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Supporting Information

The Direct Electrophilic Cyanation of *β*-Keto Esters and Amides with Cyano Benziodoxole

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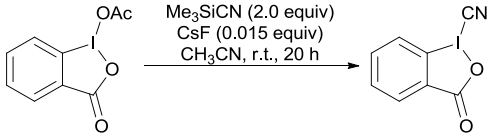
Contents

1. General Information

The ^{1}H-NMR (400 MHz) NMR, ^{13}C-NMR (100 MHz) spectra for solution in $CDCl_3$ are recorded on a Buruker Avance 400. ^{1}H NMR spectra are internally referenced to $CDCl_3$ signal (δ = 7.26 ppm) and ^{13}C NMR spectra are internally referenced to $CDCl_3$ signal (δ = 77.0 ppm). IR spectra were recorded on a Bruker ALPHA FT-IR-Spektrometer. The melting and decomposition points of **C1**, **C2** were recorded on a METTLER TOLEDO differential scanning calorimeter at a scan rate of 10 ℃ min^{-1}, the melting points of **2b-2d**, **2k-2m** and **2o** were determined on a XT4A melting point apparatus (uncorrected). HRMS was recorded on Bruker Apex IV FTMS. Analytical TLC is performed using F254 pre-coated silica gel plate. Column chromatography is performed with silica gel (200–300 mesh). Petroleum ether (PE) has a boiling point ranging 60–90 ℃. All reactions are performed in oven-dried glassware under a positive pressure of argon using typical vacuum-line techniques unless otherwise noted. Solvents are dry and transferred *via* syringe into the reaction vessels though a rubber septum. Substrate **1a-1g and 1j** was prepared according to literature procedure.[1] The tert-butyl and 1-admantyl β-keto esters **1h** and **1i** were synthesized by transesterification of the methyl ester.[2] The β-keto amides **1k-1q** was synthesized by aminolysis of the ethyl ester.

2. Synthesis of **C1**, **C2**, **C4**, **3a** and **3b**

1-Cyano-1,2-benziodoxol-3(1*H*)-one (**C1**).

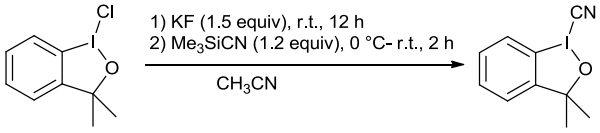


C1

Following a modified procedure,[3] CsF(27 mg, 0.015 equiv) and 1-acetoxy-1,2-benziodoxol-3(1*H*)-one[4] (4.58 g, 15.0 mmol, 1.0 equiv) were dissolved in dry acetonitrile(40 mL) under Ar atmosphere. After the addition of Me_3SiCN(4.3 mL, 30 mmol, 2.0 equiv), the mixture was stirred for 20 h at room temperature. The product was filtered off, washed with acetonitrile, and dried at 40 ℃ in Glass Oven under vacuum. Then the pure target product **C1** was obtained.

White solid, 89.8% yield; mp 194-197 ℃ (dec.) (lit.,[3] 155-158 ℃, lit.,[5] 173-175 ℃). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.31 (d, J = 7.4 Hz, 1H), 8.14 (dd, J = 7.4 Hz, 1.5 Hz, 1H), 8.03 (td, J = 7.4 Hz, 1.5 Hz, 1H), 7.90 (t, J = 7.4 Hz, 1H) ppm. IR (neat): $\tilde{\nu}$ = 2160, 1627 cm^{-1}. NMR data correspond to the reported values.[3,5]

1-Cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (**C2**)



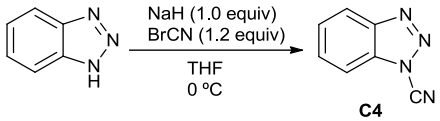
C2

The anhydrous KF (0.29 g, 5 mmol, 1.5 equiv) was flame-dried in a sheleck bottle. After the bottle was cooled to room temperature under Ar atmosphere, 1-chloro-3,3-dimethyl-1,2-benziodoxole[6] (0.99 g, 3.3 mmol, 1 equiv) followed by anhydrous MeCN (10 mL) was added. The resulting suspension was vigorously stirred for 12 h. Then the resulting suspension was cooled in an ice-salt bath to −10 ºC, and Me_3SiCN (0.63 mL, 4.3 mmol, 1.3 equiv) was injected. The reaction mixture was stirred for 2 h, allowed to warm to rt, and filtered over a 1 cm thick pad of Celite and the filter cake was washed with a little dry MeCN under Ar atmosphere. The brown solution was concentrated to dryness. The crude was washed with PE and dissolved in ether. The ether solution was filtered under Ar to remove the precipita-

tion. After addition of PE to the ether solution, the product was precipitated. The product was filtered off, washed with PE, and dried at room temperature in Glass Oven under vacuum.

White solid, 45.2% yield; mp 116-124 ℃ (lit.,[5] 97-101 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 6.8 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 6.4 Hz, 1H), 1.48 (s, 6H) ppm. ^{13}C (400 MHz, $CDCl_3$): 148.0, 131.6, 130.8, 128.2, 126.8, 111.4, 97.8, 80.3, 30.1 ppm. IR (neat): $\tilde{\nu}$ = 2138 cm^{-1}. NMR data correspond to the reported values.[5]

1-Cyanobenzo-1,2,3-triazol (**C4**)

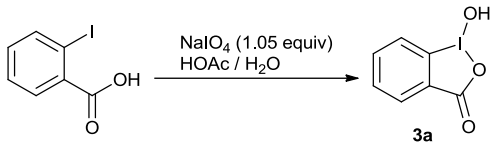


C4

Following a slightly modified procedure,[7] a solution of benzotriazole (1.49 g, 12.5 mmol, 1.0 equiv) in THF (5 mL) was added to NaH (0.5 g, 12.5 mmol, 1.0 euqiv) in THF (10 mL). The solution was stirred for 1 h, then cyanogen bromide (1.67 g, 15 mmol, 1.2 equiv) was added over 15 min in an ice bath. The reaction mixture was stirred in another 1h at room temperature. Then the solution was filtered and the solvent was evaporated to give the crude product. The crude product was sublimed at 75 ℃ (1 Torr) to give of l-cyanobenzo-1,2,3-triazole.

White crystal, 85.2% yield, mp 72-74 ℃ (lit.,[7] 73-75 ℃); IR (neat): $\tilde{\nu}$ = 2922, 2249, 1604, 1452, 1317, 1222, 956, 765 cm^{-1}.

1-Hydroxy-1,2-benziodoxol-3(1*H*)-one (**3a**).

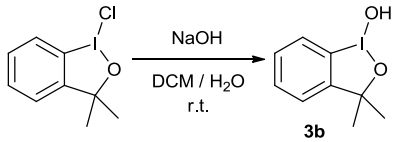


3a

Following a literature procedure,[4] To a mixture of acetic acid (15 mL) and of water (22 mL) were added 2-iodobenzoic acid (7.44 g, 30 mmol, 1.0 equiv) and $NaIO_4$ (6.9 g, 31.5 mmol, 1.05 equiv). The mixture was refluxed for 4 h and then cooled to 10 ℃ within 2 h. The mixture was charged into 180 mL of water. The solids were collected by filtration and washed with water (14 mL) and acetone (7 mL). The product was dried at 40 ℃ in a glass oven to yield g of **3a**.

White solid, 98% yield, mp 256-258 ℃ (lit.,[4] 258 ℃); IR (neat): $\tilde{\nu}$ = 2832, 2396, 1602, 1557, 1437, 1336, 739, 579 cm^{-1}.

1-Hydroxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (**3b**)

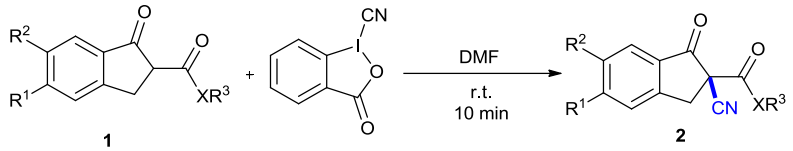


3b

Following a literature procedure,[8] the 1-chloro-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (296.5 mg, 1 mmol, 1 equiv) was dissolved in DCM (5 mL) and NaOH (40.0 mg, 1 mmol, 1.00 equiv) in water (1 mL) was added. After 3 h, the organic layer was separated, dried over $MgSO_4$, filtered over $MgSO_4$ and concentrated. The crude product was recrystallized in EtOAc, washed with PE and dried under vacuum to afford **3b**.

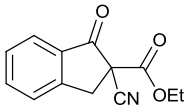
Needle crystal, 38% yield, mp 151-153 ℃ (lit.,[4] 140-142 ℃); IR (neat): $\tilde{\nu}$ = 2956, 1426, 1152, 952, 867, 767, 630 cm^{-1}.

3. General procedure for the electrophilic cyanation of β-keto esters and amides



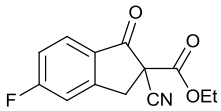
The cyclic *β*-keto ester or amide (0.1 mmol, 1.0 equiv) and cyano benziodoxole **C1** (0.12 mmol, 1.2 equiv) were added into a reaction tube. After the addition of DMF (0.2 mL), the reaction mixture was stirred at room temperature until TLC indicated the completion of the reaction (0.15 h -1 h). The crude mixture was purified directly by column chromatography on silica gel with PE/EtOAc (15:1 to 10:1) as eluent.

4. Characterization data for cyanation products



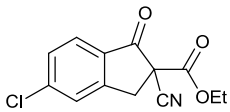
Ethyl 2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2a**)

White solid, 95% yield; mp 91-93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.94 (d, J = 17.3 Hz, 1H), 3.69 (d, J = 17.3 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 164.0, 151.5, 136.9, 132.1, 128.9, 126.5, 126.3, 115.8, 64.2, 54.3, 37.5, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2983, 2247, 1725, 1589, 1243, 1210, 902, 749 cm^{-1}. NMR data correspond to the reported values.[9]



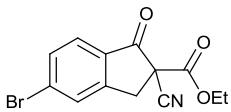
Ethyl 2-cyano-5-fluoro-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2b**)

White solid, 89% yield; mp 74-75 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, J = 8.3 Hz, 5.2 Hz, 1H), 7.23-7.18 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 3.93 (d, J = 17.5 Hz, 1H), 3.67 (d, J = 17.5 Hz, 1H), 1.35 (t, J = 7.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.8, 168.3 (d, $^{1}J_{C\text{-}F}$ = 260.3 Hz), 167.0, 163.8, 154.6 (d, $^{3}J_{C\text{-}F}$ = 10.9 Hz), 128.8 (d, $^{3}J_{C\text{-}F}$ = 10.9 Hz), 128.4 (d, $^{4}J_{C\text{-}F}$ = 1.8 Hz), 117.6 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 115.5, 113.4 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 64.4, 54.5, 37.2 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2989, 2247, 1724, 1589, 1234, 1209, 1087, 978, 863, 648 cm^{-1}. HRMS: calc. for $C_{13}H_{14}FN_2O_3$ [M+NH_4]$^{+}$: 265.0983 found: 265.0985.



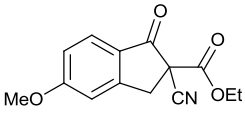
Ethyl 5-chloro-2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2c**)

White solid, 87% yield; mp 66-67 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 0.7 Hz, 1H), 7.47 (dd, J = 8.27 Hz, 1.6 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.92 (d, J = 17.4 Hz, 1H), 3.66 (d, J = 17.4 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.3, 163.7, 152.9, 143.9, 130.5, 129.9, 127.2, 126.8, 115.4, 64.4, 54.4, 37.1, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2940, 2246, 1725, 1595, 1242, 1207, 1062, 905, 759 cm^{-1}. HRMS: calc. for $C_{13}H_{14}ClN_2O_3$ [M+NH_4]$^{+}$: 281.0687 found: 281.0686.



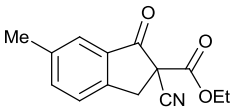
Ethyl 5-bromo-2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2d**)

White solid, 88% yield; mp 94-96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 0.8 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.64 (m, 1CH), 4.33 (q, J = 7.1 Hz, 2H), 3.92 (d, J = 17.4 Hz, 1 H), 3.66 (d, J = 17.4 Hz, 1 H), 1.34 (t, J = 7.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.5, 163.7, 152.9, 132.8, 132.7, 131.0, 129.9, 127.2, 115.4, 64.4, 54.3, 37.0, 13.9 ppm. HRMS: calc. for $C_{13}H_{10}BrNNaO_3$ [M+Na]$^+$: 329.9736 found: 329.9736.



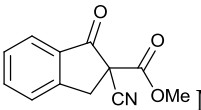
Ethyl 2-cyano-5-methoxy-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2e**)

Colorless oil, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.6 Hz, 1H), 6.99 (dd, J = 8.6, 1.9 Hz, 1H), 6.94 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 3.88 (d, J = 17.3 Hz, 1H), 3.61 (d, J = 17.3 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.5 , 167.0 , 164.4 , 154.8 , 128.0 , 124.9 , 117.2 , 116.1 , 109.5 , 64.1 , 56.0 , 54.6 , 37.4 , 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2939, 2247, 1716, 1595, 1251, 1089, 890 cm^{-1}. HRMS: calc. for $C_{14}H_{14}NO_4$ [M+H]$^+$: 260.0917 found: 260.0916.



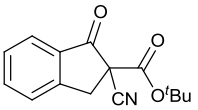
Ethyl 2-cyano-5-methyl-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2f**)

Colorless oil, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.4 (d, J = 7.9 Hz, 1H), 4.31 (q, J = 7.12Hz, 2H), 3.88 (d, J = 17.1 Hz, 1H), 3.63 (d, J = 17.1 Hz, 1H), 2.43 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 164.2, 149.0, 139.2, 138.3, 132.3, 126.1, 126.0, 115.9, 64.1, 54.6, 37.2, 21.0, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2983, 2248, 1723, 1494, 1249, 1194, 1009, 752 cm^{-1}. HRMS: calc. for $C_{14}H_{17}N_2O_3$ [M+NH_4]$^+$: 261.1234 found: 261.1231.



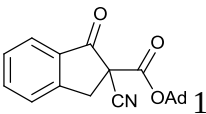
Methyl 2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2g**)

Colorless oil, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.8 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.55 (dd, J = 7.8 Hz, 0.6 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 3.95 (d, J = 17.37 Hz, 1H), 3.88 (d, J = 0.7 Hz, 3H), 3.70 (d, J = 17.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 164.6, 151.5, 137.1, 132.1, 129.1, 126.6, 126.4, 115.8, 54.7, 54.2, 37.6 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2248, 1725, 1603, 1443, 1248, 906, 750 cm^{-1}. HRMS: calc. for $C_{12}H_{13}N_2O_3$ [M+NH_4]$^+$: 233.0921 found: 233.0917.



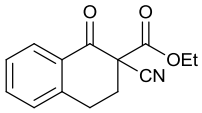
Tert-butyl 2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2h**)

Colorless oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 7.8 Hz, 1H), 7.75-7.68 (m, 1H), 7.53 (d, J = 7.8Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 3.89 (d, J = 17.2 Hz, 1H), 3.65 (d, J = 17.2 Hz, 1H), 1.50 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 162.8, 151.6, 136.7, 132.3, 128.8, 126.4, 126.1, 116.1, 85.8, 55.2, 37.5, 27.6 ppm. IR (neat): $\tilde{\nu}$ = 2981, 2247, 1725, 1604, 1251, 1146, 902, 834, 736 cm^{-1}. HRMS: calc. for $C_{15}H_{19}N_2O_3$ [M+NH_4]$^+$: 275.1390 found: 275.1390.



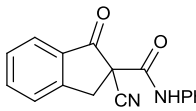
1-Adamantyl 2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**2i**)

Colorless oil, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.8 Hz, 1H), 7.74-7.68 (m, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 3.88 (d, J = 17.2 Hz, 1H), 3.64 (d, J = 17.2 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 6H), 1.64 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 162.3, 151.6, 136.7, 132.3, 128.7, 126.4, 126.1, 116.1, 85.8, 55.3, 40.8, 37.5, 35.8, 30.9 ppm. IR (neat): $\tilde{\nu}$ = 2910, 2246, 1725, 1603, 1210, 1042, 903, 724 cm^{-1}. HRMS: calc. for $C_{21}H_{21}NNaO_3$ [M+Na]$^+$: 358.1414 found: 358.1411.



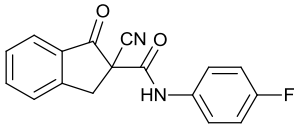
Ethyl 2-cyano-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2j**)

Colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (dd, J = 7.9 Hz, 1.1 Hz, 1H), 7.58 (td, J = 7.6 Hz, 1.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 4.40-4.32 (m, 2H), 3.33-3.25 (m, 1H), 3.15-3.08 (m, 1H), 2.92-2.81 (m, 1H), 2.68-2.58 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.0, 164.7, 142.5, 135.1, 129.4, 129.0, 129.0, 127.6, 114.8, 63.7, 55.5, 31.3, 25.4, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2983, 2245, 1742, 1692, 1599, 1223, 909, 741 cm^{-1}. HRMS: calc. for [M+H]$^+$: 244.0968 found: 244.0968.



