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Formal [3+3] Annulation of Isatin-derived 2-Bromoenals with 1, 3-Dicarbonyl Compounds Enabled by Lewis Acid/N-Heterocyclic Carbene Cooperative Catalysis

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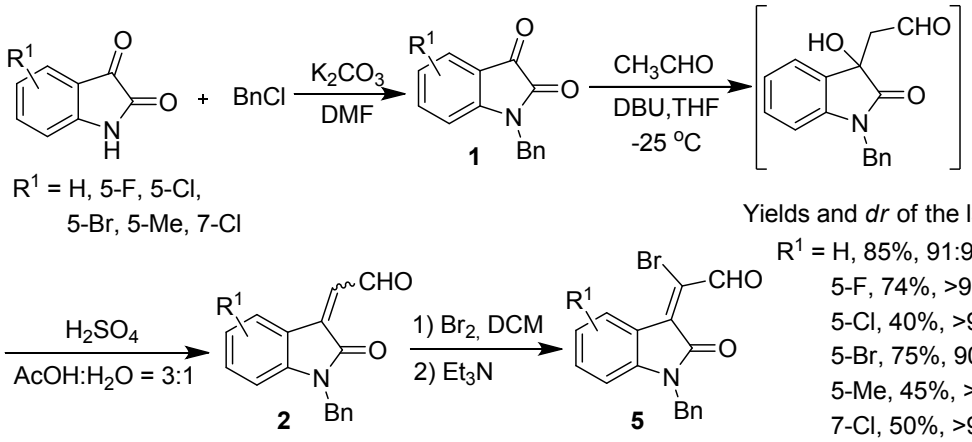
General Methods and Materials. All reactions were carried out under an atmosphere of nitrogen in dry glassware, and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200~300 mesh). All NMR spectra were recorded on Bruker spectrometers, running at 300 MHz or 500 MHz for ^{1}H and 75 MHz for ^{13}C respectively. Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hz respectively. The solvent signals were used as references (residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm, δ_c = 77.0 ppm; residual DMSO in DMSO-d_6: δ_H = 2.50 ppm, δ_c = 39.5 ppm). The following abbreviations are used to indicate the multiplicity in NMR spectra: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). High resolution mass spectrometry (HRMS) was recorded on TOF perimer for ES^+. The e.e. value was determined via chiral HPLC analysis (Diacel Chiral pack IB, methanol/H_2O = 85/15).

General procedure for the synthesis of isatin-derived 2-bromoenals 5



Isatin-derived enals **2** are prepared according to a known procedure starting from substituted isatins.[1] Isatin-derived 2-bromoenals **5** are synthesized by one-pot sequential addition of Br_2 to compounds **2** and elimination with a base.

General procedure for the synthesis of 5 from 2: To the solution of compounds **2** (263 mg, 1.0 mmol) in CH_2Cl_2 (3-4 mL) was added Br_2 (62 μL, 1.2 mmol). The resulting mixture was stirred at 5-10 °C for 15 mins followed by addition of Et_3N (235 μL, 1.7 mmol). The mixture was further stirred at 5-10 °C until the completion of the reaction as monitored by TLC. Then saturated sodium carbonate aqueous solution (20

mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3x10 mL). The organic phase was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by chromatography on silica gel using hexane/EtOAc (3:1) as the eluent to afford products **5** as red solids.

(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-2-bromoacetaldehyde **(5a)**. Red solid, mp: 188-189 °C. *E/Z* = 91:9. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.92 (s, 1H), 8.64 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.30-7.33 (m, 6H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.93 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.1, 165.0, 162.3, 145.0, 134.9, 134.8, 133.4, 128.9, 127.9, 127.7, 127.2, 122.8, 121.7, 109.7, 43.8. HRMS (ESI) calcd for $C_{17}H_{13}BrNO_2$ $(M+H)^+$: 342.0124, found 342.0129.

(*E*)-2-(1-Benzyl-5-fluoro-2-oxoindolin-3-ylidene)-2-bromoacetaldehyde (**5b**). Red solid, mp: 175-177 °C. *E/Z* = >95:5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.94 (s, 1H), 8.27 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.31-7.35 (m, 5H), 7.05-7.11 (m, 1H), 6.66 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.93 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 164.8, 158.6 (d, *J* = 241.1Hz, 1C), 141.1 (d, *J* = 1.9 Hz, 1C), 137.6 (d, *J* = 3.4 Hz, 1C), 136.1, 134.6, 129.0, 128.1, 127.2, 122.6 (d, *J* = 9.0 Hz, 1C), 119.7 (d, *J* = 24.1 Hz, 1C), 115.1 (d, *J* = 27.2 Hz, 1C), 110.2 (d, *J* = 7.9 Hz, 1C), 44.0. HRMS (ESI) calcd for $C_{17}H_{12}BrFNO_2$ $(M+H)^+$: 360.0030, found 360.0032.

(*E*)-2-(1-Benzyl-5-chloro-2-oxoindolin-3-ylidene)-2-bromoacetaldehyde (**5c**). Red solid, mp: 202-204 °C. *E/Z* = >95:5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.92 (s, 1H), 8.51 (s, 1H), 7.30-7.33 (m, 6H), 6.66 (d, *J* = 8.1 Hz, 1H), 4.93 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 164.7, 143.3, 137.1, 136.3, 134.5, 132.9, 129.0, 128.4, 128.1, 127.4, 127.2, 122.9, 110.6, 44.0. HRMS (ESI) calcd for $C_{17}H_{12}BrClNO_2$ $(M+H)^+$: 375.9734, found 375.9734.

(*E*)-2-(1-Benzyl-5-bromo-2-oxoindolin-3-ylidene)-2-bromoacetaldehyde (**5d**). Red solid, mp: 213-215 °C. *E/Z* = 90:10. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.92 (s, 1H), 8.64 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.30-7.33 (m, 5H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.93 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 164.6, 143.8, 137.0, 136.3, 135.8,

134.5, 130.2, 129.1, 128.2, 127.2, 123.3, 115.5, 111.1, 44.0. HRMS (ESI) calcd for $C_{17}H_{12}Br_2NO_2$ $(M+H)^+$: 419.9229, found 419.9232.

(*E*)-2-(1-Benzyl-5-methyl-2-oxoindolin-3-ylidene)-2-bromoacetaldehyde (**5e**). Red solid, mp: 178-180 °C. *E/Z* = >95:5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.96 (s, 1H), 8.33 (s, 1H), 7.31-7.36 (m, 5H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.91 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.2, 165.1, 142.9, 138.4, 135.0, 134.4, 133.9, 132.4, 128.9, 128.3, 127.9, 127.2, 121.7, 109.5, 43.8, 21.2. HRMS (ESI) calcd for $C_{18}H_{15}BrNO_2$ $(M+H)^+$: 356.0281, found 356.0267.

(*E*)-2-(1-Benzyl-7-chloro-2-oxoindolin-3-ylidene)-2-bromoacetaldehyde (**5f**). Red solid, mp: 166-168 °C. *E/Z* = > 95:5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.90 (s, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 7.29-7.37 (m, 6H), 7.04-7.09 (m, 1H), 5.42 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.1, 165.7, 140.7, 136.53, 136.46, 136.1, 135.7, 128.7, 127.5, 126.4, 126.1, 124.3, 123.5, 116.1, 45.2. HRMS (ESI) calcd for $C_{17}H_{12}BrClNO_2$ $(M+H)^+$: 375.9734, found 375.9734.

General procedure for the synthesis of products 7

To an oven-dried 15 mL glass cylindrical pressure vessel was charged with 2-bromoenals **5** (0.2 mmol), 1,3-dicarbonyl compounds **6** (0.4 mmol), carbene precursor **F** (8 mg, 0.03 mmol), Cs_2CO_3 (98 mg, 0.3 mmol), LiCl (9.0 mg, 0.22 mmol) and 200 mg of 4 Å MS under N_2 atmosphere. Then anhydrous 1,4-dioxane (3 mL) was added and the vessel was immediately sealed tightly. The resulting mixture was stirred at 50 ^{o}C for 2 h. The mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel to using hexane/EtOAc (5:1) as the eluent afford products **7**.

Ethyl 1-benzyl-6'-methyl-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carboxylate (**7a**). White solid, mp: 126-128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.35 (m, 5H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.04 and 4.82 (d×2, *J* = 15.6 Hz, 2H), 3.81-4.02 (m, 2H), 3.11 (d, *J* = 15.6 Hz, 1H), 2.67 (d, *J* = 15.5 Hz, 1H), 2.47 (s, 3H), 0.88 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.6, 164.5, 164.2, 163.0, 142.1, 135.4, 130.4,

129.1, 128.8, 127.8, 127.4, 123.1, 122.3, 109.6, 108.6, 60.9, 48.9, 44.2, 38.0, 19.0, 13.5. HRMS (ESI) calcd for $C_{23}H_{22}NO_5$ $(M+H)^+$: 392.1492, found 392.1488.

Ethyl 1-benzyl-2,2'-dioxo-6'-phenyl-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carboxylate (**7b**). White solid, mp: 187-189 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.53 (m, 2H), 7.29-7.46 (m, 8H), 7.20-7.24 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.93-5.04 (m, 2H), 3.69-3.88 (m, 2H), 3.29 (d, J = 15.8 Hz, 1H), 2.85 (d, J = 15.8 Hz, 1H), 0.70 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1, 164.7, 164.2, 162.3, 160.5, 142.3, 135.4, 132.7, 130.4, 129.8, 129.4, 128.8, 128.7, 128.0, 127.7, 127.3, 123.2, 122.6, 109.9, 60.9, 49.5, 44.3, 38.0, 13.1. HRMS (ESI) calcd for $C_{28}H_{24}NO_5$ $(M+H)^+$: 454.1649, found 454.1659.

Ethyl 1-benzyl-6'-(4-methoxyphenyl)-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carboxylate (**7c**). White solid, mp: 148-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, J = 8.7 Hz, 2H), 7.21-7.41 (m, 7H), 7.04 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.1 Hz, 1H), 5.02 and 4.96 (d×2, J = 15.9 Hz, 2H), 3.75-3.90 (m, 5H), 3.27 (d, J = 15.9 Hz, 1H), 2.85 (d, J = 15.9 Hz, 1H), 0.76 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.3, 165.0, 164.4, 161.4, 160.2, 142.3, 135.4, 130.5, 130.0, 129.4, 128.8, 127.7, 127.4, 124.7, 123.2, 122.6, 113.3, 109.8, 109.0, 60.9, 55.3, 49.6, 44.3, 38.1, 13.3. HRMS (ESI) calcd for $C_{29}H_{26}NO_6$ $(M+H)^+$: 484.1755, found 484.1756.

Methyl 1-benzyl-2,2'-dioxo-6'-phenyl-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carboxylate (**7d**). White solid, mp: 162-163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.53 (m, 2H), 7.29 -7.47 (m, 8H), 7.22 (d, J = 7.5 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 5.05 and 4.92 (d×2, J = 15.7 Hz, 2H), 3.30 (d, J = 15.8 Hz, 1H), 3.25 (s, 3H), 2.84 (d, J = 15.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1, 165.2, 164.1, 162.3, 160.5, 142.2, 135.4, 130.5, 129.8, 129.5, 128.8, 128.6, 128.0, 127.8, 127.4, 123.3, 122.5, 109.9, 51.7, 49.5, 44.4, 37.9. HRMS (ESI) calcd for $C_{27}H_{22}NO_5$ $(M+H)^+$: 440.1492, found 440.1501.

Methyl 1-benzyl-2,2'-dioxo-6'-(p-tolyl)-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-car-

boxylate (**7e**). White solid, mp: 201-202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.42 (m, 7H), 7.20-7.23 (m, 4H), 7.03 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 5.04 and 4.92 (d×2, J = 15.7 Hz, 2H), 3.27-3.31 (m, 4H), 2.82 (d, J = 15.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1, 165.4, 164.2, 160.6, 142.2, 140.9, 135.4, 129.8, 129.5, 129.4, 128.8, 128.7, 128.6, 127.7, 127.4, 123.2, 122.5, 109.9, 109.2, 51.6, 49.5, 44.3, 38.0, 21.5. HRMS (ESI) calcd for $C_{28}H_{24}NO_5$ $(M+H)^+$: 454.1649, found 454.1643.

Methyl 1-benzyl-6'-(4-chlorophenyl)-2,2'-dioxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carboxylate (**7f**). White solid, mp: 190-191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.48 (m, 9H), 7.18-7.24 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 5.04 and 4.91 (d×2, J = 15.7 Hz, 2H), 3.26 (s, 3H), 3.27 (d, J = 15.9 Hz, 1), 2.83 (d, J = 15.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.9, 164.9, 163.8, 159.4, 142.2, 136.7, 135.3, 130.9, 130.1, 129.6, 128.8, 128.4, 127.8, 127.5, 123.3, 122.5, 110.2, 110.0, 51.8, 49.5, 44.4, 37.9. HRMS (ESI) calcd for $C_{27}H_{21}ClNO_5$ $(M+H)^+$: 474.1103, found 474.1097.

5'-Acetyl-1-benzyl-6'-methylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7g**). White solid, mp: 150-151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.40 (m, 5H), 7.20 (m, 1H), 6.96-7.07 (m, 2H), 6.77 (d, J = 7.8 Hz, 1H), 4.96 (s, 2H), 3.11 (d, J = 15.6 Hz, 1H), 2.63 (d, J = 15.6 Hz, 1H), 2.42 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.7, 176.2, 163.8, 159.9, 141.4, 134.9, 129.5, 128.9, 128.4, 127.3, 126.9, 122.8, 121.8, 118.8, 109.6, 49.0, 43.9, 37.98, 30.4, 19.2. HRMS (ESI) calcd for $C_{22}H_{20}NO_4$ $(M+H)^+$: 362.1387, found 362.1387.

5'-Acetyl-1-benzyl-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7h**). White solid, mp: 223-224 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67-7.70 (m, 2H), 7.53 (m, 1H), 7.37-7.42 (m, 2H), 7.28-7.34 (m, 8H), 7.12-7.17 (m, 2H), 6.98 (m, 1H), 6.62 (m, 1H), 4.92 and 4.75 (d×2, J = 15.7 Hz, 2H), 3.16 (d, J = 15.8 Hz, 1H), 2.89 (d, J = 15.8 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 176.2, 164.5, 162.3, 157.7, 142.2, 138.4, 135.2, 133.1, 129.6, 129.2, 128.8, 128.7, 127.6, 127.2, 123.2,

122.5, 115.9, 109.9, 50.0, 44.2, 38.0, 19.5. HRMS (ESI) calcd for $C_{27}H_{22}NO_4$ $(M+H)^+$: 424.1543, found 424.1541.

5'-Benzoyl-1-benzyl-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7i**). White solid, mp: 266-268 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.71 (d, J = 7.2 Hz, 2H), 7.14-7.46 (m, 15H), 6.89 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 5.01 and 4.87 (d×2, J = 15.9 Hz, 2H), 3.74 (d, J = 15.9 Hz, 1H), 3.18 (d, J = 16.2 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 194.3, 175.9, 165.3, 156.1, 142.6, 136.9, 135.8, 133.0, 132.1, 130.4, 129.1, 129.0, 128.7, 128.6, 128.1, 128.0, 127.3, 127.0, 122.8, 122.7, 115.2, 109.7, 50.1, 43.2, 36.6. HRMS (ESI) calcd for $C_{32}H_{24}NO_4$ $(M+H)^+$: 486.1700, found 486.1711.

5'-Acetyl-1-benzyl-5-fluoro-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7j**). White solid, mp: 193-194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.26-7.32 (m, 5H), 6.82-6.91 (m, 2H), 6.56 (dd, J = 8.4, 3.9 Hz, 1H), 4.90 and 4.79 (d×2, J = 15.9 Hz, 2H), 3.19 (d, J = 15.9 Hz, 1H), 2.88 (d, J = 15.9 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 175.9, 164.1, 159.6 (d, J = 197.3 Hz, 1C), 157.7, 138.4, 138.1 (d, J = 2.0 Hz, 1C), 134.9, 133.3, 131.3 (d, J = 8.0 Hz, 1C), 128.87, 128.83, 128.80, 127.8, 127.1, 115.6 (d, J = 23.3 Hz, 1C), 110.8 (d, J = 14.9 Hz, 1C), 110.60, 110.57, 50.39 (d, J = 1.7 Hz, 1C), 44.4, 37.9, 19.7. HRMS (ESI) calcd for $C_{27}H_{21}FNO_4$ $(M+H)^+$: 442.1449, found 442.1445.

5'-Acetyl-1-benzyl-5-chloro-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7k**). White solid, mp: 212-213 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 7.2 Hz, 2H), 7.56 (m, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.26-7.35 (m 5H), 7.12-7.14 (m, 2H), 6.57 (d, J = 8.1 Hz, 1H), 4.90 and 4.80 (d×2, J = 15.9 Hz, 2H), 3.20 (d, J = 15.9 Hz, 1H), 2.86 (d, J = 15.9 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 175.8, 164.0, 158.5, 140.7, 138.5, 134.7, 133.3, 131.6, 129.3, 128.9, 128.8, 128.6, 127.8, 127.1, 123.0, 115.6, 111.0, 50.2, 44.3, 37.9, 19.8. HRMS (ESI) calcd for $C_{27}H_{21}ClNO_4$ $(M+H)^+$: 458.1154, found 458.1160.

5'-Acetyl-1-benzyl-5-bromo-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7l**). White solid, mp: 206-207 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.28-7.34 (m, 7H), 6.54 (d, J = 8.1 Hz, 1H), 4.91 and 4.81 (d×2, J = 15.9 Hz, 2H), 3.22 (d, J = 15.9 Hz, 1H), 2.87 (d, J = 15.9 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 175.7, 164.0, 158.5, 141.2, 138.5, 134.7, 133.3, 132.2, 131.9, 128.9, 128.8, 127.8, 127.1, 125.7, 115.8, 115.6, 111.4, 50.1, 44.3, 37.9, 19.8. HRMS (ESI) calcd for $C_{27}H_{21}BrNO_4$ $(M+H)^+$: 502.0648, found 502.0645.

5'-Acetyl-1-benzyl-5-methyl-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7m**). White solid, mp: 230-231 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.23-7.34 (m, 5H), 6.95-6.98 (m, 2H), 6.53 (d, J = 7.8 Hz, 1H), 4.90 and 4.76 (d×2, J = 15.6 Hz, 2H), 3.21 (d, J = 15.9 Hz, 1H), 2.87 (d, J = 15.9 Hz, 1H), 2.25 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7, 176.1, 164.7, 157.7, 139.7, 138.5, 135.3, 133.1, 132.9, 129.8, 129.6, 128.84, 128.76, 128.67, 127.6, 127.2, 123.3, 116.1, 109.7, 50.1, 44.2, 38.1, 21.0, 19.6. HRMS (ESI) calcd for $C_{28}H_{24}NO_4$ $(M+H)^+$: 438.1700, found 438.1687.

5'-Acetyl-1-benzyl-7-chloro-6'-phenylspiro[indoline-3,4'-pyran]-2,2'(3'H)-dione (**7n**). White solid, mp: 172-173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.23-7.33 (m, 5H), 7.16 (d, J = 8.1 Hz, 1H), 7.07 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 5.26 (s, 2H), 3.17 (d, J = 15.9 Hz, 1H), 2.87 (d, J = 15.6 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 176.8, 164.0, 158.3, 138.45, 138.35, 137.1, 133.3, 132.7, 131.9, 128.80, 128.77, 128.6, 127.2, 126.4, 124.1, 121.0, 116.2, 115.6, 49.8, 45.3, 38.3, 19.7. HRMS (ESI) calcd for $C_{27}H_{21}ClNO_4$ $(M+H)^+$: 458.1154, found 458.1152.

Procedure for the ring-opening reaction of 7k with methanol

To an oven-dried 10 mL round-bottom flask was charged with compound **7k** (46 mg, 0.1 mmol) and anhydrous methanol (1 mL). The resulting mixture was heated at 65^{o}C until the completion of the reaction as monitored by TLC. The solvent was evaporated

under reduced pressure and the residue was purified by flash chromatography on silica gel to using hexane/EtOAc (5:1) as the eluent afford 42 mg of compound **8**.

