Supplementary Information for:

Organocatalytic Enantioselective Vinylogous Mannich Reaction of α,α-Dicyanoolefins to Isatin N-Boc Ketimines

Yi Zhu,[a] Yao Li,[a] Qingbin Meng,[b,]* and Xin Li[a,]*

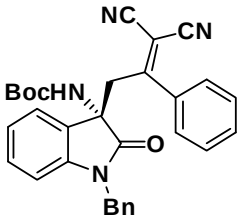
[a] *State Key Laboratory of Elemento-Organic Chemistry, CollaborativeInnovationCenterofChemical Science and Engineering, Department of Chemistry,Nankai University, Tianjin 300071;* [b] *State Key Laboratory of Toxicology and Medical Countermeasures, Beijing Institute of Pharmacology and Toxicology, Beijing, 100850, P. R. China.*

xin_li@nankai.edu.cn; nankaimqb@sina.com.

General Information: Commercial reagents were used as received, unless otherwise stated. ^{1}H and ^{13}C NMR were recorded on a Bruker-DPX 300 or 400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s= singlet, d= doublet, t= triplet, q= quartet, h= heptet, m= multiplet, br= broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer.

General procedure of the Vinylogous Mannich reaction

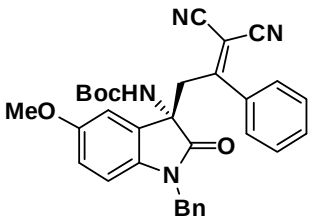
Catalyst **3k** (0.01mmol, 10mol%), α,α-dicyanoolefin[1]**2** (0.1mmol) and 4A MS (50 mg) were stirred in dry $CHCl_3$:MTBE (1:1, 0.5 mL) at -20°C. Then *N*-Bocketimines[2]**1** (0.12 mmol) in dry $CHCl_3$:MTBE (1:1, 0.5 mL) were added. After the stated reaction time, the product was purified by flash chromatography on silica gel to give the product **4**. The enantiomeric excess was determined by HPLC analysis on chiral column.



4a

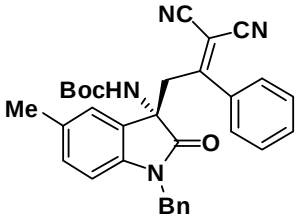
The product was synthesized according to the general procedure as white solid in 87% yield. $[\alpha]^{20}_{D}$-132.9° (c= 0.8, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 2.0 Hz, 4H), 7.20 (d, *J* = 7.4 Hz, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.15 (s, 1H), 4.64 (d, *J* = 15.8 Hz, 1H), 4.07 (d, *J* = 15.9 Hz, 1H), 3.78 (d, *J* = 13.5 Hz, 1H), 3.64 (d, *J* = 13.3 Hz, 1H), 1.24 (s, 9H);^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 171.5, 166.0, 163.4, 153.7, 141.8, 134.7, 130.3, 130.2, 129.9, 129.8, 129.8, 128.8, 128.0, 127.9, 127.5, 125.1, 123.4, 116.3, 116.1, 112.2, 112.1, 109.6, 88.9, 81.0, 61.8, 44.0, 42.6, 28.0.HRMS (ESI^+): calcd. for[$C_{31}H_{28}N_4O_3$+Na^+] 527.2059,

found 527.2058.The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 9.3 min (minor), 22.9 min (major).



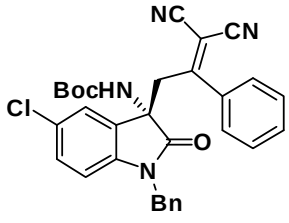
4b

The product was synthesized according to the general procedure as white solid in 80% yield. $[\alpha]^{20}_D$-103.5° (c= 0.7, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 6.1 Hz, 3H), 7.22 (dd, *J* = 15.7, 9.3 Hz, 5H), 6.71 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.48 (d, *J* = 8.5 Hz, 1H), 5.18 (s, 1H), 4.60 (d, *J* = 15.6 Hz, 1H), 4.03 (d, *J* = 15.8 Hz, 1H), 3.79 (d, *J* = 11.9 Hz, 1H), 3.77 (s, 3H), 3.66 (d, *J* = 13.2 Hz, 1H), 1.24 (d, *J* = 15.9 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 172.6, 156.3, 153.7, 135.0, 135.0, 133.8, 132.3, 129.1, 128.8, 128.8, 127.8, 127.8, 127.4, 115.0, 112.4, 112.2, 111.4, 110.2, 88.8, 80.9, 62.1, 55.8, 43.9, 42.7, 28.1.HRMS (ESI$^+$): calcd. for [$C_{32}H_{30}N_4O_4$+Na^+] 557.2165, found 557.2160. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 10.7 min (minor), 35.4 min (major).



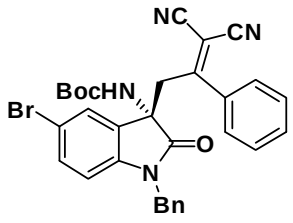
4c

The product was synthesized according to the general procedure as white solid in 80% yield. $[\alpha]^{20}_D$-127.8° (c= 0.6, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 12.1 Hz, 1H), 7.30 – 7.23 (m, 5H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 5.21 (s, 1H), 4.60 (d, *J* = 15.5 Hz, 1H), 4.14 – 4.00 (m, 1H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 13.2 Hz, 1H), 2.28 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 172.6, 153.7, 139.4, 135.0, 133.8, 132.9, 132.2, 130.1, 128.8, 127.9, 127.8, 127.7, 127.5, 125.6, 112.3, 112.3, 109.3, 88.8, 80.8, 61.9, 43.9, 42.9, 28.1, 21.1.HRMS (ESI$^+$): calcd. for [$C_{32}H_{30}N_4O_3$+Na^+] 541.2216, found 541.2215. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.7 min (minor), 21.6 min (major).



4d

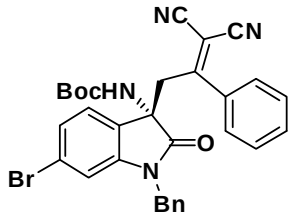
The product was synthesized according to the general procedure as white solid in 73% yield. $[\alpha]^{20}_D$-77.0° (c= 0.7, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.30 (tt, *J* = 8.3, 4.3 Hz, 5H), 7.23 – 7.18 (m, 2H), 7.12 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 5.07 (s, 1H), 4.72 (d, *J* = 15.7 Hz, 1H), 4.28 (d, *J* = 15.7 Hz, 1H), 3.79 (d, *J* = 13.4 Hz, 1H), 3.58 (d, *J* = 13.4 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 171.9, 153.6, 140.4, 134.5, 133.9, 132.3, 129.7, 129.7, 129.0, 129.0, 128.8, 128.0, 127.7, 127.5, 125.4, 112.1, 112.1, 110.6, 89.1, 81.2, 61.8, 44.2, 42.7, 28.1.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}ClN_4O_3$+Na^+] 561.1670, found 561.1665. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.6 min (minor), 13.8 min (major).



4e

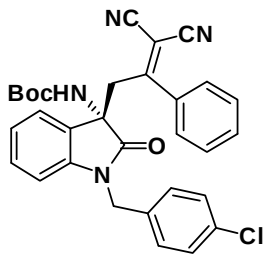
The product was synthesized according to the general procedure as white solid in 88% yield. $[\alpha]^{20}_D$-40.5° (c= 1.1, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 6.3 Hz, 4H), 7.28 – 7.22 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 2H), 6.47 (d, *J* = 8.3 Hz, 1H), 5.24 (s, 1H), 4.68 (d, *J* = 15.4 Hz, 1H), 4.29

(d, *J* = 15.6 Hz, 1H), 3.78 (d, *J* = 13.3 Hz, 1H), 3.58 (d, *J* = 13.3 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 171.8, 153.6, 140.9, 134.5, 133.8, 132.5, 132.3, 130.0, 130.0, 128.9, 128.0, 127.7, 127.5, 116.0, 112.1, 112.1, 111.0, 89.1, 81.2, 61.7, 44.2, 42.7, 28.1.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}BrN_4O_3$+Na^+] 605.1165,found 605.1163.The enantiomeric excess was determined by HPLC with an IA column at 210 nm(2-propanol/hexane=1:4), 1.0 mL/min; t_R = 8.2 min (minor), 16.6 min (major).



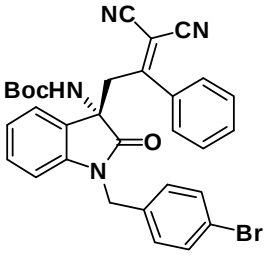
4f

The product was synthesized according to the general procedure as white solid in 92% yield. $[\alpha]^{20}_D$-57.7^o (c= 1.1, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.35 (m, 3H), 7.35 – 7.26 (m, 5H), 7.21 – 7.10 (m, 3H), 6.72 (s, 1H), 5.14 (s, 1H), 4.62 (d, *J* = 15.7 Hz, 1H), 4.08 (d, *J* = 15.8 Hz, 1H), 3.77 (d, *J* = 13.4 Hz, 1H), 3.62 (d, *J* = 13.4 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 172.0, 153.6, 143.3, 134.3, 133.6, 132.4, 129.0, 128.9, 128.0, 127.8, 127.4, 126.9, 126.1, 126.0, 123.5, 112.9, 112.2, 112.0, 89.0, 81.1, 61.4, 44.0, 42.6, 28.0.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}BrN_4O_3$+Na^+] 605.1165, found 605.1163. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.8 min (minor), 14.2 min (major).



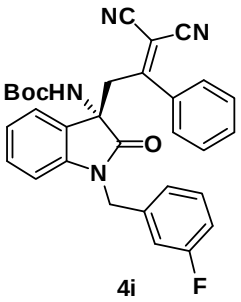
4g

The product was synthesized according to the general procedure as white solid in 87% yield. $[\alpha]^{20}_D$-183.6^o (c= 0.5, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.46 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.26 – 7.17 (m, 7H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 1H), 4.61 (d, *J* = 16.0 Hz, 1H), 3.91 (d, *J* = 16.0 Hz, 1H), 3.74 (d, *J* = 13.4 Hz, 1H), 3.60 (d, *J* = 13.4 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 172.3, 153.4, 141.6, 133.5, 133.3, 132.4, 129.9, 128.9, 128.9, 128.7, 127.8, 127.8, 124.4, 123.4, 112.3, 112.1, 109.5, 88.9, 80.9, 61.7, 43.1, 42.8, 28.0.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}ClN_4O_3$+Na^+] 561.1670, found 561.1665. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.2 min (minor), 17.5 min (major).



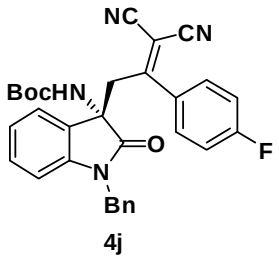
4h

The product was synthesized according to the general procedure as white solid in 88% yield. $[\alpha]^{20}_D$-165.2^o (c= 0.5, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (q, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.15 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.15 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 3.89 (d, *J* = 16.0 Hz, 1H), 3.74 (d, *J* = 13.4 Hz, 1H), 3.59 (d, *J* = 13.3 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 172.3, 153.4, 141.6, 133.8, 133.5, 132.5, 131.8, 129.9, 129.1, 128.9, 127.8, 127.8, 124.3, 123.4, 121.6, 112.3, 112.1, 109.4, 88.9, 80.9, 61.6, 43.1, 42.8, 28.0.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}BrN_4O_3$+Na^+] 605.1165, found 605.1162. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.2 min (minor), 21.5 min (major).



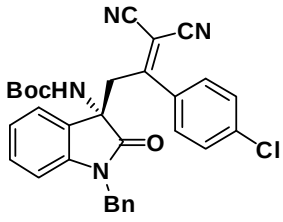
4i

The product was synthesized according to the general procedure as white solid in 83% yield. $[\alpha]^{20}_{D}$-142.0° (c= 0.3, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.47 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.15 (m, 4H), 7.10 – 7.00 (m, 3H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.24 (s, 1H), 4.50 (d, *J* = 16.1 Hz, 1H), 4.20 (d, *J* = 16.1 Hz, 1H), 3.76 (d, *J* = 13.4 Hz, 1H), 3.65 (d, *J* = 13.3 Hz, 1H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.45, 172.3, 161.6, 159.1, 153.5, 141.6, 133.5, 132.4, 123.0, 129.6, 129.5, 128.9, 127.8, 127.7, 124.7, 124.6, 124.5, 123.4, 121.9, 121.8, 115.3, 115.1, 112.3, 112.1, 109.3, 109.3, 88.8, 80.9, 61.7, 42.8, 37.0, 28.0.HRMS (ESI^+): calcd. for [$C_{31}H_{27}FN_4O_3$+Na^+] 545.1965, found 545.1962. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.7 min (minor), 23.7 min (major).



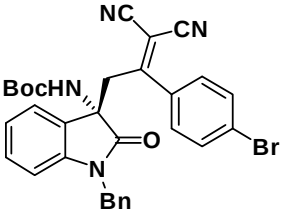
4j

The product was synthesized according to the general procedure as white solid in 80% yield. $[\alpha]^{20}_{D}$-110.1° (c= 0.9, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.25 – 7.18 (m, 3H), 7.10 (dt, *J* = 21.4, 8.0 Hz, 3H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 1H), 4.74 (d, *J* = 15.6 Hz, 1H), 4.22 (d, *J* = 15.6 Hz, 1H), 3.88 (d, *J* = 13.4 Hz, 1H), 3.64 (d, *J* = 13.4 Hz, 1H), 1.28 (s, 9H);^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 171.5, 166.0, 163.5, 153.7, 141.8, 134.7, 130.3, 130.3, 129.9, 129.8, 128.9, 128.1, 127.9, 127.5, 125.1, 123.5, 116.3, 116.1, 112.2, 112.1, 109.6, 89.0, 81.0, 61.8, 44.0, 42.6, 28.1.HRMS (ESI^+): calcd. for [$C_{31}H_{27}FN_4O_3$+Na^+] 545.1965, found 545.1960. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 9.7 min (minor), 25.5 min (major).



4k

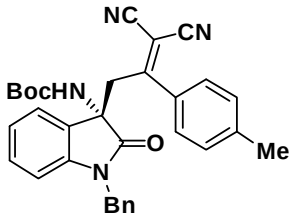
The product was synthesized according to the general procedure as white solid in 90% yield. $[\alpha]^{20}_{D}$-11.8° (c= 0.7, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 5.2 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.26 (m, 5H), 7.21 (td, *J* = 7.8, 1.1 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.04 (td, *J* = 8.3, 7.6, 0.7 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.15 (s, 1H), 4.72 (d, *J* = 15.5 Hz, 1H), 4.23 (d, *J* = 15.6 Hz, 1H), 3.89 (d, *J* = 13.4 Hz, 1H), 3.59 (d, *J* = 13.5 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 170.5, 152.7, 140.8, 137.4, 133.7, 131.2, 128.8, 128.2, 128.1, 127.9, 127.1, 126.9, 126.5, 124.2, 122.5, 111.1, 111.0, 108.6, 88.2, 80.0, 60.8, 43.0, 41.5, 27.0.HRMS (ESI^+): calcd. for [$C_{31}H_{27}ClN_4O_3$+Na^+] 561.1670, found 561.1668. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 9.0 min (minor), 25.9 min (major).



4l

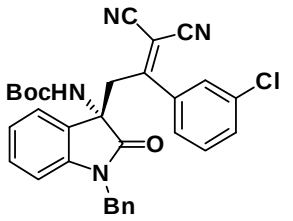
The product was synthesized according to the general procedure as white solid in 87% yield. $[\alpha]^{20}_{D}$-59.8° (c= 0.6, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.31 (d, *J* = 6.2 Hz, 5H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 7.8, 4.2 Hz, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.00 (s, 1H), 4.75 (d, *J* = 15.7 Hz, 1H), 4.23 (d, *J* = 15.6 Hz, 1H), 3.90 (d, *J* = 13.5 Hz, 1H), 3.57 (d, *J* = 13.4 Hz, 1H), 1.27 (s, 9H);^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 171.7, 153.7, 141.8, 134.7, 132.8, 132.2, 129.9, 129.3, 128.9, 128.2, 127.9, 127.5, 126.9, 125.4, 123.5, 112.1, 112.0, 109.7, 89.2,

81.0, 61.8, 44.0, 42.4, 28.1.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}BrN_4O_3$+Na^+] 605.1165, found 605.1160. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 8.8 min (minor), 26.8 min (major).



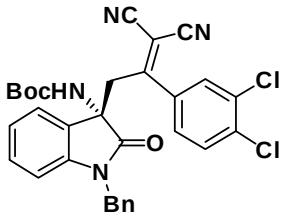
4m

The product was synthesized according to the general procedure as white solid in 83% yield. $[\alpha]^{20}_D$-114.8^o (c= 0.6, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.28 (d, *J* = 4.4 Hz, 5H), 7.25 – 7.17 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.05 (s, 1H), 4.66 (d, *J* = 15.8 Hz, 1H), 4.07 (d, *J* = 15.8 Hz, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.60 (d, *J* = 13.3 Hz, 1H), 2.42 (s, 3H), 1.23 (s, 9H);^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 172.4, 153.5, 143.3, 141.9, 134.9, 130.9, 129.7, 129.6, 128.8, 127.9, 127.9, 127.7, 127.4, 124.6, 123.2, 112.4, 112.4, 109.6, 88.0, 80.8, 61.8, 43.8, 42.7, 28.0, 21.6.HRMS (ESI$^+$): calcd. for [$C_{32}H_{30}N_4O_3$+Na^+] 541.2216, found 541.2215. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.5 min (minor), 20.9 min (major).



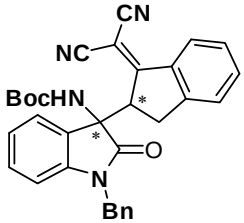
4n

The product was synthesized according to the general procedure as white solid in 95% yield. $[\alpha]^{20}_D$-97.6^o (c= 1.1, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.0 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.20 (td, *J* = 7.8, 1.2 Hz, 1H), 7.09 – 6.92 (m, 3H), 6.66 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 4.28 (d, *J* = 15.6 Hz, 1H), 3.85 (d, *J* = 13.3 Hz, 1H), 3.63 (d, *J* = 13.3 Hz, 1H), 1.27 (s, 9H);^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 171.1, 153.7, 141.8, 135.6, 134.9, 134.8, 131.8, 130.1, 129.9, 128.9, 128.0, 127.9, 127.6, 127.6, 125.8, 125.3, 123.4, 111.8, 111.6, 109.5, 90.0, 81.0, 61.7, 44.0, 42.7, 28.1.HRMS (ESI$^+$): calcd. for [$C_{31}H_{27}ClN_4O_3$+Na^+] 561.1670, found 561.1668. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 8.2 min (minor), 14.0 min (major).



4o

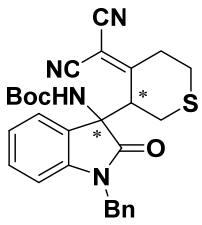
The product was synthesized according to the general procedure as white solid in 95% yield. $[\alpha]^{20}_D$-84.8^o (c= 1.4, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 1.0 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.19 (s, 1H), 7.16 – 7.11 (m, 1H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.94 (td, *J* = 7.7, 1.1 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 5.04 (s, 1H), 4.69 (d, *J* = 15.5 Hz, 1H), 4.35 (d, *J* = 15.5 Hz, 1H), 3.86 (d, *J* = 13.4 Hz, 1H), 3.50 (d, *J* = 13.4 Hz, 1H), 1.20 (s, 9H);^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 169.2, 152.8, 140.7, 135.2, 133.7, 132.8, 132.3, 129.8, 128.9, 128.5, 128.0, 127.1, 127.1, 126.6, 125.8, 124.6, 122.5, 110.7, 110.5, 108.5, 89.1, 80.1, 60.7, 43.1, 41.5, 27.0.HRMS (ESI$^+$): calcd. for [$C_{31}H_{26}Cl_2N_4O_3$+Na^+] 595.1280, found 595.1278. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 7.1 min (minor), 14.2 min (major).



4p

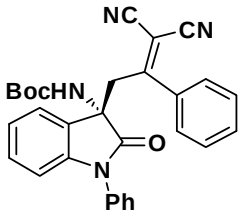
The product was synthesized according to the general procedure asyellowsolidin 96% yield. $[\alpha]^{20}_D$-100.7^o (c= 0.4, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.19 (m, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.55 (m,

2H), 7.51 – 7.36 (m, 5H), 7.35 – 7.26 (m, 14H), 7.24 (d, *J* = 7.4 Hz, 5H), 7.21 – 7.06 (m, 5H), 6.81 (t, *J* = 7.9 Hz, 3H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.48 (s, 1H), 5.15 – 4.54 (m, 7H), 4.28 – 4.18 (m, 1H), 3.81 (s, 2H), 3.48 (s, 2H), 3.22 – 2.94 (m, 4H), 1.31 (s, 9H), 1.19 (s, 17H);^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 154.0, 153.6, 150.2, 149.1, 142.8, 142.7, 136.3, 135.5, 135.3, 135.2, 134.9, 134.8, 130.0, 129.6, 128.9, 128.8, 128.7, 128.0, 127.8, 127.7, 127.6, 127.5, 127.3, 126.7, 125.9, 125.8, 125.4, 125.2, 124.9, 123.1, 122.7, 113.8, 112.6, 112.5, 109.8, 108.9, 81.1, 81.0, 79.1, 64.7, 64.1, 53.6, 52.6, 44.4, 44.3, 32.8, 32.2, 29.7, 28.1, 28.0.HRMS (ESI^+): calcd. for [$C_{32}H_{28}N_4O_3$+Na^+] 539.2059, found 539.2058. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 10.4 min (minor), 13.8 min (major), 18.1 min (minor),31.8 min (major).



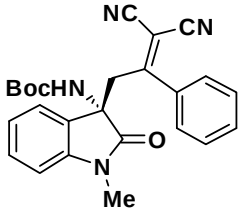
4q

The product was synthesized according to the general procedure as white solid in 90% yield. $[\alpha]^{20}_D$-34.6° (c= 0.6, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 14.2 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.33 (tt, *J* = 14.6, 7.3 Hz, 8H), 7.23 (dd, *J* = 11.8, 8.2 Hz, 3H), 7.05 (td, *J* = 7.5, 3.6 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.74 (dd, *J* = 12.6, 7.7 Hz, 2H), 4.89 (d, *J* = 60.3 Hz, 4H), 3.95 (d, *J* = 14.7 Hz, 1H), 3.71 – 3.34 (m, 4H), 3.34 – 3.21 (m, 1H), 3.11 (ddt, *J* = 18.5, 13.5, 4.0 Hz, 4H), 3.02 – 2.80 (m, 4H), 1.27 (d, *J* = 10.7 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 176.7, 176.2, 173.7, 154.1, 153.4, 142.4, 142.0, 135.2, 135.1, 129.8, 129.8, 129.6, 128.8, 128.8, 127.7, 127.6, 127.5, 127.1, 123.4, 122.9, 122.7, 122.4, 111.0, 110.9, 110.6, 110.3, 110.3, 109.6, 89.7, 87.9, 81.0, 80.9, 66.5, 64.4, 45.1, 44.6, 44.2, 44.2, 34.5, 33.9, 30.6, 30.6, 29.9, 29.7, 28.1, 28.0.HRMS (ESI^+): calcd. for [$C_{28}H_{28}N_2O_3S$+Na^+] 523.1780,found 523.1778.The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 8.7 min (minor),12.2 min (major), 15.4 min (minor), 17.0 min (major).



4r

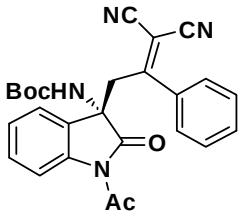
The product was synthesized according to the general procedure as white solid in 76% yield. $[\alpha]^{20}_D$-85.3° (c= 0.5, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.5 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.36 (t, *J* = 8.2 Hz, 3H), 7.29 – 7.25 (m, 1H), 7.14 (dd, *J* = 16.9, 7.7 Hz, 3H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.04 (s, 1H), 3.90 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 13.6 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 172.8, 153.6, 143.1, 134.1, 133.7, 132.4, 129.9, 129.5, 129.28, 128.4, 128.1, 127.9, 126.2, 124.8, 123.7, 112.4, 112.2, 110.0, 89.1, 80.9, 62.0, 42.7, 28.1.HRMS (ESI^+): calcd. for [$C_{30}H_{26}N_4O_3$+Na^+] 513.1903, found 513.1901. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 6.5 min (minor), 20.3 min (major).



4s

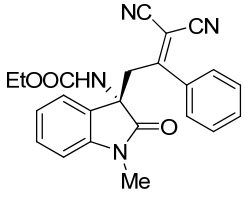
The product was synthesized according to the general procedure as white solid in 85% yield. $[\alpha]^{20}_D$-120.0°(c= 0.8, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J*= 7.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.21 – 7.09 (m, 3H), 6.68 (d, *J* = 7.7 Hz, 1H), 5.29 (s, 1H), 3.73 (d, *J* = 13.3 Hz, 1H), 3.62 (d, *J* = 13.3 Hz, 1H), 2.66 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 172.5, 153.6, 142.8, 133.3, 132.4, 130.0, 128.8, 127.9, 124.4, 123.3, 112.3, 112.2, 108.5, 88.7, 80.9, 61.7, 42.7, 28.0,

25.9.HRMS (ESI$^+$): calcd. for [$C_{25}H_{24}N_4O_3$+Na^+] 451.1746, found 451.1745. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 11.2 min (minor), 24.5 min (major).



4t

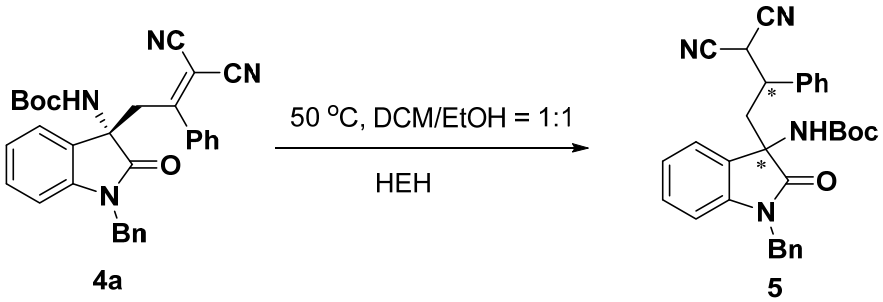
The product was synthesized according to the general procedure as white solid in 85% yield. $[\alpha]^{20}_D$-52.8^o (c= 0.6, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 – 7.39 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 5.86 (s, 1H), 3.74 – 3.58 (m, 2H), 2.13 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 171.1, 169.7, 153.4, 139.5, 132.8, 132.7, 130.4, 129.0, 128.0, 126.9, 125.8, 123.0, 116.8, 112.2, 111.6, 89.4, 81.8, 61.9, 43.7, 27.8, 26.0.HRMS (ESI$^+$): calcd. for [$C_{26}H_{24}N_4O_4$+Na^+] 479.1696, found 479.1695. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 15.0 min (minor), 19.1 min (major).



4u

The product was synthesized according to the general procedure as white solid in 88% yield. $[\alpha]^{20}_D$ -161.0^o (c= 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.22 – 7.11 (m, 3H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 4.01 – 3.74 (m, 1H), 3.62 (d, *J* = 13.4 Hz, 1H), 2.71 (s, 1H), 1.05 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 172.7, 154.6, 142.8, 133.3, 132.3, 130.2, 128.7, 128., 127.9, 127.9, 127.6, 124.8, 123.4, 112.4, 112.2, 108.6, 88.7, 61.6, 61.4, 42.2, 26.0, 14.2. HRMS (ESI$^+$): calcd. for [$C_{23}H_{20}N_4O_3$+Na^+] 423.1433, found 423.1428. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 10.0 min (minor), 16.0 min (major).

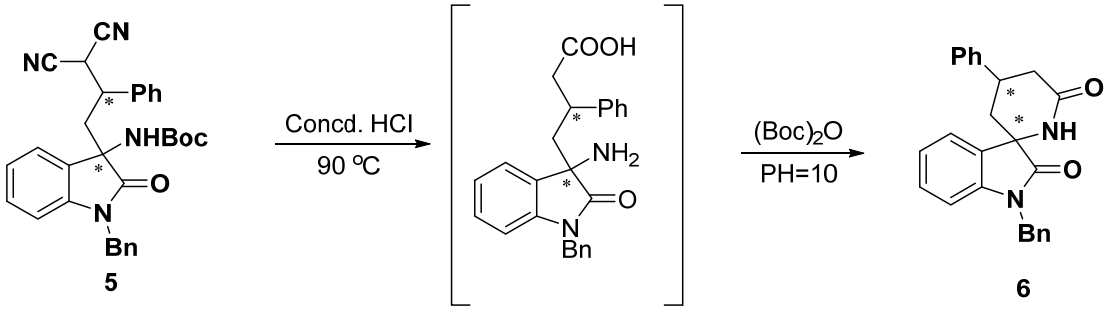
Transformations of 4a:



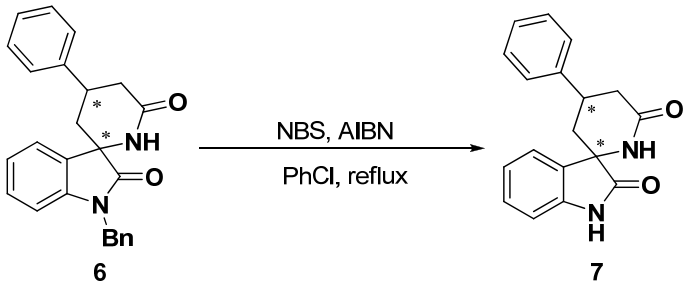
4a **5**

Hantzsch ester (582mg, 2.3mmol) was added to a stirred solution of direct vinylogousMannich product **4a** (231.8mg, 0.46mmol) in DCM/EtOH (1:1, 20.0mL). The solution was stirred at 50°C and monitored by TLC. After 96h,the mixture was concentrated and purified by flash chromatography on silica gel to give the reduced product **5**. 78% yield (181.6mg); white solid. $[\alpha]^{20}_D$-26.8^o (c= 0.2, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.34 (m, 4H), 7.30 (d, *J* = 4.3 Hz, 4H), 7.26 – 7.19 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.05 (s, 1H), 4.59 (d, *J* = 15.7 Hz, 1H), 4.36 (d, *J* = 10.4 Hz, 1H), 3.82 (d, *J* = 6.0 Hz, 1H), 3.37 (s, 1H), 2.85 (dd, *J* = 14.2, 9.0 Hz, 1H), 2.46 (dd, *J* = 14.2, 4.4 Hz, 1H), 1.59 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 153.7, 142.6, 135.9, 135.1, 129.6, 129.5, 129.4, 129.3, 128.9, 128.0, 127.7, 127.3, 123.6, 123.4,

111.5, 111.4, 109.6, 80.8, 60.6, 43.9, 41.4, 38.7, 30.5, 28.1.HRMS (ESI$^+$): calcd. for [$C_{26}H_{24}N_4O_4$+Na^+] 529.2216, found 529.2215.The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 12.4 min (minor), 22.2 min (major).