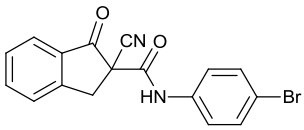
2-Cyano-*N*-phenyl-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2k**)

White solid, 94% yield; 136-139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.80-7.70 (m, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.7 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 7.43 Hz, 1H), 4.36 (d, J = 17.5 Hz, 1H), 3.64 (d, J = 17.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8, 158.1, 152.6, 137.4, 136.6, 131.8, 129.1, 128.9, 126.6, 126.1, 125.5, 120.3, 116.9, 54.1, 35.3 ppm. IR (neat): $\tilde{\nu}$ = 3331, 2250, 1718, 1598, 1535, 1272, 905, 753, 690 cm^{-1}. HRMS: calc. for [M+NH_4]$^+$: 277.0972 found: 277.0970.



2-Cyano-*N*-(4-fluorophenyl)-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2l**)

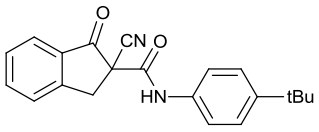
White solid, 85% yield; mp 136-139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): 8.47 (s, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.76 (t, J = 7.12, 1H), 7.58 (s, J = 7.7 Hz, 1H), 7.52-7.47(m, 3H), 7.05 (t, J = 8.6 Hz, 2H), 4,35 (d, J = 17.6 Hz, 1H), 3.65 (t, J = 17.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.6, 154.6 (d, $^1J_{C\text{-}F}$ = 290.2 Hz), 147.4, 132.3, 127.4 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 126.6, 123.7, 121.5, 121.0, 117.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 111.7, 110.7 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 104.5, 48.8, 30.1 ppm. IR (neat): $\tilde{\nu}$ = 3341, 2923, 2239, 1723, 1606, 1508, 1272, 1213, 906, 832 cm^{-1}. HRMS: calc. for $C_{17}H_{12}FN_2O_2$ [M+H]$^+$: 295.0877 found: 295.0877.



N-(4-Bromophenyl)-2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2m**)

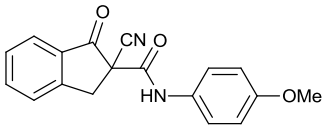
White solid, 84% yield; mp 135-140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): 8.50 (s, 1H), 7.85 (d, J = 7.1 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.51-7.43 (m, 5H), 4.35 (d, J = 17.6 Hz, 1H), 3.65 (d, J = 17.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 158.3, 152.6, 137.6, 135.7, 132.1, 131.7, 129.0, 126.7, 126.2, 121.9, 118.4, 116.7, 54.1, 35.2 ppm. IR (neat): $\tilde{\nu}$ = 3336, 2926, 2239,

1726, 1595, 1527, 1488, 1395, 1727, 1073, 906, 824 cm^{-1}. HRMS: calc. for $C_{17}H_{11}BrN_2NaO_2$ $[M+Na]^+$: 376.9896 found: 376.9894.



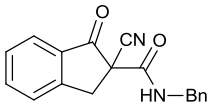
N-(4-(tert-butyl)phenyl)-2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2n**)

Colorless oil, 90% yield. ^1H NMR (400 MHz, $CDCl_3$): 8.42 (s, 1H), 7.84 (d, *J* = 7.7, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.50-7.45 (m, 3H), 7.37 (d, *J* = 8.5 Hz, 2H), 4.36 (d, *J* = 17.5 Hz, 1H), 3.64 (d, *J* = 17.5 Hz, 1H), 1.30 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8, 158.1, 152.6, 148.7, 137.4, 134.1, 131.9, 128.8, 126.6, 126.1, 126.0, 120.0, 117.0, 54.1, 35.3, 34.5, 31.3 ppm. IR (neat): $\tilde{\nu}$ = 3341, 2962, 2252, 1725, 1598, 1523, 1271, 1202, 905, 832, 727 cm^{-1}. HRMS: calc. for $C_{21}H_{20}N_2NaO_2$ $[M+Na]^+$: 355.1414 found: 355.1417.



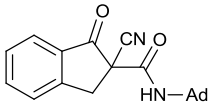
2-Cyano-*N*-(4-methoxyphenyl)-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2o**)

White solid, 95% yield; mp 109-113 ℃. ^1H NMR (400 MHz, $CDCl_3$): 8.40 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.1 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.50-7.42 (m, 3H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.35 (d, *J* = 17.5 Hz, 1H), 3.79 (s, 3H), 3.63 (d, *J* = 17.53 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 157.2, 152.7, 141.8, 137.4, 131.9, 129.7, 128.8, 126.6, 126.1, 122.2, 117.0, 114.2, 55.4, 54.0, 35.4 ppm. IR (neat): $\tilde{\nu}$ = 3350, 2923, 2237, 1711, 1531, 1230, 1176, 994, 826, 739 cm^{-1}. HRMS: calc. for $C_{18}H_{15}N_2O_3$ $[M+H]^+$: 307.1077 found: 307.1075.



N-Benzyl-2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2p**)

Colorless oil, 90% yield. ^1H NMR (400 MHz, $CDCl_3$): 7.83 (d, *J* = 7.72 Hz, 1H), 7.73 (t, *J* = 7.73 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.52 Hz, 1H), 7.38-7.34 (m, 2H), 7.32-7.26 (m, 3H), 7.08 (s, 1H), 4.56-4.46 (m, 2H), 4.28 (d, *J* = 17.5 Hz, 1H), 3.59 (d, *J* = 17.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 160.9, 152.7, 137.2, 136.6, 131.9, 128.9, 128.7, 127.8, 127.5, 126.6, 126.1, 117.2, 53.8, 44.9, 35.6 ppm. IR (neat): $\tilde{\nu}$ = 3363, 2927, 2240, 1726, 1523, 1252, 906, 744 cm^{-1}. HRMS: calc. for $C_{18}H_{14}N_2NaO_2$ $[M+Na]^+$: 313.0947 found: 313.0950. 0.



N-(1-Adamantyl) -2-cyano-1-oxo-2,3-dihydro-*1H*-indene-2-carboxamide (**2q**)

Colorless oil, 93% yield. ^1H NMR (400 MHz, $CDCl_3$): 7.80 (d, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.09 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 6.38 (s, 1H), 4.19 (d, *J* = 17.4, 1H), 3.50 (d, *J* = 17.4 Hz, 1H), 6.38 (s, 1H), 2.09 (s, 3H), 2.00 (s, 6H), 1.67 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 158.9, 152.7, 137.0, 132.0, 128.6, 126.5, 125.9, 117.6, 54.3, 53.6, 40.9, 36.1, 35.4, 29.3 ppm. IR (neat): $\tilde{\nu}$ = 3363, 2907, 2236, 1724, 1520, 1270, 1234, 906, 744 cm^{-1}. HRMS: calc. for $C_{21}H_{22}N_2NaO_2$ $[M+Na]^+$: 357.1573 found: 357.1577.

5. Reference

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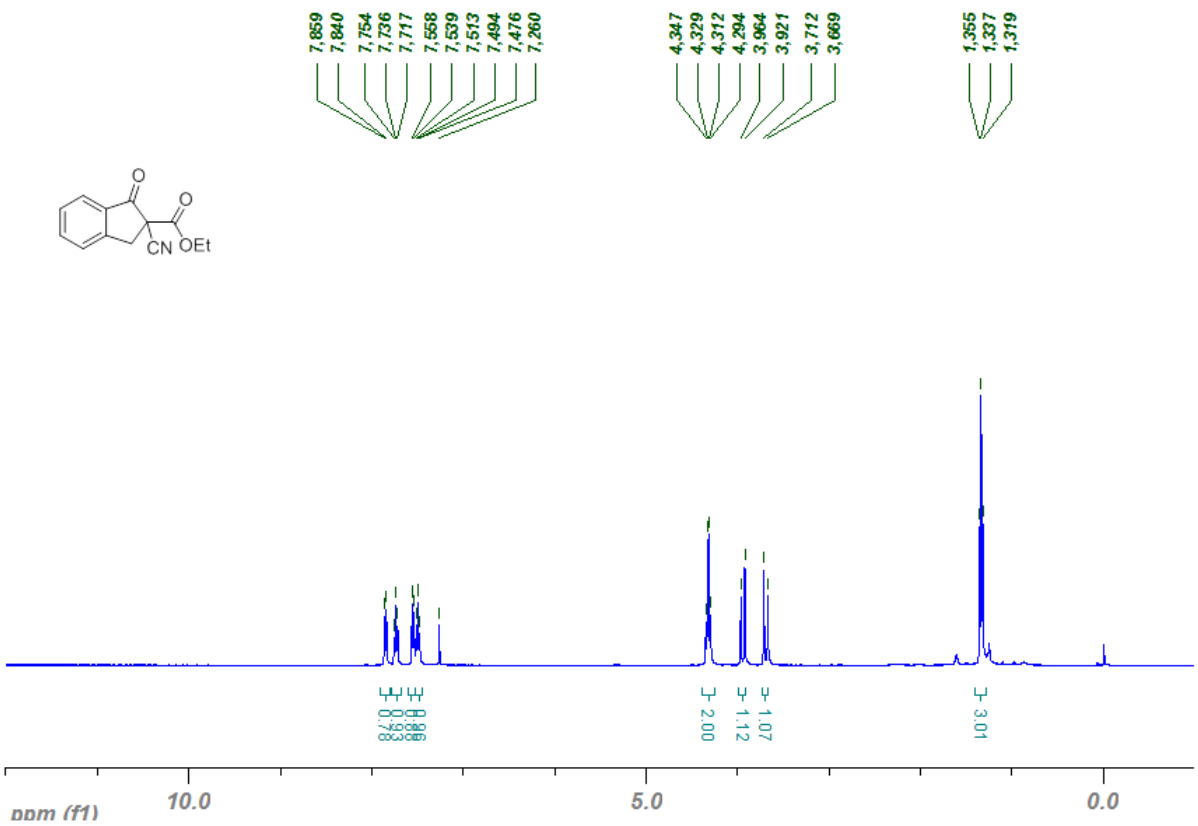
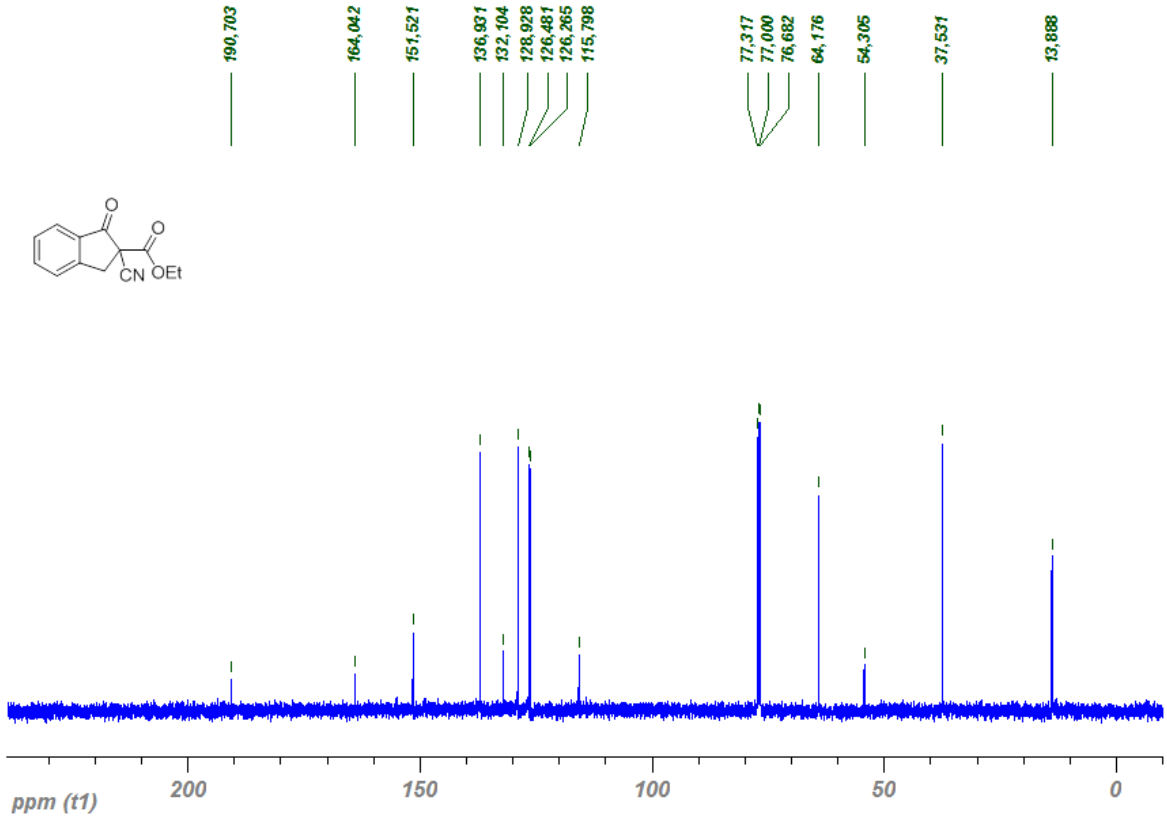
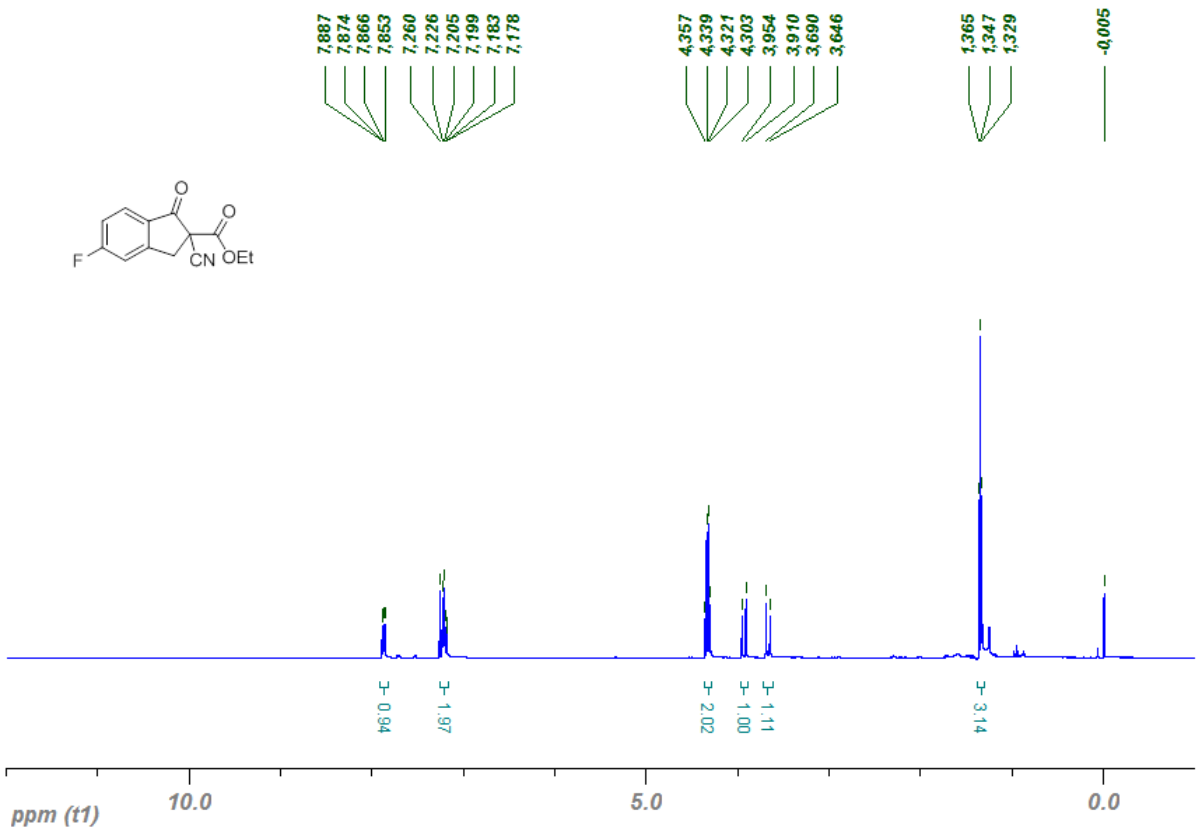
6. NMR Spectra



