Supporting Information

Transition-metal-free Oxidative Carboazidation of Acrylamides via Cascade C-N and C-C Bond-Forming Reactions

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1. General Methods

Unless stated otherwise, all reagents were purchased commercially without further purification. All reagents were weighed and handled in air at room temperature. All glassware was oven or flame dried immediately prior to use.

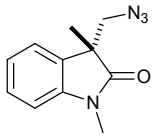
^{1}H NMR and ^{13}C NMR were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent. Chemical shifts are expressed in parts per million values (δ, ppm). ^{1}H NMR spectra were calibrated with $CDCl_3$ (δ= 7.26 ppm). ^{13}C-NMR spectra were obtained at 100 MHz and were calibrated with $CDCl_3$ (δ= 77.00 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet or unresolved, br= broad singlet, coupling constant(s) in Hz, integration). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. Purification was done by column chromatography on silica gel (200–300 mesh) with petroleum ether and ethyl acetate as the eluent to give the pure product.

2. Experimental Procedure

2.1 Synthesis of Azido Oxindoles:

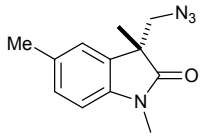
An oven-dried Schlenk tube was charge with **1** or **3** (0.5 mmol), NaN_3 (0.035g, 0.5 mmol), $K_2S_2O_8$ (2.0 equiv.) in acetone/H_2O (1:1, 5 mL).The reaction mixture was stirred at 80^{o}C for 8 h monitored by TLC. The mixture was allowed to cool to room temperature and was quenched with H_2O (10 mL).The mixture was extracted with EtOAc (3×10 mL). The combined organic layers were dried with Na_2SO_4, concentrated under reduced pressure, and dried under high vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 8:1) to obtain the desired products.

3. Characterization of the Compounds



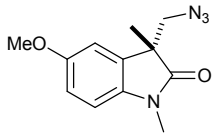
3-(Azidomethyl)-1,3-dimethylindolin-2-one (2a)[1]

Colorless liquid, (92% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.34 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.11(t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.67-3.61 (m, 2H), 3.24 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.2, 143.5, 131.4, 128.7, 123.1, 122.8, 108.4, 57.3, 48.8, 26.4, 20.5. HRMS m/z (ESI) calcd. for $C_{11}H_{12}N_4O$ $(M+Na)^+$: 239.0909, found 239.0902.



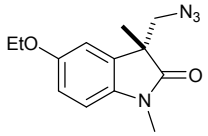
3-(Azidomethyl)-1,3,5-trimethylindolin-2-one (2b)[1]

Colorless liquid, (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.13-7.10 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.63 (s, 2H), 3.22 (s, 3H), 2.36 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.1, 141.1, 132.4, 131.4, 128.9, 123.9, 108.1, 57.3, 48.8, 26.4, 21.2, 20.5. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O$ $(M+Na)^+$: 253.1065, found 253.1054.



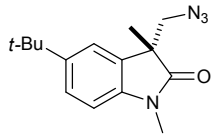
3-(Azidomethyl)-5-methoxy-1,3-dimethylindolin-2-one (2c) [1]

White solid, (96% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.91 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 2H), 3.22 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.8, 156.2, 136.9, 132.8, 112.7, 110.8, 108.7, 57.2, 55.9, 49.1, 26.5, 20.5. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O_2$ $(M+Na)^+$: 269.1014, found 269.1013.



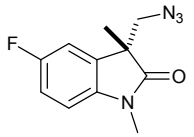
3-(Azidomethyl)-5-ethoxy-1,3-dimethylindolin-2-one (2d)

Colorless liquid, (93% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.83 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.95 (q, *J* = 13.6, 6.4 Hz, 2H), 3.55 (s, 2H), 3.14 (s, 3H), 1.34(t, *J* = 6.8 Hz, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.8, 155.5, 136.8, 132.7, 113.4, 111.5, 108.6, 64.2, 57.3, 49.1, 26.4, 20.5, 14.9. HRMS m/z (ESI) calcd. for $C_{13}H_{16}N_4O_2$ $(M+Na)^+$: 283.1171, found 283.1156.



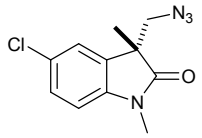
3-(Azidomethyl)-5-(tert-butyl)-1,3-dimethylindolin-2-one (2e) [1a]

Colorless liquid, (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.33 (d, *J* = 1.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.61 (q, *J* = 21.2, 12.0 Hz, 2H), 3.23 (s, 3H), 1.39 (s, 3H), 1.34(s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.3, 146.1, 141.1, 131.1, 125.3, 120.3, 107.8, 57.4, 49.0, 34.6, 31.6, 26.4, 20.5. HRMS m/z (ESI) calcd. for $C_{15}H_{20}N_4O$ $(M+Na)^+$: 295.1535, found 295.1524.



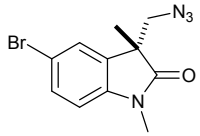
3-(Azidomethyl)-5-fluoro-1,3-dimethyli ndolin-2-one (2f) [1]

Yellow solid, (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.06-6.97 (m, 2H), 6.87-6.80 (m, 1H), 3.64 (s, 2H), 3.23 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.8, 159.4 (d, *J* = 240.0 Hz), 139.4 (d, *J* = 2.0 Hz), 131.1(d, *J* = 8.0 Hz), 114.7 (d, *J* = 5.0 Hz), 111.4 (d, *J* = 25.0 Hz), 108.8 (d, *J* = 8.0 Hz), 57.1, 49.2 (d, *J* = 2.0 Hz), 26.5, 20.4. HRMS m/z (ESI) calcd. for $C_{11}H_{11}FN_4O$ $(M+Na)^+$: 257.0815, found 257.0796.



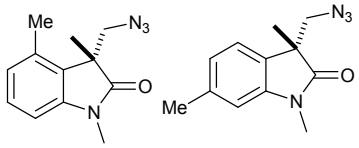
3-(Azidomethyl)-5-chloro-1,3- dimethylindolin-2-one (2g) [1a, 1b]

Colorless liquid, (86% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.64 (s, 2H), 3.23 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.7, 142.0, 133.1, 128.6, 128.2, 123.7, 109.3, 57.0, 49.9, 26.5, 20.4. HRMS m/z (ESI) calcd. for $C_{11}H_{11}ClN_4O$ $(M+Na)^+$: 273.0519, found 273.0512.



3-(Azidomethyl)-5-bromo-1,3-dimethylindolin-2-one (2h) [1a, 1b]

Colorless liquid, (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (dd, *J* =8.0, 1.6 Hz, 1H), 7.40 (d, *J* =2.0 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.67-3.61 (m, 2H), 3.22 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.6, 142.5, 133.5, 131.5, 126.4, 115.5, 109.8, 57.0, 48.9, 26.5, 20.4. HRMS m/z (ESI) calcd. for $C_{11}H_{11}BrN_4O$ $(M+Na)^+$: 317.0014, found 317.0002.



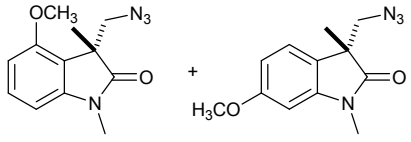
2i **2i'**

2i: 2i'= 2.2: 1

3-(Azidomethyl)-4-methyl-1, 3- dimethylindolin-2-one (2i major product) [1b]

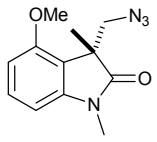
3-(Azidomethyl)-6-chloro-1, 3- dimethylindolin-2-one (2i' minor product) [1b]

Colorless liquid, (88% yield); **For 2i:** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 4.8 Hz, 1H), 3.87 (d, *J* = 12.0 Hz, 1H), 3.77 (d, *J* = 12.4 Hz, 1H), 3.24 (s, 3H), 2.41 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.4, 144.0, 134.3, 128.6, 125.3, 122.8, 106.1, 55.4, 49.8, 26.4, 20.5, 19.0. **For 2i':** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.16 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 3.62 (s, 2H), 3.22 (s, 3H), 2.41 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.5, 143.6, 138.9, 128.5, 128.0, 123.3, 109.3, 57.4, 48.6, 26.3, 21.8, 18.2. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O$ $(M+Na)^+$: 253.1065, found 253.1048.



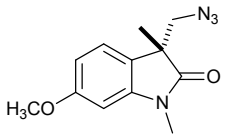
2j **2j'**

2j: 2j'= 2 : 1



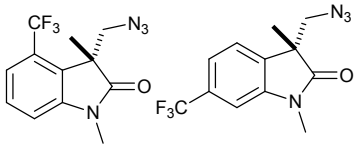
3-(Azidomethyl)-4-methoxy-1,3-dimethylindolin-2-one (2j major product) [1c]

Colorless liquid, (60% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (t, *J* =8.0 Hz, 1H), 6.65 (d, *J* =7.6 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 3.99 (d, *J* = 11.6 Hz, 1H), 3.88 (s, 3H), 3.64 (d, *J* = 11.6 Hz, 1H), 3.22 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.8, 156.2, 145.0, 130.0, 116.3, 105.8, 101.8, 55.4, 54.9, 49.4, 26.6, 18.8. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O_2$ $(M+Na)^+$: 269.1014, found 269.1004.



3-(Azidomethyl)-6-methoxy-1,3-dimethylindolin-2-one (2j' minor product) [1c]

Colorless liquid, (29% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.17 (d, *J* =8.0 Hz, 1H), 6.60 (dd, *J* =8.0, 2.0 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 3H), 3.60 (s, 2H), 3.22 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.8, 160.6, 144.8, 123.7, 123.2, 106.5, 96.5, 57.5, 55.6, 48.4, 26.4, 20.6. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O_2$ $(M+Na)^+$: 269.1014, found 269.1008.

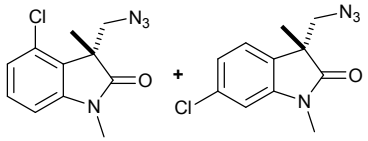


2k: 2k' = 1.4: 1

3-(Azidomethyl)-1,3-dimethyl-4-(trifluoromethyl)indolin-2-one (2k major product)

3-(Azidomethyl)-1,3-dimethyl-6-(trifluoromethyl)indolin-2-one (2k' minor product)

Yellow liquid, (75% yield); **For 2k:** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.48 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 3.94 (d, *J* = 12.0 Hz, 1H), 3.82 (d, *J* = 12.0 Hz, 1H), 3.29 (s, 3H), 1.44 (s, 3H). **For 2k':** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, *J* = 6.8 Hz, 2H), 7.09 (s, 1H), 3.68 (s, 2H), 3.28(s, 3H), 1.40 (s, 3H). HRMS m/z (ESI) calcd. for $C_{12}H_{11}F_3N_4O$ $(M+Na)^+$: 307.0783, found 307.0779.

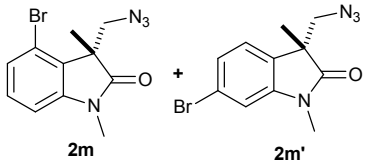


2l: 2l'= 3.3: 1

3-(Azidomethyl)-4-chloro-1,3- dimethylindolin-2-one (2l major product)

3-(Azidomethyl)-6-chloro-1,3- dimethylindolin-2-one (2l' minor product)

Yellow liquid, (84% yield); **For 2l:** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (t, *J* =8.0 Hz, 1H), 7.04 (d, *J* =8.0 Hz, 1H), 6.80(d, *J* = 7.6 Hz, 1H), 4.18 (d, *J* = 12.0 Hz, 1H), 3.72 (d, *J* = 12.0 Hz, 1H), 3.25 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.8, 145.6, 130.7, 130.0, 127.1, 124.0, 123.7, 109.2, 106.9, 54.3, 50.5, 26.7, 18.2. **For 2m':** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.20 (d, *J* =7.6 Hz, 1H), 7.08 (dd, *J* =8.0, 1.6 Hz, 1H), 6.89(d, *J* = 1.6 Hz, 1H), 3.63 (s, 2H) , 3.22 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.1, 144.7, 134.5, 131.1, 129.7, 124.4, 122.6, 107.2, 57.1, 48.5, 26.5, 20.4. HRMS m/z (ESI) calcd. for $C_{11}H_{11}ClN_4O$ $(M+Na)^+$: 273.0519, found 273.0513.



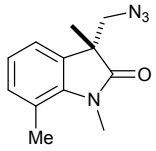
2m: 2m'= 3.1: 1

3-(Azidomethyl)-4- bromo -1,3- dimethylindolin-2-one (2m major product)

3-(Azidomethyl)-6- bromo -1,3- dimethylindolin-2-one (2m' minor product)

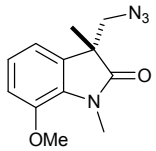
Yellow liquid, (87% yield); **For 2m:** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (d, *J* = 4.4 Hz, 2H),

6.86- 6.82 (m, 1H), 4.29 (d, J = 12.0 Hz, 1H), 3.68 (d, J = 11.6 Hz, 1H), 3.24 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.9, 145.9, 130.2, 128.8, 126.8, 118.9, 107.4, 54.0, 51.2, 26.6, 18.2. **For 2k:** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.24 (dd, J =8.0, 1.6 Hz, 1H), 7.14 (d, J =7.6 Hz, 1H), 7.04 (s, 1H), 3.63 (s, 2H) , 3.22 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.0, 144.8, 130.4, 128.8, 125.8, 111.9, 107.4, 57.1, 48.6, 26.5, 20.3. HRMS m/z (ESI) calcd. for $C_{11}H_{11}BrN_4O$ $(M+Na)^+$: 317.0014, found 317.0000.



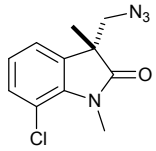
3-(Azidomethyl)-1,3,7-trimethylindolin-2-one (2n) [1a, 1b]

Colorless liquid, (65% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.11 (d, J = 7.2 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 3.66- 3.59 (m, 2H), 3.52 (s, 3H), 2.60 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 179.0, 141.3, 132.4, 132.0, 122.7, 120.9, 120.0, 57.5, 48.1, 29.7, 20.9, 19.1. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O$ $(M+Na)^+$: 253.1065, found 253.1056.



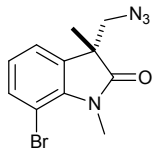
3-(Azidomethyl)-7-methoxy-1,3-dimethylindolin-2-one (2o) [1b]

White solid, (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.05 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 7.6 Hz, 2H), 3.87 (s, 3H), 3.65- 3.58 (m, 2H), 3.51 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.4, 145.5, 133.0, 131.3, 123.4, 115.6, 112.5, 57.4, 55.9, 48.8, 29.7, 20.7. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O_2$ $(M+Na)^+$: 269.1014, found 269.0094.



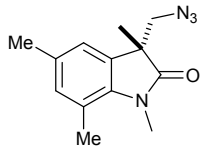
3-(Azidomethyl)-7-chloro-1,3- dimethylindolin-2-one (2p) [1b]

Colorless liquid, (79% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 3.64 (m, 2H), 3.61 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.4, 139.4, 134.2, 131.0, 123.6, 121.5, 115.9, 57.4, 48.5, 29.8, 20.8. HRMS m/z (ESI) calcd. for $C_{11}H_{11}ClN_4O$ $(M+Na)^+$: 273.0519, found 273.0507.



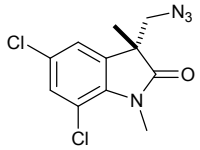
3-(Azidomethyl)-7-bromo-1,3-dimethylindolin-2-one (2q) [1a, 1b]

Colorless liquid, (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43 (d, J =8.0 Hz, 1H), 7.20 (d, J = 6.8 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 3.70-3.60 (m, 2H), 3.62 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.6, 140.9, 134.5, 134.4, 123.9, 122.1, 102.8, 57.4, 48.5, 30.0, 20.8. HRMS m/z (ESI) calcd. for $C_{11}H_{11}BrN_4O$ $(M+Na)^+$: 317.0014, found 317.0000.