To a solution of concd. HCl (6.0mL) was added hydrogenated product **5** (67.5mg, 0.14mmol). The mixture was stirred at 90°C for 8 hours and a homogeneous solution was obtained. Then excess HCl solution was removed under vacuum, and the residue was diluted with water (6 mL). After adjusting the pH of the solution is about 10 by K_2CO_3, $(Boc)_2O$ (31.5mg, 0.15mmol) in EtOH (5.0 mL) was added. The mixture was stirred at room temperature overnight. The mixture was extracted with EtOAc (3×6 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to give the cyclic product **6**. 70% yield for two steps (36.1mg);white solid. $[\alpha]^{20}_D$-50.7^o(c= 0.08, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.28 (d, *J* = 2.8 Hz, 4H), 7.24 (dt, *J* = 7.8, 1.5 Hz, 4H), 7.15 – 7.06 (m, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 5.73 (s, 1H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.19 (tt, *J* = 12.4, 3.9 Hz, 1H), 2.95 (dd, *J* = 18.3, 4.8 Hz, 1H), 2.63 (dd, *J* = 17.6, 12.3 Hz, 1H), 2.24 (dt, *J* = 38.9, 13.8 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 172.4, 142.9, 141.8, 135.3, 130.2, 129.8, 129.0, 128.9, 127.9, 127.3, 127.1, 126.8, 123.7, 123.6, 109.8, 61.3, 44.0, 39.5, 38.8, 33.1.HRMS (ESI+): calcd. for [$C_{26}H_{24}N_4O_4$+Na+] 405.1579, found 405.1578. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 16.5 min (minor), 20.9 min (major).



A solution of **6** (50 mg, 0.13 mmol) in chlorobenzene (4 mL) containing NBS (28.7 mg, 0.15 mmol) and AIBN (5 mg, 0.03 mmol) was heated to reflux under a nitrogen atmosphere. After 4 h AIBN (3 mg, 0.02 mmol) and NBS (20 mg, 0.11 mmol) were added. The solution was heated overnight then cooled to room temperature. Diethyl ether (5 mL) and water (10 mL) were added to the solution, which was stirred for 4 h, then the organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated and the crude product was purified by silica gel chromatography (DCM/MeOH, 50:1 v/v) to give **7** (22.8 mg, 60% yield). $[\alpha]^{20}_D$ -50.1^o (c= 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.31 (t, *J* = 6.5 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H),

6.91 (d, J = 7.8 Hz, 1H), 6.28 (s, 1H), 4.00 (dt, J = 11.1, 5.6 Hz, 1H), 2.91 – 2.71 (m, 1H), 2.58 (dd, J = 17.6, 12.3 Hz, 1H), 2.20 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 172.9, 142.7, 139.8, 130.4, 130.1, 128.8, 127.0, 126.7, 123.8, 123.4, 110.6, 61.6, 39.2, 38.5, 32.9. HRMS (ESI^+): calcd. for [$C_{23}H_{20}N_4O_3$+H^+] 293.1290, found 293.1293. The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol/hexane=1:4), 1.0 mL/min; t_R = 13.8 min (major), 16.4 min (minor).

Reference

1. J. Lu, F. Liu, W-J. Zhou, T.-P. Loh, *Tetrahedron Letters,* 2008, **49**, 5389
2. W. Yan, D. Wang, J. Feng, P. Li, D. Zhao, R. Wang, *Org. Lett.,*2012, **14**, 2512.

X-ray crystallography data of 4a.

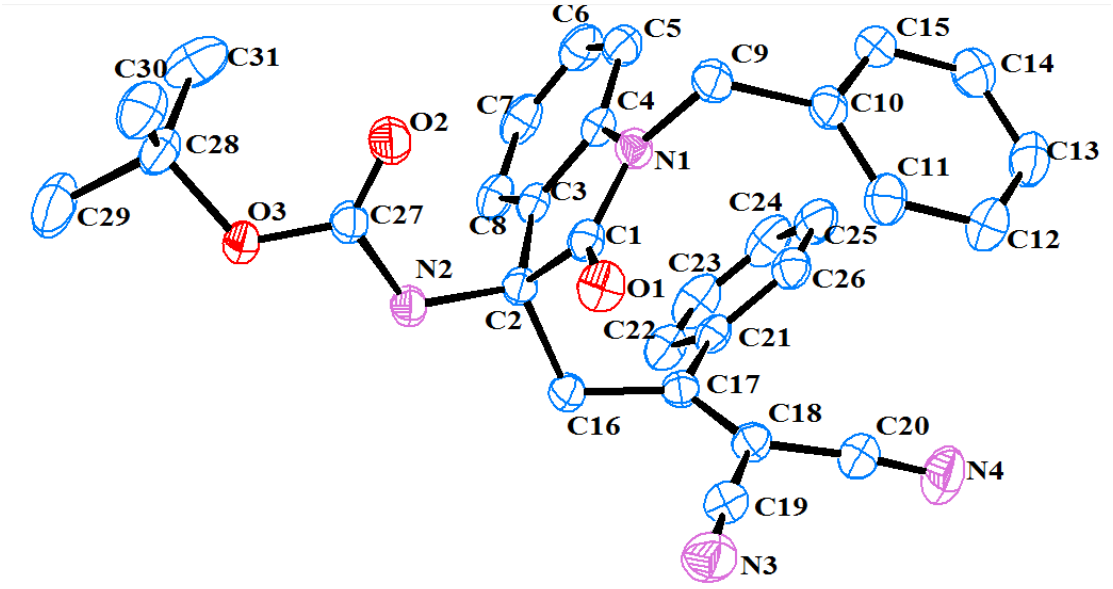
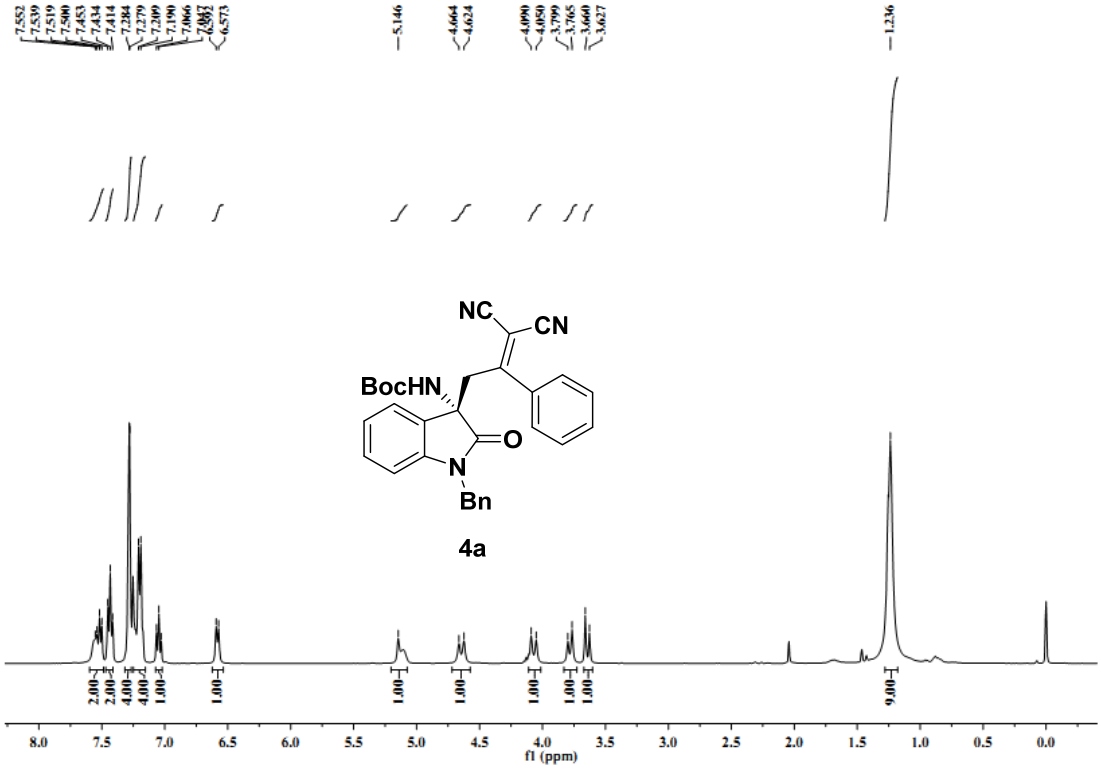
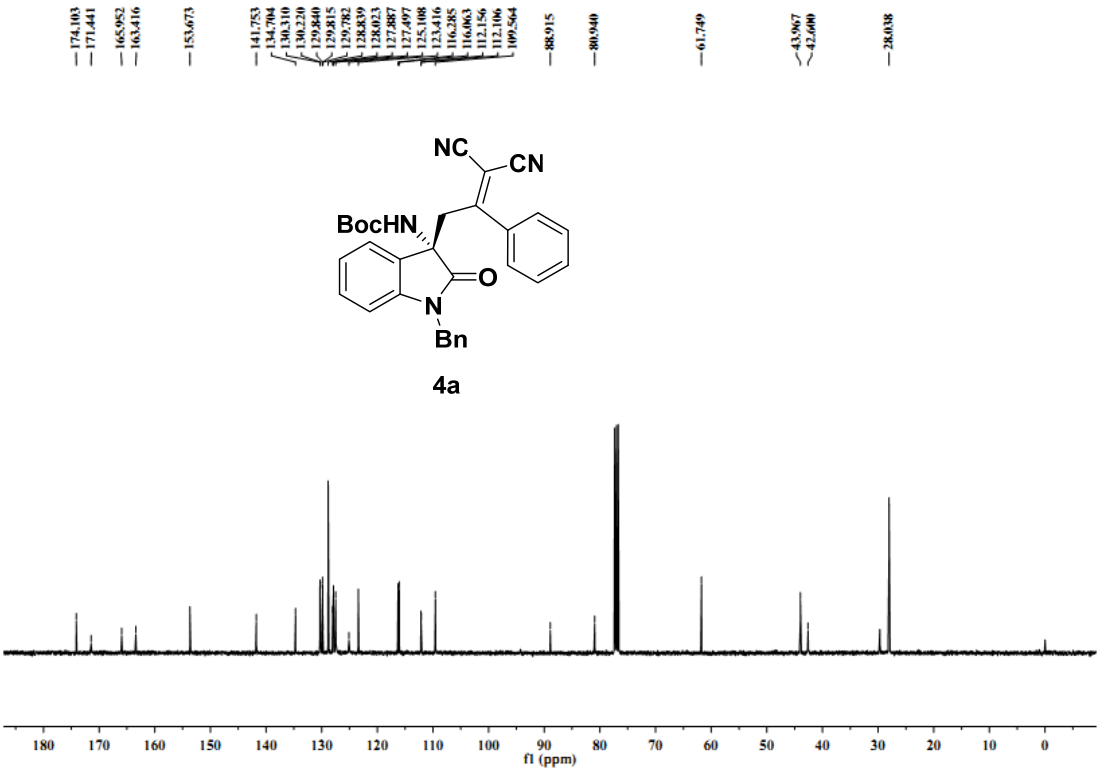


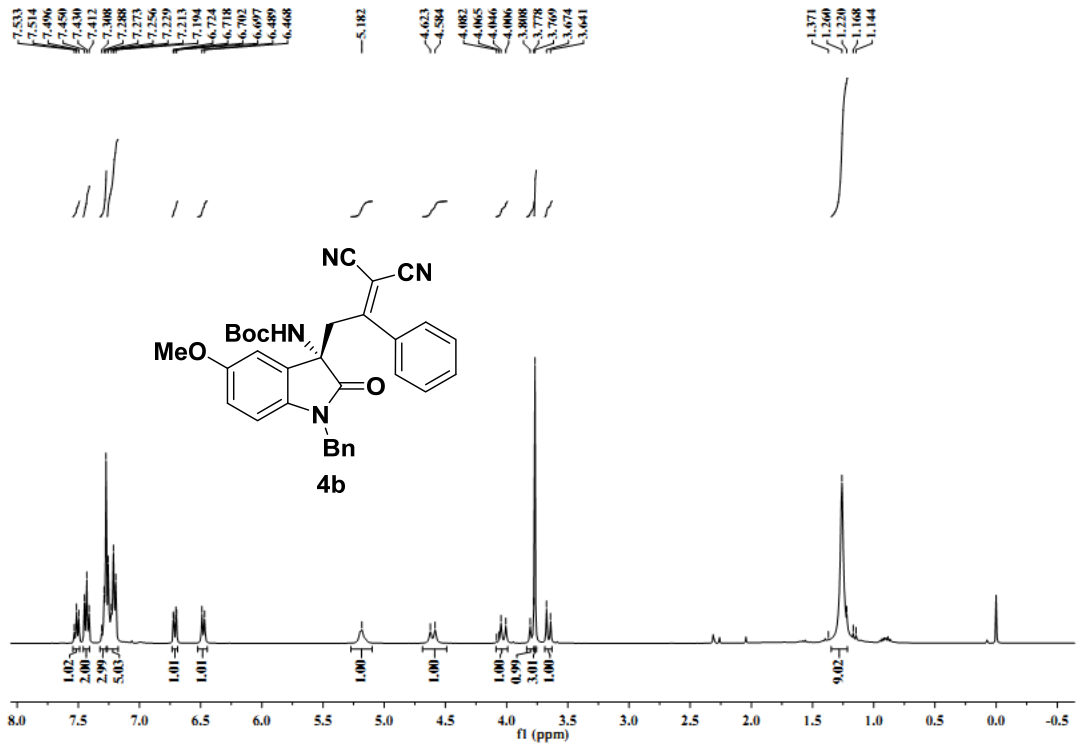
Table 1. Crystal data and structure refinement for shelxl.

Identification code	shelxl
Empirical formula	C31 H28 N4 O3
Formula weight	504.57
Temperature	173(2) K
Wavelength	1.54187 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.837(2) A alpha = 90 deg. b = 10.113(2) A beta = 106.063(8) deg. c = 14.456(3) A gamma = 90 deg.
Volume	1382.0(5) A^3
Z, Calculated density	2, 1.213 Mg/m^3
Absorption coefficient	0.638 mm^-1
F(000)	532
Crystal size	0.340 x 0.220 x 0.200 mm
Theta range for data collection	6.351 to 77.819 deg.
Limiting indices	-12<=h<=12, -11<=k<=12, -18<=l<=17
Reflections collected / unique	23289 / 5369 [R(int) = 0.0357]
Completeness to theta = 67.687	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.880 and 0.662
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5369 / 1 / 351
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0742
R indices (all data)	R1 = 0.0283, wR2 = 0.0783
Absolute structure parameter	0.08(4)
Extinction coefficient	0.0042(8)
Largest diff. peak and hole	0.158 and -0.147 e.A^-3

NMR Spectra (^{1}H NMR, ^{13}C NMR)



