Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Organocatalytic enantioselective conjugate addition of ketones to isatylidine malononitriles

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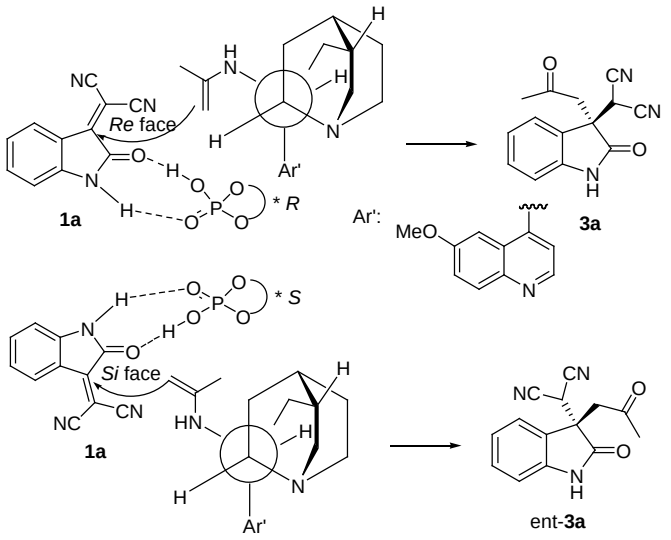
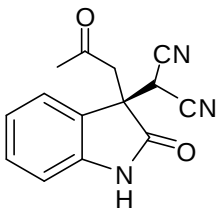
General. Commercial reagents were used as received, unless otherwise stated. The ^{1}H-NMR and ^{13}C-NMR were recorded on a Bruke DRX 400 (400 MHz) instrument. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad. Chromatography was carried out with silica gel (200-300 mesh) using mixtures of hexanes and ethyl acetate as eluents. The enantiomeric excess of products were detected on HPLC (Agilent 1200 series). Mass spectrometry was performed on a Micromass GCT CA055.

Fig. S1. Proposed models for chiral amine **I** and chiral phosphoric acid (*R*)-**5c** and (*S*)-**5c** co-catalyzed Michael addition of acetone to isatylidine malononitrile **1a.**

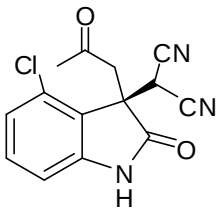


Method A: Typical Procedure for Michael Reaction (Two-component Reaction, using 3a a an example): To a solution of isatylidene malononitrile (**1a**, 98 mg, 0.5 mmol), catalyst **I** (33 mg, 0.1 mmol) and (*R*)-**5c** (66 mg, 0.2 mmol) in 5 mL of THF was added acetone (0.4 mL, 5 mmol). After suitable time of stirring at rt, TLC analysis indicated completion of the reaction. The crude reaction mixture was directly subjected to column chromatography (hexane: ethylacetate = 2:1) on silica gel to afford the corresponding product.

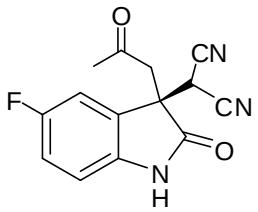
Method B: Typical Procedure for Knoevenagel-Michael Reaction (Three-component Reaction using 3a as an example): To a solution of isatin (**6a**, 73 mg, 0.5 mmol), malononitrile (33 mg, 0.5 mmol), catalyst **I** (33 mg, 0.1 mmol) and (*R*)-**5c** (66 mg, 0.2 mmol) in 5 mL of THF was added acetone (0.4 mL, 5 mmol). After suitable time of stirring at rt, TLC analysis indicated completion of the reaction. The crude reaction mixture was directly subjected to column chromatography (hexane: ethylacetate = 2:1) on silica gel to afford the corresponding product.



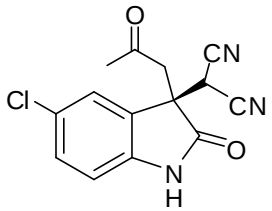
2-(2-Oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3a). The title compound was prepared according to the method B, as described above in 92% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 6.6 (2H, d, J = 33.2 Hz, Ar*H*), 6.2 (2H, d, J = 33.2 Hz, Ar*H*), 4.0 (1H, s, C*H*), 2.76 (1H, J = 17.6 Hz, C*H*), 2.53 (1H, d, J = 17.6 Hz, C*H*), 1.2 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 202.9, 175.5, 142.0, 129.1, 125.6, 122.3, 121.6, 110.0, 109.5, 48.2, 44.8, 27.8; HRMS: $C_{14}H_{11}N_3O_2$ $[M]^+$ calcd: 253.0851, found: 253.0858; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 12.1 min, t_{major} = 9.9 min, ee = 95%, $[\alpha]_D^{20}$ = -41.07° (MeOH, c = 0.3); mp: 199-200 ºC.



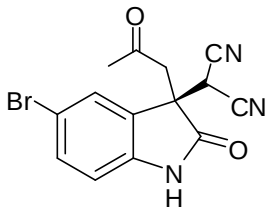
2-(4-Chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3b). The title compound was prepared according to the method B, as described above in 92% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.3 (1H, t, J = 8.0 Hz, Ar*H*), 7.0 (1H, d, J = 8.0 Hz, Ar*H*), 6.9 (1H, d, J = 8.0 Hz, Ar*H*), 3.96 (1H, d, J = 18.0 Hz, C*H*), 3.46 (1H, d, J = 18.0 Hz, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.3, 175.1, 145.4, 131.6, 129.8, 122.9, 122.7, 109.8, 109.1, 49.9, 44.3, 28.2, 23.0; HRMS: $C_{14}H_{10}N_3O_2Cl$ $[M]^+$ calcd: 287.0462, found: 287.0464; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30ºC): t_{minor} = 25.5 min, t_{major} = 28.9 min, ee = 97%, $[\alpha]_D^{20}$ = -19.4° (MeOH, c = 0.2); mp: 205-206 ºC.



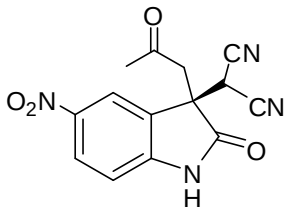
2-(5-Fluoro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3c). The title compound was prepared according to the method 2, as described above in 94% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.2 (1H, m, Ar*H*), 7.1 (1H, m, Ar*H*), 7.0 (1H, m, Ar*H*), 3.62 (1H, d, J = 18.0 Hz, C*H*), 3.39 (1H, d, J = 18.0 Hz, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.7, 176.2, 159.0 ($^2J_{C\text{-}F}$ = 179.0 Hz), 139.0, 128.1, 116.1, 111.2 ($^3J_{C\text{-}F}$ = 13.0 Hz), 110.5 ($^3J_{C\text{-}F}$ = 17.5 Hz), 49.4, 45.6, 28.4; HRMS: $C_{14}H_{10}N_3O_2F$ $[M]^+$ calcd: 271.0757, found: 271.0760; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30ºC): t_{minor} = 18.0 min, t_{major} = 33.3 min, ee = 96%, $[\alpha]_D^{20}$ = -80° (MeOH, c = 0.15); mp: 204-205 ºC.



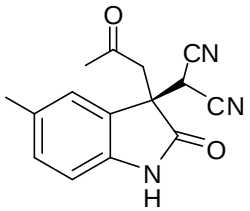
2-(5-Chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3d). The title compound was prepared according to the method B, as described above in 92% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.4 (1H, d, *J* = 2.0 Hz, Ar*H*), 7.3 (1H, m, Ar*H*), 7.0 (1H, d, *J* = 8.0 Hz, Ar*H*), 3.65 (1H, d, *J* = 18.0 Hz, C*H*), 3.39 (1H, d, *J* = 18.0 Hz, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.7, 175.9, 141.7, 129.9, 128.4, 127.5, 123.6, 111.4, 110.6, 110.0, 49.1, 45.7, 28.3, 23.0; HRMS: $C_{14}H_{10}N_3O_2Cl$ $[M]^+$ calcd: 287.0462, found: 287.0463; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30ºC): t_{minor} = 17.3 min, t_{major} = 31.3 min, ee = 95%, $[\alpha]_D^{20}$ = -130° (MeOH, *c* = 0.15); mp: 209-210 ºC.



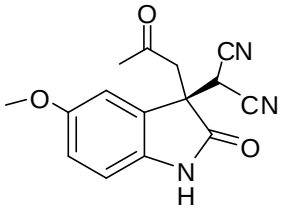
2-(5-Bromo-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3e). The title compound was prepared according to the method B, as described above in 93% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.6 (1H, d, *J* = 2.0 Hz, Ar*H*), 7.5 (H, m, Ar*H*), 6.9 (1H, d, *J* = 8.4 Hz, Ar*H*), 3.63 (1H, d, *J* = 18.4 Hz, C*H*), 3.38 (1H, d, *J* = 18.4 Hz, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.6, 175.8, 142.2, 132.8, 128.8, 126.4, 114.5, 111.9, 110.6, 49.0, 45.7, 28.3; HRMS: $C_{14}H_{10}N_3O_2Br$ $[M]^+$ calcd: 330.9956, found:330.9955; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, 30ºC): t_{minor} = 10.9 min, t_{major} = 19.2 min, ee = 94%, $[\alpha]_D^{20}$ = -55.3° (MeOH, *c* = 0.17); mp: 224-226 ºC.



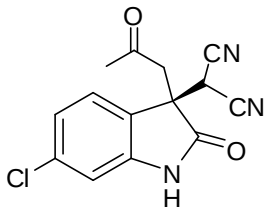
2-(5-Nitro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3f). The title compound was prepared according to the method B, as described above in 94% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ =8.3 (2H, m, Ar*H*), 7.1 (1H, d, *J* = 8.4 Hz, Ar*H*), 3.77 (1H, d, *J* = 18.4 Hz, C*H*), 3.50 (1H, d, *J* = 18.4 Hz, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 204.3, 176.3, 150.0, 142.7, 128.0,n 127.6, 120.2, 111.5, 111.2, 110.7, 48.6, 46.3, 30.0, 29.9; HRMS: $C_{14}H_{10}N_4O_4$ $[M]^+$ calcd: 298.0702, found: 298.0704; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 230 nm, 30 ºC): t_{minor} = 17.7 min, t_{major} = 23.9 min, ee = 93%, $[\alpha]_D^{20}$ = -21.88° (MeOH, *c* = 0.16); mp: 233-234 ºC.



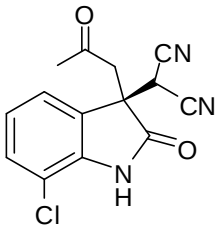
2-(5-Methyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3g). The title compound was prepared according to the method B, as described above in 95% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.2 (1H, s, Ar*H*), 7.1 (1H, d, *J* = 8.0 Hz, Ar*H*), 6.9 (1H, d, *J* = 8.0 Hz, Ar*H*), 3.55 (1H, d, *J* = 18.0 Hz, C*H*), 3.32 (1H, d, *J* = 18.0 Hz, C*H*), 2.3 (3H, s, CH_3), 2.0 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.7, 176.4, 140.3, 132.2, 130.2, 126.5, 123.7, 110.9, 110.1, 49.1, 45.6, 28.6, 19.7, 13.0; HRMS: $C_{15}H_{13}N_3O_2$ $[M]^+$ calcd: 267.1008, found: 267.1010; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 19.2 min, t_{major} = 14.6 min, ee = 95%, $[\alpha]_D^{20}$ = -161.8° (MeOH, *c* = 0.11); mp: 206-207 ºC.



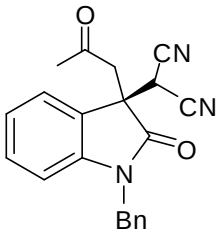
2-(5-Methoxy-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3h). The title compound was prepared according to the method B, as described above in 96% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 6.9-7.0 (3H, m, Ar*H*), 3.7 (3H, s, CH_3), 3.57 (1H, d, *J* = 18.0 Hz, C*H*), 3.33 (1H, d, *J* = 18.0 Hz, C*H*), 2.1 (3H, s, CH_3);^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.7, 176.2, 156.1, 135.9, 127.6, 114.5, 110.8, 110.3, 54.8, 49.4, 45.6, 28.6; HRMS: $C_{15}H_{13}N_3O_3$ $[M]^+$ calcd: 283.0957, found: 283.0958; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 24.2 min, t_{major} = 19.3 min, ee = 95%, $[\alpha]_D^{20}$ = -307.1° (MeOH, *c* = 0.14); mp: 202-203 ºC.



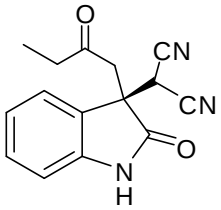
2-(6-Chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3i). The title compound as yellow oil was prepared according to the method B, as described above in 93% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.1-7.3 (3H, m, Ar*H)*, 3.58 (1H, d, *J* = 18.0 Hz, C*H*), 3.36 (1H, d, *J* = 18.0 Hz, C*H*), 2.1 (3H, s, CH_3*)*; ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.6, 176.1, 144.4, 125.6, 125.1, 124.7, 123.4, 113.5, 110.6, 110.1, 48.7, 45.6, 28.4; HRMS: $C_{14}H_{10}N_3O_2Cl$ $[M]^+$ calcd: 287.0462, found: 287.0464; HPLC (Chiralpak AS-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 19.2 min, t_{major} = 26.3 min, ee = 96%, $[\alpha]_D^{20}$ = -21.8° (MeOH, *c* = 0.16); mp: 219-220 ºC.



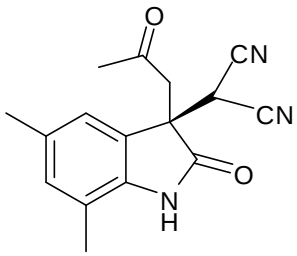
2-(7-Chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3j). The title compound was prepared according to the method B, as described above in 91% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.3 (2H, d, J = 8.0 Hz, Ar*H*) 7.1 (H, m, Ar*H)*, 3.62 (1H, d, J = 18.0 Hz, C*H*), 3.41 (1H, d, J = 18.0 Hz, C*H*), 2.3 (1H, s, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.6, 175.8, 140.8, 130.0, 128.2, 123.3, 121.6, 115.5, 110.6, 110.1, 49.6, 45.8, 28.4, 23.0; HRMS: $C_{14}H_{10}N_3O_2Cl$ $[M]^+$ calcd: 287.0462, found: 287.0461; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 25.4 min, t_{major} = 14.2 min, ee = 86%, $[\alpha]_D^{20}$ = -32.8° (MeOH, c = 0.35); mp: 197-199 ºC.



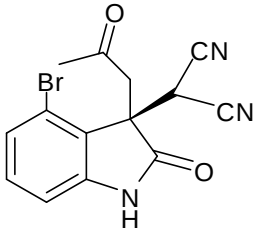
2-(1-Benzyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3k). The title compound was prepared according to the method A, as described above in 92% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 6.0-6.6 (9H, m, Ar*H*), 4.2 (2H, s, CH_2), 2.86 (1H, d, J = 18.0 Hz, C*H*), 2.63 (1H, d, J = 18.0 Hz, C*H*), 1.2 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 202.8, 173.9, 143.0, 134.4, 129.1, 127.5, 126.5, 126.3, 124.9, 122.2, 122.1, 110.1, 109.6, 109.3, 47.8, 45.1, 43.2, 27.7, 22.3; HRMS: $C_{21}H_{17}N_3O_2$ $[M]^+$ calcd: 343.1321, found: 343.1320; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 23.5 min, t_{major} = 12.1 min, ee = 46%, $[\alpha]_D^{20}$ = -12.5° (MeOH, c = 0.2).



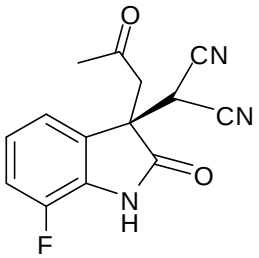
2-(2-Oxo-3-(2-oxobutyl)indolin-3-yl)malononitrile (3l). The title compound was prepared according to the method A, as described above in 97% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.0-7.4 (4H, m, Ar*H*), 3.54 (1H, d, J = 17.6 Hz, C*H*), 3.30 (1H, d, J = 17.6 Hz, C*H*), 3.3-3.5 (2H, dd, J_1 = 17.6 Hz, J_2 = 94.0 Hz, CH_2), 2.4 (2H, m, CH_2), 0.9 (3H, t, J = 6.8 Hz, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 206.4, 176.4, 142.8, 129.9, 126.5, 123.1, 122.4, 110.9, 110.3, 49.1, 44.6, 35.3, 6.2; HRMS: $C_{15}H_{13}N_3O_2$ $[M]^+$ calcd: 267.1008, found: 267.1017; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{minor} = 12.3 min, t_{major} = 10.1 min, ee = 92%, $[\alpha]_D^{20}$ = -80° (MeOH, c = 0.1); mp: 168-169 ºC.



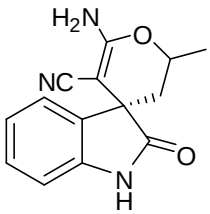
2-(5,7-Dimethyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3m). The title compound was prepared according to the method B, as described above in 85% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.08 (1H, s, Ar*H*), 7.0 (1H, s, Ar*H*), 3.53 (1H, d, *J* = 18.0 Hz, C*H*), 3.30 (1H, d, *J* = 18.0 Hz, C*H*), 2.3 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.0 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.7, 176.6, 138.8, 132.2, 131.7, 126.2, 120.9, 119.9, 110.9, 49.2, 45.6, 29.3, 28.6, 19.6, 15.2; HRMS: $C_{16}H_{15}N_3O_2$ $[M]^+$ calcd: 281.1164, found: 281.1172; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC): t_{minor} = 9.3 min, t_{major} = 7.1 min, ee = 93%, $[\alpha]_D^{16.3}$ = -11.28° (MeOH, *c* = 0.25); mp: 166-167 ºC.



2-(4-Bromo-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3n). The title compound was prepared according to the method B, as described above in 90% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.3 (1H, m, Ar*H*), 7.2 (1H, d, *J* = 8.4 Hz, Ar*H*), 7.0 (1H, d, *J* = 8.0 Hz, Ar*H*), 4.0 (1H, d, *J* = 18.0 Hz, CH_2), 3.4 (1H, d, *J* = 18.0 Hz, CH_2), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.2, 175.1, 144.4, 131.9, 128.1, 120.1, 109.7, 105.1, 53.4, 44.3, 28.2, 19.4; HRMS: $C_{14}H_{10}N_3O_2Br$ $[M]^+$ calcd: 330.9956, found:330.9955; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC): t_{minor} = 9.7 min, t_{major} = 8.6 min, ee > 99%, $[\alpha]_D^{16.5}$ = -19.1° (MeOH, *c* = 0.3); mp: 197-199 ºC.

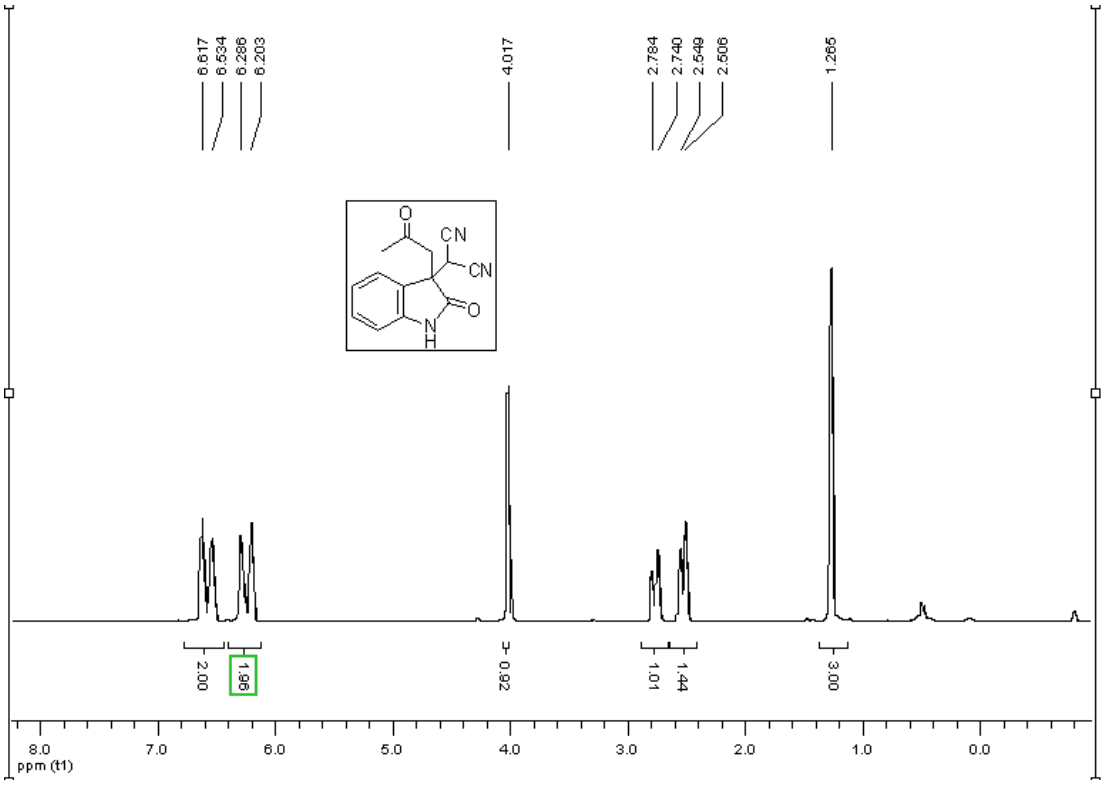


2-(7-Fluoro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (3o). The title compound was prepared according to the method B, as described above in 97% yield. ^{1}H NMR (400 MHz, MeOH-d_4): δ = 7.07-7.28 (3H, m, Ar*H*), 3.63 (1H, d, *J* = 18.0 Hz, C*H*), 3.40 (1H, d, *J* = 18.0 Hz, C*H*), 2.1 (3H, s, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 203.5, 175.8, 148.5, 146.1, 130.3, 129.4, 123.2, 119.0, 117.0, 110.6, 110.1, 49.2, 45.8, 28.4; HRMS: $C_{14}H_{10}N_3O_2F$ $[M]^+$ calcd: 271.0757, found: 271.0760; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC): t_{minor} = 18.1 min, t_{major} = 10.5 min, ee = 88%, $[\alpha]_D^{16.9}$ = -2.85° (MeOH, *c* = 0.4); mp: 217-219 ºC.