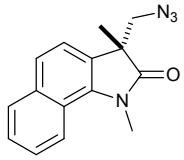
3-(Azidomethyl)-1,3,5,7-tetramethylindolin-2-one (2r) [1b, 1c]

Colorless liquid, (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.91 (s, 1H), 6.86 (s, 1H), 3.65-3.57 (m, 2H), 3.49 (s, 3H), 2.55 (s, 3H), 2.30 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.9, 138.8, 132.9, 132.2, 132.1, 121.6, 119.7, 57.5, 48.1, 29.7, 20.9, 20.8, 18.9. HRMS m/z (ESI) calcd. for $C_{13}H_{16}N_4O$ $(M+Na)^+$: 267.1222, found 267.1205.



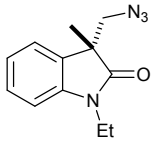
3-(Azidomethyl)-5,7-dichloro-1,3- dimethylindolin-2-one (2s)

Yellow solid, (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (s, 1H), 7.15 (s, 1H), 3.76- 3.59 (m, 2H), 3.59 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.0, 138.2, 135.5, 130.4, 128.3, 122.2, 116.2, 57.1, 48.7, 29.7, 20.7. HRMS m/z (ESI) calcd. for $C_{11}H_{10}Cl_2N_4O$ $(M+Na)^+$: 307.0129, found 307.0129.



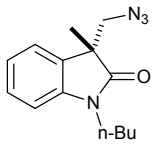
3-(Azidomethyl)-1,3-dimethyl-1H-benzo[g]indol-2(3H)-one (2t) [1a, 1b]

Yellow solid, (94% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 4.20 (d, J = 11.6 Hz, 1H), 3.68 (d, J = 12.0 Hz, 1H), 3.57 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.4, 136.4, 135.3, 133.5, 127.0, 126.9, 122.9, 119.8, 108.9, 62.1, 48.3, 29.9, 27.6. HRMS m/z (ESI) calcd. for $C_{15}H_{14}N_4O$ $(M+Na)^+$:289.1065, found 289.1061.



3-(Azidomethyl)-1-ethyl-3-methylindolin-2-one (4a) [1a]

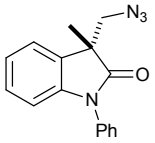
Yellow liquid, (91% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.34-7.28 (m, 2H), 7.10 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 3.87-3.71 (m, 2H), 3.63 (s, 3H), 1.37 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.8, 142.6, 131.7, 128.6, 123.2, 122.6, 108.5, 57.4, 48.7, 34.8, 20.4, 12.6. HRMS m/z (ESI) calcd. for $C_{12}H_{14}N_4O$ $(M+Na)^+$: 253.1065, found 253.1060.



3-(Azidomethyl)-1-(n-Butyl)-3-methylindolin-2-one (4b)

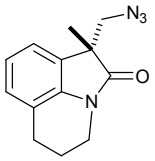
Yellow liquid, (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33-7.27 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 3.81-3.66 (m, 2H), 3.63 (s, 2H), 1.73-1.64 (m, 2H), 1.44-1.34 (m,

2H), 1.37 (s, 3H), 0.96 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.1, 143.0, 131.6, 128.6, 123.1, 122.5, 108.7, 57.4, 48.7, 39.8, 29.4, 20.6, 20.3, 13.8. HRMS m/z (ESI) calcd. for $C_{14}H_{18}N_4O$ $(M+Na)^+$: 281.1378, found 281.1378.



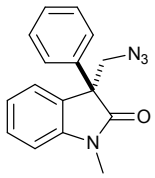
3-(Azidomethyl)-3-methyl-1-phenylindolin-2-one (4c) [1c]

Yellow liquid, (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55-7.52 (m, 2H), 7.43 (d, J = 7.6 Hz, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.28-7.23 (m, 1H), 7.14 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 3.78 (d, J = 12.0 Hz, 1H), 3.71 (d, J = 11.6 Hz, 1H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.7, 143.6, 134.4, 131.2, 129.6, 128.6, 128.2, 126.6, 123.3, 123.2, 109.7, 57.7, 49.0, 20.7. HRMS m/z (ESI) calcd. for $C_{16}H_{14}N_4O$ $(M+Na)^+$: 301.1065, found 301.1058.



1-(Azidomethyl)-1-methyl-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (4f) [1]

Colorless liquid, (93% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.12 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 3.79-3.69 (m, 2H), 3.63 (s, 2H), 2.85-2.75 (m, 2H), 2.08-1.98 (m, 2H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 177.0, 139.2, 130.6, 127.5, 122.3, 120.9, 120.5, 57.2, 50.1, 39.0, 24.6, 21.2, 20.3. HRMS m/z (ESI) calcd. for $C_{13}H_{14}N_4O$ $(M+Na)^+$: 265.1065, found 265.1066.



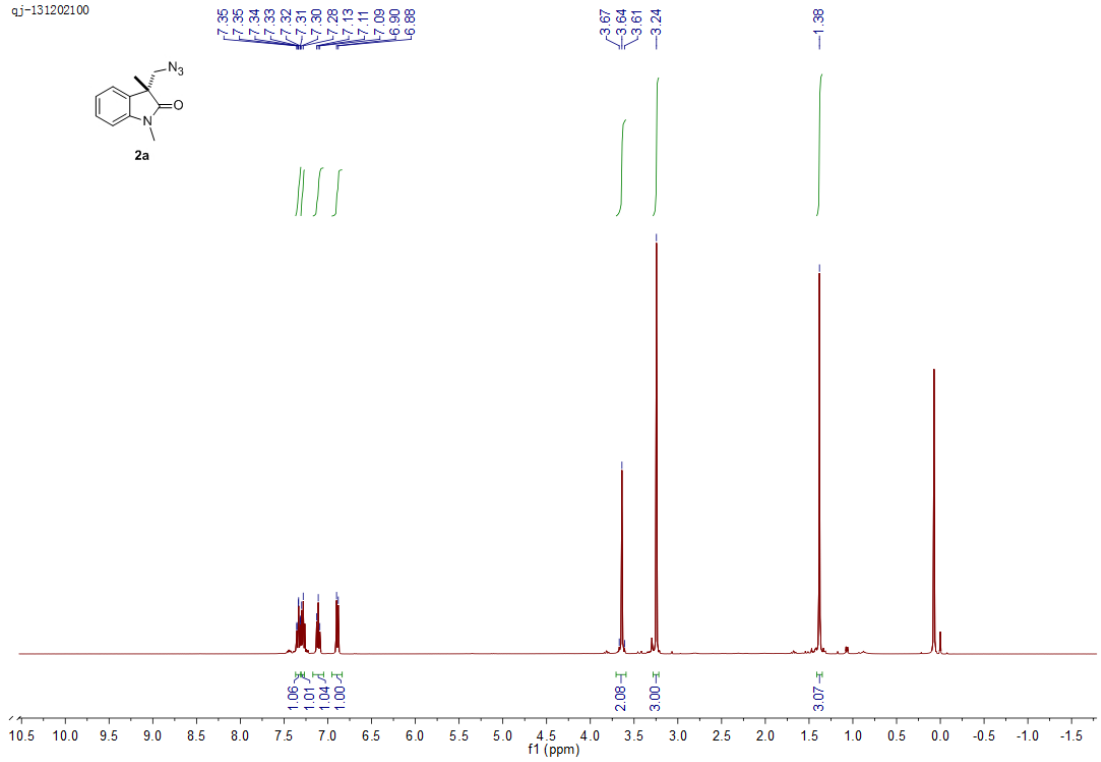
3-(Azidomethyl)-1-methyl-3-phenylindolin-2-one (4g)[1a]

Colorless liquid, (71% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.40 (m, 4H), 7.34-7.29 (m, 3H), 7.19 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 4.09 (s, 2H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 176.3, 144.3, 136.6, 129.4, 129.2, 128.8, 128.1, 127.1, 125.4, 122.8, 108.7, 57.2, 56.6, 26.6. HRMS m/z (ESI) calcd. for $C_{16}H_{14}N_4O$ $(M+Na)^+$: 301.1065, found 301.1058.

4. References

(1) *(a)* Y. Yuan, T. Shen, K. Wang, N. Jiao. *Chem. Asian J.* 2013, **8**, 2932. *(b)* Y. Li, M. Sun, H. Wang, Q. Tian, S. Yang. *Angew. Chem. Int. Ed.* 2013, **52**, 3972. *(c)* K. Matcha, R. Narayan, A. P. Antonchick, *Angew. Chem. Int. Ed.* 2013, **52**, 7985.

5. NMR Charts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7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.13
7.11
7.09
6.90
6.88
3.67
3.64
3.61
3.24
1.38
2a
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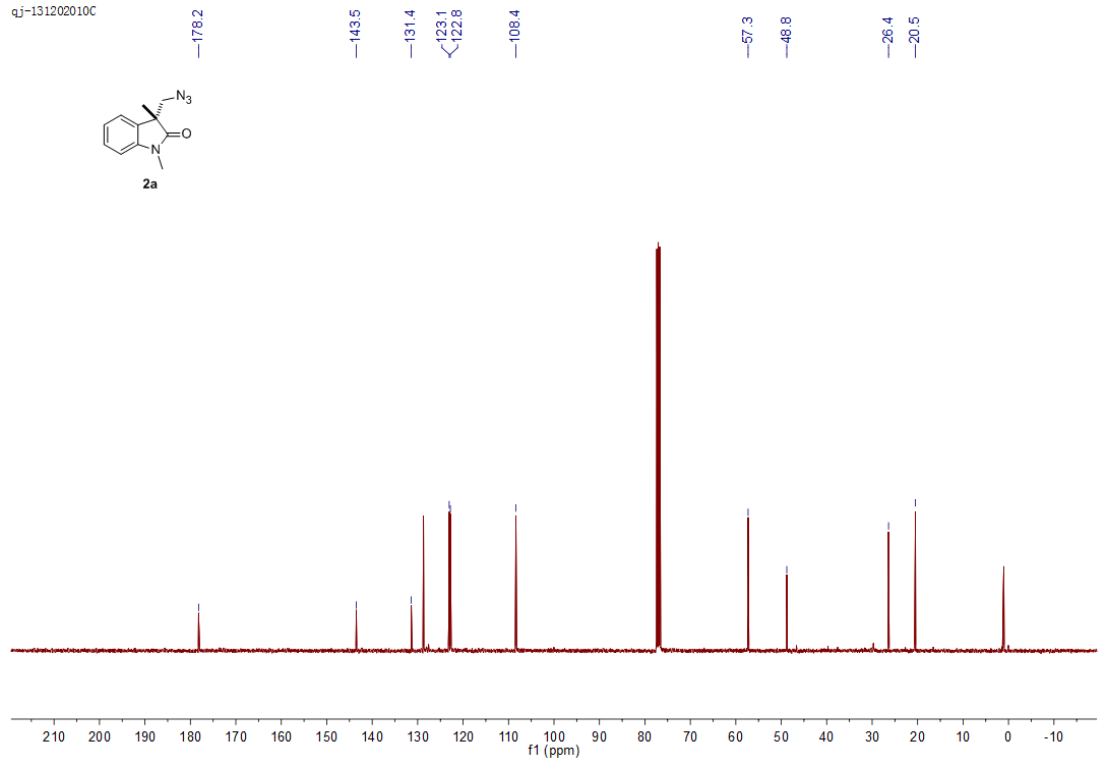
1.01
1.04
1.00
2.08
3.00
3.07
f1 (ppm)


qj-131202010C
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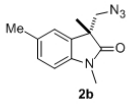
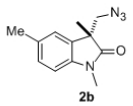
143.5
131.4
123.1
122.8
108.4
57.3
48.8
26.4
20.5
2a
f1 (ppm)

qj-13121301



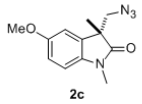
2b

qj-13121301c



2b

qj-14010801



2c

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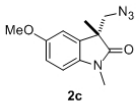

2c

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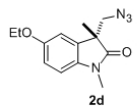

2d

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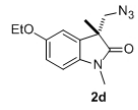
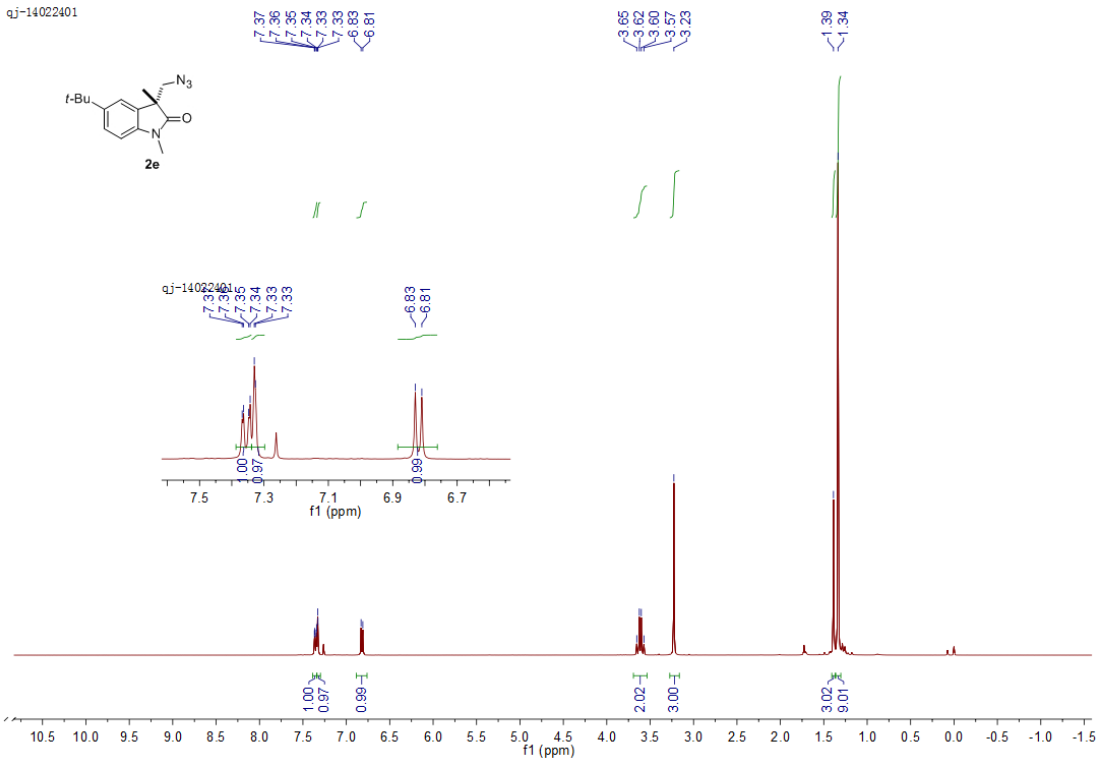