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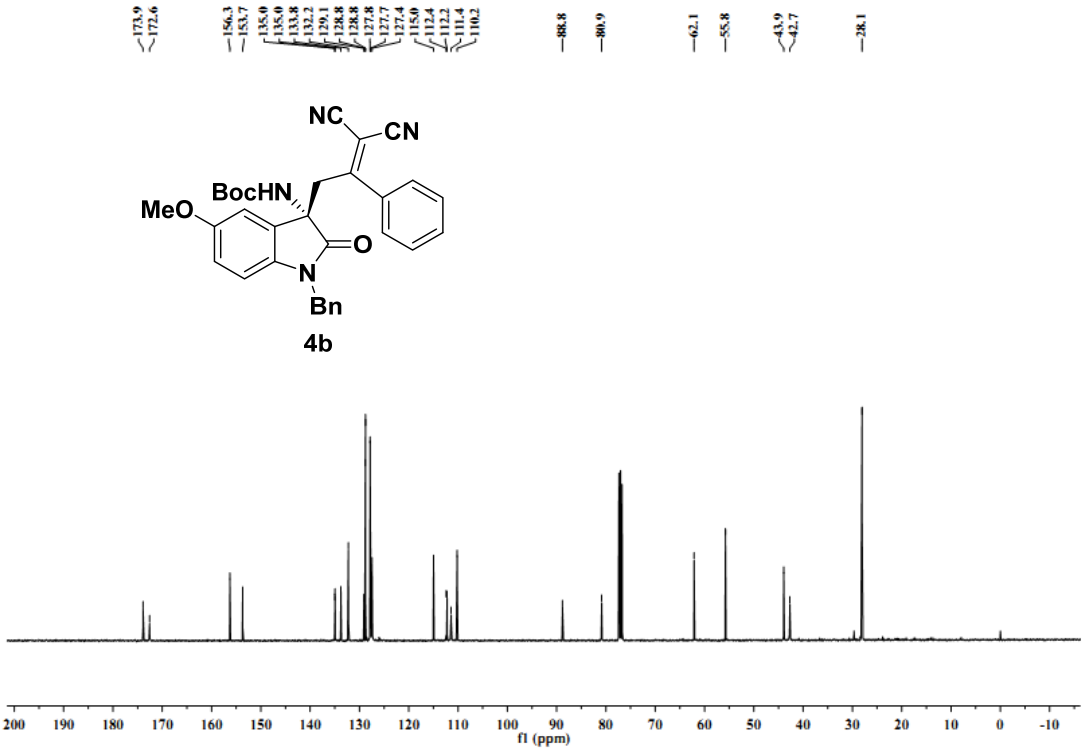
BocHN
MeO
O
N
Bn
4b
f1 (ppm)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MeO
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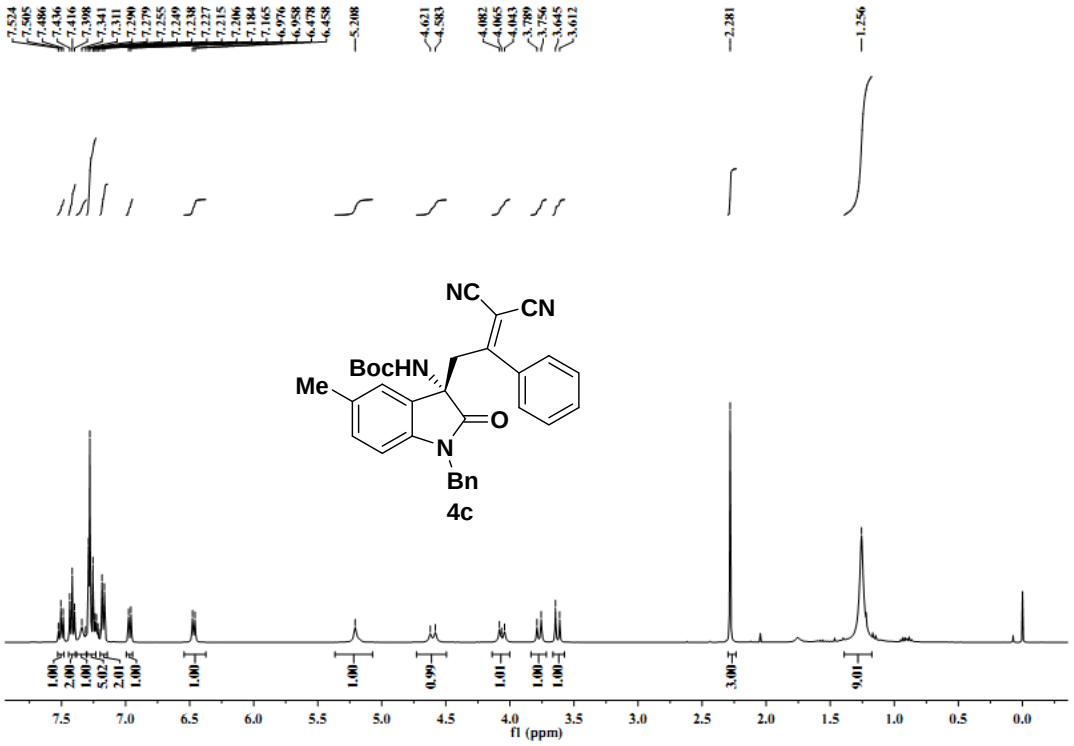
Bn
4b
f1 (ppm)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7.227
7.215
7.206
7.184
7.165
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6.958
6.478
6.458
5.208
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4.583
4.082
4.065
4.043
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3.612
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CN
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Me
O
N
Bn
4c
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2.00
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1.00
1.00
1.00
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1.01
1.00
1.00
3.00
9.01
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7.0
6.5
6.0
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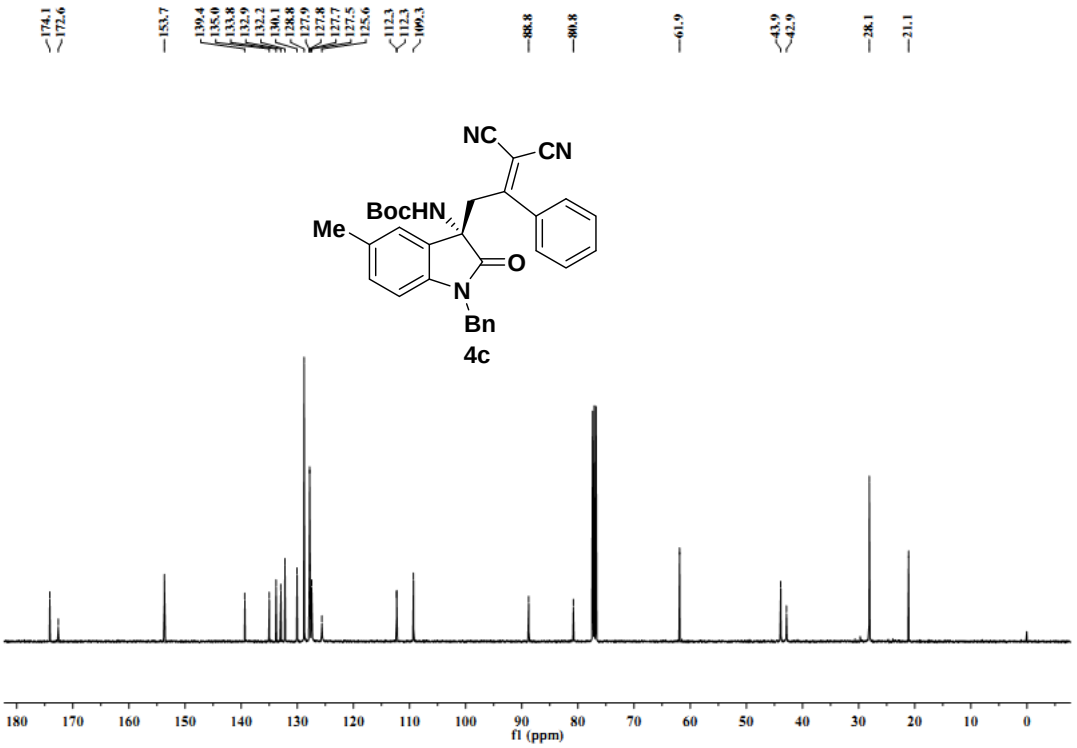
f1 (ppm)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125.6
112.3
112.3
109.3
88.8
80.8
61.9
43.9
42.9
28.1
21.1
NC
CN
BocHN
Me
O
N
Bn
4c
180
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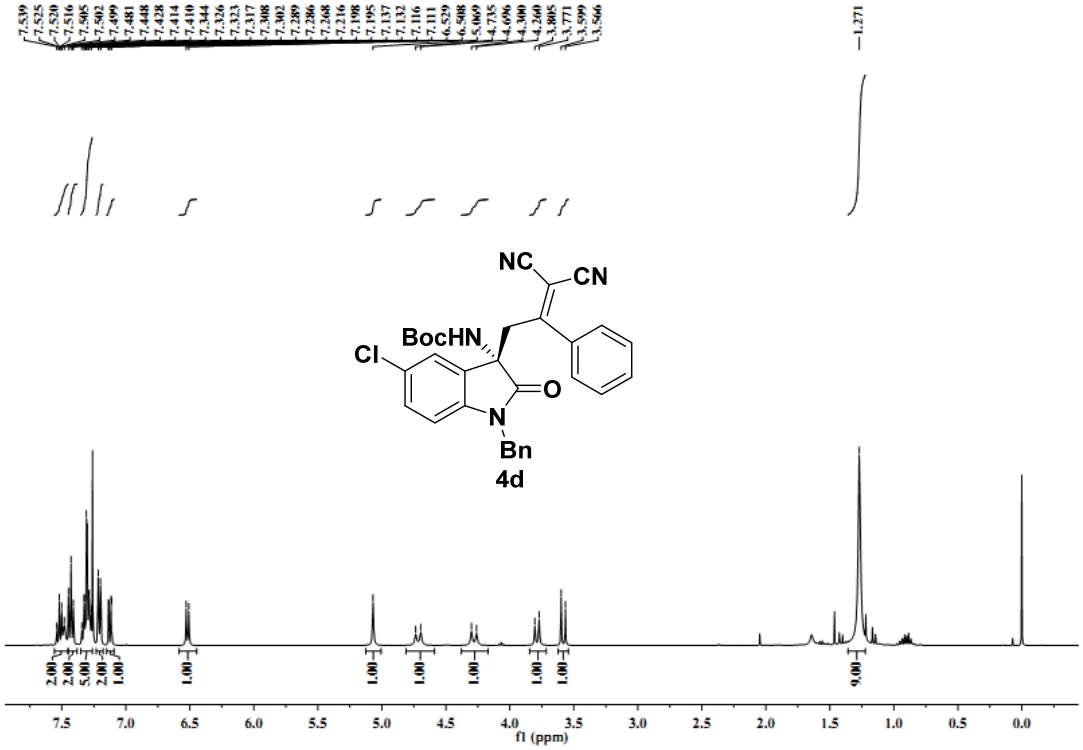
f1 (ppm)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Cl
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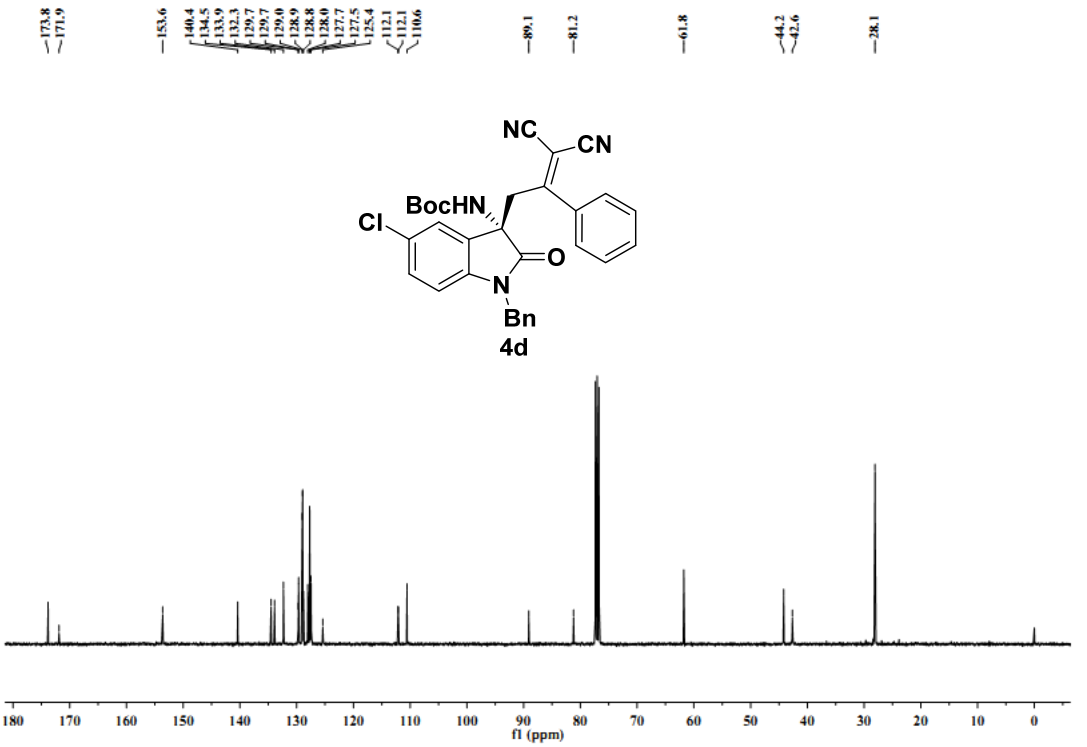
N
Bn
4d
fl (ppm)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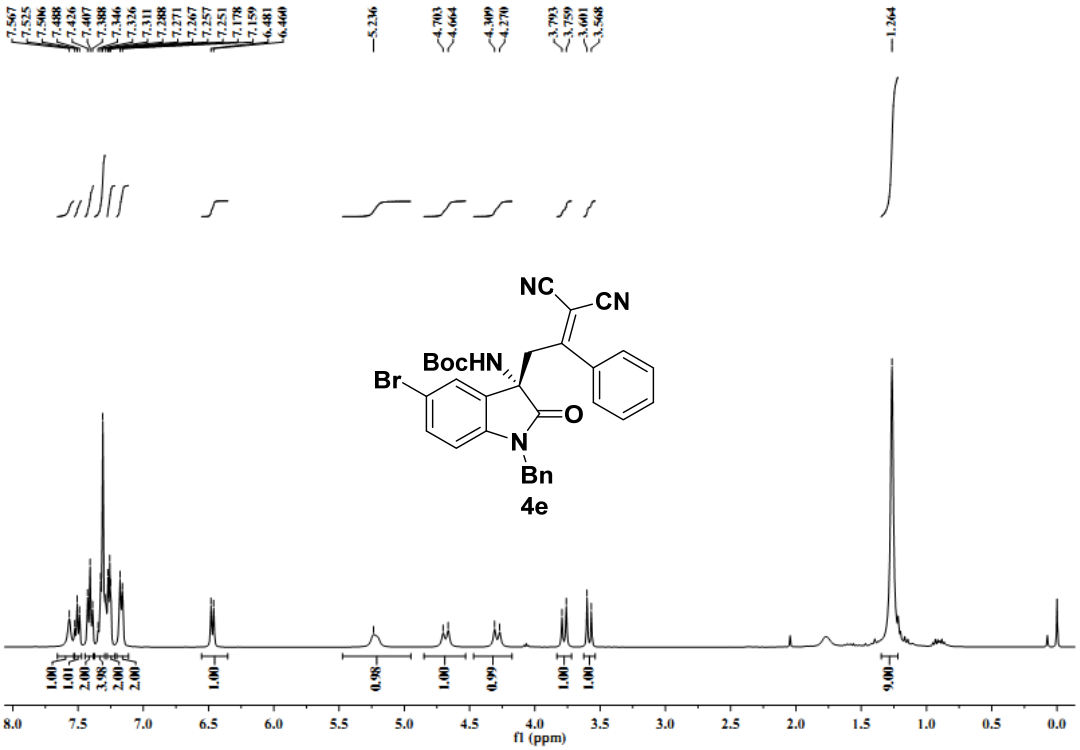
Cl
O
N
Bn
4d
fl (ppm)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7.267
7.257
7.251
7.178
7.159
6.481
6.460
5.236
4.703
4.664
4.309
4.270
3.793
3.759
3.601
3.568
1.264
NC
CN
BocHN
Br
O
N
Bn
4e
1.00
1.01
2.00
3.98
2.00
2.00
1.00
0.98
1.00
0.99
1.00
1.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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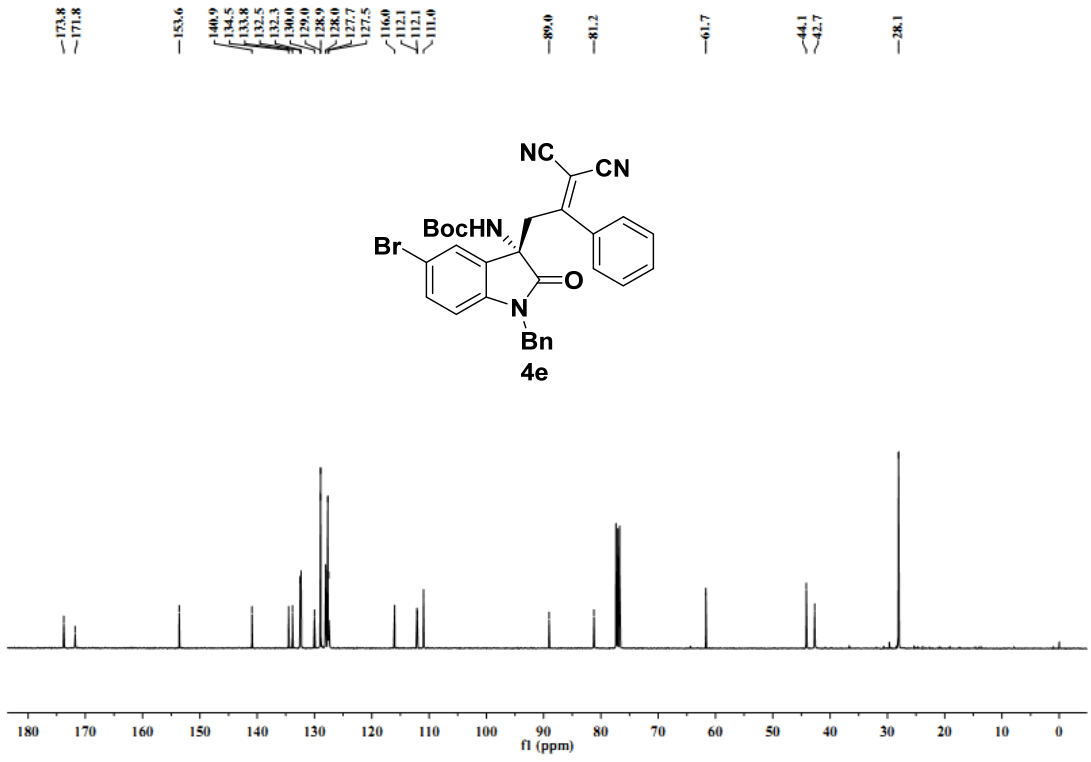
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.8
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129.0
128.9
128.0
127.7
127.5
116.0
112.1
112.1
111.0
89.0
81.2
61.7
44.1
42.7
28.1
NC
CN
BocHN
Br
O
N
Bn
4e
180
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130
120
110
100
90
80
70
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50
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30
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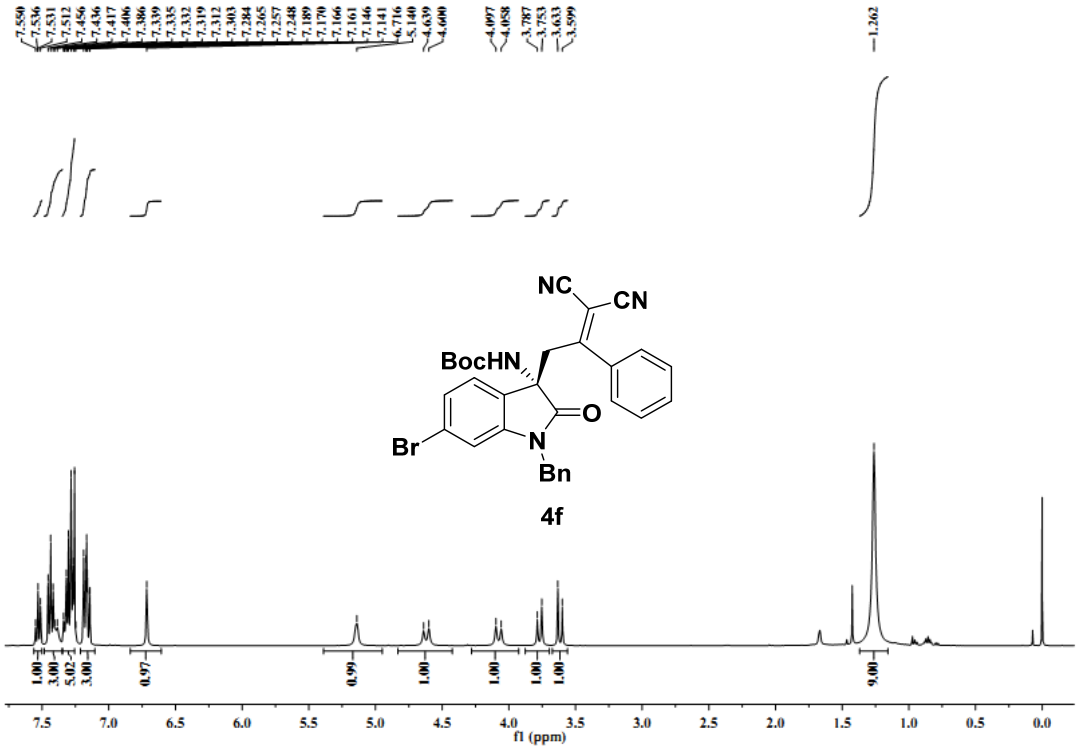
10
0
f1 (ppm)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7.166
7.161
7.146
7.141
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4.600
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3.787
3.753
3.633
3.599
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NC
CN
BocHN
O
Br
N
Bn
4f
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3.00
5.02
3.00
0.97
0.99
1.00
1.00
1.00
1.00
9.00
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7.0
6.5
6.0
5.5
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2.5
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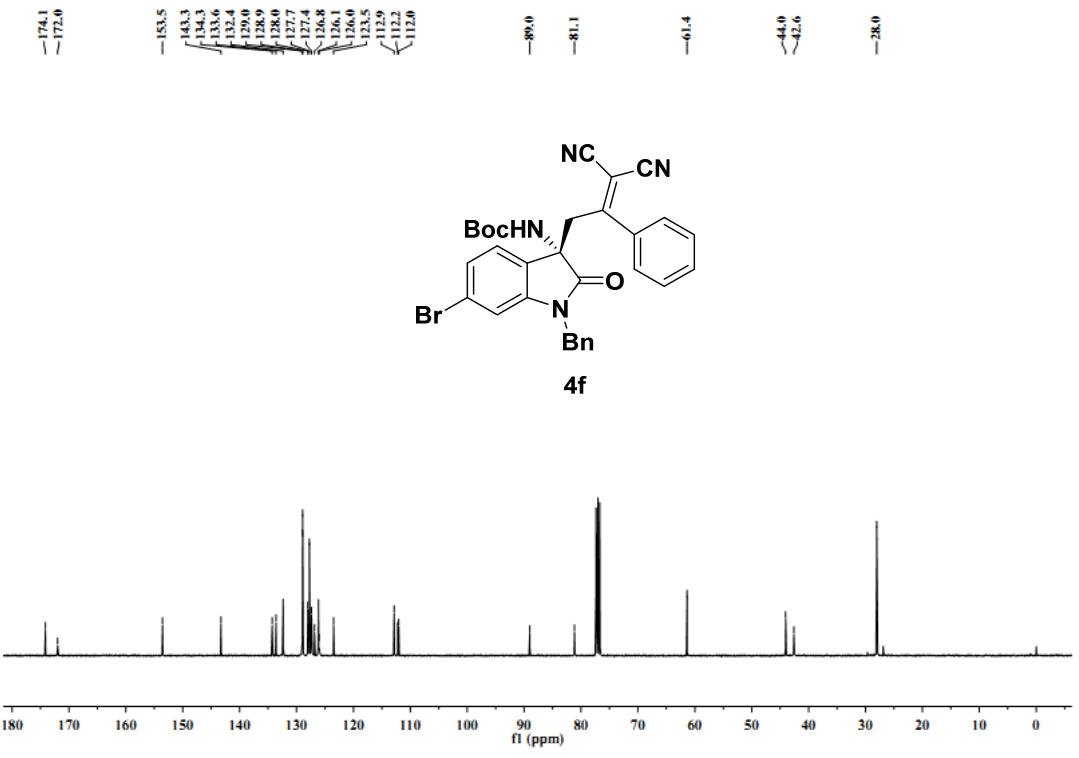
0.0
f1 (ppm)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134.3
133.6
132.4
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128.0
127.7
127.4
126.8
126.1
126.0
123.5
112.9
112.2
112.0
89.0
81.1
61.4
44.0
42.6
28.0
NC
CN
BocHN
O
Br
N
Bn
4f
180
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130
120
110
100
90
80
70
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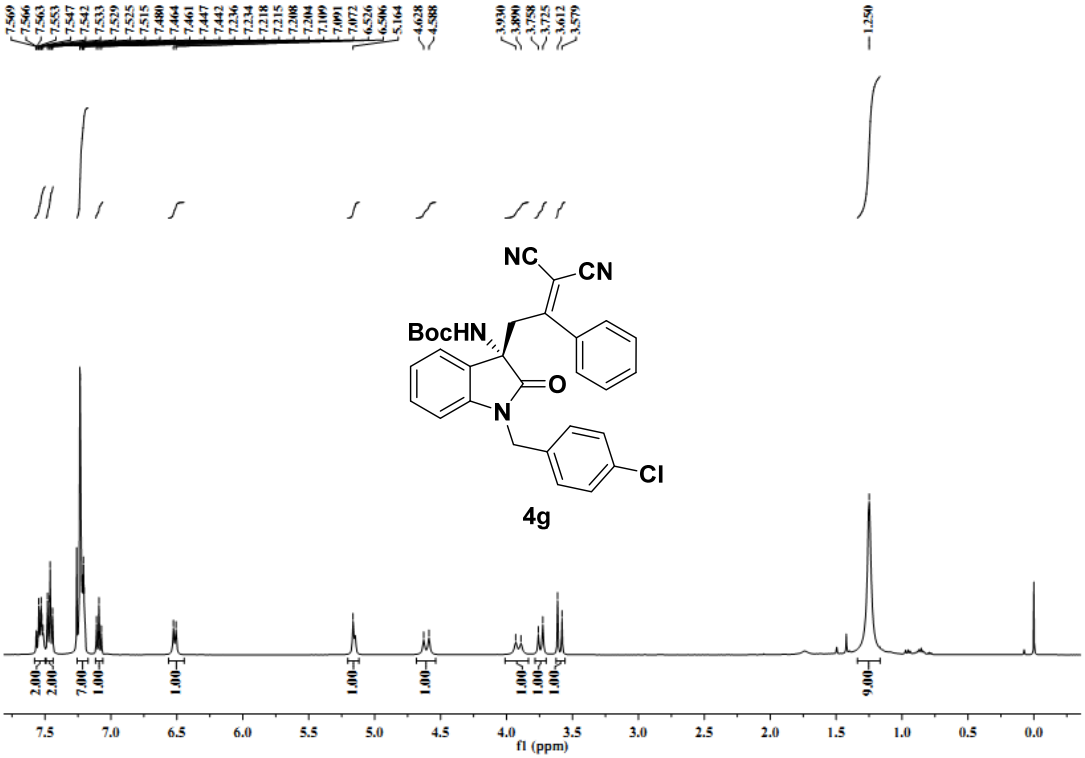
50
40
30
20
10
0
f1 (ppm)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7.515
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7.461
7.447
7.442
7.236
7.234
7.218
7.215
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7.204
7.109
7.091
7.072
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6.506
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4.588
3.930
3.890
3.758
3.725
3.612
3.579
1.250
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CN
BocHN
O
N
Cl
4g
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2.00
7.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
9.00
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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2.5
2.0
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1.0
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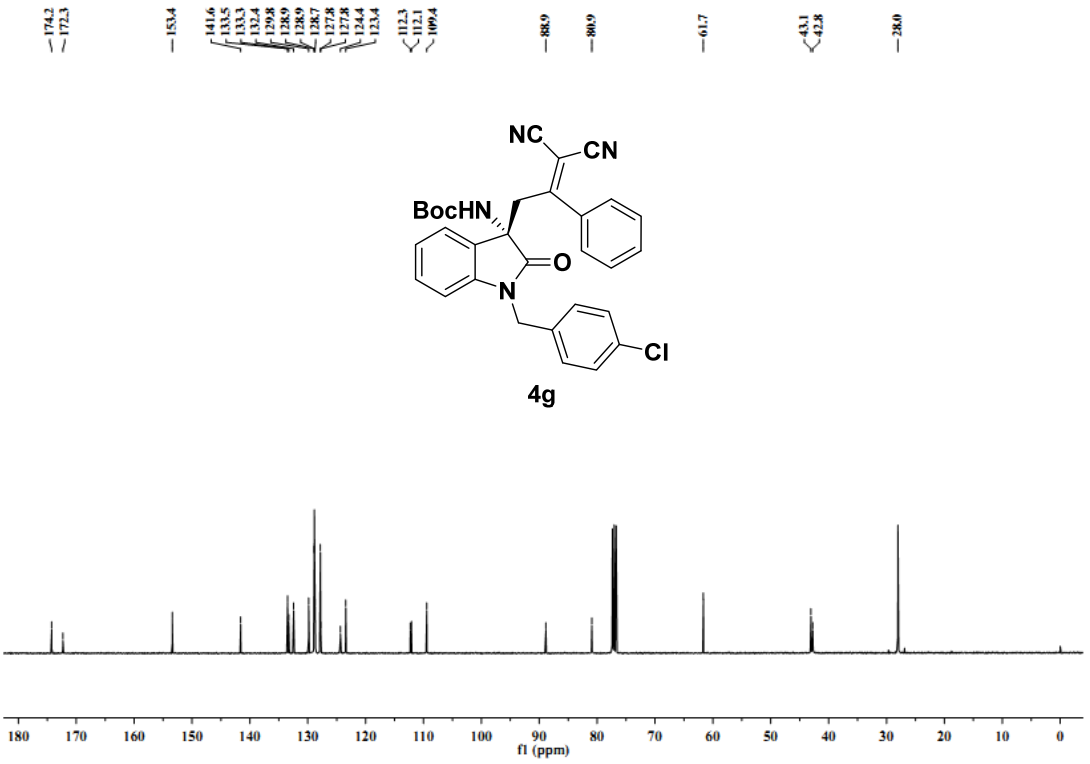
0.0
f1 (ppm)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128.9
128.7
127.8
127.8
124.4
123.4
112.3
112.1
109.4
88.9
80.9
61.7
43.1
42.8
28.0
NC
CN
BocHN
O
N
Cl
4g
180
170
160
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130
120
110
100
90
80
70
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50
40
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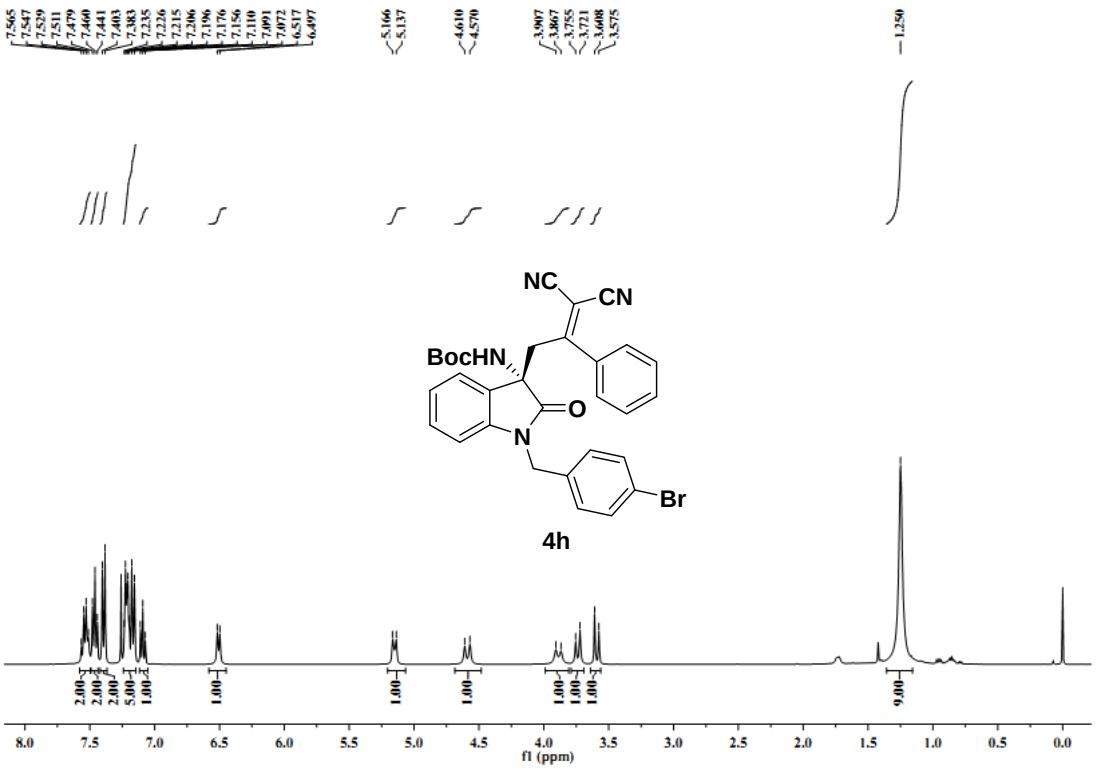
f1 (ppm)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7.156
7.110
7.091
7.072
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6.497
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5.137
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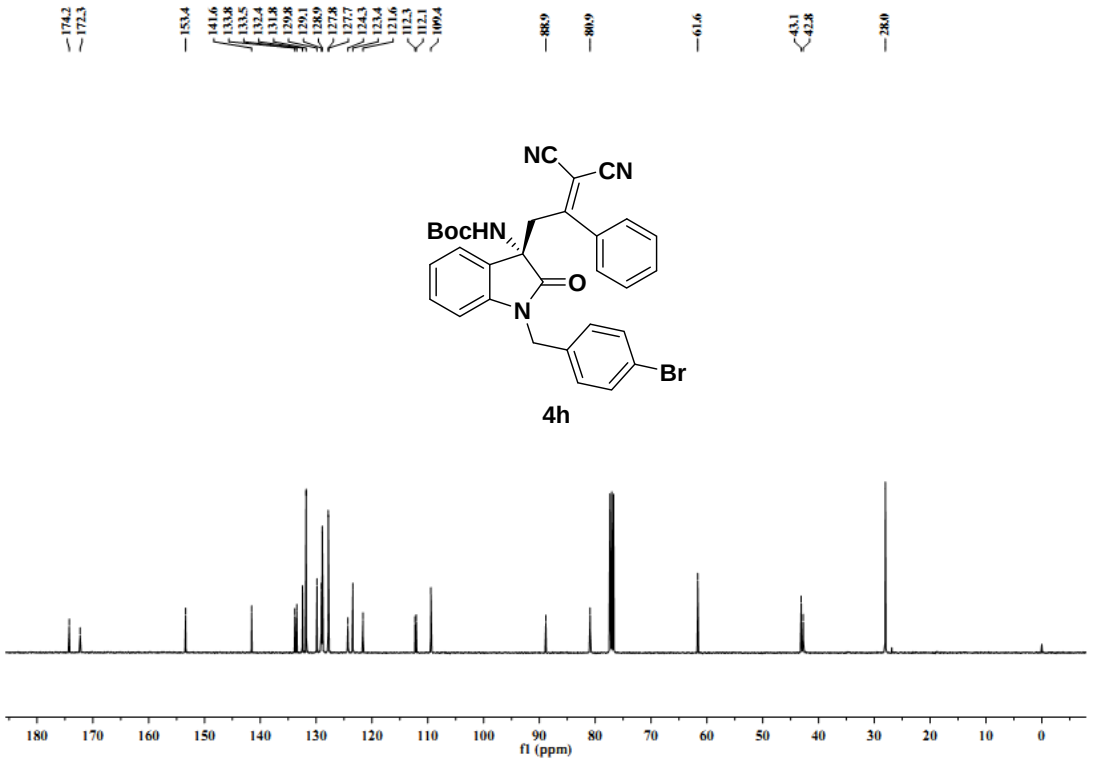
4.570
3.907
3.867
3.755
3.721
3.608
3.575
1.250
NC
CN
BocHN
O
N
Br
4h
2.00
2.00
2.00
5.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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124.3
123.4
121.6
112.3
112.1
109.4
88.9
80.9
61.6
43.1
42.8
28.0
NC
CN
BocHN
O
N
Br
4h
180
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150
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130
120
110
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90
80
70
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50
40
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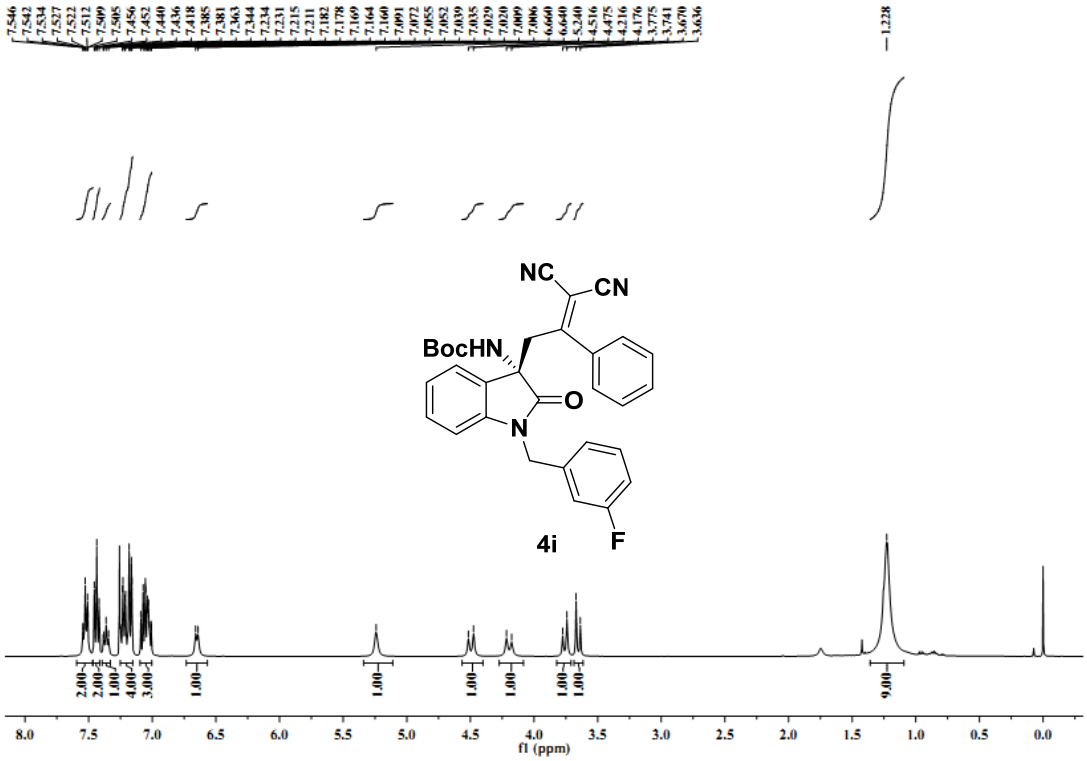
f1 (ppm)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F
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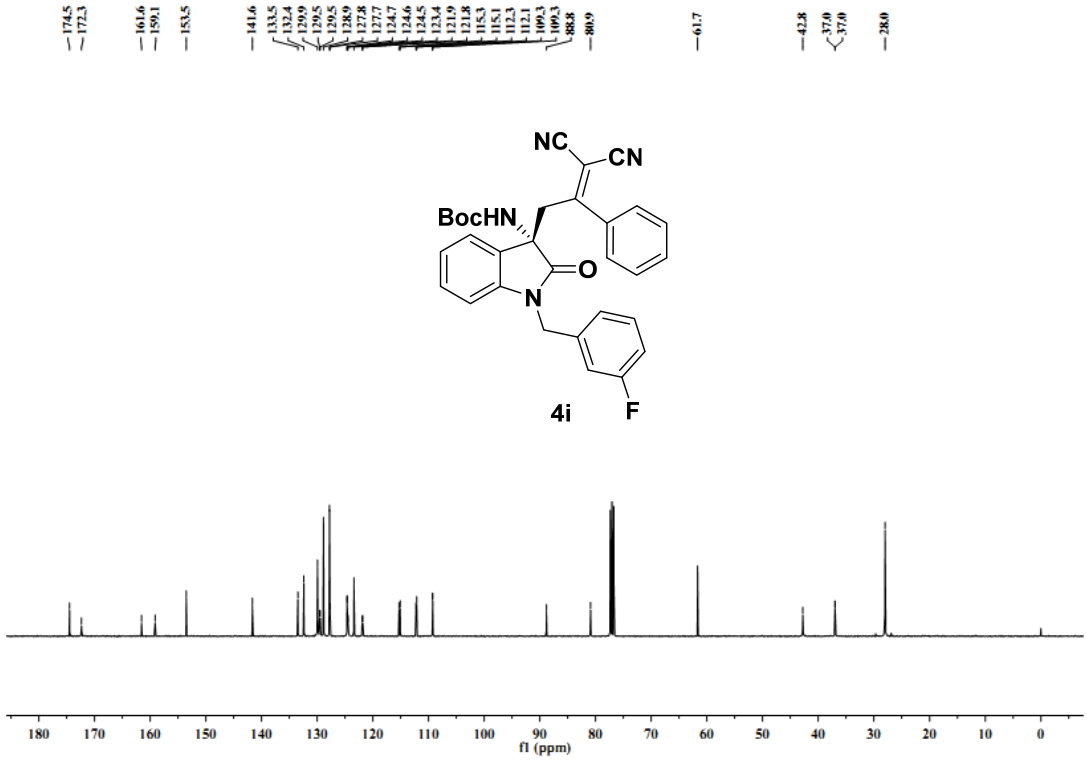
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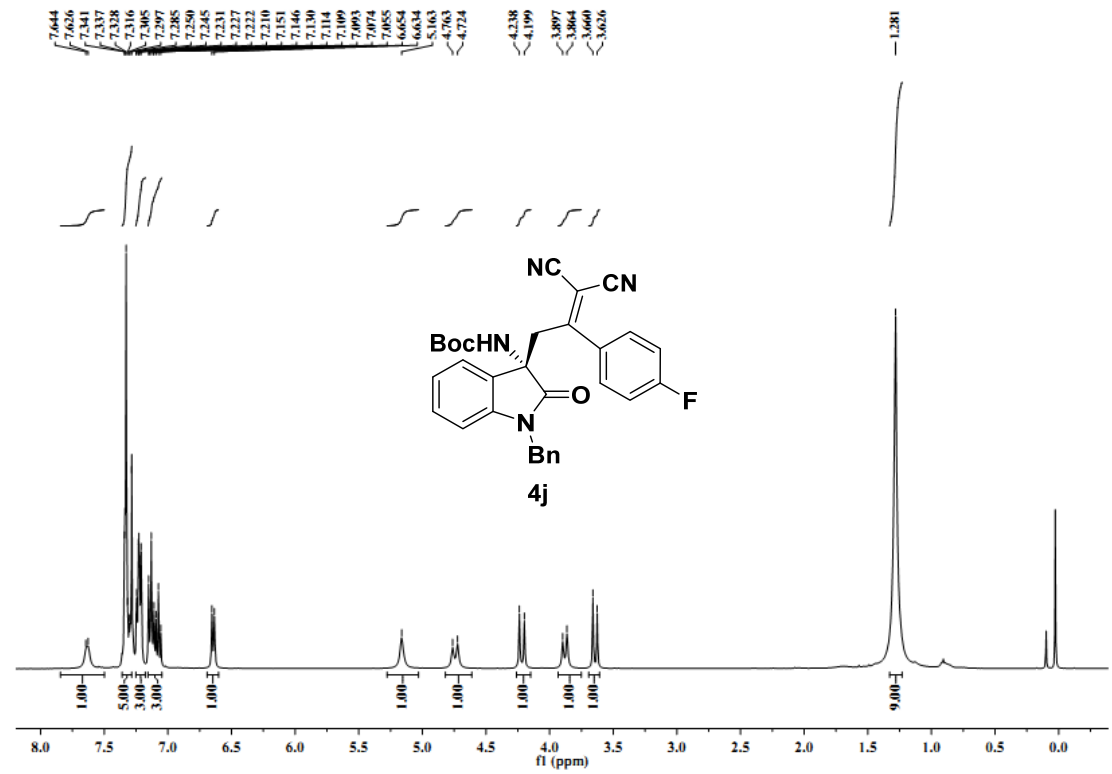
BocHN
O
N
F
4i
f1 (ppm)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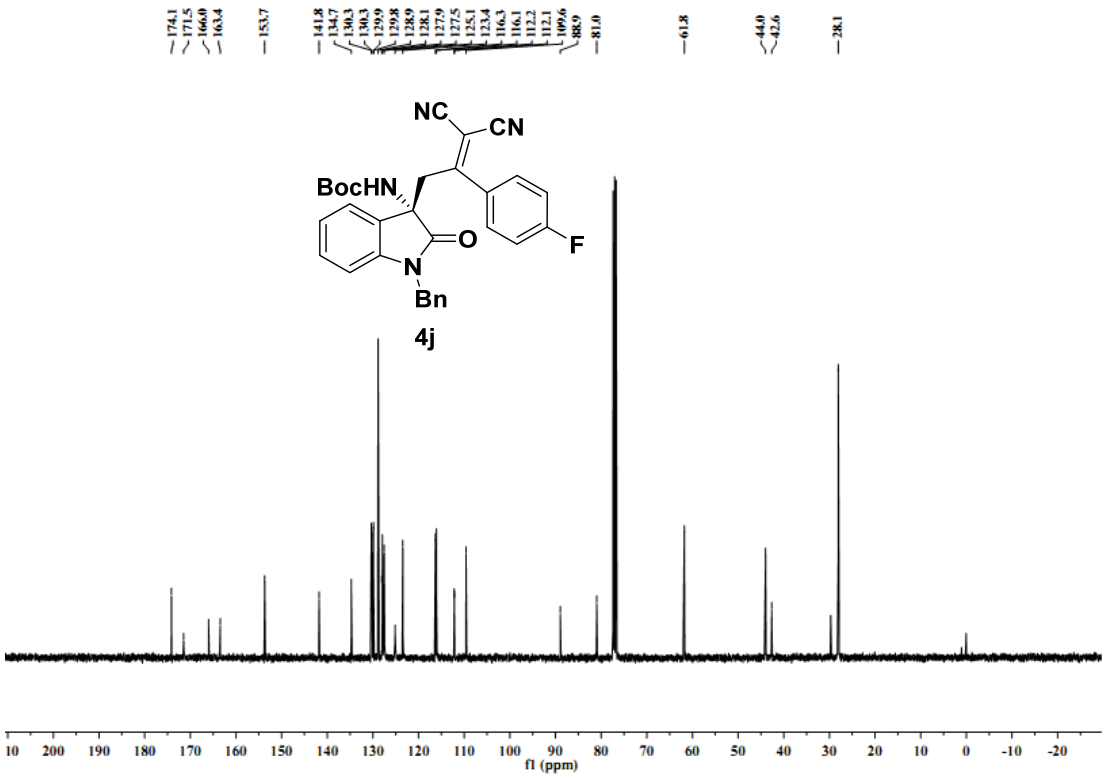
fl (ppm)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O
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Bn
F
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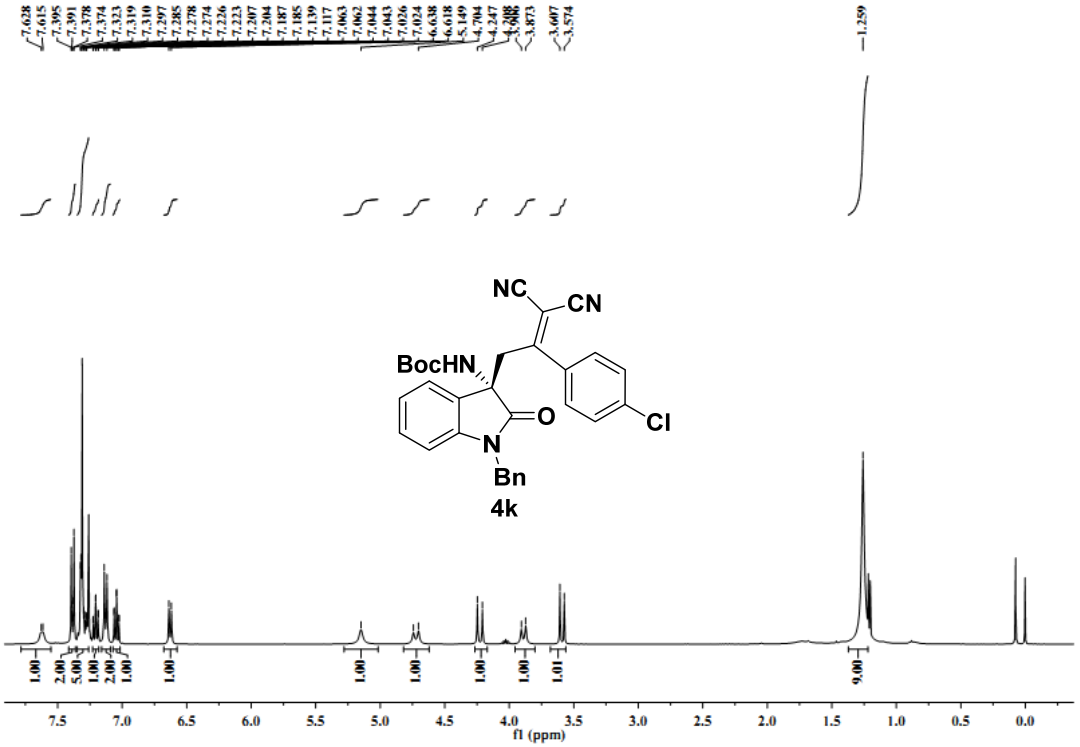
fl (ppm)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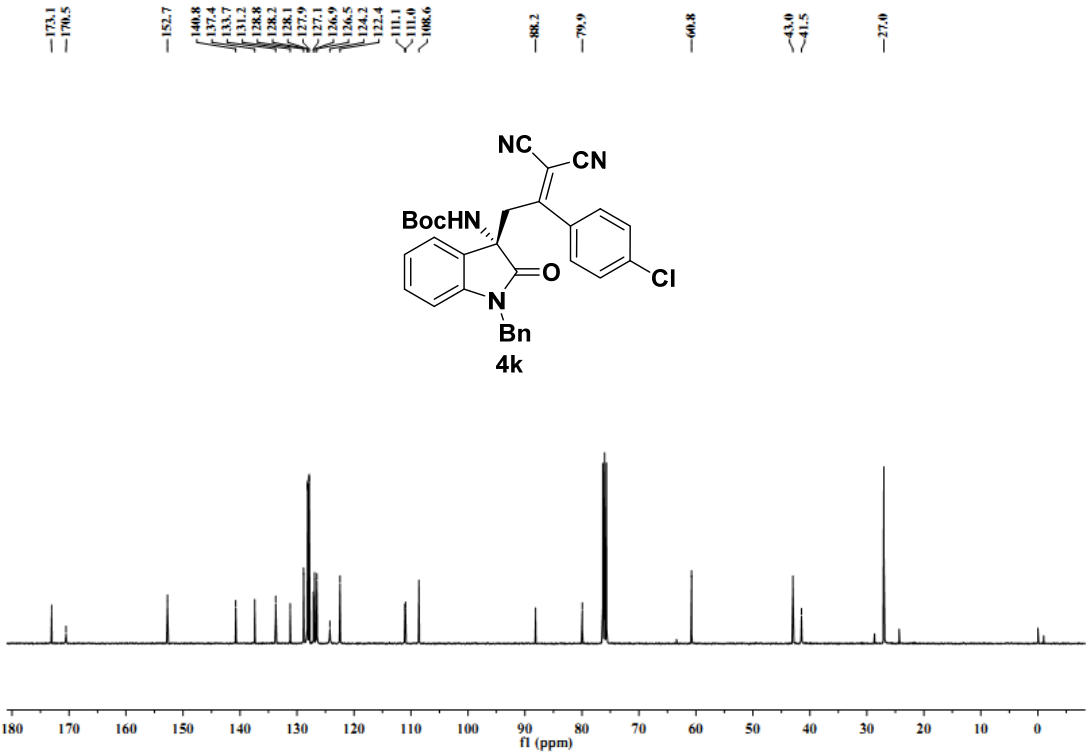
Bn
Cl
4k
fl (ppm)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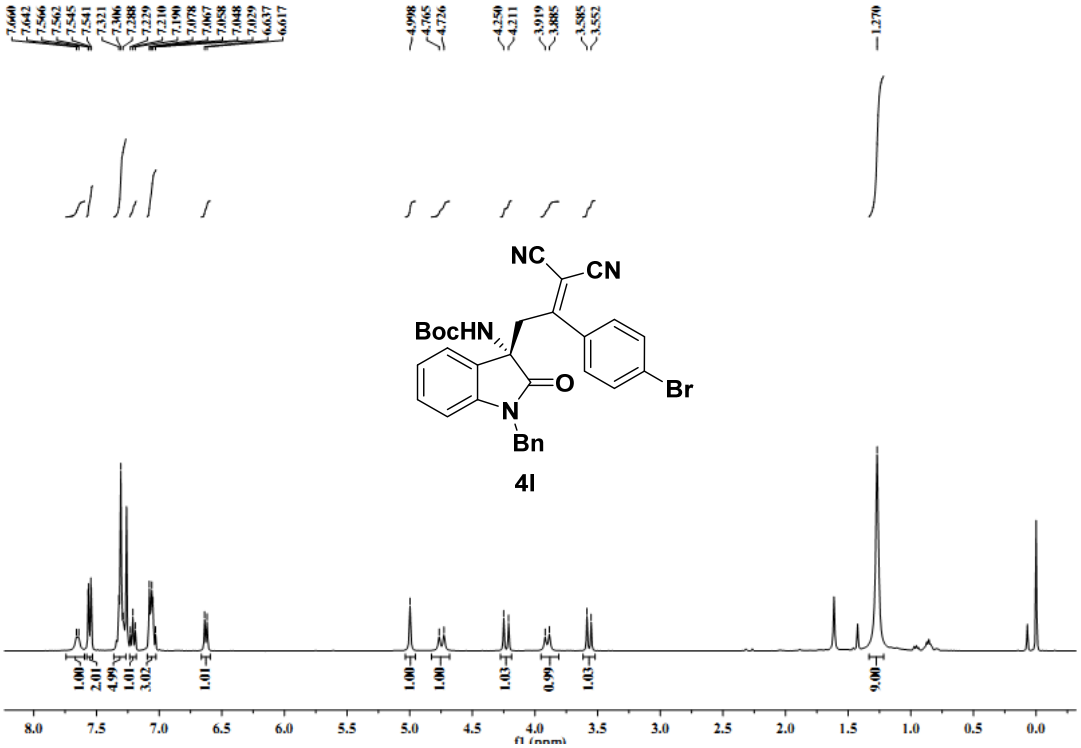
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Bn
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1.01
1.00
1.00
1.03
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1.03
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6.5
6.0
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5.0
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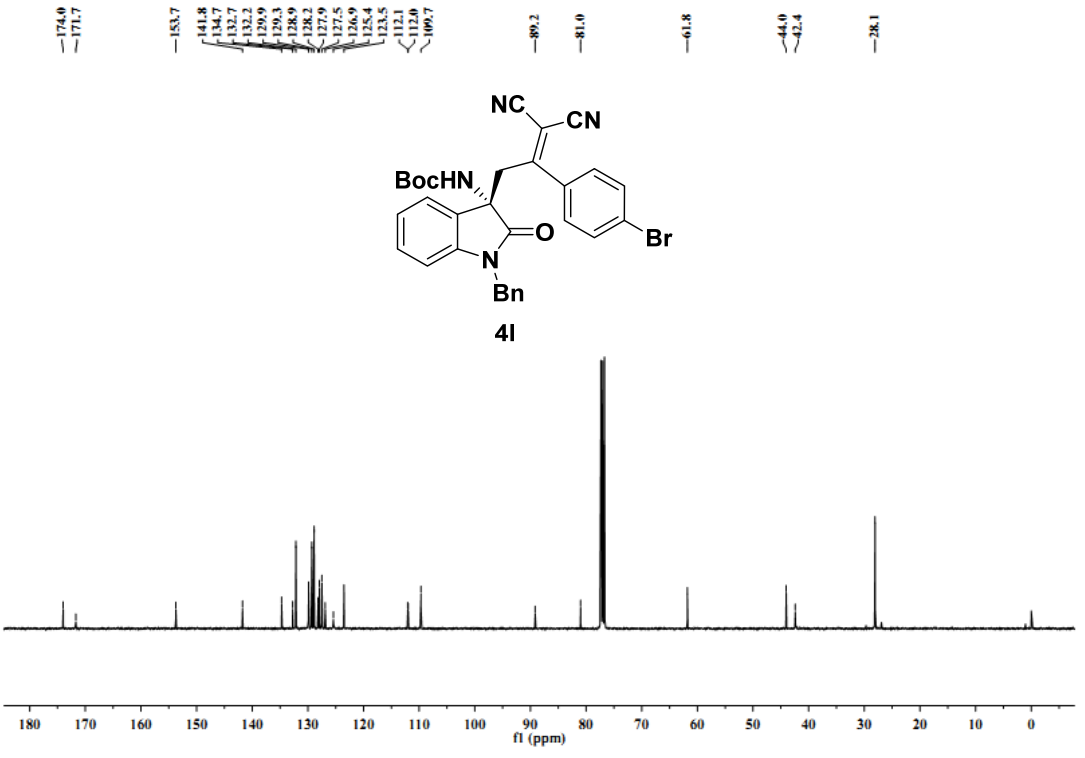
f1 (ppm)