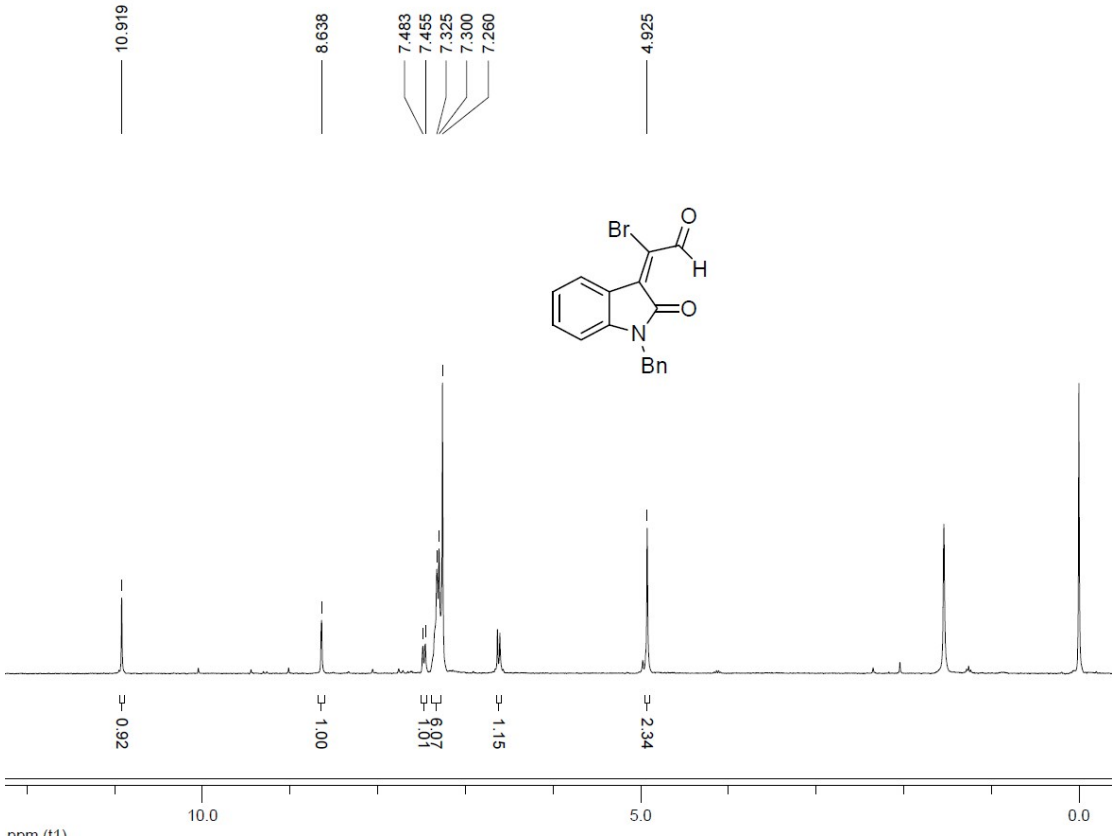
Methyl 2-(1-benzyl-5-chloro-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl)acetate (**8**). 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87-7.90 (m, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.29-7.46 (m 8H), 7.10 (dd, J = 8.4, 2.1 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 5.05 and 4.97 (d×2, J = 15.9 Hz, 2H), 4.12 (d, J = 18.0 Hz, 1H), 3.62 (d, J = 18.6 Hz, 1H), 3.59 (s, 3H), 3.16 (d, J = 16.2 Hz, 1H), 2.83 (d, J = 16.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.5, 178.7, 170.0, 142.2, 136.1, 135.6, 133.4, 132.5, 128.9, 128.8, 128.6, 128.2, 128.0, 127.6, 127.3, 124.2, 110.2, 63.4, 51.8, 47.2, 44.4, 40.9. HRMS (ESI) calcd for $C_{26}H_{23}ClNO_4$ $(M+H)^+$: 448.1310, found 448.1289.

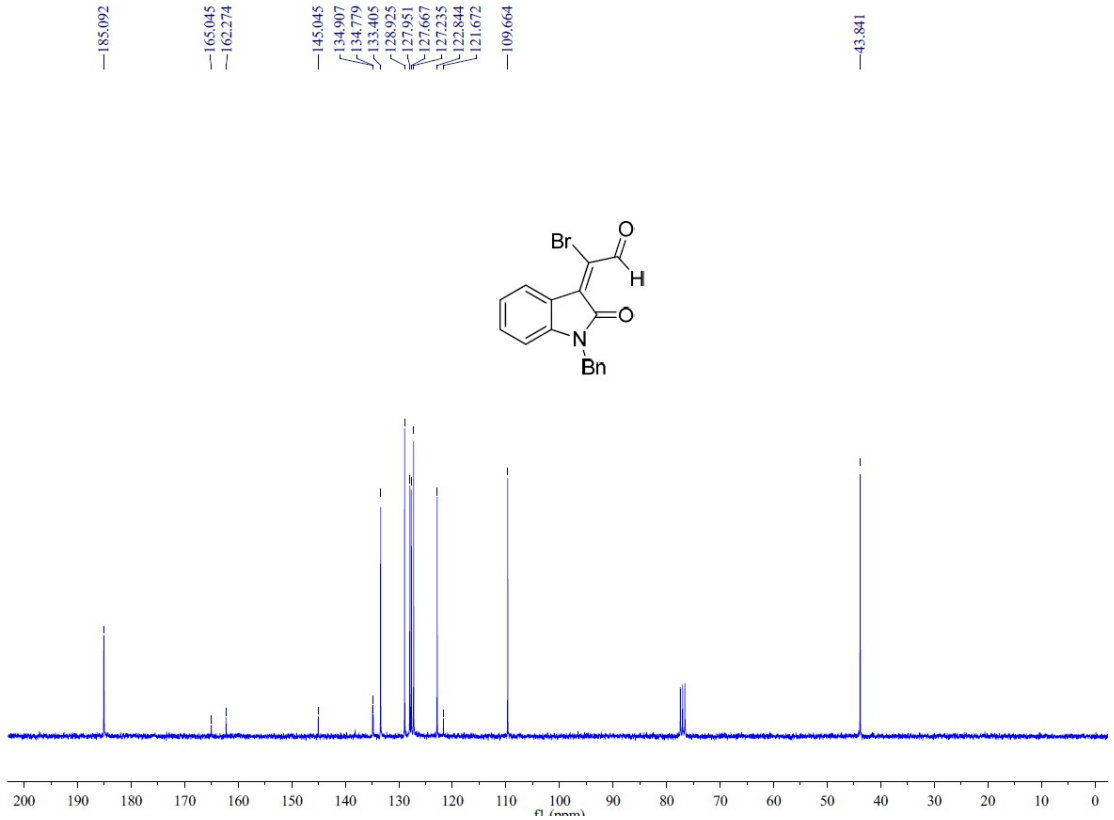
Procedure for the NHC-catalyzed reaction of 2-bromoenal 5a with ethanol

To an oven-dried 15 mL glass cylindrical pressure vessel was charged with 2-bromoenals **5a** (68 mg, 0.2 mmol), carbene precursor **F** (8 mg, 0.03 mmol), Cs_2CO_3 (98 mg, 0.3 mmol), LiCl (9.0 mg, 0.22 mmol) and 200 mg of 4 Å MS under N_2 atmosphere. Then anhydrous 1,4-dioxane (3 mL) and ethanol (0.5 mL) were added and the vessel was immediately sealed tightly. The resulting mixture was stirred at 50 ^{o}C for 2 h. The mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel to using hexane/EtOAc (5:1) as the eluent afford 48 mg of compound **13**.

(*E*)-ethyl 2-(1-benzyl-2-oxoindolin-3-ylidene)acetate (**13**).[2] 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 7.5 Hz, 1H), 7.22-7.33 (m, 6H), 7.01 (t, J = 7.5 Hz, 1H), 6.96 (s, 1H), 6.67 (d, J = 7.5 Hz, 1H), 4.92 (s, 2H), 4.32 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H).

1. T. Mukaiyama, K. Ogata, I. Sato and Y. Hayashi, *Chem. Eur. J.*, 2014, **20**, 13583.
2. C. Palumbo, G. Mazzeo, A. Mazziotta, A. Gambacorta, M. A. Loreto, A. Migliorini, S. Superchi, D. Tofani and T. Gasperi, *Org. Lett.*, 2011, **13**, 6248.

