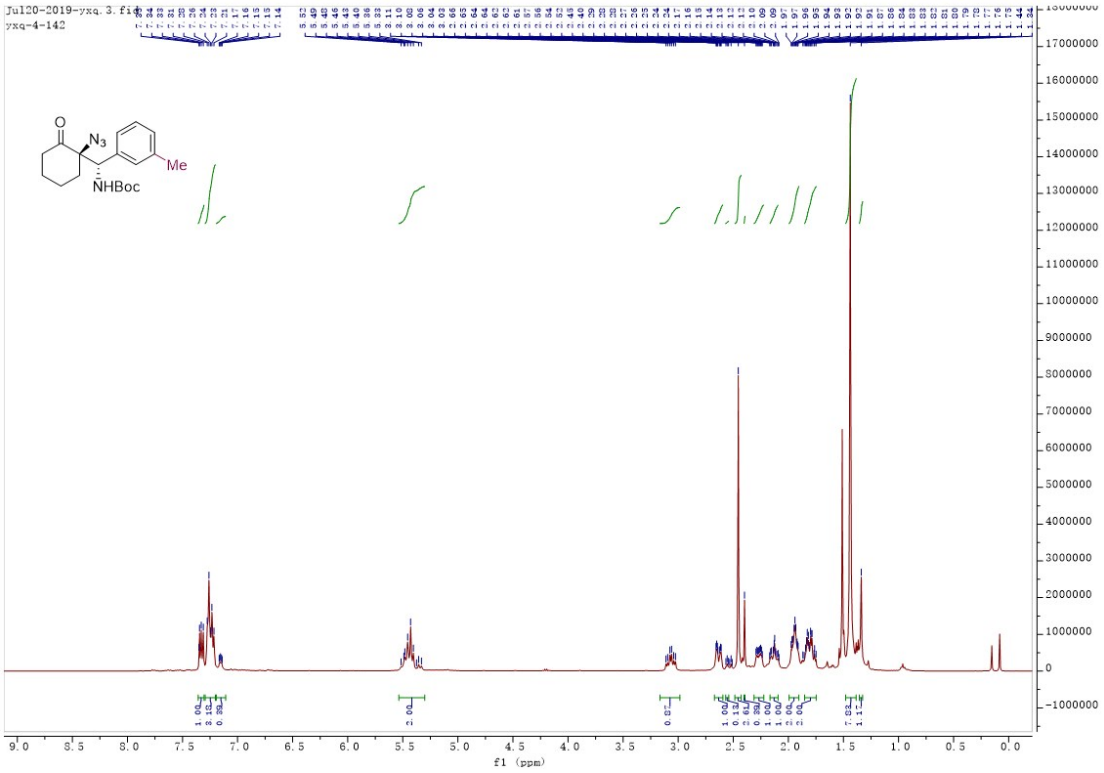


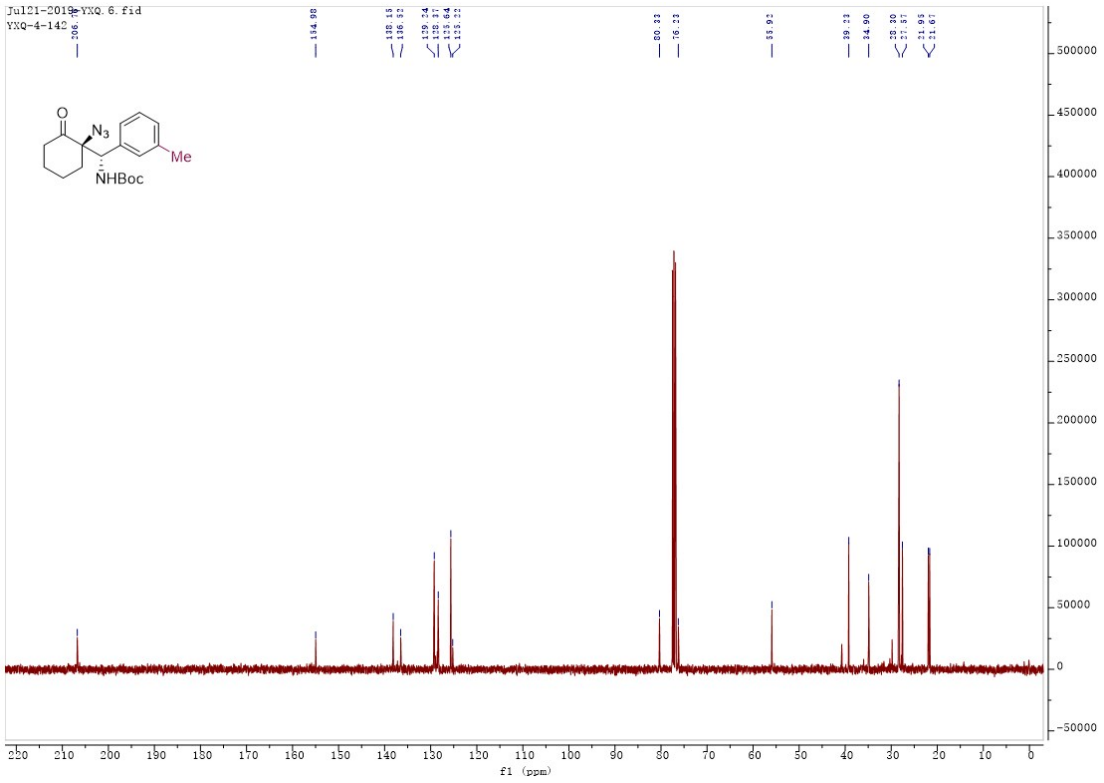
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-methoxyphenyl)methyl)carbamate **(3g)**



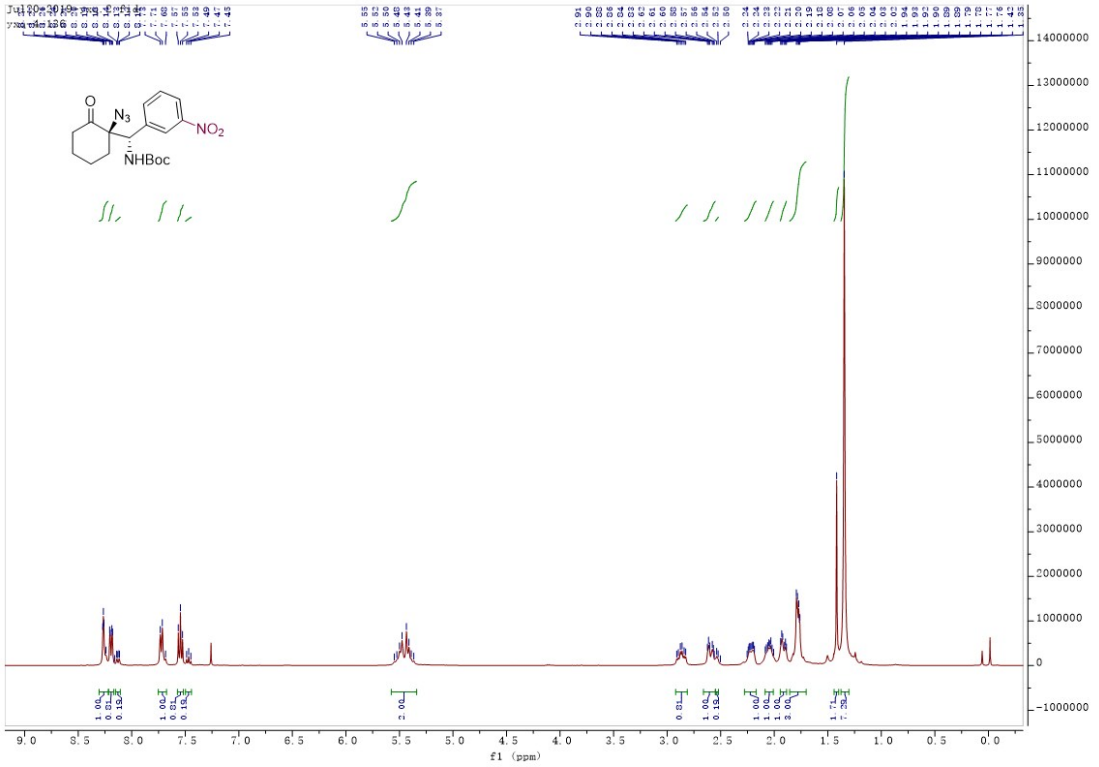


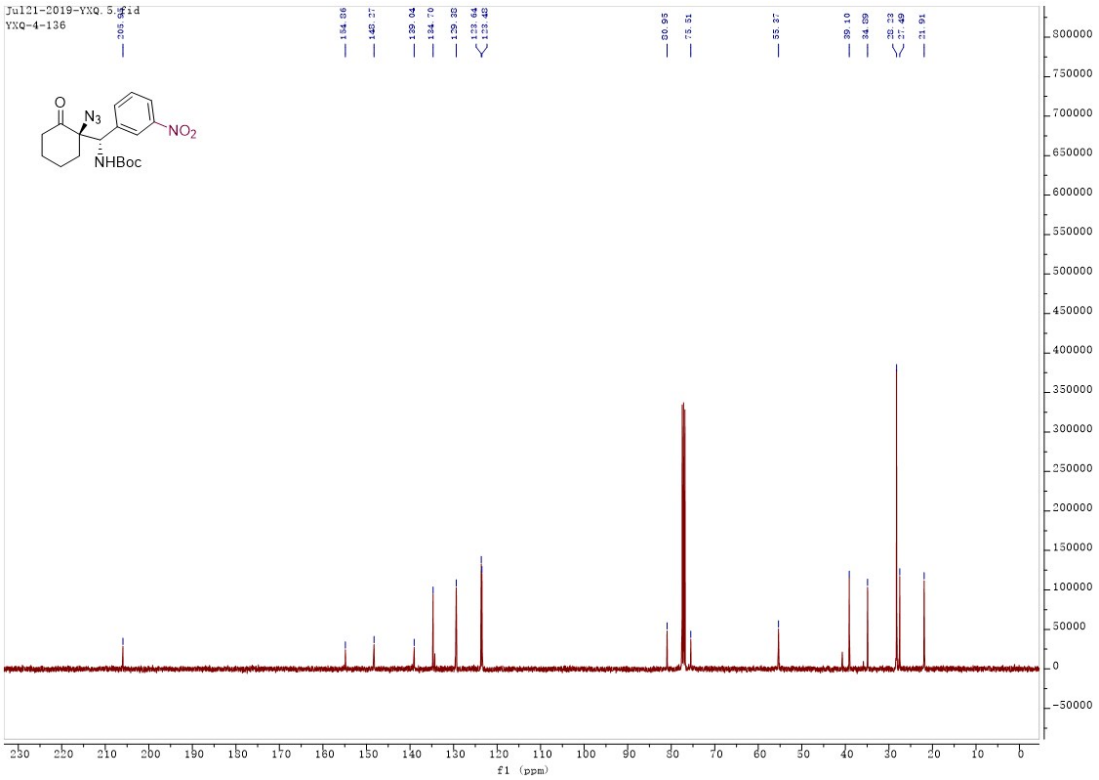
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(m-tolyl)methyl)carbamate **(3h)**