4l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132.7
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127.5
126.9
125.4
123.5
112.1
112.0
109.7
89.2
81.0
61.8
44.0
42.4
28.1
NC
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N
Bn
Br
180
170
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80
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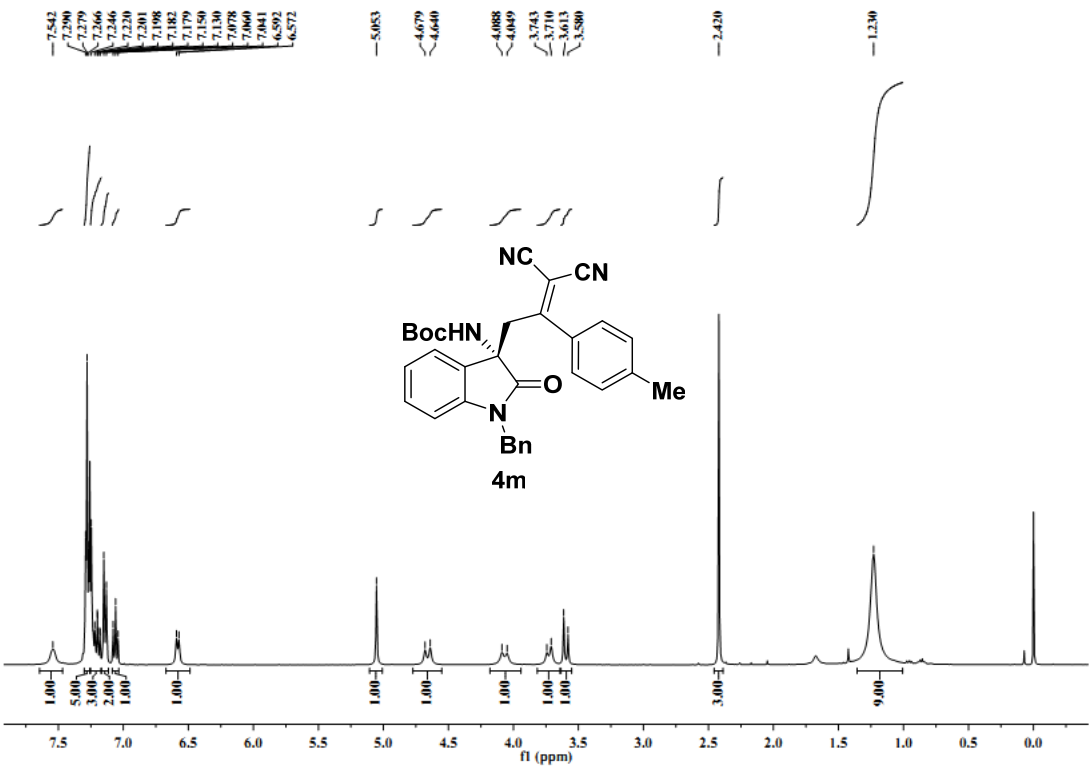
30
20
10
0
f1 (ppm)