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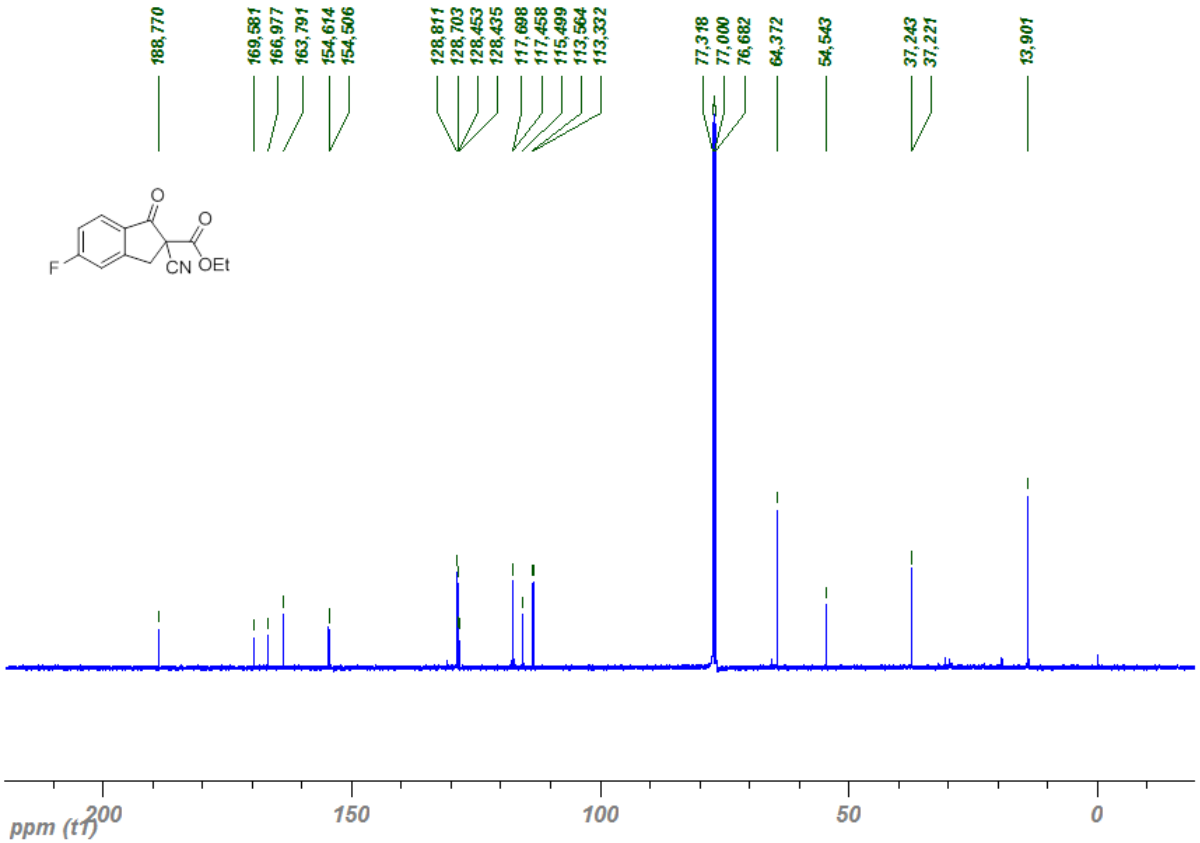
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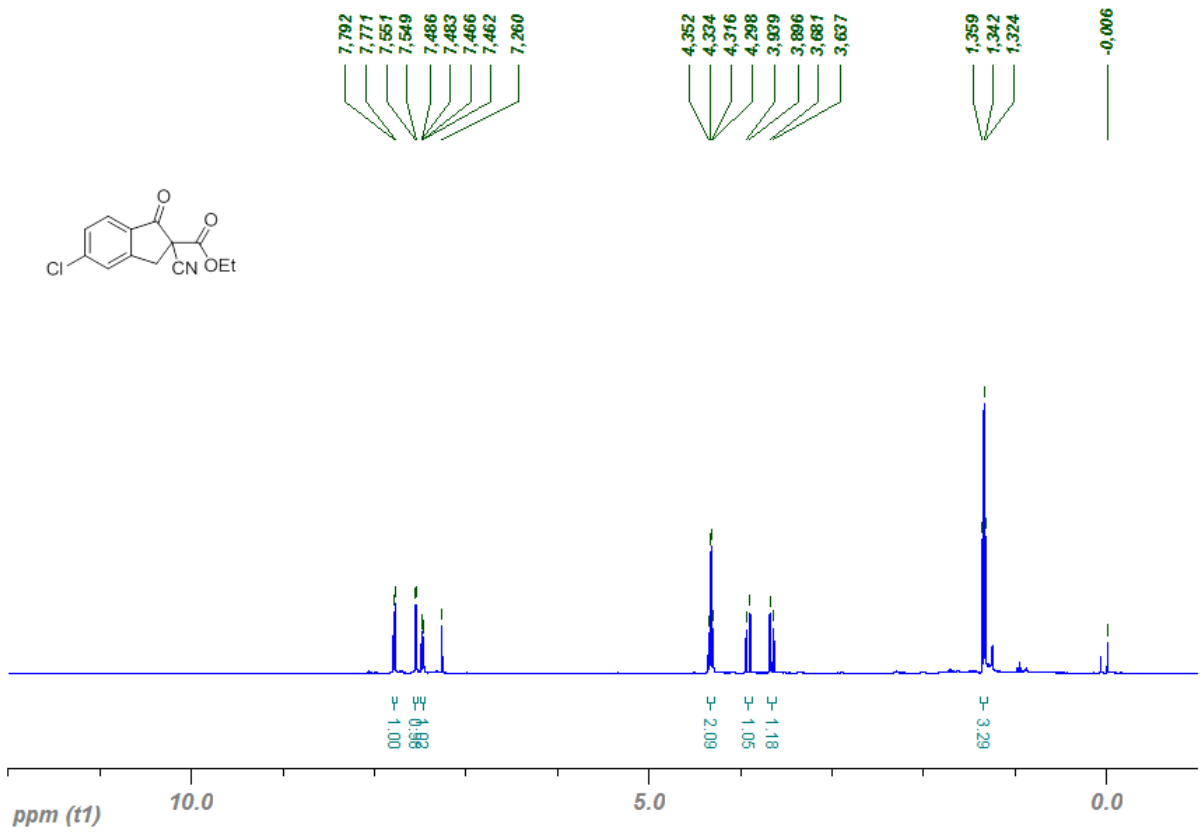
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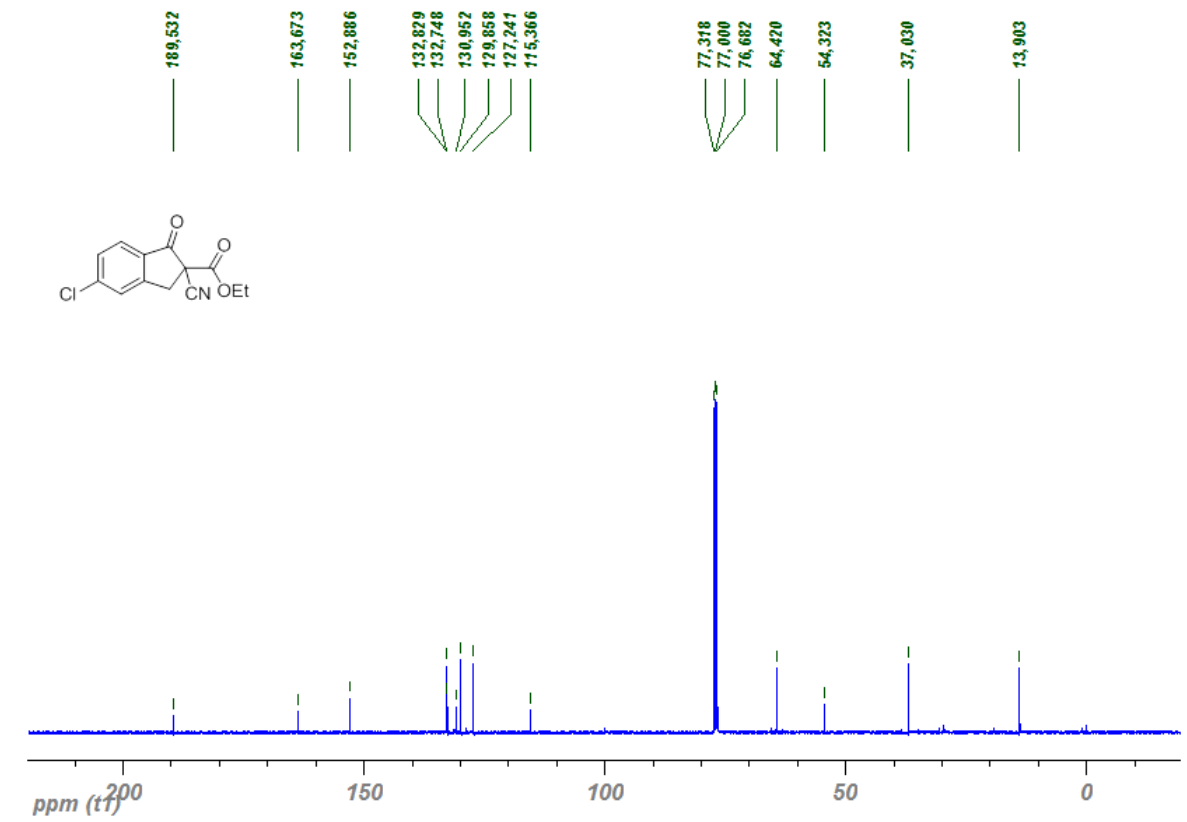
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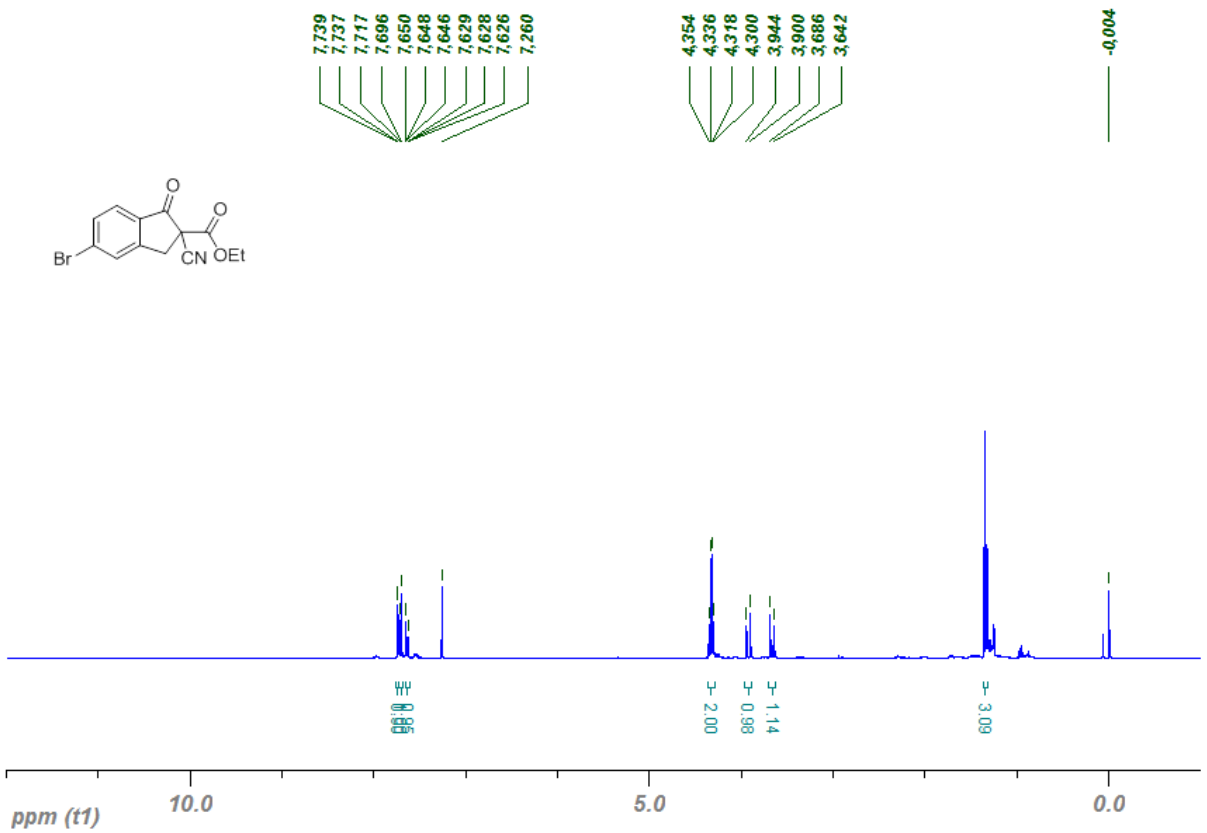
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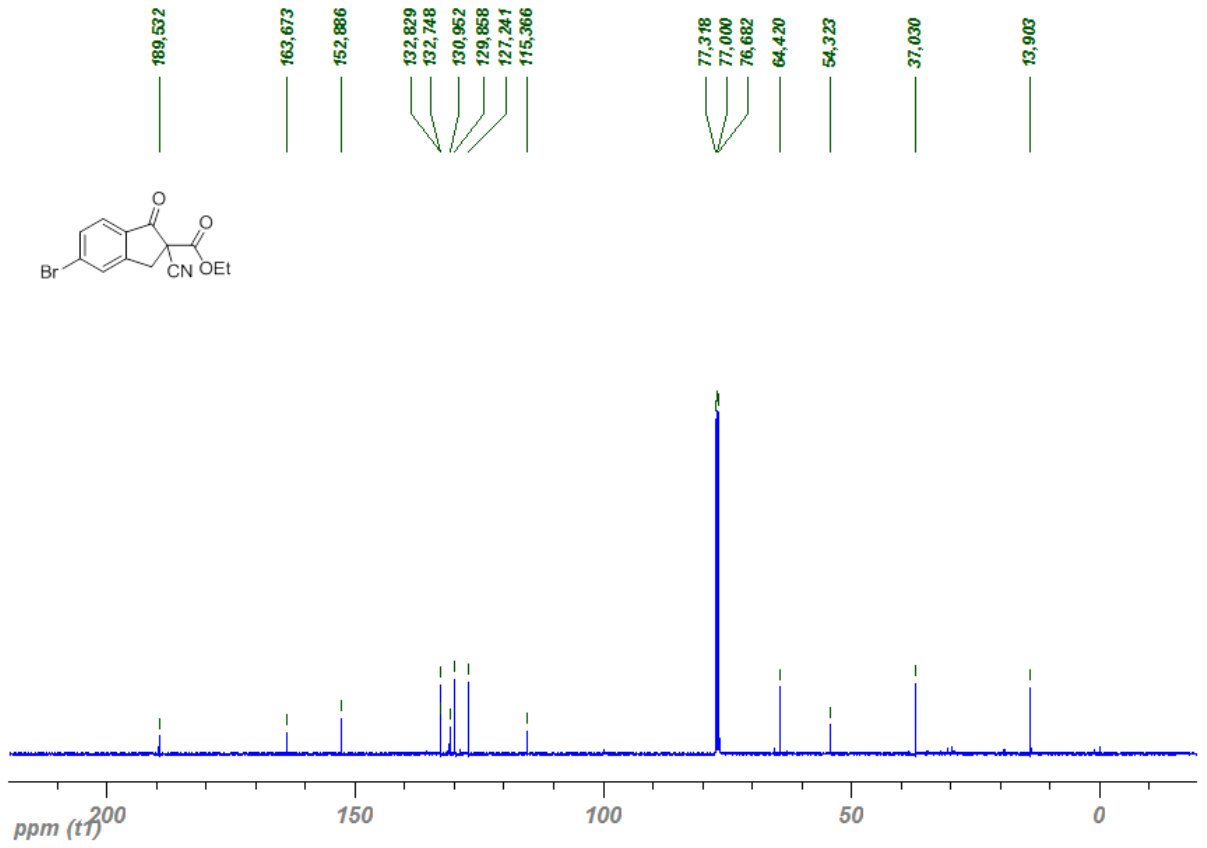
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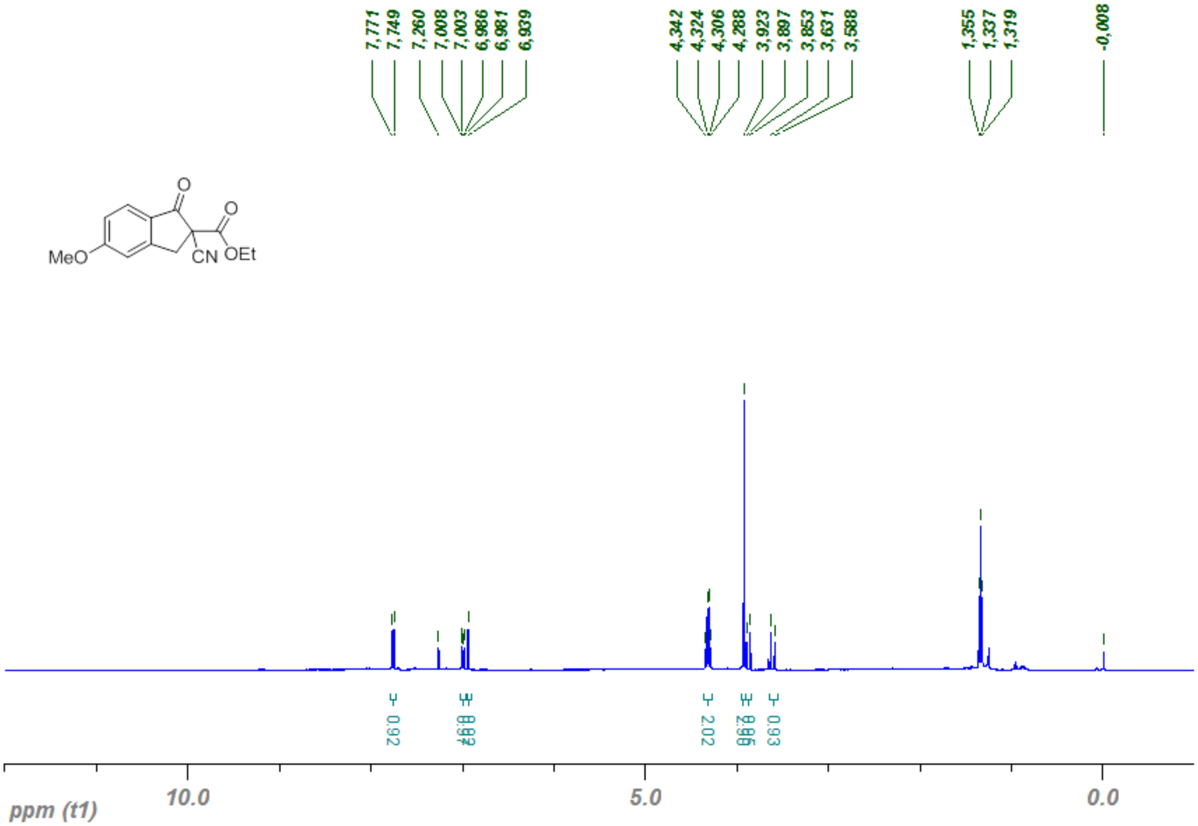