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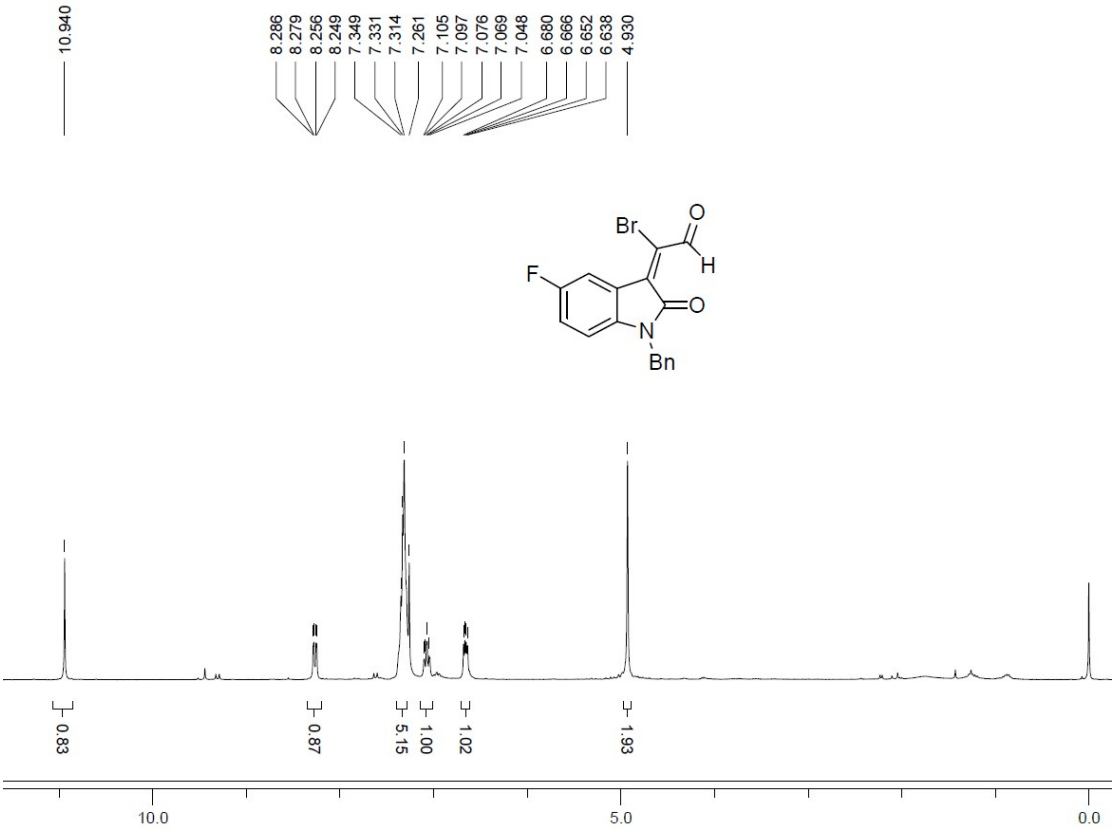
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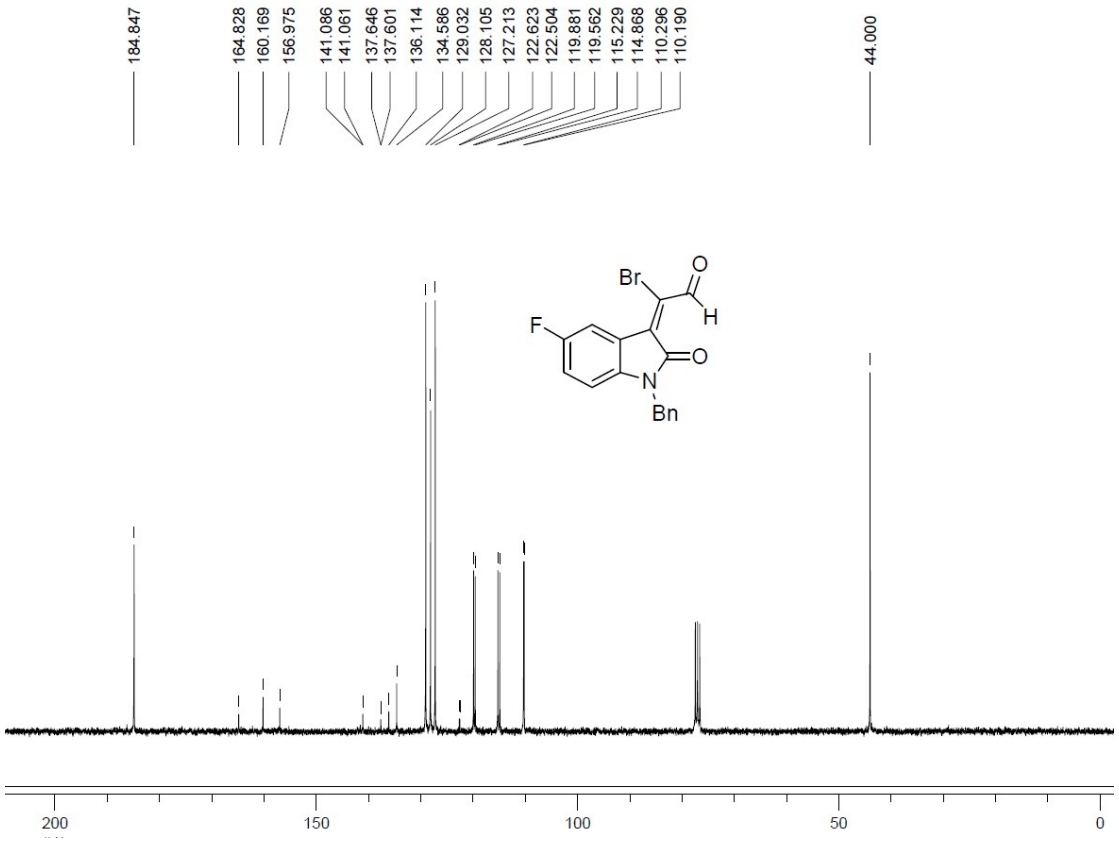
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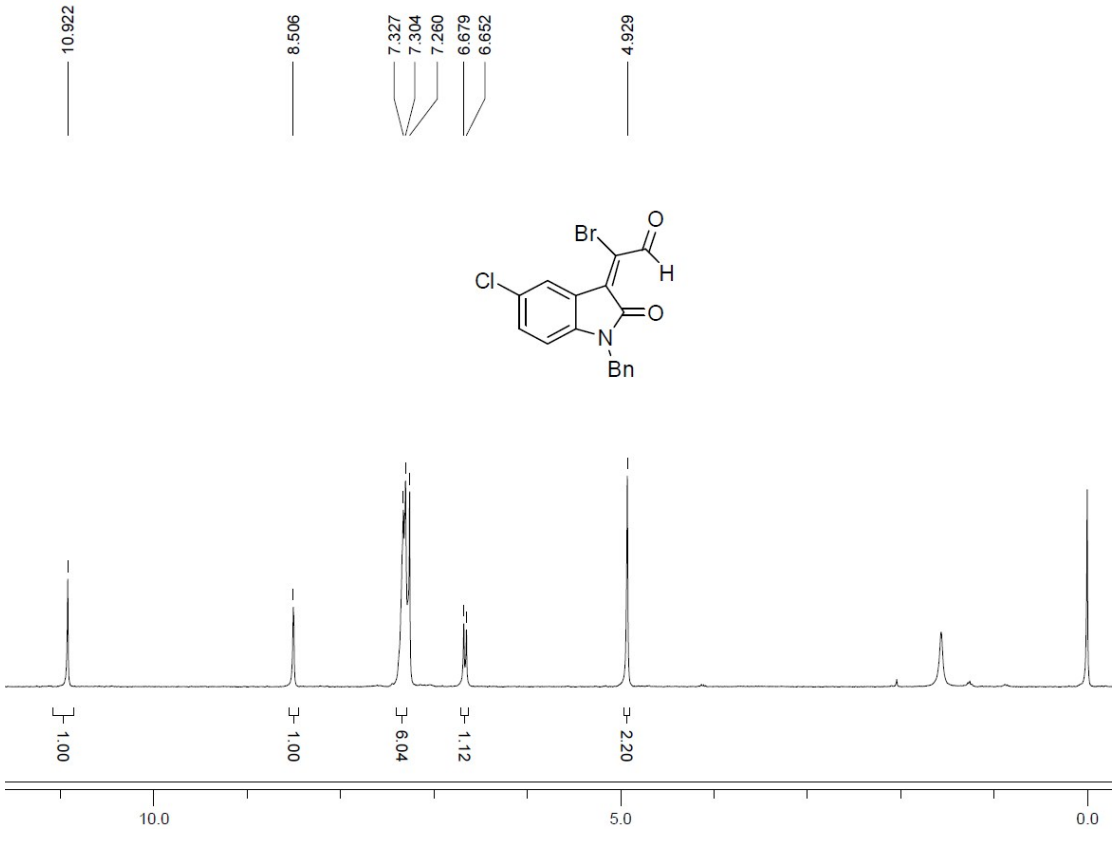
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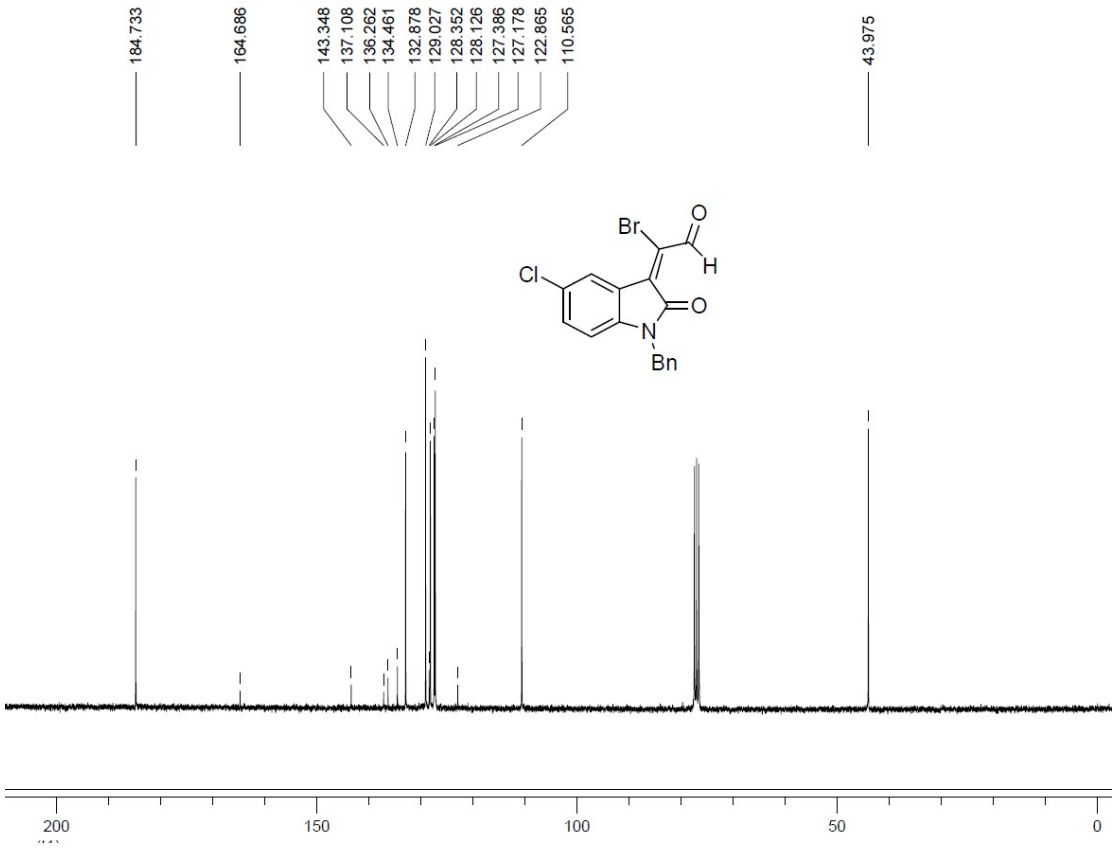
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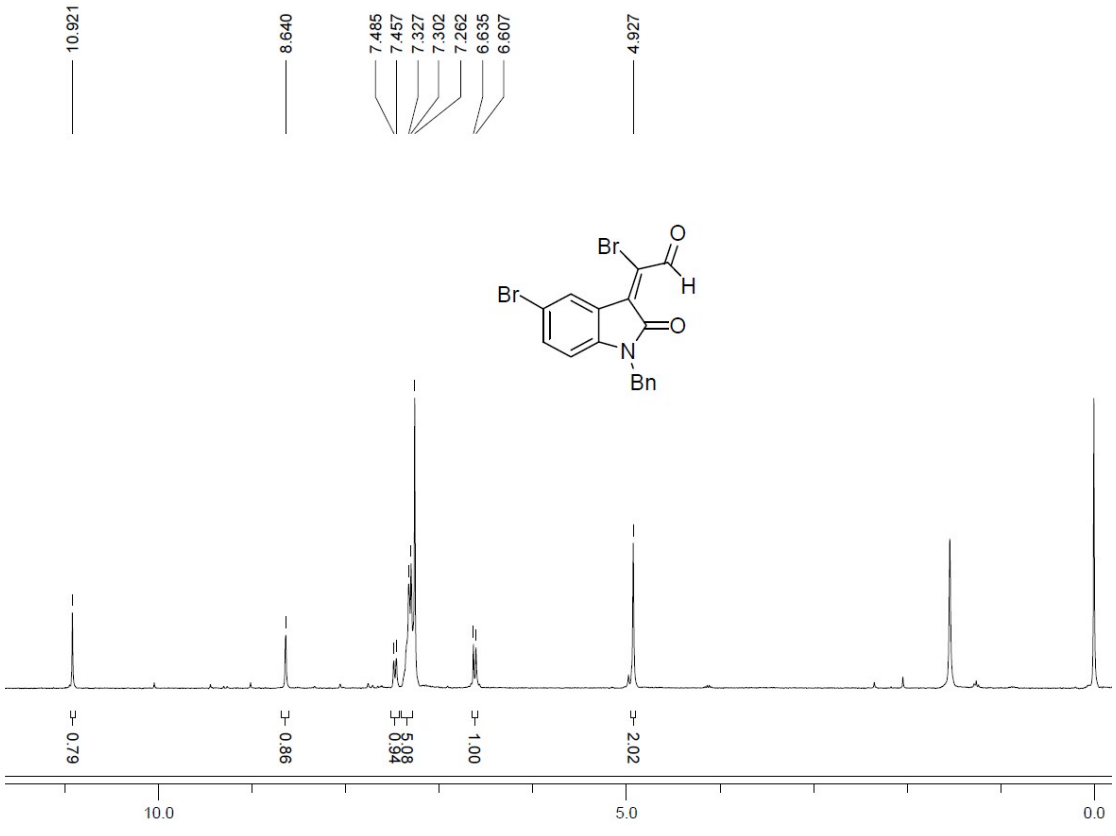
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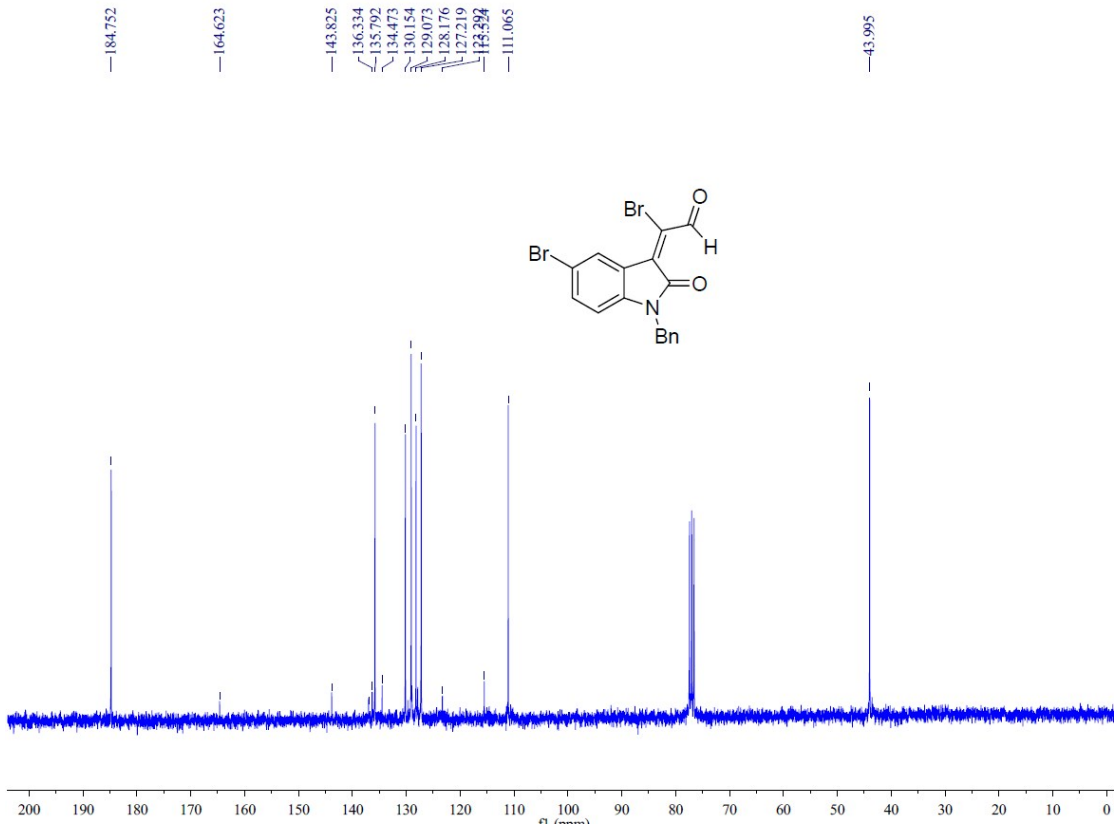
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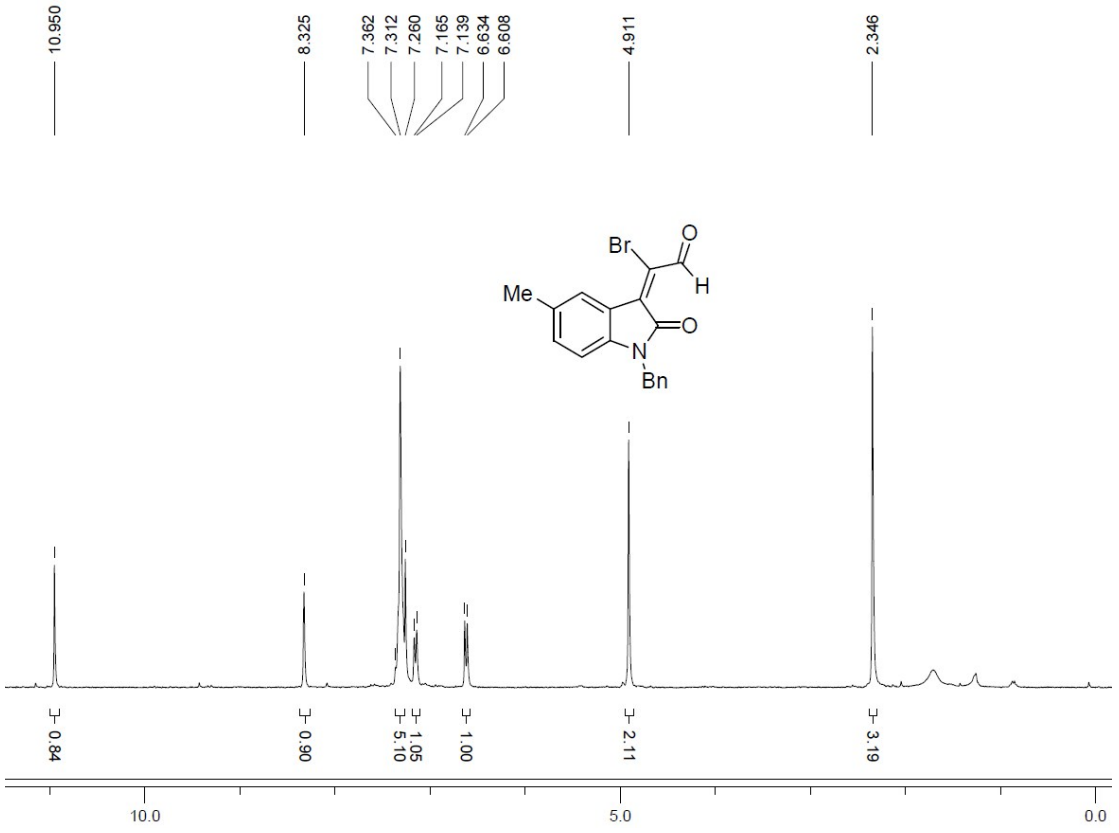
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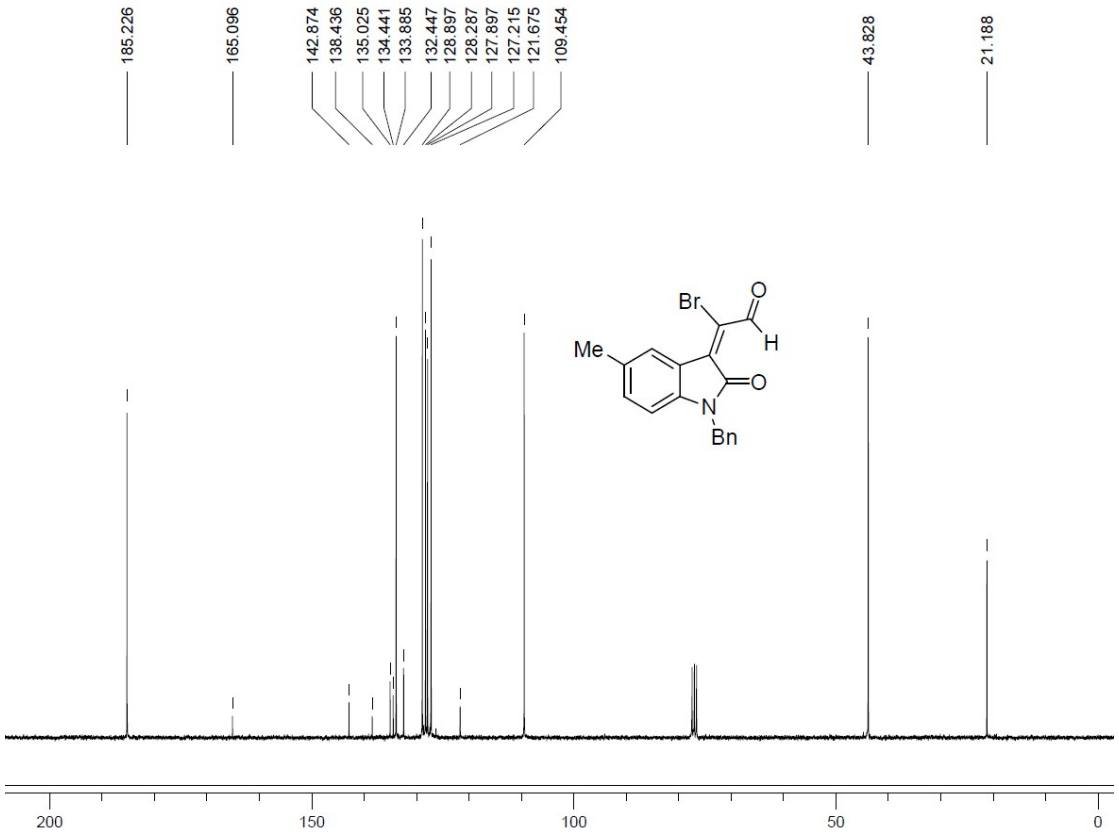
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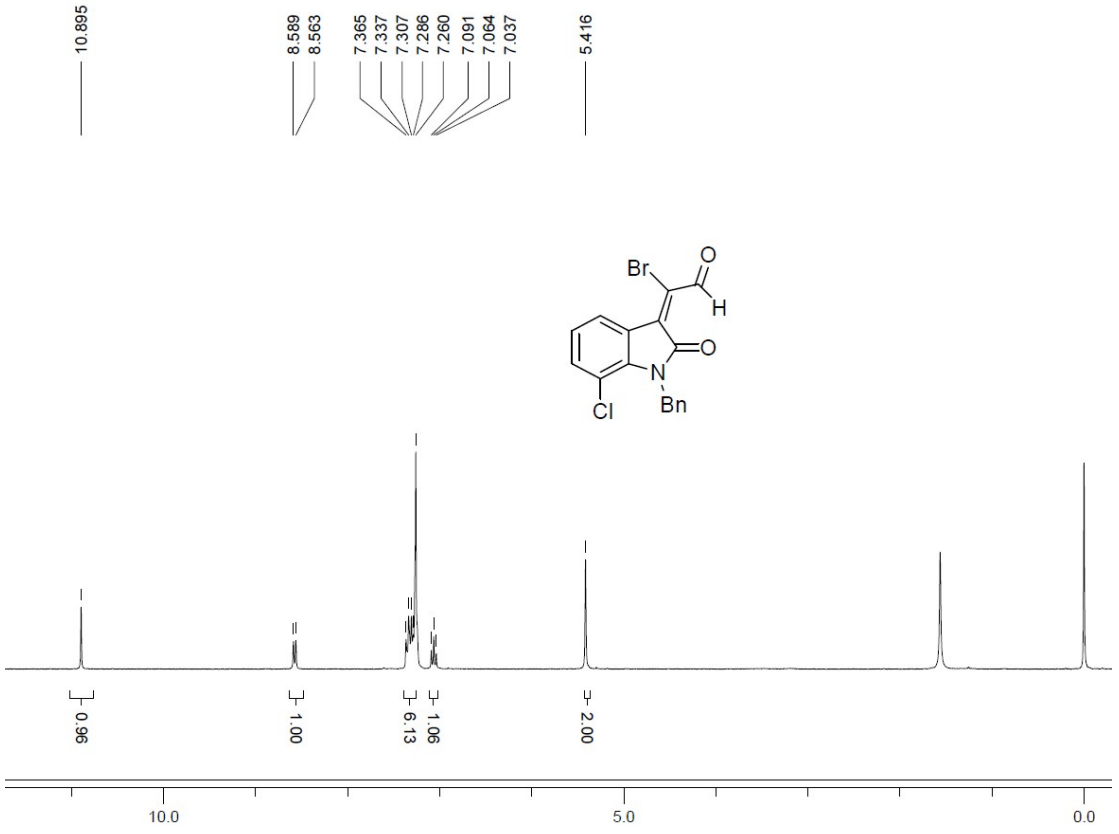
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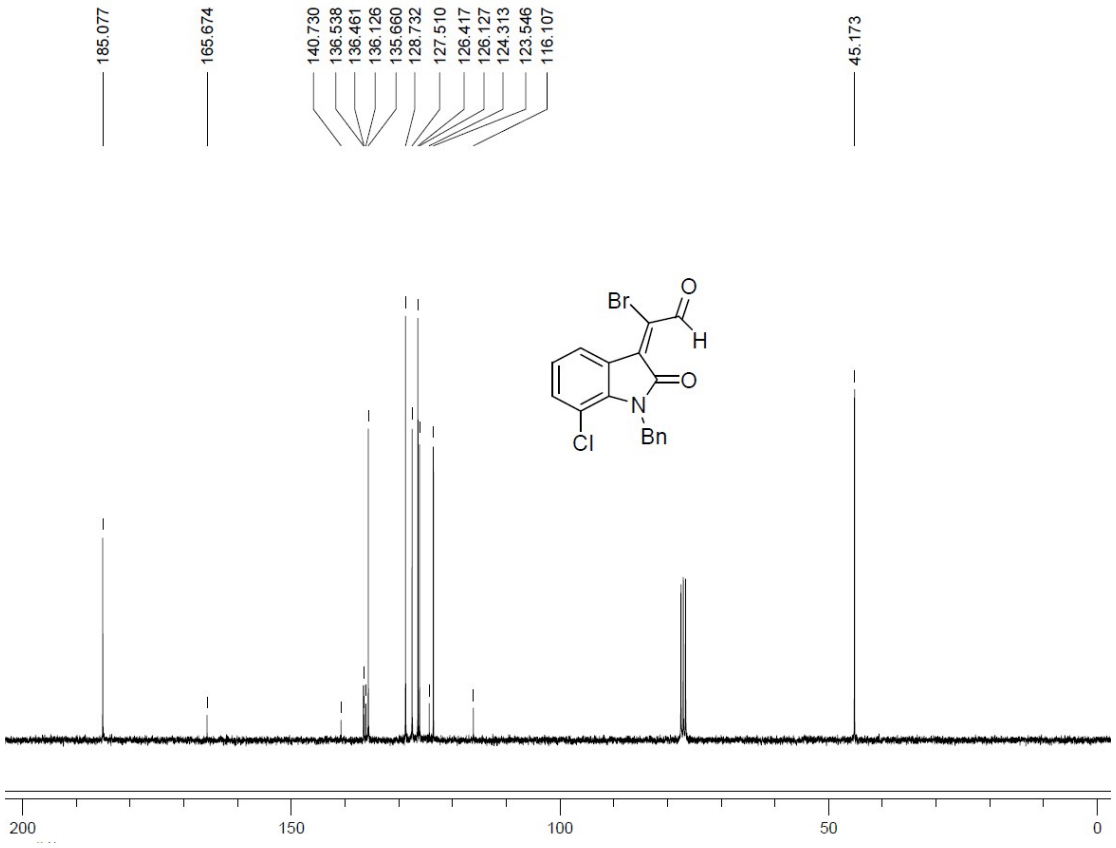
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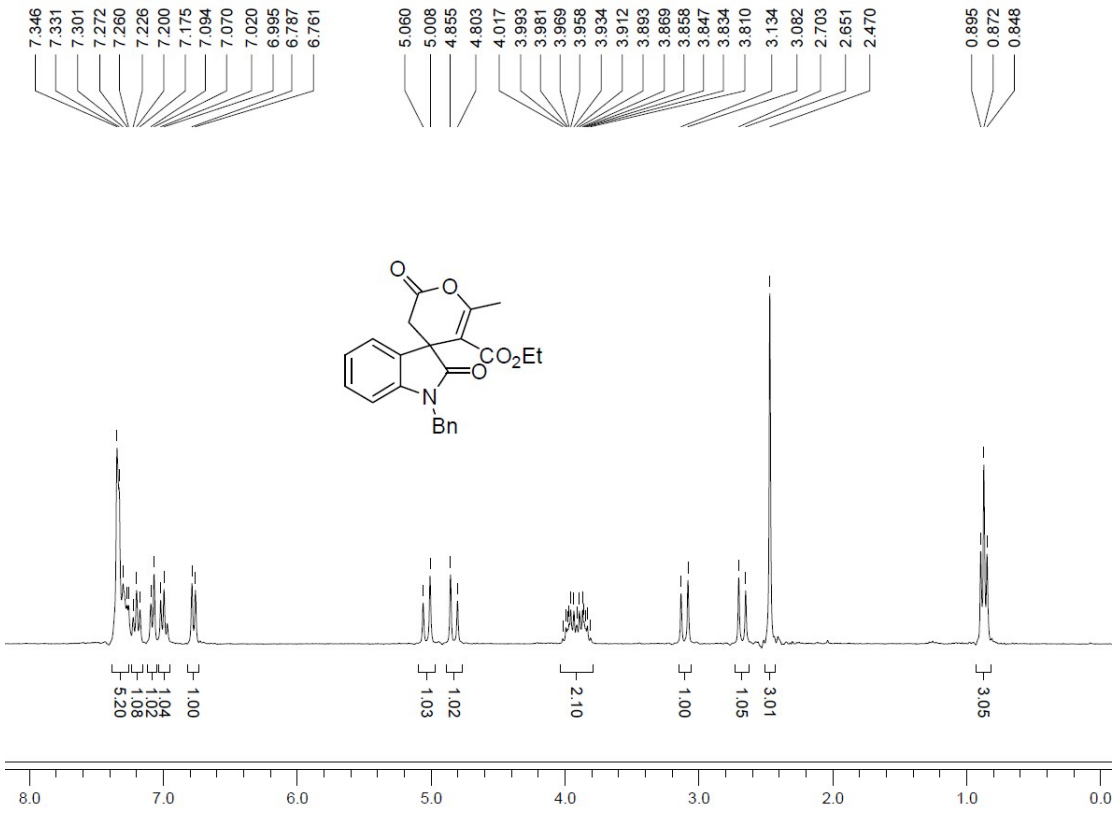
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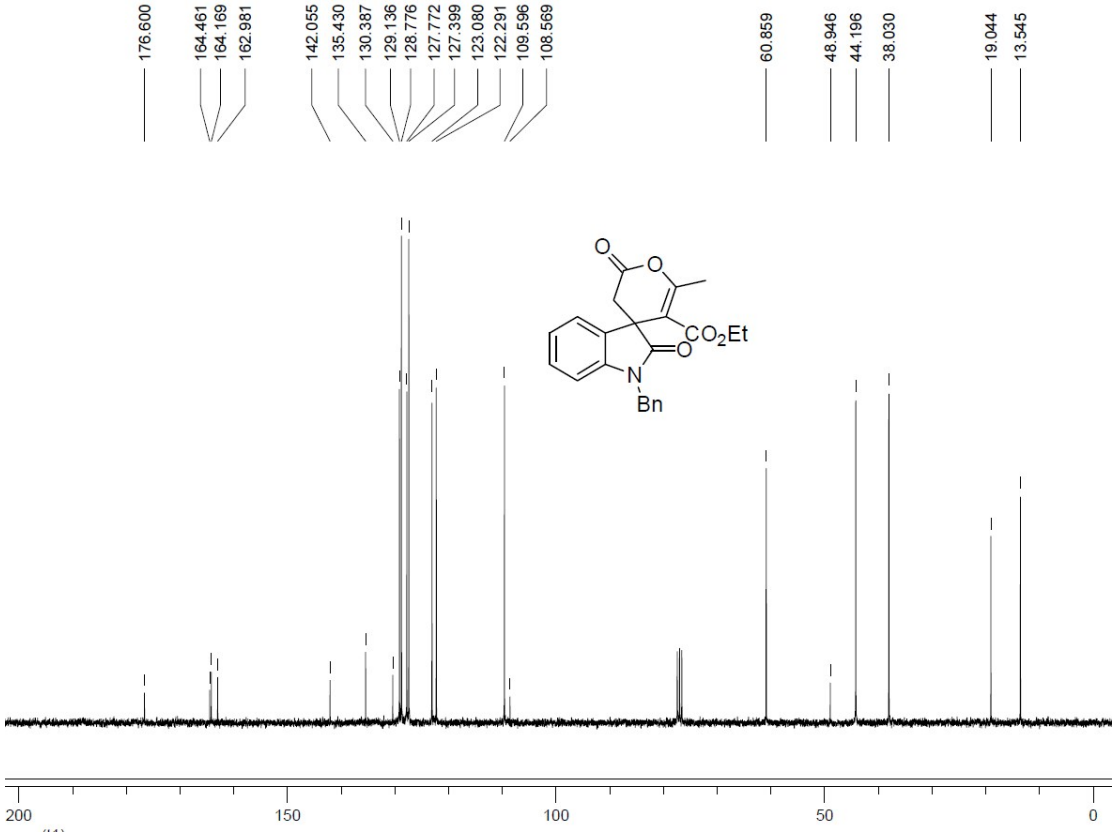
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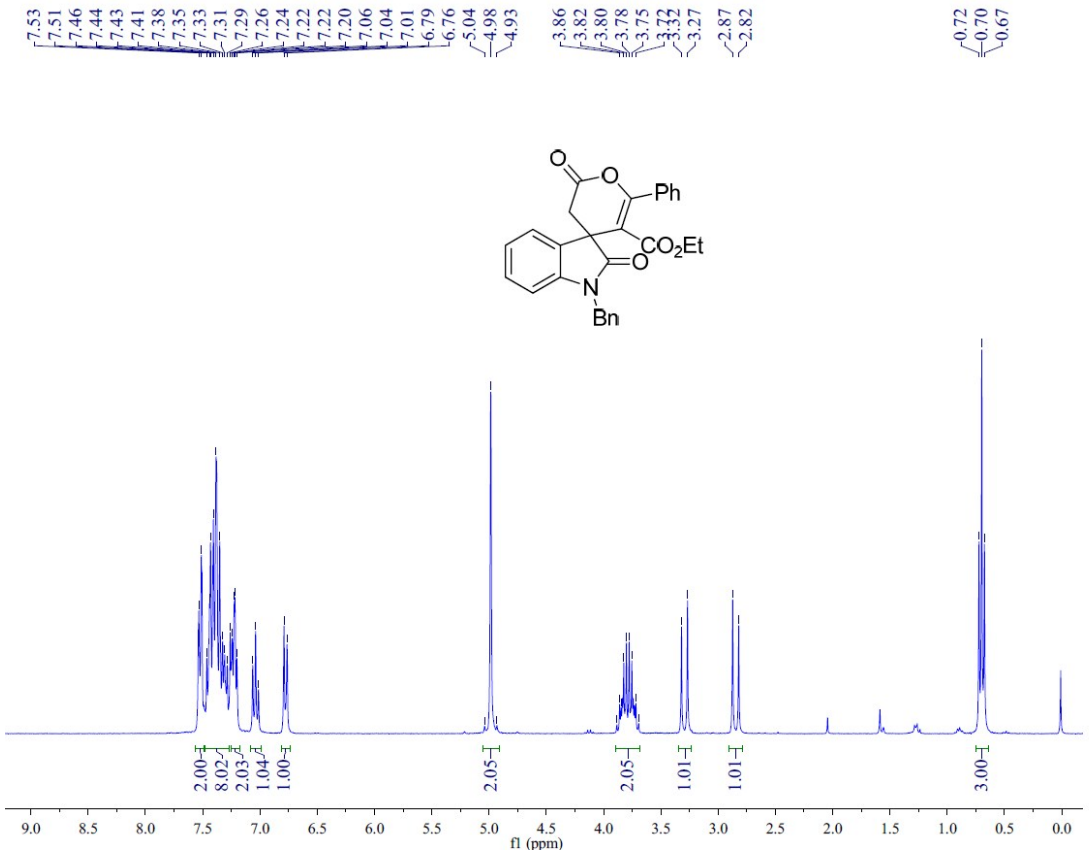
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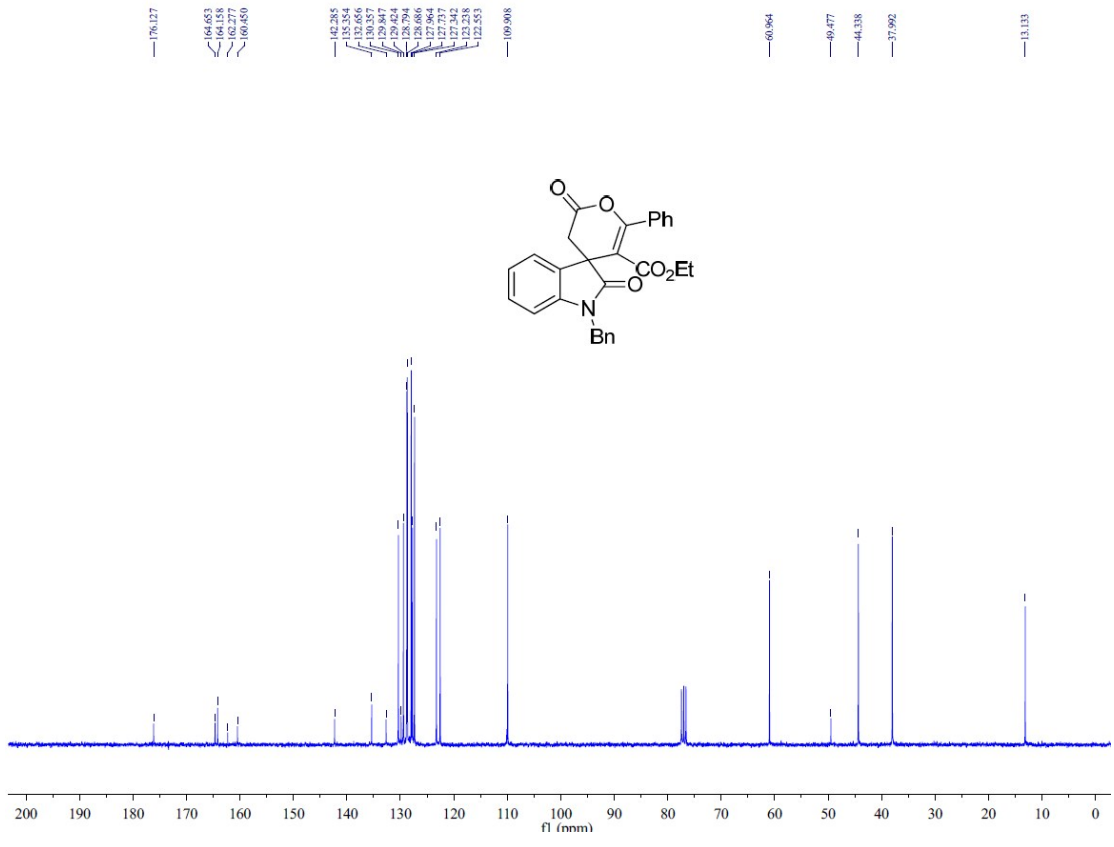
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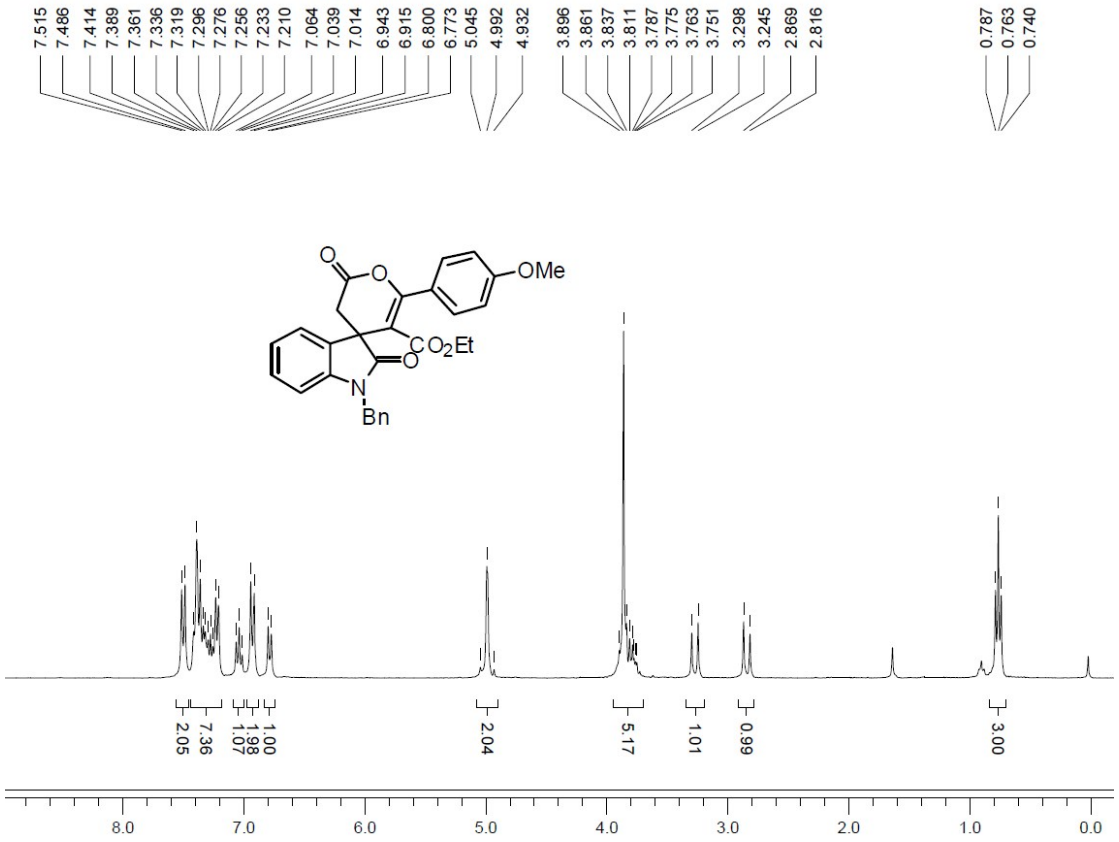
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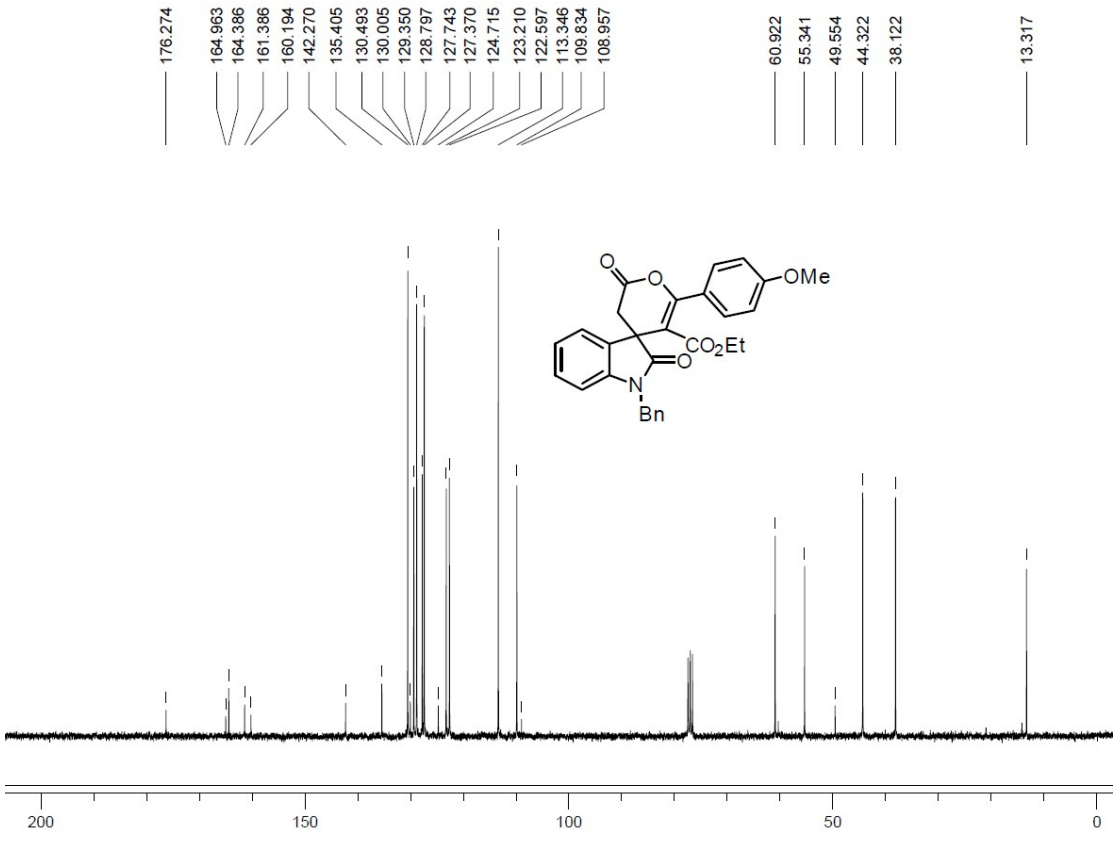
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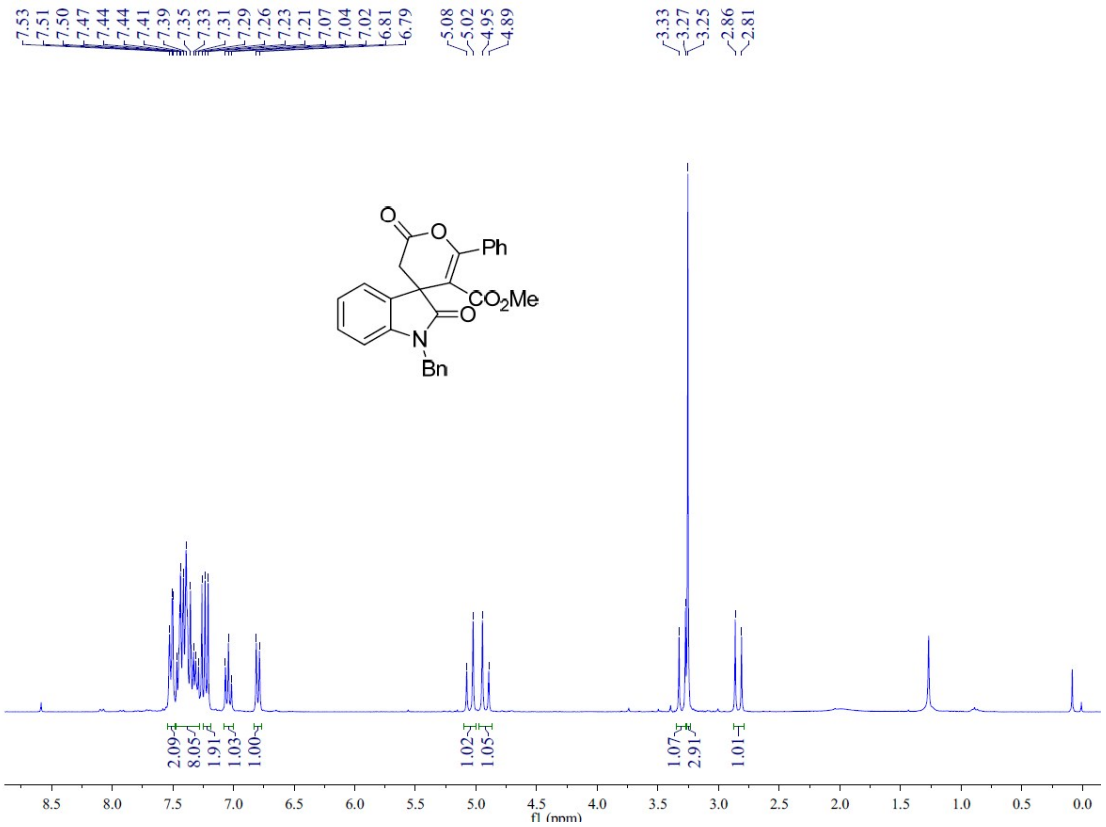
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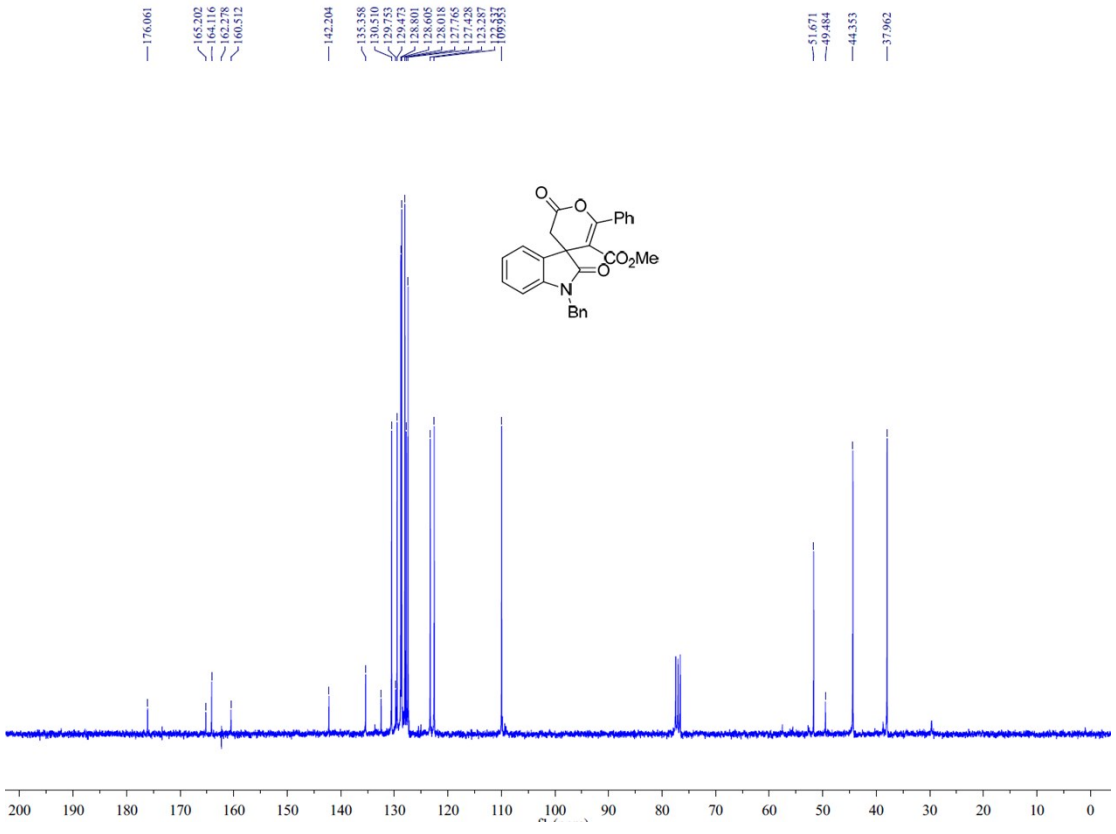
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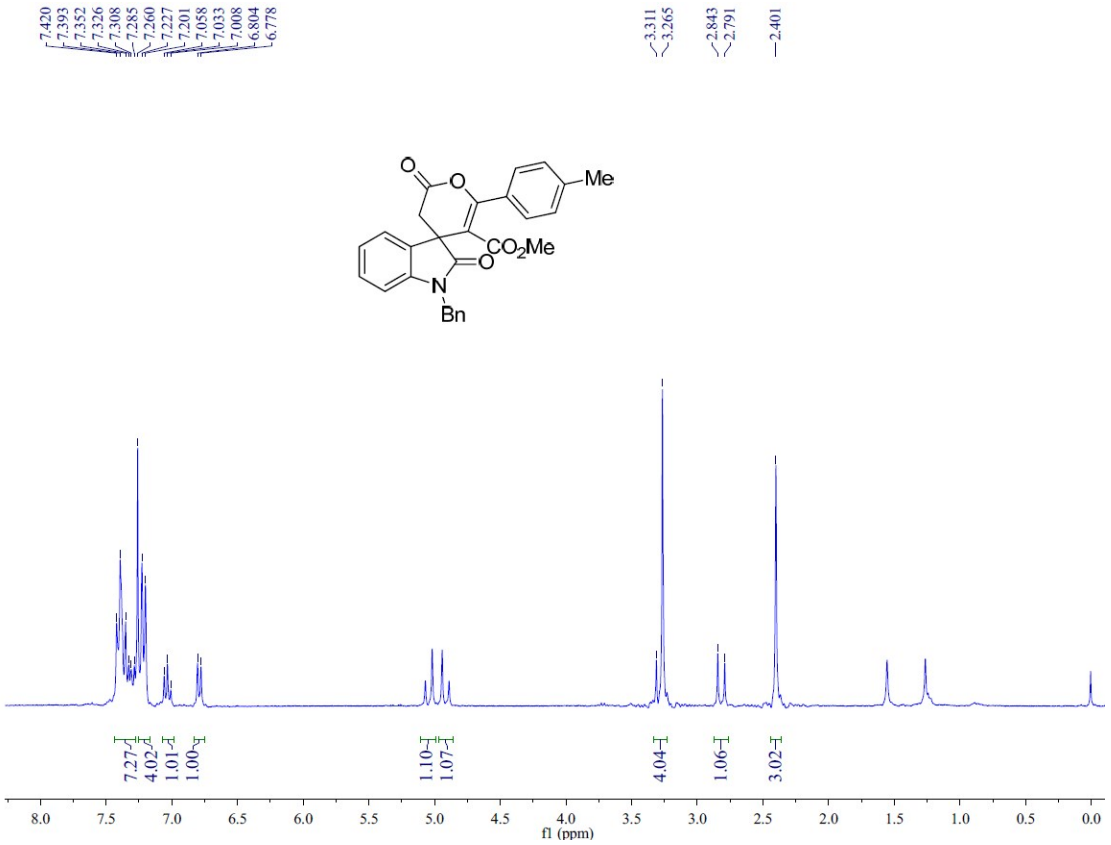
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7.008
6.804
6.778
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3.265
2.843
2.791
2.401
Me
CO2Me
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1.07
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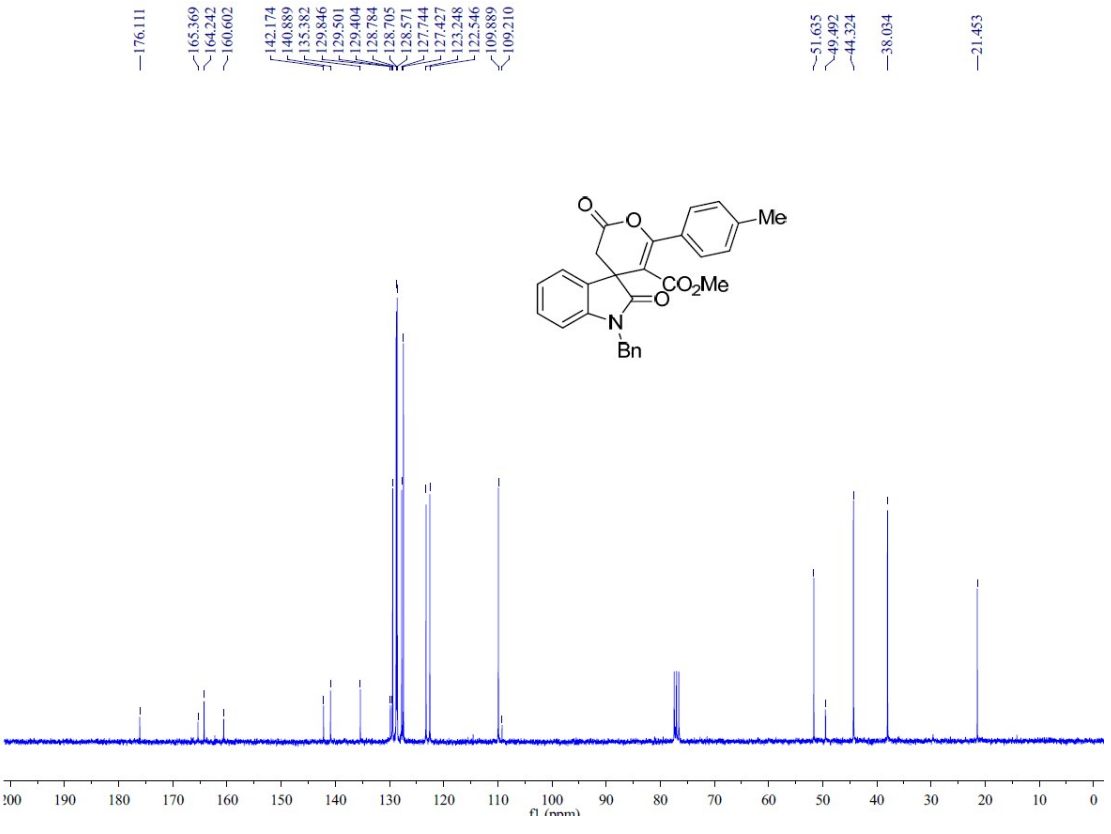