4l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7.130
7.078
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7.041
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6.572
5.053
4.679
4.640
4.088
4.049
3.743
3.710
3.613
3.580
2.420
1.230
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BocHN
O
N
Bn
Me
4m
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5.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
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3.00
9.00
7.5
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6.5
6.0
5.5
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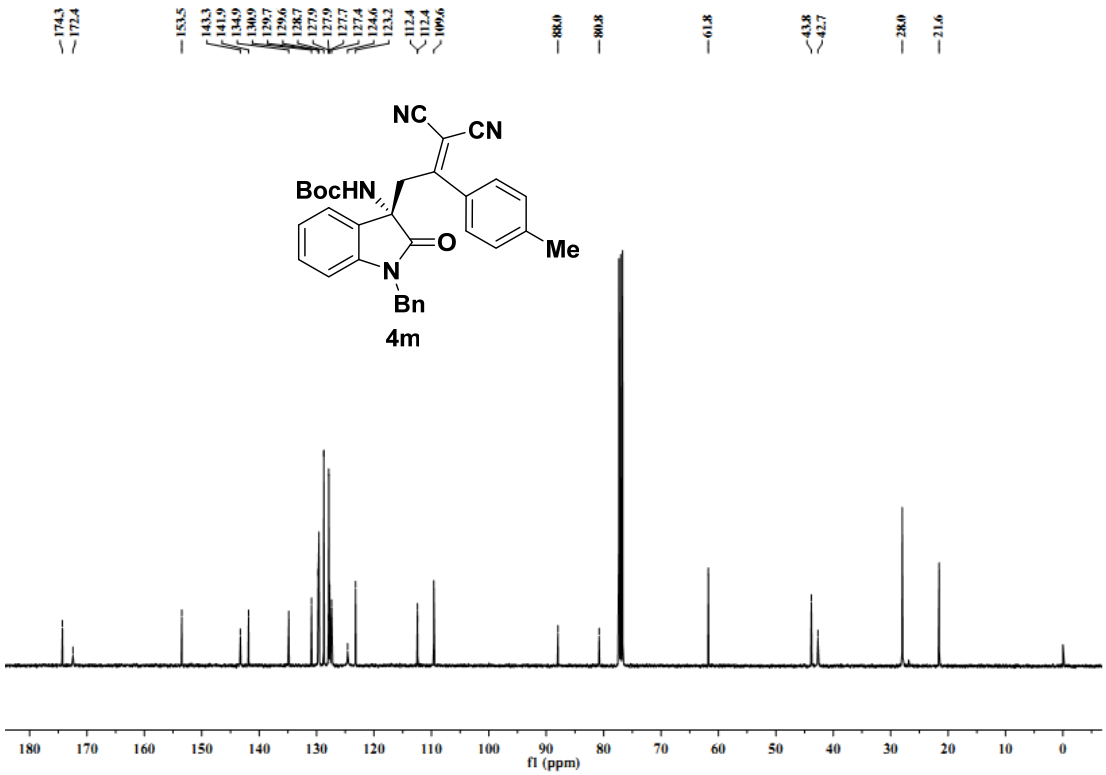
f1 (ppm)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141.9
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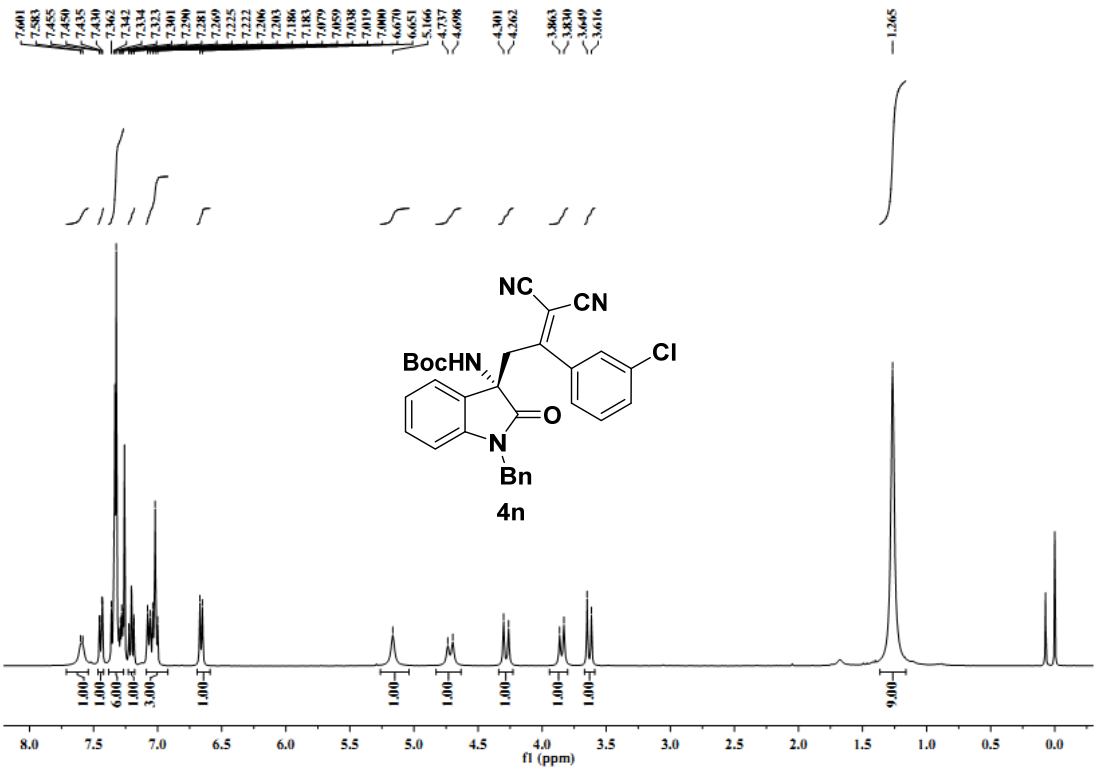
127.9
127.7
127.4
124.6
123.2
112.4
112.4
109.6
88.0
80.8
61.8
43.8
42.7
28.0
21.6
NC
CN
BocHN
O
N
Bn
Me
4m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Cl
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N
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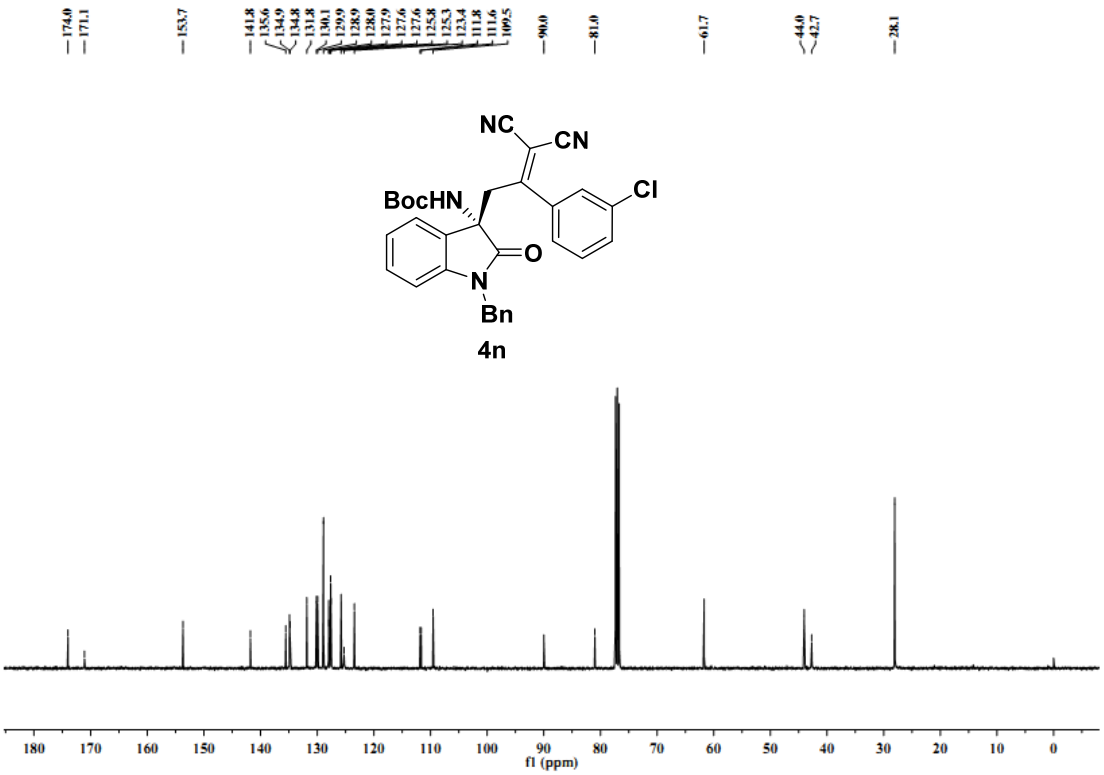
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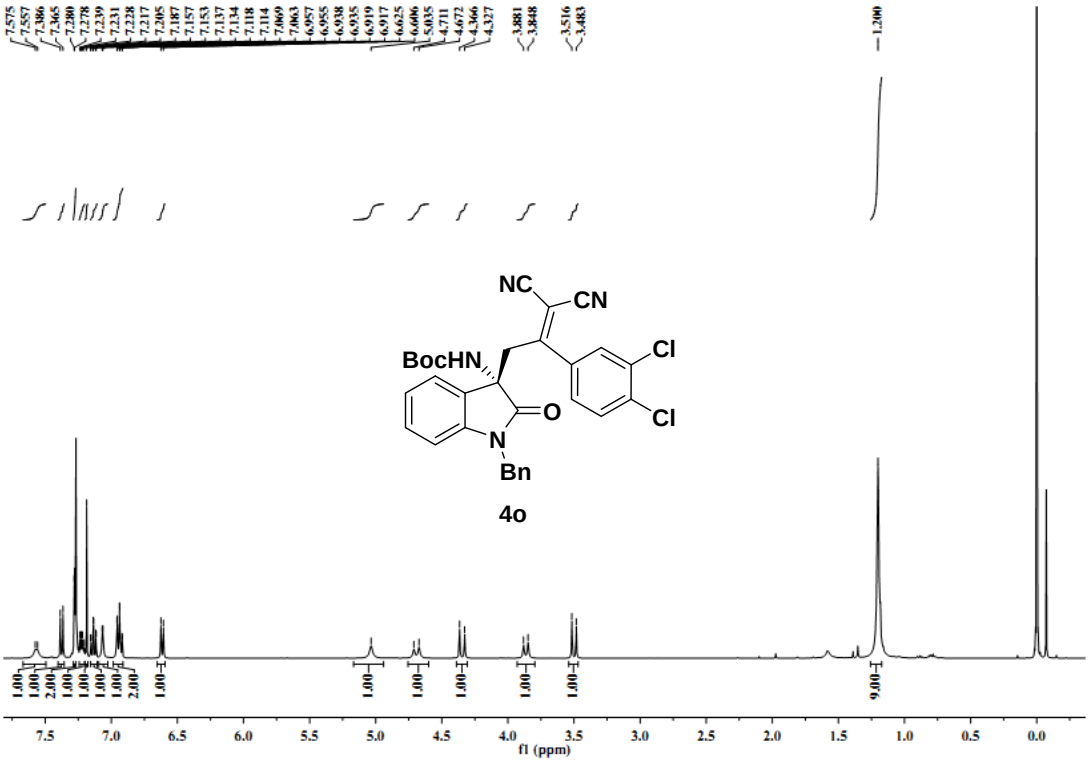
f1 (ppm)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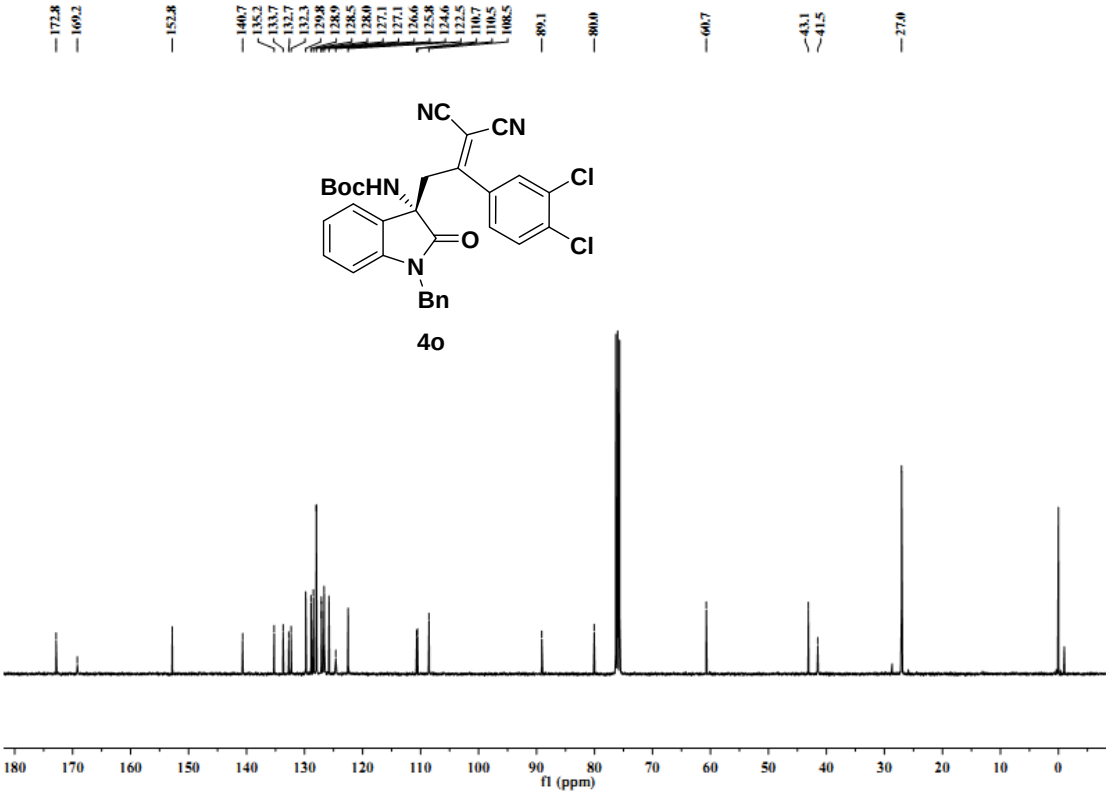
BocHN
Cl
Cl
O
N
Bn
4o
fl (ppm)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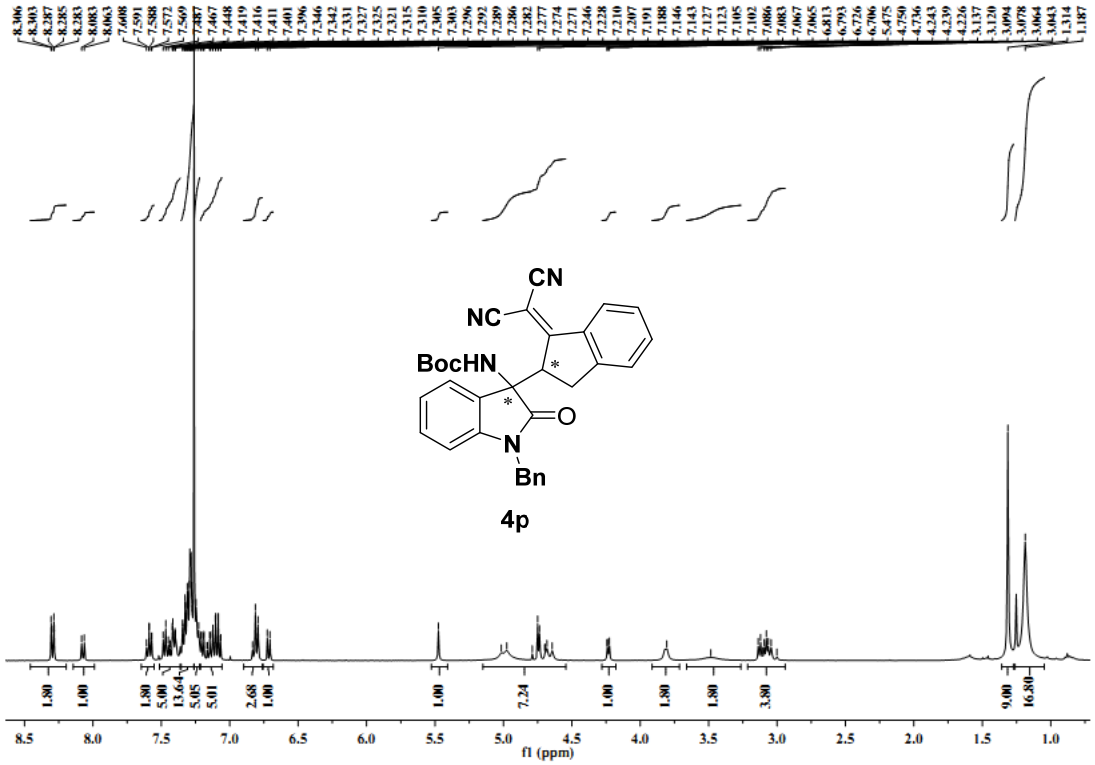
BocHN
Cl
Cl
O
N
Bn
4o
fl (ppm)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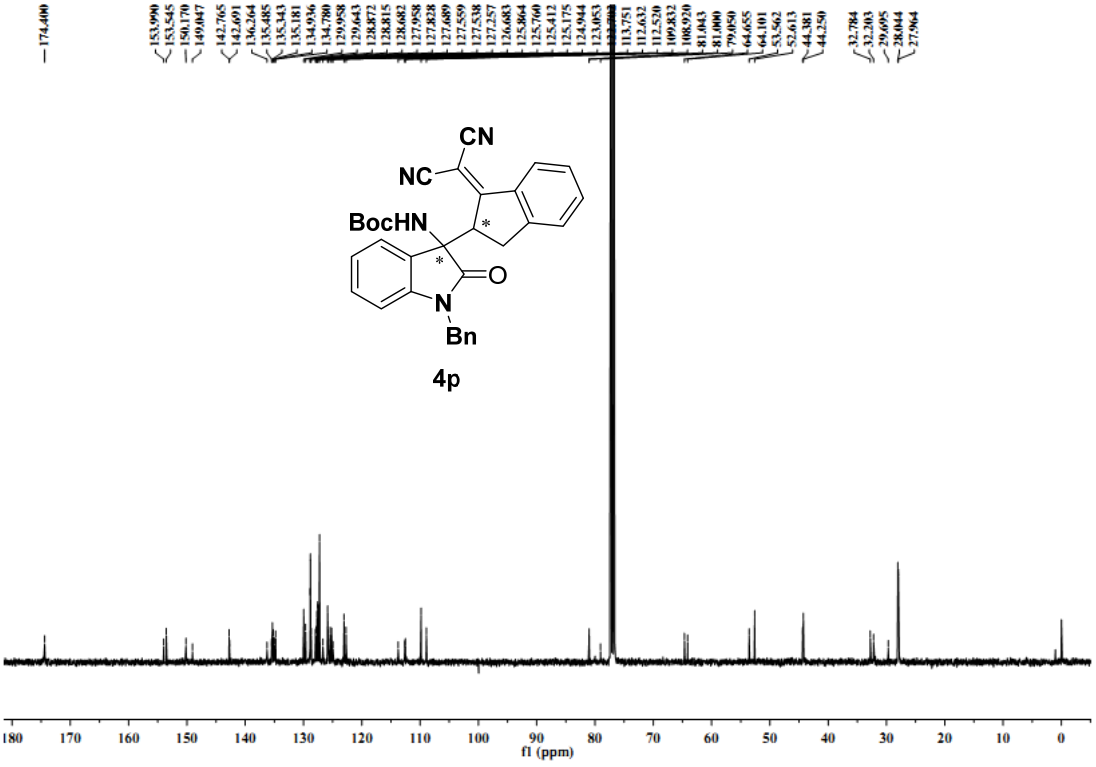
fl (ppm)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O
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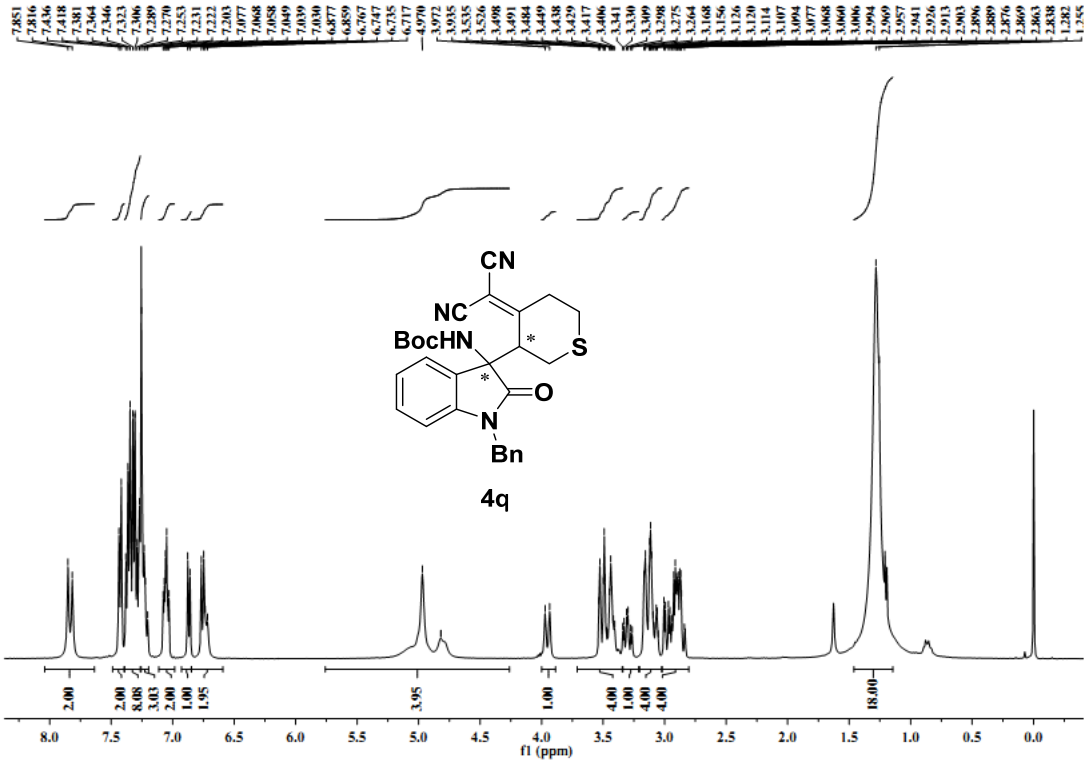
Bn
4p
fl (ppm)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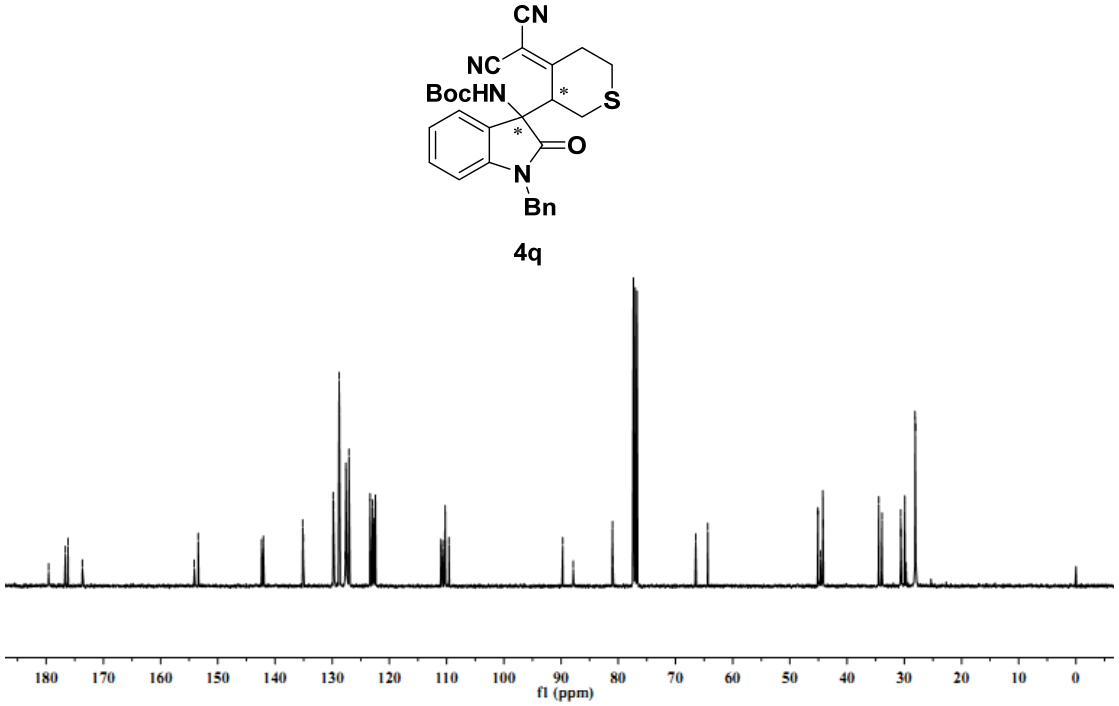
f1 (ppm)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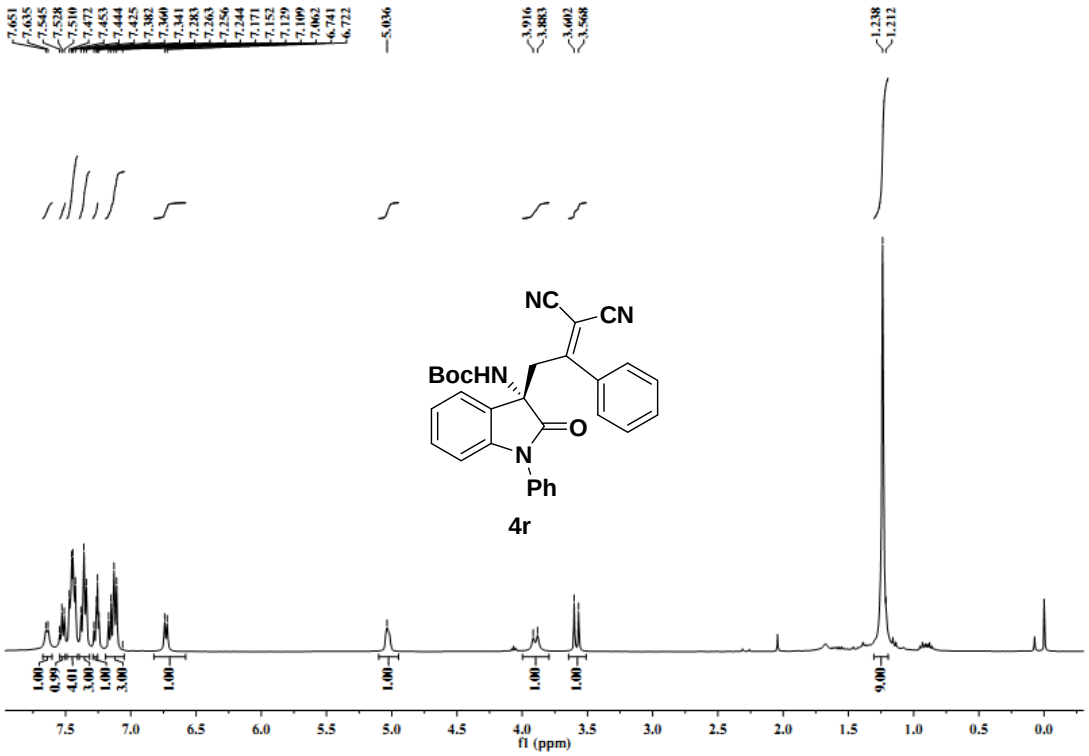
NC
BocHN
S
O
N
Bn
4q
f1 (ppm)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Ph
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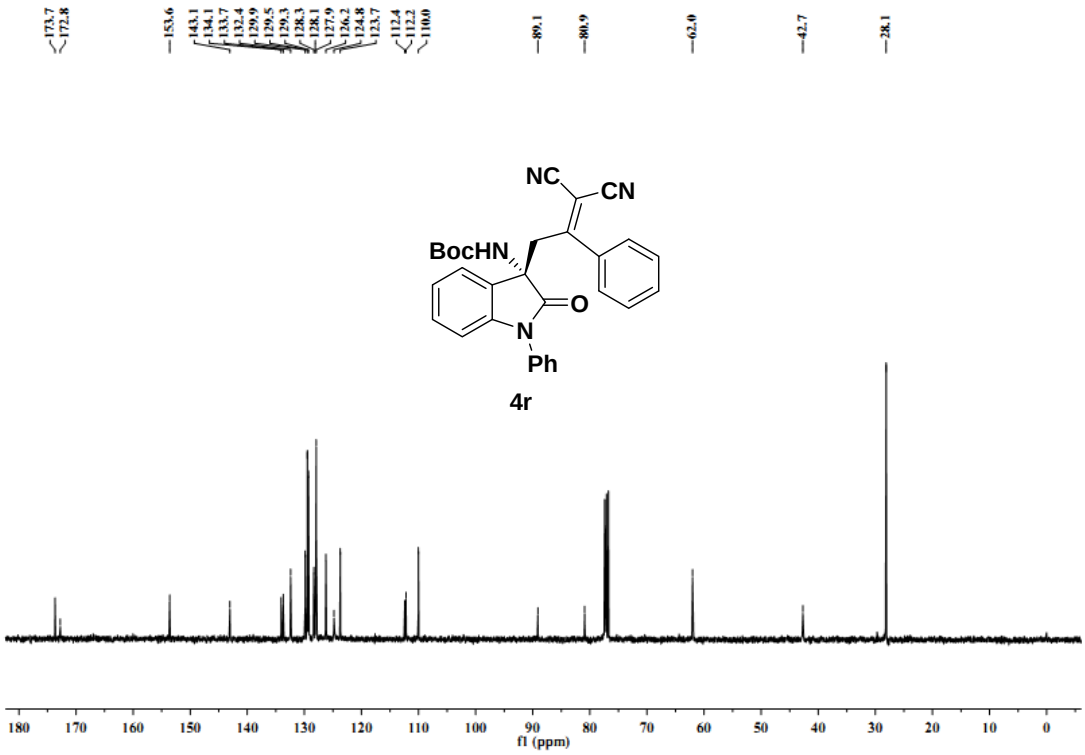
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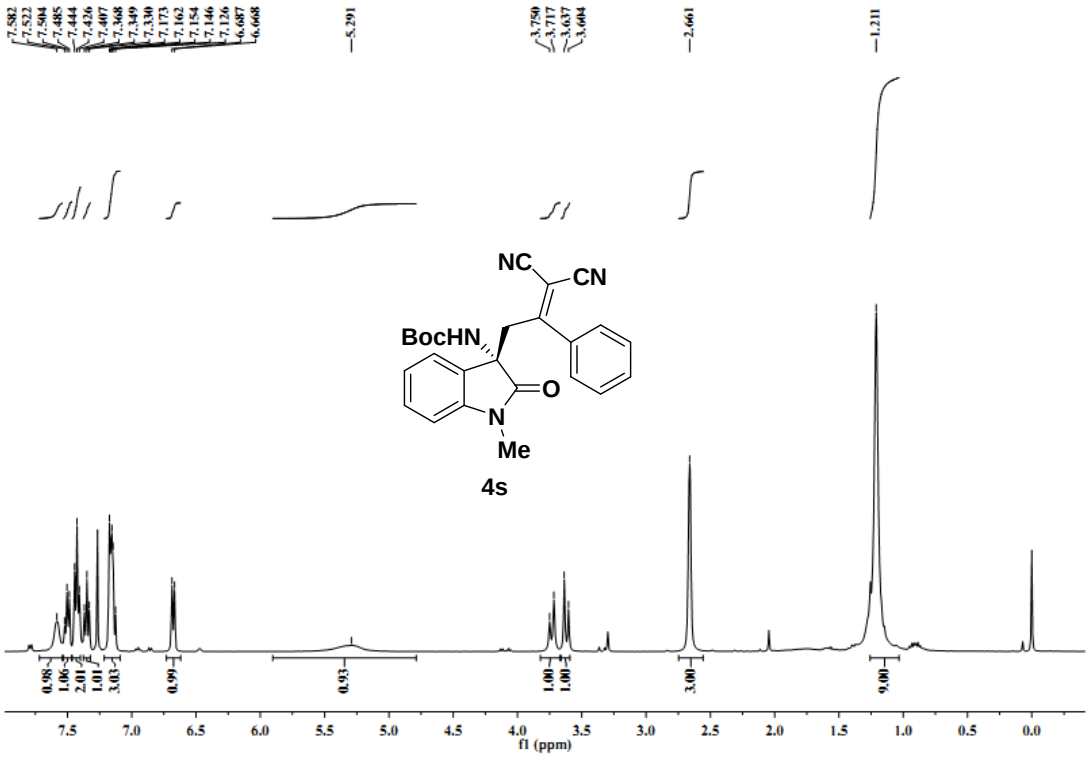
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7.173
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7.154
7.146
7.126
6.687
6.668
5.291
3.750
3.717
3.637
3.604
2.661
1.211
NC
CN
BocHN
O
N
Me
4s
0.98
1.06
2.01
1.01
3.03
0.99
0.93
1.00
1.00
3.00
9.00
7.5
7.0
6.5
6.0
5.5
5.0
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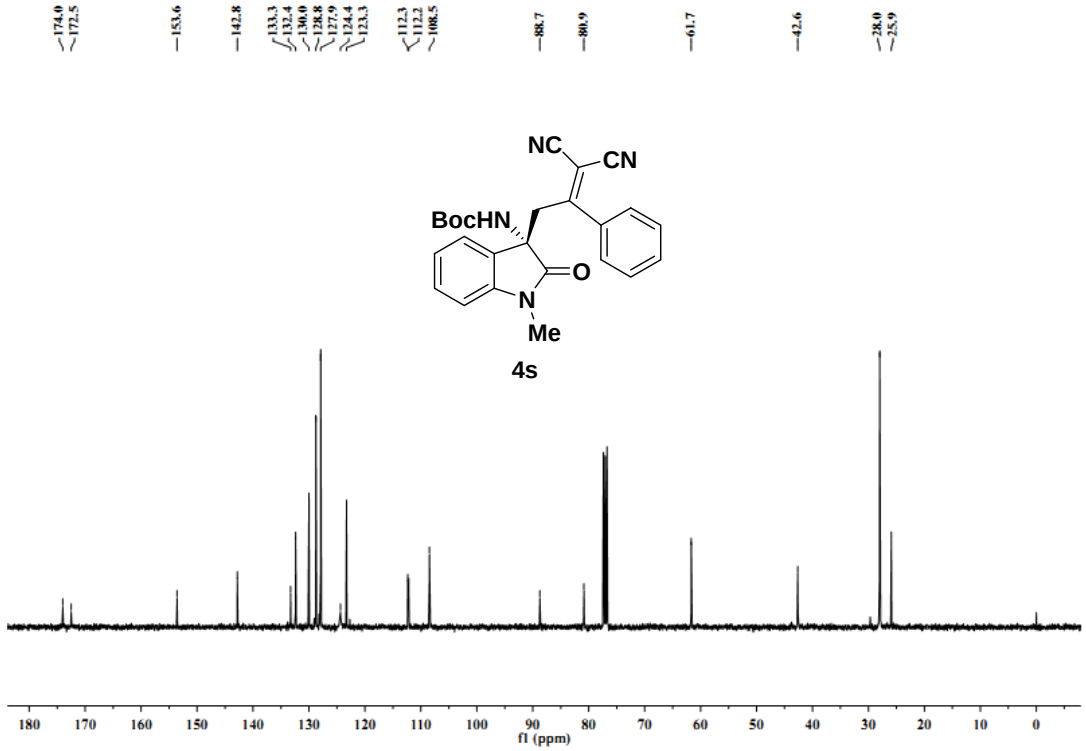
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.4
130.0
128.8
127.9
124.4
123.3
112.3
112.2
108.5
88.7
80.9
61.7
42.6
28.0
25.9
NC
CN
BocHN
O
N
Me
4s
180
170
160
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100
90
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50
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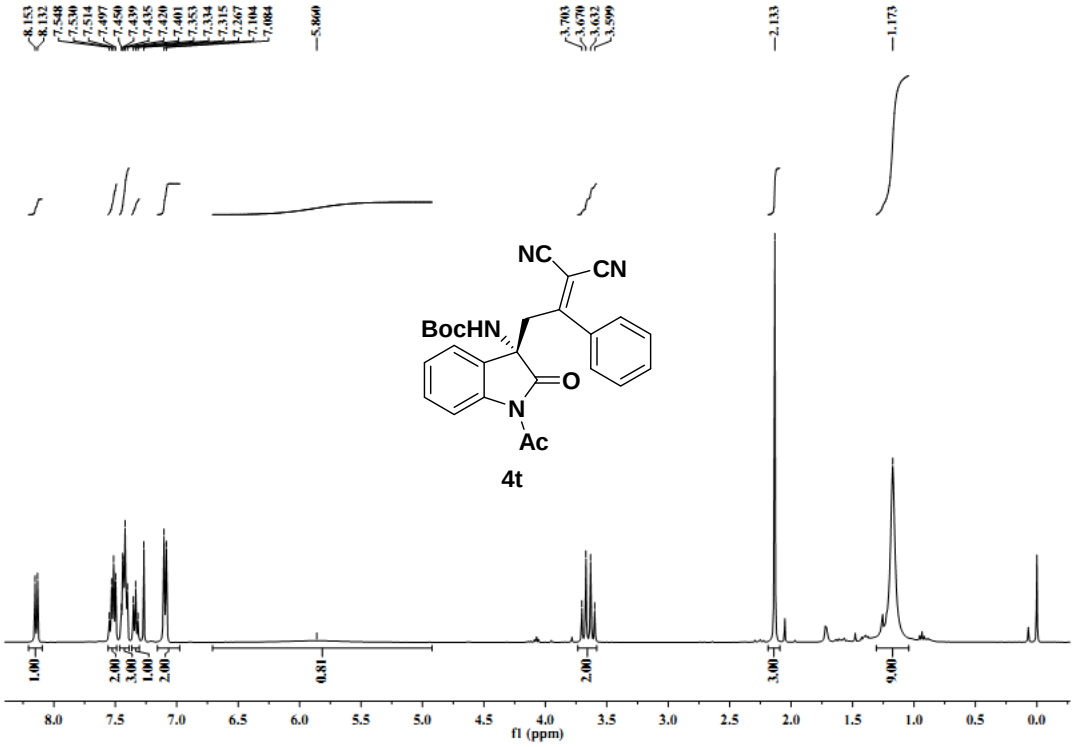
f1 (ppm)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7.439
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7.420
7.401
7.353
7.334
7.315
7.267
7.104
7.084
5.860
3.703
3.670
3.632
3.599
2.133
1.173
NC
CN
BocHN
O
N
Ac
4t
1.00
2.00
3.00
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2.00
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3.00
9.00
8.0
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6.5
6.0
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2.5
2.0
1.5
1.0
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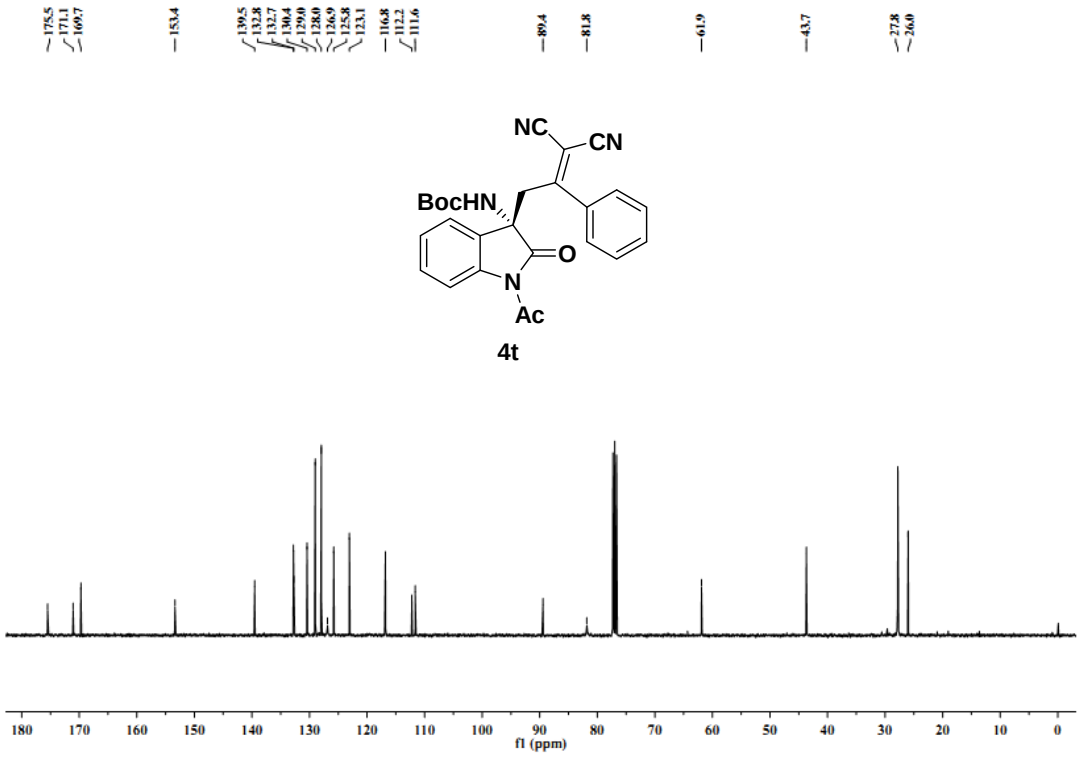
0.0
f1 (ppm)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130.4
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128.0
126.9
125.8
123.1
116.8
112.2
111.6
89.4
81.8
61.9
43.7
27.8
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NC
CN
BocHN
O
N
Ac
4t
180
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120
110
100
90
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50
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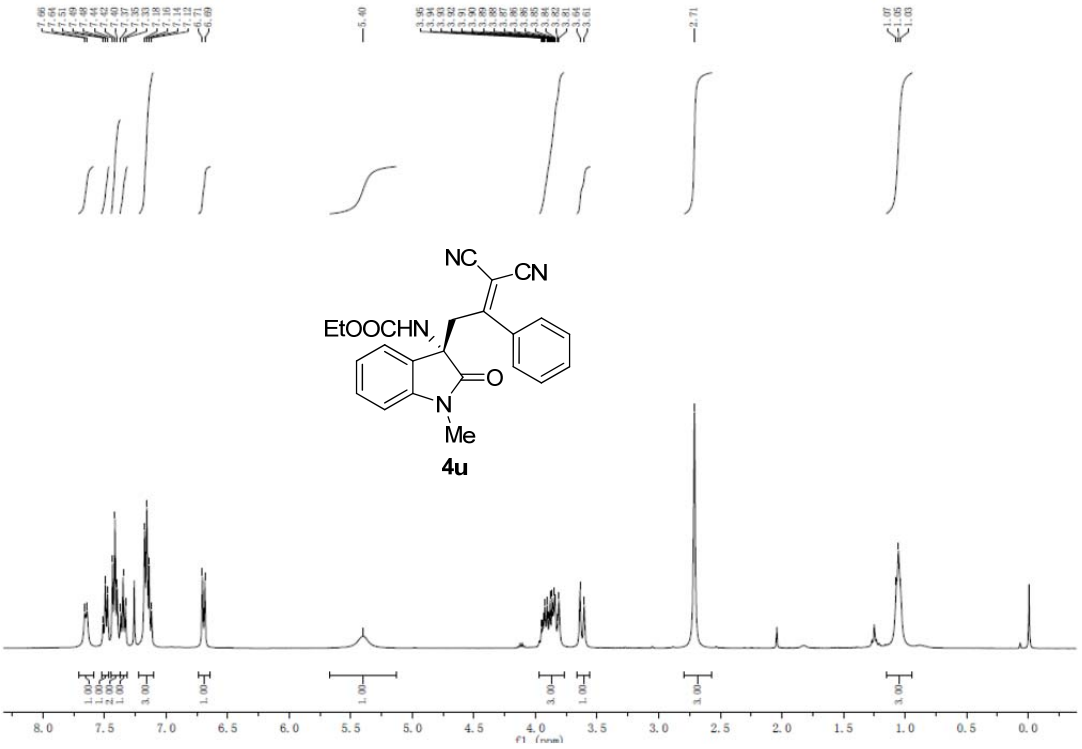
f1 (ppm)