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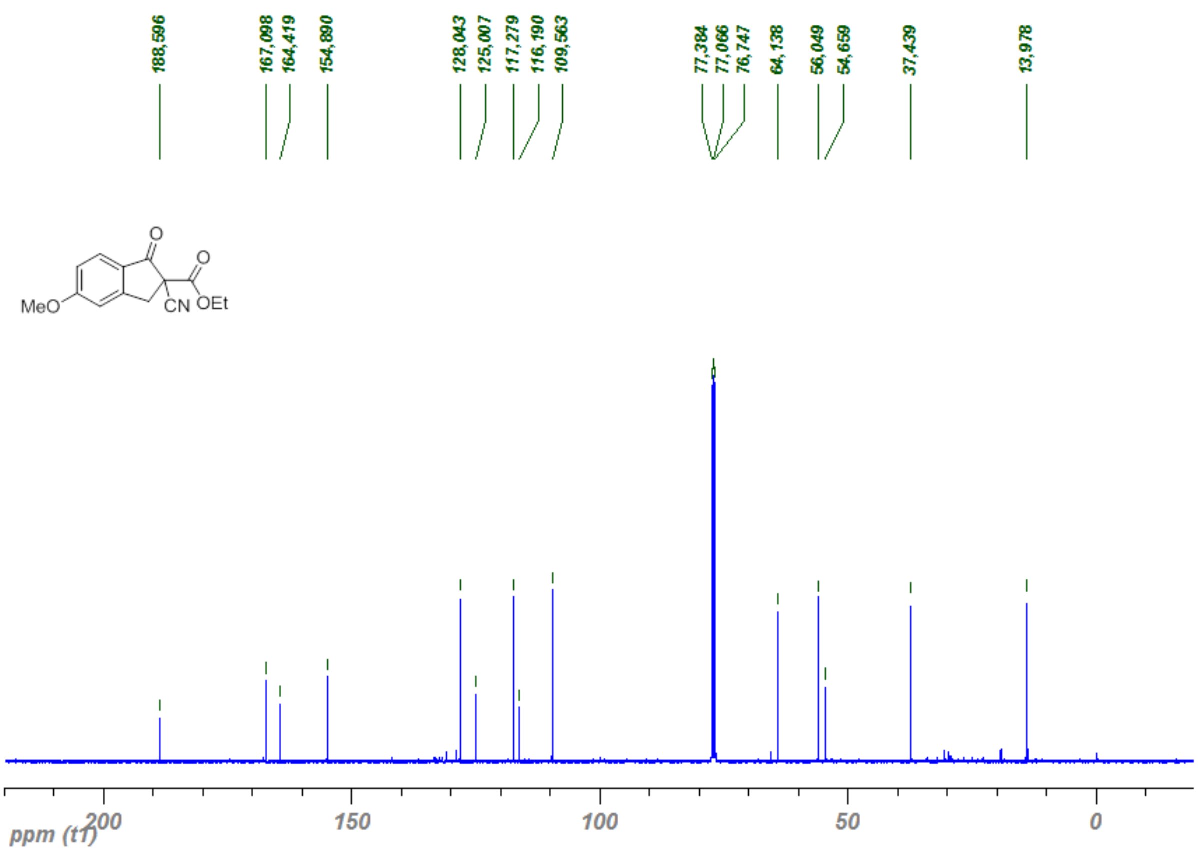
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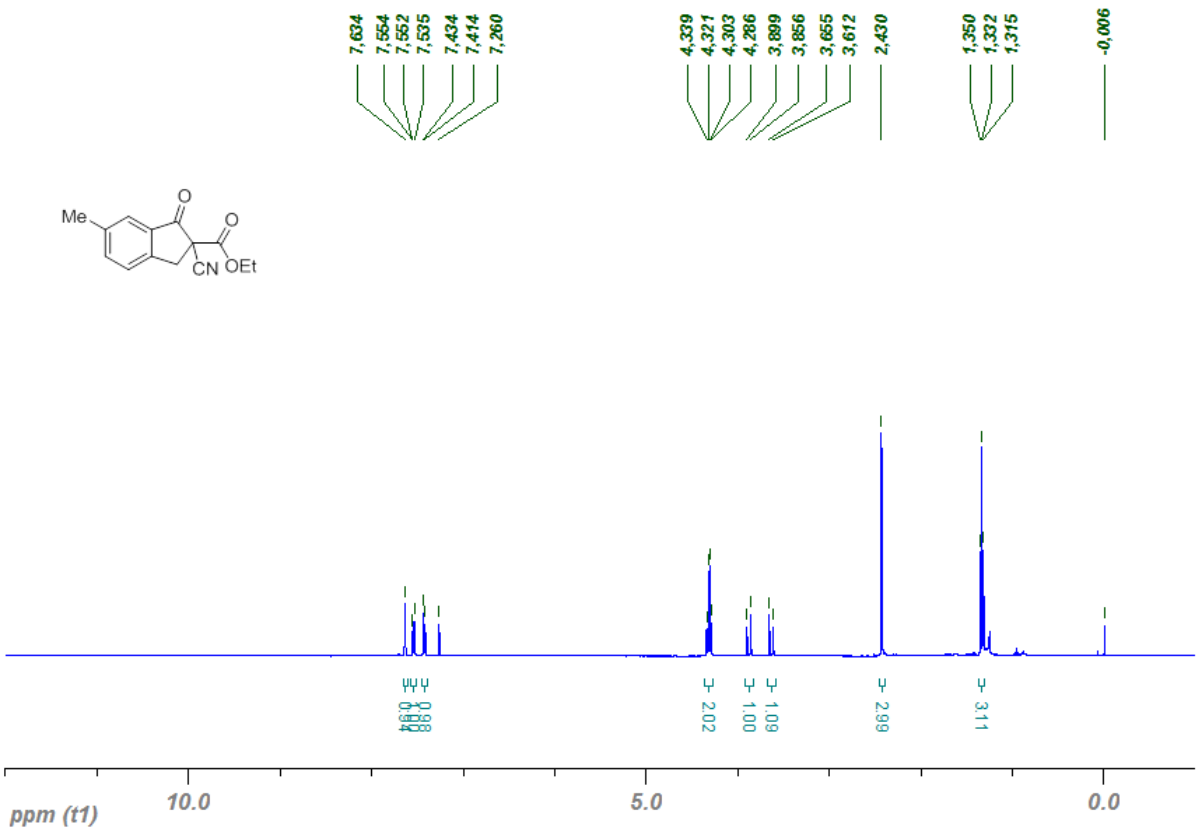
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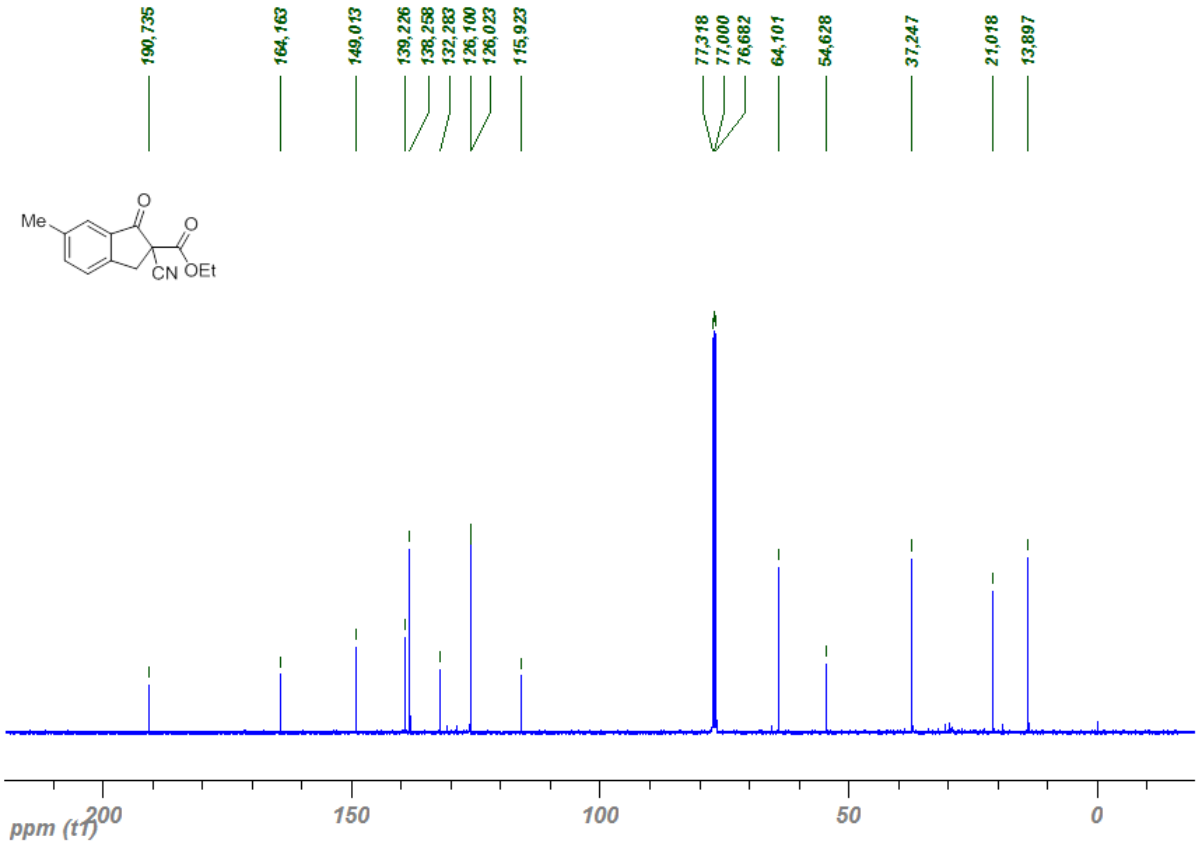
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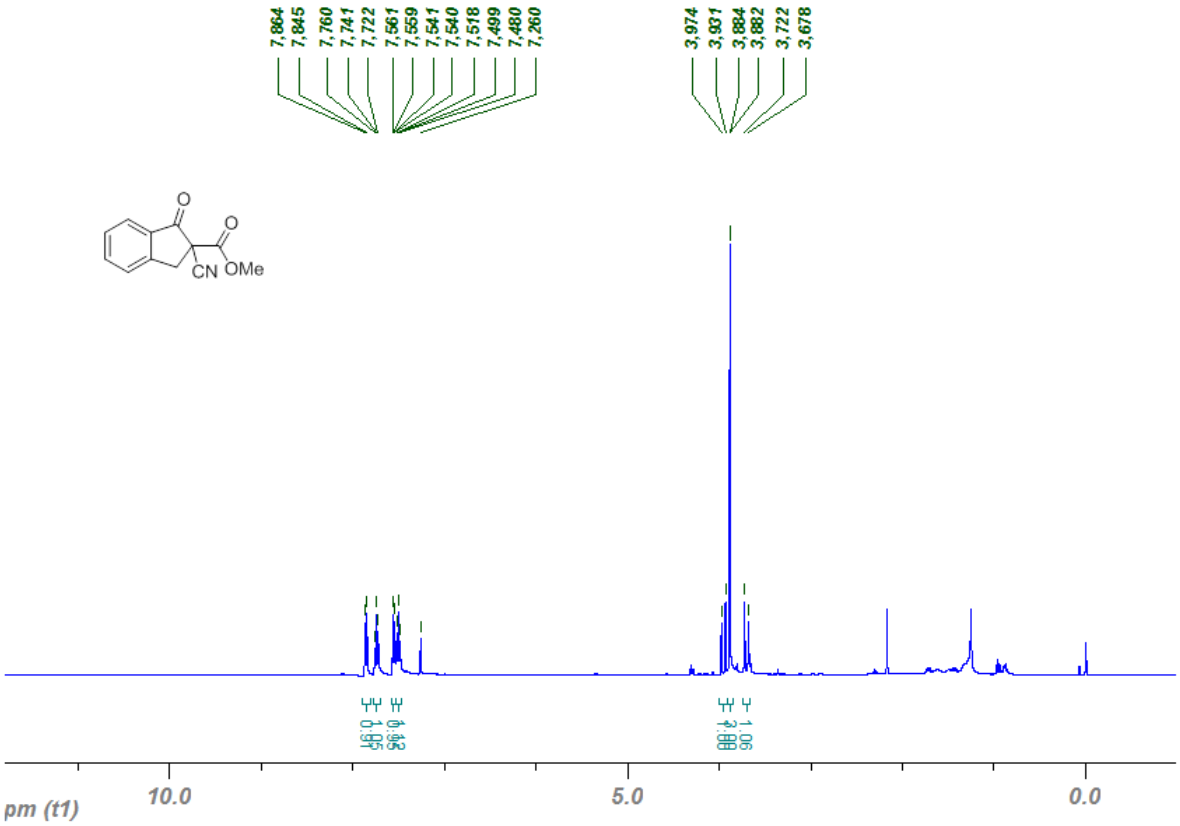
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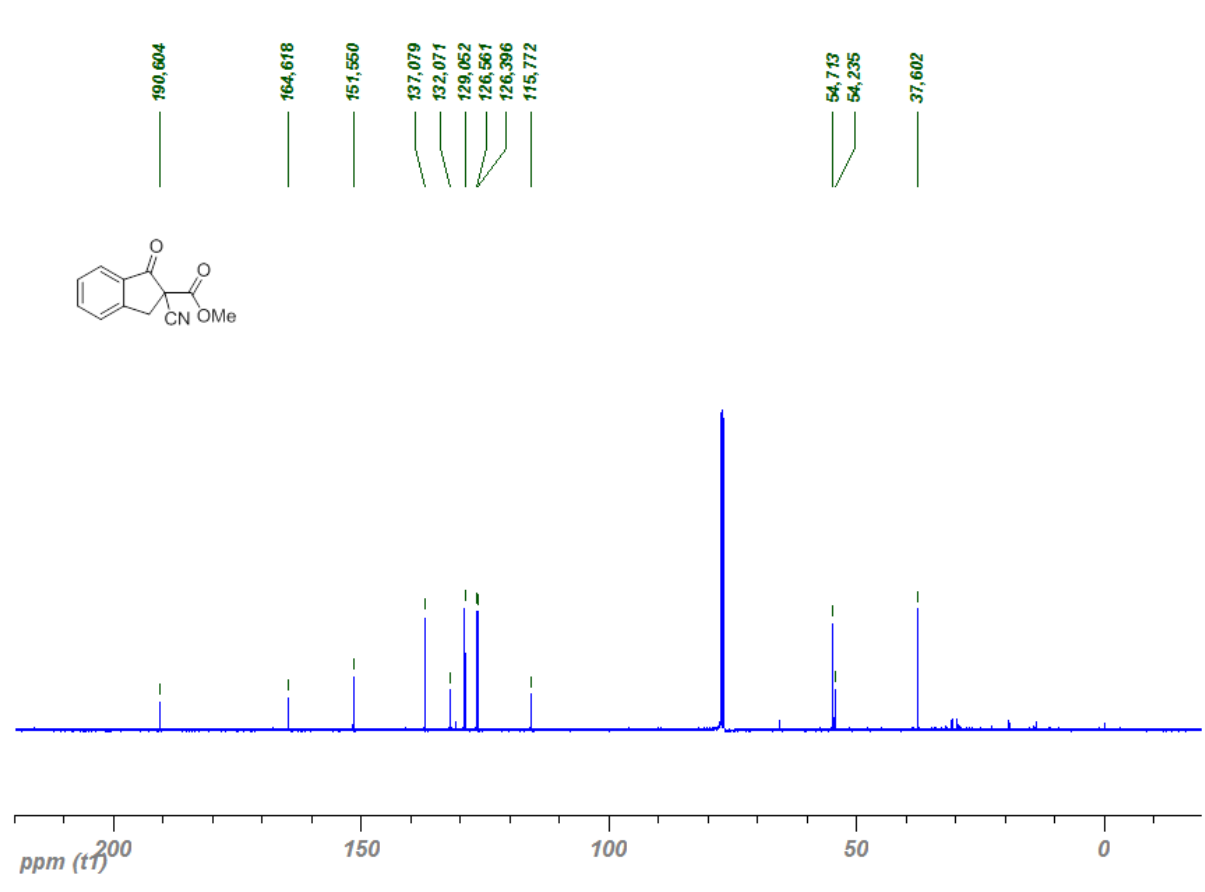