1.06
3.02
fl (ppm)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123.248
122.546
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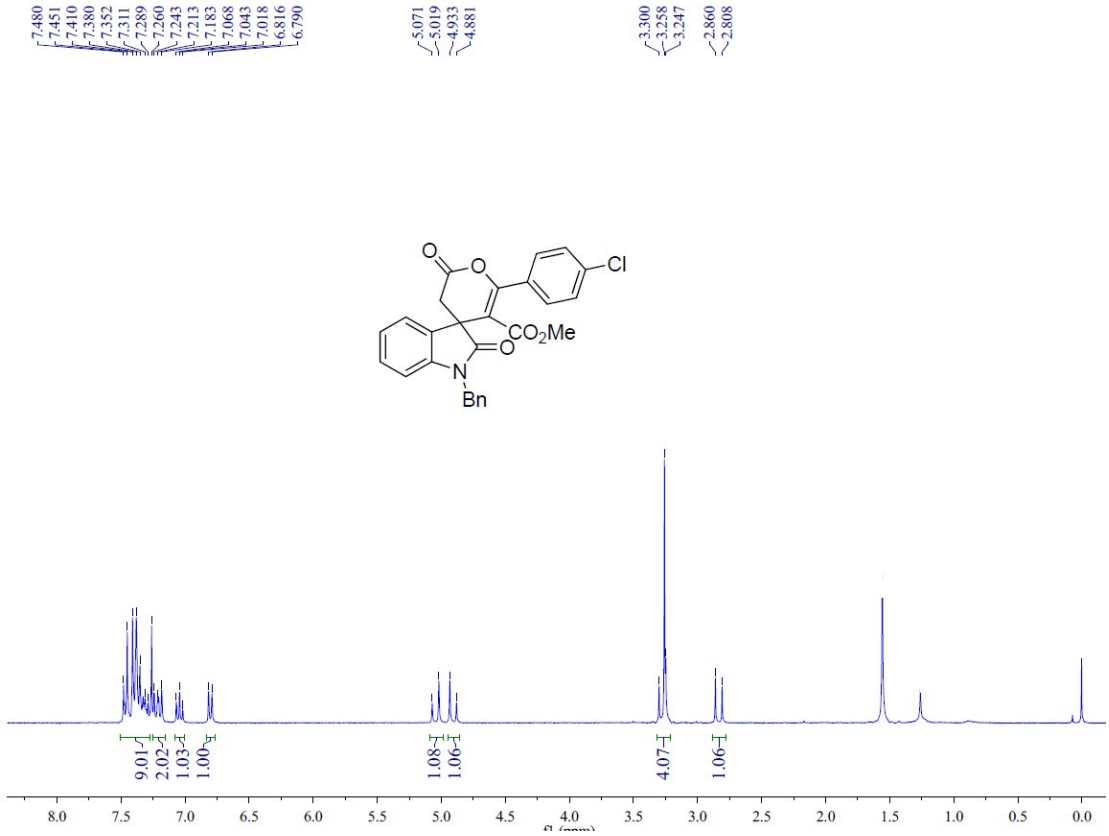
Me
CO2Me
O
N
Bn
fl (ppm)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7.018
6.816
6.790
5.071
5.019
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4.881
3.300
3.258
3.247
2.860
2.808
O
O
Cl
CO2Me
O
N
Bn
9.01
2.02
1.03
1.00
1.08
1.06
4.07
1.06
8.0
7.5
7.0
6.5
6.0
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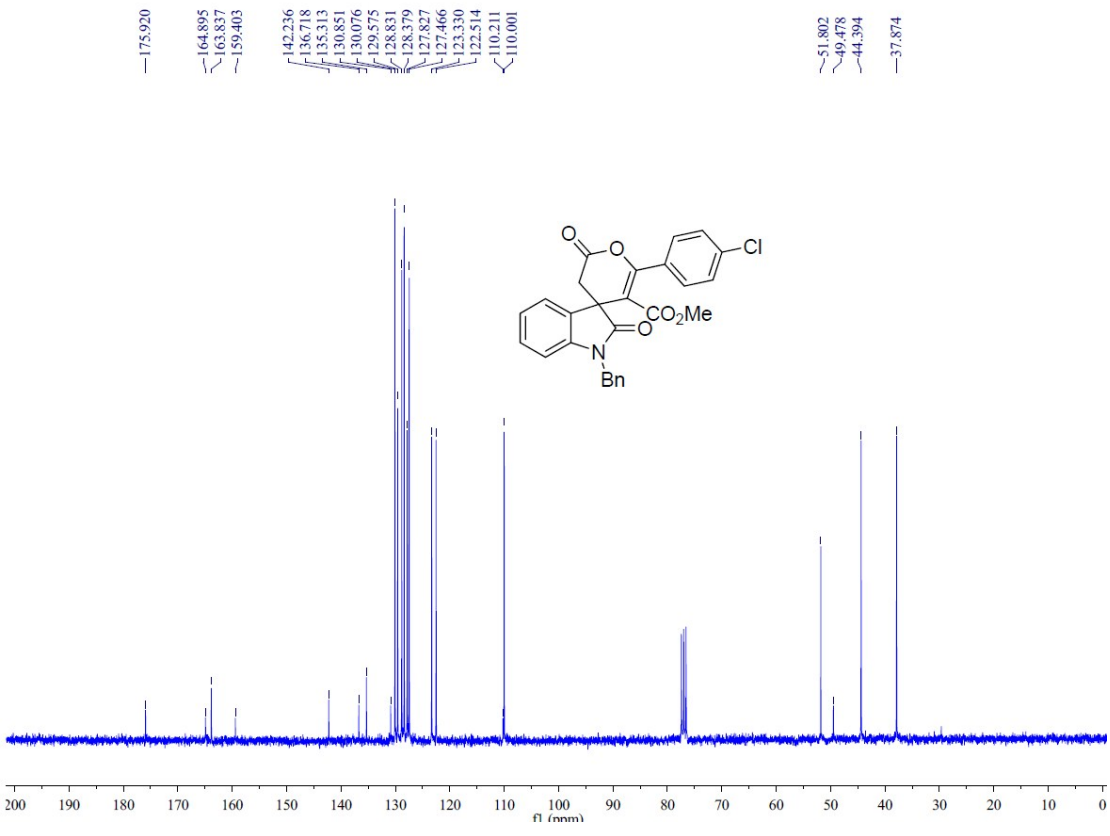
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127.466
123.330
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110.211
110.001
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49.478
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O
O
Cl
CO2Me
O
N
Bn
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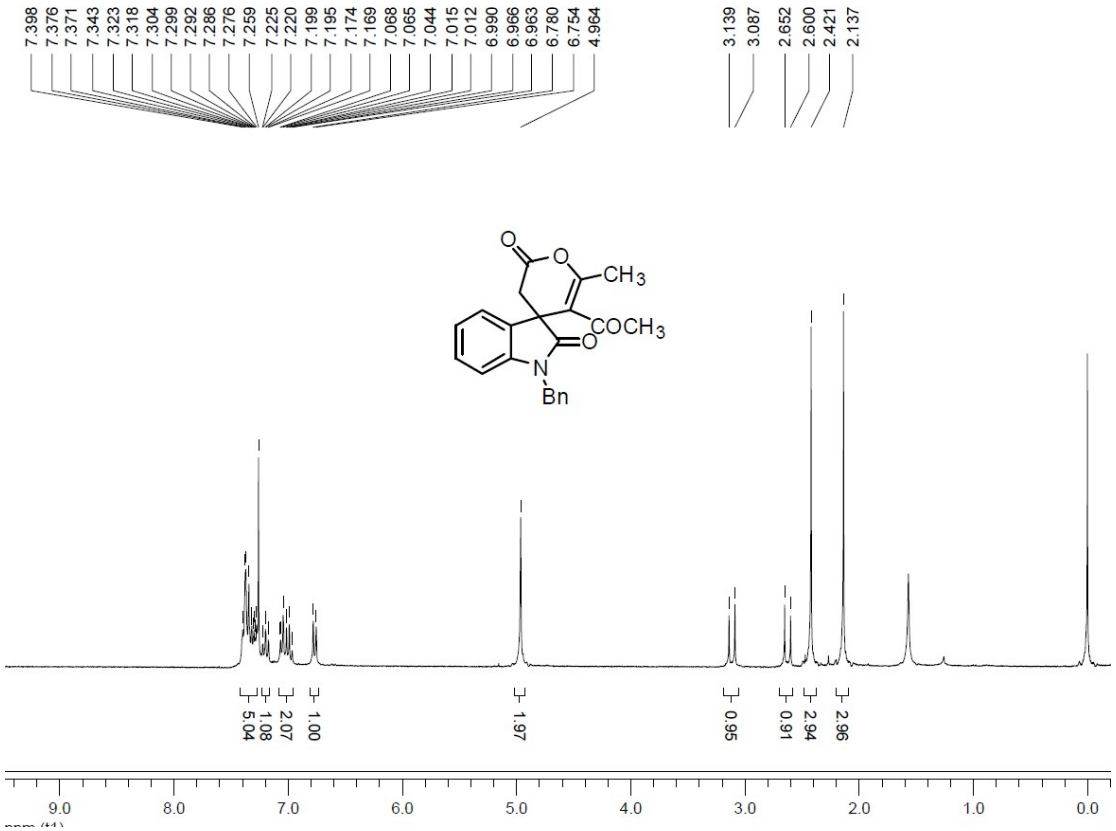
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7.220
7.199
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7.169
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7.065
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7.015
7.012
6.990
6.966
6.963
6.780
6.754
4.964
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3.087
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2.600
2.421
2.137
O
O
CH3
COCH3
O
N
Bn
5.04
1.08
2.07
1.00
1.97
0.95
0.91
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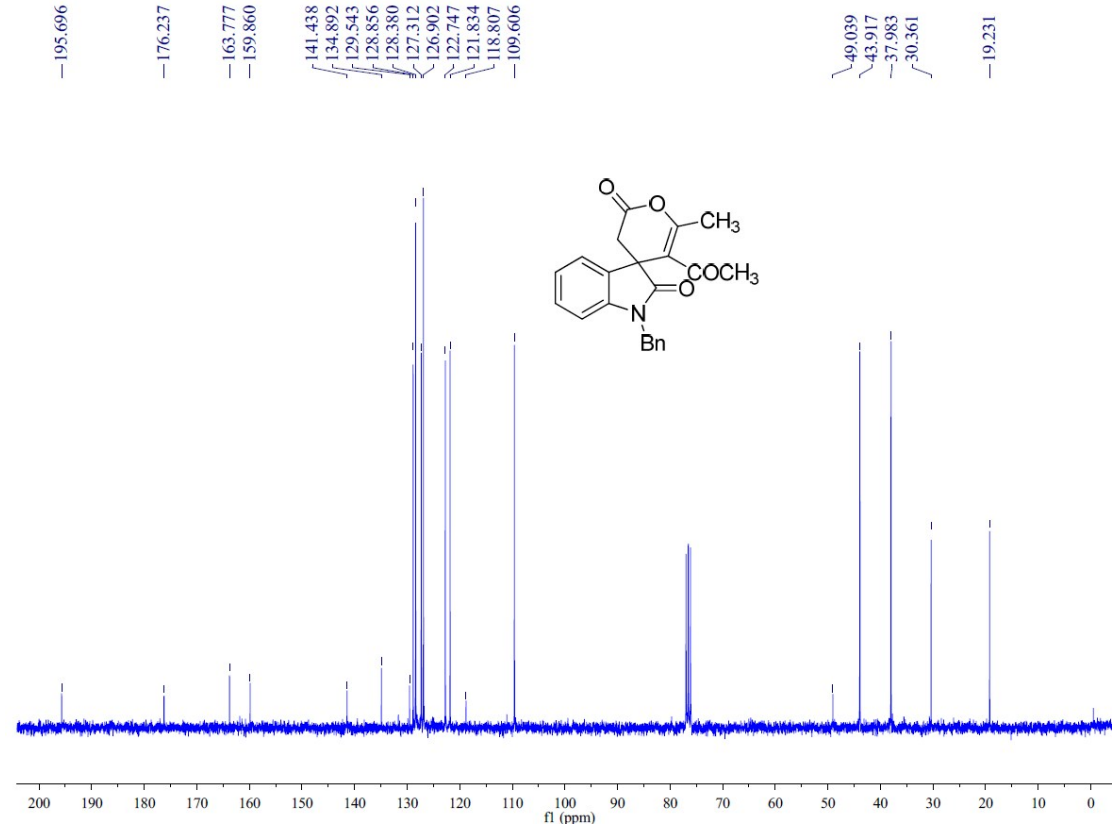
0.0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121.834
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109.606
49.039
43.917
37.983
30.361
19.231
O
O
CH3
COCH3
O
N
Bn
200
190
180
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130
120
110
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90
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50
40
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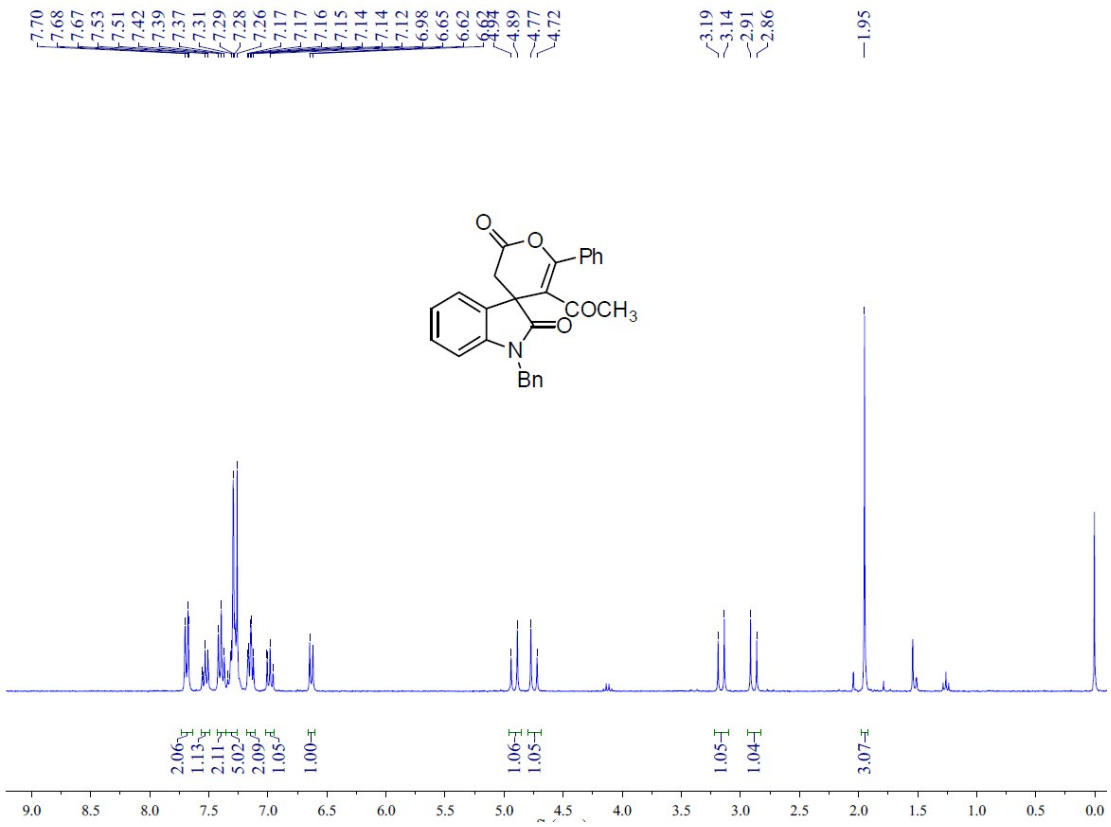
f1 (ppm)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7.28
7.26
7.17