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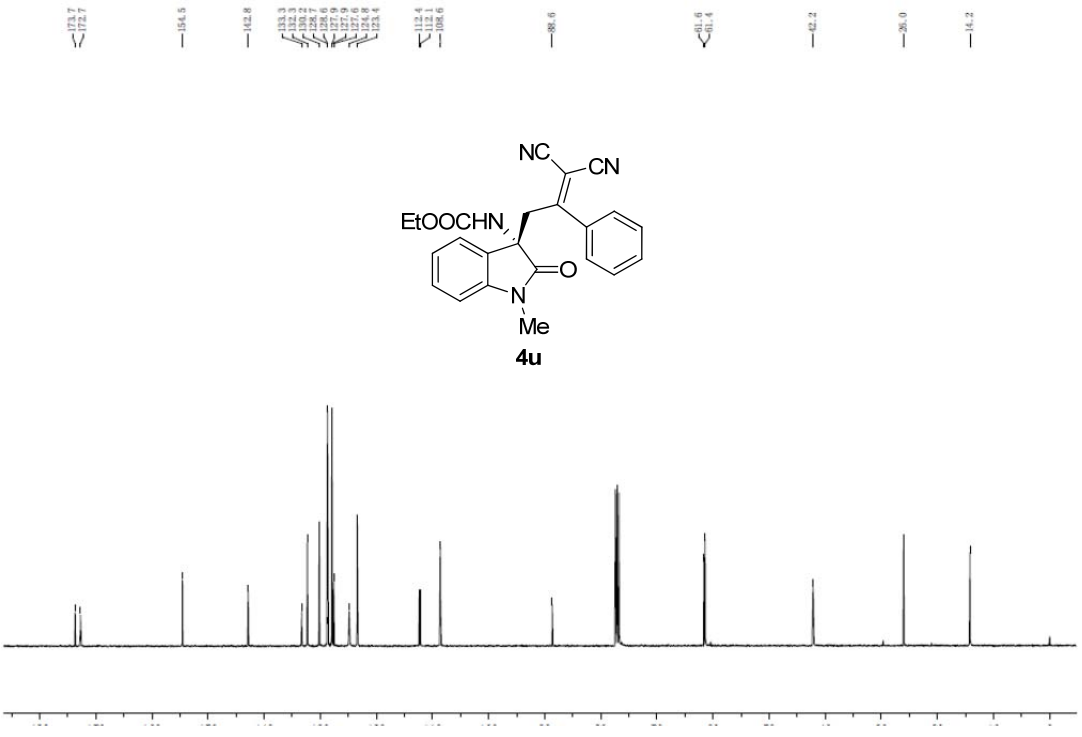

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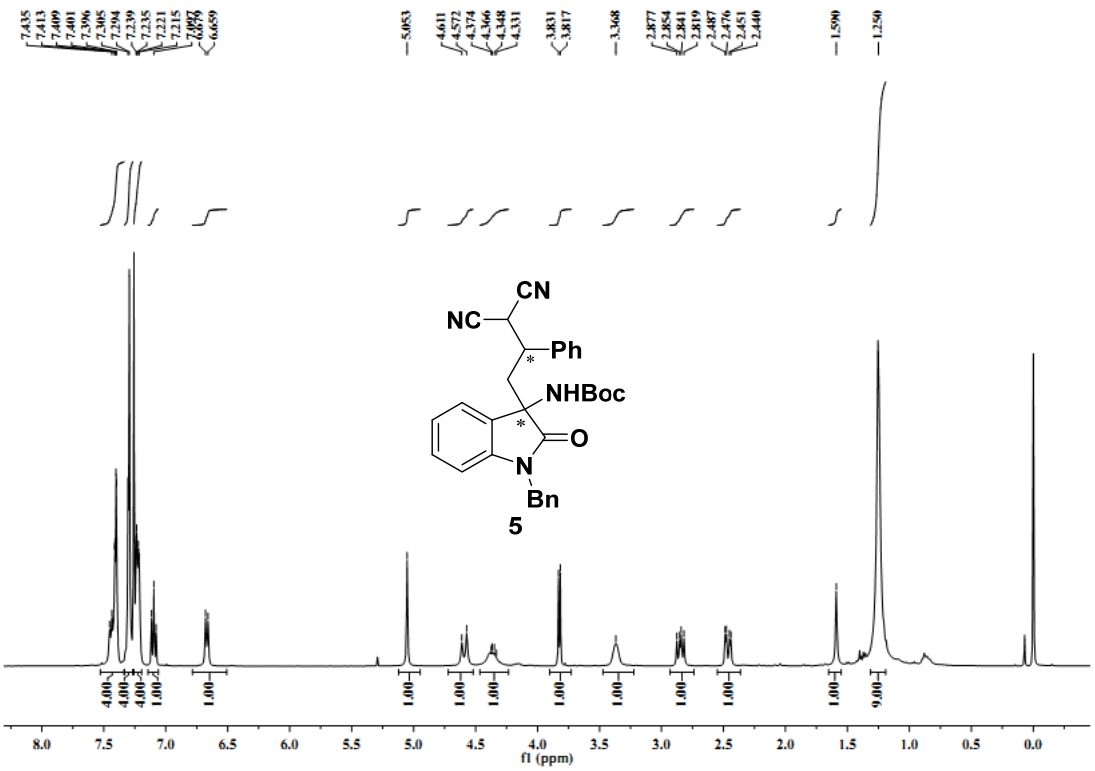
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4.572
4.374
4.366
4.348
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3.831
3.817
3.368
2.877
2.854
2.841
2.819
2.487
2.476
2.451
2.440
1.590
1.250
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NC
Ph
NHBoc
O
N
Bn
5
4.00
4.00
4.00
1.00
1.00
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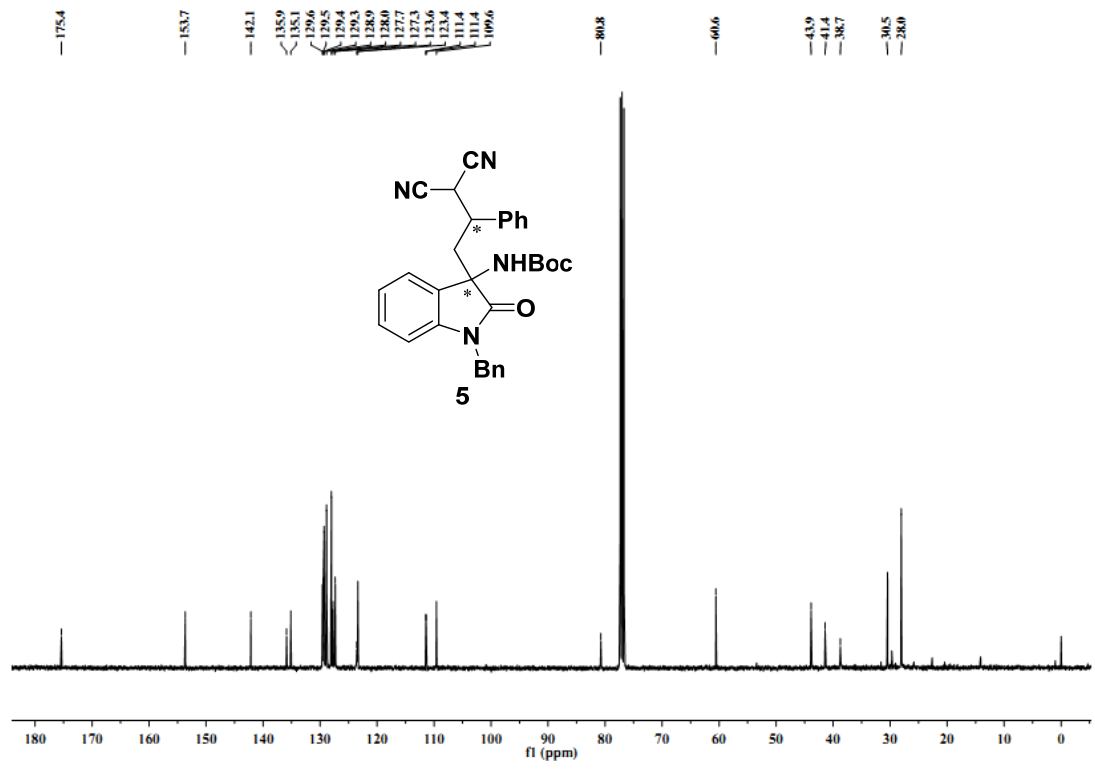
9.00
f1 (ppm)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129.4
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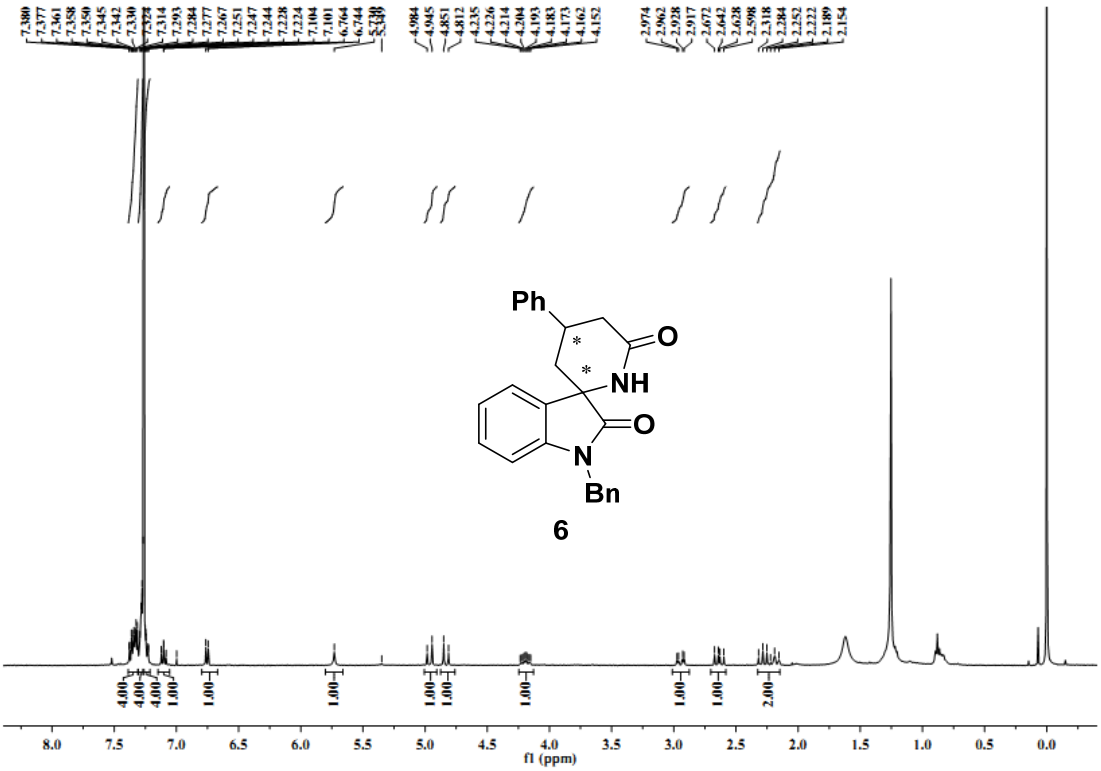
128.9
128.0
127.7
127.3
123.6
123.4
111.4
111.4
109.6
80.8
60.6
43.9
41.4
38.7
30.5
28.0
CN
NC
Ph
NHBoc
O
N
Bn
5
f1 (ppm)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NH
O
N
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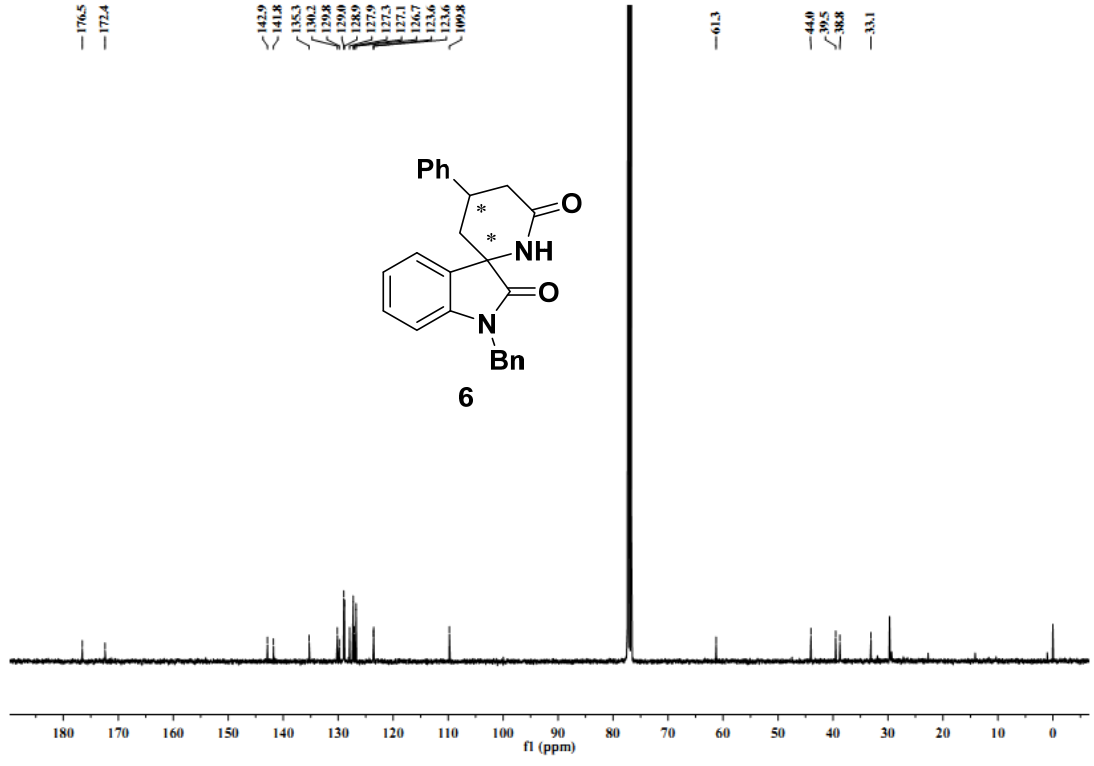
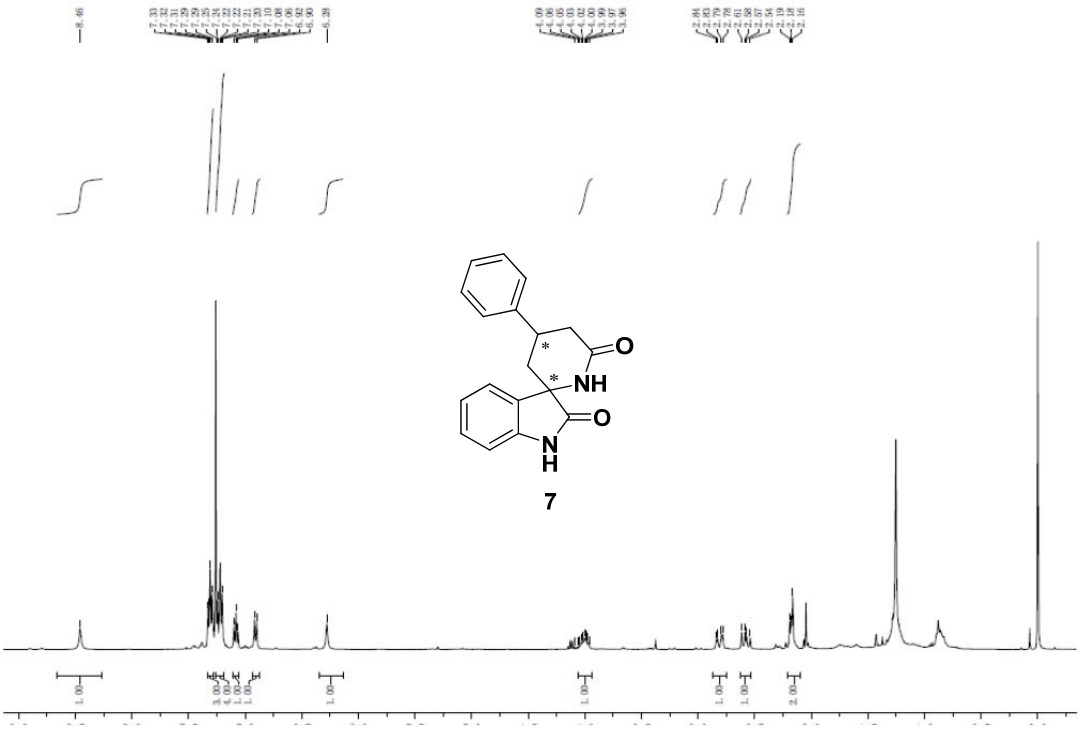
f1 (ppm)


Ph
O
NH
O
N
Bn
6
f1 (ppm)



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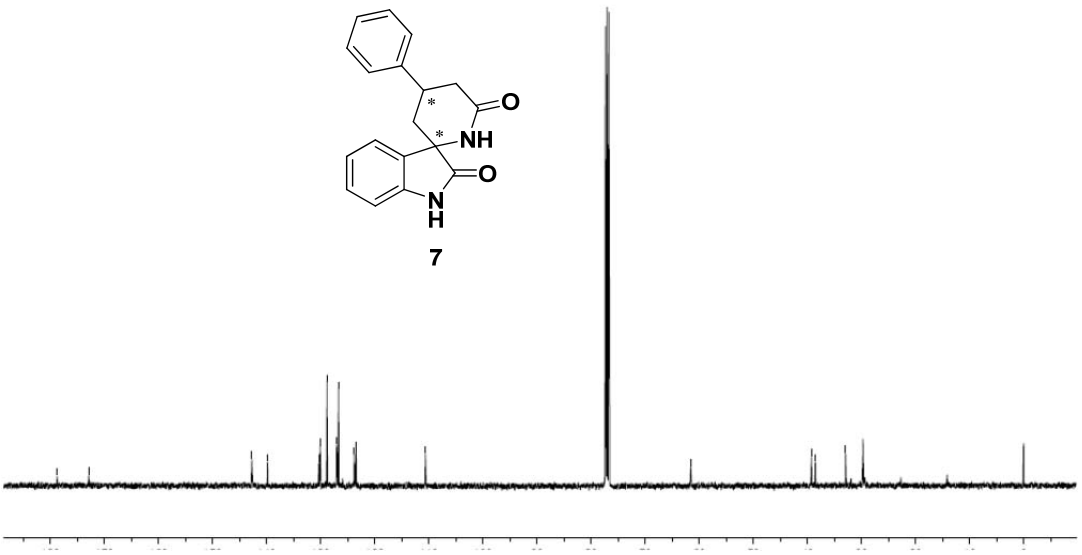
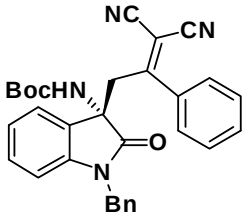


7

HPLC Spectra



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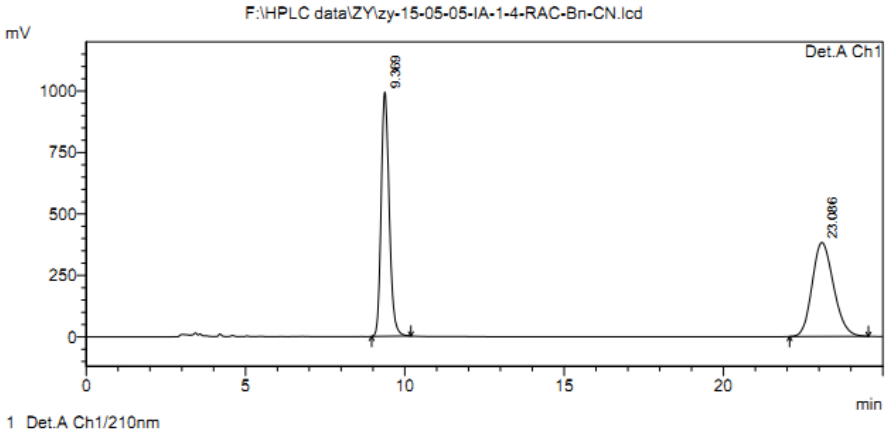


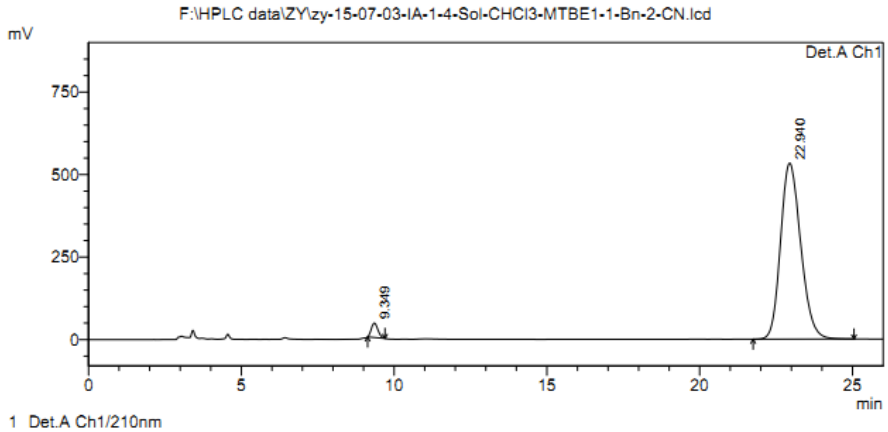
1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.369	17462031	993352	49.448	72.205
2	23.086	17852007	382381	50.552	27.795
Total		35314037	1375733	100.000	100.000

<Chromatogram>

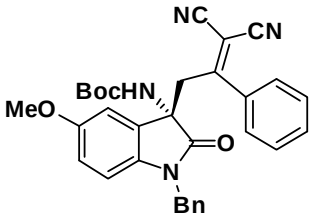


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.349	654196	43677	2.598	7.570
2	22.940	24524879	533296	97.402	92.430
Total		25179076	576972	100.000	100.000



4b

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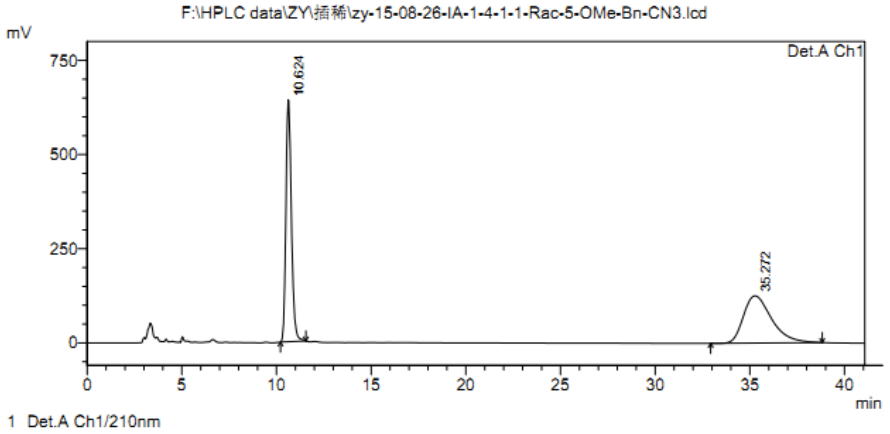

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.624	12966656	642103	50.016	83.664
2	35.272	12958202	125378	49.984	16.336
Total		25924858	767481	100.000	100.000

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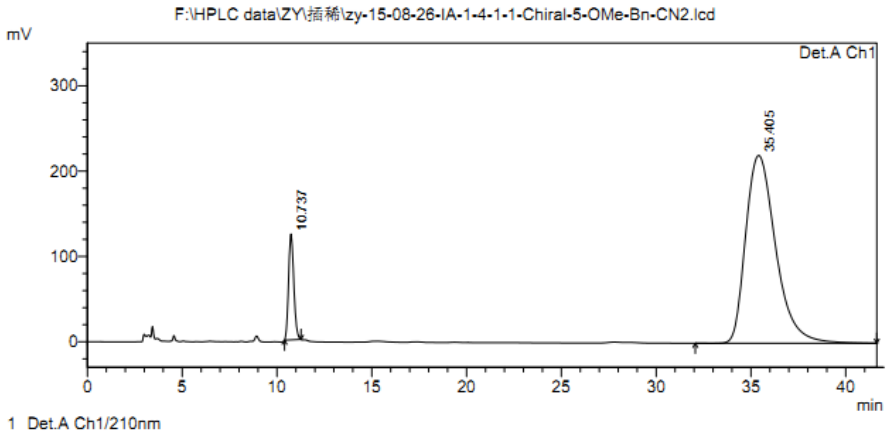
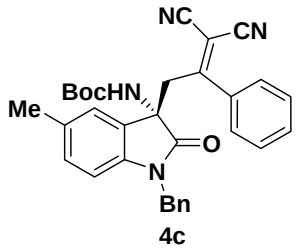


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.737	2386981	123952	8.971	36.032
2	35.405	24220914	220054	91.029	63.968
Total		26607895	344006	100.000	100.000



4c

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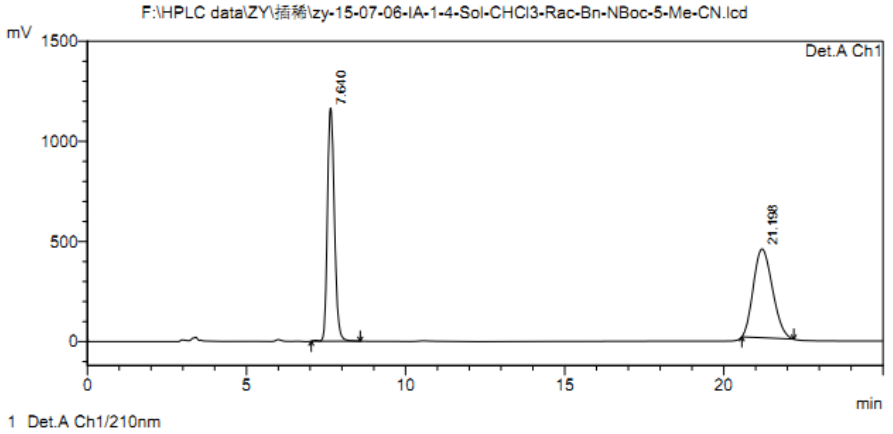

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.640	17827859	1164266	49.100	72.430
2	21.198	18481394	443164	50.900	27.570
Total		36309253	1607430	100.000	100.000

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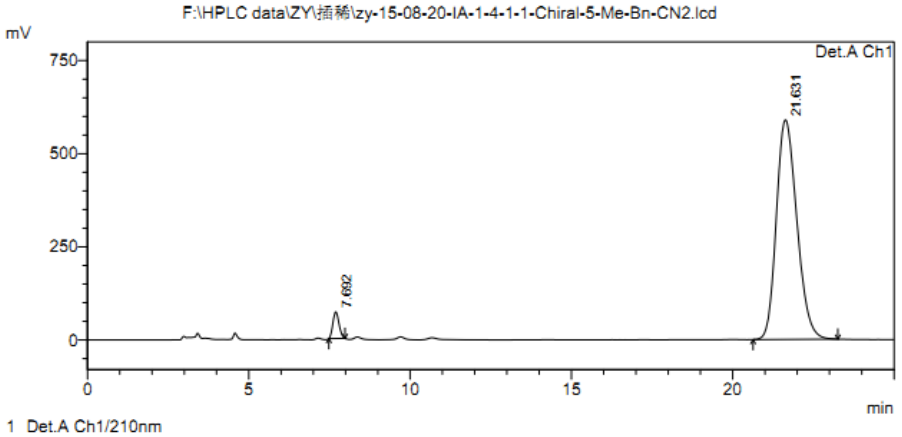
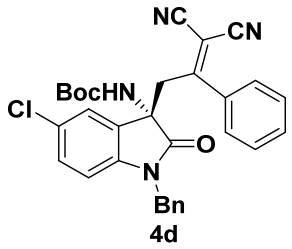


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.692	938233	71264	3.481	10.787
2	21.631	26015460	589417	96.519	89.213
Total		26953693	660681	100.000	100.000



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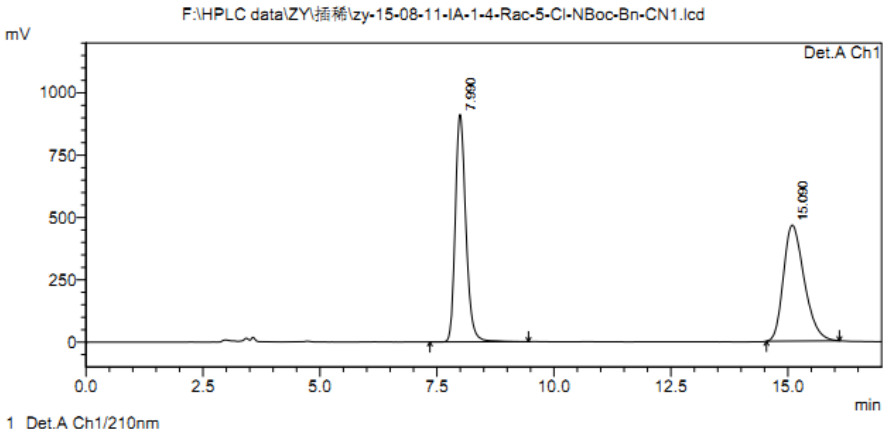

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.990	14347791	912537	49.883	66.240
2	15.090	14415350	465080	50.117	33.760
Total		28763140	1377617	100.000	100.000

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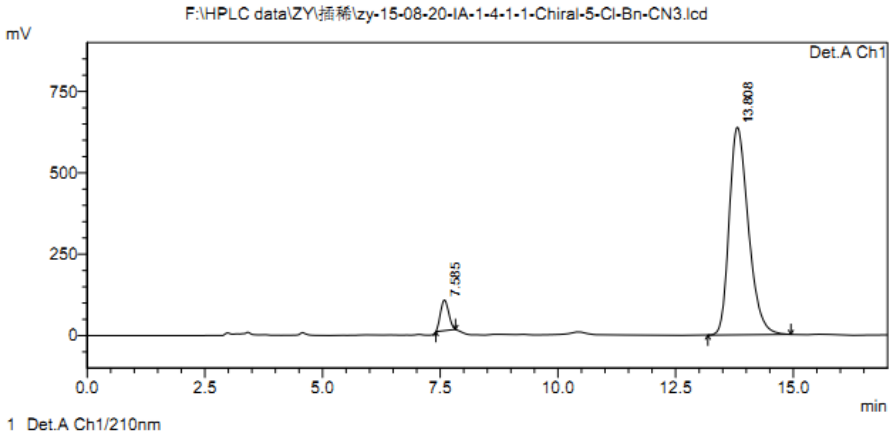
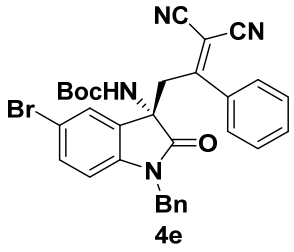


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.585	1137463	93969	5.921	12.843
2	13.808	18073174	637705	94.079	87.157
Total		19210637	731675	100.000	100.000