2d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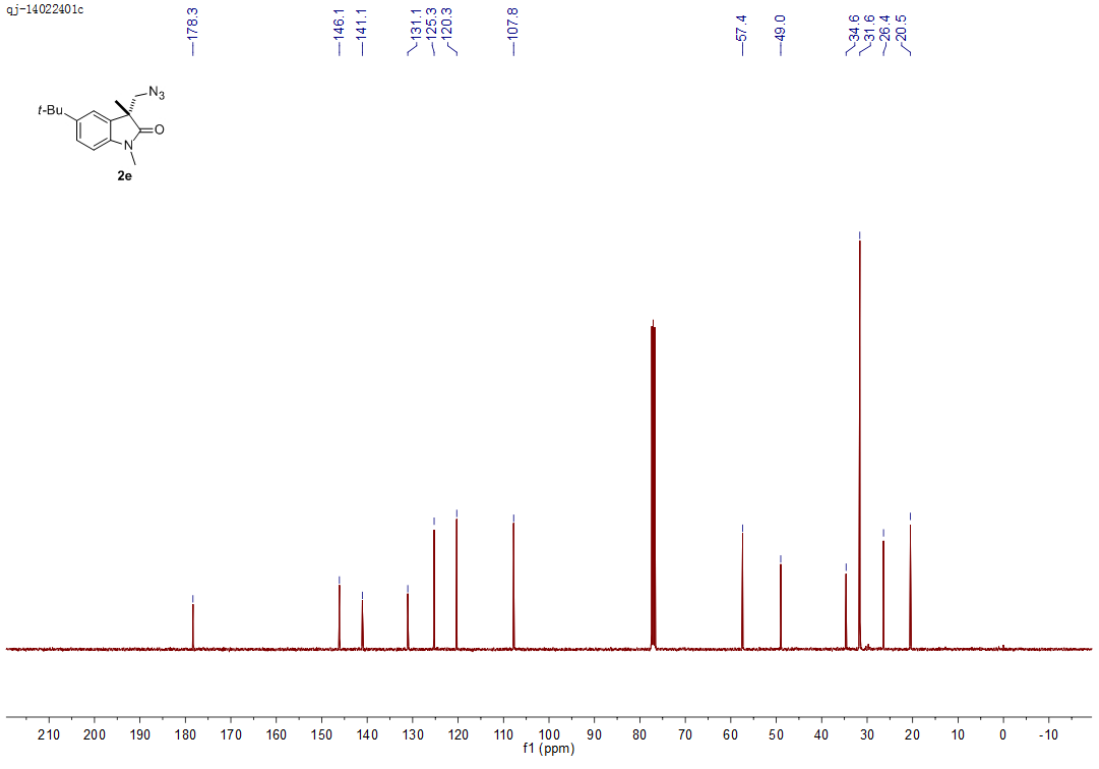
7.36
7.35
7.34
7.33
6.83
6.81
3.65
3.62
3.60
3.57
3.23
1.39
1.34
t-Bu
N3
O
N
2e
1.00
0.97
0.99
2.02
3.00
3.02
9.01
f1 (ppm)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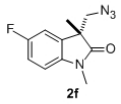
131.1
125.3
120.3
107.8
57.4
49.0
34.6
31.6
26.4
20.5
t-Bu
N3
O
N
2e
f1 (ppm)

qj-13122401



2f

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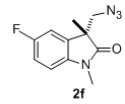
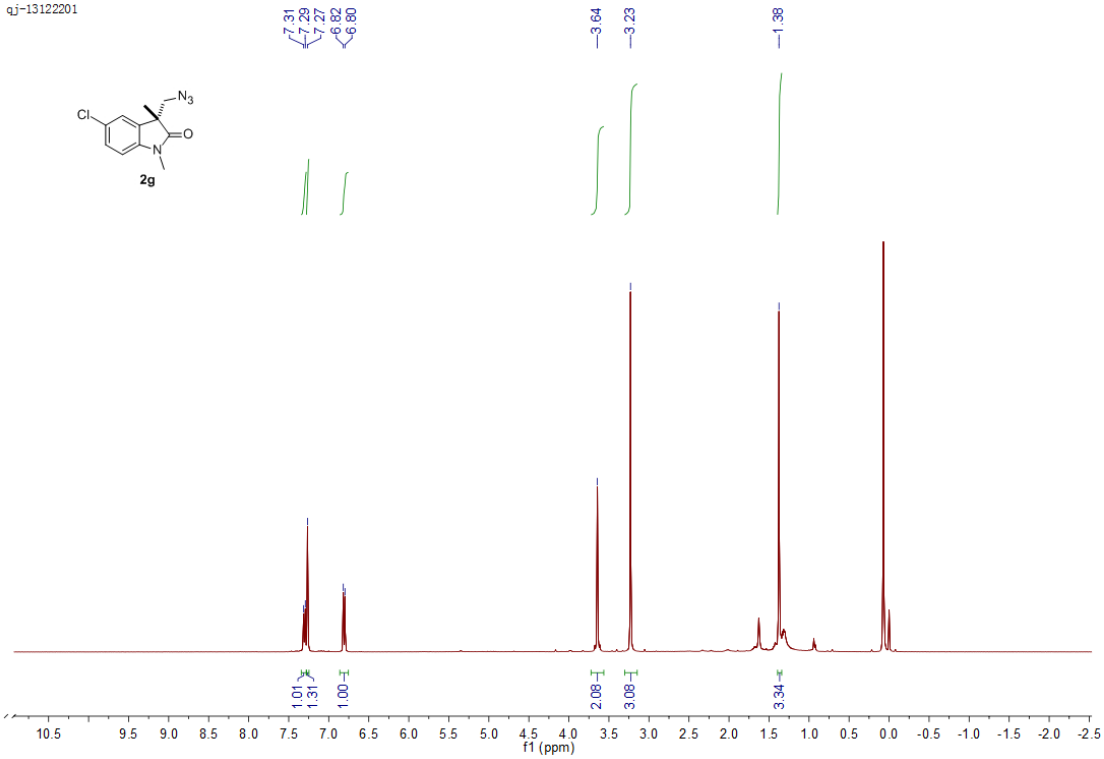
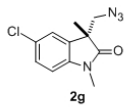


2f

qj-13122201



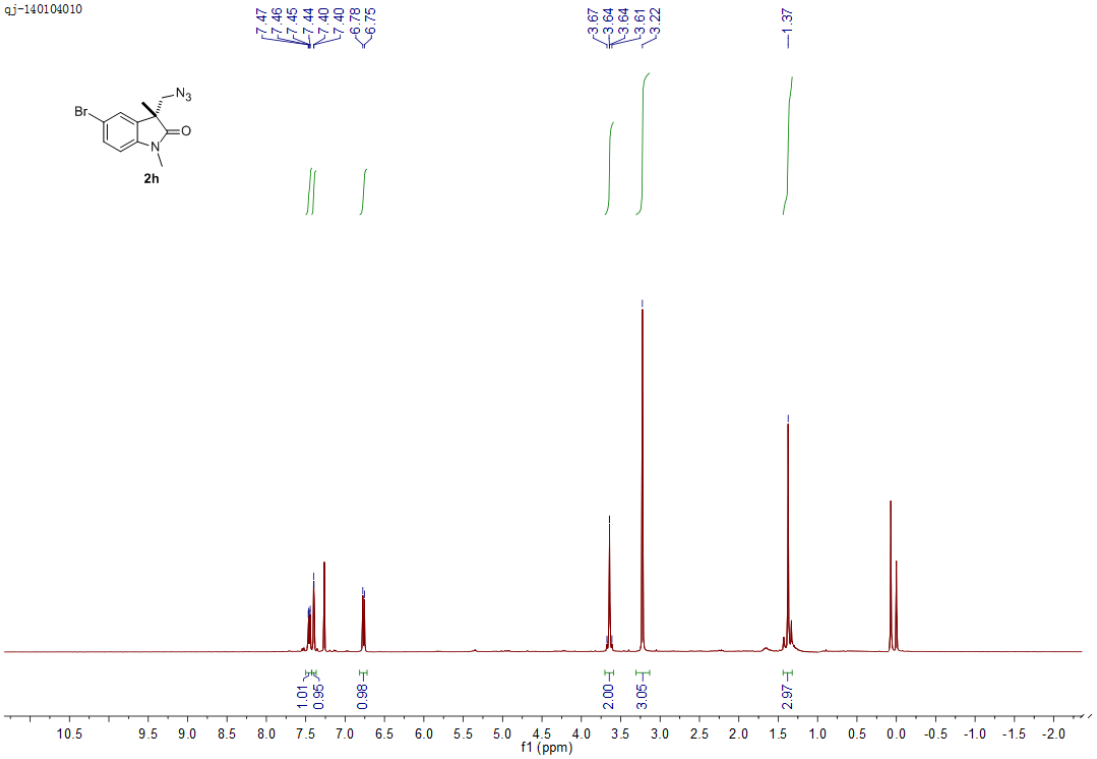


2g

qj-131222011c

2g

qj-140104010



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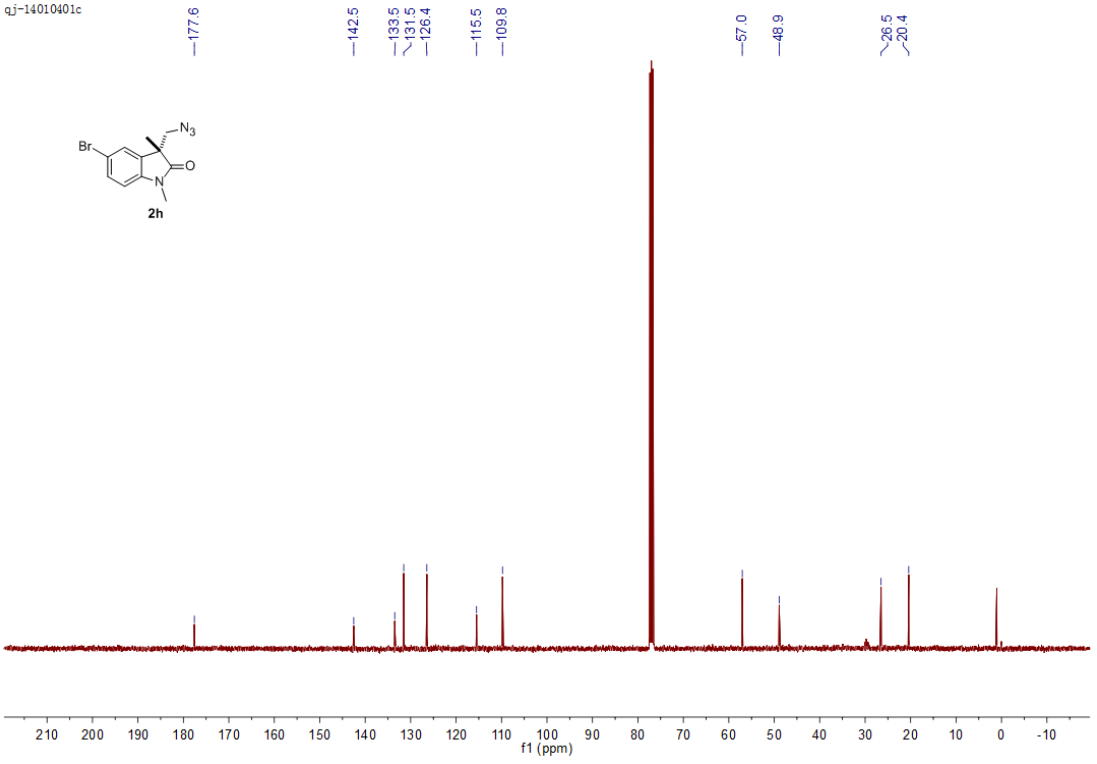