7.17
7.16
7.15
7.14
7.14
7.12
6.98
6.65
6.62
4.89
4.77
4.72
3.19
3.14
2.91
2.86
1.95
O
O
Ph
COCH3
O
N
Bn
2.06
1.13
2.11
5.02
2.09
1.05
1.00
1.06
1.05
1.05
1.04
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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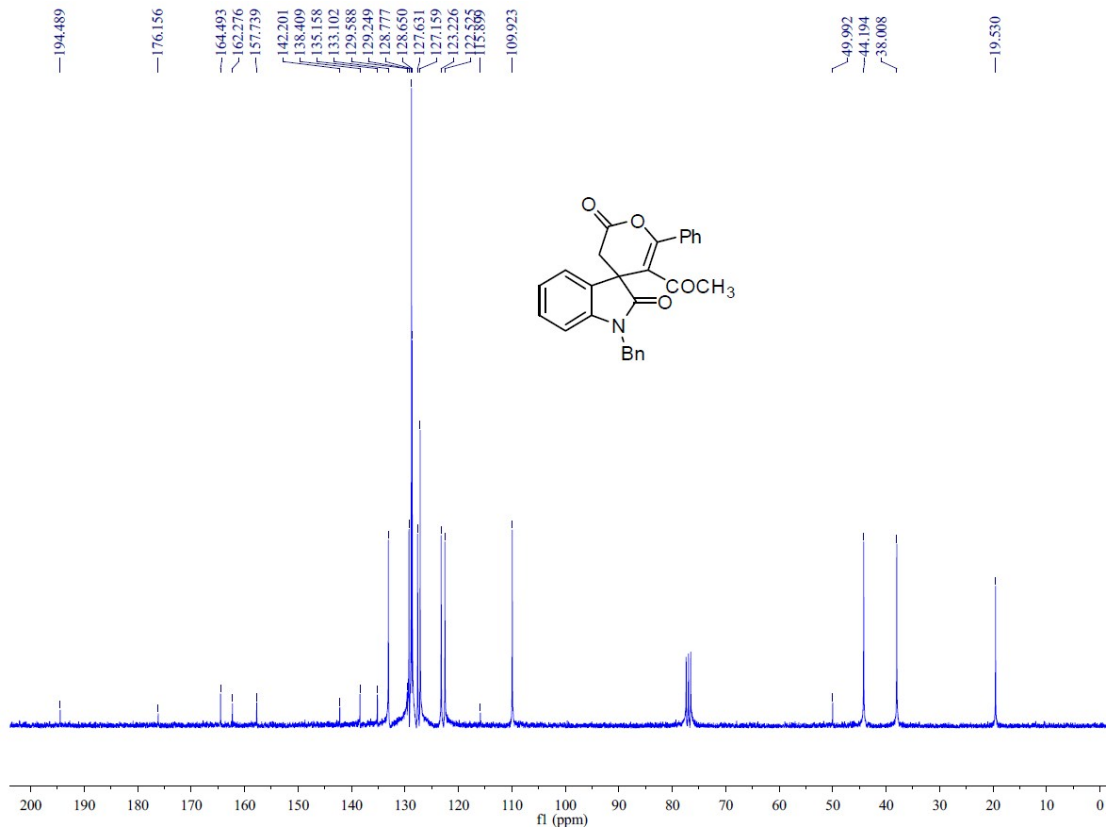
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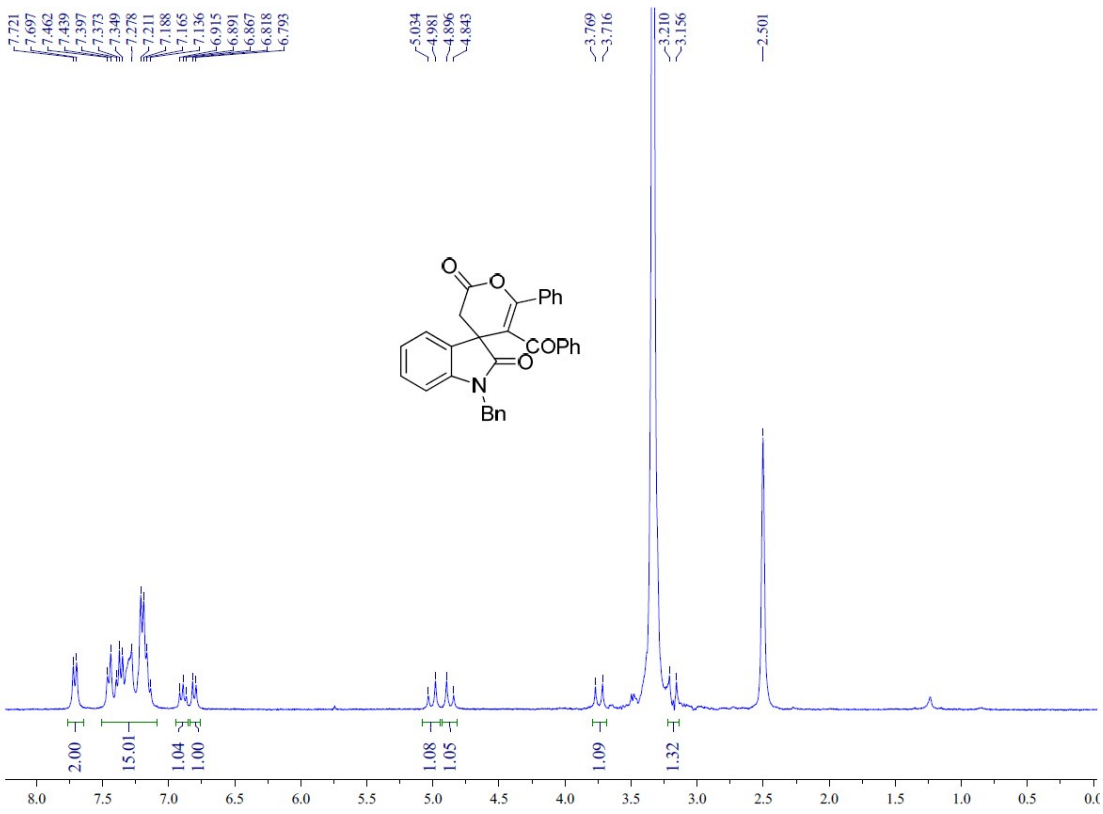
127.631
127.159
123.226
122.525
115.899
109.923
49.992
44.194
38.008
19.530
O
O
Ph
COCH3
O
N
Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.915
6.891
6.867
6.818
6.793
5.034
4.981
4.896
4.843
3.769
3.716
3.210
3.156
2.501
O
O
Ph
COPh
O
N
Bn
2.00
15.01
1.04
1.00
1.08
1.05
1.09
1.32
8.0
7.5
7.0
6.5
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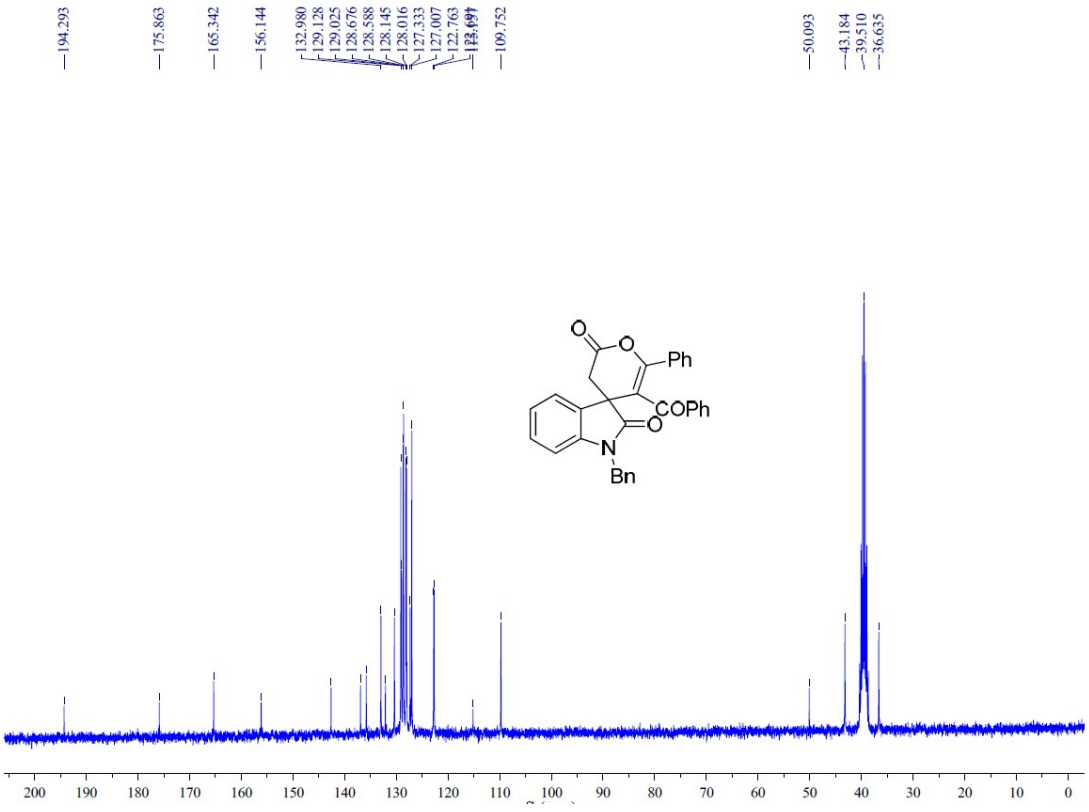
0.5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127.007
122.763
109.752
50.093
43.184
39.510
36.635
O
O
Ph
COPh
O
N
Bn
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150
140
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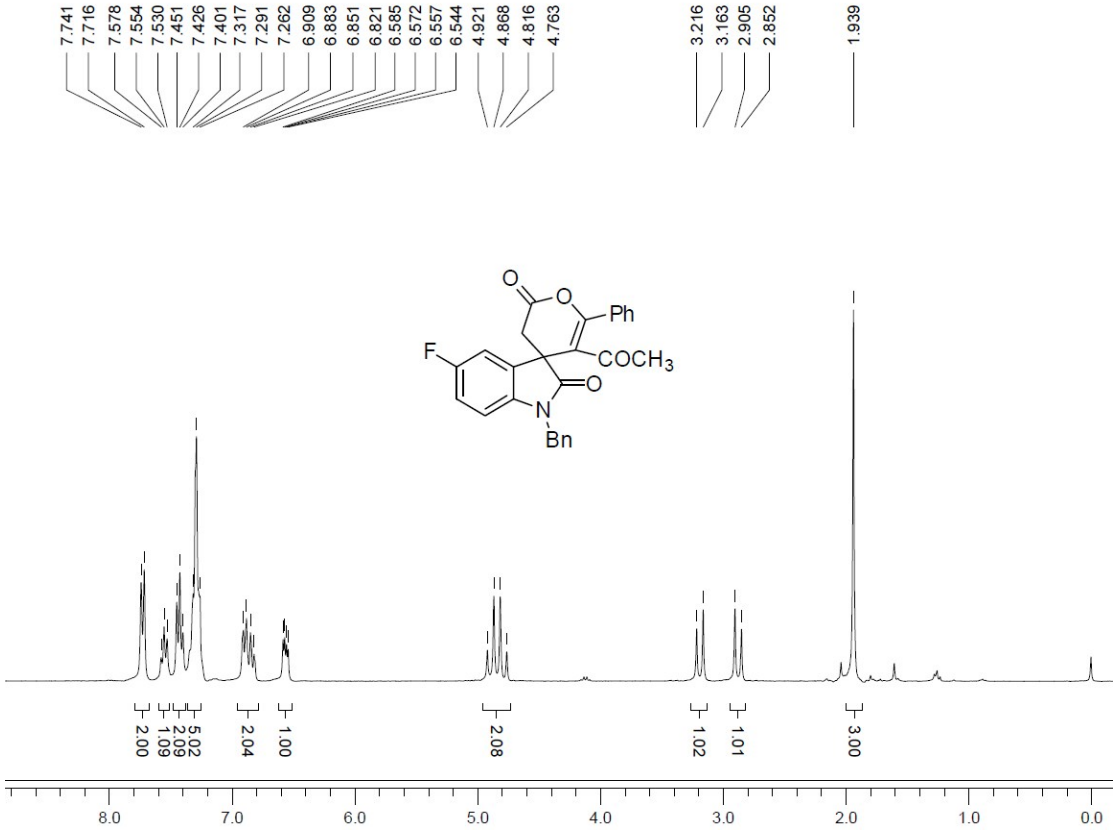
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6.572
6.557
6.544
4.921
4.868
4.816
4.763
3.216
3.163
2.905
2.852
1.939
O
O
Ph
F
COCH3
O
N
Bn
2.00
1.09
2.09
5.02
2.04
1.00
2.08
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1.01
3.00
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1.0
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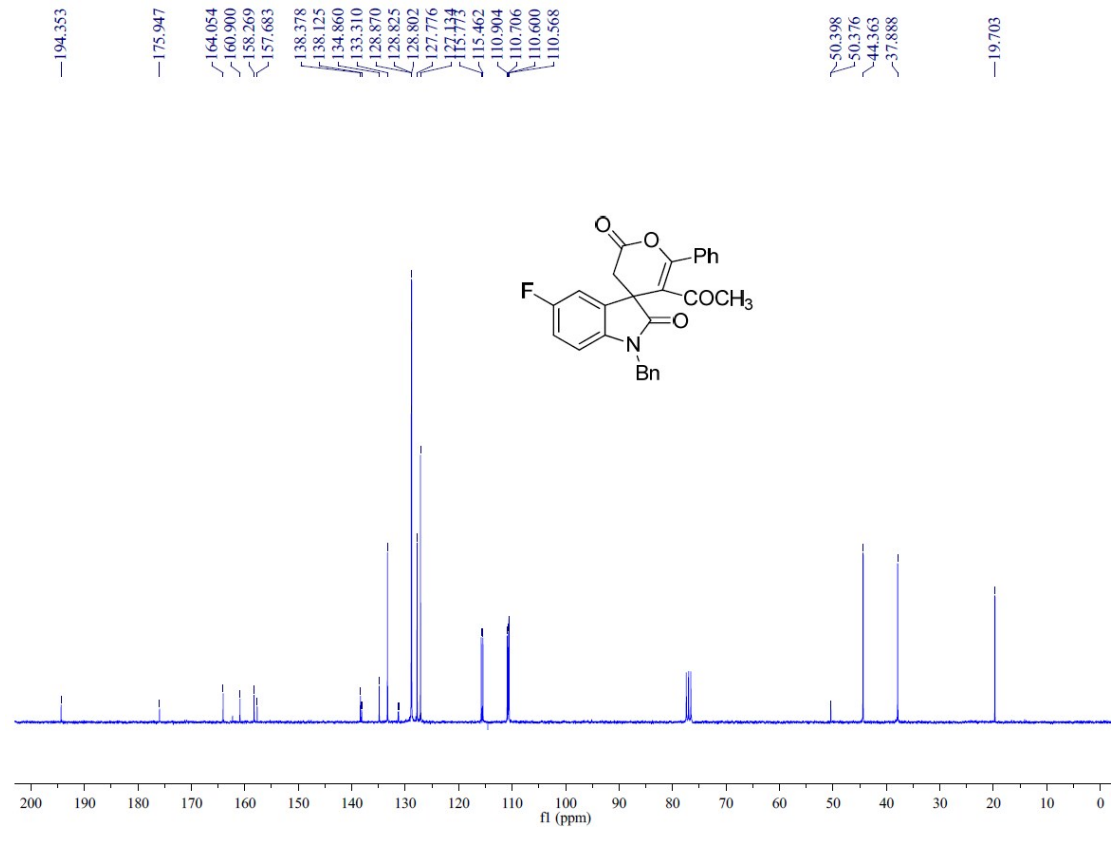
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128.802
127.776
115.462
110.904
110.706
110.600
110.568
50.398
50.376
44.363
37.888
19.703
O
O
Ph
F
COCH3
O
N
Bn
200
190
180
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140
130
120
110
100
90
80
70
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50
40
30
20
10
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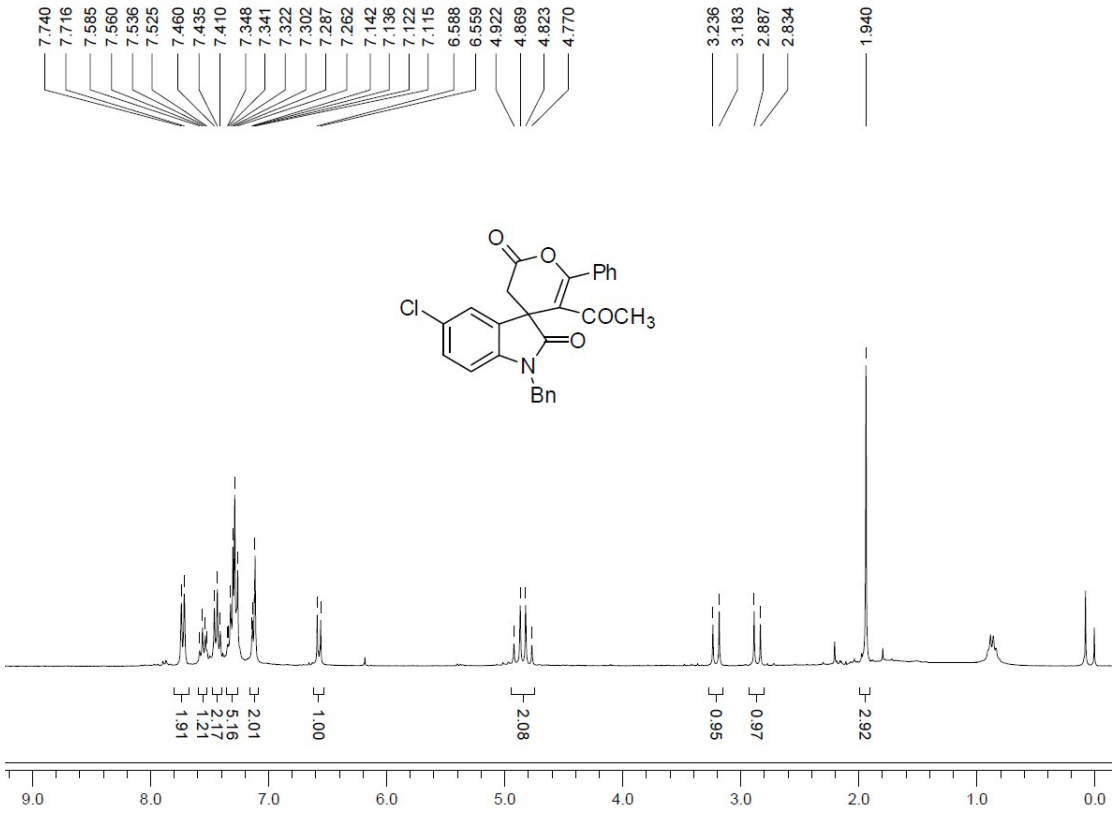
f1 (ppm)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7.460
7.435
7.410
7.348
7.341
7.322
7.302
7.287
7.262
7.142
7.136
7.122
7.115
6.588
6.559
4.922
4.869