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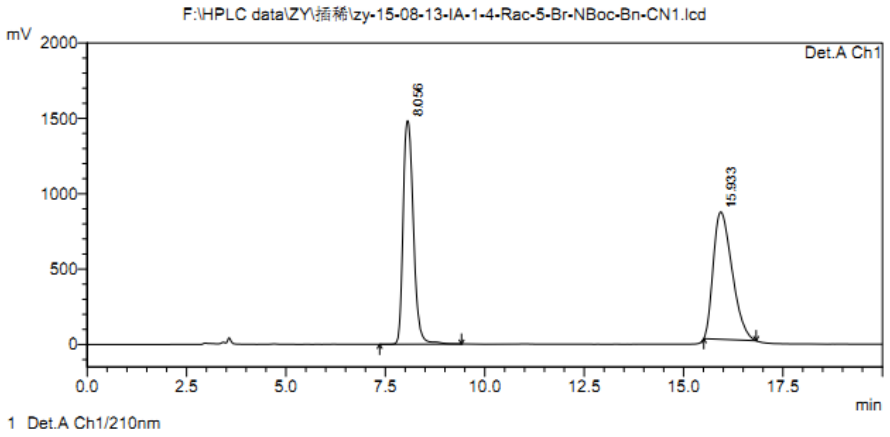
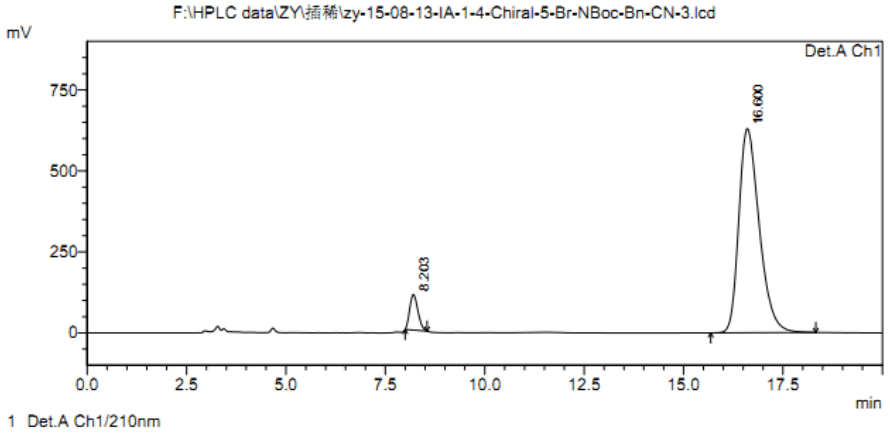


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.056	26653673	1483045	48.934	63.699
2	15.933	27815112	845164	51.066	36.301
Total		54468785	2328209	100.000	100.000

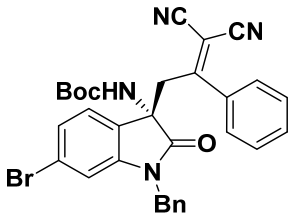
<Chromatogram>



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.203	1575768	110184	6.533	14.886
2	16.600	22543346	630007	93.467	85.114
Total		24119114	740191	100.000	100.000



4f

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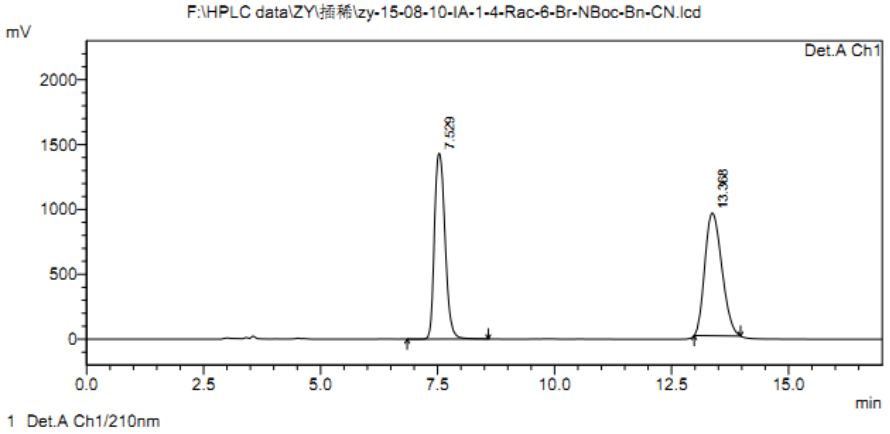

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.529	22567526	1432061	48.515	60.216
2	13.368	23949013	946138	51.485	39.784
Total		46516540	2378200	100.000	100.000

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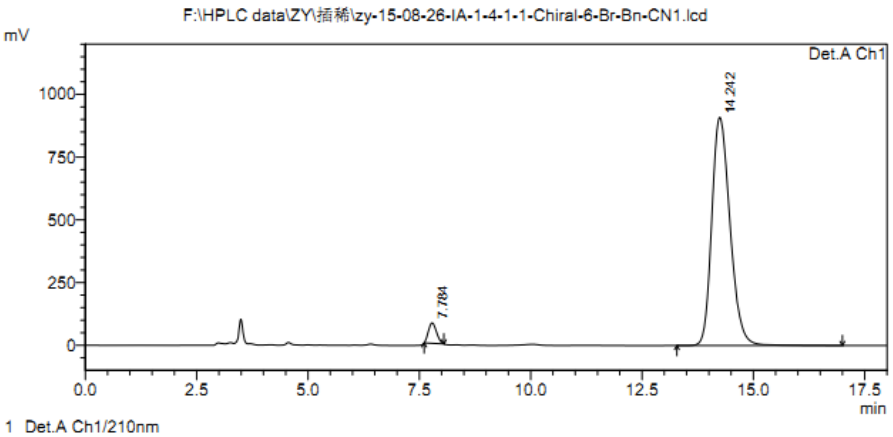
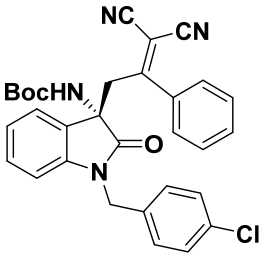


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.784	1023126	81511	3.804	8.228
2	14.242	25872784	909108	96.196	91.772
Total		26895910	990619	100.000	100.000



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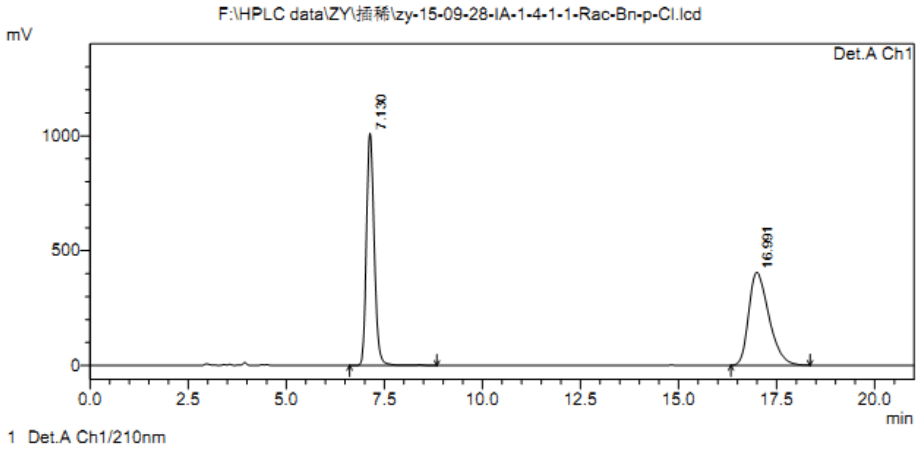


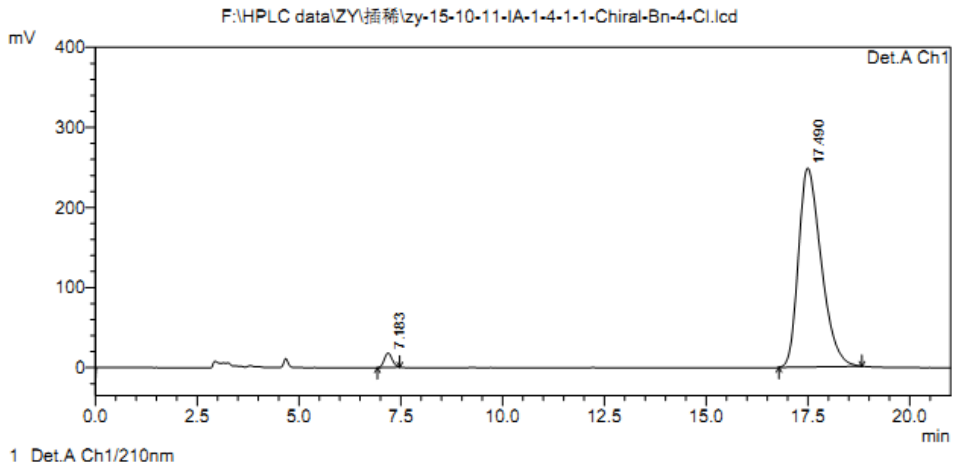
1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.130	13950031	1011054	49.042	71.416
2	16.991	14494909	404671	50.958	28.584
Total		28444941	1415725	100.000	100.000

<Chromatogram>

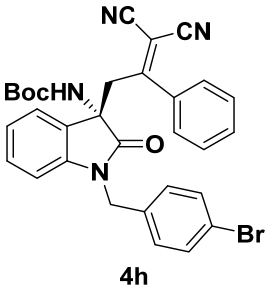


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.183	242265	18005	2.445	6.755
2	17.490	9667032	248517	97.555	93.245
Total		9909297	266521	100.000	100.000



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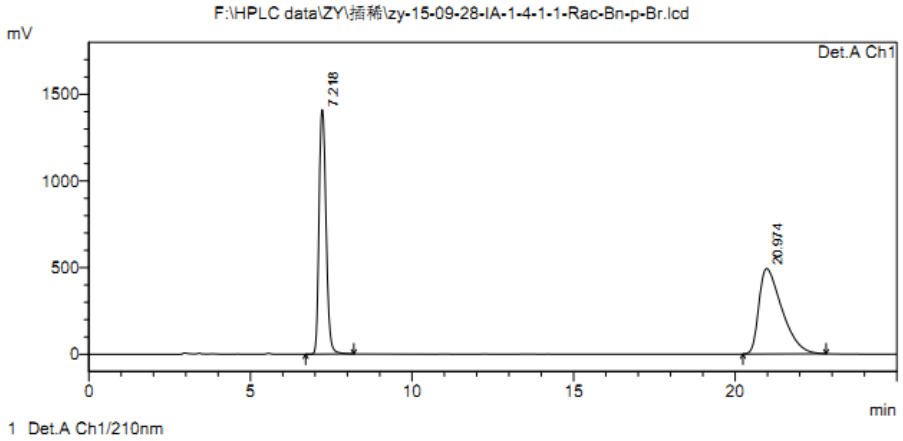

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.218	21348571	1409887	46.611	74.100
2	20.974	24453407	492796	53.389	25.900
Total		45801978	1902683	100.000	100.000

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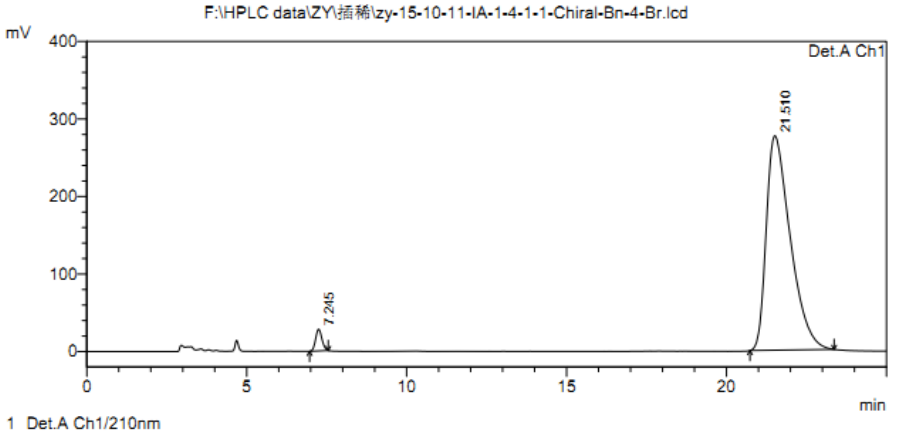
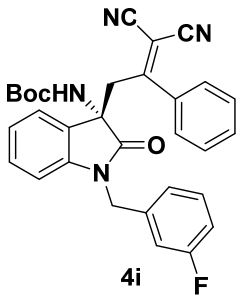


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.245	383590	27973	2.589	9.183
2	21.510	14434714	276649	97.411	90.817
Total		14818304	304623	100.000	100.000



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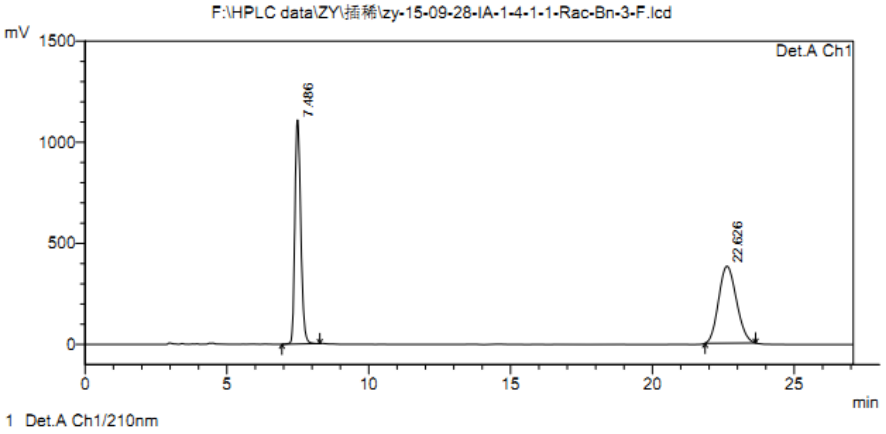

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.486	16004680	1108048	49.035	74.435
2	22.626	16634798	380558	50.965	25.565
Total		32639478	1488605	100.000	100.000

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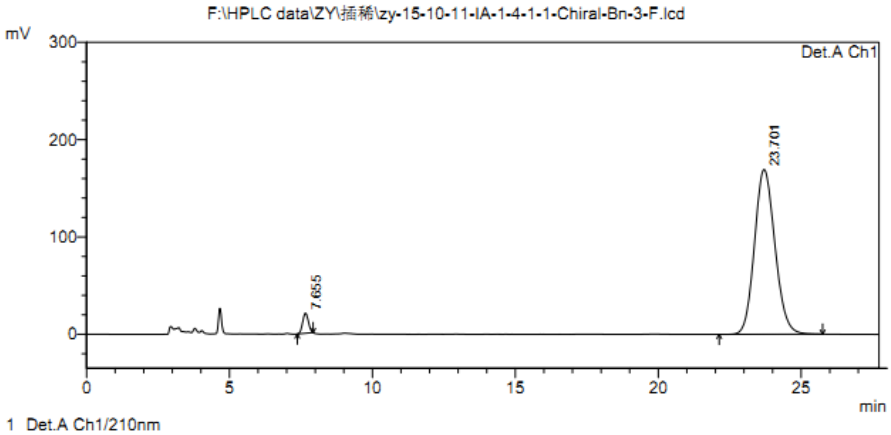
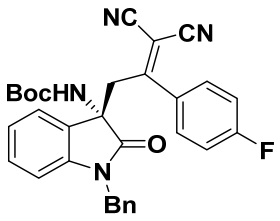


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.655	289609	20744	3.323	10.914
2	23.701	8424686	169325	96.677	89.086
Total		8714295	190069	100.000	100.000



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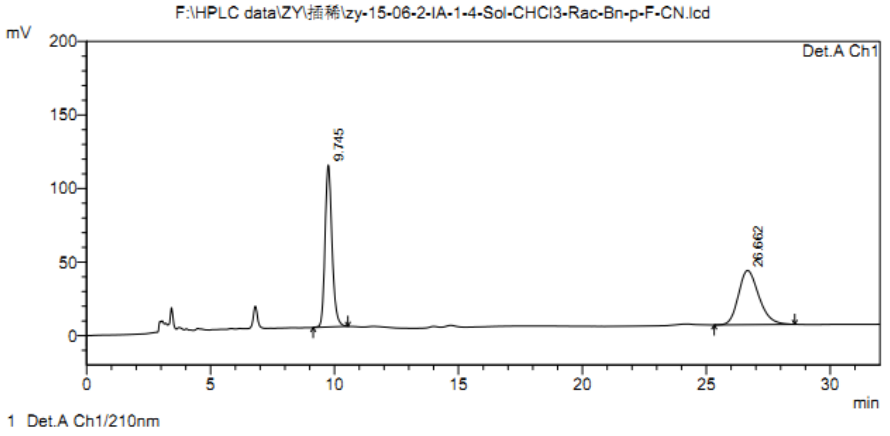

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.745	2168778	110103	50.687	74.937
2	26.662	2109979	36825	49.313	25.063
Total		4278757	146928	100.000	100.000

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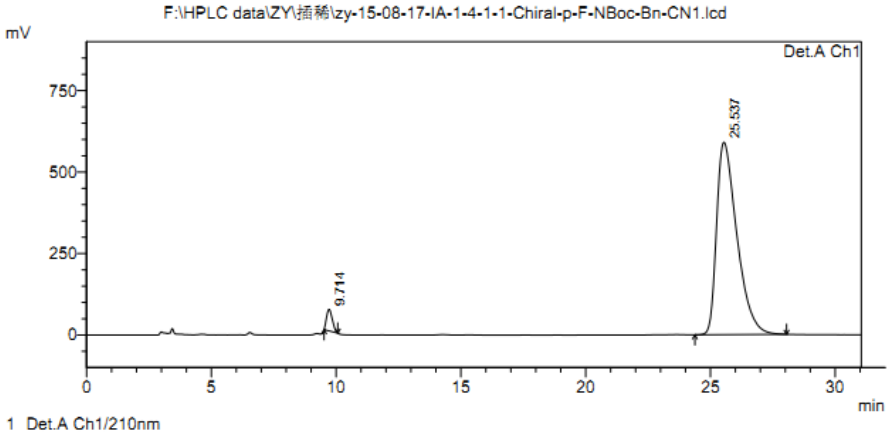
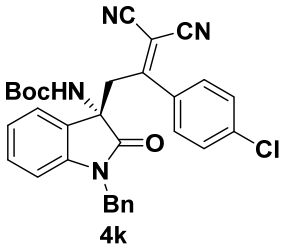


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.714	1061515	66036	3.086	10.060
2	25.537	33339046	590383	96.914	89.940
Total		34400561	656419	100.000	100.000



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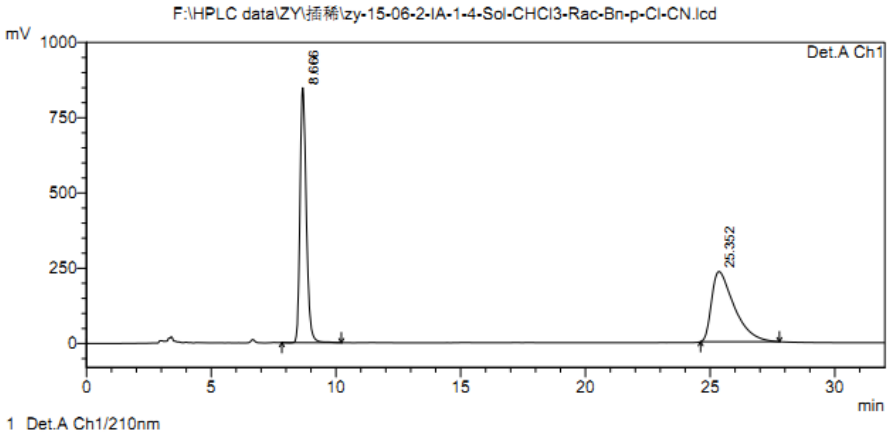

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.666	14795295	846315	50.223	78.427
2	25.352	14663792	232792	49.777	21.573
Total		29459087	1079106	100.000	100.000

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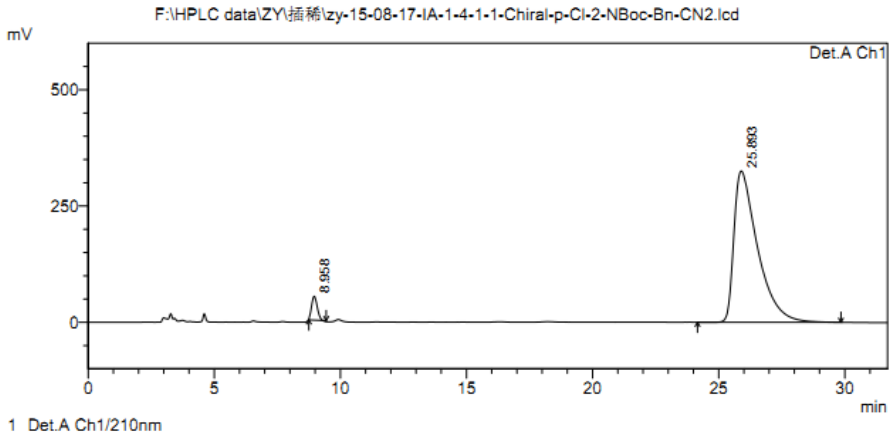
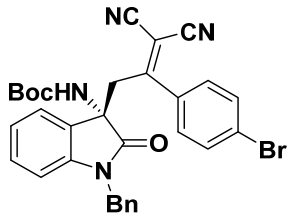


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.958	783357	51167	3.561	13.592
2	25.893	21214412	325289	96.439	86.408
Total		21997769	376456	100.000	100.000



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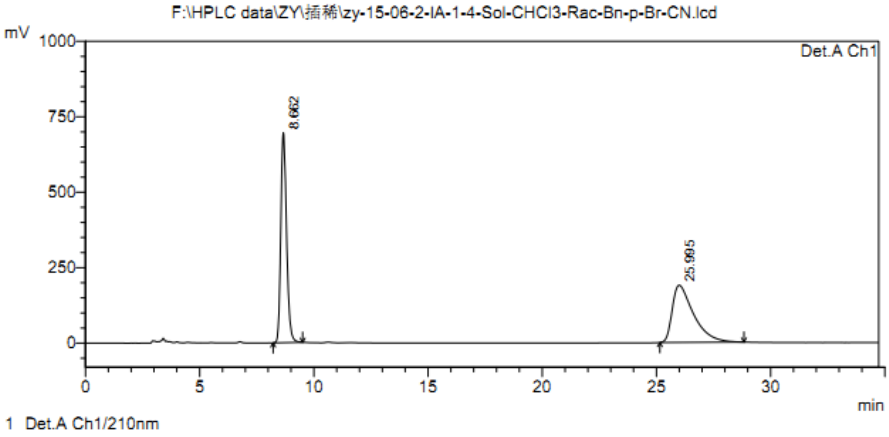

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.662	12155487	695201	49.717	78.575
2	25.995	12293690	189558	50.283	21.425
Total		24449177	884758	100.000	100.000

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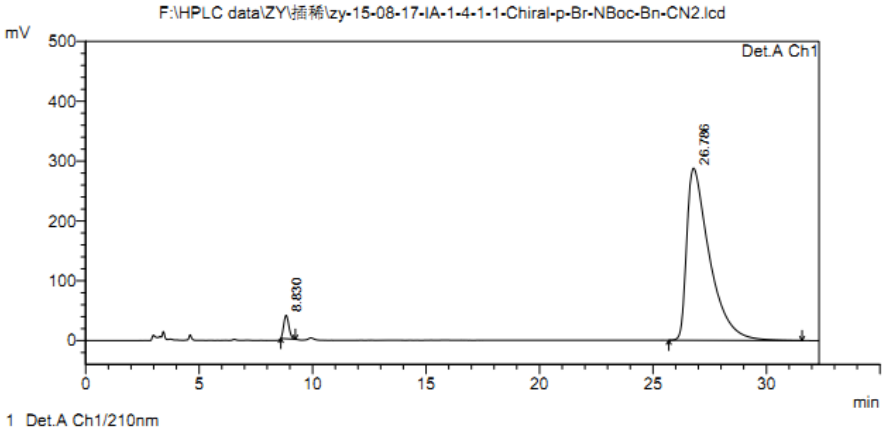
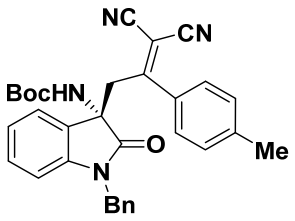


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.830	617191	39181	2.982	11.988
2	26.786	20078737	287651	97.018	88.012
Total		20695928	326832	100.000	100.000



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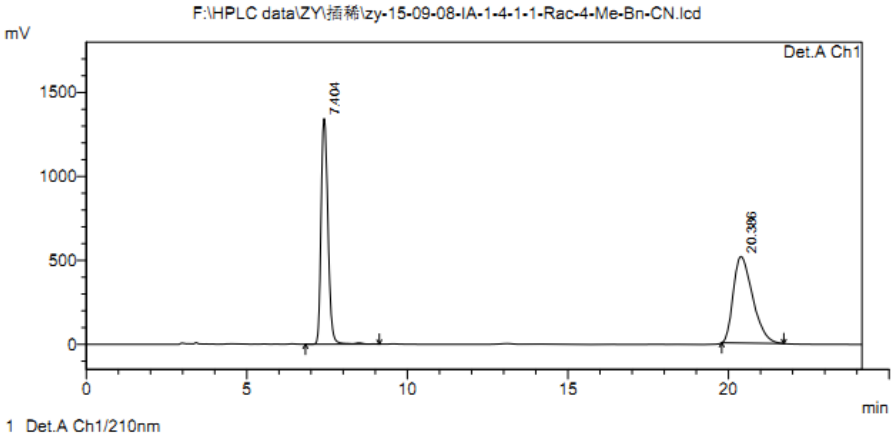

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.404	20121886	1344563	48.223	72.280
2	20.386	21605038	515640	51.777	27.720
Total		41726924	1860203	100.000	100.000

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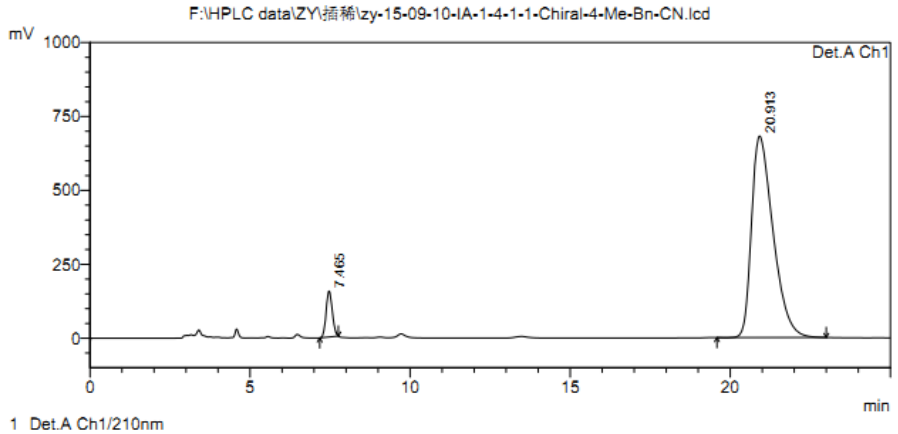
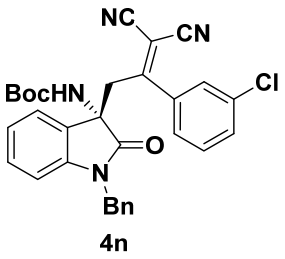


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.465	2082758	155454	6.132	18.575
2	20.913	31881708	681454	93.868	81.425
Total		33964466	836908	100.000	100.000



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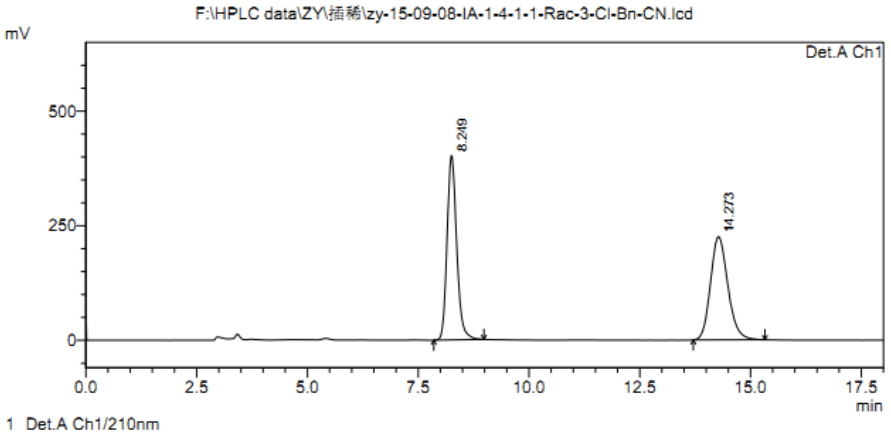

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.249	6085669	402308	49.811	64.084
2	14.273	6131884	225475	50.189	35.916
Total		12217553	627783	100.000	100.000

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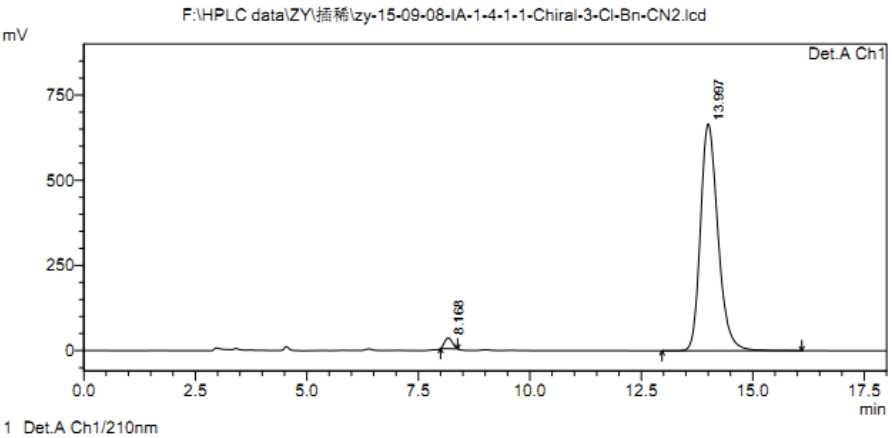
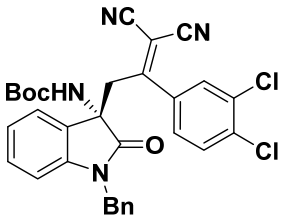


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.168	375399	31301	2.028	4.490
2	13.997	18139024	665793	97.972	95.510
Total		18514423	697094	100.000	100.000