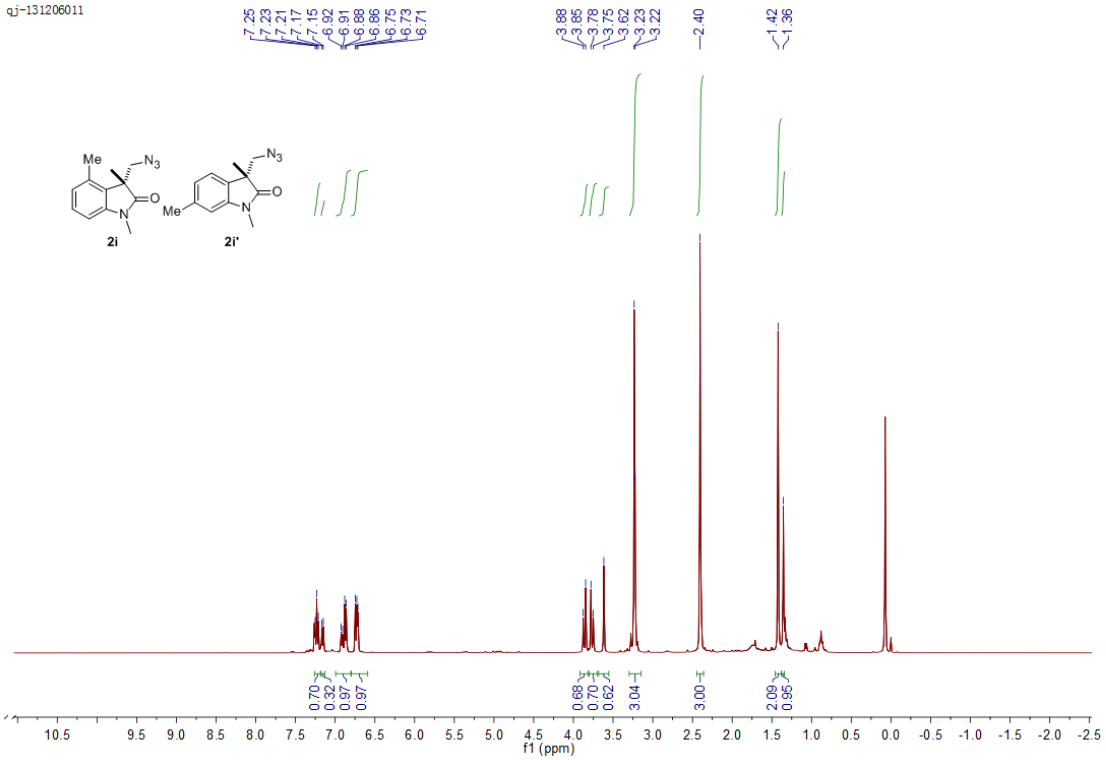
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7.23
7.21
7.17
7.15
6.92
6.91
6.88
6.86
6.75
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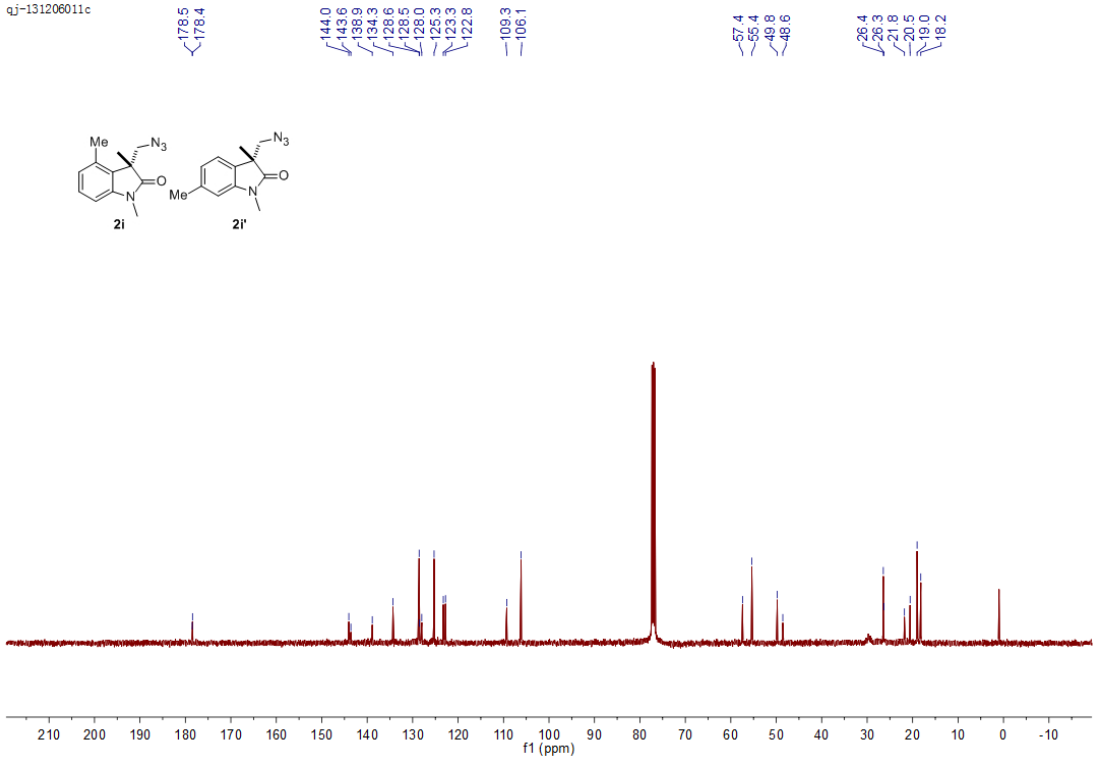
3.88
3.85
3.78
3.75
3.62
3.23
3.22
2.40
1.42
1.36
Me
N3
O
N
Me
2i
2i'
0.70
0.32
0.97
0.97
0.68
0.70
0.62
3.04
3.00
2.09
0.95
f1 (ppm)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178.4
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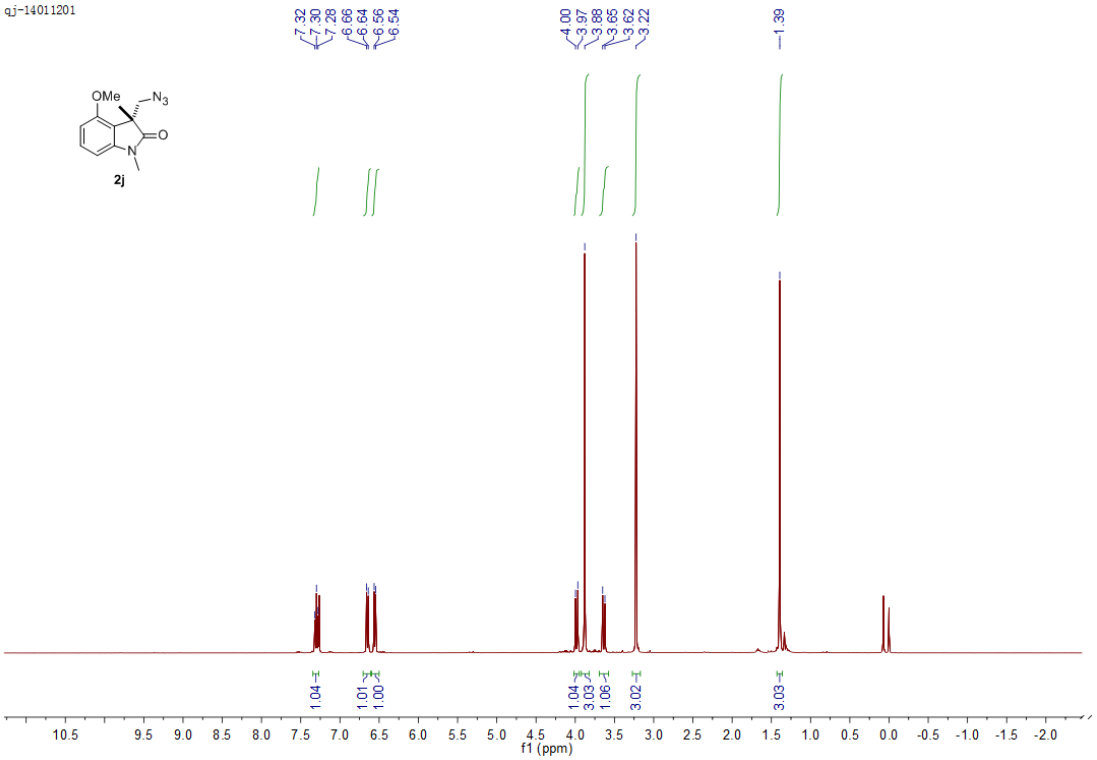
143.6
138.9
134.3
128.6
128.5
128.0
125.3
123.3
122.8
109.3
106.1
57.4
55.4
49.8
48.6
26.4
26.3
21.8
20.5
19.0
18.2
Me
N3
O
N
Me
2i
2i'
f1 (ppm)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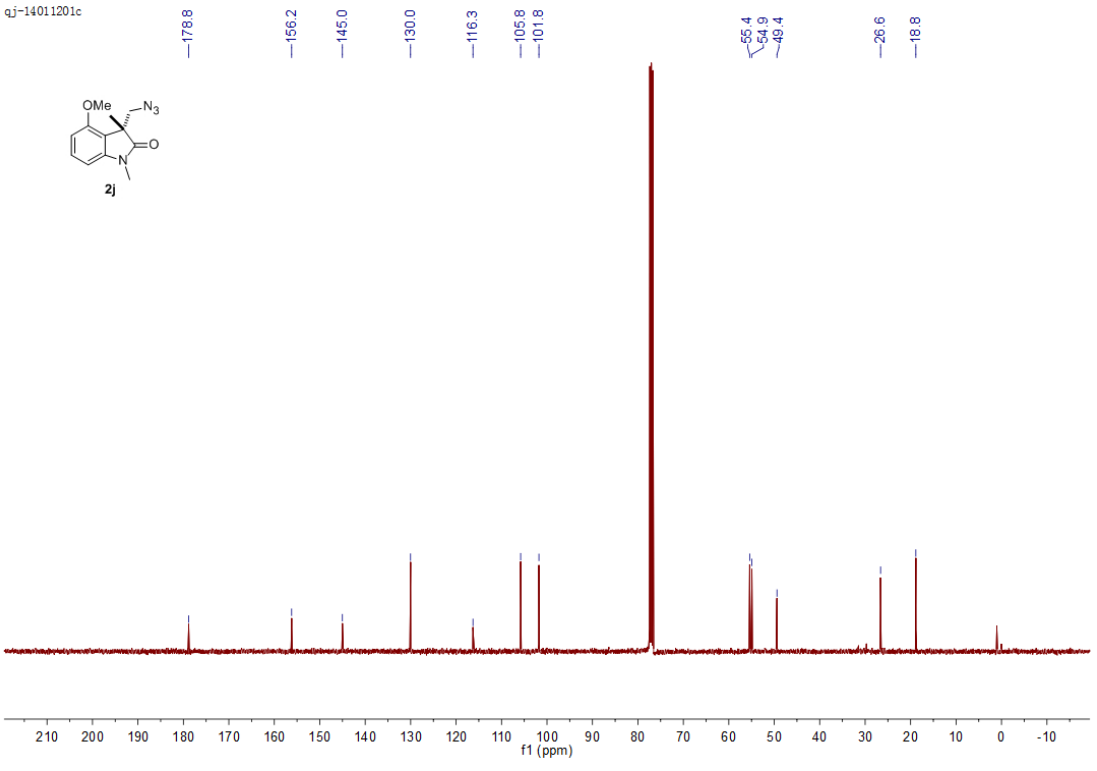
7.32
7.30
7.28
6.66
6.64
6.56
6.54
4.00
3.97
3.88
3.65
3.62
3.22
1.39
OMe
N3
O
N
2j
1.04
1.01
1.00
1.04
3.03
1.06
3.02
3.03
f1 (ppm)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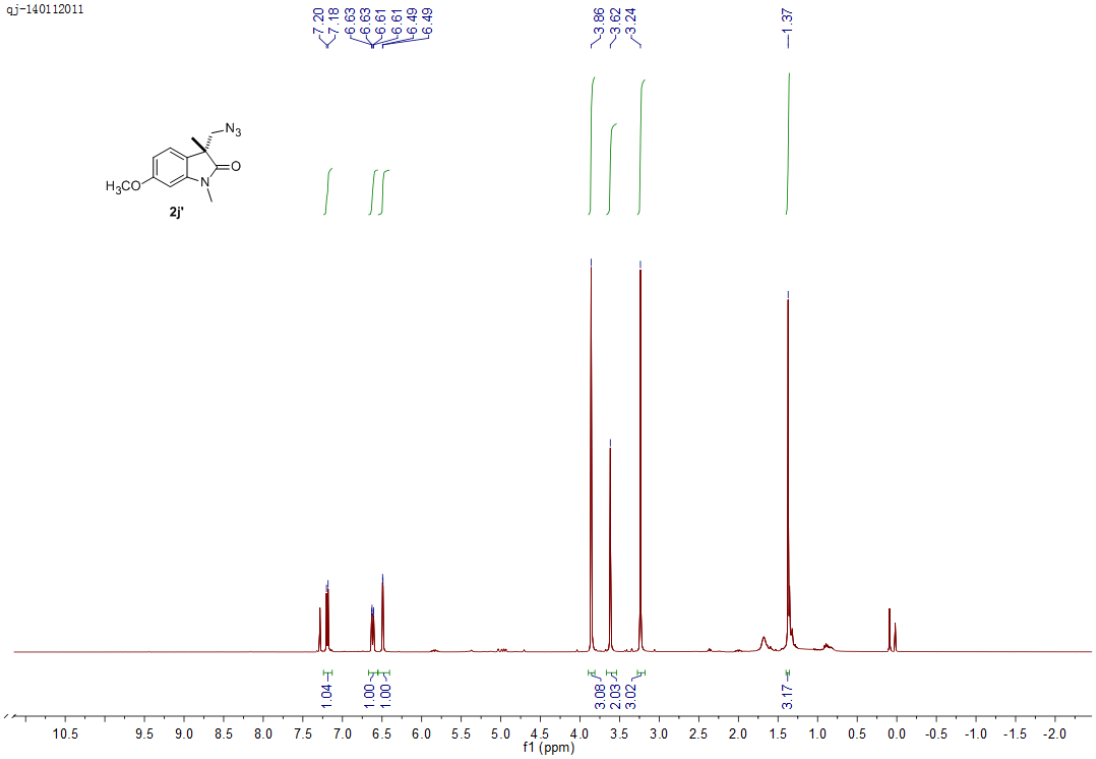
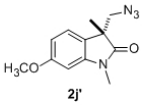
178.8
156.2
145.0
130.0
116.3
105.8
101.8
55.4
54.9
49.4
26.6
18.8
OMe
N3
O
N
2j
f1 (ppm)

qj-140112011



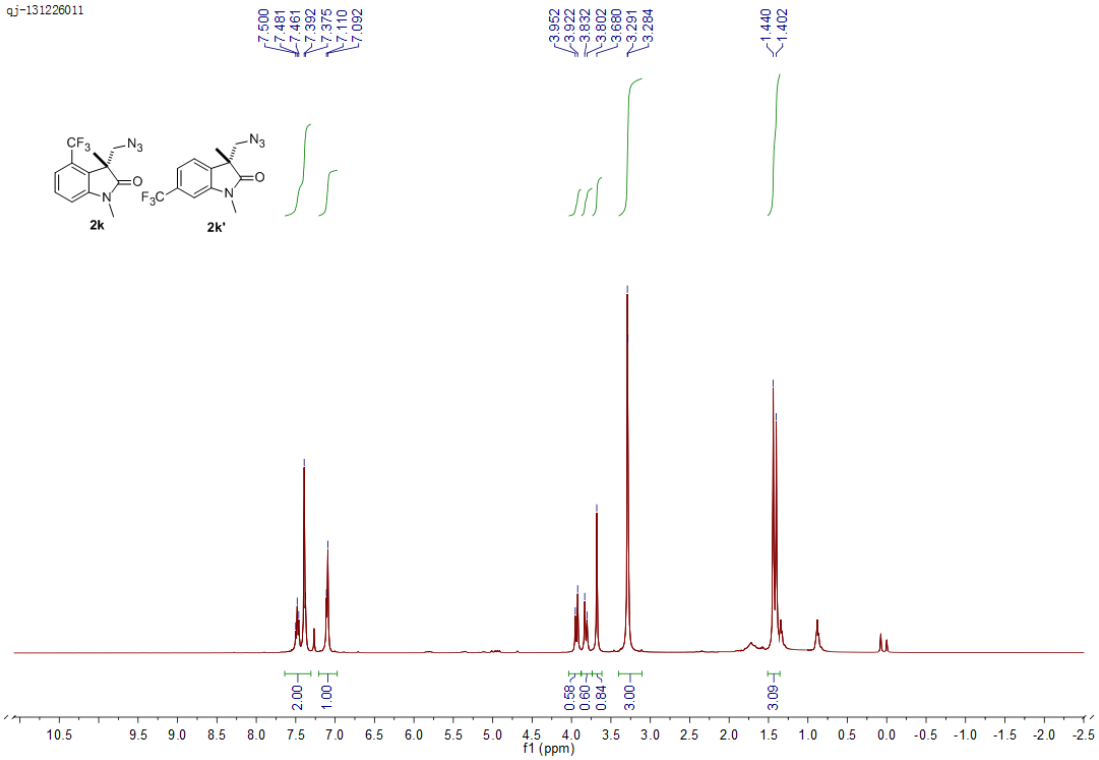


2j'

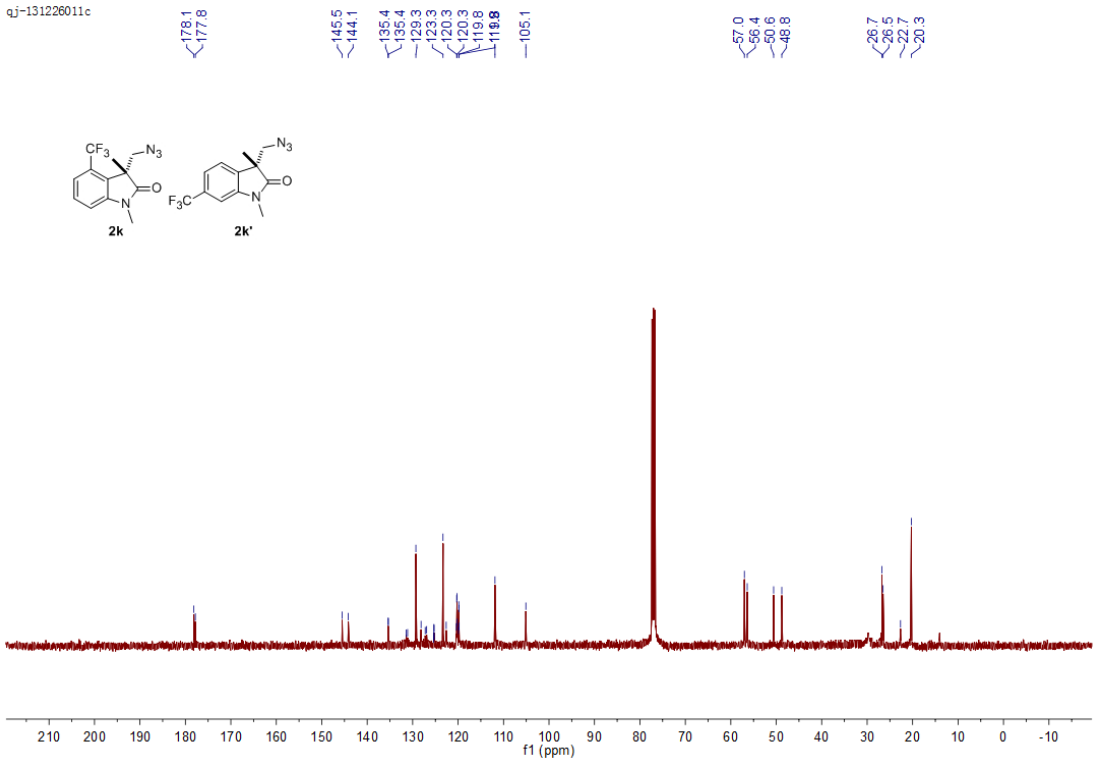
qj-140112011c

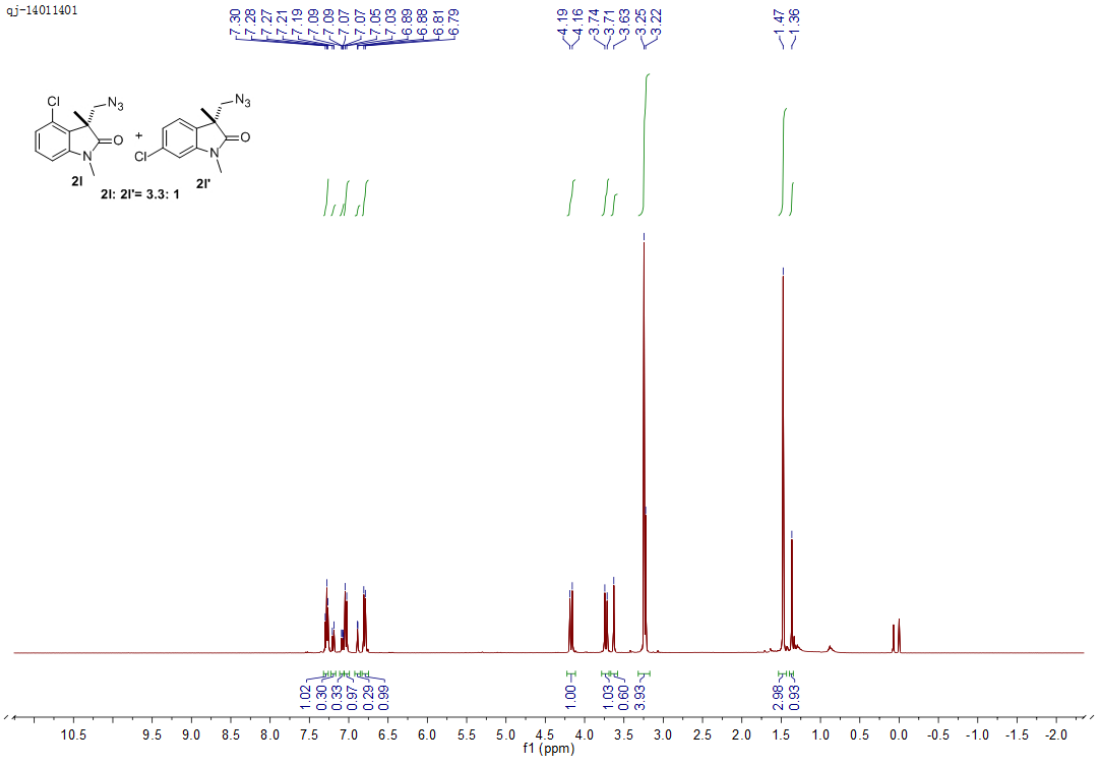
2j'