4.823
4.770
3.236
3.183
2.887
2.834
1.940
O
O
Ph
Cl
COCH3
O
N
Bn
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1.21
2.17
9.16
2.01
1.00
2.08
0.95
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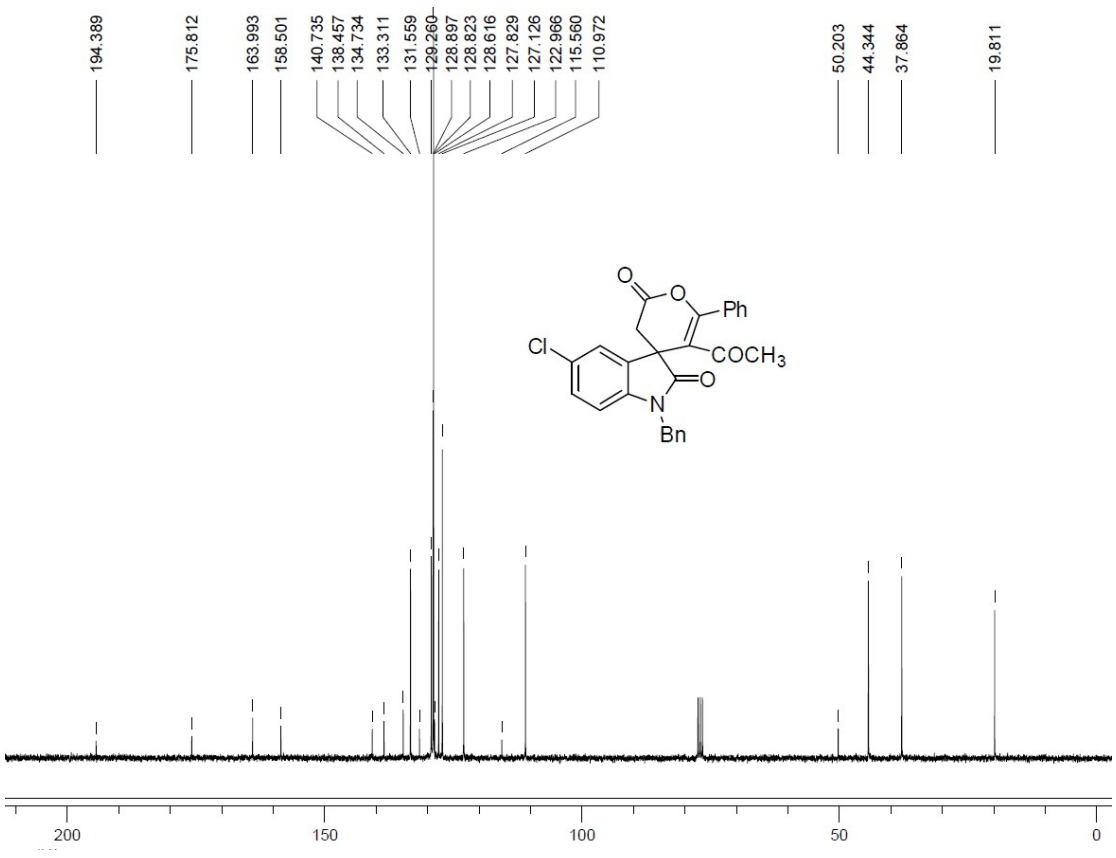
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127.829
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122.966
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110.972
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O
Ph
Cl
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O
N
Bn
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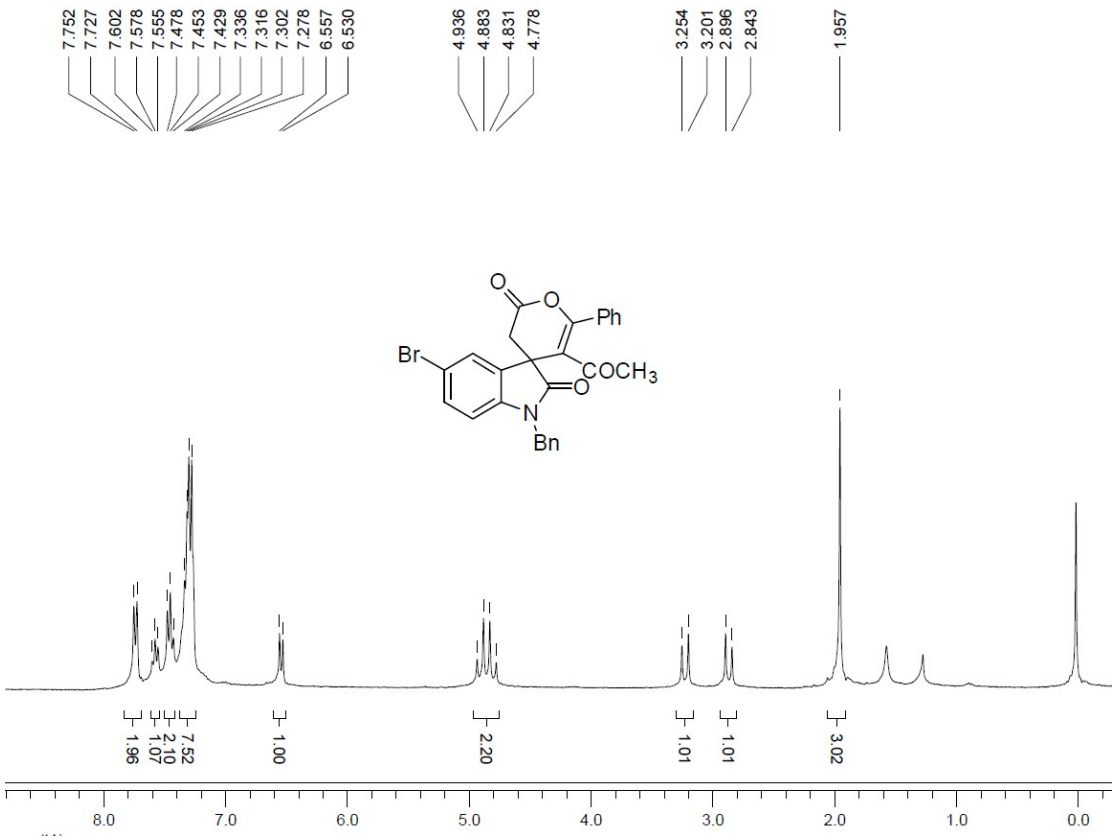
100
50
0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7.429
7.336
7.316
7.302
7.278
6.557
6.530
4.936
4.883
4.831
4.778
3.254
3.201
2.896
2.843
1.957
O
O
Ph
Br
COCH3
O
N
Bn
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1.07
1.10
7.52
1.00
2.20
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1.01
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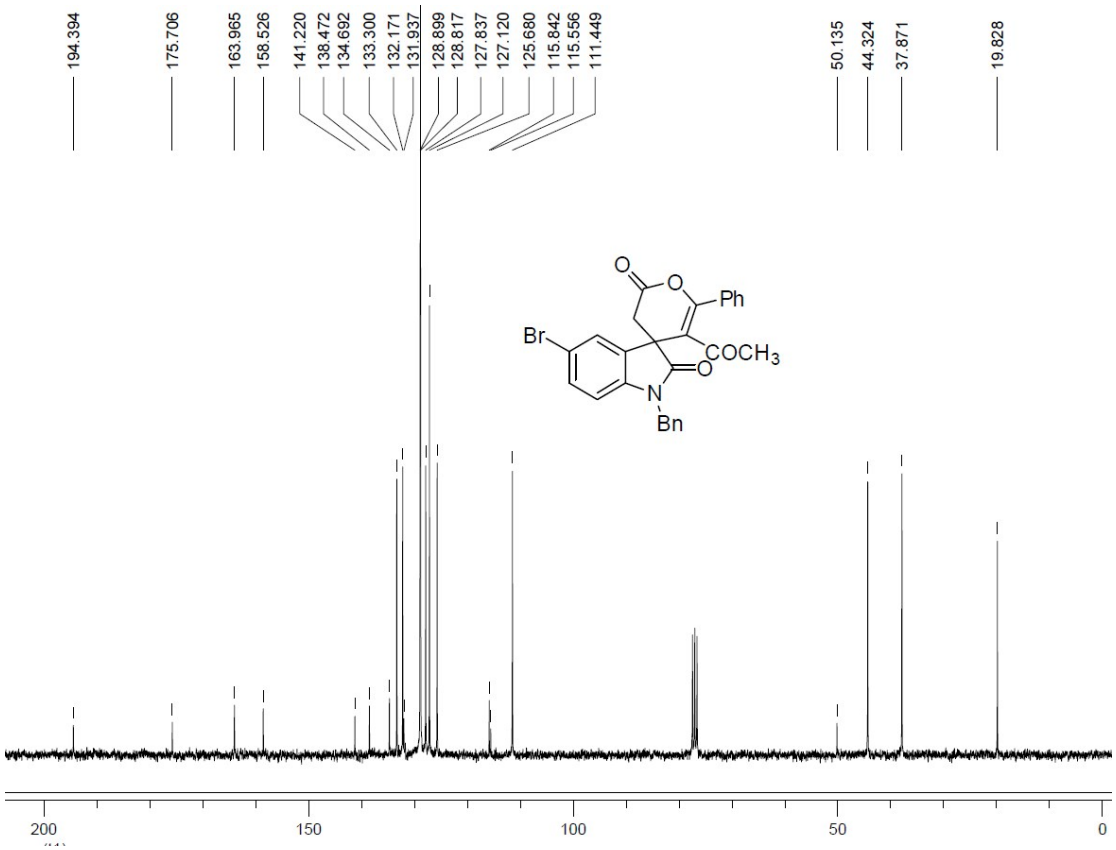
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128.817
127.837
127.120
125.680
115.842
115.556
111.449
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19.828
O
O
Ph
Br
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N
Bn
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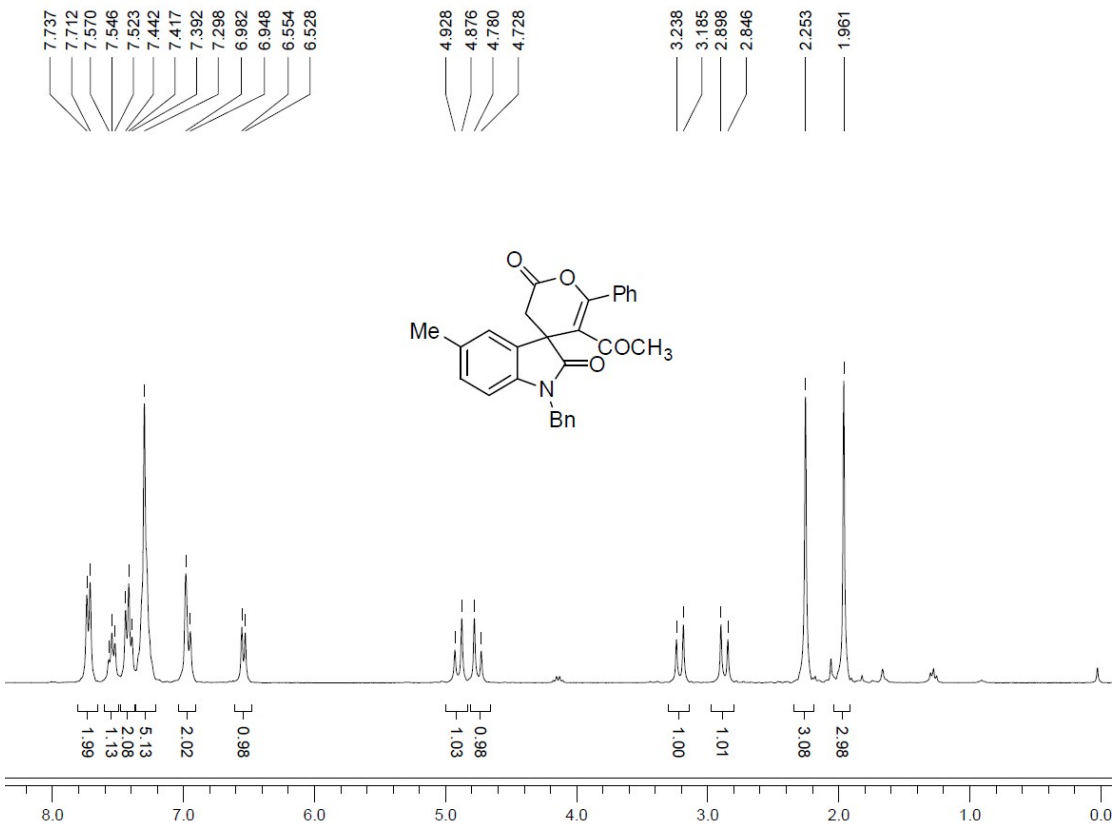
100
50
0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6.528
4.928
4.876
4.780
4.728
3.238
3.185
2.898
2.846
2.253
1.961
O
O
Ph
Me
COCH3
O
N
Bn
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1.13
2.08
5.13
2.02
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1.03
0.98
1.00
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4.0
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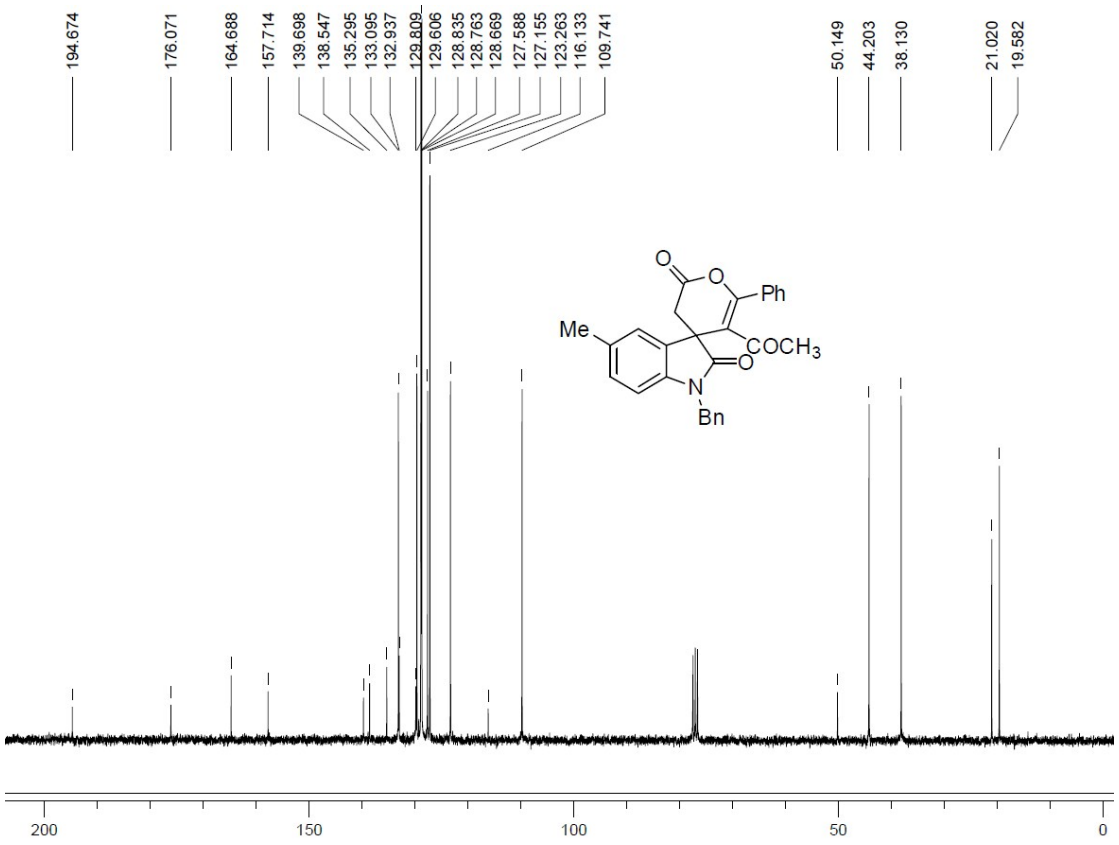
0.0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128.763
128.669
127.588
127.155
123.263
116.133
109.741
50.149
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19.582
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O