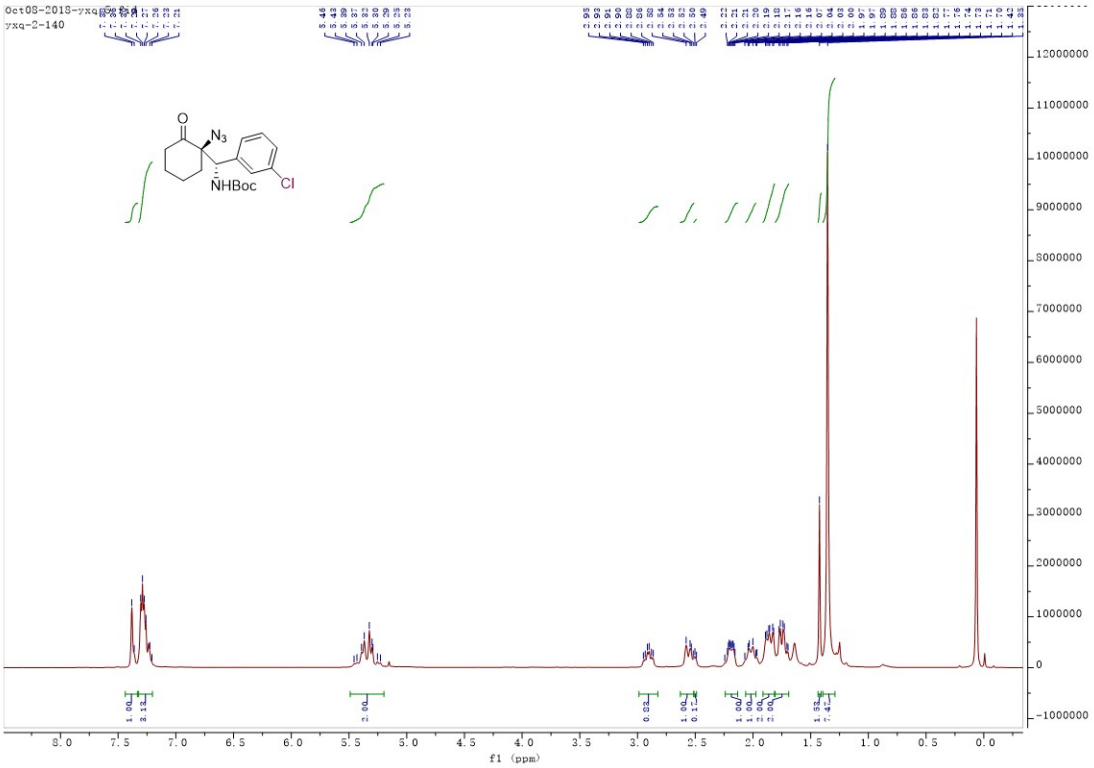


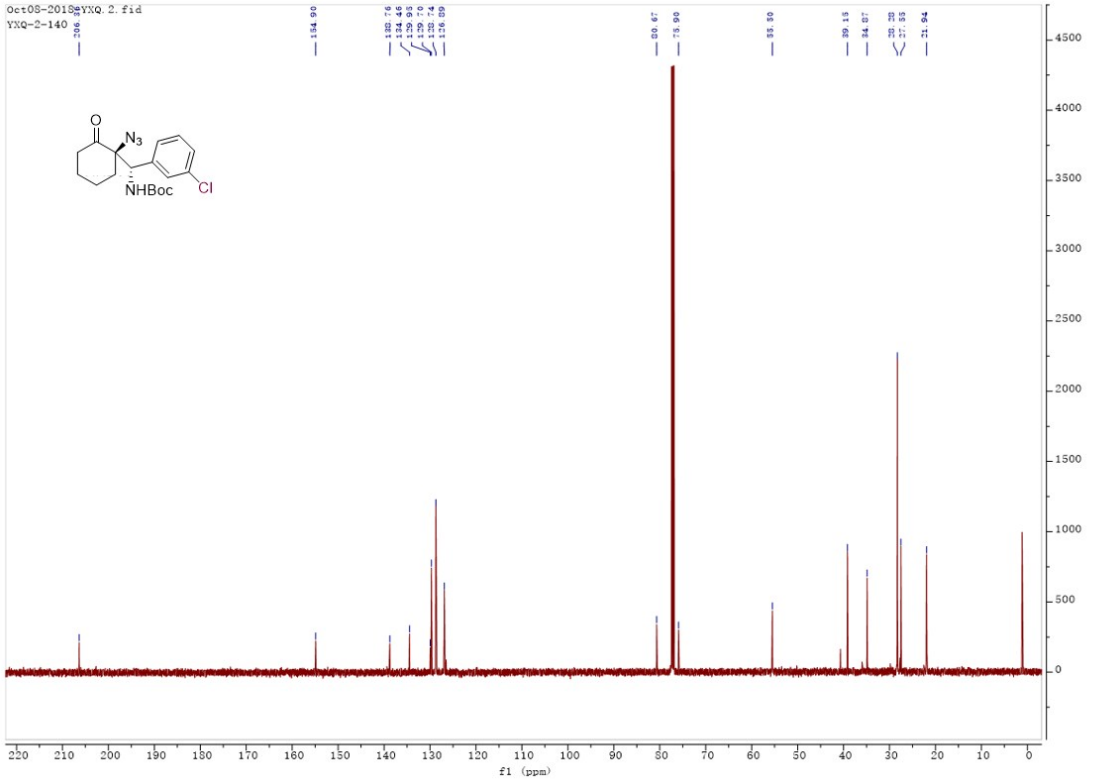
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-nitrophenyl)methyl)carbamate **(3i)**



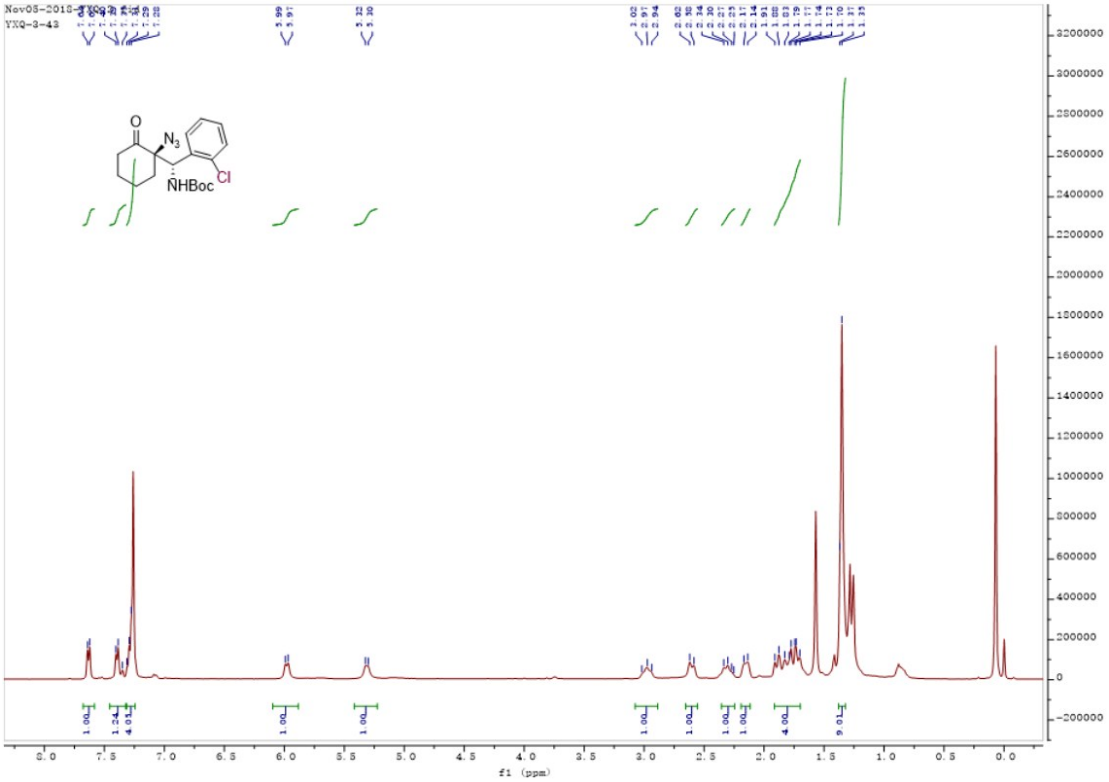


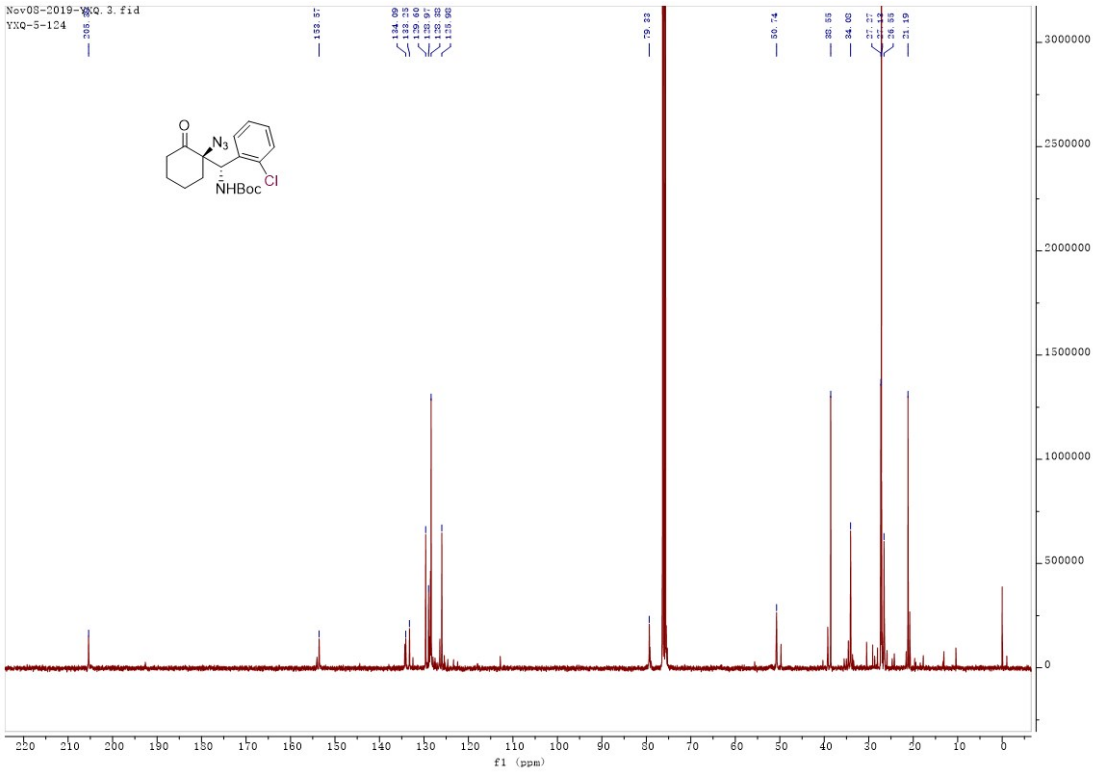
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(3-chlorophenyl)methyl)carbamate **(3j)**