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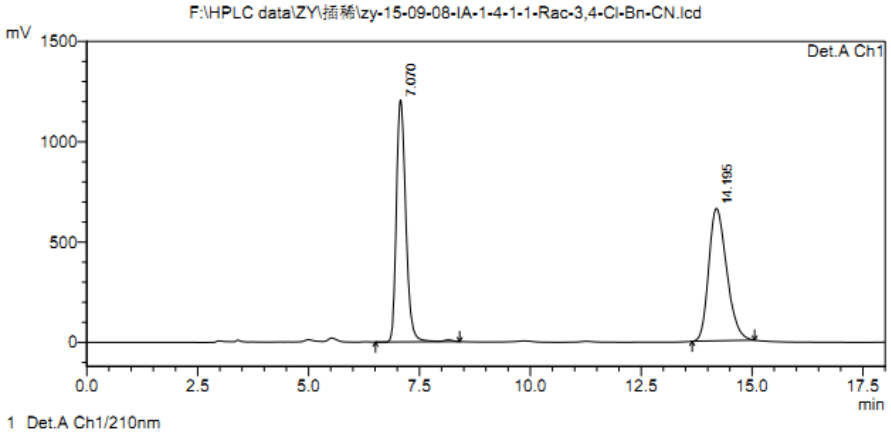

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.070	17893153	1205951	49.074	64.620
2	14.195	18568064	660265	50.926	35.380
Total		36461217	1866216	100.000	100.000

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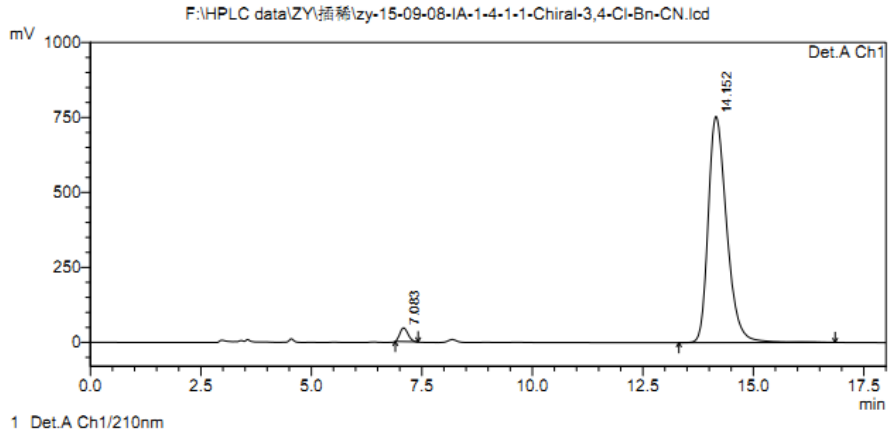
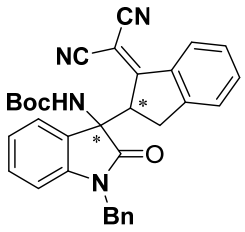


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.083	577766	45722	2.563	5.716
2	14.152	21967441	754210	97.437	94.284
Total		22545207	799932	100.000	100.000



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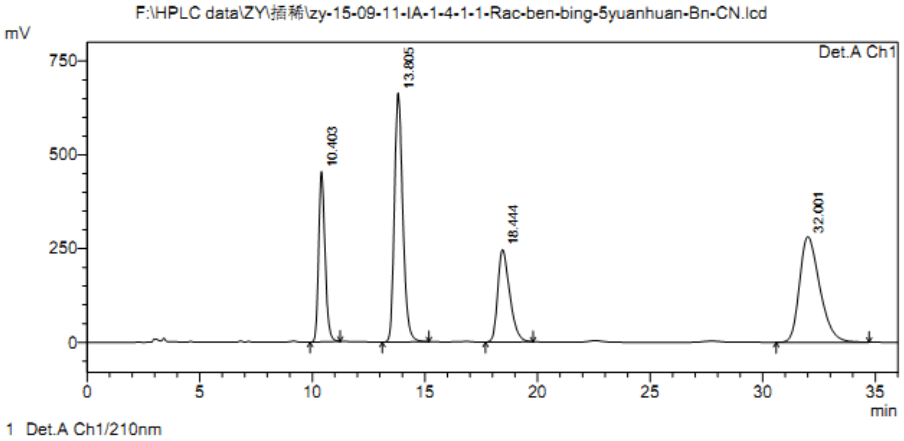

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.403	8973251	454735	16.927	27.604
2	13.805	17276954	664352	32.592	40.329
3	18.444	9133580	246481	17.230	14.962
4	32.001	17626597	281764	33.251	17.104
Total		53010381	1647332	100.000	100.000

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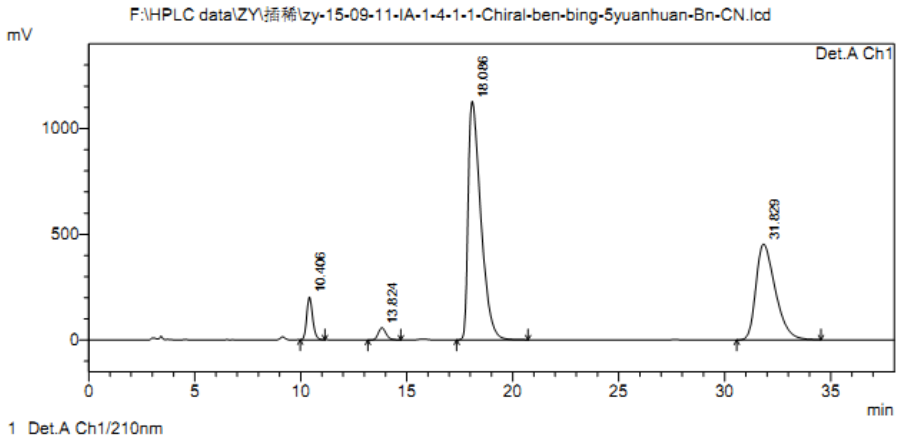
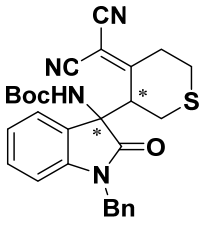


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.406	3944168	201909	4.879	10.967
2	13.824	1478303	57859	1.829	3.143
3	18.086	46556421	1128157	57.596	61.280
4	31.829	28854063	453069	35.696	24.610
Total		80832955	1840993	100.000	100.000



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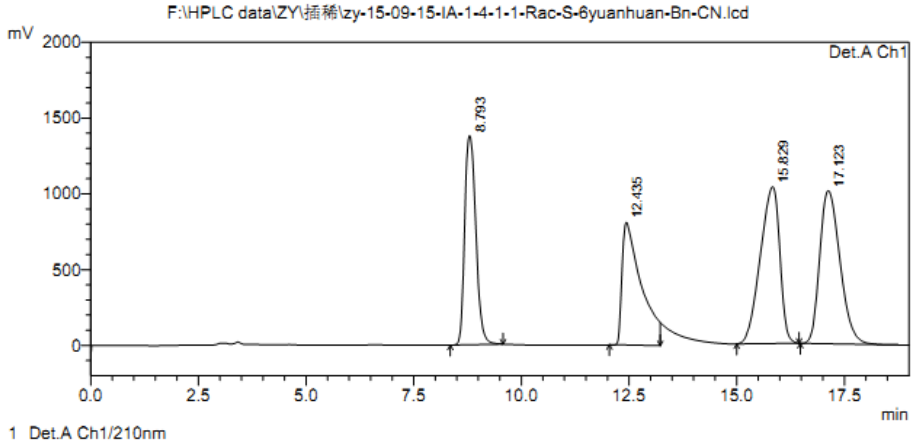

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.793	24799022	1379880	21.521	32.575
2	12.435	24789956	809499	21.513	19.110
3	15.829	32567903	1035669	28.263	24.449
4	17.123	33073457	1010965	28.702	23.866
Total		115230337	4236014	100.000	100.000

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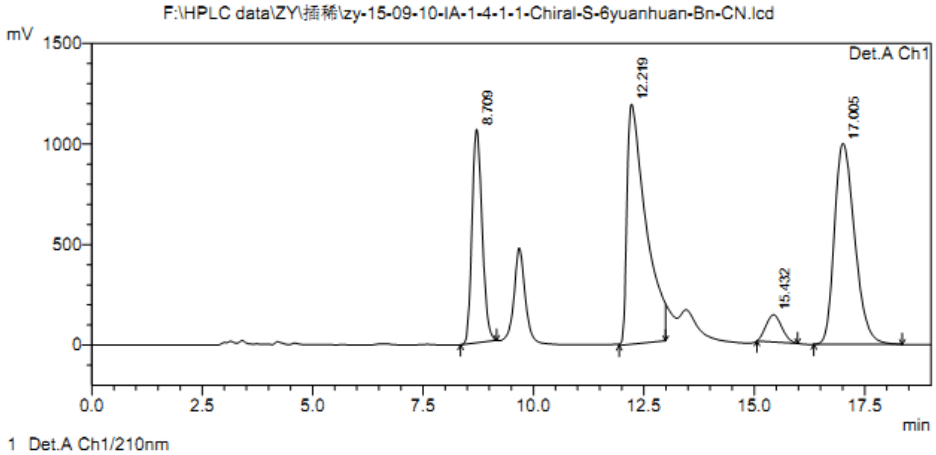
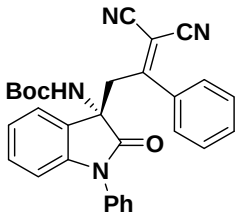


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.709	16854824	1062361	19.208	31.327
2	12.219	35424638	1193229	40.370	35.186
3	15.432	3381650	136083	3.854	4.013
4	17.005	32089722	999523	36.569	29.474
Total		87750834	3391197	100.000	100.000



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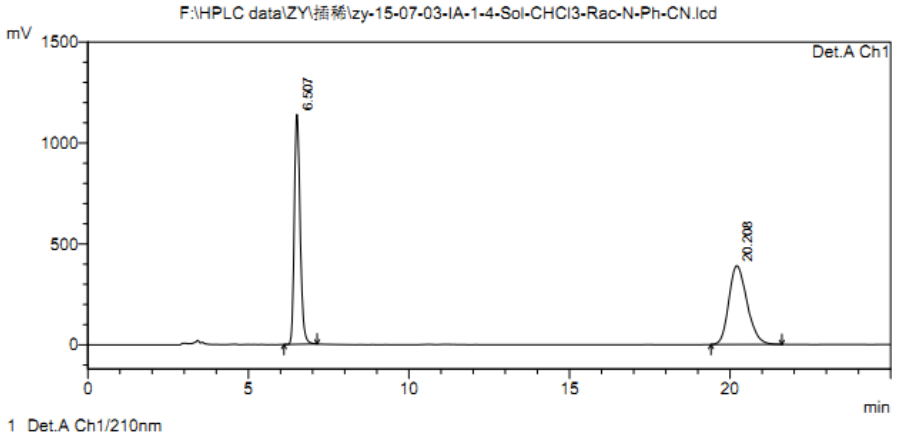

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.507	14356145	1139103	48.380	74.521
2	20.208	15317741	389464	51.620	25.479
Total		29673886	1528567	100.000	100.000

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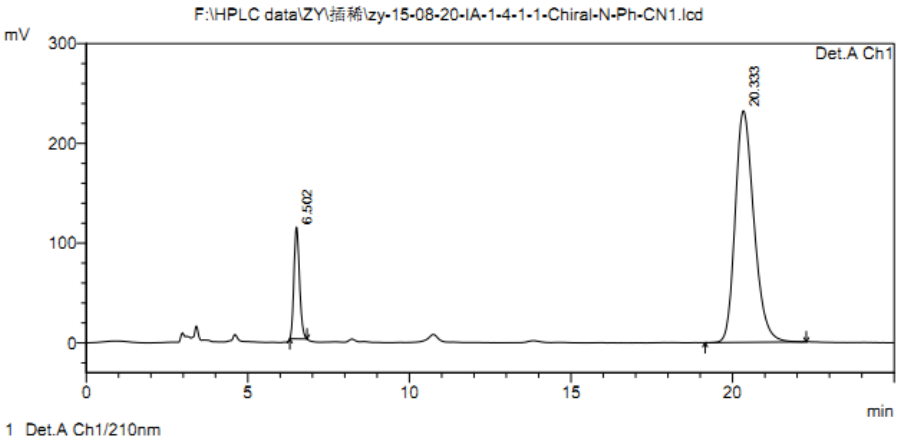
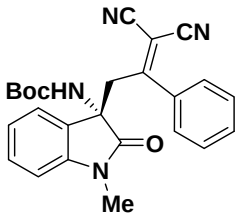


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.502	1336600	111998	12.489	32.546
2	20.333	9365205	232119	87.511	67.454
Total		10701805	344117	100.000	100.000



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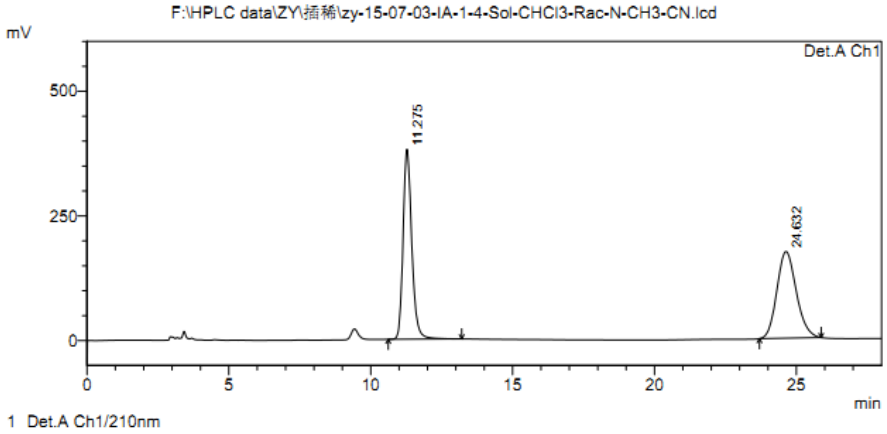

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.275	8148697	380912	49.666	68.674
2	24.632	8258173	173754	50.334	31.326
Total		16406871	554665	100.000	100.000

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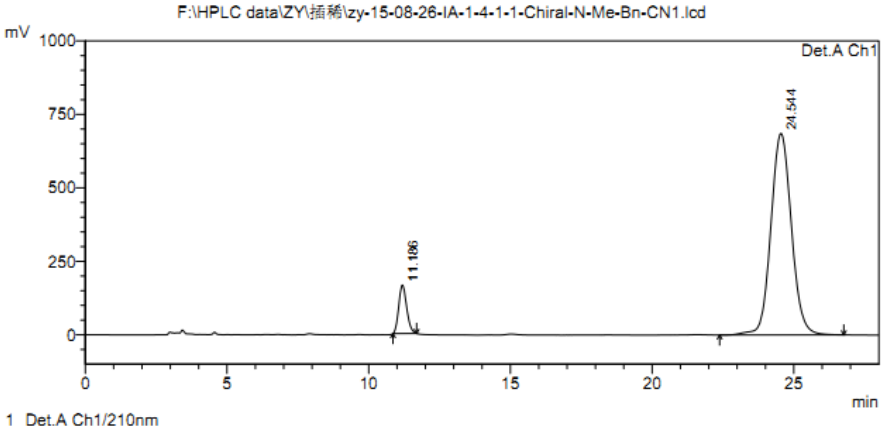
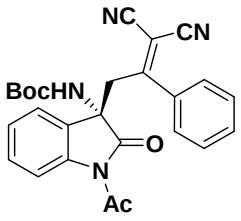


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.186	3225948	165108	8.546	19.399
2	24.544	34522793	686026	91.454	80.601
Total		37748741	851133	100.000	100.000



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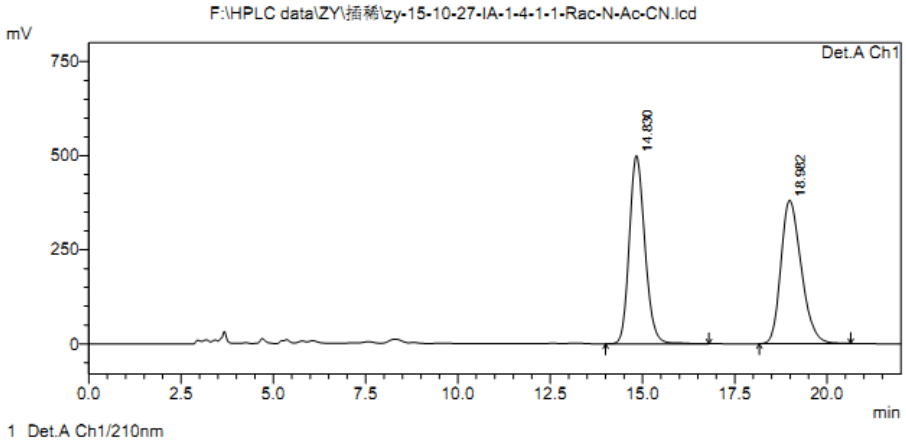

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.830	14653810	500310	50.025	56.754
2	18.982	14639036	381234	49.975	43.246
Total		29292846	881544	100.000	100.000

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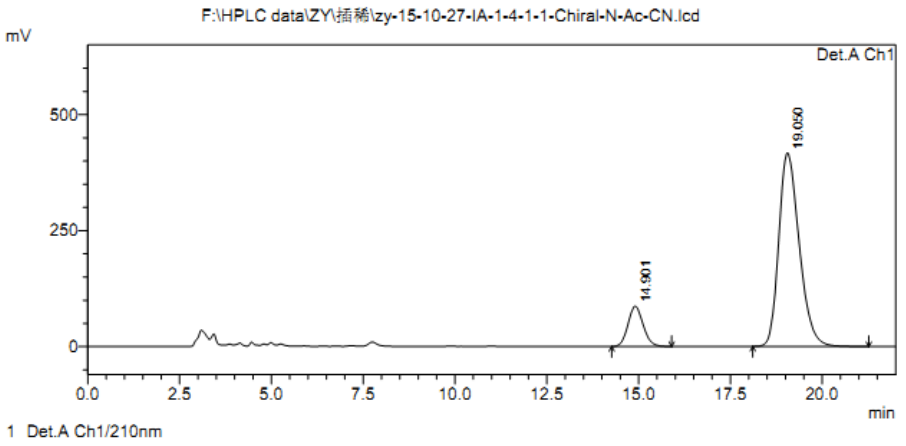
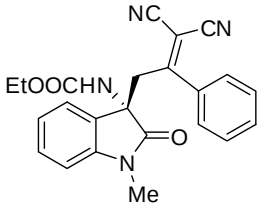


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.901	2508905	87079	13.445	17.275
2	19.050	16151813	416984	86.555	82.725
Total		18660718	504063	100.000	100.000



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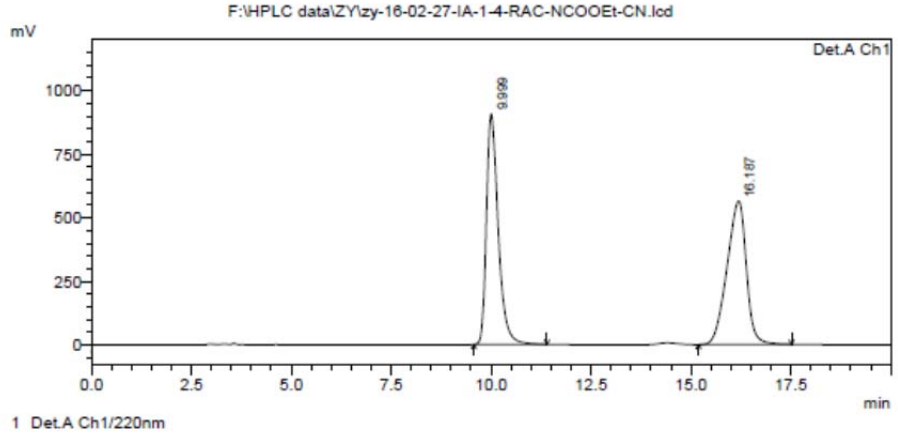

1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.999	18610562	906422	49.552	61.621
2	16.187	18947252	564552	50.448	38.379
Total		37557814	1470974	100.000	100.000

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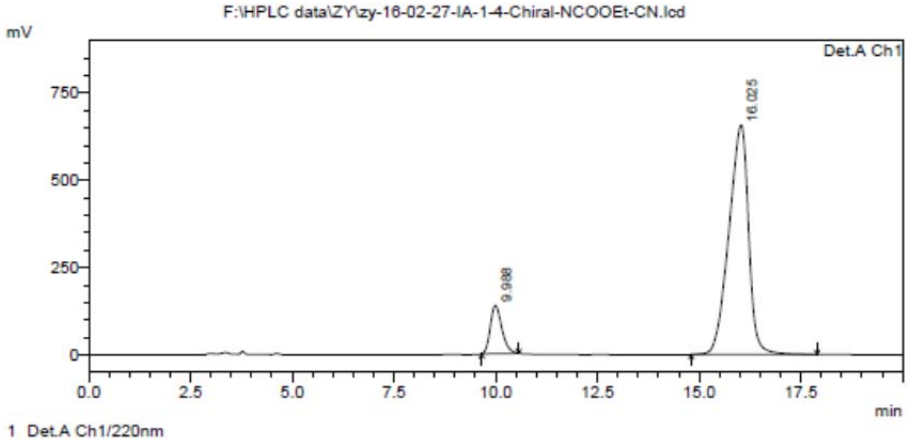
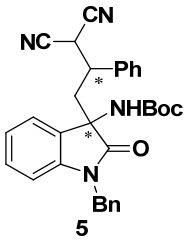


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.988	2733871	138456	10.965	17.397
2	16.025	22198237	657423	89.035	82.603
Total		24932108	795879	100.000	100.000



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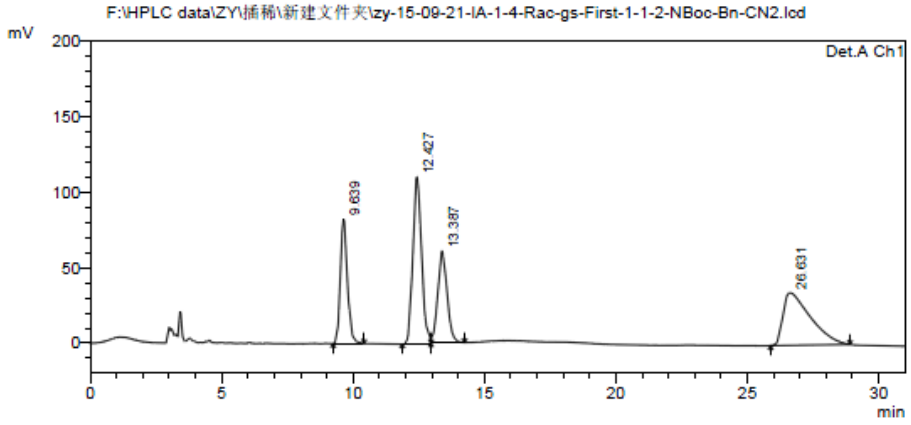

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.639	1507274	82462	18.732	28.610
2	12.427	2495001	110083	31.008	38.193
3	13.387	1524327	60699	18.944	21.059
4	26.631	2519763	34986	31.316	12.138
Total		8046364	288230	100.000	100.000

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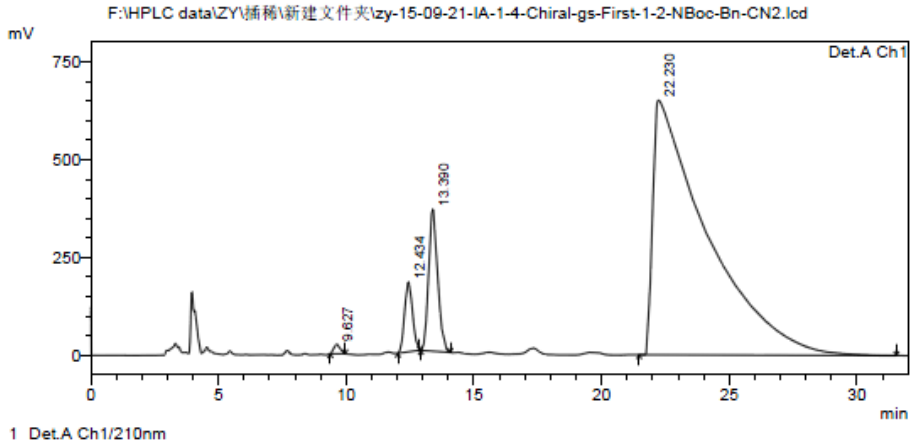
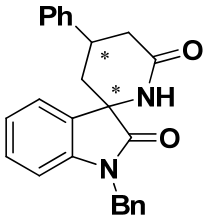


PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.627	406640	23333	0.374	1.922
2	12.434	3853757	177790	3.541	14.644
3	13.390	9052960	361820	8.319	29.802
4	22.230	95510210	651130	87.766	53.632
Total		108823566	1214072	100.000	100.000



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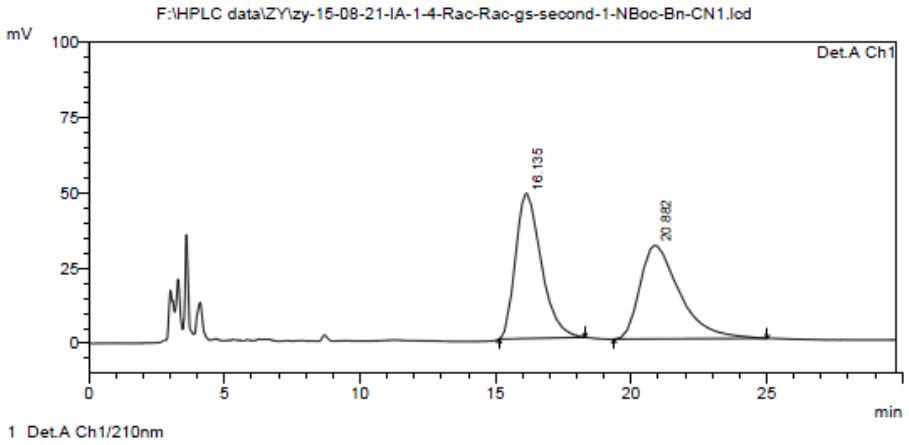

1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.135	3163363	48175	50.002	60.760
2	20.882	3163068	31112	49.998	39.240
Total		6326431	79287	100.000	100.000

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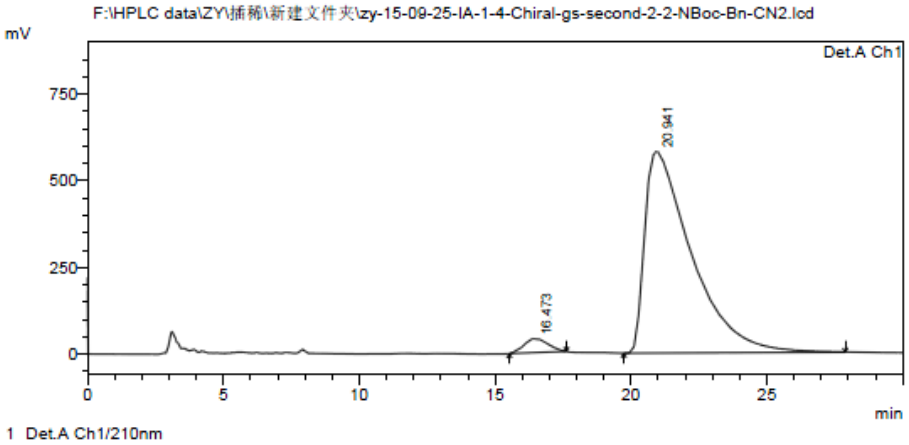
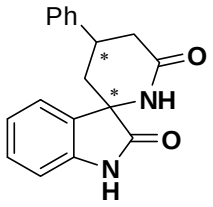


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.473	2455614	40391	3.402	6.496
2	20.941	69731787	581396	96.598	93.504
Total		72187400	621787	100.000	100.000



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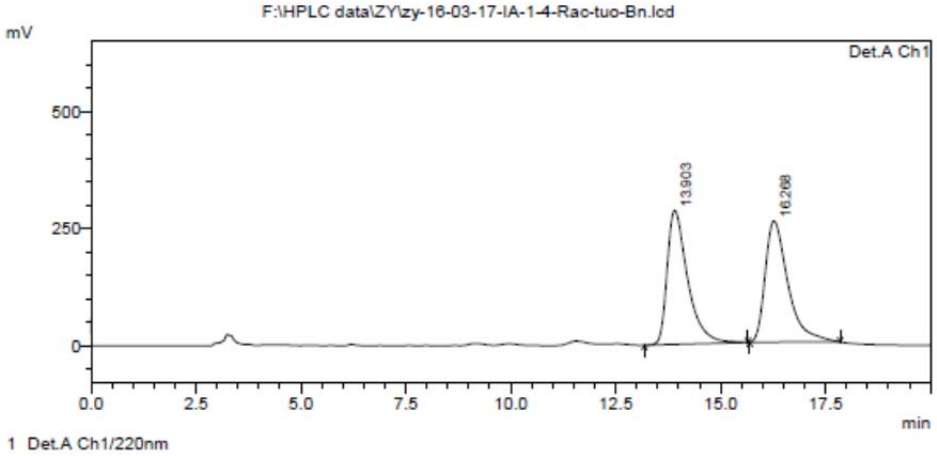

1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.903	9728113	286494	49.829	52.541
2	16.268	9795026	258780	50.171	47.459
Total		19523140	545274	100.000	100.000

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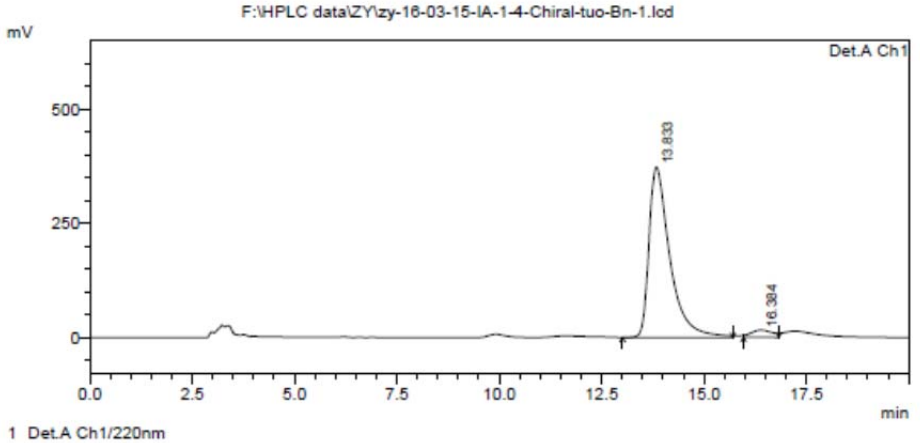

1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.833	13270096	372787	95.879	96.000
2	16.384	570362	15533	4.121	4.000
Total		13840459	388320	100.000	100.000