6'-Amino-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (7). $NaBH_4$ (4.0 mg, 0.1 mmol) was added to a solution of **3a** (13.0 mg, 0.05 mmol, 92% ee) in MeOH (0.35 mL) at rt with stirring. The reaction was stirred for 30 min then the solvent was removed. The crude reaction mixture was directly subjected to column chromatography (hexane: ethylacetate = 1:1) on silica gel to afford the corresponding product in 80% yield. ^{1}H NMR (400 MHz, acetone-d_6): δ = 6.9-7.4 (4H, m, Ar*H*), 1.7-1.9 (2H, dd, J_1 = 13.6 Hz, J_2 = 57.6 Hz, CH_2), 1.4 (3H, d, J = 6.0 Hz, CH_3); ^{13}C NMR (75 MHz, acetone-d_6): δ = 179.0, 165.6, 141.1, 134.9, 128.3, 124.1, 121.9, 109.6, 70.9, 59.6, 47.8, 39.1, 20.0; HRMS: $C_{14}H_{13}N_3O_2$ $[M]^+$ calcd: 255.1008, found: 255.1012; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC): t_{jj} = 13.2 min, t_{mj} = 14.9 min, ee = 91%, dr = 9:1, $[\alpha]_D^{20}$ = -9.4° (MeOH, *c* = 0.17); mp: 284-285 ºC.

3a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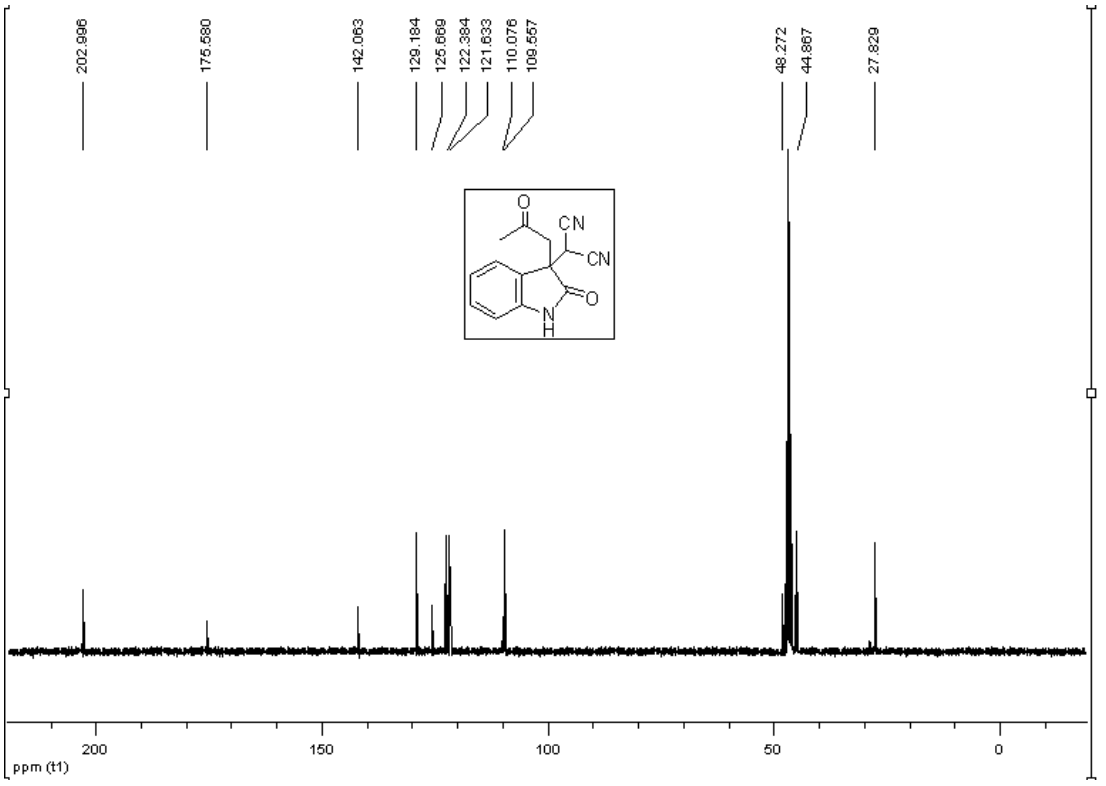
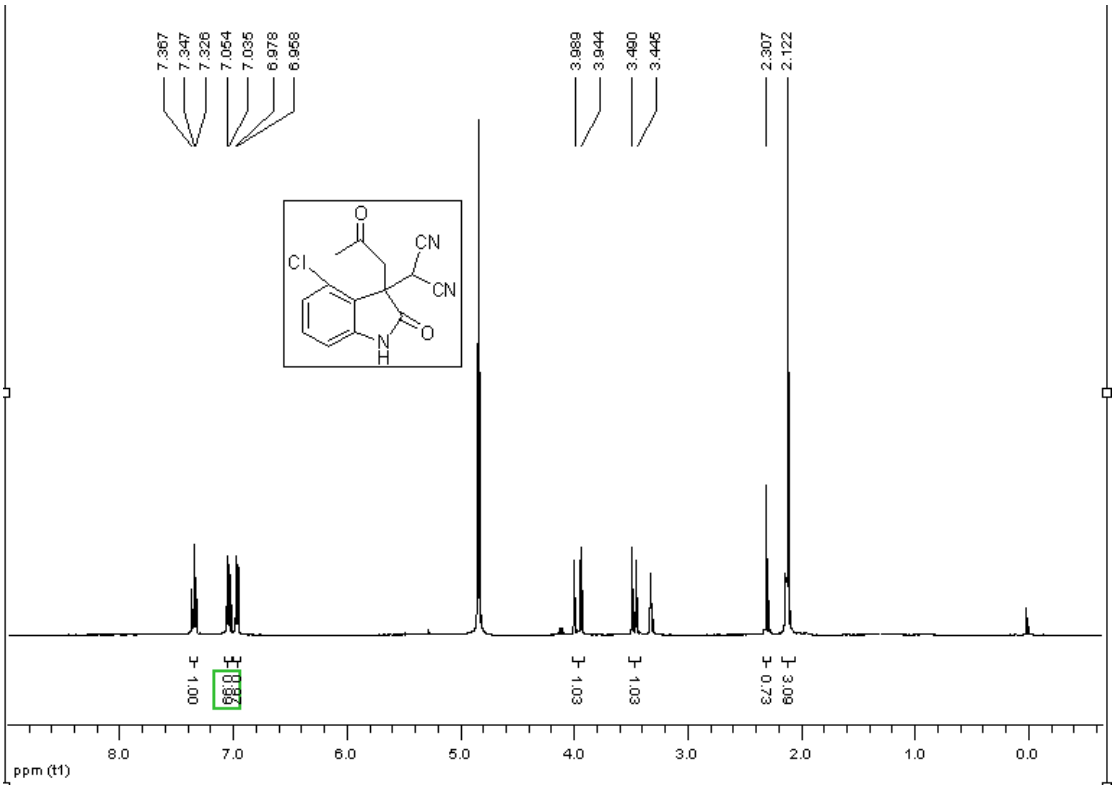
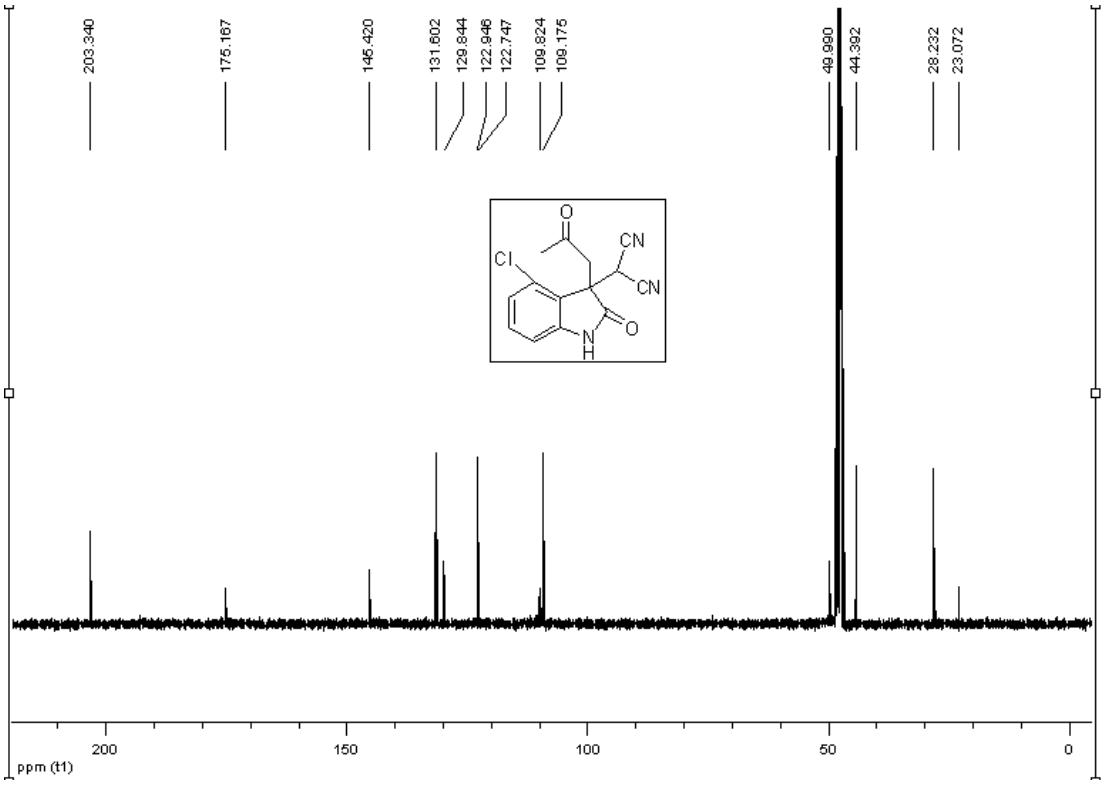
6.534
6.286
6.203
4.017
2.784
2.740
2.549
2.506
1.265
O
CN
CN
O
N
H
2.00
1.96
0.92
1.01
1.44
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


202.996
175.580
142.063
129.184
125.669
122.384
121.633
110.076
109.557
48.272
44.867
27.829
O
CN
CN
O
N
H
200
150
100
50
0
ppm (t1)

3b


7.367
7.347
7.326
7.054
7.035
6.978
6.958
3.989
3.944
3.490
3.445
2.307
2.122
O
CN
Cl
CN
O
N
H
1.00
0.98
1.03
1.03
0.73
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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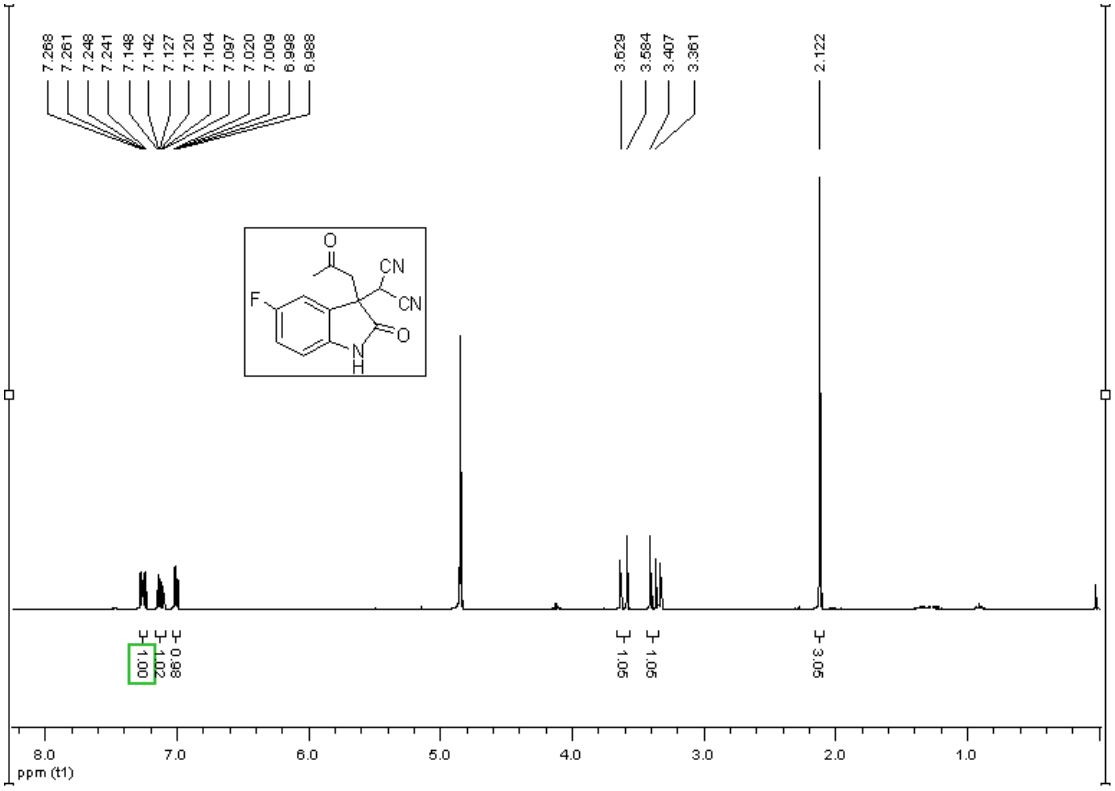
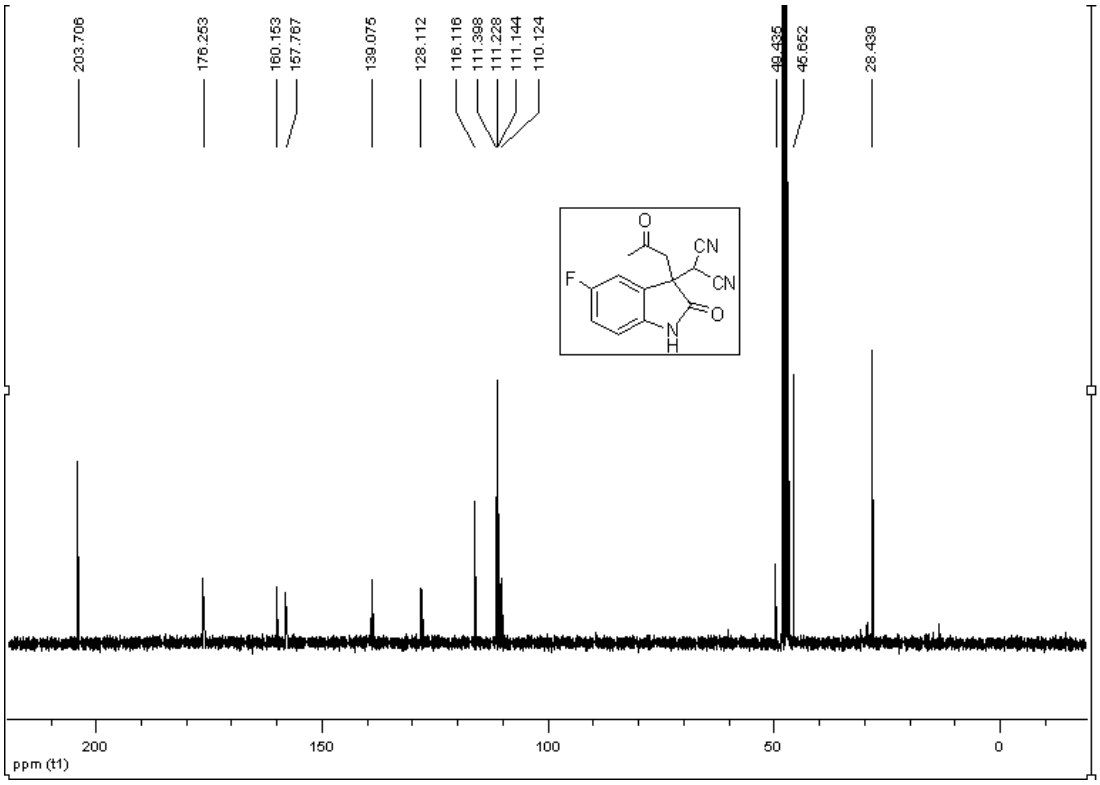
175.167
145.420
131.602
129.844
122.946
122.747
109.824
109.175
49.990
44.392
28.232
23.072
O
CN
Cl
CN
O
N
H
200
150
100
50
0
ppm (t1)

3c


7.268
7.261
7.248
7.241
7.148
7.142
7.127
7.120
7.104
7.097
7.020
7.009
6.998
6.988
3.629
3.584
3.407
3.361
2.122
1.00
1.02
0.98
1.05
1.05
3.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
O
CN
CN
F
O
N
H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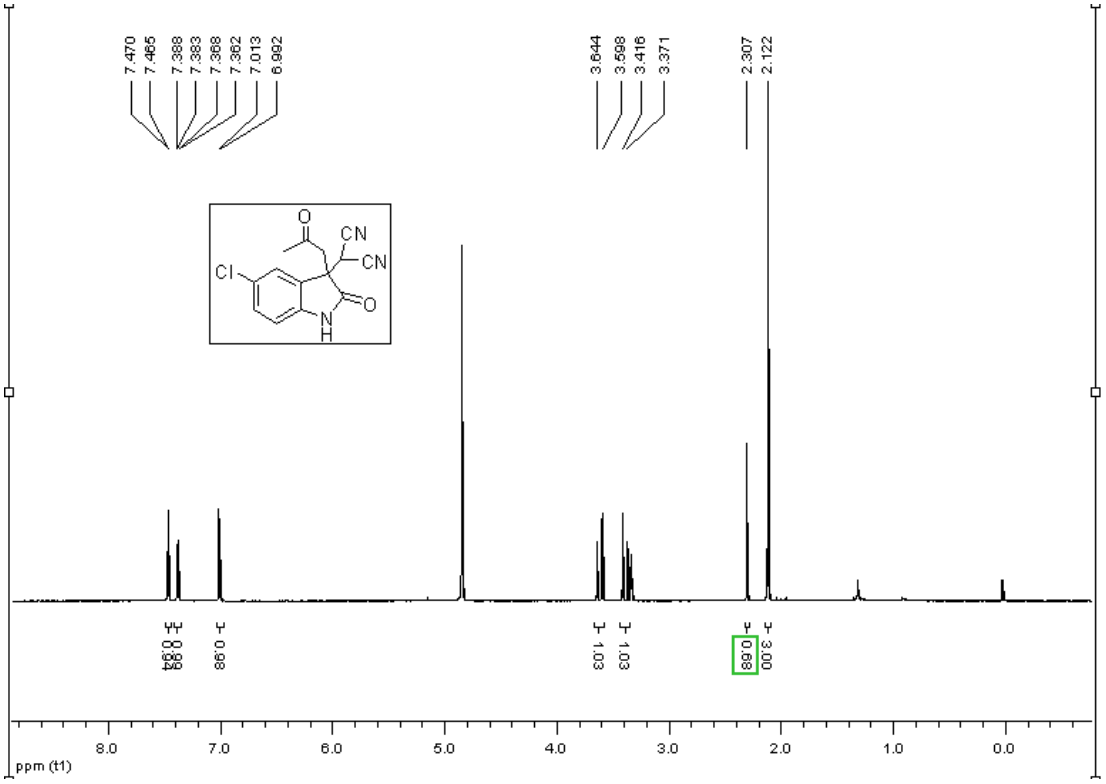
176.253
160.153
157.767
139.075
128.112
116.116
111.398
111.228
111.144
110.124
49.435
46.652
28.439
200
150
100
50
0
ppm (t1)
O
CN
CN
F
O
N
H