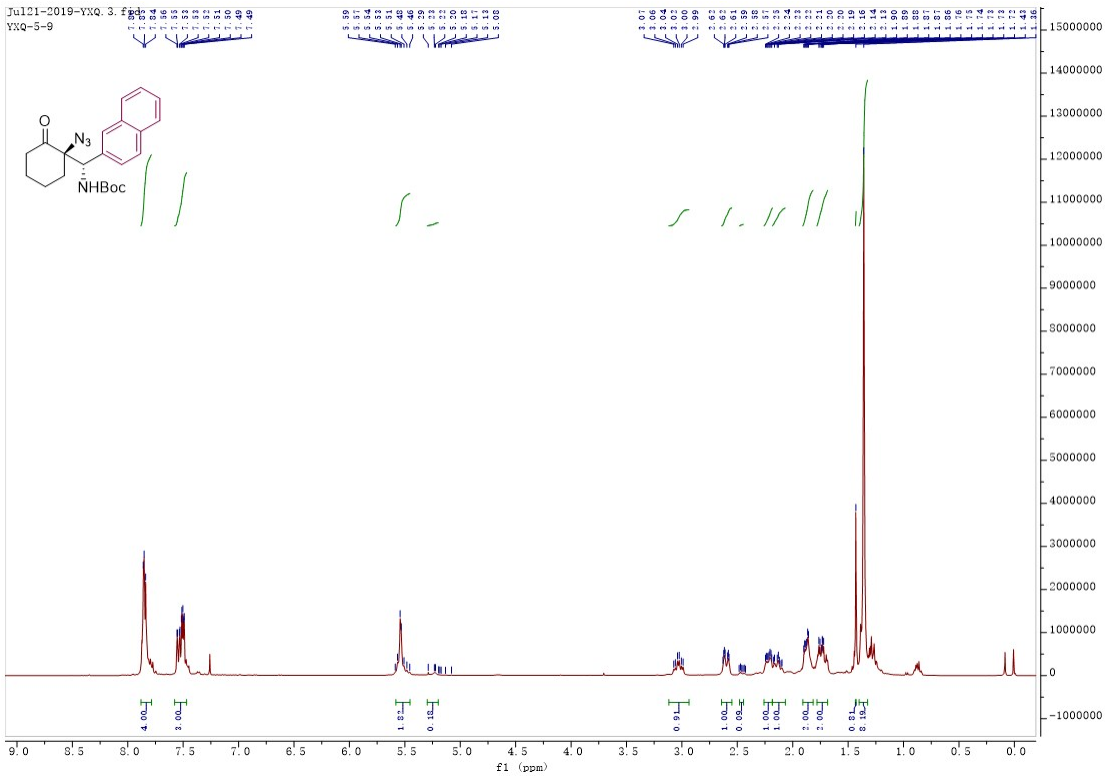


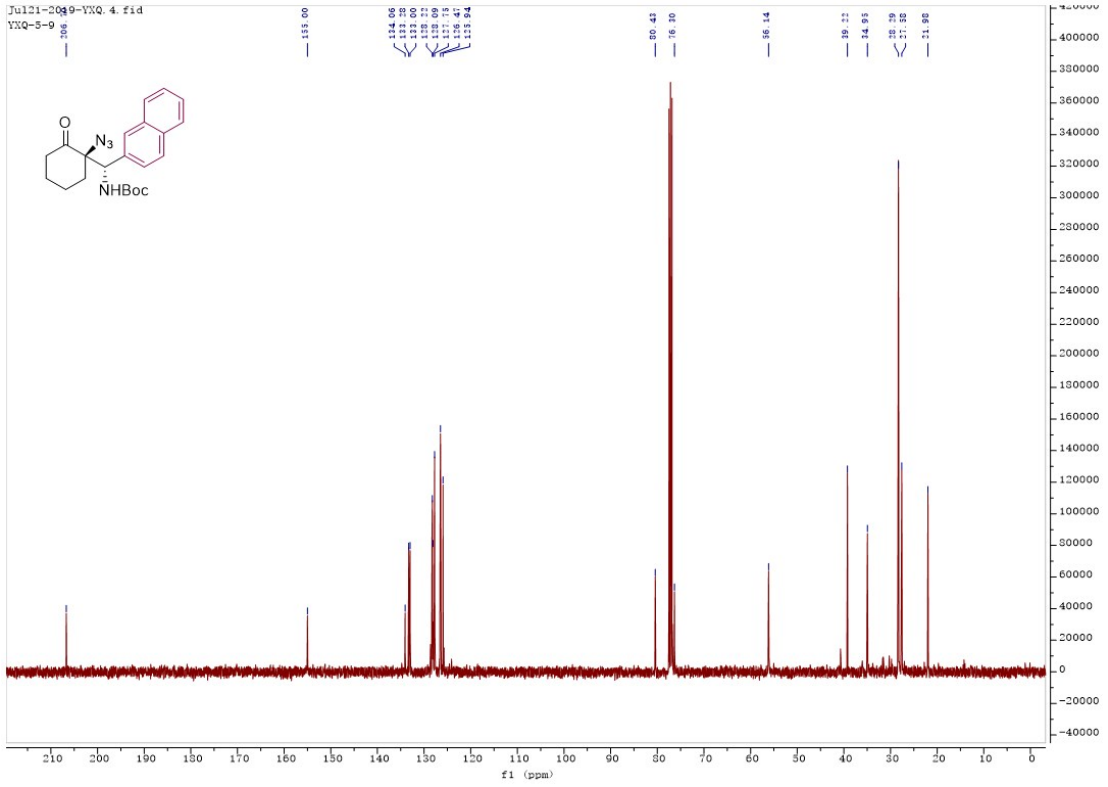
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(2-chlorophenyl)methyl)carbamate **(3k)**



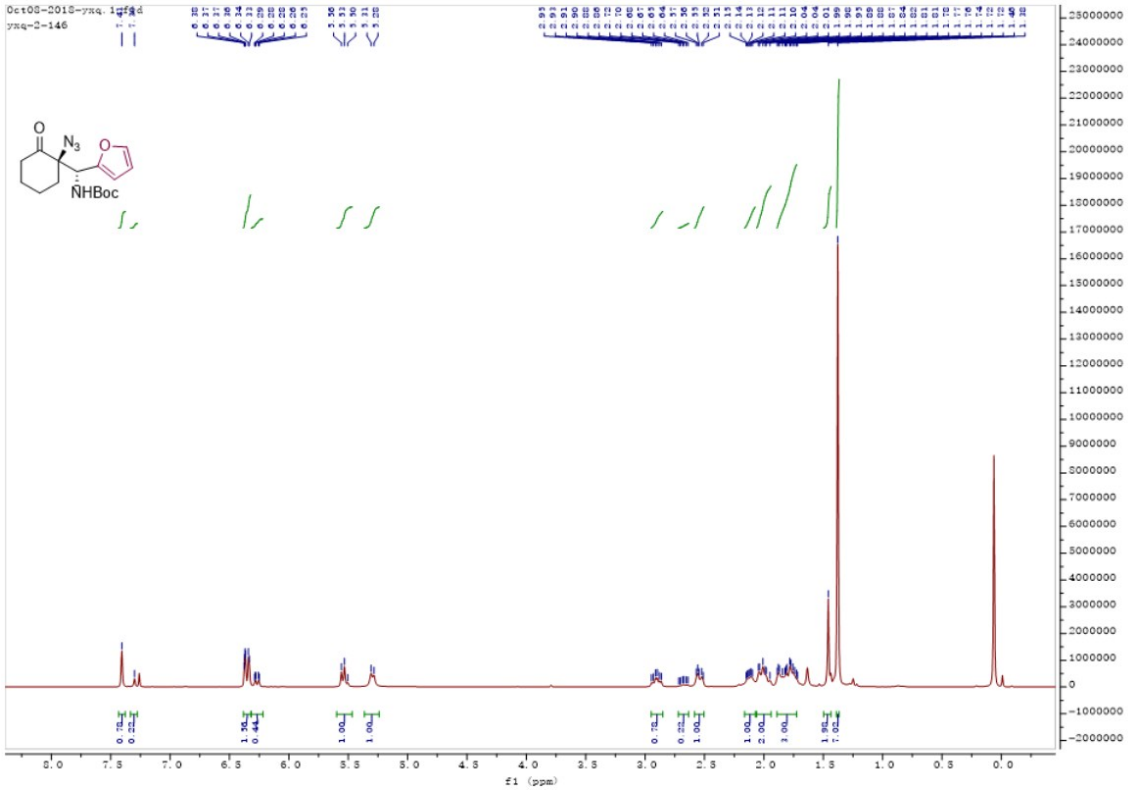


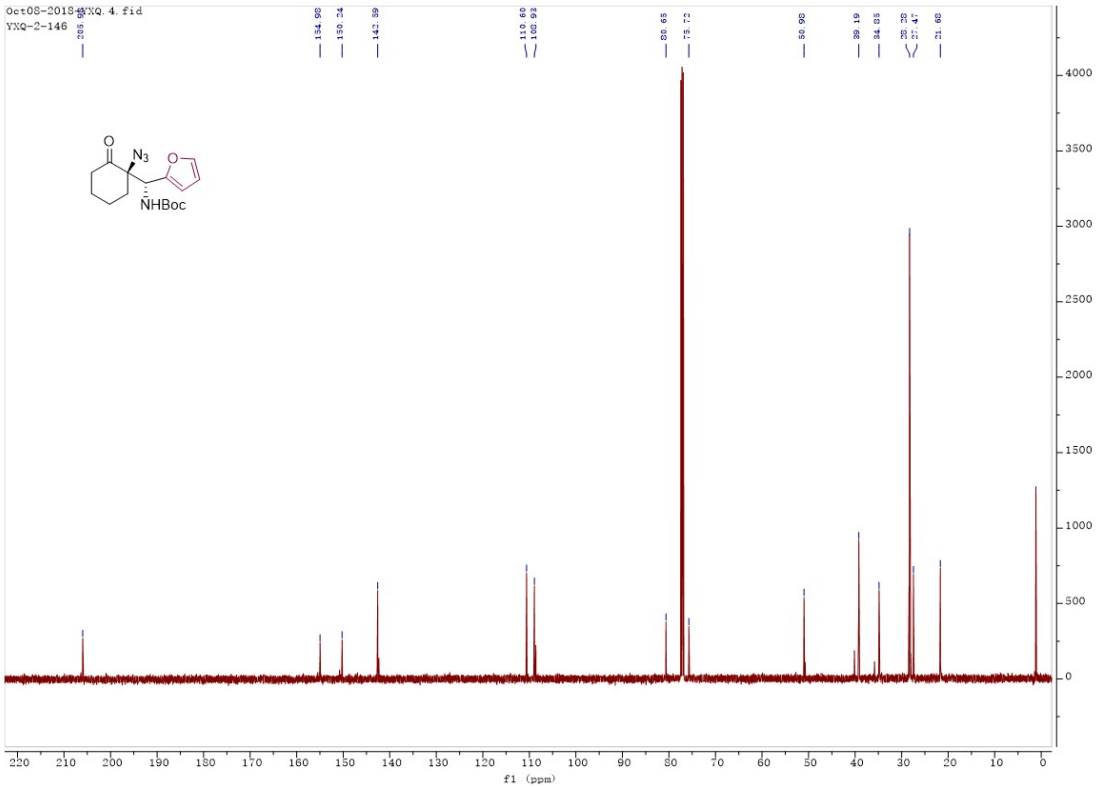
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(naphthalen-2-yl)methyl)carbamate **(3l)**



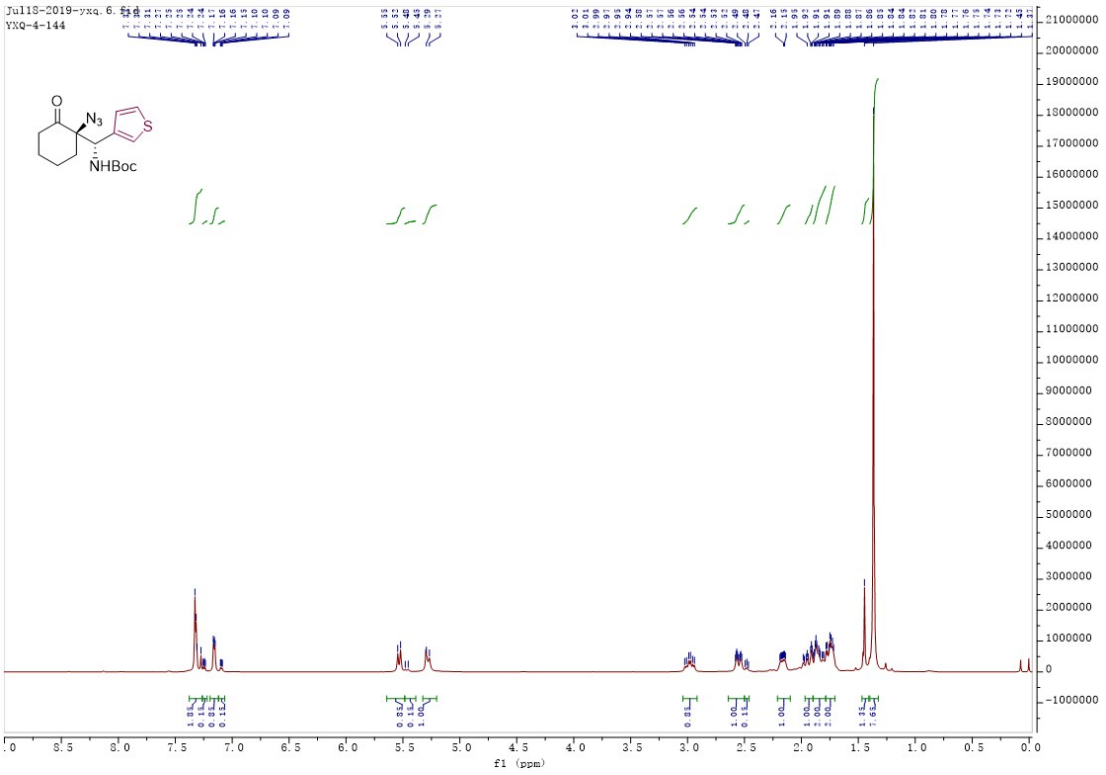


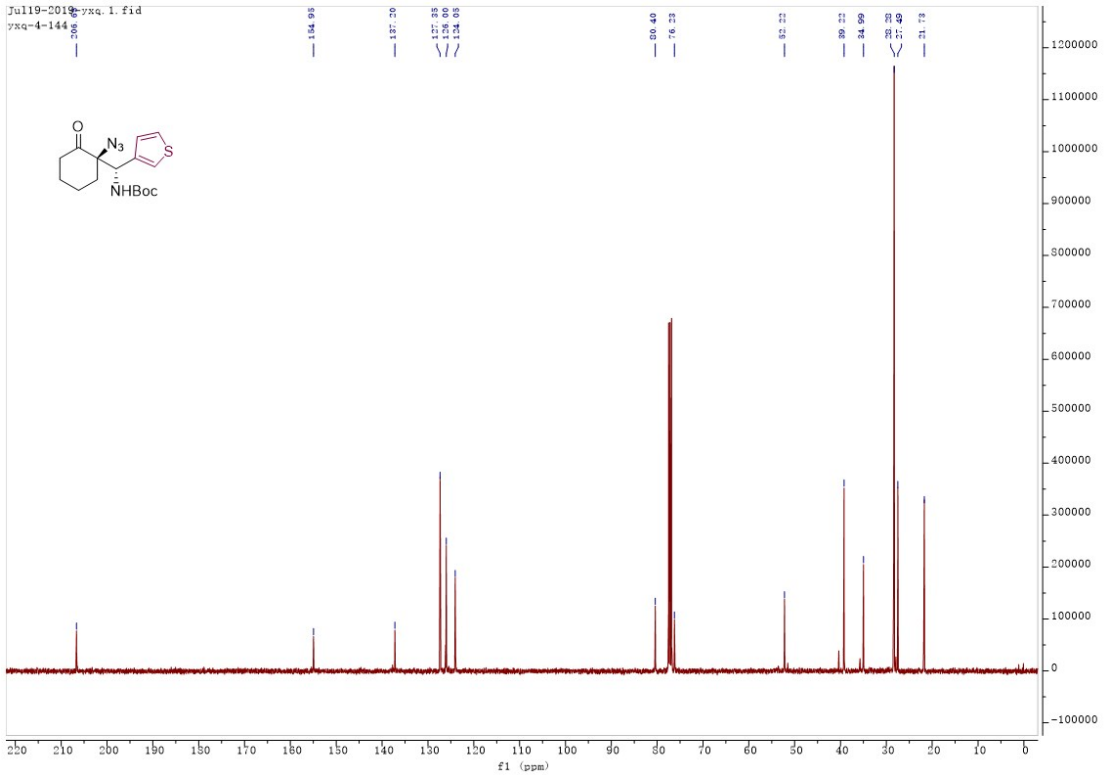
tert-butyl ((R)-((R)-1-azido-2-oxocyclohexyl)(furan-2-yl)methyl)carbamate **(3m)**