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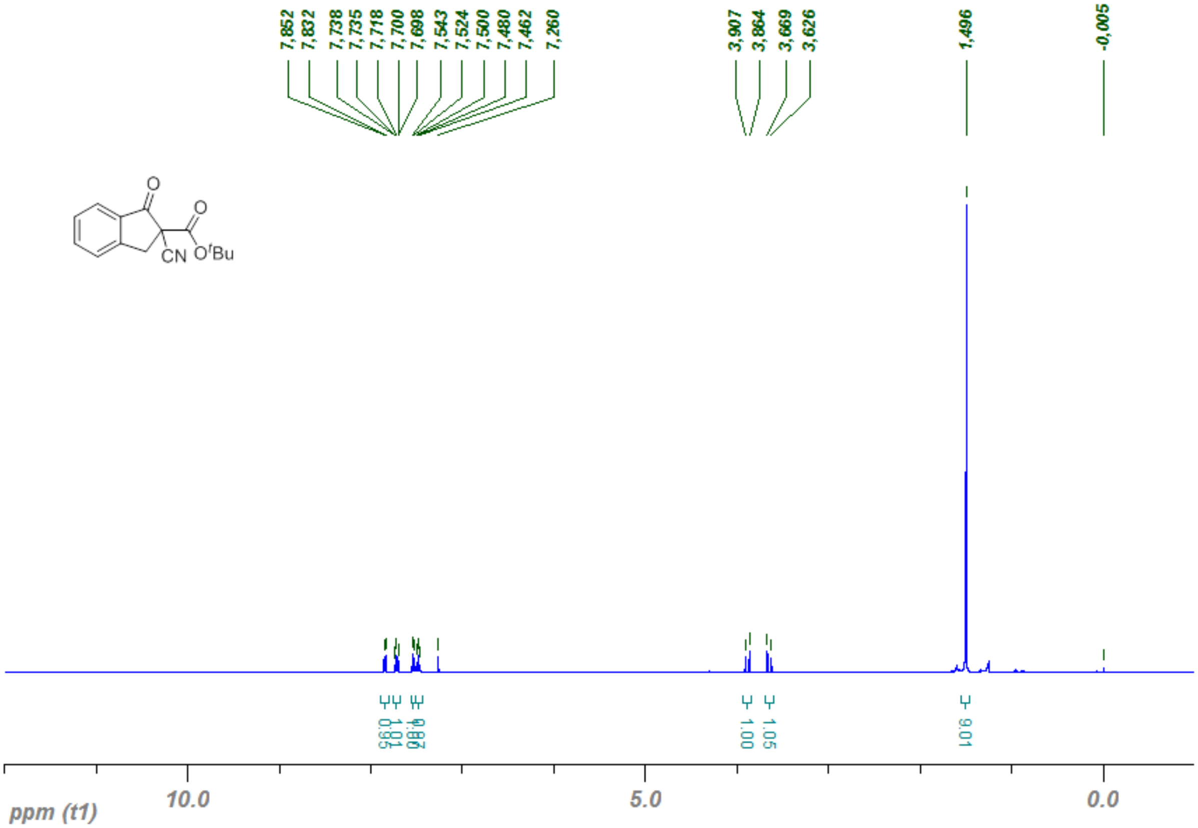
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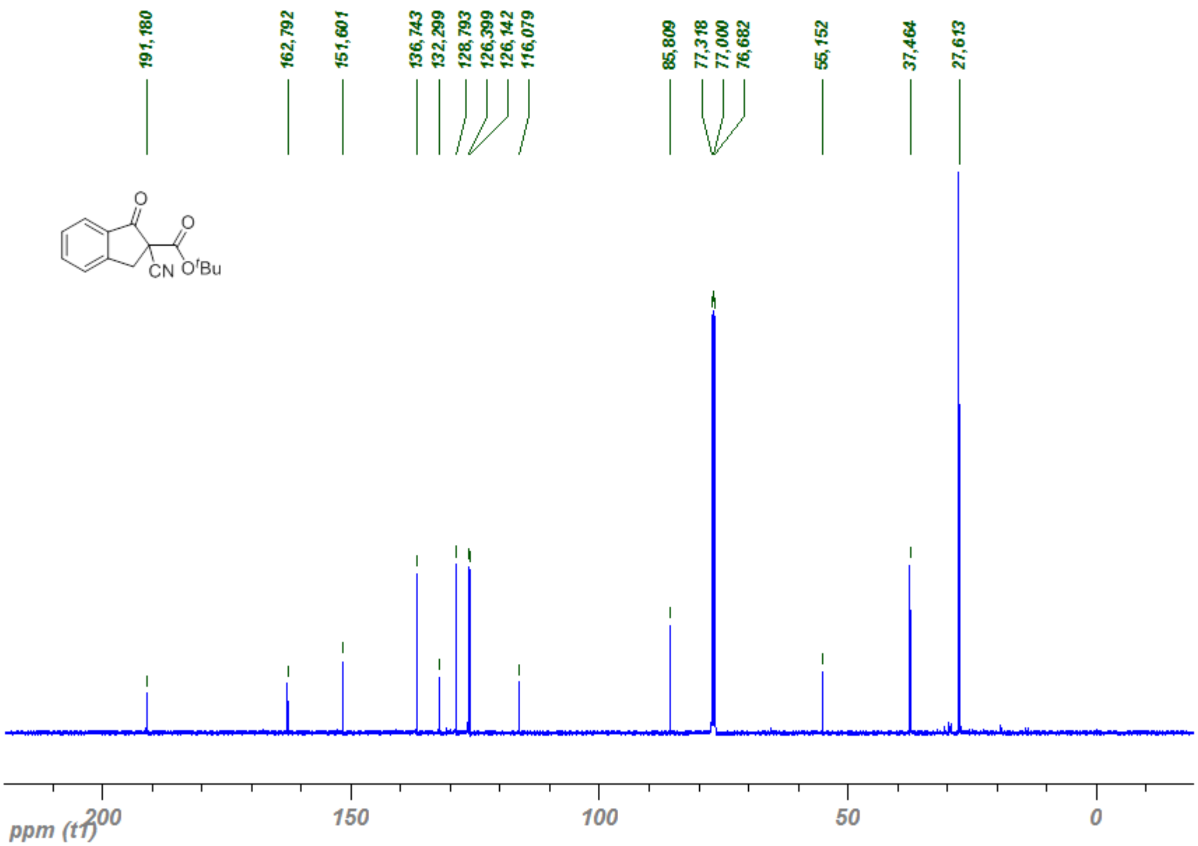
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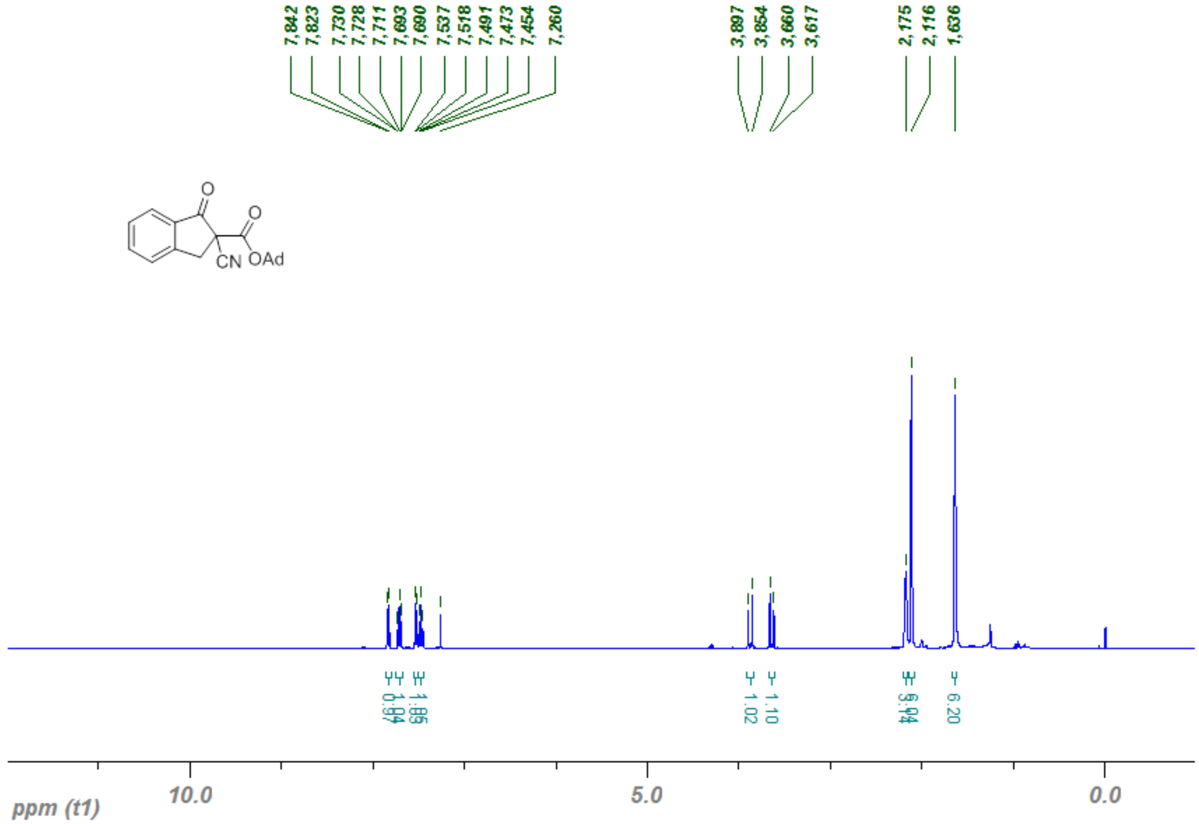
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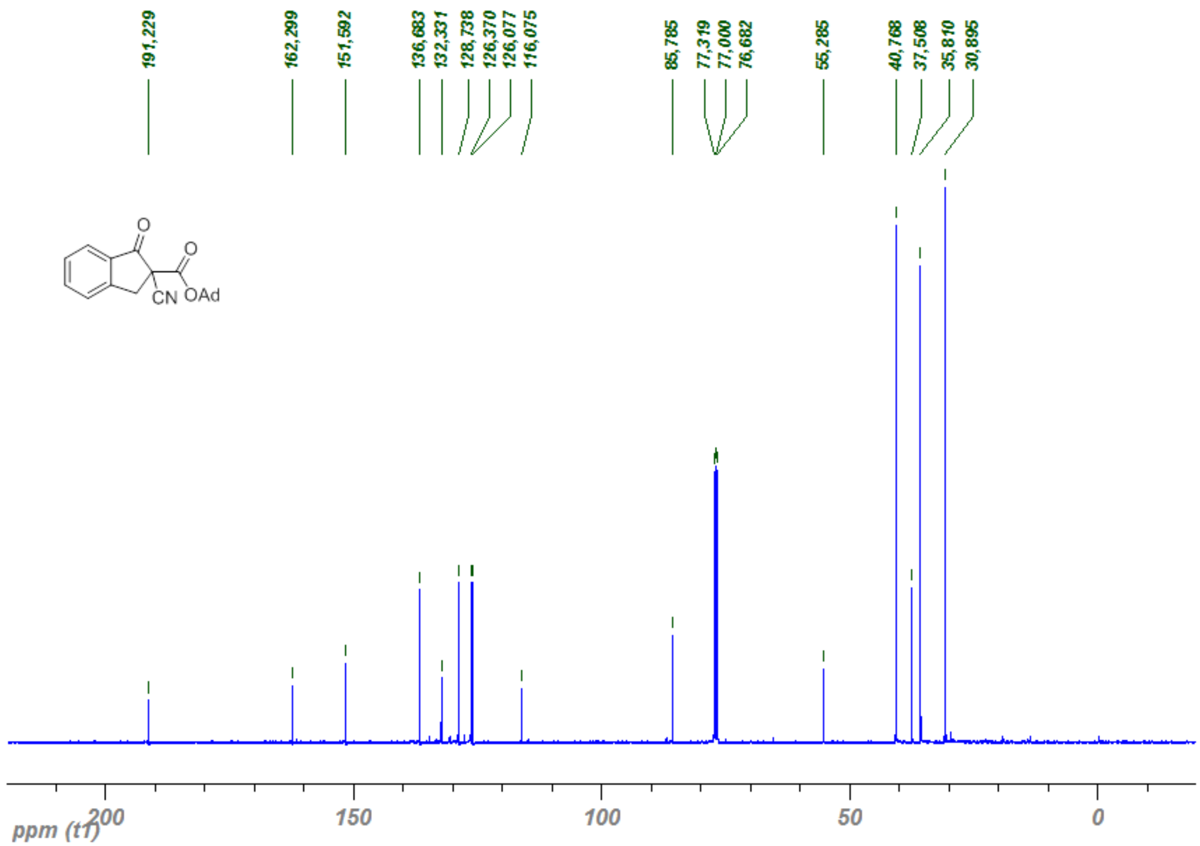
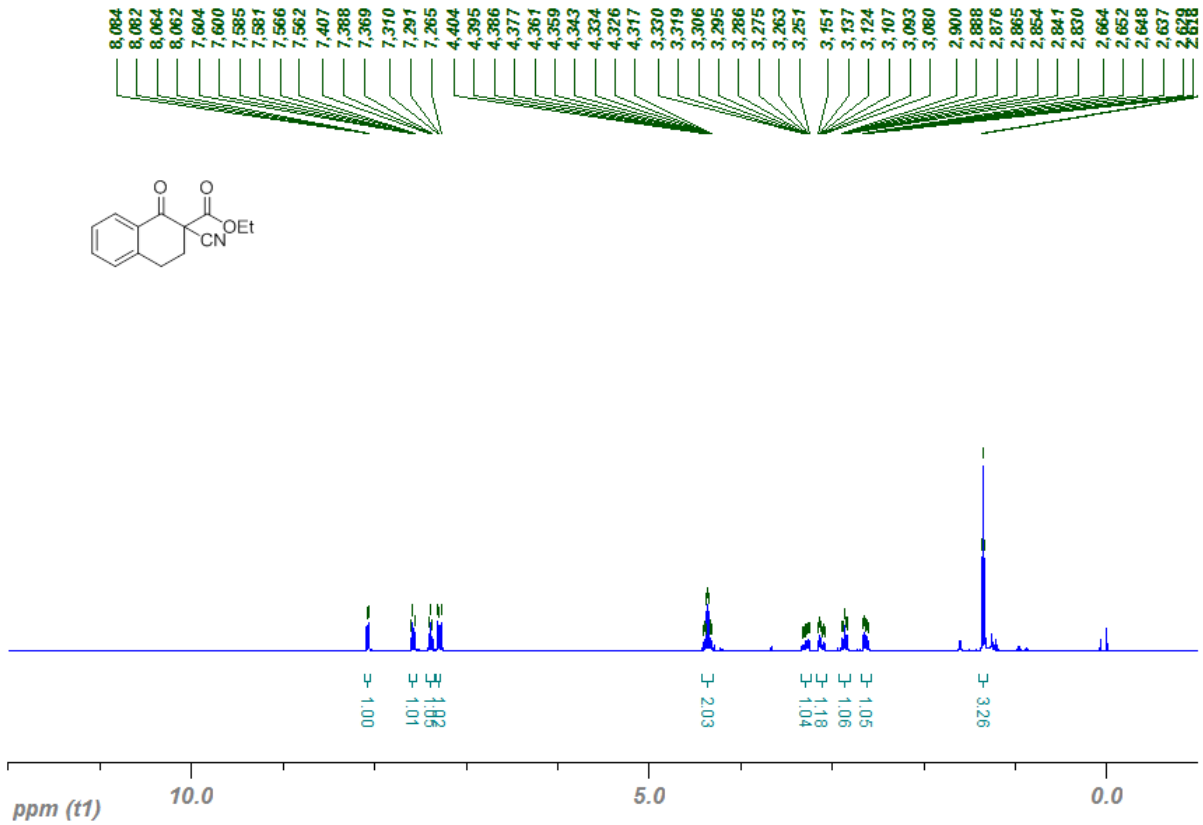
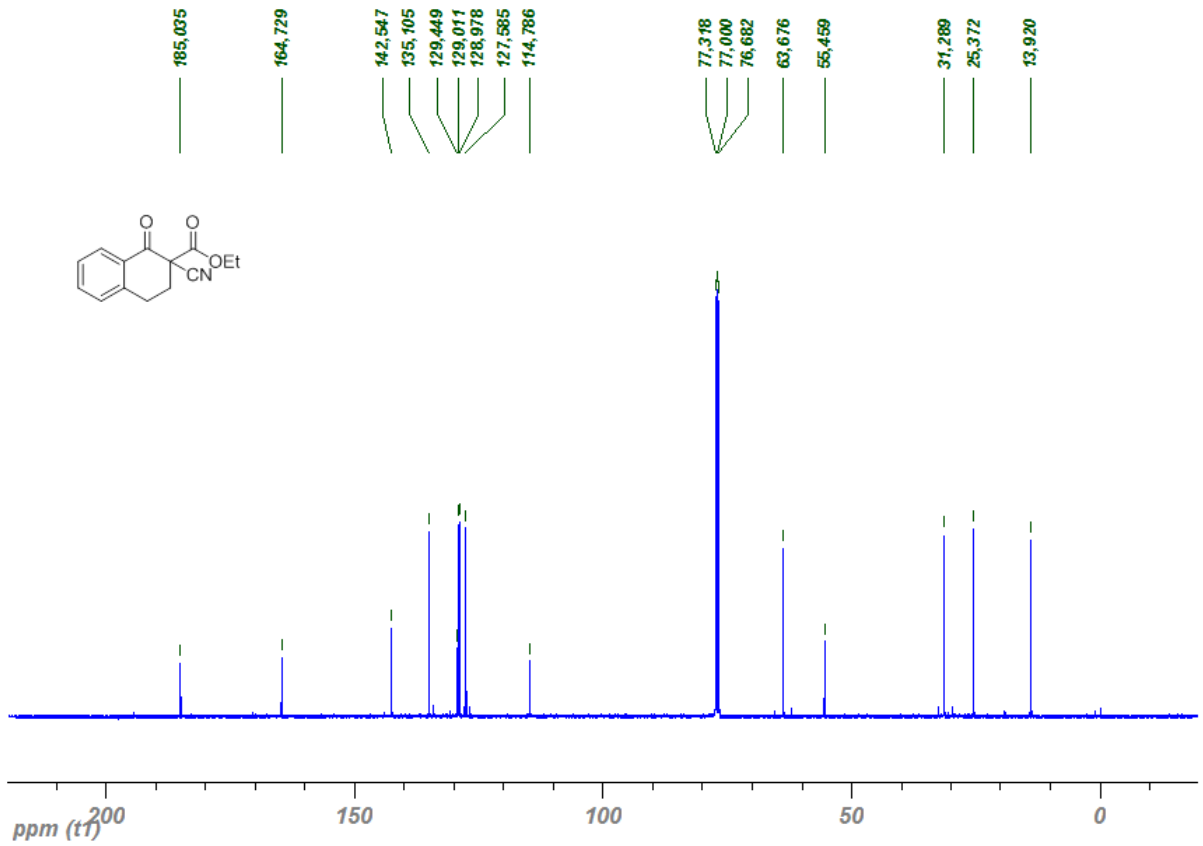
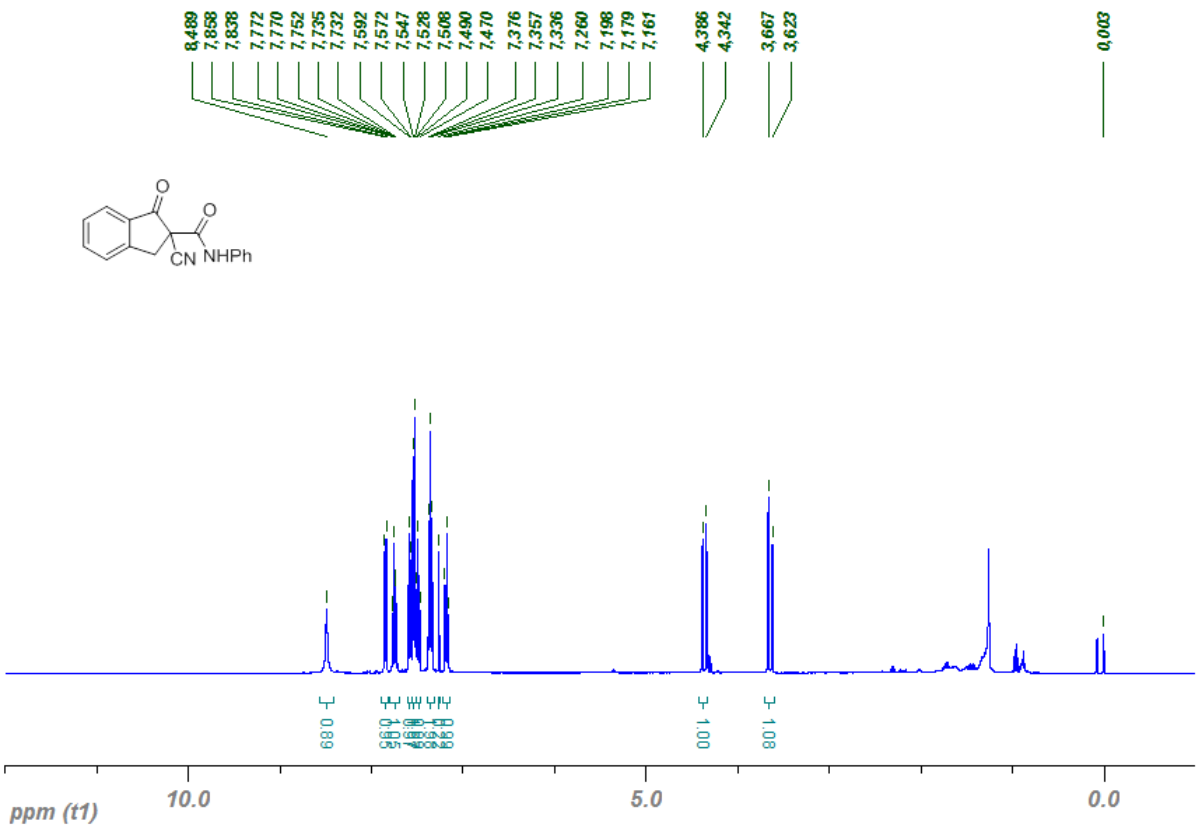
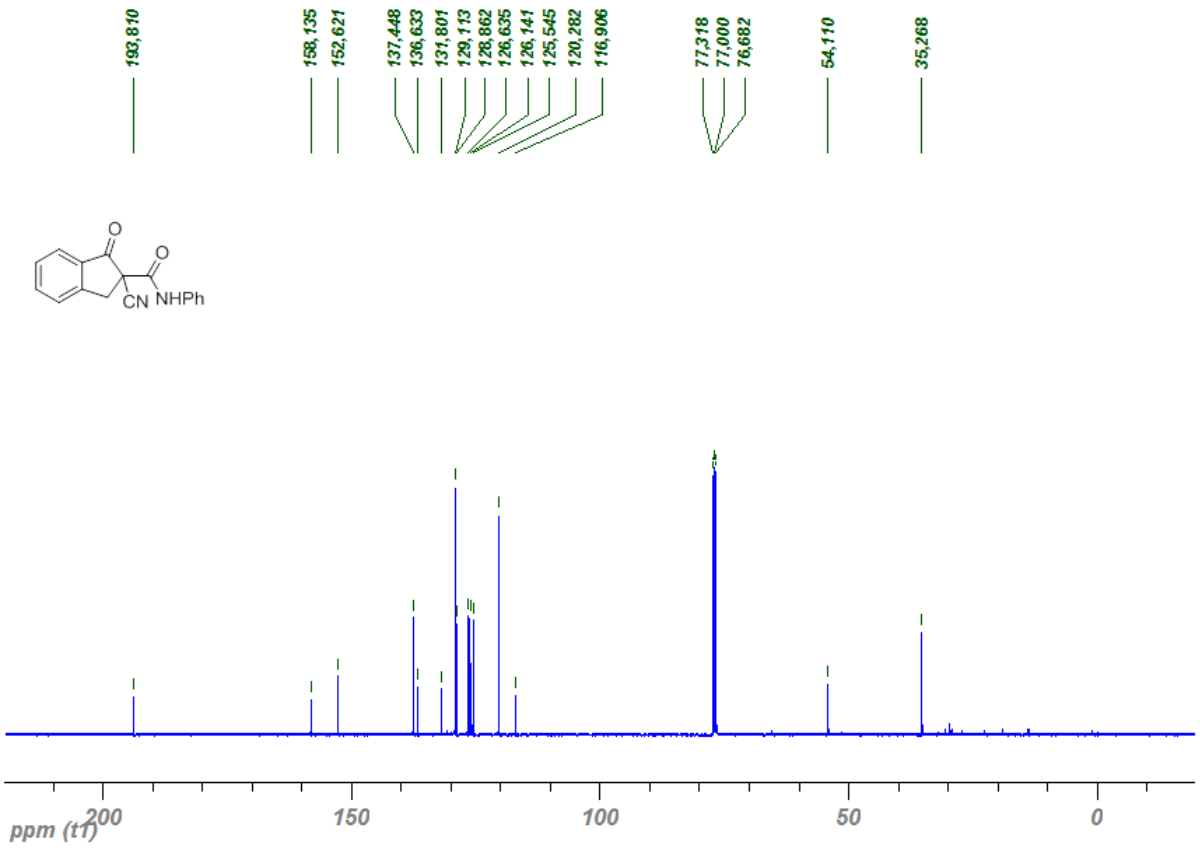
6.20
ppm (t1)
10.0
5.0
0.0