3d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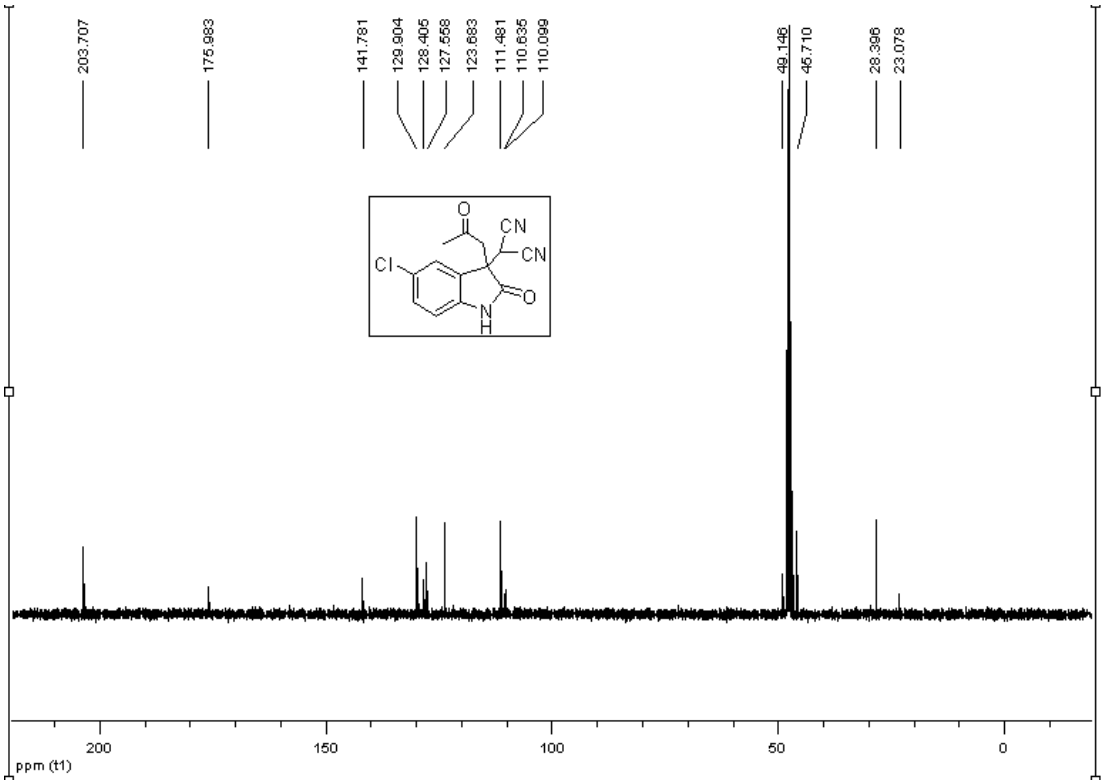
7.465
7.388
7.383
7.368
7.362
7.013
6.992
3.644
3.598
3.416
3.371
2.307
2.122
O
CN
CN
Cl
O
N
H
0.94
0.98
1.03
1.03
0.68
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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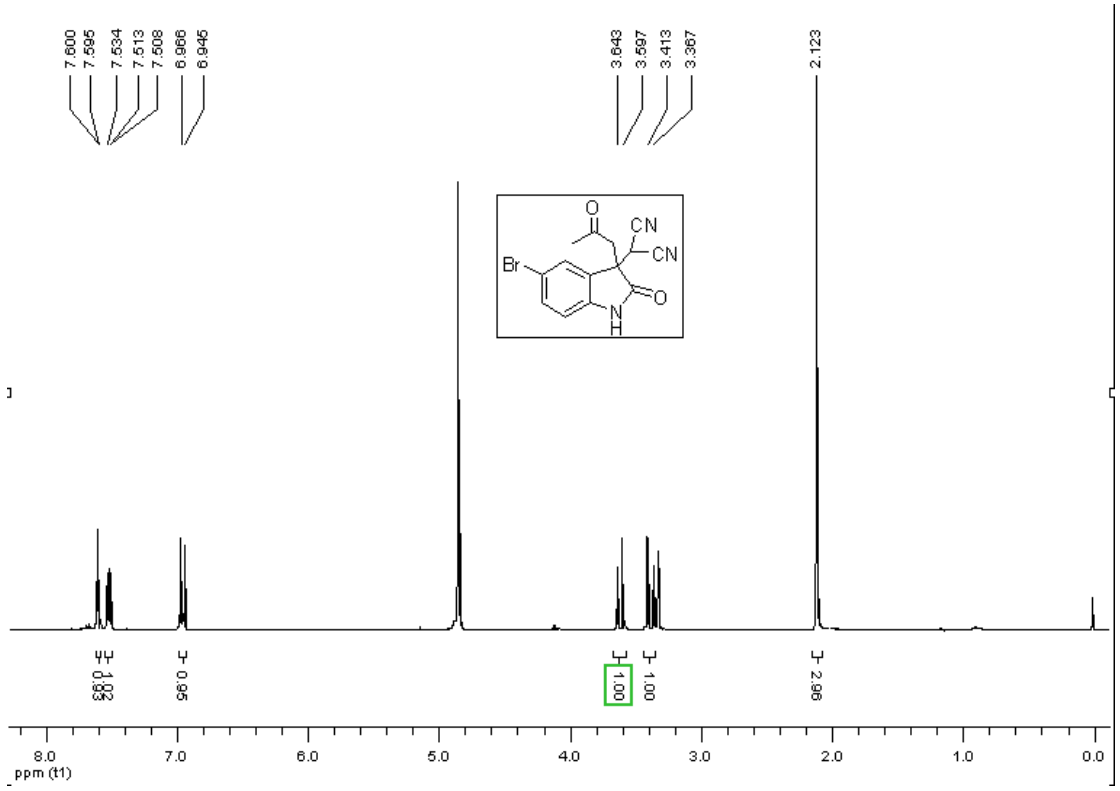
141.781
129.904
128.405
127.558
123.683
111.481
110.635
110.099
49.146
45.710
28.396
23.078
O
CN
CN
Cl
O
N
H
200
150
100
50
0
ppm (t1)

3e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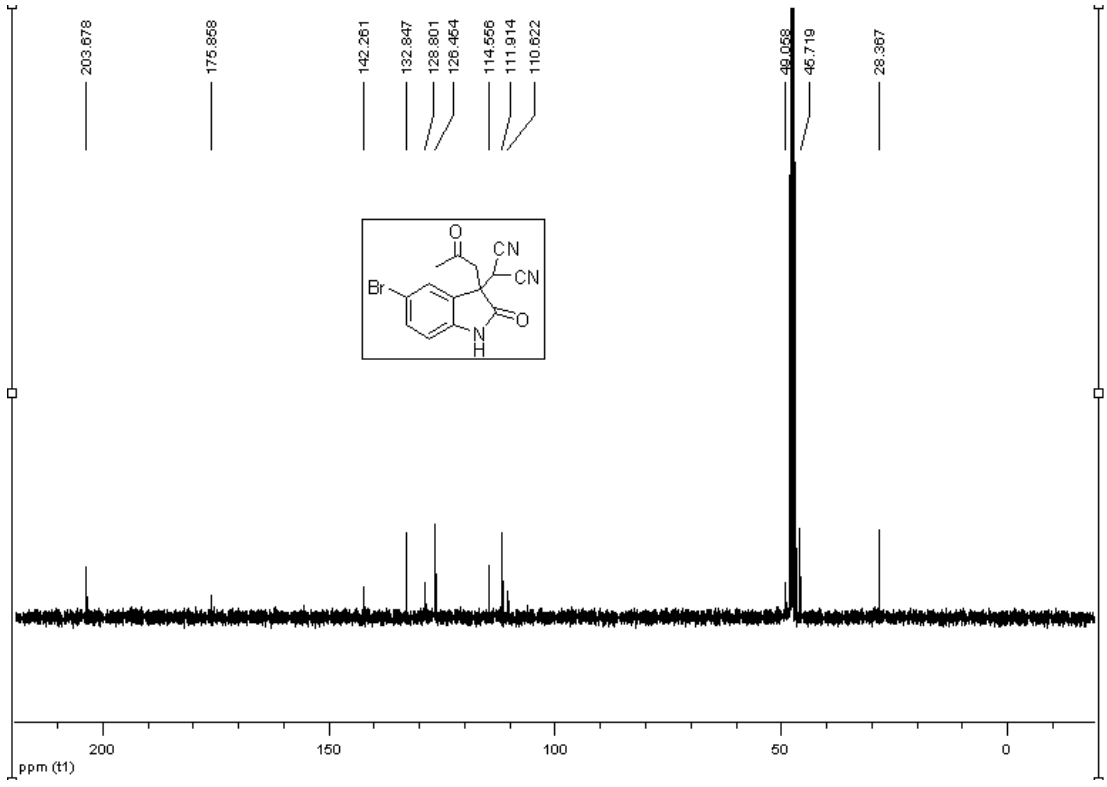
7.595
7.534
7.513
7.508
6.966
6.945
3.643
3.597
3.413
3.367
2.123
O
CN
CN
Br
O
N
H
1.03
0.96
1.00
1.00
2.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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175.858
142.261
132.847
128.801
126.454
114.556
111.914
110.622
49.058
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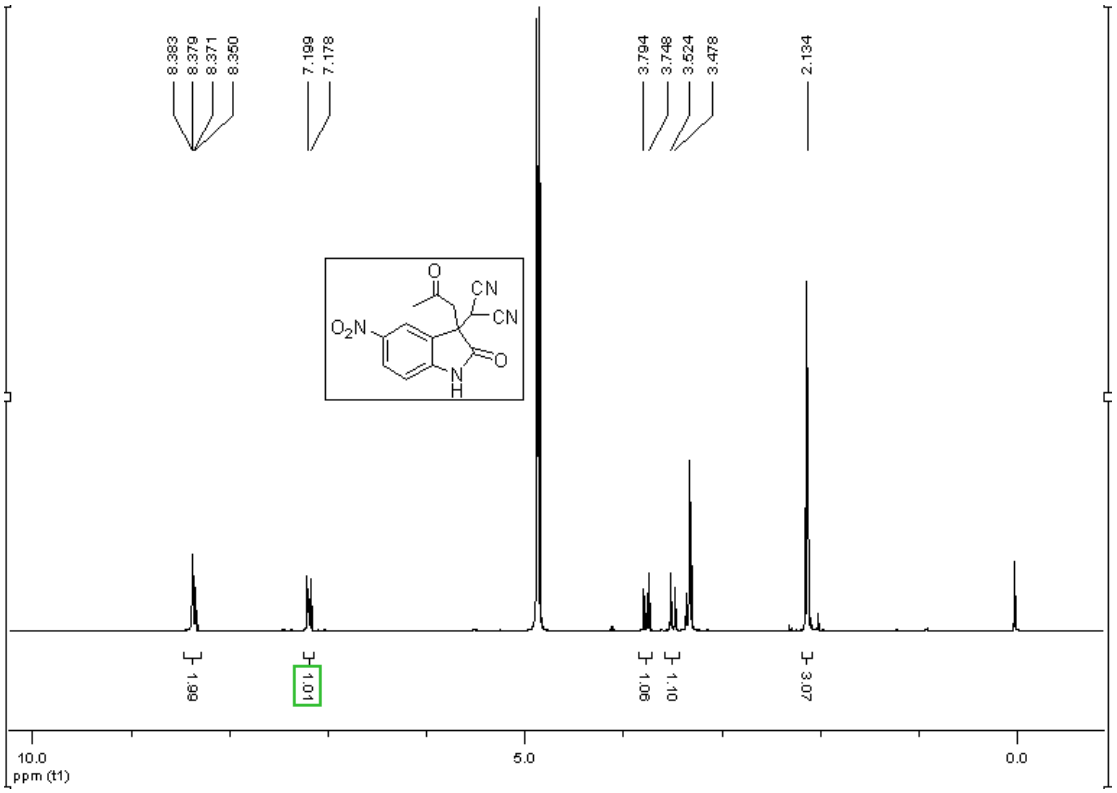
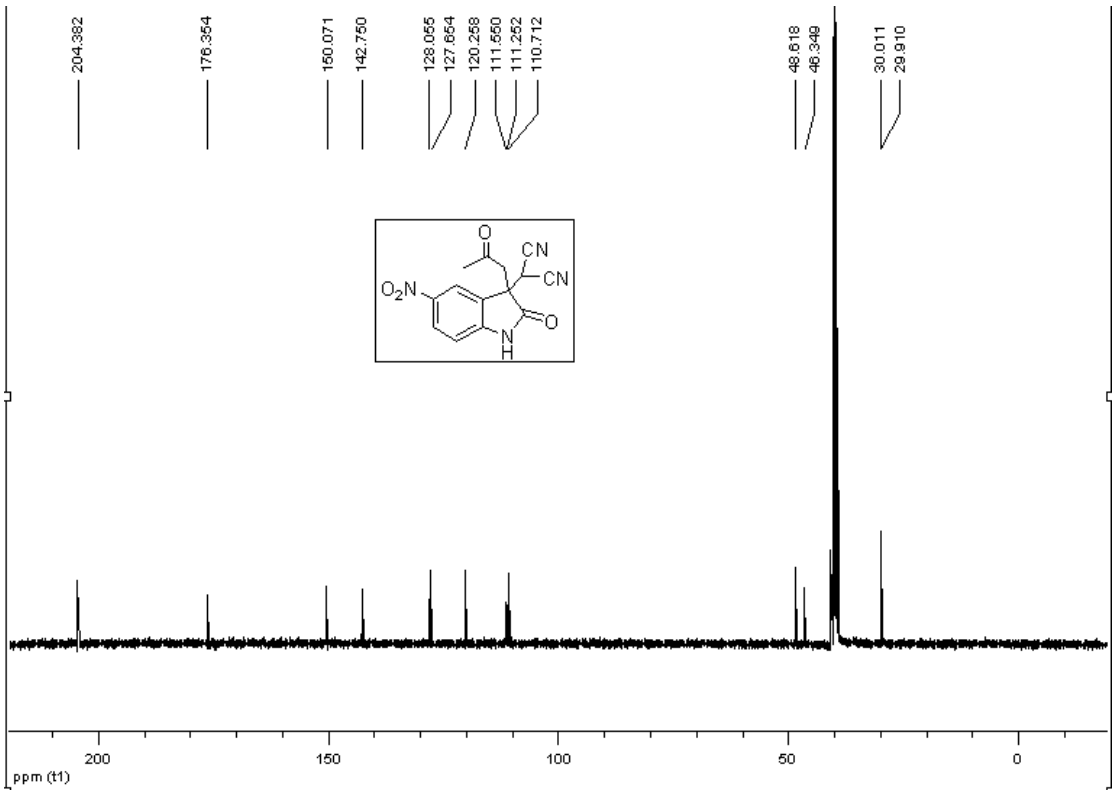
28.367
O
CN
CN
Br
O
N
H
200
150
100
50
0
ppm (t1)

3f


8.383
8.379
8.371
8.350
7.199
7.178
3.794
3.748
3.524
3.478
2.134
1.99
1.01
1.08
1.10
3.07
10.0
ppm (t1)
5.0
0.0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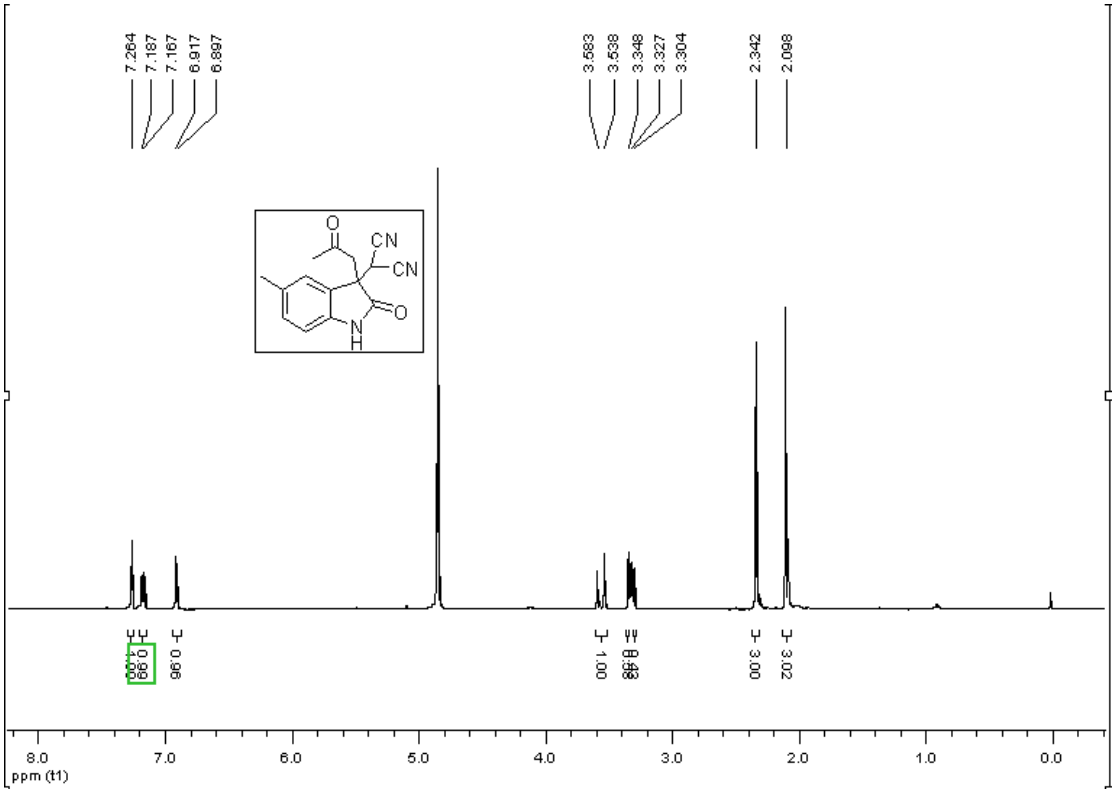
150.071
142.750
128.055
127.654
120.258
111.550
111.252
110.712
48.618
46.349
30.011
29.910
200
150
100
50
0
ppm (t1)

3g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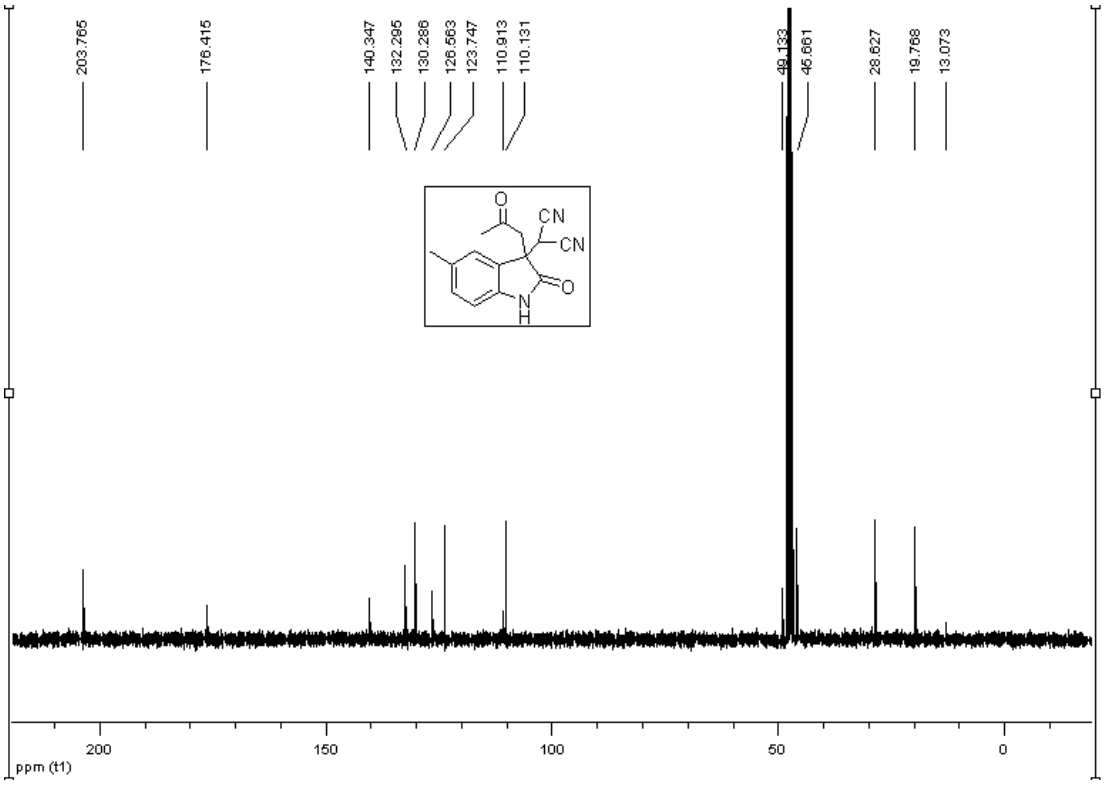
7.167
6.917
6.897
3.583
3.538
3.348
3.327
3.304
2.342
2.098
CN
CN
O
O
N
H
0.98
0.96
1.00
3.00
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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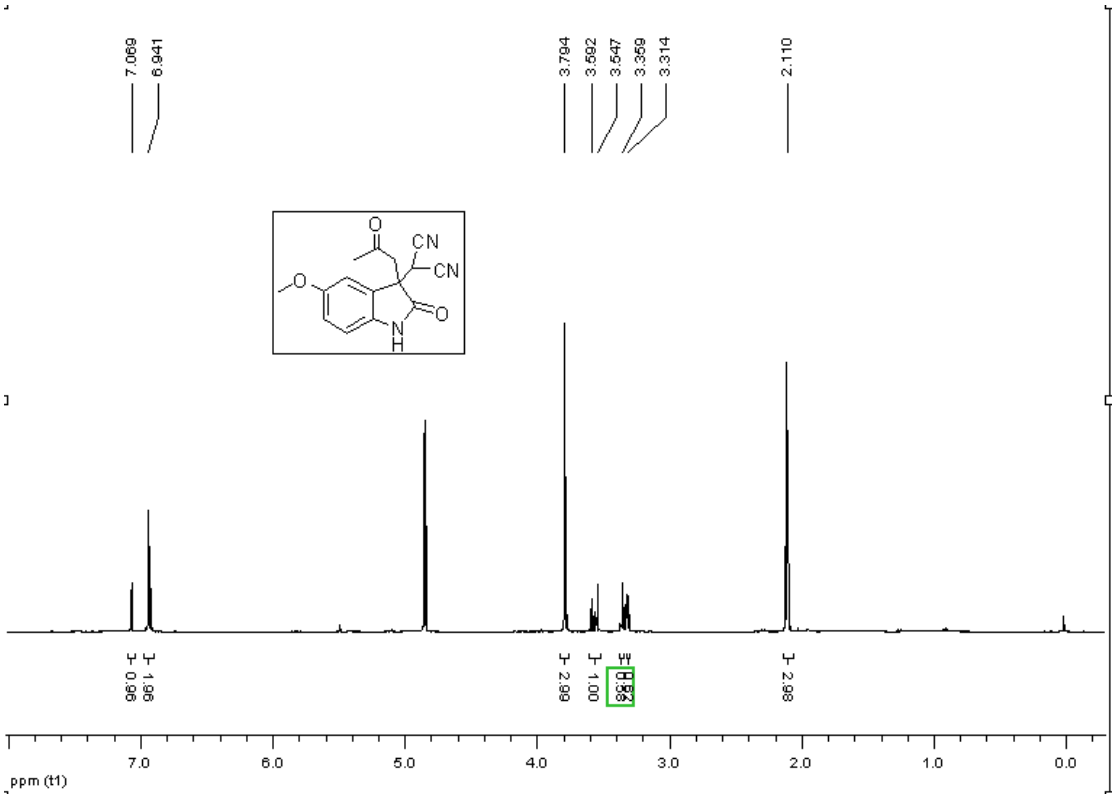
123.747
110.913
110.131
49.133
45.661
28.627
19.768
13.073
CN
CN
O
O
N
H
200
150
100
50
0
ppm (t1)