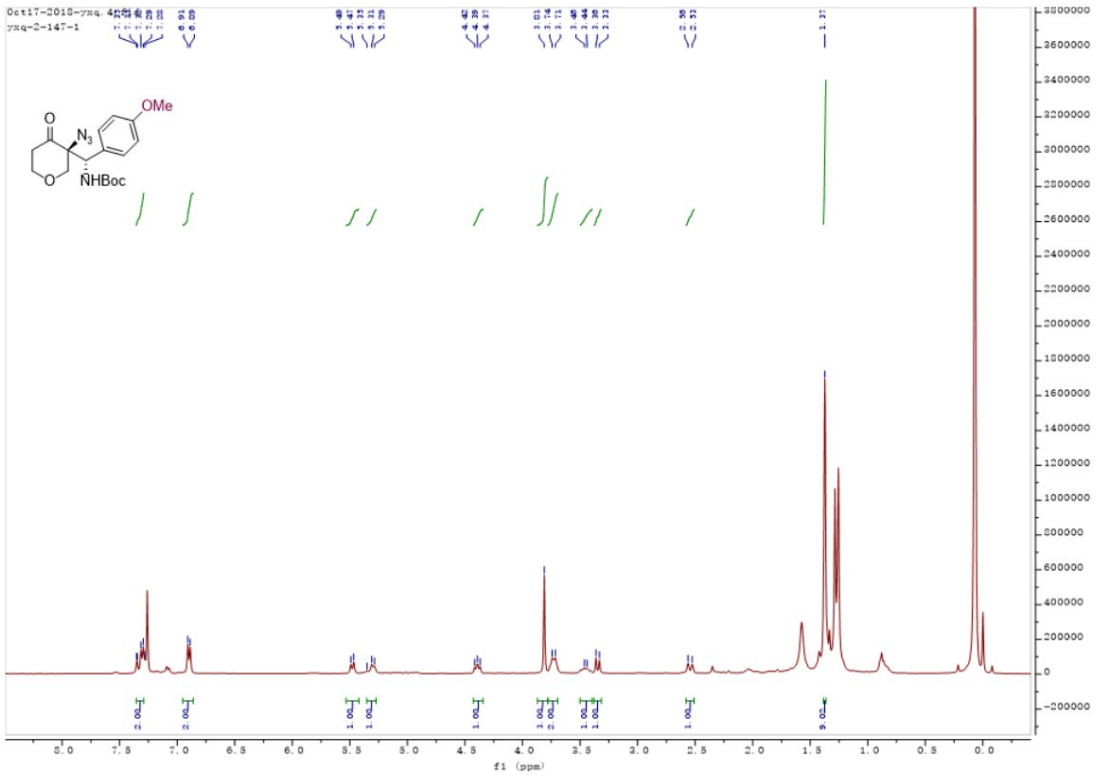


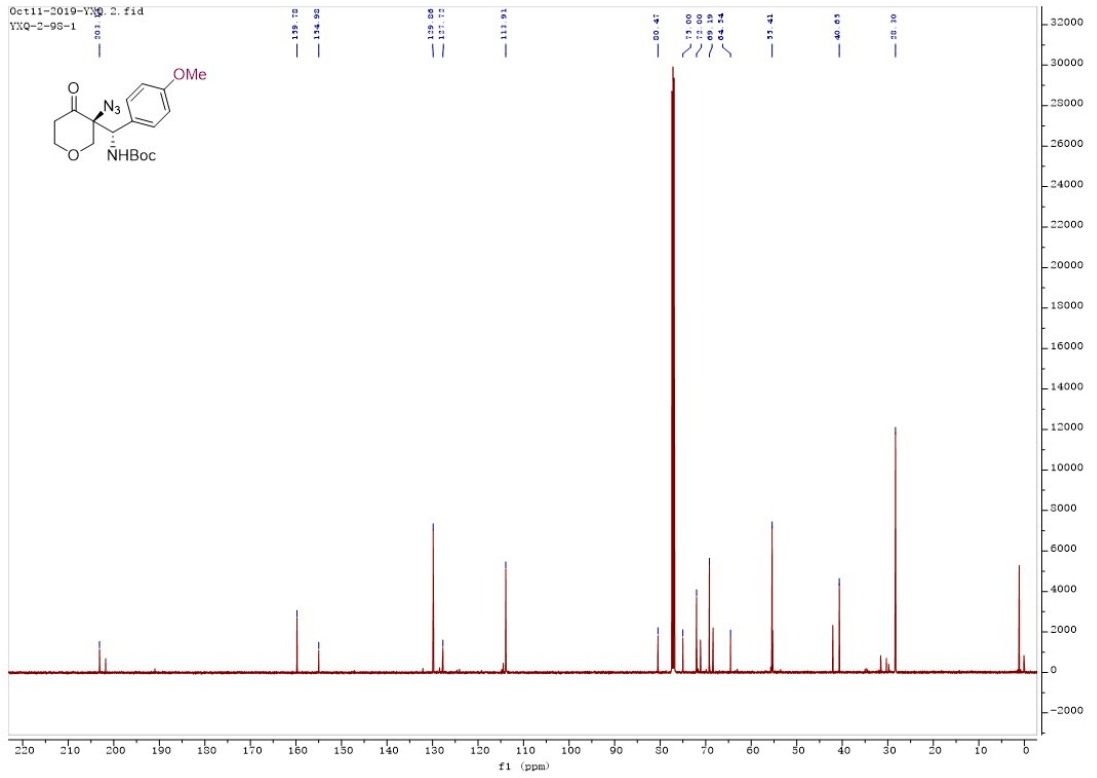
tert-butyl ((S)-((R)-1-azido-2-oxocyclohexyl)(thiophen-3-yl)methyl)carbamate **(3n)**



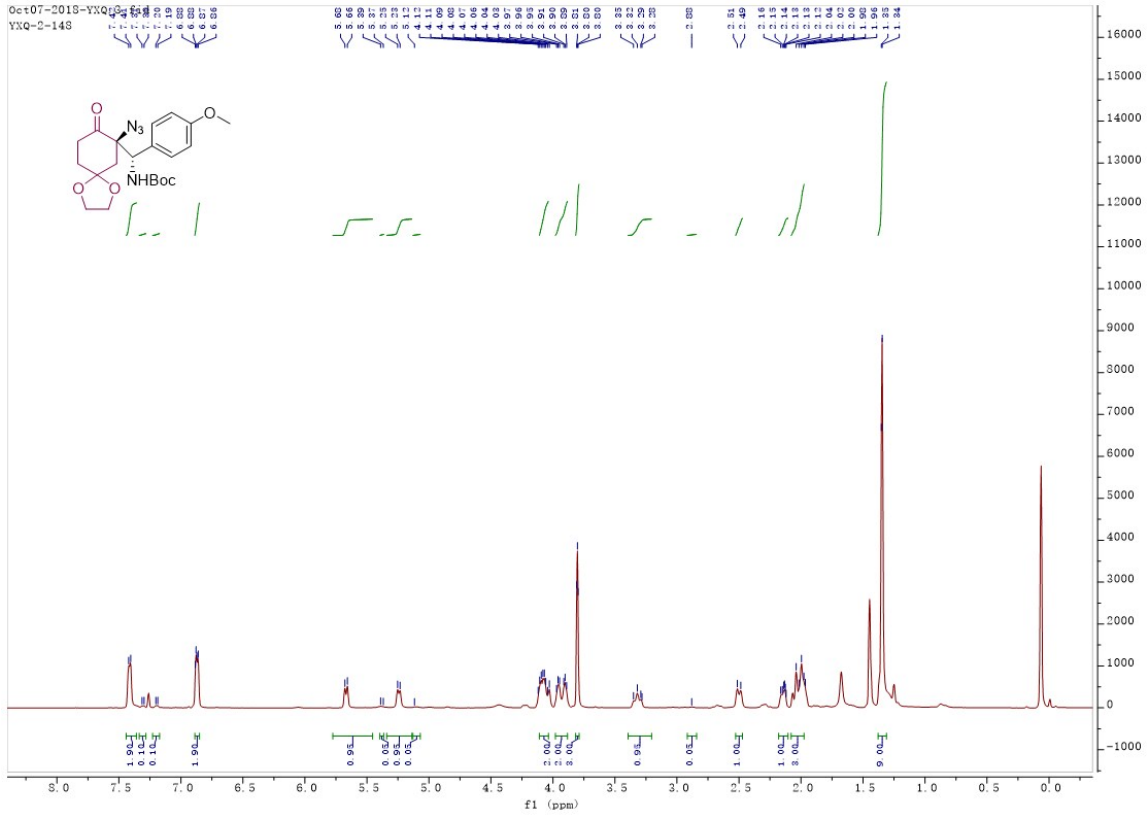


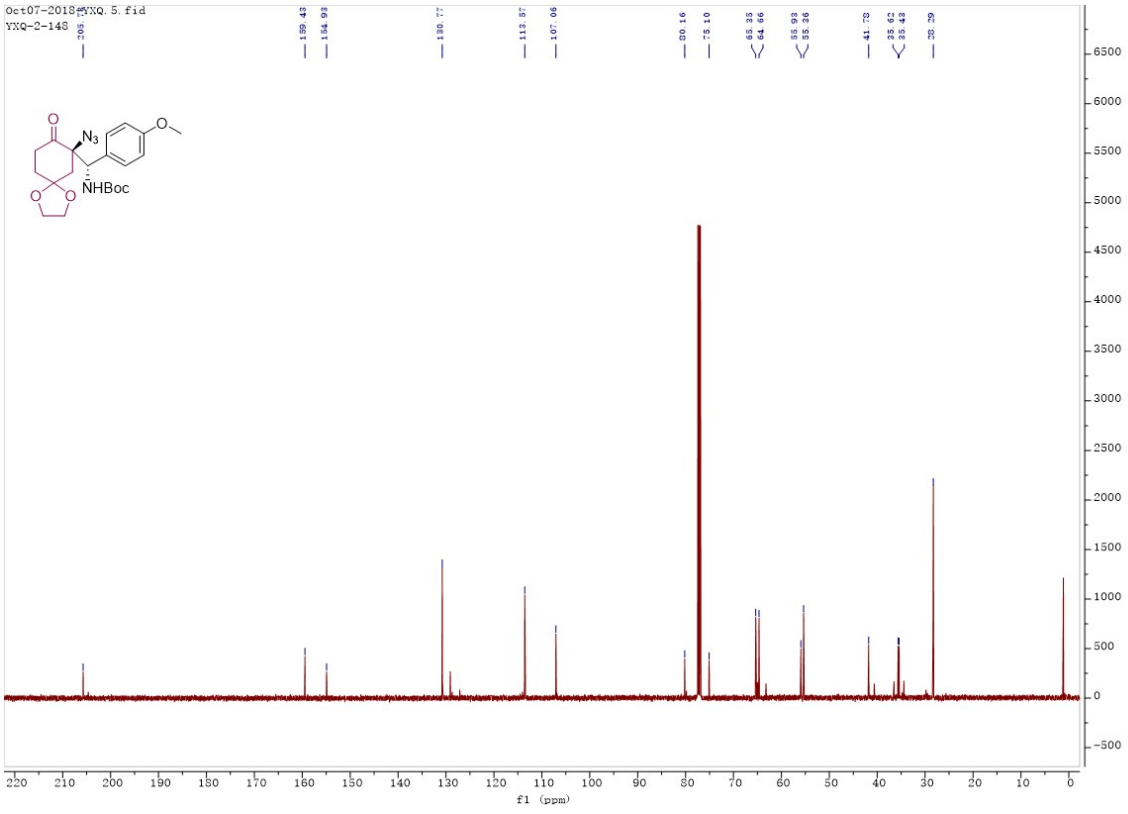
tert-butyl ((S)-((S)-3-azido-4-oxotetrahydro-2H-pyran-3-yl)(4-methoxyphenyl)methyl)carbamate **(3o)**