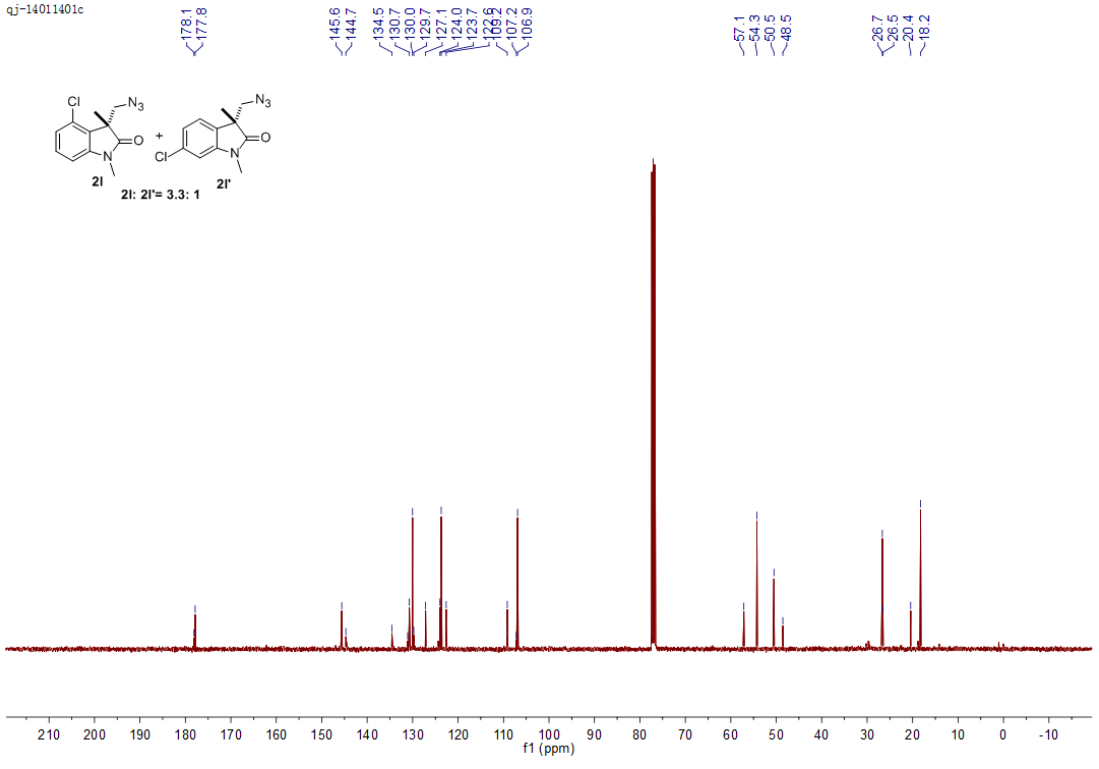
qj-131226011



qj-131226011c




qj-14011401
7.30
7.28
7.27
7.21
7.19
7.09
7.09
7.07
7.07
7.05
7.03
6.89
6.88
6.81
6.79
4.19
4.16
3.74
3.71
3.63
3.25
3.22
1.47
1.36
Cl
N3
O
N
2l
+
Cl
N3
O
N
2l'
2l: 2l'= 3.3: 1
1.02
0.30
0.33
0.97
0.29
0.99
1.00
1.03
0.60
3.93
2.98
0.93
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)


qj-14011401c
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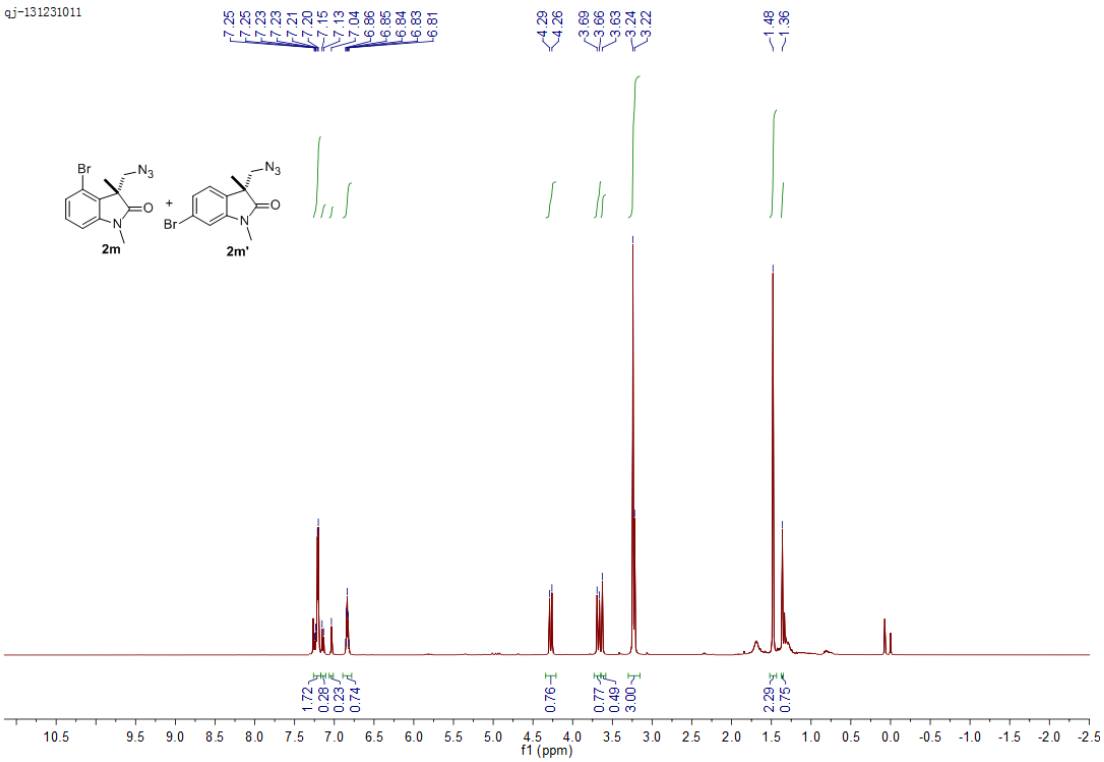
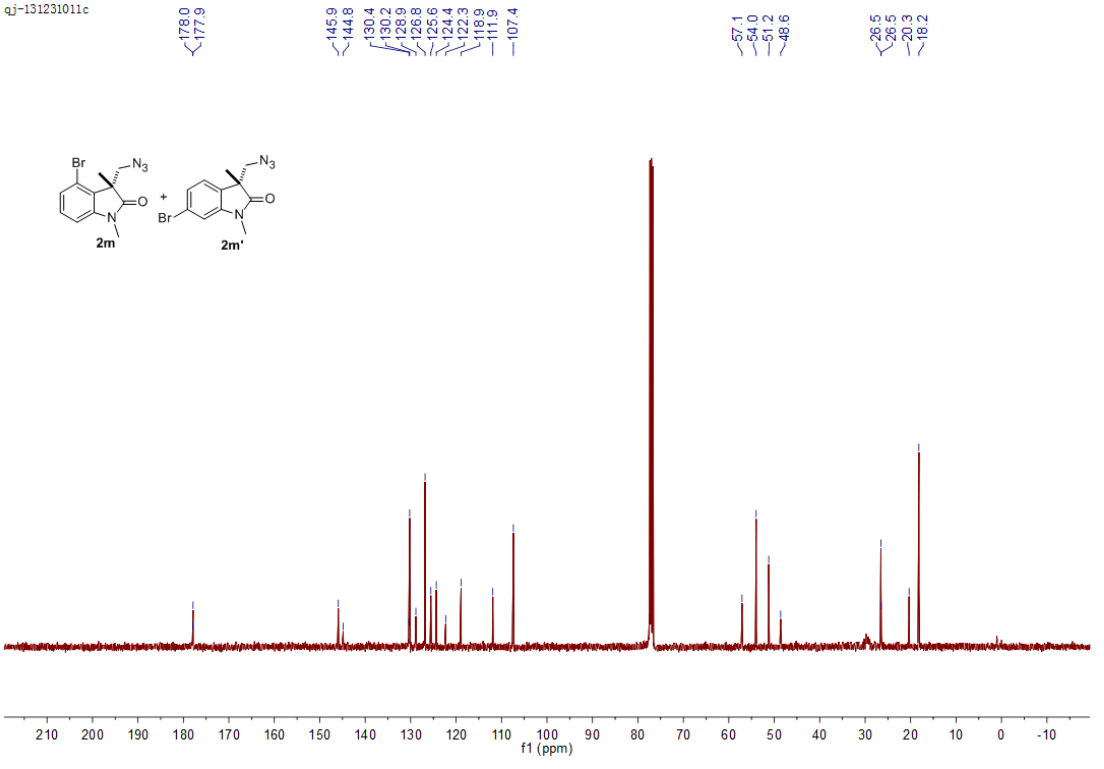
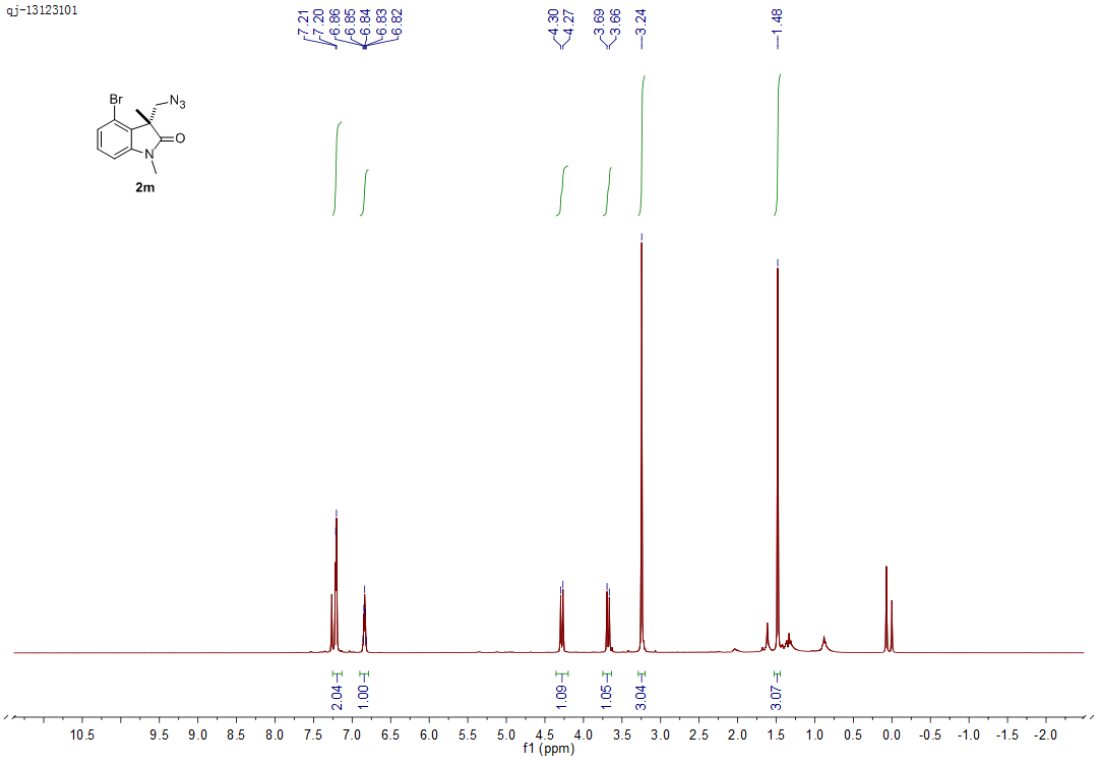
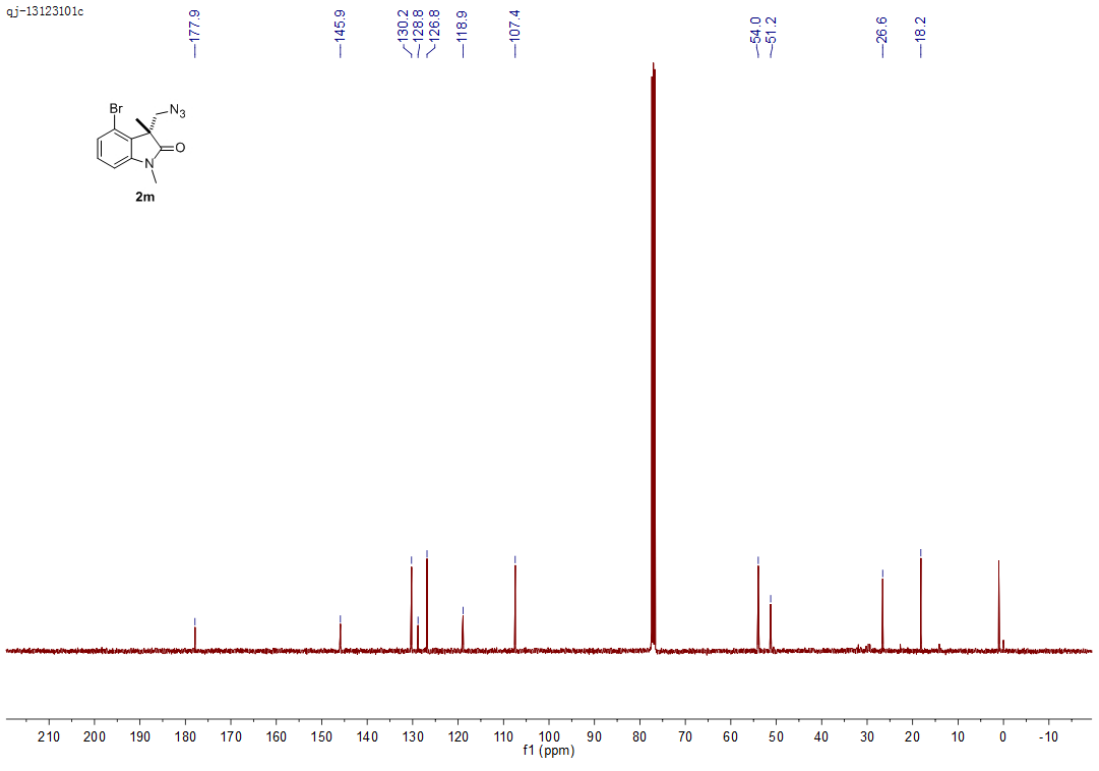
177.8
145.6
144.7
134.5
130.7
130.0
129.7
127.1
124.0
123.7
109.6
107.2
106.9
57.1
54.3
50.5
48.5
26.7
26.5
20.4
18.2
Cl
N3
O
N
2l
+
Cl
N3
O
N
2l'
2l: 2l'= 3.3: 1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