3h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3.794
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3.547
3.359
3.314
2.110
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CN
O
O
N
H
0.96
1.96
2.99
1.00
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7.0
6.0
5.0
4.0
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2.0
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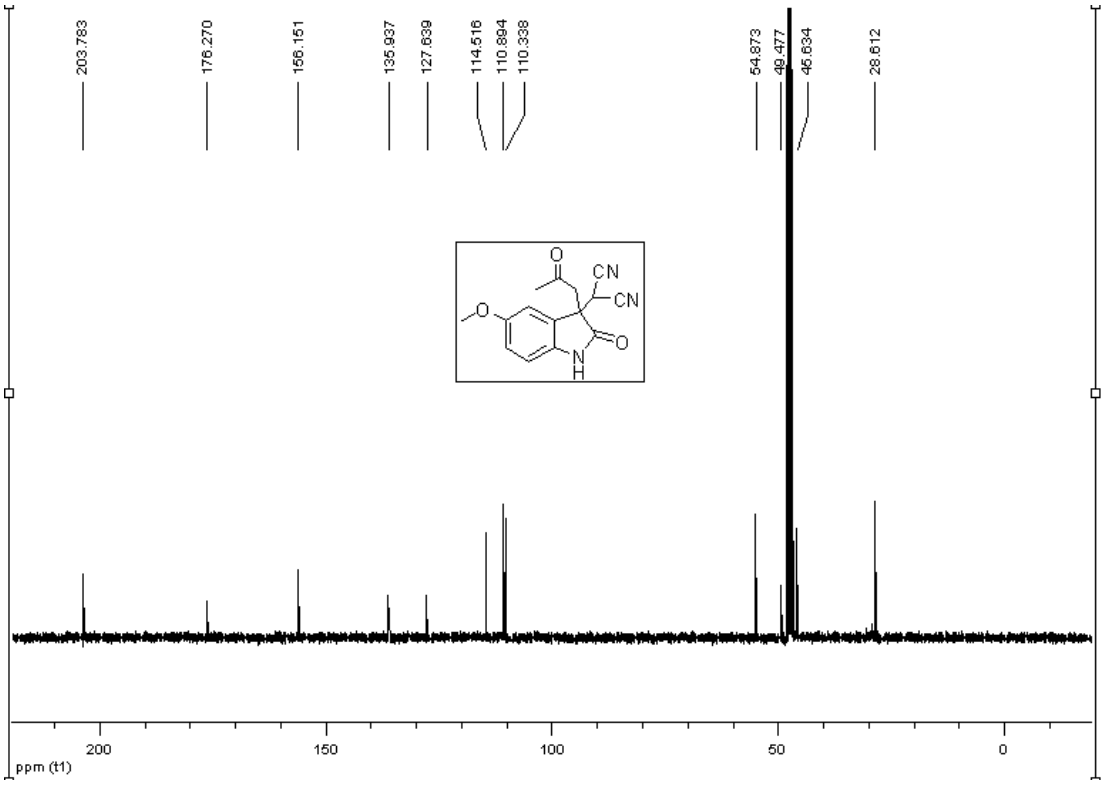
0.0
ppm (t1)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156.151
135.937
127.639
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110.338
54.873
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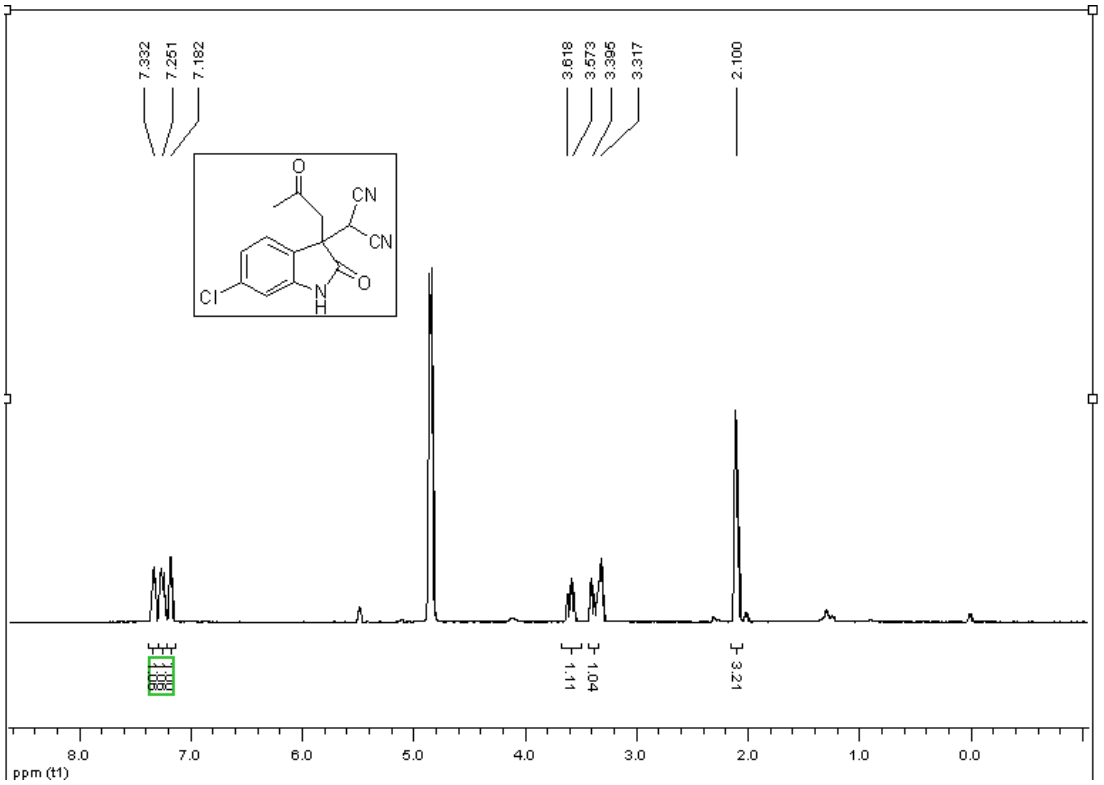
45.634
28.612
CN
CN
O
O
N
H
200
150
100
50
0
ppm (t1)

3i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CN
O
O
Cl
N
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1.00
1.11
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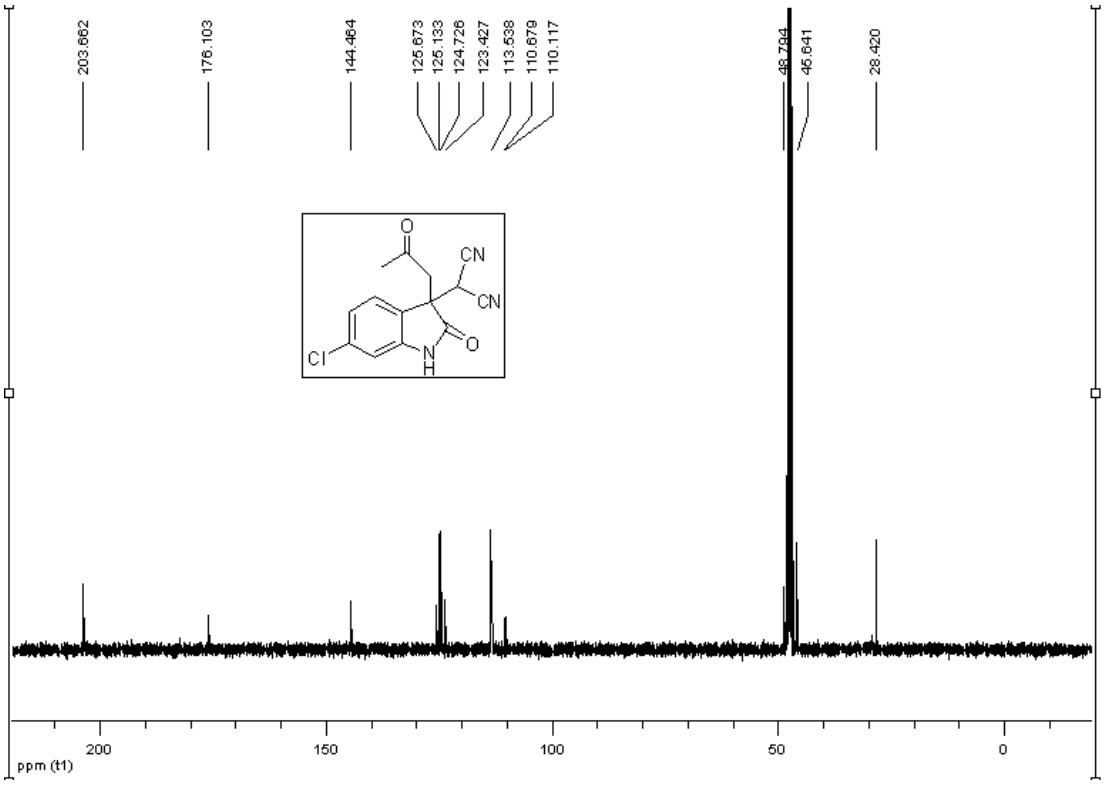
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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125.133
124.726
123.427
113.538
110.679
110.117
48.794
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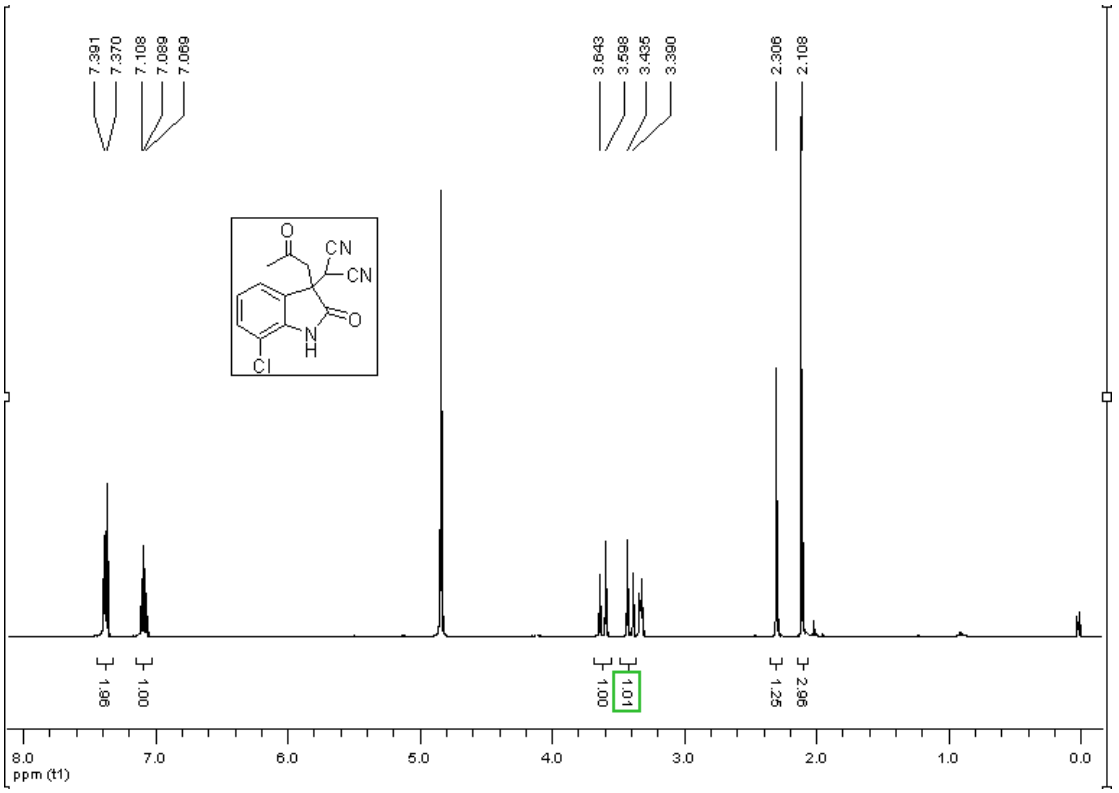
CN
CN
O
O
Cl
N
H
200
150
100
50
0
ppm (t1)

3j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3.435
3.390
2.306
2.108
O
CN
CN
O
N
H
Cl
1.96
1.00
1.00
1.01
1.25
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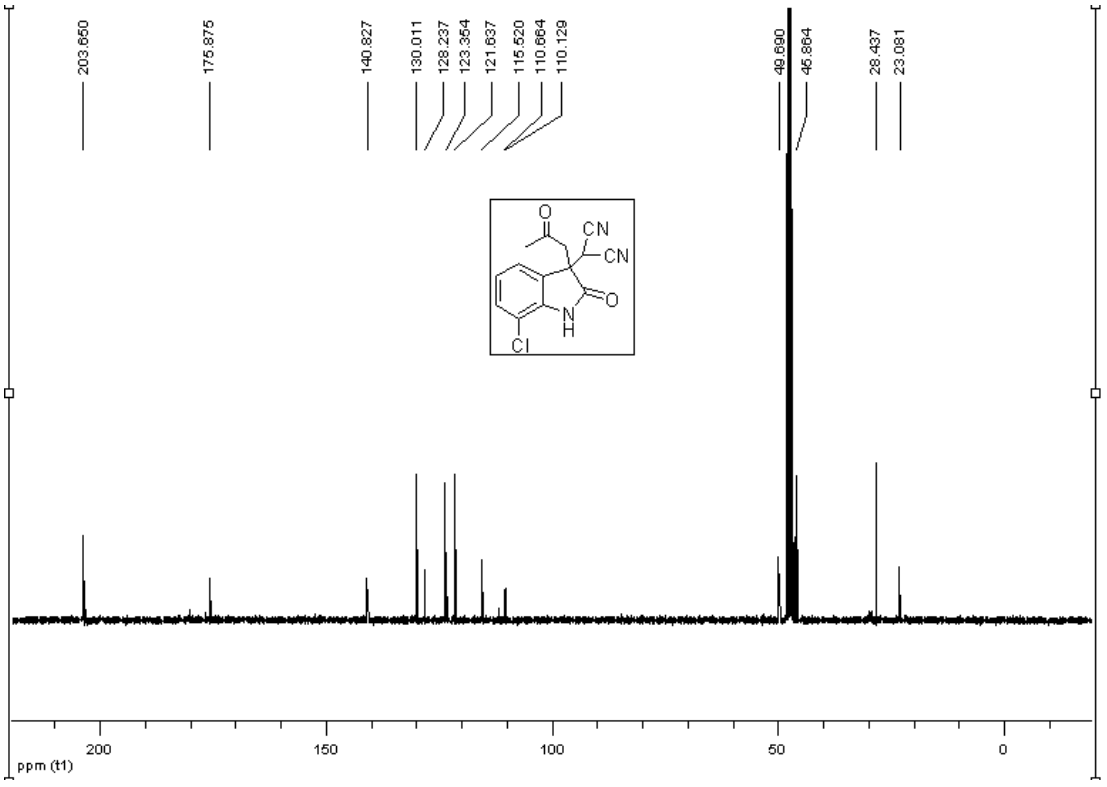
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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115.520
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110.129
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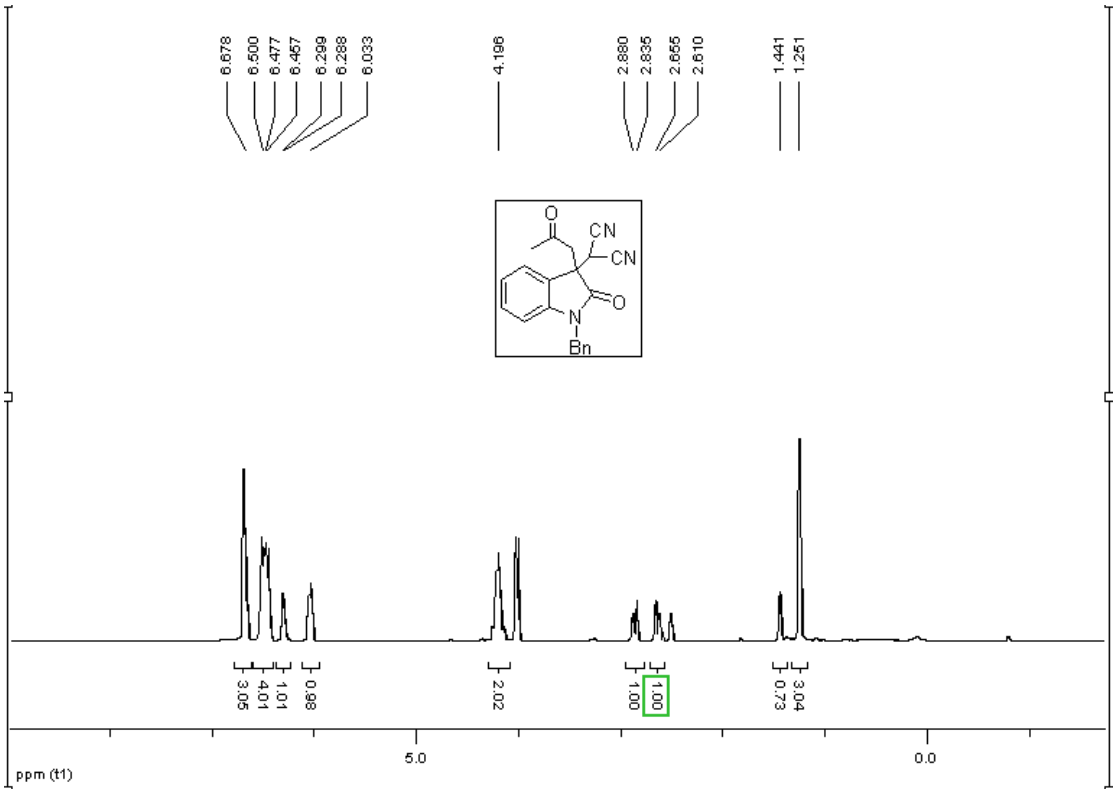
CN
O
N
H
Cl
200
150
100
50
0
ppm (t1)