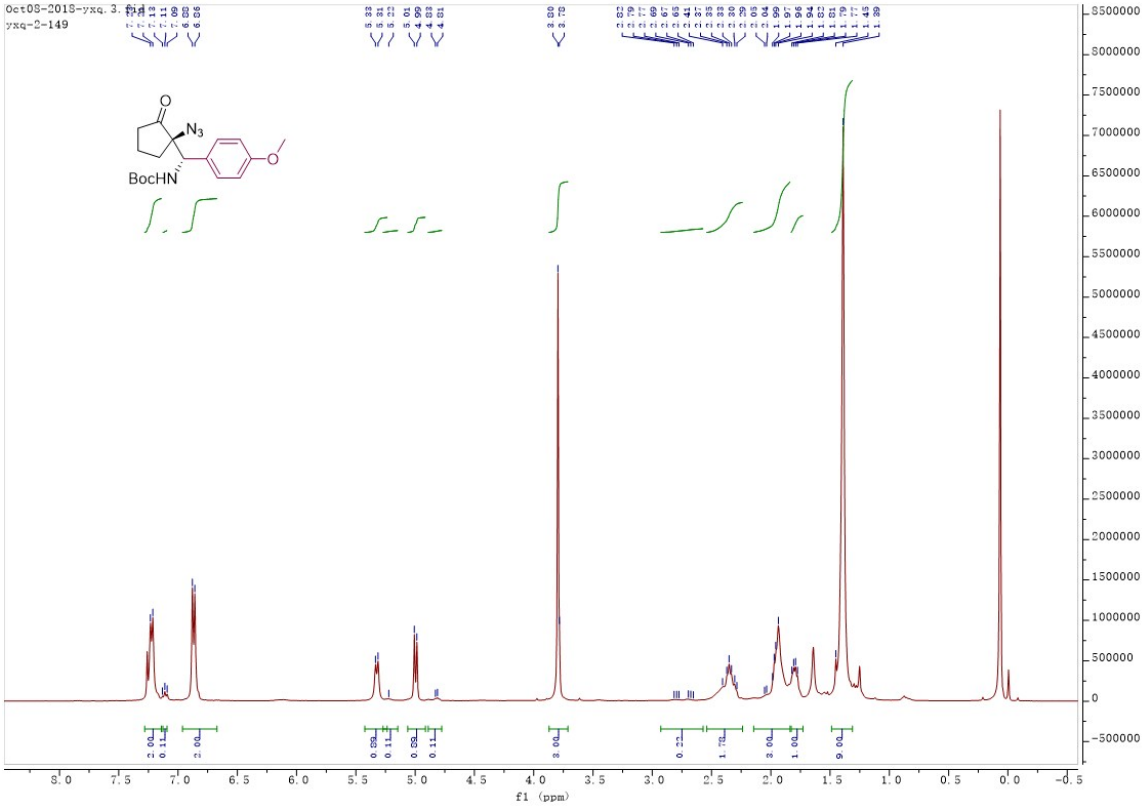


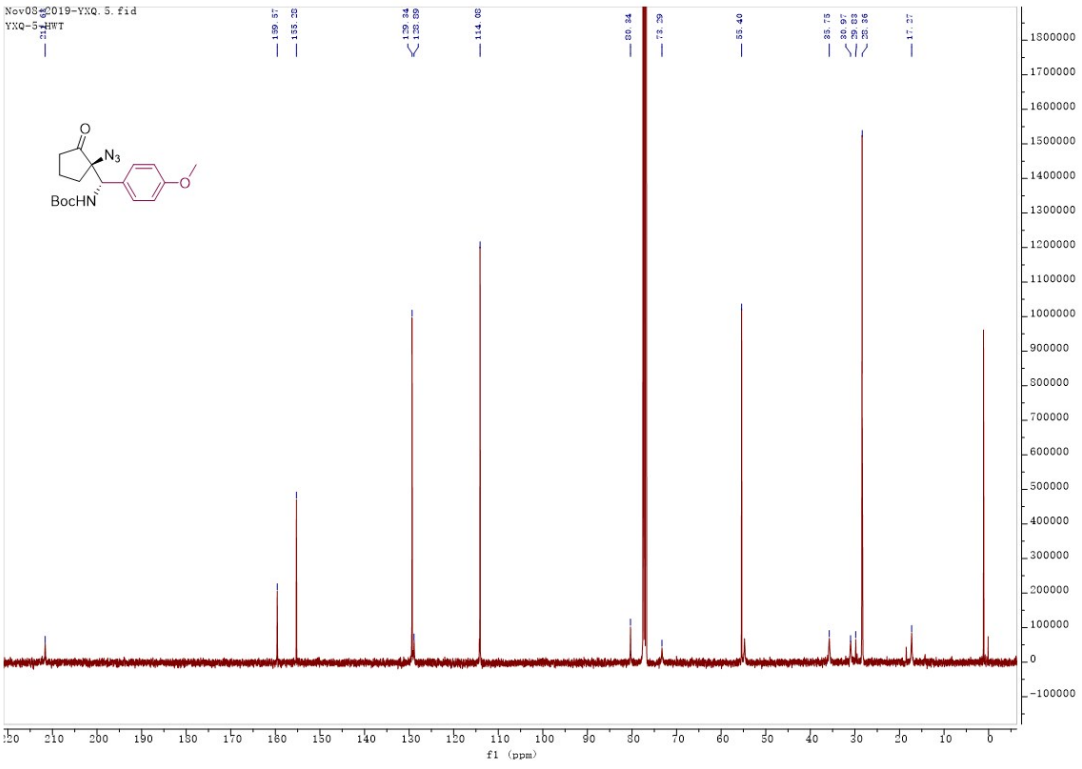
tert-butyl-((R)-((S)-7-azido-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)(4-methoxyphenyl)methyl)carbamate **(3p)**



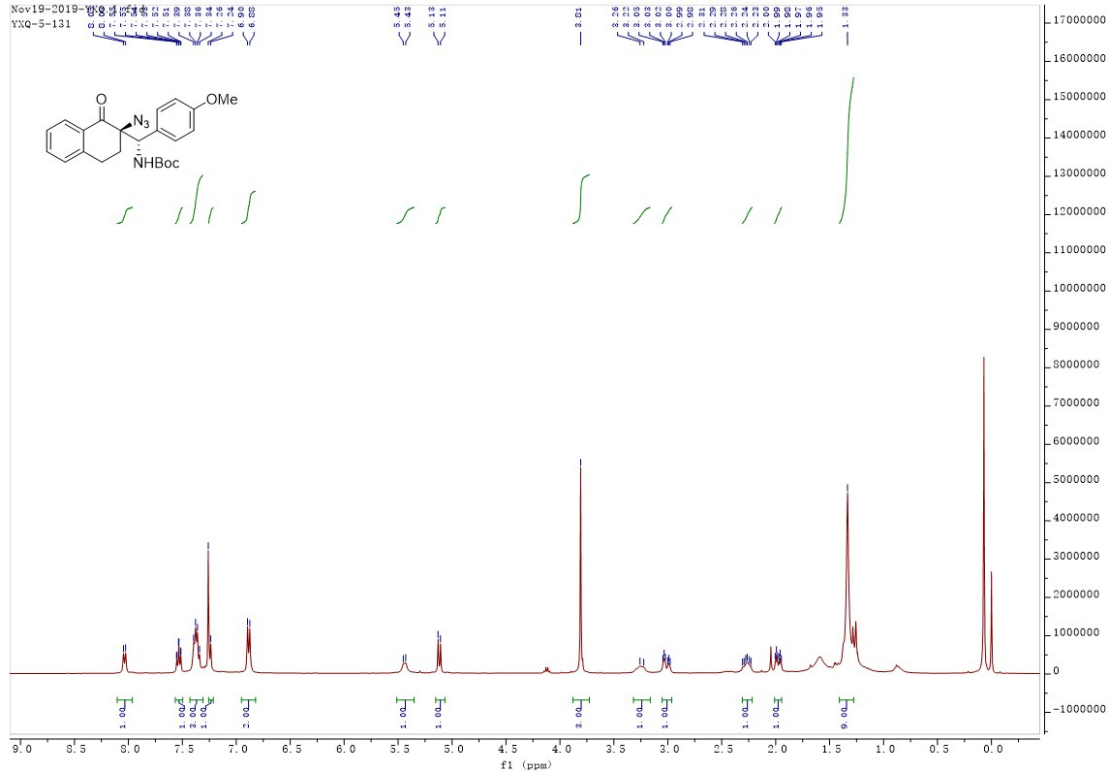


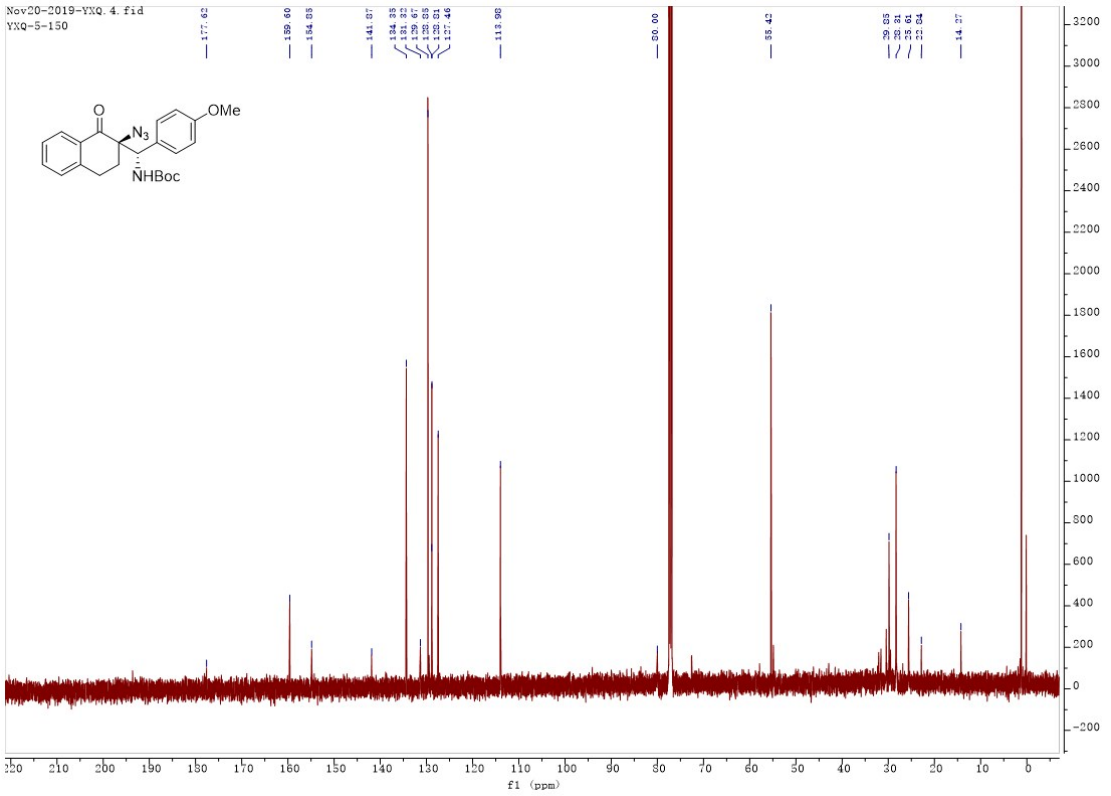
tert-butyl ((S)-((R)-1-azido-2-oxocyclopentyl)(4-methoxyphenyl)methyl)carbamate **(3q)**