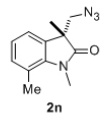

qj-131231011
7.25
7.25
7.23
7.23
7.21
7.20
7.15
7.13
7.04
6.86
6.85
6.84
6.83
6.81
4.29
4.26
3.69
3.66
3.63
3.24
3.22
1.48
1.36
Br
N3
O
N
2m
+
Br
N3
O
N
2m'
1.72
0.28
0.23
0.74
0.76
0.77
0.49
3.00
2.29
0.75
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)


qj-131231011c
178.0
177.9
145.9
144.8
130.4
130.2
128.9
126.8
125.6
124.4
122.3
118.9
111.9
107.4
57.1
54.0
51.2
48.6
26.5
26.5
20.3
18.2
Br
N3
O
N
2m
+
Br
N3
O
N
2m'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


qj-13123101
7.21
7.20
6.86
6.85
6.84
6.83
6.82
4.30
4.27
3.69
3.66
3.24
1.48
Br
N3
O
N
2m
2.04
1.00
1.09
1.05
3.04
3.07
f1 (ppm)


qj-13123101c
177.9
145.9
130.2
128.8
126.8
118.9
107.4
54.0
51.2
26.6
18.2
Br
N3
O
N
2m
f1 (ppm)

qj-14011001



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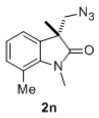
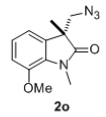
qj-14011001c



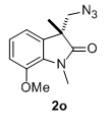
2n

qj-14021901

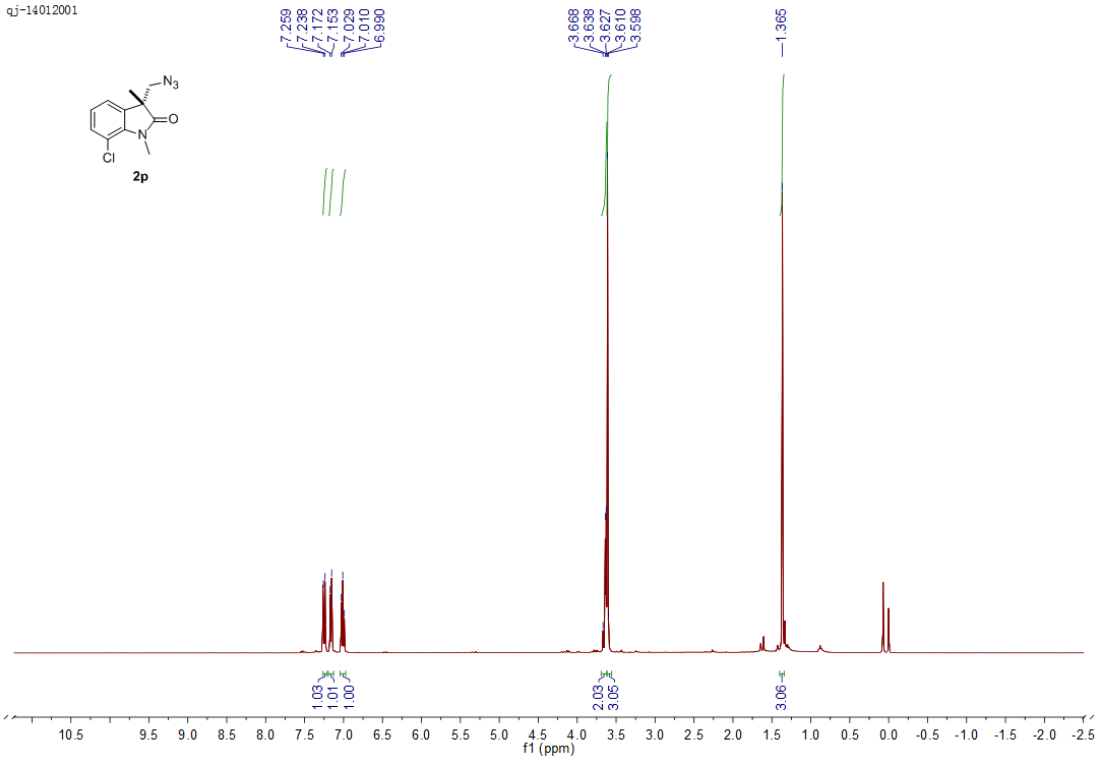


2o

qj-14021901c



2o


qj-14012001
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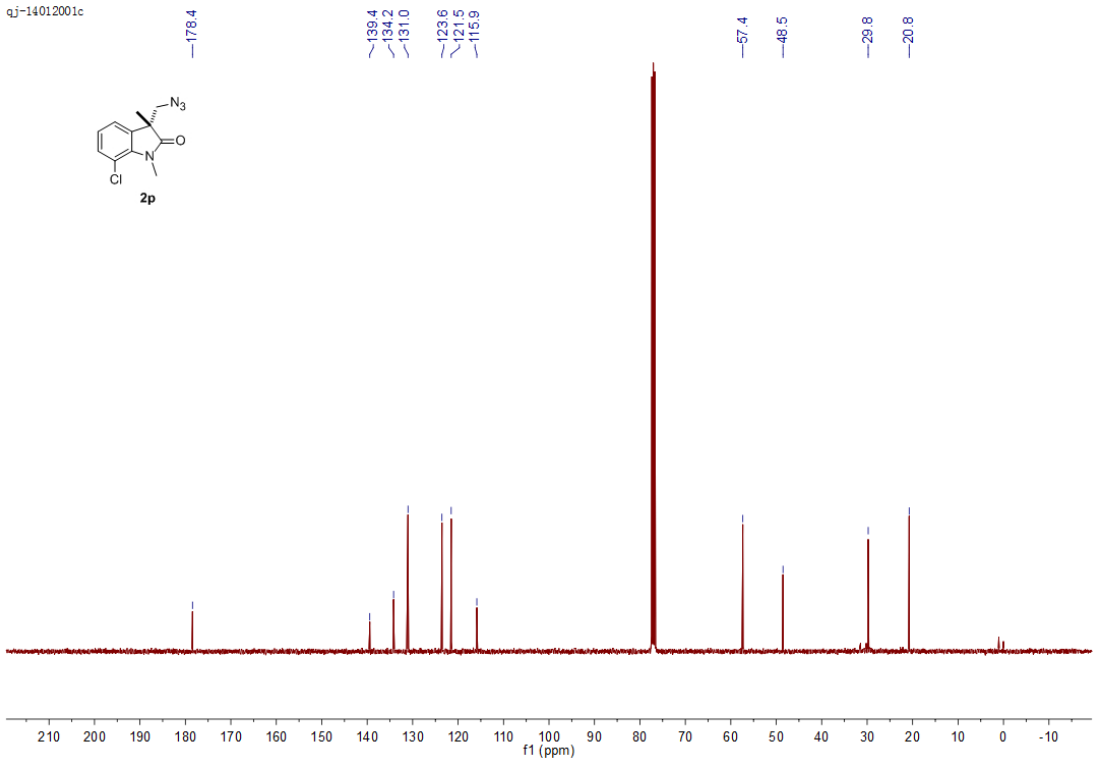
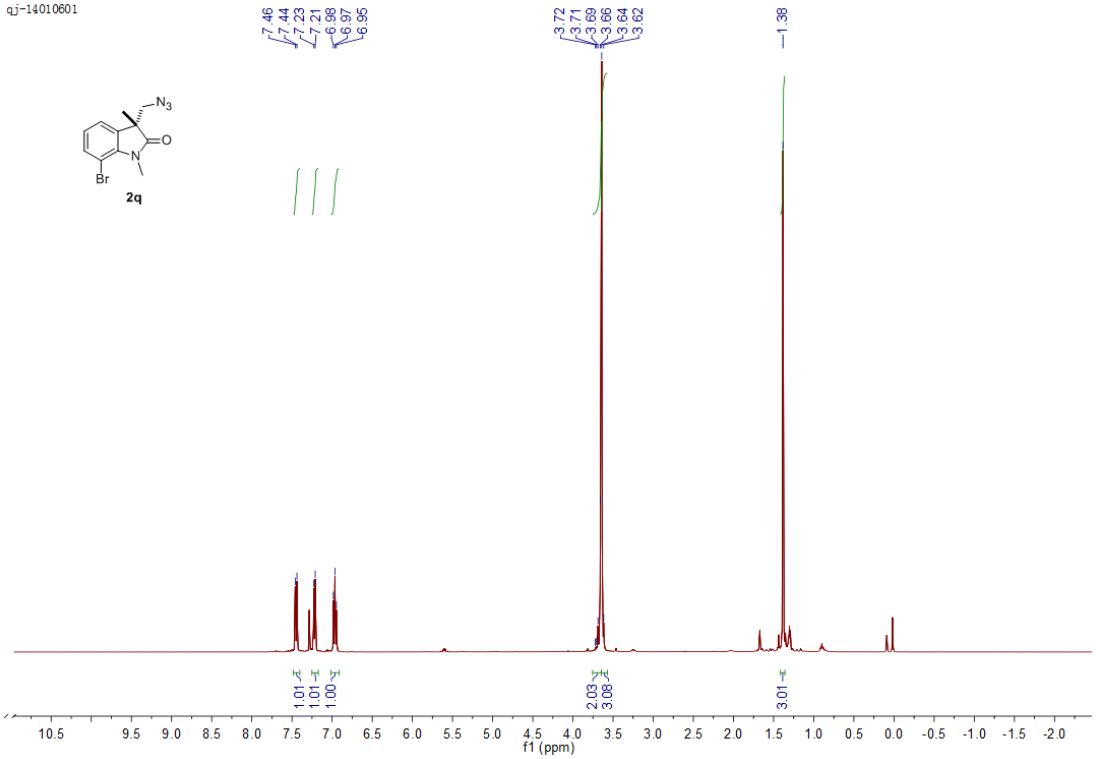
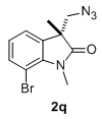
7.238
7.172
7.153
7.029
7.010
6.990
3.668
3.638
3.627
3.610
3.598
1.365
N3
O
N
Cl
2p
1.03
1.01
1.00
2.03
3.05
3.06
f1 (ppm)


qj-14012001c
178.4
139.4
134.2
131.0
123.6
121.5
115.9
57.4
48.5
29.8
20.8
N3
O
N
Cl
2p
f1 (ppm)

qj-14010601



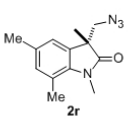


2q

qj-14010601c

2q

qj-140227010



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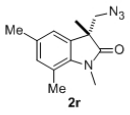
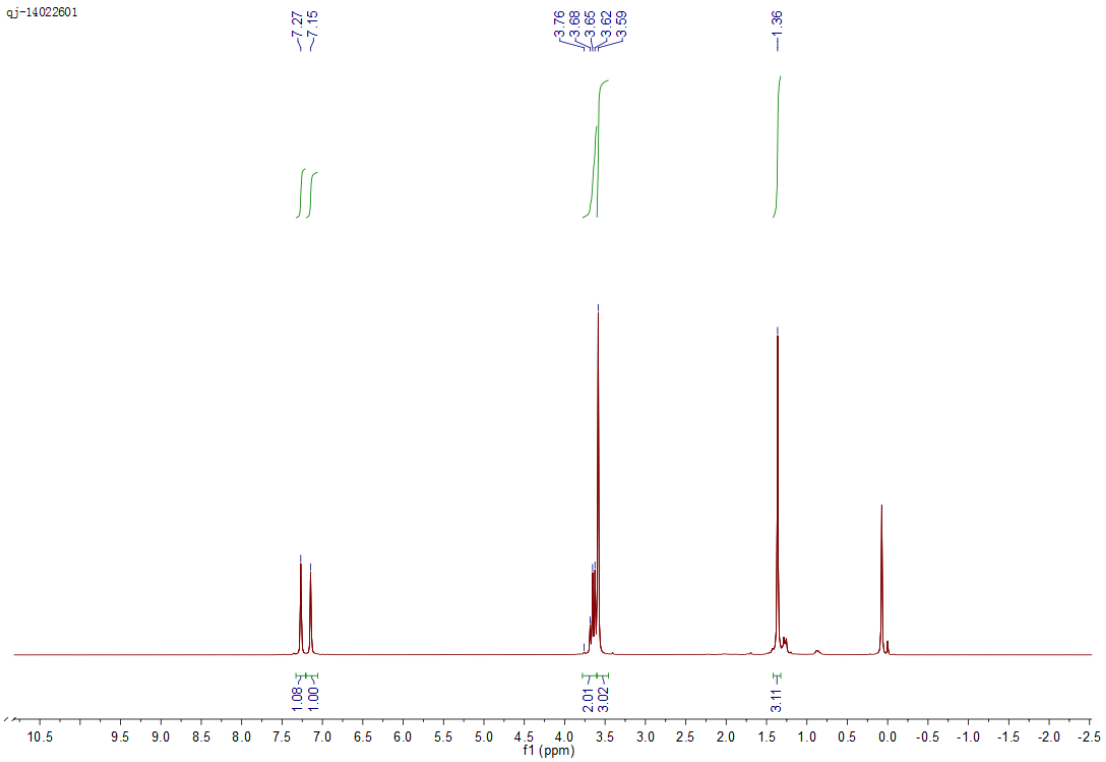
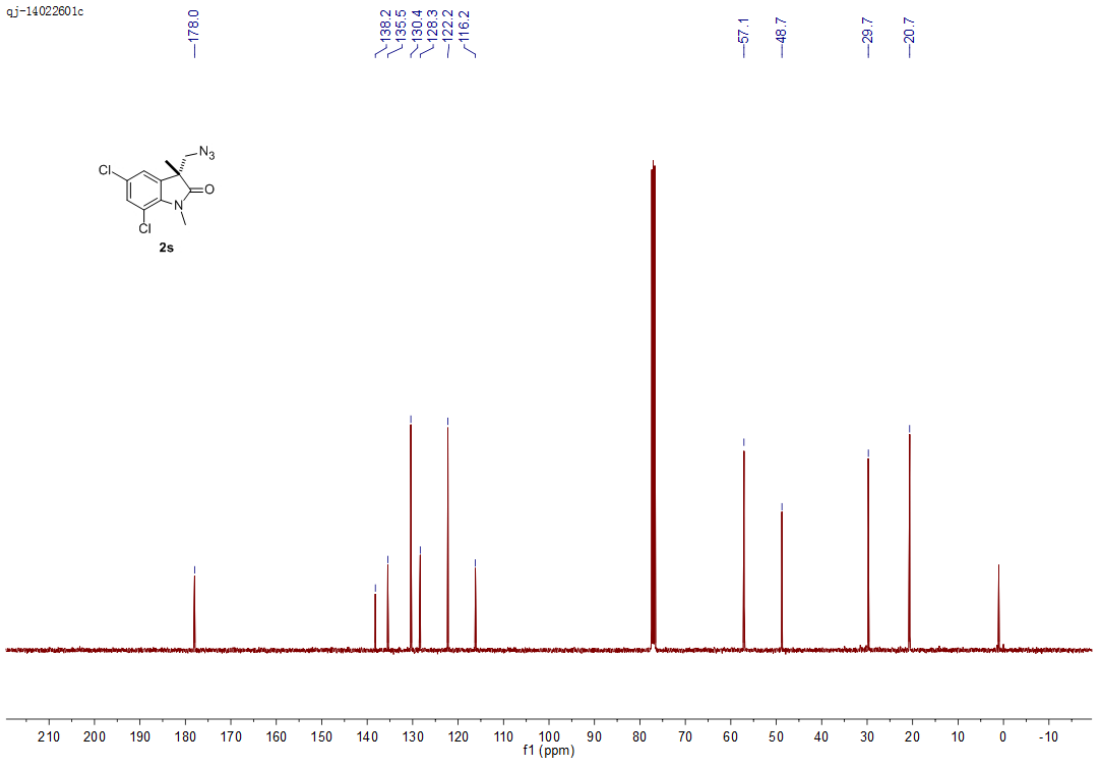
qj-14022701c