3k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4.196
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2.835
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2.610
1.441
1.251
O
CN
CN
O
N
Bn
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4.01
1.01
0.98
2.02
1.00
1.00
0.73
3.04
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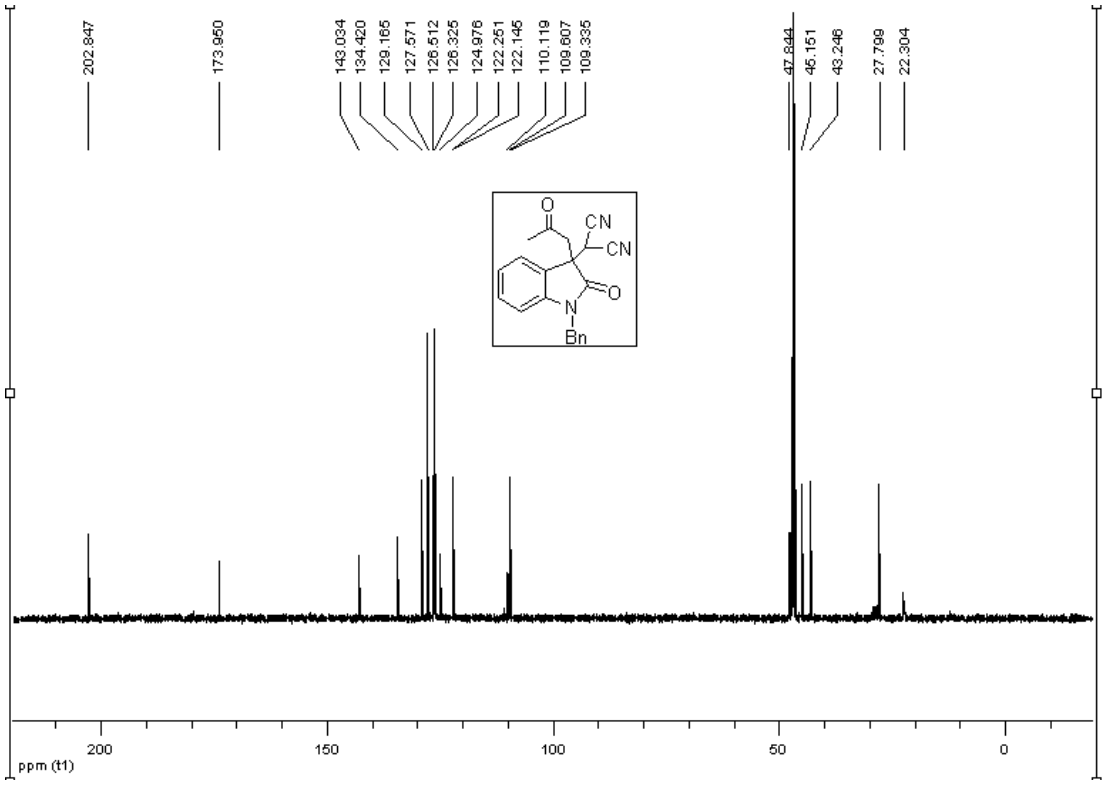
0.0
ppm (t1)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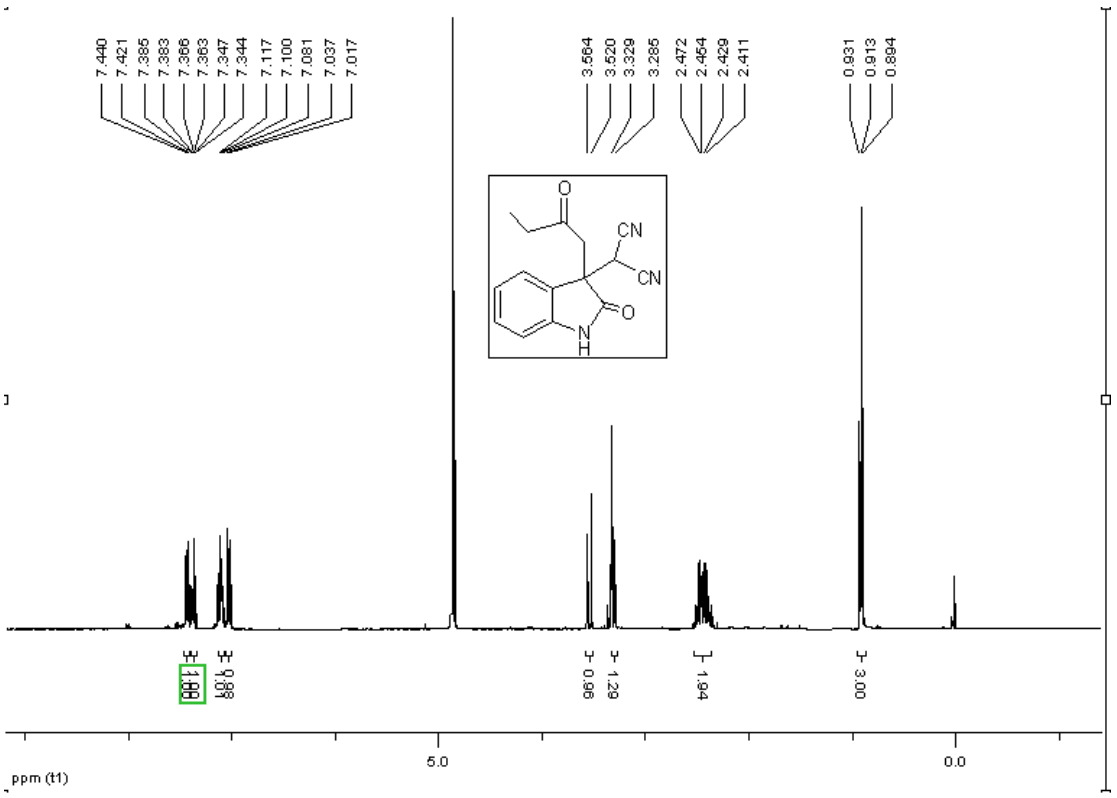
134.420
129.165
127.571
126.512
126.325
124.976
122.251
122.145
110.119
109.607
109.335
47.844
45.151
43.246
27.799
22.304
O
CN
CN
O
N
Bn
200
150
100
50
0
ppm (t1)

3l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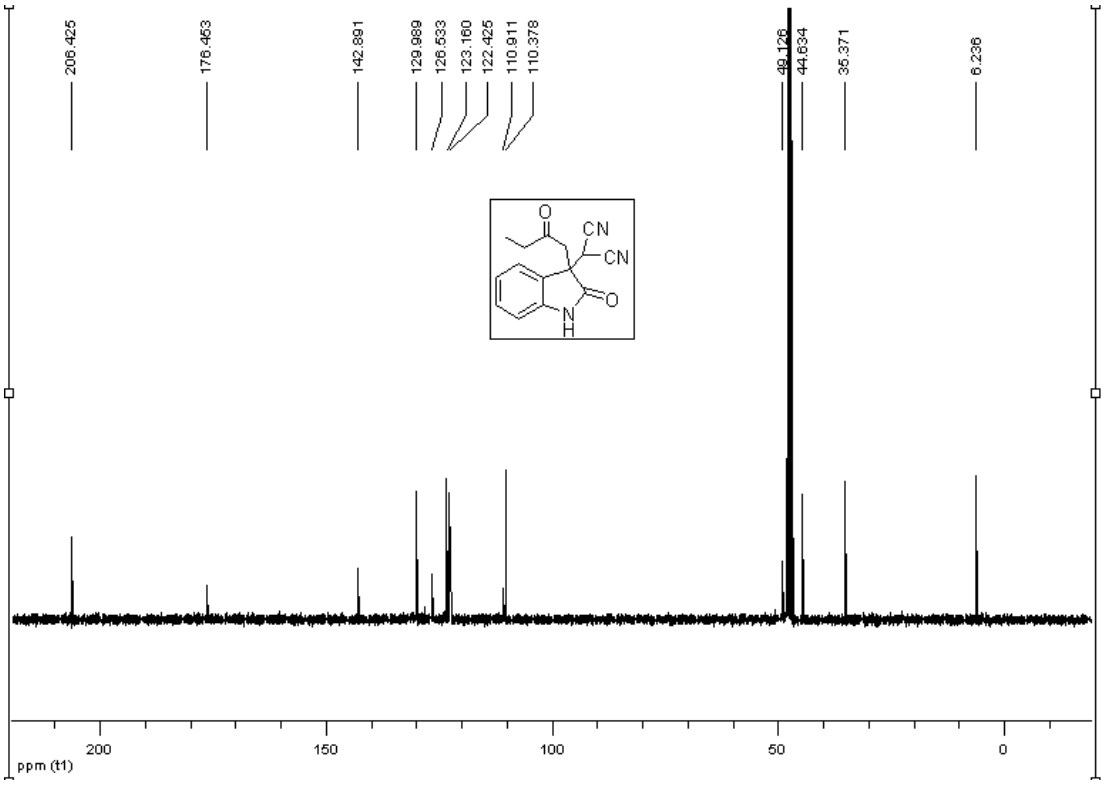
7.100
7.081
7.037
7.017
3.564
3.520
3.329
3.285
2.472
2.454
2.429
2.411
0.931
0.913
0.894
O
CN
CN
O
N
H
1.00
0.99
0.96
1.29
1.94
3.00
5.0
0.0
ppm (t1)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123.160
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110.911
110.378
49.126
44.634
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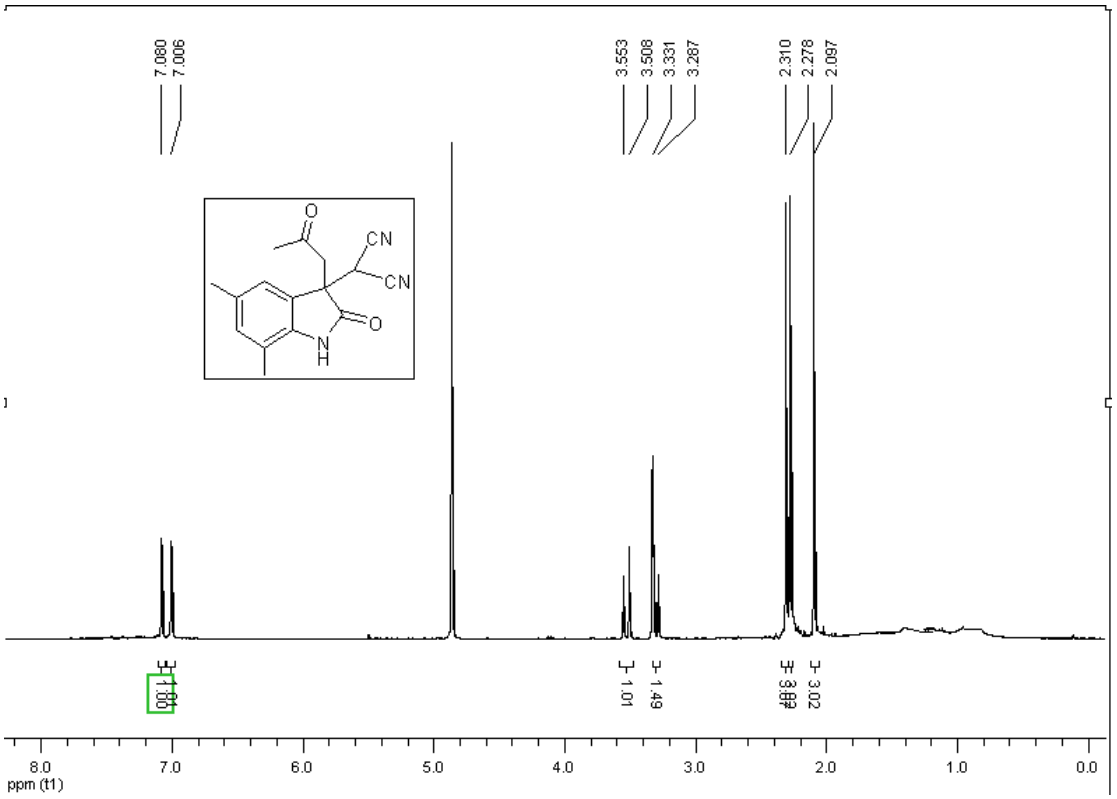
6.236
O
CN
CN
O
N
H
200
150
100
50
0
ppm (t1)

3m


7.080
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3.331
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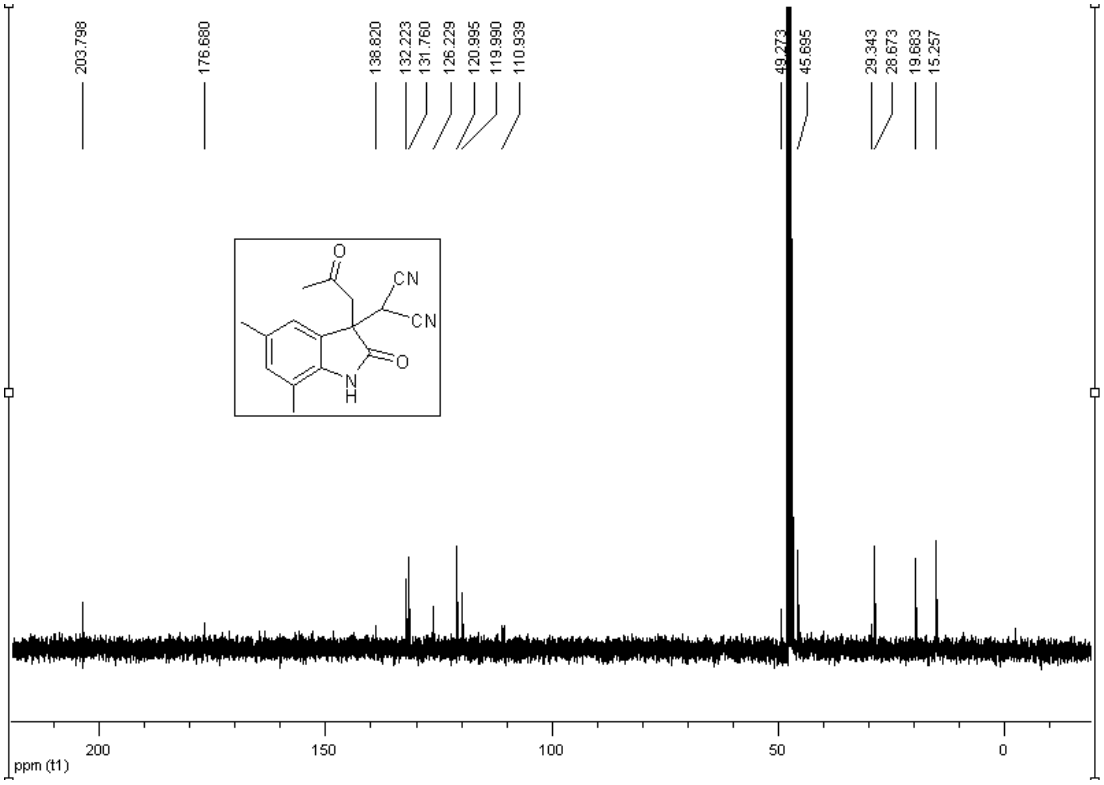
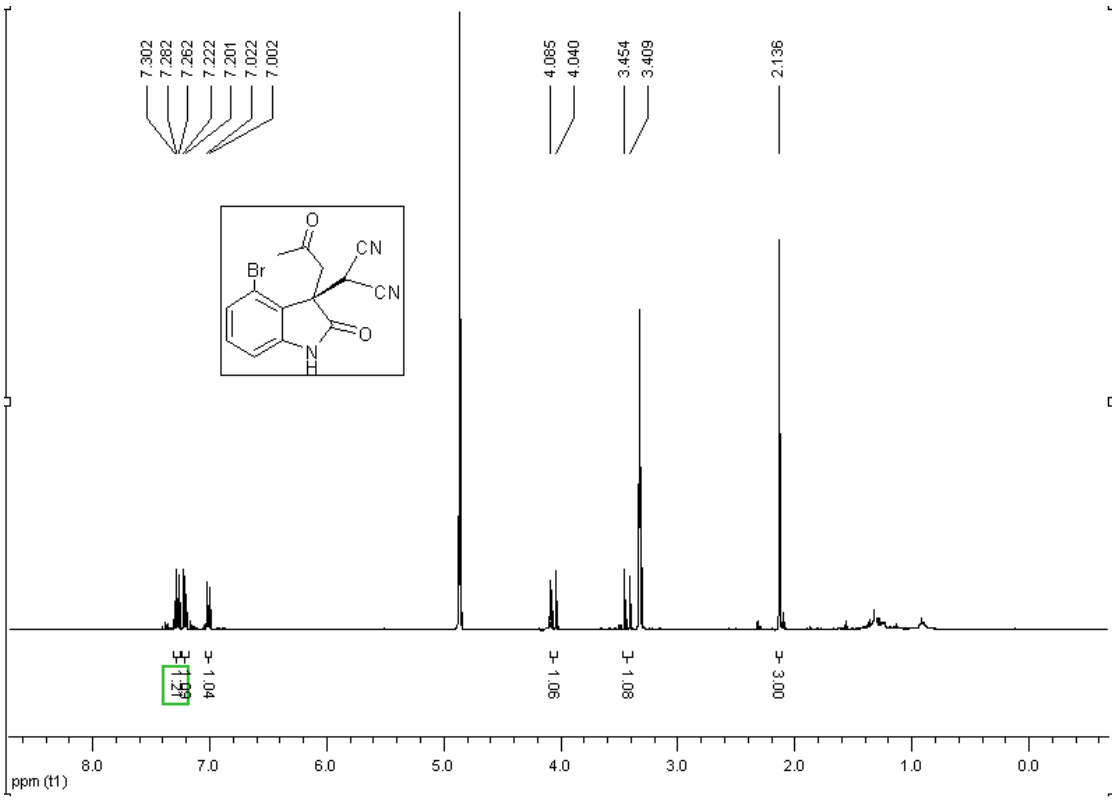
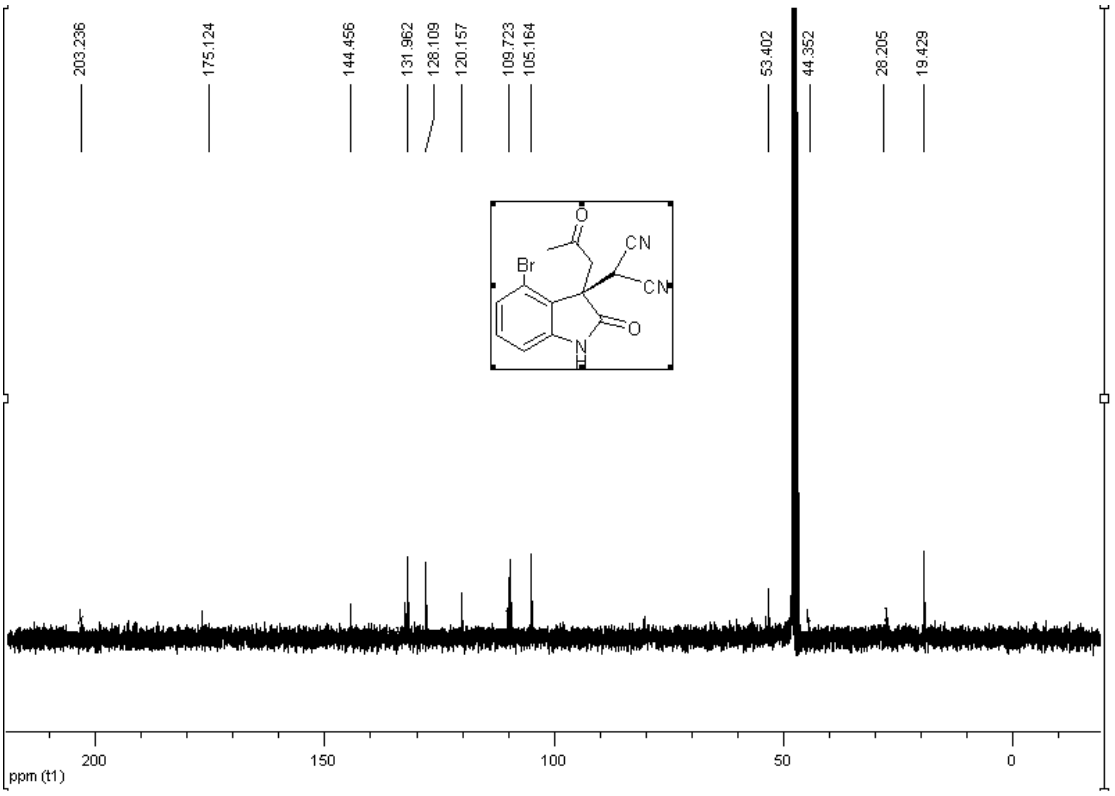
2.310
2.278
2.097
O
CN
CN
O
N
H
1.00
1.01
1.49
3.88
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


203.798
176.680
138.820
132.223
131.760
126.229
120.995
119.990
110.939
49.273
45.695
29.343
28.673
19.683
15.257
O
CN
CN
O
N
H
200
150
100
50
0
ppm (t1)

3n


7.302
7.282
7.262
7.222
7.201
7.022
7.002
4.085
4.040
3.454
3.409
2.136
O
CN
Br
CN
O
N
H
1.00
1.04
1.06
1.08
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


203.236
175.124
144.456
131.962
128.109
120.157
109.723
105.164
53.402
44.352
28.205
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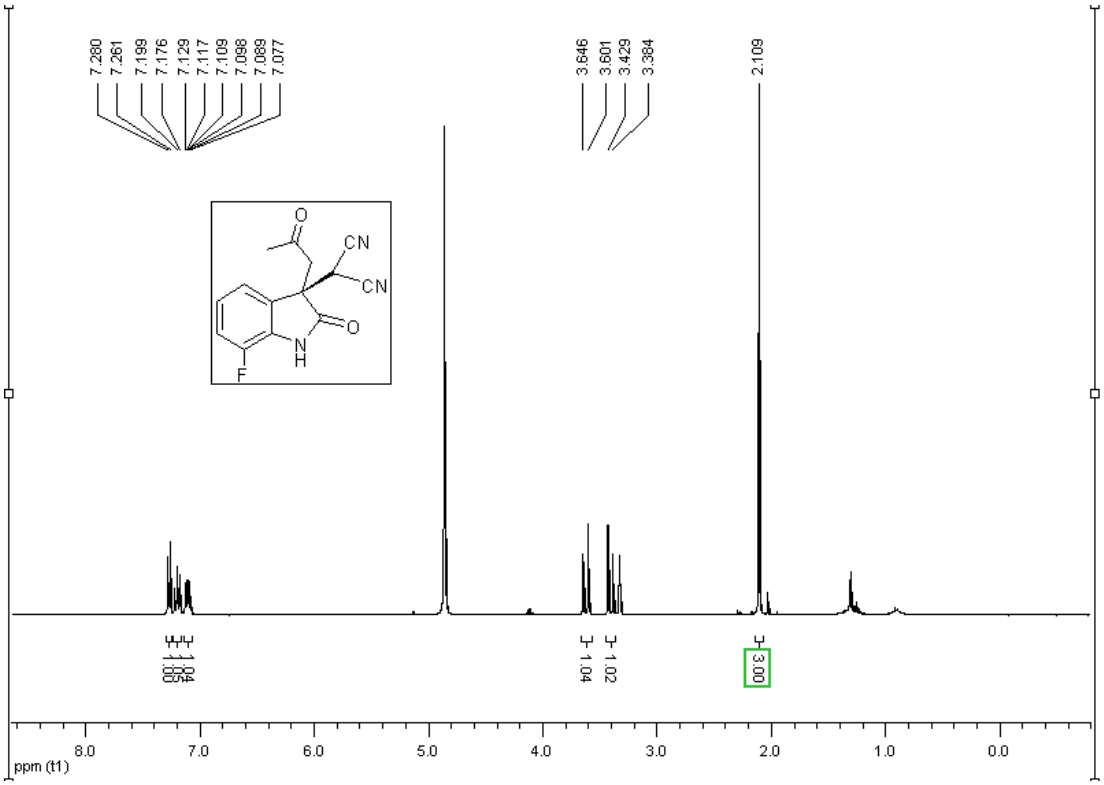
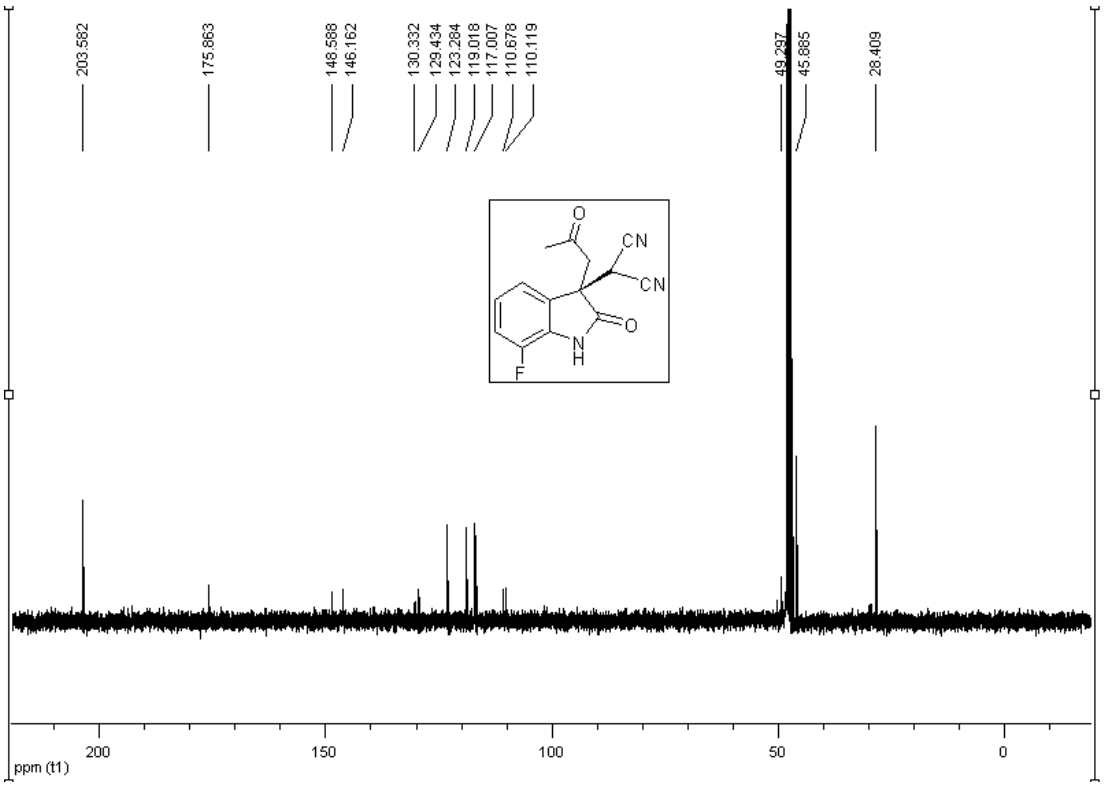
O
CN
Br
CN
O
N
H
200
150
100
50
0
ppm (t1)