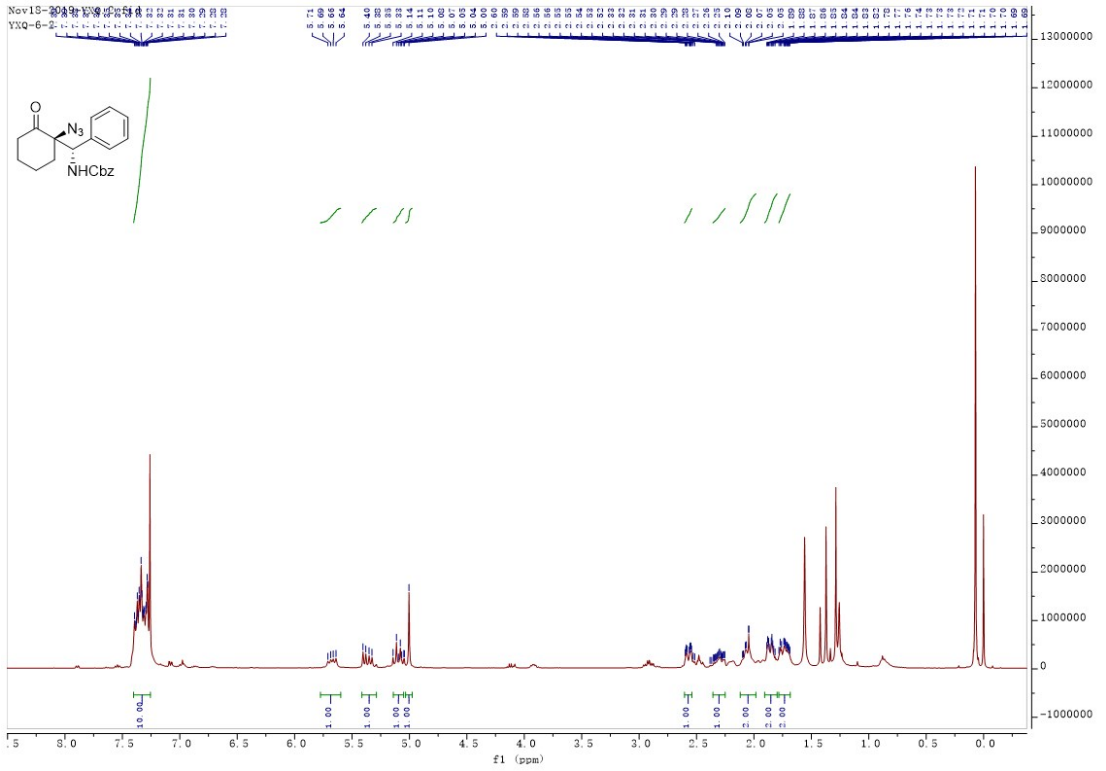


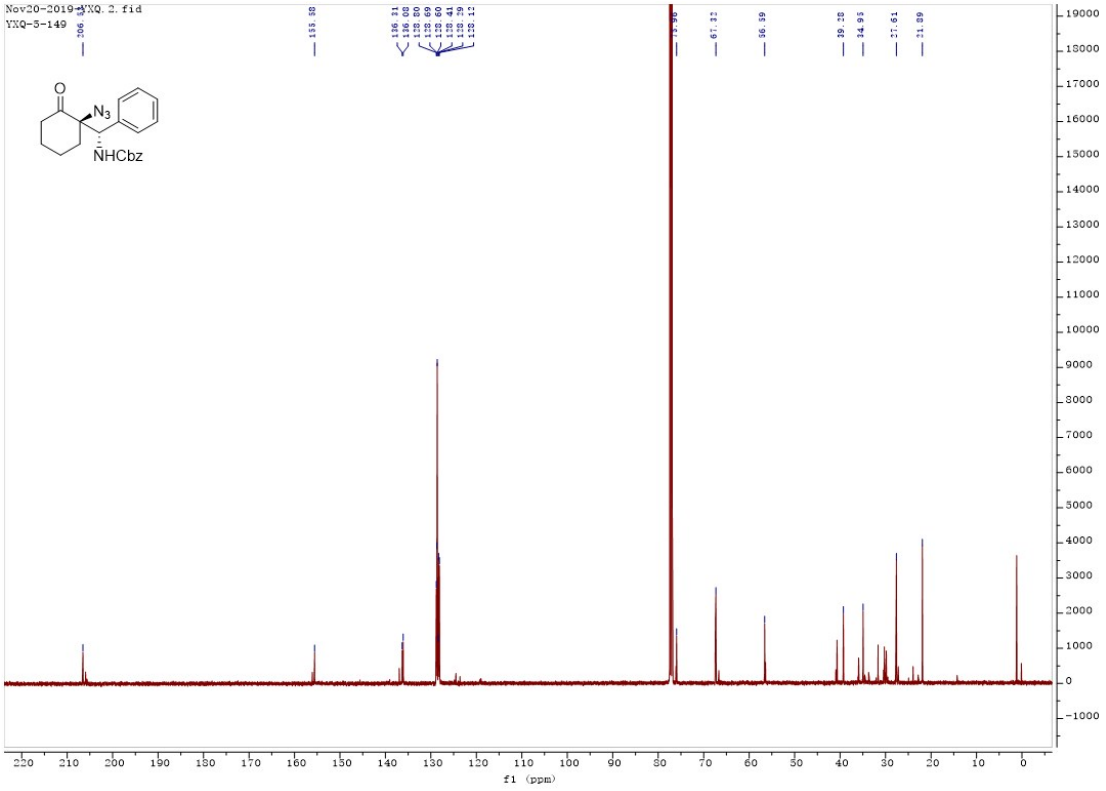
tert-butyl-((S)-((R)-2-azido-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)(4-methoxyphenyl)methyl)carbamate **(3r)**



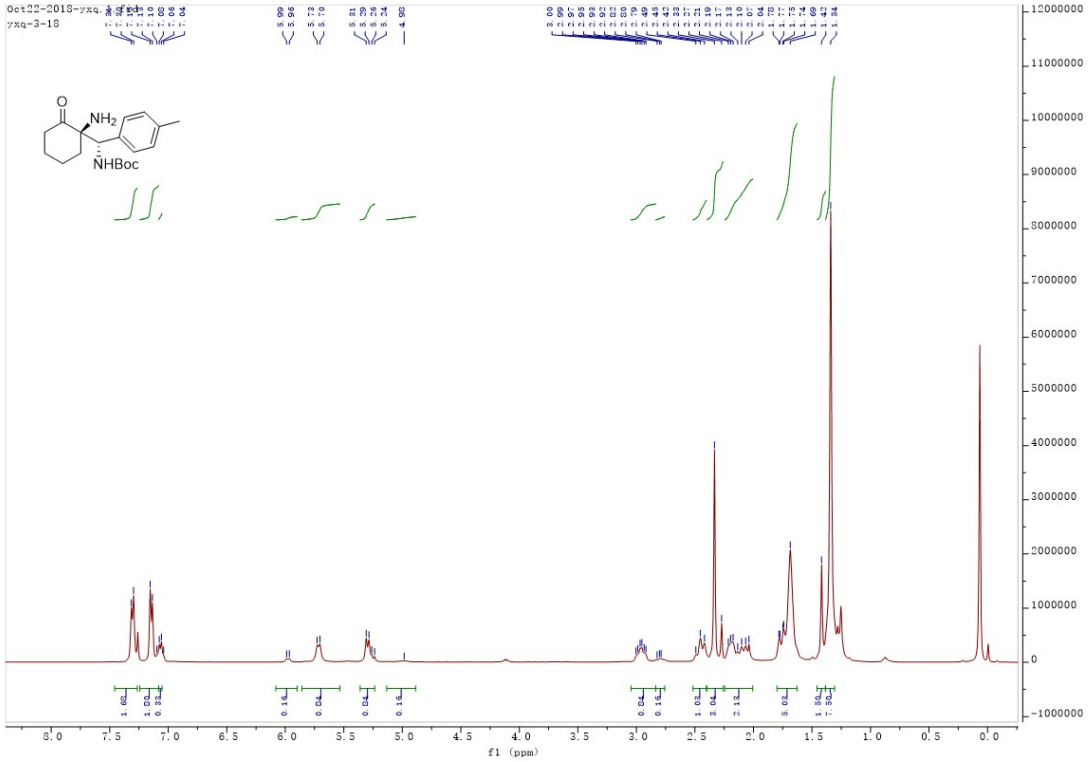


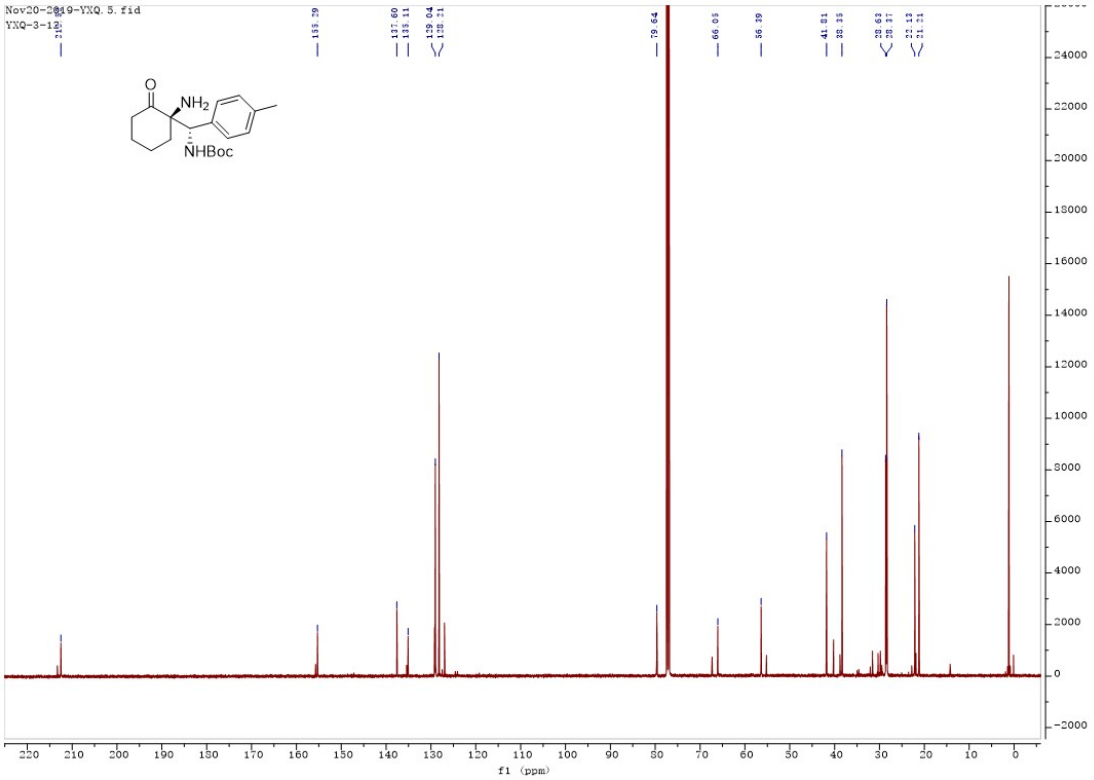
benzyl ((S)-((R)-1-azido-2-oxocyclohexyl)(phenyl)methyl)carbamate **(3s)**