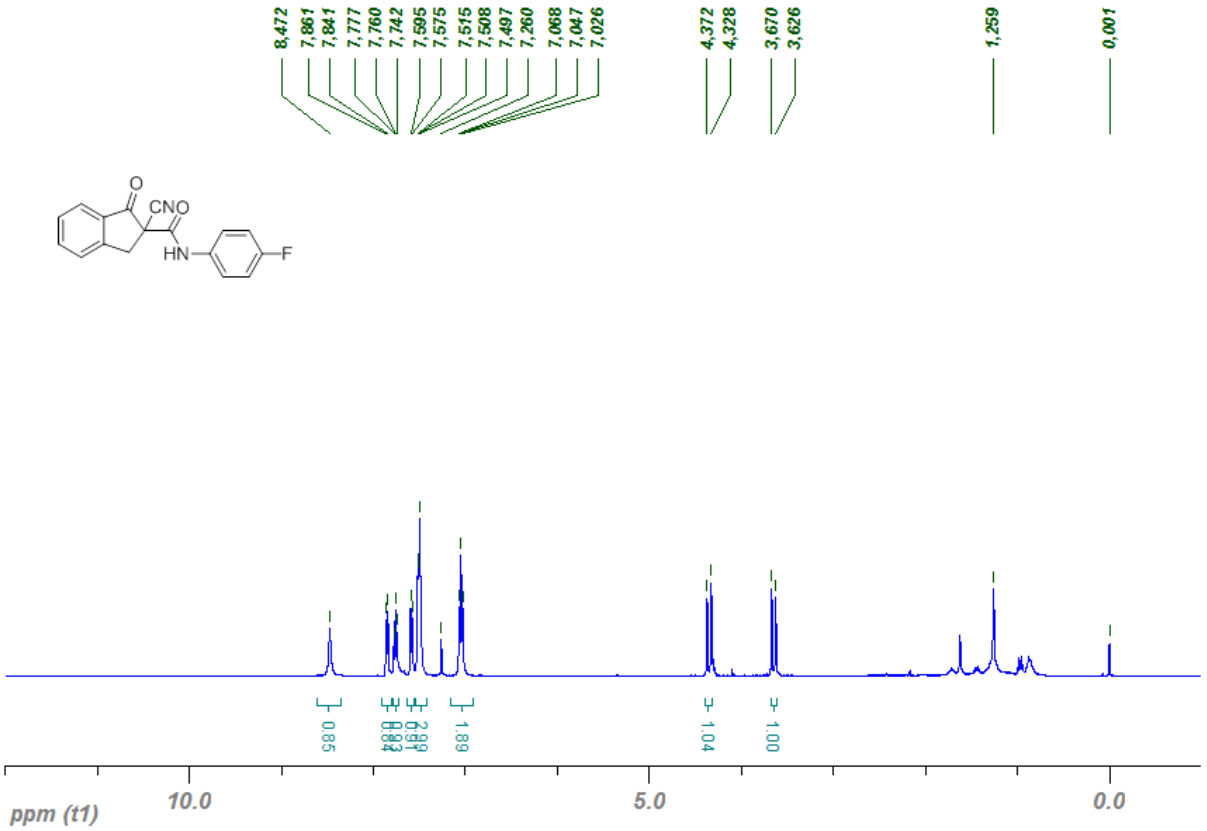

191,229
162,299
151,592
136,683
132,331
128,738
126,370
126,077
116,075
85,785
77,319
77,000
76,682
55,285
40,768
37,508
35,810
30,895
CN
OAd
ppm (t1)
200
150
100
50
0

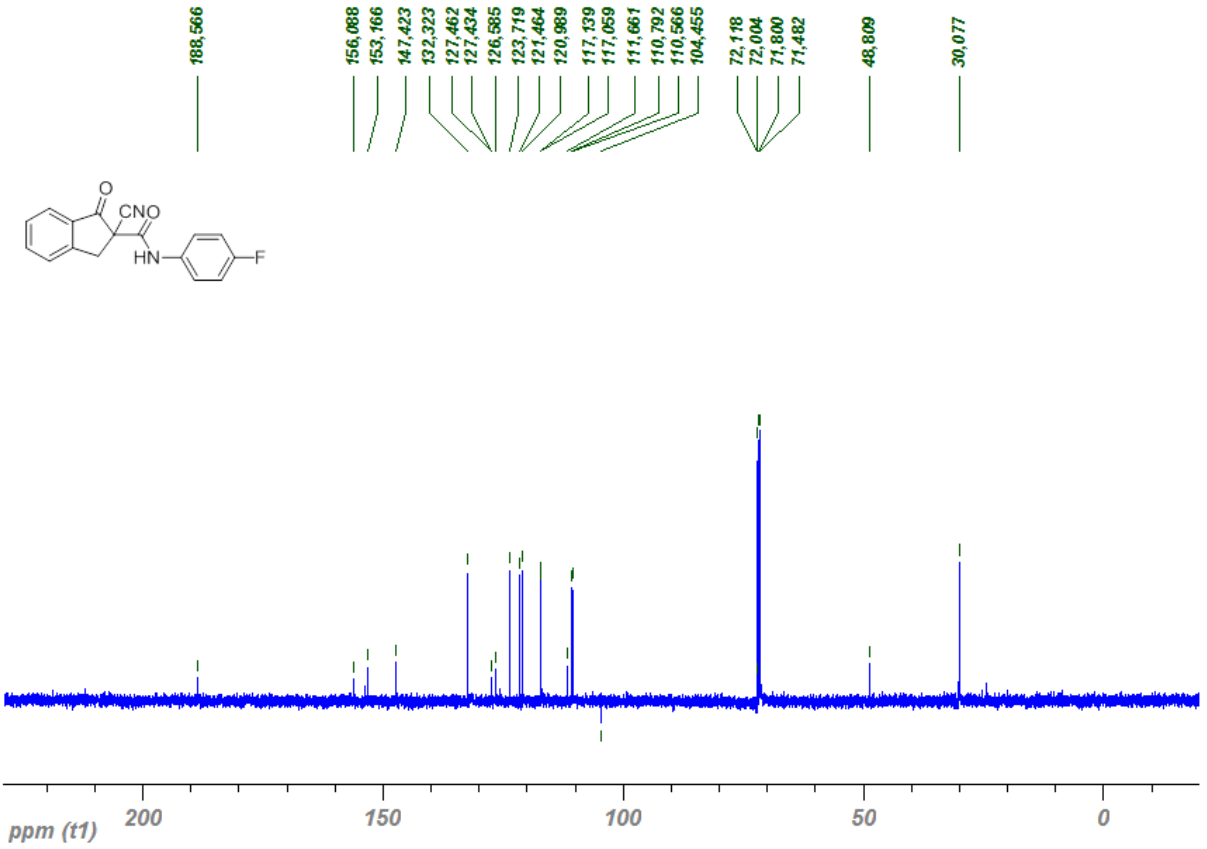

8,084
8,082
8,064
8,062
7,604
7,600
7,585
7,581
7,566
7,562
7,407
7,388
7,369
7,310
7,291
7,265
4,404
4,395
4,386
4,377
4,361
4,359
4,343
4,334
4,326
4,317
3,330
3,319
3,306
3,295
3,286
3,275
3,263
3,251
3,151
3,137
3,124
3,107
3,093
3,080
2,900
2,888
2,876
2,865
2,854
2,841
2,830
2,664
2,652
2,648
2,637
O
O
OEt
CN
1.00
1.01
2.03
1.04
1.18
1.06
1.05
3.26
10.0
5.0
0.0
ppm (t1)

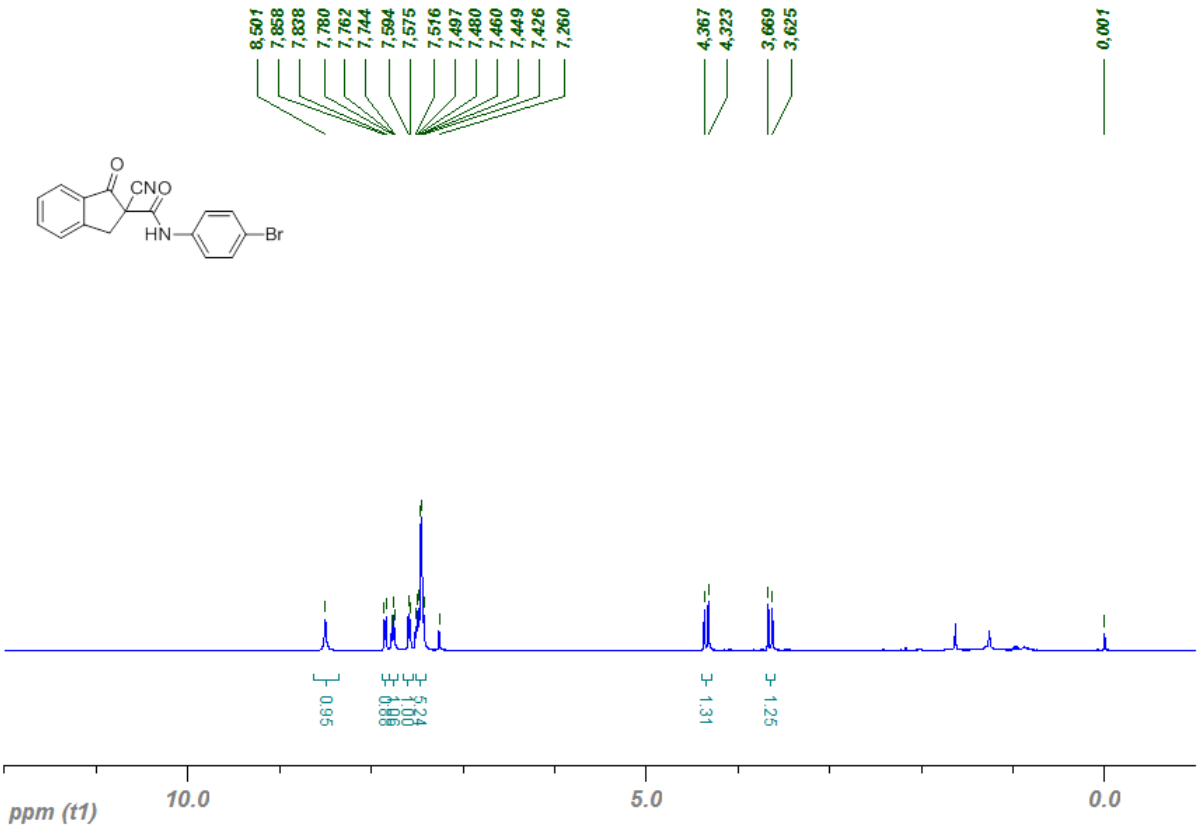

185,035
164,729
142,547
135,105
129,449
129,011
128,978
127,585
114,786
77,318
77,000
76,682
63,676
55,459
31,289
25,372
13,920
O
O
OEt
CN
200
150
100
50
0
ppm (t1)