3o


7.280
7.261
7.199
7.176
7.129
7.117
7.109
7.098
7.089
7.077
3.646
3.601
3.429
3.384
2.109
O
CN
CN
O
N
H
F
1.00
1.04
1.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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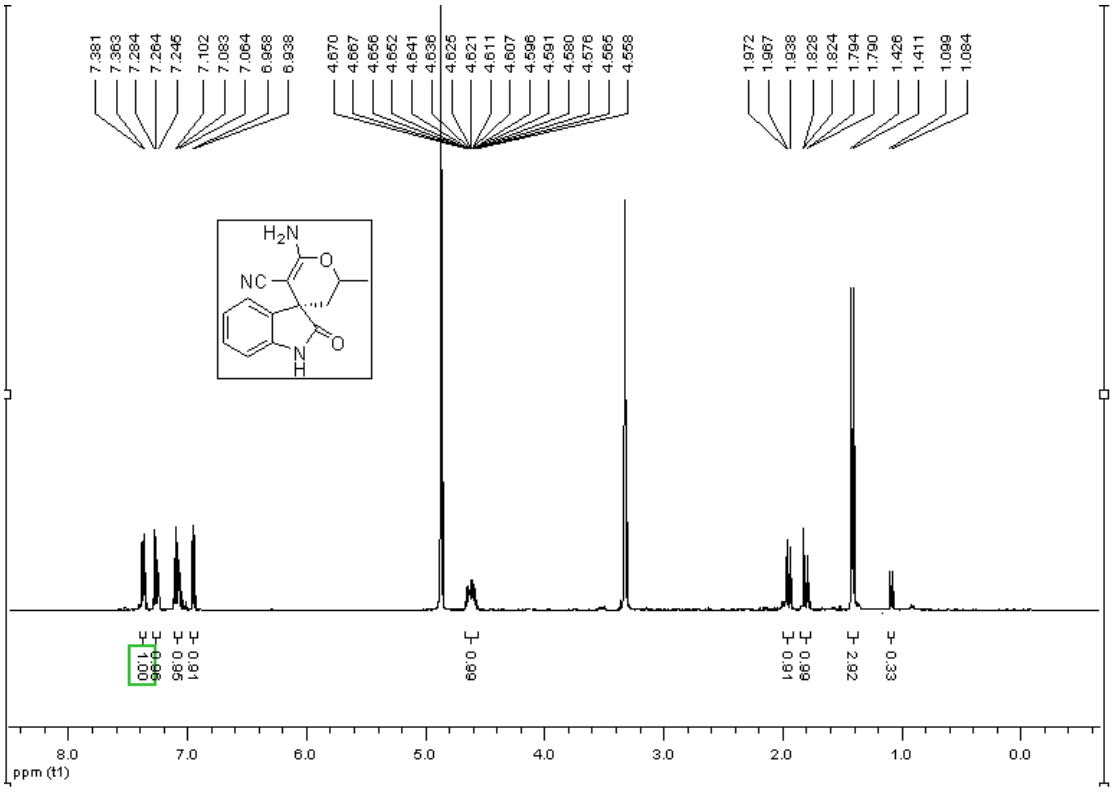
175.863
148.588
146.162
130.332
129.434
123.284
119.018
117.007
110.678
110.119
49.297
45.885
28.409
O
CN
CN
O
N
H
F
200
150
100
50
0
ppm (t1)

7


7.381
7.363
7.284
7.264
7.245
7.102
7.083
7.064
6.958
6.938
4.670
4.667
4.656
4.652
4.641
4.636
4.625
4.621
4.611
4.607
4.596
4.591
4.580
4.576
4.565
4.558
1.972
1.967
1.938
1.828
1.824
1.794
1.790
1.426
1.411
1.099
1.084
H2N
O
NC
O
N
H
1.00
0.96
0.91
0.99
0.91
0.99
2.92
0.33
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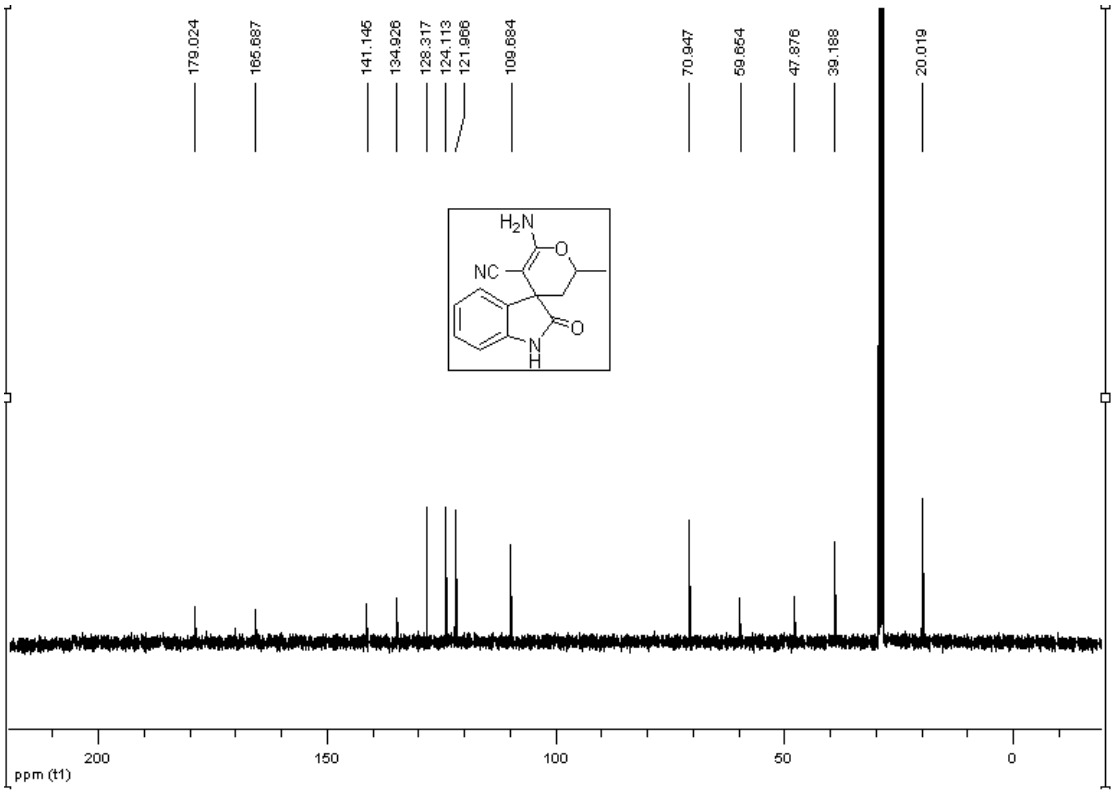
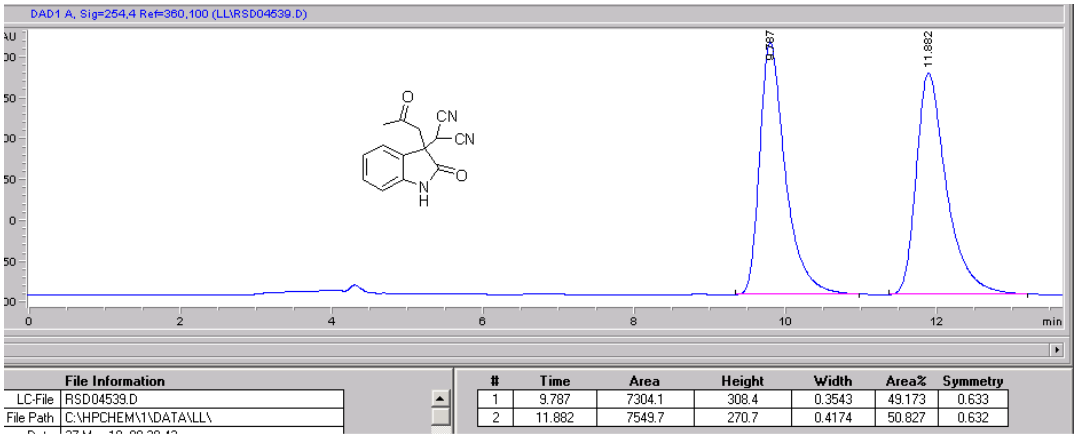
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

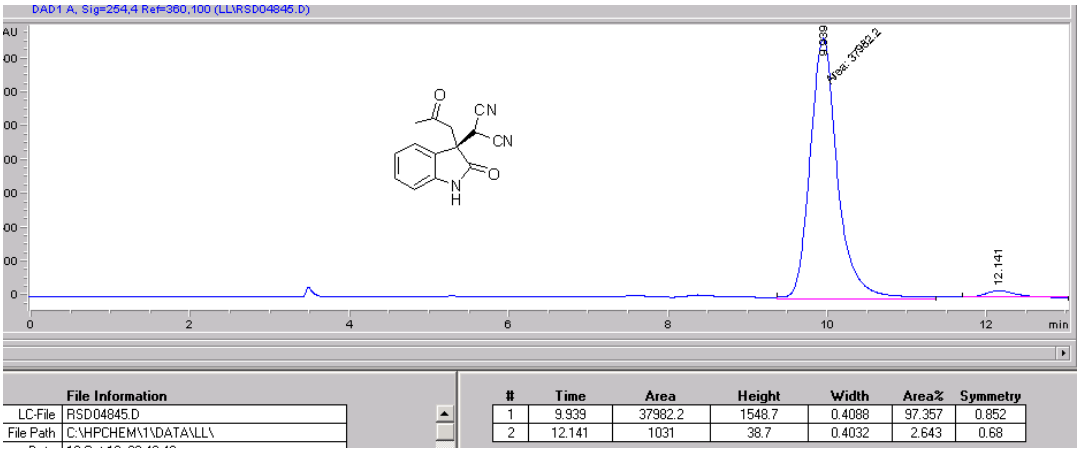

179.024
165.687
141.145
134.926
128.317
124.113
121.966
109.684
70.947
59.654
47.876
39.188
20.019
H2N
O
NC
O
N
H
200
150
100
50
0
ppm (t1)

3a



File Information	
LC-File	RSD04539.D
File Path	C:\HPCHEM\1\DATA\LL\

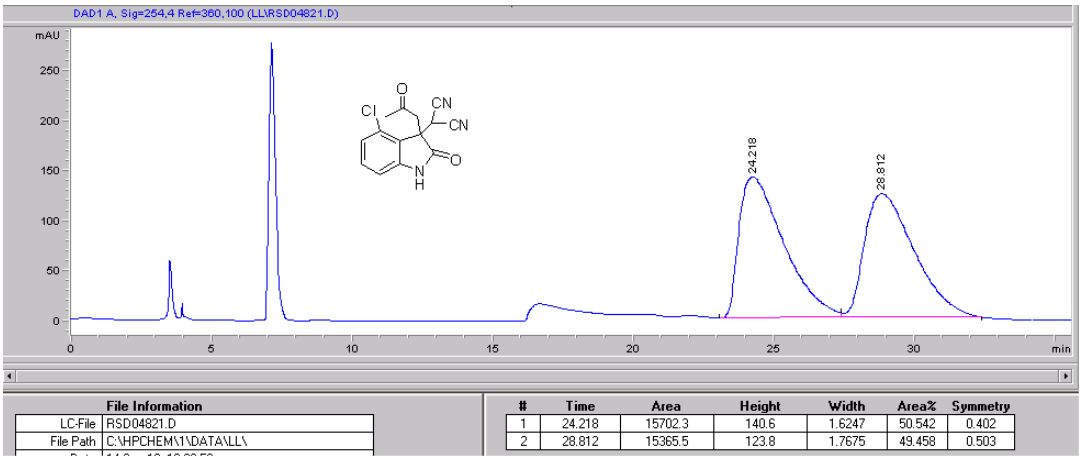
#	Time	Area	Height	Width	Area%	Symmetry
1	9.787	7304.1	308.4	0.3543	49.173	0.633
2	11.882	7549.7	270.7	0.4174	50.827	0.632



File Information	
LC-File	RSD04845.D
File Path	C:\HPCHEM\1\DATA\LL\

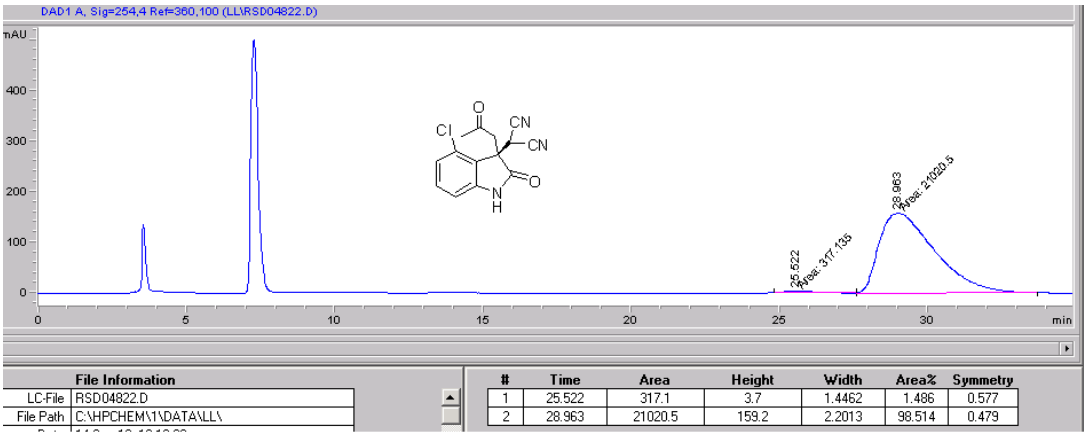
#	Time	Area	Height	Width	Area%	Symmetry
1	9.939	37982.2	1548.7	0.4088	97.357	0.852
2	12.141	1031	38.7	0.4032	2.643	0.68

3b



File Information	
LC-File	RSD04821.D
File Path	C:\HPCHEM\1\DATA\LL\

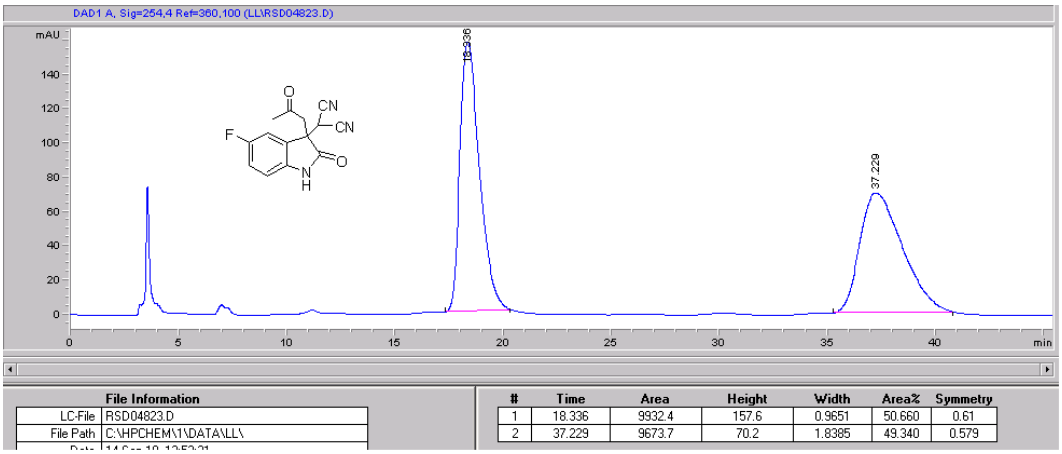
#	Time	Area	Height	Width	Area%	Symmetry
1	24.218	15702.3	140.6	1.6247	50.542	0.402
2	28.812	15365.5	123.8	1.7675	49.458	0.503



File Information	
LC-File	RSD04822.D
File Path	C:\HPCHEM\1\DATA\LL\

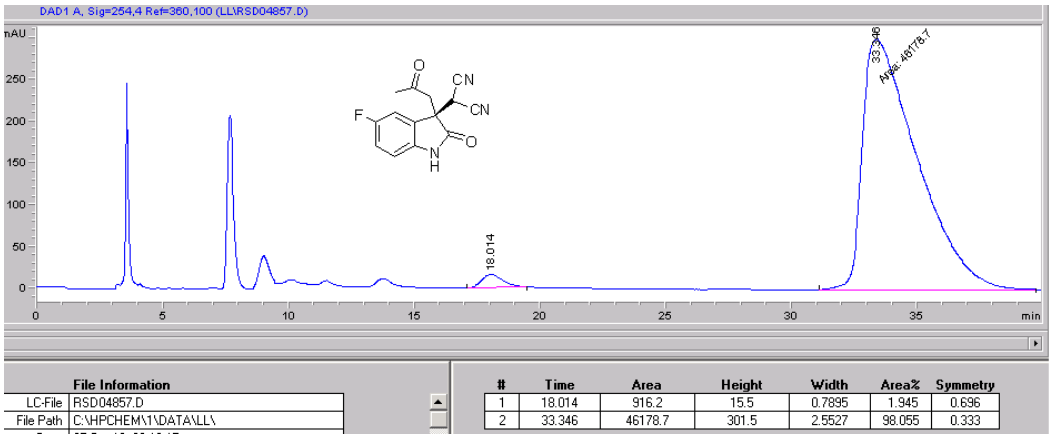
#	Time	Area	Height	Width	Area%	Symmetry
1	25.522	317.1	3.7	1.4462	1.486	0.577
2	28.963	21020.5	159.2	2.2013	98.514	0.479

3c



File Information	
LC-File	RSD04823.D
File Path	C:\HPCHEM\1\DATA\LL\

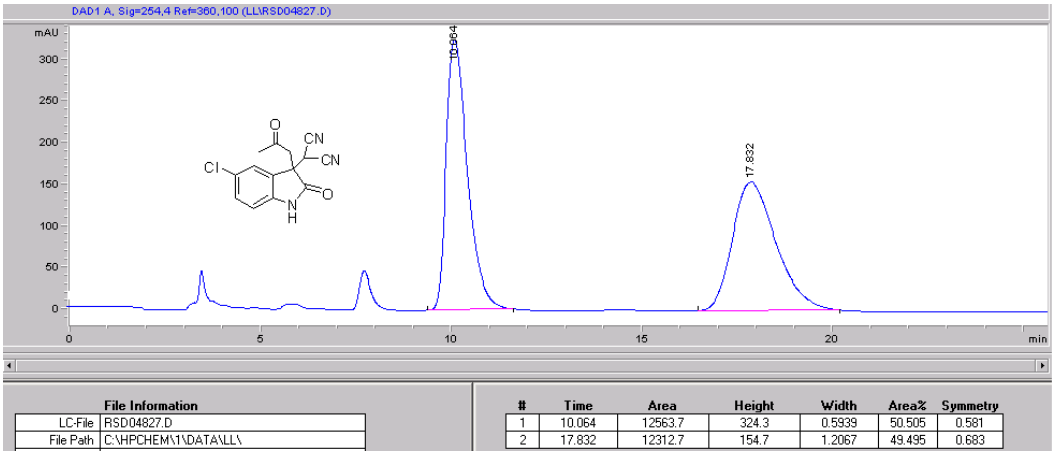
#	Time	Area	Height	Width	Area%	Symmetry
1	18.336	9932.4	157.6	0.9651	50.660	0.61
2	37.229	9673.7	70.2	1.8385	49.340	0.579