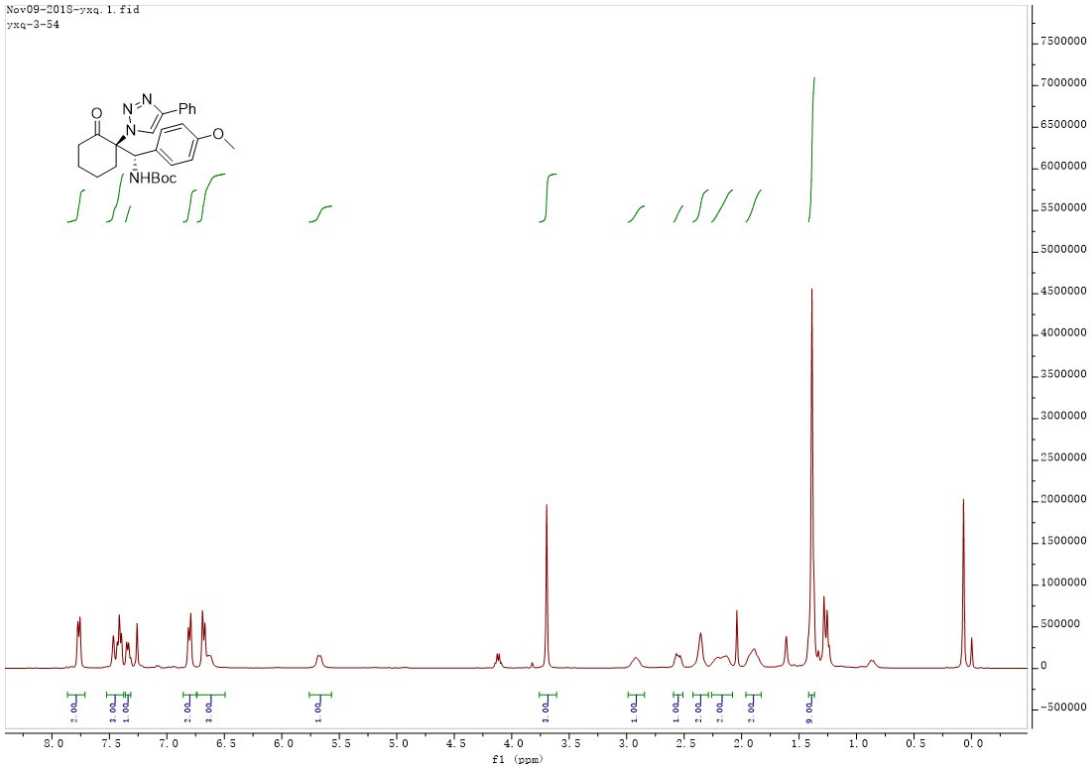


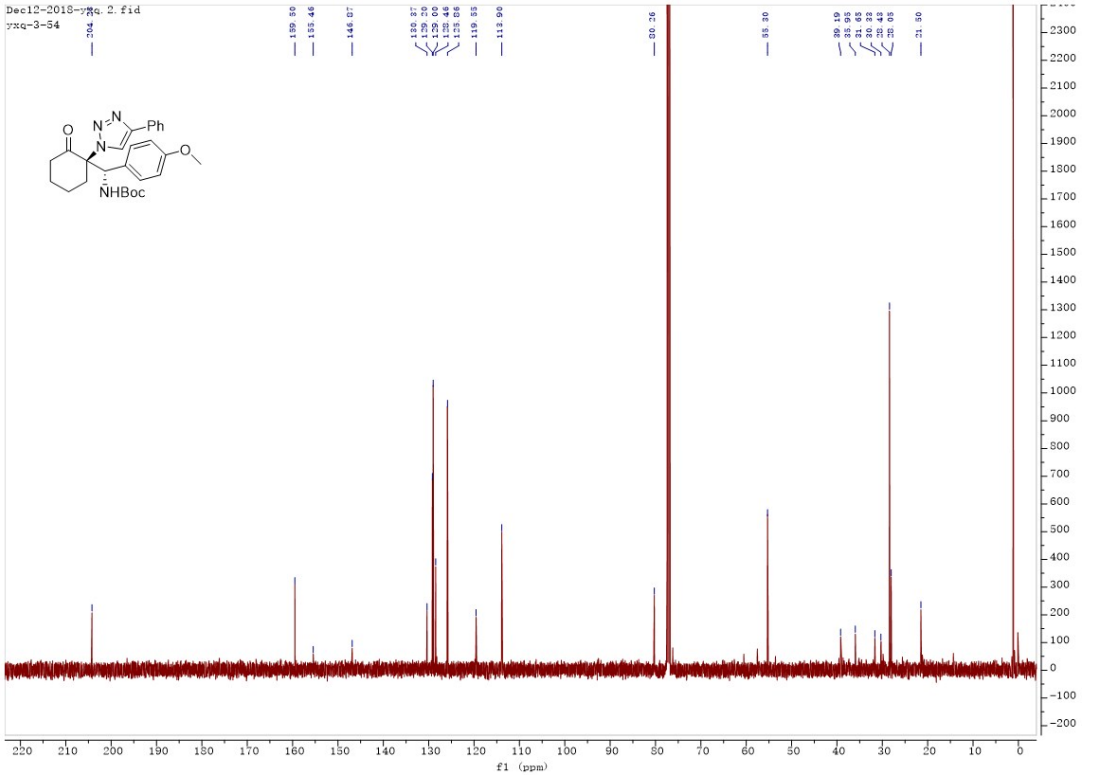
tert-butyl ((S)-((R)-1-amino-2-oxocyclohexyl)(p-tolyl)methyl)carbamate **(4c)**



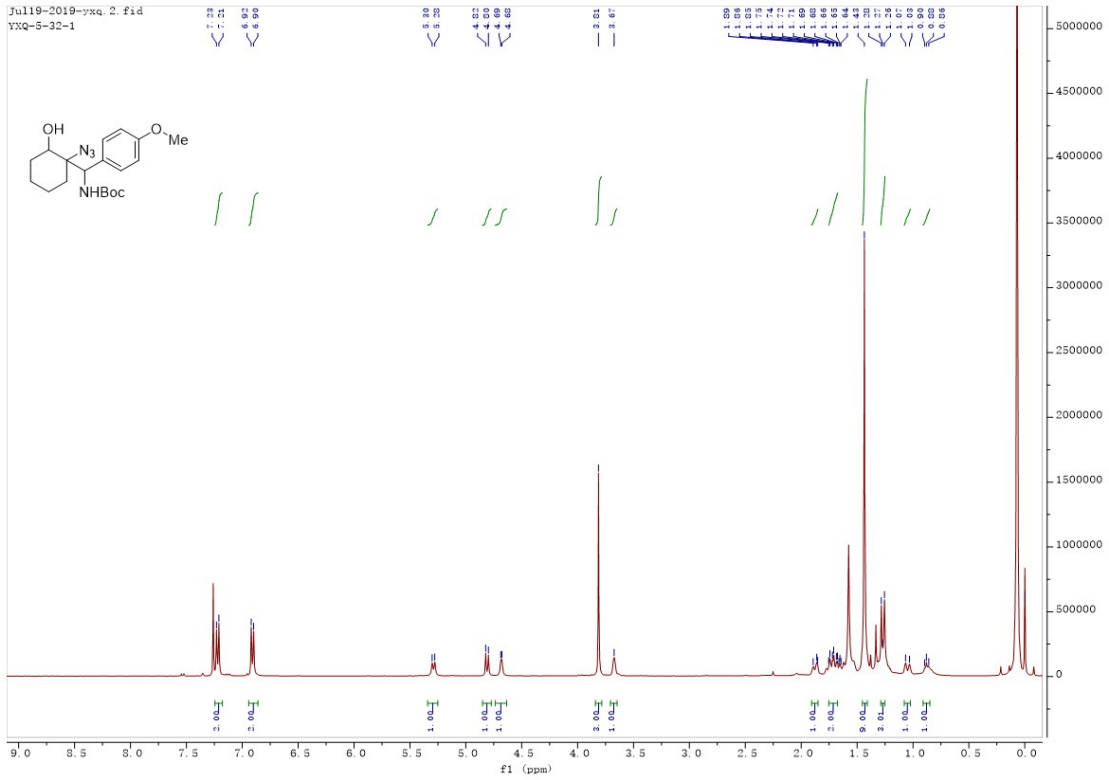


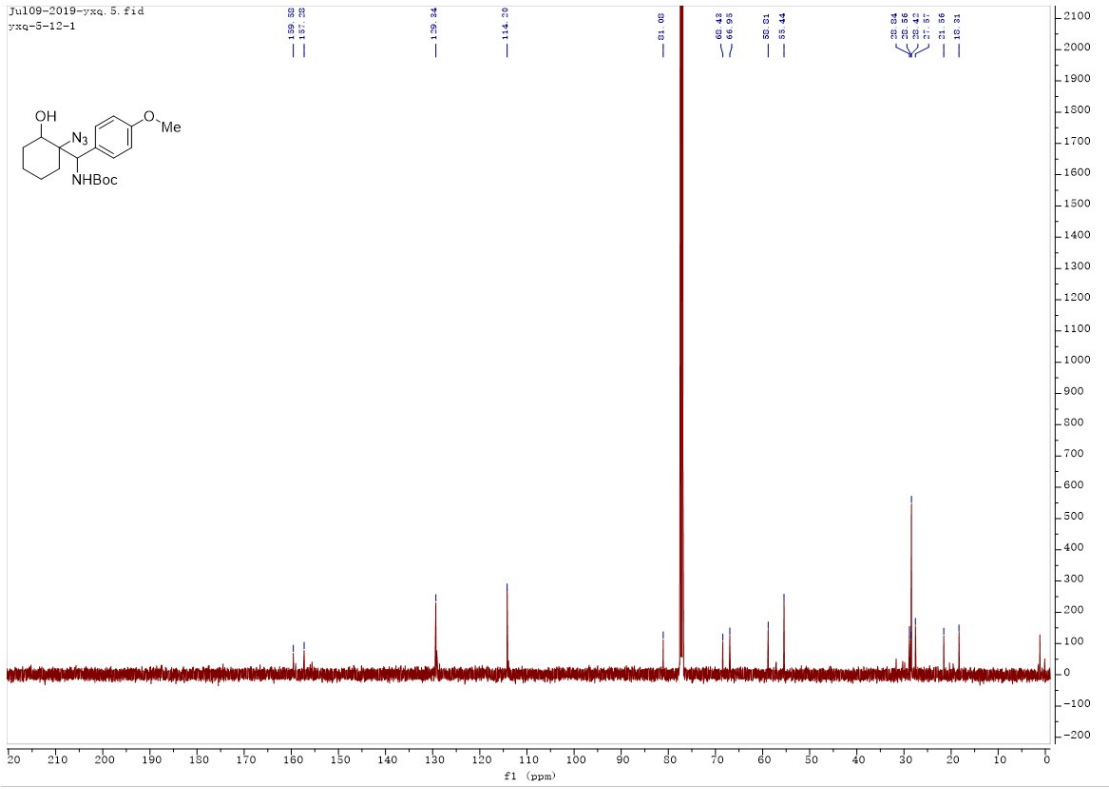
tert-butyl-((S)-(4-methoxyphenyl)((R)-2-oxo-1-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclohexyl)methyl)carbamate **(5a)**



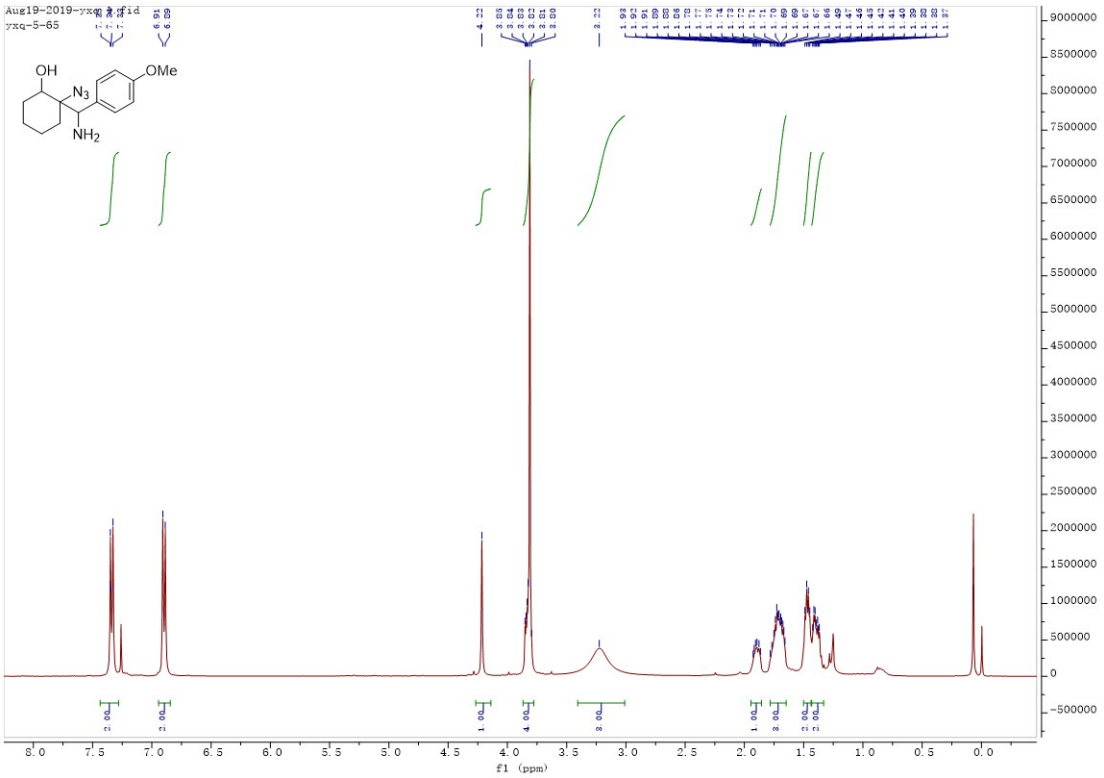


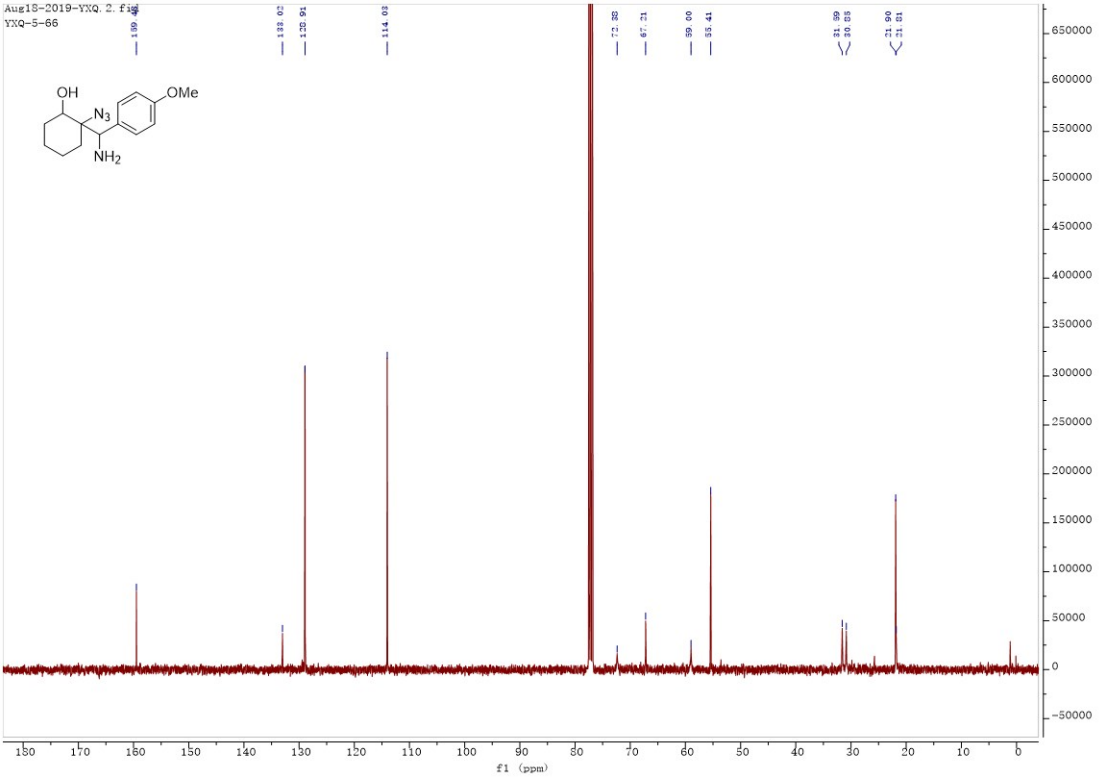
tert-butyl ((1S)-((1R)-1-azido-2-hydroxycyclohexyl)(4-methoxyphenyl)methyl)carbamate **(6a1)**