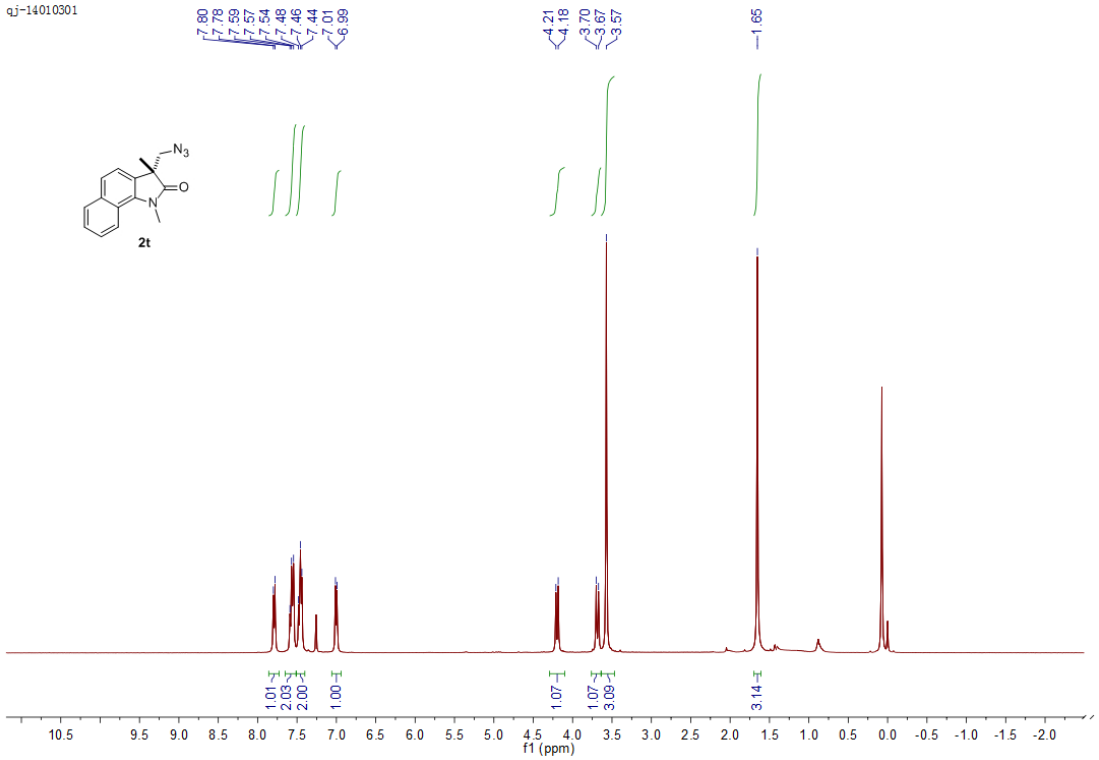


2r


qj-14022601
7.27
7.15
3.76
3.68
3.65
3.62
3.59
1.36
1.08
1.00
2.01
3.02
3.11
f1 (ppm)


qj-14022601c
178.0
138.2
135.5
130.4
128.3
122.2
116.2
57.1
48.7
29.7
20.7
Cl
N3
O
N
Cl
2s
f1 (ppm)

qj-14010301



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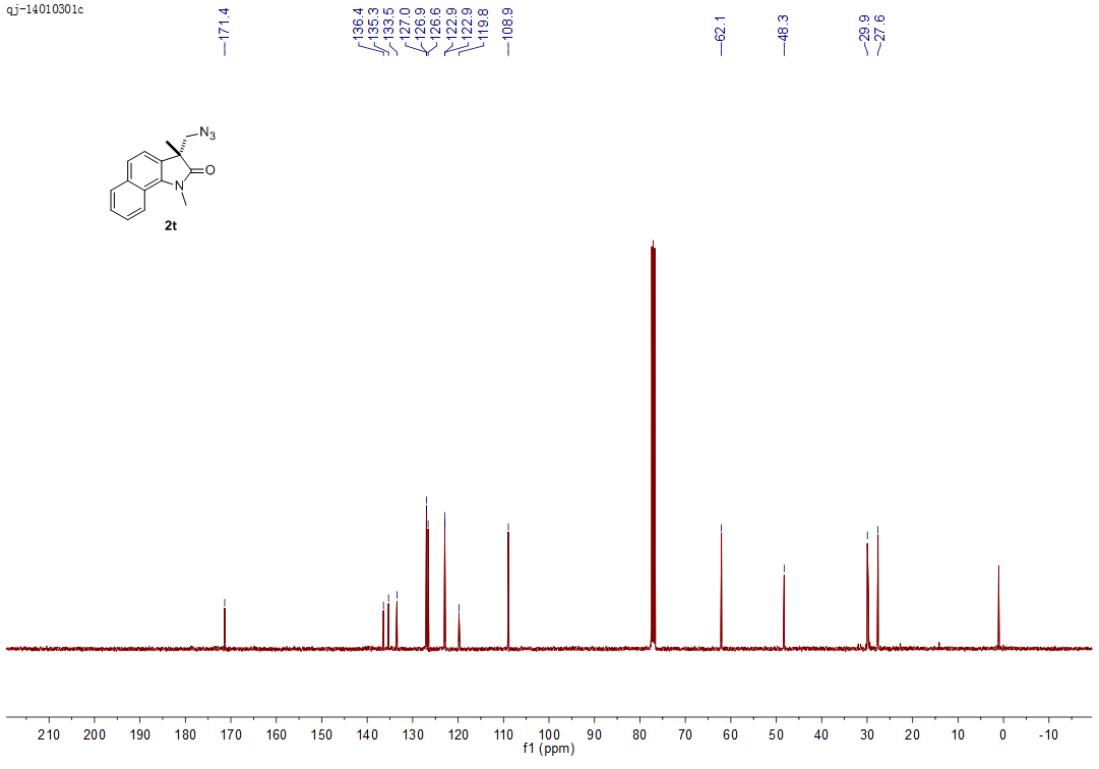
qj-14010301c



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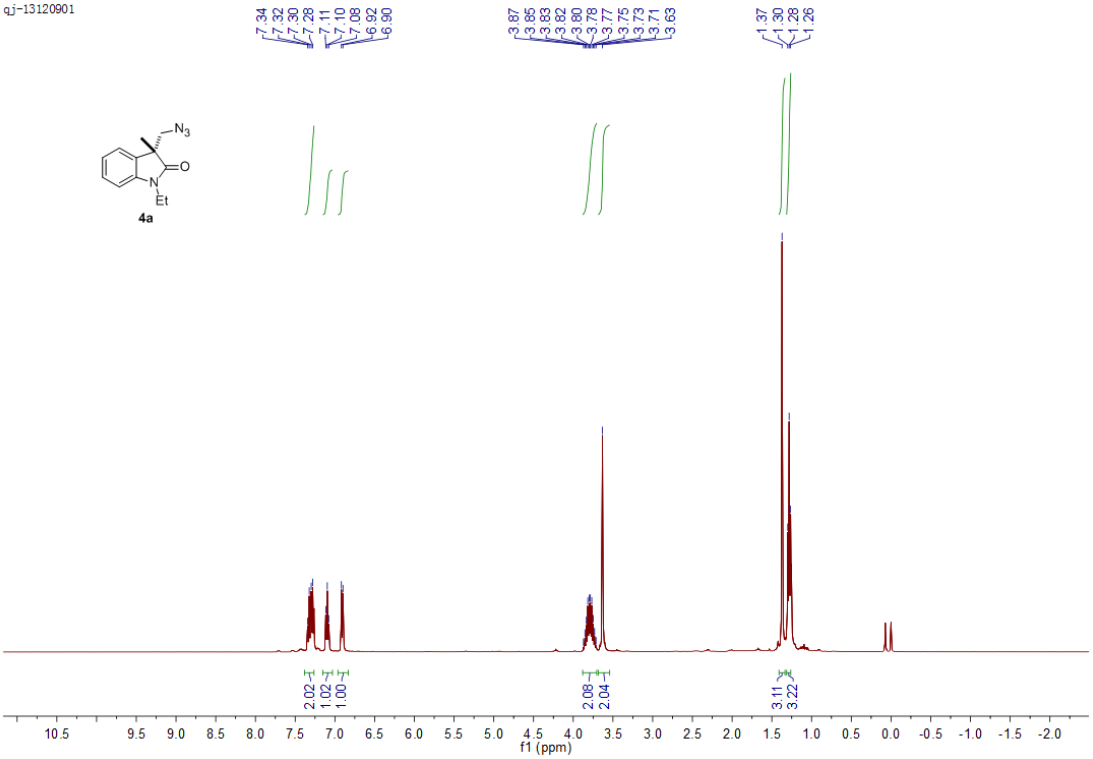
qj-13120901



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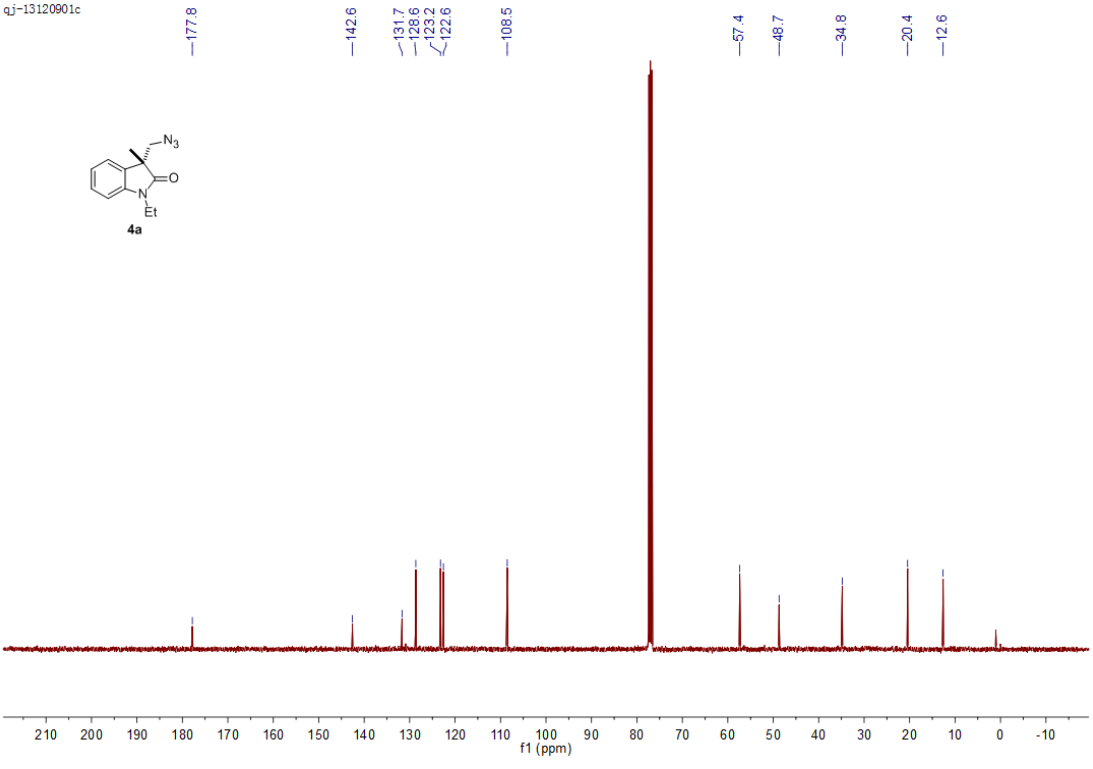

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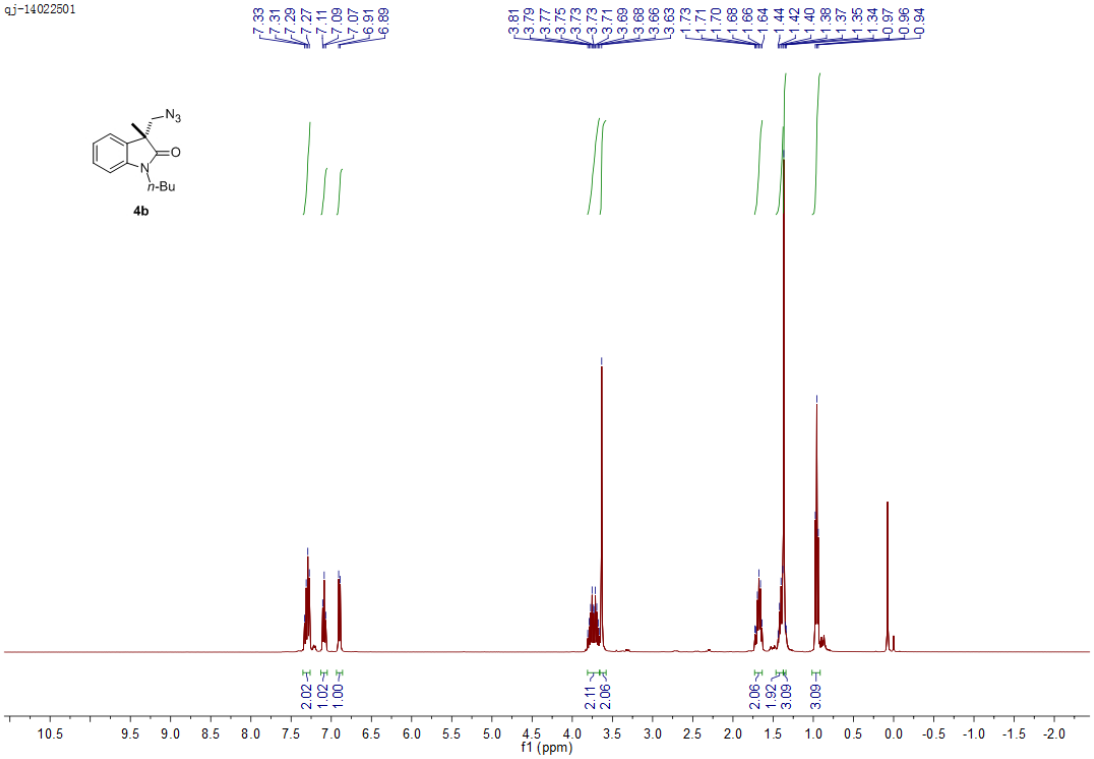
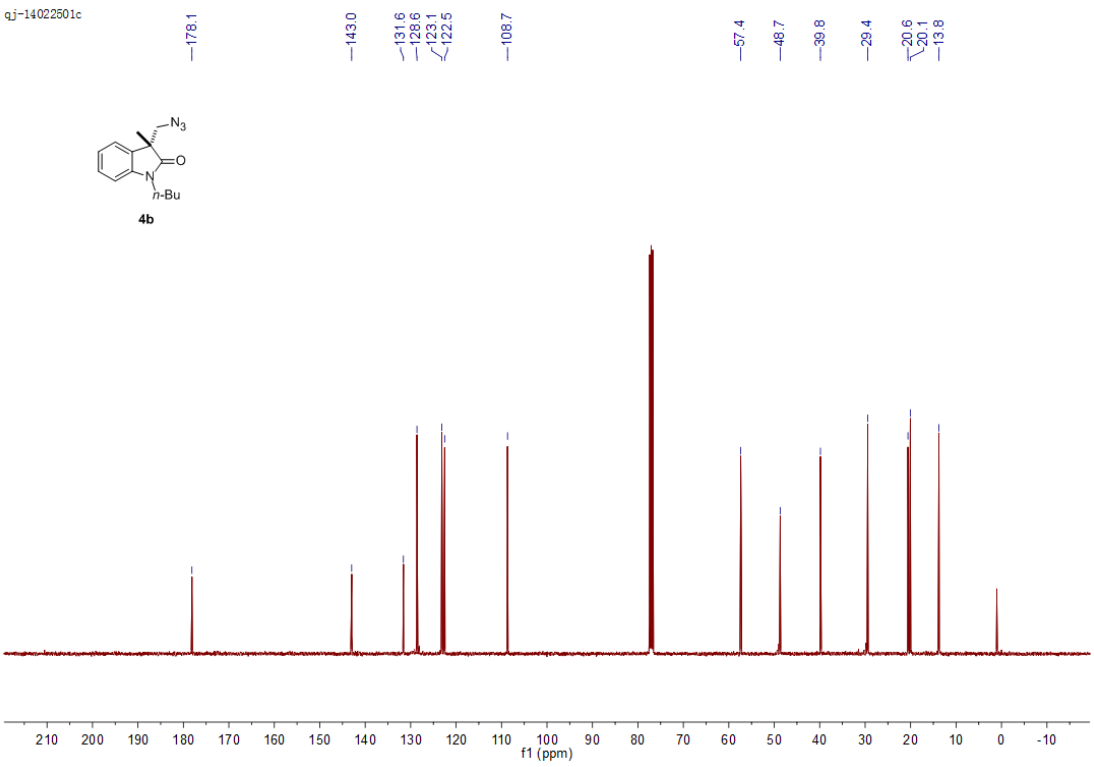