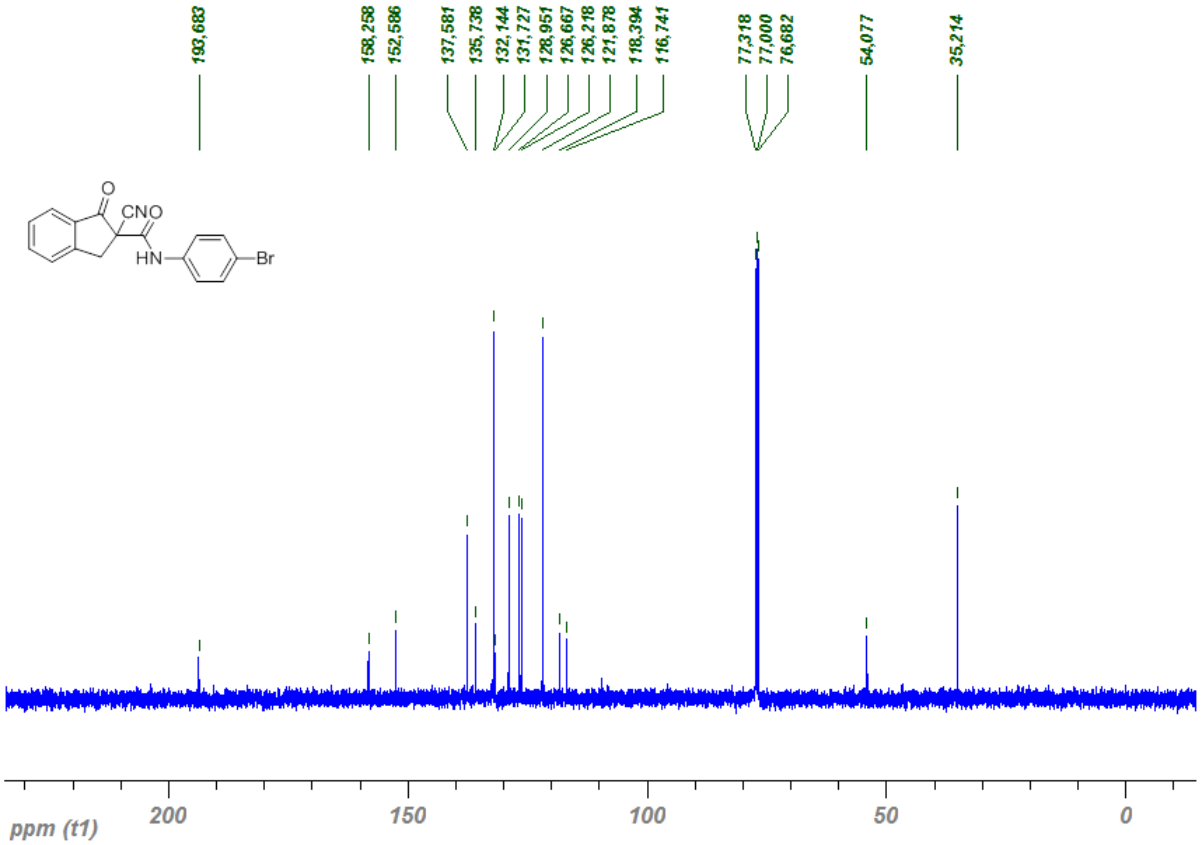

8,489
7,858
7,838
7,772
7,770
7,752
7,735
7,732
7,592
7,572
7,547
7,528
7,508
7,490
7,470
7,376
7,357
7,336
7,260
7,198
7,179
7,161
4,386
4,342
3,667
3,623
0,003
O
O
CN NHPh
1,089
1,100
1,108
10.0
5.0
0.0
ppm (t1)

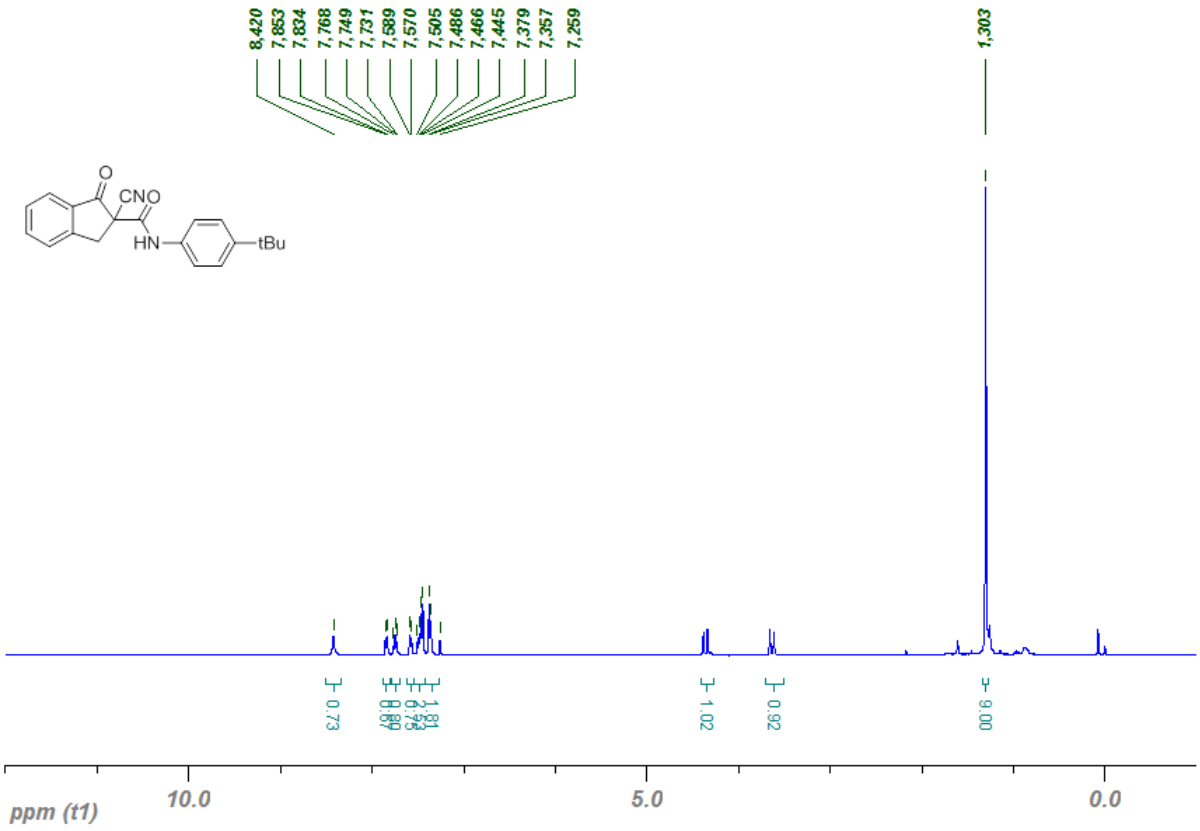

193,810
158,135
152,621
137,448
136,633
131,801
129,113
128,862
126,635
126,141
125,545
120,282
116,906
77,318
77,000
76,682
54,110
35,268
O
O
CN NHPh
200
150
100
50
0
ppm (t1)

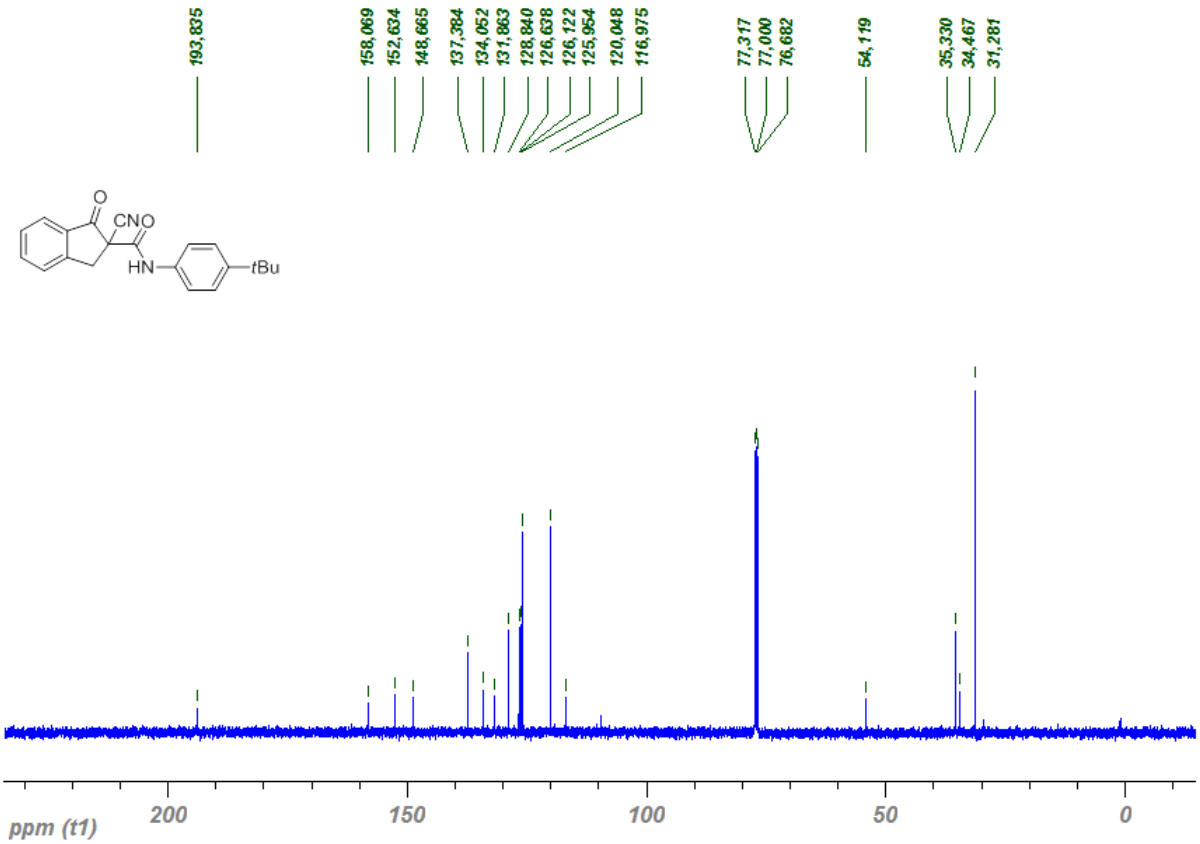

8,472
7,861
7,841
7,777
7,760
7,742
7,595
7,575
7,515
7,508
7,497
7,260
7,068
7,047
7,026
4,372
4,328
3,670
3,626
1,259
0,001
O
CNO
HN
F
0,85
1,89
1,04
1,00
ppm (t1)
10.0
5.0
0.0

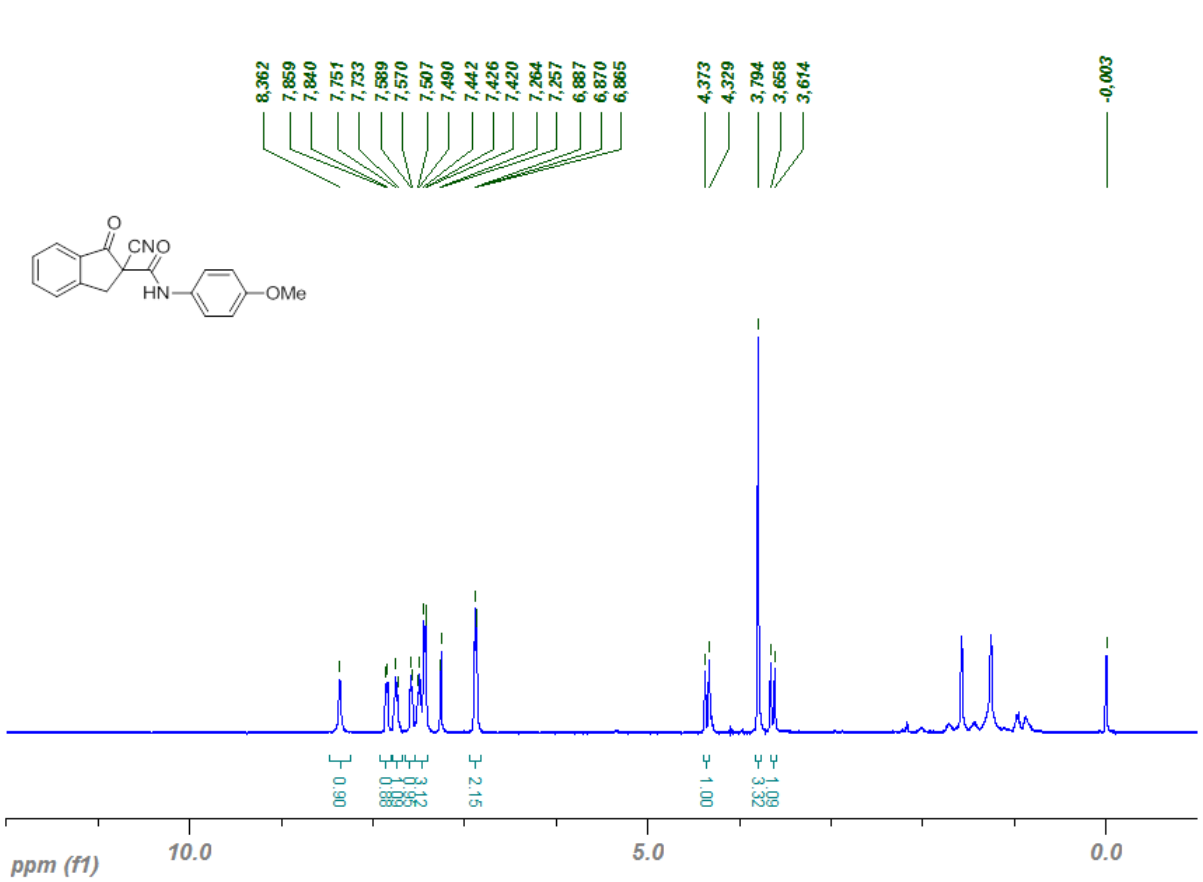

188,566
156,088
153,166
147,423
132,323
127,462
127,434
126,585
123,719
121,464
120,989
117,139
117,059
111,661
110,792
110,566
104,455
72,118
72,004
71,800
71,482
48,809
30,077
O
CNO
HN
F
ppm (t1)
200
150
100
50
0