Ph
Me
COCH3
O
N
Bn
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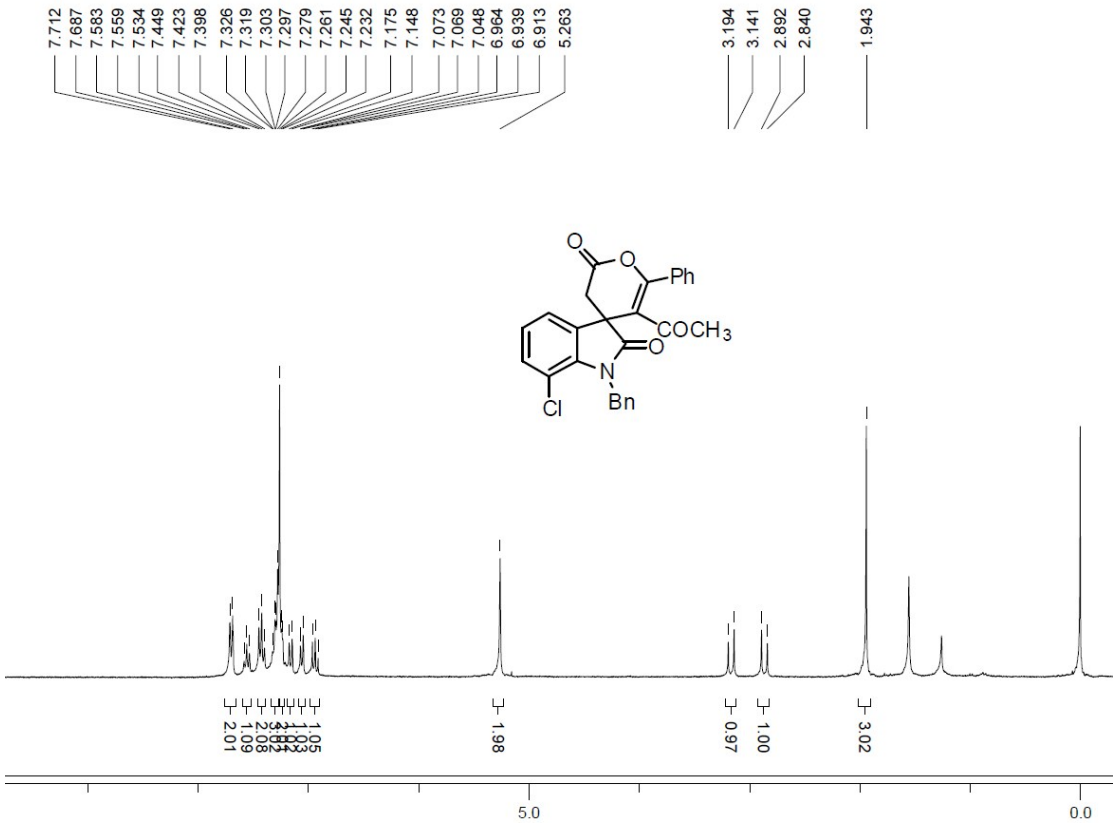
150
100
50
0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7.279
7.261
7.245
7.232
7.175
7.148
7.073
7.069
7.048
6.964
6.939
6.913
5.263
3.194
3.141
2.892
2.840
1.943
O
O
Ph
COCH3
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N
Bn
Cl
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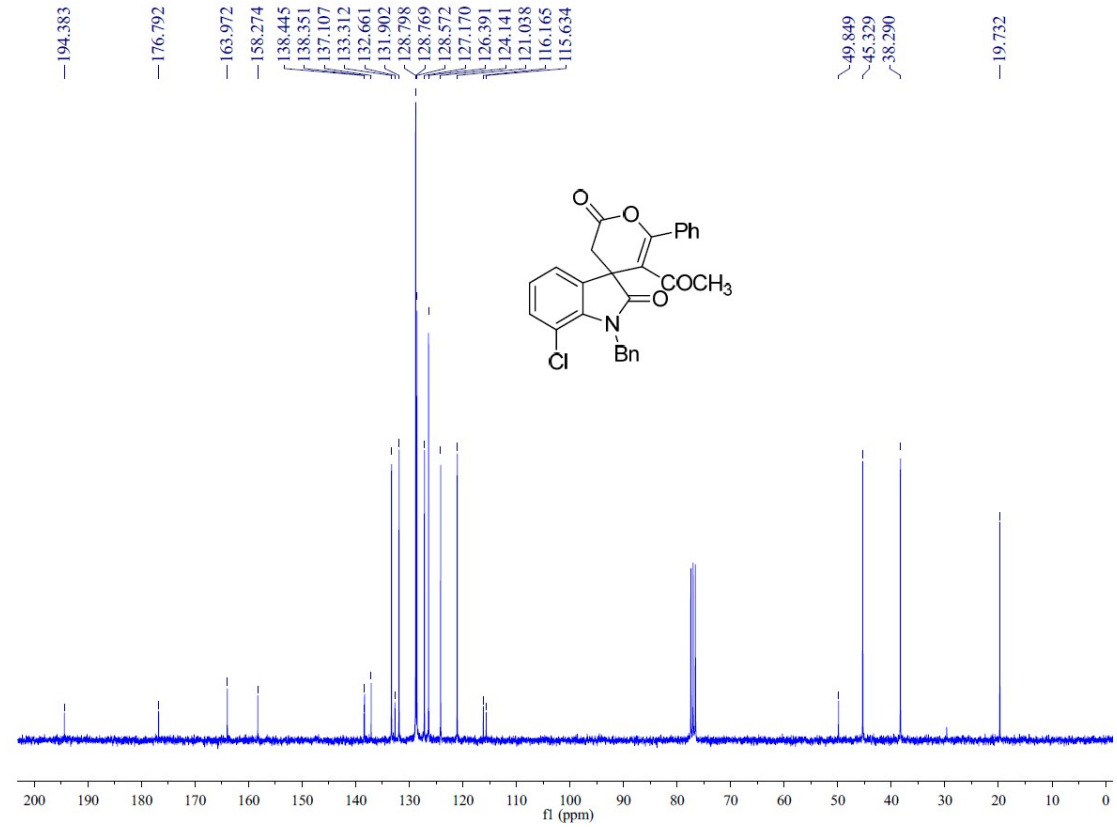
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128.572
127.170
126.391
124.141
121.038
116.165
115.634
49.849
45.329
38.290
19.732
O
O
Ph
COCH3
O
N
Bn
Cl
200
190
180
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90
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70
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50
40
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20
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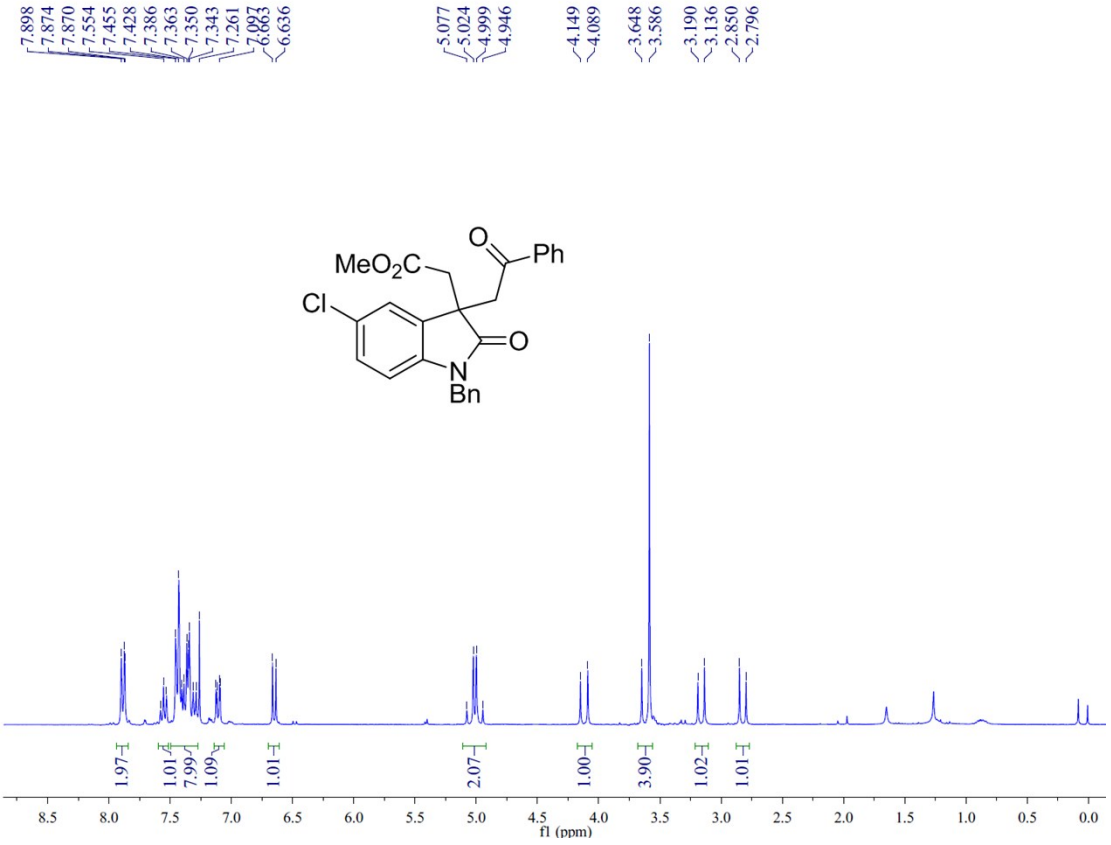
f1 (ppm)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6.636
5.077
5.024
4.999
4.946
4.149
4.089
3.648
3.586
3.190
3.136
2.850
2.796
MeO2C
Ph
O
Cl
O
N
Bn
1.97
1.01
7.99
1.09
1.01
2.07
1.00
3.90
1.02
1.01
8.5
8.0
7.5
7.0
6.5
6.0
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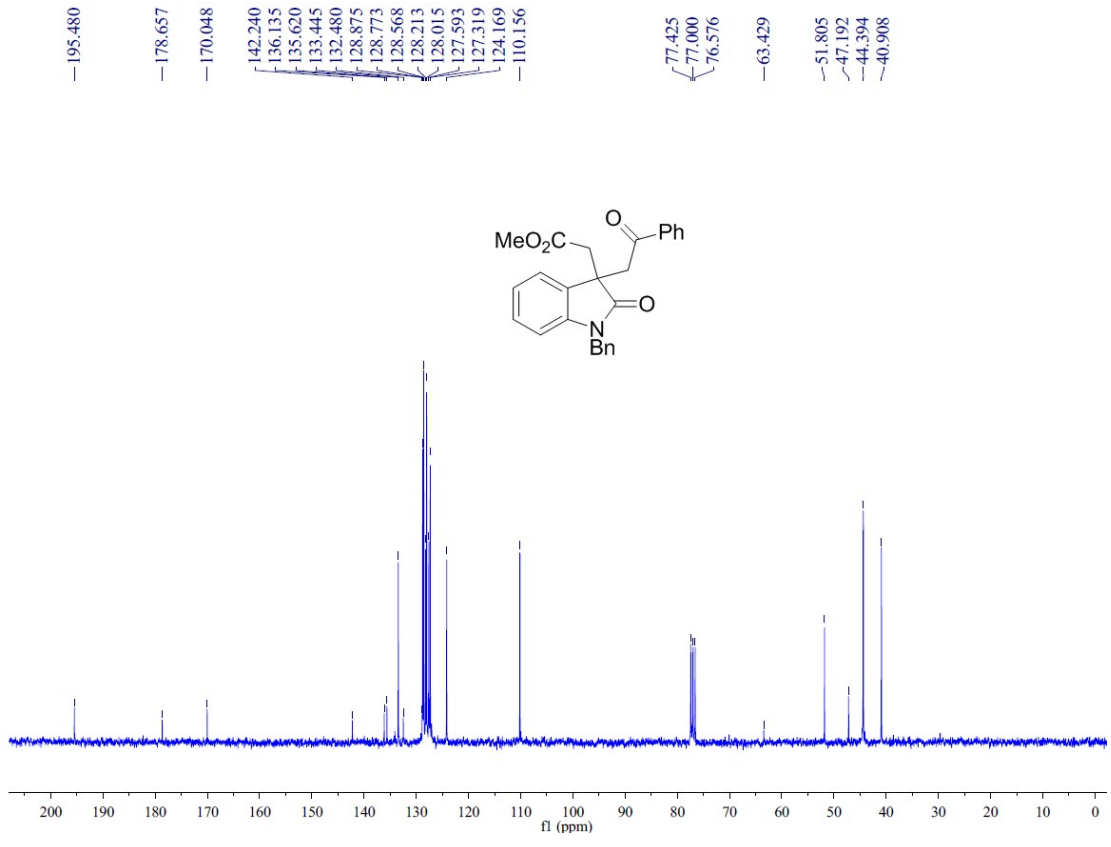
0.0
f1 (ppm)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128.568
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128.015
127.593
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76.576
63.429
51.805
47.192
44.394
40.908
MeO2C
Ph
O
O
N
Bn
200
190
180
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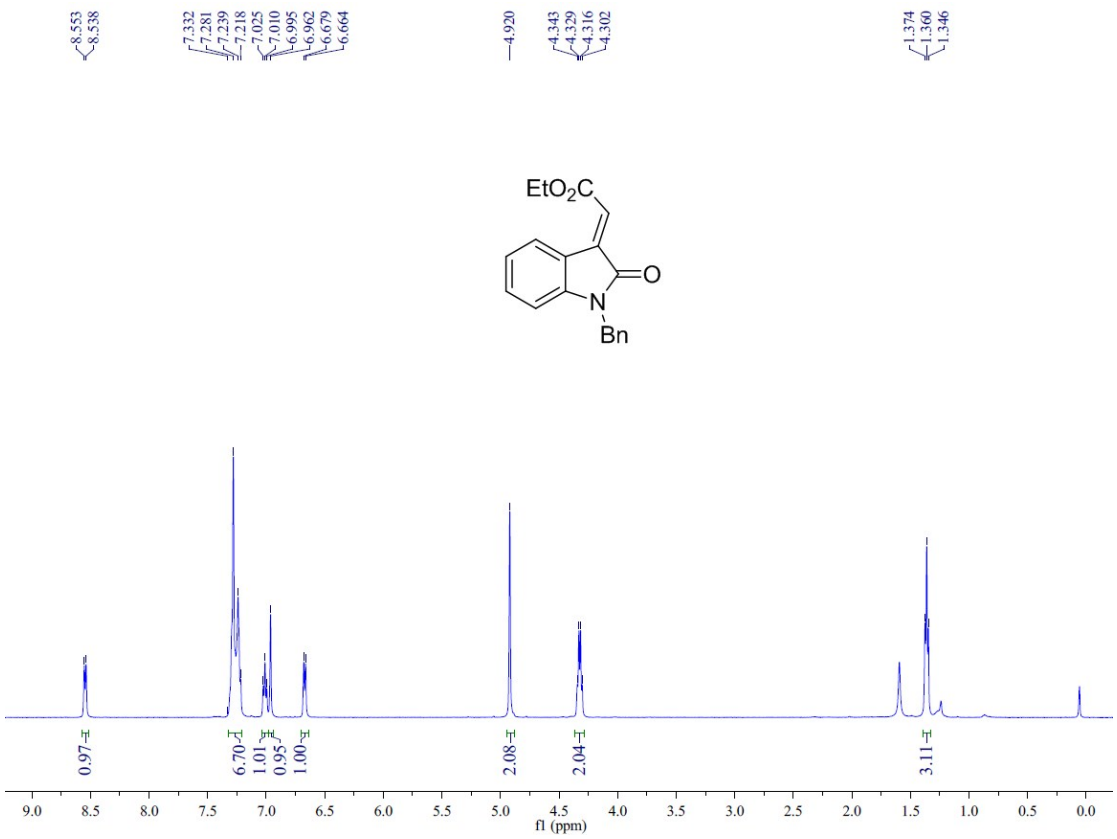
f1 (ppm)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7.010
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4.920
4.343
4.329
4.316
4.302
1.374
1.360
1.346
EtO2C
O
N
Bn
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6.70
1.01
0.95
1.00
2.08
2.04
3.11
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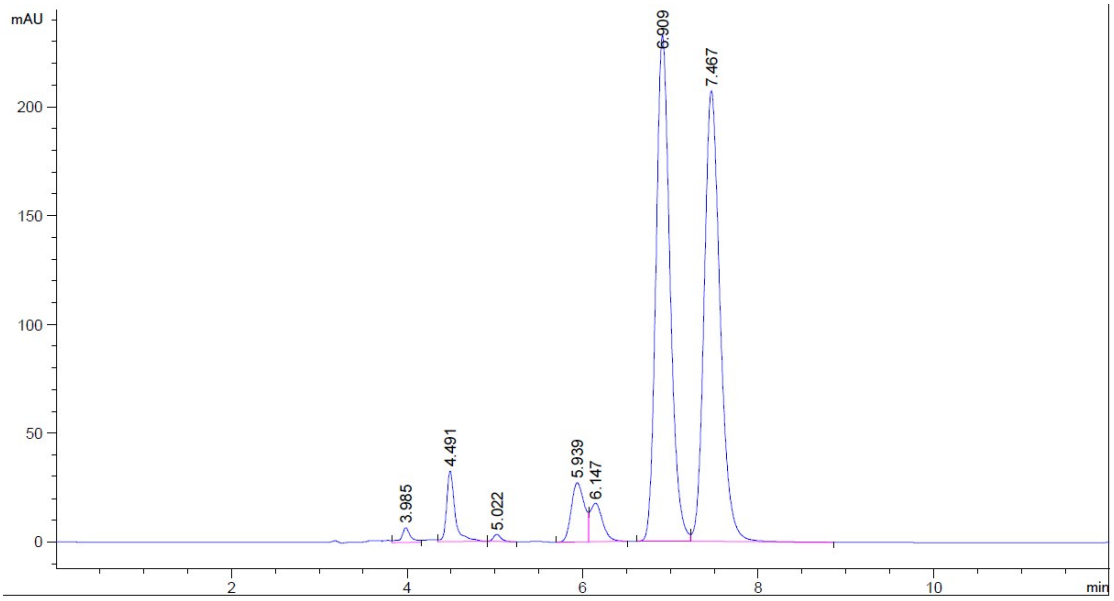
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