File Information	
LC-File	RSD04857.D
File Path	C:\HPCHEM\1\DATA\LL\

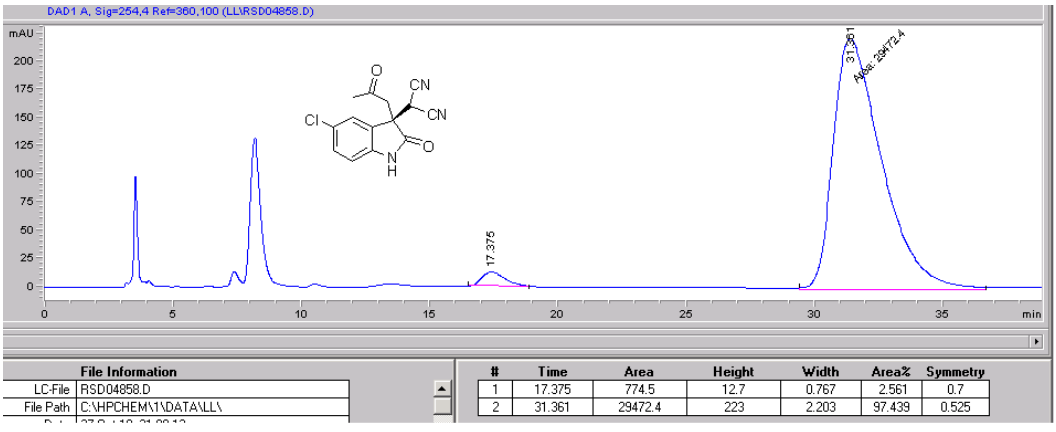
#	Time	Area	Height	Width	Area%	Symmetry
1	18.014	916.2	15.5	0.7895	1.945	0.696
2	33.346	46178.7	301.5	2.5527	98.055	0.333

3d



File Information	
LC-File	RSD04827.D
File Path	C:\HPCHEM\1\DATA\LL\

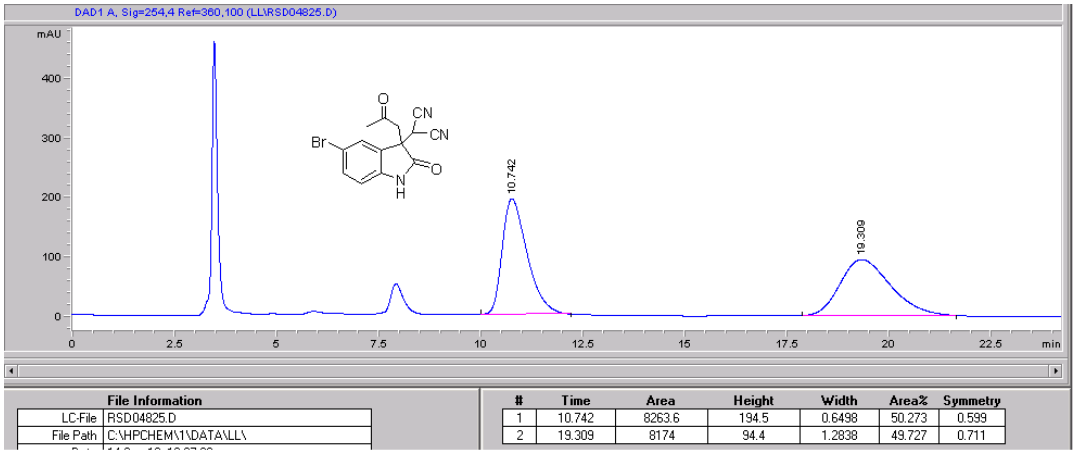
#	Time	Area	Height	Width	Area%	Symmetry
1	10.064	12563.7	324.3	0.5939	50.505	0.581
2	17.832	12312.7	154.7	1.2067	49.495	0.683



File Information	
LC-File	RSD04858.D
File Path	C:\HPCHEM\1\DATA\LL\

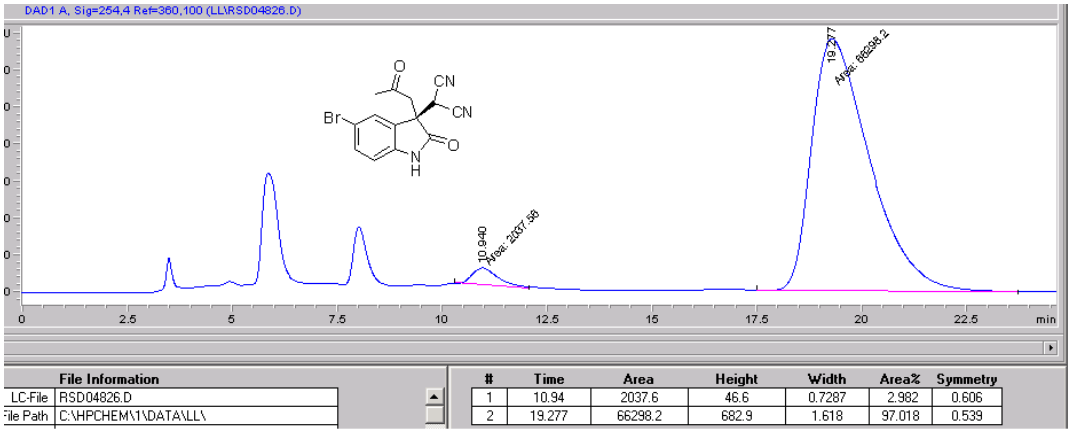
#	Time	Area	Height	Width	Area%	Symmetry
1	17.375	774.5	12.7	0.767	2.561	0.7
2	31.361	29472.4	223	2.203	97.439	0.525

3e



File Information	
LC-File	RSD04825.D
File Path	C:\HPCHEM\1\DATA\LL\

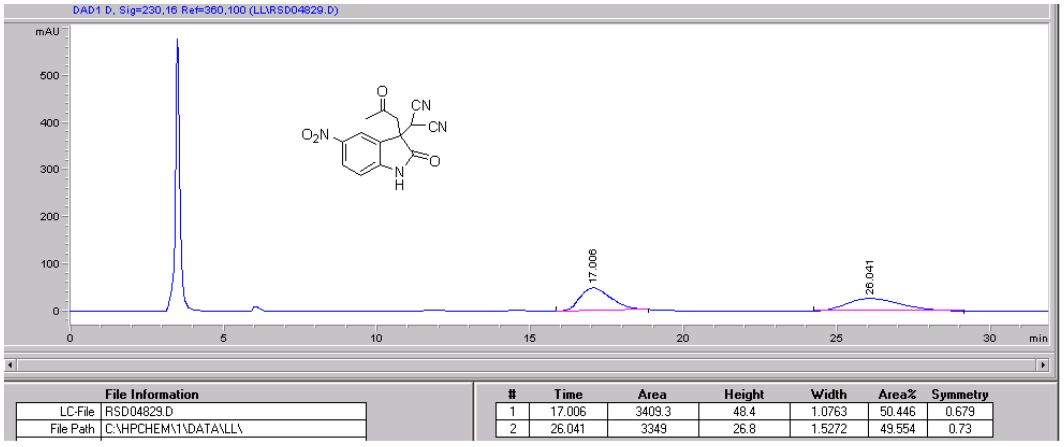
#	Time	Area	Height	Width	Area%	Symmetry
1	10.742	8263.6	194.5	0.6498	50.273	0.599
2	19.309	8174	94.4	1.2838	49.727	0.711



File Information	
LC-File	RSD04826.D
File Path	C:\HPCHEM\1\DATA\LL\

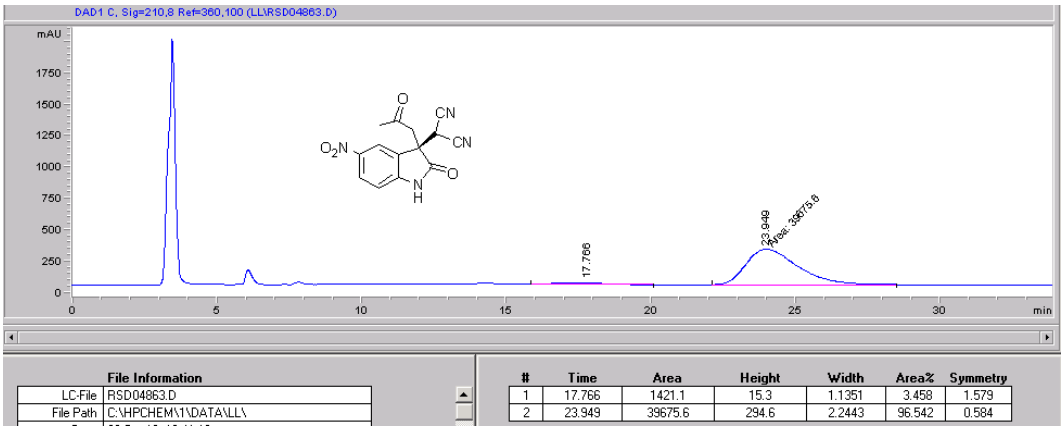
#	Time	Area	Height	Width	Area%	Symmetry
1	10.94	2037.6	46.6	0.7287	2.982	0.606
2	19.277	66298.2	682.9	1.618	97.018	0.539

3f



File Information	
LC-File	RSD04829.D
File Path	C:\HPCHEM\1\DATA\LL\

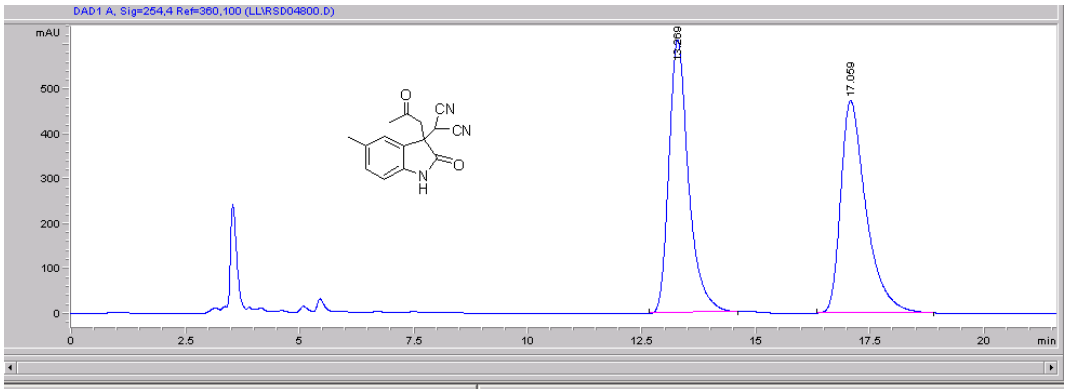
#	Time	Area	Height	Width	Area%	Symmetry
1	17.006	3409.3	48.4	1.0763	50.446	0.679
2	26.041	3349	26.8	1.5272	49.554	0.73



File Information	
LC-File	RSD04863.D
File Path	C:\HPCHEM\1\DATA\LL\

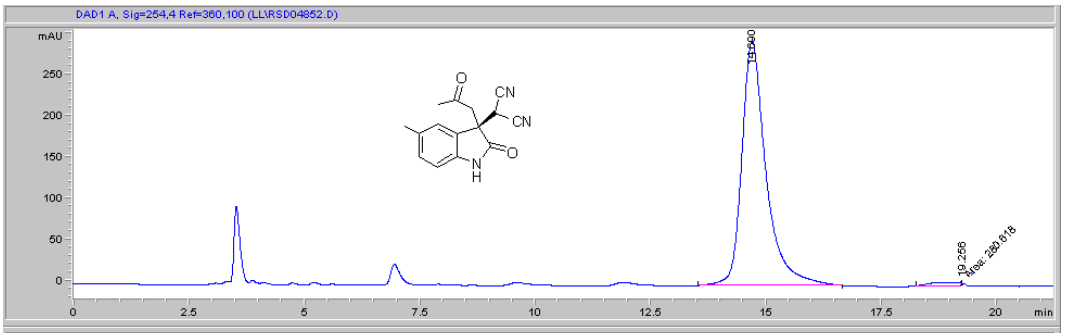
#	Time	Area	Height	Width	Area%	Symmetry
1	17.766	1421.1	15.3	1.1351	3.458	1.579
2	23.949	39675.6	294.6	2.2443	96.542	0.584

3g



File Information	
LC-File	RSD04800.D
File Path	C:\HPCHEM\1\DATA\LL\

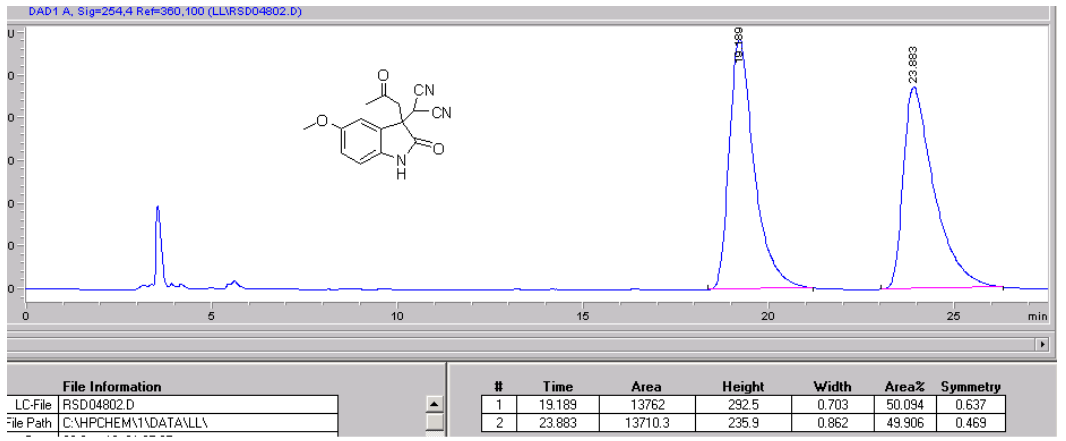
#	Time	Area	Height	Width	Area%	Symmetry
1	13.269	18243.7	609.6	0.4512	49.739	0.733
2	17.059	18435.2	474.6	0.5812	50.261	0.588



File Information	
LC-File	RSD04801.D
File Path	C:\HPCHEM\1\DATA\LL\

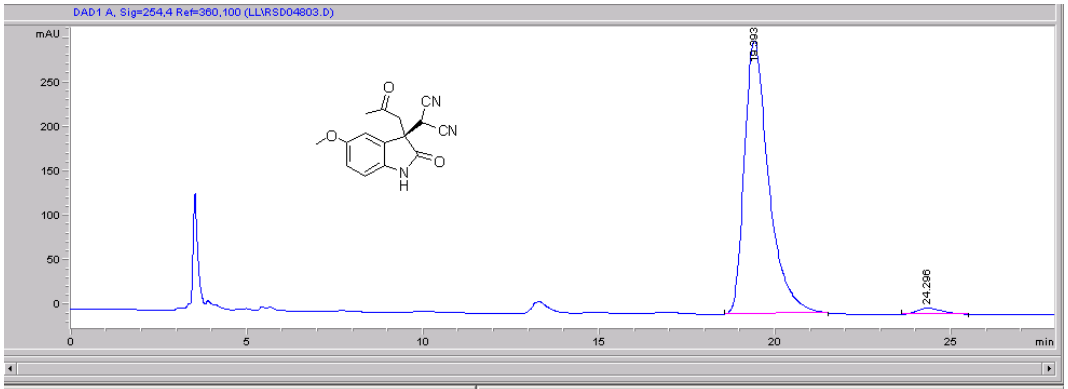
#	Time	Area	Height	Width	Area%	Symmetry
1	14.69	10944.1	296.4	0.5468	97.500	0.675
2	19.256	280.6	7.1	0.6594	2.500	0.785

3h



File Information	
LC-File	RSD04802.D
File Path	C:\HPCHEM\1\DATA\LL\

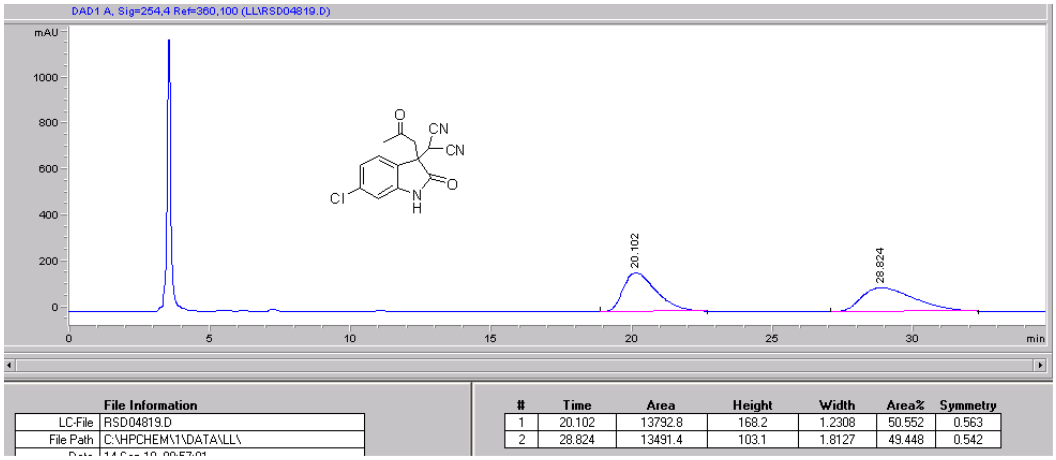
#	Time	Area	Height	Width	Area%	Symmetry
1	19.189	13762	292.5	0.703	50.094	0.637
2	23.883	13710.3	235.9	0.862	49.906	0.469



File Information	
LC-File	RSD04803.D
File Path	C:\HPCHEM\1\DATA\LL\

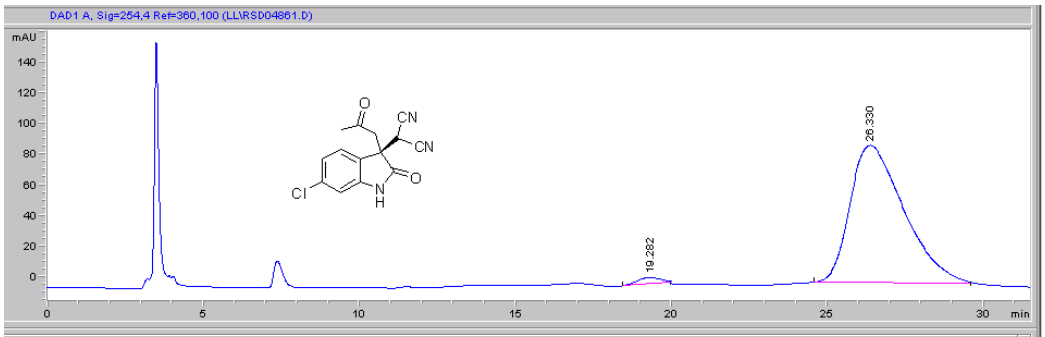
#	Time	Area	Height	Width	Area%	Symmetry
1	19.393	14831.1	307.1	0.7234	97.593	0.636
2	24.296	365.8	7	0.7021	2.407	0.653

3i



File Information	
LC-File	RSD04819.D
File Path	C:\HPCHEM\1\DATA\LL\

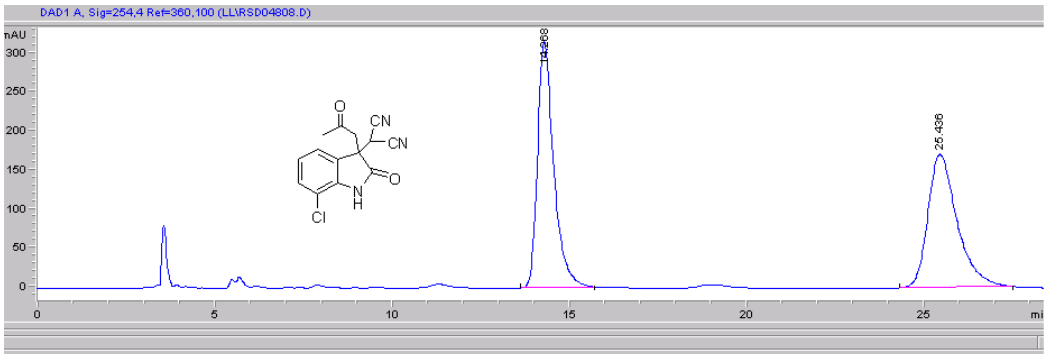
#	Time	Area	Height	Width	Area%	Symmetry
1	20.102	13792.8	168.2	1.2308	50.552	0.563
2	28.824	13491.4	103.1	1.8127	49.448	0.542