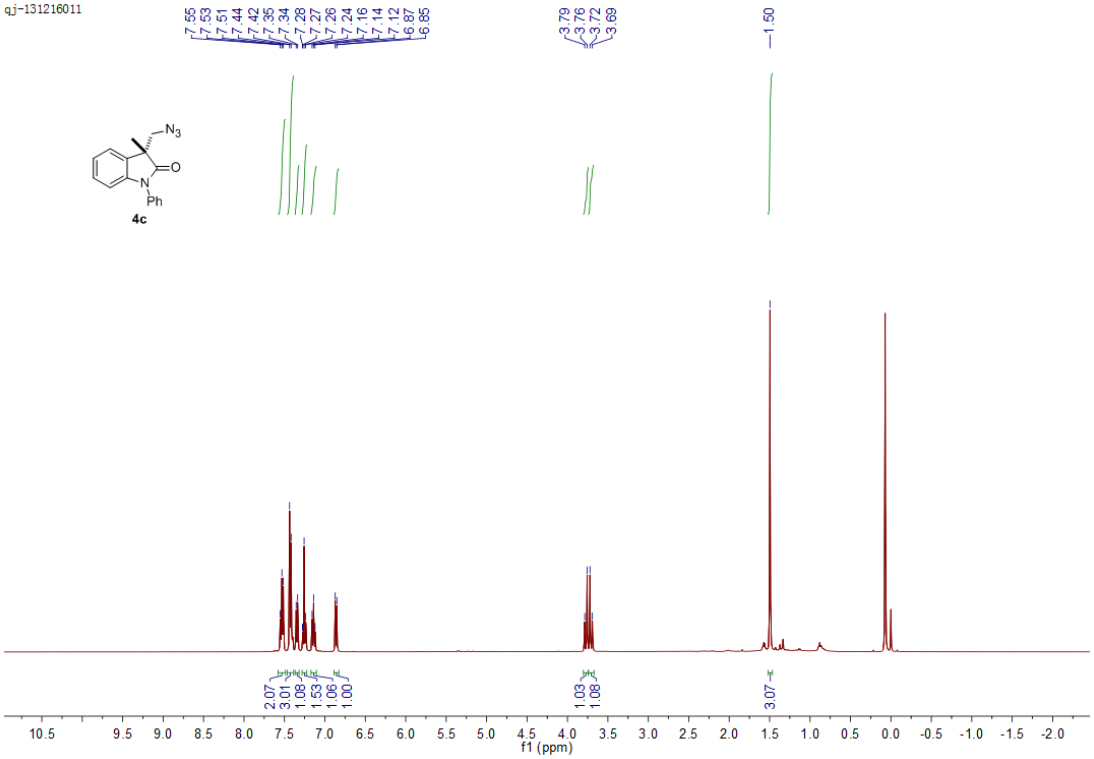
4b

qj-14022501c

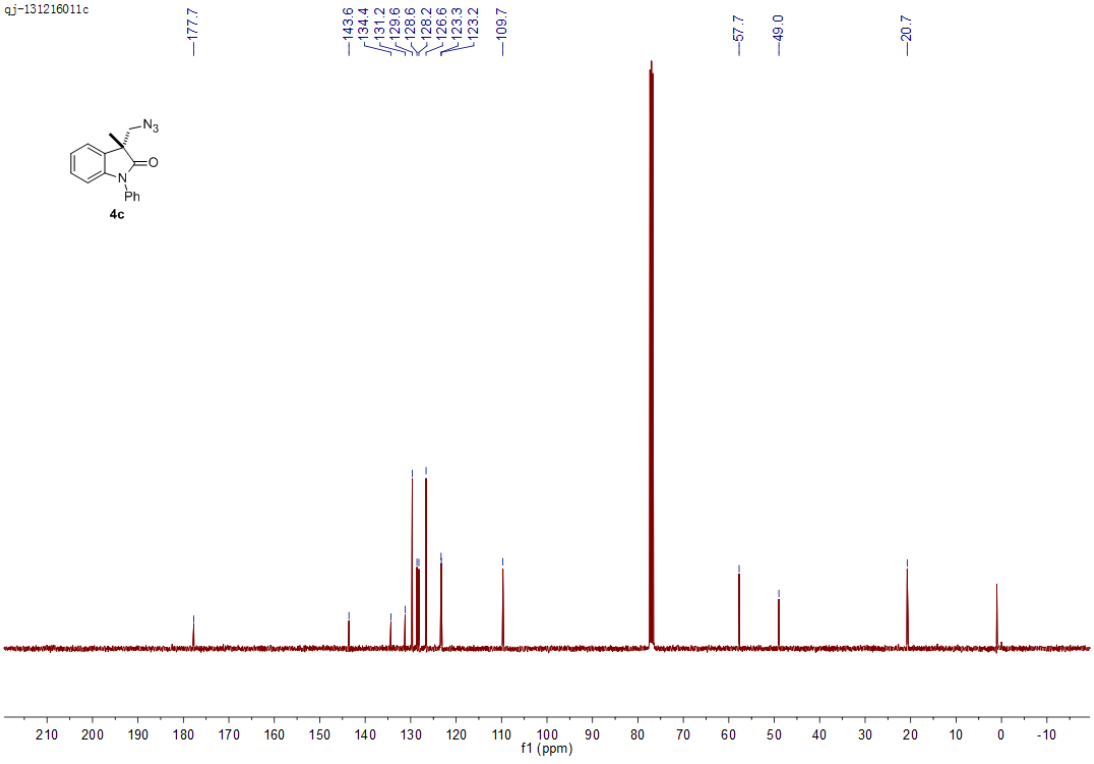


4b

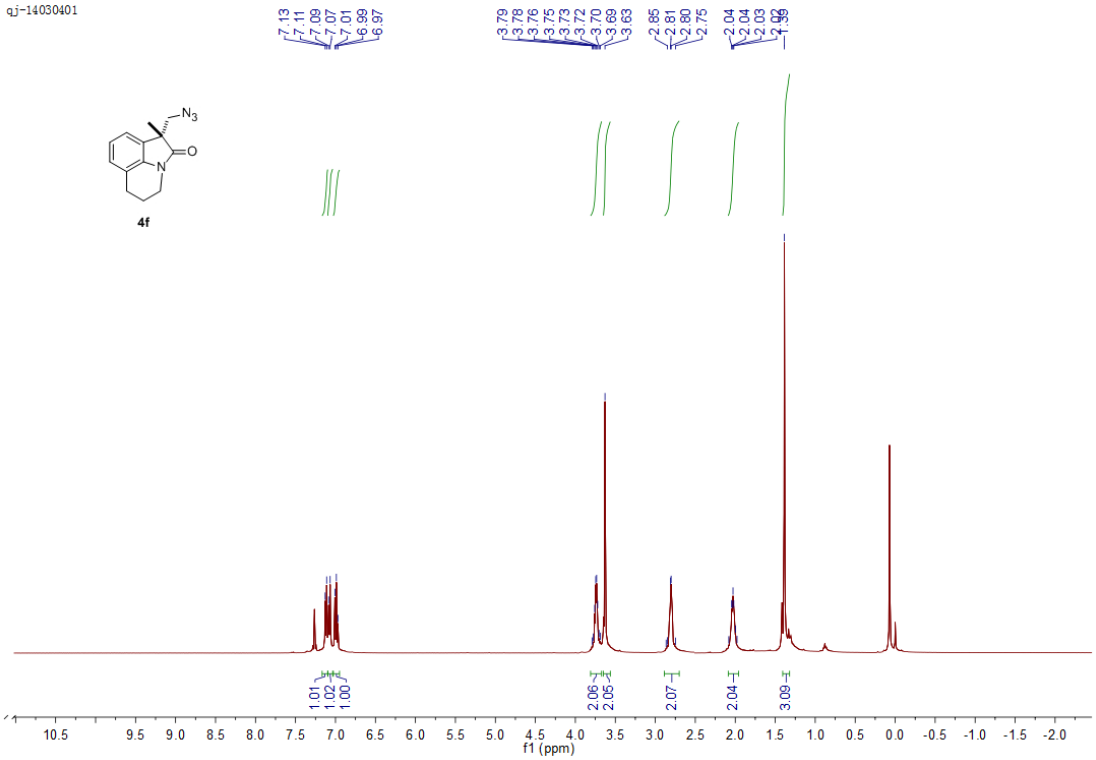
qj-131216011



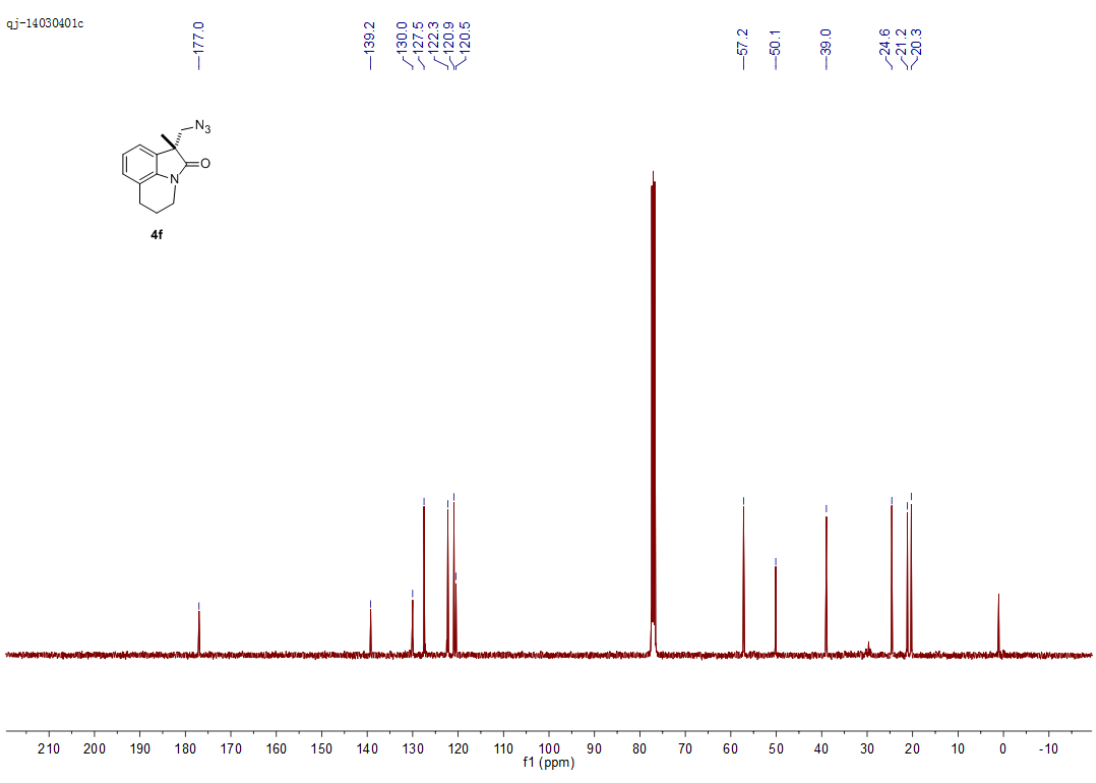
qj-131216011c



qj-14030401



qj-14030401c



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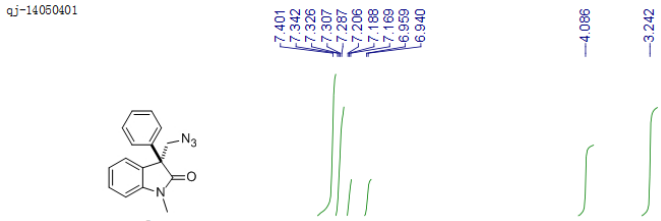

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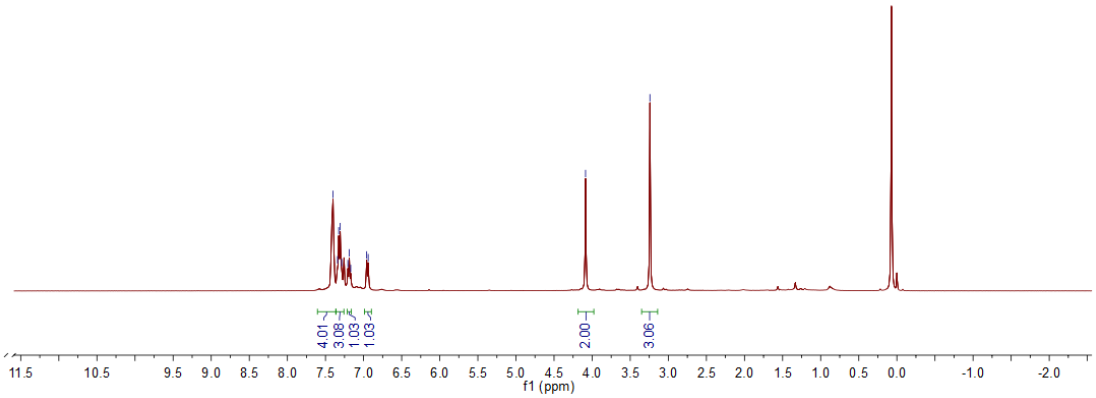
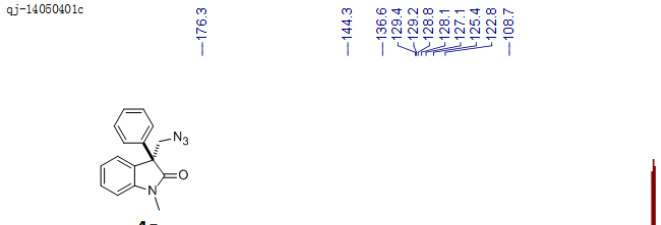


qj-14050401c



4g