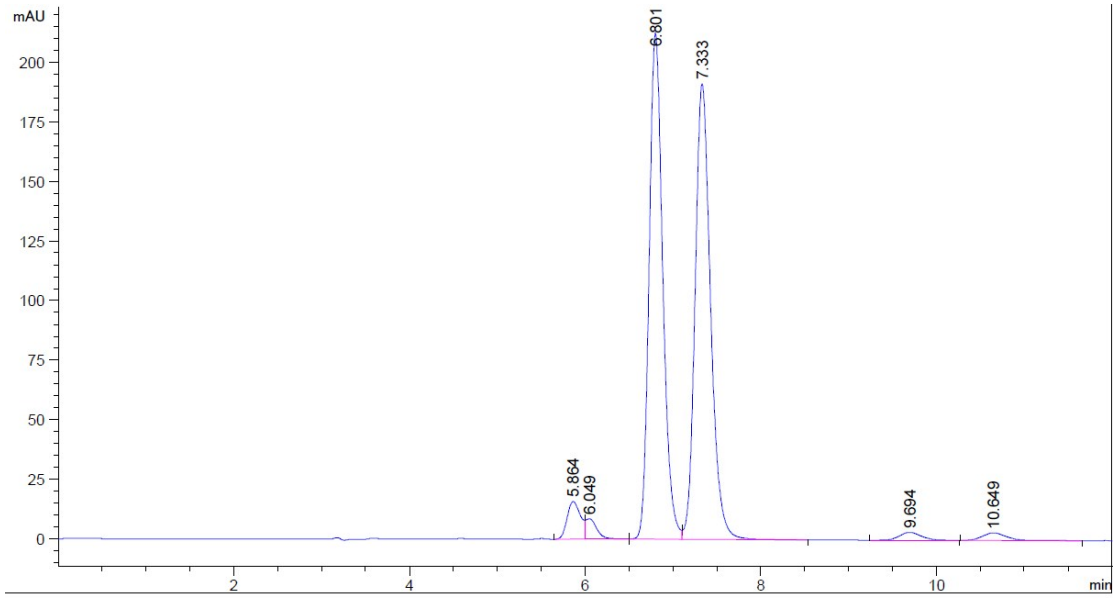
Racemic **7a**



Wavelength = 250 nm

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	3.985	VV	0.1004	47.12137	6.75049	0.7915
2	4.491	VB	0.0991	218.33531	32.59848	3.6676
3	5.022	BB	0.0926	19.78923	3.26985	0.3324
4	5.939	BV	0.1578	281.42203	27.17084	4.7273
5	6.147	VB	0.1467	174.53943	17.59498	2.9319
6	6.909	BV	0.1710	2592.20020	232.59561	43.5435
7	7.467	VB	0.1936	2619.72632	207.04919	44.0058

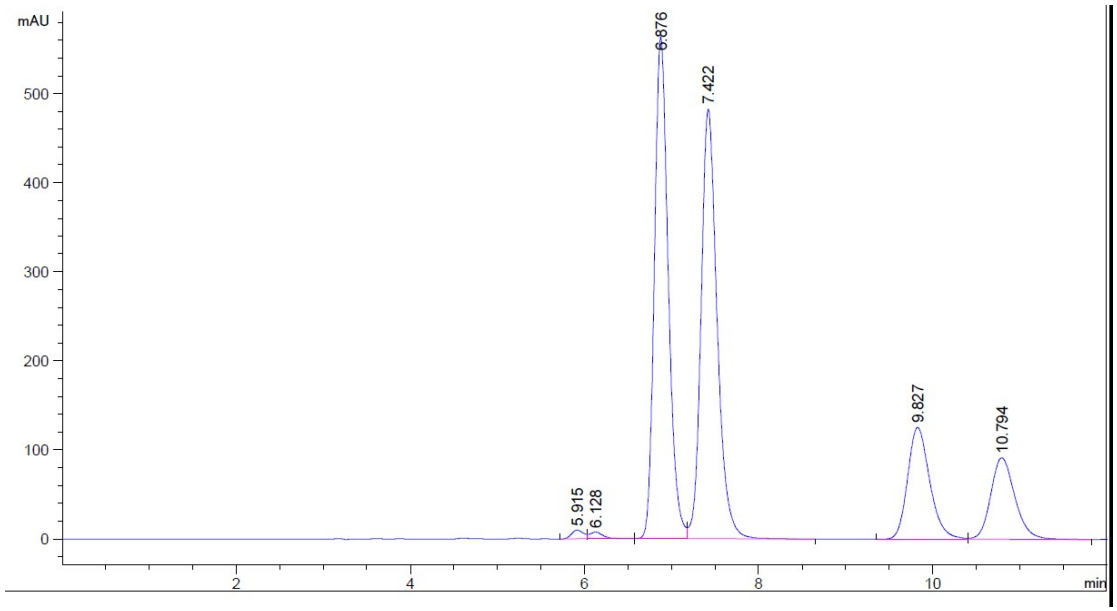
Precatalyst **G**



Wavelength = 254 nm

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	5.864	BV	0.1605	165.75880	15.78871	3.3181
2	6.049	VB	0.1324	76.55961	8.55839	1.5325
3	6.801	BV	0.1660	2296.79712	212.73007	45.9766
4	7.333	VB	0.1868	2341.61914	191.25034	46.8738
5	9.694	BB	0.2640	56.27768	3.26632	1.1265
6	10.649	BB	0.2881	58.56614	3.13337	1.1724

Precatalyst **H**



Wavelength = 254 nm

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	5.915	BV	0.1489	96.02527	9.83993	0.5800
2	6.128	VB	0.1542	78.04585	7.51224	0.4714
3	6.876	BV	0.1690	6227.41406	563.33710	37.6116
4	7.422	VB	0.1951	6170.60352	482.72256	37.2685
5	9.827	BV	0.2713	2219.40503	125.53606	13.4045
6	10.794	VB	0.2959	1765.68103	91.59210	10.6641