File Information	
LC-File	RSD04861.D
File Path	C:\HPCHEM\1\DATA\LL\

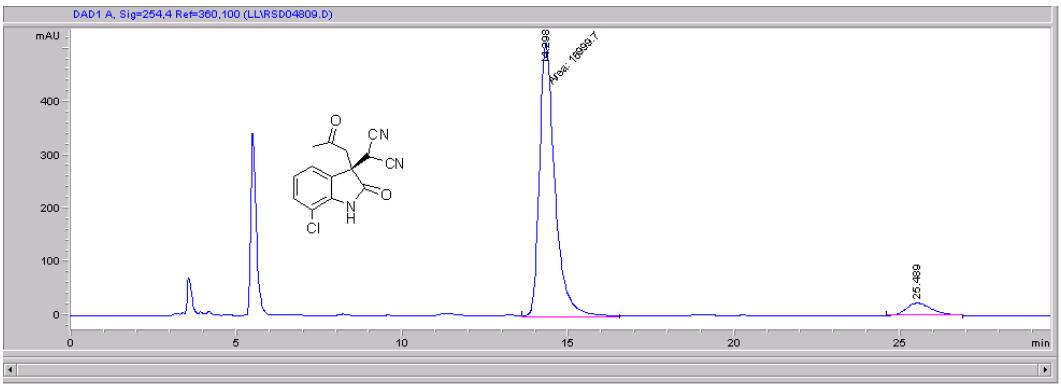
#	Time	Area	Height	Width	Area%	Symmetry
1	19.282	220.1	4.1	0.6344	2.003	1.168
2	26.33	10766.4	89.8	1.7494	97.997	0.56

3j



File Information	
LC-File	RSD04808.D
File Path	C:\HPCHEM\1\DATA\LL\

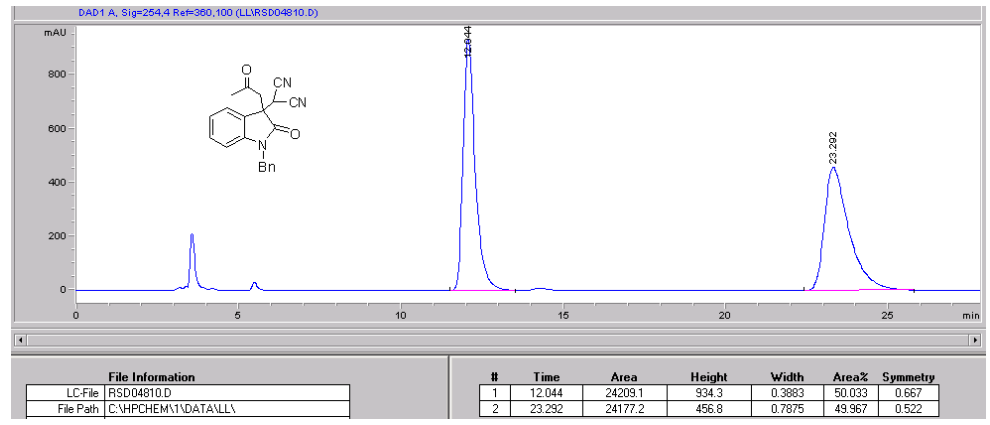
#	Time	Area	Height	Width	Area%	Symmetry
1	14.268	10084.3	317.3	0.4747	50.634	0.647
2	25.436	9831.7	171.3	0.8597	49.366	0.656



File Information	
LC-File	RSD04809.D
File Path	C:\HPCHEM\1\DATA\LL\

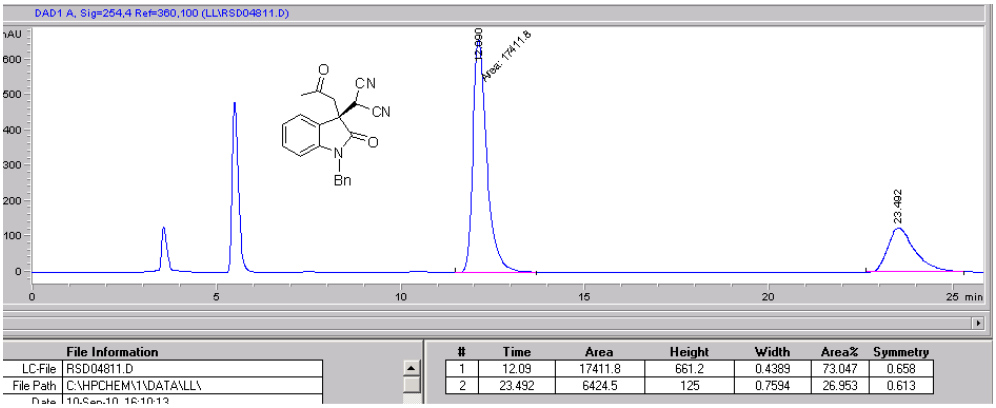
#	Time	Area	Height	Width	Area%	Symmetry
1	14.298	16999.7	515.3	0.5499	93.001	0.654
2	25.489	1279.4	23.6	0.7933	6.999	0.724

3k



File Information	
LC-File	RSD04810.D
File Path	C:\HPCHEM\1\DATA\LL\

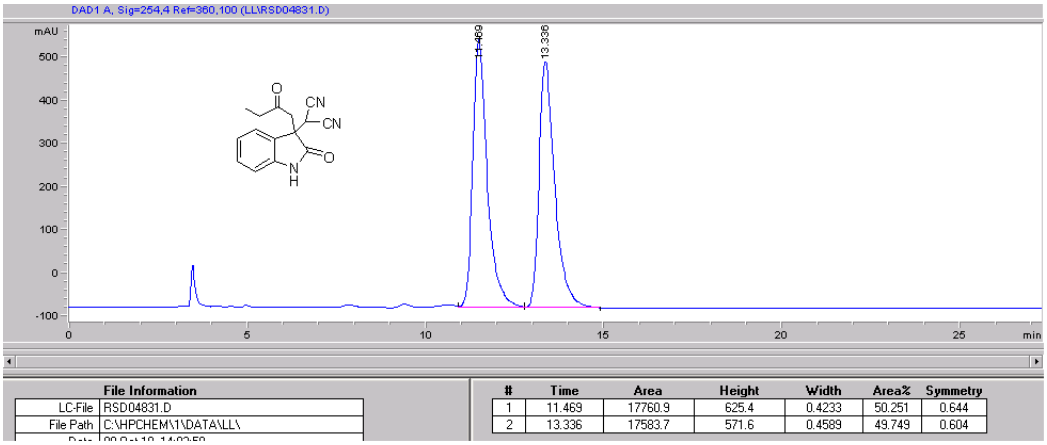
#	Time	Area	Height	Width	Area%	Symmetry
1	12.044	24209.1	934.3	0.3883	50.033	0.667
2	23.292	24177.2	456.8	0.7875	49.967	0.522



File Information	
LC-File	RSD04811.D
File Path	C:\HPCHEM\1\DATA\LL\

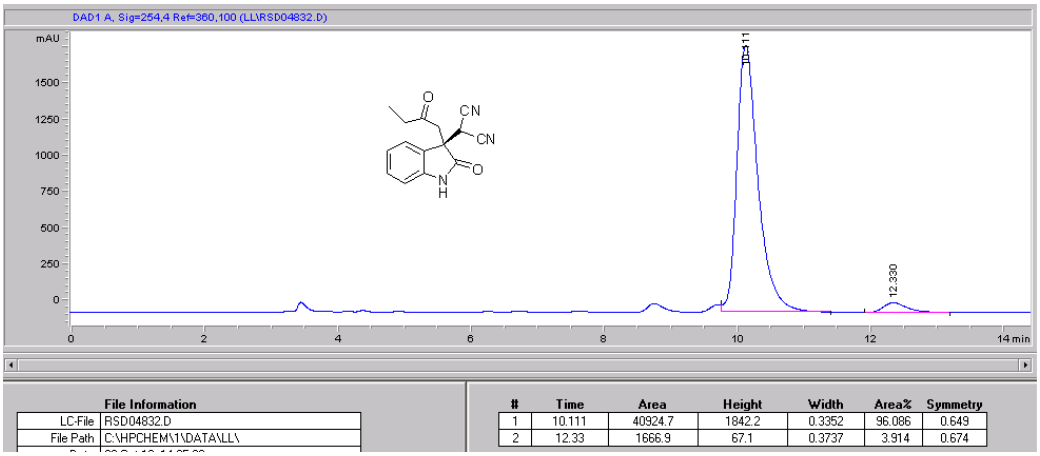
#	Time	Area	Height	Width	Area%	Symmetry
1	12.09	17411.8	661.2	0.4389	73.047	0.658
2	23.492	6424.5	125	0.7594	26.953	0.613

3l



File Information	
LC-File	RSD04831.D
File Path	C:\HPCHEM\1\DATA\LL\

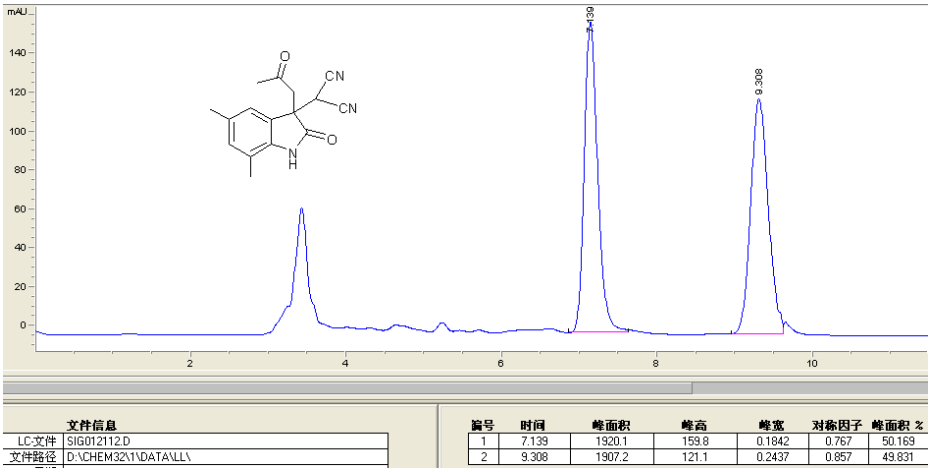
#	Time	Area	Height	Width	Area%	Symmetry
1	11.469	17760.9	625.4	0.4233	50.251	0.644
2	13.336	17583.7	571.6	0.4589	49.749	0.604



File Information	
LC-File	RSD04832.D
File Path	C:\HPCHEM\1\DATA\LL\

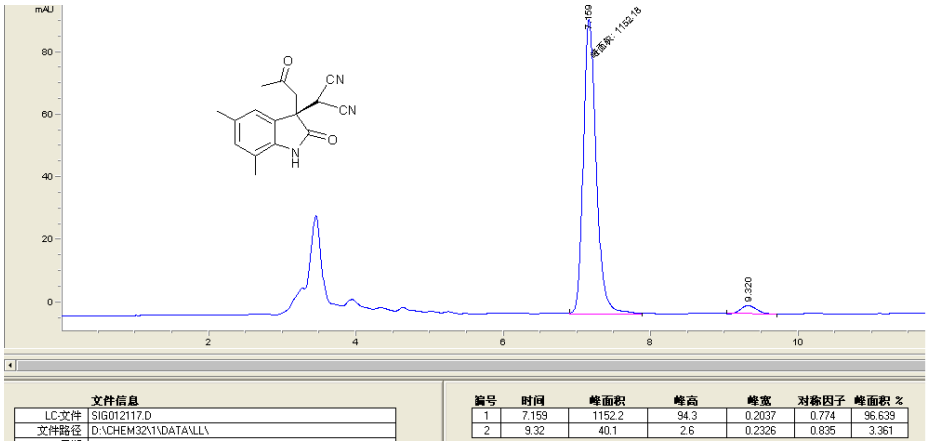
#	Time	Area	Height	Width	Area%	Symmetry
1	10.111	40924.7	1842.2	0.3352	96.086	0.649
2	12.33	1666.9	67.1	0.3737	3.914	0.674

3m



文件信息	
LC文件	SIG012112.D
文件路径	D:\CHEM32\1\DATA\LL\

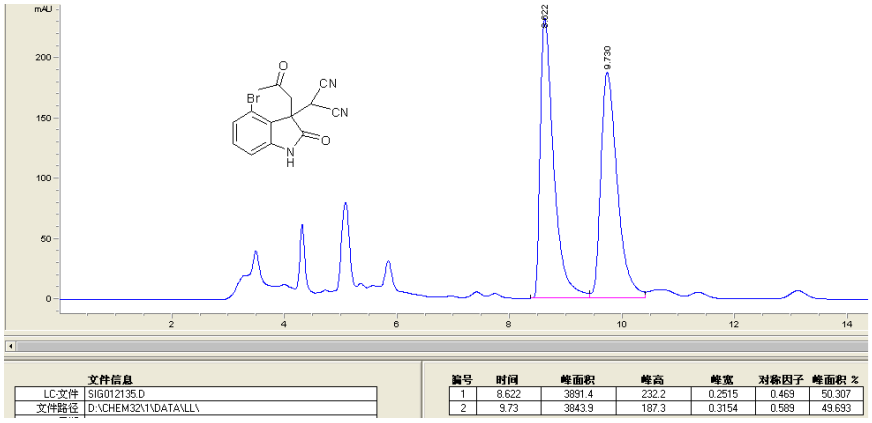
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	7.139	1920.1	159.8	0.1842	0.767	50.169
2	9.308	1907.2	121.1	0.2437	0.857	49.831



文件信息	
LC文件	SIG012117.D
文件路径	D:\CHEM32\1\DATA\LL\

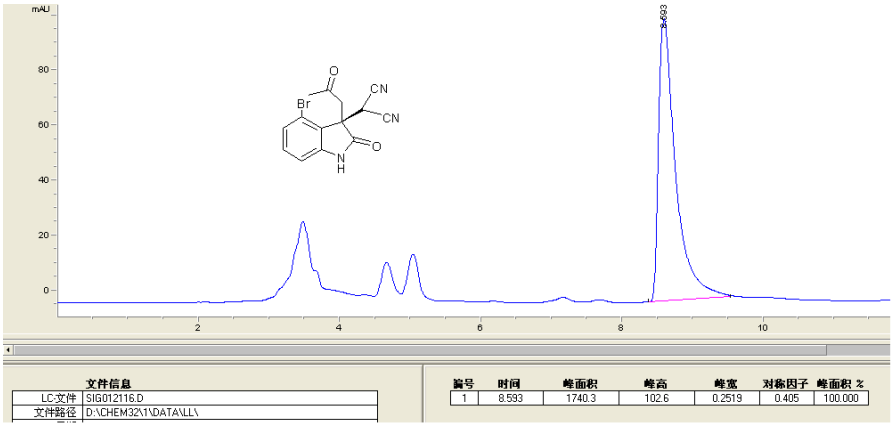
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	7.159	1152.2	94.3	0.2037	0.774	96.639
2	9.32	40.1	2.6	0.2326	0.835	3.361

3n



文件信息	
LC文件	SIG012135.D
文件路径	D:\CHEM32\1\DATA\LL\

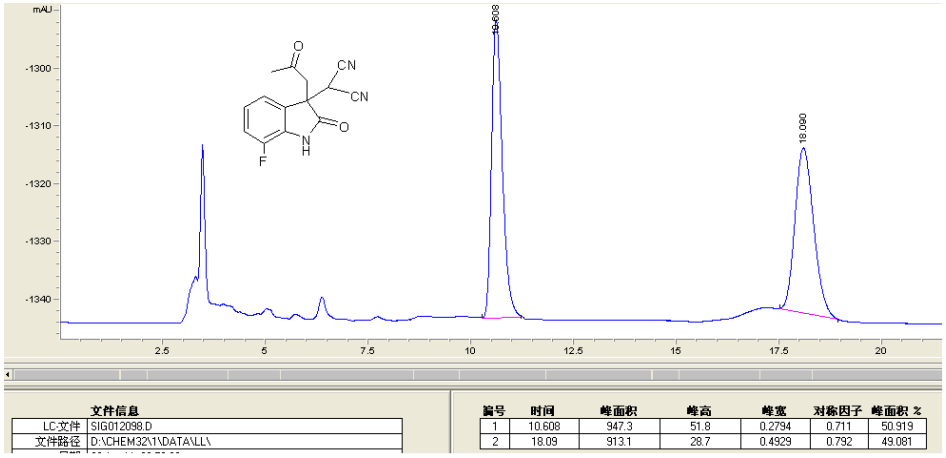
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	8.622	3891.4	232.2	0.2515	0.469	50.307
2	9.73	3843.9	187.3	0.3154	0.589	49.693



文件信息	
LC文件	SIG012116.D
文件路径	D:\CHEM32\1\DATA\LL\

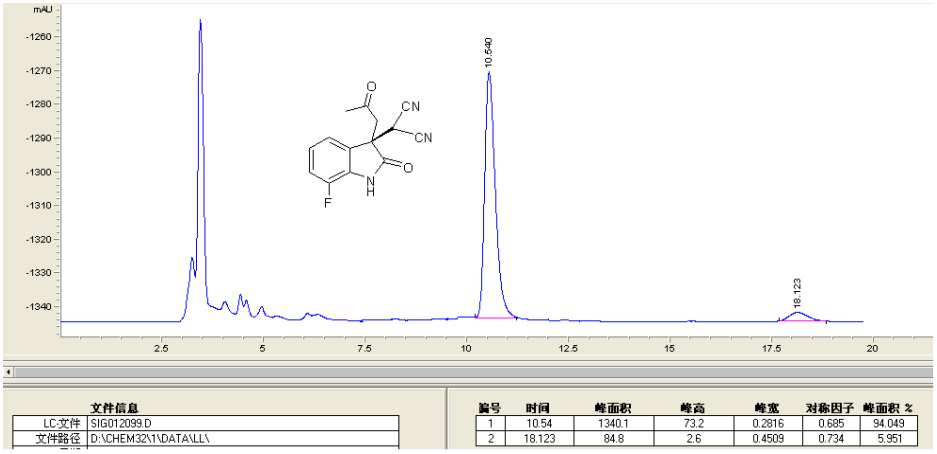
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	8.593	1740.3	102.6	0.2519	0.405	100.000

3o



文件信息	
LC-文件	SIG012098.D
文件路径	D:\CHEM32\1\DATA\LL\

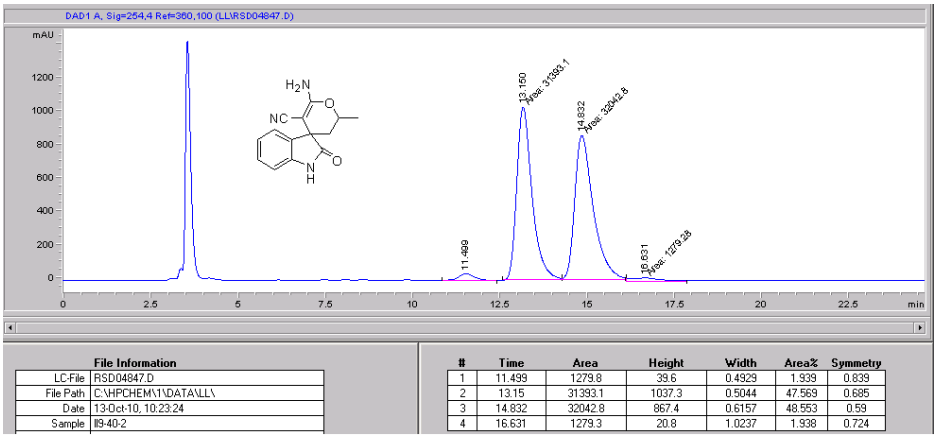
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	10.608	947.3	51.8	0.2794	0.711	50.919
2	18.09	913.1	28.7	0.4929	0.792	49.081



文件信息	
LC-文件	SIG012099.D
文件路径	D:\CHEM32\1\DATA\LL\

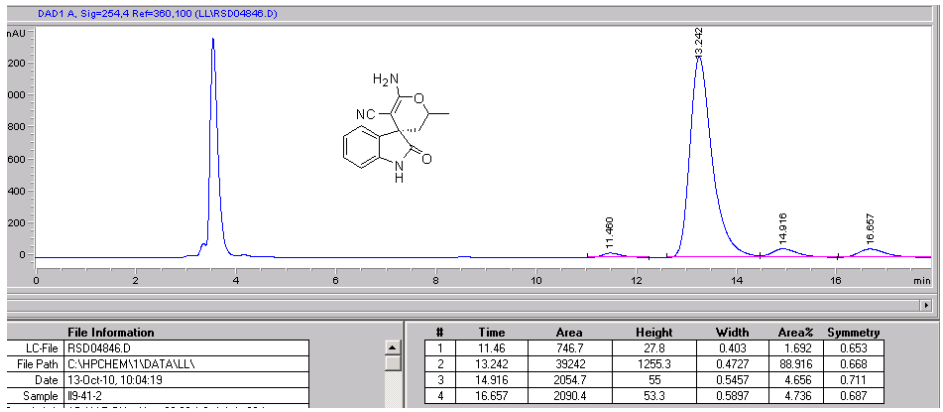
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	10.54	1340.1	73.2	0.2816	0.685	94.049
2	18.123	84.8	2.6	0.4509	0.734	5.951

7



File Information	
LC-File	RSD04847.D
File Path	C:\HPCHEM\1\DATA\LL\
Date	13-Oct-10, 10:23:24
Sample	II9-40-2

#	Time	Area	Height	Width	Area%	Symmetry
1	11.499	1279.8	39.6	0.4929	1.939	0.839
2	13.15	31393.1	1037.3	0.5044	47.569	0.685
3	14.832	32042.8	867.4	0.6157	48.553	0.59
4	16.631	1279.3	20.8	1.0237	1.938	0.724



File Information	
LC-File	RSD04846.D
File Path	C:\HPCHEM\1\DATA\LL\
Date	13-Oct-10, 10:04:19
Sample	II9-41-2

#	Time	Area	Height	Width	Area%	Symmetry
1	11.46	746.7	27.8	0.403	1.692	0.653
2	13.242	39242	1255.3	0.4727	88.916	0.668
3	14.916	2054.7	55	0.5457	4.656	0.711
4	16.657	2090.4	53.3	0.5897	4.736	0.687