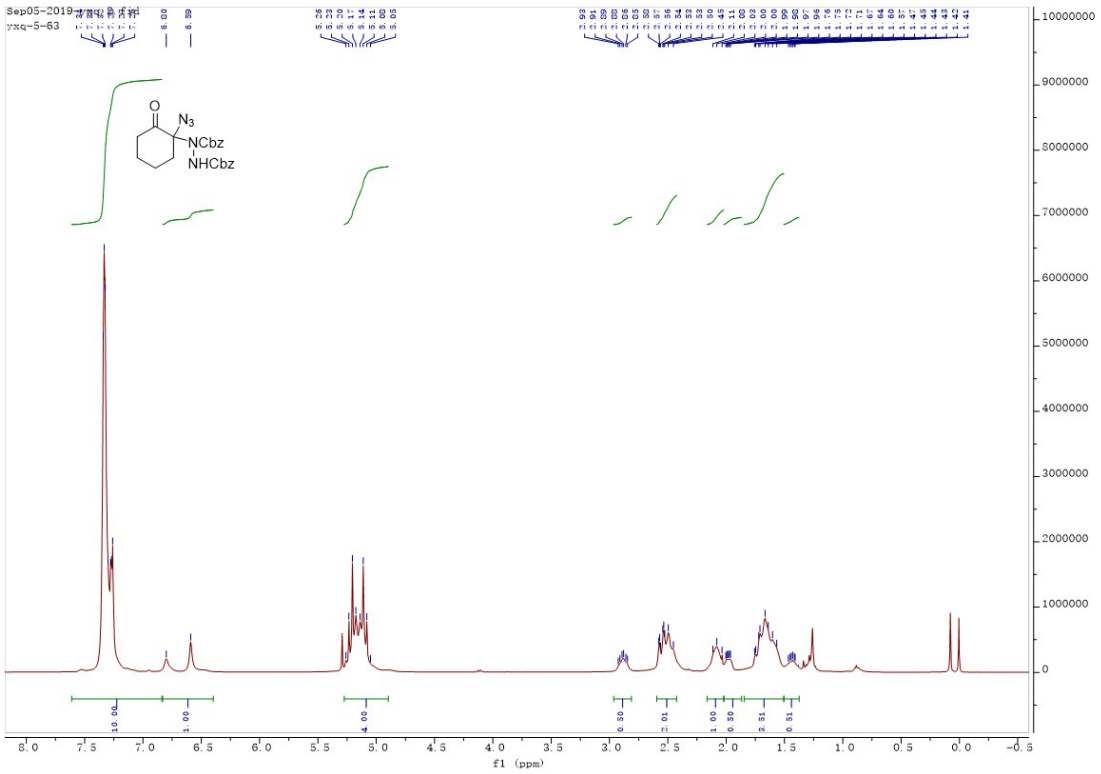


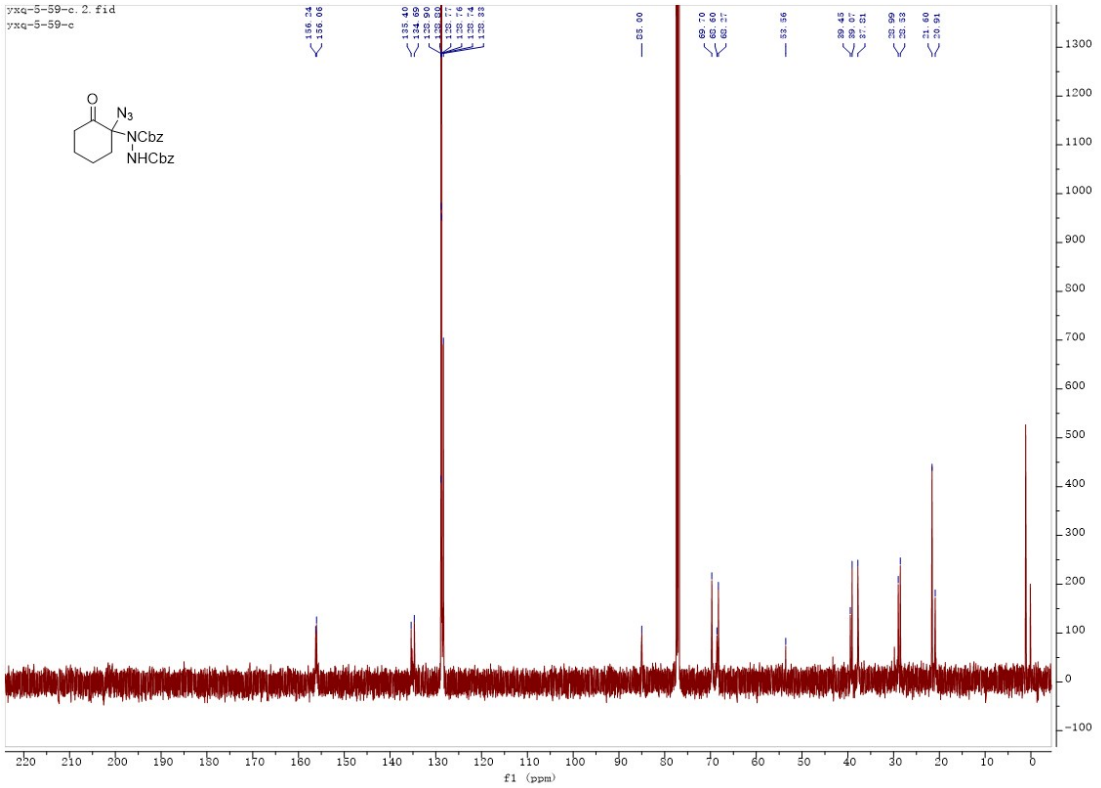
2-(amino(4-methoxyphenyl)methyl)-2-azidocyclohexan-1-ol **(7a)**



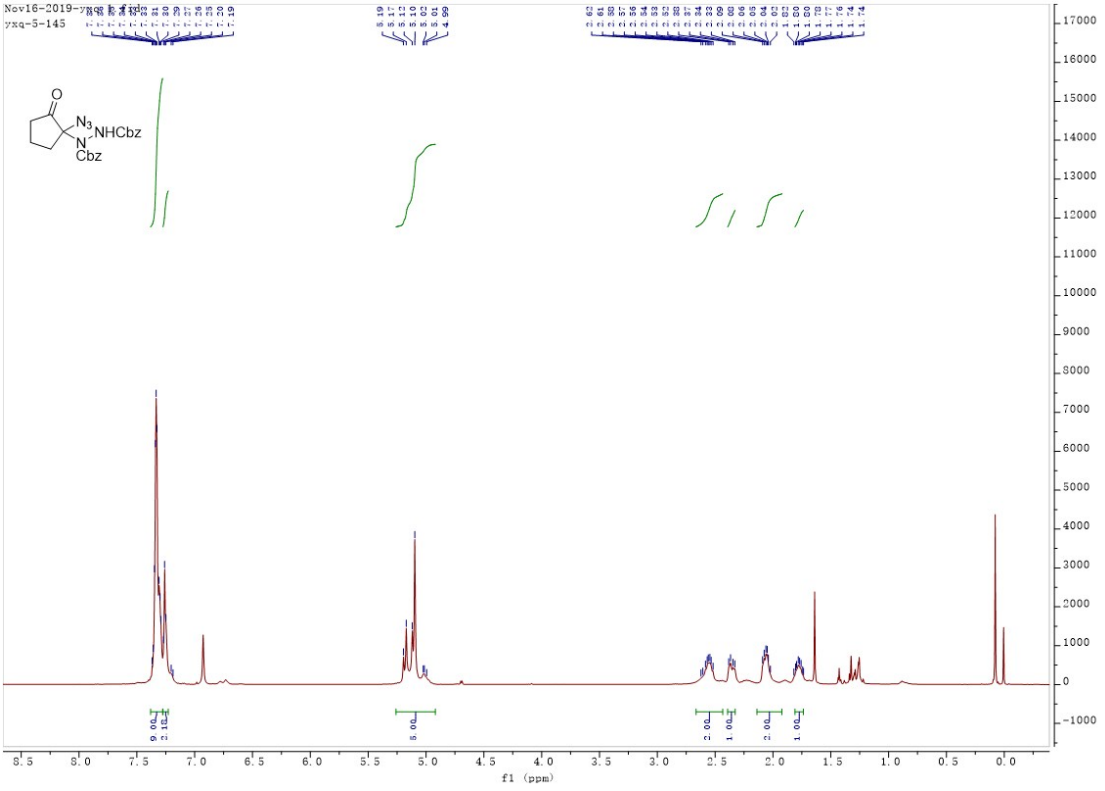


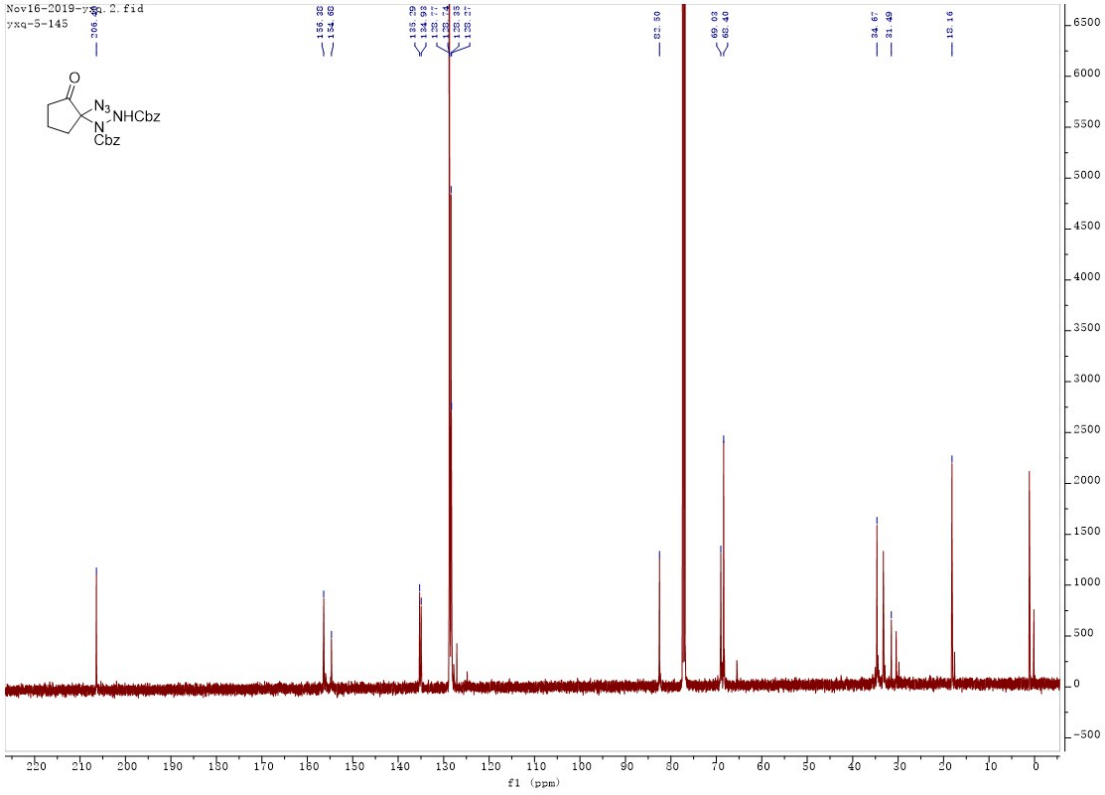
*di*benzyl 1-(1-azido-2-oxocyclohexyl)hydrazine-1,2-dicarboxylate **(9a)**





dibenzyl 1-(1-azido-2-oxocyclopentyl)hydrazine-1,2-dicarboxylate **(9b)**


yxq-5-145
O
N3
NHCbz
N
Cbz
f1 (ppm)


yxq-5-145
O
N3
NHCbz
N
Cbz
f1 (ppm)