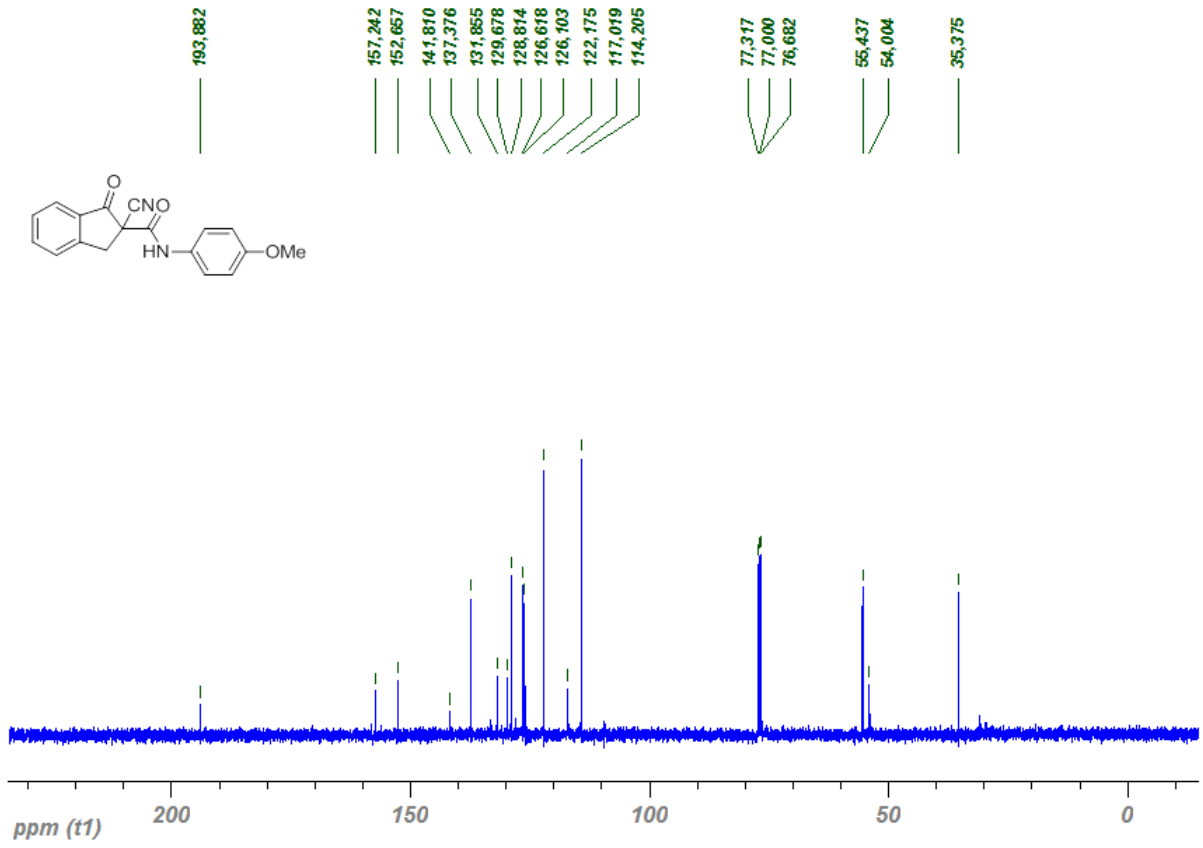

8,501
7,858
7,838
7,780
7,762
7,744
7,594
7,575
7,516
7,497
7,480
7,460
7,449
7,426
7,260
4,367
4,323
3,669
3,625
0,001
O
CNO
HN
Br
0,95
5,24
1,00
0,98
1,31
1,25
ppm (t1)
10.0
5.0
0.0

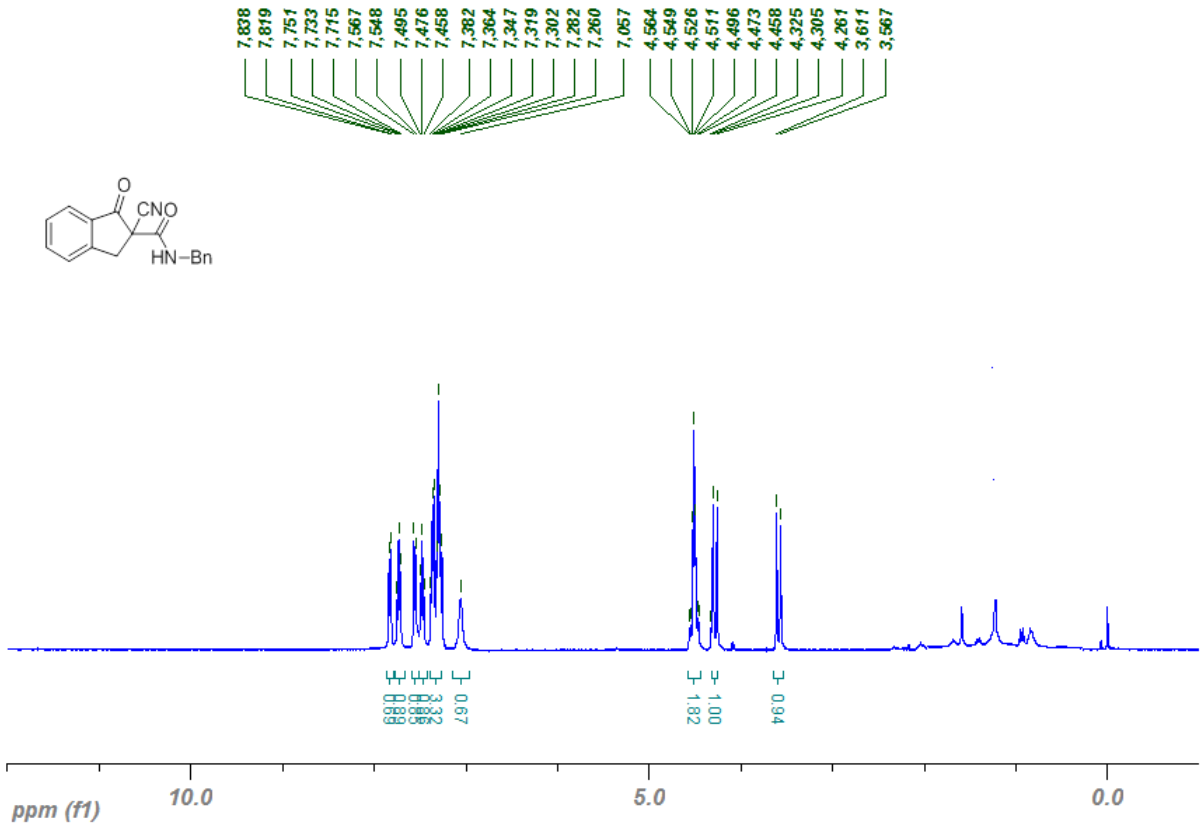

193,683
158,258
152,586
137,581
135,738
132,144
131,727
128,951
126,667
126,218
121,878
118,394
116,741
77,318
77,000
76,682
54,077
35,214
O
CNO
HN
Br
ppm (t1)
200
150
100
50
0

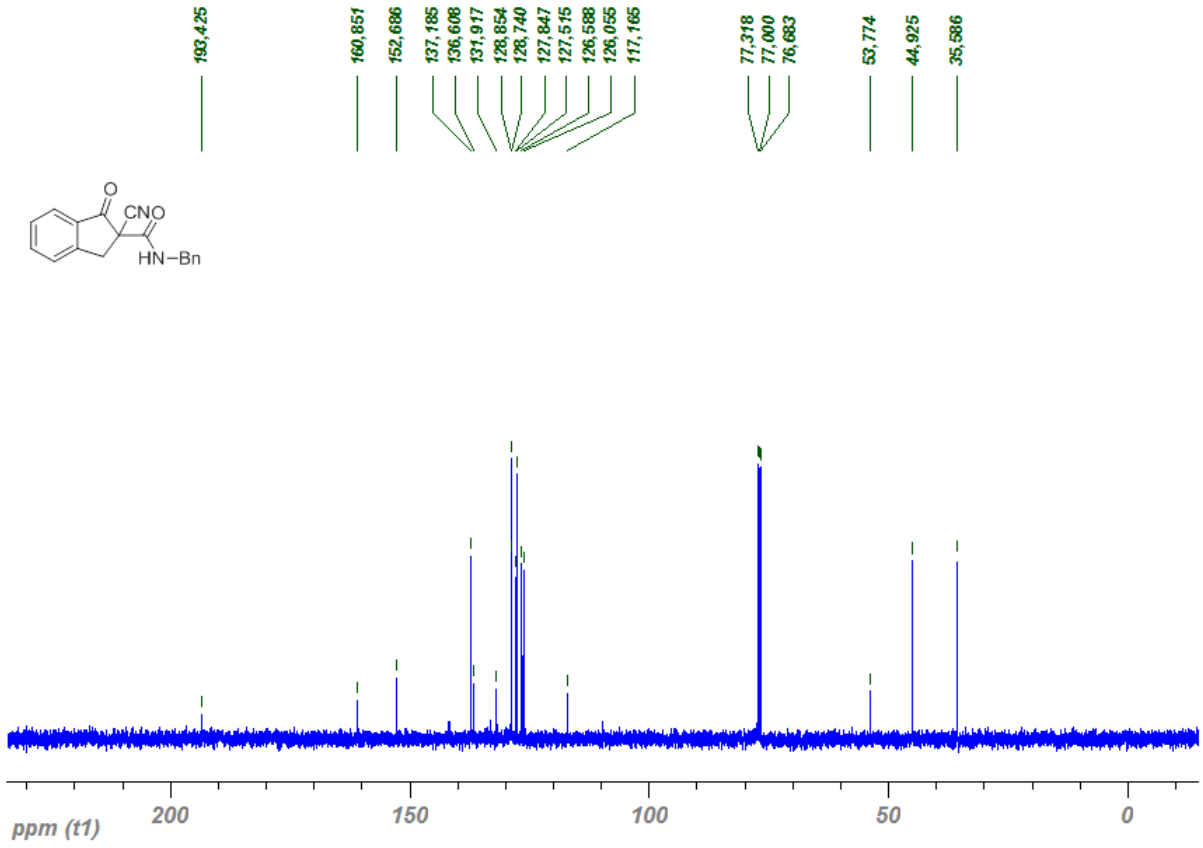

8,420
7,853
7,834
7,768
7,749
7,731
7,589
7,570
7,505
7,486
7,466
7,445
7,379
7,357
7,259
1,303
O
CNO
HN
tBu
0.73
1.81
1.02
0.92
9.00
ppm (t1)
10.0
5.0
0.0

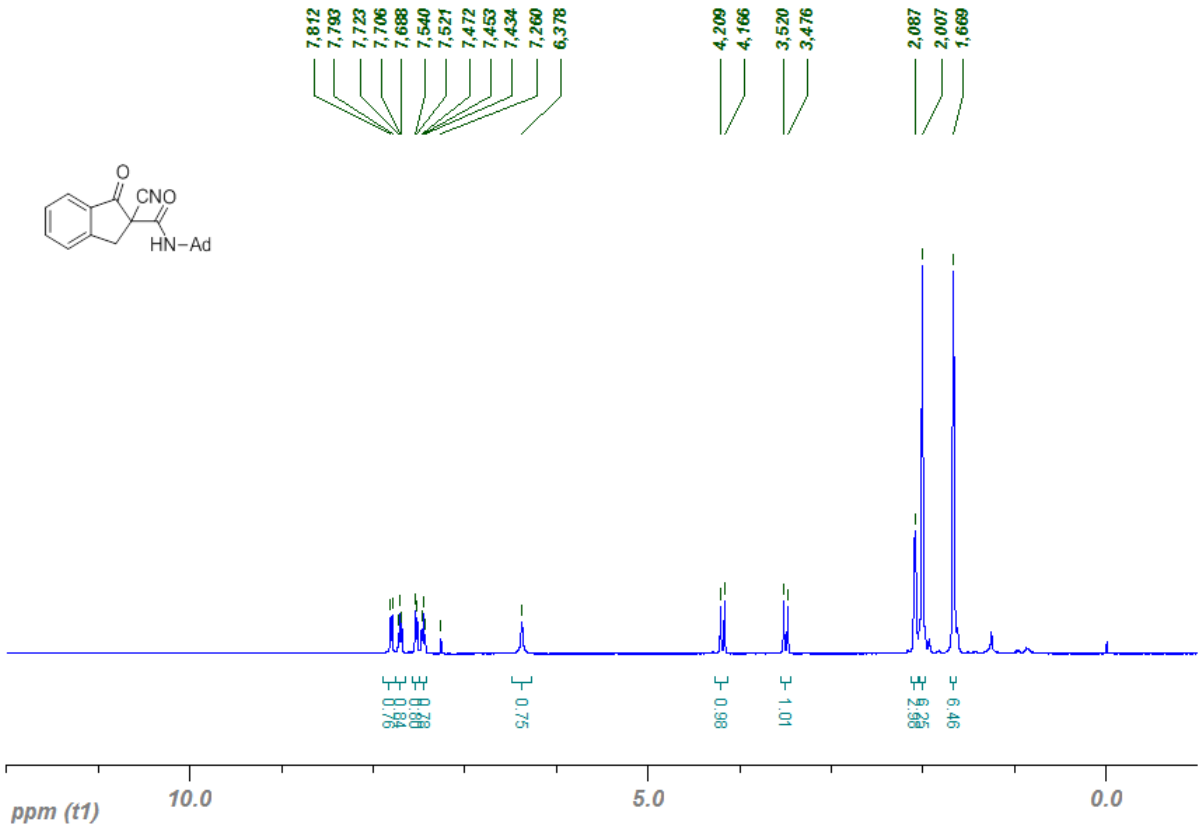

193,835
158,069
152,634
148,665
137,384
134,052
131,863
128,840
126,638
126,122
125,954
120,048
116,975
77,317
77,000
76,682
54,119
35,330
34,467
31,281
O
CNO
HN
tBu
ppm (t1)
200
150
100
50
0

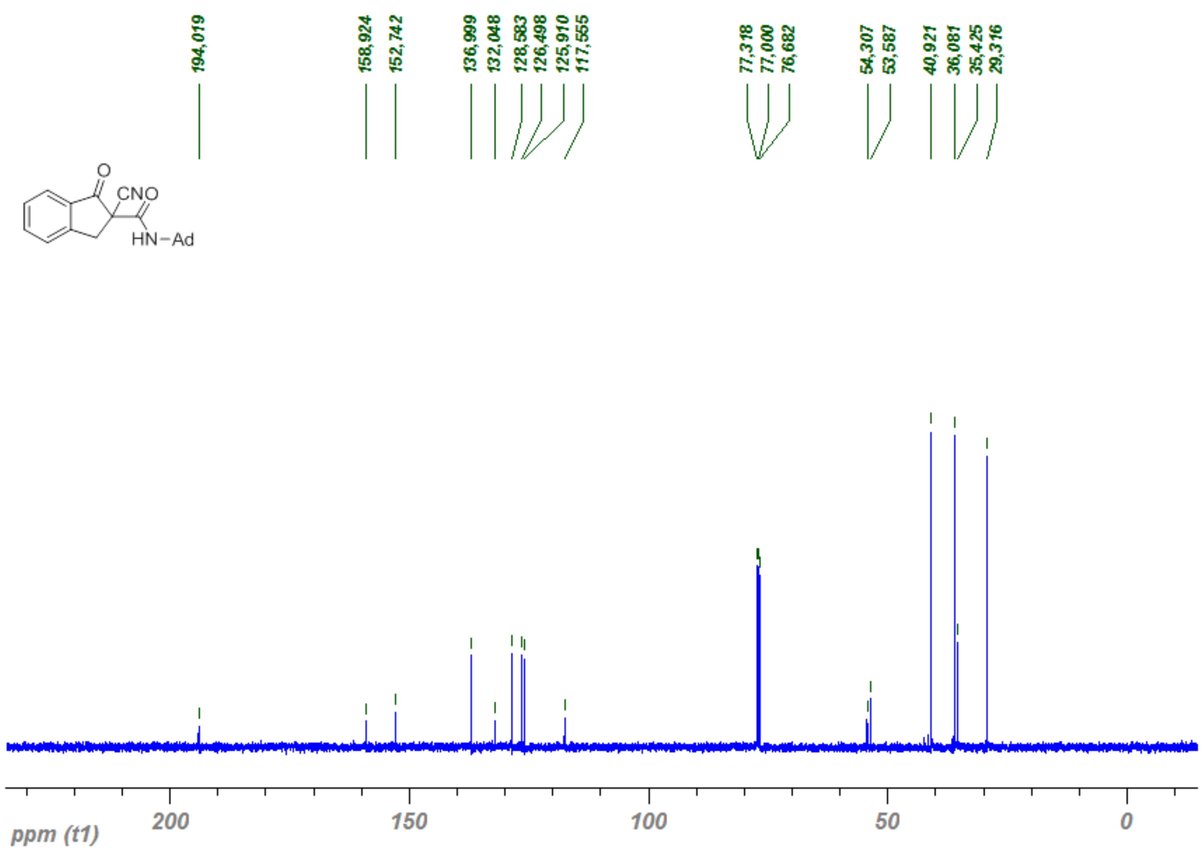

8,362
7,859
7,840
7,751
7,733
7,589
7,570
7,507
7,490
7,442
7,426
7,420
7,264
7,257
6,887
6,870
6,865
4,373
4,329
3,794
3,658
3,614
-0,003
O
CNO
HN
OMe
0,90
0,88
0,86
3,12
2,15
1,00
1,09
3,32
10.0
5.0
0.0
ppm (f1)


193,882
157,242
152,657
141,810
137,376
131,855
129,678
128,814
126,618
126,103
122,175
117,019
114,205
77,317
77,000
76,682
55,437
54,004
35,375
O
CNO
HN
OMe
200
150
100
50
0
ppm (t1)


7,838
7,819
7,751
7,733
7,715
7,567
7,548
7,495
7,476
7,458
7,382
7,364
7,347
7,319
7,302
7,282
7,260
7,057
4,564
4,549
4,526
4,511
4,496
4,473
4,458
4,325
4,305
4,261
3,611
3,567
O
CNO
HN–Bn
0,67
1,82
1,00
0,94
10.0
5.0
0.0
ppm (f1)


193,425
160,851
152,686
137,185
136,608
131,917
128,854
128,740
127,847
127,515
126,588
126,055
117,165
77,318
77,000
76,683
53,774
44,925
35,586
O
CNO
HN–Bn
200
150
100
50
0
ppm (t1)


7,812
7,793
7,723
7,706
7,688
7,540
7,521
7,472
7,453
7,434
7,260
6,378
4,209
4,166
3,520
3,476
2,087
2,007
1,669
O
CNO
HN−Ad
0.75
0.98
1.01
6.46
ppm (t1)
10.0
5.0
0.0


194,019
158,924
152,742
136,999
132,048
128,583
126,498
125,910
117,555
77,318
77,000
76,682
54,307
53,587
40,921
36,081
35,425
29,316
O
CNO
HN−Ad
ppm (t1)
200
150
100
50
0